

# Supporting Information

## Overcoming High Reduction Potentials via Consecutive Mechanical-Force-Induced Electron Transfer Strategy

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## 1. General Information of Instrumentation and Chemicals

Materials were obtained from commercial suppliers and purified by standard procedures unless otherwise noted. *tet*-BaTiO<sub>3</sub> (1-3 μm particle size, 99%, product No. A66127), *cub*-BaTiO<sub>3</sub> (100-200 nm particle size, 99%, product No. A66123), CaTiO<sub>3</sub> (~2 μm particle size, 99%, product No. A67685), PbTiO<sub>3</sub> (product No. A60705), Li<sub>2</sub>TiO<sub>3</sub> (product No. A60327), SrTiO<sub>3</sub> (0.5-5 μm particle size, 99%, product No. E061762) and LiNbO<sub>3</sub> (product No. A60320) were purchased from 3AMaterials® (<https://www.3accorematerials.com/zh/>). All reactions were performed using grinding vessels in powteq vibration ball mill GT300. Both jars and balls were made of stainless steel. Solvents for reactions were purchased from commercial suppliers. <sup>1</sup>H, <sup>19</sup>F, <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> on Bruker Avance 400 MHz spectrometers. Multiplicity was recorded as follows: s = singlet, brs = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet. The n-dodecane was used as an internal standard to determine gas chromatography (GC) yields. Recycle preparative gel permeation chromatography (GPC) was conducted with a LC-5060P (Serial No. LA5-21345) using ethyl acetate as an eluent. High-resolution mass data were recorded on a high-resolution mass spectrometer in the ESI or EI mode. The molecular ion [M+H]<sup>+</sup>, [M+NH<sub>4</sub>]<sup>+</sup>, [M+Na]<sup>+</sup> or [M]<sup>+</sup> are given in m/z units. Thin Layer Chromatography analysis was performed on silica gel coated glass plates (0.25 mm) with fluorescence indicator UV254. For detection of spots, irradiation of UV light at 254 nm or staining reagent using basic potassium permanganate solution was used. Flash column chromatography was conducted with silica gel (particle size 300-400 mesh, Huanghai) at room temperature and under elevated pressure.

## 2. Lists of Reaction Substrates

All the aryl iodides were purchased from energy chemical or bidepharm without further purification. Substrates **2i**,<sup>[1]</sup> **2j**,<sup>[1]</sup> **2p-2v**,<sup>[1]</sup> **2w-2x**,<sup>[2]</sup> **1y-1z**<sup>[3]</sup> and **1ab-1ac**<sup>[3]</sup> were synthesized according to the corresponding literature. Other substrates were purchased from energy chemical or bidepharm without further purification.

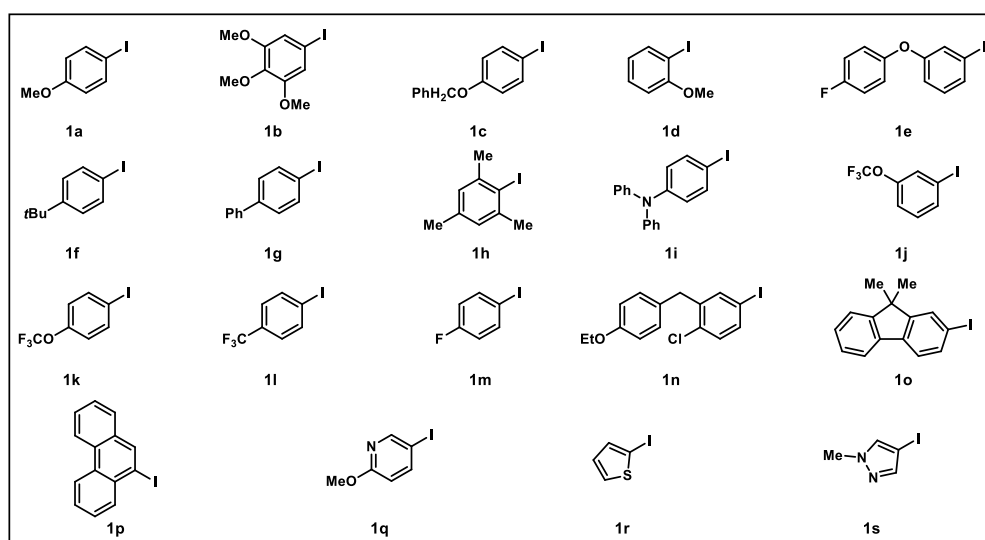
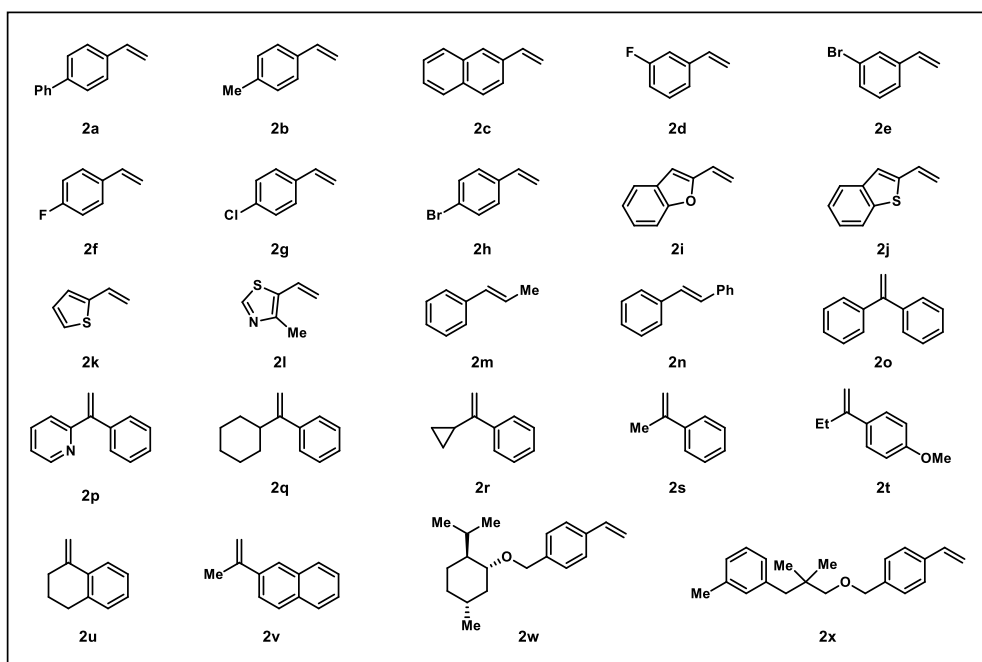
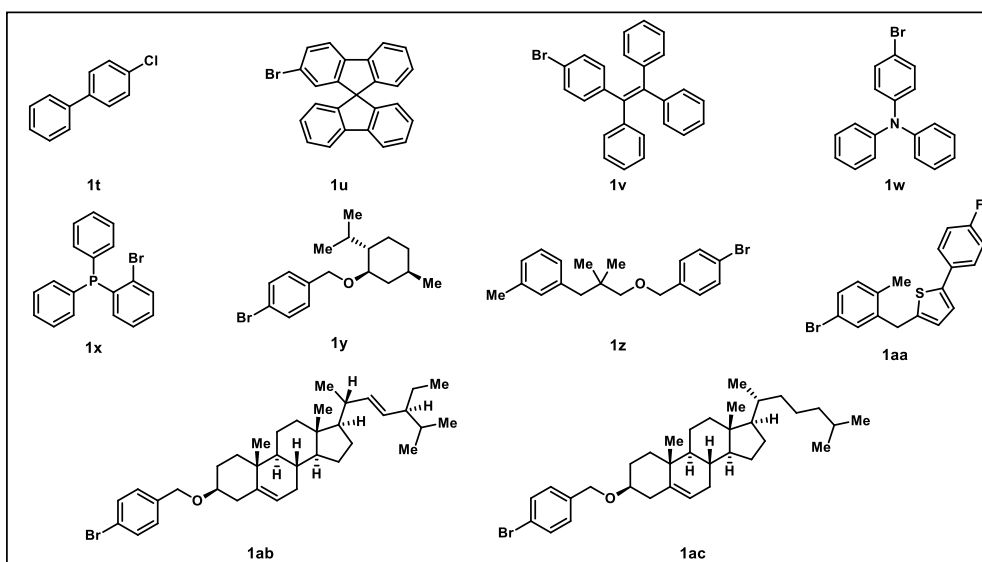


Figure S1. List of aryl iodides used in this study



**Figure S2.** List of styrenes used in this study



**Figure S3.** List of aryl bromides and aryl chlorides used in this study

### 3. General Procedure

**Method A: General Procedure for *anti*-Markovnikov Hydroarylation of Alkene:** Aryl iodides (**1**, 0.28 mmol, 1.4 equiv), styrene derivatives (**2**, 0.20 mmol, 1.0 equiv), promoter (**D1**, 0.06 mmol), NaOtBu (0.6 mmol) and CaTiO<sub>3</sub> (0.8 mmol) were placed in a stainless-steel milling jar (10.0 mL) with two stainless-steel balls (10 mm, diameter) in air. DMSO (1.2 mmol) were added into the jar in the argon fulfilled glovebox, the jar was placed in Gladman vibration ball mill GT300 (30 Hz). After grinding for 2.5 h (30 min break 5 min for five times), the reaction mixture was washed with ethyl acetate. The solvent was evaporated in vacuo and the remaining residue was purified by column chromatography on silica gel to yield products.

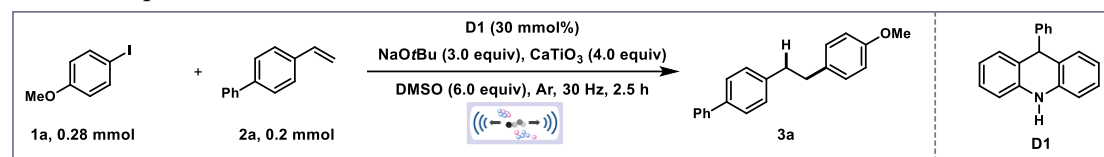
**Method B: General Procedure for Dehalogenative deuteration of aromatic bromides and aromatic chlorides:** Aryl bromides (0.2 mmol, 1.0 equiv), promoter (**D1**, 0.06 mmol), KOH (0.28 mmol) and CaTiO<sub>3</sub> (0.8 mmol) were placed in a stainless-steel milling jar (10.0 mL) with two

stainless-steel balls (10 mm, diameter) in air. DMSO (0.4 mmol) were added into the jar in the argon fulfilled glovebox, the jar was placed in Gladman vibration ball mill GT600 (35 Hz). After grinding for 3.0 h (10 min break 5 min for eighteen times), the reaction mixture was washed with ethyl acetate. The solvent was evaporated in vacuo and the remaining residue was purified by column chromatography on silica gel to yield products. Aryl chlorides (0.4 mmol, 1.0 equiv), promoter (**D1**, 0.12 mmol), KO<sup>t</sup>Bu (0.56 mmol) and CaTiO<sub>3</sub> (1.6 mmol) were placed in a stainless-steel milling jar (10.0 mL) with two stainless-steel balls (10 mm, diameter) in air. DMSO (2.4 mmol) were added into the jar in the argon fulfilled glovebox, the jar was placed in Gladman vibration ball mill GT600 (35 Hz). After grinding for 3.0 h (10 min break 5 min for eighteen times), the reaction mixture was washed with ethyl acetate. The solvent was evaporated in vacuo and the remaining residue was purified by column chromatography on silica gel to yield products.

## 4. Optimization of Reaction Conditions

4-Iodoanisole (**1a**, 0.28 mmol, 1.4 equiv), *p*-vinylbiphenyl (**2a**, 0.20 mmol, 1.0 equiv), promoter (**D1**, 0.03 mmol), bases (0.6 mmol) and piezoelectric materials (0.8 mmol) were placed in a stainless-steel milling jar (10.0 mL) with two stainless-steel balls (10 mm, diameter) in air. LAG (1.2 mmol) were added into the jar in the argon fulfilled glovebox, the jar was placed in Gladman vibration ball mill GT300 (30 Hz). After grinding for 2.5 h (30 min break 5 min for five times), the reaction mixture was washed with ethyl acetate. The yield of **3a** was determined by gas chromatography (GC) analysis of the crude reaction mixture using *n*-dodecane as an internal standard (Table S1).

**Table S1 Optimization of reaction conditions**

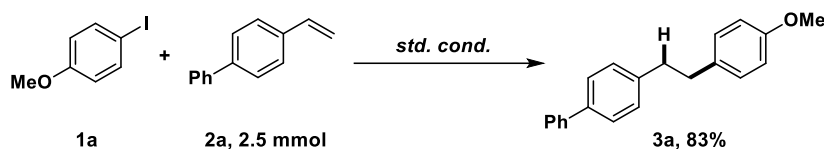


Entry	Deviation from standard conditions	Yield of <b>3a</b> <sup>a</sup> (%)
1	none	91
2	SrTiO <sub>3</sub> (0.5-5 μm) instead of CaTiO <sub>3</sub>	85
3	<i>tet</i> -BaTiO <sub>3</sub> (1-3 μm) instead of CaTiO <sub>3</sub>	71
4	LiNbO <sub>3</sub> (1-3 μm) instead of CaTiO <sub>3</sub>	71
5	Li <sub>2</sub> TiO <sub>3</sub> instead of CaTiO <sub>3</sub>	55
6	PbTiO <sub>3</sub> instead of CaTiO <sub>3</sub>	36
7	ZnO instead of CaTiO <sub>3</sub>	23
8	NMP instead of DMSO	46
9	CH <sub>3</sub> CN instead of DMSO	35
10	DMF instead of DMSO	32
11	EtOH instead of DMSO	3
12	2-Me-THF instead of DMSO	2
13	Xylene instead of DMSO	0
14	Cyclohexane instead of DMSO	0
15	DCM instead of DMSO	0
16	KO <sup>t</sup> Bu instead of NaO <sup>t</sup> Bu	78
17	NaOH instead of NaO <sup>t</sup> Bu	78
18	K <sub>3</sub> PO <sub>4</sub> instead of NaO <sup>t</sup> Bu	13



Entry	Deviation from standard conditions	Yield of 3a <sup>a</sup> (%)
19	KF instead of NaOtBu	12
20	Na <sub>2</sub> CO <sub>3</sub> instead of NaOtBu	0
21	Et <sub>3</sub> N instead of NaOtBu	0

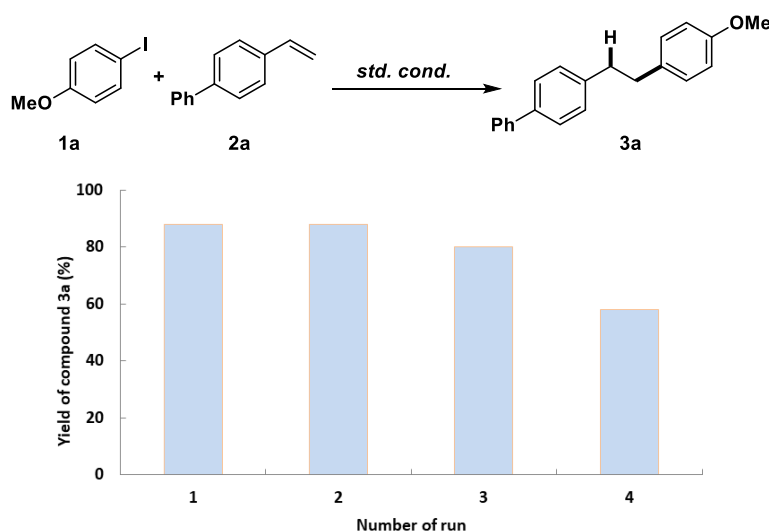
## 5. The Procedure for the Scale-up Reaction



4-Iodoanisole (**1a**, 3.50 mmol, 1.4 equiv), *p*-vinylbiphenyl (**2a**, 2.50 mmol, 1.0 equiv), promoter (**D1**, 0.75 mmol), NaOtBu (7.5 mmol) and CaTiO<sub>3</sub> (10.0 mmol) were placed in a stainless-steel milling jar (50.0 mL) with fifty stainless-steel balls (7 mm, diameter) in air. DMSO (15.0 mmol) were added into the jar in the argon fulfilled glovebox, the jar was placed in Gladman vibration ball mill GT300 (30 Hz). After grinding for 2.5 h (30 min break 5 min for five times), the reaction mixture was washed with ethyl acetate. The solvent was evaporated and the residual was purified through column chromatography on silica gel with petroleum ether/ethyl acetate (10/1) as the eluent to give pure target product (**3a**, 0.255 g, 83%).

## 6. CaTiO<sub>3</sub> Recycling Experiments

4-Iodoanisole (**1a**, 0.28 mmol, 1.4 equiv), *p*-vinylbiphenyl (**2a**, 0.20 mmol, 1.0 equiv), promoter (**D1**, 0.06 mmol), NaOtBu (0.6 mmol) and CaTiO<sub>3</sub> (0.8 mmol) were placed in a stainless-steel milling jar (10.0 mL) with two stainless-steel balls (10 mm, diameter) in air. DMSO (1.2 mmol) were added into the jar in the argon fulfilled glovebox, the jar was placed in Gladman vibration ball mill GT300 (30 Hz). After grinding for 2.5 h (30 min break 5 min for five times), the reaction mixture was washed with ethyl acetate. CaTiO<sub>3</sub> was filtrated and washed with ethyl acetate, and dried over under reduce pressure for 2 h. then can be reused for hydroarylation of *p*-vinylbiphenyl (**2a**, 0.20 mmol) with 4-Iodoanisole (**1a**, 0.28 mmol, 1.4 equiv) under the same reaction conditions for at least four times (Figure S4). The yield of **3a** was determined by gas chromatography (GC) analysis using *n*-dodecane as an internal standard.

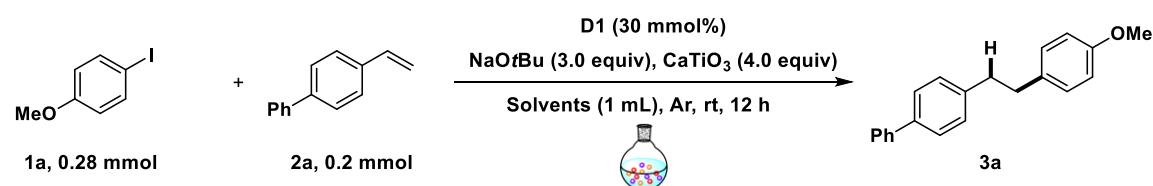


**Figure S4** CaTiO<sub>3</sub> recycling experiments using template reaction

## 7. Solution Reactions in Different Solvents

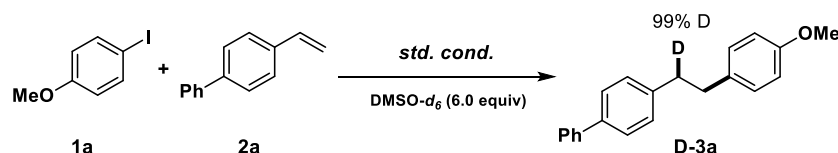
4-Iodoanisole (**1a**, 0.28 mmol, 1.4 equiv), *p*-vinylbiphenyl (**2a**, 0.20 mmol, 1.0 equiv), promoter (**D1**, 0.06 mmol), NaOtBu (0.6 mmol) and CaTiO<sub>3</sub> (0.8 mmol) were placed in a 8 mL Vail with one stirrer in air. Solvents (1.0 mL) were added into the jar in the argon fulfilled glovebox, the jar was placed in Gladman vibration ball mill GT300 (30 Hz). After grinding for 2.5 h (30 min break 5 min for five times), the reaction mixture was washed with ethyl acetate. The yield of **3a** was determined by gas chromatography (GC) analysis of the crude reaction mixture using *n*-dodecane as an internal standard (Table S2).

**Table S2** Solution reactions in different solvents



Entry	Solvent	Yield of <b>3a</b> (%)
1	DMSO	5
2	NMP	2
3	DMF	6
4	CH <sub>3</sub> CN	4

## 8. H Source Control Experiment



4-Iodoanisole (**1a**, 0.28 mmol, 1.4 equiv), *p*-vinylbiphenyl (**2a**, 0.20 mmol, 1.0 equiv), promoter (**D1**, 0.06 mmol), NaOtBu (0.6 mmol) and CaTiO<sub>3</sub> (0.8 mmol) were placed in a stainless-steel milling jar (10.0 mL) with two stainless-steel balls (10 mm, diameter) in air. DMSO-*d*<sub>6</sub> (1.2 mmol) were added into the jar in the argon fulfilled glovebox, the jar was placed in Gladman vibration ball mill GT300 (30 Hz). After grinding for 2.5 h (30 min break 5 min for five times), the reaction mixture was washed with ethyl acetate. The solvent was evaporated and the residual was purified through column chromatography on silica gel with petroleum ether/ethyl acetate (10/1) as the eluent to give pure target product (**D-3a**, 0.439 g, 76%, 99% deuteration rate). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.66 – 7.59 (m, 2H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.28 (d, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 3.82 (s, 3H), 2.98 – 2.92 (m, 3H).

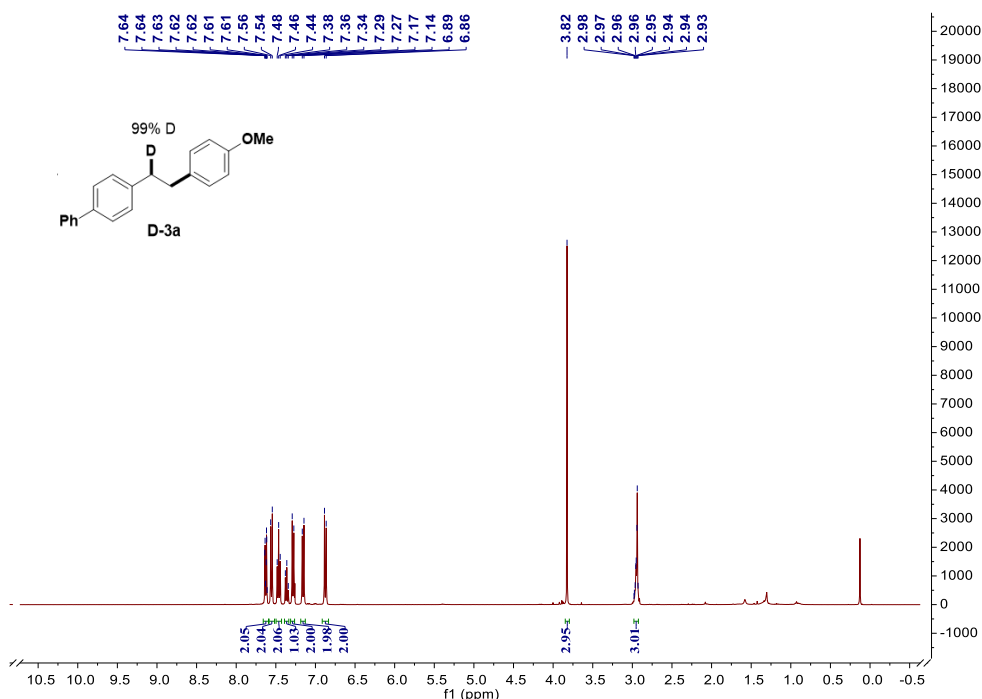
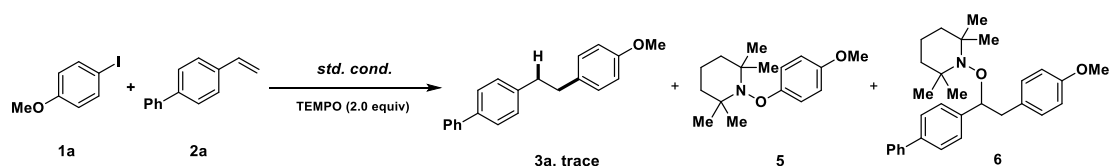


Figure S5  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) Spectrum of Compound **D-3a**

## 9. Radical-Trapping Experiments



4-Iodoanisole (**1a**, 0.28 mmol, 1.4 equiv), *p*-vinylbiphenyl (**2a**, 0.20 mmol, 1.0 equiv), promoter (**D1**, 0.06 mmol),  $\text{NaOtBu}$  (0.6 mmol),  $\text{CaTiO}_3$  (0.8 mmol) and 2,2,6,6-tetramethylpiperidinyloxy (TEMPO, 0.4 mmol) were placed in a stainless-steel milling jar (10.0 mL) with two stainless-steel balls (10 mm, diameter) in air. DMSO (1.2 mmol) were added into the jar in the argon fulfilled glovebox, the jar was placed in Gladman vibration ball mill GT300 (30 Hz). After grinding for 2.5 h (30 min break 5 min for five times), the reaction mixture was washed with ethyl acetate. The yield of target product **3a** was determined by gas chromatography (GC) analysis of the crude reaction mixture using *n*-dodecane as an internal standard. The aryl radical combined with TEMPO (**5**) and benzyl radical combined with TEMPO (**6**) were detected by HR-MS (Figure S6-S7). Compound **5**: HR-MS (ESI):  $m/z$  calcd for  $[\text{M}+\text{H}]^+$   $\text{C}_{16}\text{H}_{26}\text{NO}_2$ , 264.1958; found 264.1972 (Figure S6); Compound **6**: HR-MS (ESI):  $m/z$  calcd for  $[\text{M}+\text{H}]^+$   $\text{C}_{30}\text{H}_{38}\text{NO}_2$ , 444.2897; found 444.2895 (Figure S7).

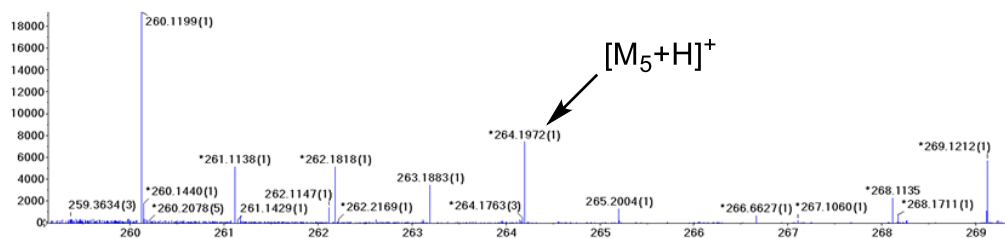
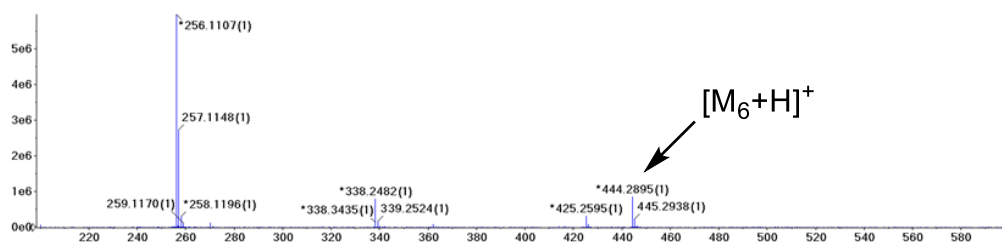


Figure S6 HRMS spectra of compound **5**

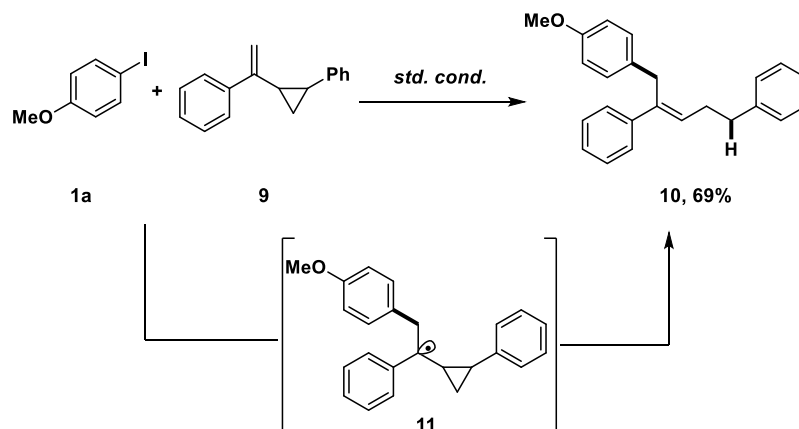


**Figure S7** HRMS spectra of compound **6**



4-Iodoanisole (**1a**, 0.28 mmol, 1.4 equiv), *p*-vinylbiphenyl (**2a**, 0.20 mmol, 1.0 equiv), promoter (**D1**, 0.06 mmol), NaOtBu (0.6 mmol), CaTiO<sub>3</sub> (0.8 mmol) and butylated hydroxytoluene (BHT, 0.4 mmol) were placed in a stainless-steel milling jar (10.0 mL) with two stainless-steel balls (10 mm, diameter) in air. DMSO (1.2 mmol) were added into the jar in the argon fulfilled glovebox, the jar was placed in Gladman vibration ball mill GT300 (30 Hz). After grinding for 2.5 h (30 min break 5 min for five times), the reaction mixture was washed with ethyl acetate. The yield of target product **3a** was determined by gas chromatography (GC) analysis of the crude reaction mixture using *n*-dodecane as an internal standard.

## 10. Radical Clock Experiment



4-Iodoanisole (**1a**, 0.28 mmol, 1.4 equiv), (1-(2-phenylcyclopropyl)vinyl)benzene (**9**, 0.20 mmol, 1.0 equiv), promoter (**D1**, 0.06 mmol), NaOtBu (0.6 mmol) and CaTiO<sub>3</sub> (0.8 mmol) were placed in a stainless-steel milling jar (10.0 mL) with two stainless-steel balls (10 mm, diameter) in air. DMSO (1.2 mmol) were added into the jar in the argon fulfilled glovebox, the jar was placed in Gladman vibration ball mill GT300 (30 Hz). After grinding for 2.5 h (30 min break 5 min for five times), the reaction mixture was washed with ethyl acetate. The solvent was evaporated and the residual was purified through column chromatography on silica gel with petroleum ether/ethyl acetate (10/1) as the eluent to give pure target product (**10**, 0.452 g, 69%). This further demonstrates that mechanical-force-induced hydroarylation of alkenes proceeds through a radical process. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.23 – 7.05 (m, 10H), 6.92 (d, *J* = 8.6 Hz, 2H), 6.65 (d, *J* =

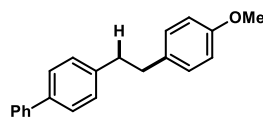
8.6 Hz, 2H), 5.89 (t,  $J$  = 7.2 Hz, 1H), 3.66 (s, 2H), 3.64 (s, 3H), 2.69 (t,  $J$  = 7.6 Hz, 2H), 2.48 (q,  $J$  = 7.4 Hz, 2H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  157.8, 143.1, 141.9, 138.5, 131.8, 129.8, 129.2, 128.7, 128.5, 128.3, 126.8, 126.4, 126.0, 113.9, 55.3, 36.1, 35.0, 31.1.

## 11. References

- [1] A. Falk, A. Cavalieri, D. Vogt, H. G. Schmalz, Enantioselective Nickel-Catalyzed Hydrocyanation using Chiral Phosphine-Phosphite Ligands: Recent Improvements and Insights. *Adv. Synth. Catal.* **2015**, 357, 3317-3320.
- [2] M. Z. Tang, S. X. Han, S. L. Huang, S. L. Huang, L. G. Xie, Carbosulfenylation of Alkenes with Organozinc Reagents and Dimethyl(methylthio)sulfonium Trifluoromethanesulfonate. *Org. Lett.* **2020**, 22, 9729-9734.
- [3] (a) M. J. Bçhm, C. Golz, I. Rüter, M. Alcarazo, Two-Step Synthesis of Unsymmetrical Diaryl Sulfides by Electrophilic Thiolation of Non-functionalized (Hetero)arenes. *Chem. Eur. J.* **2018**, 24, 15026-15035; (b) K. Harano, R. M. Gorgolla, E. Nakamura, Binding of Aromatic Molecules in the Fullerene-rich Interior of a Fullerene Bilayer Vesicle in Water. *Chem. Commun.* **2013**, 49, 7629-7631.

## 12. Characterization Data of All the Target Products

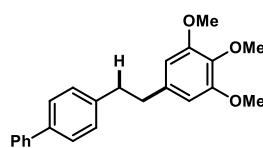
### 4-(4-methoxyphenethyl)-1,1'-biphenyl (3a)



Compound **3a** was prepared following the general procedure A, using corresponding aryl iodine and alkenes. The crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford the desired product (46.1 mg, 80%) as a yellowish solid.

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.65 (dd,  $J$  = 8.4, 1.2 Hz, 2H), 7.57 (d,  $J$  = 8.0 Hz, 2H), 7.48 (t,  $J$  = 7.6 Hz, 2H), 7.38 (t,  $J$  = 7.4 Hz, 1H), 7.30 (d,  $J$  = 8.4 Hz, 2H), 7.17 (d,  $J$  = 8.8 Hz, 2H), 6.89 (d,  $J$  = 8.4 Hz, 2H), 3.83 (s, 3H), 3.01 – 2.92 (m, 4H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  157.9, 141.1, 141.0, 138.8, 133.8, 129.5, 129.4, 129.0, 128.8, 127.1, 127.0, 113.8, 55.3, 37.9, 37.0. HR-MS (ESI):  $m/z$  calcd for  $[\text{M}+\text{H}]^+$   $\text{C}_{21}\text{H}_{21}\text{O}^+$ , 289.1587; found 289.1588.

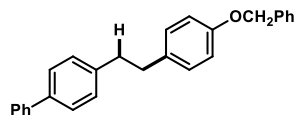
### 4-(3,4,5-trimethoxyphenethyl)-1,1'-biphenyl (3b)



Compound **3b** was prepared following the general procedure A, using corresponding aryl iodine and alkenes. The crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford the desired product (36.9 mg, 53%) as a white solid.

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.58 (dd,  $J$  = 8.4, 1.2 Hz, 2H), 7.53 (d,  $J$  = 8.4 Hz, 2H), 7.43 (t,  $J$  = 7.6 Hz, 2H), 7.33 (t,  $J$  = 7.2 Hz, 1H), 7.26 (d,  $J$  = 7.6 Hz, 2H), 6.38 (s, 2H), 3.84 (s, 3H), 3.82 (s, 6H), 3.00 – 2.85 (m, 4H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  153.1, 141.1, 140.8, 139.1, 137.5, 136.2, 129.1, 128.9, 127.19, 127.16, 127.1, 105.5, 61.0, 56.1, 38.4, 37.7. HR-MS (EI):  $m/z$  calcd for  $[\text{M}]^+$   $\text{C}_{23}\text{H}_{24}\text{O}_3^+$ , 348.1725; found 348.1724.

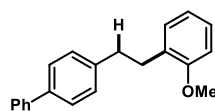
### 4-(4-(benzyloxy)phenethyl)-1,1'-biphenyl (3c)



Compound **3c** was prepared following the general procedure A, using corresponding aryl iodine and alkenes. The crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford the desired product (51.7 mg, 71%) as a white solid.

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.60 (dd,  $J$  = 8.4, 1.2 Hz, 2H), 7.53 (d,  $J$  = 8.4 Hz, 2H), 7.45 (d,  $J$  = 7.2 Hz, 4H), 7.43 – 7.41 (m, 1H), 7.40 – 7.38 (m, 2H), 7.36 – 7.33 (m, 1H), 7.26 (d,  $J$  = 8.4 Hz, 2H), 7.13 (d,  $J$  = 8.8 Hz, 2H), 6.92 (d,  $J$  = 8.8 Hz, 2H), 5.06 (s, 2H), 2.97 – 2.88 (m, 4H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  157.2, 141.2, 141.1, 138.9, 137.3, 134.2, 129.5, 129.0, 128.8, 128.7, 128.0, 127.6, 127.2, 127.14, 127.10, 114.8, 70.2, 37.9, 37.1. HR-MS (ESI):  $m/z$  calcd for  $[\text{M}+\text{H}]^+$   $\text{C}_{27}\text{H}_{25}\text{O}^+$ , 365.1900; found 365.1900.

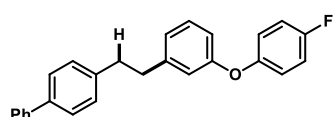
### 4-(2-methoxyphenethyl)-1,1'-biphenyl (3d)



Compound **3d** was prepared following the general procedure A, using corresponding aryl iodine and alkenes. The crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford the desired product (30.0 mg, 52%) as a white solid.

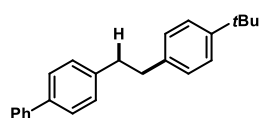
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.62 (d,  $J$  = 7.6 Hz, 2H), 7.55 (d,  $J$  = 8.0 Hz, 2H), 7.46 (t,  $J$  = 7.6 Hz, 2H), 7.36 (d,  $J$  = 7.2 Hz, 1H), 7.31 (d,  $J$  = 8.0 Hz, 2H), 7.23 (td,  $J$  = 8.0, 1.6 Hz, 1H), 7.16 (dd,  $J$  = 7.2, 1.4 Hz, 1H), 6.94 – 6.88 (m, 2H), 3.86 (s, 3H), 3.02 – 2.93 (m, 4H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  157.6, 141.8, 141.3, 138.8, 130.3, 130.0, 129.0, 128.8, 127.3, 127.1, 127.1, 120.5, 110.4, 55.4, 36.0, 32.6. HR-MS (ESI):  $m/z$  calcd for  $[\text{M}+\text{H}]^+$   $\text{C}_{21}\text{H}_{21}\text{O}^+$ , 289.1587; found 289.1587.

#### 4-(3-(4-fluorophenoxy)phenethyl)-1,1'-biphenyl (3e)



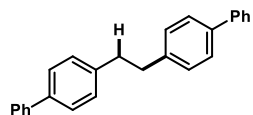
Compound **3e** was prepared following the general procedure A, using corresponding aryl iodide and alkenes. The crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford the desired product (50.8 mg, 69%) as a yellow solid. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 7.6 Hz, 2H), 7.55 (d, *J* = 7.8 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.42 – 7.34 (m, 2H), 7.30 – 7.26 (m, 3H), 7.04 (d, *J* = 9.0 Hz, 1H), 7.01 – 6.96 (m, 3H), 6.84 (d, *J* = 8.4 Hz, 2H), 2.98 (s, 4H). <sup>19</sup>F NMR (376 MHz, Chloroform-*d*) δ -120.3. <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 158.8 (d, *J* = 243.4 Hz), 157.7, 153.0 (d, *J* = 2.0 Hz), 143.9, 141.1, 140.6, 139.0, 129.7, 129.0, 128.9, 127.2, 127.2, 127.1, 123.5, 120.5 (d, *J* = 8.1 Hz), 118.5, 116.3 (d, *J* = 23.2 Hz), 116.0, 37.8, 37.4. HR-MS (EI): *m/z* calcd for [M]<sup>+</sup> C<sub>26</sub>H<sub>21</sub>FO<sup>+</sup>, 368.1576; found 368.1566.

#### 4-(4-(tert-butyl)phenethyl)-1,1'-biphenyl (3f)



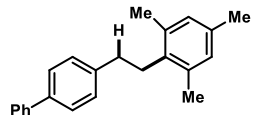
Compound **3f** was prepared following the general procedure A, using corresponding aryl iodide and alkenes. The crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford the desired product (40.0 mg, 64%) as a white solid. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 7.2 Hz, 2H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 3H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 3.04 – 2.95 (m, 4H), 1.38 (s, 9H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 148.9, 141.3, 141.2, 139.0, 138.9, 129.0, 128.9, 128.2, 127.2, 127.2, 127.1, 125.4, 37.7, 37.5, 34.5, 31.6. HR-MS (EI): *m/z* calcd for [M]<sup>+</sup> C<sub>24</sub>H<sub>26</sub><sup>+</sup>, 314.2035; found 314.2034.

#### 1,2-di([1,1'-biphenyl]-4-yl)ethane (3g)



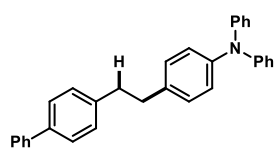
Compound **3g** was prepared following the general procedure A, using corresponding aryl iodide and alkenes. The crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford the desired product (34.8 mg, 52%) as a yellow solid. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 7.2 Hz, 4H), 7.55 (d, *J* = 8.0 Hz, 4H), 7.45 (t, *J* = 7.6 Hz, 4H), 7.34 (t, *J* = 7.4 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 4H), 3.02 (s, 4H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 141.1, 140.9, 139.0, 129.0, 128.8, 127.2, 127.2, 127.1, 37.6. HR-MS (EI): *m/z* calcd for [M]<sup>+</sup> C<sub>26</sub>H<sub>22</sub><sup>+</sup>, 334.1722; found 334.1712.

#### 4-(2,4,6-trimethylphenethyl)-1,1'-biphenyl (3h)



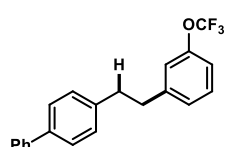
Compound **3h** was prepared following the general procedure A, using corresponding aryl iodide and alkenes. The crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford the desired product (31.2 mg, 52%) as a yellow solid. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.64 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.39 – 7.34 (m, 3H), 6.91 (s, 2H), 2.98 – 2.93 (m, 2H), 2.84 – 2.78 (m, 2H), 2.38 (s, 6H), 2.31 (s, 3H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 141.6, 141.3, 139.2, 136.2, 135.6, 135.5, 129.2, 129.0, 128.9, 127.4, 127.3, 127.2, 35.4, 32.0, 21.1, 19.9. HR-MS (EI): *m/z* calcd for [M]<sup>+</sup> C<sub>23</sub>H<sub>24</sub><sup>+</sup>, 300.1878; found 300.1879.

#### 4-(2-([1,1'-biphenyl]-4-yl)ethyl)-N,N-diphenylaniline (3i)



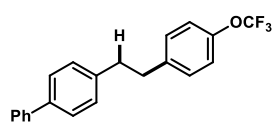
Compound **3i** was prepared following the general procedure A, using corresponding aryl iodine and alkenes. The crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford the desired product (40.0 mg, 47%) as a yellow solid. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.61 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.37 – 7.32 (m, 1H), 7.31 – 7.23 (m, 7H), 7.12 – 7.09 (m, 5H), 7.05 (d, *J* = 8.6 Hz, 2H), 7.00 (t, *J* = 7.6 Hz, 2H), 3.02 – 2.90 (m, 4H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 148.1, 145.9, 141.2, 141.1, 139.0, 136.6, 129.4, 129.3, 129.0, 128.9, 127.21, 127.18, 127.1, 124.8, 123.9, 122.5, 37.7, 37.5. HR-MS (EI): *m/z* calcd for [M]<sup>+</sup> C<sub>32</sub>H<sub>27</sub>N<sup>+</sup>, 425.2143; found 425.2133.

#### 4-(3-(trifluoromethoxy)phenethyl)-1,1'-biphenyl (3j)



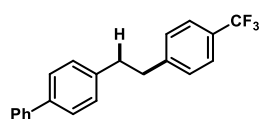
Compound **3j** was prepared following the general procedure A, using corresponding aryl iodine and alkenes. The crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford the desired product (43.0 mg, 63%) as a white solid. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 7.0 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.47 (t, *J* = 7.2 Hz, 2H), 7.38 – 7.34 (m, 1H), 7.31 (d, *J* = 8.4 Hz, 1H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.16 – 7.06 (m, 3H), 2.99 (s, 4H). <sup>19</sup>F NMR (376 MHz, Chloroform-*d*) δ -57.6. <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 149.4 (q, *J* = 3.0 Hz), 144.0, 141.1, 140.3, 139.2, 129.7, 129.0, 128.9, 127.3, 127.2, 127.1, 127.1, 120.6 (q, *J* = 257.5 Hz), 121.2, 118.6, 37.6, 37.3. HR-MS (EI): *m/z* calcd for [M]<sup>+</sup> C<sub>21</sub>H<sub>17</sub>F<sub>3</sub>O<sup>+</sup>, 342.1231; found 342.1228.

#### 4-(4-(trifluoromethoxy)phenethyl)-1,1'-biphenyl (3k)



Compound **3k** was prepared following the general procedure A, using corresponding aryl iodine and alkenes. The crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford the desired product (43.8 mg, 64%) as a white solid. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 7.8 Hz, 2H), 7.54 (d, *J* = 8.2 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.23 (dd, *J* = 14.2, 8.4 Hz, 4H), 7.15 (d, *J* = 8.8 Hz, 2H), 2.97 (s, 4H). <sup>19</sup>F NMR (376 MHz, Chloroform-*d*) δ -57.9. <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 147.6 (q, *J* = 2.0 Hz), 141.1, 140.5, 140.5, 139.1, 129.8, 129.0, 128.9, 127.2, 127.2, 127.1, 121.0 (q, *J* = 1.0 Hz), 120.6 (q, *J* = 257.6 Hz), 37.5, 37.2. HR-MS (ESI): *m/z* calcd for [M+NH<sub>4</sub>]<sup>+</sup> C<sub>21</sub>H<sub>21</sub>F<sub>3</sub>NO<sup>+</sup>, 360.1570; found 360.1565.

#### 4-(4-(trifluoromethyl)phenethyl)-1,1'-biphenyl (3l)

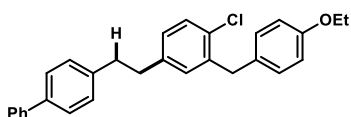


Compound **3l** was prepared following the general procedure A, using corresponding aryl iodine and alkenes. The crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford the desired product (56.0 mg, 86%) as a white solid. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.63 – 7.59 (m, 2H), 7.54 (dd, *J* = 8.0, 5.6 Hz, 4H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.2 Hz, 2H), 3.08 – 2.93 (m, 4H). <sup>19</sup>F NMR (376 MHz, Chloroform-*d*) δ -62.2. <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 145.8, 141.0, 140.3, 139.2, 129.0, 128.9, 128.9, 127.5 (q, *J* = 160.6 Hz), 127.3, 127.1, 125.8, 125.4 (q, *J* = 4.0 Hz), 124.5 (q, *J* = 273.7 Hz), 37.7, 37.2. HR-MS (EI): *m/z* calcd for [M]<sup>+</sup> C<sub>21</sub>H<sub>17</sub>F<sub>3</sub><sup>+</sup>, 326.1282; found 326.1279.

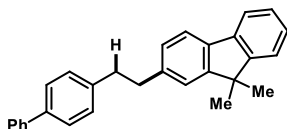


Fc1ccc(cc1)/C=C/c2ccc(cc2)C

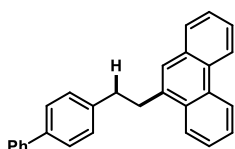
**4-(4-chloro-3-(4-ethoxybenzyl)phenethyl)-1,1'-biphenyl (3n)**



**2-(2-([1,1'-biphenyl]-4-yl)ethyl)-9,9-dimethyl-9H-fluorene (3o)**



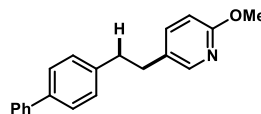
**9-(2-([1,1'-biphenyl]-4-yl)ethyl)phenanthrene (3p)**



Compound **3p** was prepared following the general procedure A, using corresponding aryl iodide and alkenes. The crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to afford the desired product (52.0 mg, 73%) as a yellow solid. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.82 (dd, *J* = 6.4, 3.2 Hz, 1H), 8.73 (d, *J* = 8.0 Hz, 1H), 8.28 – 8.23 (m, 1H), 7.91 – 7.84 (m, 1H), 7.75 – 7.61 (m, 9H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.42 (d, *J* = 7.8 Hz, 3H), 3.55 – 3.46 (m, 2H), 3.27 – 3.18 (m, 2H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 141.3, 141.2, 139.2, 136.0, 132.0, 131.3, 130.9, 129.9, 129.0, 128.9, 128.3, 127.4, 127.3, 127.2, 126.8, 126.4, 126.2, 124.4, 123.5, 122.6, 36.3, 35.5. HR-MS (ESI): *m/z* calcd for [M+H]<sup>+</sup> C<sub>28</sub>H<sub>23</sub><sup>+</sup>, 359.1794;

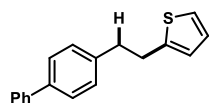
found 359.1794.

### 5-(2-([1,1'-biphenyl]-4-yl)ethyl)-2-methoxypyridine (3q)



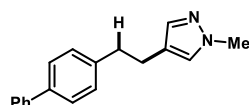
Compound **3q** was prepared following the general procedure A, using corresponding aryl iodine and alkenes. The crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3:1) to afford the desired product (33.0 mg, 57%) as a yellow solid. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.99 (d, *J* = 1.6 Hz, 1H), 7.60 (dd, *J* = 8.4, 1.6 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.40 – 7.31 (m, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 6.69 (dd, *J* = 8.4, 0.8 Hz, 1H), 3.93 (s, 3H), 2.96 – 2.85 (m, 4H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  162.9, 146.3, 141.1, 140.3, 139.2, 139.1, 129.6, 129.0, 128.9, 127.2, 127.2, 127.1, 110.5, 53.4, 37.5, 34.0. HR-MS (ESI): *m/z* calcd for [M+H]<sup>+</sup> C<sub>20</sub>H<sub>20</sub>NO<sup>+</sup>, 290.1539; found 290.1536.

### 2-(2-([1,1'-biphenyl]-4-yl)ethyl)thiophene (3r)



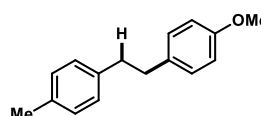
Compound **3r** was prepared following the general procedure A, using corresponding aryl iodine and alkenes. The crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford the desired product (22.2 mg, 42%) as a white solid. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.61 (dd, *J* = 8.2, 1.6 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.30 – 7.26 (m, 3H), 7.00 – 6.96 (m, 2H), 3.01 (s, 4H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  142.2, 141.1, 140.9, 139.0, 129.0, 128.8, 128.3, 127.2, 127.2, 127.1, 125.4, 120.5, 36.7, 32.3. HR-MS (EI): *m/z* calcd for [M]<sup>+</sup> C<sub>18</sub>H<sub>16</sub>S<sup>+</sup>, 264.0973; found 264.0970.

### 4-(2-([1,1'-biphenyl]-4-yl)ethyl)-1-methyl-1H-pyrazole (3s)



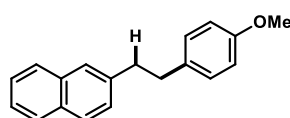
Compound **3s** was prepared following the general procedure A, using corresponding aryl iodine and alkenes. The crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3:1) to afford the desired product (24.0 mg, 33%) as a yellow solid. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.61 – 7.58 (m, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.36 – 7.31 (m, 2H), 7.27 (s, 1H), 7.25 (s, 1H), 7.10 (s, 1H), 3.85 (s, 3H), 2.93 – 2.87 (m, 2H), 2.84 – 2.79 (m, 2H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  141.1, 140.9, 139.0, 138.8, 129.0, 128.8, 128.4, 127.2, 127.1, 127.1, 121.2, 38.9, 37.1, 26.1. HR-MS (ESI): *m/z* calcd for [M+H]<sup>+</sup> C<sub>18</sub>H<sub>19</sub>N<sub>2</sub><sup>+</sup>, 363.1543; found 363.1540.

### 1-methoxy-4-(4-methylphenethyl)benzene (3t)



Compound **3t** was prepared following the general procedure A, using corresponding aryl iodine and alkenes. The crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to afford the desired product (25.8 mg, 57%) as a yellow solid. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.14 – 7.05 (m, 6H), 6.84 (d, *J* = 8.6 Hz, 2H), 3.80 (s, 3H), 2.86 (s, 4H), 2.34 (s, 3H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  157.9, 138.9, 135.4, 134.1, 129.4, 129.1, 128.4, 113.8, 55.4, 37.9, 37.3, 21.1. HR-MS (ESI): *m/z* calcd for [M+H]<sup>+</sup> C<sub>16</sub>H<sub>19</sub>O<sup>+</sup>, 227.1430; found 227.1434.

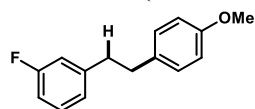
### 2-(4-methoxyphenethyl)naphthalene (3u)



Compound **3u** was prepared following the general procedure A, using corresponding aryl iodine and alkenes. The crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to afford the desired product (20.0 mg, 38%) as a white solid. <sup>1</sup>H

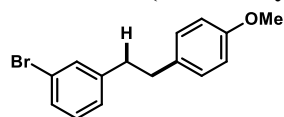
NMR (400 MHz, Chloroform-*d*)  $\delta$  7.82 (dd,  $J$  = 16.7, 7.8 Hz, 3H), 7.64 (s, 1H), 7.46 (p,  $J$  = 5.6 Hz, 2H), 7.36 (d,  $J$  = 8.4 Hz, 1H), 7.15 (d,  $J$  = 8.4 Hz, 2H), 6.86 (d,  $J$  = 8.4 Hz, 2H), 3.81 (s, 3H), 3.09 (dd,  $J$  = 9.2, 5.8 Hz, 2H), 2.99 (dd,  $J$  = 9.2, 5.8 Hz, 2H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  158.0, 139.5, 133.9, 133.7, 132.1, 129.5, 127.9, 127.7, 127.6, 127.5, 126.6, 126.0, 125.3, 113.9, 55.4, 38.5, 37.0. HR-MS (ESI):  $m/z$  calcd for  $[\text{M}+\text{H}]^+$   $\text{C}_{19}\text{H}_{19}\text{O}^+$ , 263.1430; found 263.1428.

#### 1-fluoro-3-(4-methoxyphenethyl)benzene (3v)



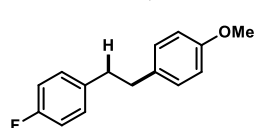
Compound **3v** was prepared following the general procedure A, using corresponding aryl iodine and alkenes. The crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to afford the desired product (30.0 mg, 65%) as a colorless oil.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.16 – 7.09 (m, 1H), 6.98 (d,  $J$  = 8.6 Hz, 2H), 6.85 – 6.72 (m, 5H), 3.69 (s, 3H), 2.81 – 2.73 (m, 4H).  $^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  -113.7.  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  163.0 (d,  $J$  = 246.4 Hz), 158.0, 144.5 (d,  $J$  = 7.1 Hz), 133.5, 129.8 (d,  $J$  = 9.1 Hz), 129.4, 124.3 (d,  $J$  = 3.0 Hz), 115.4 (d,  $J$  = 20.0 Hz), 113.9, 112.8 (d,  $J$  = 21.2 Hz), 55.3, 38.0, 36.8. HR-MS (EI):  $m/z$  calcd for  $[\text{M}]^+$   $\text{C}_{15}\text{H}_{15}\text{FO}^+$ , 230.1107; found 230.1103.

#### 1-bromo-3-(4-methoxyphenethyl)benzene (3w)



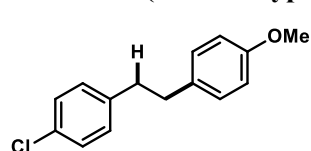
Compound **3w** was prepared following the general procedure A, using corresponding aryl iodine and alkenes. The crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to afford the desired product (34.3 mg, 59%) as a yellow oil.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.34 (d,  $J$  = 7.4 Hz, 2H), 7.14 (t,  $J$  = 7.4 Hz, 1H), 7.11 – 7.05 (m, 3H), 6.84 (d,  $J$  = 8.6 Hz, 2H), 3.80 (s, 3H), 2.86 (s, 4H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  158.0, 144.3, 133.4, 131.6, 130.0, 129.5, 129.1, 127.3, 122.5, 113.9, 55.4, 37.9, 36.9. HR-MS (ESI):  $m/z$  calcd for  $[\text{M}+\text{H}]^+$   $\text{C}_{15}\text{H}_{16}^{79}\text{BrO}^+$ , 291.0379; found 291.0378;  $\text{C}_{15}\text{H}_{16}^{81}\text{BrO}^+$ , 293.0359; found 293.0346.

#### 1-fluoro-4-(4-methoxyphenethyl)benzene (3x)



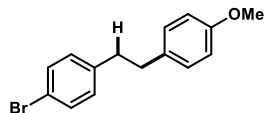
Compound **3x** was prepared following the general procedure A, using corresponding aryl iodine and alkene. The crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to afford the desired product (25.0 mg, 54%) as a yellow solid.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.14 – 7.05 (m, 4H), 6.96 (t,  $J$  = 8.8 Hz, 2H), 6.84 (d,  $J$  = 8.6 Hz, 2H), 3.80 (s, 3H), 2.92 – 2.81 (m, 4H).  $^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  -117.6.  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  161.4 (d,  $J$  = 245.4 Hz), 158.0, 137.5 (d,  $J$  = 3.0 Hz), 133.6, 129.9 (d,  $J$  = 7.1 Hz), 129.5, 115.1 (d,  $J$  = 20.2 Hz), 113.8, 55.3, 37.4, 37.2. HR-MS (EI):  $m/z$  calcd for  $[\text{M}]^+$   $\text{C}_{15}\text{H}_{15}\text{F}^+$ , 230.1107; found 230.1107.

#### 1-chloro-4-(4-methoxyphenethyl)benzene (3y)



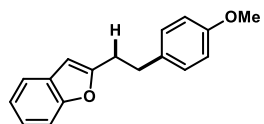
Compound **3y** was prepared following the general procedure A, using corresponding aryl iodine and alkene. The crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to afford the desired product (30.0 mg, 61%) as a yellow solid.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.24 (d,  $J$  = 8.4 Hz, 2H), 7.08 (d,  $J$  = 4.4 Hz, 2H), 7.06 (d,  $J$  = 4.6 Hz, 2H), 6.83 (d,  $J$  = 8.6 Hz, 2H), 3.79 (s, 3H), 2.91 – 2.78 (m, 4H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  158.0, 140.3, 133.4, 131.7, 130.0, 129.5, 128.5, 113.9, 55.3, 37.6, 37.0. HR-MS (EI):  $m/z$  calcd for  $[\text{M}]^+$   $\text{C}_{15}\text{H}_{15}\text{ClO}^+$ , 246.0811; found 246.0806.

#### 1-bromo-4-(4-methoxyphenethyl)benzene (3z)



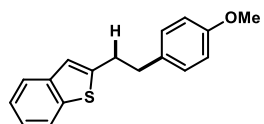
Compound **3z** was prepared following the general procedure A, using corresponding aryl iodine and alkene. The crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to afford the desired product (35.0 mg, 60%) as a colorless oil. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.40 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 8.6 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 3.80 (s, 3H), 2.86 (s, 4H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 158.0, 140.8, 133.4, 131.4, 130.4, 129.5, 119.7, 113.9, 55.4, 37.6, 36.9. HR-MS (EI): *m/z* calcd for [M]<sup>+</sup> C<sub>15</sub>H<sub>15</sub><sup>79</sup>BrO<sup>+</sup>, 290.0306; found 290.0306; C<sub>15</sub>H<sub>15</sub><sup>81</sup>BrO<sup>+</sup>, 292.0286; found 292.0281.

## 2-(4-methoxyphenethyl)benzofuran (3aa)



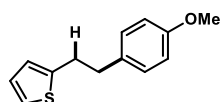
Compound **3aa** was prepared following the general procedure A, using corresponding aryl iodine and alkene. The crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to afford the desired product (35.0 mg, 69%) as a colorless oil. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.56 – 7.47 (m, 2H), 7.30 – 7.21 (m, 2H), 7.18 (d, *J* = 8.6 Hz, 2H), 6.89 (d, *J* = 8.6 Hz, 2H), 6.41 (s, 1H), 3.83 (s, 3H), 3.14 – 3.03 (m, 4H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 158.6, 158.1, 154.7, 133.1, 129.4, 129.0, 123.3, 122.5, 120.4, 113.9, 110.8, 102.4, 55.3, 33.2, 30.7. HR-MS (ESI): *m/z* calcd for [M+H]<sup>+</sup> C<sub>17</sub>H<sub>17</sub>O<sub>2</sub><sup>+</sup>, 253.1223; found 253.1227.

## 2-(4-methoxyphenethyl)benzo[b]thiophene (3ab)



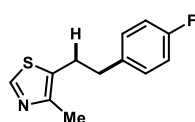
Compound **3ab** was prepared following the general procedure A, using corresponding aryl iodine and alkene. The crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to afford the desired product (34.0 mg, 63%) as a colorless oil. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 8.2 Hz, 1H), 7.56 (d, *J* = 8.8 Hz, 1H), 7.25 – 7.13 (m, 2H), 7.05 (d, *J* = 8.6 Hz, 2H), 6.88 (s, 1H), 6.75 (d, *J* = 8.6 Hz, 2H), 3.70 (s, 3H), 3.14 – 3.05 (m, 2H), 2.96 – 2.86 (m, 2H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 158.1, 145.7, 140.2, 139.4, 133.1, 129.5, 124.2, 123.6, 122.9, 122.3, 121.0, 113.9, 55.4, 36.6, 33.0. HR-MS (ESI): *m/z* calcd for [M+H]<sup>+</sup> C<sub>17</sub>H<sub>17</sub>OS<sup>+</sup>, 269.0995; found 269.1003.

## 2-(4-methoxyphenethyl)thiophene (3ac)



Compound **3ac** was prepared following the general procedure A, using corresponding aryl iodine and alkene. The crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to afford the desired product (27.0 mg, 62%) as a yellow oil. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.15 – 7.10 (m, 3H), 6.92 (dd, *J* = 5.2, 2.8 Hz, 1H), 6.85 (d, *J* = 8.4 Hz, 2H), 6.79 – 6.77 (m, 1H), 3.80 (s, 3H), 3.15 – 3.09 (m, 2H), 2.97 – 2.91 (m, 2H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 158.1, 144.6, 133.3, 129.5, 126.8, 124.4, 123.1, 113.9, 55.3, 37.3, 32.2. HR-MS (ESI): *m/z* calcd for [M+H]<sup>+</sup> C<sub>13</sub>H<sub>15</sub>OS<sup>+</sup>, 219.0838; found 219.0838.

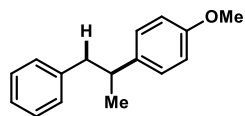
## 5-(4-fluorophenethyl)-4-methylthiazole (3ad)



Compound **3ad** was prepared following the general procedure A, using corresponding aryl iodine and alkene. The crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5:1) to afford the desired product (28.0 mg, 63%) as a yellow oil. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.53 (s, 1H), 7.11 – 7.02 (m, 2H), 6.95 (t, *J* = 8.4 Hz, 2H), 3.03 (t, *J* = 7.2 Hz, 2H), 2.87 (t, *J* = 7.6 Hz, 2H), 2.24 (s, 3H). <sup>19</sup>F NMR (376 MHz, Chloroform-*d*) δ -116.8. <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 161.6 (d, *J* = 245.4 Hz), 149.2, 149.1, 136.1 (d, *J* = 4.0 Hz), 130.5,

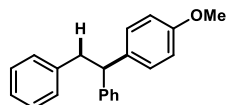
130.0 (d,  $J = 8.1$  Hz), 115.3 (d,  $J = 21.2$  Hz), 37.0, 28.4, 14.8. HR-MS (ESI):  $m/z$  calcd for  $[M+H]^+ C_{12}H_{13}FNS^+$ , 222.0747; found 222.0742.

#### 1-methoxy-4-(1-phenylpropan-2-yl)benzene (3ae)



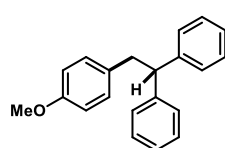
Compound **3ae** was prepared following the general procedure A, using corresponding aryl iodine and alkene. The crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to afford the desired product (23.1 mg, 51%) as a yellow oil.  $^1H$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.29 – 7.24 (m, 2H), 7.19 (t,  $J = 7.2$  Hz, 1H), 7.14 – 7.08 (m, 4H), 6.86 (d,  $J = 8.8$  Hz, 2H), 3.82 (s, 3H), 3.02 – 2.91 (m, 2H), 2.77 (dd,  $J = 13.0, 8.0$  Hz, 1H), 1.25 (d,  $J = 6.8$  Hz, 3H).  $^{13}C$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  157.9, 141.0, 139.2, 129.3, 128.1, 128.0, 125.9, 113.7, 55.3, 45.4, 41.1, 21.5. HR-MS (ESI):  $m/z$  calcd for  $[M+H]^+ C_{16}H_{19}O^+$ , 227.1430; found 227.1428.

#### (1-(4-methoxyphenyl)ethane-1,2-diyl)dibenzene (3af)



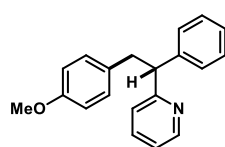
Compound **3af** was prepared following the general procedure A, using corresponding aryl iodine and alkene. The crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to afford the desired product (29.0 mg, 50%) as a white solid.  $^1H$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.25 – 7.22 (m, 2H), 7.20 – 7.14 (m, 5H), 7.13 – 7.09 (m, 3H), 7.02 – 6.98 (m, 2H), 6.79 (d,  $J = 8.8$  Hz, 2H), 4.18 (t,  $J = 7.8$  Hz, 1H), 3.75 (s, 3H), 3.33 (d,  $J = 7.8$  Hz, 2H).  $^{13}C$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  157.9, 145.0, 140.5, 136.7, 129.2, 129.0, 128.4, 128.1, 128.0, 126.2, 125.9, 113.8, 55.3, 52.3, 42.4. HR-MS (ESI):  $m/z$  calcd for  $[M+NH_4]^+ C_{21}H_{24}NO^+$ , 306.1852; found 306.1859.

#### (2-(4-methoxyphenyl)ethane-1,1-diyl)dibenzene (3ag)



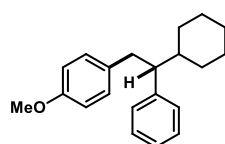
Compound **3ag** was prepared following the general procedure A, using corresponding aryl iodine and alkene. The crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to afford the desired product (44.0 mg, 76%) as a yellow solid.  $^1H$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.30 (dt,  $J = 13.0, 7.2$  Hz, 8H), 7.22 (t,  $J = 7.0$  Hz, 2H), 6.98 (d,  $J = 8.6$  Hz, 2H), 6.78 (d,  $J = 8.6$  Hz, 2H), 4.25 (t,  $J = 7.8$  Hz, 1H), 3.79 (s, 3H), 3.38 (d,  $J = 7.8$  Hz, 2H).  $^{13}C$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  157.8, 144.7, 132.5, 130.1, 128.5, 128.2, 126.3, 113.6, 55.3, 53.5, 41.3. HR-MS (ESI):  $m/z$  calcd for  $[M+H]^+ C_{21}H_{21}O^+$ , 289.1587; found 289.1589.

#### 2-(2-(4-methoxyphenyl)-1-phenylethyl)pyridine (3ah)



Compound **3ah** was prepared following the general procedure A, using corresponding aryl iodine and alkene. The crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3:1) to afford the desired product (31.0 mg, 54%) as a yellow solid.  $^1H$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  8.51 (d,  $J = 3.0$  Hz, 1H), 7.42 (td,  $J = 7.6, 2.0$  Hz, 1H), 7.24 (d,  $J = 8.0$  Hz, 2H), 7.17 (t,  $J = 7.6$  Hz, 2H), 7.08 (t,  $J = 7.2$  Hz, 1H), 7.03 – 6.96 (m, 2H), 6.87 (d,  $J = 8.6$  Hz, 2H), 6.61 (d,  $J = 8.6$  Hz, 2H), 4.23 (t,  $J = 7.8$  Hz, 1H), 3.64 (s, 3H), 3.51 (dd,  $J = 13.8, 8.0$  Hz, 1H), 3.21 (dd,  $J = 13.8, 7.6$  Hz, 1H).  $^{13}C$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  163.1, 157.8, 149.3, 143.4, 136.5, 132.5, 130.0, 128.5, 128.3, 126.5, 123.4, 121.5, 113.5, 55.8, 55.2, 40.5. HR-MS (EI):  $m/z$  calcd for  $[M]^+ C_{20}H_{19}NO^+$ , 289.1467; found 289.1464.

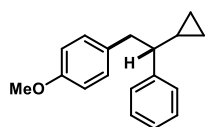
#### 1-(2-cyclohexyl-2-phenylethyl)-4-methoxybenzene (3ai)



Compound **3ai** was prepared following the general procedure A, using corresponding aryl iodine and alkene. The crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to

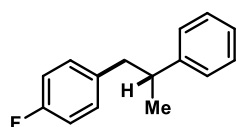
afford the desired product (34.0 mg, 58%) as a colorless oil.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.21 (t,  $J$  = 7.2 Hz, 2H), 7.14 (t,  $J$  = 6.6 Hz, 1H), 7.03 (d,  $J$  = 7.0 Hz, 2H), 6.86 (d,  $J$  = 8.6 Hz, 2H), 6.69 (d,  $J$  = 8.6 Hz, 2H), 3.73 (s, 3H), 3.12 (dd,  $J$  = 13.6, 5.2 Hz, 1H), 2.76 (dd,  $J$  = 13.6, 9.6 Hz, 1H), 2.63 – 2.55 (m, 1H), 1.97 (d,  $J$  = 12.4 Hz, 1H), 1.75 (dd,  $J$  = 12.8, 3.6 Hz, 1H), 1.67 – 1.53 (m, 3H), 1.33 – 1.24 (m, 2H), 1.14 – 1.02 (m, 2H), 0.90 – 0.74 (m, 1H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  157.5, 143.8, 133.5, 130.0, 128.9, 127.8, 125.8, 113.4, 55.2, 54.6, 42.3, 38.4, 31.9, 30.5, 26.6. HR-MS (ESI):  $m/z$  calcd for  $[\text{M}+\text{H}]^+$   $\text{C}_{21}\text{H}_{26}\text{O}^+$ , 295.2056; found 295.2056.

#### 1-(2-cyclopropyl-2-phenylethyl)-4-methoxybenzene (3aj)



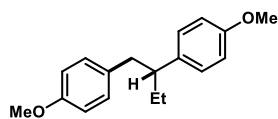
Compound **3aj** was prepared following the general procedure A, using corresponding aryl iodide and alkene. The crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to afford the desired product (36.0 mg, 72%) as a colorless oil.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.24 (d,  $J$  = 7.6 Hz, 2H), 7.16 (t,  $J$  = 7.6 Hz, 1H), 7.11 (d,  $J$  = 7.6 Hz, 2H), 6.90 (d,  $J$  = 8.4 Hz, 2H), 6.71 (d,  $J$  = 8.0 Hz, 2H), 3.74 (s, 3H), 3.02 (dd,  $J$  = 13.2, 6.4 Hz, 1H), 2.94 (dd,  $J$  = 13.2, 7.8 Hz, 1H), 2.02 (q,  $J$  = 7.8, 7.0 Hz, 1H), 1.03 (qt,  $J$  = 9.0, 4.2 Hz, 1H), 0.57 – 0.49 (m, 1H), 0.40 – 0.31 (m, 1H), 0.06 – -0.00 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  157.7, 145.2, 132.7, 130.3, 128.1, 127.9, 126.0, 113.3, 55.2, 42.6, 16.8, 5.9, 3.8. HR-MS (ESI):  $m/z$  calcd for  $[\text{M}+\text{H}]^+$   $\text{C}_{18}\text{H}_{21}\text{O}^+$ , 253.1587; found 253.1585.

#### 1-fluoro-4-(2-phenylpropyl)benzene (3ak)



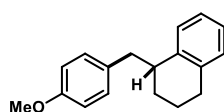
Compound **3ak** was prepared following the general procedure A, using corresponding aryl iodide and alkene. The crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to afford the desired product (37.0 mg, 86%) as a colorless oil.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.17 (q,  $J$  = 7.2 Hz, 2H), 7.12 – 7.04 (m, 3H), 6.94 – 6.85 (m, 2H), 6.81 (t,  $J$  = 8.6 Hz, 2H), 2.94 – 2.75 (m, 2H), 2.67 (dd,  $J$  = 13.2, 7.8 Hz, 1H), 1.16 (d,  $J$  = 6.8 Hz, 3H).  $^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  -117.6.  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  161.4 (d,  $J$  = 244.4 Hz), 146.6, 136.4 (d,  $J$  = 4.0 Hz), 130.6 (d,  $J$  = 7.1 Hz), 128.4, 127.1, 126.2, 114.9 (d,  $J$  = 21.2 Hz), 44.3, 42.1 (d,  $J$  = 2.0 Hz), 21.2. HR-MS (EI):  $m/z$  calcd for  $[\text{M}]^+$   $\text{C}_{15}\text{H}_{15}\text{F}^+$ , 214.1158; found 214.1154.

#### 4,4'-(butane-1,2-diyl)bis(methoxybenzene) (3al)



Compound **3al** was prepared following the general procedure A, using corresponding aryl iodide and alkene. The crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to afford the desired product (29.0 mg, 54%) as a colorless oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.01 (d,  $J$  = 8.6 Hz, 2H), 6.93 (d,  $J$  = 8.6 Hz, 2H), 6.81 (d,  $J$  = 8.6 Hz, 2H), 6.75 (d,  $J$  = 8.6 Hz, 2H), 3.79 (s, 3H), 3.76 (s, 3H), 2.85 – 2.72 (m, 2H), 2.67 – 2.56 (m, 1H), 1.75 – 1.64 (m, 1H), 1.60 – 1.50 (m, 1H), 0.76 (t,  $J$  = 7.3 Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  157.8, 157.7, 137.2, 133.2, 130.1, 128.8, 113.6, 113.4, 55.3, 49.2, 42.8, 28.5, 12.2. HR-MS (ESI):  $m/z$  calcd for  $[\text{M}+\text{NH}_4]^+$   $\text{C}_{18}\text{H}_{26}\text{O}_2^+$ , 288.1958; found 288.1960.

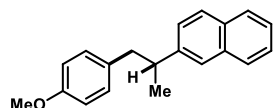
#### 1-(4-methoxybenzyl)-1,2,3,4-tetrahydronaphthalene (3am)



Compound **3am** was prepared following the general procedure A, using corresponding aryl iodide and alkene. The crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to afford the desired product (27.0 mg, 53%) as a colorless oil.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.25 – 7.20 (m, 1H), 7.18 – 7.10 (m, 5H), 6.88 (d,  $J$  = 8.8 Hz, 2H), 3.83 (s,

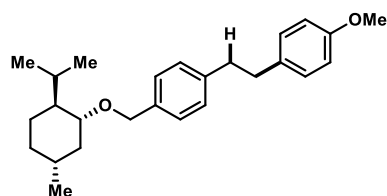
3H), 3.13 – 3.01 (m, 2H), 2.86 – 2.64 (m, 3H), 1.97 – 1.83 (m, 1H), 1.77 – 1.62 (m, 3H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 158.0, 140.8, 137.2, 133.2, 130.2, 129.3, 129.0, 125.8, 125.6, 113.8, 55.4, 42.6, 39.8, 29.9, 26.5, 19.3. HR-MS (ESI): *m/z* calcd for [M+H]<sup>+</sup> C<sub>18</sub>H<sub>21</sub>O<sup>+</sup>, 253.1587; found 253.1581.

### 2-(1-(4-methoxyphenyl)propan-2-yl)naphthalene (3an)



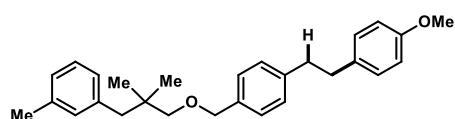
Compound **3an** was prepared following the general procedure A, using corresponding aryl iodine and alkene. The crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to afford the desired product (48.6 mg, 88%) as a white solid. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.81 – 7.76 (m, 3H), 7.59 (s, 1H), 7.46 – 7.39 (m, 2H), 7.36 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.01 (d, *J* = 8.6 Hz, 2H), 6.77 (d, *J* = 8.6 Hz, 2H), 3.76 (s, 3H), 3.17 – 3.08 (m, 1H), 2.98 (dd, *J* = 13.4, 6.6 Hz, 1H), 2.80 (dd, *J* = 13.4, 8.0 Hz, 1H), 1.32 (d, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 157.9, 144.6, 133.7, 132.9, 132.3, 130.2, 127.9, 127.7, 127.7, 126.1, 125.9, 125.3, 125.2, 113.6, 55.3, 44.1, 42.3, 21.3. HR-MS (ESI): *m/z* calcd for [M+H]<sup>+</sup> C<sub>20</sub>H<sub>21</sub>O<sup>+</sup>, 277.1587; found 277.1587.

### 1-(((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)methyl)-4-(4-methoxyphenethyl)benzene (3ao)



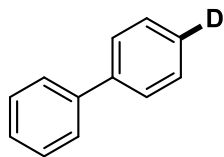
Compound **3ao** was prepared following the general procedure A, using corresponding aryl iodine and alkene. The crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to afford the desired product (40.0 mg, 53%) as a white solid. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.27 (d, *J* = 7.6 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 4.64 (d, *J* = 11.2 Hz, 1H), 4.38 (d, *J* = 11.2 Hz, 1H), 3.80 (s, 3H), 3.23 – 3.11 (m, 1H), 2.94 – 2.80 (m, 4H), 2.38 – 2.25 (m, 1H), 2.25 – 2.16 (m, 1H), 1.73 – 1.58 (m, 2H), 1.37 – 1.25 (m, 2H), 1.01 – 0.86 (m, 9H), 0.72 (d, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 157.9, 141.2, 136.7, 134.0, 129.5, 128.5, 128.1, 113.8, 78.7, 70.4, 55.3, 48.4, 40.4, 38.0, 37.2, 34.7, 31.7, 25.6, 23.3, 22.5, 21.1, 16.1. HR-MS (ESI): *m/z* calcd for [M+H]<sup>+</sup> C<sub>26</sub>H<sub>37</sub>O<sub>2</sub><sup>+</sup>, 381.2788; found 381.2794.

### 1-(3-((4-(4-methoxyphenethyl)benzyl)oxy)-2,2-dimethylpropyl)-3-methylbenzene (3ap)



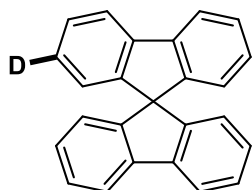
Compound **3ap** was prepared following the general procedure A, using corresponding aryl iodine and alkene. The crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to afford the desired product (34.0 mg, 42%) as a white solid. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.32 (d, *J* = 7.8 Hz, 2H), 7.20 (d, *J* = 7.8 Hz, 2H), 7.14 (t, *J* = 7.6 Hz, 3H), 7.03 (d, *J* = 7.6 Hz, 1H), 7.01 – 6.94 (m, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 4.52 (s, 2H), 3.81 (s, 3H), 3.10 (s, 2H), 2.91 (s, 4H), 2.61 (s, 2H), 2.34 (s, 3H), 0.93 (s, 6H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 157.9, 141.1, 139.1, 137.2, 136.6, 134.0, 131.6, 129.5, 128.5, 127.8, 127.7, 127.7, 126.6, 113.8, 78.3, 73.1, 55.4, 44.9, 38.0, 37.2, 35.9, 24.9, 21.6. HR-MS (ESI): *m/z* calcd for [M+H]<sup>+</sup> C<sub>28</sub>H<sub>35</sub>O<sub>2</sub><sup>+</sup>, 403.2632; found 403.2634.

#### 1,1'-biphenyl-4-d (4a)



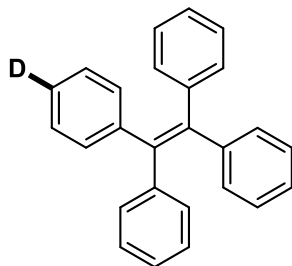
Compound **4a** was prepared following the general procedure B, using corresponding aryl chloride. The crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 50:1) to afford the desired product (21.0 mg, 67%, 97% D) as a white solid.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.60 (d,  $J$  = 7.6 Hz, 4H), 7.48 – 7.32 (m, 5H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  141.3, 128.8, 128.7, 127.3, 127.2. HR-MS (ESI):  $m/z$  calcd for  $[\text{M}+\text{H}]^+$   $\text{C}_{12}\text{H}_{10}\text{D}^+$ , 156.0918; found 156.0920.

#### 9,9'-spiro[fluorene]-2-d (4b)



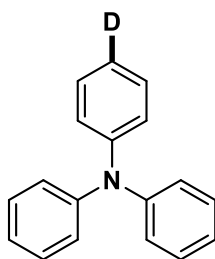
Compound **4b** was prepared following the general procedure B, using corresponding aryl bromide. The crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 50:1) to afford the desired product (50.0 mg, 79%, 93% D) as a white solid.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.76 (d,  $J$  = 7.6 Hz, 4H), 7.27 (t,  $J$  = 7.4 Hz, 4H), 7.01 (t,  $J$  = 7.5 Hz, 3H), 6.69 – 6.61 (m, 4H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  148.9, 141.9, 127.9, 127.8, 127.7, 124.1, 124.0, 120.1, 66.0. HR-MS (EI):  $m/z$  calcd for  $[\text{M}]^+$   $\text{C}_{25}\text{H}_{15}\text{D}^+$ , 317.1315; found 317.1313.

#### (2-(phenyl-4-d)ethene-1,1,2-triyl)tribenzene (4c)



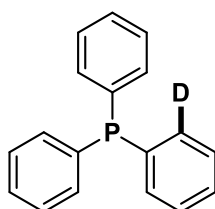
Compound **4c** was prepared following the general procedure B, using corresponding aryl bromide. The crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 50:1) to afford the desired product (35.0 mg, 52%, 99% D) as a white solid.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.17 – 7.10 (m, 12H), 7.06 (dd,  $J$  = 7.0, 2.7 Hz, 7H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  143.8, 141.0, 131.4, 127.7, 127.6, 126.5. HR-MS (EI):  $m/z$  calcd for  $[\text{M}]^+$   $\text{C}_{26}\text{H}_{19}\text{D}^+$ , 333.1628; found 333.1627.

#### N,N-diphenylaniline-4-d (4d)



Compound **4d** was prepared following the general procedure B, using corresponding aryl bromide. The crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 50:1) to afford the desired product (45.0 mg, 91%, 92% D) as a white solid.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.21 – 7.11 (m, 6H), 7.02 – 6.89 (m, 8H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  148.0, 129.3, 129.2, 124.3, 122.8. HR-MS (ESI):  $m/z$  calcd for  $[\text{M}+\text{H}]^+$   $\text{C}_{18}\text{H}_{15}\text{DN}^+$ , 247.1340; found 247.1333.

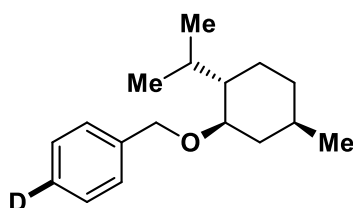
#### diphenyl(phenyl-2-d)phosphane (4e)



Compound **4e** was prepared following the general procedure B, using corresponding aryl bromide. The crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 50:1) to afford the desired product (43.0 mg, 82%, 99% D) as a colorless oil.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.23 (dq,  $J$  = 4.8, 2.1 Hz, 14H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  134.0, 133.8, 128.9, 128.6, 128.5. HR-MS (ESI):  $m/z$  calcd for  $[\text{M}+\text{H}]^+$   $\text{C}_{18}\text{H}_{15}\text{DP}^+$ , 264.1047; found 264.1041.

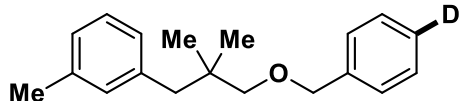


**1-(((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)methyl)benzene-4-d (4f)**



Compound **4f** was prepared following the general procedure B, using corresponding aryl bromide. The crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 50:1) to afford the desired product (33.0 mg, 67%, 89% D) as a colorless oil. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.31 (m, 4H), 4.66 (d, *J* = 11.4 Hz, 1H), 4.41 (d, *J* = 11.4 Hz, 1H), 3.18 (td, *J* = 10.6, 4.0 Hz, 1H), 2.35 – 2.27 (m, 1H), 2.23 – 2.17 (m, 1H), 1.69 – 1.60 (m, 2H), 1.41 – 1.26 (m, 3H), 1.03 – 0.95 (m, 1H), 0.94 (d, *J* = 6.6 Hz, 3H), 0.90 (d, *J* = 7.0 Hz, 3H), 0.86 (dd, *J* = 12.6, 9.2 Hz, 1H), 0.72 (d, *J* = 7.0 Hz, 3H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 139.2, 128.4, 128.3, 128.0, 127.5, 78.8, 70.5, 48.4, 40.4, 34.7, 31.7, 25.6, 23.3, 22.5, 21.1, 16.1. HR-MS (EI): *m/z* calcd for [M]<sup>+</sup> C<sub>17</sub>H<sub>25</sub>DO<sup>+</sup>, 247.2046; found 247.2043.

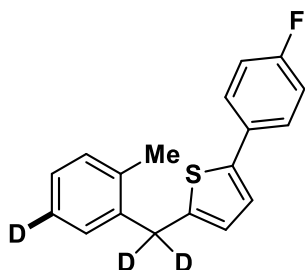
**1-((2,2-dimethyl-3-(*m*-tolyl)propoxy)methyl)benzene-4-d (4g)**



Compound **4g** was prepared following the general procedure B, using corresponding aryl bromide. The crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 50:1)

to afford the desired product (47.0 mg, 86%, 88% D) as a colorless oil. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.36 (m, 4H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 7.6 Hz, 1H), 6.98 – 6.94 (m, 2H), 4.54 (s, 2H), 3.11 (s, 2H), 2.60 (s, 2H), 2.33 (s, 3H), 0.93 (s, 6H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 139.1, 137.2, 131.5, 128.4, 128.3, 127.7, 127.6, 127.5, 127.4, 126.6, 78.4, 73.2, 44.9, 35.9, 24.9, 21.5. HR-MS (EI): *m/z* calcd for [M]<sup>+</sup> C<sub>19</sub>H<sub>23</sub>DO<sup>+</sup>, 269.1890; found 269.1885.

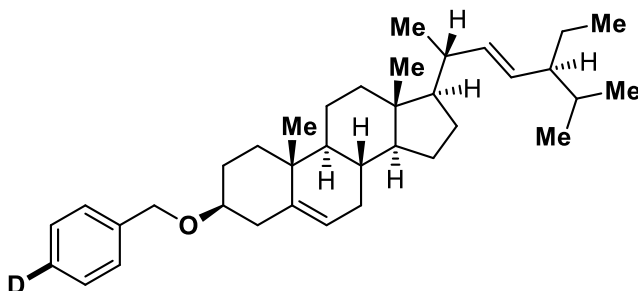
**2-(4-fluorophenyl)-5-((2-methylphenyl-5-d)methyl-d2)thiophene (4h)**



Compound **4h** was prepared following the general procedure B, using corresponding aryl bromide. The crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 50:1) to afford the desired product (48.5 mg, 85%, 99% D) as a colorless oil. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.52 – 7.47 (m, 2H), 7.23 (d, *J* = 3.6 Hz, 1H), 7.21 (s, 2H), 7.07 – 7.01 (m, 3H), 6.69 (d, *J* = 3.6 Hz, 1H), 4.14 (d, *J* = 7.4 Hz, 0.58 H), 2.35 (s, 3H). <sup>19</sup>F

NMR (376 MHz, CDCl<sub>3</sub>) δ -115.2. <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 162.2 (d, *J* = 248.5 Hz), 141.6, 136.5, 131.0 (d, *J* = 4.0 Hz), 130.6, 129.5 (d, *J* = 11.1 Hz), 127.2, 127.2, 127.1, 127.0, 126.3, 126.0, 122.8 (d, *J* = 2.0 Hz), 115.8 (d, *J* = 21.2 Hz), 34.0, 19.6. HR-MS (EI): *m/z* calcd for [M]<sup>+</sup> C<sub>18</sub>H<sub>12</sub>D<sub>2</sub>FS<sup>+</sup>, 285.1067; found 285.1039.

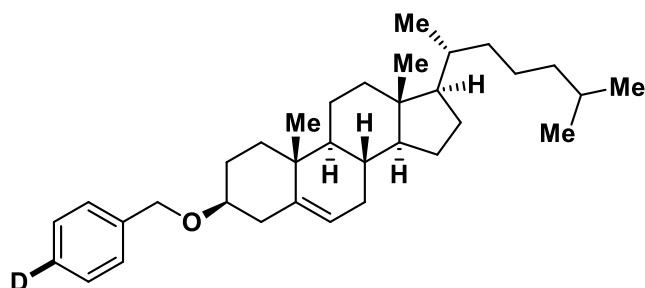
**(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-17-((2*R*,5*S*,*E*)-5-ethyl-6-methylhept-3-en-2-yl)-10,13-dimethyl-3-((phenyl-4-d)methoxy)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthrene (4i)**



Compound **4i** was prepared following the general procedure B, using corresponding aryl bromide. The crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 50:1) to afford the desired product (91.0 mg, 90%, 90% D)

as a white solid.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.45 (d,  $J$  = 8.2 Hz, 2H), 7.22 (d,  $J$  = 8.2 Hz, 2H), 5.34 (d,  $J$  = 5.0 Hz, 1H), 5.15 (dd,  $J$  = 15.2, 8.4 Hz, 1H), 5.02 (dd,  $J$  = 15.2, 8.6 Hz, 1H), 4.50 (s, 2H), 3.31 – 3.22 (m, 1H), 2.43 – 2.38 (m, 1H), 2.27 (t,  $J$  = 11.2 Hz, 1H), 2.07 – 1.85 (m, 5H), 1.73 – 1.66 (m, 1H), 1.57 – 1.40 (m, 9H), 1.32 – 1.12 (m, 5H), 1.10 – 1.05 (m, 1H), 1.02 (d,  $J$  = 6.6 Hz, 6H), 1.00 – 0.88 (m, 2H), 0.85 (d,  $J$  = 6.4 Hz, 3H), 0.81 (t,  $J$  = 7.2 Hz, 6H), 0.70 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  140.9, 138.4, 138.2, 131.5, 129.4, 129.3, 121.8, 121.3, 78.9, 69.2, 57.0, 56.0, 51.3, 50.3, 42.3, 40.6, 39.8, 39.2, 37.3, 37.0, 32.0, 32.0, 29.0, 28.5, 25.5, 24.4, 21.3, 21.2, 21.1, 19.5, 19.1, 12.3, 12.1. HR-MS (EI):  $m/z$  calcd for  $[\text{M}+\text{NH}_4]^+$   $\text{C}_{36}\text{H}_{57}\text{DNO}^+$ , 521.4576; found 521.4569.

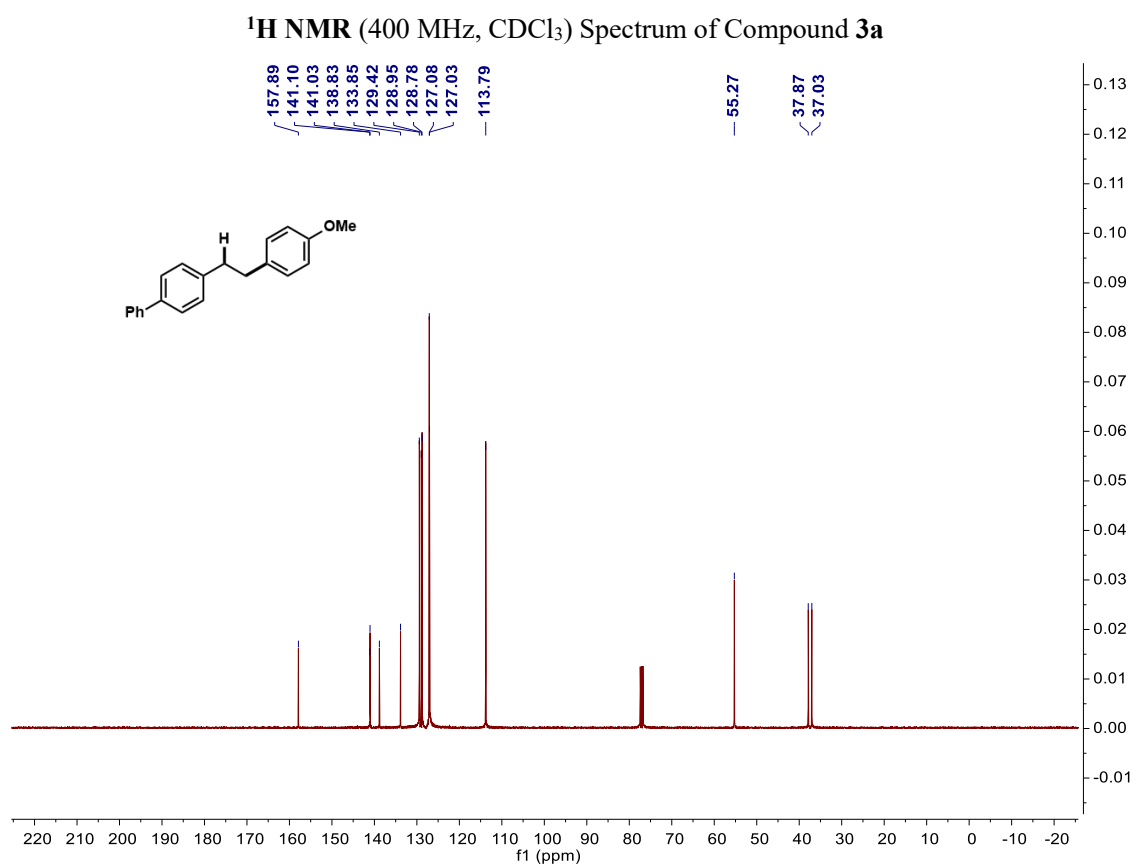
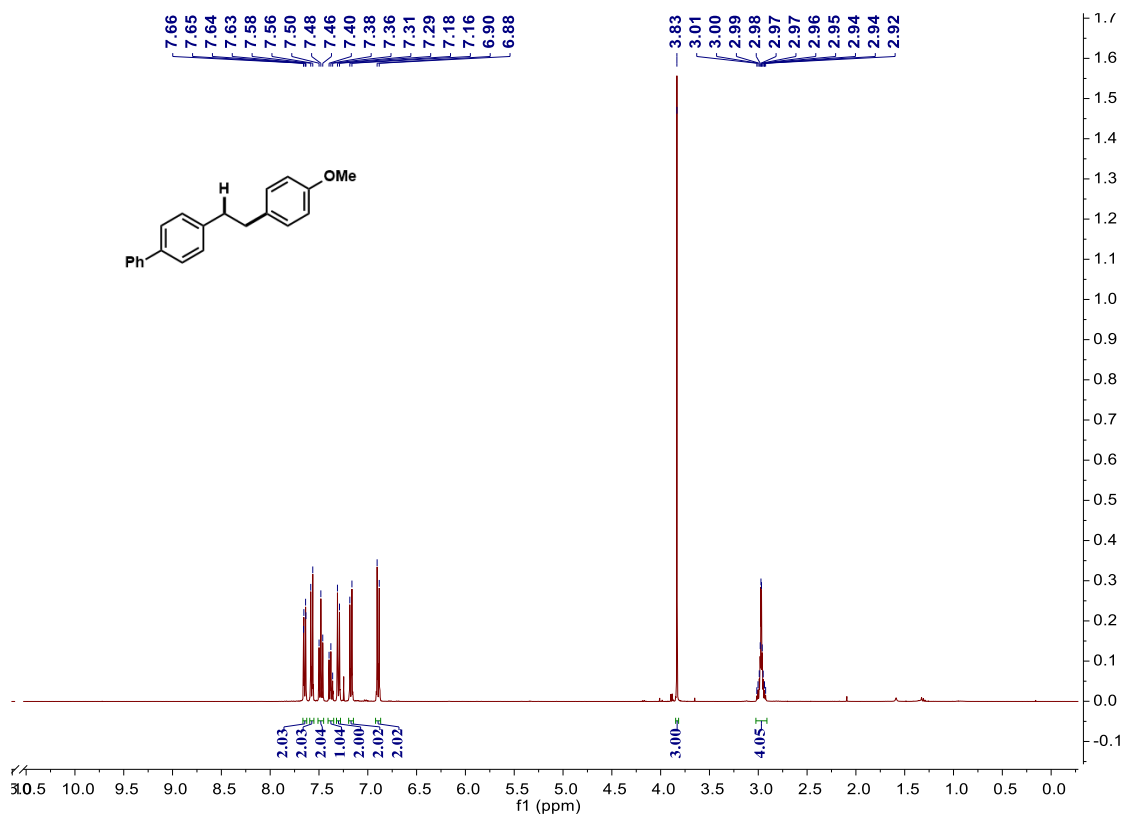
**(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-3-((phenyl-4-*d*)methoxy)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthrene (4j)**

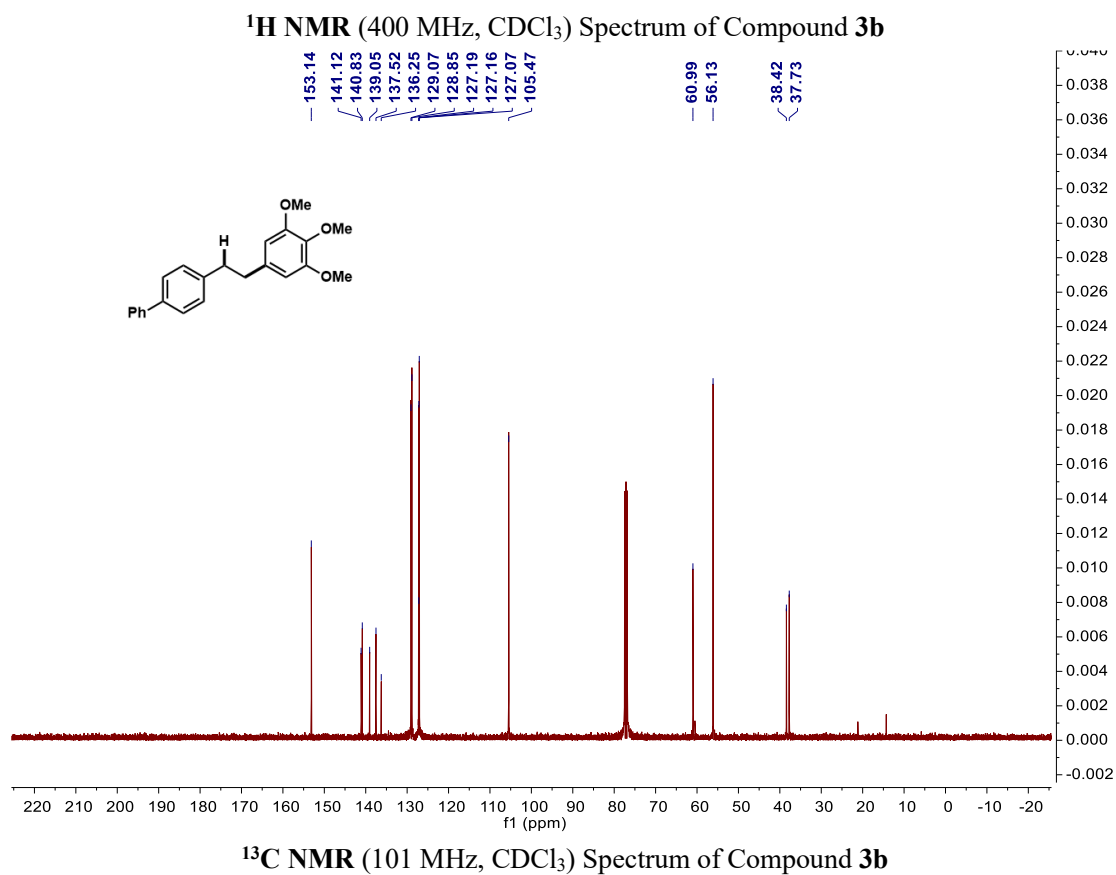
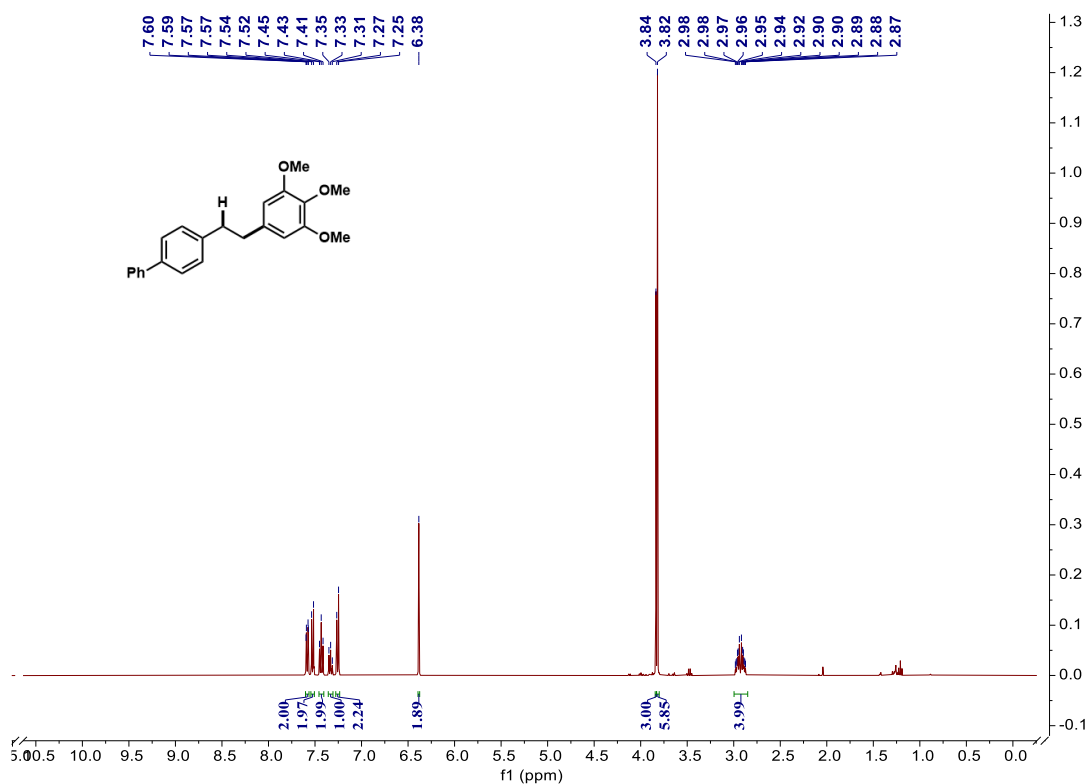


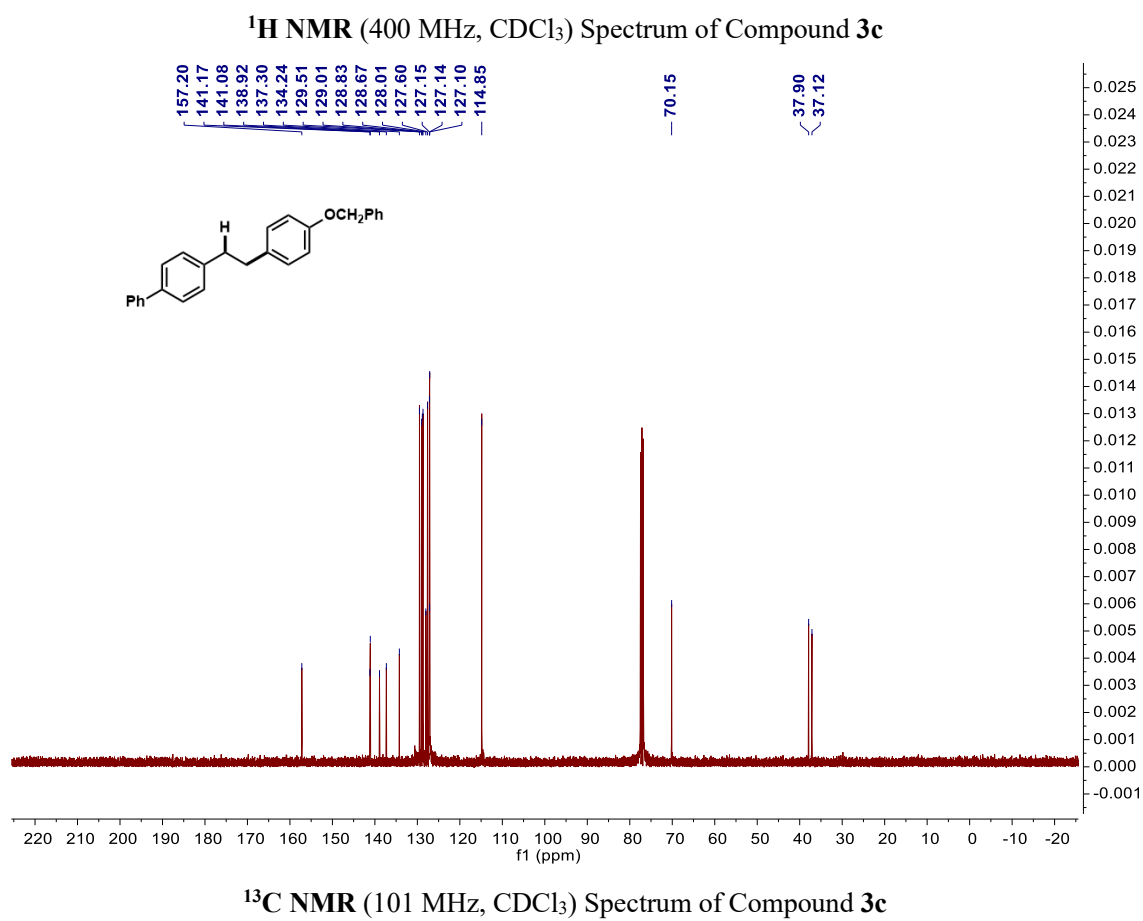
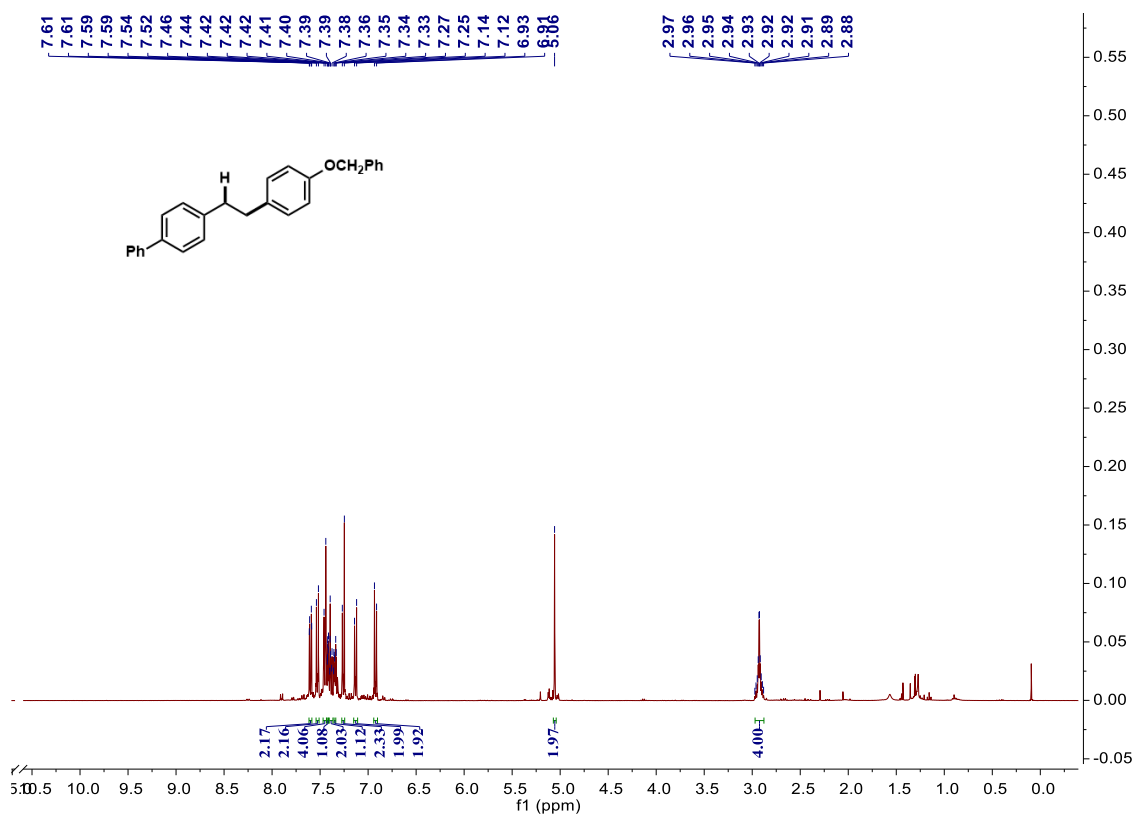
Compound **4j** was prepared following the general procedure B, using corresponding aryl bromide. The crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 50:1) to afford the desired product (77.0 mg, 81%, 99% D) as a white solid.  $^1\text{H}$

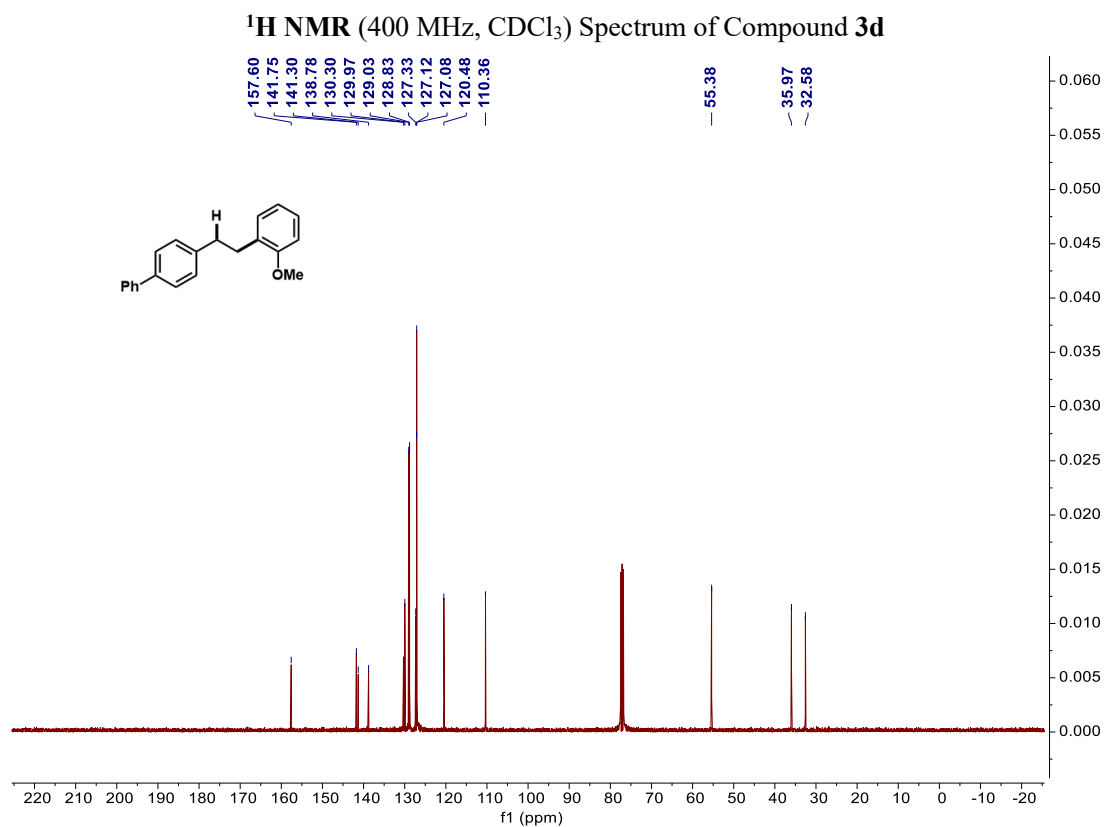
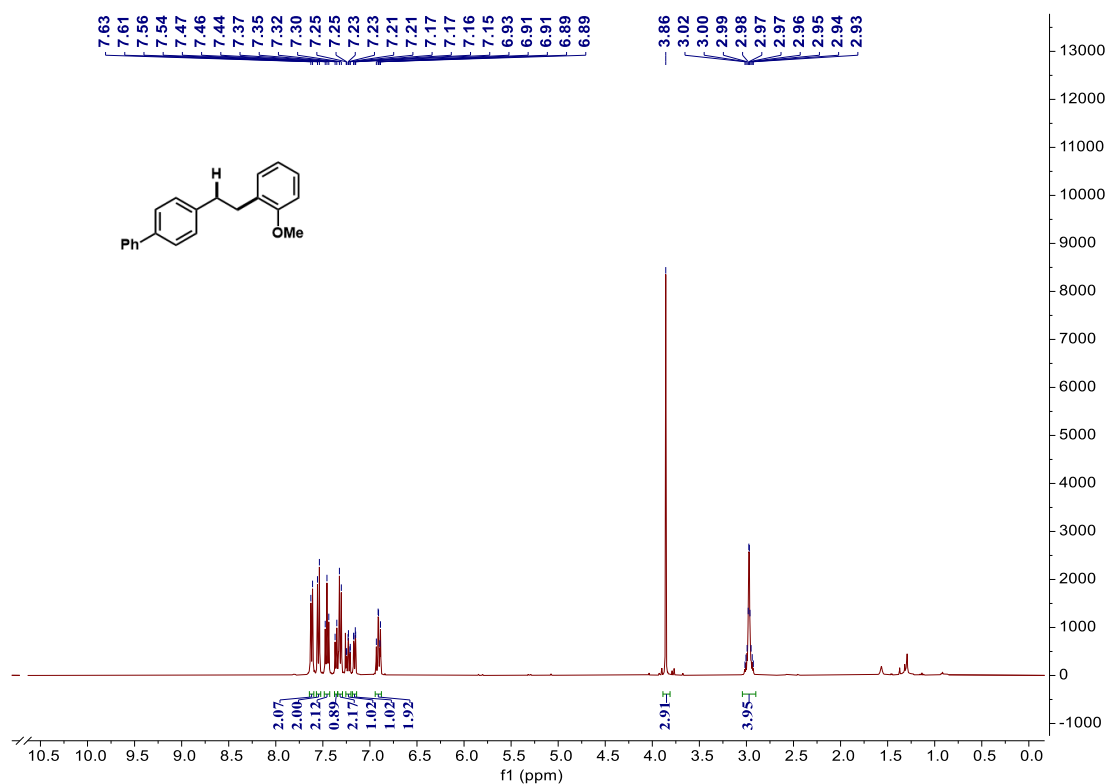
NMR (400 MHz, Chloroform-*d*)  $\delta$  7.45 (d,  $J$  = 8.2 Hz, 2H), 7.22 (d,  $J$  = 8.2 Hz, 2H), 5.35 (d,  $J$  = 5.0 Hz, 1H), 4.50 (s, 2H), 3.29 – 3.21 (m, 1H), 2.44 – 2.36 (m, 1H), 2.31 – 2.22 (m, 1H), 2.04 – 1.79 (m, 5H), 1.61 – 1.43 (m, 8H), 1.41 – 1.24 (m, 6H), 1.19 – 1.03 (m, 7H), 1.01 (s, 3H), 0.92 (d,  $J$  = 6.4 Hz, 3H), 0.87 (dd,  $J$  = 6.6, 1.6 Hz, 6H), 0.68 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  140.9, 138.2, 131.5, 129.3, 121.8, 121.3, 78.8, 69.2, 56.8, 56.2, 50.2, 42.4, 39.9, 39.6, 39.2, 37.3, 37.0, 36.3, 35.9, 32.0, 32.0, 28.5, 28.3, 28.1, 24.4, 23.9, 22.9, 22.7, 21.2, 19.5, 18.8, 12.0. HR-MS (EI):  $m/z$  calcd for  $[\text{M}+\text{H}]^+$   $\text{C}_{34}\text{H}_{52}\text{DO}^+$ , 478.4154; found 478.4155.

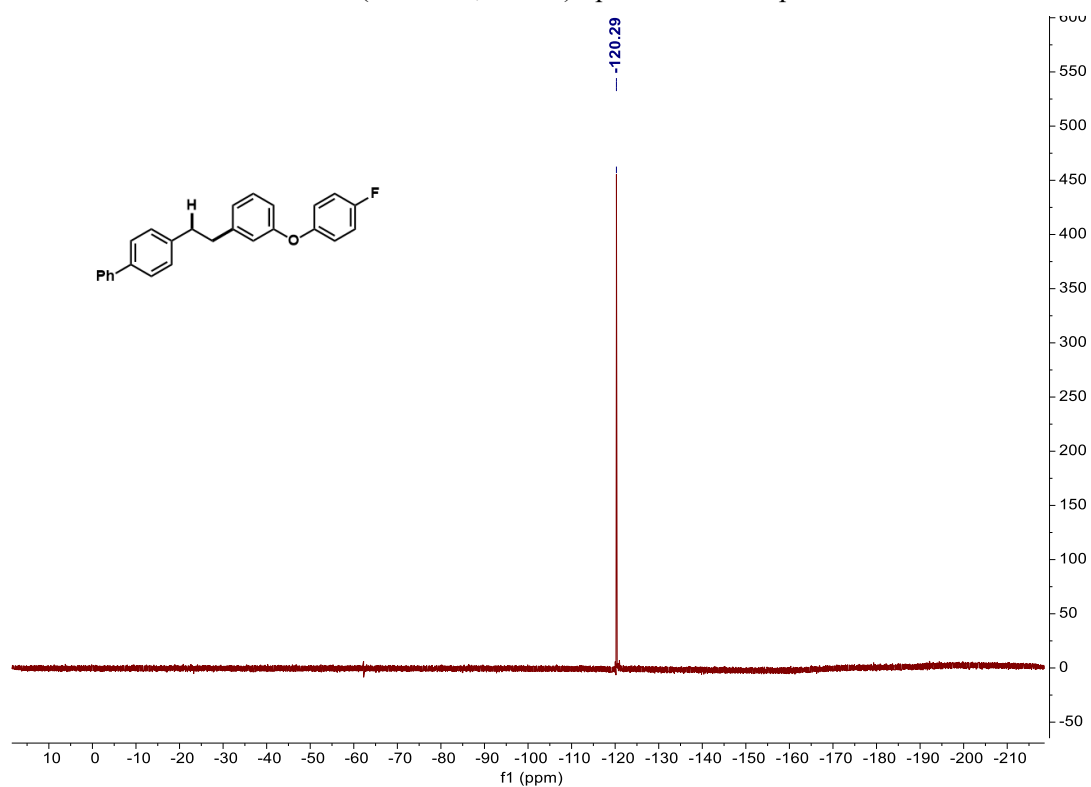
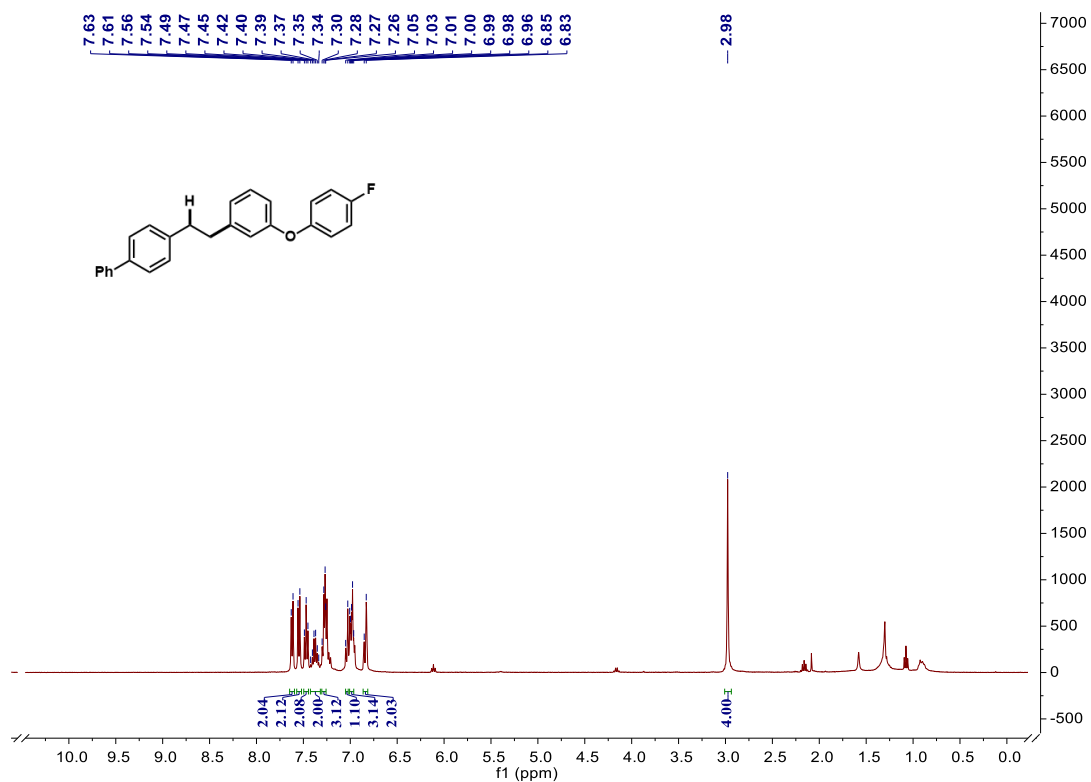
## 13. NMR Spectra

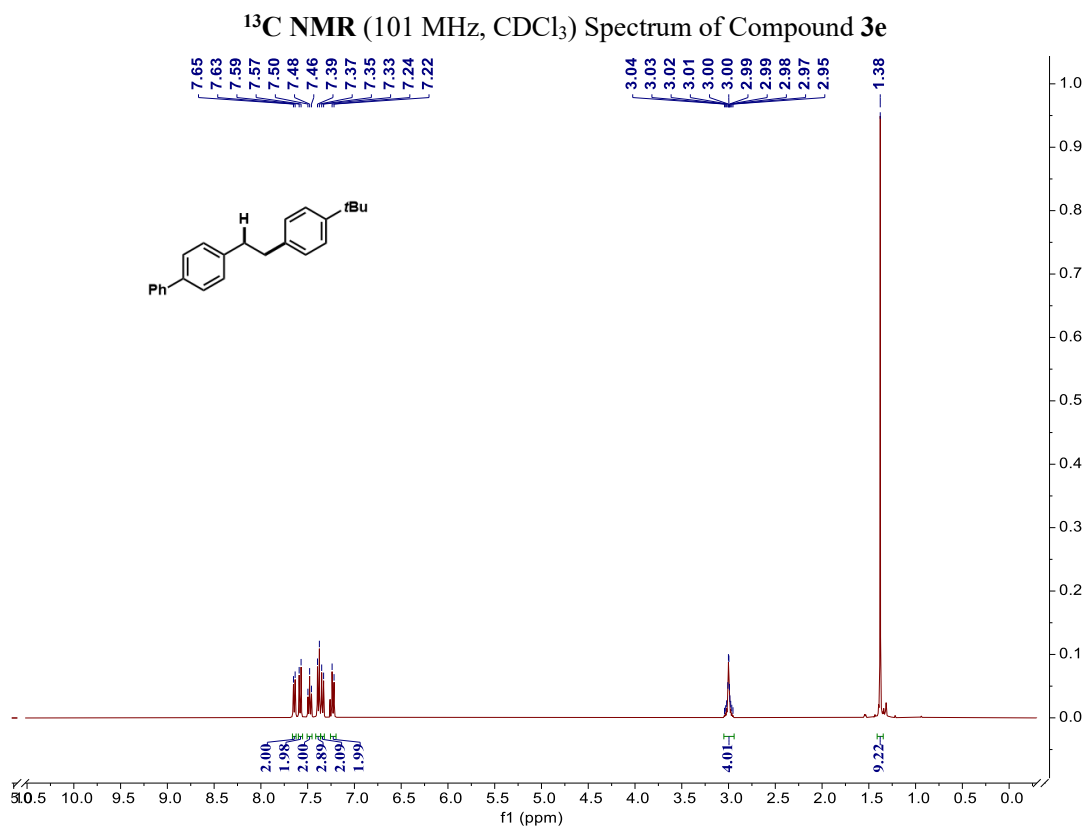
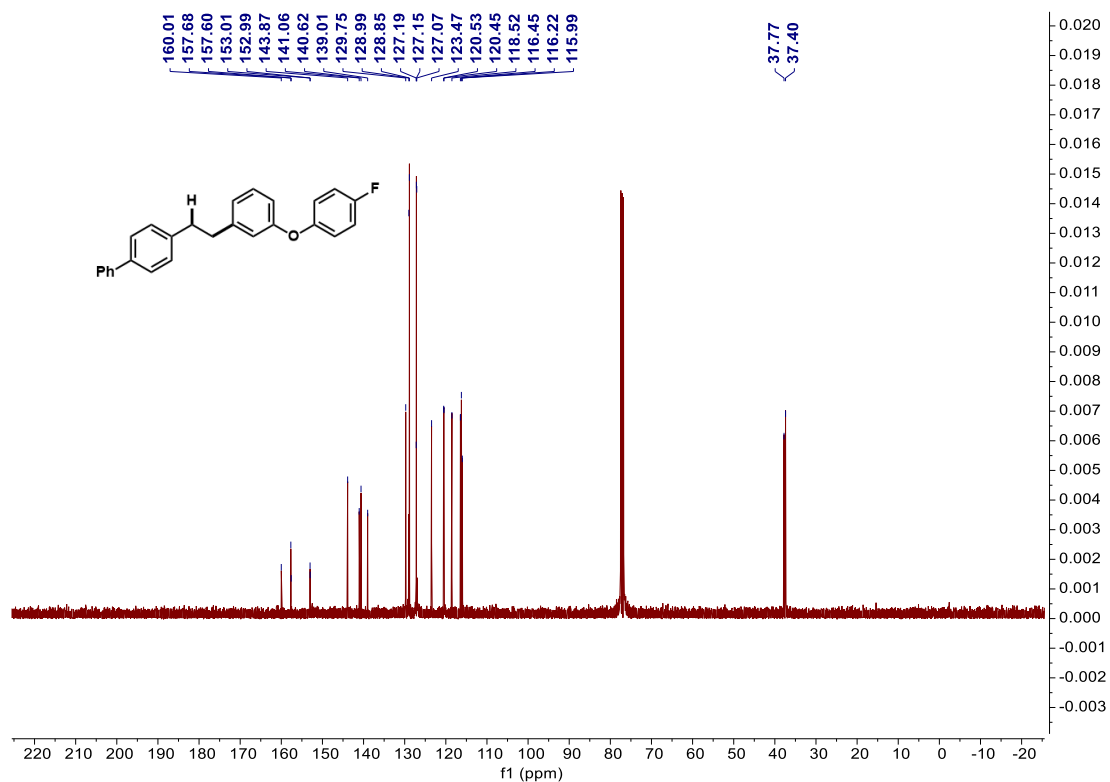




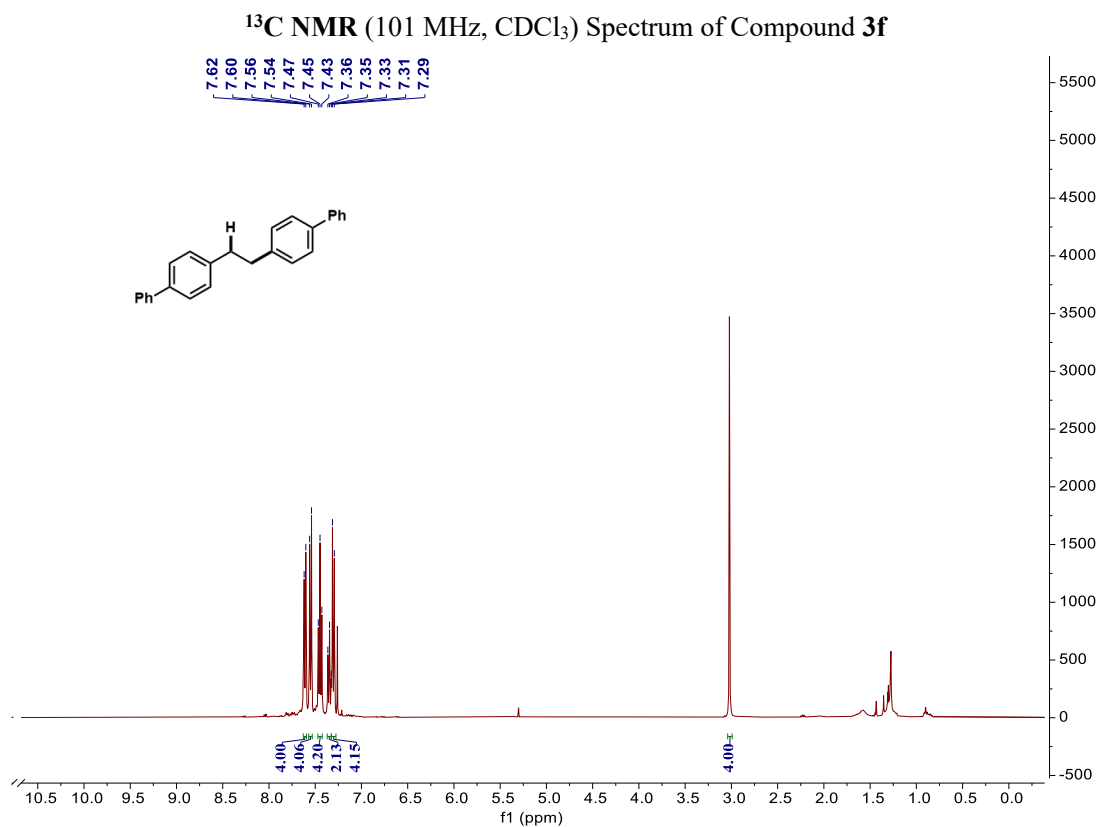
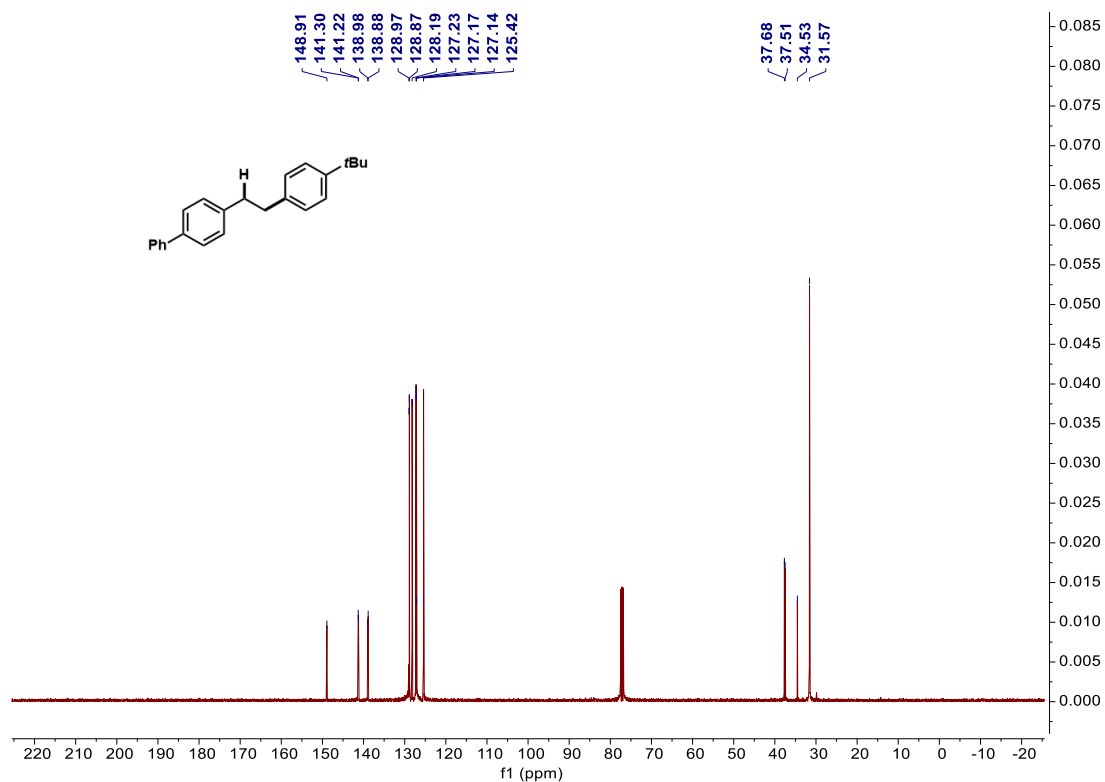


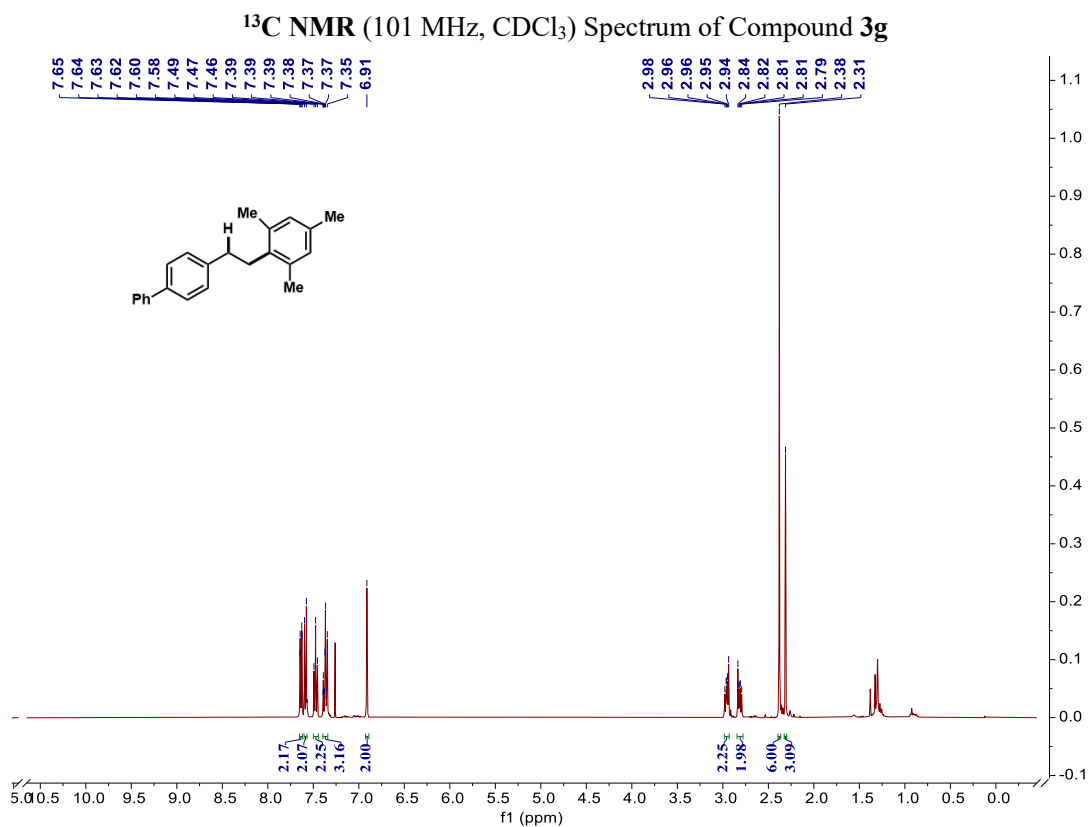
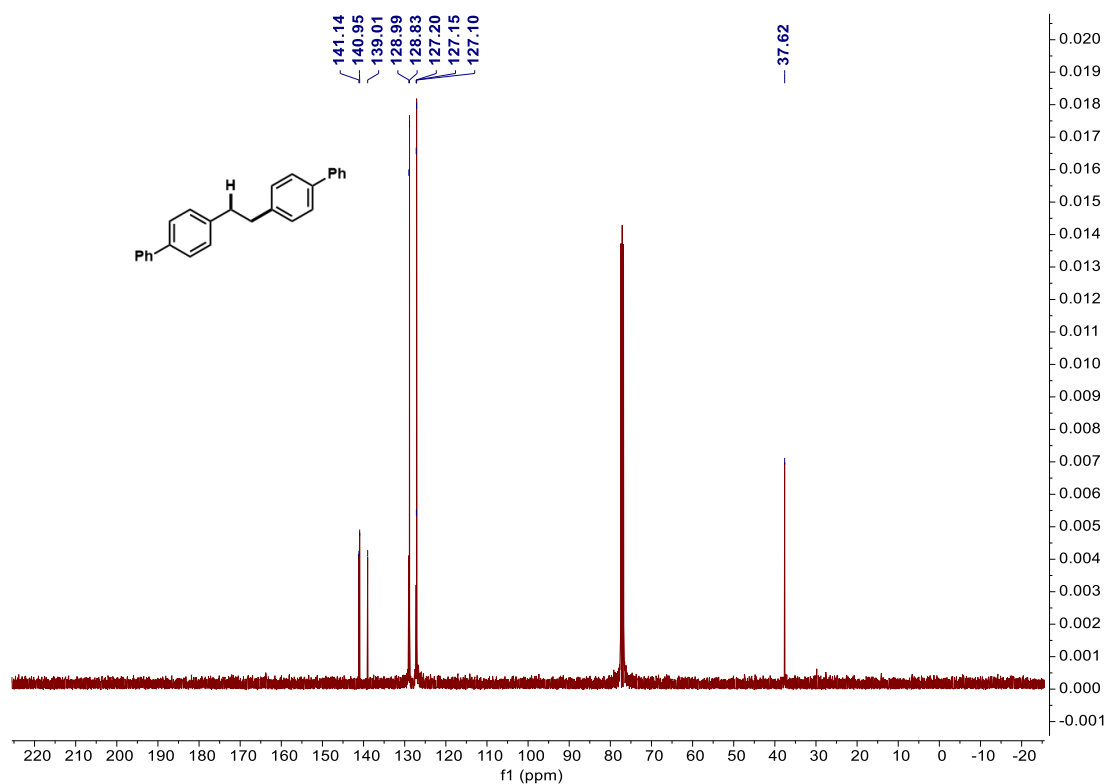


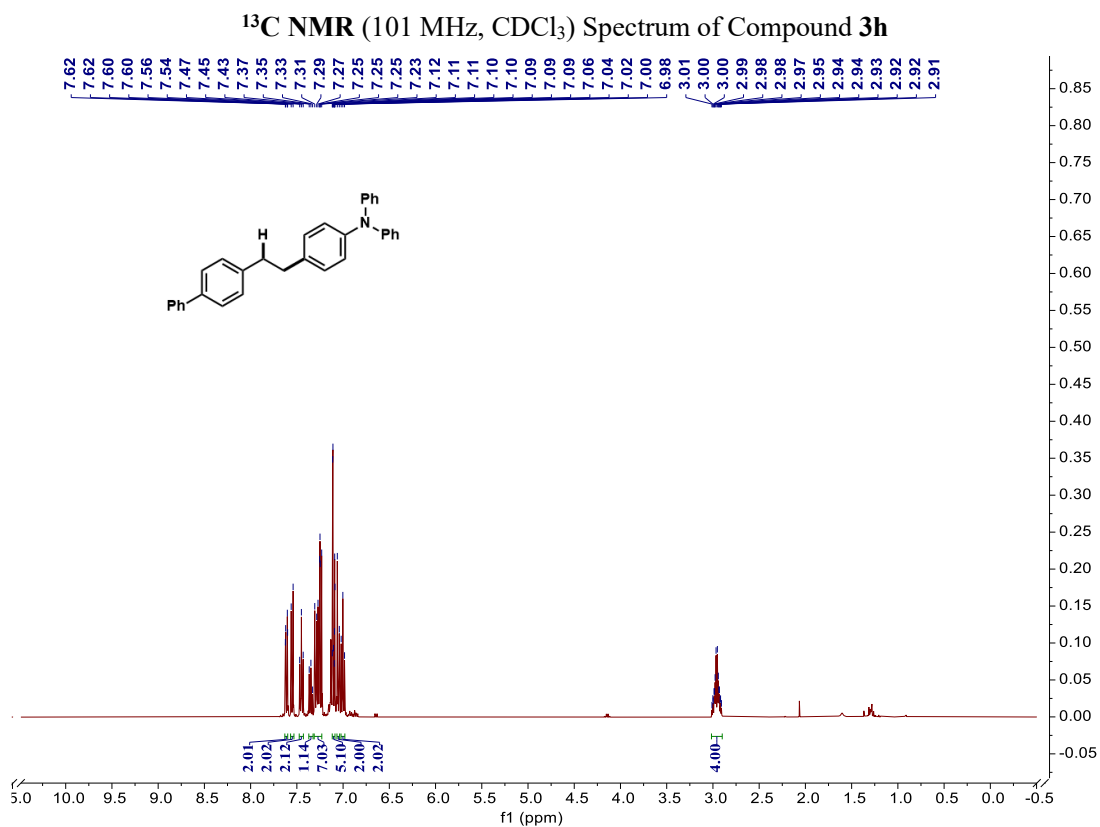
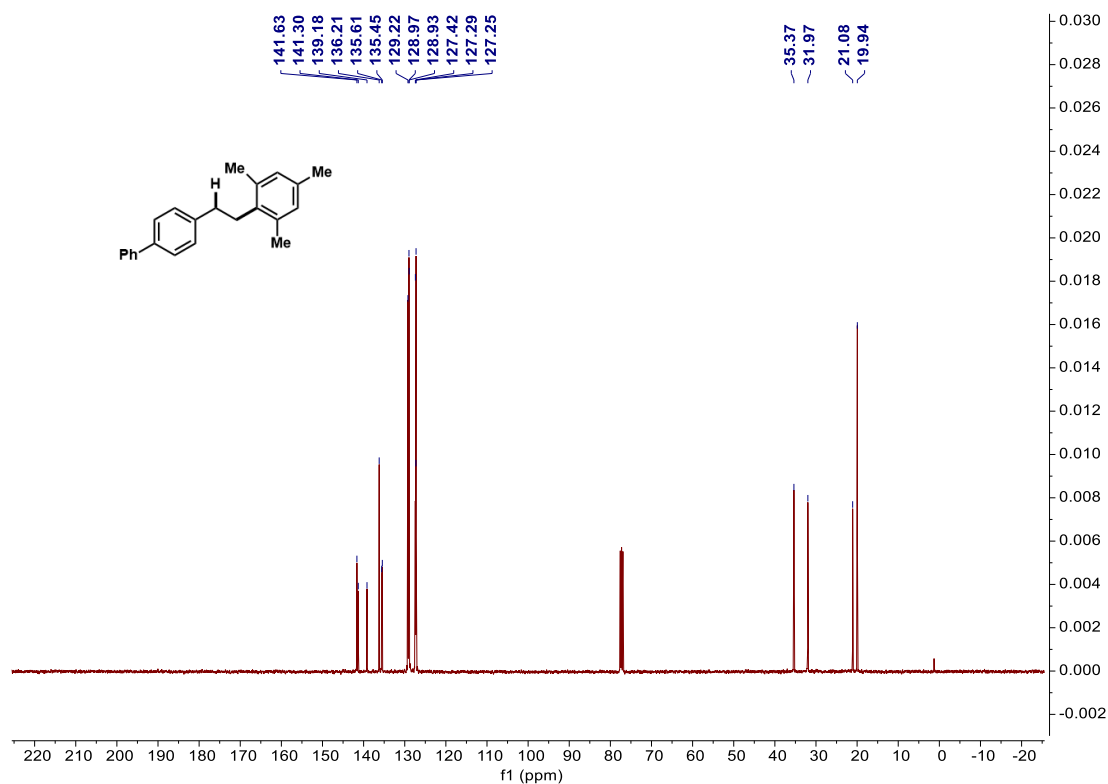


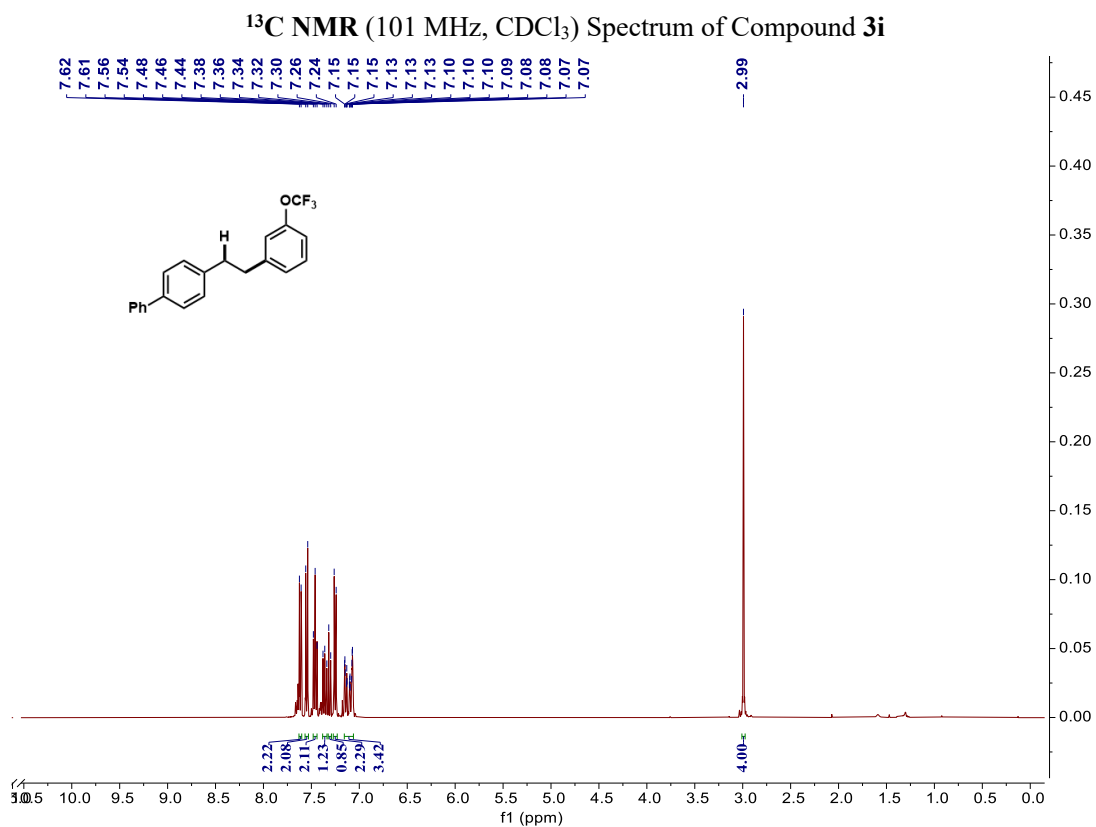
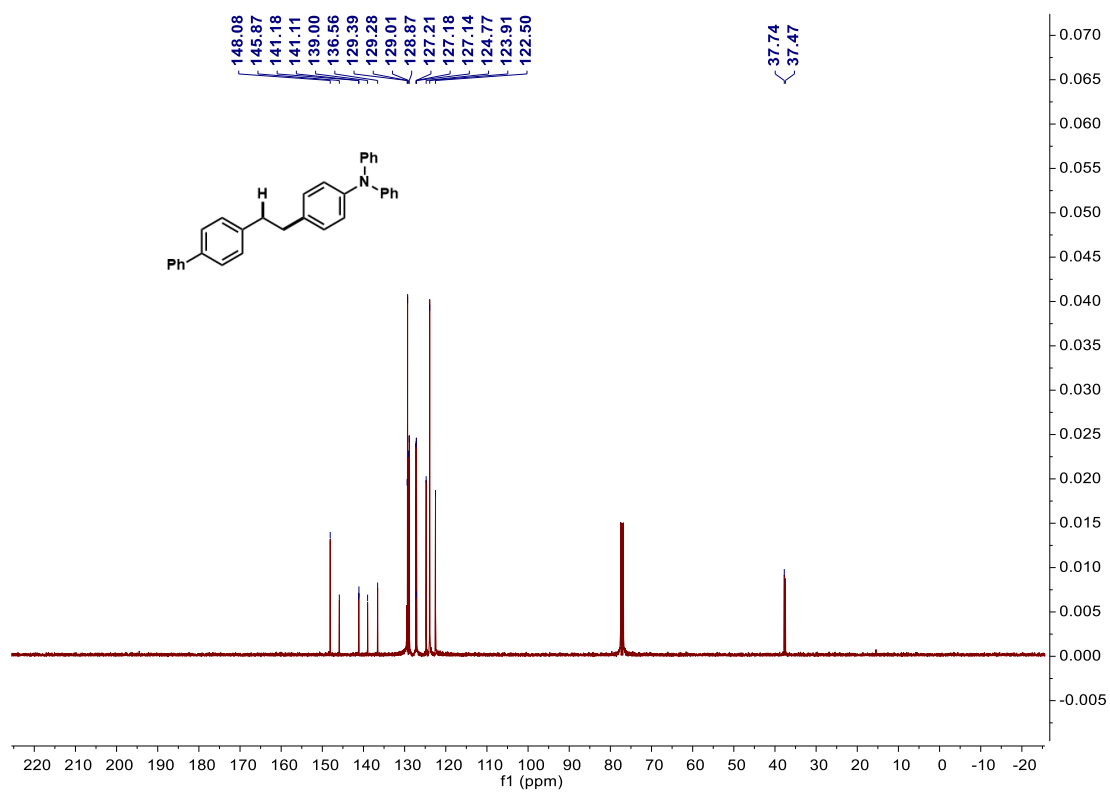


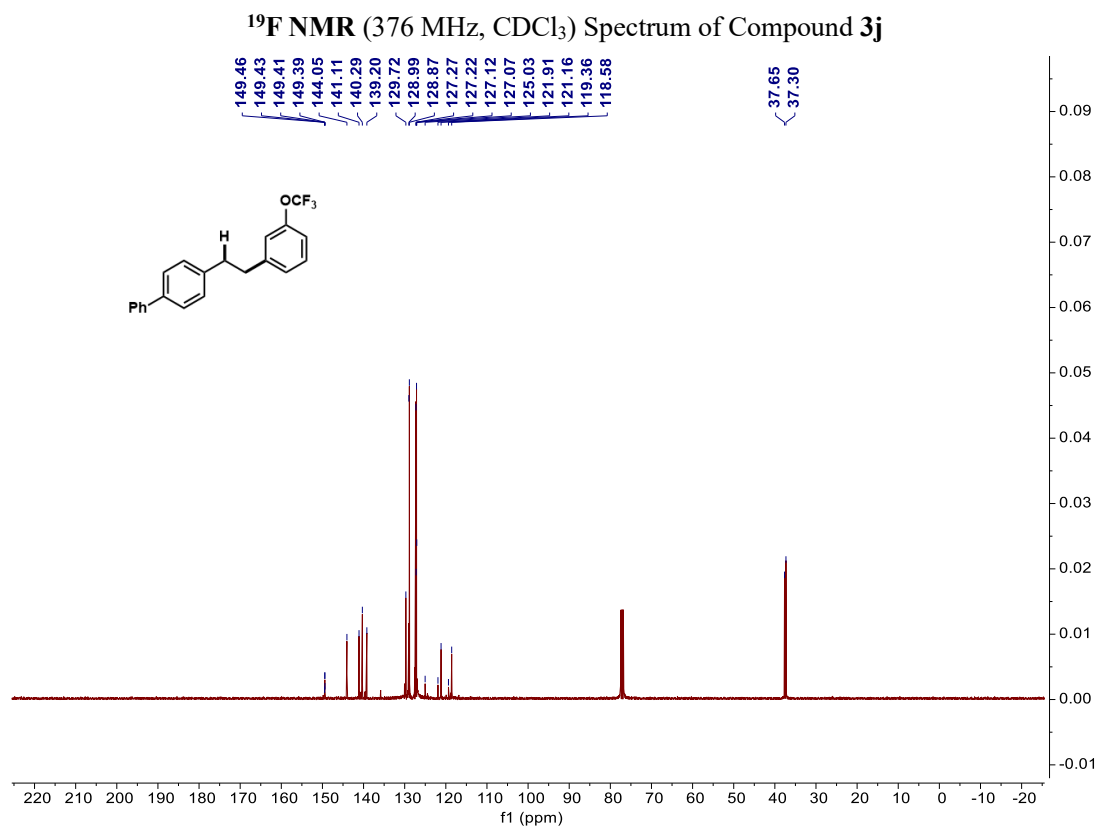
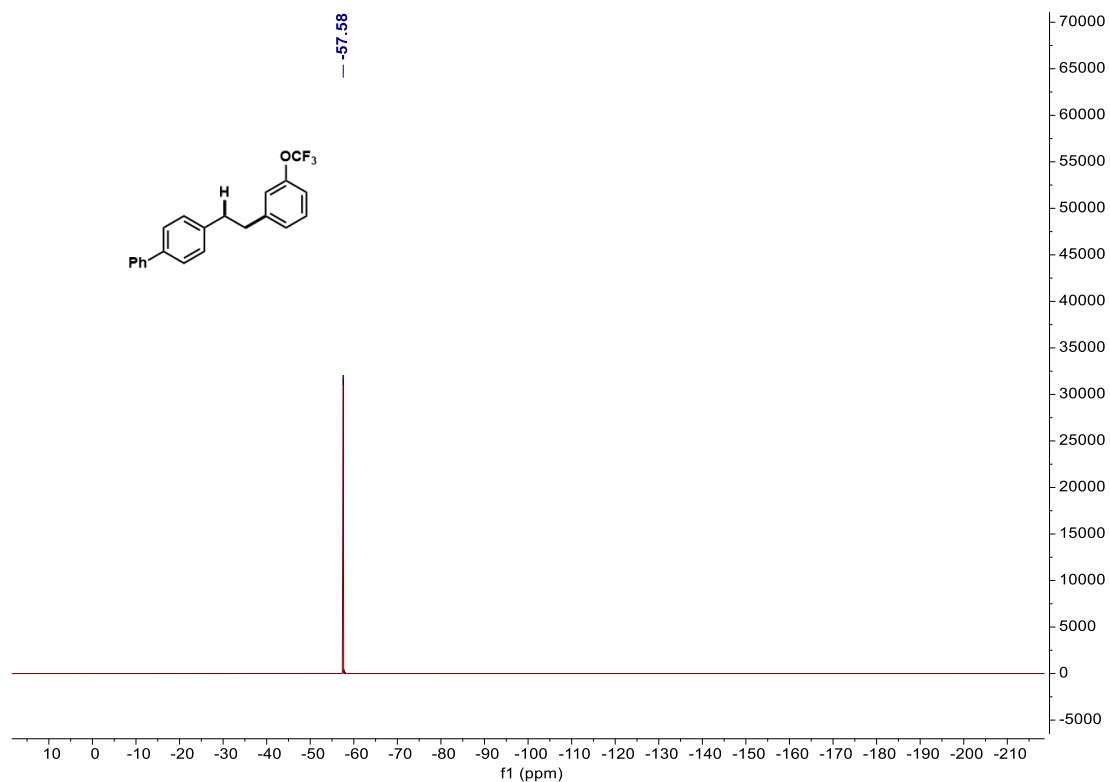


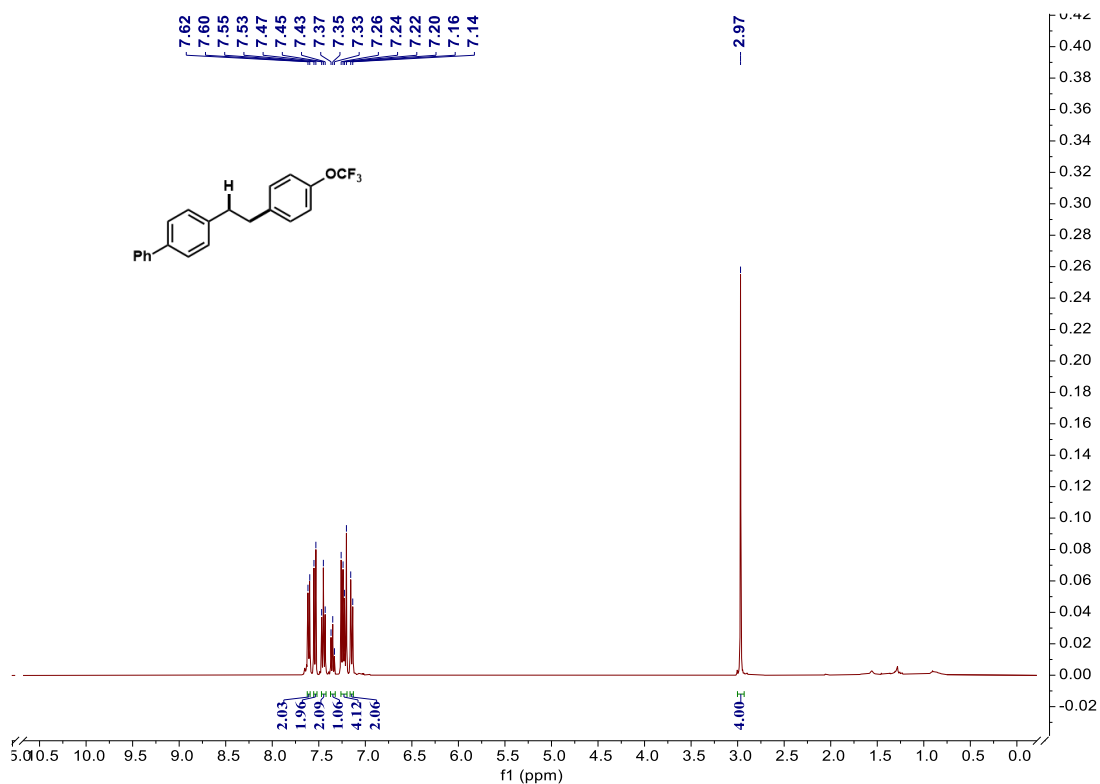




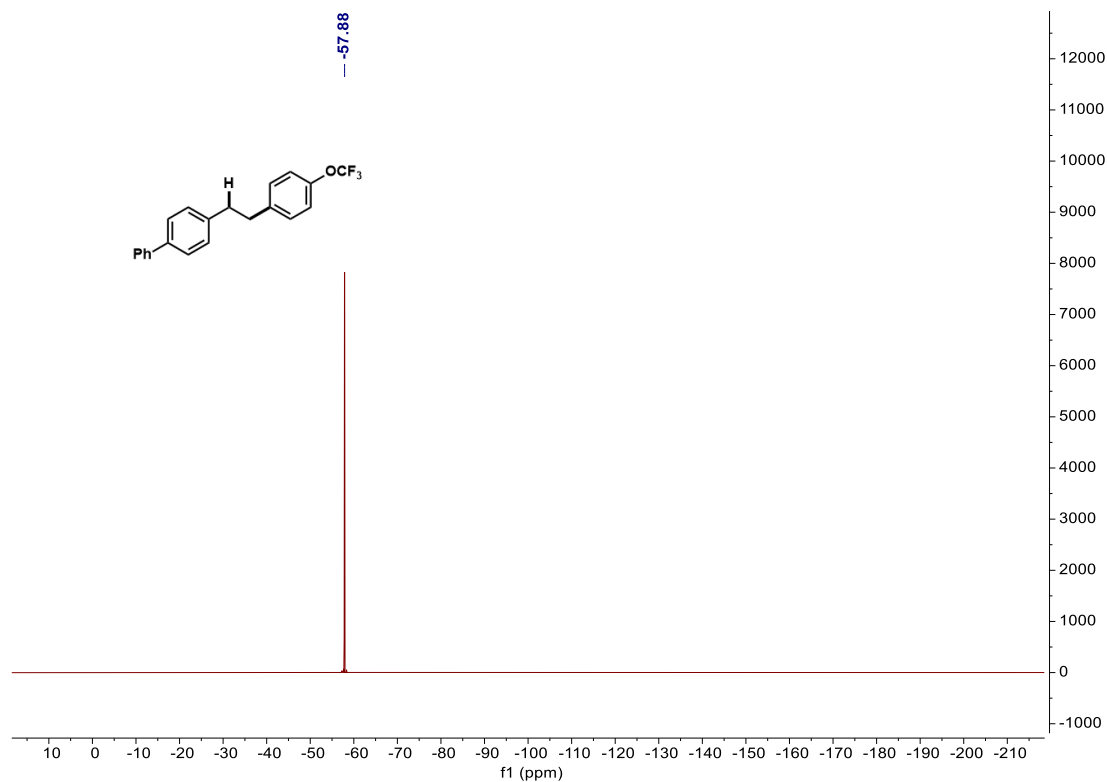




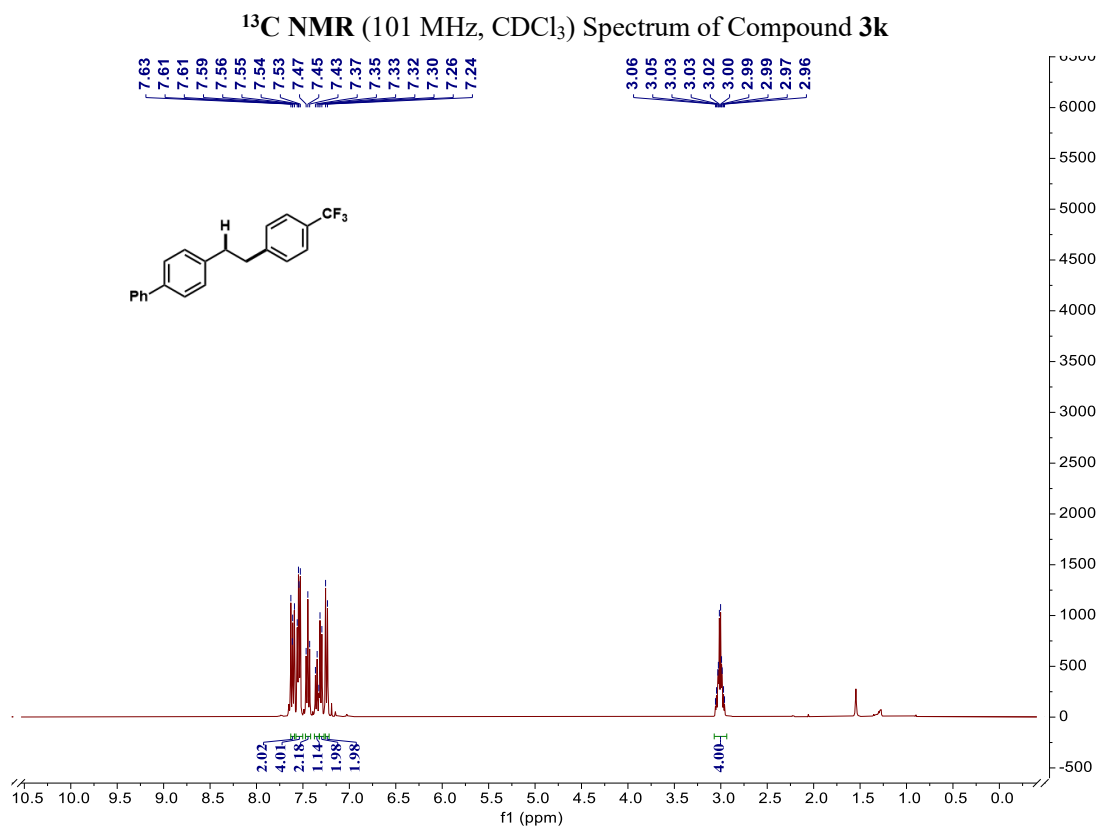
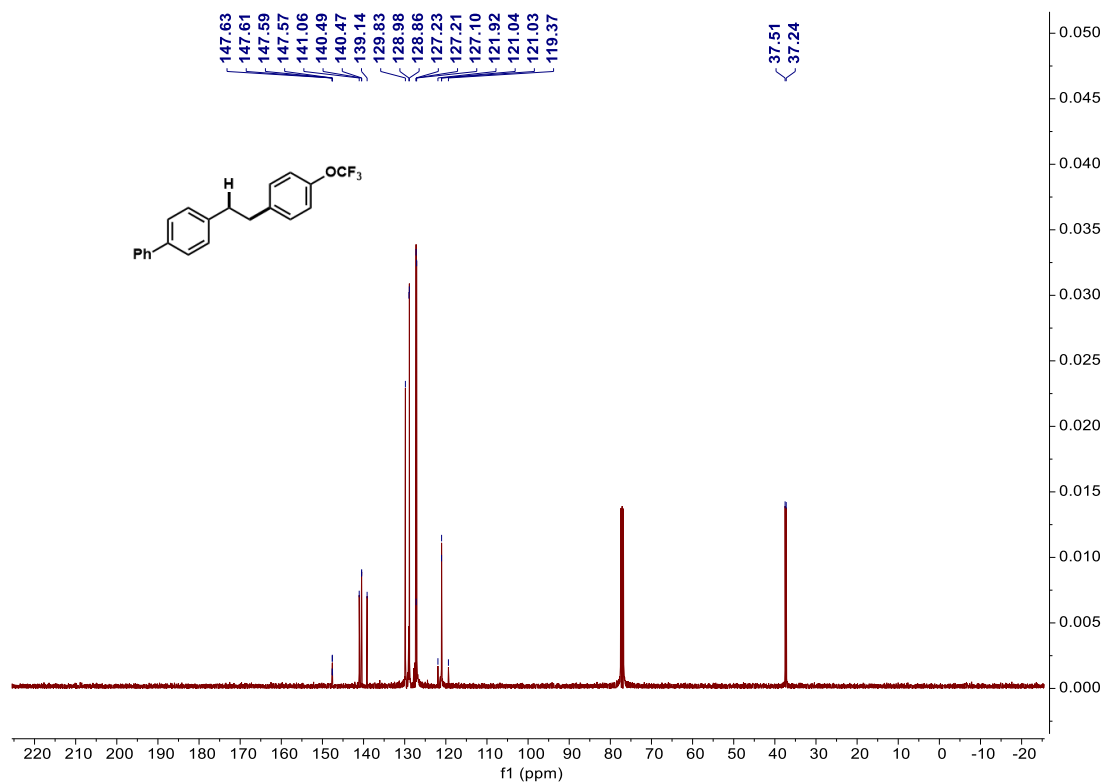




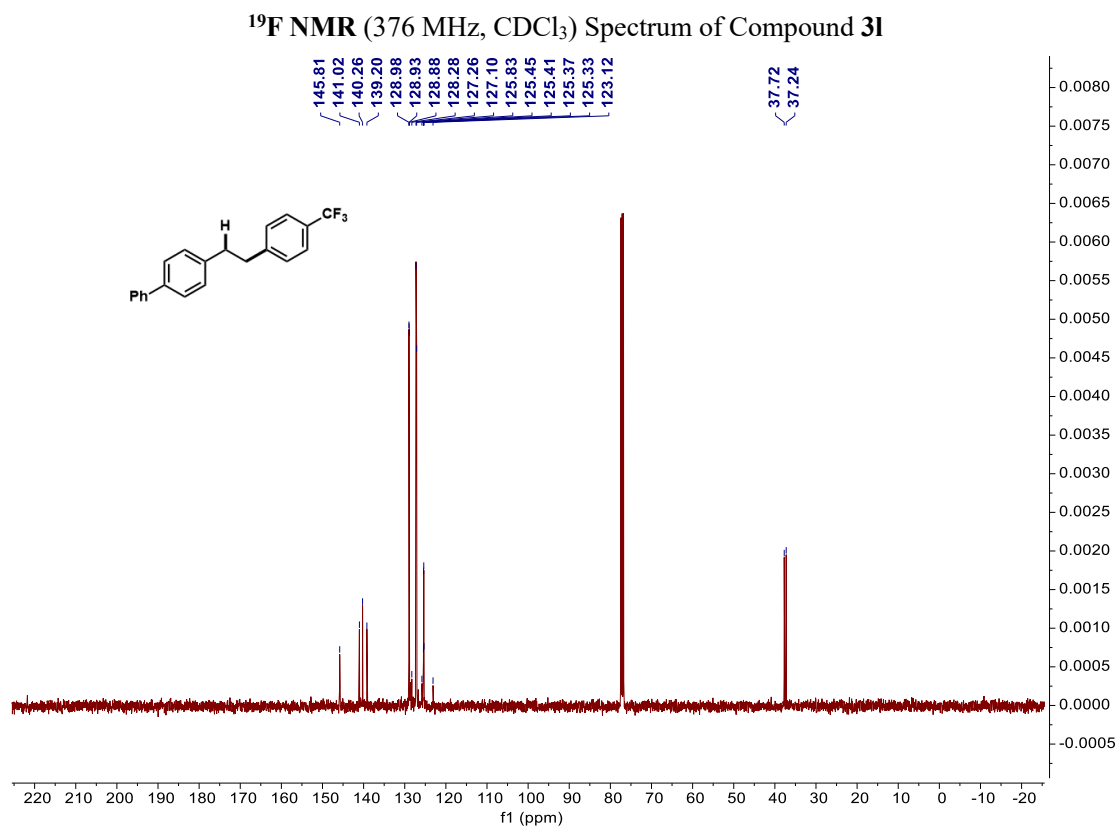
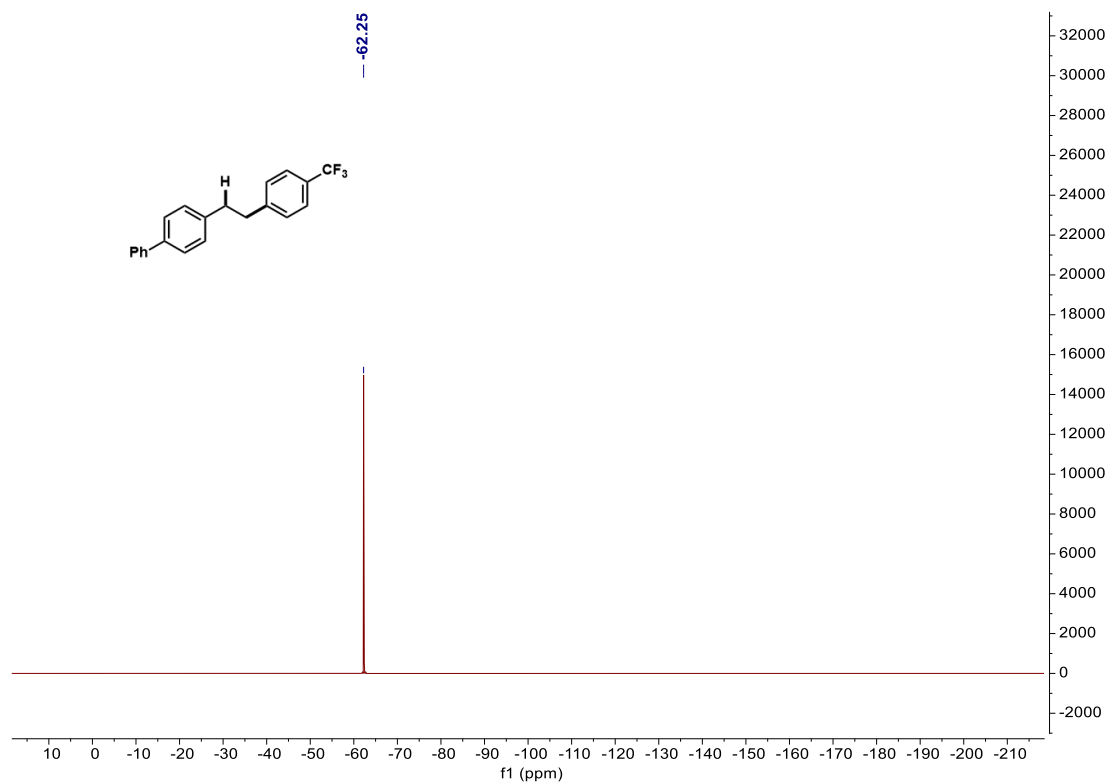
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) Spectrum of Compound **3k**



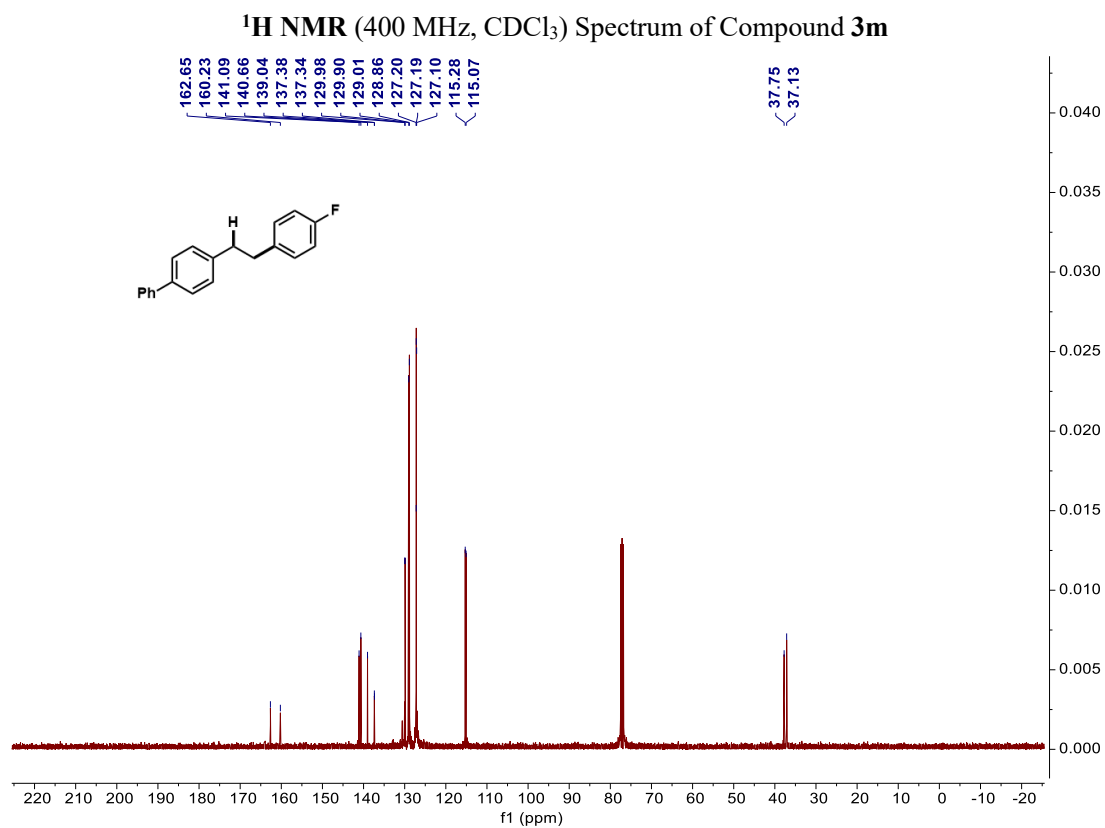
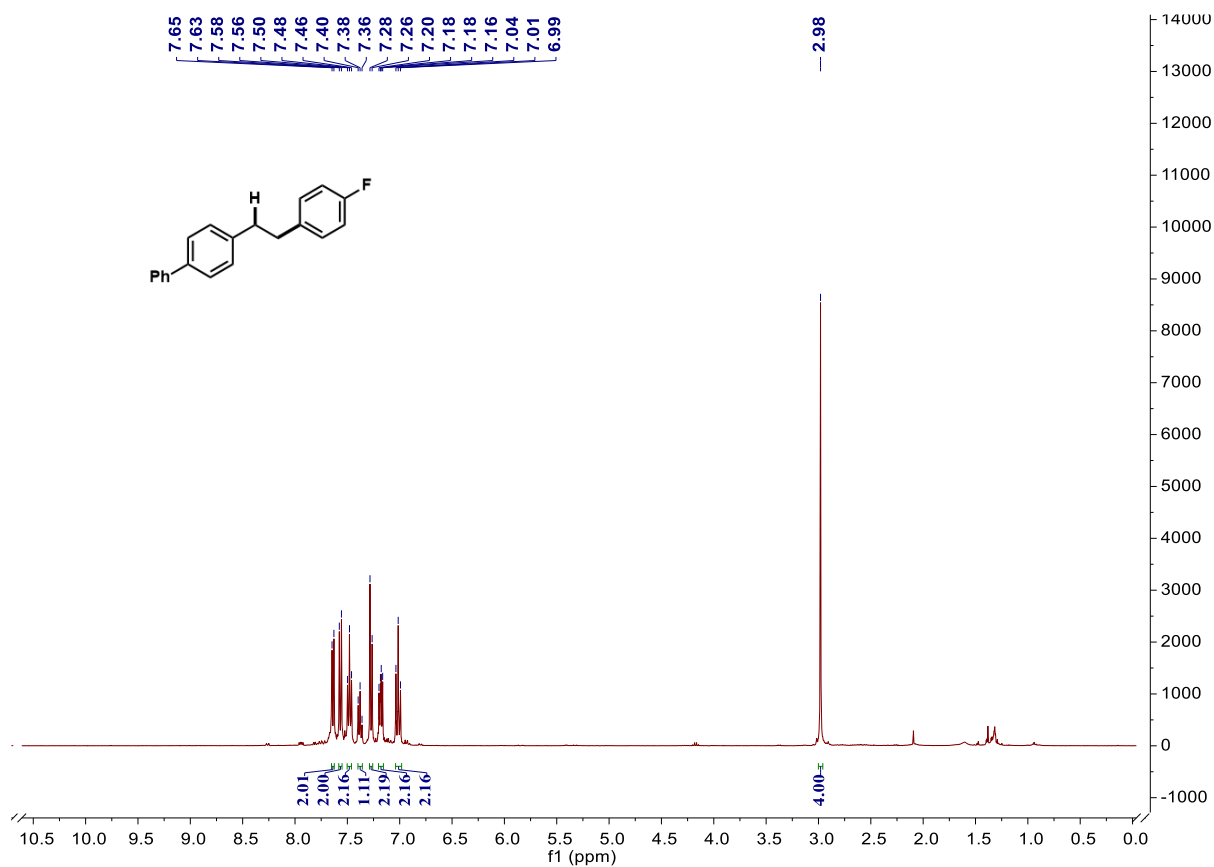
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) Spectrum of Compound **3k**

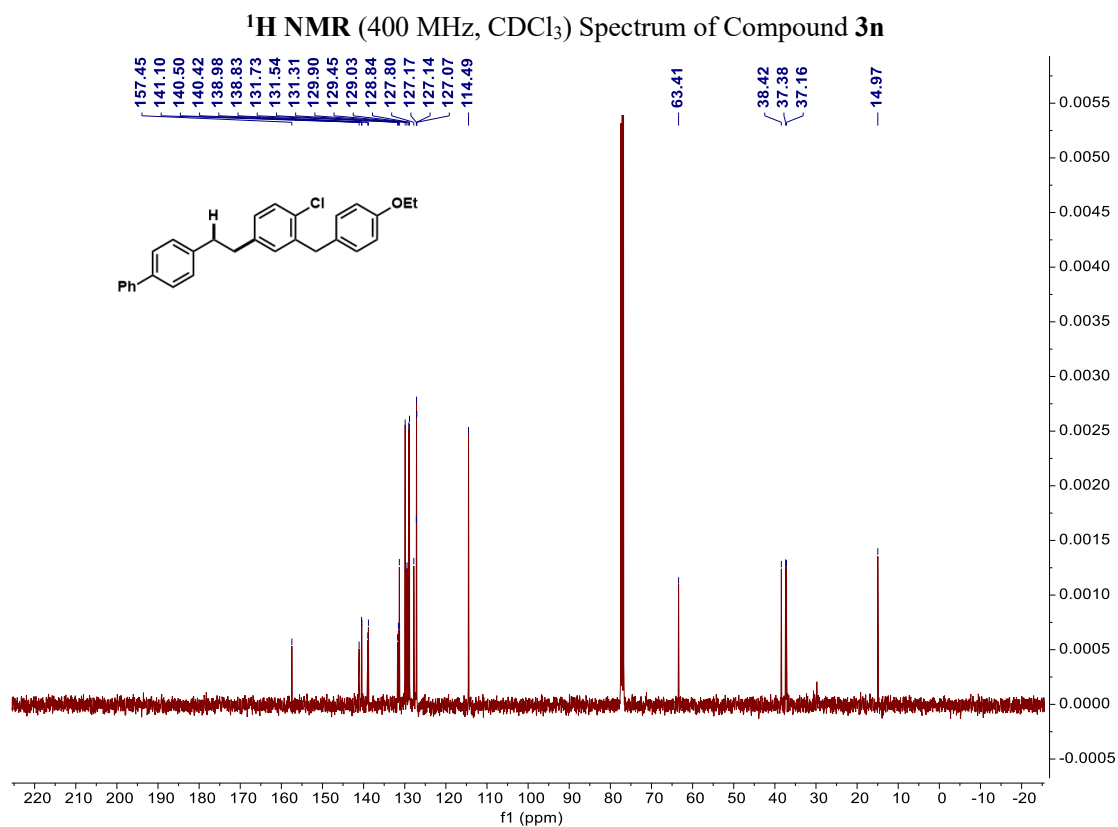
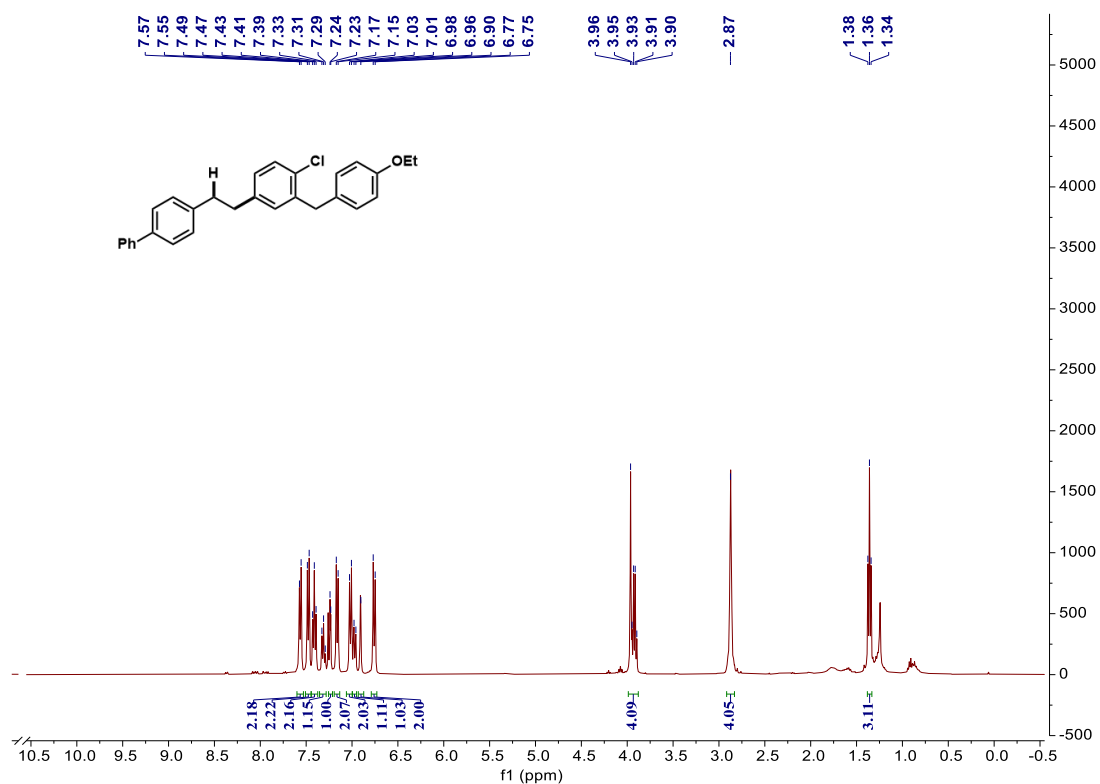


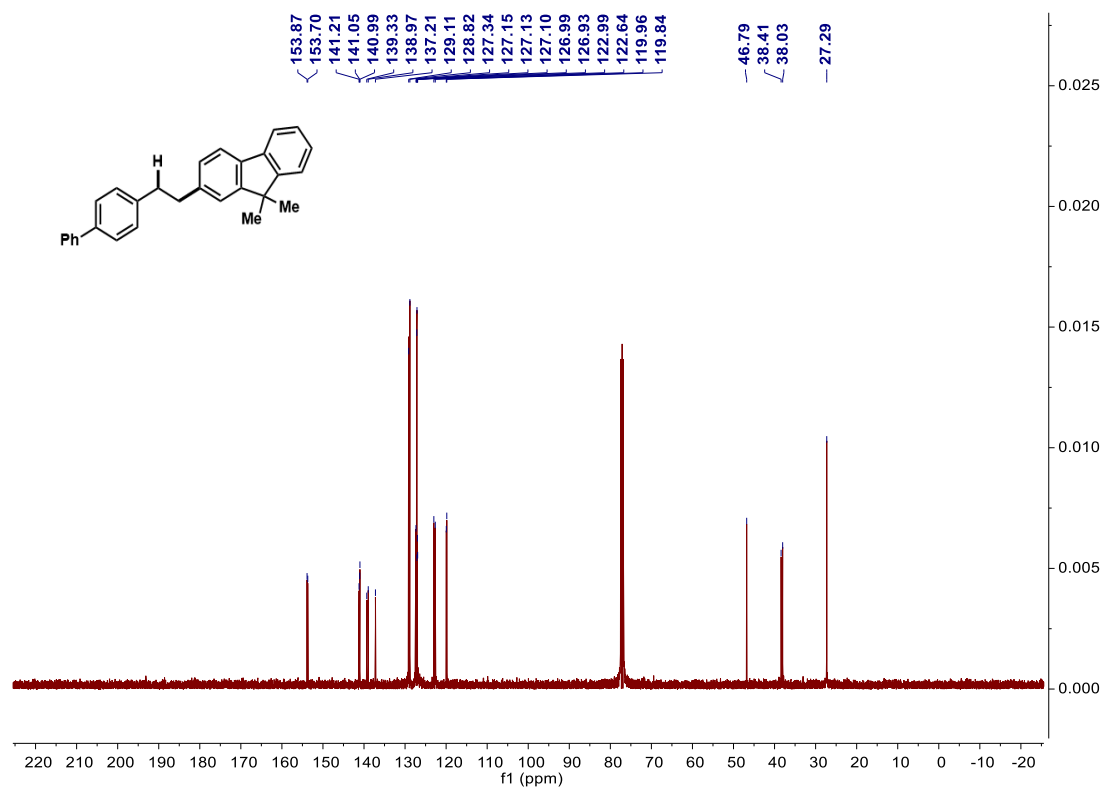
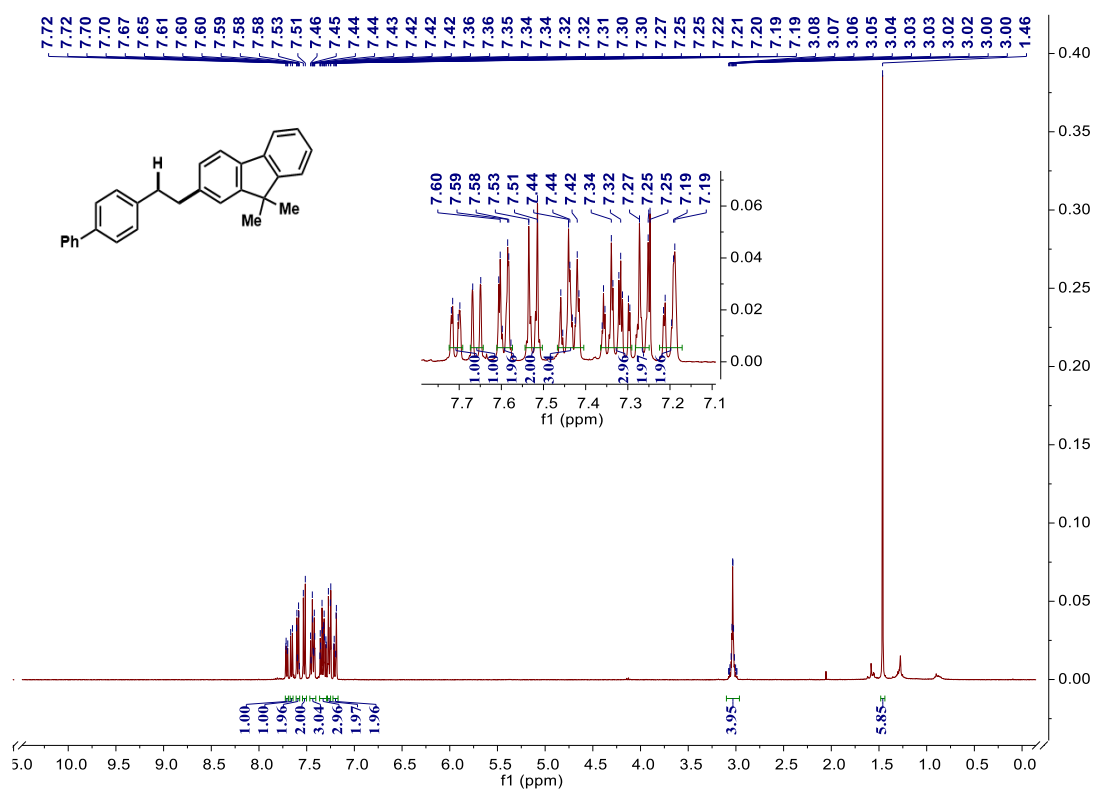
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) Spectrum of Compound 3l

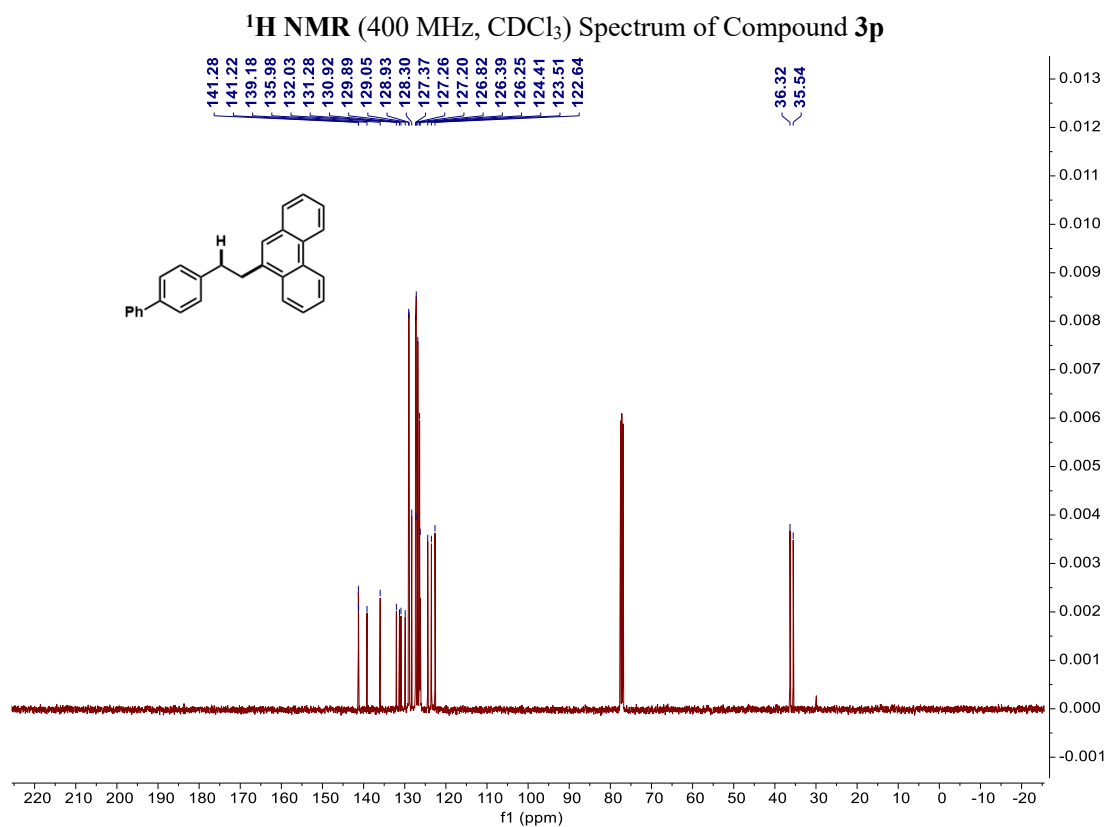
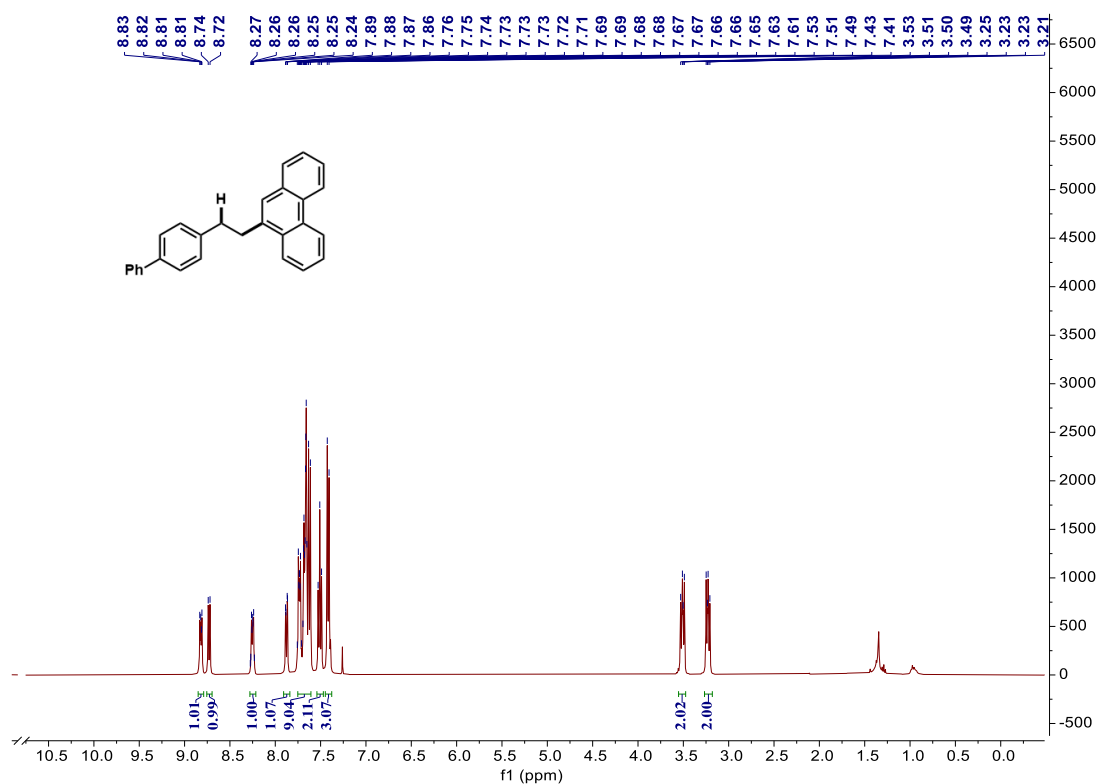


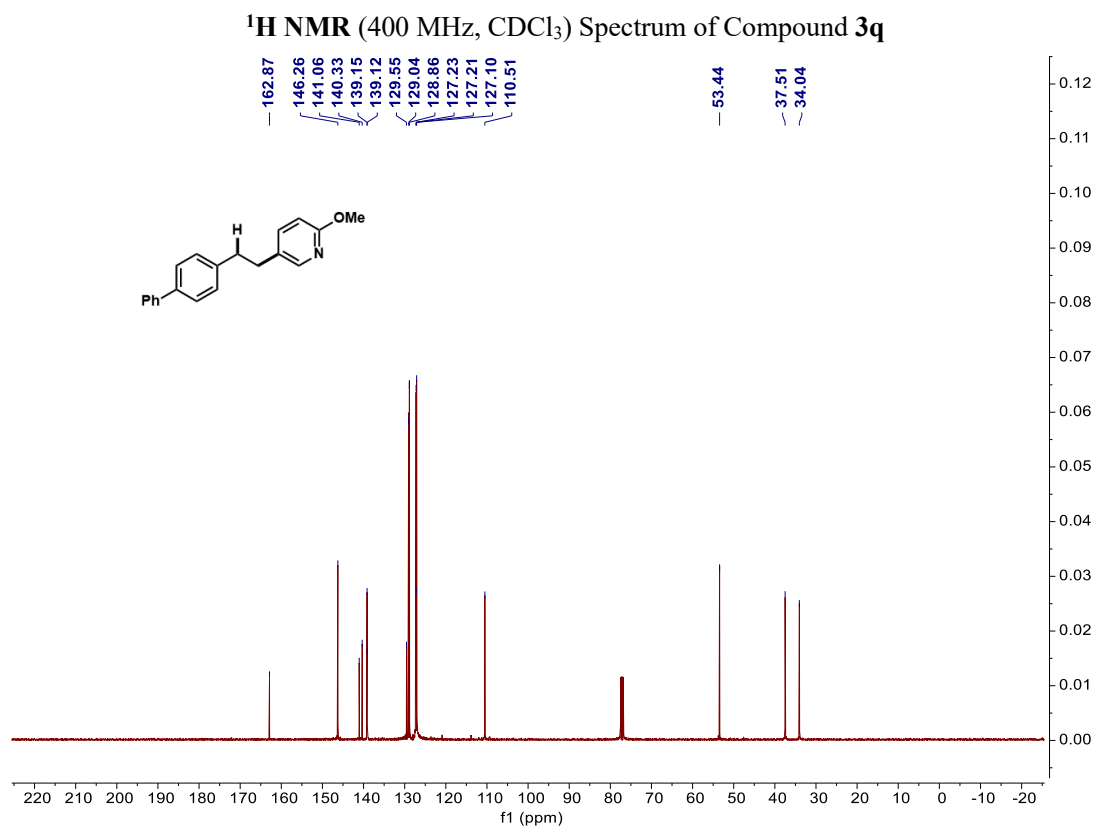
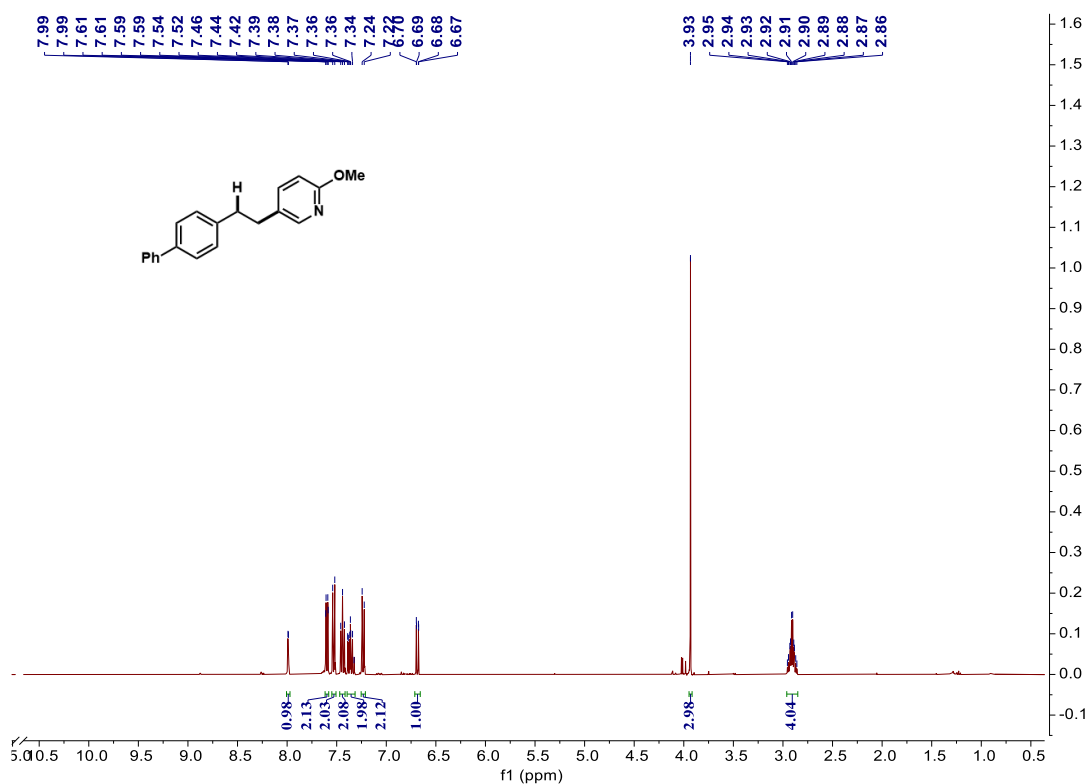


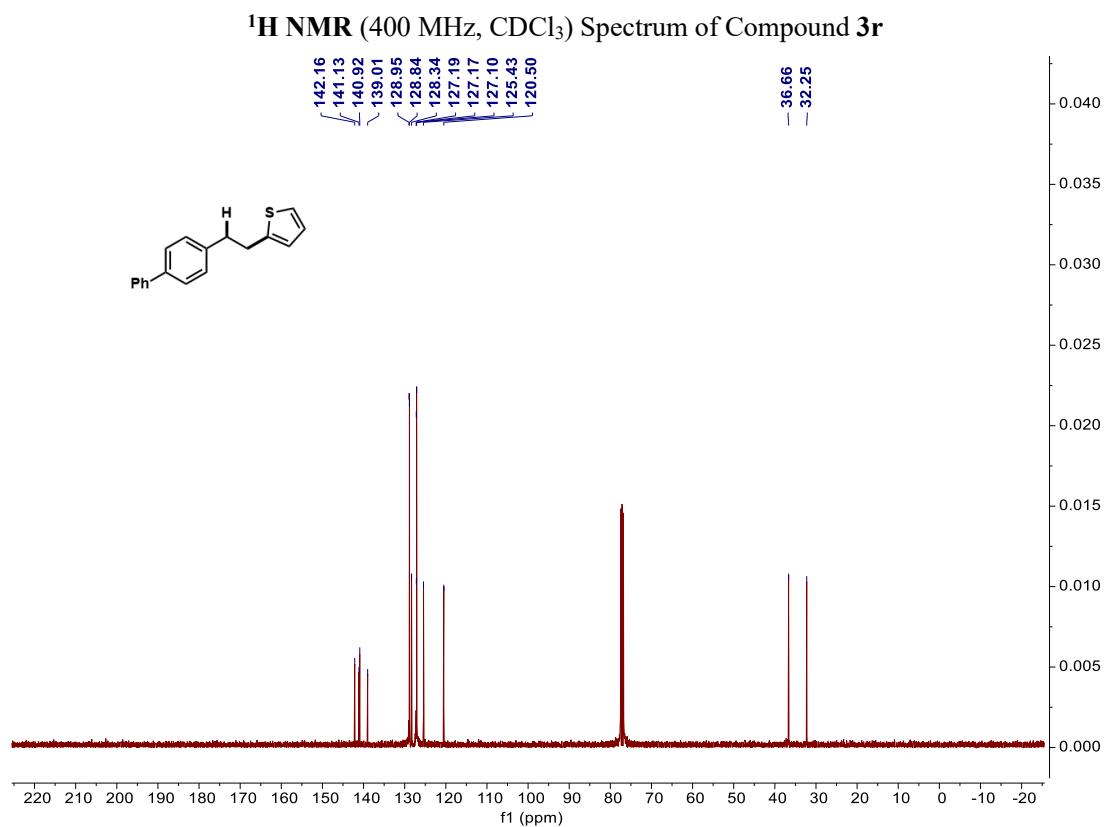
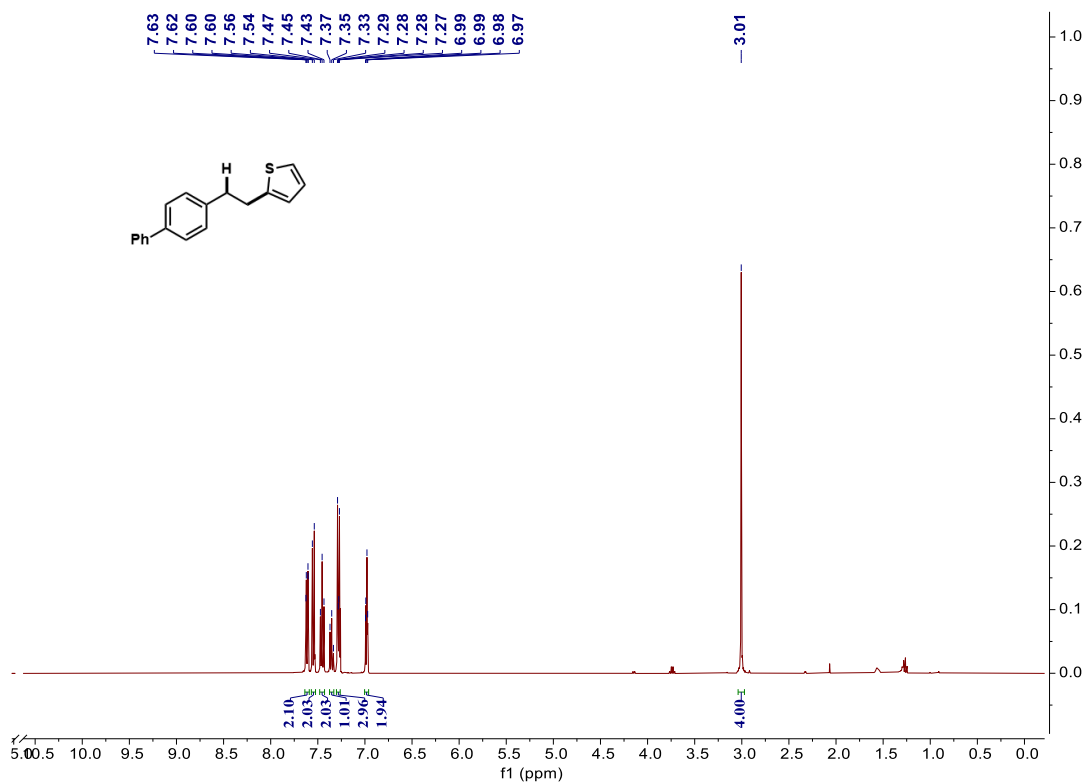


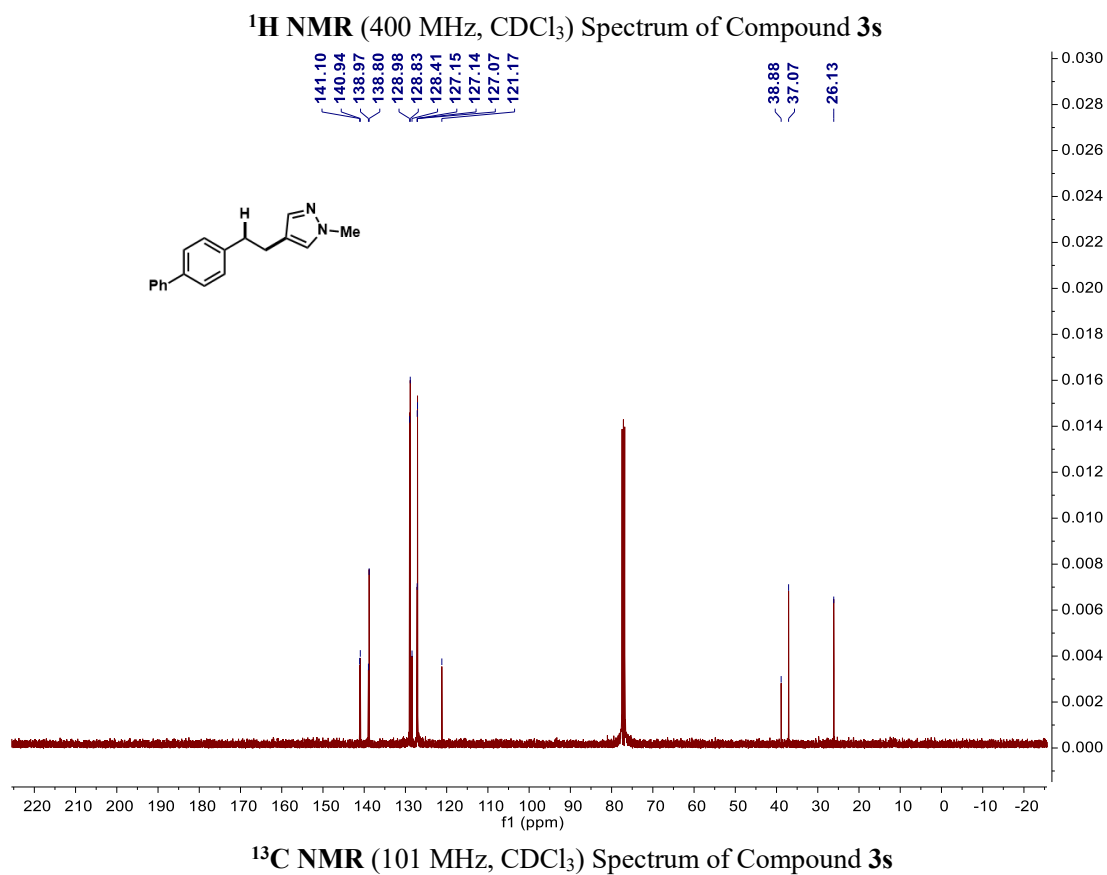
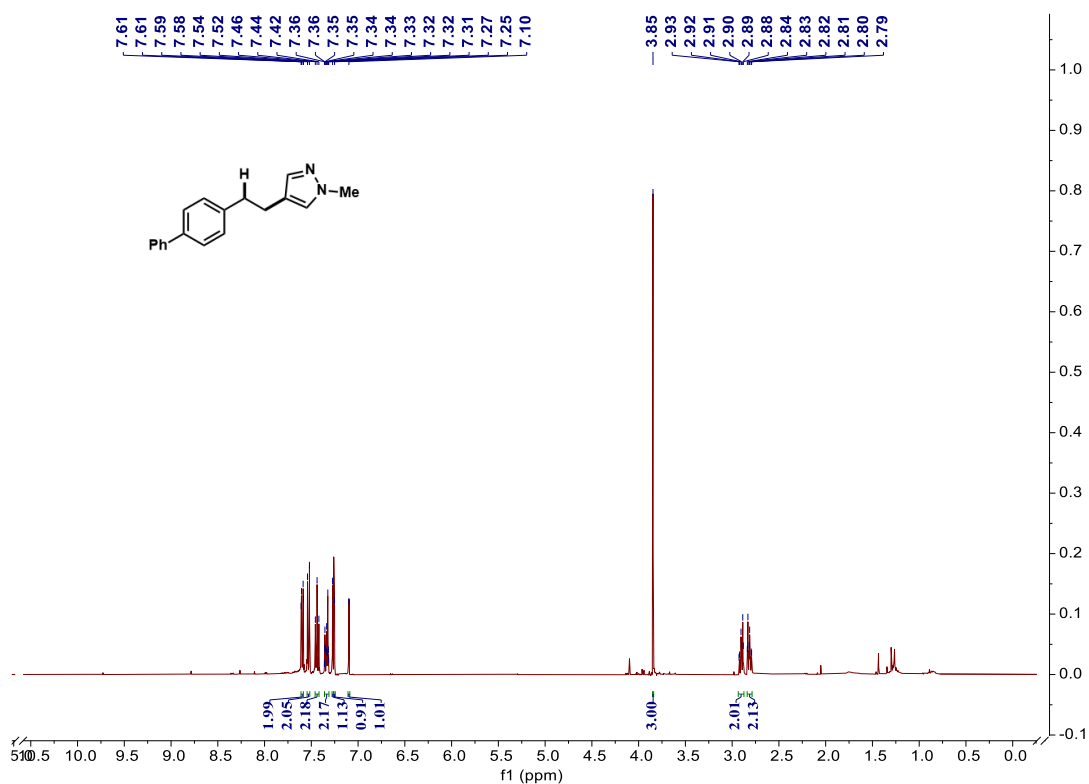


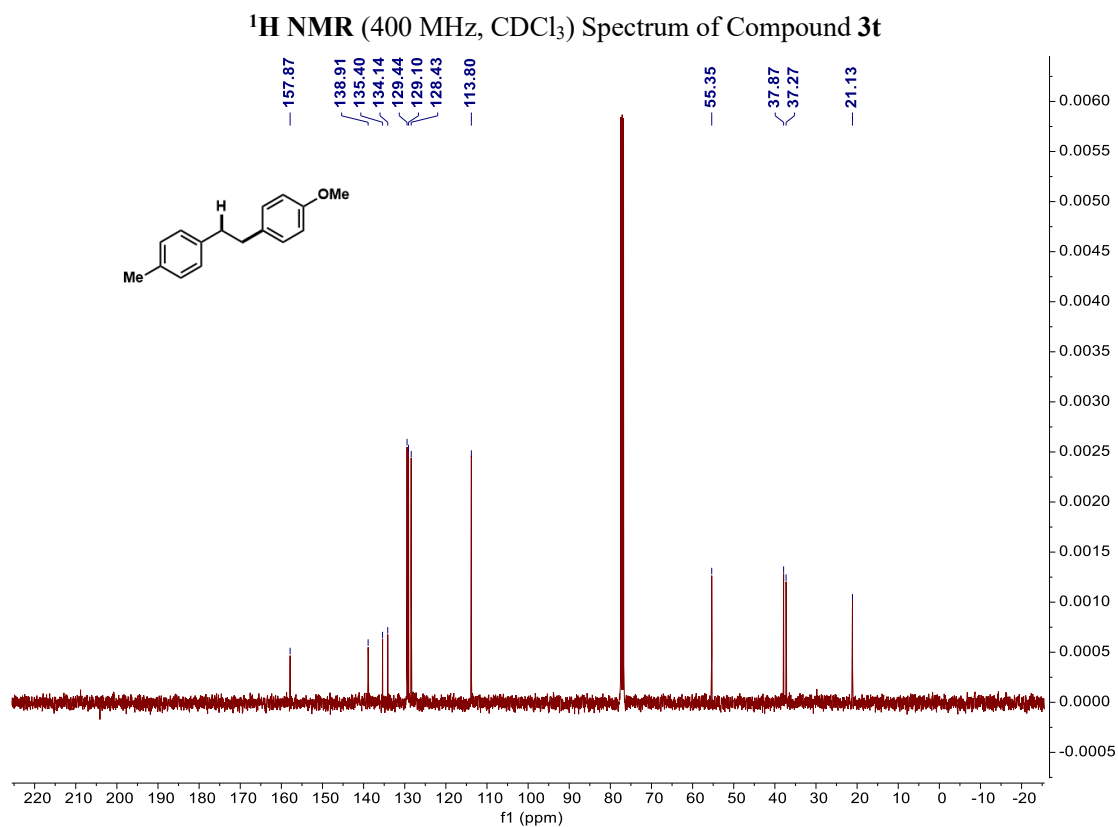
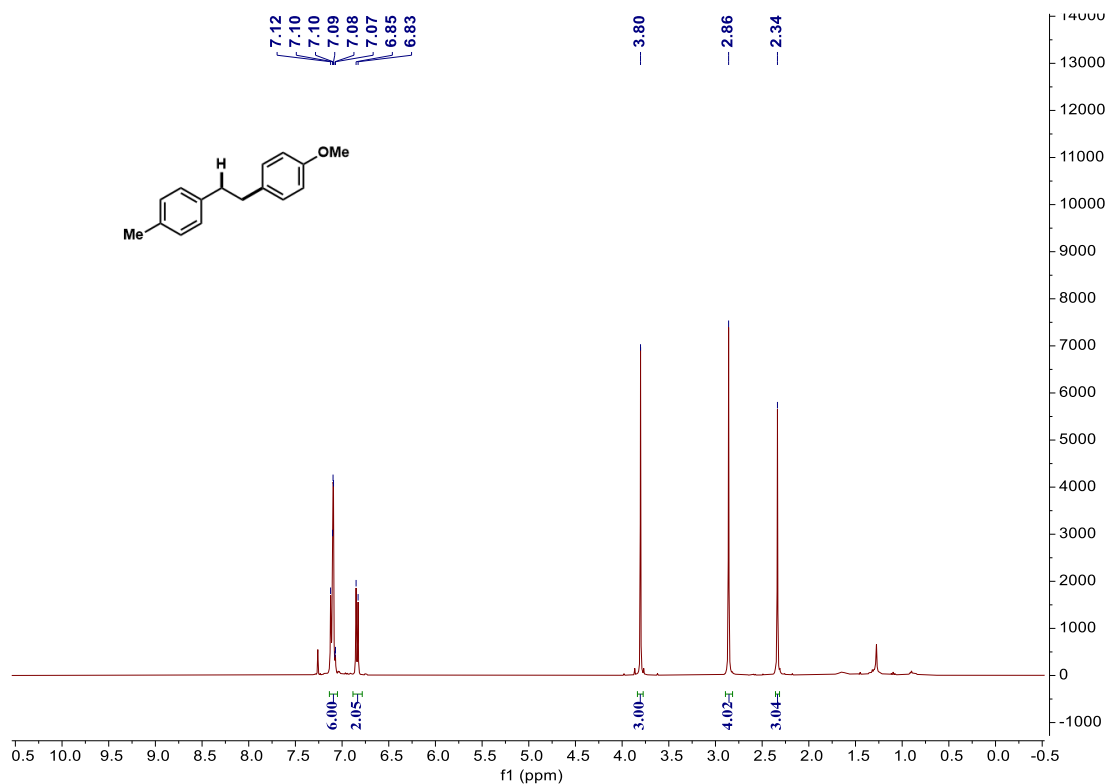




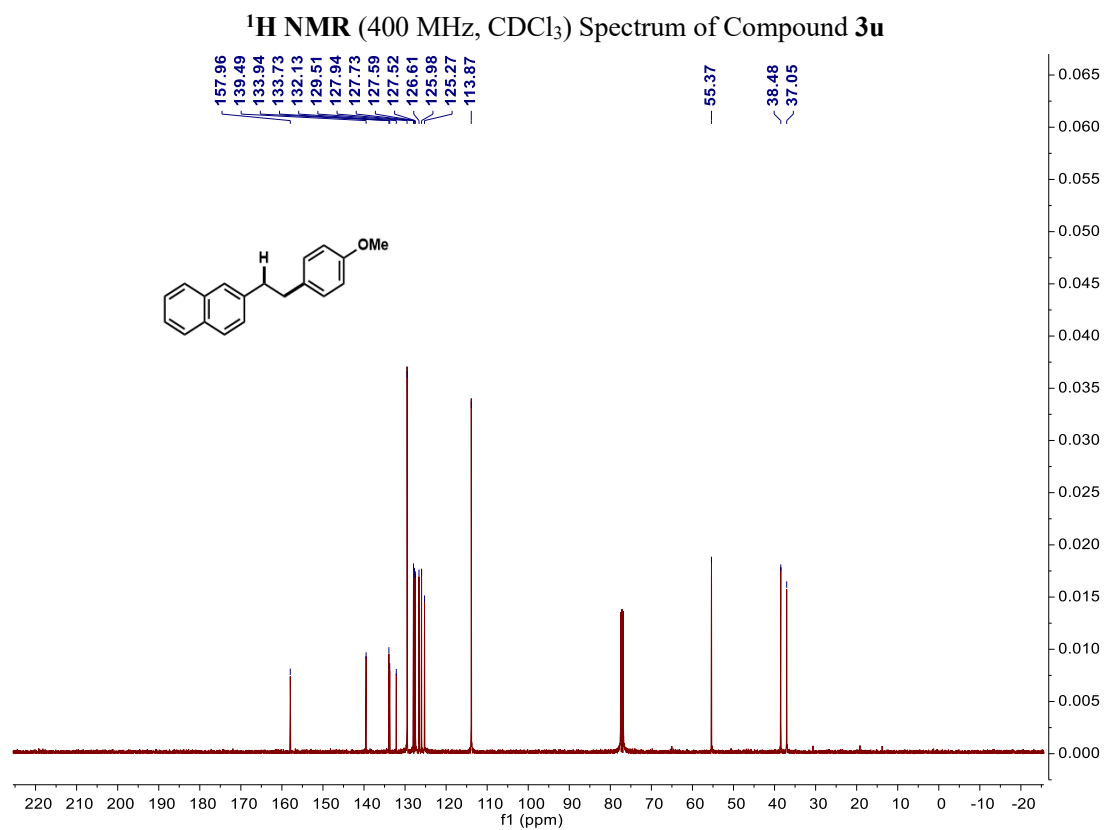
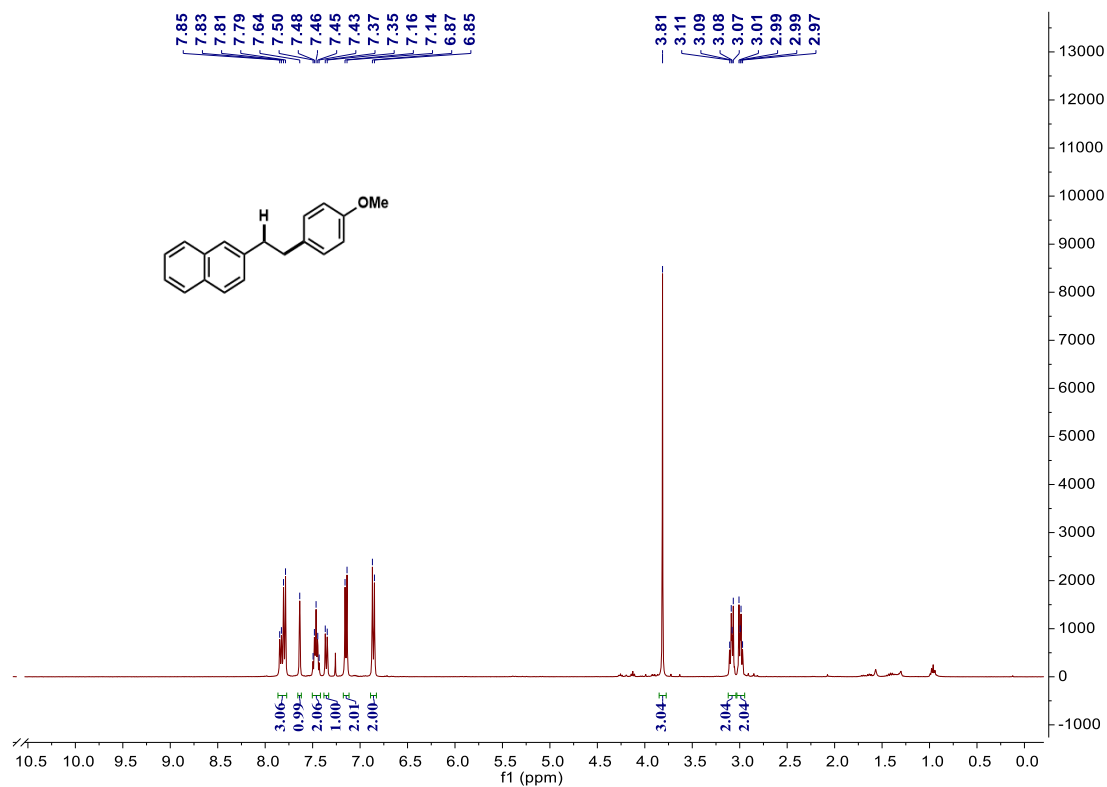


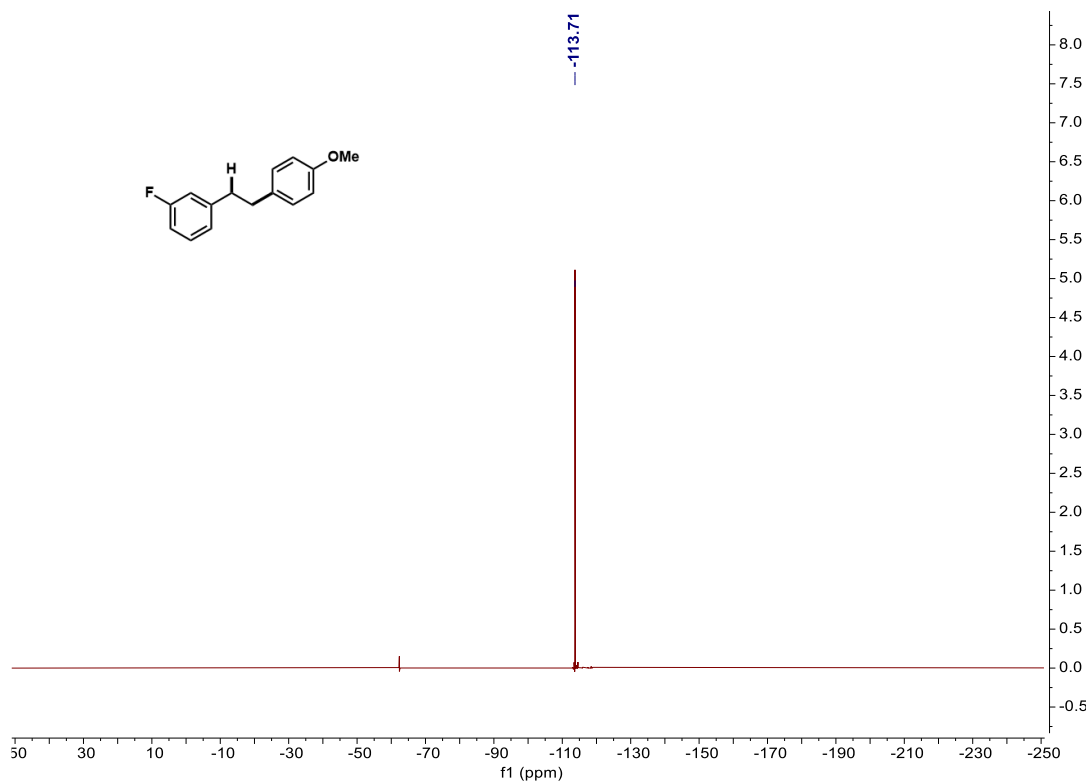
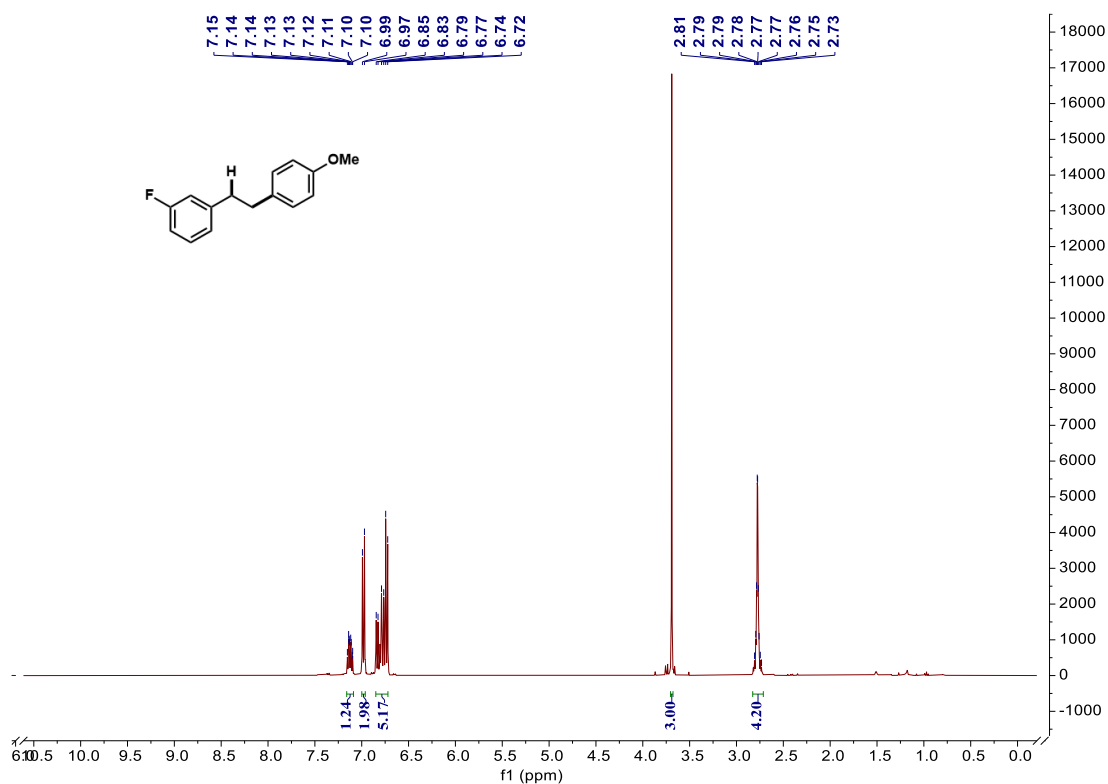


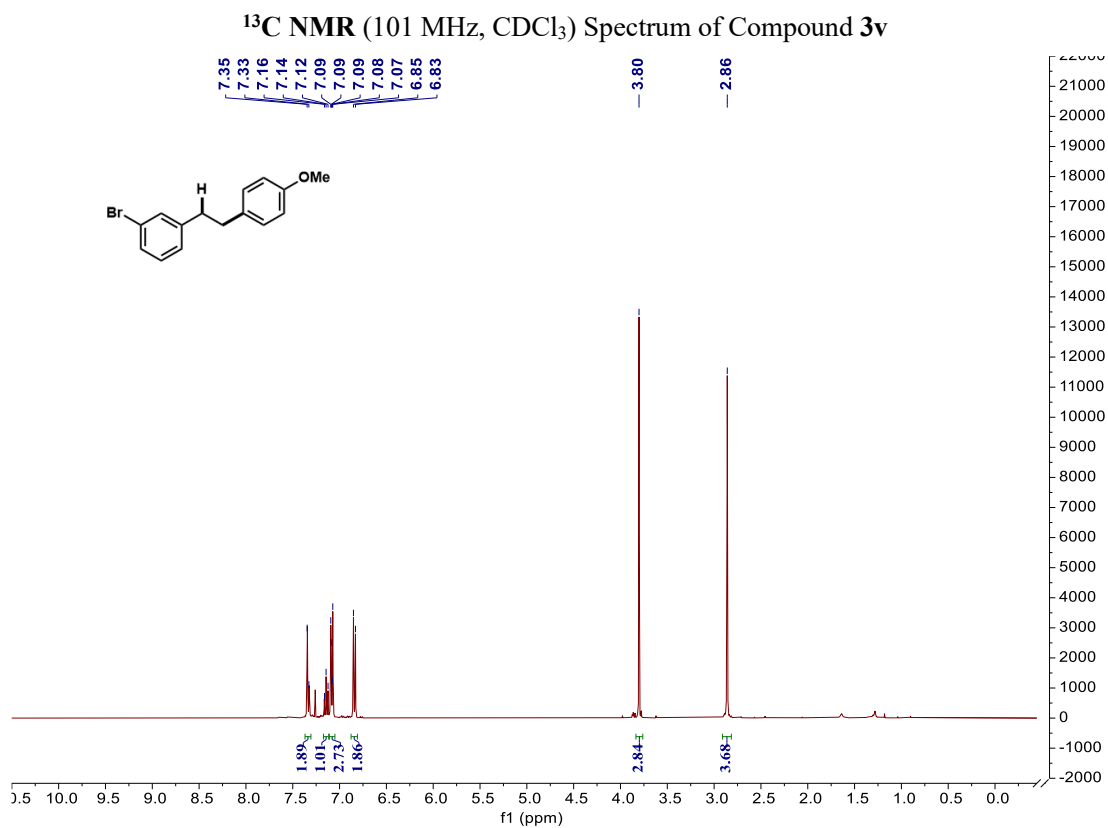
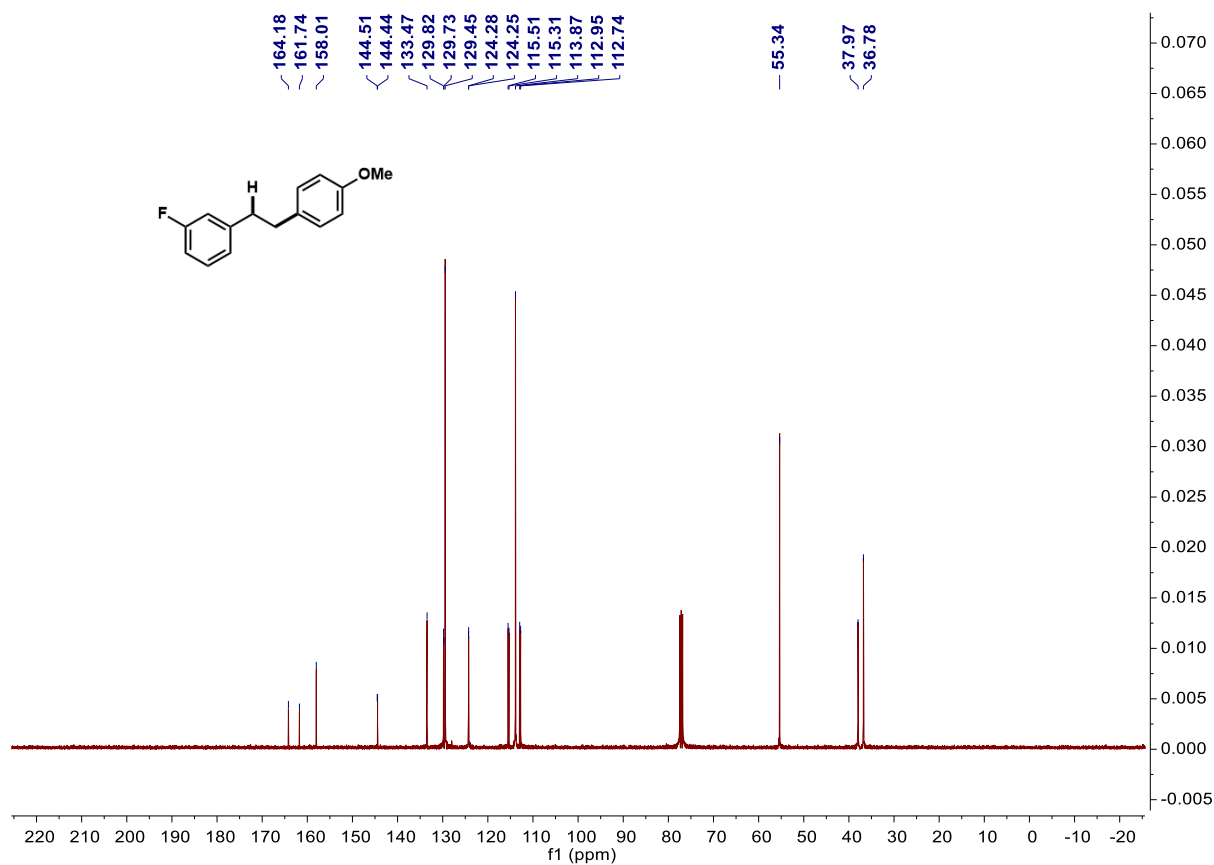


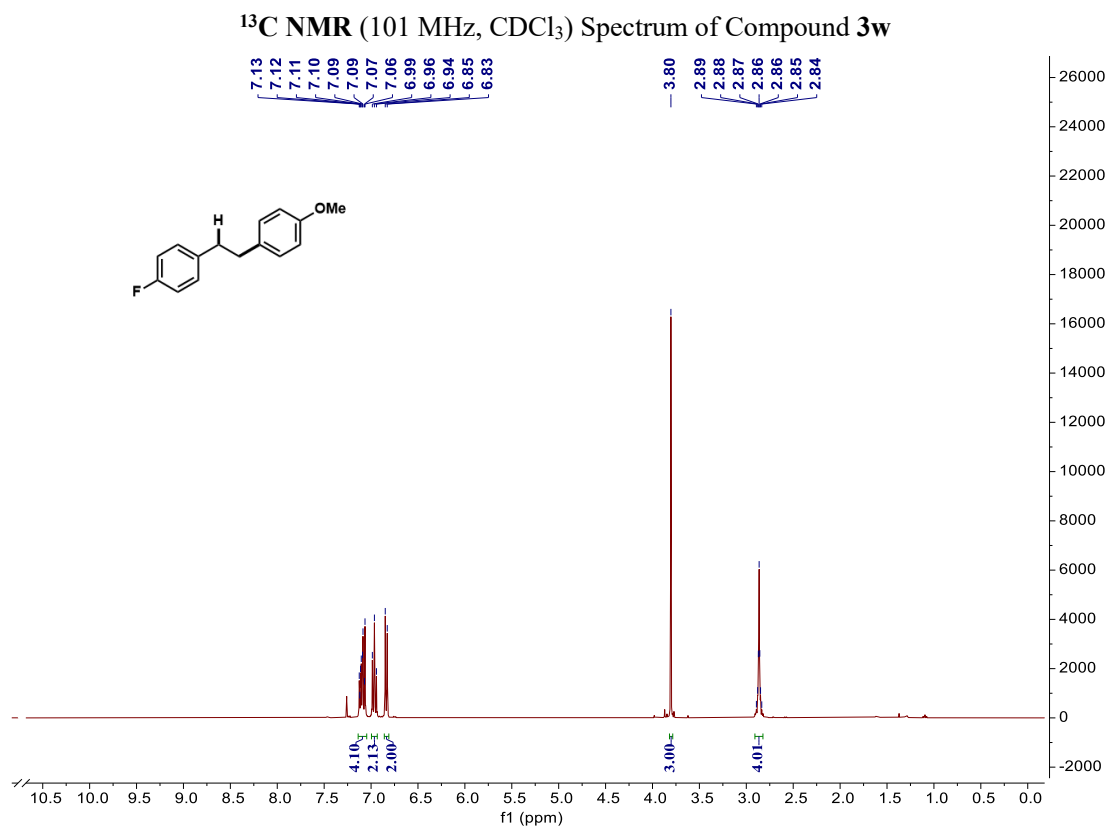
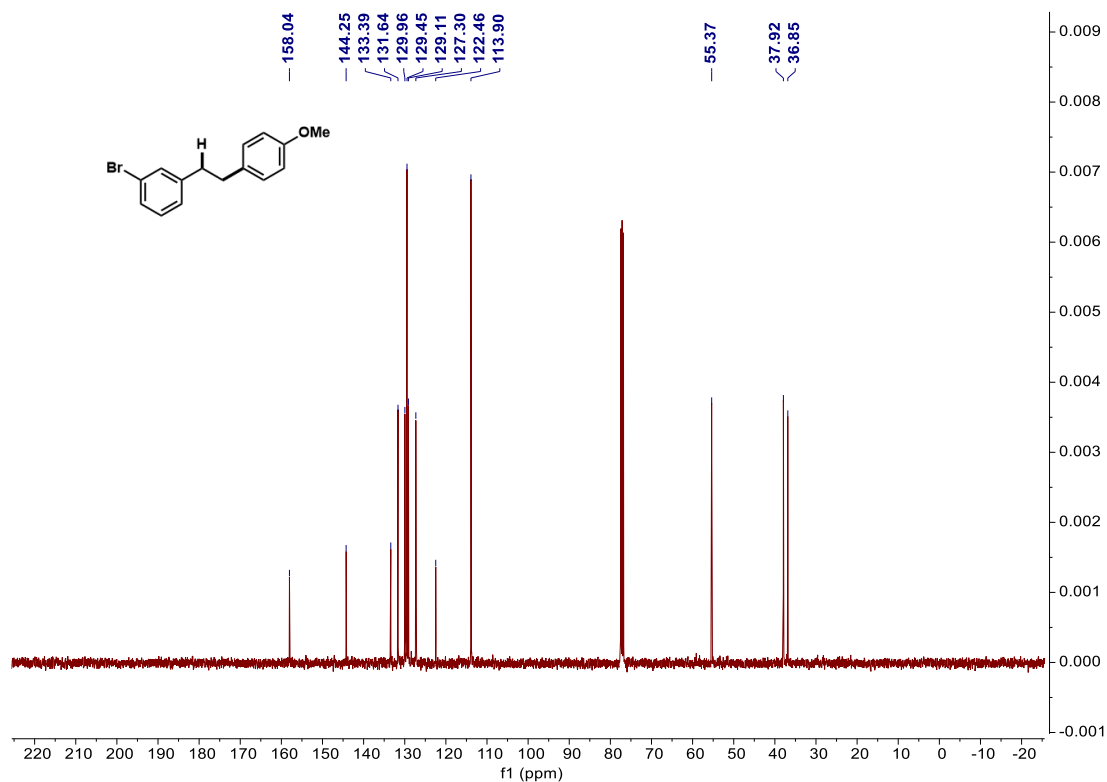


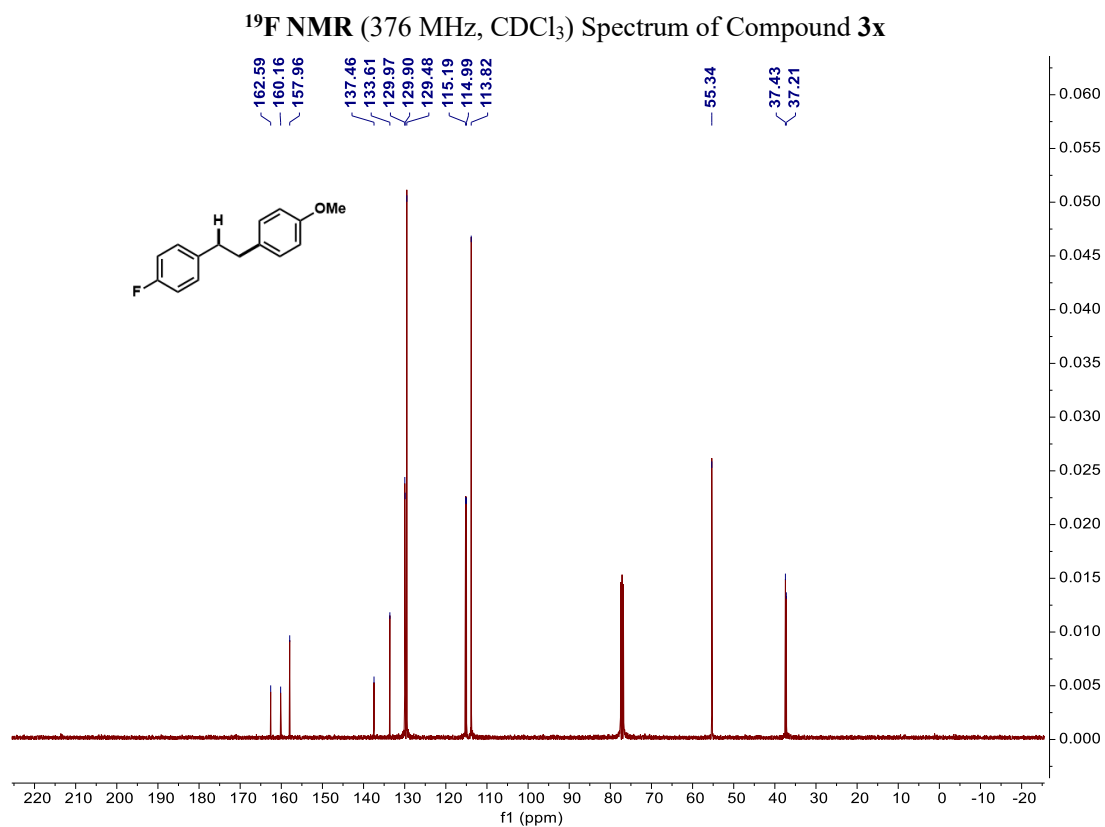
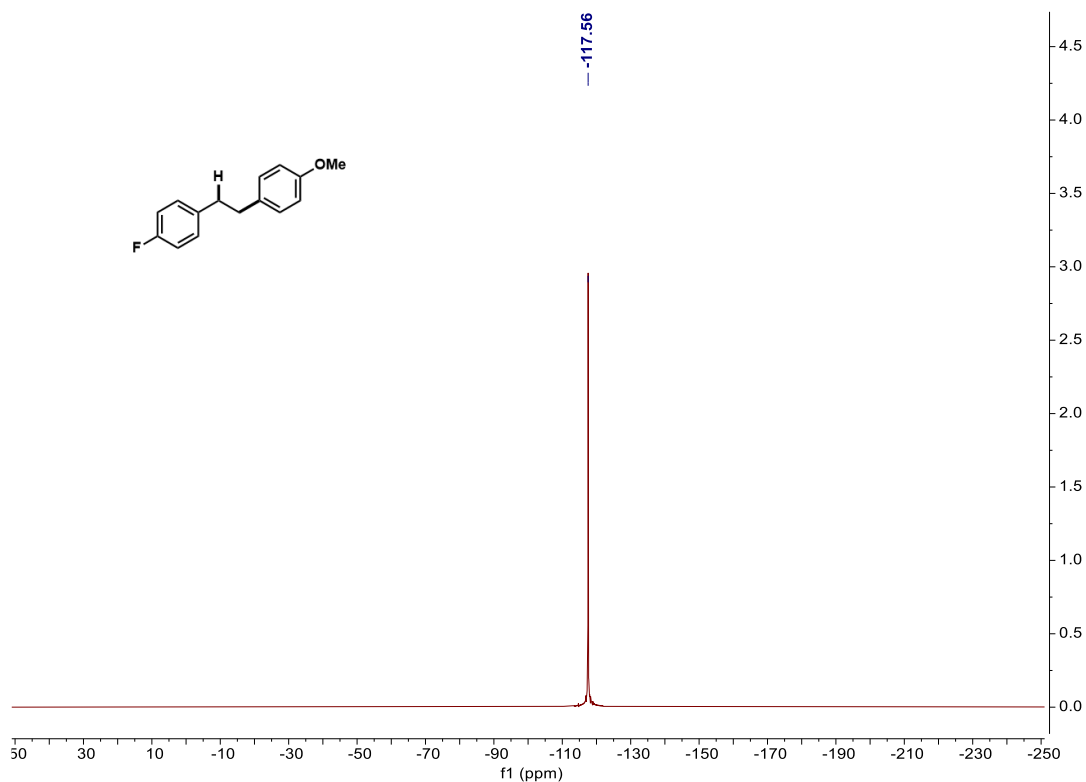


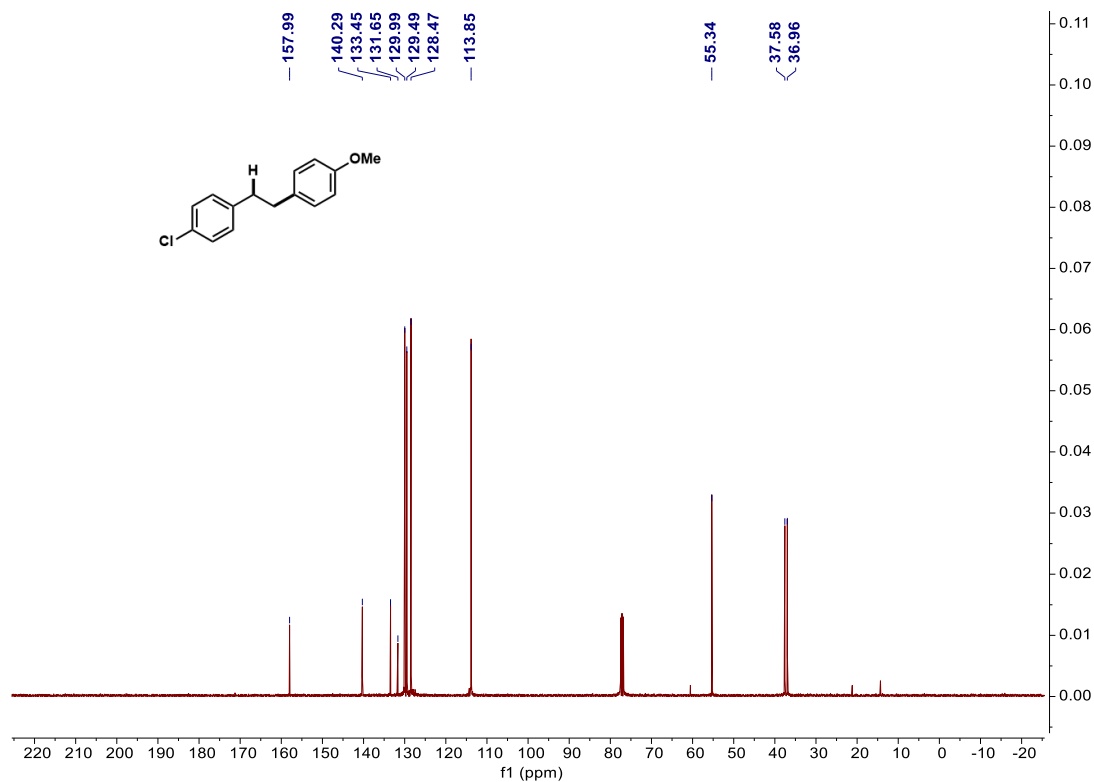
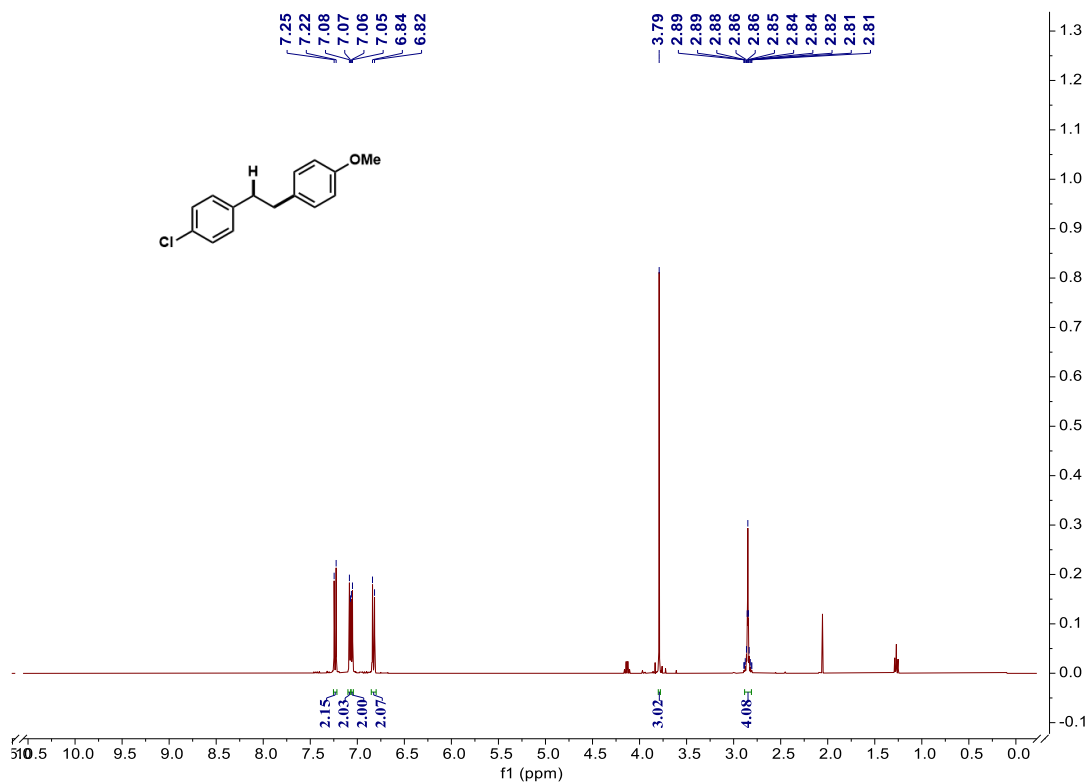


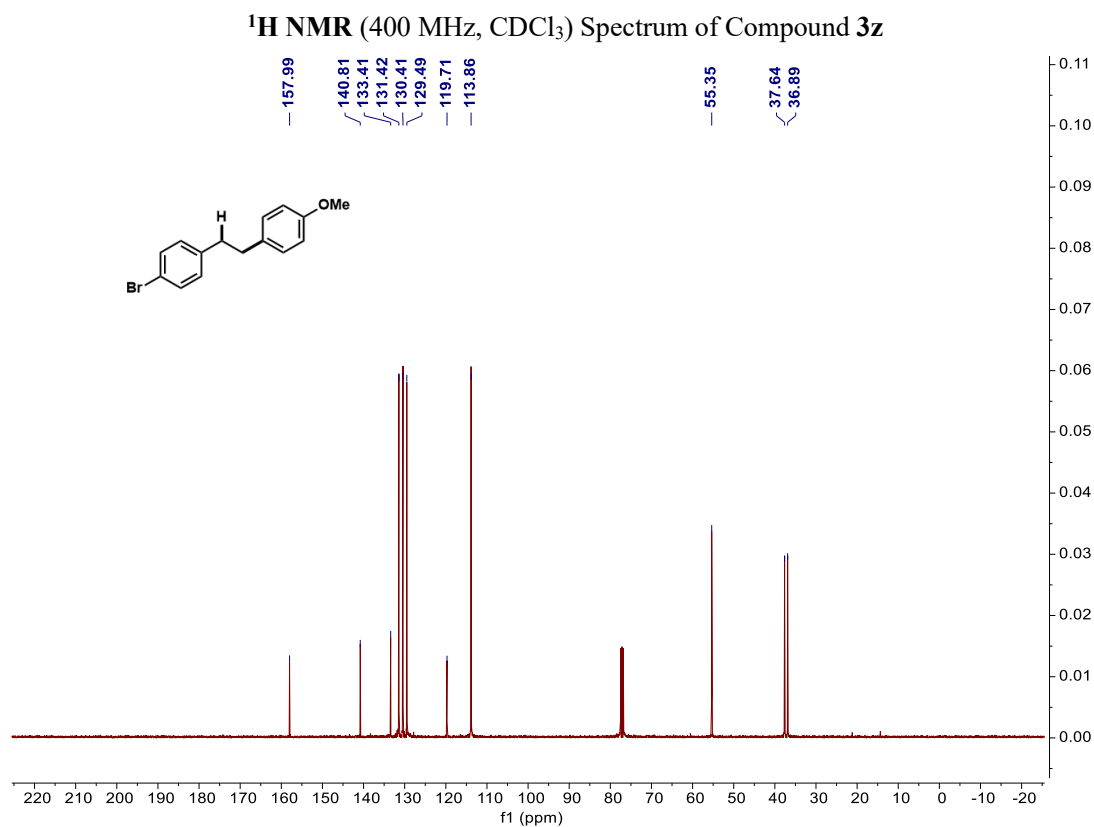
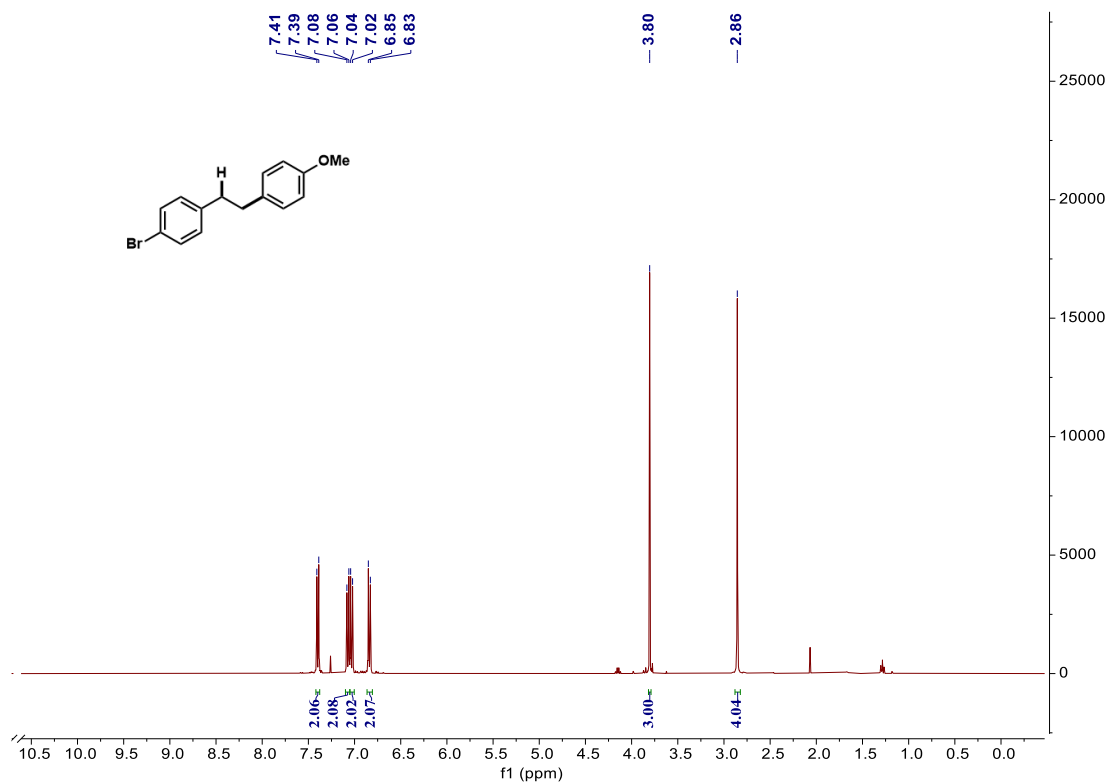


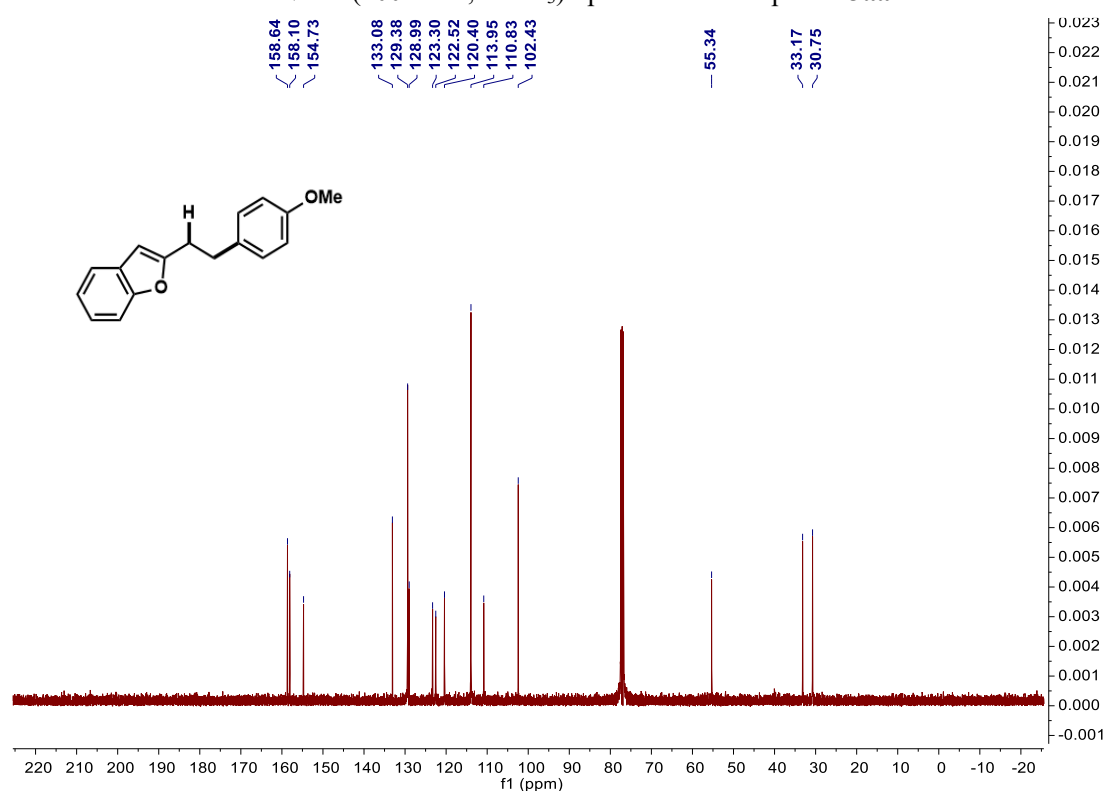
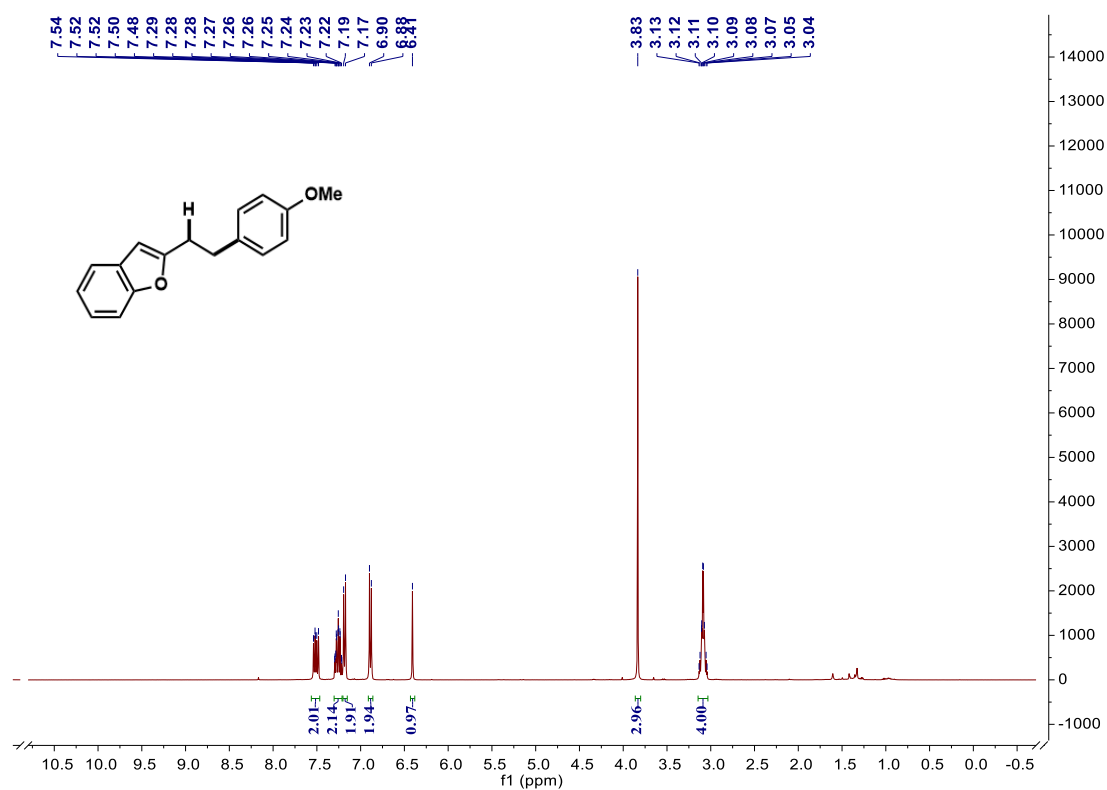




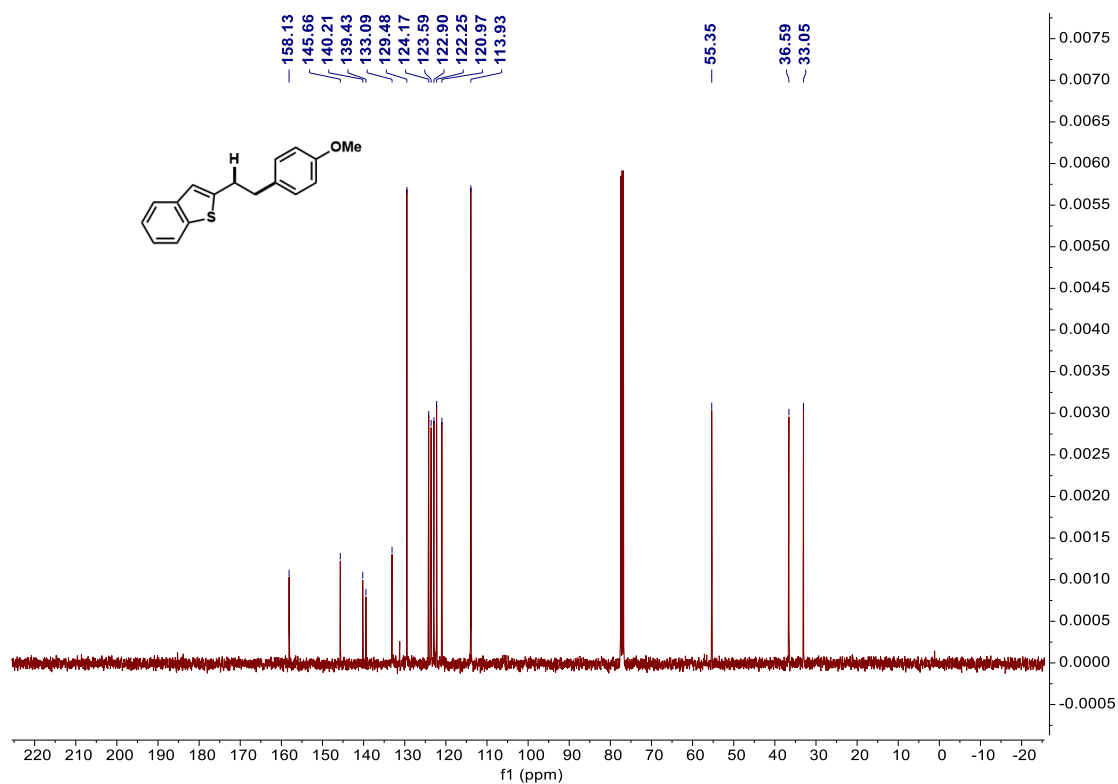
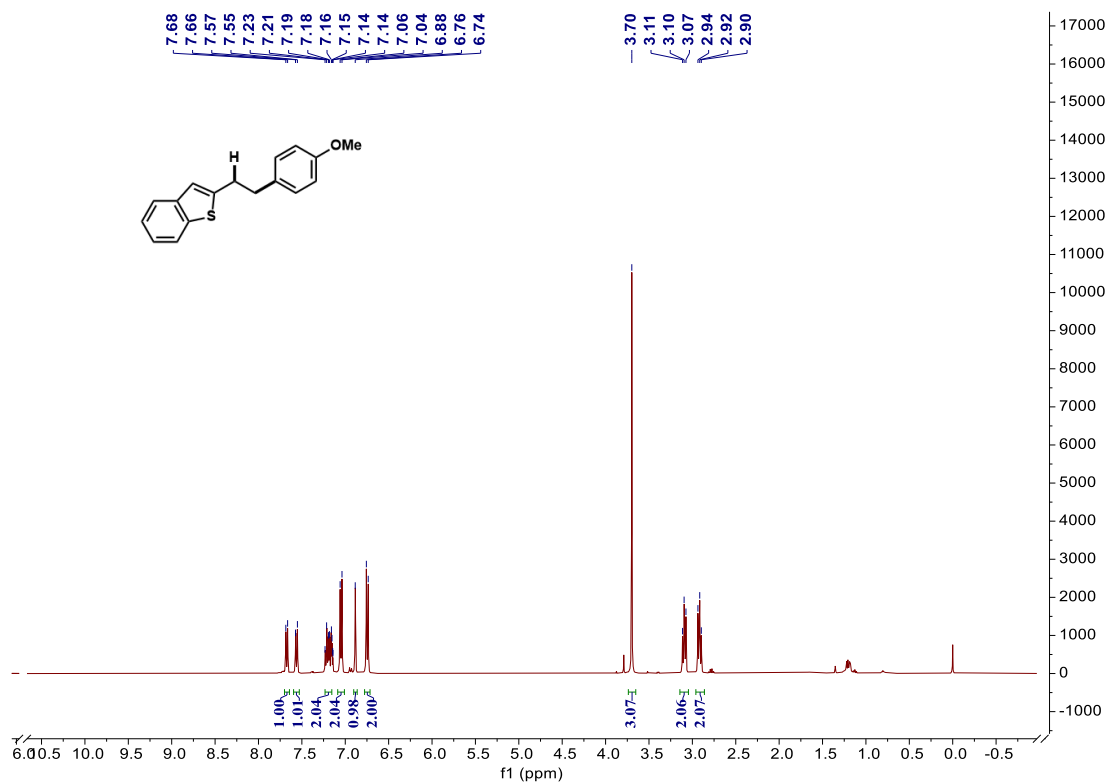


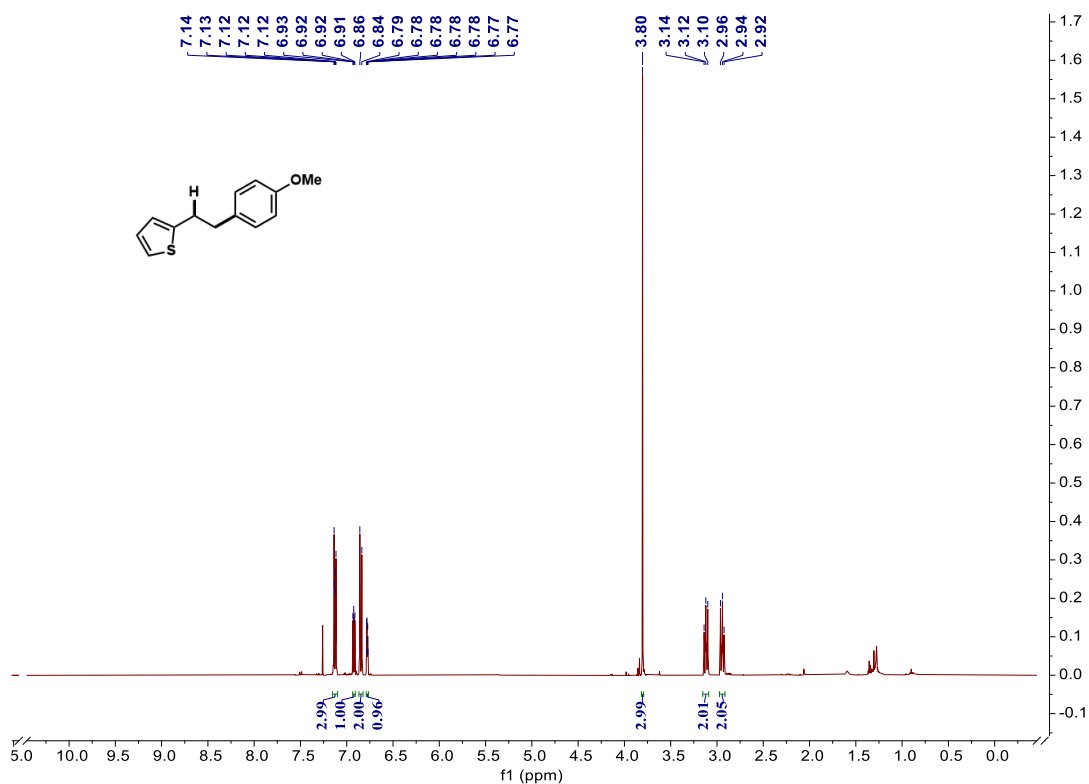




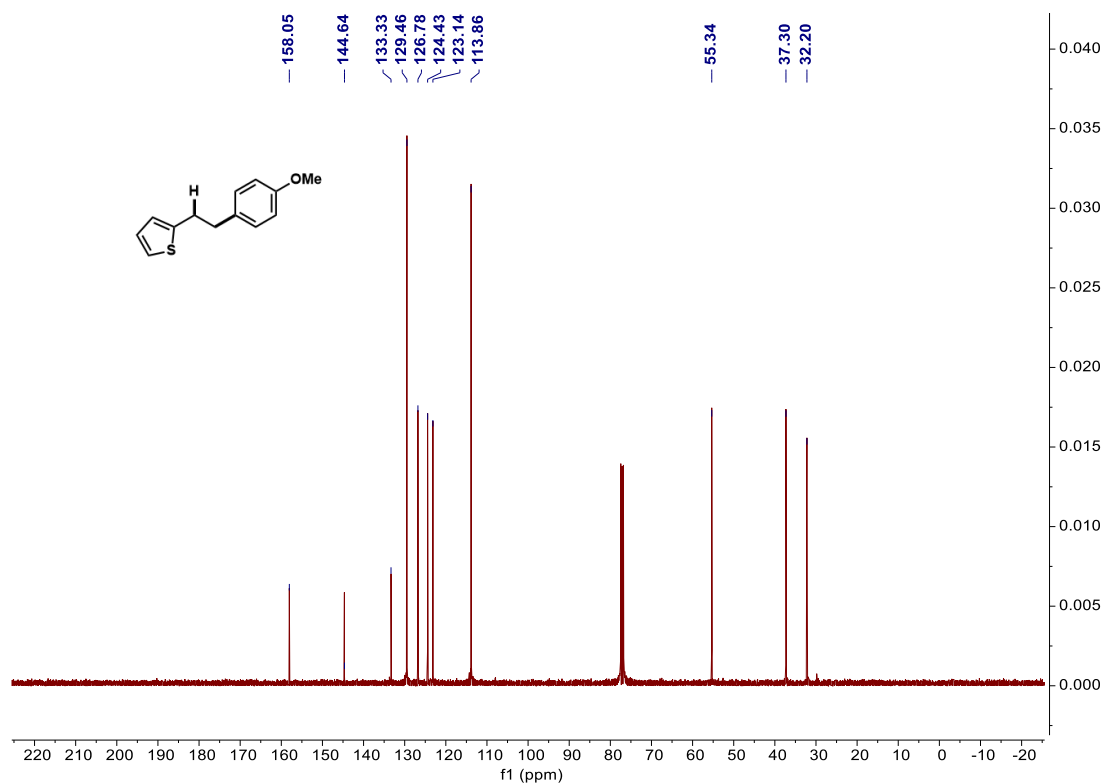




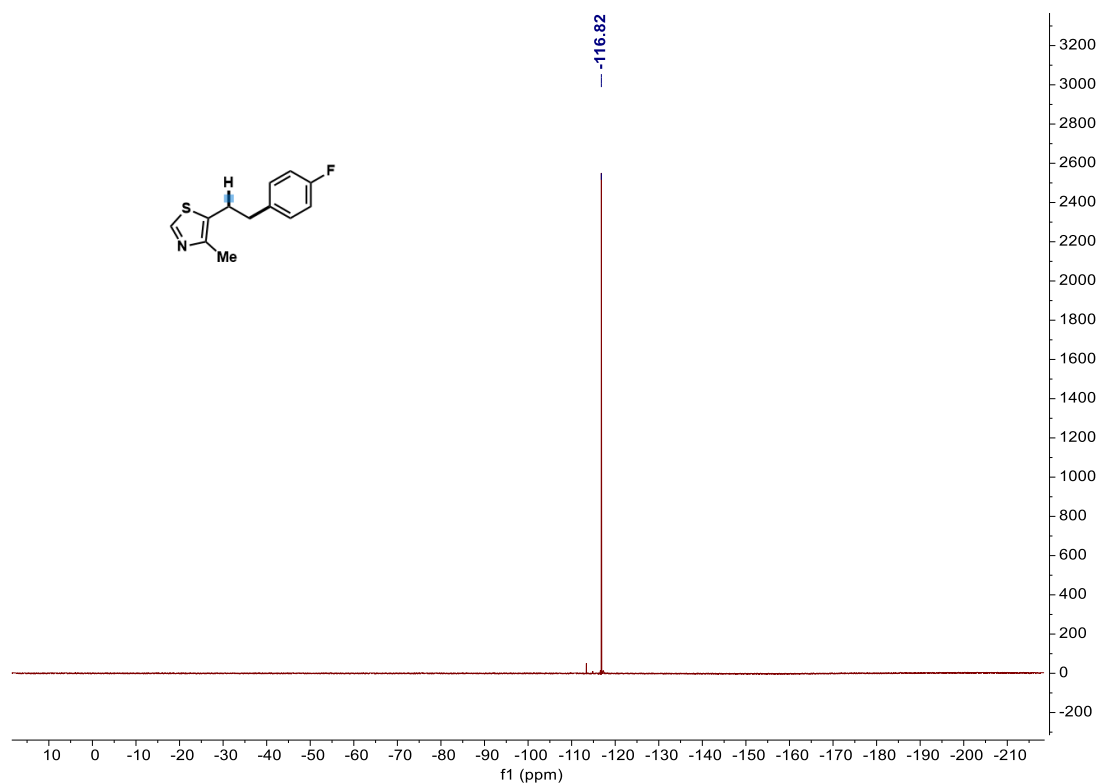
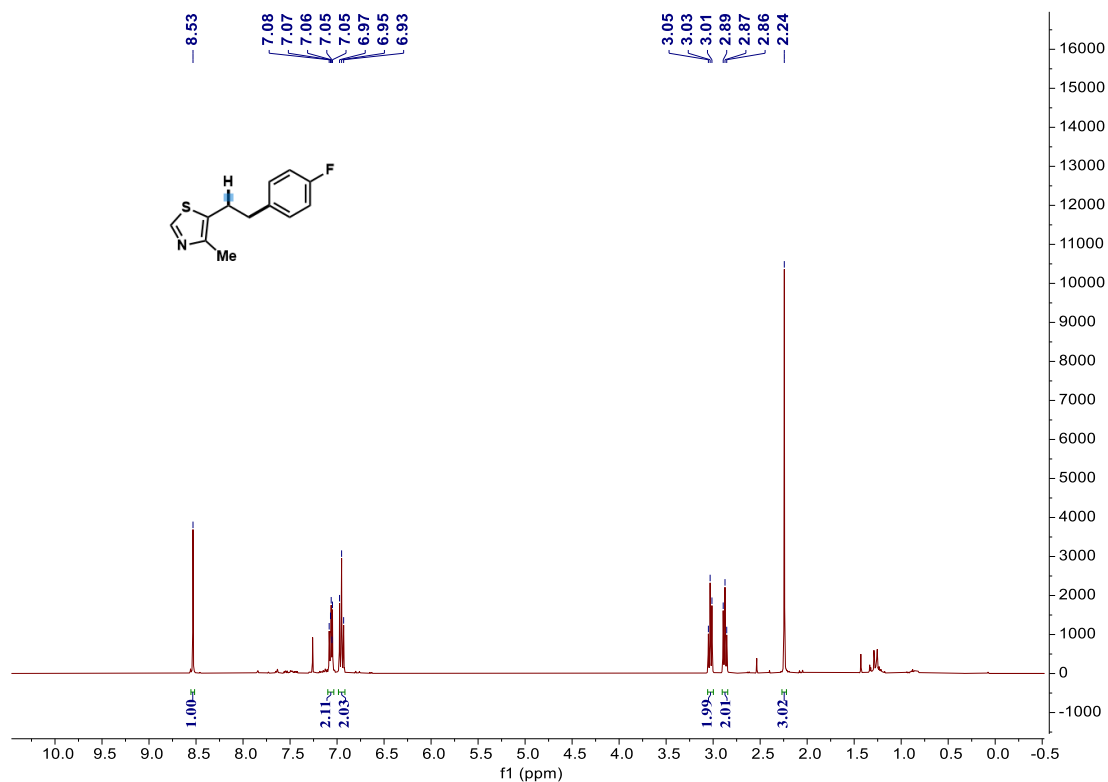


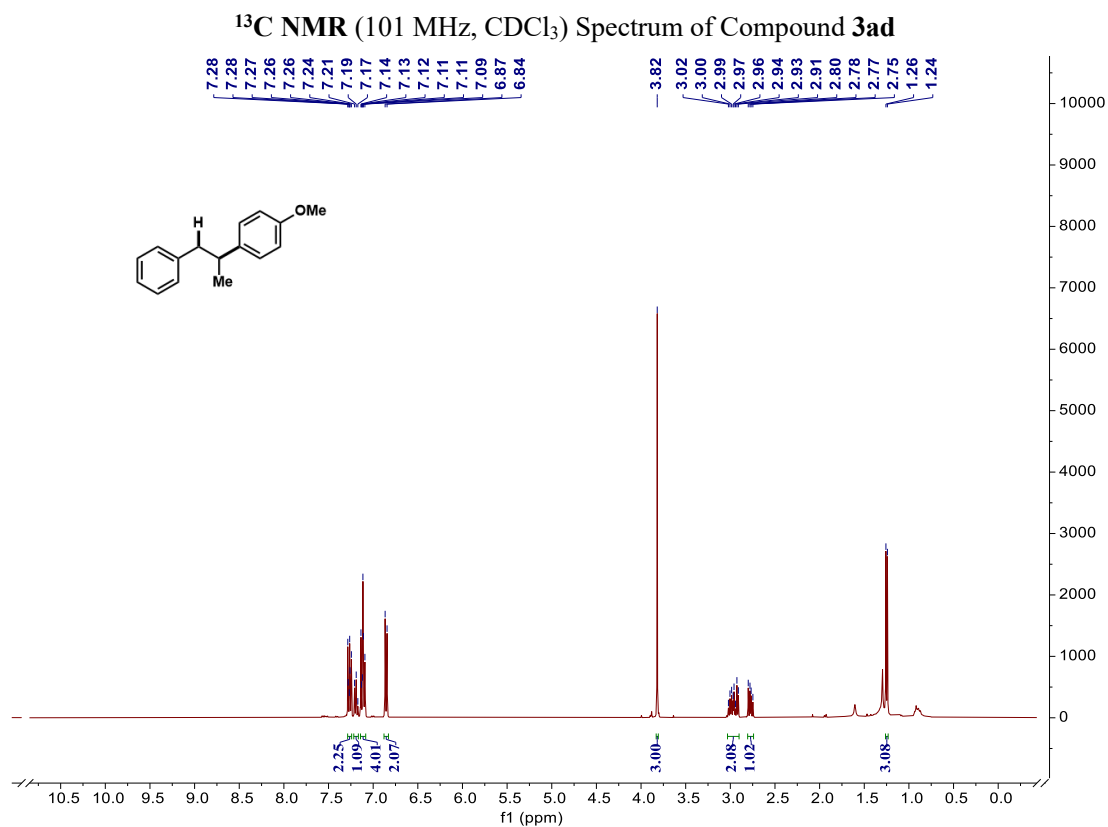
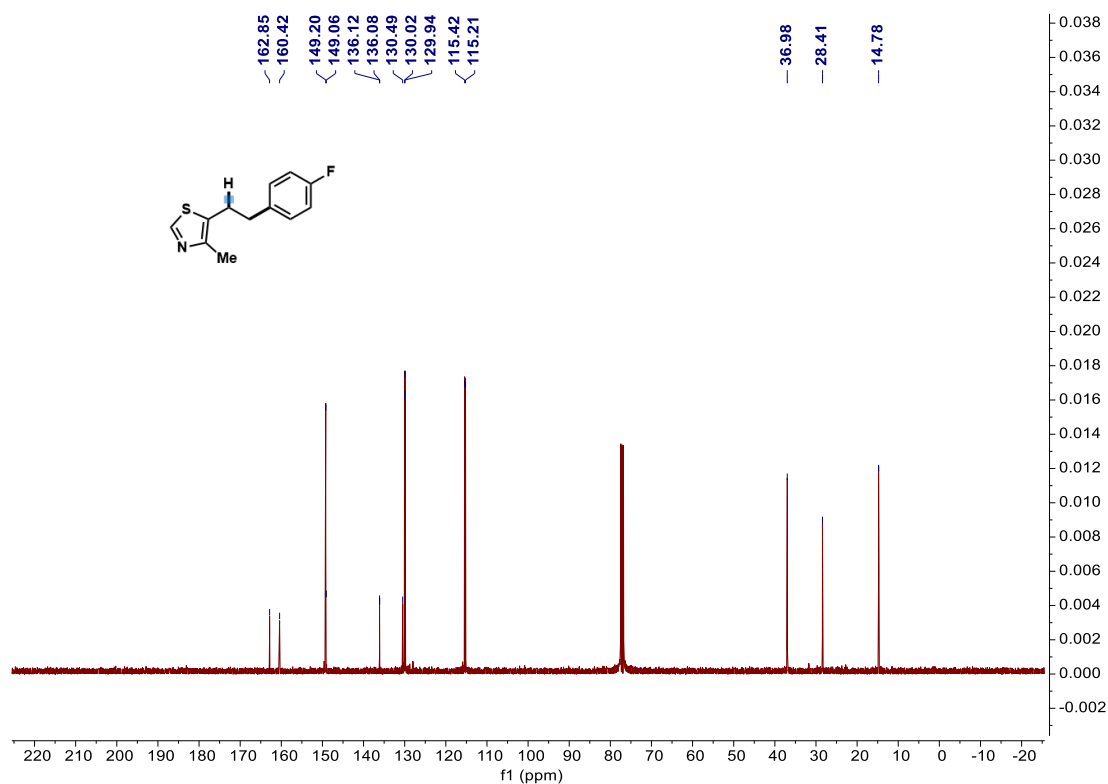


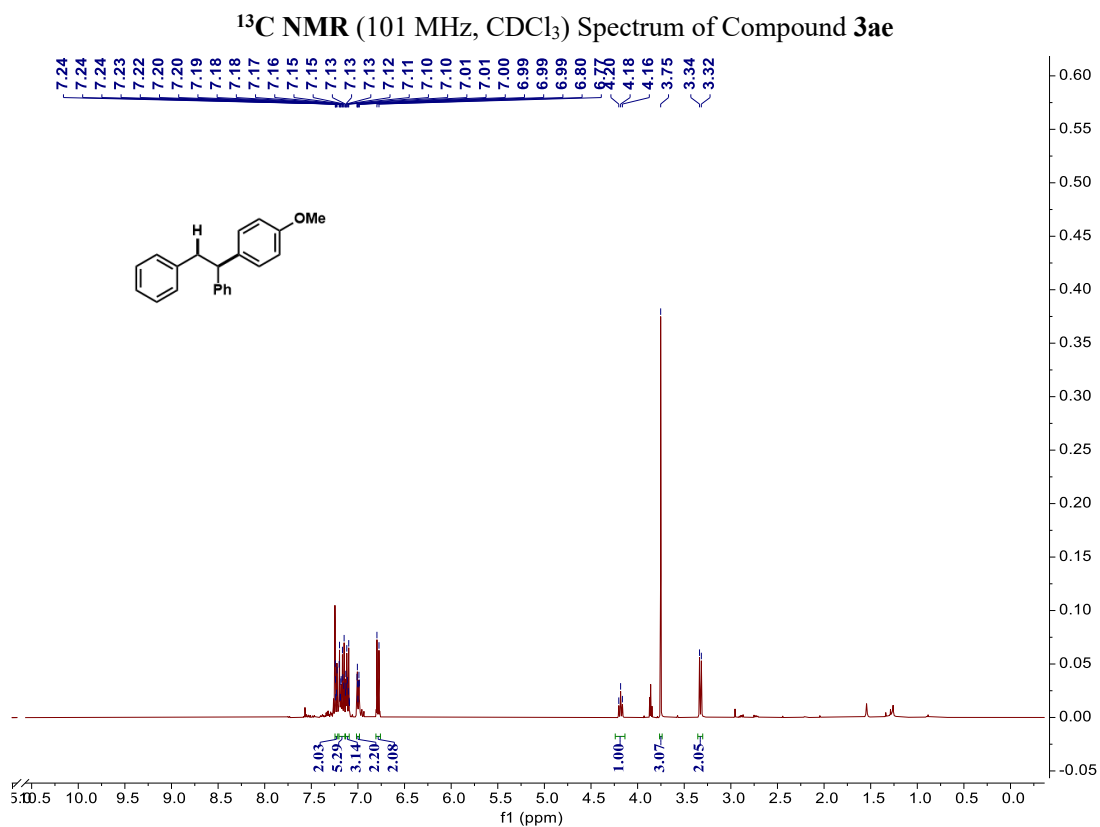
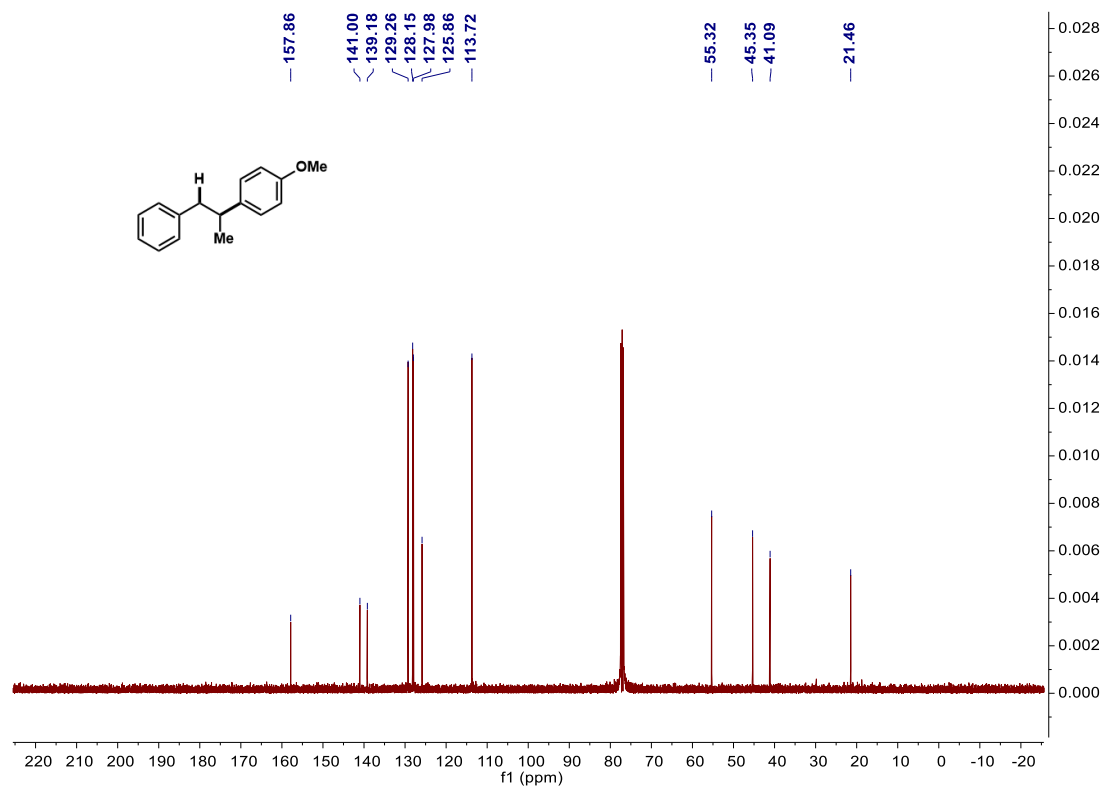
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) Spectrum of Compound **3ac**

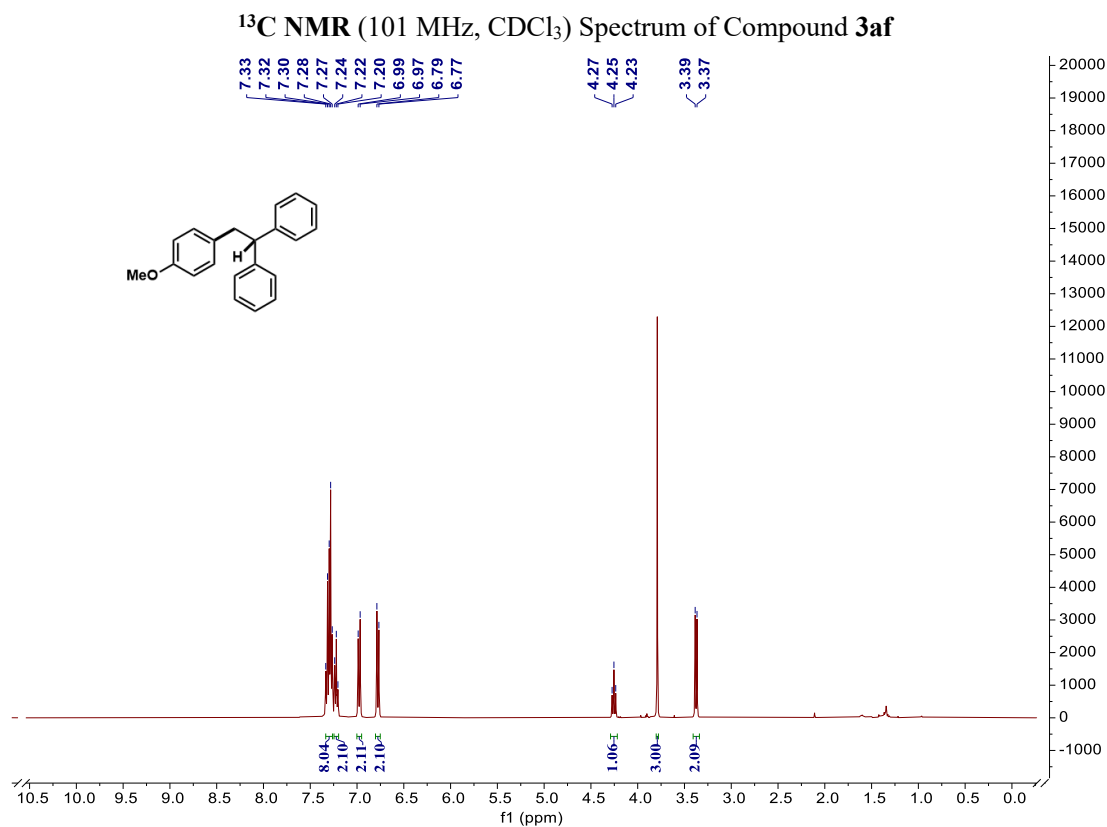
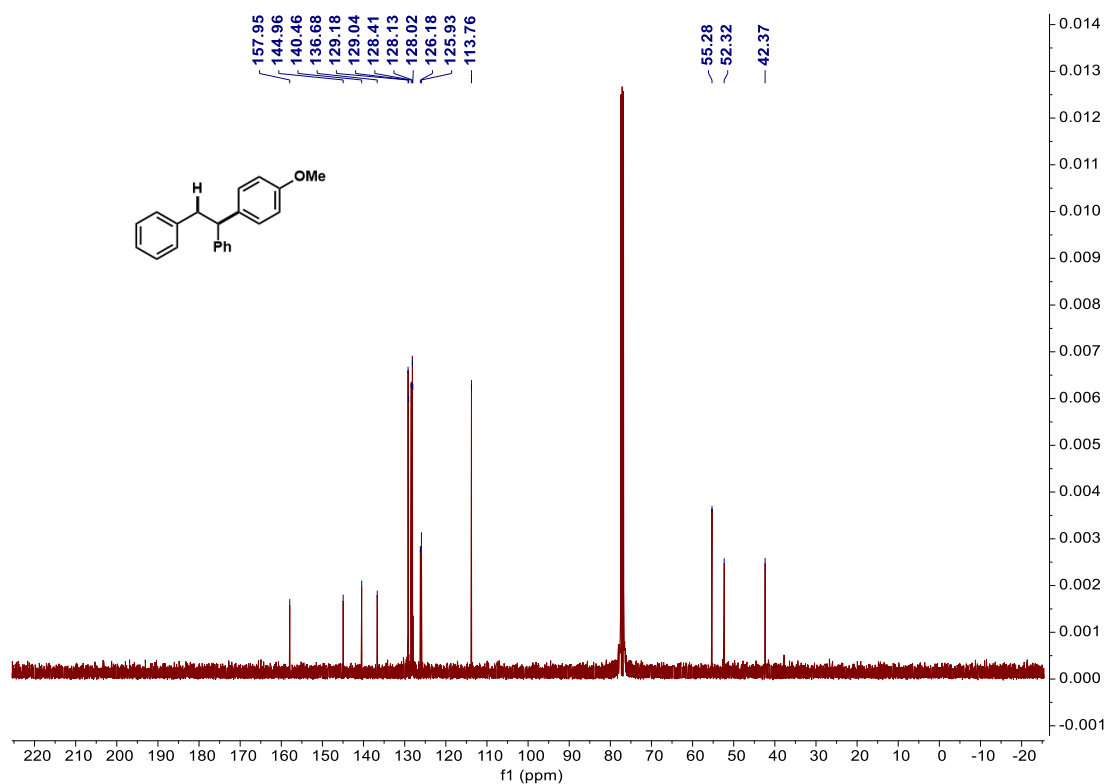


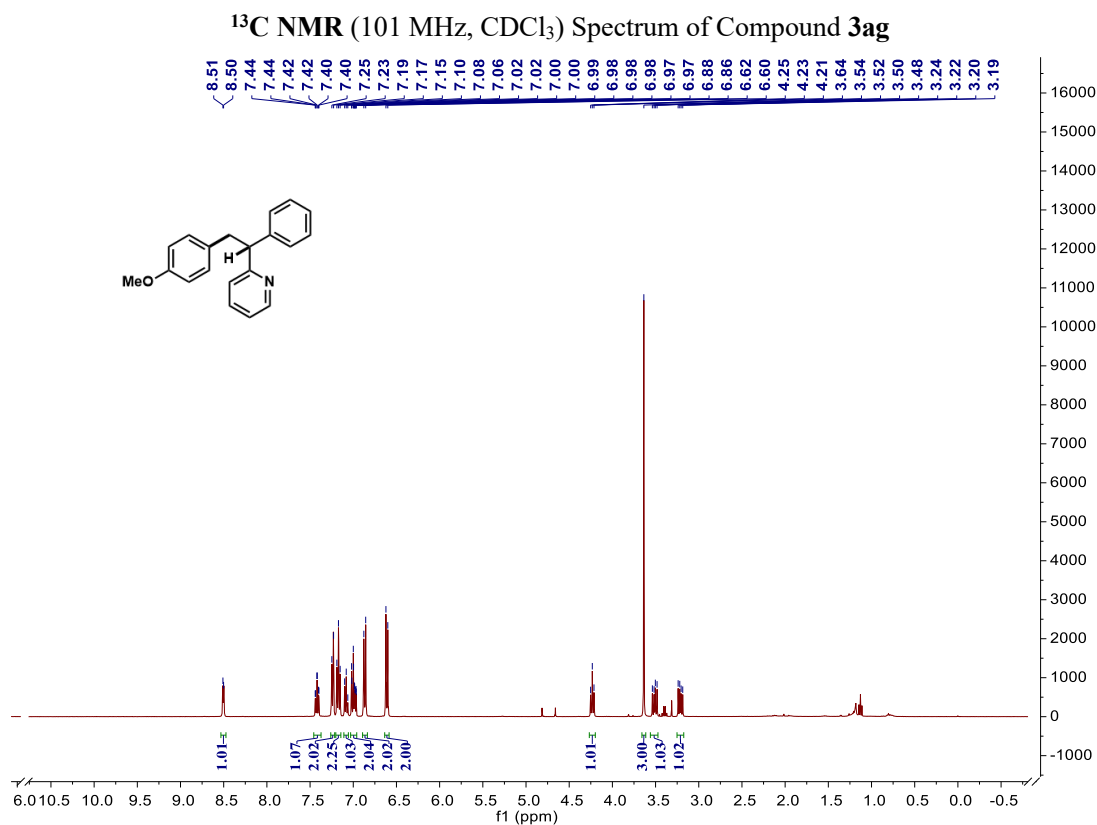
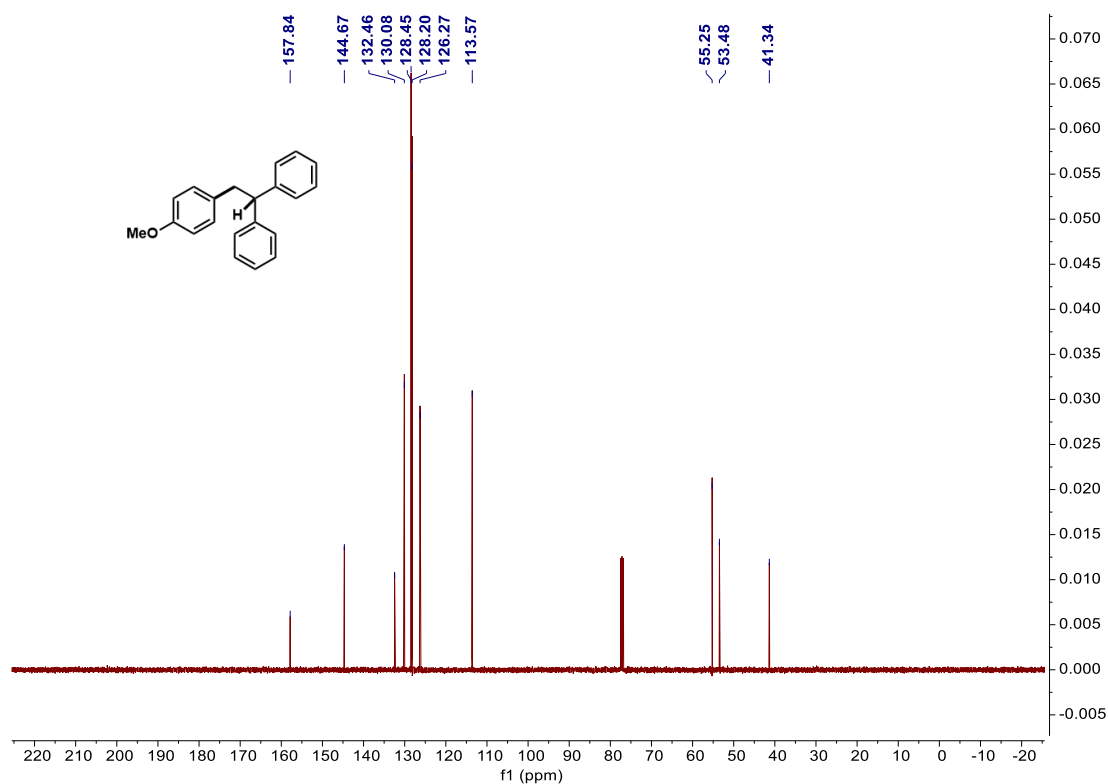
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) Spectrum of Compound **3ac**

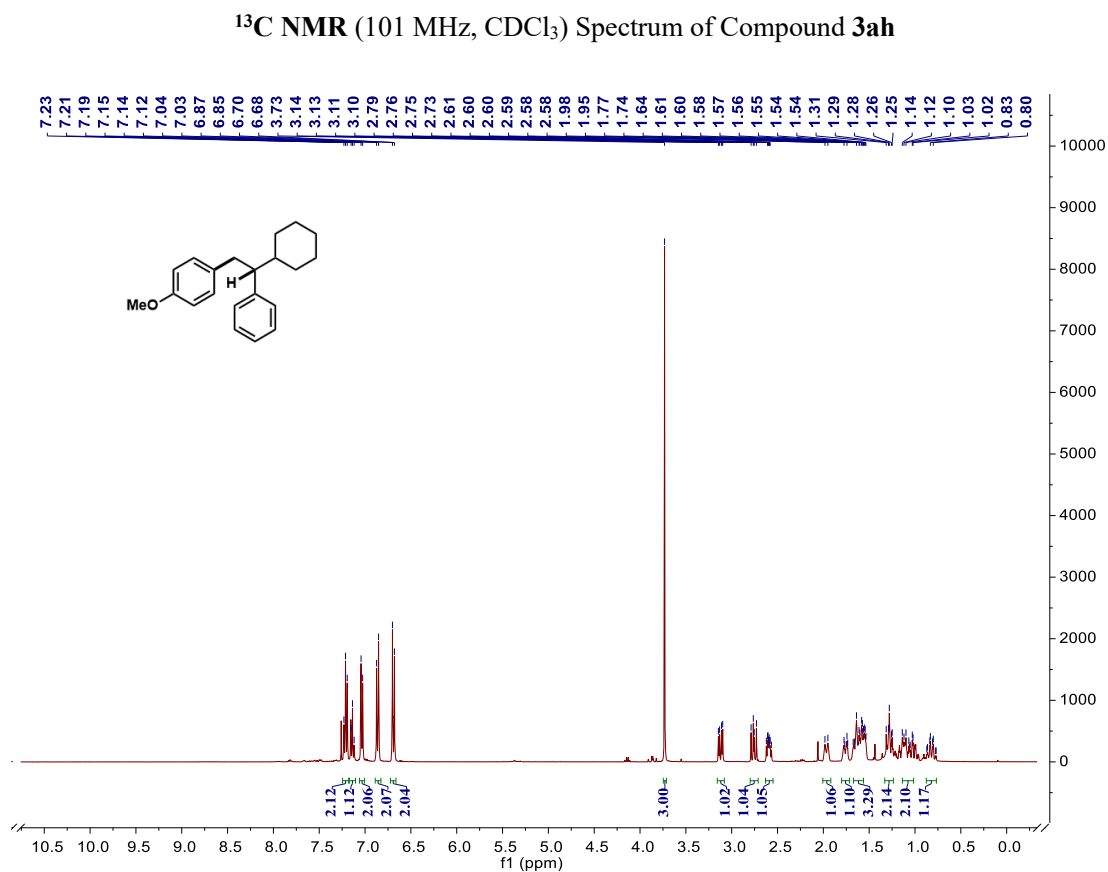
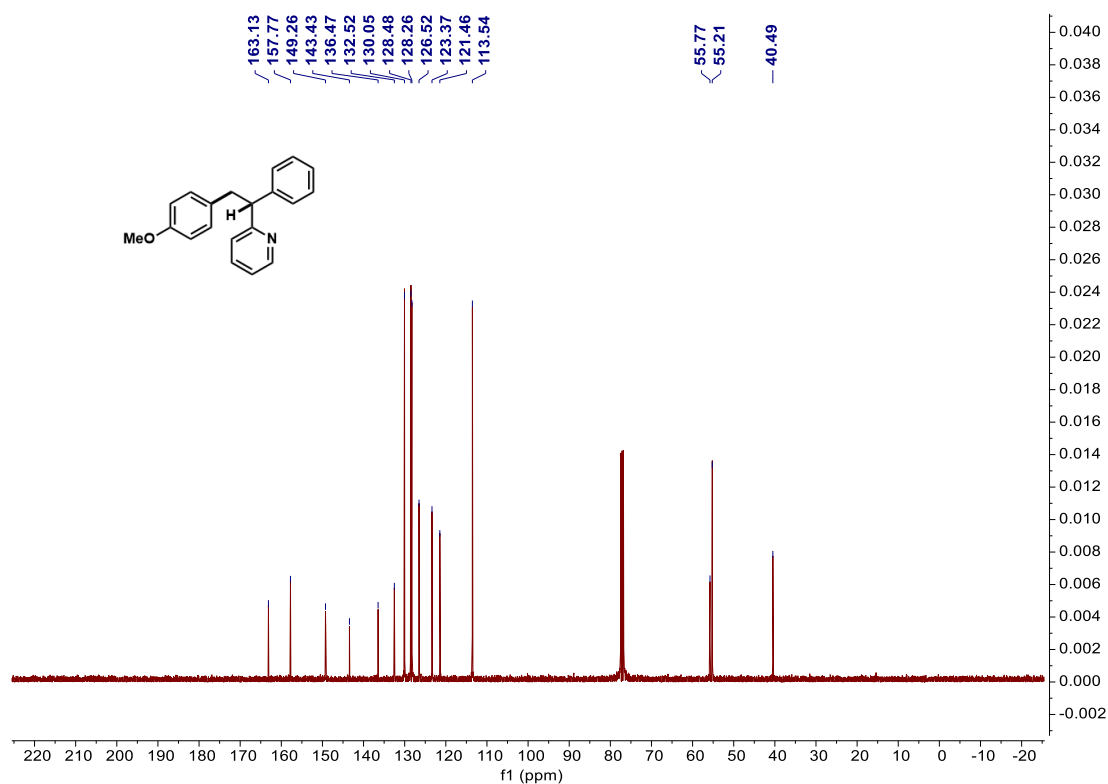




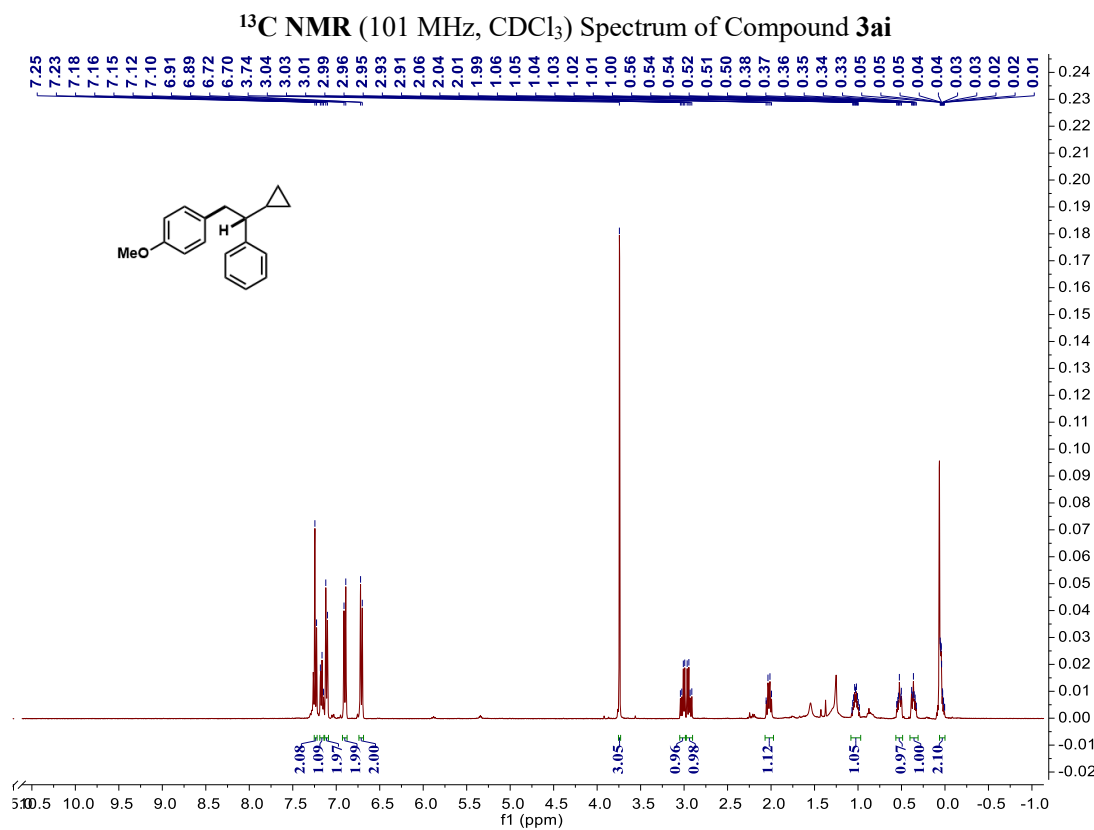
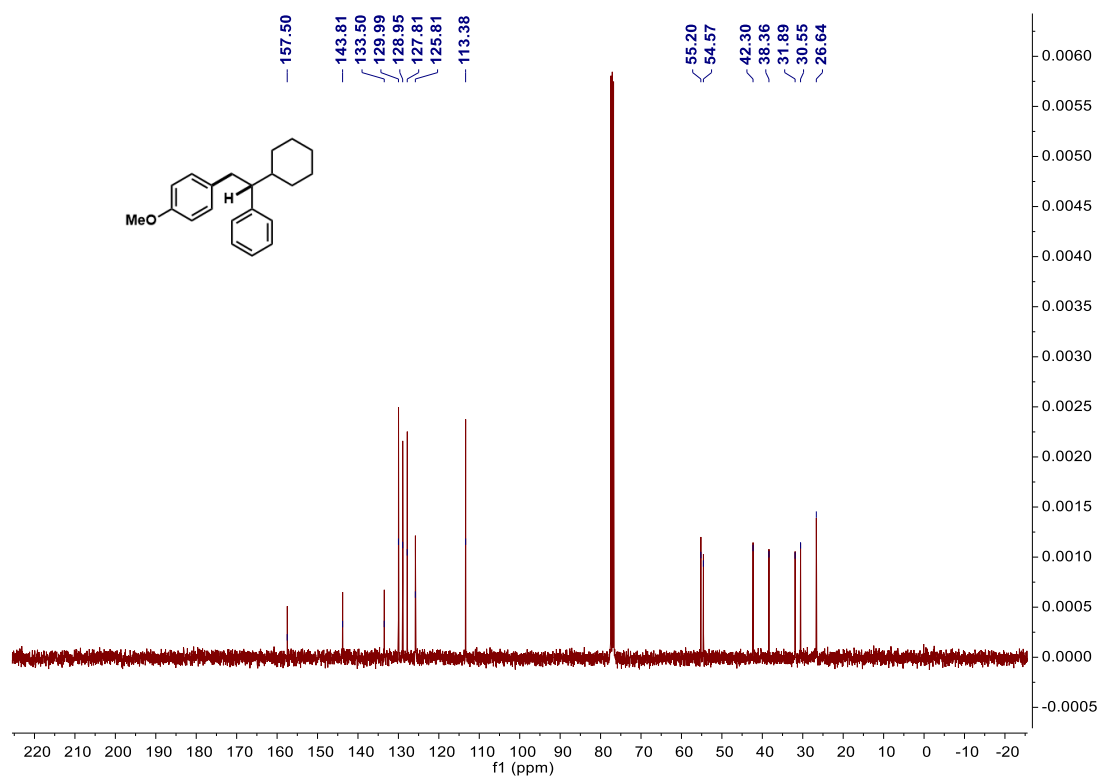


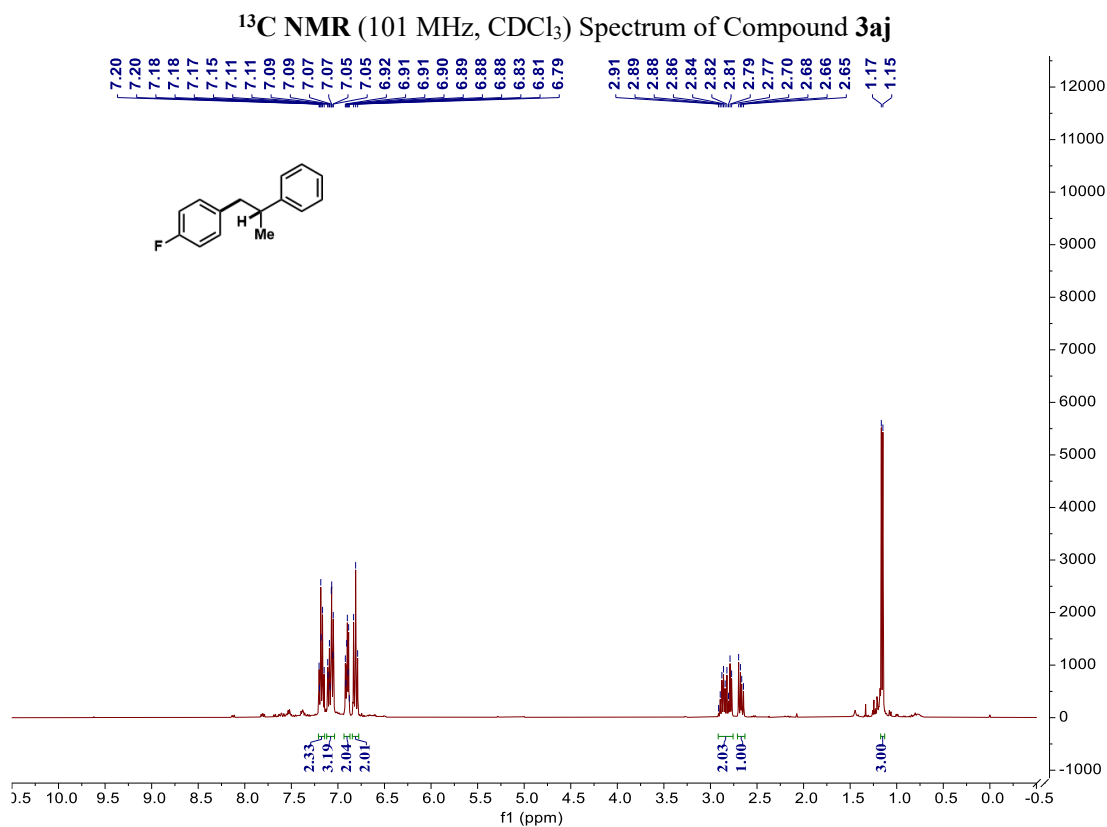
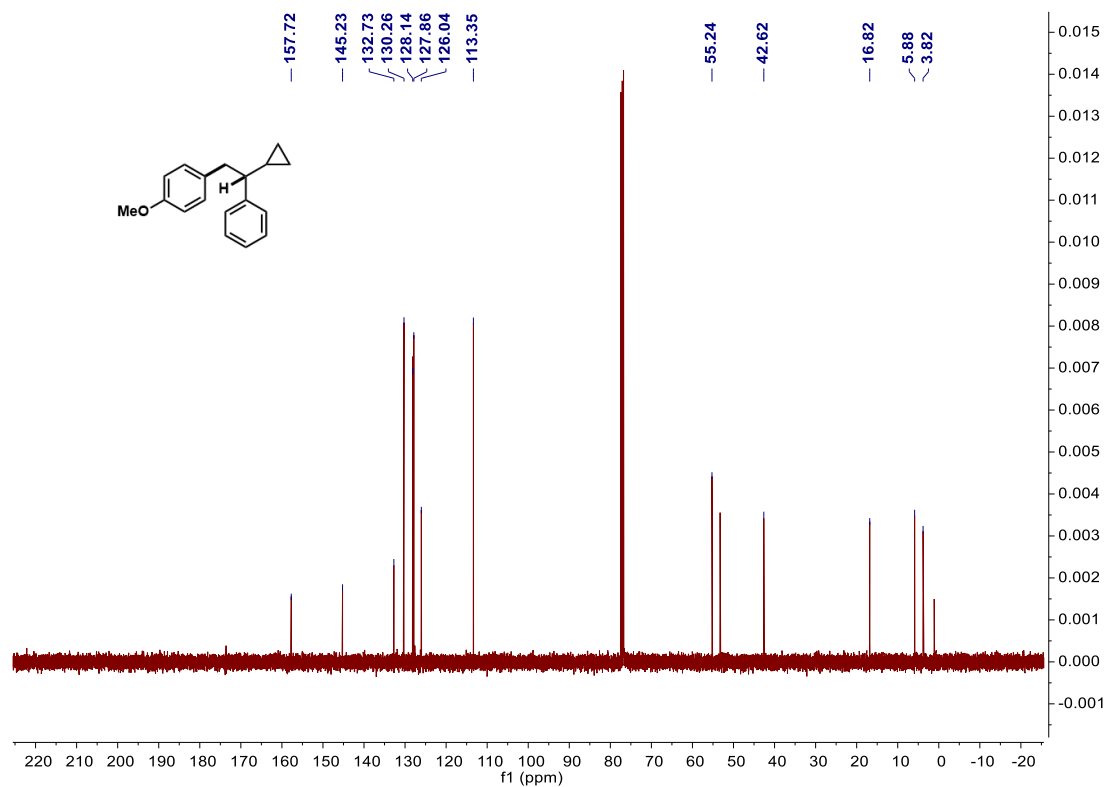


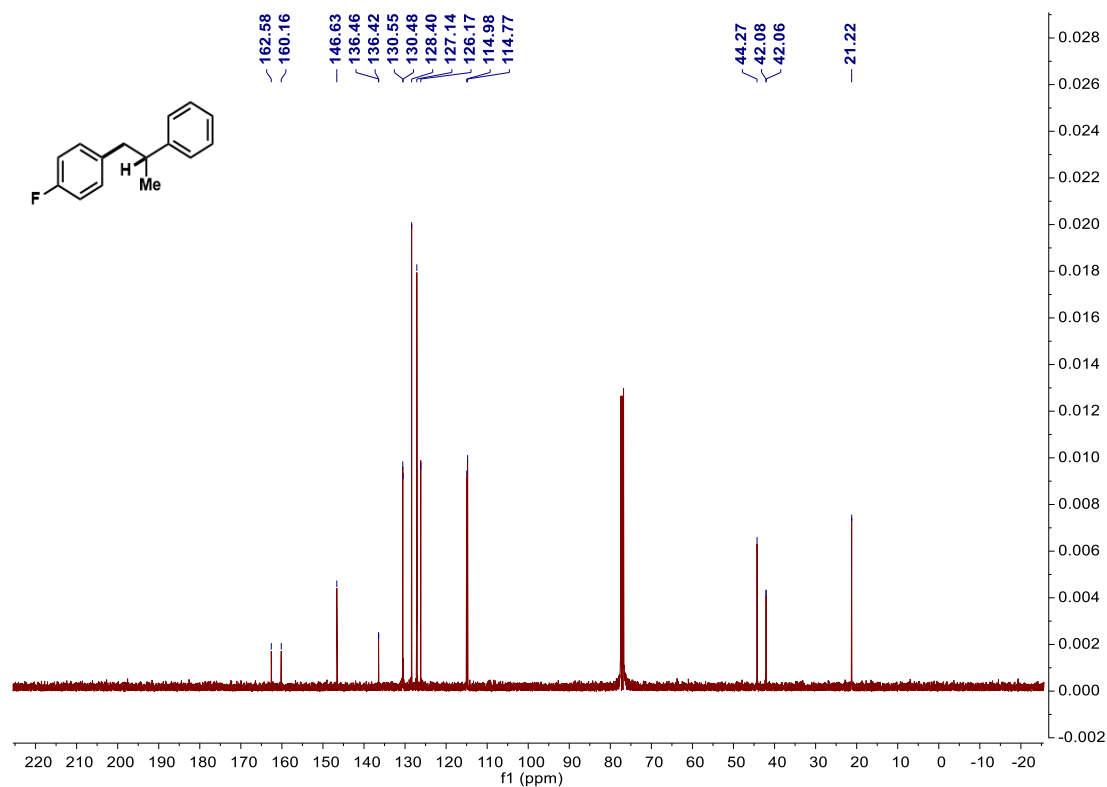
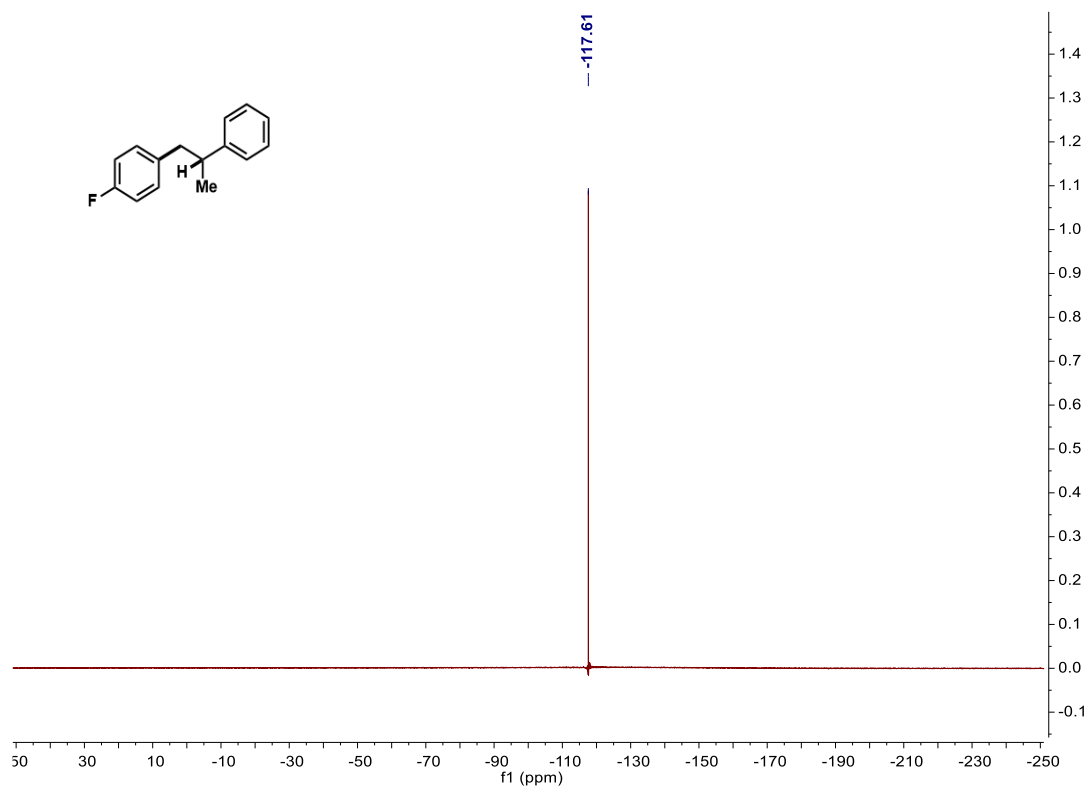




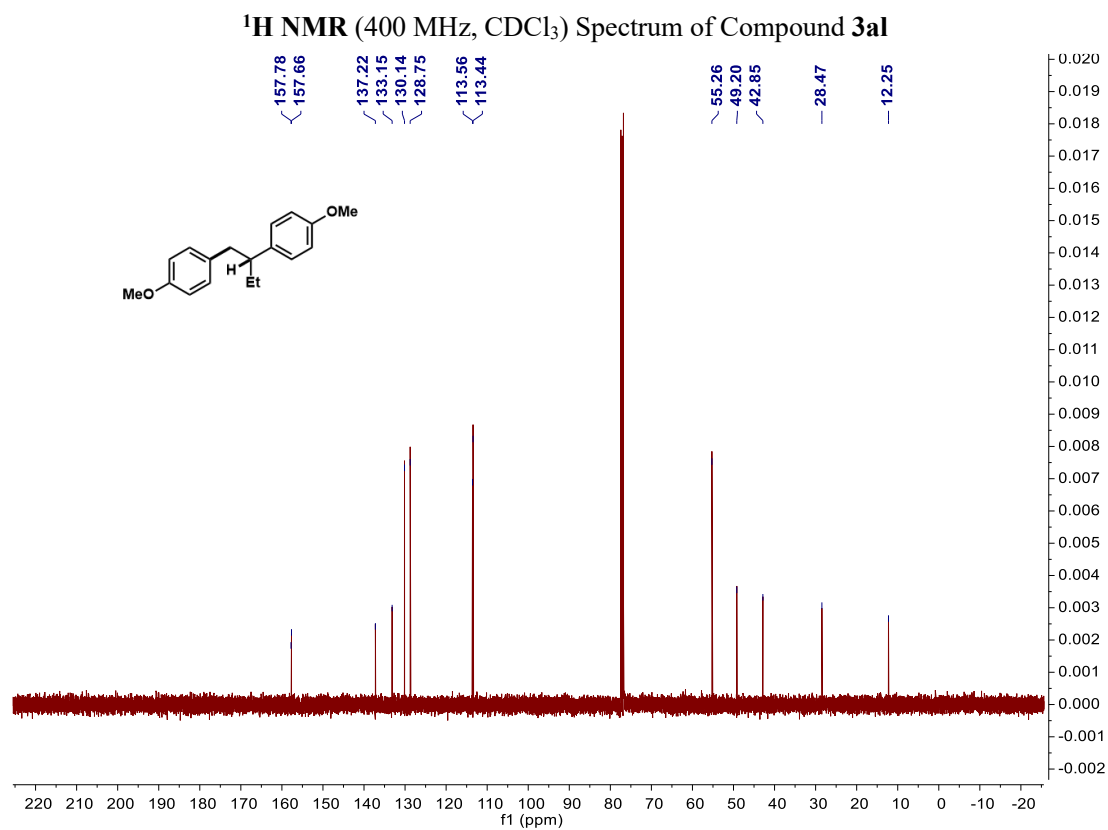
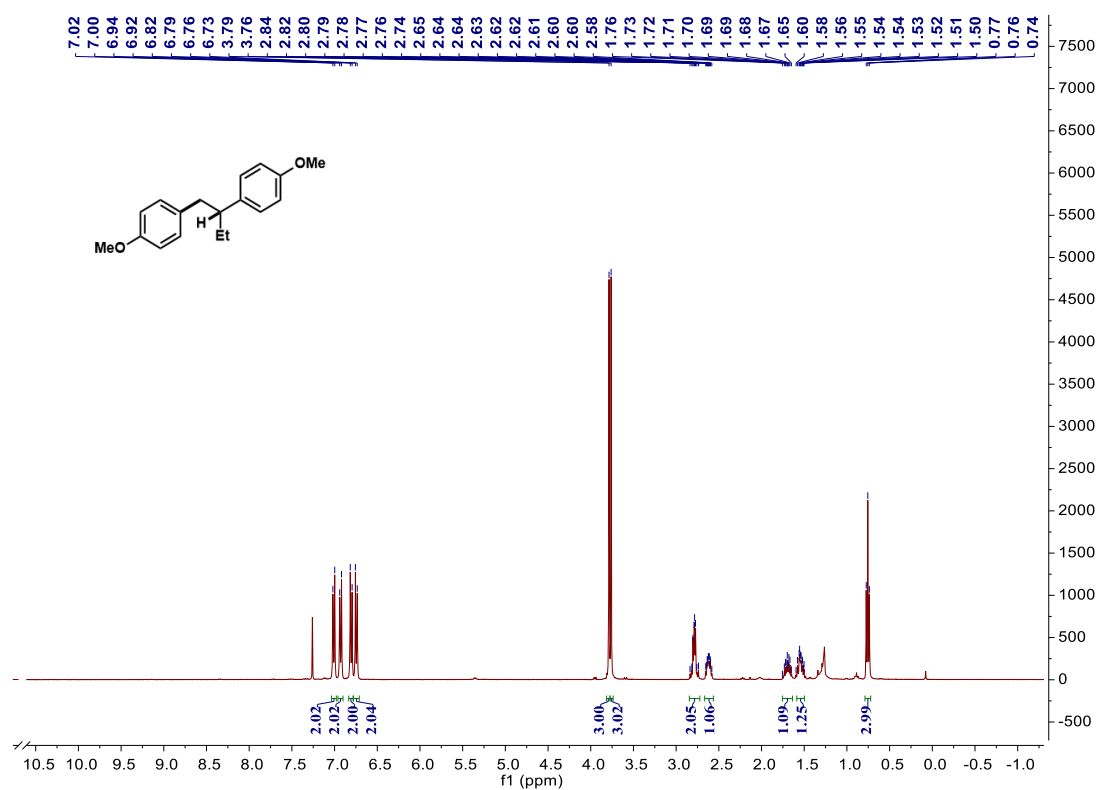


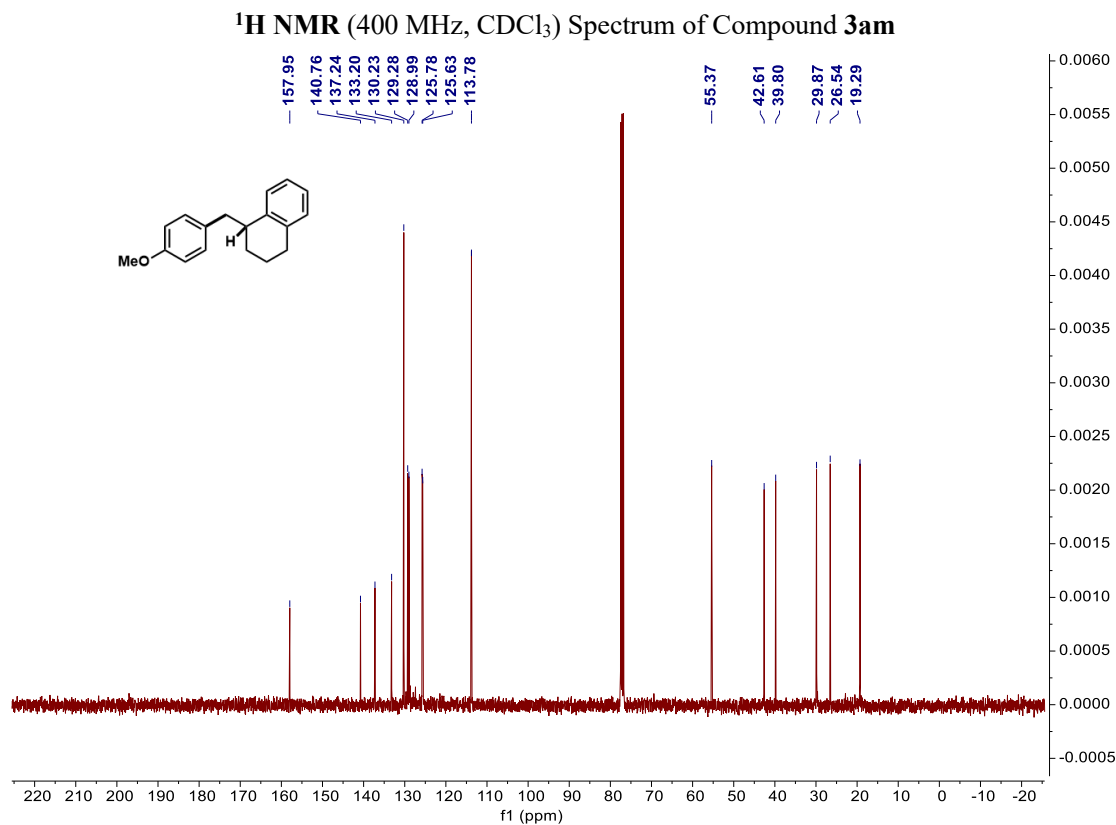
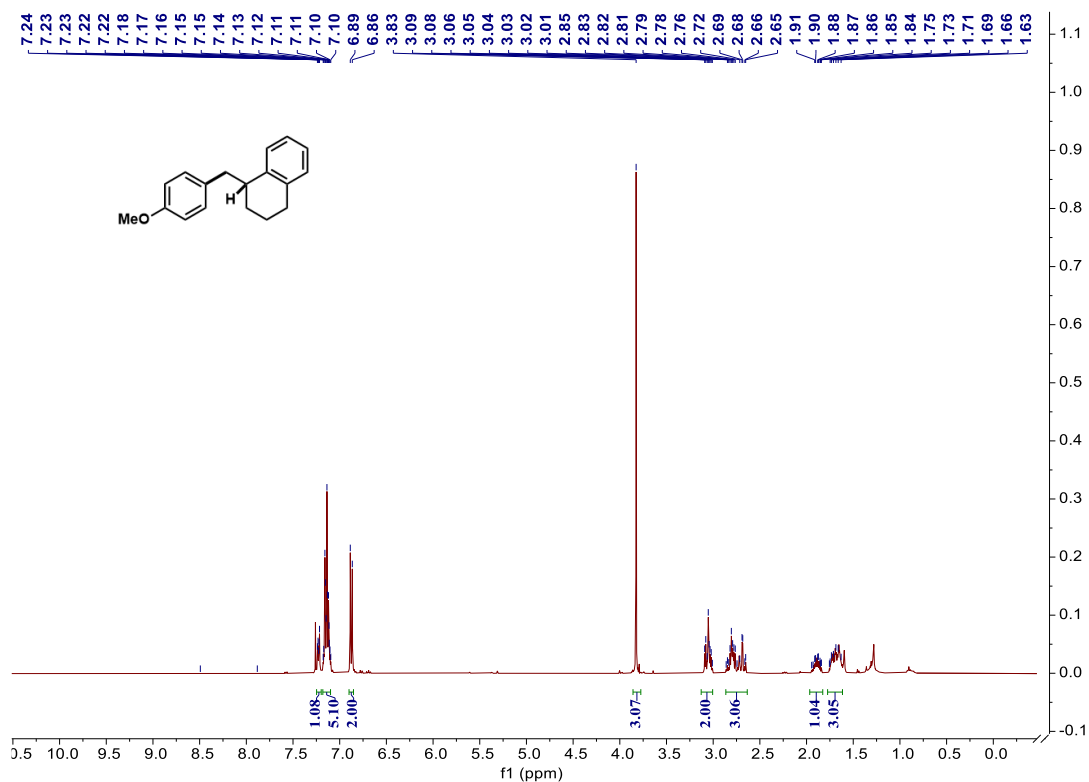


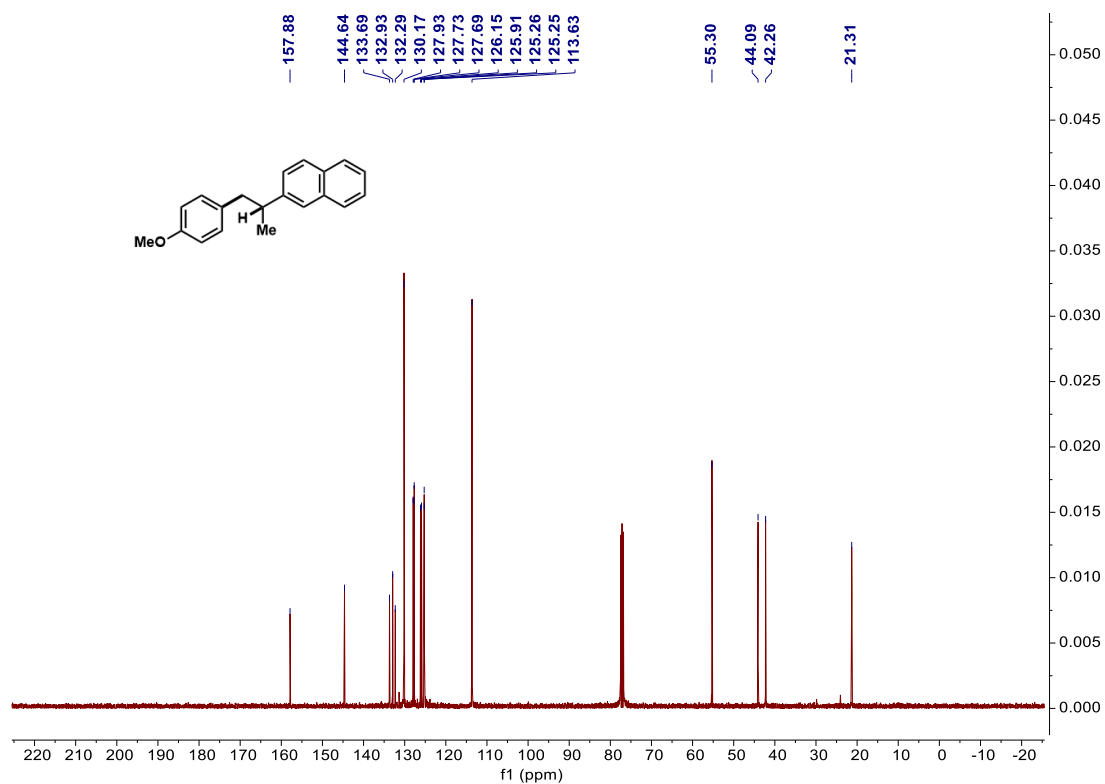
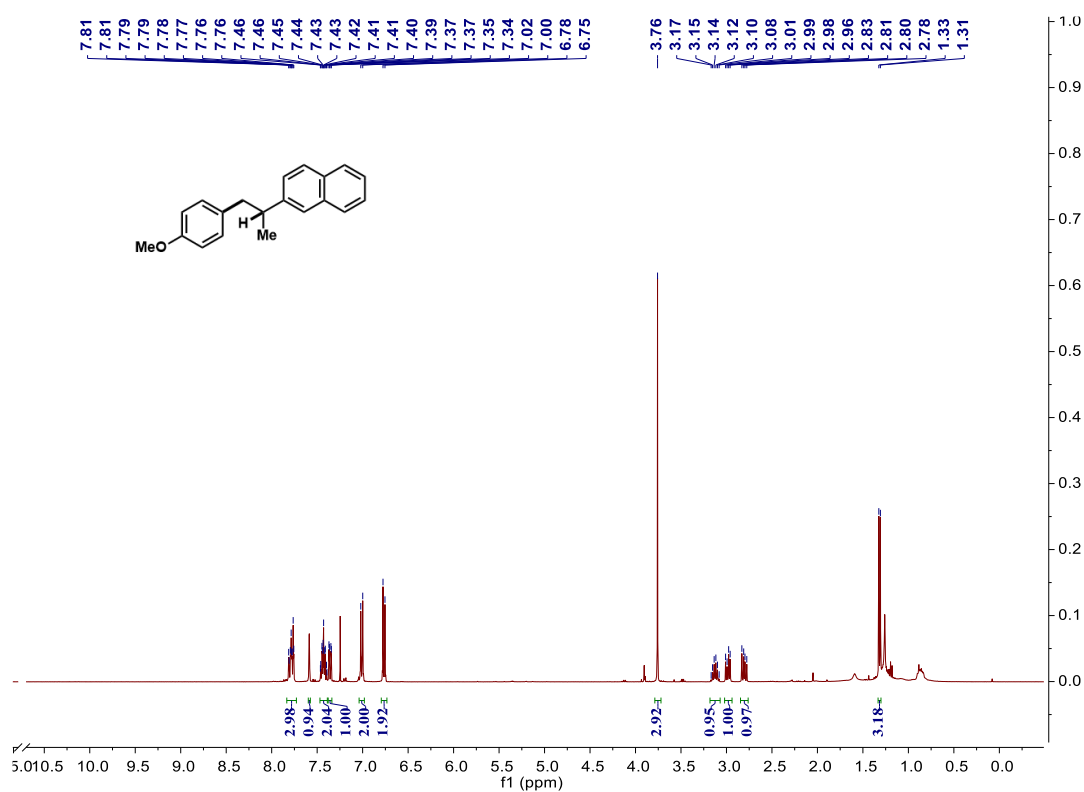


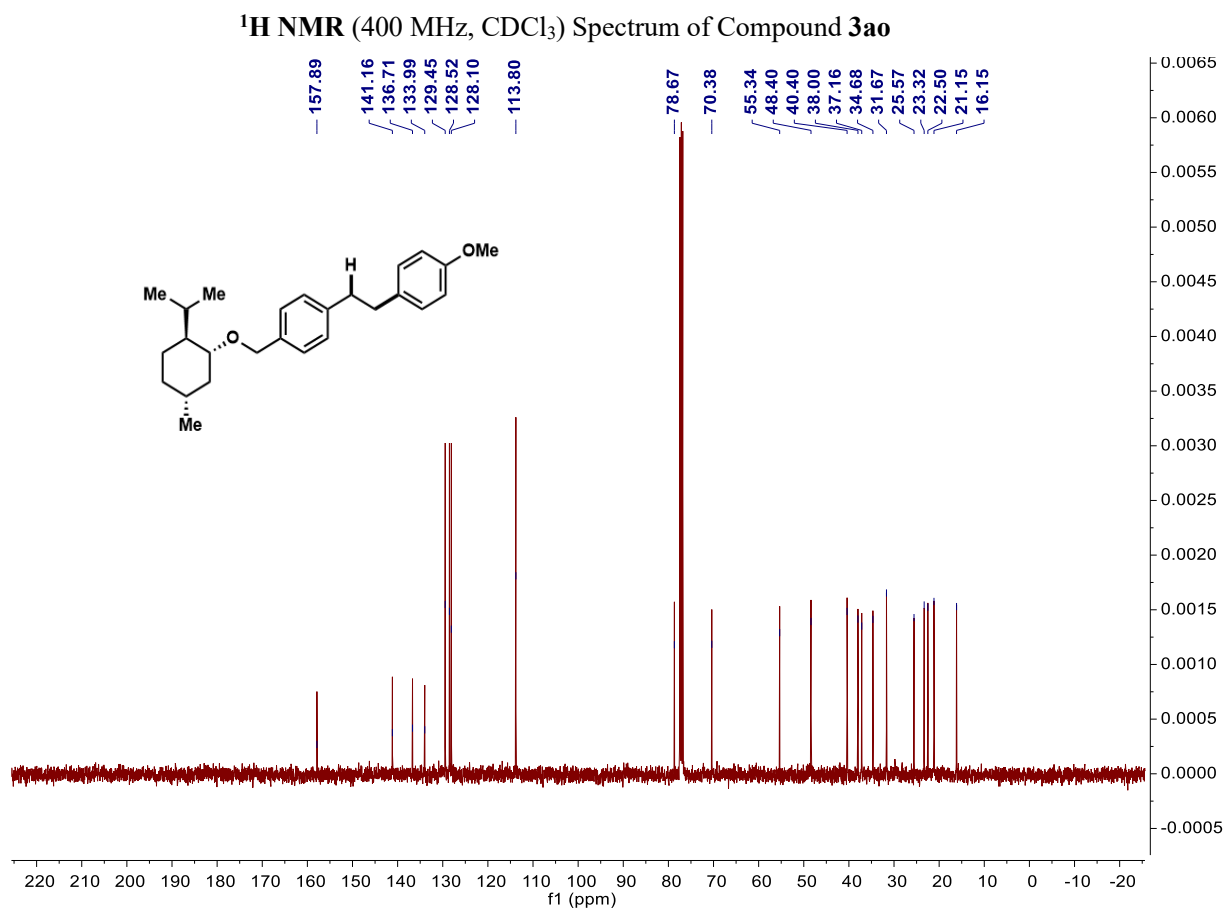
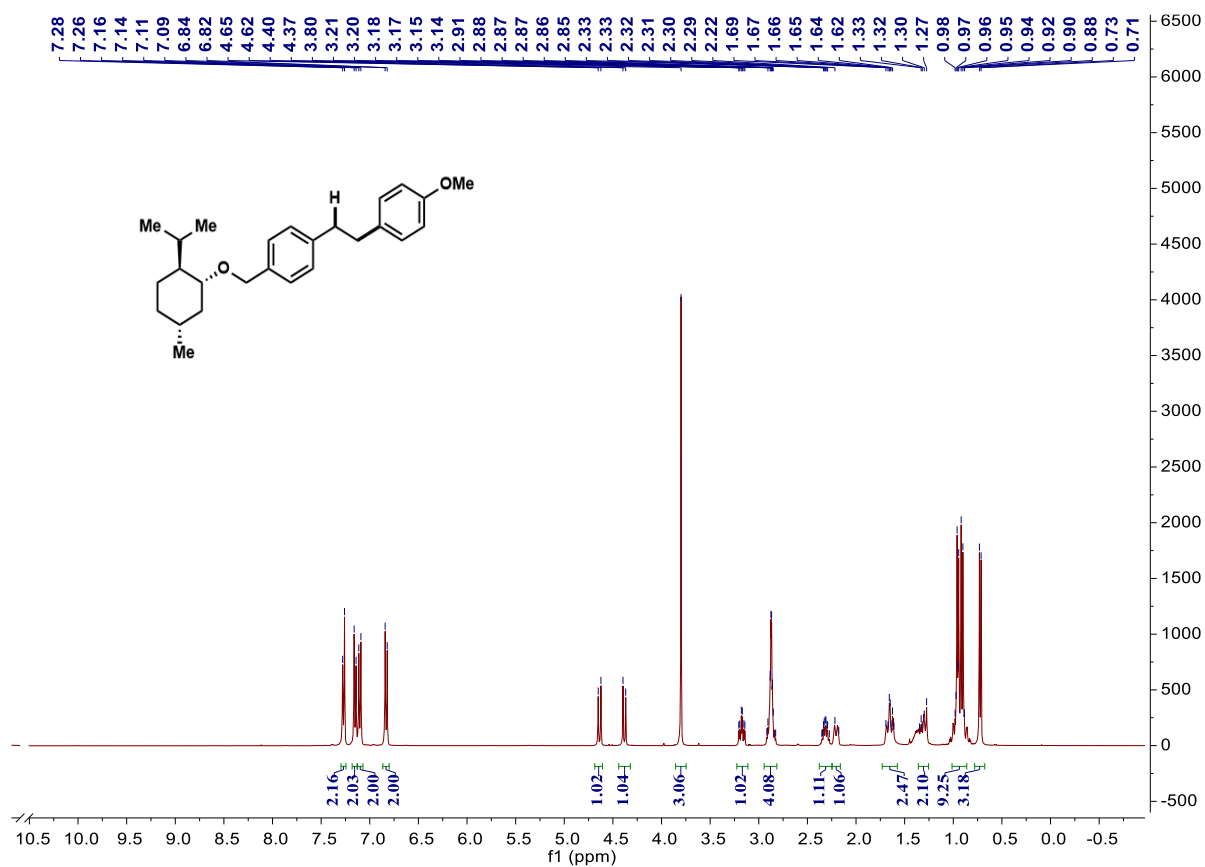


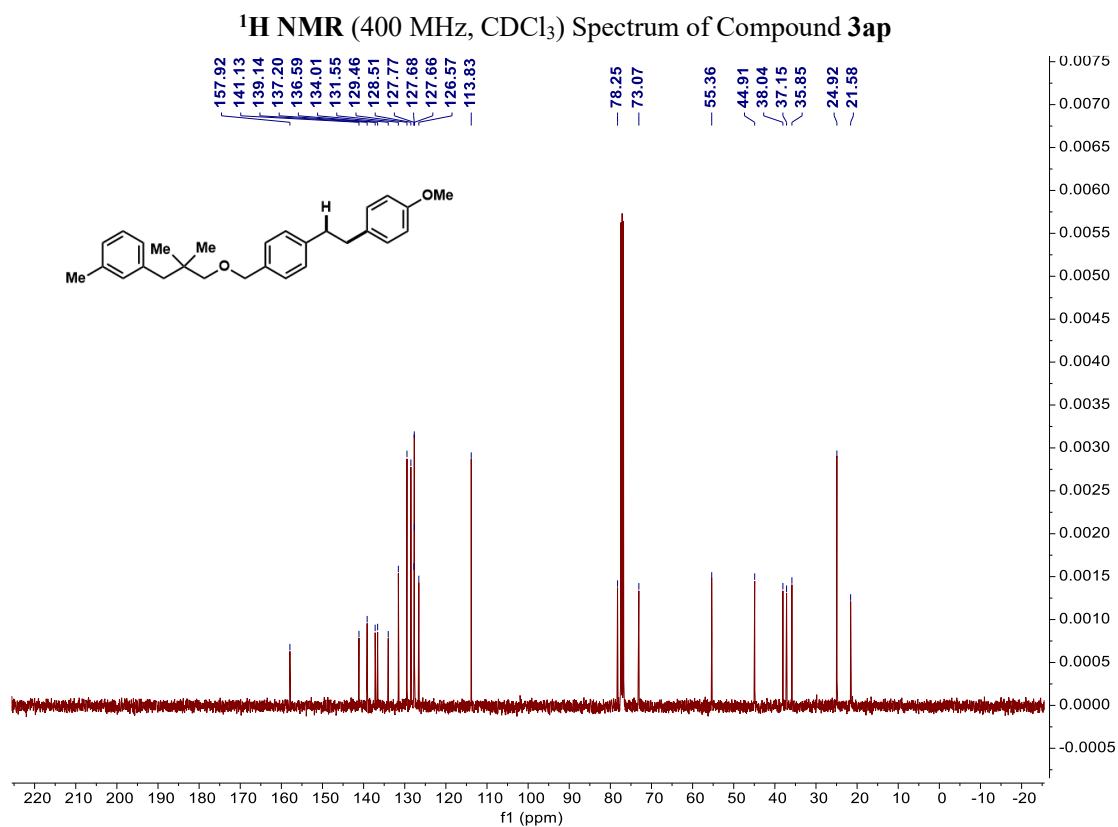
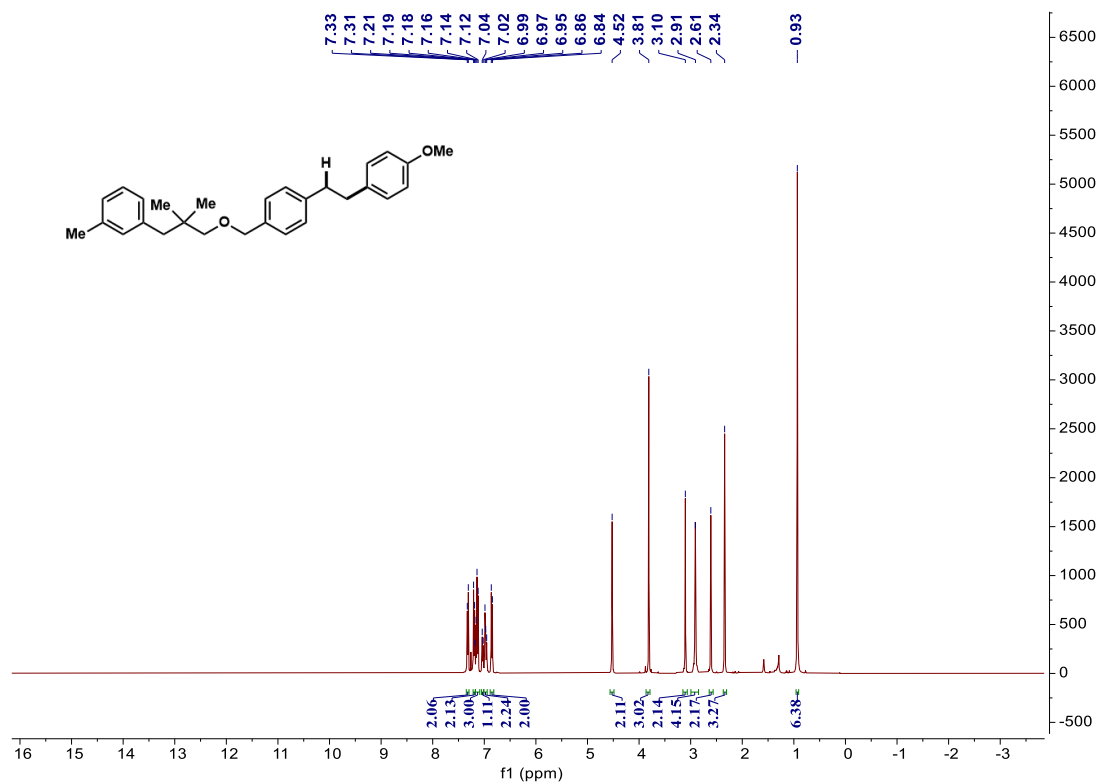
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) Spectrum of Compound 3ak



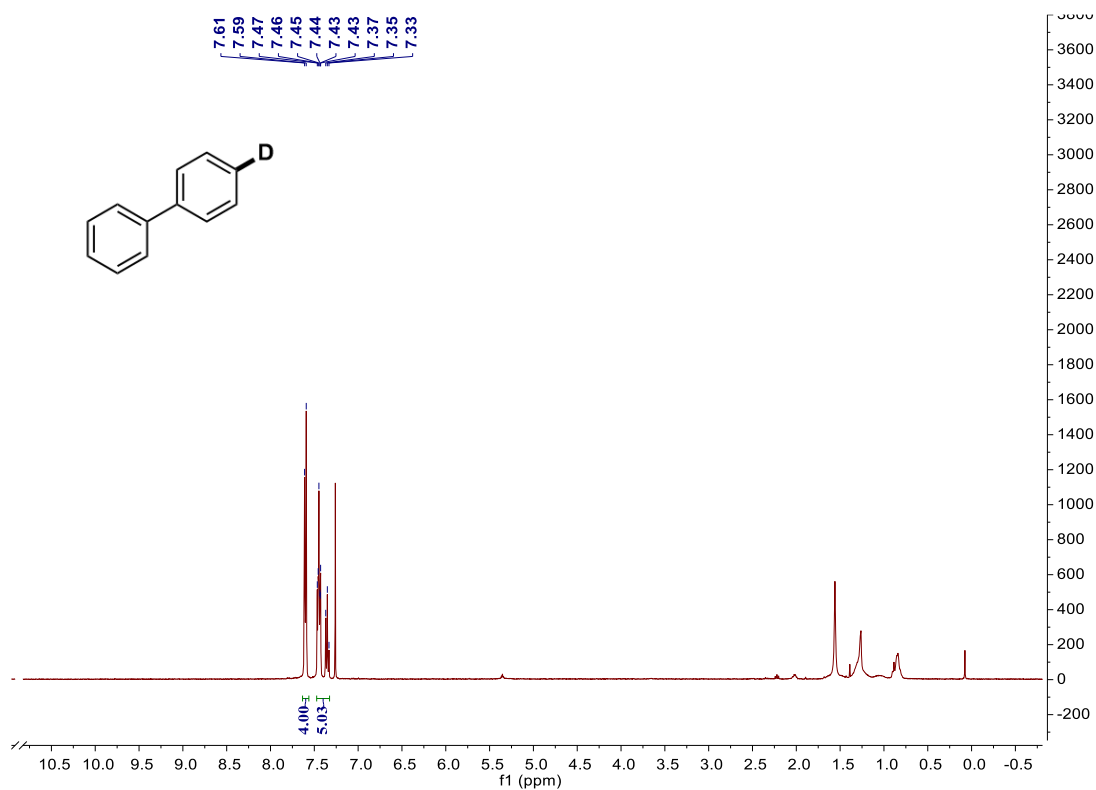




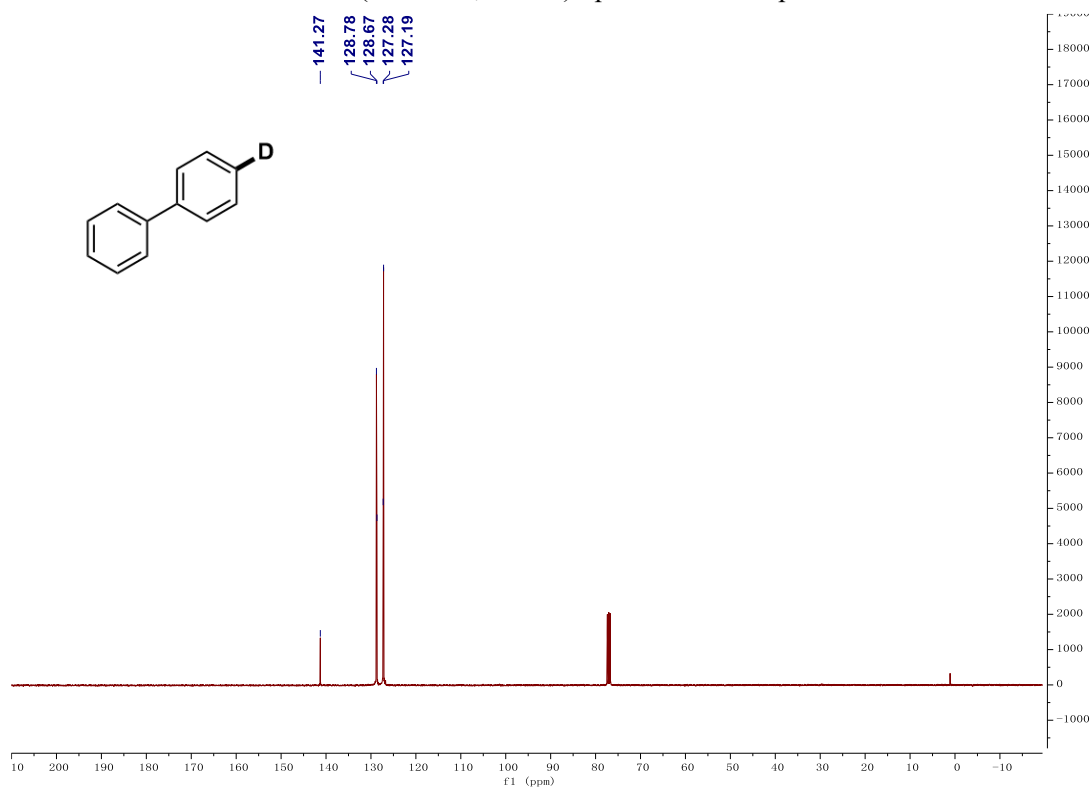




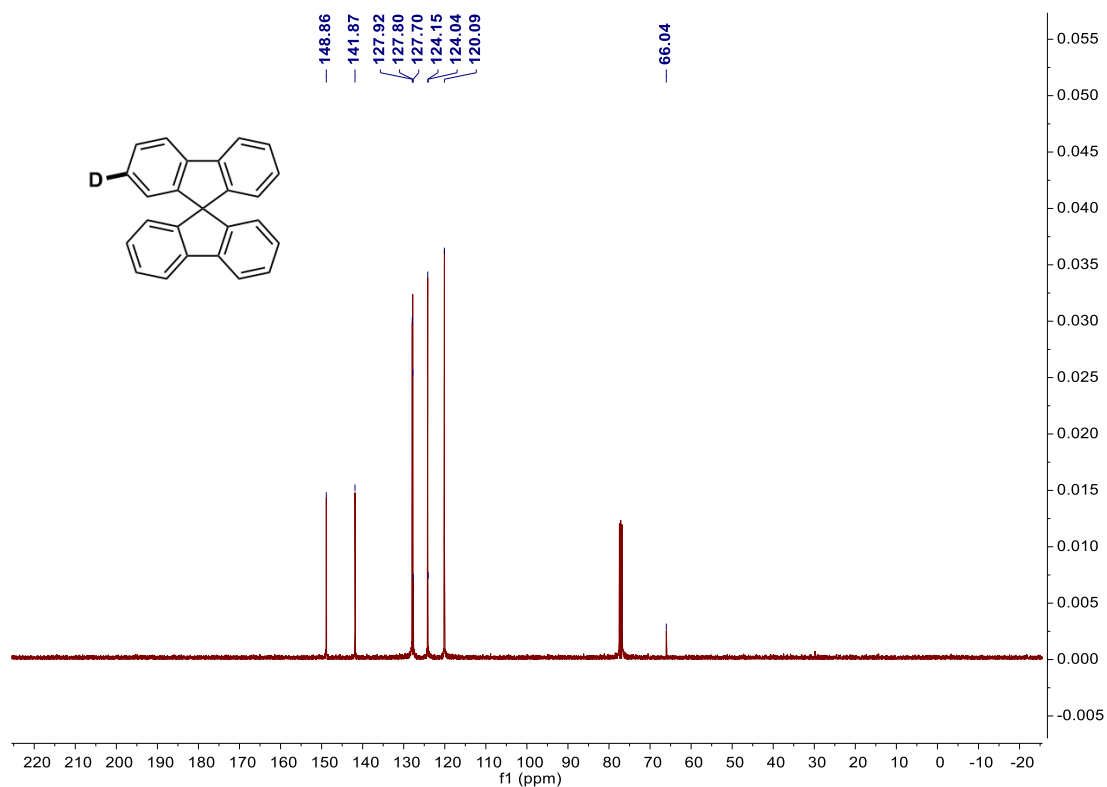
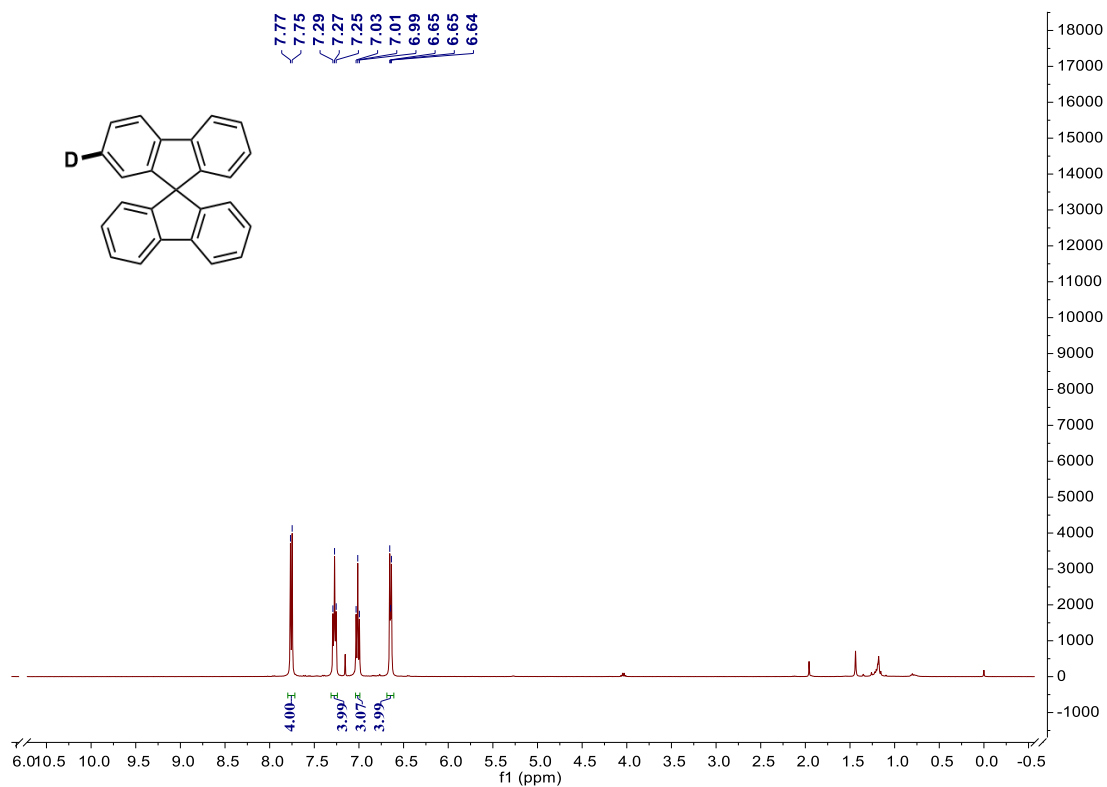


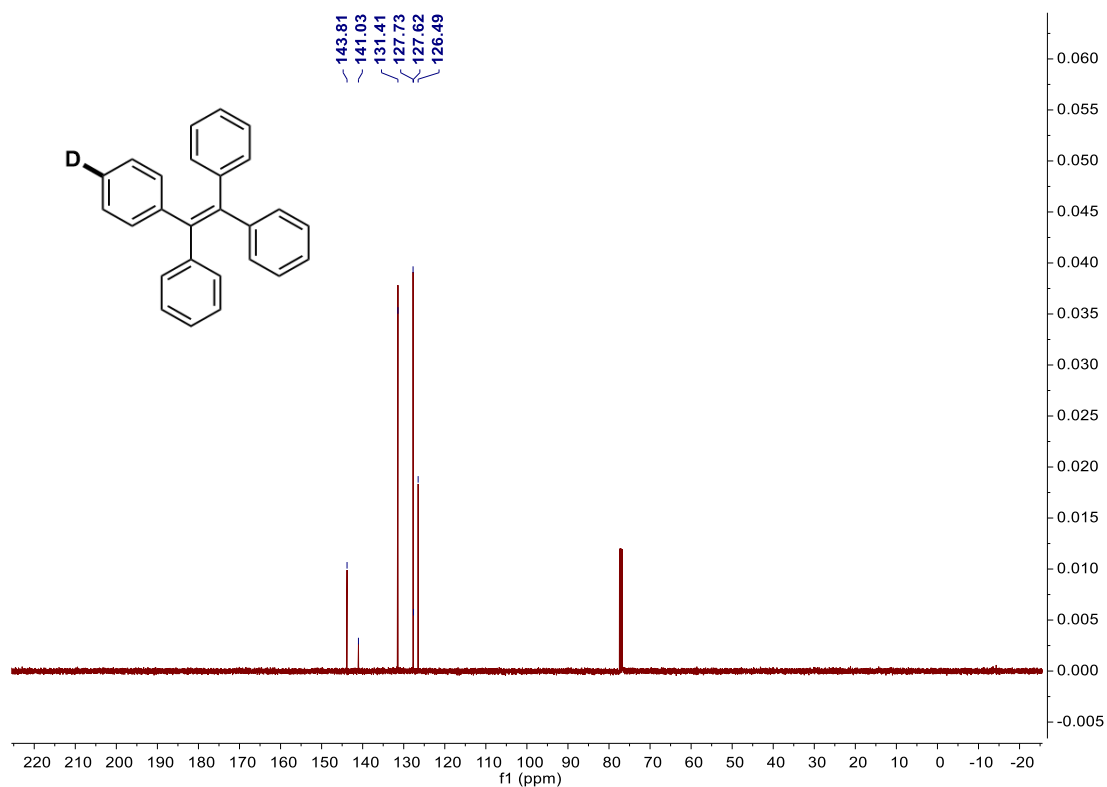
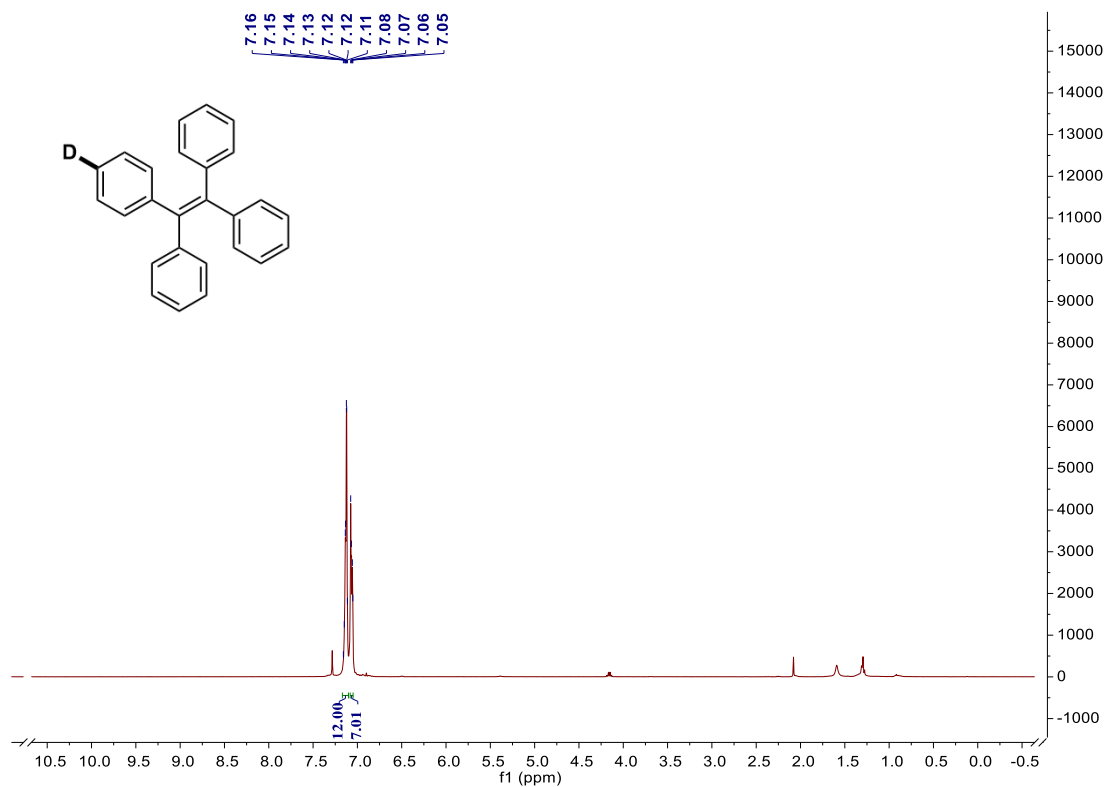


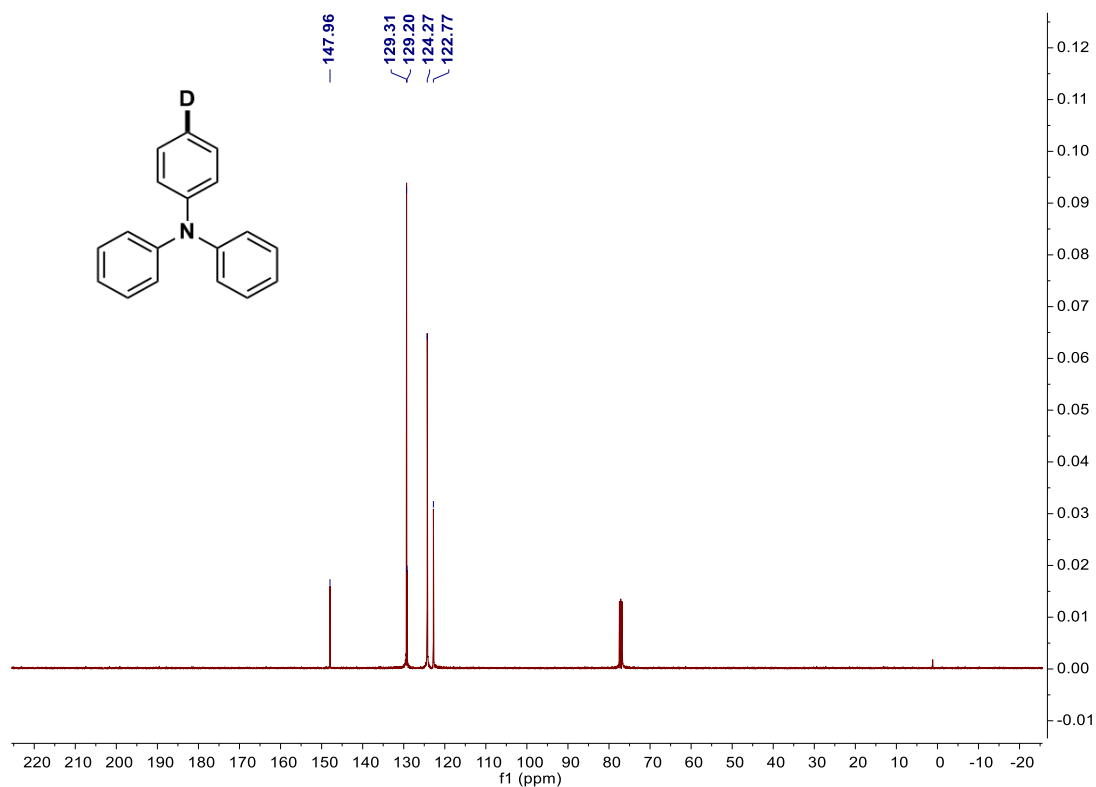
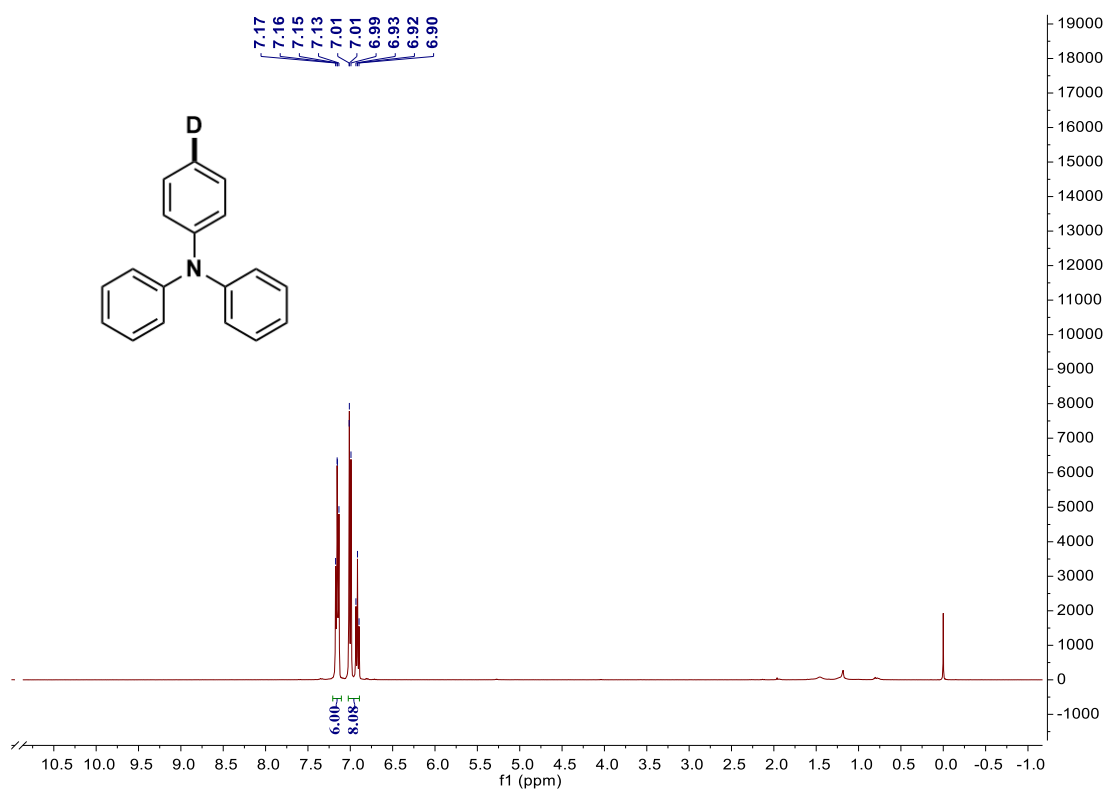
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) Spectrum of Compound 4a

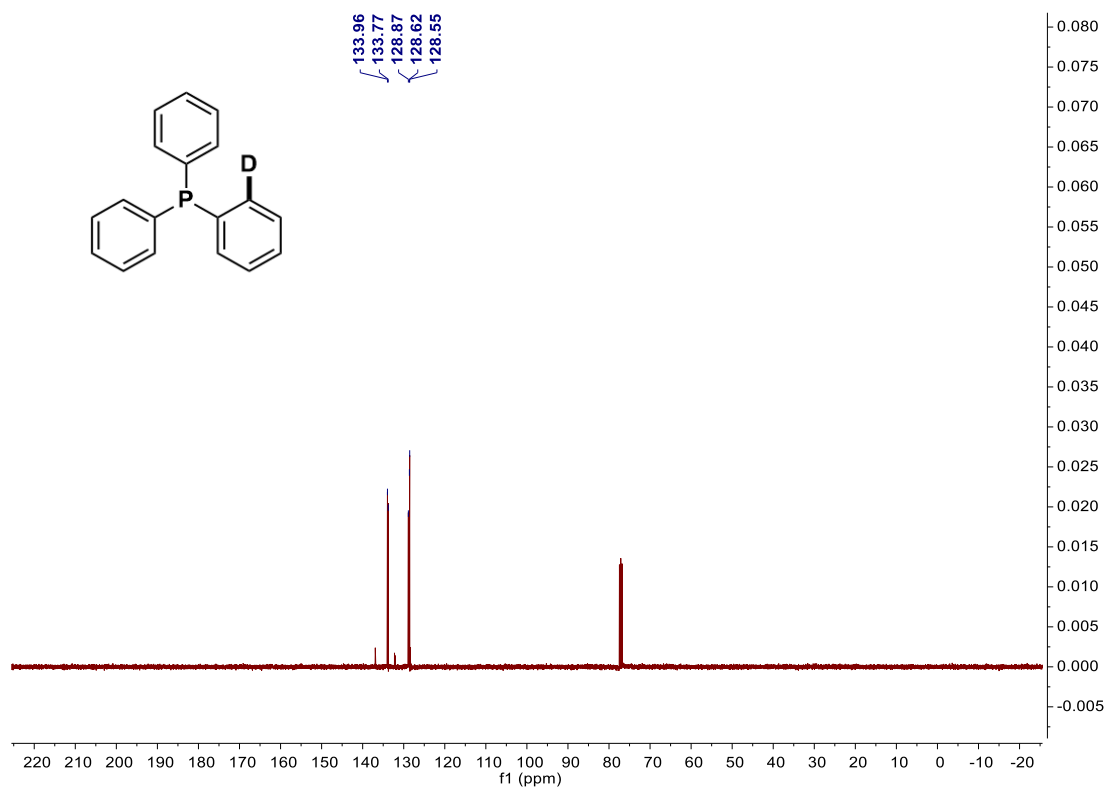
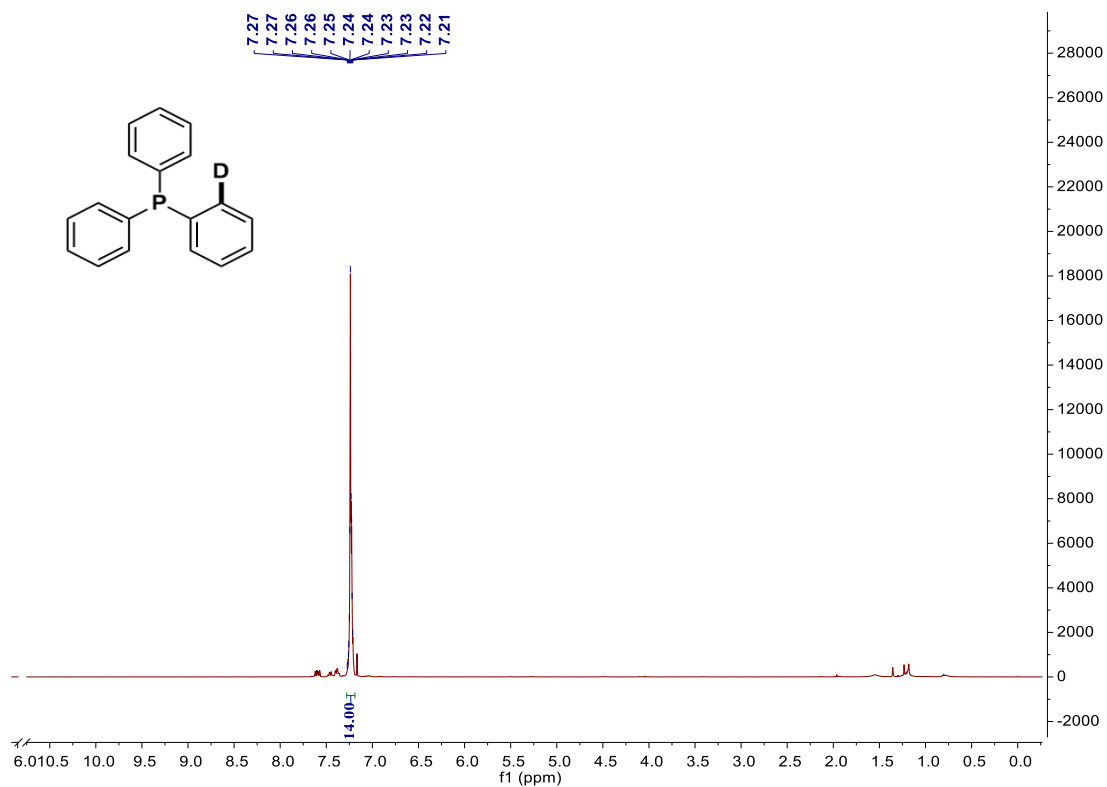


<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) Spectrum of Compound 4a

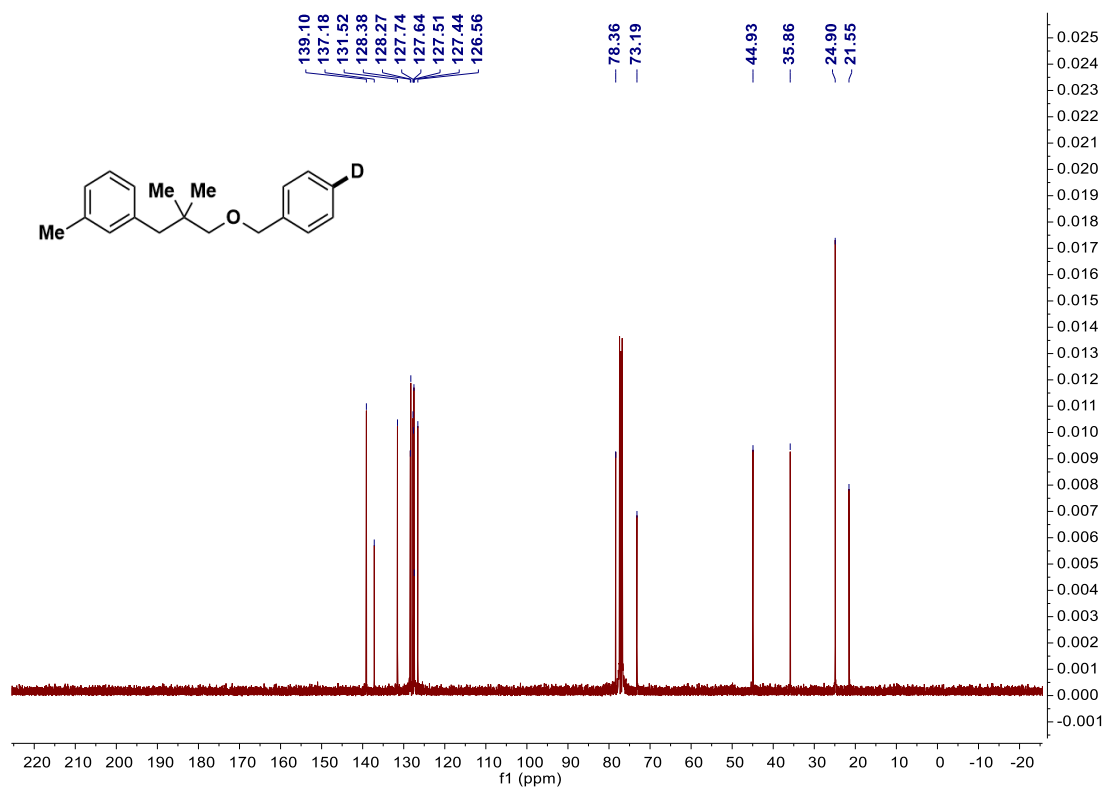
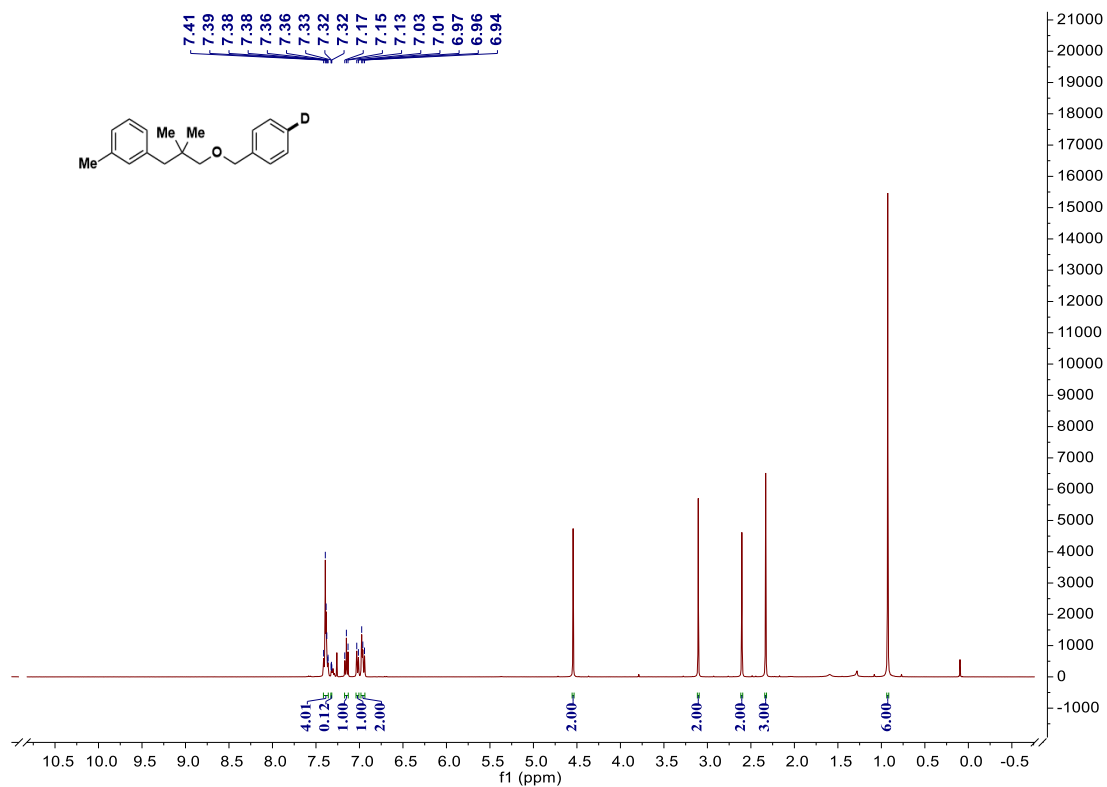


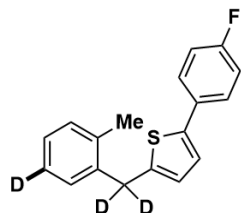
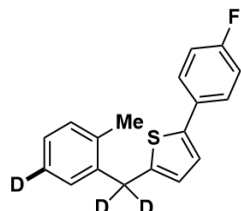










Cc1ccc(cc1C2(C)C(C)(C)C2Sc3ccc(cc3-c4ccc(F)cc4)C5=CC=CC=C5)C(F)(F)F

7



