

Site-Selective Alkoxylation of Benzylic C–H Bonds via Photoredox Catalysis

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There are relatively few methods that accomplish the selective alkoxylation of sp^3 -hybridized C–H bonds, particularly in comparison to the numerous analogous strategies for C–N and C–C bond formation. We report a photocatalytic protocol for the functionalization of benzylic C–H bonds with a wide range of readily available oxygen nucleophiles. Our strategy merges the photoredox activation of arenes with copper(II)-mediated oxidation of the resulting benzylic radicals, which enables the introduction of benzylic C–O bonds with high site selectivity, chemoselectivity, and functional group tolerance. This method enables the late-stage introduction of complex alkoxy groups into bioactive molecules, providing a practical new tool with potential applications in synthesis and medicinal chemistry.

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Site-Selective Alkoxylation of Benzylic C–H Bonds via Photoredox Catalysis

Byung Joo Lee, Kimberly S. DeGlopper, and Tehshik P. Yoon*

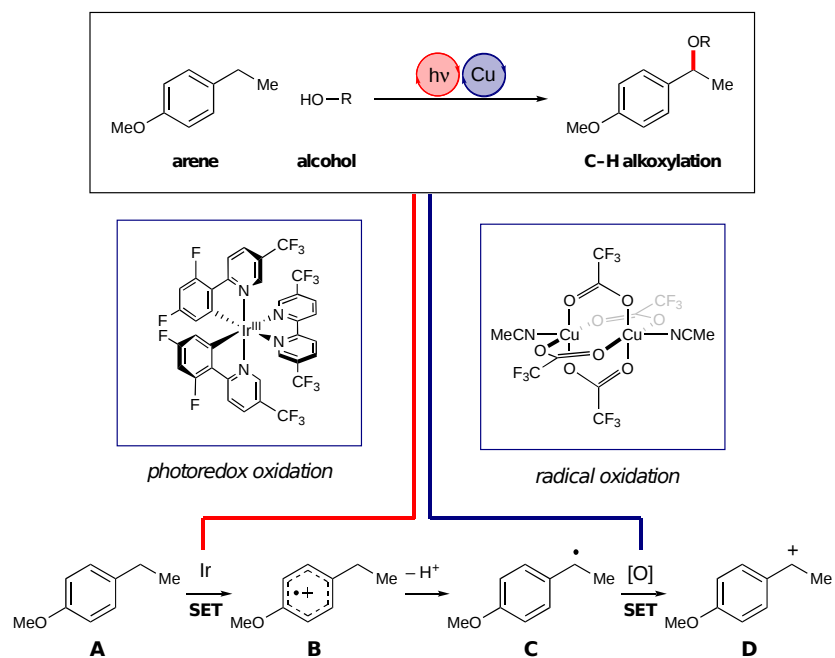
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Abstract: There are few methods that can accomplish the selective alkoxylation of sp^3 -hybridized C–H bonds, particularly in comparison to the numerous analogous strategies for C–N and C–C bond formation. We report a photocatalytic protocol for the functionalization of benzylic C–H bonds with a wide range of readily available oxygen nucleophiles. Our strategy merges the photoredox activation of arenes with copper(II)-mediated oxidation of the resulting benzylic radicals, which enables the introduction of benzylic C–O bonds with high site selectivity, chemoselectivity, and functional group tolerance. This method enables the late-stage introduction of complex alkoxy groups into bioactive molecules, providing a practical new tool with potential applications in synthesis and medicinal chemistry.

The development of methods for the site-selective functionalization of sp^3 -hybridized C–H bonds has profoundly influenced the way that organic chemists approach complex molecule synthesis.¹ Late-stage functionalization strategies that enable one-step incorporation of new functional groups are particularly important because they can provide an efficient strategy to rapidly assess structural analogues of pharmaceutical candidates for new chemical and biological properties.² Much of the recent activity in this field has centered on the introduction of fluorine, carbon, and nitrogen moieties at aliphatic positions³. These reactions are fundamentally oxidative transformations; thus, their development has benefitted from the availability of numerous electrophilic group-transfer oxidants for each of these important classes of C–H functionalizations (e.g., Selectfluor and NFSI for C–F bond formation; organohalides, Michael acceptors, and diazoesters for C–C bond formation; and azides, hydroxylamine derivatives, and iminoiodinanes for C–N bond formation).

In contrast, few methods for the direct alkoxylation of sp^3 -hybridized C–H bonds have been reported to date,⁴ despite the ubiquity of C–O bonds in bioactive compounds.⁵ Almost all of reported methods that effect the oxygenation of aliphatic C–H bonds have been hydroxyl- and ester-forming reactions,⁶ consistent with the availability of corresponding terminal oxidants (e.g., hydroperoxides and peroxyesters). Electrophilic oxidants that can be used as alkoxy group transfer reagents, on the other hand, are not well known, which has been an impediment for the development of similarly robust C–H alkoxylation reactions.

We imagined that an umpolung strategy exploiting a photoredox catalyst in combination with an appropriate terminal oxidant would enable the direct incorporation of a wide range of simple nucleophilic alcohols into Csp^3 –H bonds.⁷ A brief outline of our design strategy is summarized in Scheme 1. Photoinduced one-electron oxidation of an electron-rich arene (**A**) would afford a radical cation (**B**) whose benzylic C–H bonds are significantly acidified;⁸ facile deprotonation would afford benzylic radical intermediate **C**. A radicalophilic terminal oxidant could transform **C** into the corresponding carbocation (**D**), which could be trapped by a nucleophilic alcohol without the need to prepare a pre-oxidized electrophilic alkoxy group-transfer reagent. An analogous oxidation–deprotonation–oxidation sequence was proposed in the electrochemical benzylic methoxylation of estrone,⁹ but this method requires the use of an alcohol solvent, which limits its utility to the incorporation of simple alkoxy groups. More recently, Pandey¹⁰ and Guo¹¹ have developed photoredox protocols for benzylic ether formation using oxygen as a terminal oxidant; these photocatalytic methods, however, are limited to intramolecular bond formations. The development of a photocatalytic method for the cross-coupling of complex alcohols with complex benzylic C–H donors would be a useful new tool for organic synthesis.



Scheme 1. Design Strategy for Photocatalytic Etherification of Benzylic C–H Bonds.

We recently proposed that Cu(II) salts as relatively inexpensive, non-toxic reagents that are ideal and underutilized terminal oxidants for net-oxidative photoredox reactions.^{12,13} Seminal studies by Kochi demonstrated that a variety of organic radicals undergo oxidation by Cu(II) at diffusion-controlled rates.¹⁴ Moreover, the use of Cu(II) oxidants avoids the intermediacy of reactive open-shelled radical intermediates (e.g., oxygen-centered radicals, superoxide, singlet oxygen) that can be incompatible with highly functionalized complex organic molecules. Our previous investigations revealed that the photocatalytic oxidative oxyamination of alkenes is uniquely enabled by the use of Cu(TFA)₂ as a terminal oxidant, and that a wide range of other, more conventional terminal oxidants failed to afford the difunctionalization products. We reasoned, therefore, that a combination of photoredox catalyst and Cu(II) oxidant would be effective for performing benzylic C–H alkoxylation reactions as well.

Table 1. Optimization Studies for Methoxylation of Benzylic C–H Bonds.

Entry ^[a]	Photocatalyst	Terminal oxidant	Yield ^[b]
1	[Ir(dF(CF ₃)ppy) ₂ (5,5'-dCF ₃ bpy)]PF ₆	Cu(OAc) ₂ •H ₂ O	8%
2	[Ir(dF(CF ₃)ppy) ₂ (5,5'-dCF ₃ bpy)]PF ₆	Cu(TFA) ₂ •H ₂ O	61%
3	[Ir(dF(CF ₃)ppy) ₂ (5,5'-dCF ₃ bpy)]PF ₆	Cu(TFA) ₂ •MeCN	73%
4	[Ir(dF(CF ₃)ppy) ₂ (5,5'-dCF ₃ bpy)]PF ₆	Air, PhI(OAc) ₂ , TEMPO, MnO ₂ , FeCl ₃ , <i>t</i> -BuOOH, or benzoquinone	<10%
5	[Ir(dF(CF ₃)ppy) ₂ (bpy)]PF ₆	Cu(TFA) ₂ •MeCN	23%
6	Fukuzumi acridinium (5.0 mol%)	Cu(TFA) ₂ •MeCN	10%
7	Triphenylpyrylium (2.5 mol%)	Cu(TFA) ₂ •MeCN	5%
8	none	Cu(TFA) ₂ •MeCN	0%
9	[Ir(dF(CF ₃)ppy) ₂ (5,5'-dCF ₃ bpy)]PF ₆	none	0%
10 ^[c]	[Ir(dF(CF ₃)ppy) ₂ (5,5'-dCF ₃ bpy)]PF ₆	Cu(TFA) ₂ •MeCN	0%

[a] Unless otherwise noted, all reactions were conducted using 0.3 mmol of **1** in degassed MeCN and irradiated with a 427 nm Kessil lamp for 6 h. [b] Yields determined by ¹H NMR analysis of the crude reaction mixtures using phenanthrene as an internal standard. [c] Reaction was conducted in the dark.

To test this hypothesis, we examined the reaction of 4-ethylanisole (**1**) with 2 equiv of methanol (Table 1). [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)]PF₆ was selected as a photocatalyst because its excited-state reduction potential (+1.68 V vs SCE)¹⁵ should be sufficiently positive to oxidize **1** (+1.52 V). The use of Cu(OAc)₂ as a terminal oxidant indeed produced the desired product **2**, but in only 8% yield (entry 1). Acetoxylation was the major oxidation pathway in this experiment. We hypothesized that less nucleophilic ligands on Cu(II) might decrease the formation of this undesired product. Indeed, Cu(TFA)₂ provided a higher yield and no observable ester product (entry 2); however, benzylic alcohol was a significant byproduct, which we attributed to the presence of water in the hydrate form of the commercial salt. We thus prepared the anhydrous acetonitrile complex Cu(TFA)₂(MeCN),¹⁶ the use of which prevented formation of the hydroxylated product and afforded the desired methanol adduct in 73% yield (entry 3). Cu(II) salts were unique in their ability to promote this alkoxylation: we screened a wide range of other common terminal oxidants, and none produced significant yields of **1** (entry 4), consistent with our guiding hypothesis. Alternate photocatalysts also afforded diminished reaction efficiency. Both less-oxidizing Ir photocatalysts¹⁷ (entry 5) and more-oxidizing organic photocatalysts¹⁸ (entry 6 and 7) afforded diminished yields. Finally, control experiments validated the photocatalytic nature of this reaction and the necessity of Cu(II) co-oxidant; no product was observed in the absence of photocatalyst, Cu(II) terminal oxidant, or light (entries 8–10).

Table 2. Scope of C–H Oxygenation via Photoredox Catalysis^a

Arene Scope			Alcohol Scope		
Site Selectivity			Other Nucleophiles		
Heteroarene Scope			Incompatible Nucleophiles		

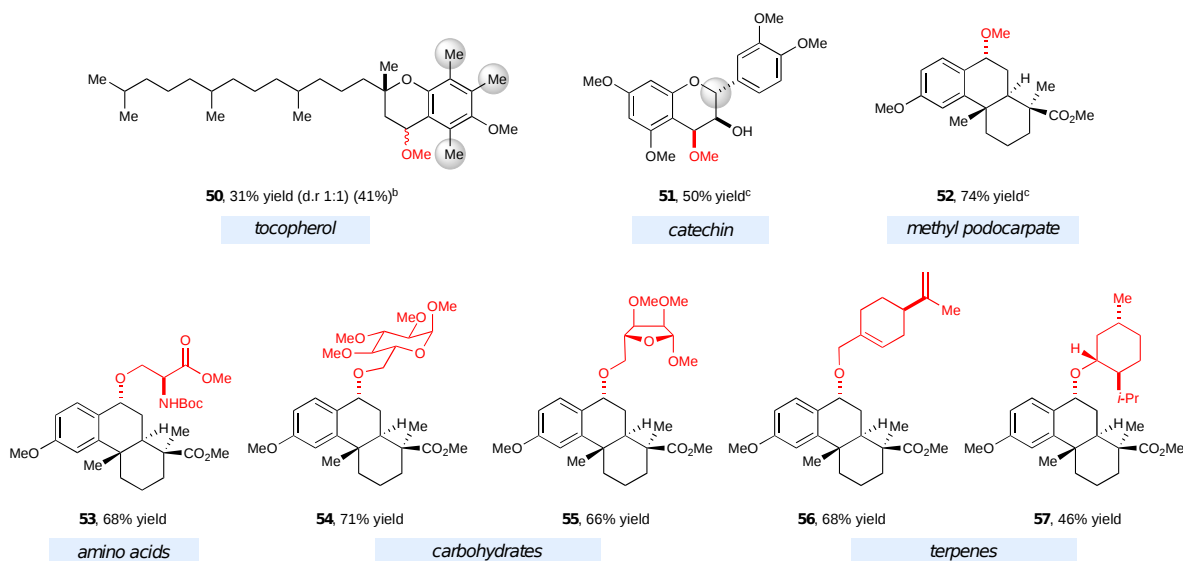
[a] Reaction condition: substrate (0.6 mmol, 1 equiv.), [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)]PF₆ (1 mol%), K₂HPO₄ (3 equiv), Cu(TFA)₂(MeCN) (1.2 equiv), methanol (2 equiv), MeCN (0.2 M) unless otherwise noted. Yields represent the averaged isolated yields from two experiments. [b] Yield determined by ¹H NMR analysis of the crude reaction mixtures using phenanthrene as an internal standard. [c] Reaction conducted at 0.1 M using 8 equiv methanol. [d] Reaction conducted using 8 equiv alcohol.

The scope of this benzylic alkoxylation protocol is summarized in Table 2. The reaction is most efficient at secondary benzylic positions; primary C–H bonds undergo competitive overoxidation that diminishes the yield of monoalkoxylation products somewhat (3), and tertiary sites undergo functionalization at significantly slower rates (4). The latter can be addressed by diluting the reaction to increase photon flux and by increasing the amount of MeOH to 8 equiv. The presence of alkoxy substituents on the arene that could stabilize the putative quinone methide intermediate is strictly required, but a variety of such groups along with additional substituents are well tolerated (5–9, 17–21). The functional group compatibility of this method is high and includes acidic heteroatoms (10 and 14), basic heterocycles (20), base-sensitive moieties (11 and 12), and boronate ester or azide groups that provide handles for further synthetic manipulation (13 and 15). In general, this reaction displayed a remarkable degree of site selectivity consistent with the predicted stability of the quinone methide intermediate (17–19). Thus functionalization of *p*-alkoxy-activated benzylic positions is highly selective even in the presence of weaker benzylic C–H bonds (20–22). Finally, the benzylic positions of a variety of electron-rich heterocycles that are also readily oxidized by the photocatalyst can also be functionalized using this protocol (23–25).

The scope of the reaction with respect to the heteroatomic nucleophile was also explored. Water, unfortunately, is not a suitable nucleophile, and overoxidation to the ketone was the major product of this reaction (26). Alcohols of increased steric bulk react more slowly, although the yields of these reactions can be increased using 8 equiv of alcohol (27–29). A variety of diverse functional groups were readily tolerated (30–40), including those containing easily oxidizable moieties (30–33, and 37) and potentially base-sensitive groups (36, 38, and 39). An unsymmetrical 1,3-diol reacted exclusively through the less-sterically-bulky primary alcohol (40). Carboxylic acids were also readily incorporated, including both simple aliphatic and more functionalized acids (41–45). Nucleophiles that are more readily oxidized than the anisole unit (47) or that bear strongly coordinating heterocycles (48) were unfortunately not suitable reaction partners. Finally, although *N*-Boc carbamate reacted with reasonable efficiency (46), other nitrogen nucleophiles were generally not effective (49), suggesting that alternate conditions will be required for the general introduction of C–N bonds using this photocatalytic strategy.

The combination of high site selectivity and significant functional group compatibility suggested to us that this method might be applicable to the diversification of highly complex bioactive organic compounds. Table 3 outlines the functionalization of a range of commercially available natural product scaffolds, all of which are selectively functionalized at the unique activated benzylic C–H position. No diastereoselectivity is observed when the substrate lacks significant stereochemical bias (50), but six-membered rings with a strong preference for a single chair conformation undergo highly selective functionalization of the axial C–H bond (51 and 52).

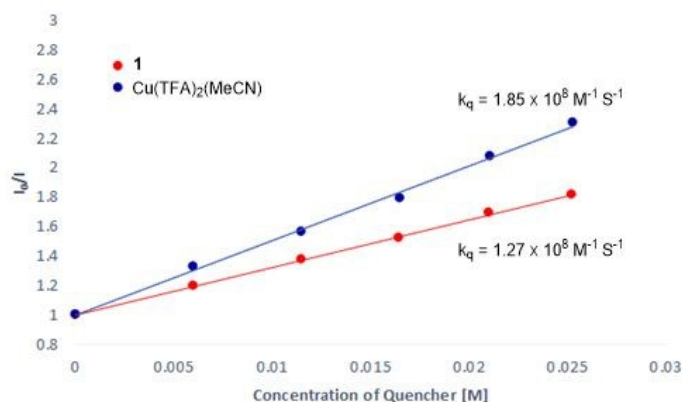
The observation that synthetically useful yields can be obtained using only two equivalents of the alcohol nucleophile also suggests that this intermolecular C–H functionalization might operate as a method to couple two high-value reaction partners. Thus, the ability to conjugate *O*-methylpodocarpate with a variety of structurally complex nucleophilic partners was explored. The alcohol moiety of a protected serine can readily be installed in good yield (53) without competitive attack of the Boc carbamate. The reaction also incorporates protected hexose and pentose moieties (54 and 55) as well as primary and secondary terpene alcohols (56 and 57) in synthetically useful yields.

Table 3. Late-Stage Functionalization via Oxidative Photoredox Catalysis^[a]

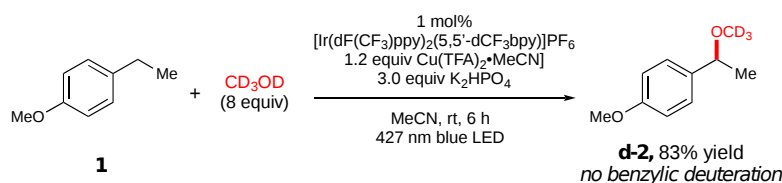
To better understand the mechanism of this transformation, we first examined the nature of the initial photoinduced electron-transfer step. The excited-state reduction and oxidation potentials of the optimal photocatalyst (+1.68 V and −0.43 V vs SCE, respectively) are sufficient to either oxidize arene substrate **1** ($E_{\text{pl}/2} = +1.52$ V) or reduce Cu(II) ($E_{1/2} = +0.38$ V). Indeed, a Stern–Volmer analysis indicates that both can quench the photocatalyst excited state at similar rates (Scheme 2A). Thus the arene radical cation might be generated either by the excited Ir*(III) photocatalyst or the Ir(IV) complex ($E_{1/2} = +1.94$ V vs SCE) resulting from oxidative quenching by Cu(II). Both mechanisms might be operative. Consistent with this hypothesis, a less strongly oxidizing photocatalyst ([Ir(dF(CF₃)ppy)₂(bpy)]PF₆, $E_{1/2}^* = +1.31$ V) that is not capable of directly oxidizing **1** nevertheless provides the methoxylation product, albeit in diminished yield (Table 1, entry 4). We also examined the photocatalytic reaction of **1** with CD₃OD, which resulted in the formation of **d-2** in 83% yield with no incorporation of deuterium at the benzylic position. This result indicates that the deprotonation step is essentially irreversible under the optimized conditions, as might be expected from Kochi's observation that the oxidation of electron-rich organoradicals by Cu(II) occurs at diffusion-controlled rates.¹⁴

A mechanistic proposal consistent with these data is outlined in Scheme 2C. Photoexcitation of the Ir(III) catalyst affords a triplet excited state that is oxidatively quenched by Cu(II) to afford a strongly oxidizing Ir(IV) complex. Subsequent oxidation of the arene affords an arene radical cation that undergoes benzylic deprotonation and rapid oxidation by Cu(II). The resulting quinone methide undergoes nucleophilic attack by the alcohol coupling partner to afford the observed benzylic ether products. The reaction proceeds to completion with only 1.2 equiv of Cu(II). Thus both oxidizing equivalents of Cu(II) are consumed in this reaction, which could be attributed to the disproportionation of the Cu(I) byproduct of either oxidation step to Cu(II) and Cu(0), the latter of which we observe precipitating from solution during the reaction.

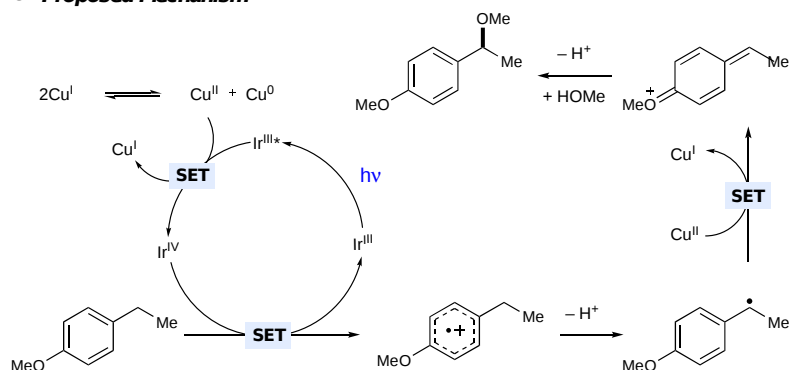
A Stern-Volmer Quenching Studies



B Hydrogen-Deuterium Exchange



C Proposed Mechanism



Scheme 2. Development of a Mechanistic Hypothesis.

In summary, we have developed a new photocatalytic strategy to introduce diverse alkoxide functionalities into complex organic molecules by functionalization of benzylic C–H bonds. The site selectivity and broad functional group compatibility of this method renders it amenable to the late-stage functionalization of complex bioactive compounds. Moreover, the efficiency of the reaction provides synthetically useful yields using only a two-fold excess of the alcohol reaction partner, which enables the formation of new benzylic ether compounds from the coupling of two structurally complex units. From a broader perspective, these results are intriguing because they demonstrate that the organoradical intermediates that are readily generated by photoredox activation can be diverted towards cationic reactivity via *in situ* oxidation by Cu(II). This combination thus provides a promising new platform to design new bond-forming oxidative functionalization reactions with broad utility in synthetic and medicinal chemistry.

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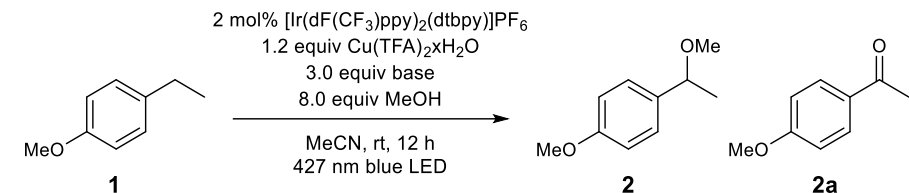
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I. General Experimental Information

All reactions were performed under an N₂ atmosphere unless otherwise stated. All glassware was dried in an oven at 120 °C for at least 2 h prior to use and allowed to cool in a desiccator cabinet. MeCN, THF, Et₂O, DMF, toluene, and CH₂Cl₂ were purified by elution through alumina as described by Grubbs.¹ Cu(TFA)₂(H₂O)_n was used as purchased from Alfa. All other chemicals were purchased from commercial suppliers and used as received. Flash column chromatography was performed with normal phase SiO₂ (Sigma-Aldrich or Macherey-Nagel, 60 Å pore size, 230-400 mesh, 40-63 µm particle size) according to the method of Still.² Reactions were monitored by thin-layer chromatography (Silicycle, 250 µm thickness), and visualization was accomplished with a 254 nm UV light or by staining with KMnO₄ solution (3.0 g of KMnO₄ and 20.0 g of K₂CO₃ in 5 mL of 5% aq. NaOH and 300 mL H₂O). ¹H, ¹³C{¹H}, and ¹¹B{¹H} NMR data for all previously uncharacterized compounds were obtained using a Bruker AVANCE-400 or Bruker AVANCE-500 spectrometer with DCH, Prodigy, or BBFO+ probes. ¹H spectra were internally referenced to tetramethyl silane (0.00 ppm). ¹³C{¹H} spectra were internally referenced to CDCl₃ (77.16 ppm). ¹H NMR spectra were tabulated as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet, br = broad), coupling constant(s), and number of protons. ¹³C NMR spectra were tabulated by observed peak. The spectrometers used for this work are supported by the NIH (S10 OD012245) and a generous gift from Paul J. and Margaret M. Bender. Mass spectrometry was performed with a Thermo Q Exactive™ Plus. This instrument is supported by the NIH (S10 OD020022) and the University of Wisconsin. IR spectra were obtained using a Bruker Alpha Platinum FTIR spectrometer equipped with an attenuated total reflectance (ATR) sampling head. UV-Vis absorption spectra were acquired using a Varian Cary® 50 UV-visible spectrophotometer with a scan rate of 300 nm/min. UV-Vis emission spectra were acquired on an ISS PC1 spectrofluorimeter. Cyclic voltammograms were acquired using a Pine Research WaveNow potentiostat/galvanostat. Melting points were obtained using a Stanford Research Systems DigiMelt apparatus.

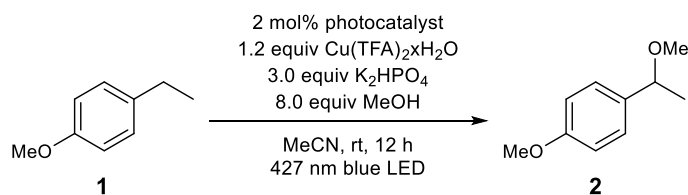
II. Optimization

A Base Screen



entry ^a	Base	2 yield (%) ^b	2a yield (%) ^b
1	NaTCA ($\text{CCl}_3\text{CO}_2\text{Na}$)	8%	0%
2	KH_2PO_4	32%	0%
3	$\text{NBu}_4\text{OP}(\text{O})(\text{OBu})_2$	5%	0%
4	NaOAc	11%	0%
5	KHCO_3	6%	0%
6	2,6-lutidine	43%	32%
7	2,4,6-trimethylpyridine	46%	11%
8	2,6-ditertbutyl-4-methylpyridine	53%	0%
9	CsCO_3	1%	0%
10	K_3PO_4	18%	0%

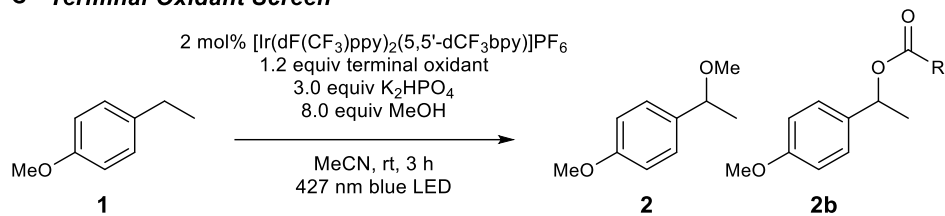
B Photocatalyst Screen



entry ^a	Photocatalyst	yield (%) ^b
1	$[\text{Ru}(\text{bpm})_3](\text{PF}_6)_2$	0%
2	$[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbpy})]\text{PF}_6$	29%
3	$[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{bpy})]\text{PF}_6$	44%
4	$[\text{Ru}(\text{bpz})_3](\text{PF}_6)_2$	0%
5	$[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(5,5'\text{-dCF}_3\text{bpy})]\text{PF}_6$	72%

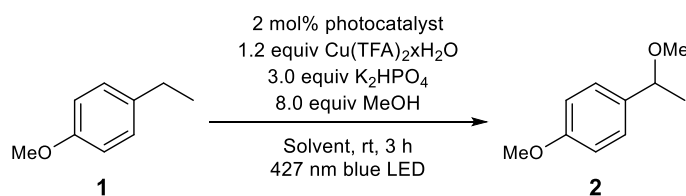
^a Unless otherwise noted, all reactions were conducted using 0.3 mmol of **1** in degassed solvent (0.1 M) and irradiated with a 427 nm Kessil lamp for 12 h. ^b Yields determined by ^1H NMR analysis of the crude reaction mixtures using phenanthrene as an internal standard.

C Terminal Oxidant Screen



entry ^a	Terminal Oxidant	2 yield (%) ^b	2b yield (%) ^b
1	MnO ₂	2%	0%
2	Mn(OAc) ₃	1%	0%
3	FeCl ₃	trace	0%
4	Fe(ClO ₄) ₃	1%	0%
5	Fe(acac) ₃	trace	0%
6	Ag(TFA)	25%	0%
7	Ag(OTf)	0%	0%
8	Ag ₂ O	2%	0%
9	CuBr ₂	0%	0%
10	Cu(OAc) ₂ ·xH ₂ O	11%	18%
11	Cu(OBz) ₂	0%	15%
12	Cu(TFA) ₂ ·xH ₂ O	45%	0%
13	Cu(OTf) ₂	9%	0%
14	CuO	0%	0%

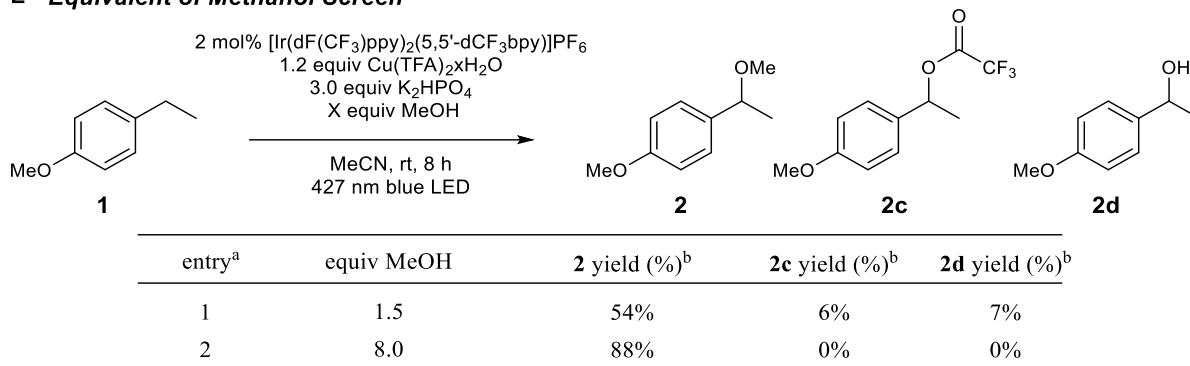
D Solvent Screen



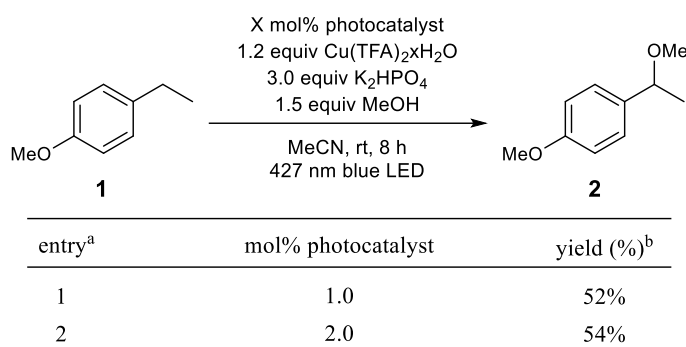
entry ^a	Solvent	yield (%) ^b
1	PhMe	15%
2	CH ₂ Cl ₂	9%
3	THF	12%
4	DMF	11%
5	MeCN	45%

^a Unless otherwise noted, all reactions were conducted using 0.3 mmol of **1** in degassed solvent (0.1 M) and irradiated with a 427 nm Kessil lamp for 3 h. ^b Yields determined by ¹H NMR analysis of the crude reaction mixtures using phenanthrene as an internal standard.

E Equivalent of Methanol Screen

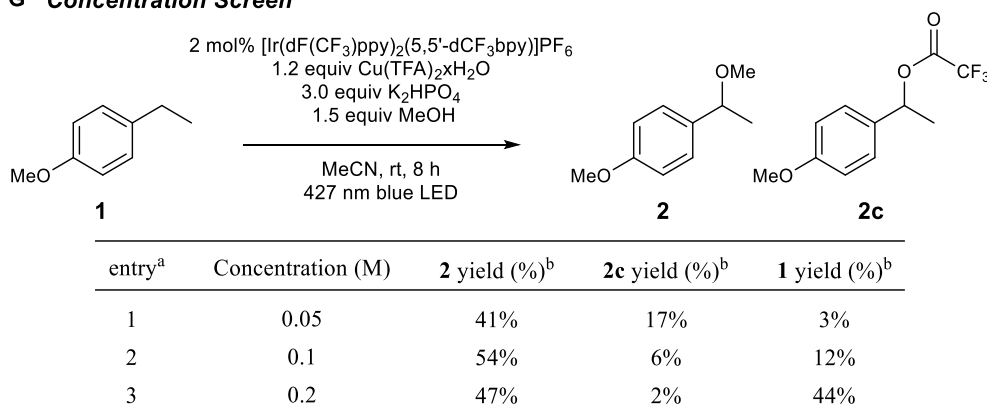


F Photocatalyst Loading Screen



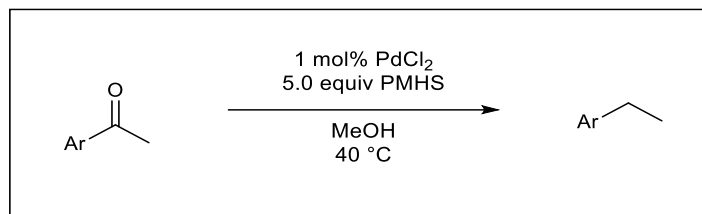
^a Unless otherwise noted, all reactions were conducted using 0.3 mmol of **1** in degassed solvent (0.1 M) and irradiated with a 427 nm Kessil lamp for 8 h. ^b Yields determined by ¹H NMR analysis of the crude reaction mixtures using phenanthrene as an internal standard.

G Concentration Screen



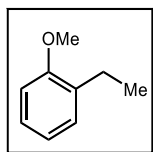
^a Unless otherwise noted, all reactions were conducted using 0.3 mmol of **1** in degassed solvent and irradiated with a 427 nm Kessil lamp for 8 h. ^b Yields determined by ¹H NMR analysis of the crude reaction mixtures using phenanthrene as an internal standard.

III. Substrate Synthesis and Characterization Data

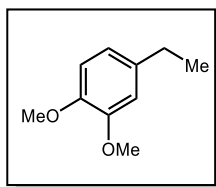


General Synthesis Procedure³

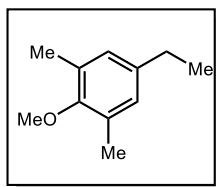
A 100-mL round-bottomed flask was charged with PdCl₂ (10 mol%) and the aromatic ketone (1 equiv). Under a nitrogen atmosphere, methanol (0.5 M with respect to substrate) was added, followed by PMHS (5 equiv, slow addition). The mixture was stirred at 40 °C for 12–24 hours, monitoring for completion by TLC. After completion of the reaction, the product was dissolved in pentane and water was added. The mixture was extracted three times into an equal volume of pentane, and the combined organic layers were dried (MgSO₄), concentrated under reduced pressure, and purified by column chromatography on silica gel to afford the pure product.



1-Ethyl-2-methoxybenzene (S1): Prepared according to the General Synthesis Procedure with 2'-methoxyacetophenone (1.99 g, 13.3 mmol). Following workup, the product was purified by flash column chromatography on silica gel (gradient 0% to 5% Et₂O/pentane) to give the title compound as a clear liquid (1.40 g, 10.3 mmol, 78%). Spectral data were consistent with those reported previously.⁴

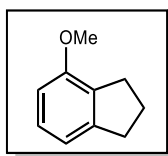


4-Ethyl-1,2-dimethoxybenzene (S2): Prepared according to the General Synthesis Procedure with 3',4'-dimethoxyacetophenone (1.02 g, 5.68 mmol). Following workup, the product was purified by flash column chromatography on silica gel (gradient 0% to 10% Et₂O/pentane) to give the title compound as a clear liquid (828 mg, 4.98 mmol, 88%). Spectral data were consistent with those reported previously.⁵



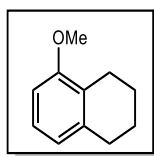
5-Ethyl-2-methoxy-1,3-dimethylbenzene (S3): Prepared according to the General Synthesis Procedure with 3',5'-dimethyl-4'-methoxyacetophenone (1.02 g, 5.68 mmol). Following workup, the product was purified by flash column chromatography on silica gel (gradient 0% to 5% Et₂O/pentane) to give the title compound as a clear liquid (858 mg, 5.23 mmol, 92%).

¹H NMR (500 MHz, CDCl₃) δ 6.84 (s, 2H), 3.70 (s, 3H), 2.54 (q, *J* = 7.62 Hz, 2H), 2.27 (s, 6H), 1.20 (t, *J* = 7.60 Hz, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 155.25, 139.91, 130.87, 128.53, 60.11, 28.54, 16.46, 16.11; **IR** (thin film): ν 2961, 2930, 2868, 1483, 1455, 1222, 1140, 1016, 866; **HRMS** (ESI) [M+H]⁺ calculated for [C₁₁H₁₆O] requires *m/z* 165.1274, found *m/z* 165.1272.

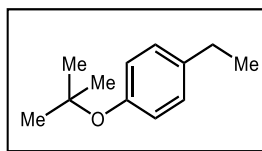


4-Methoxy-2,3-dihydro-1H-indene (S4): Prepared according to the General Synthesis Procedure with 7-methoxy-1-indanone (921 mg, 5.68 mmol). Following workup, the product was purified by flash column chromatography on silica gel (gradient 0% to 5% Et₂O/pentane) to give the title compound as a clear liquid (741 mg, 5.00 mmol, 88%).

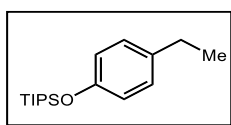
¹H NMR (500 MHz, CDCl₃) δ 7.13 (d, *J* = 7.76 Hz, 1H), 6.86 (d, *J* = 7.28 Hz, 1H), 6.67 (d, *J* = 8.05 Hz, 1H), 3.84 (s, 3H), 2.92 (t, *J* = 7.51 Hz, 2H), 2.87 (t, *J* = 7.42 Hz, 2H), 2.07 (q, *J* = 7.49 Hz, 2H); **¹³C NMR** (126 MHz, CDCl₃) δ 156.20, 146.38, 131.80, 127.61, 117.00, 107.78, 55.31, 33.37, 29.50, 25.07; **IR** (thin film): ν 2944, 2841, 1588, 1475, 1444, 1258, 1070, 764; **HRMS** (ESI) [M+H]⁺ calculated for [C₁₀H₁₂O] requires *m/z* 149.0961, found *m/z* 149.0959.



5-Methoxy-1,2,3,4-tetrahydronaphthalene (S5): Prepared according to the General Synthesis Procedure with 5-methoxy-1-tetralone (1.00 g, 5.68 mmol). Following workup, the product was purified by flash column chromatography on silica gel (gradient 0% to 5% Et₂O/pentane) to give the title compound as a clear liquid (792 mg, 4.88 mmol, 86%). Spectral data were consistent with those reported previously.⁶

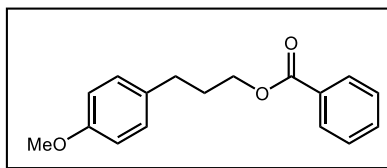


1-(tert-Butoxy)-4-ethylbenzene (S6): A 250-mL round-bottomed flask was charged with a magnetic stir bar, 10% Pd/C (2 g), and MeOH (100 mL). The stirred solution was fitted with a hydrogen balloon and purged for 20 min. 4-*tert*-Butoxystyrene (10 mmol, 1.88 mL) was then added, and the reaction was stirred at room temperature for 12 h, at which point it was passed through a Celite plug (Et₂O). The solvent was removed under reduced pressure, and the resulting residue was purified by flash column chromatography on silica gel (pentane) to afford the title compound as a clear liquid (1.50 g, 8.4 mmol, 84%). Spectral data were consistent with those reported previously.⁷



(4-Ethylphenoxy)triisopropylsilane (S7): A mixture of 4-ethylphenol (1.2 g, 10 mmol, 1 equiv) and imidazole (1.4 g, 20 mmol, 2 equiv) in dimethylformamide (DMF, 8.3 mL) was added dropwise into a solution of triisopropylsilyl chloride (1.9 g, 10 mmol, 1 equiv) in DMF (1.2 mL). After stirring for 12 h at room temperature, an aqueous solution of sodium bicarbonate was added to the reaction mixture, and the evolving two-phased system was separated. The aqueous phase was extracted with pentane three times, and the combined organic solutions were washed with water three times, dried over MgSO₄, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (pentane) to afford the product as a clear liquid (9.0 mmol, 2.5 g, 90%).

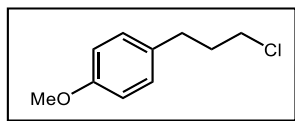
¹H NMR (500 MHz, CDCl₃) δ 7.02 (d, *J* = 8.41 Hz, 2H), 6.79 (d, *J* = 8.46 Hz, 2H), 2.57 (q, *J* = 7.61 Hz, 2H), 1.21-1.28 (m, 3H), 1.20 (t, *J* = 7.60 Hz, 3H), 1.09-1.10 (m, 18H); **¹³C NMR** (126 MHz, CDCl₃) δ 153.85, 137.31, 129.00, 120.19, 28.43, 26.11, 18.60, 16.17, -4.03; **IR** (thin film): ν 2962, 2893, 1608, 1507, 1463, 1260, 913, 882, 832, 684, 668; **HRMS** (ESI) [M+H]⁺ calculated for [C₁₇H₃₀OSi] requires *m/z* 279.2139, found *m/z* 279.2139.



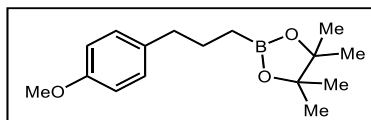
3-(4-Methoxyphenyl)propyl acetate (S8): To a solution of benzoic acid (305 mg, 2.5 mmol, 1 equiv) in CH₂Cl₂ (15 mL) were added 3-(4-methoxyphenyl)-1-propanol (830 mg, 5 mmol, 2 equiv), DCC (567 mg, 2.75 mmol, 1.1 equiv), and DMAP (31 mg, 0.25 mmol, 0.1 equiv). The mixture was stirred at room temperature for 12 h. The solid was filtered, and the filtrate was concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (10% Et₂O in pentane) to afford the product as a clear liquid (603 mg, 2.23 mmol, 89%).

¹H NMR (500 MHz, CDCl₃) δ 8.04 (dd, *J* = 8.33, 1.43 Hz, 2H), 7.56 (tt, *J* = 7.52, 1.43 Hz, 1H), 7.45 (t, *J* = 7.79 Hz, 2H), 7.13 (d, *J* = 8.57 Hz, 2H), 6.84 (d, *J* = 8.59 Hz, 2H), 4.33 (t, *J* = 6.45 Hz, 2H), 3.79 (s, 3H), 2.74 (t, *J* = 7.31 Hz, 1H), 2.08 (m, 2H); **¹³C NMR** (126 MHz, CDCl₃) δ 166.62,

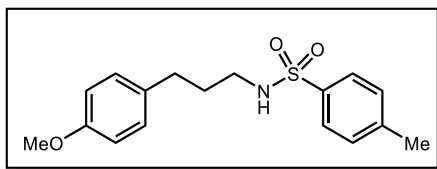
157.92, 133.23, 132.88, 130.40, 129.55, 129.35, 128.35, 113.89, 64.26, 55.27, 31.38, 30.52; **IR** (thin film): ν 2949, 2837, 1715, 1609, 1510, 1452, 1270, 1243, 1110, 1030, 749; **HRMS** (ESI) $[M+NH_4]^+$ calculated for $[C_{17}H_{18}O_3]$ requires m/z 293.1148, found m/z 293.1139.



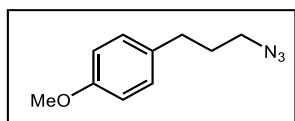
1-(3-Chloropropyl)-4-methoxybenzene (S9): A 100-mL round-bottomed flask equipped with a stir bar was charged with PPh_3 (5.24 g, 20 mmol, 2 equiv) and CCl_4 (3.23 g, 21 mmol, 2.1 equiv) under N_2 . Anhydrous CH_2Cl_2 (50 mL) was added, and the mixture was placed in an ice bath and stirred for 10 min at 0 °C. 3-(4-Methoxyphenyl)-1-propanol (1.66 g, 10 mmol, 1 equiv), diluted with CH_2Cl_2 (7.6 mL), was added dropwise at 0 °C. Upon addition of the alcohol, the ice bath was removed, and the reaction was stirred for 14 h at room temperature. The reaction mixture was concentrated under reduced pressure, and the resulting residue was purified by flash column chromatography on silica gel (5% Et_2O in pentane) to afford the product as a clear liquid (1.37 g, 7.40 mmol, 74%). Spectral data were consistent with those reported previously.⁸



3-(3-(4-Methoxyphenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (S10): Prepared as described by Watson. Spectral data were consistent with those reported previously.⁹

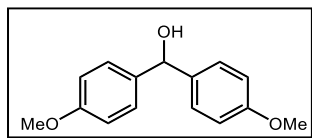


N-(3-(4-Methoxyphenyl)propyl)-4-methylbenzenesulfonamide (S11): 3-(4-Methoxyphenyl)propylamine (991 mg, 6.0 mmol, 1 equiv) was dissolved in CH_2Cl_2 and cooled to 0 °C. Triethylamine (909 mg, 9.0 mmol, 1.5 equiv) and DMAP (73 mg, 0.6 mmol, 0.1 equiv) were added. Finally, *p*-toluenesulfonyl chloride (1.26 g, 6.6 mmol, 1.1 equiv) was added portionwise. The solution was slowly warmed to room temperature and stirred for an additional 19 h. Once complete, the reaction was quenched with 1 M HCl. The aqueous layer was washed with CH_2Cl_2 , dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (gradient 50% Et_2O in pentane to 100% Et_2O) to afford the product as a white solid (1.71 g, 5.34 mmol, 89%). Spectral data were consistent with those reported previously.¹⁰

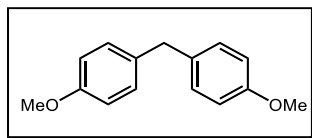


1-(3-Azidopropyl)-4-methoxybenzene (S12): To a solution of triphenylphosphine (1.44 g, 5.5 mmol, 1.1 equiv) in 23 mL of anhydrous THF at 0 °C was added diisopropyl azodicarboxylate (1.021 g, 5.05 mmol, 1.01 equiv), followed by 3-(4-methoxyphenyl)-1-propanol (830 mg, 5.0 mmol, 1 equiv) in 12 mL of anhydrous THF, followed by diphenylphosphonic azide (2.475 g, 9.0

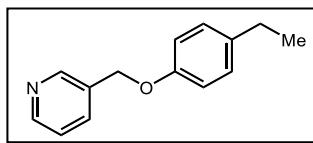
mmol, 1.8 equiv). The reaction was allowed to warm to room temperature and stir for 3 h. The reaction was diluted with Et₂O and washed with a saturated aqueous solution of NaHCO₃ and brine. The organic phase was dried over MgSO₄, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (5% Et₂O in pentane) to afford the product as a pale-yellow liquid (803 mg, 4.20 mmol, 84%). Spectral data were consistent with those reported previously.¹¹



Bis(4-methoxyphenyl)methanol (S13): To a 100-mL nitrogen-purged round-bottomed flask containing *p*-anisaldehyde (10 mmol) in Et₂O (10 mL) at 0 °C, was added 4-methoxyphenyl magnesium bromide (30 mL, 15 mmol, 1.5 equiv, 0.5 M solution in THF) dropwise over 5 min. The reaction was then allowed to warm to room temperature and left to stir overnight. A saturated aqueous solution of NH₄Cl was then added slowly and stirred for a few minutes. Et₂O was then added, and the layers were separated. The aqueous layer was extracted with Et₂O (2x), and then the combined organic extracts were washed with water and brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (20% Et₂O in pentane) to afford the product as a white solid (2.3 g, 9.2 mmol, 92%). Spectral data were consistent with those reported previously.¹²



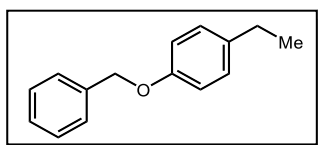
Bis(4-methoxyphenyl)methane (S14): A 100-mL round-bottomed flask was charged with PdCl₂ (123 mg, 0.7 mmol, 0.1 equiv) and bis(4-methoxyphenyl)methanol (1.71 g, 7 mmol, 1 equiv). Under a nitrogen atmosphere, MeOH (14 mL) was added, followed by PMHS (0.87 mL, 2 equiv, slow addition). The mixture was stirred at 40 °C for 12 h. After completion of the reaction, the product was dissolved in pentane, and water was added. The mixture was extracted three times into an equal volume of pentane and the combined organic layers were dried (MgSO₄), filtered, concentrated under reduced pressure, and purified by column chromatography on silica gel (gradient 0% to 5% Et₂O/pentane) to afford the pure product as a white solid (1.36 g, 5.95 mmol, 85%). Spectral data were consistent with those reported previously.⁴



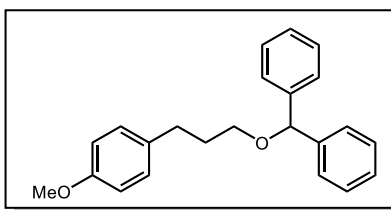
3-((4-Ethylphenoxy)methyl)pyridine (S15): A mixture of 4-ethylphenol (1.12 g, 9.16 mmol, 1 equiv), 3-(chloromethyl)pyridine hydrochloride (1.64 g, 10 mmol, 1 equiv), and K₂CO₃ (4.15 g, 30 mmol, 3 equiv) was dissolved in CH₃CN (20 mL) and heated to reflux under nitrogen for 12 h. After cooling to room temperature, the reaction mixture was filtered and washed with CH₂Cl₂. The combined organic extracts were concentrated under reduced pressure, and the resulting residue was purified by column chromatography on silica gel (30% MTBE/pentane) to afford the pure product as a clear liquid (1.1 g, 5.0 mmol, 54%).

¹H NMR (500 MHz, CDCl₃) δ 8.68 (dd, *J* = 2.16, 0.92 Hz, 1H), 8.58 (dd, *J* = 4.77, 1.68 Hz, 1H), 7.78 (dt, *J* = 8.03, 1.93 Hz, 1H), 7.32 (ddd, *J* = 7.85, 4.83, 0.88 Hz, 1H), 7.13 (d, *J* = 8.60 Hz, 2H), 6.90 (d, *J* = 8.61 Hz, 2H), 5.06 (s, 2H), 2.60 (q, *J* = 7.60 Hz, 2H), 1.21 (t, *J* = 7.60 Hz, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 156.44, 149.41, 149.04, 137.18, 135.25, 132.76, 128.85, 123.49, 114.69, 67.64, 27.99, 15.85;

IR (thin film): ν 3032, 2962, 2967, 1607, 1582, 1508, 1230, 1176, 1020, 862, 708; **HRMS** (ESI) [M-H]⁺ calculated for [C₁₄H₁₅NO] requires *m/z* 212.1070, found *m/z* 212.1068.

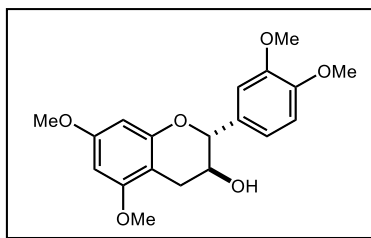


1-(Benzyloxy)-4-ethylbenzene (S16): A mixture of 4-ethylphenol (1.22 g, 10 mmol, 1 equiv), benzyl bromide (1.88 g, 11 mmol, 1.1 equiv), and CsCO₃ (3.58 g, 11 mmol, 1.1 equiv) was dissolved in CH₃CN (25 mL). The mixture was stirred at room temperature for 3 h under a nitrogen atmosphere. After 3 h, the reaction mixture was diluted with CH₂Cl₂. The organic solution was washed with water and brine, dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The resulting residue was purified by column chromatography on silica gel (pentane) to afford the pure product as a clear liquid (1.32 g, 6.2 mmol, 62%). Spectral data were consistent with those reported previously.¹³



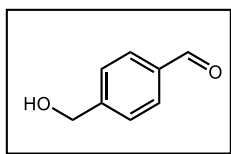
((3-(4-Methoxyphenyl)propoxy)methylene)dibenzene (S17): A 100-mL round-bottomed flask, equipped with a magnetic stir bar, was charged with 3-(4-methoxyphenyl)-1-propanol (1.66 g, 10 mmol, 1 equiv) and anhydrous THF (50 mL). The mixture was cooled to 0 °C, then treated with NaH (60% dispersion in mineral oil, 600 mg, 15 mmol, 1.5 equiv). After being stirred at room temperature for 30 min, bromodiphenylmethane (2.47 g, 10 mmol, 1 equiv) was added portion-wise. The mixture was stirred at room temperature for 24 h. The reaction mixture was diluted with Et₂O and H₂O, and the layers were separated. The aqueous layer was extracted with Et₂O (2x). The combined organic layers were dried over MgSO₄, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (10% Et₂O in pentane) to afford the product as a clear oil (1.23 g, 3.70 mmol, 37%).

¹H NMR (500 MHz, CDCl₃) δ 7.29-7.37 (m, 8H), 8.58 (dd, *J* = 4.77, 1.68 Hz, 1H), 7.22-7.26 (m, 2H), 7.08 (d, *J* = 8.58 Hz, 2H), 6.80 (d, *J* = 8.60 Hz, 2H), 5.32 (s, 1H), 3.78 (s, 3H), 3.46 (t, *J* = 6.25 Hz, 2H), 2.65-2.72 (m, 2H), 1.86-1.98 (m, 2H); **¹³C NMR** (126 MHz, CDCl₃) δ 157.68, 142.56, 134.14, 129.35, 128.34, 127.34, 126.98, 113.69, 83.61, 68.26, 55.25, 31.75, 31.54; **IR** (thin film): ν 3059, 3028, 2936, 2857, 1608, 1508, 1450, 1243, 1178, 1098, 1069, 1031, 699; **HRMS** (ESI) [M+NH₄]⁺ calculated for [C₂₃H₂₄O₂] requires *m/z* 350.2115, found *m/z* 350.2111.

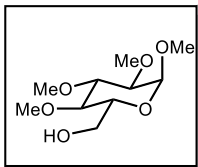


(2R,3S)-2-(3,4-Dimethoxyphenyl)-5,7-dimethoxychroman-3-ol (S18): A 100-mL round-bottomed flask, equipped with a magnetic stir bar, was charged with *trans*-3,3',4',5,7-pentahydroxyflavane (1.00 g, 3.44 mmol, 1 equiv), anhydrous K₂CO₃ (3.80 g, 27.5 mmol, 8 equiv), and anhydrous acetone (50 mL). Then MeI (1.70 mL, 27.5 mmol, 8 equiv) was added dropwise to the solution. The resulting solution was stirred for 14 days and eluted through a short pad of silica using acetone. The filtrate was concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (50% Et₂O in pentane) to afford the product as a white solid (703 mg, 2.03 mmol, 59%).

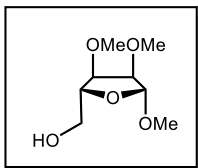
¹H NMR (400 MHz, CDCl₃) δ 6.96-7.01 (m, 2H), 6.89 (d, *J* = 8.19 Hz, 1H), 6.14 (d, *J* = 2.37 Hz, 1H), 6.10 (d, *J* = 2.30 Hz, 1H), 4.65 (d, *J* = 8.32 Hz, 1H), 4.05 (td, *J* = 8.77, 5.85 Hz, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 3.80 (s, 3H), 3.75 (s, 3H), 3.06 (dd, *J* = 16.36, 5.70 Hz, 1H), 2.58 (dd, *J* = 16.30, 9.09 Hz, 1H), 1.80 (s, 1H); **¹³C NMR** (126 MHz, CDCl₃) δ 159.73, 158.75, 155.31, 149.35, 149.33, 130.31, 119.97, 111.20, 109.96, 101.70, 93.01, 91.91, 81.81, 68.24, 55.97, 55.92, 55.52, 55.38, 27.6; **IR** (thin film): ν 3498, 3001, 2936, 3839, 1592, 1509, 1457, 1421, 1140, 1115, 1023, 730; **HRMS** (ESI) [M+Na]⁺ calculated for [C₁₉H₂₂O₆] requires *m/z* 369.1309, found *m/z* 369.1307; m.p = 139–140 °C.



4-(Hydroxymethyl)benzaldehyde (S19): A 100-mL round-bottomed flask, equipped with a magnetic stir bar, was charged with terephthalaldehyde (1.37g, 10.2 mmol, 1.00 equiv), followed by a solution of EtOH:THF (10 mL: 30 mL). NaBH₄ (102.1 mg, 2.7 mmol, 0.265 equiv) was added to the solution at 0 °C, and the mixture was stirred for 30 min. Then the reaction mixture was stirred for an additional 6 h at room temperature. The reaction mixture was neutralized with 1 N HCl to pH = 5. The solution was concentrated under reduced pressure, and the resulting residue was dissolved in water. The aqueous solution was extracted three times with EtOAc (20 mL). The combined organic layers were washed with brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (50% Et₂O/pentane) to afford the product as a white solid (1.36 g, 9.99 mmol, 66%). Spectral data were consistent with those reported previously.¹⁴

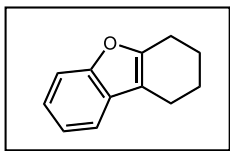


((2R,3R,4S,5R,6S)-3,4,5,6-Tetramethoxytetrahydro-2H-pyran-2-yl)methanol (S20): To a stirred suspension of methyl- α -D-glucopyranoside (5.00 g, 25.7 mmol) in CH_2Cl_2 (100 mL) at room temperature was added DABCO (5.77 g, 51.4 mmol) and triphenylmethylchloride (14.3 g, 51.4 mmol). After being stirred for 24 h, the reaction mixture was concentrated under vacuum and the resulting residue was purified by flash column chromatography on silica gel (50% EtOAc in pentane). To a solution of the tritylated product in DMF (76.0 mL) were added MeI (8.00 mL, 128 mmol) and NaH (60% in mineral oil, 3.22 g, 80.5 mmol) portion-wise at 0 °C. After being stirred for 12 h at room temperature, saturated aqueous NH_4Cl was added dropwise. The mixture was extracted with EtOAc three times, washed with H_2O , saturated aqueous NH_4Cl , dried over Na_2SO_4 , filtered, and the reaction mixture was concentrated under vacuum. The resulting residue was purified by flash column chromatography on silica gel (gradient 10% to 50% Et₂O in pentane). The methylated product was dissolved in CH_2Cl_2 (125 mL), and Et_3SiH (4.15 mL, 26.0 mmol) was added neat followed by the addition of TBSOTf (32.4 μL , 0.140 mmol). After 2 h, the yellow color disappeared, and TLC analysis indicated that the reaction was completed. Saturated aqueous NaHCO_3 solution (0.1 mL) was added, and the mixture was dried with Na_2SO_4 , filtered and concentrated under vacuum. The residue was purified by silica gel chromatography (gradient 50% to 100% Et₂O in pentane) to give **S20** as a white solid (2.60 g, 43%). Spectral data were consistent with those reported previously.¹⁵

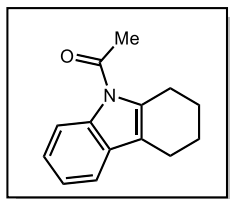


((2R,3R,4R,5R)-3,4,5-Trimethoxytetrahydrofuran-2-yl)methanol (S21): To a stirred suspension of methyl beta-D-ribofuranoside (5.00 g, 30.5 mmol) in CH_2Cl_2 (100 mL) at room temperature was added DABCO (6.83 g, 60.9 mmol) and triphenylmethylchloride (17.0 g, 60.9 mmol). After being stirred for 24 h, the reaction mixture was concentrated under vacuum and the resulting residue was purified by flash column chromatography on silica gel (50% EtOAc in pentane). To a solution of the tritylated product in DMF (47.3 mL) were added MeI (5.00 mL, 82.4 mmol) and NaH (60% in mineral oil, 3.22 g, 51.5 mmol) portion-wise at 0 °C. After being stirred for 12 h at room temperature, saturated aqueous NH_4Cl was added dropwise. The mixture was extracted with EtOAc three times, washed with H_2O , saturated aqueous NH_4Cl , dried over Na_2SO_4 , filtered, and the reaction mixture was concentrated under vacuum. The resulting residue was purified by flash column chromatography on silica gel (gradient 10% to 50% Et₂O in pentane). The methylated product was dissolved in CH_2Cl_2 (80 mL), and Et_3SiH (2.60 mL, 16.6 mmol) was added neat followed by the addition of TBSOTf (21.0 μL , 0.0910 mmol). After 2 h, the yellow color disappeared, and TLC analysis indicated that the reaction was completed. Saturated aqueous NaHCO_3 solution (0.1 mL) was added, and the mixture was dried with Na_2SO_4 , filtered, and concentrated under vacuum. The residue was purified by silica gel chromatography (gradient 50% to 100% EtOAc in pentane) to give **S21** as a colorless oil (1.10 g, 19%).

¹H NMR (500 MHz, CDCl₃) δ 4.93 (s, 1H), 4.18 (dt, *J* = 6.81, 3.31 Hz, 1H), 3.98 (dd, *J* = 6.82, 4.74 Hz, 1H), 3.85 (dt, *J* = 11.9, 3.48 Hz, 1H), 3.77 (d, *J* = 4.67 Hz, 1H), 3.63 (ddd, *J* = 12.1, 8.63, 3.65 Hz, 1H), 3.52 (s, 3H), 3.45 (s, 3H), 3.44 (s, 3H), 2.10 (dd, *J* = 8.86, 3.85 Hz, 1H); **¹³C NMR** (126 MHz, CDCl₃) δ 106.03, 82.39, 82.11, 79.26, 62.92, 58.45, 58.37, 55.67; **IR** (thin film): ν 3460, 2919, 2830, 1451, 1374, 1320, 1189, 1131, 1091, 1043, 946, 930; **HRMS** (ESI) [M+NH₄]⁺ calculated for [C₈H₁₆O₅] requires *m/z* 210.1336, found *m/z* 210.1334.

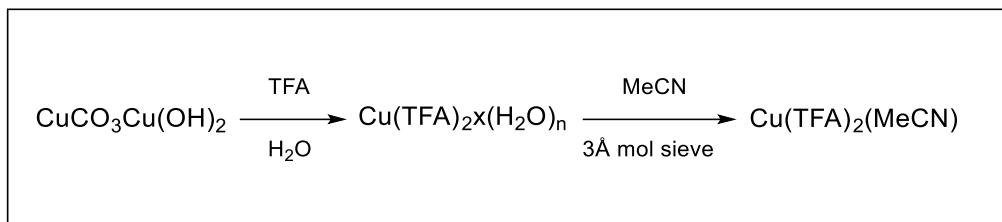


1,2,3,4-Tetrahydrodibenzo[b,d]furan (S22): Prepared as described by Tang. Spectral data were consistent with those reported previously.¹⁶



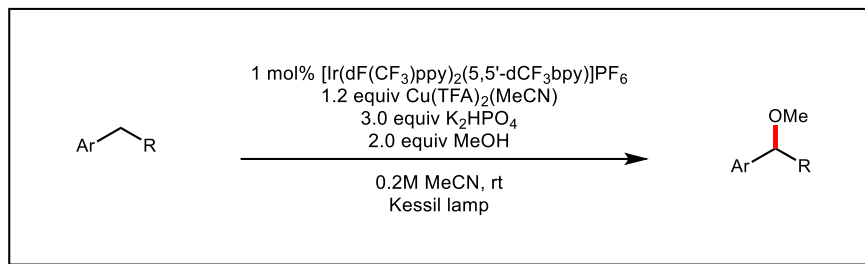
1-(1,2,3,4-tetrahydro-9H-carbazol-9-yl)ethan-1-one (S23): Prepared as described by Vincent. Spectral data were consistent with those reported previously.¹⁷

IV. Synthesis and Characterization Data for $\text{Cu}_2(\text{TFA})_4(\text{MeCN})_2$



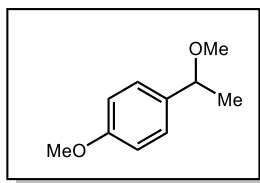
$\text{CuCO}_3\text{Cu}(\text{OH})_2$ (2.21g, 10 mmol, 1 equiv) was added to a 100-mL round-bottom flask with a stirbar. A 1:1 mixture of TFA/ H_2O (6 mL) was added slowly, and the solution was stirred until all the copper dissolved. The reaction mixture was then evaporated under reduced pressure to afford the hydrated $\text{Cu}(\text{TFA})_2$ as a blue solid. This material was then dissolved in 50 mL MeCN and stirred. After 1 h, 3.0 g of activated 3Å mol sieves were added, and the mixture was stirred for an additional 30 min. The reaction mixture was then filtered, and the sieves were washed with several portions of MeCN. The filtrate was evaporated under reduced pressure to afford the product as a blue-green powder (5.00 g, 15.1 mmol, 76%).¹⁸

V. Experimental Procedures and Characterization Data for Table 2



General Procedure A: A dry 20-mL Schlenk tube (1.5 cm diameter) was charged with $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(5,5'\text{-dCF}_3\text{bpy})]\text{PF}_6$ (6.90 mg, 0.006 mmol, 0.01 equiv), K_2HPO_4 (312 mg, 1.8 mmol, 3 equiv), and $\text{Cu}(\text{TFA})_2(\text{MeCN})$ (238 mg 0.72 mmol, 1.2 equiv). A stock solution containing the alkyl arene (0.6 mmol, 1 equiv) and MeOH (40 mg, 1.2 mmol, 2 equiv) in 0.9 mL MeCN was added. An additional 2.1 mL MeCN were added to rinse the wall of the Schlenk tube. The reaction was degassed by three freeze/pump/thaw cycles (4 cycles, 5 min each) under nitrogen in the dark before back filling with nitrogen. The reaction was then allowed to stir while being irradiated by a 40W Kessil Lamp PR160 (427nm). After a pre-determined time point, the reaction was eluted through a short pad of silica using Et_2O . After concentration under reduced pressure, the pure methoxylated alkyl arene was isolated by flash column chromatography.

General Procedure B: A dry 20-mL Schlenk tube (1.5 cm diameter) was charged with $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(5,5'\text{-dCF}_3\text{bpy})]\text{PF}_6$ (6.90 mg, 0.006 mmol, 0.01 equiv.), K_2HPO_4 (312 mg, 1.8 mmol, 3 equiv.), $\text{Cu}(\text{TFA})_2(\text{MeCN})$ (238 mg 0.72 mmol, 1.2 equiv), and MeOH (0.2 mL 5.0 mmol, 8 equiv.). A stock solution containing the alkyl arene (0.6 mmol, 1 equiv.) in 0.9 mL MeCN was then added. An additional 5.1 mL MeCN were added to rinse the wall of the Schlenk tube. The reaction was degassed by three freeze/pump/thaw cycles (4 cycles, 5 min each) under nitrogen in the dark before back filling with nitrogen. The reaction was then allowed to stir while being irradiated by a 40W Kessil Lamp PR160 (427nm). After a pre-determined time point, the reaction was eluted through a short pad of silica using Et_2O . After concentration under reduced pressure, the pure methoxylated alkyl arene was isolated by flash column chromatography.



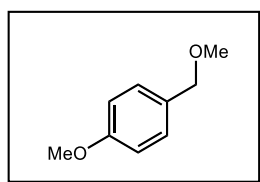
1-Methoxy-4-(1-methoxyethyl)benzene (2)

Prepared according to general procedure A using 1-ethyl-4-methoxybenzene (81.7 mg, 0.600 mmol), MeOH (40 mg, 1.2 mmol), [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)]PF₆ (6.90 mg, 0.006 mmol), K₂HPO₄ (312 mg, 1.80 mmol), and Cu(TFA)₂(MeCN) (238 mg 0.720 mmol). The crude material was purified by flash column chromatography (5% Et₂O/Pentane). (6 h)

Experiment 1: 73.2 mg of a clear liquid (73%, 0.440 mmol)

Experiment 2: 66.8 mg of a clear liquid (67%, 0.402 mmol)

Spectral data were consistent with those reported previously.¹⁹

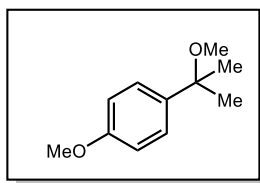


1-Methoxy-4-(methoxymethyl)benzene (3)

Prepared according to general procedure B using 1-methyl-4-methoxybenzene (73.3 mg, 0.600 mmol), MeOH (0.2 mL, 5.0 mmol), [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)]PF₆ (6.90 mg, 0.006 mmol), K₂HPO₄ (312 mg, 1.80 mmol), and Cu(TFA)₂(MeCN) (238 mg 0.720 mmol). The crude material was analyzed for NMR yield using phenanthrene as an internal standard. (12 h)

Experiment 1: 21% yield by ¹H NMR

Spectral data were consistent with those reported previously.²⁰



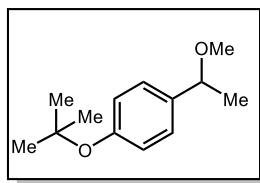
1-Methoxy-4-(2-methoxypropan-2-yl)benzene (4)

Prepared according to general procedure B using 1-isopropyl-4-methoxybenzene (90.1 mg, 0.600 mmol), MeOH (0.2 mL, 5.0 mmol), [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)]PF₆ (6.90 mg, 0.006 mmol), K₂HPO₄ (312 mg, 1.80 mmol), and Cu(TFA)₂(MeCN) (238 mg 0.720 mmol). The crude material was purified by flash column chromatography (5% Et₂O/Pentane). (13 h)

Experiment 1: 87.4 mg of a clear liquid (81%, 0.486 mmol)

Experiment 2: 86.7 mg of a clear liquid (80%, 0.480 mmol)

¹H NMR (500 MHz, CDCl₃) δ 7.33 (d, *J* = 8.75 Hz, 2H), 6.88 (d, *J* = 8.76 Hz, 2H), 3.81 (s, 3H), 3.04 (s, 3H), 1.51 (s, 6H); **¹³C NMR** (126 MHz, CDCl₃) δ 158.42, 137.86, 127.04, 113.44, 76.37, 55.23, 50.48, 27.99; **IR** (thin film): ν 2974, 2931, 1783, 1609, 1509, 1246; **HRMS** (ESI) [M-OMe]⁺ calculated for [C₁₁H₁₆O₂] requires *m/z* 149.0961, found *m/z* 149.0960.



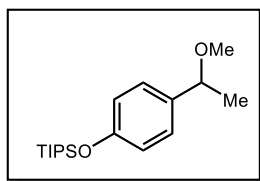
1-(*tert*-Butoxy)-4-(1-methoxyethyl)benzene (5)

Prepared according to general procedure A using 1-(*tert*-butoxy)-4-ethylbenzene (107 mg, 0.600 mmol), MeOH (40 mg, 1.2 mmol), [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)]PF₆ (6.90 mg, 0.006 mmol), K₂HPO₄ (312 mg, 1.80 mmol), and Cu(TFA)₂(MeCN) (238 mg 0.720 mmol). The crude material was purified by flash column chromatography (10% Et₂O/Pentane). (14 h)

Experiment 1: 89.9 mg of a clear liquid (72%, 0.432 mmol)

Experiment 2: 104.9 mg of a clear liquid (84%, 0.504 mmol)

¹H NMR (500 MHz, CDCl₃) δ 7.19 (d, *J* = 8.45 Hz, 2H), 6.96 (d, *J* = 8.51 Hz, 2H), 4.26 (q, *J* = 6.43 Hz, 1H), 3.20 (s, 3H), 1.42 (d, *J* = 6.53 Hz, 3H), 1.34 (s, 9H); **¹³C NMR** (126 MHz, CDCl₃) δ 154.68, 138.14, 126.69, 124.00, 79.17, 78.27, 56.27, 28.86, 23.58; **IR** (thin film): ν 2975, 2930, 1605, 1503, 1163, 1107; **HRMS** (ESI) [M+Na]⁺ calculated for [C₁₃H₂₀O₂] requires *m/z* 231.1356, found *m/z* 231.1354.



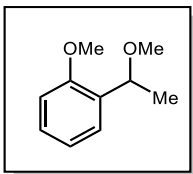
Triisopropyl(4-(1-methoxyethyl)phenoxy)silane (6)

Prepared according to general procedure B using (4-ethylphenoxy)triisopropylsilane (167 mg, 0.600 mmol), MeOH (0.2 mL, 5.0 mmol), [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)]PF₆ (6.90 mg, 0.006 mmol), K₂HPO₄ (312 mg, 1.80 mmol), and Cu(TFA)₂(MeCN) (238 mg 0.720 mmol). The crude material was purified by flash column chromatography (2% Et₂O/Pentane). (56 h)

Experiment 1: 95.2 mg of a clear liquid (52%, 0.309 mmol)

Experiment 2: 99.6 mg of a clear liquid (54%, 0.323 mmol)

¹H NMR (500 MHz, CDCl₃) δ 7.08 (d, *J* = 8.49 Hz, 2H), 6.78 (d, *J* = 8.48 Hz, 2H), 4.16 (q, *J* = 6.46 Hz, 1H), 3.11 (s, 3H), 1.34 (d, *J* = 6.42 Hz, 3H), 1.14-1.22 (m, 3H), 1.02-1.03 (m, 18H); **¹³C NMR** (126 MHz, CDCl₃) δ 155.43, 135.73, 127.33, 119.75, 79.17, 56.17, 23.65, 17.93, 12.67; **IR** (thin film): ν 2944, 2893, 2867, 1607, 1509, 1463, 1259, 1116, 911, 882, 836, 677; **HRMS** (ESI) [M+Na]⁺ calculated for [C₁₈H₃₂O₂Si] requires *m/z* 331.2064, found *m/z* 331.2063.

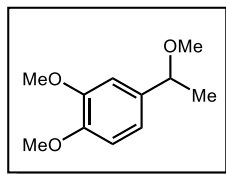


1-Methoxy-2-(1-methoxyethyl)benzene (7)

Prepared according to general procedure B using 1-ethyl-2-methoxybenzene (81.7 mg, 0.600 mmol), MeOH (0.2 mL, 5.0 mmol), [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)]PF₆ (6.90 mg, 0.006 mmol), K₂HPO₄ (312 mg, 1.80 mmol), and Cu(TFA)₂(MeCN) (238 mg 0.720 mmol). The crude material was analyzed for NMR yield using phenanthrene as an internal standard. (3 d)

Experiment 1: 38% yield by ^1H NMR

Spectral data were consistent with those reported previously.²¹



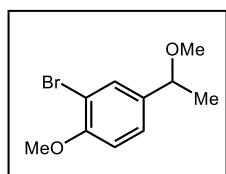
1,2-Dimethoxy-4-(1-methoxyethyl)benzene (8)

Prepared according to general procedure B using 4-ethyl-1,2-dimethoxybenzene (99.7 mg, 0.600 mmol), MeOH (0.2 mL, 5.0 mmol), $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(5,5'\text{-dCF}_3\text{bpy})]\text{PF}_6$ (6.90 mg, 0.006 mmol), K_2HPO_4 (312 mg, 1.80 mmol), and $\text{Cu}(\text{TFA})_2(\text{MeCN})$ (238 mg 0.720 mmol). The crude material was purified by flash column chromatography (20% Et₂O/Pentane). (7 d)

Experiment 1: 83.4 mg of a clear liquid (71%, 0.425 mmol)

Experiment 2: 81.1 mg of a clear liquid (69%, 0.414 mmol)

^1H NMR (500 MHz, CDCl_3) δ 6.87 (d, J = 1.28 Hz, 1H), 6.83-6.84 (m, 2H), 4.24 (q, J = 6.45, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 3.21 (s, 3H), 1.43 (d, J = 6.43 Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 149.16, 136.09, 118.66, 110.80, 108.82, 79.39, 56.29, 55.85, 23.87; IR (thin film): ν 2972, 2931, 1597, 1511, 1259, 1026; HRMS (ESI) $[\text{M-OMe}]^+$ calculated for $[\text{C}_{11}\text{H}_{16}\text{O}_3]$ requires m/z 165.0910, found m/z 165.0909.



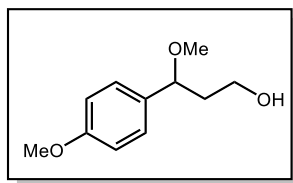
2-Bromo-1-methoxy-4-(1-methoxyethyl)benzene (9)

Prepared according to general procedure B using 2-bromo-4-ethyl-1-methoxybenzene (129 mg, 0.600 mmol), MeOH (0.2 mL, 5.0 mmol), $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(5,5'\text{-dCF}_3\text{bpy})]\text{PF}_6$ (6.90 mg, 0.006 mmol), K_2HPO_4 (312 mg, 1.80 mmol), and $\text{Cu}(\text{TFA})_2(\text{MeCN})$ (238 mg 0.720 mmol). The crude material was purified by flash column chromatography (5% Et₂O/Pentane). (60 h)

Experiment 1: 53.6 mg of a clear liquid (38%, 0.230 mmol)

Experiment 2: 58.4 mg of a clear liquid (40%, 0.250 mmol)

^1H NMR (500 MHz, CDCl_3) δ 7.50 (d, J = 2.07 Hz, 1H), 7.21 (dd, J = 8.40, 2.11 Hz, 1H), 6.88 (d, J = 8.41 Hz, 1H), 4.22 (q, J = 6.45, 1H), 3.90 (s, 3H), 3.20 (s, 3H), 1.41 (d, J = 6.41 Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 155.18, 137.21, 131.23, 126.31, 111.83, 111.65, 78.58, 56.40, 56.30, 23.79; IR (thin film): ν 2973, 2928, 1601, 1494, 1289, 1051; HRMS (ESI) $[\text{M-OMe}]^+$ calculated for $[\text{C}_{10}\text{H}_{13}\text{BrO}_2]$ requires m/z 212.9910, found m/z 212.9911.



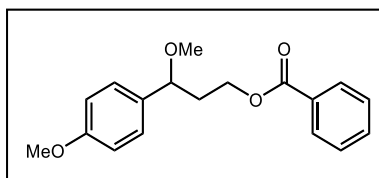
3-Methoxy-3-(4-methoxyphenyl)propan-1-ol (10)

Prepared according to general procedure B using 3-(4-methoxyphenyl)propan-1-ol (99.7 mg, 0.600 mmol), MeOH (0.2 mL, 5.0 mmol), [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)]PF₆ (6.90 mg, 0.006 mmol), K₂HPO₄ (312 mg, 1.80 mmol), and Cu(TFA)₂(MeCN) (238 mg 0.720 mmol). The crude material was purified by flash column chromatography (60% Et₂O/Pentane). (10 h)

Experiment 1: 77.4 mg of a clear liquid (69%, 0.416 mmol)

Experiment 2: 74.1 mg of a clear liquid (66%, 0.398 mmol)

¹H NMR (500 MHz, CDCl₃) δ 7.23 (d, *J* = 8.58 Hz, 2H), 6.90 (d, *J* = 8.64 Hz, 2H), 4.34 (dd, *J* = 8.92, 4.24 Hz, 1H), 3.81 (s, 3H), 3.74-3.77 (m, 2H), 3.20 (s, 3H), 2.78-2.80 (m, 1H), 2.01-2.08 (m, 1H), 1.80-1.86 (m, 1H); **¹³C NMR** (126 MHz, CDCl₃) δ 159.20, 133.45, 127.75, 113.89, 83.31, 61.12, 56.37, 55.26, 40.36; **IR** (thin film): ν 3394, 2931, 1610, 1510, 1244, 1033; **HRMS** (ESI) [M-OMe]⁺ calculated for [C₁₁H₁₆O₃] requires *m/z* 165.0910, found *m/z* 165.0909.



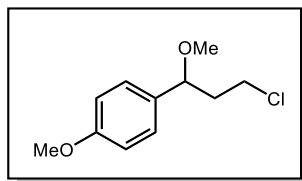
3-Methoxy-3-(4-methoxyphenyl)propyl benzoate (11)

Prepared according to general procedure A using 3-(4-methoxyphenyl)propyl benzoate (163 mg, 0.600 mmol), MeOH (40 mg, 1.2 mmol), [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)]PF₆ (6.90 mg, 0.006 mmol), K₂HPO₄ (312 mg, 1.80 mmol), and Cu(TFA)₂(MeCN) (238 mg 0.720 mmol). The crude material was purified by flash column chromatography (15% Et₂O/Pentane). (12 h)

Experiment 1: 123 mg of a clear oil (62%, 0.373 mmol)

Experiment 2: 127 mg of a clear oil (65%, 0.385 mmol)

¹H NMR (500 MHz, CDCl₃) δ 8.01 (dd, *J* = 8.33, 1.43 Hz, 2H), 7.54 (tt, *J* = 7.52, 1.43 Hz, 1H), 7.43 (t, *J* = 7.78 Hz, 2H), 7.24 (d, *J* = 8.70 Hz, 2H), 6.89 (d, *J* = 8.65 Hz, 2H), 4.43 (ddd, *J* = 11.03, 7.22, 5.87 Hz, 1H), 4.26-4.33 (m, 2H), 3.79 (s, 3H), 3.20 (s, 3H), 2.27 (ddt, *J* = 14.04, 7.91, 6.05 Hz, 1H), 2.07 (ddt, *J* = 14.09, 7.24, 5.95 Hz, 1H); **¹³C NMR** (126 MHz, CDCl₃) δ 166.45, 159.25, 133.32, 132.85, 130.34, 129.52, 128.31, 127.84, 113.92, 80.32, 62.00, 56.43, 55.22, 37.15; **IR** (thin film): ν 2934, 2830, 1716, 1608, 1511, 1453, 1271, 1244, 1174, 1104, 1029, 710; **HRMS** (ESI) [M+Na]⁺ calculated for [C₁₈H₂₀O₄] requires *m/z* 323.1254, found *m/z* 323.1250.



1-(3-Chloro-1-methoxypropyl)-4-methoxybenzene (12)

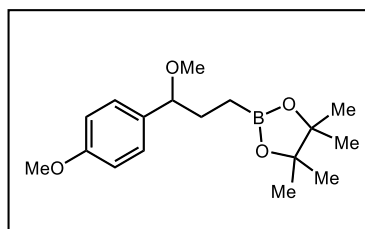
Prepared according to general procedure B using 1-(3-chloropropyl)-4-methoxybenzene (111 mg, 0.600 mmol), MeOH (0.2 mL, 5.0 mmol), [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)]PF₆ (6.90 mg, 0.006

mmol), K₂HPO₄ (312 mg, 1.80 mmol), and Cu(TFA)₂(MeCN) (238 mg 0.720 mmol). The crude material was purified by flash column chromatography (5% Et₂O/Pentane). (8 h)

Experiment 1: 106 mg of a clear liquid (83%, 0.496 mmol)

Experiment 2: 95.6 mg of a clear liquid (74%, 0.447 mmol)

¹H NMR (500 MHz, CDCl₃) δ 7.23 (d, *J* = 8.60 Hz, 2H), 6.90 (d, *J* = 8.62 Hz, 2H), 4.31 (dd, *J* = 8.26, 5.14 Hz, 1H), 3.81 (s, 3H), 3.68 (ddd, *J* = 10.75, 7.92, 5.65 Hz, 1H), 3.48 (dt, *J* = 10.76, 6.05 Hz, 1H), 3.20 (s, 3H), 2.24 (ddt, *J* = 14.22, 8.28, 5.91 Hz, 1H), 1.98 (dddd, *J* = 14.19, 7.92, 5.96, 5.08 Hz, 1H); **¹³C NMR** (126 MHz, CDCl₃) δ 159.30, 133.03, 127.85, 113.94, 79.94, 56.55, 55.28, 41.76, 40.83; **IR** (thin film): ν 2999, 2940, 2836, 1611, 1583, 1509, 1447, 1242, 1034, 814; **HRMS** (ESI) [M-OMe]⁺ calculated for [C₁₁H₁₅ClO] requires *m/z* 183.0571, found *m/z* 183.0573.



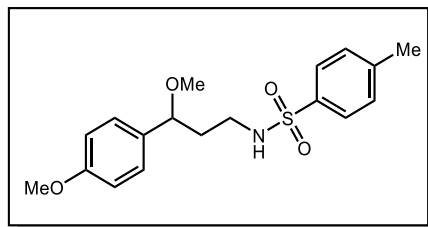
2-(3-Methoxy-3-(4-methoxyphenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (13)

Prepared according to general procedure A using 2-(3-(4-methoxyphenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (166 mg, 0.600 mmol), MeOH (40 mg, 1.2 mmol), [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)]PF₆ (6.90 mg, 0.006 mmol), K₂HPO₄ (312 mg, 1.80 mmol), and Cu(TFA)₂(MeCN) (238 mg 0.720 mmol). The crude material was purified by flash column chromatography (20% Et₂O/Pentane). (8 h and 30 min)

Experiment 1: 110 mg of a clear liquid (62%, 0.372 mmol)

Experiment 2: 104 mg of a clear liquid (57%, 0.340 mmol)

¹H NMR (500 MHz, CDCl₃) δ 7.19 (d, *J* = 8.61 Hz, 2H), 6.86 (d, *J* = 8.61 Hz, 2H), 3.98 (dd, *J* = 7.36, 5.96 Hz, 1H), 3.80 (s, 3H), 3.18 (s, 3H), 1.88 (ddt, *J* = 13.97, 9.30, 7.02 Hz, 1H), 1.72 (ddt, *J* = 13.65, 9.31, 6.18 Hz, 1H), 1.23 (s, 12H), 0.69-0.82 (m, 2H); **¹³C NMR** (126 MHz, CDCl₃) δ 158.89, 134.37, 127.93, 113.59, 85.14, 82.87, 56.45, 55.23, 32.39, 24.79, 7.39; **¹¹B NMR** (160 MHz, CDCl₃) δ 34.01; **IR** (thin film): ν 2977, 2929, 1610, 1510, 1243, 1143; **HRMS** (ESI) [M-OMe]⁺ calculated for [C₁₇H₂₇BO₄] requires *m/z* 274.1849, found *m/z* 274.1851.



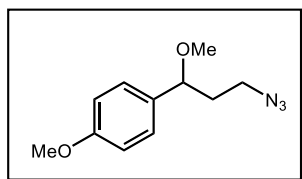
N-(3-Methoxy-3-(4-methoxyphenyl)propyl)-4-methylbenzenesulfonamide (14)

Prepared according to general procedure A using N-(3-(4-methoxyphenyl)propyl)-4-methylbenzenesulfonamide (192 mg, 0.600 mmol), MeOH (40 mg, 1.2 mmol), [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)]PF₆ (6.90 mg, 0.006 mmol), K₂HPO₄ (312 mg, 1.80 mmol), and Cu(TFA)₂(MeCN) (238 mg 0.720 mmol). The crude material was purified by flash column chromatography (60% Et₂O/Pentane). (12 h)

Experiment 1: 146 mg of a clear oil (70%, 0.418 mmol)

Experiment 2: 134 mg of a clear oil (64%, 0.384 mmol)

¹H NMR (500 MHz, CDCl₃) δ 7.75 (d, *J* = 8.26 Hz, 2H), 7.32 (d, *J* = 8.10 Hz, 2H), 7.07 (d, *J* = 8.65 Hz, 2H), 6.83 (d, *J* = 8.62 Hz, 2H), 5.24 (dd, *J* = 6.94, 4.79 Hz, 1H), 4.13 (dd, *J* = 8.39, 4.23 Hz, 1H), 3.79 (s, 3H), 3.12 (s, 3H), 2.97-3.13 (m, 1H), 3.00 (ddt, *J* = 12.43, 7.59, 4.63 Hz, 1H), 2.44 (s, 3H), 1.73-1.86 (m, 2H); **¹³C NMR** (126 MHz, CDCl₃) δ 159.24, 143.24, 137.81, 129.67, 127.57, 127.17, 113.91, 82.64, 56.41, 55.27, 41.09, 36.92, 21.55; **IR** (thin film): ν 3279, 2930, 1607, 1509, 1244, 1155; **HRMS** (ESI) [M+Na]⁺ calculated for [C₁₈H₂₃NO₄S] requires *m/z* 372.1240, found *m/z* 372.1236.



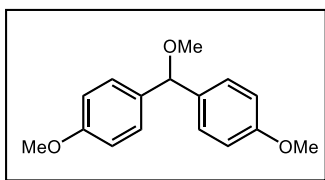
1-(3-Azido-1-methoxypropyl)-4-methoxybenzene (15)

Prepared according to general procedure A using 1-(3-azidopropyl)-4-methoxybenzene (115 mg, 0.600 mmol), MeOH (40 mg, 1.2 mmol), [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)]PF₆ (6.90 mg, 0.006 mmol), K₂HPO₄ (312 mg, 1.80 mmol), and Cu(TFA)₂(MeCN) (238 mg 0.720 mmol). The crude material was purified by flash column chromatography (5% Et₂O/Pentane). (12 h)

Experiment 1: 59.6 mg of a clear liquid (45%, 0.269 mmol)

Experiment 2: 74.0 mg of a clear liquid (56%, 0.334 mmol)

¹H NMR (500 MHz, CDCl₃) δ 7.21 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 4.19 (dd, *J* = 8.4, 5.1 Hz, 1H), 3.82 (s, 3H), 3.43 (ddd, *J* = 12.2, 7.7, 6.3 Hz, 1H), 3.27 (dt, *J* = 12.4, 6.3 Hz, 1H), 3.19 (s, 3H), 2.04 (ddt, *J* = 14.5, 8.4, 6.1 Hz, 1H), 1.84 (dddd, *J* = 14.1, 7.6, 6.6, 5.1 Hz, 1H). **¹³C NMR** (126 MHz, CDCl₃) δ 159.31, 133.13, 127.80, 113.96, 80.23, 56.44, 55.28, 48.24, 37.34; **IR** (thin film): ν 2933, 2830, 2095, 1611, 1511, 1246, 1106; **HRMS** (ESI) [M-OMe]⁺ calculated for [C₁₁H₁₅N₃O₂] requires *m/z* 190.0975, found *m/z* 190.0973.



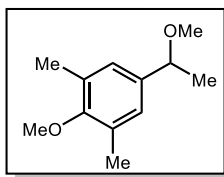
4,4'-(Methoxymethylene)bis(methoxybenzene) (16)

Prepared according to general procedure B using bis(4-methoxyphenyl)methane (137 mg, 0.600 mmol), MeOH (0.2 mL, 5.0 mmol), [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)]PF₆ (6.90 mg, 0.006 mmol), K₂HPO₄ (312 mg, 1.80 mmol), and Cu(TFA)₂(MeCN) (238 mg 0.720 mmol). The crude material was purified by flash column chromatography (10% Et₂O/Pentane). (4 h)

Experiment 1: 95.9 mg of a clear liquid (62%, 0.371 mmol)

Experiment 2: 81.9 mg of a clear liquid (55%, 0.317 mmol)

¹H NMR (500 MHz, CDCl₃) δ 7.24 (d, *J* = 8.58 Hz, 4H), 6.85 (d, *J* = 8.73 Hz, 4H), 5.16 (s, 1H), 3.78 (s, 6H), 3.34 (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 158.87, 134.52, 128.11, 113.73, 84.51, 56.79, 55.25; **IR** (thin film): ν 2995, 2932, 2829, 1609, 1507, 1459, 1241, 1171, 1085, 1031, 815; **HRMS** (ESI) [M-OMe]⁺ calculated for [C₁₅H₁₅O₂] requires *m/z* 227.1067, found *m/z* 227.1067.



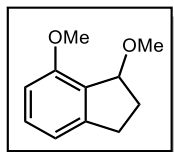
2-Methoxy-5-(1-methoxyethyl)-1,3-dimethylbenzene (17)

Prepared according to general procedure B using ((3-(4-methoxyphenyl)propoxy)methylene)dibenzene (98.6 mg, 0.600 mmol), MeOH (0.2 mL, 5.0 mmol), [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)]PF₆ (6.90 mg, 0.006 mmol), K₂HPO₄ (312 mg, 1.80 mmol), and Cu(TFA)₂(MeCN) (238 mg 0.720 mmol). The crude material was purified by flash column chromatography (5% Et₂O/Pentane). (21 h and 30 min)

Experiment 1: 62.6 mg of a clear liquid (54%, 0.322 mmol)

Experiment 2: 61.2 mg of a clear liquid (53%, 0.315 mmol)

¹H NMR (500 MHz, CDCl₃) δ 6.94 (s, 1H), 4.18 (q, *J* = 6.44 Hz, 1H), 3.72 (s, 3H), 3.21 (s, 3H), 2.28 (s, 6H), 1.40 (d, *J* = 6.43 Hz, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 156.23, 138.60, 130.70, 126.57, 79.27, 59.65, 56.39, 23.66, 16.19; **IR** (thin film): ν 2976, 2929, 1482, 1449, 1222, 1145, 1111, 1015; **HRMS** (ESI) [M+Na]⁺ calculated for [C₁₂H₁₈O₂] requires *m/z* 217.1199, found *m/z* 217.1199.



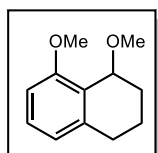
1,7-Dimethoxy-2,3-dihydro-1H-indene (18)

Prepared according to general procedure A using 4-methoxy-2,3-dihydro-1H-indene (89.0 mg, 0.600 mmol), MeOH (40 mg, 1.2 mmol), [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)]PF₆ (6.90 mg, 0.006 mmol), K₂HPO₄ (312 mg, 1.80 mmol), and Cu(TFA)₂(MeCN) (238 mg 0.720 mmol). The crude material was purified by flash column chromatography (10% Et₂O/Pentane). (28 h)

Experiment 1: 63.3 mg of a clear liquid (59%, 0.355 mmol)

Experiment 2: 64.8 mg of a clear liquid (61%, 0.364 mmol)

¹H NMR (500 MHz, CDCl₃) δ 7.24 (t, *J* = 7.76 Hz, 1H), 6.87 (d, *J* = 7.40 Hz, 1H), 6.71 (d, *J* = 8.15 Hz, 1H), 4.98 (dd, *J* = 6.08, 1.48 Hz, 1H), 3.85 (s, 3H), 3.38 (s, 3H), 3.14 (dt, *J* = 16.28, 8.28 Hz, 1H), 2.78 (ddd, *J* = 16.03, 8.58, 2.30 Hz, 1H), 2.10-2.23 (m, 2H); **¹³C NMR** (126 MHz, CDCl₃) δ 156.97, 147.33, 130.26, 130.19, 117.22, 108.21, 81.64, 56.42, 55.31, 31.65, 30.87; **IR** (thin film): ν 2931, 2825, 1732, 1591, 1474, 1262, 1075; **HRMS** (ESI) [M+Na]⁺ calculated for [C₁₁H₁₄O₂] requires *m/z* 201.0886, found *m/z* 201.0885.



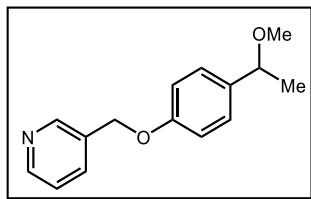
1,8-Dimethoxy-1,2,3,4-tetrahydronaphthalene (19)

Prepared according to general procedure B using 5-methoxy-1,2,3,4-tetrahydronaphthalenes (97.4 mg, 0.600 mmol), MeOH (0.2 mL, 5.0 mmol), [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)]PF₆ (6.90 mg, 0.006 mmol), K₂HPO₄ (312 mg, 1.80 mmol), and Cu(TFA)₂(MeCN) (238 mg 0.720 mmol). The crude material was purified by flash column chromatography (10% Et₂O/Pentane). (17 h)

Experiment 1: 68.7 mg of a clear liquid (60%, 0.357 mmol)

Experiment 2: 67.9 mg of a clear liquid (59%, 0.353 mmol)

¹H NMR (500 MHz, CDCl₃) δ 7.15 (t, *J* = 7.90 Hz, 1H), 6.71 (d, *J* = 7.98 Hz, 2H), 4.55 (t, *J* = 3.04 Hz, 1H), 3.85 (s, 3H), 3.45 (s, 3H), 2.77-2.87 (m, 1H), 2.66 (ddd, *J* = 17.35, 12.19, 5.96 Hz, 1H), 2.22-2.26 (m, 1H), 1.95 (dddd, *J* = 21.57, 12.93, 5.57, 2.80 Hz, 1H), 1.68-1.73 (m, 1H), 1.51 (dt, *J* = 13.71, 3.51 Hz, 1H); **¹³C NMR** (126 MHz, CDCl₃) δ 158.32, 139.05, 128.31, 125.26, 121.39, 107.77, 70.10, 56.84, 55.60, 29.13, 26.61, 17.14; **IR** (thin film): ν 2936, 1587, 1465, 1260, 1086, 904, 726; **HRMS** (ESI) [M-OMe]⁺ calculated for [C₁₁H₁₃O] requires *m/z* 161.0961, found *m/z* 161.0960.



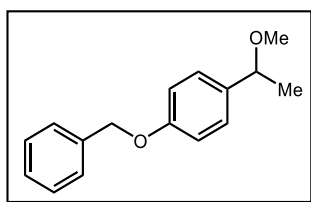
3-((4-(1-Methoxyethyl)phenoxy)methyl)pyridine (20)

Prepared according to general procedure B using 3-((4-ethylphenoxy)methyl)pyridine (128 mg, 0.600 mmol), MeOH (0.2 mL, 5.0 mmol), [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)]PF₆ (6.90 mg, 0.006 mmol), K₂HPO₄ (312 mg, 1.80 mmol), and Cu(TFA)₂(MeCN) (238 mg 0.720 mmol). The crude material was purified by flash column chromatography (40% MTBE/Pentane). (3 d)

Experiment 1: 71.3 mg of a clear oil (49%, 0.293 mmol)

Experiment 2: 70.4 mg of a clear oil (52%, 0.289 mmol)

¹H NMR (500 MHz, CDCl₃) δ 8.69 (d, *J* = 2.18 Hz, 1H), 8.59 (dd, *J* = 4.81, 1.64 Hz, 1H), 7.78 (dt, *J* = 7.98, 1.93 Hz, 1H), 7.33 (dd, *J* = 7.84 1H), 7.25 (d, *J* = 8.62 2H), 6.96 (d, *J* = 8.66 2H), 5.08 (s, 2H), 4.26 (q, *J* = 6.45 1H), 3.20 (s, 3H), 1.42 (d, *J* = 6.52 Hz, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 157.80, 149.46, 149.01, 136.33, 135.28, 132.57, 127.54, 123.52, 114.70, 79.06, 67.59, 56.27, 23.78; **IR** (thin film): ν 2975, 2928, 1608, 1508, 1233, 1106, 1021; **HRMS** (ESI) [M+H]⁺ calculated for [C₁₅H₁₇O₂N] requires *m/z* 244.1332, found *m/z* 244.1332.



1-(Benzyloxy)-4-(1-methoxyethyl)benzene (21)

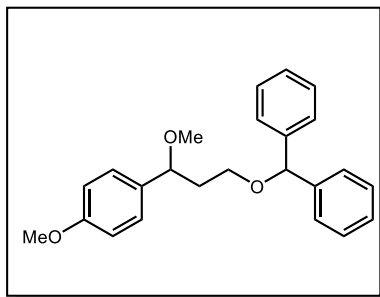
Prepared according to general procedure A using 1-(benzyloxy)-4-ethylbenzene (127 mg, 0.600 mmol), MeOH (40 mg, 1.2 mmol), [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)]PF₆ (6.90 mg, 0.006 mmol), K₂HPO₄ (312 mg, 1.80 mmol), and Cu(TFA)₂(MeCN) (238 mg 0.720 mmol). The crude material was purified by flash column chromatography (7% Et₂O/Pentane). (8 h and 30 min)

Experiment 1: 105 mg of a clear liquid (72%, 0.432 mmol)

Experiment 2: 112 mg of a clear liquid (77%, 0.462 mmol)

¹H NMR (500 MHz, CDCl₃) δ 7.43 (d, *J* = 8.16 Hz, 2H), 7.37 (t, *J* = 7.32 Hz, 2H), 7.31 (t, *J* = 8.53 Hz, 1H), 7.23 (d, *J* = 8.53 2H), 6.96 (d, *J* = 8.57 2H), 5.04 (s, 2H), 4.24 (q, *J* = 6.44 1H), 3.19 (s, 3H), 1.42 (d, *J* = 6.49 Hz, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 158.29, 137.10, 135.85, 128.62, 127.99, 127.53, 127.49, 114.76, 79.15, 70.07, 56.28, 23.83; **IR** (thin film):

ν 2974, 2926, 1608, 1507, 1227, 1106, 1019; **HRMS** (ESI) $[M-OMe]^+$ calculated for $[C_{16}H_{18}O_2]$ requires m/z 211.1117, found m/z 211.1116.



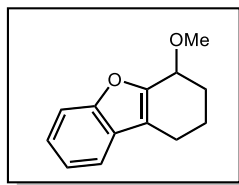
((3-Methoxy-3-(4-methoxyphenyl)propoxy)methylene)dibenzene (22)

Prepared according to general procedure A using ((3-(4-methoxyphenyl)propoxy)methylene)dibenzene (200 mg, 0.600 mmol), MeOH (40 mg, 1.2 mmol), $[Ir(dF(CF_3)ppy)_2(5,5'-dCF_3bpy)]PF_6$ (6.90 mg, 0.006 mmol), K_2HPO_4 (312 mg, 1.80 mmol), and $Cu(TFA)_2(MeCN)$ (238 mg 0.720 mmol). The crude material was purified by flash column chromatography (10% Et₂O/Pentane). (21 h)

Experiment 1: 46.4 mg of a clear liquid (23%, 0.128 mmol) (62% NMR yield)

Experiment 2: 70.9 mg of a clear liquid (33%, 0.196 mmol) (71% NMR yield)

¹H NMR (500 MHz, CDCl₃) δ 7.29-7.35 (m, 8H), 7.21-7.25 (m, 1H), 7.19 (d, J = 8.60 Hz 2H), 6.86 (d, J = 8.69 Hz 2H), 5.29 (s, 1H), 4.32 (dd, J = 7.89, 5.96 Hz, 1H), 3.80 (s, 3H), 3.56 (ddd, J = 9.31, 7.11, 5.35 Hz, 1H), 3.37 (ddd, J = 9.31, 6.45, 5.53 Hz, 1H), 3.15 (s, 3H) 2.14 (dddd, J = 14.22, 7.81, 6.48, 5.41 Hz, 1H), 1.90 (ddt, J = 13.97, 7.06, 5.67 Hz, 1H); **¹³C NMR** (126 MHz, CDCl₃) δ 159.04, 142.52, 142.45, 133.95, 128.31, 128.30, 127.96, 127.34, 127.33, 127.00, 126.98, 113.73, 83.65, 80.33, 65.70, 56.35, 55.24, 38.35; **IR** (thin film): ν 3060, 2928, 2866, 1608, 1507, 1450, 1298, 1244, 1176, 1098, 1073, 1031, 830, 699; **HRMS** (ESI) $[M+Na]^+$ calculated for $[C_{24}H_{26}O_3]$ requires m/z 385.1774, found m/z 385.1767.



4-Methoxy-1,2,3,4-tetrahydrodibenzo[b,d]furan (23)

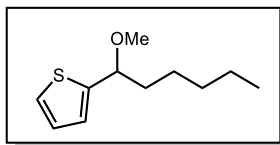
Prepared according to general procedure B using 1,2,3,4-tetrahydrodibenzo[b,d]furan (103 mg, 0.600 mmol), MeOH (0.2 mL, 5.0 mmol), $[Ir(dF(CF_3)ppy)_2(5,5'-dCF_3bpy)]PF_6$ (6.90 mg, 0.006 mmol), K_2HPO_4 (312 mg, 1.80 mmol), and $Cu(TFA)_2(MeCN)$ (238 mg 0.720 mmol). The crude material was purified by flash column chromatography (Gradient 2.5% to 5% Et₂O/Pentane). (24 h)

Experiment 1: 48.9 mg of a clear oil (40%, 0.242 mmol)

Experiment 2: 49.7 mg of a clear oil (41%, 0.246 mmol)

¹H NMR (500 MHz, CDCl₃) δ 7.47 (d, J = 7.89 Hz, 1H), 7.46 (d, J = 8.08 Hz, 1H), 7.25-7.29 (m, 1H), 7.21 (td, J = 7.89, 1.06 Hz, 1H), 4.46 (t, J = 4.09 Hz, 1H), 3.56 (s, 3H), 2.74 (td, J = 16.57, 4.52 Hz, 1H), 2.56 (ddd, J = 16.45, 9.28, 5.28 Hz, 1H), 2.11-2.19 (m, 1H), 1.96-2.05 (m, 1H), 1.81-1.97 (m, 2H); **¹³C NMR** (126 MHz, CDCl₃) δ 154.79, 152.49, 127.84, 124.32, 122.32, 119.42, 116.63, 111.41, 71.24, 57.13, 29.12, 20.67, 18.86; **IR** (thin film):

ν 2931, 2863, 2821, 1451, 1366, 1185, 743; **HRMS** (ESI) $[M-OMe]^+$ calculated for $[C_{13}H_{14}O_2]$ requires m/z 171.0804, found m/z 171.0803.



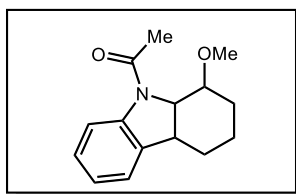
2-(1-methoxyhexyl)thiophene (24)

Prepared according to general procedure B using 2-hexylthiophene (101 mg, 0.600 mmol), MeOH (0.2 mL, 5.0 mmol), $[Ir(dF(CF_3)ppy)_2(5,5'-dCF_3bpy)]PF_6$ (6.90 mg, 0.006 mmol), K_2HPO_4 (312 mg, 1.80 mmol), and $Cu(TFA)_2(MeCN)$ (238 mg 0.720 mmol). The crude material was purified by flash column chromatography (2.5% Et₂O/Pentane). (3 d)

Experiment 1: 56.3 mg of a yellow oil (44%, 0.284 mmol)

Experiment 2: 54.5 mg of a yellow oil (44%, 0.275 mmol)

¹H NMR (500 MHz, CDCl₃) δ 7.24-7.29 (m, 1H), 6.94-6.98 (m, 2H), 4.35 (t, J = 6.80 Hz 1H), 3.25 (s, 3H), 1.91 (dddd, J = 12.5, 9.13, 7.10, 5.30 Hz 1H), 1.67-1.76 (m, 1H), 1.36-1.45 (m, 1H), 1.22-1.32 (m, 5H), 0.81-0.91 (m, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 146.40, 126.24, 125.20, 124.76, 79.46, 56.40, 38.29, 31.62, 25.49, 22.55, 14.03; **IR** (thin film): ν 2928, 2857, 2821, 1463, 1319, 1092, 827, 696; **HRMS** (ESI) $[M-OMe]^+$ calculated for $[C_{11}H_{18}OS]$ requires m/z 167.0889, found m/z 167.0890.



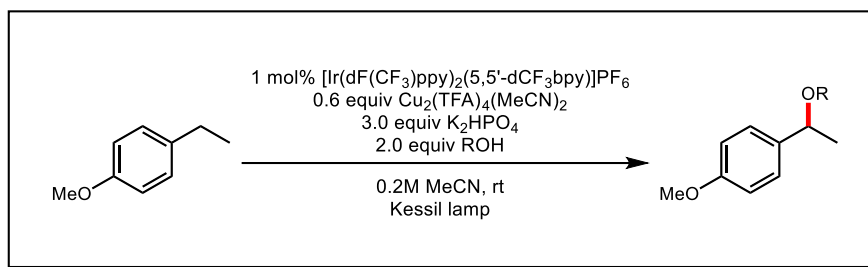
1-(1-Methoxy-1,2,3,4-tetrahydro-9H-carbazol-9-yl)ethan-1-one (25)

Prepared according to general procedure B using 1-(1,2,3,4-tetrahydro-9H-carbazol-9-yl)ethan-1-one (127 mg, 0.600 mmol), MeOH (0.2 mL, 5.0 mmol), $[Ir(dF(CF_3)ppy)_2(5,5'-dCF_3bpy)]PF_6$ (6.90 mg, 0.006 mmol), K_2HPO_4 (312 mg, 1.80 mmol), and $Cu(TFA)_2(MeCN)$ (238 mg 0.720 mmol). The crude material was purified by flash column chromatography (Gradient 20% to 30% Et₂O/Pentane). (12 h)

Experiment 1: 68.1 mg of a white solid (47%, 0.280 mmol)

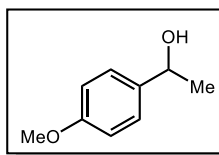
Experiment 2: 66.6 mg of a white solid (46%, 0.274 mmol)

¹H NMR (500 MHz, CDCl₃) δ 8.03 (d, J = 8.39 Hz, 1H), 7.46 (dt, J = 7.63, 1.04 Hz, 1H), 7.32 (ddd, J = 7.85, 6.92, 1.05 Hz, 1H), 7.25 (t, J = 7.52 Hz, 1H), 4.88 (t, J = 3.38 Hz, 1H), 3.46 (s, 3H), 2.83 (ddd, J = 16.7, 5.60, 2.53 Hz, 1H), 2.78 (s, 3H), 2.57 (dddd, J = 16.7, 11.1, 5.91, 1.11 Hz, 1H), 2.33 (ddt, J = 14.0, 5.50, 2.99 Hz, 1H), 1.98 (tddd, J = 13.5, 11.1, 5.60, 2.74 Hz, 1H), 1.85 (dtt, J = 13.4, 5.37, 2.73 Hz, 1H), 1.72 (tt, J = 13.6, 3.26 Hz, 1H); **¹³C NMR** (126 MHz, CDCl₃) δ 169.90, 136.48, 133.96, 129.39, 125.24, 122.95, 121.51, 118.90, 115.75, 71.22, 55.96, 26.74, 26.45, 21.27, 16.98; **IR** (thin film): ν 2954, 2931, 2901, 1687, 1604, 1401, 1170, 1150, 1070, 752; **HRMS** (ESI) $[M+Na]^+$ calculated for $[C_{15}H_{17}O_2N]$ requires m/z 266.1152, found m/z 266.1148; m.p = 76–77 °C.



General Procedure C: A dry 20-mL Schlenk tube (1.5 cm diameter) was charged with [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)]PF₆ (6.90 mg, 0.006 mmol, 0.01 equiv.), K₂HPO₄ (312 mg, 1.80 mmol, 3 equiv.), and Cu(TFA)₂(MeCN) (238 mg 0.720 mmol, 1.2 equiv.). A stock solution containing 1-ethyl-4-methoxybenzene (82 mg, 0.60 mmol, 1 equiv.) and the alcohol/ carboxylic acid (1.2 mmol, 2 equiv.) in 0.9 mL MeCN was then added. An additional 2.1 mL MeCN were added to rinse the wall of the Schlenk tube. The reaction was degassed by three freeze/pump/thaw cycles (4 cycles, 5 min each) under nitrogen in the dark before back filling with nitrogen. The reaction was then allowed to stir while being irradiated by a 40W Kessil Lamp PR160 (427nm). After a pre-determined time point, the reaction was eluted through a short pad of silica using Et₂O. After concentration under reduced pressure, the pure product was isolated by flash column chromatography.

General Procedure D: A dry 20-mL Schlenk tube (1.5 cm diameter) was charged with [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)]PF₆ (6.90 mg, 0.006 mmol, 0.01 equiv.), K₂HPO₄ (312 mg, 1.80 mmol, 3 equiv.), Cu(TFA)₂(MeCN) (238 mg 0.720 mmol, 1.2 equiv.), and the alcohol/ carbamate (5.0 mmol, 8 equiv.). A stock solution containing 1-ethyl-4-methoxybenzene (82 mg, 0.60 mmol, 1 equiv.) in 0.9 mL MeCN was then added. An additional 2.1 mL MeCN were added to rinse the wall of the Schlenk tube. The reaction was degassed by three freeze/pump/thaw cycles (4 cycles, 5 min each) under nitrogen in the dark before back filling with nitrogen. The reaction was then allowed to stir while being irradiated by a 40W Kessil Lamp PR160 (427nm). After a pre-determined time point, the reaction was eluted through a short pad of silica using Et₂O. After concentration under reduced pressure, the pure product was isolated by flash column chromatography.



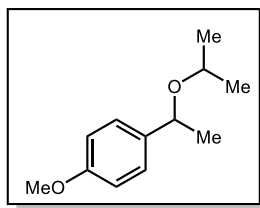
1-(1-Isopropoxyethyl)-4-methoxybenzene (26)

Prepared according to general procedure C using 1-ethyl-4-methoxybenzene (82.1 mg, 0.602 mmol), water (21.7 mg, 1.20 mmol), [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)]PF₆ (6.90 mg, 0.006 mmol), K₂HPO₄ (312 mg, 1.80 mmol), and Cu(TFA)₂(MeCN) (238 mg 0.720 mmol).

Experiment 1: 23% yield by ¹H NMR

Experiment 2: 16% yield by ¹H NMR

Spectral data were consistent with those reported previously.²²



1-(1-Isopropoxyethyl)-4-methoxybenzene (27)

Prepared according to general procedure C using 1-ethyl-4-methoxybenzene (82.0 mg, 0.600 mmol), isopropyl alcohol (72.2 mg, 1.20 mmol), $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(5,5'\text{-dCF}_3\text{bpy})]\text{PF}_6$ (6.90 mg, 0.006 mmol), K_2HPO_4 (312 mg, 1.80 mmol), and $\text{Cu}(\text{TFA})_2(\text{MeCN})$ (238 mg 0.720 mmol). The crude material was purified by flash column chromatography (5% Et_2O /Pentane). (7 h)

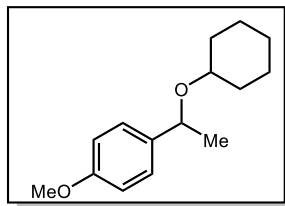
Experiment 1: 62.5 mg of a clear liquid (54%, 0.322 mmol)

Experiment 2: 65.6 mg of a clear liquid (56%, 0.338 mmol)

Prepared according to general procedure D using 1-ethyl-4-methoxybenzene (82.0 mg, 0.600 mmol), isopropyl alcohol (292 mg, 4.86 mmol), $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(5,5'\text{-dCF}_3\text{bpy})]\text{PF}_6$ (6.90 mg, 0.006 mmol), K_2HPO_4 (312 mg, 1.80 mmol), and $\text{Cu}(\text{TFA})_2(\text{MeCN})$ (238 mg 0.720 mmol). The crude material was purified by flash column chromatography (2.5 % Et_2O /Pentane). (8 h)

Experiment 1: 79.4 mg of a clear liquid (68%, 0.409 mmol)

Spectral data were consistent with those reported previously.²³



1-(1-(Cyclohexyloxy)ethyl)-4-methoxybenzene (28)

Prepared according to general procedure C using 1-ethyl-4-methoxybenzene (82.0 mg, 0.600 mmol), cyclohexanol (121 mg, 1.20 mmol), $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(5,5'\text{-dCF}_3\text{bpy})]\text{PF}_6$ (6.90 mg, 0.006 mmol), K_2HPO_4 (312 mg, 1.80 mmol), and $\text{Cu}(\text{TFA})_2(\text{MeCN})$ (238 mg 0.720 mmol). The crude material was purified by flash column chromatography (5% Et_2O /Pentane). (7 h)

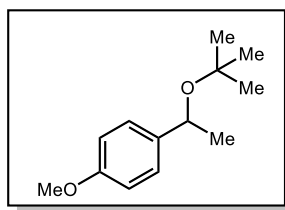
Experiment 1: 70.2 mg of a clear liquid (50%, 0.300 mmol)

Experiment 2: 73.9 mg of a clear liquid (53%, 0.315 mmol)

Prepared according to general procedure D using 1-ethyl-4-methoxybenzene (81.6 mg, 0.600 mmol), cyclohexanol (599 mg, 5.59 mmol), $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(5,5'\text{-dCF}_3\text{bpy})]\text{PF}_6$ (6.90 mg, 0.006 mmol), K_2HPO_4 (312 mg, 1.80 mmol), and $\text{Cu}(\text{TFA})_2(\text{MeCN})$ (238 mg 0.720 mmol). The crude material was purified by flash column chromatography (5% Et_2O /Pentane). (7 h)

Experiment 1: 92.7 mg of a clear liquid (66%, 0.396 mmol)

Spectral data were consistent with those reported previously.²⁴



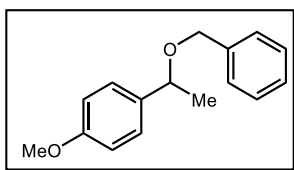
1-(1-(tert-Butoxy)ethyl)-4-methoxybenzene (29)

Prepared according to general procedure D using 1-ethyl-4-methoxybenzene (81.6 mg, 0.599 mmol), *tert*-butanol (356 mg, 4.81 mmol), [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)]PF₆ (6.90 mg, 0.006 mmol), K₂HPO₄ (312 mg, 1.80 mmol), and Cu(TFA)₂(MeCN) (238 mg 0.720 mmol). The crude material was purified by flash column chromatography (2.5% Et₂O/Pentane). (14.5 h)

Experiment 1: 57.5 mg of a clear oil (46%, 0.276 mmol)

Experiment 2: 55.0 mg of a clear oil (44%, 0.264 mmol)

Spectral data were consistent with those reported previously.²⁵



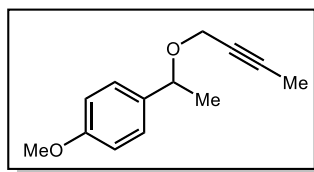
1-(1-(Benzyloxy)ethyl)-4-methoxybenzene (30)

Prepared according to general procedure C using 1-ethyl-4-methoxybenzene (81.7 mg, 0.600 mmol), benzyl alcohol (130 mg, 1.20 mmol), [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)]PF₆ (6.90 mg, 0.006 mmol), K₂HPO₄ (312 mg, 1.80 mmol), and Cu(TFA)₂(MeCN) (238 mg 0.720 mmol). The crude material was purified by flash column chromatography (1% Et₂O/Pentane). (12 h)

Experiment 1: 811.8 mg of a clear oil (59%, 0.338 mmol)

Experiment 2: 77.7 mg of a clear oil (53%, 0.321 mmol)

Spectral data were consistent with those reported previously.²⁶



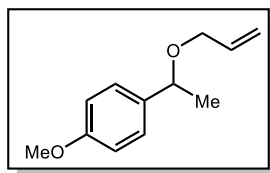
1-(1-(But-2-yn-1-yloxy)ethyl)-4-methoxybenzene (31)

Prepared according to general procedure C using 1-ethyl-4-methoxybenzene (81.5 mg, 0.599 mmol), 2-butyne-1-ol (83.8 mg, 1.20 mmol), [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)]PF₆ (6.90 mg, 0.006 mmol), K₂HPO₄ (312 mg, 1.80 mmol), and Cu(TFA)₂(MeCN) (238 mg 0.720 mmol). The crude material was purified by flash column chromatography (1% Et₂O/Pentane). (12 h)

Experiment 1: 66.8 mg of a clear oil (54%, 0.327 mmol)

Experiment 2: 63.1 mg of a clear oil (52%, 0.309 mmol)

¹H NMR (500 MHz, CDCl₃) δ 7.25 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 4.55 (q, *J* = 6.5 Hz, 1H), 3.99 (dq, *J* = 15.0, 2.4 Hz, 1H), 3.85 – 3.77 (m, 1H), 3.80 (s, 3H), 1.85 (t, *J* = 2.3 Hz, 3H), 1.45 (d, *J* = 6.5 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 159.1, 134.7, 127.7, 113.8, 81.9, 76.1, 75.4, 55.9, 55.3, 23.8, 3.7; HRMS (ESI) [M+Na]⁺ calculated for [C₁₃H₁₆O₂] requires *m/z* 227.1043, found *m/z* 227.1038; IR (thin film): ν 2974, 2931, 2856, 2837, 2293, 2244, 1243, 1082, 1034, 831.



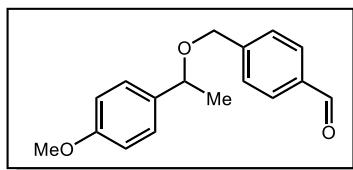
1-(1-(Allyloxy)ethyl)-4-methoxybenzene (32)

Prepared according to general procedure C using 1-ethyl-4-methoxybenzene (81.6 mg, 0.599 mmol), 2-propen-1-ol (73.5 mg, 1.27 mmol), [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)]PF₆ (6.90 mg, 0.006 mmol), K₂HPO₄ (312 mg, 1.80 mmol), and Cu(TFA)₂(MeCN) (238 mg 0.720 mmol). The crude material was purified by flash column chromatography (1% Et₂O/Pentane). (12 h)

Experiment 1: 68.0 mg of a clear oil (59%, 0.354 mmol)

Experiment 2: 66.0 mg of a clear oil (57%, 0.343 mmol)

Spectral data were consistent with those reported previously.²⁷



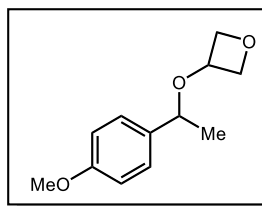
4-((1-(4-Methoxyphenyl)ethoxy)methyl)benzaldehyde (33)

Prepared according to general procedure C using 1-ethyl-4-methoxybenzene (81.8 mg, 0.601 mmol), 4-(hydroxymethyl)benzaldehyde (164 mg, 1.20 mmol), [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)]PF₆ (6.90 mg, 0.006 mmol), K₂HPO₄ (312 mg, 1.80 mmol), and Cu(TFA)₂(MeCN) (238 mg 0.720 mmol). The crude material was purified by flash column chromatography (20% MTBE/Pentane). (12 h)

Experiment 1: 73.7 mg of a clear oil (45%, 0.273 mmol)

Experiment 2: 66.1 mg of a clear oil (41%, 0.245 mmol)

¹H NMR (500 MHz, CDCl₃) δ 9.99 (s, 1H), 7.84 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 7.9 Hz, 2H), 7.28 (d, *J* = 8.6 Hz, 2H), 6.91 (d, *J* = 8.6 Hz, 2H), 4.53 – 4.31 (m, 3H), 3.81 (s, 3H), 1.50 (d, *J* = 6.5 Hz, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 192.0, 159.2, 146.0, 135.6, 135.2, 129.9, 127.7, 127.6, 114.0, 77.4, 69.4, 55.3, 24.1; **HRMS** (ESI) [M+Na]⁺ calculated for [C₁₇H₁₈O₃] requires *m/z* 293.1148, found *m/z* 293.1146; **IR** (thin film): ν 2973, 2929, 2836, 2735, 1695, 1510, 1242, 1086, 830, 810.



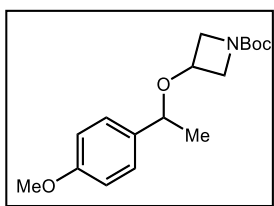
3-(1-(4-Methoxyphenyl)ethoxy)oxetane (34)

Prepared according to general procedure C using 1-ethyl-4-methoxybenzene (82.0 mg, 0.600 mmol), 1,3-epoxy-2-propanol (88.9 mg, 1.20 mmol), [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)]PF₆ (6.90 mg, 0.006 mmol), K₂HPO₄ (312 mg, 1.80 mmol), and Cu(TFA)₂(MeCN) (238 mg 0.720 mmol). The crude material was purified by flash column chromatography (20% Et₂O/Pentane). (8 h)

Experiment 1: 36.2 mg of a clear liquid (29%, 0.174 mmol)

Experiment 2: 37.1 mg of a clear liquid (30%, 0.178 mmol)

¹H NMR (500 MHz, CDCl₃) δ 7.21 (d, *J* = 8.61 Hz 2H), 6.87 (d, *J* = 8.62 Hz 2H), 4.70 (t, *J* = 6.48 Hz 1H), 4.65 (t, *J* = 6.11 Hz 1H), 4.48 (p, *J* = 6.03 Hz 1H), 4.37-4.41 (m, 2H), 4.32 (q, *J* = 6.46 Hz 1H), 3.80 (s, 3H), 1.45 (d, *J* = 6.52 Hz 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 159.33, 134.80, 127.61, 113.87, 79.38, 79.19, 76.97, 70.37, 55.29, 23.53; **IR** (thin film): ν 2953, 2872, 1611, 1511, 1456, 1243, 1177, 1123, 1031, 966, 832; **HRMS** (ESI) [M+Na]⁺ calculated for [C₁₂H₁₆O₃] requires *m/z* 231.0992, found *m/z* 231.0988.



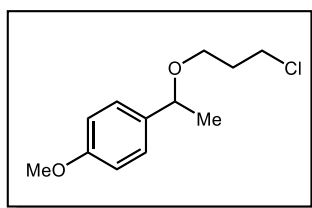
tert-Butyl 3-(1-(4-methoxyphenyl)ethoxy)azetidine-1-carboxylate (35)

Prepared according to general procedure C using 1-ethyl-4-methoxybenzene (81.9 mg, 0.601 mmol), 1-boc-3-hydroxyazetidine (209 mg, 1.21 mmol), [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)]PF₆ (6.90 mg, 0.006 mmol), K₂HPO₄ (312 mg, 1.80 mmol), and Cu(TFA)₂(MeCN) (238 mg 0.720 mmol). The crude material was purified by flash column chromatography (20% Et₂O/Pentane). (12 h)

Experiment 1: 62.0 mg of a clear liquid (34%, 0.202 mmol)

Experiment 2: 66.4 mg of a clear liquid (36%, 0.216 mmol)

¹H NMR (500 MHz, CDCl₃) δ 7.21 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 4.33 (q, *J* = 6.5 Hz, 1H), 4.13 (tt, *J* = 6.6, 4.7 Hz, 1H), 4.01 (ddd, *J* = 9.1, 6.5, 1.0 Hz, 1H), 3.86 (dd, *J* = 9.1, 4.7 Hz, 1H), 3.80 (s, 3H), 3.80 – 3.77 (m, 2H), 3.70 – 3.62 (m, 1H), 1.45 (d, *J* = 6.5 Hz, 3H), 1.41 (s, 9H); **¹³C NMR** (126 MHz, CDCl₃) δ 159.3, 156.3, 134.6, 127.6, 113.9, 79.4, 77.3, 77.1, 76.8, 76.7, 65.6, 55.3, 28.4, 23.5; **IR** (thin film): ν 2974, 2932, 2881, 2837, 1697, 1402, 1365, 1244, 1156, 1115, 1080, 1034, 832; **HRMS** (ESI) [M+Na]⁺ calculated for [C₁₇H₂₅NO₄] requires *m/z* 330.1676, found *m/z* 330.1672.



1-(1-(3-Chloropropoxy)ethyl)-4-methoxybenzene (36)

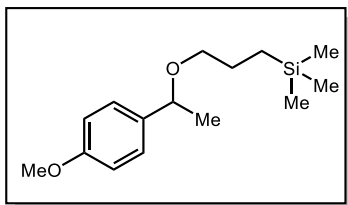
Prepared according to general procedure C using 1-ethyl-4-methoxybenzene (81.6 mg, 0.599 mmol), 3-chloro-1-propanol (116 mg, 1.23 mmol), [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)]PF₆ (6.90 mg, 0.006 mmol), K₂HPO₄ (312 mg, 1.80 mmol), and Cu(TFA)₂(MeCN) (238 mg 0.720 mmol). The crude material was purified by flash column chromatography (1% Et₂O/Pentane). (12 h)

Experiment 1: 74.7 mg of a clear oil (54%, 0.327 mmol)

Experiment 2: 66.5 mg of a clear oil (49%, 0.291 mmol)

¹H NMR (500 MHz, CDCl₃) δ 7.22 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 4.36 (q, *J* = 6.5 Hz, 1H), 3.80 (s, 3H), 3.70 – 3.55 (m, 2H), 3.41 – 3.35 (m, 2H), 1.98 (m, 2H), 1.42 (d, *J* = 6.4 Hz, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 159.0, 135.8, 127.3, 113.8, 77.7, 64.8, 55.2, 42.1, 33.0, 23.9;

HRMS (ESI) $[M+Na]^+$ calculated for $[C_{12}H_{17}ClO_2]$ required m/z 251.0809, found m/z 251.0806; **IR** (thin film): ν 2970, 2929, 2865, 1510, 1243, 1098, 1035, 8310.



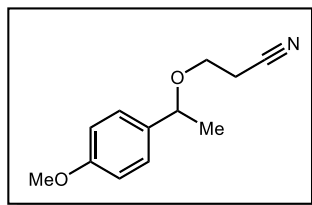
3-(1-(4-Methoxyphenyl)ethoxy)propyltrimethylsilane (37)

Prepared according to general procedure C using 1-ethyl-4-methoxybenzene (82.0 mg, 0.602 mmol), 3-(trimethylsilyl)-1-propanol (160 mg, 1.21 mmol), $[Ir(dF(CF_3)ppy)_2(5,5'-dCF_3bpy)]PF_6$ (6.90 mg, 0.006 mmol), K_2HPO_4 (312 mg, 1.80 mmol), and $Cu(TFA)_2(MeCN)$ (238 mg 0.720 mmol). The crude material was purified by flash column chromatography (1% Et_2O /Pentane). (17.5 h)

Experiment 1: 83.4 mg of a clear oil (52%, 0.313 mmol)

Experiment 2: 70.8 mg of a clear oil (43%, 0.260 mmol)

1H NMR (500 MHz, $CDCl_3$) δ 7.23 (d, J = 8.7 Hz, 2H), 6.88 (d, J = 8.7 Hz, 2H), 4.35 (q, J = 6.4 Hz, 1H), 3.80 (s, 3H), 3.22 (t, J = 7.2 Hz, 2H), 1.63 – 1.46 (m, 2H), 1.42 (d, J = 6.5 Hz, 3H), 0.41 (ddd, J = 10.0, 7.7, 4.5 Hz, 2H), -0.04 (s, 9 H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.8, 136.3, 127.3, 113.7, 77.4, 71.5, 55.2, 24.4, 24.1, 12.6, -1.7; **HRMS** (ESI) $[M+Na]^+$ calculated for $[C_{15}H_{26}O_2Si]$ requires m/z 289.1594, found m/z 289.1590; **IR** (thin film): ν 2953, 2929, 2871, 1511, 1244, 1098, 1038, 854, 830, 734.



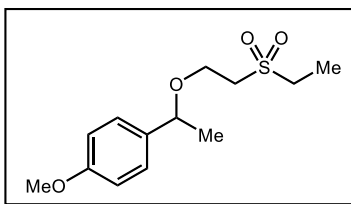
3-(1-(4-Methoxyphenyl)ethoxy)propanenitrile (38)

Prepared according to general procedure C using 1-ethyl-4-methoxybenzene (82.0 mg, 0.600 mmol), 2-cyanoethanol (85.3 mg, 1.20 mmol), $[Ir(dF(CF_3)ppy)_2(5,5'-dCF_3bpy)]PF_6$ (6.90 mg, 0.006 mmol), K_2HPO_4 (312 mg, 1.80 mmol), and $Cu(TFA)_2(MeCN)$ (238 mg 0.720 mmol). The crude material was purified by flash column chromatography (20% Et_2O /Pentane). (10 h)

Experiment 1: 60.1 mg of a clear liquid (49%, 0.293 mmol)

Experiment 2: 58.7 mg of a clear liquid (48%, 0.286 mmol)

1H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, J = 8.63 Hz 2H), 6.89 (d, J = 8.62 Hz 2H), 4.42 (q, J = 6.46 Hz 1H), 3.81 (s, 3H), 3.48 (td, J = 6.41, 2.1 Hz 2H), 2.54 (t, J = 6.41 Hz 2H), 1.45 (d, J = 6.41 Hz 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.28, 134.71, 127.43, 117.97, 113.99, 78.31, 62.82, 55.29, 23.85, 19.05; **IR** (thin film): ν 2973, 2931, 2875, 2252, 1611, 1511, 1455, 1243, 1097, 1031, 832; **HRMS** (ESI) $[M+Na]^+$ calculated for $[C_{12}H_{15}ON]$ requires m/z 228.0995, found m/z 228.0994.



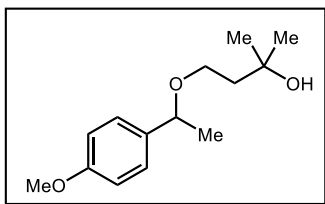
1-(1-(2-(Ethylsulfonyl)ethoxy)ethyl)-4-methoxybenzene (39)

Prepared according to general procedure C using 1-ethyl-4-methoxybenzene (81.7 mg, 0.600 mmol), 2-(ethylsulfonyl)ethanol (170 mg, 1.23 mmol), [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)]PF₆ (6.90 mg, 0.006 mmol), K₂HPO₄ (312 mg, 1.80 mmol), and Cu(TFA)₂(MeCN) (238 mg 0.720 mmol). The crude material was purified by flash column chromatography (50% Et₂O/Pentane). (24 h)

Experiment 1: 68.5 mg of a clear oil (42%, 0.251 mmol)

Experiment 2: 70.8 mg of a clear oil (43%, 0.260 mmol)

¹H NMR (500 MHz, CDCl₃) δ 7.20 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 8.6 Hz, 2H), 4.40 (q, *J* = 6.5 Hz, 1H), 3.80 (s, 3H), 3.75 – 3.61 (m, 2H), 3.22 – 3.05 (m, 4H), 1.47 – 1.37 (m, 6H); **¹³C NMR** (126 MHz, CDCl₃) δ 159.3, 134.4, 127.4, 114.0, 78.5, 62.1, 55.3, 52.7, 49.3, 23.5, 6.6; **HRMS** (ESI) [M+NH₄]⁺ calculated for [C₁₃H₂₀O₄S] requires *m/z* 290.1421, found *m/z* 290.1419; **IR** (thin film): ν 2974, 2928, 2870, 1511, 1311, 1288, 1242, 1121, 1095, 1029, 833.



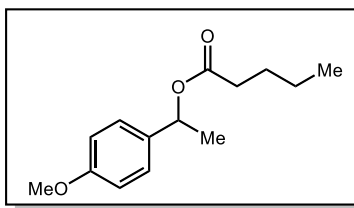
4-(1-(4-Methoxyphenyl)ethoxy)-2-methylbutan-2-ol (40)

Prepared according to general procedure C using 1-ethyl-4-methoxybenzene (81.4 mg, 0.598 mmol), 3-methyl-1,3-butanediol (127 mg, 1.22 mmol), [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)]PF₆ (6.90 mg, 0.006 mmol), K₂HPO₄ (312 mg, 1.80 mmol), and Cu(TFA)₂(MeCN) (238 mg 0.720 mmol). The crude material was purified by flash column chromatography (50% Et₂O/Pentane). (13 h)

Experiment 1: 87.5 mg of a clear oil (61%, 0.367 mmol)

Experiment 2: 88.9 mg of a clear oil (62%, 0.373 mmol)

¹H NMR (500 MHz, CDCl₃) δ 7.23 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 4.35 (q, *J* = 6.4 Hz, 1H), 3.80 (s, 3H), 3.51 (t, *J* = 5.9 Hz, 2H), 1.72 (qt, *J* = 14.5, 5.8 Hz, 2H), 1.43 (d, *J* = 6.5 Hz, 3H), 1.23 (s, 3H), 1.16 (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 159.1, 135.1, 127.4, 113.8, 78.3, 70.6, 65.8, 55.2, 41.4, 29.3, 29.2, 23.9; **HRMS** (ESI) [M+Na]⁺ calculated for [C₁₄H₂₂O₃] requires *m/z* 261.1461, found *m/z* 261.1458; **IR** (thin film): ν 3436, 2970, 2931, 2870, 2837, 1511, 1243, 1172, 1091, 1035, 831.



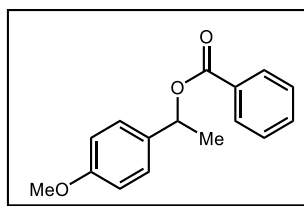
1-(4-Methoxyphenyl)ethyl pentanoate (41)

Prepared according to general procedure C using 1-ethyl-4-methoxybenzene (82.0 mg, 0.600 mmol), pentanoic acid (123 mg, 1.20 mmol), [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)]PF₆ (6.90 mg, 0.006 mmol), K₂HPO₄ (312 mg, 1.80 mmol), and Cu(TFA)₂(MeCN) (238 mg 0.720 mmol). The crude material was purified by flash column chromatography (5% Et₂O/Pentane). (24 h)

Experiment 1: 71.7 mg of a clear liquid (51%, 0.303 mmol)

Experiment 2: 71.1 mg of a clear liquid (51%, 0.301 mmol)

¹H NMR (500 MHz, CDCl₃) δ 7.29 (d, *J* = 8.66 Hz 2H), 6.87 (d, *J* = 8.70 Hz 2H), 5.86 (q, *J* = 6.60 Hz 1H), 3.80 (s, 3H), 2.30 (td, *J* = 7.45, 2.16 Hz 2H), 1.55-1.64 (m, 2H), 1.51 (d, *J* = 6.58 Hz 3H), 1.33 (sext, *J* = 7.32 Hz 2H), 0.89 (t, *J* = 7.37 Hz 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 173.17, 159.19, 133.94, 127.54, 113.80, 71.71, 55.28, 34.39, 27.03, 22.23, 22.03, 13.72; **IR** (thin film): ν 2959, 2932, 2869, 1729, 1513, 1246, 1169, 1007, 826; **HRMS** (ESI) [M+Na]⁺ calculated for [C₁₄H₂₀O₃] requires *m/z* 259.1305, found *m/z* 259.1301.



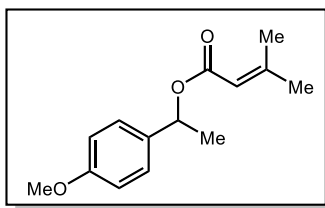
1-(4-Methoxyphenyl)ethyl benzoate (42)

Prepared according to general procedure C using 1-ethyl-4-methoxybenzene (82.0 mg, 0.600 mmol), benzoic acid (147 mg, 1.20 mmol), [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)]PF₆ (6.90 mg, 0.006 mmol), K₂HPO₄ (312 mg, 1.80 mmol), and Cu(TFA)₂(MeCN) (238 mg 0.720 mmol). The crude material was purified by flash column chromatography (5% Et₂O/Pentane). (33 h)

Experiment 1: 81.2 mg of a clear liquid (53%, 0.317 mmol)

Experiment 2: 81.9 mg of a clear liquid (54%, 0.320 mmol)

¹H NMR (500 MHz, CDCl₃) δ 8.06 (dd, *J* = 8.17, 1.42 Hz 2H), 7.51-7.58 (m, 1H), 7.43 (t, *J* = 7.77 Hz 2H), 7.39 (d, *J* = 8.66 Hz 2H), 6.90 (d, *J* = 8.64 Hz 2H), 6.10 (q, *J* = 6.57 Hz 1H), 3.80 (s, 3H), 1.66 (d, *J* = 6.57 Hz 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 165.87, 159.28, 133.86, 132.84, 130.63, 129.62, 128.30, 127.56, 113.88, 72.65, 55.28, 22.18; **IR** (thin film): ν 2977, 2933, 2837, 1712, 1610, 1512, 1244, 1029, 709; **HRMS** (ESI) [M+Na]⁺ calculated for [C₁₆H₁₆O₃] requires *m/z* 279.0992, found *m/z* 279.0988.



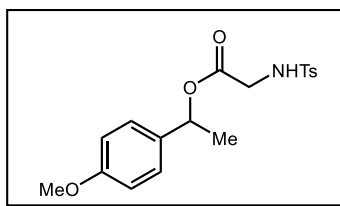
1-(4-Methoxyphenyl)ethyl 3-methylbut-2-enoate (43)

Prepared according to general procedure C using 1-ethyl-4-methoxybenzene (82.0 mg, 0.600 mmol), 3-methyl-2-butenic acid (121 mg, 1.20 mmol), [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)]PF₆ (6.90 mg, 0.006 mmol), K₂HPO₄ (312 mg, 1.80 mmol), and Cu(TFA)₂(MeCN) (238 mg 0.720 mmol). The crude material was purified by flash column chromatography (Gradient 5% to 10% Et₂O/Pentane). (24 h)

Experiment 1: 91.9 mg of a clear liquid (65%, 0.392 mmol)

Experiment 2: 70.2 mg of a clear liquid (50%, 0.300 mmol)

¹H NMR (500 MHz, CDCl₃) δ 7.30 (d, *J* = 8.70 Hz 2H), 6.87 (d, *J* = 8.72 Hz 2H), 5.87 (q, *J* = 6.58 Hz 1H), 5.70 (m, 1H), 3.79 (s, 3H), 2.15 (d, *J* = 1.29 Hz 3H), 1.87 (d, *J* = 1.36 Hz 3H), 1.53 (d, *J* = 6.62 Hz 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 165.96, 159.12, 156.69, 134.30, 127.53, 116.35, 113.81, 70.97, 55.28, 27.42, 22.20, 20.22; **IR** (thin film): ν 2979, 2936, 2838, 1709, 1650, 1513, 1226, 1143, 1034, 1006, 729; **HRMS** (ESI) [M+Na]⁺ calculated for [C₁₄H₁₈O₃] requires *m/z* 257.1148, found *m/z* 257.1149.



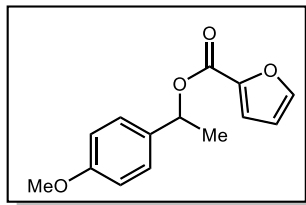
1-(4-Methoxyphenyl)ethyl tosylglycinate (44)

Prepared according to general procedure C using 1-ethyl-4-methoxybenzene (82.0 mg, 0.600 mmol), *N*-(*p*-toluenesulfonyl)glycine (275 mg, 1.20 mmol), [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)]PF₆ (6.90 mg, 0.006 mmol), K₂HPO₄ (312 mg, 1.80 mmol), and Cu(TFA)₂(MeCN) (238 mg 0.720 mmol). The crude material was purified by flash column chromatography (Gradient 50% to 75% Et₂O/Pentane). (34 h)

Experiment 1: 113.8 mg of a pale-yellow oil (52%, 0.313 mmol)

Experiment 2: 102.9 mg of a pale-yellow oil (47%, 0.283 mmol)

¹H NMR (500 MHz, CDCl₃) δ 7.71 (d, *J* = 8.35 Hz 2H), 7.25 (d, *J* = 8.82 Hz 2H), 7.19 (d, *J* = 8.70 Hz 2H), 6.86 (d, *J* = 8.73 Hz 2H), 5.76 (q, *J* = 6.60 Hz 1H), 4.98 (t, *J* = 5.49 Hz 1H), 3.80 (s, 3H), 3.80 (dd, *J* = 17.78, 5.65 Hz 1H), 3.71 (dd, *J* = 17.80, 5.31 Hz 1H), 2.40 (s, 3H), 1.45 (d, *J* = 6.58 Hz 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 168.12, 159.59, 143.78, 136.09, 132.39, 129.75, 127.69, 127.24, 113.91, 74.10, 55.30, 44.37, 21.63, 21.54; **IR** (thin film): ν 3282, 2978, 2931, 2840, 1737, 1608, 1513, 1449, 1331, 1298, 1157, 1117, 1095, 1058, 1029, 816; **HRMS** (ESI) [M+NH₄]⁺ calculated for [C₁₈H₂₁NO₅S] requires *m/z* 381.1479, found *m/z* 381.1471.



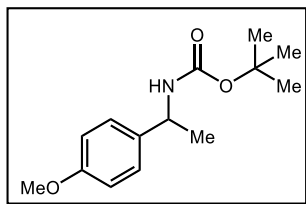
1-(4-Methoxyphenyl)ethyl furan-2-carboxylate (45)

Prepared according to general procedure C using 1-ethyl-4-methoxybenzene (81.7 mg, 0.600 mmol), 2-furoic acid (136mg, 1.21 mmol), [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)]PF₆ (6.90 mg, 0.006 mmol), K₂HPO₄ (312 mg, 1.80 mmol), and Cu(TFA)₂(MeCN) (238 mg 0.720 mmol). The crude material was purified by flash column chromatography (10% Et₂O/Pentane). (24 h)

Experiment 1: 83.9 mg of a clear oil (57%, 0.341 mmol)

Experiment 2: 80.5 mg of a clear oil (54%, 0.327 mmol)

Spectral data were consistent with those reported previously.²⁸



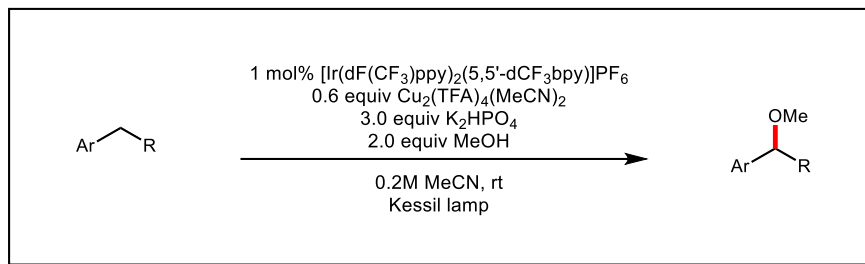
tert-Butyl (1-(4-methoxyphenyl)ethyl)carbamate (46)

Prepared according to general procedure D using 1-ethyl-4-methoxybenzene (82.0 mg, 0.600 mmol), *tert*-butyl carbamate (141 mg, 1.20 mmol), [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)]PF₆ (6.90 mg, 0.006 mmol), K₂HPO₄ (312 mg, 1.80 mmol), and Cu(TFA)₂(MeCN) (238 mg 0.720 mmol). The crude material was purified by iterative flash column chromatography; first condition (20% MTBE/Pentane) and second condition (20% Et₂O/Pentane). (6 h)

Experiment 1: 57.2 mg of a white solid (38%, 0.228 mmol)

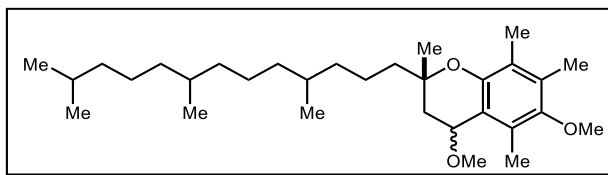
Spectral data were consistent with those reported previously.²⁹

VI. Experimental Procedures and Characterization Data for Table 3



General Procedure E: A dry 20-mL Schlenk tube (1.5 cm diameter) was charged with $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(5,5'\text{-dCF}_3\text{bpy})]\text{PF}_6$ (3.45 mg, 0.003 mmol, 0.01 equiv.), K_2HPO_4 (156 mg, 0.900 mmol, 3 equiv.), $\text{Cu}(\text{TFA})_2(\text{MeCN})$ (119 mg 0.360 mmol, 1.2 equiv.), and MeOH (0.10 mL 2.5 mmol, 8 equiv.). A stock solution containing the alkyl arene (0.3 mmol, 1 equiv.) in 0.9 mL MeCN was then added. An additional 5.1 mL MeCN were added to rinse the wall of the Schlenk tube. The reaction was degassed by three freeze/pump/thaw cycles (4 cycles, 5 min each) under nitrogen in the dark before back filling with nitrogen. The reaction was then allowed to stir while being irradiated by a 40W Kessil Lamp PR160 (427nm). After a pre-determined time point, the reaction was eluted through a short pad of silica using Et_2O . After concentration by rotary evaporation, the pure methoxylated alkyl arene was isolated by flash column chromatography.

General Procedure F: A dry 20-mL Schlenk tube (1.5 cm diameter) was charged with $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(5,5'\text{-dCF}_3\text{bpy})]\text{PF}_6$ (3.45 mg, 0.003 mmol, 0.01 equiv.), K_2HPO_4 (156 mg, 0.900 mmol, 3 equiv.), $\text{Cu}(\text{TFA})_2(\text{MeCN})$ (119 mg 0.360 mmol, 1.2 equiv.), and MeOH (0.10 mL 2.5 mmol, 8 equiv.). A stock solution containing the alkyl arene (0.3 mmol, 1 equiv.) in 0.9 mL DCM was then added. An additional 5.1 mL MeCN were added to rinse the wall of the Schlenk tube. The reaction was degassed by three freeze/pump/thaw cycles (4 cycles, 5 min each) under nitrogen in the dark before back filling with nitrogen. The reaction was then allowed to stir while being irradiated by a 40W Kessil Lamp PR160 (427nm). After a pre-determined time point, the reaction was eluted through a short pad of silica using Et_2O . After concentration by rotary evaporation, the pure methoxylated alkyl arene was isolated by flash column chromatography.



4,6-Dimethoxy-2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)chromane (50)

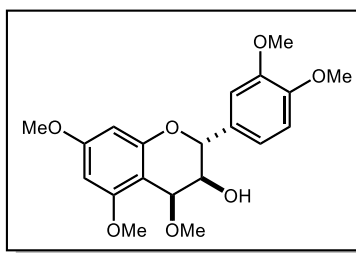
Prepared according to general procedure F using 6-methoxy-2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)chromane (134 mg, 0.300 mmol), MeOH (0.10 mL, 2.5 mmol), [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)]PF₆ (3.45 mg, 0.003 mmol), K₂HPO₄ (156 mg, 0.900 mmol), and Cu(TFA)₂(MeCN) (119 mg 0.360 mmol). The crude material was purified by flash column chromatography (Gradient 2.5% to 5% Et₂O/Pentane). (10 d)

Experiment 1: 43.0 mg of a clear oil (30%, 0.0906 mmol) 1:1 d.r.

Experiment 2: 45.6 mg of a clear oil (32%, 0.0961 mmol) 1:1 d.r.

Major: ¹H NMR (500 MHz, CDCl₃) δ 4.28 (dd, *J* = 5.02, 2.53 Hz 1H), 3.63 (s, 3H), 3.40 (s, 3H), 2.24 (s, 3H), 2.18 (s, 3H), 2.17-2.20 (m, 1H), 2.08 (s, 3H), 1.79 (dd, *J* = 14.57, 4.96 Hz 1H), 1.57-1.66 (m, 2H), 1.44-1.54 (m, 2H), 1.19-1.45 (m, 14H), 1.01-1.18 (m, 6H), 0.87 (d, *J* = 6.61 Hz 9H), 0.85 (d, *J* = 6.74 Hz 3H); ¹³C NMR (126 MHz, CDCl₃) δ 149.85, 147.67, 130.55, 127.68, 123.25, 117.78, 74.74, 71.41, 60.32, 55.07, 42.96, 42.95, 39.38, 37.56, 37.46, 37.43, 37.41, 37.40, 37.38, 37.34, 37.30, 34.26, 34.22, 32.81, 32.79, 32.69, 32.67, 27.99, 24.83, 24.81, 24.46, 24.45, 23.25, 23.23, 22.73, 22.64, 20.91, 20.89, 19.76, 19.71, 19.69, 19.68, 19.64, 19.61, 12.77, 11.90, 11.41; **IR** (thin film): ν 2924, 2864, 1456, 1405, 1375, 1253, 1085, 1015, 735; **HRMS** (ESI) [M+Na]⁺ calculated for [C₃₁H₅₄O₃] requires *m/z* 497.3965, found *m/z* 497.3959.

Minor: ¹H NMR (500 MHz, CDCl₃) δ 4.28 (dd, *J* = 5.02, 2.53 Hz 1H), 3.63 (s, 3H), 3.40 (s, 3H), 2.24 (s, 3H), 2.18 (s, 3H), 2.17-2.20 (m, 1H), 2.08 (s, 3H), 1.79 (dd, *J* = 14.57, 4.96 Hz 1H), 1.57-1.66 (m, 2H), 1.44-1.54 (m, 2H), 1.19-1.45 (m, 14H), 1.01-1.18 (m, 6H), 0.87 (d, *J* = 6.61 Hz 9H), 0.85 (d, *J* = 6.74 Hz 3H); ¹³C NMR (126 MHz, CDCl₃) δ 149.85, 147.67, 130.55, 127.68, 123.25, 117.78, 74.74, 71.41, 60.32, 55.07, 42.96, 42.95, 39.38, 37.56, 37.46, 37.43, 37.41, 37.40, 37.38, 37.34, 37.30, 34.26, 34.22, 32.81, 32.79, 32.69, 32.67, 27.99, 24.83, 24.81, 24.46, 24.45, 23.25, 23.23, 22.73, 22.64, 20.91, 20.89, 19.76, 19.71, 19.69, 19.68, 19.64, 19.61, 12.77, 11.90, 11.41; **IR** (thin film): ν 2924, 2864, 1456, 1405, 1375, 1253, 1085, 1015, 735; **HRMS** (ESI) [M+Na]⁺ calculated for [C₃₁H₅₄O₃] requires *m/z* 497.3965, found *m/z* 497.3959.



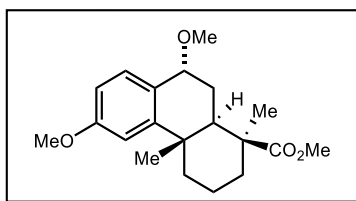
(2R,3S,4S)-2-(3,4-Dimethoxyphenyl)-4,5,7-trimethoxychroman-3-ol (51)

Prepared according to general procedure E using (2R,3S)-2-(3,4-dimethoxyphenyl)-5,7-dimethoxychroman-3-ol (104 mg, 0.300 mmol), MeOH (0.10 mL, 2.5 mmol), [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)]PF₆ (3.45 mg, 0.003 mmol), K₂HPO₄ (156 mg, 0.900 mmol), and Cu(TFA)₂(MeCN) (119 mg 0.360 mmol). The crude material was purified by flash column chromatography (Gradient 60% Et₂O/Pentane to Et₂O). (3 h)

Experiment 1: 58.9 mg of a white solid (52%, 0.157 mmol)

Experiment 2: 54.6 mg of a white solid (48%, 0.145 mmol)

¹H NMR (500 MHz, CDCl₃) δ 7.05 (dd, *J* = 8.22, 2.00 Hz 1H), 6.99 (d, *J* = 1.99 Hz 1H), 6.91 (d, *J* = 8.24 Hz 1H), 6.11 (d, *J* = 2.40 Hz 1H), 6.10 (d, *J* = 2.31 Hz 1H), 4.97 (d, *J* = 10.38 Hz 1H), 4.70 (d, *J* = 3.57 Hz 1H), 3.95 (ddd, *J* = 10.34, 9.36, 3.61 Hz 1H), 3.90 (s, 3H), 3.89 (s, 3H), 3.84 (s, 3H), 3.76 (s, 3H), 3.58 (s, 3H), 2.44 (d, *J* = 9.39 Hz 1H); **¹³C NMR** (101 MHz, acetone-*d*₆) δ 161.79, 159.74, 156.05, 149.44, 149.18, 131.99, 120.74, 111.98, 111.40, 103.67, 93.00, 91.10, 77.03, 70.81, 70.79, 58.09, 55.24, 55.23, 55.09, 54.72; **IR** (thin film): ν 3501, 2937, 2835, 1704, 1602, 1511, 1455, 1340, 1259, 1203, 1136, 1067, 1023, 812; **HRMS** (ESI) [M+H]⁺ calculated for [C₂₀H₂₄O₇] requires *m/z* 345.1333, found *m/z* 345.1331; m.p = 133–135 °C.



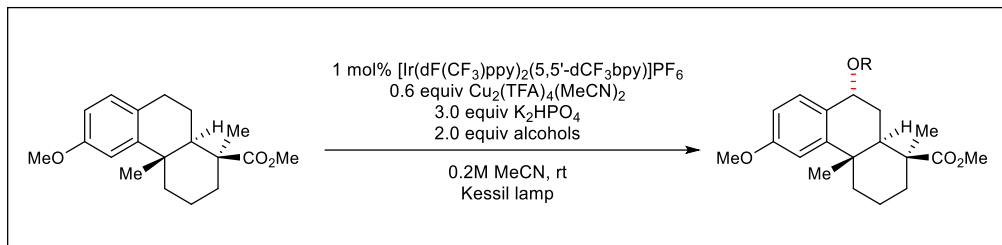
Methyl (1S,4aS,9R,10aR)-6,9-dimethoxy-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (52)

Prepared according to general procedure E using methyl (1S,4aS,10aR)-6-methoxy-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (94.0 mg, 0.300 mmol), MeOH (0.10 mL, 2.5 mmol), [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)]PF₆ (3.45 mg, 0.00300 mmol), K₂HPO₄ (156 mg, 0.900 mmol), and Cu(TFA)₂(MeCN) (119 mg 0.360 mmol). The crude material was purified by flash column chromatography (20% Et₂O/Pentane). (1 hr and 30 min)

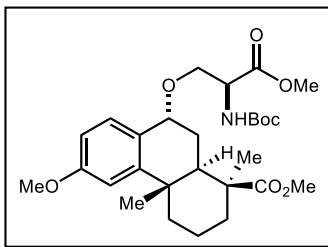
Experiment 1: 71.6 mg of a clear oil (72%, 0.215 mmol)

Experiment 2: 74.6 mg of a clear oil (75%, 0.224 mmol)

¹H NMR (500 MHz, CDCl₃) δ 7.18 (d, *J* = 8.44 Hz 1H), 6.79 (d, *J* = 2.56 Hz 1H), 6.74 (dd, *J* = 8.40, 2.58 Hz 1H), 4.23 (d, *J* = 2.83 Hz 1H), 3.77 (s, 3H), 3.67 (s, 3H), 3.45 (s, 3H), 2.47–2.55 (m, 1H), 2.25–2.31 (m, 1H), 2.15–2.23 (m, 1H), 1.91–2.02 (m, 3H), 1.63 (dtd, *J* = 14.21, 4.49, 4.34, 2.21 Hz, 1H), 1.44 (td, *J* = 13.33, 4.10 Hz, 1H), 1.29 (s, 3H), 1.14 (td, *J* = 13.61, 4.27 Hz 1H), 0.98 (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 178.03, 159.46, 150.01, 132.13, 127.09, 111.52, 110.72, 77.14, 56.24, 55.23, 51.32, 45.50, 43.62, 38.82, 38.80, 37.34, 28.33, 24.56, 21.83, 19.91.; **IR** (thin film): ν 2943, 1724, 1609, 1497, 1462, 1270, 1223, 1144, 1076; **HRMS** (ESI) [M+Na]⁺ calculated for [C₂₀H₂₈O₄] requires *m/z* 355.1880, found *m/z* 355.1874.



General Procedure G: A dry 20 mL Schlenk tube (1.5 cm diameter) was charged with $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(5,5'\text{-dCF}_3\text{bpy})][\text{PF}_6]$ (3.45 mg, 0.00300 mmol, 0.01 equiv.), K_2HPO_4 (156 mg, 0.900 mmol, 3 equiv.), $\text{Cu}(\text{TFA})_2(\text{MeCN})$ (119 mg 0.360 mmol, 1.2 equiv.), methyl (1S,4aS,10aR)-6-methoxy-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (94.0 mg, 0.300 mmol, 1 equiv.) and alcohol (0.6 mmol, 2 equiv.). 1.5 mL MeCN were then added to rinse the wall of the Schlenk tube. The reaction was degassed by three freeze/pump/thaw cycles (4 cycles, 5 min each) under nitrogen in the dark before back filling with nitrogen. The reaction was then allowed to stir while being irradiated by a 40W Kessil Lamp PR160 (427nm). After a pre-determined time point, the reaction was eluted through a short pad of silica using Et_2O . After concentration by rotary evaporation, the pure product was isolated by flash column chromatography.



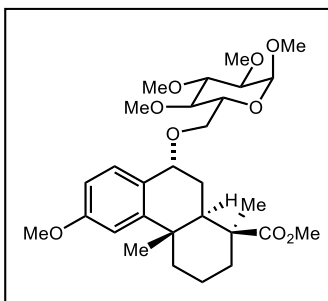
Methyl (1S,4aS,9R,10aR)-9-((S)-2-((tert-butoxycarbonyl)amino)-3-methoxy-3-oxopropoxy)-6-methoxy-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (53)

Prepared according to general procedure G using methyl (1S,4aS,10aR)-6-methoxy-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (94.0 mg, 0.300 mmol), methyl (tert-butoxycarbonyl)-L-serinate (132 mg, 0.600 mmol), $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(5,5'\text{-dCF}_3\text{bpy})]\text{PF}_6$ (3.45 mg, 0.00300 mmol), K_2HPO_4 (156 mg, 0.900 mmol), and $\text{Cu}(\text{TFA})_2(\text{MeCN})$ (119 mg 0.360 mmol). The crude material was purified by flash column chromatography (25% Et_2O /Pentane). (9 h 30 min)

Experiment 1: 106.2 mg of a white solid (68%, 0.204 mmol)

Experiment 2: 103.7 mg of a white solid (67%, 0.200 mmol)

^1H NMR (500 MHz, CDCl_3) δ 7.15 (d, J = 8.42 Hz 1H), 6.79 (d, J = 2.58 Hz 1H), 6.75 (dd, J = 8.42, 2.56 Hz 1H), 5.33 (d, J = 8.92 Hz 1H), 4.48 (dt, J = 9.23, 3.46 Hz 1H), 4.32 (d, J = 2.85 Hz 1H), 4.10 (dd, J = 9.25, 3.35 Hz 1H), 3.79 (s, 3H), 3.77-3.79 (m, 1H), 3.71 (s, 3H), 3.66 (s, 3H), 2.39 (dt, J = 14.77, 1.83 Hz 1H), 2.28 (dd, J = 13.67, 3.48 Hz 1H), 2.15-2.23 (m, 1H), 1.91-2.04 (m, 2H), 1.87 (dd, J = 12.84, 1.45 Hz 1H), 1.60-1.66 (m, 1H), 1.45 (s, 9H), 1.38-1.45 (m, 1H), 1.25 (s, 3H), 1.09 (td, J = 12.86, 3.57 Hz 1H), 0.95 (s, 3H); **^{13}C NMR** (126 MHz, CDCl_3) δ 177.88, 171.23, 159.56, 155.64, 150.09, 132.08, 126.54, 111.62, 110.66, 79.94, 76.26, 68.65, 55.21, 54.10, 52.40, 51.34, 45.62, 43.53, 38.84, 38.67, 37.44, 28.34, 28.24, 25.46, 21.75, 19.85; **IR** (thin film): ν 3443, 2946, 2873, 1715, 1576, 1206, 1160, 1097, 1068, 730; **HRMS** (ESI) $[\text{M}+\text{Na}]^+$ calculated for $[\text{C}_{28}\text{H}_{41}\text{NO}_8]$ requires m/z 542.2724, found m/z 542.2721; m.p = 48–56 °C.



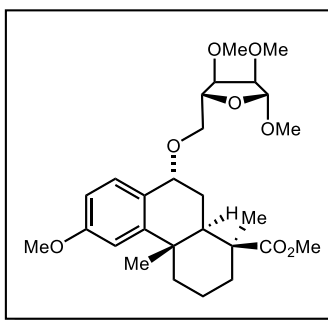
Methyl (1S,4aS,9R,10aR)-6-methoxy-1,4a-dimethyl-9-(((2R,3R,4R,5S,6S)-3,4,5,6-tetramethoxytetrahydro-2H-pyran-2-yl)methoxy)-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (54)

Prepared according to general procedure G using methyl (1S,4aS,10aR)-6-methoxy-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (94.0 mg, 0.300 mmol), ((2R,3R,4S,5R,6S)-3,4,5,6-tetramethoxytetrahydro-2H-pyran-2-yl)methanol (142 mg, 0.600 mmol), [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)]PF₆ (3.45 mg, 0.00300 mmol), K₂HPO₄ (156 mg, 0.900 mmol), and Cu(TFA)₂(MeCN) (119 mg 0.360 mmol). The crude material was purified by flash column chromatography (Gradient 50% to 75% Et₂O/Pentane). (10 h)

Experiment 1: 113.9 mg of a white solid (71%, 0.212 mmol) 20:1 d.r.

Experiment 2: 113.2 mg of a white solid (70%, 0.211 mmol) 20:1 d.r.

¹H NMR (500 MHz, CDCl₃) δ 7.21 (d, *J* = 8.46 Hz 1H), 6.79 (d, *J* = 2.56 Hz 1H), 6.72 (dd, *J* = 8.42, 2.59 Hz 1H), 4.80 (d, *J* = 3.58 Hz 1H), 4.41 (t, *J* = 2.70 Hz 1H), 3.80 (dd, *J* = 10.77, 2.01 Hz 1H), 3.78 (s, 3H), 3.70 (dd, *J* = 10.75, 4.06 Hz 1H), 3.67 (s, 3H), 3.62 (s, 3H), 3.59-3.62 (m, 1H), 3.48-3.53 (m, 1H), 3.51 (s, 3H), 3.50 (s, 3H), 3.40 (s, 3H), 3.18-3.24 (m, 2H), 2.51 (dd, *J* = 13.88, 2.29 Hz 1H), 2.26-2.32 (m, 1H), 2.17-2.19 (m, 1H), 2.06 (d, *J* = 12.81 Hz 1H), 1.93-2.03 (m, 2H), 1.60-1.67 (m, 1H), 1.43 (td, *J* = 13.39, 4.13 Hz 1H), 1.30 (s, 3H), 1.14 (td, *J* = 13.56, 4.17 Hz 1H), 0.97 (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 178.06, 159.44, 150.23, 132.20, 126.84, 111.18, 110.83, 97.39, 83.69, 81.78, 79.47, 76.27, 70.43, 66.75, 60.90, 60.42, 58.96, 55.21, 55.14, 51.31, 45.35, 43.66, 38.86, 38.72, 37.38, 28.36, 25.89, 21.92, 19.91; **IR** (thin film): ν 2937, 2836, 1722, 1609, 1497, 1148, 1095, 1040, 909, 728; **HRMS** (ESI) [M+Na]⁺ calculated for [C₂₉H₄₄O₉] requires *m/z* 559.2878, found *m/z* 559.2868; m.p = 58–67 °C.



Methyl (1S,4aS,9R,10aR)-6-methoxy-1,4a-dimethyl-9-(((2R,3S,4S,5S)-3,4,5-trimethoxytetrahydrofuran-2-yl)methoxy)-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (55)

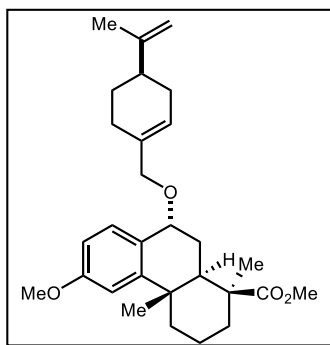
Prepared according to general procedure G using methyl (1S,4aS,10aR)-6-methoxy-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (94.0 mg, 0.300 mmol), ((2R,3R,4R,5R)-3,4,5-trimethoxytetrahydrofuran-2-yl)methanol (116 mg, 0.600 mmol),

[Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)]PF₆ (3.45 mg, 0.00300 mmol), K₂HPO₄ (156 mg, 0.900 mmol), and Cu(TFA)₂(MeCN) (119 mg 0.360 mmol). The crude material was purified by flash column chromatography (50% Et₂O/Pentane). (9 h 30 min)

Experiment 1: 98.2 mg of a white solid (66%, 0.199 mmol)

Experiment 2: 97.6 mg of a white solid (66%, 0.198 mmol)

¹H NMR (500 MHz, CDCl₃) δ 7.25 (d, *J* = 9.48 Hz 1H), 6.79 (d, *J* = 2.58 Hz 1H), 6.74 (dd, *J* = 8.43, 2.59 Hz 1H), 4.93 (d, *J* = 1.52 Hz 1H), 4.46-4.47 (m, 1H), 4.23 (td, *J* = 6.31, 4.36 Hz 1H), 3.84 (dd, *J* = 6.37, 4.72 Hz 1H), 3.78 (s, 3H), 3.75-3.79 (m, 1H), 3.72 (dd, *J* = 4.73, 1.43 Hz 1H), 3.66 (s, 3H), 3.62 (dd, *J* = 10.63, 6.23 Hz 1H), 3.48 (s, 3H), 3.40 (s, 3H), 3.38 (s, 3H), 2.47 (d, *J* = 12.95 Hz 1H), 2.25-2.31 (m, 1H), 2.17-2.20 (m, 1H), 1.92-2.04 (m, 3H), 1.63 (dt, *J* = 14.34, 3.54 Hz 1H), 1.42 (td, *J* = 13.37, 4.12 Hz 1H), 1.28 (s, 3H), 1.12 (td, *J* = 13.60, 4.27 Hz 1H), 0.97 (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 178.03, 159.41, 150.05, 132.22, 126.97, 111.46, 110.64, 105.55, 82.20, 80.92, 80.71, 75.79, 70.21, 58.36, 58.30, 55.21, 55.15, 51.31, 45.59, 43.61, 38.88, 38.75, 37.42, 28.31, 25.68, 21.78, 19.90; **IR** (thin film): ν 2936, 2839, 1724, 1609, 1460, 1271, 1196, 1140, 1106, 1068, 1041; **HRMS** (ESI) [M+Na]⁺ calculated for [C₂₇H₄₀O₈] requires *m/z* 515.2615, found *m/z* 515.2612; m.p = 102–104 °C.



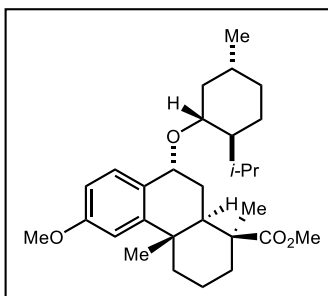
Methyl (1S,4aS,9R,10aR)-6-methoxy-1,4a-dimethyl-9-(((R)-4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)methoxy)-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (56)

Prepared according to general procedure G using methyl (1S,4aS,10aR)-6-methoxy-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (94.0 mg, 0.300 mmol), (R)-4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)methanol (91.3 mg, 0.600 mmol), [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)]PF₆ (3.45 mg, 0.00300 mmol), K₂HPO₄ (156 mg, 0.900 mmol), and Cu(TFA)₂(MeCN) (119 mg 0.360 mmol). The crude material was purified by flash column chromatography (10% Et₂O/Pentane). (10 h)

Experiment 1: 93.9 mg of a clear oil (69%, 0.207 mmol)

Experiment 2: 91.6 mg of a clear oil (67%, 0.202 mmol)

¹H NMR (500 MHz, CDCl₃) δ 7.17 (d, *J* = 8.41 Hz 1H), 6.78 (d, *J* = 2.60 Hz 1H), 6.75 (dd, *J* = 8.44, 2.63 Hz 1H), 5.75-5.79 (m, 1H), 4.71-4.73 (m, 2H), 4.36 (dd, *J* = 2.69, 2.69 Hz 1H), 4.05 (d, *J* = 11.3 Hz 1H), 3.93 (d, *J* = 11.3 Hz 1H), 3.77 (s, 3H), 3.67 (s, 3H), 2.46 (dd, *J* = 13.96, 2.23 Hz 1H), 2.25-2.32 (m, 1H), 2.15-2.21 (m, 5H), 1.91-2.05 (m, 4H), 1.84-1.90 (m, 1H), 1.74 (s, 3H), 1.57-1.66 (m, 1H), 1.41-1.56 (m, 2H), 1.29 (s, 3H), 1.14 (td, *J* = 13.57, 4.23 Hz 1H), 0.97 (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 178.06, 159.35, 150.11, 149.96, 135.03, 132.15, 127.45, 124.76, 111.63, 110.63, 108.63, 74.46, 73.24, 55.23, 51.32, 45.53, 43.68, 41.16, 38.78, 38.76, 37.37, 30.60, 28.39, 27.55, 26.97, 25.20, 21.83, 20.80, 19.93; **IR** (thin film): ν 2933, 1723, 1609, 1497, 1442, 1269, 1222, 1200, 1144, 1040, 730; **HRMS** (ESI) [M+Na]⁺ calculated for [C₂₉H₄₀O₄] requires *m/z* 475.2819, found *m/z* 475.2814.



Methyl (1S,4aS,9R,10aR)-9-(((1S,2R,5S)-2-isopropyl-5-methylcyclohexyl)oxy)-6-methoxy-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (57)

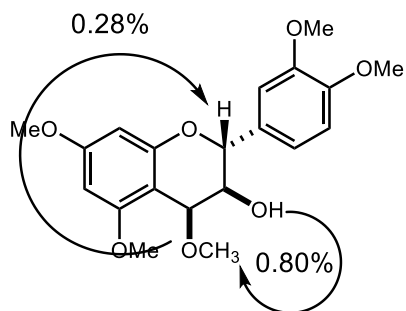
Prepared according to general procedure G using methyl (1S,4aS,10aR)-6-methoxy-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (94.0 mg, 0.300 mmol), (1R,2S,5R)-2-isopropyl-5-methylcyclohexan-1-ol (93.8 mg, 0.600 mmol), [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)]PF₆ (3.45 mg, 0.00300 mmol), K₂HPO₄ (156 mg, 0.900 mmol), and Cu(TFA)₂(MeCN) (119 mg 0.360 mmol). The crude material was purified by flash column chromatography (10% Et₂O/Pentane). (10 h)

Experiment 1: 61.2 mg of a white solid (45%, 0.134 mmol)

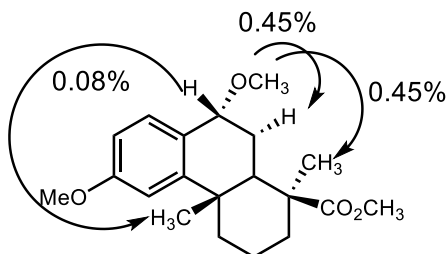
Experiment 2: 63.6 mg of a white solid (46%, 0.139 mmol)

¹H NMR (500 MHz, CDCl₃) δ 7.24 (d, *J* = 8.29 Hz 1H), 6.74-6.80 (m, 2H), 4.50 (dd, *J* = 4.15, 1.70 Hz 1H), 3.77 (s, 3H), 3.66 (s, 3H), 3.31 (td, *J* = 10.28, 4.16 Hz 1H), 2.43-2.47 (m, 1H), 2.39 (ddt, *J* = 14.85, 7.90, 3.93 Hz 1H), 2.24-2.31 (m, 2H), 2.18-2.24 (m, 1H), 2.06 (td, *J* = 14.23, 4.10 Hz 1H), 1.92-2.01 (m, 2H), 1.61-1.70 (m, 3H), 1.46 (td, *J* = 13.62, 4.17 Hz 1H), 1.37-1.43 (m, 1H), 1.27 (s, 3H), 1.20-1.24 (m, 1H), 1.14 (td, *J* = 13.56, 4.21 Hz 1H), 1.02-1.07 (m, 2H), 1.01 (d, *J* = 6.50 Hz 3H), 0.96 (s, 3H), 0.88-0.91 (m, 1H), 0.86 (d, *J* = 7.02 Hz 3H), 0.79 (d, *J* = 6.87 Hz 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 178.08, 159.08, 149.88, 132.11, 127.61, 112.14, 110.22, 76.51, 70.70, 55.24, 51.30, 47.98, 45.86, 43.99, 41.98, 38.80, 38.37, 37.63, 34.49, 31.71, 28.43, 27.01, 24.48, 23.07, 22.60, 21.88, 21.38, 19.88, 16.55; **IR** (thin film): ν 2926, 2864, 1724, 1610, 1499, 1455, 1269, 1143, 1041; **HRMS** (ESI) [M+Na]⁺ calculated for [C₂₉H₄₄O₄] requires *m/z* 479.3132, found *m/z* 479.3126; *m.p* = 62–68 °C.

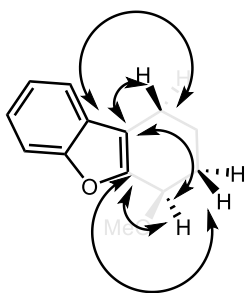
VII. Stereochemical Assignment of Major Diastereomers by 1D NOESY Experiments and Regiochemistry Assignment of Major Regioisomers by HMBC



Major isomer (**51**)

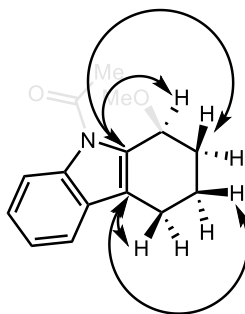


Major isomer (**52**)



Major isomer (**23**)

HMBC data



Major isomer (**25**)

HMBC data

VIII. Stern-Volmer Experiments

Stern-Volmer experiments tracking the quenching of the phosphorescence of $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(5,5'\text{-dCF}_3\text{bpy})]\text{PF}_6$ (**Ir**) and $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{bpy})]\text{PF}_6$ (**Ir-2**) were conducted on an ISS PC1 Spectrofluorimeter. Rigorously degassed (N_2) stock solutions of each component were prepared prior to each set of experiments. The solutions were irradiated at 400 nm and luminescence was measured at 580 nm. Because $\text{Cu}(\text{TFA})_2(\text{MeCN})$ absorbs at 400 nm and 580 nm, **I** for Experiment 2 was normalized for an inner filter effect as described by Albinsson.³⁰ The solutions were loaded into quartz cuvettes and sealed under inert atmosphere using a rubber septum. The concentration of photocatalyst **Ir** was 2.6×10^{-5} M. The concentration of photocatalyst **Ir-2** was 2.3×10^{-5} M.

Experiment 1: Constant Iridium; Varied 1-ethyl-4-methoxybenzene

Species	Concentration (M)
$[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(5,5'\text{-dCF}_3\text{bpy})]\text{PF}_6$	2.62E-05
1-ethyl-4-methoxybenzene	Varied

[1-ethyl-4-methoxybenzene] M	I_0/I (1)	I_0/I (2)	I_0/I (3)	I_0/I (average)
0	1.00	1.00	1.00	1.00
0.006	1.18	1.21	1.19	1.19
0.011	1.34	1.39	1.37	1.37
0.016	1.51	1.53	1.51	1.52
0.021	1.71	1.69	1.67	1.69
0.025	1.84	1.81	1.79	1.81

Table S8: Relevant concentrations and tabulated quenching data for Experiment 1.

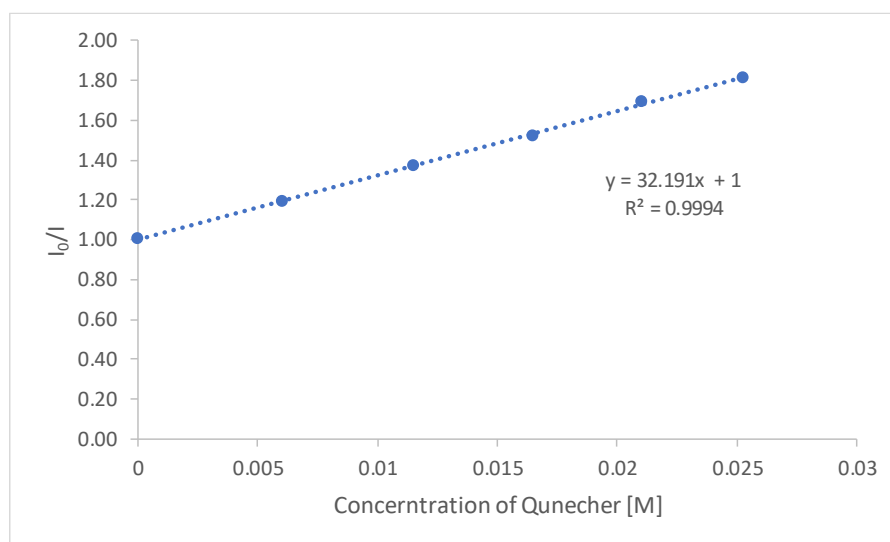
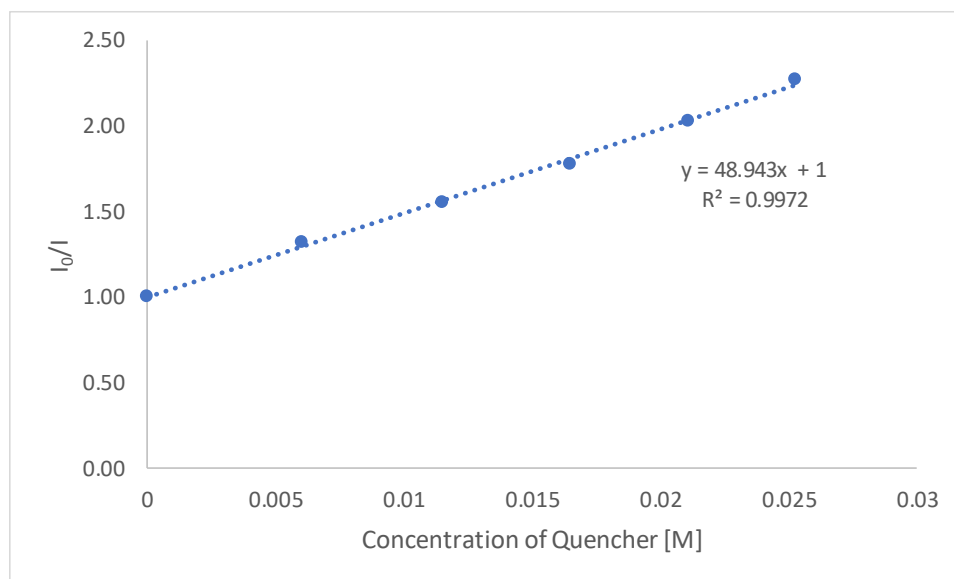


Figure S5: Graphical representation of I_0/I data collected in Experiment 1.

Experiment 2: Constant Iridium; Varied Cu(TFA)₂(MeCN)

Species	Concentration (M)
[Ir(dF(CF ₃)ppy) ₂ (5,5'-dCF ₃ bpy)]PF ₆	2.62E-05
Cu(TFA) ₂ (MeCN)	Varied

[Cu(TFA) ₂ (MeCN)] M	I ₀ /I _{norm} (1)	I ₀ /I _{norm} (2)	I ₀ /I _{norm} (3)	I ₀ /I _{norm} (average)
0	1.00	1.00	1.00	1.00
0.006	1.31	1.33	1.30	1.31
0.011	1.58	1.53	1.54	1.55
0.016	1.83	1.72	1.76	1.77
0.021	2.12	1.96	1.99	2.02
0.025	2.35	2.21	2.25	2.27

Table S9: Relevant concentrations and tabulated quenching data for Experiment 2.**Figure S6:** Graphical representation of I_0/I_{norm} data collected in Experiment 2.

Experiment 3: Constant Iridium; Varied 1-ethyl-4-methoxybenzene

Species	Concentration (M)
[Ir(dF(CF ₃)ppy) ₂ (bpy)]PF ₆	2.28E-05
1-ethyl-4-methoxybenzene	Varied

[1-ethyl-4-methoxybenzene] M	I	I ₀ /I
0	3679695	1.00
0.007	3701293	0.99
0.012	3569884	1.03
0.018	3587482	1.03
0.023	3535815	1.04
0.027	3421606	1.08

Table S10: Relevant concentrations and tabulated quenching data for Experiment 3.

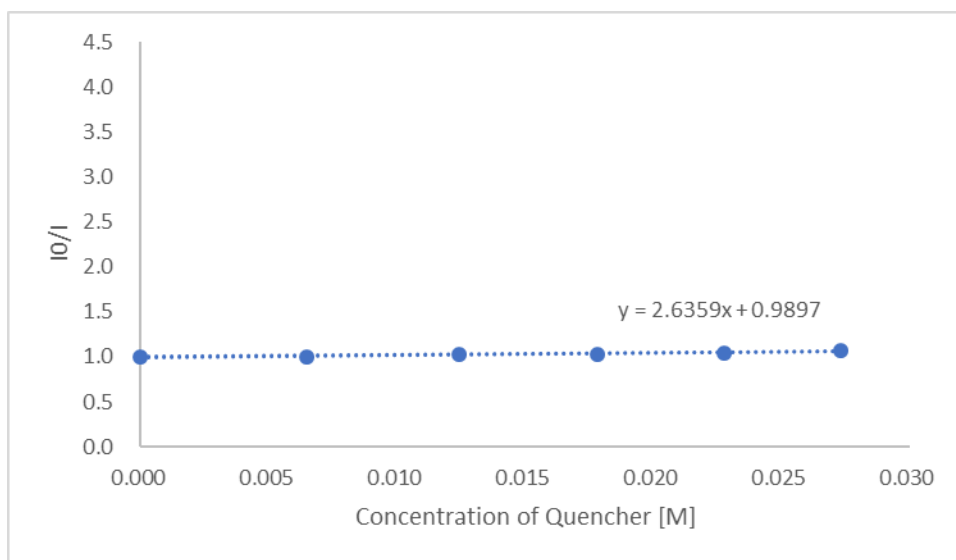


Figure S7: Graphical representation of I_0/I data collected in Experiment 3.

[Cu(TFA) ₂ (MeCN)] M	Absorbance at 400 nm	Absorbance at 580 nm
0	0.00	0.00
0.006	0.022	0.043
0.011	0.044	0.080
0.016	0.064	0.11
0.024	0.12	0.17

Table S11: Relevant concentrations and tabulated absorbance data.

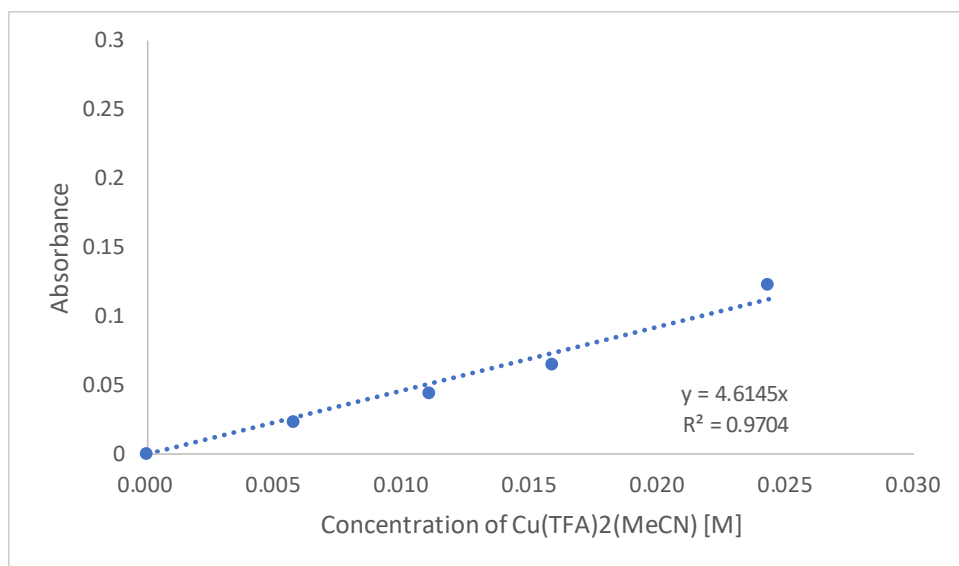


Figure S8: Graphical representation of molar absorptivity of Cu(TFA)₂(MeCN) at 400 nm.

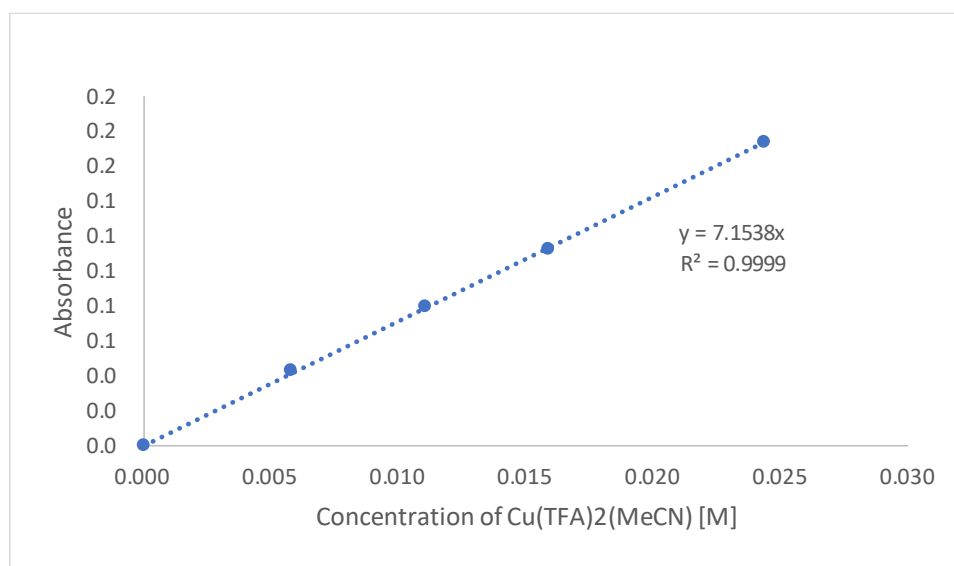


Figure S9: Graphical representation of molar absorptivity of Cu(TFA)₂(MeCN) at 580 nm.

IX. Cyclic Voltammetry Data

Cyclic voltammetry experiments were performed in MeCN with analyte (1 mM) and [(n-Bu)₄N]⁺[PF₆]⁻ (100 mM) using a glassy carbon working electrode, platinum wire counter electrode, a Ag/AgNO₃ MeCN reference electrode, and a scan rate of 50 mV/s. Ferrocene was added as an internal reference to SCE.

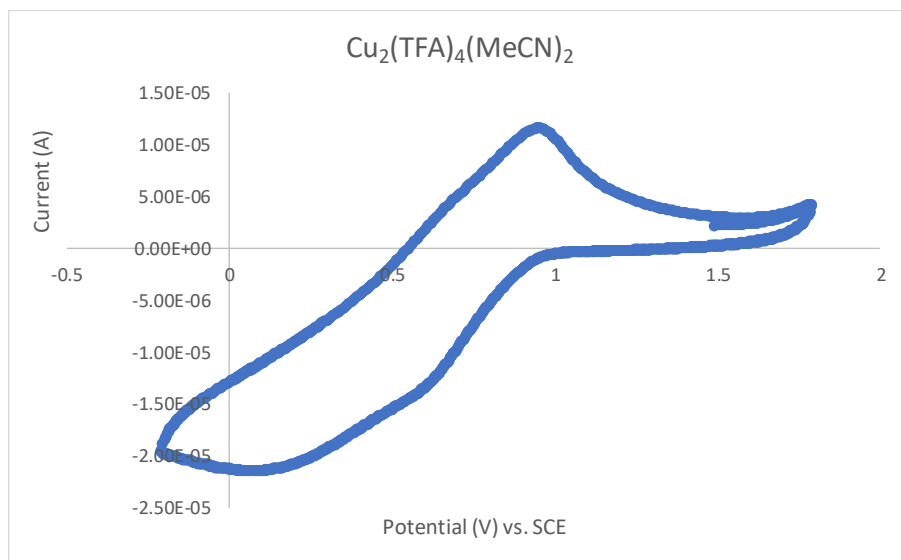


Figure S10: Cyclic voltammograms of $\text{Cu}(\text{TFA})_2(\text{MeCN})$.

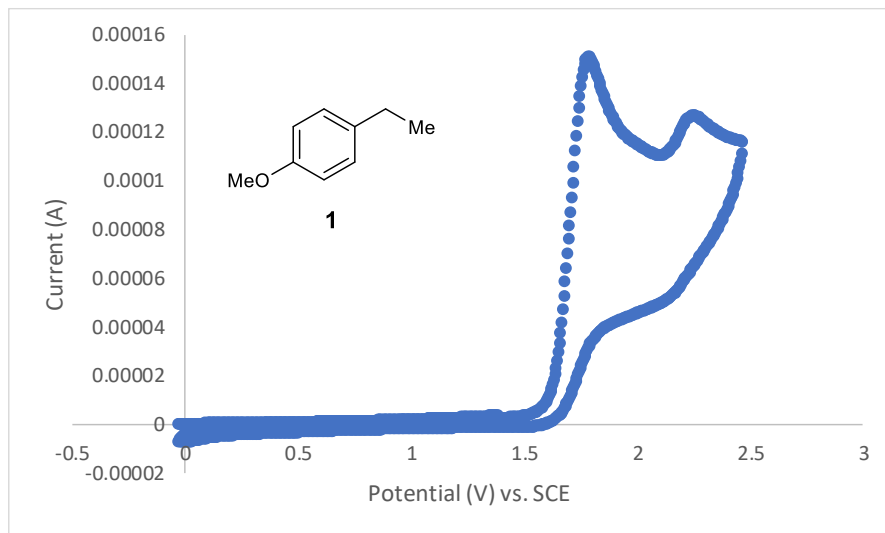
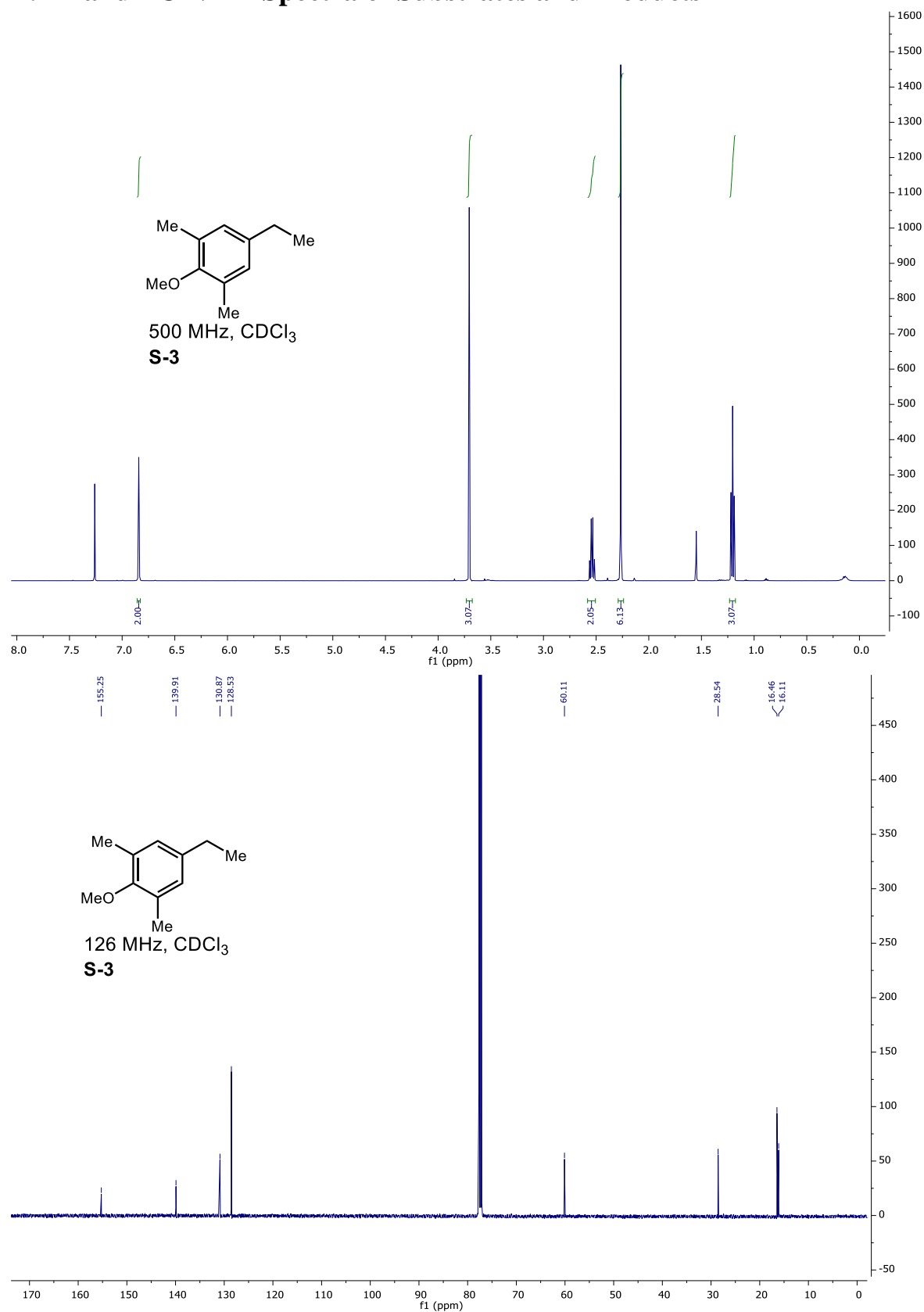


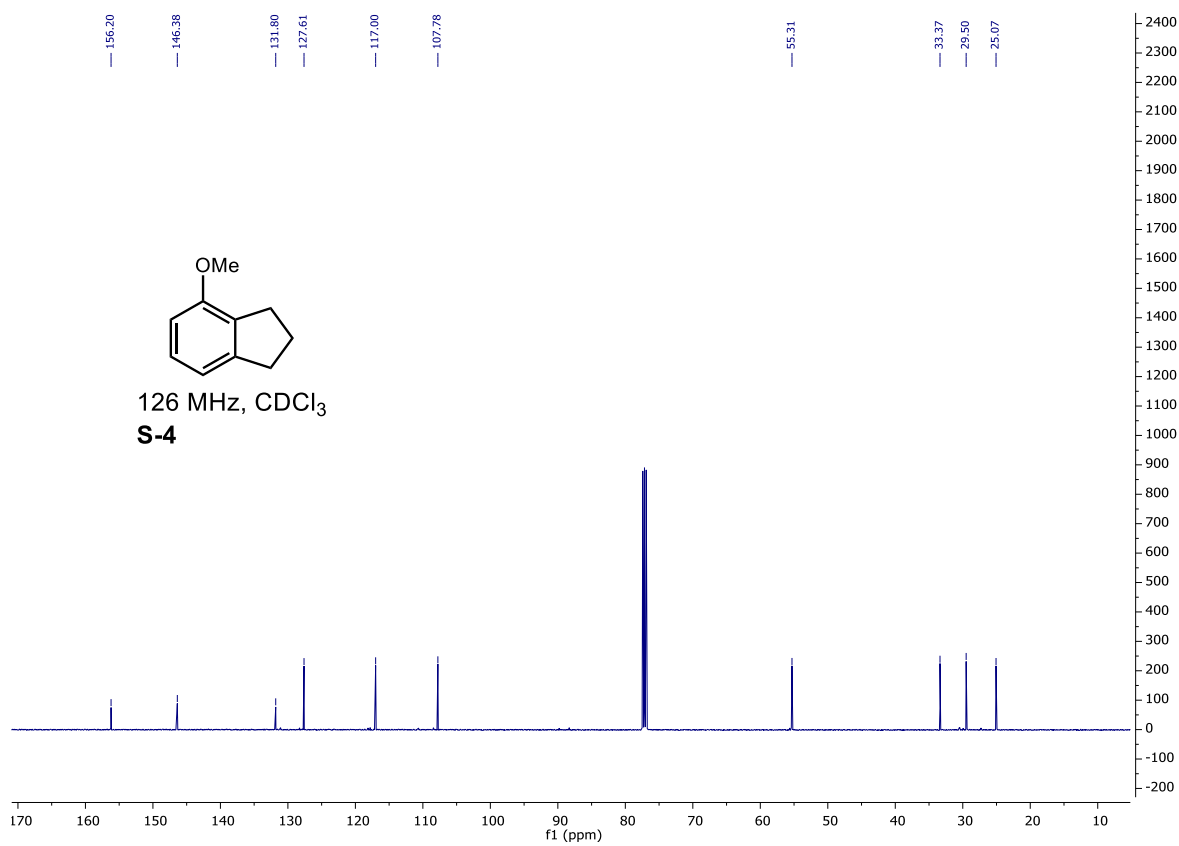
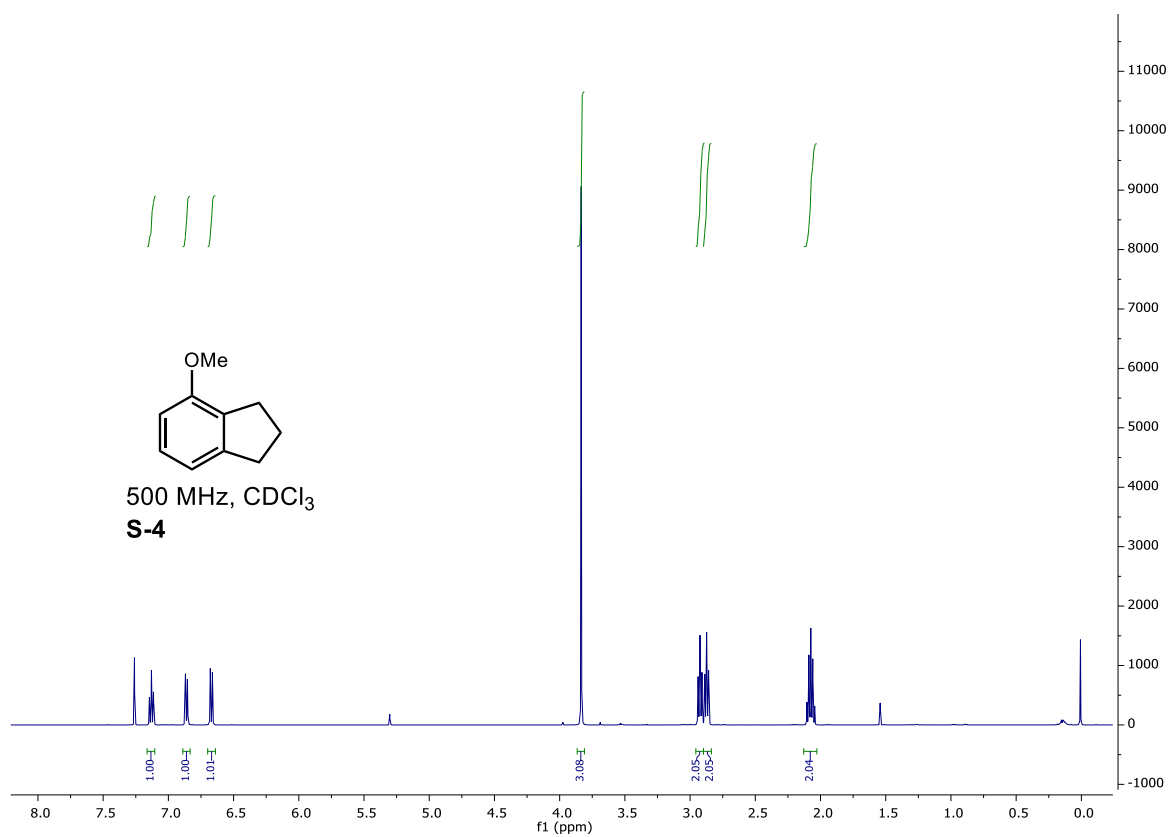
Figure S11: Cyclic voltammograms of 1-ethyl-4-methoxybenzene (**1**).

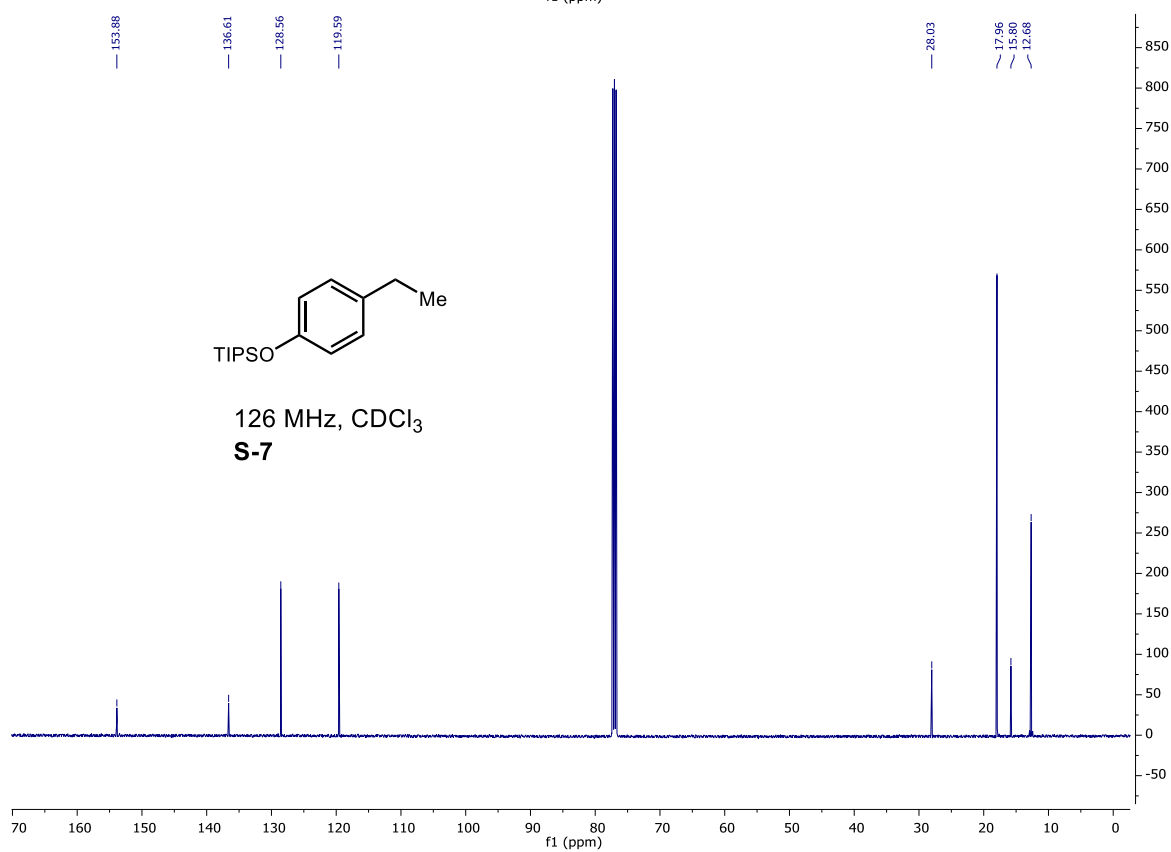
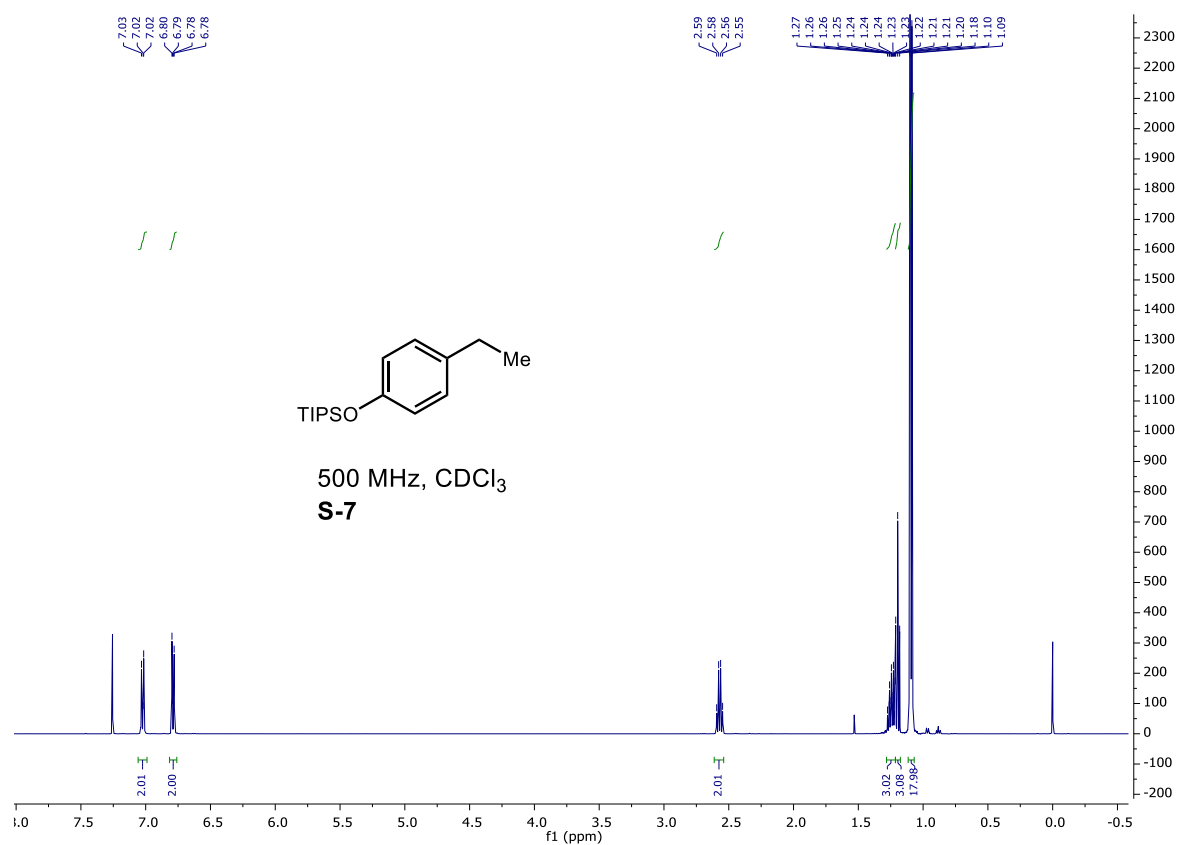
$\text{Cu}(\text{TFA})_2(\text{MeCN})$: $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}+}$ $E_{\text{p}/2} = 0.38$ V vs. SCE in MeCN

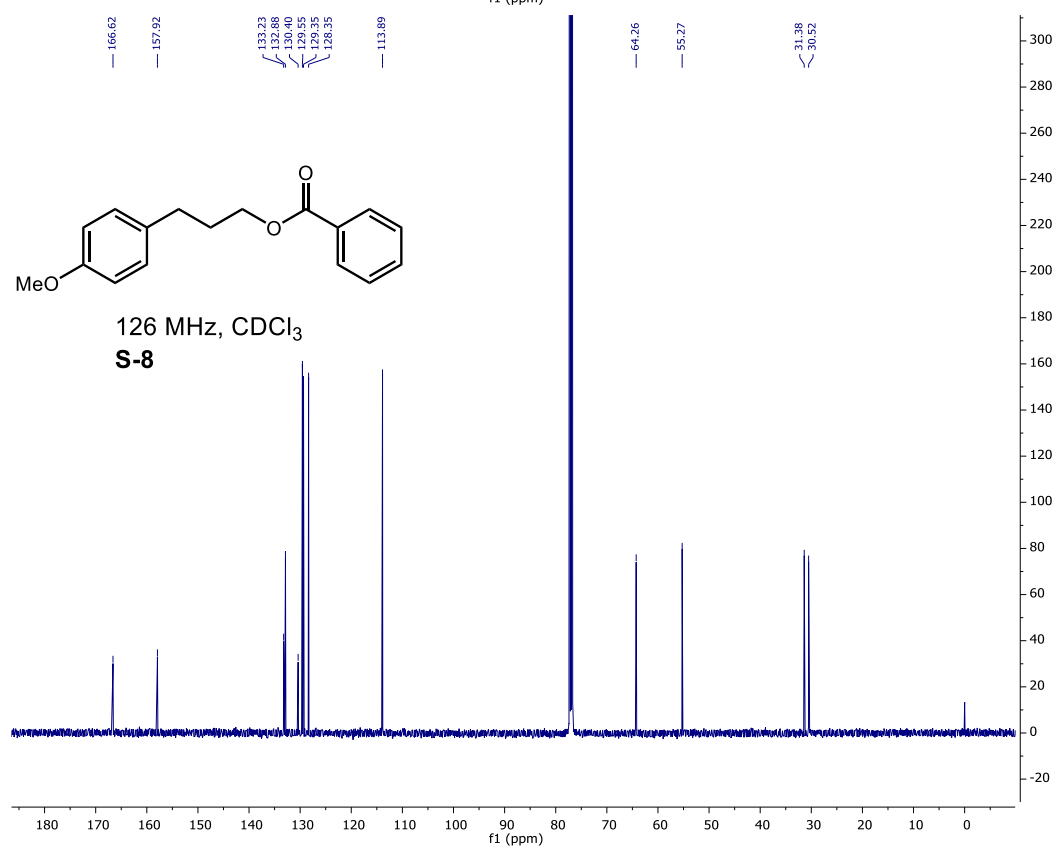
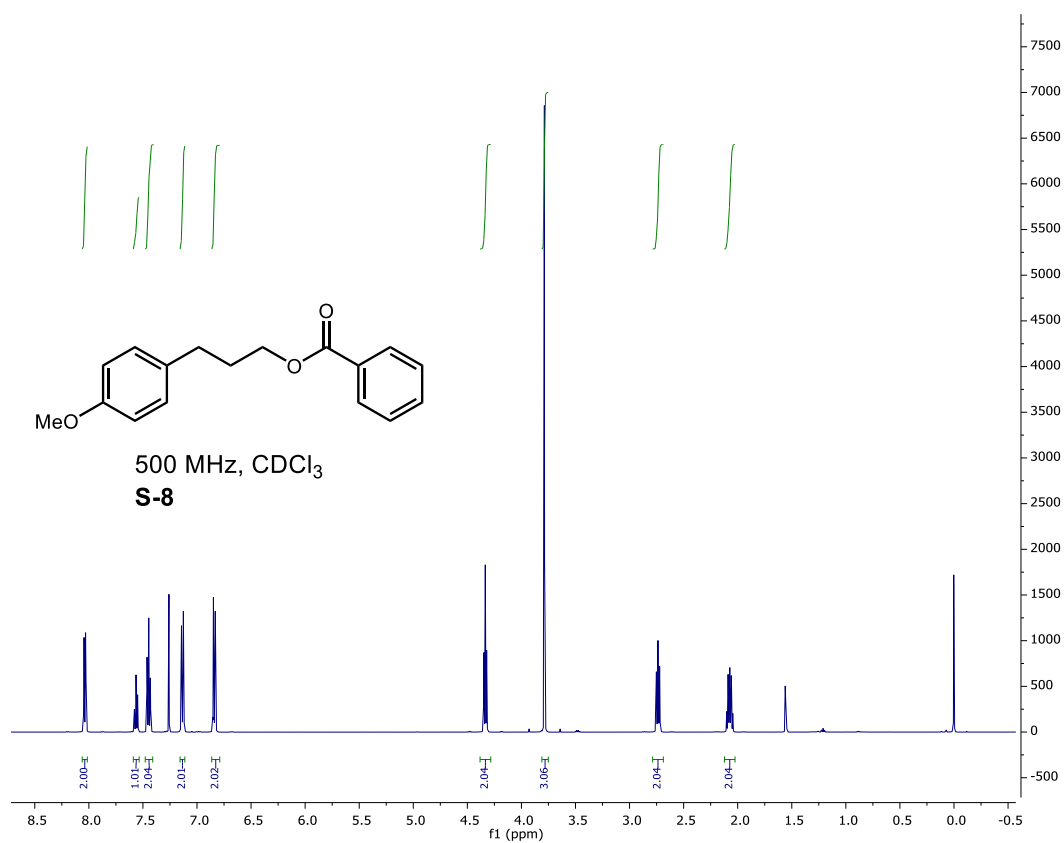
1-ethyl-4-methoxybenzene (1): $1/1^{+}$ $E_{\text{p}/2} = 1.52$ V vs. SCE in MeCN

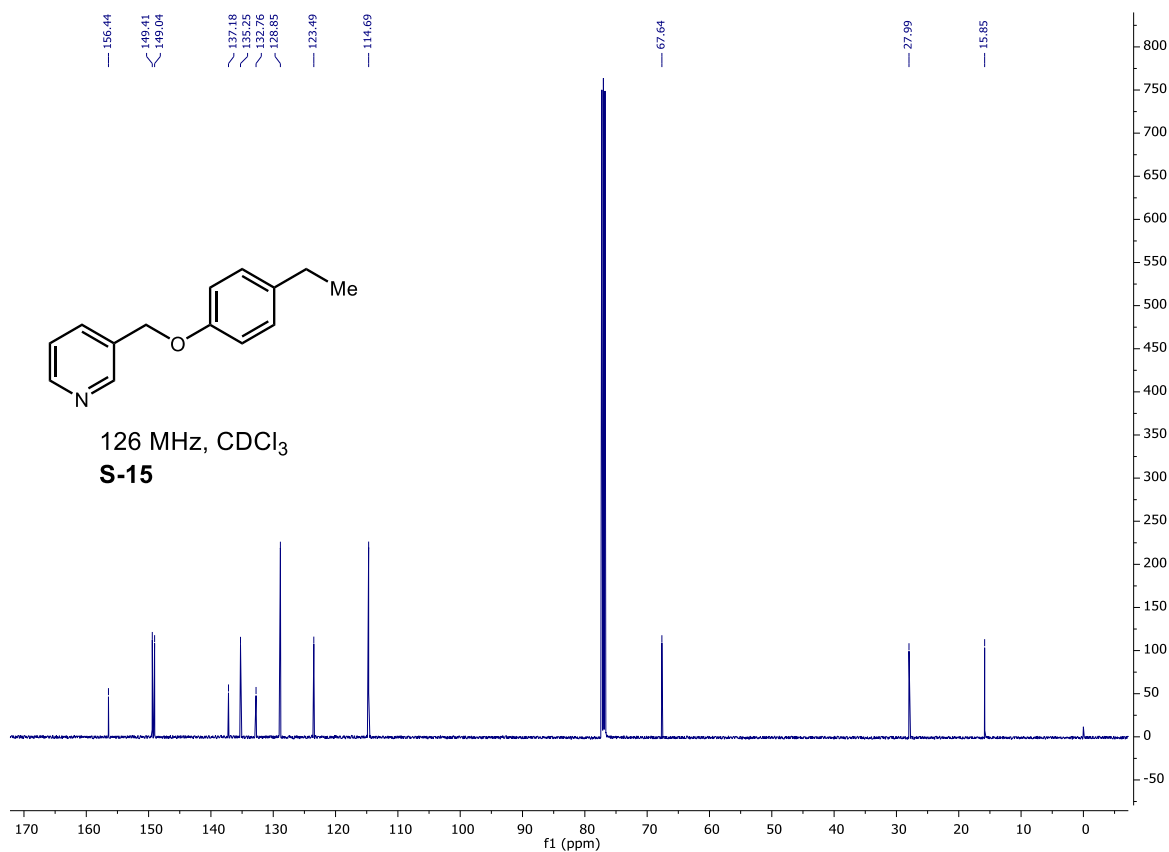
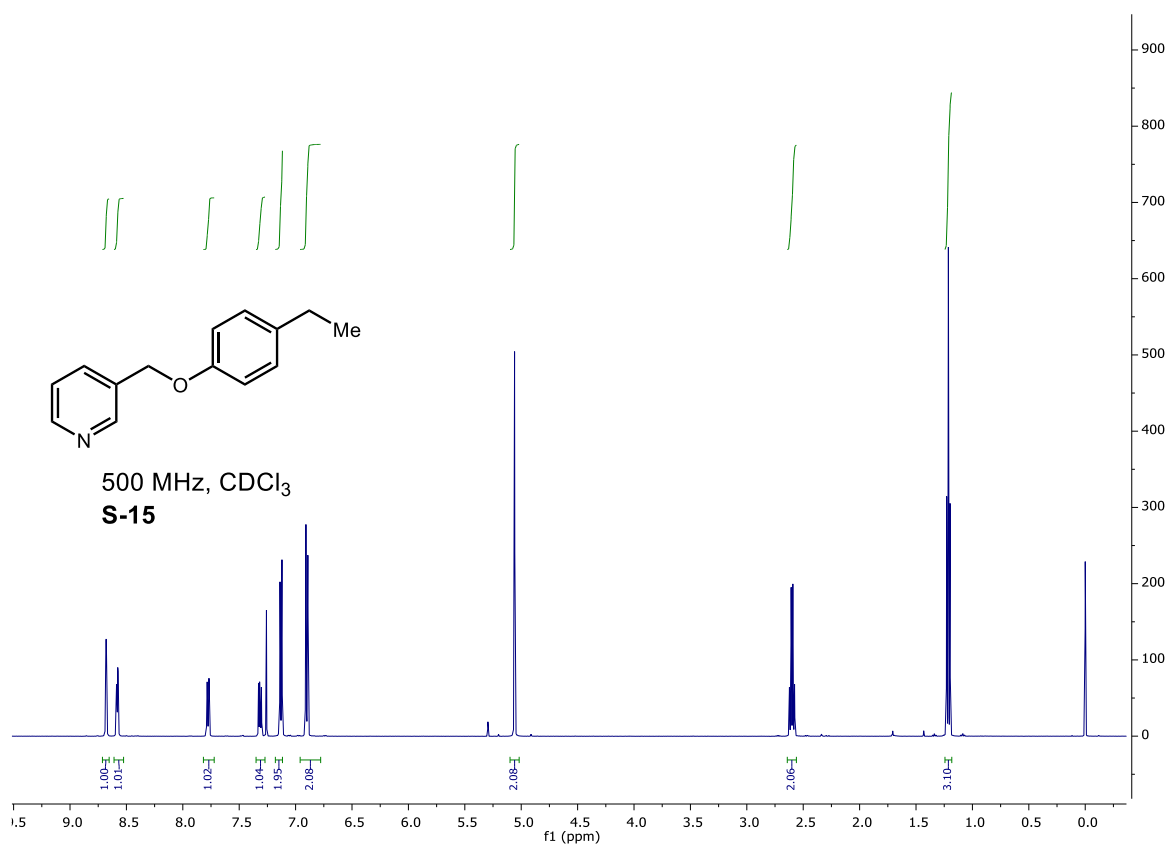
X. ^1H and ^{13}C NMR Spectra of Substrates and Products

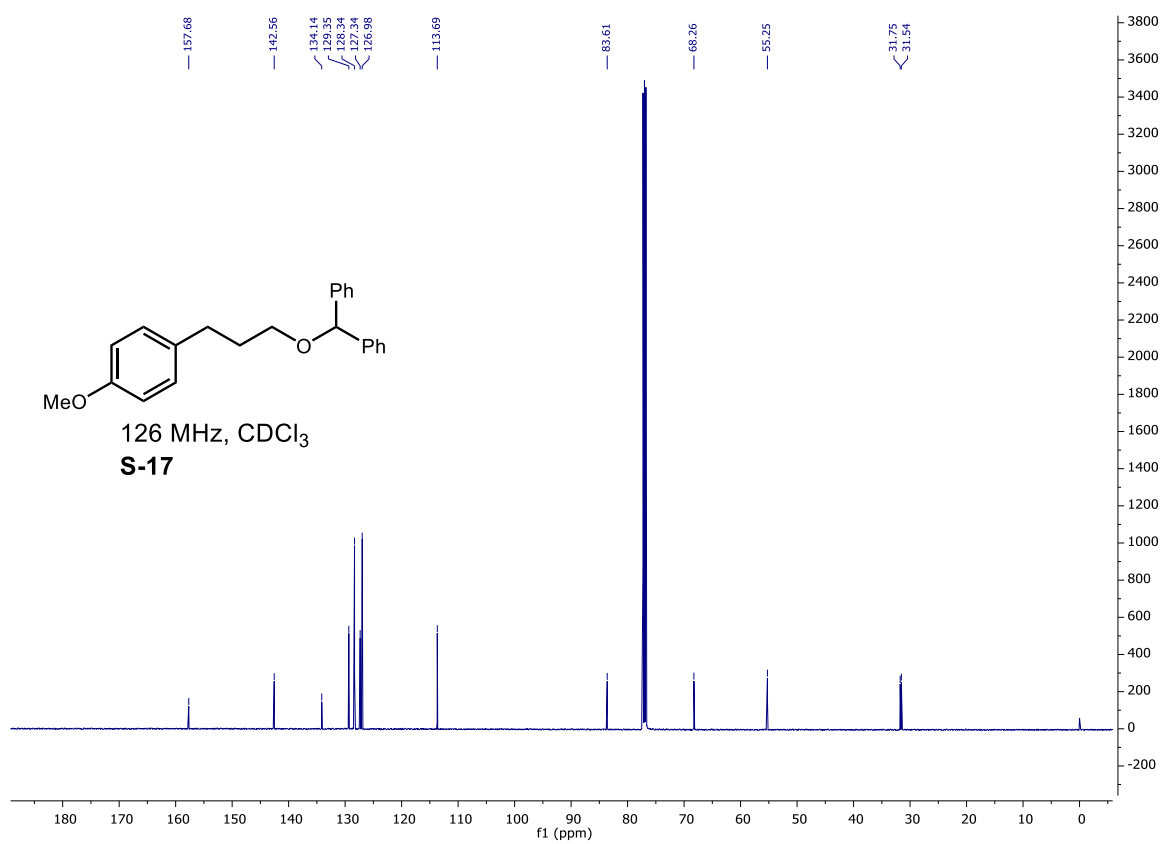
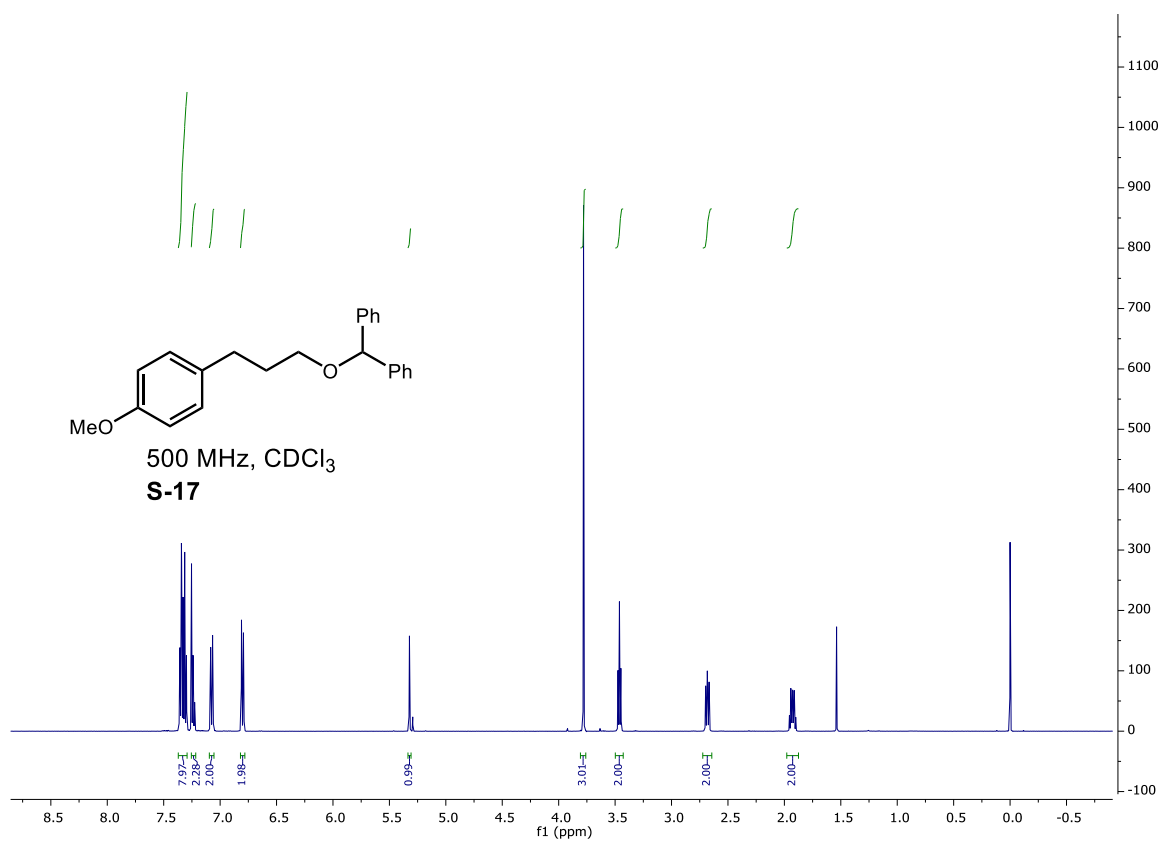


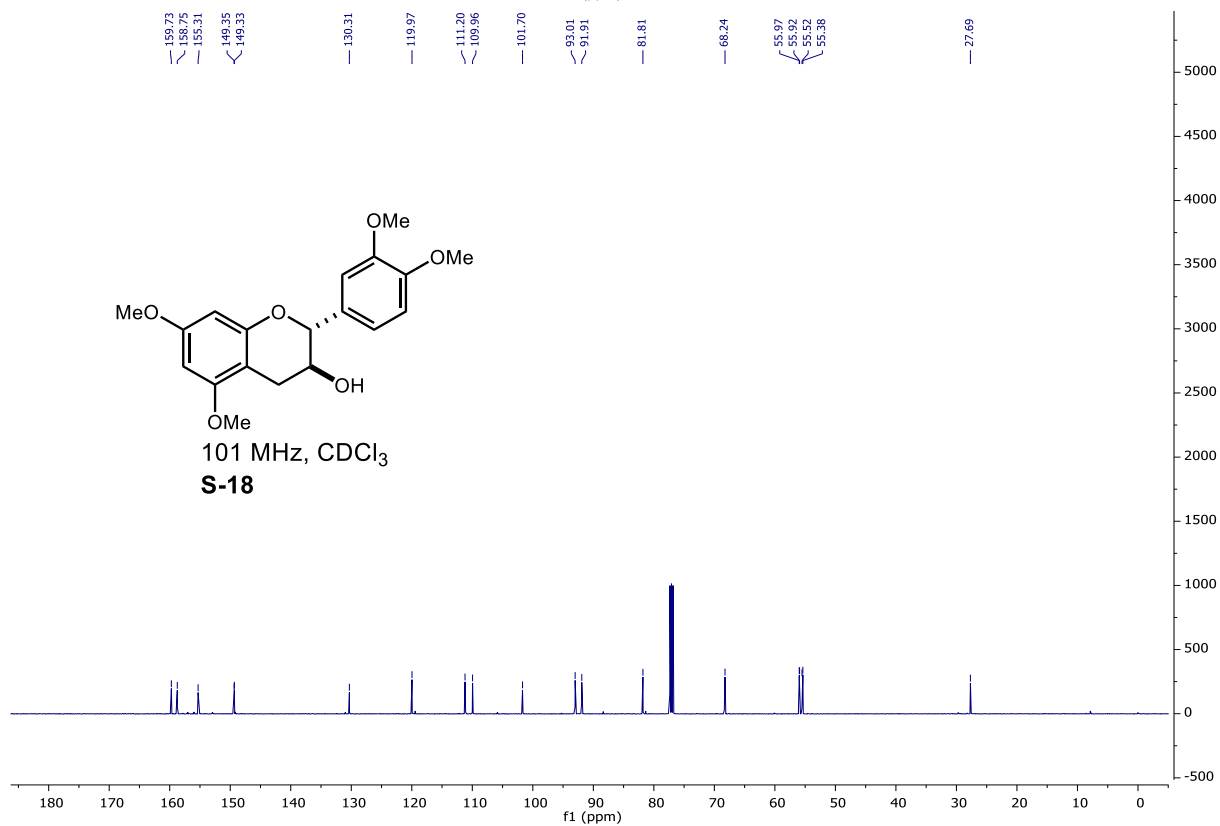
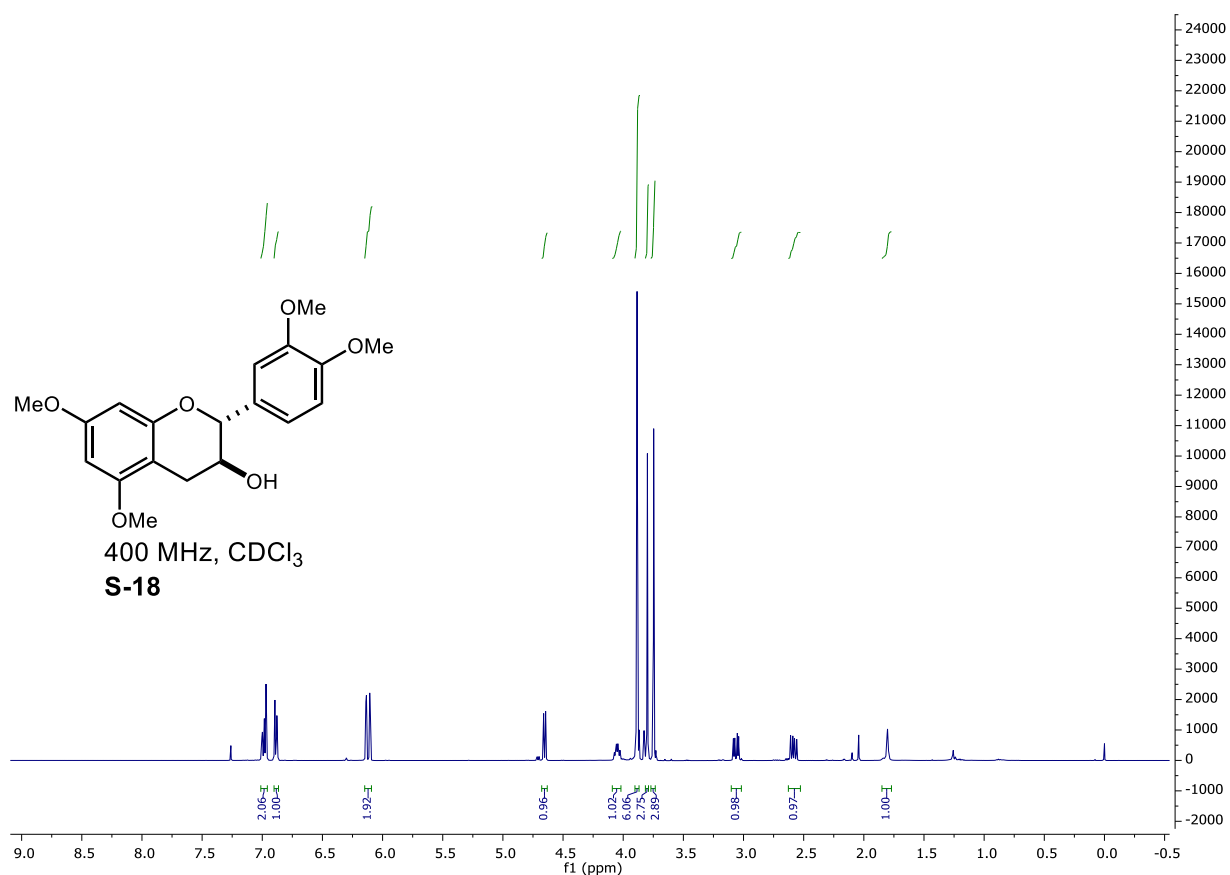


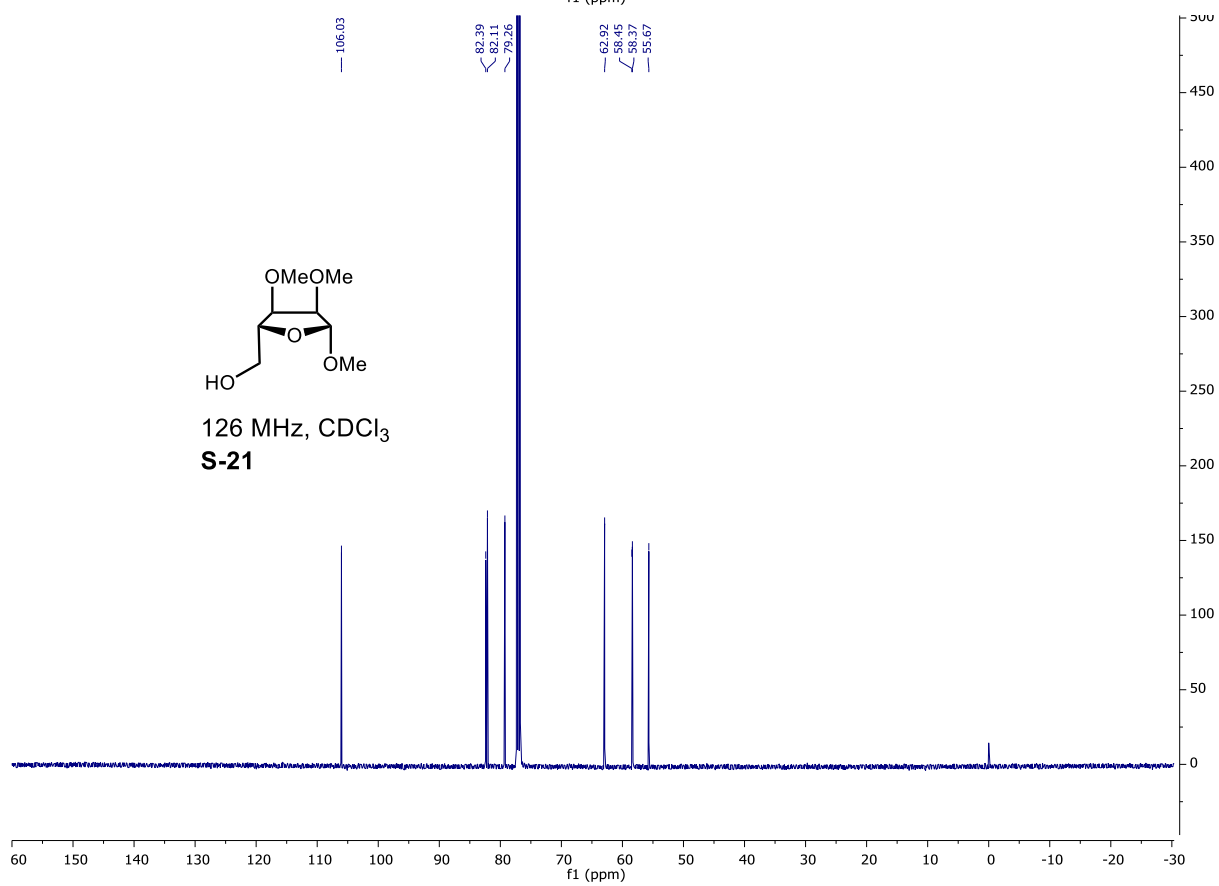
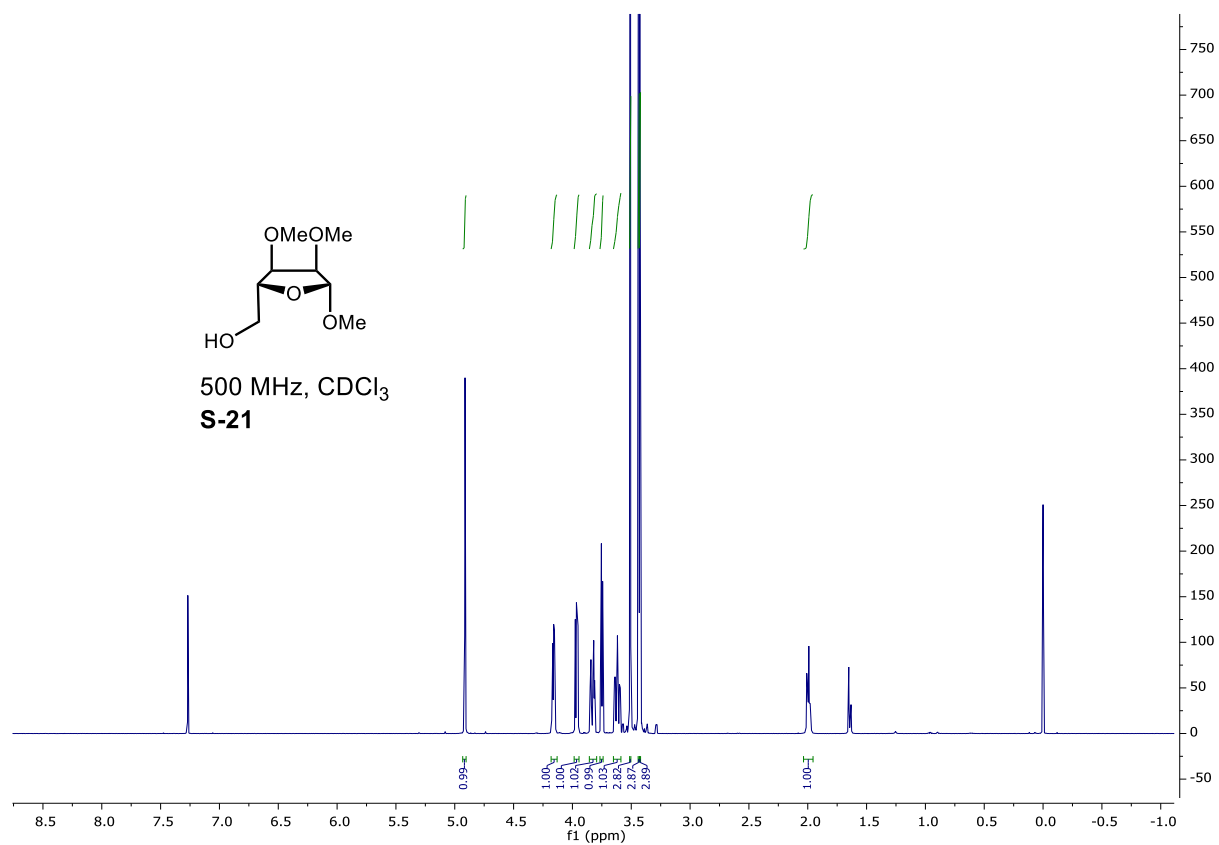


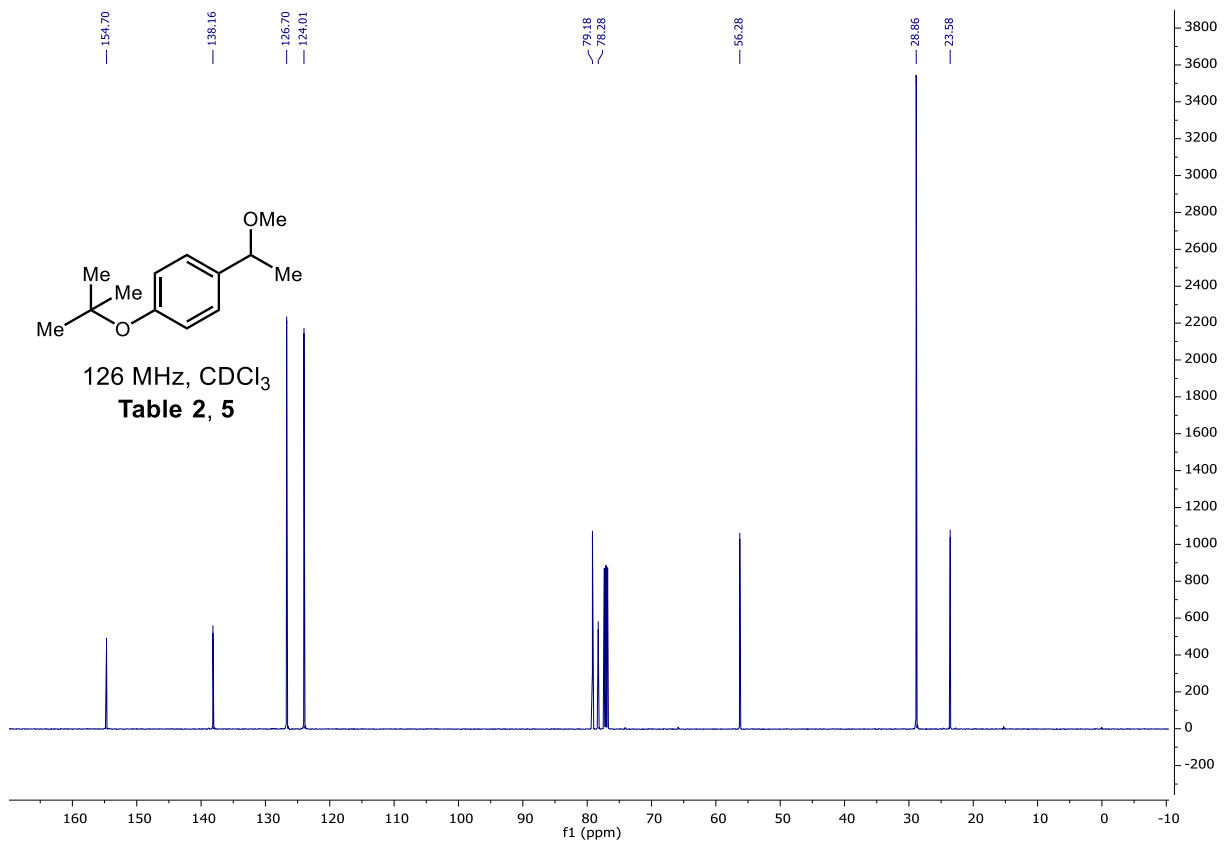
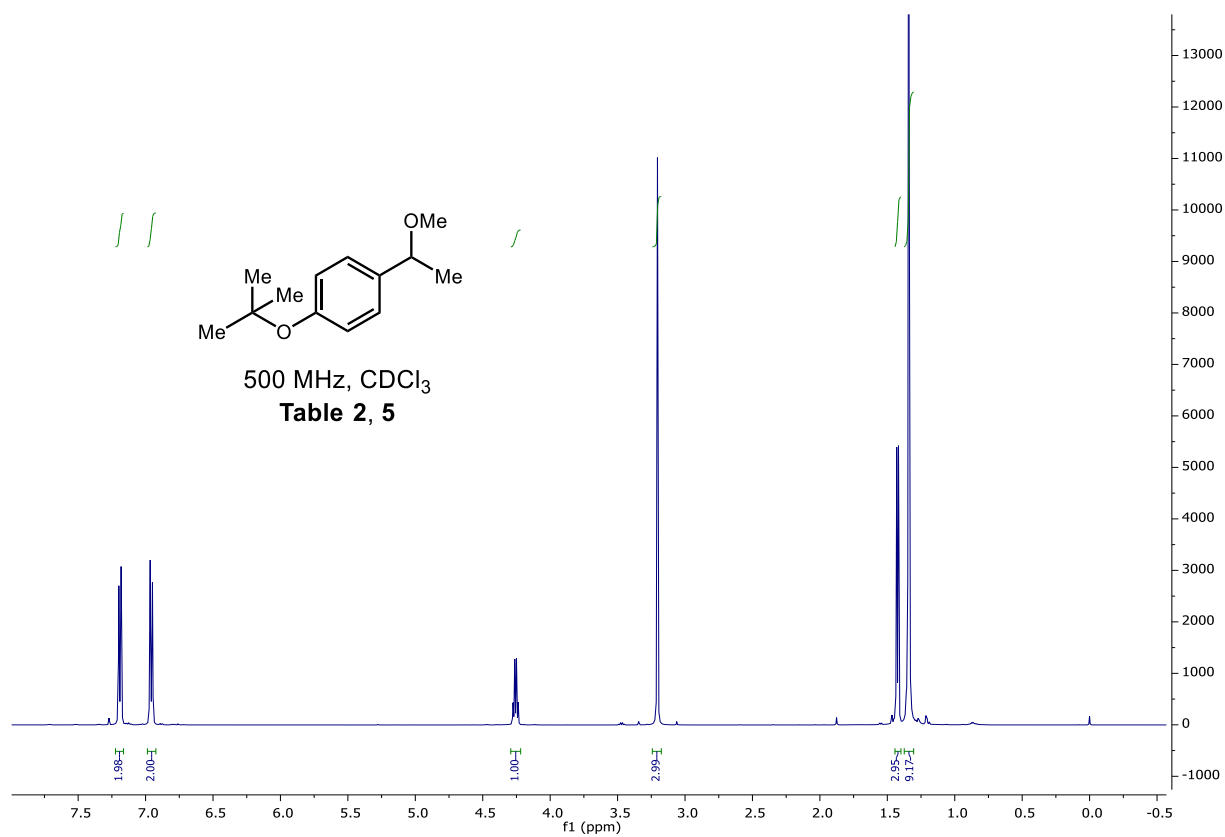


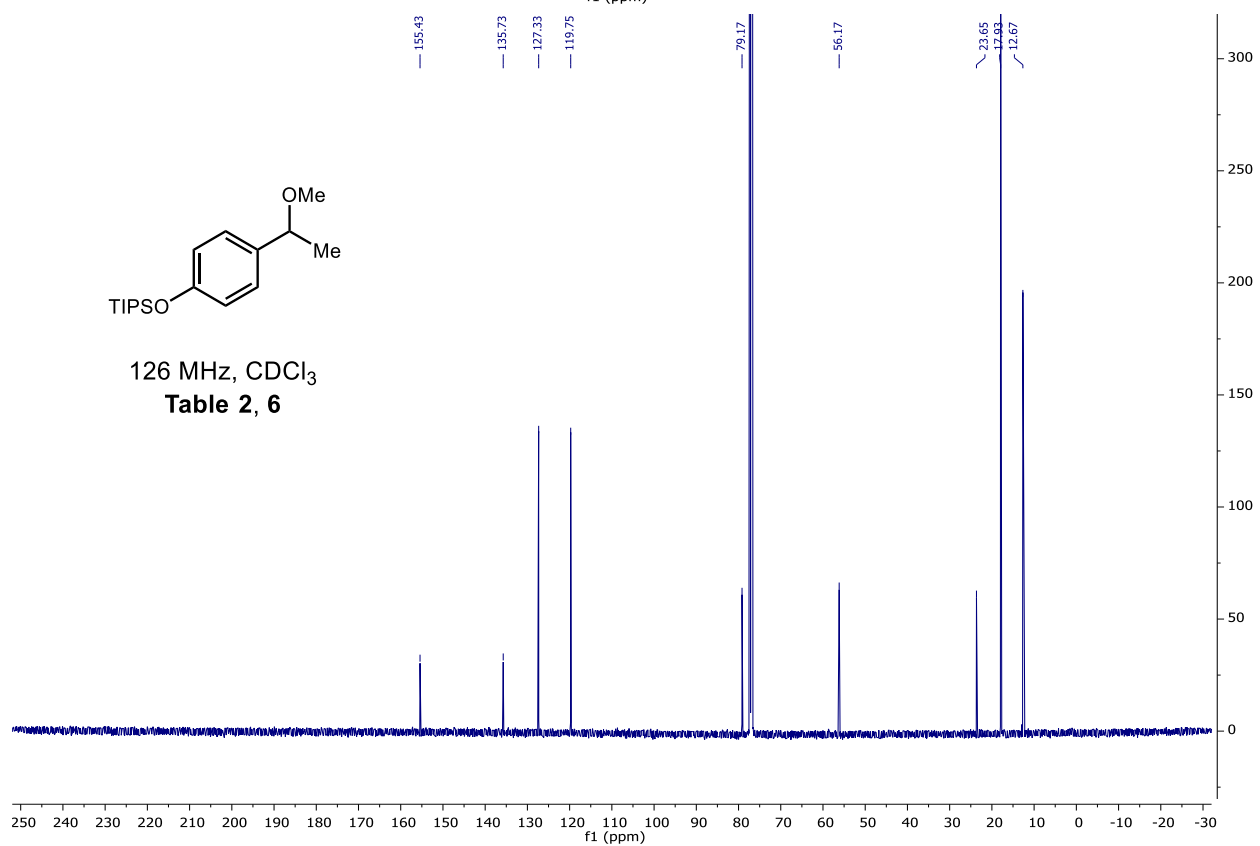
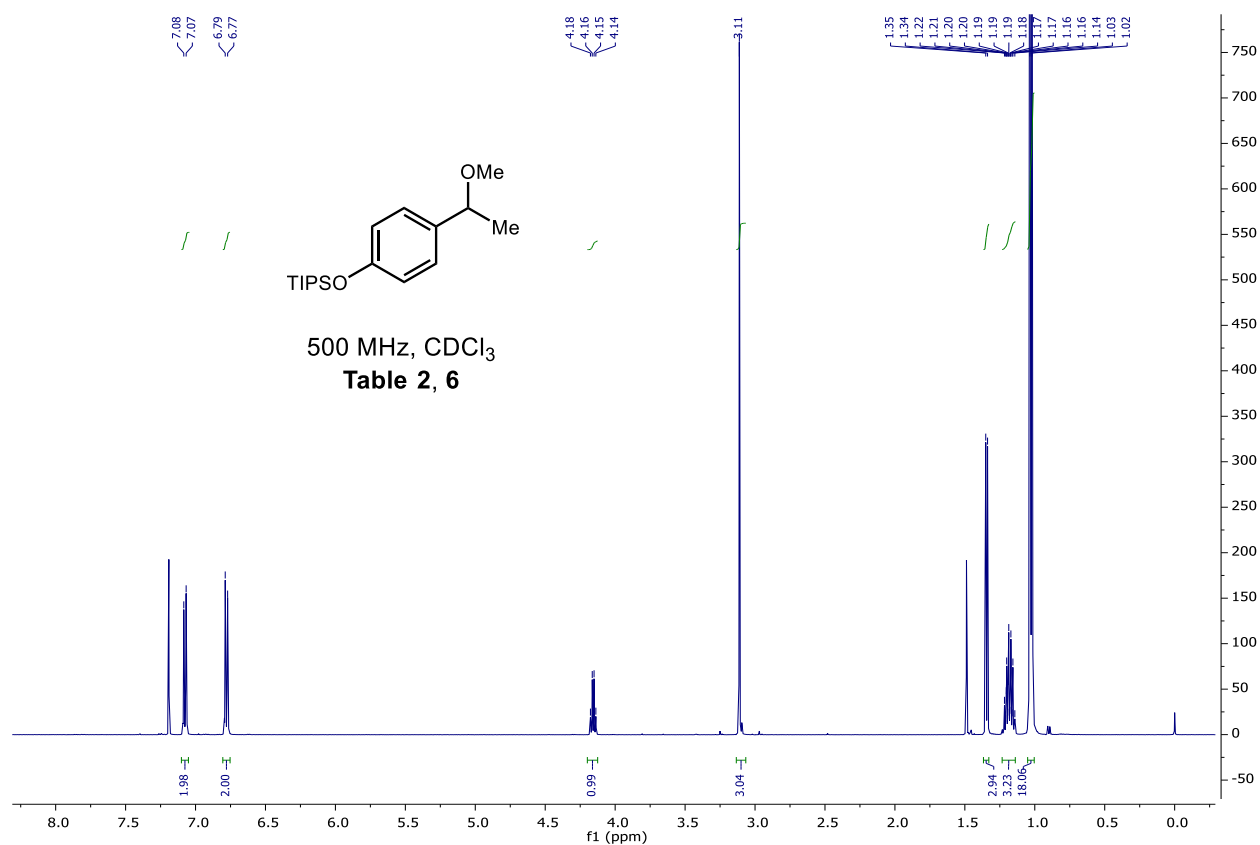


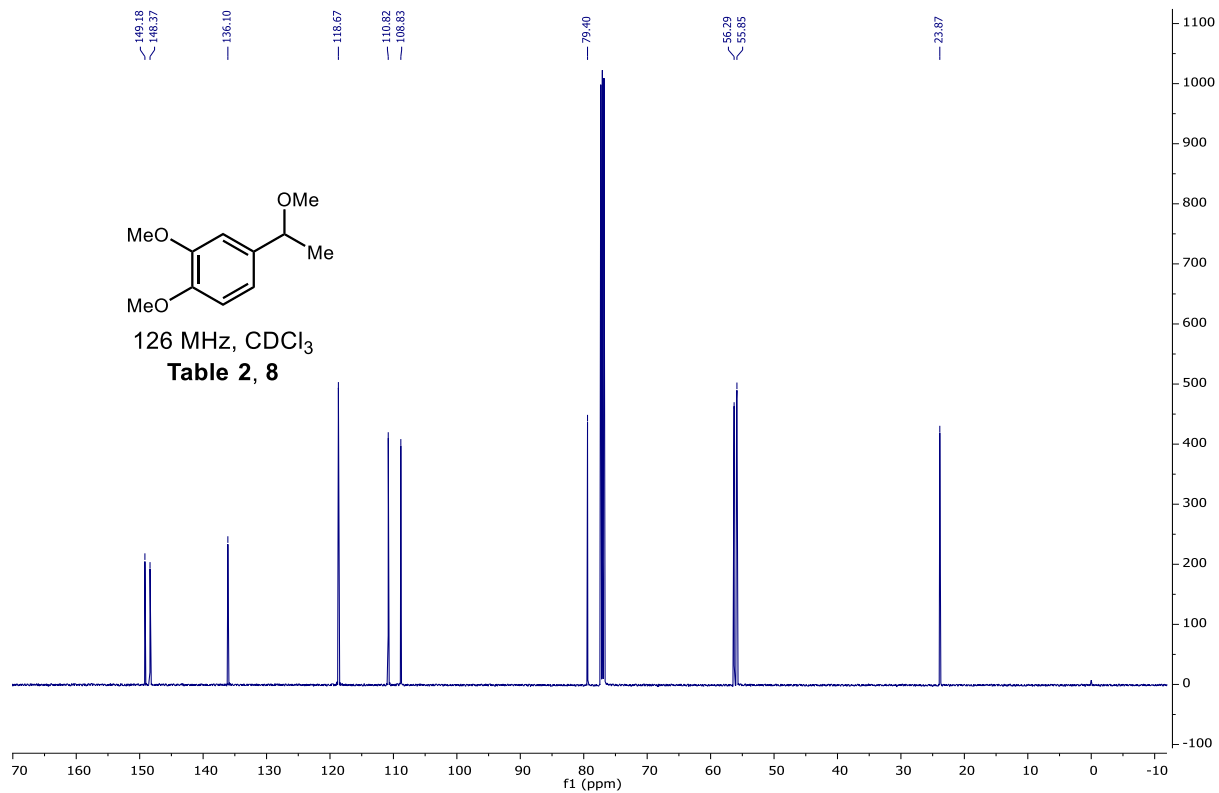
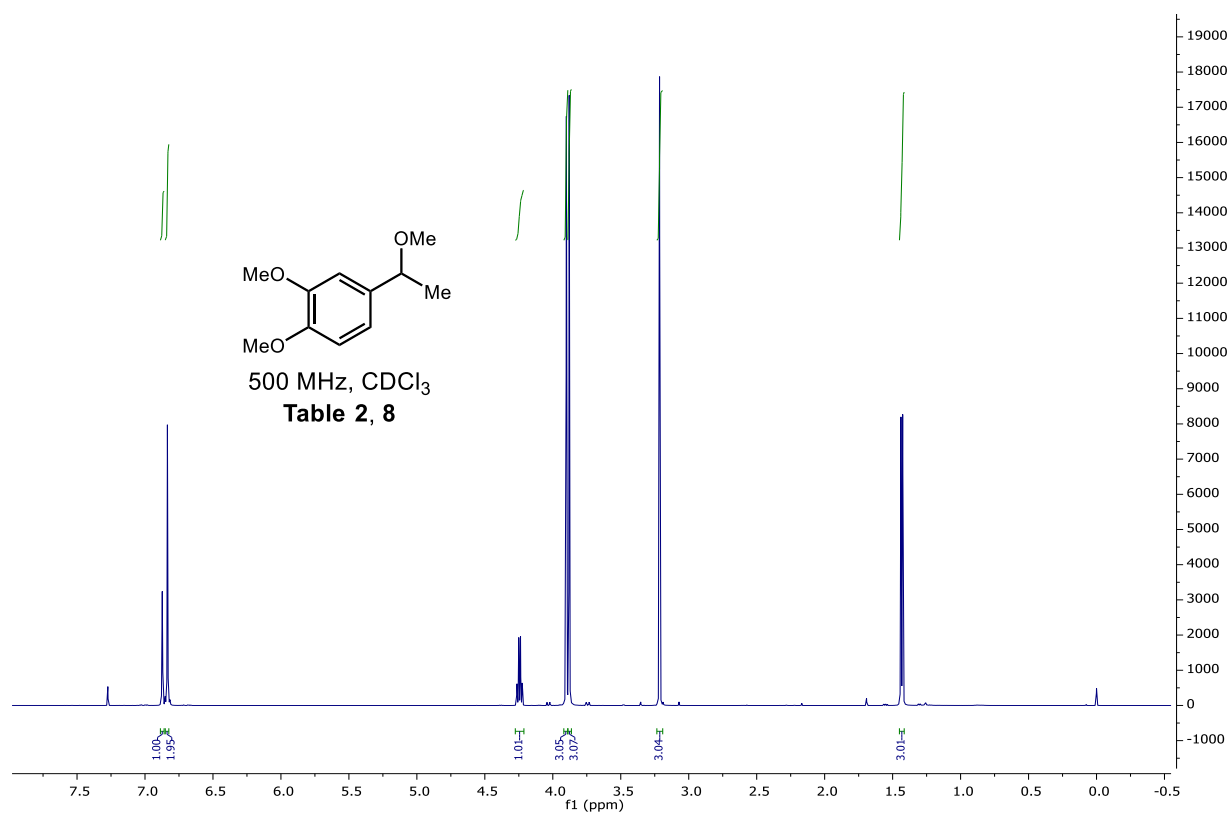


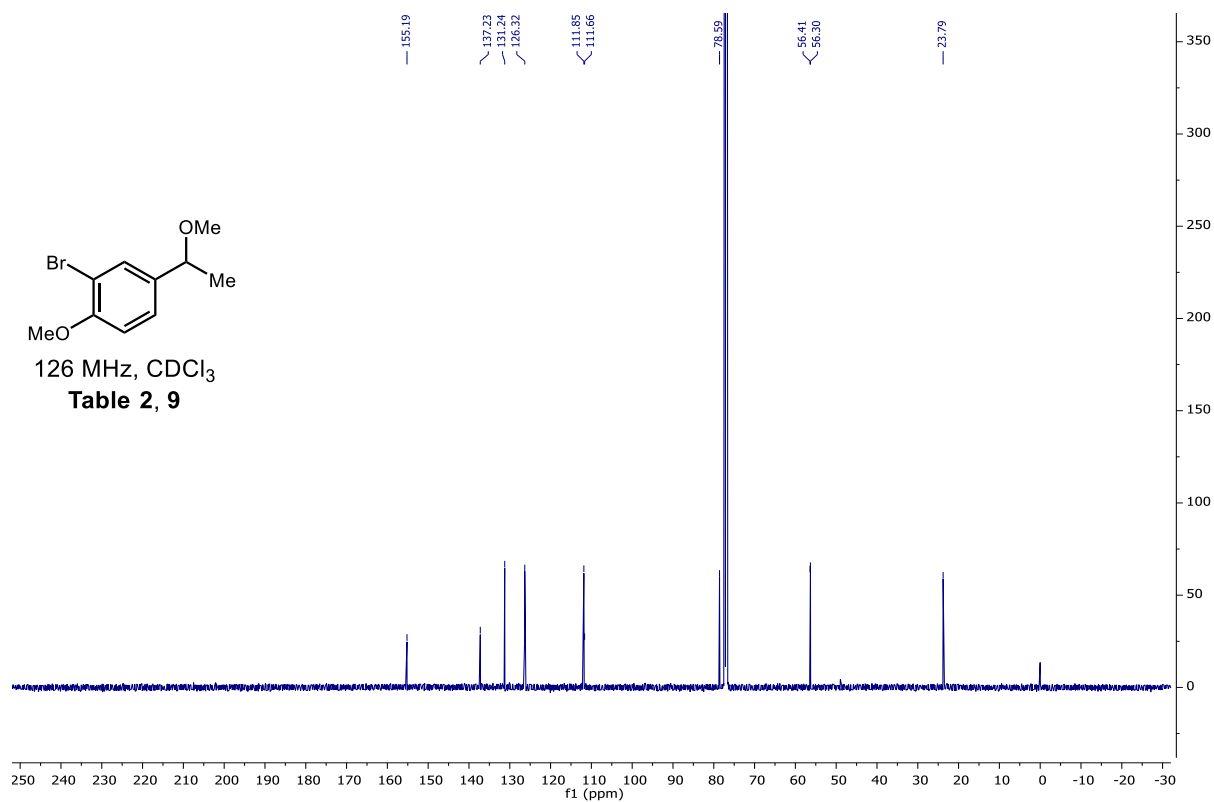
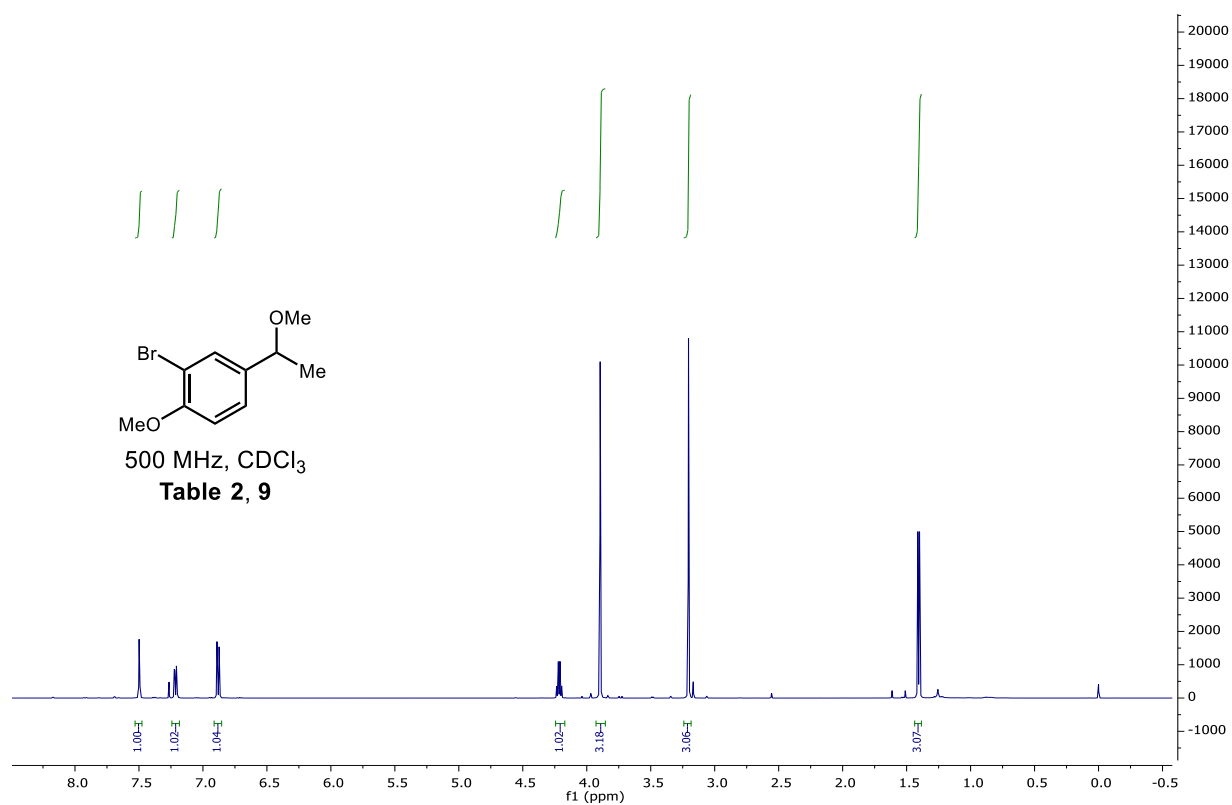


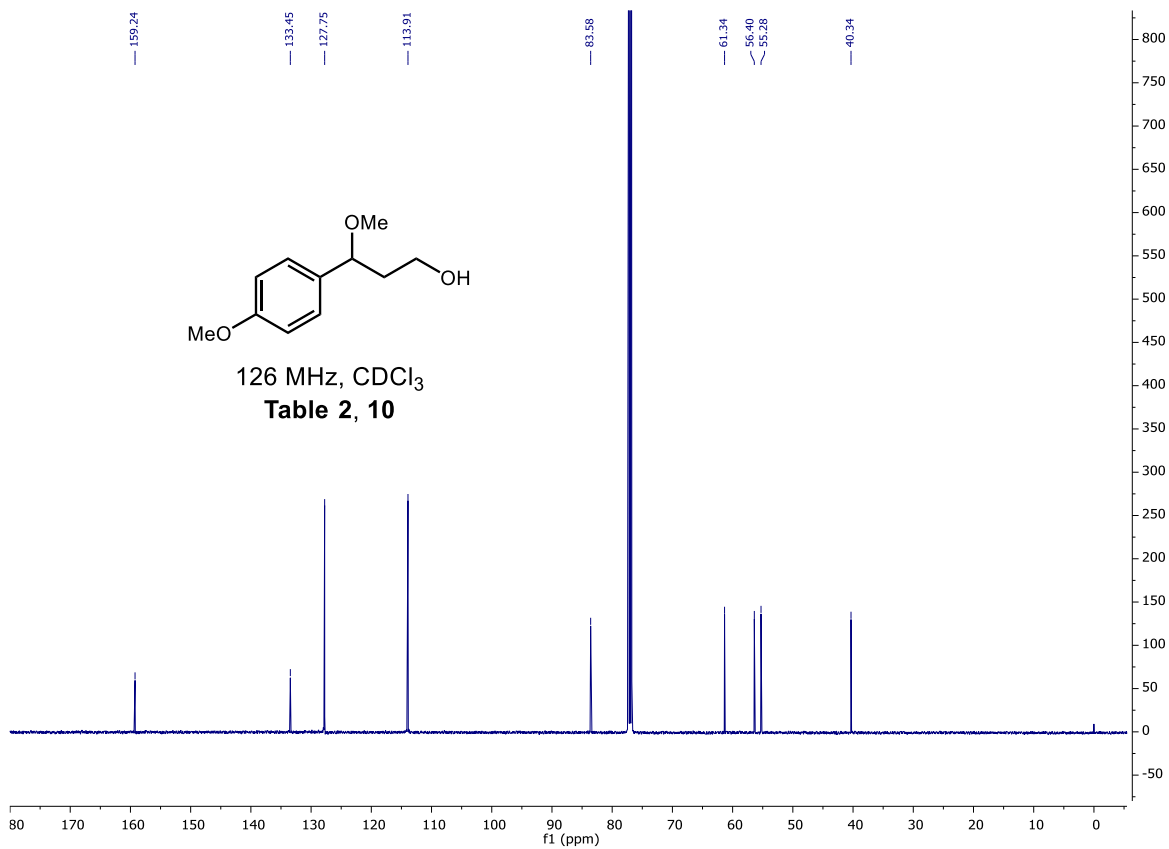
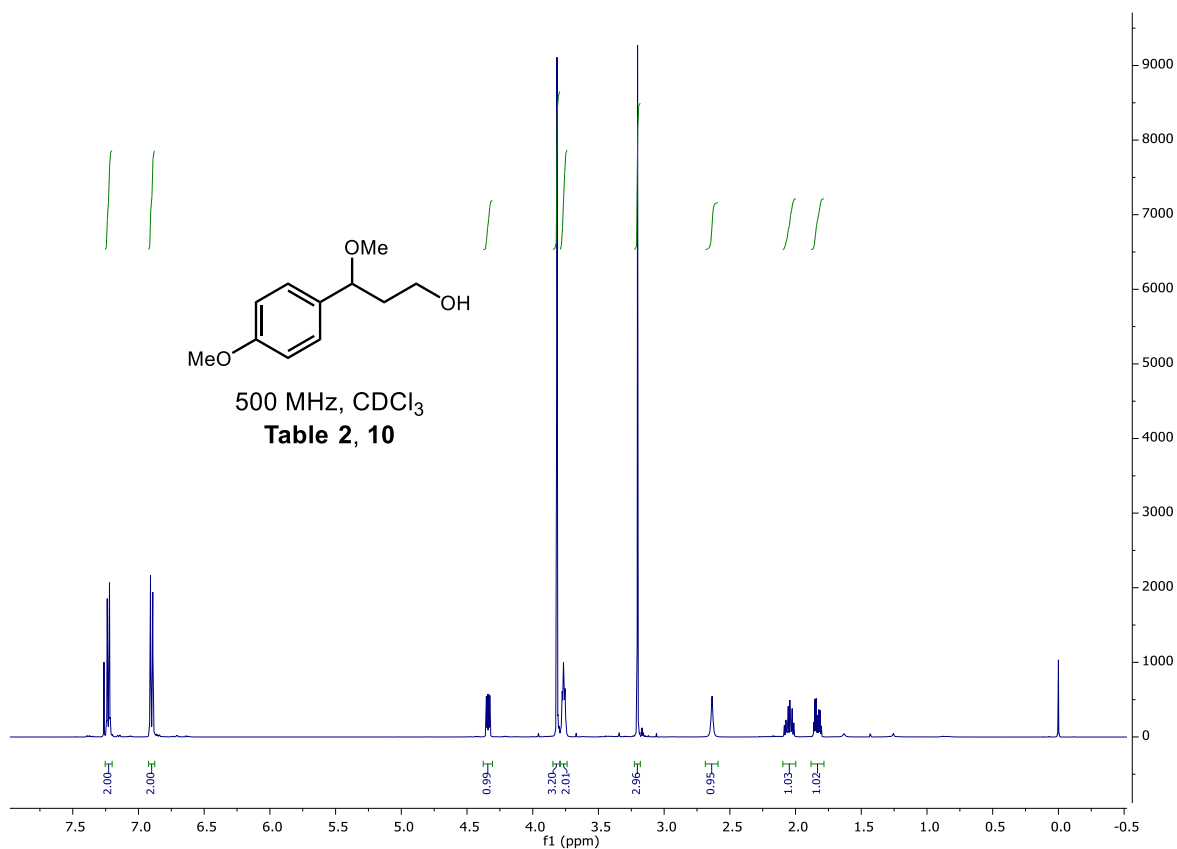


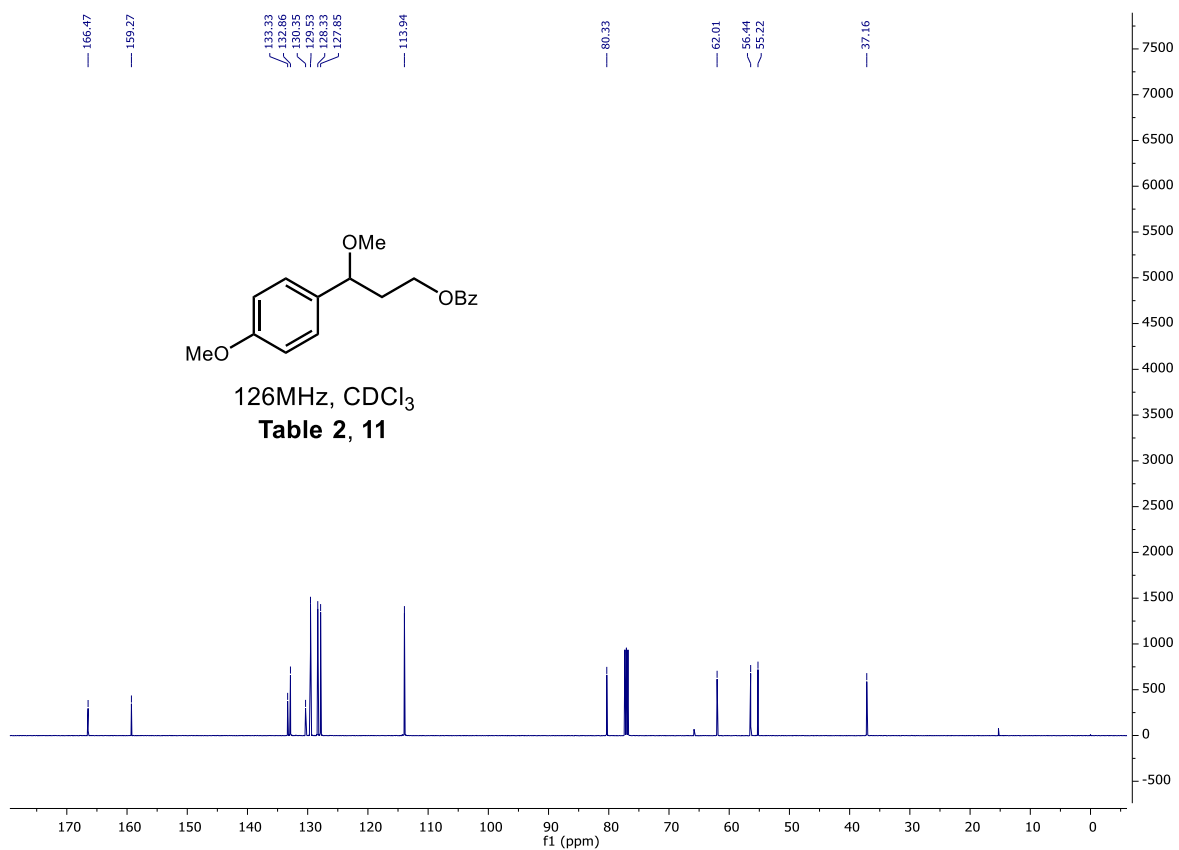
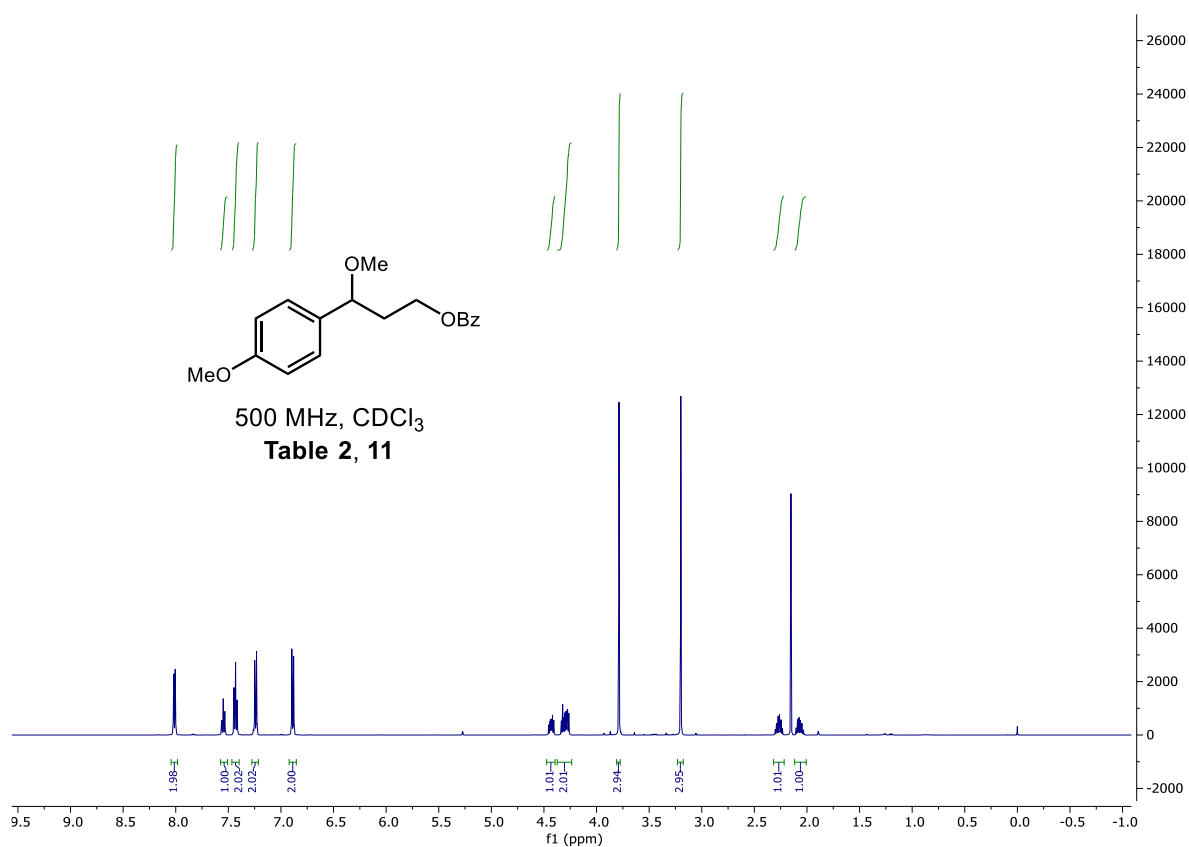


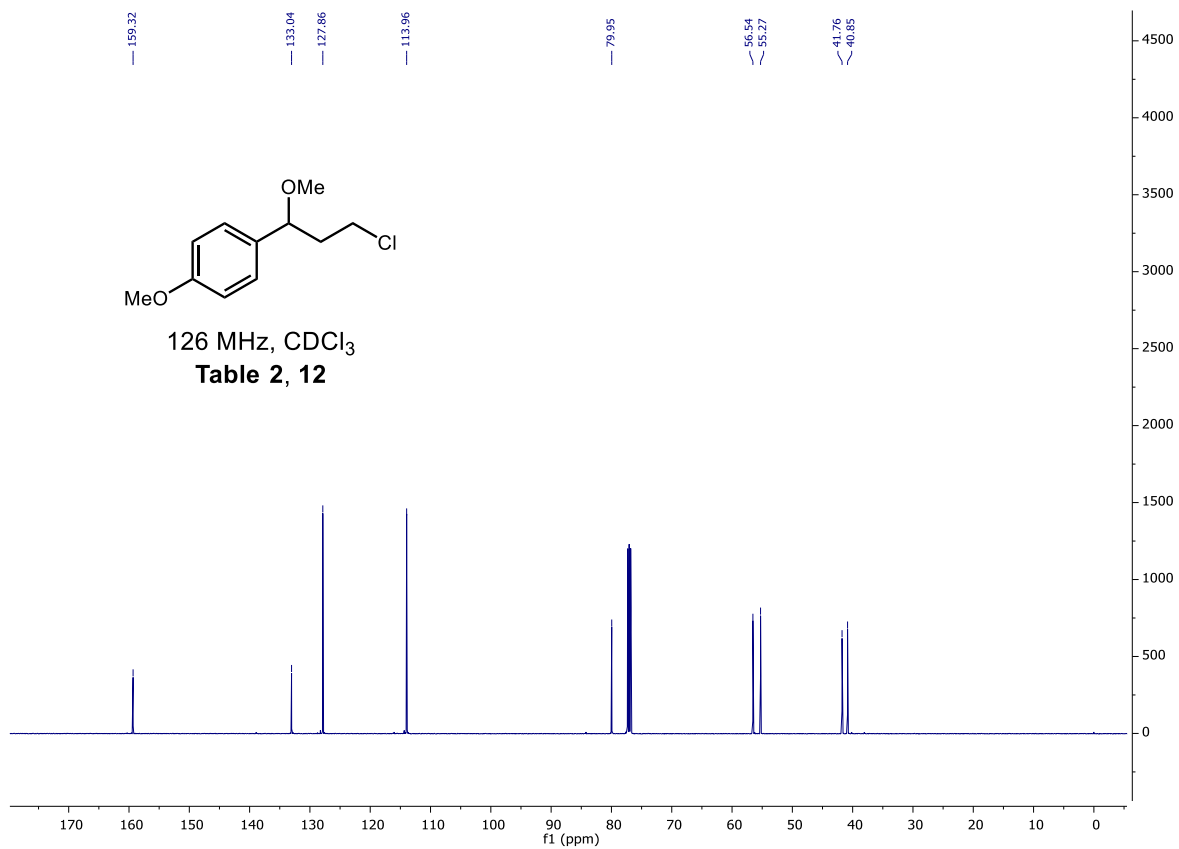
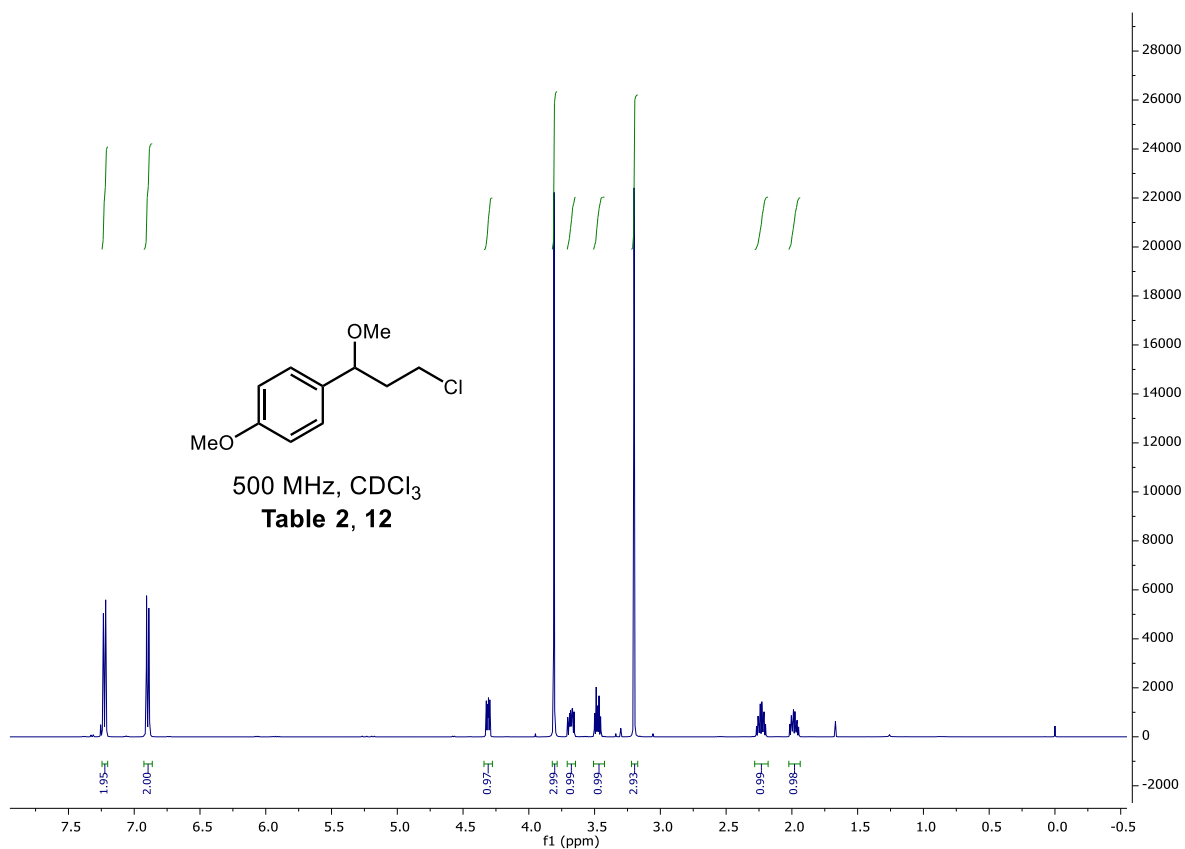


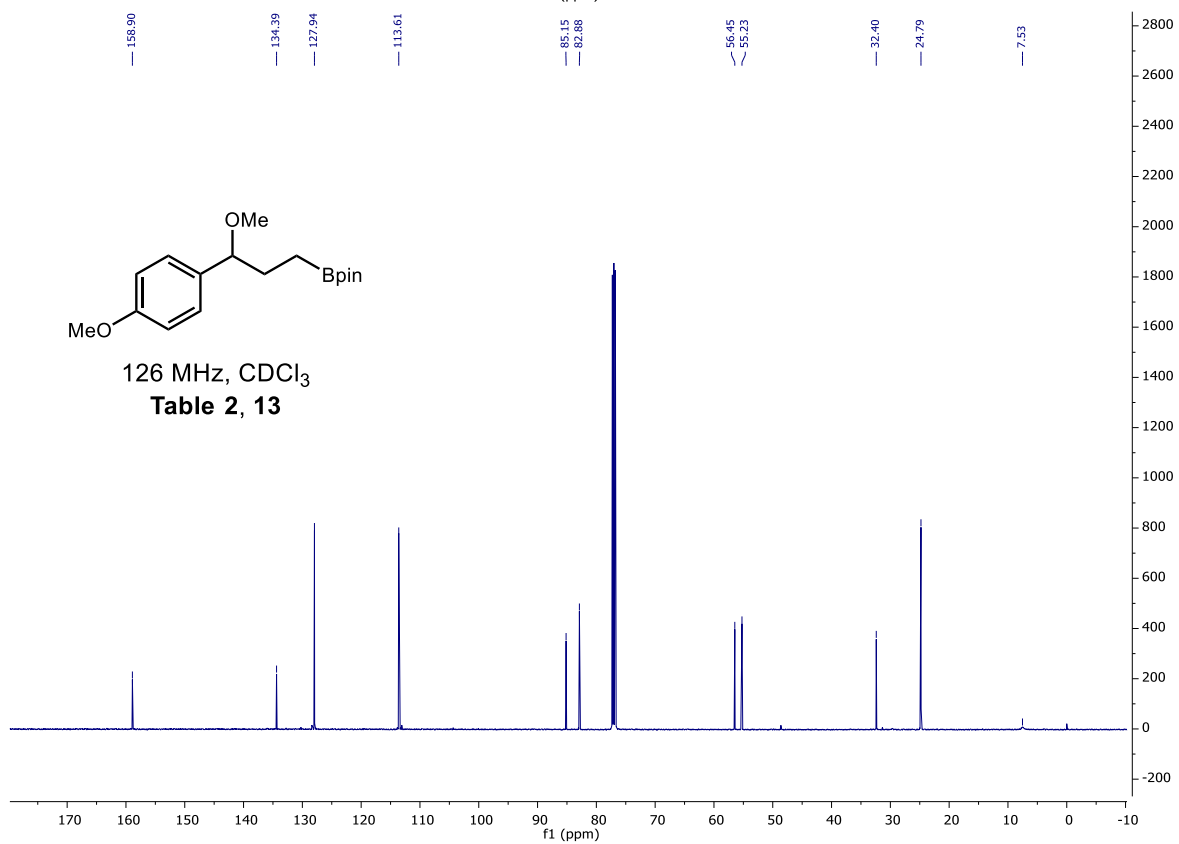
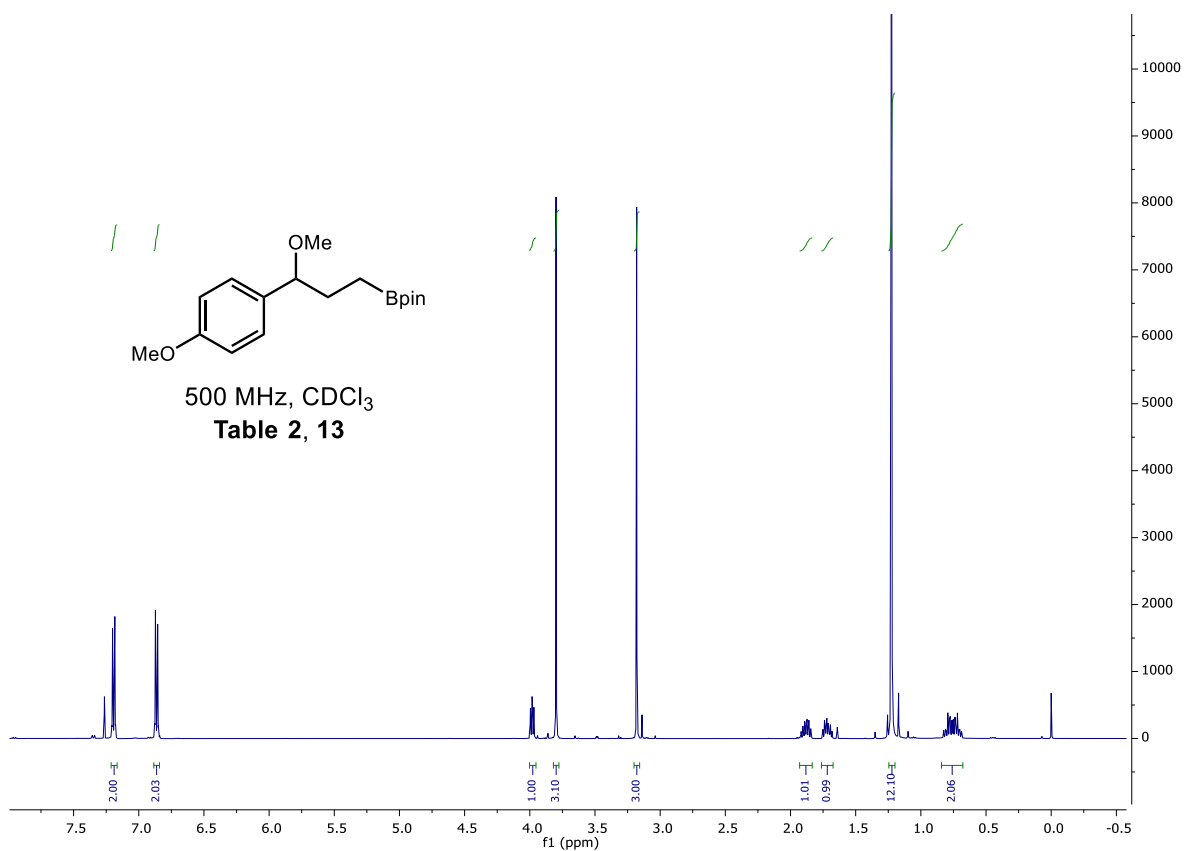


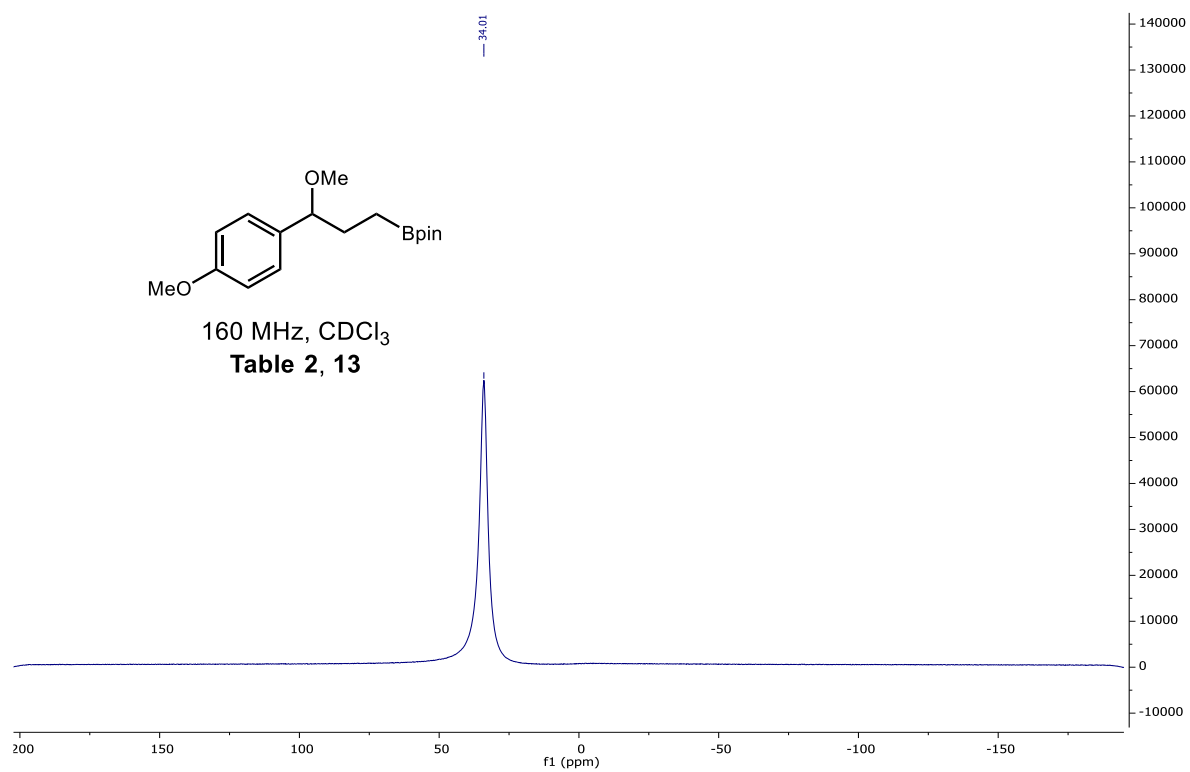


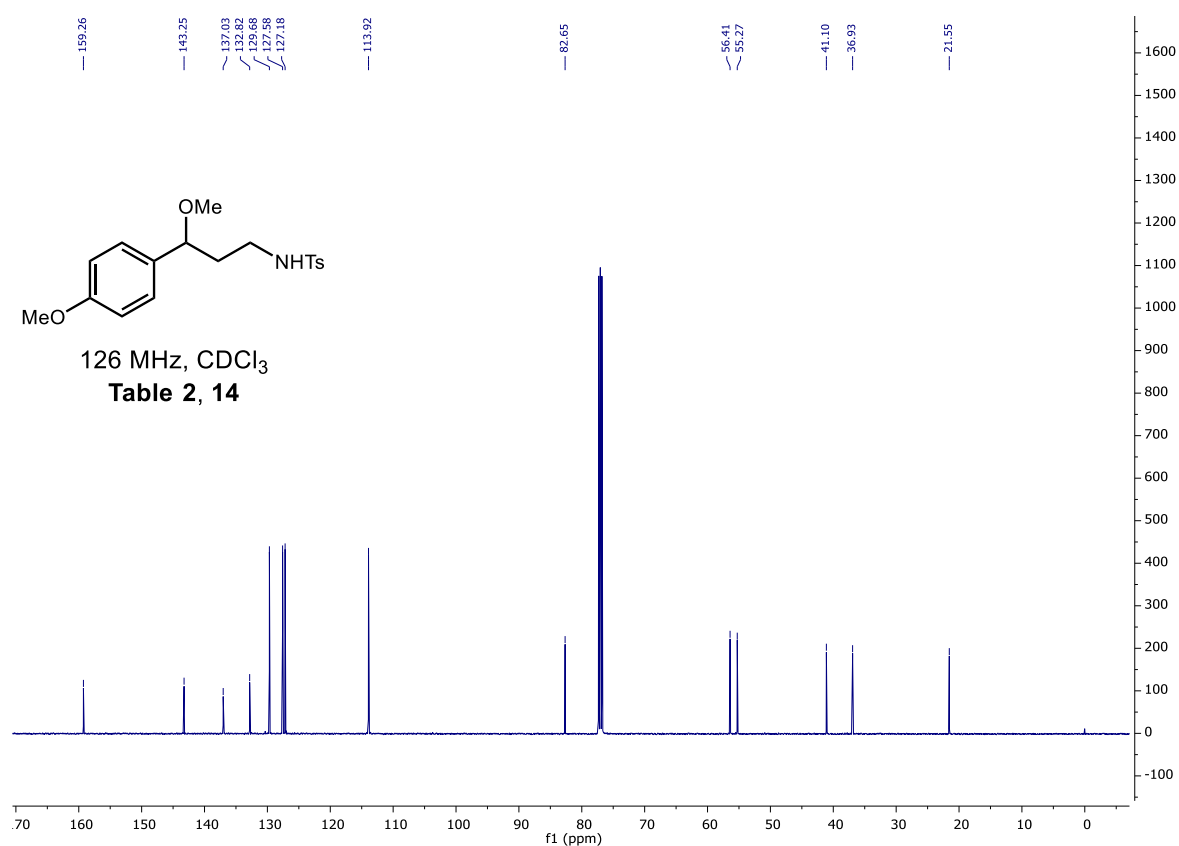
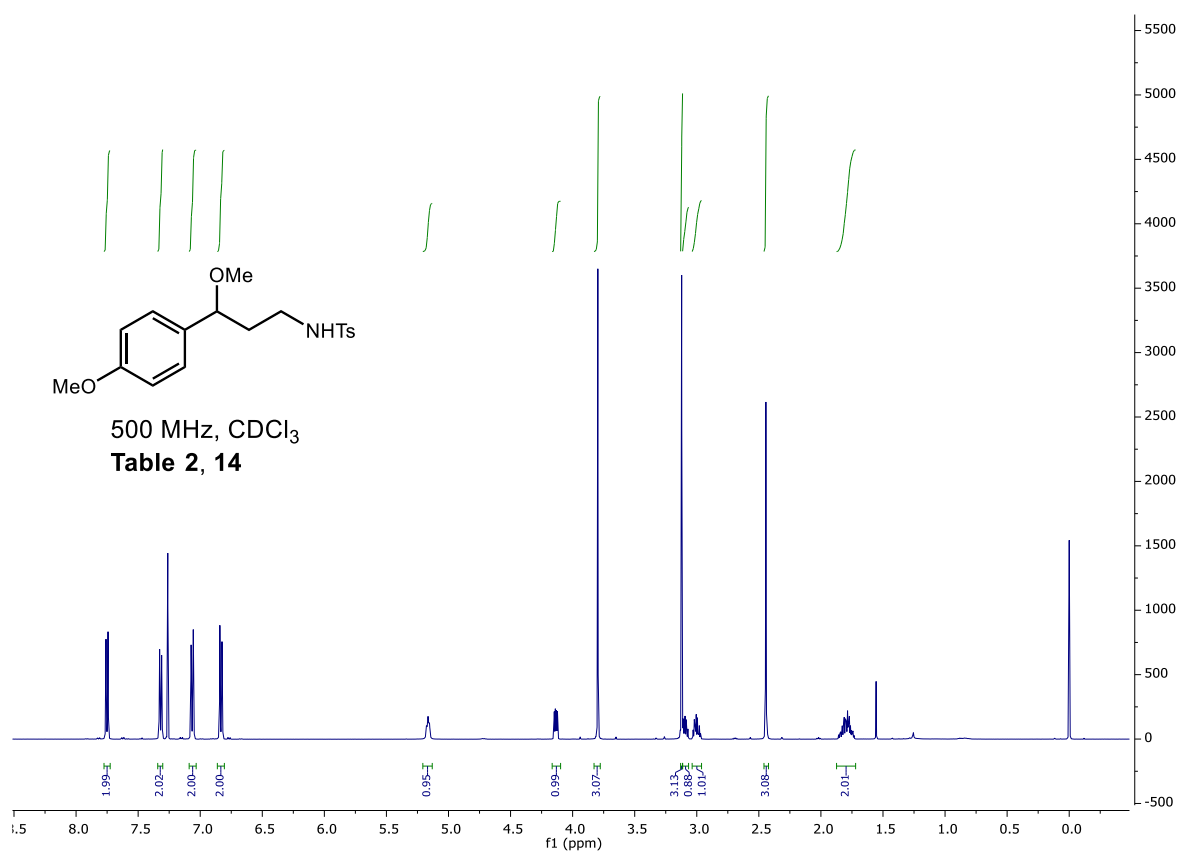


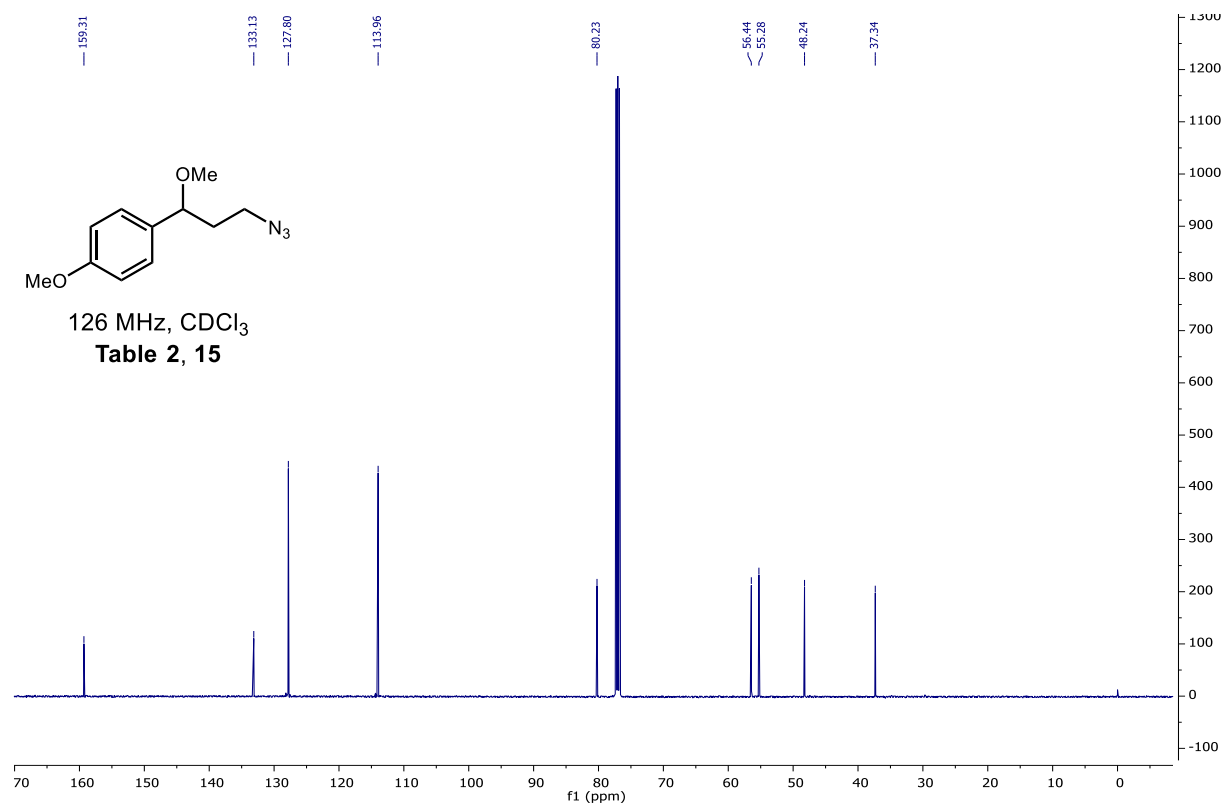
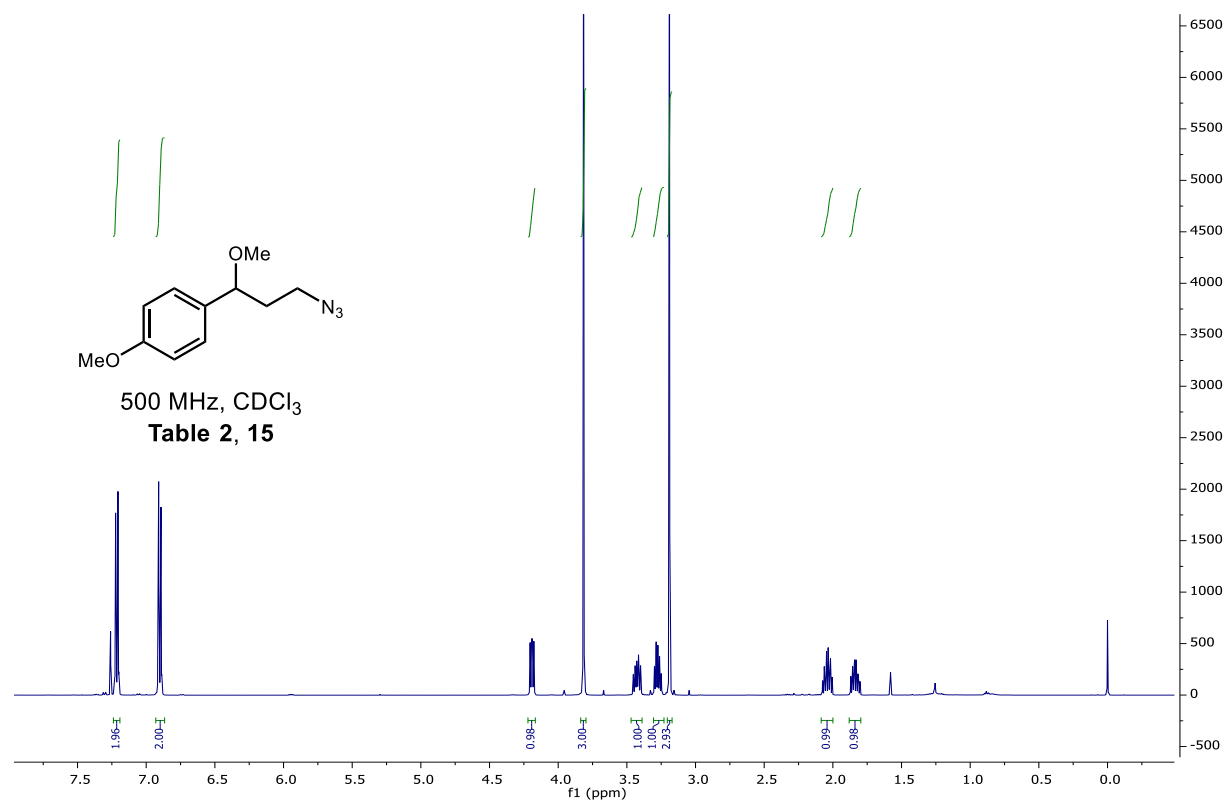


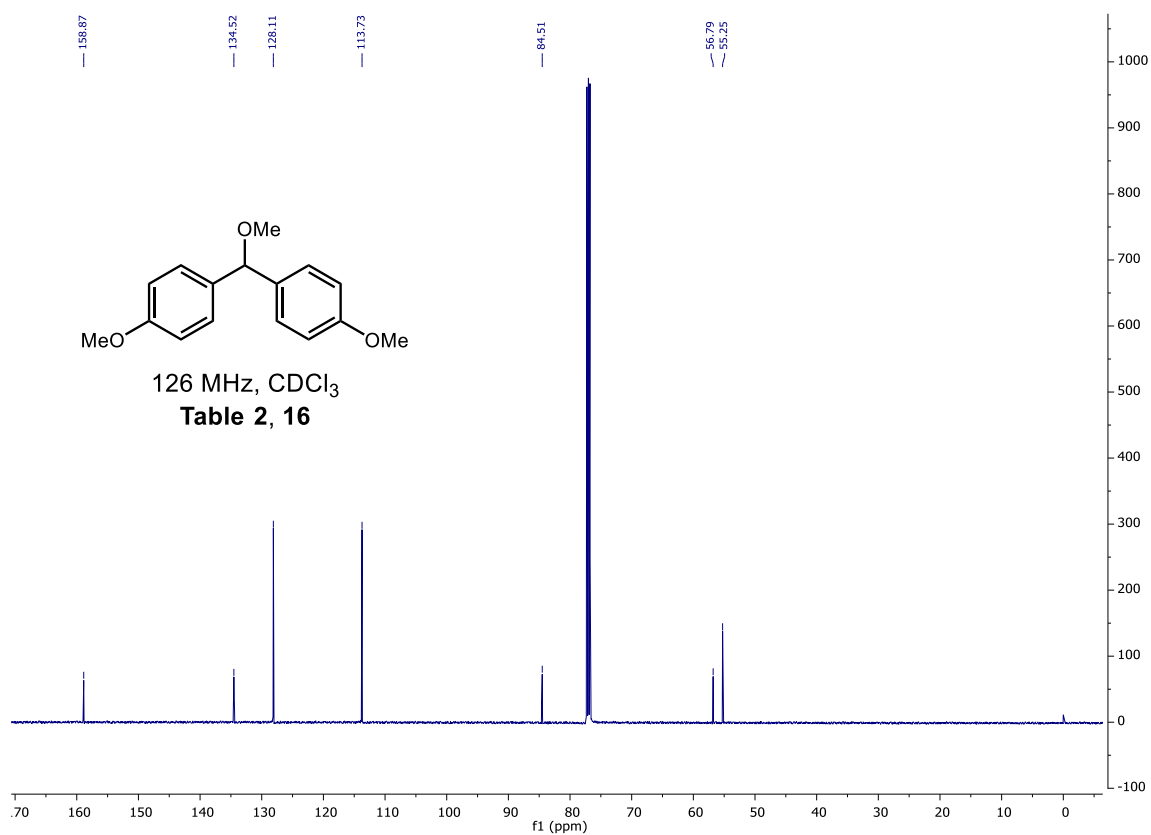
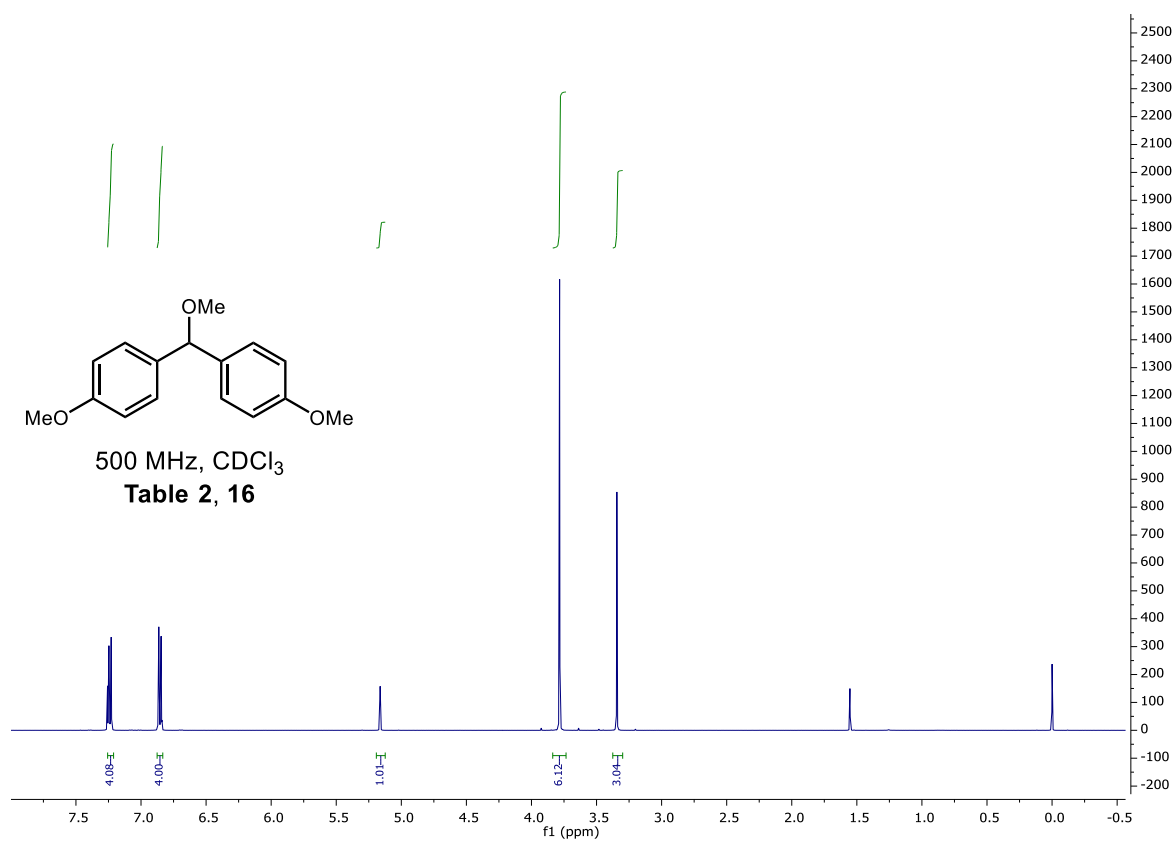


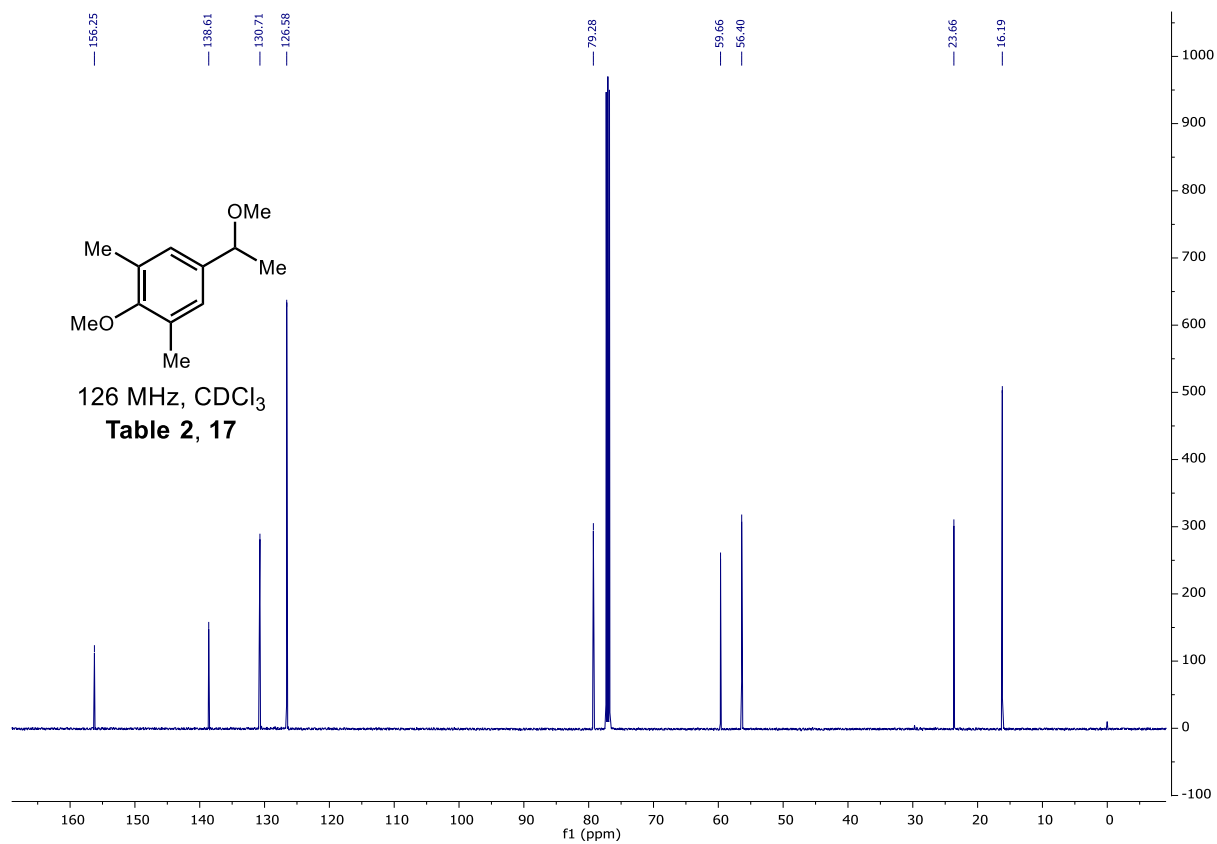
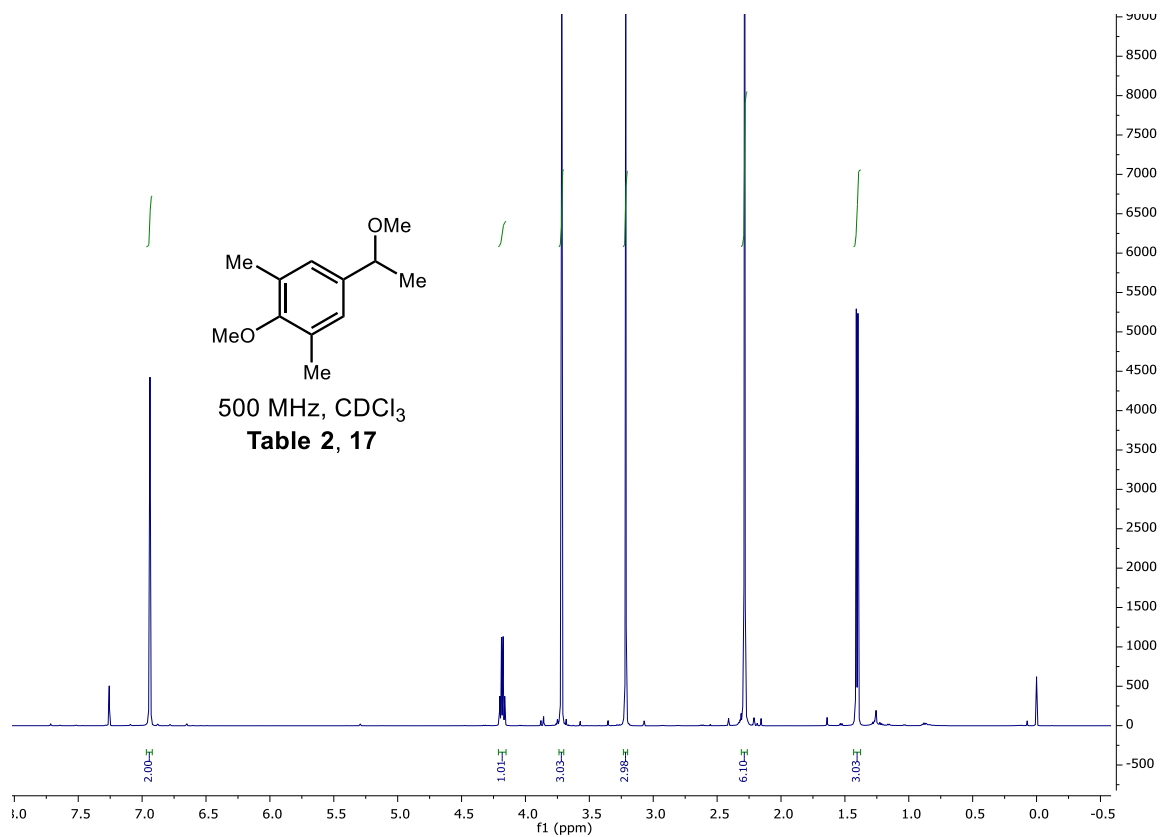


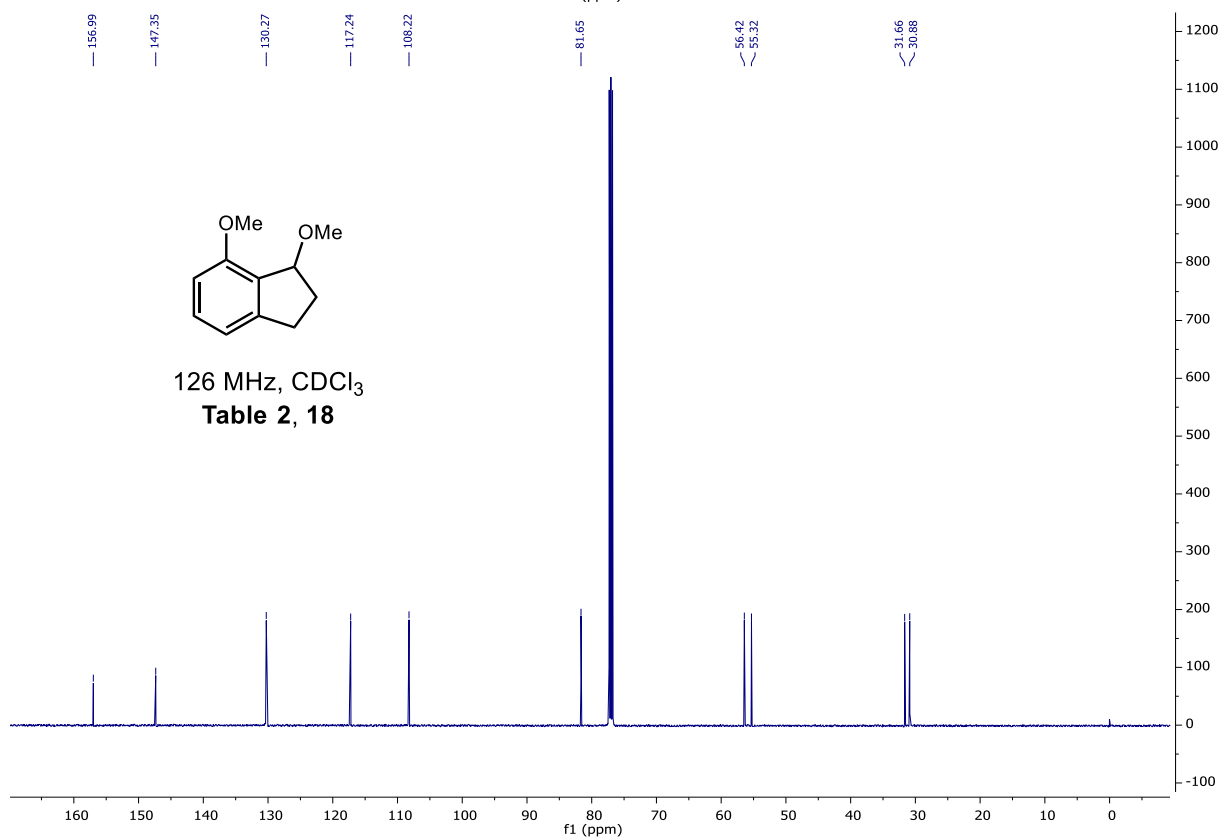
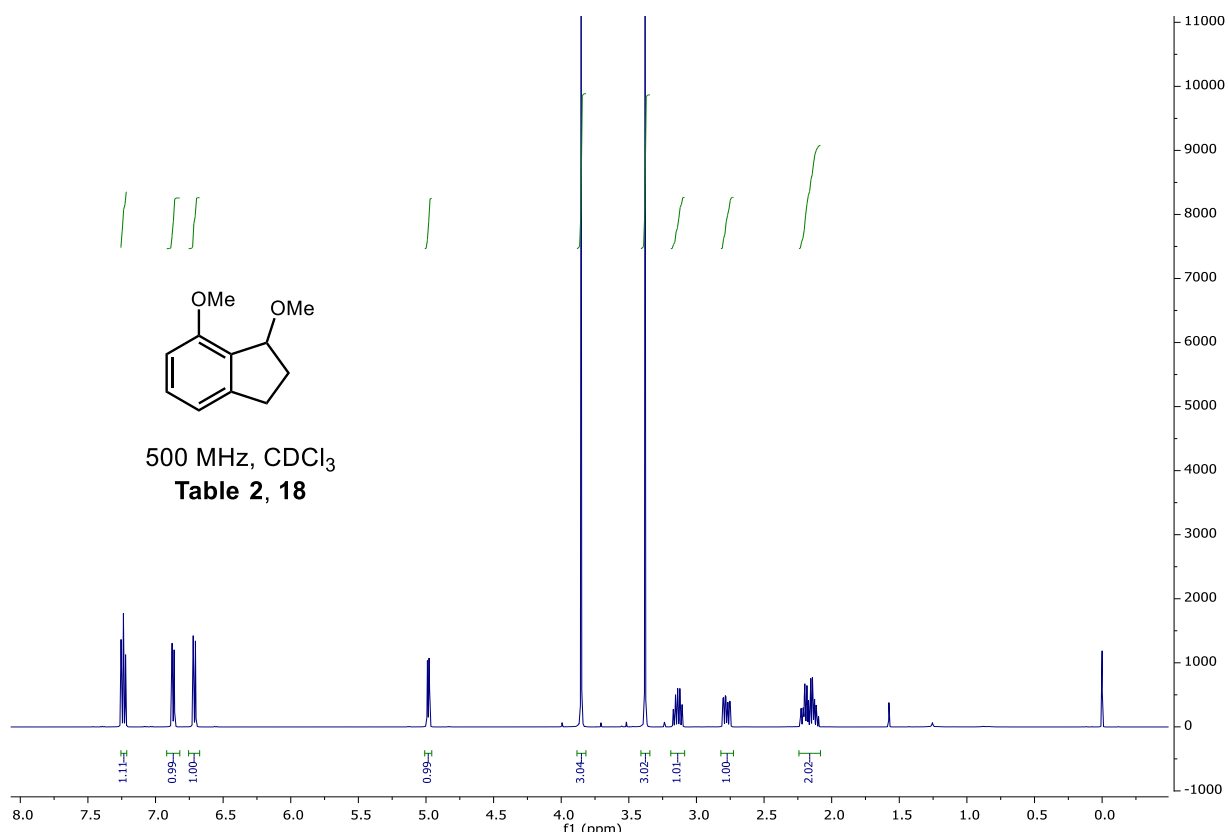


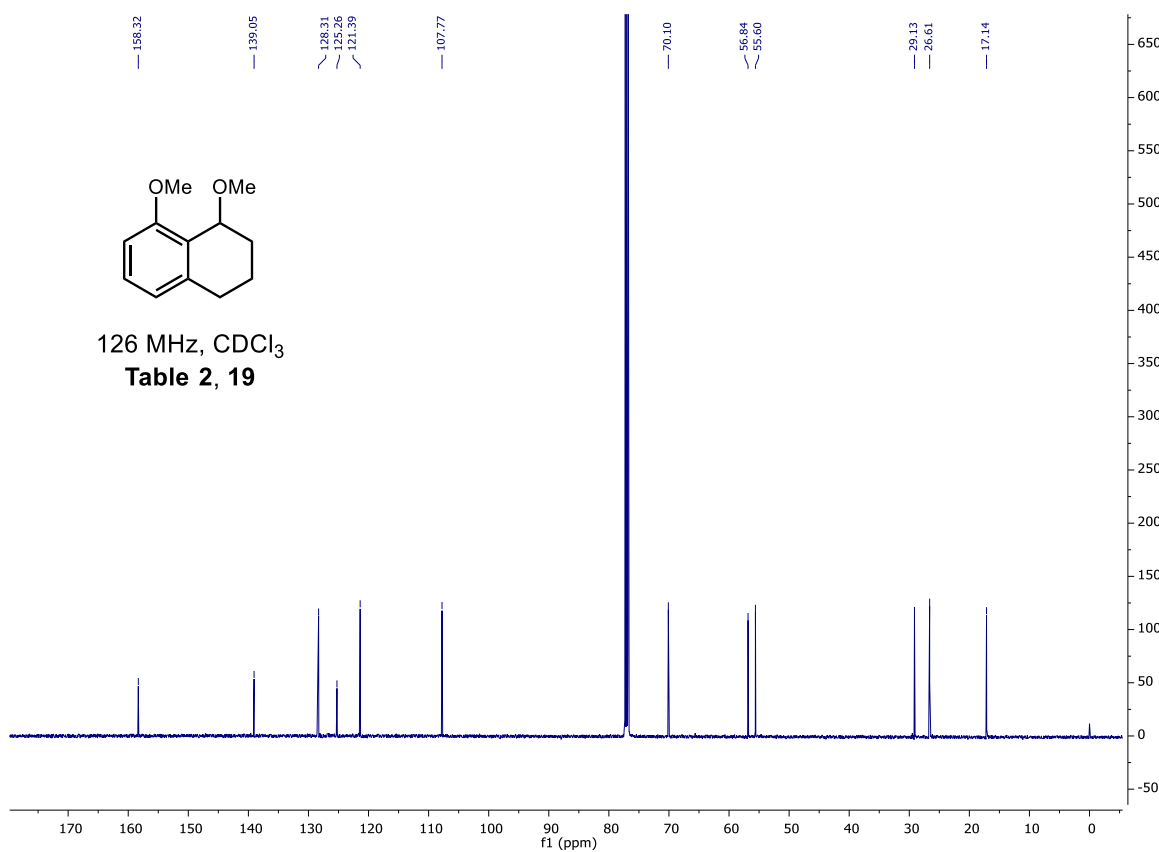
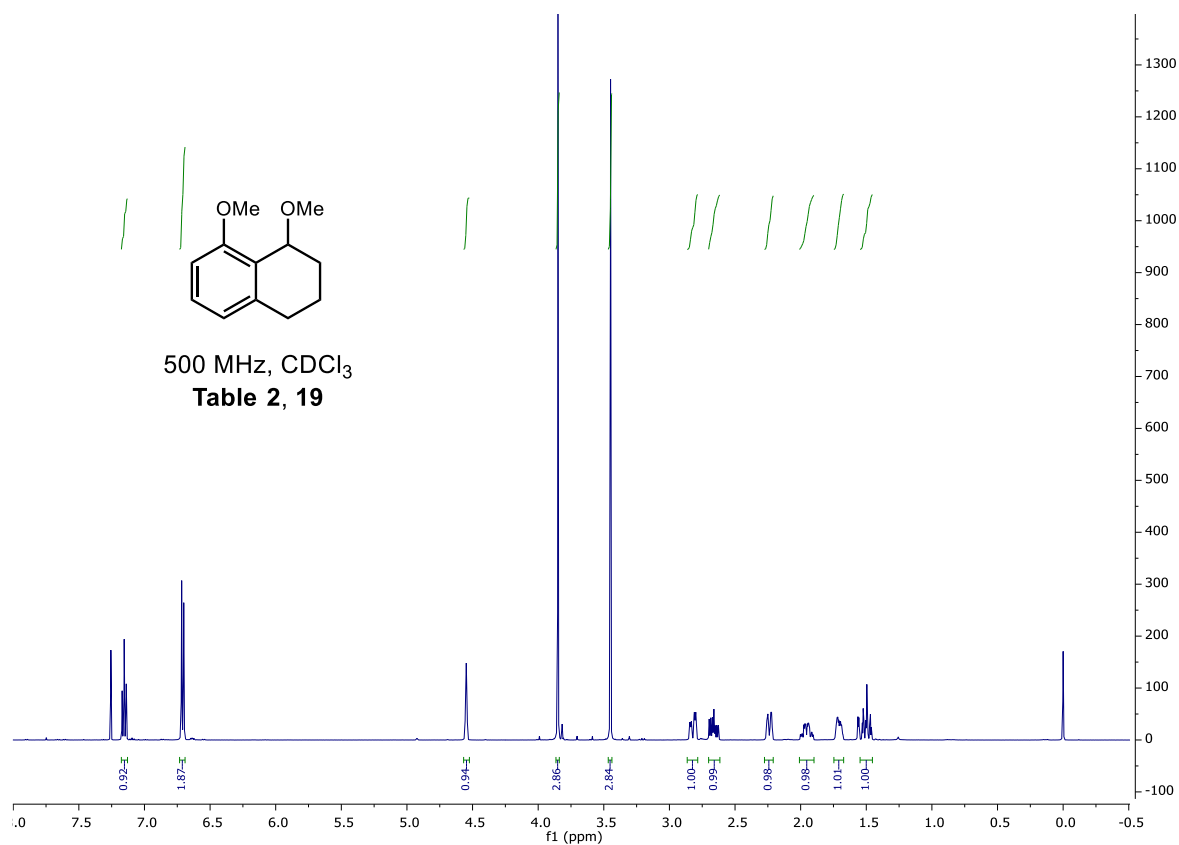


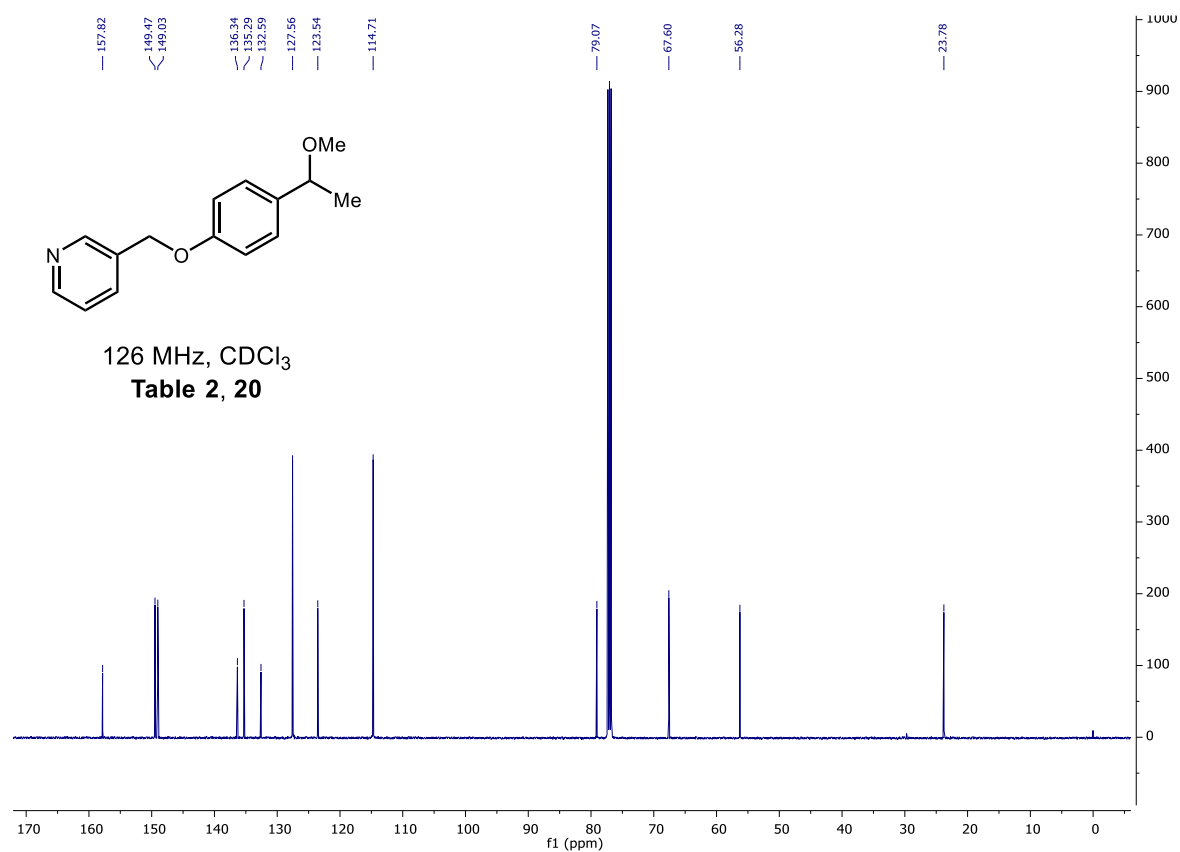
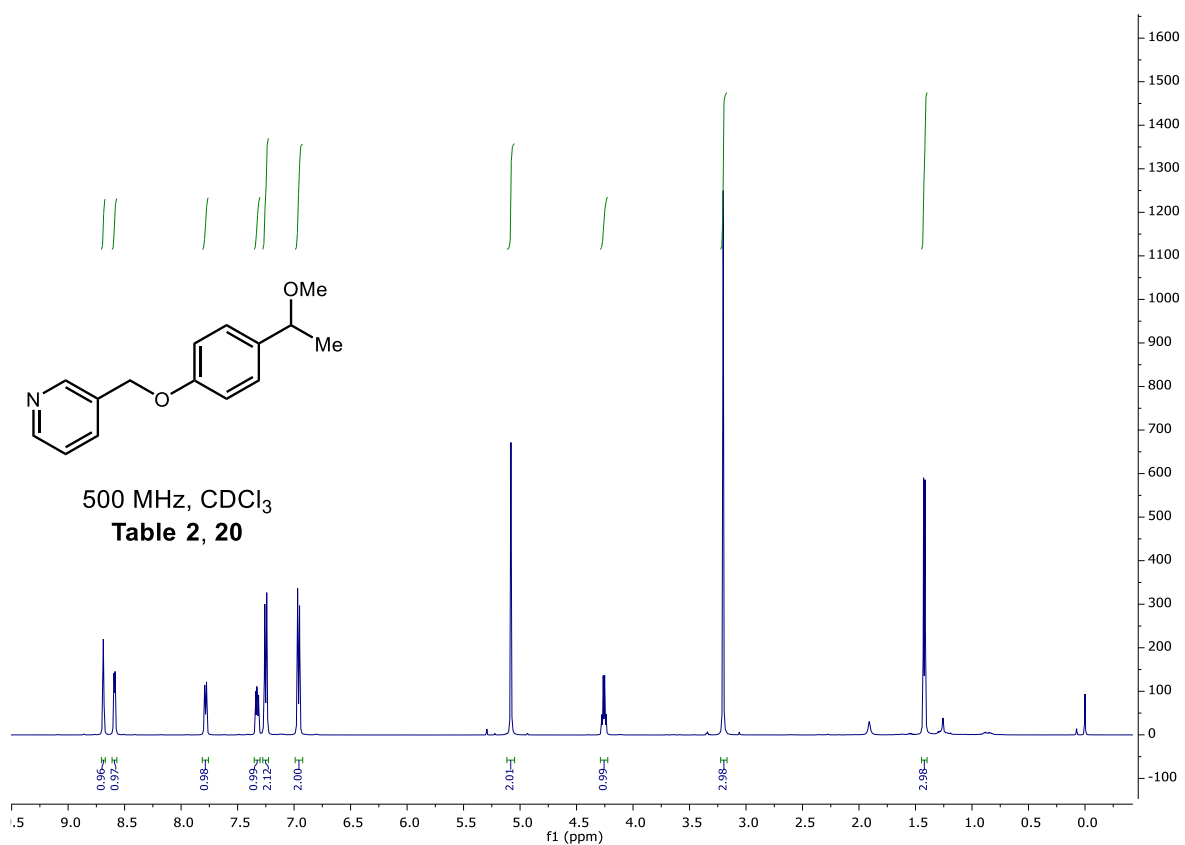


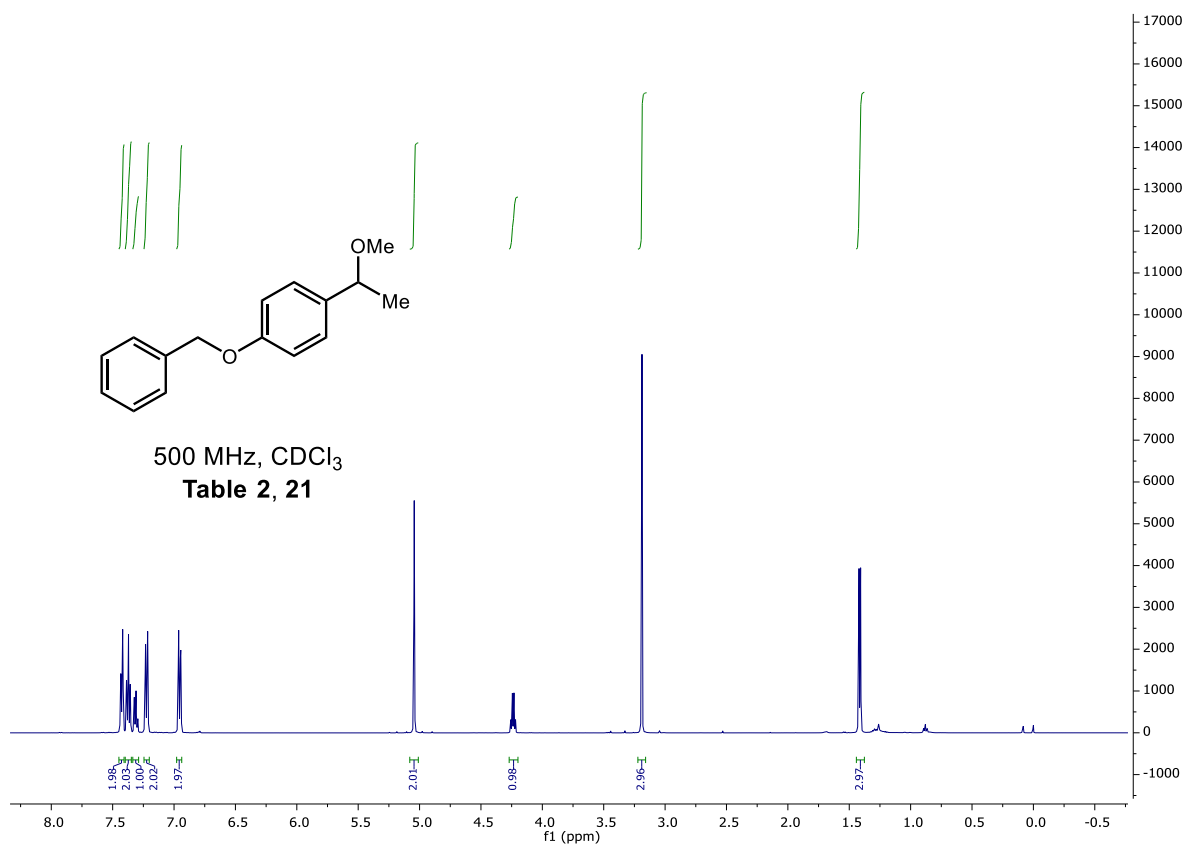


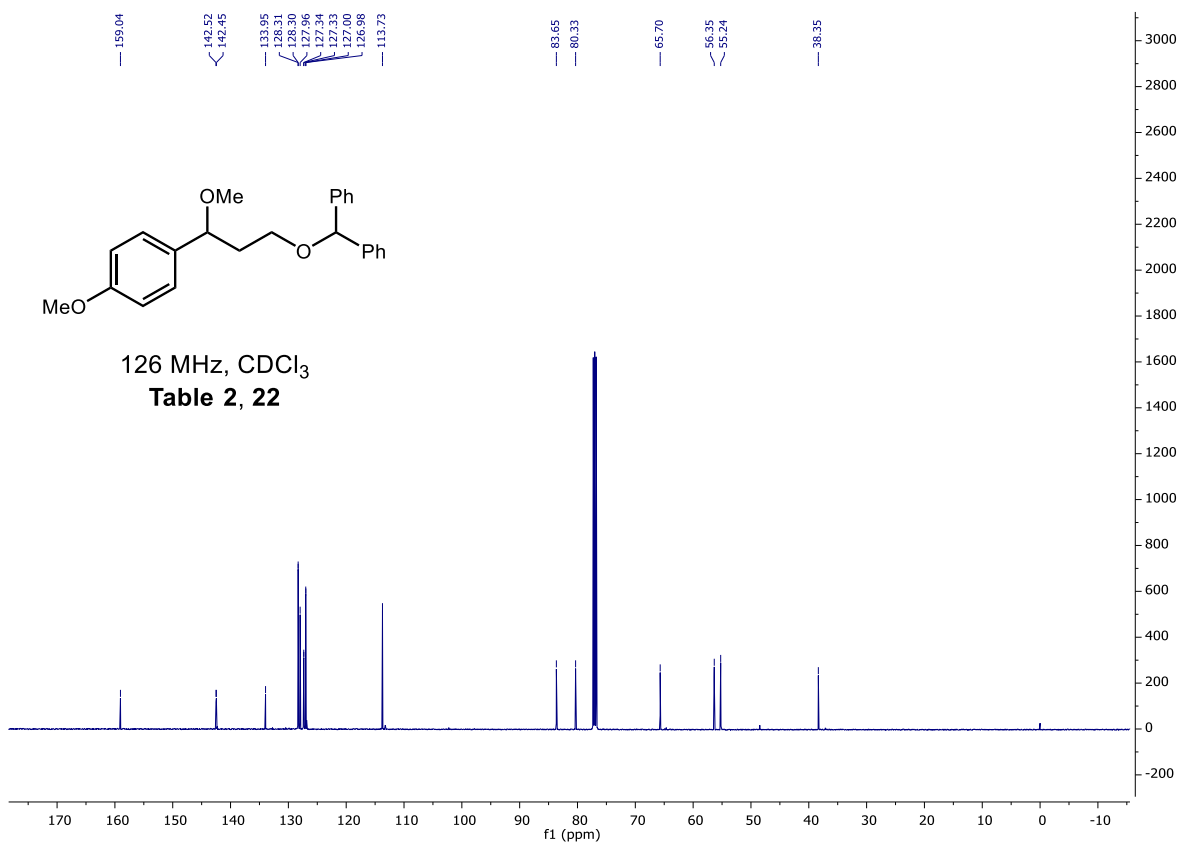
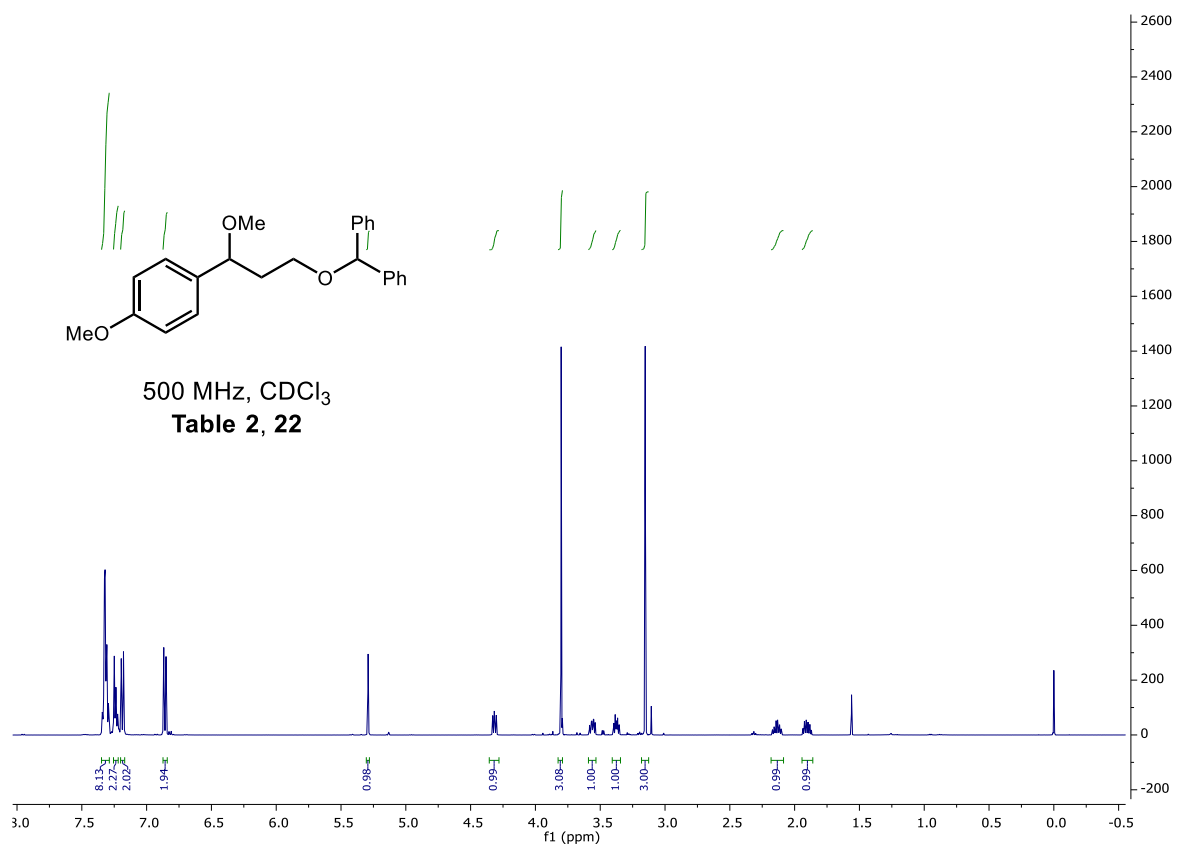


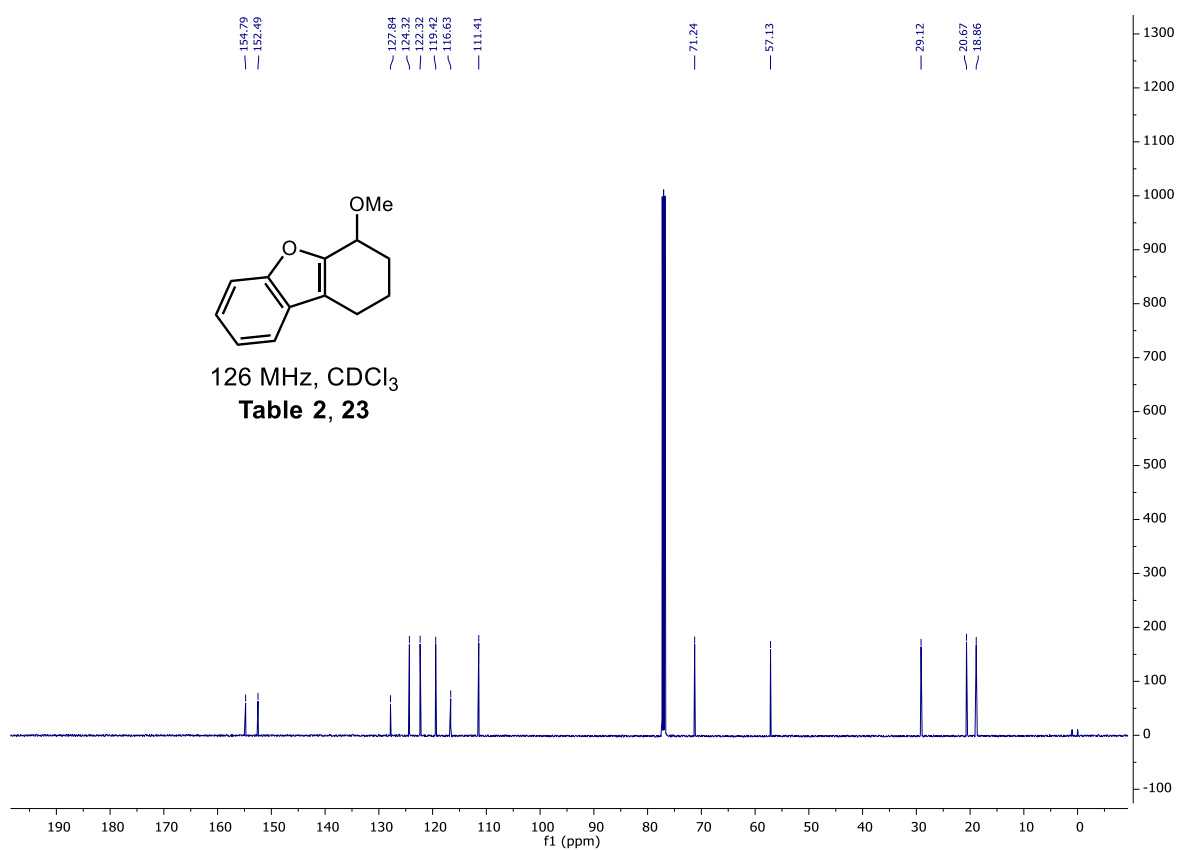
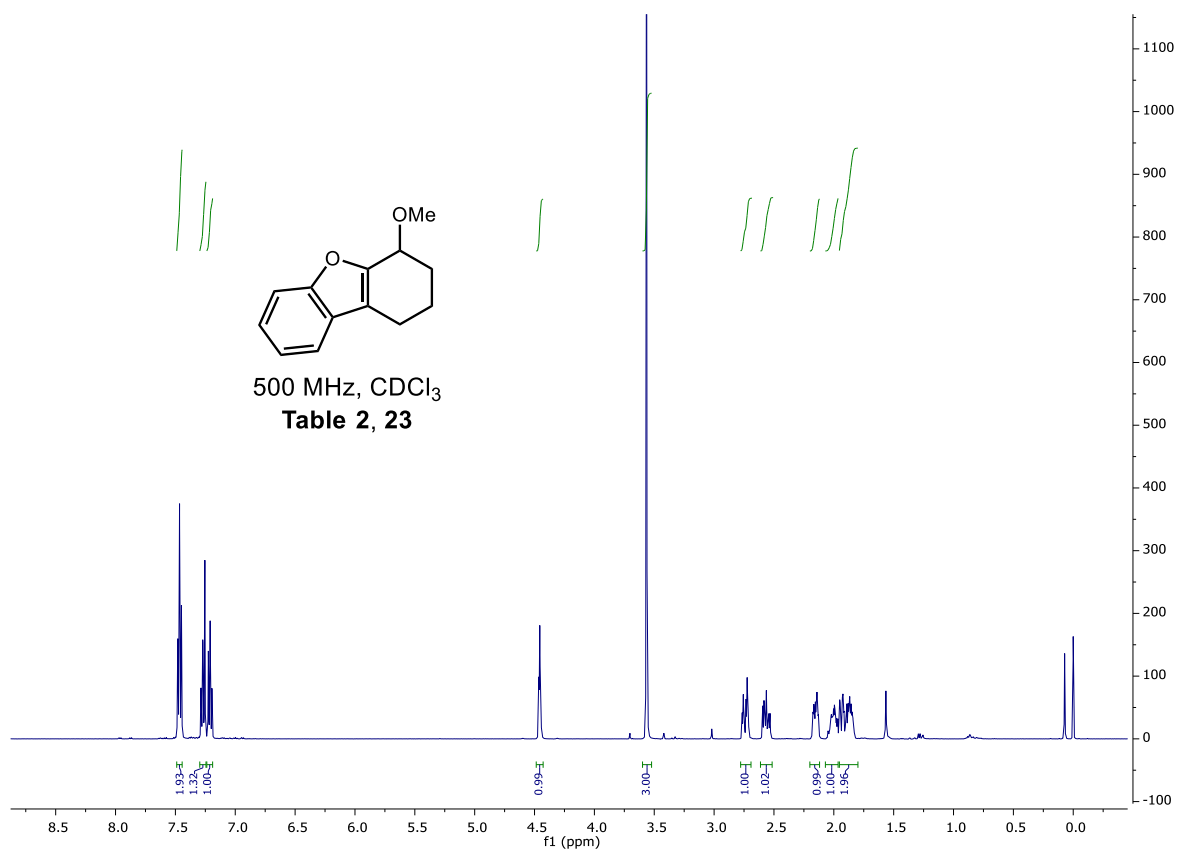


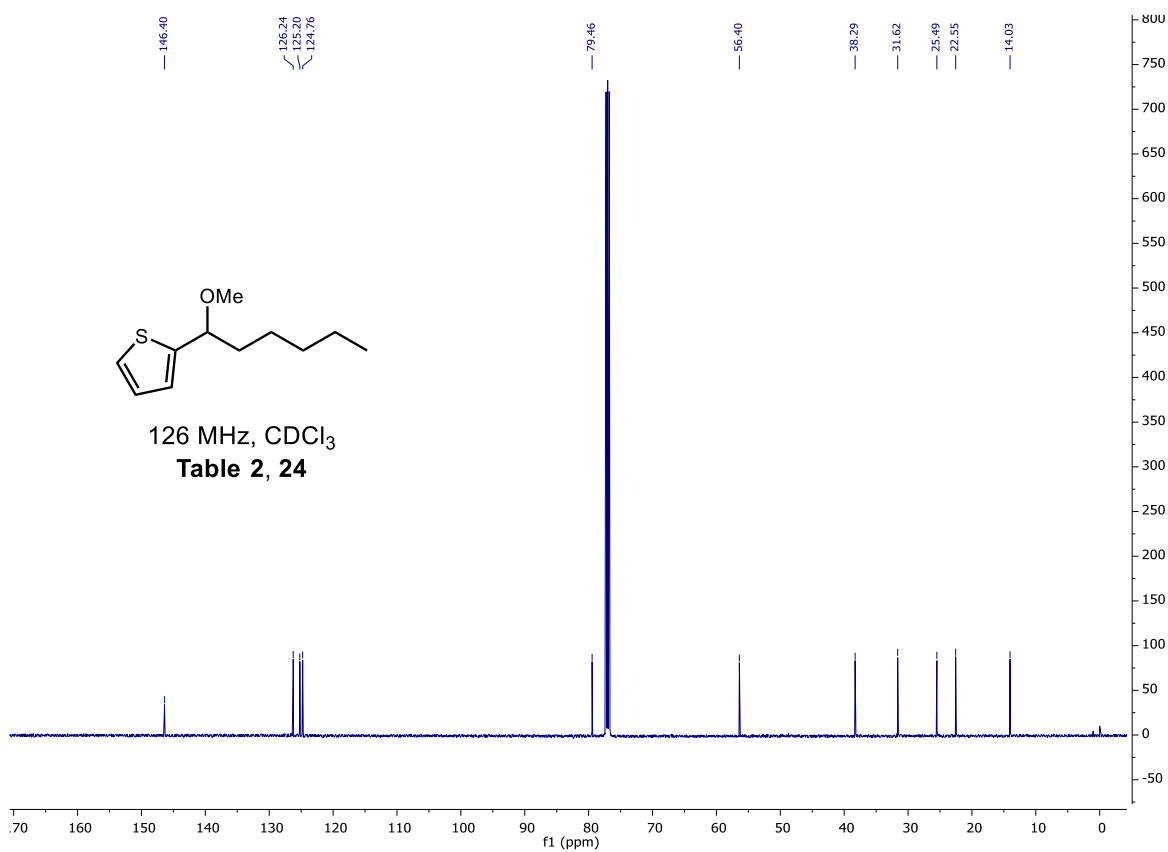
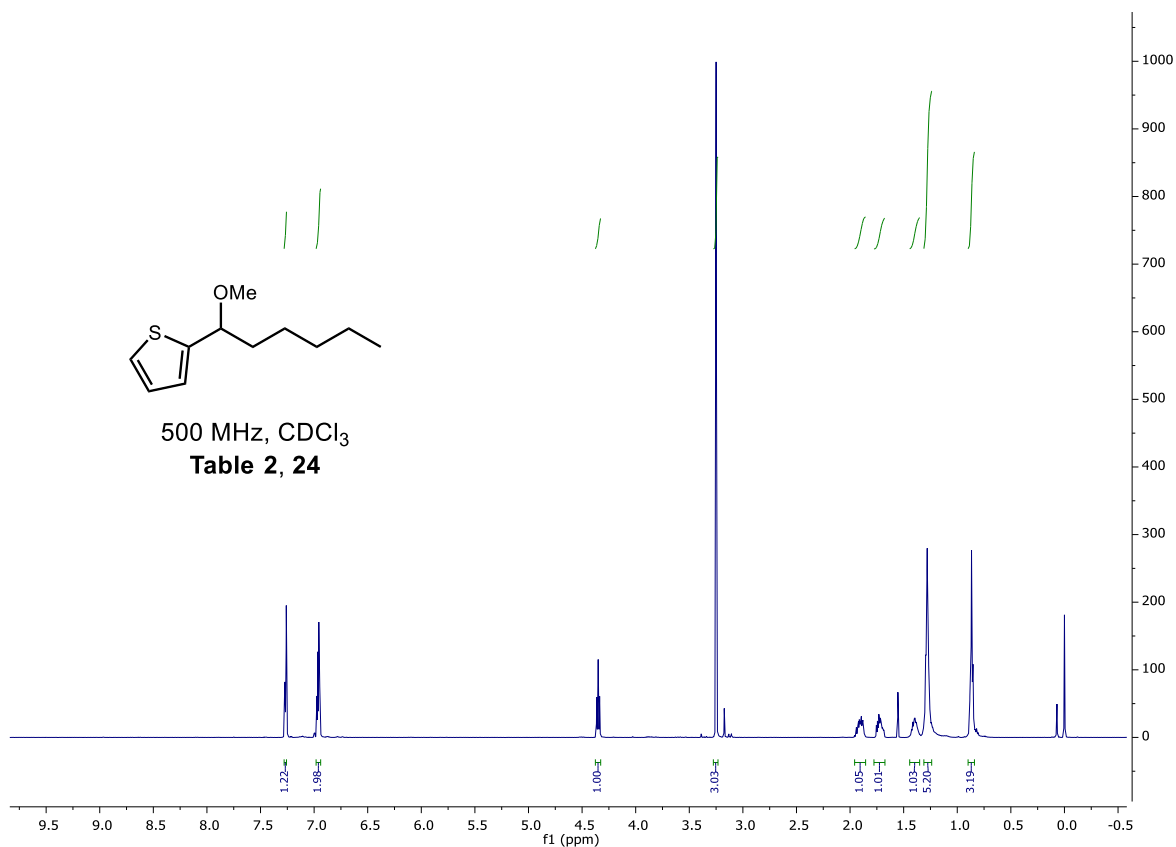


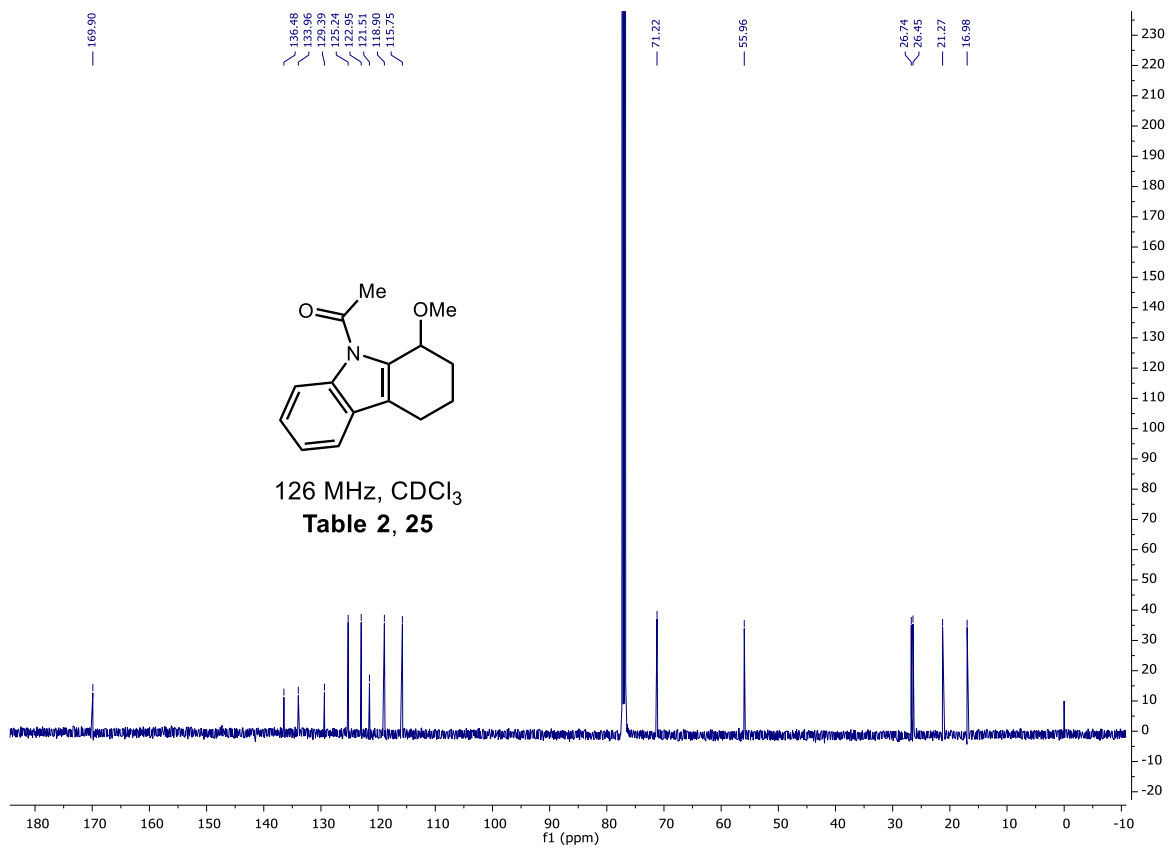
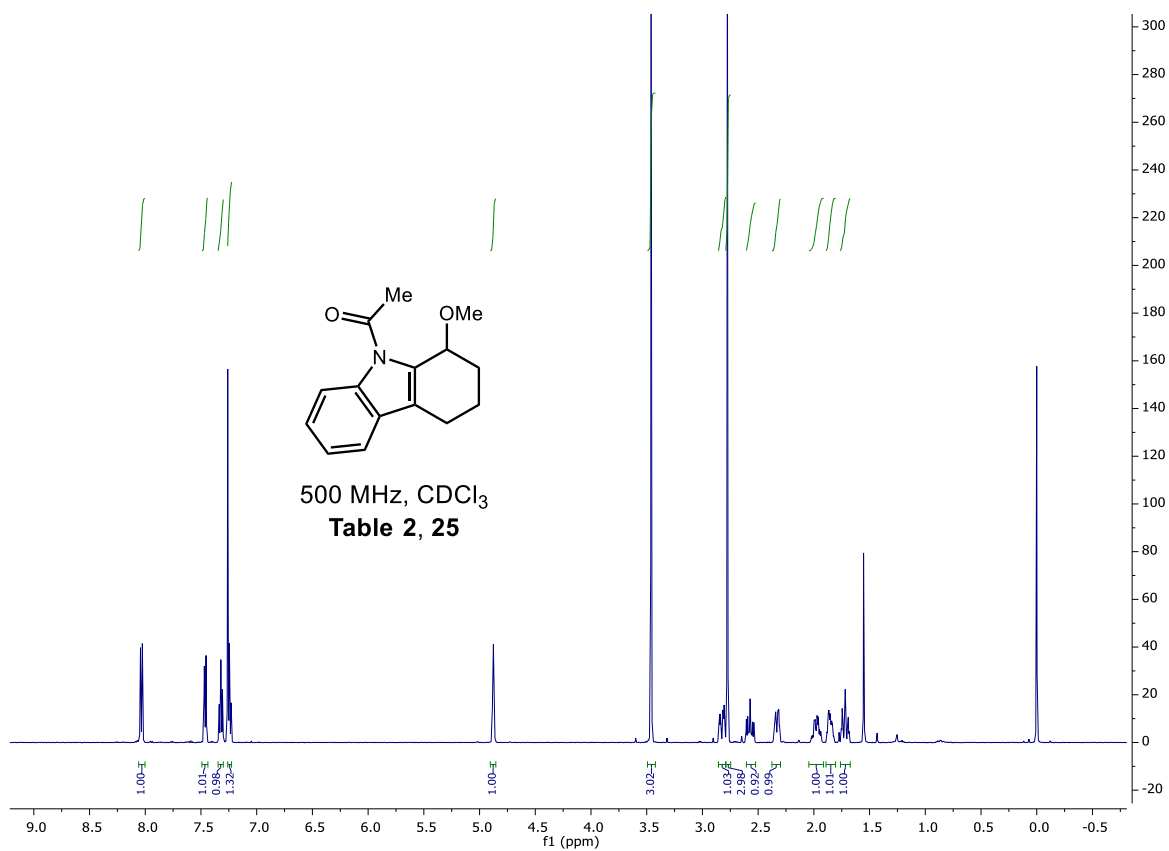


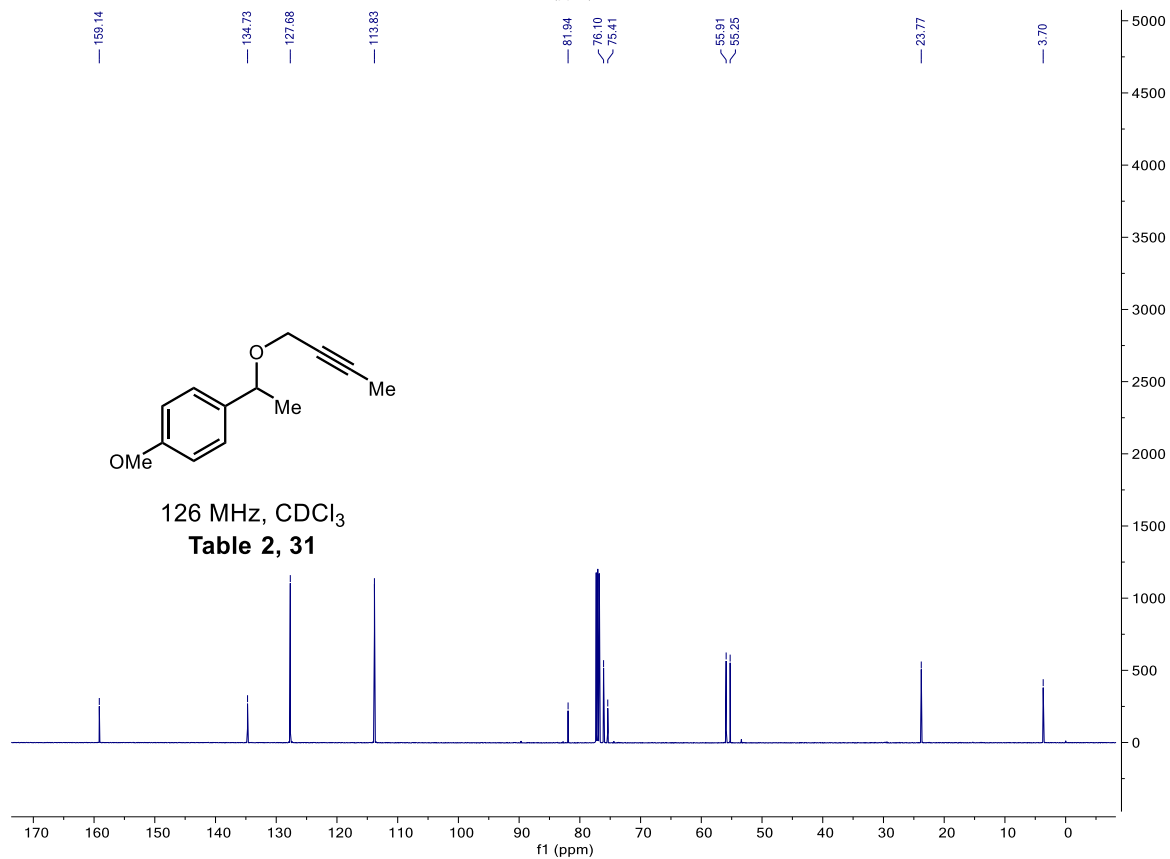
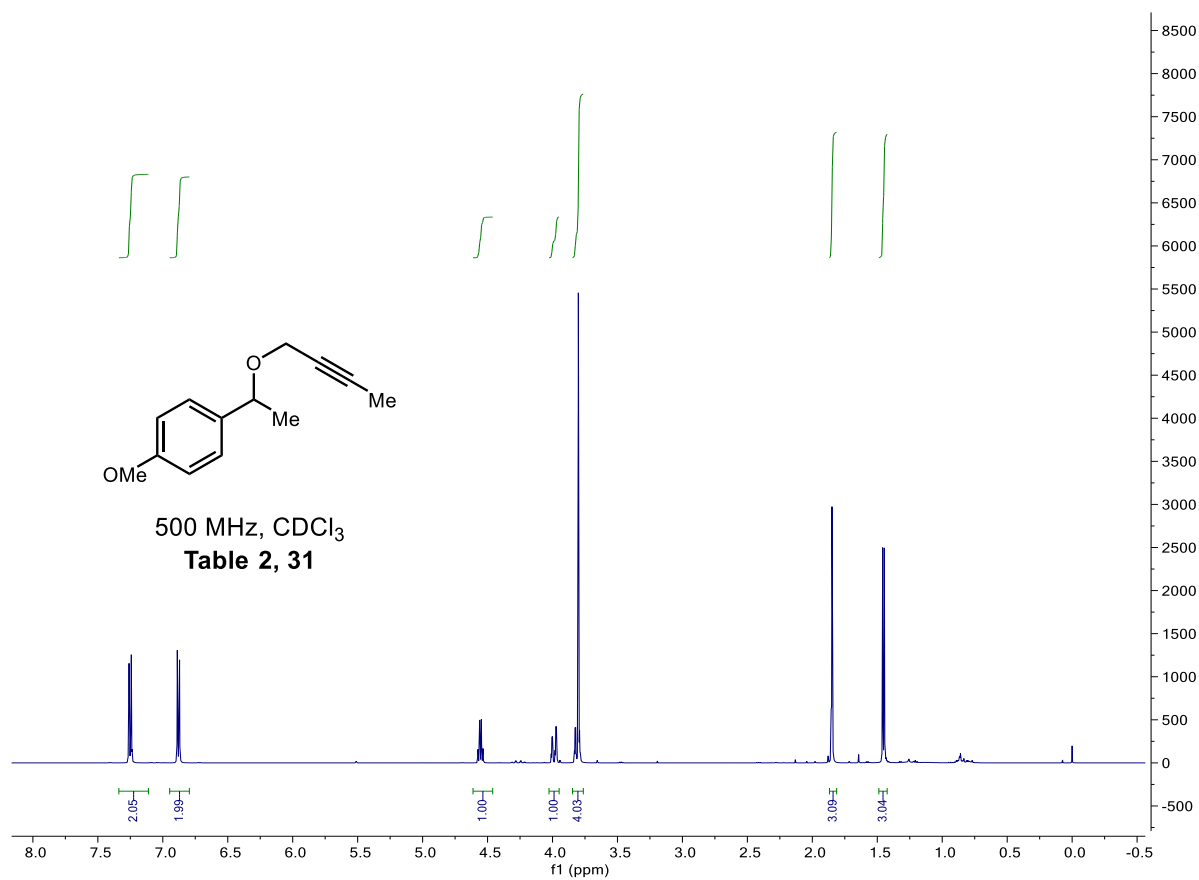


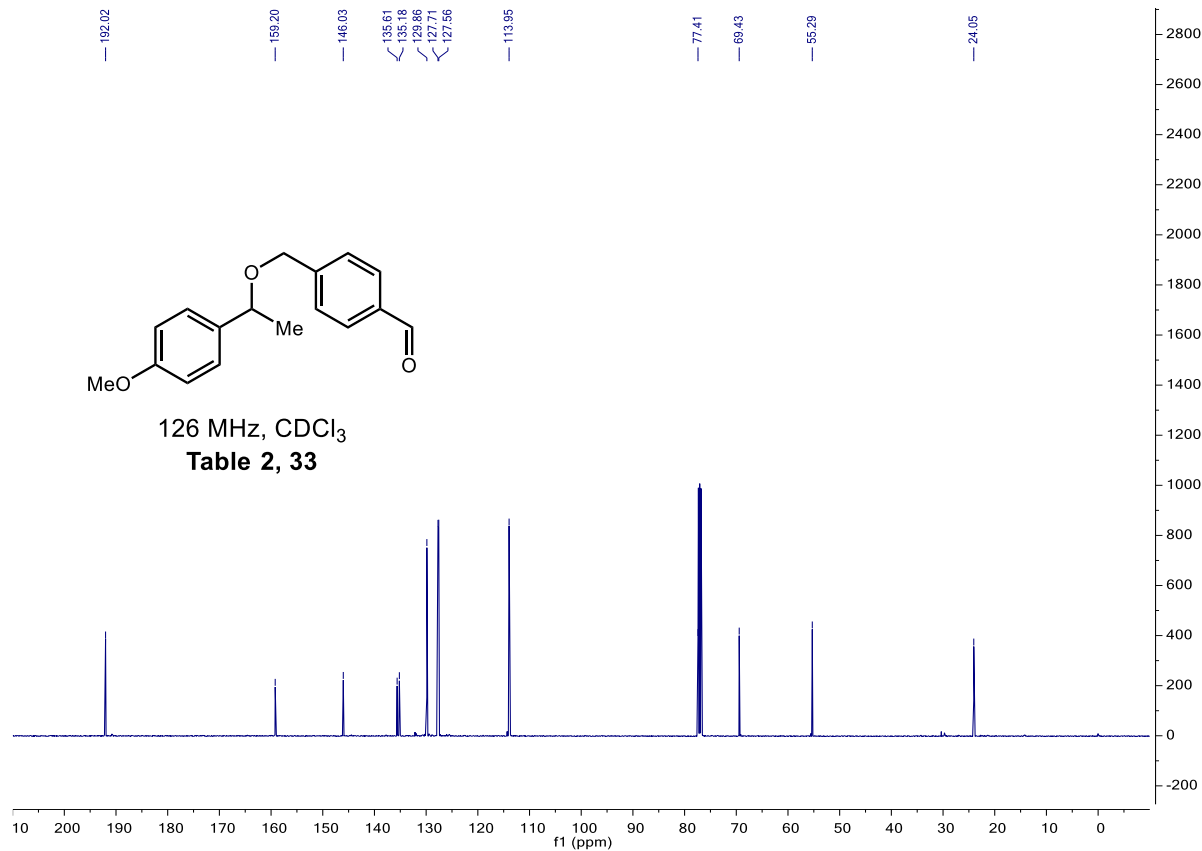
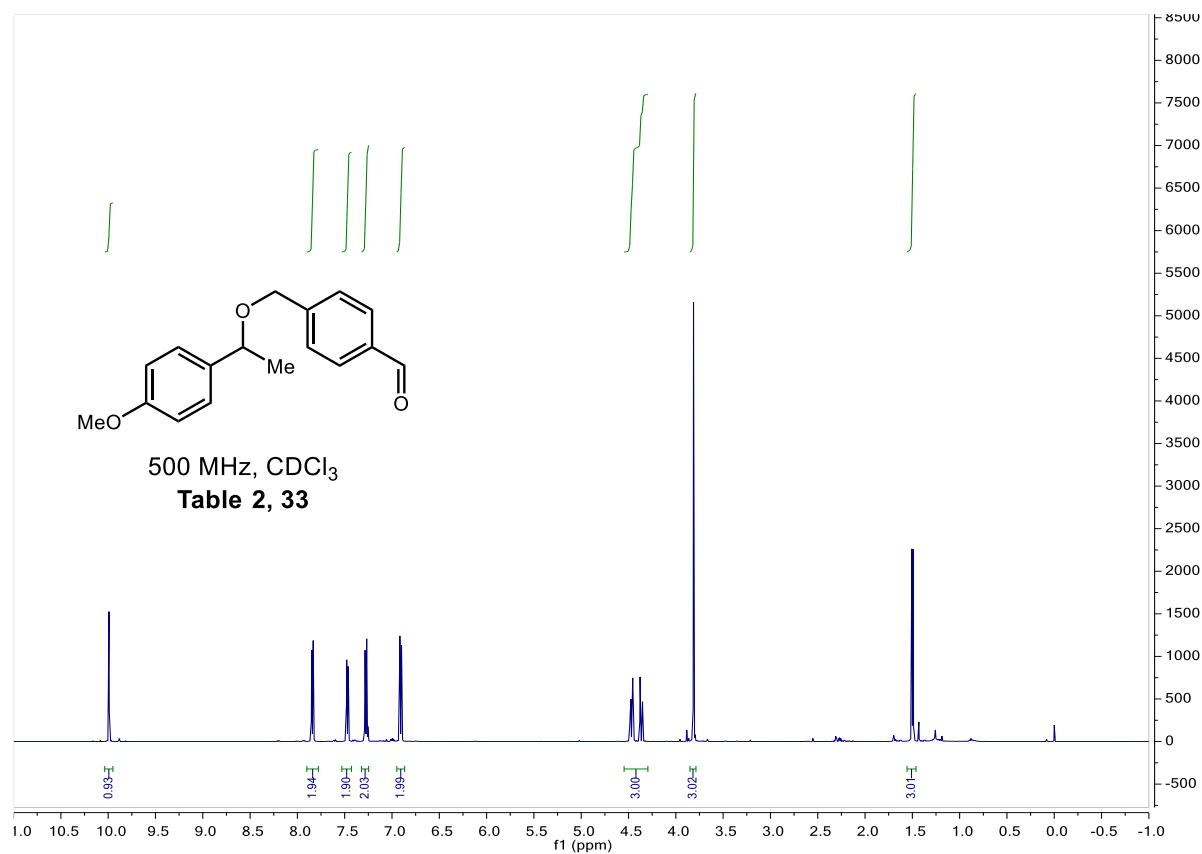


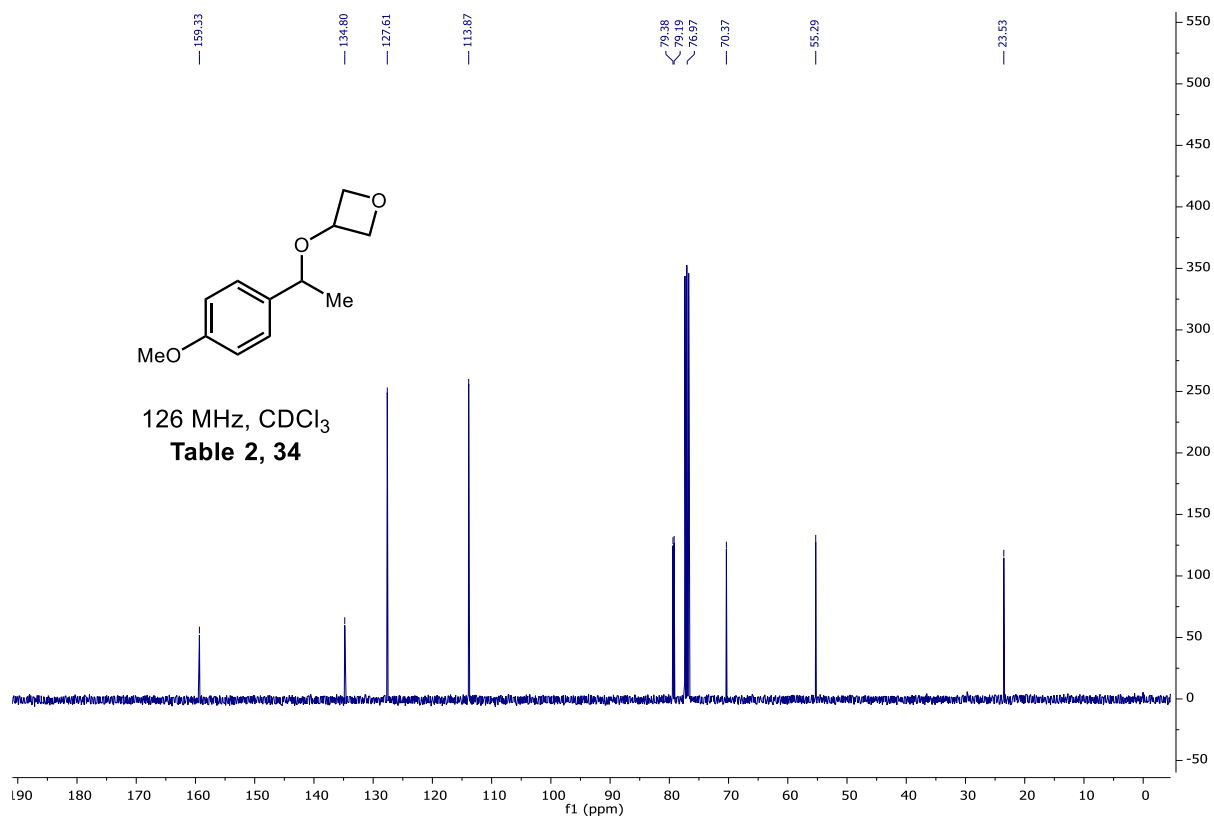
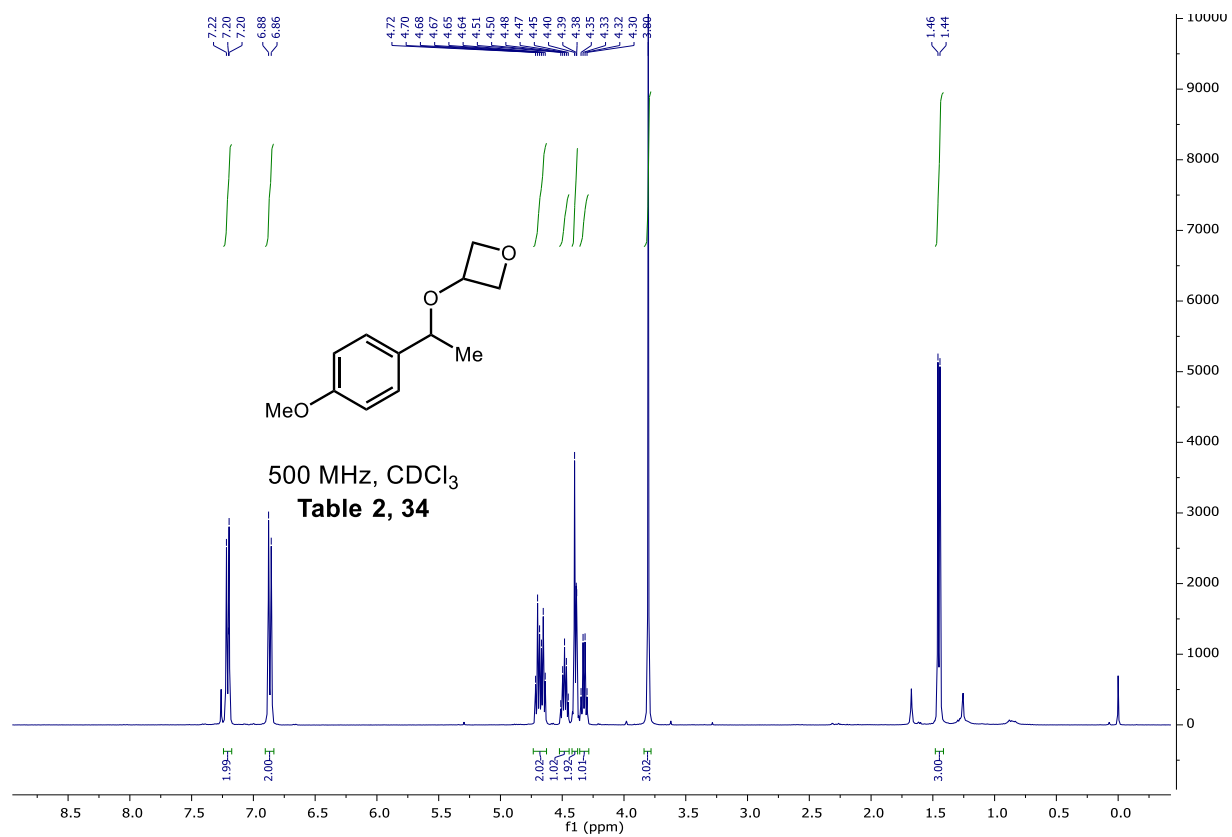


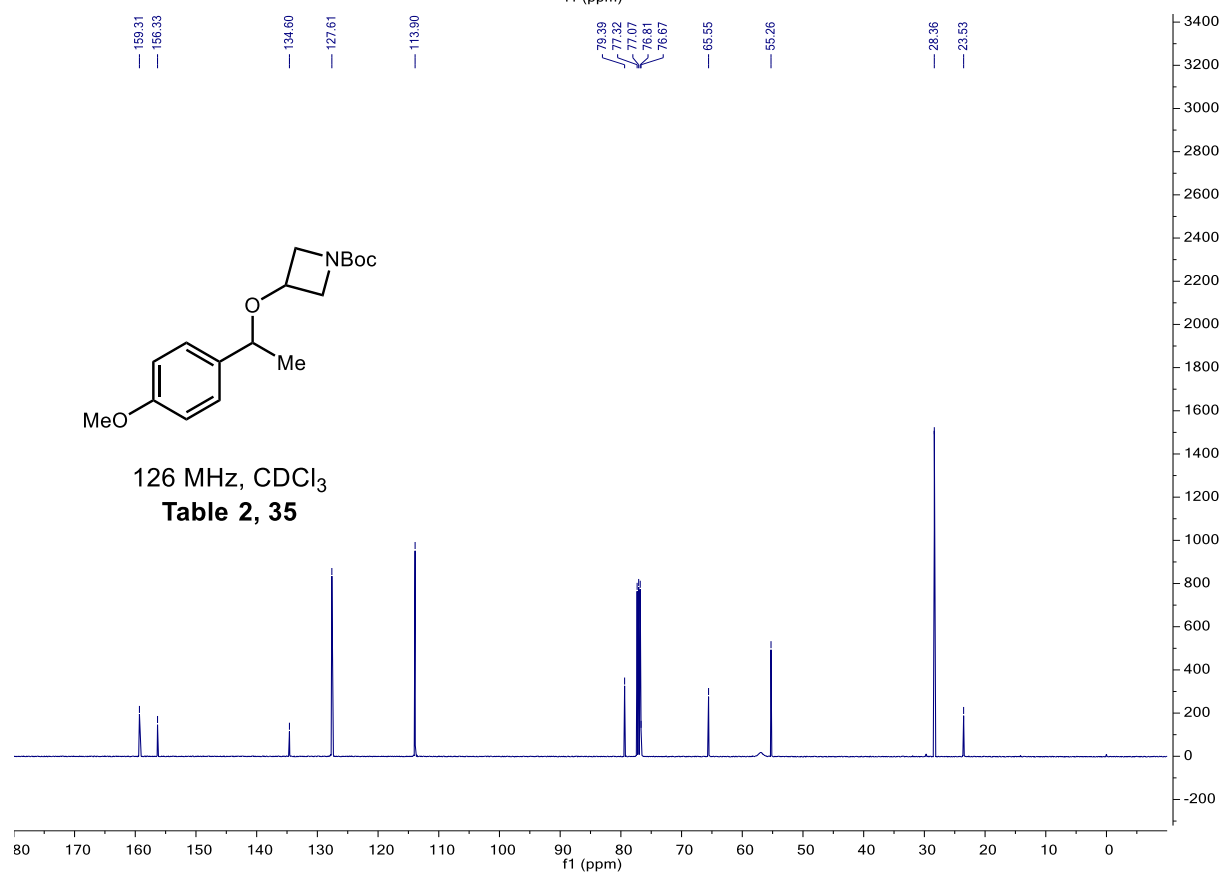
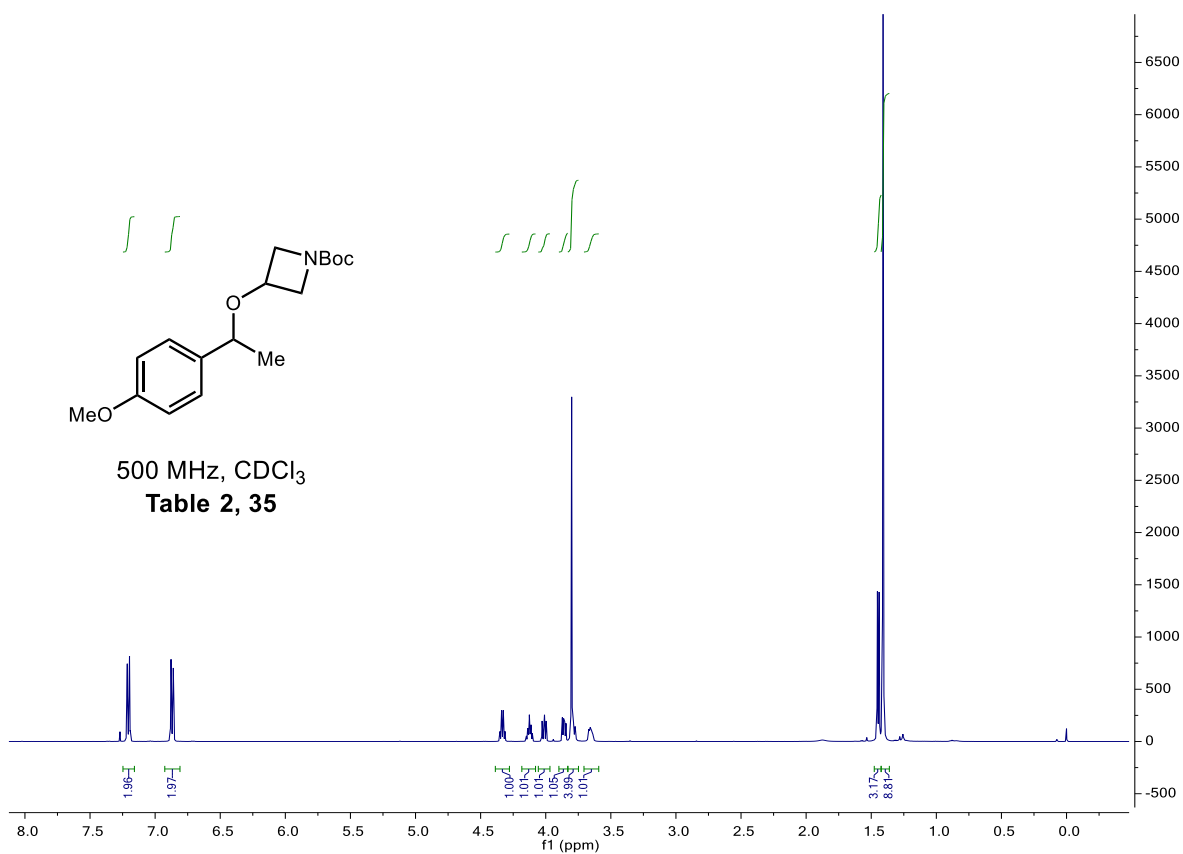


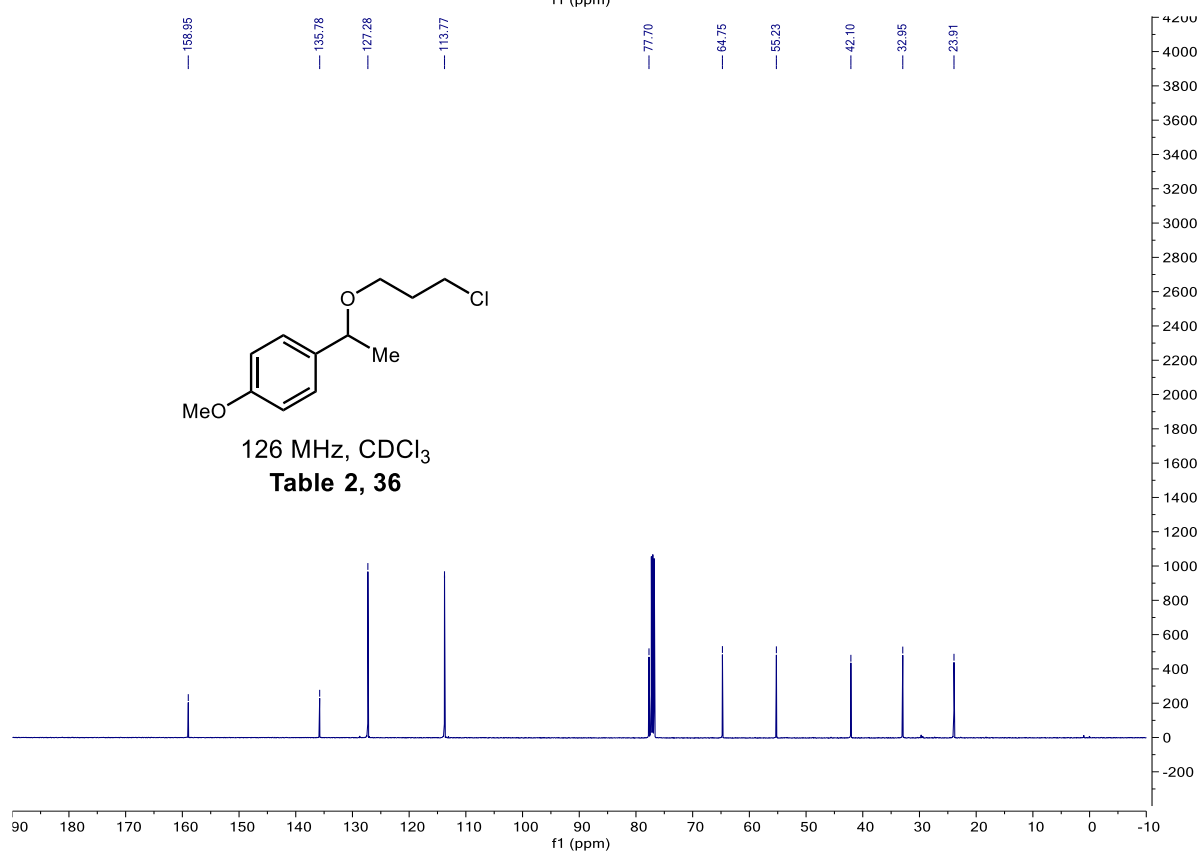
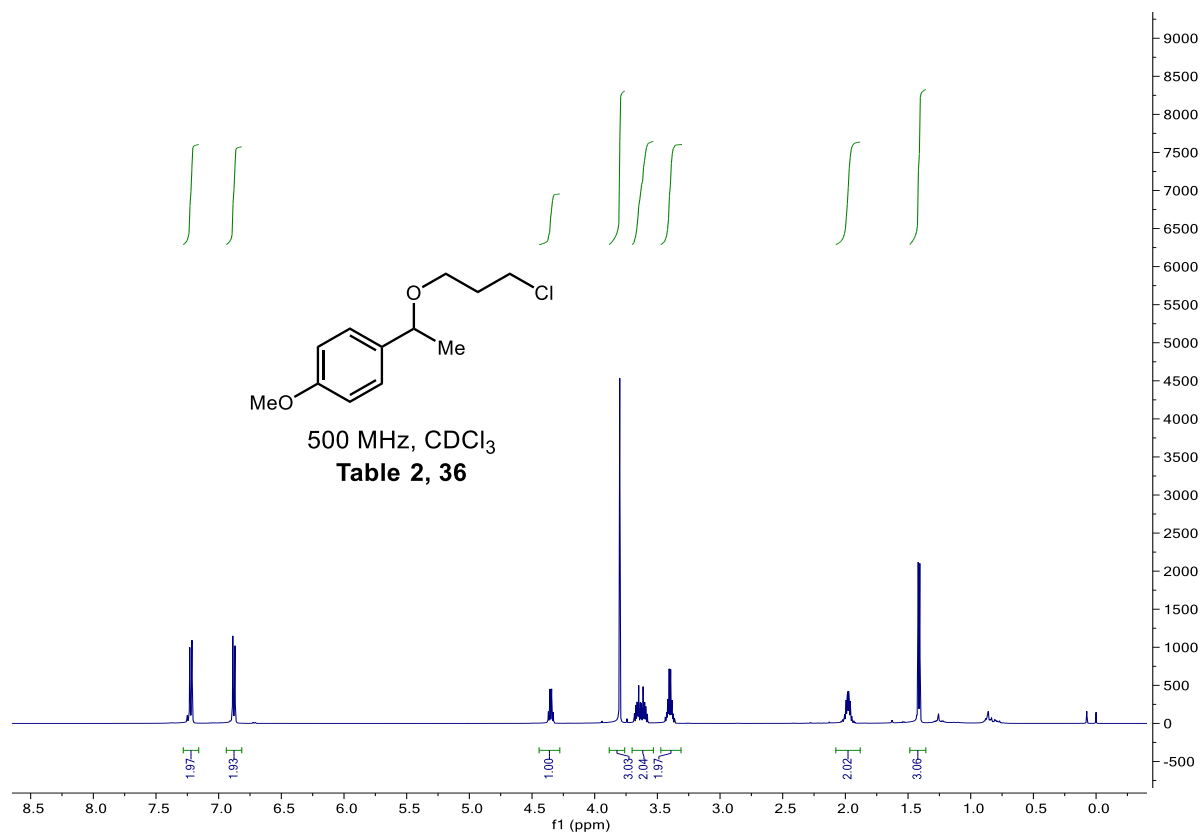


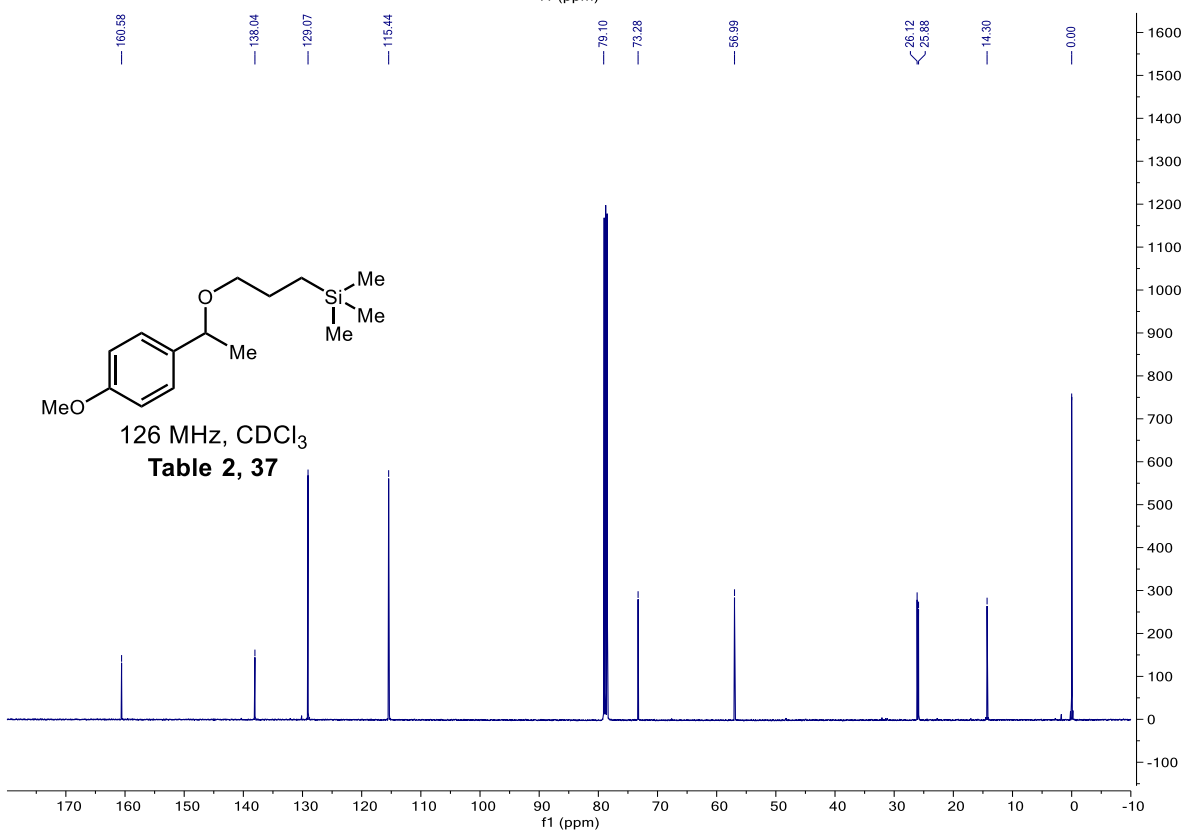
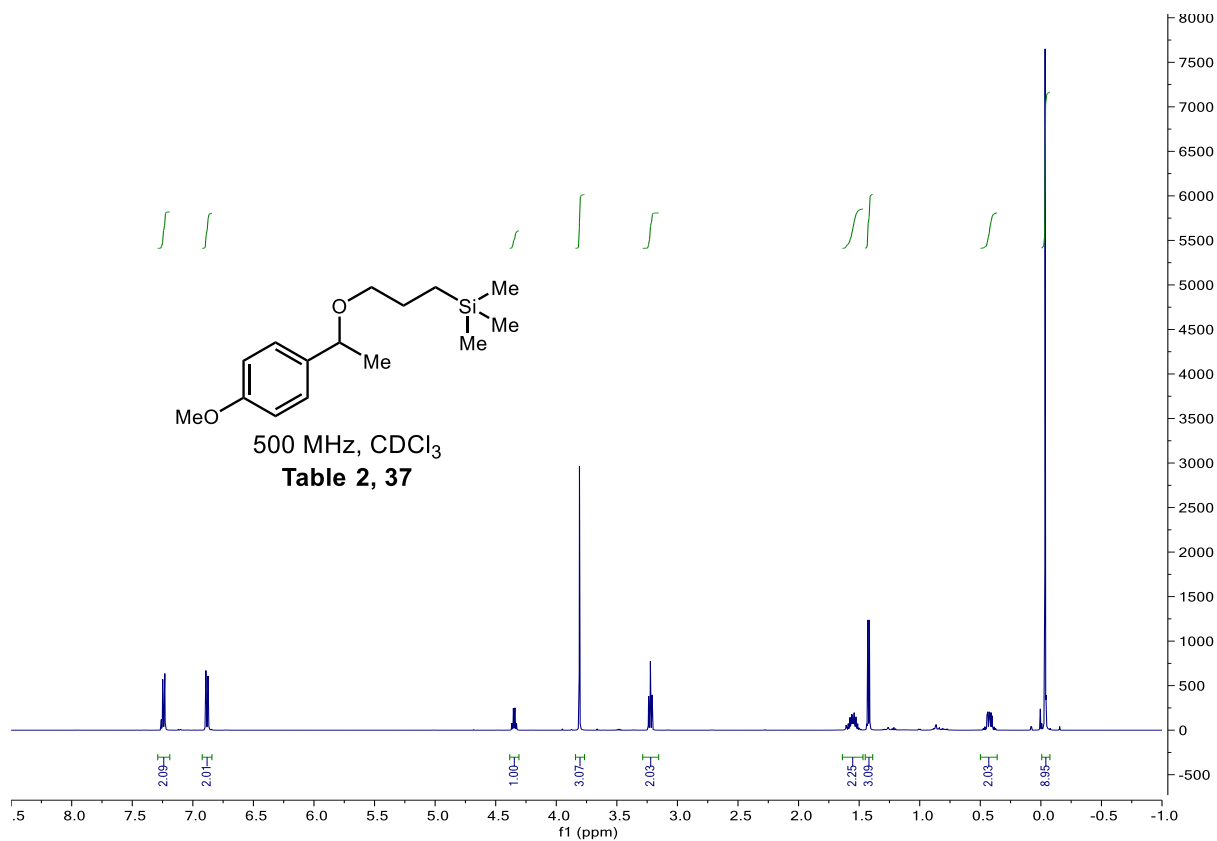


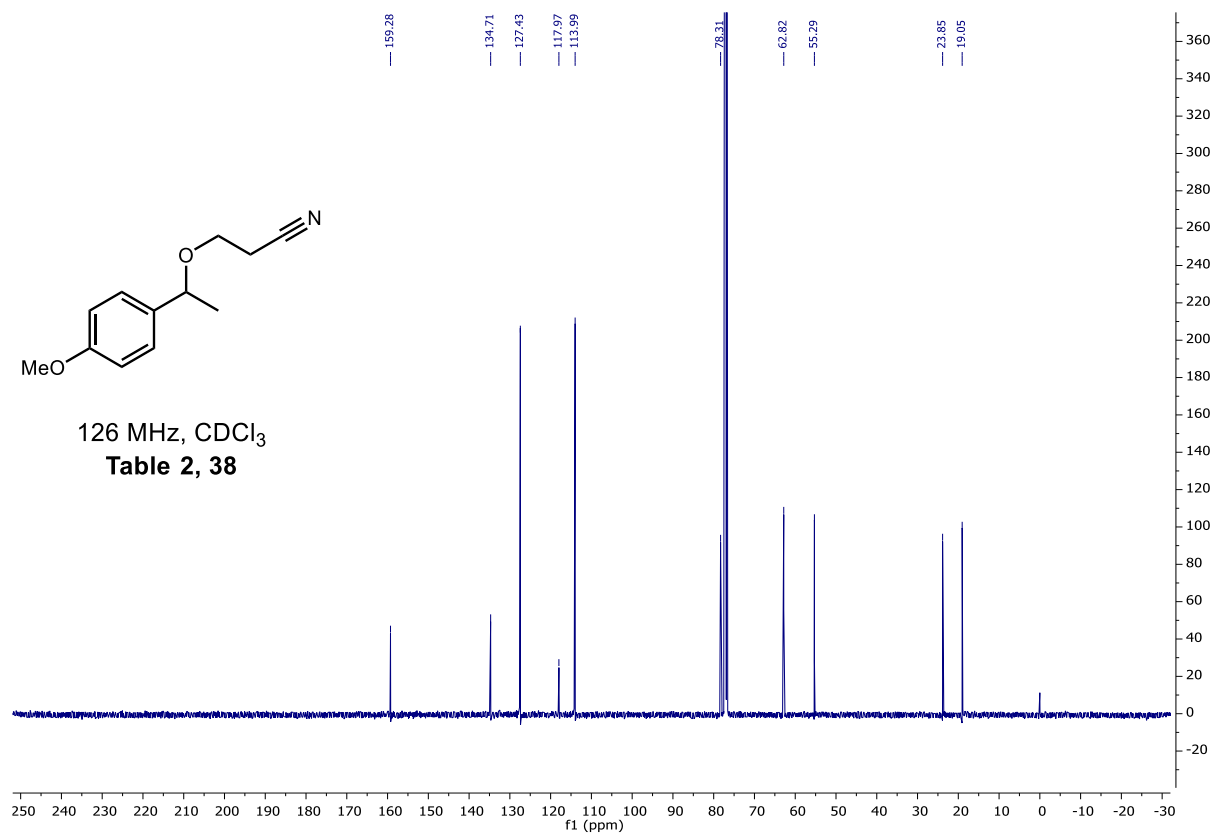
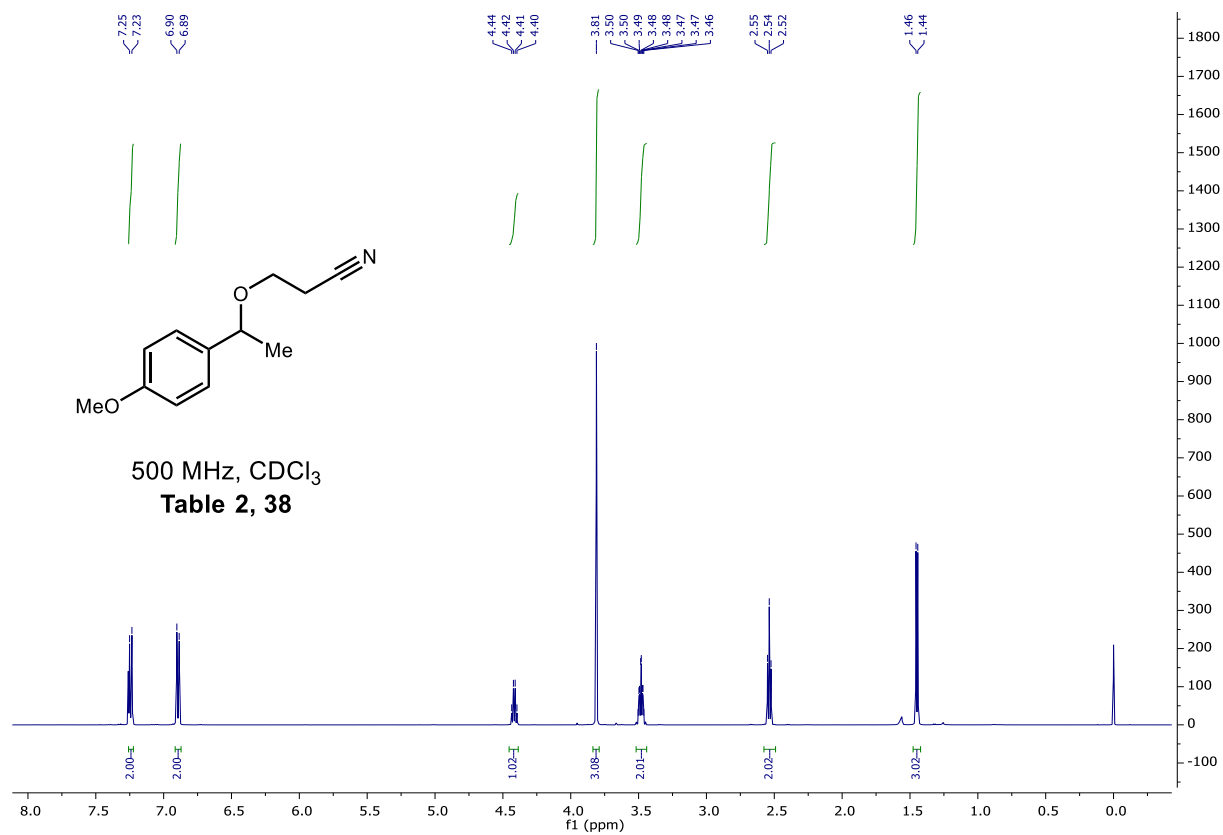


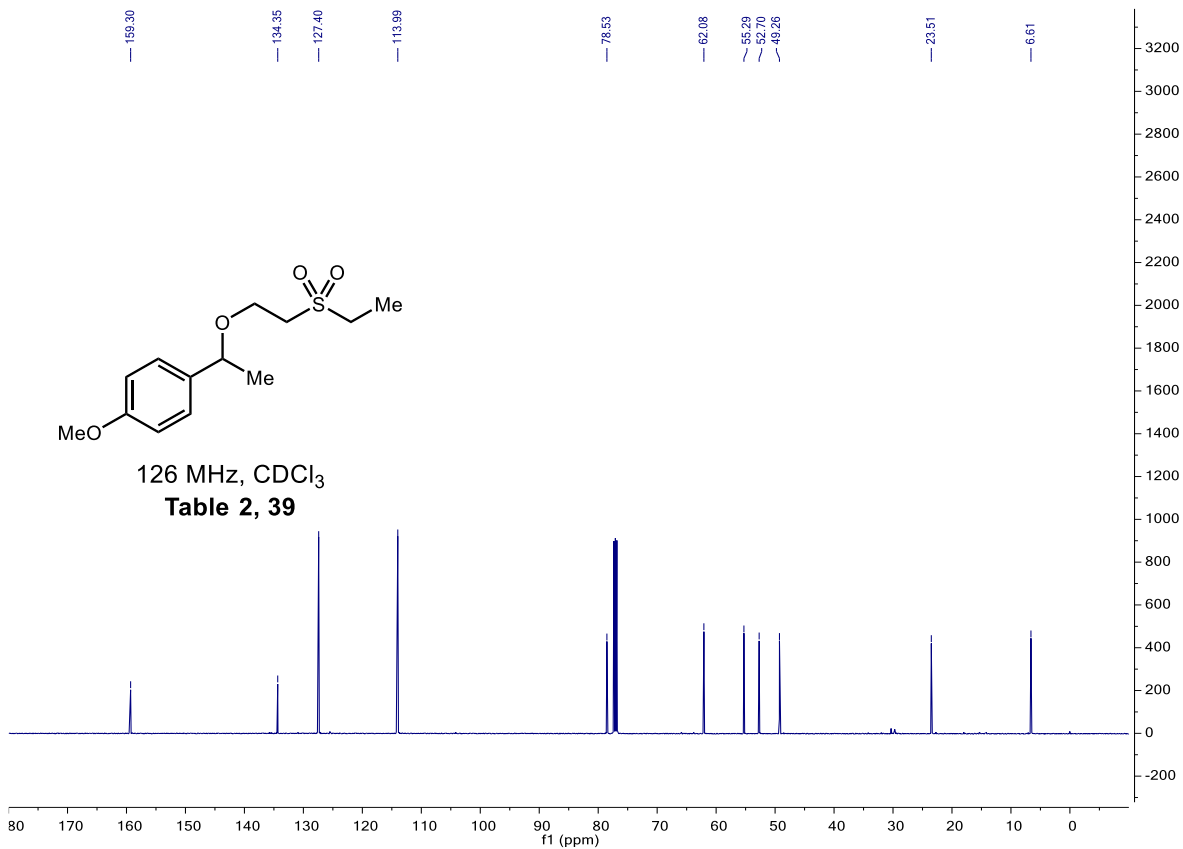
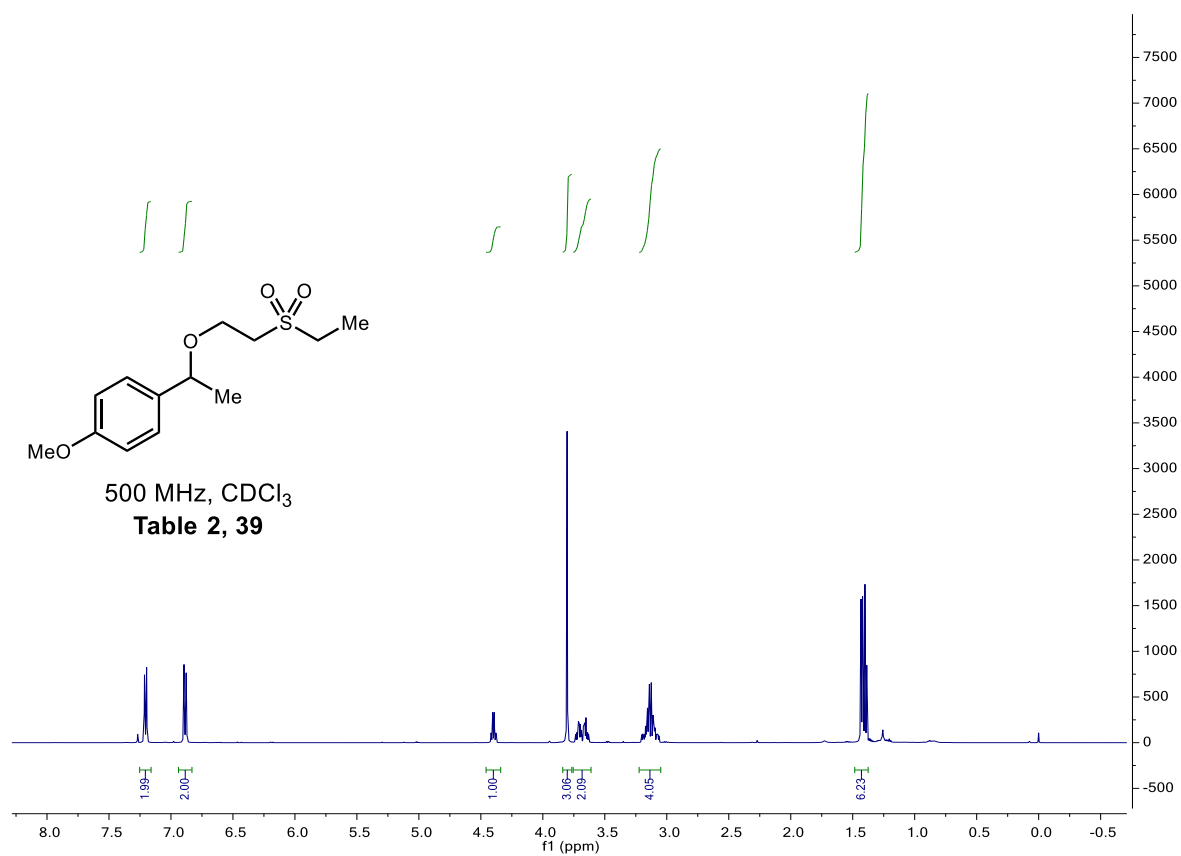


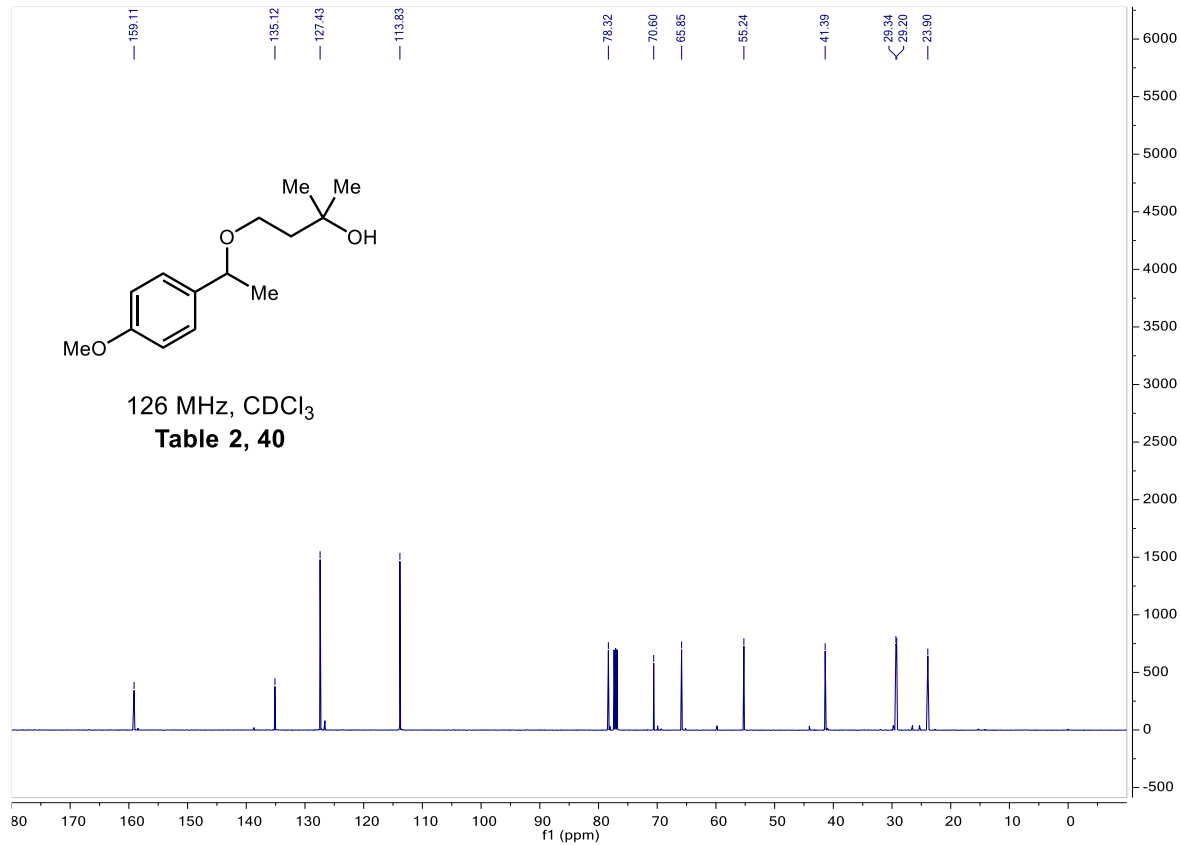
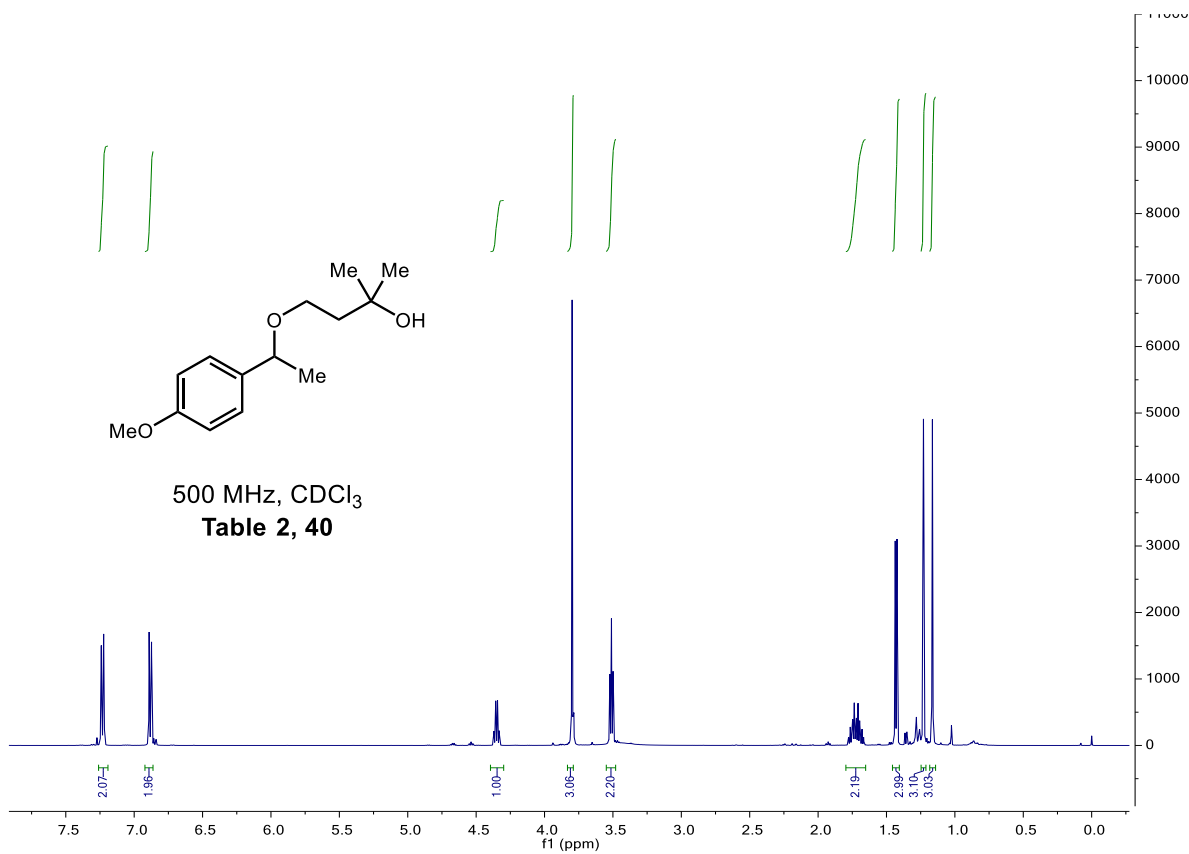


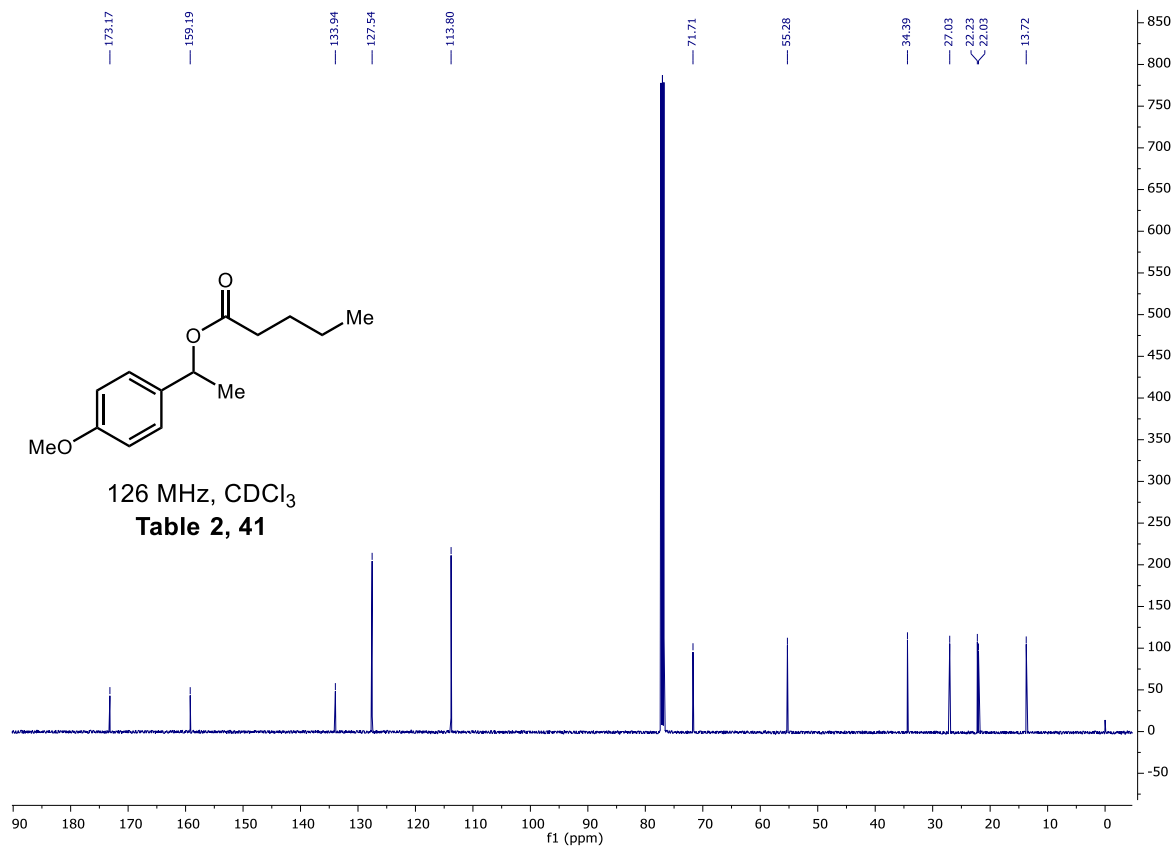
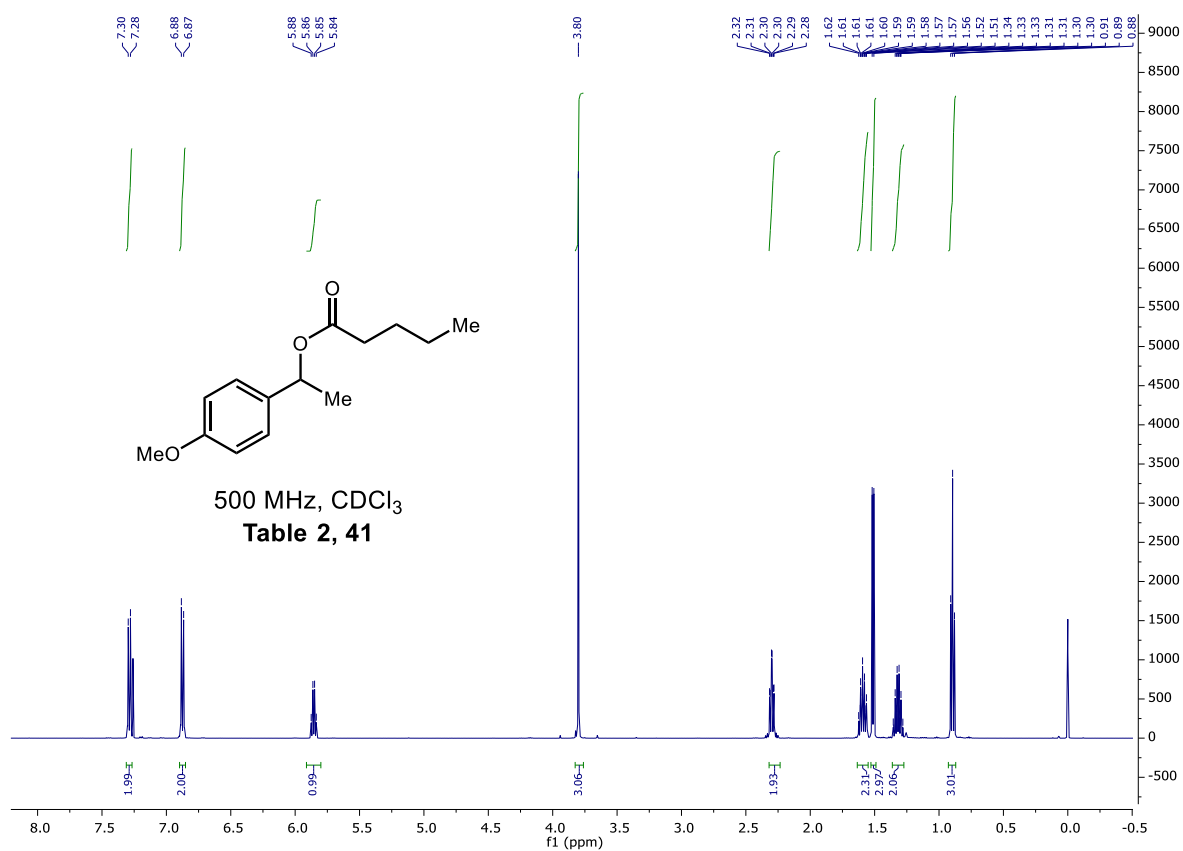


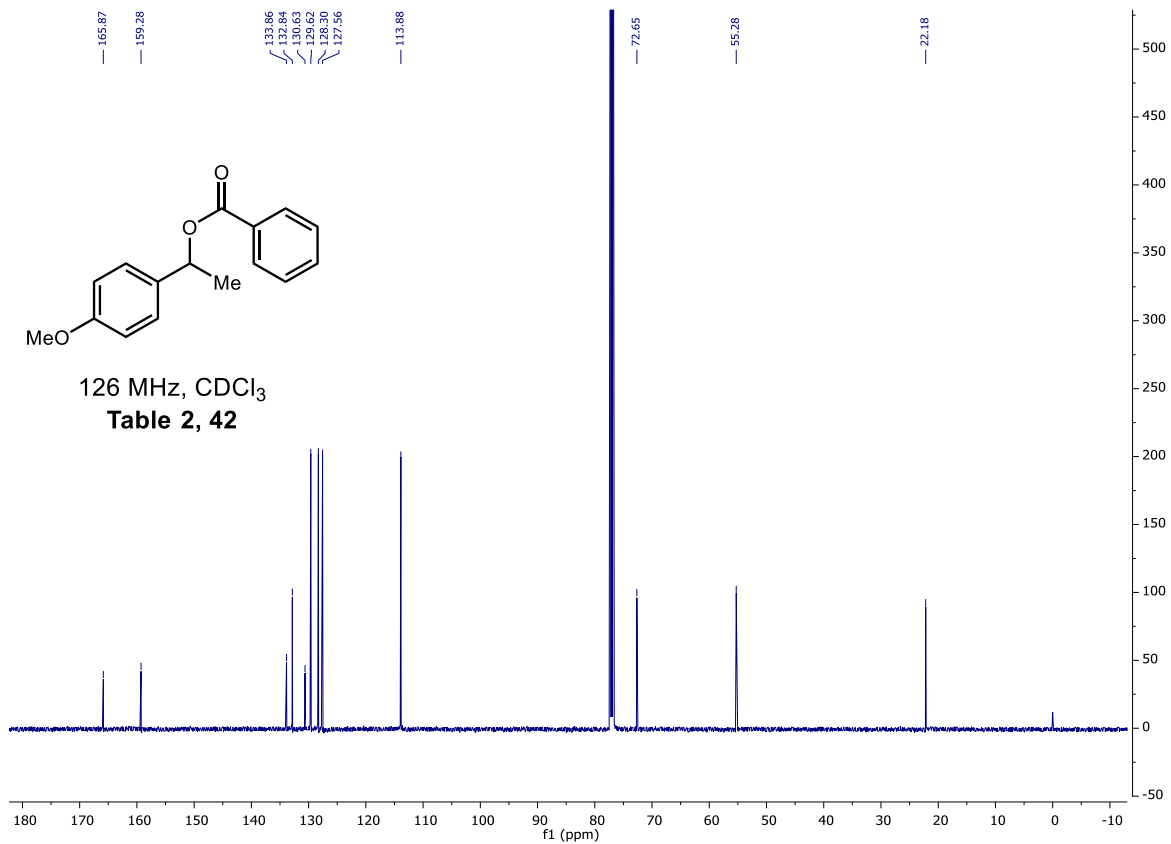
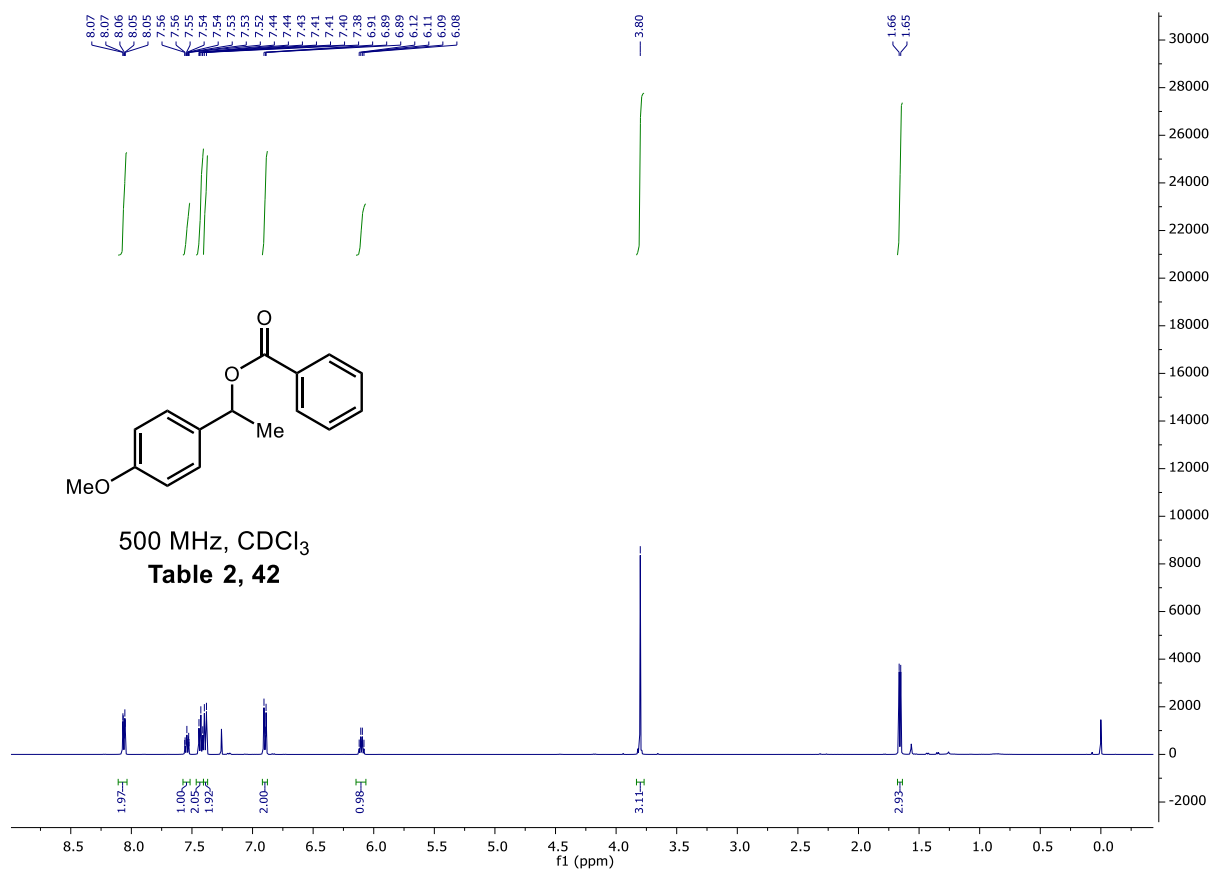


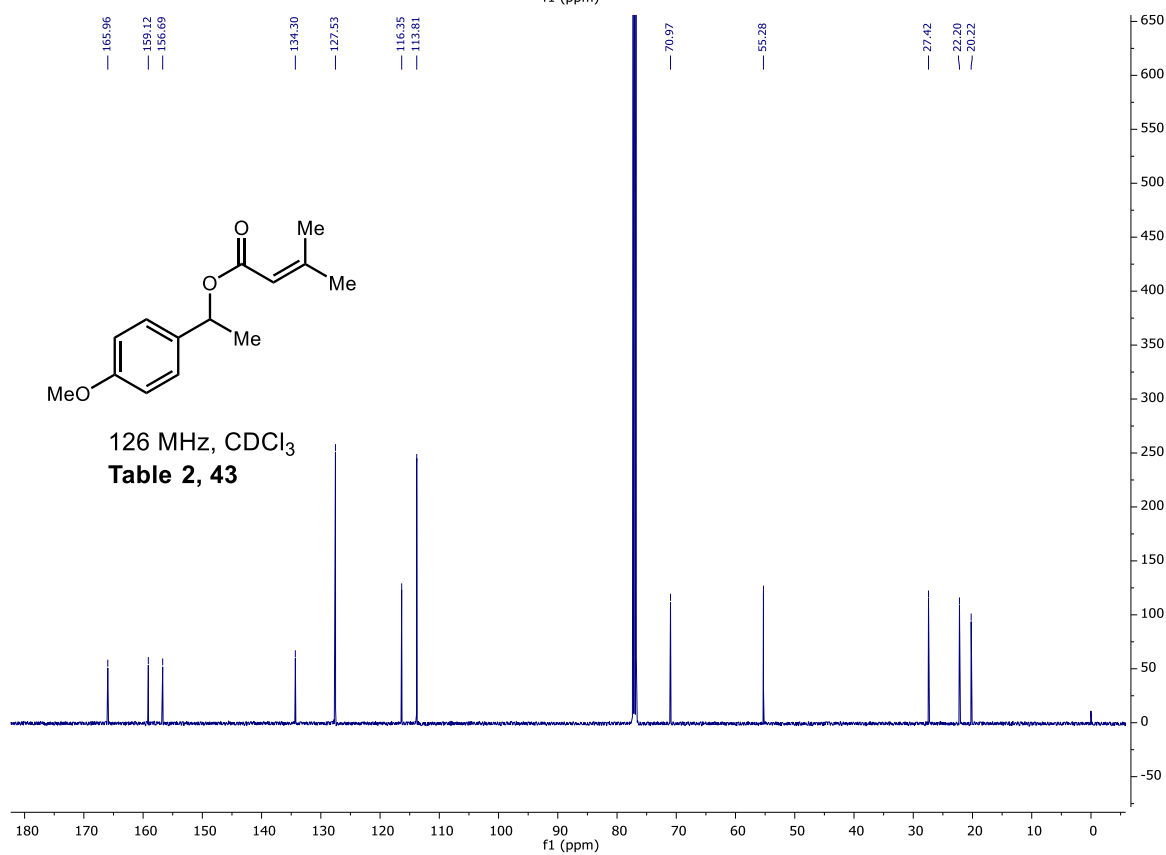
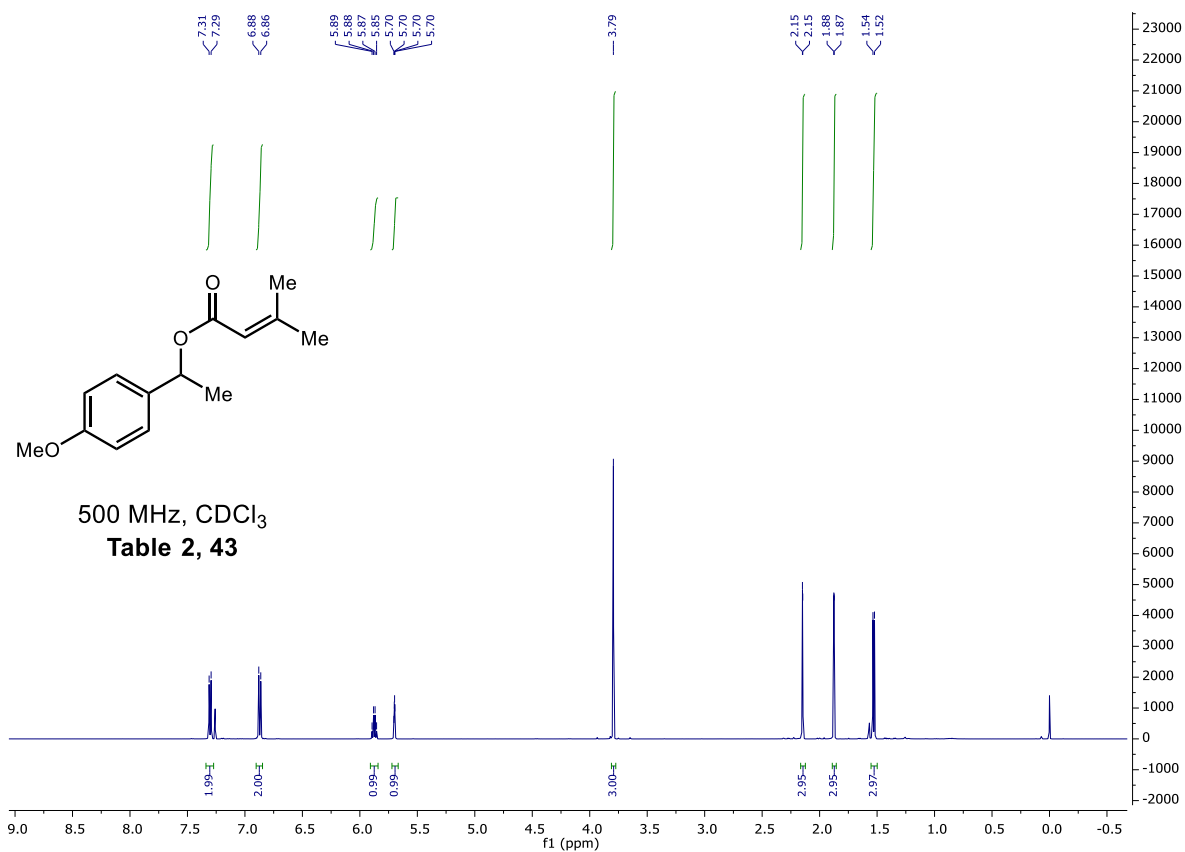


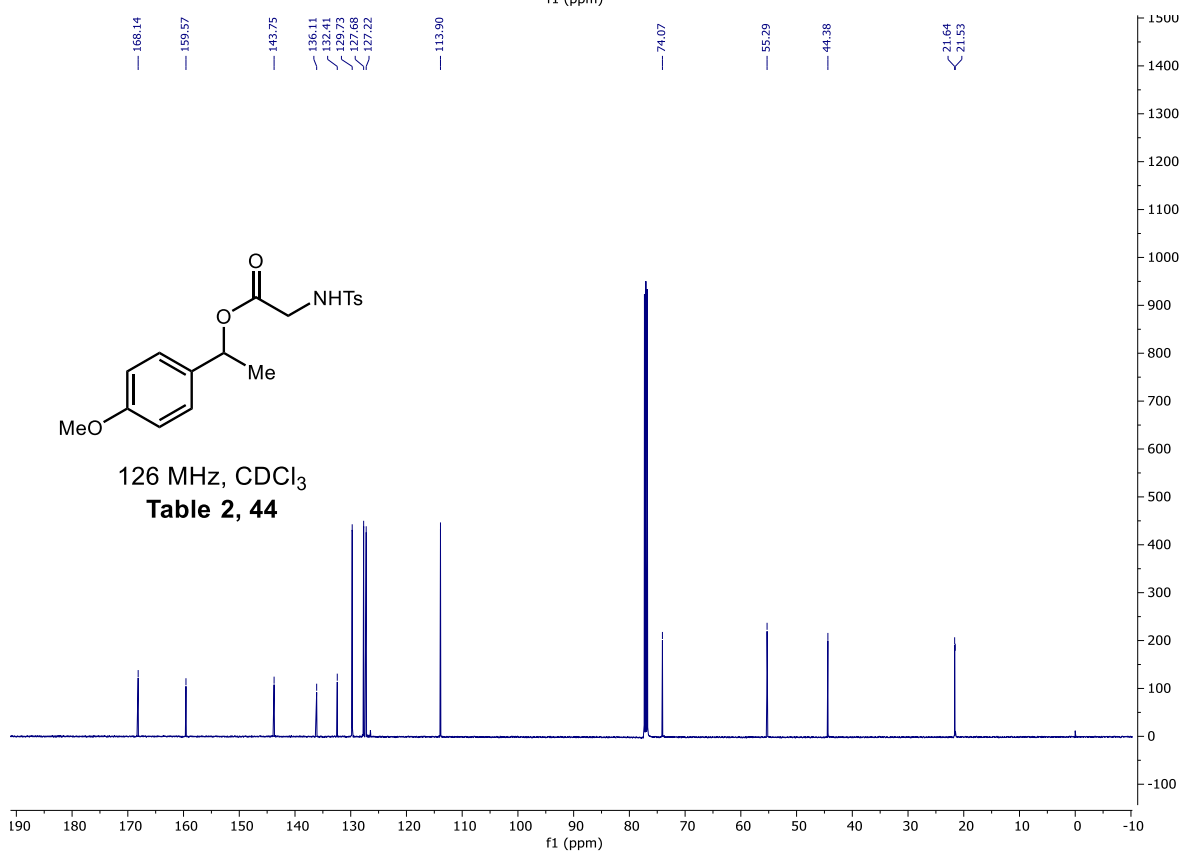
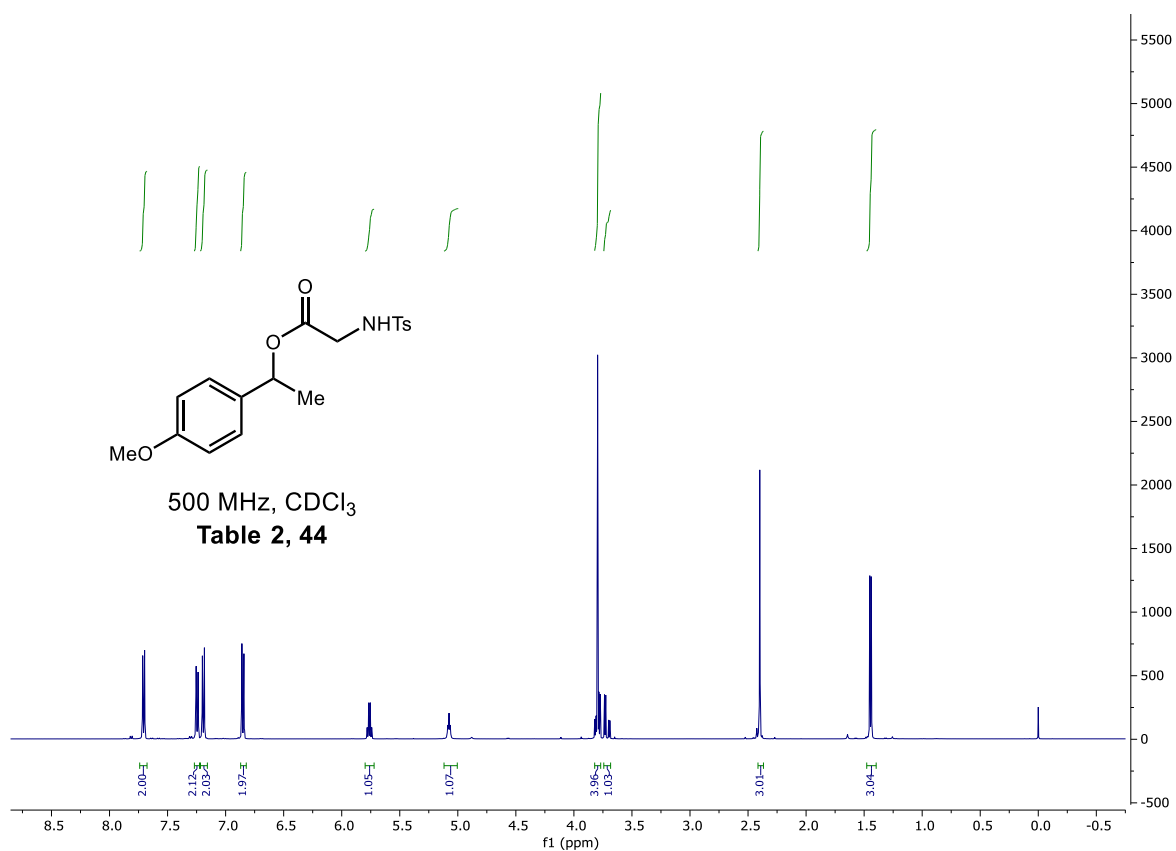


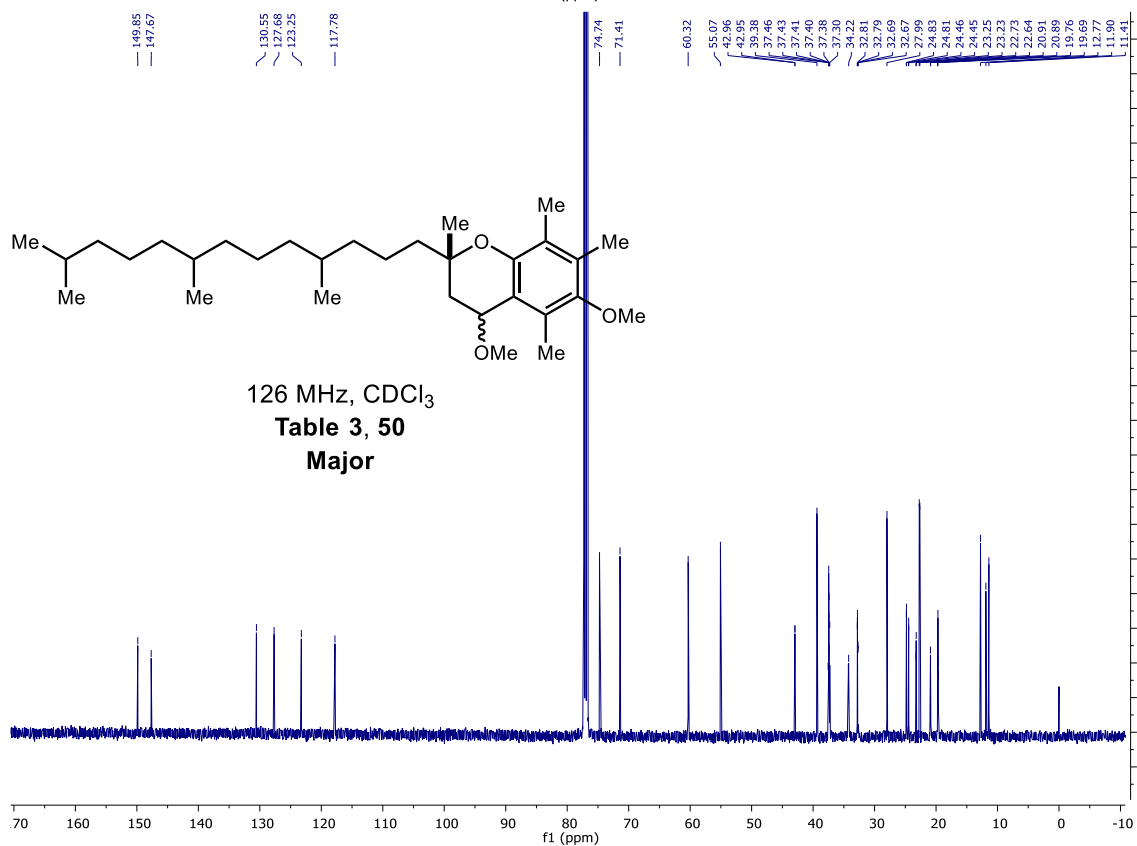
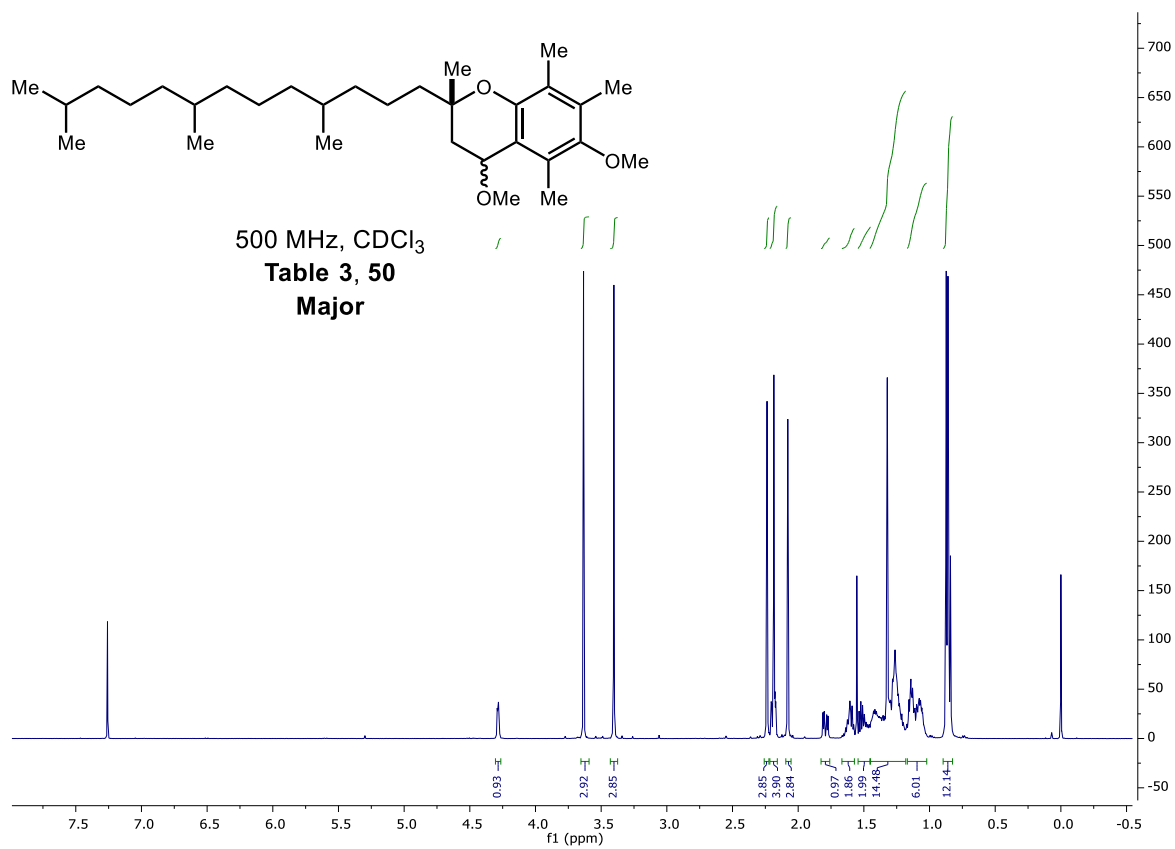


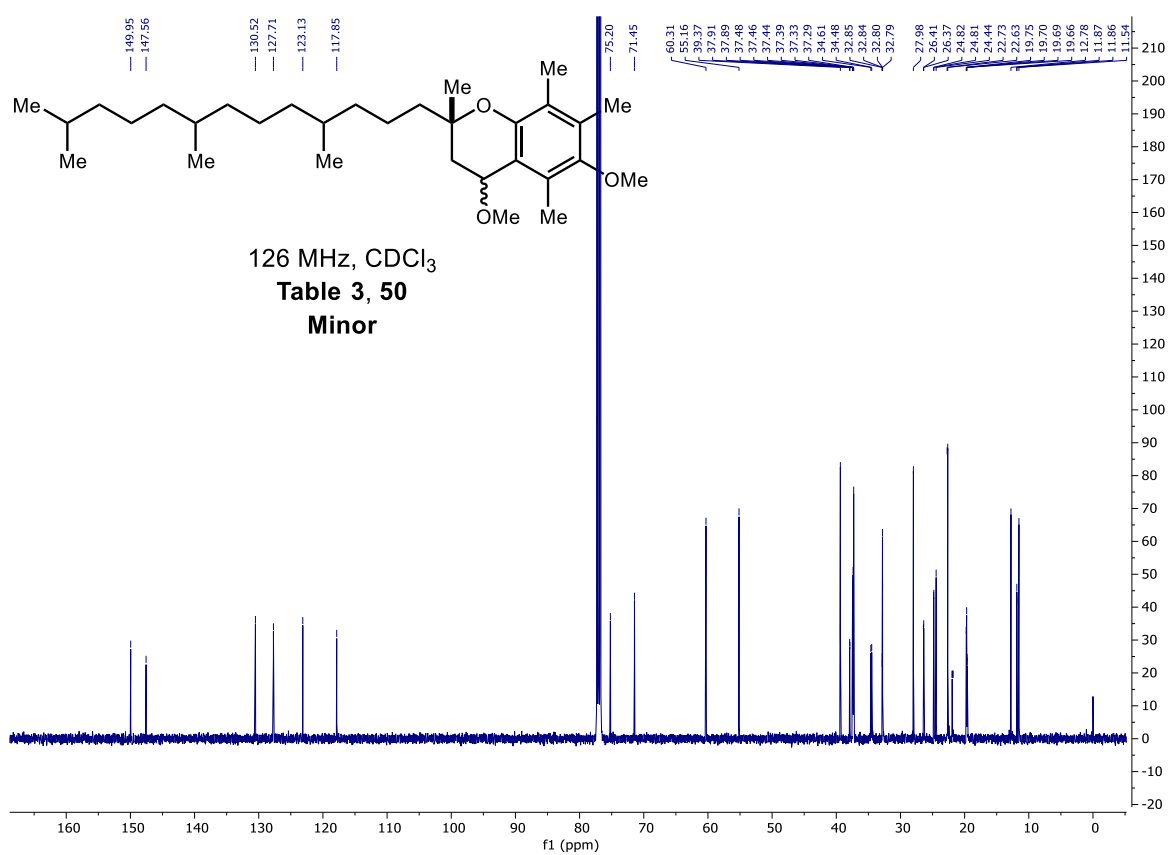


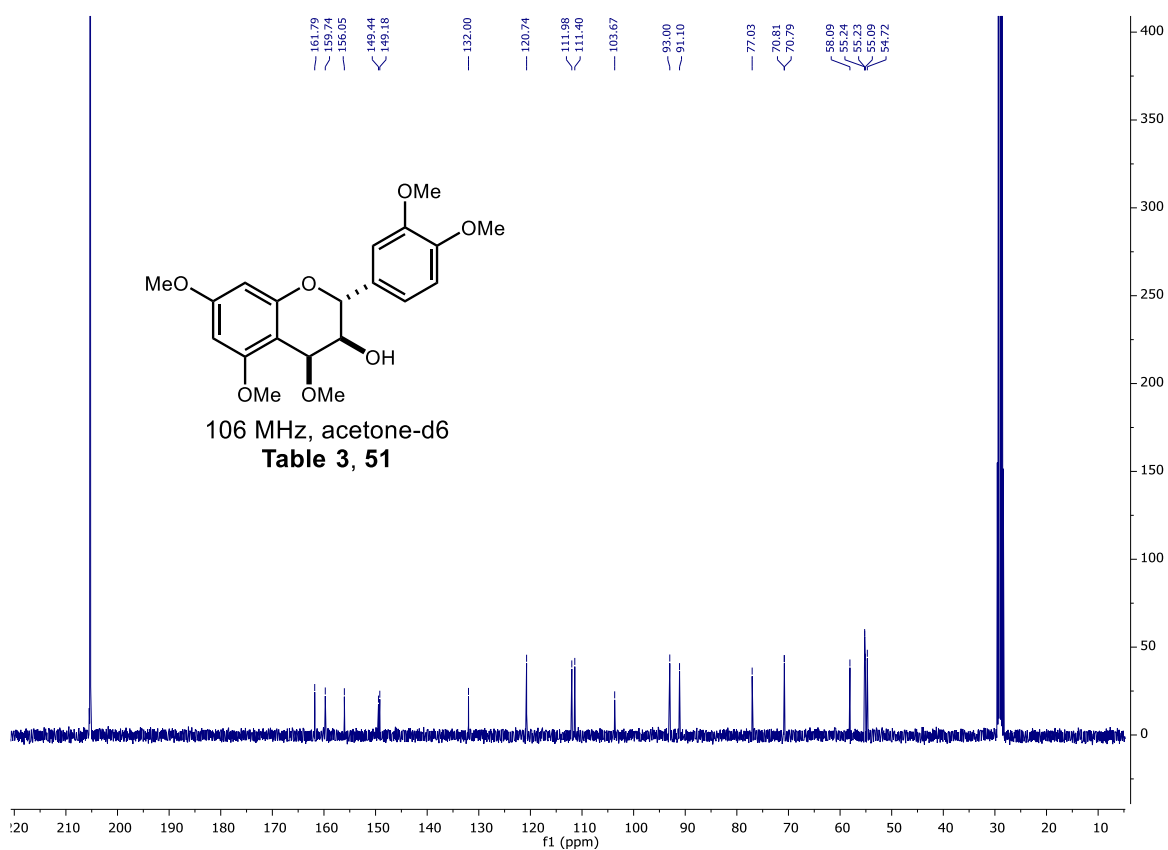
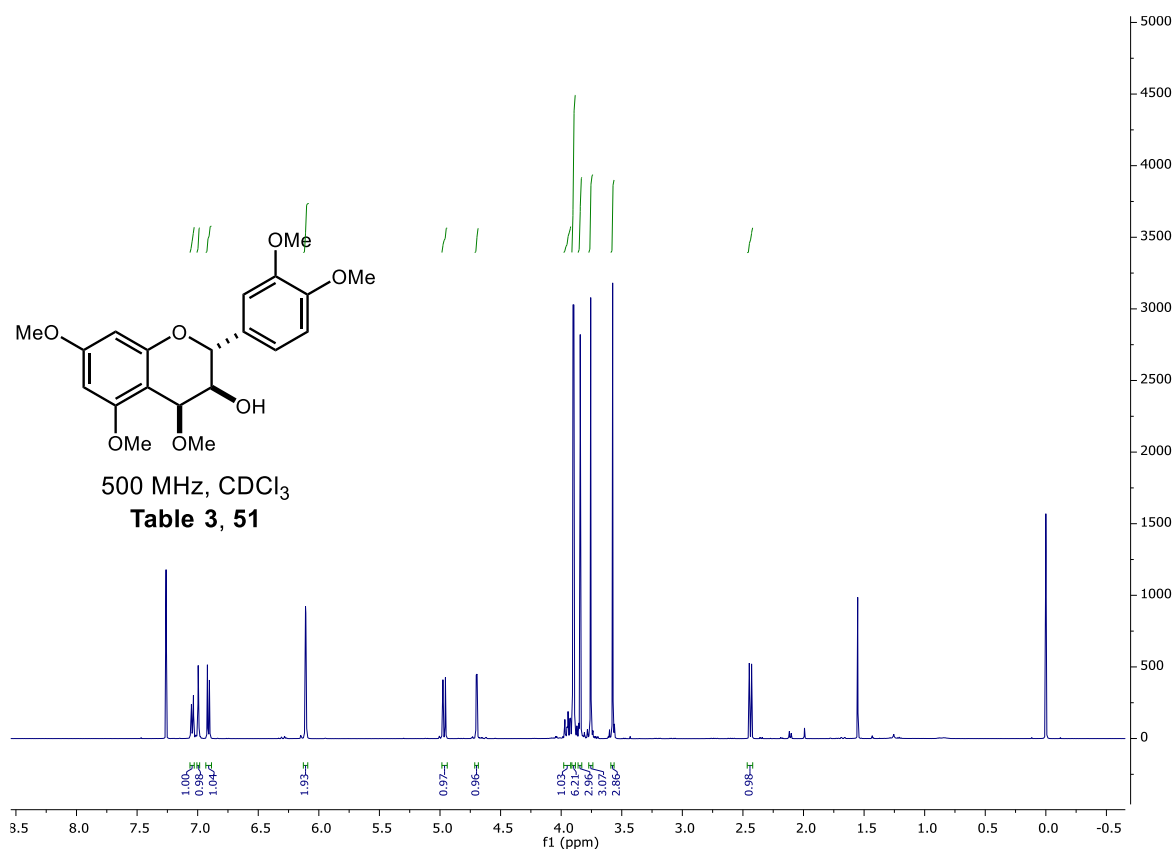


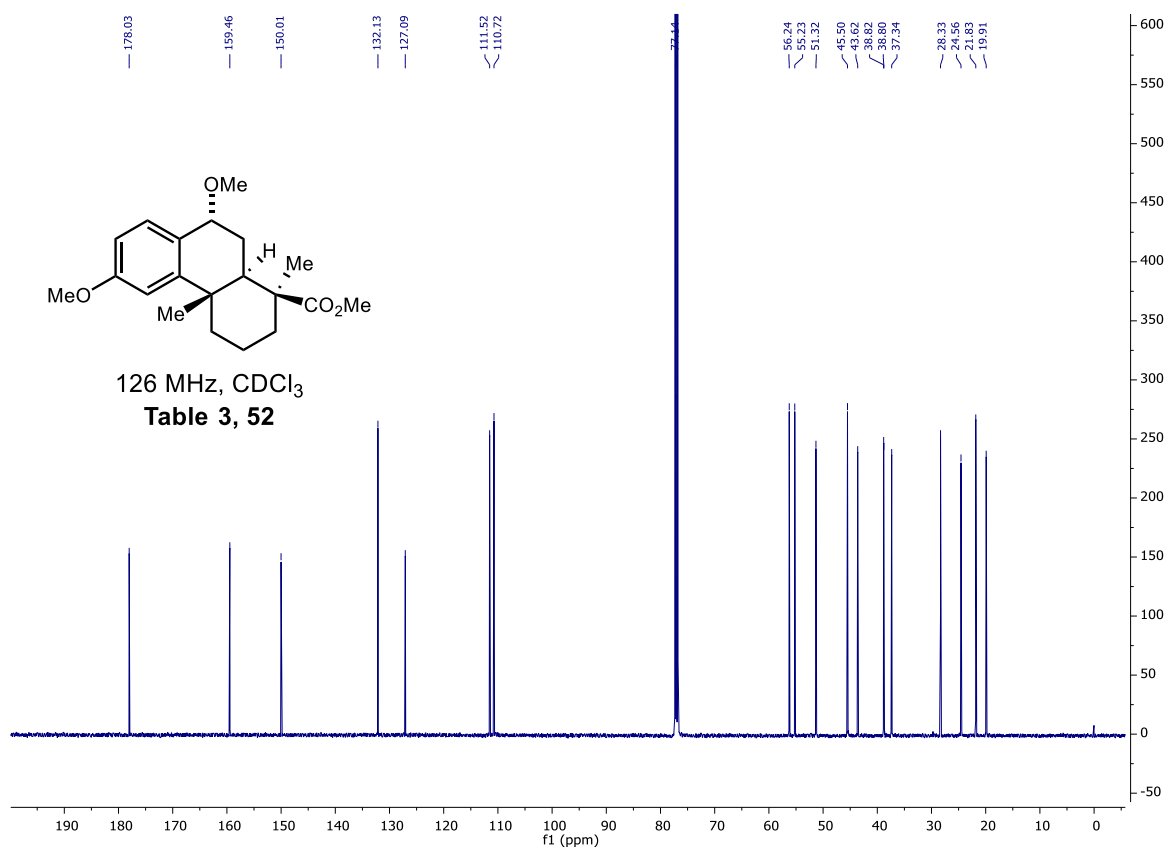
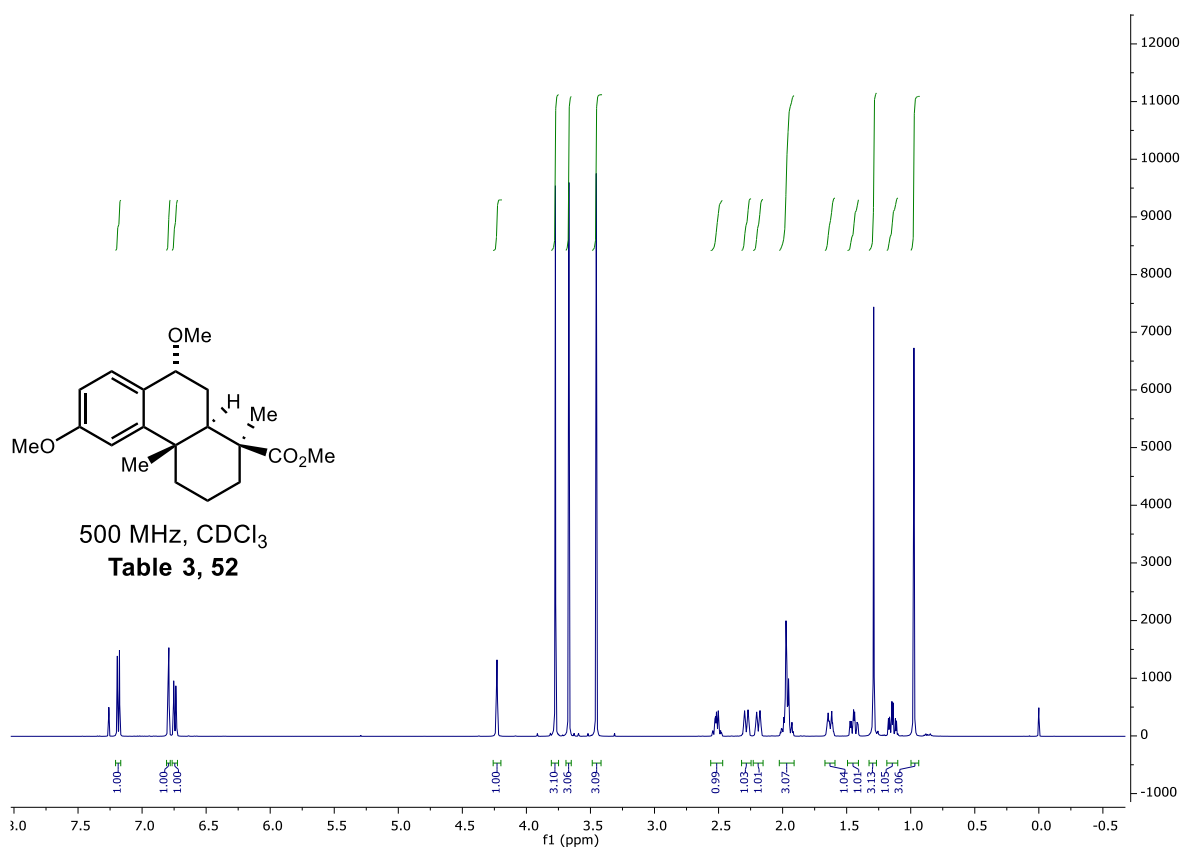


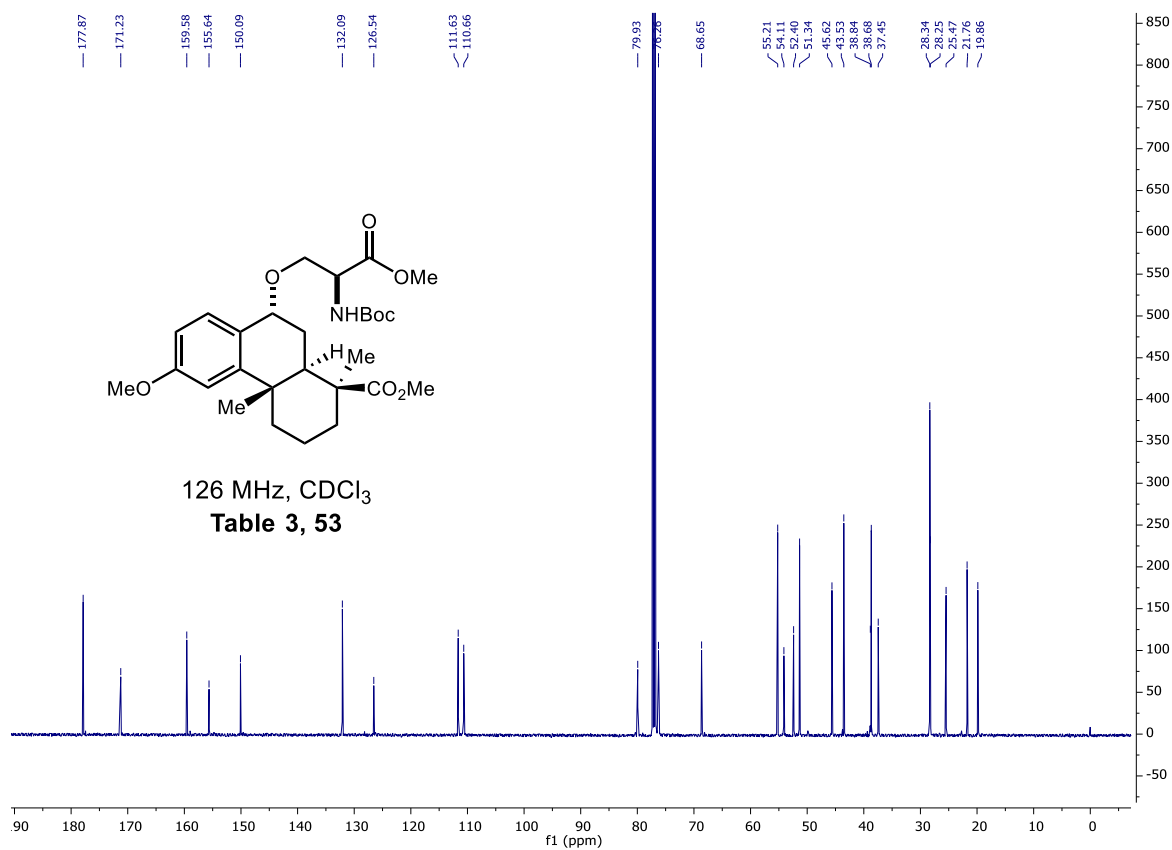
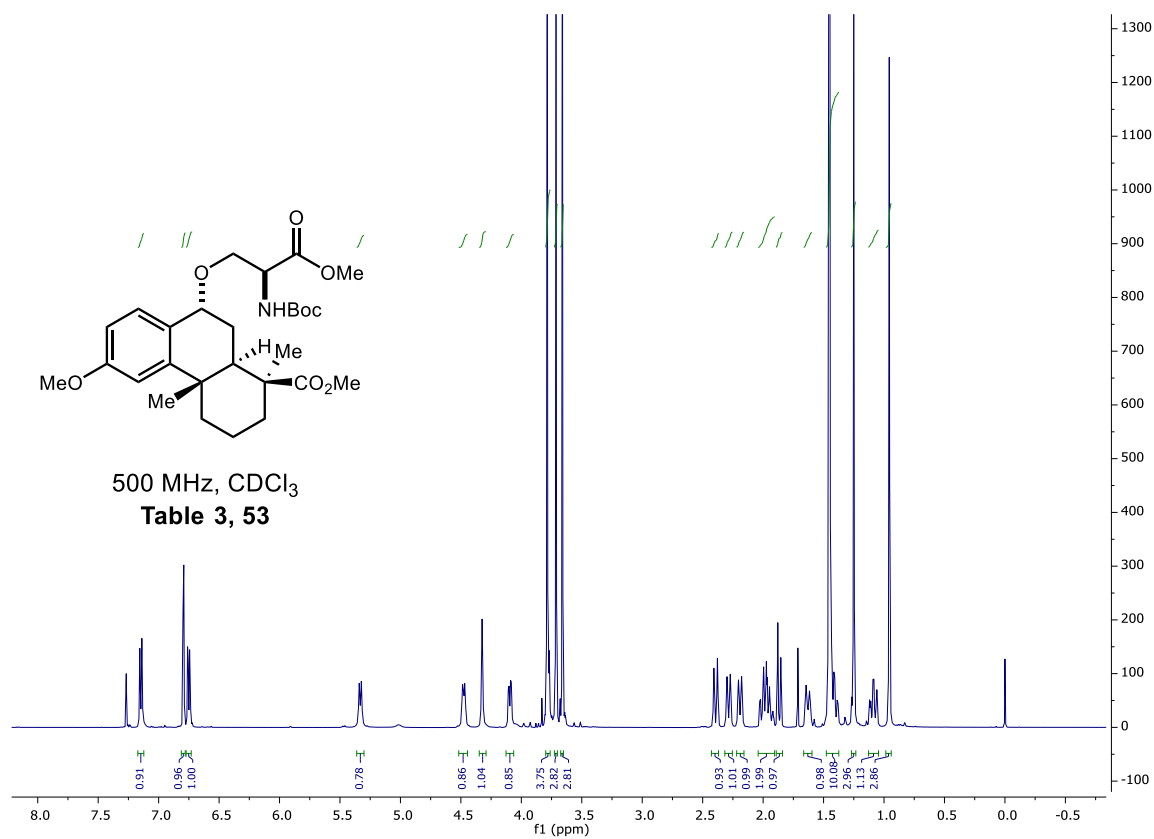


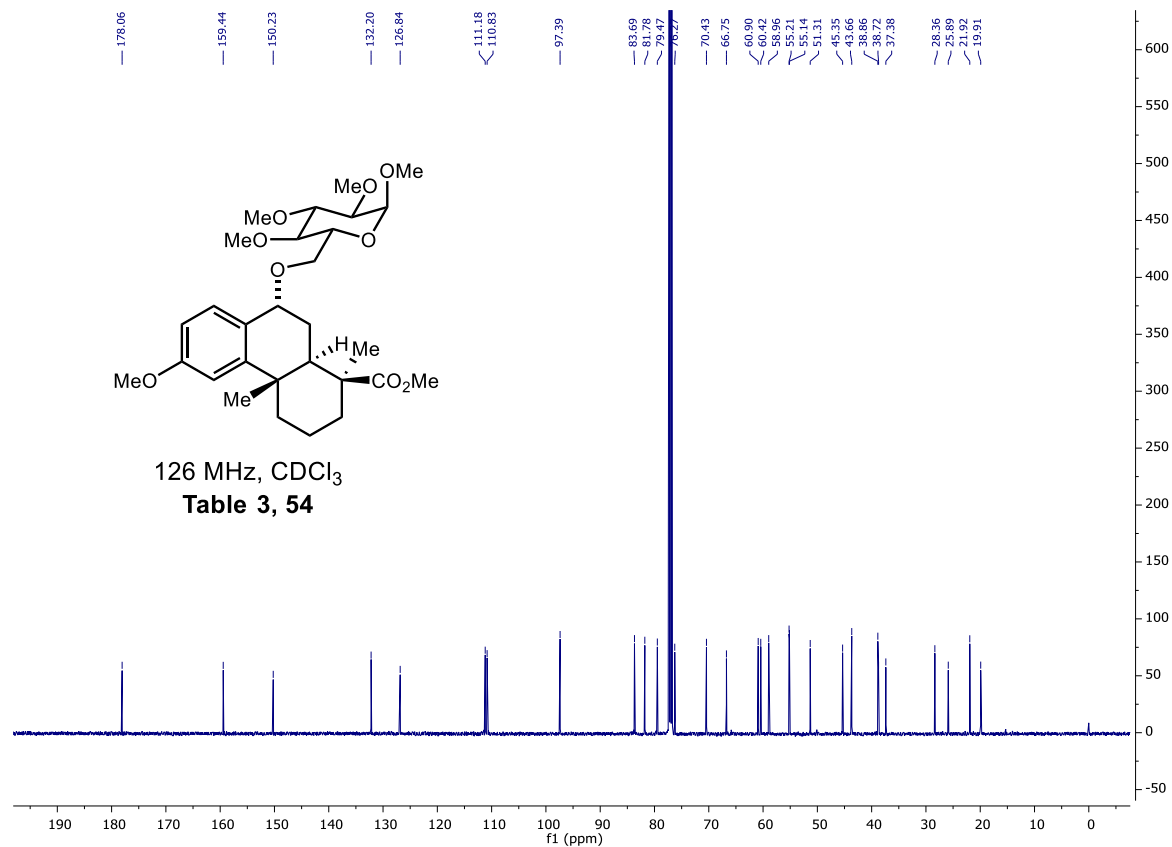
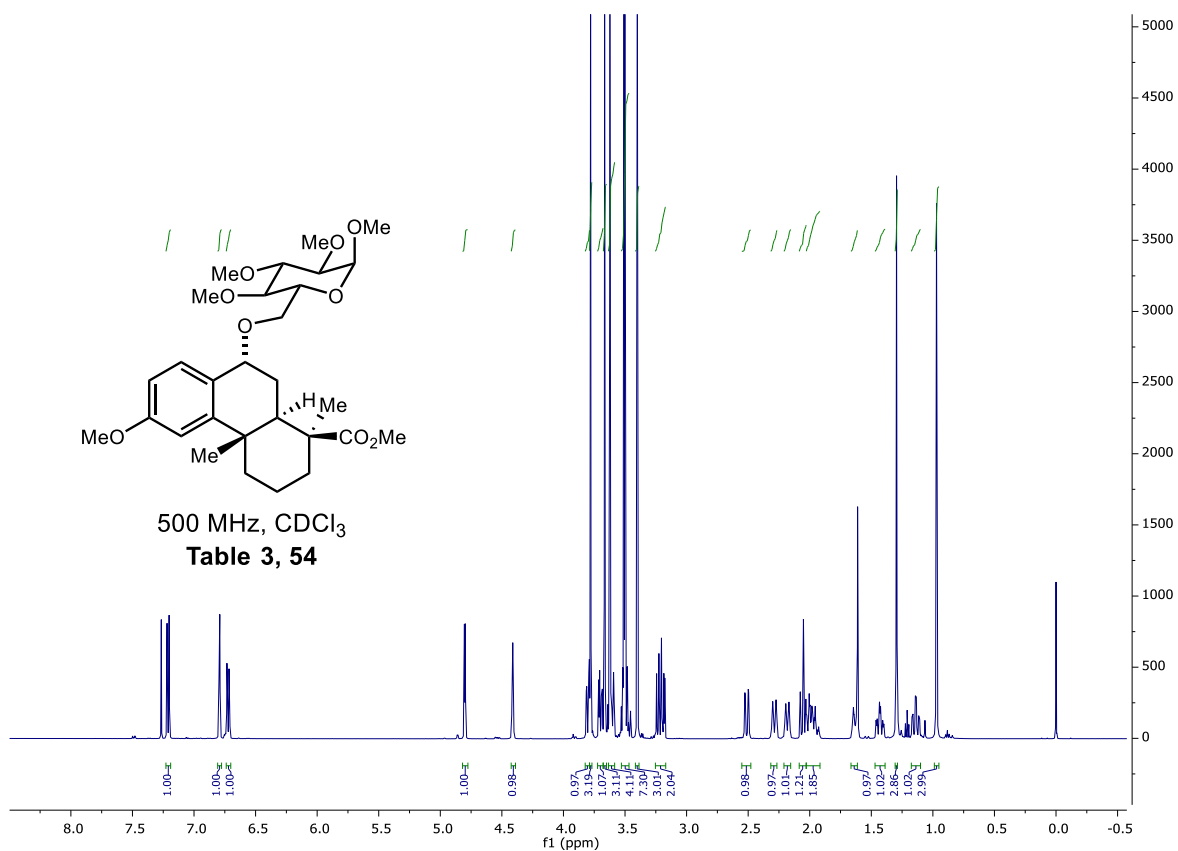


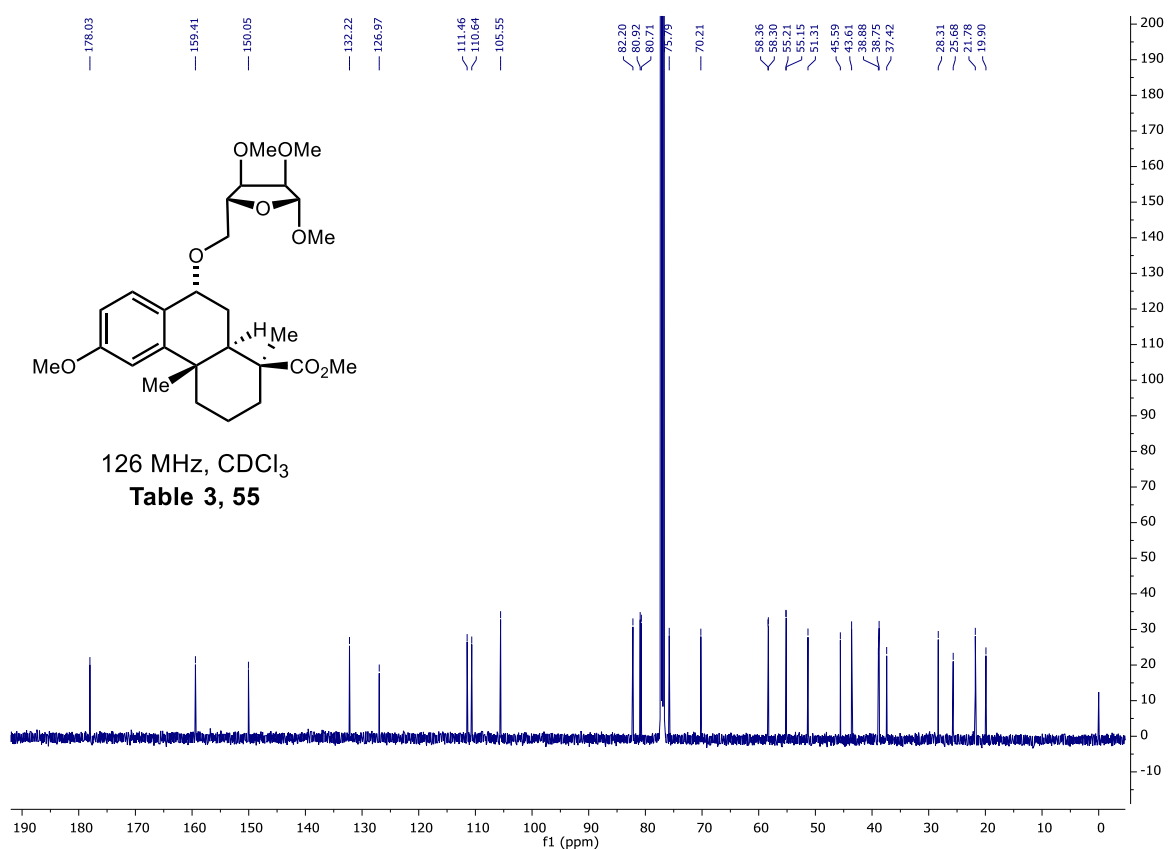
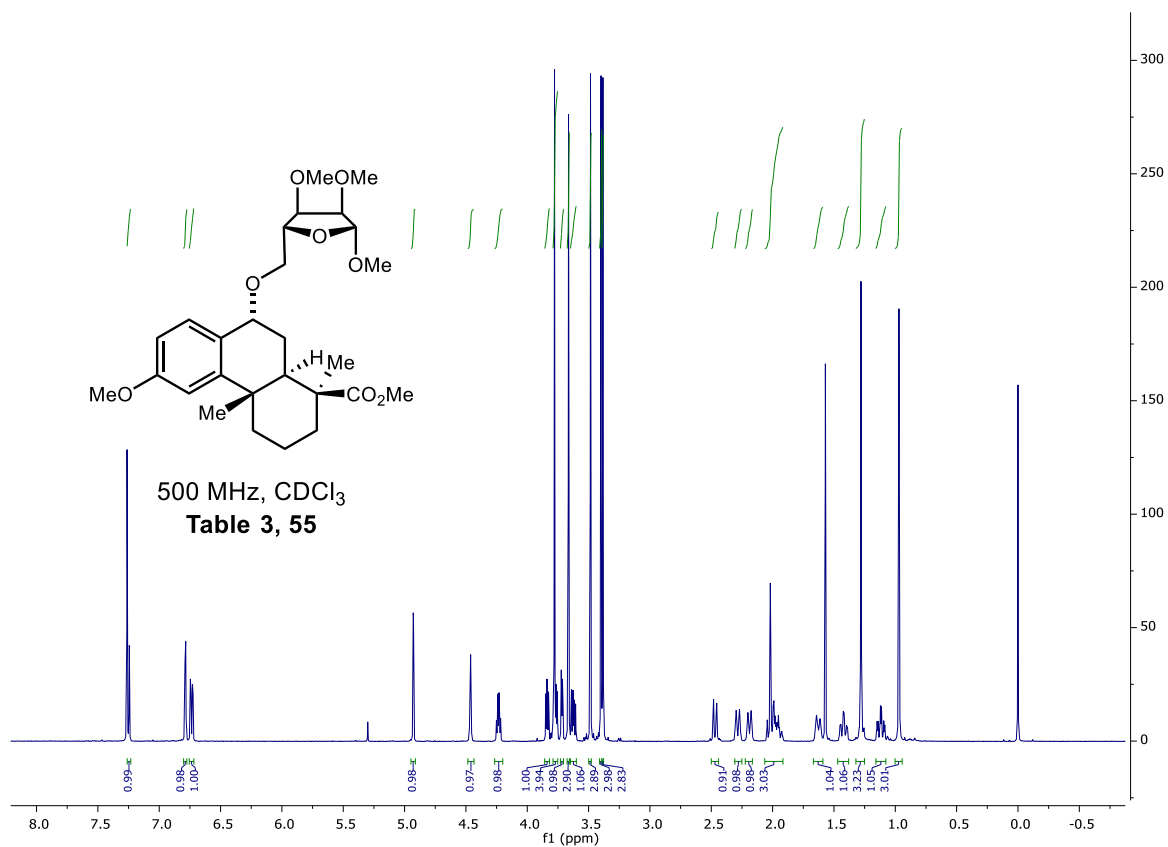


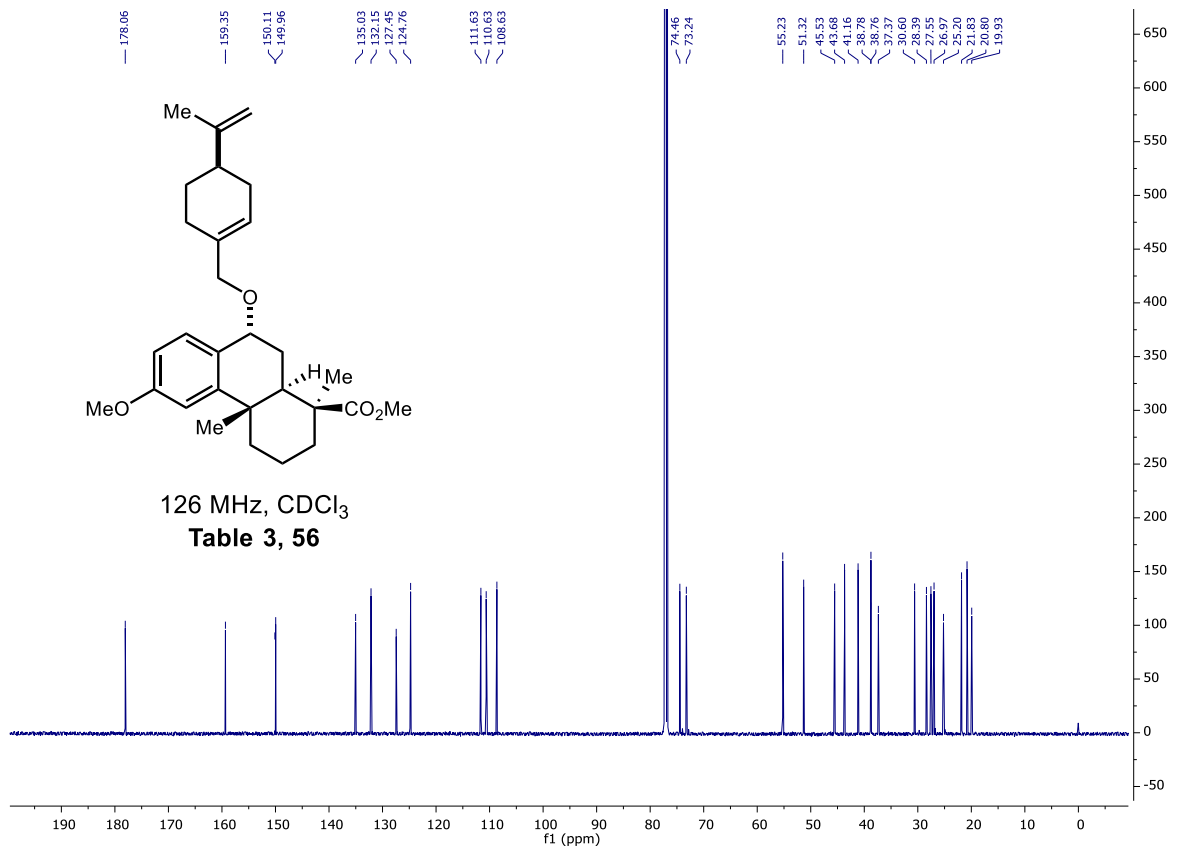
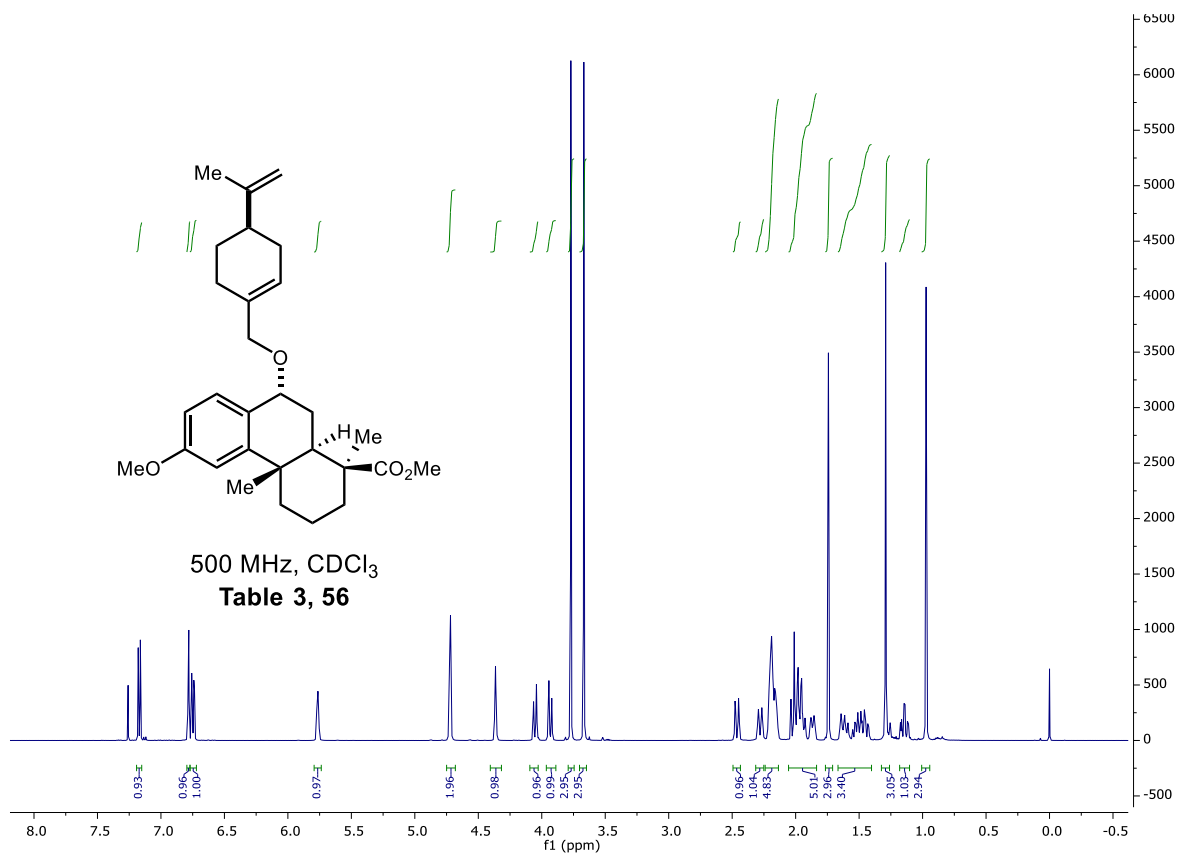


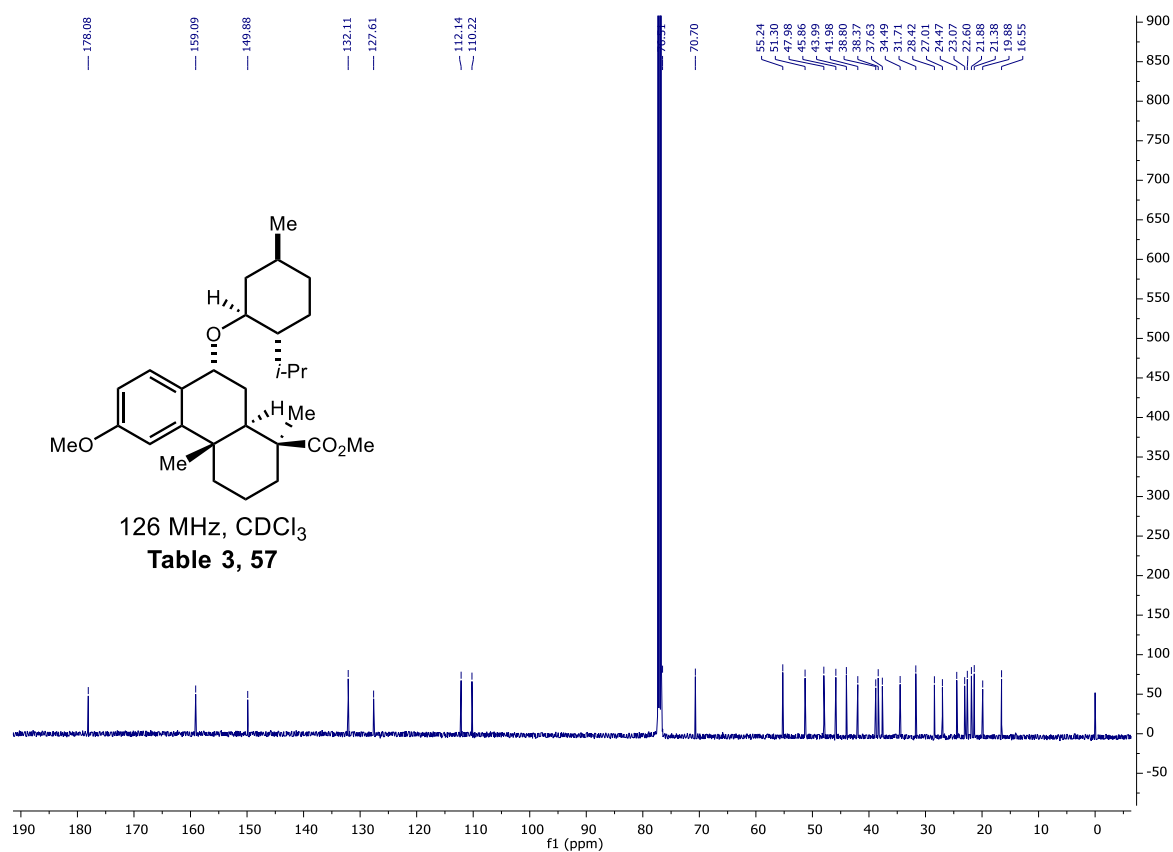
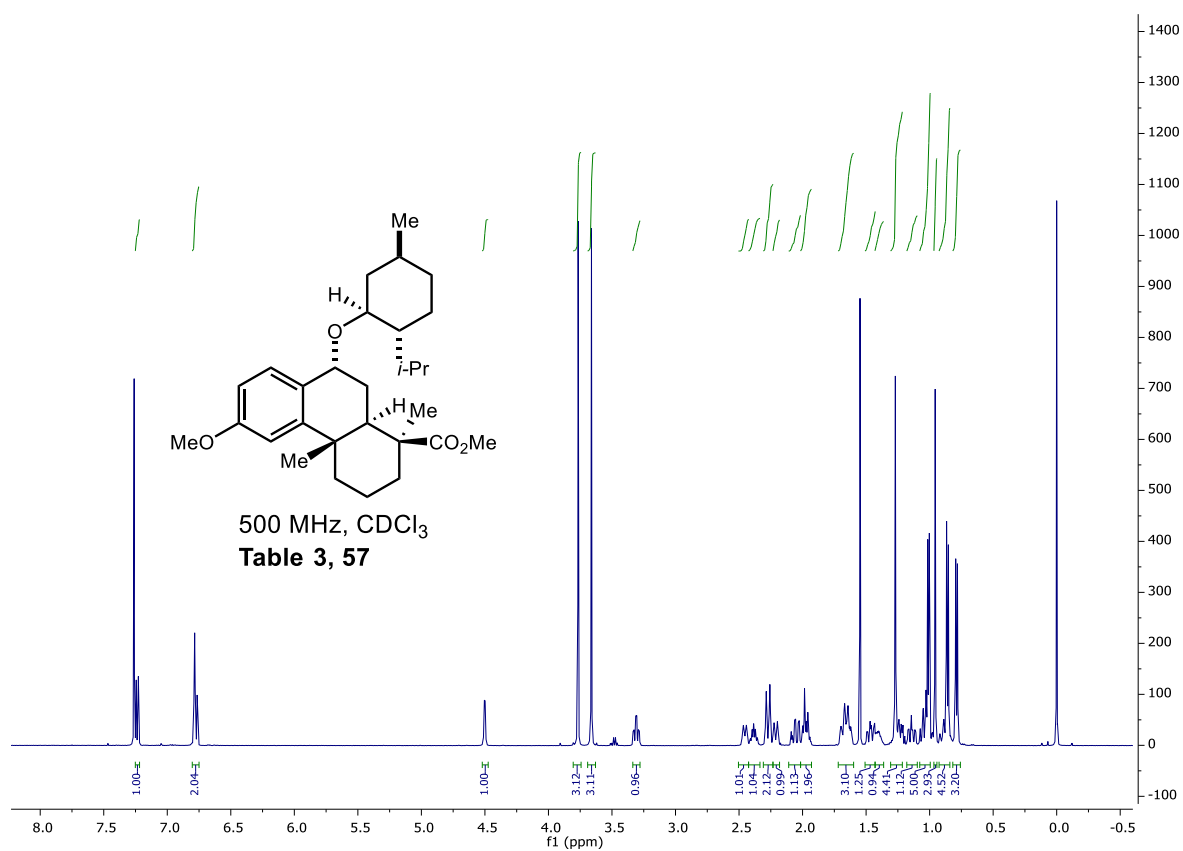












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