

Supporting Information

Nickel-Catalyzed Hydrogenolysis of Unactivated Carbon-Cyano Bonds

Tuhin Patra, Soumitra Agasti, Atanu Modak and Debabrata Maiti*

Department of Chemistry, Indian Institute of Technology Bombay
Powai, Mumbai-400076, India
dmaiti@chem.iitb.ac.in

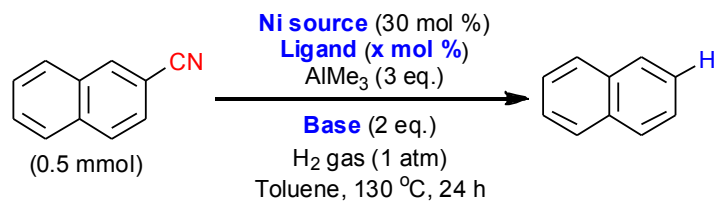
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General considerations:

Reagents. All the solvents were bought from Merck and dried using standard drying techniques before use. Dry toluene was obtained by passage through alumina and further distilled with sodium wire by using benzophenone as indicator and was purged with hydrogen gas for 1 h before use. All cyanides and ligands were bought from Aldrich and used as received. Ni(acac)₂, Ni(COD)₂ and PCy₃ were bought from Aldrich and stored under nitrogen in a vacuum atmosphere glovebox. All other reagents were purchased from commercial sources and used as received. For column chromatography silica gel (60-120 mesh or 100-200 mesh) from SRL Co. was used. Gradient elution by petroleum ether/ethyl acetate mixture was performed based on Merck aluminium TLC sheets (silica gel 60F₂₅₄).

Analytical information. All isolated products were characterized by ¹H NMR, ¹³C NMR spectroscopy, Gas chromatography mass spectra (GCMS) or HRMS. Copies of the ¹H NMR and ¹³C NMR can be found in this Supporting Information. All NMR spectra were recorded on a Bruker 400 MHz instrument. All ¹H NMR spectra are reported in parts per million (ppm) downfield of TMS and were measured relative to residual CHCl₃ (7.27 ppm). All ¹³C NMR spectra were reported in ppm relative to CDCl₃ (77.23 ppm) and were obtained with proton decoupling. Coupling constants, J, were reported in Hertz. All GC analyses were performed on a Agilent 7890A GC system connected with a FID detector using a J & W DB-1 column (10 m, 0.1 mm I.D.). All GCMS analyses were done by Agilent 7890A GC system connected with 5975C inert XL EI/CI MSD (with triple axis detector).

Optimization details for hydrogenolysis of C-CN bond:^[1]

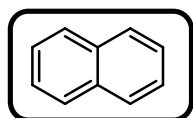


Entry	Ni source	Ligand	Ligand (mol%)	Base	GC yield (%)
1	Ni(acac) ₂	PCy ₃	60	--	35
2	Ni(acac) ₂	PCy ₃	90	--	44
3	Ni(acac) ₂	PCy ₃	90	KO ^t Bu	21
4	Ni(acac) ₂	SIPr.HCl	60	--	8
5	Ni(acac) ₂	SIPr.HCl	60	KO ^t Bu	3
6	Ni(acac) ₂		60	--	3
7	Ni(acac) ₂		60	KO ^t Bu	<1
8	Ni(acac) ₂		60	--	6
9	Ni(acac) ₂		60	KO ^t Bu	2
10	Ni(COD) ₂	PCy ₃	60	--	66
11	Ni(COD)₂	PCy₃	90	--	78
12	Ni(COD) ₂	PCy ₃	90	KO ^t Bu	41
13	Ni(COD) ₂	SIPr.HCl	60	--	11
14	Ni(COD) ₂	SIPr.HCl	60	KO ^t Bu	7

General procedure for hydrogenolysis of cyano compound using hydrogen gas.

An oven-dried screw-cap reaction tube (25 mL) was charged with 0.25 mmol of aryl cyanide and a magnetic stirbar. The reaction tube was taken inside the dry box and Ni(COD)₂ (15-30 mol%) and PCy₃ (45-90 mol%) were added. The tube was sealed and taken out from the dry box. Vacuum and hydrogen sequences were repeated for 3 times using standard schlenk technique. 67 μL of AlMe₃ in Toluene (0.75 mmol) and H₂ purged toluene (1 mL) were added by syringe and the reaction tube was immersed in a preheated oil bath at 130°C temperature for 24 hour with continuous stirring. The reaction mixture was cooled to room temperature and 3 mL of ethyl acetate was added. This diluted solution was filtered through celite using ethyl acetate (15 mL) as eluant. Filtrate was concentrated and purified by column chromatography to obtain the pure product.

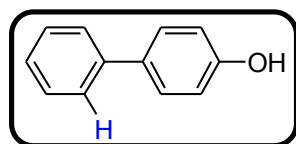
Characterization data of products:



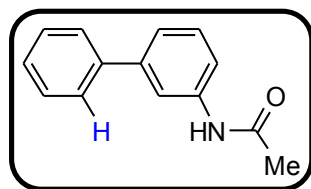
128.0 [M]⁺.

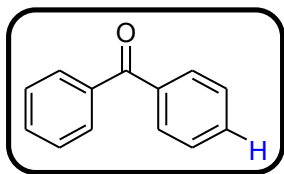
Naphthalene (Table 1, entry 1a and 1b): ¹H NMR (400 MHz, CDCl₃) δ: 7.49 – 7.55 (m, 4H), 7.89 (dd, *J* = 6.2, 3.3 Hz, 4H). ¹³C NMR (101 MHz, CDCl₃) δ: 126.01, 128.07, 133.62. **GC-MS (m/z):**

4-Hydroxybiphenyl (Table 1, entry 1c): ¹H NMR (400 MHz, CDCl₃) δ: 5.24 (b, 1H), 6.90 – 6.93 (m, 2H), 7.28 – 7.33 (m, 1H), 7.39 – 7.44 (m, 2H), 7.46 – 7.50 (m, 2H), 7.52 – 7.56 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ: 115.85, 126.88, 126.91, 128.58, 128.92, 134.11, 140.98, 155.39. **GC-MS (m/z):** 170.1 [M]⁺.



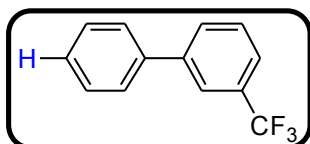
N-(biphenyl-3-yl)acetamide (Table 1, entry 1d): ¹H NMR (400 MHz, CDCl₃) δ: 2.17 (s, 3H), 7.33 (d, *J* = 8.0 Hz, 3H), 7.42 (q, *J* = 7.2 Hz, 2H), 7.54 (dd, *J* = 13.7, 7.5 Hz, 4H), 7.75 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ: 24.69, 118.93, 119.09, 123.24, 127.32, 127.62, 128.90, 129.48, 138.62, 140.85, 142.18, 169.04. **GC-MS (m/z):** 211.2 [M]⁺.





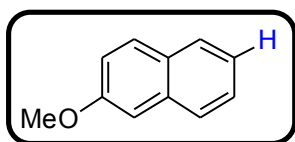
Benzophenone (Table 1, entry 1e): $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.45 – 7.51 (m, 4H), 7.56 – 7.61 (m, 2H), 7.79 – 7.83 (m, 4H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ : 128.44, 130.22, 132.59, 137.72, 196.92. **GC-MS** (m/z): 182.0 $[\text{M}]^+$.

3-Trifluoromethylbiphenyl (Table 1, entry 1f): $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.35 – 7.43 (m, 1H), 7.44 – 7.53 (m, 2H), 7.55 (d, $J = 7.8$ Hz, 1H), 7.58 (d, $J = 4.9$



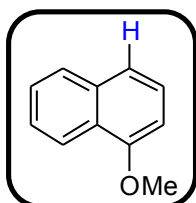
Hz, 2H), 7.59 – 7.62 (m, 1H), 7.73 – 7.78 (m, 1H), 7.83 (s, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ : 125.59 (q, $J = 272$ Hz), 123.94 (q, $J = 3$ Hz), 127.17, 128.01, 128.97, 129.20, 130.38 (q, $J = 1$ Hz), 131.16 (q, $J = 32$ Hz), 134.11, 139.75, 142.01. **GC-MS** (m/z): 222.0 $[\text{M}]^+$.

2-Methoxynaphthalene (Table 1, entry 1g): $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 3.92



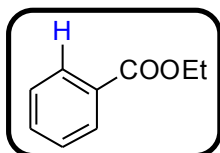
(s, 3H), 7.16 (d, $J = 8.3$ Hz, 2H), 7.35 (ddd, $J = 8.1, 6.8, 1.2$ Hz, 1H), 7.46 (ddd, $J = 8.2, 6.8, 1.3$ Hz, 1H), 7.73 – 7.80 (m, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ : 55.49, 105.93, 118.91, 123.78, 126.56, 126.93, 127.85, 129.14, 129.58, 134.75, 157.77. **GC-MS** (m/z): 158.1 $[\text{M}]^+$.

1-Methoxynaphthalene (Table 1, entry 1h): $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 4.05

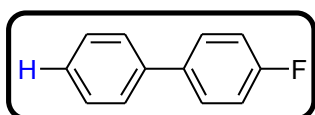


(s, 3H), 6.87 (dt, $J = 7.5, 1.2$ Hz, 1H), 7.43 – 7.54 (m, 2H), 7.54 – 7.62 (m, 2H), 7.89 (dtd, $J = 7.9, 2.9, 1.4$ Hz, 1H), 8.35 – 8.42 (m, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ : 55.59, 103.91, 120.36, 122.13, 125.34, 125.74, 126.03, 126.55, 127.61, 134.62, 155.56. **GC-MS** (m/z): 158.0 $[\text{M}]^+$.

Ethyl benzoate (Table 1, entry 1i): $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 1.36 (t, $J = 7.2$



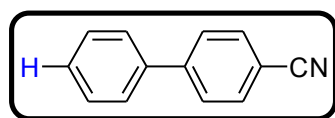
Hz, 3H), 4.35 (q, $J = 7.2$ Hz, 2H), 7.44 (m, 3H), 8.04 (dt, $J = 8.5, 1.9$ Hz, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ : 14.29, 60.88, 128.28, 129.50, 130.48, 132.77, 166.51. **GC-MS** (m/z): 150.0 $[\text{M}]^+$.



4-Fluorobiphenyl (Table 1, entry 1j): $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.15 (td, $J = 8.6, 1.4$ Hz, 2H), 7.34 – 7.40

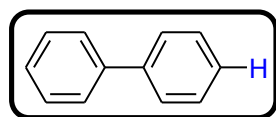
(m, 1H), 7.45 (tt, $J = 6.2, 1.5$ Hz, 2H), 7.56 (dtd, $J = 8.5, 3.5, 2.0$ Hz, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ : 115.70, 115.91, 127.21, 127.45, 128.84, 128.92, 129.01, 137.52 (d, $J = 3$ Hz), 140.44, 162.64 (d, $J = 245$ Hz). GC-MS (m/z): 172.0 $[\text{M}]^+$.

[1,1'-biphenyl]-4-carbonitrile (Table 1, entry 1k): ^1H NMR (400 MHz, CDCl_3) δ :



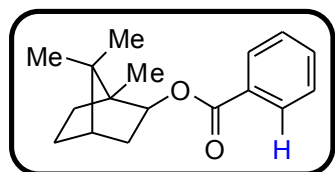
7.40 – 7.45 (m, 1H), 7.46 – 7.52 (m, 2H), 7.57 – 7.61 (m, 2H), 7.67 – 7.75 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ : 111.07, 119.15, 127.41, 127.92, 128.85, 129.30, 132.78, 139.35, 145.86. GC-MS (m/z): 179.0 $[\text{M}]^+$.

Biphenyl (Table 1, entry 1l): ^1H NMR (400 MHz, CDCl_3) δ : 7.68 (dt, $J = 8.1, 1.4$

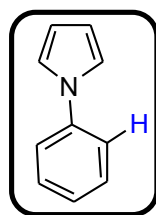


Hz, 4H), 7.48 – 7.55 (m, 4H), 7.42 (td, $J = 7.4, 1.4$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ : 127.37, 127.46, 128.96, 141.43. GC-MS (m/z): 154.0 $[\text{M}]^+$.

1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl benzoate (Table 1, entry 1m): ^1H NMR (400 MHz, CDCl_3) δ : 8.01 (dd, $J = 8.0, 1.6$, 2H), 7.54 (t, $J = 6.0$, 1H), 7.43 (t, $J = 8.0$,

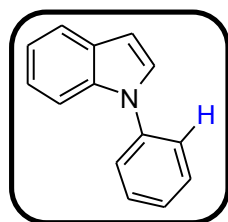


2H), 4.92 (dd, $J = 7.6, 4.0$, 1H), 1.89– 1.97 (m, 2H), 1.59– 1.77 (m, 4H), 1.11 (s, 3H), 0.90 (s, 3H), 0.88 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ : 166.25, 132.86, 131.04, 129.63, 128.52, 81.62, 49.18, 47.20, 45.28, 39.17, 34.08, 27.25, 20.32, 11.78, 1.20. HRMS calculated for ($\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}+\text{H}$): 281.1517, found 281.1522.



1-phenyl-1H-pyrrole (Table 2, entry 2a): ^1H NMR (400 MHz, CDCl_3) δ : 6.37 (t, $J = 2.2$ Hz, 2H), 7.12 (t, $J = 2.2$ Hz, 2H), 7.24 – 7.29 (m, 1H), 7.40 – 7.47 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ : 110.57, 119.51, 120.72, 125.81, 129.73, 140.94. GC-MS (m/z): 143.0 $[\text{M}]^+$.

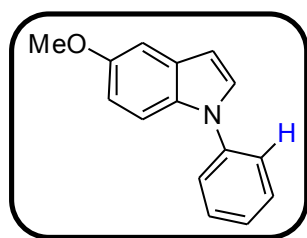
1-phenyl-1H-indole (Table 2, entry 2b): ^1H NMR (400 MHz, CDCl_3) δ : 6.75 (dt, J



$= 3.2, 0.8$ Hz, 1H), 7.22–7.32 (m, 2H), 7.37 – 7.45 (m, 2H), 7.56 (dd, $J = 4.3, 0.8$ Hz, 4H), 7.64 (dt, $J = 8.2, 1.0$ Hz, 1H), 7.77 (dq, $J = 7.4, 1.0$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ : 103.74, 110.68, 120.53, 121.31, 122.53, 124.52, 126.60, 128.12, 129.48, 129.78, 135.99, 139.97. HRMS calculated for ($\text{C}_{14}\text{H}_{11}\text{N}+\text{H}$):

194.0970, found 194.0967.

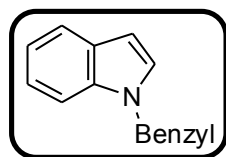
5-methoxy-1-phenyl-1*H*-indole (Table 2, entry 2c): $^1\text{H NMR}$ (400 MHz, CDCl_3)



δ : 3.90 (s, 3H), 6.64 (d, $J = 3.2$ Hz, 1H), 6.91 (dt, $J = 8.9$, 1.8 Hz, 1H), 7.17 (d, $J = 2.4$ Hz, 1H), 7.36 (dd, $J = 9.3$, 3.2 Hz, 2H), 7.48 – 7.56 (m, 5H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ : 56.02, 102.84, 103.40, 111.51, 112.65, 124.18, 126.40, 128.51, 129.77, 130.01, 131.20, 140.08, 154.70. HRMS

calculated for ($\text{C}_{15}\text{H}_{13}\text{NO}+\text{H}$): 224.1075, found 224.1077.

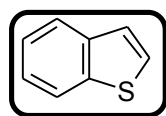
1-benzyl-1*H*-indole (Table 2, entry 2d and 2e): $^1\text{H NMR}$ (400 MHz, CDCl_3) δ :



5.22 (s, 2H), 6.47 (dd, $J = 3.2$, 1.7 Hz, 1H), 6.99 – 7.11 (m, 6H), 7.16 – 7.21 (m, 3H), 7.57 (dt, $J = 8.5$, 1.4 Hz, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ : 50.35, 101.95, 109.98, 119.81, 121.26, 121.96, 127.04, 127.87, 128.55, 128.98, 129.03, 136.56, 137.83. **GC-MS**

(m/z): 207.1 [M] $^+$.

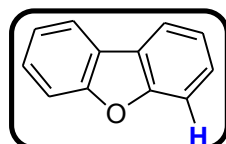
Benzo[*b*]thiophene (Table 2, entry 2f and 2g): $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.34



– 7.42 (m, 3H), 7.46 (d, $J = 5.4$ Hz, 1H), 7.83 – 7.87 (m, 1H), 7.91 (ddd, $J = 6.9$, 2.2, 0.9 Hz, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ : 122.68, 123.80, 124.03, 124.33, 124.39, 126.49, 139.76, 139.88. **GC-**

MS (m/z): 134.1 [M] $^+$.

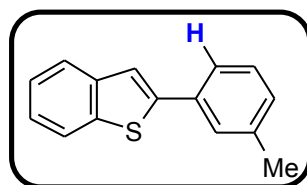
Dibenzo[*b,d*]furan (Table 2, entry 2h): $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.36 (td, $J =$



7.5, 1.0 Hz, 2H), 7.48 (ddd, $J = 8.3$, 7.3, 1.4 Hz, 2H), 7.60 (dt, $J = 8.2$, 0.9 Hz, 2H), 7.98 (ddd, $J = 7.7$, 1.4, 0.7 Hz, 2H). $^{13}\text{C NMR}$

(101 MHz, CDCl_3) δ : 111.85, 120.83, 122.87, 124.40, 127.31, 156.35. **GC-MS** (m/z): 168.0 [M] $^+$.

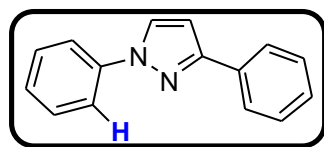
2-*m*-tolylbenzo[*b*]thiophene (Table 2, entry 2i): $^1\text{H NMR}$ (400 MHz, CDCl_3) δ :



2.43 (s, 3H), 7.17 (ddt, $J = 7.5$, 1.7, 0.8 Hz, 1H), 7.30 – 7.37 (m, 3H), 7.52 – 7.56 (m, 3H), 7.76 – 7.85 (m, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ : 21.68, 119.54, 122.46, 123.71, 123.85, 124.44, 124.67, 127.41, 129.05, 129.29, 134.41,

138.83, 139.67, 140.91, 144.62. HRMS calculated for ($\text{C}_{15}\text{H}_{12}\text{S}+\text{H}$): 225.0738, found 225.0734.

1,3-diphenyl-1*H*-pyrazole (Table 2, entry 2j): $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 6.78

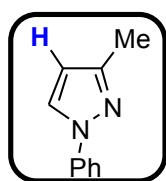


(d, $J = 2.5$ Hz, 1H), 7.34 (dd, $J = 19.5, 7.4$ Hz, 1H), 7.41 – 7.50 (m, 4H), 7.76 – 7.80 (m, 2H), 7.91 – 7.97 (m, 4H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ : 100.18, 105.23, 119.26, 126.03, 126.54, 128.23, 128.85, 129.62, 133.30, 140.41,

153.13. HRMS calculated for ($\text{C}_{15}\text{H}_{12}\text{N}_2+\text{H}$): 221.1079, found 221.1082.

3-methyl-1-phenyl-1*H*-pyrazole (Table 2, entry 2k): $^1\text{H NMR}$ (400 MHz, CDCl_3)

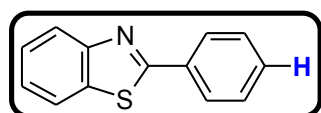


δ : 2.38 (s, 3H), 6.24 (d, $J = 2.4$ Hz, 1H), 7.21 – 7.27 (m, 1H), 7.39 – 7.45 (m, 2H), 7.63 – 7.66 (m, 2H), 7.81 (d, $J = 2.4$ Hz, 1H). $^{13}\text{C NMR}$

(101 MHz, CDCl_3) δ : 13.93, 107.71, 119.03, 126.12, 127.57, 129.5, 140.40, 150.75. HRMS calculated for ($\text{C}_{10}\text{H}_{10}\text{N}_2+\text{H}$): 159.0922,

found 159.0919.

2-phenylbenzo[*d*]thiazole (Table 2, entry 2l): $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.39

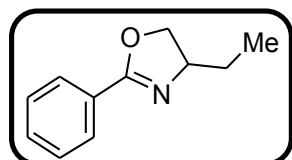


(ddd, $J = 8.3, 7.2, 1.2$ Hz, 1H), 7.48 – 7.52 (m, 4H), 7.89 – 7.93 (m, 1H), 8.06 – 8.12 (m, 3H). $^{13}\text{C NMR}$ (101 MHz,

CDCl_3) δ : 121.84, 123.45, 125.41, 126.54, 127.78, 129.24,

131.19, 133.84, 135.28, 154.36, 168.30. GC-MS (m/z): 211.2 [M] $^+$.

5-ethyl-2-phenyl-4,5-dihydrooxazole (Table 2, entry 2m and 2n): $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 0.98 (t, $J = 7.4$ Hz, 3H), 1.60 (dq, $J = 13.3, 7.4, 5.8$ Hz, 1H), 1.76



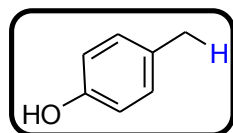
(dq, $J = 13.3, 7.4, 5.8$ Hz, 1H), 4.03 (t, $J = 7.9$ Hz, 1H), 4.22

(dtd, $J = 9.4, 7.4, 5.8$ Hz, 1H), 4.45 (dd, $J = 9.4, 8.2$ Hz, 1H),

7.35 – 7.47 (m, 3H), 7.92 – 7.96 (m, 2H). $^{13}\text{C NMR}$ (101

MHz, CDCl_3) δ : 10.13, 28.76, 68.07, 72.25, 128.00, 128.35, 128.41, 131.34, 163.61.

HRMS calculated for ($\text{C}_{11}\text{H}_{13}\text{NO}+\text{H}$): 176.1075, found 176.1079.



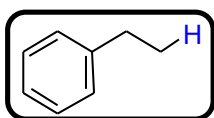
***p*-Cresol (Table 3, entry 3a):** $^1\text{H NMR}$ (400 MHz, CDCl_3) δ :

2.27 (s, 3H), 6.70 – 6.78 (m, 2H), 6.99 – 7.07 (m, 2H). $^{13}\text{C NMR}$

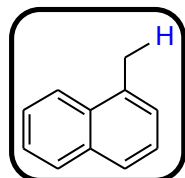
(101 MHz, CDCl_3) δ : 20.67, 115.28, 129.44, 130.22, 153.59. GC-

MS (m/z): 108.0 [M] $^+$.

Ethylbenzene (Table 3, entry 3b): Yield was determined by GC due to high

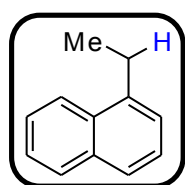


volatility of product using *n*-decane as internal standard. GC yield 73% (with 30 mol% Ni(COD)₂) and 53% (with 15 mol% Ni(COD)₂).



1-Methylnaphthalene (Table 3, entry 3c): Yield was determined by GC using *n*-decane as internal standard. GC yield 69% (with 30 mol% Ni(COD)₂) and 51% (with 15 mol% Ni(COD)₂).

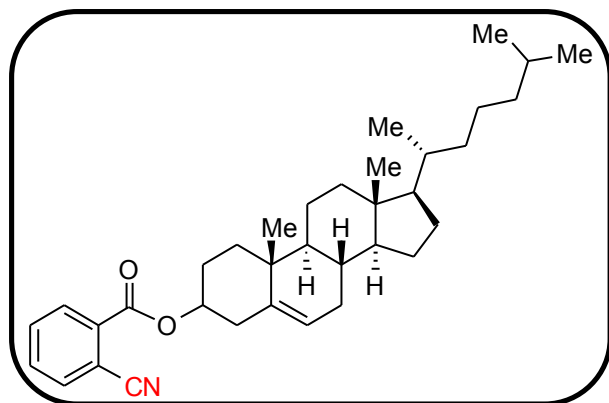
1-Ethynaphthalene (Table 3, entry 3d and side product of Table 3, entry 3c): ¹H



NMR (400 MHz, CDCl₃) δ: 8.10 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.53 (q, *J* = 8.0 Hz, 2H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 3.16 (q, *J* = 7.2 Hz, 2H), 1.42 (t, *J* = 7.2 Hz, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ: 140.44, 133.98,

131.93, 128.91, 126.55, 125.84, 125.55, 125.01, 123.90, 26.07, 15.22. GCMS (*m/z*): 156.1 [M]⁺.

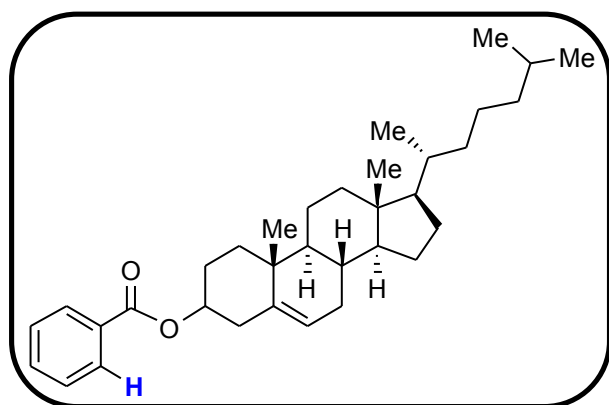
Cholesterol-3-(2-cyanobenzoate) (Scheme 2, entry 4a):^[2] ¹H NMR (400 MHz, CDCl₃) δ: 8.14 (dd, *J* = 7.6, 4.0, 1H), 7.80 (d, *J* = 8.0, 1H), 7.64- 7.69 (m, 2H), 5.43 (d, *J* = 4.8, 1H), 4.93 (m, 1H), 2.55-2.51 (m, 2H), 2.07- 1.99 (m, 4H), 1.85- 1.79 (m, 2H),



1.64 (s, 2H), 1.37- 1.31 (m, 3H), 1.27-0.98 (m, 15H), 1.07 (s, 3H), 0.92 (d, *J* = 6.4, 3H), 0.87 (d, *J* = 2.0, 3H), 0.86 (d, *J* = 2.0, 3H), 0.69 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ: 163.67, 139.50, 134.89, 133.18, 132.61, 132.57, 131.35, 123.26, 117.82, 113.07, 76.66, 56.86, 56.30,

50.18, 42.49, 39.89, 39.69, 38.12, 37.14, 36.81, 36.35, 35.97, 32.10, 32.02, 28.41, 28.19, 27.84, 24.46, 24.01, 23.00, 22.74, 21.22, 19.54, 18.89, 12.04. HRMS calculated for (C₃₅H₄₉NO₂+H): 516.3842, found 516.3848.

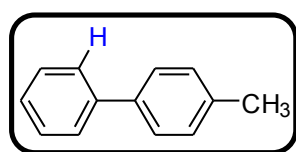
Cholesterol-3-benzoate (Scheme 2, entry 4b): $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 8.04 (dd, $J=8.0, 1.2, 2\text{H}$), 7.54 (m, 1H), 7.43 (t, $J=7.6, 2\text{H}$), 5.42 (d, $J=4.0, 1\text{H}$), 4.86 (m,



1H), 2.55-2.51 (m, 2H), 2.07- 1.99 (m, 4H), 1.85- 1.79 (m, 2H), 1.64 (s, 2H), 1.37- 1.31 (m, 3H), 1.27-0.98 (m, 15H), 1.07 (s, 3H), 0.92 (d, $J=6.4, 3\text{H}$), 0.87 (d, $J=2.0, 3\text{H}$), 0.86 (d, $J=2.0, 3\text{H}$), 0.69 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ : 166.23, 139.87, 132.94, 131.03, 129.75, 128.48, 123.00, 74.80, 56.90, 56.33,

50.24, 42.53, 39.94, 39.73, 38.43, 37.24, 36.87, 36.39, 36.02, 32.15, 32.09, 28.46, 28.24, 28.09, 24.51, 24.04, 23.05, 22.79, 21.26, 19.60, 12.47, 0.09.

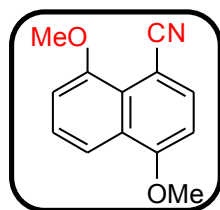
4-methyl-1,1'-biphenyl (Scheme 2, entry 4d): $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 2.45



(s, 3H), 7.29 – 7.32 (m, 2H), 7.35 – 7.40 (m, 1H), 7.45 – 7.50 (m, 2H), 7.54 – 7.57 (m, 2H), 7.62 – 7.66 (m, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ : 21.30, 127.16, 127.18, 128.90,

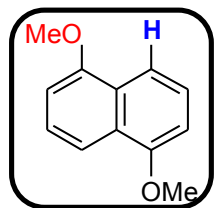
129.67, 137.19, 138.53, 141.34. **GC-MS** (m/z): 168.1 $[\text{M}]^+$.

4,8-dimethoxy-1-naphthonitrile (Scheme 2, entry 4e):^[3] $^1\text{H NMR}$ (400 MHz,



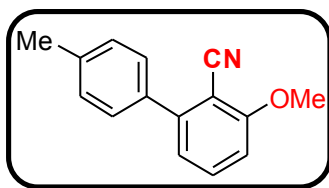
CDCl_3) δ : 4.04 (s, 6H), 6.84 (d, $J=8.2\text{ Hz}$, 1H), 6.99 (d, $J=7.7\text{ Hz}$, 1H), 7.47 (t, $J=8.2\text{ Hz}$, 1H), 7.81 – 7.93 (m, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ : 55.92, 56.21, 98.65, 104.18, 107.81, 115.05, 120.95, 125.19, 126.94, 127.05, 136.47, 154.91, 159.11. **GC-MS**

(m/z): 213.1 $[\text{M}]^+$.



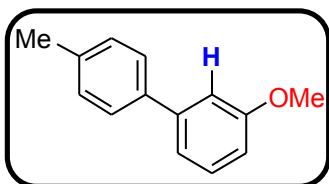
1,5-dimethoxynaphthalene (Scheme 2, entry 4f): $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 4.00 (s, 6H), 6.84 – 6.87 (m, 2H), 7.37 – 7.42 (m, 2H), 7.85 (dd, $J=8.7, 0.8\text{ Hz}$, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ : 55.73, 104.72, 114.37, 125.36, 126.78, 155.42. **GC-MS** (m/z): 188.1 $[\text{M}]^+$.

3-methoxy-4'-methylbiphenyl-2-carbonitrile (Scheme 2, entry 4g): $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 2.41 (s, 3H), 3.96 (s, 3H), 6.93 (dd, $J=8.5, 0.9\text{ Hz}$, 1H), 7.05 (dd, J



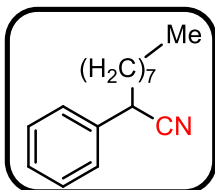
= 7.8, 0.9 Hz, 1H), 7.24 – 7.32 (m, 2H), 7.43 – 7.47 (m, 2H), 7.54 (dd, $J = 8.5, 7.8$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ : 21.47, 56.42, 109.46, 116.38, 122.04, 128.82, 129.52, 130.20, 133.84, 135.38, 138.90, 147.55, 162.38. GC-MS (m/z): 223.1 $[\text{M}]^+$.

3-methoxy-4'-methylbiphenyl (Scheme 2, entry 4h): ^1H NMR (400 MHz, CDCl_3)



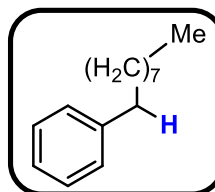
δ : 2.39 (s, 3H), 3.87 (s, 3H), 6.87 (ddd, $J = 8.3, 2.6, 1.0$ Hz, 1H), 7.11 (dd, $J = 2.6, 1.7$ Hz, 1H), 7.15 – 7.29 (m, 6H), 7.34 (t, $J = 7.9$ Hz, 1H), 7.47 – 7.51 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ : 21.31, 55.52, 112.62, 112.96, 119.74, 127.24, 128.90, 129.66, 129.90, 137.42, 142.94, 160.15. GC-MS (m/z): 198.0 $[\text{M}]^+$.

2-phenyldecanenitrile (Scheme 2, entry 4g): ^1H NMR (400 MHz, CDCl_3) δ : 0.87



(t, $J = 6.8, 6.8$ Hz, 3H), 1.23 – 1.31 (m, 12H), 1.76 – 1.96 (m, 2H), 3.75 (dd, $J = 8.6, 6.3$ Hz, 1H), 7.27 – 7.33 (m, 3H), 7.33 – 7.38 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ : 14.19, 22.72, 27.12, 29.05, 29.25, 29.35, 31.88, 36.01, 37.46, 76.91, 77.23, 77.55, 121.02, 127.29, 128.13, 129.09, 136.18. GCMS (m/z): 229.1 $[\text{M}]^+$.

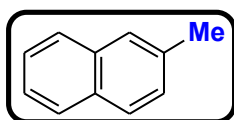
Nonylbenzene (Scheme 2, entry 4h): ^1H NMR (400 MHz, CDCl_3) δ : 0.86 – 1.04



(m, 2H), 1.25 – 1.50 (d, $J = 20.3$ Hz, 7H), 1.65 – 1.73 (q, $J = 7.6, 7.3, 7.3$ Hz, 1H), 2.63 – 2.72 (t, $J = 7.8, 7.8$ Hz, 1H), 7.23 – 7.26 (d, $J = 7.5$ Hz, 2H), 7.31 – 7.36 (t, $J = 7.5, 7.5$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ : 14.34, 22.92, 29.59, 29.78, 29.81, 31.79, 32.14, 36.23, 125.74, 128.41, 128.59, 143.14. GC-MS (m/z): 204.2 $[\text{M}]^+$.

Characterization data of side products:

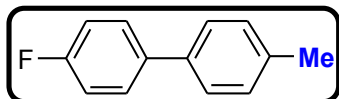
2-methylnaphthalene (Table 1, entry 1a): ^1H NMR (400 MHz, CDCl_3) δ : 2.53 (d,



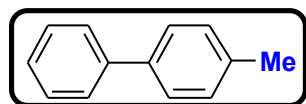
$J = 1.5$ Hz, 3H), 7.37 (dd, $J = 8.4, 1.8$ Hz, 1H), 7.47 (ttd, $J = 8.9, 3.6, 1.9$ Hz, 2H), 7.65 (s, 1H), 7.80 (dd, $J = 8.1, 4.0$ Hz, 2H), 7.84 (dd, $J = 7.7, 1.6$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ : 21.91,

125.14, 126.05, 127.02, 127.42, 127.78, 127.87, 128.30, 131.87, 133.84, 135.62. **GC-MS** (m/z): 142.1 [M]⁺.

4-fluoro-4'-methylbiphenyl (Table 1, entry 1j): ¹H NMR (400 MHz, CDCl₃) δ: 2.43 (s, 3H), 7.11 – 7.19 (m, 2H), 7.28 (d, *J* = 7.9 Hz, 2H), 7.48 (d, *J* = 7.9 Hz, 2H), 7.54 – 7.59 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ: 21.26, 115.62, 115.83, 127.03, 128.60, 128.68, 129.72, 137.21, 137.4 (d, *J* = 3 Hz), 137.56, 162.47 (d, *J* = 245 Hz). **GC-MS** (m/z): 186.2 [M]⁺.



4-methylbiphenyl (Table 1, entry 1l): ¹H NMR (400 MHz, CDCl₃) δ: 2.37 (s, 3H), 7.24 (dd, *J* = 8.2, 2.2 Hz, 2H), 7.28 – 7.35 (m, 1H), 7.42 (dd, *J* = 8.4, 6.9 Hz, 2H), 7.47 – 7.51 (m, 2H), 7.55 – 7.60 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ: 21.31, 127.17, 127.19, 128.91, 129.67, 137.21, 138.54, 141.34. **GC-MS** (m/z): 168.0 [M]⁺.



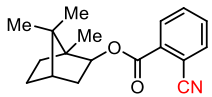
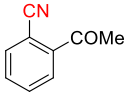
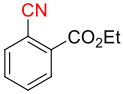
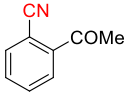

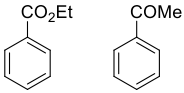
For all other cases side products were identified by GCMS, ¹H, and ¹³C NMR of the reaction mixture and yields were determined by GC.

References:

1. T. Patra, S. Agasti, Akanksha and D. Maiti, *Chem. Comm.* 2013, **49**, 69-71.
2. B. Neises and W. Steglich, *Angew. Chem. Int. Ed.* 1978, **17**, 522-524.
3. W. Li and P. Sun, *J. Org. Chem.* 2012, **77**, 8362-8366.

Control experiment for conversion of ester group into COMe:

Substrates	Condition	Products (from GCMS)
	Ni(COD)₂ (30 mol%) PCy₃ (90 mol%) AlMe ₃ (3 equiv.) Toluene, 130 °C, N ₂ atm, 24 h	 not detected
	Ni(COD)₂ (30 mol%) PCy₃ (90 mol%) AlMe ₃ (3 equiv.) Toluene, 130 °C, N ₂ atm, 24 h	 not detected

	<p>Ni(COD)₂ (30 mol%) PCy₃ (90 mol%) AlMe₃ (3 equiv.) Toluene, 130 °C, N₂ atm, 24 h</p>	 <p>not detected</p>
	<p>AlMe₃ (3 equiv.) Toluene, 130 °C, N₂ atm, 24 h</p>	 <p>not detected</p>
	<p>AlMe₃ (3 equiv.) Toluene, 130 °C, N₂ atm, 24 h</p>	 <p>~70% ~5%</p>

NMR Files:

Table 1, Entry 1a and 1b:

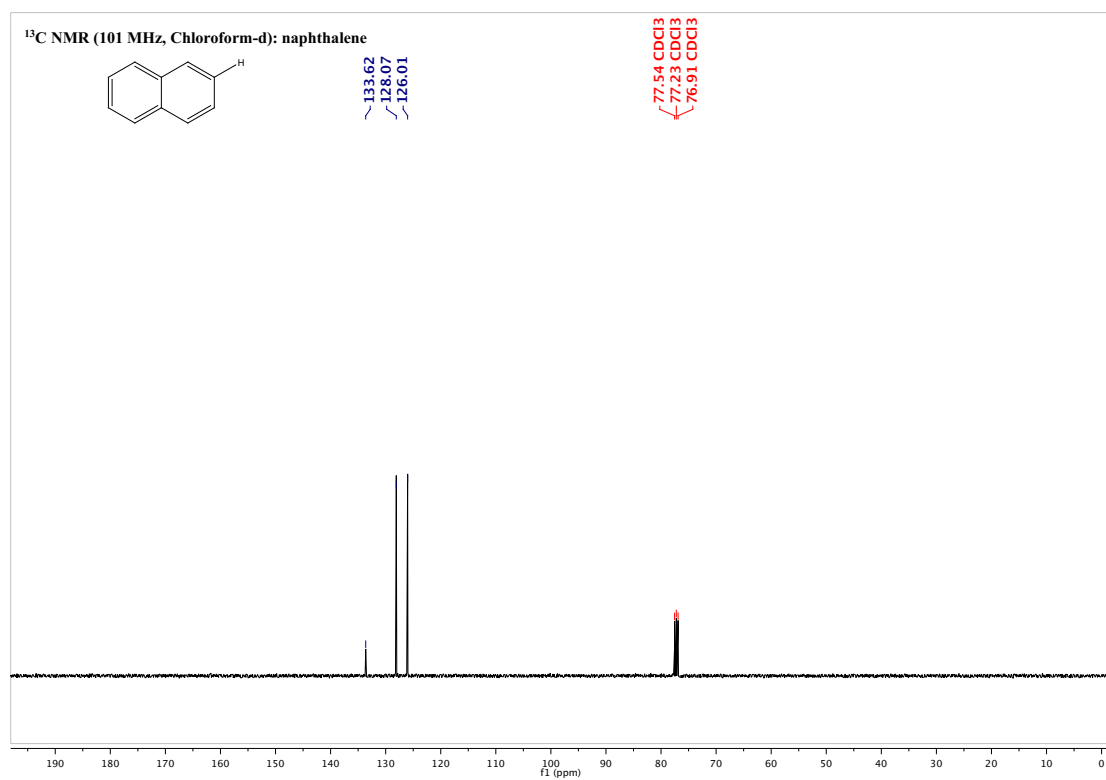
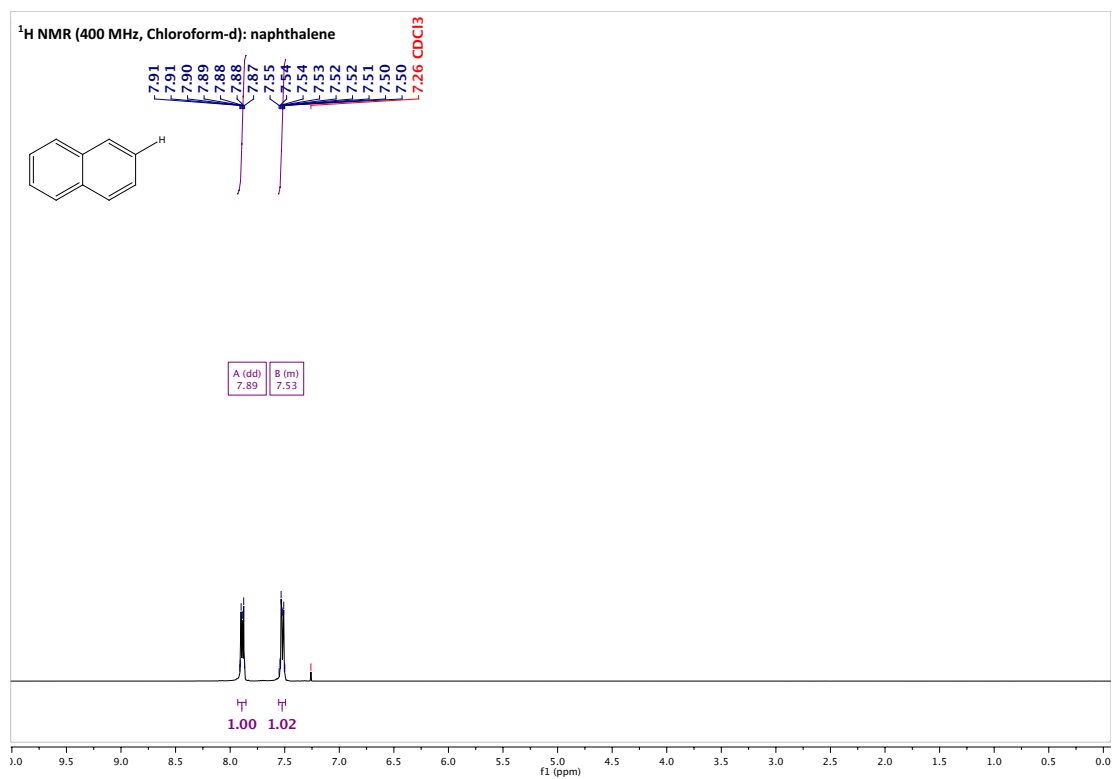


Table 1, Entry 1c:

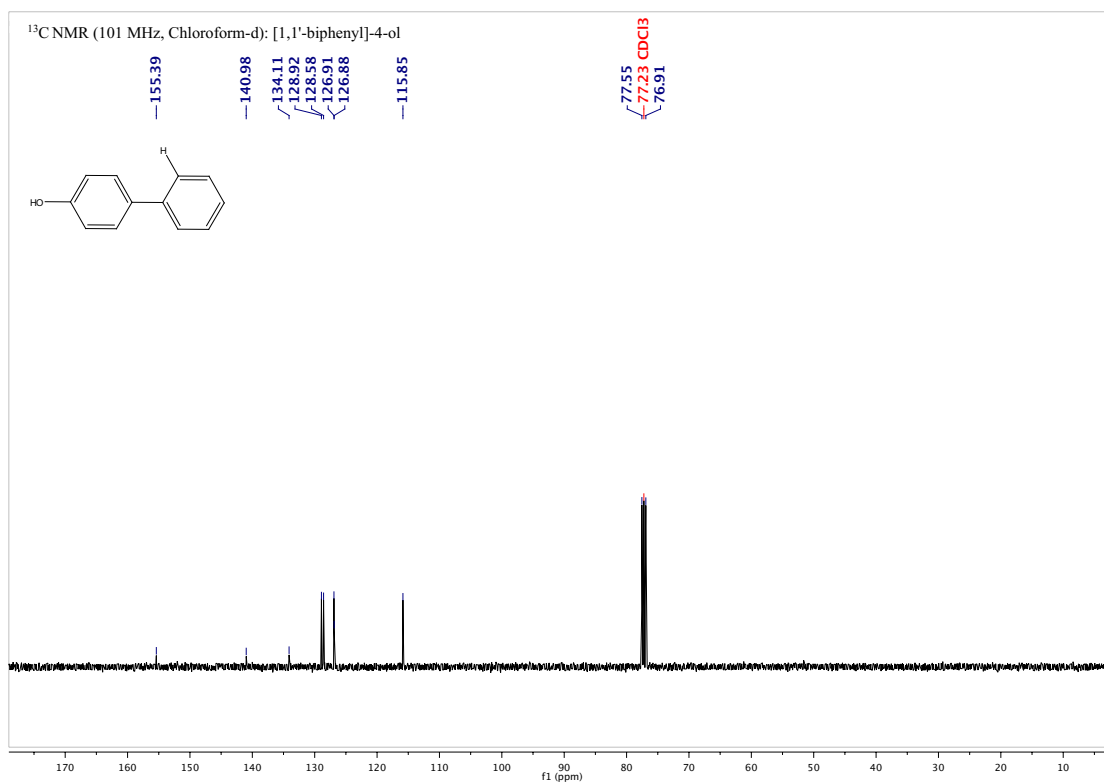
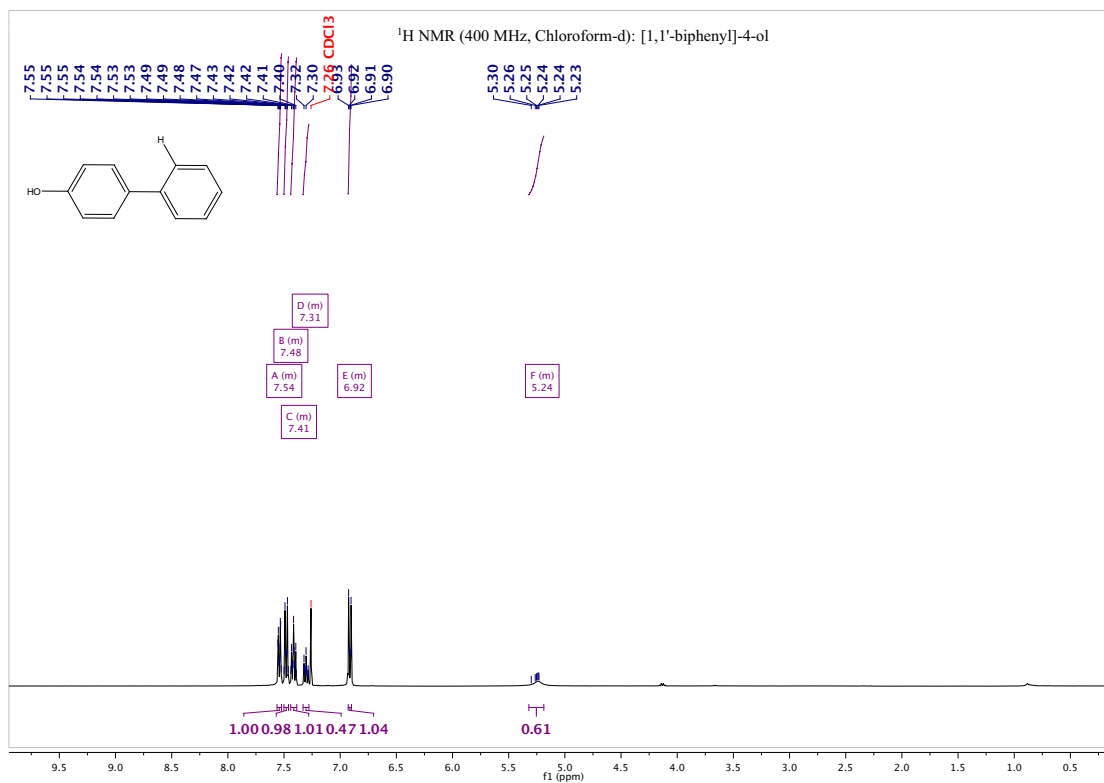


Table 1, Entry 1d:

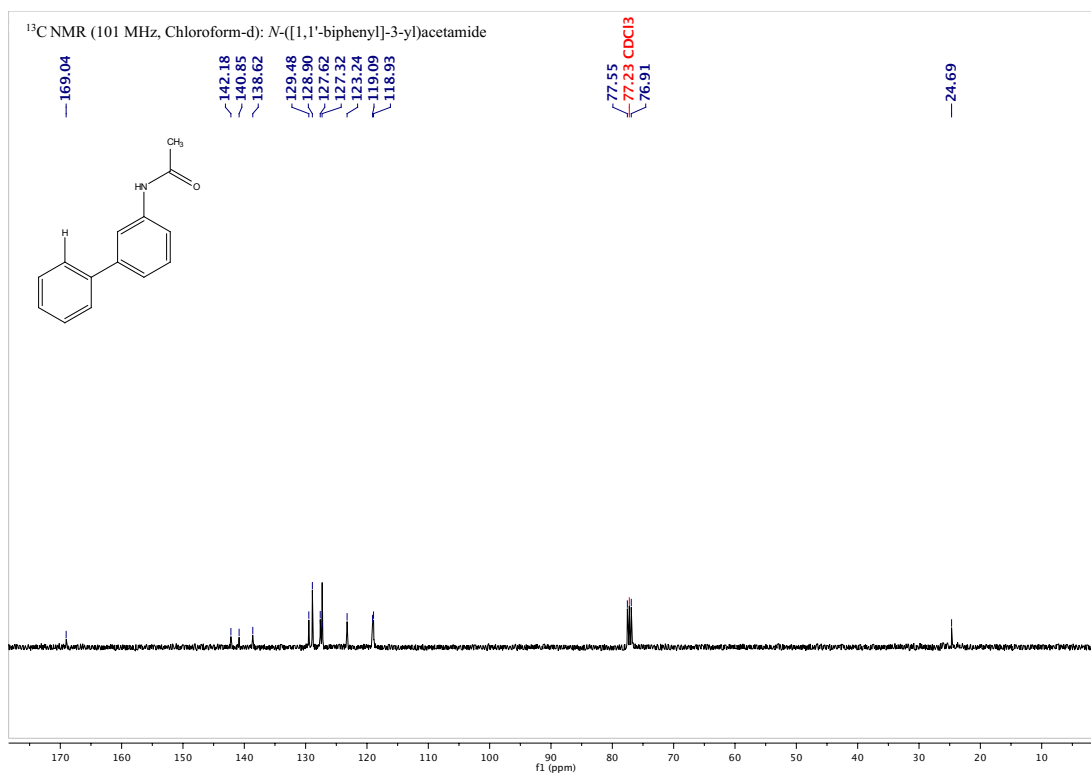
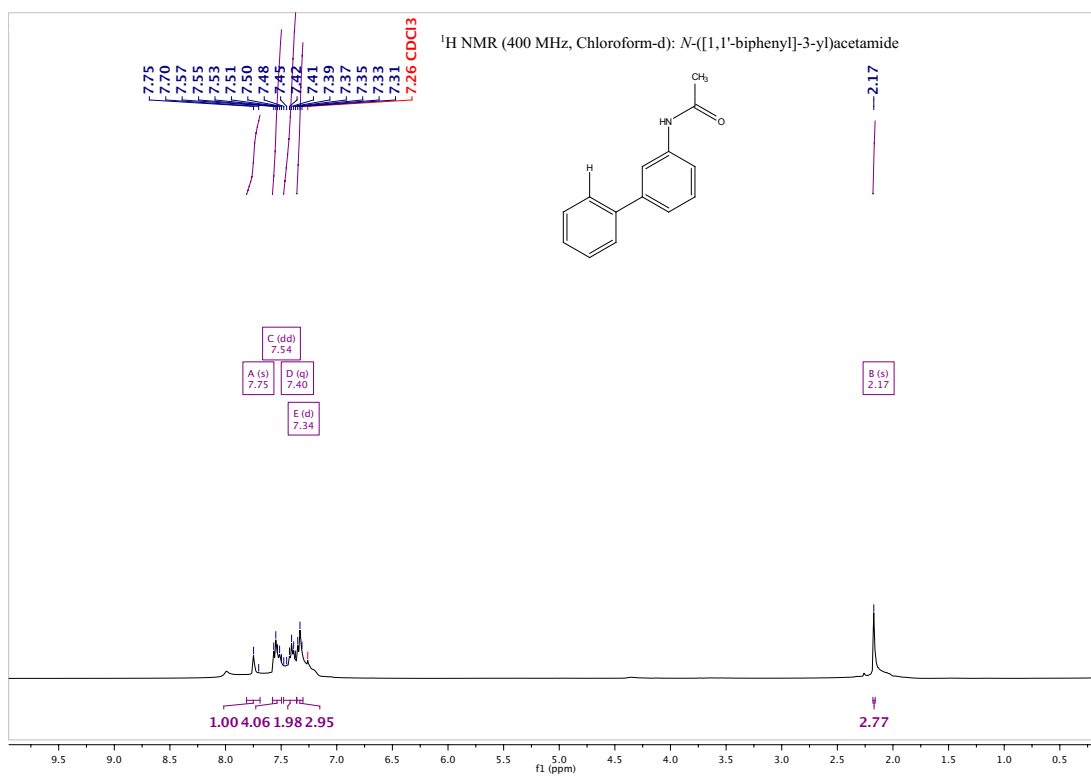


Table 1, Entry 1e:

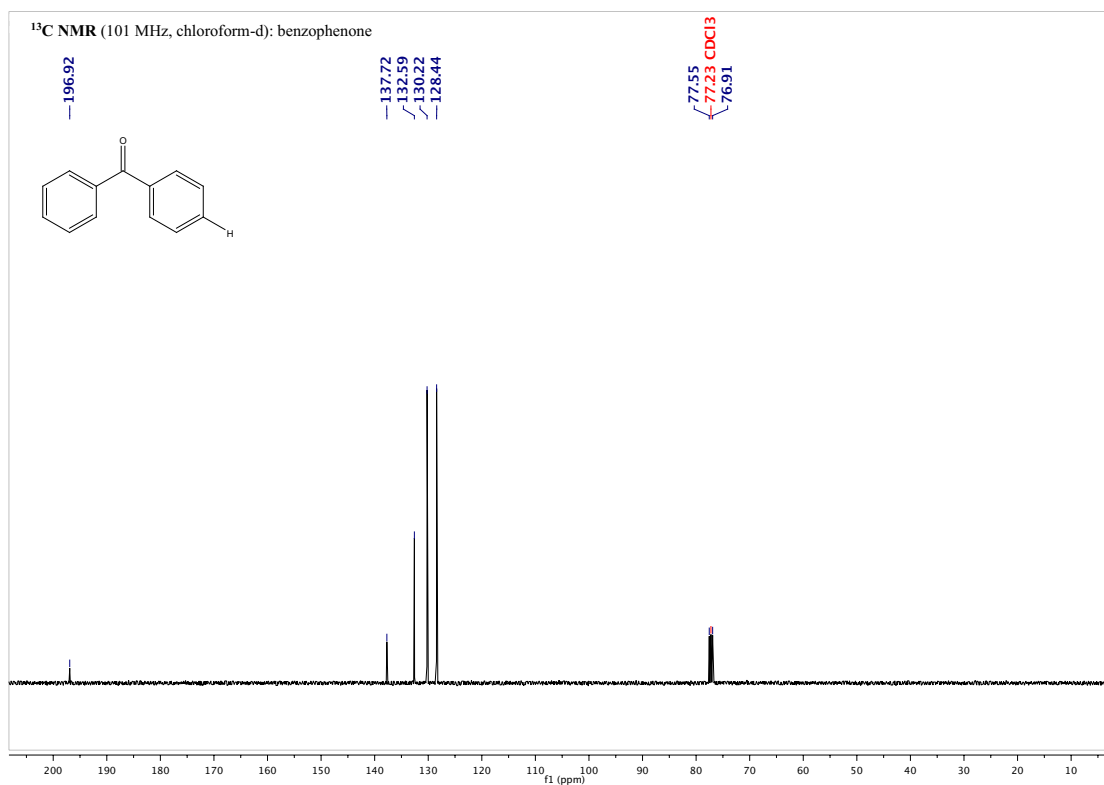
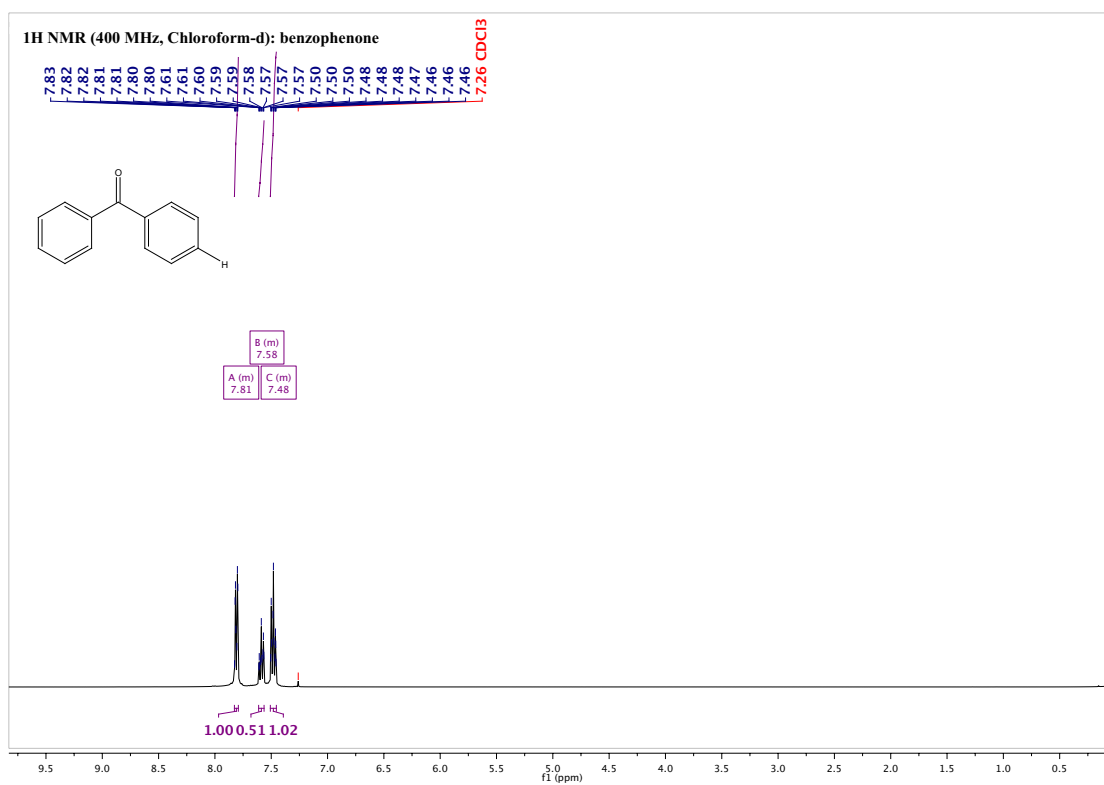


Table 1, Entry 1f:

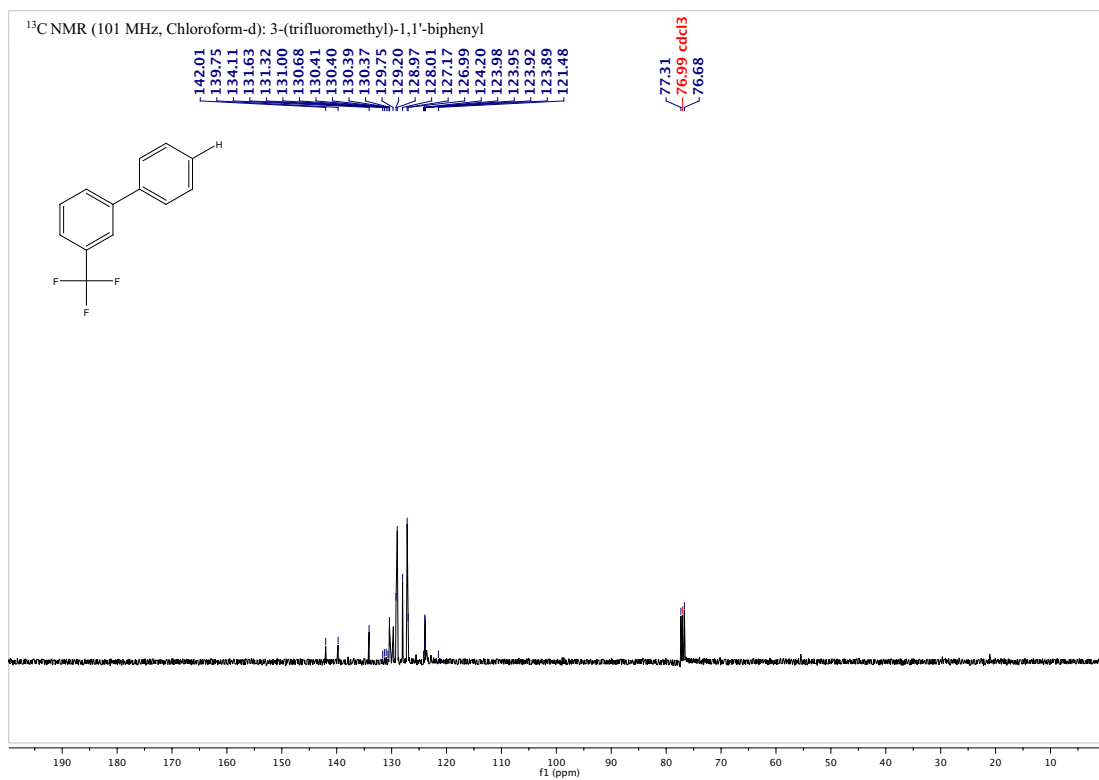
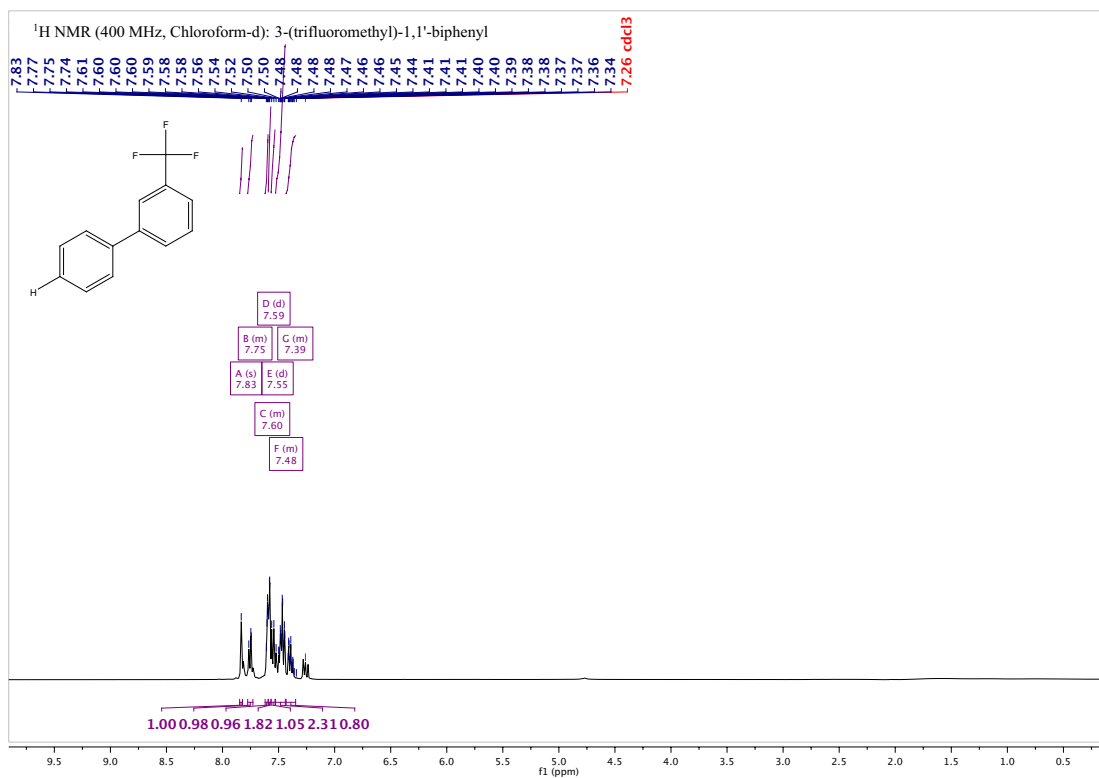


Table 1, Entry 1g:

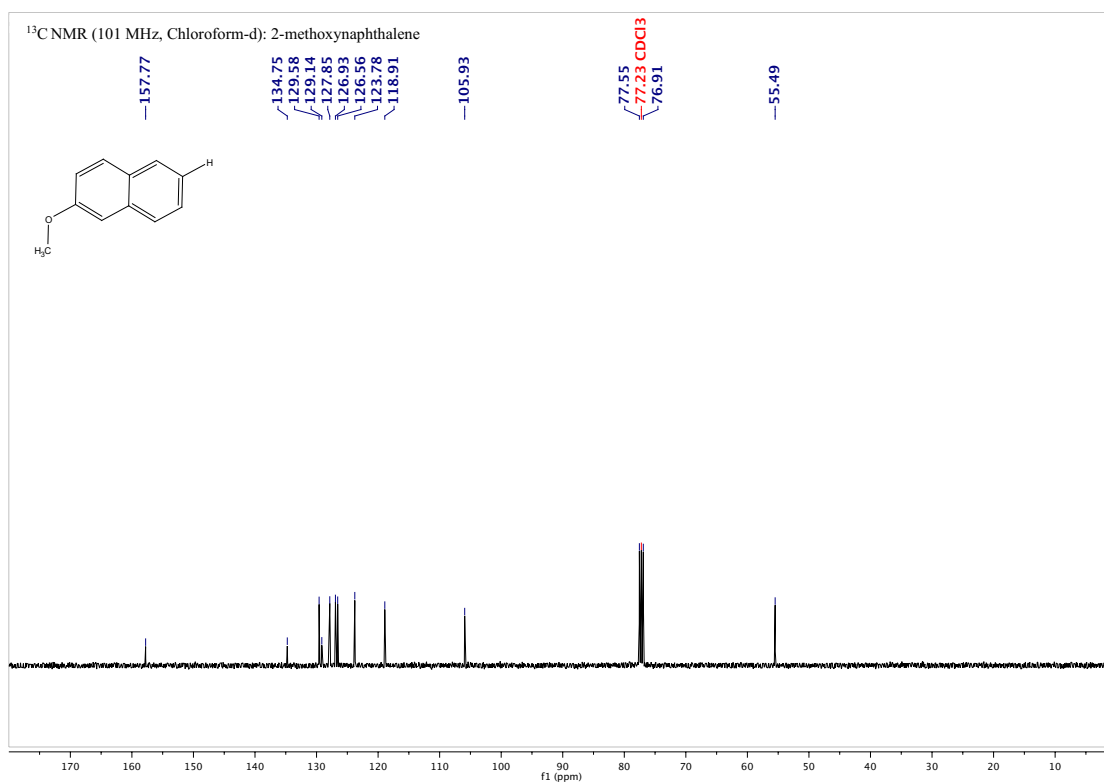
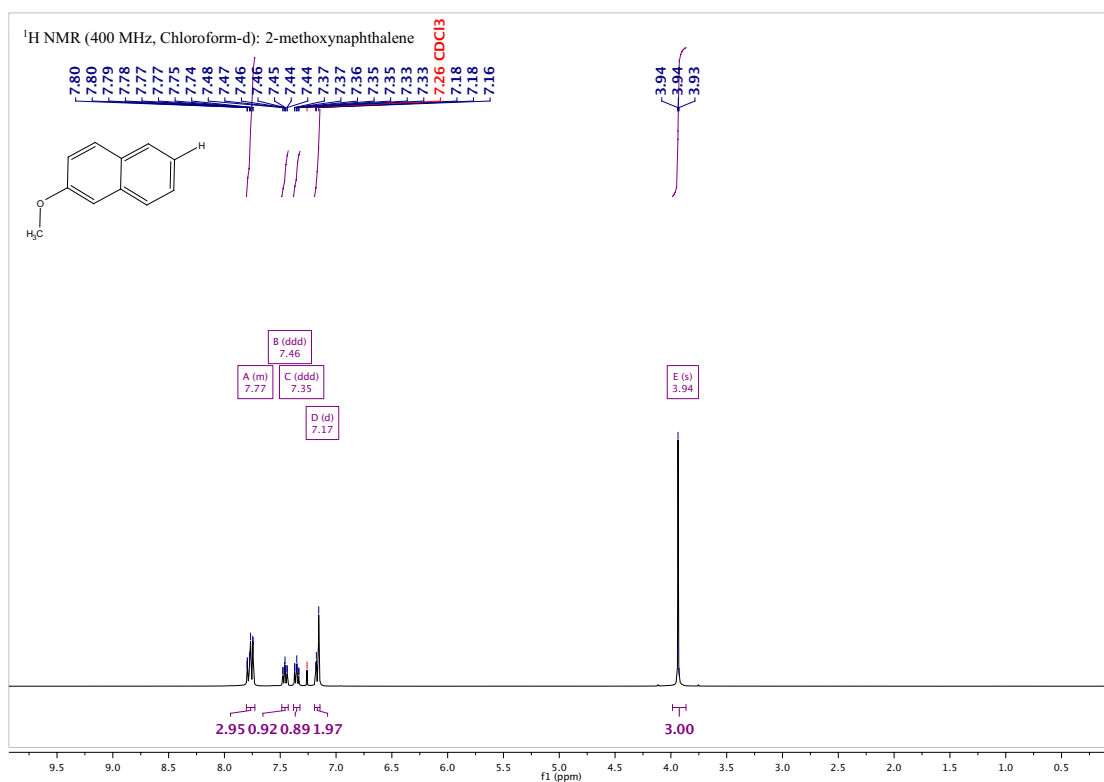


Table 1, Entry 1h:

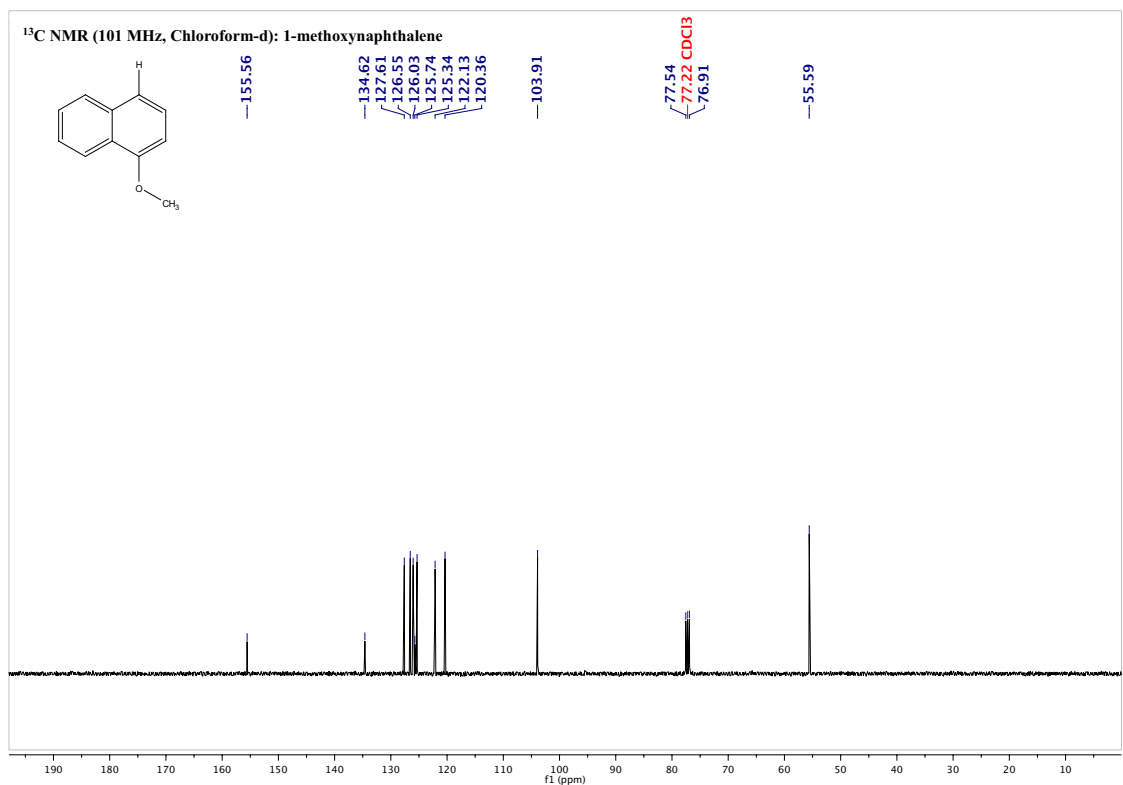
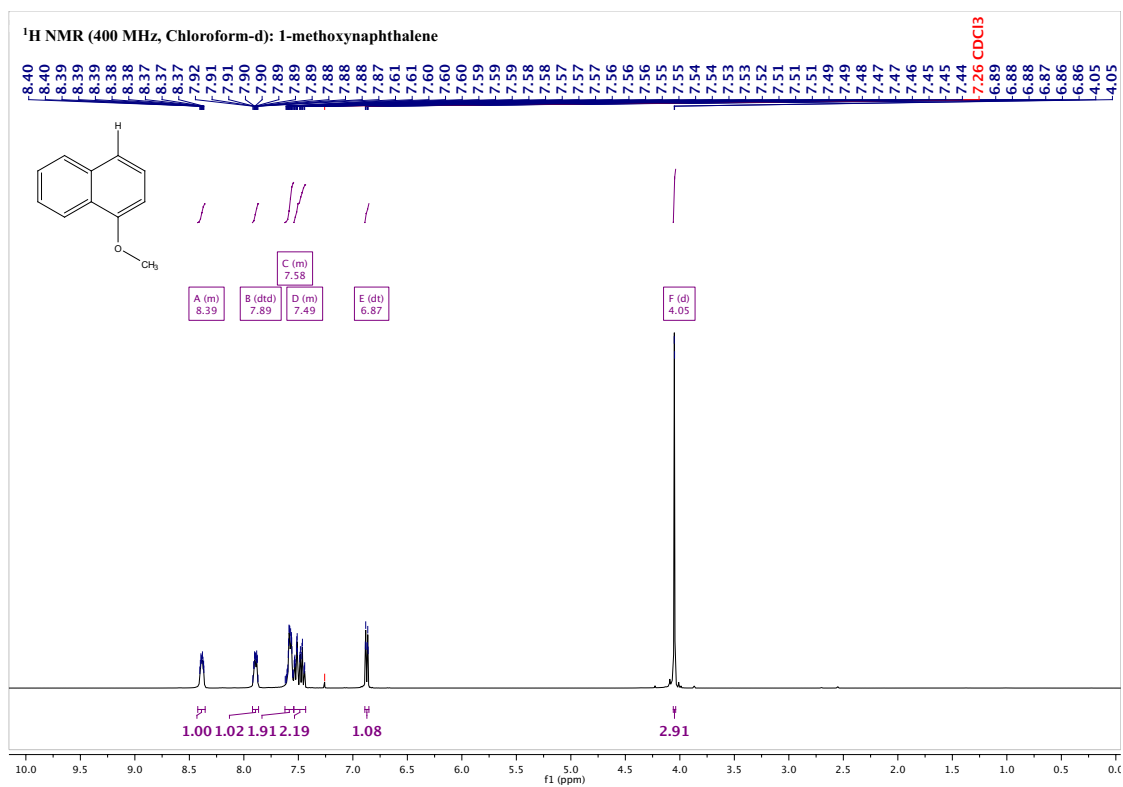


Table 1, Entry 1i:

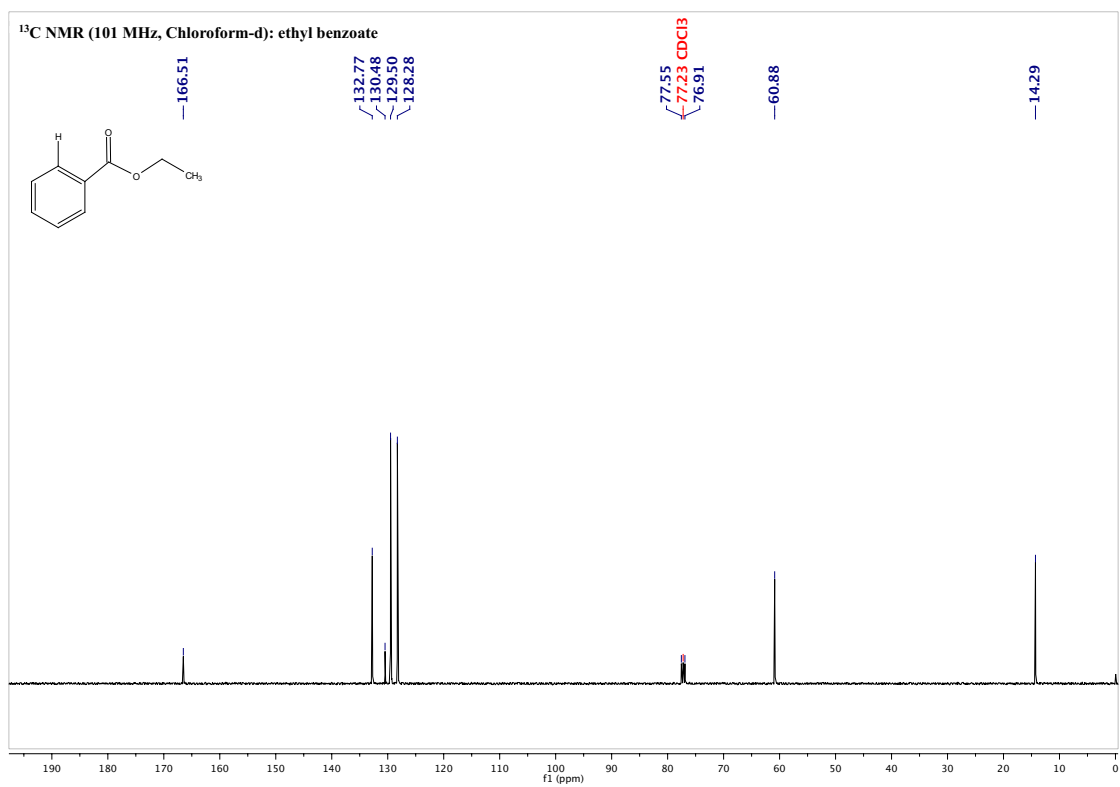
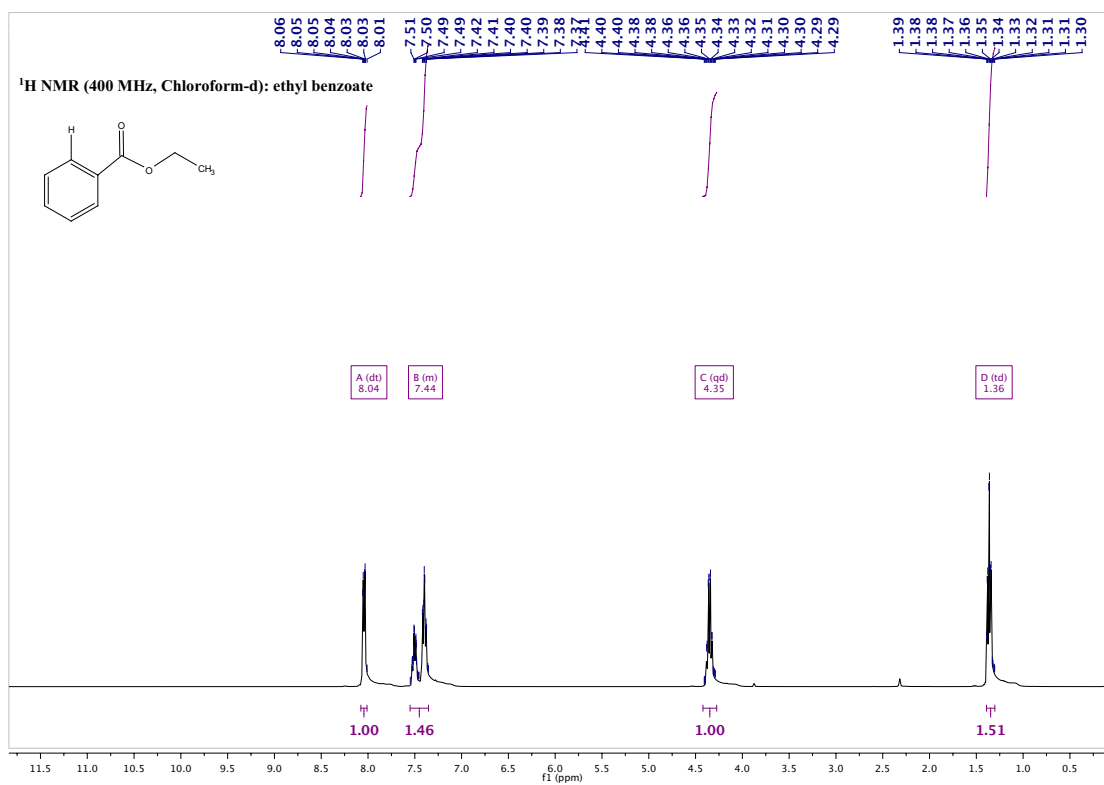


Table 1, Entry 1j:

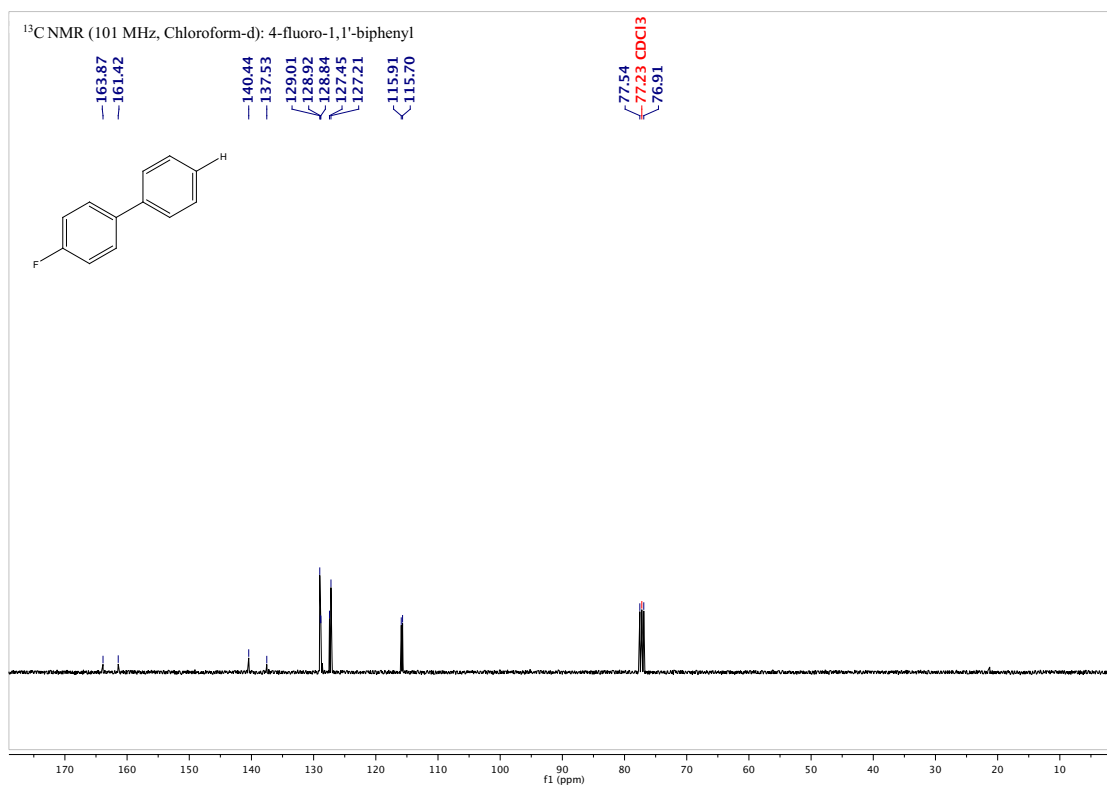
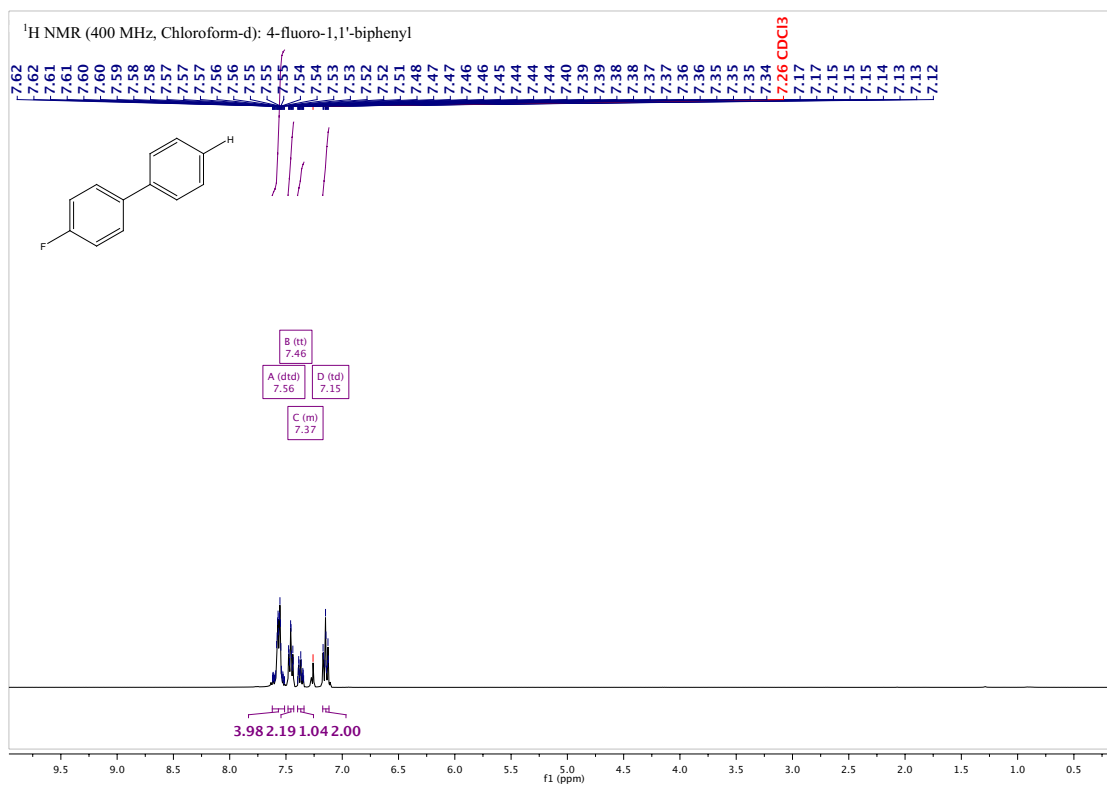


Table 1, Entry 1k:

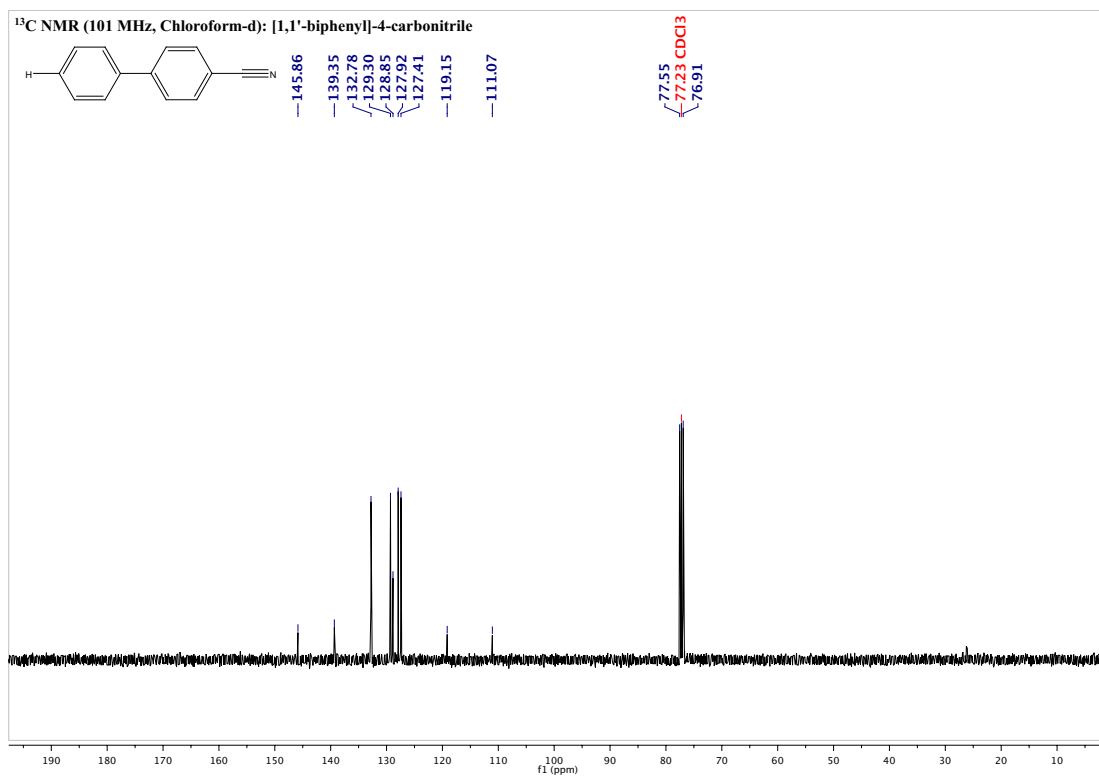
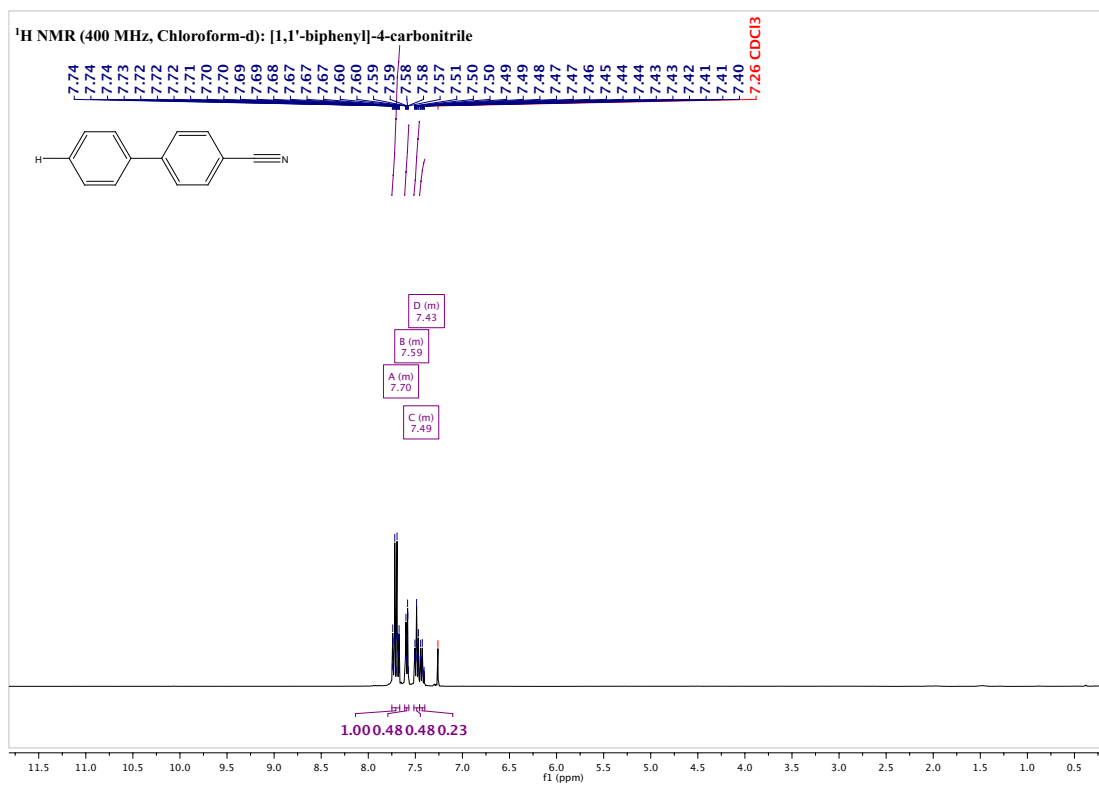


Table 1, Entry 11:

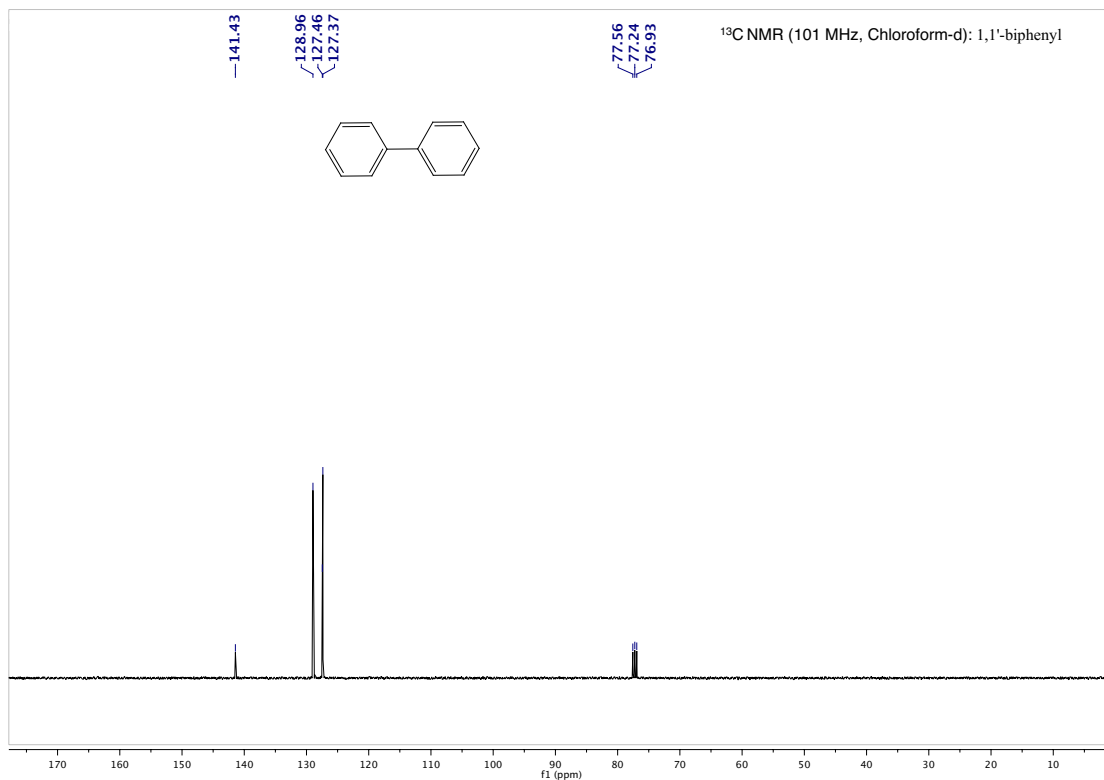
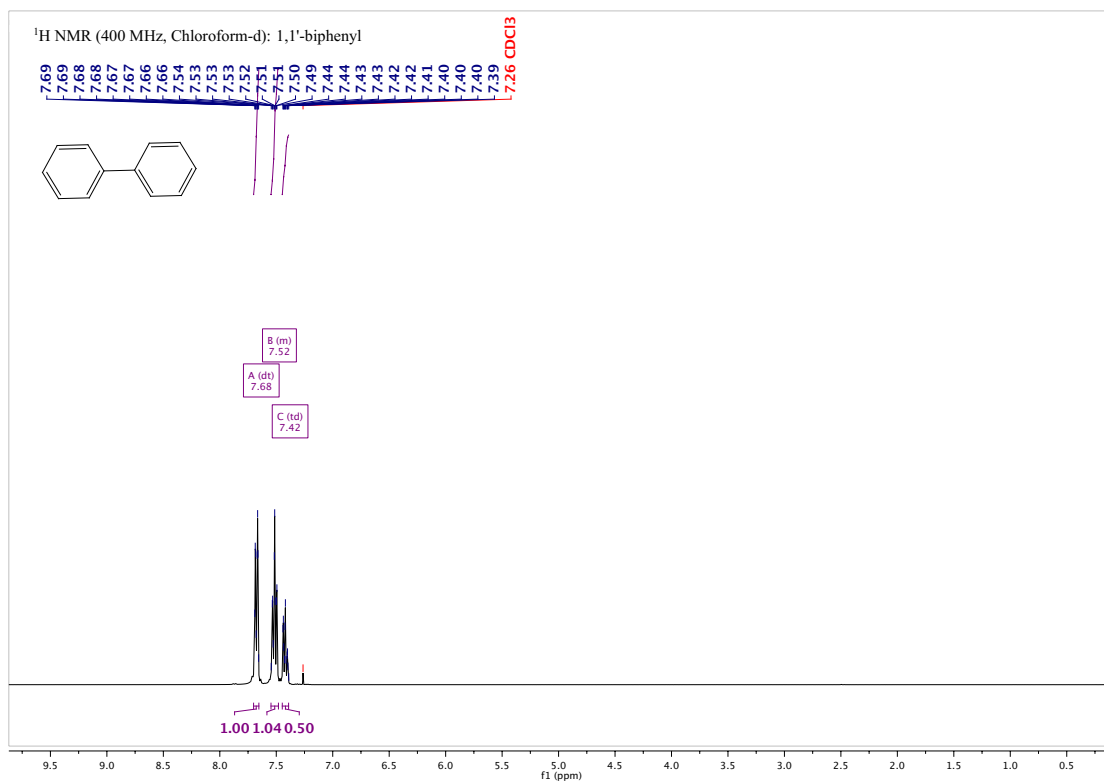


Table 1, Entry 1m:

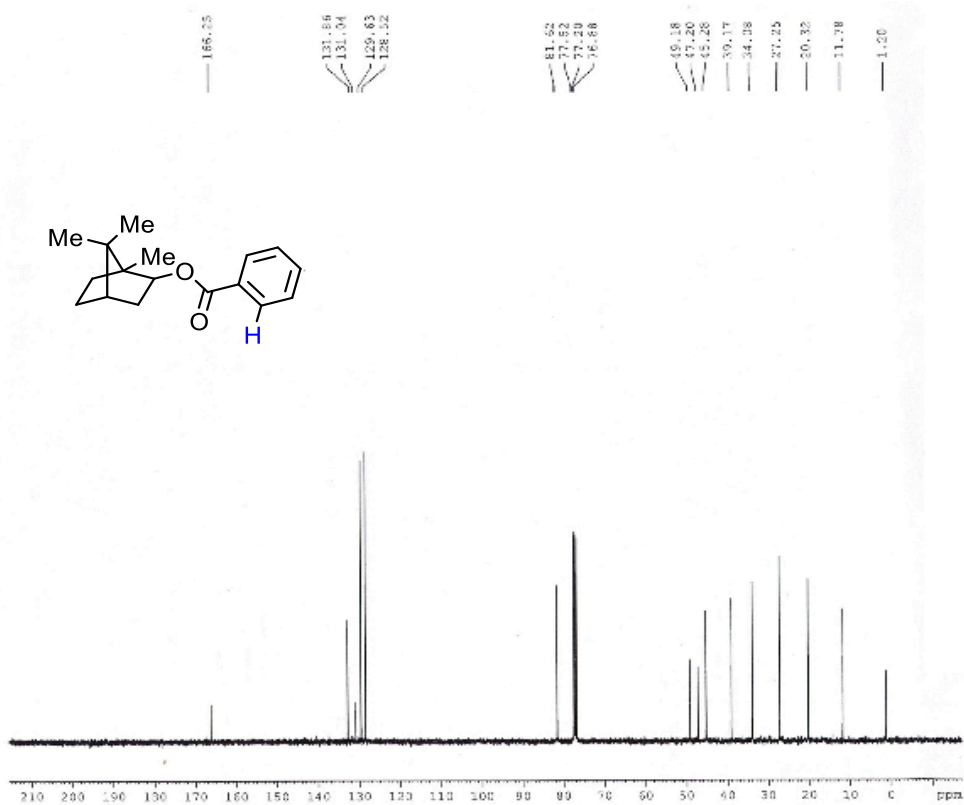
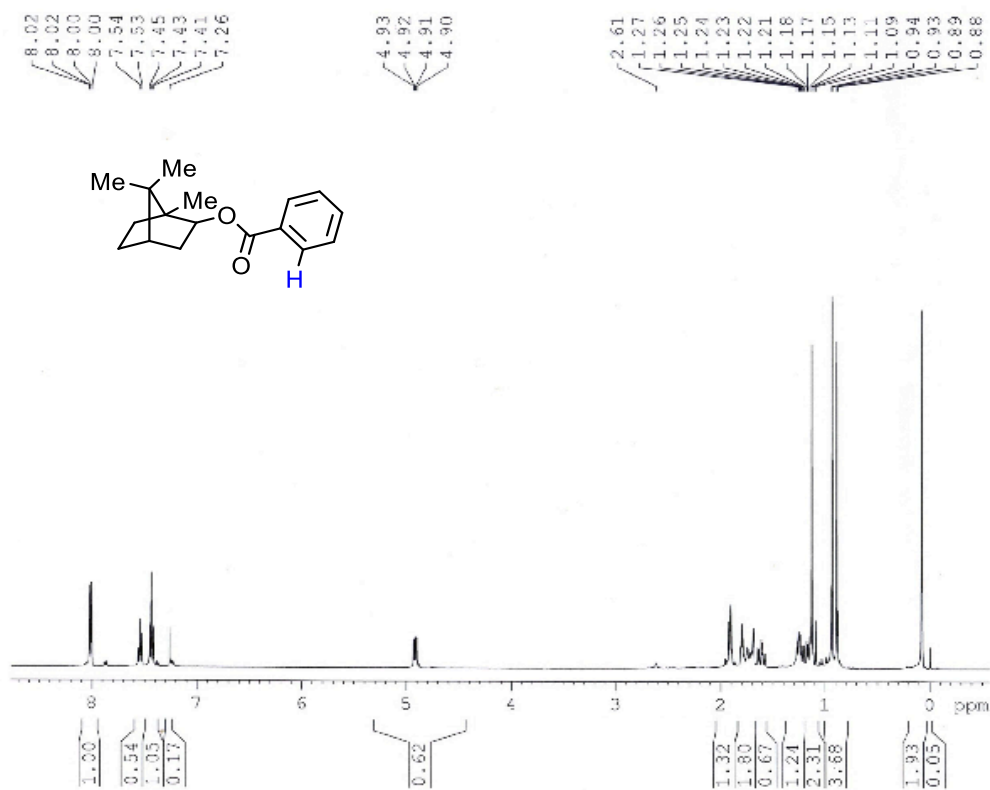


Table 2, Entry 2a:

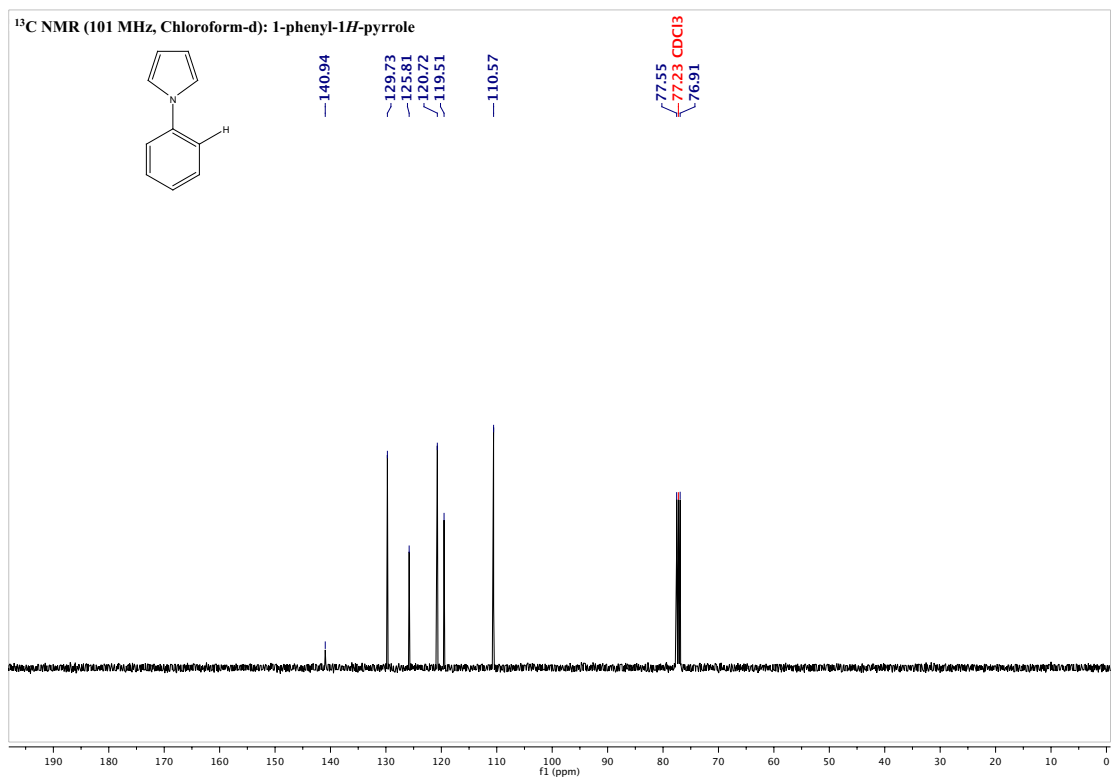
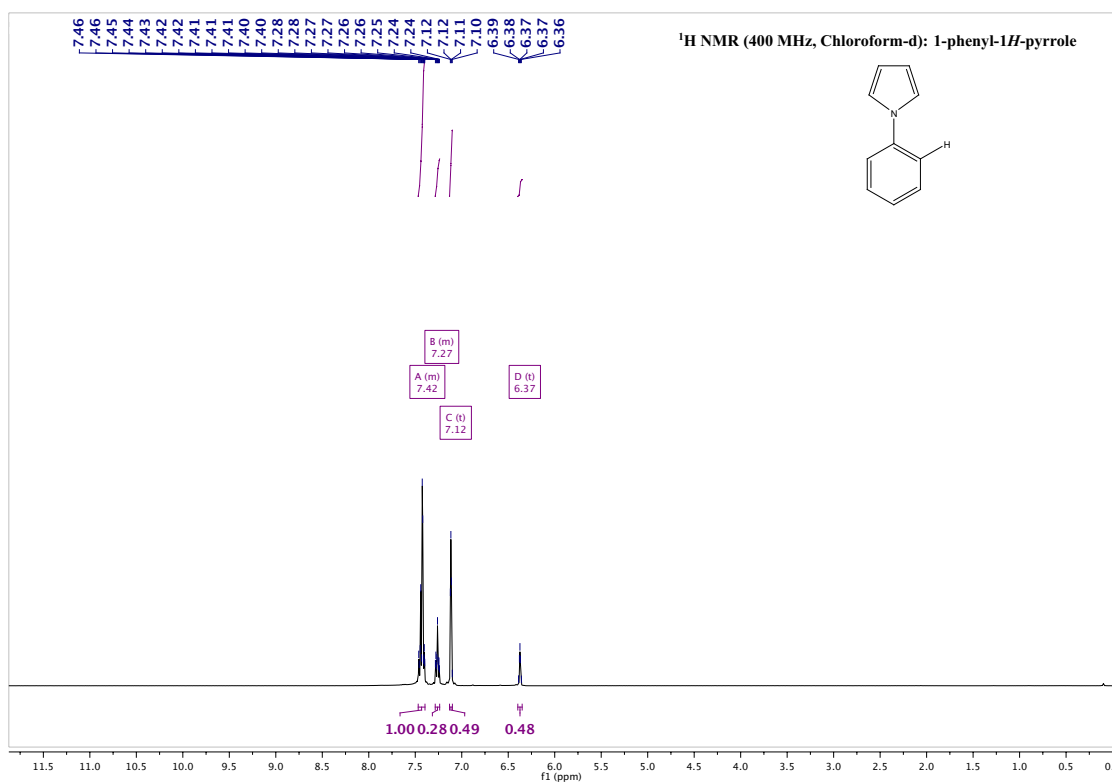


Table 2, Entry 2b:

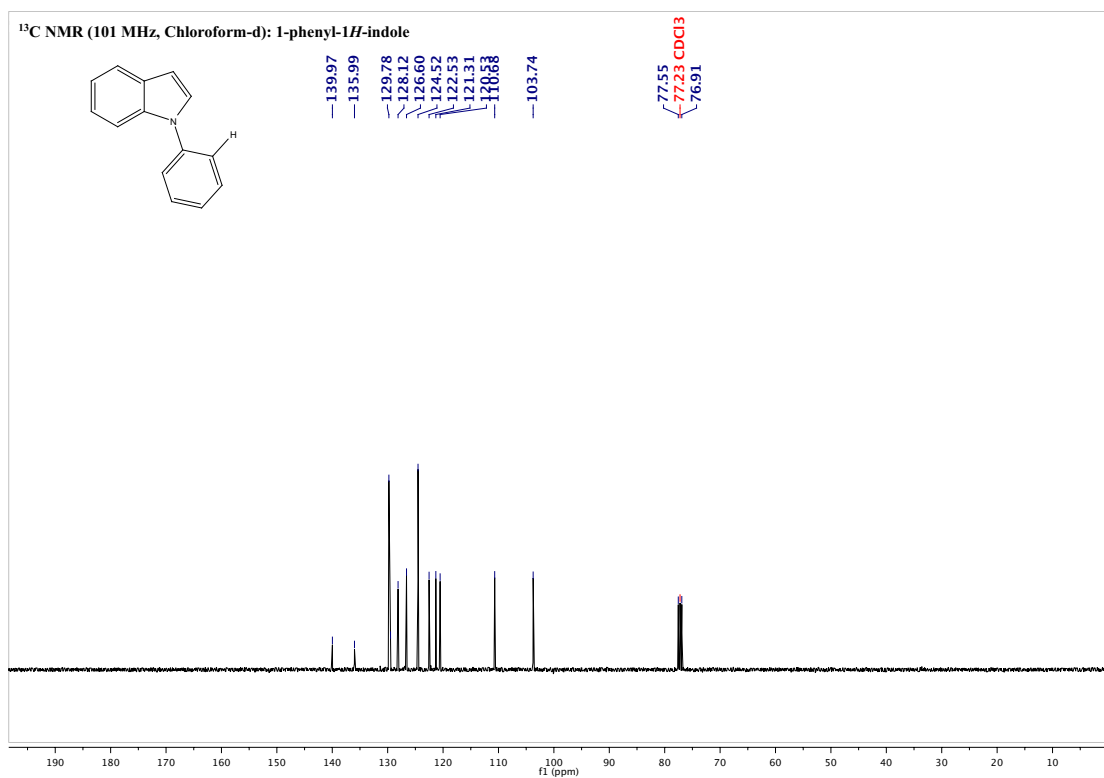
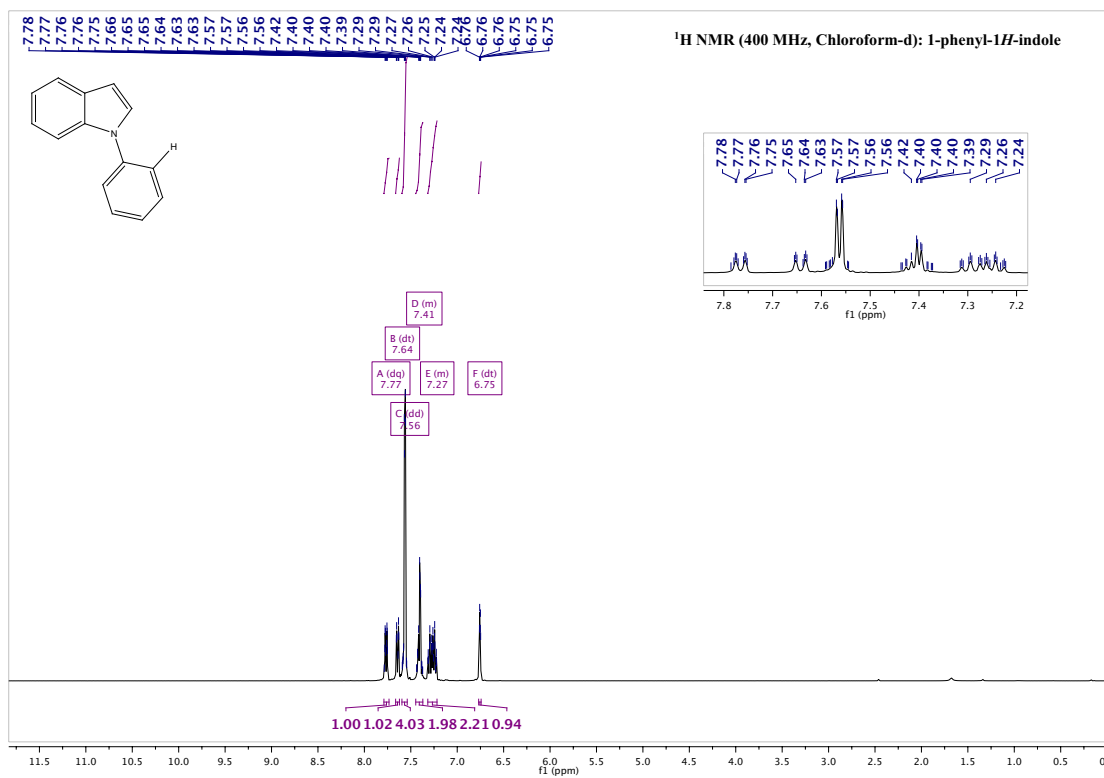


Table 2, Entry 2c:

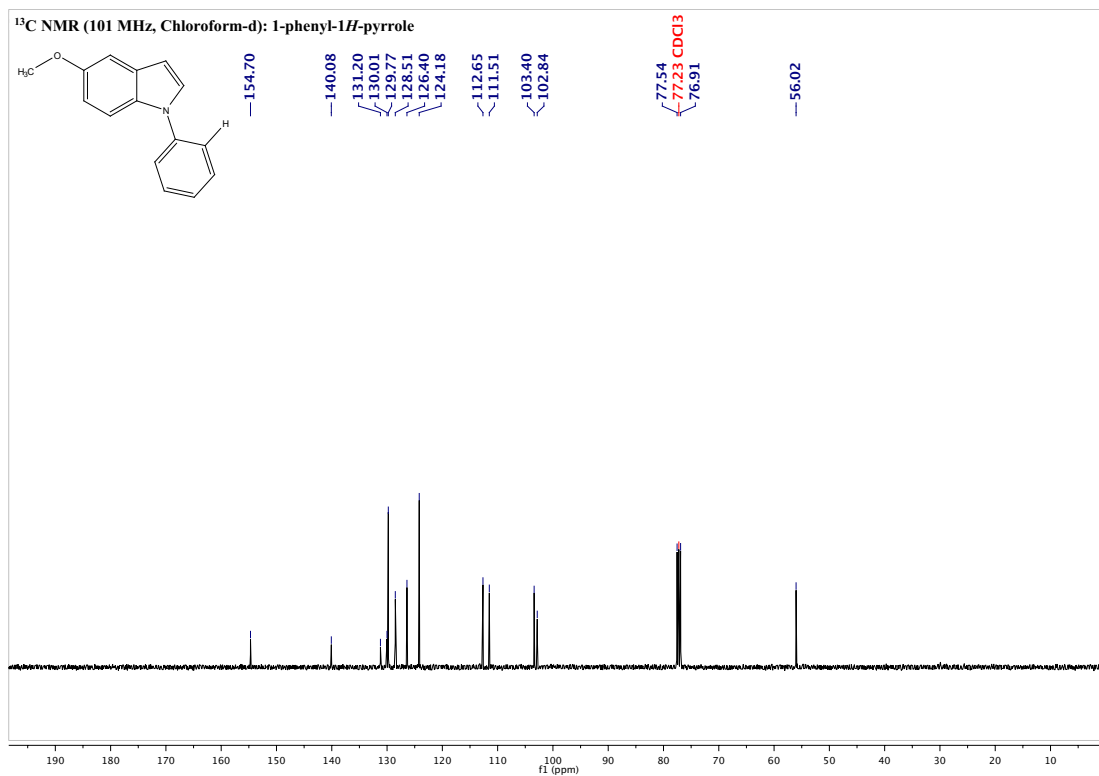
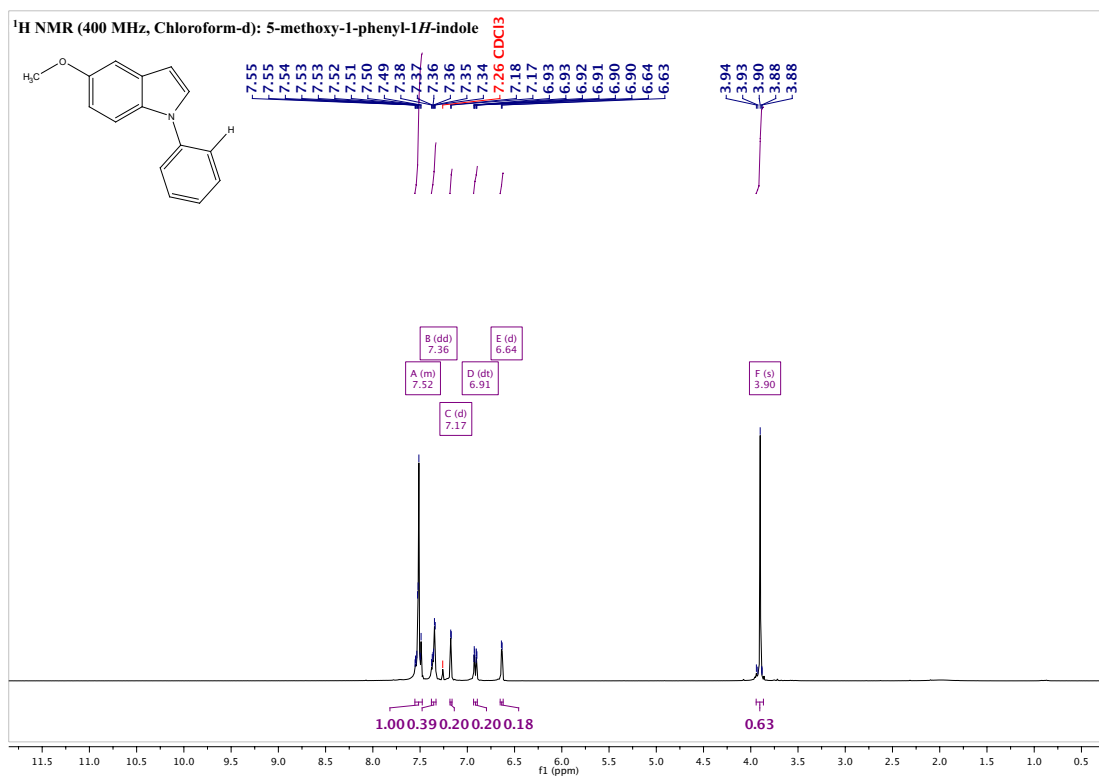


Table 2, Entry 2d and 2e:

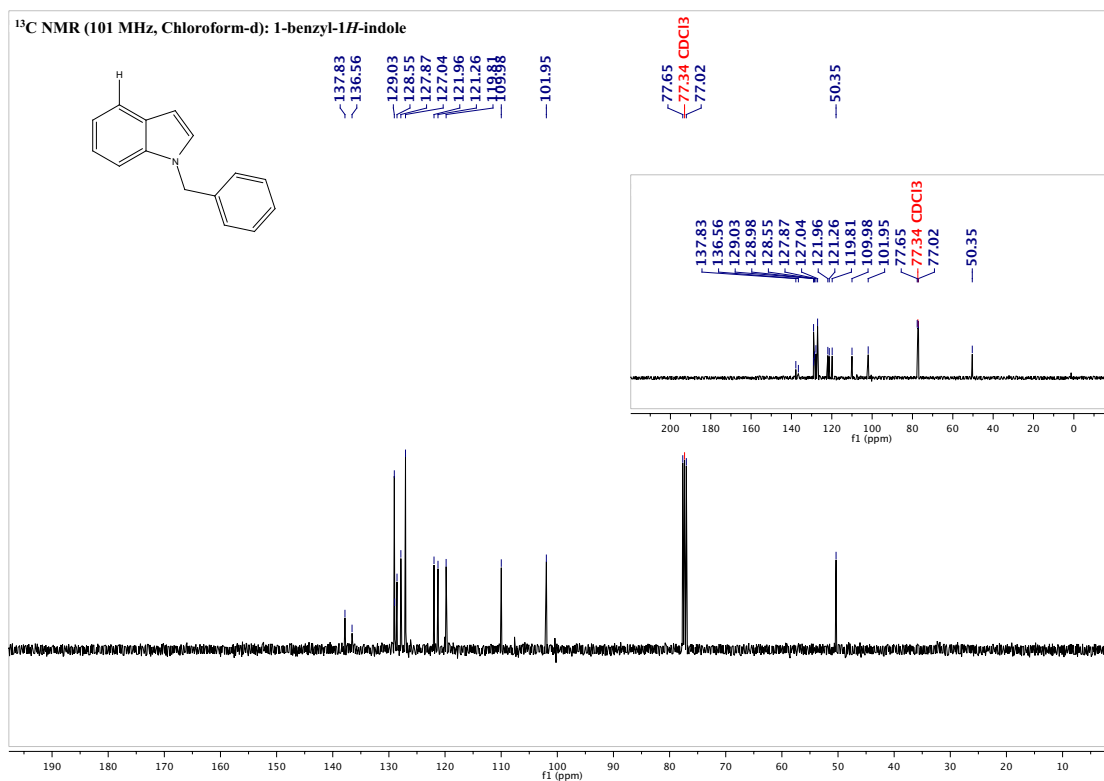
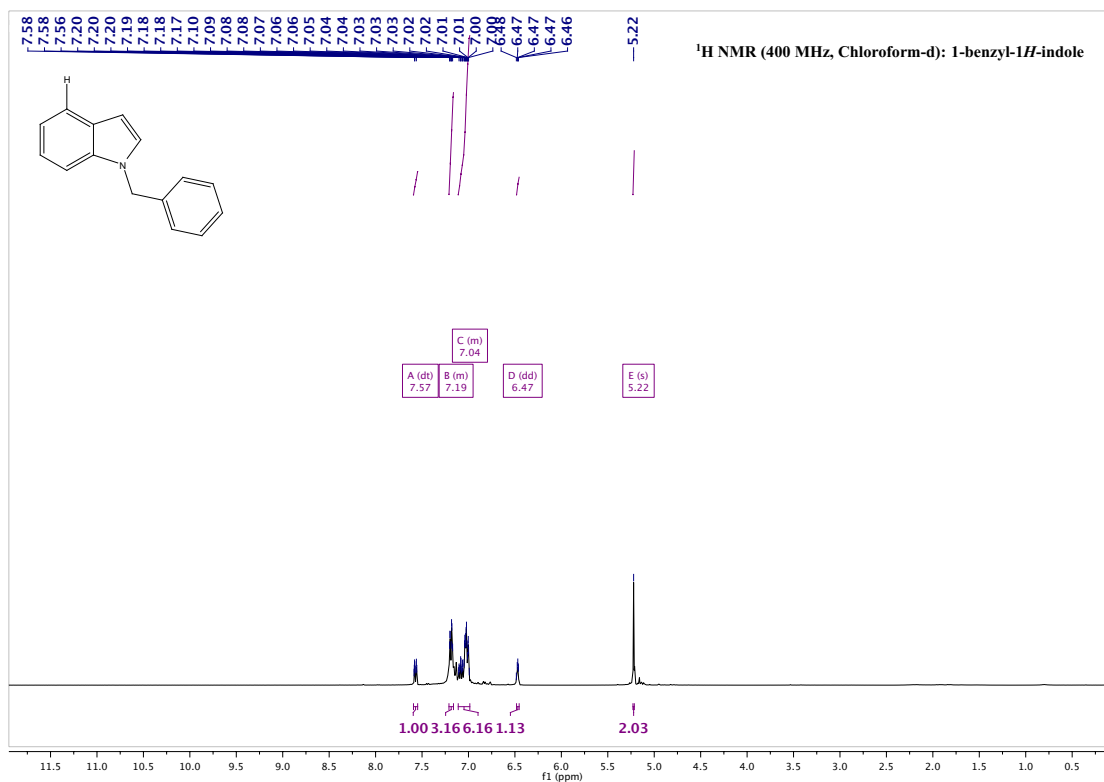


Table 2, Entry 2h:

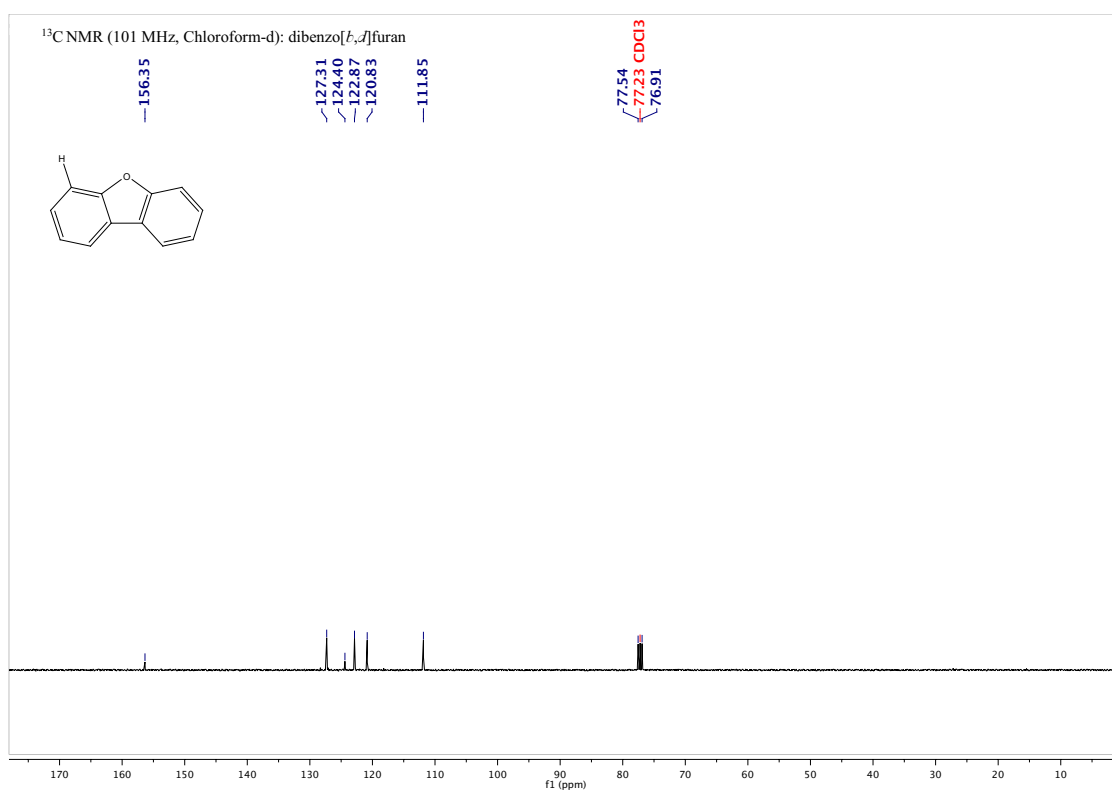
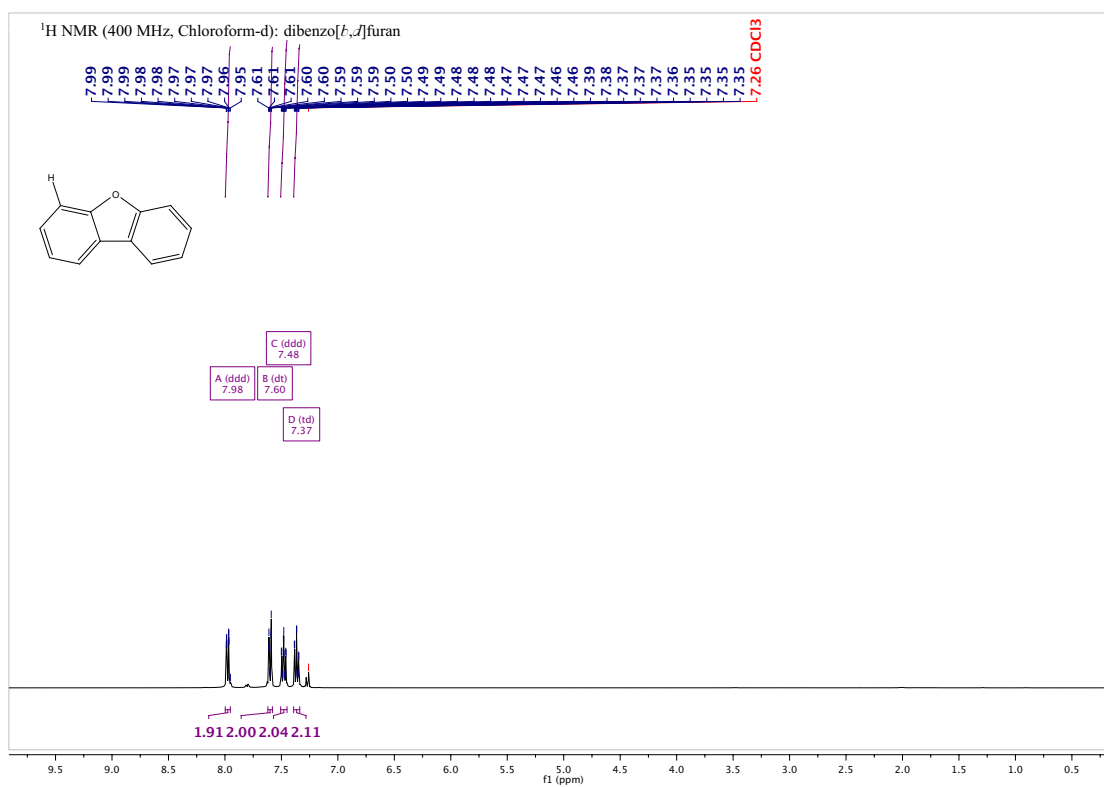


Table 2, Entry 2i:

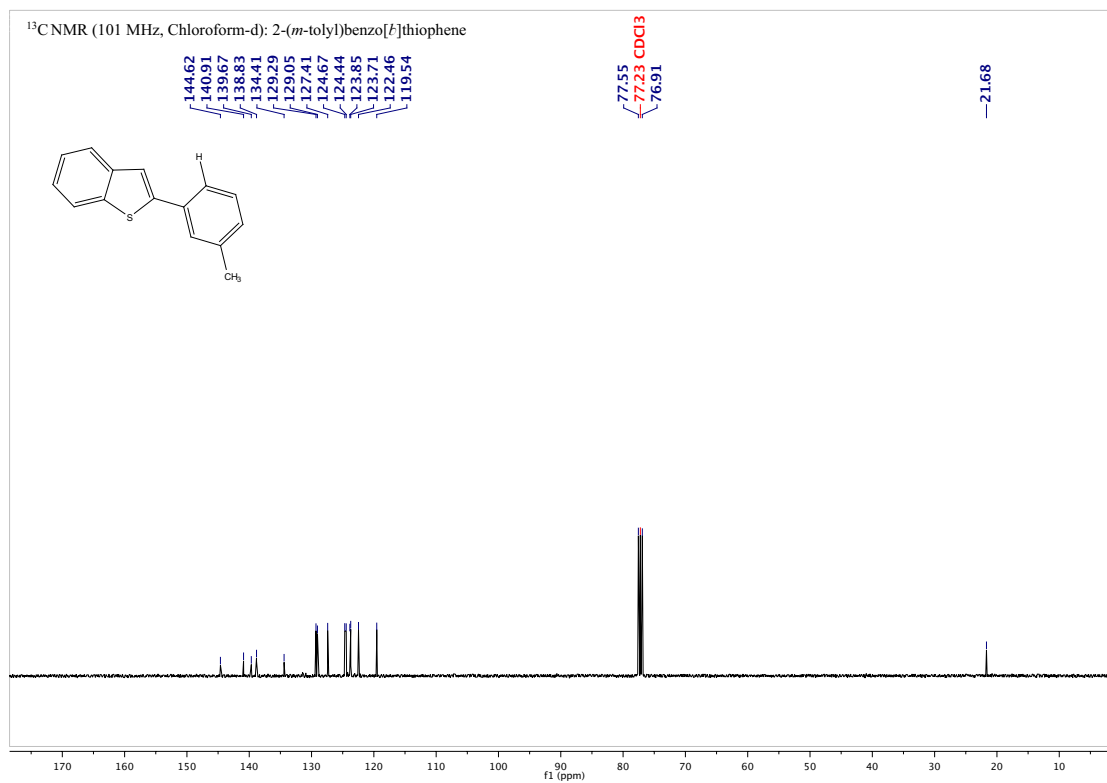
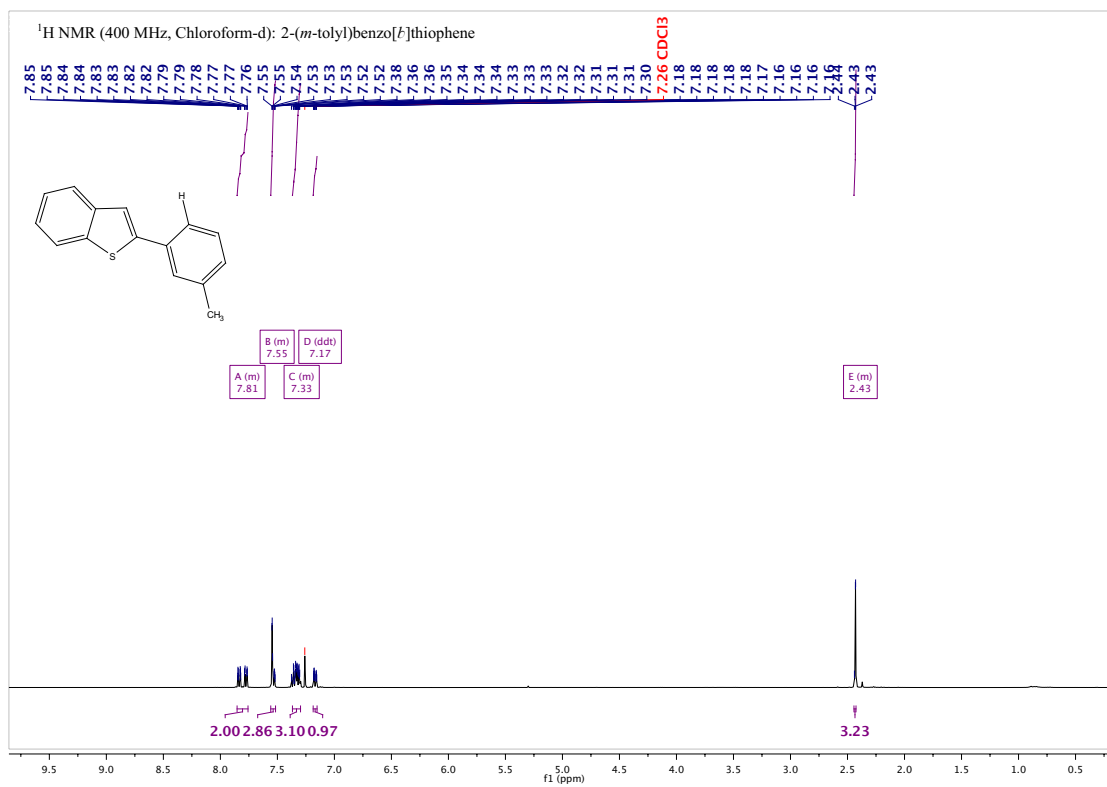


Table 2, Entry 2j:

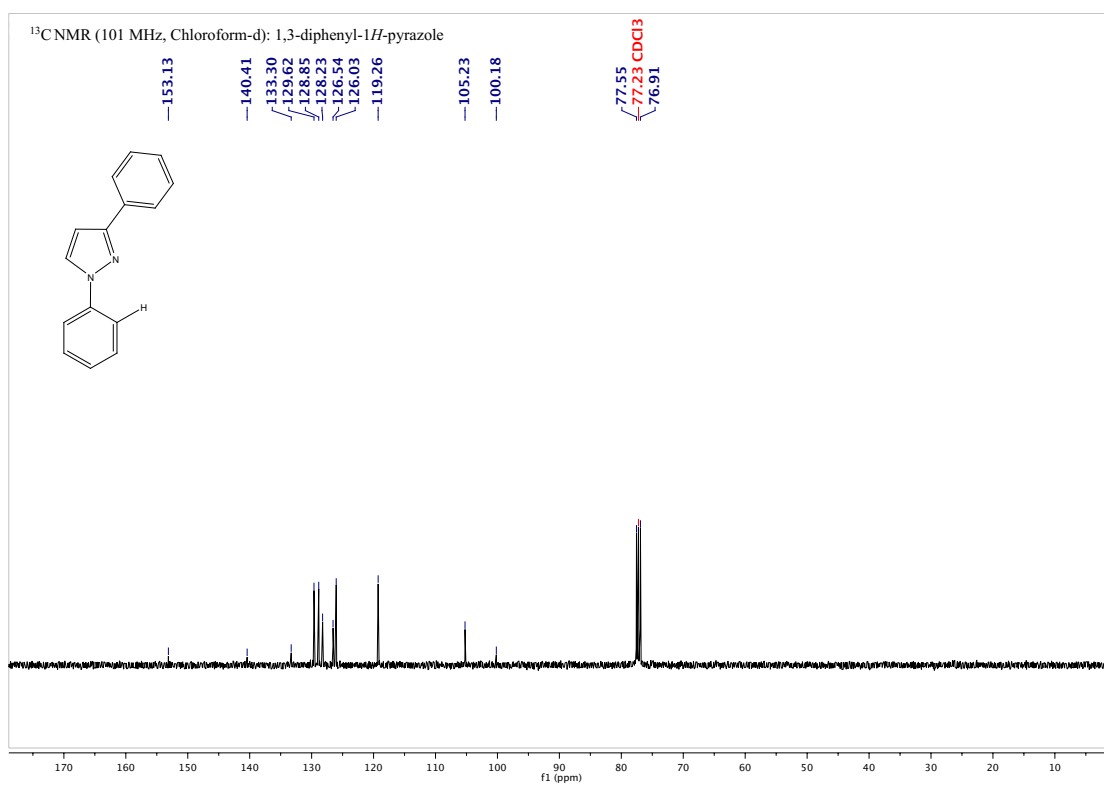
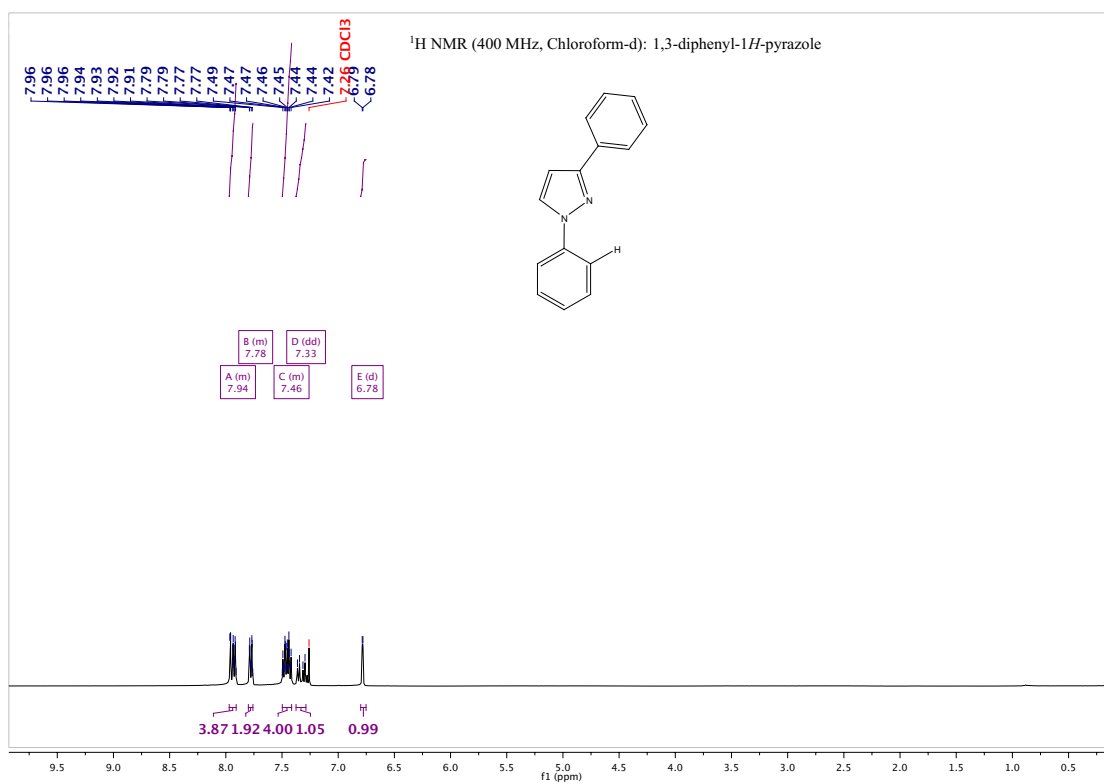


Table 2, Entry 2k:

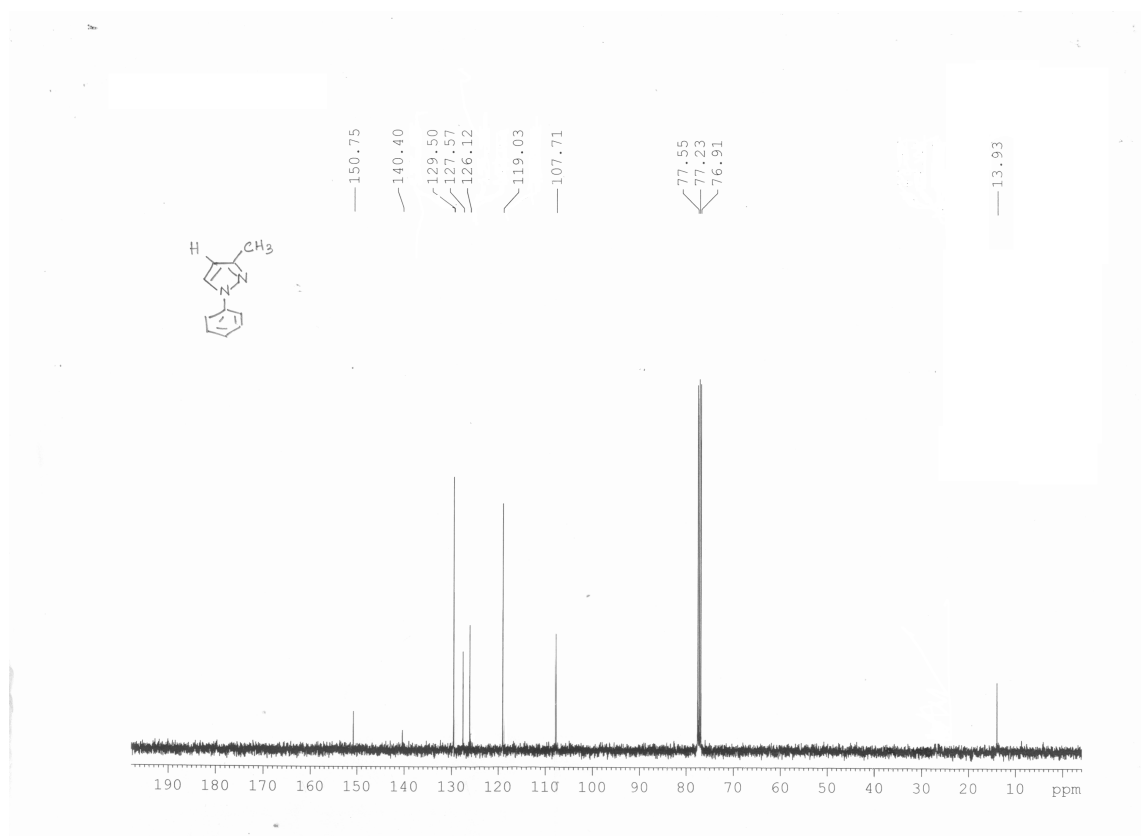
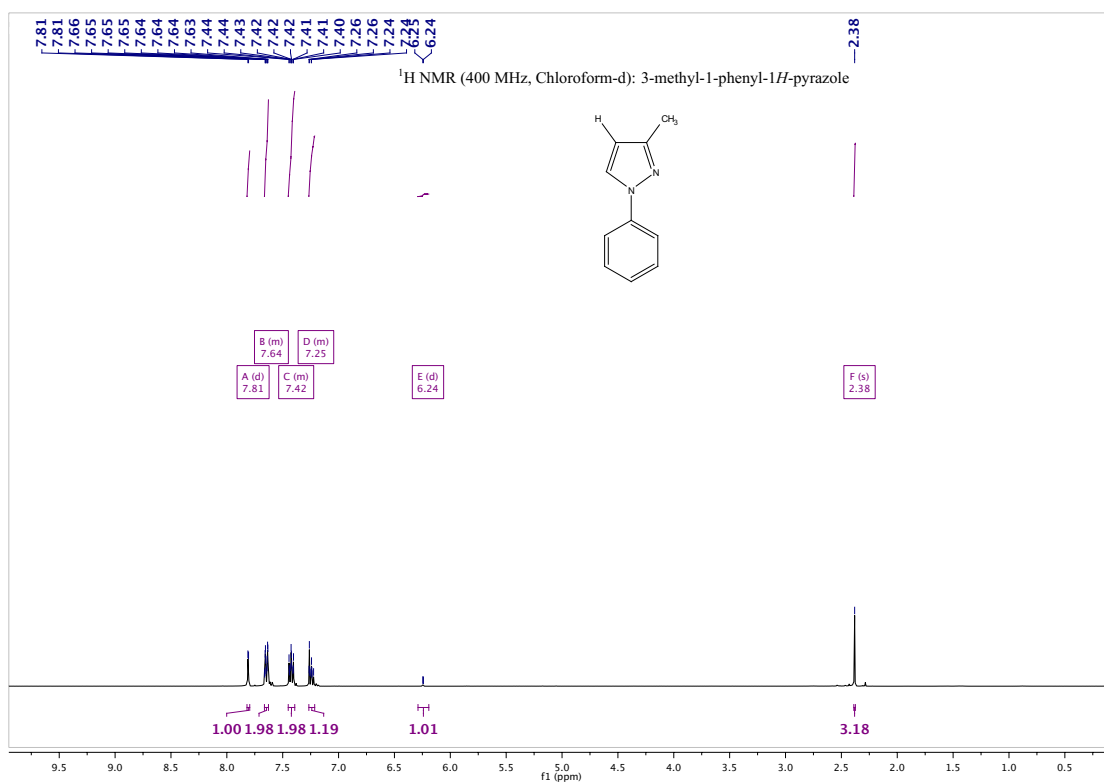


Table 2, Entry 2l:

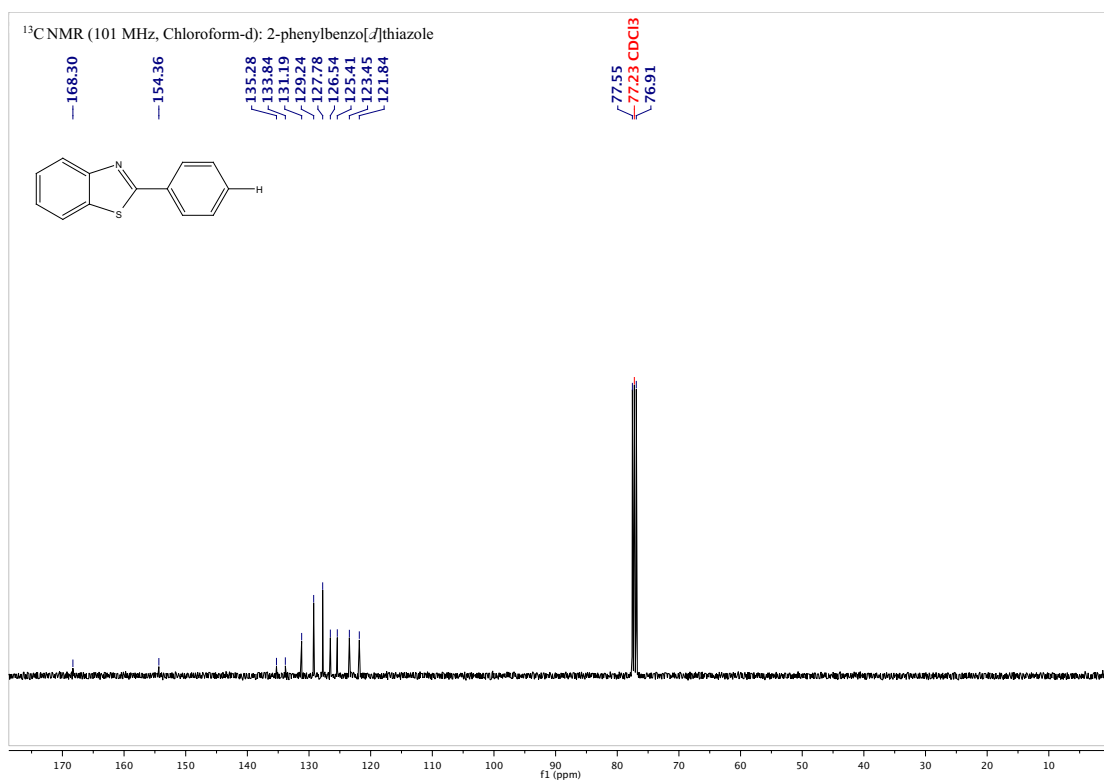
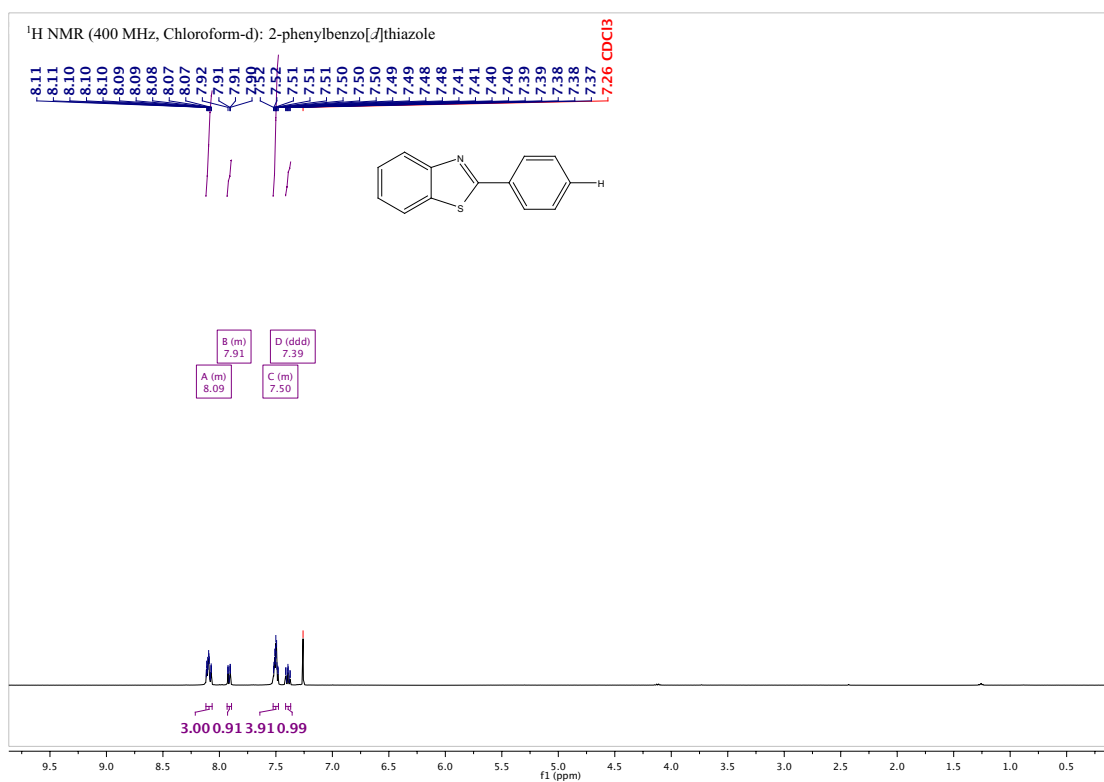


Table 2, Entry 2m and 2n:

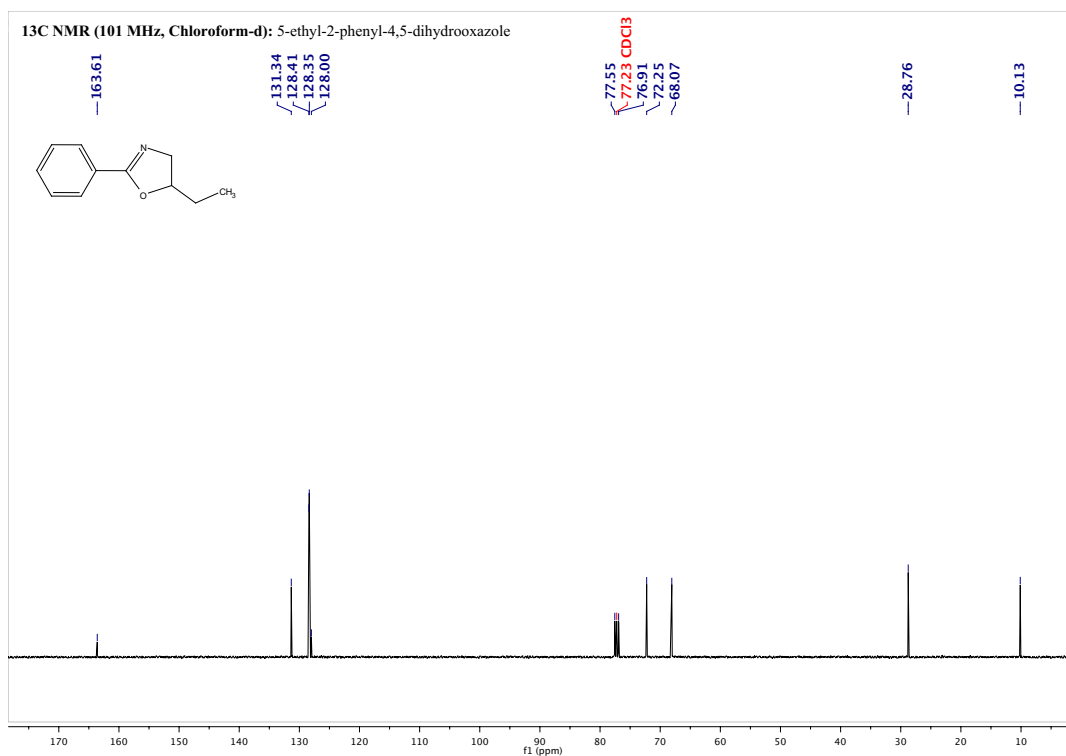


Table 3, Entry 3a:

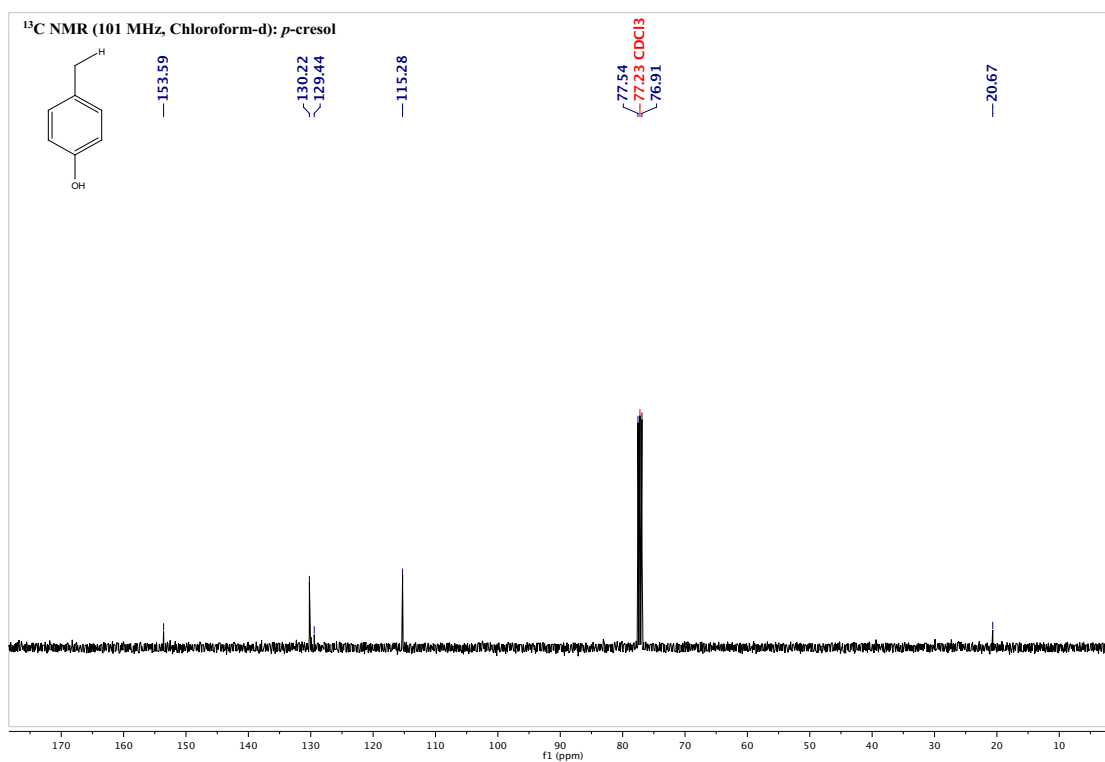
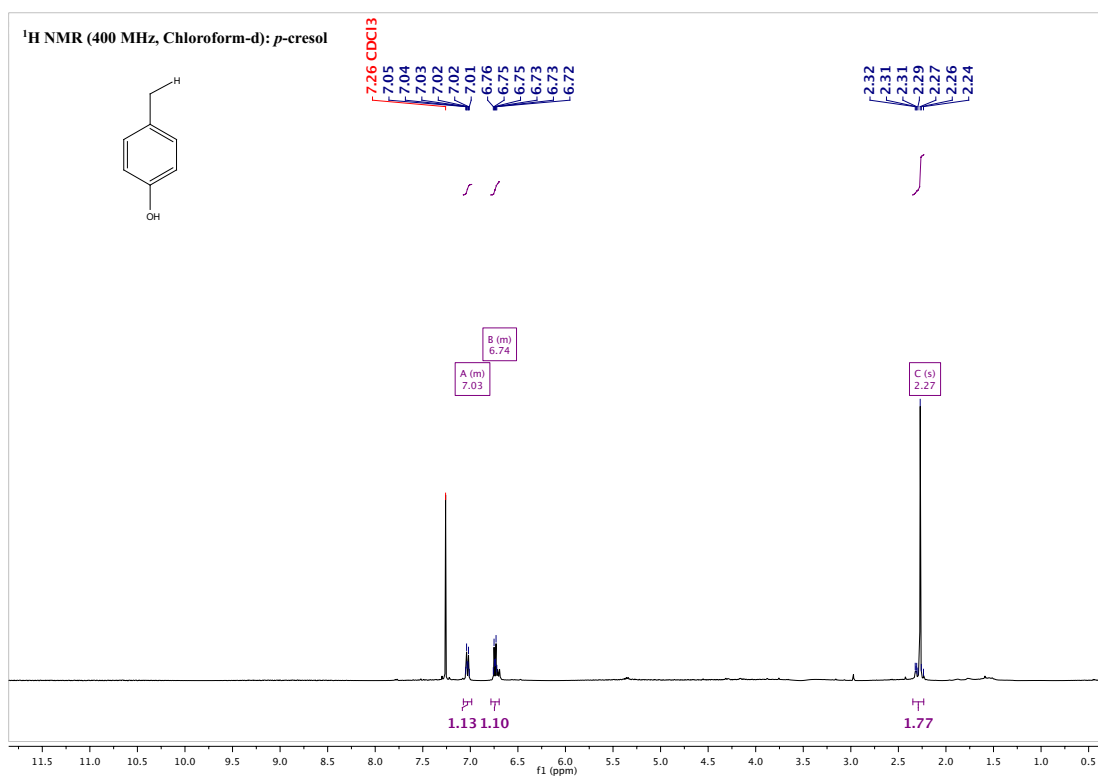
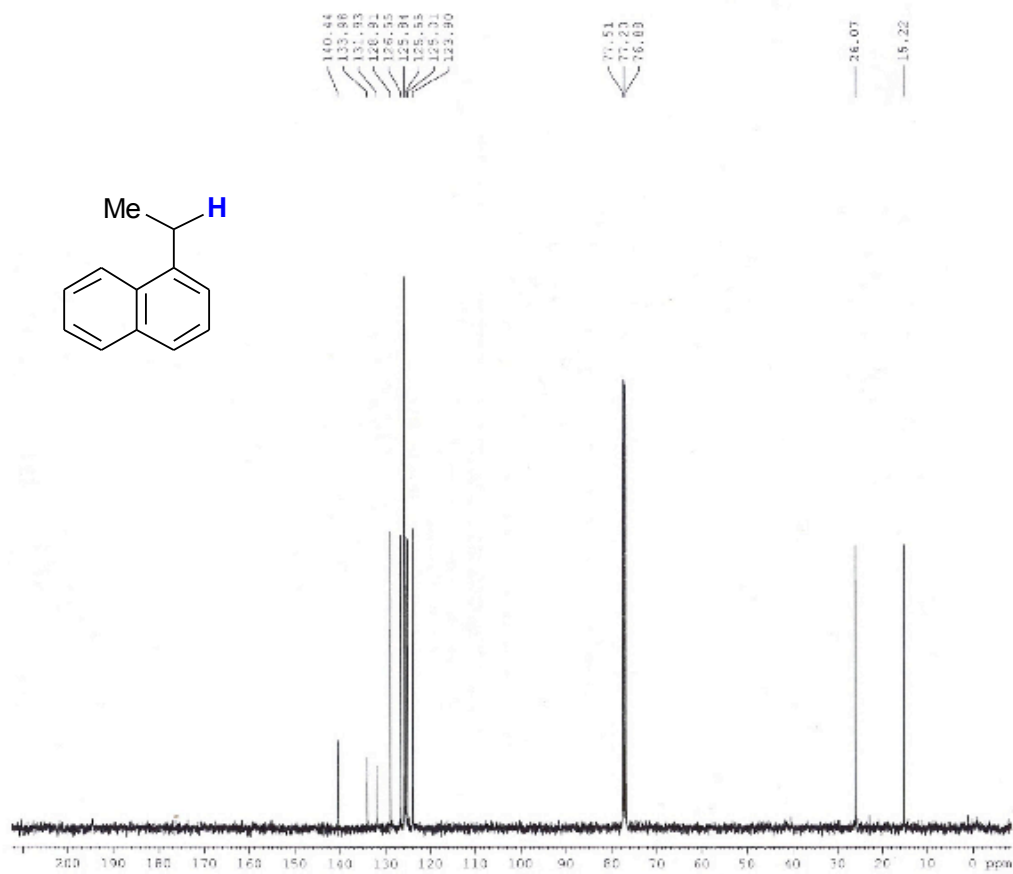
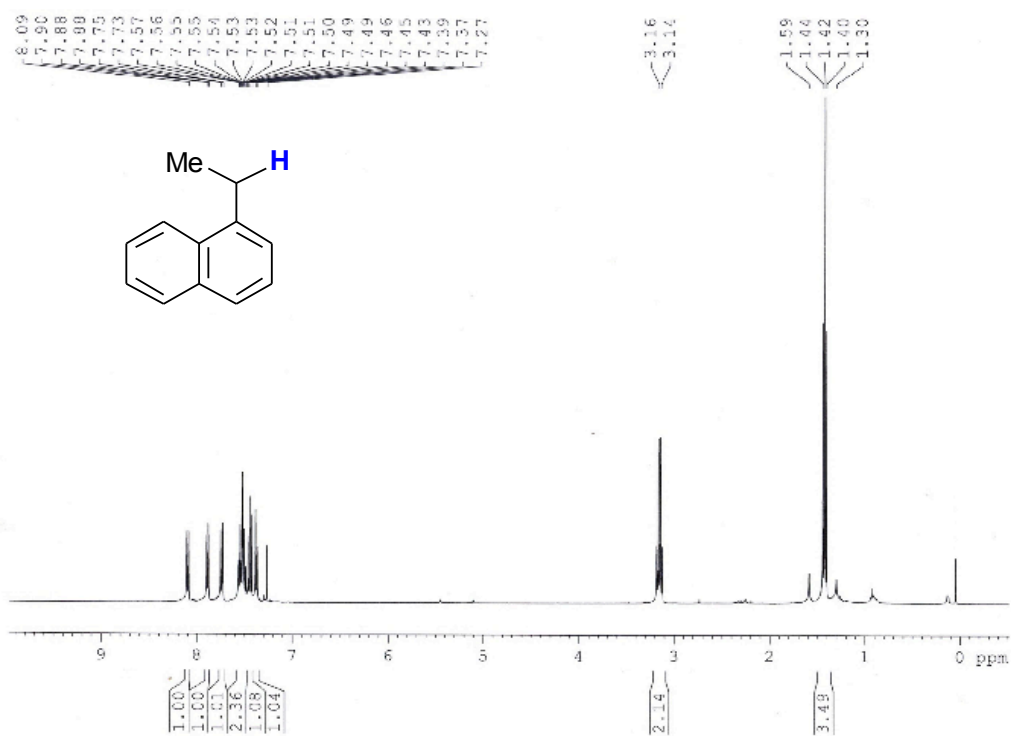
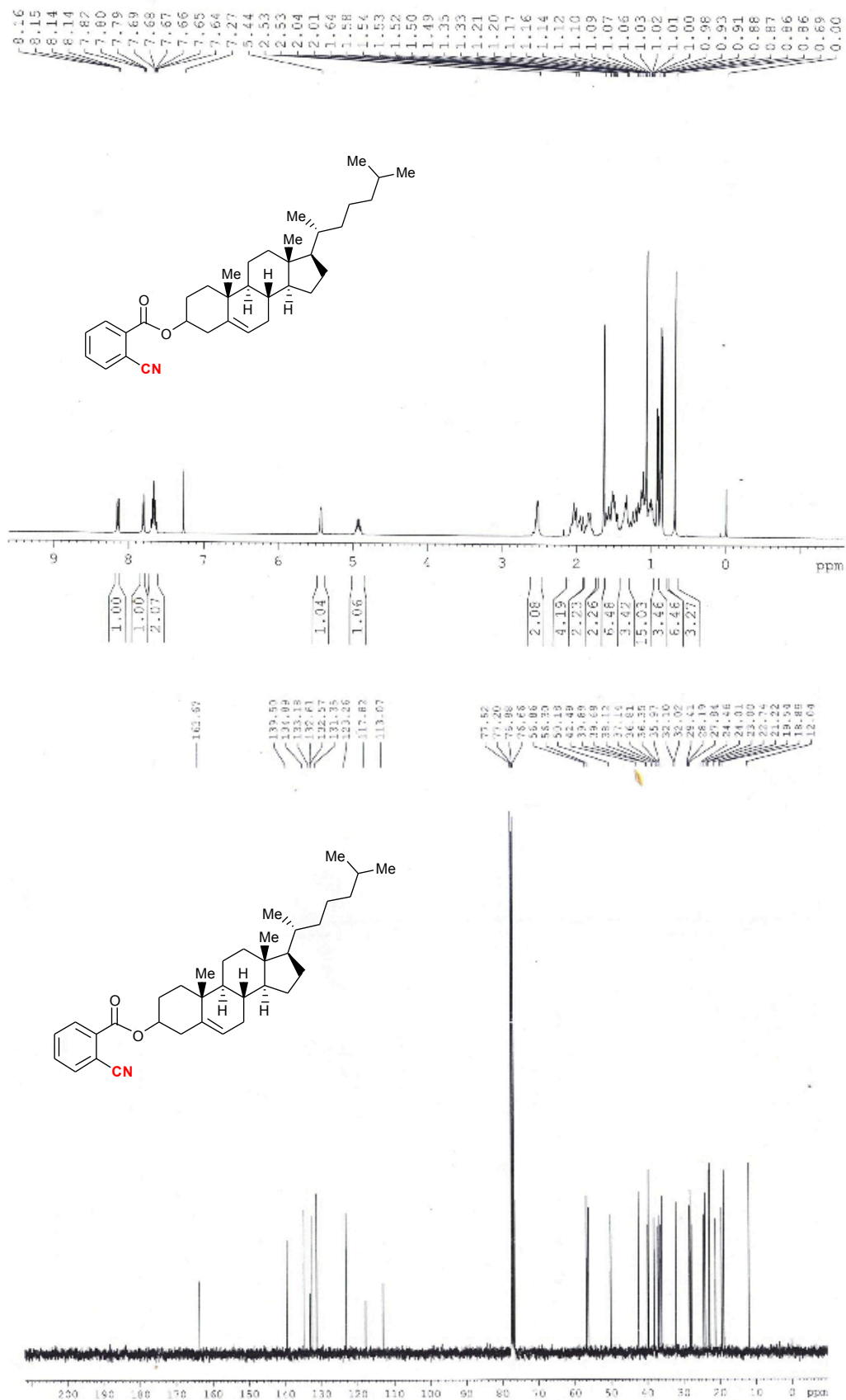


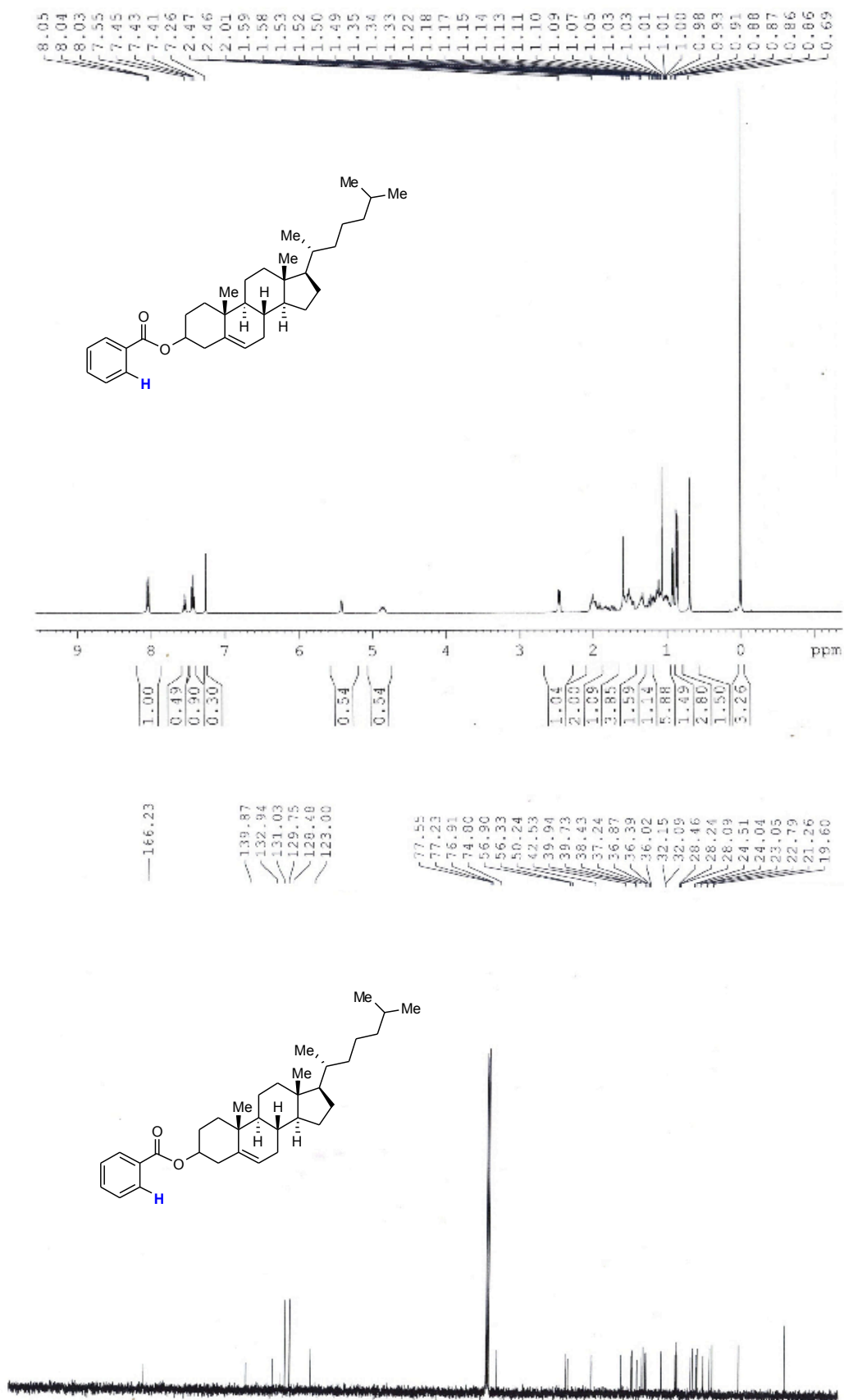
Table 3, Entry 3d and 3c side product:



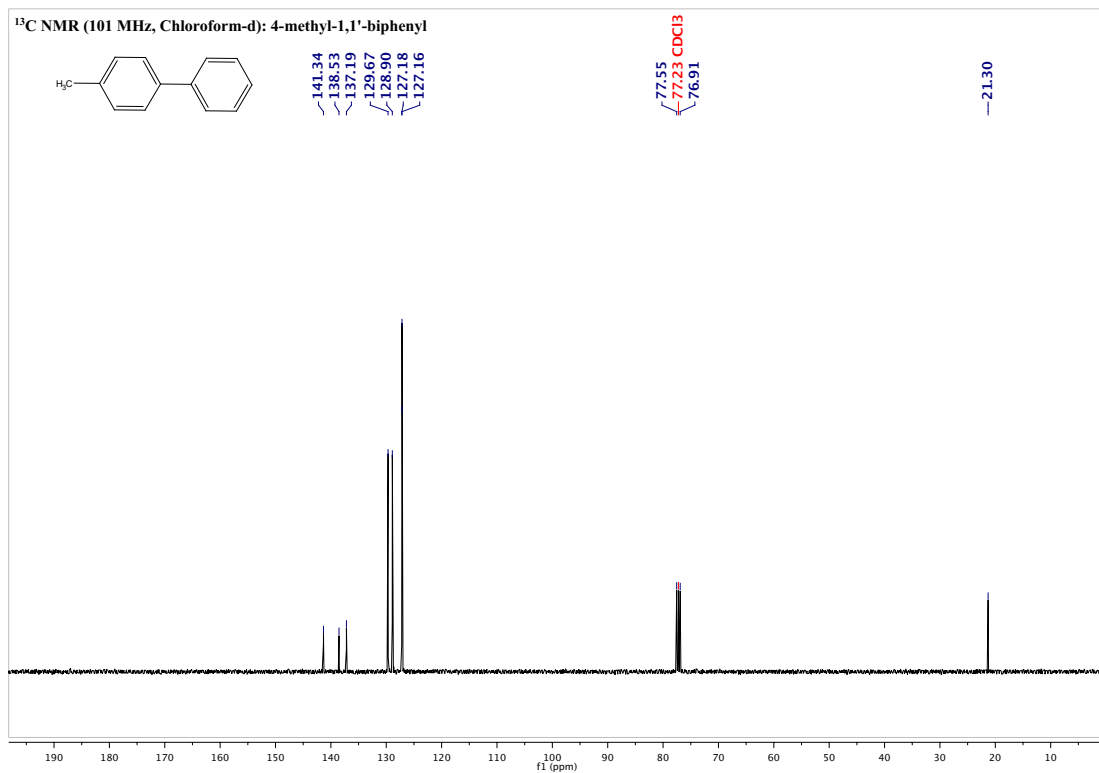
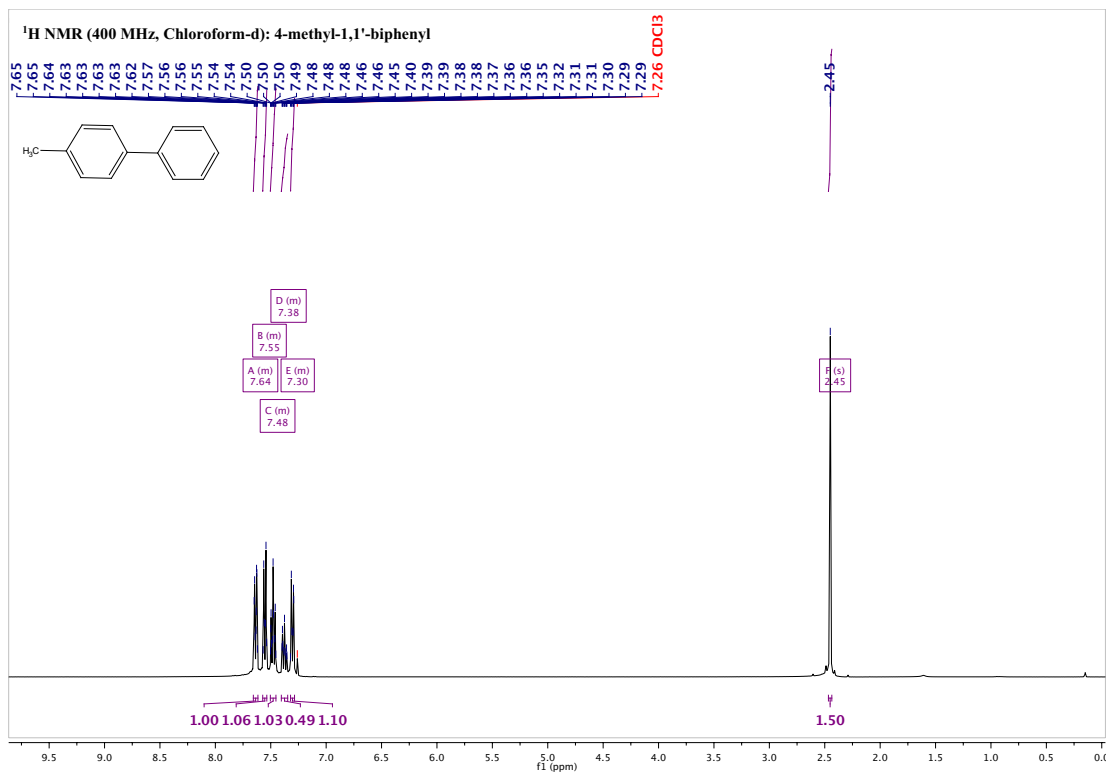
Scheme 2, Entry 4a:



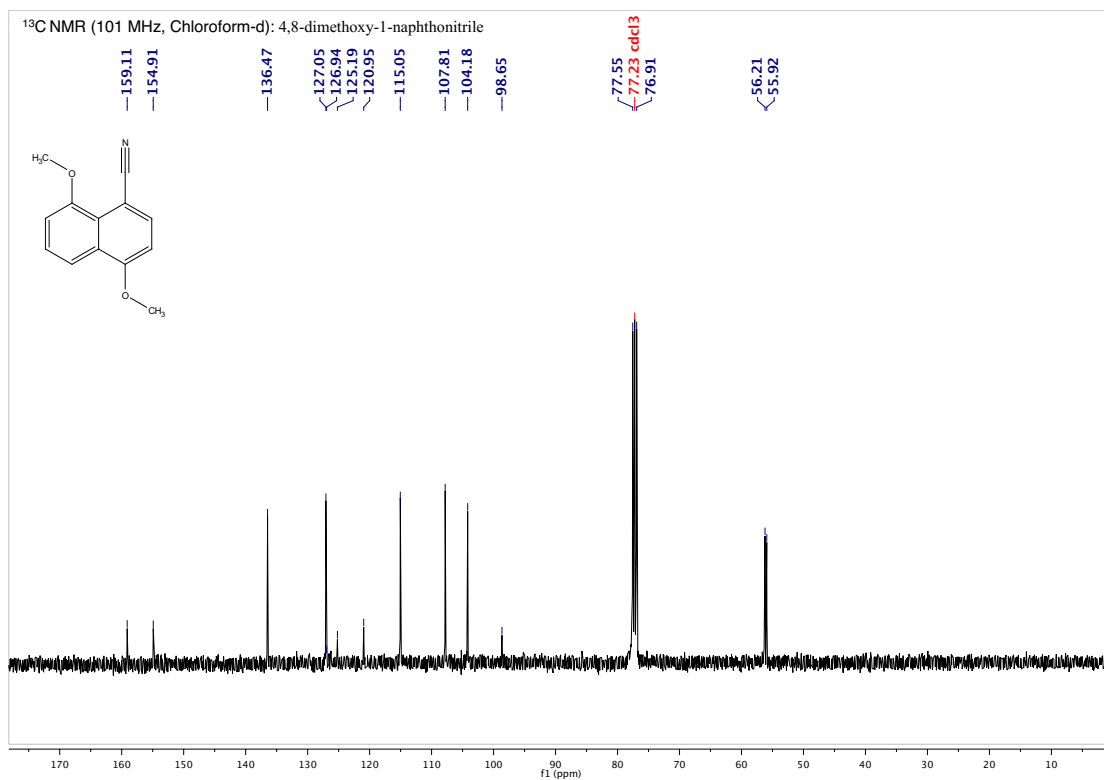
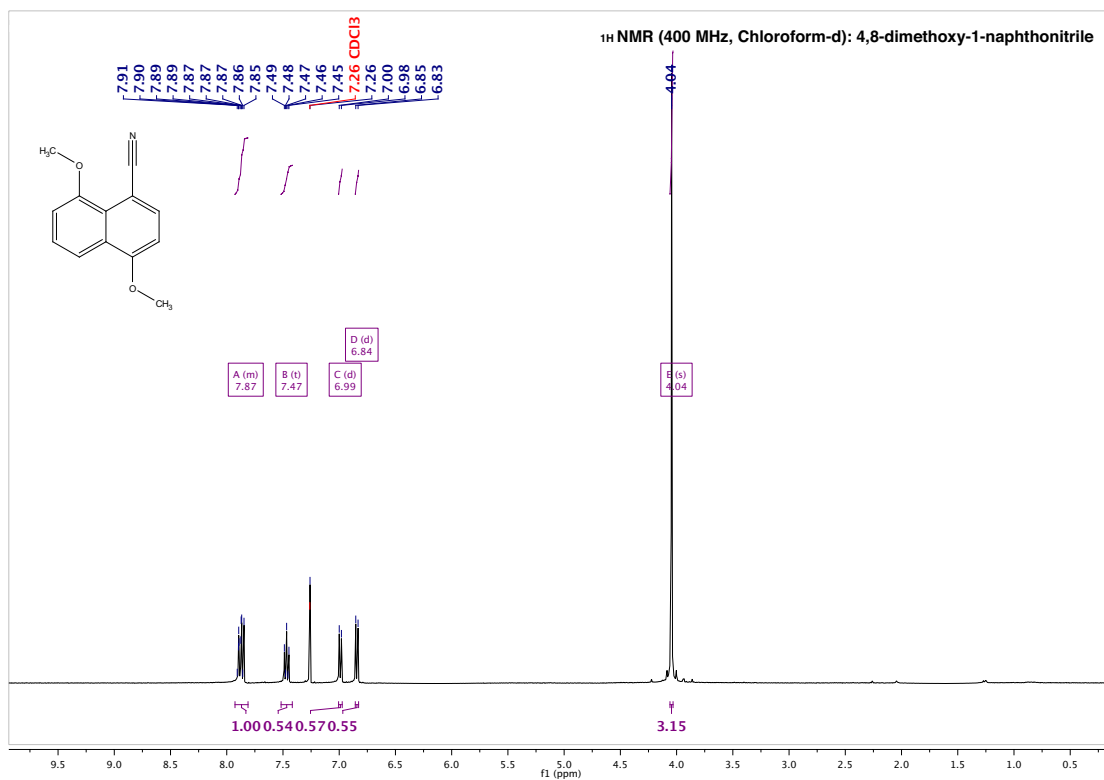
Scheme 2, Entry 4b:



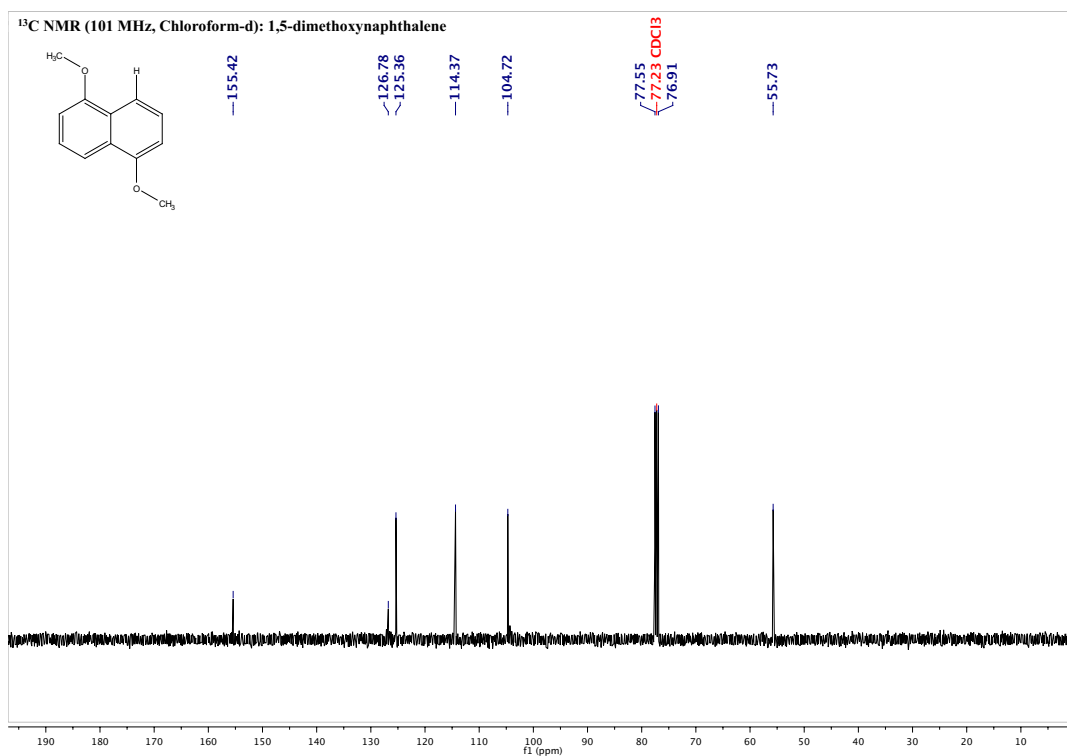
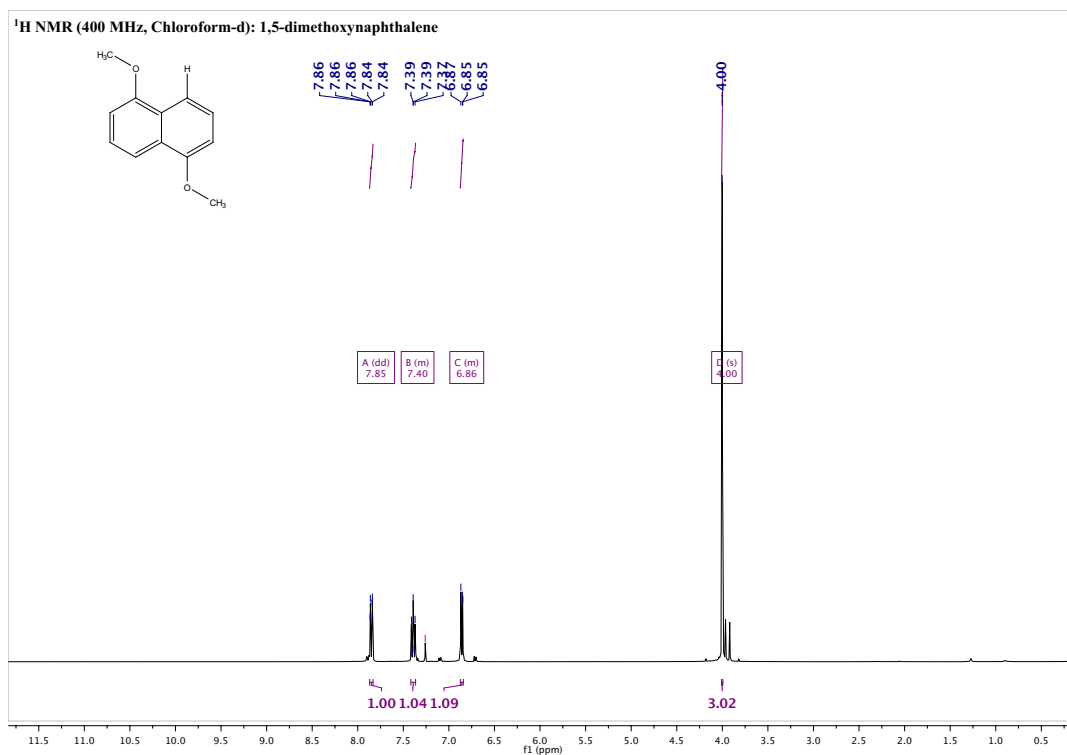
Scheme 2, Entry 4d:



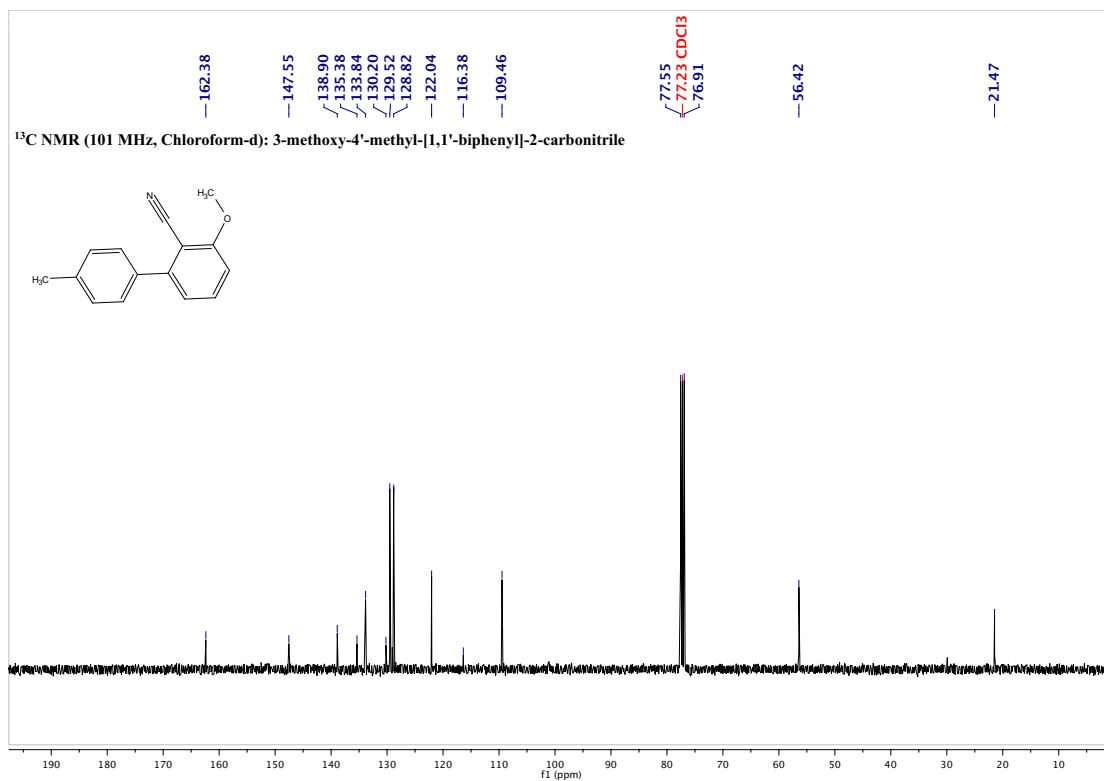
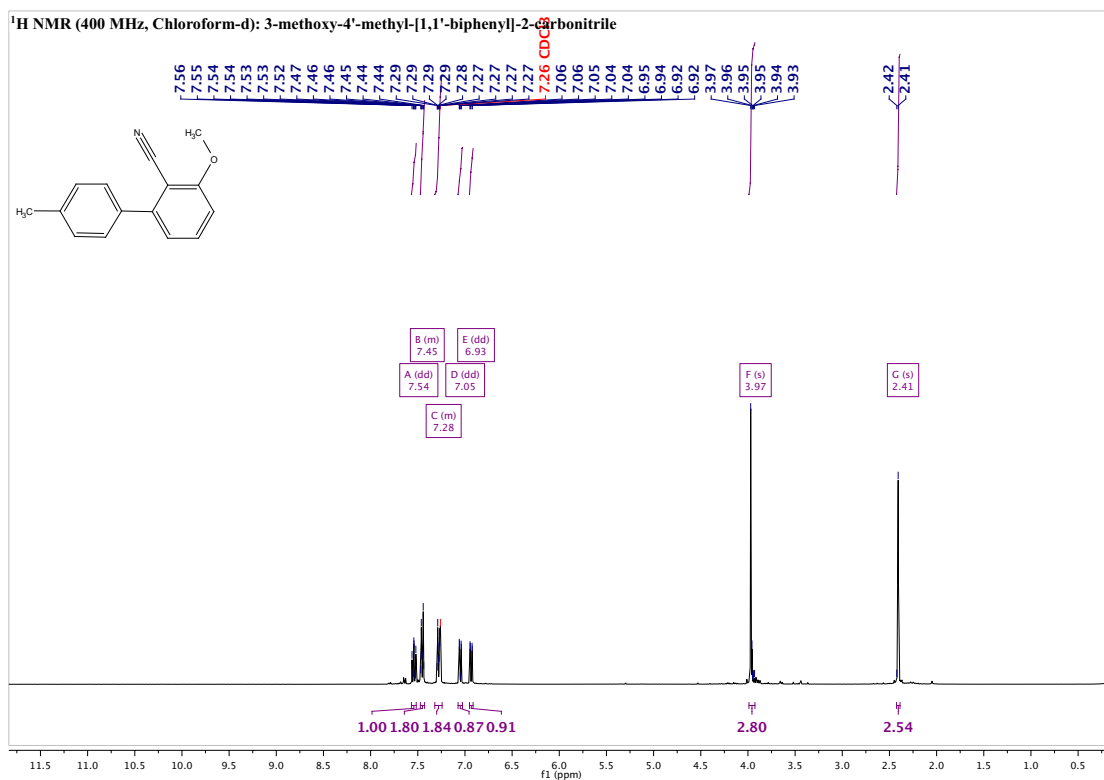
Scheme 2, Entry 4e:



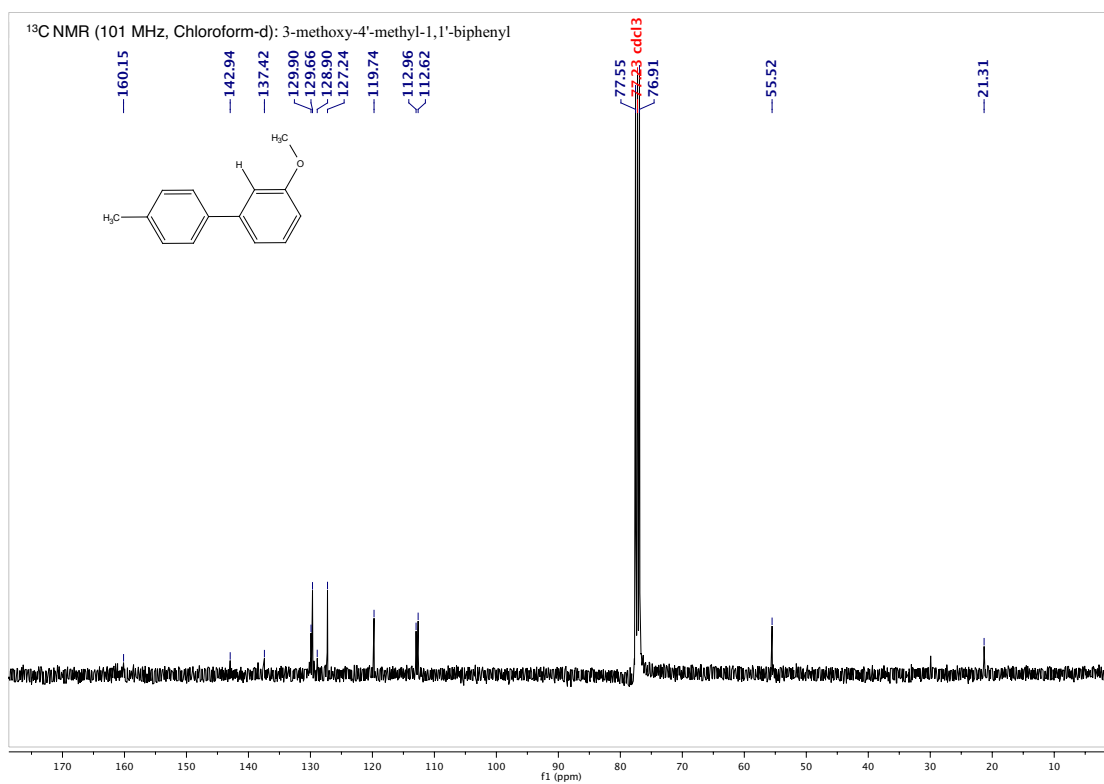
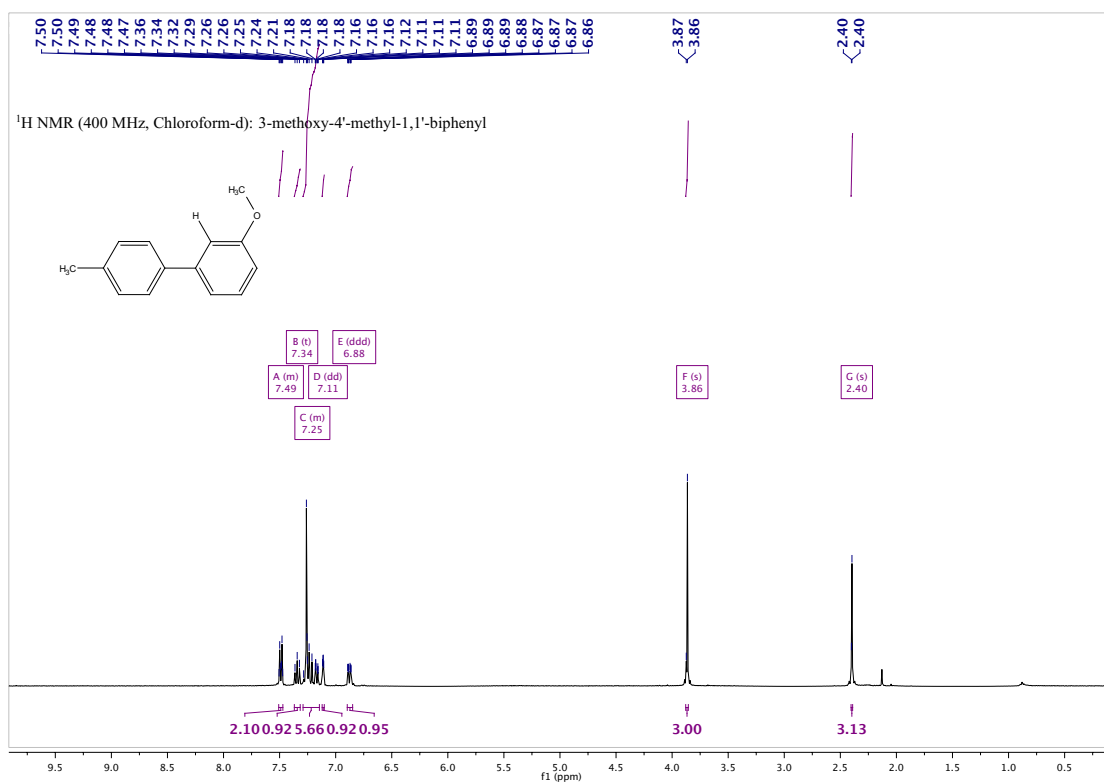
Scheme 2, Entry 4f:



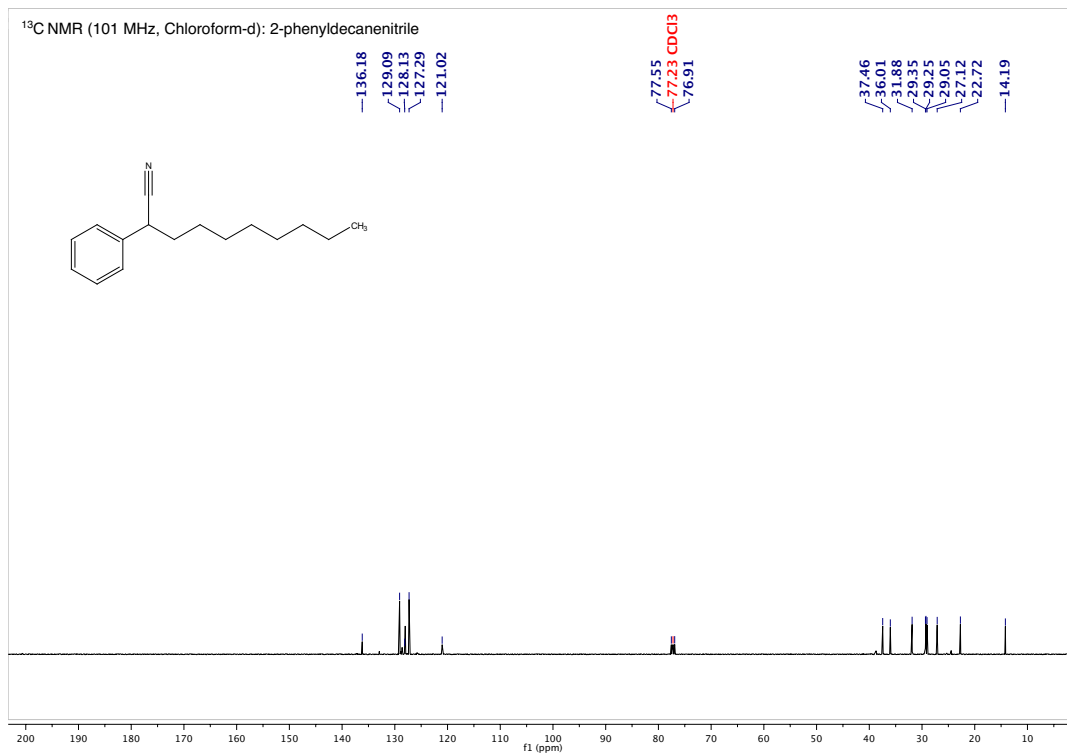
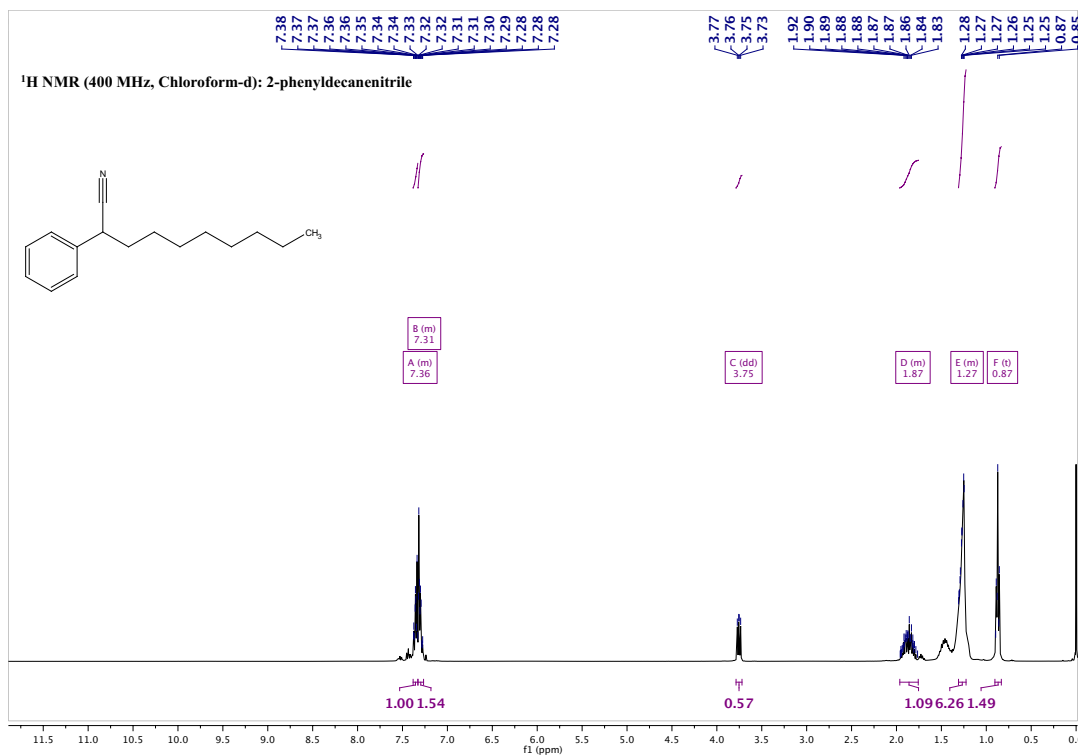
Scheme 2, Entry 4g:



Scheme 2, Entry 4h:



Scheme 2, Entry 4i:



Scheme 2, Entry 4j:

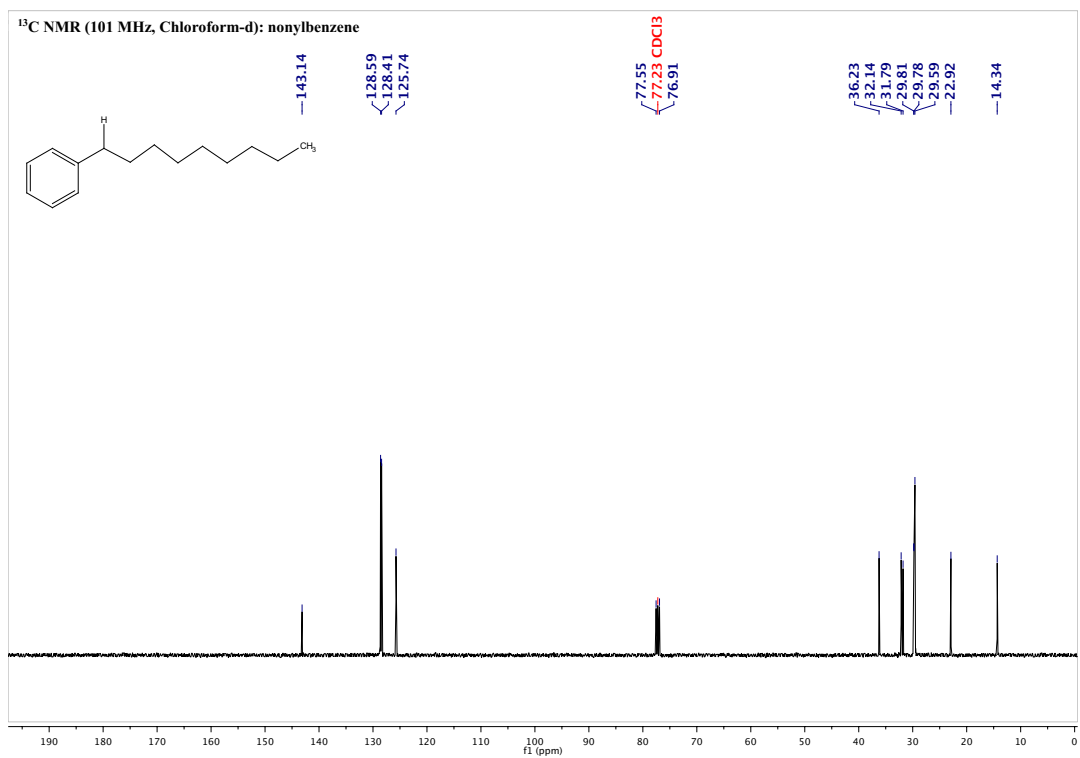
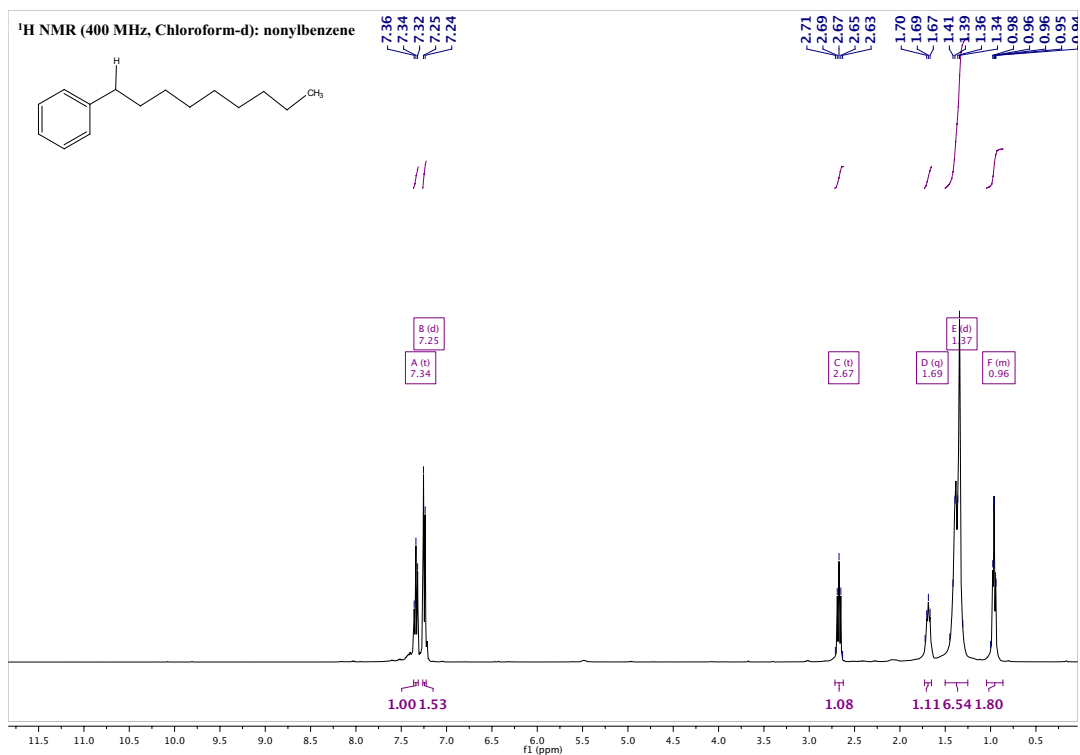


Table 1, Entry 1a (side product):

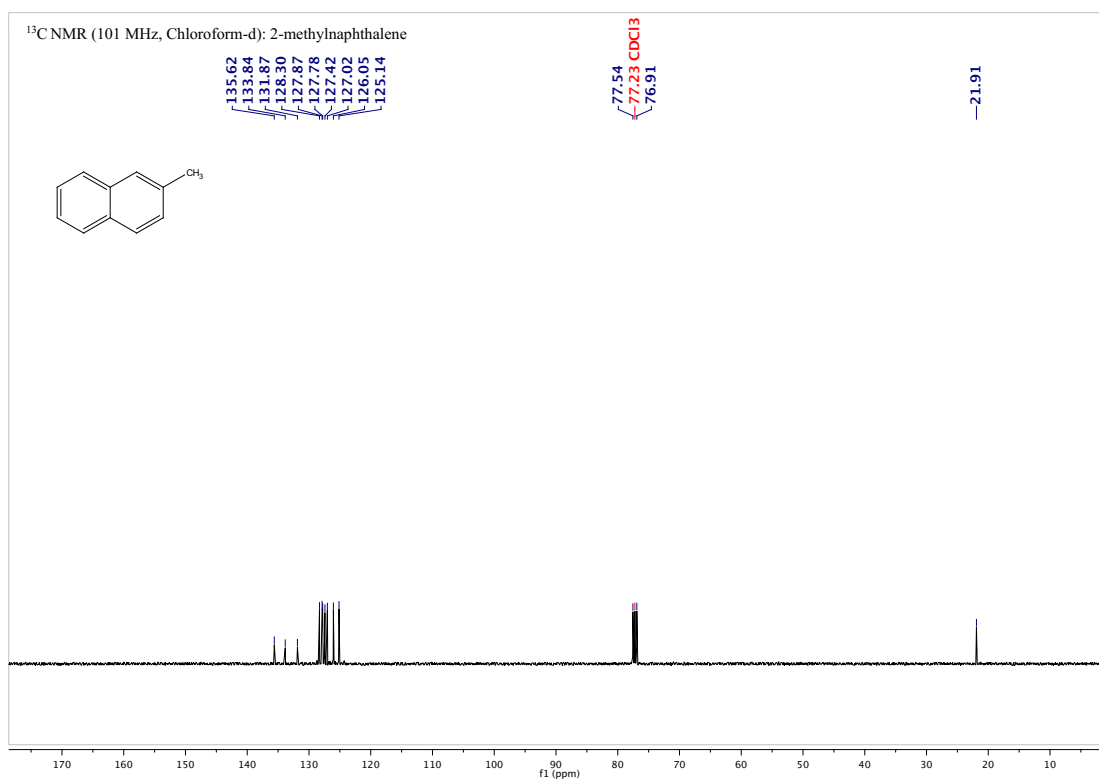
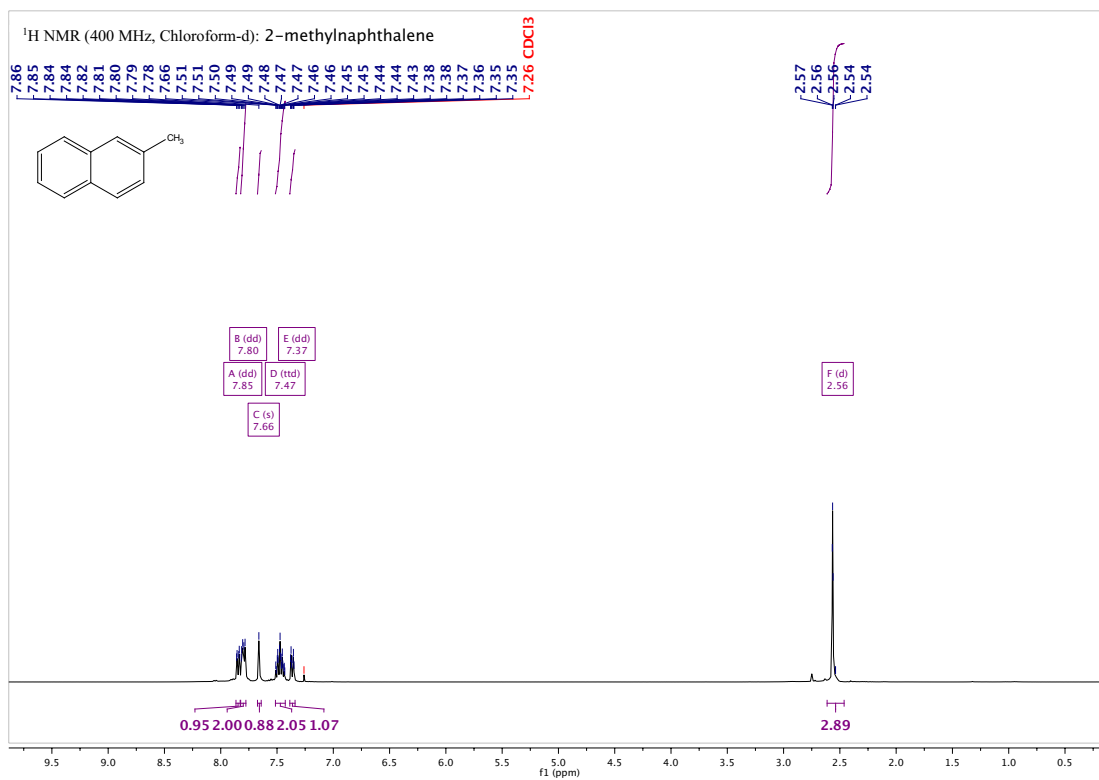


Table 1, Entry 1j (side product):

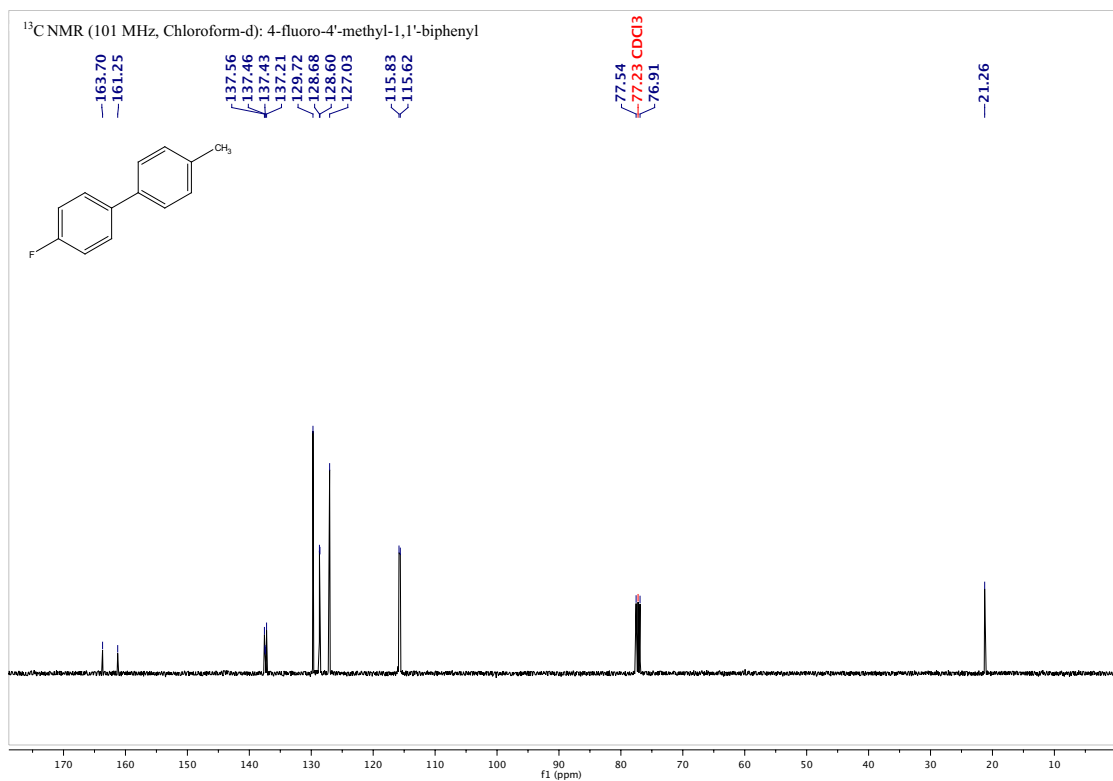
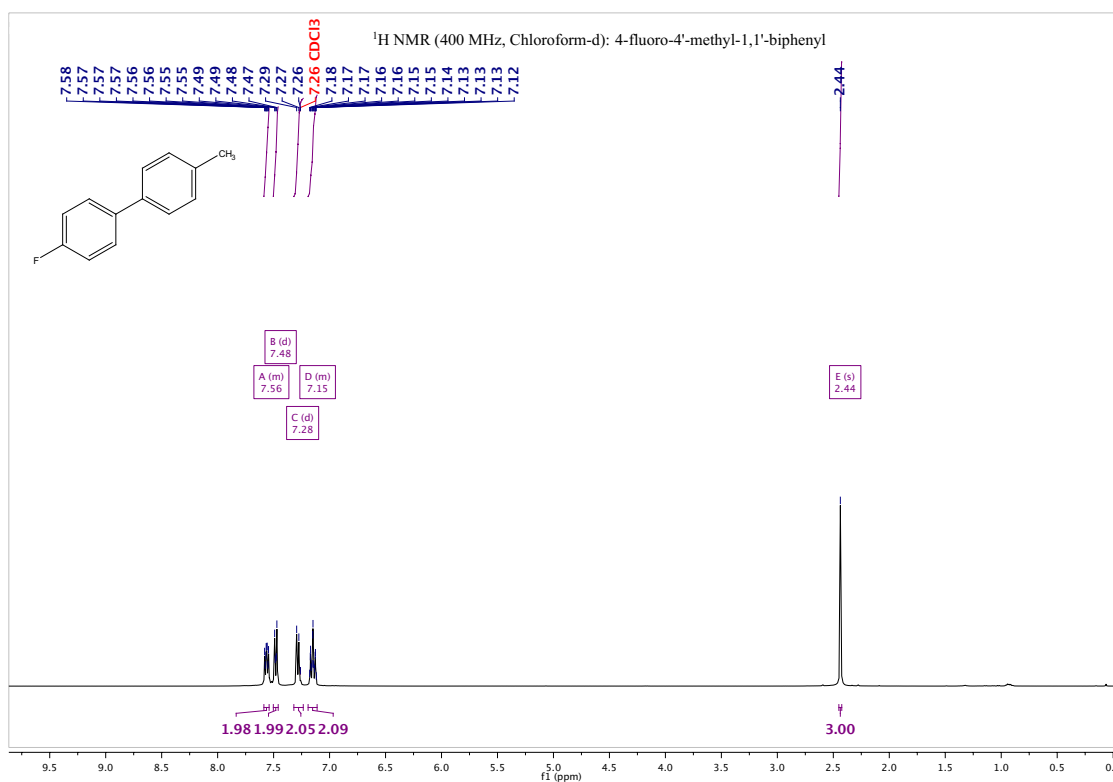


Table 1, Entry 11 (side product):

