

Supplementary Information for

**A Flexible Approach to Pd-Catalyzed Carbonylations via Aroyl
Dimethylaminopyridinium Salts**

Jeffrey S. Quesnel, Alexander Fabrikant, and Bruce A. Arndtsen*

*Department of Chemistry, McGill University, 801 Sherbrooke Street West, Montreal, Quebec,
H3A 0B8, Canada*

Table of Contents

I. General Considerations	S1
II. General Procedures and Characterization Data	
Procedure for Phosphine Screening (Table 1)	S2
Typical Procedure for the Synthesis of and Isolation of DMAP Iodide Salts (Table 2)	S2
Outside Glovebox Procedure for the Synthesis and Isolation of Aroyl-DMAP Iodide Salts (Table 2)	S2
Typical Procedure for 10 mmol Scale Synthesis of DMAP Iodide Salts (Table 3)	S3
Typical Procedure for the Synthesis of and Isolation of DMAP Bromide Salts (Table 4)	S3
Typical Procedure for Reaction of DMAP Salts with Nucleophiles (Table 5)	S3
III. Mechanistic Studies	S3
Kinetic Analysis of $[\text{PhCO-DMAP}]^+\text{T}^-$ Synthesis	S3
Control Reaction of $\text{PhCOPd}(\text{P}^t\text{Bu}_3)\text{I}$ with DMAP	S6
IV. Characterization Data of Compounds	S6
V. NMR Spectra	S18
VI. References	S79

I. General Considerations

Unless noted, all manipulations were conducted in a glovebox under a nitrogen atmosphere. All reagents were purchased from commercial sources and used without purification, unless otherwise stated. Research grade carbon monoxide (99.99%) was used as received. Solvents were dried via filtration through silica on a solvent purifier system. Deuterated acetonitrile, chloroform, and benzene were stirred over calcium hydride, degassed, vacuum transferred, and stored over 4 Å molecular sieves in the glovebox. Tetrabutylammonium chloride was dried in the glovebox by dissolving in dichloromethane, allowing to stand overnight over activated molecule sieves, filtering and removing the solvent *in vacuo*. 4-Dimethylaminopyridine was purified by hot filtering a toluene solution followed by azeotropically removal of trace amounts of water and finally recrystallization. Ethyl 4-iodobenzoate was distilled prior to use. (2-ethynylphenyl)methanol was prepared by reduction of the corresponding aldehyde with sodium borohydride.¹ $\text{Pd}_2\text{dba}_3\cdot\text{CHCl}_3$ was prepared according to literature procedure and stored at -35 °C in the glovebox to avoid decomposition.²

Nuclear magnetic resonance (NMR) characterization was performed on 200, 300, 400, and 500 MHz spectrometers for proton, 75 and 126 MHz for carbon, and 81 MHz for phosphorus. ^1H and ^{13}C NMR chemical shifts were referenced to residual solvent while ^{31}P was referenced to an

85% phosphoric acid external standard. ICP-OES were measured by Robertson Microlit Laboratories in NJ, USA. High pressure reactions were performed using 40 mL Parr stainless steel autoclaves equipped with glass liners.

II. General Procedures

Procedure for Phosphine Ligand Screening (Table 1)

In the glovebox, a 25 mL Teflon sealed, thick wall Schlenk vacuum/storage tube equipped with a stir bar was charged with iodobenzene (102 mg, 0.50 mmol), 4-dimethylaminopyridine (73 mg, 0.60 mmol), $\text{Pd}_2\text{dba}_3 \cdot \text{CHCl}_3$ (12.9 mg, 12.5 μmol , 2.5 mol%), and ligand (25 μmol , 5 mol%) in THF (1 mL). The vessel was removed from the glovebox and pressurized with 1 atm CO and heated to 45 °C for 24 hours. The volatiles were then removed *in vacuo* and the vessel was brought back into the glovebox. Benzylamine (59 mg, 0.55 mmol), and diisopropylethylamine (71 mg, 0.55 mmol) were added with dichloromethane (*ca.* 2 mL). The mixture was stirred for 5 minutes. The yield of product was based on the NMR analysis of benzylbenzamide formation using the benzyl benzoate as the standard. For entry 14, the yield is of the isolated DMAP salt, following the isolation procedure described.

Typical Procedure for the Synthesis and Isolation of Aroyl-DMAP Iodide Salts 2 (Table 2)

In the glovebox, a 25 mL Teflon sealed, thick wall Schlenk vacuum/storage tube equipped with a stir bar was charged with iodobenzene (102.0 mg, 0.5 mmol), 4-dimethylaminopyridine (73.3 mg, 0.6 mmol, 1.2 equiv), and $\text{Pd}(\text{P}^t\text{Bu}_3)_2$ (12.8 mg, 25 μmol , 5 mol%) in THF (2 mL). The vessel was charged with 1 atm CO and heated to 45 °C for 24 h. The CO atmosphere was evacuated and the vessel was brought back into the glovebox. The insoluble product was isolated by filtering over a medium glass frit, rinsing with THF (4×1 mL) to give the **2a** as a pale, yellow solid (172 mg, 97% yield). For reactions where the palladium content was analyzed, the reaction conditions were altered slightly: ArI (0.6 mmol), DMAP (73.3 mg, 0.5 mmol), $\text{Pd}(\text{P}^t\text{Bu}_3)$ (12.8 mg, 25 μmol , 5 mol%), CO (1 atm), THF (1 mL), 45 °C, 24 h. Pd content analyses: **2a** = 98 ppm; **2b** = 450 ppm (65 °C, 4 atm); **2c** = 270; **2d** = 199; **2e** = 522 ppm; **2f** = 215 ppm; **2g** = 2132; **2h** = 2635 (65 °C, 4 atm); **2j** = 1780 (65 °C, 4 atm).

Outside Glovebox Procedure for the Synthesis and Isolation of Aroyl-DMAP Iodide Salts 2 (Table 2)

In a fumehood, a 25 mL Teflon sealed, thick wall Schlenk vacuum/storage tube equipped with a stir bar was evacuated and filled with nitrogen three times, then placed under a positive pressure of nitrogen. The solid reagents: 4-dimethylaminopyridine (73.3 mg, 0.6 mmol, 1.2 equiv), $\text{Pd}_2\text{dba}_3 \cdot \text{CHCl}_3$ (12.9 mg, 12.5 μmol , 2.5 mol%), and $[\text{P}^t\text{Bu}_3\text{H}^+]\text{Cl}^-$ (6.0 mg, 25 μmol , 5 mol%), were weighed into vials in air and then quickly added neat into the briefly uncapped vessel. Iodobenzene (55.6 μmol , 0.5 mmol) was added by micropipette to the Schlenk tube, followed by syringe addition of dry and nitrogen purged THF (1 mL). The vessel was frozen with liquid N_2 , the nitrogen atmosphere evacuated, and allowed to thaw (three cycles), then charged with 1 atm CO and heated to 45 °C for 24 h. The CO atmosphere was evacuated and the product was isolated in the glovebox (to avoid slow product hydrolysis) as described above to give a pale yellow solid (142 mg, 81% yield).

Preparation of $[\text{P}^t\text{Bu}_3\text{H}^+]\text{Cl}^-$: In the glove box, a 25 mL Teflon sealed, thick wall Schlenk vacuum/storage tube equipped with a stir bar was charged with P^tBu_3 (185.0 mg, 0.92 mmol)

dissolved in diethyl ether (4 mL). The vessel was sealed then removed from the glovebox. Under a positive flow of nitrogen, HCl in diethyl ether (1M, 2 mL) was added dropwise to give a white precipitate. The mixture was left to stir for 5 minutes after which the volatiles were removed *in vacuo*. The vessel was brought back into the glove box and the solid was filtered over a medium glass sintered frit, rinsing with diethyl ether (3×2 mL) to give the product as a white solid (202.2 mg, 93% yield). ^1H -NMR (500 MHz; CD_3CN): δ 6.5 (br. d, $J \sim 480$ Hz, 1H), 1.64 (d, $J = 15.3$ Hz, 27H); $^{13}\text{C}\{^1\text{H}\}$ -NMR (126 MHz; CD_3CN): δ 36.9 (d, $J = 28.0$ Hz), 29.4; $^{31}\text{P}\{^1\text{H}\}$ -NMR (81 MHz; CD_3CN): δ 51.4 (d, $J = 64.0$ Hz from apparent H-P coupling); APCI m/z calculated for $\text{C}_{12}\text{H}_{28}\text{P}(\text{M-Cl})^+$: 203.19231; found 203.19245.

Typical Procedure for 10 mmol Scale Synthesis of Aroyl-DMAP Iodide Salts 2 (Table 2)

In the glovebox, a 40 mL Parr steel autoclave equipped with a glass liner and a magnetic stirrer was charged iodobenzene (2.04 g, 10 mmol), 4-dimethylaminopyridine (1.46 g, 12 mmol), and $\text{Pd}(\text{P}^t\text{Bu}_3)_2$ (25.6 mg, 50 μmol , 0.5 mol%) in THF (10 mL). The vessel was sealed and connected to a Parr Multiwell Reactor 5000. The system evacuated and backfilled with CO three times and finally pressurized with 20 atm. The vessel was heated to 80 $^\circ\text{C}$ for 7 h. After allowing sufficient time to cool to room temperature (*ca.* 2 h), the CO atmosphere was evacuated and the vessel was brought back into the glove box. The product was purified by filtering the precipitate over a medium glass frit, rinsing with THF (4×3 mL) to give the **2a** as a pale, yellow solid (3.51 g, 99% yield).

Typical Procedure for the Synthesis and Isolation of Aroyl-DMAP Bromide Salts 3 (Table 4)

In the glovebox, a 25 mL Teflon sealed, thick wall Schlenk vacuum/storage tube equipped with a stir bar was charged with bromobenzene (78.5 mg, 0.5 mmol), 4-dimethylaminopyridine (73.3 mg, 0.6 mmol), and $\text{Pd}(\text{P}^t\text{Bu}_3)_2$ (12.8 mg, 25 μmol , 5 mol%) in toluene (2 mL). The vessel was charged with 4 atm CO and heated to 100 $^\circ\text{C}$ for 24 h. The CO atmosphere was evacuated and the vessel was brought back into the glovebox. The product was purified by filtering the insoluble product over a medium glass frit, rinsing with toluene (4×1 mL) to give the **3b** as an off-white solid (121.7 mg, 77% yield).

Typical Procedure for Reaction of Aroyl-DMAP Salts with Nucleophiles (Table 5)

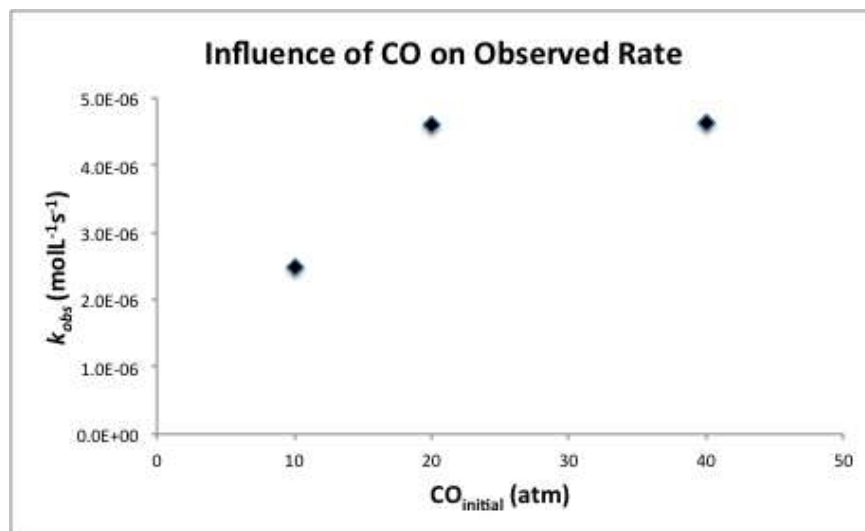
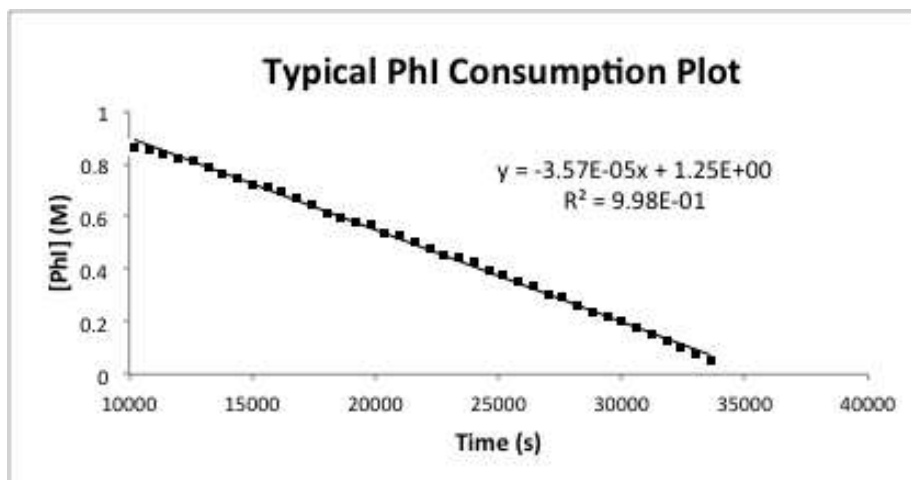
In the glovebox, a disposable 4 mL glass vial equipped with a magnetic stir bar and plastic cap was charged with aroyl-DMAP salt **2a** (177 mg, 0.50 mmol) and diisopropylethylamine (129 mg, 1.0 mmol) in dichloromethane (1 mL). The vial was then removed from the glovebox. The cap was removed and benzylamine (78.8 μL , 0.75 mmol, 1.5 equiv.) was added to the vial *via* syringe. The cap was replaced and the mixture was allowed to stir for 2 hours. The volatiles were removed *in vacuo* and the crude products were purified by silica gel column chromatography eluting with hexanes/ethyl acetate (10:1) to give benzyl benzamide **4a** as a white solid (88.1 mg, 86% yield).

III. Mechanistic Studies

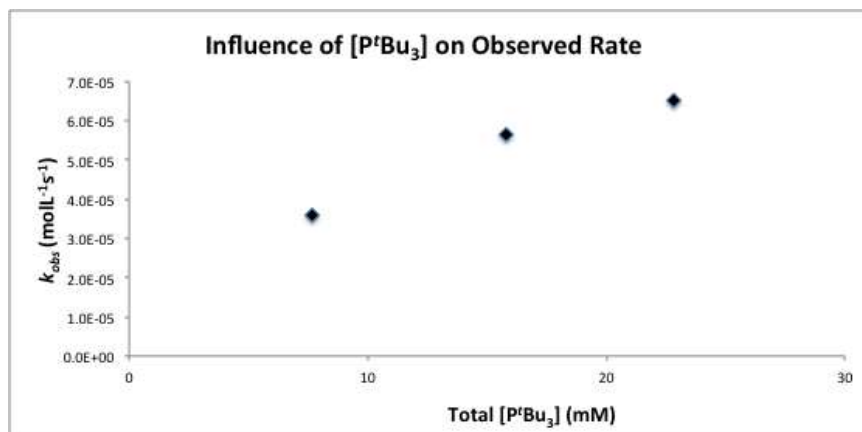
Kinetic Analysis of $[\text{PhCO-DMAP}]^+\text{I}^-$ Synthesis

Kinetic experiments were performed using the same procedure as described for the 10 mmol scale synthesis of DMAP salts. The reaction was monitored by CO pressure changes, as

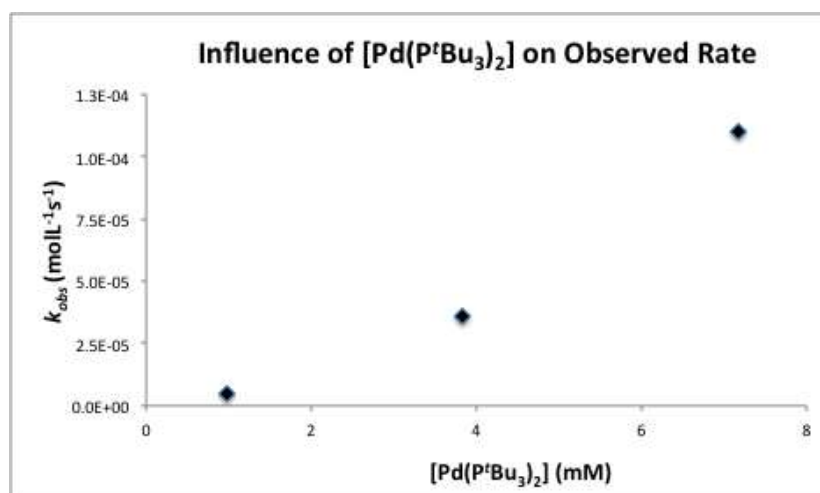
measured by a pressure transducer. The standard reaction conditions were: phenyl iodide (2.04 g, 10 mmol), DMAP (1.47 g, 12 mmol), $\text{Pd}(\text{P}^t\text{Bu}_3)_2$ (25.6 mg, 0.1 mmol, 0.5 mol%), CO (20 atm), in THF (10 mL) at 80 °C. Changes to each of these parameters is highlighted beneath each plot. A typical rate of PhI consumption vs. time plot is given below and shows the zero order formation of product. A linear fit of $[\text{PhI}]$ vs. time gives k_{obs} .



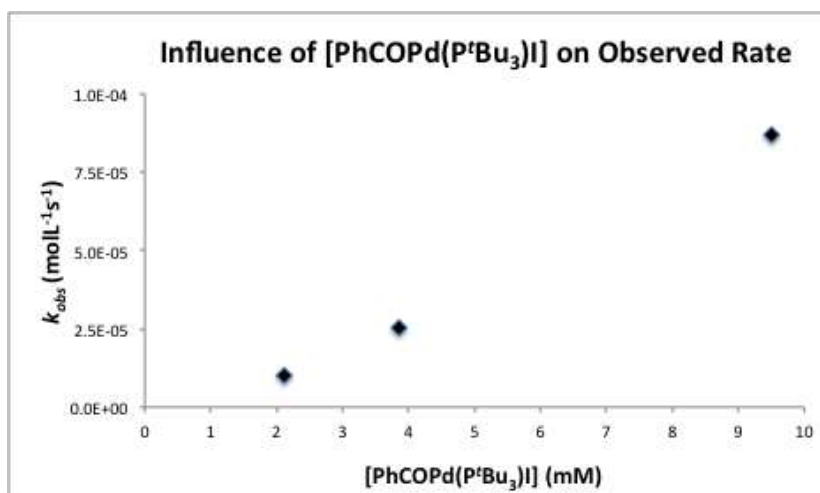
CO (10-40 atm)



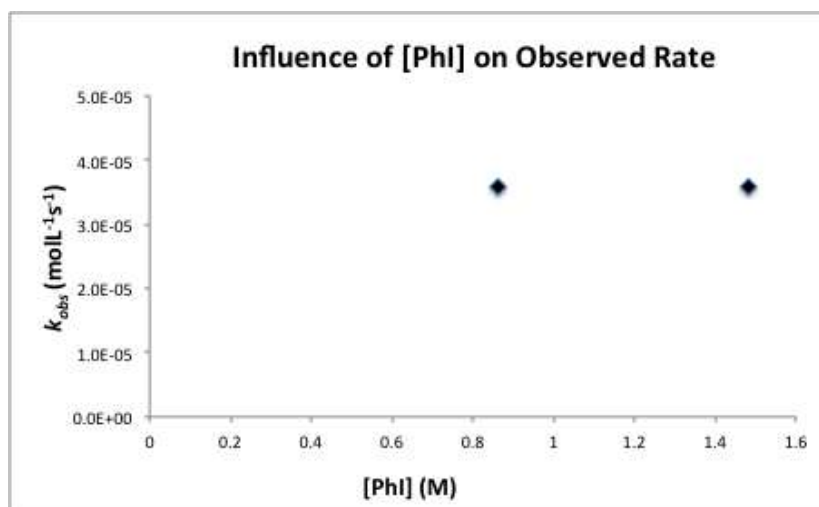
Additional P'Bu₃ (0-36.9 mg)



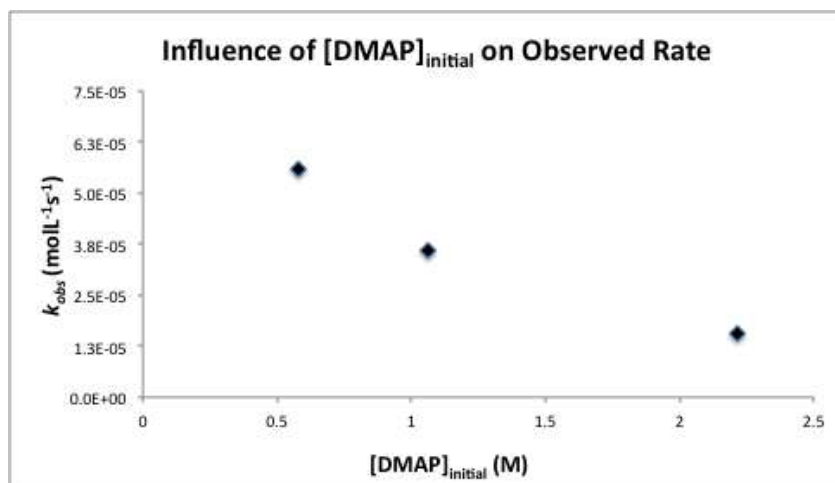
Pd(P'Bu₃)₂ (6.0-44.0 mg, 0.125-1 mol%)



Using PhCOPd(P'Bu₃)I (13.7-61.7 mg, 0.25-1.5 mol%) in place of Pd(P'Bu₃)₂



Phenyl iodide (2.04-3.63 g, 10-15 mmol)

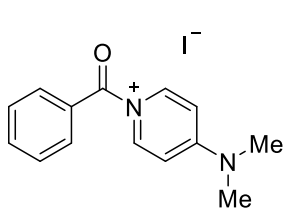


DMAP (0.85-3.24 g, 7-26.5 mmol)

Control Reaction of PhCOPd(P^tBu₃)I with DMAP

In the glove box, PhCOPd(P^tBu₃)I (3.2 mg, 5.9 μmol) and dimethylaminopyridine (2.2 mg, 18 μmol) were dissolved in C₆D₆ (0.7 mL) and added to a J-Young NMR tube. ¹H and ³¹P NMR after 5 minutes confirm the presence of PhCOPd(P^tBu₃)I (³¹P = 69.7 ppm) and free P^tBu₃ (³¹P = 61.9 ppm) in a 2.8:1 ratio.

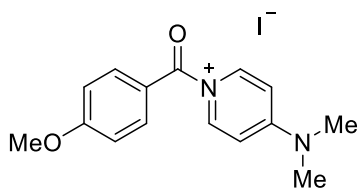
IV. Characterization Data of Compounds



1-benzoyl-4-(dimethylamino)pyridin-1-ium iodide, 2a

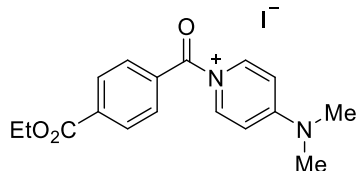
Pale yellow solid, 97% yield; ¹H-NMR (500 MHz; CDCl₃; 70 °C): δ 8.45 (d, *J* = 7.3 Hz, 2H), 7.83-7.81 (m, 2H), 7.76-7.72 (m, 1H), 7.63-7.59 (m, 2H), 7.37 (d, *J* = 6.8 Hz, 2H), 3.54 (s, 6H); ¹³C{¹H}-NMR (126 MHz; CDCl₃): δ 167.3, 158.4, 138.1, 135.2, 130.9, 129.7, 127.8, 109.2, 42.6; FT-IR (ATR, cm⁻¹): 1721.2 (C=O); APCI *m/z* calculated

for C₁₄H₁₅N₂O (M-I)⁺: 227.1179; found 227.1190.



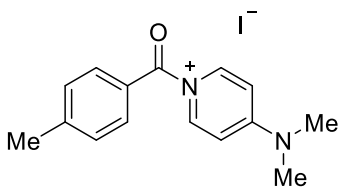
4-(dimethylamino)-1-(4-methoxybenzoyl)pyridin-1-ium iodide, 2b

Pale yellow solid, 99% yield; $^1\text{H-NMR}$ (200 MHz; CDCl_3): δ 8.44 (d, $J = 8.1$ Hz, 2H), 7.83 (d, $J = 9.0$ Hz, 2H), 7.34 (d, $J = 8.1$ Hz, 2H), 7.08 (d, $J = 9.0$ Hz, 2H), 3.92 (s, 3H), 3.52 (s, 6H); $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (75 MHz; CDCl_3): δ 166.4, 165.1, 158.0, 138.4, 133.6, 119.2, 115.0, 108.8, 56.1, 42.3; FT-IR (ATR, cm^{-1}): 1705.7 (C=O); APCI m/z calculated for $\text{C}_{15}\text{H}_{17}\text{N}_2\text{O}_2$ (M-I) $^+$: 257.1285; found 257.1290.



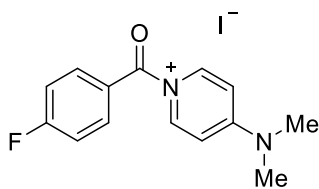
4-(dimethylamino)-1-(4-(ethoxycarbonyl)benzoyl)pyridin-1-ium iodide, 2c

Bright yellow solid, 90% yield; $^1\text{H-NMR}$ (300 MHz; CDCl_3): δ 8.46 (d, $J = 7.9$ Hz, 2H), 8.25 (dd, $J = 8.3, 1.5$ Hz, 2H), 7.92 (dd, $J = 8.3, 1.5$ Hz, 2H), 7.36 (d, $J = 7.3$ Hz, 2H), 4.43 (q, $J = 7.1$ Hz, 2H), 3.56 (s, 6H), 1.42 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (75 MHz; CDCl_3): δ 166.7, 164.8, 158.4, 138.0, 135.8, 131.7, 130.8, 130.4, 109.3, 61.9, 42.6, 14.2; FT-IR (ATR, cm^{-1}): 1735.7, 1709.2 (C=O); APCI m/z calculated for $\text{C}_{17}\text{H}_{19}\text{N}_2\text{O}_3$ (M-I) $^+$: 299.1390; found 299.1385.



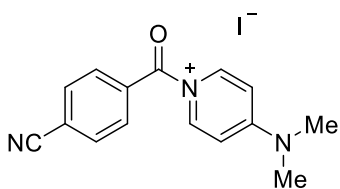
4-(dimethylamino)-1-(4-methylbenzoyl)pyridin-1-ium iodide, 2d

Yellow solid, 96% yield; $^1\text{H-NMR}$ (500 MHz; CDCl_3): δ 8.25 (d, $J = 7.9$ Hz, 2H), 7.47 (d, $J = 8.1$ Hz, 2H), 7.27 (s, 2H), 7.21 (d, $J = 8.4$ Hz, 2H), 3.36 (s, 6H), 2.28 (s, 3H); $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (126 MHz; CDCl_3): δ 167.1, 158.2, 146.6, 138.1, 130.9, 130.2, 124.8, 109.0, 42.5, 21.9; FT-IR (ATR, cm^{-1}): 1732.1 (C=O); APCI m/z calculated for $\text{C}_{15}\text{H}_{17}\text{N}_2\text{O}$ (M-I) $^+$: 241.1335; found 241.1341.



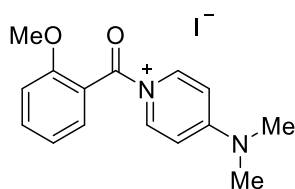
4-(dimethylamino)-1-(4-fluorobenzoyl)pyridin-1-ium iodide, 2e

Light green solid, 93% yield; $^1\text{H-NMR}$ (300 MHz; CDCl_3): δ 8.66 (d, $J = 6.4$ Hz, 2H), 8.24 (d, $J = 8.2$ Hz, 2H), 7.94 (d, $J = 8.3$ Hz, 2H), 7.30 (d, $J = 6.5$ Hz, 2H), 3.40 (s, 6H); Due to the extreme insolubility of the compound, only partial carbon data can be obtained: $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (126 MHz; CDCl_3): δ 141.0, 133.8, 133.83, 124.1, 109.6, 41.3; FT-IR (ATR, cm^{-1}): 1734.9 (C=O); APCI m/z calculated for $\text{C}_{14}\text{H}_{14}\text{FN}_2\text{O}$ (M-I) $^+$: 245.1085; found 245.1095.



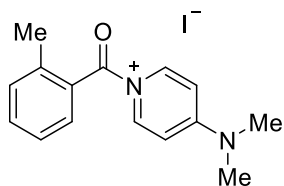
1-(4-cyanobenzoyl)-4-(dimethylamino)pyridin-1-ium iodide, 2f

Yellow solid, 90% yield; $^1\text{H-NMR}$ (500 MHz; CD_3CN ; 70 $^\circ\text{C}$): δ 8.40 (d, $J = 8.2$ Hz, 2H), 8.02-8.00 (m, 2H), 7.97-7.95 (m, 2H), 7.06 (d, $J = 8.3$ Hz, 2H), 3.41 (s, 6H); $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (126 MHz; CD_3CN ; 70 $^\circ\text{C}$): δ 166.7, 158.6, 138.2, 133.13, 133.03, 131.0, 117.4, 117.1, 107.7, 41.1; FT-IR (ATR, cm^{-1}): 2225.1 (C \equiv N), 1737.0 (C=O); APCI m/z calculated for $\text{C}_{15}\text{H}_{14}\text{N}_3\text{O}$ (M-I) $^+$: 252.1131; found 252.1128.



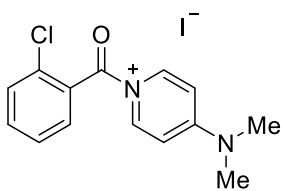
4-(dimethylamino)-1-(2-methoxybenzoyl)pyridin-1-ium iodide, 2g

Light green-yellow solid, 94% yield; $^1\text{H-NMR}$ (200 MHz; CDCl_3): δ 8.36 (d, $J = 8.3$ Hz, 2H), 7.68 (ddd, $J = 8.5, 7.4, 1.8$ Hz, 1H), 7.59 (ddd, $J = 7.7, 1.8, 0.4$ Hz, 1H), 7.34 (d, $J = 8.3$ Hz, 2H), 7.16 (td, $J = 7.6, 1.0$ Hz, 1H), 7.09 (dt, $J = 8.5, 0.4$ Hz, 1H), 3.87 (s, 3H), 3.56 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ -NMR (126 MHz; CDCl_3): δ 166.3, 158.4, 157.0, 137.4, 135.9, 131.7, 121.8, 117.4, 112.3, 108.8, 56.5, 42.7; FT-IR (ATR, cm^{-1}): 1722.1 (C=O); APCI m/z calculated for $\text{C}_{15}\text{H}_{17}\text{N}_2\text{O}_2$ (M-I) $^+$: 257.1285; found 257.1295.



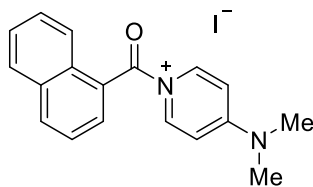
4-(dimethylamino)-1-(2-methylbenzoyl)pyridin-1-ium iodide, 2h

Bright yellow solid, 93% yield; $^1\text{H-NMR}$ (500 MHz; CDCl_3): δ 8.29 (d, $J = 8.2$ Hz, 2H), 7.49 (td, $J = 7.5, 1.7$ Hz, 1H), 7.35-7.28 (m, 5H), 3.49 (s, 6H), 2.30 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ -NMR (126 MHz; CDCl_3): δ 167.1, 158.4, 138.7, 137.3, 133.4, 132.1, 129.1, 127.8, 126.6, 109.4, 42.9, 19.9; FT-IR (ATR, cm^{-1}): 1740.7 (C=O); APCI m/z calculated for $\text{C}_{15}\text{H}_{17}\text{N}_2\text{O}$ (M-I) $^+$: 241.1335; found 241.1334.



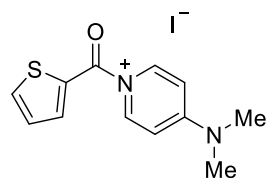
1-(2-chlorobenzoyl)-4-(dimethylamino)pyridin-1-ium iodide, 2i

Dark yellow solid, 56% yield; $^1\text{H-NMR}$ (300 MHz; CDCl_3): δ 8.36 (d, $J = 8.2$ Hz, 2H), 7.73 (d, $J = 7.6$ Hz, 1H), 7.65 (m, $J = 6.2, 2.6$ Hz, 1H), 7.55 (m, 2H), 7.36 (d, $J = 8.2$ Hz, 2H), 3.58 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ -NMR (126 MHz; CDCl_3): δ 165.1, 136.9 (br.), 134.4, 131.5, 130.9, 130.7, 128.5, 128.2, 109.5 (br.), 42.9 (br.); FT-IR (ATR, cm^{-1}): 1738.1 (C=O); APCI m/z calculated for $\text{C}_{14}\text{H}_{14}\text{ClN}_2\text{O}$ (M-I) $^+$: 261.0789; found 261.0792.



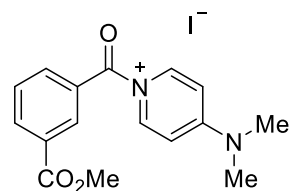
1-(1-naphthoyl)-4-(dimethylamino)pyridin-1-ium iodide, 2j

Yellow solid, 98% yield; $^1\text{H-NMR}$ (300 MHz; CDCl_3): δ 8.44 (d, $J = 8.2$ Hz, 2H), 8.21 (d, $J = 8.3$ Hz, 1H), 8.03-8.00 (m, 1H), 7.94-7.91 (m, 1H), 7.84 (dd, $J = 7.2, 1.2$ Hz, 1H), 7.70-7.64 (m, 3H), 7.29 (d, $J = 8.2$ Hz, 2H), 3.57 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ -NMR (126 MHz; CDCl_3): δ 165.1, 156.3, 135.7, 131.7, 131.5, 128.2, 127.5, 126.7, 126.3, 125.2, 123.9, 122.6, 122.0, 105.0, 38.7; FT-IR (ATR, cm^{-1}): 1728.0 (C=O); APCI m/z calculated for $\text{C}_{18}\text{H}_{14}\text{N}_2\text{O}$ (M-I) $^+$: 277.1335; found 277.1331.



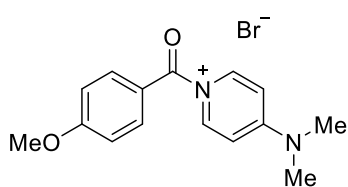
4-(dimethylamino)-1-(thiophene-2-carbonyl)pyridin-1-ium iodide, 2k

Orange solid, 92% yield; $^1\text{H-NMR}$ (300 MHz; CD_3CN): δ 8.53 (d, $J = 8.2$ Hz, 2H), 8.17 (dd, $J = 4.8, 1.0$ Hz, 1H), 7.81 (dd, $J = 4.0, 1.0$ Hz, 1H), 7.37 (dd, $J = 5.0, 4.1$ Hz, 1H), 7.01 (d, $J = 8.2$ Hz, 2H), 3.37 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ -NMR (126 MHz; CDCl_3): δ 161.7, 158.8, 139.0, 138.9, 138.2, 132.3, 129.5, 107.7, 41.2; FT-IR (ATR, cm^{-1}): 1701.0 (C=O); APCI m/z calculated for $\text{C}_{12}\text{H}_{13}\text{N}_2\text{OS}$ (M-I) $^+$: 233.0743; found 233.0732.



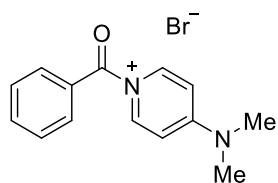
4-(dimethylamino)-1-(3-(methoxycarbonyl)benzoyl)pyridin-1-ium iodide, 2l

Light grey solid, 95% yield; ^1H -NMR (200 MHz; CDCl_3): δ 8.46 (br. d, $J = 6.3$ Hz, 2H), 8.42-8.37 (m, 2H), 8.10 (ddd, $J = 7.8, 1.9, 1.3$ Hz, 1H), 7.76 (t, $J = 8.0$ Hz, 1H), 7.35 (br. d, $J = 6.9$ Hz, 2H), 3.97 (s, 3H), 3.55 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ -NMR (126 MHz; CDCl_3): δ 166.4, 164.9, 158.3, 137.8, 135.4, 134.7, 131.5, 131.3, 130.0, 128.2, 109.1, 52.6, 42.3; FT-IR (ATR, cm^{-1}): 1743.3, 1721.4 (C=O); APCI m/z calculated for $\text{C}_{16}\text{H}_{17}\text{N}_2\text{O}_3$ (M-I) $^+$: 285.1234; found 285.1239.



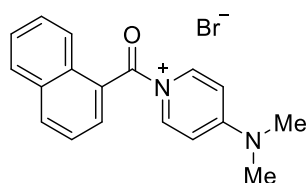
4-(dimethylamino)-1-(4-methoxybenzoyl)pyridin-1-ium bromide, 3a

Orange solid, 95% yield; ^1H -NMR (400 MHz; CDCl_3): δ 8.47 (d, $J = 8.1$ Hz, 2H), 7.83 (d, $J = 9.0$ Hz, 2H), 7.45 (d, $J = 8.2$ Hz, 2H), 7.09 (d, $J = 9.0$ Hz, 2H), 3.93 (s, 3H), 3.54 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ -NMR (75 MHz; CDCl_3): δ 166.6, 165.4, 158.4, 138.5, 133.8, 119.4, 115.2, 108.9, 56.0, 42.1; FT-IR (ATR, cm^{-1}): 1710.5 (C=O); APCI m/z calculated for $\text{C}_{15}\text{H}_{17}\text{N}_2\text{O}_2$ (M-Br) $^+$: 257.1285; found 257.1291.



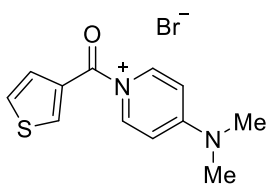
1-benzoyl-4-(dimethylamino)pyridin-1-ium bromide, 3b

Off-white solid, 77% yield; ^1H -NMR (300 MHz; CDCl_3): δ 8.45 (d, $J = 8.2$ Hz, 2H), 7.75-7.70 (m, 3H), 7.60-7.50 (m, 4H), 3.54 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ -NMR (75 MHz; CDCl_3): δ 167.3, 158.5, 138.1, 135.1, 130.7, 129.6, 128.0, 109.1, 42.3; FT-IR (ATR, cm^{-1}): 1721.6 (C=O); APCI m/z calculated for $\text{C}_{14}\text{H}_{15}\text{N}_2\text{O}$ (M-Br) $^+$: 227.1179; found 227.1184.



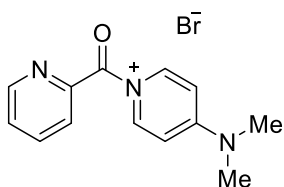
1-(1-naphthoyl)-4-(dimethylamino)pyridin-1-ium bromide, 3c

Grey solid, 96% yield; ^1H -NMR (400 MHz; CDCl_3): δ 8.42 (d, $J = 8.2$ Hz, 2H), 8.18 (d, $J = 8.2$ Hz, 1H), 8.01-7.99 (m, 1H), 7.87-7.85 (m, 1H), 7.77 (d, $J = 7.0$ Hz, 1H), 7.65-7.61 (m, 3H), 7.44 (d, $J = 8.2$ Hz, 2H), 3.57 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ -NMR (126 MHz; CDCl_3 , 70 $^\circ\text{C}$): δ 166.9, 159.0, 137.4, 134.5, 133.8, 130.5, 129.8, 129.1, 129.0, 127.6, 125.4, 124.8, 123.9, 109.1, 42.3; FT-IR (ATR, cm^{-1}): 1729.8 (C=O); APCI m/z calculated for $\text{C}_{18}\text{H}_{17}\text{N}_2\text{O}$ (M-Br) $^+$: 277.1335; found 277.1340.



4-(dimethylamino)-1-(thiophene-3-carbonyl)pyridin-1-ium bromide, 3d

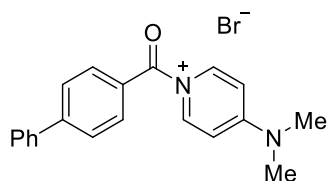
Grey solid, 97% yield; ^1H -NMR (300 MHz; CDCl_3): δ 8.63 (d, $J = 8.2$ Hz, 2H), 8.49 (t, $J = 2.3, 2.1$ Hz, 1H), 7.57 (d, $J = 2.1$ Hz, 2H), 7.46 (d, $J = 8.2$ Hz, 2H), 3.53 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ -NMR (75 MHz; CDCl_3): δ 161.4, 158.5, 138.5, 138.2, 129.5, 128.8, 110.0, 109.1, 42.0; FT-IR (ATR, cm^{-1}): 1718.6 (C=O); APCI m/z calculated for $\text{C}_{12}\text{H}_{13}\text{N}_2\text{OS}$ (M-Br) $^+$: 233.0743; found 233.0743.



4-(dimethylamino)-1-picolinoylpyridin-1-ium bromide, 3e

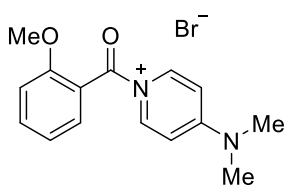
Off-white solid, 86% yield; ^1H -NMR (300 MHz; CD_3CN): δ 8.78 (ddd, $J = 4.8, 1.6, 1.0$ Hz, 1H), 8.65 (br. s, 1H), 8.27 (dt, $J = 7.9, 1.1$ Hz, 1H), 8.15 (td, $J = 7.8, 1.7$ Hz, 1H), 7.78 (ddd, $J = 7.7, 4.8, 1.3$ Hz, 1H), 6.96 (d, $J = 7.8$ Hz, 2H), 3.35 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ -NMR (126 MHz; CD_3CN , 70 $^\circ\text{C}$): δ 165.0, 158.1, 149.2, 147.4, 140.1, 138.4, 128.6, 128.0, 106.9,

40.4; FT-IR (ATR, cm^{-1}): 1733.8 (C=O); APCI m/z calculated for $\text{C}_{13}\text{H}_{14}\text{N}_3\text{O}$ (M-Br) $^{+}$: 228.1131; found 228.1122.



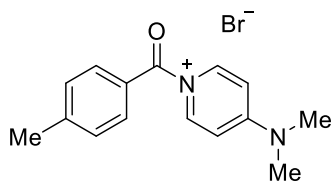
1-([1,1'-biphenyl]-4-carbonyl)-4-(dimethylamino)pyridin-1-ium bromide, 3f

White solid, 91% yield; ^1H -NMR (300 MHz; CDCl_3): δ 8.52 (d, J = 8.2 Hz, 2H), 7.89 (d, J = 8.5 Hz, 2H), 7.82 (d, J = 8.2 Hz, 2H), 7.66-7.63 (m, 2H), 7.53-7.44 (m, 5H), 3.57 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ -NMR (75 MHz; CDCl_3): δ 167.1, 158.5, 148.0, 138.7, 138.2, 131.6, 129.2, 129.0, 128.1, 127.4, 126.3, 109.1, 42.2; FT-IR (ATR, cm^{-1}): 1718.2 (C=O); APCI m/z calculated for $\text{C}_{20}\text{H}_{19}\text{N}_2\text{O}$ (M-Br) $^{+}$: 303.1492; found 303.1497.



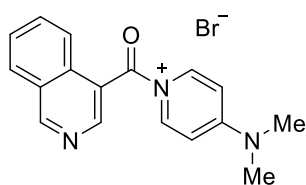
4-(dimethylamino)-1-(2-methoxybenzoyl)pyridin-1-ium bromide, 3g

Yellow solid, 83% yield; ^1H -NMR (400 MHz; CDCl_3): δ 8.38 (d, J = 8.2 Hz, 2H), 7.69 (td, J = 8.0, 1.8 Hz, 1H), 7.58 (dd, J = 7.6, 1.8 Hz, 1H), 7.45 (d, J = 8.1 Hz, 2H), 7.18 (t, J = 7.5 Hz, 1H), 7.10 (d, J = 8.6 Hz, 1H), 3.87 (s, 3H), 3.58 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ -NMR (75 MHz; CDCl_3): δ 166.4, 158.6, 157.0, 137.4, 135.9, 131.7, 121.8, 117.6, 112.2, 108.7, 56.3, 42.3; FT-IR (ATR, cm^{-1}): 1731.0 (C=O); APCI m/z calculated for $\text{C}_{15}\text{H}_{17}\text{N}_2\text{O}_2$ (M-Br) $^{+}$: 257.1285; found 257.1290.



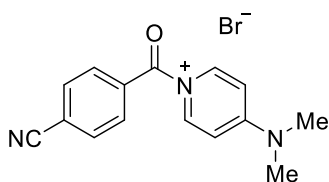
4-(dimethylamino)-1-(4-methylbenzoyl)pyridin-1-ium bromide, 3h

Yellow solid, 91% yield; ^1H -NMR (300 MHz; CDCl_3): δ 8.41 (d, J = 7.8 Hz, 2H), 7.60 (d, J = 8.2 Hz, 2H), 7.51 (d, J = 7.6 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 3.51 (s, 6H), 2.43 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ -NMR (75 MHz; CDCl_3): δ 167.2, 158.5, 146.8, 138.2, 131.0, 130.3, 125.0, 109.0, 42.2, 21.9; FT-IR (ATR, cm^{-1}): 1714.3 (C=O); APCI m/z calculated for $\text{C}_{15}\text{H}_{17}\text{N}_2\text{O}$ (M-Br) $^{+}$: 241.1335; found 241.1346.



4-(dimethylamino)-1-(isoquinoline-4-carbonyl)pyridin-1-ium bromide, 3i

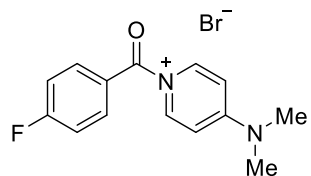
Yellow solid, 63% yield; ^1H -NMR (300 MHz; CD_3CN): δ 9.60 (s, 1H), 8.76 (s, 1H), 8.50 (d, J = 7.9 Hz, 2H), 8.31 (d, J = 7.9 Hz, 1H), 8.08 (d, J = 8.5 Hz, 1H), 7.98-7.93 (m, J = 7.0, 1.5 Hz, 1H), 7.87 (m, 1H), 7.00 (d, J = 7.9 Hz, 2H), 3.38 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ -NMR (126 MHz; CD_3CN): δ 166.9, 159.1, 158.2, 146.0, 138.4, 133.5, 133.4, 129.5, 129.4, 128.9, 124.0, 121.3, 107.9, 41.5; FT-IR (ATR, cm^{-1}): 1723.7 (C=O); APCI m/z calculated for $\text{C}_{17}\text{H}_{16}\text{N}_3\text{O}$ (M-Br) $^{+}$: 278.1288; found 278.1288.



1-(4-cyanobenzoyl)-4-(dimethylamino)pyridin-1-ium bromide, 3j

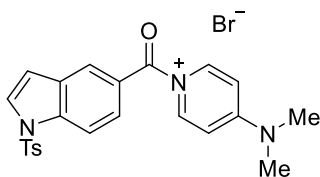
Off-white solid, 91% yield; ^1H -NMR (300 MHz; CD_3CN): δ 8.38 (d, J = 7.9 Hz, 2H), 8.02 (d, J = 8.8 Hz, 2H), 7.94 (d, J = 8.8 Hz, 2H), 7.04 (d, J = 7.9 Hz, 2H), 3.38 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ -NMR (126 MHz; CD_3CN , 70°C): δ 166.9, 158.7, 138.7, 133.4, 133.2, 133.0, 131.2, 117.6, 107.8, 41.0; FT-IR (ATR, cm^{-1}): 2233.13 ($\text{C}\equiv\text{N}$), 1720.2

(C=O); APCI m/z calculated for $C_{15}H_{14}N_3O$ (M-Br) $^+$: 252.1131; found 252.1144.



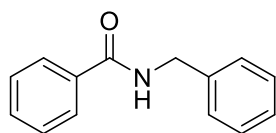
4-(dimethylamino)-1-(4-fluorobenzoyl)pyridin-1-ium bromide, 3k

Yellow solid, 96% yield; 1H -NMR (400 MHz; $CDCl_3$): δ 8.48 (d, J = 7.8 Hz, 2H), 7.87 (m, J = 9.0, 5.1 Hz, 2H), 7.47 (d, J = 8.2 Hz, 2H), 7.28 (t, J = 8.2 Hz, 2H), 3.52 (s, 6H); $^{13}C\{^1H\}$ -NMR (75 MHz; $CDCl_3$): δ 166.5 (d, J = 259.7 Hz), 166.3, 158.4, 138.3, 133.9 (d, J = 9.8 Hz), 124.2 (d, J = 2.3 Hz), 117.1 (d, J = 22.5 Hz), 109.0, 42.1; FT-IR (ATR, cm^{-1}): 1724.92 (C=O); APCI m/z calculated for $C_{14}H_{14}FN_2O$ (M-Br) $^+$: 245.1085; found 245.1075.



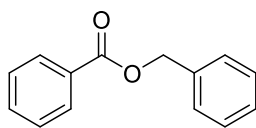
4-(dimethylamino)-1-(1-tosyl-1H-indole-5-carbonyl)pyridin-1-ium bromide, 3l

White solid, 92% yield; 1H -NMR (400 MHz; $CDCl_3$): δ 8.44 (d, J = 7.4 Hz, 2H), 8.11 (d, J = 8.6 Hz, 1H), 8.02 (s, 1H), 7.78 (d, J = 7.8 Hz, 2H), 7.70 (d, J = 9.8 Hz, 2H), 7.45 (d, J = 7.4 Hz, 2H), 7.28 (d, J = 7.8 Hz, 2H), 6.81 (d, J = 2.3 Hz, 1H), 3.51 (s, 6H), 2.34 (s, 3H); $^{13}C\{^1H\}$ -NMR (75 MHz; $CDCl_3$): δ 167.4, 158.4, 146.1, 138.4, 137.9, 134.4, 130.8, 130.4, 128.8, 126.9, 126.7, 125.8, 122.5, 114.4, 109.3, 108.9, 42.1, 21.7; FT-IR (ATR, cm^{-1}): 1736.0 (C=O); APCI m/z calculated for $C_{23}H_{22}N_3O_3S$ (M-Br) $^+$: 420.1376; found 420.1382.



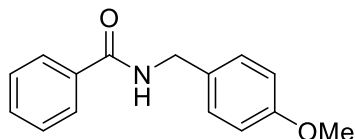
N-benzylbenzamide, ³ 4a

White solid, 86% yield; 1H -NMR (300 MHz; $CDCl_3$): δ 7.80-7.78 (m, 2H), 7.51-7.46 (m, 1H), 7.42-7.37 (m, 2H), 7.35-7.25 (m, 4H), 6.71 (br. s, 1H), 4.61 (d, J = 5.7 Hz, 2H); $^{13}C\{^1H\}$ -NMR (75 MHz; $CDCl_3$): δ 167.4, 138.2, 134.4, 131.5, 128.7, 128.5, 127.9, 127.5, 127.0, 44.1; FT-IR (ATR, cm^{-1}): 3286.2 (N-H), 1635.0 (C=O).



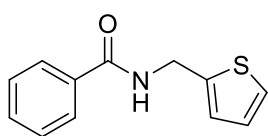
Benzyl benzoate, ⁴ 4b

Colourless oil, 97% yield; 1H -NMR (300 MHz; $CDCl_3$): δ 8.14-8.11 (m, 2H), 7.61-7.55 (m, 1H), 7.50-7.37 (m, 7H), 5.40 (s, 2H); $^{13}C\{^1H\}$ -NMR (75 MHz; $CDCl_3$): δ 166.4, 136.1, 133.0, 130.2, 129.7, 128.6, 128.4, 128.3, 128.2, 66.7; FT-IR (ATR, cm^{-1}): 1714.7 (C=O).



N-(4-methoxybenzyl)benzamide, ⁵ 4c

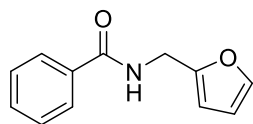
White solid, 96% yield; 1H -NMR (300 MHz; $CDCl_3$): δ 7.78 (d, J = 7.2 Hz, 2H), 7.46 (t, J = 7.3 Hz, 1H), 7.37 (t, J = 7.5 Hz, 2H), 7.24 (d, J = 8.5 Hz, 2H), 6.84 (d, J = 8.6 Hz, 2H), 6.80 (br. s, 1H), 4.52 (d, J = 5.6 Hz, 2H), 3.77 (s, 3H); $^{13}C\{^1H\}$ -NMR (75 MHz; $CDCl_3$): δ 167.4, 159.0, 134.4, 131.4, 130.4, 129.2, 128.5, 127.0, 114.1, 55.3, 43.5; FT-IR (ATR, cm^{-1}): 3333.7 (N-H), 1641.2 (C=O).



N-(thiophen-2-ylmethyl)benzamide, ⁶ 4d

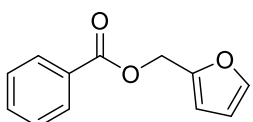
White solid, 97% yield; 1H -NMR (300 MHz; $CDCl_3$): δ 7.78 (d, J = 7.2 Hz, 2H), 7.49 (t, J = 7.2 Hz, 1H), 7.40 (t, J = 7.4 Hz, 2H), 7.23 (d, J = 4.4 Hz, 1H), 7.02 (d, J = 2.5 Hz, 1H), 6.95 (dd, J = 4.8, 3.7 Hz, 1H), 6.71 (br.

s, 1H), 4.79 (d, $J = 5.6$ Hz, 2H); $^{13}\text{C}\{^1\text{H}\}$ -NMR (75 MHz; CDCl_3): δ 167.2, 140.8, 134.1, 131.6, 128.6, 127.02, 126.93, 126.2, 125.3, 38.8; FT-IR (ATR, cm^{-1}): 3296.0 (N-H), 1634.0 (C=O).



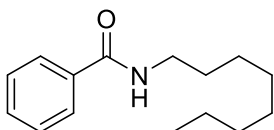
***N*-(furan-2-ylmethyl)benzamide, ⁷4e**

White solid, 80% yield; ^1H -NMR (300 MHz; CDCl_3): δ 7.79-7.76 (m, 2H), 7.51-7.45 (m, 1H), 7.42-7.40 (m, 2H), 7.38-7.35 (m, 1H), 6.62 (s, 1H), 6.32 (dd, $J = 3.1, 1.9$ Hz, 1H), 6.27 (d, $J = 3.2$ Hz, 1H), 4.62 (d, $J = 5.5$ Hz, 2H); $^{13}\text{C}\{^1\text{H}\}$ -NMR (75 MHz; CDCl_3): δ 167.2, 151.2, 142.2, 134.1, 131.6, 128.5, 127.0, 110.5, 107.6, 37.0; FT-IR (ATR, cm^{-1}): 3284.5 (N-H), 1638.4 (C=O).



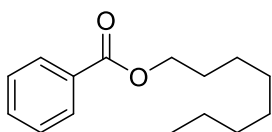
furan-2-ylmethyl benzoate, ⁸ 4f

Pale brown oil, 86% yield; ^1H -NMR (300 MHz; CDCl_3): δ 8.06 (d, $J = 7.1$ Hz, 2H), 7.57-7.51 (m, 1H), 7.45-7.39 (m, 3H), 6.49 (d, $J = 3.2$ Hz, 1H), 6.38 (dd, $J = 3.2, 1.9$ Hz, 1H), 5.32 (s, 2H); $^{13}\text{C}\{^1\text{H}\}$ -NMR (75 MHz; CDCl_3): δ 166.2, 149.5, 143.3, 133.1, 129.89, 129.73, 128.3, 110.78, 110.59, 58.5; FT-IR (ATR, cm^{-1}): 1716.4 (C=O).



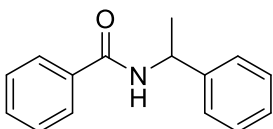
***N*-octylbenzamide, ⁹ 4g**

White solid, 99% yield; ^1H -NMR (300 MHz; CDCl_3): δ 7.76 (dd, $J = 8.2, 1.4$ Hz, 2H), 7.48-7.43 (m, 1H), 7.40-7.35 (m, 2H), 6.47 (br. s, 1H), 3.40 (q, $J = 6.5$ Hz, 2H), 1.58 (quintet, $J = 7.0$ Hz, 2H), 1.36-1.25 (m, 10H), 0.86 (t, $J = 6.7$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ -NMR (75 MHz; CDCl_3): δ 167.5, 134.8, 131.2, 128.4, 126.9, 40.1, 31.8, 29.7, 29.3, 29.2, 27.0, 22.6, 14.1; FT-IR (ATR, cm^{-1}): 3336.1 (N-H), 1629.1 (C=O).



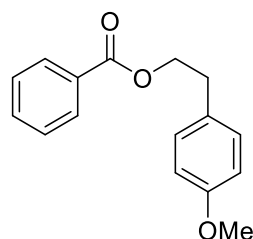
octyl benzoate, ¹⁰ 4h

Colourless oil, 92% yield; ^1H -NMR (300 MHz; CDCl_3): δ 8.05 (dd, $J = 8.4, 1.3$ Hz, 2H), 7.57-7.51 (m, 1H), 7.45-7.40 (m, 2H), 4.31 (t, $J = 6.7$ Hz, 2H), 1.76 (quintet, $J = 7.2$ Hz, 2H), 1.46-1.29 (m, 10H), 0.89 (t, $J = 6.8$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ -NMR (75 MHz; CDCl_3): δ 166.6, 132.7, 130.5, 129.5, 128.3, 65.1, 31.8, 29.3, 29.2, 28.7, 26.0, 22.6, 14.1; FT-IR (ATR, cm^{-1}): 1717.8 (C=O).



***N*-(1-phenylethyl)benzamide, ¹¹ 4i**

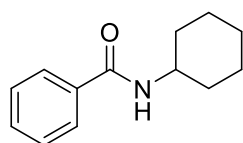
White solid, 95% yield; ^1H -NMR (300 MHz; CDCl_3): δ 7.77 (d, $J = 7.2$ Hz, 2H), 7.49-7.26 (m, 8H), 6.42 (br. s, 1H), 5.34 (quintet, $J = 7.1$ Hz, 1H), 1.60 (d, $J = 6.9$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ -NMR (75 MHz; CDCl_3): δ 166.5, 143.1, 134.6, 131.4, 128.7, 128.5, 127.4, 126.9, 126.2, 49.2, 21.7; FT-IR (ATR, cm^{-1}): 3319.7 (N-H), 1634.4 (C=O).



4-methoxyphenethyl benzoate, ¹² 4j

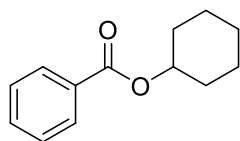
Colourless oil, 97% yield; ^1H -NMR (300 MHz; CDCl_3): δ 8.07-8.04 (m, 2H), 7.59-7.53 (m, 1H), 7.44 (t, $J = 7.5$ Hz, 2H), 7.23 (d, $J = 8.6$ Hz, 2H), 6.89 (d, $J = 8.7$ Hz, 2H), 4.52 (t, $J = 7.0$ Hz, 2H), 3.80 (s, 3H), 3.04 (t, $J = 7.0$ Hz, 2H); $^{13}\text{C}\{^1\text{H}\}$ -NMR (75 MHz; CDCl_3): δ 166.5, 158.4, 132.9, 130.4, 129.9, 129.6, 128.4, 114.0, 65.7, 55.2, 34.4; FT-IR (ATR, cm^{-1}):

1714.0 (C=O).



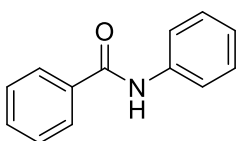
***N*-cyclohexylbenzamide,¹³ 4k**

White solid, 98% yield; ¹H-NMR (300 MHz; CDCl₃): δ 7.74 (d, *J* = 7.1 Hz, 2H), 7.44 (t, *J* = 7.2 Hz, 1H), 7.37 (t, *J* = 7.3 Hz, 2H), 6.22 (d, *J* = 5.8 Hz, 1H), 4.00-3.88 (m, 1H), 1.99 (dd, *J* = 12.2, 2.5 Hz, 2H), 1.78-1.67 (m, 2H), 1.66-1.57 (m, 1H), 1.45-1.31 (m, 2H), 1.28-1.17 (m, 3H); ¹³C{¹H}-NMR (75 MHz; CDCl₃): δ 166.6, 135.1, 131.1, 128.4, 126.9, 48.7, 33.2, 25.5, 24.9; FT-IR (ATR, cm⁻¹): 3327.3 (N-H), 1626.9 (C=O).



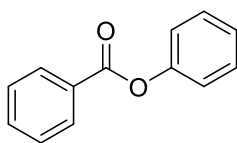
cyclohexyl benzoate,⁵ 4l

Colourless oil, 91% yield; ¹H-NMR (300 MHz; CDCl₃): δ 8.07-8.04 (m, 2H), 7.57-7.51 (m, 1H), 7.45-7.40 (m, 2H), 5.03 (tt, *J* = 8.5, 4.1 Hz, 1H), 1.98-1.91 (m, 2H), 1.84-1.75 (m, 2H), 1.65-1.31 (m, 6H); ¹³C{¹H}-NMR (75 MHz; CDCl₃): δ 165.9, 132.6, 131.0, 129.5, 128.2, 73.0, 31.6, 25.5, 23.6; FT-IR (ATR, cm⁻¹): 1712.1 (C=O).



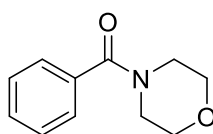
***N*-phenylbenzamide,⁷ 4m**

White solid, 79% yield; ¹H-NMR (300 MHz; CDCl₃): δ 7.90 (br. s, 1H), 7.85 (dd, *J* = 6.9, 1.6 Hz, 2H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.56-7.51 (m, 1H), 7.48-7.43 (m, 2H), 7.35 (t, *J* = 7.9 Hz, 2H), 7.14 (t, *J* = 7.4 Hz, 1H); ¹³C{¹H}-NMR (75 MHz; CDCl₃): δ 165.8, 137.9, 135.0, 131.8, 129.1, 128.8, 127.0, 124.6, 120.2; FT-IR (ATR, cm⁻¹): 3342.8 (N-H), 1653.3 (C=O).



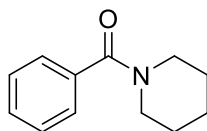
phenyl benzoate,¹⁴ 4n

White solid, 57% yield; ¹H-NMR (300 MHz; CDCl₃): δ 8.24-8.22 (m, 2H), 7.67-7.62 (m, 1H), 7.55-7.49 (m, 2H), 7.47-7.41 (m, 2H), 7.31-7.23 (m, 3H); ¹³C{¹H}-NMR (75 MHz; CDCl₃): δ 165.2, 151.0, 133.6, 130.2, 129.59, 129.50, 128.6, 125.9, 121.7; FT-IR (ATR, cm⁻¹): 1729.1 (C=O).



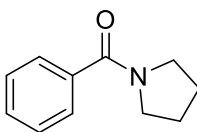
morpholino(phenyl)methanone,¹⁵ 4o

White solid, 99% yield; ¹H-NMR (300 MHz; CDCl₃): δ 7.38 (m, 5H), 3.90-3.30 (m, 8H); ¹³C{¹H}-NMR (75 MHz; CDCl₃): δ 170.4, 135.3, 129.8, 128.5, 127.0, 66.9, 48.2 (br.), 42.4 (br.); FT-IR (ATR, cm⁻¹): 1623.6 (C=O).



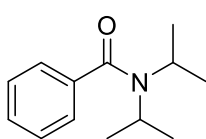
phenyl(piperidin-1-yl)methanone,¹⁵ 4p

White solid, 95% yield; ¹H-NMR (300 MHz; CDCl₃): δ 7.35 (s, 5H), 3.67 (br. s, 2H), 3.30 (br. s, 2H), 1.63 (br. m, 4H), 1.48 (br. m, 2H); ¹³C{¹H}-NMR (75 MHz; CDCl₃): δ 170.2, 136.5, 129.3, 128.3, 126.7, 48.7, 43.1, 26.5, 25.6, 24.6; FT-IR (ATR, cm⁻¹): 1622.9 (C=O).



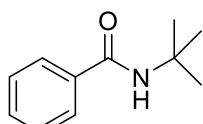
phenyl(pyrrolidin-1-yl)methanone,¹³ 4q

White solid, 94% yield; $^1\text{H-NMR}$ (300 MHz; CDCl_3): δ 7.48 (dd, $J = 6.7, 2.7$ Hz, 2H), 7.35 (dd, $J = 4.9, 1.7$ Hz, 3H), 3.61 (t, $J = 6.8$ Hz, 2H), 3.38 (t, $J = 6.5$ Hz, 2H), 1.96-1.87 (m, 2H), 1.87-1.76 (m, 2H); $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (75 MHz; CDCl_3): δ 169.7, 137.2, 129.7, 128.2, 127.0, 49.6, 46.1, 26.3, 24.4; FT-IR (ATR, cm^{-1}): 1615.7 (C=O).



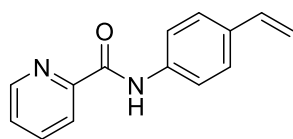
***N,N*-diisopropylbenzamide, ¹⁶ 4r**

White solid, 69% yield; $^1\text{H-NMR}$ (300 MHz; CDCl_3): δ 7.35-7.31 (m, 3H), 7.30-7.25 (m, 2H), 3.95-3.38 (br. m, 2H), 1.65-0.96 (br. m, 12H); $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (75 MHz; CDCl_3): δ 171.0, 138.9, 128.6, 128.4, 125.5, 50.6 (br.), 45.9 (br.), 20.7; FT-IR (ATR, cm^{-1}): 1625.3 (C=O).



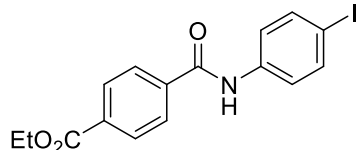
***N*-(*tert*-butyl)benzamide, ¹³ 4s**

White solid, 92% yield; $^1\text{H-NMR}$ (300 MHz; CDCl_3): δ 7.71 (d, $J = 6.8$ Hz, 2H), 7.50-7.34 (m, 3H), 5.97 (br. s, 1H), 1.46 (s, 12H); $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (75 MHz; CDCl_3): δ 166.9, 135.9, 131.0, 128.4, 126.7, 51.6, 28.9; FT-IR (ATR, cm^{-1}): 3319.7 (N-H), 1634.4 (C=O).



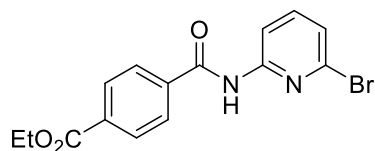
***N*-(4-vinylphenyl)picolinamide, 5a**

Off-white solid, 88% yield; $^1\text{H-NMR}$ (500 MHz; CDCl_3): δ 10.05 (s, 1H), 8.62 (ddd, $J = 4.7, 1.5, 0.8$ Hz, 1H), 8.30 (dt, $J = 7.8, 0.9$ Hz, 1H), 7.91 (td, $J = 7.7, 1.7$ Hz, 1H), 7.76 (d, $J = 8.6$ Hz, 2H), 7.48 (ddd, $J = 7.6, 4.8, 1.2$ Hz, 1H), 7.44 (d, $J = 8.6$ Hz, 2H), 6.71 (dd, $J = 17.6, 10.9$ Hz, 1H), 5.72 (dd, $J = 17.6, 0.6$ Hz, 1H), 5.21 (dd, $J = 10.9, 0.6$ Hz, 1H); $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (75 MHz; CDCl_3): δ 161.9, 149.7, 147.9, 137.7, 137.3, 136.2, 133.7, 126.9, 126.4, 122.3, 119.6, 113.0; FT-IR (ATR, cm^{-1}): 3321.1 (N-H), 1683.4 (C=O); ESI HRMS ($\text{C}_{14}\text{H}_{12}\text{N}_2\text{ONa}$): calc'd (M+Na) 247.0842, observed 247.0838.



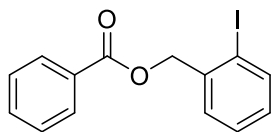
ethyl 4-((4-iodophenyl)carbamoyl)benzoate, 5b

White solid, 94% yield; $^1\text{H-NMR}$ (300 MHz; CDCl_3): δ 8.13 (d, $J = 8.6$ Hz, 2H), 7.90 (d, $J = 8.6$ Hz, 2H), 7.86 (br. s, 1H), 7.68 (d, $J = 8.8$ Hz, 2H), 7.44 (d, $J = 8.9$ Hz, 2H), 4.41 (q, $J = 7.1$ Hz, 2H), 1.42 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (75 MHz; CDCl_3): δ 165.6, 164.8, 138.3, 138.1, 137.4, 133.6, 130.0, 127.0, 122.0, 88.2, 61.5, 14.3; FT-IR (ATR, cm^{-1}): 3322.1 (N-H), 1716.4 (C=O), 1679.4 (C=O); ESI HRMS ($\text{C}_{16}\text{H}_{14}\text{INO}_3\text{Na}$): calc'd (M+Na) 417.9911, observed 417.9912.



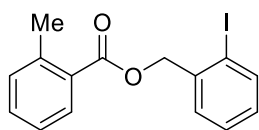
ethyl 4-((6-bromopyridin-2-yl)carbamoyl)benzoate, 5c

White solid, 95% yield; $^1\text{H-NMR}$ (300 MHz; CDCl_3): δ 8.58 (s, 1H), 8.35 (d, $J = 8.2$ Hz, 1H), 8.16 (d, $J = 8.4$ Hz, 2H), 7.96 (d, $J = 8.4$ Hz, 2H), 7.63 (t, $J = 8.0$ Hz, 1H), 7.29-7.26 (m, 1H), 4.42 (q, $J = 7.1$ Hz, 2H), 1.42 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (75 MHz; CDCl_3): δ 165.5, 164.7, 151.2, 140.8, 139.4, 137.3, 134.0, 130.1, 127.2, 124.1, 112.5, 61.5, 14.3; FT-IR (ATR, cm^{-1}): 3355.0 (N-H), 1699.8 (C=O), 1675.5 (C=O); ESI HRMS ($\text{C}_{15}\text{H}_{14}\text{BrN}_2\text{O}_3$): calc'd (M+H) 349.0182, observed 349.0175.



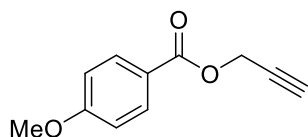
2-iodobenzyl benzoate,¹⁷ 5d

White solid, 95% yield; ¹H-NMR (300 MHz; CDCl₃): δ 8.13 (dd, *J* = 8.7, 1.6 Hz, 2H), 7.89 (dd, *J* = 7.9, 0.7 Hz, 1H), 7.60-7.55 (m, 1H), 7.50-7.43 (m, 3H), 7.37 (td, *J* = 7.5, 0.9 Hz, 1H), 7.04 (td, *J* = 7.6, 1.5 Hz, 1H), 5.39 (s, 2H); ¹³C{¹H}-NMR (75 MHz; CDCl₃): δ 166.1, 139.6, 138.5, 133.2, 129.92, 129.90, 129.81, 129.6, 128.46, 128.39, 98.5, 70.4; FT-IR (ATR, cm⁻¹): 1716.2 (C=O); ESI HRMS (C₁₄H₁₁NaO₂I): calc'd (M+Na) 360.96959, observed 360.96950.



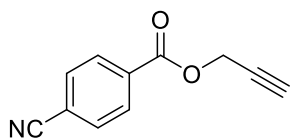
2-iodobenzyl 2-methylbenzoate, 5e

White solid, 97% yield; ¹H-NMR (400 MHz; CDCl₃): δ 8.02 (d, *J* = 8.6 Hz, 1H), 7.89 (d, *J* = 7.9 Hz, 1H), 7.48 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.44-7.35 (m, 2H), 7.26 (dt, *J* = 7.2, 3.6 Hz, 2H), 7.04 (td, *J* = 7.6, 1.3 Hz, 1H), 5.36 (s, 2H), 2.64 (s, 3H); ¹³C{¹H}-NMR (75 MHz; CDCl₃): δ 166.9, 140.6, 139.5, 138.5, 132.2, 131.8, 130.8, 129.9, 129.6, 129.1, 128.4, 125.8, 98.5, 70.3, 21.9; ESI HRMS (C₁₅H₁₃INaO₂): calc'd (M+Na) 374.9852, observed 374.9851.



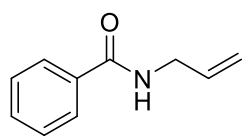
prop-2-yn-1-yl 4-methoxybenzoate, 5f

Colourless oil, 98% yield; ¹H-NMR (400 MHz; CDCl₃): δ 8.01 (d, *J* = 8.9 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 4.89 (d, *J* = 2.4 Hz, 2H), 3.85 (s, 3H), 2.50 (t, *J* = 2.4 Hz, 1H); ¹³C{¹H}-NMR (75 MHz; CDCl₃): δ 165.5, 163.6, 131.9, 121.7, 113.7, 78.0, 74.8, 55.4, 52.1; FT-IR (ATR, cm⁻¹): 3292.4 (C≡C-H), 2128.0 (C≡C), 1711.6 (C=O); ESI HRMS (C₁₁H₁₀NaO₃): calc'd (M+Na) 213.0522, observed 213.0525.



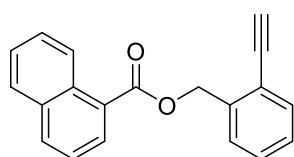
prop-2-yn-1-yl 4-cyanobenzoate, 5g

White solid, 90% yield; ¹H-NMR (400 MHz; CDCl₃): δ 8.17 (d, *J* = 8.5 Hz, 2H), 7.76 (d, *J* = 8.5 Hz, 2H), 4.96 (d, *J* = 2.5 Hz, 2H), 2.55 (t, *J* = 2.4 Hz, 1H); ¹³C{¹H}-NMR (75 MHz; CDCl₃): δ 164.2, 133.2, 132.3, 130.3, 117.8, 116.8, 75.6, 53.2; FT-IR (ATR, cm⁻¹): 3267.3 (C≡C-H), 2230.2 (C≡N), 1727.7 (C=O); APCI HRMS (C₁₁H₈NO₂): calc'd (M+H) 186.0550, observed 186.0543.



N-allylbenzamide,¹⁸ 5i

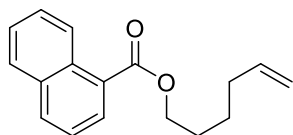
Colourless oil, 95% yield; ¹H-NMR (300 MHz; CDCl₃): δ 7.84-7.74 (br. m, 2H), 7.47-7.35 (m, 3H), 6.89 (br. s, 1H), 5.97-5.79 (br. m, 1H), 5.24-5.08 (br. m, 2H), 4.01 (br. s, 2H); ¹³C{¹H}-NMR (75 MHz; CDCl₃): δ 167.5, 134.4, 134.2, 131.4, 128.4, 127.0, 116.3, 42.4; FT-IR (ATR, cm⁻¹): 3303.1 (N-H), 1635.1 (C=O).



2-ethynylbenzyl 1-naphthoate, 5j

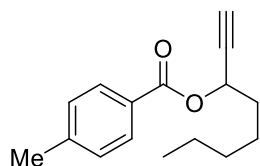
White solid, 95% yield; ¹H-NMR (400 MHz; CDCl₃): δ 8.99 (d, *J* = 8.6 Hz, 1H), 8.28 (dd, *J* = 7.2, 0.9 Hz, 1H), 8.03 (d, *J* = 8.1 Hz, 1H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.64-7.48 (m, 5H), 7.40 (td, *J* = 7.6, 1.2 Hz, 1H), 7.33 (td, *J* = 7.5, 0.9 Hz, 1H), 5.64 (s, 2H), 3.37 (s, 1H); ¹³C{¹H}-NMR

(75 MHz; CDCl₃): δ 167.2, 138.3, 133.8, 133.5, 133.0, 131.4, 130.5, 129.1, 128.53, 128.44, 128.1, 127.8, 126.8, 126.2, 125.8, 124.5, 121.6, 82.3, 81.0, 65.1; FT-IR (ATR, cm⁻¹): 3254.7 (C≡C-H), 1705.3 (C=O); ESI HRMS (C₂₀H₁₄NaO₂): calc'd (M+Na) 309.0886, observed 309.0878.



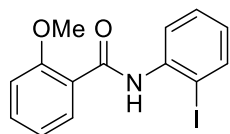
hex-5-en-1-yl 1-naphthoate, 5h

Colourless oil, 98% yield; ¹H-NMR (300 MHz; CDCl₃): δ 8.92 (d, *J* = 8.7 Hz, 1H), 8.19 (dd, *J* = 7.3, 1.2 Hz, 1H), 8.02 (d, *J* = 8.2 Hz, 1H), 7.89 (d, *J* = 7.4 Hz, 1H), 7.62 (ddd, *J* = 8.5, 6.9, 1.6 Hz, 1H), 7.57-7.48 (m, 2H), 5.85 (ddt, *J* = 17.0, 10.3, 6.7 Hz, 1H), 5.09 (dq, *J* = 17.2, 1.7 Hz, 1H), 5.02-4.97 (m, 1H), 4.40-4.38 (m, 2H), 2.17 (q, *J* = 7.1 Hz, 2H), 1.91-1.81 (m, 2H), 1.66-1.56 (m, 2H); ¹³C{¹H}-NMR (75 MHz; CDCl₃): δ 167.6, 138.3, 133.8, 133.2, 131.3, 130.0, 128.5, 127.7, 127.4, 126.2, 125.8, 124.5, 114.9, 65.0, 33.3, 28.2, 25.4; FT-IR (ATR, cm⁻¹): 1710.3 (C=O); ESI HRMS (C₁₇H₁₈O₂Na): calc'd (M+Na) 277.1199, observed 277.1203.



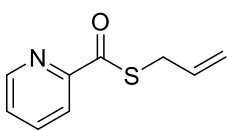
oct-1-yn-3-yl 4-methylbenzoate, 5k

Colourless oil, 96% yield; ¹H-NMR (300 MHz; CDCl₃): δ 7.96 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 5.58 (td, *J* = 6.6, 2.1 Hz, 1H), 2.47 (d, *J* = 2.2 Hz, 1H), 2.41 (s, 3H), 1.93-1.89 (m, 2H), 1.58-1.48 (m, 2H), 1.39-1.28 (m, 4H), 0.90 (t, *J* = 7.0 Hz, 3H); ¹³C{¹H}-NMR (75 MHz; CDCl₃): δ 165.6, 143.9, 129.8, 129.1, 127.1, 81.5, 73.4, 64.1, 34.7, 31.3, 24.6, 22.5, 21.7, 14.0; FT-IR (ATR, cm⁻¹): 3296.4 (C≡C-H), 2121.8 (C≡C), 1719.6 (C=O); ESI HRMS (C₁₆H₂₀O₂Na): calc'd (M+Na) 267.1356, observed 267.1360.



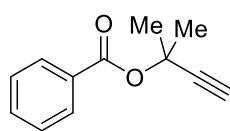
N-(2-iodophenyl)-2-methoxybenzamide, 5l

Light brown solid, 90% yield; ¹H-NMR (400 MHz; CDCl₃): δ 10.19 (br. s, 1H), 8.50 (dd, *J* = 8.3, 1.5 Hz, 1H), 8.31 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.84 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.52 (ddd, *J* = 8.3, 7.3, 1.8 Hz, 1H), 7.41-7.36 (m, 1H), 7.16-7.12 (m, 1H), 7.06 (d, *J* = 8.4 Hz, 1H), 6.85 (td, *J* = 7.6, 1.4 Hz, 1H), 4.12 (s, 3H); ¹³C NMR (75 MHz; CDCl₃): δ 163.4, 157.3, 139.8, 139.1, 133.5, 132.7, 129.0, 125.6, 122.9, 121.45, 121.42, 111.4, 89.6, 56.2; FT-IR (ATR, cm⁻¹): 3294.5 (N-H), 1658.7 (C=O); ESI HRMS (C₁₄H₁₂INNaO₂): calc'd (M+Na) 375.9805, observed 375.9804.



S-allyl pyridine-2-carbothioate, 5m

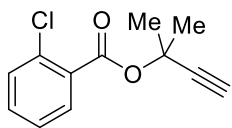
Yellow oil, 90% yield; ¹H-NMR (400 MHz; CDCl₃): δ 8.67-8.66 (m, 1H), 7.94 (d, *J* = 7.8 Hz, 1H), 7.83 (td, *J* = 7.7, 1.7 Hz, 1H), 7.49 (ddd, *J* = 7.5, 4.8, 1.2 Hz, 1H), 5.89 (ddt, *J* = 16.9, 10.0, 6.9 Hz, 1H), 5.31 (dd, *J* = 16.9, 1.3 Hz, 1H), 5.12 (dd, *J* = 10.0, 1.0 Hz, 1H), 3.68 (d, *J* = 6.9 Hz, 2H); ¹³C{¹H}-NMR (75 MHz; CDCl₃): δ 193.0, 151.8, 149.1, 137.2, 133.0, 127.8, 120.4, 118.0, 31.6; FT-IR (ATR, cm⁻¹): 1666.0 (C=S); ESI HRMS (C₉H₉NNaOS): calc'd (M+Na) 202.0297, observed 202.0301.



2-methylbut-3-yn-2-yl benzoate, 5n

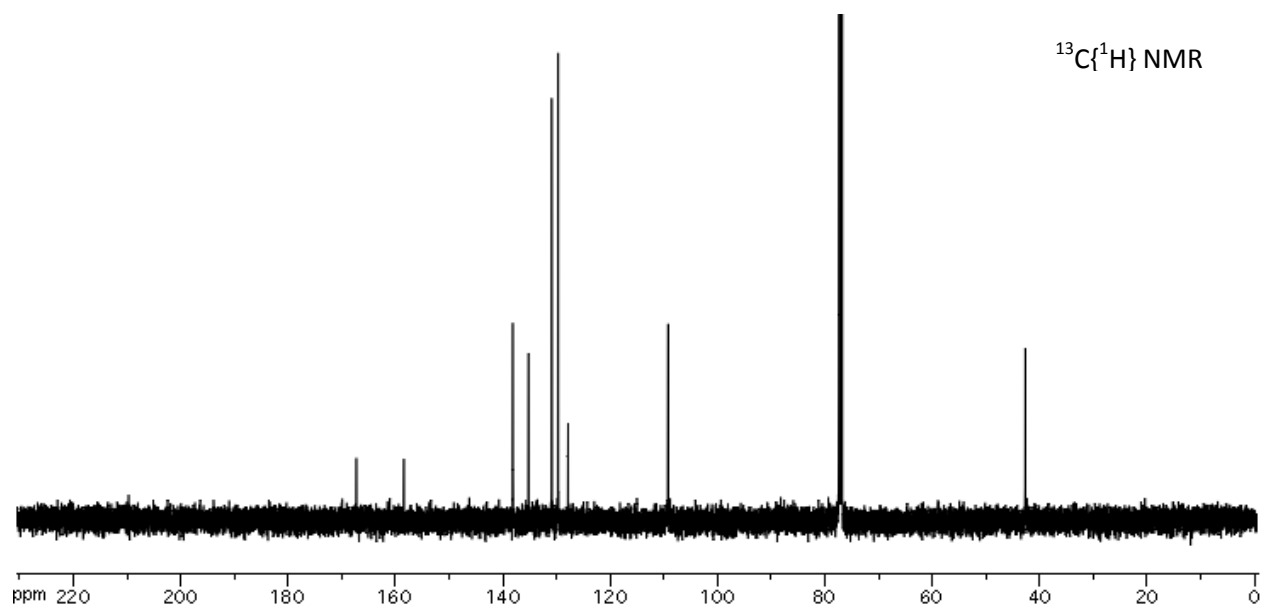
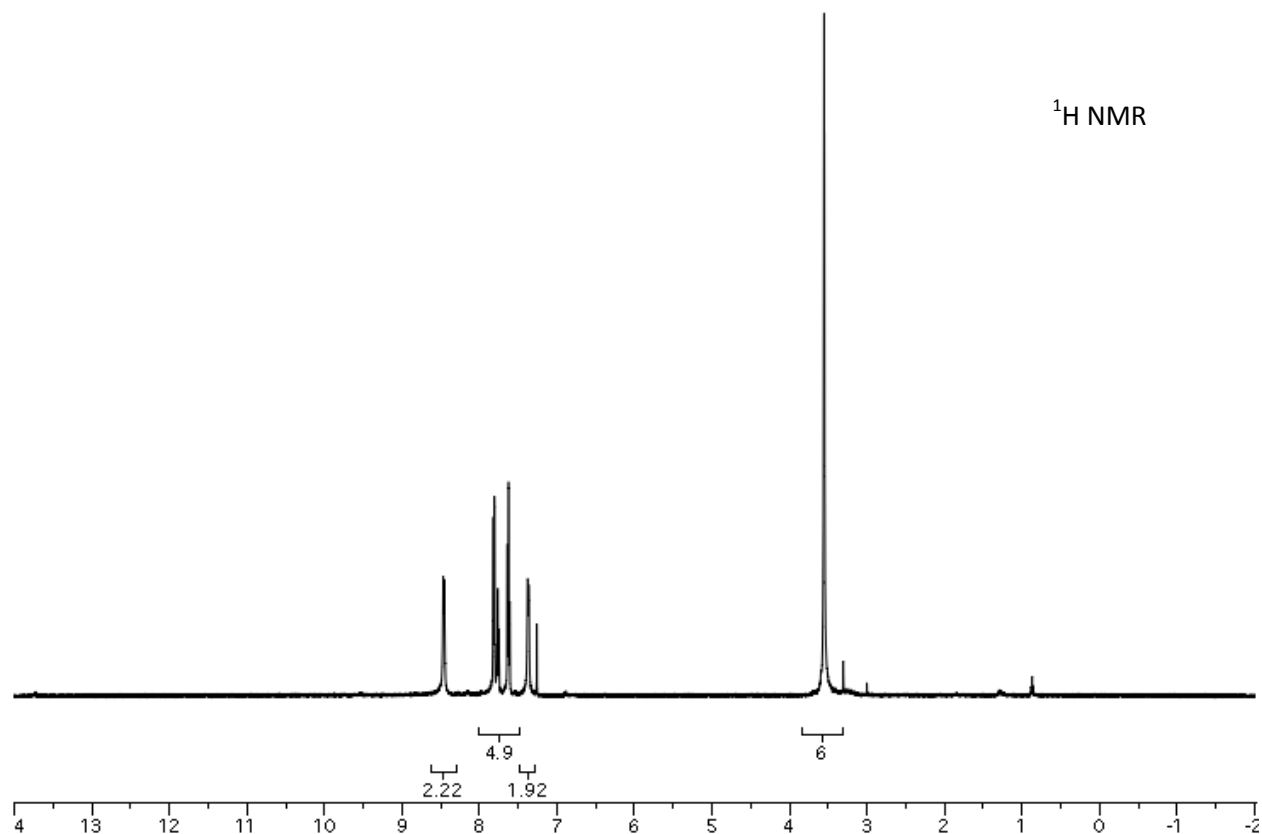
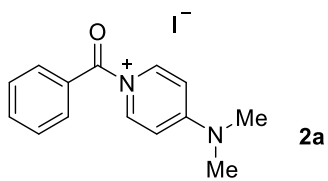
Colourless oil, 95% yield; ¹H-NMR (300 MHz; CDCl₃): δ 8.05-8.01 (m, 2H), 7.58-7.52 (m, 1H), 7.45-7.40 (m, 2H), 2.59 (s, 1H), 1.82 (s, 6H); ¹³C NMR (75 MHz; CDCl₃): δ 164.8, 132.9, 130.8, 129.6, 128.3, 84.7, 72.5,

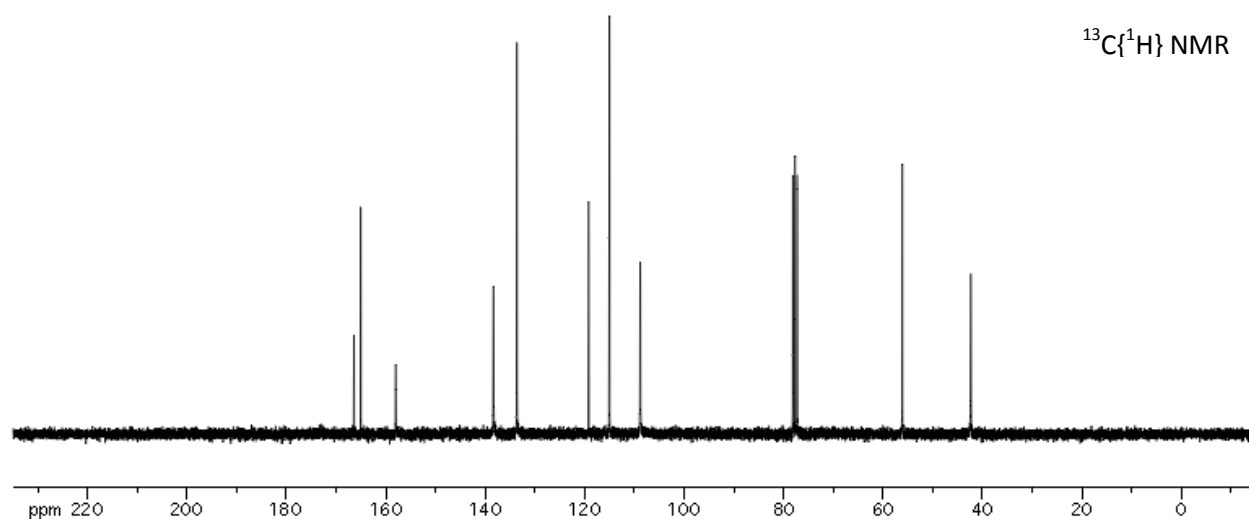
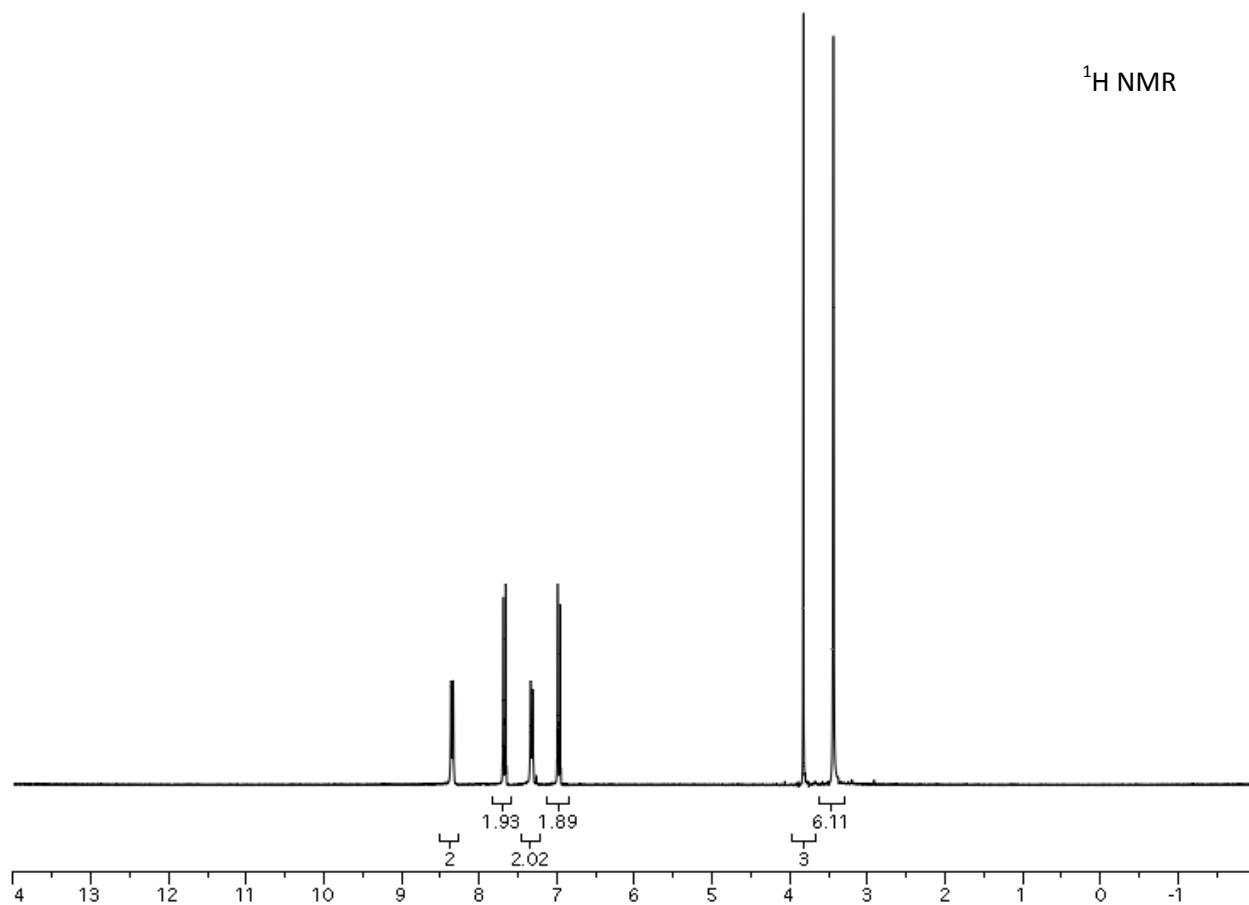
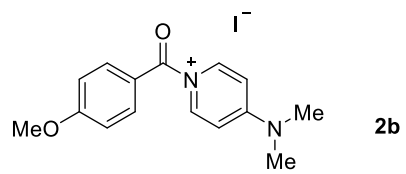
72.2, 29.0; FT-IR (ATR, cm^{-1}): 3296.4 ($\text{C}\equiv\text{C-H}$), 2123.9 ($\text{C}\equiv\text{C}$), 1718.6 (C=O).

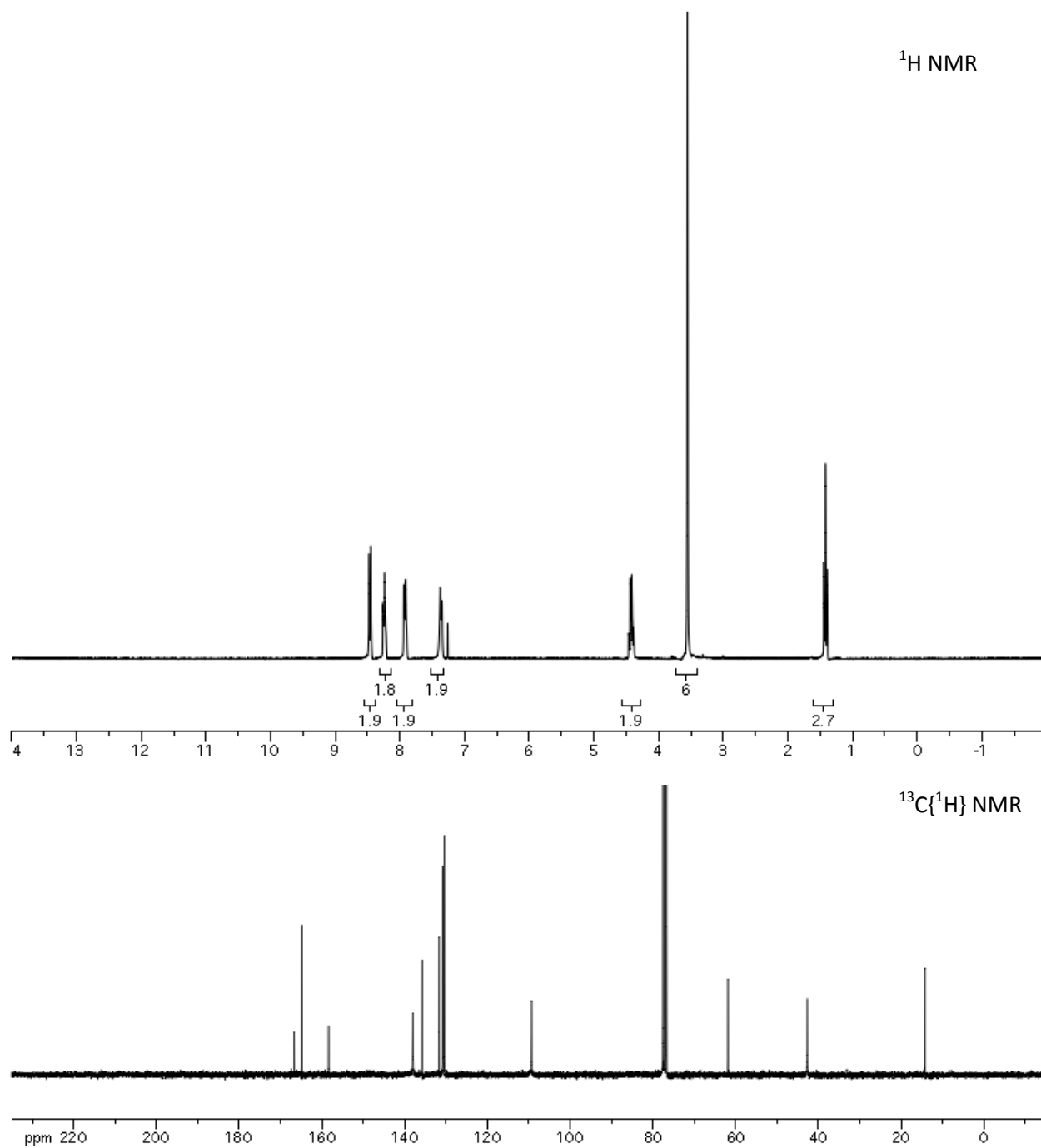
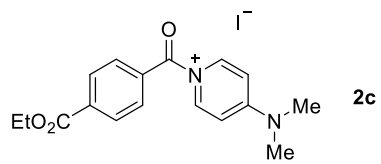


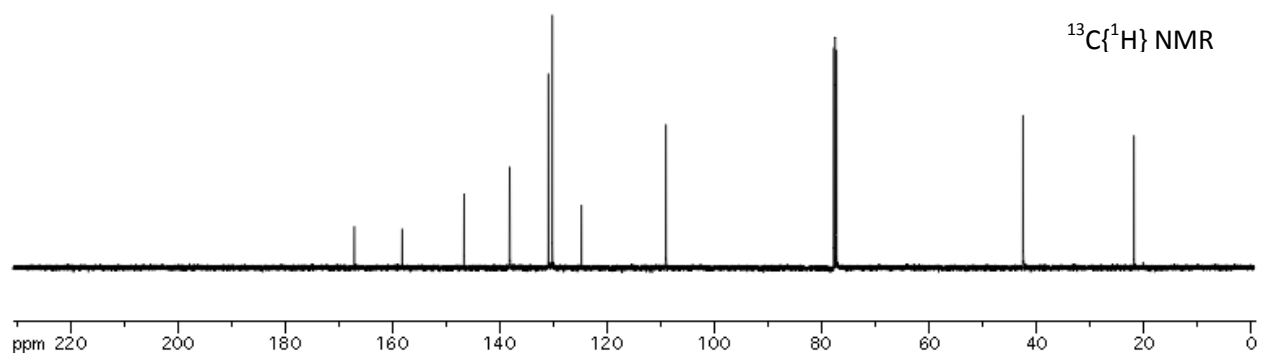
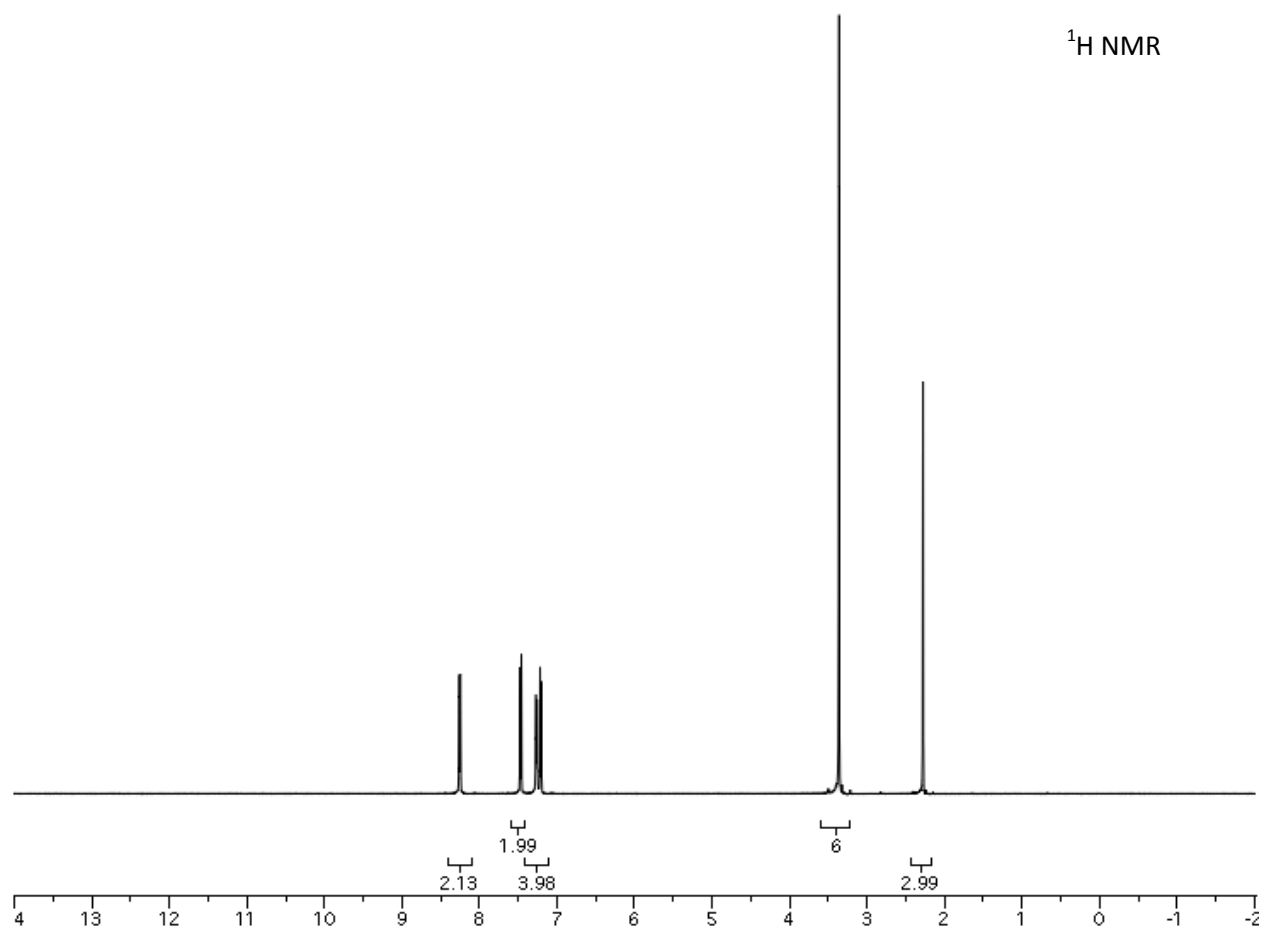
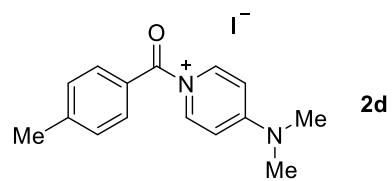
2-methylbut-3-yn-2-yl 2-chlorobenzoate, 5o

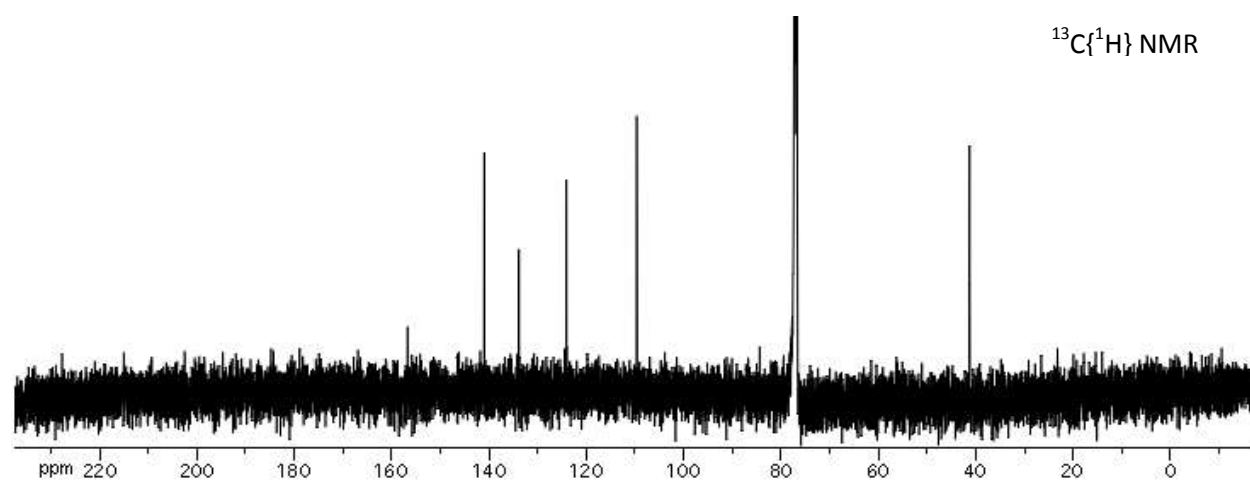
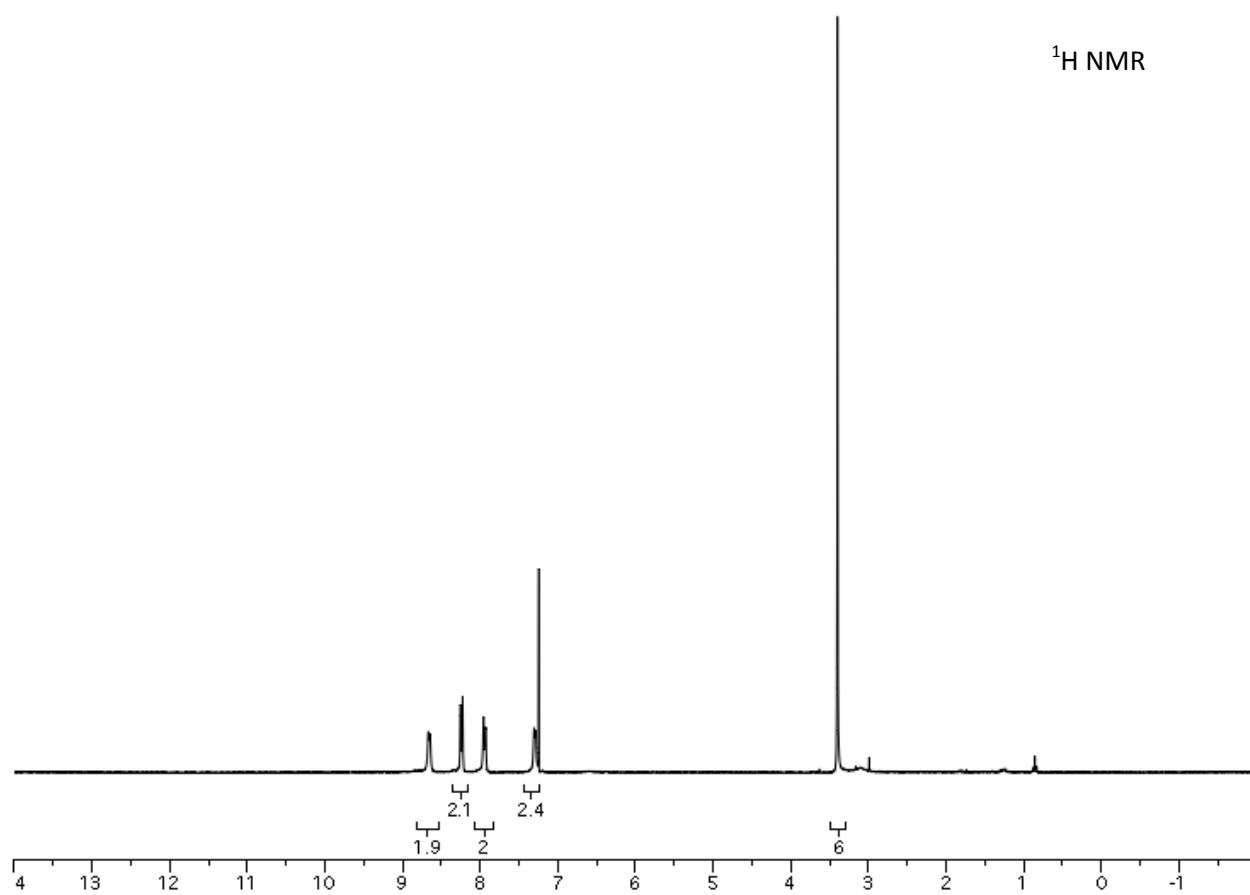
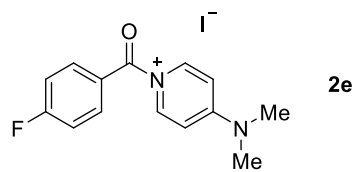
Colourless oil, 90% yield: ^1H -NMR (400 MHz; CDCl_3): δ 7.79 (dd, $J = 7.7$, 1.6 Hz, 1H), 7.44-7.37 (m, 2H), 7.32-7.28 (m, 1H), 2.61 (s, 1H), 1.82 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ -NMR (75 MHz; CDCl_3): δ 164.0, 133.5, 132.4, 131.3, 131.0, 130.7, 126.5, 84.3, 73.2, 72.9, 29.0; FT-IR (ATR, cm^{-1}): 3300.0 ($\text{C}\equiv\text{C-H}$), 2123.8 ($\text{C}\equiv\text{C}$), 1732.9 (C=O); ESI HRMS ($\text{C}_{12}\text{H}_{11}\text{ClNaO}_2$): calc'd ($\text{M}+\text{Na}$) 245.0340, observed 245.0336.

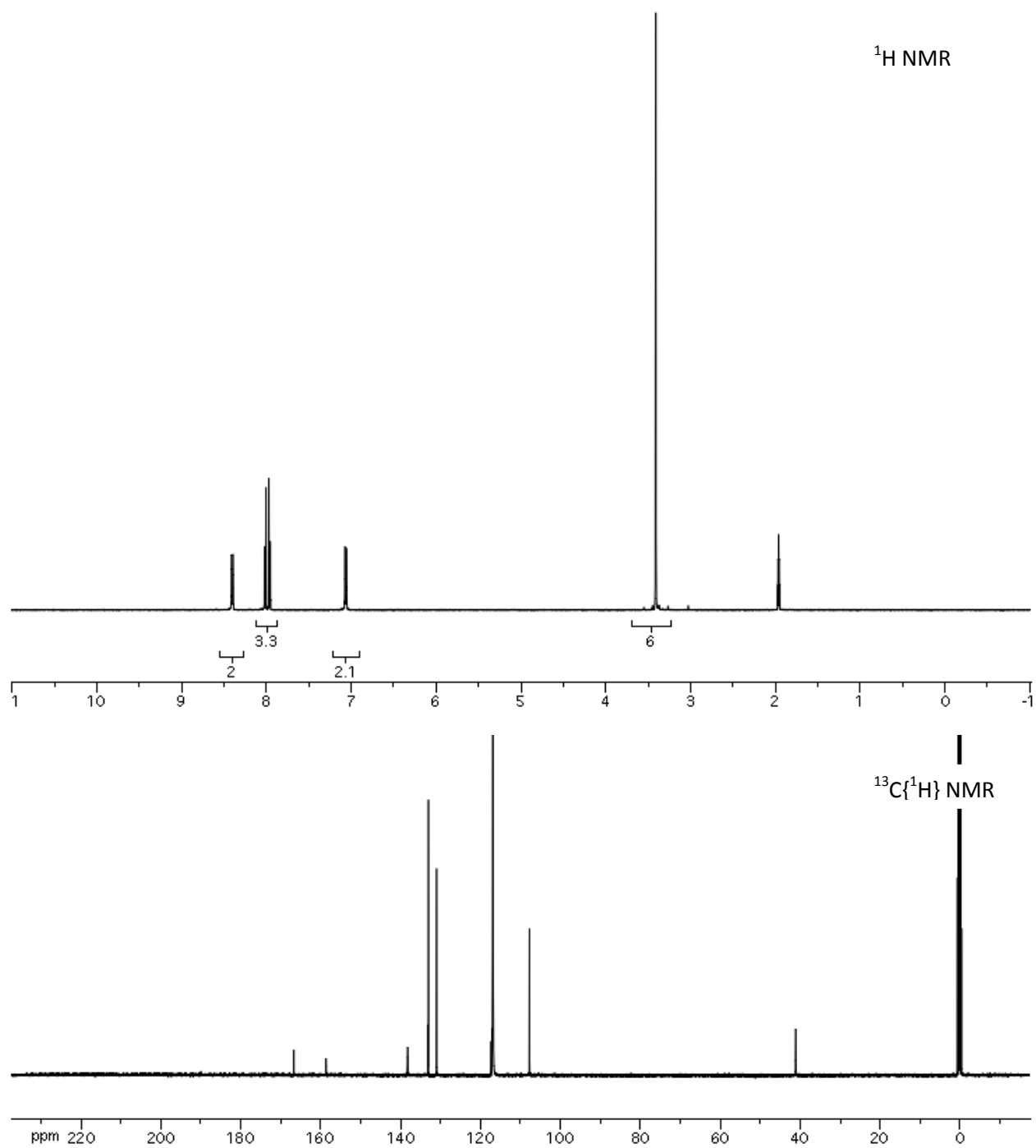
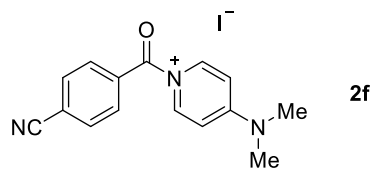


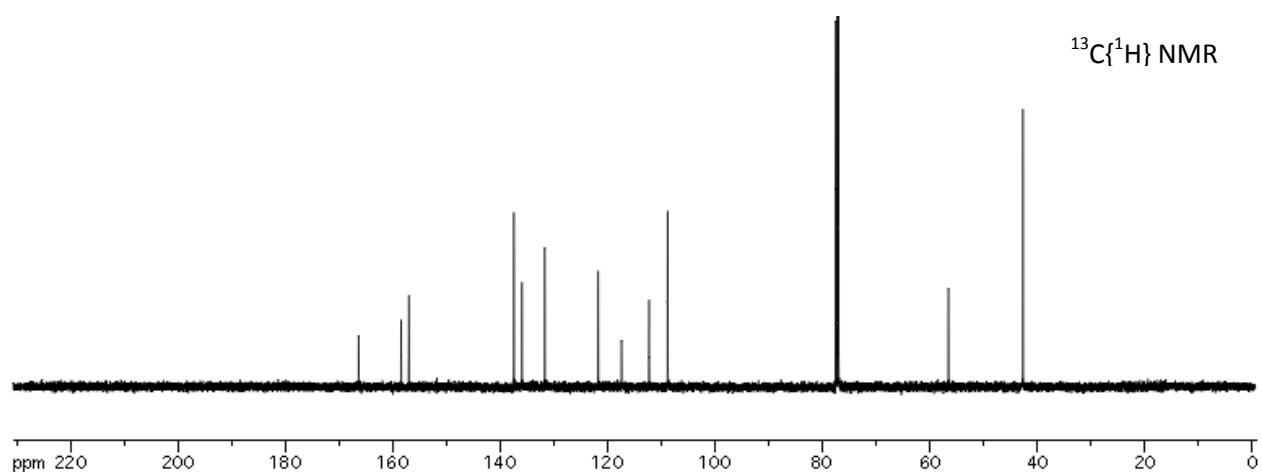
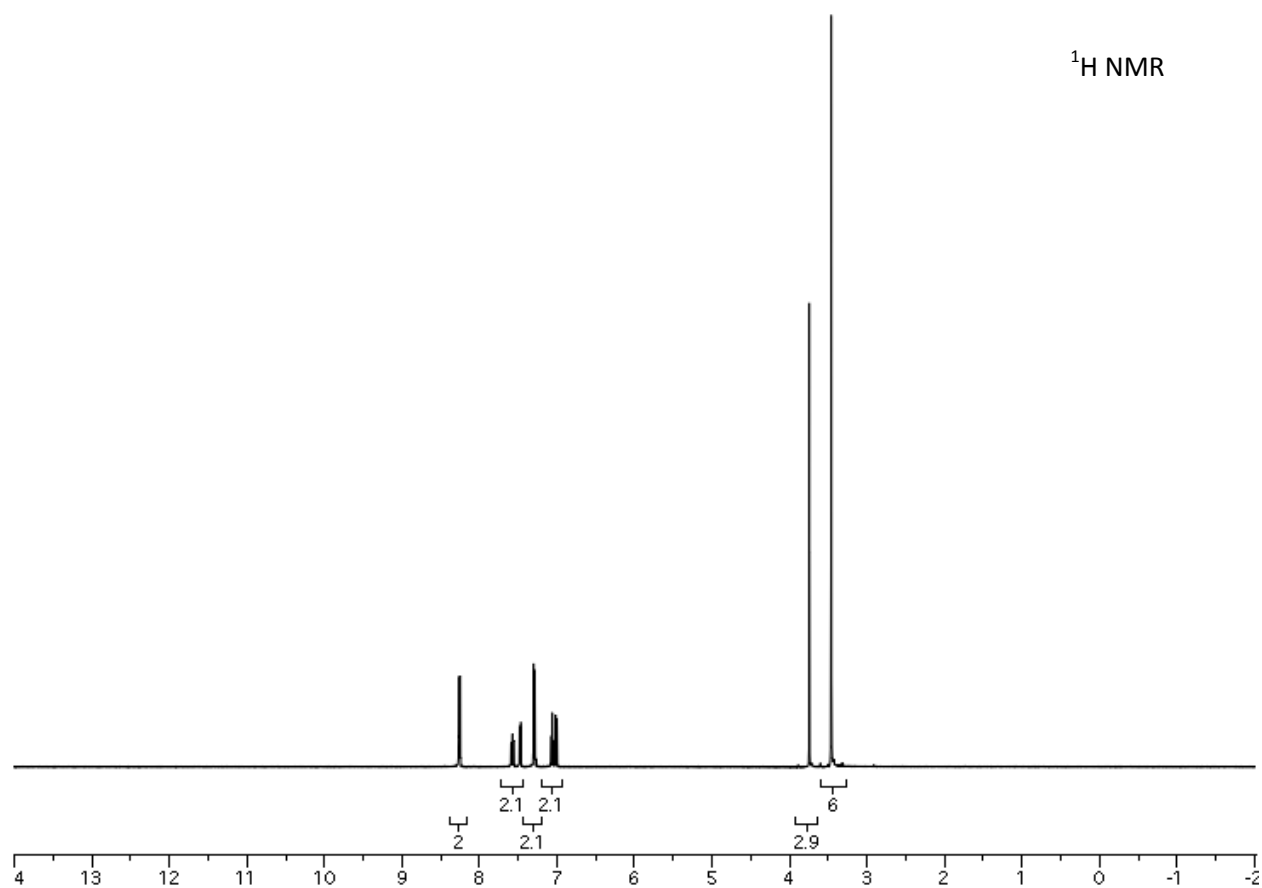
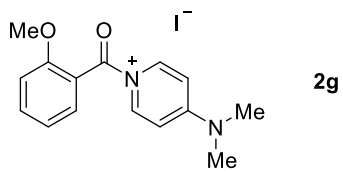


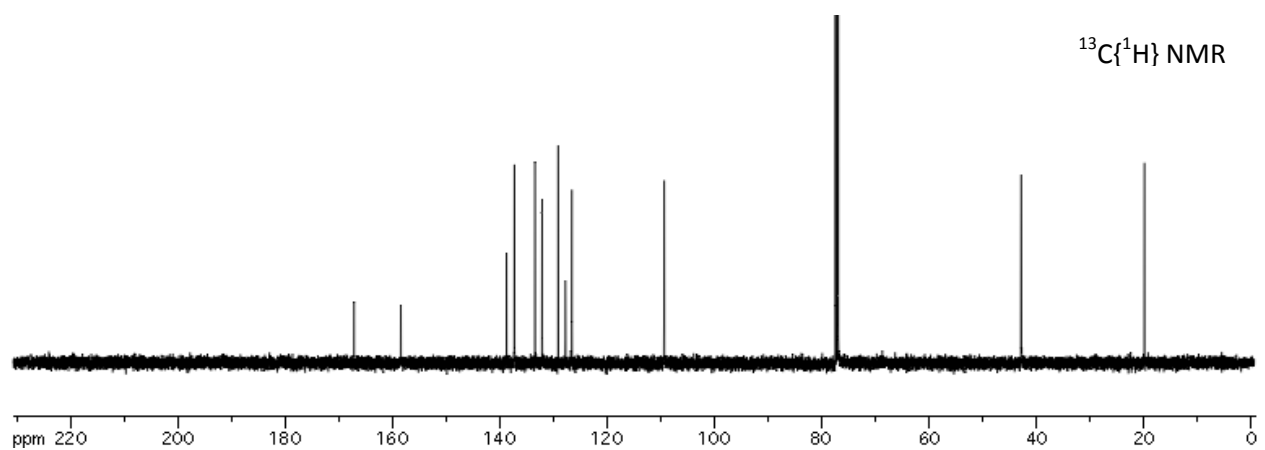
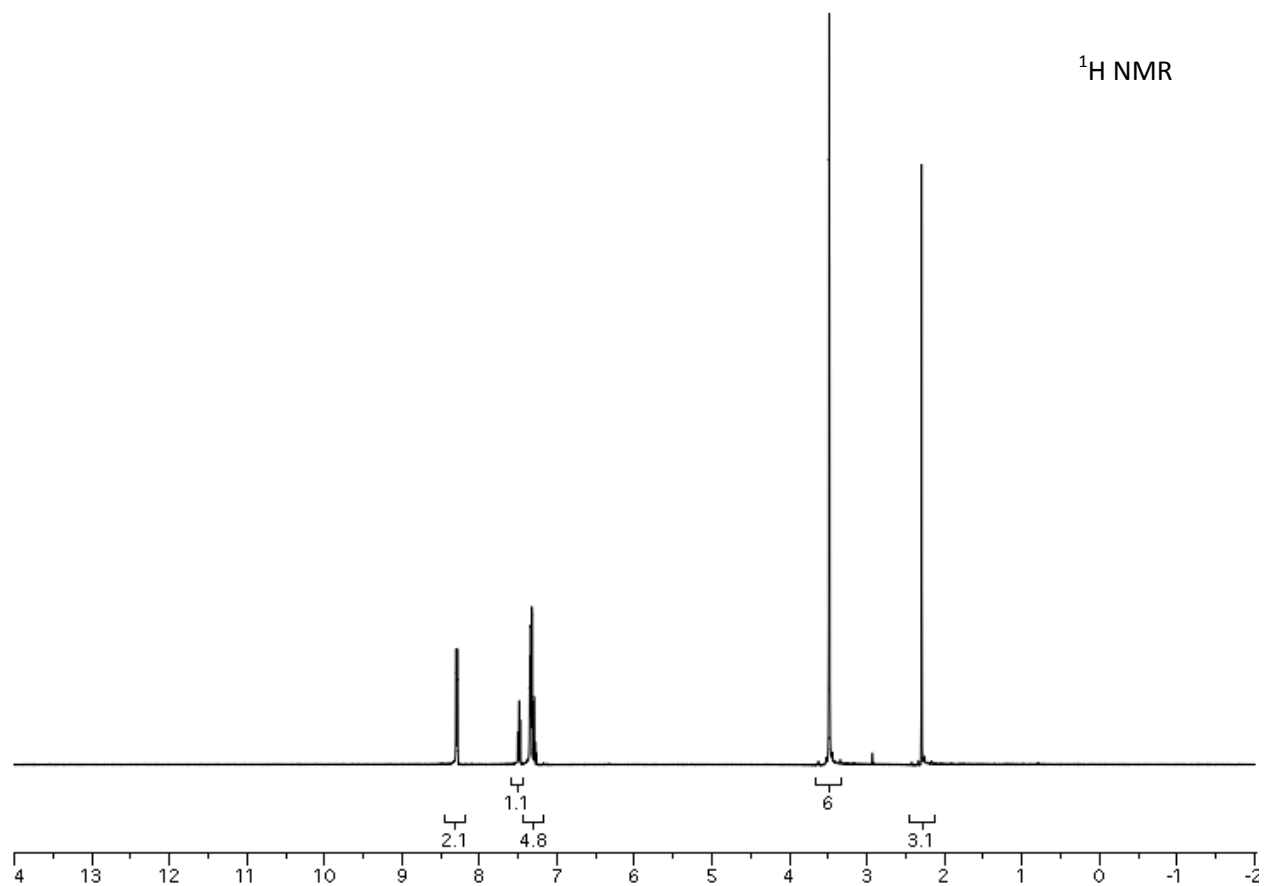
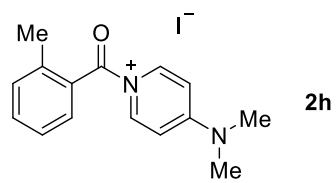


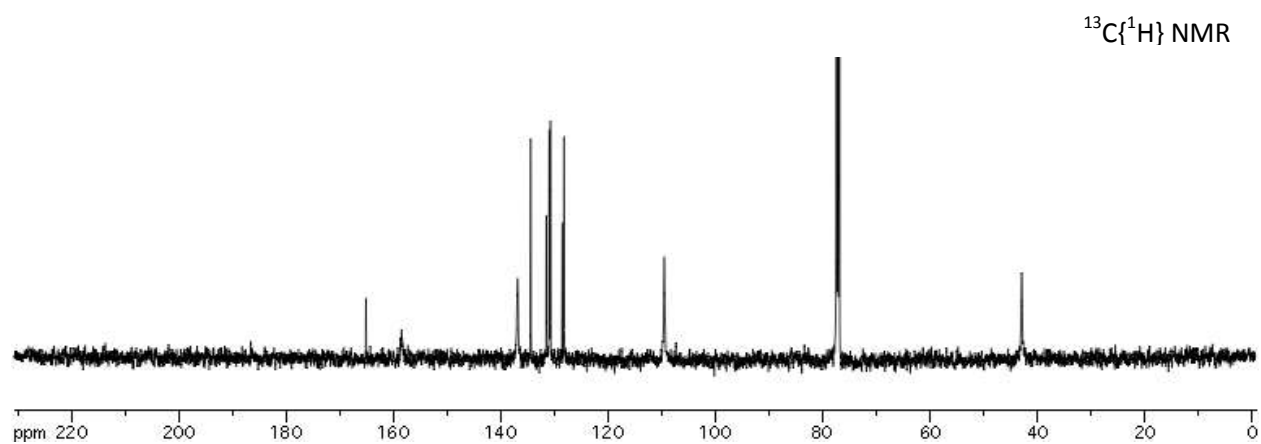
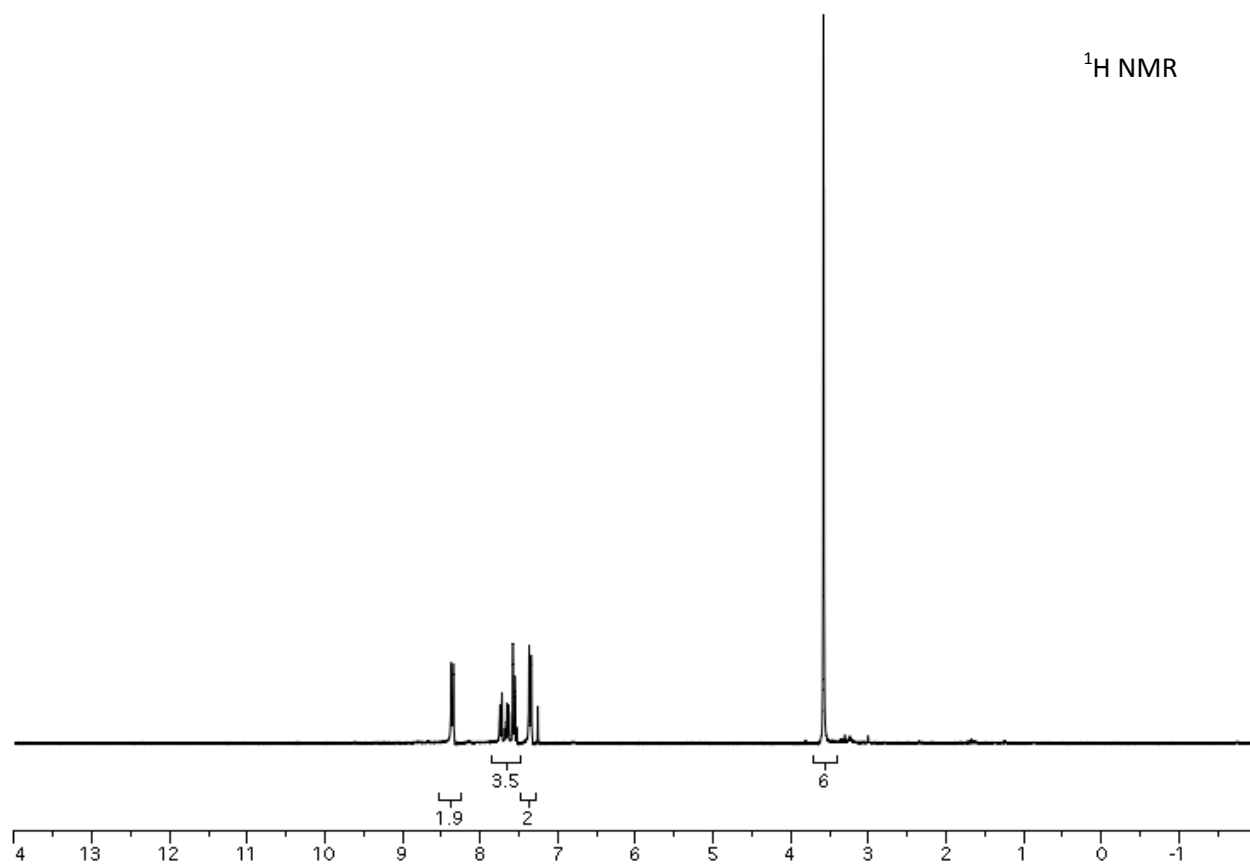
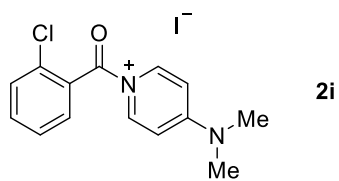


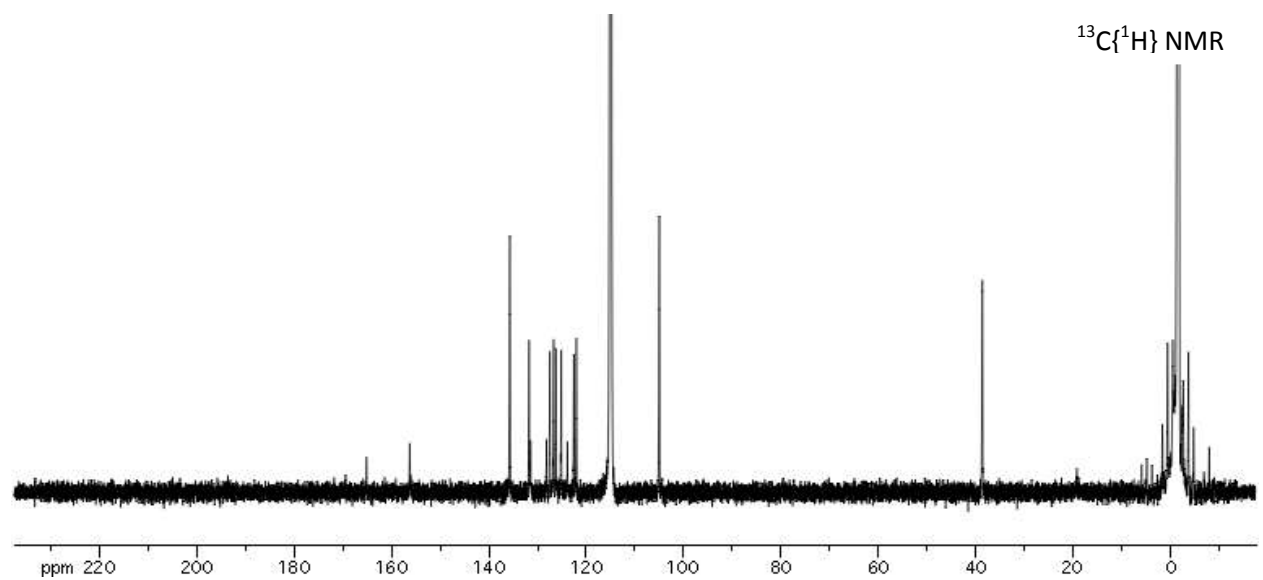
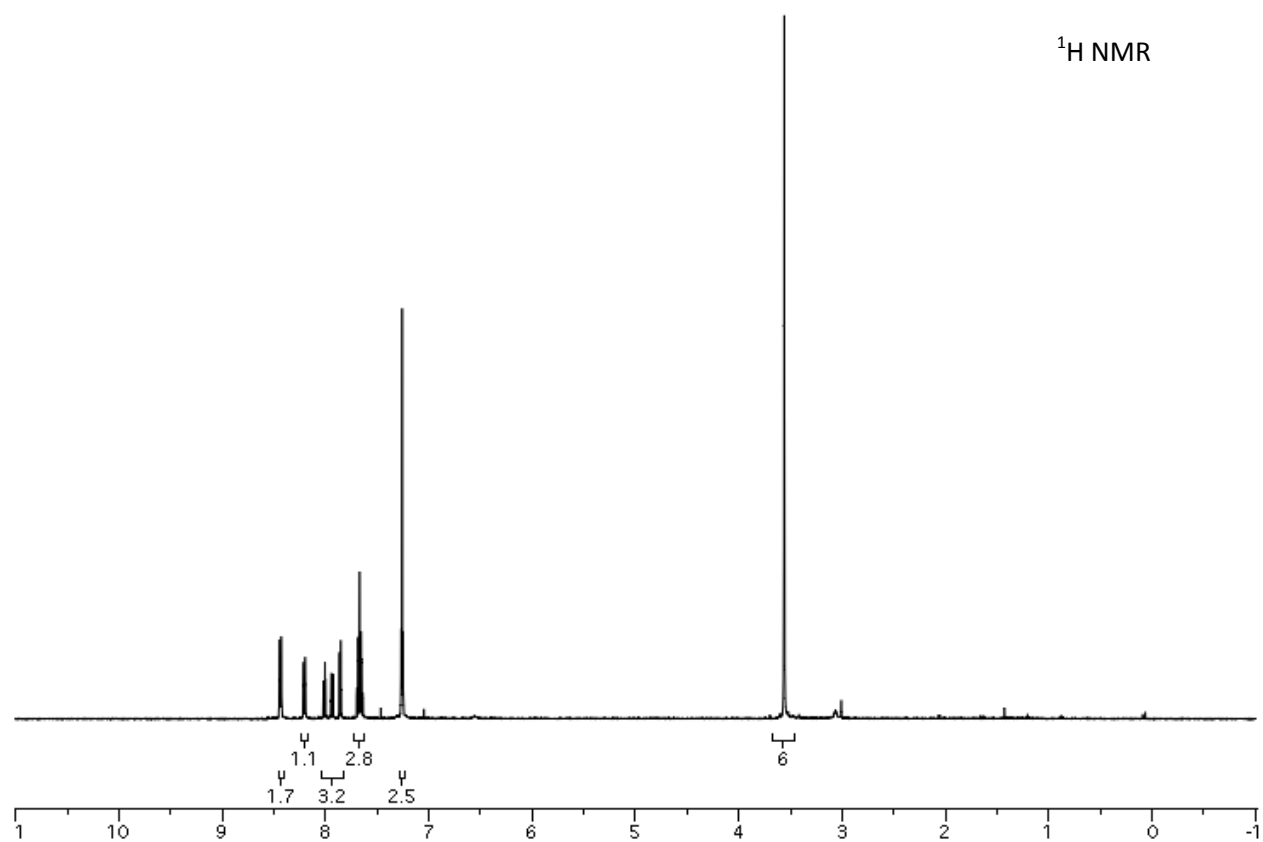
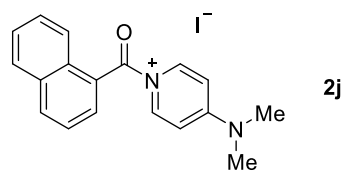


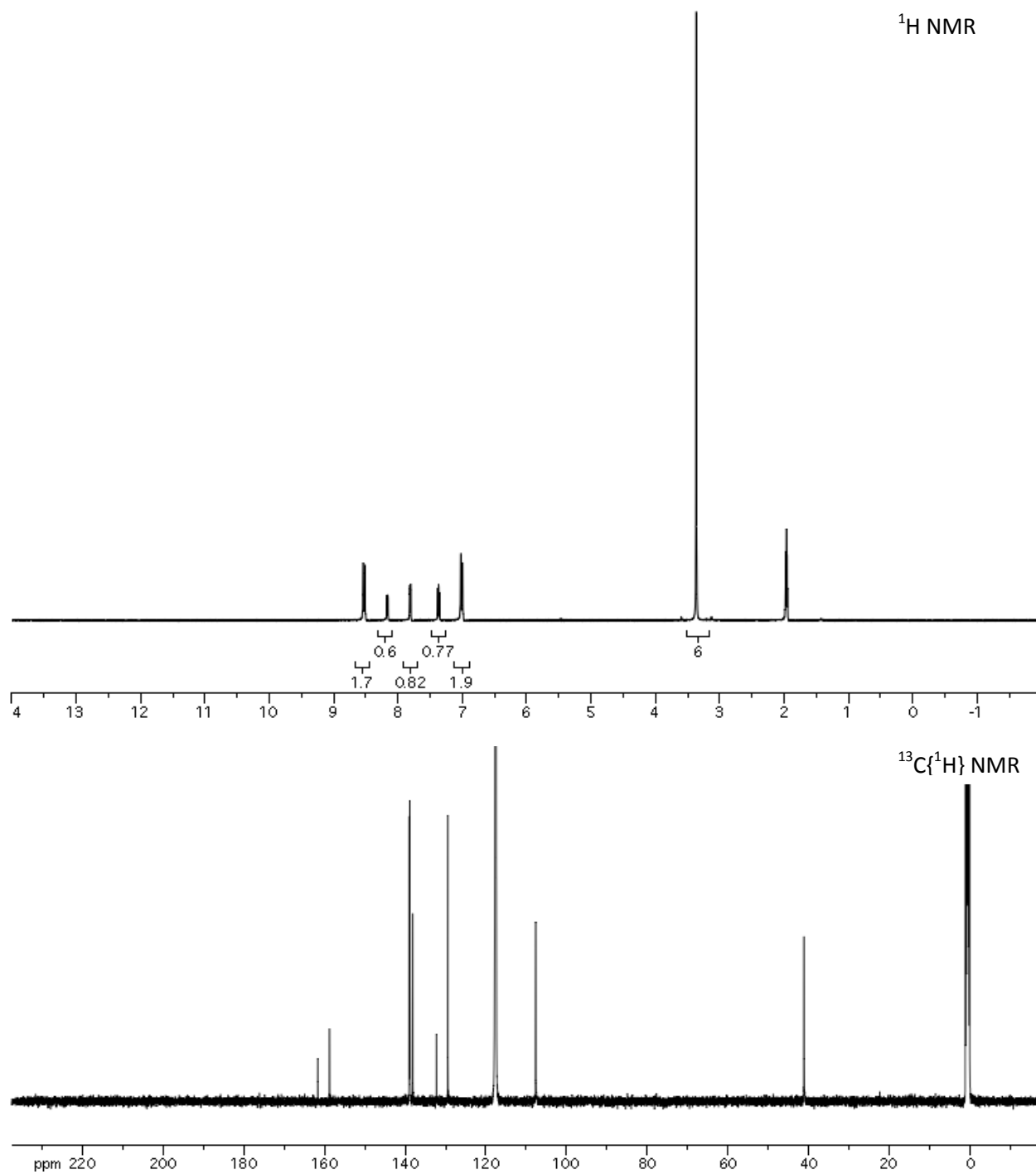
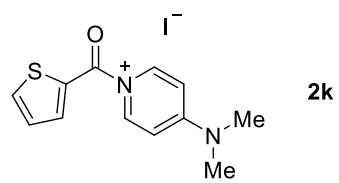


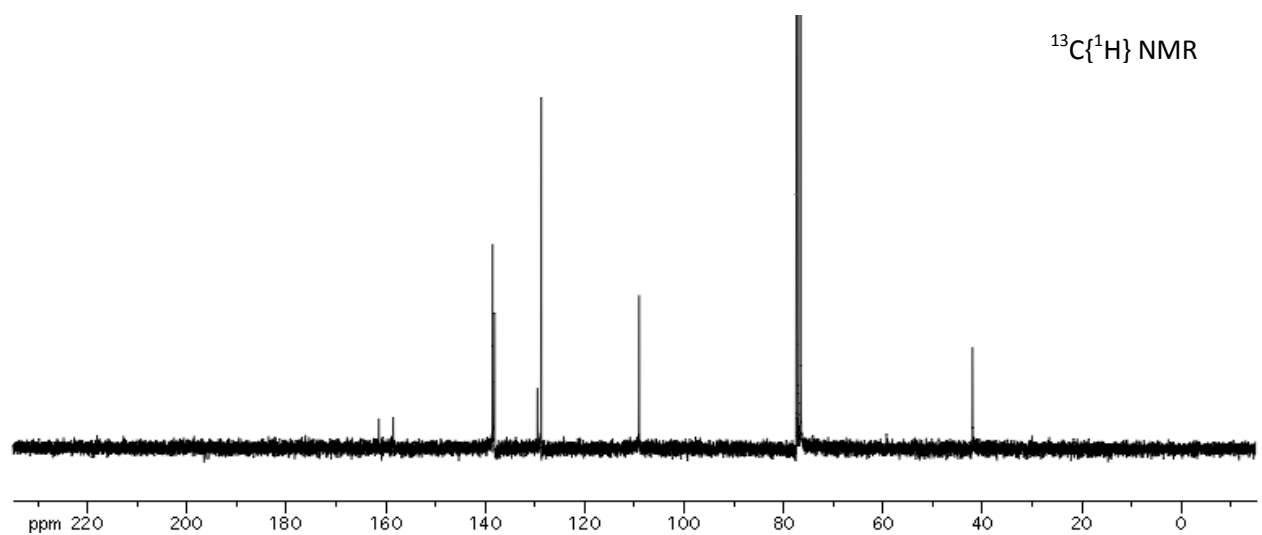
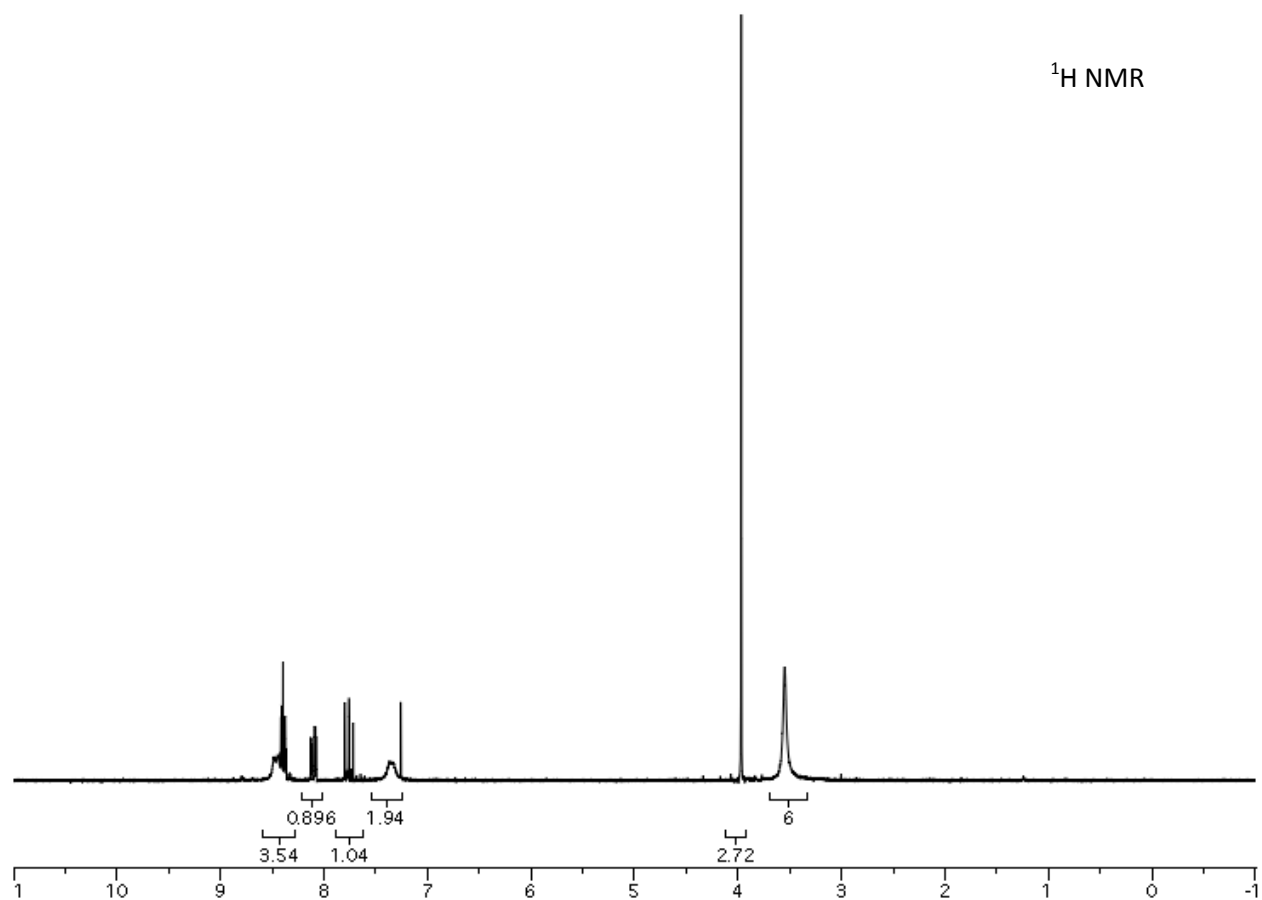
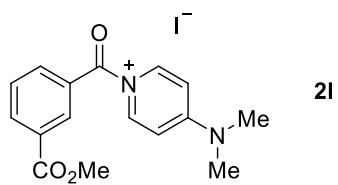


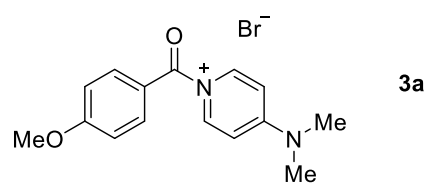




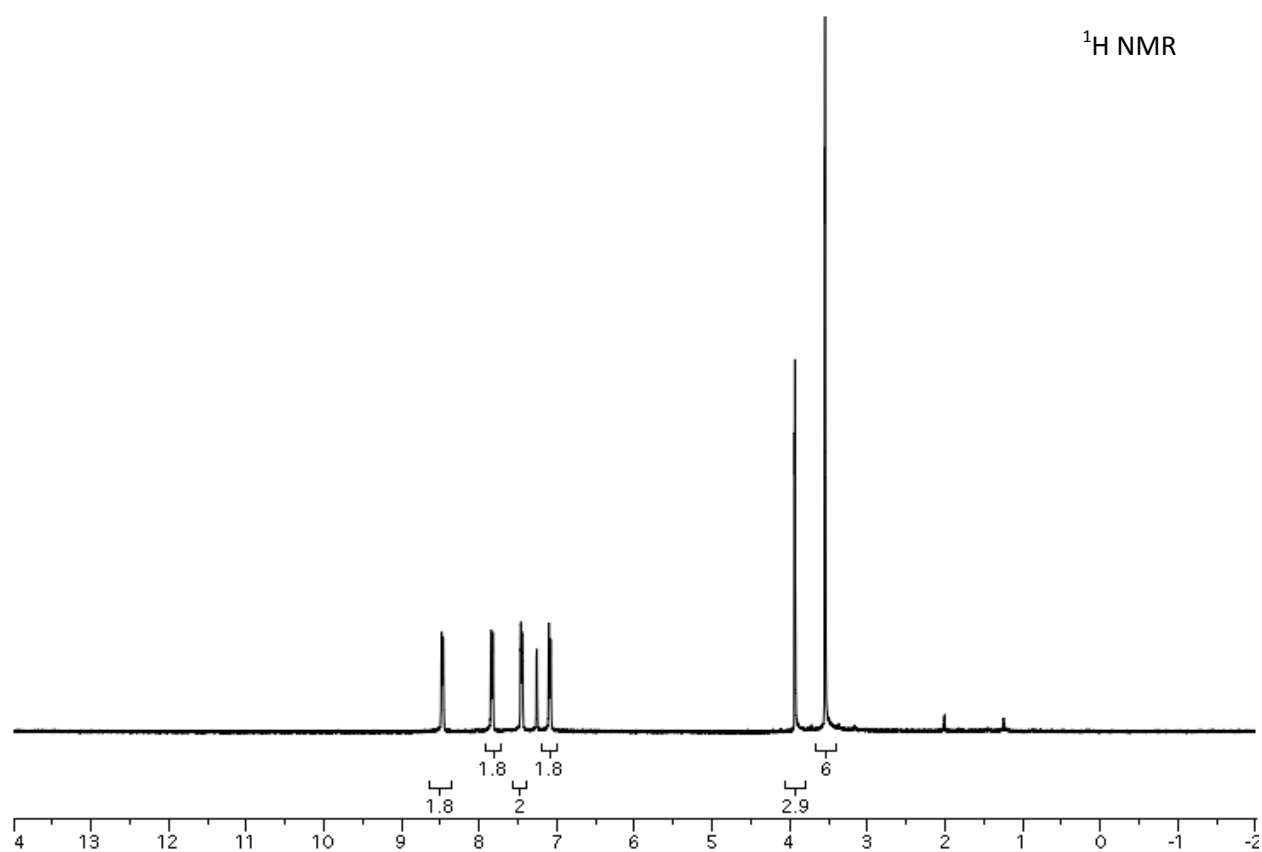


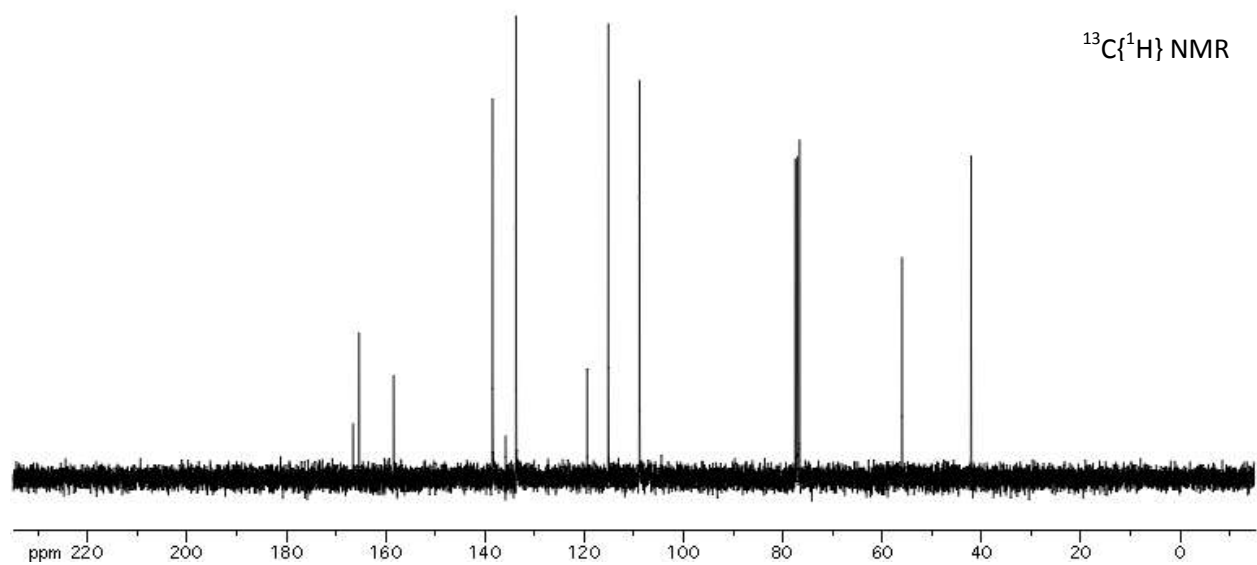


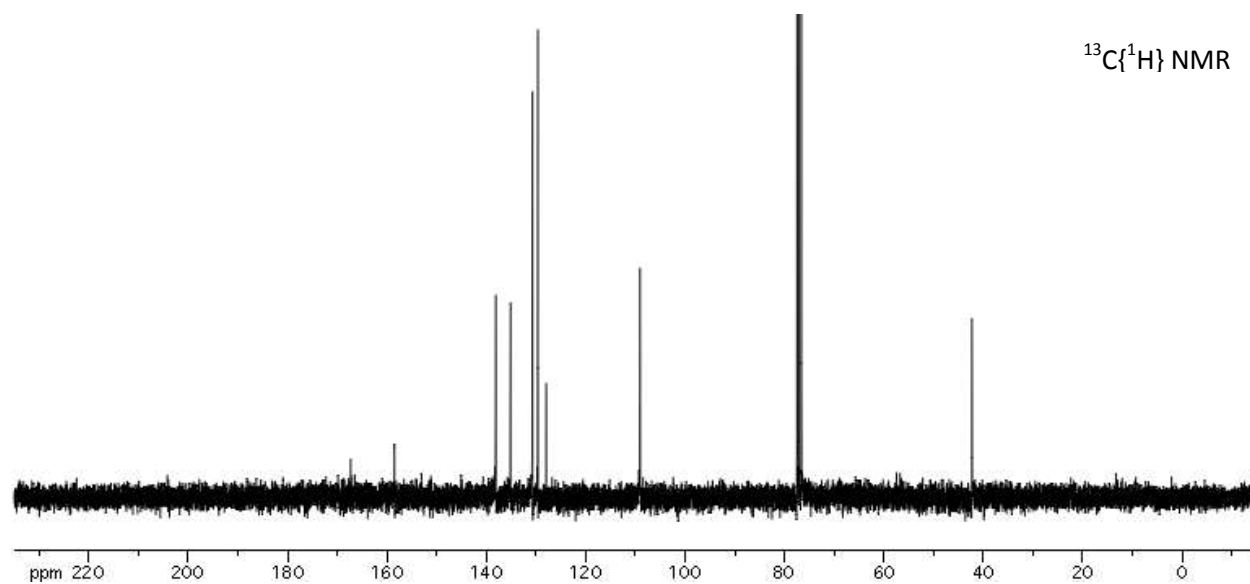
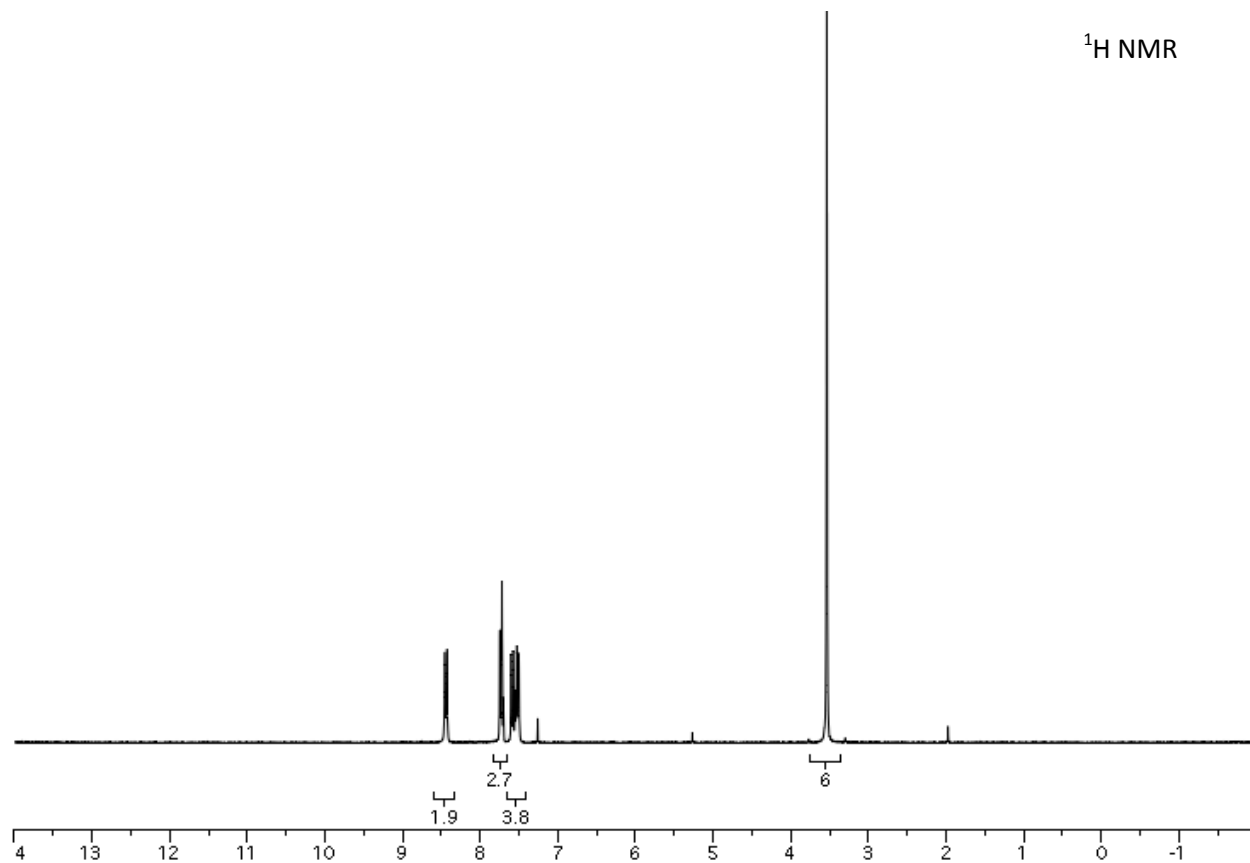
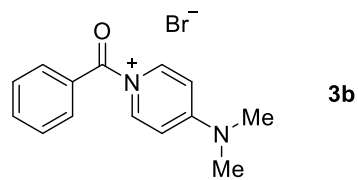


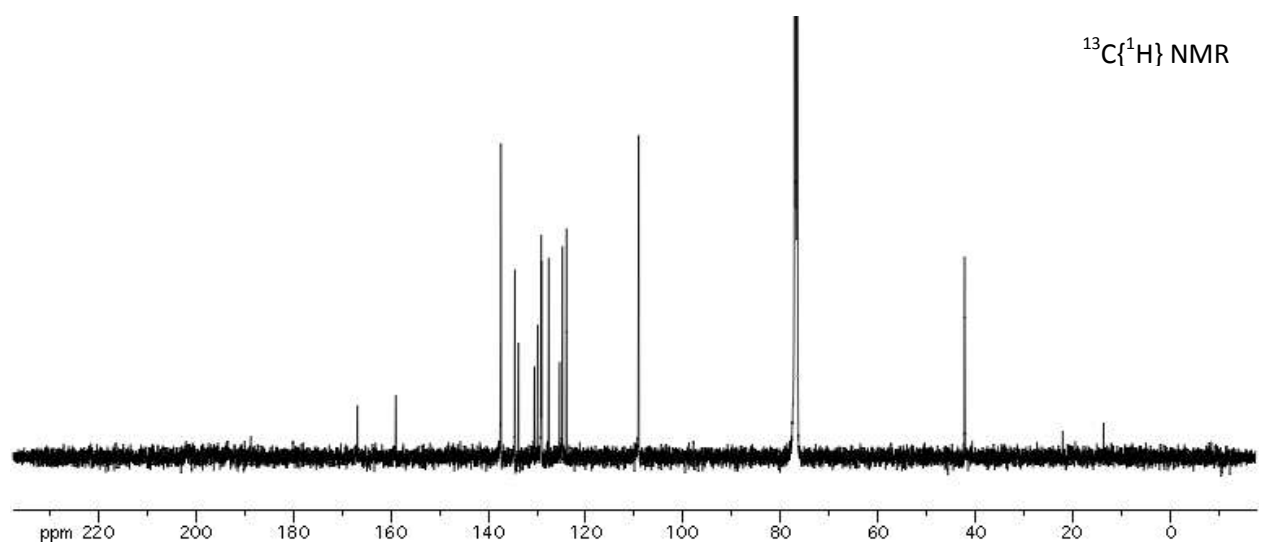
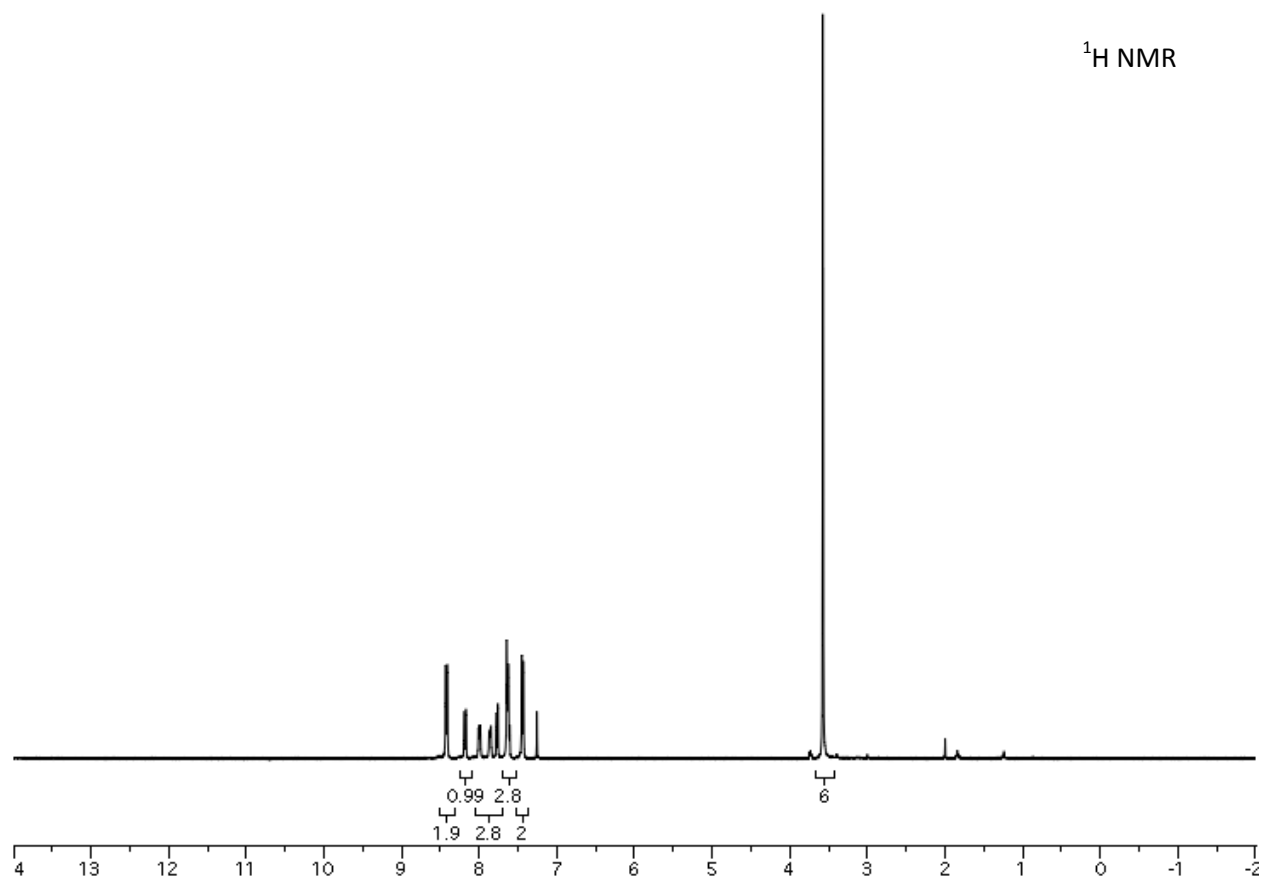
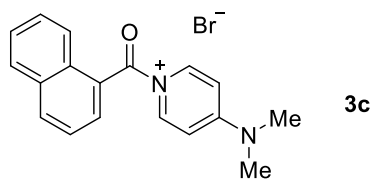


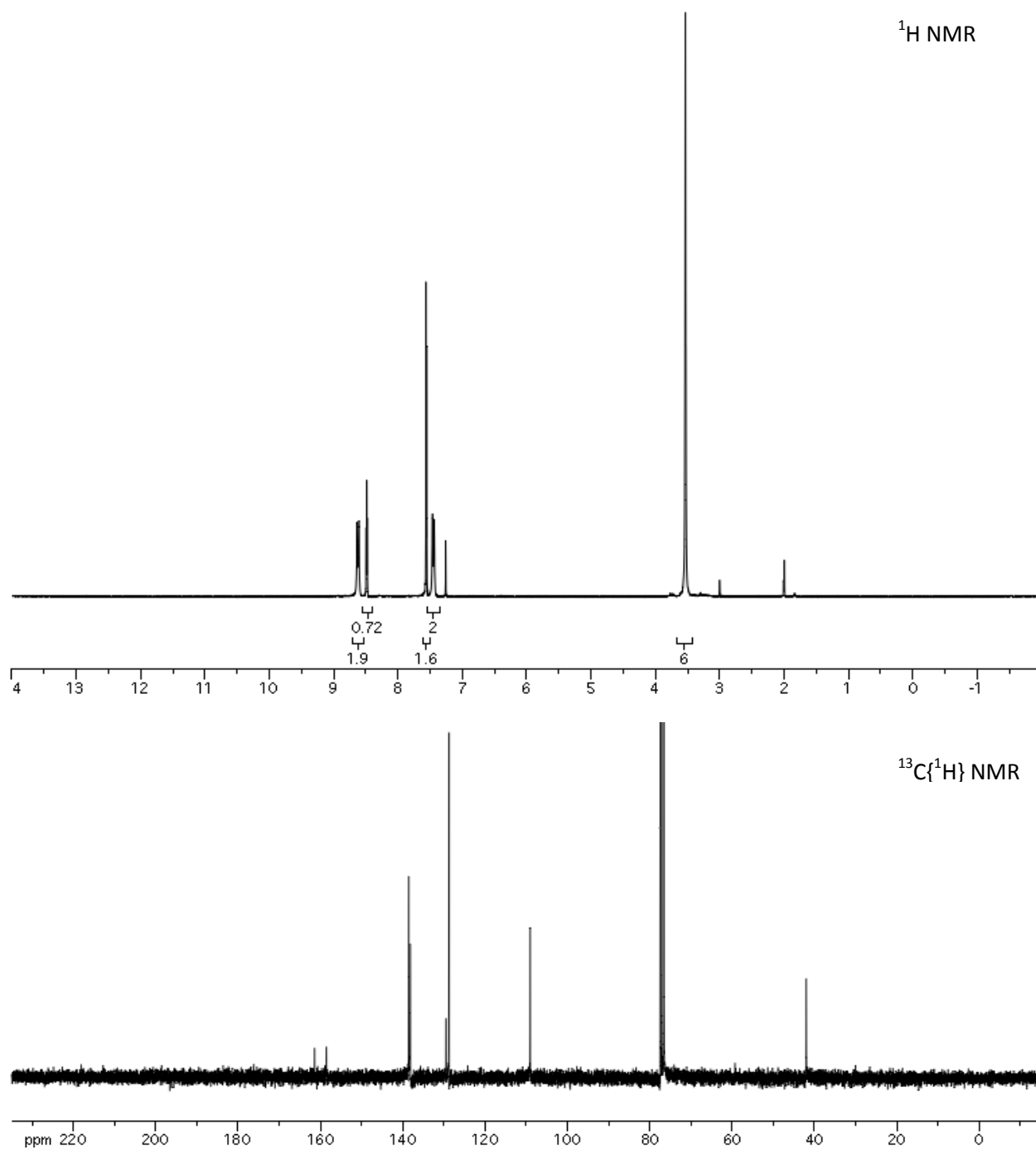
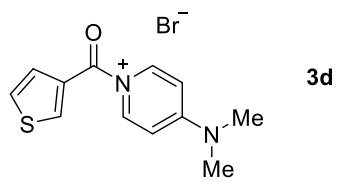
3a

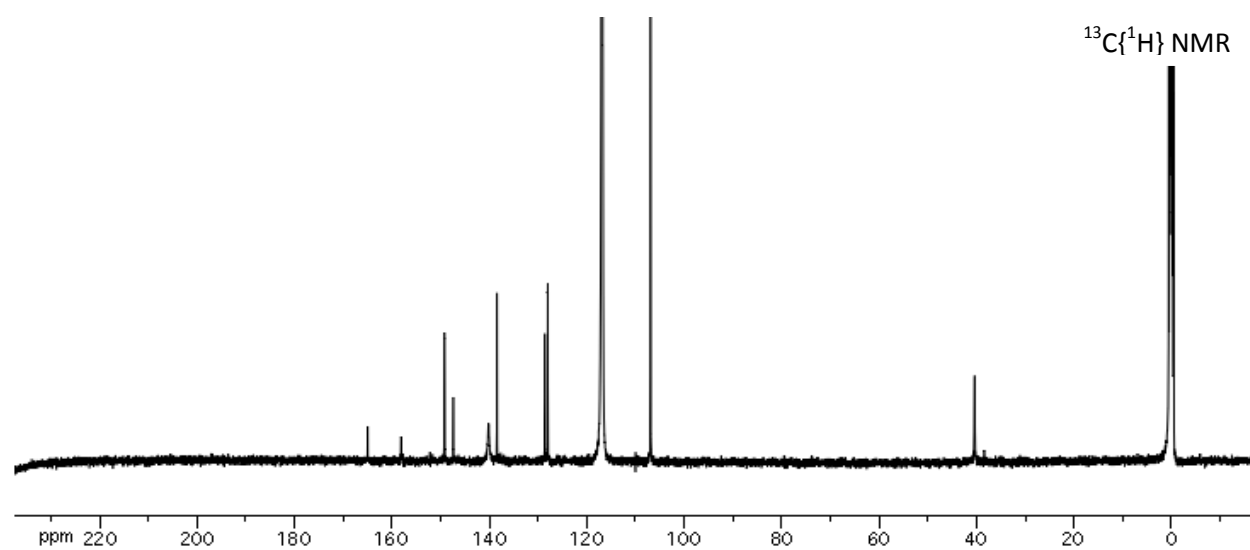
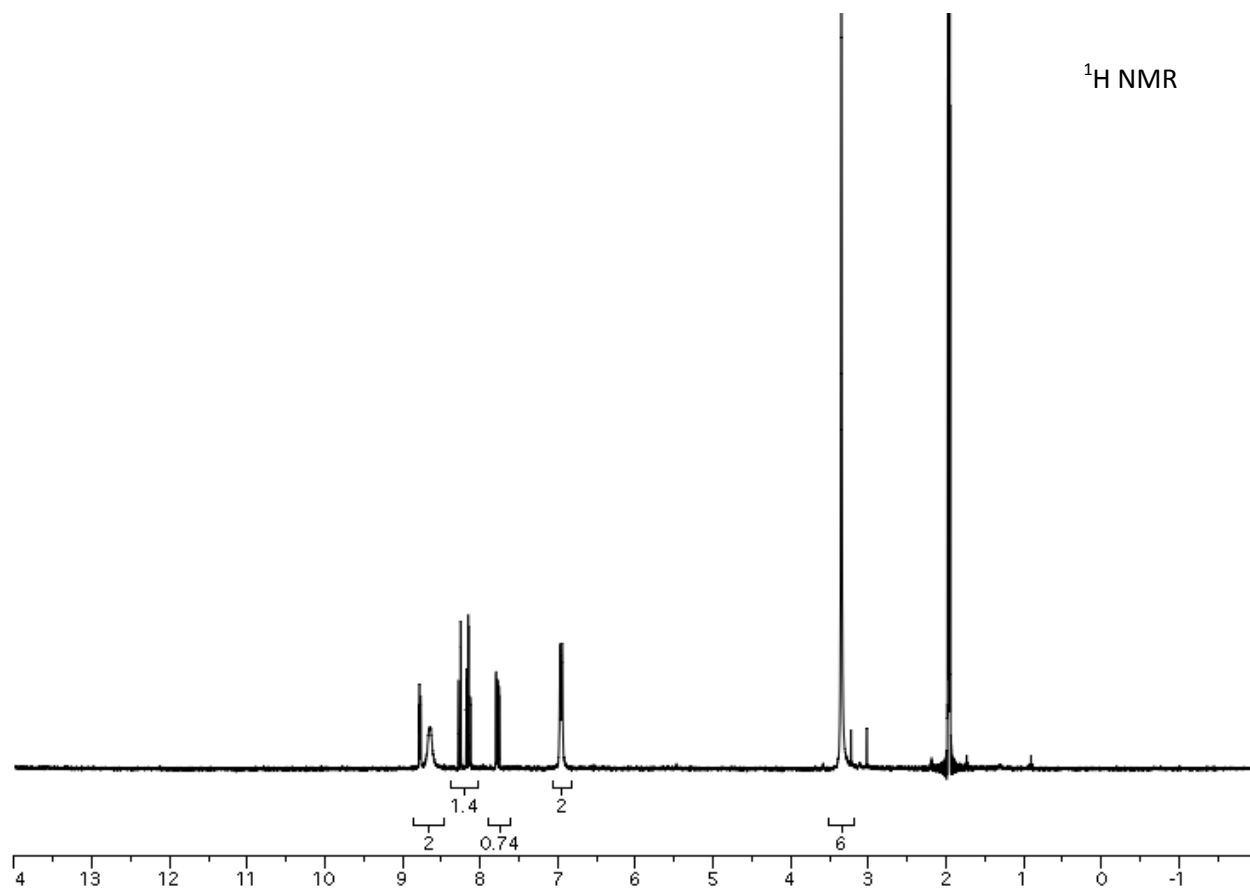
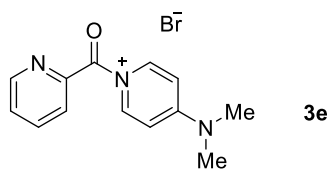


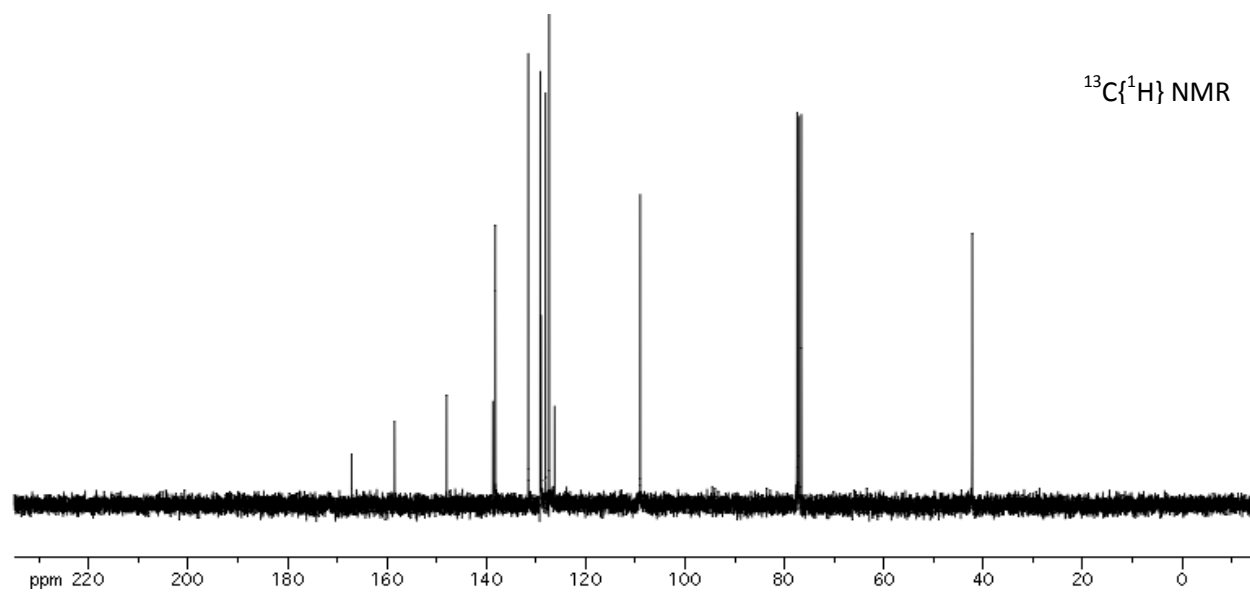
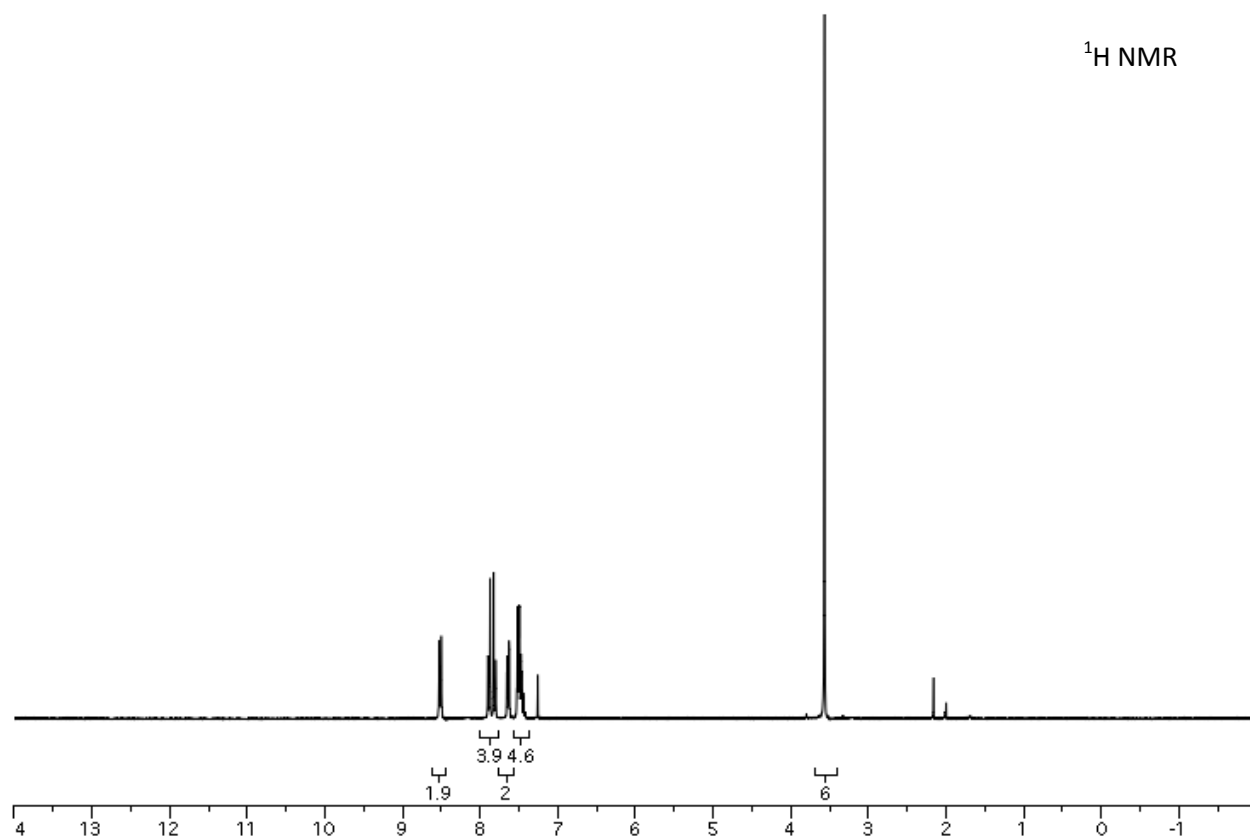
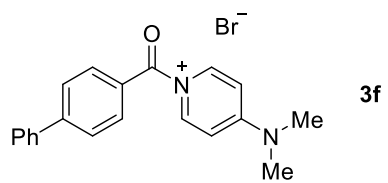


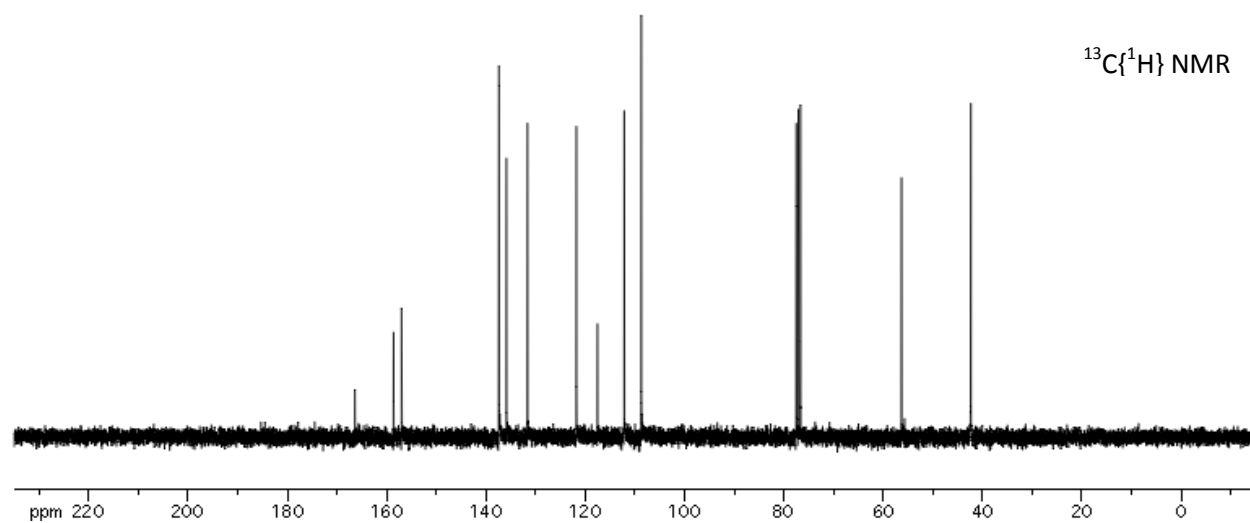
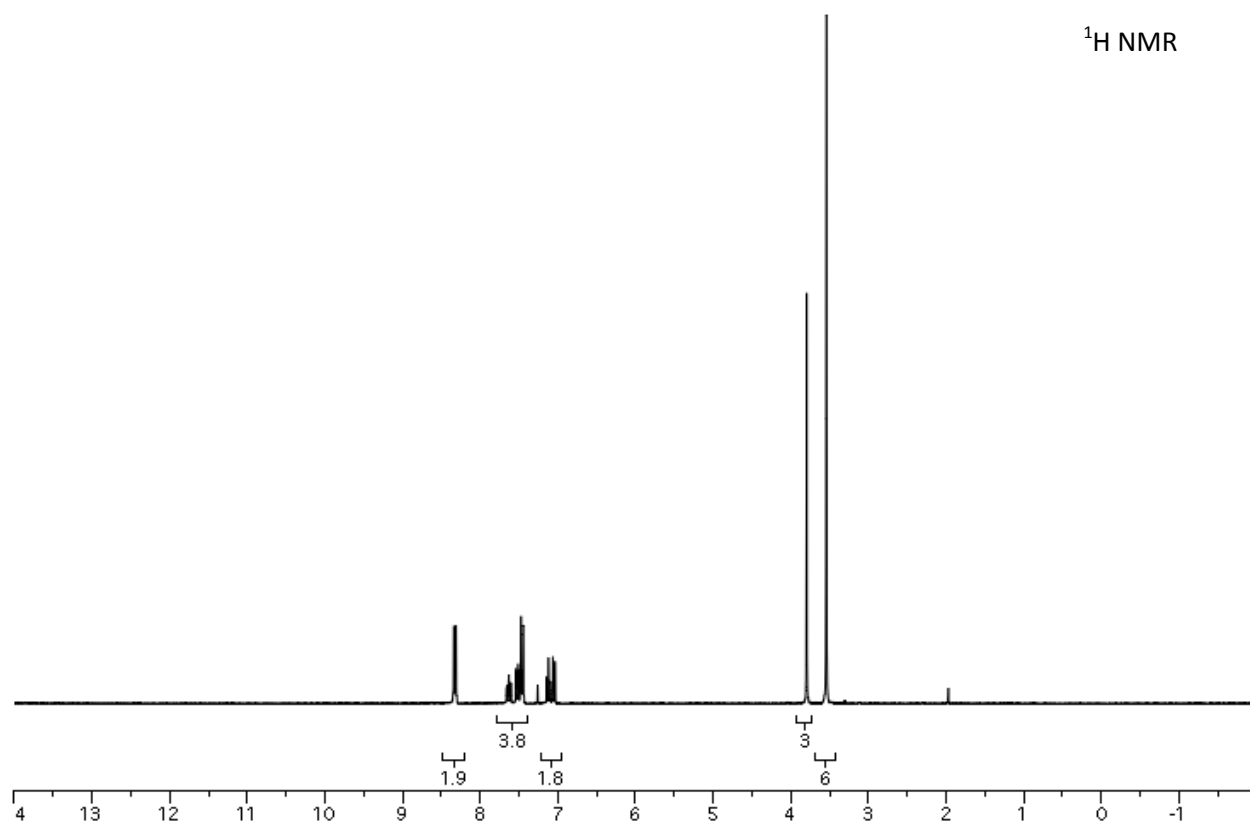
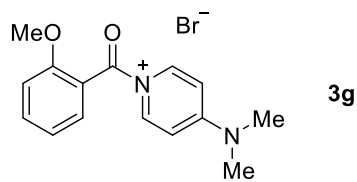


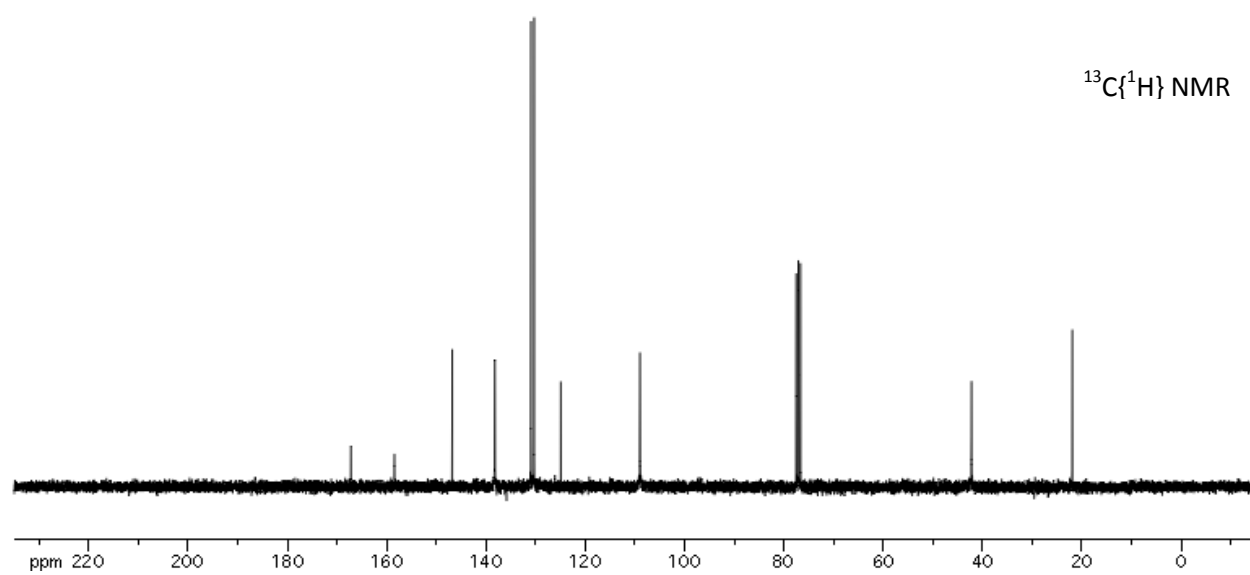
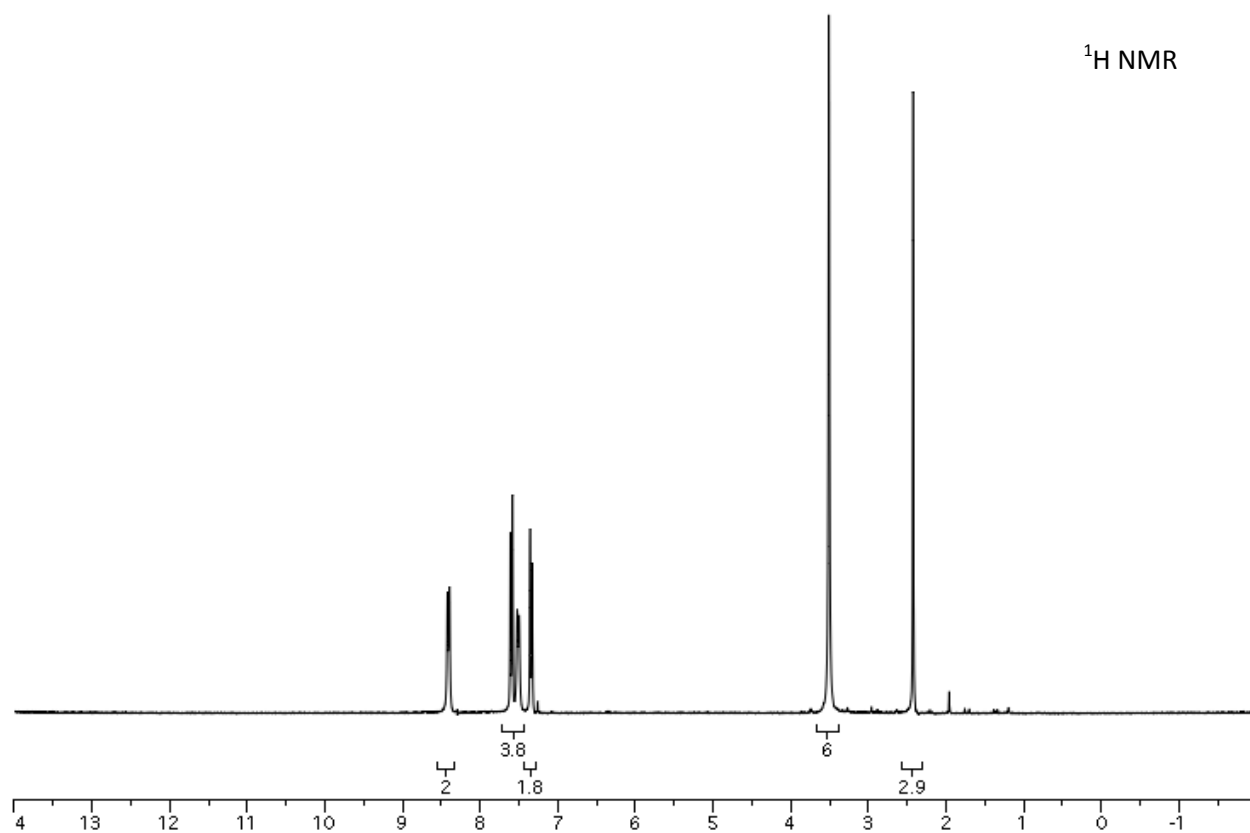
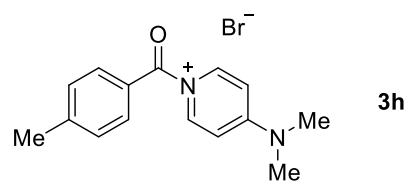




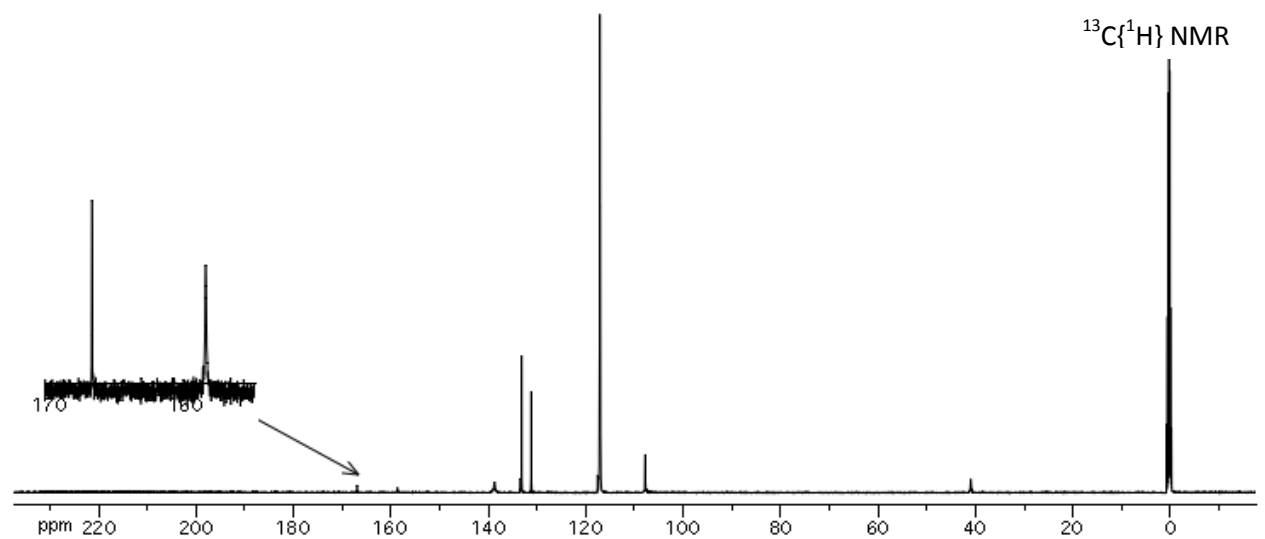
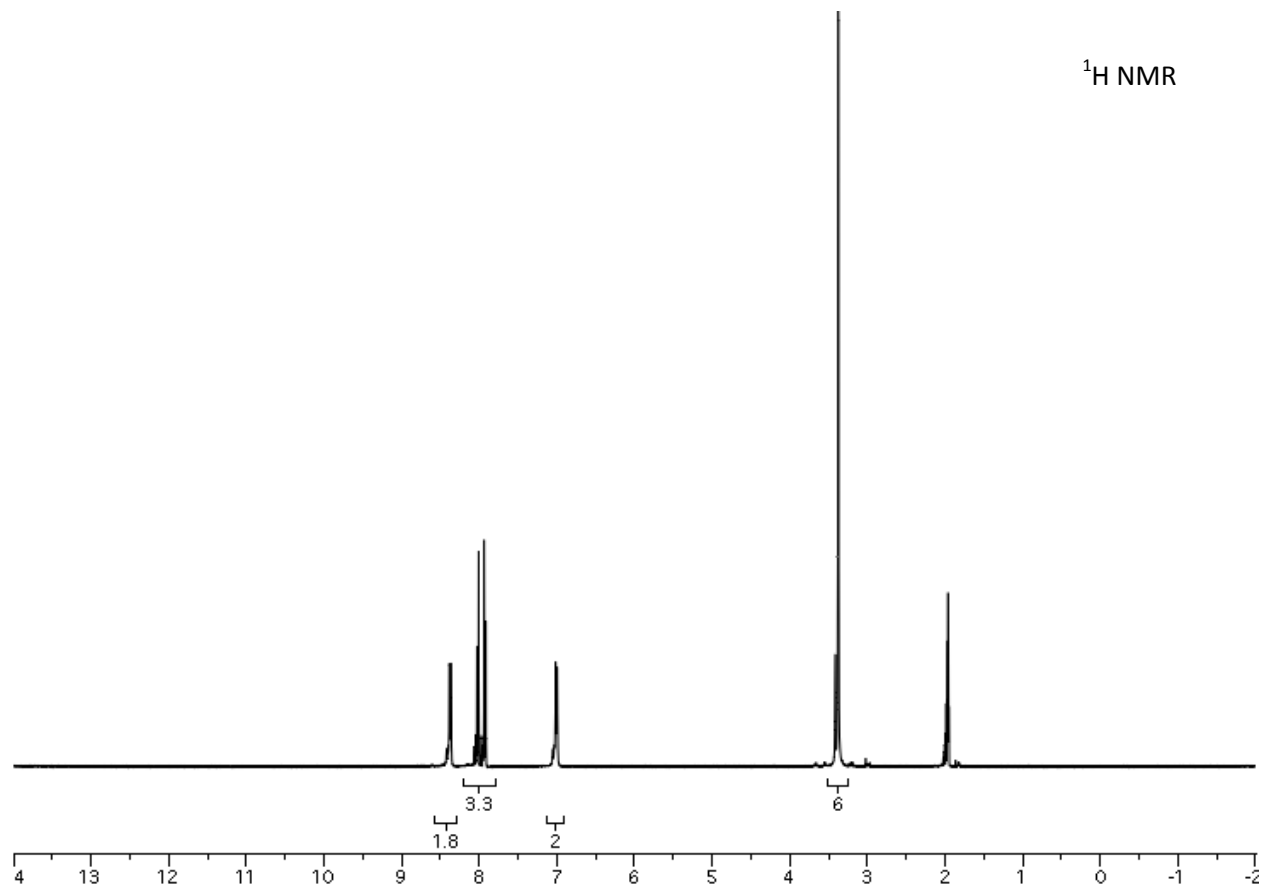
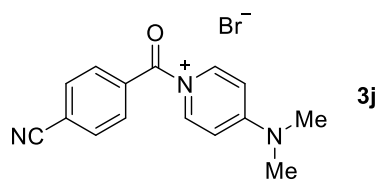


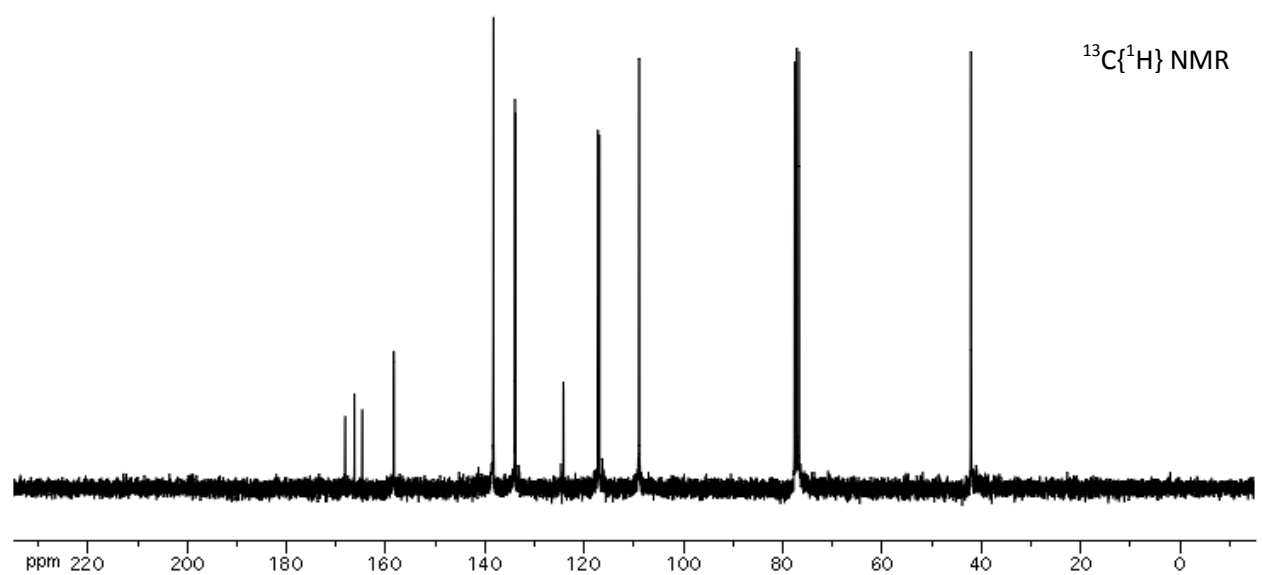
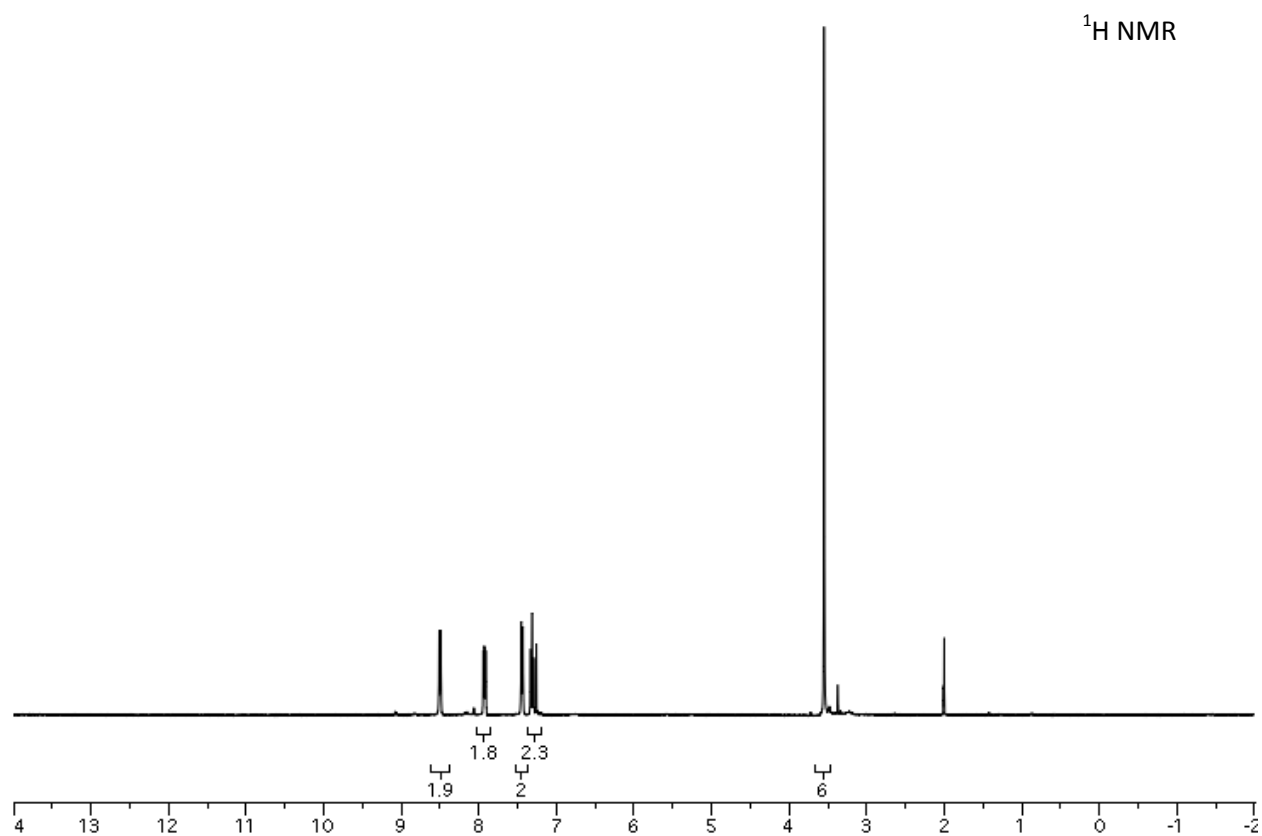
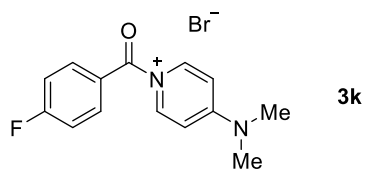


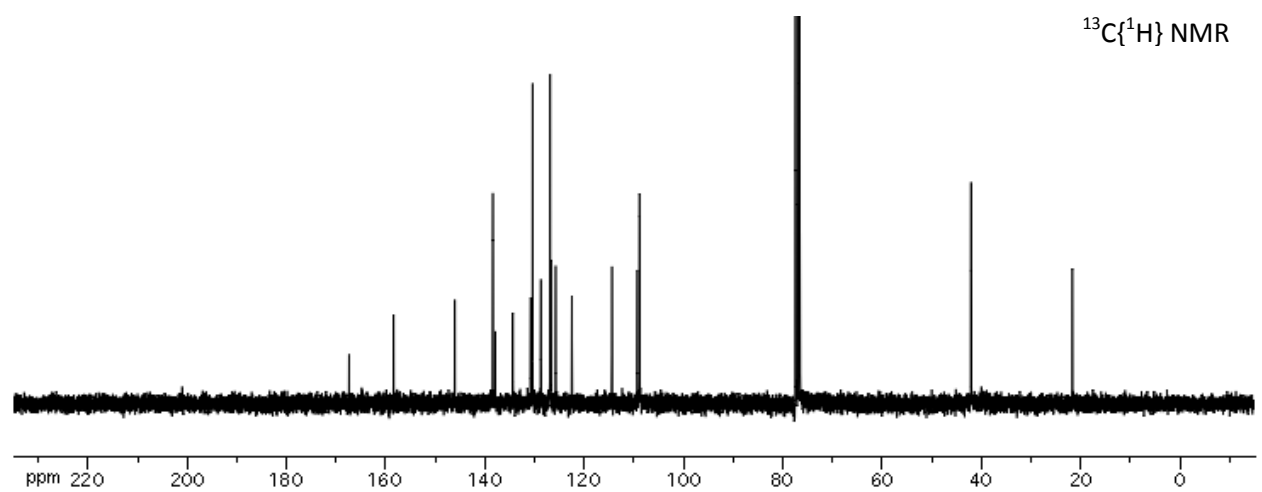
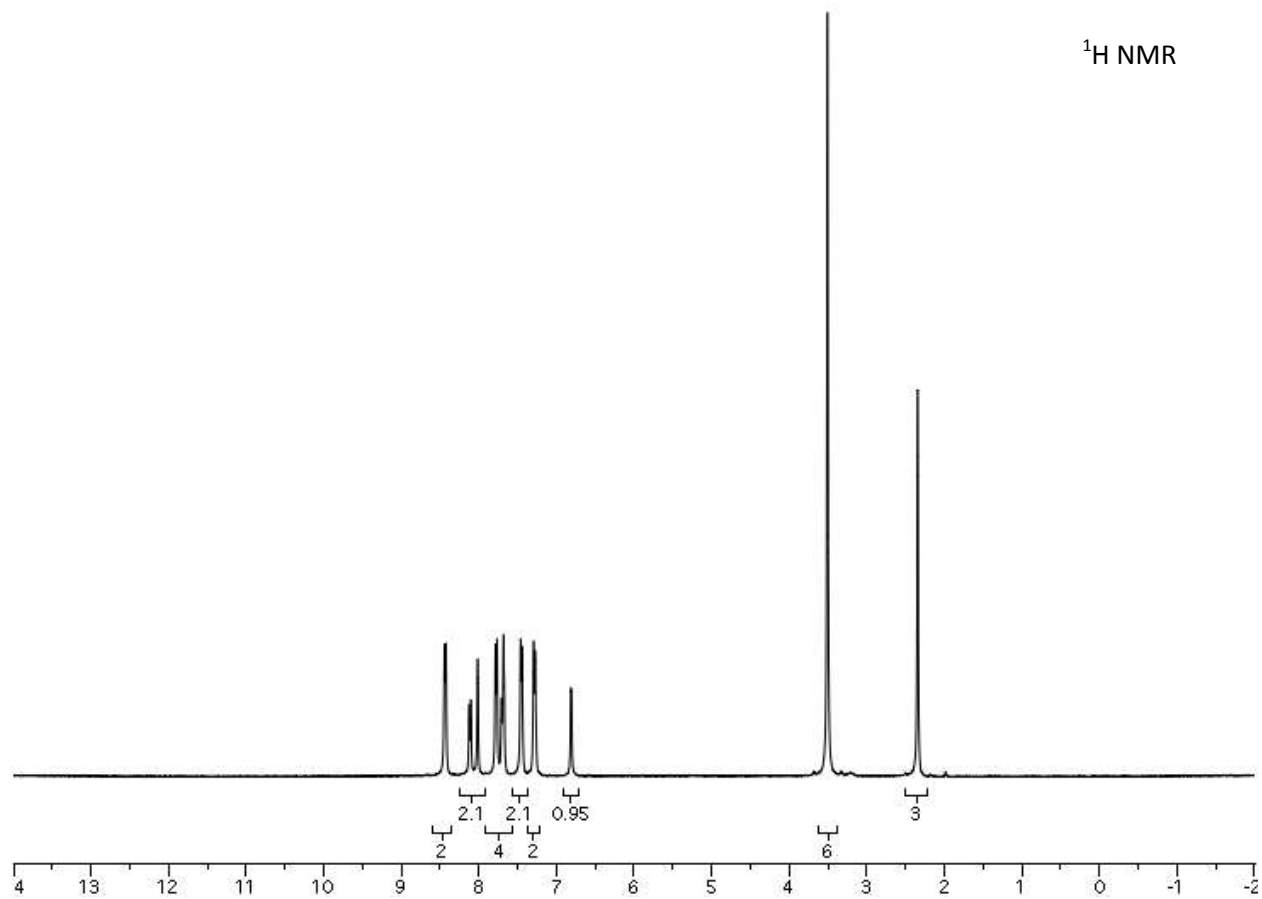
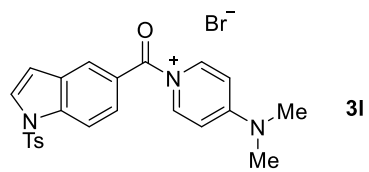


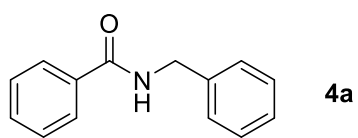




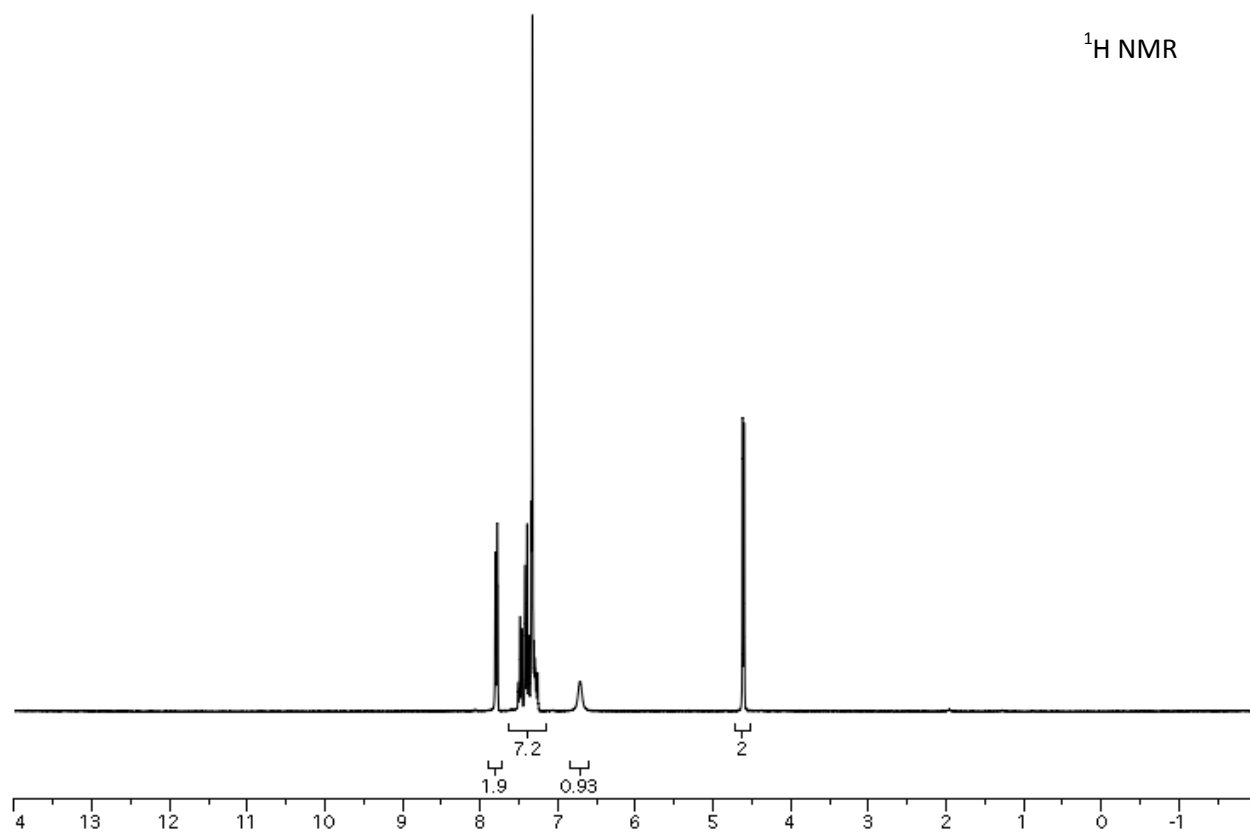




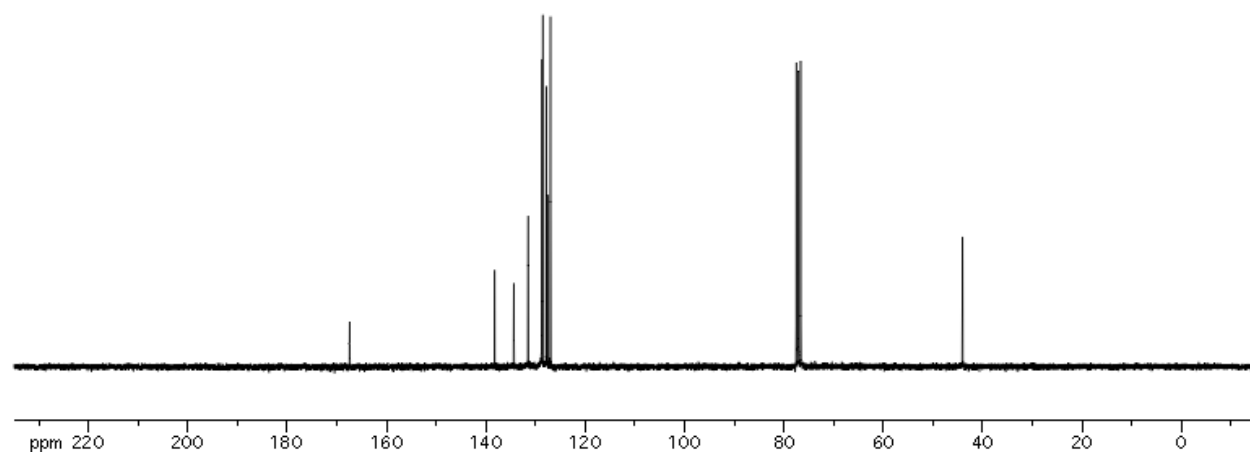


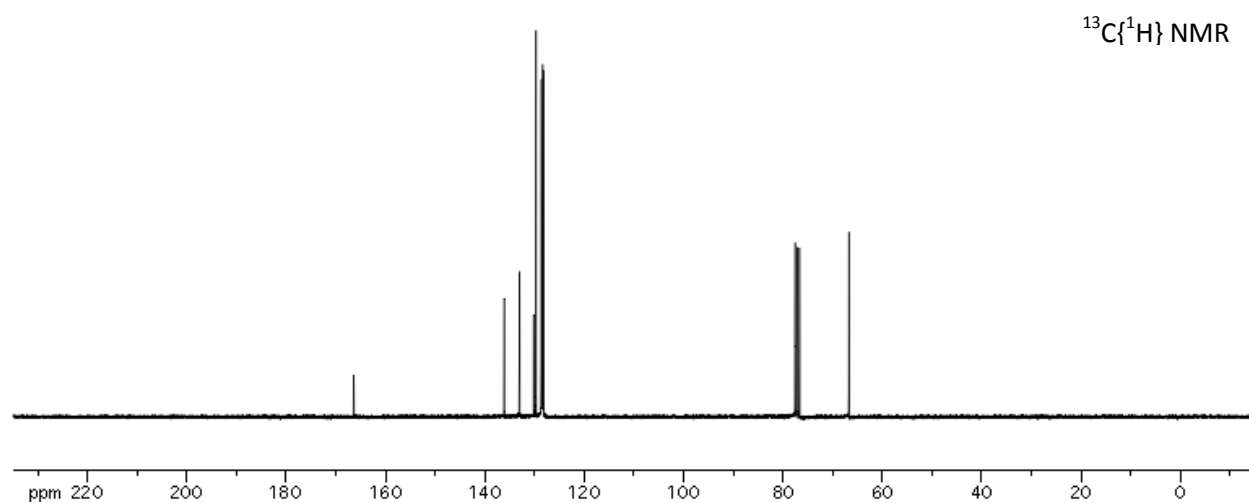
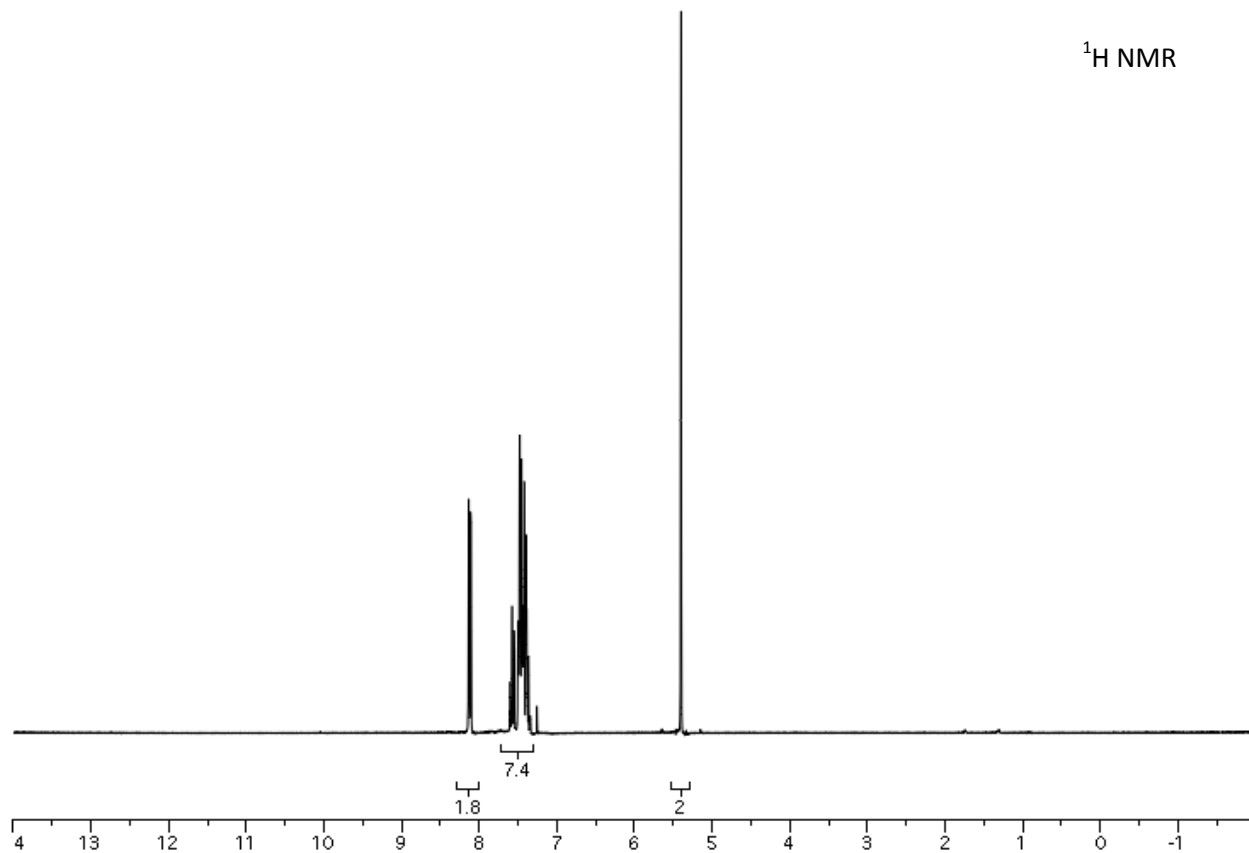
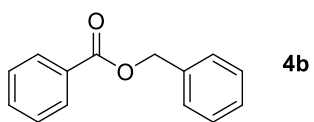


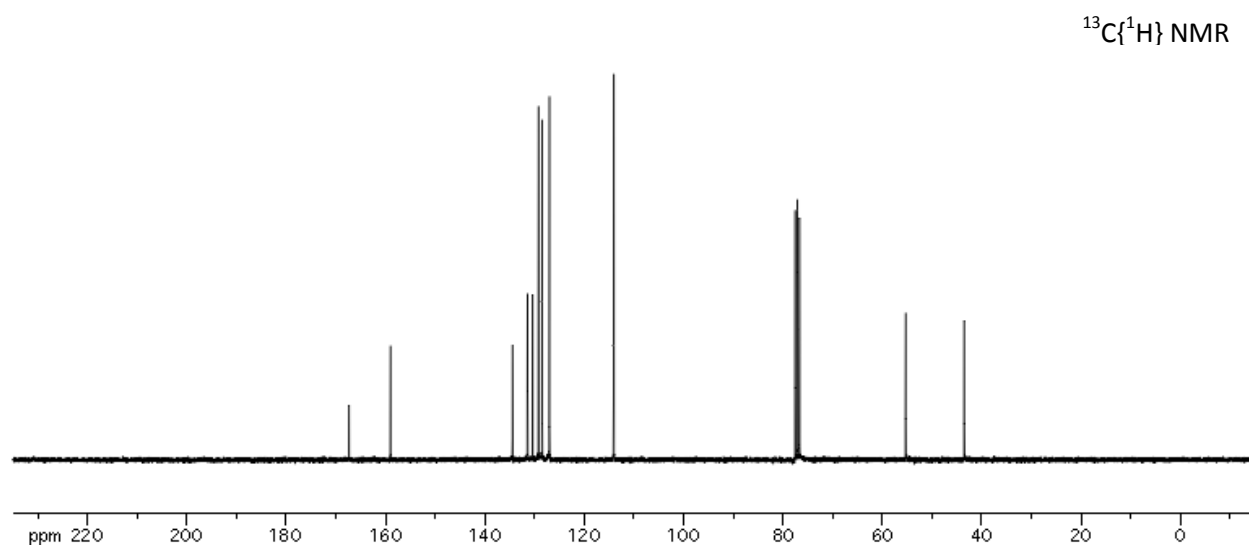
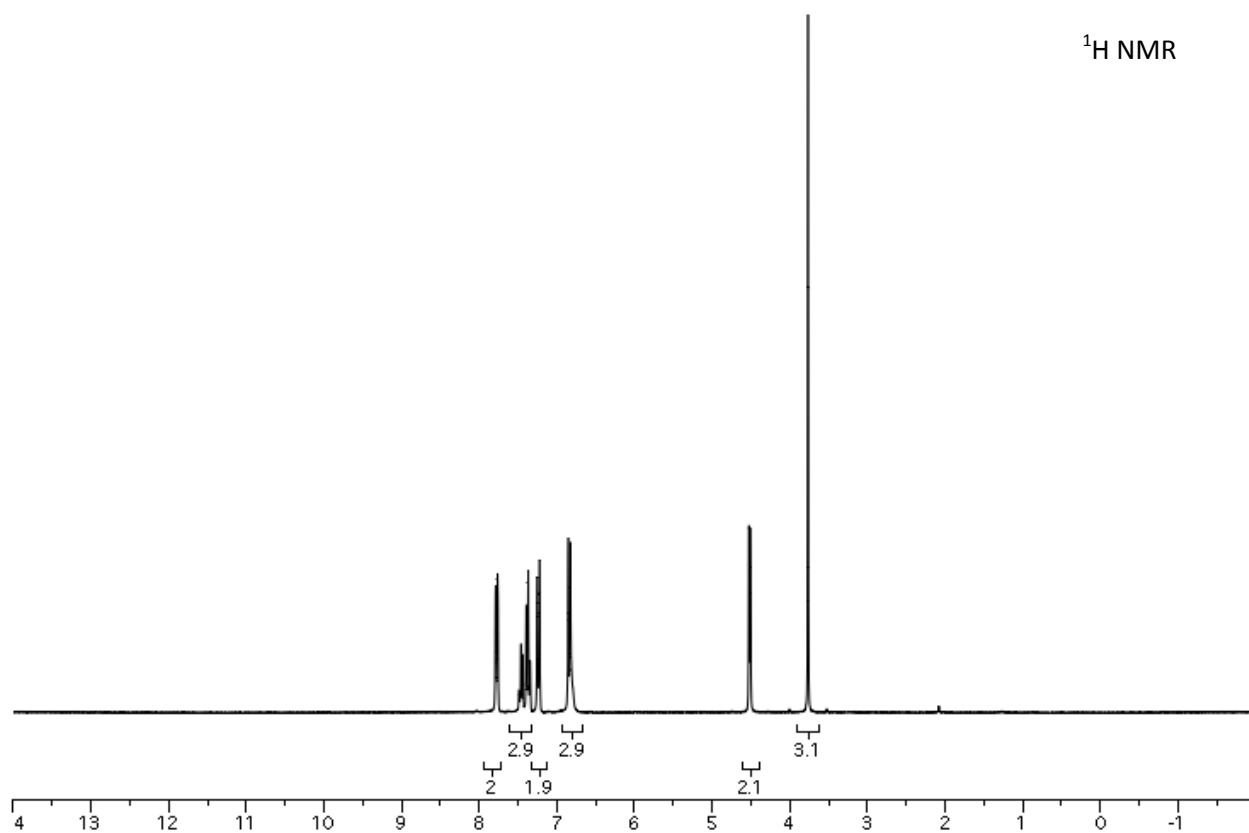
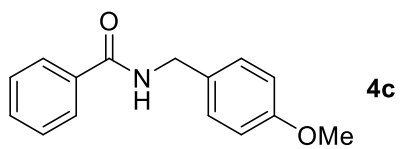
^1H NMR

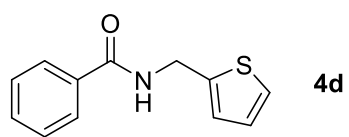


$^{13}\text{C}\{^1\text{H}\}$ NMR

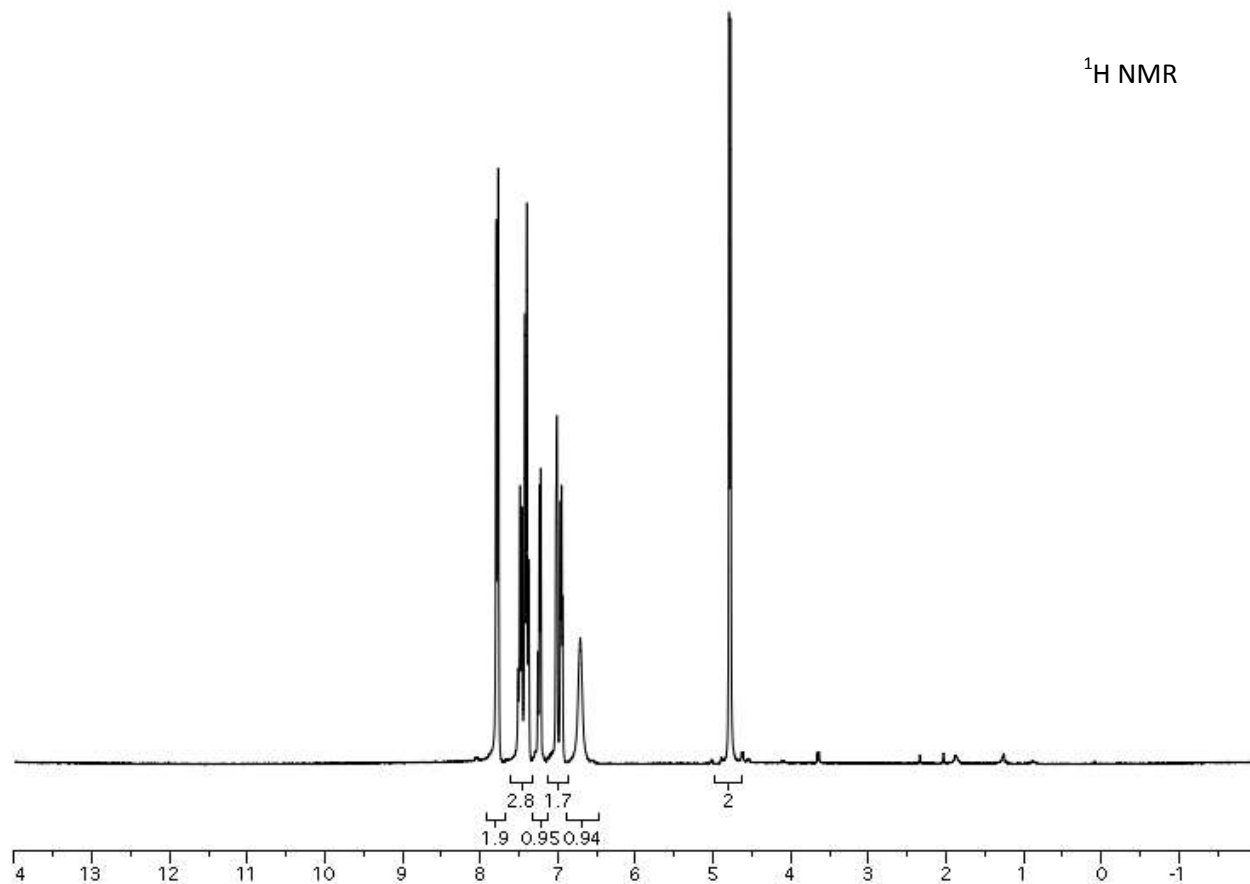




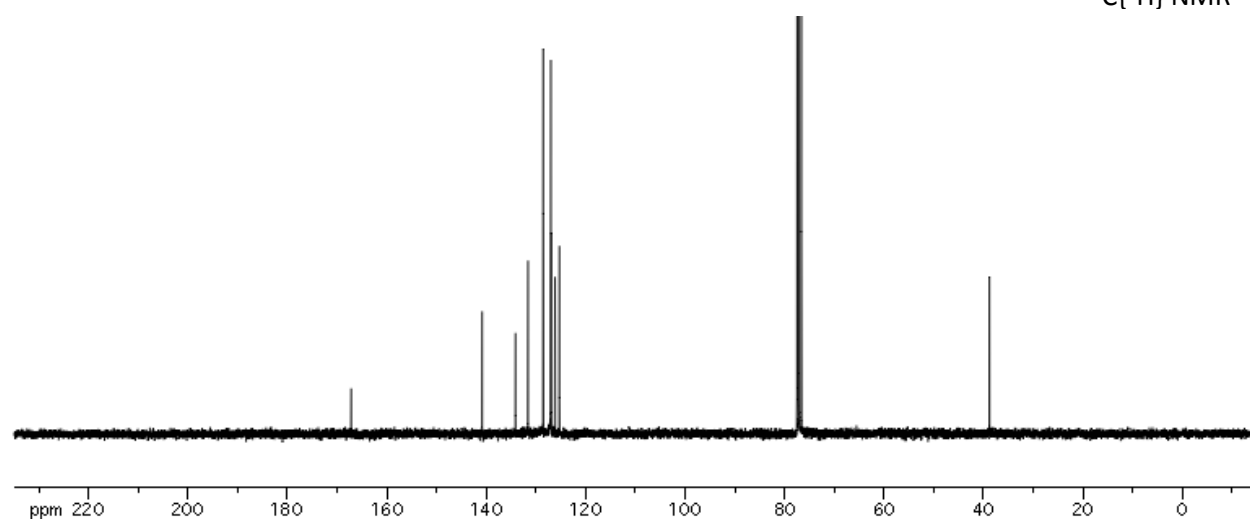


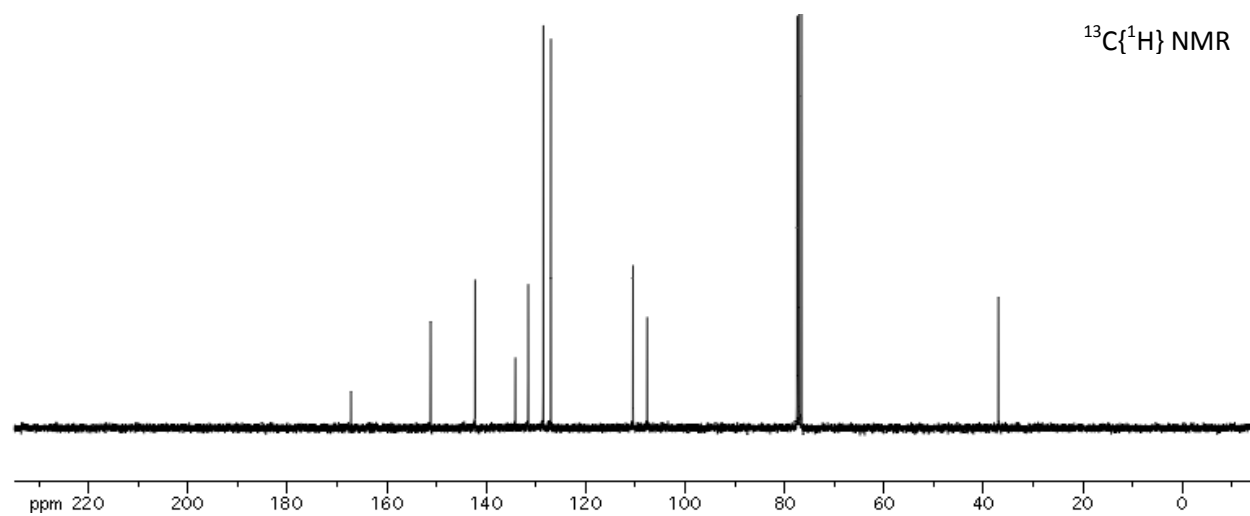
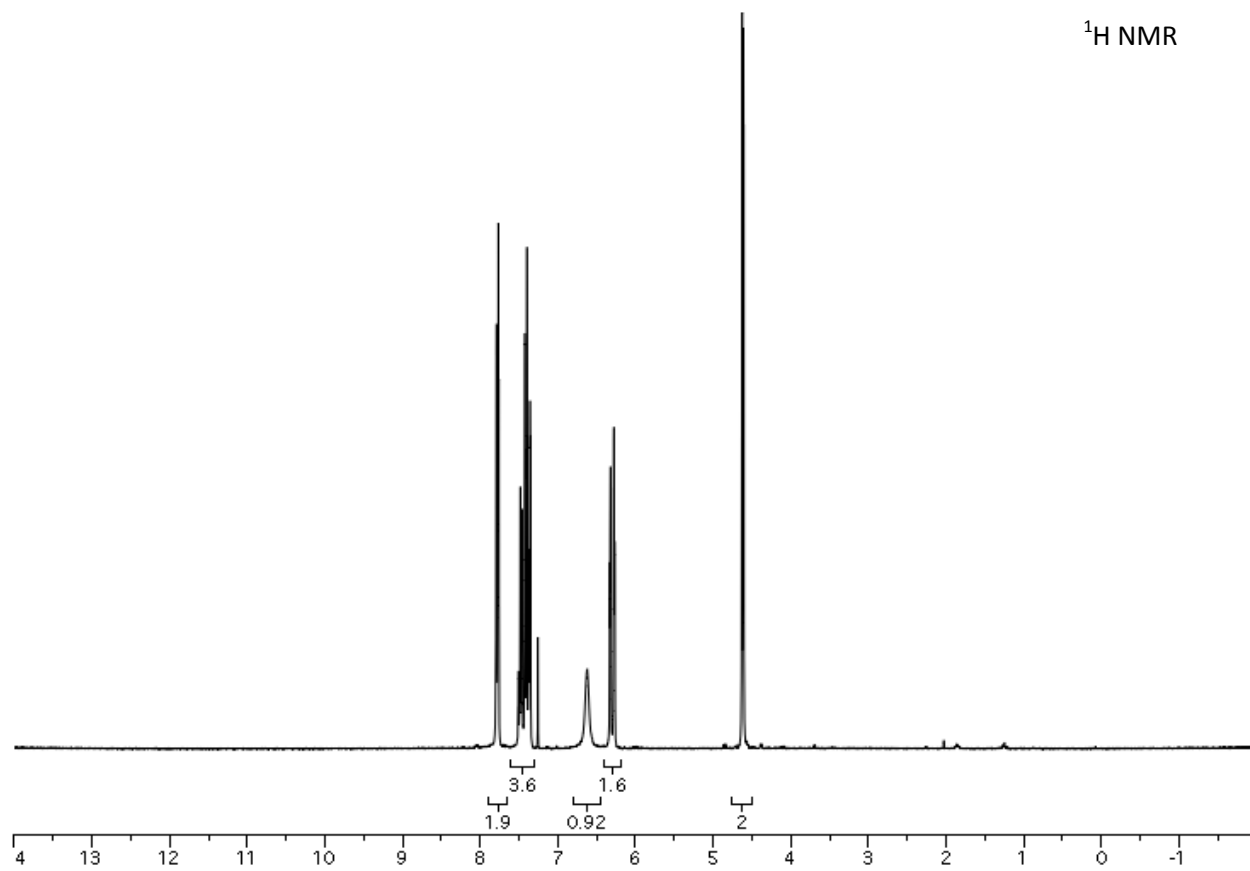
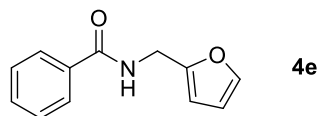


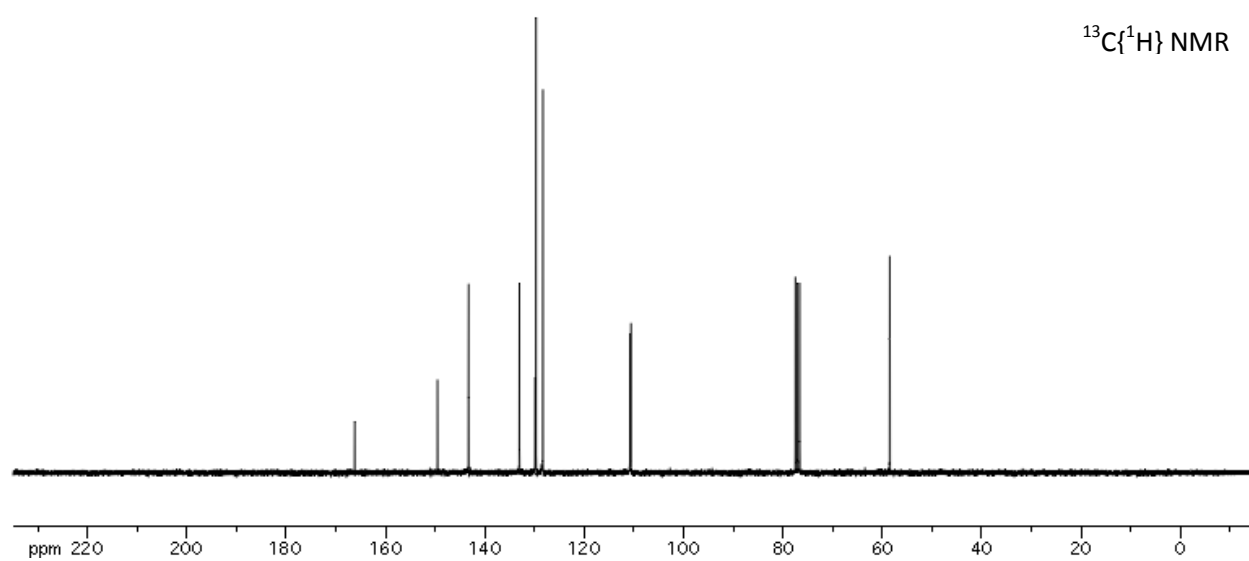
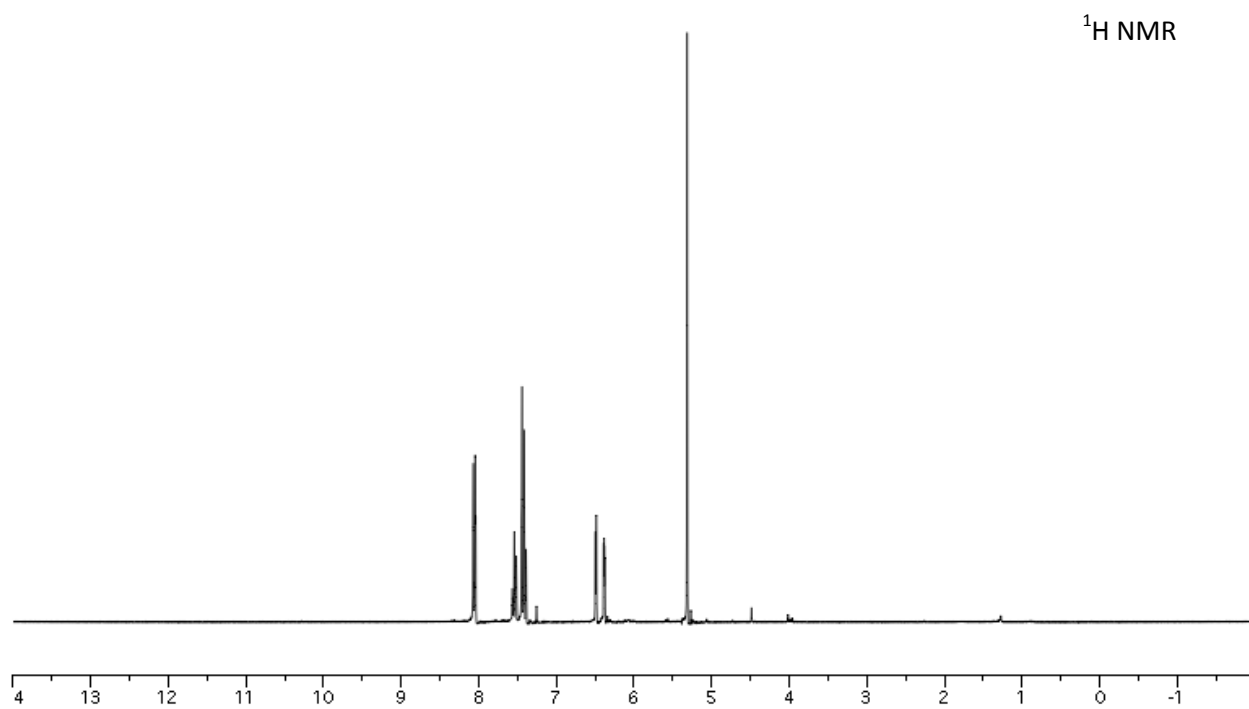
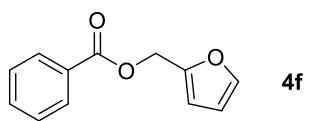
^1H NMR

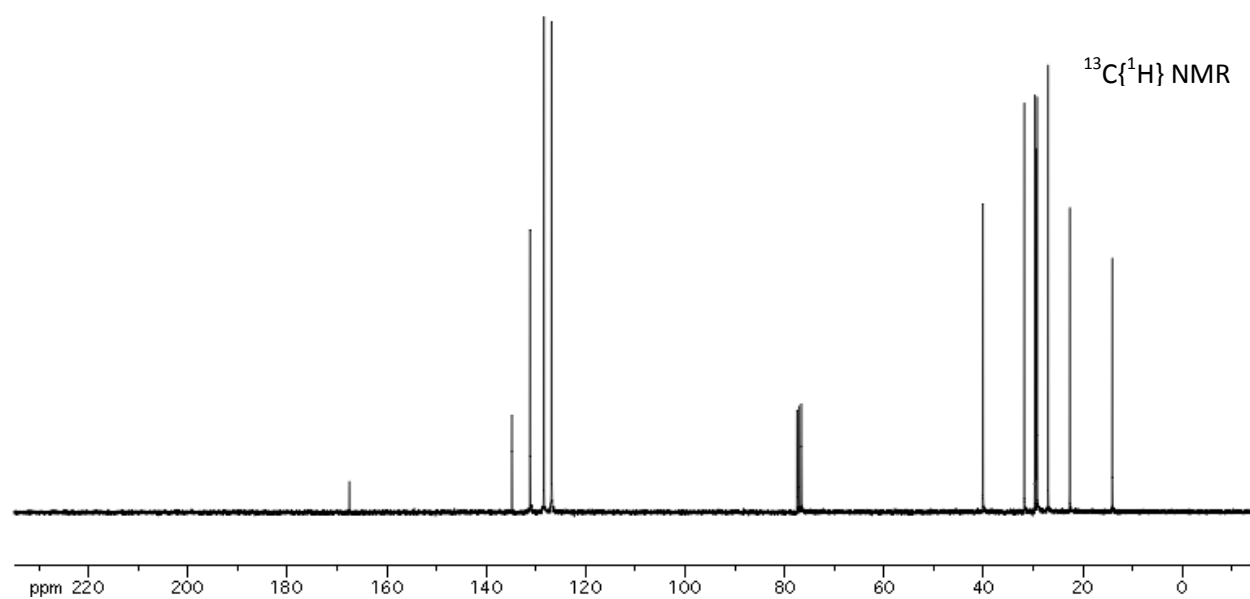
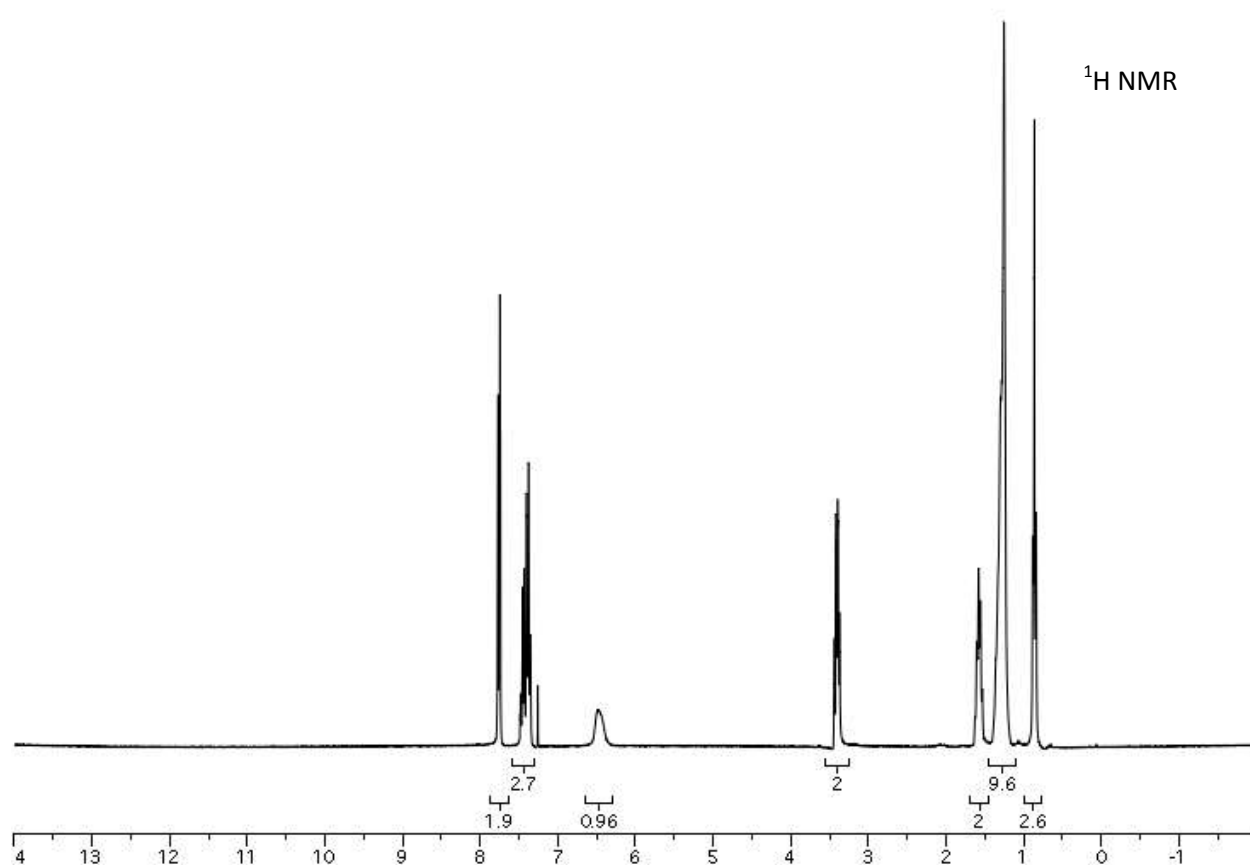
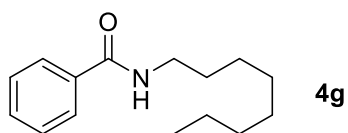


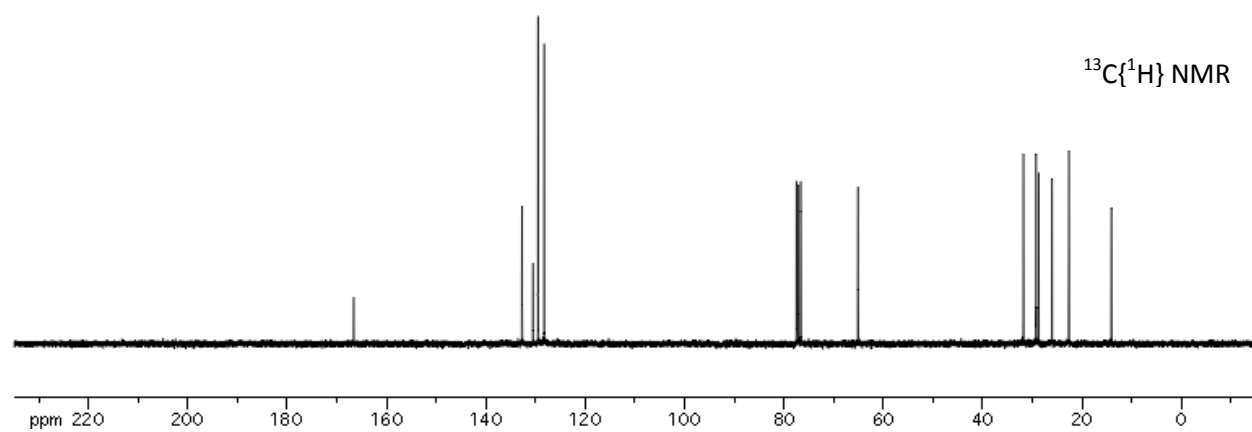
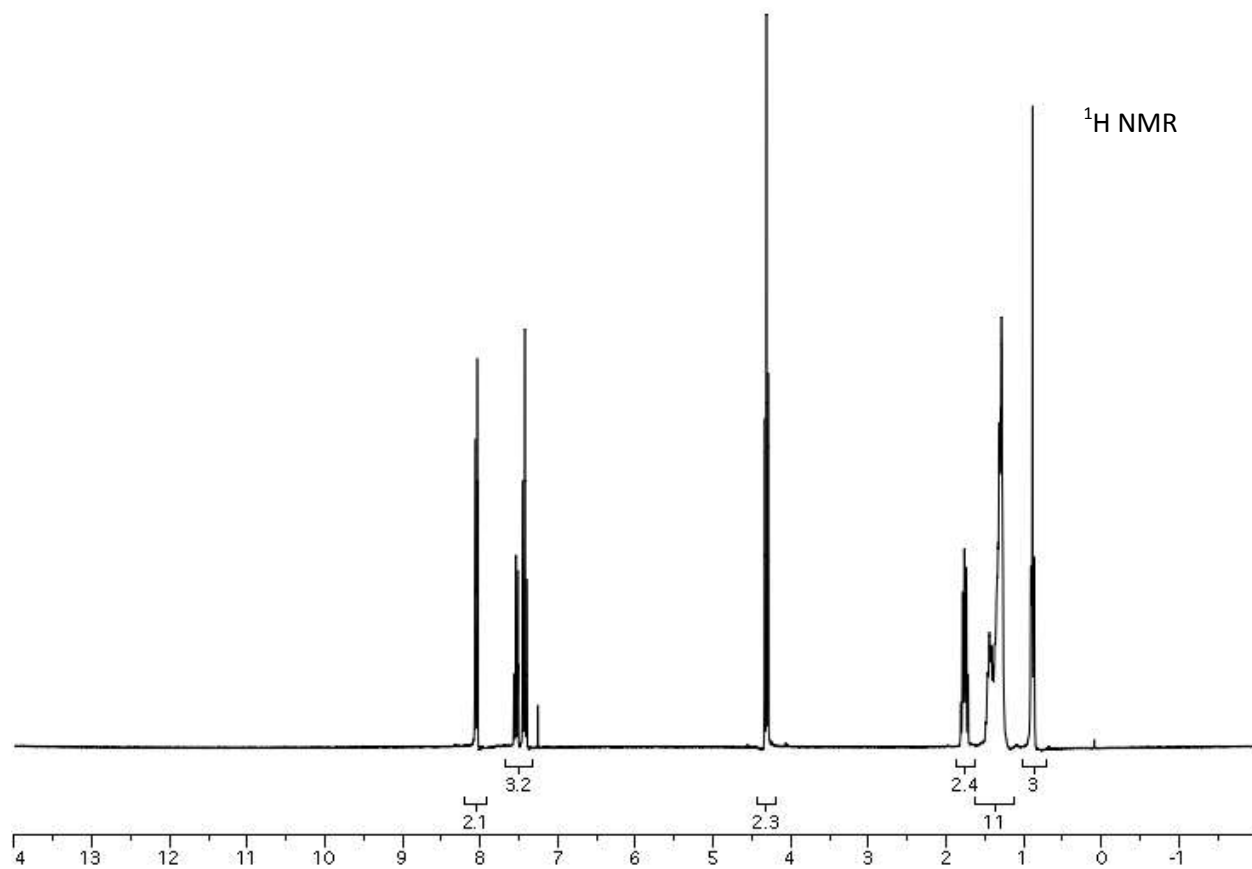
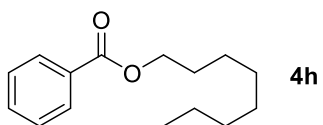
$^{13}\text{C}\{^1\text{H}\}$ NMR

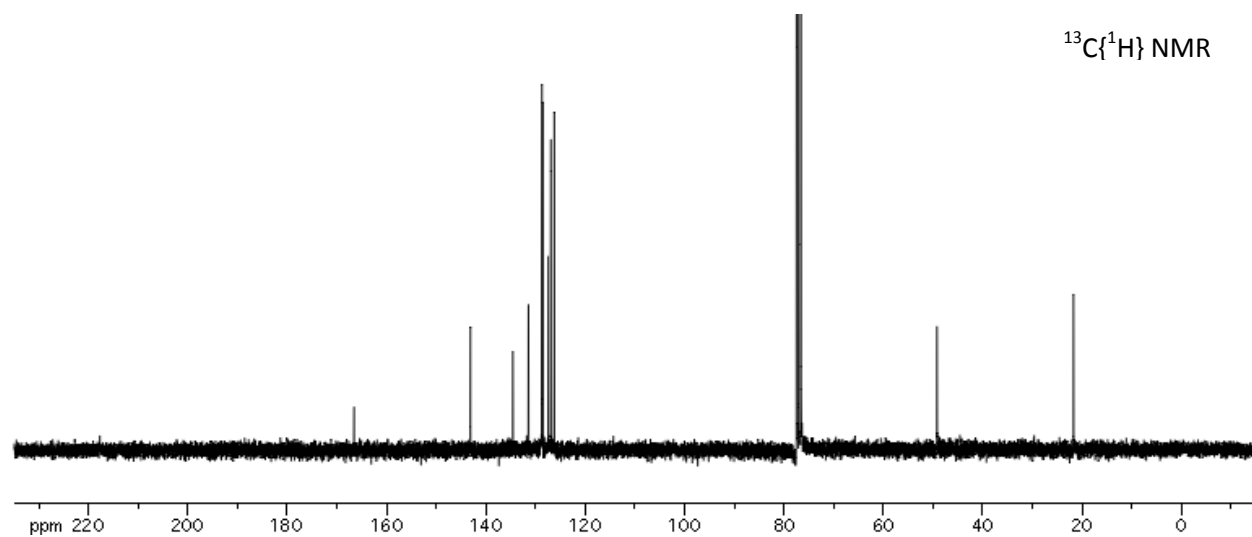
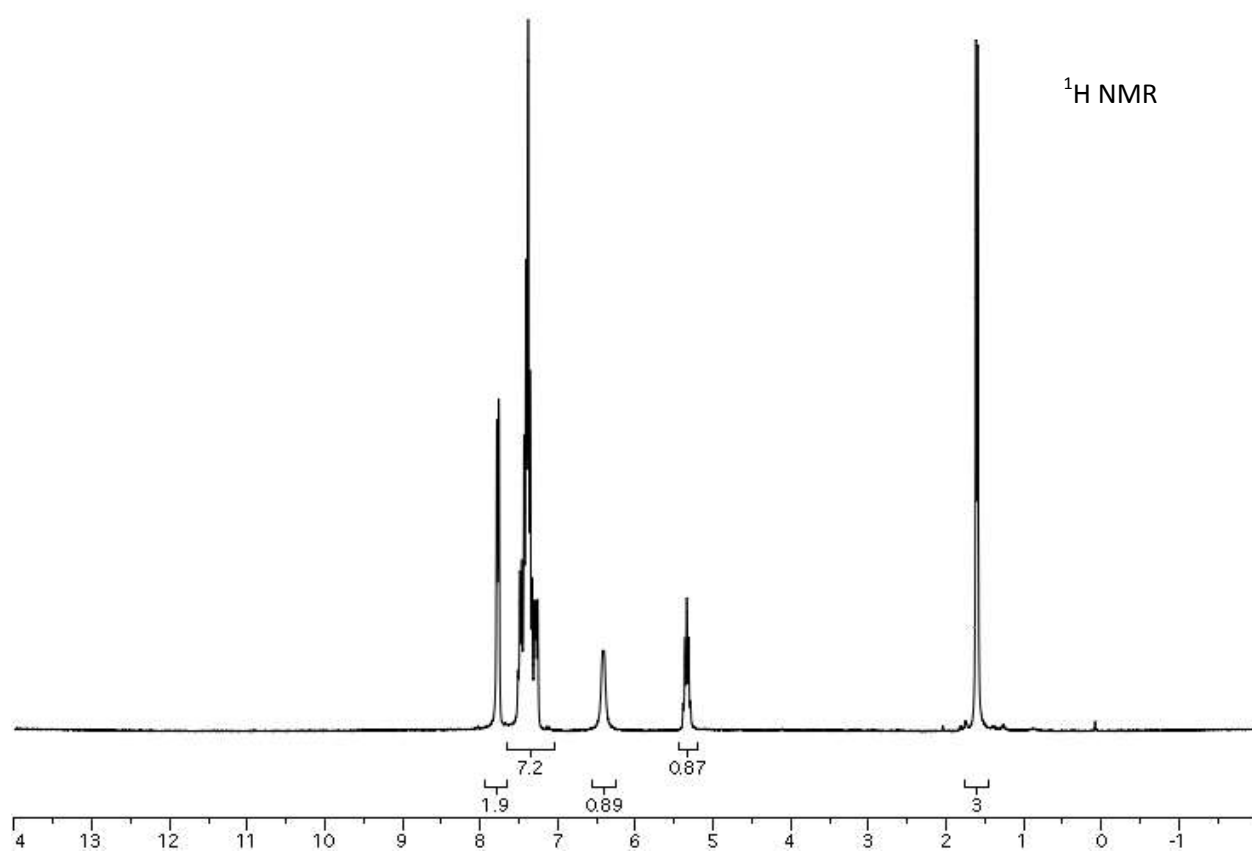
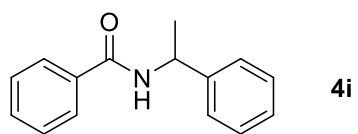


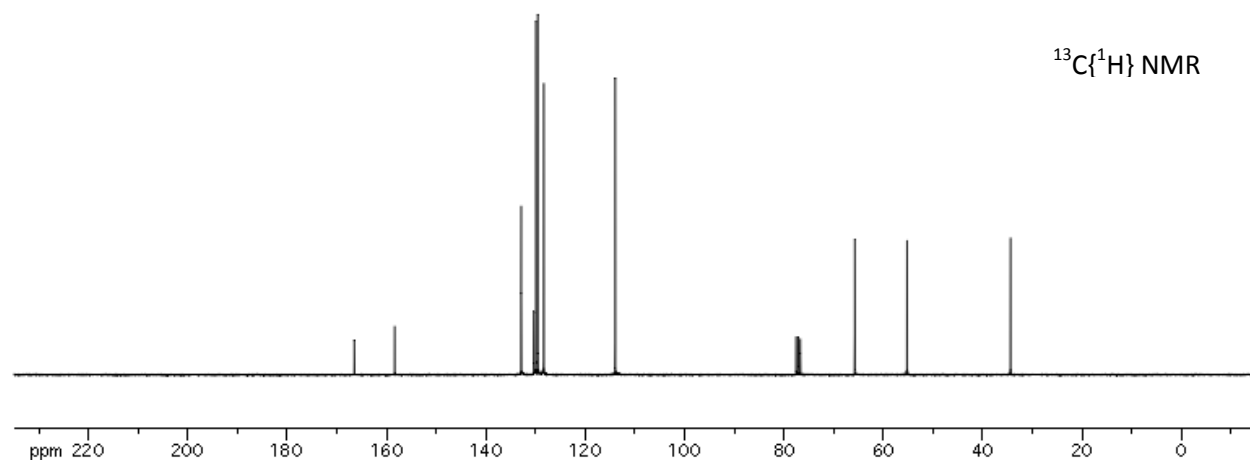
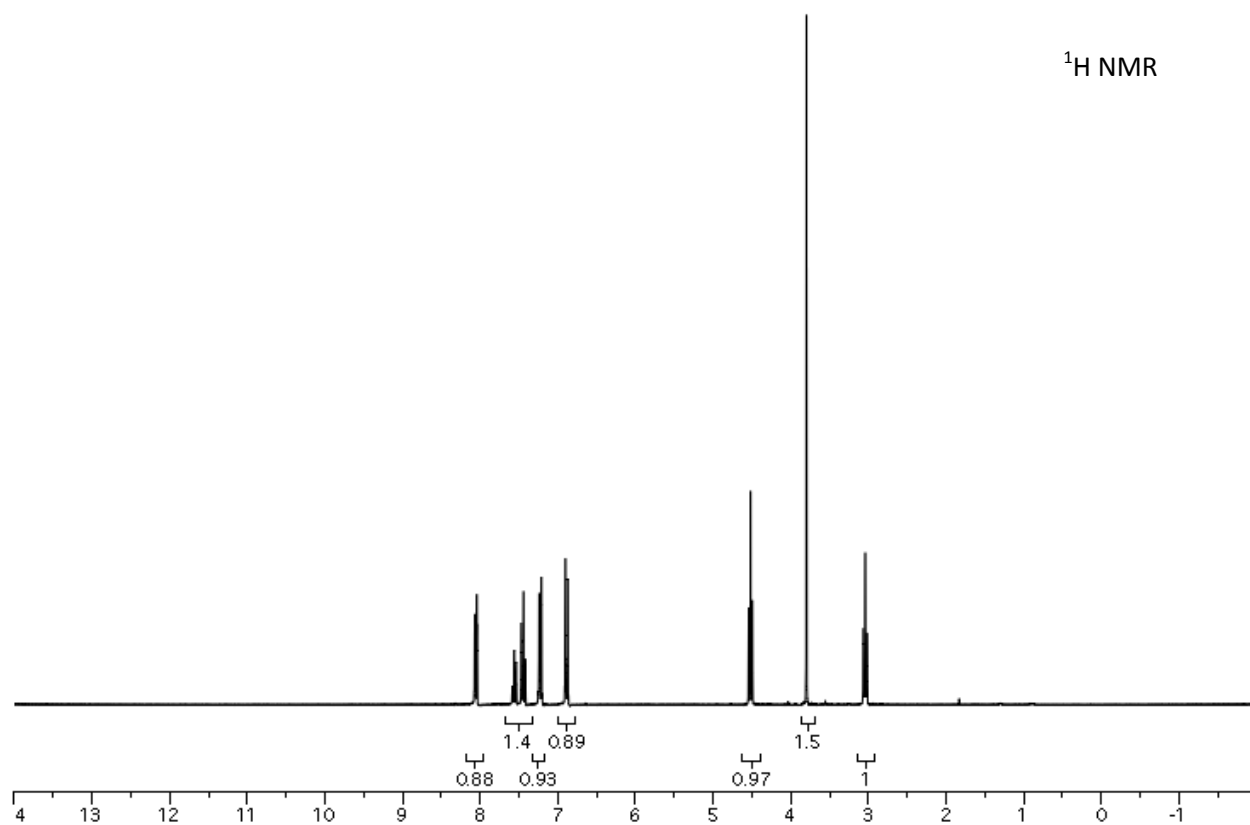
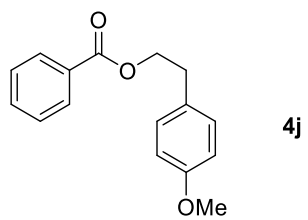


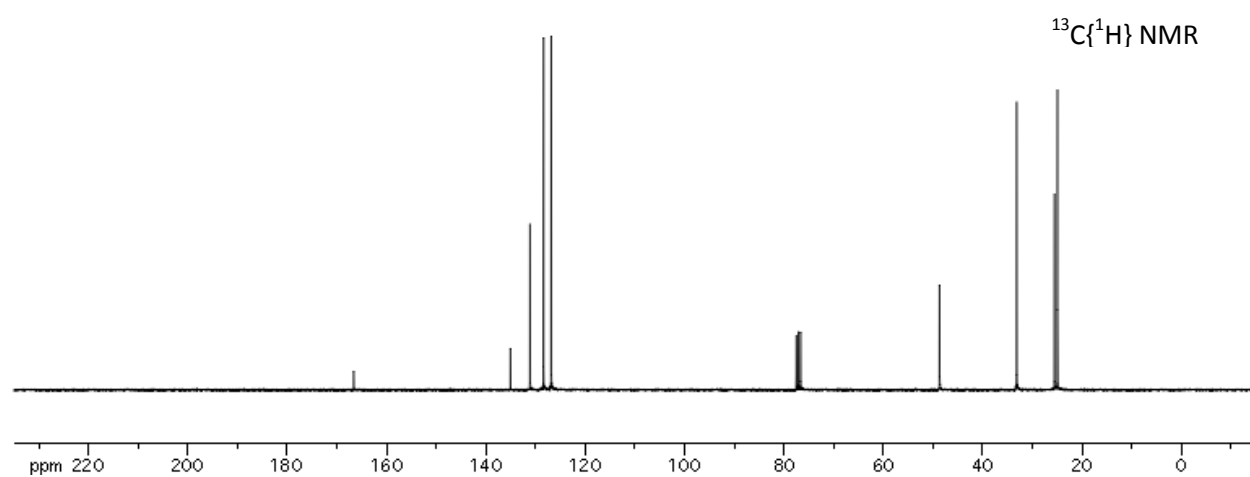
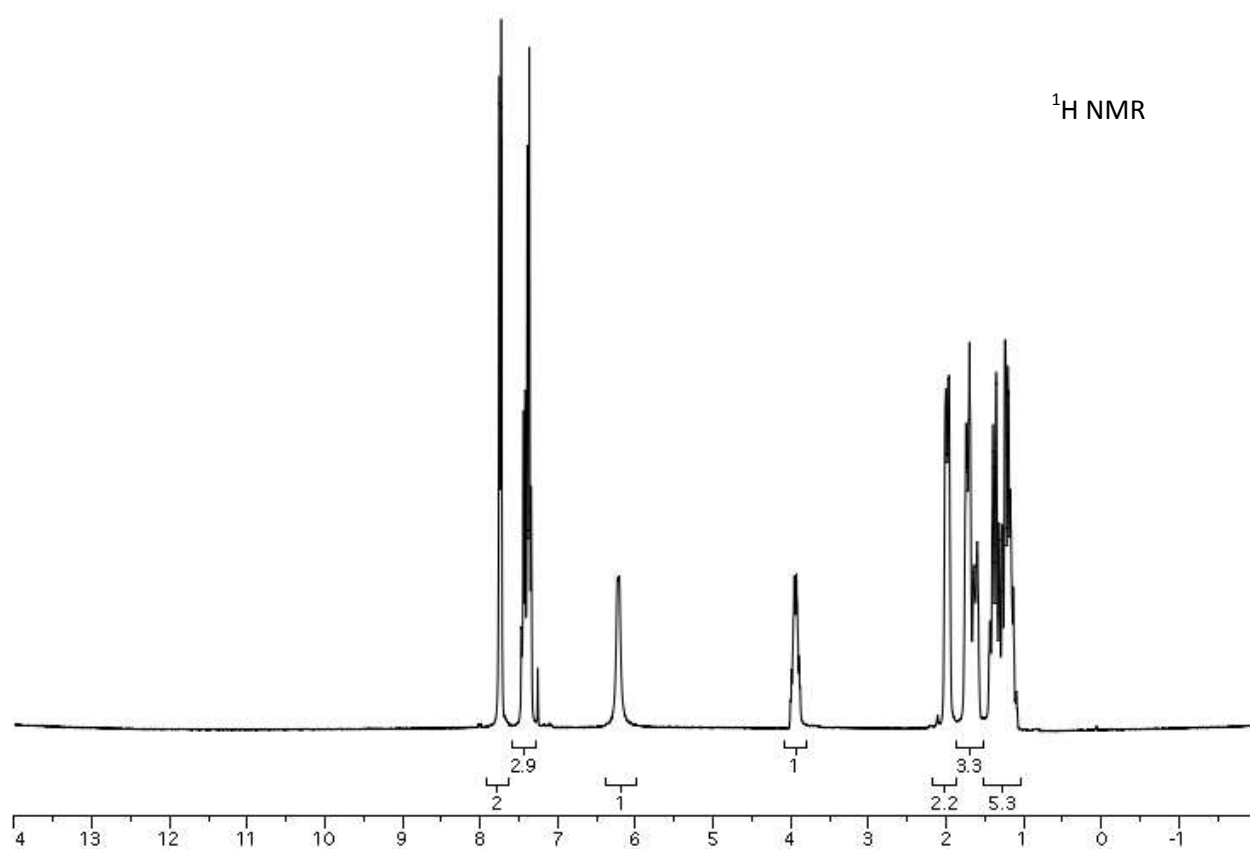
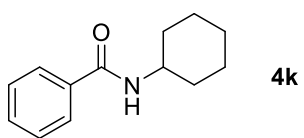


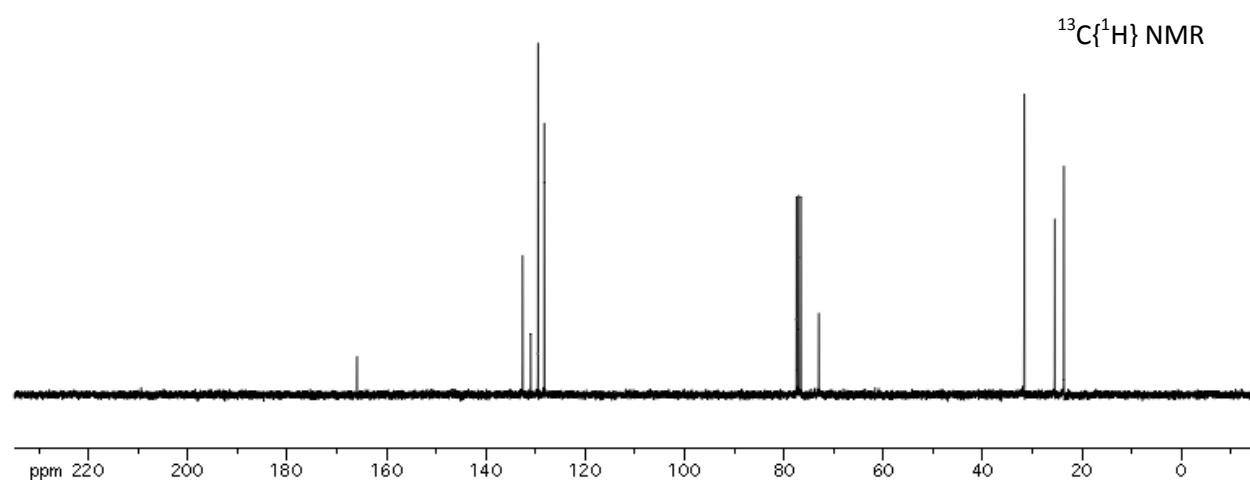
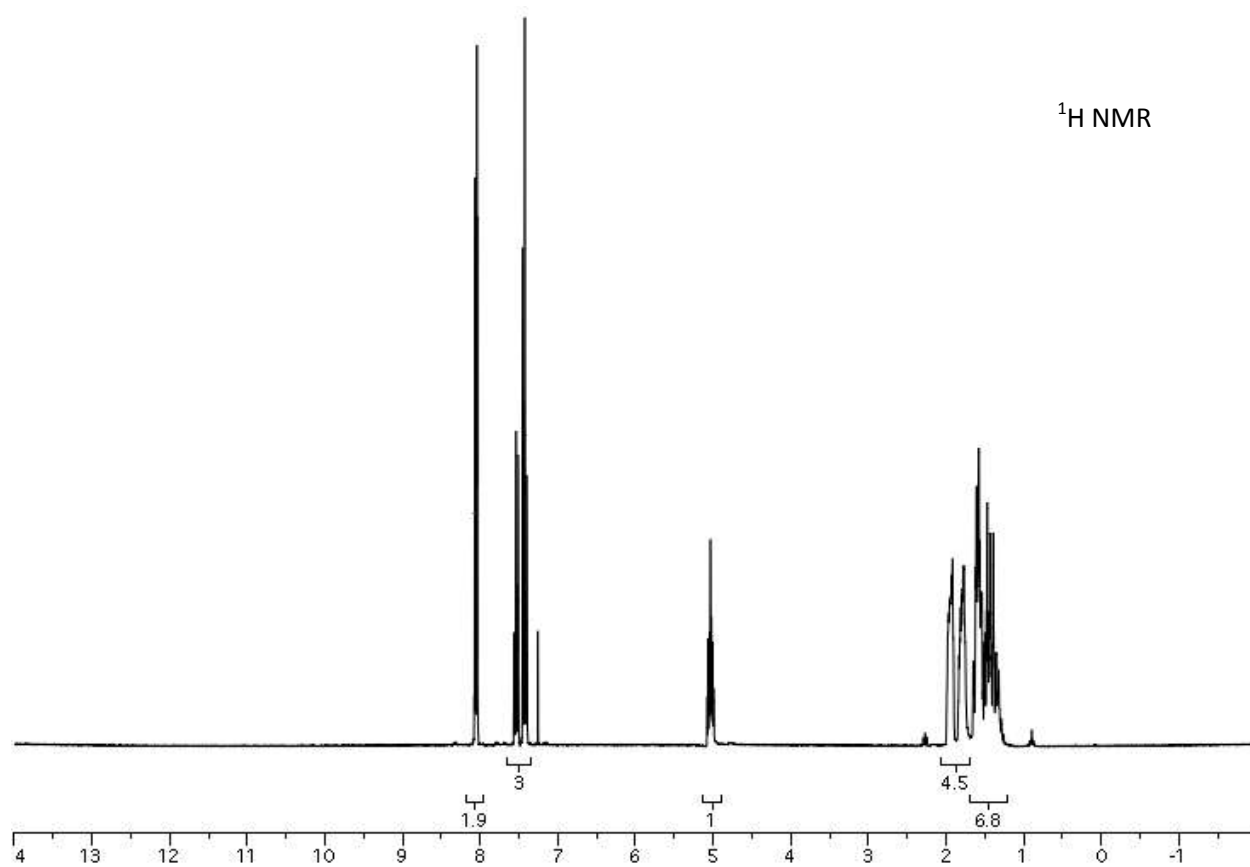
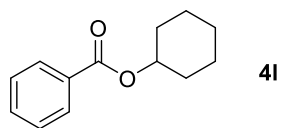


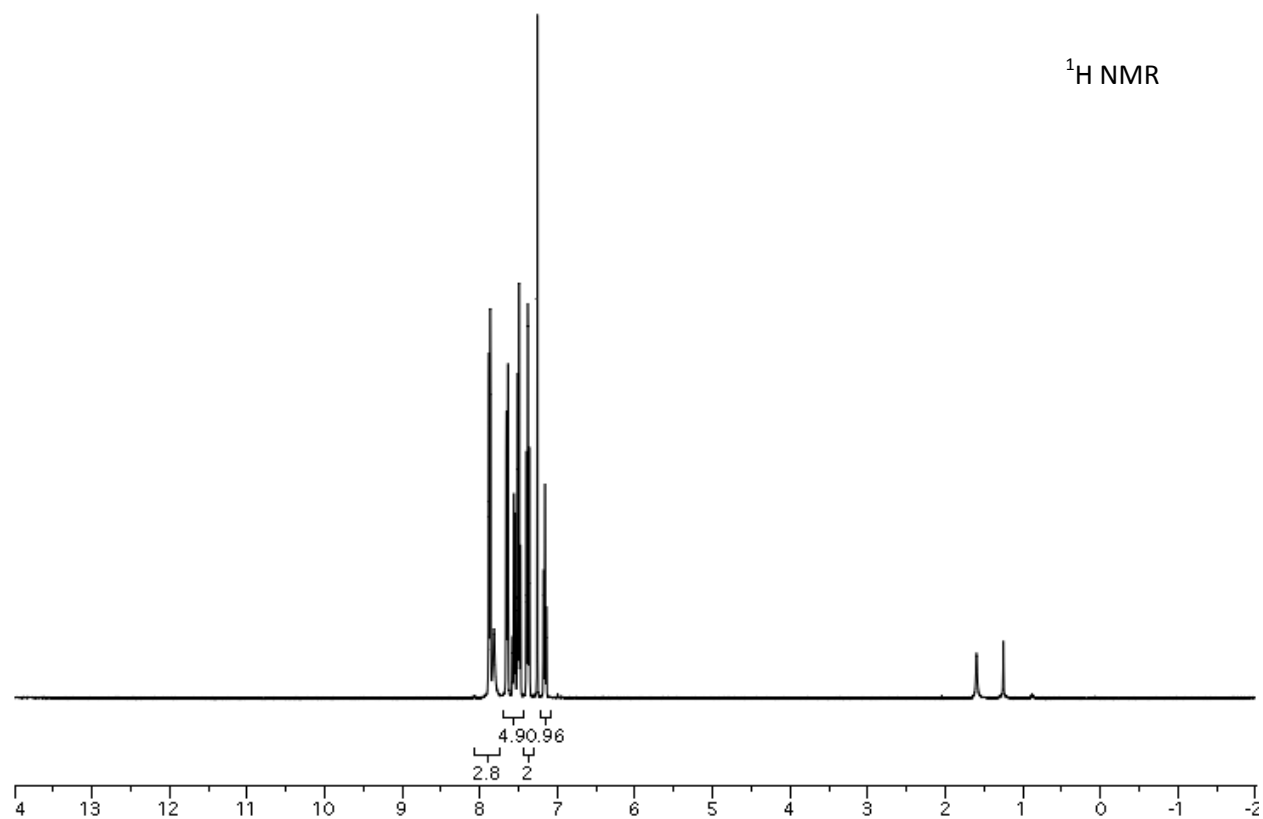
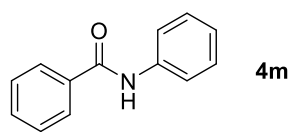


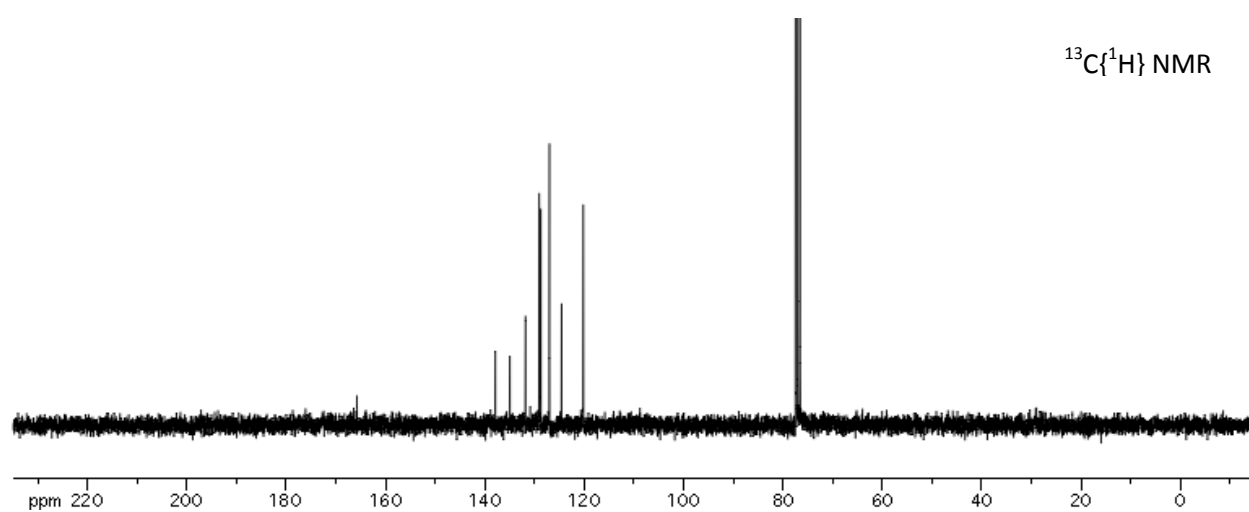
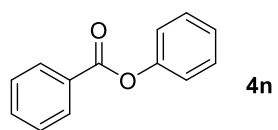


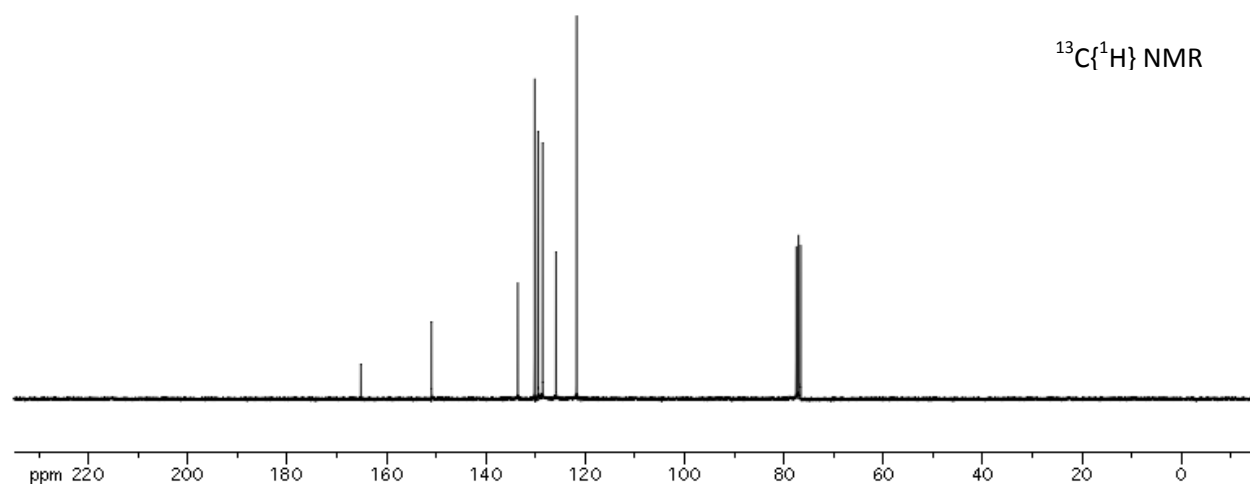
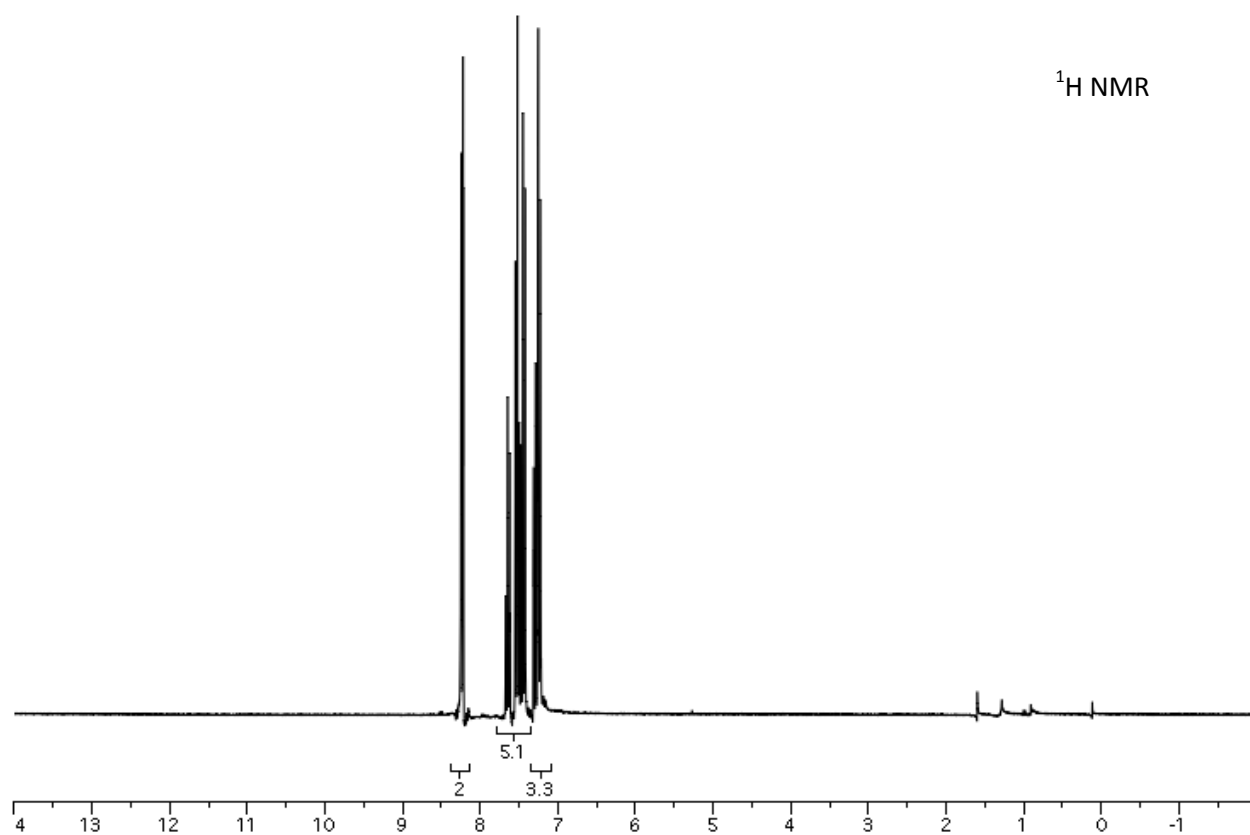


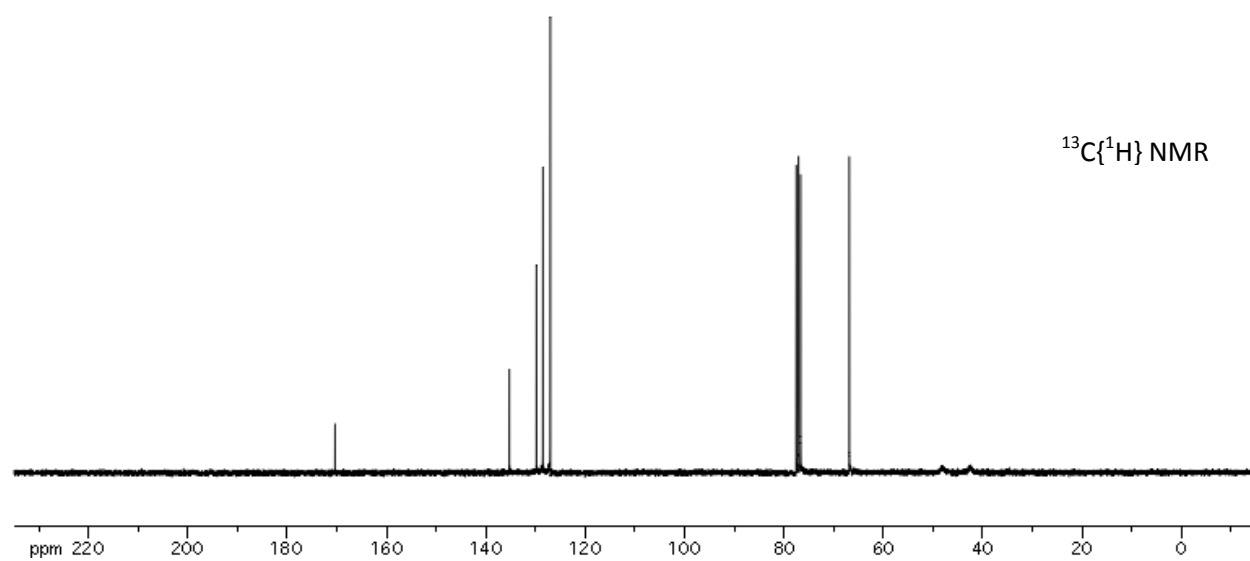
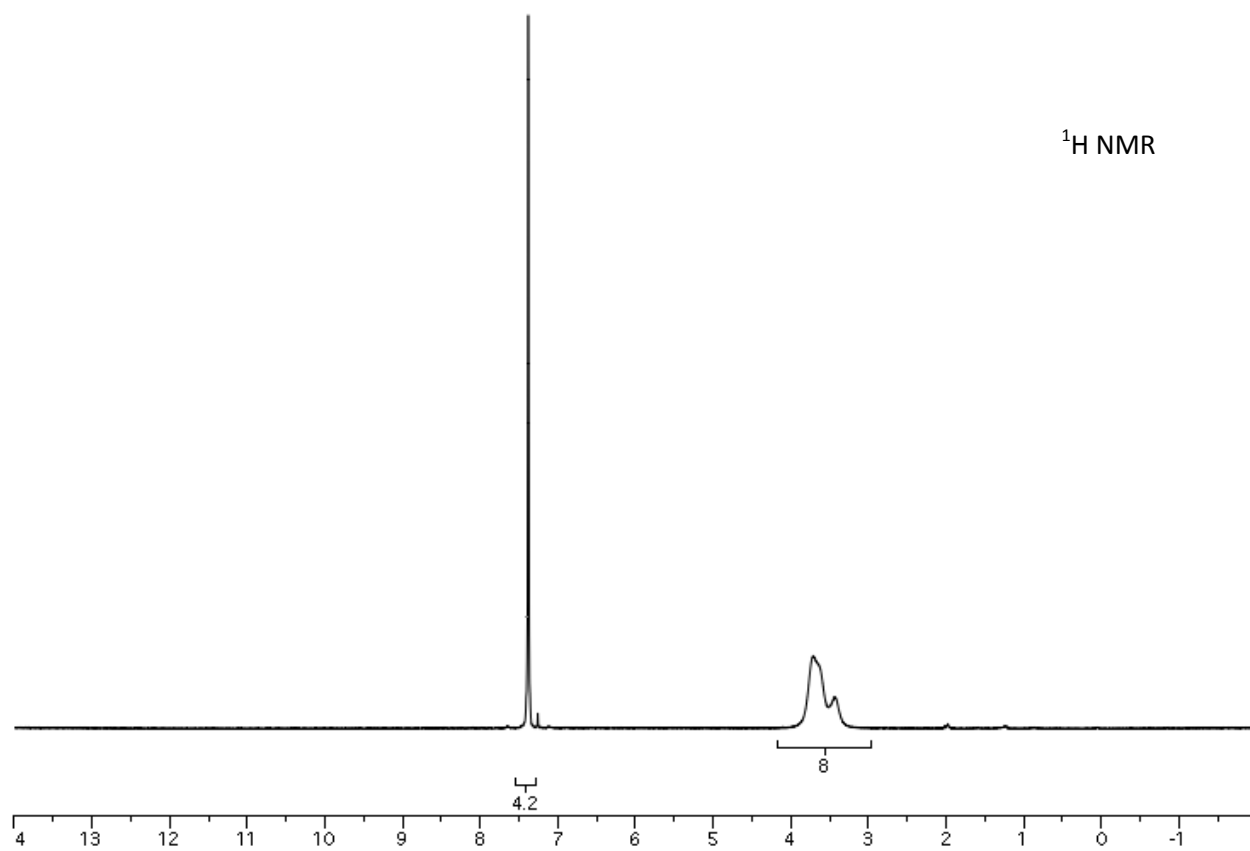
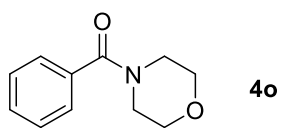


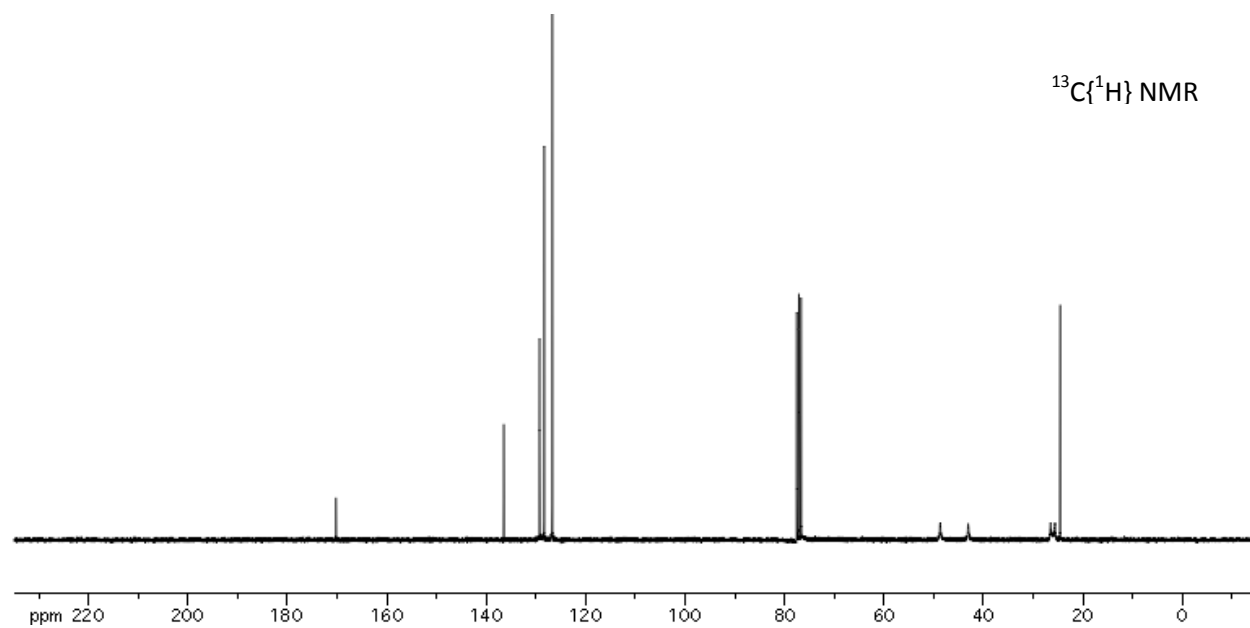
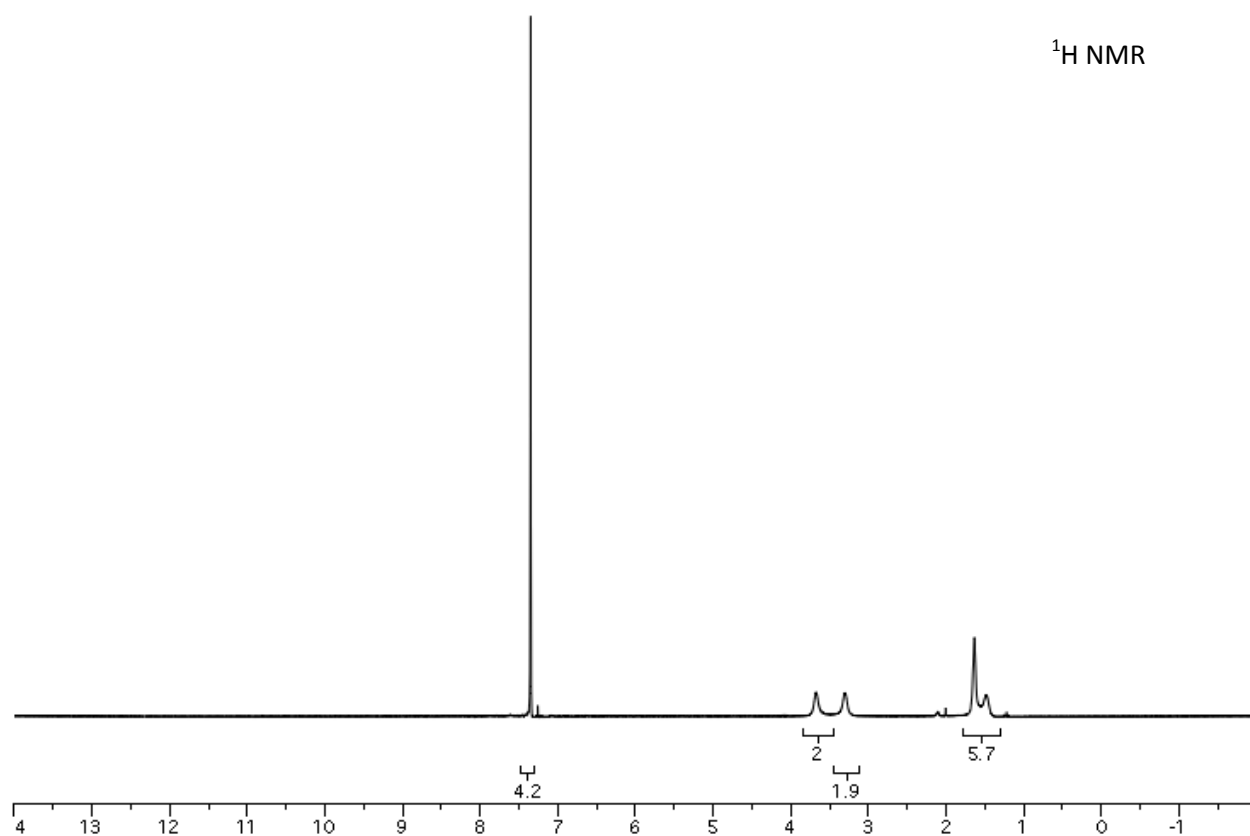
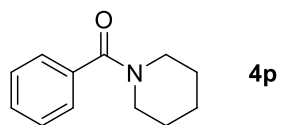


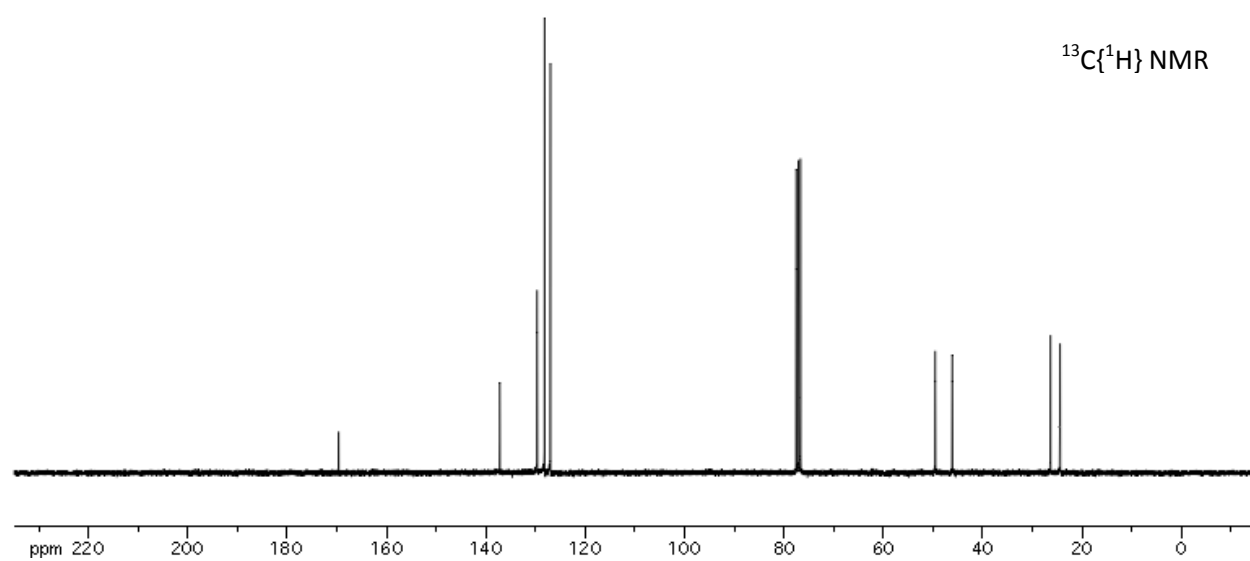
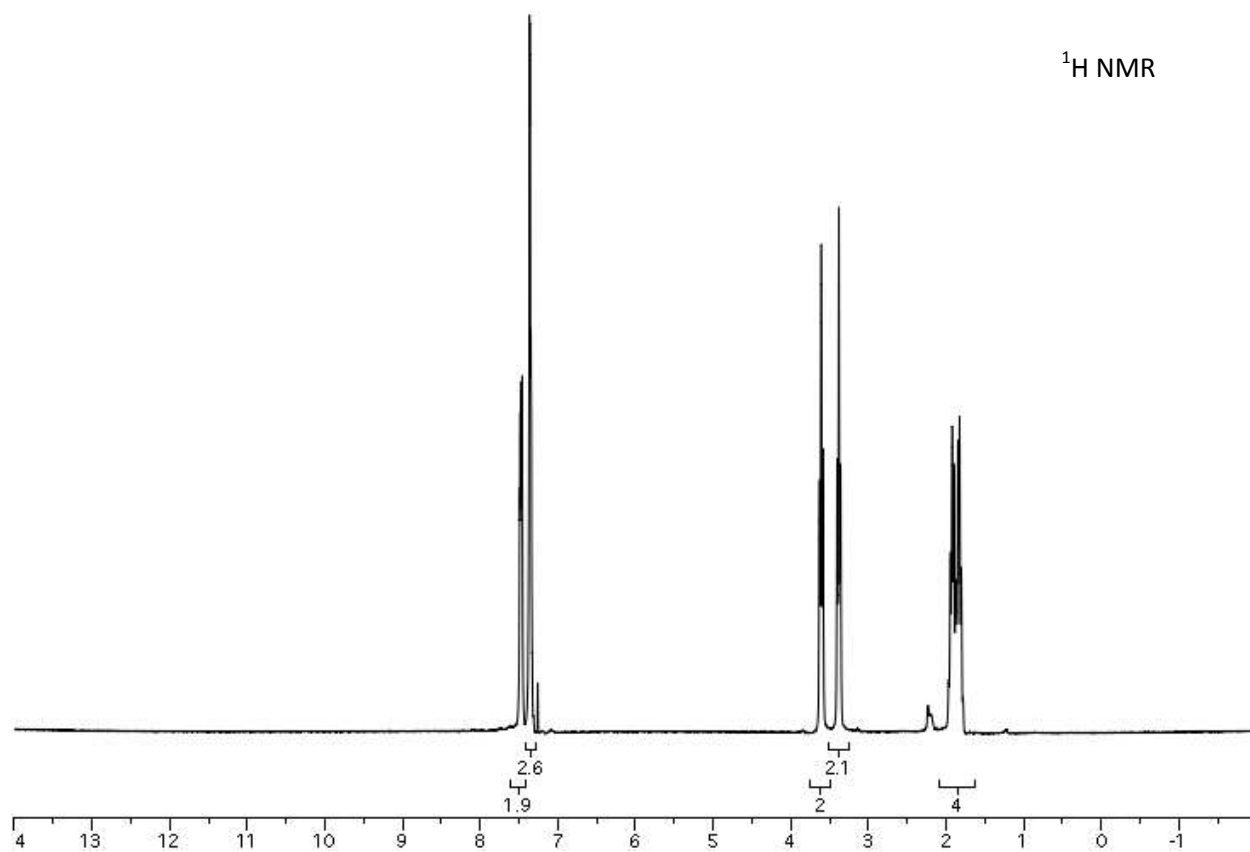
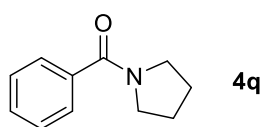


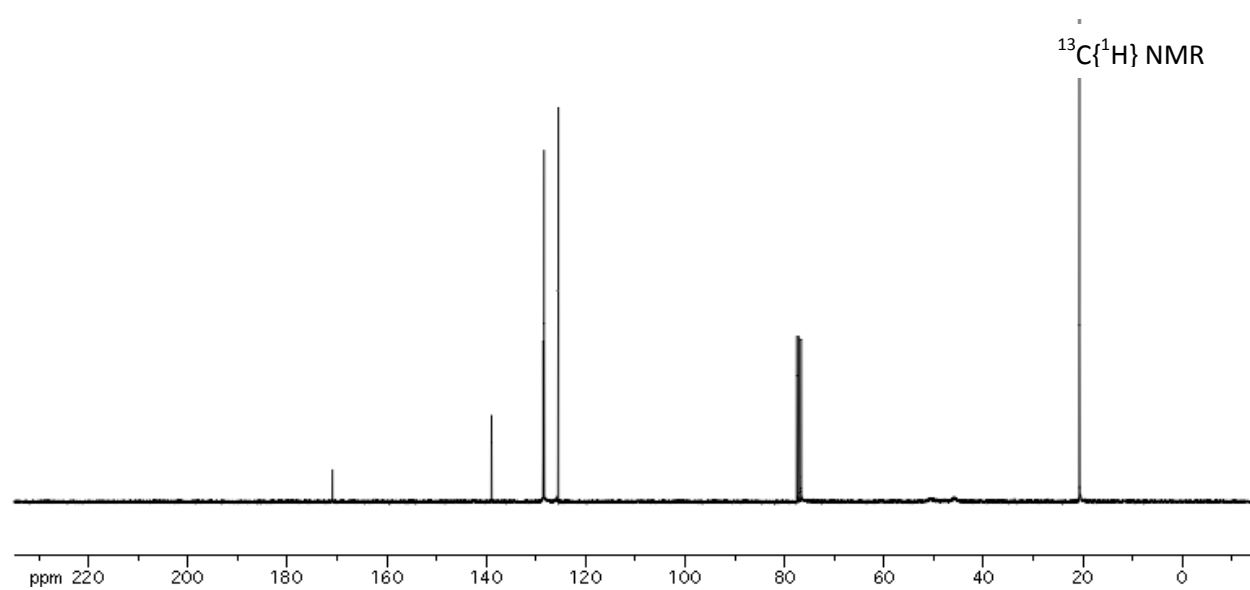
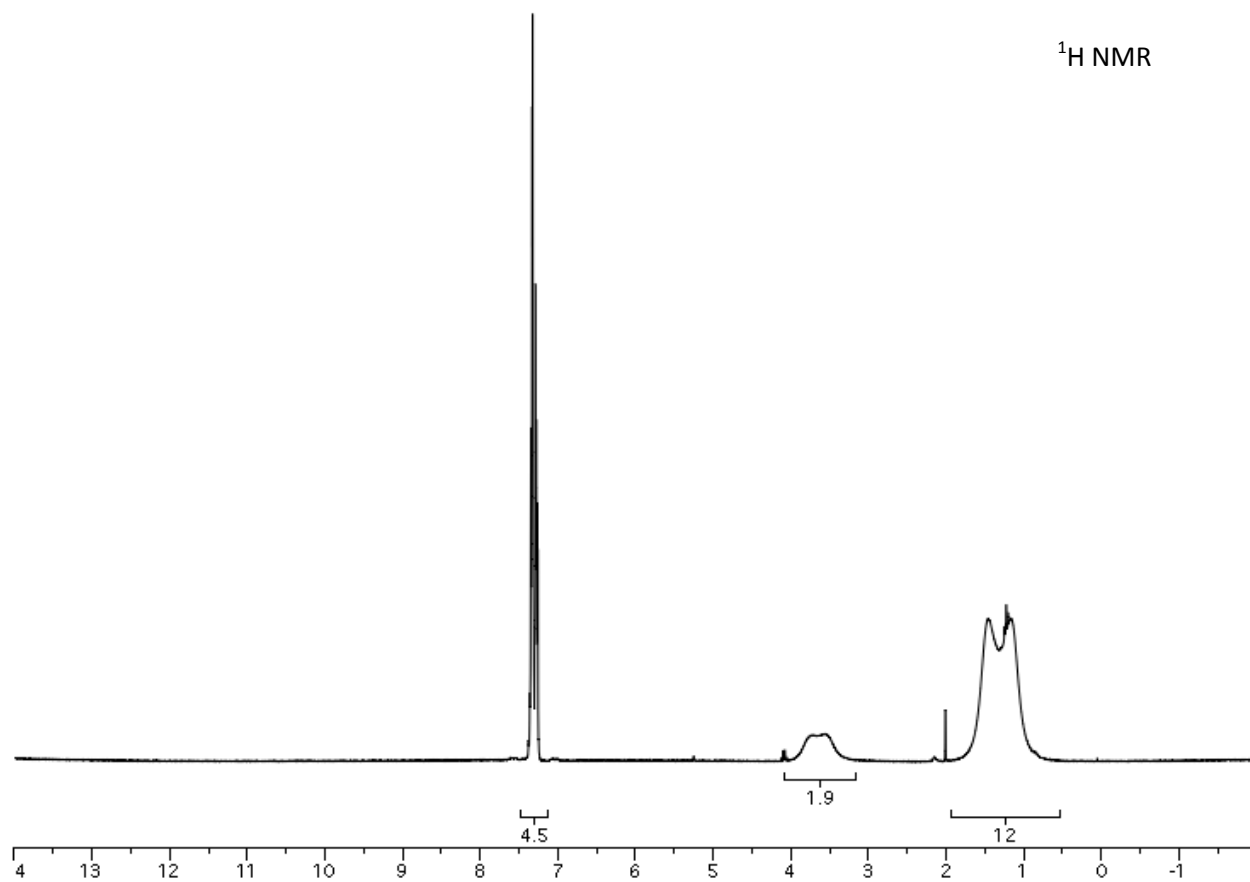
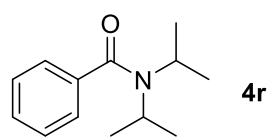


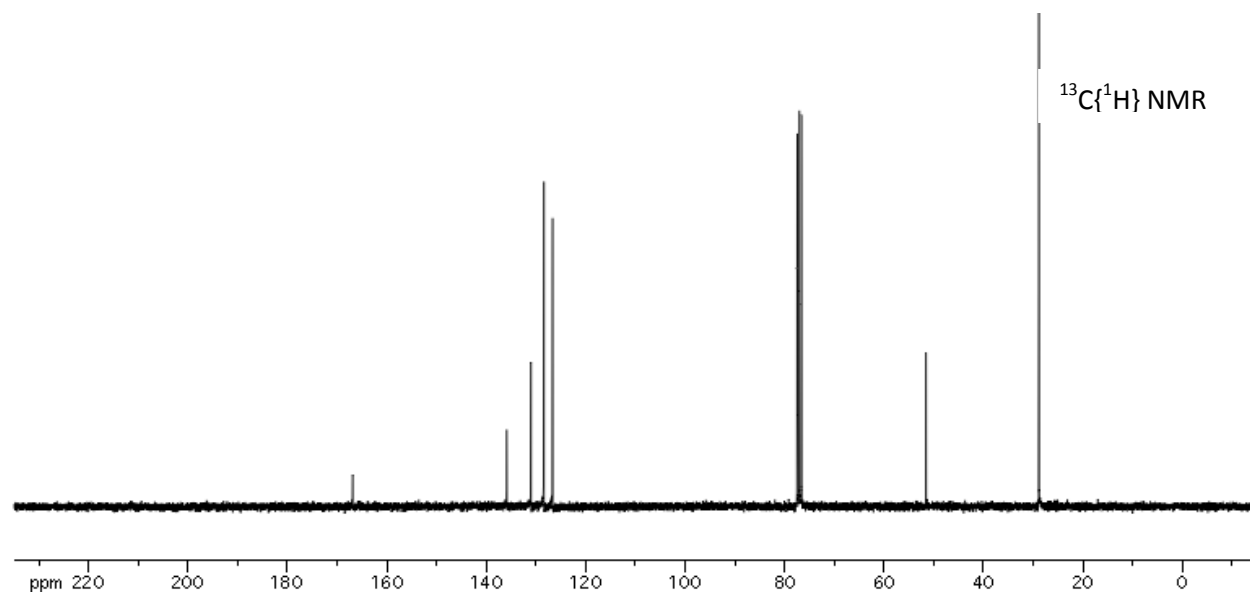
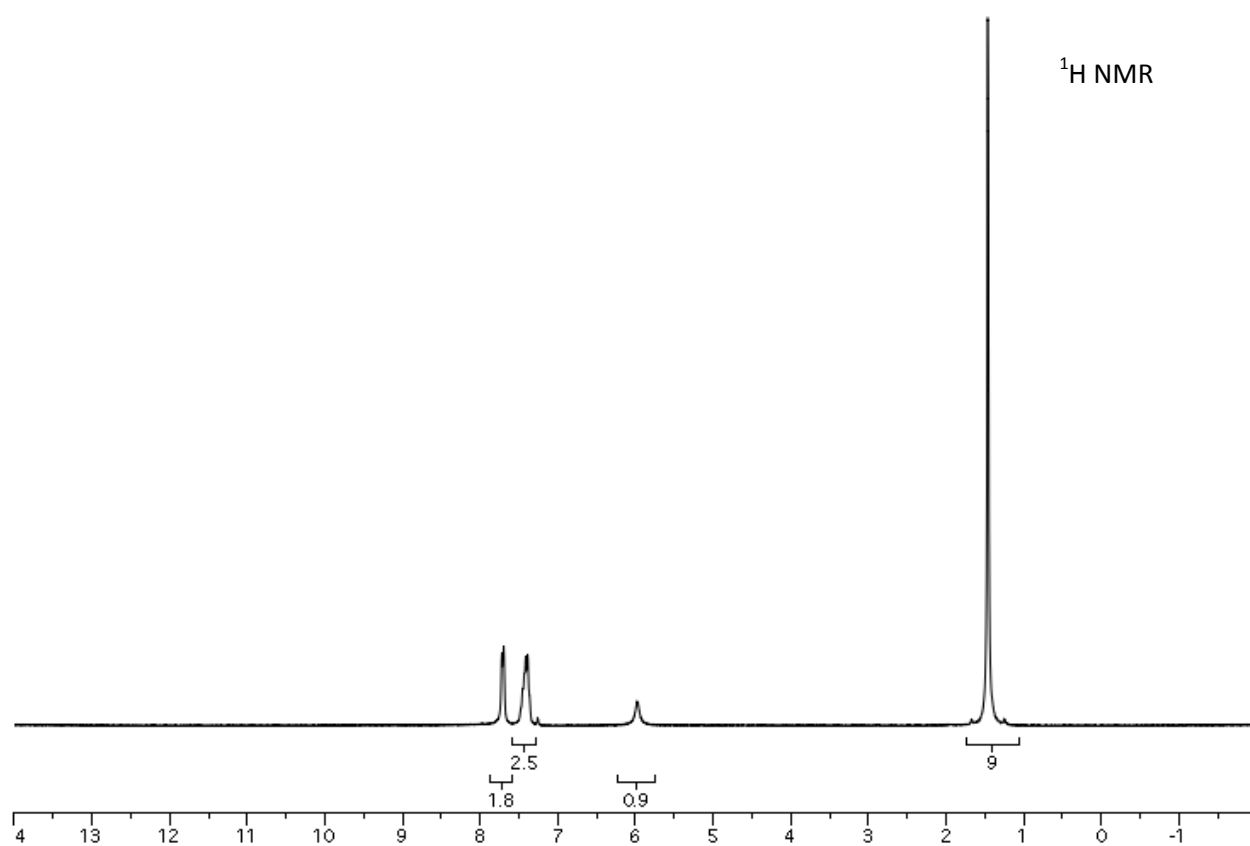
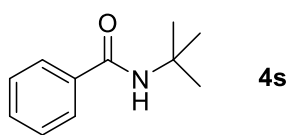


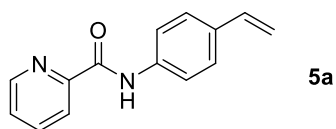




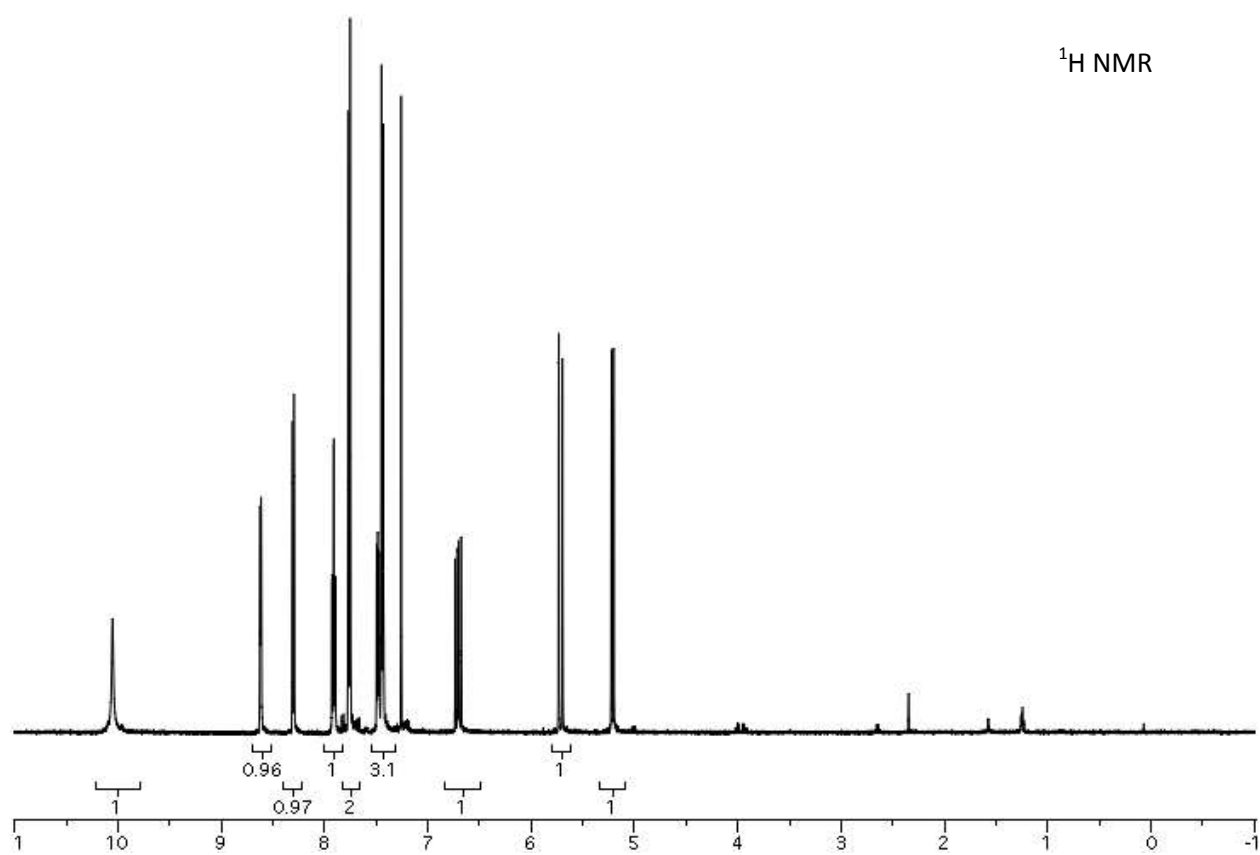




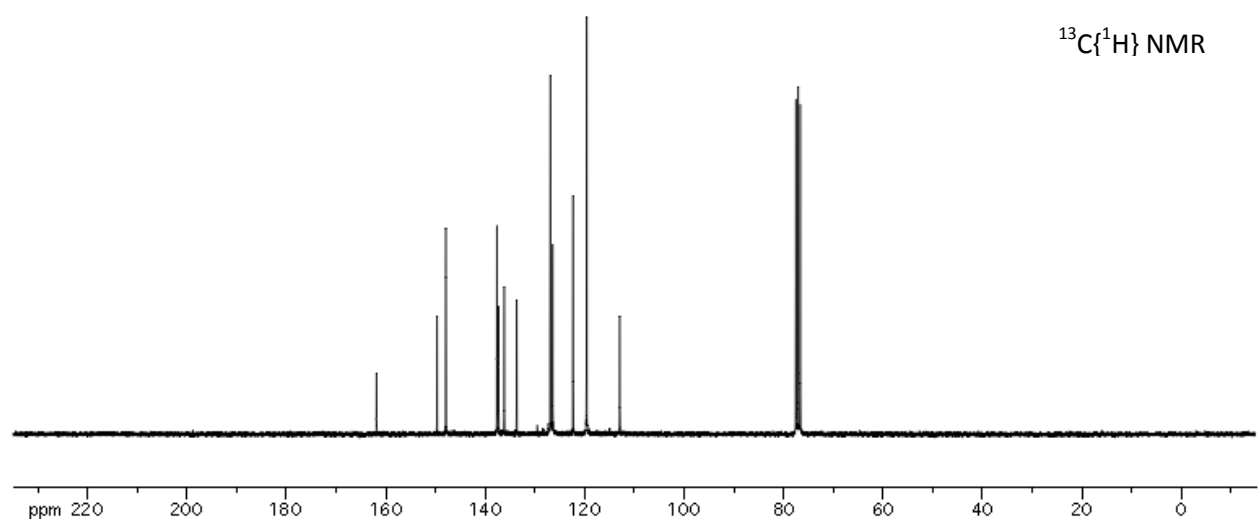


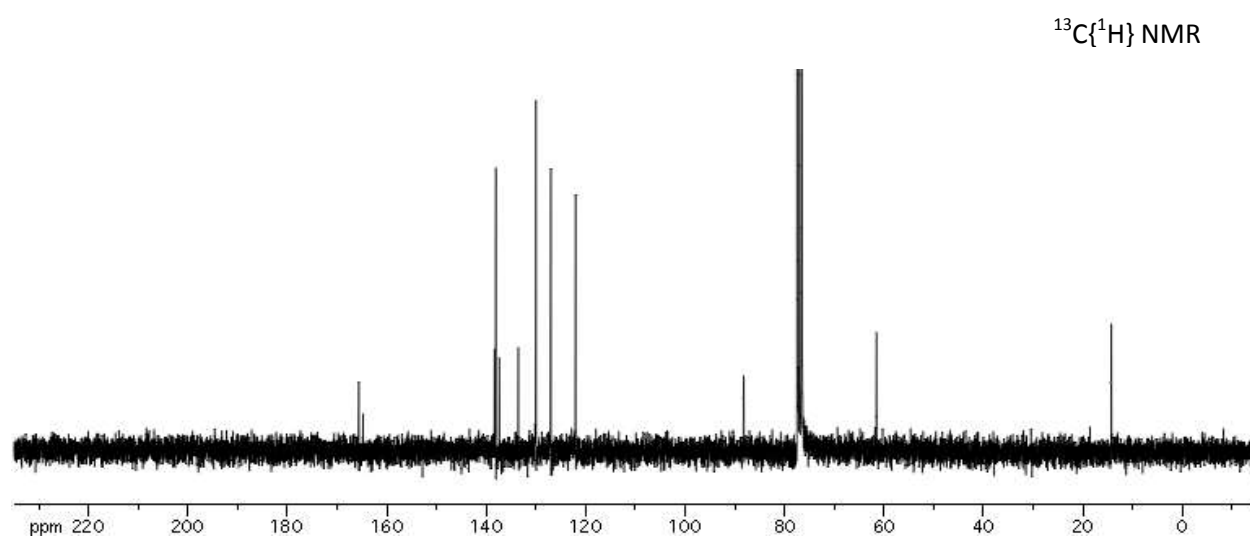
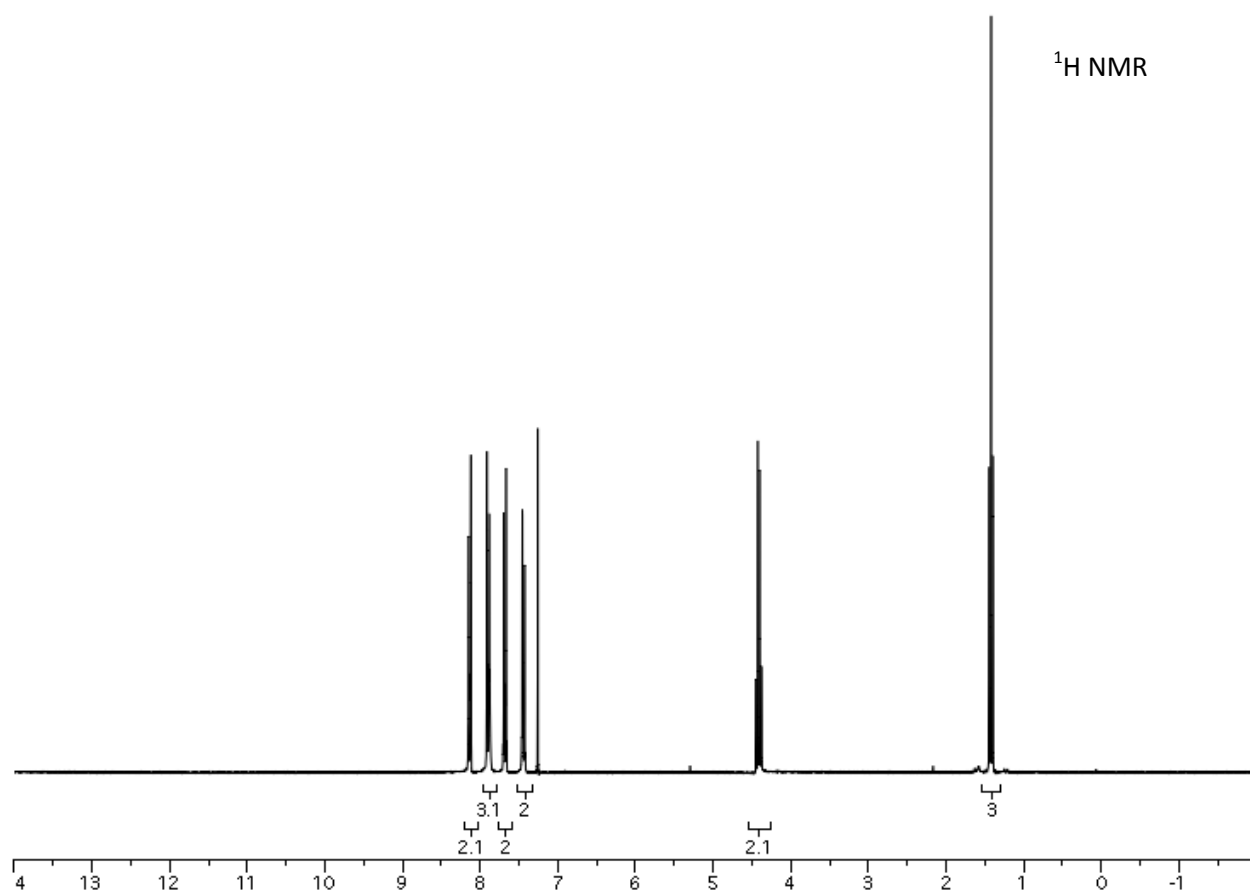
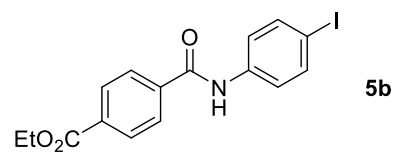


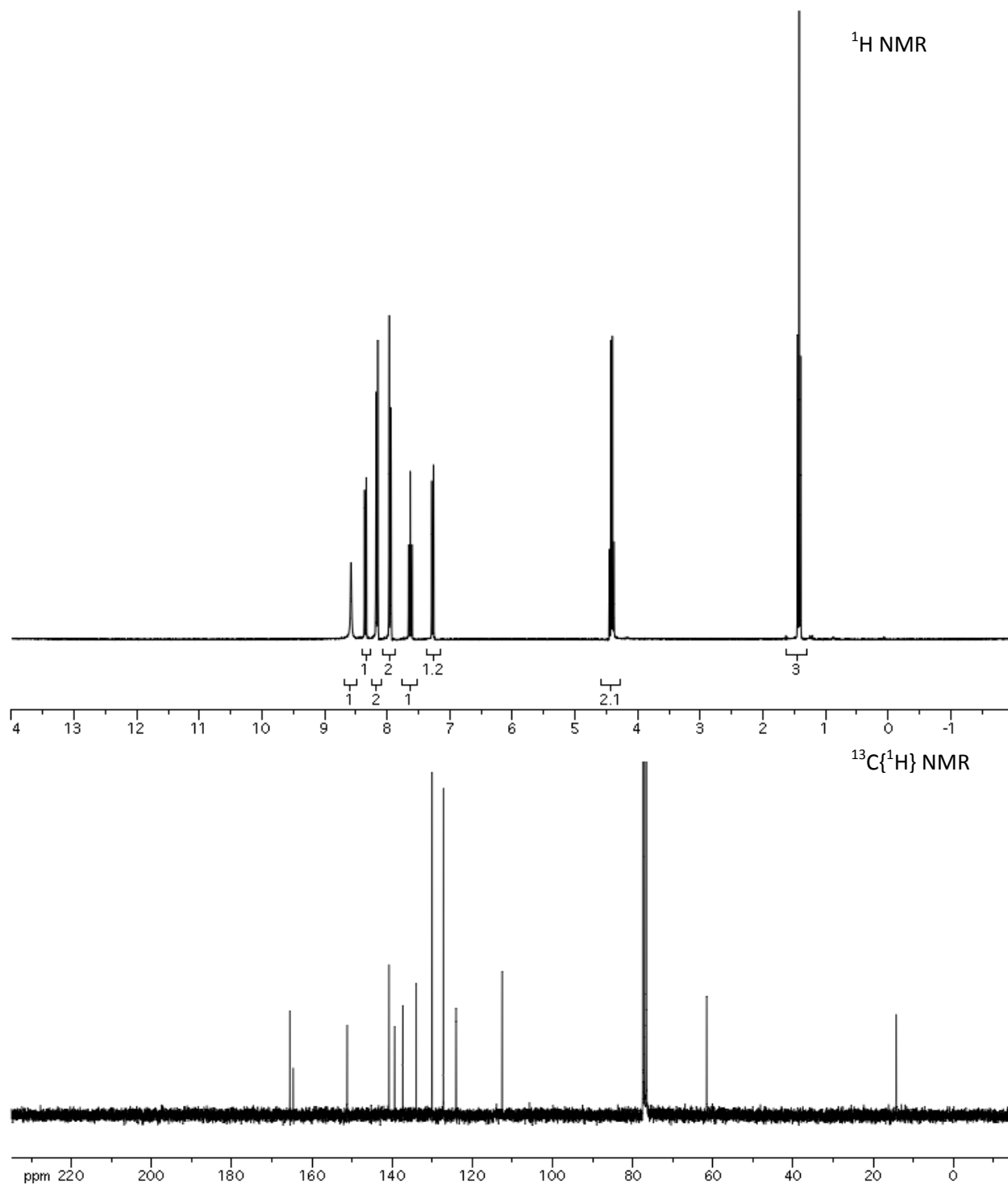
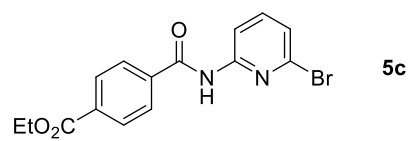
^1H NMR

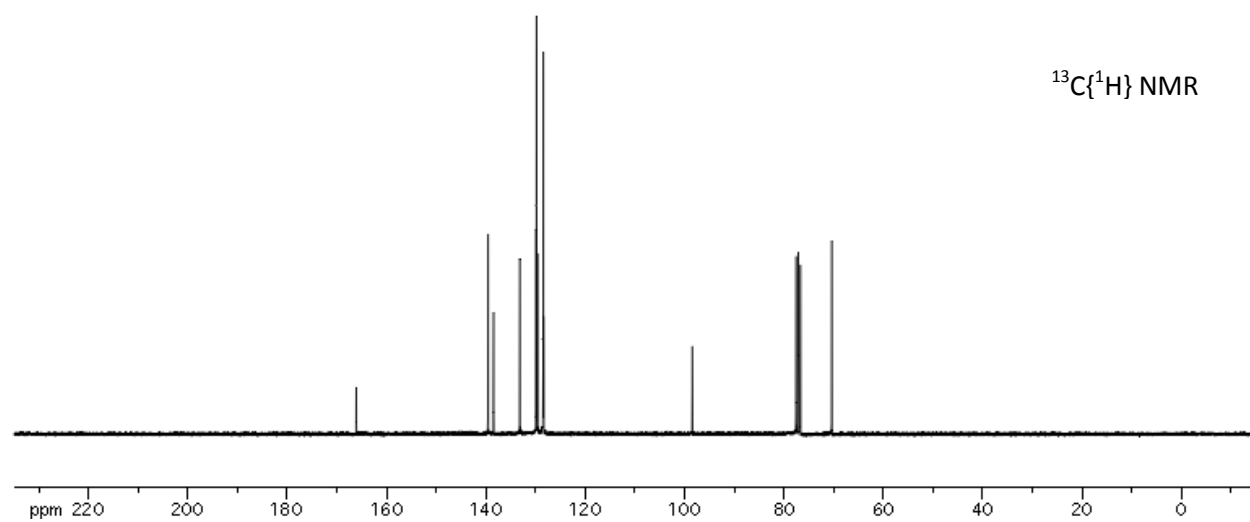
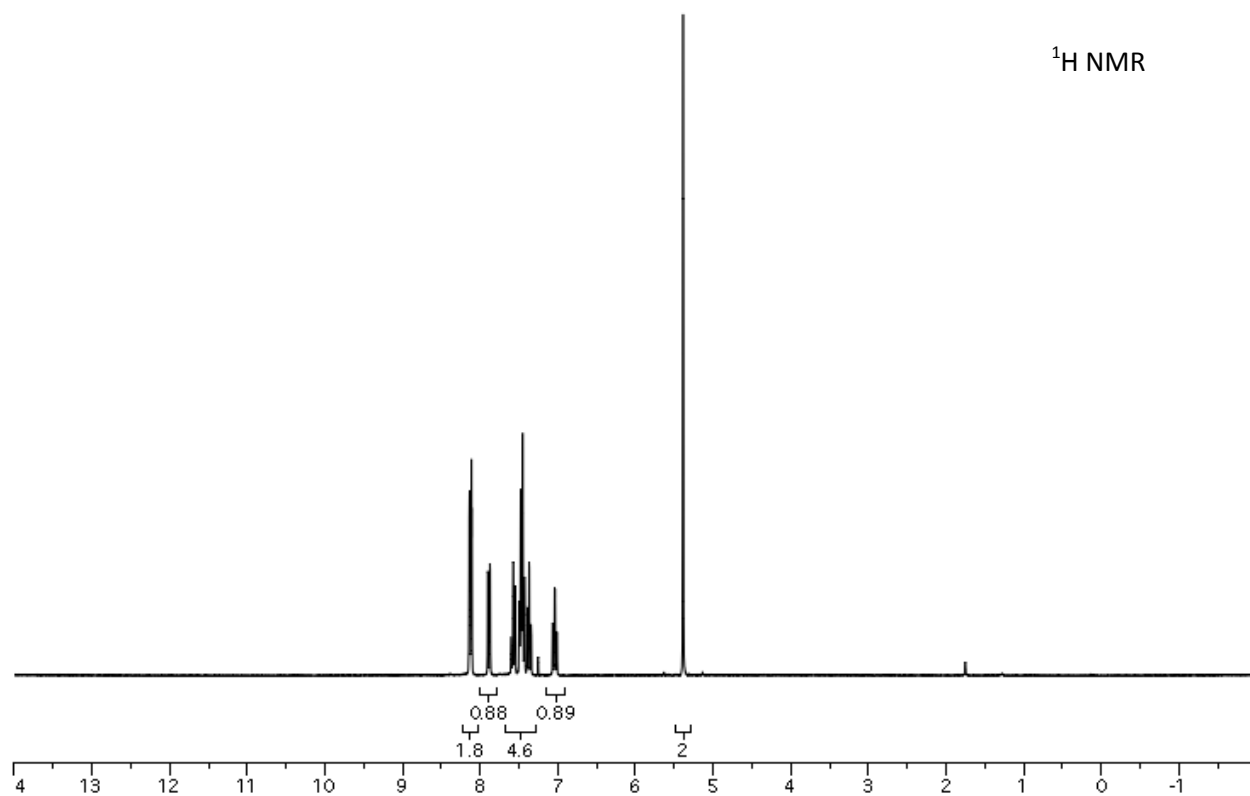
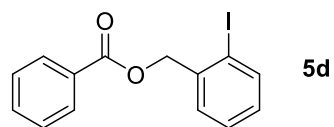


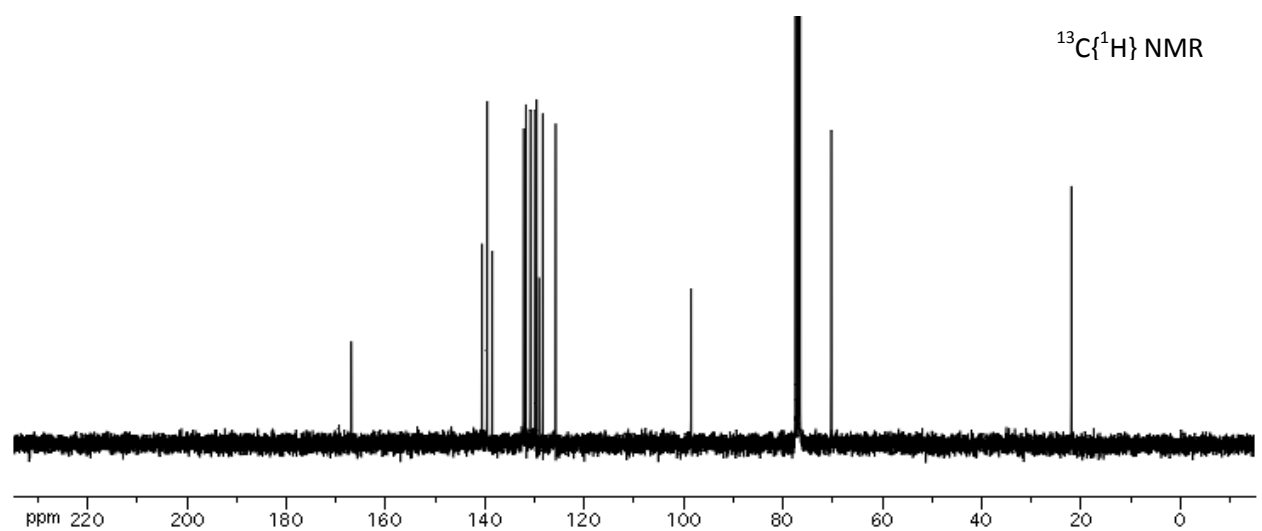
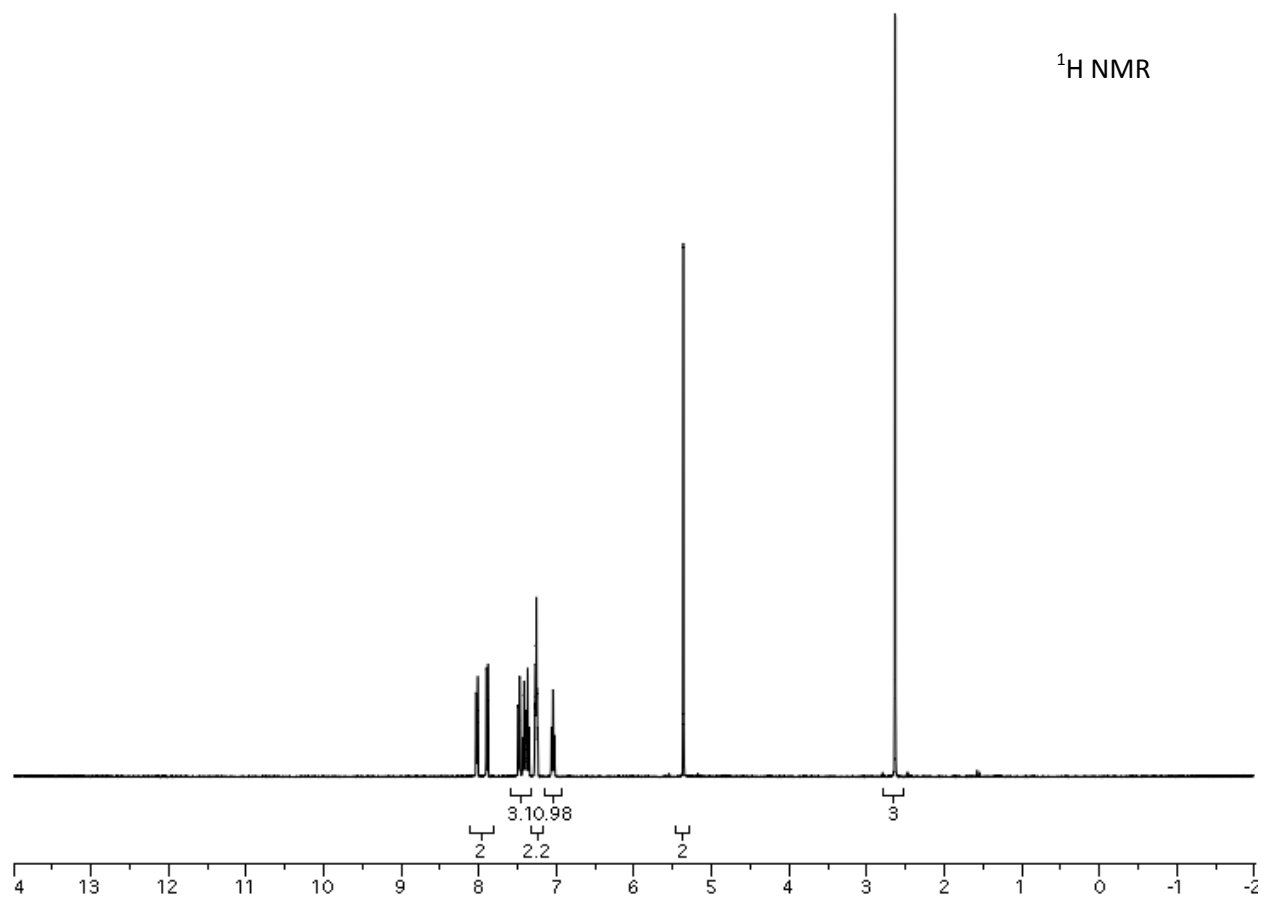
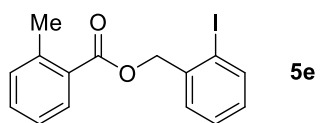
$^{13}\text{C}\{^1\text{H}\}$ NMR

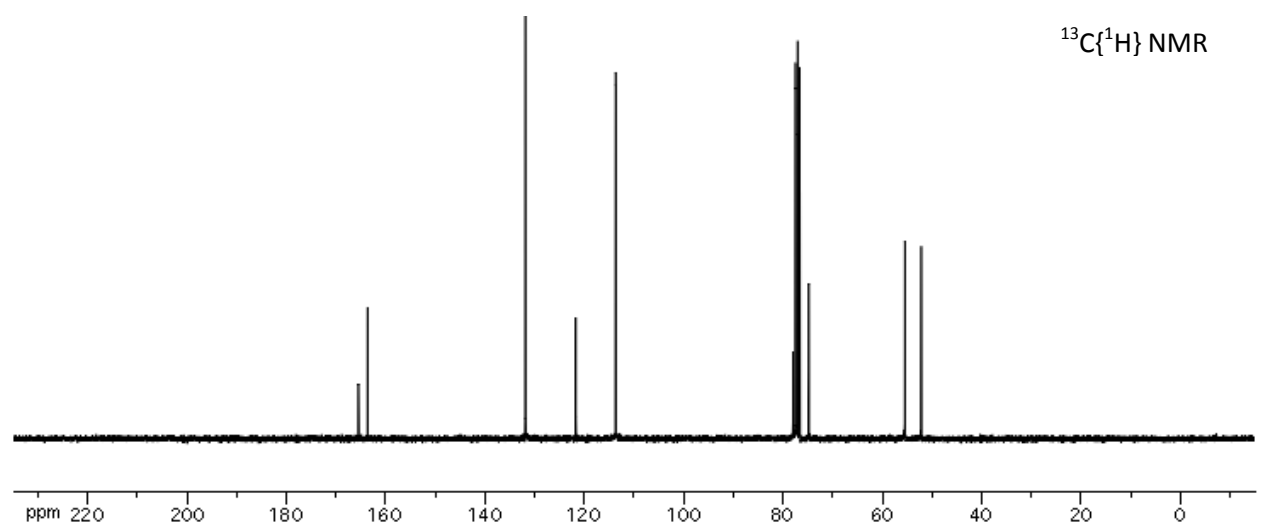
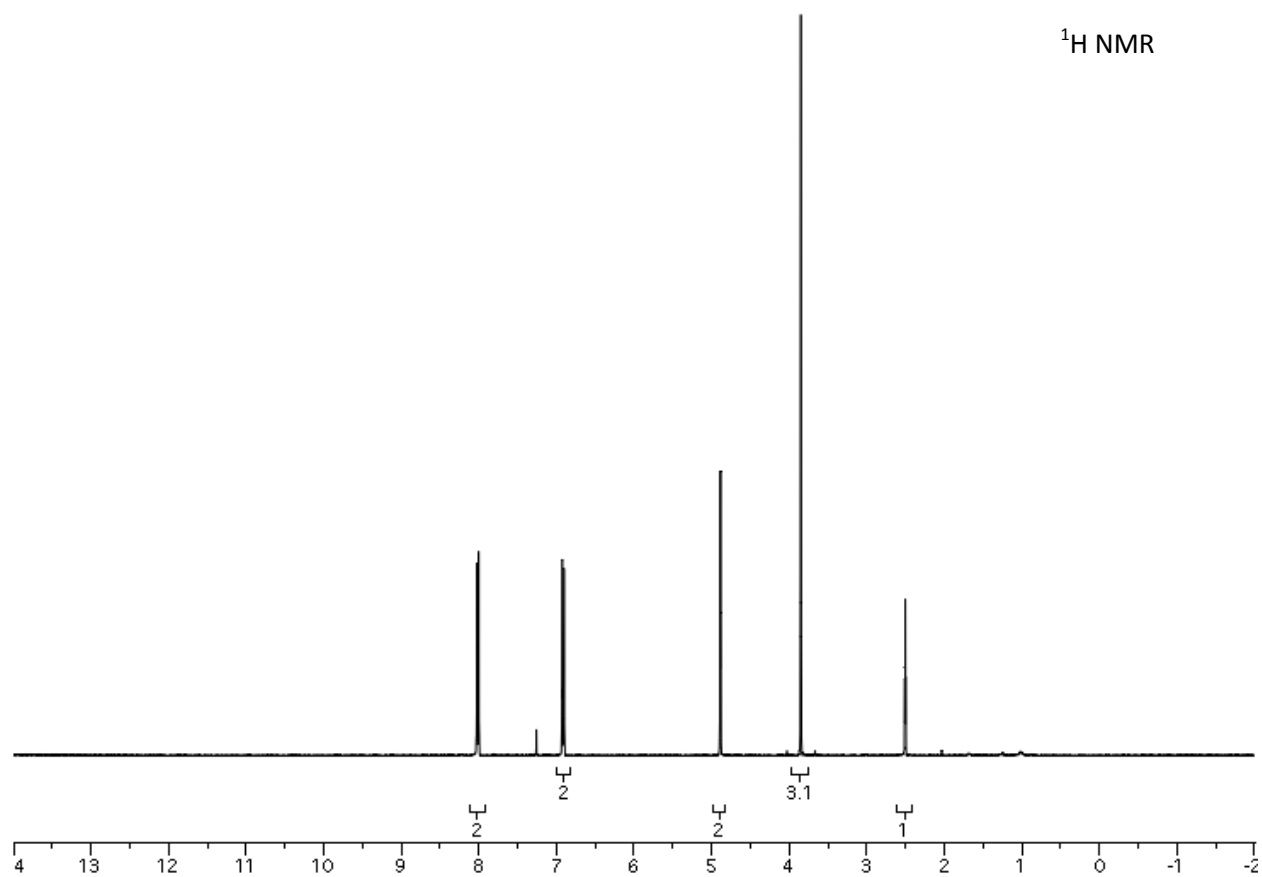
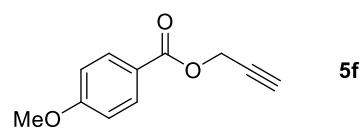


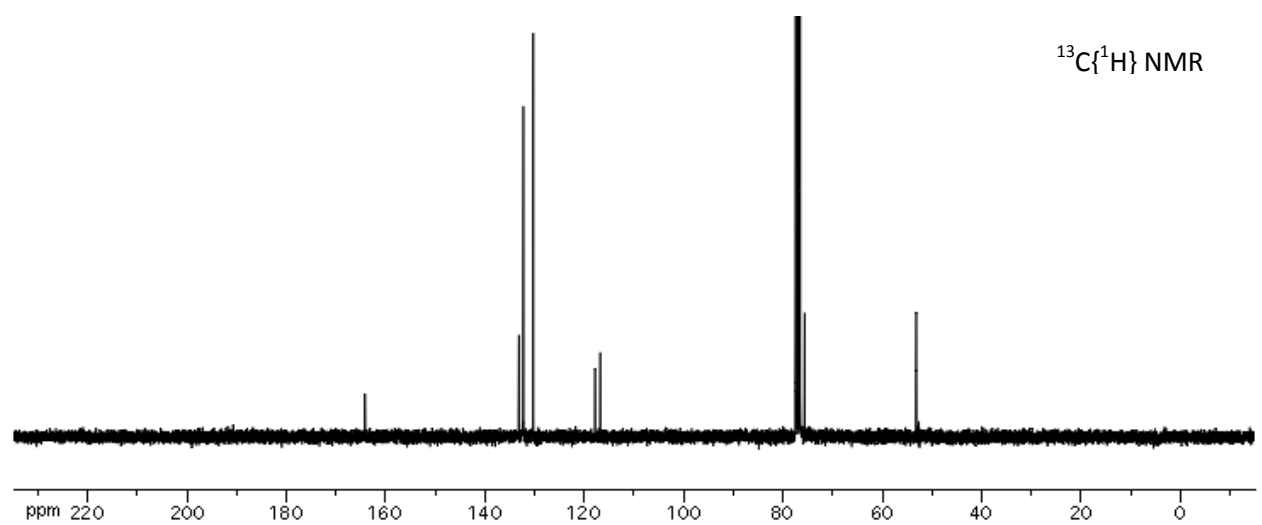
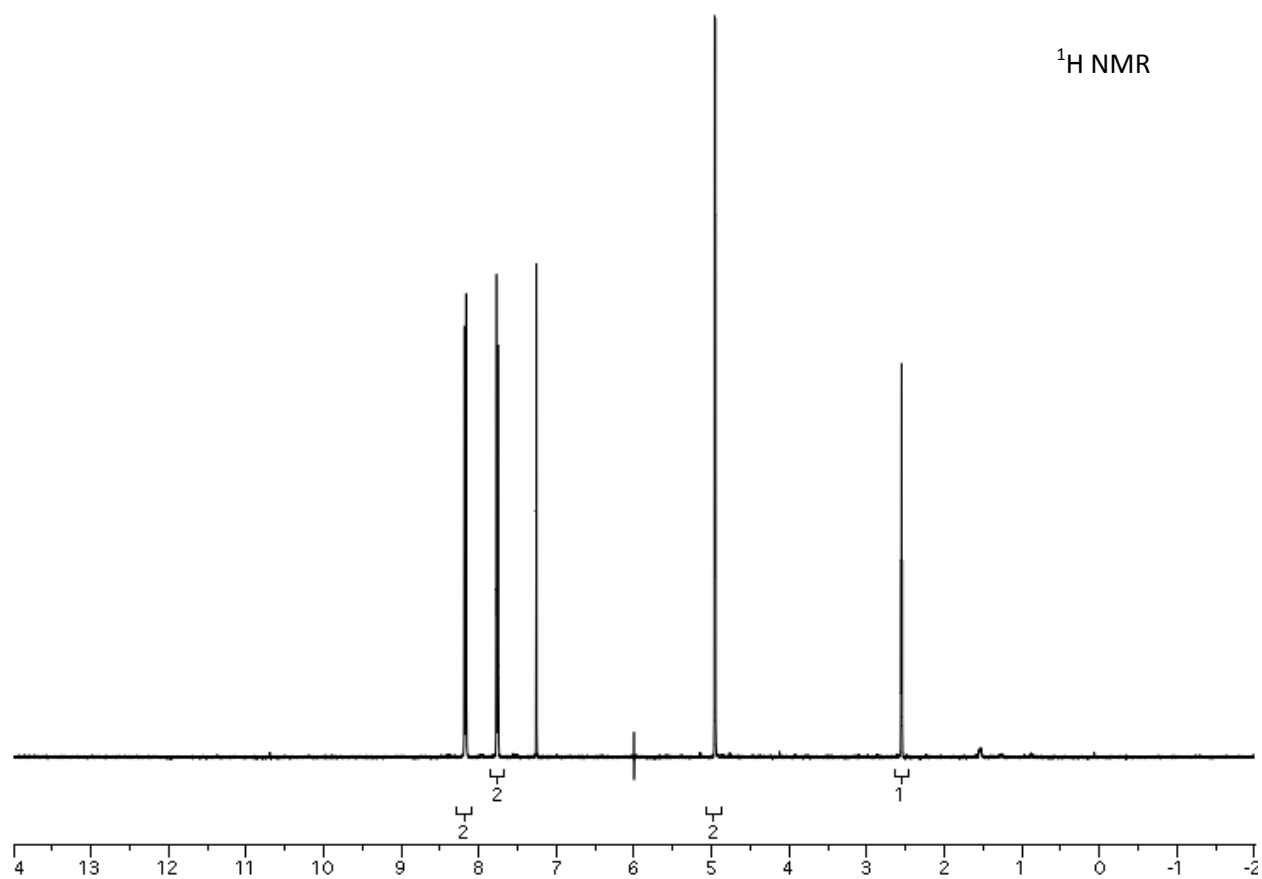
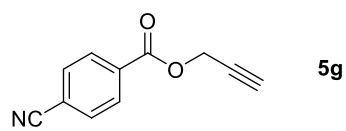


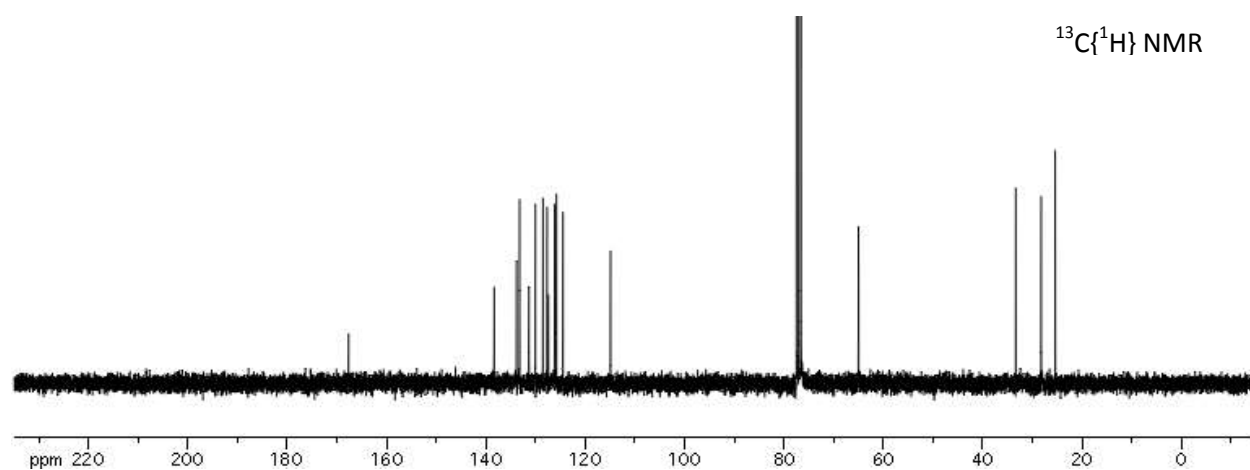
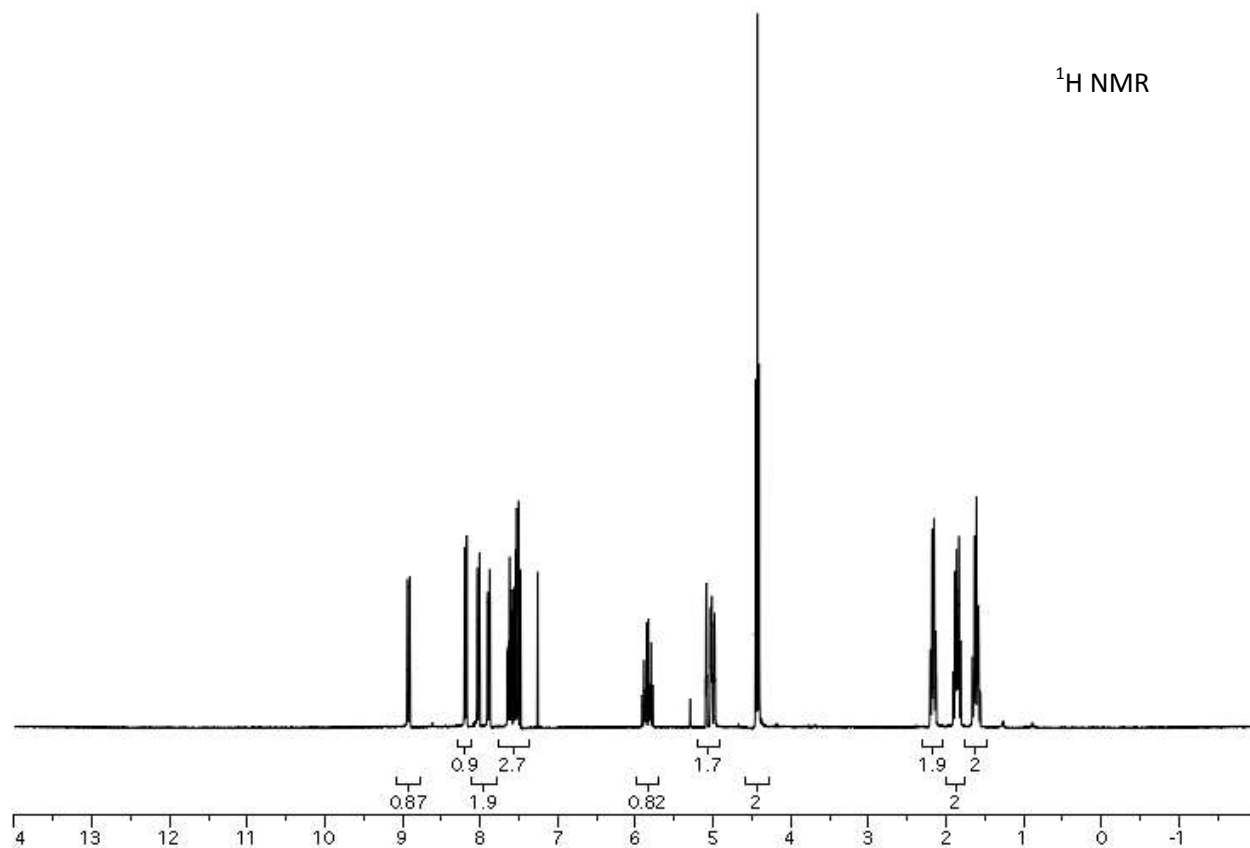
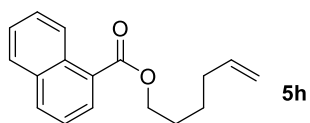


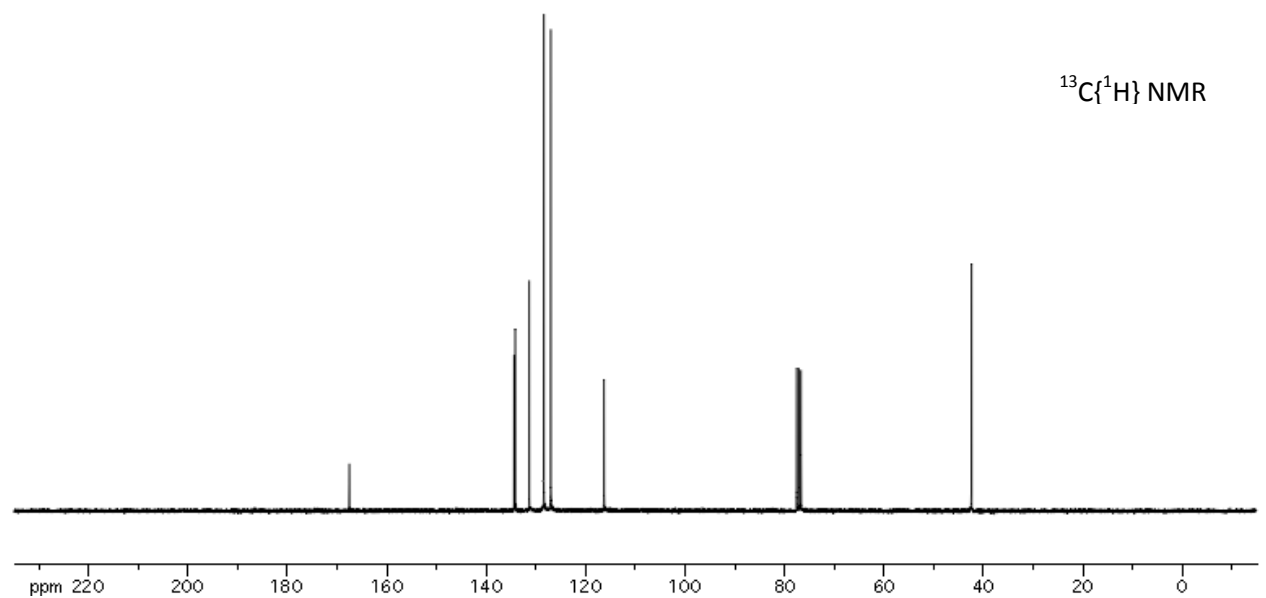
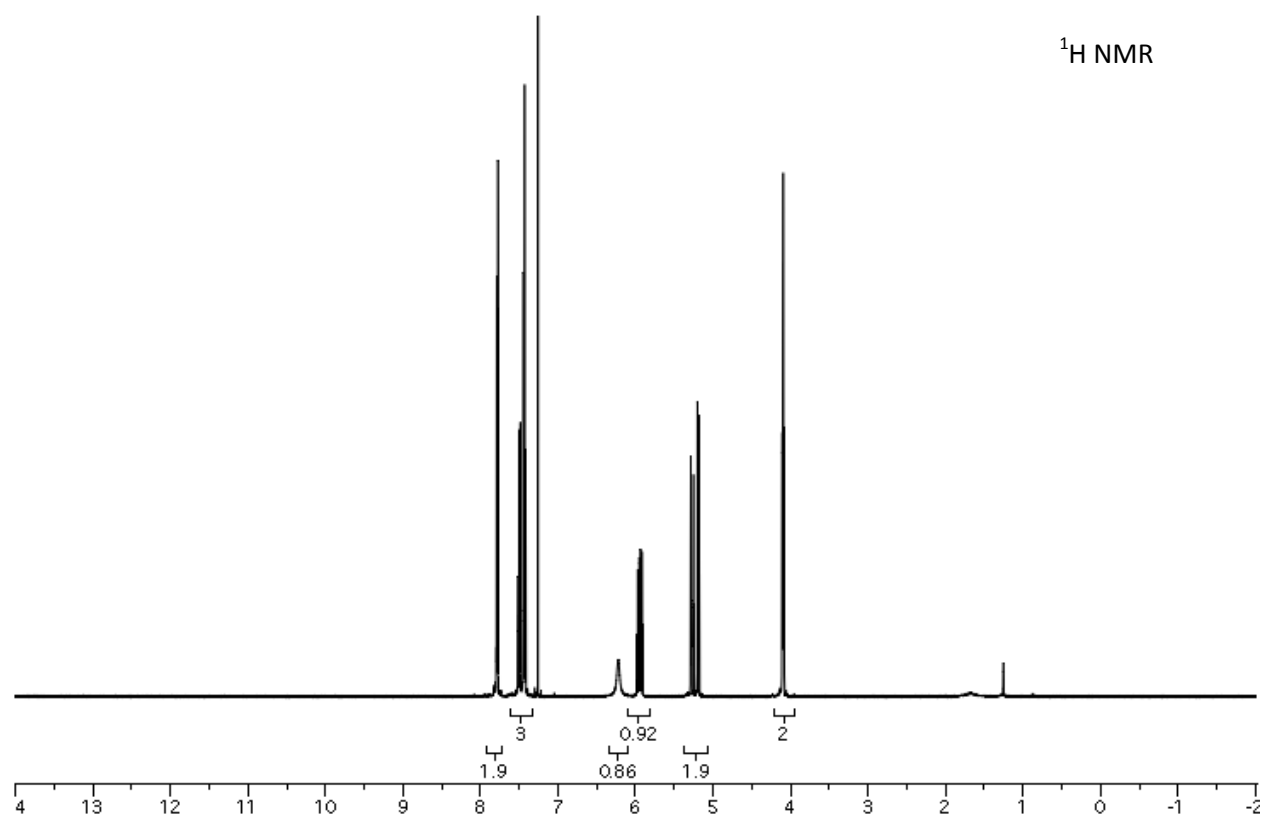
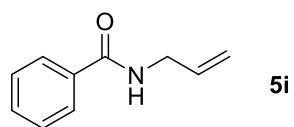


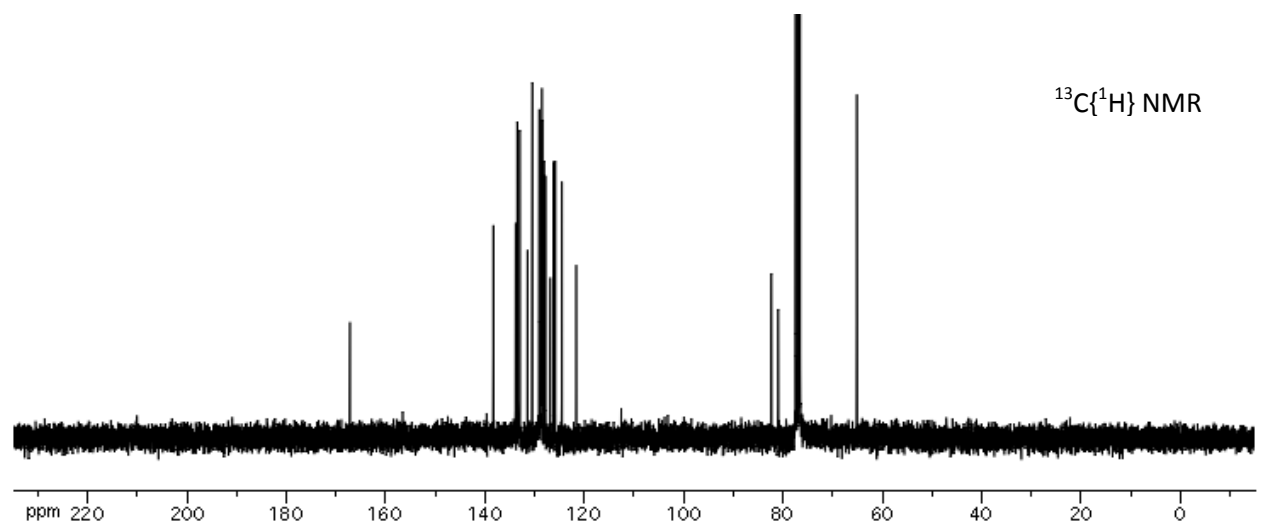
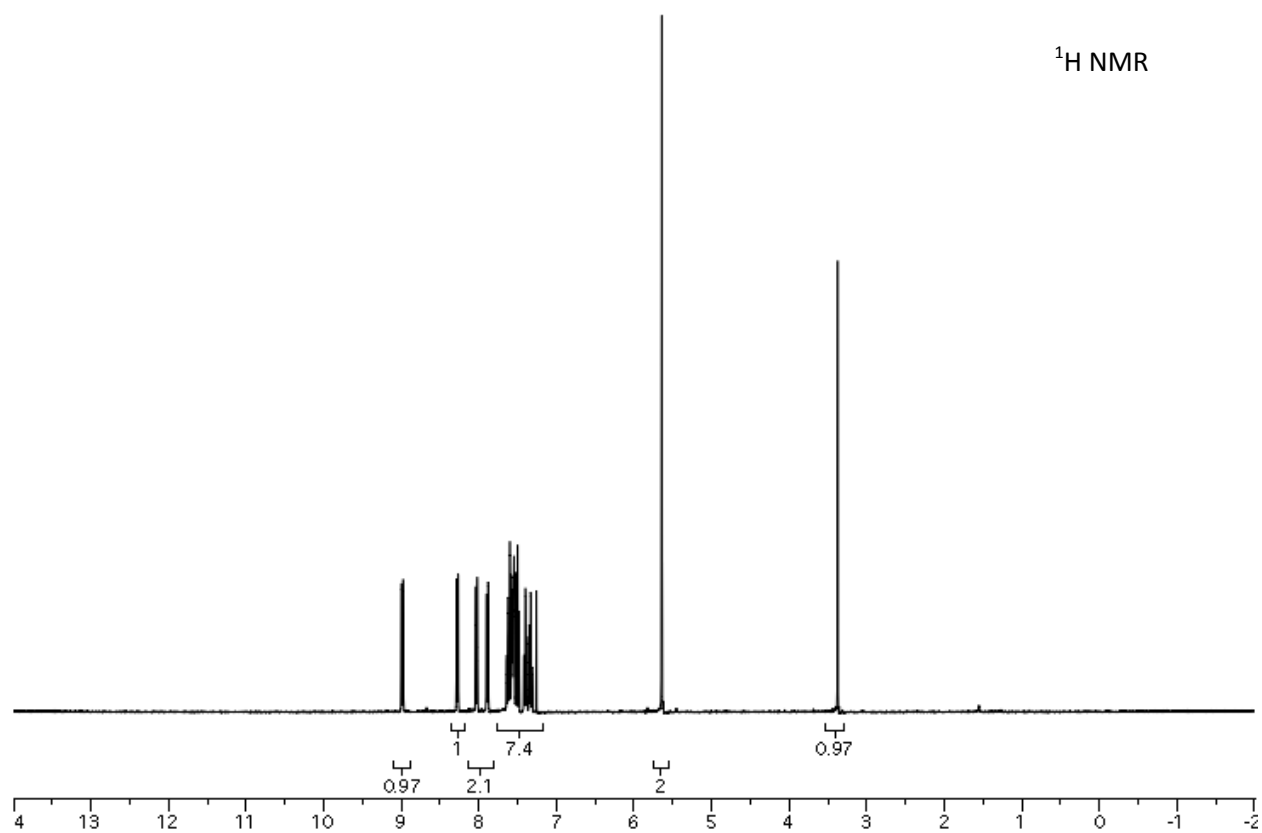
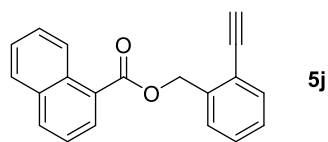


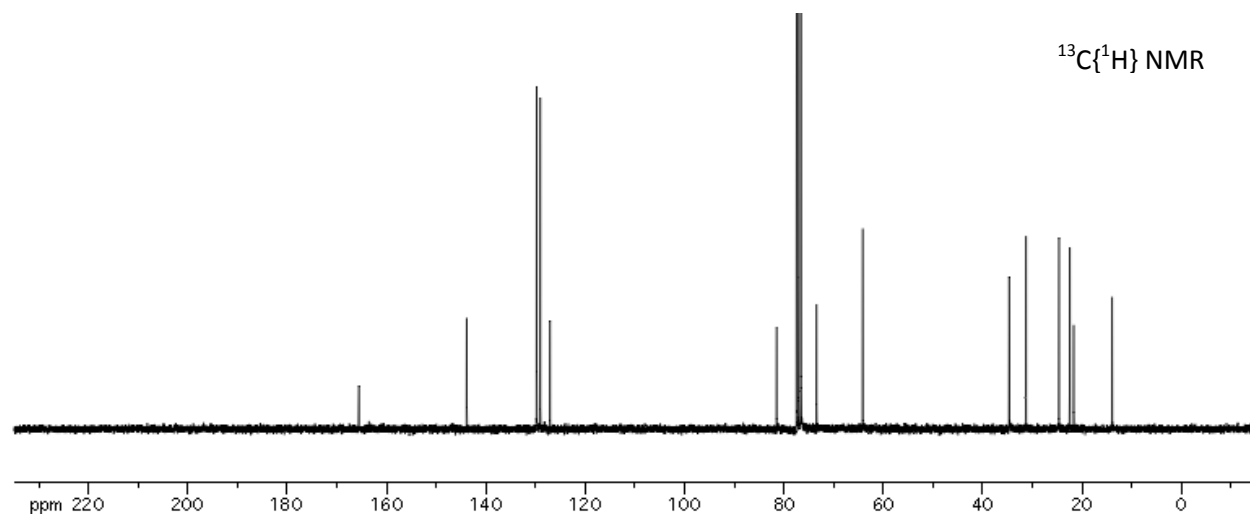
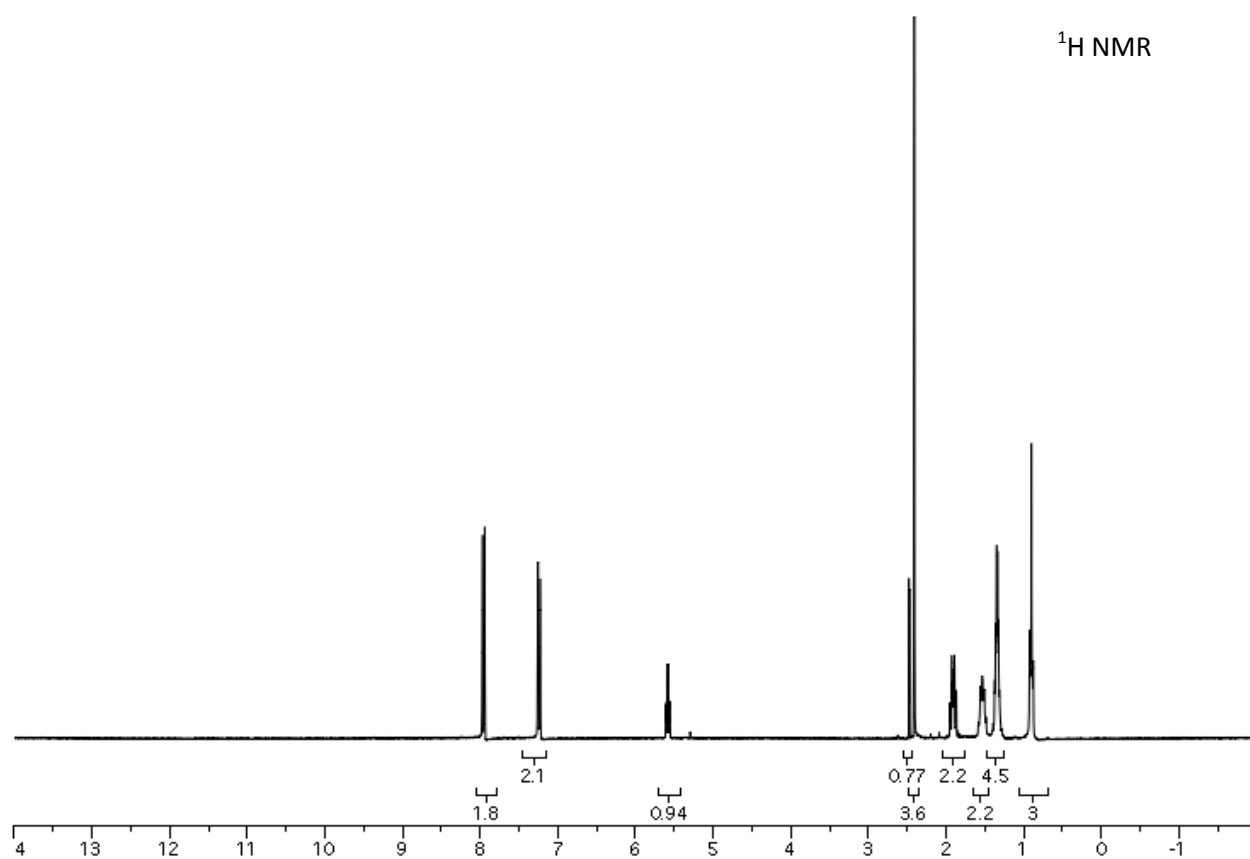
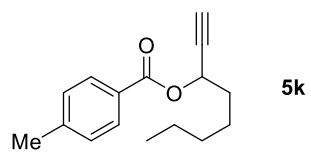


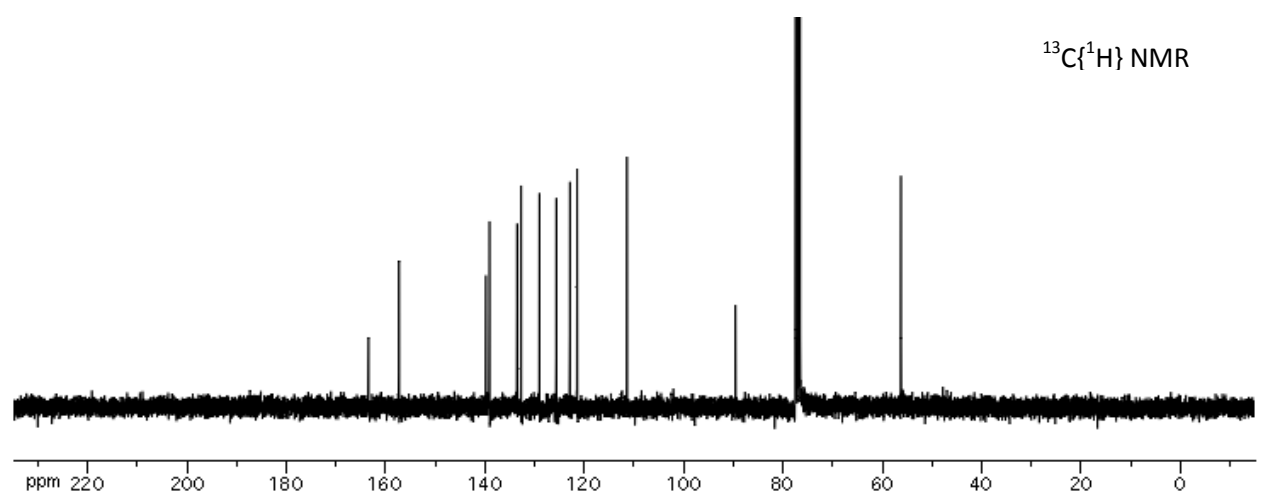
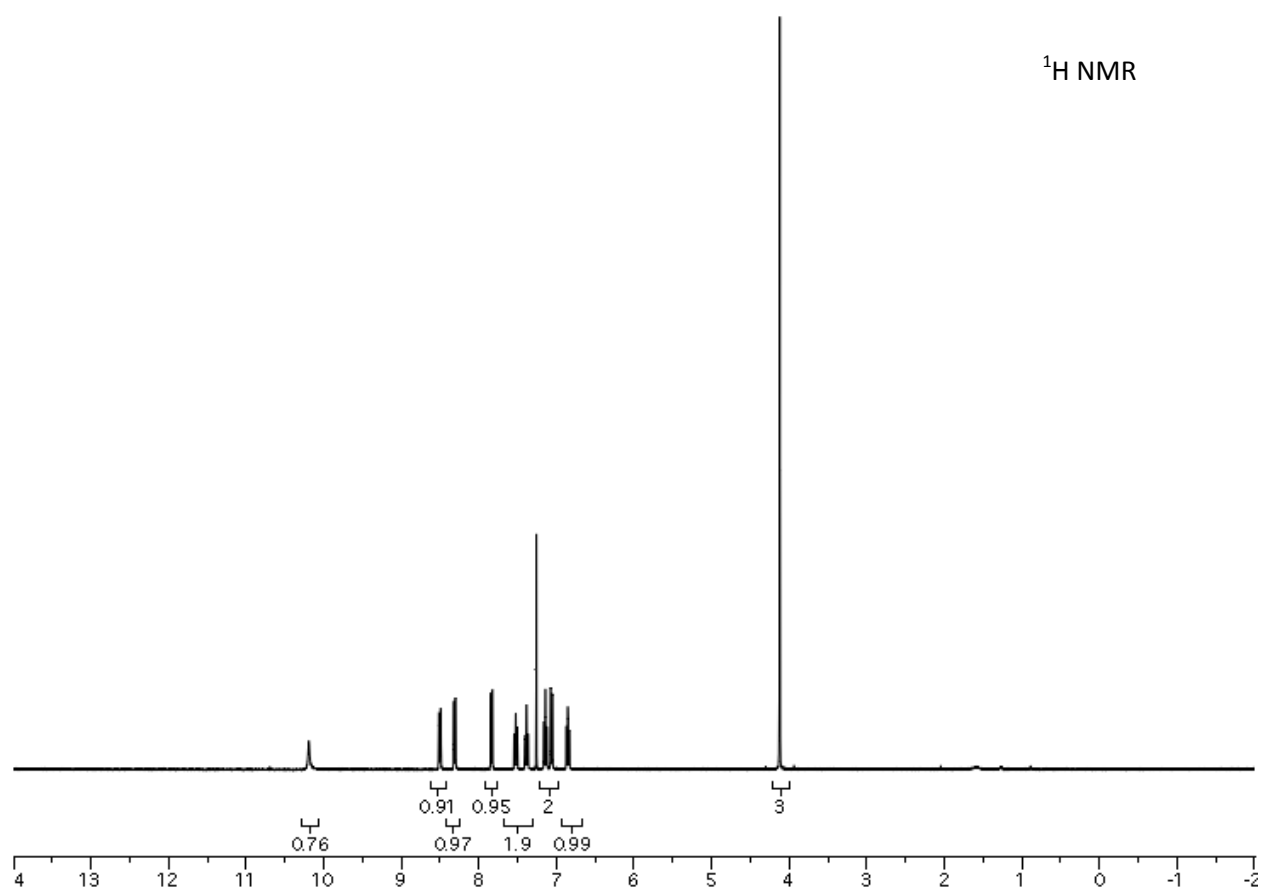
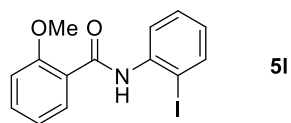


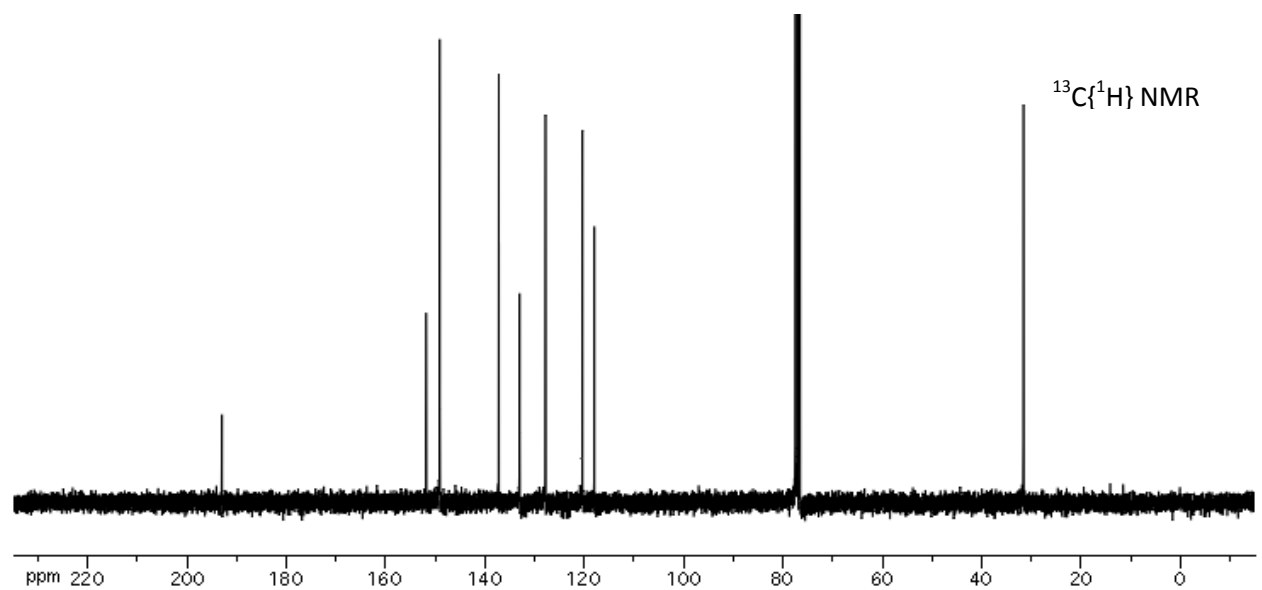
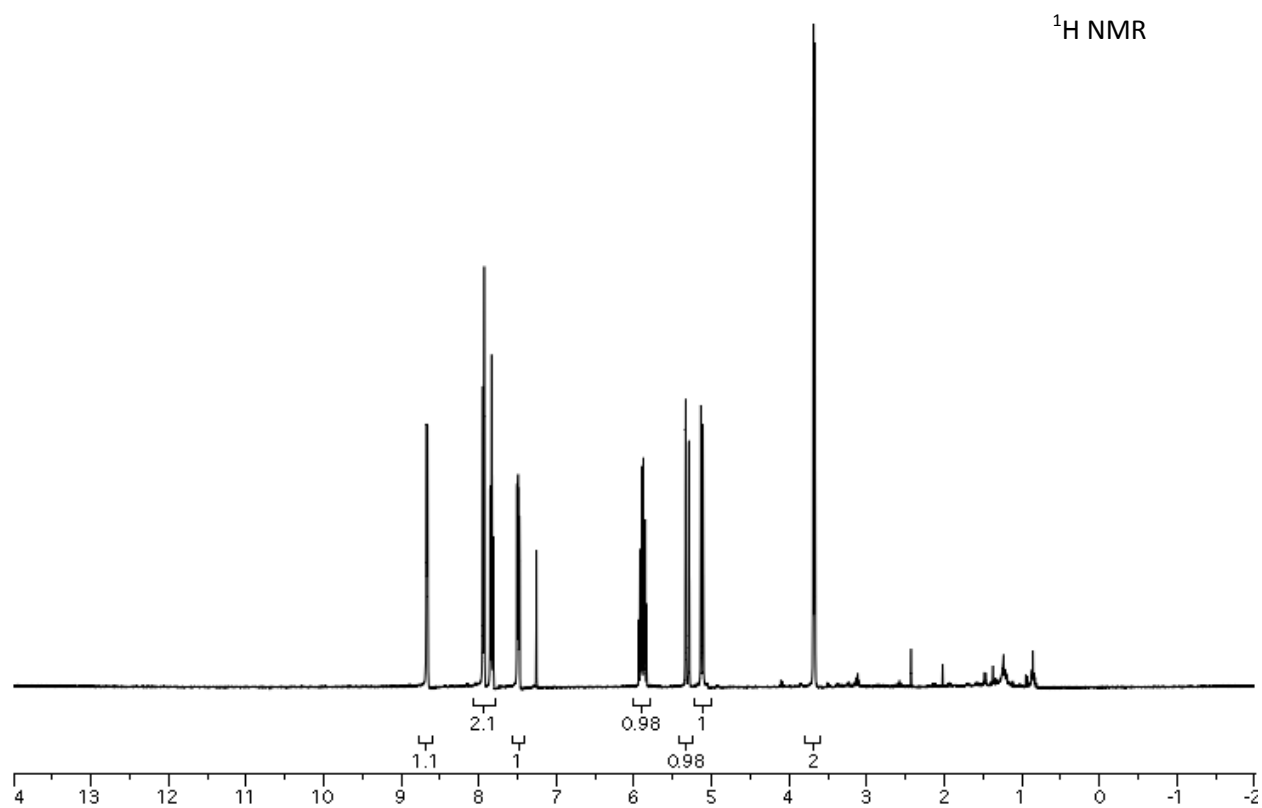
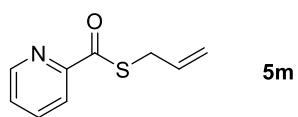


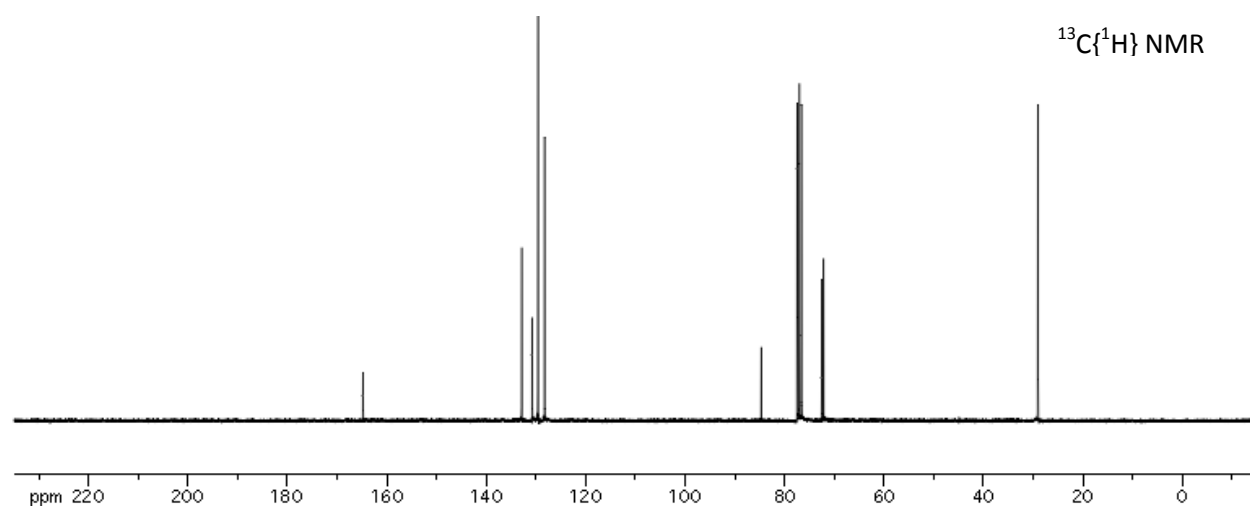
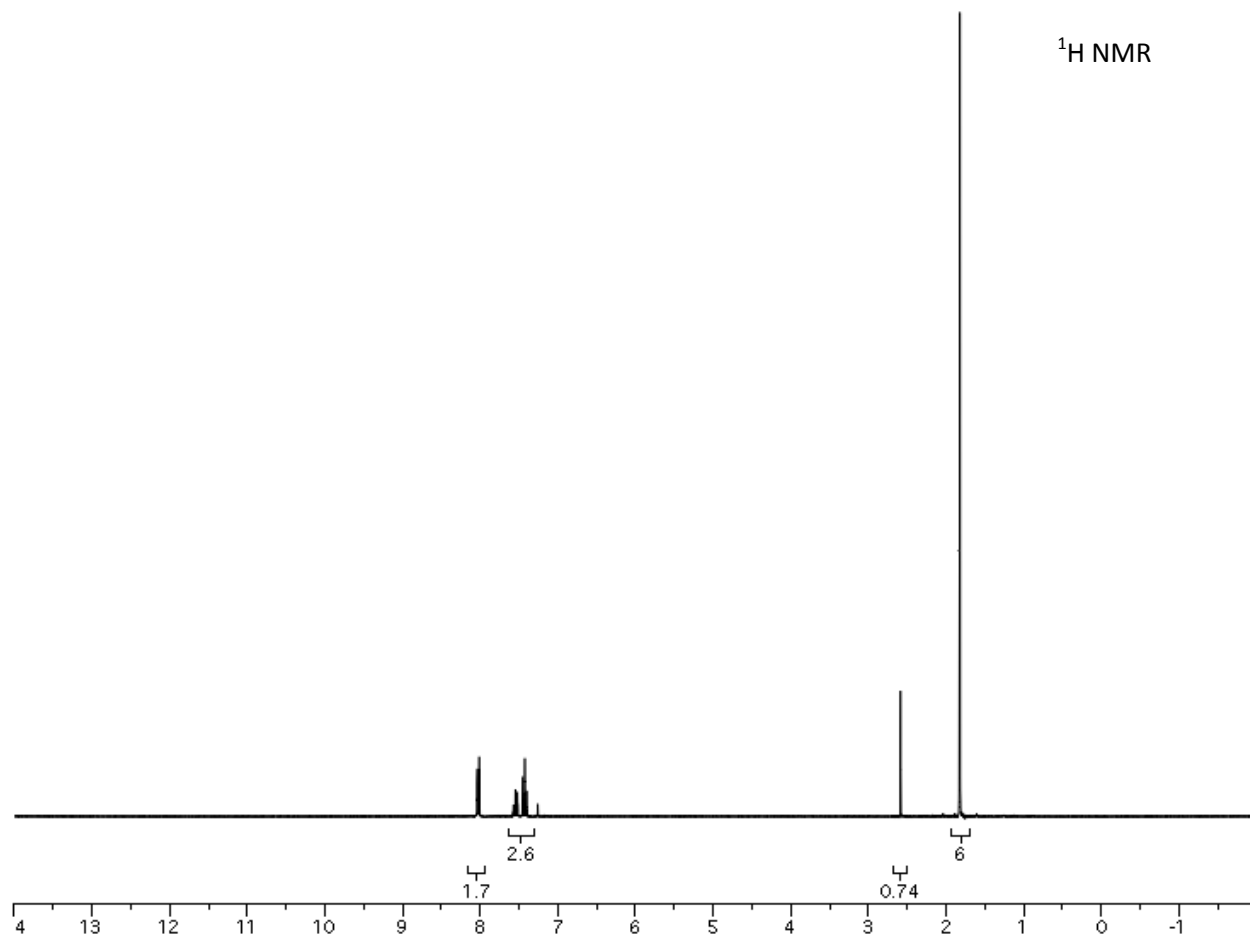
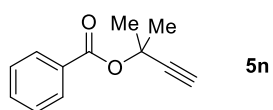


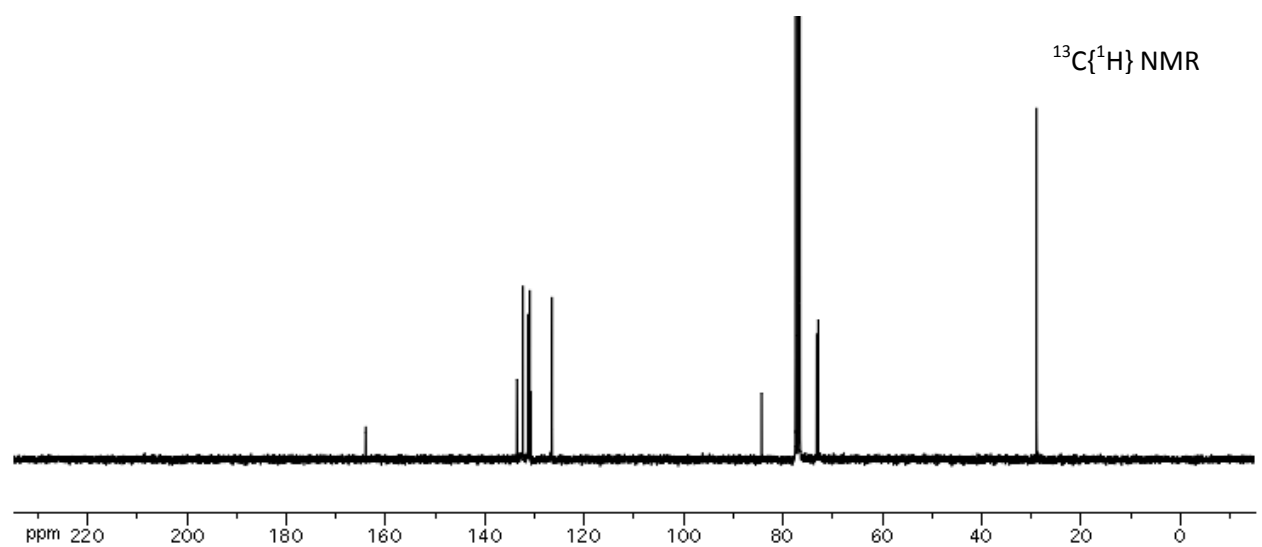
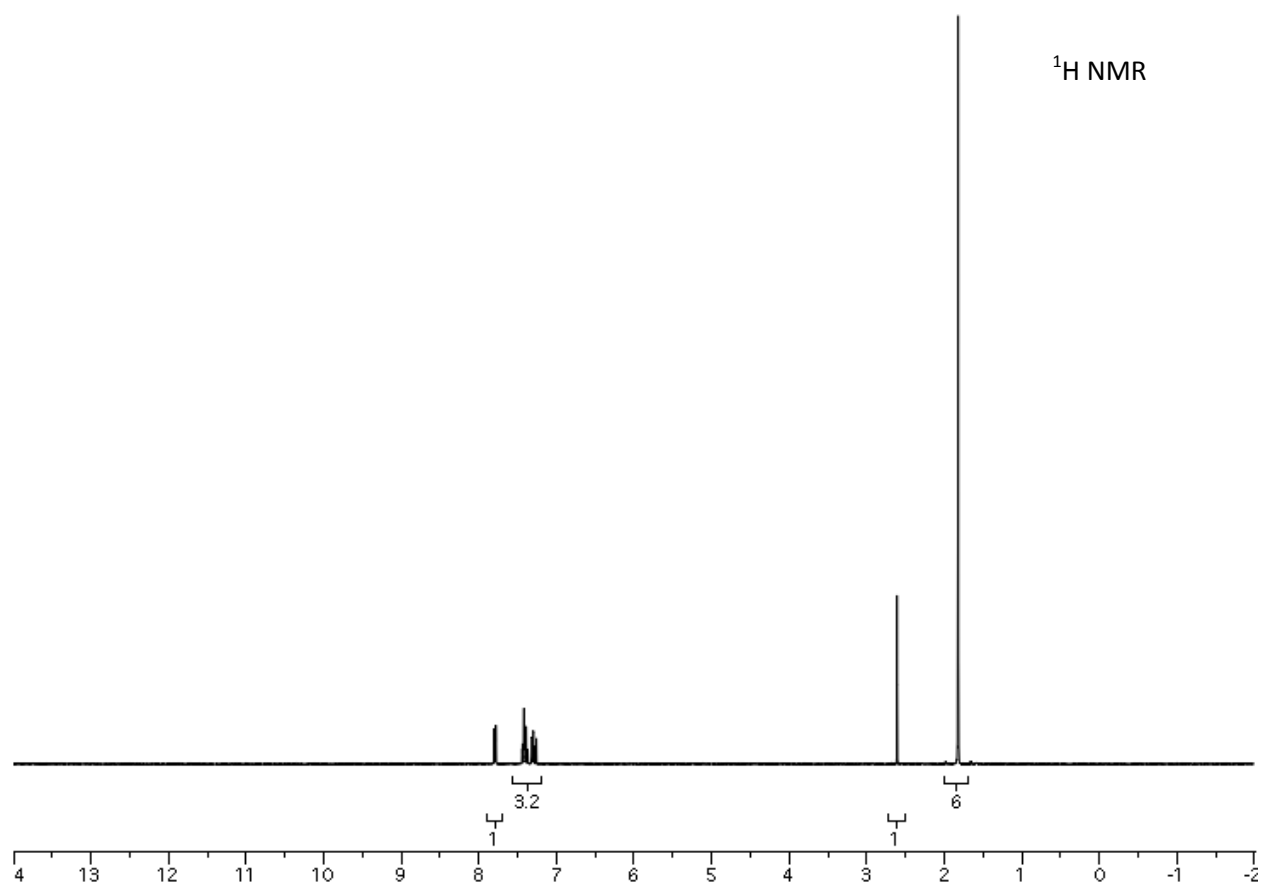
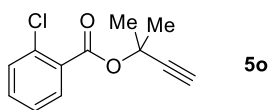


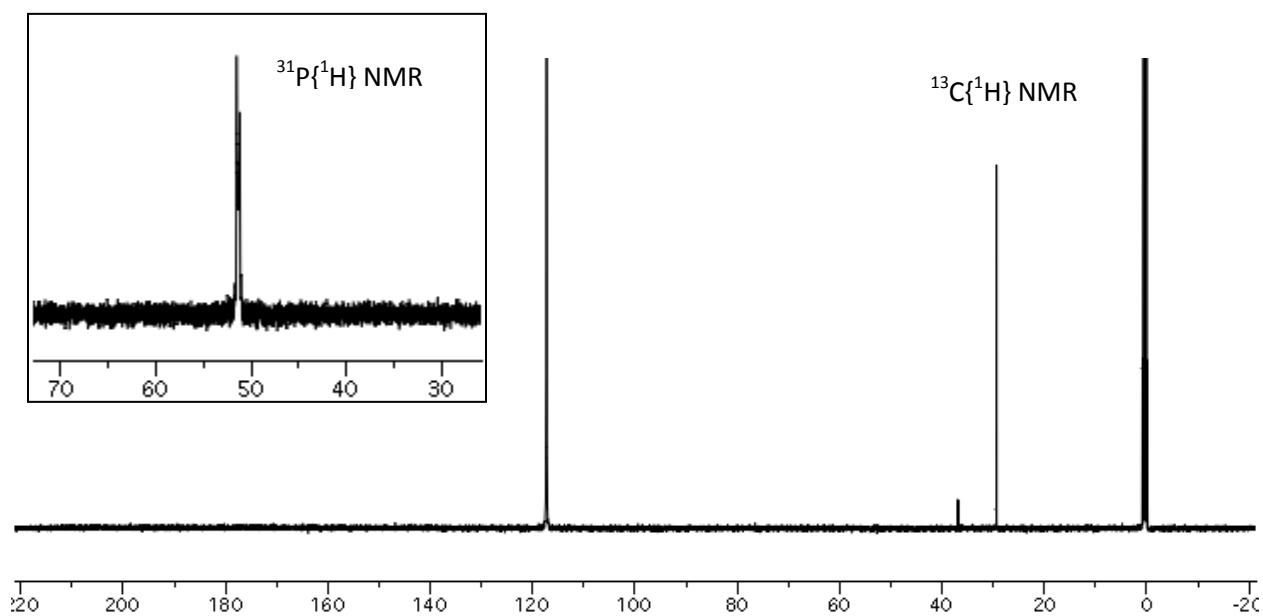
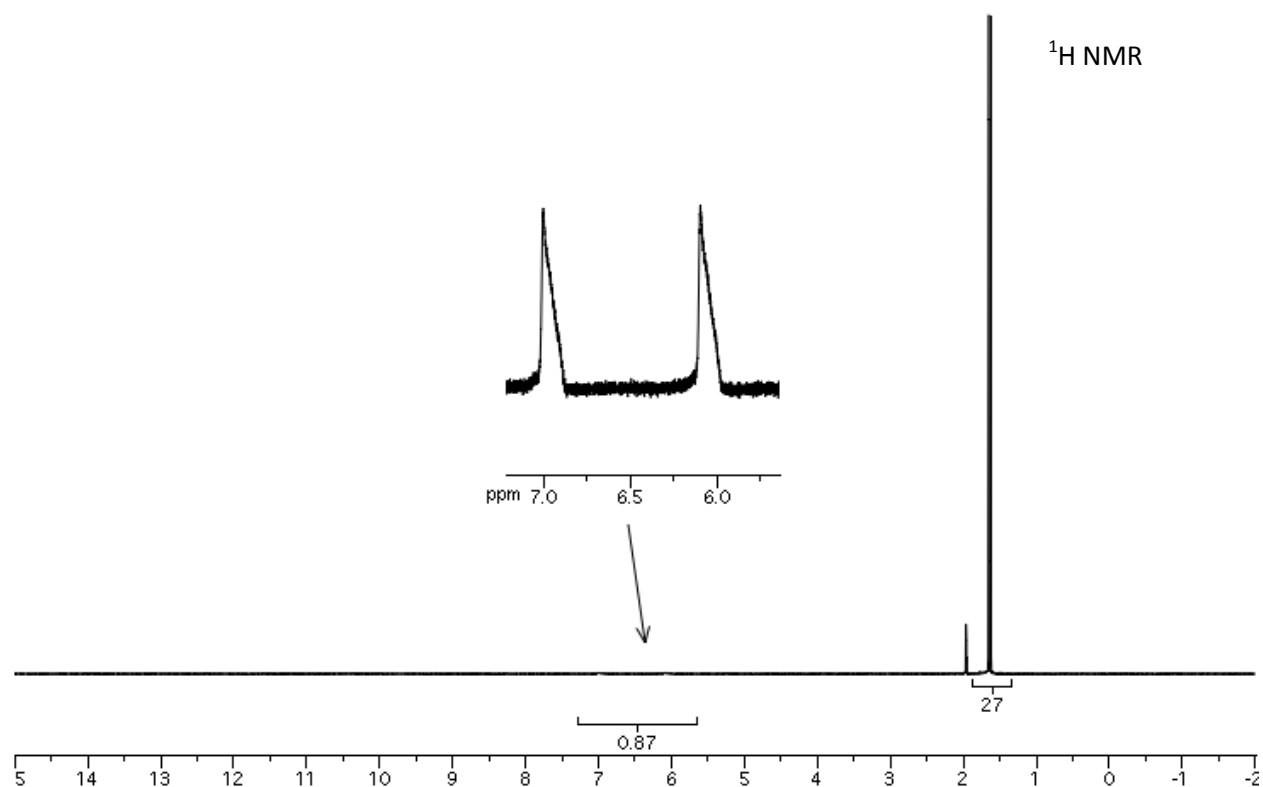
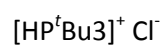












V. References

- 1) Xu, X.; Park, C.-M. *Angew. Chem. Int. Ed.* **2012**, *51*, 9372.
- 2) Zaleskiy, S. S.; Ananikov, V. P. *Organometallics* **2012**, *31*, 2302.
- 3) Tsukamoto, H.; Suzuki, R.; Kondo, Y. *J. Comb. Chem.* **2006**, *8*, 289.
- 4) Burgstein, M. R.; Berberich, H.; Roesky, P. W. *Chem. Eur. J.* **2001**, *7*, 3078.
- 5) Salvadori, J.; Balducci, E.; Zaza, S.; Petricci, E.; Taddei, M. *J. Org. Chem.* **2010**, *75*, 1841.
- 6) Molander, G. A.; Hiebel, M.-A. *Org. Lett.* **2010**, *12*, 4876.
- 7) Takeda, K.; Tsuboyama, K.; Takayanagi, H.; Ogura, H. *Synthesis* **1987**, 560.
- 8) Morcillo, S. P.; Álvarez de Cienfuegos, L.; Mota, A. J.; Justicia, J.; Robles, R. *J. Org. Chem.* **2011**, *76*, 2277.
- 9) McNulty, J.; Nair, J. J.; Cheekoori, S.; Larichev, V.; Capretta, A.; Robertson, A. J. *Chem. Eur. J.* **2006**, *12*, 9314.
- 10) Yadav, S.; Subba Reddy, B. V.; Pandurangam, T.; Jayasudan Reddy, Y.; Gupta, M. K. *Catal. Commun.* **2008**, *9*, 1297.
- 11) Zhang, C.; Feng, P.; Jiao, N. *J. Am. Chem. Soc.* **2013**, *135*, 15257.
- 12) Allen, C. L.; Atkinson, B. N.; Williams, J. M. J. *Angew. Chem. Int. Ed.* **2012**, *51*, 1383.
- 13) Lee, C. K.; Yu, J. S.; Kim, S. H. *J. Heterocycl. Chem.* **1998**, *35*, 835.
- 14) Ohshima, T.; Iwasaki, T.; Maegawa, Y.; Yoshiyama, A.; Mashima, K. *J. Am. Chem. Soc.* **2008**, *130*, 2944.
- 15) Barbe, G.; Charette, A. B. *J. Am. Chem. Soc.* **2007**, *130*, 18.
- 16) Yoo, W.-J.; Li, C.-J. *J. Am. Chem. Soc.* **2006**, *128*, 13064.
- 17) Liu, L.; Yun, L.; Wang, Z.; Fu, X.; Yan, C.-H. *Tet. Lett.* **2013**, *54*, 5383.
- 18) Prediger, P. C.; Barbosa, L. S. F.; Génisson, Y.; Correia, C. R. D. *J. Org. Chem.* **2011**, *76*, 7737.
- 19) Pagar, V. V.; Jadhav, A. M.; Liu, R.-S. *J. Am. Chem. Soc.* **2011**, *133*, 20728.