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Synthesis of 2,5-Diaryl-1,5-Dienes from Allylic Bromides Using Visible-Light Photoredox Catalysis

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Abstract

Visible-light photoreductive coupling of 2-arylallyl bromides in the presence of the photocatalyst $Ru(bpy)_3(PF_6)_2$, a Hantzsch ester, and *i*-Pr_2NEt gives 2,5-diaryl-1,5-dienes in high yield. This method avoids the use of stoichiometric metal reductants and is compatible with the presence of halogen, alkyl, electron-donating and electron-withdrawing substituents on the aromatic ring.

INTRODUCTION

The importance of visible-light photocatalysis in organic synthesis has increased substantially in recent years, as it is a sustainable and green method and offers unique opportunities for controlling selectivity.[1,2] In the area of free radical reactions, visible-light photocatalysis is allowing a variety of such processes to be accomplished without the use of stoichiometric adjuvants such as tin reagents. A variety of precursors such as halides,[1d,1f,3] selenosulfonates,[4] sulfonium[5] and sulfonyl[6] derivatives, diazonium salts,[7] carboxylic acids,[8] (*N*-acyloxy)phthalimides,[9] *N*-phthalimidoyl oxalates,[10] enamines,[11] and other α-amino substituted compounds[12] can be used to generate carbon radicals under these conditions. In a recent study of the reaction of tertiary radicals generated from *N*-(acyloxy)phthalimides under visible-light photoredox conditions with allylic halides as acceptors,[9b] we observed the formation of substantial amounts of 2,5-diphenylhexa-1,5-diene as a side product in attempted couplings with α-(bromomethyl)styrene. Inasmuch as the formation of 1,5-dienes by reductive coupling of allylic halides is typically accomplished using stoichiometric metal reductants (Wurtz couplings),[13] and no fully satisfactory method appears to be available for the synthesis of 2,5-diaryl-1,5-dienes,[14] we decided to explore the utility of visible-light photoredox catalysis for preparing such dienes. The outcome of these investigations, which led to a general, high-yielding method for preparing 2,5-diaryl-1,5-dienes by utilizing allylic bromides as radical precursors for the first time in photoredox catalysis, is reported herein.

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Supporting Information. Copies of ^1H and ^{13}C NMR spectra of compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

Notes

The authors declare no competing financial interest.

RESULTS AND DISCUSSION

Salient results of our initial optimization of the synthesis of 2,5-diphenylhexa-1,5-diene (**1a**) from α-(bromomethyl)styrene (**2a**) are summarized in Table 1. By simple omission of the *N*-(acyloxy)phthalimide radical precursor, diene **1a** was obtained in 78% yield under the conditions employed in our earlier cross-coupling studies (entry 1).[9b] Control experiments showed that the photocatalyst, $Ru(bpy)_3(PF_6)_2$, light, and Hünig's base (*i*-Pr_2NEt) are essential (entries 2–4). In the absence of the Hantzsch ester (diethyl 1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylate, **3**), diene **1a** was formed in low yield (24%), with 62% of bromide **2a** being recovered (entry 5). Subsequent optimization reactions revealed that the product yield and conversion was lower when the catalyst loading was decreased to 0.5 mol % and unchanged when increased from 1.0 to 1.5 mol% (entries 6 and 7). One equiv of Hantzsch ester **3** and 2 equiv of Hünig's base appeared optimal (entries 8–12). Dichloromethane was preferred over MeCN or THF as the reaction solvent, and increasing the starting concentration of bromide **2a** to 0.4 M was also beneficial (entries 13–16). The reaction was nearly complete after 6 h at room temperature with conversion not increasing further after 18 h (entries 17–19). Finally, combining the optimum reaction parameters led to full conversion of allylic bromide **2a** and clean formation of 2,5-diphenylhexa-1,5-diene (**1a**) in about 80% yield at scales up to 2 mmol (entry 20).

To investigate the scope of this synthesis of 2,5-diaryl-1,5-dienes, a broad selection of α-(bromomethyl)styrenes **2** was prepared from commercially available acetophenones by the two-step sequence illustrated in Scheme 1. Whereas the initial Wittig methylenation was easily accomplished,[15] the allylic bromination step required some optimization (see Supporting Information for details).[16]

With a reliable access to various substituted α-(bromomethyl)styrenes **2** in hand, the scope of the visible-light photoredox catalyzed formation of the 2,5-diaryl-1,5-dienes **1** was explored (Table 2). Substrates containing halogen substituents at the *meta* or *para* position gave diene products **1b**–**1d** in yields in excess of 80% (entries 2–4), comparable to the yield realized with the unsubstituted precursor (entry 1). A fluoro substituent at the *ortho* position prevented full conversion of the allylic bromide, resulting in a 68% yield of **1e** (entry 5). In this case, increasing the reaction time led to higher conversions of **2e**; however, the yields of **1e** remained in the same range. Similar results were observed in the synthesis of dienes **1f**–**1h** containing tolyl substituents, with *ortho* substitution leading to lower conversion and lower yield (entries 6–8). Both strong electron-donating (OMe) and electron-withdrawing (CN) substituents were tolerated, giving the corresponding diene products **1i**–**1m** in yields of 60–70% (entries 9–13). The presence of an ortho substituent again resulted in much lower conversion and yield of diene product **1k**. However in this case, increasing the catalyst loading to 1.5 mol% and the reaction time to 48 h, resulted in diene **1k** being formed in 67% yield (entry 11). Substrates containing nitro substituents were partially consumed under our standard reaction conditions, however no 1,5-diene products were formed.[17] Overall, this visible-light photoredox catalyzed Wurtz-type coupling protocol offers – in contrast to other literature-known methods[14] – a mild, catalytic and broadly tolerant access to 2,5-diarylhexa-1,5-dienes from easily accessible starting materials in one step and high yields.

The likely mechanism for the formation of 2,5-diaryl-1,5-dienes under the conditions we report is summarized in Scheme 2.[18] After visible-light photoexcitation of the catalyst $Ru(bpy)_3^{2+}$, the corresponding excited state $Ru(bpy)_3^{2+*}$ is quenched by a stoichiometric reductant (Hantzsch ester **3** or *i*-Pr_2NEt). Single-electron transfer from the resulting Ru(I)-species to the allylic bromide **2** generates allylic radical **A** with loss of bromide anion. Dimerization of **A** would yield the 2,5-diaryl-1,5-diene product **1**. Alternatively, addition of allylic radical **A** to allylic bromide **2**, followed by loss of bromide radical from **B**, or single-electron reduction of **B** followed by expulsion of bromide anion, would yield product **1**.[9b]

To explore whether product formation occurs preferentially via radical dimerization or an addition-fragmentation mechanism, we examined the reaction of the unsymmetrical allylic precursors (1-bromobut-2-en-2-yl)benzene (**4**) and (3-bromobut-1-en-2-yl)benzene (**5**) (Scheme 3). Both allylic bromides would generate the same delocalized radical, but should exhibit different reactivity towards allylic substitution, with addition of a radical to the exomethylene double bond of **5** being faster than addition to allylic isomer **4** having a trisubstituted double bond. As an addition-fragmentation mechanism would be inconsistent with the formation of diene **8** containing two disubstituted double bonds in equal amounts from both bromide precursors, dimerization of allylic radicals is undoubtedly the major pathway. The somewhat higher yield of diene **6** harboring two trisubstituted double bonds from allylic precursor **5** suggests that an addition-fragmentation pathway occurs to a limited extent, a conclusion that was exploited later in the reaction depicted in Scheme 4.

After investigating the behavior of various substituted α-(bromomethyl)styrene derivatives in visible-light photocatalyzed coupling, allylic bromides with substitution other than an aryl moiety in the 2-postion were tested (Table 3). Methyl 2-(bromomethyl)acrylate (**9**) gave diene product **10** in moderate yield. However, 2-bromoallyl bromide (**11**) delivered dibromodiene **12** in low yield only, whereas attempted coupling of 2-methylallyl bromide gave no 1,5-diene product. In all reactions summarized in Table 3, no starting material was recovered after a reaction time of 18 h.[19] Attempted extension of the method to 2-aryl-substituted allylic chlorides was briefly examined; however, only starting material was recovered in all cases. Even the more strongly reducing photocatalyst $Ir(ppy)_3$ did not convert α-(chloromethyl)styrene to diene product **1**.

In order to access non-symmetrically substituted 2,5-diaryl-1,5-dienes, reaction conditions that would favor the addition-fragmentation pathway over radical dimerization were examined. The investigations were conducted with 4-chloro-α-(bromomethyl)styrene (**2b**) as the radical precursor and α-(chloromethyl)styrene (**14**) as the acceptor (Scheme 4). Employing **14** in excess (5 equiv) under otherwise identical standard conditions led to a 1:1 mixture of dienes **1b** and **15** (67% overall yield). However, the addition of the bromide precursor **2b** over 7 h using a syringe pump, which ensures a low concentration of allylic radicals in solution, and increasing the catalyst and reagent loading gave exclusively the unsymmetrical 2,5-diaryl-1,5-diene **15** in 60% yield.

CONCLUSION

2,5-Diaryl-1,5-hexadienes are formed in high yields at room temperature by reductive coupling of 2-arylallyl bromides in the presence 1 mol% of the commercially available photocatalyst $Ru(bpy)_3(PF_6)_2$, Hantzsch ester **3**, *i*-Pr_2NEt, and visible light. This attractive method avoids the use of stoichiometric metals and is believed to proceed largely via dimerization of photogenerated allylic radical intermediates. By slightly adapting the reaction conditions the addition-fragmentation pathway is favored that grants access to non-symmetrically substituted 2,5-diaryl-1,5-dienes.

EXPERIMENTAL SECTION

Materials and Methods

Unless stated otherwise, reactions were conducted in oven-dried glassware under an atmosphere of argon using anhydrous solvents (either freshly distilled or passed through activated alumina columns). For all photoredox-catalyzed coupling reactions, CH_2Cl_2 was sparged with argon for 5 minutes prior to use. All commercially obtained reagents were used as received. $Ru(bpy)_3(PF_6)_2$ and other photocatalysts were obtained from Sigma Aldrich. Methyl vinyl ketone (MVK), 2,3-dibromopropene (**11**) and TMS-Cl were distilled prior to use. The reaction components Hantzsch ester **3**[20], methyl 2-(bromomethyl)acrylate (**9**)[21] and α-(chloromethyl)styrene (**14**)[22] were prepared according to literature procedures. Usually one representative coupling reaction and yield of the product is described in detail; isolated yields reported in the Results and Discussion section are the average yields obtained from duplicate experiments. Reaction temperatures were controlled using a temperature modulator, and unless stated otherwise, reactions were performed at room temperature (rt, approximately 23 °C). Thin-layer chromatography (TLC) was conducted with silica gel 60 F254 pre-coated plates, (0.25 mm) and visualized by exposure to UV light (254 nm) or by anisaldehyde, ceric ammonium molybdate, iodine, and potassium permanganate staining. Silica gel 60 (particle size 0.040–0.063 mm) was used for flash column chromatography. ^1H NMR spectra were recorded at 500 or 600 MHz and are reported relative to deuterated solvent signals. Data for ^1H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. ^{13}C NMR spectra were recorded at 125 or 150 MHz. Data for ^{13}C NMR spectra are reported in terms of chemical shift. IR spectra were recorded on a FT-IR spectrometer and are reported in terms of frequency of absorption (cm^{-1}). High-resolution mass spectra were obtained with a LCT spectrometer. Blue LEDs (30 cm, 1 watt) were purchased from http://www.creativelightings.com (product code CL-FRS5050-12WP-12V) and powered by 8 AA batteries.

Preparation of α-Methylstyrene Derivatives via Wittig Olefination (Scheme 1)

General Procedure for the Wittig Olefination of Acetophenone Derivatives.[15]— A mixture of methyltriphenylphosphonium bromide (12.0–15.0 mmol, 4.32–5.40 g, 1.2–1.5 equiv) in dry THF (18.3 mL) under argon atmosphere was cooled to 0 °C in an ice bath. Then *n*-BuLi (2.5 M solution in hexanes, 12.0–15.0 mmol, 4.8–6.0 mL, 1.2–1.5 equiv) was added slowly over 10–15 minutes under stirring. After the resulting orange mixture was maintained at 0 °C for 1 hour, a solution of the acetophenone derivative (10.0 mmol, 1.0

equiv) in dry THF (7.0 mL) was added dropwise over 10–15 minutes at 0 °C. The reaction was allowed to warm up to room temperature, stirred overnight and finally quenched with a saturated aqueous solution of sodium chloride (75 mL). The resulting mixture was extracted with pentane (3 × 100 mL) or diethylether (3 × 100 mL). The combined organic phases were washed with a saturated aqueous solution of sodium chloride, dried over sodium sulfate and concentrated under reduced pressure. The crude residue was purified by silica gel chromatography.

4-Chloro-α-methylstyrene—Following the general procedure, title compound was synthesized from 4-chloroacetophenone (10.0 mmol, 1.55 g, 1.0 equiv), methyltriphenylphosphonium bromide (15.0 mmol, 5.40 g, 1.5 equiv) and *n*-BuLi (2.5 M solution in hexanes, 15.0 mmol, 6.0 mL, 1.5 equiv). Extraction with pentane and purification by silica gel chromatography (100% pentane) provided 4-chloro-α-methylstyrene (9.51 mmol, 1.45 g, 95%) as a colorless oil. R_f 0.77 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 (d, *J* = 8.7, 2H), 7.29 (d, *J* = 8.7, 2H), 5.36 (s, 1H), 5.11–5.09 (m, 1H), 2.14–2.13 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 142.3, 139.8, 133.3, 128.5, 126.9, 113.1, 21.9. Characterization data obtained matched those previously reported in literature.[22]

4-Bromo-α-methylstyrene—Following the general procedure, title compound was synthesized from 4-bromoacetophenone (10.0 mmol, 1.99 g, 1.0 equiv), methyltriphenylphosphonium bromide (15.0 mmol, 5.40 g, 1.5 equiv) and *n*-BuLi (2.5 M solution in hexanes, 15.0 mmol, 6.0 mL, 1.5 equiv). Extraction with pentane and purification by silica gel chromatography (100% pentane) provided 4-bromo-α-methylstyrene (8.82 mmol, 1.74 g, 88%) as a colorless oil. R_f 0.76 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 (d, *J* = 8.7, 2H), 7.33 (d, *J* = 8.6, 2H), 5.36 (s, 1H), 5.11–5.10 (m, 1H), 2.13–2.12 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 142.3, 140.2, 131.4, 127.3, 121.5, 113.2, 21.8. Characterization data obtained matched those previously reported in literature.[23,24]

3-Bromo-α-methylstyrene—Following the general procedure, title compound was synthesized from 3-bromoacetophenone (10.0 mmol, 1.99 g, 1.0 equiv), methyltriphenylphosphonium bromide (15.0 mmol, 5.40 g, 1.5 equiv) and *n*-BuLi (2.5 M solution in hexanes, 15.0 mmol, 6.0 mL, 1.5 equiv). Extraction with pentane and purification by silica gel chromatography (100% pentane) provided 3-bromo-α-methylstyrene (9.53 mmol, 1.88 g, 95%) as a colorless oil. R_f 0.78 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60 (t, *J* = 1.8, 1H), 7.41–7.38 (m, 2H), 7.20 (t, *J* = 7.9, 1H), 5.38 (s, 1H), 5.14–5.12 (m, 1H), 2.13 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.5, 142.1, 130.4, 129.9, 128.8, 124.2, 122.6, 113.8, 21.8. Characterization data obtained matched those previously reported in literature.[25]

2-Fluoro-α-methylstyrene—Following the general procedure, title compound was synthesized from 2-fluoroacetophenone (10.0 mmol, 1.38 g, 1.0 equiv), methyltriphenylphosphonium bromide (15.0 mmol, 5.40 g, 1.5 equiv) and *n*-BuLi (2.5 M solution in hexanes, 15.0 mmol, 6.0 mL, 1.5 equiv). Extraction with pentane and purification by silica gel chromatography (100% pentane) provided 2-fluoro-α-methylstyrene (8.84 mmol, 1.20 g, 88%) as a colorless oil. R_f 0.67 (100% hexanes); ^{1}H NMR (500 MHz,

$CDCl_3$): δ 7.31 (dt, *J* = 7.8, 0.6, 1H), 7.25–7.21 (m, 1H), 7.10 (t, *J* = 7.5, 1H), 7.04 (dd, *J* = 11.1, 8.3, 1H), 5.24–5.22 (m, 2H), 2.16–2.14 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.1 (d, *J* = 248.1), 140.3 (d, *J* = 0.8), 130.4 (d, *J* = 13.6), 129.5 (d, *J* = 4.4), 128.8 (d, *J* = 8.4), 124.0 (d, *J* = 3.5), 116.7 (d, *J* = 4.0), 116.0 (d, *J* = 23.0), 23.2 (d, *J* = 3.4); IR (thin film): 3083, 2974, 2924, 2855, 1633, 1573, 1489, 1448, 1216, 1092 cm^{-1}; HRMS-CI (*m/z*) $[M]^+$ calculated for C_9H_9F 136.0688, found 136.0687.

4-Methyl-α-methylstyrene—Following the general procedure, title compound was synthesized from 4-methylacetophenone (10.0 mmol, 1.34 g, 1.0 equiv), methyltriphenylphosphonium bromide (15.0 mmol, 5.40 g, 1.5 equiv) and *n*-BuLi (2.5 M solution in hexanes, 15.0 mmol, 6.0 mL, 1.5 equiv). Extraction with pentane and purification by silica gel chromatography (100% pentane) provided 4-methyl-α-methylstyrene (8.76 mmol, 1.16 g, 88%) as a colorless oil. R_f 0.69 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 (d, *J* = 8.2, 2H), 7.15 (d, *J* = 7.9, 2H), 5.35 (s, 1H), 5.05–5.04 (m, 1H), 2.36 (s, 3H), 2.16–2.14 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.2, 138.5, 137.3, 129.0, 125.5, 111.7, 22.0, 21.2. Characterization data obtained matched those previously reported in literature.[22,23]

3-Methyl-α-methylstyrene—Following the general procedure, title compound was synthesized from 3-methylacetophenone (10.0 mmol, 1.34 g, 1.0 equiv), methyltriphenylphosphonium bromide (15.0 mmol, 5.40 g, 1.5 equiv) and *n*-BuLi (2.5 M solution in hexanes, 15.0 mmol, 6.0 mL, 1.5 equiv). Extraction with pentane and purification by silica gel chromatography (100% pentane) provided 3-methyl-α-methylstyrene (8.62 mmol, 1.14 g, 86%) as a colorless oil. R_f 0.69 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 (d, *J* = 8.9, 2H), 7.24 (t, *J* = 7.4, 1H), 7.11 (d, *J* = 7.6, 1H), 5.38–5.37 (m, 1H), 5.09–5.08 (m, 1H), 2.39 (s, 3H), 2.18–2.16 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.5, 141.4, 137.8, 128.3, 128.2, 126.4, 122.8, 112.4, 22.0, 21.7. Characterization data obtained matched those previously reported in literature.[26]

2-Methyl-α-methylstyrene—Following the general procedure, title compound was synthesized from 2-methylacetophenone (10.0 mmol, 1.34 g, 1.0 equiv), methyltriphenylphosphonium bromide (15.0 mmol, 5.40 g, 1.5 equiv) and *n*-BuLi (2.5 M solution in hexanes, 15.0 mmol, 6.0 mL, 1.5 equiv). Extraction with pentane and purification by silica gel chromatography (100% pentane) provided 2-methyl-α-methylstyrene (8.28 mmol, 1.09 g, 83%) as a colorless oil. R_f 0.50 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.19–7.11 (m, 4H), 5.21–5.19 (m, 1H), 4.86–4.85 (m, 1H), 2.33 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.0, 144.0, 134.6, 130.2, 128.0, 126.9, 125.7, 114.8, 24.5, 20.0. Characterization data obtained matched those previously reported in literature.[22]

4-Methoxy-α-methylstyrene—Following the general procedure, title compound was synthesized from 4-methoxyacetophenone (10.0 mmol, 1.50 g, 1.0 equiv), methyltriphenylphosphonium bromide (15.0 mmol, 5.40 g, 1.5 equiv) and *n*-BuLi (2.5 M solution in hexanes, 15.0 mmol, 6.0 mL, 1.5 equiv). Extraction with pentane and purification by silica gel chromatography (100% pentane) provided 4-methoxy-α-methylstyrene (8.61 mmol, 1.28 g, 86%) as a colorless oil. R_f 0.21 (100% hexanes); ^{1}H NMR (500 MHz,

$CDCl_3$): δ 7.43 (d, *J* = 8.9, 2H), 6.88 (d, *J* = 8.9, 2H), 5.31–5.30 (m, 1H), 5.02–5.00 (m, 1H), 3.83 (s, 3H), 2.16–2.14 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.2, 142.7, 133.9, 126.7, 113.7, 110.8, 55.4, 22.1. Characterization data obtained matched those previously reported in literature.[23,24,26]

3-Methoxy-α-methylstyrene—Following the general procedure, title compound was synthesized from 3-methoxyacetophenone (10.0 mmol, 1.50 g, 1.0 equiv), methyltriphenylphosphonium bromide (15.0 mmol, 5.40 g, 1.5 equiv) and *n*-BuLi (2.5 M solution in hexanes, 15.0 mmol, 6.0 mL, 1.5 equiv). Extraction with pentane and purification by silica gel chromatography (100% pentane) provided 3-methoxy-α-methylstyrene (9.05 mmol, 1.34 g, 90%) as a colorless oil. R_f 0.25 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26 (t, *J* = 8.0, 1H), 7.08 (d, *J* = 7.9, 1H), 7.02–7.01 (m, 1H), 6.83 (dd, *J* = 8.2, 2.3, 1H), 5.38 (s, 1H), 5.11–5.09 (m, 1H), 3.83 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.6, 143.3, 142.9, 129.3, 118.2, 112.8, 112.7, 111.6, 55.4, 22.0. Characterization data obtained matched those previously reported in literature.[23,24]

2-Methoxy-α-methylstyrene—Following the general procedure, title compound was synthesized from 2-methoxyacetophenone (10.0 mmol, 1.50 g, 1.0 equiv), methyltriphenylphosphonium bromide (15.0 mmol, 5.40 g, 1.5 equiv) and *n*-BuLi (2.5 M solution in hexanes, 15.0 mmol, 6.0 mL, 1.5 equiv). Extraction with pentane and purification by silica gel chromatography (100% pentane) provided 2-methoxy-α-methylstyrene (7.98 mmol, 1.18 g, 80%) as a colorless oil. R_f 0.32 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28–7.24 (m, 1H), 7.21 (dd, *J* = 7.5, 1.8, 1H), 6.94 (dt, *J* = 7.4, 1.0, 1H), 6.90 (d, *J* = 8.2, 1H), 5.18–5.16 (m, 1H), 5.09–5.07 (m, 1H), 3.85 (s, 3H), 2.15–2.13 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.7, 144.5, 132.9, 129.5, 128.4, 120.6, 115.2, 110.9, 55.5, 23.3. Characterization data obtained matched those previously reported in literature.[24]

4-Cyano-α-methylstyrene—Following the general procedure, title compound was synthesized from 4-acetylbenzonitrile (10.0 mmol, 1.45 g, 1.0 equiv), methyltriphenylphosphonium bromide (15.0 mmol, 5.40 g, 1.5 equiv) and *n*-BuLi (2.5 M solution in hexanes, 15.0 mmol, 6.0 mL, 1.5 equiv). Extraction with diethyl ether and purification by silica gel chromatography (10% diethyl ether/hexanes) provided 4-cyano-α-methylstyrene (4.66 mmol, 667 mg, 47%) as a yellow oil. R_f 0.52 (10% ethyl acetate/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.5, 2H), 7.54 (d, *J* = 8.5, 2H), 5.47 (s, 1H), 5.25–5.24 (m, 1H), 2.16 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.8, 141.9, 132.2, 126.2, 119.1, 115.8, 111.0, 21.6. Characterization data obtained matched those previously reported in literature.[27,28]

3-Cyano-α-methylstyrene—Following the general procedure, title compound was synthesized from 3-acetylbenzonitrile (10.0 mmol, 1.45 g, 1.0 equiv), methyltriphenylphosphonium bromide (12.0 mmol, 4.32 g, 1.2 equiv) and *n*-BuLi (2.5 M solution in hexanes, 12.0 mmol, 4.8 mL, 1.2 equiv). Extraction with diethyl ether and purification by silica gel chromatography (10% diethyl ether/hexanes) provided 3-cyano-α-methylstyrene (6.47 mmol, 926 mg, 65%) as a colorless oil. R_f 0.55 (10% ethyl acetate/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72 (s, 1H), 7.68 (dd, *J* = 8.0, 1.0, 1H), 7.55 (dd,

J = 8.0, 1.0, 1H), 7.43 (t, *J* = 7.8, 1H), 5.42 (s, 1H), 5.21–5.19 (m, 1H), 2.16–2.14 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 142.5, 141.4, 130.9, 129.9, 129.3, 129.2, 119.1, 114.8, 112.6, 21.6; IR (thin film): 3089, 2976, 2947, 2921, 2359, 2230, 1630, 1596, 1575, 1481, 1441, 1377, 1192 cm^{-1}; HRMS-ESI (*m/z*) $[M + Na]^+$ calculated for $C_{10}H_9NNa$ 166.0633, found 166.0641.

But-1-en-2-ylbenzene—Following the general procedure, title compound was synthesized from propiophenone (10.0 mmol, 1.34 g, 1.0 equiv), methyltriphenylphosphonium bromide (15.0 mmol, 5.40 g, 1.5 equiv) and *n*-BuLi (2.5 M solution in hexanes, 15.0 mmol, 6.0 mL, 1.5 equiv). Extraction with pentane and purification by silica gel chromatography (100% pentane) provided but-1-en-2-ylbenzene (8.06 mmol, 1.07 g, 81%) as a colorless oil. R_f 0.75 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42 (d, *J* = 7.6, 2H), 7.33 (t, *J* = 7.5, 2H), 7.26 (t, *J* = 7.3, 1H), 5.28 (s, 1H), 5.07–5.05 (m, 1H), 2.52 (q, *J* = 7.4, 2H), 1.11 (t, *J* = 7.4, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.2, 141.7, 128.4, 127.4, 126.1, 111.1, 28.2, 13.1. Characterization data obtained matched those previously reported in literature.[29]

But-2-en-2-ylbenzene—Following the general procedure, title compound was synthesized from acetophenone (10.0 mmol, 1.20 g, 1.0 equiv), ethyltriphenylphosphonium bromide (15.0 mmol, 5.57 g, 1.5 equiv) and *n*-BuLi (2.5 M solution in hexanes, 15.0 mmol, 6.0 mL, 1.5 equiv). Extraction with pentane and purification by silica gel chromatography (100% pentane) provided a 1.7:1 mixture of *E*/*Z* isomers of but-2-en-2-ylbenzene (7.30 mmol, 966 mg, 73%) as a colorless oil. R_f 0.72 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$, mixture of isomers = 0.6:0.4): δ 7.40–7.29 (m, 3.4H), 7.25–7.20 (m, 1.6H), 5.88 (dq, *J* = 6.9, 1.1, 0.6H), 5.58 (dq, *J* = 6.8, 1.1, 0.4H), 2.05 (s, 3.0H), 1.82 (d, *J* = 6.9, 1.8H), 1.63–1.59 (m, 1.2H); ^{13}C NMR (125 MHz, $CDCl_3$, mixture of isomers): δ 144.2, 142.0, 136.9, 135.6, 128.3, 128.2, 128.1, 126.6, 126.5, 125.7, 122.6, 121.7, 25.5, 15.6, 15.0, 14.5. Characterization data obtained matched those previously reported in literature.[30]

Preparation of α-(Bromomethyl)styrene Derivatives via Allylic Bromination (Scheme 1)

General Procedure for the Allylic Bromination of α-Methylstyrene Derivatives.[16]—

To a mixture of the α-methylstyrene derivative (0.50 mmol, 1.0 equiv) and TMS-Cl (0.50–50 μmol, 1–6 μL, 0.1–10 mol%) in dry CH_2Cl_2/THF (4:1, 1.5 mL) under argon atmosphere, NBS (0.60 mmol, 106 mg, 1.2 equiv) and $Yb(OTf)_3$ (0.50–50 μmol, 0.3–31 mg, 0.1–10 mol%) were added in one portion. After stirring for one hour, the mixture was concentrated under reduced pressure. The resulting residue was filtered three times with pentane or diethyl ether and the combined filtrates were concentrated under reduced pressure. The crude product mixture was then purified by silica gel chromatography.

α-(Bromomethyl)styrene (2a)—Following the general procedure, **2a** was synthesized from commercially available α-methylstyrene (0.50 mmol, 65 μL, 1.0 equiv), TMS-Cl (5.0 μmol, 1 μL, 1 mol%), NBS (0.60 mmol, 106 mg, 1.2 equiv) and $Yb(OTf)_3$ (5.0 μmol, 3 mg, 1 mol%). Filtration with pentane and purification by silica gel chromatography (100% pentane) provided **2a** (0.22 mmol, 43 mg, 43%) as a colorless oil. R_f 0.41 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52–7.49 (m, 2H), 7.41–7.37 (m, 2H), 7.36–7.32

(m, 1H), 5.57 (s, 1H), 5.50 (s, 1H), 4.40 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.4, 137.7, 128.7, 128.4, 126.2, 117.2, 34.4. Characterization data obtained for **2a** matched those previously reported in literature.[22]

4-Chloro-α-(bromomethyl)styrene (2b)—Following the general procedure, **2b** was synthesized from 4-chloro-α-methylstyrene (0.50 mmol, 76 mg, 1.0 equiv), TMS-Cl (5.0 μmol, 1 μL, 1 mol%), NBS (0.60 mmol, 106 mg, 1.2 equiv) and $Yb(OTf)_3$ (5.0 μmol, 3 mg, 1 mol%). Filtration with pentane and purification by silica gel chromatography (100% pentane) provided **2b** (0.26 mmol, 60 mg, 52%) as a colorless oil. R_f 0.40 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43 (d, *J* = 8.8, 2H), 7.35 (d, *J* = 8.8, 2H), 5.54 (s, 1H), 5.50 (s, 1H), 4.35 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.3, 136.1, 134.3, 128.8, 127.6, 117.8, 34.0. Characterization data obtained for **2b** matched those previously reported in literature.[22]

4-Bromo-α-(bromomethyl)styrene (2c)—Following the general procedure, **2c** was synthesized from 4-bromo-α-methylstyrene (0.50 mmol, 94 mg, 1.0 equiv), TMS-Cl (5.0 μmol, 1 μL, 1 mol%), NBS (0.60 mmol, 106 mg, 1.2 equiv) and $Yb(OTf)_3$ (5.0 μmol, 3 mg, 1 mol%). Filtration with pentane and purification by silica gel chromatography (100% pentane) provided **2c** (0.25 mmol, 69 mg, 50%) as a colorless oil. R_f 0.41 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50 (d, *J* = 8.5, 2H), 7.36 (d, *J* = 8.6, 2H), 5.55 (s, 1H), 5.51 (s, 1H), 4.35 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.4, 136.6, 131.8, 127.9, 122.5, 117.8, 33.9; IR (thin film): 2359, 2340, 1682, 1588, 1490, 1394, 1276, 1211, 1072, 1008 cm^{-1}; HRMS-CI (*m/z*) $[M]^+$ calculated for $C_9H_8Br_2$ 273.8993, found 273.8994.

3-Bromo-α-(bromomethyl)styrene (2d)—Following the general procedure, **2d** was synthesized from 3-bromo-α-methylstyrene (0.50 mmol, 94 mg, 1.0 equiv), TMS-Cl (25 μmol, 3 μL, 5 mol%), NBS (0.60 mmol, 106 mg, 1.2 equiv) and $Yb(OTf)_3$ (25 μmol, 16 mg, 5 mol%). Filtration with pentane and purification by silica gel chromatography (100% pentane) provided **2d** (0.29 mmol, 81 mg, 59%) as a colorless oil. R_f 0.42 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64–7.62 (m, 1H), 7.48–7.45 (m, 1H), 7.42–7.39 (m, 1H), 7.27–7.23 (m, 1H), 5.55 (s, 1H), 5.26 (s, 1H), 4.34 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.3, 139.9, 131.4, 130.2, 129.4, 124.9, 122.9, 118.5, 33.8; IR (thin film): 3062, 2969, 2359, 1623, 1591, 1556, 1476, 1395, 1297, 1210, 1070 cm^{-1}; HRMS-CI (*m/z*) $[M]^+$ calculated for $C_9H_8Br_2$ 273.8993, found 273.8984.

2-Fluoro-α-(bromomethyl)styrene (2e)—Following the general procedure, **2e** was synthesized from 2-fluoro-α-methylstyrene (0.50 mmol, 76 mg, 1.0 equiv), TMS-Cl (25 μmol, 3 μL, 5 mol%), NBS (0.60 mmol, 106 mg, 1.2 equiv) and $Yb(OTf)_3$ (25 μmol, 16 mg, 5 mol%). Filtration with pentane and purification by silica gel chromatography (100% pentane) provided **2e** (0.24 mmol, 51 mg, 48%) as a colorless oil. R_f 0.46 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37–7.29 (m, 2H), 7.15 (dt, *J* = 7.5, 0.8, 1H), 7.10–7.05 (m, 1H), 5.61 (s, 1H), 5.42 (s, 1H), 4.39 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.0 (d, *J* = 247.9), 141.4, 130.6 (d, *J* = 4.0), 130.0 (d, *J* = 8.5), 126.6 (d, *J* = 13.8), 124.3 (d, *J* = 3.6), 120.8 (d, *J* = 2.7), 116.0 (d, *J* = 22.6), 35.5 (d, *J* = 5.3). Characterization data obtained for **2e** matched those previously reported in literature.[31]

4-Methyl-α-(bromomethyl)styrene (2f)—Following the general procedure, **2f** was synthesized from 4-methyl-α-methylstyrene (0.50 mmol, 76 mg, 1.0 equiv), TMS-Cl (0.50 μmol, 1 μL, 0.1 mol%), NBS (0.60 mmol, 106 mg, 1.2 equiv) and $Yb(OTf)_3$ (0.50μmol, 0.3 mg, 0.1 mol%). Filtration with pentane and purification by silica gel chromatography (100% pentane) provided **2f** (0.12 mmol, 25 mg, 24%) as a colorless oil. R_f 0.38 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 (d, *J* = 8.2, 2H), 7.19 (d, *J* = 7.9, 2H), 5.53 (s, 1H), 5.44 (s, 1H), 4.38 (s, 2H), 2.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.2, 138.3, 134.7, 129.4, 126.1, 116.5, 34.5, 21.3. Characterization data obtained for **2f** matched those previously reported in literature.[22]

3-Methyl-α-(bromomethyl)styrene (2g)—Following the general procedure, **2g** was synthesized from 3-methyl-α-methylstyrene (0.50 mmol, 76 mg, 1.0 equiv), TMS-Cl (5.0 μmol, 1 μL, 1 mol%), NBS (0.60 mmol, 106 mg, 1.2 equiv) and $Yb(OTf)_3$ (5.0 μmol, 3 mg, 1 mol%). Filtration with pentane and purification by silica gel chromatography (100% pentane) provided **2g** (0.22 mmol, 45 mg, 43%) as a colorless oil. R_f 0.35 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31–7.25 (m, 3H), 7.16 (d, *J* = 6.6, 1H), 5.54 (s, 1H), 5.48 (s, 1H), 4.38 (s, 2H), 2.39 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.5, 138.2, 137.7, 129.2, 128.5, 127.0, 123.3, 117.2, 34.5, 21.7; IR (thin film): 3031, 2921, 2361, 2341, 1602, 1489, 1442, 1278, 1210 cm^{-1}; HRMS-CI (*m/z*) $[M]^+$ calculated for $C_{10}H_{11}Br$ 210.0044, found 210.0046.

2-Methyl-α-(bromomethyl)styrene (2h)—Following the general procedure, **2h** was synthesized from 2-methyl-α-methylstyrene (0.50 mmol, 76 mg, 1.0 equiv), TMS-Cl (5.0 μmol, 1 μL, 1 mol%), NBS (0.60 mmol, 106 mg, 1.2 equiv) and $Yb(OTf)_3$ (5.0 μmol, 3 mg, 1 mol%). Filtration with pentane and purification by silica gel chromatography (100% pentane) provided **2h** (0.28 mmol, 58 mg, 55%) as a colorless oil. R_f 0.52 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25–7.16 (m, 3H), 5.64 (s, 1H), 5.15–5.14 (m, 1H), 4.25 (s, 2H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.1, 139.4, 135.4, 130.4, 128.9, 127.9, 125.7, 119.6, 37.0, 19.9. Characterization data obtained for **2h** matched those previously reported in literature.[22]

4-Methoxy-α-(bromomethyl)styrene (2i)—A mixture of 4-methoxy-α-methylstyrene (2.00 mmol, 296 mg, 1.0 equiv), NBS (1.23 mmol, 220 mg, 0.62 equiv) and benzoyl peroxide (0.10 mmol, 24 mg, 5 mol%) in CCl_4 (18 mL) was refluxed at 78 °C under argon atmosphere. After three hours, a second portion of NBS (1.23 mmol, 220 mg, 0.62 equiv) and benzoyl peroxide (0.10 mmol, 24 mg, 5 mol%) was added and the reaction mixture was refluxed for three additional hours. After cooling to room temperature, the resulting precipitate was removed by filtration and the filtrate was concentrated under reduced pressure. Purification of the crude product by silica gel chromatography (2% diethyl ether/ hexanes) provided **2i** (0.91 mmol, 207 mg, 46%) as a colorless oil. R_f 0.37 (5% ethyl acetate/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 (d, *J* = 8.8, 2H), 6.91 (d, *J* = 8.8, 2H), 5.48 (s, 1H), 5.40 (s, 1H), 4.37 (s, 2H), 3.83 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.8, 143.7, 130.1, 127.7, 115.6, 114.0, 55.4, 34.6. Characterization data obtained for **2i** matched those previously reported in literature.[32]

3-Methoxy-α-(bromomethyl)styrene (2j)—Following the general procedure, **2j** was synthesized from 3-methoxy-α-methylstyrene (0.50 mmol, 74 mg, 1.0 equiv), TMS-Cl (5.0 μmol, 1 μL, 1 mol%), NBS (0.60 mmol, 106 mg, 1.2 equiv) and $Yb(OTf)_3$ (5.0 μmol, 3 mg, 1 mol%). Filtration with diethyl ether and purification by silica gel chromatography (2% diethyl ether/hexanes) provided **2j** (0.22 mmol, 49 mg, 43%) as a colorless oil. R_f 0.53 (5% ethyl acetate/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 (t, *J* = 8.0, 1H), 7.08 (d, *J* = 7.7, 1H), 7.04–7.02 (m, 1H), 6.88 (dd, *J* = 8.2, 2.5, 1H), 5.56 (s, 1H), 5.49 (s, 1H), 4.37 (s, 2H), 3.84 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.8, 144.3, 139.3, 129.6, 118.7, 117.6, 113.6, 112.3, 55.4, 34.3; IR (thin film): 2957, 2833, 2364, 1599, 1577, 1490, 1453, 1427, 1323, 1288, 1237, 1211, 1046 cm^{-1}; HRMS-CI (*m/z*) $[M]^+$ calculated for $C_{10}H_{11}BrO$ 225.9993, found 225.9983.

2-Methoxy-α-(bromomethyl)styrene (2k)—A mixture of 2-methoxy-α-methylstyrene (2.00 mmol, 296 mg, 1.0 equiv), NBS (1.23 mmol, 220 mg, 0.62 equiv) and benzoyl peroxide (0.10 mmol, 24 mg, 5 mol%) in CCl_4 (18 mL) was refluxed at 78 °C under argon atmosphere. After three hours, a second portion of NBS (1.23 mmol, 220 mg, 0.62 equiv) and benzoyl peroxide (0.10 mmol, 24 mg, 5 mol%) was added and the reaction mixture was refluxed for three additional hours. After cooling to room temperature, the resulting precipitate was removed by filtration and the filtrate was concentrated under reduced pressure. Purification of the crude product by silica gel chromatography (2% diethyl ether/ hexanes) provided **2k** (0.90 mmol, 204 mg, 45%) as a colorless oil. R_f 0.50 (5% ethyl acetate/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36–7.32 (m, 1H), 7.27 (dd, *J* = 7.5, 1.8, 1H), 6.99 (dt, *J* = 7.4, 0.8, 1H), 6.92 (d, *J* = 8.4, 1H), 5.53 (s, 1H), 5.29–5.28 (m, 1H), 4.49 (s, 2H), 3.85 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.6, 145.1, 131.0, 129.5, 128.3, 120.7, 119.3, 110.7, 55.5, 36.1; IR (thin film): 2936, 2834, 1626, 1598, 1490, 1461, 1434, 1242, 1211, 1026 cm^{-1}; HRMS-CI (*m/z*) $[M + NH_4]^+$ calculated for $C_{10}H_{11}BrONH_4$ 244.0337, found 244.0335.

4-Cyano-α-(bromomethyl)styrene (2l)—Following the general procedure, **2l** was synthesized from 4-cyano-α-methylstyrene (0.50 mmol, 72 mg, 1.0 equiv), TMS-Cl (50 μmol, 6 μL, 10 mol%), NBS (0.60 mmol, 106 mg, 1.2 equiv) and $Yb(OTf)_3$ (50 μmol, 31 mg, 10 mol%). Filtration with diethyl ether and purification by silica gel chromatography (10% diethyl ether/hexanes) provided **2l** (0.26 mmol, 58 mg, 52%) as a colorless solid. R_f 0.34 (10% ethyl acetate/hexanes); mp: 58–59 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.2, 2H), 7.59 (d, *J* = 8.2, 2H), 5.65 (s, 1H), 5.63 (s, 1H), 4.36 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.1, 142.2, 132.5, 127.0, 120.0, 118.7, 112.0, 33.2; IR (thin film): 2921, 2360, 2227, 1606, 1506, 1447, 1403, 1212 cm^{-1}; HRMS-ESI (*m/z*) $[M + Na]^+$ calculated for $C_{10}H_8NBrNa$ 243.9738, found 243.9729.

3-Cyano-α-(bromomethyl)styrene (2m)—Following the general procedure, **2m** was synthesized from 3-cyano-α-methylstyrene (0.50 mmol, 72 mg, 1.0 equiv), TMS-Cl (50 μmol, 6 μL, 10 mol%), NBS (0.60 mmol, 106 mg, 1.2 equiv) and $Yb(OTf)_3$ (50 μmol, 31 mg, 10 mol%). Filtration with diethyl ether and purification by silica gel chromatography (10% diethyl ether/hexanes) provided **2m** (0.21 mmol, 47 mg, 43%) as a colorless solid. R_f 0.33 (10% ethyl acetate/hexanes); mp: 61–63 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76 (s,

1H), 7.71 (d, *J* = 8.0, 1H), 7.62 (d, *J* = 7.7, 1H), 7.49 (t, *J* = 7.8, 1H), 5.59 (s, 2H), 4.35 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 142.6, 139.0, 131.7, 130.6, 130.0, 129.5, 119.3, 118.7, 112.9, 33.3; IR (thin film): 2920, 2360, 2340, 2229, 1573, 1481, 1277, 1260, 1212 cm^{-1}; HRMS-ESI (*m/z*) $[M + Na]^+$ calculated for $C_{10}H_8NBrNa$ 243.9738, found 243.9746.

(*Z*)-(1-Bromobut-2-en-2-yl)benzene (4)—Following the general procedure, **4** was synthesized from but-1-en-2-ylbenzene (0.50 mmol, 66 mg, 1.0 equiv), TMS-Cl (12.5 μmol, 2 μL, 2.5 mol%), NBS (0.60 mmol, 106 mg, 1.2 equiv) and $Yb(OTf)_3$ (12.5 μmol, 8 mg, 2.5 mol%). Filtration with pentane and purification by silica gel chromatography (100% pentane) provided **4** (0.30 mmol, 62 mg, 59%) as a colorless oil. R_f 0.32 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44 (d, *J* = 7.9, 2H), 7.35 (t, *J* = 7.6, 2H), 7.29 (d, *J* = 7.4, 1H), 6.09 (q, *J* = 7.1, 1H), 4.40 (s, 2H), 1.92 (d, *J* = 7.1, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.6, 137.0, 129.5, 128.6, 127.5, 125.9, 29.3, 14.6; IR (thin film): 3027, 2977, 2918, 1600, 1493, 1446, 1207 cm^{-1}; HRMS-CI (*m/z*) $[M + NH_4]^+$ calculated for $C_{10}H_{11}BrNH_4$ 228.0388, found 228.0383.

(3-Bromobut-1-en-2-yl)benzene (5)—Following the general procedure, **5** was synthesized from but-2-en-2-ylbenzene (0.50 mmol, 66 mg, 1.0 equiv), TMS-Cl (12.5 μmol, 2 μL, 2.5 mol%), NBS (0.60 mmol, 106 mg, 1.2 equiv) and $Yb(OTf)_3$ (12.5 μmol, 8 mg, 2.5 mol%). Filtration with pentane and purification by silica gel chromatography (100% pentane) provided **5** (0.35 mmol, 74 mg, 70%) as a colorless oil. R_f 0.38 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 (d, *J* = 7.0, 2H), 7.39–7.31 (m, 3H), 5.53 (s, 1H), 5.40 (s, 1H), 5.12 (q, *J* = 6.7, 1H), 1.94 (d, *J* = 6.8, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.4, 139.9, 128.5, 128.1, 127.0, 115.3, 48.9, 24.9; IR (thin film): 3056, 2975, 2925, 2362, 1624, 1574, 1494, 1443, 1374, 1172, 1071 cm^{-1}; HRMS-CI (*m/z*) $[M]^+$ calculated for $C_{10}H_{11}Br$ 210.0044, found 210.0034.

Visible-Light Photoredox Catalyzed Wurtz-Type Coupling Reactions (Tables 1, 2, 3 and Scheme 3)

General Procedure for the Wurtz-type coupling reaction of substituted allylic bromides—A 1-dram vial was charged with $Ru(bpy)_3(PF_6)_2$ (2.0 μmol, 2 mg, 1 mol%), Hantzsch ester **3** (0.20 mmol, 51 mg, 1.0 equiv) and a magnetic stir bar under argon. After sequential addition of CH_2Cl_2 (0.5 mL, sparged with argon for five minutes), *i*-Pr_2NEt (0.40 mmol, 63 μL, 2.0 equiv) and the substituted allylic bromide (0.20 mmol, 1.0 equiv), the vial was capped and placed in the center of a 30 cm-loop of blue LEDs. After stirring for 18 hours, the reaction mixture was concentrated under reduced pressure. The crude product was then purified by silica gel chromatography.

2,5-Diphenylhexa-1,5-diene (1a)—Following the general procedure, **1a** was synthesized from $Ru(bpy)_3(PF_6)_2$ (2.0 μmol, 2 mg, 1 mol%), Hantzsch ester **3** (0.20 mmol, 51 mg, 1.0 equiv), *i*-Pr_2NEt (0.40 mmol, 63 μL, 2.0 equiv) and α-(bromomethyl)styrene (**2a**, 0.20 mmol, 39 mg, 1.0 equiv) in CH_2Cl_2 (0.5 mL). Purification by silica gel chromatography (100% pentane) provided **1a** (81 μmol, 19 mg, 81%) as a colorless solid.

Under the same conditions, coupling product **1a** (94 mg, 80%) was obtained from $Ru(bpy)_3(PF_6)_2$ (0.01 mmol, 8.5 mg, 1 mol%), Hantzsch ester **3** (1.00 mmol, 255 mg, 1.0 equiv), *i*-Pr_2NEt (2.00 mmol, 0.32 mL, 2.0 equiv) and α-(bromomethyl)styrene (**2a**, 1.00 mmol, 197 mg, 1.0 equiv) in CH_2Cl_2 (2.5 mL). In the same fashion, product **1a** (184 mg, 78%) was obtained from $Ru(bpy)_3(PF_6)_2$ (0.02 mmol, 17 mg, 1 mol%), Hantzsch ester **3** (2.00 mmol, 510 mg, 1.0 equiv), *i*-Pr_2NEt (4.00 mmol, 0.63 mL, 2.0 equiv) and α-(bromomethyl)styrene (**2a**, 2.00 mmol, 394 mg, 1.0 equiv) in CH_2Cl_2 (5 mL).

R_f 0.37 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42 (d, *J* = 7.5, 4H), 7.35 (t, *J* = 7.4, 4H), 7.32–7.28 (m, 2H), 5.31 (d, *J* = 1.2, 2H), 5.07 (s, 2H), 2.68 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.1, 141.2, 128.4, 127.5, 126.3, 112.7, 34.4. Characterization data obtained for **1a** matched those previously reported in literature.[33]

2,5-Bis-(4-chlorophenyl)hexa-1,5-diene (1b)—Following the general procedure, **1b** was synthesized from $Ru(bpy)_3(PF_6)_2$ (2.0 μmol, 2 mg, 1 mol%), Hantzsch ester **3** (0.20 mmol, 51 mg, 1.0 equiv), *i*-Pr_2NEt (0.40 mmol, 63 μL, 2.0 equiv) and 4-chloro-α-(bromomethyl)styrene (**2b**, 0.20 mmol, 46 mg, 1.0 equiv) in CH_2Cl_2 (0.5 mL). Purification by silica gel chromatography (100% pentane) provided **1b** (81 μmol, 25 mg, 81%) as a colorless solid. R_f 0.44 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29 (s, 8H), 5.26 (s, 2H), 5.03 (s, 2H), 2.59 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.8, 139.5, 133.3, 128.6, 127.6, 113.5, 34.2. Characterization data obtained for **1b** matched those previously reported in literature.[14k]

2,5-Bis-(4-bromophenyl)hexa-1,5-diene (1c)—Following the general procedure, **1c** was synthesized from $Ru(bpy)_3(PF_6)_2$ (2.0 μmol, 2 mg, 1 mol%), Hantzsch ester **3** (0.20 mmol, 51 mg, 1.0 equiv), *i*-Pr_2NEt (0.40 mmol, 63 μL, 2.0 equiv) and 4-bromo-α-(bromomethyl)styrene (**2c**, 0.20 mmol, 55 mg, 1.0 equiv) in CH_2Cl_2 (0.5 mL). Purification by silica gel chromatography (100% pentane) provided **1c** (83 μmol, 32 mg, 83%) as a colorless solid. R_f 0.41 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 (d, *J* = 8.4, 4H), 7.23 (d, *J* = 8.4, 4H), 5.26 (s, 2H), 5.03 (s, 2H), 2.59 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.8, 140.0, 131.5, 127.9, 121.5, 113.6, 34.1. Characterization data obtained for **1c** matched those previously reported in literature.[14k]

2,5-Bis-(3-bromophenyl)hexa-1,5-diene (1d)—Following the general procedure, **1d** was synthesized from $Ru(bpy)_3(PF_6)_2$ (2.0 μmol, 2 mg, 1 mol%), Hantzsch ester **3** (0.20 mmol, 51 mg, 1.0 equiv), *i*-Pr_2NEt (0.40 mmol, 63 μL, 2.0 equiv) and 3-bromo-α-(bromomethyl)styrene (**2d**, 0.20 mmol, 55 mg, 1.0 equiv) in CH_2Cl_2 (0.5 mL). Purification by silica gel chromatography (100% pentane) provided **1d** (87 μmol, 34 mg, 87%) as a colorless oil.

Under the same conditions, coupling product **1d** (154 mg, 79%) was obtained from $Ru(bpy)_3(PF_6)_2$ (0.01 mmol, 8.5 mg, 1 mol%), Hantzsch ester **3** (1.00 mmol, 255 mg, 1.0 equiv), *i*-Pr_2NEt (2.00 mmol, 0.32 mL, 2.0 equiv) and 3-bromo-α-(bromomethyl)styrene (**2d**, 1.00 mmol, 275 mg, 1.0 equiv) in CH_2Cl_2 (2.5 mL).

R_f 0.50 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50 (t, *J* = 1.8, 2H), 7.42–7.39 (m, 2H), 7.30–7.26 (m, 2H), 7.20 (t, *J* = 7.8, 2H), 5.28 (d, *J* = 1.0, 2H), 5.07 (s, 2H), 2.59 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.6, 143.3, 130.5, 130.0, 129.4, 124.9, 122.7, 114.2, 34.1; IR (thin film): 3081, 2942, 2859, 1806, 1626, 1589, 1556, 1473, 1407, 1291, 1068 cm^{-1}; HRMS-CI (*m/z*) $[M + NH_4]^+$ calculated for $C_{18}H_{16}Br_2NH_4$ 407.9962, found 407.9958.

2,5-Bis-(2-fluorophenyl)hexa-1,5-diene (1e)—Following the general procedure, **1e** was synthesized from $Ru(bpy)_3(PF_6)_2$ (2.0 μmol, 2 mg, 1 mol%), Hantzsch ester **3** (0.20 mmol, 51 mg, 1.0 equiv), *i*-Pr_2NEt (0.40 mmol, 63 μL, 2.0 equiv) and 2-fluoro-α-(bromomethyl)styrene (**2e**, 0.20 mmol, 43 mg, 1.0 equiv) in CH_2Cl_2 (0.5 mL). Purification by silica gel chromatography (100% pentane) provided **1e** (66 μmol, 18 mg, 66%) as a colorless oil. R_f 0.45 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25–7.18 (m, 4H), 7.08 (dt, *J* = 7.5, 1.1, 2H), 7.02 (ddd, *J* = 10.7, 8.3, 0.9, 2H), 5.17 (s, 2H), 5.15 (s, 2H), 2.58 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.0 (d, *J* = 247.3), 144.4, 130.3 (d, *J* = 4.4), 129.8 (d, *J* = 14.3), 128.9 (d, *J* = 8.4), 124.0 (d, *J* = 3.5), 116.3 (d, *J* = 2.3), 115.8 (d, *J* = 22.9), 35.0 (d, *J* = 3.2); IR (thin film): 3082, 2933, 2860, 1799, 1631, 1573, 1487, 1447, 1214, 1090, 1033 cm^{-1}; HRMS-CI (*m/z*) $[M + H]^+$ calculated for $C_{18}H_{16}F_2H$ 271.1298, found 271.1292.

2,5-Bis-(4-methylphenyl)hexa-1,5-diene (1f)—Following the general procedure, **1f** was synthesized from $Ru(bpy)_3(PF_6)_2$ (2.0 μmol, 2 mg, 1 mol%), Hantzsch ester **3** (0.20 mmol, 51 mg, 1.0 equiv), *i*-Pr_2NEt (0.40 mmol, 63 μL, 2.0 equiv) and 4-methyl-α-(bromomethyl)styrene (**2f**, 0.20 mmol, 42 mg, 1.0 equiv) in CH_2Cl_2 (1.0 mL). Purification by silica gel chromatography (100% pentane) provided **1f** (82 μmol, 22 mg, 82%) as a colorless solid. R_f 0.19 (100% hexanes); mp: 56–57 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29 (d, *J* = 8.1, 4H), 7.14 (d, *J* = 7.9, 4H), 5.25 (d, *J* = 1.3, 2H), 5.00 (s, 2H), 2.62 (s, 4H), 2.35 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.0, 138.3, 137.2, 129.1, 126.1, 111.8, 34.5, 21.3; IR (thin film): 3082, 3023, 2921, 2861, 1624, 1512, 1453 cm^{-1}; HRMS-CI (*m/z*) $[M + H]^+$ calculated for $C_{20}H_{22}H$ 263.1800, found 263.1804.

2,5-Bis-(3-methylphenyl)hexa-1,5-diene (1g)—Following the general procedure, **1g** was synthesized from $Ru(bpy)_3(PF_6)_2$ (2.0 μmol, 2 mg, 1 mol%), Hantzsch ester **3** (0.20 mmol, 51 mg, 1.0 equiv), *i*-Pr_2NEt (0.40 mmol, 63 μL, 2.0 equiv) and 3-methyl-α-(bromomethyl)styrene (**2g**, 0.20 mmol, 42 mg, 1.0 equiv) in CH_2Cl_2 (1.0 mL). Purification by silica gel chromatography (100% pentane) provided **1g** (88 μmol, 23 mg, 88%) as a colorless oil. R_f 0.36 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.24–7.18 (m, 6H), 7.10 (d, *J* = 6.9, 2H), 5.27 (d, *J* = 1.4, 2H), 5.04 (s, 2H), 2.63 (s, 4H), 2.36 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.3, 141.2, 137.9, 128.3, 128.2, 127.0, 123.4, 112.5, 34.5, 21.7; IR (thin film): 3035, 2919, 2859, 2360, 1787, 1626, 1600, 1575, 1486, 1452 cm^{-1}; HRMS-CI (*m/z*) $[M + H]^+$ calculated for $C_{20}H_{22}H$ 263.1800, found 263.1792.

2,5-Bis-(2-methylphenyl)hexa-1,5-diene (1h)—Following the general procedure, **1h** was synthesized from $Ru(bpy)_3(PF_6)_2$ (2.0 μmol, 2 mg, 1 mol%), Hantzsch ester **3** (0.20 mmol, 51 mg, 1.0 equiv), *i*-Pr_2NEt (0.40 mmol, 63 μL, 2.0 equiv) and 2-methyl-α-

(bromomethyl)styrene (**2h**, 0.20 mmol, 42 mg, 1.0 equiv) in CH_2Cl_2 (0.5 mL). Purification by silica gel chromatography (100% pentane) provided **1h** (72 μmol, 19 mg, 72%) as a colorless oil.

Under the same conditions, coupling product **1h** (90 mg, 69%) was obtained from $Ru(bpy)_3(PF_6)_2$ (0.01 mmol, 8.5 mg, 1 mol%), Hantzsch ester **3** (1.00 mmol, 255 mg, 1.0 equiv), *i*-Pr_2NEt (2.00 mmol, 0.32 mL, 2.0 equiv) and 2-methyl-α-(bromomethyl)styrene (**2h**, 1.00 mmol, 210 mg, 1.0 equiv) in CH_2Cl_2 (2.5 mL).

R_f 0.39 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.18–7.11 (m, 6H), 7.06 (d, *J* = 6.9, 2H), 5.20 (s, 2H), 4.89 (d, *J* = 1.9, 2H), 2.45 (s, 4H), 2.26 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.6, 143.0, 134.9, 130.2, 128.5, 126.9, 125.5, 114.1, 35.9, 20.0; IR (thin film): 3070, 3016, 2924, 2360, 1634, 1487, 1452, 1211, 1045 cm^{-1}; HRMS-CI (*m/z*) $[M + H]^+$ calculated for $C_{20}H_{22}H$ 263.1800, found 263.1804.

2,5-Bis-(4-methoxyphenyl)hexa-1,5-diene (1i)—Following the general procedure, **1i** was synthesized from $Ru(bpy)_3(PF_6)_2$ (2.0 μmol, 2 mg, 1 mol%), Hantzsch ester **3** (0.20 mmol, 51 mg, 1.0 equiv), *i*-Pr_2NEt (0.40 mmol, 63 μL, 2.0 equiv) and 4-methoxy-α-(bromomethyl)styrene (**2i**, 0.20 mmol, 45 mg, 1.0 equiv) in CH_2Cl_2 (0.5 mL). Purification by silica gel chromatography (5% diethyl ether/hexanes) provided **1i** (63 μmol, 19 mg, 63%) as a colorless solid. R_f 0.45 (10% ethyl acetate/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35 (d, *J* = 8.5, 4H), 6.87 (d, *J* = 8.4, 4H), 5.22 (s, 2H), 4.97 (s, 2H), 3.82 (s, 6H), 2.62 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.2, 147.5, 133.6, 127.3, 113.7, 111.1, 55.4, 34.5. Characterization data obtained for **1i** matched those previously reported in literature.[14f]

2,5-Bis-(3-methoxyphenyl)hexa-1,5-diene (1j)—Following the general procedure, **1j** was synthesized from $Ru(bpy)_3(PF_6)_2$ (2.0 μmol, 2 mg, 1 mol%), Hantzsch ester **3** (0.20 mmol, 51 mg, 1.0 equiv), *i*-Pr_2NEt (0.40 mmol, 63 μL, 2.0 equiv) and 3-methoxy-α-(bromomethyl)styrene (**2j**, 0.20 mmol, 45 mg, 1.0 equiv) in CH_2Cl_2 (0.5 mL). Purification by silica gel chromatography (5% diethyl ether/hexanes) provided **1j** (74 μmol, 22 mg, 74%) as a colorless oil. R_f 0.50 (10% ethyl acetate/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27–7.23 (m, 2H), 6.99 (d, *J* = 7.8, 2H), 6.94–6.92 (m, 2H), 6.83 (dd, *J* = 8.2, 2.5, 2H), 5.29 (d, *J* = 1.2, 1H), 5.06 (s, 2H), 3.82 (s, 6H), 2.64 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.7, 148.1, 142.8, 129.4, 118.6, 112.9, 112.8, 112.2, 55.3, 34.5; IR (thin film): 3078, 2934, 2833, 1602, 1575, 1487, 1460, 1427, 1286, 1231, 1047 cm^{-1}; HRMS-CI (*m/z*) $[M + H]^+$ calculated for $C_{20}H_{22}O_2H$ 295.1698, found 295.1700.

2,5-Bis-(2-methoxyphenyl)hexa-1,5-diene (1k)—Following the general procedure, **1k** was synthesized from $Ru(bpy)_3(PF_6)_2$ (3.0 μmol, 3 mg, 1.5 mol%), Hantzsch ester **3** (0.20 mmol, 51 mg, 1.0 equiv), *i*-Pr_2NEt (0.40 mmol, 63 μL, 2.0 equiv) and 2-methoxy-α-(bromomethyl)styrene (**2k**, 0.20 mmol, 45 mg, 1.0 equiv) in CH_2Cl_2 (0.5 mL). The reaction time was extended from 18 hours to 42 hours. Purification by silica gel chromatography (5% diethyl ether/hexanes) provided **1k** (69 μmol, 20 mg, 69%) as a colorless solid. R_f 0.44 (5% ethyl acetate/hexanes); mp: 98–100 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26–7.22 (m, 2H), 7.10 (dd, *J* = 7.4, 1.7, 2H), 6.90 (dt, *J* = 7.4, 1.0, 2H), 6.85 (d, *J* = 8.2, 2H), 5.12 (s, 2H),

5.00 (d, *J* = 2.0, 2H), 3.75 (s, 6H), 2.55 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.6, 148.9, 132.2, 130.4, 128.4, 120.5, 114.2, 110.7, 55.5, 35.0; IR (thin film): 3072, 2944, 2837, 1633, 1597, 1489, 1458, 1435, 1239, 1024 cm^{-1}; HRMS-CI (*m/z*) $[M]^+$ calculated for $C_{20}H_{22}O_2$ 294.1620, found 294.1625.

2,5-Bis-(4-cyanophenyl)hexa-1,5-diene (1l)—Following the general procedure, **1l** was synthesized from $Ru(bpy)_3(PF_6)_2$ (2.0 μmol, 2 mg, 1 mol%), Hantzsch ester **3** (0.20 mmol, 51 mg, 1.0 equiv), *i*-Pr_2NEt (0.40 mmol, 63 μL, 2.0 equiv) and 4-cyano-α-(bromomethyl)styrene (**2l**, 0.20 mmol, 44 mg, 1.0 equiv) in CH_2Cl_2 (0.5 mL). Purification by silica gel chromatography (10% → 20% diethyl ether/hexanes) provided **1l** (73 μmol, 21 mg, 73%) as a colorless solid. R_f 0.18 (10% ethyl acetate/hexanes); mp: 115–116 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62 (d, *J* = 8.4, 4H), 7.44 (d, *J* = 8.4, 4H), 5.37 (s, 2H), 5.15 (s, 2H), 2.63 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.1, 145.5, 132.4, 126.9, 118.9, 116.1, 111.2, 33.6; IR (thin film): 3065, 2917, 2852, 2360, 2341, 2226, 1623, 1604, 1504, 1401, 1128 cm^{-1}; HRMS-ESI (*m/z*) $[M + Na]^+$ calculated for $C_{20}H_{16}N_2Na$ 307.1211, found 307.1213.

2,5-Bis-(3-cyanophenyl)hexa-1,5-diene (1m)—Following the general procedure, **1m** was synthesized from $Ru(bpy)_3(PF_6)_2$ (2.0 μmol, 2 mg, 1 mol%), Hantzsch ester **3** (0.20 mmol, 51 mg, 1.0 equiv), *i*-Pr_2NEt (0.40 mmol, 63 μL, 2.0 equiv) and 3-cyano-α-(bromomethyl)styrene (**2m**, 0.20 mmol, 44 mg, 1.0 equiv) in CH_2Cl_2 (1.0 mL). Purification by silica gel chromatography (20% diethyl ether/hexanes) provided **1m** (74 μmol, 21 mg, 74%) as a colorless solid. R_f 0.51 (20% ethyl acetate/hexanes); mp: 64–65 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61–7.59 (m, 2H), 7.58–7.55 (m, 4H), 7.46–7.42 (m, 2H), 5.32 (s, 2H), 5.12 (s, 2H), 2.61 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.6, 142.2, 131.1, 130.6, 129.9, 129.4, 118.9, 115.4, 112.7, 33.6; IR (thin film): 3082, 2921, 2851, 2360, 2229, 1627, 1574, 1480 cm^{-1}; HRMS-ESI (*m/z*) $[M + Na]^+$ calculated for $C_{20}H_{16}N_2Na$ 307.1211, found 307.1224.

Wurtz-type coupling of (*Z*)-(1-bromobut-2-en-2-yl)benzene (4)—Following the general procedure, the reaction of $Ru(bpy)_3(PF_6)_2$ (2.0 μmol, 2 mg, 1 mol%), Hantzsch ester **3** (0.20 mmol, 51 mg, 1.0 equiv), *i*-Pr_2NEt (0.40 mmol, 63 μL, 2.0 equiv) and (*Z*)-(1-bromobut-2-en-2-yl)benzene (**4**, 0.20 mmol, 42 mg, 1.0 equiv) in CH_2Cl_2 (0.5 mL) gave a crude product. Purification by silica gel chromatography (100% pentane) provided a mixture of the three regioisomers **6** (36 μmol, 10 mg, 36%), **7** (43 μmol, 11 mg, 43%) and **8** (15 μmol, 4 mg, 15%). Analytical samples were obtained by an automated flash chromatography system.

Data for 6: colorless solid; R_f 0.45 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31–7.28 (m, 8H), 7.24–7.20 (m, 2H), 5.72 (q, *J* = 6.9, 2H), 2.54 (s, 4H), 1.67 (d, *J* = 6.9, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.1, 140.5, 128.3, 126.6, 126.4, 123.4, 28.1, 14.2. Characterization data obtained for **6** matched those previously reported in literature.[34]

Data for 7: colorless oil; R_f 0.50 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30–7.19 (m, 10H), 5.75 (q, *J* = 6.8, 1H), 5.17 (d, *J* = 0.9, 1H), 5.08–5.07 (m, 1H), 2.70–2.64 (m,

2H), 2.50–2.45 (m, 1H), 1.77 (d, *J* = 6.9, 3H), 1.07 (d, *J* = 6.9, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.1, 143.3, 142.9, 140.1, 128.3, 128.2, 127.3, 126.9, 126.7, 126.6, 124.6, 111.0, 36.4, 35.7, 18.6, 14.6; IR (thin film): 3022, 3961, 2925, 2360, 1493, 1442, 1371, 1028 cm^{-1}; HRMS-CI (*m/z*) $[M + H]^+$ calculated for $C_{20}H_{22}H$ 263.1800, found 263.1797.

Data for 8 (1:1 mixture of diastereomers): colorless oil; R_f 0.53 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$, mixture of diastereomers): δ 7.34–7.24 (m, 16H), 7.20–7.16 (m, 4H), 5.20–5.19 (m, 2H), 5.19 (s, 2H), 5.06 (s, 2H), 5.01–5.00 (m, 2H), 2.79–2.72 (m, 4H), 1.18 (d, *J* = 6.2, 6H), 0.94 (d, *J* = 6.8, 6H). Characterization data obtained for **8** matched those previously reported in literature.[34]

Wurtz-type coupling of (3-bromobut-1-en-2-yl)benzene (5)—Following the general procedure, the reaction of $Ru(bpy)_3(PF_6)_2$ (2.0 μmol, 2 mg, 1 mol%), Hantzsch ester **3** (0.20 mmol, 51 mg, 1.0 equiv), *i*-Pr_2NEt (0.40 mmol, 63 μL, 2.0 equiv) and (3-bromobut-1-en-2-yl)benzene (**5**, 0.20 mmol, 42 mg, 1.0 equiv) in CH_2Cl_2 (0.5 mL) gave a crude product. Purification by silica gel chromatography (100% pentane) provided the three regioisomers **6** (45 μmol, 12 mg, 45%), **7** (39 μmol, 10 mg, 39%) and **8** (14 μmol, 4 mg, 14%). Characterization data obtained for **6**, **7** and **8** matched those reported above.

Dimethyl 2,5-dimethylenehexanedioate (10)—Following the general procedure, **10** was synthesized from $Ru(bpy)_3(PF_6)_2$ (2.0 μmol, 2 mg, 1 mol%), Hantzsch ester **3** (0.20 mmol, 51 mg, 1.0 equiv), *i*-Pr_2NEt (0.40 mmol, 63 μL, 2.0 equiv) and methyl 2-(bromomethyl)acrylate[2] (**9**, 0.20 mmol, 36 mg, 1.0 equiv) in CH_2Cl_2 (0.5 mL). Purification by silica gel chromatography (10% diethyl ether/hexanes) provided **10** (57 μmol, 11 mg, 57%) as a colorless oil. R_f 0.37 (10% ethyl acetate/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.17 (d, *J* = 1.3, 2H), 5.54 (s, 2H), 3.76 (s, 6H), 2.50 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.6, 139.6, 125.7, 52.0, 31.0; IR (thin film): 2923, 2851, 2361, 1721, 1632, 1439, 1203, 1141 cm^{-1}; HRMS-CI (*m/z*) $[M + H]^+$ calculated for $C_{10}H_{14}O_4H$ 199.0970, found 199.0976.

2,5-Dibromohexa-1,5-diene (12)—Following the general procedure, **12** was synthesized from $Ru(bpy)_3(PF_6)_2$ (2.0 μmol, 2 mg, 1 mol%), Hantzsch ester **3** (0.20 mmol, 51 mg, 1.0 equiv), *i*-Pr_2NEt (0.40 mmol, 63 μL, 2.0 equiv) and 2,3-dibromopropene (**11**, 0.20 mmol, 40 mg, 1.0 equiv) in CH_2Cl_2 (0.5 mL). Purification by silica gel chromatography (100% pentane) provided **12** (15 μmol, 4 mg, 15%) as a colorless oil. R_f 0.78 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.64 (d, *J* = 1.7, 2H), 5.45 (d, *J* = 1.8, 2H), 2.68 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 132.0, 118.3, 39.9. Characterization data obtained for **12** matched those previously reported in literature.[35]

Visible-Light Photoredox Catalyzed Coupling to Activated Olefins (Scheme 4)

2-(4-Chlorophenyl)-5-phenylhexa-1,5-diene (15)—A 1-dram vial was charged with $Ru(bpy)_3(PF_6)_2$ (2.0 μmol, 2 mg, 2 mol%), Hantzsch ester **3** (0.20 mmol, 51 mg, 2.0 equiv) and a magnetic stir bar under argon. After sequential addition of CH_2Cl_2 (0.5 mL, sparged with argon for five minutes), *i*-Pr_2NEt (0.40 mmol, 63 μL, 4.0 equiv) and α-(chloromethyl)styrene (**14**, 0.50 mmol, 76 mg, 5.0 equiv), the vial was placed in the center

of a 30 cm-loop of blue LEDs. A solution of 4-chloro-α-(bromomethyl)styrene (**2b**, 0.10 mmol, 23 mg, 1.0 equiv) in CH_2Cl_2 (1.0 mL, sparged with argon for five minutes) was added over a time period of seven hours with a syringe pump. After additional stirring for 11 hours, the reaction mixture was concentrated under reduced pressure. Purification by silica gel chromatography (100% pentane) provided **15** (60 μmol, 16 mg, 60%) as a colorless oil. R_f 0.31 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39–7.27 (m, 9H), 5.27 (d, *J* = 1.1, 1H), 5.26 (d, *J* = 1.1, 1H), 5.05 (d, *J* = 0.9, 1H), 5.03 (d, *J* = 0.9, 1H), 2.66–2.58 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.0, 147.0, 141.1, 139.6, 133.3, 128.6, 128.5, 128.4, 127.6, 127.5, 126.3, 113.3, 112.9, 34.3, 34.2; IR (thin film): 3081, 2939, 2361, 1626, 1492, 1443, 1394, 1095, 1012 cm^{-1}; HRMS-CI (*m/z*) $[M + H]^+$ calculated for $C_{18}H_{17}ClH$ 269.1097, found 269.1090.

Supplementary Material

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18. Although the generation of allylic radicals from allylic bromides by visible-light photoredox catalysis has not to our knowledge been reported, the mechanism we suggest has much precedent from previous reports of the formation of a variety of stabilized radicals from bromide precursors, see: 3g and 3h.
19. In the reactions with 11 and 13, no starting material or any side products were observed after workup by NMR analysis, suggesting that volatile products were formed, most likely by hydrogen-atom transfer to the allylic radical.
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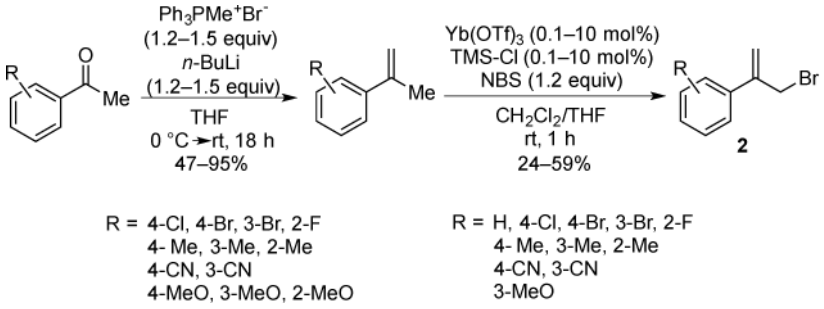
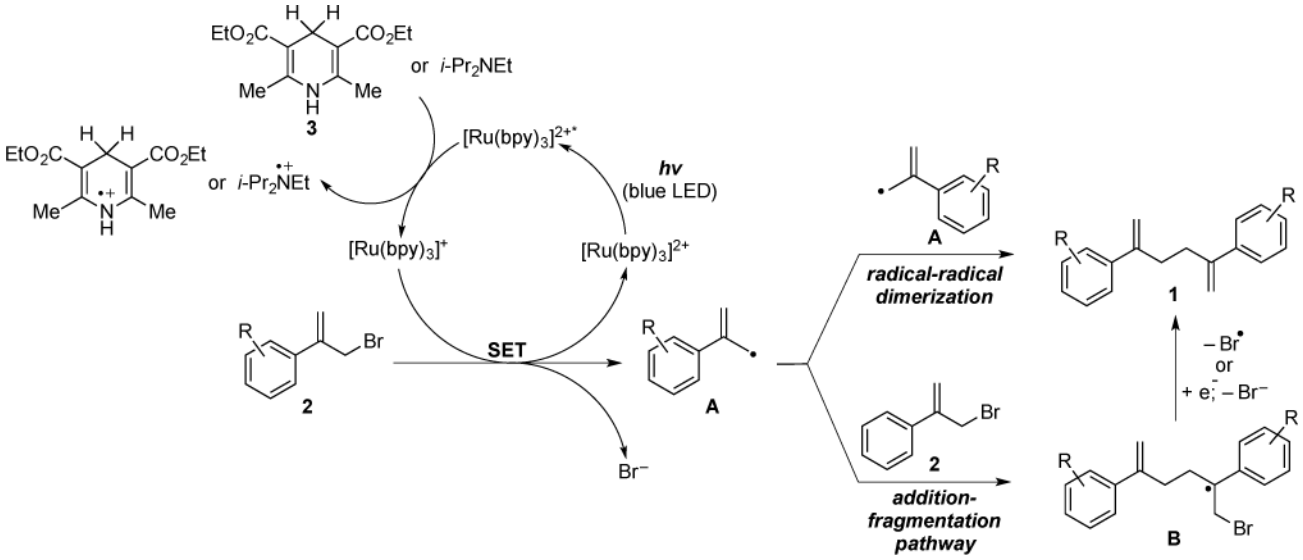


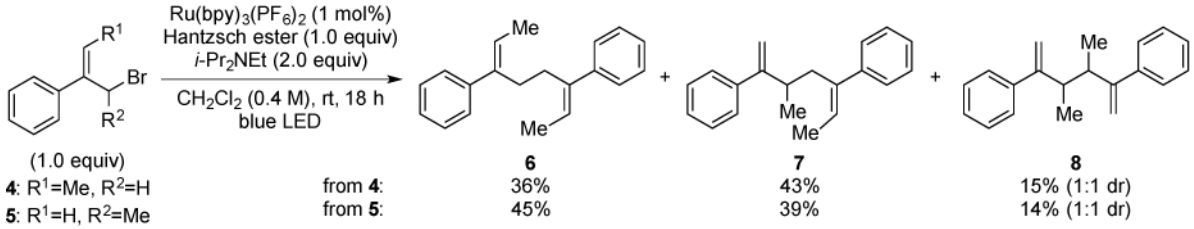
Scheme 1.

Synthesis of α-(bromomethyl)styrenes **2** from acetophenones.



Scheme 2.

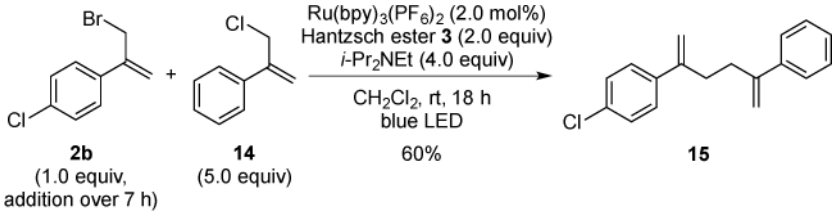
Proposed mechanism for the $Ru(bpy)_3^{2+}$-catalyzed generation of allylic radicals from the corresponding bromides and possible reaction pathways.



Scheme 3.

Investigation of the reaction pathways leading to the observed Wurtz-type coupling products.[a]

[a]Isolated yield after silica gel chromatography (average of two experiments).



Scheme 4.

Synthesis of non-symmetrically substituted 2,5-diaryl-1,5-dienes by reaction via the addition-fragmentation pathway.

Table 1

Optimization and control experiments for the coupling of α-(bromomethyl)styrene (**2a**) to form 2,5-diphenylhexa-1,5-diene (**1a**).

Entry	Modification	Yield of 1a (%)[a]	Recovery of 2a (%)[a]
1	–	78	4
2	no $Ru(bpy)_3(PF_6)_2$	ND	92
3	no light	ND	65
4	no *i*-Pr_2NEt	6	69
5	no Hantzsch ester **3**	24	62
6	$Ru(bpy)_3(PF_6)_2$ (0.5 mol%)	47	35
7	$Ru(bpy)_3(PF_6)_2$ (1.5 mol%)	79	<2
8	Hantzsch ester **3** (0.5 equiv)	57	25
9	Hantzsch ester **3** (0.75 equiv)	71	11
10	*i*-Pr_2NEt (0.5 equiv)	43	35
11	*i*-Pr_2NEt (1.0 equiv)	73	7
12	*i*-Pr_2NEt (2.0 equiv)	82	2
13	MeCN (0.2 M)	61	28
14	THF (0.2 M)	52	38
15	CH_2Cl_2 (0.1 M)	69	16
16	CH_2Cl_2 (0.4 M)	80	ND
17	2 h	48	43
18	6 h	72	13
19	24 h	76	6
20	*i*-Pr_2NEt (2.0 equiv) CH_2Cl_2 (0.4 M)	81,80[b],78[c]	ND

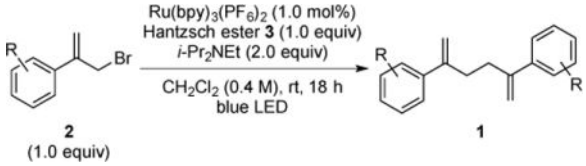
[a] Isolated yield of **1a** and recovery of **2a** after silica gel chromatography, 0.2 mmol scale.

[b] 1.0 mmol scale.

[c] 2.0 mmol scale. ND = not detected.

Table 2

Scope of the visible-light photoredox catalyzed synthesis of 2,5-diaryl-1,5-dienes **1**.



Entry	R	Product (Yield in %)[a]
1	H (**2a**)	**1a** (81%, 80%[b])
2	4-Cl (**2b**)	**1b** (80%)
3	4-Br (**2c**)	**1c** (82%)
4	3-Br (**2d**)	**1d** (84%, 79%[b])
5	2-F (**2e**)	**1e** (66%)[c]
6	4-Me (**2f**)	**1f** (79%)[d]
7	3-Me (**2g**)	**1g** (85%)[d]
8	2-Me (**2h**)	**1h** (71%[e], 69%[f])
9	4-OMe (**2i**)	**1i** (59%)
10	3-OMe (**2j**)	**1j** (72%)
11	2-OMe (**2k**)	**1k** (67%)[g]
12	4-CN (**2l**)	**1l** (70%)
13	3-CN (**2m**)	**1m** (70%)[d]

[a] Isolated yield of **1** after silica gel chromatography (average of two experiments).

[b] 1.0 mmol scale.

[c] 26% recovered SM **2e** (89% brsm).

[d] CH_2Cl_2 (0.2 M).

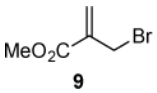
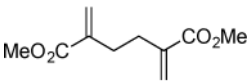
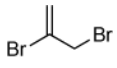
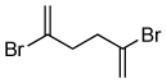
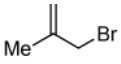
[e] 29% recovered SM **2h** (*quant.* brsm).

[f] 1.0 mmol scale, 25% recovered SM **2h** (91% brsm).

[g] $Ru(bpy)_3(PF_6)_2$ (1.5 mol%), 42 h reaction time, 18% recovered SM **2k** (81% brsm).

Table 3

Visible-light-mediated photocatalytic Wurtz-type coupling of various allylic bromides.[a]

Starting Material	Product (Yield in %)[b]
 **9**	 **10** (57%)
 **11**	 **12** (15%)
 **13**	ND

[a] Reaction conditions from Table 2.

[b] Isolated yield after silica gel chromatography.

ND = not detected.