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Los Angeles

Novel Transformations using Uranium and Group 5 Metal Complexes

Supported by 1,1'-diamidoferrocene Ligands

A thesis submitted in partial satisfaction of the requirements for the degree

Master of Science in Chemistry

by

Michael Joseph Lopez

2013

ABSTRACT OF THE THESIS

Novel Transformations using Uranium and Group 5 Metal Complexes Supported by 1,1'-diamidoferrocene Ligands

by

Michael Joseph Lopez

Master of Science in Chemistry

University of California, Los Angeles, 2013

Professor Craig A. Merlic, Chair

These studies describe the use of the redox-active 1,1'-diamidoferrocene ligand on uranium and group 5 metals. A novel terminal uranium-imide complex was synthesized using the bulky 2,6-dimesitylphenyl imide substituent as support. Although the uranium-imide was shown to be sterically accessible through the accommodation of another 2,6-dimesitylphenyl amide group, further reactivity was not seen, with the exception of sulfur. Electron transfer between the iron contained in the 1,1'-diamidoferrocene ligand and group 5 metals was more apparent than with uranium. A control reaction between ferrocene and niobium pentachloride suggested the formation of ferrocenium via electron transfer from iron to niobium. The use of a reduced tantalum and niobium precursors is required for coordination by 1,1'-diamidoferrocene ligands to prevent side reactions.

The thesis of Michael Joseph Lopez is approved.

Catherine F. Clarke

Richard B. Kaner

Craig A. Merlic, Committee Chair

University of California, Los Angeles

2013

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Introduction

The impact of organometallic catalysts in organic transformations has grown in recent years, as exemplified by the Noble Prizes awarded in 2001, 2005, and 2010. While these reactions are considerably efficient, to be applicable in an industrial setting the cost of the catalyst must be considered, specifically, the catalytic metal center. For example, an academic scaled palladium-catalyzed Heck cross coupling between *p*-bromoanisole and phenylboronic acid has turn over numbers (TON) on the order of 10^5 and catalyst loading as low as 1 mmol%, but on the industrial scale catalyst loading must be increased as high as 10 mol% with lowered TON due to costly recovery.¹ Only when the reaction products have high commercial value, such as pharmaceutical drugs, are the costs of expensive catalysts endurable. To avoid or reduce the cost of catalytic transformations, early and first row transition metals are used. The costs of common metal chlorides are given in Table 1, and the prohibitive cost of metals such as rhodium, platinum, and palladium is seen.

Table 1 Costs of metal chlorides (per gram) with indicated purity from Sigma Aldrich.

Metal Chloride	Purity	Cost per Gram
TiCl ₄	≥ 99.995 %	9.90
VCl ₃	97 %	31.10
NbCl ₅	≥ 99.9 %	8.57
TaCl ₅	99.99 %	9.38
FeCl ₂	98 %	2.90
CoCl ₂	97 %	7.92
NiCl ₂	98 %	0.74
CuCl ₂	99.999 %	7.48
RuCl ₃ hydrate	99.98 %	67.40
RhCl ₃	98 %	303.00
IrCl ₃	99.8 %	234.50
PdCl ₂	99.999 %	113.50
PtCl ₂	≥ 99.9 %	240.00
AuCl ₃	≥ 99.9 %	270.00

Although there are clear financial incentives to replace late platinum group metals, several common reaction classes are more difficult for early and first row transition metals. For example, palladium is often used in Heck cross-coupling reactions as palladium readily reacts with aryl halides through oxidative addition to initiate the catalytic cycle, eventually leading to reductive elimination to regenerate the palladium catalyst.² These processes require a formal oxidation state change of two, to make and break the desired chemical bonds.³ Both early and (the majority of) first row transition metals are considered hard Lewis acids, which make strong bonds with hard Lewis bases.^{4,5} Hard Lewis bases induce weak ligand fields and thus readily allow radical reactions.⁴ The opposite is true for late transition metals that bind strong-field inducing, soft Lewis acids.⁴ This is further exemplified by the nickel-catalyzed Heck cross coupling reaction, in which both the two electron oxidative addition/reductive elimination reactions and a radical promoted pathway can be invoked.⁶ A method to promote two-electron chemistry in early/first row transition metals is to use redox-active ligands, a method inspired by metalloenzymes.⁷

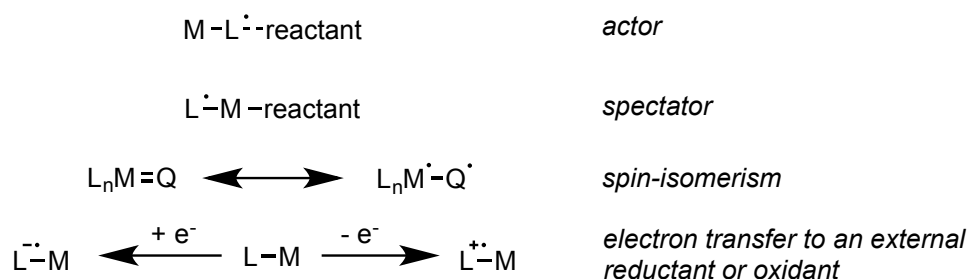
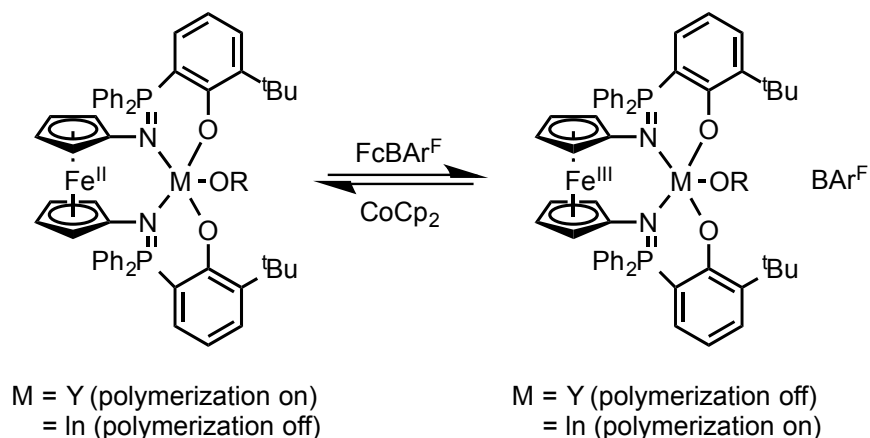


Figure 1 Four main categories of redox-active ligands as described by Crabtree.^{8a}

Crabtree classifies redox-active ligands in four main categories, as shown in Figure 1. The actor and spectator categories are related as the reactant interacts with either the

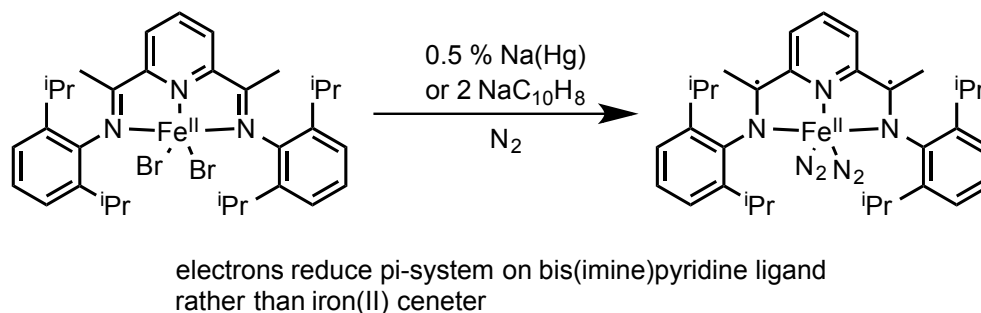
oxidized/reduced ligand or the oxidized/reduced metal, respectively. The Diaconescu group has utilized this reversibly to control the polymerization of lactide by oxidizing/reducing the ferrocene backbone contained in the ligand (Figure 2).⁹ When yttrium is used as the metal center and the iron is in the +2 oxidation state, L-lactide is readily polymerized, but by oxidizing the iron to +3, polymerization is halted. The last two classes of redox-active ligands are also related, as shown by Chirik's group (Figure 2). They have shown instead of reducing an iron(II) bis(imino)pyridine complex to iron(0) in the presence of sodium amalgam or sodium naphthalene, two electrons are placed in the conjugated pi-system on the bis(imino)pyridine ligand.^{10a} This reduced ligand complex has been used to catalyze formal [2 + 2] cycloadditions, 1,6-enyne cyclizations, hydrogenation, hydrosilylations, and most interestingly, carbon-carbon activation via oxidative addition.¹⁰ Using a combination of spectroscopy and density functional theory, Chirik's group has proposed during the carbon-carbon oxidative addition to the iron metal center, one electron is from the iron and the other is from the ligand resulting in a formal iron(III) metal center and a radical contained on the bis(imino)pyridine ligand.^{10e} The two unpaired electrons couple anti-ferromagnetically to give a diamagnetic complex.

Diaconescu's Redox Switchable Catalyst



Broderick, E. M.; et al. *J. Am. Chem. Soc.* **2011**, 133, 9278.

Chirik's Non-innocent Ligand



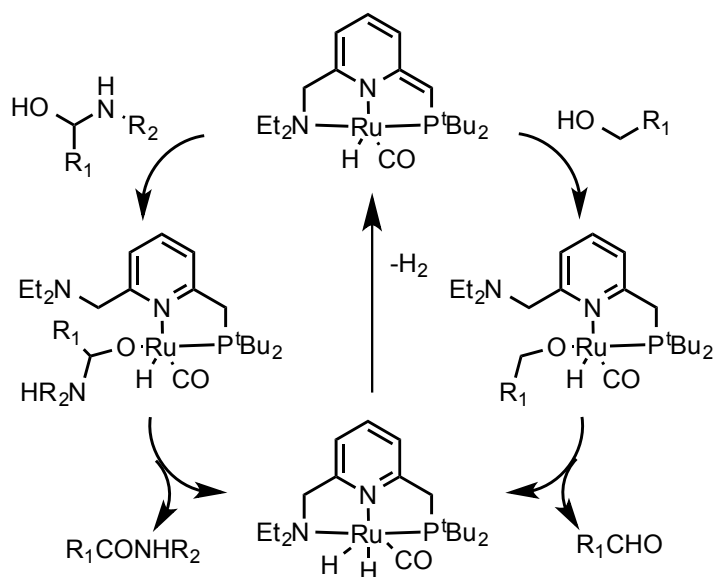
Bouwkamp, M. W.; et al. *J. Am. Chem. Soc.* **2006**, 128, 13340.

Figure 2 Examples of Crabtree's categories of redox-active ligands.

Redox-active ligands have allowed for new types of reactivity for both early and late transition metals. Amide synthesis usually requires activated acid derivatives, such as acid chlorides, or rearrangement reactions.¹¹ Milstein's group has shown amide formation through the coupling of alcohols and amines (with coproduction of hydrogen gas) via a ruthenium(II), pyridine containing, PNN pincer ligand complex (Figure 3).^{12a} The primary alcohol is first dehydrogenated to an aldehyde, in which one hydrogen hydrogenates the ligand backbone

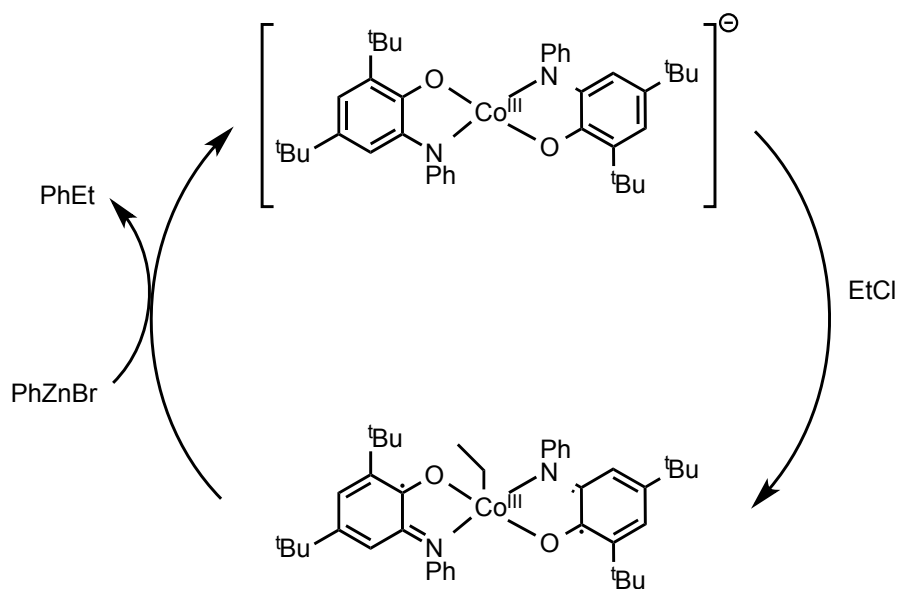
inducing aromaticity and the other forms a hydride. This complex readily loses dihydrogen, disrupting the aromaticity of the pyridine backbone, and dehydrogenates the newly formed hemiaminal to form the amide. The same ruthenium(II) PNN ligand complex was also used for thermal and light induced water splitting.^{12b} In an effort to replace late transition metals, Soper et al. used a cobalt(III) amidophenolate complex for the Negishi cross-coupling of alkyl halides and organozinc reagents (Figure 3).¹³ They propose the two electrons required for reactivity come from the ligand, even though the cobalt(III) metal center goes through formal oxidative addition and reductive elimination steps.

Milstein's Catalytic Production of Amides



Gunanathan, C.; et al. *Science* **2007**, 317, 790

Soper's Negishi Cross Coupling using Co(III)



Smith, A. L.; et al. *J. Am. Chem. Soc.* **2010**, 132, 14358.

Figure 3 Examples of new reactivity allowed by redox-active ligands.

In order to further expand utility of redox-active ligands, substituted 1,1'-diamidoferrocene ligands were placed (or attempted to be placed) on uranium and group 5 metals, respectively, as shown in Figure 4. Previously, the Diaconescu group discovered a weak interaction between the uranium center and the supported di-substituted 1,1'-diamidoferrocene ligands.¹⁴ Utilizing this interaction, the group successfully ring-opened imidazoles through two consecutive C-H activations and C-C coupling, as well as the intermolecular hydroamination of terminal alkynes with primary amines and the intramolecular hydroamination of terminal alkynes and alkenes.¹⁵ The catalytically active species in uranium hydroamination reactions can contain either a terminal imido or amido.¹⁶ Due to the large ionic radius of uranium, synthesizing terminal imides are usually difficult and require careful manipulation of the imide substituent to avoid the synthesis of bridging imides.¹⁷ Using a bulky terphenyl substituent in combination with the di-substituted 1,1'-diamidoferrocene ligand, a terminal uranium imide was synthesized with interesting agostic interactions suggesting novel reactivity. This uranium imido and its corresponding reactivity will be discussed in detail in Chapter 1.

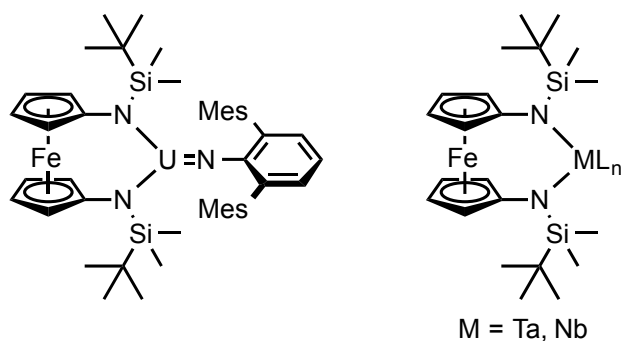


Figure 4 Target metal complexes supported by redox-active 1,1'-diamidoferrocene ligands.

Despite evidence of electronic communication between the coordinated metal centers and 1,1'-disubstituted ferrocene ligands, there are no reports showing direct reduction or oxidation between the metal center and corresponding ligand. Based upon control studies ferrocene, it appears the 1,1'-diamidoferrocene ligands reduce niobium pentachloride before coordination. Reactions between the di-substituted 1,1'-diamidoferrocene ligands and group 5 metal starting materials will further be discussed in Chapter 2.

References

- (1) Alper, H.; Arya, P.; Bourque, S. C.; Jefferson G. R.; Manzer, L. E. *Can. J. Chem.* **2010**, 78, 920.
- (2) (a) Heck, R. F. *Acc. Chem. Res.* **1979**, 12, 146. (b) Kambe, N.; Iwasaki, T.; Terao, J. *Chem. Soc. Rev.* **2011**, 40, 4937. (c) Seechurn, C. J.; Kitching, M. O.; Colacot, T. J. C.; Snieckus, V. *Angew. Chem. Int. Ed.* **2012**, 51, 5062.
- (3) For example, see: *Organotransition Metal Chemistry, from Bonding to Catalysis*; Hartwig, J. F.; University Science Books: New York, 2010.
- (4) For example, see: *Inorganic Chemistry (2nd edition)*; Miessler, G. L., Tarr, D. A.; Pearson Education, Inc. Pearson Prentice Hall: Upper Saddle River, New Jersey, 1998.
- (5) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, 85, 3533.
- (6) (a) Liu, C.; Tang, S.; Liu, S.; Yuan, S.; Zheng, L.; Meng, L.; Lei, A. *Angew. Chem. Int. Ed.* **2012**, 51, 3638. (b) Matsubara, R.; Gutierrez, A. C.; Jamison, T. F. *J. Am. Chem. Soc.* **2011**, 133, 19020. (c) Tang, S.; Liuz, C.; Lei, A. *Chem Commun.* **2013**, 49, 2442.
- (7) For examples about non-innocent ligands in Moco and cytochrome P450, see: (a) George, G. N.; Costa, C.; Moura, J. J. G.; Moura, I. *J. Am. Chem. Soc.* **1999**, 121, 2625. (b) Rittle, J.; Green, M. T. *Science* **2010**, 330, 933.
- (8) For a recent review of redox-active ligands, see: (a) Luca, O. R.; Crabtree, R. H. *Chem. Soc. Rev.* **2013**, 42, 1440. (b) Praneeth, V. K. K.; Ringenberg, M. R.; Ward, T. R. *Angew. Chem. Int. Ed.* **2012**, 51, 10228.
- (9) Broderick, E. M.; Guo, N.; Vogel, C. S.; Xu, C.; Sutter, J.; Miller, J. T.; Meyer, K.; Mehrkhodavandi, P.; Diaconescu, P. L. *J. Am. Chem. Soc.* **2011**, 133, 9278.
- (10) (a) Bouwkamp, M. W.; Bowman, A. C.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2006**, 128, 13340. (b) Sylvester, K. T.; Chirik, P. J. *J. Am. Chem. Soc.* **2009**, 131, 8772. (c) Bart, S. C.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2004**, 126, 13794. (d) Tondreau, A. M.; Atienza, C. C. H.; Weller, K. J.; Nye, S. A.; Lewis, K. M.; Delis, J. G. P.; Chirik, P. J. *Science* **2012**, 335, 567. (e) Darmon, J. M.; Stieber, C. E.; Sylvester, K. T.; Fernandez, I.; Lobkovsky, E.; Semproni, S. P.; Bill, E.; Wieghardt, K.; DeBeer, S.; Chirik, P. J. *J. Am. Chem. Soc.* **2012**, 134, 17125.
- (11) For example, see: *Compendium of Organic Synthetic Methods*; Smith, M. B.; Wiley: New York, 2001.
- (12) (a) Gunanthan, C.; Ben-David, Y.; Milstein, D. *Science* **2007**, 317, 790. (b) Kohl, S. W.; Weiner, L.; Schwartzburd, L.; Konstantinovski L.; Shimon, L. J. W.; Ben-David, Y.; Iron, M. A.; Milstein, D. *Science* **2009**, 324, 74.

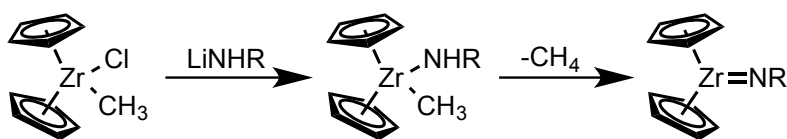
- (13) Smith, A. L.; Hardcastle, K. I.; Soper, J. D. *J. Am. Chem. Soc.* **2010**, 132, 14358.
- (14) (a) Monreal, M. J.; Diaconescu, P. L. *Organometallics* **2008**, 27, 1702. (b) Duhovic, S.; Oria, J. V.; Odoh, S. O.; Schreckenbach, G.; Batista, E. R.; Diaconescu, P. L. *Organometallics* **2013**, ASAP.
- (15) (a) Monreal, M. J.; Khan, S.; Diaconescu, P. L. *Angew. Chem. Int. Ed.* **2009**, 48, 8352. (b) Broderick, E. M.; Gutzwiller, N. P.; Diaconescu, P. L. *Organometallics* **2010**, 29, 3242.
- (16) (a) Straub, T.; Haskel, A.; Neyroud, T. G.; Kapon, M.; Botoshansky, M.; Eisen, M. S. *Organometallics* **2001**, 20, 5017. (b) Stubbert, B. D.; Marks, T. J. *J. Am. Chem. Soc.* **2007**, 129, 6149.
- (17) Spencer, L. P.; Yang, P.; Scott, B. L.; Batista, E. R.; Boncella, J. M. *Inorg. Chem.* **2009**, 48, 11615.

Chapter 1 Introduction

The field of organoactinide chemistry has grown significantly in the past decade.¹ Uranium is the most studied actinide, due the stability of uranium-238 and uranium involvement in nuclear power. Despite interest in uranium nitrides, the number of uranium multiple bonded nitrogen complexes have only increased in recent years.^{1b} The synthesis of uranium organometallic complexes has been hindered by the divergent reactivity of f-block compounds. Even in comparison to other elements within the f-block, uranium shows different modes of reactivity than the lanthanides or thorium.² Thorocene is able to reversibly bind neutral Lewis bases, while uranocene only binds anionic ligands.² Uranium is also unique in its ability to access several stable oxidation states, trivalent to hexavalent.

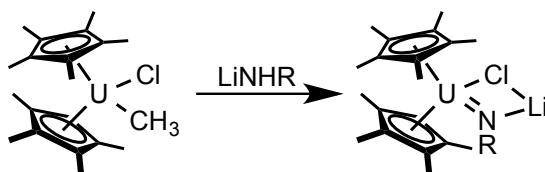
Currently, several research groups are studying f-orbital contributions and reactivity in ligand multiple bonds. Transition metal-based terminal imides are typically generated by heating an alkyl/aryl and amido containing metal complex to eliminate the alkane/arene and generate the corresponding imide (Figure 5).³ However, reacting $(\eta^5\text{-C}_5\text{Me}_5)_2\text{UMeCl}$ ($\text{Me}=\text{CH}_3$) with a lithium amide should generate the amido ligand but instead results in methane evolution rather than lithium chloride elimination.⁴ Thermolysis of the related compound $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}(\text{NHPh})_2$ ($\text{Ph} = \text{C}_6\text{H}_5$) also failed to produce the imide.⁴

a common route to a terminal early transition metal imide



Walsh, P. J.; et al. *J. Am. Chem. Soc.* **1988**, 110, 8729.

the same reaction with lithium/potassium amides result in salt formation



Arney, D. S. J.; Burns, C. J. *J. Am. Chem. Soc.* **1995**, 117, 9448.

Figure 5 Synthetic routes to install terminal imides on uranium(IV) versus zirconium(IV).

Despite these complications, several routes for synthesizing uranium imides have been developed. Salt metathesis of uranium tetrachloride with lithium amides generates a trans-bis(imide) complex, due to the inverse trans effect.^{5a} Using two bulky tridentate hydrotris(3,5-dimethylpyrazolyl)borate ligands, benzyl elimination could be initiated through the introduction of organic azides, resulting in uranium-imide formation.^{5b} Other methods to synthesize uranium-imides involve the use of reduced uranium starting materials, such as the reduction of diazenes/azides with uranium(III) or inverse sandwich complexes.^{5c,d} Despite the recent growth of complexes containing a uranium-imido bond, their corresponding reactivity remains undeveloped. The covalent nature of the uranium nitrogen double bond is assumed to affect the reactivity.⁶

Current literature is limited to reactions involving imido exchange, hydroamination of alkynes and alkenes, carbon dioxide activation, intramolecular C-H activation, and the cleavage of diphenyl dichalcogenides.⁷ For example, $(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr(=NR)}$ activates benzene C-H bonds intermolecularly while the related $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U(=NAd)}_2$ (Ad = $\text{C}_{10}\text{H}_{15}$) only intramolecularly C-H activates the pentamethylcyclopentadienyl ligand (Figure 6).^{3a,7g} Recently, the Diaconescu group discovered a novel terminal uranium imide featuring agostic interactions between the terphenyl substituent and uranium metal center. This agostic interaction in combination with the use of 1,1'-diamidoferrocene ligands was hypothesized to lead to new reactivity of uranium-imido complexes. The use of redox-active ligands on uranium is currently limited primarily to the use of α -diimine and bis(imine)pyridine ligands.⁸

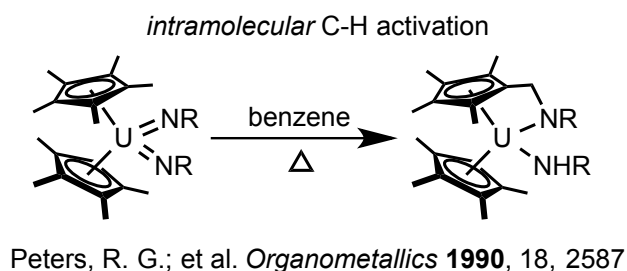
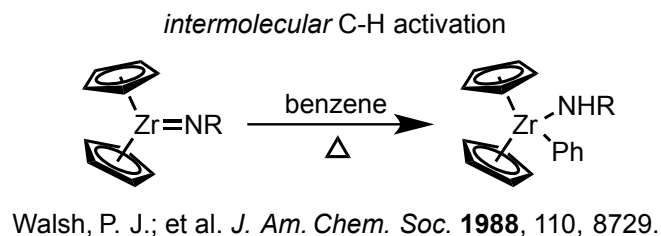


Figure 6 Exemplifying the divergent reactivity between uranium(IV)-imides and zirconium(IV)-imides.

Ligand Synthesis

Following previous reports by Arnold et al., the Diaconescu group synthesized several derivatives of 1,1'-diamidoferrocene ligands (Figure 7).^{9,10} Both cyclopentadiene rings of ferrocene are lithiated by the slow addition of *n*-butyl lithium in the presence of tetramethylethylenediamine (TMEDA). 1,1'-dilithioferrocene is suspended in diethyl ether, cooled to -78 °C, and diluted tetrabromoethane (TBE) is added dropwise to the cooled reaction mixture. The reaction mixture is slowly warmed to room temperature and allowed to react overnight, generating the product 1,1'-dibromoferrocene **B**. The reaction was quenched with water, extracted with diethyl ether, and the dark red product was crystallized in boiling methanol.

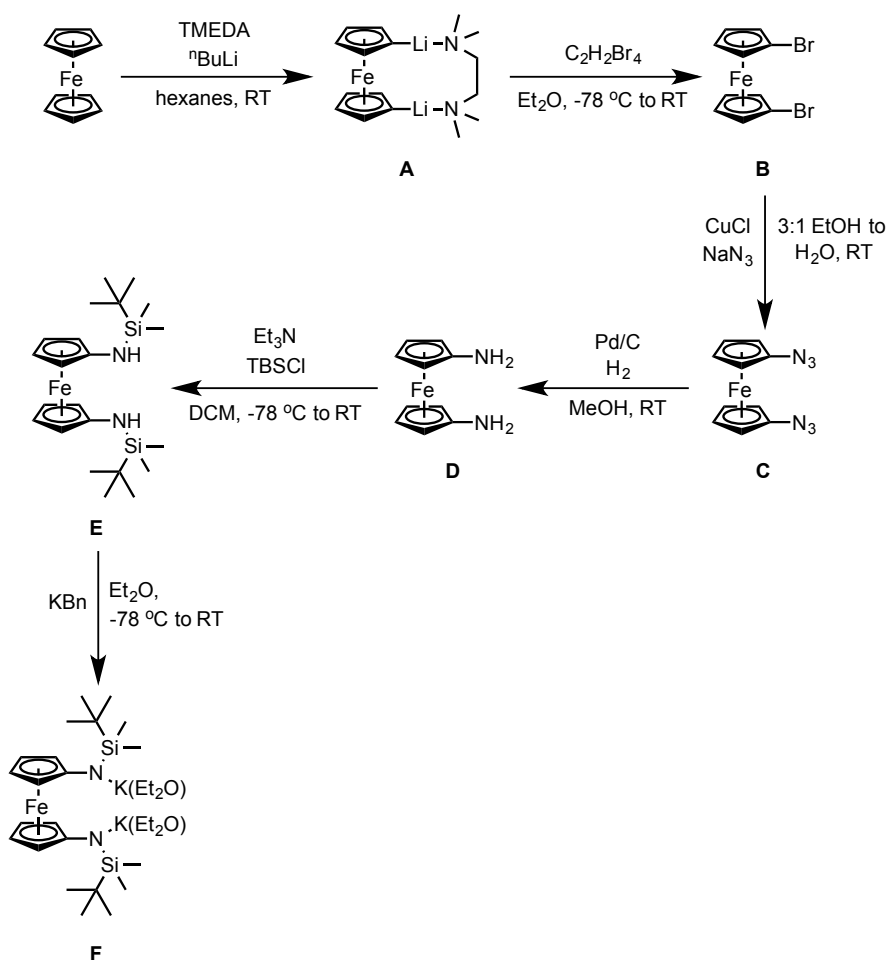


Figure 7 Synthetic route to potassium salt of the ligand, **F**.

The catalytic system of copper(I) chloride and sodium azide are used to generate the diazidoferrocene product over 48 hours. After two days, the reaction is filtered and hexanes are used to extract the product from the solid filtrate. The crimson red product was crystallized in diethyl ether. The corresponding amine is then generated via hydrogenation with palladium on carbon in methanol. The resulting oxygen-sensitive, yellow 1,1'-diamineferrocene (**D**) compound is purified with several diethyl ether washes. All subsequent manipulations and reactions are carried out under a nitrogen atmosphere due to oxygen and water sensitivity.

To synthesize the silyl substituted 1,1'-diamineferrocene, **E**, triethyl amine and *tert*-butyldimethylsilyl chloride in dichloromethane were added to a frozen dichloromethane solution of 1,1'-diamineferrocene.⁹ The ammonium chloride salt was easily removed by drying the reaction mixture and then extracting the product with hexanes. The red-orange silyl substituted 1,1'-diamineferrocene required no further purification.

Uranium Reactions

The synthesis of the uranium complex supported by the 1,1'-diamidoferrocene, **G**, required the addition of the potassium ligand salt to a frozen THF solution of excess uranium tetraiodide (Figure 8).¹¹ When uranium tetraiodide is added to the ligand salt, the bis(ligand) (bis(ligand) = two 1,1'-diamidoferrocene ligands on one uranium metal center) complex forms. When performed at higher concentrations, the yield decreases significantly due to increased bis(ligand) complex formation with ligand redistribution.^{5d} The uranium complex is then reduced to the inverse sandwich complex, **H**, using potassium graphite in toluene over 24 h, although reaction times up to 48 h are sometimes required.¹² The reaction mixture requires monitoring via ¹H NMR spectroscopy to ensure consumption of the uranium starting material. The yields of the inverse sandwich complex are highly variable (about 40-75 %) despite using potassium graphite

from the same batch. Due to the unreliability of potassium graphite, we investigated using potassium. With potassium as the reducing agent, the bis(ligand) uranium complex is exclusively formed within minutes. The slower reaction times with potassium graphite might be required to allow for the proper orientation to form of inverse sandwich complex, although the mechanism for inverse sandwich compound formation remains unclear.¹³

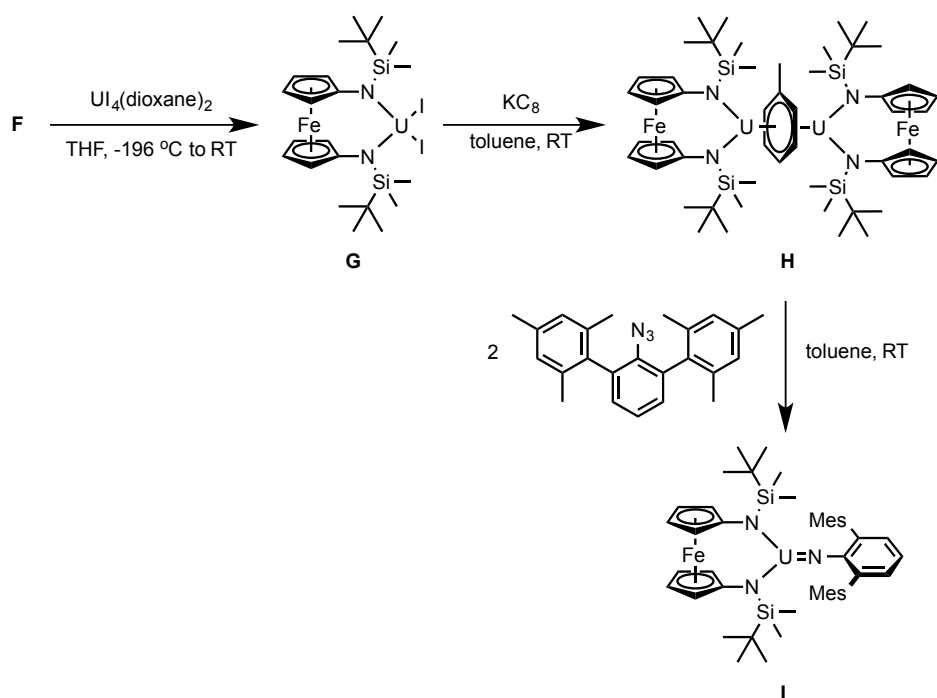


Figure 8 Synthetic route to uranium-imide complex, **I**.

The terminal uranium-imido complex, **I**, was synthesized by reacting the uranium inverse sandwich complex **H** with 2,6-dimesitylphenyl azide (Figure 8). The bulky 2,6-dimesitylphenyl amide and related terphenyl ligands have been previously utilized to stabilize two and three coordinate geometries around highly reactive early transition metals.¹⁴ Due to the large ionic radii of uranium, a large imide substituent is required to synthesize a terminal imide with the

small 1,1'-diamidoferrocene ligands and prevent imide bridging between uranium metal centers. A new unknown product, observable by ^1H NMR spectroscopy, was formed while heating the uranium-imido complex to 85 °C overnight in benzene- d_6 . Unfortunately, even heating for an extended time period (up to a week) did not force the reaction to reach completion. Attempting to drive the reaction to completion by heating to higher temperatures, was also unsuccessful. The unknown product was unable to be purified due to similar solubility of the starting uranium-imido and unknown product. Due to the unprecedented agostic interactions observed in the X-ray crystal structure between the uranium metal center and a mesityl group from the imide ligand, the unknown product was hypothesized to be the C-H activation product of benzene, analogous to the previously mentioned $(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(=\text{NR})$ 1,2-addition.^{3a}

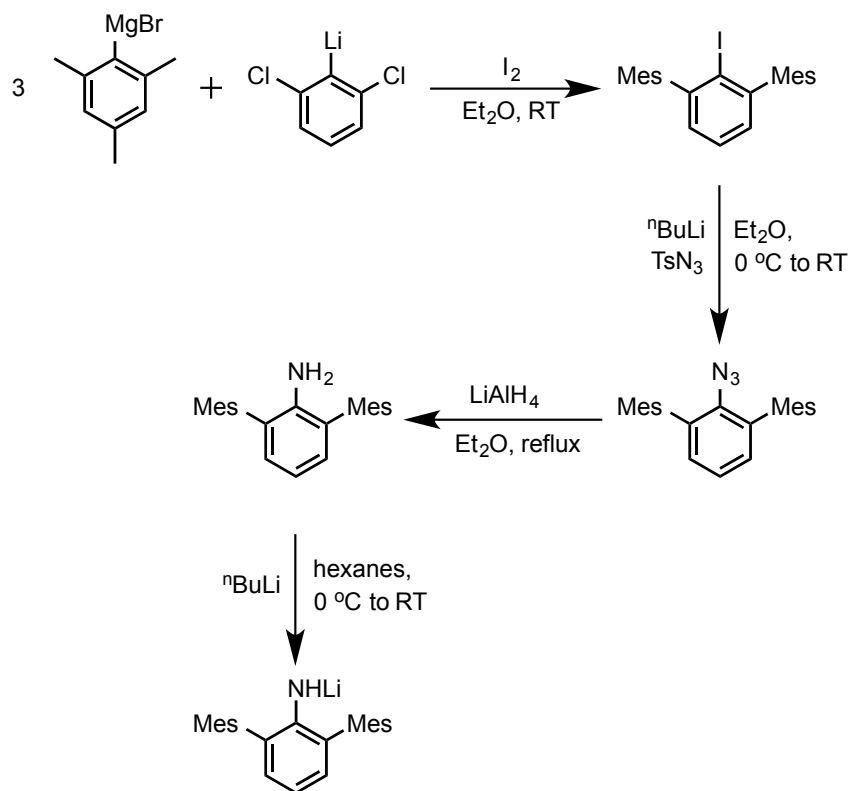


Figure 9 Synthesis of terphenyl ligand.¹⁵

In order to identify if C-H activation was occurring, the proposed uranium intermediates of the proposed C-H activation were generated and the ^1H NMR spectra were compared. The lithium amide was synthesized via a multi-step synthetic procedure from Tilley et al. (Figure 9).^{15,17} 2,6-dichlorobenzene was lithiated at the one-position using *n*-butyl lithium at reduced temperatures. The Grignard derived from 2-bromomesitylene was added and the reaction mixture was allowed to stir overnight. After refluxing the reaction mixture for 2 hours, the reaction was quenched with excess iodine in diethyl ether.

To exchange the iodide with azide, 2,6-dimesitylphenyl iodide was lithiated with *n*-butyl lithium.¹⁷ Salt metathesis between 2,6-dimesitylphenyl iodide and *p*-toluenesulfonyl azide generated the azide-substituted terphenyl. Although the product, 2,6-dimesitylphenyl azide, is not heat sensitive, both azides are light sensitive thus the reaction was shielded from both heat and light. To exemplify the stability of 2,6-dimesitylphenyl azide, reduction of the azide to an amine requires the use of lithium aluminum hydride heated to reflux.¹⁷ From the amine, *n*-butyl lithium or potassium benzyl was used to form lithium amide or potassium amide, respectively.¹⁷ Unfortunately, subsequent salt metatheses reactions using the potassium amide and phenyl lithium gave a ^1H NMR spectra unlike the spectra seen when heating the original uranium-imide complex in benzene.

The C-H activating potential of the uranium-imide was evaluated using different substrates. Toluene contains a weak benzylic proton that is easily removed in the presence of organometallic reagents. Heating the uranium-imide complex in toluene resulted in the same ^1H NMR spectra as heating in benzene, although the ^1H NMR spectra are expected to be similar albeit the presence of methylene protons. To determine if C-H activation occurred, the uranium-imide was allowed to react in the presence of cyclohexane or 1,4-cyclohexadiene. While 1,4-

cyclohexadiene has shown high reactivity in C-H activation, cyclohexane rarely undergoes C-H activation.¹⁸ Unfortunately, reactions with both substrates led to very similar ¹H NMR spectra. Thus we conclude the unknown uranium product is not forming via an *intermolecular* C-H activation reaction.

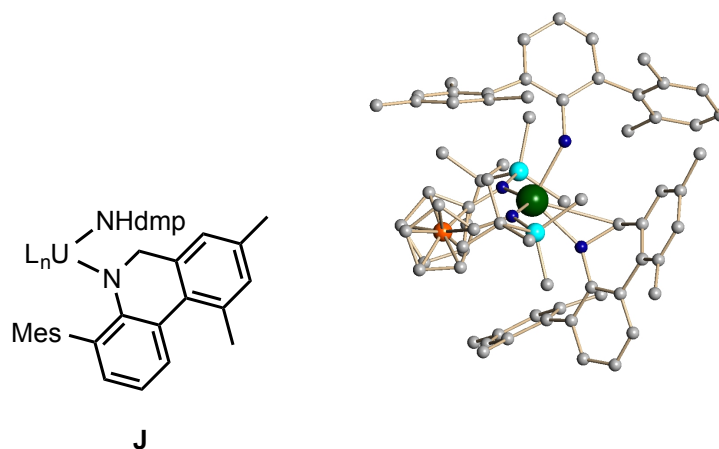


Figure 10 Formation of N-heterocycle **J**. Unrefined X-ray crystal structure is shown to the right, showing two terphenyl ligands can fit around the uranium metal center.

Interestingly, *intramolecular* C-H activation does occur when two eq of 2,6-dimesitylphenyl azide was used, generating a N-heterocycle (Figure 10). The second equivalent of azide was expected to coordinate to the uranium metal center after the initial formation of the uranium-imide complex. Dinitrogen was readily lost, generating a reactive nitrogen species that then C-H activates the methyl contained on the mesityl ring of the terphenyl ligand, generating the N-heterocycle. This C-H activation can also be viewed as a formal 1,2-addition across the

uranium nitrogen double bond. This is similar to the reported *intramolecular* C-H activation shown in Figure 6.^{7g}

In exploring additional reactivity, the uranium-imide complex is shown to be sensitive to compounds containing an acidic proton, such as *tert*-butyl alcohol, phenol, and aniline. These reactions result solely in the formation of protonated ligand and 2,6-dimesitylphenyl amine. No reaction is observed with internal alkynes (which can be attributed to the steric bulk of the 2,6-dimesitylphenyl substituent), alkylsilyl halides, or white phosphorus. However, a reaction did occur between the uranium-imide complex and one equivalent of elemental sulfur. Boncella et al. previously observed the oxidative addition of elemental sulfur and selenium across a dimer of uranium(V) imides yielding bridged chalcogenide species.¹⁹ Interestingly, the ¹H NMR spectra obtained was diamagnetic suggesting the formation of a uranium(VI) species, but despite many attempts a solid state structure to aid interpretation has not been obtained.

Conclusion

A novel, terminal uranium-imide complex with a redox-active ligand was synthesized and characterized by X-ray crystallography and ¹H NMR spectroscopy. While no *intermolecular* C-H bond activation occurred with small molecules, *intramolecular* C-H bond activation of the terphenyl substituent was reported and characterized by X-ray crystallography, ¹H NMR spectroscopy, and elemental analysis. Progress in reactivity studies was seen in reactions with elemental sulfur and future research directions should focus on characterizing the mentioned reaction product. Future NMR spectroscopy experiments should also be performed to assign proton signals for both the terminal uranium imide complex and *intramolecular* C-H bond activation product.

Supporting Information

Materials and Methods

Unless otherwise stated, reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques or in an MBraun inert-gas glovebox. Solvents were purified using a two-column solid-state purification system developed by Grubbs and transferred into the glovebox via Schlenk bomb. NMR solvents were purchased from Cambridge Isotope Laboratories, degassed, and stored over 4 Å molecular sieves until use. Uranium turnings were purchased from Argonne National Laboratories. Potassium graphite was obtained from the Kaner Laboratory (UCLA). Compounds **A-F**,⁹ **G**,¹⁰ **H**,¹¹ *p*-toluenesulfonyl azide,²⁰ lithium 2,6-dimesitylphenyl amide,¹⁷ and $\text{UI}_4(\text{dioxane})_2$ ²¹ were prepared using published procedures. All other materials were used as received. ¹H NMR spectra were recorded on Bruker300 spectrometers at room temperature in C₆D₆ or CDCl₃. Chemicals shifts are reported with respect to solvent residual peaks, 7.16 ppm for C₆D₆ and 7.26 for CDCl₃. Elemental analyses was performed on an Exeter Analytical, Inc. CE-440 Elemental Analyzer.

Experimental Procedures

Synthesis of $\text{UI}_4(\text{dioxane})_2$. In a glovebox, a Schlenk tube was charged with a stir bar, nitric acid-washed uranium turnings (1.199 g, 5.03 mmol), iodine (2.352 g, 9.33 mmol, 2.1 eq), and 6 mL of *p*-dioxane. The reaction mixture was sealed, taken out of the glovebox, and heated to 50 °C overnight. The Schlenk tube was returned to the glovebox and the resulting suspension was filtered through a medium-porosity fritted filter, collecting the red-orange solid. The solid was washed with hexanes until the filtrate became colorless, and the solid was dried under vacuum. Yield: 4.62 g, 90 %.

Synthesis of *p*-toluenesulfonyl azide. A solution of *p*-toluenesulfonyl chloride (13.180 g, 69.13 mmol) in 70 mL of 100 % ethanol was heated to 45 °C. Sodium azide (5.098 g, 78.43 mmol, 1.1 eq) was dissolved in 30 mL of 90 % aqueous ethanol. The heated *p*-toluenesulfonyl chloride solution was added to the sodium azide solution. Sodium chloride precipitated from the reaction mixture following the addition and the reaction mixture was allowed to stir for 2.5 hours.

Sodium chloride was removed via filtration with a Buchner funnel, and the volume was reduced using a rotary evaporator at 35 °C. The resulting residue was washed with 85 mL then two 15 mL portions of water and dried over magnesium sulfate. Yield: 11.451 g, 84 %. Characterization consistent with reported literature values.²⁰

Synthesis of 2,6-dimesitylphenyl iodide. A solution of 1,3-dichlorobenzene (5.0351 g, 0.0342 mol) in 85 mL THF was cooled to -70 °C for 30 min. Over 20 min, *n*-butyl lithium (13.7 mL, 0.1454 mol, 2.5 M in hexanes) was added and the reaction mixture was allowed to stir for 1.5 hours. While the reaction mixture was stirring, magnesium turnings (24.96 g, 1.0140 mol, 10 eq) were activated with iodine in THF. A solution of 2-bromomesitylene (20.457 g, 0.1027 mol) in THF was slowly added to the magnesium suspension, to generate the corresponding Grignard *in situ*. The Grignard was added to the lithium salt mixture at -70 °C and the reaction mixture was warmed to room temperature. After stirring overnight, the reaction was quenched with excess iodine in diethyl ether. After refluxing for 2 h, the solution was washed with aqueous sodium sulfite, followed by three diethyl ether extractions. The organics were combined and washed with water, brine, and then dried over magnesium sulfate. After removing solvent under vacuum, the crude solid was dissolved in boiling hexanes and crystallized at -35 °C. The crystals were decanted and washed with diethyl ether to yield a white solid (6.215 g, 41.2 %). Characterization consistent with reported literature values.¹⁵

Synthesis of 2,6-dimesitylphenyl azide. A solution of *n*-butyl lithium (3.5 mL, 37.15 mmol, 2.5 M in hexanes) was added dropwise to a slurry of 2,6-dimesitylphenyl iodide (3.389 g, 7.69 mmol) in hexanes at 0 °C. The yellow slurry was warmed to room temperature and allowed to stir for an additional 16 h. A solution of *p*-toluenesulfonyl azide (1.920 g, 9.74 mmol, 1.2 eq) in diethyl ether was added dropwise at 0 °C. After stirring for 2 h at 0 °C, the reaction was quenched with water. The aqueous phase was separated and extracted three times with diethyl ether. The organic phases were combined, washed with water and dried over magnesium sulfate. After drying, the solid residue was crystallized from diethyl ether at -35 °C. Solvent was decanted and the remaining yellow solid was dried (1.969 g, 72 %). Characterization consistent with reported literature values.¹⁷

Synthesis of 2,6-dimesitylphenyl amine. A solution of 2,6-dimesitylphenyl azide (1.346 g, 3.78 mmol) in diethyl ether was added dropwise to a stirred diethyl ether mixture of lithium aluminum hydride (743.8 mg, 19.59 mmol, 5 eq). After refluxing for 4.5 h, the solution was then cooled to room temperature and quenched with diethyl ether. Filtration through a medium-porosity fritted filter, followed by separation of aqueous phase. The organics were dried over magnesium sulfate and the solvents were removed in vacuum. Solid was crystallized from diethyl ether at -35 °C. Solvent was decanted and the remaining white solid was dried (953.6 mg, 76.4 %). Characterization consistent with reported literature values.¹⁷

Synthesis of potassium 2,6-dimesitylphenyl amide. A slurry of potassium benzyl (36.5 mg, 0.28 mmol) was added to a solution of 2,6-dimesitylphenyl amine (90.0 mg, 0.27 mmol) in diethyl ether at -35 °C. After stirring for 2 h, the solvent was removed under vacuum to yield a light yellow powder (93.3 mg, 92.9 %). Characterization was consistent with similarly reported lithium 2,6-dimesitylphenyl amide.¹⁷

Synthesis of phenyl lithium. A solution of *n*-butyl lithium (2.09 mL, 22.18 mmol, 2.5 M in hexanes) was added to a solution of phenyl iodide (1.0697 g, 5.24 mmol) in diethyl ether at 0 °C. After stirring for 30 min, solvents were removed under vacuum. Washed the solid with hexanes and dried. Yield: 181.8 mg, 93.7 %. ¹H NMR (300 MHz, C₆D₆), δ (ppm): 8.36 (d, 2H, Ph), 7.22 (m, 3H, Ph), 2.98 (q, 4H, C₂H₄O), 0.58 (t, 6H, C₂H₆).

Synthesis of 1,1'-dilithioferrocene, A (Figure 7). A solution of *n*-butyl lithium (74.91 mL, 0.79 mmol, 2.5 M in hexanes, 2 eq) was added dropwise to a solution of ferrocene (20.000 g, 0.1075 mol) and TMEDA (14.994 g, 0.1290 mol, 1.2 eq) in 200 mL of hexanes. After stirring overnight, the solution was filtered through medium-porosity fritted filter, washed with hexanes until the filtrate was colorless, and dried under vacuum to give a pale orange solid (28.600 g, 84.7 %).⁹

Synthesis of 1,1'-dibromoferrocene, B (Figure 7). A solution of TBE (69.310 g, 0.2005 mol, 2.2 eq) in 90 mL of diethyl ether was added dropwise to a solution of 1,1'-dilithioferrocene (28.600 g, 0.0911 mol) in 250 mL of diethyl ether at -70 °C over the course of 30 min. After stirring at -70 °C for 2 h, the reaction was warmed to room temperature and stirred overnight. The reaction was quenched with water and filtered through Celite. After phase separation, the water layer was extracted with diethyl ether three times. The organic phases were collected and dried over magnesium sulfate. After removing solvents under vacuum, the resulting oily red residue was dissolved in boiling methanol and set at -35 °C to crystallize. The solvent was decanted to yield dark red crystals (22.323 g, 71 %). Characterization consistent with reported literature values.⁹

Synthesis of 1,1'-diazidoferrocene, C (Figure 7). 1,1'-dibromoferrocene (10.270 g, 0.0298 mol) and copper(I) chloride (6.357 g, 0.0642 mol, 2.15 eq) were dissolved in 95 % ethanol.

Sodium azide (8.152 g, 0.1254 mol, 4 eq) was dissolved in minimal water, and added to the 1,1'-dibromoferrocene solution. Immediately, the solution turned brown. The reaction mixture was vented and stirred for 48 h, while being shielded from light. The reaction mixture was quenched with water and filtered through Celite. The filtrate was extracted three times with hexanes. The solid collected on the Celite was then extracted with hexanes until the filtrate was colorless. The organic phases were combined and dried over magnesium sulfate. Solvent was removed under vacuum and the red residue was crystallized in diethyl ether at -35 °C. The solvent was decanted to yield red crystals. Yield: 3.580 g, 44 %. Characterization consistent with reported literature values.⁹

Synthesis of 1,1'-diamineferrocene, D (Figure 7). In a glovebox, a Schlenk tube was charged with a stir bar, 1,1'-diazidoferrrocene (2.394 g, 0.0088 mol), spatula tip full of palladium on carbon, and methanol. The sealed Schlenk tube was removed and connected to a hydrogen line. Over the course of two days, six cycles of evacuating and refilling the Schlenk tube with hydrogen were performed. After the tube was brought back into the glovebox, the solution was filtered through Celite. The solvent was removed under vacuum and the solid was washed with diethyl ether until filtrate was golden. After removing solvent, the yellow solid was generated. Yield: 1.666 g, 87 %. Characterization consistent with reported literature values.⁹

Synthesis of E (Figure 7). A solution of *tert*-butyldimethylsilyl chloride (3.556 g, 23.59 mmol, 3 eq) and triethyl amine (1.761 g, 17.40 mmol, 2.25 eq) in dichloromethane was slowly added to a frozen solution of 1,1'-diamineferrocene (1.666 g, 7.71 mmol). The reaction mixture was allowed to stir overnight. Solvent was removed, the solid was extracted with hexanes, and filtered through Celite to yield a red solution. Drying the solution gave a red-orange solid (2.245 g, 65 %). Characterization consistent with reported literature values.⁹

Synthesis of F (Figure 7). Solid potassium benzyl (505.8 mg, 3.88 mmol, 2 eq to synthesize a terminal imide using the small 1,1'-diamidoferrocene ligands) was added to a frozen solution of **E** (866.3 mg, 1.94 mmol) in diethyl ether. After stirring for 6 h, solvent was removed under vacuum. The red solid was washed with hexanes and dried to yield a light red solid (912.5 mg, 70 %).¹⁰

Synthesis of G (Figure 8). A solution of **F** (806.4 mg, 1.20 mmol, 0.9 eq) in THF was added to a frozen solution of $\text{UI}_4(\text{dioxane})_2$ (1.245 g, 1.35 mmol) in THF. Initially, the solution turned purple, but after 1.5 hours the color changed to light brown. After stirring for 3 h, solvent was removed under vacuum and the solid was extracted with toluene. After filtering through Celite, solvent was removed. A second extraction by toluene, filtering through Celite, and drying was performed. The solid was washed with hexanes and dried, resulting in a light yellowish-brown solid (1.057 g, 87 %). Characterization consistent with reported literature values.¹¹

Synthesis of H (Figure 8). A slurry of potassium graphite (295.2 mg, 2.18 mmol, 4 eq) in toluene was added to a solution of **G** (530.2 mg, 0.52 mmol) in toluene. The reaction mixture was allowed to stir at room temperature for 24 to 48 h. After 24 h, aliquots were taken to measure reaction completion via disappearance of starting material. The solution was filtered through Celite, dried under vacuum, and washed with hexanes. After drying, an ash-black solid was generated (232.1 mg, 60 %). Characterization consistent with reported literature values.¹²

Synthesis of I (Figure 8). A solution of 2,6-dimesitylphenyl azide (56.2 mg, 0.15 mmol, 2 eq) in toluene was added to a solution of **H** (101.9 mg, 0.07 mmol) in toluene. The reaction reached completion immediately upon addition of the terphenyl azide. Solvent was removed under vacuum, dissolved in hexane and filtered through Celite. After drying, a redish-brown solid formed (126.0 mg, 89 %).

Note: Dr. Monreal initially discovered and crystallized complex I. However, specific synthetic conditions could not be found. Thus the reaction was optimized again including modification of reaction time and solvents.

Attempted synthesis of H using potassium metal. A solution of **H** (118.4 mg, 0.11 mmol) in toluene was added to a potassium mirror (18.4 mg, 0.47 mmol, 4 eq). After stirring for 15 min, an aliquot was taken and dried. ^1H NMR showed the formation of the uranium bis(ligand) complex. Characterization consistent with reported literature values.¹⁰

Attempted synthesis of uranium-amide monoiodide. A melt solution of potassium 2,6-dimesitylphenyl amide (36.3 mg, 0.09 mmol) in diethyl ether was added to a frozen solution of **G** (99.1 mg, 0.09 mmol) in diethyl ether. After stirring for 3 hours, the solution was filtered through Celite and solvent was removed under vacuum. The product was extracted in hexanes, filtered through Celite, and dried, yielding a redish-brown solid (72.0 mg, 64.5 %). A similar result is given when lithium 2,6-dimesitylphenyl amide is used. ^1H NMR spectrum has not been interpreted.

Attempted synthesis of phenyl uranium-amide. A solution of uranium-amide monoiodide (43.0 mg, 0.03 mmol) in diethyl ether was added to a solution of phenyl lithium (4.7 mg, 0.03) in diethyl ether. Reaction was immediately dried and ^1H NMR was taken revealing a different spectrum compared to the spectrum of heating the uranium-imide in benzene. ^1H NMR spectrum has not been interpreted.

Synthesis of J (Figure 8). A solution of 2,6-dimesitylphenyl azide (53.9 mg, 0.15 mmol, 4 eq) in toluene was added to a solution of **H** (54.2 mg, 0.03 mmol) in toluene. The reaction was allowed to stir at room temperature for 2 h. Solvent was removed under vacuum, dissolved in hexane and

filtered through Celite. After drying, a redish-brown solid formed (97.2 mg, 64 %). Anal. calcd. for $C_{76}H_{102}FeN_4Si_2U$: C, 64.21%; H, 7.23%; N, 3.93%. Found: C, 63.45%; H, 7.44%; N, 3.72%.

Note, Professor Paula L. Diaconescu mounted and collected data for complex J, while Dr. Saeed I. Khan solved the X-ray crystal structure. Elemental analysis was performed by Brianna Upton.

General Procedure for uranium-imide reactions.

Uranium-imide complex, generated *in-situ* (1 eq), and substrate (1 eq) were combined in 0.7 mL of C_6D_6 (toluene was used for C-H activation of toluene and cyclohexane- d_{12} was used for C-H activation with cyclohexane). Also, monitoring of the C-H activation reactions were done after heating the sample to 85 °C. Reactions were monitored via 1H NMR spectroscopy starting from zero to four hours.

Details for reaction between J and benzene- d_6 . 1H NMR shows characteristic peaks for **I** as well as for an unknown product(s).

Details for reaction between J and toluene. 1H NMR shows characteristic peaks for **I** as well as for an unknown product(s). While the reaction is in not in a deuterated solvent, peaks outside of 0-10 ppm are similar to the reaction between **I** and benzene- d_6 .

Details for reaction between J and 1,4-cyclohexadiene. 1H NMR shows characteristic peaks for **I** and an unknown product(s). The 1H NMR spectrum pattern is similar to the reaction between **I** and benzene- d_6 .

Details for reaction between J and cyclohexane- d_{12} . 1H NMR shows characteristic peaks for **I** and an unknown product(s). The 1H NMR spectrum pattern is similar to the reaction between **I** and benzene- d_6 .

Details for reaction between J and diphenylacetylene. 1H NMR shows characteristic peaks for **I** and for diphenylacetylene.

Details for reaction between J and white phosphorus. ^1H NMR shows characteristic peaks for **I**.

Details for reaction between J and trimethylsilyl chloride. ^1H NMR shows characteristic peaks for **I**, as well as for trimethylsilyl chloride.

Details for reaction between J and *tert*-butyl alcohol. ^1H NMR shows protonated ligand⁹ and 2,6-dimesitylphenyl amine.¹⁷

Details for reaction between J and phenol. ^1H NMR shows protonated ligand⁹ and 2,6-dimesitylphenyl amine.¹⁷

Details for reaction between J and aniline. ^1H NMR shows protonated ligand⁹ and 2,6-dimesitylphenyl amine.¹⁷

Details for reaction between J and sulfur. ^1H NMR shows new unknown product formation.

Appendix

^1H NMR spectra

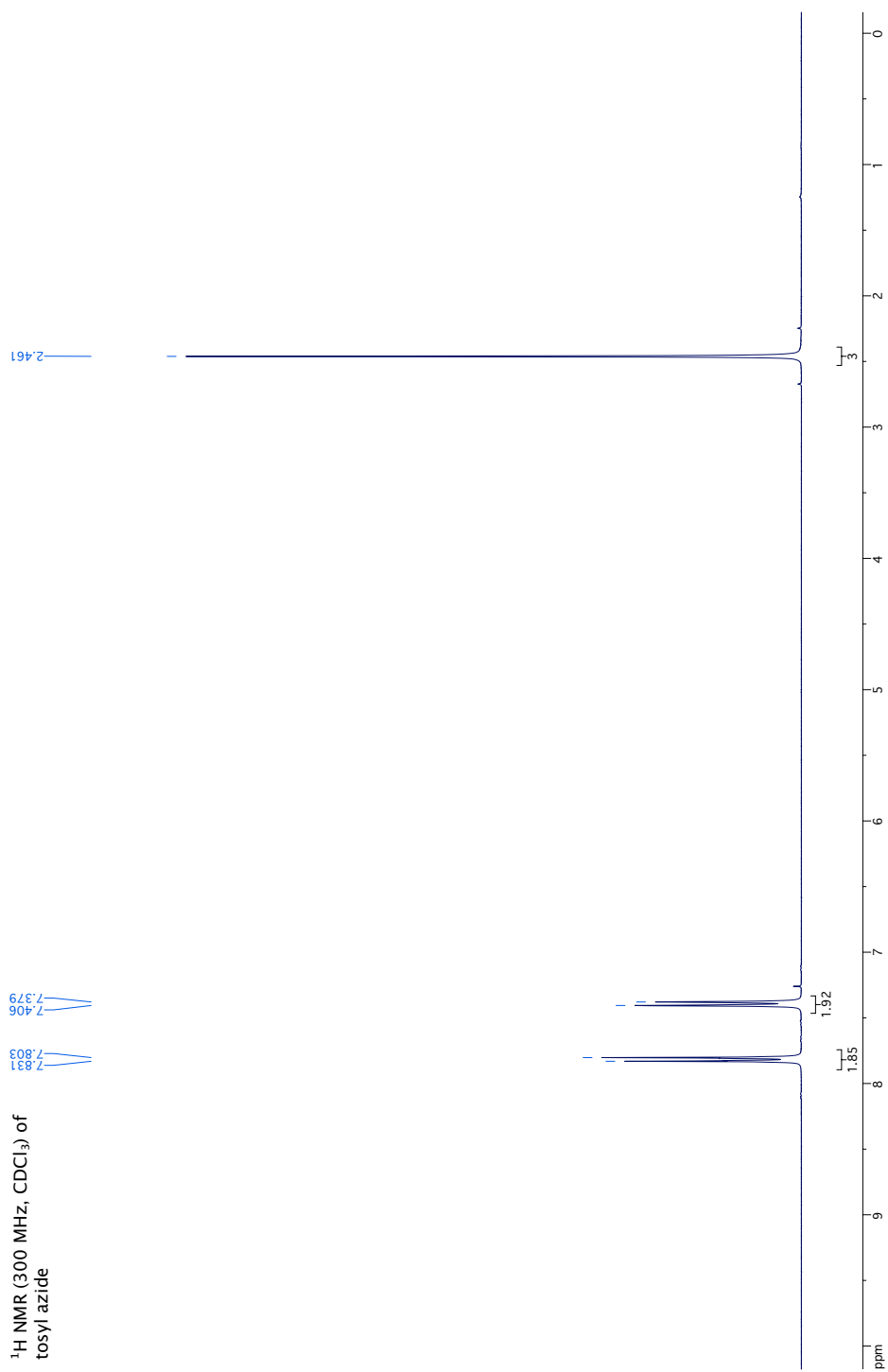


Figure A1 ¹H NMR (300 MHz, CDCl₃) of tosyl azide.

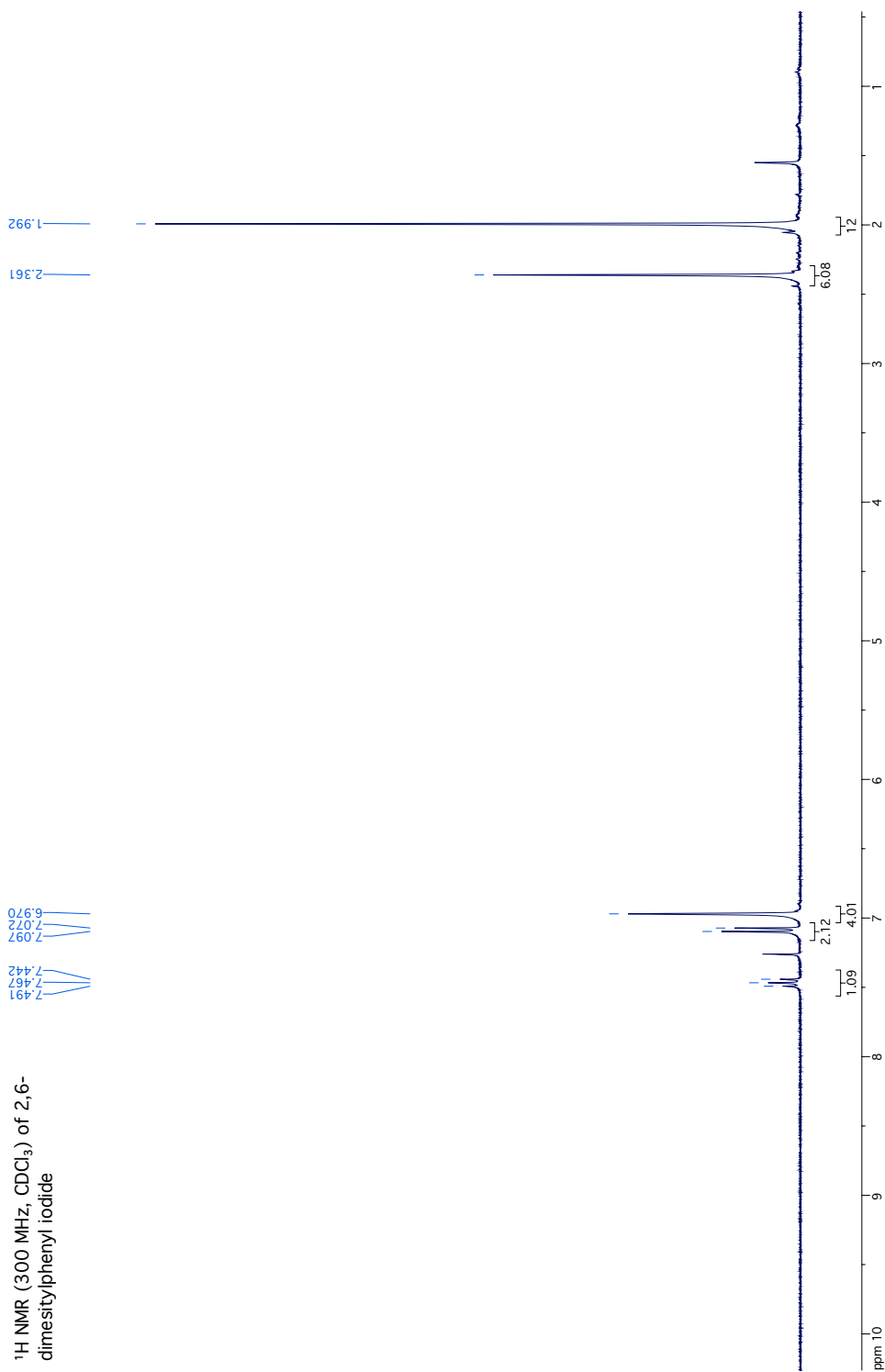


Figure A2 ¹H NMR (300 MHz, CDCl₃) of 2,6-dimesitylphenyl iodide.

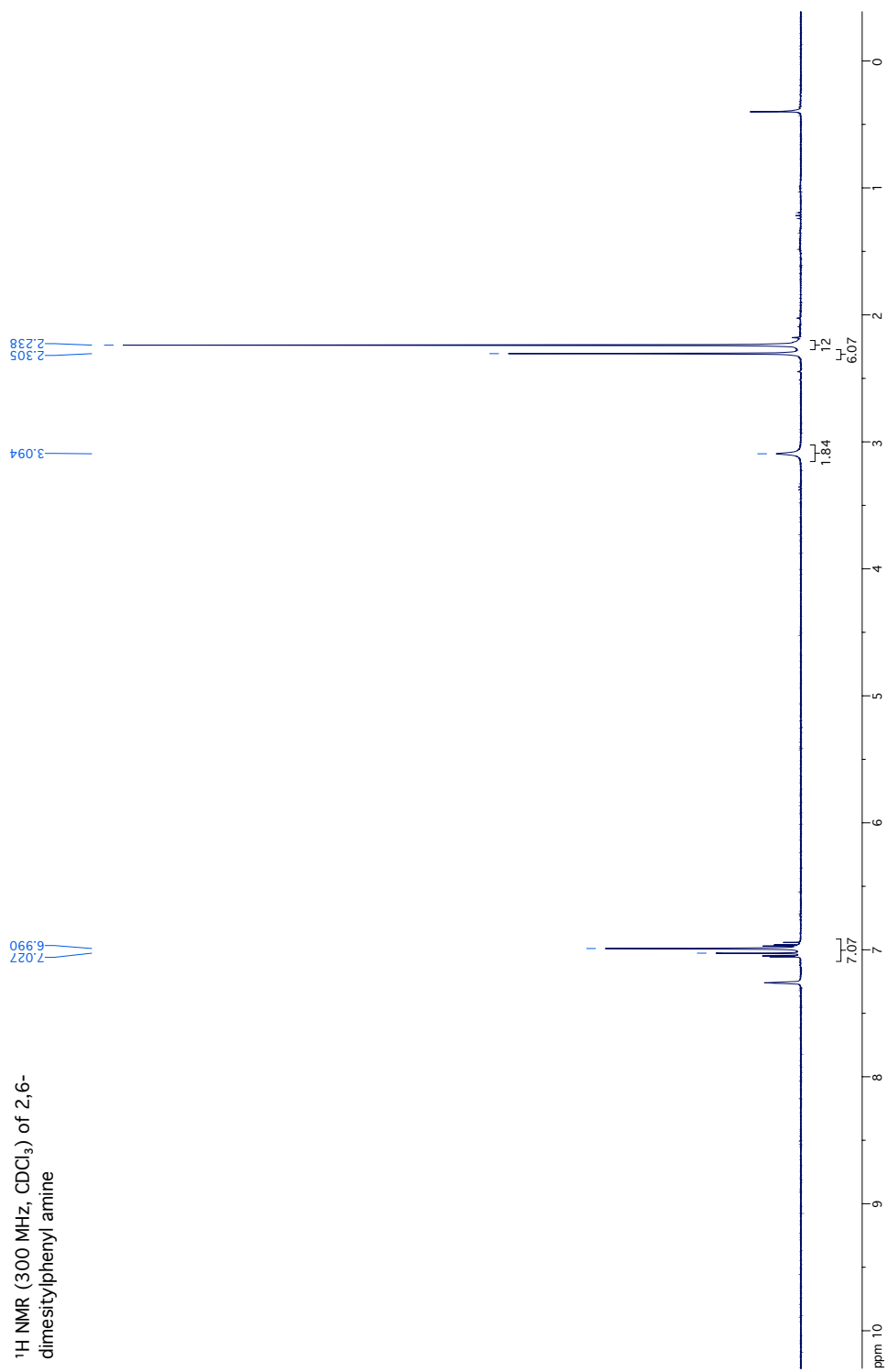


Figure A4 ¹H NMR (300 MHz, CDCl₃) of 2,6-dimesitylphenyl amine.

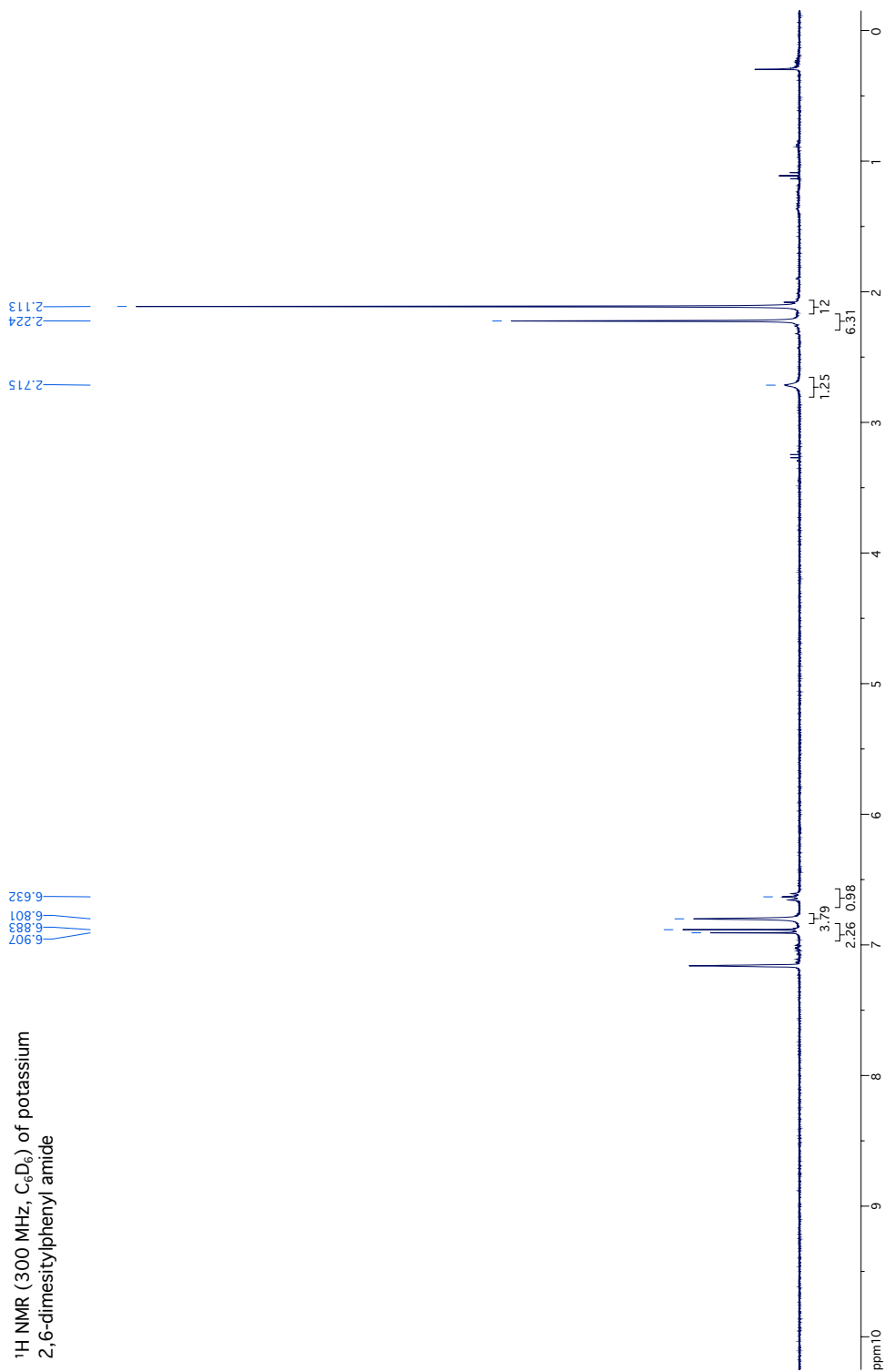
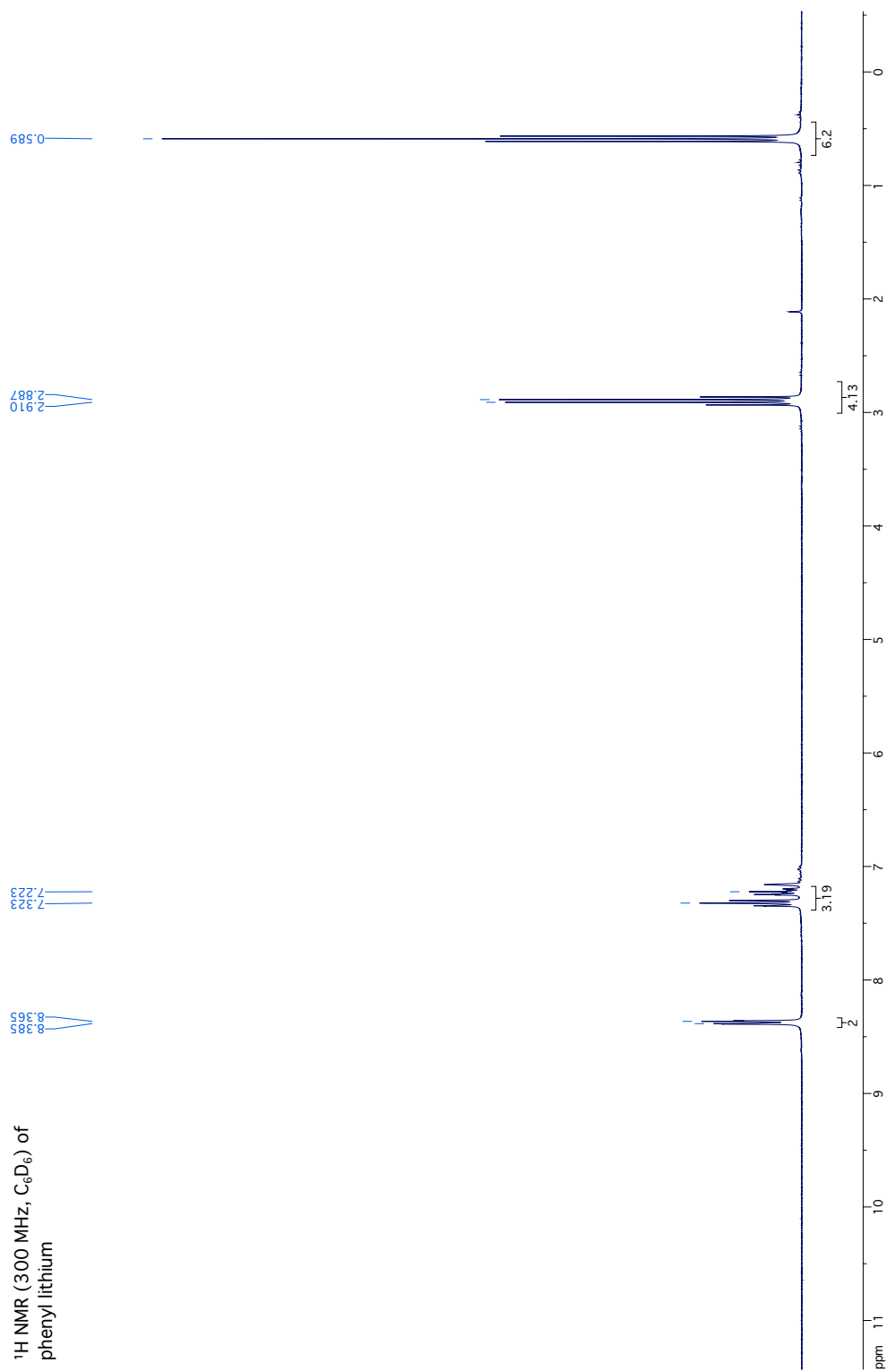


Figure A5 ¹H NMR (300 MHz, C₆D₆) of potassium 2,6-dimesitylphenyl amide.



¹H NMR (300 MHz, C₆D₆) of 1,1'-
dibromoferrocene

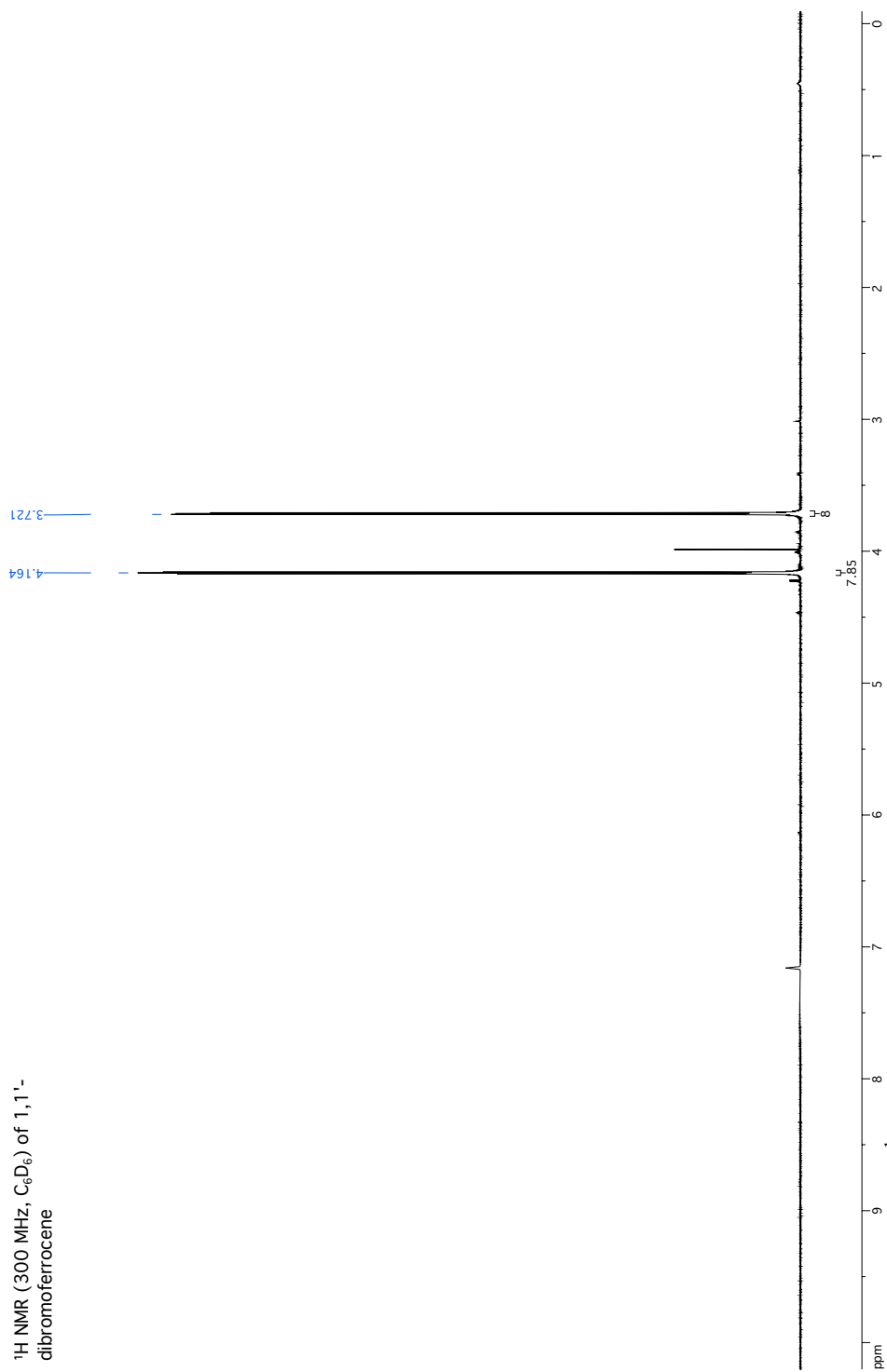


Figure A7 ¹H NMR (300 MHz, C₆D₆) of 1,1-dibromoferrocene with ferrocene at 4ppm.

^1H NMR (300 MHz, C_6D_6) of 1,1'-
diazidobiphenylene

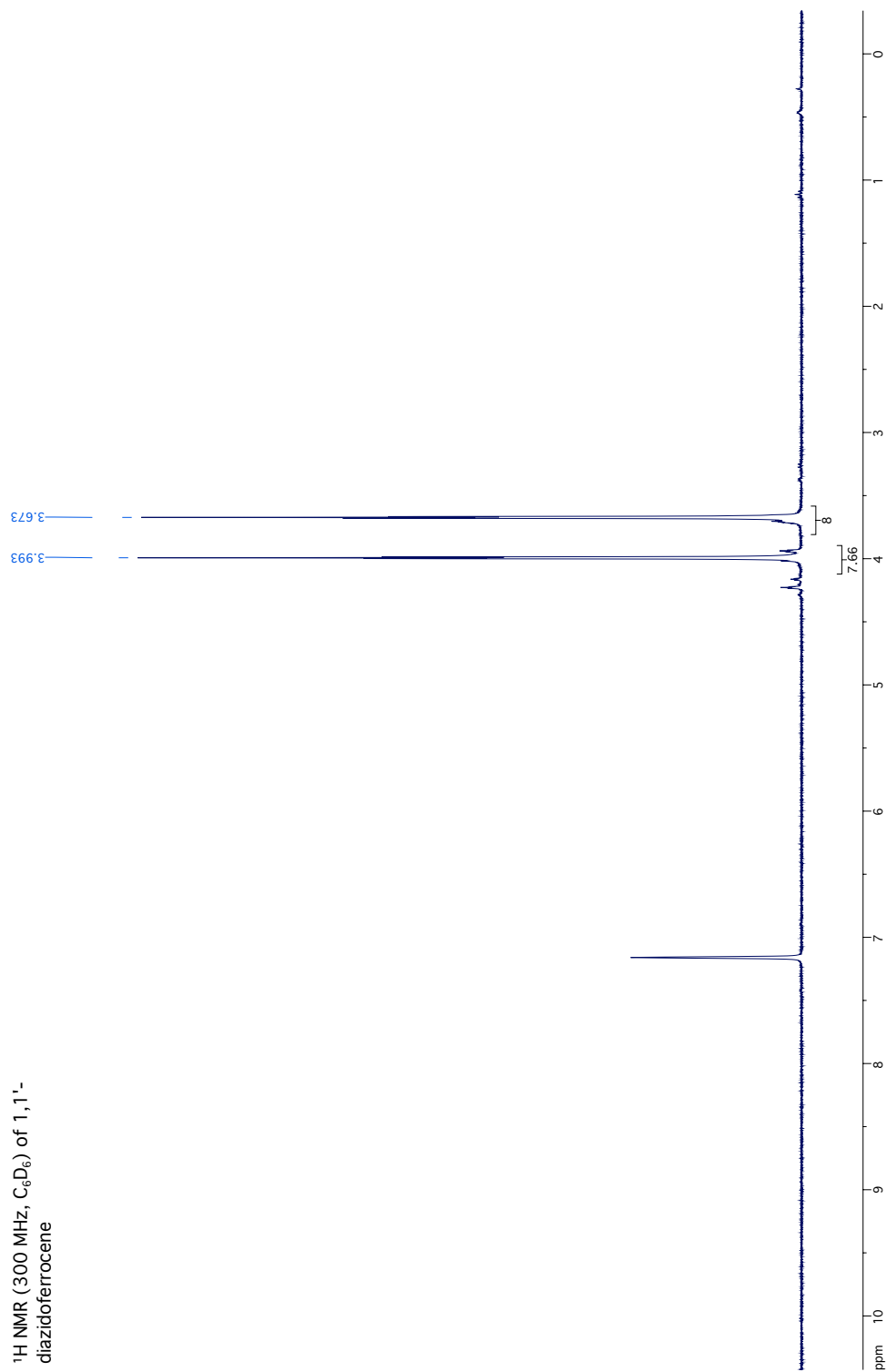


Figure A8 ^1H NMR (300 MHz, C_6D_6) of 1,1'-diazidobiphenylene.

^1H NMR (300 MHz, C_6D_6) of 1,1'-diamineferrocene

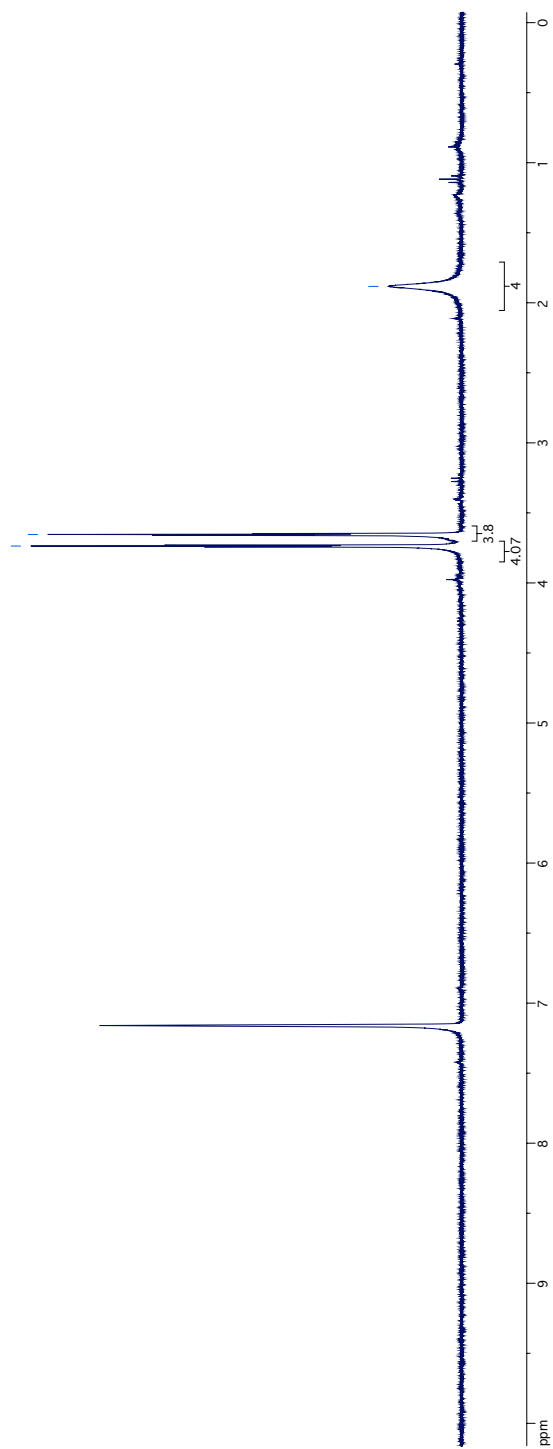


Figure A9 ^1H NMR (300 MHz, C_6D_6) of 1,1'-diamineferrocene.

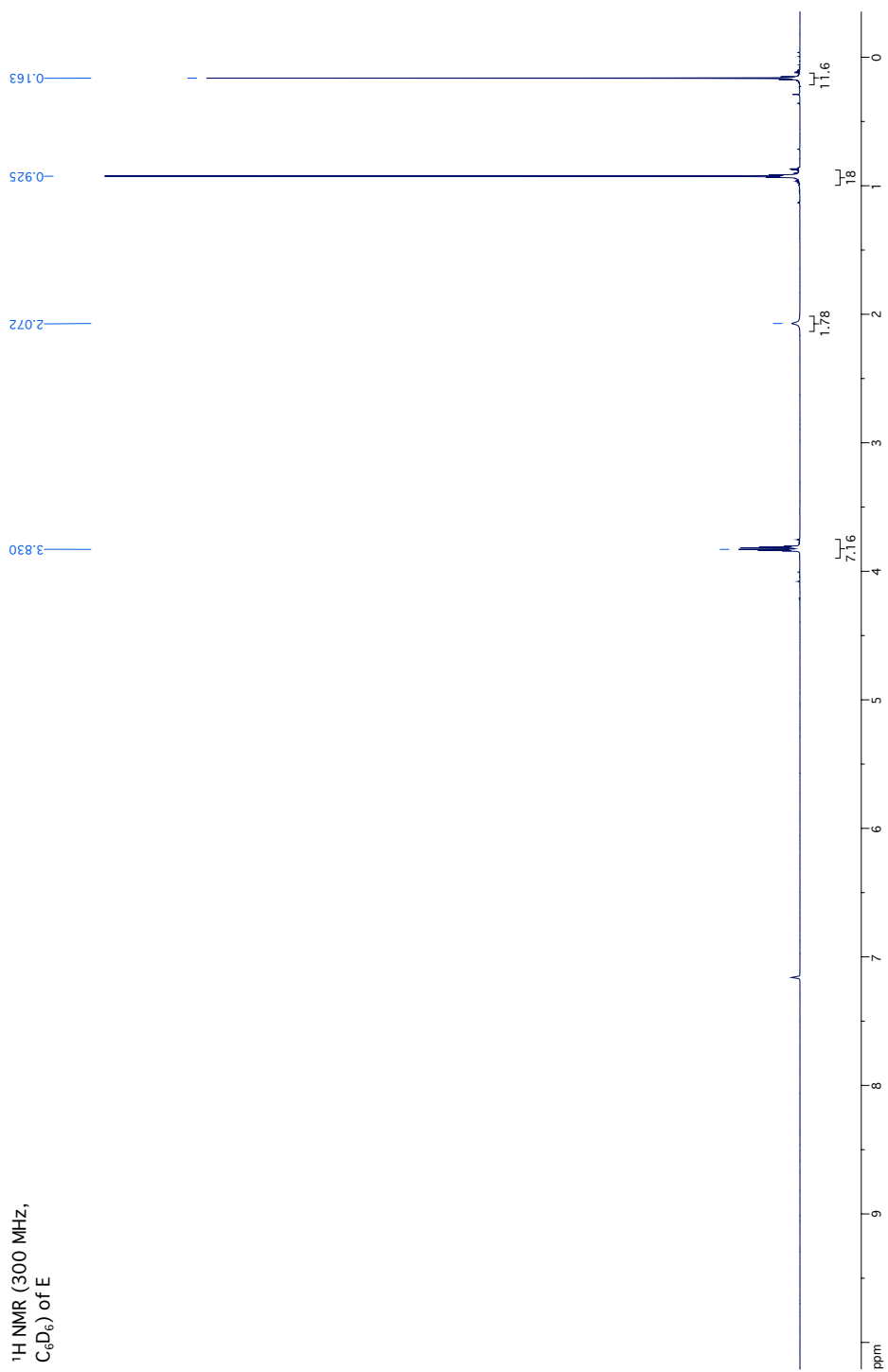


Figure A10 ^1H NMR (300 MHz, C_6D_6) of E.

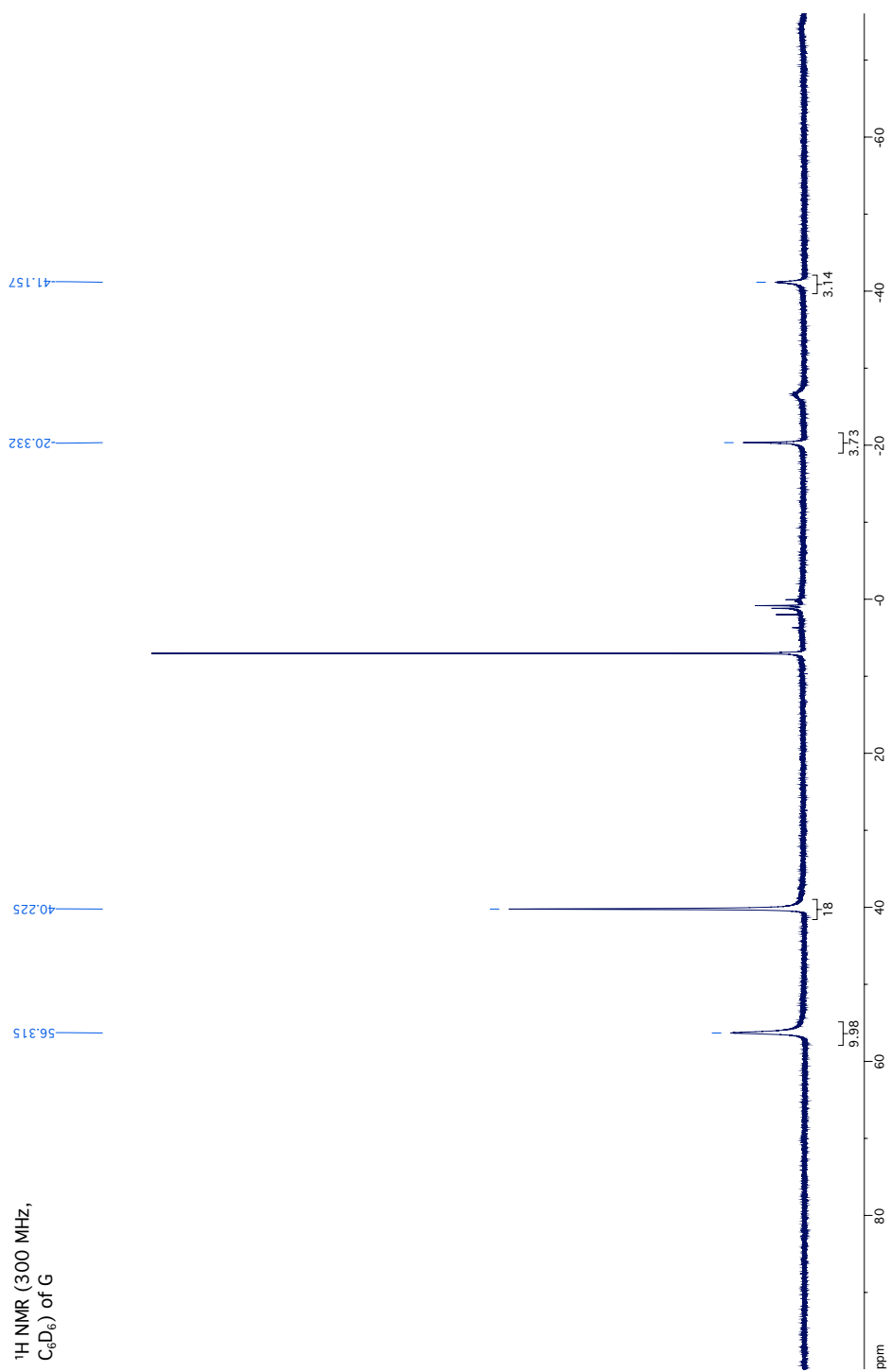


Figure A11 ^1H NMR (300 MHz, C_6D_6) of G.

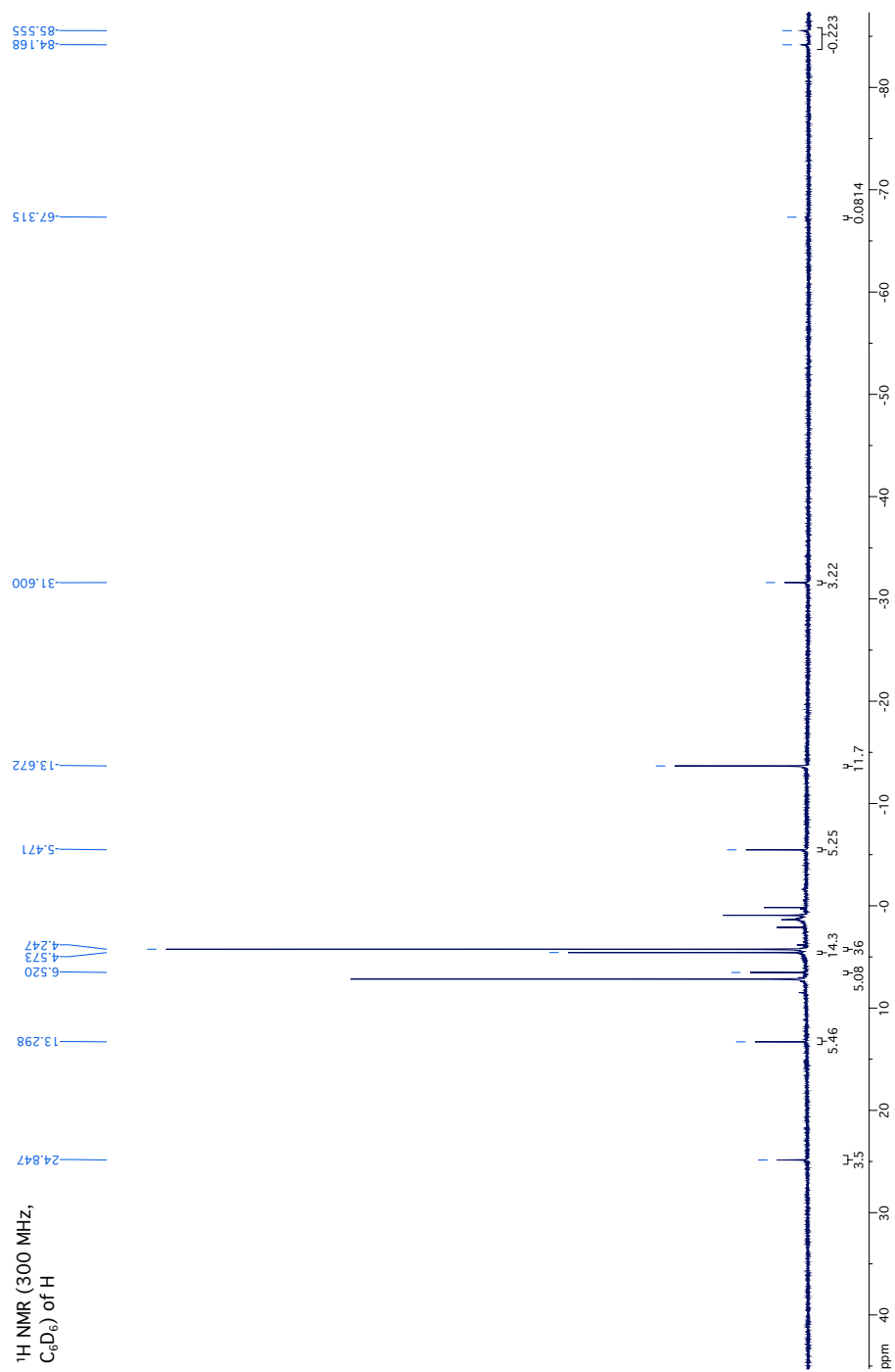


Figure A12 ¹H NMR (300 MHz, C₆D₆) of H.

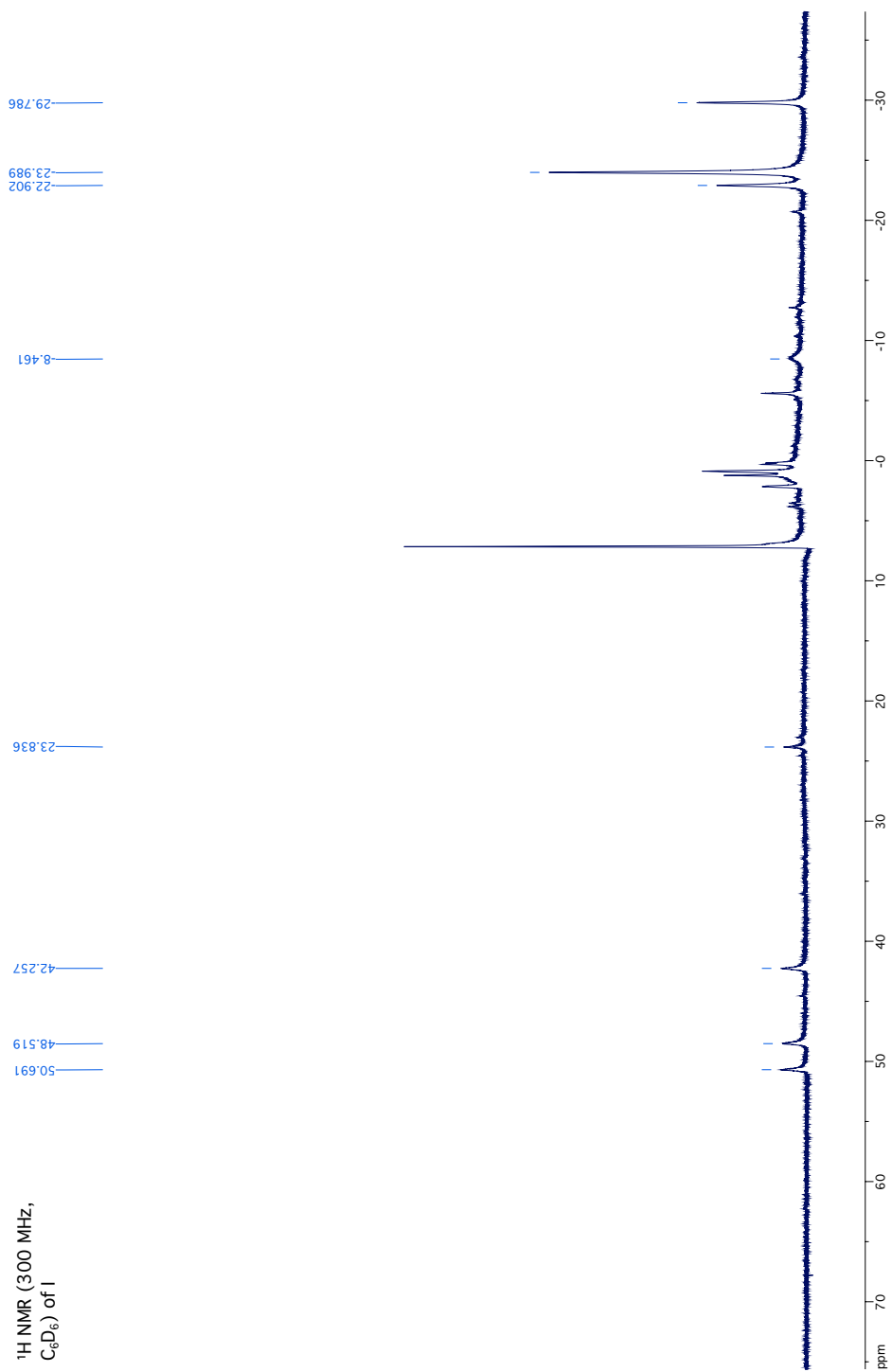
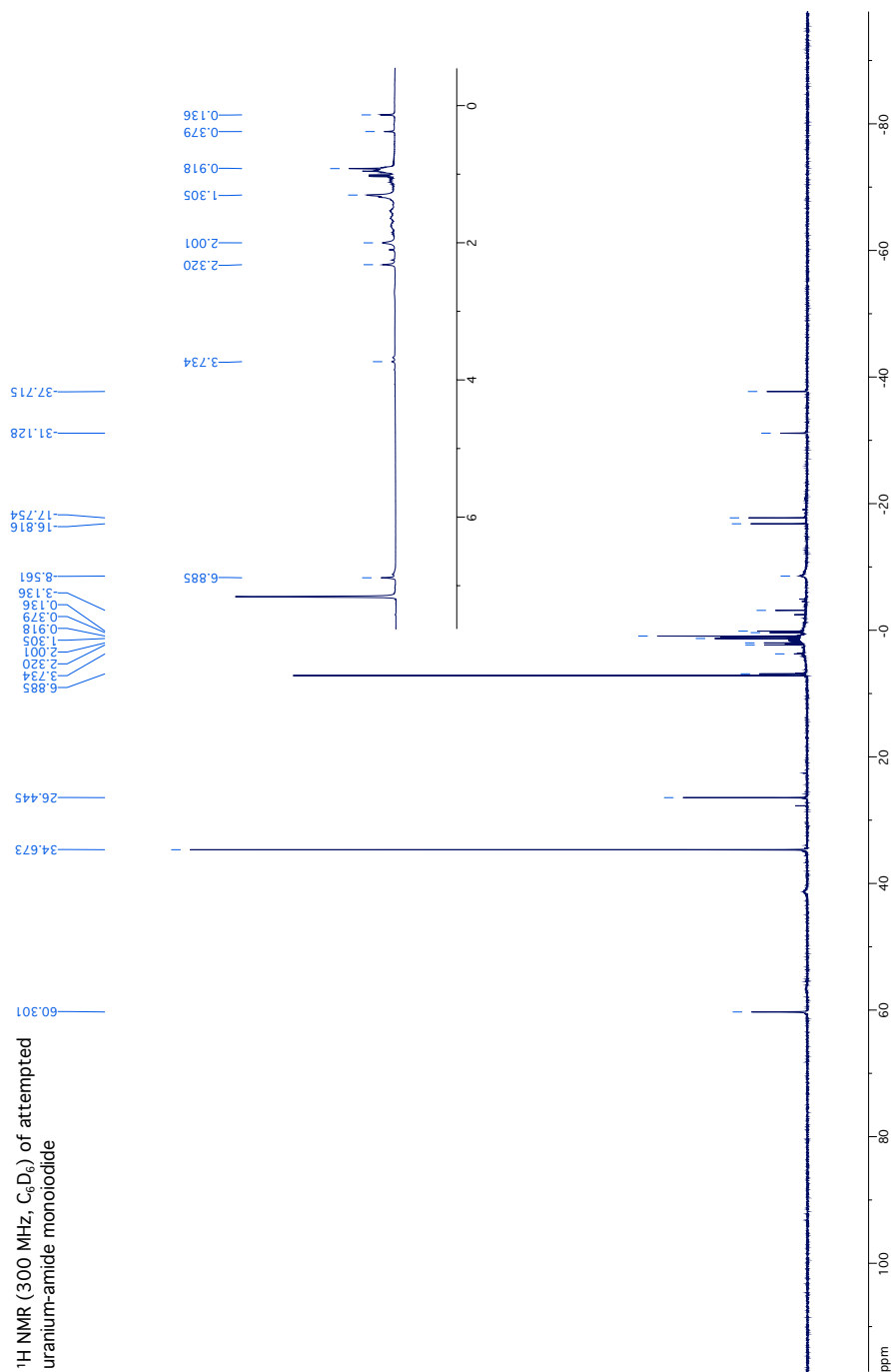
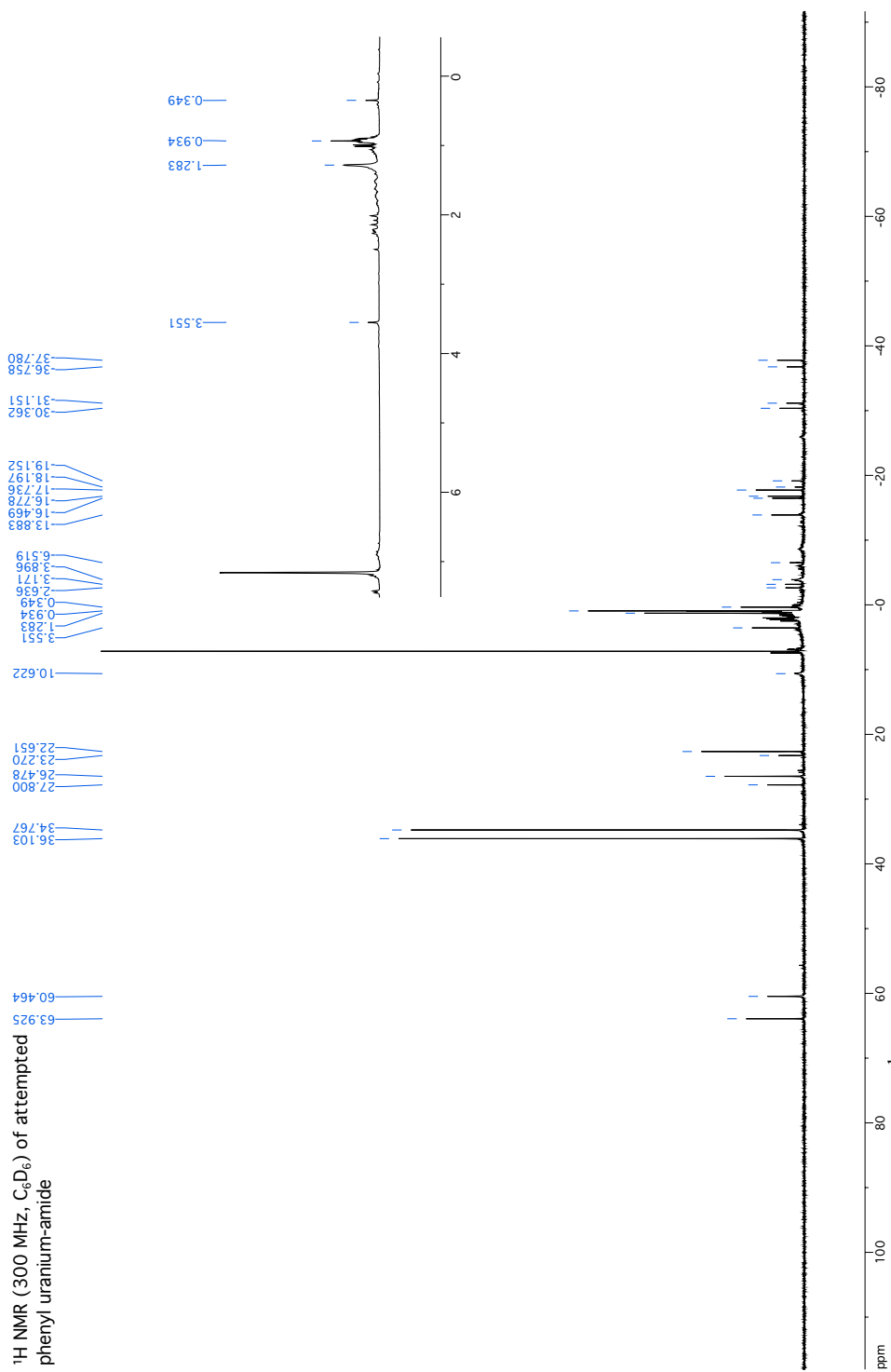


Figure A13 ¹H NMR (300 MHz, C₆D₆) of **I**.





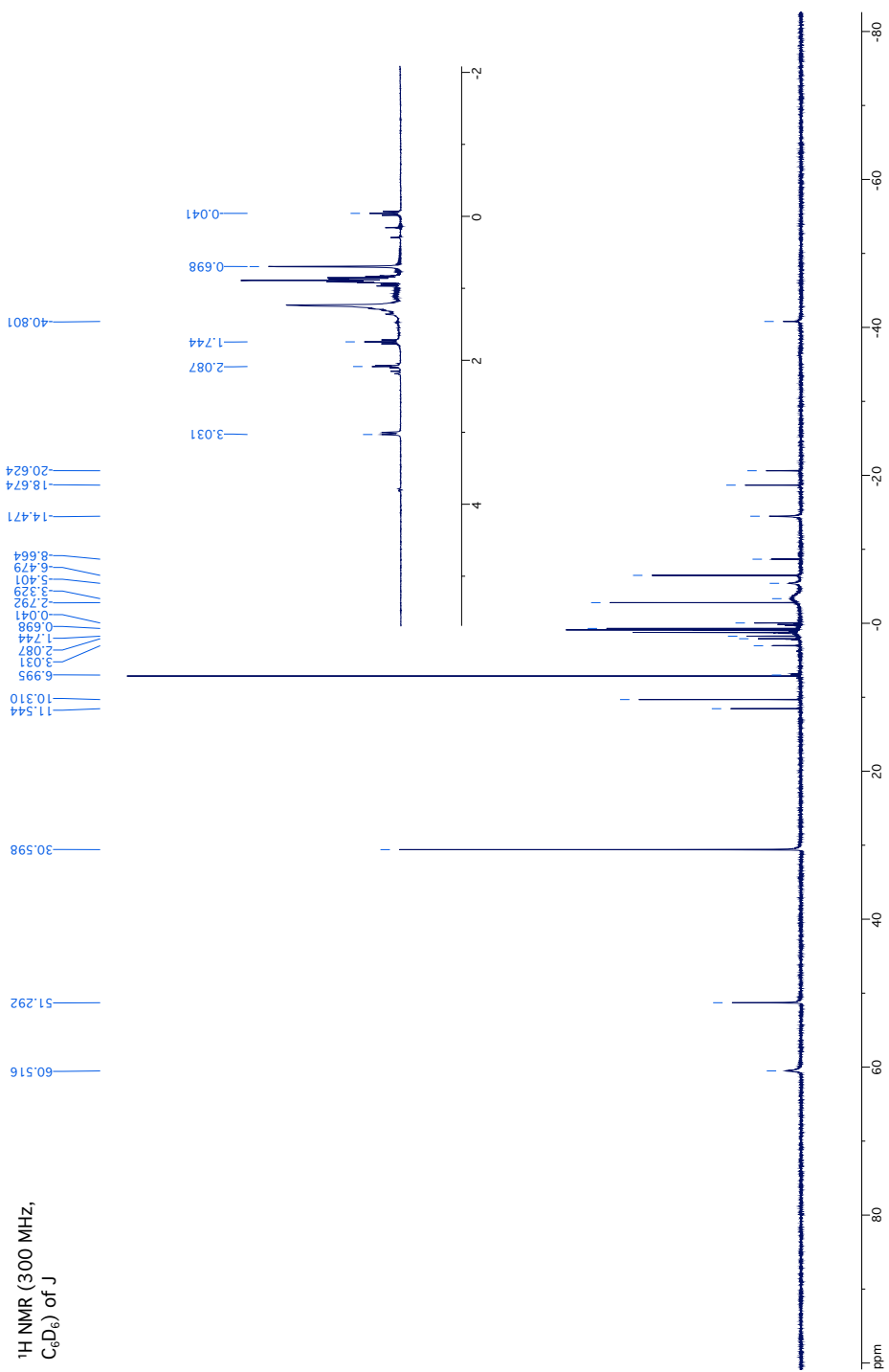


Figure A16 ¹H NMR (300 MHz, C₆D₆) of J.

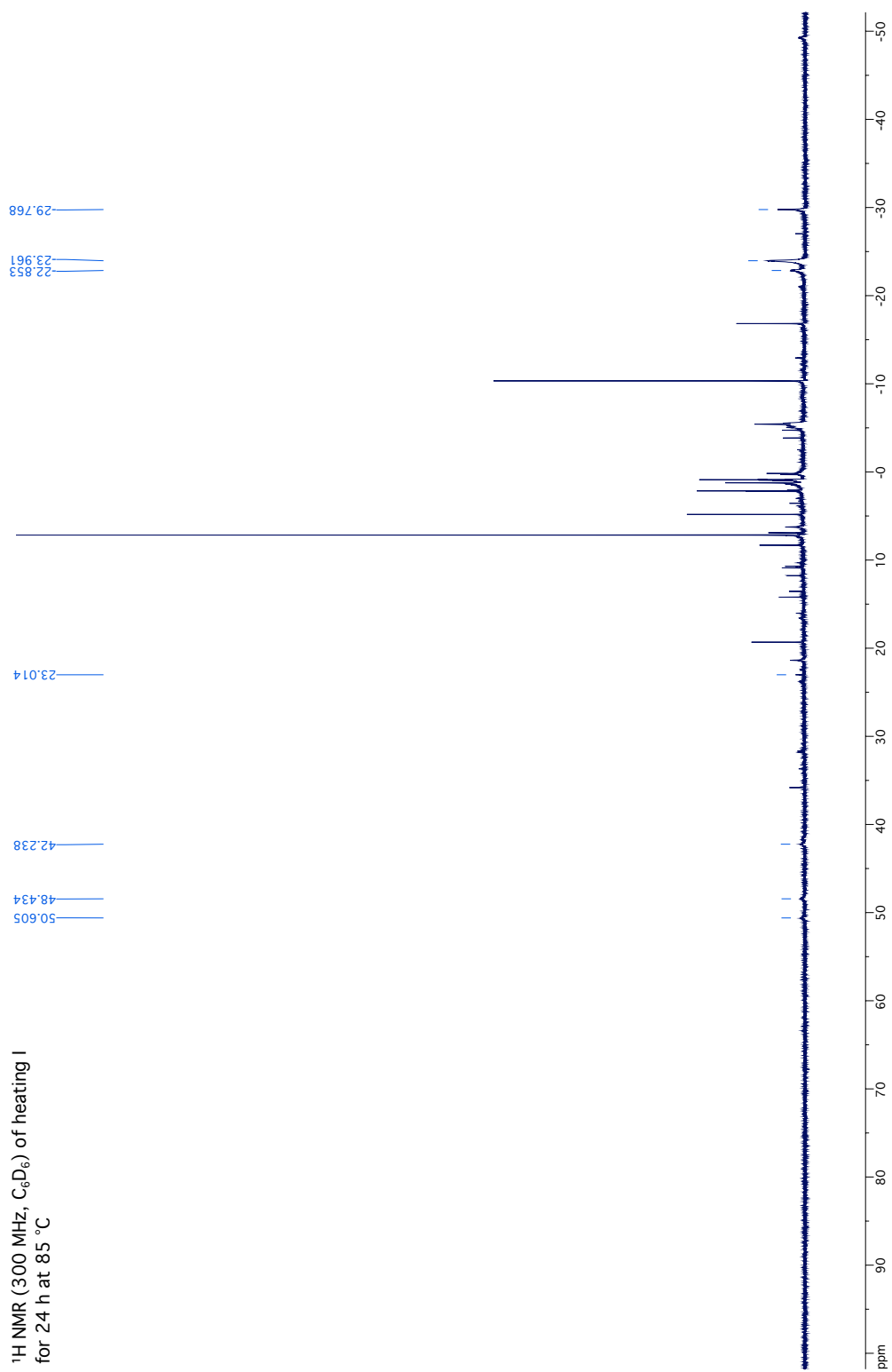


Figure A17 ¹H NMR (300 MHz, C₆D₆) of heating **I** for 24 h at 85 °C. Picked peaks for **I**.

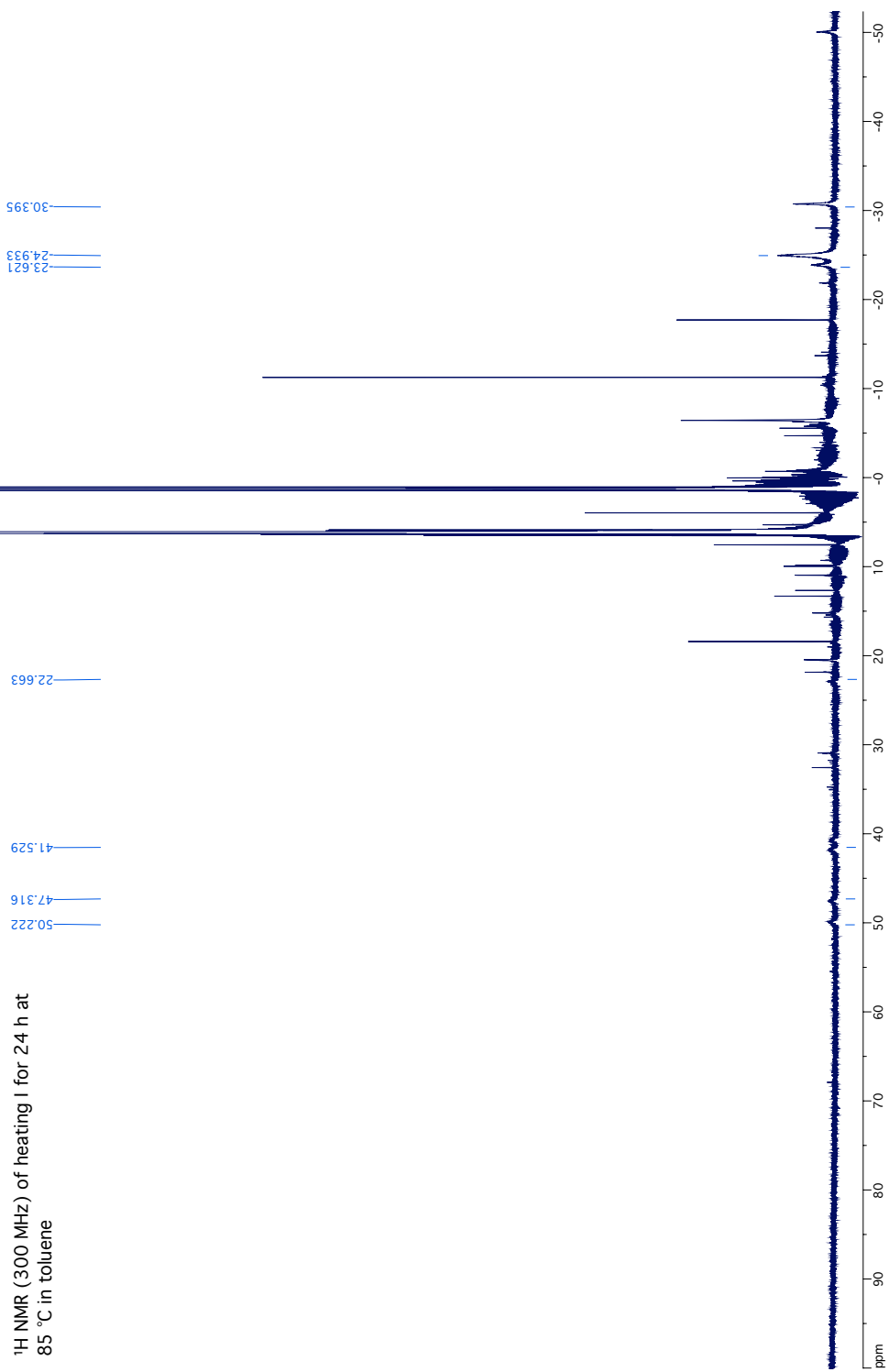


Figure A18 ¹H NMR (300 MHz) of heating **I** for 24 h at 85 °C in toluene. Picked peaks for **I**.

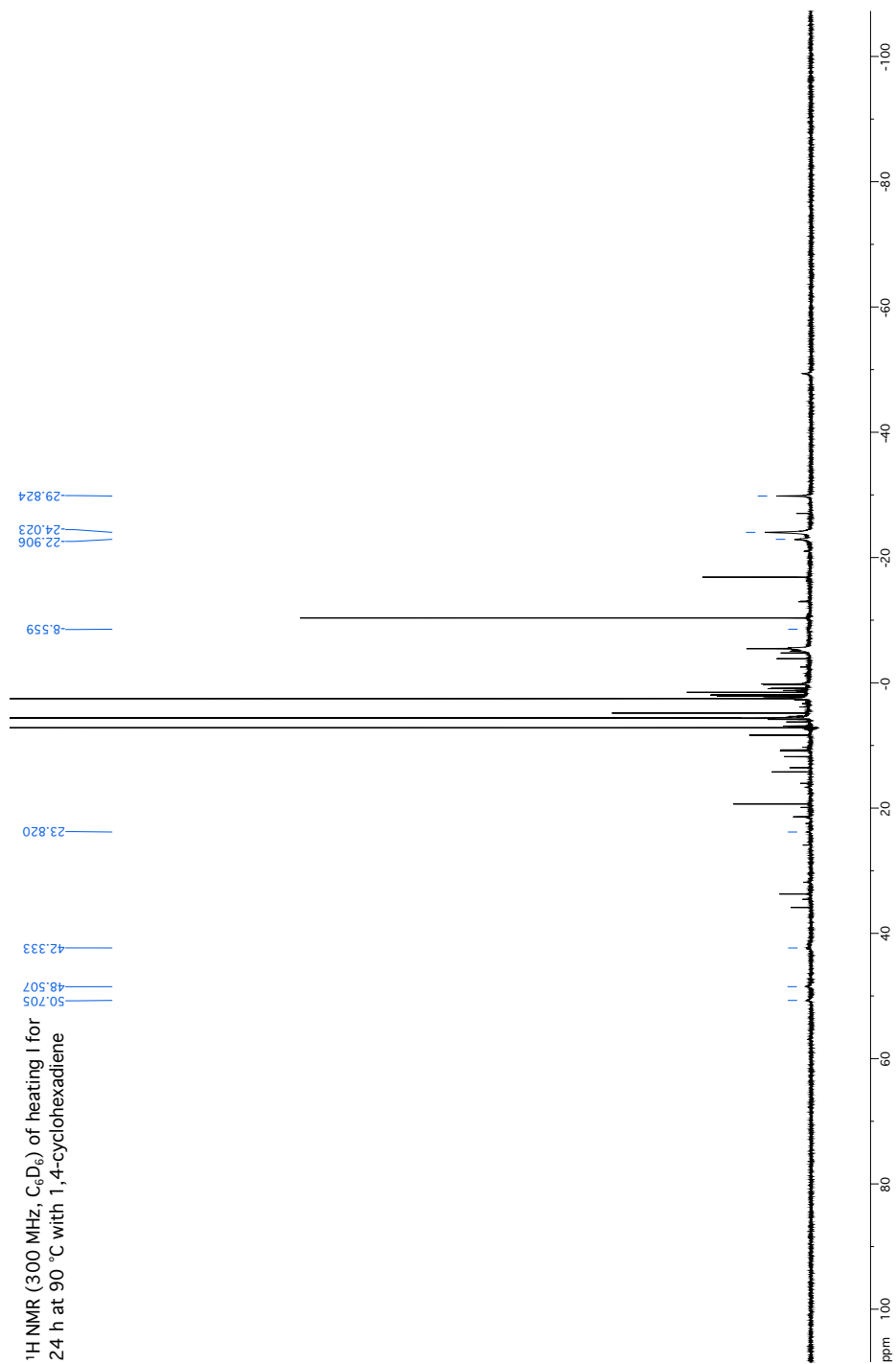


Figure A19 ¹H NMR (300 MHz, C₆D₆) of heating **I** with 1,4-cyclohexadiene for 24 h at 90 °C. Picked peaks for **I**.

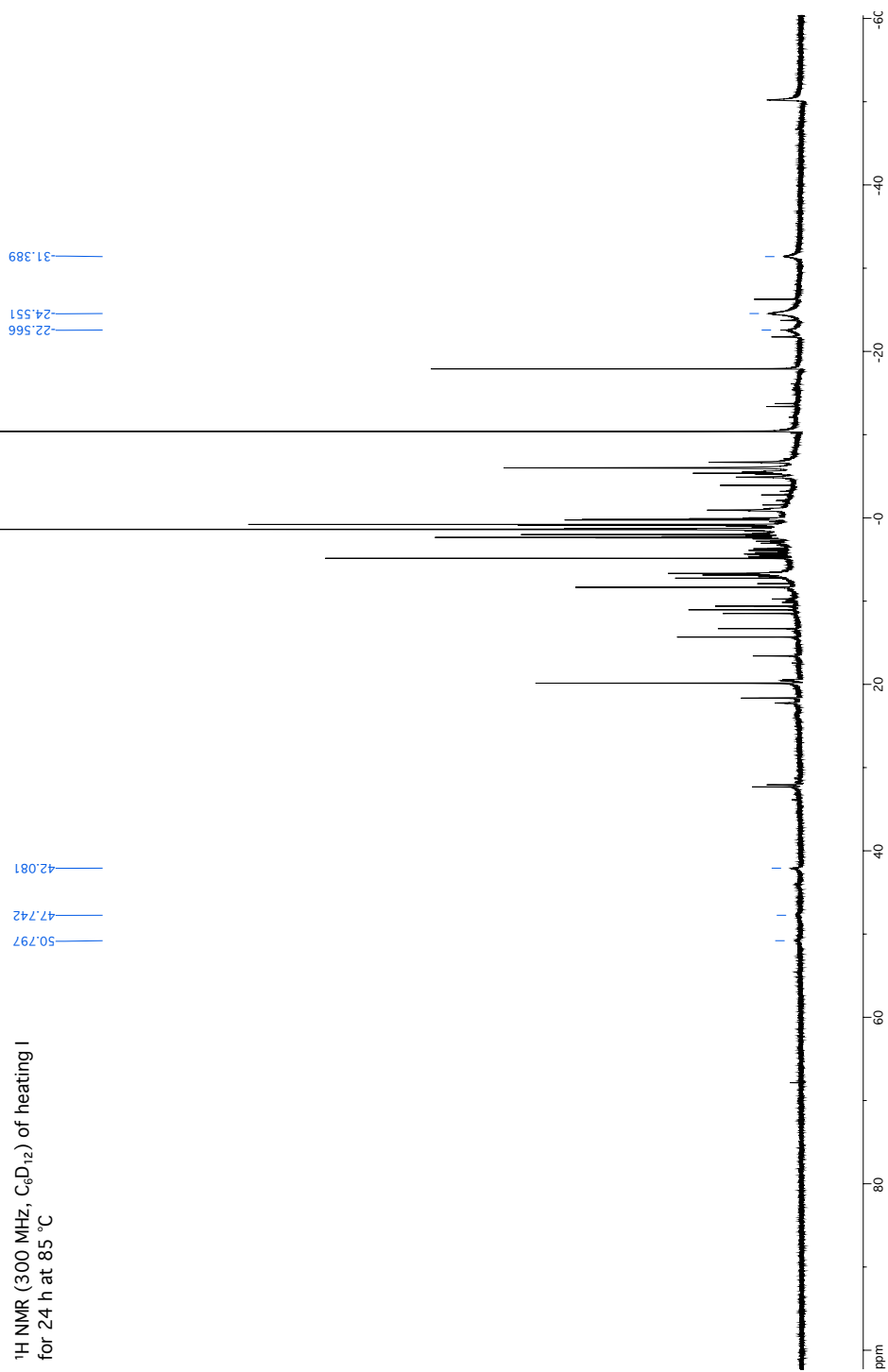


Figure A20 ^1H NMR (300 MHz, C_6D_{12}) of heating **I** for 24 h at 85 °C. Picked peaks for **I**.

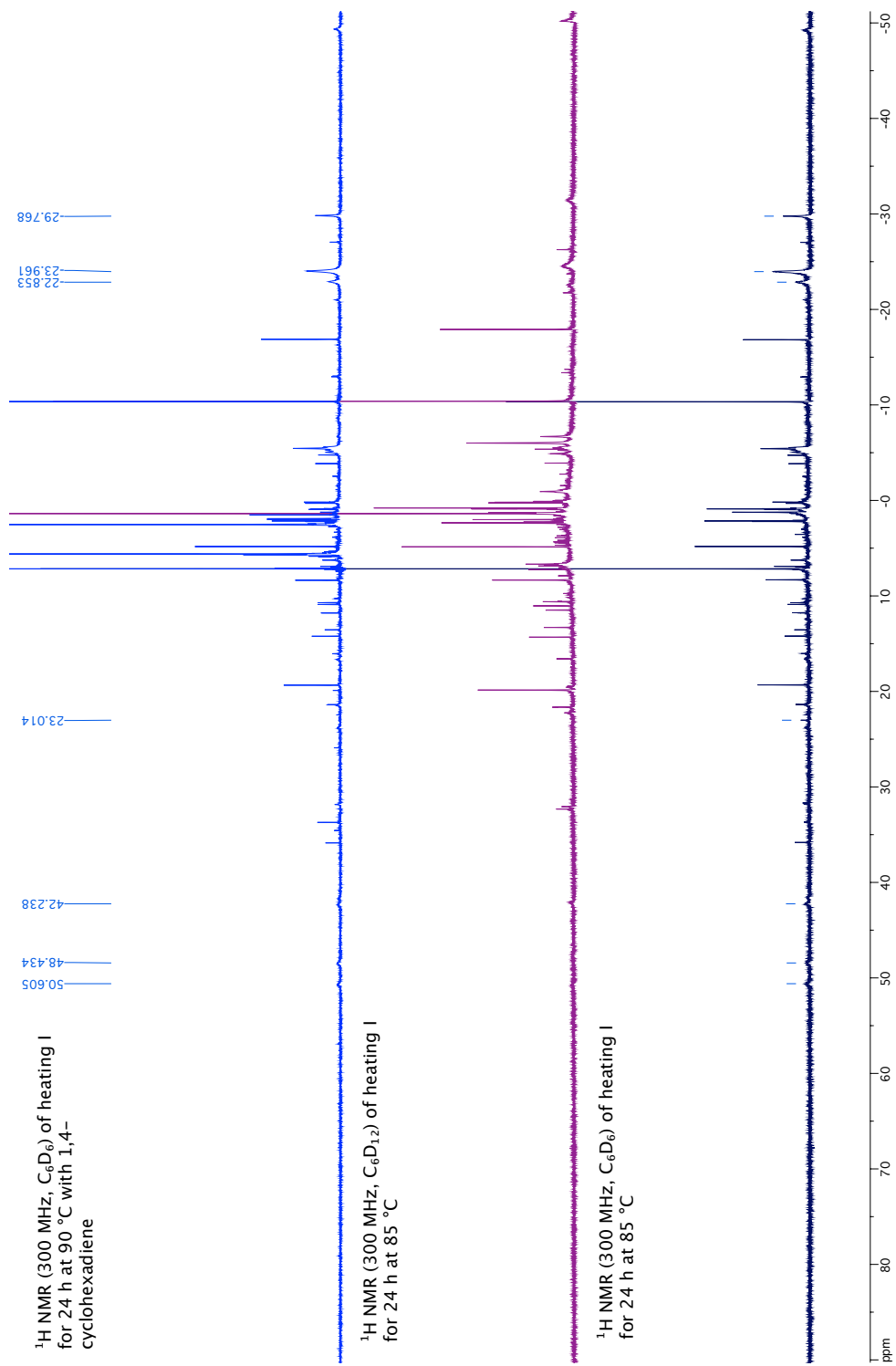


Figure A21 Comparison of Figures A17, A19, and A20 showing similar pattern with **I** present in all three.

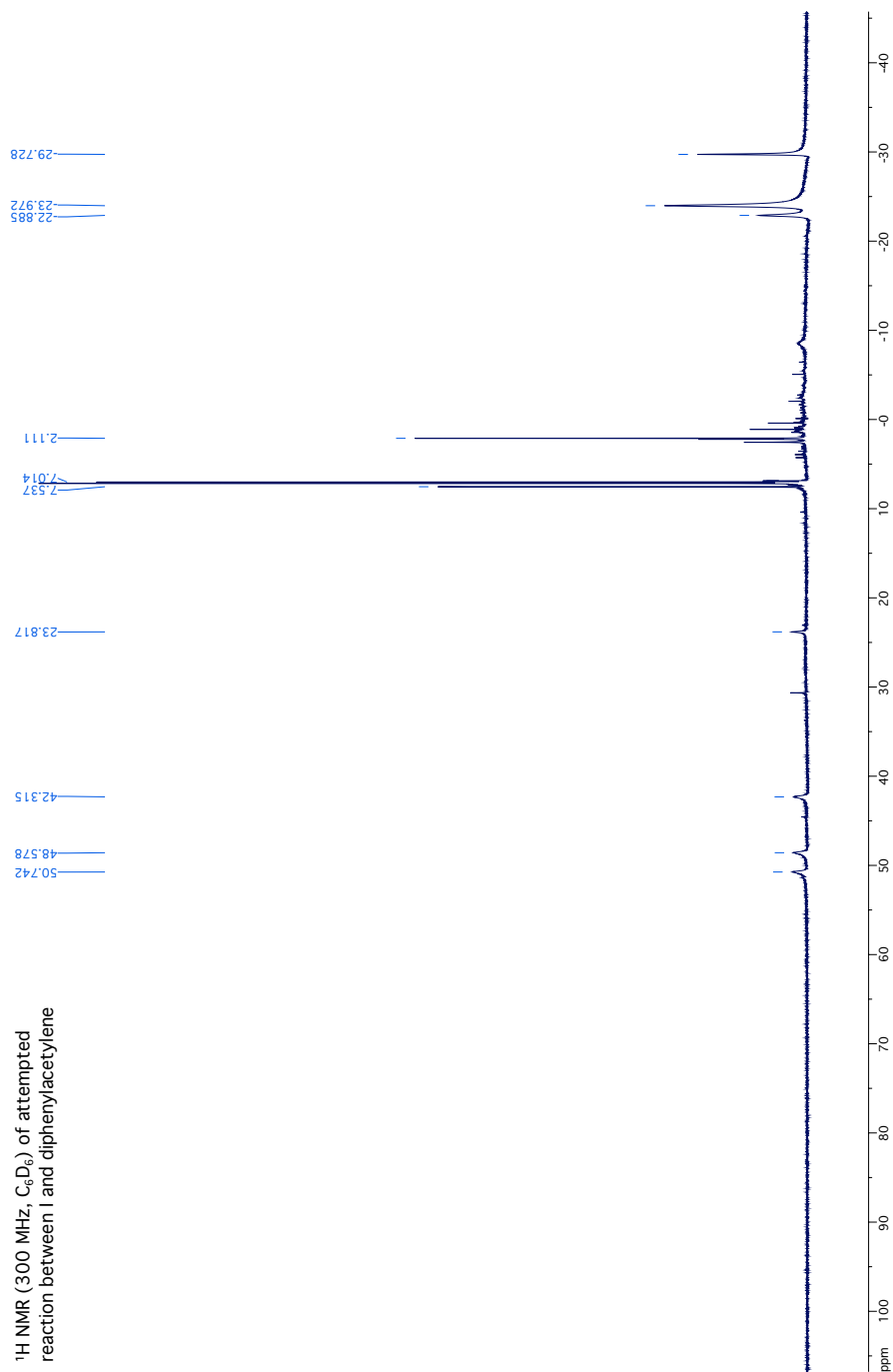
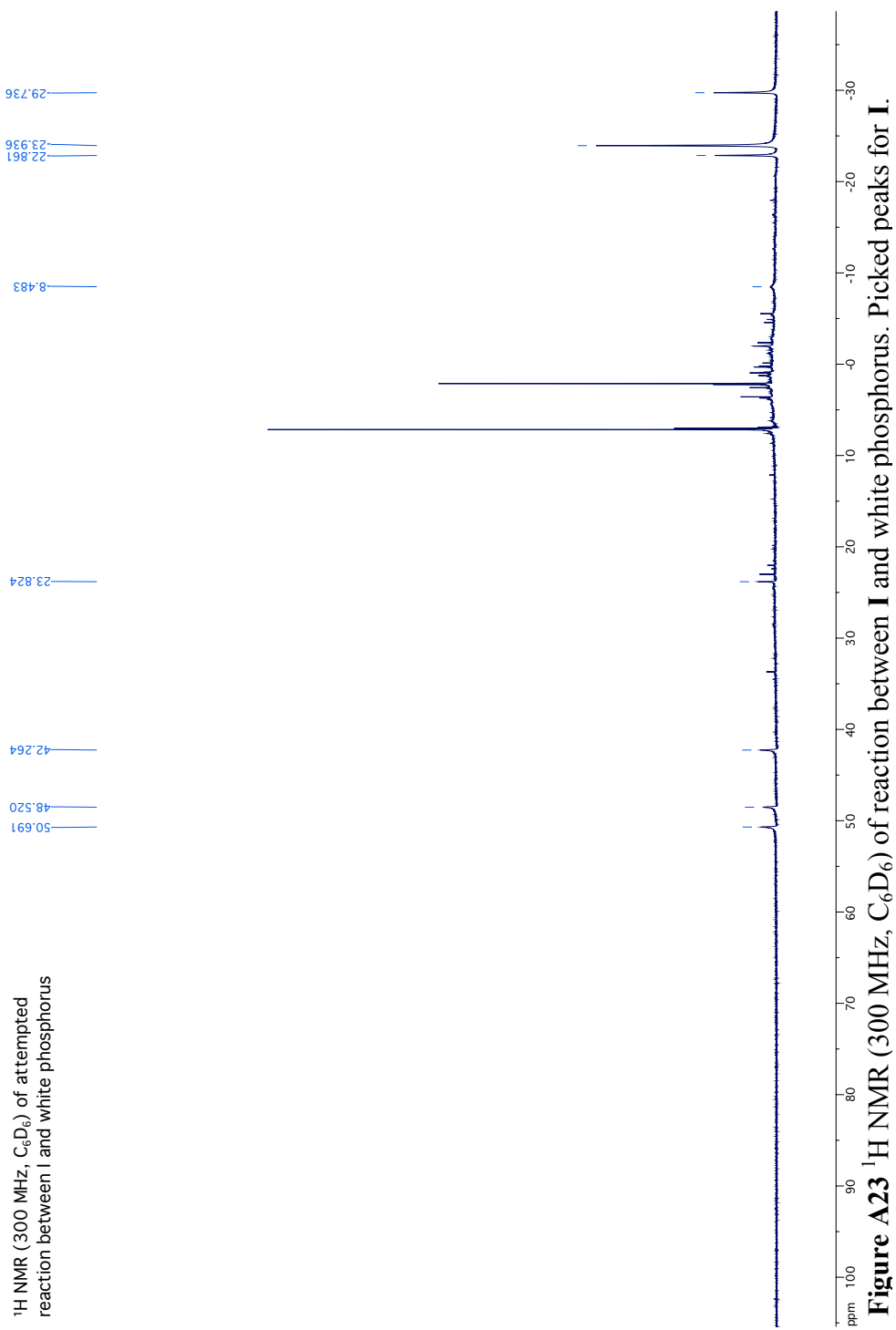


Figure A22 ¹H NMR (300 MHz, C₆D₆) of reaction between **I** and diphenylacetylene. Picked peaks for **I**.



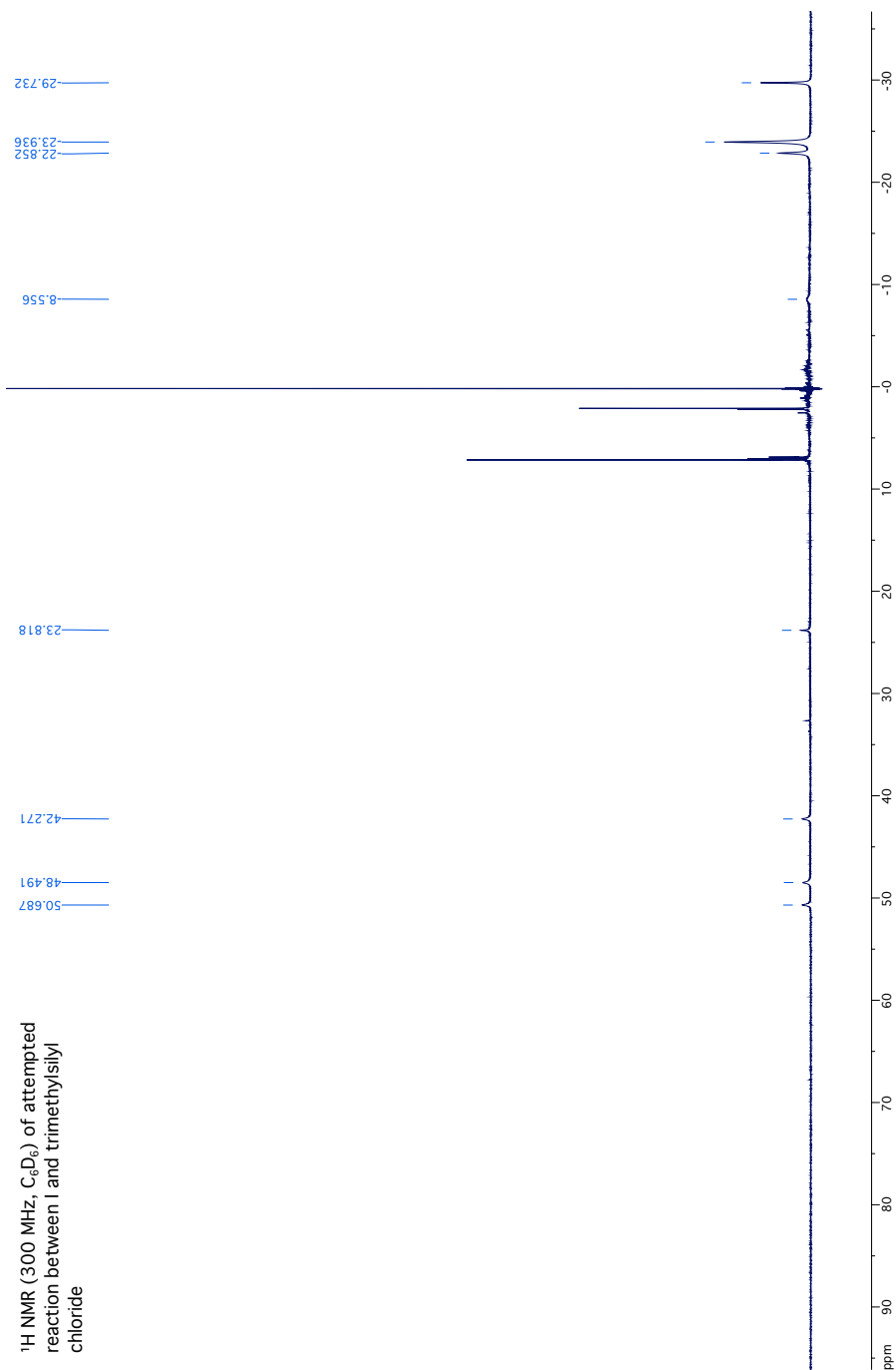


Figure A24 ¹H NMR (300 MHz, C₆D₆) of reaction between **I** and TMSCl. Picked peaks for **I**.

^1H NMR (300 MHz, C_6D_6) of attempted reaction between **1** and tert-butyl alcohol

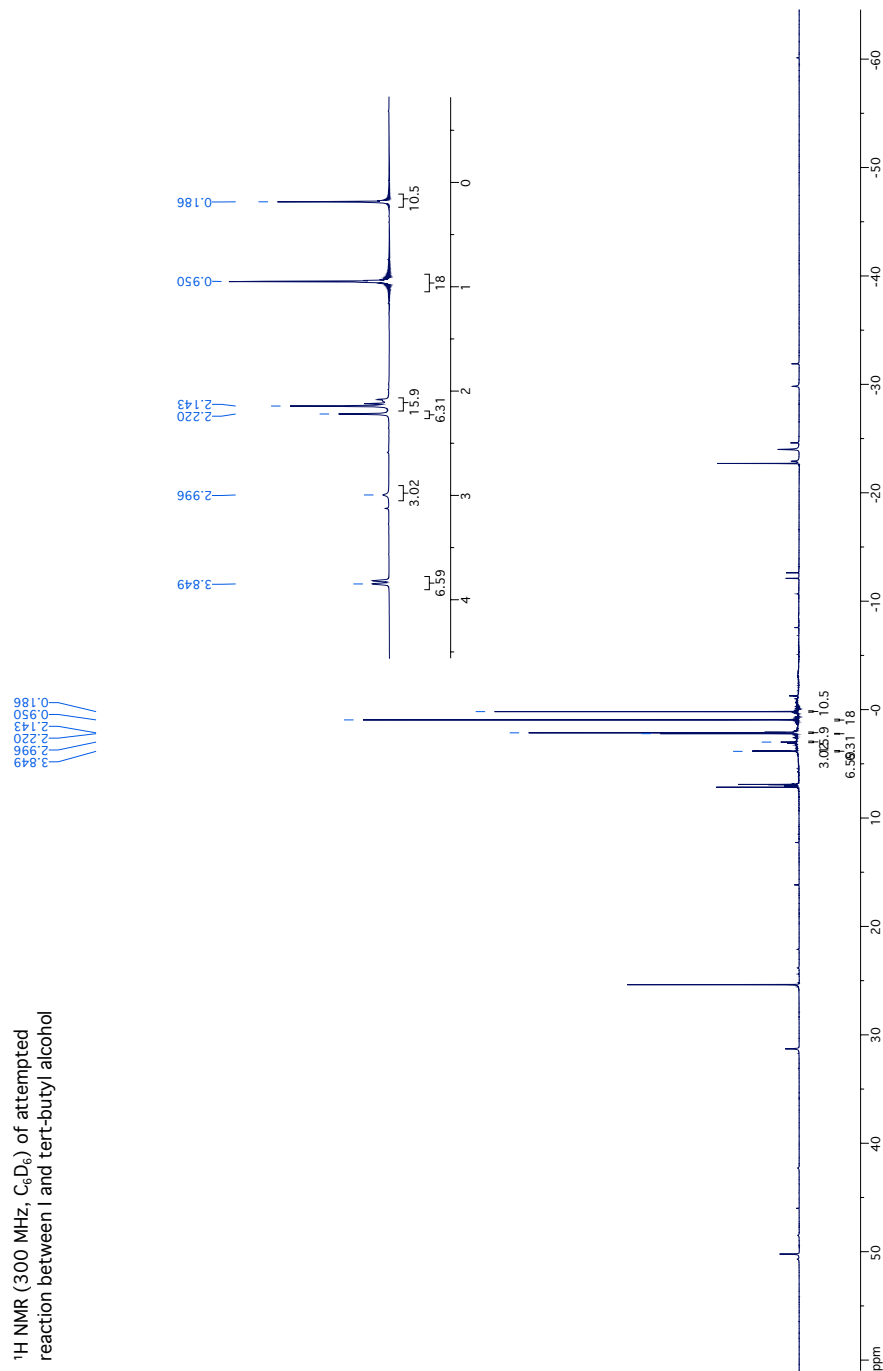


Figure A25 ^1H NMR (300 MHz, C_6D_6) of reaction between **1** and *t*-BuOH. Peaks picked for **E** and terphenyl amine.

^1H NMR (300 MHz, C_6D_6) of attempted reaction between **I** and phenol

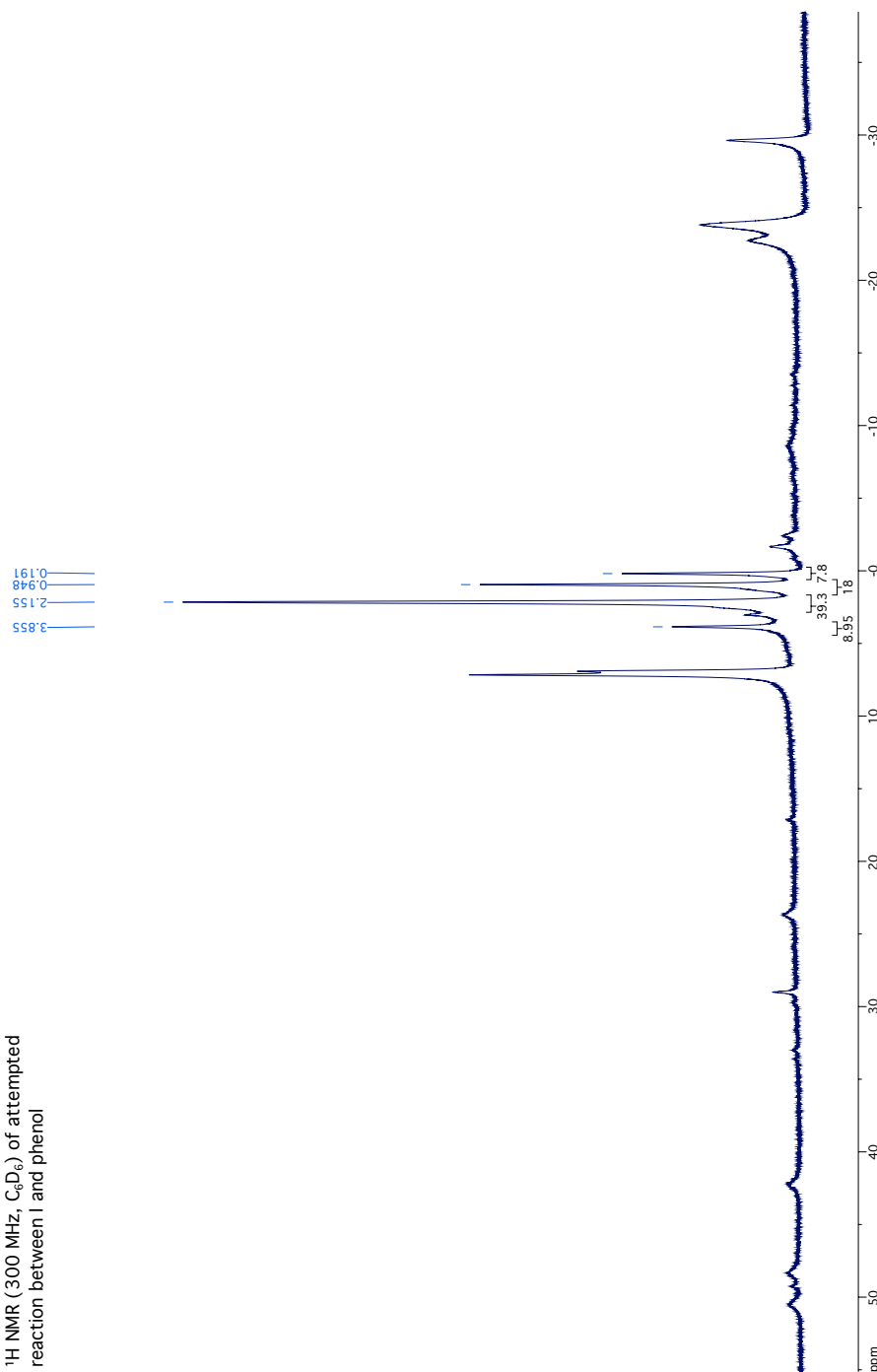


Figure A26 ^1H NMR (300 MHz, C_6D_6) of reaction between **I** and phenol. Peaks picked for **E** and terphenyl amine.

¹H NMR (300 MHz, C₆D₆) of attempted
reaction between **I** and aniline

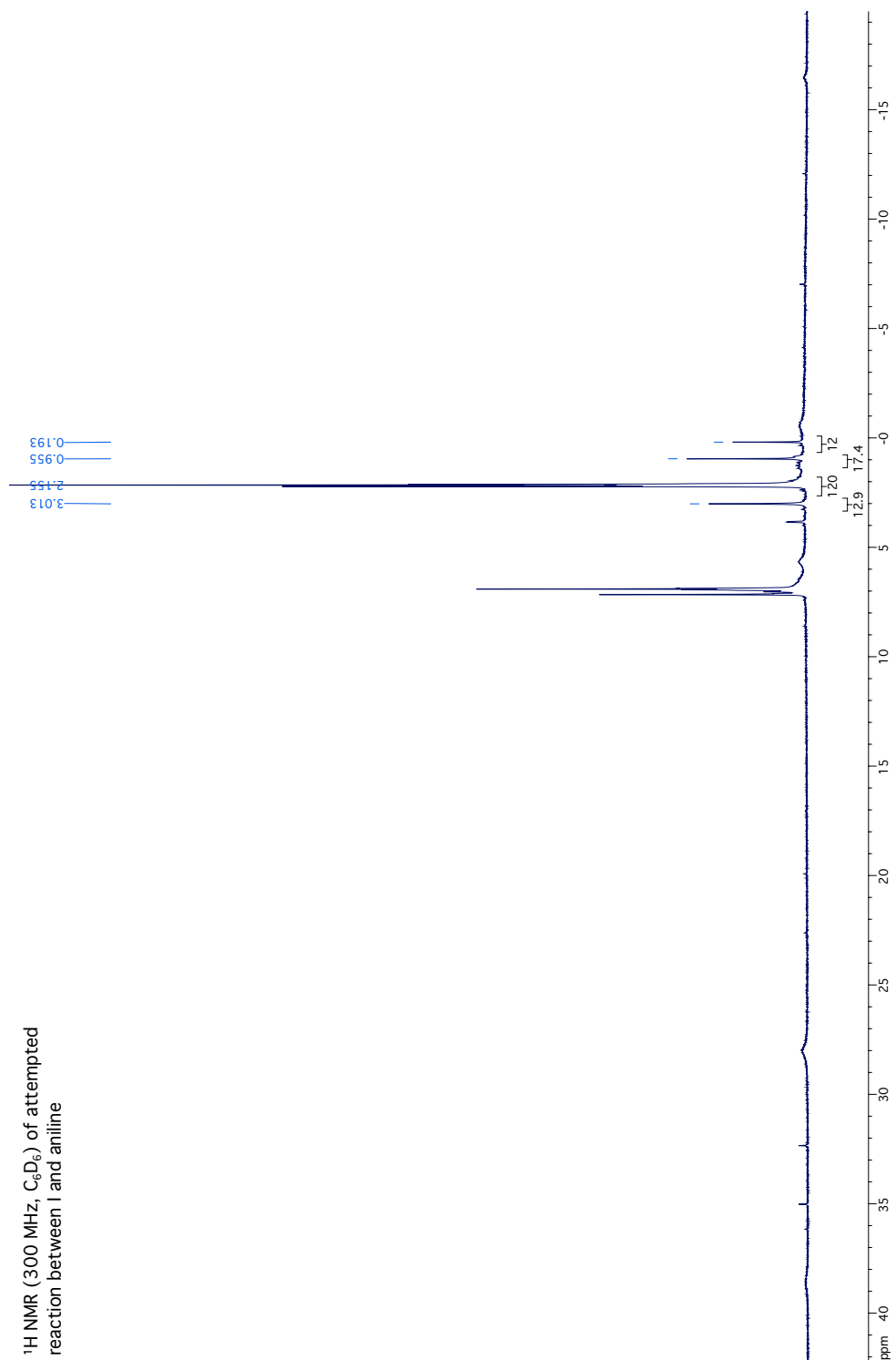


Figure A27 ¹H NMR (300 MHz, C₆D₆) of reaction between **I** and aniline. Peaks picked for **E** and terphenyl amine.

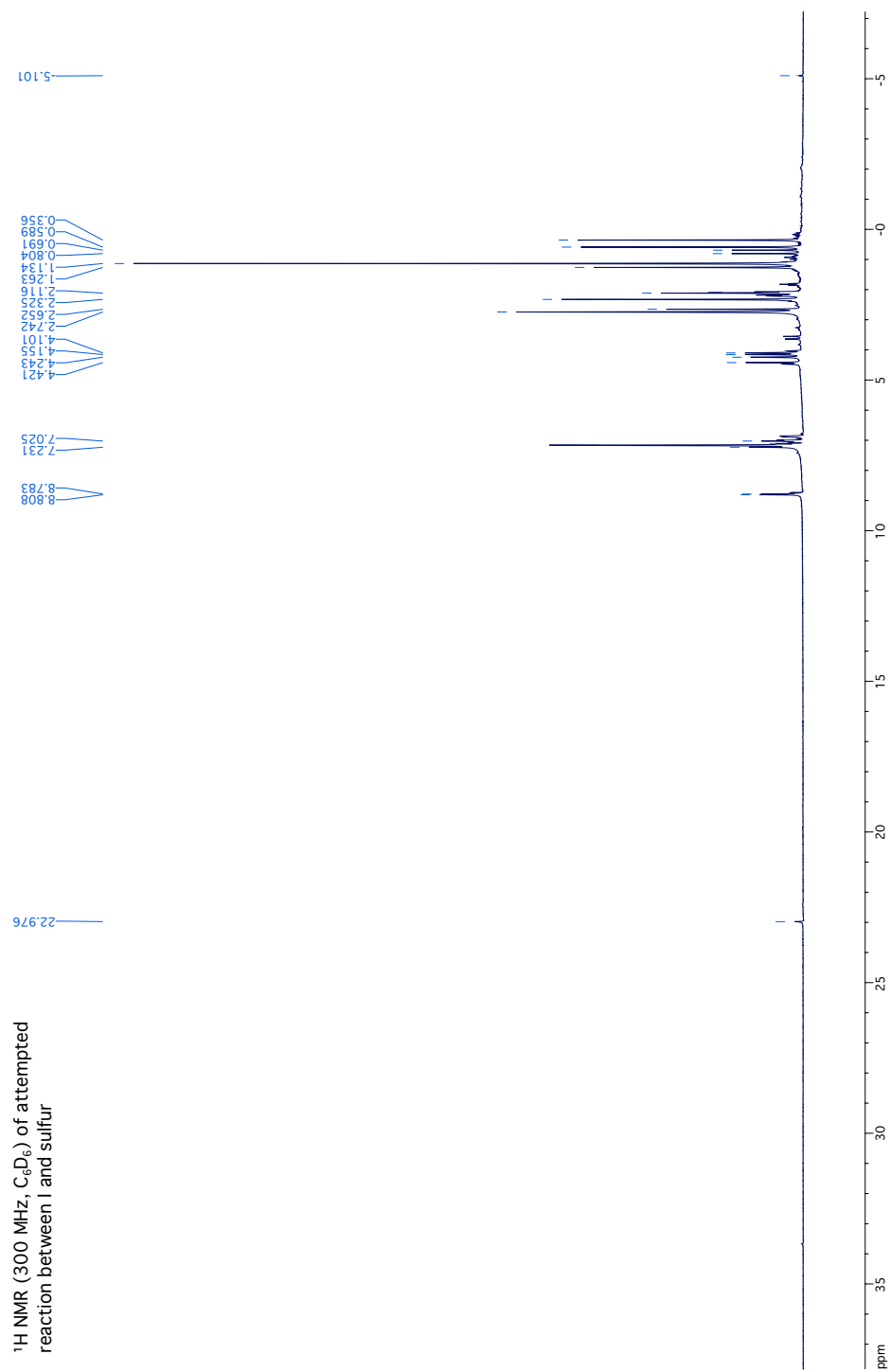


Figure A28 ¹H NMR (300 MHz, C₆D₆) of reaction between **1** and sulfur.

References

- (1) (a) Fox, A. R.; Bart, S. C.; Meyer, K.; Cummins, C. C. *Nature* **2008**, 455, 341. (b) Hayton, T. W. *Chem. Commun.* **2013**, 49, 2956.
- (2) Berthet, J. c.; Thuery, P.; Garin, N.; Dognon, J. P.; Cantat, T.; Ephritikhine, M. *J. Am. Chem. Soc.* **2013**, 135, 10003.
- (3) (a) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, 110, 8729. (b) Schaller, C. P.; Cummins, C. C.; Wolzanski, P. T. *J. Am. Chem. Soc.* **1996**, 118, 591.
- (4) Arney, D. S. J.; Burns, C. J. *J. Am. Chem. Soc.* **1995**, 117, 9448.
- (5) (a) Jilek, R. E.; Spencer, L. P.; Lewis, R. A.; Scott, B. L.; Hayton, T. W.; Boncella, J. M. *J. Am. Chem. Soc.* **2012**, 134, 9876. (b) Matson, E. M.; Crestani, M. G.; Fanwick, P. E.; Bart, S. C. *Dalton Trans.* **2012**, 41, 7952. (c) Warner, B. P.; Scott, B. L.; Burns, C. J. *Angew. Chem. Int. Ed.* **1998**, 37, 959. (d) Evans, W. J.; Traina, C. A.; Ziller, J. W. *J. Am. Chem. Soc.* **2009**, 131, 17473.
- (6) Zi, G.; Bloesch, L. L.; Jia, L.; Andersen, R. A.; *Organometallics* **2005**, 24, 4602.
- (7) (a) Spencer, L. P.; Yang, P.; Scott, B. L.; Batista E. R.; Boncella J. M. *J. Am. Chem. Soc.* **2008**, 130, 2930. (b) Broderick, E. M.; Gutzwiller, N. P.; Diaconescu, P. L. *Organometallics* **2010**, 29, 3242. (c) Haskell, A.; Straub, T.; Eisen, M. S. *Organometallics* **1996**, 15, 3773. (d) Stubbert, B. D.; Marks, T. J. *J. Am. Chem. Soc.* **2007**, 129, 4253. (e) Zi, G.; Bloesch, L. J.; Andersen, R. A. *Organometallics* **2005**, 24, 4602. (f) Bart, S. C. et al. *J. Am. Chem. Soc.* **2008**, 130, 12536. (g) Peters, R. G.; Warners, B. P.; Scott, B. L.; Burns, C. J. *Organometallics* **1999**, 18, 2587. (h) Graves, C. R.; Scott, B. L.; Morris, D. E.; Kiperlinger, J. L. *Chem. Commun.* **2009**, 7, 776.
- (8) (a) Kraft, S. J.; Williams, U. J.; Daly, S. R. L. Schelter, E. J.; Kozimor, S. A.; Boland, K. S. L. Kikkawa, J. M. L. Forrest, W. P.; Christensen, C. N.; Schwarz, D. E.; Fanwick, P. E.; Clark, D. L.; Conradson, S. D.; Bart, S. C. *Inorg. Chem.* **2011**, 50, 9838. (b) Cladis, D. P.; Kiernicki, J. J.; Fanwick, P. E.; Bart, S. C. *Chem. Commun.* **2013**, 49, 4169.
- (9) Shafir, A.; Power, M. P.; Whitener, G. D.; Arnold, J. *Organometallics* **2001**, 20, 1365.
- (10) Monreal, M. J.; Carver, C. T.; Diaconescu, P. L. *Inorg. Chem.* **2007**, 46, 7226.
- (11) Monreal, M. J.; Diaconescu, P. L. *Organometallics* **2008**, 27, 1702.
- (12) Monreal, M. J.; Khan, S. I.; Kiplinger, J. L.; Diaconescu, P. L. *Chem Commun.* **2011**, 479, 9119.
- (13) Gianetti, T. L.; Nocton, G.; Minasian, S. G.; Tomson, N. C.; Kilcoyne D.; Kozimor, S. A.; Shuh, D. K.; Tyliczszak, T.; Bergman, R. G.; Arnold J. *J. Am. Chem. Soc.* **2013**, 135, 3224.

- (14) (a) Boynton, J. N.; Guo, J. D.; Fetting, J. C.; Melton, C. E.; Nagase, S.; Power, P. P. *J. Am. Chem. Soc.* **2013**, 135, 10720. (b) Merrill, W. A.; Stich, T. A.; Brynda, M.; Yeagle, G. J.; Fetting, J. C.; Hont, R. D.; Reiff, W. M.; Schulz, C. E.; Britt, R. D.; Power, P. P. *J. Am. Chem. Soc.* **2009**, 131, 12693.
- (15) Du, C. F.; Hart, H.; Ng, K. D. *J. Org. Chem.* **1986**, 51, 3162.
- (16) Akbar, S.; Harold, H. *Synthesis* **1996**, 12, 1455.
- (17) Gavenonis, J.; Tilley, T. D. *Organometallics* **2002**, 21, 5549.
- (18) (a) Hoyt, H. M.; Michael, F. E.; Bergman, R. G. *J. Am. Chem. Soc.* **2004**, 126, 1018. (b) Cowley, R. E.; Eckert, N. A.; Vaddadi, S.; Figg, T. M.; Cundari, T. R.; Holland, P. L. *J. Am. Chem. Soc.* **2011**, 133, 9796.
- (19) Spencer, L. P.; Yang, P.; Scott, B. L.; Batista, E. R.; Boncella, J. M. *Inorg. Chem.* **2009**, 48, 11615.
- (20) Regitz, M.; Hocker, J.; Liedhegener, A. *Org. Synth.* **1968**, 48, 36.
- (21) Monreal, M. J.; Thomson, R. K.; Cantat, T.; Travia, N. E.; Scott, B. L.; Kiplinger, J. L. *Organometallics* **2011**, 30, 2031.

Chapter 2 Introduction

Synthetic derivatives of 1-alkenylboron have enabled chemists to carry out a wide range of reactions. They are versatile precursors in several carbon cross-coupling reactions including the Suzuki-Miyaura reactions, for which the 2010 Nobel Prize was awarded. Several alkenylboron syntheses are available including: palladium cross-coupling of alkenyl halides/triflates with B_2pin_2 (B_2pin_2 = bis(pinacolato)diboron), reaction of 1-halo-1-lithioalkenes and HBpin (HBpin = pinacolborane) at -110 °C, platinum-catalyzed 1,2-diboration of alkynes, palladium-catalyzed diboration of methylenecyclopropenes, ruthenium-catalyzed olefin metathesis of vinyl boronates with alkenes. While all the above methods have been fully developed, each synthetic route possesses limitations hampering general applications in both academia and industry.^{1a-c} Most importantly, most all the above reactions use expensive, late transition metals and feature a limited reagent scope.

Known reactions for the synthesis of cyclic 1-alkenylboron compounds include the hydroboration of a cyclic alkyne, multi-step syntheses using lithium/Grignard reagents, or palladium cross-coupling. Some alkenylboron derivatives, such as 1,1-disubstituted vinyl boronate esters, cannot be made using hydroboration techniques. A potential solution would be to use dehydrogenative borylation to generate the desired alkenylboron derivatives. Dehydrogenative borylation offers high tolerance of starting materials, including both linear and cyclic functionalized products. To date, the metals employed in catalytic dehydrogenative borylation have been primarily late transition metals (Rh, Ru, Pd, Pt) with the exception of titanium.¹ The titanium complex $(\eta^5-C_5Me_5)_2Ti(C_2H_4)$, as developed by Smith et al., splits hydrogen-boron bonds forming a hydride and boron addition to the alkene (Figure 11).^{1d} A dihydrido complex forms via β -hydrogen elimination from the newly generated hydridoalkyl

species. This mechanism is preferred over reductive elimination, giving the corresponding saturated alkane. Upon titanium reduction, hydrogen gas is liberated from the reaction giving a η^2 -coordinated alkenylboron, which is then displaced by an unborylated alkene. To expand the field of early transition metal mediated dehydrogenative borylation catalysis, the Diaconescu group proposed the development of group 5 metal catalysts (tantalum and niobium) supported by 1,1'-diamidoferrocene ligands.

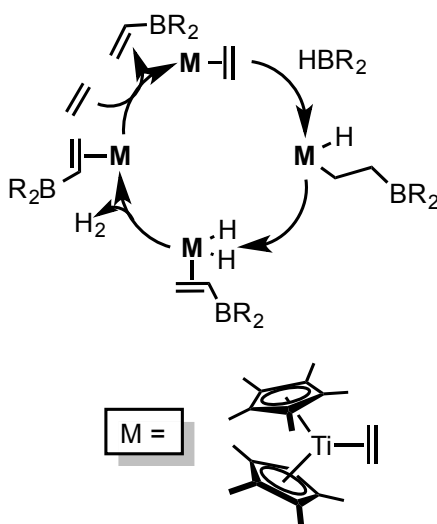


Figure 11 Catalytic cycle of dehydrogenative borylation featuring Smith's titanium catalyst^{1d}

Niobium was chosen for use in dehydrogenative borylation as group 5 metals form stronger hydride bonds than titanium, which could facilitate the β -hydrogen abstraction step in dehydrogenative borylation.² Niobium also has a smaller propensity than tantalum to activate dihydrogen, which is an important byproduct of the catalytic cycle. Favoring dihydrogen production and subsequent release would assist in driving the reaction toward the desired

alkenylboron product. The differences between tantalum and niobium have been recently highlighted by a study of the related hydroboration reaction that indicated that the coordination of HBCat (HBCat = catecholborane) to $(\eta^5\text{-C}_5\text{Me}_5)_2\text{M}$ ($\text{M} = \text{Nb}, \text{Ta}$) is different. The tantalum derivative is described as having two hydrides and a BCat bond and thus is formally tantalum(V), while the niobium complex prefers one hydride and an η^2 -coordination of the H-Bcat bond thus is formally niobium(III).³ Overall, niobium is expected to be superior at β -hydrogen elimination than titanium and better at releasing hydrogen than tantalum.

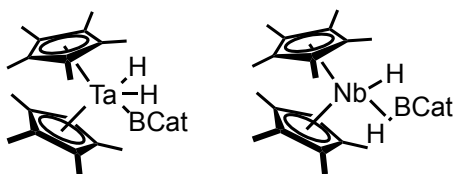


Figure 12 Structural differences between tantalum and niobium HBCat activation.³

Search for Suitable Ta/Nb Precursors

Initial salt metathesis reactions between the potassium salt of the 1,1'-diamidoferrocene ligand and tantalum pentachloride led to a mixture of intractable products. Based upon suggestions from the Mashima group at Osaka University, two group 5 metal complexes were identified to be possibly useful starting materials. Trimethyldichlorotantalum and trimethyldichloroniobium both contain σ -bonded alkyl groups for alkane elimination and chlorides for salt metathesis.⁴ These starting materials provide several potential pathways of 1,1'-diamidoferrocene coordination. Unfortunately, the synthesis of both group 5 starting materials requires dimethyl zinc, a costly reagent. Efforts to synthesize more cost effective group 5 starting materials containing σ -bonded alkyl groups led to intractable and unknown products. For

example, reacting niobium pentachloride with potassium benzyl generated bibenzyl rather than the desired benzylchloroniobium complex. Unfortunately, both the protonated and salt form of the ligand failed to generate the desired group 5 complex when reacted with trimethyldichlorotantalum.

To further elucidate possible mechanisms for the observed reactivity, a control reaction between ferrocene and niobium pentachloride was performed. Upon the addition of niobium pentachloride, the red-orange solution became blue-green in color, suggesting the formation of a ferrocenium cation. Moreover, niobium halide salts are well known to be able to carry a negative charge.⁵ From this control reaction, we postulated that electron transfer from 1,1'-diamidoferrocene to the group 5 starting material was occurring prior to coordination. To avoid the issue of electron transfer, reduced group 5 starting materials were pursued. Procedures for reduced monomeric tantalum complexes were unreliable and required strong reducing agents, such as sodium amalgam or potassium graphite.⁶ However, a method for reducing niobium pentachloride by aluminum powder in acetonitrile proved to be more reproducible.⁷ Acetonitrile was easily exchanged for THF (THF = tetrahydrofuran), generating the bis(THF)tetrachloroniobium compound. Salt metathesis between the potassium salt of the 1,1'-diamidoferrocene ligand and the reduced niobium(IV) starting material (Figure 13) resulted in a purple solution, suggestive of a niobium(IV) complex.⁸

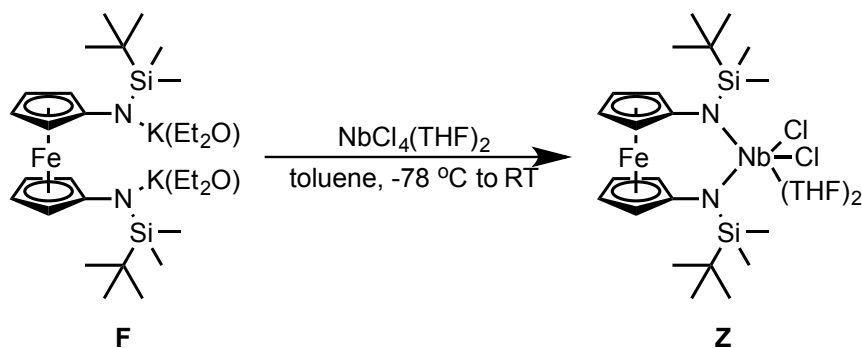


Figure 13 Synthetic scheme for the formation proposed niobium(IV) product.

Conclusion

Based upon on the control reaction with ferrocene, the 1,1'-diamidoferrocene ligand appears to reduce niobium pentachloride. ^1H NMR spectrum of the product from reacting ligand **F** with niobium tetrachloride suggests complex **Z** as a likely structure. Current work should be focused on further characterizing niobium complex **Z** using X-ray crystallography, EPR spectroscopy, and cyclic voltammetry. Also, reactivity studies with olefins and boranes should be conducted, working toward catalyzing dehydrogenative borylation with niobium complex **Z**.

Supporting Information

Materials and Methods

Unless otherwise stated, reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques or in an MBraun inert-gas glovebox. Solvents were purified using a two-column solid-state purification system developed by Grubbs and transferred into the glovebox via Schlenk bomb. NMR solvents were purchased from Cambridge Isotope Laboratories, degassed, and stored over 4 Å molecular sieves until use. Potassium graphite was obtained from the Kaner laboratory (UCLA). $\text{Ta/NbMe}_3\text{Cl}_2$,⁴ $\text{NbCl}_4(\text{THF})_2$,⁷ $\text{TaCl}_3(\text{py})_3$,^{6a} $\text{TaCl}_4(\text{PEt}_3)_2$,^{6b} and 1,1'-diamidoferrocene ligand^{9,10} were prepared using published procedures.

All other materials were used as received. ^1H NMR spectra were recorded on Bruker300 spectrometers at room temperature in C_6D_6 . Chemicals shifts are reported with respect to solvent residual peaks, 7.16 ppm for C_6D_6 .

Experimental Procedures

Attempted Synthesis of Trichlorodibenzyl niobium. Solid potassium benzyl (60.4 mg, 0.46 mmol, 2 eq) was added to a frozen solution of niobium pentachloride (62.7 mg, 0.23 mmol) in toluene. The reaction mixture was allowed to stir at room temperature for 3 h. It was then filtered through Celite and the filtrate was dried. ^1H NMR (300 MHz, C_6D_6), δ (ppm): 7.10 (m, 8H, - C_6H_5), 2.84 (s, 4H, C_2H_4). ^1H NMR showed the formation of bibenzyl.

Attempted Synthesis of Trimethyldichloroniobium using Dimethylaluminum Chloride. A solution of dimethylaluminum chloride (1.1 mL, 9.08 mmol, 1.5 eq) in hexanes was added to a frozen hexanes mixture of niobium pentachloride (202.5 mg, 0.74 mmol) in hexanes. The reaction mixture was warmed to room temperature and allowed to stir overnight. The solution was filtered through Celite to yield a golden-yellow solution. Solvent was removed under vacuum. ^1H NMR (300 MHz, C_6D_6), δ (ppm): 2.30 (s, 9H), 0.42 (s, 9H). ^1H NMR showed the formation of unknown product(s).

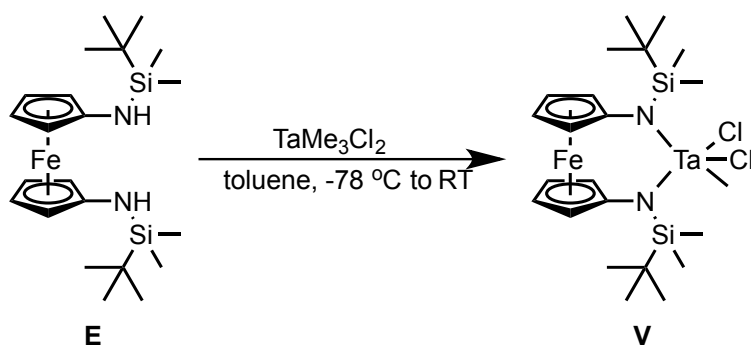
Synthesis of Trimethyldichlorotantalum using Dimethyl Zinc. A solution of dimethyl zinc (2.3 mL, 17.4 mmol, 1.5 eq) in heptane was slowly added to a frozen solution of tantalum pentachloride (548.5 mg, 1.5 mmol) in hexanes. The reaction mixture was warmed to room temperature and allowed to stir overnight. The solution was filtered through Celite and solvents were removed under vacuum. Yield: 311.2 mg, 64.0 %. ^1H NMR (300 MHz, C_6D_6), δ (ppm): 1.64 (s, 9H).⁴

Synthesis of Trimethyldichloroniobium using Dimethyl Zinc. Procedure was identical to that used for the trimethyldichlorotantalum. Yield: 286.3 mg, 66.3 %. ^1H NMR (300 MHz, C_6D_6), δ (ppm): 1.49 (s, 9H).⁴

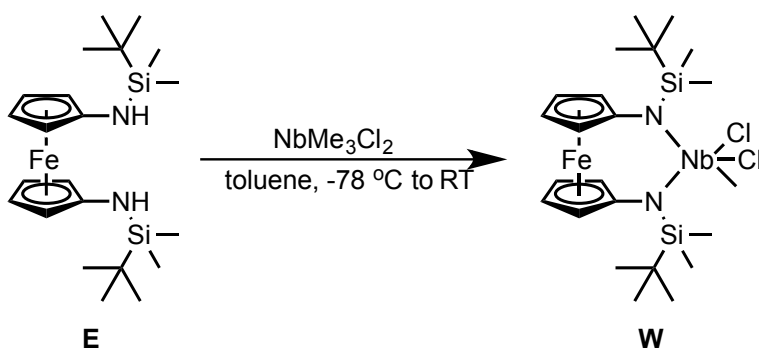
Synthesis of $\text{NbCl}_4(\text{THF})_2$. Solid niobium pentachloride (3.0807 g, 0.011 mol) was added to a slurry of aluminum powder (0.1125 g, 4.16 mmol, 0.33 eq) in acetonitrile. After 2 h of stirring, the reaction mixture was filtered through Celite to yield a dark orange-brown solution. Solvent was removed under vacuum to give a redish-brown solid. The solid was dissolved in THF and stirred vigorously for 3 h. After the solution was filtered, the remaining solid was washed with THF, then pentane yielding a pale yellow solid. Solvent was removed under vacuum. Yield: 215.0 mg, 54.2 %.⁷

Synthesis of $\text{TaCl}_3(\text{py})_3$. A stirred suspension of potassium graphite (648.2 mg, 4.79 mmol, 3.7 eq) in diethyl ether was added to solid tantalum pentachloride (459.4 mg, 1.28 mmol), followed the addition of 10 mL of pyridine. The solution was stirred for 1 h, filtered and allowed to precipitate at $-35\text{ }^\circ\text{C}$. Yield 74.6 mg, 11.1 %.^{6a}

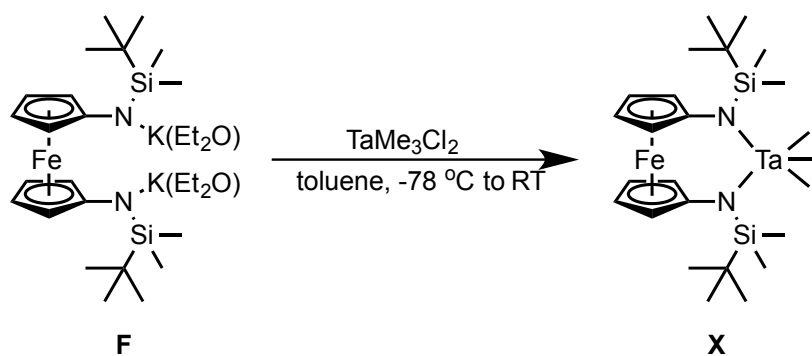
Synthesis of $\text{TaCl}_4(\text{PET}_3)_2$. Triethylphosphine (384.2 mg, 3.25 mmol, 2.2 eq) and sodium amalgam (41.4 mg, 1.80 mmol Na in 0.79 mL Hg) were added to a solution of tantalum pentachloride (537.0 mg, 1.49 mmol) in toluene. The solution was stirred for 1 h, filtered, concentrated and allowed to precipitate at $-35\text{ }^\circ\text{C}$. Yield: 74.1 mg, 8.8 %.^{6b}



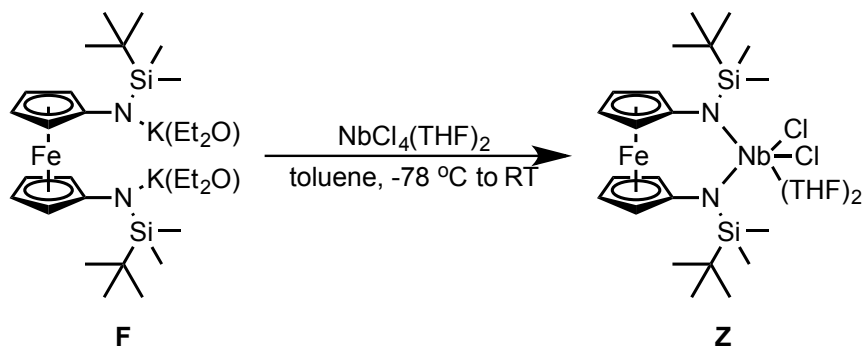
Attempted Synthesis of V using E. A solution of **E** (122.1 mg, 0.27 mmol, 0.9 eq) in toluene was added dropwise to a frozen solution trimethyldichlorotantalum (100.1 mg, 0.31 mmol) in toluene. After 30 min, the color of the solution turned dark-orange. Solvent was removed under vacuum. ^1H NMR (300 MHz, C_6D_6), δ (ppm): 3.82 (d, 8H, CpH), 2.06 (s, 2H, -NH), 0.92 (s, 18H, -Si(*t*-Bu)), 0.16 (s, 12H, -SiMe₂). The ^1H NMR spectrum showed protonated ligand.



Attempted Synthesis of W using E. Procedure was identical to that used for the trimethyldichlorotantalum. ^1H NMR (300 MHz, C_6D_6), δ (ppm): 3.82 (d, 8H, CpH), 2.06 (s, 2H, -NH), 0.92 (s, 18H, -Si(*t*-Bu)), 0.16 (s, 12H, -SiMe₂). The ^1H NMR spectrum showed protonated ligand.



Attempted Synthesis of X using F. A slurry of F (107.9 mg, 0.33 mmol, 0.9 eq) in toluene was added to a frozen solution of trimethyldichlorotantalum (137.0 mg, 0.20 mmol) in toluene. The solution was warmed to room temperature and allowed to stir for 3 hours. After the solution was filtered through Celite and solvent was removed under vacuum. The ^1H NMR spectrum showed protonated ligand (^1H NMR (300 MHz, C_6D_6), δ (ppm): 3.82 (d, 8H, CpH), 2.06 (s, 2H, -NH), 0.92 (s, 18H, -Si(*t*-Bu)), 0.16 (s, 12H, -SiMe₂)) along with peaks from unknown product(s).



Proposed Synthesis of Z. A slurry of F (95.1 mg, 0.14 mmol, 0.9 eq) in toluene was added to a frozen solution of $\text{NbCl}_4(\text{THF})_2$ (66.4 mg, 0.17 mmol) in toluene. The solution became purple within 1 h of addition. After stirring for 6 h, the solution was filtered through Celite and volatiles

were removed under vacuum. The resulting solid was washed with hexanes and dried. Yield: 55.1 mg, 64.1 %. ^1H NMR (300 MHz, C_6D_6), δ (ppm): 3.83 (d, 8H, CpH), 3.21 (q, 8H, CH_2O), 1.11 (t, 8H, CH_2), 0.92 (s, 18H, $-\text{Si}(t\text{-Bu})$), 0.16 (s, 12H, $-\text{SiMe}_2$). Peaks at 7.02 and 2.11 ppm are toluene and 1.36 ppm is hexanes.

Appendix

^1H NMR Spectra

^1H NMR (300 MHz, C_6D_6) of attempted reaction between NbCl_5 and potassium benzyl

2.842

7.108

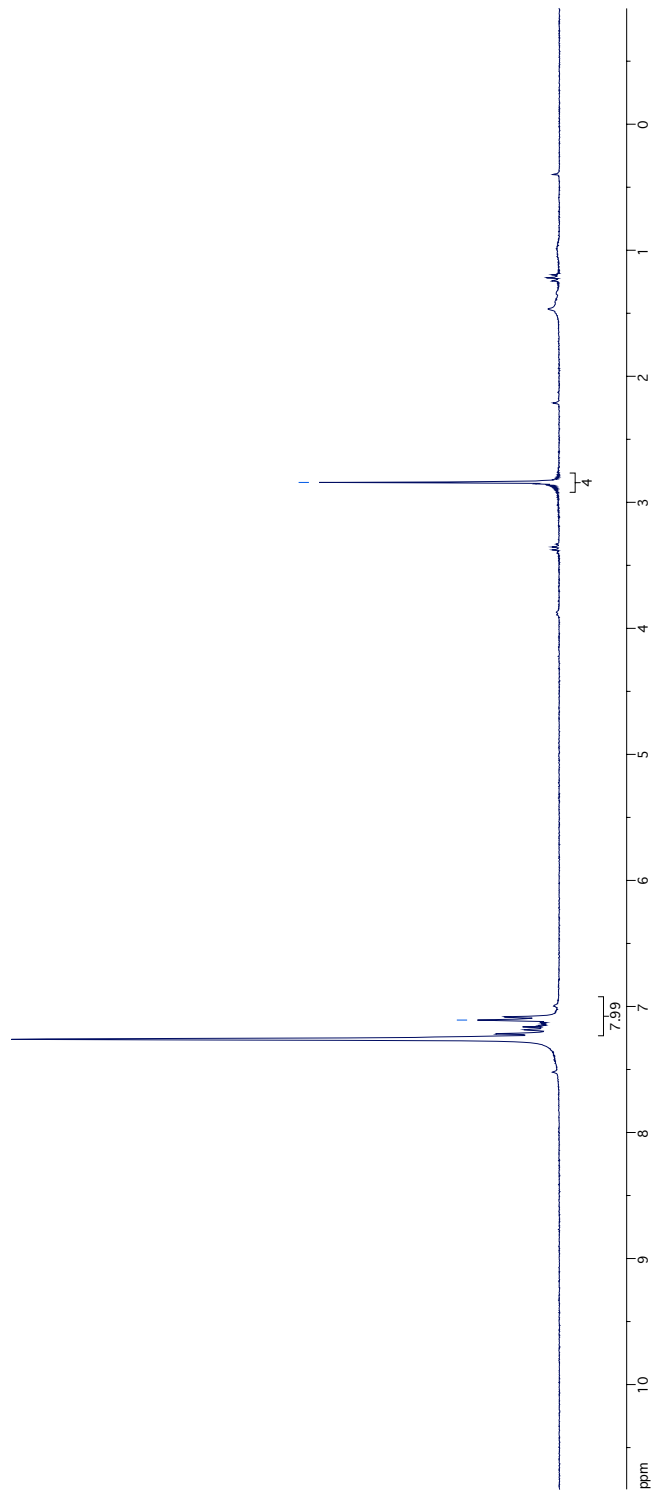


Figure B1 ^1H NMR (300 MHz, C_6D_6) of reaction between NbCl_5 and potassium benzyl.

¹H NMR (300 MHz, C₆D₆) of attempted reaction between NbCl₅ and dimethylaluminum chloride

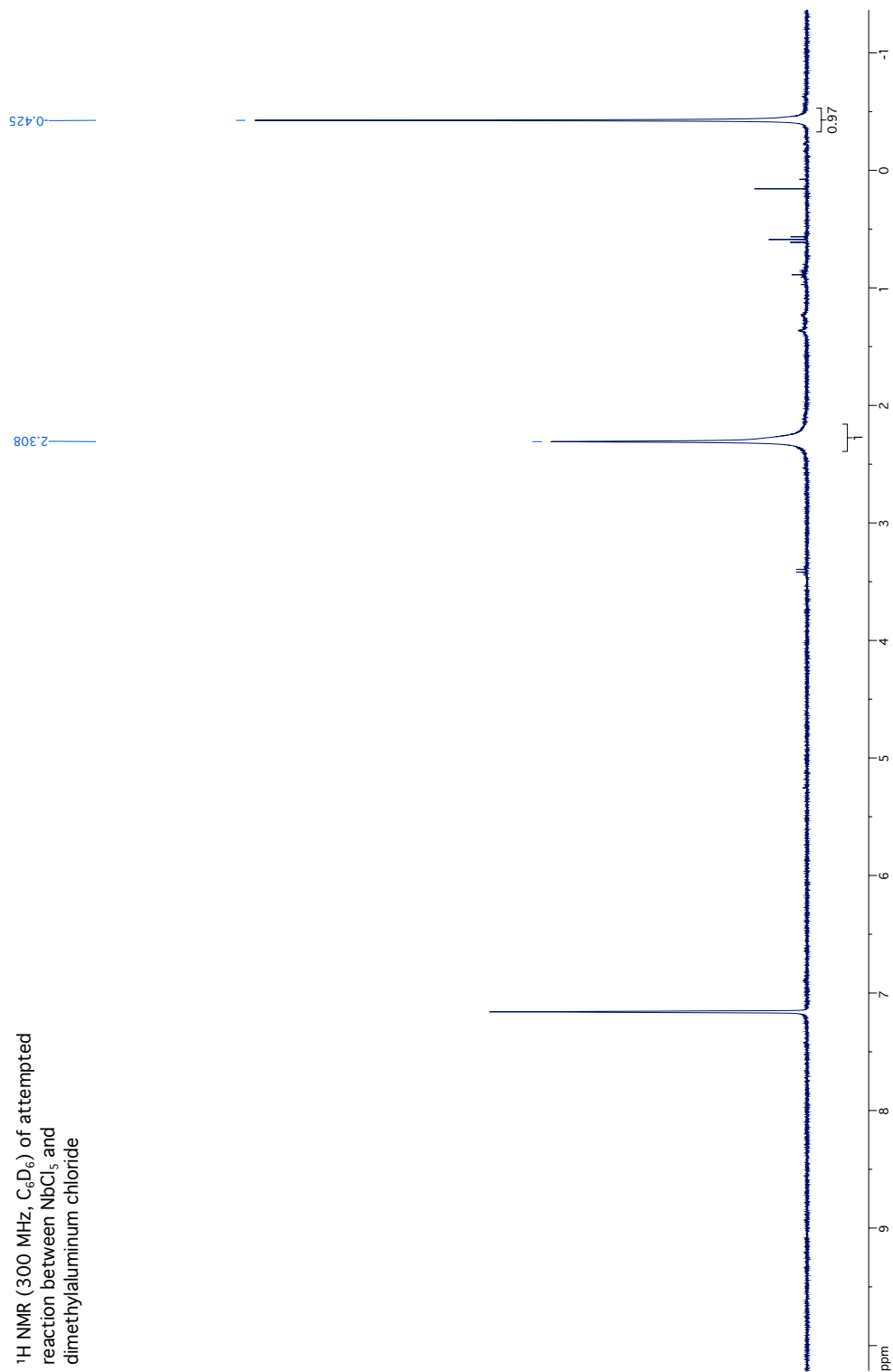


Figure B2 ¹H NMR (300 MHz, C₆D₆) of reaction between NbCl₅ and Me₂AlCl.

^1H NMR (300 MHz, C_6D_6) of
trimethyldichloro tantalum

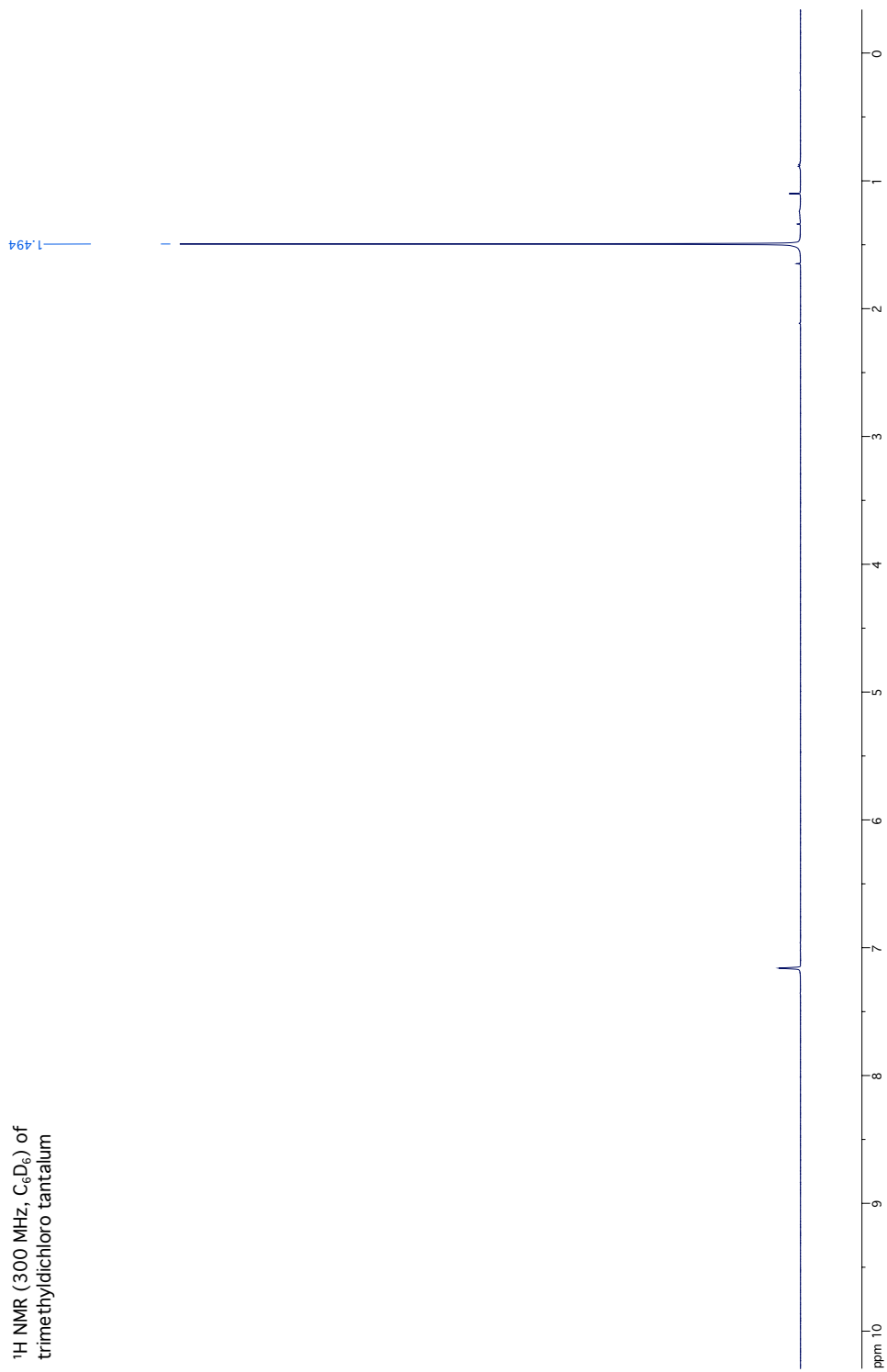


Figure B3 ^1H NMR (300 MHz, C_6D_6) of trimethyldichloro tantalum.

^1H NMR (300 MHz, C_6D_6) of
trimethyldichloro niobium

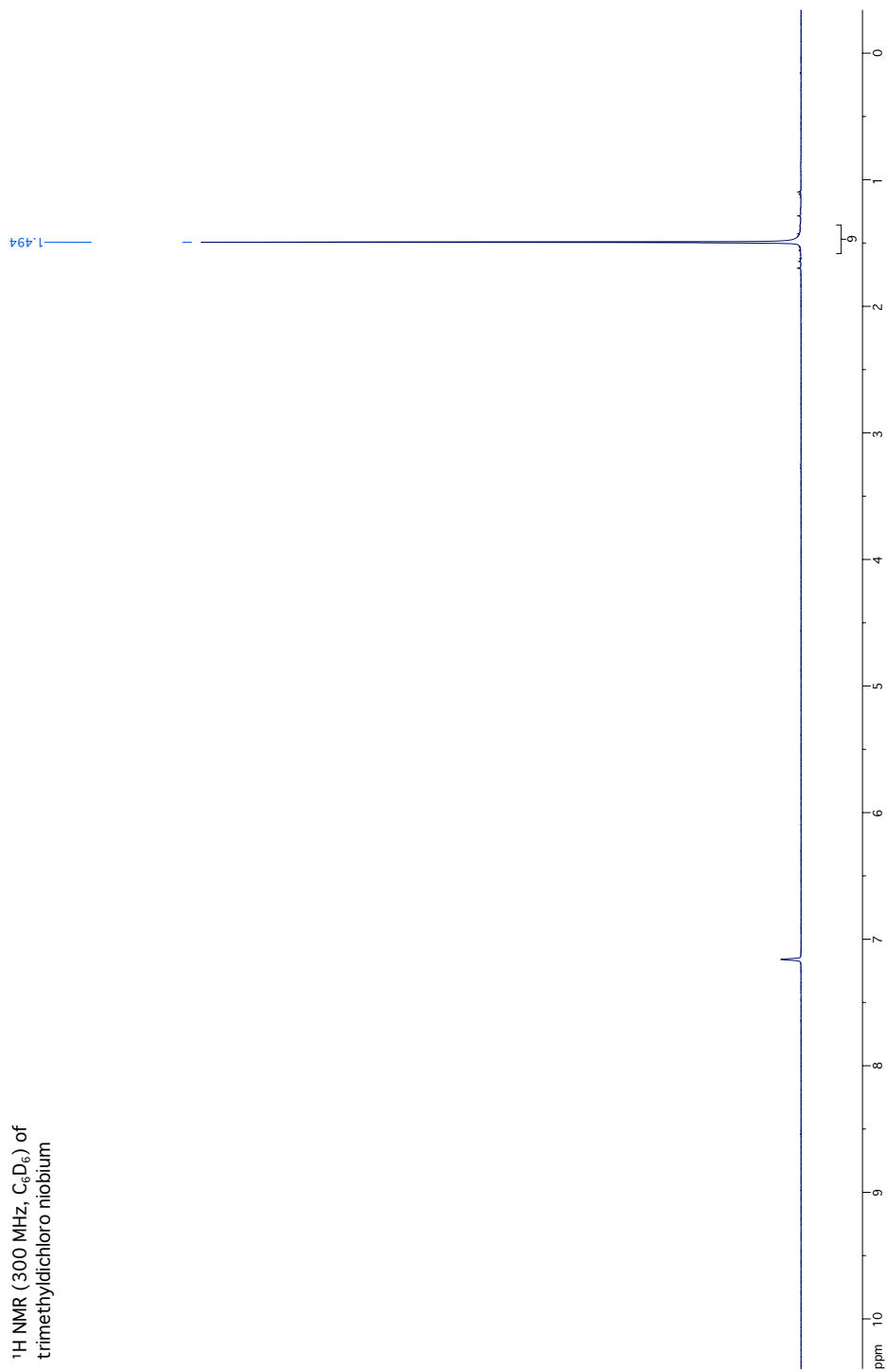


Figure B4 ^1H NMR (300 MHz, C_6D_6) of trimethyldichloro niobium.

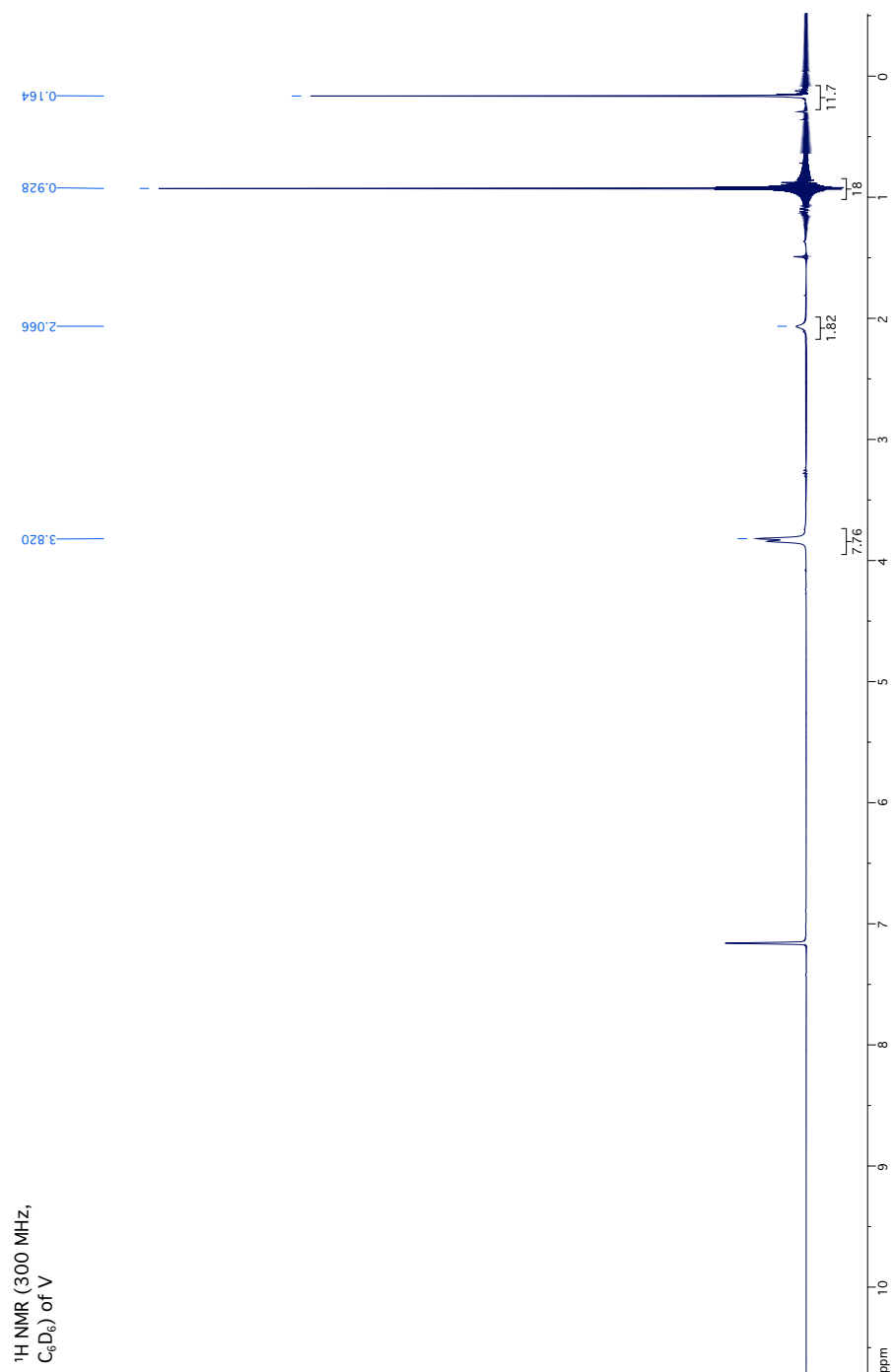


Figure B5 ¹H NMR (300 MHz, C₆D₆) of reaction between **E** and TaMe₃Cl₂. Peaks picked for **E**.

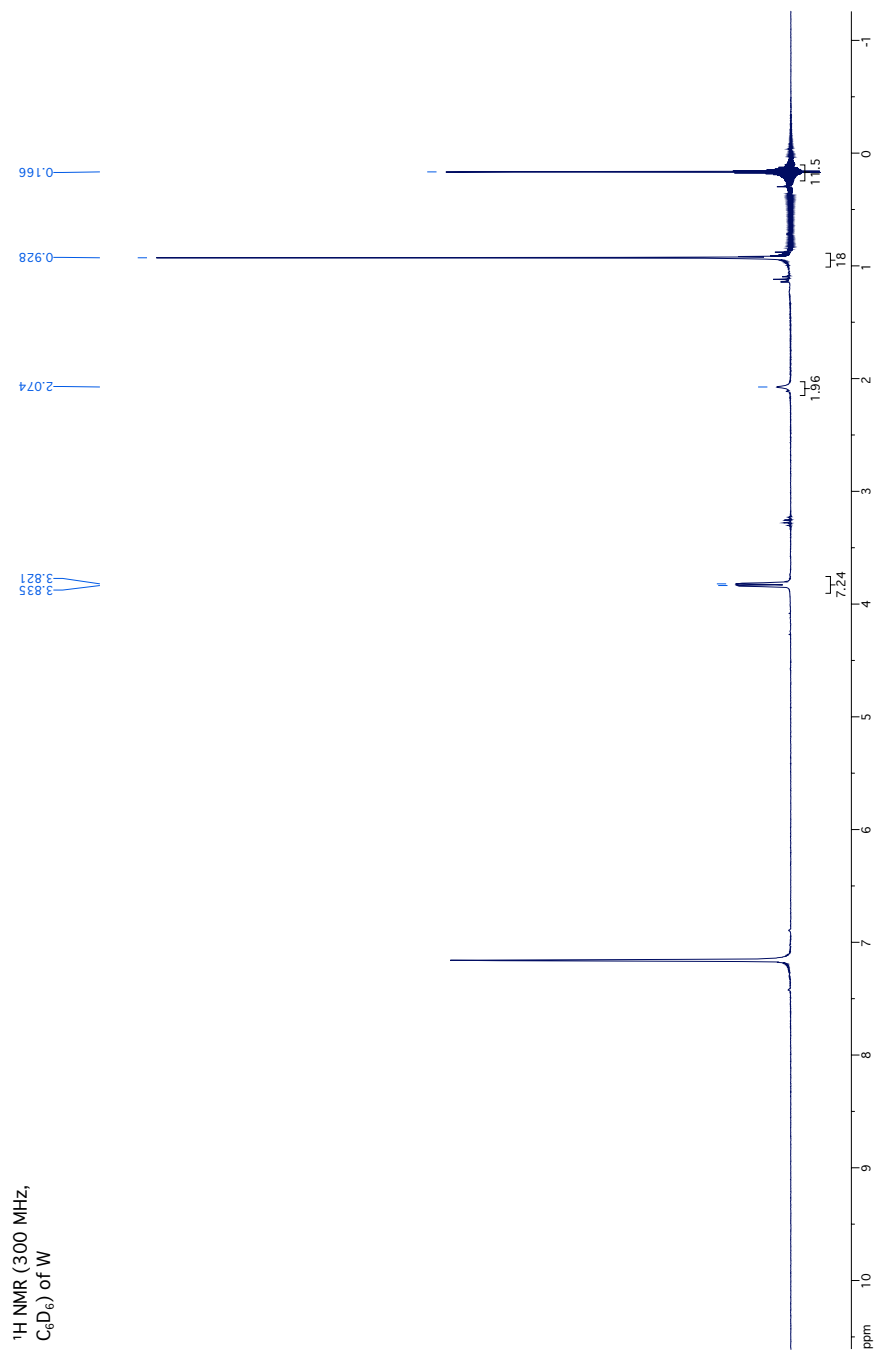


Figure B6 ^1H NMR (300 MHz, C_6D_6) of reaction between **E** and NbMe_3Cl_2 . Peaks picked for **E**.

¹H NMR (300 MHz,
C₆D₆) of X

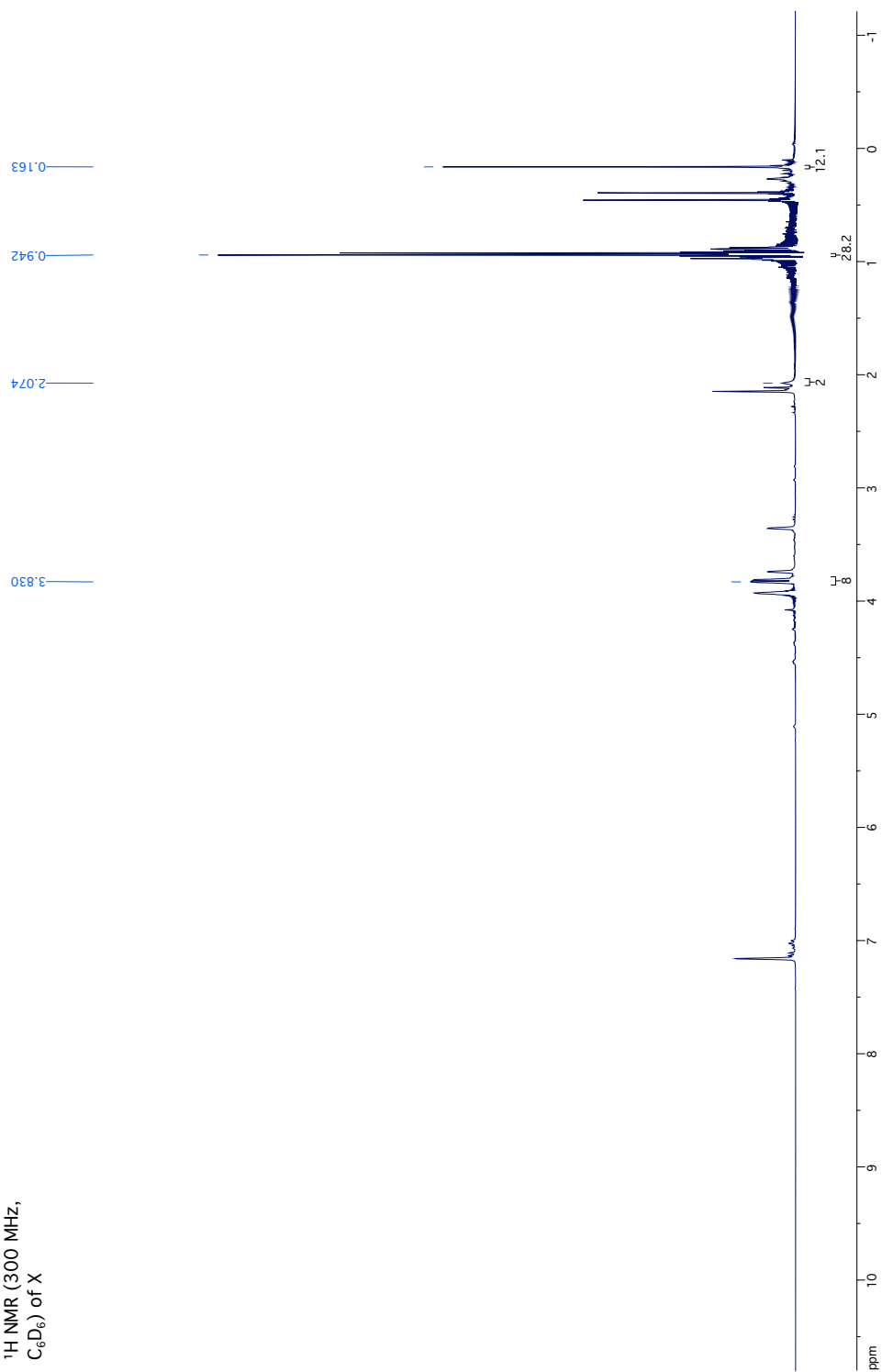


Figure B7 ¹H NMR (300 MHz, C₆D₆) of reaction between **F** and TaMe₃Cl₂. Peaks picked for **E**.

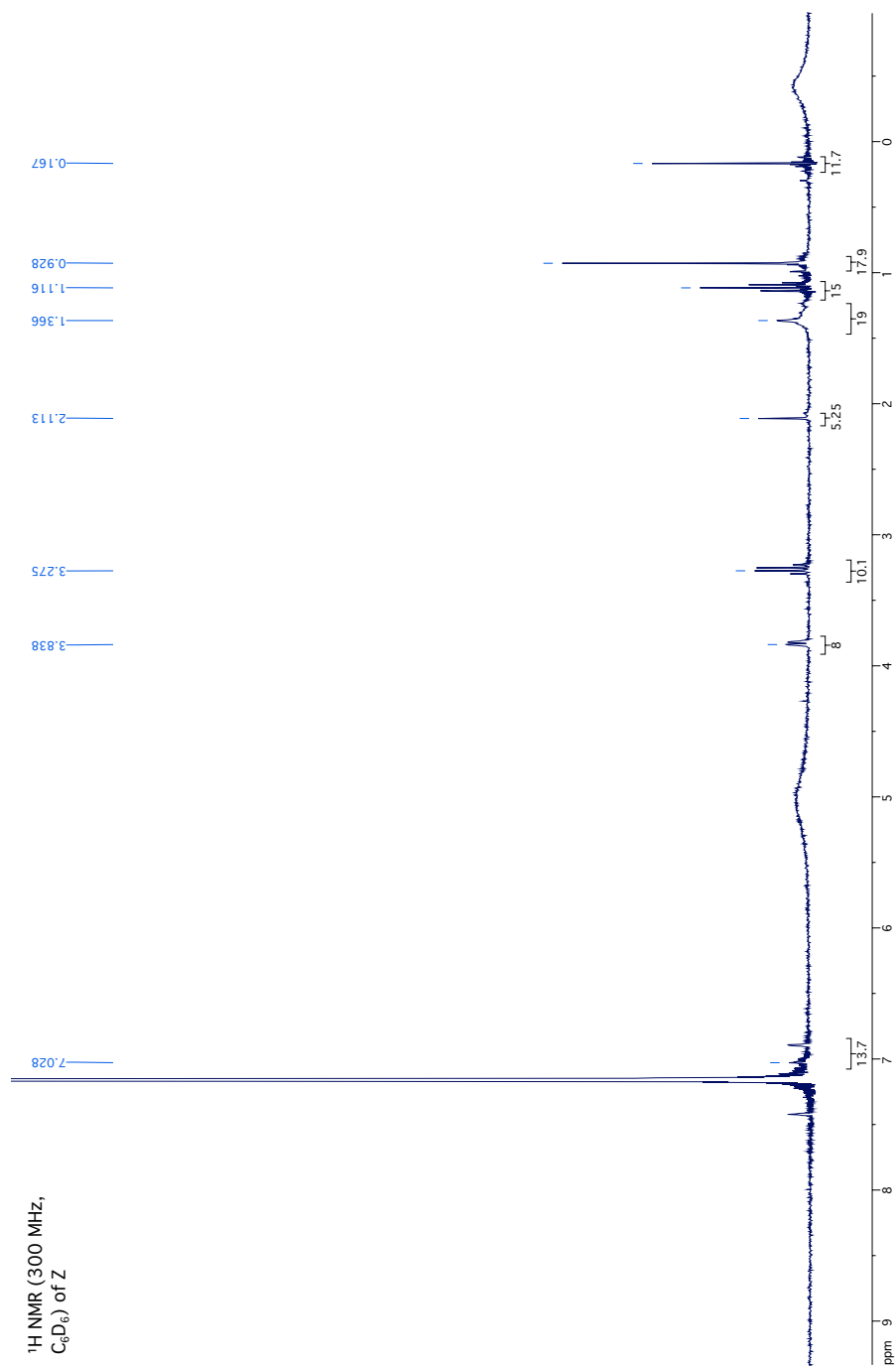


Figure B8 ¹H NMR (300 MHz, C₆D₆) of **Z**.

References

- (1) (a) Kondoh, A.; Jamison, T. F. *Chem. Commun.* **2010**, 46, 907. (b) Mikhalid, I. A. I.; Coaper, B.; Edes, S. N.; Coventry, D. N.; Souza, F. E. S.; Thomas, R. L.; Hall, J. J.; Bi, S. W.; Lin, Z.; Marger, T. B. *Dalton Trans.* **2008**, 8, 1055. (c) Ohmura, T.; Takasaki, Y.; Furukawa, H.; Sugimoto, M. *Angew. Chem. Int. Ed.* **2009**, 48, 2372. (d) Wadepohl, H. *Angew. Chem. Int. Ed.* **1997**, 36, 2441.
- (2) Skinner, H. A.; Connor, J. A. *Pure & Appl. Chem.* **1985**, 57, 79.
- (3) Lantero, D. R.; Miller, S. L.; Cho, S. Y.; Ward, D. L.; Smith, M. R. *Organometallics* **1999**, 18, 235.
- (4) Juvinall, G. L. *J. Am. Chem. Soc.* **1964**, 86, 4202.
- (5) Fowles, G. W. A.; Rice, D. A.; Wilkins, J. D. *J. Chem. Soc., Dalton Trans.* **1974**, 10, 1080.
- (6) (a) Cotton, F. A.; Murillo, C. A.; Wang, X. *Inorg. Chim. Acta.* **1996**, 245, 115. (b) Cotton, F. A.; Duraj, S. A.; Roth, W. J. *Inorg. Chem.* **1984**, 23, 4046.
- (7) Manzer, L. E. *Inorg. Chem.* **1977**, 16, 525.
- (8) Acedo, L.; Otero, A.; Royo, P. *J. Organomet. Chem.* **1983**, 258, 181.
- (9) Shafir, A.; Power, M. P.; Whitener, G. D.; Arnold, J. *Organometallics* **2001**, 20, 1365.
- (10) Monreal, M. J.; Carver, C. T.; Diaconescu, P. L. *Inorg. Chem.* **2007**, 46, 7226.