Supporting Information

Boron carbonitride photocatalysts for direct decarboxylation: the construction of C(sp^3)-N or C(sp^3)-C(sp^2) bonds with visible light

Jiale Shi, Tao Yuan, Rong Wang, Meifang Zheng*, Xinchen Wang*

State Key Laboratory of Photocatalysis on Energy and Environment, College of Chemistry, Fuzhou University, Fuzhou, 350116. China

* E-mail: mfzheng@fzu.edu.cn; xcwang@fzu.edu.cn.

Table of Contents

Experimental procedures

General information

If no special indicated, other reagents and solvents were used as commercially available without further purification. Column chromatographic purification of products was accomplished using 200-300 mesh silica gel. NMR spectrum were measured on a Bruker Avance spectrometer in the solvents indicated; Coupling constants are reported in Hz with multiplicities denoted as s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). Gas chromatography mass spectra (GC-MS) were taken at Thermo Trace 1300 gas chromatograph mass spectrometer and a TR-5MS column (0.25 mm × 30 m, Film: 0.25 μm).

Synthesis of ceramic BCN

Ceramic BCN was synthesized according to Ref. [1] with slight modification. Typically, 0.5 g boric acid, 1.0 g urea and 5 g glucose were grinded fully in an agate mortar. Later, the mixed precursor was put into a horizontal tube furnace. A flow of ammonia (0.25 L min^{-1}) was pumped into the tube for about 10 min to expel air before heating up. Then the mixture was first heated to 373K for 30min and went on heating to 1523 K for 5 h at a heating rate of 5 K min^{-1}. Next, the mixture was cooled to 773 K for 100 min at a cooling rate of 5 K min^{-1}. Finally, the mixture is naturally cooled to room temperature. The obtained sample was wash with water and EtOH three times and dried, denoted as BCN.

Optical and structure characterization of ceramic BCN

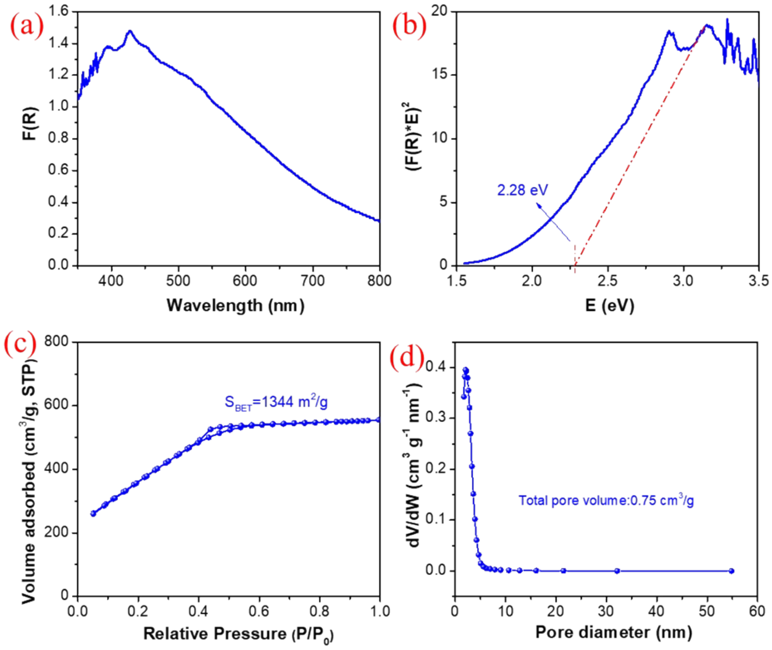


Figure S1. (a) UV-vis DRS of BCN; (b) The $(F(R)*E)^2$ versus E plot of BCN; (c) N_2 adsorption and desorption isotherms of BCN; (d) BJH pore size distribution curves of BCN.

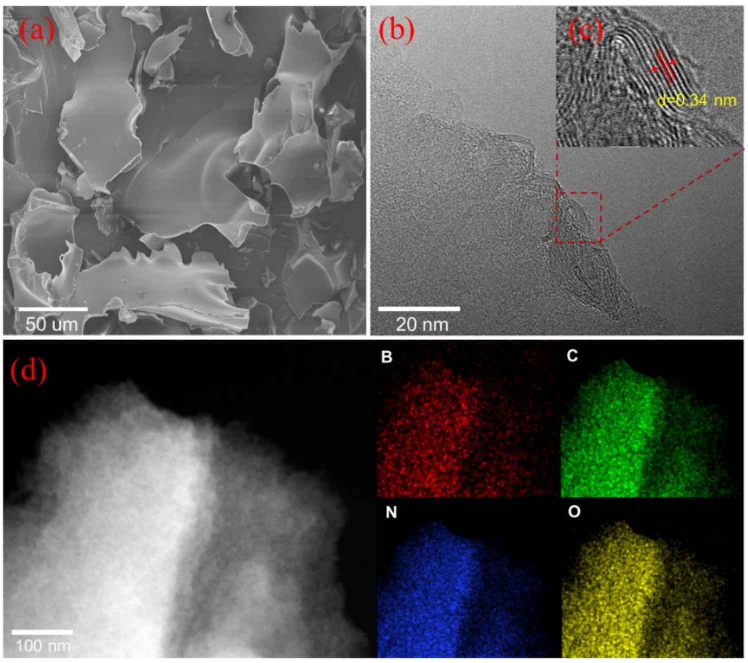


Figure S2. (a) SEM image of BCN; (b) TEM image of BCN; (c) HR-TEM image highlighted by the red dashed box in (b); (d) High-Angle Annular Dark Field (HAADF) image of BCN and elemental mapping images of B, C, N, O.

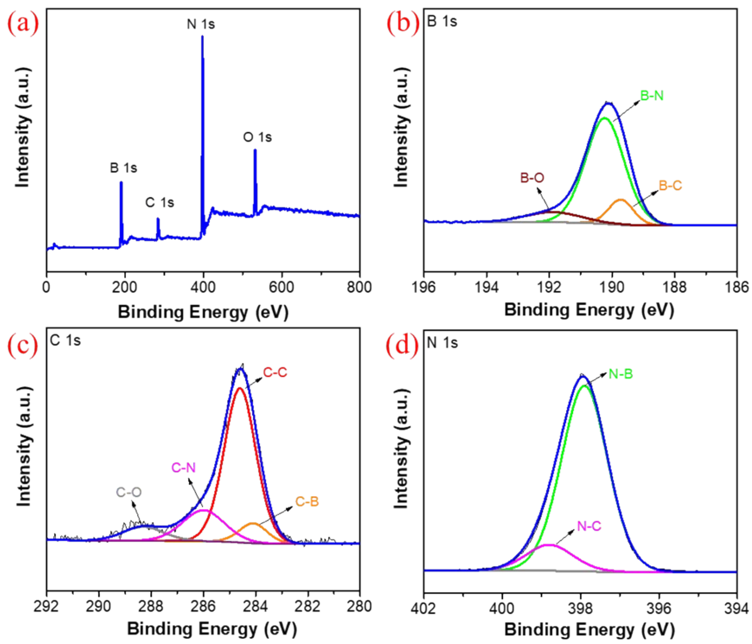


Figure S3. XPS spectra of BCN: (a) survey spectrum and the high resolution spectrum of (b) B 1s, (c) C 1s, (d) N 1s.

Photoreactor configuration

Reactions were irradiated using a simple photoreactor consisting of Eaglerise ELP8X3LS 3W blue LEDs (λ = 420 nm), which was connected to HAAKE-FK cyclic water cooling system at 25 ^{o}C.

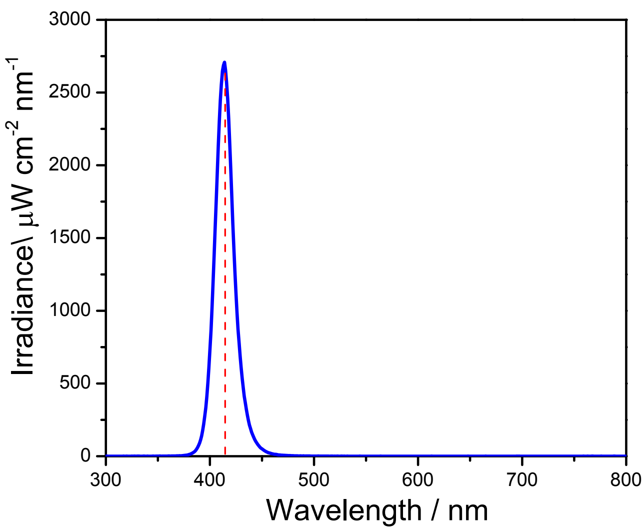
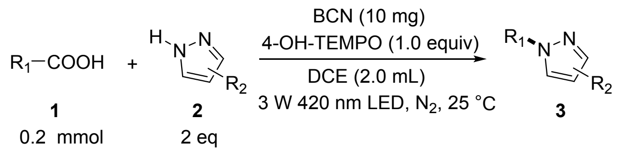


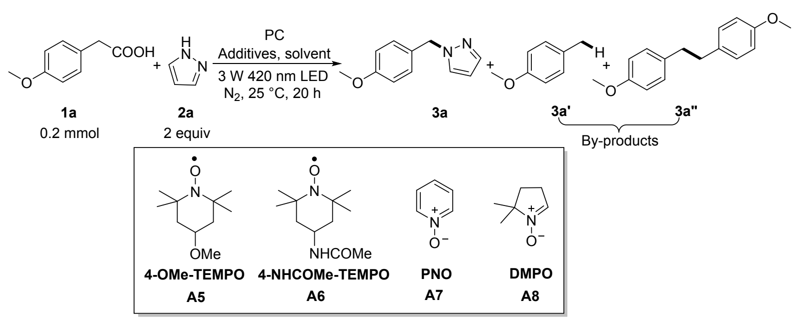
Figure S4. The optical spectrum of a 420 nm LED.

General procedure A for direct decarboxylative N-H functionalization



A solution of aryl acetic acids **1** (0.2 mmol, 1 equiv), **2** (0.4 mmol, 2 equiv), BCN (10 mg) and 4-OH-TEMPO (0.2 mmol, 1 equiv) in DCE (2 mL) were added into a Schlenk tube equipped with a stirring bar. The Schlenk tube was purged with nitrogen for three times. After degassing by freeze-pump-thaw process for three cycles, the reaction mixture was irradiated with a 3 W 420 nm LED at 25 ºC for 20-40 hours, at which time the mixture was transferred into a centrifuge to separate the heterogeneous catalyst and solution. Then the solution was washed with brine and extracted with acetyl acetate three times. The combined organic extracts were dried over Na_2SO_4, and then concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using light petroleum ether/ethyl acetate as eluent to afford the final compounds **3**. The product was analyzed by GC-MS, ^{1}H NMR, and ^{13}C NMR.

Table S1. Screening of optimal reaction conditions.[a]

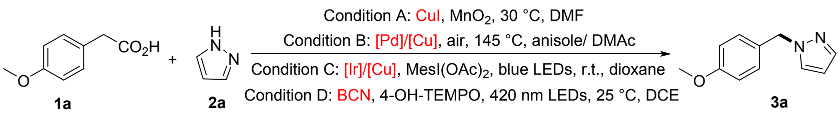


Entry	PC	Solvent	Additives	Conv. **1a** (%)	Yield. **3a/3a'/3a''** (%)
1	BCN	DCE	**A5**	91	59/8/12
2	BCN	DCE	**A6**	80	56/14/5
3	BCN	DCE	**A7**	38	8/4/13
4	BCN	DCE	**A8**	24	0/15/9
5[b]	BCN	DCE	**A4**	80	46/8/13
6[c]	BCN	DCE	**A4**	43	15/20/4
7[d]	BCN	DCE	**A4**	72	32/18/11
8	[Ir]	DCE	**A4**	14	10/2/1

9	[Ru]	DCE	**A4**	-	-
10[e]	BCN	DCE	-	trace	-
11[e]	BCN	DCE	**A4**	50	19/8/2

[a] Reactions conditions: 0.2 mmol of **1a**, 2 equiv of **2a**, 1.0 equiv of additive and 10 mg of photocatalysts in the 2 mL of solvents for 20 h at 25 °C under a 3 W 420 nm LED illumination. Yield was determined by gas chromatography. PNO is short for 2-picoline-*N*-oxide. DMPO is short for 5,5-dimethyl-1-pyrroline-*N*-oxide. [b] 2 equiv of trifluoroacetic acid (TFA) was added. [c] 1 equiv of Et_3N was added. [d] 1 equiv of K_2CO_3 was added. [e] The reaction is operated in air instead of N_2. Benzaldehyde and benzoic acid are detected in the air.

Table S2. Efficiency of various transition metal catalytic systems for decarboxylative C-N coupling reaction.



Entry	Condition	The amount of **1a**/mmol	Reaction time/h	Yield of **3a**/%	TON	Refs.
1	A	0.2	20	-	-	[4a]
2	B	0.2	16	-	-	[4b]
3	C	0.2	20	-	-	[6c]
4	D	0.2	20	60	-	This work

Low reactivity & unsuccessful substrates for direct decarboxylative N-H functionalization

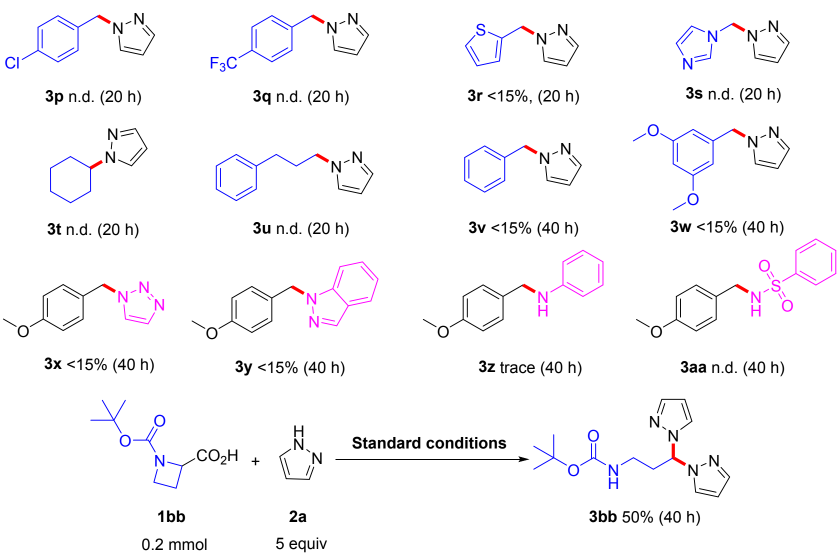
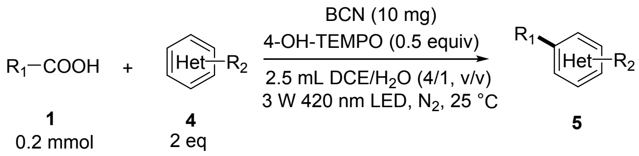


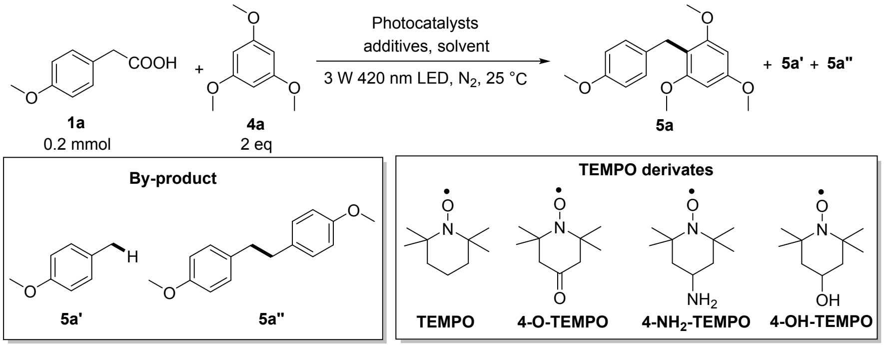
Figure S5. Low reactivity & unsuccessful substrates run under the standard conditions described in general procedure A.

General procedure B for direct decarboxylative C(sp^2)-H functionalization



A solution of aryl acetic acids **1** (0.2 mmol, 1 equiv), **4** (0.4 mmol, 2 equiv), BCN (10 mg) and 4-OH-TEMPO (0.1 mmol, 0.5 equiv) in 2.5 mL DCE/H_2O (4/1, v/v) were added into a Schlenk tube equipped with a stirring bar. The Schlenk tube was purged with nitrogen for three times. After degassing by freeze-pump-thaw process for three cycles, the reaction mixture was irradiated with a 3 W 420 nm LED at 25 ºC for 20-40 hours, at which time the mixture was transferred into a centrifuge to separate the heterogeneous catalyst and solution. Then the solution was washed with brine and extracted with acetyl acetate three times. The combined organic extracts were dried over Na_2SO_4, and then concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using light petroleum ether/ethyl acetate as eluent to afford the final compounds **5**. The product was analyzed by GC-MS, ^{1}H NMR, and ^{13}C NMR.

Table S3. Screening for optimal reaction conditions. [a]

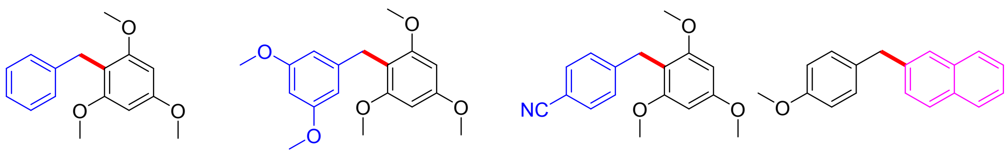


Entry	Photocalysts	Solvent	Additives	Conv. **1a** (%)	Yield. **5a/5a'/5a''** (%)
1	BCN	DCE	TEMPO	30	27/1/1
2	BCN	H_2O	TEMPO	42	36/2/2
3	BCN	DMSO	TEMPO	0	-
4	BCN	MeCN	TEMPO	trace	trace
5	BCN	DMF	TEMPO	trace	trace

6	BCN	DCE/H_2O	TEMPO	82	52/6/12
7	CdS	DCE/H_2O	TEMPO	81	26/9/23
8	TiO_2	DCE/H_2O	TEMPO	0	-
9	BCN	DCE/H_2O	4-NH_2-TEMPO	82	54/8/10
10	BCN	DCE/H_2O	4-O-TEMPO	89	45/2/20
11	BCN	DCE/H_2O	4-OH-TEMPO	89	62/13/7
12	BCN	DCE/H_2O	DDQ	5	5/0/0
13	BCN	DCE/H_2O	$Na_2S_2O_8$	8	8/0/0
14	-	DCE/H_2O	4-OH-TEMPO	0	-
15	BCN	DCE/H_2O	-	21	15/2/2
16[b]	BCN	DCE/H_2O	4-OH-TEMPO	0	-

[a] Unless otherwise noted, the reactions were conducted with 0.2 mmol of **1a**, 2 equiv of **2a**, 0.5 equiv of additives and 10 mg of photocatalysts in the 2.5 mL of solvents for 20 h at 25 °C under 3 W 420 nm LED illumination. Yield was determined by gas chromatography. [b] No light.

Low reactivity & unsuccessful substrates for direct decarboxylative C-H functionalization

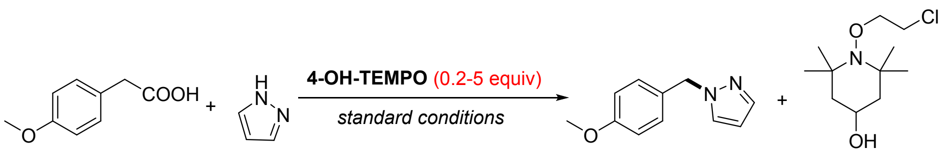


5p <15% (40 h) **5q** <15% (40 h) **5r** n.d. (20 h) **5s** n.d. (20 h)

Figure S6. Low reactivity & unsuccessful substrates run under the standard conditions described in general procedure B.

Mechanistic studies

a) Effect of different equivalents of 4-OH-TEMPO in the decarboxylative C(sp^3)-N coupling



1a **2a** **3a** **10**

A solution of compound **1a** (0.2 mmol), **2a** (0.4 mmol, 2 equiv), 4-OH-TEMPO (0.2- 5 equiv) and BCN (10 mg) in DCE (2 mL) were added into a Schlenk tube equipped with a stirring bar. The Schlenk tube was purged with nitrogen for three times. After degassing by freeze-pump-thaw process for three cycles, the reaction mixture was irradiated with a 3 W 420 nm LED at 25 °C for 20 hours. After completion of the reaction, GC-MS analysis showed that compound **3a** and **10** were formed.

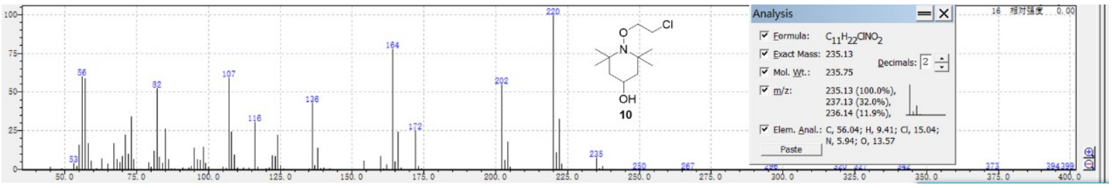
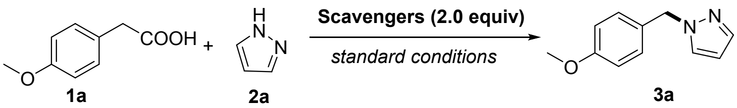


Figure S7. GC-MS spectrum of compound **10**.

b) Effect of different scavengers in the decarboxylative C(sp^3)-N coupling



A solution of compound **1a** (0.2 mmol), **2a** (0.4 mmol, 2 equiv), 4-OH-TEMPO (0.2 mmol, 1 equiv), BCN (10 mg) and scavengers (0.4 mmol, 2 equiv) in DCE (2 mL) were added into a Schlenk tube equipped with a stirring bar. The Schlenk tube was purged with nitrogen for three times. After degassing by freeze-pump-thaw process for three cycles, the reaction mixture was irradiated with a 3 W 420 nm LED at 25 °C for 20 hours. After completion of the reaction, analysis by GC-MS.

When the model reaction was treated with widely used radical scavenger, 1,1-diphenylethene (DPE), under standard conditions, the reaction was suppressed. The radical adducts **13** was detected by GC-MS, indicating the formation of benzyl radical in this process.

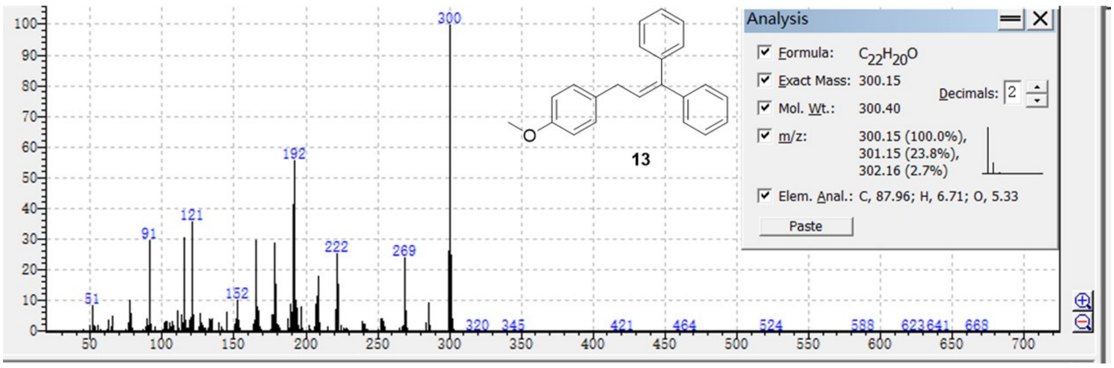
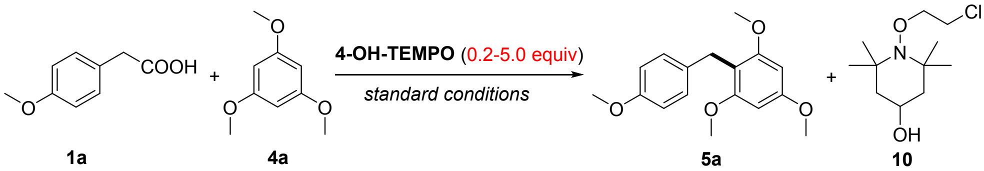


Figure S8. GC-MS spectrum of compound **13**.

c) Effect of different equivalents of 4-OH-TEMPO in the decarboxylative C(sp^3)-C(sp^2) coupling



A solution of compound **1a** (0.2 mmol), **4a** (0.4 mmol, 2 equiv), 4-OH-TEMPO (0.2-5 equiv) and BCN (10 mg) in 2.5mL of DCE/H_2O (4/1, v/v) were added into a Schlenk tube equipped with a stirring bar. The Schlenk tube was purged with nitrogen for three times. After degassing by freeze-pump-thaw process for three cycles, the reaction mixture was irradiated with a 3 W 420 nm LED at 25 °C for 20 hours. After completion of the reaction, GC-MS analysis showed that compound **5a** and **10** were formed.

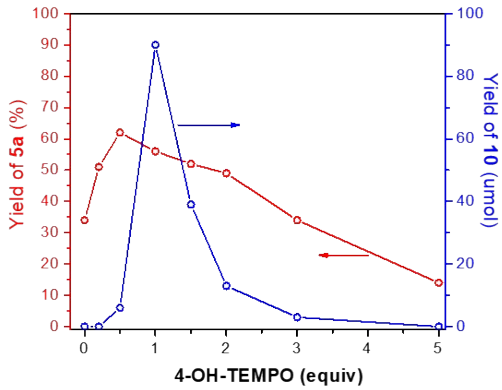
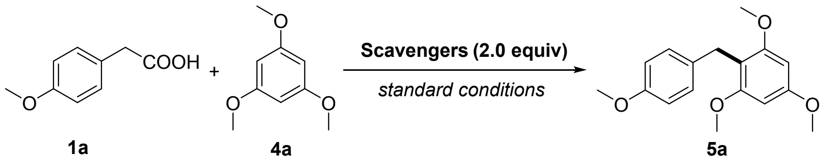


Figure S9. Effect of different equivalents of 4-OH-TEMPO in the decarboxylative C(sp^3)-C(sp^2) coupling.

d) Effect of different scavengers in the decarboxylative C(sp^3)-C(sp^2) coupling



A solution of compound **1a** (0.2 mmol), **4a** (0.4 mmol, 2 equiv), 4-OH-TEMPO (0.1 mmol, 0.5 equiv), BCN (10 mg) and scacengers (0.4 mmol, 2 equiv) in 2.5mL of DCE/H_2O (4/1, v/v) were added into a Schlenk tube equipped with a stirring bar. The Schlenk tube was purged with nitrogen for three times. After degassing by freeze-pump-thaw process for three cycles, the reaction mixture was irradiated with a 3 W 420 nm LED at 25 °C for 20 hours. After completion of the reaction, analysis by GC-MS.

When the model reaction was treated with widely used radical scavenger, 1,1-diphenylethene (DPE), under standard conditions, the reaction was suppressed. The radical adducts **13** was detected by GC-MS, indicating the formation of benzyl radical in this process.

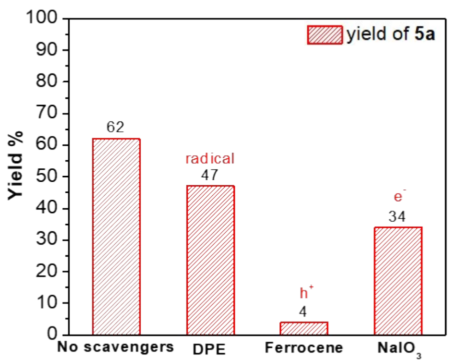


Figure S10. Effect of different scavengers in the decarboxylative C(sp^3)-C(sp^2) coupling.

Recycling test:

A solution of 4-methoxyphenylacetic acid (0.2 mmol), 1,3,5-trimethoxybenzene (0.4 mmol, 2 equiv), 4-OH-TEMPO (0.1 mmol, 0.5 equiv) and BCN (10 mg) in 2.5mL of DCE/H_2O (4/1, v/v) were added into a Schlenk tube equipped with a stirring bar. The Schlenk tube was purged with nitrogen for three times. After degassing by freeze-pump-thaw process for three cycles, the reaction mixture was irradiated with a 3 W 420 nm LED at 25 °C for 20 hours. After completion, the reaction mixture was centrifuged to separate BCN and the liquid mixture. The photocatalyst BCN was washed thoroughly with EtOH and H_2O many times and reused in the subsequent recycling reaction.

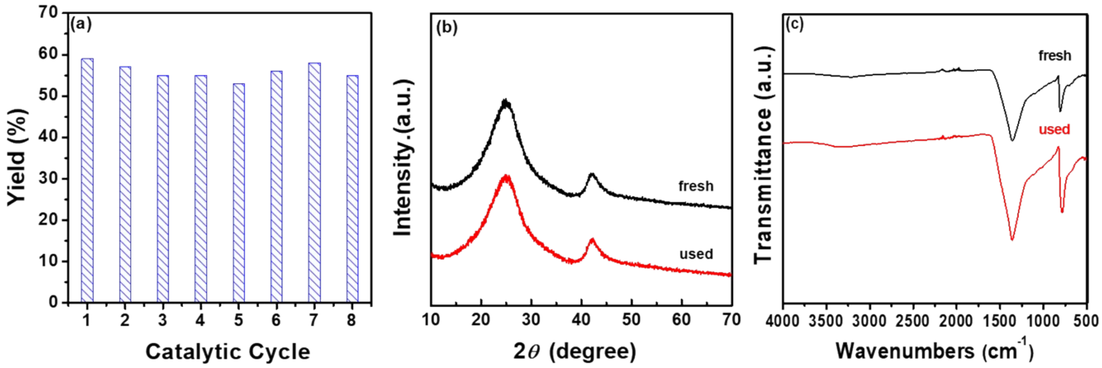
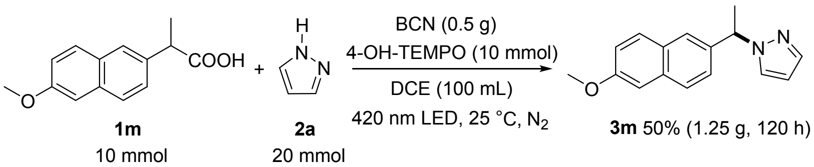


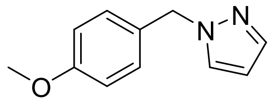
Figure S11. (a) Activity test with recycled BCN. (b) XRD pattern of fresh and used BCN. (c) FT-IR pattern of fresh and used BCN.

Gram-scale reaction:



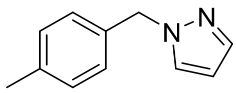
A solution of naporxen **1m** (10 mmol, 2.30 g), pyrazole **2a** (20 mmol, 1.36 g), BCN (0.5 g) and 4-OH-TEMPO (10 mmol, 1.72 g) in DCE (100 mL) were added into a Schlenk tube equipped with a stirring bar. The Schlenk tube was purged with nitrogen for three times. After degassing by freeze-pump-thaw process for three cycles, the reaction mixture was irradiated with a 3 W 420 nm LED at 25 °C for 120 hours, at which time the mixture was transferred into a centrifuge to separate the heterogeneous catalyst and solution. Then the solution was washed with brine and extracted with acetyl acetate three times. The combined organic extracts were dried over Na_2SO_4, and then concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using light petroleum ether/ethyl acetate as eluent to afford the final compounds **3m**.

Characterization data for products



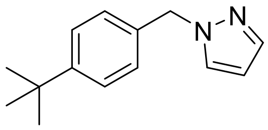
1-(4-Methoxybenzyl)-1*H*-pyrazole (**3a**)[2]

19.5 mg, 52% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.53 (s, 1H), 7.34 (s, 1H), 7.17 (d, *J*=7.8 Hz, 2H), 6.86 (d, *J*=7.8 Hz, 2H), 6.25 (s, 1H), 5.24 (s, 2H), 3.77 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 159.17, 139.17, 128.98, 128.70, 128.42, 113.95, 105.58, 55.19, 55.04. MS (m/z, EI): 51, 77, 121 (100), 188.



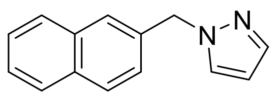
1-(4-Methylbenzyl)-1*H*-pyrazole (**3b**)

12.4 mg, 36% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.56 – 7.50 (m, 1H), 7.37 – 7.33 (m, 1H), 7.15 (d, *J*=7.8 Hz, 2H), 7.12 (d, *J*=8.2 Hz, 2H), 6.26 (t, *J*=2.1 Hz, 1H), 5.28 (s, 2H), 2.33 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 139.38, 137.74, 133.53, 129.42, 129.00, 127.69, 105.80, 55.68, 21.07. MS (m/z, EI): 51, 77, 105 (100), 144, 172.



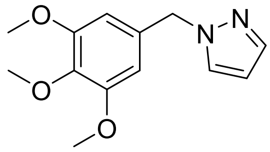
1-(4-tert-Butylbenzyl)-1*H*-pyrazole (**3c**)

15.0 mg, 35% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.55 (d, *J*=1.6 Hz, 1H), 7.39 (d, *J*=2.4 Hz, 1H), 7.37 (d, *J*=8.4 Hz, 2H), 7.16 (d, *J*=8.4 Hz, 2H), 6.27 (t, *J*=2.1 Hz, 1H), 5.30 (s, 2H), 1.31 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 150.91, 139.39, 133.55, 129.09, 127.37, 125.65, 105.75, 55.56, 34.47, 31.22. MS (m/z, EI): 53, 91, 117, 131, 199 (100), 214.



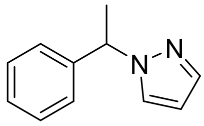
1-(Naphthalene-2-ylmethyl)-1*H*-pyrazole (**3d**)[2]

10.8 mg, 26% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.82 (d, *J*=8.4 Hz, 3H), 7.67 (s, 1H), 7.58 (s, 1H), 7.51 – 7.46 (m, 2H), 7.42 (s, 1H), 7.33 (d, *J*=8.5 Hz, 1H), 6.30 (s, 1H), 5.49 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 139.56, 134.00, 133.27, 132.94, 129.26, 128.68, 127.90, 127.68, 126.69, 126.36, 126.21, 125.37, 106.04, 56.10. MS (m/z, EI): 55, 81, 115, 141 (100), 180, 208.



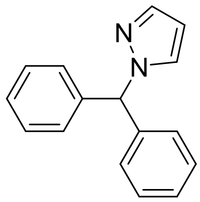
1-(3,4,5-Trimethoxybenzyl)-1*H*-pyrazole (**3e**)

33.3 mg, 67% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.55 (s, 1H), 7.40 (s, 1H), 6.42 (s, 2H), 6.28 (s, 1H), 5.24 (s, 2H), 3.81 (s, 3H), 3.80 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 153.44, 139.56, 137.62, 132.19, 129.22, 105.97, 104.64, 60.76, 56.06, 56.04. MS (m/z, EI): 52, 81, 109, 148, 181, 233, 248 (100).



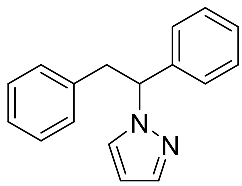
1-(1-phenylethyl)-1*H*-pyrazole (**3f**)

13.8 mg, 40% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.55 (d, *J*=1.6 Hz, 1H), 7.41 (d, *J* = 2.4 Hz, 1H), 7.32 (d, *J*=7.6 Hz, 2H), 7.28 – 7.25 (m, 1H), 7.19 (d, *J* = 7.1 Hz, 2H), 6.29 – 6.26 (m, 1H), 5.54 (q, *J*=7.1 Hz, 1H), 1.90 (d, *J*=7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 141.98, 139.05, 128.64, 127.71, 127.66, 126.20, 105.36, 60.95, 21.44. MS (m/z, EI): 51, 77, 105 (100), 157, 172.



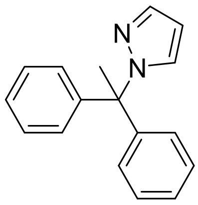
1-Benzhydryl-1*H*-pyrazole (**3g**)

26.6 mg, 57% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.57 (s, 1H), 7.28 (q, *J*=6.1 Hz, 6H), 7.22 (s, 1H), 7.06 (d, *J*=6.7 Hz, 4H), 6.76 (s, 1H), 6.23 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 139.74, 139.55, 129.40, 128.61, 128.20, 127.99, 105.39, 69.40. MS (m/z, EI): 51, 77, 115, 157, 167 (100), 234.



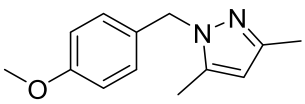
1-(1,2-Diphenylethyl)-1*H*-pyrazole (**3h**)

23.8 mg, 48% yield. [1]H NMR (400 MHz, $CDCl_3$) δ = 7.58 (s, 1H), 7.30 (d, *J* = 5.9 Hz, 6H), 7.21 (d, *J*=6.0 Hz, 1H), 7.18 (d, *J*=7.3 Hz, 2H), 7.02 (d, *J*=7.1 Hz, 2H), 6.23 – 6.15 (m, 1H), 5.51 – 5.43 (m, 1H), 3.84 (dd, *J*=13.8, 9.1 Hz, 1H), 3.43 (dd, *J*=13.8, 6.1 Hz, 1H). [13]C NMR (151 MHz, $CDCl_3$) δ = 140.26, 139.34, 137.79, 128.99, 128.92, 128.53, 128.26, 127.85, 126.88, 126.47, 105.11, 67.62, 41.68. MS (m/z, EI): 51, 77, 103, 157 (100), 180, 248.



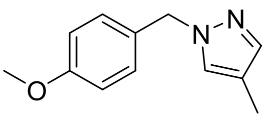
1-(1,1-Diphenylethyl)-1*H*-pyrazole (**3i**)

24.3 mg, 49% yield. [1]H NMR (400 MHz, $CDCl_3$) δ = 7.65 (s, 1H), 7.32 (d, *J*=5.9 Hz, 6H), 7.12 (s, 1H), 6.98 (d, *J*=7.2 Hz, 4H), 6.29 – 6.21 (m, 1H), 2.48 (s, 3H). [13]C NMR (151 MHz, $CDCl_3$) δ = 144.85, 139.26, 130.30, 128.16, 127.50, 127.35, 104.75, 69.89, 29.36. MS (m/z, EI): 51, 77, 103, 181 (100), 233, 248.



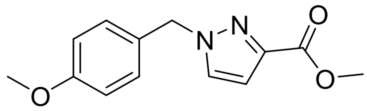
1-(4-Methoxybenzyl)-3,5-dimethyl-1*H*-pyrazole (**3j**)

27.6 mg, 64% yield. [1]H NMR (600 MHz, $CDCl_3$) δ = 7.03 (d, *J*=8.8 Hz, 2H), 6.83 (d, *J*=8.7 Hz, 2H), 5.82 (s, 1H), 5.14 (s, 2H), 3.76 (s, 3H), 2.24 (s, 3H), 2.14 (s, 3H). [13]C NMR (151 MHz, $CDCl_3$) δ = 158.87, 147.32, 138.91, 129.43, 127.91, 113.98, 105.44, 55.17, 52.07, 13.45, 11.08. MS (m/z, EI): 51, 77, 121 (100), 216.



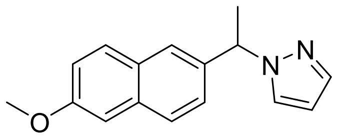
1-(4-methoxybenzyl)-4-methyl-1*H*-pyrazole (**3k**)

25.0 mg, 62% yield. [1]H NMR (400 MHz, $CDCl_3$) δ = 7.32 (s, 1H), 7.17 (d, *J*=8.2 Hz, 2H), 7.10 (s, 1H), 6.86 (d, *J*=8.2 Hz, 2H), 5.16 (s, 2H), 3.78 (s, 3H), 2.04 (s, 3H). [13]C NMR (101 MHz, $CDCl_3$) δ = 159.33, 139.72, 129.18, 128.93, 127.75, 116.39, 114.14, 55.38, 55.28, 8.93. MS (m/z, EI): 51, 77, 121 (100), 202.



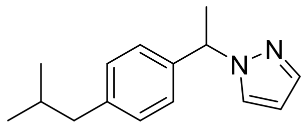
Methyl 1-(4-methoxybenzyl)-1*H*-pyrazole-3-carboxylate (**3l**)

22.1 mg, 45% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.52 (d, *J* =2.0 Hz, 1H), 7.25 (d, J=8.7 Hz, 2H), 6.85 (d, *J* =2.0 Hz, 1H), 6.83 (d, *J* =8.7 Hz, 2H), 5.70 (s, 2H), 3.85 (s, 3H), 3.76 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 160.25, 159.25, 138.45, 131.66, 130.40, 129.25, 113.97, 111.83, 55.30, 54.46, 51.98. MS (m/z, EI): 51, 77, 121 (100), 139, 187, 215, 246.



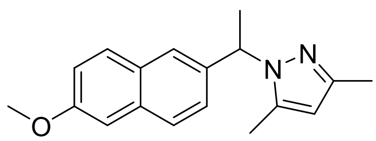
1-(1-(6-methoxynaphthalen-2-yl)ethyl)-1*H*-pyrazole (**3m**)

28.7 mg, 57% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.70 (d, *J*=8.7 Hz, 2H), 7.59 (d, *J*=9.1 Hz, 2H), 7.42 (d, *J*=1.7 Hz, 1H), 7.29 (d, *J*=8.5 Hz, 1H), 7.17 – 7.10 (m, 2H), 6.30 – 6.24 (m, 1H), 5.67 (q, *J*=7.0 Hz, 1H), 3.91 (s, 3H), 1.98 (d, *J*=7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 157.89, 139.11, 136.97, 134.09, 129.53, 128.69, 127.78, 127.42, 125.01, 124.98, 119.13, 105.62, 105.46, 61.05, 55.33, 21.43. MS (m/z, EI): 63, 115, 141, 185 (100), 252.



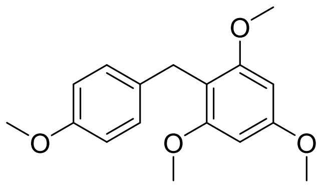
1-(1-(4-Isobutylphenyl)ethyl)-1*H*-pyrazole (**3n**)

19.1 mg, 42% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.55 (d, *J* =1.7 Hz, 1H), 7.39 (d, *J* =2.3 Hz, 1H), 7.10 (d, *J* = 0.3 Hz, 4H), 6.26 (t, *J* =2.1 Hz, 1H), 5.52 (q, *J* =7.1 Hz, 1H), 2.44 (d, *J* =7.2 Hz, 2H), 1.89 (d, *J* =7.1 Hz, 3H), 1.83 (dd, *J* =13.5, 6.7 Hz, 1H), 0.89 (d, *J* =6.6 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 141.38, 139.25, 139.07, 129.48, 127.74, 126.16, 105.39, 60.89, 45.11, 30.23, 22.46, 22.44, 21.59. MS (m/z, EI): 51, 91, 117, 161, 185, 213 (100), 228.



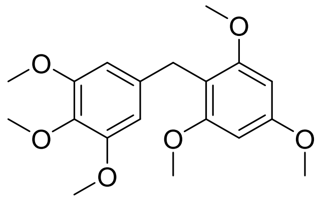
1-(1-(6-Methoxynaphthalen-2-yl)ethyl)-3,5-dimethyl-1*H*-pyrazole (**3o**)

35.2 mg, 63% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.68 (d, *J* =3.5 Hz, 1H), 7.67 (d, *J* =3.2 Hz, 1H), 7.47 (s, 1H), 7.25 (d, *J* =8.4 Hz, 1H), 7.14 (d, *J* =8.8 Hz, 1H), 7.09 (s, 1H), 5.85 (s, 1H), 5.48 (q, *J* =6.8 Hz, 1H), 3.88 (s, 3H), 2.33 (s, 3H), 2.11 (s, 3H), 1.99 (d, *J* =6.9 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 156.84, 146.11, 138.12, 137.30, 132.93, 128.62, 127.89, 126.48, 124.01, 123.45, 118.11, 104.80, 104.78, 56.62, 54.48, 20.89, 12.97, 10.43. MS (m/z, EI): 63, 115, 141, 185 (100), 222, 280.



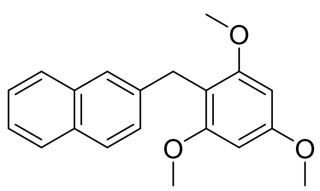
1-(4-Methoxybenzyl)-2,4,6-trimethoxybenzene (**5a**)[3]

28.7 mg, 50% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.17 (d, *J* =7.5 Hz, 2H), 6.78 (d, *J* =7.1 Hz, 2H), 6.16 (s, 2H), 3.88 (s, 2H), 3.81 (s, 3H), 3.80 (s, 6H), 3.76 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 159.57, 158.79, 157.39, 134.47, 129.31, 113.41, 110.73, 90.68, 55.73, 55.34, 55.21, 27.37. MS (m/z, EI): 51, 91, 121, 181, 257, 288 (100).



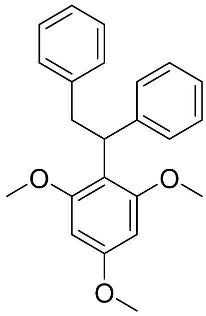
1-(3,4,5-Trimethoxybenzyl)-2,4,6-trimethoxybenzene (**5b**)

46.5 mg, 67% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.51 (s, 2H), 6.17 (s, 2H), 3.88 (s, 2H), 3.85 – 3.75 (m, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 159.76, 158.81, 152.77, 138.04, 135.80, 110.08, 105.50, 90.73, 60.78, 55.93, 55.71, 55.32, 28.53. MS (m/z, EI): 53, 121, 151, 181, 259, 333, 348 (100).



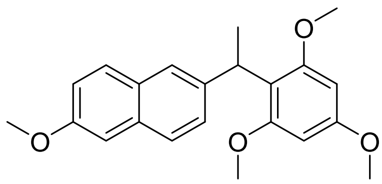
1-(Naphthalen-2-ylmethyl)-2,4,6-trimethoxybenzene (**5c**)

26.3 mg, 43% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.73 (dt, *J* = 14.6, 8.7 Hz, 3H), 7.61 (s, 1H), 7.39 (dq, *J*=13.7, 7.4, 6.5 Hz, 3H), 6.19 (s, 2H), 4.11 (s, 2H), 3.83 (s, 3H), 3.80 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 159.84, 159.06, 139.93, 133.72, 131.97, 127.81, 127.61, 127.58, 127.43, 126.21, 125.53, 124.77, 110.15, 90.79, 55.84, 55.42, 28.61. MS (m/z, EI): 51, 121, 141, 181, 277, 308 (100).



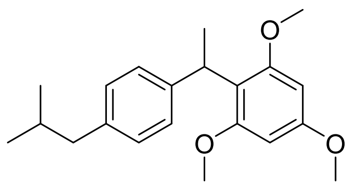
1-(1,2-Diphenylethyl)-2,4,6-trimethoxybenzene (**5d**)

23.0 mg, 33% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.38 (d, *J*=7.6 Hz, 2H), 7.23 (d, *J*=7.1 Hz, 2H), 7.18 – 7.13 (m, 3H), 7.09 (d, *J*=7.1 Hz, 3H), 6.06 (s, 2H), 4.95 (t, *J*=7.9 Hz, 1H), 3.76 (s, 3H), 3.63 (s, 6H), 3.52 (t, *J*=9.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 159.51, 159.18, 145.35, 141.96, 128.99, 128.01, 127.69, 127.62, 125.35, 125.21, 113.74, 91.44, 55.76, 55.17, 41.04, 38.19. MS (m/z, EI): 51, 91, 141, 165, 226, 257 (100), 348.



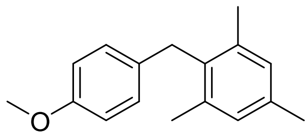
2-Methoxy-6-(1-(2,4,6-trimethoxyphenyl)ethyl)naphthalene (**5e**)

43.6 mg, 62% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.68 (d, *J* =17.3 Hz, 2H), 7.59 (s, 1H), 7.38 (s, 1H), 7.10 (d, *J* =8.5 Hz, 2H), 6.15 (s, 2H), 4.91 – 4.85 (m, 1H), 3.90 (s, 3H), 3.81 (s, 3H), 3.69 (s, 6H), 1.74 (d, *J* =7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 159.56, 159.18, 156.94, 142.00, 132.63, 129.27, 129.01, 127.60, 125.81, 124.69, 118.13, 115.95, 105.62, 91.55, 55.87, 55.33, 33.00, 17.89. MS (m/z, EI):53, 89, 128, 153, 171, 202, 263, 306, 337 (100), 352.



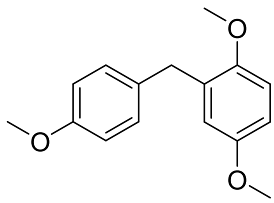
2-(1-(4-Isobutylphenyl)ethyl)-1,3,5-trimethoxybenzene (**5f**)

29.5 mg, 45% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.17 (d, *J* =7.9 Hz, 2H), 6.99 (d, *J* =8.0 Hz, 2H), 6.13 (s, 2H), 4.72 (q, *J* =7.2 Hz, 1H), 3.79 (s, 3H), 3.68 (s, 6H), 2.42 (d, *J* =7.2 Hz, 2H), 1.82 (dp, *J* = 13.5, 6.8 Hz, 1H), 1.63 (d, *J* =7.3 Hz, 3H), 0.89 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 159.41, 159.12, 143.93, 138.04, 128.35, 126.99, 116.36, 91.63, 55.85, 55.31, 45.15, 32.69, 30.31, 22.52, 22.47, 17.98. MS (m/z, EI): 55, 91, 105, 147, 195, 271, 313 (100), 328.



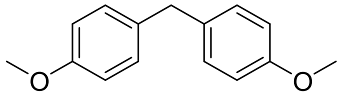
1-(4-Methoxybenzyl)-2,4,6-trimethylbenzene (**5g**)[3]

22.0 mg, 46% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.92 (d, *J* =10.6 Hz, 4H), 6.81 (s, 2H), 3.98 (s, 2H), 3.78 (s, 3H), 2.31 (s, 3H), 2.23 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 157.71, 136.98, 135.59, 134.20, 132.10, 128.92, 128.75, 113.81, 55.25, 33.82, 20.94, 20.13. MS (m/z, EI): 51, 91, 121, 132 (100), 165, 225, 240.



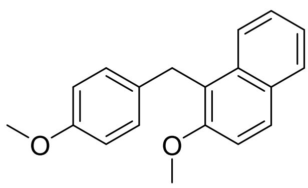
1-(4-Methoxybenzyl)-2,5-dimethoxybenzene (**5h**)

16.4 mg, 32% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.13 (d, *J*=7.2 Hz, 2H), 6.85 – 6.75 (m, 3H), 6.70 (d, *J*=8.8 Hz, 1H), 6.64 (s, 1H), 3.89 (s, 2H), 3.78 (s, 6H), 3.72 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 157.90, 153.61, 151.72, 132.90, 131.50, 129.96, 116.81, 113.82, 111.48, 111.17, 56.13, 55.71, 55.32, 35.15. MS (m/z, EI): 51, 91, 121, 183, 227, 258 (100).



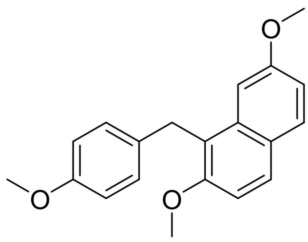
Bis(4-methoxyphenyl)methane (**5i**)[3]

13.2 mg, 29% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.10 (d, *J*=7.4 Hz, 4H), 6.83 (d, *J*=7.3 Hz, 4H), 3.87 (s, 2H), 3.79 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 157.93, 133.75, 129.75, 113.87, 55.27, 40.14. MS (m/z, EI): 51, 91, 121, 197, 228 (100).



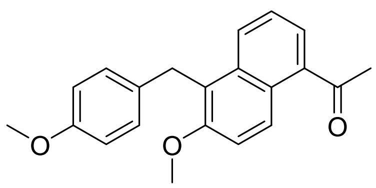
1-(4-Methoxybenzyl)-2-methoxynaphthalene (**5j**)

26.5 mg, 48% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.94 (d, *J*=8.4 Hz, 1H), 7.81 (d, *J*=8.4 Hz, 2H), 7.44 (d, *J*=6.9 Hz, 1H), 7.34 (t, *J*=8.3 Hz, 2H), 7.13 (d, *J*=7.8 Hz, 2H), 6.78 (d, *J*=7.7 Hz, 2H), 4.45 (s, 2H), 3.96 (s, 3H), 3.74 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 157.65, 154.81, 133.41, 133.34, 129.40, 129.18, 128.47, 128.29, 126.48, 123.84, 123.32, 122.13, 113.75, 113.63, 56.70, 55.23, 29.72. MS (m/z, EI): 51, 91, 121, 141, 202, 247, 278 (100).



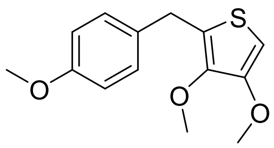
2,7-Dimethoxy-1-(4-methoxybenzyl)naphthalene (**5k**)

29.5 mg, 48% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.69 (dd, *J* = 16.6, 8.9 Hz, 2H), 7.18 (d, *J* = 9.0 Hz, 2H), 7.12 (d, *J*=8.3 Hz, 2H), 6.98 (s, 1H), 6.76 (d, *J*=8.6 Hz, 2H), 4.36 (s, 2H), 3.94 (s, 3H), 3.80 (s, 3H), 3.74 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 158.19, 157.66, 155.40, 134.68, 133.36, 130.00, 129.21, 127.98, 124.89, 121.15, 115.92, 113.80, 110.97, 102.57, 56.62, 55.29, 55.20, 30.05. MS (m/z, EI): 51, 91, 121, 131, 201, 245, 277, 308 (100).



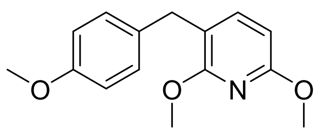
1-Acetyl-5-(4-methoxybenzyl)-6-methoxy-naphthalene (**5l**)

19.8 mg, 31% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.42 (s, 1H), 7.96 (s, 2H), 7.92 (d, *J*=9.0 Hz, 1H), 7.39 (d, *J*=9.0 Hz, 1H), 7.08 (d, *J*=7.9 Hz, 2H), 6.76 (d, *J*=7.8, 2H), 4.41 (s, 2H), 3.98 (s, 3H), 3.73 (s, 3H), 2.68 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 197.86, 157.74, 156.87, 135.75, 132.77, 132.13, 130.95, 130.23, 129.09, 128.11, 124.56, 124.20, 122.31, 113.91, 113.79, 56.43, 55.22, 29.64, 26.55. MS (m/z, EI): 51, 91, 121, 152, 189, 202, 245, 305, 320 (100).



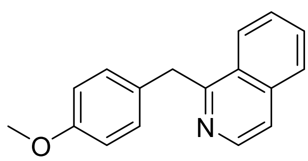
2-(4-Methoxybenzyl)-3,4-dimethoxythiophene (**5m**)

15.8 mg, 30% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.16 (d, *J*=7.9 Hz, 2H), 6.83 (d, *J*=7.9, 2H), 5.99 (s, 1H), 3.96 (s, 2H), 3.81 (s, 3H), 3.78 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 158.26, 150.71, 143.46, 132.23, 129.59, 126.68, 113.95, 93.05, 60.86, 57.12, 55.33, 31.75. MS (m/z, EI): 45, 91, 121, 157, 233, 264 (100).



3-(4-Methoxybenzyl)-2,6-dimethoxypyridine (**5n**)

19.5 mg, 38% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.22 (d, *J*=7.2 Hz, 1H), 7.11 (d, *J*=7.6 Hz, 2H), 6.83 (d, *J*=7.5 Hz, 2H), 6.22 (d, *J*=7.4 Hz, 1H), 3.95 (s, 3H), 3.90 (s, 2H), 3.79 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 161.58, 160.26, 157.97, 141.06, 132.81, 129.83, 114.99, 113.86, 100.14, 55.31, 53.56, 53.35, 33.79. MS (m/z, EI): 51, 91, 121, 228, 259 (100).



1-(4-Methoxybenzyl)isoquinoline (**5o**)[4]

17.4 mg, 35% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.49 (d, *J*=5.3 Hz, 1H), 8.16 (d, *J*=8.1 Hz, 1H), 7.81 (d, *J*=8.0 Hz, 1H), 7.63 (d, *J*=7.3 Hz, 1H), 7.58 – 7.49 (m, 2H), 7.20 (d, *J*=7.4 Hz, 2H), 6.79 (d, *J*=7.2 Hz, 2H), 4.62 (s, 2H), 3.74 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 160.53, 158.14, 141.83, 136.73, 131.54, 130.03, 129.64, 127.45, 127.33, 127.20, 125.96, 119.91, 114.04, 55.27, 41.13. MS (m/z, EI): 51, 77, 121, 234, 248 (100), 249.

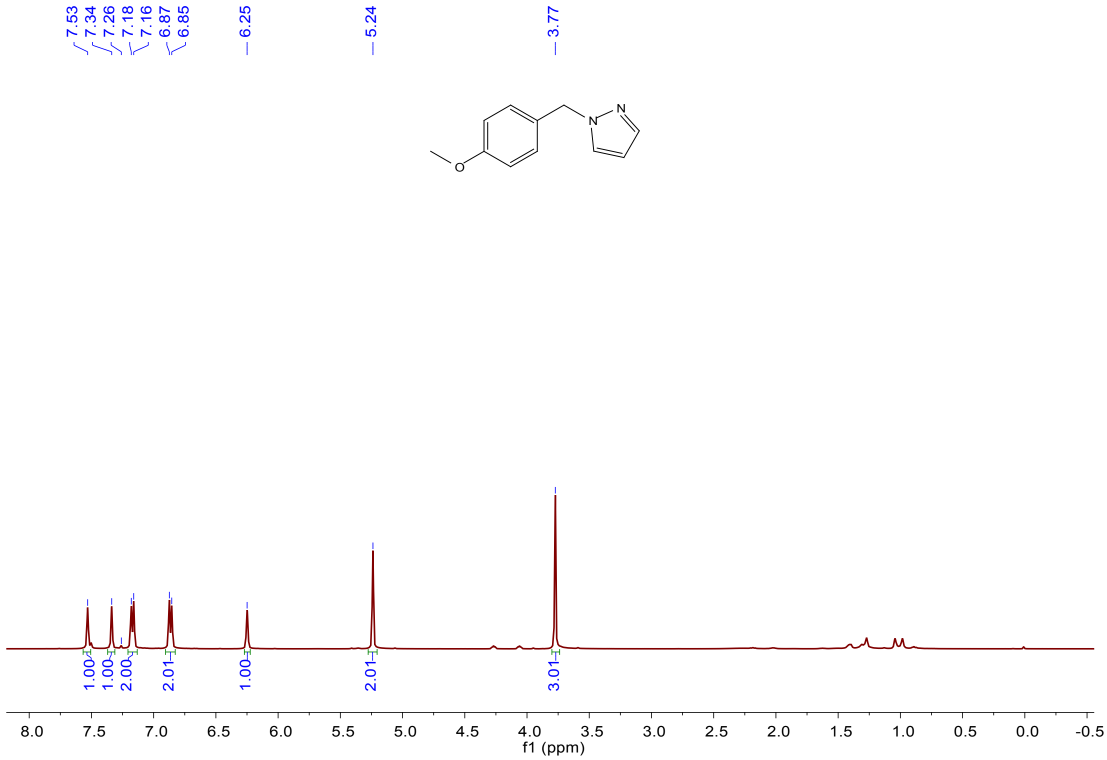
Reference

1. C. Huang, C. Chen, M. Zhang, L. Lin, X. Ye, S. Lin, M. Antonietti and X. Wang, *Nat. Commun.* 2015, **6**, 7698.
2. G. A. Molander, D. Ryu, M. Hosseini-Sarvari, R. Devulapally and D. G. Seapy, *J. Org. Chem.*, 2013, **78**, 6648.
3. M. Hofmann, N. Hampel, T. Kanzian and H. Mayr, *Angew. Chem. Int. Ed.* 2004, **43**, 5402.
4. F. Lima, M. A. Kabeshov, D. N. Tran, C. Battilocchio, J. Sedelmeier, G. Sedelmeier, B. Schenkel and S. V. Ley, *Angew. Chem. Int. Ed.*, 2016, **55**, 14085.

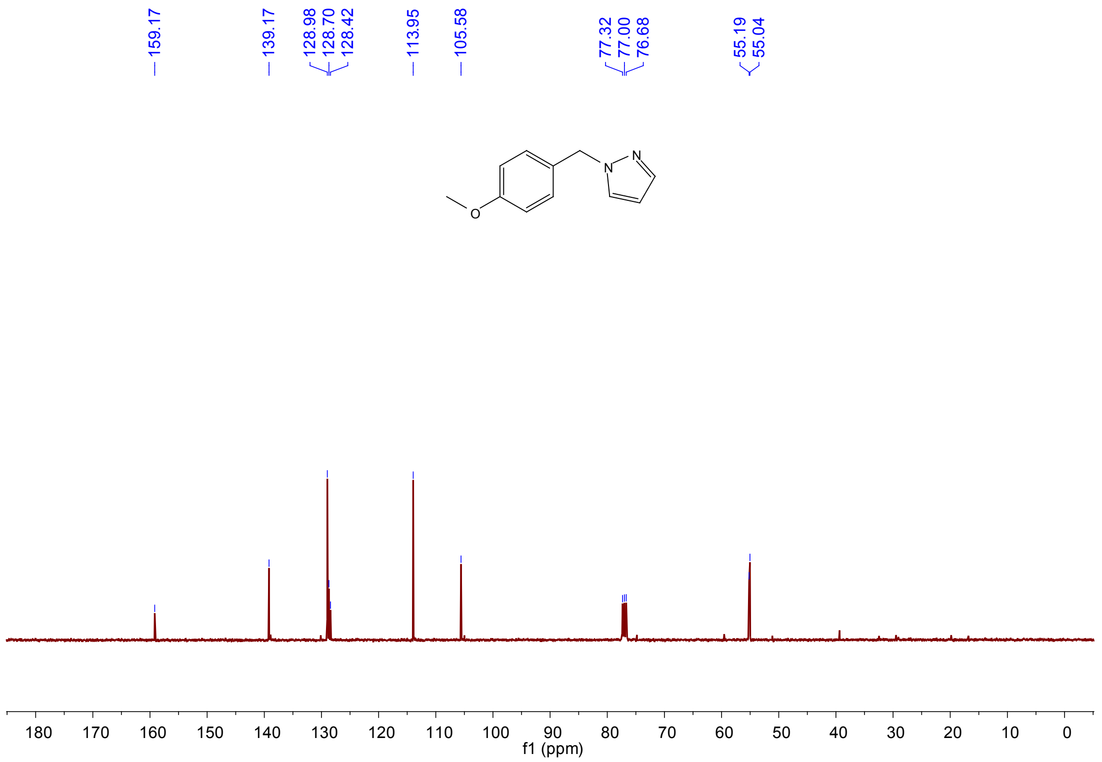
NMR spectra

3a

^{1}H NMR for **3a** (400 MHz, $CDCl_3$)

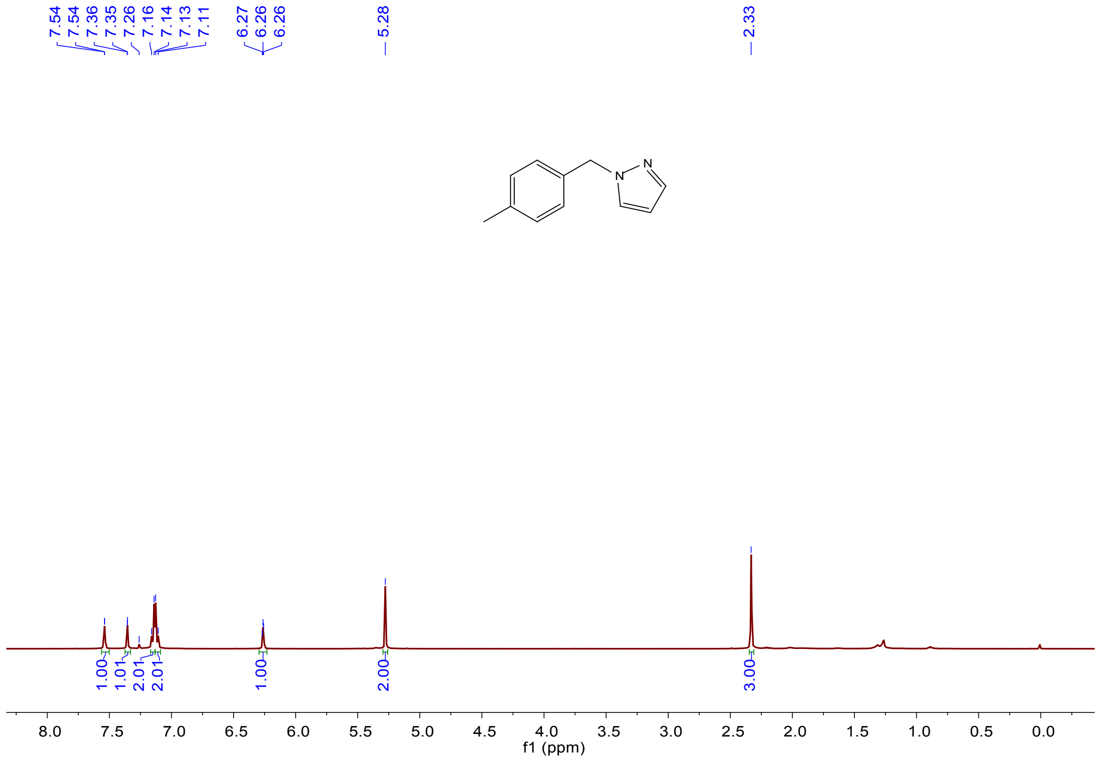


^{13}C NMR for **3a** (101 MHz, $CDCl_3$)

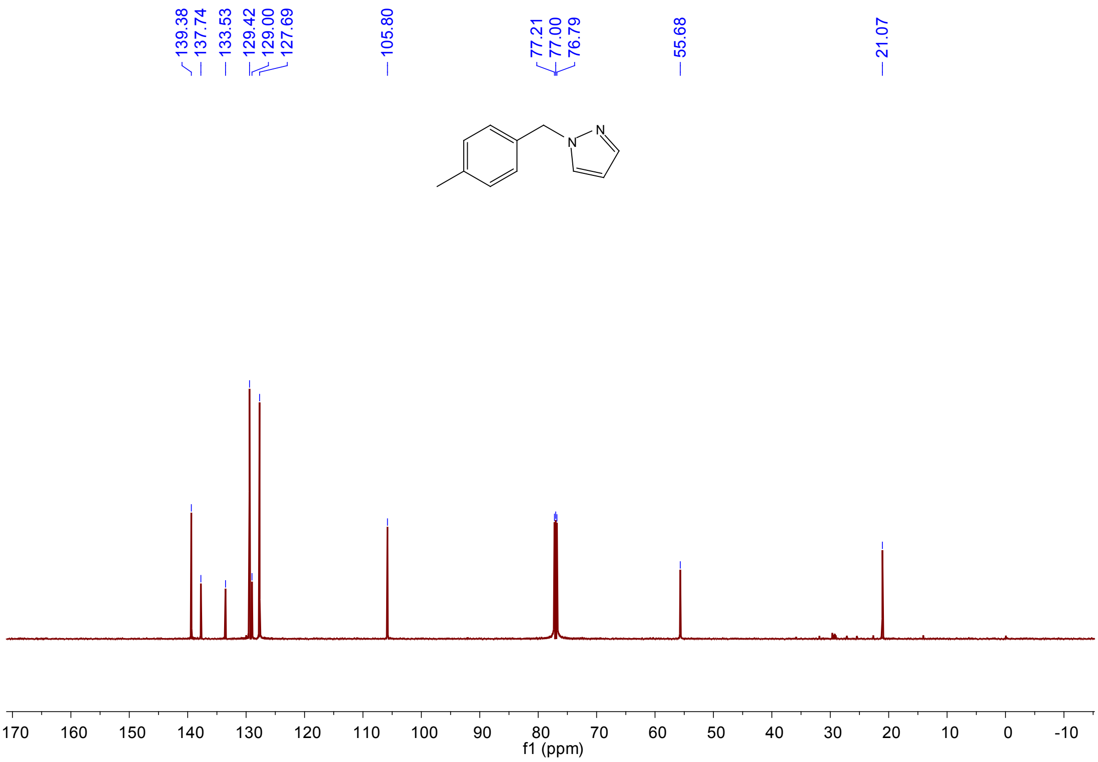


3b

^{1}H NMR for **3b** (400 MHz, $CDCl_3$)

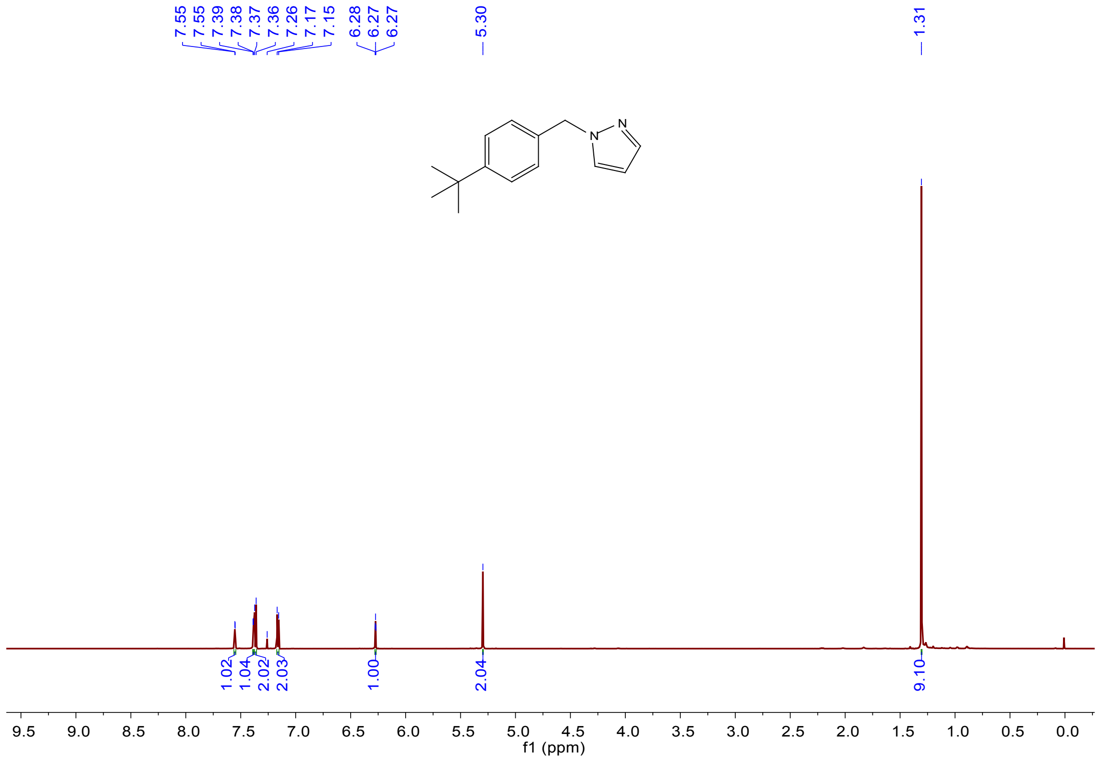


^{13}C NMR for **3b** (151 MHz, $CDCl_3$)

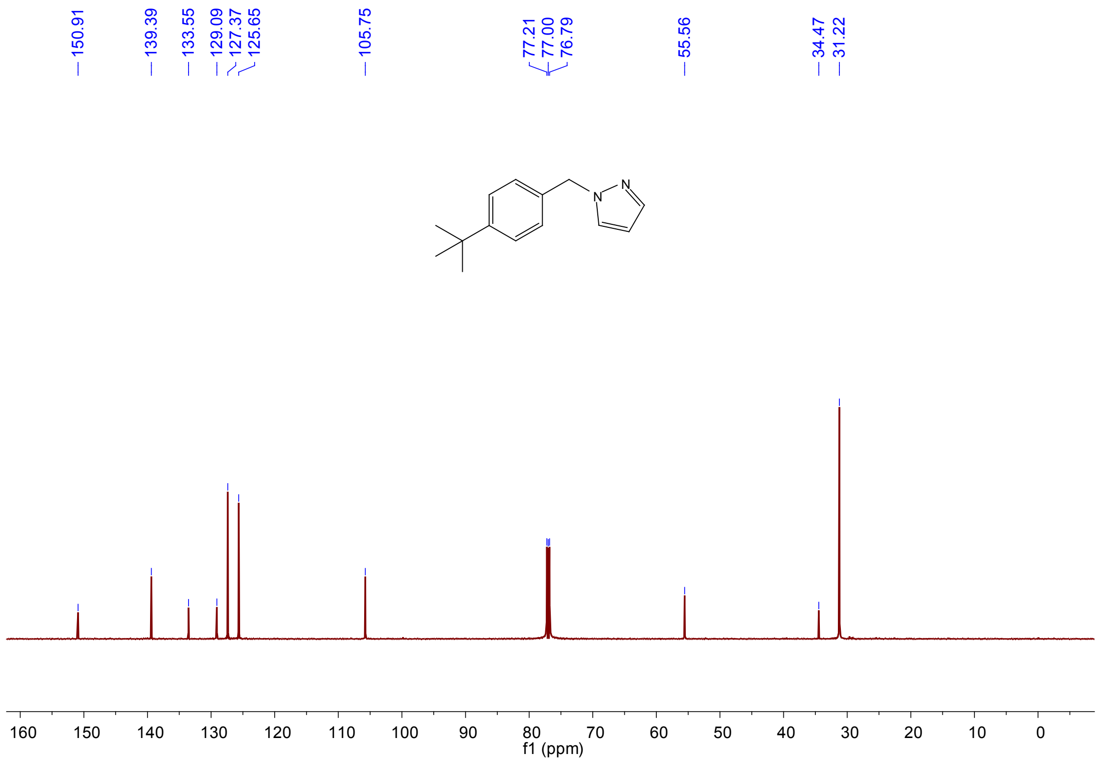


3c

^{1}H NMR for **3c** (600 MHz, $CDCl_3$)

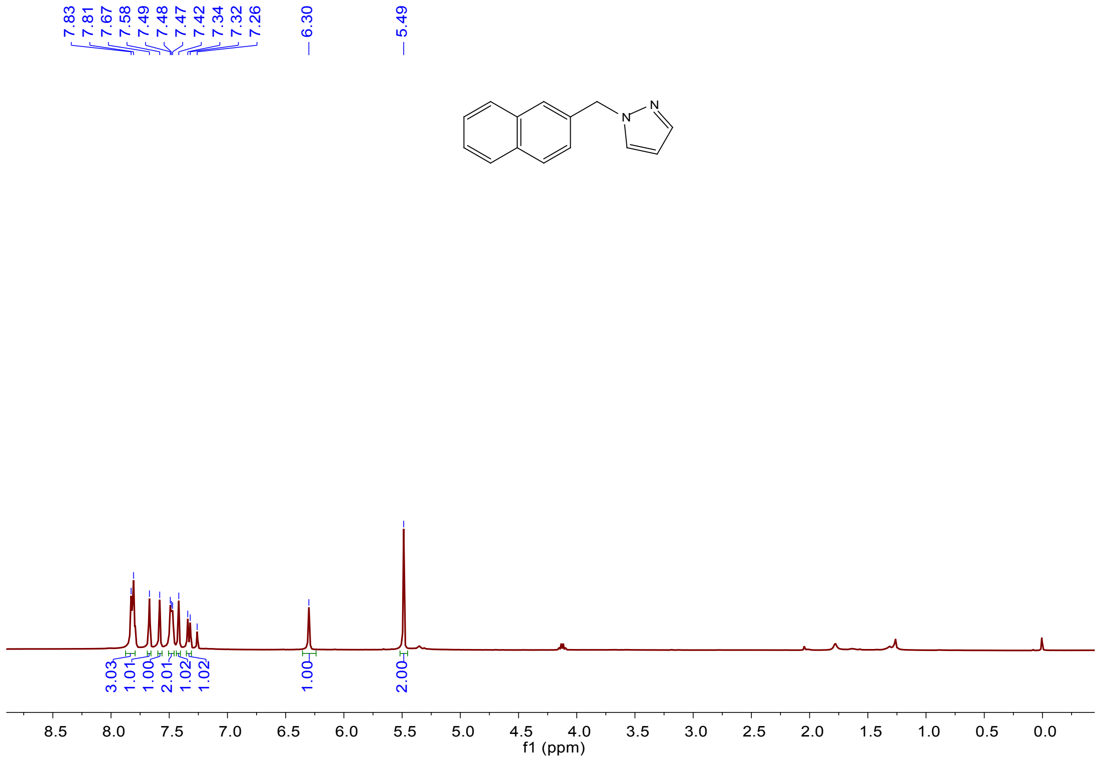


^{13}C NMR for **3c** (151 MHz, $CDCl_3$)

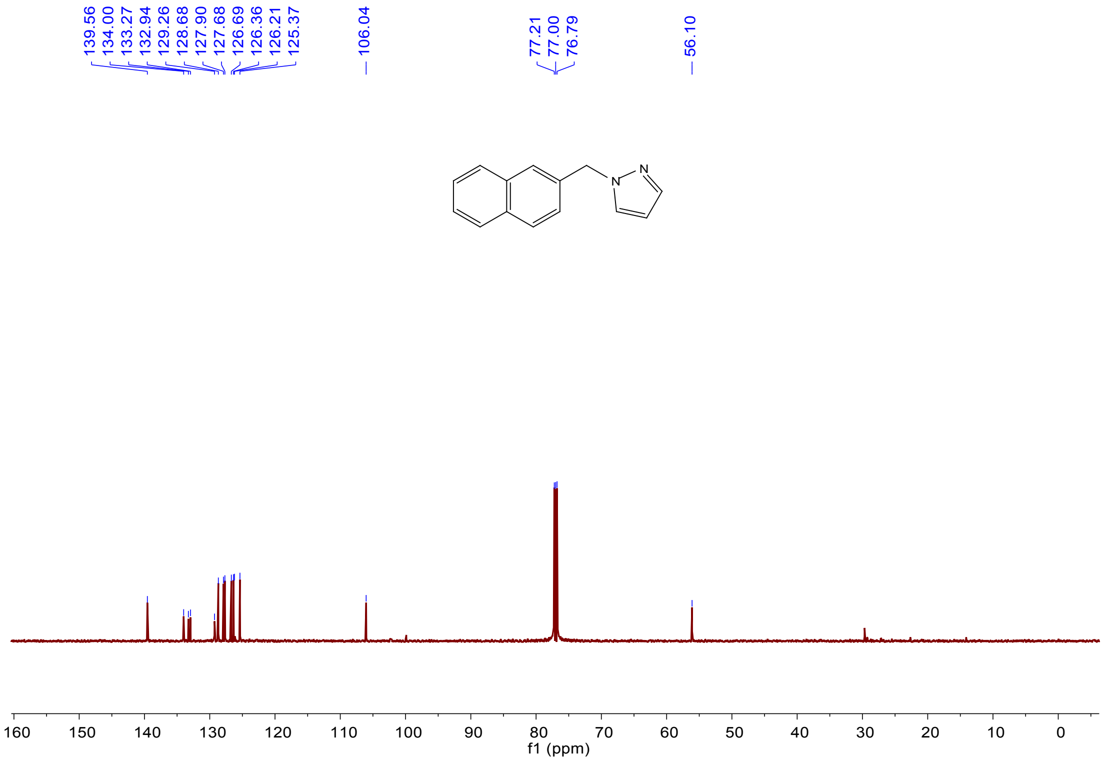


3d

^{1}H NMR for **3d** (400 MHz, $CDCl_3$)

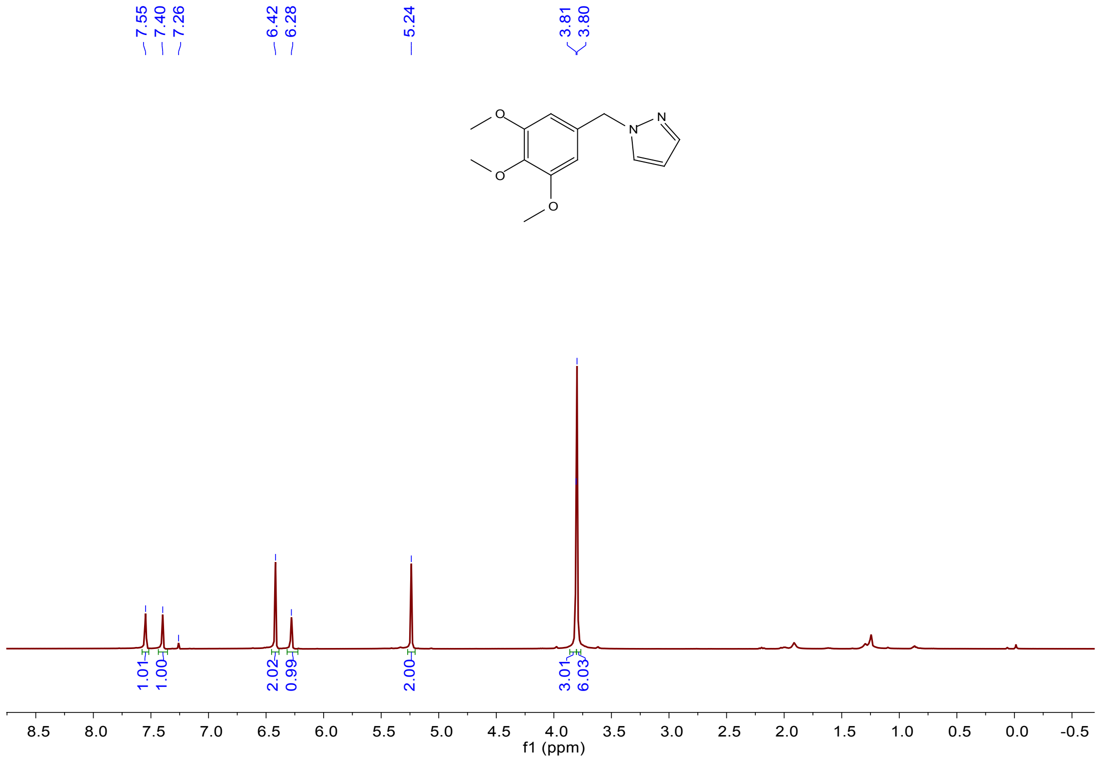


^{13}C NMR for **3d** (151 MHz, $CDCl_3$)

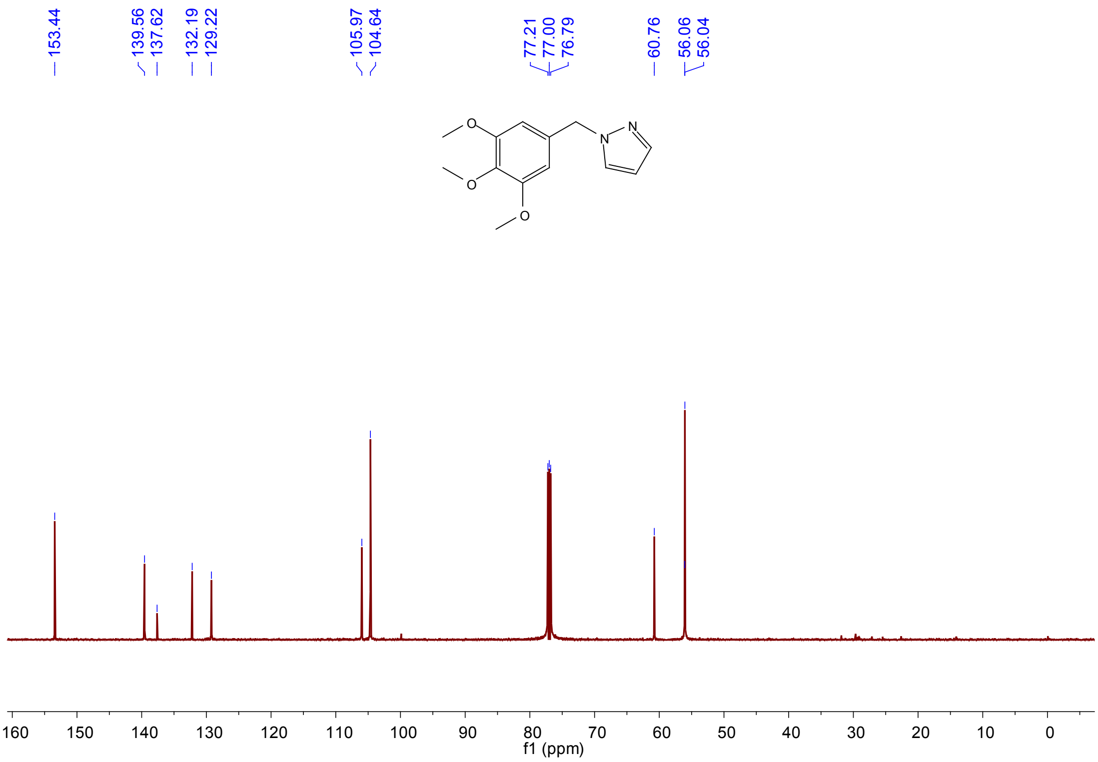


3e

^{1}H NMR for **3e** (400 MHz, $CDCl_3$)

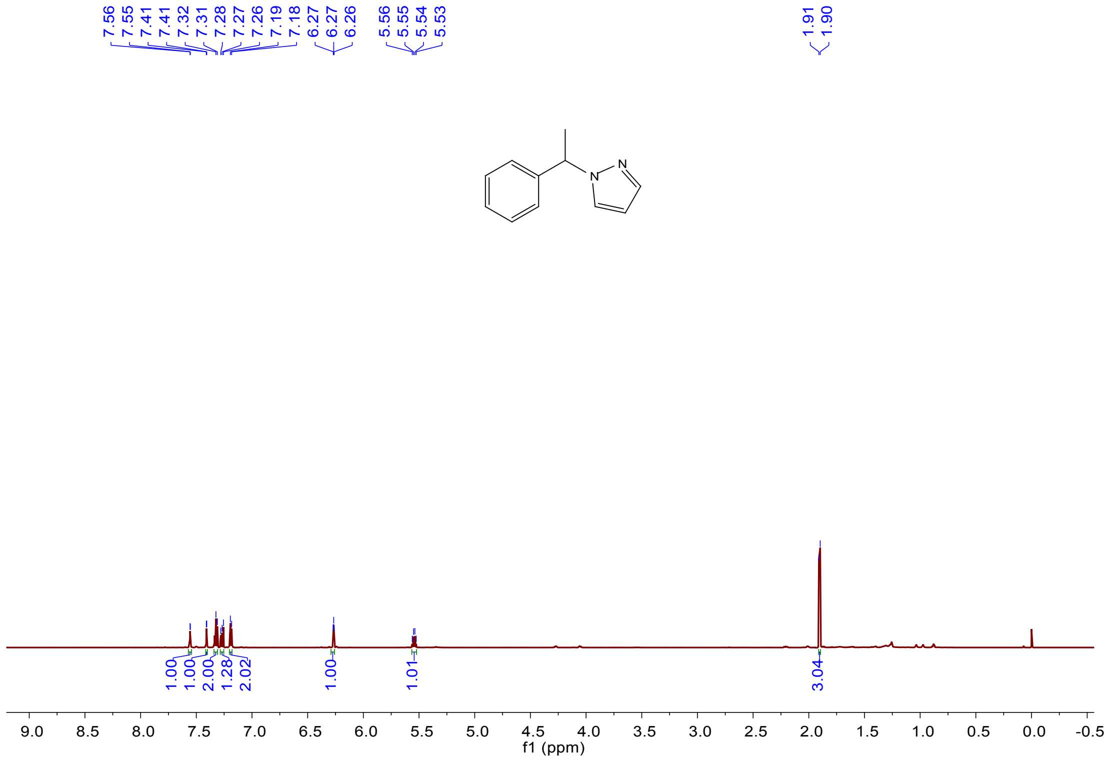


^{13}C NMR for **3e** (151 MHz, $CDCl_3$)

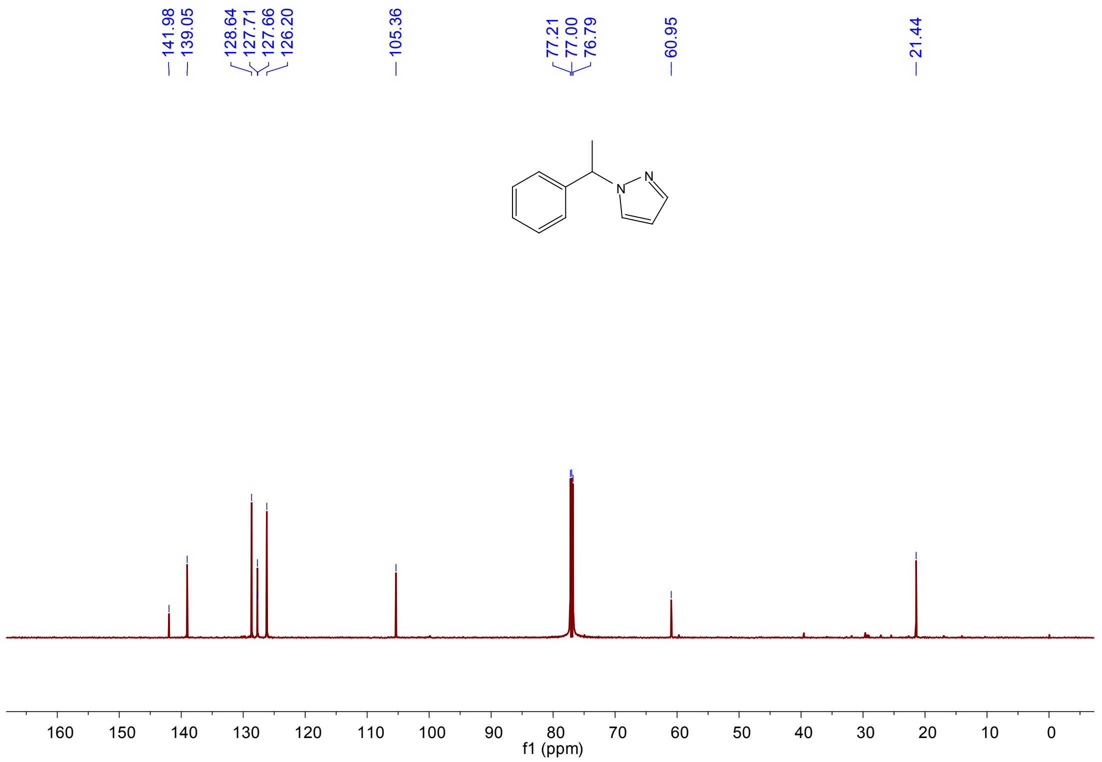


3f

[1]H NMR for **3f** (600 MHz, $CDCl_3$)

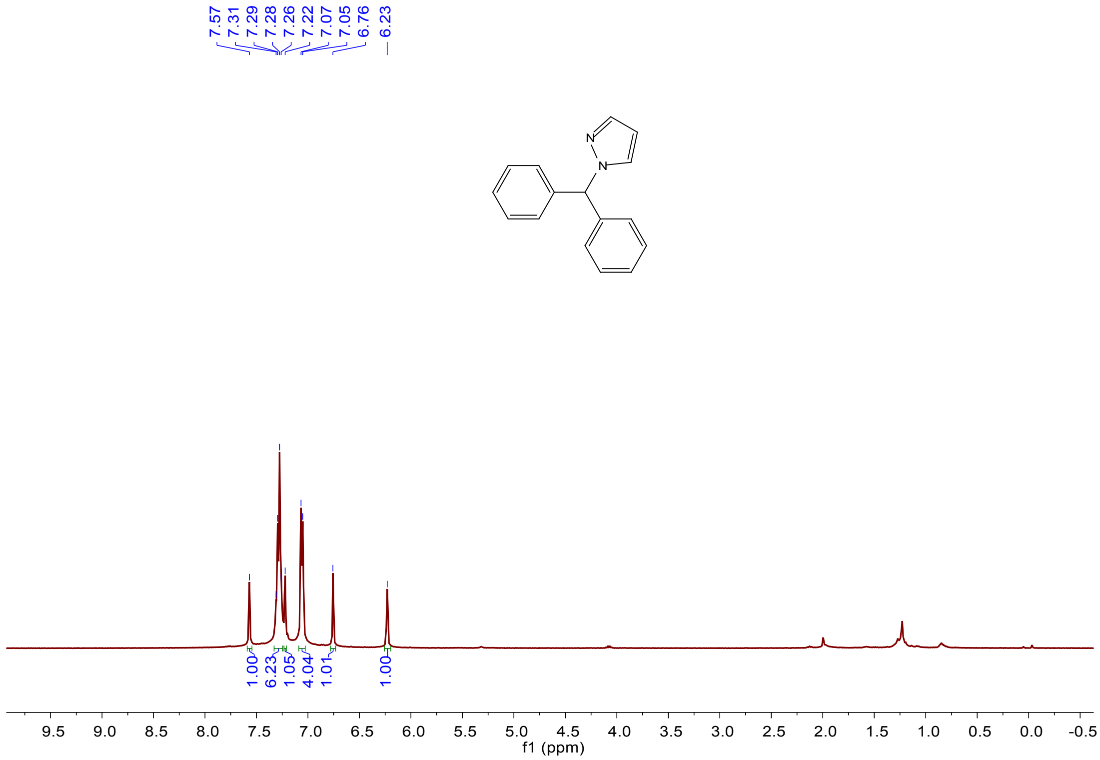


[13]C NMR for **3f** (151 MHz, $CDCl_3$)

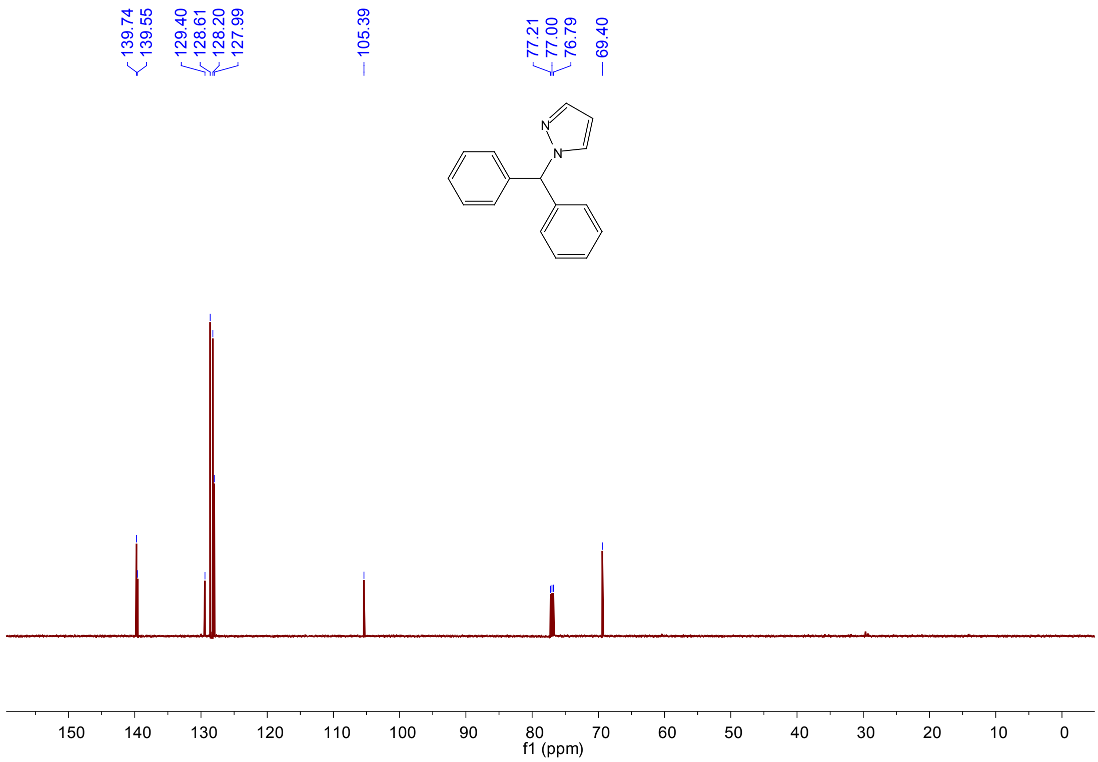


3g

^{1}H NMR for **3g** (400 MHz, $CDCl_3$)

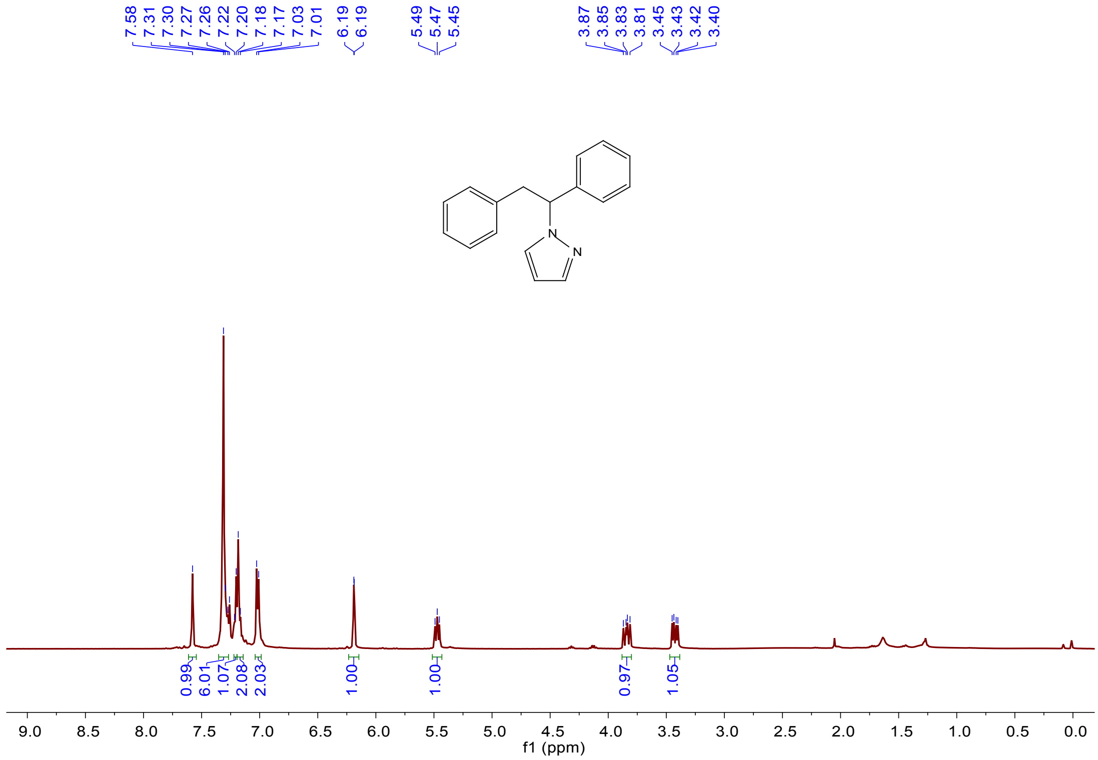


^{13}C NMR for **3g** (151 MHz, $CDCl_3$)

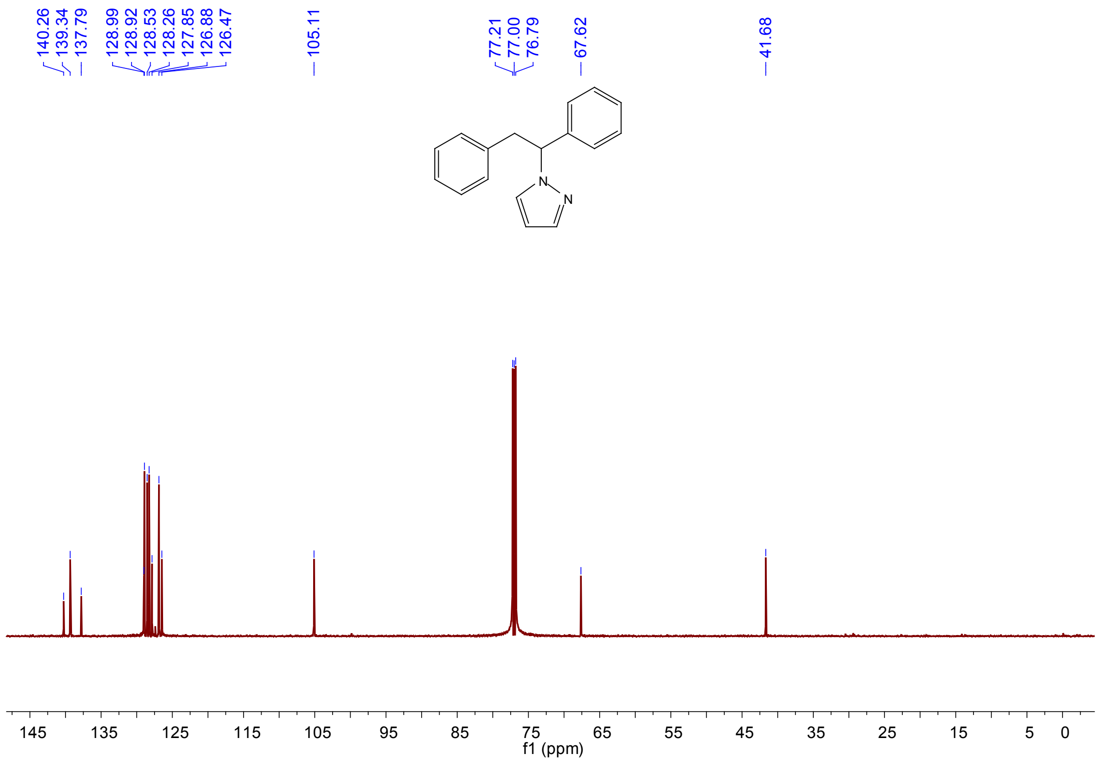


3h

^{1}H NMR for **3h** (400 MHz, $CDCl_3$)

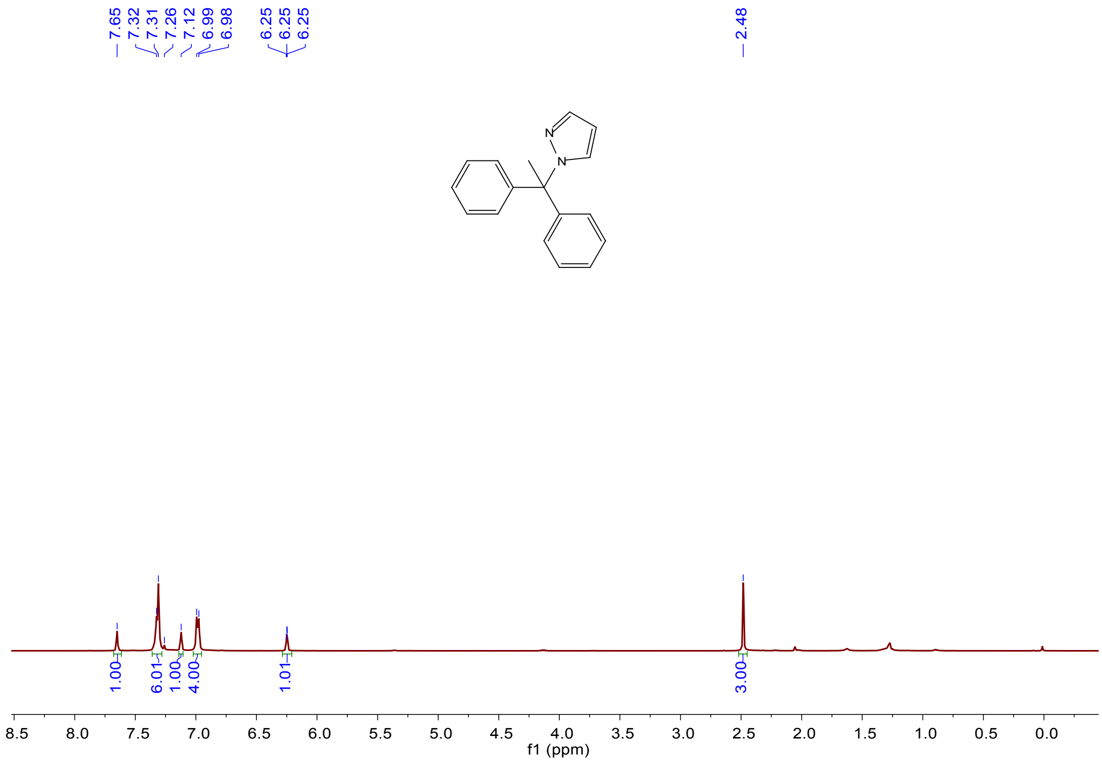


^{13}C NMR for **3h** (151 MHz, $CDCl_3$)

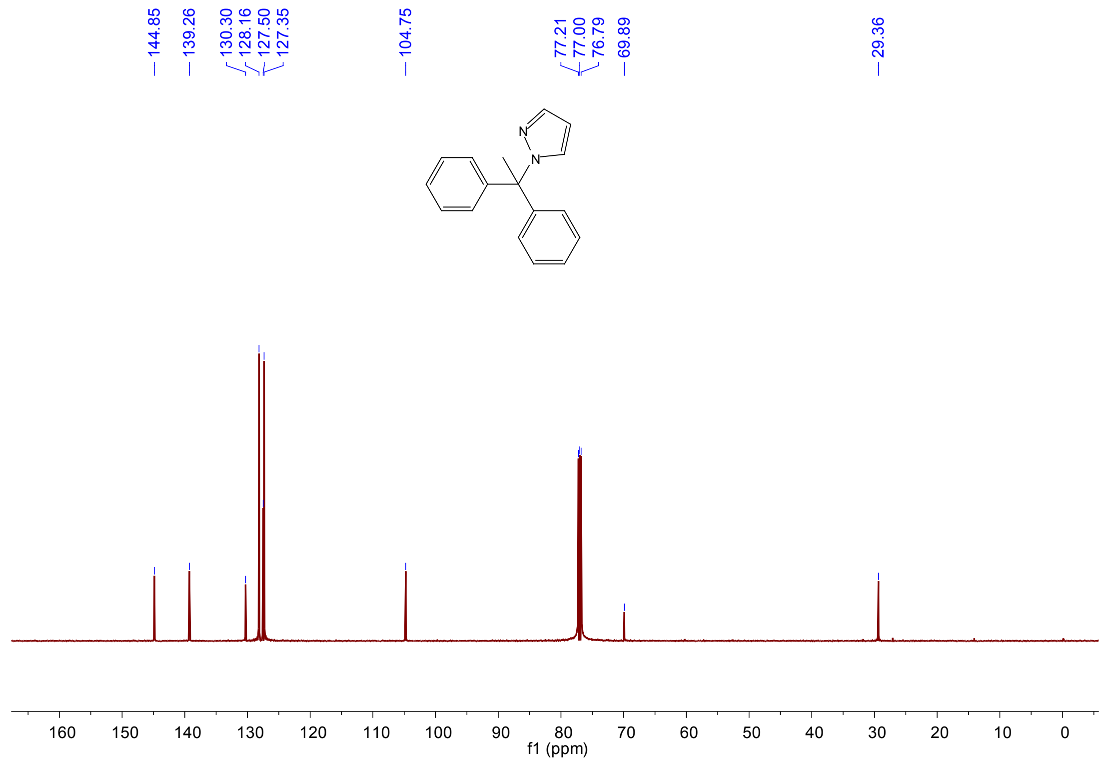


3i

^{1}H NMR for **3i** (400 MHz, $CDCl_3$)

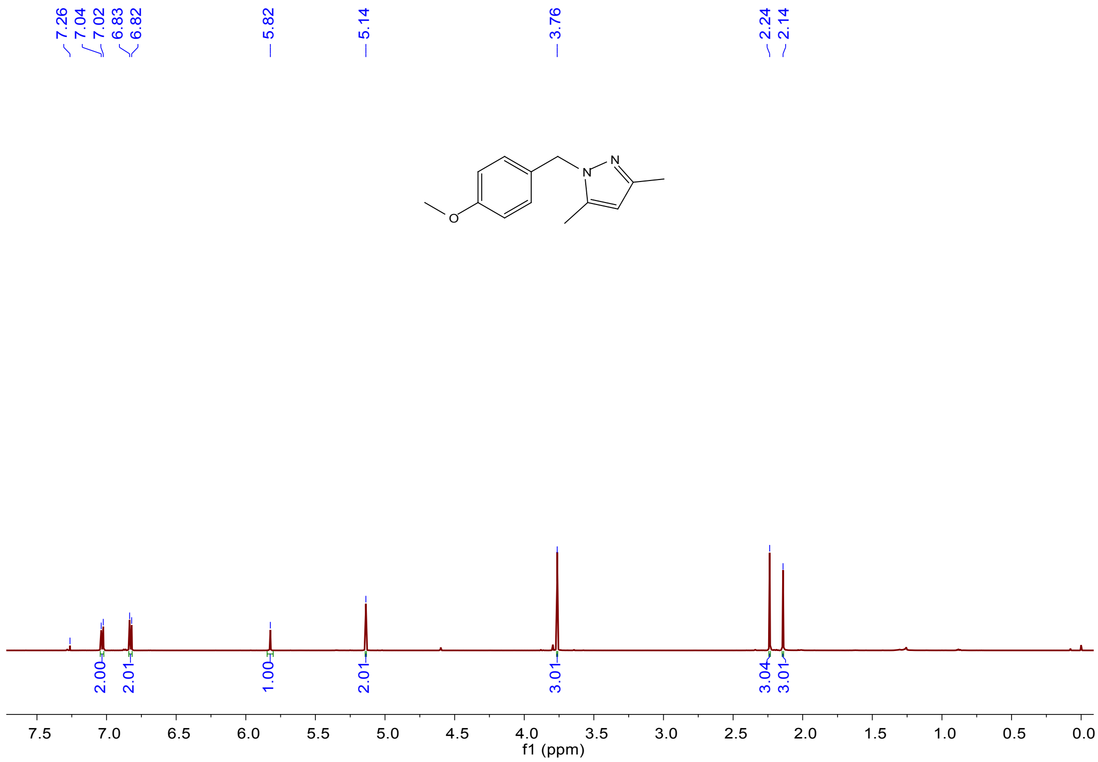


^{13}C NMR for **3i** (151 MHz, $CDCl_3$)

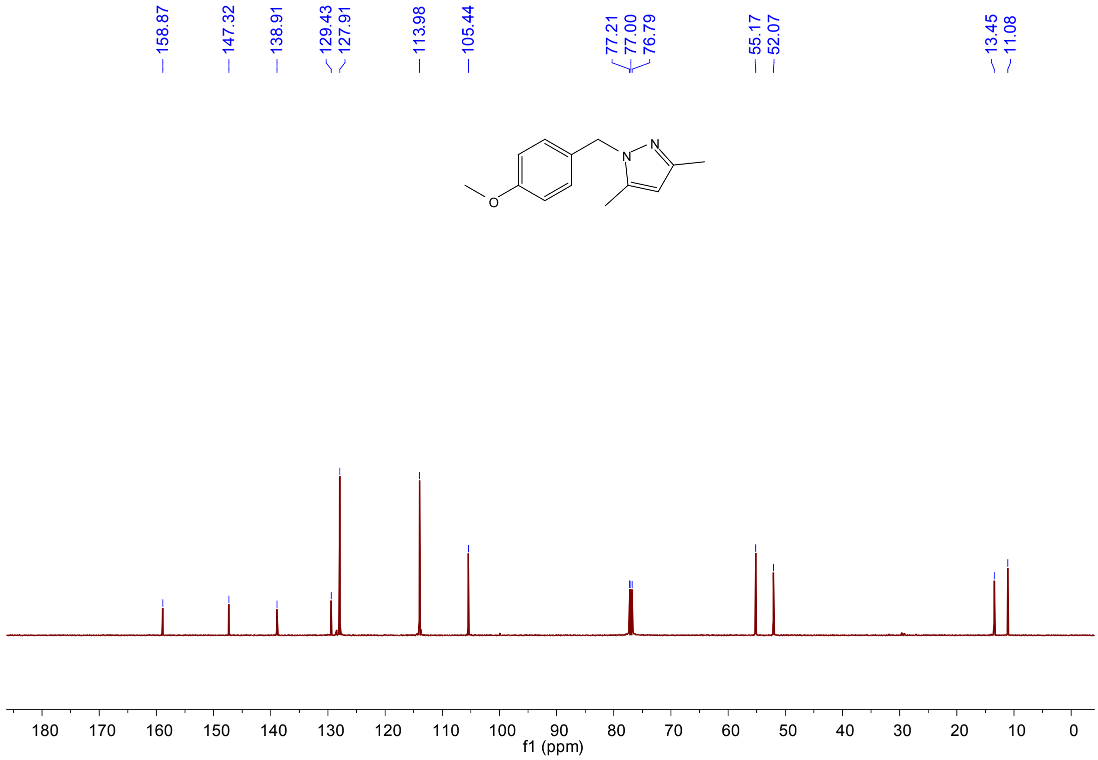


3j

^1H NMR for **3j** (600 MHz, $CDCl_3$)

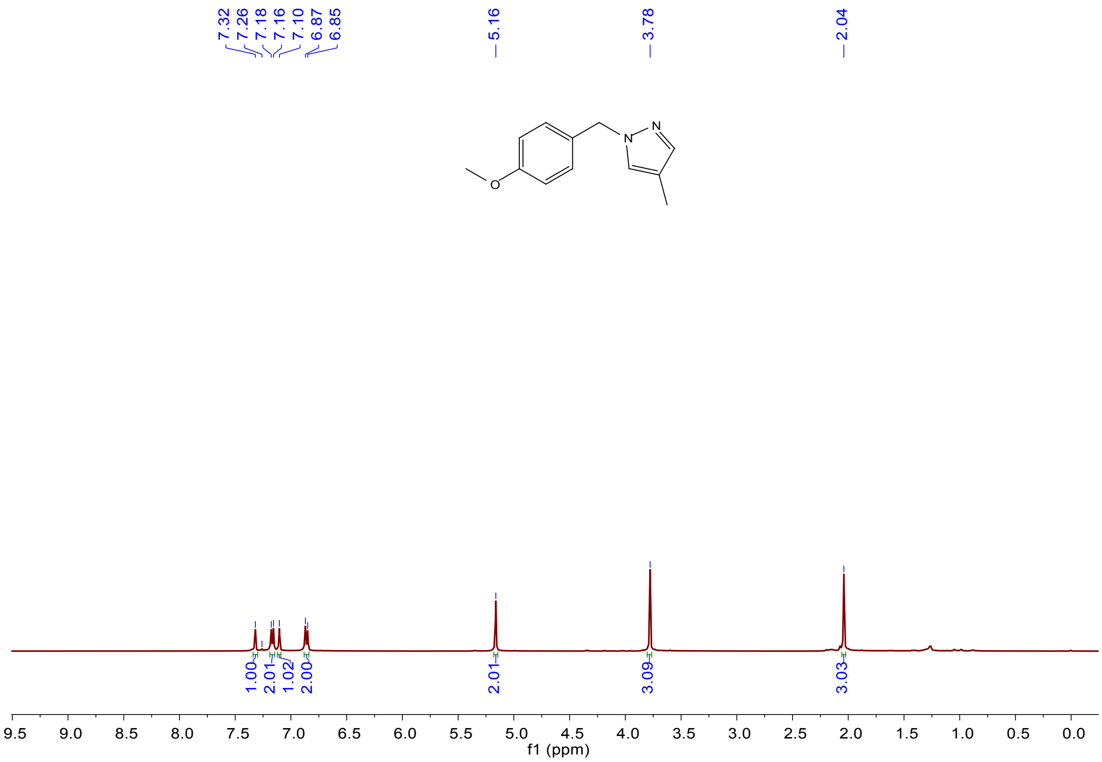


^{13}C NMR for **3j** (151 MHz, $CDCl_3$)

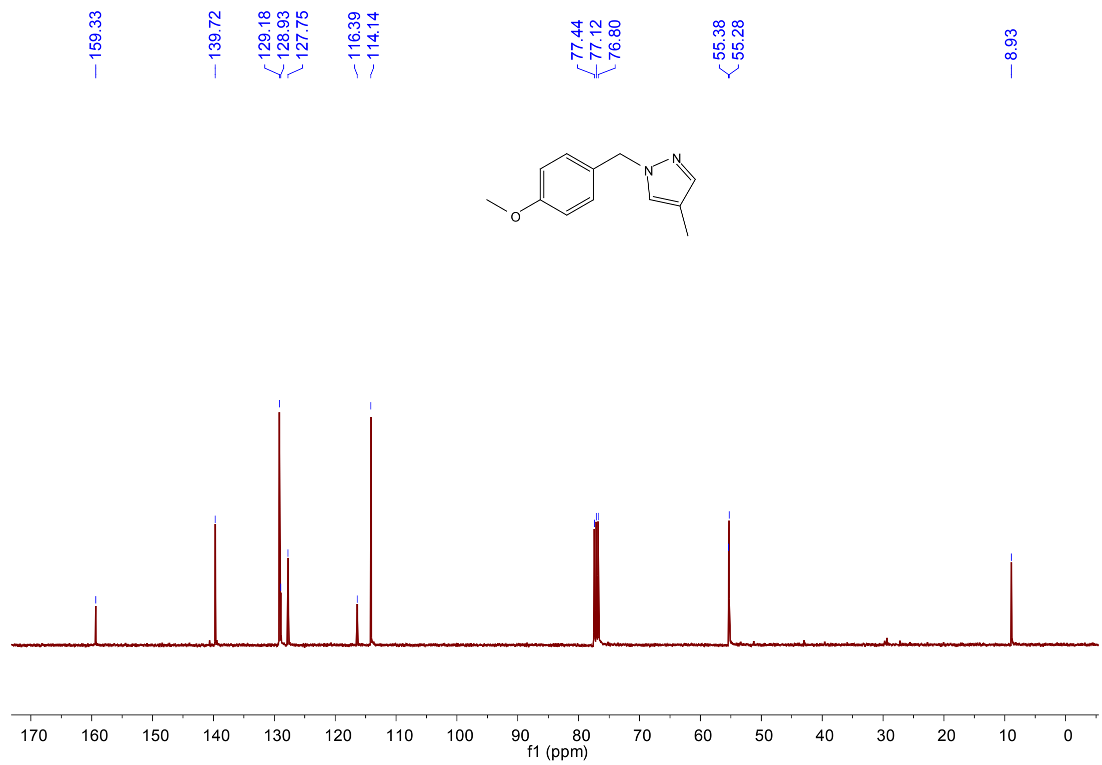


3k

^{1}H NMR for **3k** (400 MHz, $CDCl_3$)

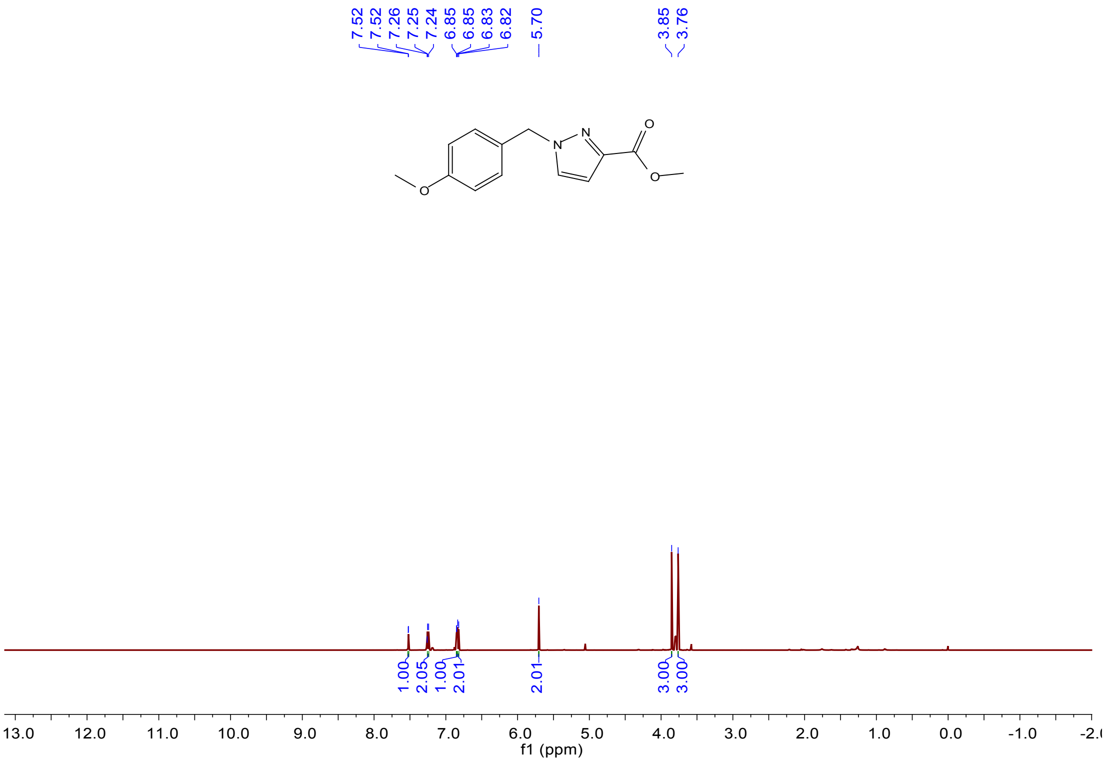


^{13}C NMR for **3k** (101 MHz, $CDCl_3$)

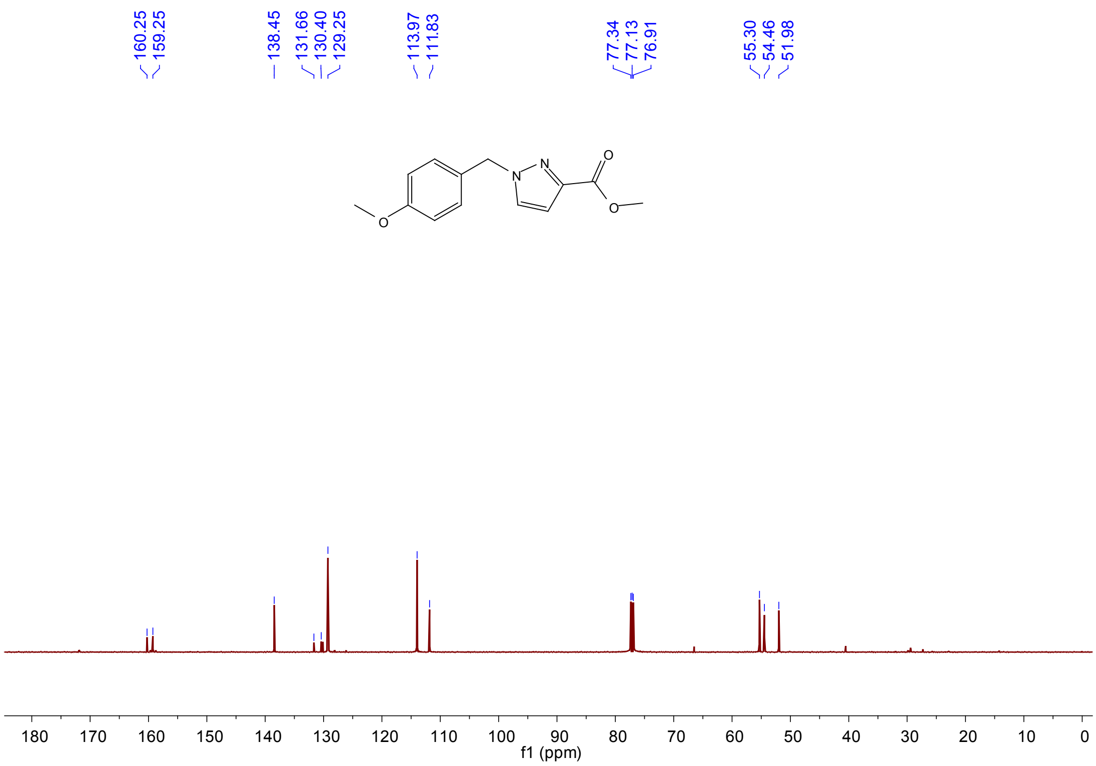


3l

^{1}H NMR for **3l** (600 MHz, $CDCl_3$)

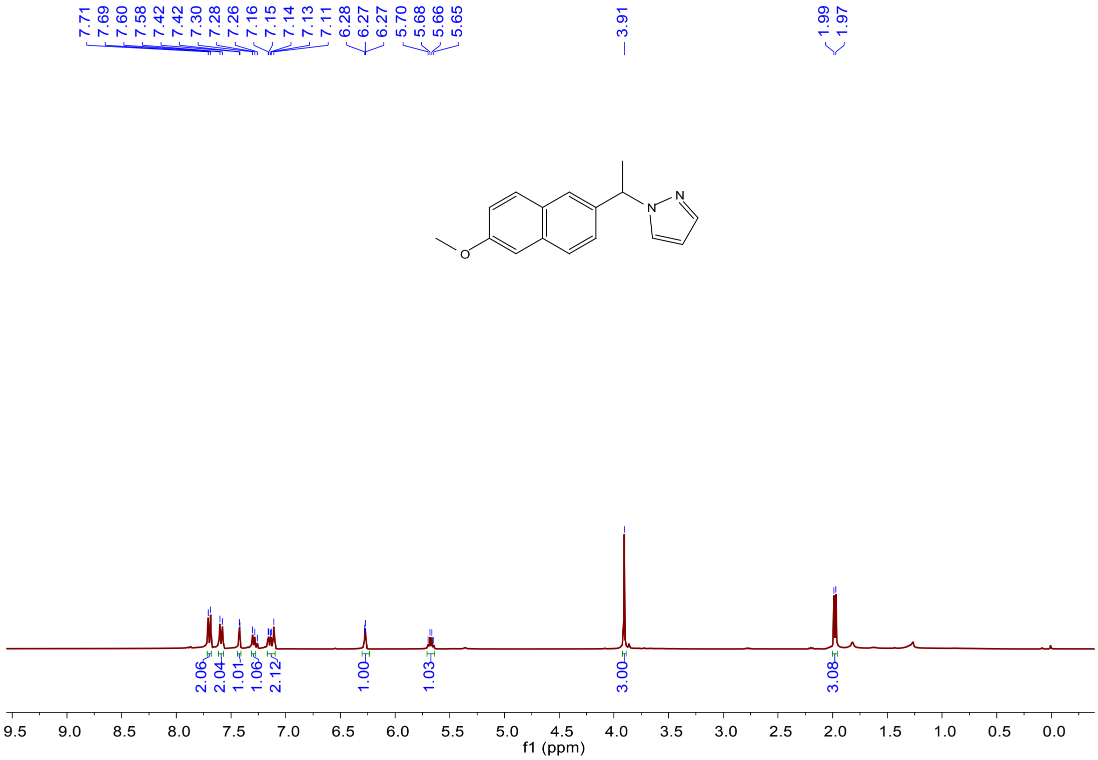


^{13}C NMR for **3l** (151 MHz, $CDCl_3$)

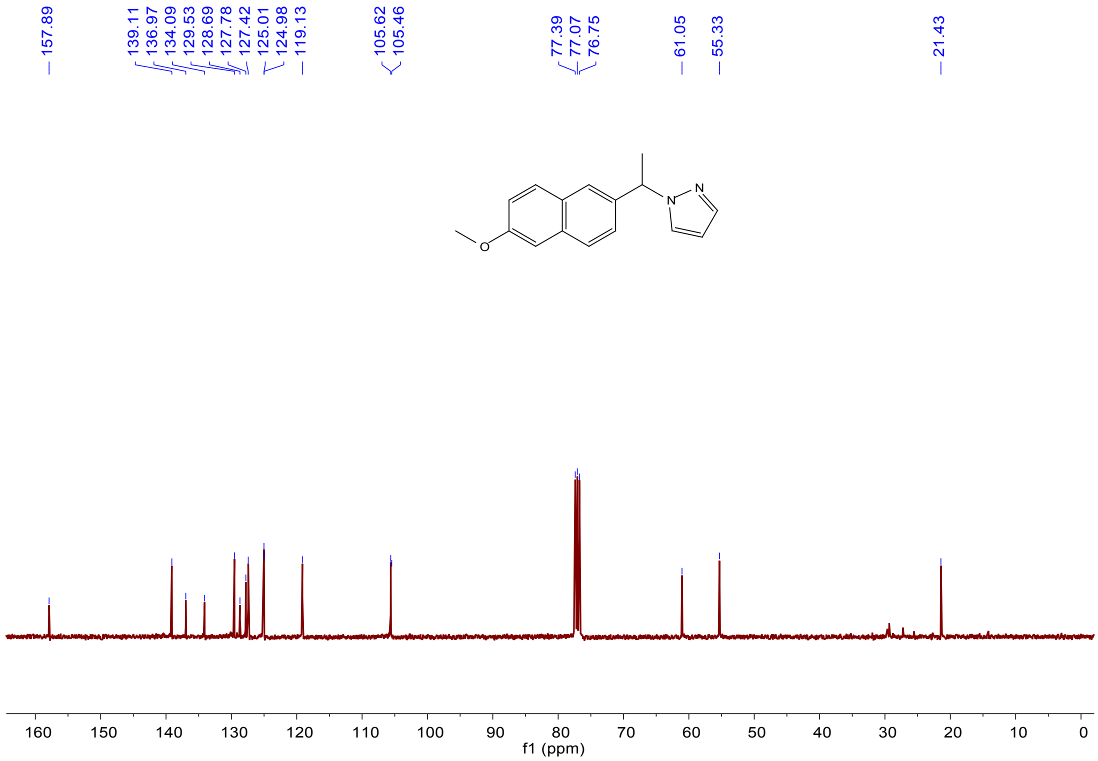


3m

^{1}H NMR for **3m** (400 MHz, $CDCl_3$)

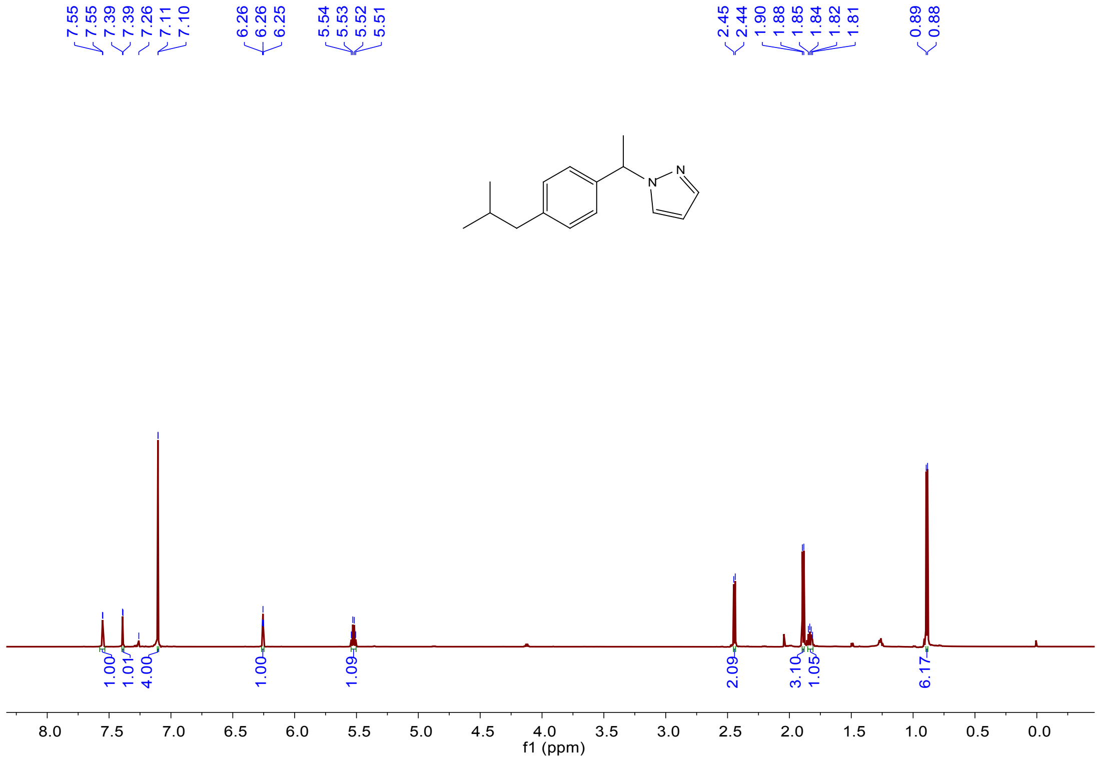


^{13}C NMR for **3m** (101 MHz, $CDCl_3$)

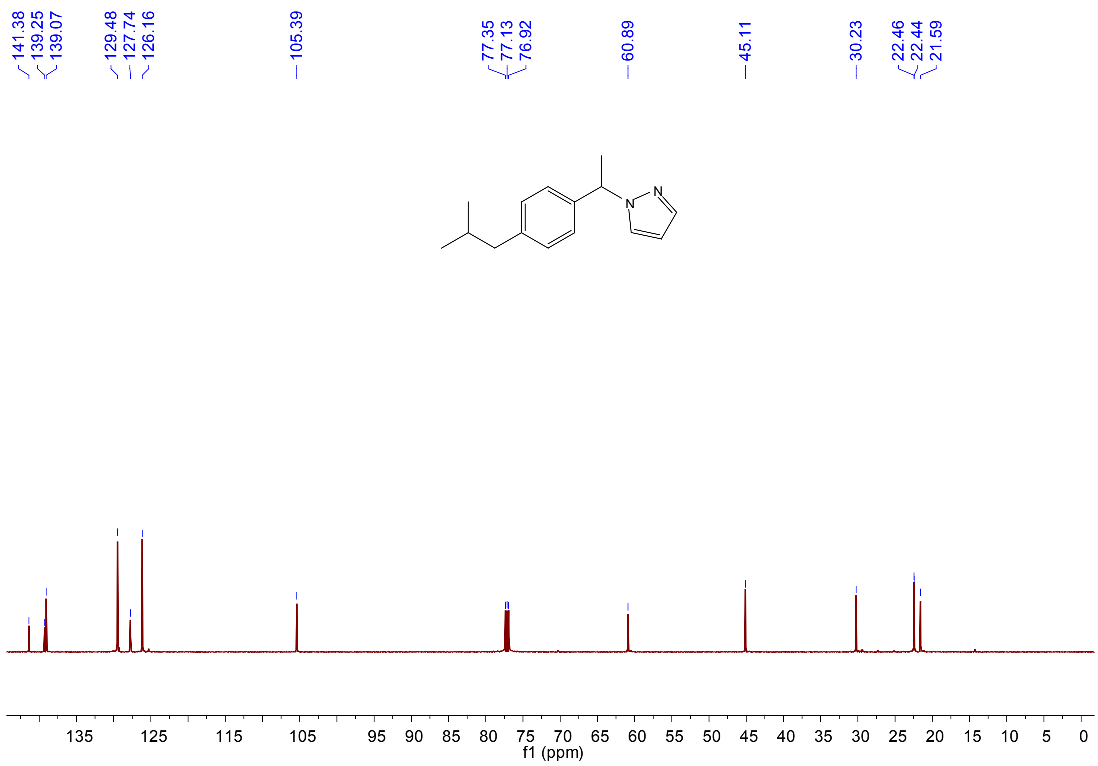


3n

[1]H NMR for **3n** (600 MHz, $CDCl_3$)

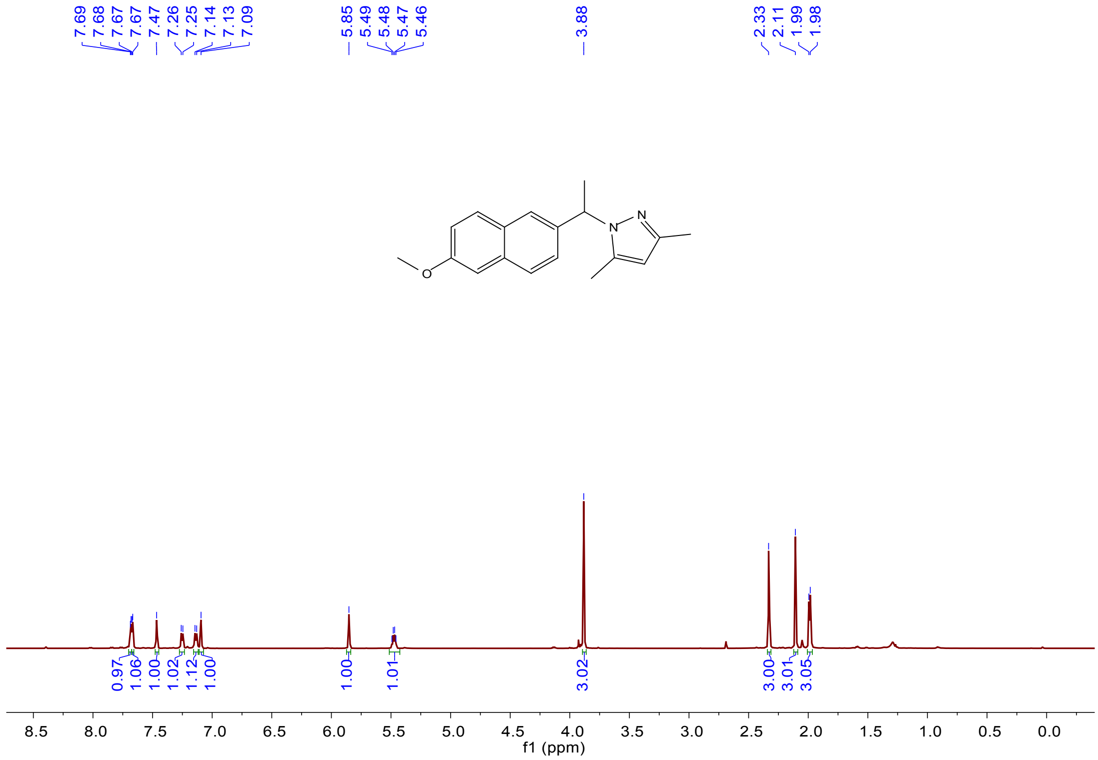


[13]C NMR for **3n** (151 MHz, $CDCl_3$)

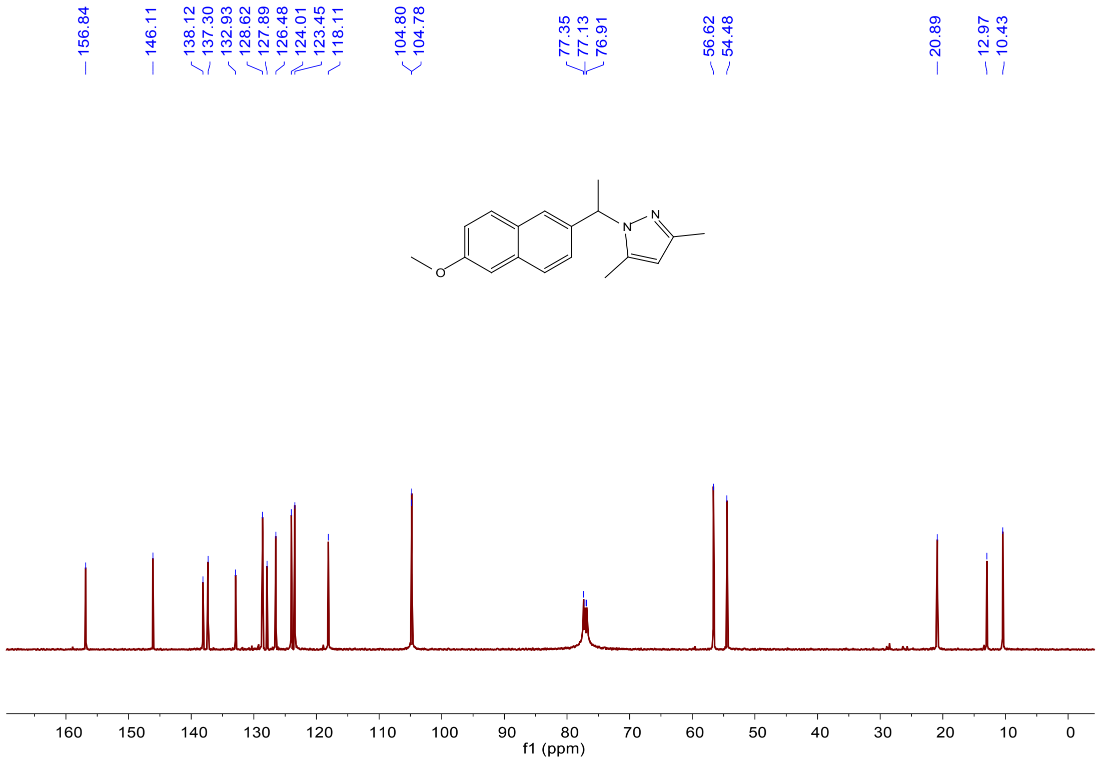


3o

^{1}H NMR for **3o** (600 MHz, $CDCl_3$)

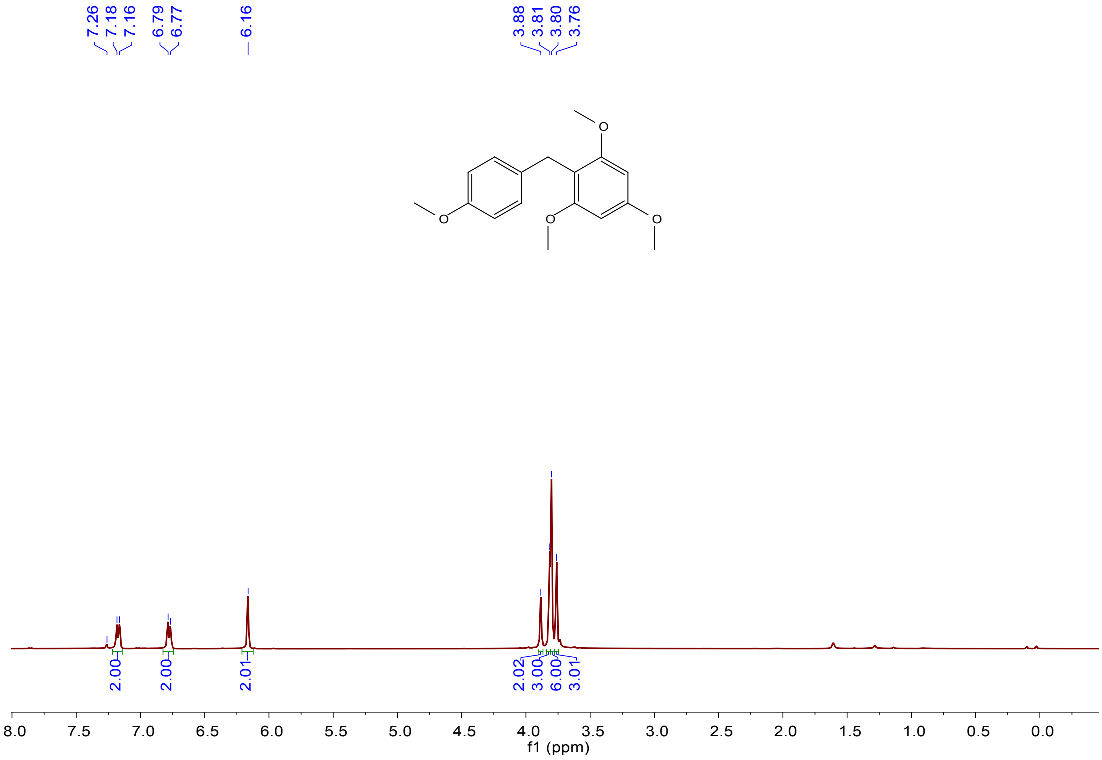


^{13}C NMR for **3o** (151 MHz, $CDCl_3$)

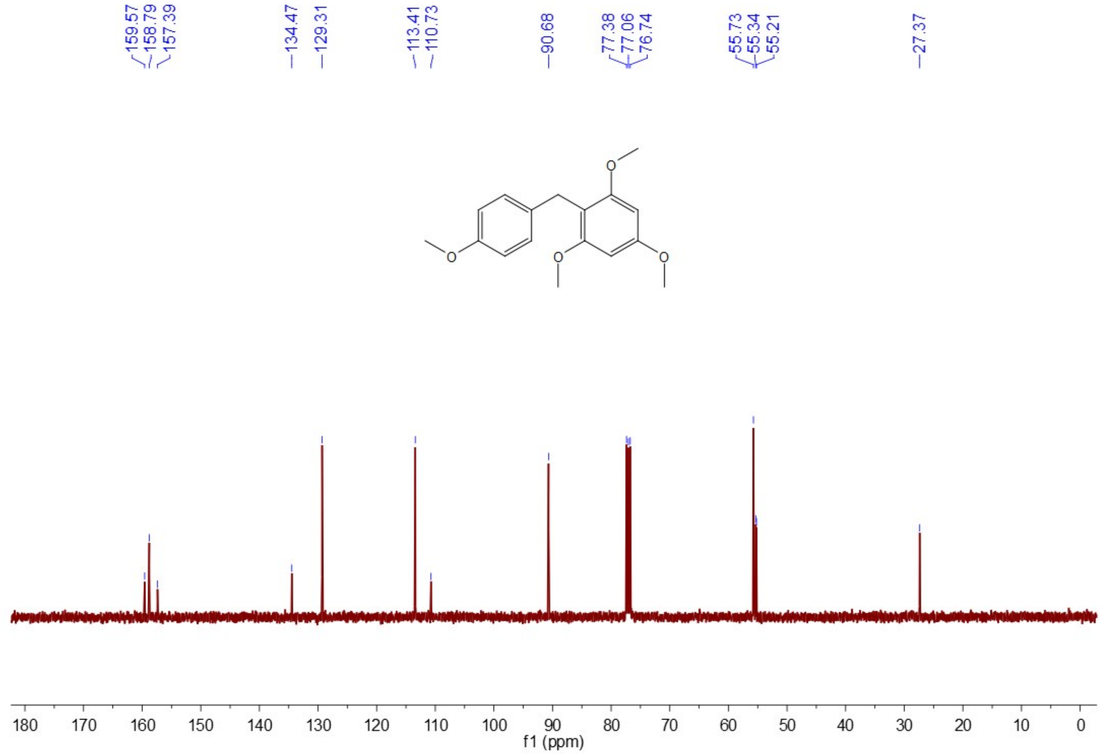


5a

^{1}H NMR for **5a** (400 MHz, $CDCl_3$)

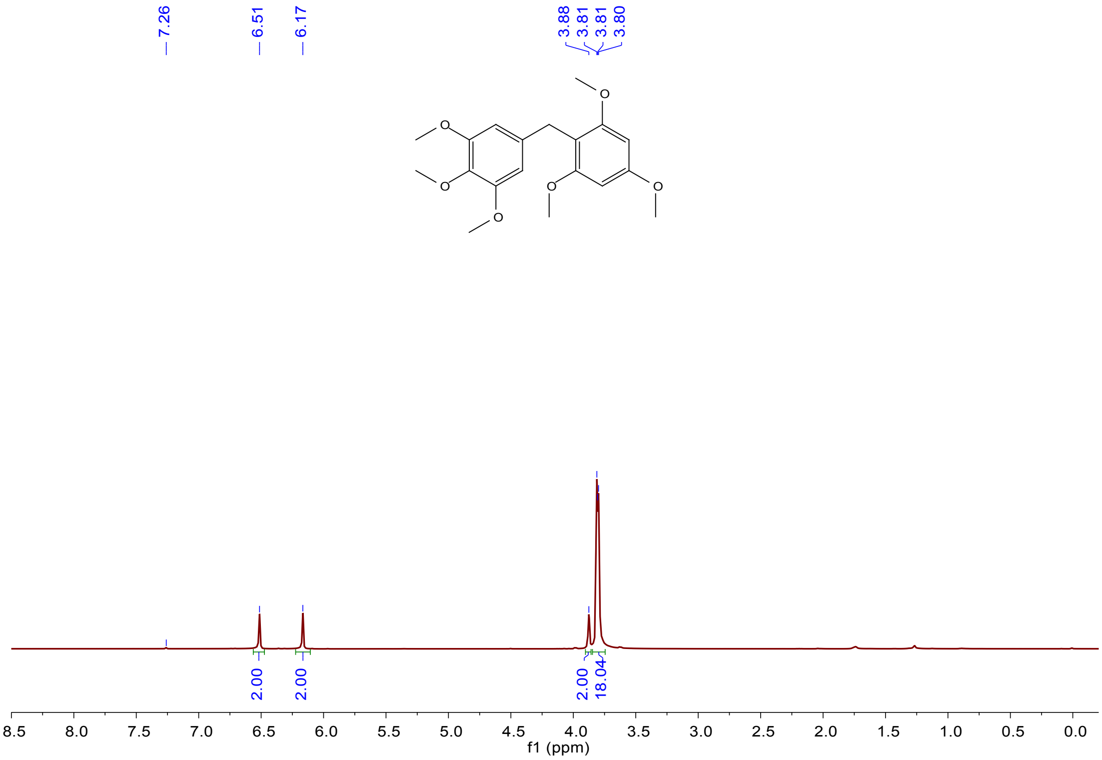


^{13}C NMR for **5a** (101 MHz, $CDCl_3$)

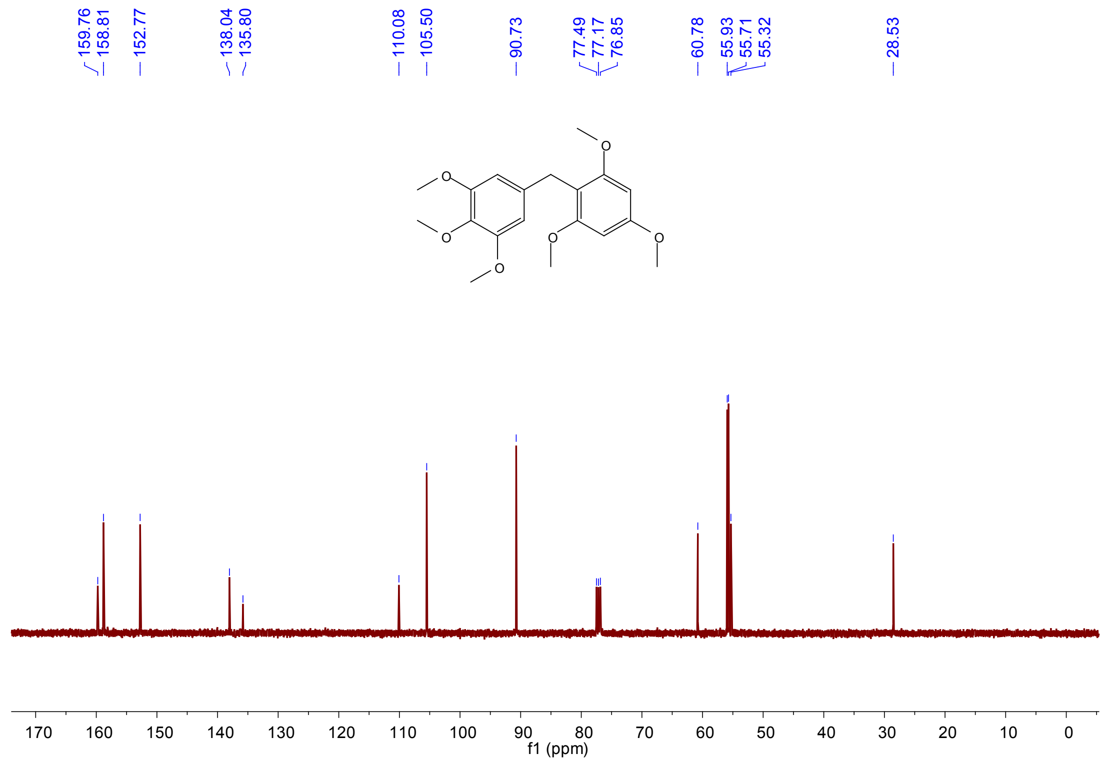


5b

[1]H NMR for **5b** (400 MHz, $CDCl_3$)

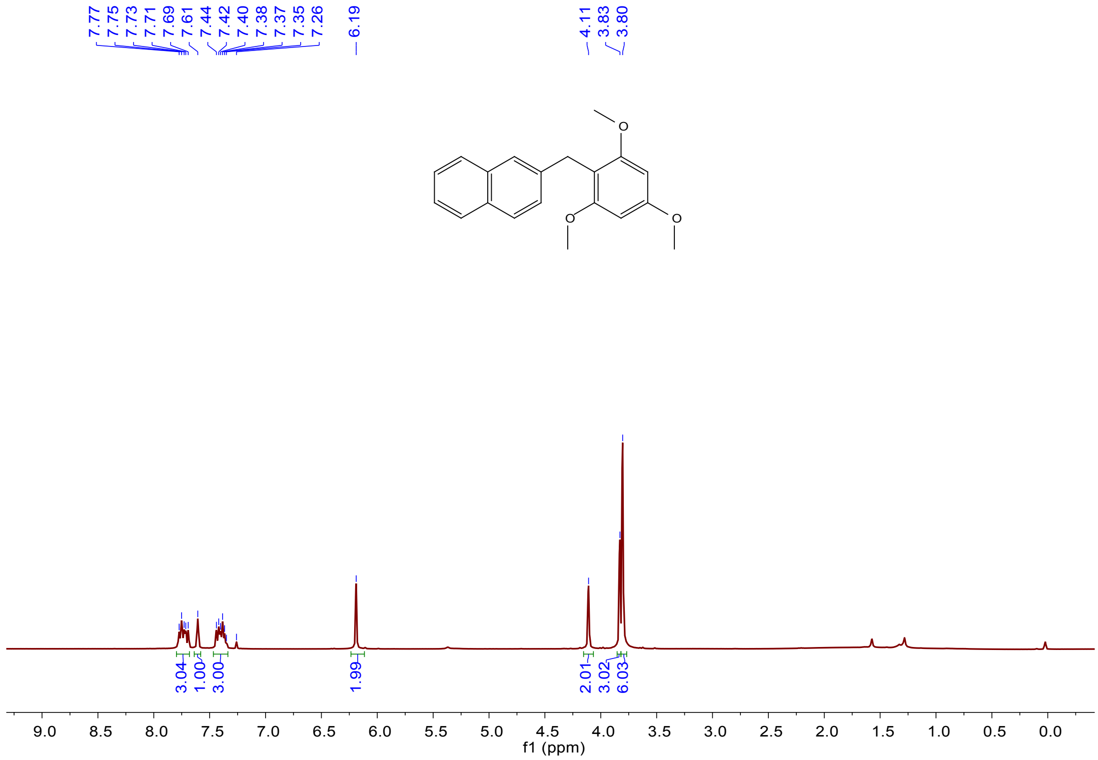


[13]C NMR for **5b** (101 MHz, $CDCl_3$)

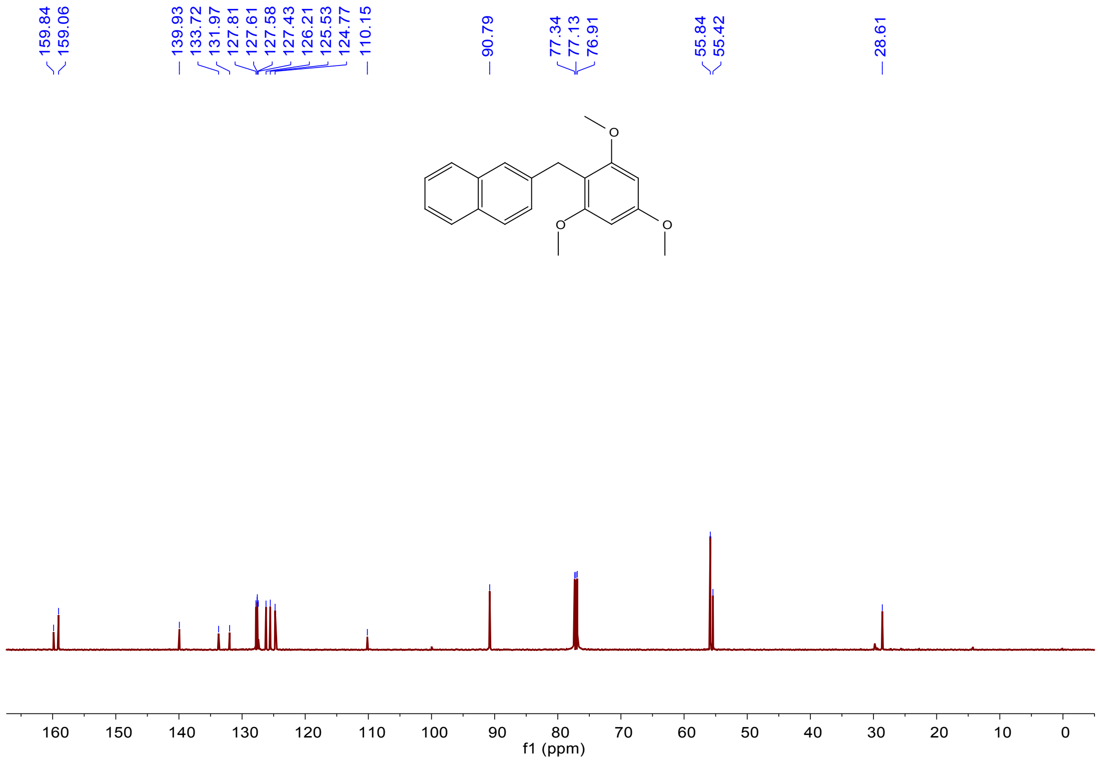


5c

[1]H NMR for **5c** (400 MHz, $CDCl_3$)

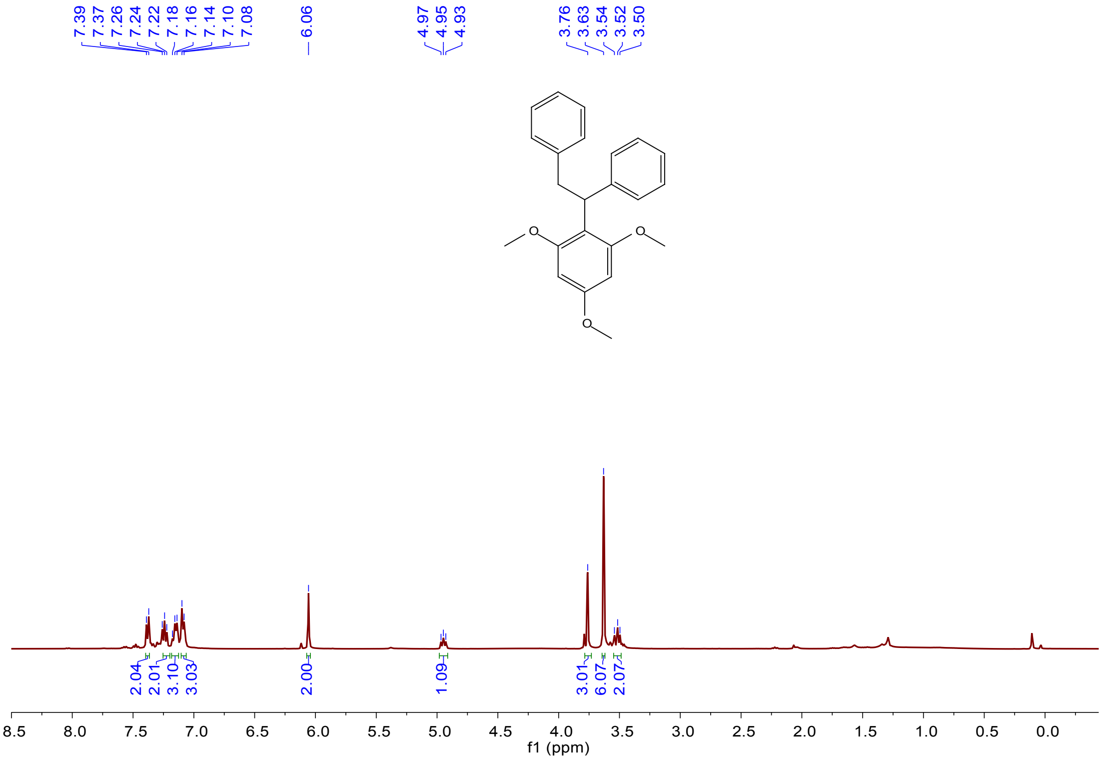


[13]C NMR for **5c** (151 MHz, $CDCl_3$)

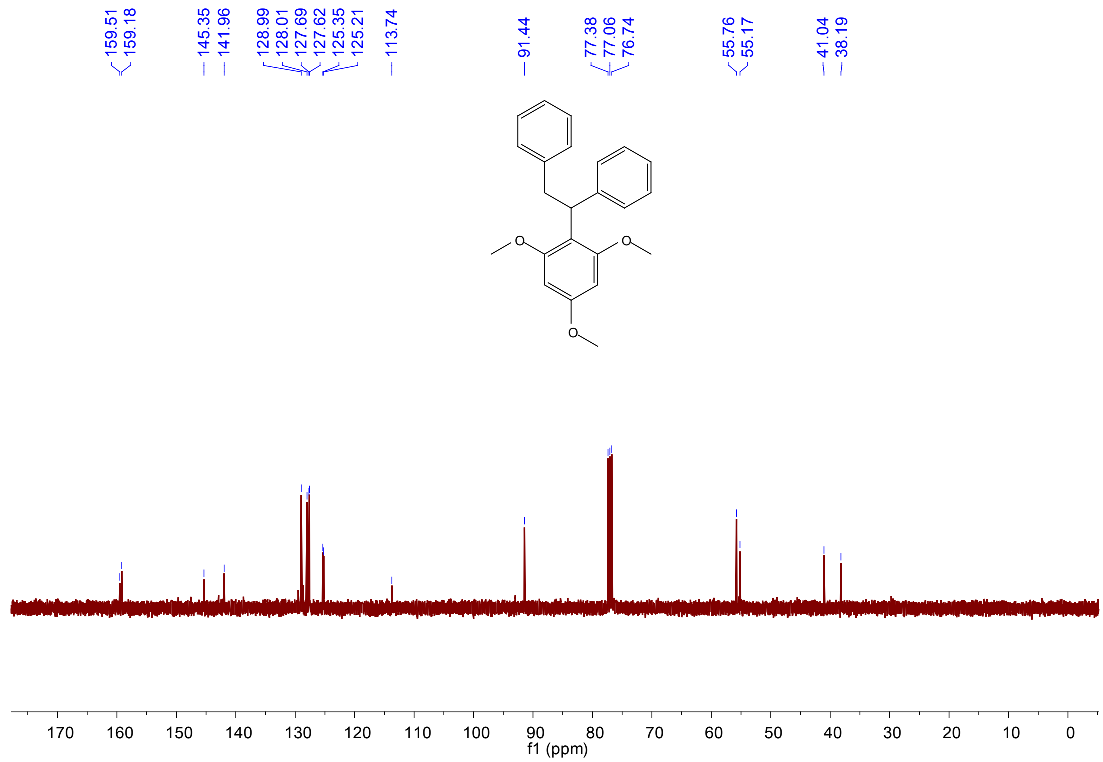


5d

^{1}H NMR for **5d** (400 MHz, $CDCl_3$)

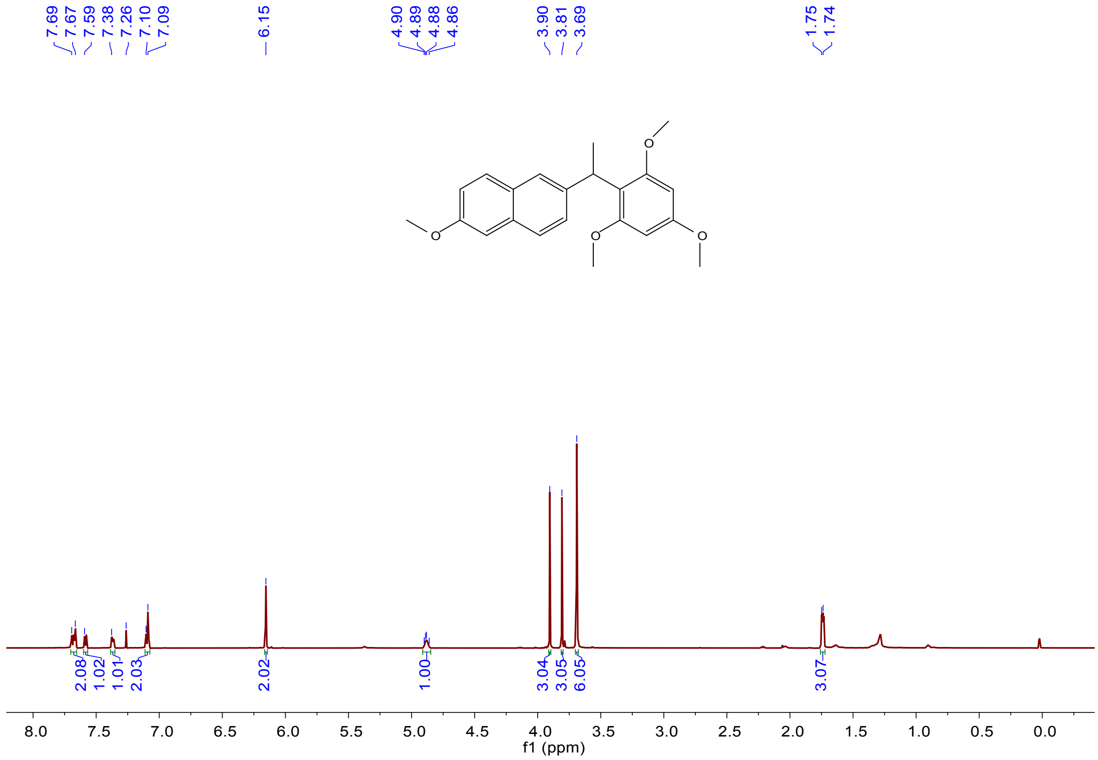


^{13}C NMR for **5d** (101 MHz, $CDCl_3$)

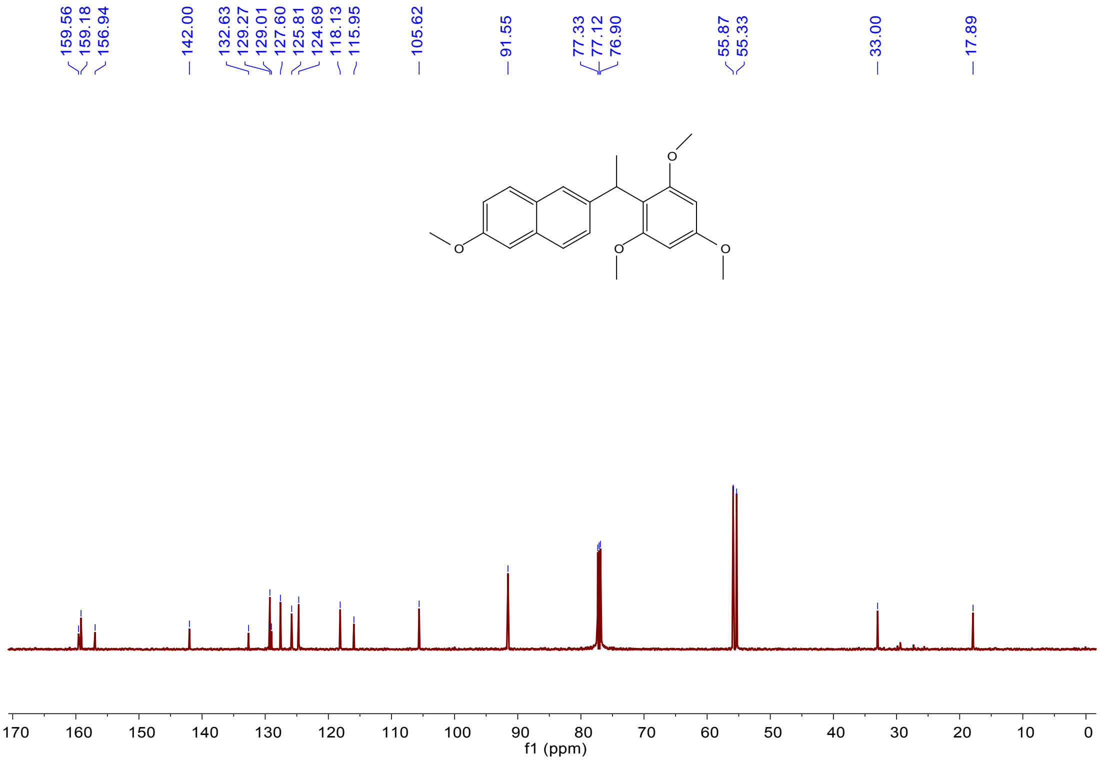


5e

[1]H NMR for **5e** (600 MHz, $CDCl_3$)

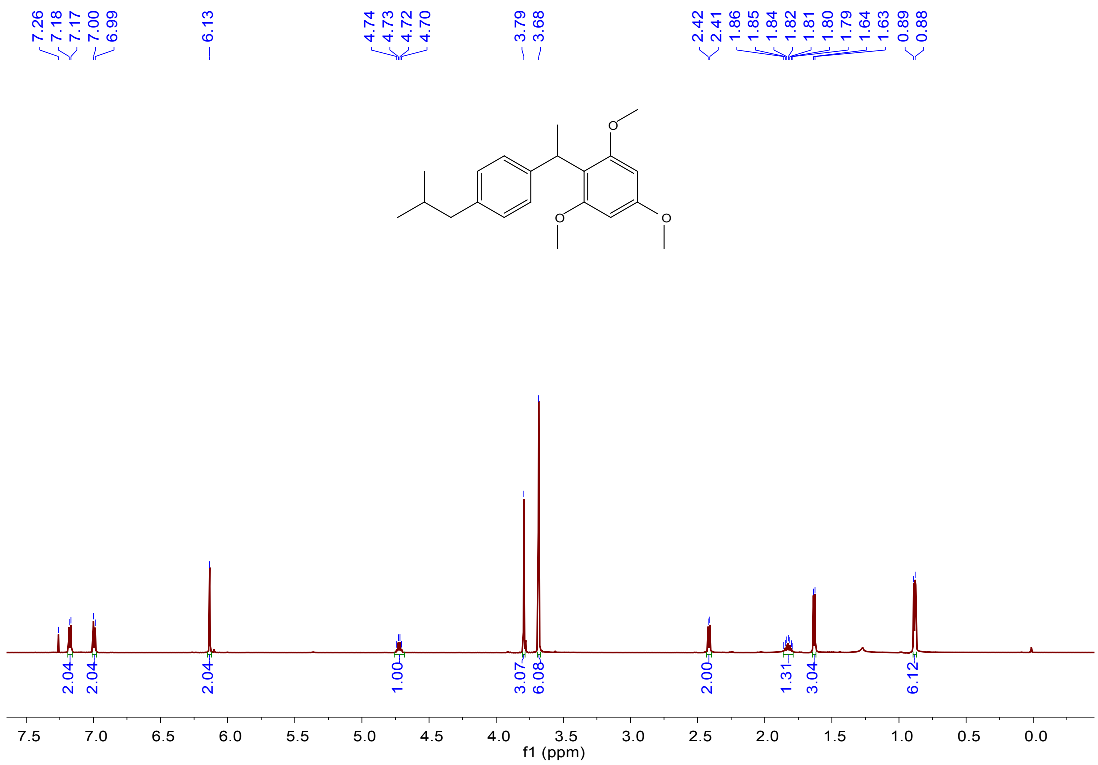


[13]C NMR for **5e** (151 MHz, $CDCl_3$)

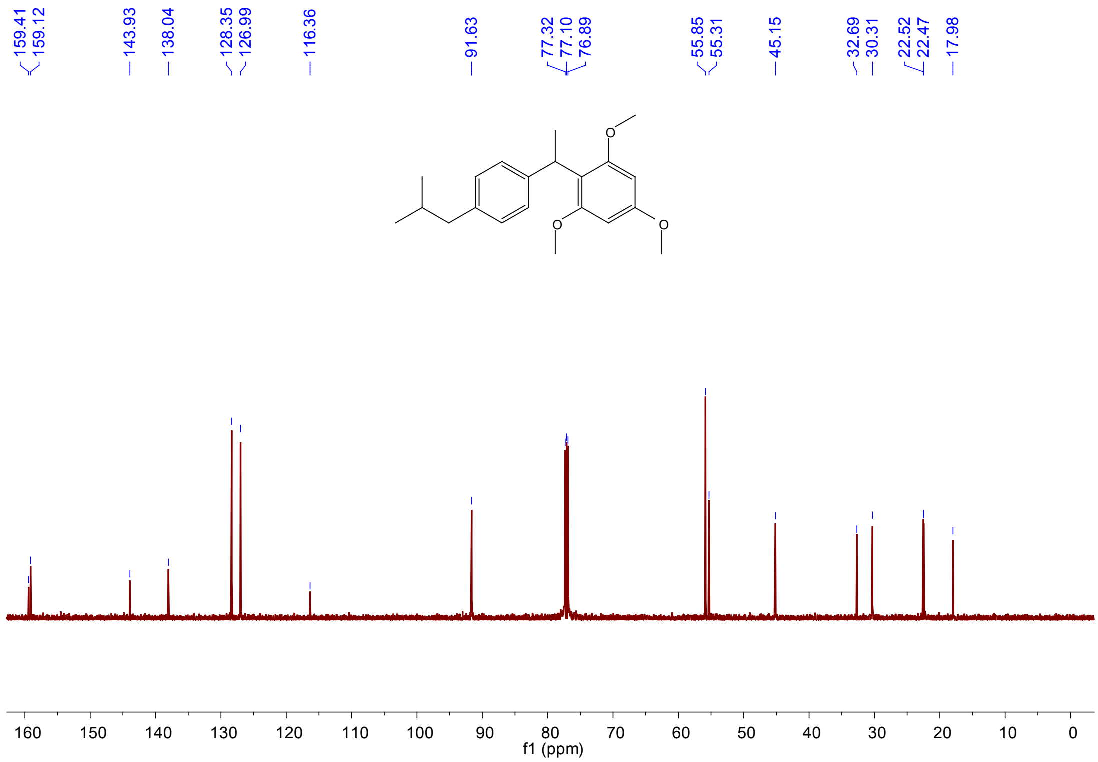


5f

^{1}H NMR for **5f** (600 MHz, $CDCl_3$)

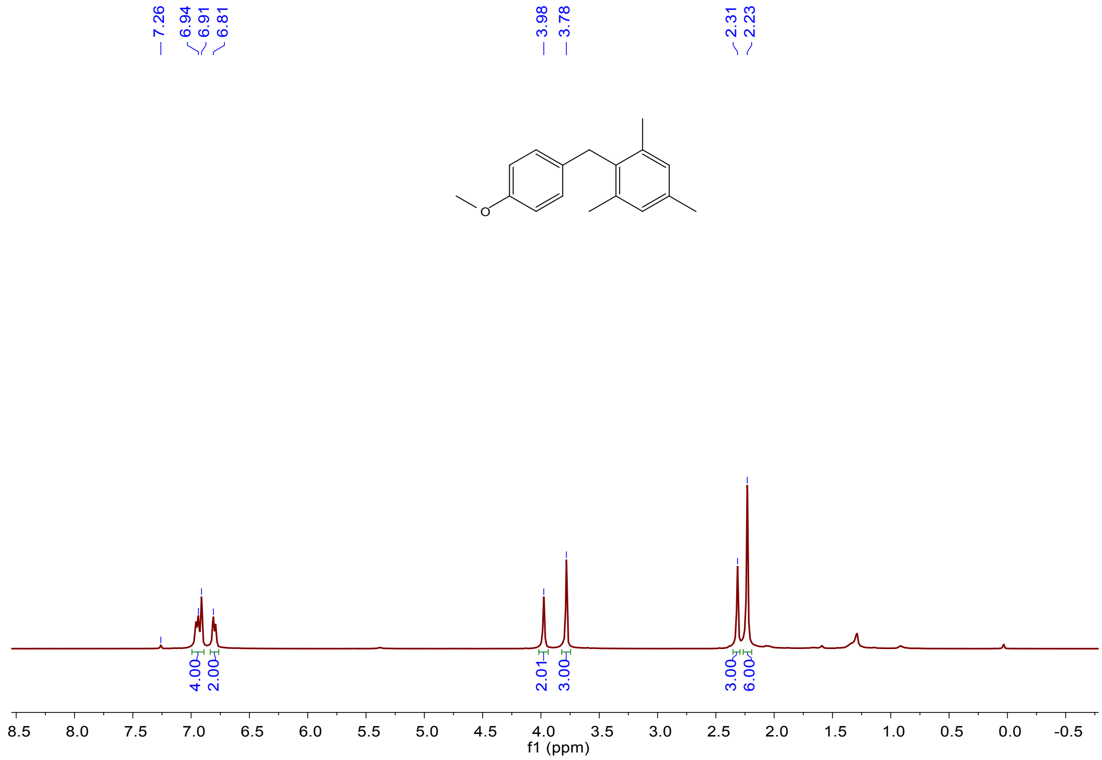


^{13}C NMR for **5f** (151 MHz, $CDCl_3$)

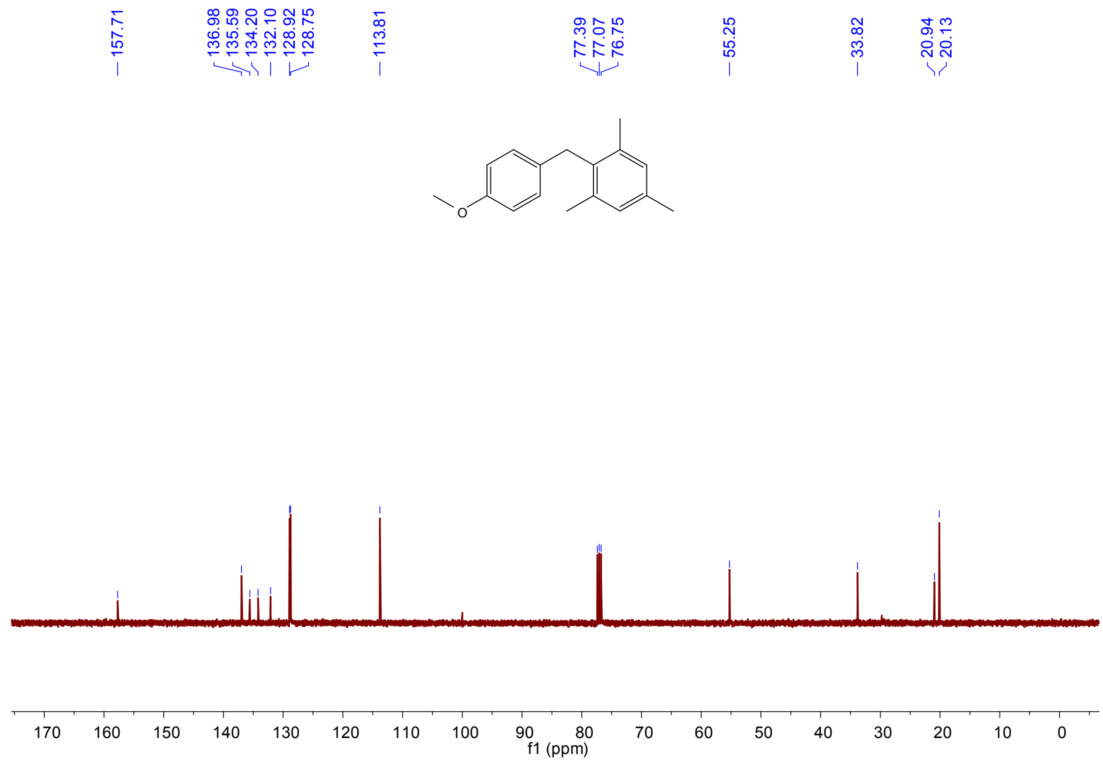


5g

^{1}H NMR for **5g** (400 MHz, $CDCl_3$)

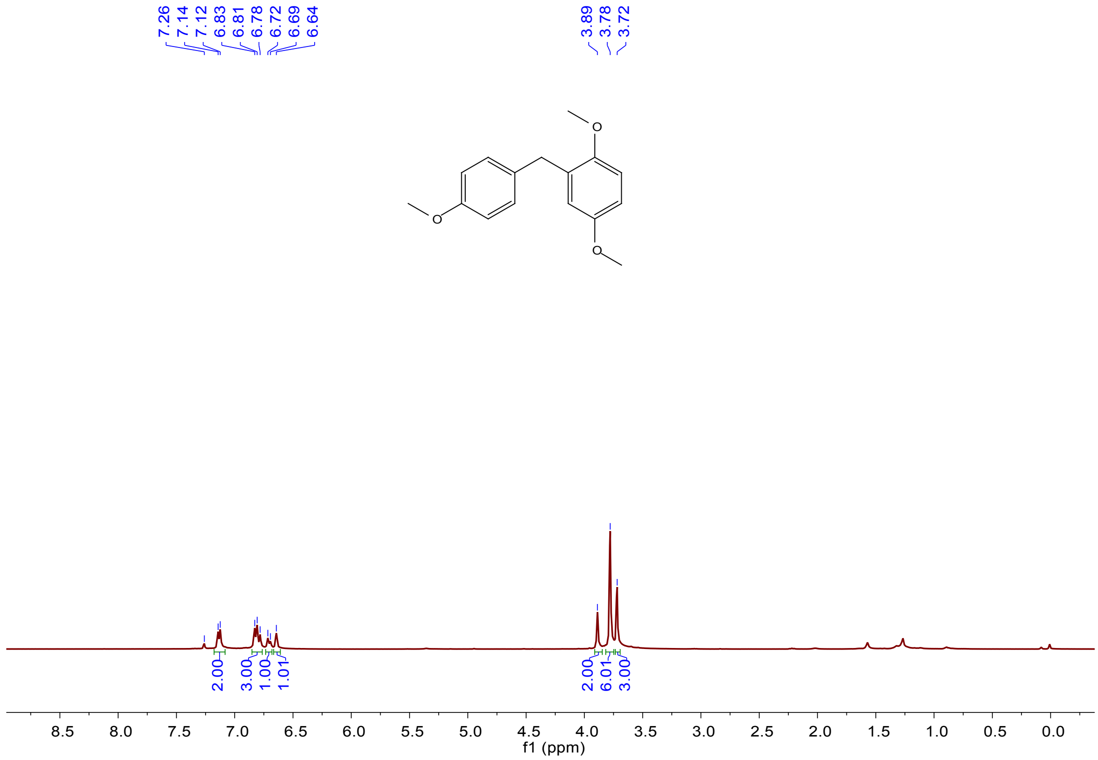


^{13}C NMR for **5g** (101 MHz, $CDCl_3$)

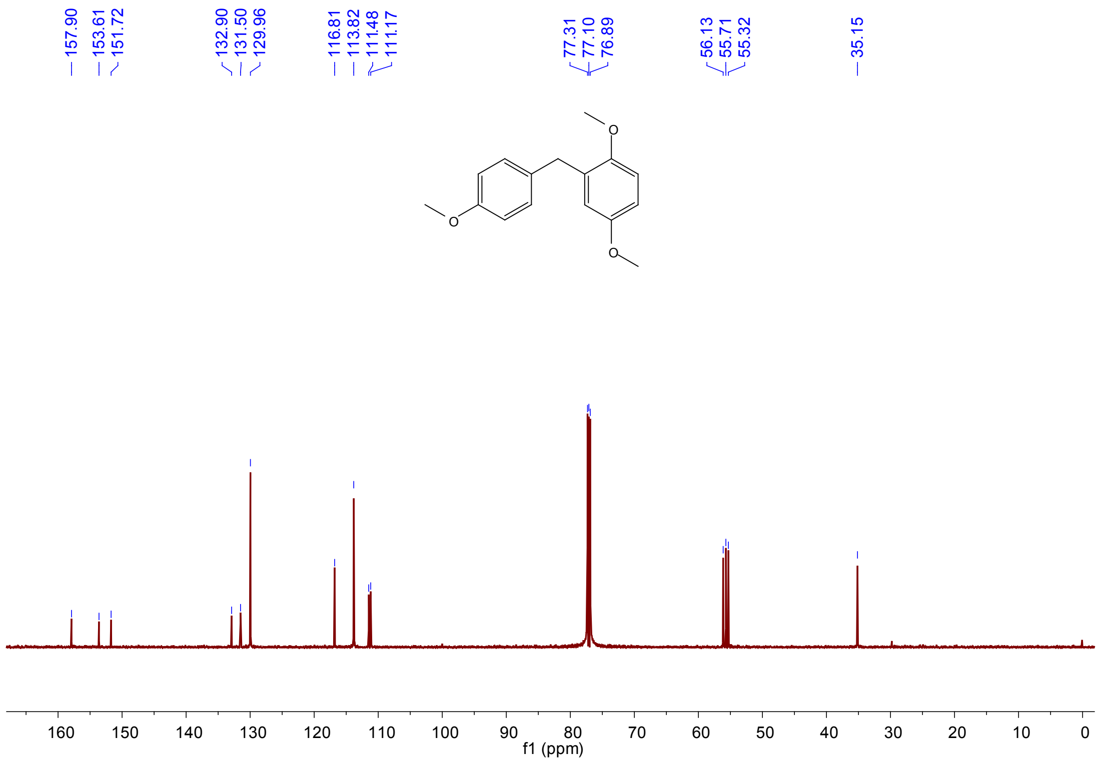


5h

^{1}H NMR for **5h** (400 MHz, $CDCl_3$)

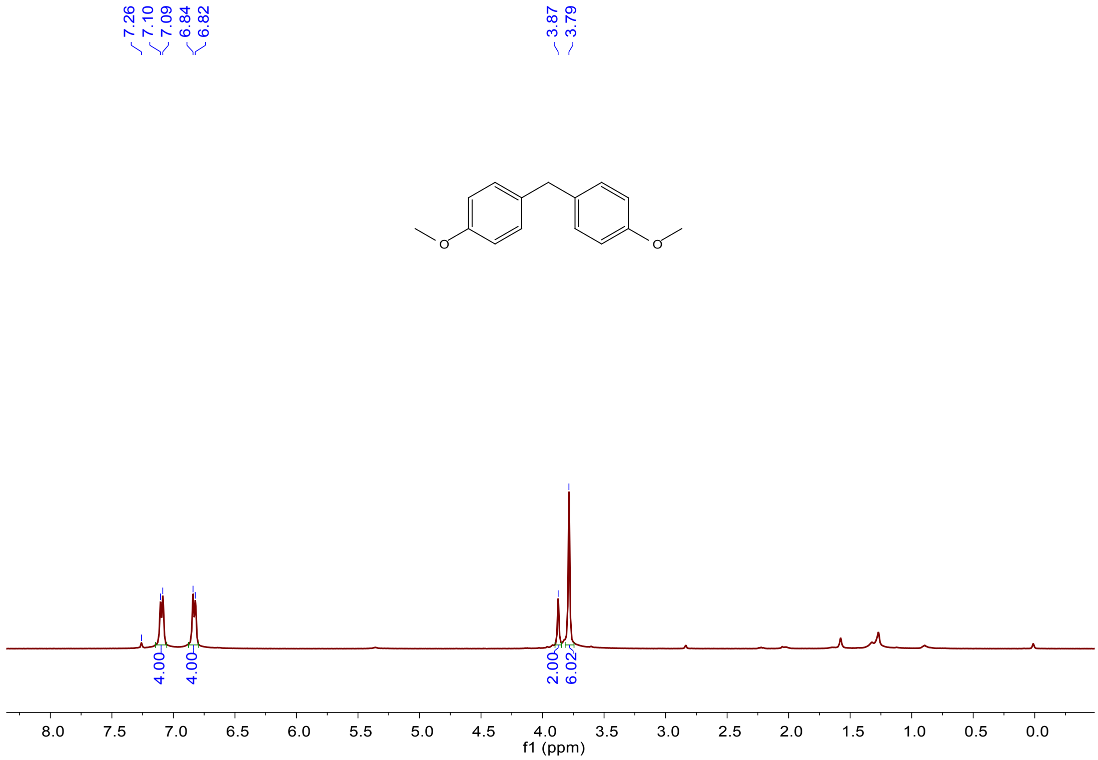


^{13}C NMR for **5h** (151 MHz, $CDCl_3$)

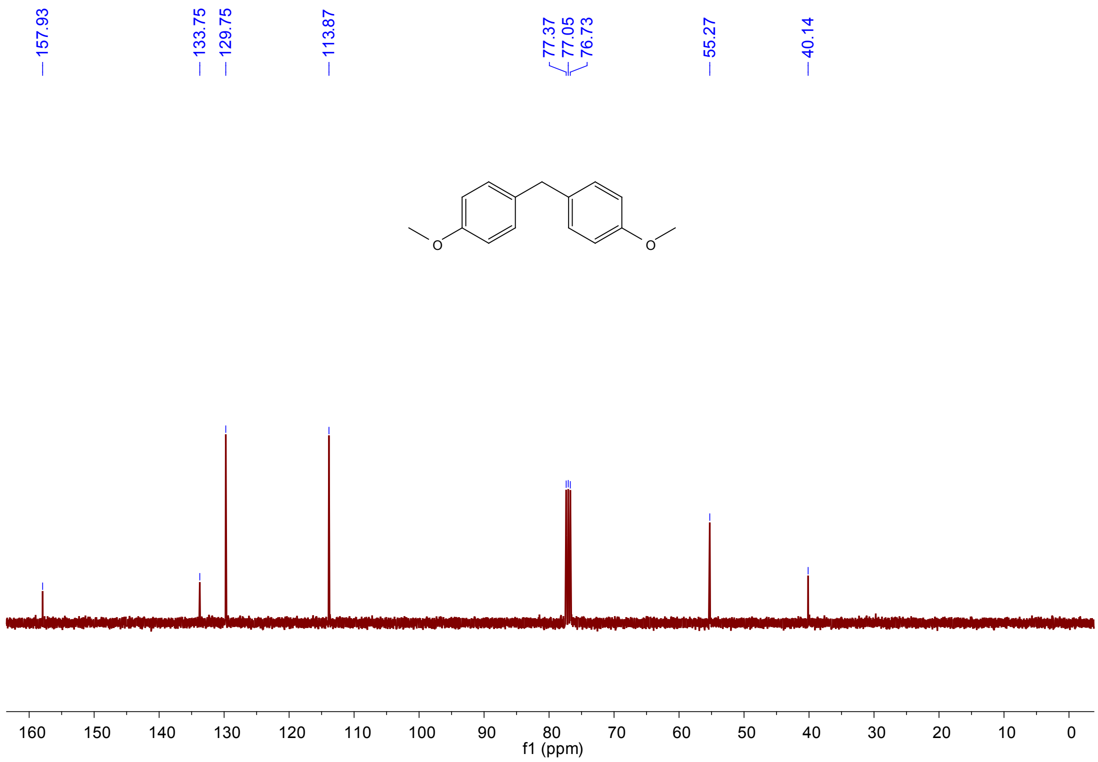


5i

^{1}H NMR for **5i** (400 MHz, $CDCl_3$)

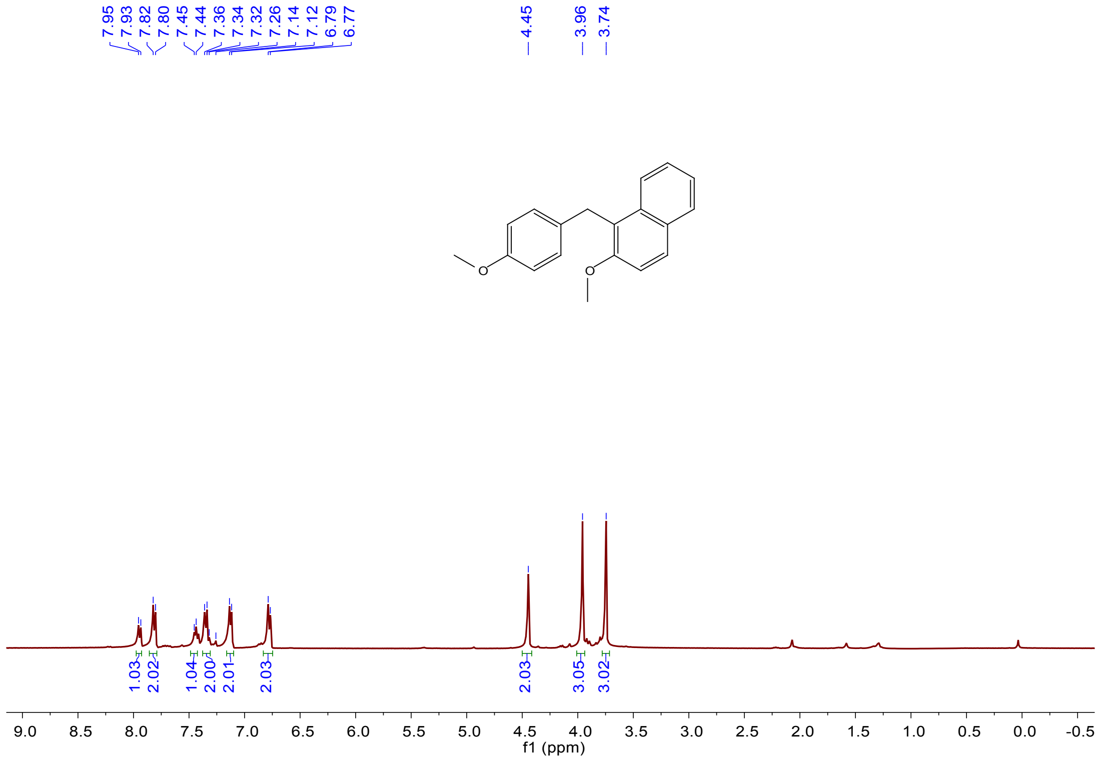


^{13}C NMR for **5i** (101 MHz, $CDCl_3$)

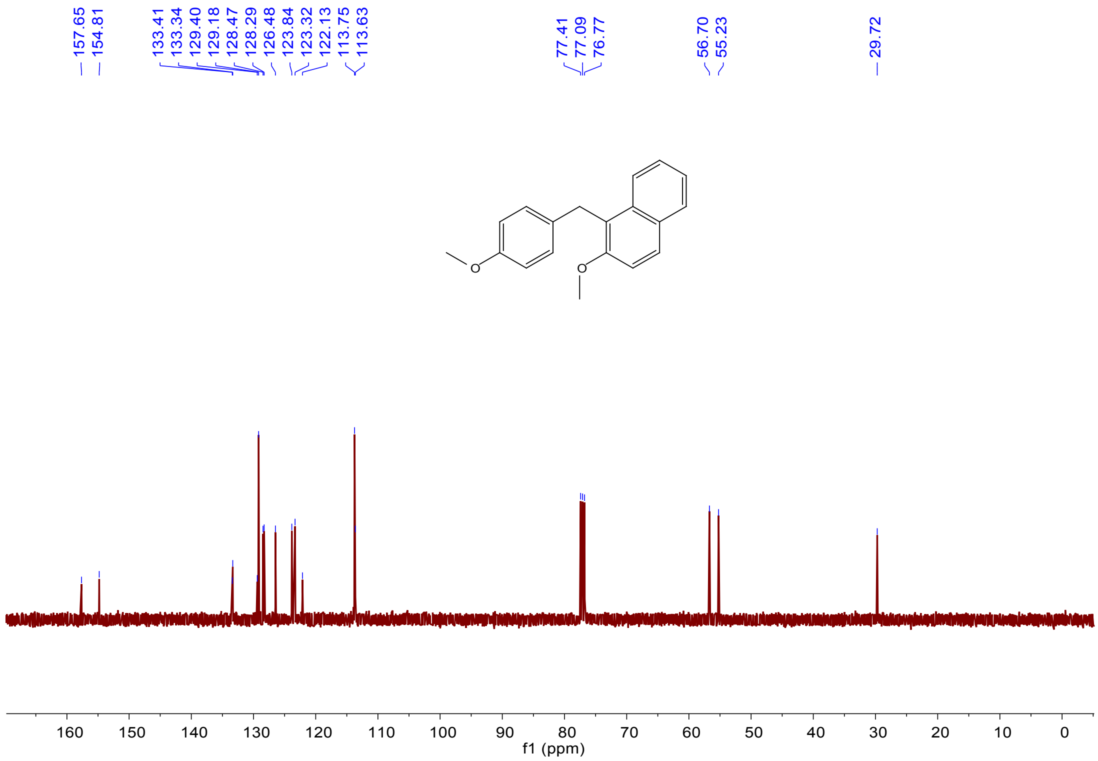


5j

^{1}H NMR for **5j** (400 MHz, $CDCl_3$)

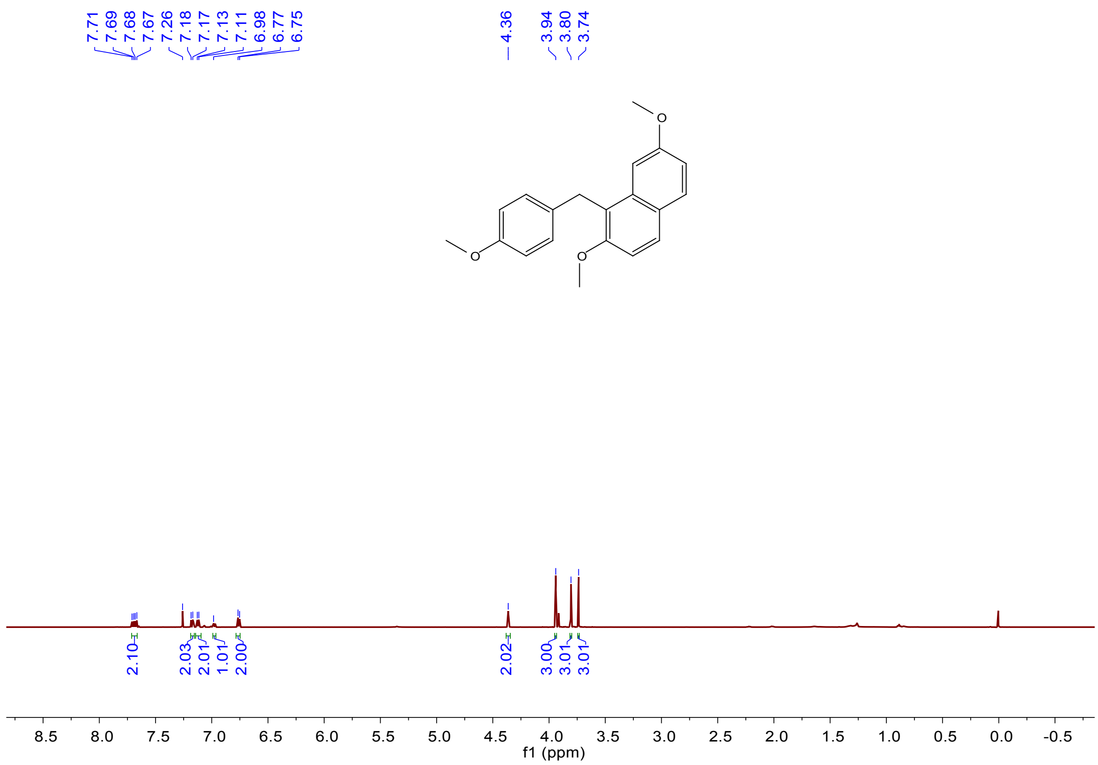


^{13}C NMR for **5j** (101 MHz, $CDCl_3$)

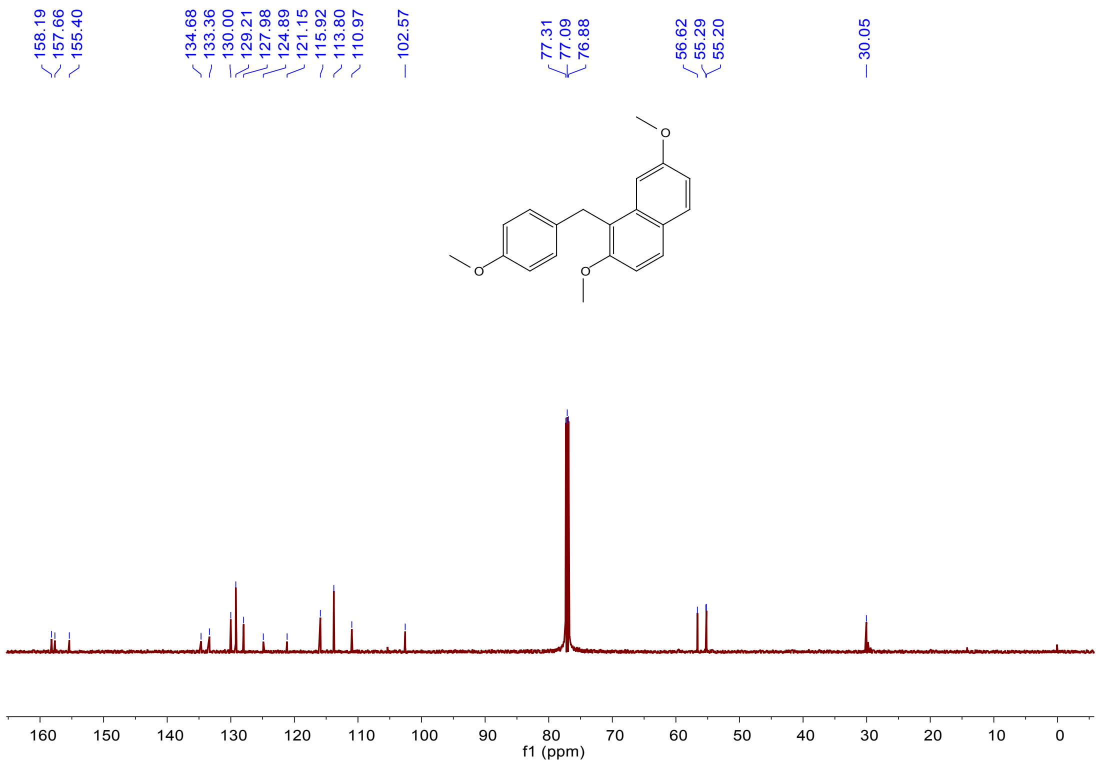


5k

[1]H NMR for **5k** (600 MHz, $CDCl_3$)

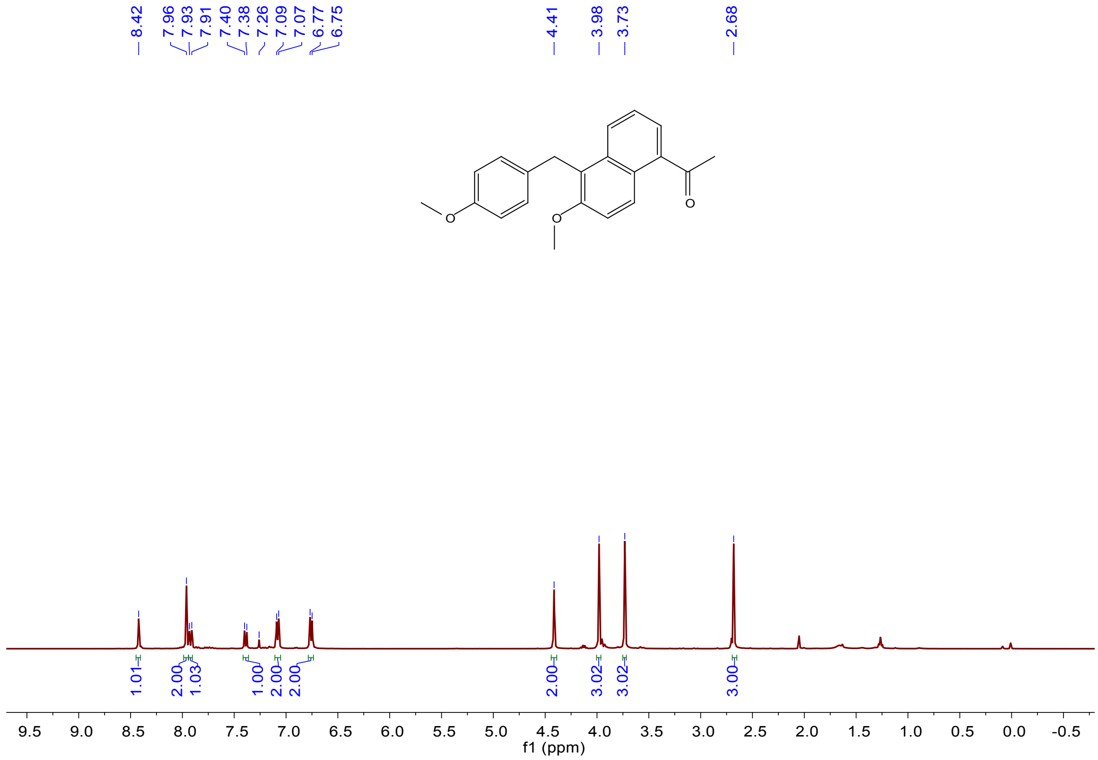


[13]C NMR for **5k** (151 MHz, $CDCl_3$)

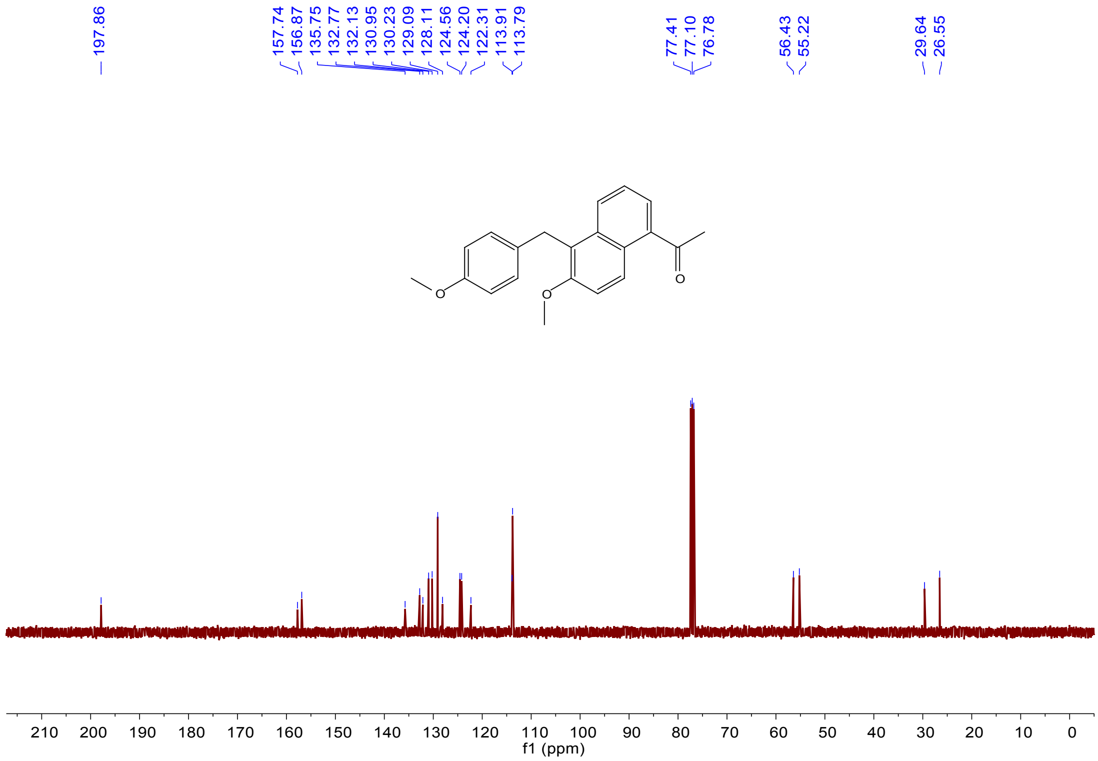


5l

[1]H NMR for **5l** (400 MHz, $CDCl_3$)

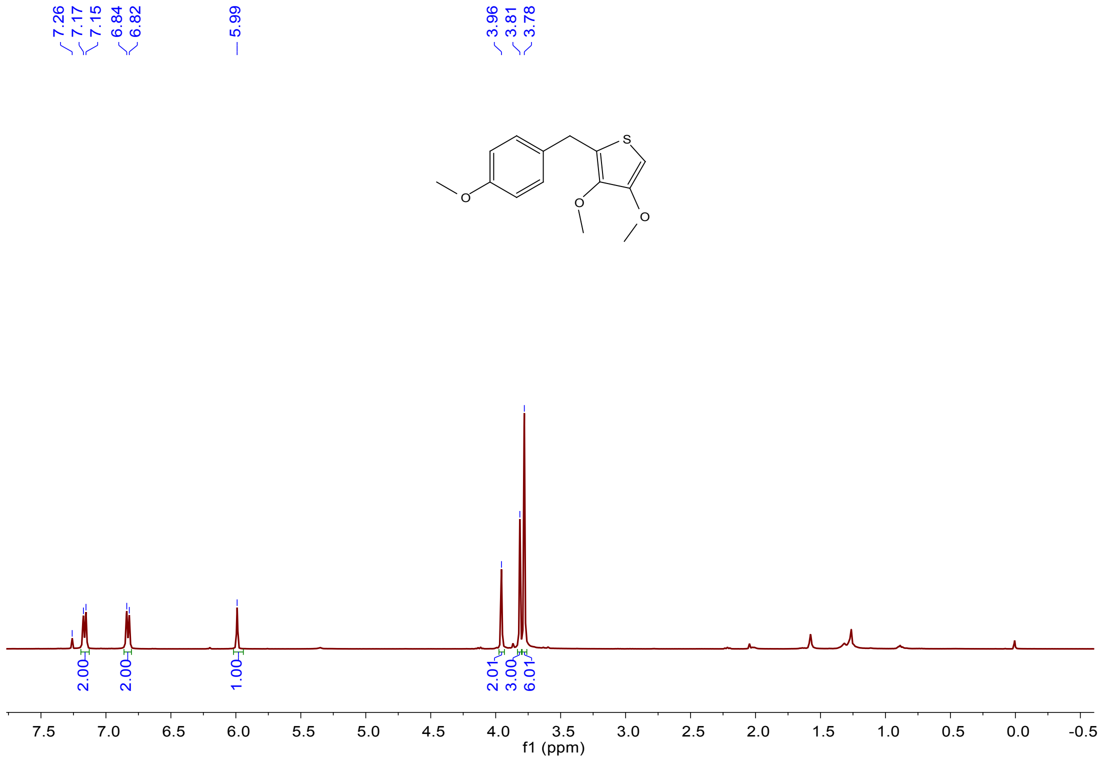


[13]C NMR for **5l** (101 MHz, $CDCl_3$)

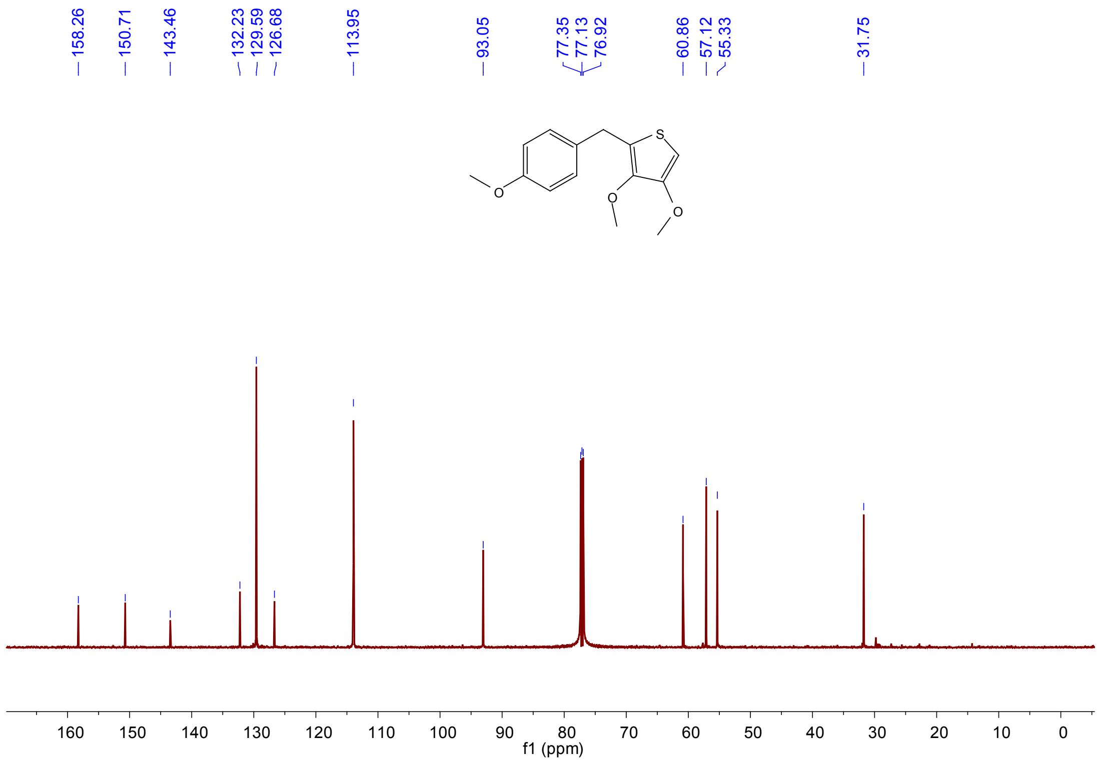


5m

^{1}H NMR for **5m** (400 MHz, $CDCl_3$)

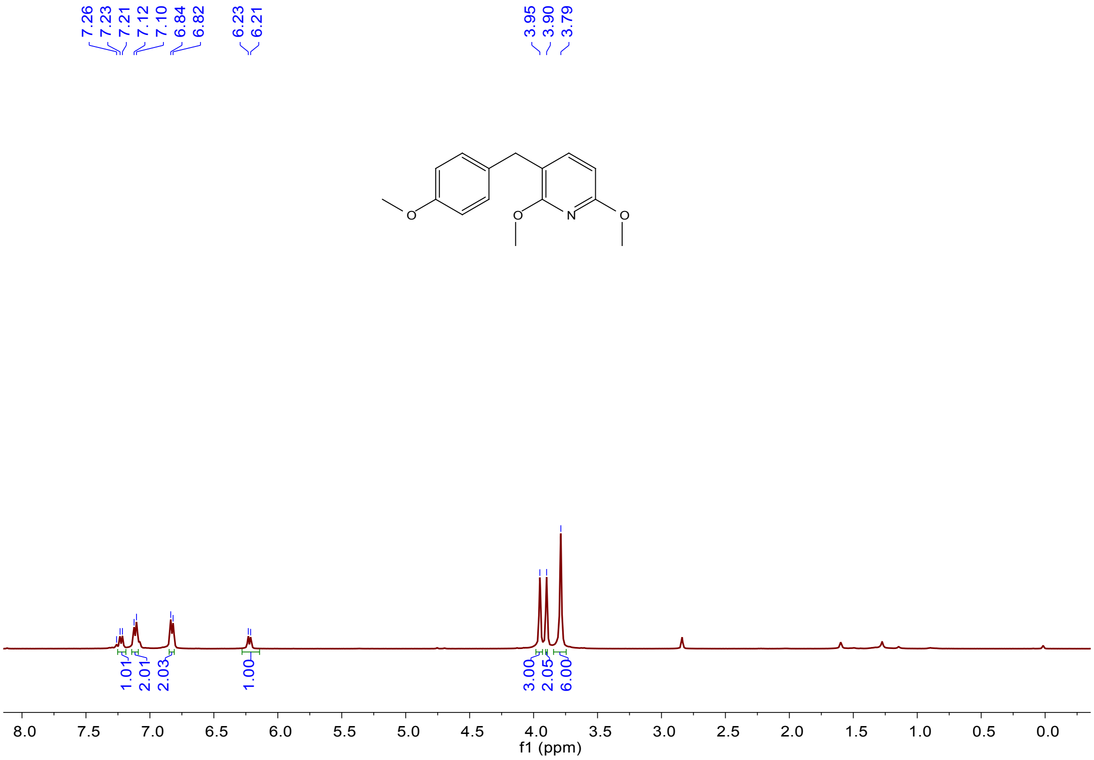


^{13}C NMR for **5m** (151 MHz, $CDCl_3$)

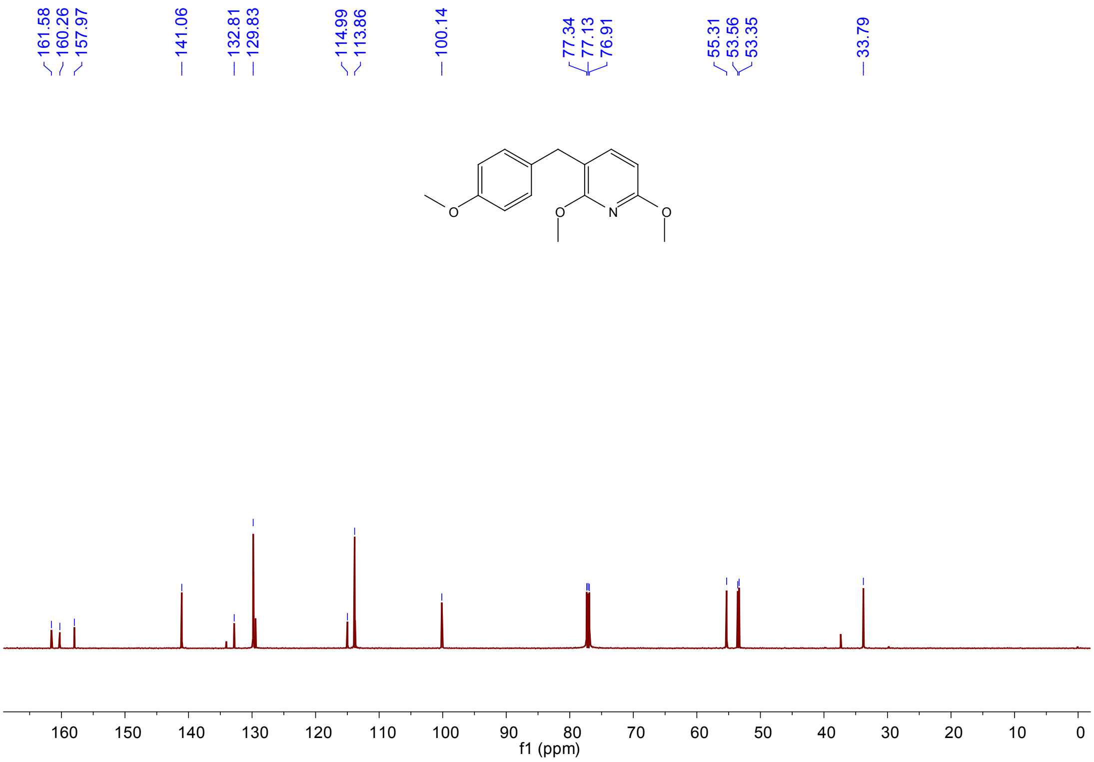


5n

^{1}H NMR for **5n** (400 MHz, $CDCl_3$)

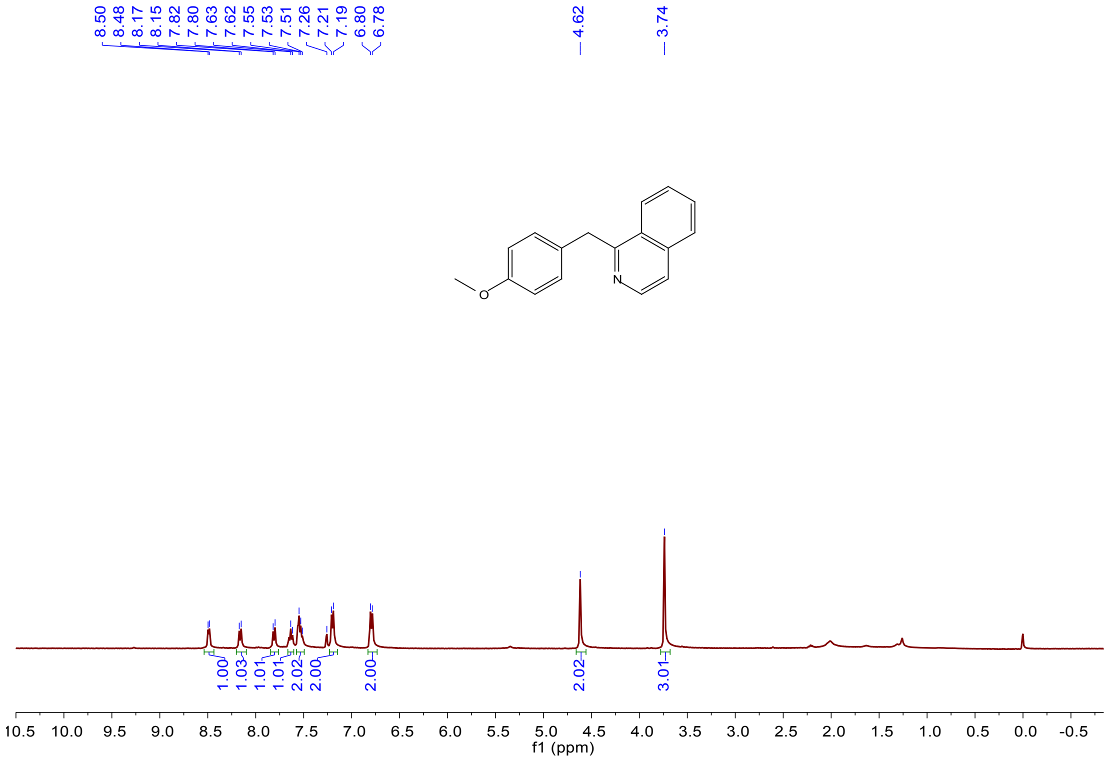


^{13}C NMR for **5n** (151 MHz, $CDCl_3$)



5o

^{1}H NMR for **5o** (400 MHz, $CDCl_3$)



^{13}C NMR for **5o** (151 MHz, $CDCl_3$)