Applications of Organo Selenides in the Suzuki, Negishi, Sonogashira and Kumada Cross-Coupling Reactions

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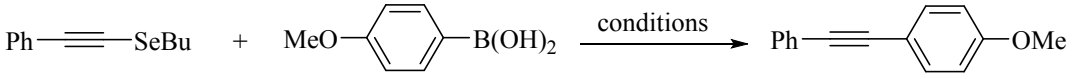
SUPPORTING INFORMATION

Materials and Methods

Proton nuclear magnetic resonance spectra (^{1}H NMR) were obtained on a NMR spectrometer at 400 MHz. Spectra were recorded in $CDCl_3$ solutions. Chemical shifts are reported in ppm, referenced to the solvent peak of $CDCl_3$ or tetramethylsilane (TMS) as the external reference. Data are reported as follows: chemical shift (δ), multiplicity, coupling constant *(J)* in Hertz and integrated intensity. Carbon-13 nuclear magnetic resonance spectra (^{13}C NMR) were obtained on a 400 NMR spectrometer at 100 MHz. Spectra were recorded in $CDCl_3$ solutions. Chemical shifts are reported in ppm, referenced to the solvent peak of $CDCl_3$. Abbreviations to denote the multiplicity of a particular signal are s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sex (sextet), dt (double triplet), td (triple doublet) and m (multiplet). High resolution mass spectra were recorded on a mass spectrometer using electrospray ionization (ESI). Column chromatography was performed using Silica Gel (230-400 mesh) following the methods described by Still. Thin layer chromatography (TLC) was performed using Gel GF_{254}, 0.25 mm thickness. For visualization, TLC plates were either placed under ultraviolet light, or stained with iodine vapor, or acidic vanillin. Most reactions were monitored by TLC for disappearance of starting material. The following solvents were dried and purified by distillation from the reagents indicated: tetrahydrofuran from sodium with a benzophenone ketyl indicator. All other solvents were ACS or HPLC grade unless otherwise noted. Air- and moisture-sensitive reactions were conducted in flame-dried or oven dried glassware equipped with tightly fitted rubber septa and under a positive atmosphere of dry nitrogen or argon. Reagents and solvents were handled using standard syringe techniques.

Table S1:



entry	palladium (mol%)	$Cu(OAc)_2.H_2O$ (equiv)	solvent	temperature ºC	time	Yield[a] (%)
1	$Pd(PPh_3)_4$ (10)	$Cu(OAc)_2.H_2O$ (2)	DMF	100	45 min	94[b]
2	$Pd(PPh_3)_4$ (10)	$Cu(OAc)_2.H_2O$ (2)	DMF	80	45 min	93[b]

3	$Pd(PPh_3)_4$ (10)	$Cu(OAc)_2.H_2O$ (2)	DMF	60	2 h	73[b]
4	$Pd(PPh_3)_4$ (10)	$Cu(OAc)_2.H_2O$ (2)	DMF	r.t.	24 h	63[b]
5	$Pd(PPh_3)_4$ (10)	$Cu(OAc)_2.H_2O$ (2)	DMF	80	45 min	87
6	_	$Cu(OAc)_2.H_2O$ (2)	DMF	80	24 h	36[c]
7	$Pd(PPh_3)_4$ (10)	-	DMF	80	24 h	_[c]
8	$Pd(PPh_3)_4$ (10)	$Cu(OAc)_2.H_2O$ (1)	DMF	80	45 min	76
9	$Pd(PPh_3)_4$ (10)	$Cu(OAc)_2.H_2O$ (0.5)	DMF	80	45 min	50
10	$Pd(PPh_3)_4$ (10)	$Cu(OAc)_2.H_2O$ (1.2)	DMF	80	45 min	94
11	$Pd(PPh_3)_4$ (5)	$Cu(OAc)_2.H_2O$ (1.2)	DMF	80	45 min	76
12	$Pd(PPh_3)_4$ (2)	$Cu(OAc)_2.H_2O$ (1.2)	DMF	80	45 min	50
13	$PdCl_2(PPh_3)_2$ (10)	$Cu(OAc)_2.H_2O$ (1.2)	DMF	80	5h	65
14	$PdCl_2$ (10)	$Cu(OAc)_2.H_2O$ (1.2)	DMF	80	15h	32[c]
15	$Pd_2(dba)_3$ (10)	$Cu(OAc)_2.H_2O$ (1.2)	DMF	80	2h	72
16	$Pd(PPh_3)_4$ (10)	$Cu(OAc)_2.H_2O$ (1.2)	EtOH	78	3h	72
17	$Pd(PPh_3)_4$ (10)	$Cu(OAc)_2.H_2O$ (1.2)	THF	66	2h	83
18	$Pd(PPh_3)_4$ (10)	$Cu(OAc)_2.H_2O$ (1.2)	DMSO	80	1h	72
19	$Pd(PPh_3)_4$ (10)	$Cu(OAc)_2.H_2O$ (1.2)	CH_3CN	80	1h	68
20	$Pd(PPh_3)_4$ (10)	$Cu(OAc)_2.H_2O$ (1.2)	DMF	80	45 min	-[c, d]

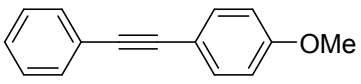
[a] The reactions were performed by using organo selenides **1** (0.25 mmol), boronic acid (1.2 equiv), palladium salt, copper salt, in solvent (3 mL) at 80 ^oC for 45 min. [b] Boronic acid (2 equiv) was used. [c] The starting material was recovered. [d] The reaction was carried out in the presence of K_2CO_3 (2 equiv) and H_2O (1mL).

General Experimental Procedures

General procedure for Suzuki cross-coupling reaction of organo selenides with boronic acids: A mixture of organo selenide (0.25 mmol), $Pd(PPh_3)_4$ (0.1 equiv) and boronic acid (1.2 equiv) were dissolved in DMF (3 mL). After this, the $Cu(OAc)_2.H_2O$ (1.2 equiv) were added. This mixture was then heated in oil bath for 1h at 80 °C. After the reaction was cooled to ambient temperature, diluted with ethyl acetate (3 mL) and then washed with saturated solution of NH_4Cl (20 mL). The organic phase was separated, dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by flash chromatography and eluted with hexane.

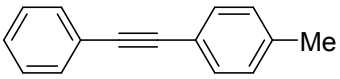
General procedure for Negishi cross-coupling reaction of organo selenides with organo zinc reagents: A mixture of organo selenide (0.25 mmol) and $Pd(PPh_3)_4$ (0.1 equiv) were dissolved in THF (3 mL). After this, the organo zinc reagente (2 equiv) were added. The mixture was then heated in oil bath for 3h at 60 °C. After the reaction was cooled to ambient temperature, the crude reaction mixture was diluted with ethyl acetate (3 mL) and then washed with saturated solution of NH_4Cl (20 mL). The organic phase was separated, dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by flash chromatography and eluted with hexane.

General procedure for Kumada cross-coupling reaction of organo selenides with organo magnesium reagents: A mixture of organo selenide (0.25 mmol) and $Pd(PPh_3)_4$ (0.1 equiv) were dissolved in THF (3 mL). After this, the organo magnesium reagent (2 equiv) were added. The mixture was then heated in oil bath for 2h at 60 °C. After the reaction was cooled to ambient temperature, the crude reaction mixture was diluted with ethyl acetate (3 mL) and then washed with saturated solution of NH_4Cl (20 mL). The organic phase was separated, dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by flash chromatography and eluted with hexane.

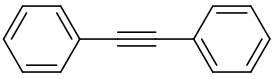


1-methoxy-4-(phenylethynyl)benzene[1] **($C_{15}H_{12}O$) 3a**. Yield: 0.049g (94%). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.55-7.49 (m, 4H), 7.39-7.32 (m,

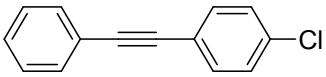
3H), 6.91 (d, J = 8.8 Hz, 2H), 3.91 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.6, 133.1, 131.4, 128.3, 127.9, 123.6, 115.4, 114.0, 89.4, 88.1, 55.3. MS (EI, 70 eV; *m/z* (relative intensity)): 208 (100), 193 (54), 165 (66), 63 (6).



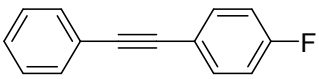
1-methyl-4-(phenylethynyl)benzene[1] **($C_{15}H_{12}$) 3b**. Yield: 0.039g (81%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.56-7.54 (m, 2H), 7.46 (d, J = 8.2 Hz, 2H), 7.37-7.35 (m, 3H), 7.19 (d, J = 8.2 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.4, 131.5, 131.4, 129.1, 128.3, 128.1, 123.5, 120.2, 89.6, 88.7, 21.5. MS (EI, 70 eV; *m/z* (relative intensity)): 192 (100), 165 (24), 64 (11), 51 (4).



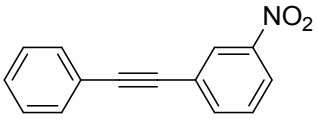
1,2-diphenylethyne[1] **($C_{14}H_{10}$) 3c**. Yield: 0.039g (89%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.55-7.49 (m, 4H), 7.64-7.58 (m, 4H), 7.44-7.37 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 131.7, 128.4, 128.3, 123.4, 89.5. MS (EI, 70 eV; *m/z* (relative intensity)): 178 (100), 152 (18), 89 (10), 76 (15).



1-choro-4-(phenylethynyl)benzene[1] **($C_{14}H_9Cl$) 3d**. Yield: 0.043g (81%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.57-7.54 (m, 2H), 7.50-7.47 (m, 2H), 7.40-7.37 (m, 5H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 134.3, 132.8, 131.6, 129.7, 128.5, 128.4, 122.9, 121.8, 90.3, 88.3. MS (EI, 70 eV; *m/z* (relative intensity)): 212 (100), 176 (59), 151 (16), 88 (12), 75 (10).

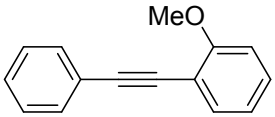


1-fluoro-4-(phenylethynyl)benzene[1] **($C_{14}H_9F$) 3e**. Yield: 0.035g (72%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.58-7.52 (m, 4H), 7.41-7.36 (m, 3H), 7.10-7.04 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.5 (d, J = 249.6 Hz), 133.5 (d, J = 8.1 Hz), 131.6, 128.3, 128.2, 1213.2, 119.5 (d, J = 3.6 Hz), 115.6 (d, J = 22.1 Hz), 89.1, 88.3. MS (EI, 70 eV; *m/z* (relative intensity)): 196 (100), 170 (22), 98 (15), 85 (11).

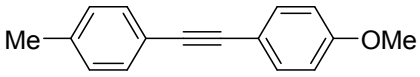


1-nitro-3-(phenylethynyl)benzene[1] **($C_{14}H_9NO$) 3f**. Yield: 0.030g (54%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.40-8.39 (m, 1H), 8.20 (ddd, J = 8.3, 2.3, 1.1 Hz, 2H), 3.91 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.2, 131.8, 129.3,

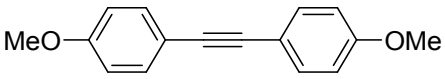
129.0, 128.5, 126.4, 125.2, 122.9, 122.2, 91.9, 86.9. MS (EI, 70 eV; *m/z* (relative intensity)): 223 (100), 176 (98), 151 (38), 88 (15).



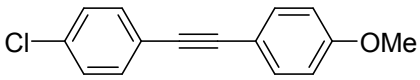
1-methoxy-2-(phenylethynyl)benzene[1] **($C_{15}H_{12}O$) 3g**. Yield: 0.034g (65%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.60-7.52 (m, 3H), 7.39-7.31 (m, 4H), 6.96 (ddd, J = 10.9, 8.7, 4.7 Hz, 1H), 3.95 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 160.1, 133.6, 131.7, 129.7, 128.2, 128.0, 123.7, 120.5, 112.7, 110.9, 93.4, 85.8, 55.9. MS (EI, 70 eV; *m/z* (relative intensity)): 208 (100), 165 (28), 131 (20), 73 (15).



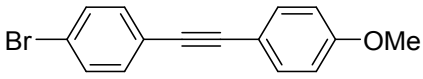
1-methoxy-4-(tolylethynyl)benzene[1] **($C_{16}H_{14}O$) 3h**. Yield: 0.041g (73%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.51-7.44 (m, 4H), 7.18 (d, J = 7.9 Hz, 2H), 6.91 (d, J = 8.8 Hz, 2H), 3.85 (s, 3H), 2.40 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.6, 138.0, 133.0, 131.3, 129.0, 120.6, 115.7, 114.0, 88.7, 88.2, 55.3, 21.4. MS (EI, 70 eV; *m/z* (relative intensity)): 222(39), 207 (100), 178 (26), 133 (16), 77 (14).



1,2-bis(4-metoxyphenyl)ethyne[1] **($C_{16}H_{14}O_2$) 3i**. Yield: 0.050g (84%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.49-7.46 (m, 4H), 6.91-6.87 (m, 4H), 3.85 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.4, 132.9, 115.8, 114.0, 88.0, 55.3. MS (EI, 70 eV; *m/z* (relative intensity)): 238 (100), 223 (92), 152 (47), 119 (15), 63 (28).

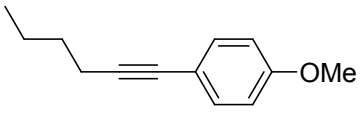


1-choro-4-((4-methoxyphenyl)ethynyl)benzene[1] **($C_{15}H_{11}ClO$) 3j**. Yield: 0.043g (71%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.50-7.44 (m, 4H), 7.35-7.31 (m, 2H), 6.92-6.89 (m, 2H), 3.85 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.9, 133.9, 133.1, 132.6, 128.6, 122.2, 115.1, 114.1, 90.4, 87.0, 55.3. MS (EI, 70 eV; *m/z* (relative intensity)): 243 (70), 206 (100), 192 (13), 76 (8).

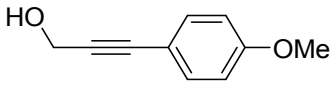


1-bromo-4-((4-methoxyphenyl)ethynyl)benzene[1] **($C_{15}H_{11}BrO$) 3k**. Yield: 0.022g (77%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.55-7.48 (m, 4H), 7.36-7.34 (m, 2H), 6.93-6.89 (m, 2H), 3.86 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz):

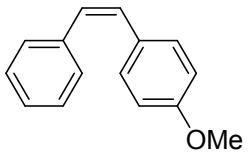
δ 159.7, 135.4, 133.0, 131.4, 128.3, 127.9, 123.7, 114.0, 89.4, 88.1, 55.3. MS (EI, 70 eV; *m/z* (relative intensity)): 287 (70), 207 (100), 198 (68), 165 (50), 63 (5).



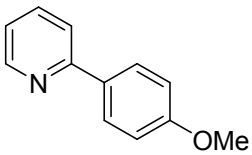
1-(hex-1-ynyl)-4-methoxybenzene[1] **($C_{13}H_{16}O$) 3l**. Yield: 0.080g (77%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.35 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 3.82 (s, 3H), 2.42 (t, J = 7.2 Hz, 2H), 1.63-1.43 (m, 4H), 0.93 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.0, 132.8, 116.4, 113.8, 88.7, 80.2, 55.2, 30.9, 22.0, 13.6. MS (EI, 70 eV; *m/z* (relative intensity)): 188 (13), 159 (9), 149 (47), 145 (100).



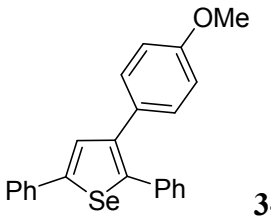
3-(4-methoxyphenyl)prop-2-yn-1-ol[1] **($C_{10}H_{10}O_2$) 3m**. Yield: 0.021g (53%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.41-7.36 (m, 2H), 6.86-6.84 (m, 2H), 4.49 (s, 2H), 3.82 (s, 3H), 1.96 (sl, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.8, 133.2, 129.9, 113.9, 86.0, 85.7, 55.3, 51.7. MS (EI, 70 eV; *m/z* (relative intensity)): 162 (59), 148 (100), 131 (34), 91 (33), 65 (28).



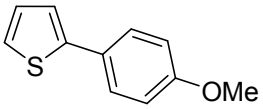
(*Z*)-1-methoxy-4-styrylbenzene[2] **($C_{15}H_{14}O$) 3n**. Yield: 0.040g (77%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.30-7.21 (m, 6H), 6.79 (d, J = 8.8 Hz, 2H), 6.56-6.55 (m, 2H), 3.81 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.7, 137.6, 130.2, 129.8, 129.7, 128.8, 128.7, 128.2, 126.9, 113.6, 55.2. MS (EI, 70 eV; *m/z* (relative intensity)): 210 (100), 16.5 (60), 152 (47), 63 (10).



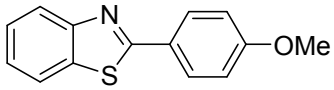
2-(4-methoxypheny)pyridine[3] **($C_{12}H_{11}NO$) 3o**. Yield: 0.033g (72%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.67 (dd, J = 4.8, 0.7 Hz, 1H), 7.97 (d, J = 8.8 Hz, 2H), 7.75-7.67 (m, 2H), 7.19 (ddd, J = 7.0, 4.8, 1.4 Hz, 1H), 7.02 (d, J = 8.8 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 160.6, 157.2, 149.5, 136.6, 132.1, 128.3, 119.7, 114.2, 55.3. MS (EI, 70 eV; *m/z* (relative intensity)): 185 (100), 170 (51), 142 (47), 51 (4).



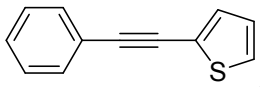
3-(4-methoxyphenyl)-2,5-diphenylselenophene[4] **($C_{23}H_{18}OSe$) 3p**. Yield: 0.052g (54%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.63-7.60 (m, 3H), 7.43-7.39 (m, 2H), 7.34-7.25 (m, 8H), 6.86 (d, J = 8.8 Hz, 2H), 3.84 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.6, 148.2, 143.2, 140.5, 136.4, 136.2, 130.3, 130.2, 129.6, 129.2, 128.9, 128.4, 127.7, 127.2, 126.1, 113.8, 55.2. MS (EI, 70 eV; *m/z* (relative intensity)): 389 (5), 281 (36), 207 (100), 191 (20), 73 (43).



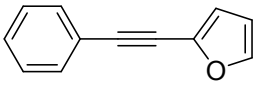
2-(4-methoxyphenyl)thiophene[5] **($C_{11}H_{10}OS$) 3q**. Yield: 0.028g (58%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.56 (d, J = 8.8 Hz, 2H), 7.24-7.22 (m, 2H), 7.08-7.06 (m, 1H), 6.94 (d, J = 8.8 Hz, 2H), 3.86 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.2, 144.3, 127.9, 1127.3, 127.2, 123.8, 122.1, 114.3, 55.4. MS (EI, 70 eV; *m/z* (relative intensity)): 190 (77), 175 (100), 115 (12), 77 (10).



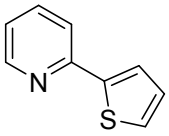
2-(4-methoxyphenyl)benzo[*d*]thiazole[6] **($C_{14}H_{11}NOS$) 3r**. Yield: 0.020g (32%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.08-8.04 (m, 3H), 7.89 (ddd, J = 8.0, 1.3, 0.6 Hz, 1H), 7.51-7.47 (m, 1H), 7.37 (ddd, J = 8.0, 7.2, 1.2 Hz, 1H), 7.02 (d, J = 8.8 Hz, 2H), 3.90 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.8, 161.9, 154.3, 134.9, 129.1, 126.6, 126.2, 124.8, 122.9, 121.5, 114.4, 55.4. MS (EI, 70 eV; *m/z* (relative intensity)): 245 (100), 225 (46), 198 (59), 73 (43).



2-(phenylethynyl)thiophene[1] **($C_{12}H_8S$) 4a**. Yield: 0.038g (82%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.57-7.53 (m, 2H), 7.39-7.36 (m, 3H), 7.32-7.30 (m, 2H), 7.05-7.03 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 132.5, 131.8, 131.4, 129.2, 128.3, 127.2, 127.1, 123.0, 93.0, 82.6. MS (EI, 70 eV; *m/z* (relative intensity)): 184 (100), 152 (24), 139 (23), 51 (2).

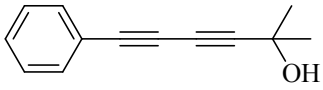


2-(phenylethynyl)furan[1] **($C_{12}H_8O$) 4b**. Yield: 0.024g (58%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.56-7.54 (m, 2H), 7.45-7.44 (m, 1H), 7.38-7.35 (m, 3H), 6.68-6.67 (m, 1H), 6.46-6.44 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.6, 137.3, 131.4, 128.6, 128.3, 122.4, 115.1, 110.9, 93.2, 74.4. MS (EI, 70 eV; *m/z* (relative intensity)): 168 (75), 139 (100), 113 (13), 63 (10).

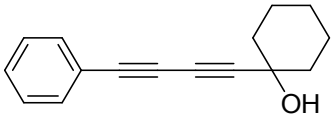


2-(thiophen-2-yl)pyridine[3] **(C_9H_7NS) 4c**. Yield: 0.033g (82%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.59 (ddd, J = 4.9, 1.7, 1.1 Hz, 1H), 7.72-7.61 (m, 3H), 7.41 (dd, J = 5.1, 1.1 Hz, 1H), 7.17-7.12 (m, 2H),). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 152.6, 149.5, 141.2, 136.6, 128.0, 127.5, 124.6, 121.8, 118.8. MS (EI, 70 eV; *m/z* (relative intensity)): 161 (100), 117 (26), 89 (13), 51 (8).

General procedure for Sonogashira cross-coupling reaction of organo selenides with terminal alkynes: A mixture of organo selenide (0.25 mmol), $PdCl_2(PPh_3)_2$ (0.1 equiv), terminal alkyne (4 equiv) and Et_3N (1.0 equiv) were dissolved in DMF (3 mL). After this, the $Cu(OAc)_2.H_2O$ (0.2 equiv) were added. The Schlenk was then heated in oil bath for 24h at 80 °C. After the reaction was cooled to ambient temperature, the crude reaction mixture was diluted with ethyl acetate (3 mL) and then washed with saturated solution of NH_4Cl (20 mL). The organic phase was separated, dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by flash chromatography and eluted with a mixture of hexane/acetate (9:1).

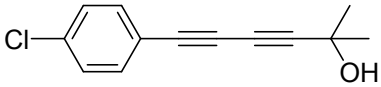


2-methyl-6-phenylhexa-3,5-diyn-2-ol[7] **($C_{13}H_{12}O$) 5a**. Yield: 0.042g (93%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.49-7.26 (m, 5H), 2.09 (sl, 1H), 1.58 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 132.5, 129.2, 128.4, 121.5, 86.7, 78.8, 73.1, 67.0, 65.7, 31.1. MS (EI, 70 eV; *m/z* (relative intensity)): 184 (42), 169 (100), 141 (57), 115 (48), 75 (9).

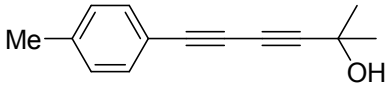


1-(phenylbuta-1,3-diynyl)cyclohexanol[7] **($C_{16}H_{16}O$) 5b**. Yield: 0.035g (63%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.53-7.50 (m, 2H), 7.40-7.32 (m,

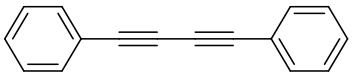
3H), 2.07-1.98 (m, 3H), 1.77-1.57 (m, 8H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 132.5, 129.2, 128.4, 121.7, 86.2, 78.5, 73.4, 69.3, 68.9, 39.7, 25.1, 23.1. MS (EI, 70 eV; *m/z* (relative intensity)): 224 (65), 181 (100), 167 (87), 126 (67), 55 (57).



6-(4-chlorophenyl)-2-methylhexa-3,5-diyn-2-ol[7] **($C_{13}H_{11}ClO$) 5c**. Yield: 0.042g (88%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.42-7.27 (m, 4H), 2.34 (sl, 1H), 1.58 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 135.4, 133.7, 128.8, 120.0, 87.3, 74.1, 69.0, 66.8, 65.7, 31.1. MS (EI, 70 eV; *m/z* (relative intensity)): 184 (42), 169 (100), 141 (57), 115 (48), 75 (9).



2-methyl-6-*p*-tolylhexa-3,5-diyn-2-ol[7] **($C_{14}H_{14}O$) 5d**. Yield: 0.044g (88%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.25 (d, J = 7.9 Hz, 2H), 7.00 (d, J = 7.9 Hz, 2H), 2.23-2.13 (m, 4H), 1.42 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 139.6, 132.4, 129.2, 118.5, 86.5, 79.1, 72.6, 67.2, 65.7, 31.2, 21.5. MS (EI, 70 eV; *m/z* (relative intensity)): 198 (75), 139 (100), 113 (13), 63 (10).



1,4-diphenylbuta-1,3-diyne[7] **($C_{16}H_{10}$) 5e**. Yield: 0.047g (93%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.58-7.55 (m, 4H), 7.42-7.34 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 132.5, 129.2, 128.4, 121.9, 81.6, 74.0. MS (EI, 70 eV; *m/z* (relative intensity)): 202 (100), 150 (13), 133 (12), 101 (12), 73 (18).

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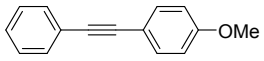

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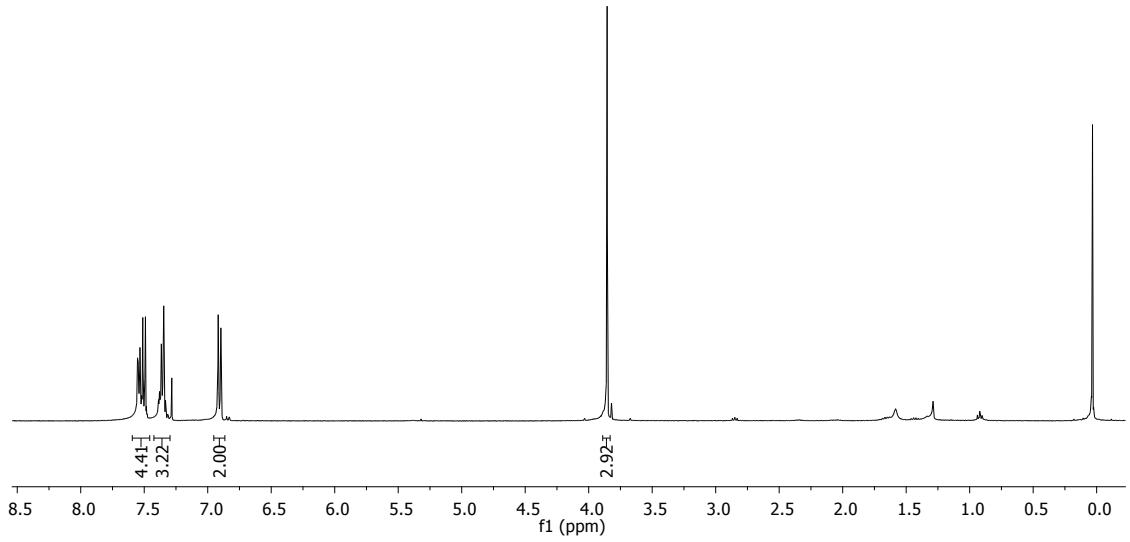

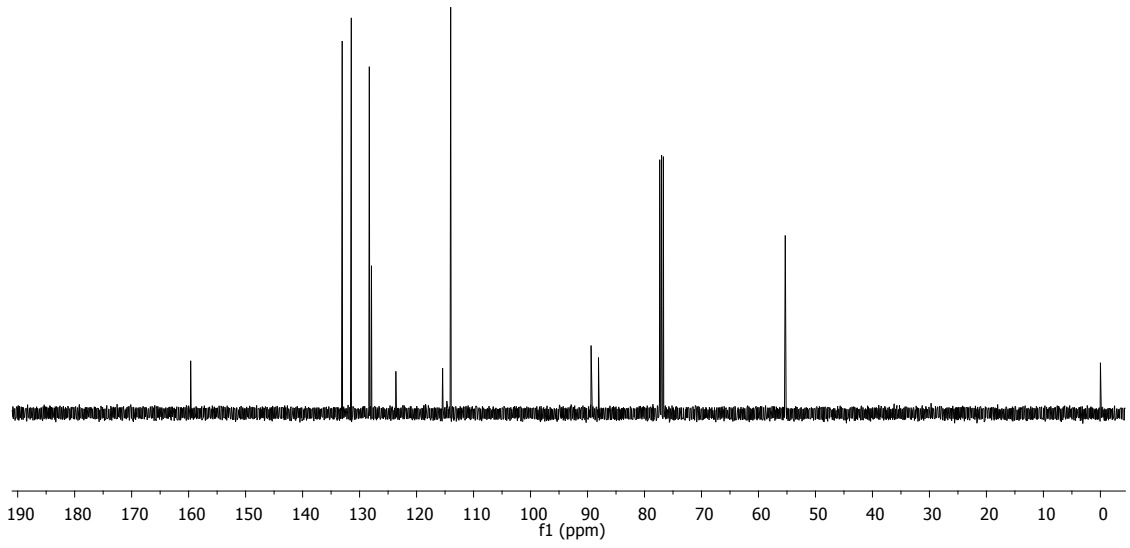

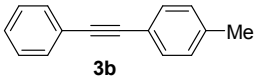
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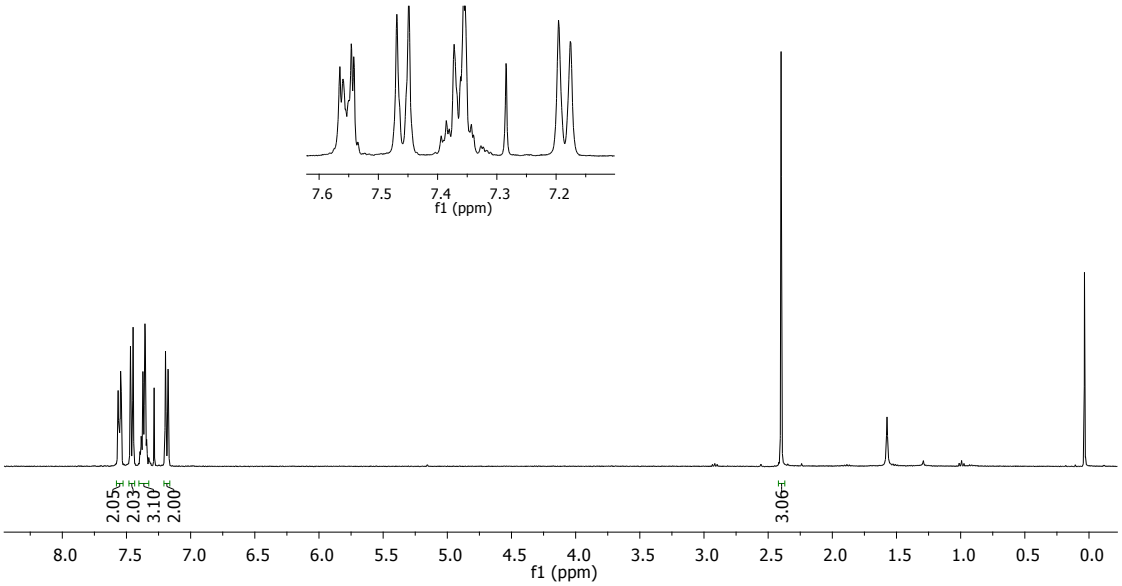
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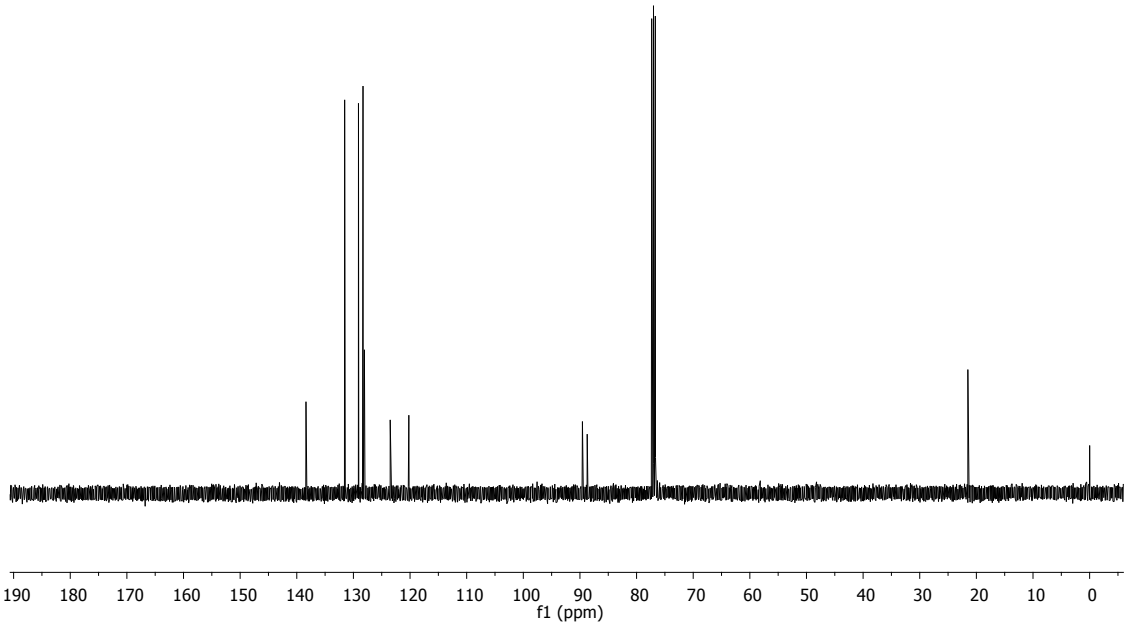
f1 (ppm)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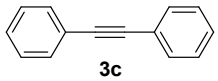
f1 (ppm)



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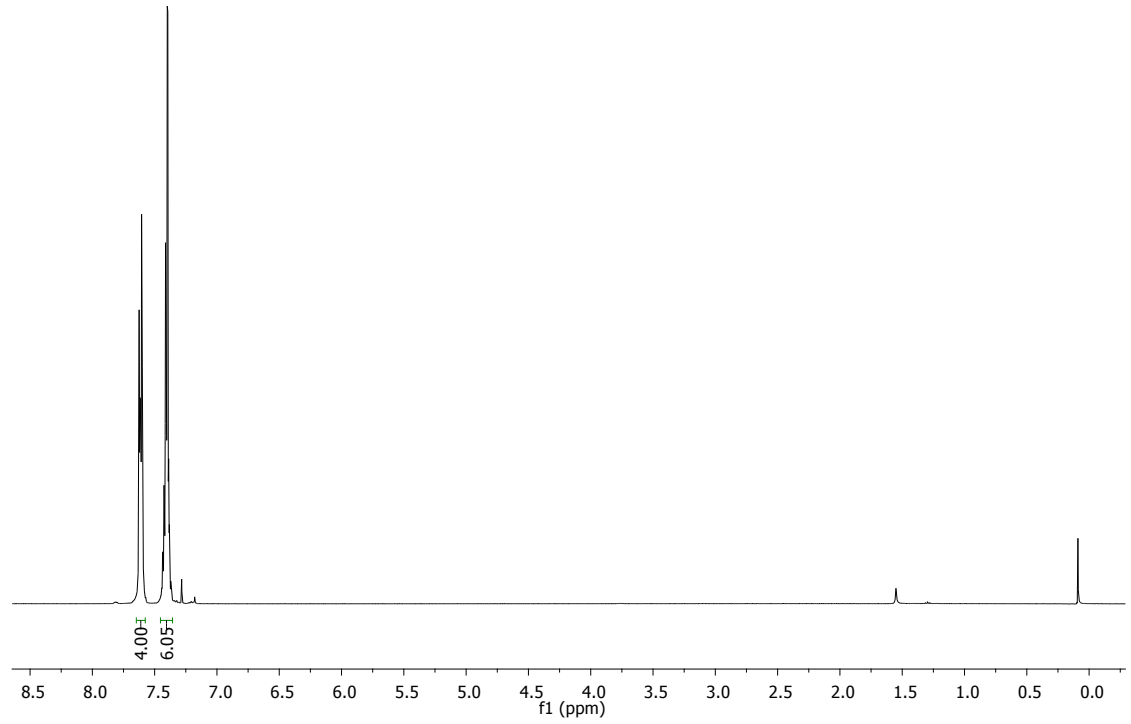
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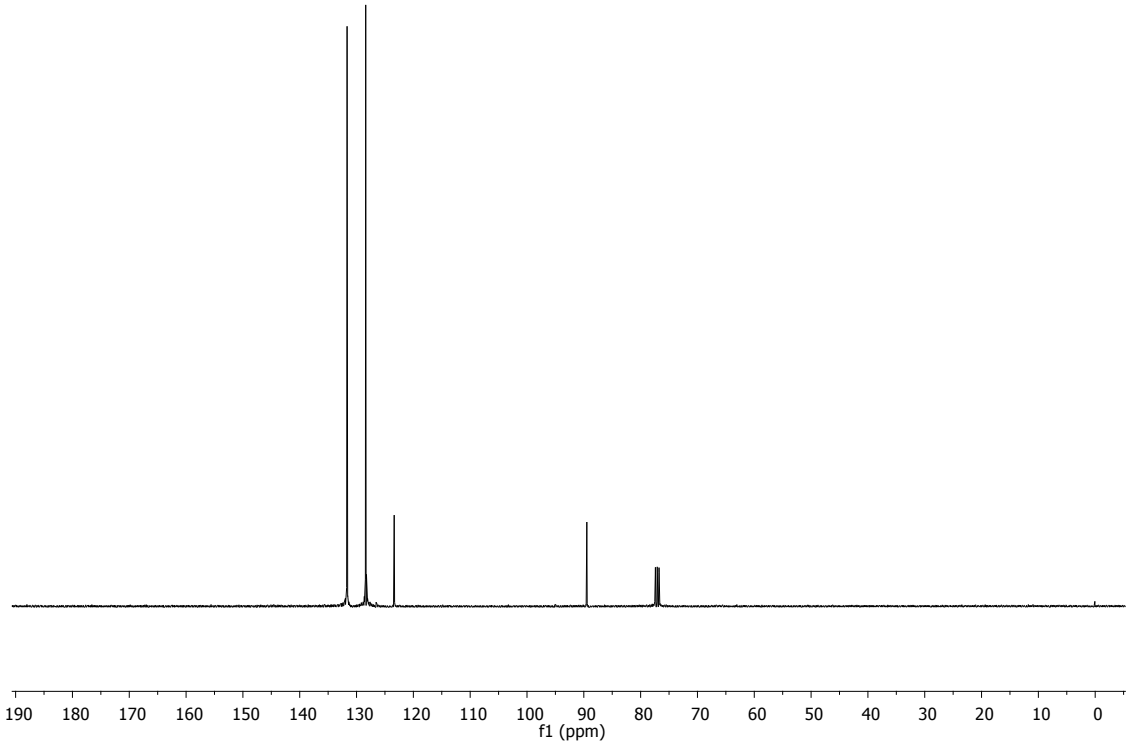
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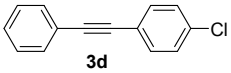
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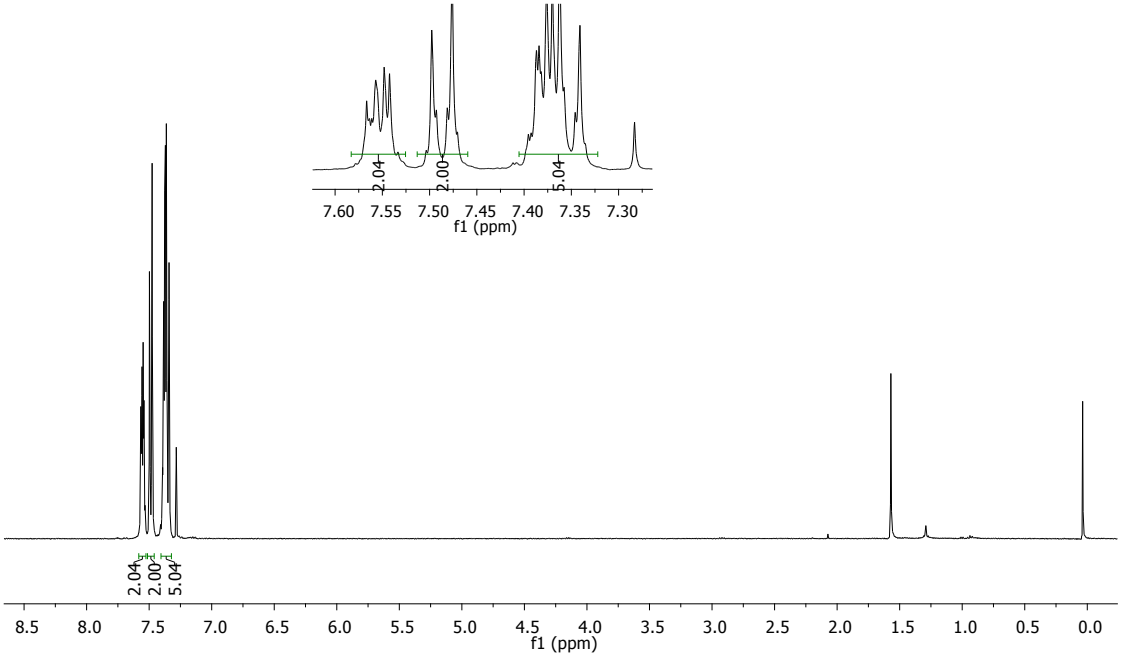
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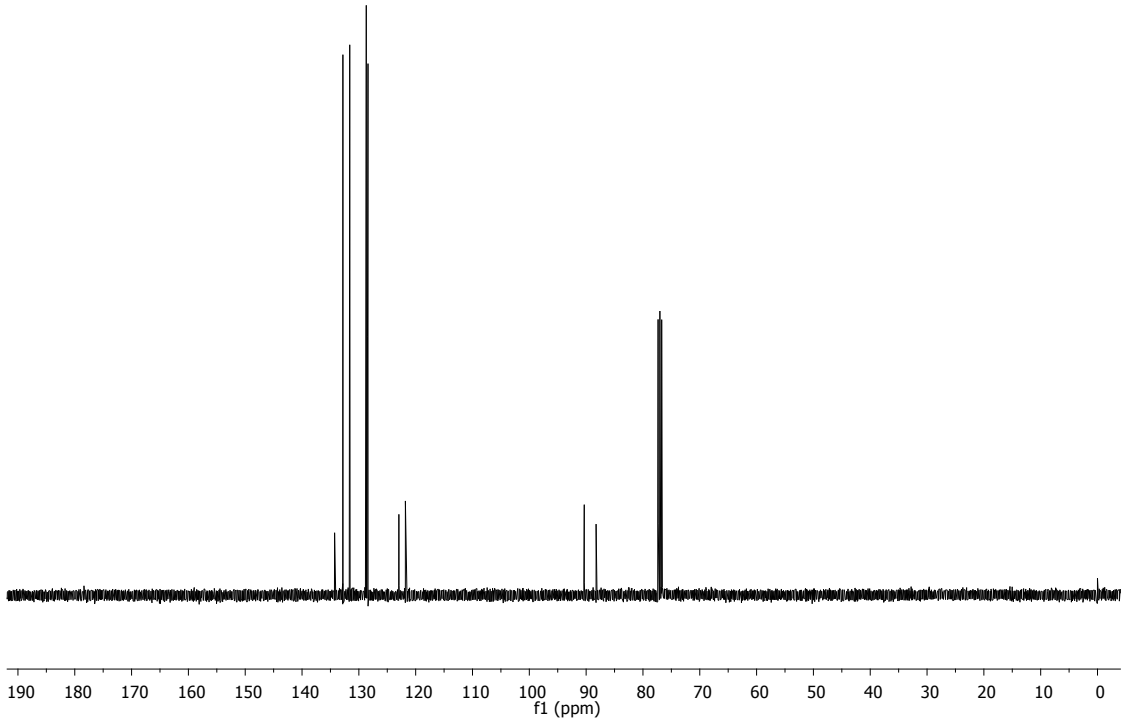
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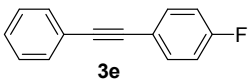
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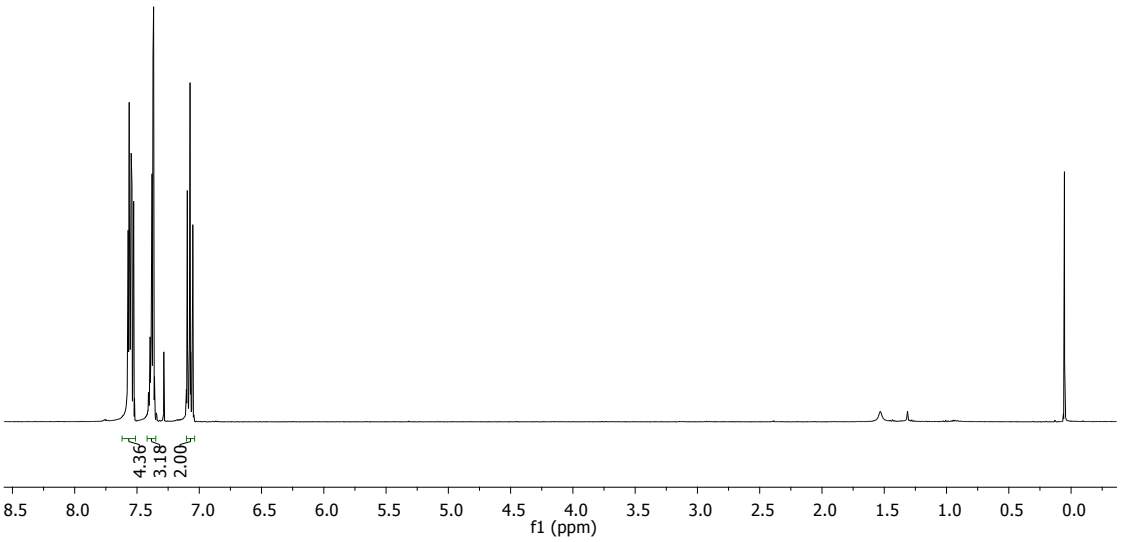
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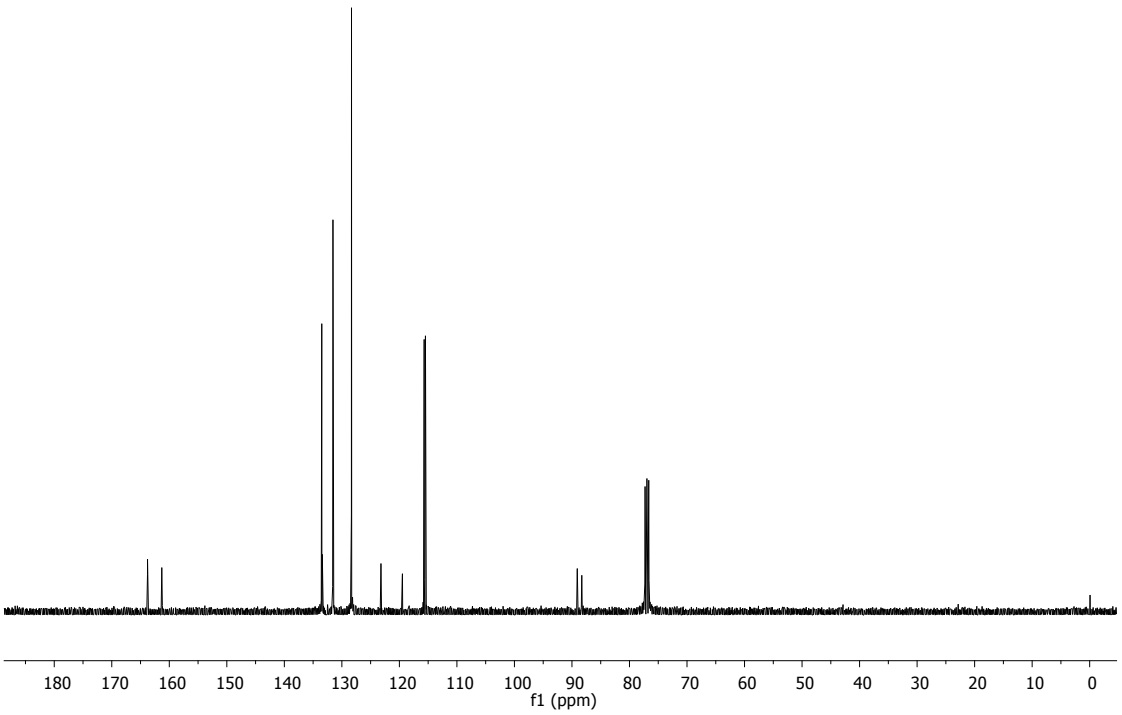
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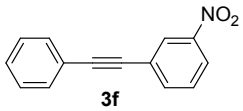
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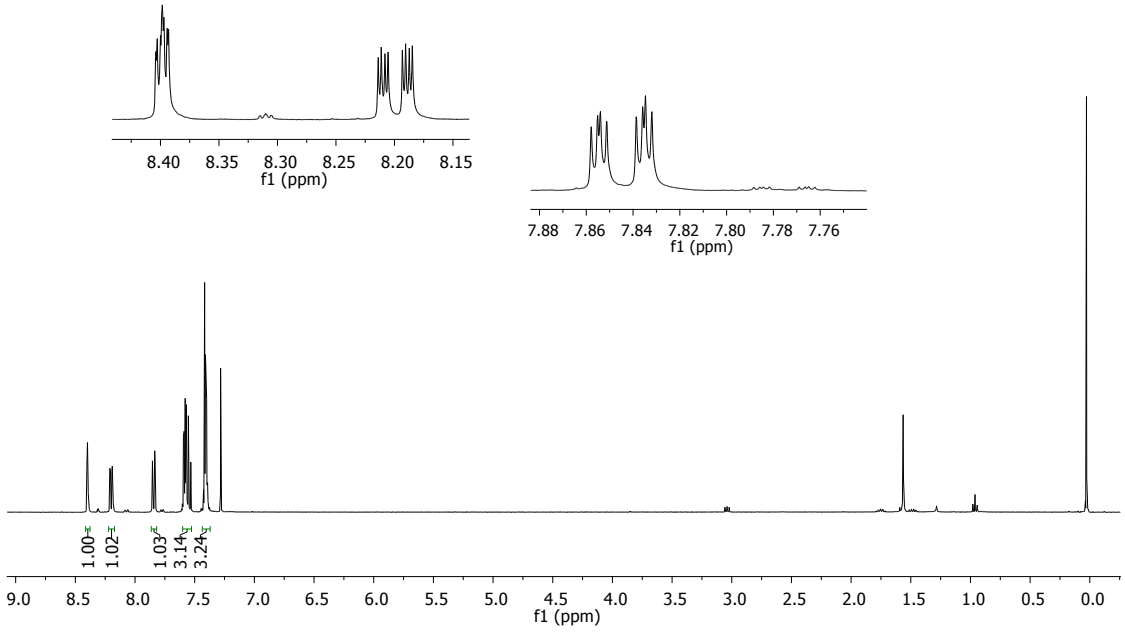
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3.14
3.24
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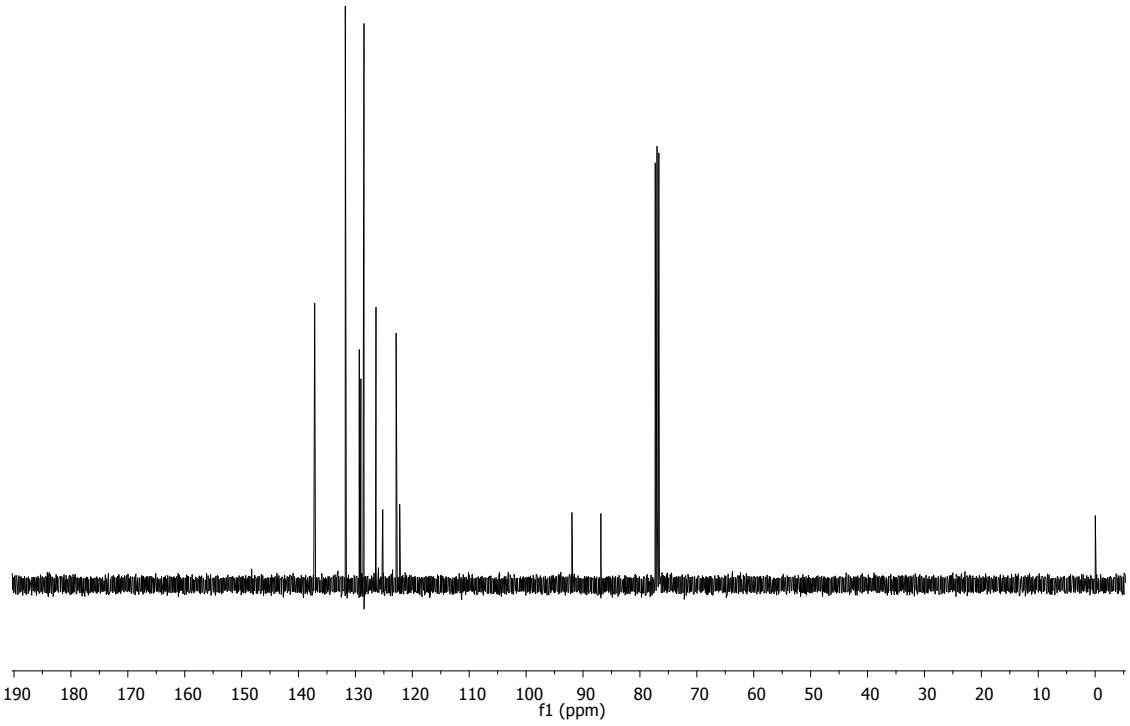
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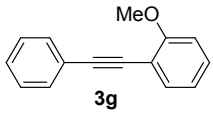
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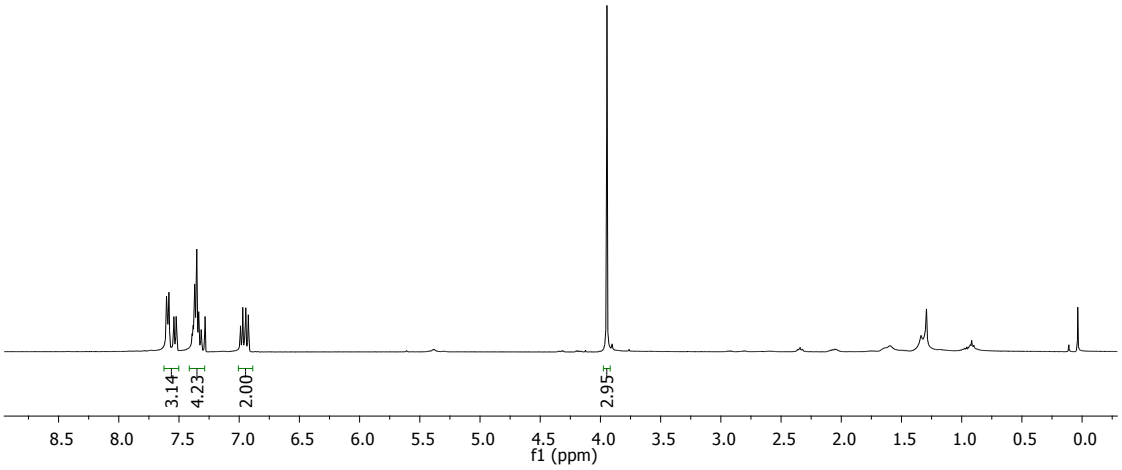
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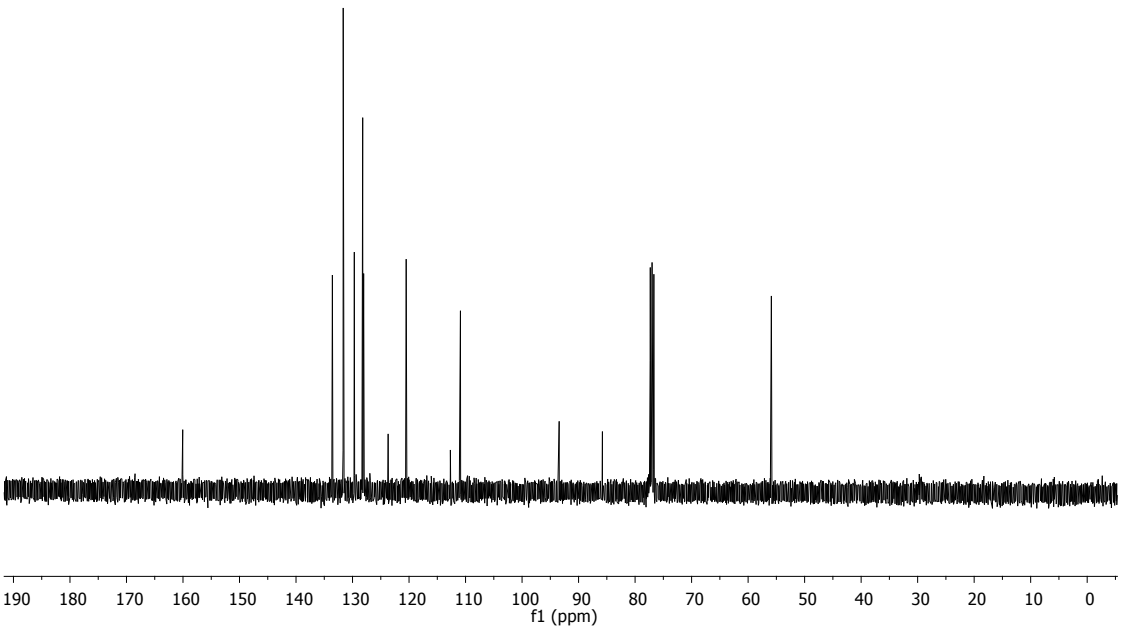
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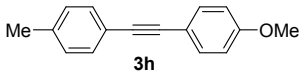
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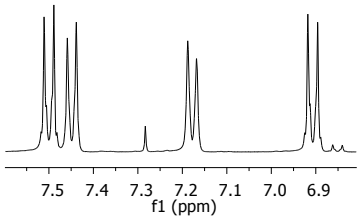
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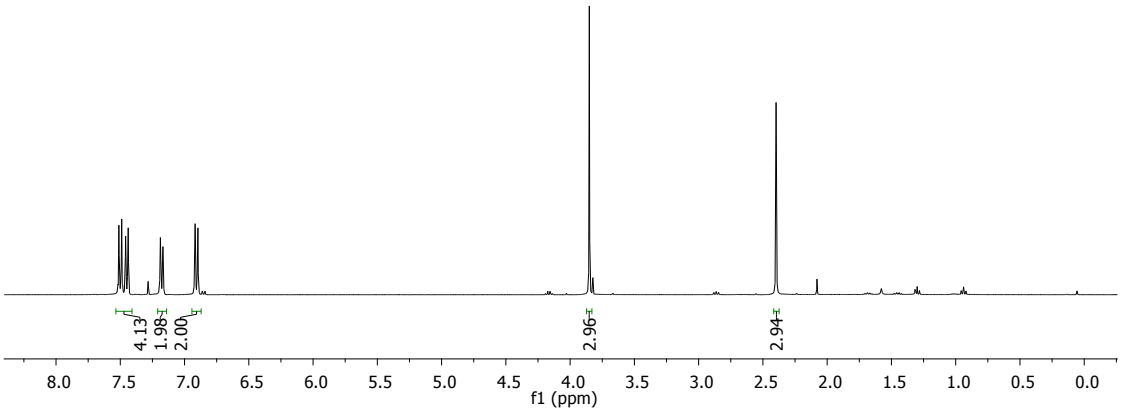
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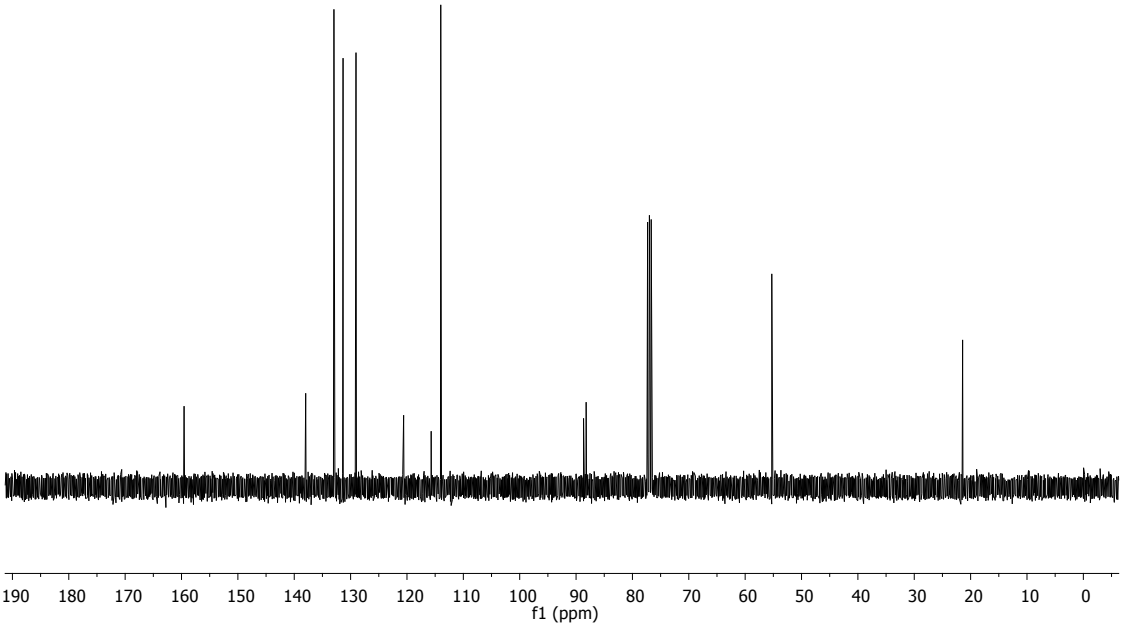
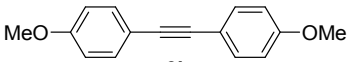
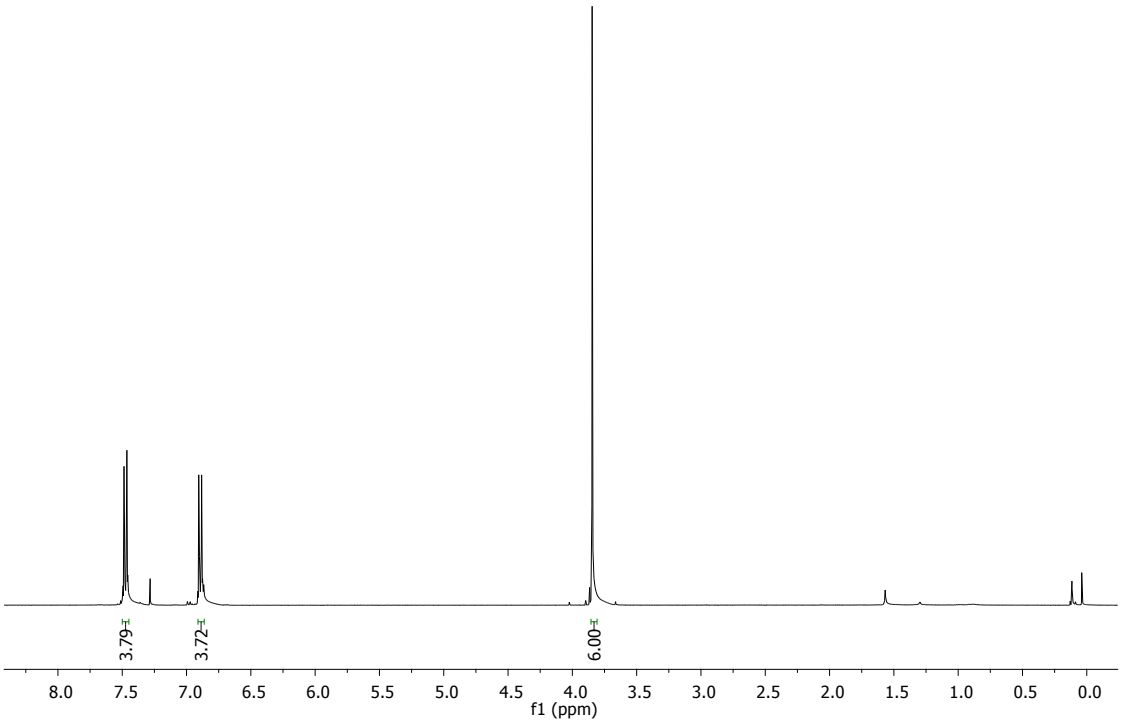
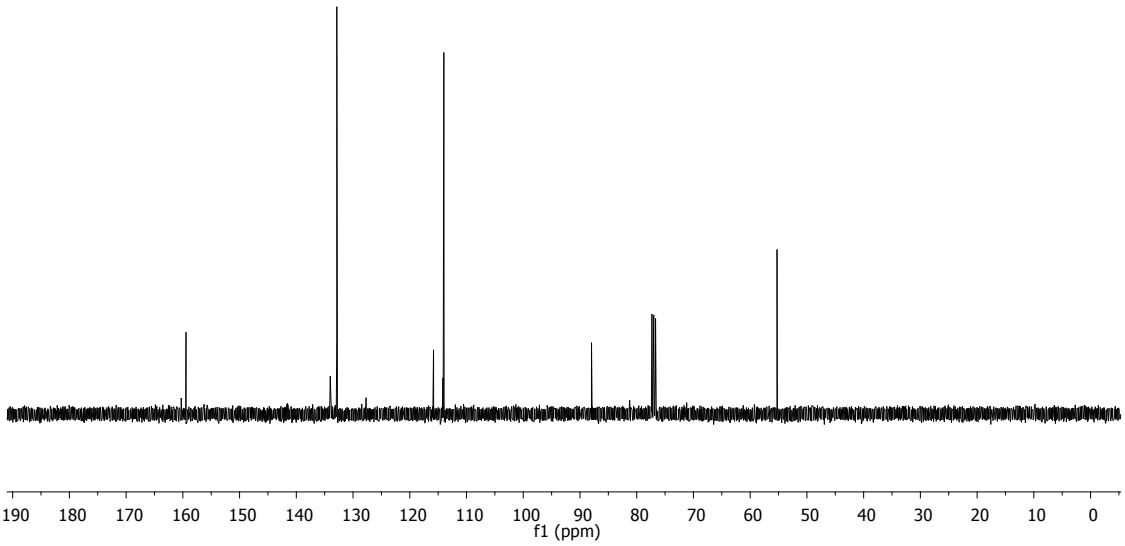
1.98
2.00
2.96
2.94
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

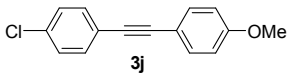

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


MeO
OMe

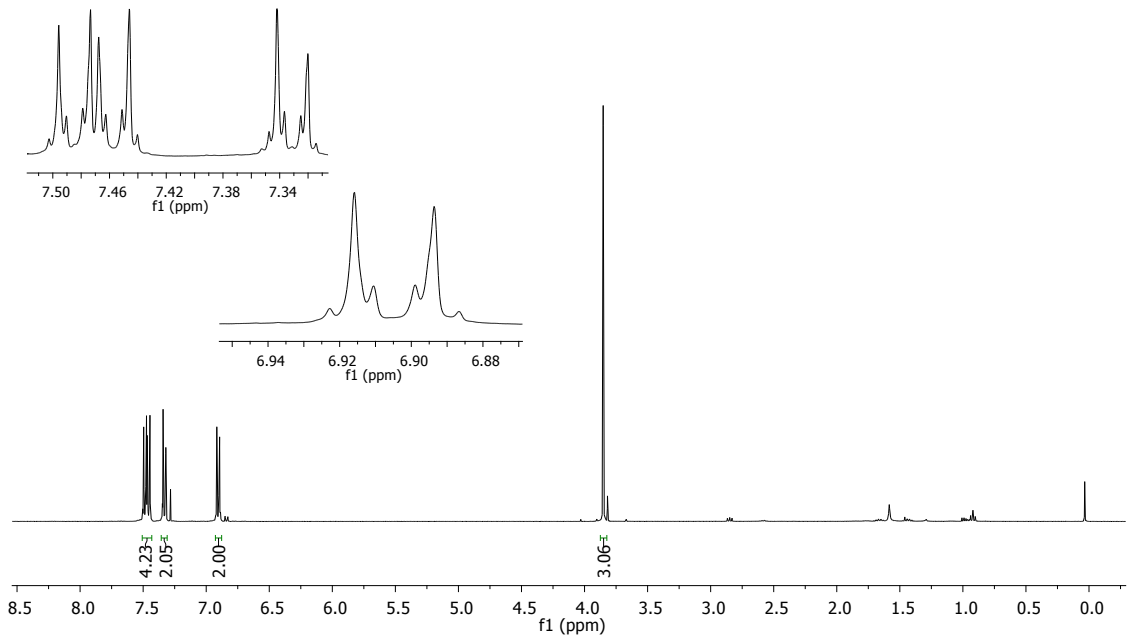
3i

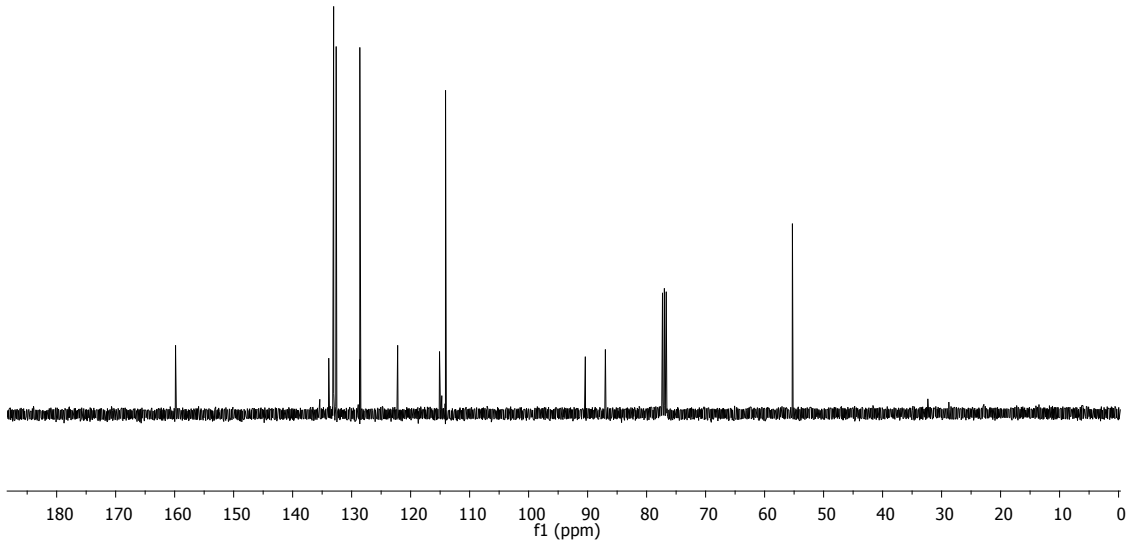

3.79
3.72
6.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

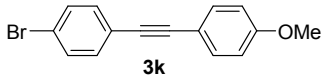

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Cl
OMe

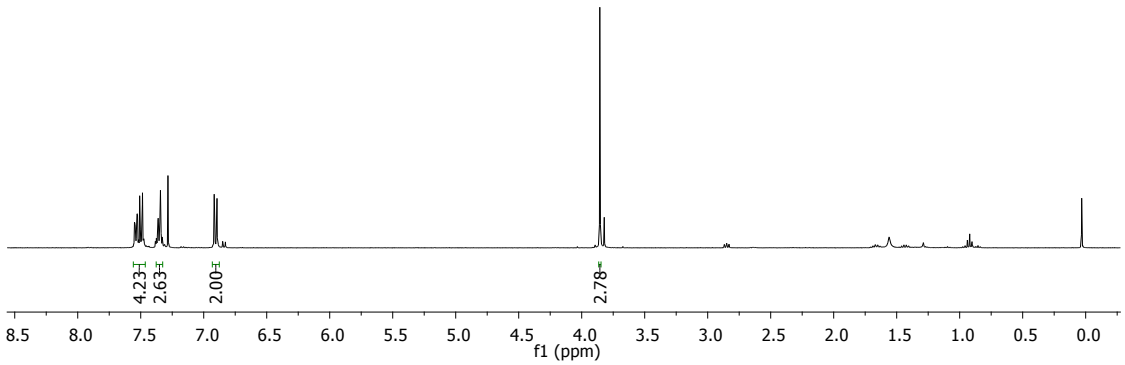
3j

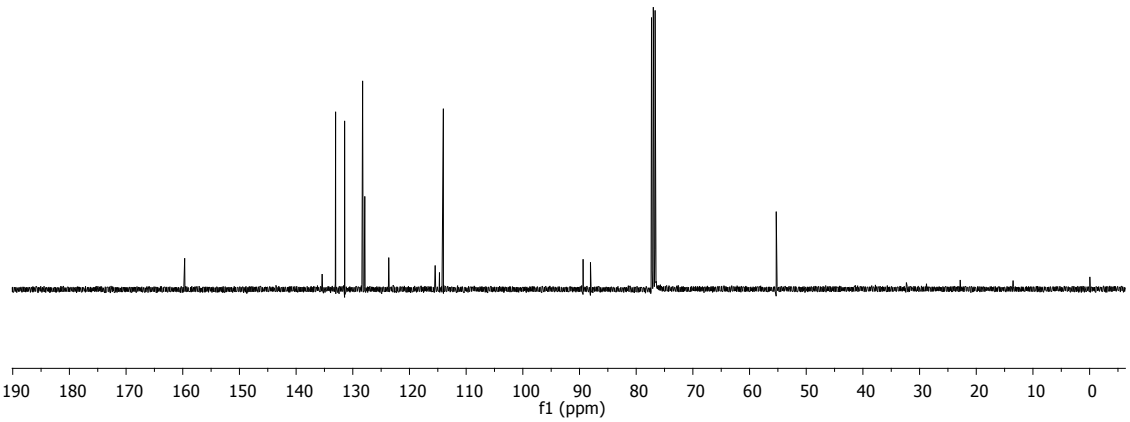

7.50
7.46
7.42
7.38
7.34
f1 (ppm)
6.94
6.92
6.90
6.88
f1 (ppm)
4.23
2.05
2.00
3.06
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

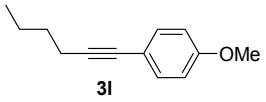

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Br
OMe

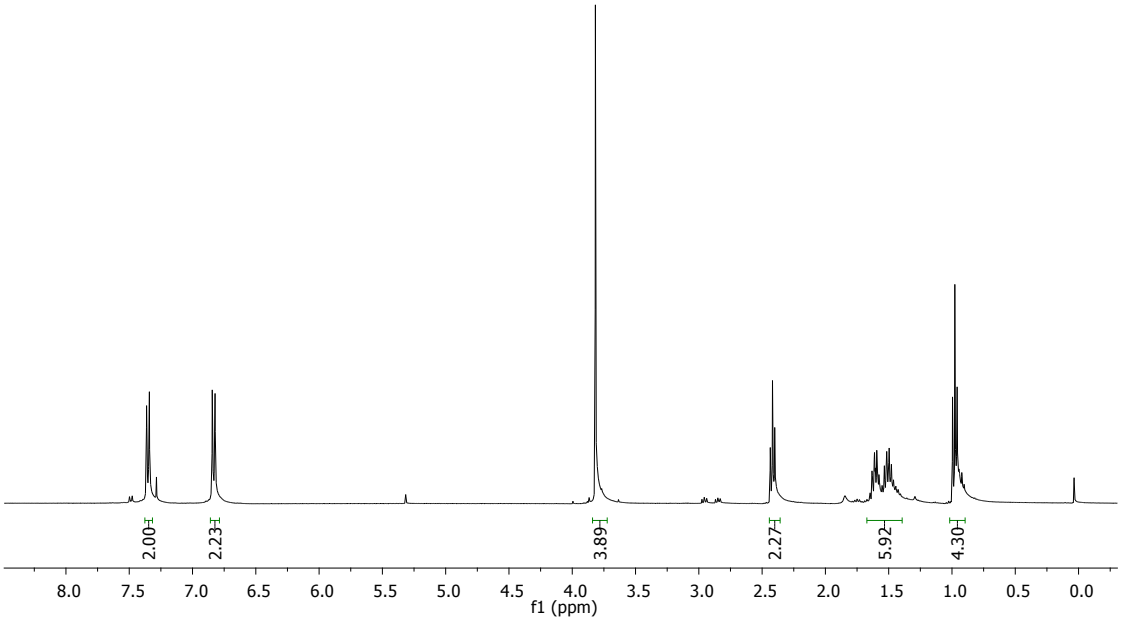
3k

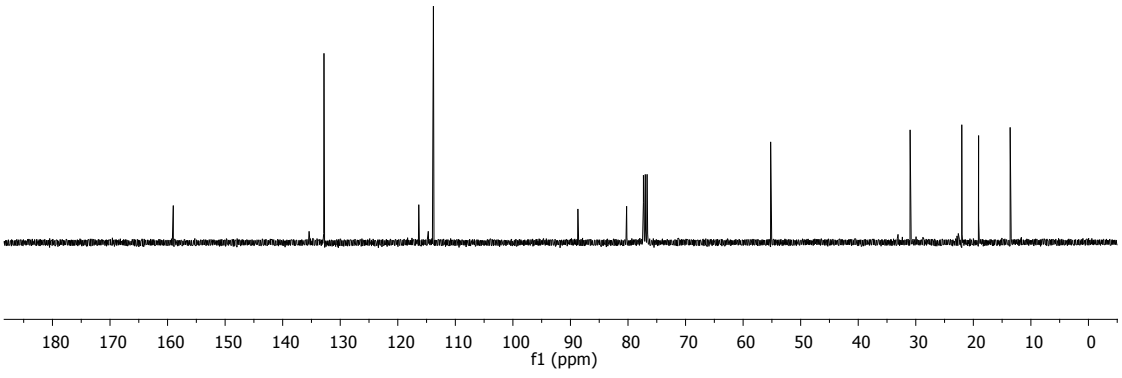

4.23
2.63
2.00
2.78
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

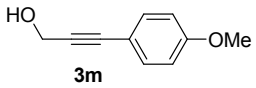

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


OMe

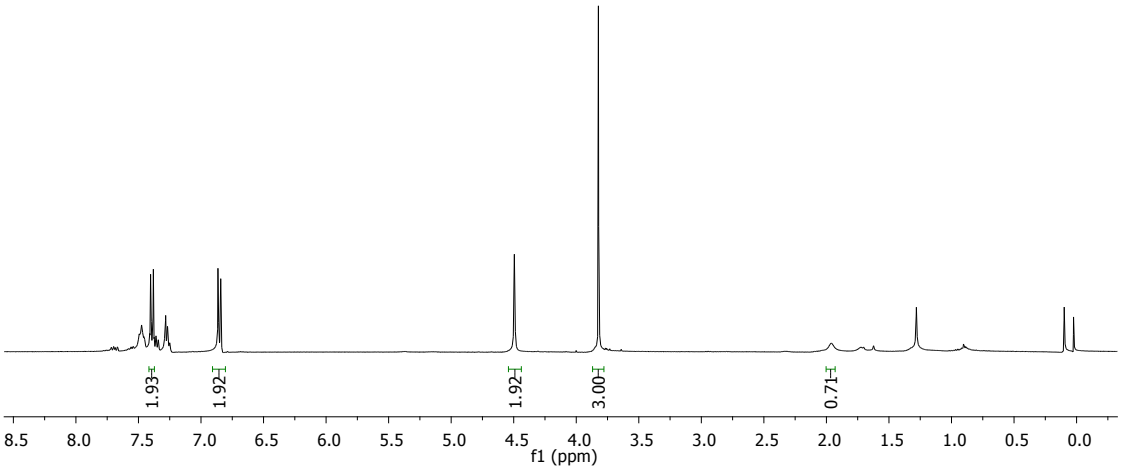
3l

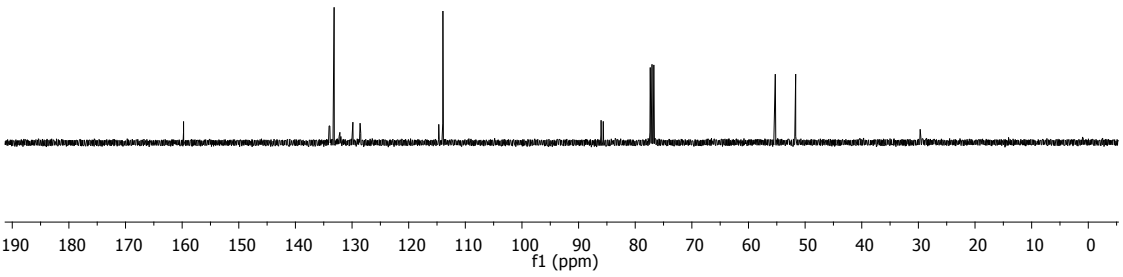

2.00
2.23
3.89
2.27
5.92
4.30
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

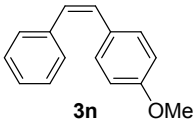

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


HO
OMe

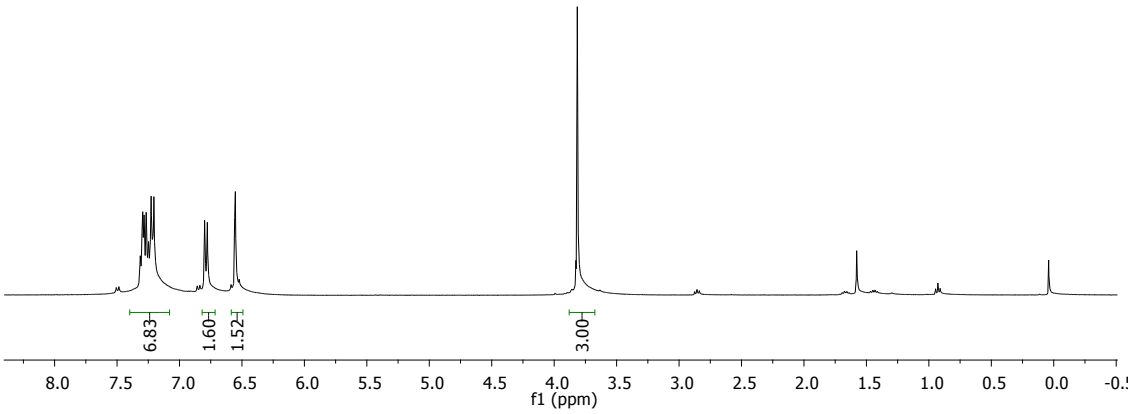
3m

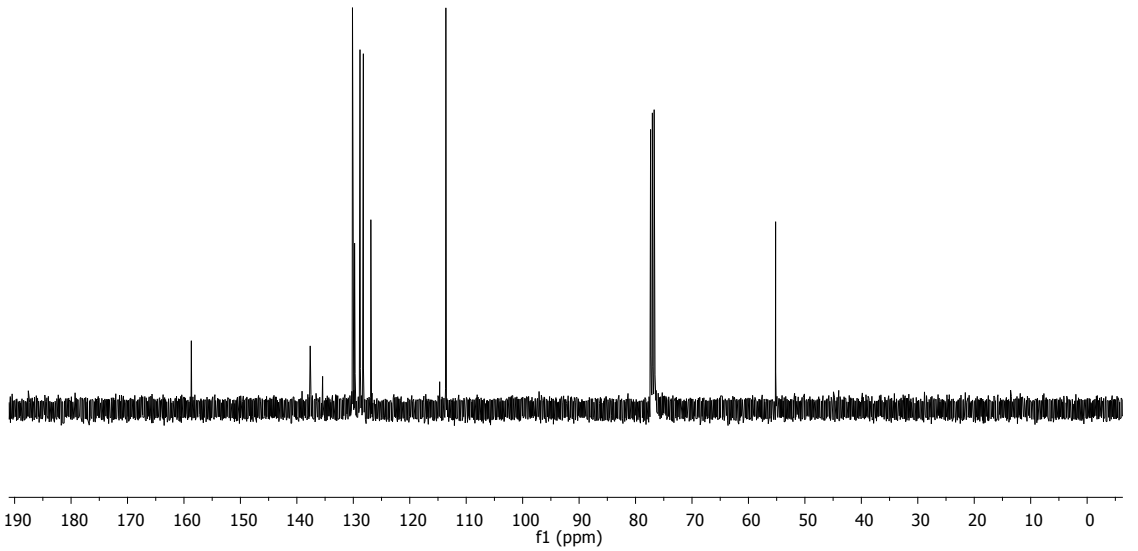

1.93
1.92
1.92
3.00
0.71
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

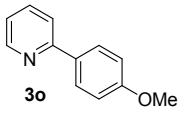

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


OMe

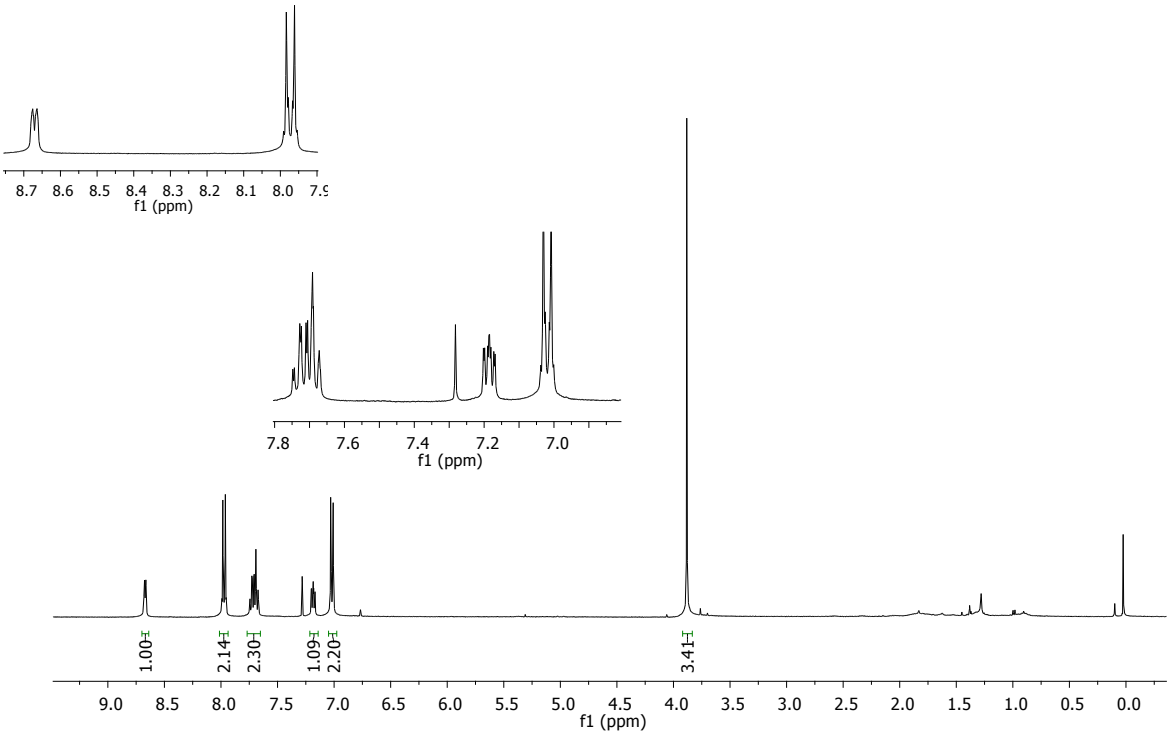
3n

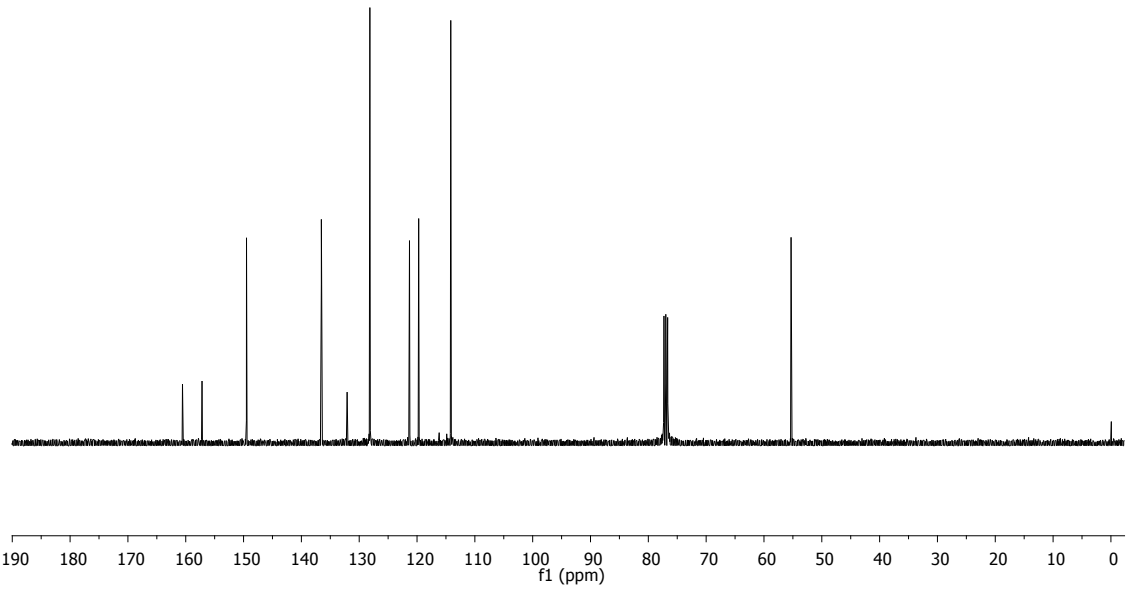

6.83
1.60
1.52
3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

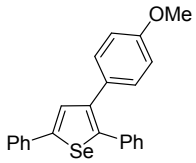

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


N
OMe

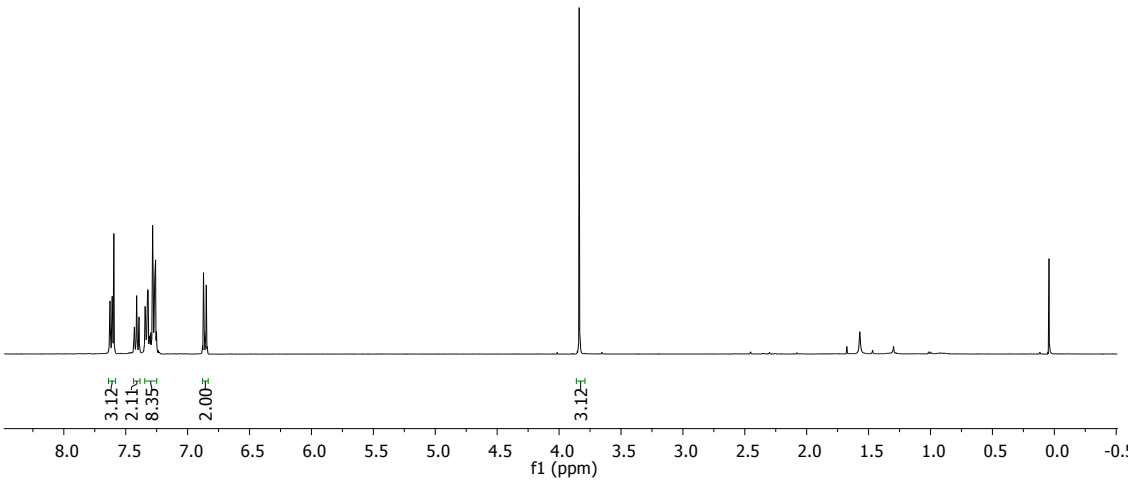
3o

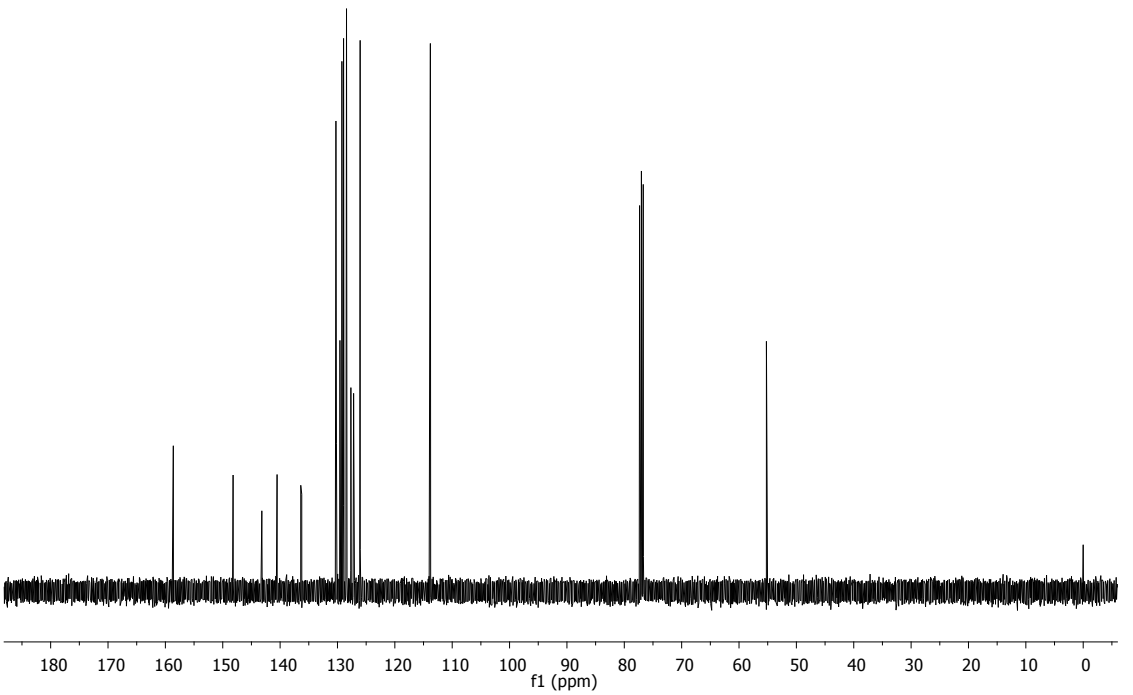

8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9
f1 (ppm)
7.8 7.6 7.4 7.2 7.0
f1 (ppm)
1.00
2.14
2.30
1.09
2.20
3.41
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

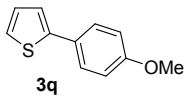

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


OMe
Ph
Se
Ph

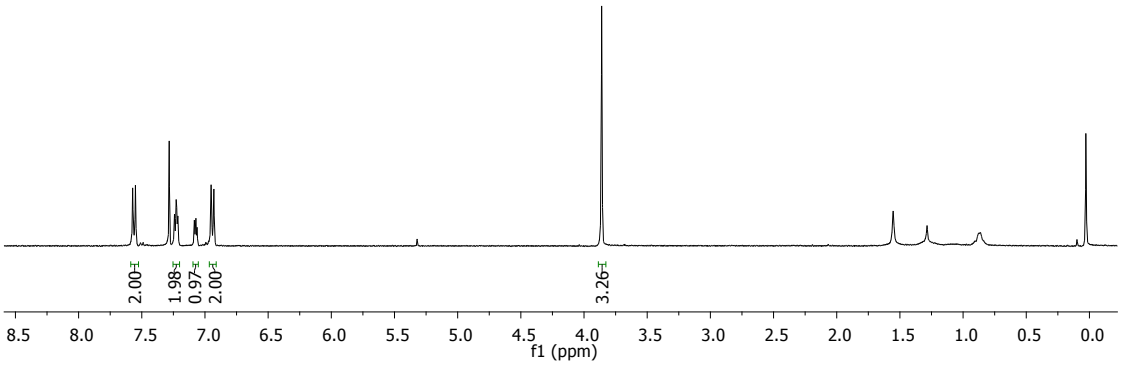
3p

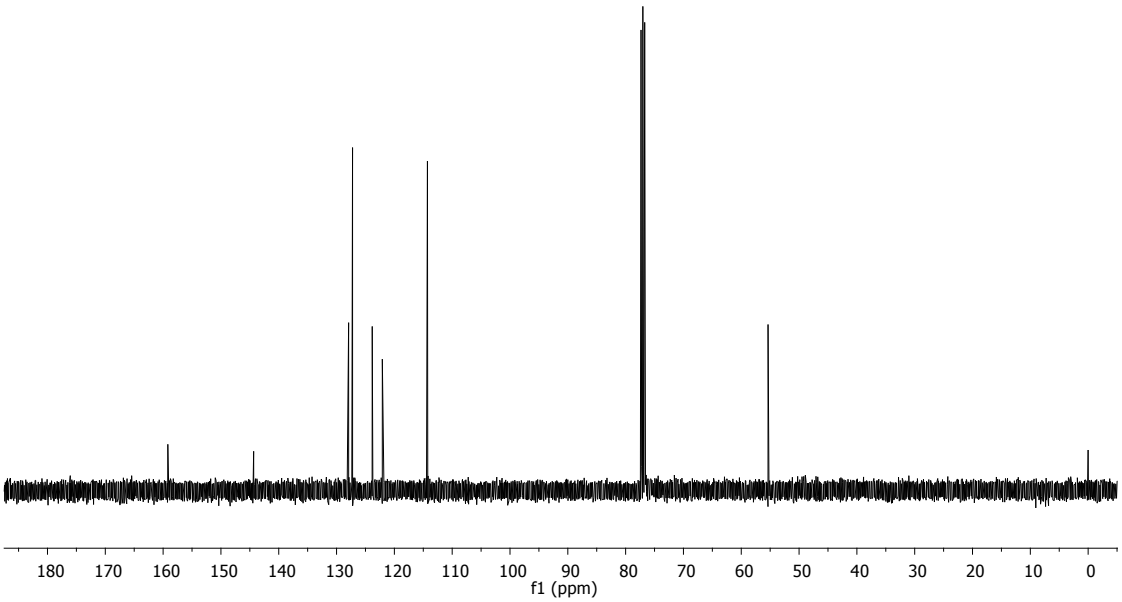

3.12
2.11
8.35
2.00
3.12
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

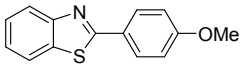

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


S
OMe

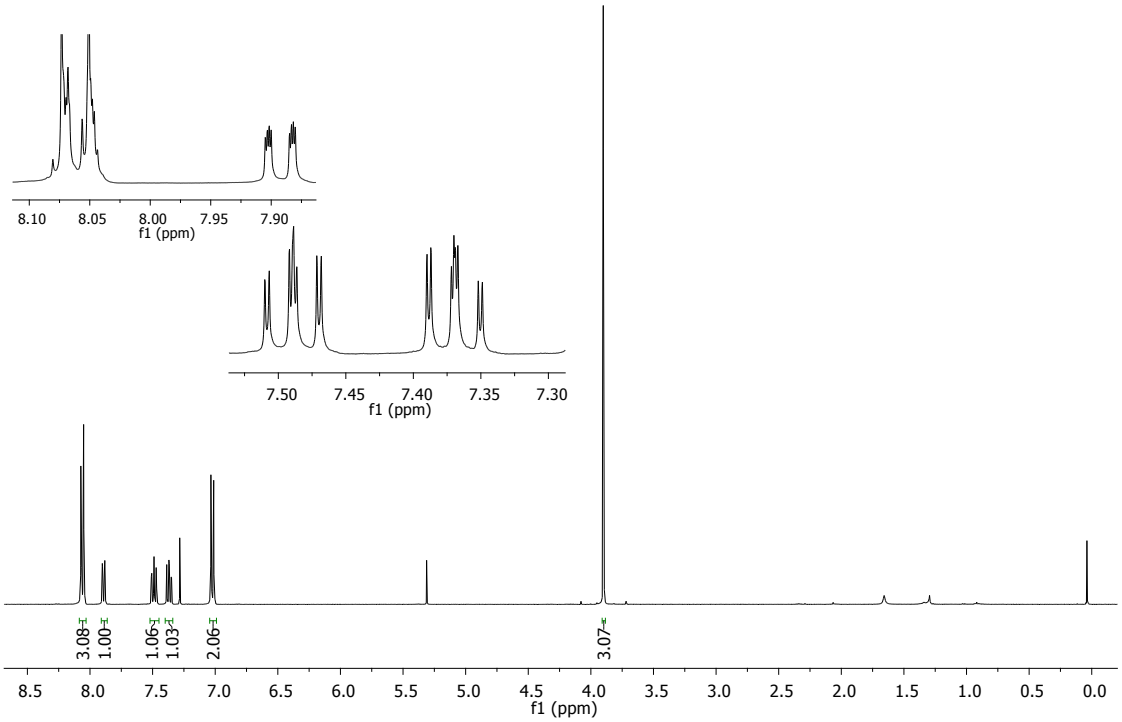
3q

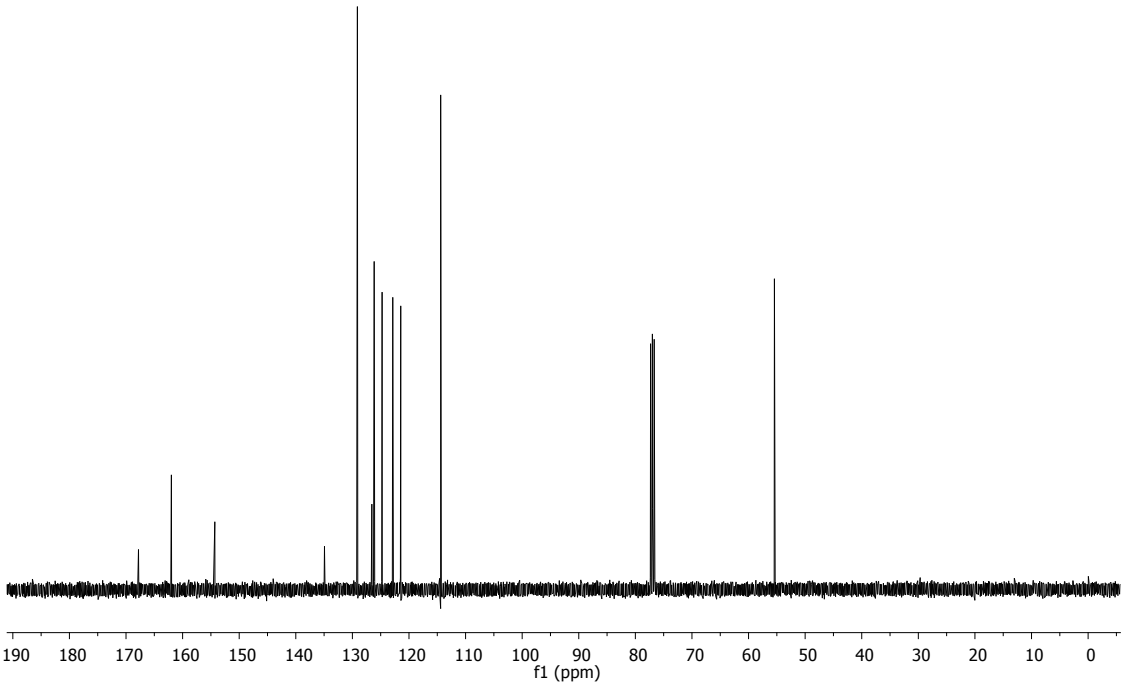

2.00
1.98
0.97
2.00
3.26
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

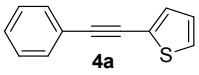

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


N
S
OMe

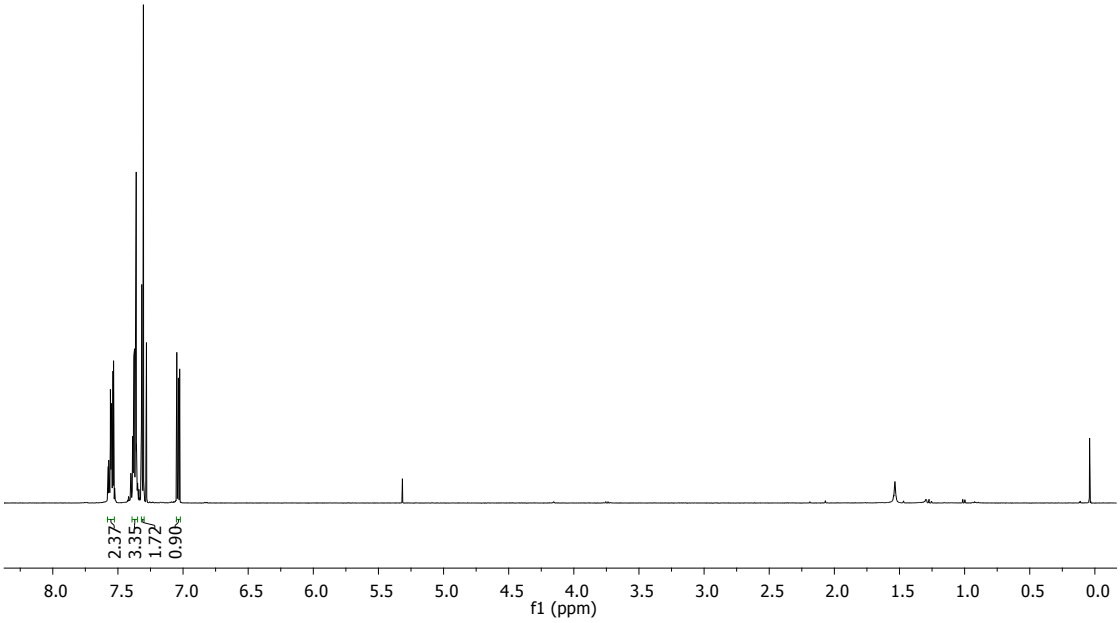
3r

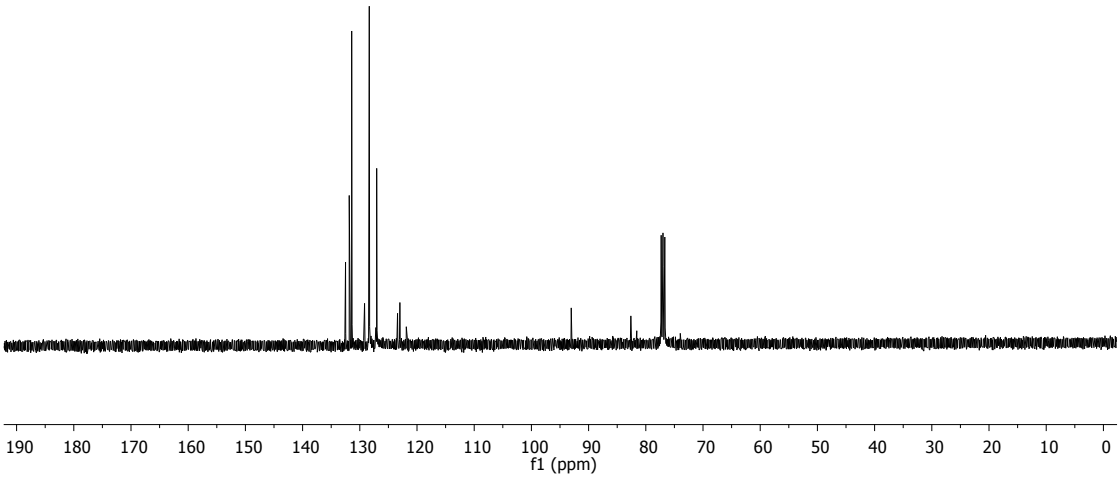

8.10
8.05
8.00
7.95
7.90
f1 (ppm)
7.50
7.45
7.40
7.35
7.30
f1 (ppm)
3.08
1.00
1.06
1.03
2.06
3.07
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

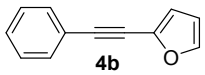

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


S

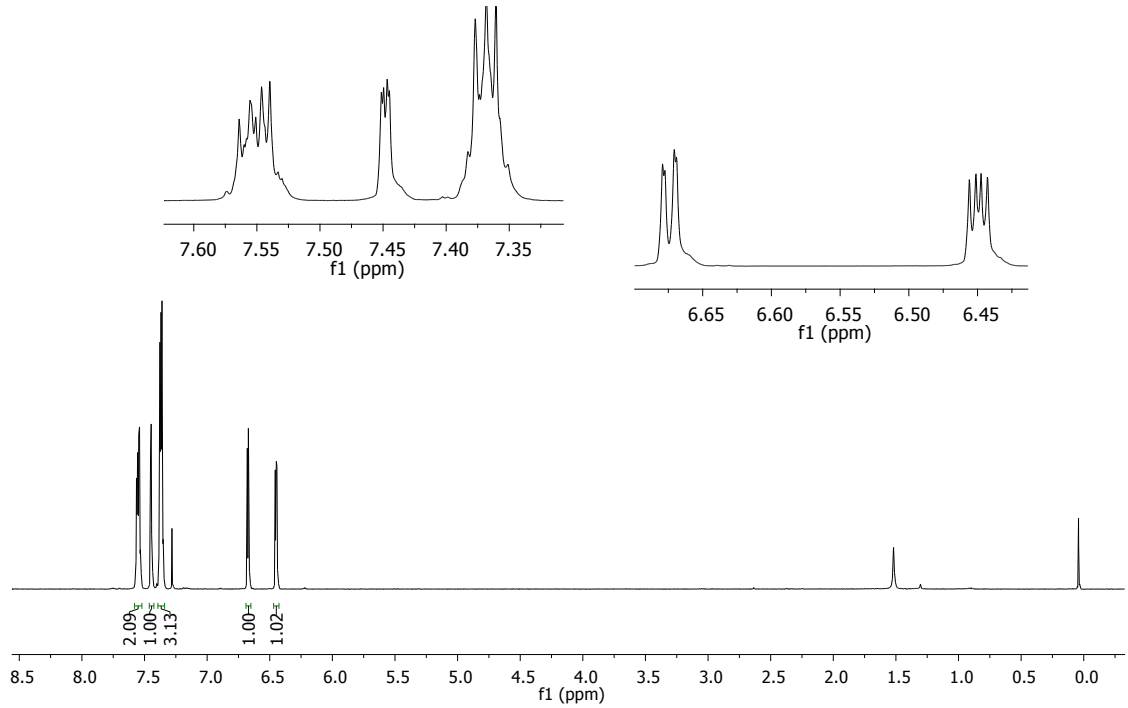
4a

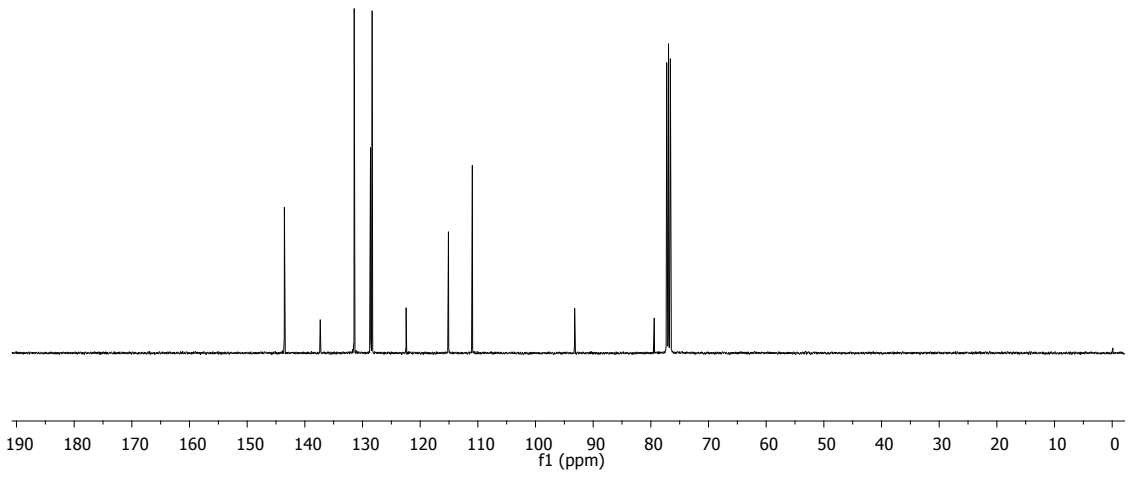

2.37
3.35
1.72
0.90
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

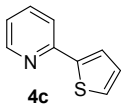

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



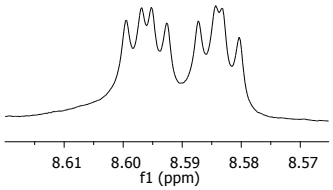
4b

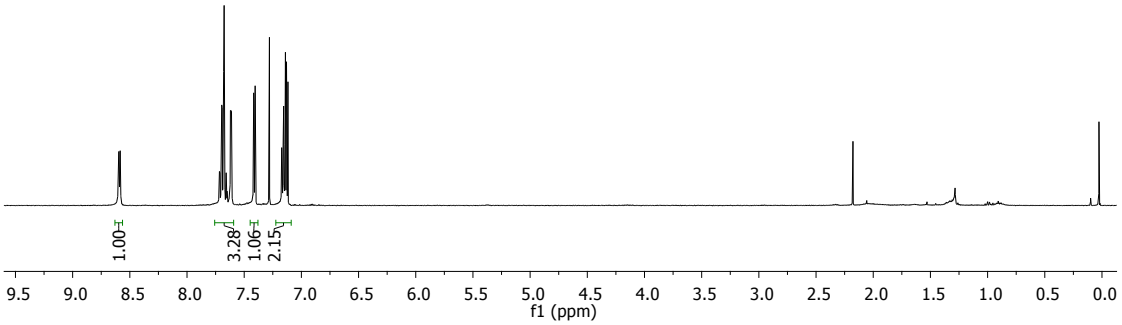

7.60 7.55 7.50 7.45 7.40 7.35
f1 (ppm)
6.65 6.60 6.55 6.50 6.45
f1 (ppm)
2.09
1.00
3.13
1.00
1.02
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

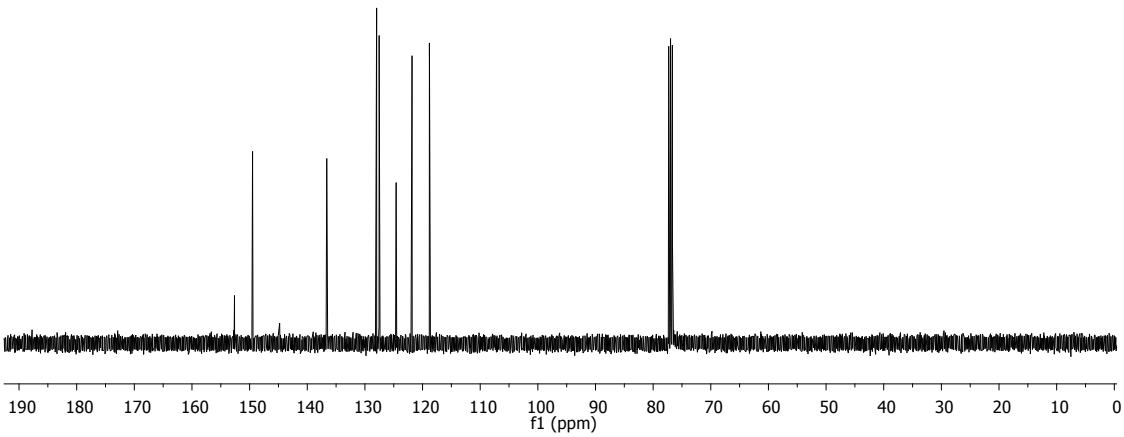

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

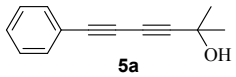

N
S

4c

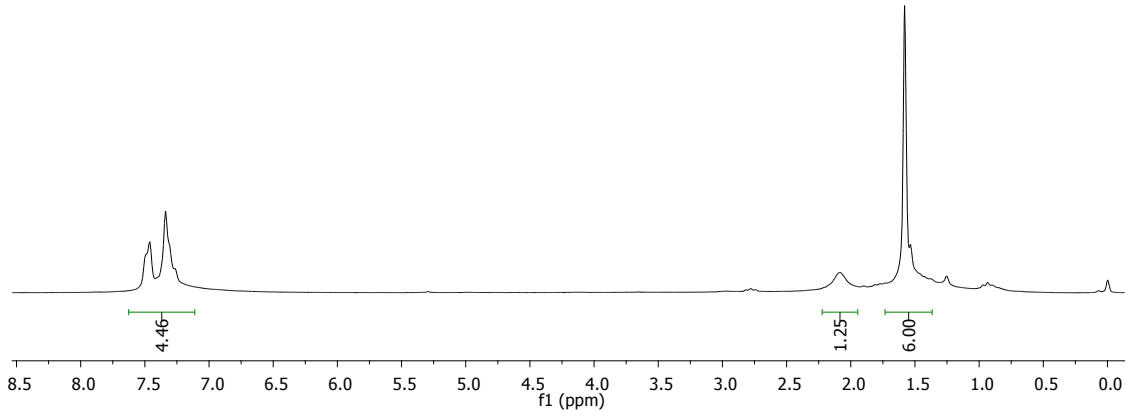

8.61
8.60
8.59
8.58
8.57
f1 (ppm)

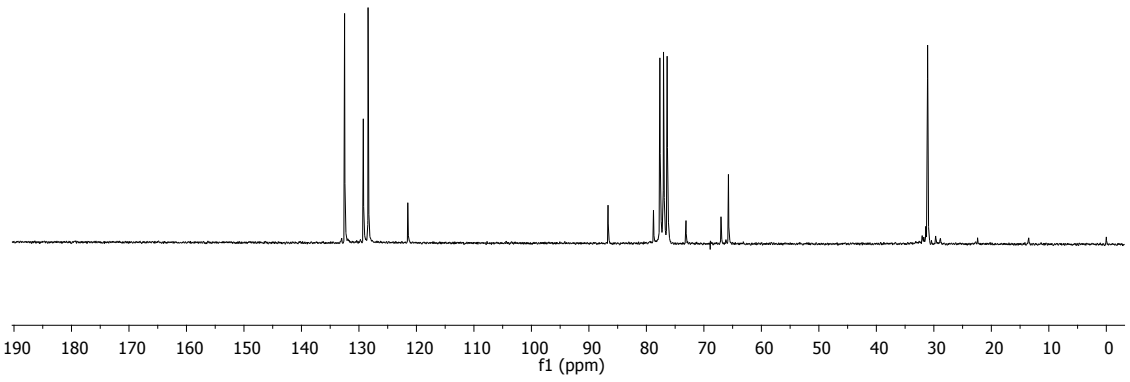

1.00
3.28
1.06
2.15
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

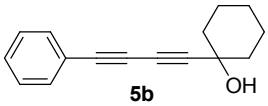

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OH

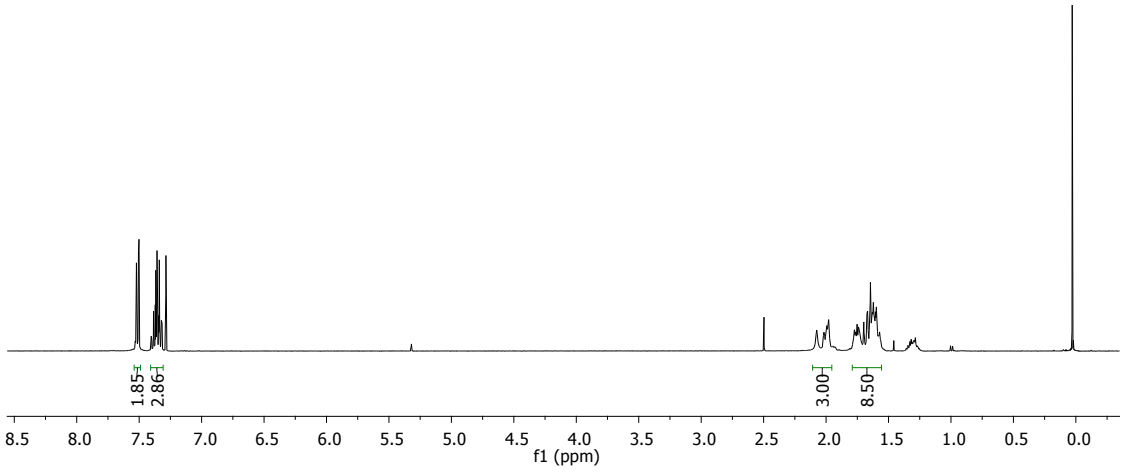
5a

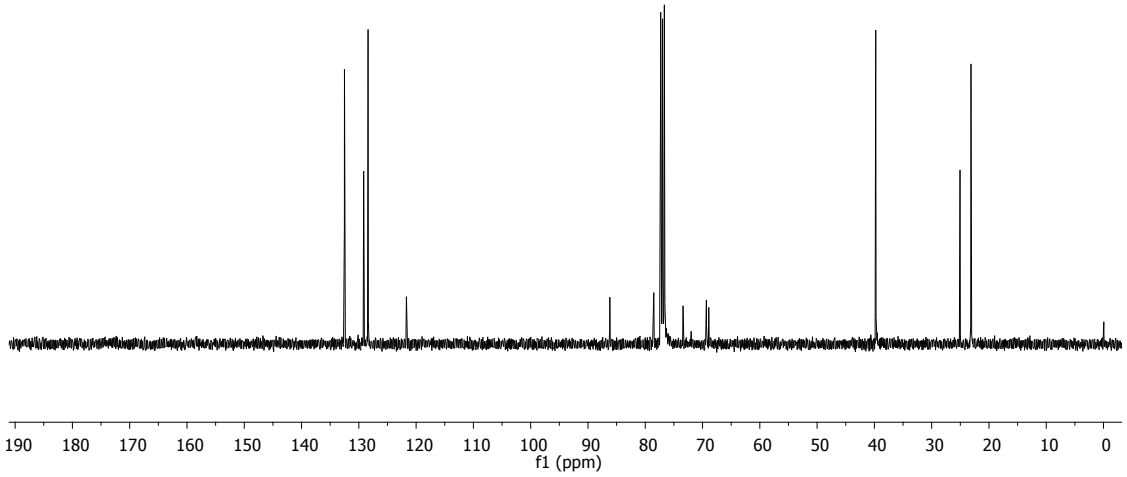

4.46
1.25
6.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

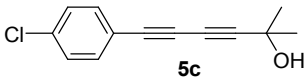

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


OH

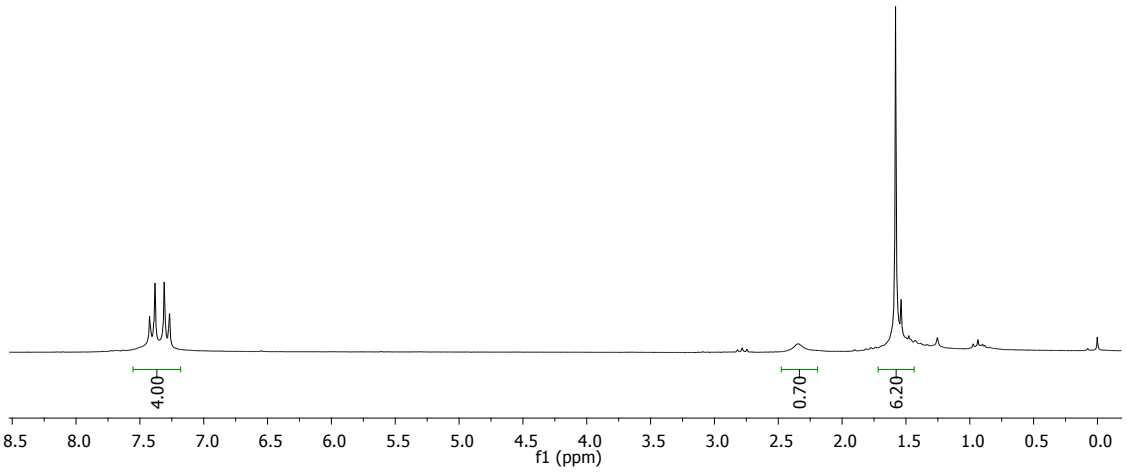
5b

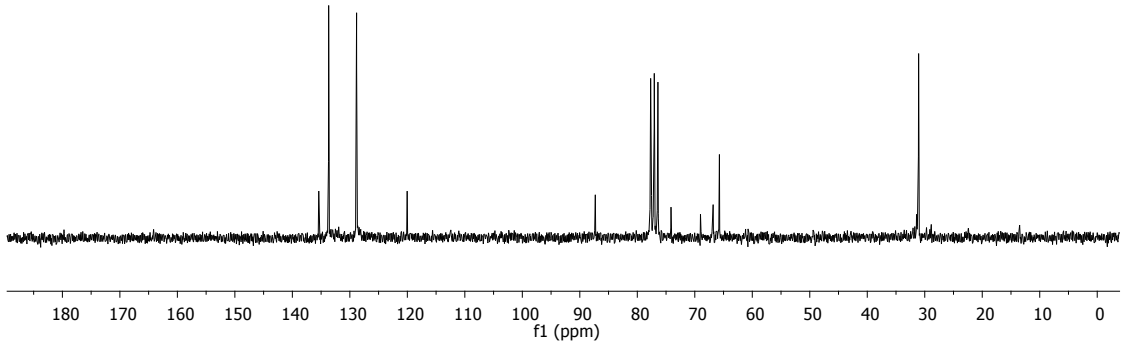

1.85
2.86
3.00
8.50
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

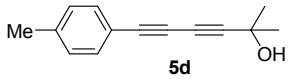

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Cl
OH

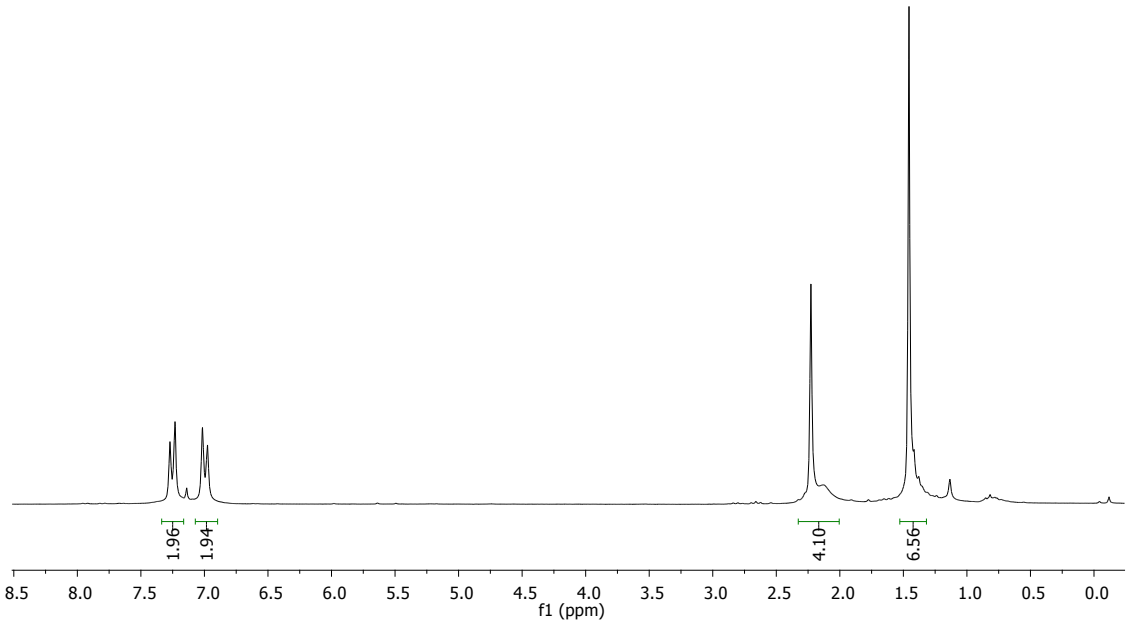
5c

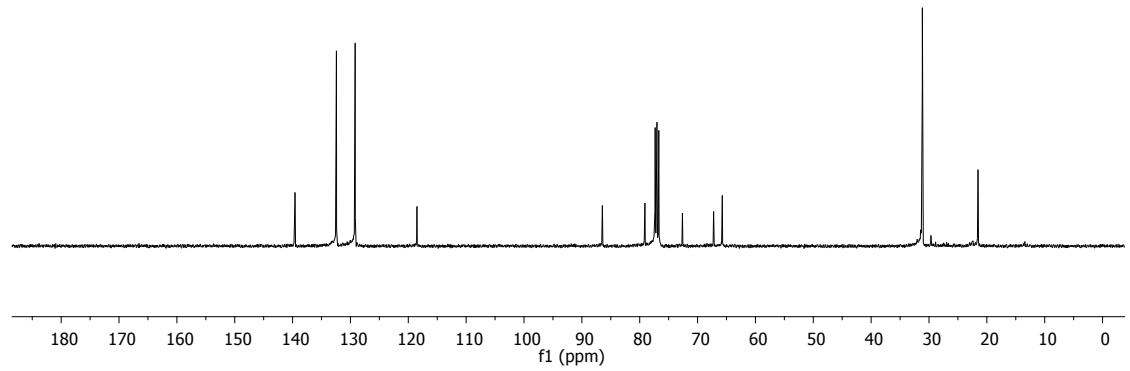

4.00
0.70
6.20
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

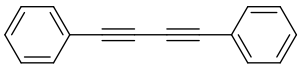

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Me
OH

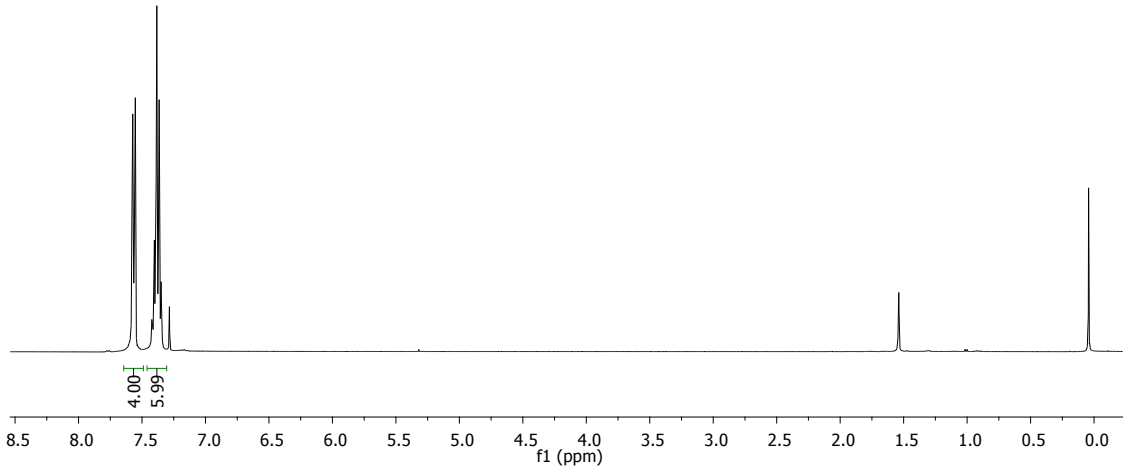
5d

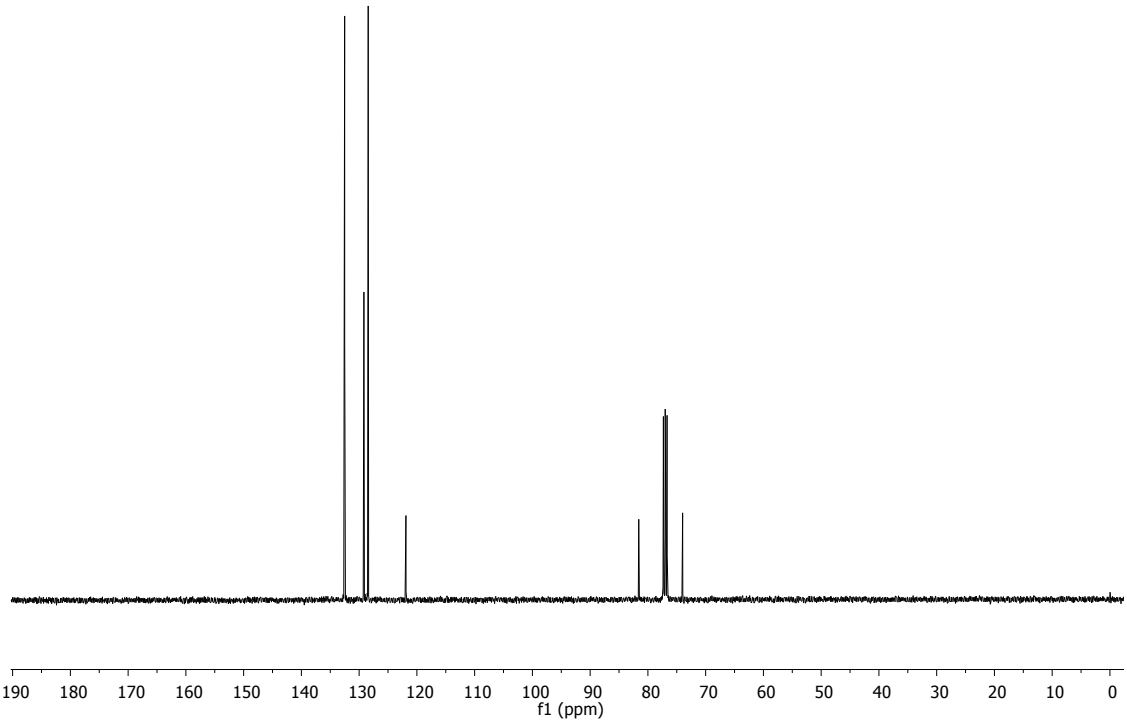

1.96
1.94
4.10
6.56
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



5e


4.00
5.99
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)