UNIVERSITY OF CALIFORNIA, MERCED

$HB(C_6F_5)_4$-Catalyzed Intramolecular Hydroarylations of Alkenes, and the Design and Synthesis of Modular Promesogenic Organic Ligands for Quantum Dot Nanoparticle Self-Assembly

A dissertation submitted in partial satisfaction of the
requirements for the degree Doctor of Philosophy

in

Chemistry and Chemical Biology

by

Amir Keshavarz

Committee in Charge:

Professor Ryan D. Baxter, Chair

Professor Linda S. Hirst

Professor Erik J. Menke

Professor Benjamin J. Stokes, Advisor

The Dissertaton of Amir Keshavarz is approved, and it is acceptable in quality and form for publication on microfilm and electronically:

Professor Ryan D. Baxter (Chair)

Professor Linda S. Hirst

Professor Erik J. Menke

Professor Benjamin J. Stokes (Advisor)

University of California, Merced

2019

DEDICATION

TO MY FAMILY

TABLE OF CONTENTS

LIST OF ABBREVIATION

Å	Angstrom
Boc	*tert*-butoxylcarbonyl
br	broad
Bu	butyl (C_4H_9)
C–C	carbon–carbon
d	doublet
DCE	1,2-dichloroethane
DCM	dichloromethane
dd	doublet of doublet
DMF	*N*,*N*-dimethylformamide
EAS	electrophilic aromatic substitution
Equiv	molar equivalent
ESI	electrospray ionization
Et	ethyl
EI	electron impact
FT	Fourier transform
GC	gas chromatography
H	hour
Hex	hexyl (C_6H_{13})
HRMS	high-resolution mass spectrometry
Hz	hertz
IR	infrared

LIST OF ABBREVIATIONS (continued)

J	coupling constant
LC	liquid crystal
M	molarity
m	multiple
Me	methyl
mmol	millimole
Ms	methanesulfonyl
m/z	mass-to-charge
np	nanoparticle
NMR	nuclear magnetic resonance
pen	pentet
Ph	phenyl
ppm	parts per million
Pr	propyl
q	quartet
rt	room temperature
s	singlet
t	triplet
TPFPB	tetrakis(pentafluorophenyl)borate
THF	tetrahydrofuran

LIST OF SCHEMES

LIST OF TABLES

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my PhD. advisor, Dr. Benjamin J Stokes. None of my accomplishments would have been possible without his support, encouragements, motivations and patience. His guidance helped me to become a better chemist.

I like to thank my dissertation committee members, Professors Ryan Baxter, Linda Hirst, Erik Menke and Matthew Meyer (former member) for providing valued feedback during my PhD career.

I like to thank the members of Stokes and Baxter lab for creating a positive and friendly environment in the lab.

I also like to thank our collaborators at professor Hirst lab, particularly Sheida T Riahinasab.

I also wish to thank the UC Merced chemistry and chemical biology faculties, administrative support, research support staff and Dr. Rice and Dr. Russell for their help with NMR instruments.

And finally, I like to thank my parents and sister for their endless support and encouragements.

VITA

Education

August 2019 Ph.D. Candidate in Organic Chemistry (advisor: Prof. Benjamin J Stokes)
University of California at Merced

August 2014 M.Sc. in Chemistry (advisor: the late Prof. Joseph Hajdu)
California State University at Northridge

May 2012 B.Sc. in Biochemistry (advisor: the late Prof. Joseph Hajdu)
California State University at Northridge

Publications

(7) Keshavarz, A.; Riahinasab, S. T.; Hirst, L. S.; Stokes, B. J. "New Promesogenic Ligands for Host Medium Microencapsulation by Quantum Dots via Liquid Crystal Phase Transition."*ACS Applied Nano Materials* **2019,** *2,* 2542.
(6) Riahinasab, S. T.; Keshavarz, A.; Elbaradei, A.; Melton, C. N.; Warren, G. I.; Stokes, B. J.; Hirst, L. S. "Solid Nanoparticle Foams Formed by Double Nematic Nucleation and Growth." *Nat. Commun.* **2019**, *10*, 894.
(5) Melton, C. N.; Riahinasab, S. T.; Keshavarz, A.; Stokes, B. J.; Hirst, L. S. "Phase Transition-Driven Nanoparticle Assembly in Liquid Crystal Droplets." *Nanomaterials* **2018**, *8*, 146.
(4) Quint, M. T.; Sarang, S.; Quint, D. A.; Keshavarz, A.; Stokes, B. J.; Subramaniam, A. B.; Huang, K. C.; Gopinathan, A.; Hirst, L. S.; Ghosh, S. "Plasmon-Actuated Nano-Assembled Microshells." *Sci. Rep*. **2017**, *7*, 17788.
(3) Cai, X.; Keshavarz, A.; Omaque, J.; Stokes, B. J. "Brønsted Acid-Catalyzed Intramolecular Hydroarylation of *β*-Benzylstyrenes." *Org Lett.* **2017**, *19*, 2626.
(2) Riahinasab, S. T.; Elbaradei, A.; Keshavarz, A.; Stokes, B. J.; Hirst, L. S. "Nanoparticle Microstructures Templated by Liquid Crystal Phase-Transition Dynamics." *Proc. SPIE.* **2017**, *10125*, 1012503.
(1) Keshavarz, A.; Zelaya, L.; Singh, J.; Ranganathan, R.; Hajdu, J. "Activity-Based Targeting of Secretory Phospholipase A_2 Enzymes: A Fatty Acid Binding Protein-Assisted Approach." *ChemPhysLipids.* **2017***, 202*, 38.

PATENT APPLICATION (no. PCT/US2018/058271)
Organic Ligands for Templatable Mesoscale Nanocapsules *(Inventors: Benjamin J. Stokes and Amir Keshavarz)*.

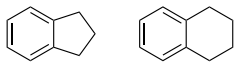
ABSTRACT

$Ph_3CB(C_6F_5)_4$ is a highly effective and easily handled Brønsted acid precatalyst for intramolecular hydroarylations of *β*-benzylalkenes and *β*-homobenzylalkenes. These cyclizations produce a wide variety of indanes and tetralins, including those found in important pharmaceuticals. My research in this area has focused on delineating how subtle structural changes can dictate the regioselectivity of intramolecular alkylation of arenes towards either the electronically or sterically preferred position. In an unrelated project, I designed and synthesized a new modular class of promesogenic organic ligands that direct CdSe/ZnS quantum dot nanoparticle self-assembly in a liquid crystal host using phase transition templating. Hollow micrometer-sized capsules are formed that resist thermal decomposition up to 350 °C and may therefore be useful for encapsulation applications.

CHAPTER 1

A Literature Review of Regioselectivity Outcomes of Acid-Catalyzed Intramolecular Alkylations of Arenes Using Alkenes

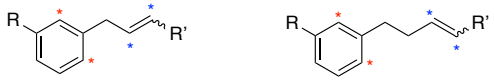
140 years have passed since the discovery of the Friedel–Crafts (FC) alkylation reaction,[1] and it remains a powerful method for the attachment of alkyl groups aromatic carbon atoms.[2] FC alkylation products are widely used in chemical industry as pharmaceuticals and agrochemicals.[3] FC reactions are typically carried out under strong acidic conditions proceeding by electrophilic aromatic substitution (EAS).[4] FC-type intramolecular hydroarylation of olefins represent an atom-economical synthetic route to the development of carbocylic compounds, particularly five- and six-membered rings (indane **1.1** and tetralin **1.2** nuclei are depicted in Scheme 1).



1.1 **1.2**

Scheme 1. Depiction of indane and tetralin skeletons.

Intramolecular hydroarylation of alkenes is challenging because their reactivity with protons is relatively low compared to alkynes and allenes. Therefore, the activation of a C–C double bond to generate a highly electrophilic carbon atom becomes difficult. In such reactions, the hydrogen of the arene nucleophile is usually replaced by an electrophile, thus making a new bond. A polysubstituted arene may contain two sites for substitution that could lead to distinct cyclization products, termed *regioisomers* (see **1.3**, Scheme 2). In general, the preference for alkylation is dictated by the electronic effects or the steric environment imparted by the substituent. In addition, there could be competition between five- and six-membered ring formation (not shown). The six-membered ring has less strain and typically occurs faster than five-membered rings. Arene regioselectivity outcomes in FC reactions have been of longstanding interest to chemists, although mainly in intermolecular reactions.[5]

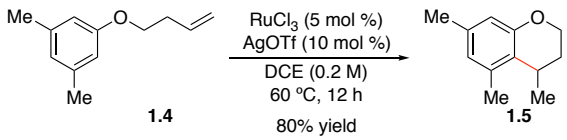


1.3 **1.3a**

Scheme 2. Potential nucleophilic (red stars) and electrophilic (blue stars) sites for alkylation.

Numerous synthetic methods have been developed for the catalytic intramolecular hydroarylation of alkenes to furnish a wide variety of tetralins and indanes. However, the evaluation of regioselective variants of such reactions has been much less emphasized, and is a main focus of Chapters 2 and 3. Thus, the remainder of this chapter will review examples of regioselective Lewis and Brønsted acid-catalyzed intramolecular FC-type hydroarylations of alkenes.

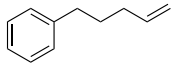
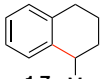
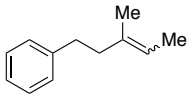
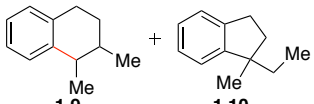
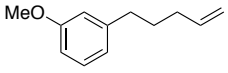
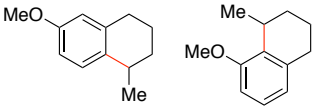
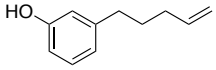
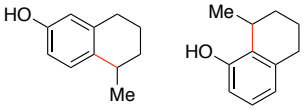
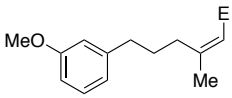
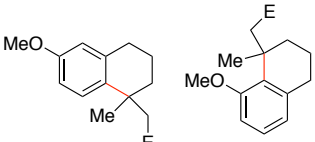
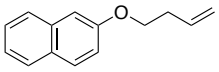
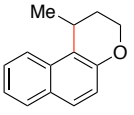
Tetralins (1,2,3,4-tetrahydronaphthalenes, see **1.2** in Scheme 1) are common motifs found in many natural products,[6] pharmaceutical drugs,[7] materials,[8] and polymers.[9] Due to the importance of tetralins, chemists have given a lot of attention to developing synthetic methods to access their skeletons.[10] One of the methods to showcase multiple regioselective examples of via acid-catalyzed intramolecular hydroarylation of alkenes was reported by Sames and coworkers (Scheme 3).[11]



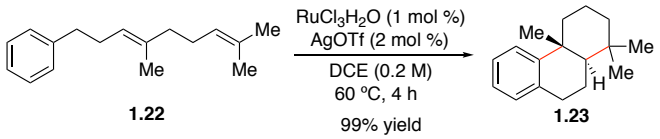
Scheme 3. Optimized reaction conditions for the cyclization of homoallylic aryl ether.

They explored the intramolecular cyclization of arene-olefin molecules for which they found that the cyclic products could be obtained by employing catalytic amount of ruthenium (III) chloride (5 mol %) and silver triflate (10 mol %) in 1,2-dichloroethane, at 60 ºC for a period of 12 h. Even though Ru based transition metals are expensive but $RuCl_3$ is easily handled. A wide variety of products could be obtained yielding tetralins, chromanes, dihydrobenzofurans, dihydrocoumarins, tetrahydroquinolines and indoles. Although, it was noted that the formation of side products was inevitable; for example, when using substrate 1-(but-3-en-1-yloxy)-3,5-dimethylbenzene **1.4**, a total of eight products were obtained.

Table 1. Ru(III)-catalyzed cyclization of arene-olefin substrates via intramolecular electrophilic hydroarylation.

entry	substrate	products	combined yield (%)
1	 **1.6**	 **1.7**	82
2	 **1.8**	 **1.9** + **1.10** (82:18)	80
3	 **1.11**	 **1.12** + **1.13** (65:35)	77
4	 **1.14**	 **1.15** + **1.16** (57:43)	79
5	 **1.17** $E=CO_2Et$	 **1.18** + **1.19** (64:36)	85
6	 **1.20**	 **1.21**	73

Cyclization of pent-4-en-1-ylbenzene **1.6** resulted in formation of the tetralin product in decent yield (82%). Interesting substrate scope shed some light on the regioselectivity. When the olefin **1.8** was subjected to hydroarylation, six- and five-membered ring products were obtained in 82:18 ratio respectively. This result indicates that six-membered ring occurred faster than five-membered ring, perhaps due to the less ring strain. Five-membered ring was formed because the generated carbocation is on a tertiary carbon, and therefore more stable than the other carbocation that gives rise to the six-membered ring. By manipulating the stability of carbocation, we can change the regioselectivity ratio. For the reaction where methoxy was used as the substituent **1.11**, the ratio obtained was 65:35, while it was 57:43 when the substituent was a hydroxyl group **1.14**. Surprisingly, a very similar ratio, 64:36, was obtained when the methoxy group was retained but instead a CO_2Et group was added at the terminal side of the olefin, **1.17**; one could have expected this ester group, being bulkier than a hydrogen atom, could have a greater influence on promoting the cyclization to the less steric site, however, even though the less steric tetralin was obtained, its yield was not enhanced. Unlike substrate **1.8**, no five-membered ring was observed in this example. The methoxy substituent, being an electron donating group could enhance the rate of cyclization and predominantly favors the formation of six-membered ring which has less angle strain. Interestingly, when the substrate 2-(but-3-en-1-yloxy)naphthalene **1.20** was submitted to the reaction conditions, two regiosomeric products could be obtained; however, cyclization only took place at the most nucleophilic carbon, showing the nucleophilicity had a bigger effect than sterics. Lastly, they sought to apply their methodology to a more complex substrate. Acid-catalyzed cyclizations to access polycyclic terpenoids are commonly used.[12] Interestingly, through hydroarylation of **1.22**, the polycyclic terpenoid **1.23** was obtained quantitatively in 99% yield with using a combination of 1 mol % of $RuCl_3H_2O$ and 2 mol % of AgOTf (Scheme 4).



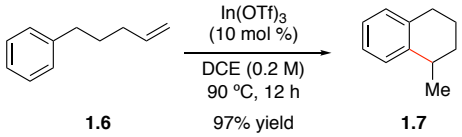
Scheme 4. Synthesis of polycyclic terpenoid through intramolecular hydroarylation.

In summary, a variety of carbocycles, chromane, terpenoid and dihydrocoumarin derivitavies could be obtained in good yields by employing catalytic amount of $RuCl_3$/AgOTf. A more detailed substrate scope containing modifications on different moieties of the substrate with various substituents is needed in order to understand the regioselectivity trends better.

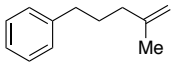
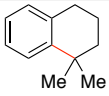
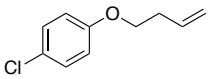
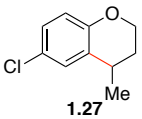
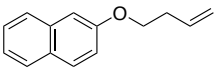
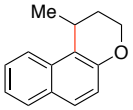
In another work, Tan et al. employed $In(OTf)_3$ as a catalyst for the cyclization of φ-aryl-1-alkenes to form tetralin and chromane derivatives (Table 2).[13] This work showed to be as effective methodology as what Sames[11] had reported earlier. They screened different Lewis acid catalysts for the optimization. They found that when submitting pent-4-en-1-ylbenzene **1.6** to Sames' conditions, the cyclized product **1.7** was obtained in 85% yield which was consistent with the results previously reported; however, they

observed that an additional 8% yield was due to a mixture of isomerization products. Initial catalytic tests with indium (III) chloride proved to be unsuccessful as no reaction was observed; thus, they decided to test a stronger Lewis acid, indium(III) triflate.

Table 2. Indium-catalyzed intramolecular hydroarylation under optimized conditions.



1.6 97% yield **1.7**

entry	substrate	product	yield (%)
1	 **1.24**	 **1.25**	89
2	 **1.26**	 **1.27**	62
3	 **1.20**	 **1.21**	61

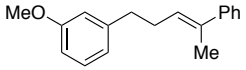
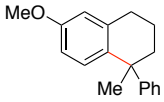
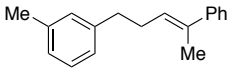
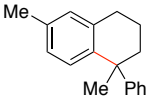
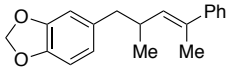
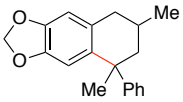
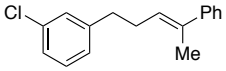
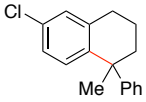
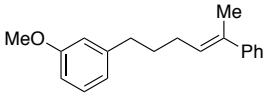
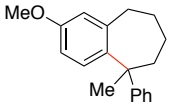
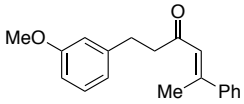
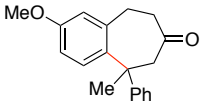
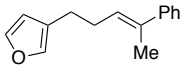
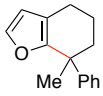
This acid gave really good results as the desired cyclic product **1.7** was obtained in 97% yield with no side products. They also found that the reaction worked with iron (III) chloride but this acid required stoichiometric amounts to yield 81% when 1.1 equivalent of the catalyst was used.

The reaction for tetralin formation worked well for monosubstituted and disubstituted olefins. When substituting the phenyl ring at the *para* position, chromanes were formed with electron withdrawing group, for example, compound **1.27** was obtained in 62%. By replacing the phenyl moiety with a naphthyl one, **1.20**, the reaction preceded in a 61% yield exclusively by cyclizing at the most nucleophilic position, **1.21**. This reaction was limited to the olefins that were three methylenes away from the phenyl group as 4-phenyl-1-butene failed to give the cyclized product. It was also limited to terminal alkenes because the intenal alkene, (*E*)-hex-4-en-1-ylbenzene did not cyclize. It was believed that the indium triflate would complex with the olefin allowing for the cyclization via EAS from which after a series of deprotonation/protonation, the desired product could form. $In(OTf)_3$ was found to be an effective catalyst for these types of cyclization. However, the less Lewis acidic $InCl_3$ was ineffective and $FeCl_3$ worked only when stoichiometric amount was used. Main limitation of this methodology was failing to cyclize the internal alkenes efficiently. The attempts to make polycyclic terpenoids also failed. One advantage of using In(III) salts over the Ru(III) catalysts is the cost, especially when the reaction had to be run on large scales. In conclusion, the scope of the $RuCl_3$/AgOTf is broader than the $In(OTf)_3$ catalyzed reactions.

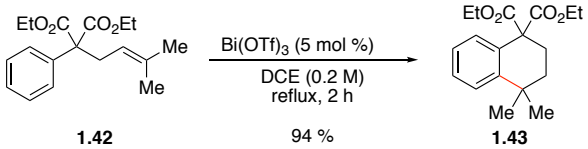
In a related work, West et al. reported atom-economic synthetic route toward tetralins through Brønsted acid-catalyzed intramolecular hydroarylation of 1,1-disubstituted olefin by employing trifluoromethanesulfonimide as a catalyst (Table 3).[14] Even though no optimization was done, most reactions proceeded in similar conditions by employing 0.5–1 mol % acid in DCE or DCM with microwave heating or reflux. This methodology gives access to five- to seven-membered carbocycles with good to excellent yields. In Table. 3 (entry 1–7), two possible regioisomers could potentially form. However, only one isomer was observed throughout the scope. For substrates **1.28**, **1.30** and **1.36** (entry 1, 2, 5) no microwave heating was required perhaps due to the electron donating abilities of methoxy and methyl functional groups. Substrate **1.32** (entry 3) gave a diastereomeric product. Substrate **1.34** also gave single regioisomer **1.35**. For this reaction, microwave heating was perhaps needed to push the reaction forward due to the electron withdrawing nature of *chloro* functional group. Interestingly, substrate **1.36** gave seven-membered carbocycle **1.37** in 60% yield. The enone substrate **1.38** was unreactive under the employed reaction conditions and yielded no cyclized product. And finally, furan **1.40** gave single regioisomer product **1.41** in 56% yield. In some reported examples by West, microwave heating was needed to push the reaction forward. In this system, the formation of the minor regioisomer is diminished, most likely due to the highly substituted olefin substrates. Due to the steric bias in this system, the electronic effects could not be evaluated.

Tetralin formation via intramolecular hydroarylation has also been studied by Duñach et al. (Scheme 5).[15a,b] They submitted substrate diethyl 2-(3-methylbut-2-en-1-yl)-2-phenylmalonate **1.42** to different catalytic conditions employing metal triflate catalysts. They observed that this type of metals allowed for the reaction to occur although only scandium (III), indium (III) and bismuth (III) afforded the tetralin product **1.43** in yields above 90%; bismuth (III) triflate, being a more benign compound, was opted as the catalyst employing 1, 5 or 10 mol % depending on the substrate. The reaction was run either in 1,2-dicloroethane or nitromethane under reflux.

Table 3. Superacid-catalyzed FC cyclization of unactivated alkenes.

entry	substrate	reaction conditions	products	combined yield (%)
1	 **1.28**	0.5 mol % Tf_2NH, 0.05 DCM, reflux 1 h	 **1.29**	94
2	 **1.30**	0.5 mol % Tf_2NH, 0.05 DCM, reflux 2 h	 **1.31**	92
3	 **1.32**	1.0 mol % Tf_2NH, 0.05 DCE, 180 °C (microwave), 15 min	 **1.33**	90 (2.8:1) dr
4	 **1.34**	1.0 mol % Tf_2NH, 0.05 DCE, 180 °C (microwave), 2 h	 **1.35**	87
5	 **1.36**	1.0 mol % Tf_2NH, 0.05 DCM, reflux, 20 h	 **1.37**	60
6	 **1.38**	1.0 mol % Tf_2NH, 0.05 CD_2Cl_2, reflux, 21 h; then 100 °C (microwave), 30 min	 **1.39**	0
7	 **1.40**	1.0 mol % Tf_2NH, 0.05 DCE, 180 °C (microwave), 5 min	 **1.41**	56

1.42 to different catalytic conditions employing metal triflate catalysts. They observed that this type of metals allowed for the reaction to occur although only scandium (III), indium (III) and bismuth (III) afforded the tetralin product **1.43** in yields above 90%; bismuth (III) triflate, being a more benign compound, was opted as the catalyst employing 1, 5 or 10 mol % depending on the substrate. The reaction was run either in 1,2-dicloroethane or nitromethane under reflux.



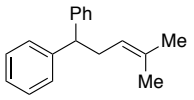
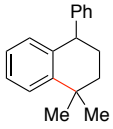
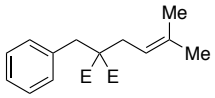
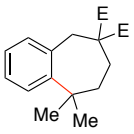
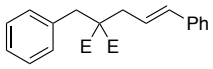
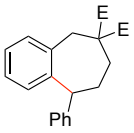
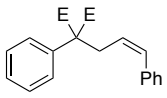
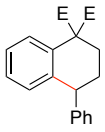
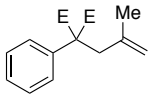
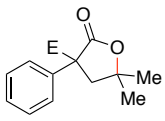
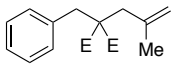
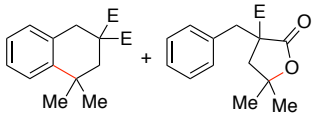
1.42 94 % **1.43**

Scheme 5. Intramolecular hydroarylation catalyzed by $Bi(OTf)_3$.

The arene-olefin substrates employed in this work contained either 1 or 2 electron withdrawing groups (-CN and/or $–CO_2Et$) and one electron donating group (Ph) at their

homoallylic position. The intramolecular cyclization was most likely promoted by the presence

Table 4. Scope of $Bi(OTf)_3$-catalyzed intramolecular hydroarylation of alkenes.

entry	substrate	products	combined yield (%)
1	 **1.44**	 **1.45**	95
2	 **1.46**	 **1.47**	51
3	 **1.48**	 **1.49**	80
4	 **1.50**	 **1.51**	97
5	 **1.52**	 **1.53**	96
6	 **1.54**	 **1.55** (56:44) **1.56**	95

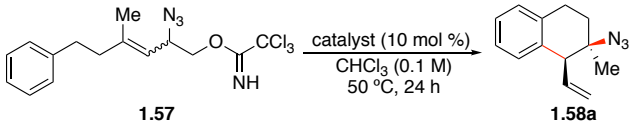
E = CO_2Et

of the electron withdrawing groups (Table 4). Interestingly, one of their substrates, (4-methylpent-3-ene-1,1-diyl)dibenzene **1.44** did not contain electron withdrawing groups yet it gave the tetralin product in good yield, 95%. It seemed that the substituents on the olefin played a major role on the regioselective outcome of the reaction probably due to the different stabilities of the formed carbocations. Trisubstituted olefins gave the carbon–carbon cyclic products in yields around 90% for the most part in the case of tetralins, and 51% and 80% for the benzosuberan products **1.47** and **1.49** respectively. The benzosuberan yields were not as high as those of tetralins probably due to the greater stability of 6-membered ring over 7-membered ring. Disubstituted alkenes presented interesting regioselective results. When submitting **1.50**, a 1,2-disubstituted olefins with a phenyl substituent, to the reaction conditions, only the tetralin product was obtained in 97% yield. In the case of 1,1-disubstituted olefins, the lactone product was obtained

either as the only product or as the major one; for example, in the case of **1.52**, the product **1.53** was the only one observed, whereas, in the case of **1.54**, a 56:44 mixture of tetralin to lactone, respectively, was obtained.

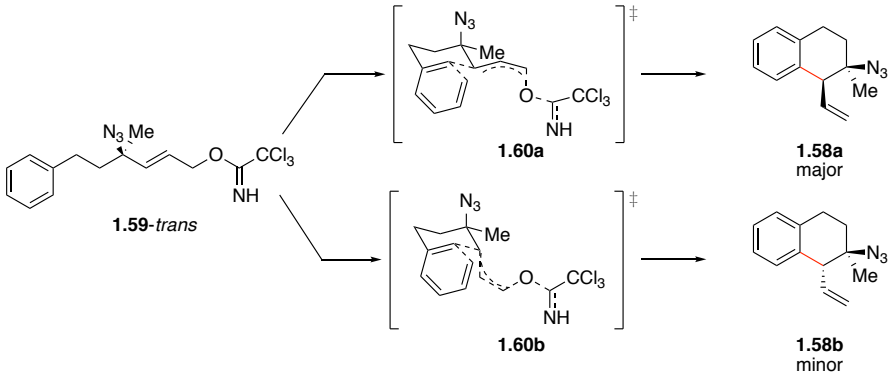
In a related intramolecular acid-catalyzed reaction, Corey et al. reported the cyclization of a β-homobenzylbutene substrate.[16] In their efforts of proving the catalytic activity of the combined triflimide and titanium (IV) chloride, they submitted (4-methylpent-3-en-1-yl)benzene to different catalytic conditions. They showed that the biscoordinating Lewis acid enhances the acidity of an exceedingly strong protic acid like triflimide.

Table 5. Hydroarylation optimization of allylic azides.



1.57 **1.58a**

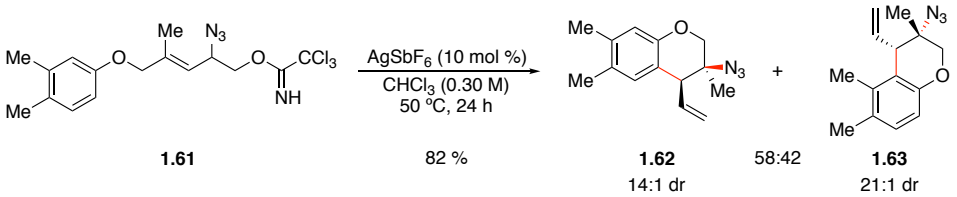
entry	catalyst	yield (%)	dr
1	BF_3•OEt_2	35	28:1
2	Tf_2NH	80	13:1
3	JohnPhosAuSbF$_6$	75	21:1
4	$AgClO_4$	81	7:1
5	$AgSbF_6$	92	21:1



Scheme 6. Proposed transition states for the stereochemical outcome.

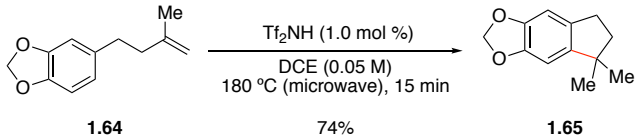
Recently, Topczewski et al. accomplished the stereoselective synthesis of 3-azido-tetralins and chromanes via a tandem allyluc azide rearrangement and FC alkylation.[17] In their strategy, trichloroamide was used as the protecting group because it could readily get activated under electrophilic conditions (Table 5). Reaction optimization on allylic azide **1.57** with numerous Lewis, Brønsted acids and transition metal complexes gave different percent yields and diasterselectivity. Although the BF_3OEt_2 gave excellent diastereoselectivity (entry one), but thpercent yield was diminished to 35%. Silver salts

with noncoordinating counterions (entry 4-5) showed to be effective catalysts for this transformation. Reaction with AgSbF6 (entry 5) is mild, high yielding, highly stereselective. The stereochemical outcome was described based on chair like transition states (Scheme 6). Th diastereoselectivity is shown in two pathways in which the orientation of the vinyl groups is different. The major diastereomer is fromed through a pseudoequatorial orientation when the hydrogen of the vinyl group is facing anti to the methyl group. When a bigger group than methyl was used, the diastereoselectivity improved and when methyl was replaced by hydrogen, the diastereoselectivity was decreased. When cyclization was conducted on substrate **1.61**, two regioisomers **1.62** and **1.63** were formed in 58:42 ratio respectively. Even though, this reaction is highly stereoselective, but only slight preference was given to the formation of less hindered product. No other regioselective example was attempted in this report.



Scheme 7. Stereoselective $AgSbF_6$-catalyzed hydroarylation of allylic azides.

In addition to the tetralin synthesis, chemists have also been interested in making indanes. Indanes are backbone for many natural products and pharmaceutical drugs.[18] Moreover, they have been found to have application in material science.[19] One classical approach to indane analogs synthesis is through dimerization of α-methyl styrene precursors.[20] The main drawback to dimerization is that only limited number of compounds can be made, and further functionalization becomes very difficult. It may also be challenging to control the reaction to avoid formation of linear dimer or cyclic trimer. Blunt and coworkers have also reported the formation of a 1,1,3-trisubstituted through intramolecular hydroarylation of the olefin using TsOH as a catalyst. However, the focus of Blunt's work wasn't indane synthesis, no scope or further investigation was performed.

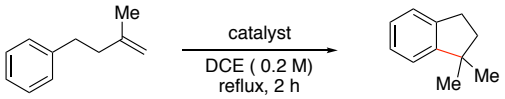


Scheme 8. Superacid-catalyzed FC cyclization of unactivated alkenes to form indane.

West et al.[14] were also able to synthesize indane **1.65** through intramolecular hydroarylation of the olefin **1.64** by employing catalytic amount of trifluoromethanesulfonimide (Scheme 8). Interestingly only one regioisomer was formed. The selectivity could be attributed to both the sterics and electronics. No six-membered ring was formed due to the stability of the carbocation at the more substituted position.

Duñach and coworkers also reported synthesis of indane **1.67** in excellent yield under Bi(III) and In(III) catalysis.[15b] The reaction can work with as low as 1 mol % catalyst loading under reflux (Table 6). The acidity of the catalyst is enhanced through coordination with water molecules. Therefore, the proton that is added to the carbocationic intermediate comes from the Bi(III)- or In(III)-activated water molecules. Furthermore, this atom-economic methodology gives access to a variety of carbocyclic products.

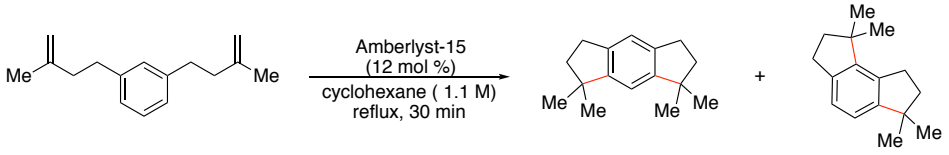
Table 6. FC-type cyclization to form indane under Bi(III) and In(III) catalysis.



1.66 **1.67**

entry	conditions	yield (%)
1	$Bi(OTf)_3 \cdot 4H_2O$ (5 mol %)	97
2	$Bi(OTf)_3 \cdot 4H_2O$ (1 mol %)	97
3	$In(OTf)_3 \cdot H_2O$ (5 mol %)	96
4	$In(OTf)_3 \cdot H_2O$ (1 mol %)	96

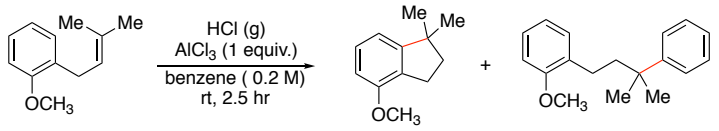
The acid-catalyzed hydroarylation yielding indane products was investigated by Flanagan et al. in which they used Amberlyst-15 to induce cyclization of the 1,3-diolefinic benzene substrate **1.68** (Scheme 9).[21] The cyclization occurred by employing 12 mol % of the catalysts Amberlyst-15 and allowing the reaction mixture to reflux for 30 minutes; the reaction resulted in a 98% yield of a 1:1 isomeric mixture of **1.69** and **1.70**. It was surprising to observed how this resulted in a 1:1 isomeric mixture even though statistically the products should have resulted in a 2:1 ratio of **1.70** and **1.69**, respectively. This is probably due to the greater sterics present in isomer **1.70**.



1.68 98 % **1.69** 50:50 **1.70**

Scheme 9. Amberlyst-15- catalyzed FC cyclization of alkenes to form indane.

In 1981, Okogun and Fatope discovered that a mixture of aluminum (III) chloride and hydrogen chloride made *in situ* from concentrated hydrochloric acid and concentrated sulfuric acid could promote the hydroarylation of 2-olefinic anisole, **1.71**, in benzene at ambient temperature, which yielded the indole product **1.72** in 60%.[22] This methodology was later on used by Xia et al. (Scheme. 10).[23] Initially, Xia's group wanted to make 1,1-dimethyl-4-indanol compounds by performing the hydroarylation on olefins **1.74** and **1.77**. The reaction was carried out under acidic conditions employing aluminum (III) chloride and hydrogen chloride which this time was generated from sodium chloride and sulfuric acid. As seen on Table 7, substrate **1.74** was submitted to these condition;



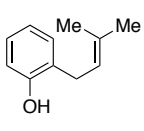
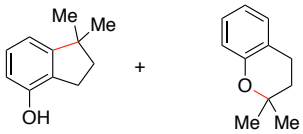
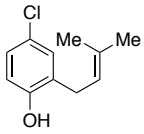
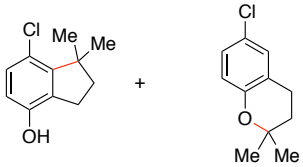
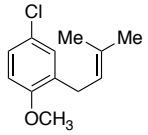
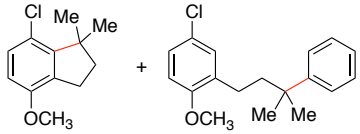
1.71 60 % [a] 63 % [b] **1.72** 100:0 21:79 **1.73**

[a]Results obtained by Okogun and Fatope. [b]Results obtained by Xia's group

Scheme 10. Acid-catalyzed hydroarylation of *β*-benzylisobutenes to form indanes.

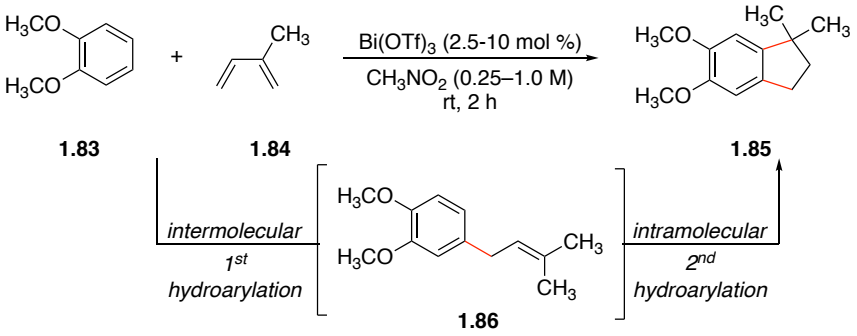
however; this reaction gave chemoisomeric products in which the major isomer was that in which cyclization occurred between the vinyllic carbon and the oxygen forming a six-membered ring, **1.76**, in 73%, while the desired product, the indane, **1.75**, was obtained as the minor product in only 15%. This reaction was performed on an additional substrate, **1.77**, which contained a *chloro* group at position 4. Once again, the indane product **1.78** was the minor one which was obtained in 12%, while the chromane product **1.79** was the major one, although this time it was formed in a lower yield, 39%. The reduced yield for the chromane **1.79** compared to its analogous **1.76** is probably due to electron density being pulled away from the oxygen atom by the electronegative *chloro* atom; thus, resulting in a decrease on the nucleophilicity of the oxygen. In attempts of forming only the indane product, the olefins **1.74** and **1.77** were protected with a methoxy group and then they were submitted to the aforementioned conditions. This route suppressed formation of the chromane product; however, a mixture of intramolecular and intermolecular products was obtained. In the case of substrate **1.71**, the indane product **1.72** was obtained in a 13% yield, while the intermolecular product, **1.73**, formed by addition of the solvent to the olefin, resulted in a 50% yield. This result was significantly different from that

Table 7. Scope of acid-catalyzed hydroarylation of *β*-benzylisobutenes.

entry	substrate	products		combined yield (%)
1	 **1.74**	 **1.75** + **1.76**	17:83	88
2	 **1.77**	 **1.78** + **1.79**	24:76	51
3	 **1.80**	 **1.81** + **1.82**	58:42	55

obtained by Okogun since only about one fourth of the indane product was obtained and an
additional product was observed. The only difference between these procedures is the way in which hydrogen chloride was generated. In the case of substrate **1.80**, the indane product **1.81** was obtained in a 32 % yield and the intermolecular product **1.82** in a 23% yield. The substrate with the *chloro* substituent gave better results as the indane product was the major one; the electronegativity of this atom influences the electronics of the phenol, making the cyclization at carbon 3 more suitable. In order to eliminate the formation of the intermolecular product different solvents were screened; employing substrate **1.71**, the used of hexane resulted in the formation of indane exclusively, although the yield was diminished, 8% yield; cyclohexane also gave solely the indane product in 19% yield; the use of carbon disulfide resulted in formation of two products, the indane in 38% yield and a tricyclic compound in 3% yield. Carbon disulfide was a better solvent for this reaction since the nature of this compound prevented it from reacting with the substrate and perhaps the solubility was better as well.

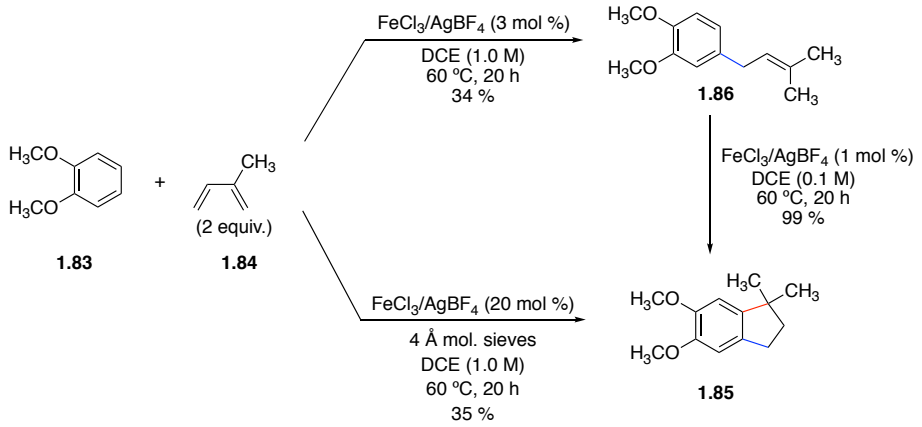
Table 8. Intermolecular hydroarylation catalyzed by $Bi(OTf)_3$ optimization for the formation of indane.



entry	reaction conditions	yield (%)
1	0.25 mmol **1.83**, 6 equiv. **1.84**, 5 mol % cat., 0.25 M	54
2	0.50 mmol **1.83**, 3 equiv. **1.84**, 5 mol % cat., 0.50 M	61
3	1.00 mmol **1.83**, 1.5 equiv. **1.84**, 5 mol % cat., 1.0 M	79
4	1.00 mmol **1.83**, 1.5 equiv. **1.84**, 2.5 mol % cat., 1.0 M	42
5	1.00 mmol **1.83**, 1.5 equiv. **1.84**, 10 mol % cat., 1.0 M	33
6	1.00 mmol **1.83**, 1.5 equiv. **1.84**, 5 mol % cat., 1.00 M, 40 ºC	44

It is noteworthy that gem-dimethyl moeities have shown importance in medicinal chemistry.[24] Duñach and coworkers reported synthesis of indanes through double hydroarylation of unactivated 1,3-dienes by employing $Bi(OTf)_3$ as acatalyst.[25] In this reaction, 1,2-dimethoxy benzene was reacted with isoprene in the presence of a variety of different lewis acids. During the optimization studies, the formation of intermolecular molecular as asole product was observed when 1 mol% of catalyst was used. By increasing the catalyst loading to 5 mol%, the reaction went into completion and afforded the indane **1.85** in 79% yield. This reaction was also highly regioselective. There are two potential sites for cyclization. However, a single regioisomer at the less hindered position is formed.

In a very similar work, Eichman's group reported synthesis of prenylated arenes and 2,2-dimethylchromanes through FC-type coupling between activated arenes and isoprenes.[26] They observed an interesting transformation in which the formation of intermolecular and intramolecular products could be controlled by changing the reaction conditions (Scheme 11). When optimized conditions was conducted on veratrole **1.83**, the desired intermolecular product **1.86** was formed in 34% yield. However, trace amounts of indane products were formed as well. By subjecting the intermolecular product to the optimized condition with the exception of using 1 mol % catalyst, the intramolecular product, indane **1.85** was formed in quantitative yield. Interestingly, only 35% of indane product could be obtained upon a one-pot reaction. A high catalyst loading perhaps polymerized the reactive alkenes and caused the percent yield to diminish. These studies are a good indication that the reaction perhaps goes through a carbocationic intermediate first before cyclization. Some regioselective studies were attempted in which the veratrole was replaced by phenol (Table 9). In this reaction, two new bonds are formed (C–C and C–O). Substrate **1.87a** with a methyl substituent group gave two regioisomers **1.88a** and **1.89a** in equal amounts. When methyl was replaced by isopropyl which is bulkier, substrate **1.87b** gave the less hindered product **1.88b** as the major product. Substrate **1.87c** also gave the less hindered product **1.88c** as the major product. These studies show that the steric dictated the regioselectivity. In the case of naphthol **1.87d**, the cyclization happened exclusively at the more nucleophilic carbon and gave the product in 94% yield.

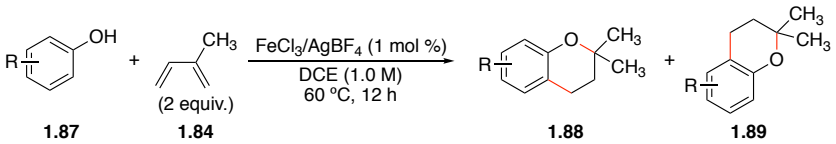


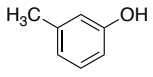
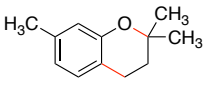
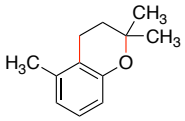
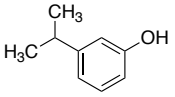
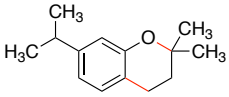
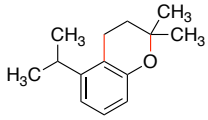
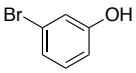
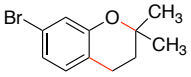
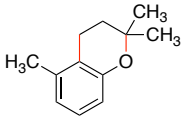
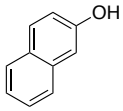
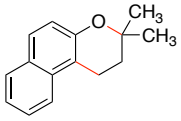
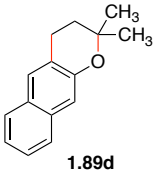
Scheme 11. Intramolecular and intermolecular hydroarylation catalyzed by $FeCl_3/AgBF_4$

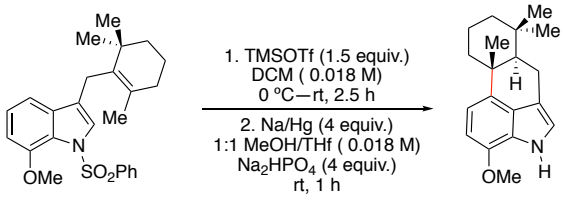
1,1-diaryl compounds are important building blocks for numerous pharmacophores.[24] Acid-catalyzed intramolecular hydroarylation of alkenes is one method that can give access to their skeletons. Recently Mahapatra[27] reported the regioselective intramolecular hydroarylation of indoles at the C–4 position (Scheme 12). In their efforts of synthesizing (-)-Mycoleptodiscin, the group planned on working with indoles substituted at their position 3 with an olefinic moiety to promote an intramolecular hydroarylation at position 4 on the indole. With the purpose of preventing cyclization at position 2, which is more nucleophilic than carbon 4, the group modified the electronics of the indole. The nitrogen was protected with a phenyl sulfonyl, an electron withdrawing group, which via

resonance decreases the nucleophilicity at position 2; also, a methoxy, an electron donating group, was introduced at position 7 in order to increase the nucleophilicity at position 4. Different Lewis and Brønsted acids were tested for their catalytic activity promoting the intramolecular hydroarylation of **1.90**, of which, only aluminum (III) chloride, tin (IV) chloride, and trimethylsilyl trifluoromethanesulfonate allowed for the cyclization to take place. Trimethylsilyl trifluoromethanesulfonate was opted as the optimal catalyst as 1.5 equivalents of it resulted in an overall yield, following cyclization and desulfonation, of 63%, which was about twice of that afforded with the Lewis acids. The reaction worked for both terminal and internal alkenes giving similar yields (Table 10).

Table 9. Regioselective intermolecular hydroarylation catalyzed by $FeCl_3/AgBF_4$.



entry	substrate	products			combined yield (%)
1			+		41
	1.87a	**1.88a**	50:50	**1.89a**	
2			+		54
	1.87b	**1.88b**	75:25	**1.89b**	
3			+		69
	1.87c	**1.88c**	67:33	**1.89c**	
4			+		94
	1.87d	**1.88d**	>95:5	**1.89d**	

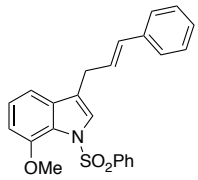
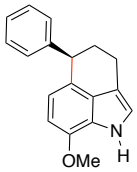
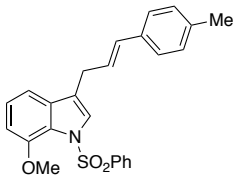
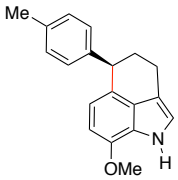
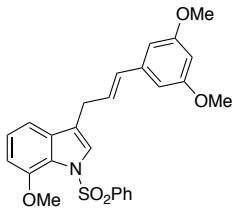
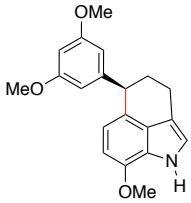
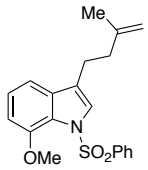
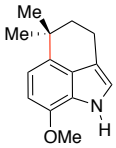
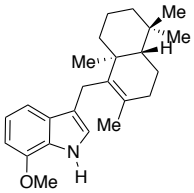
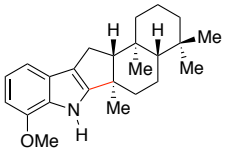
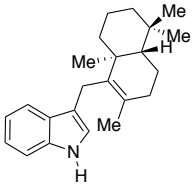
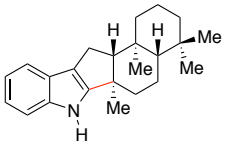


1.90 63 % **1.91**

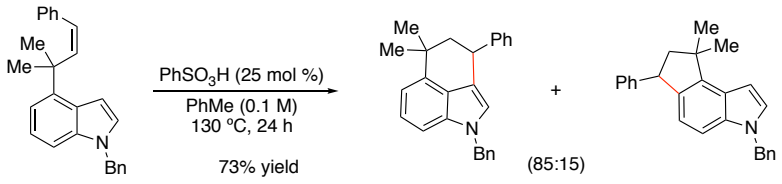
Scheme 12. Optimized reaction conditions for acid-catalyzed C–4 cyclization and desulfonation.

For internal alkenes, the styrene moieties were used. When no substituents were added to the phenyl ring, **1.92a**, the reaction proceeded with a 65% yield after desulfonation. Similar yields were obtained when the phenyl ring was functionalized with electron donating groups, for example, when a methyl group was added at the *para* position, **1.92b**, the product **1.93b** was obtained in a 64%, while functionalizing the phenyl ring with methoxy groups at positions 3 and 5, **1.92c**, resulted in a 57% yield. In the case of the external alkene, **1.94**, the product **1.95** was obtained in a 68% yield. In order to test if the methoxy group at position 7 and the phenyl sulfonyl were required to promote the cyclization selectively, these groups were omitted. When substrate **1.96**, which did not contain the phenyl sulfonyl group, was submitted to the reaction conditions, the cyclization took place exclusively at position 2 in an 80% yield. This showed the need of the electron withdrawing group in order to decrease the nucleophilicity of carbon 2 in the indole. Substrate **1.98**, which did not contain the phenyl sulfonyl nor the methoxy group also resulted in the cyclization at position 2 in 86% yield. The slight increase in the yield of this compound compared to its analog **1.97** shows that the inductive effect of the methoxy group might have slowed down the cyclization at carbon 2. The strategy of using both the methoxy group at carbon 7 and protecting the nitrogen with trimethylsilyl trifluoromethanesulfonate in order to bias the nucleophilicity of the carbon at position 2 in the indole proved to be efficient as the reaction conditions afforded the desired isomer exclusively.

Table 10. Intramolecular hydroarylation of various C–4 indoles.

entry	substrate	product	yield (%)
1	 **1.92a**	 **1.93a**	65
2	 **1.92b**	 **1.93b**	64
3	 **1.92c**	 **1.93c**	57
4	 **1.94**	 **1.95**	68
5	 **1.96**	 **1.97**	80
6	 **1.98**	 **1.99**	86

In a related work, dispersion-controlled Brønsted acid-catalyzed hydroarylation of *cis*-Methindolystyrenes was reported by Stokes group.[28] Tetrahydrobenzo[*cd*]indole and tetrahydrocyclopenta[*e*]indole were synthesized as regioisomeric products of the intramolecular hydroarylation of *cis*-indole-olefins. It was expressed that *cis* isomers were necessary for the hydroarylation reaction to occur since the *trans* isomers usually gave oligomeric products. The cyclization of **1.100a** was possible by protecting the indole moiety, employing catalytic amount of benzenesulfonic acid, 25 mol %, and allowing the reaction to reflux in toluene for a period of 24 hours. The cyclization to form six-membered ring is attributed to nucleophilicity and the dispersive interactions between the indole and styrenyl moieties via concerted protonation and C–C bond formation. A regioisomeric mixture of products was obtained in an 85:15 ratio, tetrahydrobenzo[*cd*]indole **1.101a** and tetrahydrocyclopenta[*e*]indole **1.102a**, respectively, showing that in addition to the dispersive intractions, electronics also dictate the regioselective outcome of the reaction (Scheme 13).

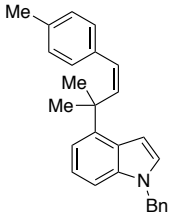
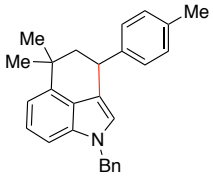
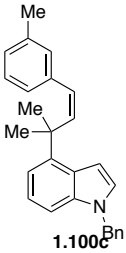
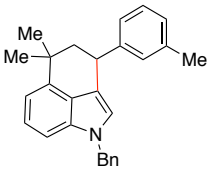
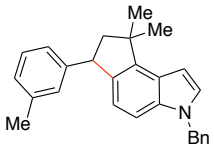
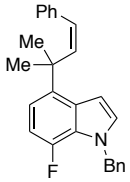
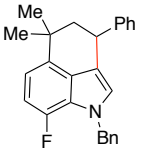
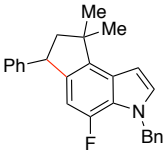
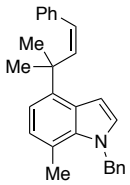
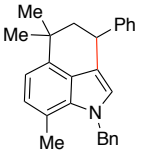
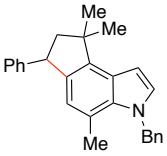
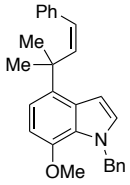
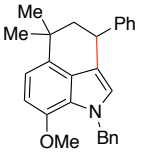
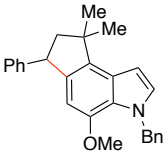


1.100a **1.101a** **1.102a**

Scheme 13. Acid-catalyzed intramolecular hydroarylation of *cis*-methindolylstyrenes.

The regioselectivity was studied by modifying both the phenyl in the styrene moiety and the phenyl in the indole moiety (Table 11). When a methyl group was added *para* to the styrene moiety, **1.100b**, it was observed that this particular substrate cyclized exclusively at the most nucleophilic carbon affording the tetrahydrobenzo[*cd*]indole product **1.101b** in good yield, 85 %. On the other hand, when this methyl group was placed at the *meta* position, **1.100c**, a combined 74 % yield of both regioisomers was obtained in an 84:16 ratio, in which the tetrahydrobenzo[*cd*]indole **1.101c**, a fused tricycle compound, was once again the predominant product. The indole moiety was substituted with electron donating and electron withdrawing groups at position 7. When fluorine, an electron withdrawing group, **1.100d**, was employed, the reaction proceed in good yield, 90%, of which it was a regiosomeric mixture 95:5 containing mainly the fuse tricyclic product **1.101d**. However, the yield decreased when the indole was substituted with electron donating groups; probably due to the decrease in nucleophilicity at carbon 2. Specifically, when a methyl substituent was used, **1.100e**, the yield obtained was 55 % of a 79:21 mixture, containing mainly the tetrahydrobenzo[*cd*]indole **1.101e**. Surprisingly, when a stronger donating group, methoxy, was used, **1.100f** the main product formed was the tetrahydrocyclopenta[*e*]indole **1.102f**; the combined yield was 32 % and the regioisomeric ratio was 95:5. In conclusion, the regioselectivity was dictated by nucleophilicity and dispersive interactions between the indole and styrenyl moieties, which are forced into close proximity due to the geminal dimethyl group.

Table 11. Scope of the cyclization of *cis*-methindolylstyrenes analogs.

entry	substrate	products			combined yield (%)
1	 **1.100b**	 **1.101b**			85
2	 **1.100c**	 **1.101c**	84:16	 **1.102c**	74
3	 **1.100d**	 **1.101d**	95:5	 **1.102d**	90
4	 **1.100e**	 **1.101e**	79:21	 **1.102e**	55
5	 **1.100f**	 **1.101f**	<5:95	 **1.102f**	32

References

1) Friedel, C.; Crafts, J. M. *J. Chem. Soc.* **1877**, *32*, 725.
2) Rueping, M.; Nachtsheim, B. J. *Beilstein J. Org. Chem*. **2010**, *6*, 6.
3) Bhattacharya, A.; Shukla, P. M.; Maji, B. *R. Soc. Open Sci.* **2017**, *4*, 170748.
4) Galabov, B.; Nalbantova, D.; Schleyer, P. V. R.; Schaefer III, H. F. *Acc. Chem. Res.* **2016**, *49*, 1191.
5) (a) Fievez, T.; Pinter, B.; Geerlings, P.; Bickelhaupt, M.; De Proft, F. *Eur. J. Org. Chem.* **2011**, *16*, 2958. (b) Liu, S. *J. Chem. Phys.* **2014**, *141*, 194109. (c) Liu, S. *J. Phys. Chem. A*. **2015**, *119*, 3107. (d) Galabov, B.; Nalbantova, D.; Schleyer, P. V. R.; Schaefer III, H. F. *Acc. Chem. Res.* **2016**, *49*, 1191. (e) Kromann, J. C.; Jensen, J. H.; Kruszyk, M.; Jessing, M.; Jørgensen, M. *Chem. Sci*. **2018**, *9*, 660.
6) (a) Hatfield, M. J.; Tsurkan, L. G.; Hyatt, J. L. Edwards, C. C.; Lemoff, A.; Jeffries, C.; Yan, B.; Potter, P. M. *J. Nat. Prod.* **2013**, *76*, 36. (b) Zhu, S.; Liang, R.; Jiang, H.; Wu, W. *Angew. Chem. Int. Ed.* **2012**, *51*, 10861.
7) (a) Brewster, W. K.; Nichols, D. E.; Riggs, R. M.; Mottola, D. M.; Lovenberg, T. W.; Lewis, M. H; Mailman, R. B. *J. Med. Chem.* **1990**, *33*, 1756. (b) Monte, A. P.; Marona-Lewicka, D.; Cozzi, N. V.; Nichols, D. E. *J. Med. Chem.* **1993**, *36*, 3700. (c) Boehm, M. F.; Zhang, L.; Badea, B. A.; White, S. K.; Mais, D. E.; Berger, E.; Suto, C. M.; Goldman, M. E.; Heyman, R. A. *J. Med. Chem.* **1994**, *37*, 2930. (d) Vukics, K.; Fodor, T.; Fischer, J.; Fellegvári, I.; Lévai, S. *Org. Proc. Res. Dev.* **2002**, *6*, 82. (e) Yao, B.; Ji, H.; Cao, Y.; Zhou, Y.; Zhu, J.; Lu, J.; Li, Y.; Chen, J.; Zheng, C.; Jiang, Y.; Liang, R.; Tang, H. *J. Med. Chem.* **2007**, *50*, 5293. (f) Tang, G.; Wong, J. C.; Zhang, W.; Wang, Z.; Zhang, N.; Peng, Z.; Zhang, Z.; Rong, Y.; Li, S.; Zhang, M.; Yu, L.; Feng, T.; Zhang, X.; Wu, X.; Wu, J. Z; Chen, L. *J. Med. Chem*. **2014**, *57*, 8026. (g) Diaz, Philippe.; Huang, W.; Keyari, C. M.; Buttrick, B.; Price, L.; Guilloteau, N.; Tripathy, S.; Sperandio, V. G.; Fronczek, F. R.; Astruc-Diaz, F. *J. Med. Chem*. **2016**, *59*, 2579. (h) Heck, M. C.; Wagner, C. E.; Shahani, P. H.; MacNeill, M.; Grozic, A.; Darwaiz, T.; Shimabuku, M.; Deans, D. G.; Robinson, N. M.; Salama, S. H.; Ziller, J. W.; Ma, N.; Vaart, A.; Marshall, P. A.; Jurutka, P. W. *J. Med. Chem*. **2016**, *59*, 8924. (i) Bao, X.; Qiao, X.; Bao, C.; Liu, Y.; Zhao, X.; Lu, Y. Chen, G. *Org. Process Res. Dev.* **2017**, *21*, 748.
8) (a) Martin, N.; Navarro, J. A.; Seoane, C.; Albert, A.; Cano, F. H. *J. Org. Chem.* **1992**, *57*, 5726. (b) Zhang, S.-F.; Shearman, J. R.; Domin, M.; Lazaro, M.-J.; Herod, A. A.; Kandiyoti, R. *Fuel* **1997**, *76*, 207. (c) Kraus, A.; Schneider, M.; Gugel, A.; Mullen, K. *J. Mater. Chem.* **1997**, *7*, 763.
9) (a) Hahn, S. F.; Martin, S. J.; McKelvy, M. L. Macromolecules **1992**, *25*, 1539. (b) Jordan, G. K.; Farona, M. F. *Polym. Bull.* **1998**, *40*, 9.
10) (a) Bright, S. T.; Coxon, J. M.; Steel, P. *J. Org. Chem.* **1990**, *55*, 1338. (b) Parlow, J. J. *Tetrahedron* **1994**, *50*, 3297. (c) Liebert, C.; Brinks, M. K.; Capacci, A. G.; Fleming, M. J.; Lautens, M. *Org lett*. **2011**, *13*, 3000. (d) Nammalwar, B.; Bunce, R. A. *Tetrahedron Lett* **2013**, *54*, 4330. (e) Begouin, J.-M.; Capitta, F; Wu, X.; Niggemann, M. *Org. Lett.* **2013**, *15*, 1370. (f) Jefferies, L. R.; Cook, S. P.; *Org. Lett*. **2014**, *16*, 2026. (g) Zhang, F.; Das, S.; Walkinshaw, A. J.; Casitas, A.; Taylor, M.; Suero, M. G.; Gaunt, M. J. *J. Am. Chem. Soc*. **2014**, *136*, 8851. (h) Chang, M.-Y.; Cheng, Y.-C.; Lu, Y.-J. *Org. Lett.* **2015**, *17*, 3142. (i) Gogoi, D.; Davi, R.; Pahari, P.; Sarma, B.; Das, S. K. *Beilstein J.*

Org. Chem. **2016**, *12*, 2816. (j) Reddel, J. C. T.; Wang, W.; Koukounas, K.; Thomson, R. *J. Chem. Sci.* **2017**, *8*, 2156. (k) Yoshida, T.; Mori, K. *Chem. Commun*. **2017**, *53*, 4319. (l) Watson, R. B.; Schindler, C. S. *Org. Lett.* **2018**, *20*, 68.
11) Youn, S. W.; Pastine, S. J.; Sames, D. *Org. Lett.* **2004**, *6*, 581.
12) Bartlett, P. A. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, **1984**; *3B*, 341.
13) Xie, K.; Wang, S.; Li, P.; Li, X.; Yang, Z.; An, X.; Guo, C.; Tan, Z. *Tetrahedron Lett*. **2010**, *51*, 4466.
14) Bonderoff, S. A.; West, F. G.; Tremblay, M. *Tetrahedron Letters* **2012**, *53*, 4600.
15) (a) Cacciuttolo, B.; Poulain-Martini, S.; Duñach E. *Eur. J. Org. Chem.* **2011**, 3710. (b) Cacciuttolo, B.; Poulain-Martini, S.; Fontaine-Vive, F.; Abdo, M. A. H.; El-Kashef, H.; Duñach E. *Eur. J. Org. Chem.* **2014**, 7458.
16) Thirupathi, B.; Breitler, S.; Reddy, K. M.; Corey, E. J. *J. Am. Chem. Soc.* **2016**, *138*, 10842.
17) Porter, M. R.; Shaker, R. M.; Calcanas, C.; Topczewski J. J. *J. Am. Chem. Soc.* **2018**, *140*, 1211.
18) Gabriele, B.; Mancuso, R.; Veltri, L. *Chem. Eur. J*. **2016**, *22*, 5056.
19) (a) Morales, A. R.; Frazer, A.; Woodward, A. W.; Ahn-White, H.-Y.; Tongwa, P.; Timofeeva,T.; Belfield, K. D. *J. Org. Chem*. **2013**, *78*, 1014. (b) Acikbas, Y.; Capan, R.; Namli, H.; Turhan, O.; Stanciu, J. *Optoelectron. Adv. Mater*. **2007**, *9*, 56. (c) Yang, J.; Lakshmikantham, M. V.; Cava, M. P.; Lorcy, D.; Bethelot, J. R. *J. Org. Chem*. **2000**, *65*, 6739.
20) Petropoulous, J. C.; Fisher, J. J. *J. Am. Chem. Soc.* **1958**, *80*, 1938.
21) Eisenbraun, E. J.; Harms, W. M.; Burnham, J. W.; Dermer, O. C.; Laramy, R. E.; Hamming, M. C.; Keen, G. W.; Flanagan, P. W. *J. Org. Chem.* **1977**, *42*(11) 1967
22) Okogun, J. I.; Fatope, M. O. *Bull. Soc. Chim. Belg.* **1981**, *90*(8), 847
23) Wang, Y.; Wu, J.; Xia, P. *Synth. Commun*. **2006**, *36*, 2685.
24) Ameen, D.; Snape, T. J. *Med. Chem. Commun*. *2013*, **4**, 893.
25) Cacciuttolo B.; Ondet, P.; Poulain-Martini, S. Lemière G.; Duñach E. *Org. Chem. Front.* **2014**, *1*, 765.
26) Villani-Gale, A. J.; Eichman, C. C. *Eur. J. Org. Chem.* **2016**, 2925.
27) Dethe, D. H.; Sau, S.K; Mahapatra, S. *Org. Lett.* **2016**, *18*, 6392.
28) Cai, X.; Tohti, A.; Ramirez, C.; Harb, H.; Fettinger, J. C.; Hratchian, H. P.; Stokes, B. J. *Org. Lett.* **2019**, *21*, 1574.

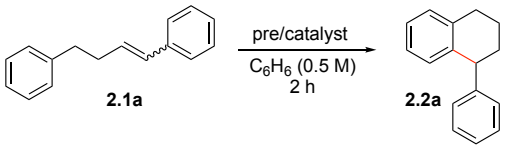
CHAPTER 2

Synthesis of Tetralins by $HB(C_6F_5)_4$-Catalyzed Intramolecular Hydroarylation of β-Homobenzylstyrenes, Isobutenes, and Propenes

Results and Discussion

We envisioned that one approach to make polysubstituted tetralins and evaluate the regioselectivity outcomes is through acid-catalyzed intramolecular hydroarylation of alkenes. To have a clear understanding of electronic and steric effects on cyclization reactions, we designed three different systems—herein *β*-homobenzylstyrenes, *β*-homobenzylbutenes, *β*-homobenzylpropenes. The olefin substrates were readily available by Wittig olefination of aldehyde. We conducted our optimization by treating *β*-homobenzylstyrenes with various acids under different conditions. Cyclization works with a number of different acids but we opted to use tetrakis(pentafluorophenyl)borate (TPFPB)[1]. TPFPB is an easily handled convenient Brønsted acid precatalyst that is an air-stable solid. Under our optimized conditions, only 2 mol % of precatalyst loading is needed to convert the olefin **2.1a** to tetralin **2.2a** (Table 9).

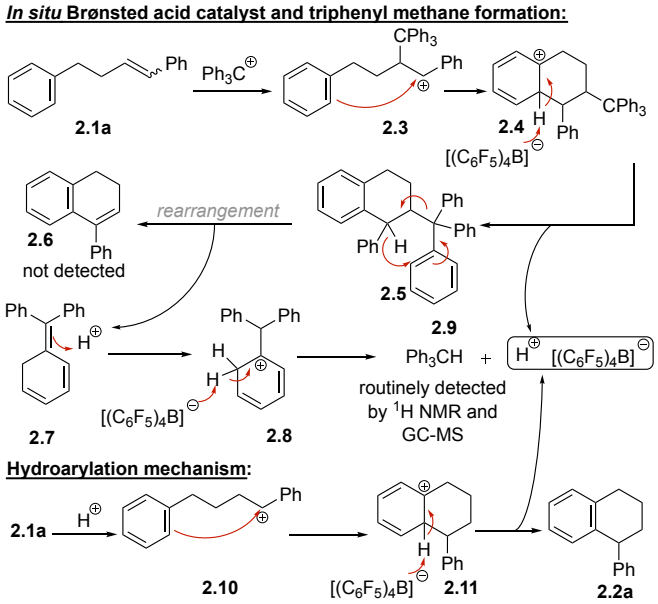
Table 12. Optimization of the intramolecular hydroarylation of *β*-homobenzylstyrenes.



entry	precatalyst or catalyst	catalyst loading (mol %)	temp (°C)	conv (%)[a] of **2.1a**	yield (%)[a] of **2.2a**
1[b]	$Ph_3CB(C_6F_5)_4$	2	rt	<5	0
2[b]	$Ph_3CB(C_6F_5)_4$	5	rt	30	28
3	$Ph_3CB(C_6F_5)_4$	2	75	100	93
4	$Ph_3CB(C_6F_5)_4$	2	50	100	93
5	HOTf	10	0→50	100	88
6	H_2SO_4	10	50	100	67
7	$Sm(OTf)_3$	10	50	<5	0
8	$Ga(OTf)_3$	10	50	<5	0
9	$InCl_3$	10	50	<5	0

All reactions were conducted on 0.1 mmol scale in a sealed dram vial. [a]Determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. [b]Reaction was run for 24 hours.

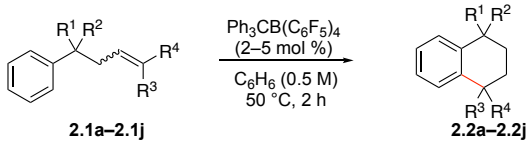
Later, we found out that 5 mol % of precatalyst loading is needed for cyclization of *β*-homobenzylbutenes and *β*-homobenzylpropenes. Otherwise, percent yield diminishes significantly. With this information in hand, we then started to study the influence of substituents along the linear substrate backbone (Table 13). We propose that the reaction gets initiated through binding of the trityl cation to the olefin starting material **2.1a**, generating a stable benzylic carbocation **2.3** which then gets attacked by the nucleophilic arene to give the cyclized intermediate **2.4** (Scheme 14). The $[B(C_6F_5)_4]^-$ will grab a proton to regenerate the aromaticity forming **2.5** via substrate sacrifice. It has been shown that $Ph_3CB(C_6F_5)_4$ enhances the stabilization of the cationic intermediates due to its weakly coordination properties.[2] Through rearrangement and protonation/deprotonation, triphenyl methane **2.9** can form which has been observed routinely by ^{1}H NMR and GC-MS. Once $H^+[B(C_6F_5)_4]^-$ is generated *in situ*, it reacts with the starting material **2.1a** to form the cationic intermediate **2.10** which gets attacked by the nucleophilic arene

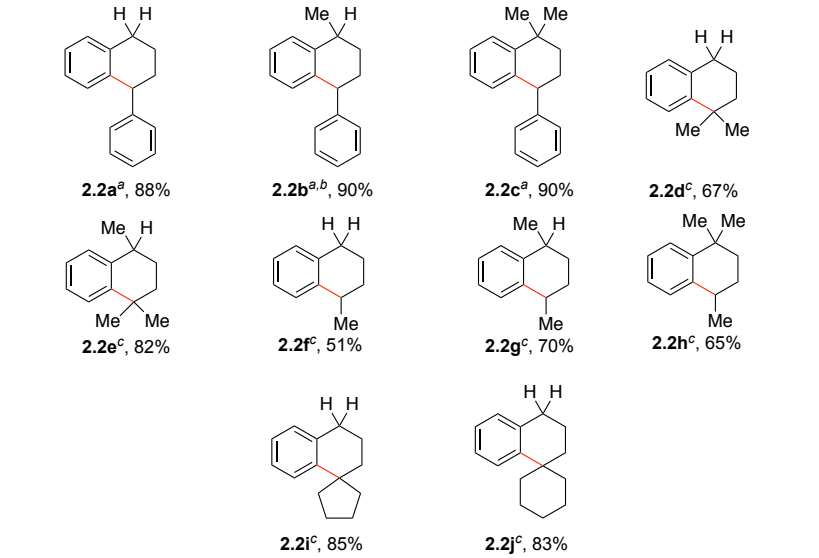


Scheme 14. Hypothesized Brønsted acid-catalyzed mechanism.

followed by deprotonattion with $[B(C_6F_5)_4]^-$ and aromatization of **2.11** to form the tetralin product **2.2a**. We wanted to see if dialkyl substituents R^1 and R^2 would play any role in enhancing the cyclization. We also wanted to see how the percent yield would change when the substituents on the olefins are styrenyl, isobutynyl or propenyl (Table 13). The

Table 13. Scope of substituents along the linear substrate backbone.





Isolated yields are reported. Substrates were fully consumed in all cases. [a] 2 mol % of precatalyst was used. [b] ^{1}H NMR of the crude reaction mixture showed diastereomeric ratio of 1:1. [c] 5 mol % of precatalyst was used.

Thorpe–Ingold[3] effect is perhaps minimal in six-membered ring formation because the yields for **2.2a**, **2.2b** and **2.2c** are similar. However, the percent yields for **2.2a**, **2.2d** and **2.2f** were different, indicating that the stability of generated carbocation is important. Spirotetralin compounds **2.2i** and **2.2j** could also be obtained in decent yield. Next, we studied the effect of substitution on the arene ring (Table 14). Reactions work fairly well with *chloro* in the *para* position **2.13a**. However, the yield significantly decreases when methyl is in the *para* position **2.13b**. Interestingly, no conversion was observed on **2.12c** and only 42% yield was obtained when our optimized condition was applied to substrate **2.12d**. Mr. Thanh Lien who is a graduate student in Stokes lab prepared **2.1c** and **2.2c**. Ms. Jessica Lopez Lara who is an undergraduate student in Stokes lab helped me with the synthesis of **2.12c** and **2.13d**.

Table 14. Scope of arene substitution.

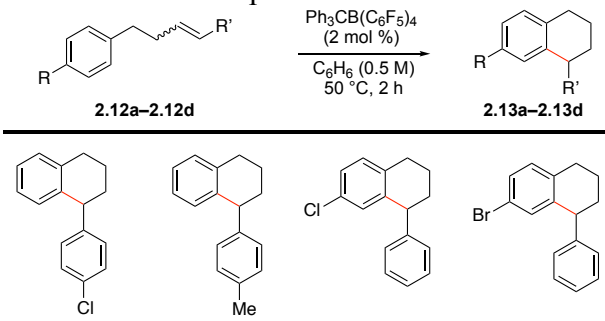
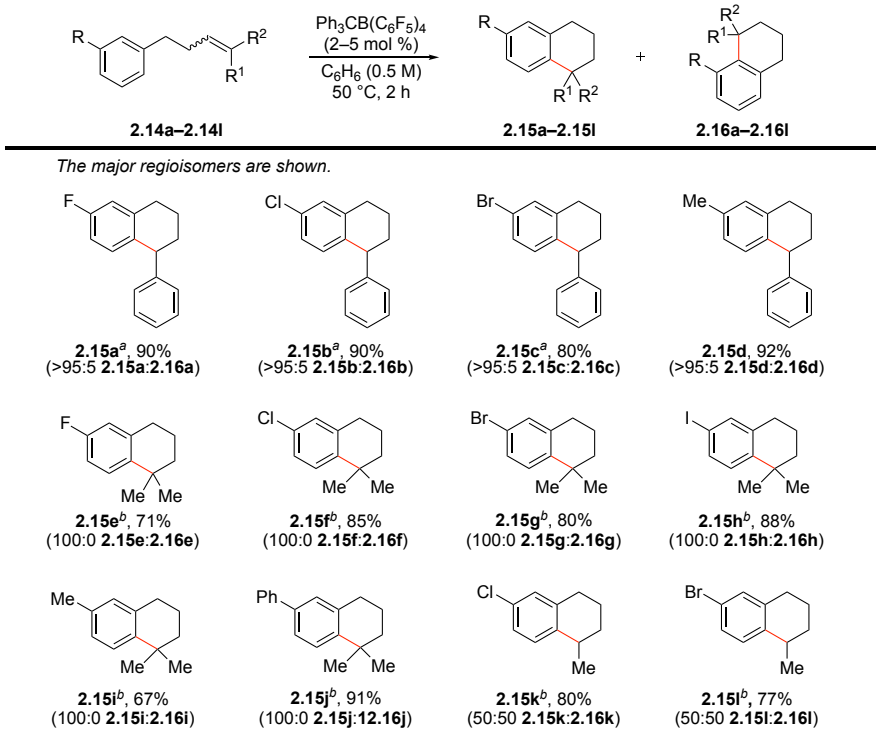


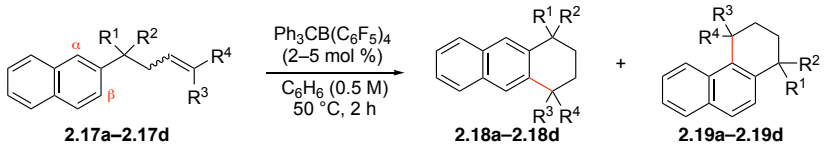
Table 15. Evaluating the regioselectivity of intramolecular hydroarylation of *β*-homobenzylstyrenes, *β*-homobenzylbutenes and *β*-homobenzylpropenes.



Isolated yields of the mixture isomers are reported. Substrates were fully consumed in all cases.
[a] 2 mol % of precatalyst was used. [b] 5 mol % of precatalyst was used.

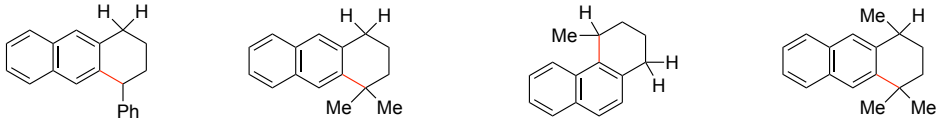
We next investigated the regioselectivity outcomes in three different systems by varying the alkene substituents–herein *β*-homobenzylstyrenes **2.14a–2.14d,** *β*-homobenzylbutenes **2.14e–2.14j** and *β*-homobenzylpropenes **12.14k–12.14l** (Table 15). In the case of herein *β*-homobenzylstyrene drivatives, we observed cyclizations at the less hindered position and only trace amounts of the minor isomers were formed. Good percent yields were also obtained for **2.15a–2.15d**. In the case of *β*-homobenzylbutenes **12.14e–12.14j**, the formation of the more hindered product was completely blocked**.** These results indicate that steric resulted from the clash between the *gem*-dimethyl and the *meta*-substituent (R group) completely dictates the regioselectivity. In the *β*-homobenzylpropenes system **12.14k–12.14l**, we began to see the electronic effects since there was less sterics involeved. The cyclization of *β*-homobenzylpropenes gave both regioisomers in equal amount. Mr. Lien synthesized **2.14c** and **2.15c**.

Table 16. Evaluating the regioselectivity of intramolecular alkylation of naphthalene analogs.



2.17a–2.17d **2.18a–2.18d** **2.19a–2.19d**

The major regioisomers are shown.



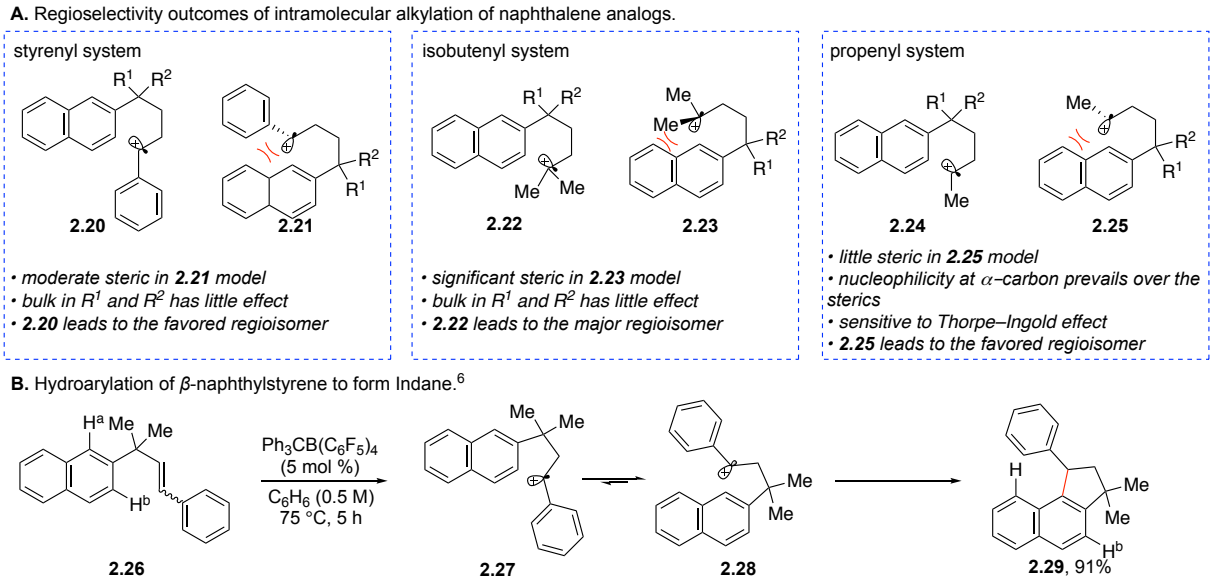
2.18a[a], 93% (62:38 **2.18a**:**2.19a**) **2.18b**[b], 83% (89:11 **2.18b**:**2.19b**) **2.19c**[b], 80% (13:87 **2.18c**:**2.19c**) **2.18d**[b], 91% (100:0 **2.18d**:**2.19d**)

Isolated yields of the mixture of isomers are reported. Substrates were fully consumed in all cases.
[a] 2 mol % of precatalyst was used. [b] 5 mol % of precatalyst was used.

We next evaluated the regioselectivity of intramolecular alkylation of naphthalene analogs (Table 16). Both benzene and naphthalene are aromatic compounds but naphthalene has a total of 10π electrons, whereas one isolated aromatic like benzene would have 6π electrons. So two isolated aromatic rings would have a total of 12π electrons. Therefore, there is smaller amount of electron density on naphthalene, resulting in higher resonance energy than benzene. (Naphthalene's resonance energy is 61 kcal/mol and benzene's resonance energy is 36 kcal/mol). Another great comparison would be the differences in bond-length. It is important to note that the individual bond's lengths in bicyclic systems are different that a benzene molecule.[4] Therefore, the reactivity will differ significantly. Naphthalene, which consists of two fused benzene rings with three Kekule resonance structures, is best represented by Erlenmeyer's symmetrical formula[5] as depicted in Table 16. The C–C bond lengths from the α to β positions to the fused ring system is shorter than β to β. This shortness of bond gives α–β carbons more double bond characteristics than β–β bond, thus making it more nucleophilic for EAS-type reactions. Armed with this knowledge, we were interested to

see how the steric and nucleophilicity would dictate the regioselectivity in naphthalene analogs. Cyclization of substrate **2.17a** gave a mixture of regioisomers **2.18a** and **2.19a** in 62:38 ratios. Consistent with

our previous observations, cyclization of olefin **2.17b** gave the less hindered regioisomer **2.18b** as the major product. In the less hindered system **2.17c**, the more congested isomer **2.19c** was formed as the major product. And finally, the cyclization of **2.17d** gave regioisomer **2.18d** exclusively in 91% yield. To have a better understanding of our results, we designed a simple model to see if any trends exists based on the steric or electronic. In the case of styrenyl systems, moderate steric exist in model **2.21**, therefore we see both regioisomers in decent amounts, even though the less hindered product is the major regioisomer (Scheme 15). In the isobutynyl system, significant steric exists due to the presence of geminal dimethyl group. Therefore, cyclization of model **2.22** is preferred over **2.23**. In the case of propenyl system, since there is relatively less sterics compared to the two previous systems, the nucleophilicity will play a bigger role. Therefore, cyclization happens at the more nucleophilic position to yield model **2.25** as the major regioisomer. Interestingly, olefin substrate **2.26** gave **2.29** in near exclusively in 91% yield[6], but its tetralin analog, gave a mixture of regioisomers in 70:30 ratio (less hindered one being the major product). This result shows that regioselectivity for five- and six-membered ring formations is significantly different.



Scheme 15. Regioselectivity rationale for intramolecular alkylation of naphthalene analogs.

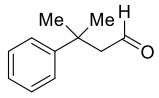
In conclusion, we have developed a method to synthesize tetralins by utilizing an easily handled precatalyst TPFPB. In addition, we have studied the regioselectivity in three different systems in detail. Formation of six-membered ring is favored over five-memberd and many products were obtained in good yields. We have shown that the steric hindrance dictates the arene substitution position for hydroarylation of styrenyl and

isobutenyl substrates; whereas, propenyls alkylate at the most nucleophilic position. The regioselectivity in the propenyl system can also be altered by the presence of geminal dimethyl group in the benzylic position. Our studies contribute to an improved general understanding of both electronic and steric effects in EAS-type reactions. Ongoing efforts are directed toward the better understanding of reaction mechanism and regioselectivity trends, particularly in the naphthyl derivatives.

Experimental

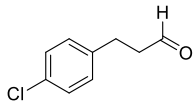
A. Synthesis of aldehydes via sequential reduction/oxidation of carboxylic acids or esters.

General Procedure I: To a round bottom flask equipped with a PTFE-coated magnetic stir bar were added 1.0 equivalent of carboxylic acid or ester in 0.1 M diethyl ether. The reaction mixture was placed in an ice bath, and then 3.0 equivalents of lithium aluminum hydride were added slowly in four different portions. The reaction mixture was stirred for two hours at room temperature. After complete consumption of the carboxylic acid or ester was observed by TLC, the reaction mixture was placed in ice bath again and quenched with 1 M aqueous HCl. The product was extracted three times with diethyl ether. The combined organic layers were dried over anhydrous sodium sulfate, filtered and concentrated under vacuum. No further purification was needed for the primary alcohol product. 1.0 equivalent of this alcohol was dissolved in 0.5 M DCM and then 1.5 equivalent of pyridiniumchlorochromate (PCC) was added. The oxidation was monitored by TLC and it was completed within three hours. The crude mixture was passed through a pad of Celite and washed with ethyl acetate. Solvent was removed under vacuum. Purification by flash column chromatography (100:0→90:10 hexanes:EtOAc) afforded the aldehyde.

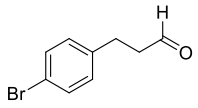


S1

3-methyl-3-phenylbutanal S1: General procedure I was followed using 2.0 g of 3-methyl-3-phenylbutanoic acid (11.2 mmol) and 1.28 g of $LiAlH_4$ (33.6 mmol) in 112 mL Et_2O. (1.80 g, 98% yield). The alcohol was then oxidized using 3.54 g of PCC (16.5 mmol) in 22 mL DCM. Purification by flash chromatography (100:0 → 90:10 hexanes:EtOAc) afforded **S1** as a colorless oil. (0.94 g, 53% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.51 (t, J = 3.0 Hz, 1H), 7.41−7.32 (m, 4H), 7.25−7.20 (m, 1H), 2.68 (d, J = 3.0 Hz, 2H), 1.47 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.1 (CO), 147.4 (C), 128.4 (2CH), 126.3 (CH), 125.5 (2CH), 56.5 (CH_2), 36.7 (C), 29.4 ($2CH_3$).

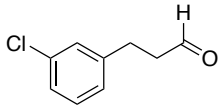


3-(4-chlorophenyl)propanal S2: General procedure I was followed using 1.00 g of 3-(4-chlorophenyl)propanoic acid (5.41 mmol) and 0.62 g of $LiAlH_4$ (16.2 mmol) in 54.2 mL Et_2O. (0.32 g, 34 % yield). The alcohol was then oxidized using 0.60 g of PCC (2.78 mmol) in 3.72 mL DCM. Purification by flash chromatography (100:0 → 90:10 Hexanes:EtOAc) afforded **S2** as a colorless oil. (0.16 g, 51 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.79 (t, *J* = 1.3 Hz, 1H), 7.24 (d, *J* = 8.32 Hz, 2H), 7.12 (d, *J* = 8.5 Hz, 2H), 2.91 (t, *J* = 7.4 Hz, 2H), 2.76 (t, *J* = 7.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.0 (CO), 138.7 (C), 131.9 (C), 129.6 (2CH), 128.6 (2CH), 45.0 (CH_2), 27.3 (CH_2); ATR-FTIR (neat): 2927, 2827, 1727, 1492, 1440 cm^{-1}.



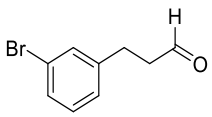
S3

3-(4-bromophenyl)propanal S3: General procedure I was followed using 2.00 g of 3-(4-bromophenyl)propanoic acid (8.73 mmol) and 0.99 g of $LiAlH_4$ (26.2 mmol) in 87.3 mL Et_2O. (0.94 g, 50 % yield). The alcohol was then oxidized using 1.40 g of PCC (6.53 mmol) in 8.7 mL DCM. Purification by flash chromatography (100:0 → 90:10 hexanes:EtOAc) afforded **S3** as a colorless oil. (0.61 g, 65 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.81 (t, *J* = 1.3 Hz, 1H), 7.44–7.37 (m, 2H), `7.10–7.04 (m, 2H), 2.91 (t, *J* = 7.4 Hz, 2H), 2.80–2.73 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.9 (CO), 139.3 (C), 131.6 (2CH), 130.0 (2CH), 120.0 (C), 45.0 (CH_2), 27.4 (CH_2); ATR-FTIR (neat): 3030, 2923, 1727, 1488, 1436 cm^{-1}.



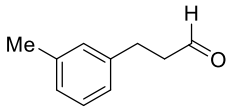
S4

3-(3-chlorophenyl)propanal S4: General procedure I was followed using 1.0 g of 3-(3-chlorophenyl)propanoic acid (5.4 mmol) and 0.62 g of $LiAlH_4$ (16.2 mmol) in 54 mL Et_2O. (0.81 g, 88% yield). The alcohol was then oxidized using 1.53 g of PCC (7.1 mmol) in 9.5 mL DCM. Purification by flash chromatography (100:0 → 90:10 hexanes:EtOAc) afforded **S4** as a colorless oil. (0.66 g, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.80 (s, 1H), 7.24–7.16 (m, 3H), 7.08 (d, *J* = 7.3 Hz, 1H), 2.97–2.89 (m, 2H), 2.77 (t, *J* = 7.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.8 (CO), 142.4 (C), 134.2 (C), 129.8 (CH), 128.4 (CH), 126.5 (CH), 126.4 (CH), 44.8 (CH_2), 27.6 (CH_2).



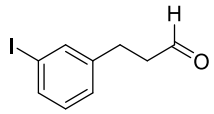
S5

3-(3-bromophenyl)propanal S5: General procedure I was followed using 3.00 g of 3-(3-bromophenyl)propanoic acid (13.0 mmol) and 1.49 g of $LiAlH_4$ (39.0 mmol) in 130.9 mL Et_2O. (2.51 g, 77% yield). The alcohol was then oxidized using 0.70 g of PCC (3.25 mmol) in 4.33 mL DCM. Purification by flash chromatography (100:0 → 90:10 hexanes:EtOAc) afforded **S5** as a colorless oil. (0.217 mg, 46% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.81 (s, 1H), 7.37–7.32 (m, 2H), 7.19–7.10 (m, 2H), 2.99–2.89 (m, 2H), 2.78 (t, J = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.8 (CO), 142.7 (C), 131.6 (CH), 131.2 (CH), 129.6 (CH), 128.4 (CH), 122.6 (C), 45.0 (CH_2), 27.6 (CH_2); ATR-FTIR (neat): 2929, 2824, 1713, 1567, 1475 cm^{-1}.



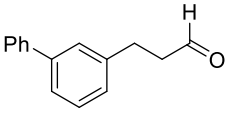
S6

3-(*m*-tolyl)propanal S6: General procedure I was followed using 1.00 g of 3-(*m*-tolyl)propanoic acid (6.09 mmol) and 0.81 g of $LiAlH_4$ (21.3 mmol) in 60.9 mL Et_2O. (0.89 g, 89 % yield). The alcohol was then oxidized using 1.92 g of PCC (8.92 mmol) in 11.9 mL DCM. Purification by flash chromatography (100:0 → 90:10 hexanes:EtOAc) afforded **S6** as a colorless oil. (0.33 g, 36 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.82 (s, 1H), 7.19 (t, J = 7.4 Hz, 1H), 7.06–6.96 (m, 3H), 2.93 (t, J = 7.5 Hz, 2H), 2.77 (t, J = 7.9 Hz, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.7 (CO), 140.2 (C), 138.2 (C), 129.0 (CH), 128.4 (CH), 127.0 (CH), 125.2 (CH), 45.3 (CH_2), 28.0 (CH_2), 21.4 (CH_3); ATR-FTIR (neat): 3026, 2922, 1707, 1610, 1590 cm^{-1}.



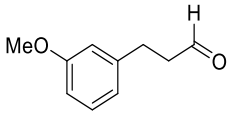
S7

3-(3-iodophenyl)propanal S7: General procedure I was followed using 1.0 g of 3-(3-iodophenyl)propanoic acid (3.6 mmol) and 0.41 g of $LiAlH_4$ (10.8 mmol) in 36 mL Et_2O. (0.68 g, 72% yield). The alcohol was then oxidized using 0.842 g of PCC (3.91 mmol) in 5.21 mL DCM. Purification by flash chromatography (100:0 → 90:10 hexanes:EtOAc) afforded **S7** as a light yellow oil. (0.45 g, 67 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.79 (t, J = 1.2 Hz, 1H), 7.56−7.50 (m, 2H), 7.15 (d, J = 7.7 Hz, 1H), 7.01 (t, J = 7.7 Hz, 1H), 2.88 (t, J = 7.1 Hz, 2H), 2.79−2.73 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.8 (CO), 142.7 (C), 137.2 (CH), 135.3 (CH), 130.2 (CH), 127.6 (CH), 94.5 (C), 44.8 (CH_2), 27.4 (CH_2). ATR-FTIR (neat): 2926, 2853, 1711, 1590, 1562 cm^{-1}.



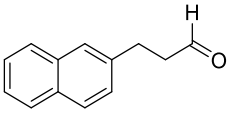
S8

3-([1,1'-biphenyl]-3-yl)propanal S8: General procedure I was followed using 0.90 g of 3-([1,1'-biphenyl]-3-yl)propan-1-ol (4.24 mmol) and 1.37 g of PCC (6.34 mmol) in 8.47 mL DCM. Purification by flash chromatography (100:0 → 90:10 hexanes:EtOAc) afforded **S8** as a colorless oil. (0.60 g, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.85 (t, *J* = 1.4 Hz, 1H), 7.60−7.56 (m, 2H), 7.47−7.32 (m, 6H), 7.19 (d, *J* = 7.5 Hz, 1H), 3.04 (t, *J* = 7.5 Hz, 2H), 2.88−2.81 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.5 (CO), 141.6 (C), 141.0 (C), 140.8 (C), 129.0 (CH), 128.7 (2CH), 127.3 (CH), 127.2 (2CH), 127.1 (2CH), 125.2 (CH), 45.3 (CH_2), 28.2 (CH_2).



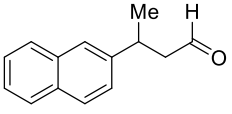
S9

3-(3-methoxyphenyl)propanal S9: General procedure I was followed using 1.9 g of 3-(3-methoxyphenyl)propanoic acid (10.2 mmol) and 1.34 g of $LiAlH_4$ (35.6 mmol) in 101.8 mL Et_2O. (1.88 g, 98.7 % yield). The alcohol was then oxidized using 3.62 g of PCC (16.8 mmol) in 22.5 mL DCM. Purification by flash chromatography (100:0 → 90:10 hexanes:EtOAc) afforded **S9** as a colorless oil. (0.80 g, 42 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.82 (t, *J* = 1.4 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 6.74 (m, 3H), 3.80 (s, 3H), 2.94 (t, *J* = 7.5 Hz, 2H), 2.79 (t, *J* = 7.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.5 (CO), 159.7 (C), 141.9 (C), 129.5 (CH), 120.5 (CH), 114.1 (CH), 111.5 (CH), 55.2 (CH_3), 45.2 (CH_2), 28.1 (CH_2); ATR-FTIR (neat): 3204, 2937, 1723, 1602, 1585 cm^{-1}.



S10

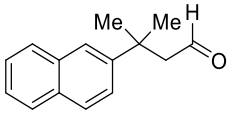
3-(naphthalen-2-yl)propanal S10: General procedure I was followed using 1.8 g of 3-(naphthalen-2-yl)propanoic acid (9.0 mmol) and 1.02 g of $LiAlH_4$ (27.0 mmol) in 90 mL Et_2O. (1.49 g, 89% yield). The alcohol was then oxidized using 2.59 g of PCC (12 mmol) in 16 mL DCM. Purification by flash chromatography (100:0 → 90:10 hexanes:EtOAc) afforded **S10** as a colorless oil. (1.08 g, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.83 (s, 1H), 7.86–7.79 (m, 3H), 7.65 (s, 1H), 7.54–7.45 (m, 2H), 7.34 (dd, *J* = 1.8, 8.6 Hz, 1H), 3.11 (t, *J* = 7.6 Hz, 2H), 2.82 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.2 (CO), 137.7 (C), 133.4 (C), 131.9 (C), 128.0 (CH), 127.4 (CH), 127.3 (CH), 126.7 (CH), 126.2 (CH), 125.9 (CH), 125.3 (CH), 44.9 (CH_2), 28.0 (CH_2); ATR-FTIR (neat): 2931, 2858, 1738, 1600, 1493 cm^{-1}.



S11

3-(naphthalen-2-yl)butanal S11: General procedure I was followed using 1.0 g of ethyl 3-(naphthalen-2-yl)butanoate (4.12 mmol) and 0.470 g of $LiAlH_4$ (12.4 mmol) in 41 mL

Et_2O. (0.80 g, 97% yield). The alcohol was then oxidized using 1.29 g of PCC (5.99 mmol) in 7.99 mL DCM. Purification by flash chromatography (100:0 → 90:10 hexanes:EtOAc) afforded **S11** as a colorless oil. (0.55 g, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.72 (s, 1H), 7.92−7.80 (m, 3H), 7.70 (s, 1H), 7.59−7.45 (m, 3H), 7.40 (d, J = 8.3 Hz, 1H), 3.53 (q, J = 7.1 Hz, 1H), 2.88−2.65 (m, 2H), 1.42 (d, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.4 (CO), 142.7 (C), 133.3 (C), 132.1 (C), 128.1 (CH), 127.4 (2CH), 125.9 (CH), 125.3 (CH), 125.2 (CH), 124.7 (CH), 51.2 (CH_2), 34.0 (CH), 21.8 (CH_3); ATR-FTIR (neat): 3025, 2924, 1600, 1495, 1452 cm^{-1}.

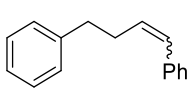


S12

3-methyl-3-(naphthalen-2-yl)butanal S12: General procedure I was followed using 2.80 g of ethyl 3-methyl-3-(naphthalen-2-yl)butanoate (11.5 mmol) and 0.328 g of $LiAlH_4$ (34.5 mmol) in 115.5 mL Et_2O. (0.65 g, 26% yield). The alcohol was then oxidized using 0.98 g of PCC (4.54 mmol) in 6.1 mL DCM. Purification by flash chromatography (100:0 → 90:10 hexanes:EtOAc) afforded **S12** as a colorless oil. (0.38 g, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.58 (t, J = 2.9 Hz, 1H), 7.93–7.87 (m, 3H), 7.85 (s, 1H), 7.59 (dd, J = 8.7, 2.1 Hz, 1H), 7.56–7.50 (m, 2H), 2.79 (d, J = 3.0 Hz, 2H), 1.59 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.5 (CO), 144.6 (C), 133.1 (C), 131.7 (C), 128.0 (CH), 127.8 (CH), 127.2 (CH), 126.0 (CH), 125.6 (CH), 124.0 (CH), 123.5 (CH), 55.9 (CH_2), 36.6 (C), 29.0 ($2CH_3$); ATR-FTIR (neat): 2965, 2871, 1714, 1599, 1505 cm^{-1}.

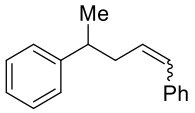
B. Synthesis of alkenes via Wittig olefination

General procedure II. In a dry 25-50 mL round bottom flask charged with PTFE coated magnetic stir bar under an atmosphere of nitrogen, the Wittig salt (1.5 eq.) was dissolved in 0.3 M dry THF. The reaction flask was then sealed with a rubber septum before 1.7 equivalents of *t*-BuOK (1.7 M in THF solution) was syringed into the mixture at room temperature. After 20 minutes, the reaction flask was cooled to 0 ºC. A solution of aldehyde dissolved in minimal amount of dry THF was slowly added to the ylide drop-wise through syringe. The reaction mixture was then brought to room temperature and allowed to stir for 18 hours. After all the aldehyde was consumed, the reaction was quenched with saturated aqueous NH_4Cl solution. The mixture was extracted with ethyl acetate three times and the organic phase was dried over anhydrous sodium sulfate before it was concentrated under reduced pressure to afford crude alkene product. Purification by silica gel chromatography (100% hexanes) afforded the alkene product.



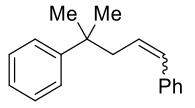
2.1a

(*Z*)- and (*E*)-but-1-ene-1,4-diyldibenzene 2.1a: General procedure II was followed using 500 mg of aldehyde 3-phenylpropanal (3.73 mmol), 2.42 g of benzyltriphenylphosphonium bromide (5.59 mmol), 12.4 mL of dry THF and 3.73 mL of a 1.7 M solution of *t*-BuOK in THF. Purification by flash column chromatography (hexanes) afforded the alkene product **2.1a** (0.61 mg, 79% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36−7.27 (m, 5H), 7.25−7.17 (m, 5H), 6.48−6.39 (m, 1H), 6.32−5.68 (m, 1H), 2.83−2.75 (m, 2H), 2.71−2.51 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.0 (C), 137.7 (C), 130.4 (CH), 130.0 (CH), 128.7 (CH), 128.5 (2CH), 128.4 (3CH), 128.1 (CH), 126.9 (CH), 126.0 (2CH), 35.9 (CH_2), 34.9 (CH_2), ; ATR-FTIR (neat): 3026, 2925, 1601, 1494, 1451 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{16}H_{16}$ $[M]^+$: 208.1252, found: 208.1245.
Minor isomer: ^{13}C NMR (100 MHz, $CDCl_3$): 146.8 (C), 137.5 (C), 131.8 (CH), 131.1 (CH), 129.4 (CH), 128.8 (CH), 128.1 (CH), 127.0 (CH), 126.6 (CH), 125.9 (2CH), 37.0 (CH_2), 30.4 (CH_2).



2.1b

(*Z*)- and (*E*)-pent-1-ene-1,4-diyldibenzene 2.1b: General procedure II was followed using 500 mg of aldehyde 3-phenylbutanal (3.37 mmol), 2.19 g of benzyltriphenylphosphonium bromide (5.1 mmol), 11.2 mL of dry THF and 3.37 mL of a 1.7 M solution of *t*-BuOK in THF. Purification by flash column chromatography (hexanes) afforded the alkene product **2.1b** (384 mg, 51% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35−7.27 (m, 9H), 7.24−7.16 (m, 6H), 6.45−6.40 (m, 1H), 6.40−6.34 (m, 1H), 6.19−6.08 (m, 1H), 5.65−5.56 (m, 1H), 2.93−2.81 (m, 2H), 2.66−2.60 (m, 2H), 2.59−2.50 (m, 1H), 2.48−2.39 (m, 1H), 1.31 (d, J = 7.0 Hz, 3H), 1.29 (d, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.0 (C), 137.7 (C), 128.7 (CH), 128.4 (2CH), 128.3 (3CH), 128.1 (CH), 127.1 (CH), 127.0 (2CH), 126.0 (2CH), 40.2 (CH), 37.0 (CH_2), 21.4 (CH_3); ATR-FTIR (neat): 3025, 2960, 1601, 1493, 1450 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{17}H_{18}$ $[M]^+$: 222.1409, found: 222.1408.
Minor isomer: ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.8 (C), 137.6 (C), 131.2 (CH), 131.1 (CH), 129.7 (CH), 129.1 (CH), 126.9 (CH), 126.5 (CH), 41.9 (CH_2), 40.4 (CH), 21.8 (CH_3).

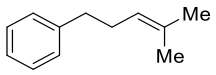


2.1c

(*Z*) and (*E*)-(4-methylpent-1-ene-1,4-diyl)dibenzene 2.1c: General procedure II was followed using 255 mg of aldehyde 3-methyl-3-phenylbutanal (1.57 mmol), 1.02 g of benzyltriphenylphosphonium bromide (2.35 mmol), 5.23 mL of dry THF and 1.57 mL of a 1.7 M solution of *t*-BuOK in THF. Purification by flash column chromatography (Hexane) afforded the alkene product **2.1c** (304 mg, 82 % yield) as a colorless oil. ^{1}H

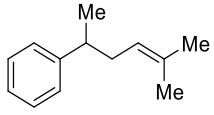
NMR (400 MHz, $CDCl_3$): δ 7.66–7.40 (m, 10H), 7.40–7.23 (m, 10H), 6.74–6.43 (m, 2H), 6.11 (m, 1H), 5.58 (m, 1H), 2.83 (d, J = 1.96 Hz, 2H), 2.65 (d, J = 1.36 Hz, 2H), 1.49 (s, 6H), 1.46 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.2 (C), 137.7 (C), 128.7 (2CH), 128.4 (2CH), 128.1 (3CH), 128.0 (CH), 126.0 (2CH), 125.8 (2CH), 48.0 (CH_2), 38.1 (C), 28.8 ($2CH_3$); ATR-FTIR (neat): 3023, 2962, 1599, 1495, 1445 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{18}H_{20}[M]^+$: 236.1565, found: 236.1569.

Minor isomer: ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.8 (C), 137.8 (C), 132.1 (CH), 130.1 (CH), 129.5 (CH), 127.5 (CH), 126.8 (CH), 126.4 (CH), 125.5 (CH), 42.4 (CH_2), 38.0 (C), 28.6 ($2CH_3$),



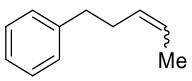
2.1d

(4-methylpent-3-en-1-yl)benzene 2.1d: General procedure II was followed using 700 mg of aldehyde 3-phenylpropanal (5.22 mmol), 3.38 g of isobutyltriphenylphosphonium iodide (7.83 mmol), 17.4 mL of dry THF and 5.22 mL of a 1.7 M solution of *t*-BuOK in THF. Purification by flash column chromatography (hexanes) afforded the alkene product **2.1d** (0.65 mg, 78% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33–7.26 (m, 2H), 7.23–7.16 (m, 3H), 5.23–5.15 (m, 1H), 2.65 (t, J = 8.4 Hz, 2H), 2.31 (q, J = 7.7 Hz, 2H), 1.71 (s, 3H), 1.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.4 (C), 132.1 (C), 128.4 (2CH), 128.2 (2CH), 125.6 (CH), 123.7 (CH), 36.2 (CH_2), 30.1 (CH_2), 25.7 (CH_3), 17.6 (CH_3); ATR-FTIR (neat): 2918, 2856, 1604, 1496, 1453 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{12}H_{16}[M]^+$: 160.1252, found: 160.1255.



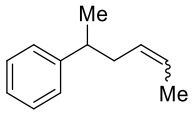
2.1e

(5-methylhex-4-en-2-yl)benzene 2.1e: General procedure II was followed using 500 mg of aldehyde 3-phenylbutanal (3.38 mmol), 2.03 g of isobutyltriphenylphosphonium iodide (5.1 mmol), 11.2 mL of dry THF and 3.38 mL of a 1.7 M solution of *t*-BuOK in THF. Purification by flash column chromatography (hexanes) afforded the alkene product **2.1e** (401 mg, 68% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32–7.26 (m, 2H), 7.23–7.14 (m, 3H), 5.12–5.04 (m, 1H), 2.72 (sex, J = 7.0 Hz, 1H), 2.33–2.17 (m, 2H), 1.66 (s, 3H), 1.55 (s, 3H), 1.24 (d, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.6 (C), 132.4 (C), 128.2 (2CH), 127.0 (2CH), 125.7 (CH), 122.9 (CH), 40.3 (CH), 36.8 (CH_2), 25.7 (CH_3), 21.4 (CH_3), 17.8 (CH_3); ATR-FTIR (neat): 2964, 2942, 1602, 1494, 1452 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{13}H_{18}[M]^+$: 174.1409, found: 174.1415.



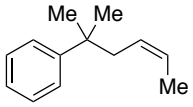
2.1f

(*Z*)-pent-3-en-1-ylbenzene 2.1f: General procedure II was followed using 500 mg of aldehyde 3-phenylpropanal (3.7 mmol), 2.1 g of ethyltriphenylphosphonium bromide (5.6 mmol), 12.3 mL of dry THF and 3.7 mL of a 1.7 M solution of *t*-BuOK in THF. Purification by flash column chromatography (hexanes) afforded the alkene product **2.1f** (324 mg, 60% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (s, 1H), 7.32–7.24 (m, 1H), 7.23–7.16 (m, 3H), 5.53–5.39 (m, 2H), 2.67 (t, *J* = 8.8 Hz, 2H), 2.37 (q, *J* = 8.7 Hz, 2H), 1.57 (d, *J* = 4.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.2 (C), 129.6 (CH), 128.4 (2CH), 128.2 (2CH), 125.7 (CH), 124.5 (CH), 35.8 (CH_2), 28.8 (CH_2), 12.7 (CH_3); ATR-FTIR (neat): 3025, 2924, 1601, 1495, 1452 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{11}H_{14}[M]^+$: 146.1095, found: 146.1098.
Minor isomer: ^{13}C NMR (100 MHz, $CDCl_3$): δ 130.6 (C), 128.3 (CH), 125.7 (CH), 125.4 (CH), 36.1 (CH_2), 34.5 (CH_2),17.9 (CH_3).



2.1g

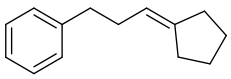
(*Z*)- and (*E*)-hex-4-en-2-ylbenzene 2.1g: General procedure II was followed using 500 mg of aldehyde 3-phenylbutanal (3.38 mmol), 1.88 g of ethyltriphenylphosphonium bromide (5.10 mmol), 11.2 mL of dry THF and 3.38 mL of a 1.7 M solution of *t*-BuOK in THF. Purification by flash column chromatography (hexanes) afforded the alkene product **2.1g** (398 mg, 74% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38–7.32 (m, 2H), 7.29–7.21 (m, 3H), 5.57–5.47 (m, 1H), 5.47–5.36 (m, 1H), 2.82 (septet, *J* = 7.0 Hz, 1H), 2.39 (t, *J* = 6.8 Hz, 2H), 1.62 (d, *J* = 6.8 Hz, 3H), 1.33 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.3 (C), 128.8 (CH), 128.2 (2CH), 126.9 (2CH), 125.8 (CH), 124.8 (CH), 40.1 (CH), 35.5 (CH_2), 21.5 (CH_3), 12.9 (CH_3); ATR-FTIR (neat): 2961, 2927, 1604, 1494, 1452 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{12}H_{16}[M]^+$: 160.1252, found: 160.1251.
Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.30–2.20 (m, 1H), 1.68 (d, *J* = 5.9 Hz, 3H), 1.52–1.43 (m, 2H), 1.29 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 129.6 (CH), 126.3 (CH), 125.8 (CH), 41.5 (CH), 17.9 (CH_3).



2.1h

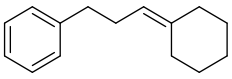
(*Z*)-(2-methylhex-4-en-2-yl)benzene 2.1h: General procedure II was followed using 255 mg of aldehyde 3-methyl-3-phenylbutanal (1.57 mmol), 0.87 g of ethyltriphenylphosphonium bromide (2.35 mmol), 5.23 mL of dry THF and 1.57 mL of a 1.7 M solution of *t*-BuOK in THF. Purification by flash column chromatography (hexanes) afforded the alkene product **2.1h** (168.3 mg, 66 % yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (t, *J* = 7.4 Hz, 2H), 7.31 (t, *J* = 6.9 Hz, 2H), 7.18 (t, *J* = 6.7 Hz, 1H), 5.46 (m, 1H), 5.19 (m, 1H), 2.36 (d, *J* = 7.3 Hz, 2H), 1.55 (s, 3H), 1.31 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.4 (C), 127.9 (2CH), 127.2 (CH), 125.8 (2CH),

125.5 (CH), 125.4 (CH), 41.2 (CH_2), 38.1 (C), 28.4 ($2CH_3$), 12.9 (CH_3); ATR-FTIR (neat): 2924, 2854, 1558, 1495, 1463 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{13}H_{18}[M]^+$: 174.1409, found: 174.1415.



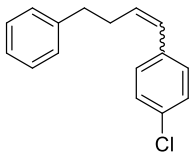
2.1i

(3-cyclopentylidenepropyl)benzene 2.1i: General procedure II was followed using 500 mg of aldehyde 3-phenylpropanal (3.72 mmol), 2.30 g of cyclopentyltriphenylphosphonium bromide (5.59 mmol), 12.5 mL of dry THF and 3.7 mL of a 1.7 M solution of *t*-BuOK in THF. Purification by flash column chromatography (hexanes) afforded the alkene product **2.1i** (513 mg, 74% yield) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.34–7.28 (m, 2H), 7.25–7.18 (m, 3H), 5.37–5.30 (m, 1H), 2.69 (t, *J* = 8.9 Hz, 2H), 2.33 (q, *J* = 7.2 Hz, 2H), 2.26 (t, *J* = 6.9 Hz, 2H), 2.15 (t, *J* = 7.0 Hz, 2H), 1.71–1.57 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.9 (C), 142.5 (C), 128.5 (2CH), 128.2 (2CH), 125.6 (CH), 119.2 (CH), 36.0 (CH_2), 33.6 (CH_2), 31.6 (CH_2), 28.6 (CH_2), 26.4 (CH_2), 24.3 (CH_2) ; ATR-FTIR (neat): 2938, 2865, 1603, 1496, 1452 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{14}H_{18}[M]^+$: 186.1409, found: 186.1416.



2.1j

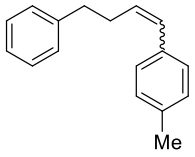
(3-cyclohexylidenepropyl)benzene 2.1j: General procedure II was followed using 300 mg of aldehyde 3-phenylpropanal (2.23 mmol), 1.43 g of cyclohexyltriphenylphosphonium bromide (0.0033 mmol), 7.4 mL of dry THF and 2.23 mL of a 1.7 M solution of *t*-BuOK in THF. Purification by flash column chromatography (hexanes) afforded the alkene product **2.1j** (323 mg, 72% yield) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.32–7.27 (m, 2H), 7.23–7.17 (m, 3H), 5.15 (t, *J* = 7.3 Hz, 1H), 2.66 (t, *J* = 8.7 Hz, 2H), 2.33 (q, *J* = 7.5 Hz, 2H), 2.12–2.05 (m, 4H), 1.58–1.47 (m, 4H), 1.46–1.37 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.3 (C), 140.3 (C), 128.5 (2CH), 128.1 (2CH), 125.6 (CH), 120.2 (CH), 37.2 (CH_2), 36.5 (CH_2), 29.1 (CH_2), 28.7 ($2CH_2$), 27.7 (CH_2), 26.9 (CH_2); ATR-FTIR (neat): 2925, 2854, 1601, 1495, 1452 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{15}H_{20}[M]^+$: 200.1565, found: 200.1565.



2.12a

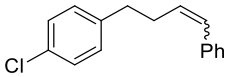
(*Z*)- and (*E*)-1-chloro-4-(4-phenylbut-1-en-1-yl)benzene 2.12a: General procedure II was followed using 560 mg of aldehyde 3-phenylpropanal (4.17 mmol), 2.7 g of (4-chlorobenzyl)triphenylphosphonium chloride (6.26 mmol), 14 mL of dry THF and 4.2 mL of a 1.7 M solution of *t*-BuOK in THF. Purification by flash column chromatography

(hexanes) afforded the alkene product **2.12a** (623 mg, 62% yield) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34−7.11 (m, 9H), 6.42−6.33 (m, 1H), 6.29−5.68 (m, 1H), 2.83−2.73 (m, 2H), 2.67−2.50 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.6 (C), 136.2 (C), 135.9 (C), 128.6 (2CH), 128.4 (5CH), 128.3 (2CH), 127.2 (2CH), 35.7 (CH_2), 34.8 (CH_2); ATR-FTIR (neat): 3026, 2927, 1603, 1491, 1453 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{16}H_{15}Cl$ $[M]^+$: 242.0862, found: 242.0864.
Minor isomer: ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.4 (C), 132.5 (CH), 130.7 (CH), 130.0 (2CH), 129.2 (CH), 126.0 (2CH), 35.9 (CH_2), 30.4 (CH_2).



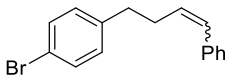
2.12b

(*Z*)- and (*E*)-1-methyl-4-(4-phenylbut-1-en-1-yl)benzene 2.12b: General procedure II was followed using 1000 mg of aldehyde 3-phenylpropanal (7.45 mmol), 5.0 g of (4-methylbenzyl)triphenylphosphonium bromide (11.2 mmol), 7.45 mL of dry THF and 4.8 mL of a 1.7 M solution of *t*-BuOK in THF. Purification by flash column chromatography (hexanes) afforded the alkene product **2.12b** (758 mg, 46% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33−7.26 (m, 2H), 7.25−7.17 (m, 4H), 7.16−7.07 (m, 3H), 6.45−6.34 (m, 1H), 6.25−5.61 (m, 1H), 2.83−2.73 (m, 2H), 2.70−2.46 (m, 2H), 2.33 (d, *J* = 4.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.8 (C), 136.6 (C), 134.9 (C), 129.2 (2CH), 128.9 (CH), 128.8 (CH), 128.6 (CH), 128.5 (2CH), 128.3 (2CH), 125.8 (2CH), 35.9 (CH_2), 34.9 (CH_2), 21.1 (CH_3); ATR-FTIR (neat): 3024, 2920, 1603, 1512, 1495 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{17}H_{18}$ $[M]^+$: 222.1409, found: 222.1406.
Minor isomer: ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.7 (C), 131.1 (C), 130.1 (CH), 129.2 (CH), 125.8 (CH), 36.1 (CH_2), 30.5 (CH_2).



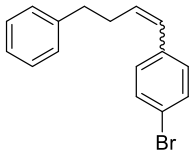
2.12c

(*Z*)- and (*E*)-1-chloro-4-(4-phenylbut-3-en-1-yl)benzene 2.12c: General procedure II was followed using 160 mg of aldehyde **S2** (0.95 mmol), 0.62 g of benzyltriphenylphosphonium bromide (1.42 mmol), 3.16 mL of dry THF and 0.95 mL of a 1.7 M solution of *t*-BuOK in THF. Purification by flash column chromatography (hexane) afforded the alkene product **2.12c** (56 mg, 24 % yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55−7.26 (m, 5H), 7.24−7.09 (m, 4H), 6.48−6.37 (m, 1H), 6.27−5.62 (m, 1H), 2.82−2.70 (m, 2H), 2.68−2.47 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.1 (C), 137.5 (C), 131.6 (C); 129.8 (2CH), 129.4 (CH), 128.7 (CH), 128.5 (2CH), 128.4 (2CH), 127.0 (CH), 126.0 (2CH), 35.2 (CH_2), 34.7 (CH_2); ATR-FTIR (neat): 3025, 2933, 1597, 1491, 1447 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{16}H_{15}Cl$ $[M]^+$: 242.0862, found: 242.0864.
Minor Isomer: ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.3 (CH), 130.7 (CH), 129.7 (CH), 128.2 (CH), 127.6 (CH), 126.5 (CH), 35.3 (CH_2), 30.2 (CH_2).



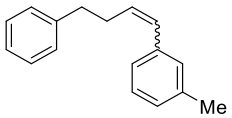
2.12d

(*Z*)- and (*E*)-1-bromo-4-(4-phenylbut-3-en-1-yl)benzene 2.12d: General procedure II was followed using 230 mg of aldehyde 3-(4-bromophenyl)propanal (1.08 mmol), 0.70 g of benzyltriphenylphosphonium bromide (1.62 mmol), 3.59 mL of dry THF and 1.08 mL of a 1.7 M solution of *t*-BuOK in THF. Purification by flash column chromatography (hexane) afforded the alkene product **2.12d** (72 mg, 31 % yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44−7.27 (m, 3H), 7.25−7.17 (m, 5H), 7.12−7.03 (m, 2H), 6.48−6.37 (m, 1H), 6.26−5.62 (m, 1H), 2.79−2.68 (m, 2H), 2.67−2.47 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.5 (C), 137.5 (C), 131.4 (2CH), 131.2 (CH), 130.2 (2CH), 129.7 (CH), 128.7 (CH), 128.5 (CH), 128.2 (CH), 126.6 (CH), 126.0 (CH), 119.6 (C), 35.4 (CH_2), 30.1 (CH_2); ATR-FTIR (neat): 2933, 2852, 1714, 1487, 1447 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{16}H_{18}$ $[M]^+$: 286.0357, found: 286.0359.
Minor Isomer: ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.6 (C), 137.4 (C), 130.7 (CH), 129.4 (CH), 127.0 (CH), 119.6 (C), 35.2 (CH_2), 34.6 (CH_2).



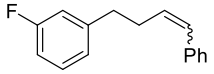
2.12e

(*Z*)- and (*E*)-1-bromo-4-(4-phenylbut-1-en-1-yl)benzene 2.12e: General procedure II was followed using 500 mg of aldehyde 3-phenylpropanal (3.72 mmol), 2.86 g of (4-bromobenzyl)triphenylphosphonium bromide (5.58 mmol), 12.4 mL of dry THF and 3.72 mL of a 1.7 M solution of *t*-BuOK in THF. Purification by flash column chromatography (hexanes) afforded the alkene product **2.12e** (44 mg, 8.8 % yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50−7.34 (m, 2H), 7.33−7.27 (m, 2H), 7.24−7.16 & 7.10−7.01 (m, 5H), 6.39−6.32 (m, 1H), 6.29−5.69 (m, 1H), 2.82−2.74 (m, 2H), 2.65−2.48 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.5 (C), 136.6 (C),131.5 (2CH), 130.8 (CH), 129.3 (CH), 128.4 (2CH), 128.3 (2CH), 127.5 (2CH), 125.9 (CH), 120.5 (C), 35.7 (CH_2), 34.8 (CH_2); ATR-FTIR (neat): 2924, 2852, 1649, 1487, 1453 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{16}H_{15}Br$ $[M]^+$: 286.0357, found: 286.0353.
Minor isomer: ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.6 (CH), 132.6 (CH), 131.8 (CH), 131.2 (CH), 130.3 (CH), 128.3 (CH), 128.0 (CH), 126.0 (CH), 120.4 (C), 35.9 (CH_2), 30.4 (CH_2).



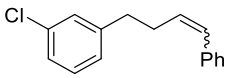
2.12f

(*Z*)- and (*E*)-1-methyl-3-(4-phenylbut-1-en-1-yl)benzene 2.12f: General procedure II was followed using 500 mg of aldehyde 3-phenylpropanal (3.72 mmol), 2.25 g of (3-methylbenzyl)triphenylphosphonium bromide (5.58 mmol), 12.4 mL of dry THF and 3.72 mL of a 1.7 M solution of *t*-BuOK in THF. Purification by flash column chromatography (hexanes) afforded the alkene product **2.12f** (600 mg, 72 % yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41−7.35 (m, 2H), 7.34−7.27 (m, 4H), 7.25−7.09 (m, 3H), 6.54−6.44 (m, 1H), 6.39−5.73 (m, 1H), 2.87 (q, *J* = 7.5 Hz, 2H), 2.79−2.57 (m, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.7 (C), 137.9 (C), 137.7 (C), 130.4 (CH), 129.7 (CH), 128.4 (2CH), 128.3 (3CH), 127.7 (CH), 126.7 (CH), 125.8 (CH), 123.1 (CH), 35.8 (CH_2), 34.8 (CH_2), 21.4 (CH_3); ATR-FTIR (neat): 3025, 2920, 1602, 1495, 1453 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{17}H_{18}$ $[M]^+$: 222.1409, found: 222.1410.
Minor isomer: ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.7 (C), 137.4 (C), 131.6 (CH), 129.4 (2CH), 128.4 (CH), 128.3 (CH), 128.0 (CH), 127.3 (CH), 126.0 (CH), 125.8 (CH), 125.7 (CH), 36.1 (CH_2), 30.4 (CH_2), 21.4 (CH_3).



2.14a

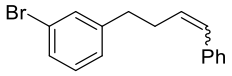
(Z)- and (E)-1-fluoro-3-(4-phenylbut-3-en-1-yl)benzene 2.14a: General procedure II was followed using 320 mg of aldehyde 3-(3-fluorophenyl)propanal (2.1 mmol), 1.37 g of benzyltriphenylphosphonium bromide (3.15 mmol), 7 mL of dry THF and 2.1 mL of a 1.7 M solution of *t*-BuOK in THF. Purification by flash column chromatography (hexanes) afforded the alkene product **2.14a** (230 mg, 48% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55−7.25 (m, 9H), 7.23−7.08 (m, 3H), 7.02−6.85 (m, 6H), 6.50−6.38 (m, 2H), 6.31−6.19 and 5.75−5.64 (m, 2H), 2.84−2.73 (m, 4H), 2.70−2.49 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.8 (d, *J* = 243.9 Hz, 2CF), 144.2 (d, *J* = 7.2 Hz, C), 144.1 (d, *J* = 7.1 Hz, C),137.5 (C), 137.3 (C), 131.2 (CH), 130.6 (CH), 129.7 (d, *J* = 7.0 Hz, 2CH), 129.6 (CH), 129.3 (CH), 128.6 (CH), 128.5 (2CH), 128.1 (CH), 127.0 (CH), 126.6 (CH), 125.9 (2CH), 124.0 (q, *J* = 2.7 Hz, 4CH), 115.2 (d, *J* = 20.7 Hz, 2CH), 112.7 (d, *J* = 20.9 Hz, 2CH), 35.7 (CH_2), 35.5 (CH_2), 34.5 (CH_2), 30.0 (CH_2); ^{19}F NMR (376 MHz, $CDCl_3$): δ -113.7; ATR-FTIR (neat): 3026, 2929, 1589, 1488, 1448 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{16}H_{15}F$ $[M]^+$: 226.1158, found: 226.1158.



2.14b

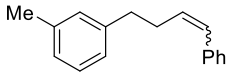
(*Z*)- and (*E*)-1-chloro-3-(4-phenylbut-3-en-1-yl)benzene 2.14b: General procedure II was followed using 231 mg of aldehyde **S4** (1.37 mmol), 0.89 g of benzyltriphenylphosphonium bromide (2.05 mmol), 4.56 mL of dry THF and 1.37 mL of a 1.7 M solution of *t*-BuOK in THF. Purification by flash column chromatography (hexanes) afforded the alkene product **2.14b** (199 mg, 60% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55−7.25 (m, 8H), 7.26−7.15 (m, 8H), 7.14−7.04 (m, 2H), 6.49−6.38 (m, 2H), 6.31–6.14 and 5.75–5.58 (m, 2H), 2.83–2.69 (m, 4H), 2.69–2.60 (m,

2H), 2.57–2.48 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.7 (C), 143.6 (C), 137.5 (C), 137.4 (C), 134.1 (2C), 131.2 (CH), 130.7 (CH), 129.8 (CH), 129.6 (CH), 129.3 (CH), 128.9 (CH), 128.7 (CH), 128.6 (2CH), 128.5 (2CH), 128.2 (2CH), 127.0 (2CH), 126.7 (2CH), 126.5 (CH), 126.1 (2CH), 126.0 (2CH), 35.7 (CH_2), 35.5 (CH_2), 34.6 (CH_2), 30.0 (CH_2); ATR-FTIR (neat): 3024, 2929, 1598, 1574, 1476 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{16}H_{15}Cl$ $[M]^+$: 242.0862, found: 242.0864.



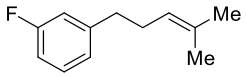
2.14c

(*Z*)- and (*E*)-1-bromo-3-(4-phenylbut-3-en-1-yl)benzene 2.14c: General procedure II was followed using 200 mg of aldehyde **S5** (0.94 mmol), 0.61 g of benzyltriphenylphosphonium bromide (1.40 mmol), 3.12 mL of dry THF and 0.93 mL of a 1.7 M solution of *t*-BuOK in THF. Purification by flash column chromatography (hexane) afforded the alkene product **2.14c** (129 mg, 64 % yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56−7.27 (m, 10H), 7.24−7.09 (m, 8H), 6.50−6.39 (m, 2H), 6.33−5.63 (m, 2H), 2.82−2.72 (m, 4H), 2.69−2.49 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.0 (C), 143.9 (C), 137.5 (C), 137.4 (C), 131.5 (CH), 130.7 (CH), 129.9 (2CH), 129.3 (CH), 129.0 (2CH), 128.7 (2CH), 128.5 (4CH), 128.3 (CH), 128.2 (CH), 128.1 (CH), 127.1 (CH), 127.0 (CH), 126.7 (CH), 126.0 (3CH), 122.4 (2C), 35.6 (CH_2), 35.5 (CH_2), 34.6 (CH_2), 30.0 (CH_2); ATR-FTIR (neat): 3025, 2928, 1597, 1567, 1495 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{16}H_{15}Br$ $[M]^+$: 286.0357, found: 286.0358.



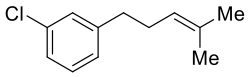
2.14d

(*Z*)- and (*E*)-1-methyl-3-(4-phenylbut-3-en-1-yl)benzene 2.14d: General procedure II was followed using 300 mg of aldehyde **S6** (2.02 mmol), 1.31 g of benzyltriphenylphosphonium bromide (3.03 mmol), 6.75 mL of dry THF and 2.02 mL of a 1.7 M solution of *t*-BuOK in THF. Purification by flash column chromatography (hexanes) afforded the alkene product **2.14d** (310 mg, 69% yield) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37−7.26 (m, 8H), 7.24−7.15 (m, 4H), 7.08−6.98 (m, 6H), 6.44−6.39 (m, 2H), 6.33−6.22 (m, 1H), 5.76−5.67 (m, 1H), 2.80−2.70 (m, 4H), 2.70−2.62 and 2.57−2.48 (m, 4H), 2.34 (d, J = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.7 (C), 141.6 (C), 137.9 (2C), 137.7 (C), 137.6 (C), 131.9 (CH), 130.2 (CH), 130.1 (CH), 129.3 (4CH), 128.7 (CH), 128.5 (3CH), 128.2 (CH), 128.1 (CH), 126.9 (CH), 126.6 (3CH), 126.5 (CH), 126.0 (3CH), 125.4 (CH), 36.0 (CH_2), 35.8 (CH_2), 34.9 (CH_2), 30.4 (CH_2), 21.4 (2CH_3); ATR-FTIR (neat): 3024, 2922, 1608, 1494, 1448 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{17}H_{18}$ $[M]^+$: 222.1409, found: 222.1408.



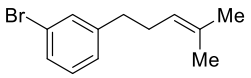
2.14e

1-fluoro-3-(4-methylpent-3-en-1-yl)benzene 2.14e: General procedure II was followed using 280 mg of aldehyde 3-(3-fluorophenyl)propanal (1.84 mmol), 1.19 g of isopropyltriphenylphosphonium iodide (2.76 mmol), 6.1 mL of dry THF and 1.84 mL of a 1.7 M solution of *t*-BuOK in THF. Purification by flash column chromatography (hexanes) afforded the alkene product **2.14e** (109.4 mg, 40% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (q, *J* = 6.3 Hz, 1H), 6.95 (d, *J* = 7.5 Hz, 1H), 6.91–6.83 (m, 2H), 5.16–5.10 (m, 1H), 2.62 (t, *J* = 8.2 Hz, 2H), 2.29 (q, *J* = 7.6 Hz, 2H), 1.68 (s, 3H), 1.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.8 (d, *J* = 243.6 Hz, CF), 144.9 (d, *J* = 7.0 Hz, C), 132.4 (C), 129.5 (d, *J* = 8.3 Hz, CH), 124.0 (d, *J* = 2.6 Hz, CH), 123.2 (CH), 115.2 (d, *J* = 20.6 Hz, CH), 112.5 (d, *J* = 20.9 Hz, CH), 35.8 (CH_2), 29.6 (CH_2), 25.6 (CH_3), 17.6 (CH_3); ^{19}F (376 MHz, $CDCl_3$): -114.18; ATR-FTIR (neat): 2927, 2858, 1616, 1590, 1448 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{12}H_{15}F[M]^+$: 178.1158, found: 178.1160.



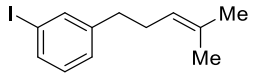
2.14f

1-chloro-3-(4-methylpent-3-en-1-yl)benzene 2.14f: General procedure II was followed using 500 mg of aldehyde **S4** (2.96 mmol), 1.92 g of isopropyltriphenylphosphonium iodide (4.44 mmol), 9.9 mL of dry THF and 2.96 mL of a 1.7 M solution of *t*-BuOK in THF. Purification by flash column chromatography (hexanes) afforded the alkene product **2.14f** (354.3 mg, 61% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23–7.13 (m, 3H), 7.06 (d, *J* = 7.6 Hz, 1H), 5.18–5.10 (m, 1H), 2.61 (t, *J* = 7.8 Hz, 2H), 2.28 (q, *J* = 7.8 Hz, 2H), 1.69 (s, 3H), 1.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.4 (C), 133.9 (C), 132.6 (C), 129.4 (CH), 128.6 (CH), 126.6 (CH), 125.8 (CH), 123.2 (CH), 35.8 (CH_2), 29.7 (CH_2), 25.7 (CH_3), 17.6 (CH_3); ATR-FTIR (neat): 2926, 2857, 1598, 1573, 1477 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{12}H_{15}Cl[M]^+$: 194.0862, found: 194.0864.



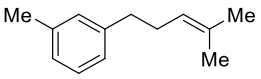
2.14g

1-bromo-3-(4-methylpent-3-en-1-yl)benzene 2.14g: General procedure II was followed using 300 mg of aldehyde **S5** (1.41 mmol), 0.912 g of isopropyltriphenylphosphonium iodide (2.11 mmol), 4.7 mL of dry THF and 1.41 mL of a 1.7 M solution of *t*-BuOK in THF. Purification by flash column chromatography (hexanes) afforded the alkene product **2.14g** (150 mg, 44% yield) as a colorless oil.^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33–7.26 (m, 2H), 7.20–7.07 (m, 2H), 5.16–5.08 (m, 1H), 2.59 (t, *J* = 7.9 Hz, 2H), 2.26 (q, *J* = 8.3 Hz, 2H), 1.68 (s, 3H), 1.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.7 (C), 132.6 (C), 131.5 (CH), 129.7 (CH), 128.7 (CH), 127.1 (CH), 123.1 (CH), 122.2 (C), 35.7 (CH_2), 29.7 (CH_2), 25.7 (CH_3), 17.6 (CH_3); ATR-FTIR (neat): 2926, 2857, 1567, 1473,1425 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{12}H_{15}Br[M]^+$: 238.0357, found: 238.0358.



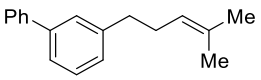
2.14h

1-iodo-3-(4-methylpent-3-en-1-yl)benzene 2.14h: General procedure II was followed using 197.6 mg of aldehyde **S7** (0.76 mmol), 0.5 g of isopropyltriphenylphosphonium iodide (1.14 mmol), 2.6 mL of dry THF and 0.76 mL of a 1.7 M solution of *t*-BuOK in THF. Purification by flash column chromatography (hexanes) afforded the alkene product **2.14h** (110.3 mg, 51% yield) as a colorless oil.^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (s, 1H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.14 (d, *J* = 7.7 Hz, 1H), 7.00 (t, *J* = 7.7 Hz, 1H), 5.13 (t, *J* = 7.1 Hz, 1H), 2.56 (8.8 Hz, 2H), 2.26 (q, *J* = 8.2 Hz, 2H), 1.69 (s, 3H), 1.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.8 (C), 137.5 (CH), 134.7 (CH), 132. 6 (C), 129.9 (CH), 127.7 (CH), 123.1 (CH), 94.3 (C), 35.6 (CH_2), 29.8 (CH_2), 25.7 (CH_3), 17.7 (CH_3); ATR-FTIR (neat): 2925, 2855, 1590, 1563, 1470 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{12}H_{15}I[M]^+$: 286.0219, found: 286.0217.



2.14i

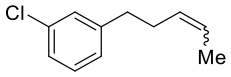
1-methyl-3-(4-methylpent-3-en-1-yl)benzene 2.14i: General procedure II was followed using 250 mg of aldehyde **S6** (1.68 mmol), 1.09 g of isopropyltriphenylphosphonium iodide (2.52 mmol), 5.6 mL of dry THF and 1.68 mL of a 1.7 M solution of *t*-BuOK in THF. Purification by flash column chromatography (hexanes) afforded the alkene product **2.14i** (173 mg, 69% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (t, *J* = 7.4 Hz, 1H), 7.09–7.03 (m, 3H) , 5.27–5.21 (m, 1H), 2.65 (t, *J* = 7.6 Hz, 2H), 2.39 (s, 3H), 2.36 (q, *J* = 8.0 Hz, 2H), 1.76 (s, 3H), 1.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.3 (C), 137.7 (C), 132.0 (C), 129.2 (CH), 128.1 (CH), 126.4 (CH), 125.4 (CH), 123.8 (CH), 36.1 (CH_2), 30.1 (CH_2), 25.6 (CH_3), 21.4 (CH_3), 17.6 (CH_3); ATR-FTIR (neat): 2920, 2856, 1609, 1488, 1376 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{13}H_{18}[M]^+$: 174.1409, found: 174.1413.



2.14j

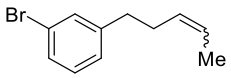
3-(4-methylpent-3-en-1-yl)-1,1'-biphenyl 2.14j: General procedure II was followed using 206 mg of aldehyde **S8** (0.97 mmol), 0.63 g of isopropyltriphenylphosphonium iodide (1.45 mmol), 3.24 mL of dry THF and 0.97 mL of a 1.7 M solution of *t*-BuOK in THF. Purification by flash column chromatography (hexanes) afforded the alkene product **2.14j** (160 mg, 69% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66–7.62 (m, 2H), 7.52–7.36 (m, 7H), 7.62–7.21 (m, 1H), 5.30–5.23 (m, 1H), 2.75 (t, *J* = 8.0 Hz, 2H), 2.40 (q, *J* = 7.5 Hz, 2H), 1.76 (s, 3H), 1.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.9 (C), 141.5 (C), 141.2 (C), 132.3 (C), 128.7 (3CH), 127.4 (2CH), 127.2 (3CH), 124.6 (CH), 123.7 (CH), 36.3 (CH_2), 30.2 (CH_2), 25.8 (CH_3), 17.7 (CH_3); ATR-

FTIR (neat): 2966, 2924, 1600, 1479, 1452 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{18}H_{20}[M]^+$: 236.1565, found: 236.1572.



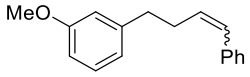
2.14k

(*Z*)-1-chloro-3-(pent-3-en-1-yl)benzene 2.14k: General procedure II was followed using 400 mg of aldehyde **S4** (2.37 mmol), 1.32 g of ethyltriphenylphosphonium bromide (3.56 mmol), 7.9 mL of dry THF and 2.37 mL of a 1.7 M solution of *t*-BuOK in THF. Purification by flash column chromatography (hexanes) afforded the alkene product **2.14k** (257 mg, 60% yield) as a colorless oil.^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23–7.13 (m, 3H), 7.07 (d, *J* = 6.9 Hz, 1H), 5.53–5.34 (m, 2H), 2.63 (t, *J* = 8.6 Hz, 2H), 2.35 (q, *J* = 7.3 Hz, 2H), 1.55 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.1 (C), 133.9 (C), 129.4 (CH), 129.0 (CH), 128.6 (CH), 126.6 (CH), 125.9 (CH), 124.9 (CH), 35.4 (CH_2), 28.4 (CH_2), 12.7 (CH_3); ATR-FTIR (neat): 2933, 2859, 1598, 1574, 1476 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{11}H_{13}Cl[M]^+$: 180.0706, found: 180.0703.



2.14l

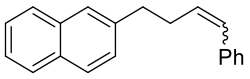
(*Z*)-1-bromo-3-(pent-3-en-1-yl)benzene 2.14l: General procedure II was followed using 286 mg of aldehyde **S5** (1.34 mmol), 0.747 g of ethyltriphenylphosphonium bromide (2.01 mmol), 4.5 mL of dry THF and 1.34 mL of a 1.7 M solution of *t*-BuOK in THF. Purification by flash column chromatography (hexanes) afforded the alkene product **2.14l** (150 mg, 50% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (s, 1H), 7.30 (d, *J* = 7.4 Hz, 1H), 7.13 (q, *J* = 7.8 Hz, 2H), 5.53–5.33 (m, 2H), 2.62 (t, *J* = 7.8 Hz, 2H), 2.34 (q, *J* = 7.5 Hz, 2H), 1.55 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.5 (C), 131.5 (CH), 129.8 (CH), 129.0 (CH), 128.8 (CH), 127.1 (CH), 124.9 (CH), 122.3 (C), 35.4 (CH_2), 28.5 (CH_2), 12.7 (CH_3); ATR-FTIR (neat): 2931, 2870, 1590, 1479, 1456 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{11}H_{13}Br[M]^+$: 224.0201, found: 224.0207.



2.14m

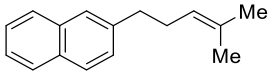
(*Z*)- and (*E*)-1**-methoxy-3-(4-phenylbut-3-en-1-yl)benzene 2.14m**: General procedure II was followed using 312 mg of aldehyde **S9** (1.9 mmol), 1.23 g of benzyltriphenylphosphonium bromide (2.85 mmol), 6.33 mL of dry THF and 1.9 mL of a 1.7 M solution of *t*-BuOK in THF. Purification by flash column chromatography (100:0 → 90: 10 Hexanes:EtOAc) afforded the alkene product **2.14m** (334 mg, 74% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45−7.22 (m, 12H), 6.92−6.78 (m, 6H), 6.54−6.45 (m, 2H), 6.37−6.27 and 5.81−5.73 (m, 2H), 3.84 (d, *J* = 7.1 Hz, 6H), 2.88−2.69 (m, 5H), 2.64−2.55 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6 (2C), 143.3 (C), 143.2 (C), 137.6 (C), 137.4 (C), 131.7 (CH), 130.3 (2CH), 129.8 (CH), 129.4

(CH), 129.2 (2CH), 128.6 (CH), 128.4 (2CH), 128.1 (CH), 126.9 (2CH), 126.5 (CH), 125.9 (2CH), 120.8 (2CH), 114.1 (2CH), 111.1 (2CH), 55.0 ($2CH_3$), 36.0 (CH_2), 35.8 (CH_2), 34.7 (CH_2), 30.4 (CH_2); ATR-FTIR (neat): 2935, 2834, 1600, 1489, 1453 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{17}H_{18}O$ $[M]^+$: 238.1358, found: 238.1357.



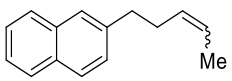
2.18a

(*Z*)- and (*E*)-2-(4-phenylbut-3-en-1-yl)naphthalene 2.18a: General procedure II was followed using 247 mg of aldehyde **S10** (1.34 mmol), 0.871 g of benzyltriphenylphosphonium bromide (2.01 mmol), 4.47mL of dry THF and 1.34 mL of a 1.7 M solution of *t*-BuOK in THF. Purification by flash column chromatography (hexanes) afforded the alkene product **2.18a** (200 mg, 58% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84−7.74 (m, 6H), 7.69−7.63 (m, 2H), 7.54−7.10 (m, 16H), 6.54−6.45 (m, 2H), 6.39−5.74 (m, 2H), 2.99 (m, 4H), 2.85−2.62 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.2 (2C), 139.1 (2C), 137.6 (C), 137.5 (C), 133.6 (C), 133.5 (C), 131.7 (CH), 130.4 (CH), 129.8 (CH), 129.5 (CH), 128.7 (CH), 128.4 (3CH), 128.1 (CH), 127.8 (2CH), 127.6 (2CH), 127.4 (2CH), 127.3 (2CH), 126.9 (CH), 126.6 (CH), 126.4 (2CH), 126.0 (3CH), 125.9 (2CH), 125.1 (2CH), 36.2 (CH_2), 36.0 (CH_2), 34.8 (CH_2), 30.2 (CH_2); ATR-FTIR (neat): 2924, 2849, 1713, 1598, 1448 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{20}H_{18}$ $[M]^+$: 258.1408, found: 258.1408.



2.18b

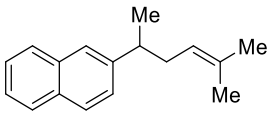
2-(4-methylpent-3-en-1-yl)naphthalene 2.18b: General procedure II was followed using 253 mg of aldehyde **S10** (1.37 mmol), 0.89 mg of isopropyltriphenylphosphonium iodide (2.06 mmol), 4.57 mL of dry THF and 1.37 mL of a 1.7 M solution of *t*-BuOK in THF. Purification by flash column chromatography (hexanes) afforded the alkene product **2.18b** (214.5 mg, 74% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83–7.73 (m, 3H), 7.62 (s, 1H), 7.47–7.38 (m, 2H), 7.34 (dd, J = 1.7, 8.5 Hz, 1H), 5.24–5.18 (m, 1H), 2.18 (t, J = 8.0 Hz, 2H), 2.38 (q, J = 8.0 Hz, 2H), 1.69 (s, 3H), 1.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.9 (C), 133.6 (C), 132.2 (C), 131.9 (C), 127.7 (CH), 127.6 (CH), 127.4 (2CH), 126.3 (CH), 125.8 (CH), 125.0 (CH), 123.7 (CH), 36.3 (CH_2), 29.9 (CH_2), 25.7 (CH_3), 17.7 (CH_3); ATR-FTIR (neat): 2924, 2855, 1600, 1508, 1450 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{16}H_{18}[M]^+$: 210.1409, found: 210.1415.



2.18c

(*Z*)- and (*E*)-2-(pent-3-en-1-yl)naphthalene 2.18c: General procedure II was followed using 460.5 mg of aldehyde **S10** (2.50 mmol), 1.39 g of ethyltriphenylphosphonium bromide (3.75 mmol), 8.33 mL of dry THF and 2.50 mL of a 1.7 M solution of *t*-BuOK

in THF. Purification by flash column chromatography (hexanes) afforded the alkene product **2.18c** (317.2 mg, 65% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82–7.74 (m, 3H), 7.63 (m, 1H), 7.43–7.30 (m, 3H), 5.53–5.41 (m, 2H), 2.83 (t, J = 8.7 Hz, 2H), 2.50–2.41 (m, 2H), 1.70–1.53 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.7 (C), 133.6 (C), 131.9 (C), 129.5 (CH), 127.7 (CH), 127.6 (CH), 127.4 (2CH), 126.4 (CH), 125.8 (CH), 125.0 (CH), 124.6 (CH), 35.9 (CH_2), 28.6 (CH_2), 12.8 (CH_3); ATR-FTIR (neat): 2919, 2855, 1600, 1508, 1438 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{15}H_{16}[M]^{+}$: 196.1252, found: 196.1247.

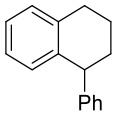


2.18d

(*Z*)- and (*E*)-2-(5-methylhex-4-en-2-yl)naphthalene 2.18d: General procedure II was followed using 250 mg of aldehyde **S11** (1.26 mmol), 818 mg of isopropyltriphenylphosphonium iodide (1.89 mmol), 4.2 mL of dry THF and 1.26 mL of a 1.7 M solution of *t*-BuOK in THF. Purification by flash column chromatography (hexanes) afforded the alkene product **2.18d** (282.6 mg, 75% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08−8.00 (m, 3H), 7.90 (s, 1H), 7.73−7.60 (m, 3H), 5.42 (s, 1H), 3.17 (q, J = 7.0 Hz, 1H), 2.65 (q, J = 7.8 Hz, 2H), 1.95 (s, 3H), 1.86 (s, 3H), 1.62 (d, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.9 (C), 133.6 (C), 132.3 (C), 132.1 (C), 127.7 (CH), 127.5 (2CH), 125.9 (CH), 125.7 (CH), 125.0 (2CH), 122.9 (CH), 40.4 (CH), 36.7 (CH_2), 25.8 (CH_3), 21.4 (CH_3), 17.8 (CH_3); ATR-FTIR (neat): 2962, 2912, 1600, 1506, 1452 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{17}H_{20}$ $[M]^{+}$: 224.1565, found: 224.1561.

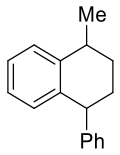
C. Synthesis of tetralins via intramolecular hydroarylation of alkenes.

General procedure III: In a dry 4 mL (1 dram) glass vial charged with PTFE coated magnetic stir bar, 1 equivalent of alkene was dissolved in 0.5 M of dry benzene 0.5 M. Depending on the alkene substrate, 0.020 or 0.050 mmol TPFBP was added to vial. The reaction mixture was then sealed and allowed to stir for 2 h at 50 ºC, at which point the reaction was cooled to room temperature before it was quenched with 1 mL of saturated $NaHCO_3$. The cyclized product was extracted with 2 mL of CH_2Cl_2 thrice and dried over anhydrous Na_2SO_4. The dry solution was then concentrated in vacuo to furnish the crude product as oil. Purification by silica gel chromatography (100% hexanes) afforded the tetralin product.



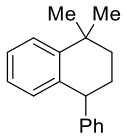
2.2a

1-phenyl-1,2,3,4-tetrahydronaphthalene 2.2a: General procedure III, was followed using amount 104.2 mg of alkene **2.1a** (0.5 mmol), 9.23 mg of tritylium TPFBP (0.01 mmol) and amount 1 mL of benzene. Purification by silica gel chromatography (100% hexanes) afforded tetralin **2.2a** (94 mg, 90%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37−7.30 (m, 2H), 7.28−7.13 (m, 5H), 7.09−7.06 (m, 1H), 6.91 (d, J = 7.7 Hz, 1H), 4.18 (t, J = 6.8 Hz, 1H), 3.04−2.85 (m, 2H), 2.28−2.18 (m, 1H), 2.02−1.74 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.5 (C), 139.3 (C), 137.5 (C), 130.1 (CH), 128.9 (CH), 128.8 (2CH), 128.2 (2CH), 125.9 (CH), 125.8 (CH), 125.6 (CH), 45.6 (CH), 33.2 (CH_2), 29.7 (CH_2), 20.9 (CH_2) ; ATR-FTIR (neat): 2980, 2868, 1600, 1492, 1449 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{16}H_{16}$ $[M]^+$: 208.1252, found: 208.1259.



2.2b

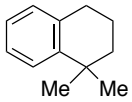
1-methyl-4-phenyl-1,2,3,4-tetrahydronaphthalene 2.2b: General procedure III, was followed using amount 120.8 of alkene **2.1b** (0.54 mmol), 10.02 mg of tritylium TPFBP (0.1009 mmol) and 1.09 mL of benzene. Purification by silica gel chromatography (100% hexanes) afforded tetralin **2.2b** (110 mg, 91%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36−7.27 (m, 6H), 7.26−7.17 (m, 4H), 7.17−7.11 (m, 3H), 7.11−7.04 (m, 3H), 6.87 (d, J = 7.8 Hz, 2H), 4.17 (t, J = 6.7 Hz, 1H), 4.12 (t, J = 7.7 Hz, 1H), 3.12−2.99 (m, 2H), 2.32−2.23 (m, 1H), 2.15−1.83 (m, 5H), 1.72−1.63 (m, 1H), 1.58−1.48 (m, 1H), 1.43 (d, J = 7.1 Hz, 3H), 1.39 (d, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.5 (C), 147.4 (C), 142.7 (C), 142.5 (C), 139.0 (2C), 130.1 (CH), 130.0 (CH), 128.8 (2CH), 128.8 (2CH), 128.2 (5CH), 127.7 (CH), 126.0 (2CH), 125.9 (2CH), 125.6 (2CH), 46.0 (2CH), 32.7 (CH), 32.7 (CH), 30.6 (CH_2), 29.7 (CH_2), 29.2 (CH_2), 28.6 (CH_2), 23.3 (CH_3), 22.9 (CH_3); ATR-FTIR (neat): 2924, 2855, 1601, 1490, 1455 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{17}H_{18}$ $[M]^+$: 222.1409, found: 222.1410.



2.2c

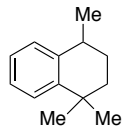
1,1-dimethyl-4-phenyl-1,2,3,4-tetrahydronaphthalene 2.2c: General procedure III, was followed using 85.0 mg of alkene **2.1c** (0.36 mmol), 6.62 mg of tritylium TPFBP (0.007 mmol) and 0.71 mL of benzene. Purification by silica gel chromatography (100% hexanes) afforded tetralin **2.2c** (76.7 mg, 90 %) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, J = 7.9 Hz, 1H); 7.32–7.27 (m, 2H), 7.23–7.16 (m, 2H), 7.11–7.06 (m, 2H), 7.03 (t, J = 7.5 Hz, 1H), 6.83 (d, J = 7.6 Hz, 1H) ,4.12 (t, J = 8.0 Hz, 1H), 2.21–2.12 (m, 1H), 1.99–1.88 (m,1H), 1.78–1.69 (m, 1H), 1.68–1.59 (m, 1H), 1.37 (d, J = 12.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.5 (C), 146.4 (C), 138.2 (C), 130.2 (CH), 128.9 (2CH), 128.2 (2CH), 126.5 (CH), 126.3 (CH), 125.9 (CH), 125.4 (CH), 46.4 (CH), 36.2

(CH_2), 34.0 (C), 32.1 (CH_3), 31.9 (CH_3), 29.3 (CH_2); ATR-FTIR (neat): 3024, 2959, 2932, 1601, 1489 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{18}H_{20}[M]^+$: 236.1565, found: 236.1566.



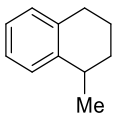
2.2d

1,1-dimethyl-1,2,3,4-tetrahydronaphthalene 2.2d: General procedure III, was followed using amount 79.8 mg of alkene **2.1d** (0.50 mmol), amount 23 mg of tritylium TPFBP (0.025 mmol) and 1.0 mL of benzene. Purification by silica gel chromatography (100% hexanes) afforded tetralin **2.2d** (53.5 mg, 67%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, *J* = 8.2 Hz, 1H), 7.18–7.12 (m, 1H), 7.10–7.02 (m, 2H), 2.78 (t, *J* = 6.3 Hz, 2H), 1.86–1.78 (m, 2H), 1.70–1.65 (m, 2H), 1.30 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.8 (C), 136.1 (C), 129.0 (CH), 126.6 (CH), 125.8 (CH), 125.2 (CH), 39.3 (CH_2), 33.8 (C), 31.9 ($2CH_3$), 30.7 (CH_2), 19.7 (CH_2); ATR-FTIR (neat): 2958, 2929, 2865, 1489, 1446 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{12}H_{16}[M]^+$: 160.1252, found: 160.1248.



2.2e

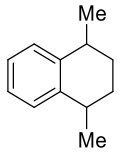
1,1,4-trimethyl-1,2,3,4-tetrahydronaphthalene 2.2e: General procedure III, was followed using 80.0 mg of alkene **2.1e** (0.46 mmol), 21.1 mg of tritylium TPFBP (0.023 mmol) and 0.91 mL of benzene. Purification by silica gel chromatography (100% hexanes) afforded tetralin **2.2e** (65.6 mg, 82 %) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37–7.32 (m, 1H), 7.21–7.10 (m, 3H), 2.92 (sex, *J* = 6.7 Hz, 1H), 2.02–1.92 (m, 1H), 1.84–1.75 (m, 1H), 1.65–1.54 (m, 2H), 1.33 (s, 3H), 1.31 (d, *J* = 6.9 Hz, 3H), 1.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.4 (C), 141.1 (C), 128.2 (CH), 126.6 (CH), 125.7 (CH), 125.4 (CH), 35.9 (CH_2), 34.0 (C), 33.4 (CH), 32.0 (CH_3), 31.9 (CH_3), 27.6 (CH_2), 23.0 (CH_3); ATR-FTIR (neat): 2934, 2860, 1589, 1481, 1450 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{13}H_{18}$ $[M]^+$: 175.1487, found: 175.1490.



2.2f

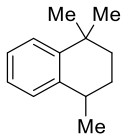
1-methyl-1,2,3,4-tetrahydronaphthalene 2.2f: General procedure III, was followed using 107 mg of alkene **2.1f** (0.73 mmol), 34 mg of tritylium TPFBP (0.0366 mmol) and 1.46 mL of benzene. Purification by silica gel chromatography (100% hexanes) afforded tetralin **2.2f** (57 mg, 53%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (d, *J* = 7.4 Hz, 1H), 7.18–7.06 (m, 3H), 2.93 (sex, *J* = 6.5 Hz, 1H), 2.86–2.72 (m, 2H), 2.00–1.84

(m, 2H), 1.81–1.70 (m, 1H), 1.61–1.52 (m, 1H), 1.32 (d, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.2 (C), 136.9 (C), 129.0 (CH), 128.1 (CH), 125.6 (CH), 125.4 (CH), 32.5 (CH), 31.5 (CH_2), 30.0 (CH_2), 22.9 (CH_3), 20.4 (CH_2); ATR-FTIR (neat): 2952, 2924, 2854, 1465, 1376 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{11}H_{14}[M]^+$: 146.1090, found: 146.1087.



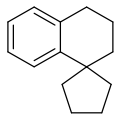
2.2g

1,4-dimethyl-1,2,3,4-tetrahydronaphthalene 2.2g: General procedure III, was followed using 81 mg of alkene **2.1g** (0.505 mmol), 23.3 mg of tritylium TPFBP (0.025 mmol) and 1.01 mL of benzene. Purification by silica gel chromatography (100% hexanes) afforded tetralin **2.2g** (59 mg, 73 %) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25–7.19 (m, 2H), 7.19–7.13 (m, 2H), 3.00–2.84 (m, 2H), 2.10–1.98 (m, 1H), 1.95–1.82 (m, 1H), 1.69–1.56 (m, 1H), 1.56–1.45 (m, 1H), 1.34 (d, J = 7.0 Hz, 3H), 1.31 (d, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.9 (C), 141.8 (C), 128.2 (CH), 127.8 (CH), 125.6 (CH), 125.5 (CH), 32.8 (2CH), 28.7 (CH_2), 28.3 (CH_2), 23.2 (CH_3), 22.6 (CH_3); ATR-FTIR (neat): 2960, 2931, 1594, 1485, 1461 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{12}H_{16}[M]^+$: 160.1252, found: 160.1260.



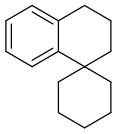
2.2h

1,1,4-trimethyl-1,2,3,4-tetrahydronaphthalene 2.2h: General procedure III, was followed using 80.0 mg of alkene **2.1h** (0.46 mmol), 21.1 mg of tritylium TPFBP (0.023 mmol) and 0.91 mL of benzene. Purification by silica gel chromatography (100% hexanes) afforded tetralin **2.2h** (65.6 mg, 82 %) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37–7.32 (m, 1H), 7.21–7.10 (m, 3H), 2.92 (sex, J = 6.7 Hz, 1H), 2.02–1.92 (m, 1H), 1.84–1.75 (m, 1H), 1.65–1.54 (m, 2H), 1.33 (s, 3H), 1.31 (d, J = 6.9 Hz, 3H), 1.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.4 (C), 141.1 (C), 128.2 (CH), 126.6 (CH), 125.7 (CH), 125.4 (CH), 35.9 (CH_2), 34.0 (C), 33.4 (CH), 32.0 (CH_3), 31.9 (CH_3), 27.6 (CH_2), 23.0 (CH_3); ATR-FTIR (neat): 2934, 2860, 1589, 1481, 1450 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{13}H_{18}$ $[M]^+$: 175.1487, found: 175.1490.



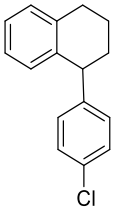
2.2i

3',4'-dihydro-2'H-spiro[cyclopentane-1,1'-naphthalene 2.2i: General procedure III, was followed using 92.7 mg of alkene **2.1i** (0.50 mmol), 22.9 mg of tritylium TPFBP (0.025 mmol) and 0.99 mL of benzene. Purification by silica gel chromatography (100% hexanes) afforded tetralin **2.2i** (78.7 mg, 85%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, J = 7.9 Hz, 1H), 7.17 (t, J = 7.9 Hz, 1H), 7.10–7.02 (m, 2H), 2.79 (t, J = 6.3 Hz, 2H), 1.97–1.73 (m, 10H), 1.73–1.66 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.4 (C), 136.9 (C), 128.7 (CH), 127.0 (CH), 126.0 (CH), 125.0 (CH), 45.8 (C), 43.6 ($2CH_2$), 37.3 (CH_2), 30.6 (CH_2), 26.0 ($2CH_2$), 20.8 (CH_2); ATR-FTIR (neat): 3014, 2935, 2866, 1488, 1447 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{14}H_{18}[M]^+$: 186.1409, found: 186.1404.



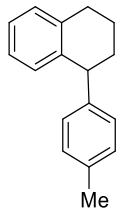
2.2j

3',4'-dihydro-2'H-spiro[cyclohexane-1,1'-naphthalene] 2.2j: General procedure III, was followed using 64.7 mg of alkene **2.1j** (0.32 mmol), 14.89 mg of tritylium TPFBP (0.016 mmol) and 0.65 mL of benzene. Purification by silica gel chromatography (100% hexanes) afforded tetralin **2.2j** (52.6 mg, 81%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, J = 7.8 Hz, 1H), 7.18 (t, J = 8.2 Hz, 1H), 7.12–7.04 (m, 2H), 2.77 (t, J = 6.2 Hz, 2H), 1.87–1.82 (m, 2H), 1.81–1.70 (m, 5H), 1.68–1.53 (m, 6H), 1.38–1.25 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.6 (C), 137.1 (C), 129.0 (CH), 126.8 (CH), 125.7 (CH), 125.1 (CH), 38.8 ($2CH_2$), 37.0 (C), 31.0 ($2CH_2$), 26.2 (CH_2), 22.0 ($2CH_2$), 19.2 (CH_2); ATR-FTIR (neat): 3014, 2927, 2858, 1487, 1446 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{15}H_{20}[M]^+$: 200.1565, found: 200.1562.



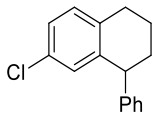
2.13a

1-(4-chlorophenyl)-1,2,3,4-tetrahydronaphthalene 2.13a: General procedure III, was followed using 106 mg of alkene **2.12a** (0.436 mmol), 8.1 mg of tritylium TPFBP (0.0087 mmol) and 0.87 mL of benzene. Purification by silica gel chromatography (100% hexanes) afforded tetralin **2.13a** (74 mg, 70%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (d, J = 8.3 Hz, 2H), 7.18–7.13 (m, 2H), 7.09–7.02 (m, 3H), 6.83 (d, J = 7.8 Hz, 1H), 4.12 (t, J = 6.6 Hz, 1H), 2.98–2.80 (m, 2H), 2.23–2.12 (m, 1H), 1.95–1.72 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.0 (C), 138.7 (C), 137.5 (C), 131.6 (C), 130.1 (2CH), 130.0 (CH), 129.0 (CH), 128.3 (2CH), 126.1 (CH), 125.7 (CH), 45.0 (CH), 33.2 (CH_2), 29.6 (CH_2), 20.8 (CH_2); ATR-FTIR (neat): 2932, 2859, 1708, 1599, 1490 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{16}H_{15}Cl[M]^+$: 242.0862, found: 242.0861.



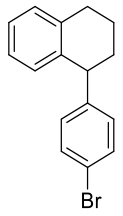
2.13b

1-(p-tolyl)-1,2,3,4-tetrahydronaphthalene 2.13b: General procedure III, was followed using 114 mg of alkene **2.12b** (0.512 mmol), amount mg of tritylium TPFBP (0.0102 mmol) and amount 1.0 mL of benzene. Purification by silica gel chromatography (100% hexanes) afforded tetralin **2.13b** (32 mg, 28%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17–7.08 (m, 4H), 7.08–6.99 (m, 3H), 6.87 (d, J = 7.7 Hz, 1H), 4.11 (t, J = 6.8 Hz, 1H), 3.00–2.78 (m, 2H), 2.35 (s, 3H), 2.23–2.09 (m, 1H), 1.99–1.71 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.5 (C), 139.6 (C), 137.6 (C), 135.4 (C), 130.2 (CH), 128.9 (3CH), 128.7 (2CH), 125.8 (CH), 125.6 (CH), 45.2 (CH), 33.3 (CH_2), 29.8 (CH_2), 21.0 (CH_2), 21.0 (CH_3); ATR-FTIR (neat): 2930, 2857, 1601, 1512, 1491 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{17}H_{18}[M]^+$: 222.1409, found: 222.1409.



2.13c

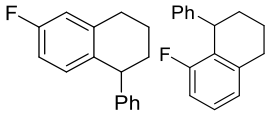
7-chloro-1-phenyl-1,2,3,4-tetrahydronaphthalene 2.13c: General procedure III, was followed using 54.7 mg of alkene **2.12c** (0.22 mmol), 4.16 mg of tritylium TPFBP (0.0045 mmol) and 0.45 mL of benzene. No tetralin product **2.13c** was formed.



2.13e

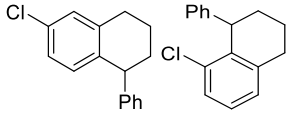
1-(4-bromophenyl)-1,2,3,4-tetrahydronaphthalene 2.13e: General procedure III, was followed using 44 mg of alkene **2.12e** (0.15 mmol), 2.82 mg of tritylium TPFBP (0.003 mmol) and 0.31 mL of benzene. Purification by silica gel chromatography (100% hexanes) afforded tetralin **2.13e** (38 mg, 86 %) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43−7.35 (m, 2H), 7.23−7.10 (m, 2H), 7.09−6.94 (m, 3H), 6.81 (d, J = 7.6 Hz, 1H), 4.09 (t, J = 6.6 Hz, 1H), 2.97−2.78 (m, 2H), 2.22−2.08 (m, 1H), 1.92−1.68 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.5 (C), 138.7 (C), 137.5 (C), 131.3 (2CH), 130.6 (2CH), 130.0 (CH), 129.1 (CH) 126.1 (CH), 125.7 (CH), 119.7 (C), 45.1 (CH), 33.2

(CH_2), 29.7 (CH_2), 20.8 (CH_2); ATR-FTIR (neat): 2929, 2857, 1601, 1487, 1448 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{16}H_{15}Br$ $[M]^+$: 286.0357, found: 286.0359.



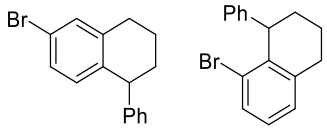
2.15a:2.16a

6-fluoro-1-phenyl-1,2,3,4-tetrahydronaphthalene 2.15a: General procedure III, was followed using amount 81.4 mg of alkene **2.14a** (0.36 mmol), 6.6 mg of tritylium TPFBP (0.0072 mmol) and 0.72 mL of benzene. Purification by silica gel chromatography (100% hexanes) afforded tetralin **2.15a** (73.1 mg, 90%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34−7.27 (m, 2H), 7.27−7.20 (m, 1H), 7.13−7.08 (m, 2H), 6.89−6.79 (m, 2H), 6.77 (dd, *J* = 8.4, 2.7 Hz, 1H), 4.10 (t, *J* = 6.8 Hz, 1H), 2.98−2.79 (m, 2H), 2.23−2.13 (m, 1H), 1.96−1.83 (m, 2H), 1.82−1.70 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161 (d, *J* = 242.6 Hz, CF), 147.3 (C), 139.6 (d, *J* = 7.0 Hz, C), 134.9 (d, *J* = 3.0 Hz, C), 131.7 (2CH), 131.6 (d, *J* = 1.4 Hz, CH), 128.7 (d, *J* = 30.0 Hz, CH), 115.0 (d, *J* = 3.0 Hz, CH), 114.8 (2CH), 112.9 (d, *J* = 3.8 Hz, CH), 45.0 (d, *J* = 18.2 Hz, CH), 33.2 (m, CH_2), 29.9 (CH_2), 20.6 (CH_2); ^{19}F (376 MHz, $CDCl_3$): δ -117.7; ATR-FTIR (neat): 2932, 2859, 1617, 1494, 1450 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{16}H_{15}F$ $[M]^+$: 226.1158, found: 226.1157.
8-fluoro-1-phenyl-1,2,3,4-tetrahydronaphthalene 2.16a: ^{13}C NMR (100 MHz, $CDCl_3$): δ 128.3 (d, *J* = 33.8 Hz, CH), 126.1 (q, *J* = 33.3 Hz, CH), 112.7 (d, *J* = 5.1 Hz, CH). Other peaks were obscured by major isomer peaks.



2.15b:2.16b

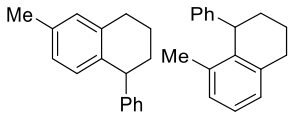
6-chloro-1-phenyl-1,2,3,4-tetrahydronaphthalene 2.15b: General procedure III, was followed using 80 mg of alkene **2.14b** (0.33 mmol), 6.01 mg of tritylium TPFBP (amount mmol) and amount 0.0066 of benzene. Purification by silica gel chromatography (100% hexanes) afforded tetralin **2.15b** 72 mg, 90%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32−7.26 (m, 2H), 7.23−7.11 (m, 2H), 7.11−7.06 (m, 2H), 7.02−6.94 (m, 1H), 6.78 (d, *J* = 8.3 Hz, 1H), 4.07 (t, *J* = 6.8 Hz, 1H), 2.95−2.75 (m, 2H), 2.21−2.11 (m, 1H), 1.95−1.81 (m, 2H), 1.80−1.69 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.9 (C), 139.4 (2C), 137.9 (C), 131.5 (CH), 128.7 (2CH), 128.6 (CH), 128.3 (2CH), 126.1 (CH), 125.8 (CH), 45.1 (CH), 33.1 (CH_2), 29.7 (CH_2), 20.7 (CH_2); ATR-FTIR (neat): 2934, 2859, 1595, 1482, 1450 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{16}H_{15}Cl$ $[M]^+$: 242.0862, found 242.0858.
8-chloro-1-phenyl-1,2,3,4-tetrahydronaphthalene 2.16b: ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.50−4.47 (m, 1H), 2.10−2.01 (m, 1H), 1.69−1.62 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.4 (CH). Other peaks were obscured by major isomer peaks.



2.15c:2.16c

6-bromo-1-phenyl-1,2,3,4-tetrahydronaphthalene 2.15c: General procedure III with the exception of running the reaction for 5 hours, was followed using 75.8 mg of alkene **2.14c** (0.26 mmol), 4.79 mg of tritylium TPFBP (0.0052 mmol) and 0.52 mL of benzene. Purification by silica gel chromatography (100% hexanes) afforded tetralin **2.15c** (60.3 mg, 80%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44−6.94 (m, 7H), 6.75 (d, *J* = 8.2 Hz, 1H), 4.08 (t, *J* = 6.8 Hz, 1H), 2.98−2.79 (m, 2H), 2.23−2.05 (m, 1H), 1.97−1.62 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.8 (C), 139.8 (C), 138.3 (C), 131.8 (CH), 131.5 (CH), 128.7 (3CH), 128.3 (2CH), 126.1 (CH), 119.5 (C), 45.1 (CH), 33.0 (CH_2), 29.6 (CH_2), 20.6 (CH_2); ATR-FTIR (neat): 2933, 2857, 1670, 1589, 1493 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{16}H_{15}Br[M]^+$: 286.0357, found: 286.0356.

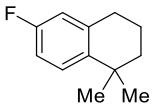
8-bromo-1-phenyl-1,2,3,4-tetrahydronaphthalene 2.16c: ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.98 (d, *J* = 7.8 Hz, 1H), 4.49 (s, 1H), 2.12−2.05 (m, 1H), 1.70−1.62 (m, 1H). Other peaks were obscured by major isomer peaks.



2.15d:2.16d

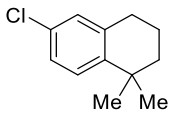
6-methyl-1-phenyl-1,2,3,4-tetrahydronaphthalene 2.15d: General procedure III, was followed using 91 mg of alkene **2.14d** (0.41 mmol), 7.6 mg of tritylium TPFBP (0.0082 mmol) and 0.82 mL of benzene. Purification by silica gel chromatography (100% hexanes) afforded tetralin **2.15d**, rr: 88:12 (84 mg, 92%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35−7.26 (m, 2H), 7.24−7.07 (m, 3H), 7.04−6.98 (m, 1H), 6.92−6.87 (m, 1H), 6.78 (d, *J* = 7.9 Hz, 1H), 4.12 (t, *J* = 6.8 Hz, 1H), 2.98−2.80 (m, 2H), 2.34 (s, 3H), 2.24−2.15 (m, 1H), 1.97−1.86 (m, 2H), 1.84−1.75 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.6 (C), 137.3 (C), 136.3 (C), 135.3 (C), 130.0 (CH), 129.4 (CH), 128.8 (2CH), 128.1 (2CH), 126.5 (CH), 125.8 (CH), 45.3 (CH), 33.4 (CH_2), 29.7 (CH_2), 21.1 (CH_2), 20.9 (CH_3); ATR-FTIR (neat): 2929, 2857, 1601, 1299, 1450 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{17}H_{18}$ $[M]^+$: 222.1409, found 222.1407.

8-methyl-1-phenyl-1,2,3,4-tetrahydronaphthalene 2.16d: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09 (d, *J* = 7.1 Hz, 1H), 4.30–4.26 (m, 1H), 1.98 (s, 3H), 1.73–1.63 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.4 (C), 137.7 (C), 128.4 (2CH), 128.0 (2CH), 126.9 (CH), 126.0 (CH), 125.5(CH), 41.7 (CH), 32.4 (CH_2), 29.8 (CH_2), 22.6 (CH_2), 19.6 (CH_3). Other peaks were obscured by major isomer peaks.



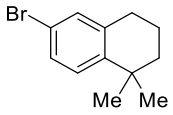
2.15e

6-fluoro-1,1-dimethyl-1,2,3,4-tetrahydronaphthalene 2.15e: General procedure III, was followed using 80.0 mg of alkene **2.14e** (0.45 mmol), 20.7 mg of tritylium TPFBP (0.022 mmol) and 0.9 mL of benzene. Purification by silica gel chromatography (100% hexanes) afforded tetralin **2.15e** (56.6 mg, 71 %) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30–7.24 (m, 1H), 6.83 (t, *J* = 8.6 Hz, 1H), 6.73 (d, *J* = 9.5 Hz, 1H), 2.75 (t, *J* = 6.4 Hz, 2H), 1.84–1.76 (m, 2H), 1.69–1.63 (m, 2H), 1.27 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.4 (d, *J* = 242.0 Hz, CF), 141.3 (d, *J* = 2.9 Hz, C), 138.2 (d, *J* = 6.9 Hz, C), 128.1 (d, *J* = 7.0 Hz, CH), 114.8 (d, *J* = 19.7 Hz, CH), 112.7 (d, *J* = 20.8 Hz, CH), 39.1 (CH_2), 33.5 (C), 31.9 ($2CH_3$), 30.9 (CH_2), 19.5 (CH_2); ^{19}F (376 MHz, $CDCl_3$): δ -118.9; ATR-FTIR (neat): 2958, 2931, 2868, 1611, 1494 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{12}H_{15}F[M]^+$: 178.1158, found: 178.1158.



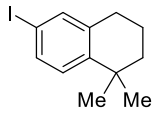
2.15f

6-chloro-1,1-dimethyl-1,2,3,4-tetrahydronaphthalene 2.15f: General procedure III, was followed using amount 100.1 mg of alkene **2.14f** (0.514 mmol), 23.7 mg of tritylium TPFBP (0.0257 mmol) and 1.03 mL of benzene. Purification by silica gel chromatography (100% hexanes) afforded tetralin **2.15f** (85 mg, 85%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (d, *J* = 8.6 Hz, 1H), 7.09 (d, *J* = 8.6 Hz, 1H), 7.01 (s, 1H), 2.72 (t, *J* = 6.3 Hz, 2H), 1.83–1.74 (m, 2H), 1.67–1.61 (m, 2H), 1.25 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.3 (C), 138.1 (C), 130.6 (C), 128.6 (CH), 128.1 (CH), 125.9 (CH), 39.0 (CH_2), 33.6 (C), 31.7 ($2CH_3$), 30.6 (CH_2), 19.5 (CH_2); ATR-FTIR (neat): 2960, 2932, 2867, 1594, 1484 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{12}H_{15}Cl$ $[M]^+$: 194.0862, found: 194.0872.



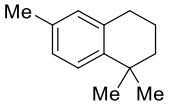
2.15g

6-bromo-1,1-dimethyl-1,2,3,4-tetrahydronaphthalene 2.15g: General procedure III, was followed using 75 mg of alkene **2.14g** (0.313 mmol), 14.5 mg of tritylium TPFBP (0.0157 mmol) and 0.63 mL of benzene. Purification by silica gel chromatography (100% hexanes) afforded tetralin **2.15g** (60 mg, 80%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27–7.22 (m, 1H), 7.21–7.16 (m, 2H), 2.74 (t, *J* = 6.4 Hz, 2H), 1.83–1.74 (m, 2H), 1.68–1.61 (m, 2H), 1.26 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.8 (C), 138.6 (C), 131.6 (CH), 128.8 (CH), 128.5 (CH), 118.8 (C), 39.0 (CH_2), 33.7 (C), 31.7 ($2CH_3$), 30.6 (CH_2), 19.5 (CH_2); ATR-FTIR (neat): 2930, 1589, 1481, 1439, 1141 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{12}H_{15}Br$ $[M]^+$: 238.0357, found: 238.0355.



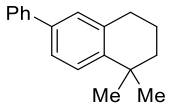
2.15h

6-iodo-1,1-dimethyl-1,2,3,4-tetrahydronaphthalene 2.15h: General procedure III, was followed using 100 mg of alkene **2.14h** (0.266 mmol), 12.3 mg of tritylium TPFBP (0.013 mmol) and amount mL of benzene. Purification silica gel chromatography (100% hexanes) afforded tetralin **2.15h** (85 mg, 85%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, J = 8.3 Hz, 1H), 7.40 (s, 1H), 7.05 (d, J = 8.3 Hz, 1H), 2.71 (t, J = 6.4 Hz, 2H), 1.82–1.73 (m, 2H), 1.67–1.61 (m, 2H), 1.25 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.6 (C), 138.9 (C), 137.7 (CH), 134.8 (CH), 128.7 (CH), 90.5 (C), 38.9 (CH_2), 33.7 (C), 31.7 ($2CH_3$), 30.4 (CH_2), 19.4 (CH_2); ATR-FTIR (neat): 2930, 2866, 1582, 1479, 1458 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{12}H_{15}I$ $[M]^+$: 286.0219, found: 286.0220.



2.15i

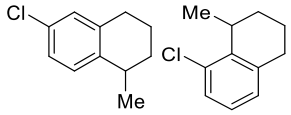
1,1,6-trimethyl-1,2,3,4-tetrahydronaphthalene 2.15i: General procedure III, was followed using 76.8 mg of alkene **2.14i** (0.44 mmol), 20.3 mg of tritylium TPFBP (0.022 mmol) and 0.88 mL of benzene. Purification by silica gel chromatography (100% hexanes) afforded tetralin **2.15i** (51.4 mg, 67 %) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (d, J = 8.0 Hz, 1H), 6.99 (d, J = 8.0 Hz, 1H), 6.90 (s, 1H), 2.76 (t, J = 6.3 Hz, 2H), 2.30 (s, 3H), 1.86–1.77 (m, 2H), 1.71–1.64 (m, 2H), 1.30 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.8 (C), 136.0 (C), 134.6 (C), 129.6 (CH), 126.7 (CH), 126.6 (CH), 39.4 (CH_2), 33.5 (C), 31.9 ($2CH_3$), 30.7 (CH_2), 20.8 (CH_3), 19.8 (CH_2); ATR-FTIR (neat): 2924, 2855, 1736, 1614, 1498 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{13}H_{18}$ $[M]^+$: 174.1409, found: 174.1413.



2.15j

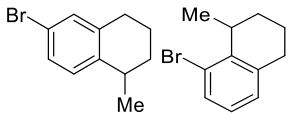
1,1-dimethyl-6-phenyl-1,2,3,4-tetrahydronaphthalene 2.15j: General procedure III, was followed using 75.9 mg of alkene **2.14j** (0.32 mmol), 14.8 mg of tritylium TPFBP (0.016 mmol) and 0.64 mL of benzene. Purification by silica gel chromatography (100% hexanes) afforded tetralin **2.15j** (68.9 mg, 91 %) as a white solid, mp = 39−41°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64–7.60 (m, 2H), 7.48–7.40 (m, 4H), 7.37–7.25 (m, 2H), 2.88 (t, J = 6.3 Hz, 2H), 1.93–1.84 (m, 2H), 1.77–1.71 (m, 2H), 1.37 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.0 (C), 141.1 (C), 138.1 (C), 136.5 (C), 128.6 (2CH), 127.6 (CH), 127.1 (CH), 127.0 (2CH), 126.8 (CH), 124.6 (CH), 39.3 (CH_2), 33.7 (C), 31.8

($2CH_3$), 30.9 (CH_2), 19.7 (CH_2); ATR-FTIR (neat): 2955, 2927, 1734, 1602, 1484, cm^{-1}; HRMS (EI) *m/z* calculated for $C_{18}H_{20}[M]^+$: 236.1565, found: 236.1564.



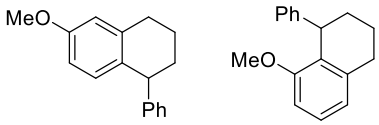
2.15k:2.16k

6-chloro-1-methyl-1,2,3,4-tetrahydronaphthalene 2.15k and 8-chloro-1-methyl-1,2,3,4-tetrahydronaphthalene 2.16k: General procedure III, was followed using 91.5 mg of alkene **2.14k** (0.51 mmol), 23.4 mg of tritylium TPFBP (0.025 mmol) and 1.01 mL of benzene. Purification by silica gel chromatography (100% hexanes) afforded tetralins **2.15k** and **2.16k** (73 mg, 80%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22–6.91 (m, 6H), 3.37–3.17 (m, 1H), 2.92–2.66 (m, 5H), 1.96–1.66 (m, 7H), 1.58–1.48 (m, 1H), 1.26 (d, *J* = 7.0 Hz, 3H), 1.25 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.6 (C), 139.8 (C), 138.7 (2C), 134.3 (C), 130.8 (C), 129.4 (CH), 128.6 (CH), 127.8 (CH), 126.9 (CH), 126.3 (CH), 125.7 (CH), 32.0 (CH), 31.2 (CH_2), 29.8 (CH), 29.8 ($2CH_2$), 29.6 (CH_2), 22.8 (CH_3), 20.6 (CH_3), 20.1 (CH_2), 17.6 (CH_2); ATR-FTIR (neat): 2933, 2870, 1595, 1482, 1458 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{11}H_{13}Cl$ $[M]^+$: 180.0706, found: 180.0714.



2.15l:2.16l

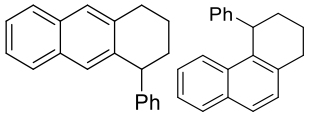
6-bromo-1-methyl-1,2,3,4-tetrahydronaphthalene 2.15l and 8-bromo-1-methyl-1,2,3,4-tetrahydronaphthalene 2.16l: General procedure III, was followed using 73.6 mg of alkene **2.14l** (0.327 mmol), 15.0 mg of tritylium TPFBP (0.0163 mmol) and 0.65 mL of benzene. Purification by silica gel chromatography (100% hexanes) afforded tetralin **2.15l** and **2.16l** (rr, 50:50) (amount mg, %) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, *J* = 7.8 Hz, 1H), 7.25 – 7.19 (m, 2H), 7.09 – 6.99 (m, 2H), 6.98–6.92 (m, 1H), 3.28–3.19 (m, 1H), 2.90–2.67 (m, 5H), 1.97–1.66 (m, 7H), 1.55–1.45 (m, 1H), 1.27 (d, *J* = 7.0 Hz, 3H), 1.26 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.3 (C), 141.1 (C), 139.2 (C), 138.9 (C), 131.6 (CH), 130.4 (CH), 129.8 (CH), 128.6 (2CH), 126.7 (CH), 125.4 (C), 118.9 (C), 32.2 (CH), 32.1 (CH), 31.1 (CH_2), 29.8 ($2CH_2$), 29.7 (CH_2), 22.7 (CH_3), 20.8 (CH_3), 20.1 (CH_2), 17.7 (CH_2); ATR-FTIR (neat): 2931, 2870, 1591, 1559, 1479 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{11}H_{13}Br[M]^+$: 224.0201, found: 224.0202.



2.15m:2.16m

6-methoxy-1-phenyl-1,2,3,4-tetrahydronaphthalene 2.15m: General procedure III, was followed using 87.9 mg of alkene **2.14m** (0.369 mmol), 6.8 mg of tritylium TPFBP (0.0073 mmol) and 0.74 mL of benzene. Purification by silica gel chromatography (100% hexanes) afforded tetralin **2.15m** (79 mg, 90%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (t, *J* = 8.9 Hz, 2H), 7.24–7.20 (m, 1H), 7.12 (d, *J* = 8.9 Hz, 2H), 6.78 (d, *J* = 7.9 Hz, 1H), 6.72–6.59 (m, 2H), 4.08 (t, *J* = 6.8 Hz, 1H), 3.80 (s, 3H), 2.99–2.78 (m, 2H), 2.22–2.11 (m, 1H), 19.4–1.72 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.5 (C), 147.7 (C), 138.7 (C), 131.6 (C), 131.1 (CH), 128.7 (2CH), 128.1 (2CH), 125.8 (CH), 113.2 (CH), 112.0 (CH), 55.1 (CH_3), 44.9 (CH), 33.4 (CH_2), 30.1 (CH_2), 20.9 (CH_2); ATR-FTIR (neat): 2929, 2856, 1734, 1608, 1499 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{17}H_{18}O$ $[M]^+$: 238.1358, found: 238.1356.

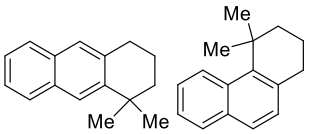
8-methoxy-1-phenyl-1,2,3,4-tetrahydronaphthalene 2.16m: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (s, 1H), 7.20–714 (m, 1H), 7.01 (d, *J* = 7.3 Hz, 1H), 6.83 (d, *J* = 7.3 Hz, 1H), 4.43–4.39 (m, 1H), 3.57 (s, 3H), 2.99–2.78 (m, 1H), 2.10–1.96 (m, 1H), 1.69–1.61 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.5 (C), 139.1 (C), 128.3 (2CH), 127.9 (CH), 127.6 (CH), 126.7 (CH), 125.1 (CH), 121.3 (CH), 107.7 (CH), 55.3 (CH_3), 38.3 (CH), 31.8 (CH_2), 29.4 (CH_2), 17.6 (CH_2). Other peaks were obscured by major isomer peaks.



2.18a:2.19a

1-phenyl-1,2,3,4-tetrahydroanthracene 2.18a: General procedure III, was followed using 100 mg of alkene **2.17a** (0.387 mmol), 7.14 mg of tritylium TPFBP (0.0077 mmol) and amount 0.77 mL of benzene. Purification by silica gel chromatography (100% hexanes) afforded tetralin **2.18a** and **2.19a** (rr, 68:32) (93 mg, 93%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41−7.25 (m, 7H), 7.26−7.13 (m, 4H), 4.35−4.28 (m, 1H), 3.18−3.05 (m, 2H), 2.31−2.12 (m, 2H), 1.91−1.70 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.4 (C), 138.7 (C), 136.3 (C), 132.1 (2C), 128.9 (2CH), 128.5 (CH), 128.3 (2CH), 128.1 (CH), 127.3 (CH), 126.8 (CH), 126.0 (CH), 125.2 (CH), 124.8 (CH), 46.1 (CH), 33.3 (CH_2), 30.2 (CH_2), 21.4 (CH_2); ATR-FTIR (neat): 2932, 2861, 1600, 1493, 1449 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{20}H_{18}$ $[M]^+$: 258.1408, found: 258.1406.

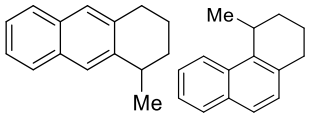
4-phenyl-1,2,3,4-tetrahydrophenanthrene 2.19a: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80−7.57 (m, 5H), 7.08–7.04 (m, 1H), 4.85−4.80 (m, 1H), 3.05−3.01 (m, 2H), 2.07−1.94 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.9 (C), 135.4 (C), 132.5 (C), 132.4 (C), 132.3 (C), 128.3 (3CH), 128.0 (CH), 126.6 (CH), 125.8 (CH), 125.6 (CH), 124.5 (CH), 124.2 (CH), 40.8 (CH), 32.3 (CH_2), 30.3 (CH_2), 17.4 (CH_2). Other peaks were obscured by major isomer peaks.



2.18b:2.19b

1,1-dimethyl-1,2,3,4-tetrahydroanthracene 2.18b: General procedure III, was followed using 94 mg of alkene **2.17b** (0.45 mmol), 20.6 mg of tritylium TPFBP (0.022 mmol) and 0.90 mL of benzene. Purification by silica gel chromatography (100% hexanes) afforded tetralins **2.18b** and **2.19b** (78 mg, 83%) rr 89:11as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (s, 1H), 7.78–7.67 (m, 2H), 7.54 (s, 1H), 7.39–7.33 (m, 2H), 3.00 (t, *J* = 7.0 Hz, 2H), 1.94–1.86 (m, 2H), 1.79–1.74 (m, 2H), 1.41 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.0 (C), 135.3 (C), 132.3 (C), 131.7 (C), 127.3 (CH), 126.7 (2CH), 125.1 (CH), 125.0 (CH), 124.7 (CH), 39.5 (CH_2), 34.3 (C), 32.5 ($2CH_3$), 31.2 (CH_2), 19.9 (CH_2); ATR-FTIR (neat): 2957, 2929, 1597, 1497, 1461 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{16}H_{18}$ $[M]^+$: 210.1409, found: 210.1410.

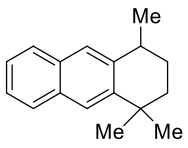
4,4-dimethyl-1,2,3,4-tetrahydrophenanthrene 2.19b: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J* = 8.4 Hz, 1H), 7.52–7.41 (m, 2H), 3.14 (t, *J* = 6.4 Hz, 2H), 2.02–1.95 (m, 2H), 1.38 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.6 (C), 128.2 (CH), 126.0 (CH), 125.8 (CH), 125.2 (CH), 124.8 (CH), 123.4 (CH), 38.9 (CH_2), 31.5 (CH_3), 19.5 (CH_2). Other peaks were obscured by major isomer peaks.



2.18c:2.19c

1-methyl-1,2,3,4-tetrahydroanthracene 2.18c: General procedure III, was followed using 101 mg of alkene **2.17c** (0.51 mmol), 23.7 mg of tritylium TPFBP (0.0257 mmol) and 1 mL of benzene. Purification by silica gel chromatography (100% hexanes) afforded tetralin **2.18c and 2.19c** rr, 13:87 (81 mg, 80%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, *J* = 8.5 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.57–7.46 (m, 1H), 7.46–7.32 (m, 1H), 7.19 (d, *J* = 8.4 Hz, 1H), 3.72–3.64 (m, 1H), 2.96–2.90 (t, *J* = 4.2 Hz, 2H), 2.11–1.83 (m, 4H), 1.40 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.7 (C), 133.2 (C), 132.5 (C), 131.8 (C), 128.6 (CH), 128.3 (CH), 125.9 (CH), 125.6 (CH), 124.4 (CH), 123.2 (CH), 30.2 (CH_2), 30.1 (CH_2), 28.1 (CH), 22.0 (CH_3), 17.7 (CH_2); ATR-FTIR (neat): 2929, 2867, 1600, 1509, 1456 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{15}H_{16}[M]^+$: 196.1252, found: 196.1255.

4-methyl-1,2,3,4-tetrahydrophenanthrene 2.19c: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.8 Hz, 1H), 7.89–7.83 (m, 1H), 7.77–7.63 (m, 4H), 3.22–2.96 (m, 1H), 2.88–2.63 (m, 2H), 2.11–1.83 (m, 2H), 1.82–1.55 (m, 2H), 1.41 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.0 (C), 132.4 (C), 132.2 (C), 131.9 (C), 127.3 (CH), 127.2 (CH), 126.8 (CH), 126.4 (CH), 124.9 (CH), 123.2 (CH), 31.7 (CH), 30.6 (CH_2), 26.0 (CH_2), 20.9 (CH_2), 19.6 (CH_3).



2.18d

1,1,4-trimethyl-1,2,3,4-tetrahydroanthracene 2.18d: General procedure III, was followed using amount 84.4 of alkene **2.17d** (0.376 mmol), 17 mg of tritylium TPFBP (0.0188 mmol) and 0.75 mL of benzene. Purification by silica gel chromatography (100% hexanes) afforded tetralin **2.18d** (77 mg, 91%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (s, 1H), 7.83−7.76 (m, 2H), 7.71 (s, 1H), 7.44−7.39 (m, 2H), 3.21−3.11 (m, 1H), 2.12−2.02 (m, 1H), 1.96−1.86 (m, 1H), 1.78−1.65 (m, 2H), 1.49−1.43 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.7 (C), 140.4 (C), 132.1 (C), 131.8 (C), 127.1 (CH), 126.9 (CH), 126.0 (CH), 125.0 (CH), 124.9 (2CH), 36.3 (CH_2), 34.4 (C), 33.7 (CH), 32.6 (CH_3), 32.5 (CH_3), 27.8 (CH_2), 23.4 (CH_3); ATR-FTIR (neat): 2959, 2856, 1594, 1494, 1466 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{17}H_{20}$ $[M]^+$: 224.1565, found: 224.1563.

References

1) (a) Anderson, L. L.; Arnold, J.; Bergman, R. G. *J. Am. Chem. Soc*. **2005**, *127*, 14542. (b) Arii, H.; Yano, Y.; Nakabayashi, K.; Yamaguchi, S.; Yamamura, M.; Mochida, K.; Kawashima, T. *J. Org. Chem*. **2016**, *81*, 6314. (c) Huang, Y.; Qui, C.; Li, Z.; Feng, W.; Gan, H.; Liu, J.; Gua, K. *ACS Sustainable Chem. Eng.* **2016**, *4*, 47.

2) (a) Albers, L.; Meshghi, M. A.; Baumgartner, J.; Marschner, C.; Müller, T. *Organometallics* **2015**, *34*, 3756. For a review, see: (b) Krossing, I.; Raabe, I. *Angew. Chem., Int. Ed.* **2004**, *43*, 2066.

3) (a) Beesley, R. M.; Ingold, C. K.; Thorpe, J. F. *J. Chem. Soc., Trans*. **1915**, *107*, 1080. For a recent review on Thorpe–Ingold effect, see: (b) Jung, M. E.; Piizzi, G. *Chem. Rev.* **2005**, *105*, 1735.

4) Coulson, C. A.; Daudel, R.; Robertson, J. M.; *Proc. R. Soc. London, Ser. A*. **1951**, *207*, 306.

5) (a) Erlenmeyer, E. *Ann. Chem.* **1866**, *137*, 327. (b) Fieser, L.; Lothrop, W. C. *J. Am. Chem. Soc.* **1935**, *57*, 1459.

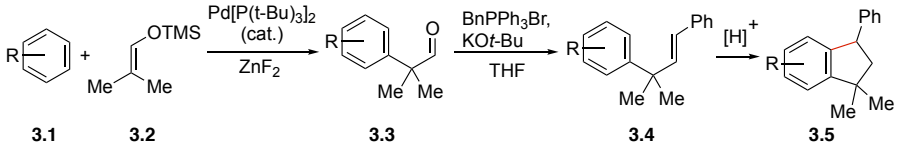
6) Cai, X.; Keshavarz, A.; Omaque, J. D.; Stokes, B. J. *Org. Lett.* **2017**, *19*, 2626.

CHAPTER 3

$HB(C_6F_5)_4$-Catalyzed Intramolecular Hydroarylation of *β*-Benzylstyrenes

Results and Discussion

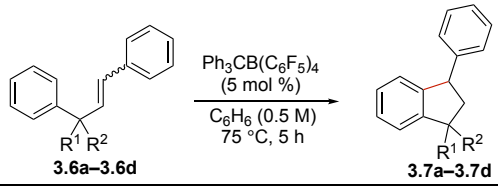
Our lab has recently published a work on electrophilic aromatic cyclizations of 3-aryl-1-propene starting materials to form polysubstituted indanes (Scheme 16).[1] We hypothesized that hydroarylation to form five-membered ring was possible because the styrenyl and phenyl substituents could get compressed into close proximity as a result of steric repulsion between the geminal dimethyl groups via Thorpe–Ingold effect.[2] In addition to studying the effect of geminal dialky on cyclization, I studied the regioselectivity outcomes extensively. Herein, we report an efficient method for the formation of the indane nucleus through intramolecular Thorpe–Ingold-assisted Brønsted–Lowry acid catalyzed hydroarylation of alkenes.

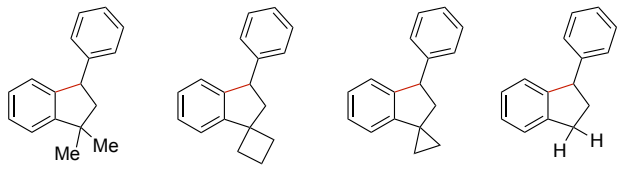


Scheme 16. Our synthetic route for indane synthesis.

The formation of a 5-membered ring poses a synthetic challenge due to ring strain. 5-*endo-trig* cyclizations are generally disfavored according to Baldwin's rules,[3] therefore the bond angles need to become distorted in order to reach the optimal trajectory. Modification to the chemical structure via the alkene substrate may allow Baldwin's rules to be overcome, specifically through the Thorpe-Ingold geminal dialkyl effect. Since the two reactive sites (electrophilic and nucleophilic) for intramolecular reactions are on the same molecule, they need to be in close proximity to enhance the rate of cyclization. After screening *β*-benzylstyrene **3.6a** with different acids, we were delighted to see that tritylium tetrakis(pentafluorophenyl)borate (TPFPB)[4] works efficiently to yield the cyclized product **3.7a** (Table 17). The importance of germinal dialkyl group become

Table. 17 The influence of alkyl substitution at the benzylic position of *β*-benzylstyrenes.





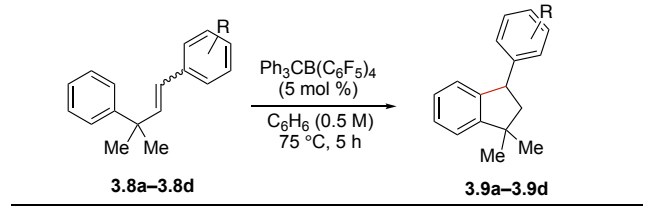
3.7a, 94%[a] **3.7b**, 48% **3.7c**, 0% 100% conv. **3.7d**, 7%[a]

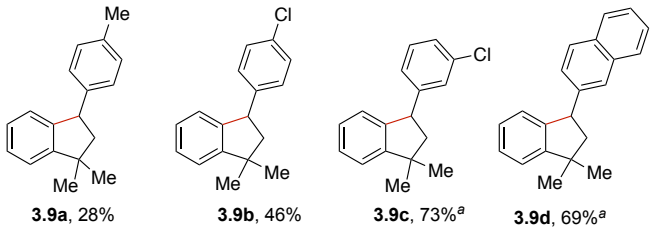
[a] Determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard.

more obvious because only 7% NMR yield was observed for indane **3.7d**. Due to the high percent yield for indane **3.7a**, we used *β*-benzylstyrenes as a model substrate for our further investigations.

We next turned our attention into cyclization of *β*-(α,α-dimethylbenzyl)styrenes **3.8** (Table 18). The yield for substrate **3.8a** was low, indicating that electronics plays an important role in cyclization. When olefin **3.8b** was subjected to hydroarylation, 46% of indane **3.9b** was obtained. Surprisingly, substrate **3.8c** required more precatalyst loading for cyclization to afford good yield. Substrate **3.8d,** which contains a 2-naphthyl substituent gave the desired product **3.9d** in 69% yield. Mr. Xiao Cai who is a graduate student in Stokes lab, synthesized **3.6a** and **3.7a**. Mr. Justin Omaque, who was an undergraduate student in Stokes lab, synthesized **3.8a**.

Table 18. Scope of the intramolecular hydroarylation of *β*-(α,α-dimethylbenzyl)styrenes.





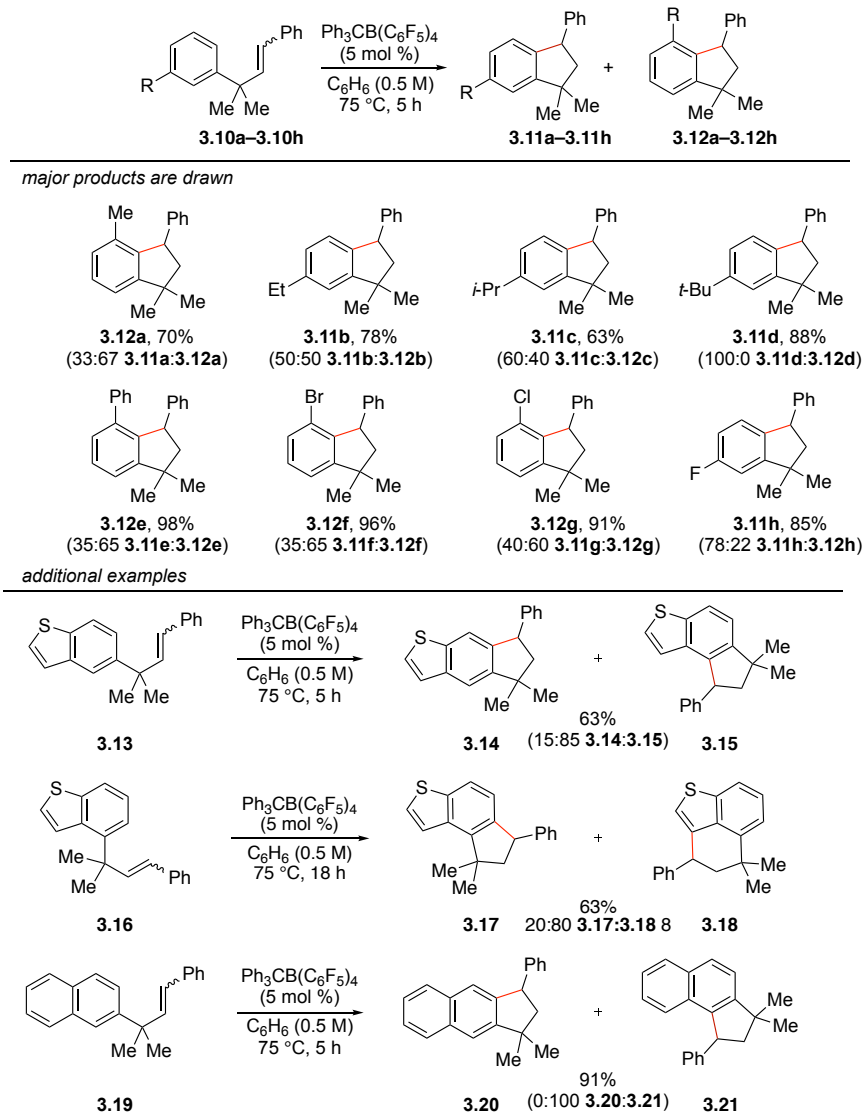
3.9a, 28% **3.9b**, 46% **3.9c**, 73%[a] **3.9d**, 69%[a]

[a] Reaction employed 15 mol % of $Ph_3CB(C_6F_5)_4$.

In the course of our group's investigations of catalytic Thorpe–Ingold assisted formal 5-*endo-trig* cyclizations, I began investigating the outcomes of *meta*-substituted substrates. By placing a substituent group in the *meta*-position, we break the symmetry of the molecule, thus creating two potential sites for cyclization. Regioselectivity can be influenced by few factors such as steric, electronic and the reaction conditions (e.g. temperature, solvent, concentration). I began my investigation by evaluating the regioselectivity outcome for *meta*-alkyl substituent groups (Table 19). Alkyl groups have no unshared electrons but they are *para* and *ortho* directing. They are weakly activating due to the inductive donating effect. We envisioned that alky groups could contribute through both steric and electronic, yet it was a mystery to us as to which effect would prevail over the other. Therefore, I began the study with the least substituent group (methyl in the *meta* position). NMR analysis of **3.11a** and **3.12a** indicates a regioisomer ratio of *ca.* 1:2. By changing the *meta*-substituent group to ethyl, we observed a product ratio of 1:1 for **3.11b** and **3.12b**. This result increased our curiosity. Therefore, we also investigated isopropyl group as the *meta*-substituant. As expected, the ratio of **3.11c** to **3.12c** was 60:40, suggesting sterics dominate over the electronic effect. Determined to

only get one isomer by varying the size of the alkyl group, we synthesized the *t*-butyl *meta*-substituted **3.10d**. Analysis of the crude sample indicated the presence of only one regioisomer **3.11d**, proving the *t*-butyl group was bulky enough to block one of the potential cyclization sites. Cyclization of **3.10e** gave regioisomer **3.12e** as the major isomer in quantitative yield. It was important for us to synthesize aryl halide derivatives of indanes. Not only because halides could be turned into other useful functional groups, but mostly because of our curiosity over regioselectivity outcomes. Halides are electron-withdrawing groups and very electronegative. They are also capable of donating a pair of electrons through resonance; therefore they are weakly activating for *ortho* and *para* directing groups. NMR analysis of halogenated samples showed that the fluorinated compound **3.10h** behaves differently than that of the brominated and chlorinated samples (**3.10f** and **3.10g**) since opposite regioselectivity was observed. Out of the three *meta* halogen susbtituted substrates that we studied, fluorine has the highest electronegativity and electron-withdrawing ability. There is evidence in literature for the *para* selectivity of electrophilic attack on fluorobenzene.[5] We applied our optimized conditions to aromatic heterocycles as well.

Table 19. Regioselectivity outcomes of intramolecular hydrorylations of *β*-(α,α-dimethylbenzyl)styrenes.



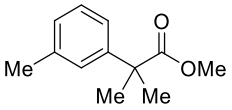
Starting material was fully consumed within 5 hours. Yields refer to the sum of regioisomers.

Heterocycles, such as benzothiophenes, are found in many bioactive molecules and pharmaceutical drugs.[6] We were delighted to see that olefin **3.13** cyclized to give mixture of regioisomers (15:85, **3.14**:**3.15**) in 63% yield. And finally, naphthyl analog **3.19** cyclized at the more nucleophilic position to give **3.21** in 91% yield exclusively. Our obtained results contribute to a better understanding of regioselectivity outcomes in EAS-type reactions.

Experimental

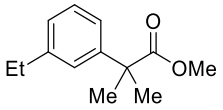
A. Synthesis of Esters and Aldehydes via Negishi-Type Cross-Coupling

General Procedure IV: In a dry 250 mL round bottom flask charged with a PTFE-coated magnetic stir bar, the *bromo*-aryl (1.00 equiv.), 0.08 equiv. of zinc fluoride and 0.10 equiv. of bis(dibenzylideneacetone) palladium (0) were dissolved in 0.1 M DMF at room temperature. The reaction flask was then sealed with a rubber septum, degassed and back-filled with argon. To this mixture were added 0.2 equiv. of tri-*tert*-butylphosphine (1.0 M in toluene) and 1.5 equiv. of trimethyl(2-methylprop-1-enyloxy) silane. The reaction mixture was heated to 80 ºC, continuously purged with argon, and was allowed to stir for 18 hours. The reaction mixture was cooled to room temperature before filtration through Celite® and the Celite® cake was washed with 30 mL of ethyl acetate. The filtrate was concentrated under reduced pressure. The crude product was purified by silica gel chromatography using a mixture of hexanes and ethyl acetate.



S13

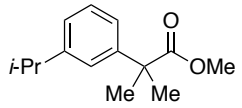
Methyl 2-methyl-2-(*m*-tolyl)propanoate S13: General procedure IV was followed using 1.0 g of 3-bromo toluene (5.85 mmol), 0.48 g of zinc fluoride (4.68 mmol), 260 mg of bis(dibenzylideneacetone) palladium (0) (0.58 mmol), 1.17 mL of tri-*tert*-butylphosphine (1.17 mmol), and 1.53 g of trimethyl(2-methylprop-1-enyloxy) silane (8.78 mmol) in 58 mL DMF. Purification by silica gel chromatography (100:0→85:15 hexanes:ethyl acetate) afforded **S13** (0.67 g, 60% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27-7.21 (m, 1H), 7.18-7.14 (m, 1H), 7.08 (d, J = 7.7 Hz, 1H) 3.67 (s, 3H), 2.38 (s, 3H), 1.60 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.4 (C=O), 144.6 (C), 137.9 (C), 128.3 (CH), 127.5 (CH), 126.3 (CH), 122.6 (CH), 52.2 (CH_3), 46.4 (C), 26.6 (CH_3), 21.6 (CH_3).



S14

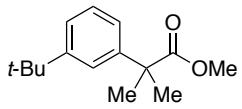
Methyl 2-(3-ethylphenyl)-2-methylpropanoate S14: General procedure IV was followed using 1.0 g of 1-bromo-3-ethylbenzene (5.40 mmol), 0.44 g of zinc fluoride (4.32 mmol), 0.31 g of bis(dibenzylideneacetone) palladium(0) (0.54 mmol), 1.08 mL of tri-*tert*-butylphosphine (1.08 mmol), and 1.41 g of trimethyl(2-methylprop-1-enyloxy)silane (8.10 mmol) in 54 mL of DMF. Purification by flash column chromatography (100:0→85:15 hexanes:ethyl acetate) afforded **S14** (0.63 g, 57% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.23 (m, 1H), 7.18-7.14 (m, 1H), 7.09 (d, J = 7.3 Hz, 1H) 3.66 (s, 3H), 2.66 (q, J = 7.6 Hz, 2H), 1.58 (s, 6H), 1.25 (t, J = 7.3 Hz, 3H) ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.4 (C=O), 144.6 (C), 144.3 (C), 128.3

(CH), 126.2 (CH), 125.2 (CH), 122.9 (CH), 52.2 (CH_3), 46.5 (C), 29.0 (CH_2) 26.6 (CH_3), 15.6 (CH_3).



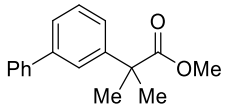
S15

Methyl 2-(3-isopropylphenyl)-2-methylpropanoate S15: General procedure IV was followed using 1.0 g of 1-bromo-3-isopropylbenzene (5.02 mmol), 0.42 g of zinc fluoride (4.02 mmol), 0.29 g of bis(dibenzylideneacetone) palladium(0) (0.50 mmol), 1.15 mL of tri-*tert*-butylphosphine (1.15mmol), and 1.31 g of trimethyl(2-methylprop-1-enyloxy)silane (7.53 mmol) in 50 mL of DMF. Purification by silica gel chromatography (100:0→85:15 hexanes:ethyl acetate) afforded crude **S15** (0.67g, 64% yield) as a yellow oil, which was carried forward to next step. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43-7.36 (m, 1H), 7.18-7.05 (m, 5H), 3.66 (s, 3H), 2.90 (sep, *J* = 6.9 Hz, 1H), 1.58 (s, 6H), 1.25 (d, J= 7.0 Hz, 6H).



S16

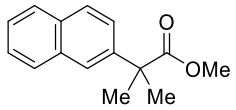
Methyl 2-(3-(tert-butyl)phenyl)-2-methylpropanoate S16: General procedure IV was followed using 1.0 g of 1-bromo-3-tert-butylbenzene (4.69 mmol), 0.39 g of zinc fluoride (3.75 mmol), 0.27 g of bis(dibenzylideneacetone) palladium(0) (0.47 mmol), 0.94 mL of tri-*tert*-butylphosphine (0.94 mmol), and 1.23 g of trimethyl(2-methylprop-1-enyloxy)silane (7.04 mmol) in 47 mL of DMF. Purification by silica gel chromatography (100:0→85:15 hexanes:ethyl acetate) afforded **S16** (0.60 g, 55% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.25 (m, 3H), 7.15 (d, *J* = 7.4, 1H), 3.64 (s, 3H), 1.56 (s, 6H), 1.25 (s, 9H).



S17

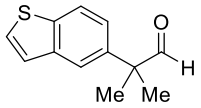
Methyl 2-([1,1'-biphenyl]-3-yl)-2-methylpropanoate S17: General procedure IV was followed using 1.0 g of 3-bromobiphenyl (4.29 mmol), 0.35 g of zinc fluoride (3.43 mmol), 0.25 g of bis(dibenzylideneacetone) palladium(0) (0.43 mmol), 0.86 mL of tri-*tert*-butylphosphine (0.86 mmol), and 1.7 g of trimethyl(2-methylprop-1-enyloxy)silane (6.44 mmol) in 43 mL of DMF. Purification by silica gel chromatography (100:0→85:15 hexanes: ethyl acetate) afforded **S17** (0.80 g, 73% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60-7.51 (m, 3H), 7.48-7.29 (m, 6H), 3.67 (s, 3H), 1.68 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.2 (C=O), 145.2 (C), 141.4 (C), 141.3 (C), 129.0 (CH),

128.6 (CH), 127.5 (CH), 127.1(CH), 125.9 (CH), 125.5 (CH), 124.8 (CH), 124.5 (CH), 52.2 (C), 46.6 (CH_3), 26.7 (CH_3).



S18

Methyl 2-methyl-2-(naphthalen-2-yl)propanoate S18: General procedure IV was followed using 1.0 g of 2-bromonaphthalene (4.83 mmol), 0.39 g of zinc fluoride (3.75 mmol), 0.28 g of bis(dibenzylideneacetone) palladium(0) (0.48 mmol), 0.97 mL tri-*tert*-butylphosphine (0.97 mmol), and 1.26 g of trimethyl(2-methylprop-1-enyloxy)silane (7.24 mmol) in 48 mL of DMF. Purification by silica gel chromatography (100:0→85:15 hexanes: ethyl acetate) afforded **S18** (0.91 g, 83% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85-7.75 (m, 3H), 7.50-7.41 (m, 4H), 3.66 (s, 3H), 1.68 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.3 (C=O), 142.0 (C), 133.3 (C), 132.2 (C),128.0 (2CH), 127.4 (CH), 126.1 (CH), 125.8 (CH), 124.5 (CH), 123.8 (CH), 52.3 (CH_3), 46.7 (C), 26.5 (CH_3).



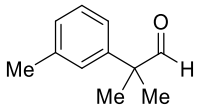
S19

2-(benzo[b]thiophen-5-yl)-2-methylpropanal S19: General procedure IV was followed using 1.0 g of 5-bromobenzo[b]thiopheme (4.70 mmol), 0.39 g of zinc fluoride (3.76 mmol), 0.27 g of bis(dibenzylideneacetone) palladium(0) (0.47 mmol), 0.90 mL (0.90 mmol) tri-*tert*-butylphosphine, and 1.30 mL of trimethyl((2-methylprop-1-en-1-yl)oxy)silane (7.05 mmol) in 47 mL of DMF. Purification by silica gel chromatography (100:0→70:30 hexanes: benzene) afforded **S19** (0.58 g, 61% yield) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.54 (s, 1H), 7.88 (d, J = 8.6 Hz, 1H), 7.75 (d, J = 1.8 Hz, 1H), 7.47 (d, J = 5.5 Hz), 7.34 (d, J = 5.4 Hz, 1H), 7.25 (dd, J = 6.7, 1.9 Hz, 1H), 1.54 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.2 (C=O), 140.1 (C), 138.8 (C), 137.4 (C), 127.3 (CH), 123.9 (CH), 123.2 (CH), 122.9 (CH), 121.6 (CH), 50.4 (C), 22.7 (CH_3).

B. Synthesis of Geminal Dialkyl Homobenzaldehydes From Esters

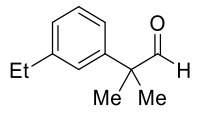
General Procedure V: Into a dry 250 mL round bottom flask charged with a PTFE-coated magnetic stir bar were added 1.00 equiv. of ester and 40 mL of diethyl ether. The solution was chilled in an ice bath and purged with argon. To this mixture, 2.25 equiv. of lithium aluminum hydride was added in four approximate equal portions over 10 minutes. The reaction was allowed to warm to room temperature and stir for additional 30 minutes. After TLC monitoring showed complete consumption of the methyl ester, the flask was returned to an ice bath and quenched with 10 mL of 1 M aqueous HCl. The primary alcohol product was extracted with diethyl ether (3 x 20 mL). The combined organic

layers were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was then dissolved in 20 mL of DCM. To this solution were added 1.10 equiv. pyridinium chlorochromate and 1.10 equiv. of KOAc at room temperature. The oxidation was monitored by TLC and was complete after two hours. The reaction mixture was then diluted in 20 mL of EtOAc and the organic layer was filtered through a path of Celite® cake. The combined organic layer was dried over anhydrous Na_2SO_4, concentrated *in vacuo* and the crude product was transferred to a packed silica gel column and flushed with a mixture of hexane and EtOAc.



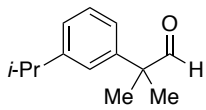
S20

2-methyl-2-(*m*-tolyl)propanal S20: General procedure V was followed using 0.50 g of 2-methyl-2-(*m*-tolyl)propanoate **S13** (2.60 mmol) and 0.222 g of $LiAlH_4$ (5.85 mmol) in 26 mL of Et_2O. The crude isolate was then oxidized using 0.617 g of PCC (2.86 mmol) and 0.281 g of KOAc (2.86 mmol) in 26 mL of DCM. Purification by flash column chromatography (100:0→70:30 hexanes: benzene) afforded **S20** as a light yellow oil (0.340 mg, 73% yield over two steps). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.51 (s, 1H), 7.32-7.25 (m, 1H), 7.14-7.07 (m, 3H), 2.38 (s, 3H), 1.47 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.3 (C=O), 141.2 (C), 138.5 (C), 128.8 (CH), 128.0 (CH), 127.5 (CH), 123.7 (CH) 50.4 (C), 22.5 (CH_3), 21.6 (CH_3).



S21

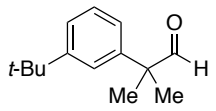
2-(3-Ethylphenyl)-2-methylpropanal S21: General procedure V was followed using 0.50 g of 2-(3-ethylphenyl)-2-methylpropanoate **S14** (2.42 mmol) and 0.206 g of $LiAlH_4$ (5.45 mmol) in 24 mL of Et_2O. The crude isolate was then oxidized using 0.573 g of PCC (2.66 mmol) and 0.261 g of KOAc (2.66 mmol) in 12 mL of DCM. Purification by flash column chromatography (100:0→70:30 hexanes: benzene) afforded **S21** as a light yellow oil (0.321 mg, 75% yield over two steps).^{1}H NMR (400 MHz, $CDCl_3$): δ 9.50 (s, 1H), 7.33-7.24 (m, 1H), 7.16-7.06 (m, 3H), 2.66 (q, J = 8.6 Hz, 2H), 1.46 (s, 6H), 1.24 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.4 (C=O), 144.9 (C), 141.2 (C), 128.8 (CH), 126.8 (CH), 126.3 (CH), 123.9 (CH) 50.4 (C), 29.0 (CH_2), 22.5 (CH_3), 15.6 (CH_3).



S22

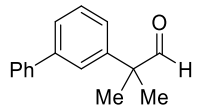
2-(3-*iso*-Propylphenyl)-2-methylpropanal S22: General procedure V was followed using 0.50 g of 2-(3-isopropylphenyl)-2-methylpropanoate **S15** (2.27 mmol) and 0.194 g

of $LiAlH_4$ (5.11 mmol) in 23 mL of Et_2O. The crude isolate was then oxidized using 0.538 g of PCC (2.50 mmol) and 0.245 g of KOAc (2.50 mmol) in 12 mL of DCM. Purification by flash column chromatography (100:0→70:30 hexanes: benzene) afforded **S22** as a light yellow oil (0.302 mg, 69% yield over two steps). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.50 (s, 1H), 7.30 (t, *J* = 8.0 Hz, 1H), 7.19-7.15 (m, 1H), 2.91 (sep, *J* = 7.2 Hz, 1H), 1.47 (s, 6H), 1.26 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.4 (C=O), 149.5 (C), 141.1 (C), 128.8 (CH), 125.2 (CH), 125.0 (CH), 124.1 (CH) 50.5 (C), 34.3 (CH), 24.0 (CH_3), 22.5 (CH_3).



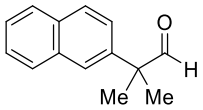
S23

2-(3-(*tert*-Butyl)phenyl)-2-methylpropanal S23: General procedure V was followed using 0.50 g of 2-(3-(*tert*-butyl)phenyl)-2-methylpropanoate **S16** (2.13 mmol) and 0.182 g of $LiAlH_4$ (4.79 mmol) in 21 mL of Et_2O. The crude isolate was then oxidized using 0.505 g of PCC (2.34 mmol) and 0.230 g of KOAc (2.34 mmol) in 11 mL of DCM. Purification by flash column chromatography (100:0→70:30 hexanes: benzene) afforded **S23** as a light yellow oil (0.314 mg, 72% yield over two steps). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.50 (s, 1H), 7.33-7.25 (m, 3H), 7.13-7.08 (m, 1H), 1.47 (s, 6H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.5 (C=O), 151.7 (C), 140.8 (C), 128.5 (CH), 124.3 (CH), 123.7 (CH), 123.6 (CH) 50.6 (C), 34.9 (C), 31.3 (CH3), 22.5 (CH_3).



S24

2-([1,1'-Biphenyl]-3-yl)-2-methylpropanal S24: General procedure V was followed using 0.50 g of 2-([1,1'-biphenyl]-3-yl)-2-methylpropanoate **S17** (1.97 mmol) and 0.168 g of $LiAlH_4$ (4.43 mmol) in 20 mL of Et_2O. The crude isolate was then oxidized using 0.468 g of PCC (2.17 mmol) and 0.213 g of KOAc (2.17 mmol) in 10 mL of DCM. Purification by flash column chromatography (100:0→70:30 hexanes: benzene) afforded **S24** as a light yellow oil (0.371 mg, 76% yield over two steps). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.56 (s, 1H), 7.60-7.55 (m, 2H), 7.53-7.42 (m, 5H), 7.39-7.34 (m, 1H), 7.29-7.27 (m, 1H), 1.52 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.2 (C=O), 141.9 (C), 141.7 (C), 141.0 (C), 129.3 (CH), 128.8 (CH), 128.3 (CH),127.5 (CH), 127.3 (CH), 126.2 (CH), 125.7 (CH), 125.6 (CH), 50.6 (C), 22.6 (CH_3).

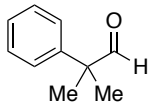


S25

2-Methyl-2-(naphthalen-2-yl)propanal S25: General procedure V was followed using 0.50 g of 2-methyl-2-(naphthalen-2-yl)propanoate **S18** (2.19 mmol) and 0.187 g of $LiAlH_4$ (4.93 mmol) in 22 mL of Et_2O. The crude isolate was then oxidized using 0.519 g of PCC (2.41 mmol) and 0.237 g of KOAc (2.41 mmol) in 11 mL of DCM. Purification by flash column chromatography (100:0→70:30 hexanes: benzene) afforded **S25** as a colorless oil (0.332 mg, 76% yield over two steps). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.61 (s, 1H), 7.91-7.83 (m, 3H), 7.78 (s, 1H), 7.56-7.49 (m, 2H), 7.43-7.39 (m, 1H), 1.60 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.2 (C=O), 138.6 (C), 133.5 (C), 132.4 (C), 128.6 (CH), 128.4 (CH), 128.0 (CH),127.6 (CH), 126.4 (CH), 126.3 (CH), 125.6 (CH), 124.9 (CH), 50.7 (C), 22.5 (CH_3).

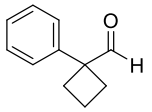
C. Synthesis of Aryl Geminal Dialkyl Aldehyde Intermediates via Sequential Reduction-Oxidation of Carboxylic Acid

General Procedure VI: To a dry 250 mL round bottom flask charged with a PTFE-coated magnetic stir bar was added 1.00 equiv. carboxylic acid in 0.05 M diethyl ether. The solution was then cooled to 0 ºC and purged with argon for 5 minutes. To the chilled mixture was added 3.25 equiv. $LiAlH_4$ in 4 portions over 10 minutes. The reaction was then warmed to room temperature and stirred for one hour. The reaction was monitored by TLC. Once all carboxylic acid was consumed, the reaction was carefully quenched by addition of 1 M aqueous HCl (~10 mL) at 0 ºC. The primary alcohol intermediate was extracted with diethyl ether three times. The ether solution was dried over anhydrous magnesium sulfate before it was concentrated *in vacuo*. The crude product was then dissolved in 0.25 M DCM. The solution was chilled in an ice bath and allowed to purge with argon. To this inert gas-protected mixture, 1.2 equiv. PCC and 1.20 equiv. KOAc were added. The reaction was allowed to stir at 0 ºC for 2 hours until all primary alcohol had been consumed as determined by TLC. The mixture was then diluted with EtOAc (20 mL) and the organic solution was filtered through a pad of Celite®. The combined liquid was dried over anhydrous sodium sulfate. All organic solvents were removed under reduced pressure and the residue was purified by flash column chromatography on SiO_2 using a mixture of hexanes and EtOAc to afford aldehyde.



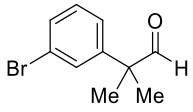
S26

2-methyl-2-phenylpropanal S26. General procedure VI was followed using 1.0 g 2-methyl-2-phenylpropanoic acid (6.1 mmol) and 753.4 mg $LiAlH_4$ (19.8 mmol) in 122 mL of Et_2OAc. The crude isolate was then oxidized using 1.60 g PCC (7.32 mmol) and 718 mg KOAc (7.32 mol) in 25 mL DCM. Purification by flash chromatography (100:0→92:8 hexanes:EtOAc) afforded **S26** (701 mg, 77% yield), which was prone to decomposition over time. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.50 (s, 1H), 7.40-7.27 (m, 5H), 1.47 (s, 6H); ^{13}C NMR (100 MHz, CDCl3) δ: 202.3, 141.4, 129.0, 127.4, 126.8, 50.6, 22.6.



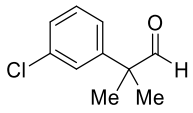
S27

1-Phenylcyclobutane-1-carbaldehyde S27: General procedure VI was followed using 1.07 g of 1-phenylcyclobutane-1-carboxylic acid (6.1 mmol) and 0.753 g of $LiAlH_4$ (19.8 mmol) in 122 mL of Et_2O. The crude isolate was then oxidized using 1.60 g of PCC (7.32 mmol) and 718 mg of KOAc (7.32 mmol) in 25 mL of DCM. Purification by flash column chromatography (100:0 → 95:5 hexanes:EtOAc) afforded **S27** as a light yellow oil (723.2 mg, 74% over two steps). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.55 (s, 1H), 7.41-7.37 (m, 2H), 7.28 (t, *J* = 7.1 Hz, 1H), 7.17 (d, *J* = 7.7 Hz, 2H), 2.78-2.70 (m, 2H), 2.46-2.38 (m, 2H), 2.08-1.88 (m, 2H);^{13}C NMR (100 MHz, $CDCl_3$): δ 199.4 (C=O), 130.9 (C), 128.8 (CH), 127.0 (CH), 126.4 (CH), 57.6 (C), 28.3 (CH_2), 15.8 (CH_2).



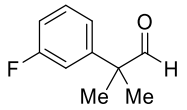
S28

2-(3-Bromophenyl)-2-methylpropanal S28: General procedure VI was followed using 1.21 g of 2-(3-bromophenyl)-2-methylpropanoic acid (6.1 mmol) and 0.753 g of $LiAlH_4$ (19.8 mmol) in 122 mL of Et_2O. The crude isolate was then oxidized using 1.60 g of PCC (7.32 mmol) and 718 mg of KOAc (7.32 mmol) in 25 mL of DCM. Purification by flash column chromatography (100:0 → 90:10 hexanes:EtOAc) afforded **S28** as a light yellow oil (702.1 mg, 50% over two steps). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.48 (s, 1H), 7.45-7.39 (m, 2H), 7.27-7.24 (m, 1H), 7.21-7.16 (m, 1H), 1.45 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.4 (C=O), 143.6 (C), 130.4 (CH), 130.3 (CH), 129.9 (CH), 125.5 (CH), 123.1 (C), 50.4 (C), 22.5 (CH_3).



S29

2-(3-Chlorophenyl)-2-methylpropanal S29: General procedure VI was followed using 1.21 g of 2-(3-chlorophenyl)-2-methylpropanoic acid (6.1 mmol) and 0.753 g of $LiAlH_4$ (19.8 mmol) in 122 mL of Et_2O. The crude isolate was then oxidized using 1.60 g of PCC (7.32 mmol) and 718 mg of KOAc (7.32 mmol) in 25 mL of DCM. Purification by flash column chromatography (100:0 → 90:10 hexanes:EtOAc) afforded **S29** as a light yellow oil (642 mg, 58% over two steps). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.48 (s, 1H), 7.38-7.22 (m, 3H), 7.14 (dd, *J* = 7.3 Hz, 1.2 Hz, 1H), 1.45 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.4 (C=O), 143.4 (C), 134.8 (C), 130.0 (CH), 127.4 (CH), 127.0 (CH), 125.0 (CH), 50.4 (C), 22.4 (CH_3).

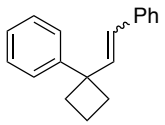


S30

2-(3-Fluorophenyl)-2-methylpropanal S30: General procedure VI was followed using 1.10 g of 2-(4-fluorophenyl)-2-methylpropanoic acid (6.1 mmol) and 0.753 g of $LiAlH_4$ (19.8 mmol) in 122 mL of Et_2O. The crude isolate was then oxidized using 1.60 g of PCC (7.32 mmol) and 718 mg of KOAc (7.32 mmol) in 25 mL of DCM. Purification by flash column chromatography (100:0 → 90:10 hexanes:EtOAc) afforded **S30** as a light yellow oil. (497 mg, 49% yield over two steps). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.49 (s, 1H), 7.39-7.30 (m, 1H), 7.06-6.95 (m, 3H), 1.46 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): 201.5 (C=O), 163.1 (d, J = 246.3 Hz, C), 130.3 (d, J = 8.3 Hz), 122.4 (d, J = 2.9 Hz, C), 114.2 (d, J = 21.0 Hz, CH), 113.9 (d, J = 22.2 Hz, CH), 50.4 (C), 22.5 (CH_3); ^{19}F (376 MHz, $CDCl_3$): δ -112.1.

D. Synthesis of β-Benzylstyrenes via Wittig Olefination of Homobenzaldehydes

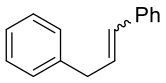
General Procedure VII: In a dry 25-50 mL round bottom flask charged with PTFE coated magnetic stir bar, benzyl triphenylphosphonium bromide (1.6 eq.) was dissolved in 2mL THF. The reaction flask was then sealed with a rubber septum before *t*-BuOK (1.6 M in THF solution) was syringed into the mixture at room temperature. The reaction mixture immediately turned red and was continuously being stirred for an additional 20 minutes before it was chilled to 0 ºC. A solution of aryl-dialkyl-aldehydes in minimal amount of THF (0.5 mmol-2.5 mmol, 1.0 eq.) was then added to the ylides drop-wise through syringe. The reaction was then brought to room temperature and allowed to stir for 18 hours. After all the aldehyde was consumed, the reaction was quenched with saturated aqueous NH_4Cl solution. Based on the polarity of the product, the alkene was extracted with a mixture solution of hexane and ethyl acetate three times. The combined organic solution was collected and dried over sodium sulfate anhydrous before it was concentrated under reduced pressure to afford crude alkene product as a mixture of *E* and *Z* isomers. Purification by silica gel chromatography using gradient elution afforded analytically pure *E* and *Z* alkenes as a mixture. The impurity is not tabulated in the following characterizations, and does not substantially affect the yield.



3.6b

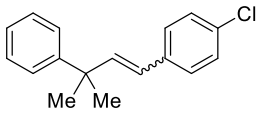
(*Z*)- and (*E*)-2-(1-Phenylcyclobutyl)vinyl)benzene 3.6b: The general procedure was followed using 294 mg of 1-phenylcyclobutane-1-carbaldehyde **S29** (1.84 mmol), 1.28 g of triphenyl phosphonium bromide (2.94 mmol) and 1.84 mL of a 1.6 M solution of *t*-BuOK in THF. Purification by flash column chromatography (100:0→85:15 hexanes:EtOAc) afforded inseparable Z/E (66:34) stereoisomers of **3.6b** (363 mg, 84% yield) as a colorless oil. Selected spectral data for *Z* isomer: ^{1}H NMR (400 MHz, $CDCl_3$):

6.55 (d, J = 12.5 Hz, 1H), 6.10 (d, J = 12.5 Hz, 1H), other peaks were obscured by E isomer. ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.5 (C), 140.3 (CH), 137.1 (C), 129.0 (2CH), 128.4 (CH), 128.2 (CH), 128.1 (CH), 127.6 (CH), 126.6 (CH), 126.2 (CH), 125.9 (CH), 48.0 (C), 36.2 (CH2), 16.0 (CH_2). Selected spectral data for E isomer: 6.59 (d, J = 16.3 Hz, 1H), 6.26 (d, J = 16.3 Hz, 1H), other peaks were obscured by Z isomer. ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.6 (C), 138.3 (CH), 137.6 (C), 128.9 (CH), 128.7 (CH) 128.4 (CH), 128.2 (CH), 126.9 (CH), 126.5 (CH), 126.0 (CH), 125.6 (CH), 49.2 (C), 33.4 (CH_2), 16.3 (CH_2). Spectral data for the mixture: HRMS (EI) *m/z* calculated for $C_{18}H_{18}$ $[M]^+$: 234.1403, found: 234.1392.



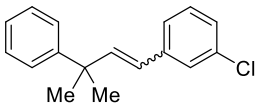
3.6d

(*Z*)- and (*E*)-Prop-1-ene-1,3-diyldibenzene 3.6d: General procedure VII was followed using 301 mg of 2-phenylacetaldehyde (2.5 mmol), 1.7 g of triphenyl phosphonium bromide (4.0 mmol) and 2.5 mL of a 1.6 M solution of *t*-BuOK in THF. Purification by flash column chromatography (100:0→90:10 hexanes:benzene) afforded inseparable *Z*/*E* (51:49) stereoisomers of **3.6d** (423 mg, 87% yield) as a colorless oil. The spectral data for the *Z* isomer matched those reported by Lipshutz and coworkers.6 The spectral data for the *E* isomer matched those reported by Alacid.[7]



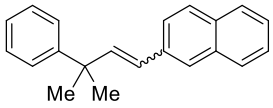
3.8b

(*Z*)- and (*E*)- 1-Chloro-4-(3-methyl-3-phenylbut-1-en-1-yl)benzene 3.8b: General procedure VII was followed using 247 mg of 2-methyl-2-phenylpropanal **S26** (1.67 mmol), 1.06 g of (4-chlorobenzyl)triphenylphosphonium chloride (2.505 mmol) and 1.67 mL of a 1.6 M solution of *t*-BuOK in THF. Purification by flash column chromatography (100:0→85:15 hexanes:EtOAc) afforded inseparable Z/E (75:25) stereoisomers of **3.8b** (332 mg, 77% yield) as a colorless oil. The NMR data matched those reported by Blunt and coworkers.[8]Selected spectral data for Z isomer: ^{1}H NMR (400 MHz, $CDCl_3$): 7.05 (d, J = 8.2 Hz, 1H), 6.82 (d, J = 8.2 Hz, 1H), 6.44 (d, J = 13.7 Hz, 1H), 5.99 (d, J = 13.7 Hz, 1H), 1.42 (s, 6H), other peaks in the aromatic region were obscured by E isomer. (100 MHz, $CDCl_3$): δ 149.7 (C), 142.5 (CH), 136.4 (CH), 132.0 (C), 130.1 (CH), 128.2 (CH), 127.5 (CH), 126.1 (CH), 125.7 (CH), 40.9 (C), 31.1 (CH_3). Selected spectral data for E isomer: 6.43 (d, J = 16.1 Hz, 1H), 6.36 (d, J = 16.1 Hz, 1H), 1.53 (s, 6H), other peaks in the aromatic region were obscured by Z isomer. ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.4 (C), 140.9 (CH), 136.2 (C). 132.6 (C), 128.6 (CH), 128.2 (CH), 127.4 (CH), 126.2 (CH), 126.0 (CH), 125.0 (CH), 40.8 (C), 28.7 (CH_3). Selected spectral data for the mixture: HRMS (EI) *m/z* calculated for $C_{17}H_{17}Cl$ $[M]^+$: 256.1013, found: 256.1012.



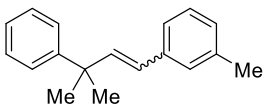
3.8c

(*Z*)- and (*E*)-1-chloro-3-(3-methyl-3-phenylbut-1-en-1-yl)benzene 3.8c: General procedure VII was followed using 400 mg of 2-methyl-2-phenylpropanal **S26** (2.70 mmol), 1.83 g (3-chlorobenzyl)triphenylphosphonium chloride (4.32 mmol) and 2.7 mL of a 1.6 M solution of *t*-BuOK in THF. Purification by flash column chromatography (100:0→85:15 hexanes:EtOAc) afforded inseparable *Z/E* (67:33) stereoisomers of **3.8c** (555 mg, 80% yield) as a colorless oil. The spectral data matched those reported by Blunt and coworkers.[8] Selected spectral data for *Z* isomer: ^{1}H NMR (400 MHz, $CDCl_3$): 6.42 (d, J = 12.6 Hz, 1H), 5.99 (d, J = 12.6 Hz, 1H), 1.40 (s, 6H). other peaks were obscured by *E* isomer. ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.4 (C), 143.0 (CH), 139.7 (C), 133.2 (C), 127.2 (CH), 40.9 (C), 31.0 (CH_3). Aromatic peaks were obscured. Selected spectral data for *E* isomer: ^{1}H NMR (400 MHz, $CDCl_3$): 6.45 (d, J = 16.1 Hz, 1H), 6.35 (d, J = 16.1 Hz, 1H), 1.52 (s, 6H). other peaks were obscured by *Z* isomer. ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.2 (C), 141.7 (CH), 139.6 (C), 134.5 (C), 124.9 (CH), 40.9 (C), 28.6 (CH_3).



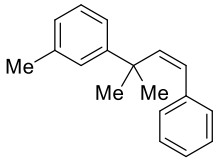
3.8d

(*Z*)- and (*E*)-2-(3-Methyl-3-phenylbut-1-en-1-yl)naphthalene 3.8d: General procedure VII was followed using 250 mg of 2-methyl-2-phenylpropanal **S26** (1.69 mmol), 1.23 g (Naphthalen-2-ylmethyl)triphenyl-phosphonium bromide (2.535 mmol, 1.5 eq.) and 1.69 mL of a 1.6 M solution of *t*-BuOK in THF. Purification by flash column chromatography (100:0→85:15 hexanes:EtOAc) afforded inseparable *Z/E* (66:34) stereoisomers of **3.8d** (377 mg, 82% yield) as a colorless oil. Selected spectral data for *Z* isomer: ^{1}H NMR (400 MHz, $CDCl_3$): 6.65 (d, J = 12.7 Hz, 1H), 6.07 (d, J = 12.7 Hz, 1H), 1.42 (s, 6H), other peaks in the aromatic region were obscured by *E* isomer. ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.5 (C), 142.2 (CH), 135.5 (C), 132.8 (C), 131.9 (C), 128.8 (CH), 128.2 (CH), 127.9 (CH), 127.9 (CH), 127.7 (CH), 127.4 (CH), 127.3 (CH), 126.3 (CH), 126.1 (CH), 125.8 (CH), 125.5 (CH), 40.9 (C), 31.1 (CH_3). Selected spectral data for *E* isomer: 6.61 (d, J = 16.6 Hz, 1H), 6.56 (d, J = 16.6 Hz, 1H), 1.58 (s, 6H), other peaks in the aromatic region were obscured by *Z* isomer. ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.7 (C), 140.6 (CH), 135.2 (C), 133.7 (C), 131.9 (C), 128.2 (CH), 128.1 (CH), 127.8 (CH), 127.6 (CH), 126.8 (CH), 126.2 (CH), 126.1 (CH), 126.0 (CH), 125.8 (CH), 125.5 (CH), 123.7 (CH), 40.9 (C), 28.8 (CH_3). Selected spectral data for the mixture: HRMS (EI) *m/z* calculated for $C_{18}H_{18}$ $[M]^+$:272.1565, found: 272.1452.



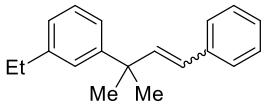
3.8e

(*Z*)- and (*E*)- 1-Methyl-3-(3-methyl-3-phenylbut-1-en-1-yl)benzene 3.8e: General procedure VII was followed using 400 mg of 2-methyl-2-phenylpropanal **S26** (2.70 mmol), 1.93 g of (4-methylbenzyl)triphenylphosphonium bromide (4.32 mmol) and 2.7 mL of a 1.6 M solution of *t*-BuOK in THF. Purification by flash column chromatography (100:0→85:15 hexanes:EtOAc) afforded inseparable *Z/E* (67:33) stereoisomers of **3.8e** (568 mg, 89% yield) as a colorless oil. The spectral data matched those reported by Blunt and coworkers.[8] Selected spectral data for *Z* isomer: ^{1}H NMR (400 MHz, $CDCl_3$): 6.92 (d, *J* = 7.8 Hz, 2H), 6.83 (d, *J* = 7.9 Hz, 2H), 6.48 (d, *J* = 12.6 Hz, 1H), 5.90 (d, *J* = 12.6 Hz, 1H), 2.26 (s, 3H), 1.38 (s, 6H). Other peaks were obscured by *E* isomer. ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.3 (C), 141.0 (CH), 135.8 (C), 135.1 (C), 128.7 (CH), 40.9 (C), 31.1 (CH_3), 21.1 (CH_3). Aromatic peaks were obscured. Selected spectral data for *E* isomer: ^{1}H NMR (400 MHz, $CDCl_3$): 6.38 (app. s, 2H), 2.33 (s, 3H), 1.51 (s, 6H). Other peaks were obscured by Z isomer. ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.6 (C), 139.1 (CH), 136.7 (C), 134.9 (C), 125.8 (CH), 40.7 (C), 28.6 (CH_3), 21.1 (CH_3).



3.10a

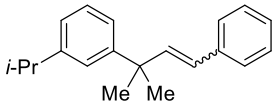
(*Z*)-1-methyl-3-(2-methyl-4-phenylbut-3-en-2-yl)benzene 3.10a: General procedure VII was followed using 397 mg of 2-(3-methylphenyl)-2-methylpropanal **S20** (2.13 mmol), 1.48 g of triphenyl phosphonium bromide (3.41 mmol) and 2.13 mL of a 1.6 M solution of *t*-BuOK in THF. Purification by flash column chromatography (100:0→85:15 hexanes:EtOAc) afforded the alkene **3.10a** (405 mg, 80% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ7.19-7.07 (m, 6H), 6.95 (d, *J* = 6.7 Hz, 3H), 6.52 (d, *J* = 12.6 Hz,1H), 5.92 (d, *J* = 12.5 Hz, 1H), 2.30 (s, 3H), 1.37 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 149.9 (C), 141.6 (CH), 138.2 (C), 130.2 (C), 128.8 (2CH), 128.5 (CH), 127.9 (CH), 127.3 (2CH), 127.0 (CH), 126.2 (CH), 126.1 (CH), 123.0 (CH), 40.9 (C), 31.0 (CH_3), 21.6 (CH_3); HRMS (EI) *m/z* calculated for $C_{18}H_{20}$ $[M]^+$:236.1560, found: 236.1552.



3.10b

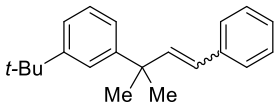
(*Z*)- and (*E*)-1-Ethyl-3-(2-methyl-4-phenylbut-3-en-2-yl) 3.10b: General procedure VII was followed using 397 mg of 2-(3-ethylphenyl)-2-methylpropanal **S21** (2.25 mmol), 1.56 g of triphenyl phosphonium bromide (3.6 mmol) and 2.25 mL of a 1.6 M solution of *t*-BuOK in THF. Purification by flash column chromatography (100:0→85:15 hexanes:EtOAc) afforded inseparable Z/E (72:28) stereoisomers of **3.10b** (438 mg, 78% yield) as a colorless oil. Selected spectral data for (*Z*)-1-ethyl-3-(2-methyl-4-phenylbut-3-en-2-yl)benzene isomer: ^{1}H NMR (400 MHz, $CDCl_3$): 6.50 (d, *J* = 12.6 Hz,1H), 5.92 (d, *J* = 12.6 Hz, 1H), 2.58 (q, *J* = 7.6 Hz, 2H), 1.37 (s, 6H), 1.18 (t, *J* = 8.1 Hz, 3H), other

peaks in aromatic region were obscured by *E* isomer. ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.9 (C), 143.8 (C), 141.7 (CH), 138.1 (C), 128.8 (2CH), 128.5 (CH), 127.9 (CH), 127.3 (CH), 126.1 (CH), 125.8 (CH), 125.0 (CH), 123.4 (CH), 40.9 (C), 31.0 (CH_3), 29.0 (CH_2), 15.7 (CH_3). Selected spectral data for (*E*)-1-ethyl-3-(2-methyl-4-phenylbut-3-en-2-yl)benzene isomer: ^{1}H NMR (400 MHz, $CDCl_3$): 6.44 (d, J = 16.4 Hz, 1H), 6.40 (d, J = 16.4 Hz, 1H), 2.64 (q, J = 7.6 Hz, 2H), 1.50 (s, 6H), 1.23 (t, J = 8.1 Hz, 3H), other peaks in aromatic region were obscured by *Z* isomer. ^{13}C NMR (100 MHz, $CDCl_3$): δ ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.7 (C), 144.1 (C), 140.3 (CH), 137.8 (C), 128.7 (CH), 128.5 (CH), 128.1 (CH), 126.9 (CH), 126.5 (CH), 126.2 (2CH), 125.8 (CH), 125.4 (CH), 123.6 (CH), 40.7(C), 31.1 (CH_3), 28.7 (CH_2), 15.7 (CH_3); HRMS (EI) *m/z* calculated for $C_{19}H_{22}$ $[M]^+$:250.1716, found: 250.1709.



3.10c

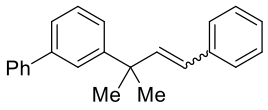
(*Z*)- and (*E*)-1-isopropyl-3-(2-methyl-4-phenylbut-3-en-2-yl)benzene 3.10c: General procedure VII was followed using 348 mg of 2-(3-isopropylphenyl)-2-methylpropanal **S22** (1.83 mmol), 1.27 g of triphenyl phosphonium bromide (2.93 mmol) and 1.83 mL of a 1.6 M solution of *t*-BuOK in THF. Purification by flash column chromatography (100:0→85:15 hexanes:EtOAc) afforded inseparable *Z/E* (68:32) stereoisomers of **3.10c** (391 mg, 81% yield) as a colorless oil. Selected spectral data for *Z* isomer: ^{1}H NMR (400 MHz, $CDCl_3$): 6.50 (d, J = 12.6 Hz, 1H), 5.93 (d, J = 12.6 Hz, 1H), 2.83 (sep, J = 7.1 Hz, 1H), 1.39 (s, 6H), 1.20 (d, J = 6.9 Hz, 6H), other peaks in aromatic region were obscured by *E* isomer. ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.4 (C), 141.8 (CH), 141.7 (C), 34.2 (CH), 31.1 (CH_3), 24.0 (CH_3). Selected spectral data for *E* isomer: ^{1}H NMR (400 MHz, $CDCl_3$): 6.45 (d, J = 16.4 Hz, 1H), 6.40 (d, J = 16.4 Hz, 1H), 2.83 (sep, J = 7.1 Hz, 1H), 1.52 (s, 6H), 1.25 (d, J = 6.9 Hz, 6H), other peaks in aromatic region were obscured by *Z* isomer. δ ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.7 (C), 140.4 (CH), 34.3 (CH), 28.8 (CH_3), 24.1(CH_3). Mixture of Z/E: ^{13}C NMR (100 MHz, $CDCl_3$): δ 128.9 (CH), 128.8 (CH), 128.5 (CH), 128.2 (CH), 127.9 (CH), 127.6 (CH), 127.3 (CH), 127.1 (CH), 126.9 (CH), 126.5 (CH), 126.2 (CH), 126.1 (CH), 125.9 (CH), 124.6 (CH), 124.4 (CH), 123.7 (CH), 123.6 (CH), 123.4 (CH); HRMS (EI) *m/z* calculated for $C_{20}H_{24}$ $[M]^+$:264.1873, found: 250.1874.



3.10d

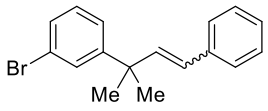
(*Z*)- and (*E*)-1-(*tert*-Butyl)-3-(2-methyl-4-phenylbut-3-en-2-yl)benzene 3.10d: General procedure VII was followed using 354 mg of 2-(3-(*tert*-butyl)phenyl)-2-methylpropanal **S23** (1.73 mmol), 1.20 g of triphenyl phosphonium bromide (2.77 mmol) and 1.73 mL of a 1.6 M solution of *t*-BuOK in THF. Purification by flash column chromatography (100:0→85:15 hexanes:EtOAc) afforded inseparable *Z/E* (67:33) stereoisomers of **3.10d**

(401 mg, 83% yield) as a colorless oil. Selected spectral data for *Z* isomer: ^{1}H NMR (400 MHz, $CDCl_3$): 6.50 (d, *J* = 12.6 Hz, 1H), 5.94 (d, *J* = 12.6 Hz, 1H), 1.40 (s, 6H), 1.27 (s, 9H), other peaks in aromatic region were obscured by *E* isomer. ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.5 (C), 149.2 (C), 141.8 (CH), 138.0 (C), 128.8 (2CH), 128.5 (CH), 128.4 (CH), 127.6 (CH), 127.3 (CH), 126.1 (CH), 126.0 (CH), 123.2 (CH), 122.4 (CH), 41.2 (C), 34.7 (C), 31.4 (CH_3), 31.4 (CH_3); Selected spectral data for *E* isomer: ^{1}H NMR (400 MHz, $CDCl_3$): 6.40 (d, *J* = 16.6 Hz, 1H), 6.45 (d, *J* = 16.6 Hz, 1H), 1.52 (s, 6H), 1.32 (s, 9H), other peaks in aromatic region were obscured by *Z* isomer. ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.8 (C), 148.2 (C), 140.4 (CH), 137.9 (C), 128.8 (CH), 128.5 (CH), 127.8 (CH), 127.3 (CH), 126.9 (CH), 126.2 (CH), 125.8 (CH), 123.4 (CH), 123.1 (CH), 122.8 (CH) 40.9 (C), 34.8 (C), 31.2 (CH_3), 28.8 (CH_3). Selected spectral data for the mixture: HRMS (EI) *m/z* calculated for $C_{21}H_{26}$ $[M]^+$: 278.2029, found: 278.2029.



3.10e

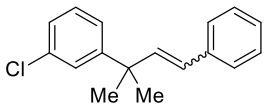
(*Z*)- and (*E*)-3-(2-Methyl-4-phenylbut-3-en-2-yl)-1,1'-biphenyl 3.10e: General procedure VII was followed using 400 mg of 2-methyl-2-(naphthalen-2-yl)propanal **S24** (1.78 mmol), 1.24 g of triphenyl phosphonium bromide (2.85 mmol) and 1.78 mL of a 1.6 M solution of *t*-BuOK in THF. Purification by flash column chromatography (100:0→85:15 hexanes:EtOAc) afforded inseparable *Z/E* (74:26) stereoisomers of **3.10e** (415 mg, 78% yield) as a colorless oil. Selected spectral data for *Z* isomer: ^{1}H NMR (400 MHz, $CDCl_3$): 6.59 (d, *J* = 12.4 Hz, 1H), 6.01 (d, *J* = 12.4 Hz, 1H), 1.49 (s, 6H), other peaks in aromatic region were obscured by *E* isomer. ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.3 (C), 141.8 (C), 141.6 (CH), 141.0 (C), 138.0 (C), 128.9 (CH), 41.1 (C), 31.2 (CH_3). Selected spectral data for *E* isomer: ^{1}H NMR (400 MHz, $CDCl_3$): 6.53 (d, *J* = 16.2 Hz, 1H), 6.49 (d, *J* = 16.2 Hz, 1H), 1.62 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.3 (C), 141.7 (C), 141.6 (CH), 141.2 (C), 140.1 (C), 137.7 (C), 126.3 (CH), 41.0 (C), 28.8 (CH_3). Selected spectral data for the mixture: HRMS (EI) *m/z* calculated for $C_{23}H_{22}$ $[M]^+$: 298.1716, found: 298.1706.



3.10f

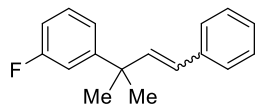
(*Z*)- and (*E*)-1-Bromo-3-(2-methyl-4-phenylbut-3-en-2-yl)benzene 3.10f: General procedure VII was followed using 450 mg of 2-(2-bromophenyl)-2-methylpropanal **S28** (1.99 mmol), 1.38 g of triphenyl phosphonium bromide (3.18 mmol) and 2.0 mL of a 1.6 M solution of *t*-BuOK in THF. Purification by flash column chromatography (100:0→85:15 hexanes:EtOAc) afforded **3.10f** as an inseparable mixture of *Z/E* (59:41) stereoisomers (427 mg, 71% yield) as a colorless oil. Selected spectral data for *Z* isomer: ^{1}H NMR (400 MHz, $CDCl_3$): 6.92 (d, *J* = 7.2 Hz, 2H), 6.57 (d, *J* = 12.4 Hz,1H), 5.91 (d, *J* = 12.6 Hz, 1H), 1.40 (s, 6H), other peaks in aromatic region were obscured by *E*

isomer. ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.2 (C), 140.8 (CH), 137.7 (C), 129.6 (2CH), 129.4 (CH), 128.7 (CH), 128.6 (CH), 127.5 (CH), 126.3 (CH), 124.9 (CH), 122.3 (C–Br), 41.0 (C), 31.1 (CH_3). Selected spectral data for *E* isomer: ^{1}H NMR (400 MHz, $CDCl_3$): 6.45 (d, *J* = 16.6 Hz,1H), 6.39 (d, *J* = 16.4 Hz, 1H), 1.53 (s, 6H), other peaks in aromatic region were obscured by *Z* isomer. δ 151.3 (C), 139.2 (CH), 137.4 (C), 129.8 (CH), 129.5 (CH), 129.1 (CH), 128.7 (CH), 128.6 (CH), 127.5 (CH), 126.7 (CH), 126.4 (CH), 125.1 (CH), 122.5 (C–Br), 40.9 (C), 28.7 (CH_3) Selected spectral data for the mixture: HRMS (EI) *m/z* calculated for $C_{17}H_{17}Br$ $[M]^+$:300.0508, found: 300.0514.



3.10g

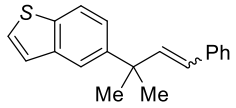
(*Z*)- and (*E*)-1-chloro-3-(2-methyl-4-phenylbut-3-en-2-yl)benzene 3.10g: General procedure VII was followed using 300 mg of 2-(2-chlorophenyl)-2-methylpropanal **S29** (1.6 mmol), 1.10 g of triphenyl phosphonium bromide (2.56 mmol) and 1.6 mL of a 1.6 M solution of *t*-BuOK in THF. Purification by flash column chromatography (100:0→85:15 hexanes:EtOAc) afforded **3.10g** as inseparable *Z/E* (81:19) stereoisomers (330 mg, 73% yield) as a colorless oil. Selected spectral data for *Z* isomer: ^{1}H NMR (400 MHz, $CDCl_3$): 6.90 (d, *J* = 7.4 Hz, 2H), 6.55 (d, *J* = 12.8 Hz,1H), 5.90 (d, *J* = 12.8 Hz, 1H), 1.39 (s, 6H), other peaks in aromatic region were obscured by E isomer. ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.9 (C), 140.8 (CH), 137.7 (C), 133.8 (C–Cl), 129.3 (CH), 129.2 (CH), 128.7 (CH), 127.5 (CH), 126.6 (CH), 126.3 (CH), 125.6 (CH), 124.4 (CH), 41.0 (C), 31.0 (CH_3). Selected spectral data for *Z* isomer: ^{1}H NMR (400 MHz, $CDCl_3$): 6.43 (d, *J* = 16.8 Hz,1H), 6.38 (d, *J* = 16.8 Hz, 1H), 1.51 (s, 6H), other peaks in aromatic region were obscured by *Z* isomer. ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.9 (C), 139.2 (CH), 137.4(C), 134.1 (C–Cl), 129.4 (CH), 128.9 (CH), 128.6 (CH), 128.2 (CH), 127.2 (CH), 126.6 (CH), 126.2 (CH), 126.1 (CH), 124.6 (CH), 40.9 (C), 28.6 (CH_3); HRMS (EI) *m/z* calculated for $C_{17}H_{17}Cl$ $[M]^+$: 256.1013, found: 250.1021.



3.10h

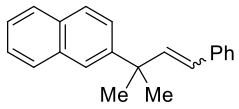
(*Z*)- and (*E*)-1-fluoro-3-(2-methyl-4-phenylbut-3-en-2-yl)benzene 3.10h: General procedure VII was followed using 450 mg of 2-(3-fluorophenyl)-2-methylpropanal **S30** (2.7 mmol), 1.87 g of triphenyl phosphonium bromide (4.32 mmol) and 2.7 mL of a 1.6 M solution of *t*-BuOK in THF. Purification by flash column chromatography (100:0→85:15 hexanes:EtOAc) afforded **3.10h** as inseparable *Z/E* (61:39) stereoisomers (490 mg, 75% yield) as a colorless oil. Selected spectral data for *Z* isomer: ^{1}H NMR (400 MHz, $CDCl_3$): 6.53 (d, *J* = 12.4 Hz, 1H), 5.89 (d, *J* = 12.4 Hz, 1H), 1.37 (s, 6H), other peaks in aromatic region were obscured by *E* isomer. ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.9 (d, *J* = 243.7 Hz, C–F), 152.7 (C), 140.8 (CH), 137.8 (C), 41.0 (C), 31.1 (CH_3). ^{19}F NMR (376 MHz, $CDCl_3$): δ -113.8; Selected spectral data for *E* isomer: ^{1}H NMR (400

MHz, $CDCl_3$): 6.42 (d, J = 16.8 Hz, 1H), 6.37 (d, J = 16.8 Hz, 1H), 1.50 (s, 6H), other peaks in aromatic region were obscured by Z isomer. ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.0 (d, J = 244.7 Hz, C–F), 151.6 (C), 139.5 (CH), 137.5 (C), 40.9 (C), 28.7 (CH_3). ^{19}F NMR (376 MHz, $CDCl_3$): δ –113.4. Selected spectral data for the mixture: HRMS (EI) *m/z* calculated for $C_{17}H_{17}F[M]^+$: 240.1309, found: 240.1300.



3.13

(*Z*)- and (*E*)-6-(2-Methyl-4-phenylbut-3-en-2-yl)benzo[*b*]thiophene 3.13: General procedure VII was followed using 520 mg of 2-(benzo[*b*]thiophen-6-yl)-2-methylpropanal **S19** (2.55 mmol), 1.66 g of triphenyl phosphonium bromide (4.08 mmol) and 2.55 mL of a 1.6 M solution of *t*-BuOK in THF. Purification by flash column chromatography (100:0→85:15 hexanes:EtOAc) afforded **3.13** as an inseparable mixture of *Z/E* (53:47) stereoisomers (495 mg, 70% yield) as light yellow oil. Selected spectral data for *Z* isomer: ^1H NMR (400 MHz, $CDCl_3$): 6.56 (d, J = 12.6 Hz, 1H), 5.99 (d, J = 12.6 Hz, 1H), 1.44 (s, 6H), other peaks in aromatic region were obscured by *E* isomer. ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.4 (C), 141.6 (CH), 138.0 (C), 128.9 (CH), 123.5 (CH), 122.0 (CH), 120.5 (CH), 41.0 (C), 31.3 (CH_3). Selected spectral data for the *E* isomer: ^1H NMR (400 MHz, $CDCl_3$): 6.49 (d, J = 16.4 Hz,1H), 6.43 (d, J = 16.4 Hz, 1H), 1.59 (s, 6H), other peaks in aromatic region were obscured by *Z* isomer. ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.0 (C), 140.2 (CH), 137.6 (C), 126.2 (CH), 123.6 (CH), 122.1 (CH), 120.7 (CH), 40.8 (C), 29.0 (CH_3). Mixture of *Z/E*: ^{13}C NMR (100 MHz, $CDCl_3$): δ 128.9 (CH), 128.8 (CH), 128.5 (CH), 127.3 (CH), 127.1 (CH), 126.5 (CH), 126.2 (CH), 124.0 (CH), 123.6 (CH), 123.5 (CH). HRMS (EI) *m/z* calculated for $C_{19}H_{18}S$ $[M]^+$:278.1129, found: 278.1120.



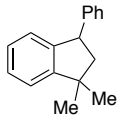
22.10

(*Z*)- and (*E*)-2-(2-methyl-4-phenylbut-3-en-2-yl)naphthalene 3.19: General procedure VII was followed using 400 mg of 2-methyl-2-(naphthalen-2-yl)propanal **S25** (2.02 mmol), 1.40 g of triphenyl phosphonium bromide (3.23 mmol) and 2.0 mL of a 1.6 M solution of *t*-BuOK in THF. Purification by flash column chromatography (100:0→85:15 hexanes:EtOAc) afforded **3.19** as inseparable Z/E (64:36) stereoisomers (449 mg, 82% yield) as a colorless oil. Selected spectral data for Z isomer: ^1H NMR (400 MHz, $CDCl_3$): 6.59 (d, J = 12.4 Hz, 1H), 6.02 (d, J = 12.4 Hz, 1H), 1.48 (s, 6H), other peaks in aromatic region were obscured by E isomer. ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.6 (C), 141.3 (CH), 141.0 (C), 138.0 (C), 133.4 (C), 131.7 (C), 129.1 (CH), 128.8 (CH), 127.9 (CH), 127.7 (CH), 127.3 (CH), 125.7 (CH), 125.6 (CH), 125.2 (CH), 123.6 (CH), 41.1 (C), 31.0 (CH_3); Selected spectral data for E isomer: ^1H NMR (400 MHz, $CDCl_3$): 6.51 (d, J = 16.2

Hz, 1H), 6.44 (d, J = 16.2 Hz, 1H), 1.62 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.1 (C), 140.0 (CH), 137.7 (C), 133.4 (C), 131.9 (C), 128.8 (CH), 127.9 (CH), 127.4 (CH), 127.1 (CH), 126.5 (CH), 126.2 (CH), 125.9 (CH), 125.7 (CH), 125.6 (CH), 125.5 (CH), 123.9 (CH), 41.0 (C), 28.7 (CH_3); ATR-FTIR: (thin film): cm^{-1}. HRMS (EI) *m/z* calculated for $C_{21}H_{20}$ $[M]^+$:272.1560, found: 272.1553.

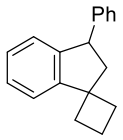
E. Synthesis of 1-Aryl-3,3-Dialkylindanes via Tritylium TPFPB-Catalyzed Hydroarylation

General Procedure VIII: In a dry 4 mL glass vial charged with PTFE coated magnetic stir bar, the alkenes (mixture of *E*, *Z* isomers, 0.25 mmol, 1.0 eq.) were dissolved with 0.50 mL dry benzene (0.5 M). To the solution, 11.5 mg of tritylium TPFPB (0.0125 mmol) was added. The vial was then capped with a septum and purged with argon for 1 min. The reaction mixture was then sealed with a PTFE cap and was allowed to stir for 5 h at 75 ºC. After the *E*, *Z* isomeric spots on TLC plate (visualized under UV Lamp, 254 nm) merged to one, the reaction was cooled to room temperature before it was quenched with 1 mL of saturated $NaHCO_3$. The cyclized product was extracted with 1 mL of CH_2Cl_2 twice and the combined organic layers were then washed with brine (2 mL) and dried over anhydrous Na_2SO_4. After filtration, the dry solution was concentrated *in vacuo* to furnish crude product as a light brown oil. Purification by silica gel chromatography using gradient elution afforded analytically pure cyclized product. The impurity is not tabulated in the following characterizations, and does not substantially affect the yield.



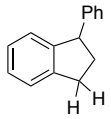
3.7a

1,1-Dimethyl-3-phenyl-2,3-dihydro-1*H*-indene 3.7a: General procedure VIII was followed using 224.0 mg of alkene **3.6a** (1.00 mmol), 12.0 mg of tritylium TPFPB (0.050 mmol) and 2.0 mL of benzene. Purification by flash column chromatography (100% hexanes) afforded indane **3.7a** (211.0 mg, 94% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.34 (m, 2H), 7.34-7.16 (m, 4H), 7.15-7.14 (m, 2H), 6.91 (dd, J = 7.5, 0.7 Hz, 1H), 4.42 (dd, J = 10.1, 7.7 Hz, 1H), 2.43 (dd, J = 12.5, 7.5 Hz, 1H), 2.01 (dd, J = 12.4, 10.3 Hz, 1H), 1.45 (s, 3H), 1.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.7 (C), 145.4 (C),145.1 (C), 128.4 (2CH), 126.9 (CH), 126.5 (CH), 126.3 (CH), 125.0 (CH), 121.9 (CH), 52.8 (CH_2), 49.0 (CH), 43.1 (C), 29.1 (CH_3), 28.7 (CH_3); ATR-FTIR: (thin film): 3061, 2948, 2858, 1599, 1493, 1452, 1152 cm^{-1}. HRMS (ESI/APCI) *m/z* calculated for $C_{17}H_{17}[M–H]^+$: 221.1325, found: 221.1327.



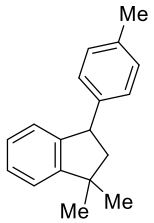
3.7b

1-Cyclobutane-3-phenyl)-indane 3.7b: General procedure VIII was followed using 62 mg of alkene **3.6b** (0.26 mmol), 12.0 mg of tritylium TPFPB (0.013 mmol) and 0.49 mL of benzene. Purification by flash column chromatography (100% hexanes) afforded indane **3.7b** (25.0 mg, 48% yield) as a colorless oil. (R_f = 0.40 hexanes, visualized by 254 nm light).[1]H NMR (400 MHz, $CDCl_3$) : δ 7.49 (d, *J*= 8.2 Hz, 1H), 7.35-7.12 (m, 9H), 6.91 (d, *J* = 7.8 Hz,1H), 4.32 (dd, *J* = 8.2 Hz, 1H), 2.80 (dd, *J* = 7.6, 12.8 Hz,1H), 2.59 (q, *J* = 9.4 Hz), 2.35-2.25 (m, 1H), 2.24-2.00 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.0 (C), 145.9 (C),145.1 (C), 128.4 (CH), 128.2 (CH), 127.0 (CH), 126.6 (CH), 126.3 (CH), 124.6 (CH), 122.0 (CH), 51.6 (CH_2), 49.8 (C), 49.2 (CH), 35.8 (CH_2), 33.7 (CH_2), 16.5 (CH_2); ATR-FTIR: (thin film): 3024, 2942, 2848, 1800, 1494, 1474, 1453 cm^{-1}. HRMS (EI) *m/z* calculated for $C_{18}H_{20}[M]^+$: 234.1403, found: 234.1408.



3.7d

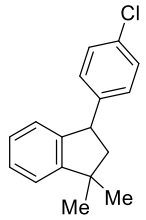
1-Phenyl-2,3-dihydro-1H-indene 3.7d: General procedure VIII was followed using 48.5 mg of alkene **3.6d** (0.25 mmol), 11.5 mg of tritylium TPFPB (0.0125 mmol) and 0.5 mL of benzene, while allowing the reaction to stir for 16 h rather than 5 h. The product **3.7d** was not isolated due to low NMR yield (7%). The NMR data matched those reported by Sun and coworkers:[9] [1] H NMR (500 MHz, $CDCl_3$): δ 7.40-7.37 (m, 3H), 7.32-7.25 (m, 4H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.04 (dd, *J* = 0.5, 7.5 Hz, 1H), 4.42 (t, *J* = 8.5 Hz, 1H), 3.16-3.11 (m, 1H), 3.07-3.00 (m, 1H), 2.70-2.63 (m, 1H), 2.19-2.11 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 147.2, 145.7, 144.6, 128.8, 128.4, 126.9, 126.7, 126.6, 125.2, 124.7, 52.0, 36.9, 32.2.



3.9a

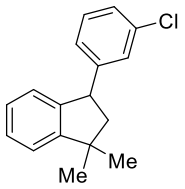
1,1-Dimethyl-3-(4-mehtylphenyl)-indane 3.9a: General procedure VIII was followed using 53 mg of alkene **3.8a** (0.22 mmol), 10.0 mg of tritylium TPFPB (0.011 mmol) and 0.42 mL of benzene. Purification by flash column chromatography (100% hexanes) afforded indane **3.9a** (20 mg, 28% yield) as a colorless oil (R_f = 0.40 hexanes, visualized by 254 nm light). The spectral data matched those reported by Blunt and co-workers.[8] [1]H NMR (400 MHz, $CDCl_3$): δ7.27–7.19 (m, 3H), 7.17–7.10 (m, 5H), 6.89 (d, *J* = 7.6 Hz,1H), 4.37 (dd, *J* = 7.9, 10.5 Hz, 1H) 2.40 (dd, *J* = 3.2, 10.5 Hz, 1H), 2.36 (s, 3H), 1.96 (dd, *J* = 10.8, 12.9 Hz, 1H), 1.43 (s, 3H) 1.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.7 (C), 145.6 (C), 142.0 (C), 135.8 (C), 129.2 (CH), 129.1 (CH), 128.3 (2CH), 126.8 (CH), 126.5 (CH), 124.9 (CH), 121.8 (CH), 52.8 (CH_2), 48.6 (CH), 43.1 (C), 29.0 (CH_3),

28.6 (CH_3), 21.0 (CH_3); ATR-FTIR: (thin film): 2956, 2924, 2360, 1738, 1372, 1236, 1044 cm^{-1}. HRMS (EI) *m/z* calculated for $C_{18}H_{20}$ $[M]^+$: 236.1565, found: 236.1549.



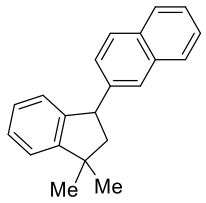
3.9b

3-(4-Chlorophenyl)-1,1-dimethy-indane 3.9b: General procedure VIII was followed using 62 mg of alkene **3.8b** (0.33 mmol), 15.0 mg of tritylium TPFPB (0.017 mmol) and 0.61 mL of benzene. Purification by flash column chromatography (100% hexanes) afforded indane **3.9b** (39 mg, 46% yield) as colorless solid, mp = 63 ºC. (R_f = 0.44 hexanes, visualized by 254 nm light). The spectral data matched those reported by Blunt and co-workers.[1] ^{1}H NMR (400 MHz, $CDCl_3$): δ7.30-7.19 (m, 5H), 7.17-7.11 (m, 3H), 6.85 (d, *J* = 8.3 Hz,1H), 4.37 (dd, *J* = 8.0, 10.2 Hz, 1H), 2.38 (dd, *J* = 7.4, 12.3 Hz, 1H), 1.92 (dd, *J* = 10.5, 13.1 Hz, 1H), 1.42 (s, 3H) 1.26 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.7 (C), 144.8 (C), 143.7 (C), 132.0 (C), 129.7 (2CH), 128.6 (2CH), 127.1 (CH), 126.6 (CH), 124.8 (CH), 122.0 (CH), 52.7 (CH_2), 48.3 (CH), 43.1 (C), 29.0 (CH_3), 28.6 (CH); ATR-FTIR: (thin film): 2984, 1737, 1373, 1236, 1044 cm^{-1}. HRMS (EI) *m/z* calculated for $C_{17}H_{17}Cl[M]^+$: 256.1013, found 256.101.



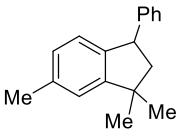
3.9c

3-(3-Chlorophenyl)-1,1-dimethyl-2,3-dihydro-1*H*-indene 3.9c: General procedure VIII was followed using 70.4 mg of alkene **3.8c** (0.27 mmol), 25 mg of tritylium TPFPB (0.027 mmol) and 0.55 mL of benzene. Purification by flash column chromatography (100% hexanes) afforded indane **3.9c** (51.4 mg, 73% yield) as a colorless oil.^{1}H NMR (400 MHz, $CDCl_3$): 7.36-7.09 (m, 8H), 6.89 (d, *J* = 7.4 Hz, 1H), 4.38 (dd, *J* = 10.2, 7.9 Hz, 1H), 2.40 (dd, *J* = 13.1, 8.0 Hz, 1H), 1.95 (dd, *J* = 12.2, 10.4 Hz, 1H), 1.43 (s, 3H), 1.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.7 (C), 147.3 (C), 144.5 (C), 134.3 (C), 129.7 (CH), 128.5 (CH), 127.2 (CH), 126.7 (2CH), 126.5 (CH), 124.9 (CH), 122.0 (CH), 52.6 (CH_2), 48.7 (CH), 43.2 (C), 29.0 (CH_3), 28.6 (CH_3).

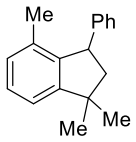


3.9d

2-(3,3-Dimethyl-2,3-dihydro-1H-inden-1-yl)naphthalene 3.9d: General procedure VIII was followed using 87.6 mg of alkene **3.8d** (0.32 mmol), 19.4 mg of tritylium TPFPB (0.016 mmol) and 0.61 mL of benzene (0.5M). Purification by flash column chromatography (100% hexanes) afforded indane **3.9d** (60.1 mg, 69% yield) as a colorless oil. (R_f = 0.30 hexanes, visualized by 254 nm light). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85-7.78 (m, 3H), 7.73 (s, 1H), 7.50-7.40 (m, 2H), 7.31(dd, *J* = 2.0, 8.5 Hz,1H), 7.28-7.24 (m, 3H), 7.18-7.11 (m, 1H), 6.90 (d, *J* = 7.6Hz), 4.58 (dd, *J* = 7.8, 10.4 Hz, 1H), 2.46 (dd, *J* = 7.5, 12.6 Hz, 1H), 2.09 (dd, *J* = 10.1, 12.6 Hz, 1H), 1.46 (s, 3H) 1.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.8 (C), 145.3 (C), 142.4 (C), 133.6 (C), 132.4 (C), 128.2 (CH), 127.6 (CH), 127.5 (CH), 127.0 (CH), 126.9 (CH), 126.8 (CH), 126.6 (CH), 216.0 (CH), 125.3 (CH), 125.0 (CH), 122.0 (CH), 52.3 (CH_2), 49.2 (CH), 43.3 (C), 29.1 (CH_3), 28.7 (CH_3); HRMS (EI) *m/z* calculated for $C_{21}H_{20}$ $[M]^+$: 272.1565 , found: 272.1537.



3.11a

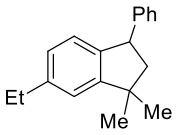


3.12a

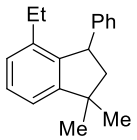
1,1,6-Trimethyl-3-phenyl-2,3-dihydro-1*H*-indene 3.11a and 1,1,4-trimethyl-3-phenyl-2,3-dihydro-1*H*-indene 3.12a: General procedure VIII was followed using 60 mg of alkene **3.10a** (0.25 mmol), 12 mg of tritylium TPFPB (0.012 mmol) and 0.47 mL of benzene. Purification by flash column chromatography (100% hexanes) afforded indane **3.11a** and **3.12a** as an inseparable 33:67 mixture, respectively (42 mg, 70% yield), a colorless oil.

3.11a: ^{1}H NMR (400 MHz, $CDCl_3$): 7.38-7.18 (m, 5H), 7.16-6.95 (m, 2H), 6.80 (d, *J* = 7.8 Hz, 1H), 4.38 (app. t, *J* = 8.8 Hz, 1H), 2.43 (dd, *J* = 12.6, 7.6 Hz, 1H), 2.40 (s, 3H), 1.99 (dd, *J* = 12.2, 9.7 Hz, 1H), 1.44 (s, 3H), 1.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.9 (C), 145.3 (C), 142.5 (C), 136.5 (C), 128.4 (CH), 127.4 (CH), 126.2 (CH) 124.7 (CH), 122.6 (CH), 53.0 (CH_2), 48.7 (CH), 43.0 (C) 29.1 (CH_3), 28.7 (CH_3), 21.5 (CH_3).

3.12a: ^{1}H NMR (400 MHz, $CDCl_3$): 7.38-7.18 (m, 5H), 7.16-6.95 (m, 3H), 4.46 (app. t, *J* = 7.7Hz, 1H), 2.53 (dd, *J* = 8.9, 12.8 Hz, 1H), 1.97 (dd, *J* = 13.0, 6.9 Hz, 1H), 1.88 (s, 3H), 1.33 (s, 3H), 1.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.4 (C), 146.5 (C), 142.4 (C), 135.2 (C), 128.4 (CH), 128.3 (CH), 127.8 (CH), 127.5 (CH), 125.8 (CH), 119.7 (CH), 52.6 (CH_2), 48.7 (CH), 43.5 (C) 30.2 (CH_3), 29.8 (CH_3), 19.4 (CH_3). ATR-FTIR (neat): 3090, 3074, 2953, 1478, 1034 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{18}H_{20}$ $[M–H]^+$: 236.1560, found 236.1552.



3.11b

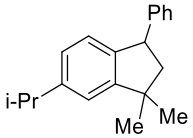


3.12b

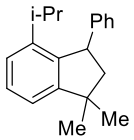
6-ethyl-1,1-dimethyl-3-phenyl-2,3-dihydro-1*H*-indene 3.11b and 4-ethyl-1,1-dimethyl-3-phenyl-2,3-dihydro-1*H*-indene 3.12b: General procedure VIII was followed using 88.0 mg of alkene **3.10b** (0.35 mmol), 16 mg of tritylium TPFPB (0.017 mmol) and 0.65 mL of benzene. Purification by flash column chromatography (100% hexanes) afforded indanes **3.11b** and **3.12b** as an inseparable 50:50 mixture, respectively (68.5 mg, 78% yield), as a colorless oil.

3.11b: ^{1}H NMR (400 MHz, $CDCl_3$): 7.34-7.20 (m, 6H), 7.12-6.96 (m, 3H), 6.80 (d, J = 7.9 Hz, 1H), 4.36 (dd, J = 10.6, 7.9 Hz, 1H), 2.66. (q, J = 8.4 Hz, 2H), 2.39 (dd, J = 12.3, 7.4 Hz, 1H), 1.97 (dd, J = 12.8, 12.3 Hz, 1H), 1.41 (s, 3H), 1.26 (s, 3H), 1.26 (t, J = 7.9 Hz). 152.8 (C), 145.3 (C), 143.0 (C), 142.7 (C), 128.4 (CH), 127.8 (CH), 126.2 (CH), 126.1 (CH), 124.7 (CH), 121.3 (CH), 53.0 (CH_2), 48.6 (CH), 43.0 (C), 29.0 (CH_3), 28.9 (CH_3), 28.6 (CH_2), 15.8 (CH_3).

3.12b: ^{1}H NMR (400 MHz, $CDCl_3$): 7.28-7.15 (m, 4H), 7.13-7.03 (m, 4H), 4.48 (dd, J = 9.4, 6.5 Hz), 2.50 (dd, J = 12.7, 8.9 Hz), 2.27-2.11 (m, 2H), 1.94 (app. q, J = 6. 4 Hz, 1H), 1.30 (s, 3H), 1.26 (s, 3H), 0.96 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 153.4 (C), 146.8 (C), 141.8 (C), 141.1 (C), 128.3 (CH), 127.8 (CH), 127.7 (CH), 126.3 (C), 125.8 (C), 119.7 (C), 52.5 (CH_2), 48.4 (CH), 43.4 (C), 30.4 (CH_3), 29.9 (CH_3), 25.5 (CH_2), 13.9 (CH_3); ATR-FTIR (neat): 3024, 2954, 2926, 2860, 1493 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{19}H_{22}$ $[M–H]^+$: 250.1711, found 250.1716.



3.11c



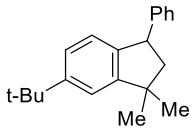
3.12c

6-*iso*-Propyl-1,1-dimethyl-3-phenyl-2,3-dihydro-1*H*-indene 3.11c and 4-*iso*-Propyl-1,1-dimethyl-3-phenyl-2,3-dihydro-1*H*-indene 3.12c: General procedure VIII was followed using 132 mg of alkene **3.10c** (0.50 mmol), 23 mg of tritylium TPFPB (0.025 mmol) and 0.99 mL of benzene. Purification by flash column chromatography (100% hexanes) afforded indane **3.11c** and **3.12c** in a 60:40 mixture, respectively (109 mg, 83% yield), a colorless oil.

3.11c: ^{1}H NMR (400 MHz, $CDCl_3$): 7.36-7.30 (m, 2H), 7.28-7.24 (m, 2H), 7.08-7.00 (m, 2H), 6.82 (d, J = 7.8 Hz, 1H), 4.38 (dd, J = 9.9, 7.5 Hz, 1H), 2.94 (sep, J = 6.7 Hz, 1H), 2.40 (dd, J = 12.3, 7.0 Hz, 1H), 1.99 (dd, J = 12.6, 10.6 Hz, 1H), 1.43 (s, 3H), 1.29 (d, 6H), 1.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.7 (C), 147.7 (C), 145.3 (C), 142.8 (C), 128.6 (2CH), 128.2 (2CH), 126.2 (CH), 124.6 (2CH), 119.8 (CH), 52.0 (CH_2), 48.6 (CH), 43.1 (C), 34.1 (CH), 29.1 (CH_3), 28.7 (CH_3), 24.3 (CH_3), 24.2 (CH_3). ATR-FTIR

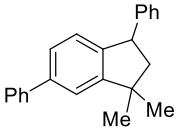
(neat): 2955, 2927, 2863, 1493, 1454, 1361 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{20}H_{24}$ $[M]^+$: 264.1873, found 264.1860.

3.12c: ^1H NMR (400 MHz, $CDCl_3$): 7.32-7.22 (m, 4H), 7.19-7.14 (m, 5H), 4.52 (dd, *J* = 9.1, 5.6 Hz, 1H), 2.62 (sep, *J*= 7.2 Hz, 1H), 2.50 (dd, *J* = 12.9, 9.0 Hz, 1H), 1.94 (dd, *J* = 12.9, 5.7 Hz, 1H), 1.27 (s, 3H), 1.25 (s, 3H), 1.07 (d, *J* = 6.7 Hz, 3H), 0.89 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.4 (C), 147.4 (C), 146.0 (C), 141.0 (C), 128.0 (2CH), 127.9 (CH), 127.6 (2CH), 125.8 (CH), 123.8 (CH), 119.6 (CH), 52.1 (CH_2), 48.1 (CH), 43.5 (C), 30.0 (CH), 24.5 (CH_3), 24.3 (CH_3), 22.4 (CH_3), 22.2 (CH_3). ATR-FTIR (neat): 2955, 2927, 2863, 1493, 1454, 1361 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{20}H_{24}$ $[M]^+$: 264.1873, found 264.1860.

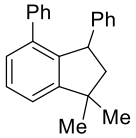


3.11d

1,1-Dimethyl-3-phenyl-7-(tert-butyl)-indane 3.11d: General procedure VIII was followed using 89 mg of alkene **3.10d** (0.33 mmol), 15.0 mg of tritylium TPFPB (0.017 mmol) and 0.59 mL of benzene. Purification by flash column chromatography (100% hexanes) afforded indane **3.11d** (77.0 mg, 88% yield) as a colorless oil. (R_f = 0.32 in hexanes, visualized by 254 nm light). ^1H NMR (400 MHz, $CDCl_3$): δ 7.39-7.32 (m, 2H), 7.31-7.25 (m, 4H), 7.24-7.20 (dd, *J* = 2.1, 8.2 Hz, 1H), 6.87 (d, *J* = 8.1 Hz,1H) 4.41 (dd, *J* = 7.5, 10.5 Hz, 1H) 2.44 (dd, *J* = 7.6, 12.2 Hz, 1H), 2.03 (dd *J* = 9.8, 12.2 Hz, 1H), 1.47 (s, 3H), 1.39 (s, 9H) 1.32 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.4 (C), 150.0 (C), 145.3 (C), 142.4 (C), 128.4 (CH), 128.4 (CH), 126.2 (CH), 124.3 (CH), 123.7 (CH), 118.6 CH), 53.1 (CH_2), 48.6 (CH), 43.2 (C), 34.8 (C), 31.7 (CH_3), 29.2 (CH_3), 28.8(CH_3)); ATR-FTIR: (thin film): 3035, 2955, 2863, 1478, 1362 cm^{-1}. HRMS (EI) *m/z* calculated for $[M]^+$: 278.2029, found: 278.2029.



3.11e

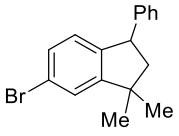


3.12e

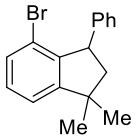
1,1-dimethyl-3,6-diphenyl-2,3-dihydro-1*H*-indene 3.11e and 1,1-dimethyl-3,4-diphenyl-2,3-dihydro-1*H*-indene 3.12e: General procedure VIII was followed using 103.0 mg of alkene **3.10e** (0.34 mmol), 16 mg of tritylium TPFPB (0.017 mmol) and 0.64 mL of benzene. Purification by flash column chromatography (100% hexanes) afforded **3.11e** and **3.12e** as an inseparable 35:65 mixture, respectively (100 mg, 98% yield), a colorless oil.

3.11e: ^1H NMR (400 MHz, $CDCl_3$): 7.69-7.45 (m, 2H), 7.40-6-82 (m, 8H), 4.49 (dd, *J* = 10.2, 7.9 Hz, 1H), 2.50 (dd, *J* = 12.6, 7.3 Hz, 1H), 2.10 (dd, *J* = 12.3, 10.6 Hz, 1H), 1.53 (s, 3H), 1.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.4 (C), 145.0 (C), 144.7 (C), 141.8 (C), 140.3 (C), 128.7 (CH), 128.5 (CH), 128.2 (CH), 127.6 (CH), 127.0 (CH), 125.3 (CH), 120.8 (CH), 53.0 (CH_2), 48.8 (CH), 43.2 (C), 29.2 (CH_3), 28.7 (CH_3).

3.12e: ^{1}H NMR (400 MHz, $CDCl_3$): 7.69-7.45 (m, 2H), 7.40-6-82 (m, 8H), 4.71 (app. t, *J* = 7.8 Hz, 1H), 2.54 (dd, *J* = 12.3, 7.9 Hz, 1H), 1.98 (dd, *J* = 13.2, 7.0 Hz, 1H), 1.45 (s, 3H), 1.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.1 (C), 145.8 (C), 142.1 (C), 141.0 (C), 140.0 (C), 128.6 (CH), 128.5 (CH), 128.4 (CH), 128.0 (CH), 127.5 (CH), 127.3 (CH), 126.2 (CH), 125.2 (CH), 121.1 (CH), 53.1 (CH_2), 48.7 (CH), 43.3 (C), 30.4 (CH_3), 28.3 (CH_3). ATR-FTIR (neat): 3025, 2952, 2859, 1600, 1453 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{23}H_{22}$ $[M–H]^+$: 298.1716, found 298.1714.



3.11f

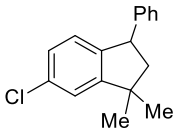


3.12f

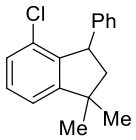
6-bromo-1,1-dimethyl-3-phenyl-2,3-dihydro-1*H*-indene 3.11f and 4-bromo-1,1-dimethyl-3-phenyl-2,3-dihydro-1*H*-indene 3.12f: General procedure VIII was followed using 87.0 mg of alkene **3.10f** (0.29 mmol), 13 mg of tritylium TPFPB (0.014 mmol) and 0.53 mL of benzene. Purification by flash column chromatography (100% hexanes) afforded **3.11f** and **3.12f** as an inseparable 35:65 mixture, respectively (83 mg, 96% yield), a colorless oil.

3.11f: ^{1}H NMR (400 MHz, $CDCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$): 7.38-7.12 (m, 7H), 7.01 (d, 8.0 Hz, 2H), 4.50 (dd, *J* = 5.8, 9.4 Hz, 1H), 2.53 (dd, *J* = 8.9, 12.9 Hz, 1H), 1.99 (dd, *J* = 5.8, 13.8 Hz, 1H), 1. 27 (s, 3H), 1.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.9(C), 145.3 (C), 143.2 (C), 130.7 (CH), 129.2 (CH), 128.3 (CH), 128.0 (CH), 125.9 (CH), 121.4 (CH), 121.1 (C), 51.5 (CH_2), 50.3 (CH), 44.5 (C), 30.3 (CH_3), 29.9 (CH_3).

3.12f: ^{1}H NMR (400 MHz, $CDCl_3$): 7.35-7.13 (m, 7H), 6.7 (d, 8.6 Hz, 1H), 4.32 (app. t, *J* = 9.7 Hz, 1H), 2.38 (dd, *J* = 7.5, 12.4 Hz, 1H), 1.97 (dd, *J* = 10.4, 12.2 Hz, 1H), 1.39 (s, 3H), 1.25 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.2(C), 144.4 (C), 143.2 (C), 129.6 (CH), 128.5 (CH), 128.3 (CH), 126.6 (CH), 126.5 (CH), 125.3 (CH), 120.7 (C), 52.7 (CH_2), 48.6 (CH), 43.3 (C), 28.9 (CH_3), 28.4 (CH_3). ATR-FTIR (neat): 3025, 2953, 2928, 2861, 1446, 1565 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{17}H_{17}Br$ $[M]^+$: 300.0508, found 300.0515.



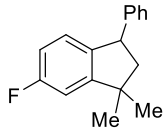
3.11g



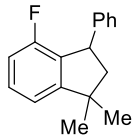
3.12g

6-Chloro-1,1-dimethyl-3-phenyl-2,3-dihydro-1*H*-indene 3.11g and 4-chloro-1,1-dimethyl-3-phenyl-2,3-dihydro-1*H*-indene 3.12g: General procedure VIII was followed using 65.0 mg of alkene **3.10g** (0.25 mmol), 12 mg of tritylium TPFPB (0.012 mmol) and 0.47 mL of benzene. Purification by flash column chromatography (100% hexanes) afforded **3.11g** and **3.12g** as an inseparable 40:60 mixture, respectively (58.5 mg, 91% yield), a colorless oil.

3.11g: ^{1}H NMR (400 MHz, $CDCl_3$): 7.40-7.102 (m, 7H), 6.81 (d, 9.4 Hz, 1H), 4.37 (app. t, *J* = 9.0 Hz, 1H), 2.05-1.96 (m, 1H (dd, *J* = 10.4, 12.2 Hz, 1H), 1.42 (s, 3H), 1.28 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.8(C), 144.5 (C), 143.9 (C), 132.6 (C), 128.3 (CH), 128.1 (CH), 126.7 (CH), 126.5 (CH), 126.2 (CH), 122.4 (CH), 52.9 (CH_2), 48.5 (CH), 43.3 (C), 28.9 (CH_3), 28.4 (CH_3).
3.12g: ^{1}H NMR (400 MHz, $CDCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$): 7.40-7.02 (m, 8H), 4.56 (app. t, *J* = 7.4 Hz, 1H), 2.54 (dd, *J* = 9.4, 13.7 Hz, 1H), 2.05-1.96 (m, 1H), 1. 30 (s, 3H), 1.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.8(C), 145.2 (C), 141.4 (C), 131.7 (C), 129.0 (CH), 128.3 (CH), 127.7 (CH),127.5 (CH), 125.9 (CH), 120.7 (CH), 51.9 (CH_2), 48.8 (CH), 44.3 (C), 30.2 (CH_3), 29.8 (CH_3). ATR-FTIR (neat): 3025, 2954, 2923, 1572, 1494, 1448 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{17}H_{17}Br$ $[M]^+$: 256.1013, found 256.1015.

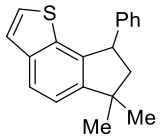


3.11h



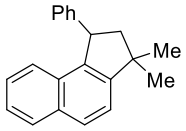
3.12h

6-Fluoro-1,1-dimethyl-3-phenyl-2,3-dihydro-1*H*-indene 3.11h and 4-fluoro-1,1-dimethyl-3-phenyl-2,3-dihydro-1*H*-indene 3.12h: General procedure VIII was followed using 123.5 mg of alkene **22.8** (0.51 mmol), 28 mg of tritylium TPFPB (0.025 mmol) and 0.95 mL of benzene. Purification by flash column chromatography (100% hexanes) afforded indanes **3.11h** and **3.12h** as an inseparable 78:22 mixture, respectively (105 mg, 90% yield), a colorless oil.
3.11h: ^{1}H NMR (400 MHz, $CDCl_3$): 7.37-7.31 (m, 2H), 7.26-7.20 (m, 3H), 6.88 (d, *J* = 8.6 Hz, 1H), 6.82-6.80 (m, 2H), 4.36 (appr. t, *J* = 8.8 Hz, 1H), 2.42 (dd, *J* = 12.5, 7.5 Hz, 1H), 2.01 (dd, *J* = 12.3 Hz, 10.4 Hz, 1H), 1.40 (s, 3H), 1.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 162.6 (d, *J* = 243.6 Hz, C), 155.1 (d, *J* = 7.0 Hz, C), 144.8 (C), 140.7 (d, *J* = 2.4 Hz, C), 128.5 (CH), 128.3 (CH), 126.4 (CH), 126.0 (d, *J*= 8.7 Hz, CH), 113.4 (d, *J* = 22.5 Hz, CH), 108.9 (d, *J* = 21.7 Hz, CH), 53.1 (CH2), 48.4 (CH), 43.2 (d, *J* = 1.9 Hz, C), 28.9 (CH3), 28.4 (CH3); ^{19}F NMR (282 MHz, $CDCl_3$): -116.5.
3.12h: ^{1}H NMR (400 MHz, $CDCl_3$): 7.39-7.20 (m, 6H), 7.16-7.10 (m, 1H), 7.03 (d, J = 7.5 Hz, 1H), 4.58 (app. t, *J* = 8.2 Hz, 1H), 2.51 (dd, *J* = 12.8, 8.3 Hz, 1H), 2.01 (dd, *J* = 11.6, 7.0 Hz, 1H), 1.38 (s, 3H), 1.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 159.6 (d, *J* = 249.4, C-F), 156.7 (d, *J* = 4.7 Hz, C), 144.7 (C), 143.4 (d, *J* = 4.1 Hz, C), 129.3 (d, *J* = 7.3 Hz, CH), 128.4 (CH), 127.4 (CH), 126.2 (CH), 117.8 (d, *J* = 3.3 Hz), 113.6 (d, *J* = 20.6 Hz, CH), 52.9 (CH_2), 46.5 (d, *J* = 1.2 Hz, CH), 44.3 (d, *J* = 1.2 Hz, C), 29.7 (CH_3), 29.1 (CH_3). ^{19}F NMR (282 MHz, $CDCl_3$): -116.1; ATR-FTIR: (thin film): 3035, 2925, 1478, 906, 730 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{17}H_{17}F$ $[M–H]^+$: 240.1309, found 240.1318.



3.15

6,6-Dimethyl-8-phenyl-7,8-dihydro-6*H*-indeno[5,4-*b*]thiophene 3.15: General procedure VIII was followed using 67 mg of alkene **3.13** (0.24 mmol), 11 mg of tritylium TPFPB (0.012 mmol) and 0.48 mL of benzene. Purification by flash column chromatography (100% hexanes) afforded indane **3.15** (42 mg, 63% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): 7.82 (d, J = 8.3 Hz, 1H), 7.35-7.19 (m, 8H), 6.56 (d, J = 6.9 Hz, 1H), 4.71 (app. t, J = 10.2 Hz, 1H), 2.59 (dd, J = 12.8, 8.2 Hz, 1H), 2.07 (dd, J = 13.5, 9.4 Hz, 1H), 1.48 (s, 3H), 1.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.1 (C), 145.6 (C), 139.0 (C), 138.2 (C), 136.5 (C), 128.5 (CH), 128.3 (CH), 126.3 (CH), 121.9 (CH), 121. 6 (CH), 118.8 (CH), 53.5 (CH_2), 49. 4 (CH), 43.7 (C) 29.7 (CH_3), 29.4 (CH_3). HRMS (ESI) *m/z* calculated for $C_{19}H_{18}S$ $[M–H]^+$: 278.1129, found 278.1120.



3.21

1,1-Dimethyl-3-phenyl-naphthalene-indane 3.21: General procedure VIII was followed using 110 mg of alkene **3.19** (0.40 mmol), 19.0 mg of tritylium TPFPB (0.02 mmol) and 0.75 mL of benzene. Purification by flash column chromatography (100% hexanes) afforded indane **3.21** (100.0 mg, 91% yield) as colorless solid, mp = 57 ºC (R_f = 0.35 hexanes, visualized by 254 nm light). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88-7.80 (m, 2H), 7.42 (d, J = 8.4Hz, 1H), 7.39-7.33 (m, 2H), 7.31-7.17 (m, 6 H), 7.16-7.11 (m, 2H), 4.90-4.83 (dd, J = 6.4, 8.9 Hz, 1H), 2.74-2.72 (dd, J = 9.0, 13.0 Hz,1 H), 2.12-2.05 (dd J = 6.6, 12.9 Hz, 1H), 1.41 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.7 (C), 147.0 (C), 138.2 (C), 133.4 (C), 130.5 (C), 129.5 (CH) 128.6 (CH), 127.9 (CH), 126.0 (CH), 125.7 (CH), 125.1 (CH), 124.7 (CH), 121.1 (CH), 52.8 (CH_2), 48.7 (CH), 44.2 (C), 30.1 (CH_3), 29.8 (CH_3)); ATR-FTIR: (thin film): 3089, 3033, 2953, 2861, 1478, 1033 cm^{-1}. HRMS (EI) *m/z* calculated for $C_{21}H_{20}$ $[M]^+$:272.1560, found: 272.1552. The connectivity was confirmed using ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC NMR analyses.

References

1) Cai, X.; Keshavarz, A.; Omaque, J. D.; Stokes, B. J. *Org. Lett*. **2017**, *19*, 2626.
2) (a) Beesley, R. M.; Ingold, C. K.; Thorpe, J. F. *J. Chem. Soc., Trans*. **1915**, *107*, 1080. For a recent review on Thorpe–Ingold effect, see: (b) Jung, M. E.; Piizzi, G. *Chem. Rev.* **2005**, *105*, 1735.
3) Baldwin, J. *J.C.S. Chem. Comm*. **1976**, 734.
4) For examples of the use of tritylium TPFPB salt as a catalyst/precatalyst, see: (a) Anderson, L. L.; Arnold, J.; Bergman, R. G. *J. Am. Chem. Soc.* **2005,** *127*, 14542. (b) Arii, H.; Yano, Y.; Nakabayashi, K.; Yamaguchi, S.; Yamamura, M.; Mochida, K.; Kawashima, T. *J. Org. Chem.* **2016,** *81*, 6314. For another recent method utilizing a tritylium catalyst, see: (c) Huang, Y.; Qiu, C.; Li, Z.; Feng, W.; Gan, H.; Liu, J.; Guo, K. *ACS Sustainable Chem. Eng.* **2016**, *4*, 47. For a recent report on the structure and

properties of tritylium and related salts, see: (d) Follet, E.; Mayer, P.; Berionni, G. *Chem. Eur. J.* **2016**, *23*, 263.
5) Rosenthal, J.; Schuster, D. I. *J. Chem. Educ.* **2003**, *80*, 679.
6) (a) Ai, T.; Xu, Y.; Qiu, L.; Geraghty, R. J.; Chen, L. *J. Med. Chem.* **2015**, *58*, 785. (b) Masuya, Y.; Tobisu, M.; Chatani, N. *Org. Lett.* **2016**, *18*, 4312.
7) Alacid, E.; Nájera, C. *J. Org. Chem.* **2008**, *73*, 2315.
8) Blunt, J. W.; Coxon, J. M.; Robinson, W. T.; Schuyt, H. A. *Australian J. Chem.* **1983**, *36*, 565.
9) Deng, R.; Sun, L.; Li, Z. *Org. Lett*. **2017**, *9*, 5207.

CHAPTER 4

Synthesis of Promesogenic Organic Ligands for Host Medium Microencapsulation by CdSe/ZnS Quantum Dots

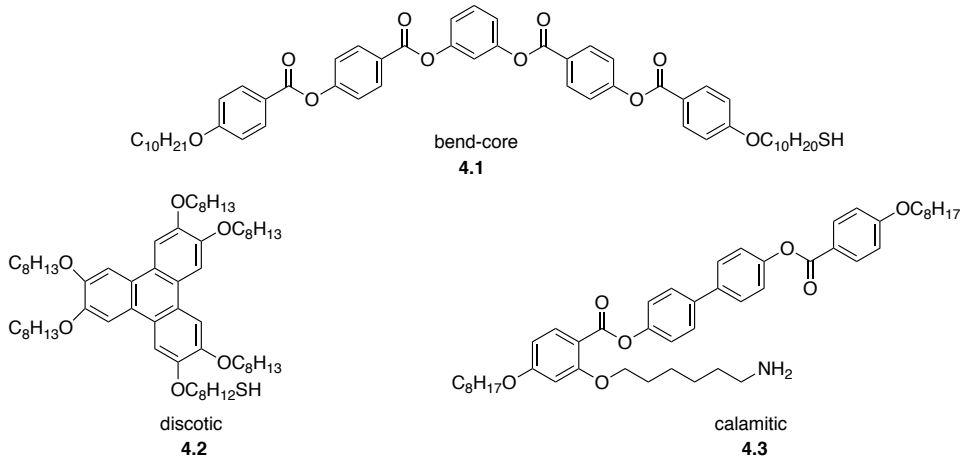
Background

Liquid Crystals (LC) are fluid-like materials that maintain some orientational order and have anisotropy, presenting different properties depending on the directionality they are being measured or observed. The LC phases have many characteristics such as being anisotropic or exhibiting short range ordering. The molecules can also move throughout the material, fluctuate and rotate freely. Liquid crystal phases can be classified as thermotropic and lyotropic. Thermotropic phases are those that occur due to changes in temperature while lyotropic phases take place due to changes in concentration. Among the thermotropic phases, the simplest and most well known LC phase is nematic in which there is orientational ordering; this phase tends to be the most fluid-like phase and exhibit lower viscosity. Smectic phases are fluid-like sheets of molecules in a stack, which contain both orientational order and 1D positional order. The columnar phases are formed from discotic materials and have 2D positional order.[1] In order to enhance the properties of the LC, significant work has recently been contributed to development of hybrid LC/nanoparticles system[2] and modification by small organic molecules[3].

The shape of the coating small organic molecules, ligands, classifies them in three categories: discotic, bend-core or banana, and calamitic or rod-like (Scheme 17). Discotic ligands are characterized by having an axis that is much shorter than the rest; they are composed of fused aromatic ring that allow for a planar conformation, just as a disk.[4] Bent-core ligands are long chains that have a bending in their structure due to the preferable orientations adopted by the bonds in order to minimize sterics;[5] carbonyl groups are usually employed in this kind of ligands as a good functional group to induce the bending. Calamitic ligands are the ones that have been explored the most. They are characterized by containing a linkage moiety and a mesogenic one; the linkage moiety allows for flexibility of the ligand, while the mesogenic portion is more rigid by containing aromatic groups attached to each other and that give the long dimension to the ligand. Studies on the design and synthesis of calamitic ligands have been conducted for the past years.[3,6-7] A variety of changes have been introduced to these ligands in order to understand the types of properties they can have when dispersed in the liquid crystal. The first calamitic ligand was synthesized by Ikeda's group,[7] in which the linking moiety was composed of a thiol binding group and a 10 carbon chain that was connected in a *para* position with the mesogenic moiety, a side-end attachment arm, while the mesogenic moiety was composed of a phenyl ring and a cyclohexane directly attached to each other. Modifications of calamitic ligand emerged over time by changing the length of the side arm as well as its position in the phenyl ring, a 1,2- position which in known as side-on attachment arm. Also the mesogenic moiety has been modified increasing rigidity by replacing the cyclohexane group by a phenyl group and increasing its length by addition of carbonyl groups and aliphatic groups.

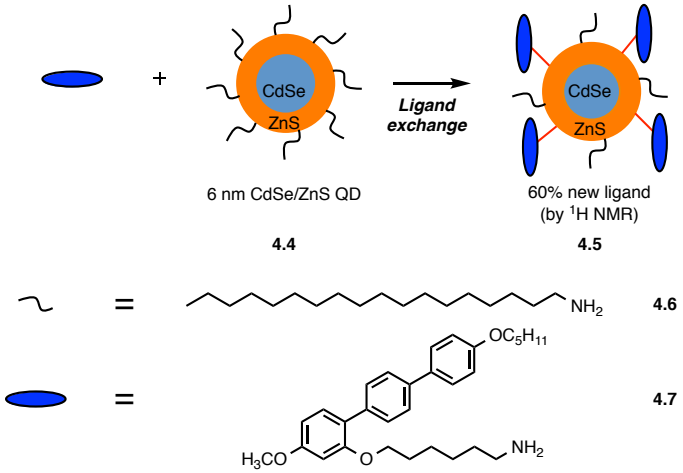
Ligands can bind nanoparticles either covalently[8] or via Van der Waals interactions[9]. Covalent bonds, being stronger, would allow for greater coating of the nanoparticles and this would have a higher impact on the properties of the hybrid nanoparticles. Therefore,

the linking atom plays a major role on the efficient binding of the ligands. One of the most widely used functional groups for binding is the thiol group as the sulfur atom has strong interactions with precious metals such as gold and silver, metal oxides such as iron oxide, and with semiconductor quantum dots such as CdSe. These nanoparticles can also be linked to amine groups as the nitrogen atom also has a strong binding affinity towards those atoms. Metal oxides have a strong affinity towards the oxygen atom; thus, it would be preferred to functionalize it with ligands containing functional groups such as carboxylic acids, alcohols, and phosphonic acids.

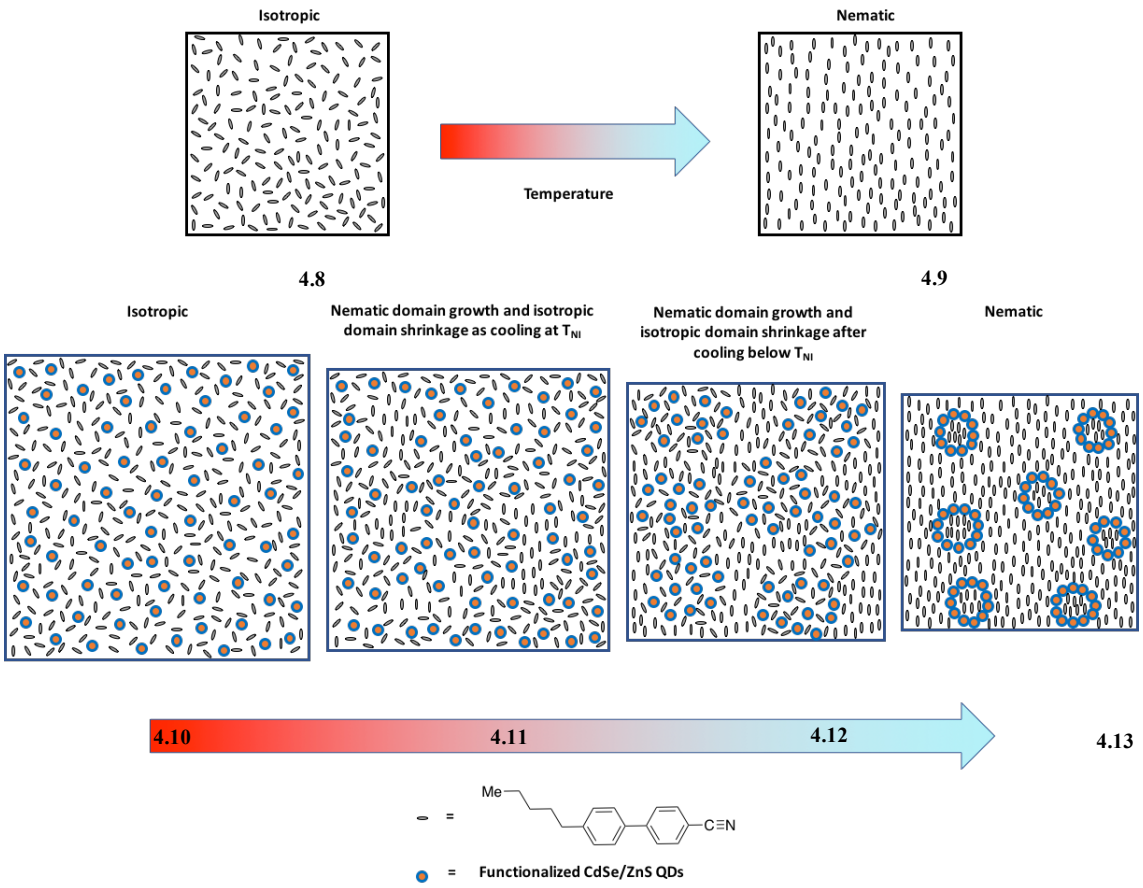


Scheme 17. Classification of ligands based on their shapes.

Functionalization of the metal nanopartcile with ligands can take place via three methods: the direct functionalization on the surface, ligand exchange, and synthetic extension by adhering ligands on already binding organic molecules. Direct functionalization is performed via the Brust-Schiffrin protocol, in which cloroauric acid is reacted with the ligand to yield dense hybrid nanoparticles.[10] In ligand exchange, a nanoparticle previously coated with a simple aliphatic organic molecule undergoes an SN_2 reaction with the desired ligand (Scheme 18).[11] Since the nanoparticles were previously coated, this method requires of ligands with stronger binding affinities and usually gives nanoparticles that are functionalized with both initial and desired ligands; there have been studies that show that the ratios between these two ligands can give rise to different morphologies.[12] The third method requires hybrid nanoparticles containing functional groups at their ends that can be easily modified; this method can yield dense nanoparticles but control over the ratio of unmodified ligand versus modified ligand can be difficult.[13] Metal nanoparticles functionalized with mesogenic (liquid crystalline) calamitic side-on ligands self-assemble into different morphologies based on cooling rate when suspended in a liquid crystal host, such as 4-cyano-4'-pentylbiphenyl (5CB). Once attached to core–shell quantum dot nanoparticles and suspended in a liquid crystal medium, the functionalized nanoparticles self-assemble[14] into different morphologies like rods, spheres and capsules that could potentially be used for biochemical sensors,[15] optoelectronic[16] and photovoltaic devices[17].



Scheme 18. Ligand exchange process.



Scheme 19. Schematic representation of phase transition.

My research has focused on the design and synthesis of promesogenic rod-shaped calamitic ligands with a side-on attaching arm bearing a nitrogen or sulfur atom terminus.

The ligand's flexible alkylamine tether promotes alignment with the local liquid crystal host, 5CB, increasing dispersibility in the isotropic phase and stabilizes the QD (Scheme 19). It is important to mention that the solutions are very dense, in a couple of microliter of sample one can find millions of QDs; thus Scheme 19 is not a quantitative representation of the QDs in solution. 5CB makes the isotropic-to-nematic phase transition T_{NI} at approximately 34 ºC. Our ligand stabilizes QDs through this phase transition, which causes a depression in the T_{NI} in regions nearby the QDs. Upon cooling, the liquid crystal starts growing nematic domains, which forces the QDs regions to spread out segregating themselves into isotropic domains. As the temperature drops below the T_{NI}, these isotropic domains start changing into nematic forcing the functionalized QDs to move to the surface of these domains and come in close proximity. The rod-like aromatic core enables attractive interaction between closely packed particles. Thus close QD proximity promotes ligand–ligand interactions causing formation of thousands of capsules or shells. In addition to the design and synthesis, I have been interested to see how the interparticle spacing is correlated to the flexible tether chain.

Results and Discussion

I initially started synthesizing ligand **4.3** which was originally reported by Rodarte, et al[18]. We provided improved synthetic procedures and complete characterization data for all the intermediates and the final ligand[19]. We also quantified the ligand exchange process by calculating the average ratio of mesogenic ligand to remaining octadecylamine ligand on the particle surface by ^{1}H NMR.[11] The same ligand was used for the modification of AuNPs to form stable rigid shell wall for encapsulation of fluorescent dye.[20] In other work, our collaborator at Hirst lab reported a method to form closed-cell foams, spherical shells and tubular networks.[21]

Table 20. Synthesis of mesogenic ligand.

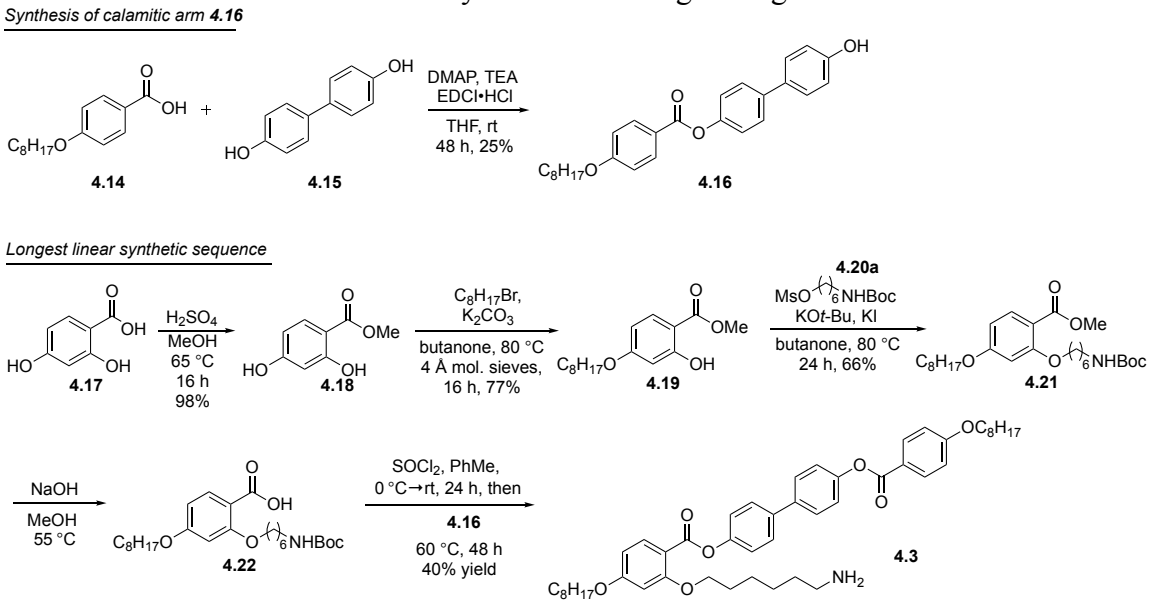
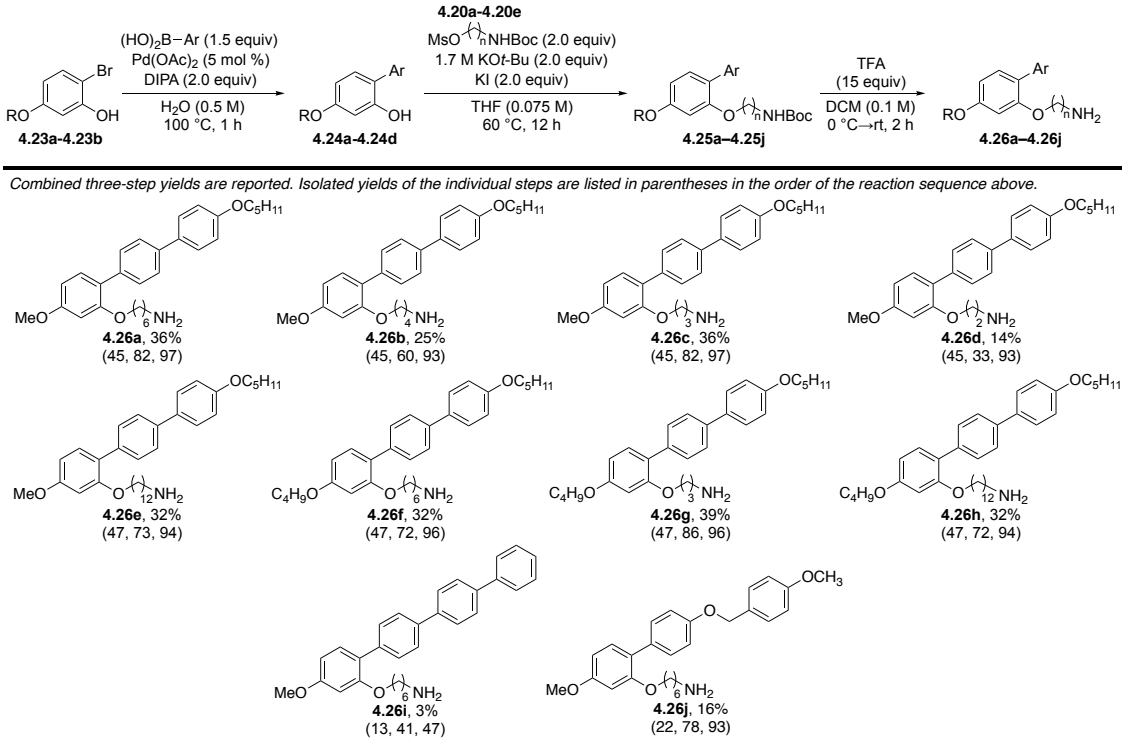


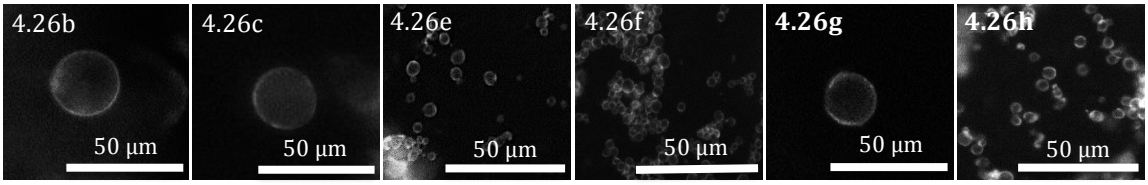
Table 21. Promesogenic ligand library synthesis.



Ligand **4.3** was prepared in eight steps with a longest linear sequence of five steps (Table 20). Rod-like arm **4.16** could be prepared by coupling of carboxylic acid **4.14** and biphonol **4.15** through EDCI.HCl/DMAP. Carboxylic acid **4.17** was esterified to form **4.18** followed by nucleophilic substitution to give alcohol **4.19**. Boc protected tether **4.20a** was prepared in two steps (see the experimental section for full detail). Reaction of alcohol **4.19** with **4.20a** gave **4.21**. The ester **4.21** was turned into carboxylic acid **4.22** through a base catalyzed reaction. One pot synthesis of **4.3** was obtained by reacting carboxylic acid with thionyl chloride followed by addition of alcohol **4.16** Due to the synthetic challenges and difficulty in purification, we decided to design a modular, scalable, ester-free ligand **4.26** that could be synthesized in few steps with high binding efficiency to QD and capable of making shells (Table 21). We designed a library of ligands to see their effectiveness in binding to CdSe/ZnS quantum dots core and their ability to self-assemble.[22] We started the synthesis with a bench top Suzuki cross-coupling[23] between arylbromides **4.23** and commercially available areneboronic acids in just 1 hour. Next the phenol oxygen of **4.24** is alkylated by Boc protected amino mesylate **4.20** to afford the *N*-protected ligand **4.25**. Finally, the Boc deprotection gives the final ligand **4.26** in near quantitative yield. It's important to note that these ligands can be prepared in less than 48 hours. We attached the ligands to quantum dot through ligand-exchange process. We then dispersed the ligand modified QD into the liquid crystal host, 5CB. After cooling from the isotropic to nematic phase the ligand modified QD's self-assembled into microcapsules. Crystal mosphologies of the ligands were confirmed by

polarized optical microscopy (POM) and differential scanning calorimetry (DSC). We used scanning electron microscopy (SEM) to further characterize the morphology of the QD shells. The images confirm that the shells are hollow with a relatively thin wall (Selected examples of shells are shown in Table 22). Gabrielle I Warren who was an undergraduate researcher in Stokes lab helped with the synthesis of ligand **4.3** and all its intermediates in the summer of 2016.

Table 22. Fluorescence microscopy images of QD mesostructures formed from 6.2 nm CdSe/ZnS QDs (λmax= 540 nm) functionalized with different ligands.

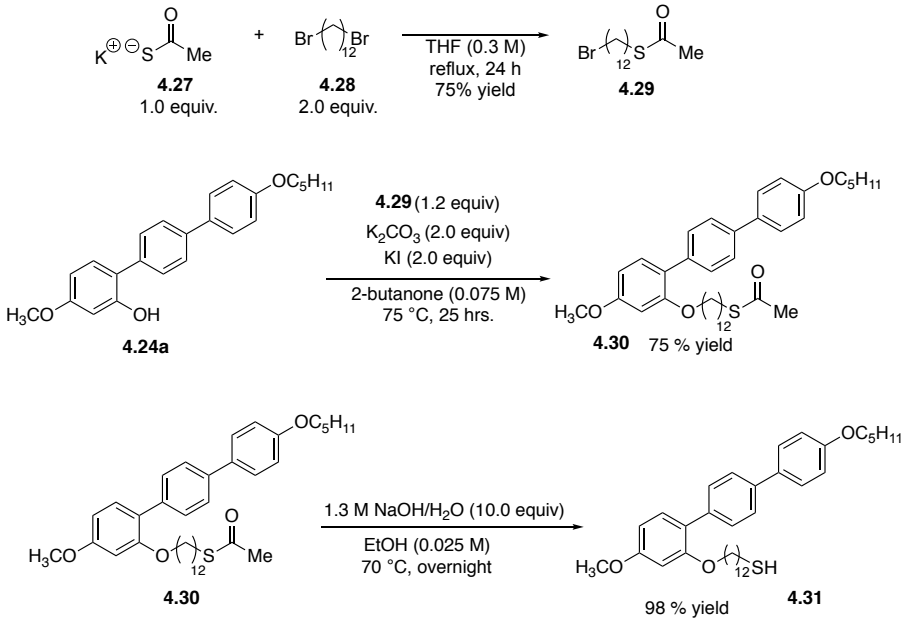


These microcapsules are highly stable up to 350 ºC and they bode well for encapsulation applications where stability under high temperature is required. Employing our method for small-angle X-ray scattering (SAXS) measurements. The nanoparticle packing in the shell was quantified. The average quantum dot separation within a shell wall, d, is inversely proportional to the scattering vector, q, as stated by the equation $q = 2\pi/d$; thus, the scattering intensity can be plotted as a function of q (refer to Figure 5, Keshavarz et al).[22] It shows that when comparing homologous ligands **4.26c**, **4.26b**, **4.26a** and **4.26e**, as the amine linker arm increases from 3 to 4, 6, and 12 methylenes, respectively, the interdot separation results on being 10.15, 11.79, 12.94, and 13.25 nm, which gives the impression of a logarithmic correlation. Therefore, the linker arm significantly has an effect on the interparticle separation. On the other hand, when the ethereal arm length was increased by changing a methoxy group into a *n*-butoxy group, no correlation between the aminoalkyl chain length and the interparticle spacing was observed as going from 3 methylenes to 6 and 12, **4.26g**, **4.26f**, and **4.26h**, the interdot distance resulted on being 11.27, 10.44, and 10.11 nm, respectively. Florescence microscopy images and shell formation was done by graduate student, Ms. Sheida T. Riahinasab from Hirst lab.

We were also able to design and synthesize a thiol-terminus promesogenic ligand **4.31** to be used for gold nanoparticles. The synthesis of **4.31** consists of four steps (Table 23). This route was chosen due to the low cost and availability of the starting materials. To prepare bromothiol **4.29**, potassium thioacetate **4.27**, and 1,12-dibromododecane **4.28** are refluxed for a day to afford 75% isolated yield. The three-step linear sequence starts with a 1-hour aqueous Suzuki cross-coupling between 2-bromo-5-methoxyphenol and aryl boronic acid, which affords **4.24a**. The next reaction is a day-long nucleophilic substitution to attach **4.24a** and **4.29**, affording **4.30** in 75% yield. Finally, deprotection of the thiol under basic conditions overnight at 70 ºC affords the target ligand **4.31** in

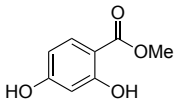
near-quantitative yield. Synthesis of the ligand **4.31** was done with the help of Ms. Jocelyn Ochoa who is a former graduate student in Stokes lab.

Table 23. Synthesis of calamitic thiolated ligand.



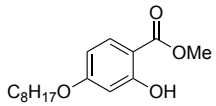
Experimental

A. Preparation of the Mesogenic Ligand **4.3**



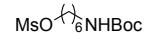
4.18

Methyl 2,4-dihydroxybenzoate 4.18. To a 100 mL round bottom flask equipped with a PTFE-coated magnetic stir barwereadded 30 mL of methanol and 6.00 g (39.0 mmol) of 2,4-dihydroxybenzoic acid **4.17**. The reaction mixture was placed in an ice bath, then 5.0 mL of concentrated sulfuric acid was added slowly. The reaction flask was heated to reflux for 16 hours. After cooling to ambient temperature, the solvent was removed under vacuum and the residue was poured into 100 mL of ice water. Analytically pure methyl 2,4-dihydroxybenzoate **4.18** (6.40 g, 98%) was isolated upon filtration. This product is also available commercially.



4.19

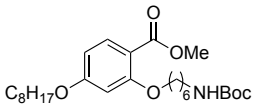
Methyl 2-hydroxy-4-(octyloxy)benzoate 4.19. To a 250 mL round bottom flask equipped with a PTFE-coated magnetic stir bar, 10 g of 4 Å molecular sieves, and 80 mL of butanone were added 3.9 g (23.2 mmol) of methyl 2,4-dihydroxybenzoate **4.18** and 16.0 g (116 mmol) of potassium carbonate. The reaction flask was heated to reflux followed by the slow addition of 4.93 g of 1-bromooctane (25.5 mmol) in 30 mL of butanone over a period of one hour. After 16 hours, the reaction was cooled to room temperature and the solids were filtered off. The solution was concentrated under vacuum and the residue was purified by flash column chromatography on SiO_2(100:0→0:100 hexanes:toluene) to afford **4.19** (4.99 g, 77%) as a white solid, mp = 38 ºC. H NMR (400 MHz, $CDCl_3$): δ 10.95 (s, 1H), 7.72 (d, J = 9.6 Hz, 1H), 6.43 (s, 1H), 6.43–6.40 (m, 1H), 3.96 (t, J = 6.7 Hz, 2H), 3.91 (s, 3H), 1.78 (p, J = 8.2 Hz, 2H), 1.47–1.39 (m, 2H), 1.35–1.24 (m, 8H), 0.88 (t, J = 7.0 Hz, 3H); ^{13}C NMR(100 MHz, $CDCl_3$): δ 170.4 (CO), 165.2 (C), 163.7 (C), 131.1 (CH), 107.9 (CH), 105.2 (C), 101.1 (CH), 68.3 (CH_2), 51.9 (CH_3), 31.8 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 29.0 (CH_2), 25.9 (CH_2), 22.6 (CH_2), 14.1 (CH_3). ATR-FTIR (thin film): 3207, 2923, 2850, 1674, 1618, 1577, 1444, 1332, 1247, 1181 cm^{-1}.



4.20a

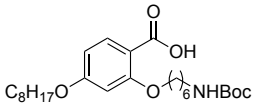
6-((*tert*-Butoxycarbonyl)amino)hexyl methanesulfonate 4.20a. Into a 250 mL round bottom flask charged with a PTFE-coated magnetic stir bar were added 47 mL of dry DCM, 2.00 g (9.4 mmol) of alcohol, and 1.7 mL (12.2 mmol) of triethylamine. The reaction flask was placed in an ice bath and 0.9 mL (11.3 mmol) of methanesulfonyl

chloride was added dropwise. After 6 hours, the reaction was quenched with 50 mL of water and separated, and the organic layer was dried over anhydrous sodium sulfate and removed under reduced pressure to afford **4.20a** (2.72 g, 98%) as alight yellow solid.



4.21

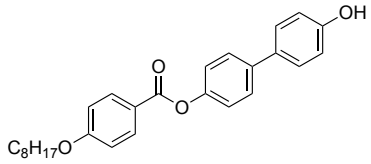
Methyl 2-((6-((*tert*-butoxycarbonyl)amino)hexyl)oxy)-4-(octyloxy)benzoate 4.21. To a 150 mL round bottom flask charged with a PTFE-coated magnetic stir bar were added 45 mL of butanone, 1.20 g (4.28 mmol) of methyl 2-hydroxy-4-(octyloxy)benzoate **4.19** and 1.39 g (4.71 mmol) of **4.20a**. Then, 1.07 g (6.42 mmol) of potassium iodide and 0.58 g (5.14 mmol) of potassium tertbutoxide powder were added to the reaction vessel and heated to reflux for 24 hours. The solvent was then removed under reduced pressure and the residue was extracted with DCM and water. The organic layer was collected and dried over anhydrous sodium sulfate before it was concentrated under vacuum. Purification by flash column chromatography (100:0→90:10 chloroform:methanol) on SiO_2 afforded **4.21** (1.35 g, 66%) as a light yellow oil. The spectral data matched those reported by Hirst and coworkers.[18] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, J = 8.6 Hz, 1H), 6.68–6.43 (m, 2H), 4.57 (br s, 1H), 3.98 (q, J = 6.4 Hz, 4H), 3.84 (s, 3H), 3.16–3.06 (m, 2H), 1.89–1.72 (m, 4H), 1.53–1.45 (m, 5H), 1.43 (s, 9H), 1.37–1.22 (m, 11H), 0.88 (t, J = 7.0, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.3 (C), 163.7 (C), 160.8 (C), 156.0 (C), 133.8 (CH), 112.2 (C), 105.1 (CH), 100.3 (CH), 77.2 (C), 68.7 (CH_2), 68.2 (CH_2), 51.6 (CH_3), 40.5 (CH_2), 31.8 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 29.1 (CH_2), 29.0 (CH_2), 28.8 (CH_2), 28.4 ($3CH_3$), 26.4 (CH_2), 26.0 (CH_2), 25.7 (CH_2), 22.6 (CH_2), 14.1 (CH_3). ATR-FTIR (neat): 3375, 2927, 2856, 1704, 1608, 1506, 1250, 1175 cm^{-1}.



4.22

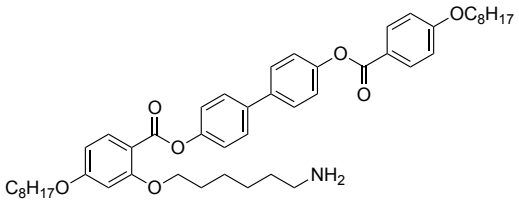
2-((6-((*tert*-butoxycarbonyl)amino)hexyl)oxy)-4-(octyloxy)benzoic acid 4.22. To a 150 mL round bottom flask charged with a PTFE-coated magnetic stir bar were added 57 mL of methanol and 1.32 g (2.75 mmol) of **4.21**. Then, a solution of 1.13 g of NaOH in 14 mL of deionized water was added slowly to the flask. The reaction was stirred at 55 ºC for 16 hours. After cooling to room temperature, the solvent was removed under reduced pressure and the aqueous residue was acidified with dilute HCl prior to extraction with DCM. The organic layer was dried over anhydrous sodium sulfate before it was concentrated under vacuum. Purification by flash column chromatography (100:0→90:10 chloroform:methanol)afforded **4.22** (1.20 g, 94%) as a white solid, mp= 86 °C. The spectral data matched those reported by Hirst and coworkers.[18] ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.72 (br s, 1H), 8.10 (d, J = 8.7 Hz, 1H), 6.61 (dd, J = 8.8, 2.3 Hz, 1H), 6.48 (d, J = 2.3 Hz, 1H), 4.53 (br s, 1H), 4.19 (t, J = 6.7 Hz, 2H), 4.00 (t, J = 6.7 Hz, 2H), 3.16–3.07 (m, 2H), 1.91 (p, J = 7.8 Hz,2H), 1.79 (p, J = 8.2 Hz,2H), 1.56–1.45 (m, 5H),

1.43 (s, 9H), 1.42–1.24 (m, 11H), 0.88 (t, J = 6.6, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ165.3 (C), 164.6 (C), 158.9 (C), 156.0 (C), 135.4 (CH), 110.2 (C), 107.1 (CH), 99.8 (CH), 77.2 (C), 70.0 (CH_2), 68.6 (CH_2), 40.3 (CH_2), 31.8 (CH_2), 29.9 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 29.0 (CH_2), 28.8 (CH_2), 28.4 ($3CH_3$), 26.3 (CH_2), 25.9 (CH_2), 25.6 (CH_2), 22.6 (CH_2), 14.1 (CH_3). ATR-FTIR (neat): 3303, 2927, 1608, 1533, 1439, 1267, 1197, 1126 cm^{-1}. HRMS (ESI) m/z calculated for $C_{26}H_{43}NO_6$ $[M]^+$: 466.3163, found: 466.3117.



4.16

4'-Hydroxy-[1,1'-biphenyl]-4-yl 4-(octyloxy)benzoate 4.16. To a 100 mL round bottom flask charged with a PTFE-coated magnetic stir bar were added 44 mL of THF, 2.00 g (8.00 mmol) of 4-(octyloxy)benzoic acid **4.14**, 0.20 g (1.63 mmol) of DMAP, and 1.49 g (8.00 mmol) of **4.15**. Then, 2.6 mL (18.4 mmol) of triethylamine was added to the reaction flask, followed by 1.84 g (9.60 mmol) of EDCI•HCl.The reaction was allowed to stir for 48 hours at room temperature. The solids were then filtered and washed with a minimal amount of cold DCM. The solvent was removed under vacuum and the residue was treated with ethanol and heated to reflux and filtered immediately once hot. The filtrate was cooled to room temperature and filtered again. The solid residues were collected and purified by flash column chromatography (100:0→80:20 hexanes:EtOAc) to afford **4.16** (0.84 g, 25%) as a white solid, mp = 168 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, J = 8.8 Hz, 2H), 7.56 (d, J = 8.7 Hz, 2H), 7.45 (d, J = 8.7 Hz, 2H), 7.24 (d, J = 8.7 Hz, 2H), 6.98 (d, J = 8.7 Hz, 2H), 6.89 (d, J = 8.7 Hz, 2H), 4.05 (t, J = 6.8 Hz, 2H), 1.83 (p, J = 6.8 Hz, 2H), 1.48 (p, J = 6.8 Hz, 2H), 1.38–1.26 (m, 8H), 0.89 (t, J = 6.7 Hz, 3H): ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.1 (C), 163.5 (C), 155.1 (C), 150.0 (C), 138.4 (C), 133.2 (C), 132.3 (2CH),128.4 (2CH), 127.7 (2CH), 122.0 (2CH), 121.5 (C), 115.6 (2CH), 114.3 (2CH), 68.3 (CH_2), 31.8 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 29.1 (CH_2), 26.0 (CH_2), 22.6 (CH_2), 14.1 (CH_3). ATR-FTIR (neat): 3458, 2920, 2853, 1748, 1606, 1497, 1254, 1166 cm^{-1}.



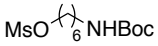
4.3

4'-((4-(Octyloxy)benzoyl)oxy)-[1,1'-biphenyl]-4-yl 2-((6-aminohexyl)oxy)-4-(octyloxy)benzoate 4.3. To a 25 mL round bottom flask charged with a PTFE-coated magnetic stir bar were added 7.6 mL of anhydrous toluene and 0.64 g of **4.22** (1.37 mmol). Then, 0.2 mL of thionyl chloride (2.5 mmol) was added dropwise at 0 ºC and the reaction was allowed to warm to room temperature and stir for 24 hours. Finally, 0.45 g

(1.07 mmol) of **4.16** was added to the flask and the reaction was heated to 60 ºC for 48 hours. After cooling to room temperature and concentration under vacuum, purification of the residue by flash column chromatography (80:20:00 hexanes:ethyl acetate:methanol→00:50:50 hexanes:ethyl acetate:methanol on Et_3N-treated SiO_2) afforded **4.3** (0.330 g, 40%) as a white solid, R_f = 0.89 (50:50EtOAc:MeOH on an Et_3N-treated SiO_2 TLC plate, visualized by 254 nm light), mp = 94 ºC.^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, *J* = 8.8 Hz, 2H), 8.05 (d, *J* = 9.1 Hz, 1H), 7.61 (d, *J* = 8.6 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 6.98 (d, *J* = 8.7 Hz, 2H), 6.53 (dd, *J* = 9.0, 6.5 Hz, 1H), 6.49 (d, *J* = 2.5 Hz, 1H), 4.05 (t, *J* = 6.5 Hz, 2H), 4.02 (t, *J* = 6.5 Hz, 2H), 4.01 (t, *J* = 6.5 Hz, 2H), 2.81 (br s, 2H), 2.67 (t, *J* = 6.4 Hz, 2H), 1.91–1.77 (m, 6H), 1.57–1.43 (m, 9H), 1.41–1.26 (m, 17H),0.91 (t, *J* = 6.5 Hz, 3H), 0.90 (t, *J* = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.9(C),167.3 (C), 166.8 (C), 166.3 (C), 164.5 (C), 153.2 (C), 153.1 (C), 140.7 (C), 140.3 (C), 137.1 (CH), 135.0 (2CH), 130.9 (4CH), 125.0 (2CH), 124.8 (2CH), 124.0 (C), 117.0 (2CH), 113.3 (C), 108.2 (CH), 102.8 (CH), 71.4 (CH_2), 71.0 ($2CH_2$), 42.6 (CH_2), 34.5 (CH_2), 32.0 ($2CH_2$), 31.9 ($2CH_2$), 31.8 (CH_2), 31.7 (CH_2), 31.3 (CH_2), 29.7 (CH_2), 28.7 ($2CH_2$), 28.6 (CH_2), 28.0 (CH_2), 26.8 (CH_2), 25.3 ($2CH_2$), 16.8 ($2CH_3$). ATR-FTIR (neat): 2923, 2854, 1726, 1605, 1251, 1196, 1162 cm^{-1}. HRMS (ESI) *m*/*z* calculated for $C_{48}H_{63}NO_7$ $[M]^+$: 766.4677, found: 766.4659.

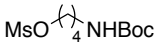
B. Preparation of the Amine Linkers **4.20a-4.20e**.

General Procedure IX: Into a round bottom flask charged with a PTFE-coated magnetic stir bar were added 1.0 equivalent of alcohol in 0.2 M dry DCM and 1.3 equivalent of triethylamine. The reaction mixture was placed in an ice bath and 1.2 equivalent of methanesulfonyl chloride was added dropwise. After 18 hours, the reaction mixture was quenched with water and separated. The organic layer was dried over anhydrous sodium sulfate and removed under reduced pressure to afford **4.20a-4.20e**.



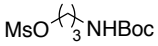
4.20a

6-((*tert*-butoxycarbonyl)amino)hexyl methanesulfonate 4.20a: General procedure IX was followed by using 1.0 g *tert*-butyl (6-hydroxyhexyl)carbamate (4.60 mmol), 0.83 mL of TEA (5.98 mmol), 0.43 mL of MsCl (5.52 mmol) and 23 mL of DCM. 1.20 g of **4.20a** (88%) was obtained as an off-white solid, mp = 44–45 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.51 (s, 1H), 4.22 (t, *J* = 6.5 Hz, 2H), 3.11 (q, *J* = 6.8 Hz, 2H), 3.00 (s, 3H), 1.75 (p, *J* = 6.5 Hz, 2H), 1.55–1.45 (m, 3H), 1.44 (s, 9H), 1.42–1.31 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.0 (C), 79.1 (C), 69.9 (CH_2), 40.4 (CH_2), 37.4 (CH_3), 29.9 (CH_2), 29.0 (CH_2), 28.4 ($3CH_3$), 26.2 (CH_2), 25.1 (CH_2). ATR-FTIR (neat): 3347, 2936, 2863, 1695, 1519, 1352, 1173 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{12}H_{25}NO_5S[M]^+$: 296.1526, found: 296.1517.



4.20b

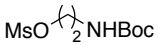
4-((*tert*-butoxycarbonyl)amino)butyl methanesulfonate 4.20b: General procedure IX was followed by using 1.0 g of *tert*-butyl (4-hydroxybutyl)carbamate (5.28 mmol), 0.96 mL of TEA (6.86 mmol), 0.49 mL of MsCl (6.34 mmol) and 26 mL of DCM. 1.21 g of **4.20b** (86%) was obtained as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.58 (br s, 1H), 4.24 (t, *J* = 6.3 Hz, 2H), 3.20–3.11 (m, 2H), 3.00 (s, 3H), 1.78 (p, *J* = 6.5 Hz, 2H), 1.60 (p, *J* = 6.5 Hz, 2H), 1.43 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.0 (C), 79.3 (C), 69.6 (CH_2), 39.7 (CH_2), 37.4 (CH_3), 28.4 ($3CH_3$), 26.4 (CH_2), 26.3 (CH_2). ATR-FTIR (neat): 3380, 2975, 2938, 1694, 1522, 1344, 1173 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{10}H_{21}NO_5S[M]^+$: 268.1213, found: 268.1205.



4.20c

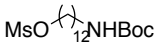
3-((*tert*-butoxycarbonyl)amino)propyl methanesulfonate 4.20c: General procedure IX was followed by using 1.0 g *tert*-butyl (3-hydroxypropyl)carbamate (5.7 mmol), 1.0 mL of TEA (7.4 mmol), 0.53 mL of MsCl (6.8 mmol) and 29 mL of DCM. 1.26 g of **4.20c** (87%) was obtained as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.67 (s, 1H), 4.29 (t, *J* = 6.0 Hz, 2H), 3.26 (q, *J* = 6.2 Hz, 2H), 3.03 (s, 3H), 1.94 (p, *J* = 6.2 Hz, 2H),

1.44 (s, 9H). δ 156.0 (C), 79.6 (C), 67.4 (CH_2), 37.4 (CH_3), 36.7 (CH_2), 28.4 ($3CH_3$), 27.4 (CH_2). This product is also commercially available. The spectral data matched those reported by Sarafiano and coworkers.[24]



4.20d

2-((*tert*-butoxycarbonyl)amino)ethyl methanesulfonate 4.20d: General procedure IX was followed by using 2.0 g of *tert*-butyl (2-hydroxyethyl)carbamate (12.4 mmol), 2.2 mL of TEA (16.1 mmol), 1.15 mL of MsCl (14.9 mmol) and 62 mL of DCM. 2.41 g **4.20d** (81%) was obtained as a viscous yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.98 (s, 1H), 4.26 (t, J = 5.2 Hz, 2H), 3.45 (q, J = 5.4 Hz, 2H), 3.02 (s, 3H), 1.42 (s, 9H). This compound is not stable and was used immediately. The spectral data matched those reported by Borbas and coworkers.[25]

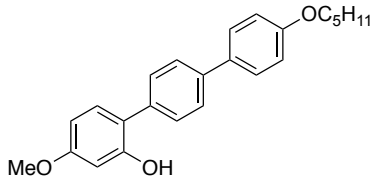


4.20e

12-((*tert*-butoxycarbonyl)amino)dodecyl methanesulfonate 4.20e: General procedure IX was followed by using 1.7 g *tert*-butyl (12-hydroxydodecyl)carbamate (5.64 mmol), 1.02 mL of TEA (7.33 mmol), 0.52 mL of MsCl (6.77 mmol) and 28 mL of DCM. 1.99 g of **4.20e** (93%) was obtained as a white solid, mp = 54–55 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.49 (br s, 1H), 4.22 (t, J = 6.6 Hz, 2H), 3.10 (q, J = 6.7 Hz, 2H), 3.00 (s, 3H), 1.73 (p, J = 6.5 Hz, 2H), 1.44 (s, 9H), 1.42–1.21 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.0 (C), 79.0 (C), 70.2 (CH_2), 40.6 (CH_2), 37.4 (CH_3), 30.1 (CH_2), 29.5 ($2CH_2$), 29.4 ($2CH_2$), 29.3 (CH_2), 29.1 (CH_2), 29.0 (CH_2), 28.4 ($3CH_3$), 26.8 (CH_2), 25.4 (CH_2). ATR-FTIR (neat): 3374, 2918, 2852, 1687, 1523, 1361, 1169 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{18}H_{37}NO_5S[M]^+$: 380.2465, found: 380.2454.

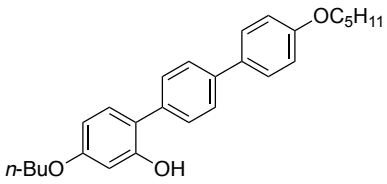
C. Preparation of the Rod-Like Ligand Backbone via Suzuki Cross-Coupling **4.24a–4.24d.**

General Procedure X: Into a 20 mL vial charged with a PTFE-coated magnetic stir bar were added 1.0 equivalent of arylbromide, 1.5 equivalent of arylboronic acid and 0.05 equivalent of palladium (II) acetate. The vial was sealed with septa and placed under vacuum and then it was filled with nitrogen. To this vial was added 0.5 M degassed water and 2.0 equivalent of degassed diisopropylamine. The reaction mixture was stirred for an hour at 100 ºC. The mixture was extracted with ethyl acetate and passed through a pad of celite. The residue was then dried over anhydrous sodium sulfate and removed under reduced pressure. Purification by column chromatography (100:0→80:20 hexanes: EtOAc) on SiO_2 afforded **4.24a–4.24d** as a solid.



4.24a

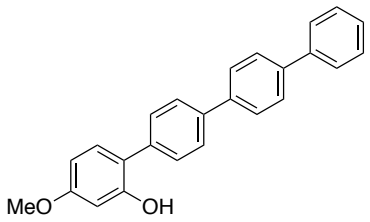
4-methoxy-4''-(pentyloxy)-[1,1':4',1''-terphenyl]-2-ol 4.24a: General procedure X was followed by using 0.50 g of 2-bromo-5-methoxyphenol **4.23a** (2.46 mmol), 1.05 g of (4'-(pentyloxy)-[1,1'-biphenyl]-4-yl)boronic acid (3.69 mmol), 28 mg of palladium (II) acetate (0.12 mmol), 4.9 mL water and 0.69 mL diisopropylamine (4.92 mmol). Purification by column chromatography (100:0→80:20 hexanes: EtOAc) on SiO_2 afforded **4.24a** (0.398 g, 45%) as a beige solid, mp = 168–169 ºC. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.6 Hz, 2H), 7.57 (d, *J* = 8.6 Hz, 2H), 7.49 (d, *J* = 8.6 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 1H), 7.00 (d, *J* = 8.6 Hz, 2H), 6.63–6.58 (m, 2H), 5.30 (s, 1H), 4.02 (t, *J* = 6.6 Hz, 2H), 3.85 (s, 3H), 1.83 (pen, *J* = 6.8 Hz, 2H), 1.49–1.38 (m, 4H), 0.96 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.2 (C), 161.6 (C), 156.1 (C), 142.7 (C), 137.8 (C), 135.4 (C), 133.4 (CH), 132.0 (2CH), 130.7 (2CH), 130.2 (2CH), 123.2 (C), 117.5 (2CH), 109.7 (CH), 104.0 (CH), 70.7 (OCH_2), 58.1 (OCH_3), 31.7 (CH_2), 30.9 (CH_2), 25.2 ($2CH_2$), 16.7 (CH_3); ATR-FTIR (neat): 3392, 2932, 2859, 1615, 1495, 1288, 1127 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{24}H_{26}O_3[M]^+$: 363.1955, found: 363.1956.



4.24b

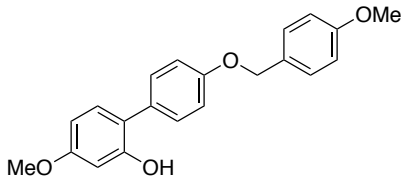
4-butoxy-4''-(pentyloxy)-[1,1':4',1''-terphenyl]-2-ol 4.24b: Into a 250 mL volumetric flask charged with a PTFE-coated magnetic stir bar were added 1.0 g of 3 butoxyphenol (6.0 mmol) in 150 mL dry DCM. Reaction flask was placed in ice bath and 1.01 g of *N*-bromosuccinimide (6.0 mmol) was added to the reaction mixture slowly in four portions over a period of two hours. Then, the reaction was brought to room temperature and stirred for another hour. Purification by column chromatography (100:0→85:15 hexanes: EtOAc) on SiO_2 afforded 2-bromo-5-butoxyphenol **4.23b** (1.2 g, 82%) as a white solid, mp = 32–33 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (d, *J* = 8.9 Hz, 1H), 6.59 (d, *J* = 2.8 Hz, 1H), 6.40 (dd, *J* = 8.9, 2.9 Hz, 1H), 5.49 (s, 1H), 3.91 (t, *J* = 6.5 Hz, 2H), 1.75 (pen, *J* = 7.9 Hz, 2H), 1.47 (sex, *J* = 7.6 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.1 (C), 152.9 (C), 131.9 (CH), 109.9 (CH), 102.2 (CH), 100.6 (C), 68.0 (OCH_2), 31.1 (CH_2), 19.2 (CH_2), 13.8 (CH_3); ATR-FTIR (neat): 3507, 2958, 2873, 1588, 1488, 1175 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{10}H_{13}BrO_2[M]^+$: 245.1172, found: 245.1172 General procedure II was followed by using 0.50 g of 2-bromo-5-butoxyphenol (2.04 mmol), 0.87 g of (4'-(pentyloxy)-[1,1'-biphenyl]-4-yl)boronic acid (3.06 mmol), 23 mg of palladium (II) acetate (0.12 mmol), 4.1 mL water and 0.58 mL diisopropylamine

(4.08 mmol). Purification by column chromatography (100:0→80:20 hexanes: EtOAc) on SiO_2 afforded **4.24b** (0.386 g, 47%) as a white solid, mp = 114–115 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, *J* = 8.6 Hz, 2H), 7.55 (d, *J* = 8.6 Hz, 2H), 7.48 (d, *J* = 8.6 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 1H), 6.99 (d, *J* = 8.6 Hz, 2H), 6.61–6.53 (m, 2H), 5.30 (s, 1H), 4.01 (t, *J* = 6.6 Hz, 2H), 3.99 (t, *J* = 6.6 Hz, 2H), 1.87–1.72 (m, 4H), 1.53–1.36 (m, 6H), 0.99 (t, *J* = 7.5 Hz, 3H), 0.95 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.1 (C), 158.9 (C), 153.4 (C), 140.0 (C), 135.2 (C), 132.8 (C), 130.7 (CH), 129.4 (2CH), 128.0 (2CH), 127.5 (2CH), 120.3 (C), 114.9 (2CH), 107.6 (CH), 101.8 (CH), 68.1 (OCH_2), 67.8 (OCH_2), 31.3 (CH_2), 29.0 (CH_2), 28.2 (CH_2), 22.5 (CH_2), 19.3 (CH_2), 14.0 (CH_3), 13.9 (CH_3); ATR-FTIR (neat): 3501, 2957, 2872, 1610, 1495, 1253, 1144 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{27}H_{32}O_3[M]^+$: 405.2424, found: 405.2412.



4.24c

4-methoxy-[1,1':4',1'':4'',1'''-quaterphenyl]-2-ol 4.24c: General procedure X was followed by using 0.50 g of 2-bromo-5-methoxyphenol **4.23a** (2.46 mmol), 1.01 g of [1,1':4',1"-terphenyl]-4-ylboronic acid (3.69 mmol), 28 mg of palladium (II) acetate (0.12 mmol), 4.9 mL water and 0.69 mL diisopropylamine (4.92 mmol). Purification by column chromatography (100:0→70:30 hexanes: EtOAc) on SiO_2 afforded **4.24c** (0.112 g, 13%) as a beige solid, mp = 226–227 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.71 (d, *J* = 1.1 Hz, 4H), 7.68–7.64 (m, 2H), 7.54 (d, *J* = 8.2 Hz, 2H), 7.47 (t, *J* = 6.4 Hz, 2H), 7.40–7.30 (m, 1H) 7.22 (d, *J* = 8.1 Hz, 1H), 6.63–6.53 (m, 2H), 5.29 (s, 1H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.6 (C), 153.4 (C), 140.6 (C), 140.3 (C), 139.8 (C), 139.4 (C), 136.0 (C), 130.8 (2CH), 129.5 (2CH), 128.8 (2CH), 127.9 (2CH), 127.6 (2CH), 127.4 (2CH), 127.0 (2CH), 120.4 (C), 107.1 (CH), 101.4 (CH), 55.4 (OCH_3); ATR-FTIR (neat): 3265, 1613, 1523, 1368, 1281, 1164, 1131 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{25}H_{20}O_2[M]^+$: 353.1536, found: 353.1531.



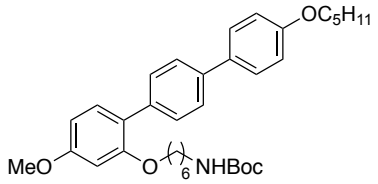
4.24d

4-methoxy-4'-((4-methoxybenzyl)oxy)-[1,1'-biphenyl]-2-ol 4.24d: General procedure X was followed by using 0.50 g of 2-bromo-5-methoxyphenol **4.23a** (2.46 mmol), 0.95 g of (4'-((4-methoxybenzyl)oxy)-[1,1'-biphenyl]-4-yl)boronic acid (3.69 mmol), 28 mg of palladium (II) acetate (0.12 mmol), 4.9 mL water and 0.69 mL disopropylamine (4.92

mmol). Purification by column chromatography (100:0→80:20 hexanes: EtOAc) on SiO_2 afforded **4.24d** (0.182 g, 22%) as a white solid, mp = 118–119 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.11 (d, *J* = 8.1 Hz, 1H), 7.07 (d, *J* = 8.1 Hz, 2H), 6.94 (d, *J* = 8.2 Hz, 2H), 6.57–6.52 (m, 2H), 5.23 (br s,1H), 5.03 (s, 2H), 3.83 (s, 3H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.3 (C), 159.5 (C), 158.4 (C), 153.4 (C), 130.7 (C), 130.3 (CH), 130.2 (CH), 129.3 (CH),129.2 (C), 129.1 (CH), 128.8 (CH), 120.5 (C), 115.7 (2CH), 114.0 (2CH), 101.2 (CH), 101.1 (CH), 69.9 (OCH_2), 55.4 (OCH_3), 55.3 (OCH_3); ATR-FTIR (neat): 3401, 2960, 2839, 1614, 1503, 11237, 1169 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{21}H_{20}O_4[M]^+$: 337.1434, found: 337.1423.

D. Preparation of *N*-Boc Protected Promesogenic Organic Ligands **4.25a–4.25j**.

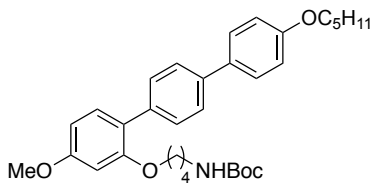
General Procedure XI: Into a 20 mL vial charged with a PTFE-coated magnetic stir bar were added 1.0 equivalent of **4.24a–4.24d**, 2.0 equivalent of **4.20a–4.20e**, 2.0 equivalent of potassium iodide in 0.075 M dry THF. 2.0 equivalent of 1.7 M KO*t*-Bu in THF was added to the vial drop wise. The reaction mixture was capped and stirred for 12 hours at 60 ºC. The solvent was removed under reduced pressure and the solid residue was extracted with water and DCM. The organic layer was collected and dried over anhydrous sodium sulfate and removed under reduced pressure. Purification by column chromatography (100:0→85:15 hexanes:ethyl acetae) on SiO_2 afforded **4.25a–4.25j** as a solid.



4.25a

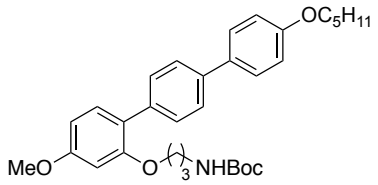
***tert*-butyl (6-((4-methoxy-4''-(pentyloxy)-[1,1':4',1''-terphenyl]-2-yl)oxy)hexyl)carbamate 4.25a:** General procedure XI was followed by using 210 mg of **4.24a** (0.579 mmol), 342 mg **4.20a** (1.16 mmol), 192 mg of KI (1.16 mmol), and 0.68 mL of KO*t*-Bu solution in 7.72 mL THF. Purification by column chromatography (100:0→85:15 hexanes: EtOAc) on SiO_2 afforded **4.25a** (266 mg, 82%) as a white solid, mp = 87–88 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61–7.55 (m, 6H), 7.30 (d, *J* = 8.2 Hz, 1H), 6.98 (d, *J* = 8.2 Hz, 2H), 6.61–6.53 (m, 2H), 4.46 (br s, 1H), 4.01 (t, *J* = 6.6 Hz, 2H), 3.96 (t, *J* = 6.4 Hz, 2H), 3.85 (s, 3H), 3.07 (q, *J* = 6.7 Hz, 2H), 1.83 (pen, *J* = 6.6 Hz, 2H), 1.75 (pen, *J* = 6.6 Hz, 2H), 1.52–1.45 (m, H), 1.44 (s, 9H), 1.40–1.24 (m, 6H), 0.96 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.2 (C), 158.6 (C), 157.0 (C), 156.0 (C), 138.7 (C), 136.8 (C), 133.3 (C), 131.1 (CH), 129.8 (2CH), 128.0 (2CH), 126.0 (2CH), 123.3 (C), 114.8 (2CH), 104.8 (CH), 100.0 (CH), 79.0 (C), 68.3 (OCH_2), 68.1 (OCH_2), 55.4 (OCH_3), 40.5 (CH_2), 30.0 (CH_2), 29.0 ($2CH_2$), 28.4 ($3CH_3$), 28.2 (CH_2), 26.4 (CH_2), 25.8 (CH_2), 22.5 (CH_2), 14.0 (CH_3); ATR-FTIR (neat): 3358, 2933, 2860,

1711, 1609, 1509, 1491, 1248, 1167 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{35}H_{47}NO_5[M]^+$: 562.3527, found: 562.3522.



4.25b

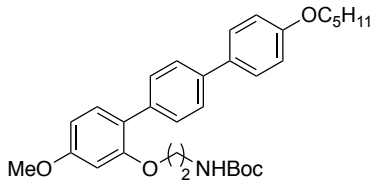
***tert*-butyl (4-((4-methoxy-4''-(pentyloxy)-[1,1':4',1''-terphenyl]-2-yl)oxy)butyl)carbamate 4.25b:** General procedure XI was followed by using 150 mg of **4.24a** (0.414 mmol), 221 mg **4.20b** (0.828 mmol), 137 mg of KI (0.828 mmol), and 0.49 mL of KO*t*-Bu solution in 5.52 mL THF. Purification by column chromatography (100:0→85:15 hexanes: EtOAc) on SiO_2 afforded **4.25b** (132 mg, 60%) as a white solid, mp = 98–99 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61–7.51 (m, 6H), 7.29 (d, *J* = 8.3 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 2H), 6.58 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.55 (d, *J* = 2.4 Hz, 1H), 4.46 (br s, 1H), 4.01 (t, *J* = 6.6 Hz, 2H), 3.98 (t, *J* = 6.6 Hz, 2H), 3.85 (s, 3H), 3.11 (q, *J* = 6.6 Hz, 2H), 1.89–1.71 (m, 4H), 1.59 (pen, *J* = 7.2 Hz, 2H), 1.51–1.42 (m, 4H), 1.40 (s, 9H) 0.95 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.2 (C), 158.6 (C), 156.8 (C), 155.9 (C), 138.8 (C), 136.7 (C), 133.3 (C), 131.2 (CH), 129.8 (CH), 129.7 (CH), 128.1 (CH), 128.0 (CH), 126.2 (CH), 126.1 (CH), 123.4 (C), 114.7 (2CH), 105.0 (CH), 100.1 (CH), 79.1 (C), 68.1 ($2OCH_2$), 55.5 (OCH_3), 40.1 (CH_2), 29.0 (CH_2), 28.4 ($3CH_3$), 28.2 (CH_2), 26.8 (CH_2), 26.4 (CH_2), 22.4 (CH_2), 14.0 (CH_3); ATR-FTIR (neat): 3308, 2932, 2869, 1673, 1609, 1249, 1172 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{33}H_{43}NO_5$ $[M]^+$: 534.3214, found: 534.3190.



4.25c

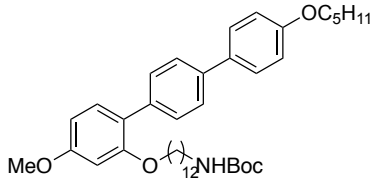
***tert*-butyl (3-((4-methoxy-4''-(pentyloxy)-[1,1':4',1''-terphenyl]-2-yl)oxy)propyl)carbamate 4.25c:** General procedure XI was followed by using 150 mg of **4.24a** (0.414 mmol), 210 mg **4.20c** (0.828 mmol), 137 mg of KI (0.828 mmol), and 0.49 mL of KO*t*-Bu solution in 5.52 mL THF. Purification by column chromatography (100:0→85:15 hexanes: EtOAc) on SiO_2 afforded **4.25c** (177 mg, 82%) as a white solid, mp = 105–106 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61–7.51 (m, 6H), 7.29 (d, *J* = 8.3 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 2H), 6.62–6.55 (m, 2H), 4.59 (br s, 1H), 4.01 (t, *J* = 6.6 Hz, 4H), 3.85 (s, 3H), 3.24 (q, *J* = 6.4 Hz, 2H), 1.93 (pen, *J* = 6.3 Hz, 2H), 1.82 (pen, *J* = 6.4 Hz, 2H), 1.51–1.40 (m, 4H), 1.39 (s, 9H) 0.95 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.2 (C), 158.6 (C), 156.7 (C), 155.9 (C), 138.9 (C), 136.6 (C), 133.2 (C), 131.2 (CH), 129.7 (2CH), 128.0 (2CH), 126.2 (2CH), 123.5 (C), 114.7 (2CH), 105.3

(CH), 100.2 (CH), 80.0 (C), 68.1 ($2OCH_2$), 55.4 (OCH_3), 38.0 (CH_2), 29.0 (CH_2), 28.4 ($3CH_3$), 28.4 (CH_2), 28.2 (CH_2), 22.5 (CH_2), 14.0 (CH_3); ATR-FTIR (neat): 3359, 2956, 2871, 1713, 1609, 1248, 1136 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{32}H_{41}NO_5[M]^+$: 520.3057, found: 520.3043.



4.25d

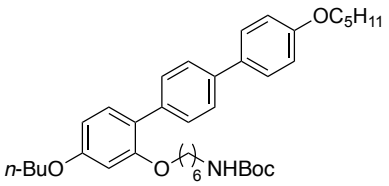
***tert*-butyl (2-((4-methoxy-4''-(pentyloxy)-[1,1':4',1''-terphenyl]-2-yl)oxy)ethyl)carbamate 4.25d:** General procedure XI was followed by using 150 mg of **4.24a** (0.414 mmol), 99.1 mg **4.20d** (0.828 mmol), 137 mg of KI (0.828 mmol), and 0.49 mL of KO*t*-Bu solution in 5.52 mL THF. Purification by column chromatography (100:0→85:15 hexanes: EtOAc) on SiO_2 afforded **4.25d** (69 mg, 33%) as an off-white solid, mp = 102–103 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63–7.50 (m, 6H), 7.30 (d, *J* = 8.4 Hz, 1H), 6.98 (d, *J* = 8.6 Hz, 2H), 6.61 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.56 (d, *J* = 2.4 Hz, 1H), 4.80 (br s, 1H), 4.05–3.97 (m, 4H), 3.85 (s, 3H), 3.45 (q, *J* = 5.4 Hz, 2H), 1.82 (pen, *J* = 8.0 Hz, 2H), 1.51–1.42 (m, 4H), 1.41 (s, 9H), 0.95 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.2 (C), 158.7 (C), 156.4 (C), 155.8 (C), 139.0 (C), 136.6 (C), 133.2 (C), 131.2 (CH), 129.7 (2CH), 128.0 (2CH), 126.3 (2CH), 123.6 (C), 114.8 (2CH), 105.9 (CH), 100.5 (CH), 79.5 (C), 68.1 ($2OCH_2$), 55.5 (OCH_3), 40.0 (CH_2), 29.0 (CH_2), 28.4 ($3CH_3$), 28.2 (CH_2), 22.5 (CH_2), 14.0 (CH_3); ATR-FTIR (neat): 3374, 2955, 2870, 1681, 1608, 1510, 1250, 1163 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{31}H_{39}NO_5[M]^+$: 506.2901, found: 506.2888.



4.25e

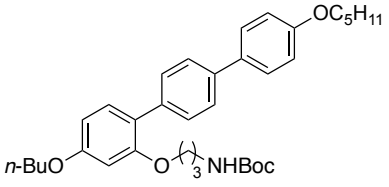
***tert*-butyl (12-((4-methoxy-4''-(pentyloxy)-[1,1':4',1''-terphenyl]-2-yl)oxy)dodecyl)carbamate 4.25e:** General procedure XI was followed by using 100 mg of **4.24a** (0.276 mmol), 209 mg **4.20e** (0.552 mmol), 92 mg of KI (0.552 mmol), and 0.32 mL of KO*t*-Bu solution in 3.68 mL THF. Purification by column chromatography (100:0→85:15 hexanes: EtOAc) on SiO_2 afforded **4.25e** (130 mg, 73%) as a white solid, mp: 80–81 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60–7.53 (m, 6H), 7.30 (d, *J* = 8.3 Hz, 1H), 6.98 (d, *J* = 8.6 Hz, 2H), 6.60 –6.54 (m, 2H), 4.49 (br s, 1H), 4.01 (t, *J* = 6.6 Hz, 2H), 3.96 (t, *J* = 6.5 Hz, 2H), 3.85 (s, 3H), 3.09 (q, *J* = 6.7 Hz, 2H), 1.82 (pen, *J* = 6.4 Hz, 2H), 1.75 (pen, *J* = 6.2 Hz, 2H), 1.52–1.45 (m, 4H), 1.44 (s, 9H), 1.43–1.20 (m, 18H),

0.95 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.2 (C), 158.6 (C), 157.1 (C), 156.0 (C), 138.7 (C), 136.8 (C), 133.4 (C), 131.1 (CH), 129.7 (2CH), 128.0 (2CH), 126.1 (2CH), 123.3 (C), 114.7 (2CH), 104.7 (CH), 99.9 (CH), 79.0 (C), 68.4 (OCH_2), 68.0 (OCH_2), 55.4 (OCH_3), 40.6 (CH_2), 30.1 (CH_2), 29.5 ($4CH_2$), 29.3 (CH_2), 29.2 (CH_2), 29.1 (CH_2), 29.0 (CH_2), 28.4 ($3CH_3$), 28.2 (CH_2), 26.8 (CH_2), 26.1 (CH_2), 22.5 (CH_2), 14.0 (CH_3); ATR-FTIR (neat): 3359, 2956, 2871, 1713, 1609, 1248, 1136 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{41}H_{59}NO_5[M]^+$: 646.4466, found: 646.4447.



4.25f

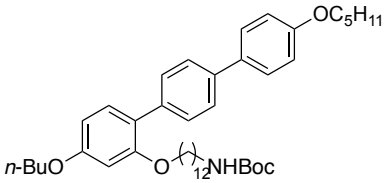
***tert*-butyl (6-((4-butoxy-4''-(pentyloxy)-[1,1':4',1''-terphenyl]-2-yl)oxy)hexyl)carbamate 4.25f:** General procedure XI was followed by using 150 mg of **4.24b** (0.371 mmol), 219 mg **4.20a** (0.742 mmol), 123 mg of KI (0.742 mmol), and 0.44 mL of KO*t*-Bu solution in 4.95 mL THF. Purification by column chromatography (100:0→85:15 hexanes: EtOAc) on SiO_2 afforded **4.25f** (162 mg, 72%) as a white solid, mp = 97–98 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61–7.51 (m, 6H), 7.27 (d, J = 8.3 Hz, 1H), 6.97 (d, J = 8.4 Hz, 2H), 6.60–6.53 (m, 2H), 4.40 (br s, 1H), 4.00 (t, J = 6.6 Hz, 4H), 3.95 (t, J = 6.4 Hz, 2H), 3.11–3.00 (m, 2H), 1.88–1.66 (m, 6H), 1.55–1.45 (m, 6H), 1.44 (s, 9H), 1.36–1.27 (m, 6H), 0.99 (t, J = 7.4 Hz, 3H), 0.94 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7 (C), 158.6 (C), 156.9 (C), 156.0 (C), 138.6 (C), 136.9 (C), 133.4 (C), 131.0 (CH), 129.7 (2CH), 128.0 (2CH), 126.0 (2CH), 123.1 (C), 114.7 (2CH), 105.4 (CH), 100.4 (CH), 79.0 (C), 68.3 (OCH_2), 68.1 (OCH_2), 67.8 (OCH_2), 40.5 (CH_2), 31.4 (CH_2), 30.0 (CH_2), 29.0 ($2CH_2$), 28.4 ($3CH_3$), 28.2 (CH_2), 26.4 (CH_2), 25.8 (CH_2), 22.5 (CH_2), 19.3 (CH_2), 14.0 (CH_3), 13.9 (CH_3); ATR-FTIR (neat): 3358, 2927, 2857, 1716, 1608, 1492, 1178 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{38}H_{53}NO_5[M]^+$: 604.3997, found: 604.399.



4.25g

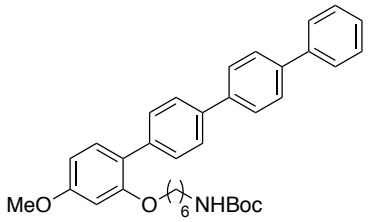
***tert*-butyl (3-((4-butoxy-4''-(pentyloxy)-[1,1':4',1''-terphenyl]-2-yl)oxy)propyl)carbamate 4.25g:** General procedure XI was followed by using 115 mg of **4.24b** (0.284 mmol), 219 mg **4.20c** (0.568 mmol), 94 mg of KI (0.568 mmol), and 0.33 mL of KO*t*-Bu solution in 3.79 mL THF. Purification by column chromatography (100:0→85:15 hexanes: EtOAc) on SiO_2 afforded **4.25g** (138 mg, 86%) as a white solid, mp = 80–81 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): mp = 105 °C. ^{1}H NMR (400 MHz,

$CDCl_3$): δ 7.62–7.50 (m, 6H), 7.28 (d, *J* = 8.3 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 2H), 6.61–6.55 (m, 2H), 4.60 (br s, 1H), 4.00 (t, *J* = 6.5 Hz, 6H), 3.24 (q, *J* = 6.4 Hz, 2H), 1.93 (pen, *J* = 6.3 Hz, 2H), 1.87–1.73 (m, 4H), 1.58–1.41 (m, 6H), 1.40 (s, 9H), 1.00 (t, *J* = 7.4 Hz, 3H), 0.95 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.8 (C), 158.6 (C), 156.7 (C), 156.0 (C), 138.8 (C), 136.7 (C), 133.3 (C), 131.1 (CH), 129.7 (2CH), 128.0 (2CH), 126.2 (2CH), 123.3 (C), 114.7 (2CH), 105.9 (CH), 100.7 (CH), 79.1 (C), 68.1 (CH_2), 67.8 (CH_2), 66.4 (CH_2), 38.0 (CH_2), 29.4 (CH_2), 29.0 (CH_2), 28.4 ($3CH_3$), 28.2 (CH_2), 27.8 (CH_2), 22.5 (CH_2), 19.3 (CH_2), 14.0 (CH_3), 13.9 (CH_3); ATR-FTIR (neat): 3376, 2930, 2871, 1693, 1491, 1294, 1181 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{35}H_{47}NO_5[M]^+$: 562.3527, found: 562.3512.



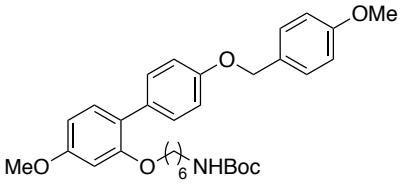
4.25h

***tert*-butyl (12-((4-butoxy-4''-(pentyloxy)-[1,1':4',1''-terphenyl]-2-yl)oxy)dodecyl)carbamate 4.25h:** General procedure XI was followed by using 90 mg of **4.24b** (0.222 mmol), 168 mg **4.20e** (0.444 mmol), 52 mg of KI (0.444 mmol), and 0.26 mL of KO*t*-Bu solution in 2.96 mL THF. Purification by column chromatography (100:0→85:15 hexanes: EtOAc) on SiO_2 afforded **4.25h** (109 mg, 72%) as a white solid, mp = 80–81 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64–7.53 (m, 6H), 7.30 (d, *J* = 8.3 Hz, 1H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.60–6.54 (m, 2H), 4.56 (br s, 1H), 4.01 (t, *J* = 6.5 Hz, 4H), 3.97 (t, *J* = 6.4 Hz, 2H), 3.11 (q, *J* = 6.7 Hz, 2H), 1.89–1.70 (m, 6H), 1.60–1.38 (m, 10H), 1.47 (s, 9H), 1.35–1.20 (m, 14H), 1.02 (t, *J* = 7.4 Hz, 3H), 0.97 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.8 (C), 158.6 (C), 157.1 (C), 156.0 (C), 138.6 (C), 136.9 (C), 133.4 (C), 131.0 (CH), 129.8 (2CH), 127.9 (2CH), 126.0 (2CH), 123.1 (C), 114.7 (2CH), 105.3 (CH), 100.4 (CH), 78.9 (C), 68.4 (CH_2), 68.1 (CH_2), 67.8 (CH_2), 40.6 (CH_2), 31.4 (CH_2), 30.5 (CH_2), 29.6 ($2CH_2$), 29.5 (CH_2), 29.3 (CH_2), 29.3 (CH_2), 29.1 (CH_2), 29.0 (CH_2), 28.5 ($3CH_3$), 28.3 ($2CH_2$), 26.8 (CH_2), 26.1 (CH_2), 22.5 (CH_2), 19.3 (CH_2), 14.1 (CH_3), 13.9 (CH_3); ATR-FTIR (neat): 3369, 2923, 2850, 1686, 1609, 1518, 1490, 1248, 1180 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{44}H_{65}NO_5[M]^+$: 688.4936, found: 688.4928.



4.25i

***tert*-butyl (6-((4-methoxy-[1,1':4',1'':4'',1'''-quaterphenyl]-2-yl)oxy)hexyl)carbamatemp 4.25i:** General procedure XI was followed by using 93 mg of **4.24c** (0.263 mmol), 156 mg **4.20a** (0.526 mmol), 87 mg of KI (0.526 mmol), and 0.31 mL of KO*t*-Bu solution in 3.5 mL THF. Purification by column chromatography (100:0→85:15 hexanes: EtOAc) on SiO_2 afforded **4.25i** (60 mg, 41%) as an off-white solid, mp = 130–131 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76–7.57 (m, 10H), 7.46 (t, *J* = 6.4 Hz, 2H), 7.39–7.33 (m, 1H), 7.32 (d, *J* = 8.2 Hz, 1H), 6.63–6.53 (m, 2H), 4.4 (s, 1H), 3.97 (t, *J* = 6.4 Hz, 2H), 3.86 (s, 3H), 3.15–3.01 (m, 2H), 1.80–1.71 (m, 2H), 1.48–1.45 (m, 2H), 1.42 (s, 9H), 1.37–1.30 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.3 (C), 157.0 (C), 140.7 (C), 139.9 (2C), 138.5 (C), 137.6 (C), 131.1 (CH), 129.9 (2CH), 128.8 (2CH), 127.5 (2CH), 127.3 (3CH), 127.0 (2CH), 126.4 (2CH), 123.2 (C), 104.8 (CH), 100.0 (CH), 79.0 (C), 68.3 (OCH_2), 55.4 (OCH_3), 40.5 (CH_2), 30.0 (CH_2), 29.0 (CH_2), 28.4 ($3CH_3$), 26.4 (CH_2), 25.8 (CH_2); ATR-FTIR (neat): 3365, 2927, 2857, 1677, 1609, 1515, 1143 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{36}H_{41}NO_4[M]^+$: 552.3108, found: 552.3101.



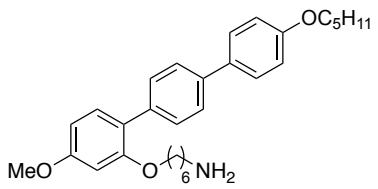
4.25j

***tert*-butyl (6-((4-methoxy-4'-((4-methoxybenzyl)oxy)-[1,1'-biphenyl]-2-yl)oxy)hexyl)carbamate 4.25j:** General procedure XI was followed by using 120 mg of **4.24d** (0.357 mmol), 263 mg **4.20a** (0.714 mmol), 119 mg of KI (0.714 mmol), and 0.42 mL of KO*t*-Bu solution in 4.8 mL THF. Purification by column chromatography (100:0→85:15 hexanes: EtOAc) on SiO_2 afforded **4.25j** (149 mg, 78%) as a white solid, mp = 71–72 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 8.1 Hz, 1H), 6.99 (d, *J* = 8.2 Hz, 2H), 6.93 (d, *J* = 8.2 Hz, 2H), 6.58–6.51 (m, 2H), 5.02 (s, 2H), 4.50 (br s, 1H), 3.93 (t, *J* = 6.3 Hz, 2H), 3.83 (s, 3H), 3.82 (s, 3H), 3.08 (q, *J* = 6.7 Hz, 2H), 1.72 (pen, *J* = 6.8 Hz, 2H), 1.50–1.45 (m, 2H), 1.44 (s, 9H), 1.43–1.25 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.8 (C), 159.4 (C), 157.5 (C), 156.8 (C), 156.0 (C), 131.1 (C), 130.9 (CH), 130.4 (2CH), 129.2 (2CH), 129.2 (C), 123.4 (C), 114.2 (2CH), 114.0 (2CH), 104.7 (CH), 100.0 (CH), 79.0 (C), 69.8 (OCH_2), 68.2 (OCH_2), 55.4 ($2OCH_3$), 40.5 (CH_2), 30.0 (CH_2), 29.0 (CH_2), 28.4 ($3CH_3$), 26.4 (CH_2), 25.8 (CH_2); ATR-FTIR (neat): 3412, 2999, 2837, 1697, 1607, 1515, 1173 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{32}H_{41}NO_6[M]^+$: 536.3007, found: 536.3002.

E. Preparation of the Promesogenic Organic Ligands **4.26a–4.26j**.

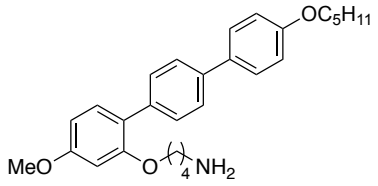
General Procedure XII: Into a 20 mL vial charged with a PTFE-coated magnetic stir bar were added 1.0 equivalent of **4.25** in 0.1 M dry DCM. The reaction mixture was placed in an ice bath, and then 15 equivalents of trifluoroacetic acid were added slowly. After 2 hours, the reaction mixture was quenched with saturated sodium bicarbonate and

extracted three times with DCM. The organic layer was passed through a pad of anhydrous sodium sulfate and removed under reduced pressure to afford **4.26** as a solid.



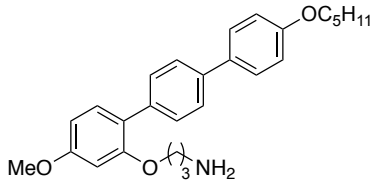
4.26a

6-((4-methoxy-4''-(pentyloxy)-[1,1':4',1''-terphenyl]-2-yl)oxy)hexan-1-amine 4.26a: General procedure XII was followed by using 260 mg of **4.25a** (0.463 mmol), 0.53 mL TFA and 4.6 mL DCM. **4.26a** (207 mg, 97%) was obtained as a white solid, mp = 125–126 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59–7.48 (m, 6H), 7.27 (d, *J* = 8.4 Hz, 1H), 6.95 (d, *J* = 8.8 Hz, 2H), 6.58–6.51 (m, 2H), 3.97 (t, *J* = 6.6 Hz, 2H), 3.91 (t, *J* = 6.4 Hz, 2H), 3.82 (s, 3H), 2.75 (t, *J* = 7.4 Hz, 2H), 1.80 (pen, *J* = 6.5 Hz, 2H), 1.71 (pen, *J* = 6.5 Hz, 2H), 1.57–1.24 (m, 12H), 0.93 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.2 (C), 158.6 (C), 156.9 (C), 138.6 (C), 136.8 (C), 133.2 (C), 131.1 (CH), 129.7 (2CH), 127.9 (2CH), 126.0 (2CH), 123.3 (C), 114.7 (2CH), 104.9 (CH), 99.9 (CH), 68.1 (OCH_2), 68.0 (OCH_2), 55.4 (OCH_3), 40.5 (CH_2), 29.5 (CH_2), 29.0 (CH_2), 28.8 (CH_2), 28.2 (CH_2), 26.0 (CH_2), 25.6 (CH_2), 22.5 (CH_2), 14.0 (CH_3); ATR-FTIR (neat): 2936, 2869, 1678, 1607, 1491, 1201 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{30}H_{39}NO_3[M]^+$: 462.3003, found: 462.3002.



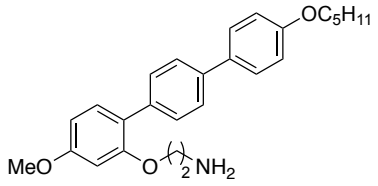
4.26b

4-((4-methoxy-4''-(pentyloxy)-[1,1':4',1''-terphenyl]-2-yl)oxy)butan-1-amine 4.26b: General procedure XII was followed by using 115 mg of **4.25b** (0.215 mmol), 0.25 mL TFA and 2.2 mL DCM. **4.26b** (83 mg, 93%) was obtained as a white solid, mp = 130–131 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58–7.48 (m, 6H), 7.27 (d, *J* = 8.4 Hz, 1H), 6.94 (d, *J* = 8.7 Hz, 2H), 6.56 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.51 (d, *J* = 3.9 Hz, 1H), 5.68 (br s, 2H), 3.97 (t, *J* = 6.6 Hz, 2H), 3.92 (t, *J* = 6.1 Hz, 2H), 3.82 (s, 3H), 2.75 (br s, 2H), 1.83–1.61 (m, 6H), 1.49–1.33 (m, 4H), 0.94 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.1 (C), 158.6 (C), 156.6 (C), 138.7 (C), 136.7 (C), 133.1 (C), 131.2 (CH), 129.7 (2CH), 127.9 (2CH), 126.0 (2CH), 123.3 (C), 114.7 (2CH), 105.1 (CH), 100.0 (CH), 68.0 (OCH_2), 67.7 (OCH_2), 55.4 (OCH_3), 39.8 (CH_2), 29.0 (CH_2), 28.2 (CH_2), 26.3 (CH_2), 26.2 (CH_2), 22.5 (CH_2), 14.0 (CH_3); ATR-FTIR (neat): 2935, 2871, 1607, 1490, 1253, 1201 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{28}H_{35}NO_3[M]^+$: 434.2690, found: 434.2672.



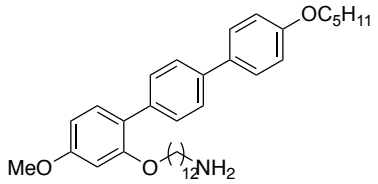
4.26c

3-((4-methoxy-4''-(pentyloxy)-[1,1':4',1''-terphenyl]-2-yl)oxy)propan-1-amine 4.26c: General procedure XII was followed by using 160 mg of **4.25c** (0.308 mmol), 0.35 mL TFA and 3.1 mL DCM. **4.26c** (125 mg, 97%) was obtained as a white solid, mp = 147–150 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 8.8 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.32 (br s, 2H), 7.21 (d, *J* = 8.4 Hz, 1H), 6.89 (d, *J* = 8.7 Hz, 2H), 6.60 (dd, *J* = 8.41, 2.33 Hz, 1H), 6.47 (d, *J* = 2.37, 1H), 3.96 (t, *J* = 5.6 Hz, 2H), 3.89 (t, *J* = 6.6 Hz, 2H), 3.84 (s, 3H), 2.65 (br s, 2H), 1.89 (pen, *J* = 5.7 Hz, 2H), 1.75 (pen, *J* = 5.8 Hz, 2H), 1.46–1.42 (m, 4H), 0.93 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.3 (C), 158.7 (C), 155.7 (C), 139.0 (C), 136.3 (C), 133.6 (C), 131.0 (CH), 129.8 (2CH), 127.9 (2CH), 126.4 (2CH), 123.2 (C), 114.8 (2CH), 105.6 (CH), 99.5 (CH), 68.1 (OCH_2), 67.3 (OCH_2), 55.4 (OCH_3), 38.6 (CH_2), 29.0 (CH_2), 28.2 (CH_2), 26.2 (CH_2), 22.5 (CH_2), 14.0 (CH_3); ATR-FTIR (neat): 2934, 2872, 1609, 1492, 1249, 1202, 1137 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{27}H_{33}NO_3[M]^+$: 420.2533, found: 420.2521.



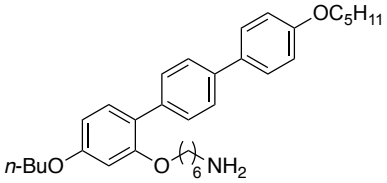
4.26d

2-((4-methoxy-4''-(pentyloxy)-[1,1':4',1''-terphenyl]-2-yl)oxy)ethan-1-amine 4.26d: General procedure XII was followed by using 60 mg of **4.25d** (0.119 mmol), 0.136 mL TFA and 1.2 mL DCM. **4.26d** (45 mg, 93%) was obtained as an off-white solid, mp = 147–150 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 8.1 Hz, 2H), 7.52 (d, *J* = 8.6 Hz, 2H), 7.45 (d, *J* = 8.6 Hz, 2H), 7.27 (d, *J* = 8.7 Hz, 1H), 6.93 (d, *J* = 8.6 Hz, 2H), 6.66 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.54 (d, *J* = 2.4 Hz, 1H), 4.07 (t, *J* = 4.9 Hz, 2H), 3.95 (t, *J* = 6.6 Hz, 2H), 3.82 (s, 3H), 3.13 (t, *J* = 4.8 Hz, 2H), 1.79 (pen, *J* = 6.8 Hz, 3H), 1.48–1.37 (m, 5H), 0.94 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, CD_2Cl_2): δ 160.3 (C), 158.9 (C), 155.3 (C), 139.0 (C), 132.6 (C), 132.5 (C) 131.4 (CH), 129.5 (2CH), 127.7 (2CH), 126.3 (2CH), 123.6 (C), 114.7 (2CH), 107.3 (CH), 101.2 (CH), 68.0 (OCH_2), 64.9 (OCH_2), 55.4 (OCH_3), 39.5 (CH_2), 29.0 (CH_2), 28.1 (CH_2), 22.5 (CH_2), 13.8 (CH_3); ATR-FTIR (neat): 2933, 2870, 1608, 1531, 1248, 1141 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{26}H_{31}NO_3[M]^+$: 420.2533, found: 420.2521.



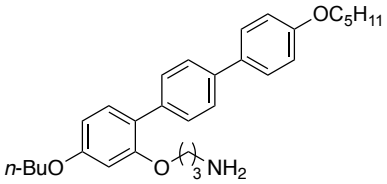
4.26e

12-((4-methoxy-4''-(pentyloxy)-[1,1':4',1''-terphenyl]-2-yl)oxy)dodecan-1-amine 4.26e: General procedure XII was followed by using 120 mg of **4.25e** (0.186 mmol), 0.213 mL TFA and 1.9 mL DCM. **4.26e** (95 mg, 94%) was obtained as a white solid, mp = 109–110 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (br s, 2H), 7.62–7.50 (m, 6H), 7.29 (d, *J* = 8.4 Hz, 1H), 6.96 (d, *J* = 8.4 Hz, 2H), 6.59–6.52 (m, 2H), 3.99 (t, *J* = 6.6 Hz, 2H), 3.94 (t, *J* = 6.5 Hz, 2H), 3.84 (s, 3H), 1.81 (pen, *J* = 7.2 Hz, 2H), 1.74 (pen, *J* = 7.2 Hz, 2H), 1.62 (pen, *J* = 7.4 Hz, 2H), 1.50–1.39 (m, 6H), 1.32–1.20 (m, 14H), 0.94 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.2 (C), 158.6 (C), 157.0 (C), 138.7 (C), 136.8 (C), 133.4 (C), 131.0 (CH), 129.7 (2CH), 127.9 (2CH), 126.0 (2CH), 123.2 (C), 114.7 (2CH), 104.7 (CH), 99.9 (CH), 68.4 (OCH_2), 68.1 (OCH_2), 55.4 (OCH_3), 40.0 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 29.1 (CH_2), 29.0 (CH_2), 28.9 (CH_2), 28.2 (CH_2), 27.5 (CH_2), 26.3 (CH_2), 26.1 (CH_2), 22.5 (CH_2), 14.0 (CH_3); ATR-FTIR (neat): 2925, 2855, 1607, 1490, 1202, 1139 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{36}H_{51}NO_3[M]^+$: 546.3942, found: 546.3924.



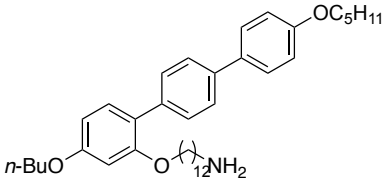
4.26f

6-((4-butoxy-4''-(pentyloxy)-[1,1':4',1''-terphenyl]-2-yl)oxy)hexan-1-amine 4.26f: General procedure XII was followed by using 150 mg of **4.25f** (0.248 mmol), 0.28 mL TFA and 2.5 mL DCM. **4.26f** (120 mg, 96%) was obtained as a white solid, mp = 100–101 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59–7.52 (m, 6H), 7.26 (d, *J* = 8.4 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 2H), 6.58–6.50 (m, 2H), 4.02–3.95 (m, 4H), 3.91 (t, *J* = 6.4 Hz, 2H), 2.76 (t, *J* = 7.4 Hz, 2H), 1.84–1.75 (m, 4H), 1.75–1.66 (m, 2H), 1.58–1.29 (m, 12H), 0.98 (t, *J* = 7.1 Hz, 3H), 0.93 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.9 (C), 158.6 (C), 156.9 (C), 139.0 (C), 136.8 (C), 132.2 (C), 131.1 (CH), 129.7 (2CH), 128.0 (2CH), 126.0 (2CH), 123.0 (C), 114.7 (2CH), 105.5 (CH), 100.4 (CH), 68.1 (OCH_2), 68.0 (OCH_2), 67.8 (OCH_2), 40.3 (CH_2), 31.4 (CH_2), 29.0 (CH_2), 28.9 (CH_2), 28.8 (CH_2), 28.2 (CH_2), 26.0 (CH_2), 25.6 (CH_2), 22.5 (CH_2), 19.3 (CH_2), 14.0 (CH_3), 13.9 (CH_3); ATR-FTIR (neat): 2956, 29354, 2871, 1677, 1609, 1530, 1202, 1182 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{30}H_{39}NO_3[M]^+$: 504.3472, found: 504.3481.



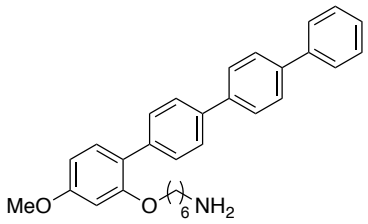
4.26g

3-((4-butoxy-4''-(pentyloxy)-[1,1':4',1''-terphenyl]-2-yl)oxy)propan-1-amine 4.26g: General procedure XII was followed by using 130 mg of **4.25g** (0.231 mmol), 0.26 mL TFA and 2.31 mL DCM. **4.26g** (102 mg, 96%) was obtained as a white solid, mp = 122–123 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60–7.51 (m, 4H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.3 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 2H), 6.59 (dd, *J* = 8.4, 2.3 Hz, 1H), 6.48 (d, *J* = 2.3 Hz, 1H), 4.03–3.95 (m, 4H), 3.90 (t, *J* = 6.6 Hz, 2H), 2.63 (t, *J* = 5.9 Hz, 2H), 1.92–1.85 (m, 2H), 1.85–1.70 (m, 4H), 1.56–1.25 (m, 8H), 1.00 (t, *J* = 7.4 Hz, 3H), 0.93 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.9 (C), 158.7 (C), 155.7(C), 139.0 (C), 136.4 (C), 132.6 (C), 131.0 (CH), 129.8 (2CH), 128.0 (2CH), 126.4 (2CH), 123.0 (C), 114.7 (2CH), 106.2 (CH), 99.8 (CH), 68.0 (OCH_2), 67.9 (OCH_2), 67.5 (OCH_2), 38.7 (CH_2), 31.3 (CH_2), 29.0 (CH_2), 28.2 (CH_2), 26.4 (CH_2), 22.5 (CH_2), 19.3 (CH_2), 14.0 (CH_3), 13.9 (CH_3); ATR-FTIR (neat): 2958, 2935, 2873, 1677, 1609, 1492, 1202 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{30}H_{39}NO_3[M]^+$: 462.3003, found: 462.3000.



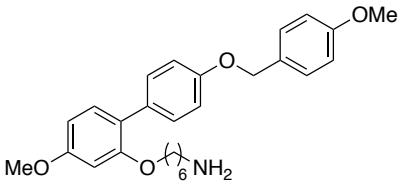
4.26h

12-((4-butoxy-4''-(pentyloxy)-[1,1':4',1''-terphenyl]-2-yl)oxy)dodecan-1-amine 4.26h: General procedure XII was followed by using 100 mg of **4.25h** (0.145 mmol), 0.17 mL TFA and 1.5 mL DCM. **4.26h** (80 mg, 94%) was obtained as a white solid, mp = 70–72 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62–7.53 (m, 6H), 7.29 (d, *J* = 8.4 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 2H), 6.59–6.53 (m, 2H), 5.16 (br s, 2H), 4.00 (t, *J* = 6.5 Hz, 4H), 3.96 (t, *J* = 6.5 Hz, 2H), 2.79 (t, *J* = 7.4 Hz, 2H), 1.86–1.70 (m, 6H), 1.58–1.35 (m, 10H), 1.34–1.20 (m, 14H), 1.00 (t, *J* = 7.4 Hz, 3H), 0.99 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.8 (C), 158.6 (C), 157.0 (C), 138.6 (C), 136.9 (C), 133.4 (C), 131.0 (CH), 129.7 (2CH), 127.9 (2CH), 126.0 (2CH), 123.0 (C), 114.7 (2CH), 105.3 (CH), 100.4 (CH), 68.5 (OCH_2), 68.1 (OCH_2), 67.8 (OCH_2), 40.9 (CH_2), 31.4 (CH_2), 30.3 (CH_2), 29.6 (CH_2), 29.5 ($2CH_2$), 29.3 (CH_2), 29.2 (CH_2), 29.1 (CH_2), 29.0 (CH_2), 28.2 ($2CH_2$), 26.6 (CH_2), 26.1 (CH_2), 22.5 (CH_2), 19.3 (CH_2), 14.0 (CH_3), 13.9 (CH_3); ATR-FTIR (neat): 2926, 2854, 1609, 1491, 1247, 1182 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{39}H_{57}NO_3[M]^+$: 588.4411, found: 588.4398.



4.26i

6-((4-methoxy-[1,1':4',1'':4'',1'''-quaterphenyl]-2-yl)oxy)hexan-1-amine 4.26i: General procedure XII was followed by using 52 mg of **4.25i** (0.148 mmol), 0.23 mL TFA (20 equiv) and 1.5 mL DCM. A mixture of hexanes:EtOAC (4:1) was added to the solid and the product was filtered to afford **4.26i** (20 mg, 47%) as a light yellow solid, mp = 125–126 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73–7.55 (m, 11H), 7.48–7.40 (m, 2H), 7.29 (d, *J* = 8.4 Hz, 1H), 6.57 (dd, *J* = 8.3, 2.4 Hz, 1H), 6.53 (d, *J* = 2.4 Hz, 1H), 3.92 (t, *J* = 6.4 Hz, 2H), 3.83 (s, 3H), 3.38 (br s, 2H), 2.74 (br, s, 2H), 1.72 (pen, *J* = 6.7 Hz, 2H), 1.59–1.45 (m, 2H), 1.40 (pen, *J* = 7.1 Hz, 2H), 1.31–1.27 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.3 (C), 156.9 (C), 156.9 (C), 140.7 (C), 139.9 (C), 138.4 (C), 137.6 (C), 131.2 (CH), 129.8 (2CH), 128.8 (2CH), 127.5 (2CH), 127.4 (CH), 127.3 (2CH), 127.0 (2CH), 126.4 (2CH), 123.1 (C), 104.9 (CH), 100.0 (CH), 68.1 (OCH_2), 55.4 (OCH_3), 28.8 ($2CH_2$), 26.2 (CH_2), 25.7 ($2CH_2$); ATR-FTIR (neat): 2956, 29354, 2871, 1677, 1609, 1530, 1202, 1182 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{31}H_{33}NO_2[M]^+$: 452.2584, found: 452.2585.

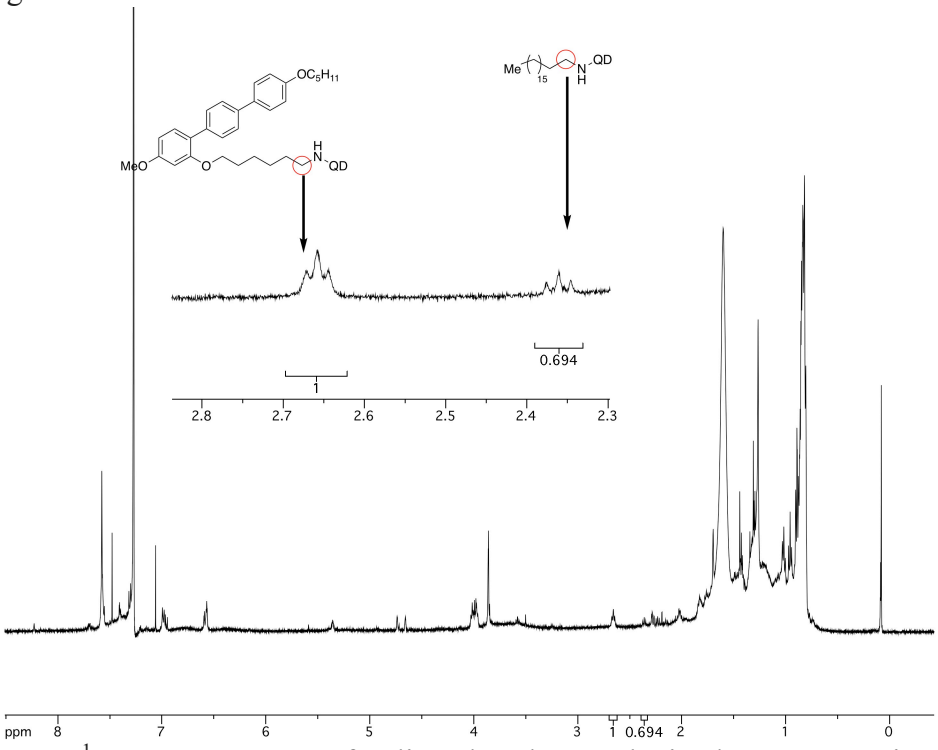


4.26j

6-((4-methoxy-4'-((4-methoxybenzyl)oxy)-[1,1'-biphenyl]-2-yl)oxy)hexan-1-amine 4.26j: General procedure XII was followed by using 124 mg of **4.25j** (0.231 mmol), 0.27 mL TFA and 2.3 mL DCM. (94 mg, 93%) of **4.26j** was obtained as a white solid, mp = 36–37 ºC. This ligand is prone to decomposion at room temperature and has to be stored in the fridge. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (d, *J* = 8.3 Hz, 2H), 7.14 (d, *J* = 8.3 Hz, 2H), 7.01 (s, 1H), 6.85–6.76 (m, 5H), 6.50 (s, 1H), 5.22 (s, 2H), 3.86 (br s, 2H), 3.81 (s, 3H), 3.76 (t, *J* = 8.6 Hz, 2H), 3.72 (s, 3H), 2.61 (t, *J* = 7.5 Hz, 2H), 1.63–1.58 (m, 2H), 1.40–1.35(m, 2H), 1.30–1.25(m, 2H), 1.20–1.13(m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.6 (C), 157.0 (C), 155.5 (C), 155.3 (C), 133.5 (C), 131.7 (CH), 130.8 (2CH), 129.7 (3CH), 123.5 (C), 122.6 (C), 115.2 (2CH), 113.6 (2CH), 98.0 (CH), 69.4 ($2OCH_2$), 55.6 (OCH_3), 55.2 (OCH_3), 40.9 (CH_2), 34.4 (CH_2), 31.3 (CH_2), 29.1 (CH_2), 26.1 (CH_2), 25.9 (CH_2); ATR-FTIR (neat): 2932, 2857, 1609, 1510, 1244, 1175 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{27}H_{33}NO_4[M]^+$: 436.2482, found: 436.2472.

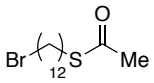
F. Ligand Exchange Process and Quantification by ^{1}H NMR Spectroscopy

For surface modification of quantum dots, we exchanged the ODA ligand with a mesogenic ligand (LC-QDs). This exchange involves 1 ml of quantum dot (CdSe/ZnS nanocrystal) solution with an octadecylamine ligand (ODA) attached and mixed with 1 mL of acetone. Free ligand was removed by centrifugation at 7000 rpm for 10 mins. The supernatant was discarded and then the last step was repeated again with the precipitate two times by adding 1 mL of acetone. Once washing is done, the precipitate was dissolved in 1 mL of chloroform and mixed with 1 mL solution of the synthesized ligand in chloroform (0.05 g/ml). ODA was then exchanged with the new ligand on the QD surface by heating at 40 ºC and stirring the solution at 200 rpm for 5 hours. The mixture was then removed from the heating stage and left to cool to room temperature. The free ligand was removed by washing it with 1 mL of ethyl acetate and centrifuged for 10 min, and then washed again twice by adding 1 mL of ethyl acetate. Finally, the precipitate was dissolved in 1 mL toluene. We quantified the ligand exchange using ^{1}H NMR (shown next page). The percent ratio of promesogenic ligand attached to the surface compared to remaining ODA is 60% to 40%.



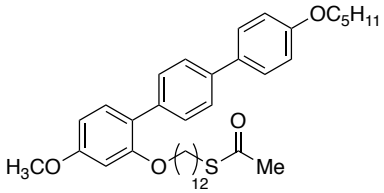
Scheme 20. ^{1}H NMR spectrum after ligand exchange obtained at 500 MHz in $CDCl_3$.

G. Individual steps procedures for thiolated ligand **4.31**



4.29

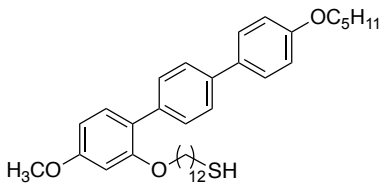
***S*-(12-bromododecyl) ethanethioate 4.29:** Into a round bottom flask charged with a PTFE-coated magnetic stir bar, 1.2562 g of potassium thioacetate **4.27** (11 mmol) were added. The flask was purged with nitrogen gas. Then, 10 mL of dry THF were added. Into a separate round bottom flask charged with a PTFE-coated magnetic stir bar, 7.2189 g of 1,12-dibromododecane **4.28** (22 mmol) were added. The flask was purged with nitrogen and then 10 mL of dry THF were added. Once the 1,12-dibromododecane was completely dissolved, it was transferred via syringe to the flask containing the potassium thioacetate solution and rinsed with additional 15 mL of THF. The mixture was allowed to reflux for 24 hours. The mixture was extracted with DCM, the organic residue was dried over anhydrous sodium sulfate, and the solvent was removed *in vacuo*. Purification by column chromatography (95:5 hexane:EtOAc) on SiO_2 afforded **4.29** (2.6675, 75%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.39 (t, J = 6.9 Hz, 2H), 2.85 (t, *J* = 7.4, 2H), 2.31(s, 3H), 1.84 (pen, *J* = 7.1, 2H), 1.55 (pen, *J* = 7.3, 2H), 1.48–1.18 (m, 16H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.0 (CO), 34.0 (CH_2), 32.8 (CH_3), 30.6 (CH_2), 29.5 ($2CH_2$), 29.5 (CH_2), 29.4 (CH_2), 29.4 (CH_2), 29.1 (CH_2), 29.1 (CH_2), 28.8 (CH_2), 28.7 (CH_2), 28.2 (CH_2).



4.30

***S*-(12-((4-methoxy-4''-(pentyloxy)-[1,1':4',1''-terphenyl]-2-yl)oxy)dodecyl) ethanethioate 4.30**: Into a 20 mL vial charged with a PTFE-coated magnetic stir bar were added 89.8 mg of 4-methoxy-4''-(pentyloxy)-[1,1':4',1''-terphenyl]-2-ol (0.248 mmol) **4.24a** and 96.2 mg of *S*-(12-bromododecyl) ethanethioate **4.29** (0.297 mmol) in 3.3 mL of 2-butanone (0.075 M). 68.6 mg of K_2CO_3 (0.496 mmol) and 82.3 mg of KI (0.496 mmol) were added to the reaction mixture. Reaction was heated to 75 ºC and stopped after 25 hours. The solvent was evaporated and the crude mixture was extracted with water and EtOAc. The organic layer was passed through a pad of anhydrous sodium sulfate and removed under reduced pressure. Purification by column chromatography (100:0→95:5 hexanes: EtOAc) on SiO_2 afforded **4.30** (111.6 mg, 75%) white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60–7.55 (m, 6H), 7.30 (dd, *J* = 7.6, 1.1 Hz, 1 H), 6.99–6.96 (m, 2H), 6.59–6.56 (m, 2H), 4.00 (t, *J* = 6.6 Hz, 2H), 3.96 (t, *J* = 6.4 Hz, 2H), 3.85 (s, 3H), 2.85 (t, *J* = 7.2 Hz, 2H), 2.32 (s, 3H), 1.82 (pen, *J* = 6.8, 2H), 1.75 (pen, *J* = 6.8 Hz, 2H), 1.56–1.24, (m, 22H), 0.95 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.2 (CO), 160.3 (C), 158.7 (C), 157.2 (C), 138.8 (C), 136.9 (C), 133.6 (C), 131.2 (CH), 129.9 (2CH), 128.1 (2CH), 126.2 (2CH), 123.5 (C), 114.9 (2CH), 104.8 (CH), 100.1 (CH), 68.6 (OCH_2), 68.2 (OCH_2), 55.6 (OCH_3), 30.8 (CH_3), 29.7 ($2CH_2$), 29.7 (CH_2S), 29.6 (CH_2), 29.6 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 29.2 (CH_2), 29.0 (CH_2), 28.4

(CH_2), 26.2 (CH_2), 22.6 (CH_2), 14.2 (CH_3). ATR-FTIR (neat): 2921, 2853, 1695, 1609, 1491 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{38}H_{53}O_4S$ $[M]^+$: 605.3637, found: 605.3659.



4.31

12-((4-methoxy-4''-(pentyloxy)-[1,1':4',1''-terphenyl]-2-yl)oxy)dodecane-1-thiol 4.31: Into a 20 mL vial charged with a PTFE-coated magnetic stir bar were added 183.9 mg of *S*-(12-((4-methoxy-4"-(pentyloxy)-[1,1':4',1"-terphenyl]-2-yl)oxy)dodecyl) ethanethioate **4.30** (0.304 mmol) in 12.2 mL of EtOH. 121.6 mg of NaOH (3.04 mmol) in 2.34 mL of water was added to the reaction mixture. Reaction was heated to 70 ºC overnight. The solvent was evaporated and the crude mixture was extracted with DCM. The organic layer was passed through a pad of anhydrous sodium sulfate and removed under reduced pressure to afford **4.31** (167.5 mg, 98%) as a beige solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62–7.49 (m, 6H), 7.30 (d, *J* = 8.4 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.63–6.53 (m, 2H), 4.00 (t, *J* = 6.6 Hz, 2H), 3.96 (t, *J* = 6.5 Hz, 2H), 3.85 (s, 3H), 2.66 (t, *J* = 7.4 Hz, 2H), 1.82 (pen, *J* = 7.1, 2H), 1.74 (pen, *J* = 7.0, 2H), 1.65 (pen, *J* = 7.3, 2H), 1.51–1.20 (m, 21H), 0.95 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.2 (C), 158.6 (C), 157.1 (C), 138.7 (C), 136.8 (C), 133.4 (C), 131.1 (CH), 129.8 (2CH), 128.0 (2CH), 126.1 (2CH), 123.3 (C), 114.7 (2CH), 104.7 (CH), 99.9 (CH), 68.4 (OCH_2), 68.1 (OCH_2), 55.4 (OCH_3), 39.2 (CH_2), 29.59 (CH_2), 29.57 (CH_2), 29.54 (CH_2), 29.52 (CH_2), 29.3 ($2CH_2$), 29.2 (CH_2), 29.1 (CH_2), 29.0 (CH_2), 28.5 (CH_2), 28.2 (CH_2), 26.1 (CH_2), 22.5 (CH_2) 14.1 (CH_3); ATR-FTIR (neat): 2959, 2852, 1609, 1490, 1276 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{36}H_{50}SO_3[M]^+$: 563.3553, found: 563.3531.

References

1) Hirst, Linda. Fundamentals of Soft Matter Science. *CRC Press*, **2012**, 1st edition.
2) Hines, D. A.; Kamat, P. V. Recent Advances in Quantum Dot Surface Chemistry. *ACS Appl. Mater. Interfaces*, **2014**, *6*, 3041–3057.
3) Nealon, G. L.; Greget, R.; Dominguez, C.; Nagy, T. Z.; Guillon, D.; Gallani, J-L.; Donnio, B. Beilstein *J. Org. Chem*. **2012**, *8*, 349.
4) Wöhrle, T.; Wurzbach, I.; Kirres, J.; Kostidou, A.; Kapernaum N.; Litterscheidt, J.; Haenle, J. C.; Staffeld, P.; Baro, A.; Giesselmann, F.; Laschat, S. *Chem. Rev.* **2016**, *116*(3), 1139–1241.
5) Yang, B.; Shen, G.; Huang, X.; Liu, R. *Molecules* **2019**, *24*(4), 698.
6) Lewandoski, W.; Wojcik, M.; Goreka, E.; *Chem. Phys. Chem.* **2014**, *15*, 1283.
7) Kanayama, N.; Tsutsumi, O.; Kanazawa, A.; Ikeda, T. *Chem. Comm*. **2001**, 2640.
8) Grzelak, J.; Zuk, M.; Tupikowska, M.; Lewandowski, W. *Nanomaterials* **2018**, *8*(3), 147.
9) Noda, Y.; Noro, S.-I.; Akutagawa, T.; Nakamura, T. *Scientific Reports*. **2014**, *4*, 3758.
10) Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D. J.; Whyman, R. *Chem Comm.* **1994**, 801.
11) Riahinasab, S. T.; Elbaradei, A.; Keshavarz, A.; Stokes, B. J.; Hirst, L. S. *Proc. SPIE* **2017**, *10125*, 1012503.
12) Wojcik, M.; Kolpaczynska, M.; Pociecha, D.; Mieczkowski, J.; Gorecka, E. *Soft Matter* **2010**, *6*, 5397.
13) Templeton, a. C.; Hostetler, M. J.; Kraft, C. T.; Murray, R. W. *J. Am. Chem. Soc.* **1998**, *120*, 1906.
14) Whitesides, G. M.; Grzybowski, B. Self-Assembly at all Scales. *Science* **2002**, *295*, 2418–2421.
15) Costa-Fernández, J. M.; Pereiro, R.; Sanz-Medel, A. The Use of Luminescent Quantum Dots for Optical Sensing. *Trends Anal. Chem.* **2006**, *25*, 207–218.
16) Jaiswal, J. K.; Mattoussi, H.; Mauro, J. M.; Simon, S. M. Long-Term Multiple Color Imaging of Live Cells Using Quantum Dot Bioconjugates. *Nature Biotechnology* **2003**, *21*, 47–51.
17) (a)Dabbousi, B. O.; Rodriguez-Viejo, J.; Mikulec, F. V.; Heine, J. R.; Mattoussi, H.; Ober, R.; Jensen, K. F.; Bawendi, G. (CdSe)ZnS Core–Shell Quantum Dots: Synthesis and Characterization of a Size Series of Highly Luminescent Nanocrystallites. *J. Phys. Chem. B*. **1997**, *101*, 9463–9475. (b) Brus, L. Quantum Crystalline and Nonlinear Optics. *Applied Physics A*. **1991**, *53*, 465–474. (c) Nozik, A. J. Quantum Dot Solar Cells. *Physica E* **2002**, *14*, 115–120.
(d) Dayal, S.; Kopidakis, N.; Olson, D. C.; Ginley, D. S.; Rumbles, G. *Nano Lett.* **2010**, *10*, 239–242.
18) Rodarte, A. L.; Nuno, Z. S.; Cao, B. H.; Pandolfi, R. J.; Quint, M. T.; Ghosh, S.; Hein, J. E.; Hirst, L. S. *ChemPhysChem.* **2014**, *15*, 1413.
19) Melton, C.; Riahinasab, S.; Keshavarz, A.; Stokes, B.; Hirst, L. Phase Transition-Driven Nanoparticle Assembly in Liquid Crystal Droplets. *Nanomaterials* **2018,** *8*, 146.
20) Quint, M. T.; Sarang, S.; Quint, D. A.; Keshavarz, A.; Stokes, B. J.; Subramaniam, A. B.; Huang, K. C.; Gopinathan, A.; Hirst, L. S.; Ghosh, S. Plasmon-Actuated Nano-Assembled Microshells. *Sci. Rep*. **2017**, *7*, 17788.

21) Riahinasab, S. T.; Keshavarz, A.; Melton, C. N.; Elbaradei, A.; Warren, G. I.; Selinger, R. L. B.; Stokes, B. J.; Hirst, L. S. Nanoparticle-Based Hollow Microstructures Formed by Two-Stage Nematic Nucleation and Phase Separation. *Nat. Commun*. **2019**, *10*, 894.
22) Keshavarz, A.; Riahinasab, S.; Hirst, L. S.; Stokes, B. J. *ACS Appl. Nano Mater*. **2019**, *2*, 2542.
23) Liu, C.; Zhang, Y.; Liu, N.; Qiu, J. *Green Chem.* **2012**, *14,* 2999.
24) Sarafianos, S.G.; Clark Jr, A. D, Tuske, S.; Squire, C. J.; Das, K. D.; Sheng, D.; Ilankumaran, P.; Ramesha, A. D.; Kroth, H.; Sayer, J. M.; Jerina, D. M.; Boyer, P. L.; Hughes, S. H.; Arnold, E. *J. Biol. Chem*. **2003**, *278*, 16280.
25) Borbas, K. E.; Bruce, J. I. *Org. Biomol. Chem*. **2007**, *5*, 2274.

CONCLUSION

By utilizing $Ph_3CB(C_6F_5)_4$ as an easily handled Brønsted acid precatalyst, we have developed methods that give access to a wide variety of polysubstituted indanes and polysubstituted tetralins. I have studied the regioselectivity outcomes in β-benzylalkenes and β-homobenzylalkenes systems in detail. In β-benzylalkenes system, six-membered ring formation is favored over five-memberd. We have shown that the steric hindrance dictates the arene substitution position for hydroarylation of styrenyl and isobutenyl substrates; whereas, propenyls alkylate at the most nucleophilic position. The regioselectivity in the propynyl system can also be altered by the presence of geminal dimethyl group in the benzylic position. Our studies contribute to an improved general understanding of both electronic and steric effects in EAS-type reactions;

In addition, I have designed and synthesized a new modular class of promesogenic organic ligands that direct CdSe/ZnS quantum dot nanoparticle self-assembly in liquid crystal host (5CB), using phase transition templating. Hollow micrometer-sized capsules are formed that resist thermal decomposition up to 350 °C and may therefore be useful for encapsulation applications where stability is required under high temperatures.