Supporting Information

Phosphine-Mediated Iterative Arene Homologation Using Allenes

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1. General Information

All reactions were performed in dry solvents under an Ar atmosphere and anhydrous conditions. DCM, THF, and MeCN were freshly distilled over CaH_2 prior to use. All other reagents were used as received from commercial sources. Reactions were monitored through thin layer chromatography (TLC) on 0.25-mm SiliCycle silica gel plates and visualized under UV light. Flash column chromatography (FCC) was performed using SiliCycle Silica-P Flash silica gel (60-Å pore size, 40–63 μm). IR spectra were recorded using a Jasco FT-IR 4100 spectrometer. NMR spectra of the naphthalenes **4** and **6** were recorded using Bruker Avance-300, Bruker Avance-400 and Bruker Avance-500 instruments, calibrated to $CD(H)Cl_3$ as the internal reference (7.26 and 77.0 ppm for ^1H and ^{13}C NMR spectra, respectively). ^1H NMR spectral data are reported in terms of chemical shift (δ, ppm), multiplicity, coupling constant (Hz), and integration. ^{13}C NMR spectral data are reported in terms of chemical shift (δ, ppm) and multiplicity, with the coupling constant (Hz) in the case of J_{CF} and J_{CP} coupling. Data for ^{31}P NMR spectra are reported in terms of chemical shift. The following abbreviations indicate the multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. High-resolution mass spectra were recorded using a Waters LCT Premier XE time-of-flight instrument controlled by MassLynx 4.1 software. Samples were infused using direct loop injection from a Waters Acquity UPLC into the multi-mode ionization source. The lock mass standard for accurate mass determination was leucine enkephalin (Sigma L9133). X-ray crystallographic data were collected using a Bruker SMART CCD-based diffractometer equipped with a low-temperature apparatus operated at 100 K. UV–Vis spectra were recorded

using an Ocean Optics USB2000 spectrophotometer equipped with a DT-MINI-2-GS light source. The spectra were recorded using a 1-mm quartz cuvette, with spectra-grade DCM as the solvent. The conversions of the reactions were determined through chiral HPLC using a Shimadzu CBM Lite system and a REGIS (*R*,*R*)-DACH DNB analytical (diameter: 4.5 mm) column, with CH_2Cl_2/hexane (9:1) as the eluent.

2. Substrate Preparation

2.1 Allenoate Preparation

Ethyl 2,3-butadienoate,[1] benzyl 2,3-butadienoate,[2] 2-trimethylsilylethyl 2,3-butadienoate,[3] 2,6-dimethylphenyl buta-2,3-dienoate,[4] penta-3,4-dien-2-one,[5] ethyl penta-2,3-dienoate,[6] ethyl hepta-2,3-dienoate,[7] ethyl 5-cyclopentylpenta-2,3-dienoate,[7] benzyl penta-2,3-dienoate,[8] and *tert*-butyl penta-2,3-dienoate[9] were prepared using reported methods.

2.2 Dialdehyde Preparation

Naphthalene-2,3-dicarbaldehyde,[10] 4,5-dichlorophthalaldehyde,[10] 4-methylphthalaldehyde,[11] 4-nitrophthalaldehyde[11], and benzene-1,2,4,5-tetracarbaldehyde[12] were prepared using reported methods.

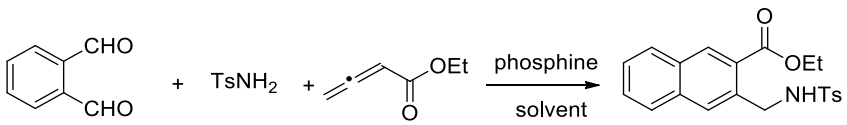
3. Multicomponent Reaction

3.1. Optimization of Conditions of Multicomponent Reaction

To determine the optimal reaction conditions, several reaction variables were tested, including

solvents, phosphines, ratios of starting materials, and reaction temperatures. The conditions were established for the reaction of *o*-phthalaldehyde (**1a**), *p*-toluenesulfonamide (**2a**), and ethyl buta-2,3-dienoate (**3a**) (Table S1). First, several nucleophilic phosphines were screened, with triphenylphosphine giving the best yield (33%) (Table 1, Entry 1). Tris(4-chlorophenyl)phosphine, tris(3-fluorophenyl)phosphine, and tris(3,5-bis(trifluoromethyl)phenyl)phosphine also gave the desired product (entries 2–4), but with yields lower than that obtained using triphenylphosphine. Tributylphosphine, ethyldiphenylphosphine, and tri-(*o*-tolyl)phosphine failed to facilitate this reaction (entries 5–7). Having selected triphenylphosphine as the optimal phosphine, solvents were screened. Toluene, benzene, THF, DCM, and dioxane failed to improve the yield of the reaction (entries 8–12).

Table S1. Optimization of solvents and phosphines for the multicomponent reaction.



1 **2a** **3a** **4a**

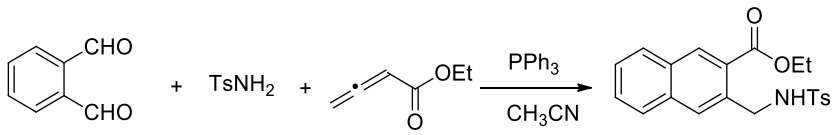
entry	solvent	catalyst	yield (%)[a]
1	CH_3CN	PPh_3	33
2	CH_3CN	P(*p*-ClC_6H_4)$_3$	26
3	CH_3CN	P(*m*-FC_6H_4)$_3$	22
4	CH_3CN	P[*m*,*m*-$(CF_3)_2C_6H_3$]$_3$	14
5	CH_3CN	P(*n*-Bu)$_3$	NR
6	CH_3CN	$PEtPh_2$	NR
7	CH_3CN	P(*o*-$CH_3C_6H_4$)$_3$	NR

8	benzene	PPh_3	26
9	toluene	PPh_3	25
10	THF	PPh_3	6
11	CH_2Cl_2	PPh_3	28
12	1,4-dioxane	PPh_3	–

[a] Based on ^1H NMR spectroscopic analysis of the crude product (using 2,4-dinitro-1-chlorobenzene as the internal standard).

After screening the phosphines and solvents, the reaction was still producing low yields. It was suspected that the yields could be improved by changing the concentration of the reaction mixture and the ratio of the substrates, as well as by slowing the addition of the allenoate **3a**. First, different ratios of the substrates were tested: the yield increased to 54% when the **1**:**2a**:**3a**:PPh_3 ratio was 1:2:3:1 (Table S2, entries 1–4). Running the reaction in more-dilute solutions improved the yield to 62% (Table 2, entry 5). Using a syringe pump to add the allenoate, as a solution in CH_3CN (8 mL) at a rate of 2 mL/h, to the reaction mixture improved the yield to 73% (Table S2, entry 6). Varying the reaction temperature, the naphthalene **4a** was obtained in 84% yield when the reaction was run at 0 °C (Table 2, entries 7 and 8). The yield did not improve, however, when the reaction system was either more dilute or more concentrated (Table 2, entries 9 and 10). Thus, the optimized reaction conditions were established with a **1**:**2a**:**3a**:PPh_3 ratio of 1:2:3:1, triphenylphosphine as the mediator, in CH_3CN at 0 °C.

Table S2. Optimization of the ratio of the substrates, the concentration, and the temperature of the multicomponent reaction.



1a 2a 3a 4a

entry	ratio (1:2a:3a:PPh_3)	concentration (M)[a]	temp. (°C)	yield (%)[b]
1	1:1:1:1	0.080	rt	33
2	1:2:2:2	0.080	rt	50
3	1:2:2:1	0.080	rt	52
4	1:2:3:1	0.080	rt	54
5	1:2:3:1	0.042	rt	62
6	1:2:3:1	0.042	rt	73
7	1:2:3:1	0.042	50	53
8	1:2:3:1	0.042	0	84
9	1:2:3:1	0.036	0	78
10	1:2:3:1	0.050	0	65

[a]Concentration of *o*-phthalaldehyde. [b]Based on ^{1}H NMR spectroscopic analysis of the crude product (using 2,6-dinitro-1-chlorobenzene as the internal standard).

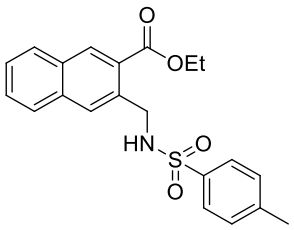
3.2 Experimental Procedures

General Procedure for the Synthesis of the Naphthalene Derivatives 4a–t.

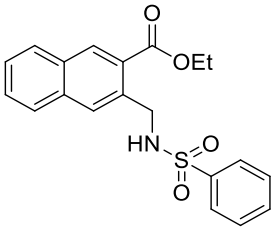
The dialdehyde **1** (0.5 mmol), the nucleophilic reagent **2** (2 equiv), Ph_3P (1 equiv, 131 mg),

and MeCN (4 mL) were added sequentially to a flame-dried flask (25 mL) and then the mixture was cooled to 0 °C. A solution of the allenoate **3** (3 equiv) in MeCN (8 mL) was added dropwise over 4 h, and then the reaction mixture was stirred under Ar at 0 °C. After completion of the reaction (TLC), the solvent was evaporated under reduced pressure and the product was purified through silica gel FCC to yield the desired naphthalene products **4a**–**u**.

Characterization Data for Naphthalene Derivatives 4a–u.

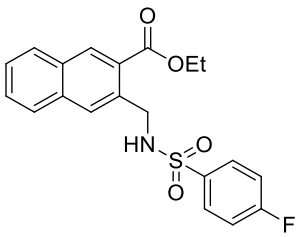


Ethyl 3-((4-Methylphenylsulfonamido)methyl)-2-naphthoate (4a). Pale yellow solid (160 mg, 84% yield); m.p. 146 °C; R_f = 0.52 (hexane/EtOAc, 3:1); IR (film) ν_{max} 3252, 2927, 1710, 1321, 1282, 1157, 1044 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.65 (s, 1H), 7.61–7.58 (m, 3H), 7.54–7.50 (m, 1H), 7.01 (d, J = 8.0 Hz, 2H), 6.00 (t, J = 7.2 Hz, 1H), 4.51 (d, J = 6.8 Hz, 2H), 4.40 (q, J = 7.2 Hz, 2H), 2.21 (s, 3H), 1.44 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 142.7, 138.0, 134.8, 133.2, 132.9, 131.8, 130.9, 129.2, 128.8, 128.7, 127.6, 127.0, 126.9, 126.3, 61.5, 47.4, 21.3, 14.3; HRMS (ESI-TOF) Calcd for $C_{21}H_{21}NO_4S$ $[M + H]^+$ m/z 384.1270, found 384.1256.

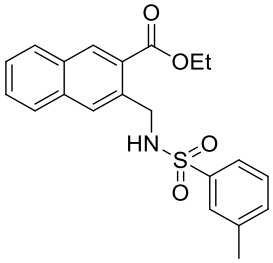


Ethyl 3-(Phenylsulfonamidomethyl)-2-naphthoate (4b). White solid (163 mg, 88% yield);

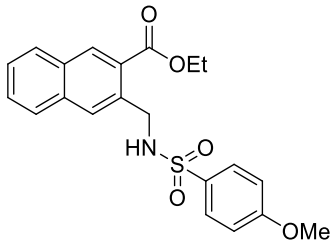
m.p. 154 °C; R_f = 0.52 (hexane/EtOAc, 3:1); IR (film) ν_{max} 3271, 3058, 2980, 1705, 1283, 1160, 1031 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.75 (d, J = 8.4 Hz, 1H), 7.72–7.70 (m, 3H), 7.60–7.57 (m, 1H), 7.54–7.51 (m, 1H), 7.33–7.30 (m, 1H), 7.27–7.23 (m, 2H), 6.08 (t, J = 7.2 Hz, 1H), 4.53 (d, J = 7.2 Hz, 2H), 4.38 (q, J = 7.2 Hz, 2 H), 1.42 (t, J = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.5, 141.0, 134.8, 133.2, 133.0, 132.0, 131.9, 130.9, 128.8, 128.7 (2C), 127.7, 127.1, 126.8, 126.3, 61.5, 47.4, 14.3; HRMS (ESI-TOF) Calcd for $C_{20}H_{18}NO_4S$ $[M - H]^+$ m/z 368.0956, found 368.0971.



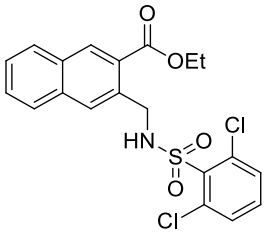
Ethyl 3-((4-Fluorophenylsulfonamido)methyl)-2-naphthoate (4c). Pale yellow oil (150 mg, 78% yield); R_f = 0.61 (hexane/EtOAc, 3:1); IR (film) ν_{max} 3206, 3067, 2982, 1708, 1281, 1134, 1091 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.88–7.86 (m, 1H), 7.78–7.77 (m, 1H), 7.70–7.67 (m, 3H), 7.63–7.59 (m, 1H), 7.56–7.53 (m, 1H), 6.89–6.86 (m, 2H) , 6.09 (t, J = 7.0 Hz, 1H), 4.53 (d, J = 7.0 Hz, 2H), 4.39 (q, J = 7.0 Hz, 2H), 1.44 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.5, 164.5 (d, J_{CF} = 252.5 Hz), 137.1 (d, J_{CF} = 3.3 Hz), 134.7, 133.1, 132.9, 131.9, 131.0, 129.5 (d, J_{CF} = 9.1 Hz), 129.0, 128.8, 127.6, 127.2, 126.1, 115.7 (d, J_{CF} = 22.5 Hz), 61.6, 47.5, 14.3; ^{19}F (376 MHz, $CDCl_3$) δ –106.4; HRMS (ESI-TOF) Calcd for $C_{20}H_{17}FNO_4S$ $[M - H]^+$ m/z 386.0862, found 386.0872.



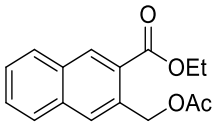
Ethyl 3-((3-Methylphenylsulfonamido)methyl)-2-naphthoate (4d). Pale yellow oil (134 mg, 70% yield); R_f = 0.55 (hexane/EtOAc, 3:1); IR (film) ν_{max} 3284, 2981, 1708, 1218, 1154, 1035 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.70 (s, 1H), 7.59–7.53 (m, 2H), 7.52–7.48 (m, 1H), 7.37 (s, 1H), 7.12–7.06 (m, 2H), 6.07 (t, J = 6.8 Hz, 1H), 4.54 (d, J = 6.8 Hz, 2H), 4.38 (q, J = 7.2 Hz, 2H), 2.06 (s, 3H), 1.42 (t, J = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.4, 140.9, 138.8, 134.7, 133.1, 132.9, 132.6, 131.9, 131.0, 128.8, 128.7, 128.5, 127.7, 127.2, 127.1, 126.1, 123.8, 61.5, 47.6, 20.9, 14.3; HRMS (ESI-TOF) Calcd for $C_{21}H_{20}NO_4S$ $[M - H]^+$ m/z 382.1113, found 382.1111.



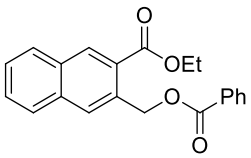
Ethyl 3-((4-Methoxyphenylsulfonamido)methyl)-2-naphthoate (4e). Colorless oil (120 mg, 60% yield); R_f = 0.44 (hexane/EtOAc, 3:1); IR (film) ν_{max} 3144,1715, 1490, 1275, 1185, 1026 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.72 (d, J = 8.0 Hz, 1H), 7.64 (s, 1H), 7.60 (d, J = 8.5 Hz, 2H), 7.56 (t, J = 8.0 Hz, 1H); 7.51 (t, J = 7.5 Hz, 1H), 6.64 (d, J = 9.0 Hz, 2H), 6.00 (t, J = 6.5 Hz, 1H), 4.49 (d, J = 7.0 Hz, 2H), 4.38 (q, J = 7.0 Hz, 2H), 3.65 (s, 3H), 1.42 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.4, 162.3, 134.7, 133.2, 133.0, 132.6, 131.8, 130.8, 128.9, 128.8, 128.7, 127.6, 127.0, 126.2, 113.8, 61.5, 55.4, 47.4, 14.3; HRMS (ESI-TOF) Calcd for $C_{21}H_{22}NO_5S$ $[M + H]^+$ m/z 400.1219, found 400.1210.



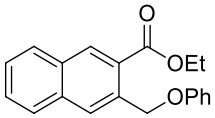
Ethyl 3-((2,6-Dichlorophenylsulfonamido)methyl)-2-naphthoate (4f). White solid (186 mg, 85% yield); m.p. 154 °C; R_f = 0.62 (hexane/EtOAc, 3:1); IR (film) ν_{max} 3092, 2927, 1711, 1489, 1219, 1187, 1033 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.71 (d, J = 7.5 Hz, 1H), 7.66 (s, 1H), 7.57–7.54 (m, 1H), 7.50–7.48 (m, 1H), 6.98 (t, J = 7.0 Hz, 1H), 6.80 (d, J = 8.0 Hz, 2H), 6.57 (t, J = 8.5 Hz, 1H), 4.78 (d, J = 7.0 Hz, 2H), 4.44 (q, J = 7.0 Hz, 2H), 1.47 (q, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.2, 136.7, 134.3, 134.0, 133.2, 132.0, 131.8, 130.8, 130.7, 130.5, 128.9, 128.6, 127.7, 127.1, 125.4, 61.6, 48.1, 14.4; HRMS (ESI-TOF) Calcd for $C_{20}H_{18}Cl_2NO_4S$ $[M + H]^+$ m/z 438.0334, found 438.0335.



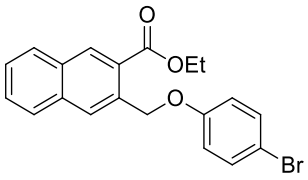
Ethyl 3-(Acetoxymethyl)-2-naphthoate (4g). White solid (125 mg, 92% yield); m.p. 76 °C; R_f = 0.73 (hexane/EtOAc, 3:1); IR (film) ν_{max} 3178, 1715, 1489, 1268, 1184, 1031 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.56 (s, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.90 (s, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.61–7.58 (m, 1H), 7.56–7.53 (m, 1H), 5.64 (s, 2H), 4.43 (q, J = 7.0 Hz, 2H), 2.16 (s, 3H), 1.42 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.7, 170.0, 134.7, 132.9, 132.5, 131.9, 128.8, 128.5, 128.2, 127.7, 127.0, 65.2, 61.3, 21.1, 14.3; HRMS (ESI-TOF) Calcd for $C_{16}H_{16}O_4Na$ $[M + Na]^+$ m/z 295.0946, found 295.0955.



Ethyl 3-((Benzoyloxy)methyl)-2-naphthoate (4h). Pale yellow solid (117 mg, 70% yield); m.p. 78 °C; R_f = 0.80 (hexane/EtOAc, 3:1); IR (film) ν_{max} 2981, 1717, 1451, 1274, 1167, 1061 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.13–8.10 (m, 2H), 7.98 (s, 1H), 7.95–7.92 (m, 1H), 7.88–7.85 (m, 1H), 7.62–7.54 (m, 3H), 7.49–7.43 (m, 2H), 5.90 (s, 2H), 4.41 (q, J = 7.2 Hz, 2H), 1.41 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.2, 166.3, 134.7, 133.0, 132.5, 132.0, 130.3, 130.1, 129.8, 128.8, 128.5 (2C), 128.2, 127.8, 127.2, 127.0, 65.7, 61.4, 14.4; HRMS (ESI-TOF) Calcd for $C_{21}H_{19}O_4$ $[M + H]^+$ m/z 335.1283, found 335.1268.

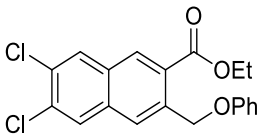


Ethyl 3-(Phenoxymethyl)-2-naphthoate (4i). White solid (190 mg, 99% yield); m.p. 80 °C; R_f = 0.85 (hexane/EtOAc, 3:1); IR (film) ν_{max} 3020, 2978, 1700, 1279, 1173, 1014 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.16 (s, 1H), 7.94 (d, J = 8.1 Hz, 1H), 7.87 (d, J = 8.1 Hz, 1H), 7.62–7.51 (m, 2H), 7.37–7.32 (m, 2H), 7.11–7.08 (m, 2H), 7.03–6.98 (m, 1H), 5.62 (d, J = 0.9 Hz, 2H), 4.43 (q, J = 7.2 Hz, 2H), 1.43 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.1, 157.9, 134.9, 134.0, 132.5, 132.3, 131.7, 128.8, 128.6, 127.8, 126.9, 126.8, 126.2, 116.8, 113.1, 68.9, 61.3, 14.4; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}O_3$ $[M + H]^+$ m/z 307.1334, found 307.1342.

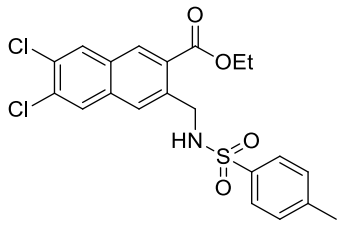


Ethyl 3-((4-Bromophenoxy)methyl)-2-naphthoate (4j). Brown oil (182 mg, 95% yield); R_f

= 0.86 (hexane/EtOAc, 3:1); IR (film) ν_{max} 3057, 2979, 1707, 1486, 1278, 1199, 1028 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.08 (s, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.61–7.53 (m, 2H), 7.40 (d, J = 9.0 Hz, 2H), 6.94 (d, J = 9.0 Hz, 2H), 5.57 (s, 2H), 4.41 (q, J = 7.0 Hz, 2H), 1.42 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.2, 158.9, 134.9, 134.6, 132.4, 131.7, 129.6, 128.8, 128.7, 127.9, 126.9, 126.7, 126.4, 121.0, 115.0, 68.7, 61.3, 14.4; HRMS (ESI-TOF) Calcd for $C_{20}H_{18}BrO_3$ $[M + H]^+$ m/z 387.0421, found 387.0406.

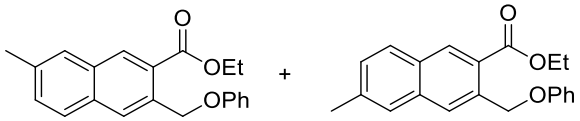


Ethyl 6,7-Dichloro-3-(phenoxymethyl)-2-naphthoate (4k). White solid (142 mg, 76% yield); m.p. 152 °C; R_f = 0.85 (hexane/EtOAc, 3:1); IR (film) ν_{max} 3041, 2930, 1737, 1417, 1268, 1133, 1105 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.48 (s, 1H), 8.07 (s, 1H), 8.04 (s, 1H), 7.99 (s, 1H), 7.33–7.30 (m, 2H), 7.05–7.03 (m, 2H), 7.00–6.97 (m, 1H), 5.58 (s, 2H), 4.41 (q, J = 7.0 Hz, 2H), 1.42 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.5, 158.6, 136.3, 133.7, 133.0, 131.1, 130.5, 129.60 (2C), 128.9, 127.5, 125.5, 121.2, 114.9, 68.2, 61.5, 14.3; HRMS (ESI-TOF) Calcd for $C_{20}H_{17}Cl_2O_3$ $[M + H]^+$ m/z 375.0555, found 375.0557.

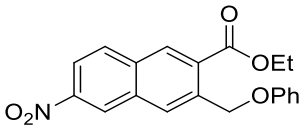


Ethyl 6,7-Dichloro-3-((4-methylphenylsulfonamido)methyl)-2-naphthoate (4l). White solid (169 mg, 75% yield); m.p. 152 °C; R_f = 0.62 (hexane/EtOAc, 3:1); IR (film) ν_{max} 3282, 1716, 1488, 1216, 1185, 957 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.98 (s, 1H),

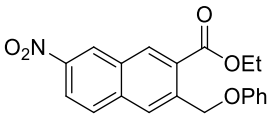
7.84 (s, 1H), 7.60–7.59 (m, 2H), 7.56 (s, 1H), 7.08 (d, J = 8.0 Hz, 2H), 5.91 (t, J = 7.0 Hz, 1H), 4.48 (d, J = 7.0 Hz, 2H), 4.40 (q, J = 7.0 Hz, 2H), 2.27 (s, 3H), 1.43 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.8, 143.0, 137.9, 134.9, 133.4, 133.3, 131.7, 131.6, 130.7, 129.6, 129.5, 129.4, 128.6, 127.6, 126.9, 61.8, 47.0, 21.3, 14.3; HRMS (ESI-TOF) Calcd for $C_{21}H_{20}Cl_2NO_4S$ $[M + H]^+$ m/z 452.0409, found 452.0482.



Ethyl 7-Methyl-3-(phenoxymethyl)-2-naphthoate (4m) and Ethyl 6-Methyl-3-(phenoxymethyl)-2-naphthoate (4m′). White solid (147 mg, 92% yield); m.p. 86 °C; R_f = 0.85 (hexane/EtOAc, 3:1); IR (film) ν_{max} 3038, 2979, 2920, 1709, 1598, 1495, 1271, 1238, 1195, 1138, 1037 cm^{-1}; Major isomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.09 (s, 1H), 7.77 (d, J = 8.4 Hz, 1H), 7.70 (s, 1H), 7.35–7.30 (m, 4H), 7.01–6.96 (m, 2H), 5.59 (s, 2H), 4.41 (d, J = 7.2 Hz, 2H), 2.53 (s, 3H), 1.42 (t, J = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.3, 158.9, 136.5, 135.2, 133.6, 132.2, 131.8, 129.9, 129.5, 128.6, 127.7, 126.6, 126.1, 125.4, 115.0, 68.7, 61.2, 21.7, 14.3. Minor isomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.57 (s, 1H), 8.05 (s, 1H), 7.83 (d, J = 8.4 Hz, 1H), 7.64 (s, 1H), 7.44–7.38 (m, 2H), 7.09–7.06 (m, 4H), 5.61 (s, 2H), 4.41 (d, J = 7.2 Hz, 2H), 2.53 (s, 3H), 1.42 (t, J = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.3, 158.9, 138.6, 134.7, 133.2, 131.9, 130.8, 130.0, 129.5, 129.0, 127.7, 126.9, 126.4, 125.7, 120.9, 68.7, 61.1, 21.9, 14.4. HRMS (ESI-TOF) Calcd for $C_{21}H_{20}O_3Na$ $[M + Na]^+$ m/z 343.1310, found 343.1310.

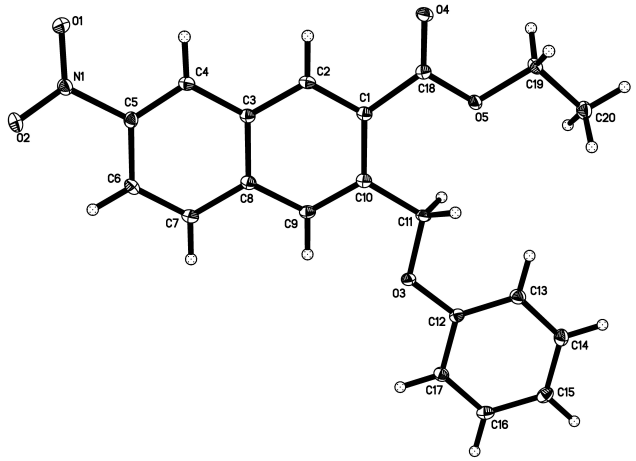


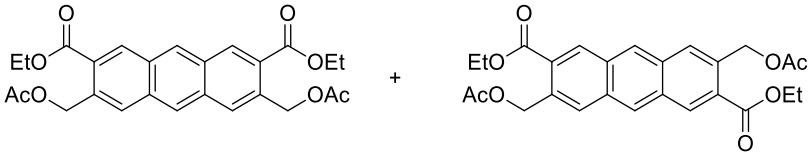
Ethyl 6-Nitro-3-(phenoxymethyl)-2-naphthoate (4n). White solid (176 mg, 50% yield); m.p. 136 °C; R_f = 0.80 (hexane/EtOAc, 3:1); IR (film) ν_{max} 3088, 2979, 1714, 1598, 1538, 1345, 1281, 1246, 1190, 1042 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.83 (d, J = 2.0 Hz, 1H), 8.66 (s, 1H), 8.39 (s, 1H), 8.29 (dd, J = 2.0, 9.0 Hz, 1H), 8.08 (d, J = 9.0 Hz, 1H), 7.35–7.32 (m, 2H), 7.07–7.05 (m, 2H), 7.02–6.99 (m, 1H), 5.62 (d, J = 1.0 Hz, 2H), 4.45 (q, J = 7.0 Hz, 2H), 1.44 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.4, 158.4, 147.1, 137.2, 134.0, 133.6, 131.8, 130.5, 129.9, 129.7, 128.6, 124.4, 121.3, 120.0, 114.9, 68.0, 61.8, 14.3; HRMS (ESI-TOF) Calcd for $C_{20}H_{16}NO_5$ $[M - H]^+$ m/z 350.1028, found 350.1039.



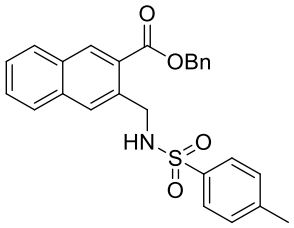
Ethyl 7-Nitro-3-(phenoxymethyl)-2-naphthoate (4n′). White solid (160 mg, 46% yield); m.p. 144 °C; R_f = 0.85 (hexane/EtOAc, 3:1); IR (film) ν_{max} 3088, 2982, 1712, 1598, 1494, 1340, 1241, 1195, 1192, 1042 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.90 (d, J = 2.0 Hz, 1H), 8.78 (s, 1H), 8.35 (dd, J = 2.0, 9.0 Hz, 1H), 8.32 (s, 1H), 8.02 (d, J = 9.0 Hz, 1H), 7.35–7.32 (m, 2H), 7.08–7.06 (m, 2H), 7.02–6.99 (m, 1H), 5.65 (d, J = 1.0 Hz, 2H), 4.46 (q, J = 7.0 Hz, 2H), 1.46 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.2, 158.5, 146.0, 139.3, 137.2, 134.0, 130.2, 129.7, 129.6, 128.3, 126.5, 125.4, 121.8, 121.3, 114.9, 68.2, 61.7, 14.3; HRMS (ESI-TOF) Calcd for $C_{20}H_{16}NO_5$ $[M - H]^+$ m/z 350.1028, found 350.1025.

ORTEP Representation of the Solid State Structure of Compound 4n´

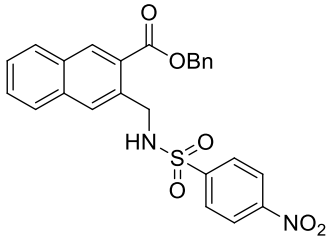




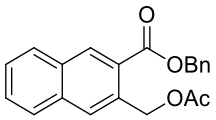
Diethyl 3,6-Bis(acetoxymethyl)anthracene-2,7-dicarboxylate (4o) and Diethyl 3,7-Bis(acetoxymethyl)anthracene-2,6-dicarboxylate (4o´). Yellow solid (163 mg, 70% yield); m.p. 170 °C; R_f = 0.32 (hexane/EtOAc, 3:1); IR (film) ν_{max} 3055, 2975, 2940, 1732, 1714, 1294, 1238, 1158, 1037 cm^{-1}; **4o**: ^1H NMR (500 MHz, $CDCl_3$) δ 8.77 (s, 2H), 8.64 (s, 1H), 8.45 (s, 1H), 8.06 (s, 2H), 5.67 (s, 4H), 4.46 (d, J = 7.5 Hz, 4H), 2.19 (s, 6H), 1.47 (t, J = 7.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.7, 166.8, 133.5, 133.4, 132.5, 131.4, 130.3, 128.5, 128.1, 127.3, 65.2, 61.5, 21.1, 14.3. **4o´**: ^1H NMR (500 MHz, $CDCl_3$) δ 8.75 (s, 2H), 8.55 (s, 2H), 8.07 (s, 2H), 5.67 (s, 4H), 4.46 (d, J = 7.5 Hz, 4H), 2.19 (s, 6H), 1.47 (t, J = 7.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.7, 166.7, 133.8, 133.1, 132.3, 130.0, 128.2, 127.9, 126.3, 65.2, 61.5, 21.1, 14.3. HRMS (ESI-TOF) Calcd for $C_{26}H_{26}O_8Na$ $[M + Na]^+$ m/z 489.1525, found 489.1530.



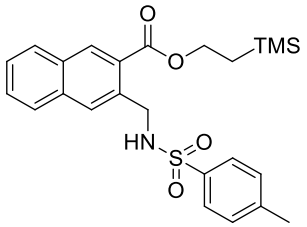
Benzyl 3-((4-Methylphenylsulfonamido)methyl)-2-naphthoate (4p). Pale yellow oil (222 mg, 99% yield); R_f = 0.52 (hexane/EtOAc, 3:1); IR (film) ν_{max} 3277, 3031, 2944, 1707, 1278, 1150, 1040 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.82 (d, J = 8.4 Hz, 1H), 7.73 (d, J = 8.0 Hz, 1H), 7.66 (s, 1H), 7.60–7.56 (m, 1H), 7.54–7.44 (m, 7 H), 7.39–7.36 (m, 3H), 6.95 (d, J = 8.0 Hz, 2H), 5.99 (t, J = 6.8 Hz, 1H), 4.53 (d, J = 6.8 Hz, 2H), 2.20 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.2, 142.7, 138.0, 135.7, 134.8, 133.2 (2C), 131.8, 130.9, 129.2, 128.9, 128.8 (2C), 128.6 (2C), 128.5, 127.7, 127.1, 126.9, 67.2, 47.4, 21.3; HRMS (ESI-TOF) Calcd for $C_{26}H_{24}NO_4S$ $[M + H]^+$ m/z 446.1426, found 446.1430.



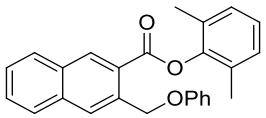
Benzyl 3-((4-Nitrophenylsulfonamido)methyl)-2-naphthoate (4q). White solid (95 mg, 40% yield); m.p. 122 °C; R_f = 0.52 (hexane/EtOAc, 3:1); IR (film) ν_{max} 3187, 1715, 1597, 1490, 1274, 1217, 1185, 1132, 957 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.80–7.73 (m, 4H), 7.64–7.60 (m, 4H), 7.55–7.51 (m, 1H), 7.50–7.42 (m, 5H), 6.27 (t, J = 7.0 Hz, 1H), 5.38 (s, 2H), 4.61 (d, J = 7.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.2, 149.0, 147.0, 135.5, 134.5, 133.5, 132.2, 131.8, 131.4, 129.5, 128.9, 128.8 (2C), 128.6, 127.8, 127.6, 127.4, 125.5, 123.5, 67.4, 47.7; HRMS (ESI-TOF) Calcd for $C_{25}H_{21}N_2O_6S$ $[M + H]^+$ m/z 477.1120, found 477.1106.



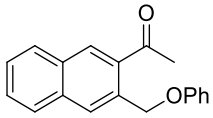
Benzyl 3-(Acetoxymethyl)-2-naphthoate (4r). White solid (142 mg, 85% yield); m.p. 74 °C; R_f = 0.65 (hexane/EtOAc, 3:1); IR (film) ν_{max} 3061, 2985, 1716, 1455, 1278, 1240, 1130, 959 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.60 (s, 1H), 7.92–7.90 (m, 2H), 7.87–7.85 (m, 1H), 7.61–7.58 (m, 1H), 7.55–7.53 (m, 1H), 7.52–7.50 (m, 2H), 7.44–7.41 (m, 2H), 7.39–7.37 (m, 1H), 5.65 (s, 2H), 5.42 (s, 2H), 2.11 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.7, 166.7, 135.9, 134.7, 133.1, 132.8, 131.9, 128.9, 128.7 (2C), 128.5, 128.4, 128.3, 127.7, 127.0, 126.5, 67.0, 65.1, 21.0; HRMS (ESI-TOF) Calcd for $C_{21}H_{18}O_4Na$ $[M + Na]^+$ *m/z* 357.1103, found 357.1115.



2-(Trimethylsilyl)ethyl 3-((4-Methylphenylsulfonamido)methyl)-2-naphthoate (4s). Colorless oil (198 mg, 87% yield); R_f = 0.53 (hexane/EtOAc, 3:1); IR (film) ν_{max} 3300, 3058, 2953, 1701, 1280, 1157, 1042 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.85–7.82 (m, 1H), 7.75–7.72 (m, 1H), 7.64 (s, 1H), 7.61–7.56 (m, 3H), 7.54–7.49 (m, 1H), 7.01–6.98 (m, 2H), 6.03 (t, J = 6.9 Hz, 1H), 4.51 (d, J = 6.9 Hz, 2H), 4.46–4.40 (m, 2H), 2.20 (s, 3H), 1.20–1.15 (m, 2H), 0.12 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.7, 142.7, 138.1, 134.7, 133.2, 133.0, 131.9, 130.9, 129.2, 128.7 (2C) , 127.7, 127.0, 126.9, 126.5, 63.9, 47.5, 21.3, 17.6, –1.4; HRMS (ESI-TOF) Calcd for $C_{24}H_{30}NO_4SSi$ $[M + H]^+$ *m/z* 456.1665, found 456.1674.



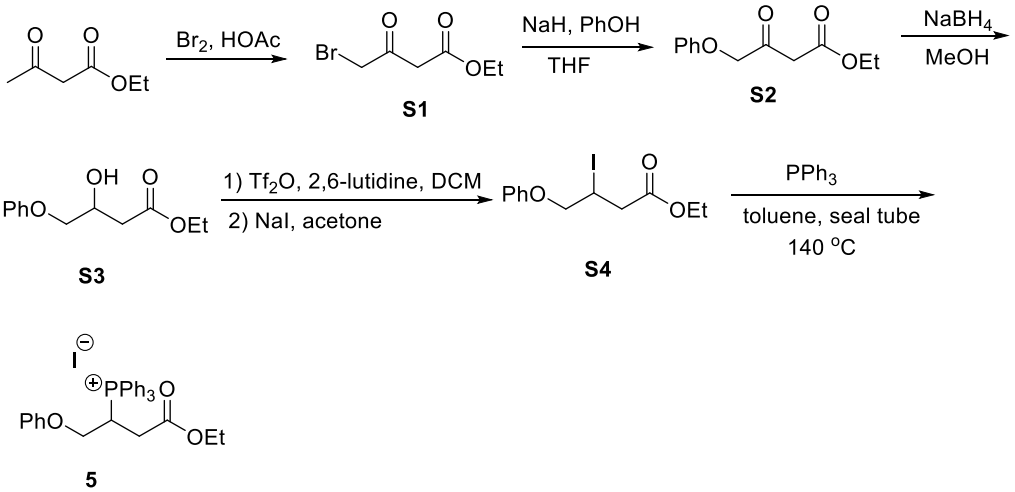
2,6-Dimethylphenyl 3-(Phenoxymethyl)-2-naphthoate (4t). Colorless oil (160 mg, 73% yield); R_f = 0.85 (hexane/EtOAc, 3:1); IR (film) ν_{max} 3033, 2920, 1726, 1280, 1162, 1110 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.96 (s, 1H), 8.29 (s, 1H), 8.02 (d, J = 8.1 Hz, 1H), 7.94 (d, J = 8.1 Hz, 1H), 7.69–7.63 (m, 1H), 7.62–7.57 (m, 1H), 7.33–7.28 (m, 2H), 7.17–7.12 (m, 3H), 7.10–7.06 (m, 2H), 7.00–6.95 (m, 1H), 5.67 (s, 2H), 2.27 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.7, 158.8, 148.3, 135.4 (2C), 133.2, 131.6, 130.4, 129.5, 129.0, 128.8, 128.0, 127.1, 126.9, 126.1, 124.5, 121.0, 114.8, 68.4, 16.5; HRMS (ESI-TOF) Calcd for $C_{26}H_{22}O_3Na$ $[M + Na]^+$ m/z 405.1467, found 405.1463.



1-(3-(Phenoxymethyl)naphthalen-2-yl)ethanone (4u). White solid (135 mg, 98% yield); m.p. 72 °C; R_f = 0.72 (hexane/EtOAc, 3:1); IR (film) ν_{max} 3144, 1738, 1597, 1490, 1217, 1186, 956 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.36 (s, 1H), 8.19 (s, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.64–7.53 (m, 2H), 7.35–7.32 (m, 2H), 7.11–7.08 (m, 2H), 7.02–6.99 (m, 1H), 5.57 (s, 2H), 2.76 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.0, 158.8, 134.8, 133.8, 131.8, 131.5, 129.7, 129.6, 128.8, 128.0, 126.9, 126.8, 121.0, 115.0, 68.7, 28.8; HRMS (ESI-TOF) Calcd for $C_{19}H_{17}O_2$ $[M + H]^+$ m/z 277.1229, found 277.1231.

4. Mechanistic Studies

4.1 Synthesis of the Phosphonium Salt 5.

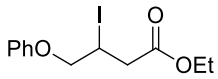


Ethyl 4-Bromo-3-oxobutanoate (S1). Prepared using the reported method[13] in 65% yield.

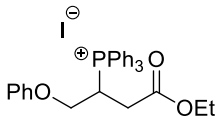
Ethyl 3-Oxo-4-phenoxybutanoate (S2). Prepared using the reported method[14] in 80% yield.

Ethyl 3-Hydroxy-4-phenoxybutanoate (S3). $NaBH_4$ (2 equiv) was added slowly to a stirring solution of the ketone **S2** (1.2 mmol) in MeOH at 0 °C. Upon completion (TLC), the reaction was quenched through slow addition of water at 0 °C. The aqueous phase was extracted with EtOAc. The combined organic phases were dried (Na_2SO_4) and concentrated in vacuo. The residue was purified through FCC to yield a pale yellow oil (70%). R_f = 0.30 (hexane/EtOAc, 1:1); IR (film) ν_{max} 3466, 3015, 2970, 1730, 1599, 1495, 1172, 1041 cm^{-1}; ^1H NMR (300

MHz, $CDCl_3$) δ 7.36–7.30 (m, 2H), 7.04–6.94 (m, 3H), 4.51–4.43 (m, 1H), 4.24 (q, J = 7.2 Hz, 2H), 4.05 (d, J = 5.4 Hz, 2H), 3.16 (s, 1H), 2.73 (d, J = 2.1 Hz, 1H), 2.71 (d, J = 4.5 Hz, 1H), 1.33 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.2, 158.4, 129.6, 121.2, 114.6, 70.7, 66.8, 60.9, 38.1, 14.2; HRMS (ESI-TOF) Calcd for $C_{12}H_{17}O_4$ $[M + H]^+$ m/z 225.1127, found 225.1126.

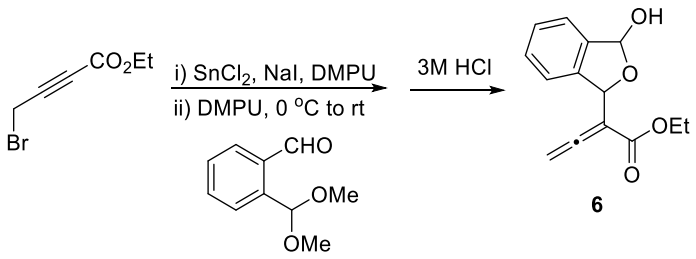


Ethyl 3-Iodo-4-phenoxybutanoate (S4). 2,6-Lutidine (1.2 equiv) and trifluoromethanesulfonic anhydride (1.1 equiv) were added dropwise and successively to a solution of the alcohol **S3** (0.2 mmol) in dry DCM at 0 °C under an inert atmosphere. The mixture was then stirred at the same temperature and monitored (TLC) for consumption of the starting material. After 1.5 h, the mixture was dried (Na_2SO_4) and concentrated under reduced pressure to obtain the crude product. Without purification, the crude product was dissolved in acetone and sodium iodide (1 equiv) was added. The resulting mixture was heated under reflux for 2 h and monitored (TLC) for consumption of the starting material. The reaction was quenched with water and the aqueous phase was extracted with DCM. The combined organic phases were dried (Na_2SO_4) and concentrated in vacuo. The residue was purified through FCC to yield a yellow/brown oil (80% over two steps). R_f = 0.72 (hexane/EtOAc, 3:1); IR (film) ν_{max} 3043, 2979, 1733, 1597, 1494, 1185, 1029 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36–7.30 (m, 2H), 7.06–7.00 (m, 1H), 6.96–6.93 (m, 2H), 4.70–4.60 (m, 1H), 4.35 (dd, J = 2.1, 10.2 Hz, 1H), 4.28–4.13 (m, 3H), 3.36 (dd, J = 2.4, 16.5 Hz, 1H), 3.03 (dd, J = 3.1, 16.5 Hz, 1H), 1.32 (t, J = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.5, 157.8, 129.6, 121.6, 114.8, 72.7, 61.1, 42.2, 20.6, 14.2; HRMS (ESI-TOF) Calcd for $C_{12}H_{16}IO_3$ $[M + H]^+$ m/z 335.0144, found 335.0155.

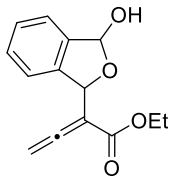


(4-Ethoxy-4-oxo-1-phenoxybutan-2-yl)triphenylphosphonium Iodide (5). The alkyl iodide **S4** (668 mg, 2 mmol) and PPh_3 (1.2 equiv) were added to degassed dry toluene. The tube was sealed and heated at 140 °C for 7 days. The mixture was concentrated under reduced pressure and then purified through FCC to obtain the phosphonium salt **5** as a yellow oil (4%). IR (film) ν_{max} 3088, 3027, 2874, 1732, 1603, 1495, 1177, 1030 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.91–7.87 (m, 6H), 7.78–7.75 (m, 3H), 7.69–7.65 (m, 6H), 7.16–7.13 (m, 2H), 6.92–6.89 (m, 1H), 6.54–6.52 (m, 2H), 5.43–5.38 (m, 1H), 4.54–4.44 (m, 2H), 4.08 (q, J = 7.0 Hz, 2H), 3.18–3.11 (m, 1H), 3.00–2.92 (m, 1H), 1.18 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.7 (d, J_{CP} = 12.6 Hz), 156.7, 135.0 (d, J_{CP} = 3.0 Hz), 134.5 (d, J_{CP} =9.9 Hz), 130.3 (d, J_{CP} = 12.5 Hz), 129.6, 122.2, 117.6 (d, J_{CP} = 84.5 Hz), 114.2, 65.9 (d, J_{CP} = 5.1 Hz), 62.1, 33.1, 32.3 (d, J_{CP} = 50.1 Hz), 14.2; ^{31}P NMR (121 MHz, $CDCl_3$) δ 30.3; HRMS (ESI-TOF) Calcd for $C_{30}H_{30}O_3P$ $[M - I]^+$ *m/z* 469.1933, found 469.1944.

4.2 Synthesis of the Lactol 6.

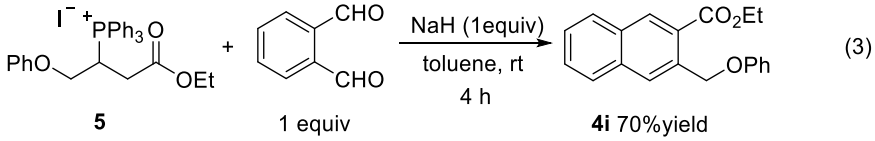


The starting material, ethyl 4-bromobut-2-ynoate, was prepared according to a reported procedure.[15]

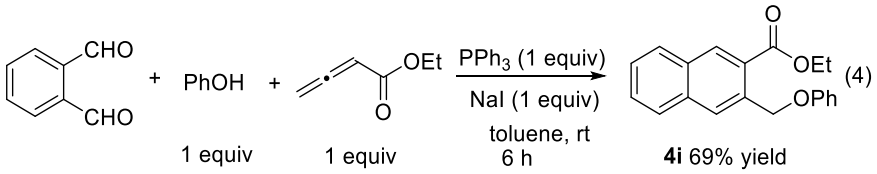


Ethyl 2-(3-Hydroxy-1,3-dihydroisobenzofuran-1-yl)buta-2,3-dienoate (6). Prepared using the reported method in 30% yield.[15] R_f = 0.32 (hexane/EtOAc, 3:1); IR (film) ν_{max} 3439, 3178, 2987, 1739, 1268 cm^{-1}. Major isomer: ^1H NMR (300 MHz, $CDCl_3$) δ 7.46–7.39 (m, 3H), 7.25–7.22 (m, 1H), 6.42 (d, J = 12.0 Hz, 1H), 5.81 (s, 1H), 5.38 (s, 2H), 4.68 (d, J = 12.0 Hz, 1H), 4.21–4.08 (m, 2H), 1.25 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 215.2, 165.7, 140.1, 139.6, 129.3, 128.7, 123.0, 121.2, 102.2, 100.9, 81.8, 80.0, 61.4, 14.1. Minor isomer: 7.52–7.47 (m, 3H), 7.33–7.30 (m, 1H), 6.61 (dd, J = 2.1, 8.4 Hz, 1H), 6.25 (s, 1H), 5.29 (dd, J = 1.5, 14.4 Hz, 1H), 5.22 (dd, J = 1.5, 14.4 Hz, 1H), 4.25 (q, J = 7.2 Hz, 2H), 3.41 (d, J = 8.4 Hz, 1H), 1.29 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 213.7, 165.5, 140.8, 139.4, 129.4, 128.5, 122.9, 122.2, 102.4, 101.6, 81.4, 79.9, 61.3, 14.2. HRMS (ESI-TOF) Calcd for $C_{14}H_{14}O_4Na$ $[M + Na]^+$ m/z 269.0790, found 269.0791.

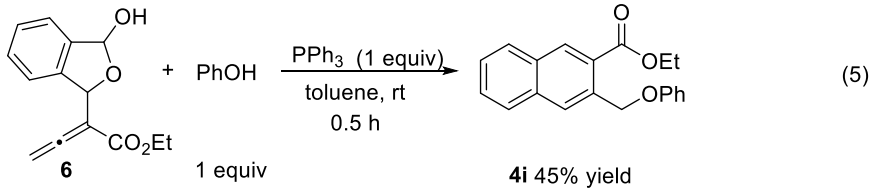
4.3 Experimental Procedures for Eqs 3–6.



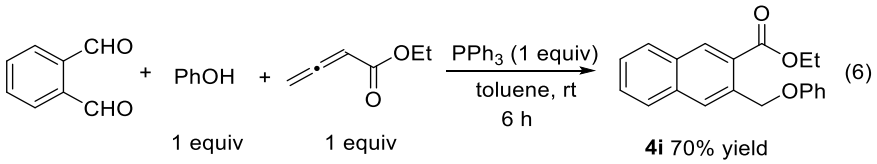
NaH (1 equiv) was added slowly to a solution of the phosphonium salt **5** (1 equiv) and *o*-phthalaldehyde (13.4 mg, 0.10 mmol) in toluene (1 mL) at room temperature. After stirring the mixture at room temperature for 4 h, the solvent was evaporated under reduced pressure. The residue was purified through FCC to yield the naphthalene derivative **4i** (70%).



Ethyl buta-2,3-dienoate was added in one batch to a solution of triphenylphosphine (1 equiv), *o*-phthalaldehyde (13.4 mg, 0.10 mmol), phenol (1 equiv), and sodium iodide (1 equiv) in toluene (1 mL) at room temperature. After stirring the mixture at room temperature for 4 h, the solvent was evaporated under reduced pressure. The residue was purified through FCC to yield the naphthalene derivative **4i** (69%).



Phenol (9.4 mg, 0.1 mmol) was added to a solution of the lactol **6** (1 equiv) and triphenylphosphine (1 equiv) in toluene (1 mL) at room temperature. After stirring the mixture at room temperature for 30 min, the solvent was evaporated under reduced pressure. The residue was purified through FCC to yield the naphthalene derivative **4i** (45%).



Ethyl buta-2,3-dienoate was added in one batch to a solution of triphenylphosphine (1 equiv), *o*-phthalaldehyde (13.4 mg, 0.1 mmol), and phenol (1 equiv) in toluene (1 mL) at room temperature. After stirring the mixture at room temperature for 6 h, the solvent was evaporated under reduced pressure. The residue was purified through FCC to yield the naphthalene derivative **4i** (70%).

4.4 HRMS Traces of the Reaction

Whereas peaks corresponding to triphenylphosphine ($[M + H]^+$, *m*/*z* 263.0990), triphenylphosphine oxide ($[M + H]^+$, *m*/*z* 279.0939), the phosphonium dienolate **A** ($[M + H]^+$, *m*/*z* 375.1514), the γ-umpolung addition adduct **B** ($[M + Na]^+$, *m*/*z* 491.1752), and the aldol addition product **F** ($[M + H]^+$, *m*/*z* 509.1882) were clearly visible in the HRMS traces of the crude reaction mixture, the signal for the product **4i** (M + H = 307.1334) was not detected during the entire duration of the reaction. Therefore, parallel multicomponent reactions were set up and analyzed using HPLC to monitor the progress of the reaction.

Ethyl buta-2,3-dienoate (1 equiv) was added in one batch to a solution of triphenylphosphine (1 equiv), *o*-phthalaldehyde (13.4 mg, 0.1 mmol), and phenol (1 equiv) in toluene (1 mL) at room temperature. After 1 min, 3 min, 5 min, 10 min, 40 min, 2 h, 4 h, and 6 h, an aliquot (5 μL) of the reaction mixture was taken and diluted with DCM (1 mL). A portion (5 μL) of each solution was dissolved in methanol (1 mL) and then a sample (0.2 μL) was injected for HRMS analysis. The desired product **4i** was formed at 3 min (8.3% yield according to the HPLC analysis), at which point the peak corresponding to the γ-addition product **B** ($[M + Na]^+$, *m*/*z* 491.1752) was clearly visible, while the peak corresponding to the aldol adduct **F** ($[M + H]^+$, *m*/*z* 509. 1882) was barely visible. The reaction steadily progressed (according to HPLC analysis, with a growing phosphine oxide peak ($[M + H]^+$, *m*/*z* 279.0939)), but the aldol adduct **F** peak was clearly visible only after 2 h (52.4% yield of **4i**). After 6 h (72.2% yield of **4i**), the reaction had reached completion, with the peaks corresponding to both **B** and **F** being barely visible.

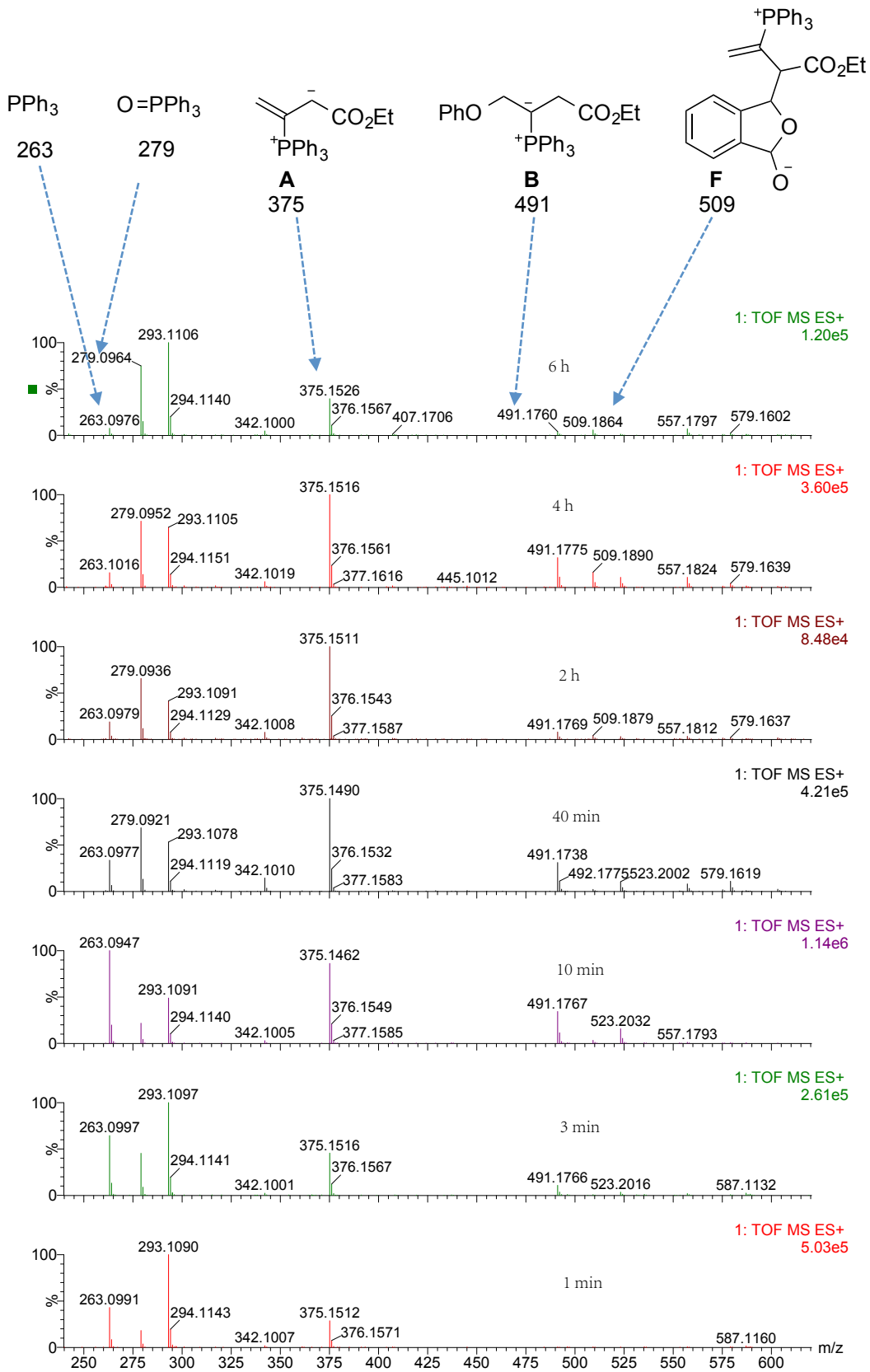
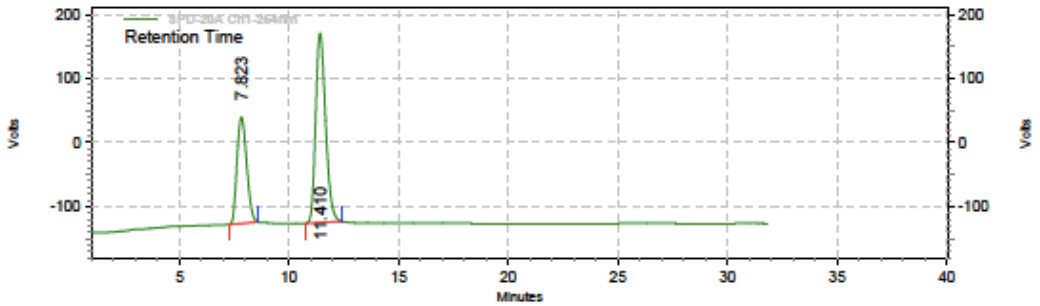


Figure S1. HRMS monitoring of the reaction.

4.5 HPLC Monitoring of the Conversion

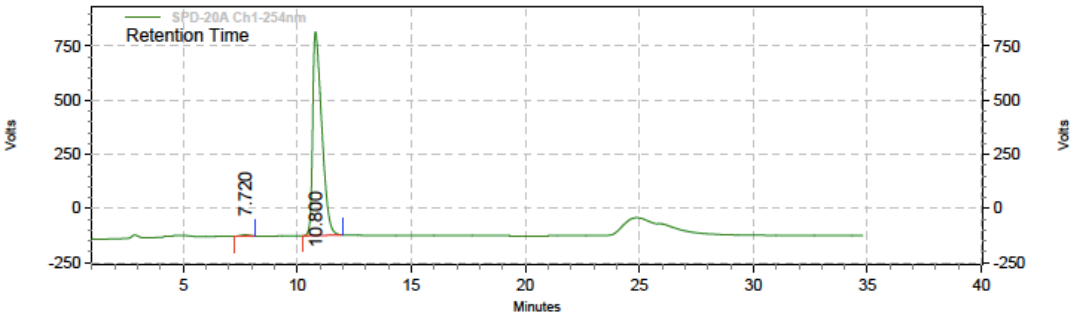
Eight parallel multicomponent reactions were set up. Ethyl buta-2,3-dienoate (1 equiv) was added in one batch to a solution of triphenylphosphine (1 equiv), *o*-phthalaldehyde (13.4 mg, 0.1 mmol), and phenol (1 equiv) in toluene (1 mL) at room temperature. The reactions were quenched after 1 min, 3 min, 10 min, 40 min, 2 h, 4 h, 6 h, and 8 h by passing the reaction mixtures through a small pipette column, elution with EtOAc (10 mL). 1-Chloro-2,4-dinitrobenzene (0.1 mmol) was added as the internal standard to each collected solution. An aliquot (0.1 mL) of each of the above solutions was diluted with DCM (1 mL) and then a sample (10 μL) was injected into the HPLC apparatus. The conversions of the reaction were determined through HPLC using a Shimadzu CBM Lite system and a REGIS (*R*,*R*)-DACH DNB analytical (diameter: 4.5 mm) column, with CH_2Cl_2/hexane (9:1) as the eluent.

1. Product **4i** and internal standard 1-chloro-2,4-dinitrobenzene in 1:1 ratio



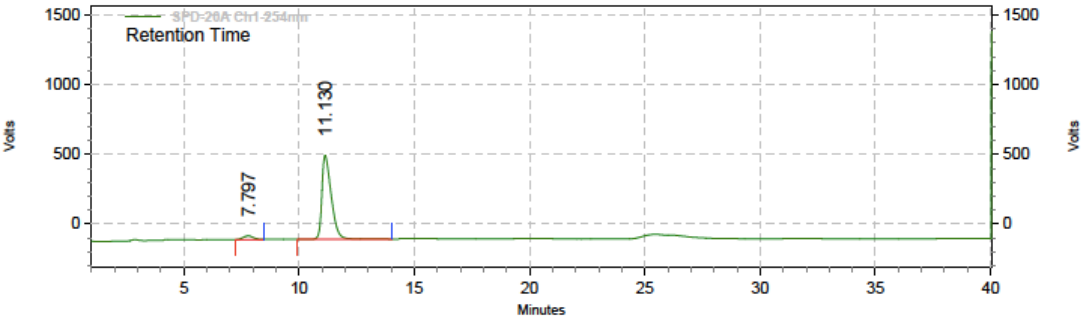
Retention Time	Area	Area %	Height	Height %
7.823	5102521	35.41	166234	35.97
11.410	9308566	64.59	295976	64.03
Totals	14411087	100.00	462210	100.00

2. Product **4i** and internal standard 1-chloro-2,4-dinitrobenzene after 1 min



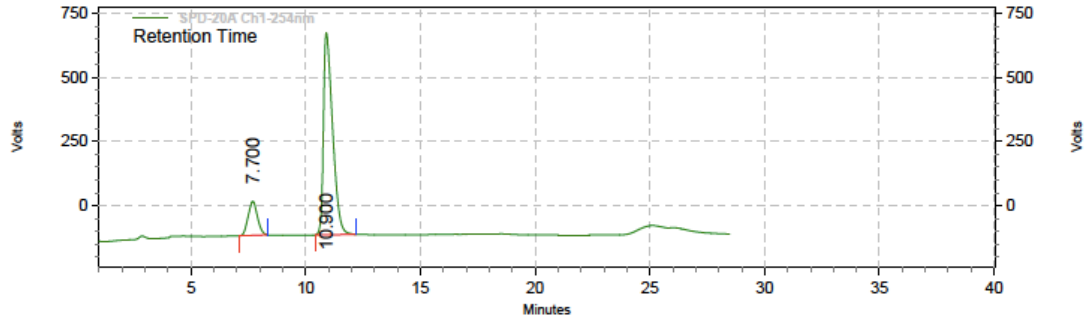
Retention Time	Area	Area %	Height	Height %
7.720	144429	0.55	6054	0.64
10.800	26050969	99.45	940567	99.36
Totals	26195398	100.00	946621	100.00

3. Product **4i** and internal standard 1-chloro-2,4-dinitrobenzene after 3 min



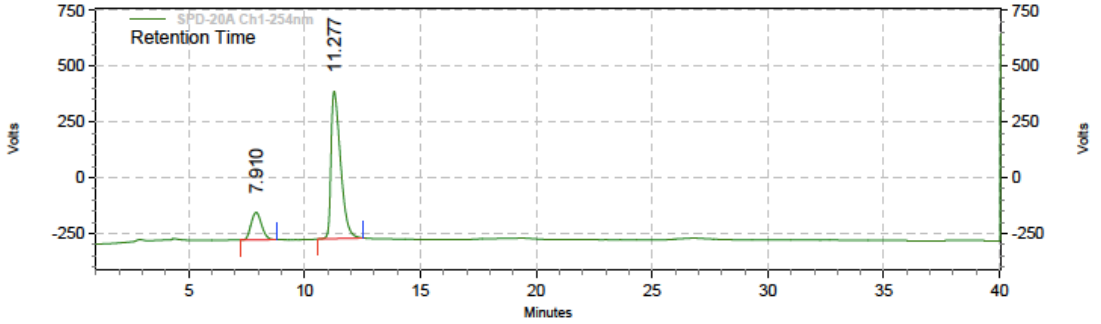
Retention Time	Area	Area %	Height	Height %
7.797	776470	4.36	26364	4.19
11.130	17015474	95.64	602713	95.81
Totals	17791944	100.00	629077	100.00

4. Product **4i** and internal standard 1-chloro-2,4-dinitrobenzene after 10 min



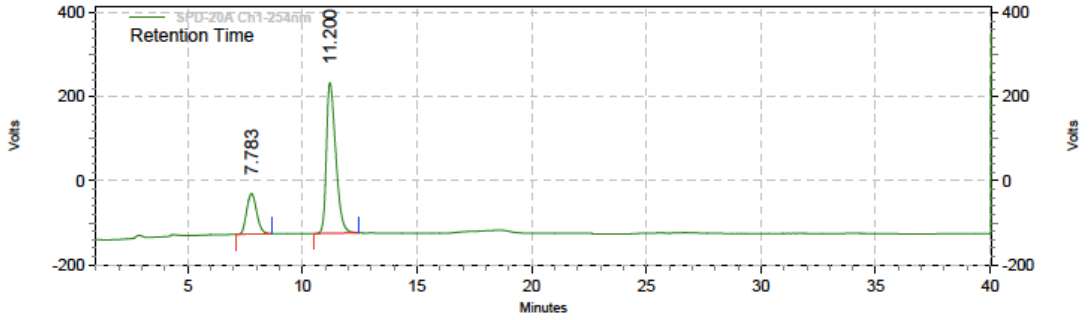
Retention Time	Area	Area %	Height	Height %
7.700	3738723	14.66	132606	14.38
10.900	21760967	85.34	789418	85.62
Totals	25499690	100.00	922024	100.00

5. Product **4i** and internal standard 1-chloro-2,4-dinitrobenzene after 40 min



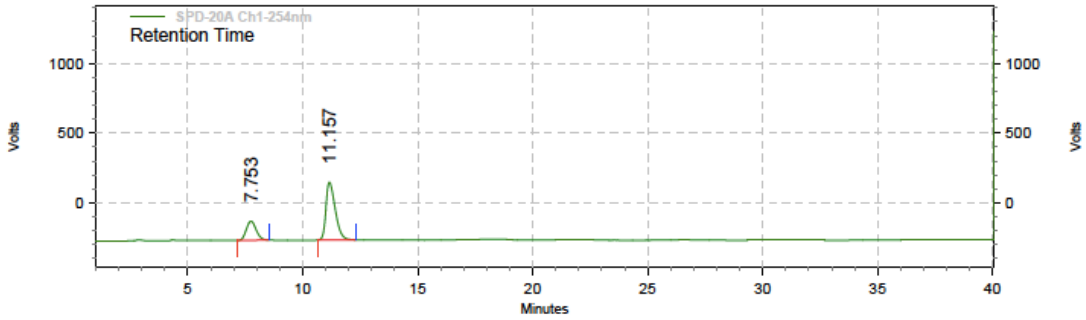
Retention Time	Area	Area %	Height	Height %
7.910	3875210	17.06	122957	15.67
11.277	18837736	82.94	661652	84.33
Totals	22712946	100.00	784609	100.00

6. Product **4i** and internal standard 1-chloro-2,4-dinitrobenzene after 2 h



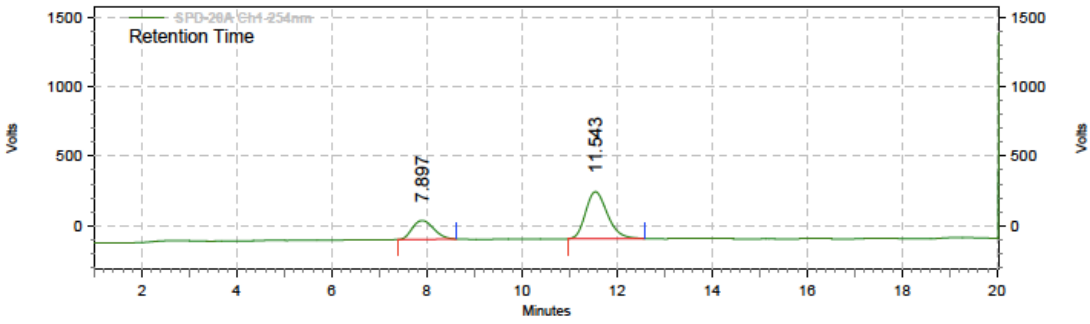
Retention Time	Area	Area %	Height	Height %
7.783	2919579	22.31	96464	21.17
11.200	10165845	77.69	359139	78.83
Totals	13085424	100.00	455603	100.00

7. Product **4i** and internal standard 1-chloro-2,4-dinitrobenzene after 4 h



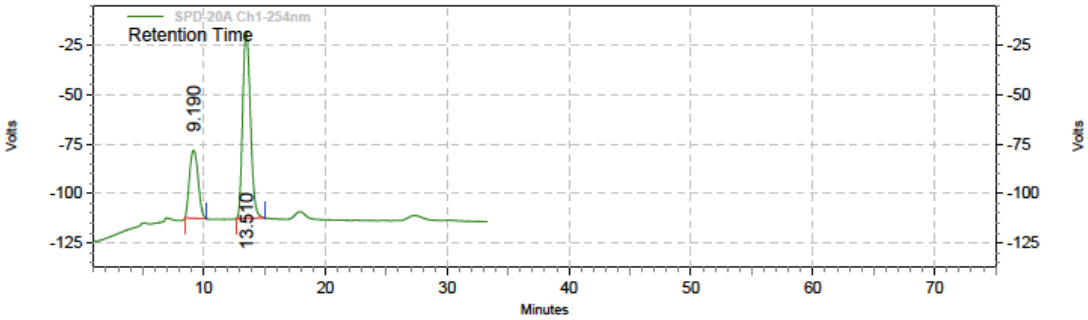
Retention Time	Area	Area %	Height	Height %
7.753	4035710	25.74	136414	24.73
11.157	11640263	74.26	415279	75.27
Totals	15675973	100.00	551693	100.00

8. Product **4i** and internal standard 1-chloro-2,4-dinitrobenzene after 6 h



Retention Time	Area	Area %	Height	Height %
7.897	4263689	28.37	136147	28.65
11.543	10763259	71.63	339076	71.35
Totals	15026948	100.00	475223	100.00

9. Product **4i** and internal standard 1-chloro-2,4-dinitrobenzene after 8 h



Retention Time	Area	Area %	Height	Height %
9.190	1686979	28.74	34429	26.70
13.510	4182371	71.26	94512	73.30
Totals	5869350	100.00	128941	100.00

Time	Yield of **4i**
1 min	1%
3 min	8.3%
10 min	31.3%
40 min	37.5%
2 h	52.4%
4 h	63.2%
6 h	72.2%
8 h	73.5%

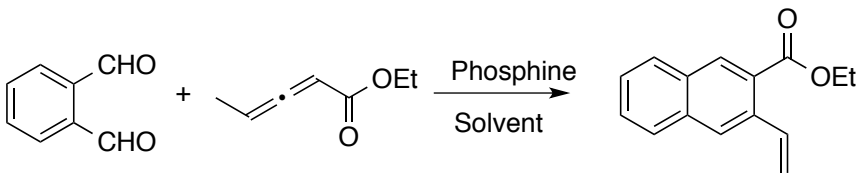
5. Aldol/Wittig reaction

5.1 Optimization of Conditions for the Two-Component Reaction

To determine the optimal reaction conditions, several reaction variables were tested, including

solvents, phosphines, and reaction temperatures. The reaction of *o*-phthalaldehyde (**1a**), ethyl 2,3-pentadienoate, and triphenylphosphine as mediator was tested to establish the reaction conditions (Table S3). A screen of several solvents revealed that toluene gave the best yield (80%) (entries 1–7). Having selected toluene as the best solvent, several other phosphines were examined. Tris(4-fluorophenyl)phosphine also gave the desired product, but the yield was lower that that obtained using triphenylphosphine (entry 8). Tris(2-furyl)phosphine failed to produce any desired product (entry 9). When tributylphosphine and ethyldiphenylphosphine were used as mediators, the yields of the desired product increased to 87 and 94%, respectively (entries 10–11). An examination of the reaction temperature revealed that the naphthalene **7a** was obtained from reactions run at 0 and 50 °C in 97 and 84% yields, respectively (entries 12–13). Thus, the optimized reaction conditions were established as using ethyldiphenylphosphine as the mediator in toluene at room temperature. Although the reaction yield was slightly higher when run at 0 °C, the reaction was performed at room temperature for ease of operation.

Table S3. Optimization for the aldol/Wittig reaction.[a]



7a

entry	solvent	phosphine	temp (°C)	yield (%)[b]
1	DCM	PPh_3	rt	70
2	$CHCl_3$	PPh_3	rt	58

3	CH_3CN	PPh_3	rt	42
4	THF	PPh_3	rt	67
5	PhH	PPh_3	rt	77
6	toluene	PPh_3	rt	80
7	1,4-dioxane	PPh_3	rt	66
8	toluene	Tris(4-fluorophenyl)phosphine	rt	70
9	toluene	Tris(2-furyl)phosphine	rt	NR
10	toluene	PBu_3	rt	87
11	toluene	$EtPh_2P$	rt	94 (95)[c]
12	toluene	$EtPh_2P$	0	97
13	toluene	$EtPh_2P$	50	84

[a]Conditions: **1a** (0.2 mmol), a phosphine (1 equiv), and ethyl 2,3-pentadienoate (2 equiv) were dissolved in a tested solvent (8 mL). [b]Based on ^{1}H NMR spectroscopic analysis of the crude product (using 2,4-dinitro-1-chlorobenzene as the internal standard). [c]Isolated yield.

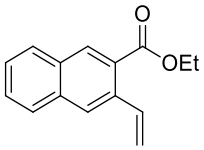
5.2 Experimental Procedures

General Procedure for the Synthesis of the Naphthalene Derivatives 7a–g

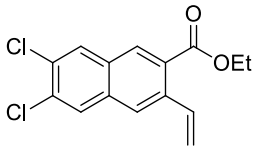
o-Phthalaldehyde (0.2 mmol), $EtPh_2P$ (1 equiv), and toluene (4 mL) were added sequentially to a flame-dried flask (25 mL) at room temperature. A γ-substituted allenoate (2 equiv) was added to the flask and then the mixture was stirred under Ar at room temperature. After completion of the reaction (TLC), the solvent was evaporated under reduced pressure and the

product purified through silica gel FCC to yield the desired naphthalene product **7a–g**.

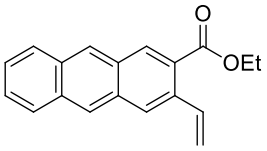
Characterization Data for Naphthalene Derivatives 7a–g



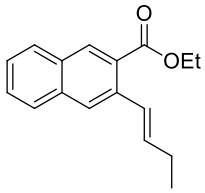
Ethyl 3-Vinyl-2-naphthoate (7a). Pale yellow oil (43 mg, 97% yield); R_f = 0.72 (hexane/EtOAc, 3:1); IR (film) ν_{max} 3025, 2979, 1726, 1258, 1226, 1075, 737 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.98 (s, 1H), 7.90–7.84 (m, 2H), 7.59–7.47 (m, 3H), 5.72 (dd, J = 1.5, 17.1 Hz, 1H), 5.38 (dd, J = 1.5, 10.8 Hz, 1H), 4.43 (q, J = 7.2 Hz, 2H), 1.45 (t, J = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.5, 136.5, 136.1, 134.9, 131.9, 131.5, 128.7, 128.3, 127.8, 127.4, 126.6, 126.5, 115.9, 61.2, 14.4; HRMS (ESI-TOF) Calcd for $C_{15}H_{15}O_2$ $[M + H]^+$ m/z 227.1072, found 227.1065.



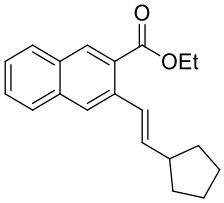
Ethyl 6,7-Dichloro-3-vinyl-2-naphthoate (7b). Pale yellow oil (54 mg, 93% yield); R_f = 0.75 (hexane/EtOAc, 3:1); IR (film) ν_{max} 3286, 3178, 3144, 1716, 1598, 1490, 1185, 1027, 957 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.99 (s, 1H), 7.95 (s, 1H), 7.86 (s, 1H), 7.48 (dd, J = 11, 17.5 Hz, 1H) 5.71 (dd, J = 1.5, 17.5 Hz, 1H), 5.41 (dd, J = 1.5, 11 Hz, 1H), 4.43 (q, J = 7.0 Hz, 2H), 1.44 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.8, 137.4, 135.8, 133.6, 132.8, 131.0, 130.6, 130.3, 129.5, 128.6 (2C), 125.3, 116.9, 61.5, 14.3; HRMS (ESI-TOF) Calcd for $[M + H]^+$ m/z $C_{15}H_{13}Cl_2O_2$ 295.0293, found 295.0282.



Ethyl 3-Vinylanthracene-2-carboxylate (7c). Pale yellow oil (55 mg, 100% yield); R_f = 0.72 (hexane/EtOAc, 3:1); IR (film) ν_{max} 2982, 1720, 1277, 1228, 1075, 748 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.46 (s, 1H), 8.38 (s, 1H), 8.10 (s, 1H), 8.00 (t, J = 7.0 Hz, 2H), 7.57–7.47 (m, 3H), 5.76 (dd, J = 1.5, 17 Hz, 1H), 5.39 (dd, J = 1.5, 16 Hz, 1H), 4.46 (q, J = 7.0 Hz, 2H), 1.48 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.4, 136.7, 135.0, 133.2, 132.7, 132.2, 132.0, 129.8, 128.5, 128.2, 128.0, 127.3, 126.5, 126.2, 125.8, 115.6, 61.2, 14.4; HRMS (ESI-TOF) Calcd for $C_{19}H_{17}O_2$ $[M + H]^+$ m/z 277.1229, found 277.1227.

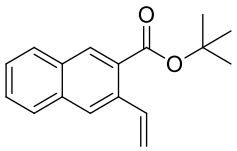


(*E*)-Ethyl 3-(But-1-en-1-yl)-2-naphthoate (7d). Pale yellow oil (48 mg, 95% yield); R_f = 0.72 (hexane/EtOAc, 3:1); IR (film) ν_{max} 3178, 2987, 1715, 1597, 1266, 1185, 1028, 958 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.93 (s, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.82 (d, J = 8.5 Hz, 1H), 7.54 (t, J = 7.0 Hz, 1H), 7.46 (t, J = 7.0 Hz, 1H), 7.19 (d, J = 15.5 Hz, 1H), 6.25 (dt, J = 6.5, 15.5 Hz, 1H), 4.43 (q, J = 7.0 Hz, 2H), 2.35–2.29 (m, 2H), 1.45 (t, J = 7.0 Hz, 3H), 1.16 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.8, 136.0, 135.0, 134.9, 131.4 (2C), 128.7, 128.1, 128.0, 127.5, 127.4, 126.1 (2C), 61.1, 26.3, 14.4, 13.6; HRMS (ESI-TOF) Calcd for $C_{17}H_{19}O_2$ $[M + H]^+$ m/z 255.1385, found 255.1382.

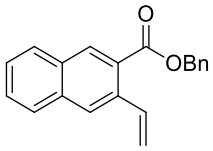


(*E*)-Ethyl 3-(2-Cyclopentylvinyl)-2-naphthoate (7e). Pale yellow oil (56 mg, 96% yield); R_f = 0.82 (hexane/EtOAc, 3:1); IR (film) ν_{max} 3178, 2952, 1723, 1266, 1200, 1059 cm^{-1}; ^1H

NMR (500 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.94 (s, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.53 (t, J = 7.5 Hz, 1H), 7.46 (t, J = 7.5 Hz, 1H), 7.18 (d, J = 16 Hz, 1H), 6.20 (dd, J = 7.5, 15.5 Hz, 1H), 4.43 (q, J = 7.0 Hz, 2H), 2.75–2.67 (m, 1H), 1.96–1.90 (m, 2H), 1.78–1.70 (m, 2H), 1.69–1.60 (m, 2H), 1.51–1.48 (m, 2H), 1.45 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.8, 137.9, 135.9, 135.0, 131.4 (2C), 128.7, 128.1, 127.5 (2C), 127.0, 126.1, 125.9, 61.1, 44.0, 33.2, 25.3, 14.4; HRMS (ESI-TOF) Calcd for $C_{20}H_{23}O_2$ $[M + H]^+$ m/z 295.1690, found 295.1698.



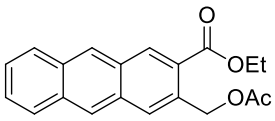
***tert*-Butyl 3-Vinyl-2-naphthoate (7f).** Pale yellow oil (49 mg, 97% yield); R_f = 0.75 (hexane/EtOAc, 3:1); IR (film) ν_{max} 3292, 2978, 1771, 1597, 1287, 1168, 1097, 957 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.95 (s, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 8.5 Hz, 1H), 7.54 (t, J = 7.0 Hz, 1H), 7.50–7.44 (m, 2H), 5.70 (dd, J = 1.5, 17 Hz, 1H), 5.36 (dd, J = 1.5, 11 Hz, 1H), 1.65 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.9, 136.8, 135.9, 134.7, 131.9, 131.1, 129.1, 128.6, 128.0, 127.7, 126.4 (2C), 115.5, 81.7, 28.3; HRMS (ESI-TOF) Calcd for $C_{17}H_{19}O_2$ $[M + H]^+$ m/z 255.1385, found 255.1381.



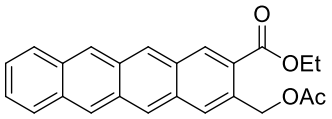
Benzyl 3-Vinyl-2-naphthoate (7g). Pale yellow oil (54 mg, 93% yield); R_f = 0.75 (hexane/EtOAc, 3:1); IR (film) ν_{max} 3289, 3178, 3144, 1713, 1598, 1490, 1186, 1028, 957 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (s, 1H), 7.98 (s, 1H), 7.89–7.85 (m, 2H), 7.58–7.55 (m, 2H), 7.51–7.50 (m, 3H), 7.44–7.41 (m, 2H), 7.38–7.37 (m, 1H), 5.73 (dd, J = 1.5, 17 Hz, 1H), 5.42 (s, 2H), 5.38 (dd, J = 1.5, 11 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.2,

136.5, 136.3, 136.0, 135.0, 131.8 (2C), 128.8, 128.7, 128.4 (2C), 128.3, 127.8, 126.8, 126.6 (2C), 116.0, 67.3; HRMS (ESI-TOF) Calcd for $C_{20}H_{17}O_2$ $[M + H]^+$ *m*/*z* 289.1229, found 289.1227.

6. Application



Ethyl 3-(Acetoxymethyl)anthracene-2-carboxylate (9). Pale yellow solid (85%); m.p. 142 °C; R_f = 0.51 (hexane/EtOAc, 3:1); IR (film) ν_{max} 3286, 3176, 1737, 1490, 1217, 1184, 1030 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.51 (s, 1H), 8.41 (s, 1H), 8.03–8.00 (m, 3H), 7.54–7.49 (m, 2H), 5.65 (s, 2H), 4.45 (q, *J* = 7.0 Hz, 2H), 2.18 (s, 3H), 1.46 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.8, 167.0, 133.8, 133.3, 132.2, 131.8, 131.6, 129.8, 128.5, 128.4, 128.2, 128.2, 126.7, 126.3, 126.0, 65.4, 61.3, 21.1, 14.4; HRMS (ESI-TOF) Calcd for $C_{20}H_{18}O_4Na$ $[M + Na]^+$ *m*/*z* 345.1103, found 345.1114.



Ethyl 3-(Acetoxymethyl)tetracene-2-carboxylate (11). Red solid (72%); m.p. 356 °C; R_f = 0.32 (hexane/EtOAc, 1:1); IR (film) ν_{max} 3053, 2983, 1740, 1456, 1217, 1177, 1031 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.82–8.80 (m, 2H), 8.74–8.69 (m, 3H), 8.08–8.04 (m, 3H), 7.50–7.47 (m, 2H), 5.69 (s, 2H), 4.50 (q, *J* = 7.0 Hz, 2H), 2.23 (s, 3H), 1.52 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.8, 166.9, 134.4, 132.3, 131.8, 131.3, 131.1, 131.0,

130.5, 129.5, 128.9, 128.7, 128.4, 128.3, 127.0, 126.5 (2C), 125.9, 125.7, 86.8, 65.5, 61.3, 21.1, 14.4; HRMS (ESI-TOF) Calcd for $C_{24}H_{21}O_4$ $[M + H]^+$ *m*/*z* 373.1440, found 373.1447.

7. Photophysical Studies

7.1 Absorption and Fluorescence Spectra of 4g, 9, and 11

UV–Vis spectra were recorded using an Ocean Optics USB2000 spectrophotometer equipped with a DT-MINI-2-GS light source. The spectra were recorded using a 1-mm quartz cuvette, with spectra-grade DCM as the solvent.

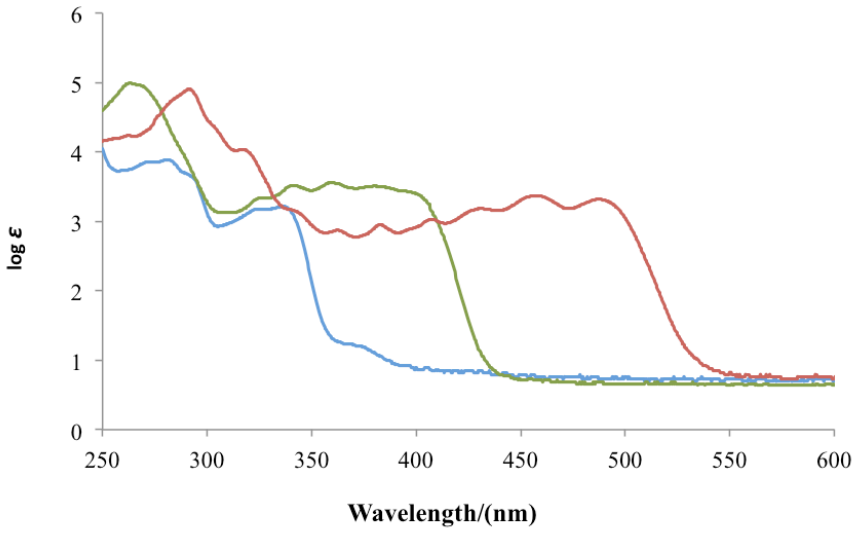


Figure S2. UV–Vis absorbance spectra of compounds **4g** (blue line), **9** (green line), and **11** (red line), with logarithms of extinction coefficients.

7.2 Fluorescence Quantum Yield in the Solution State

Fluorescence spectra were recorded using an Edinburgh Instruments FLSP920 spectrometer equipped with a Xe900 xenon bulb. The spectra were recorded using a 1-mm quartz cuvette, with spectra-grade cyclohexane as the solvent. The relative fluorescence quantum yield was

measured using anthracene (Φ_f = 0.27 in ethanol) as the standard, using the following equation

$$\Phi_u = \Phi_s \frac{A_s F_u \eta_r^2}{A_u F_s \eta_s^2}$$

where A_s and A_u are the absorbances of the standard and unknown samples, respectively, at the excitation wavelength; F_s and F_u are the integrated fluorescence intensities, respectively; and η is for the refractive index of the solvent used.[16] Here, the samples herein excited at 315 nm, with the absorbance at the excitation wavelength being less than 0.1. The lifetime of the compounds was not obtained because of the low absorbance at 303 nm (the emitting wavelength of the equipped pulsed diode laser).

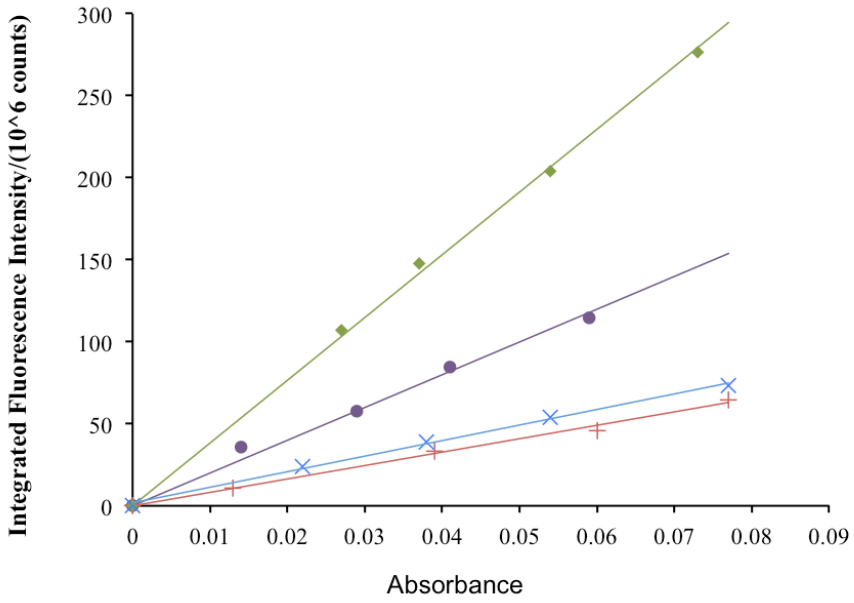
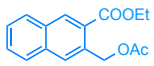
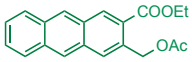
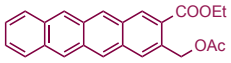


Figure S3. Linear plots of the absorbance and fluorescence intensities for anthracene (purple line) and compounds **4g** (blue line), **9** (green line), and **11** (red line).

Table S4: Summary of photophysical data.

compound	ε (M^{-1} cm^{-1})	excitation (nm)	emission (nm)	quantum yield
	7.7×10^3 (281 nm), 1.6×10^3 (336 nm)	280, 290, 326, 336	342, 359, 376	0.18
	9.7×10^4 (263 nm), 3.6×10^3 (359 nm)	270, 341, 358, 378, 396	406, 431, 461, 488	0.69
	7.9×10^4 (291 nm), 2.4×10^3 (457 nm)	289, 317, 452, 480	495, 531, 574	0.15

8. References

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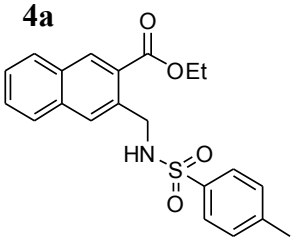
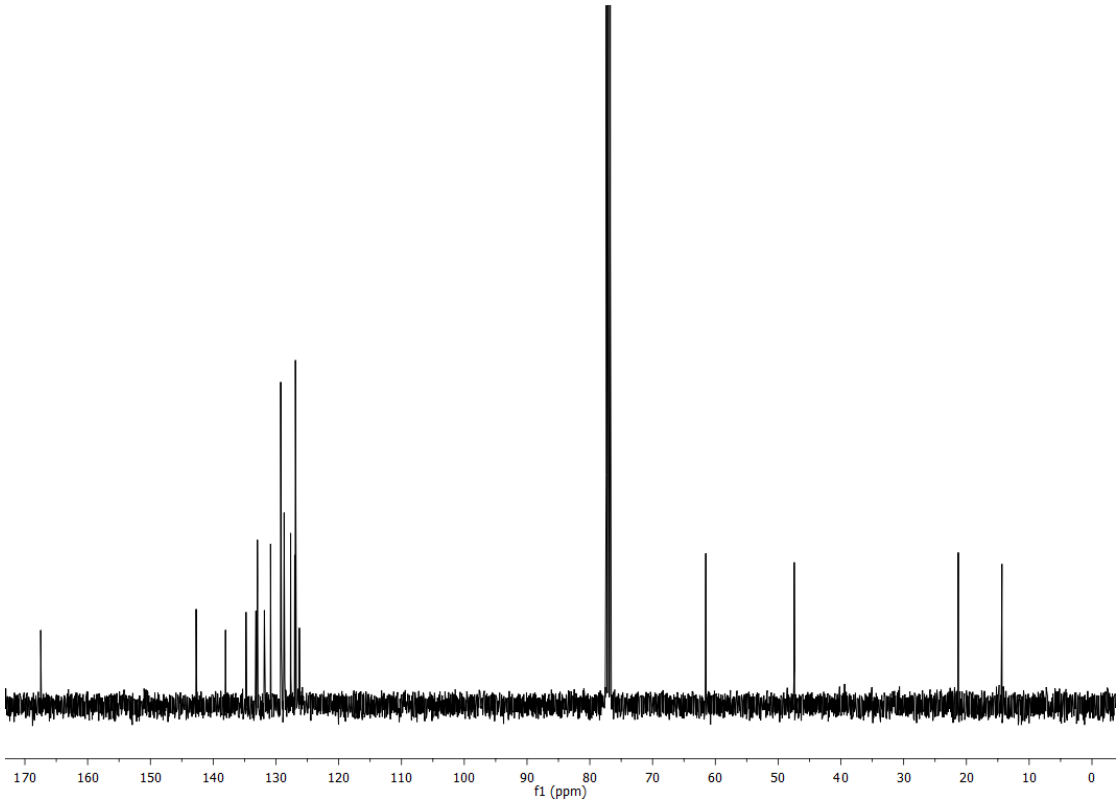
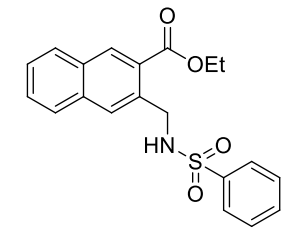
9. 1H and 13C NMR Spectra of All New Compounds

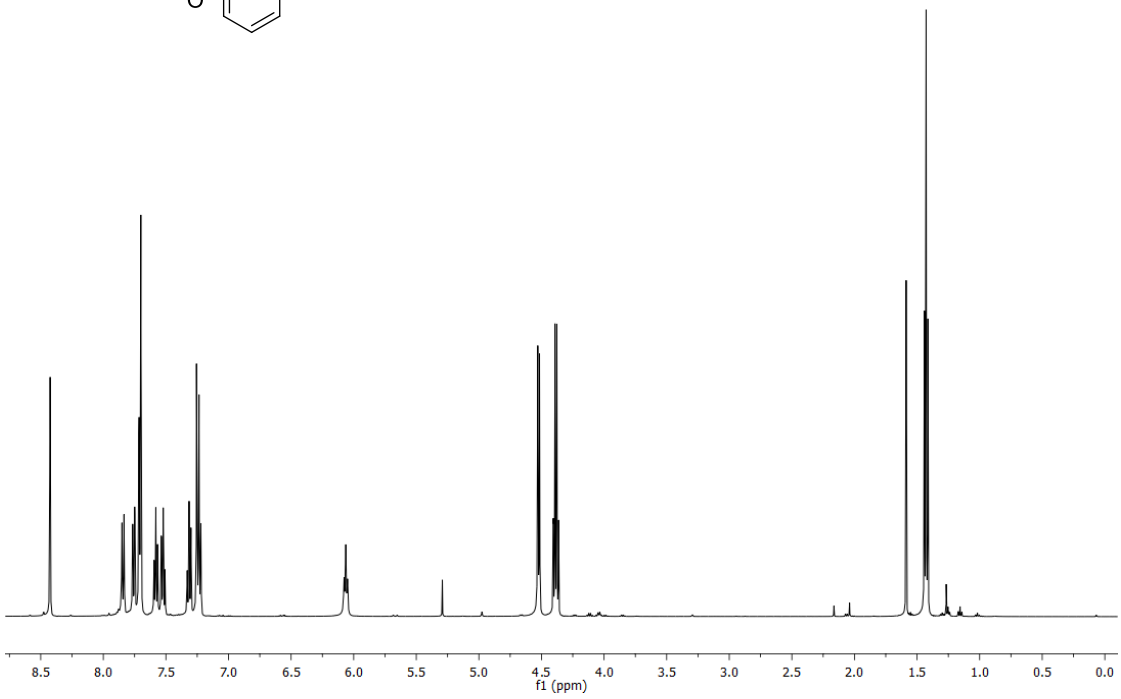
4a

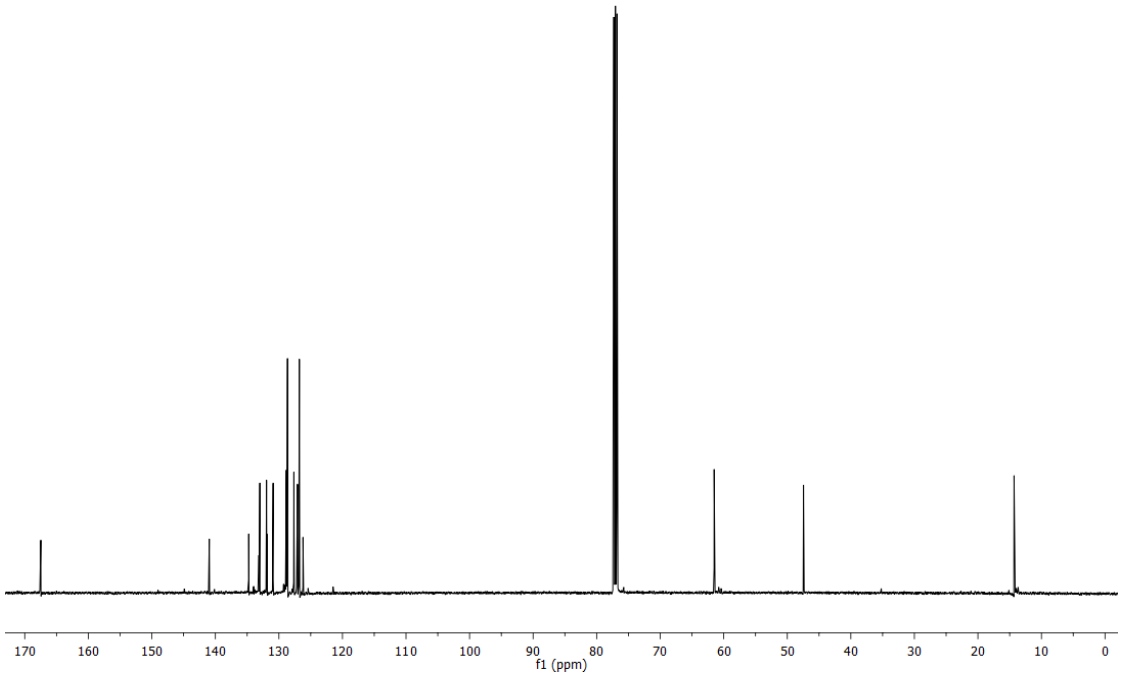




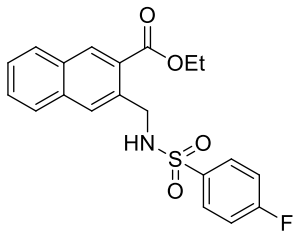
4b

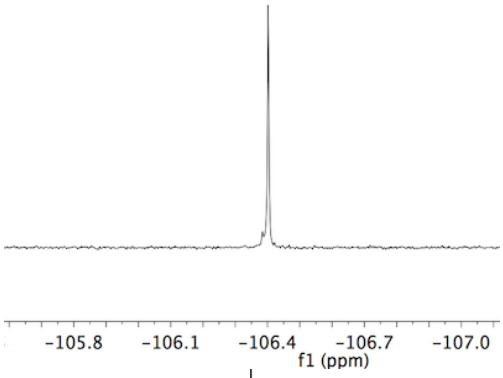

O
OEt
HN
S
O
O


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)


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

4c


O
OEt
HN
S
O
O
F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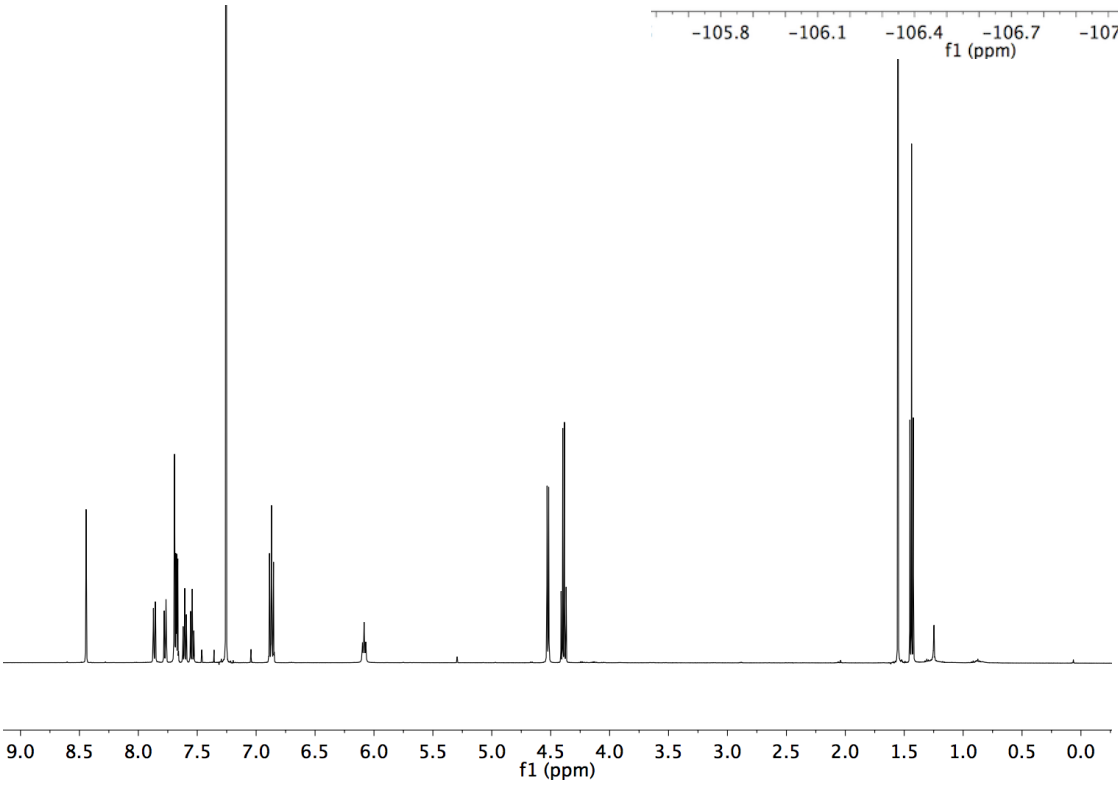
f1 (ppm)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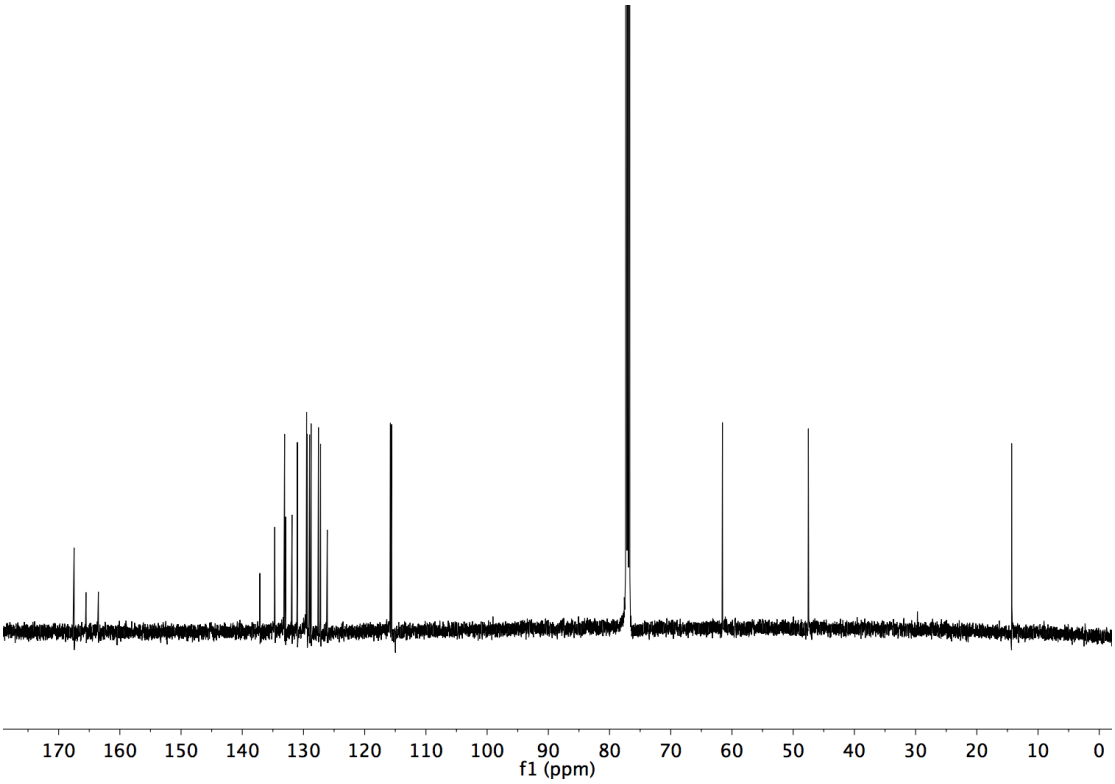
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


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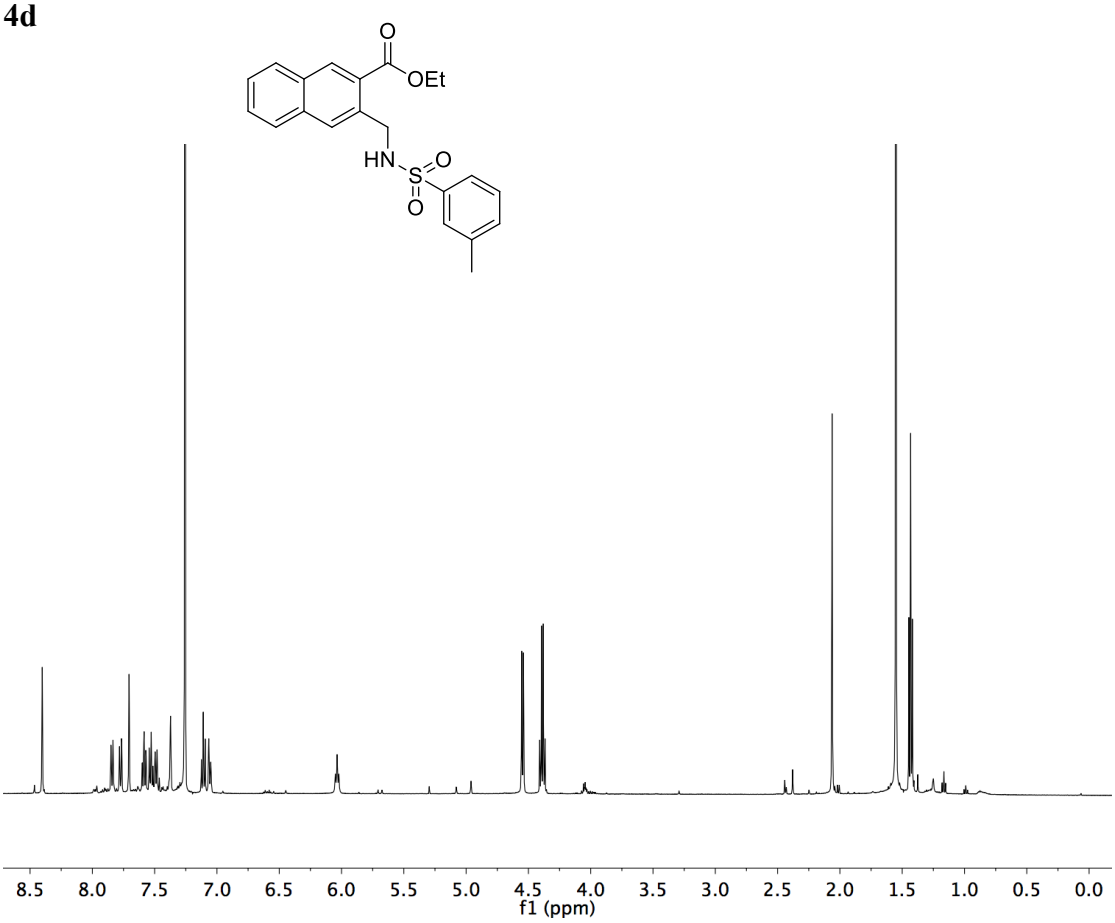
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

4d


O
OEt
HN
S
O
O
8.5
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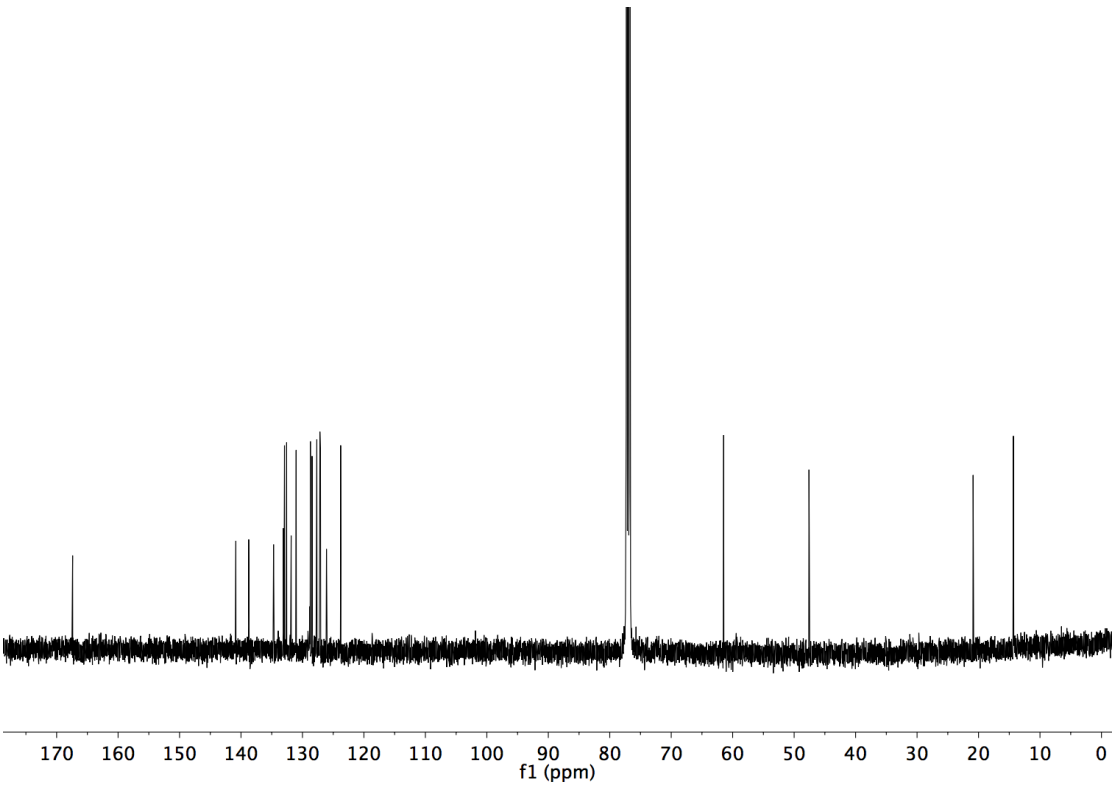
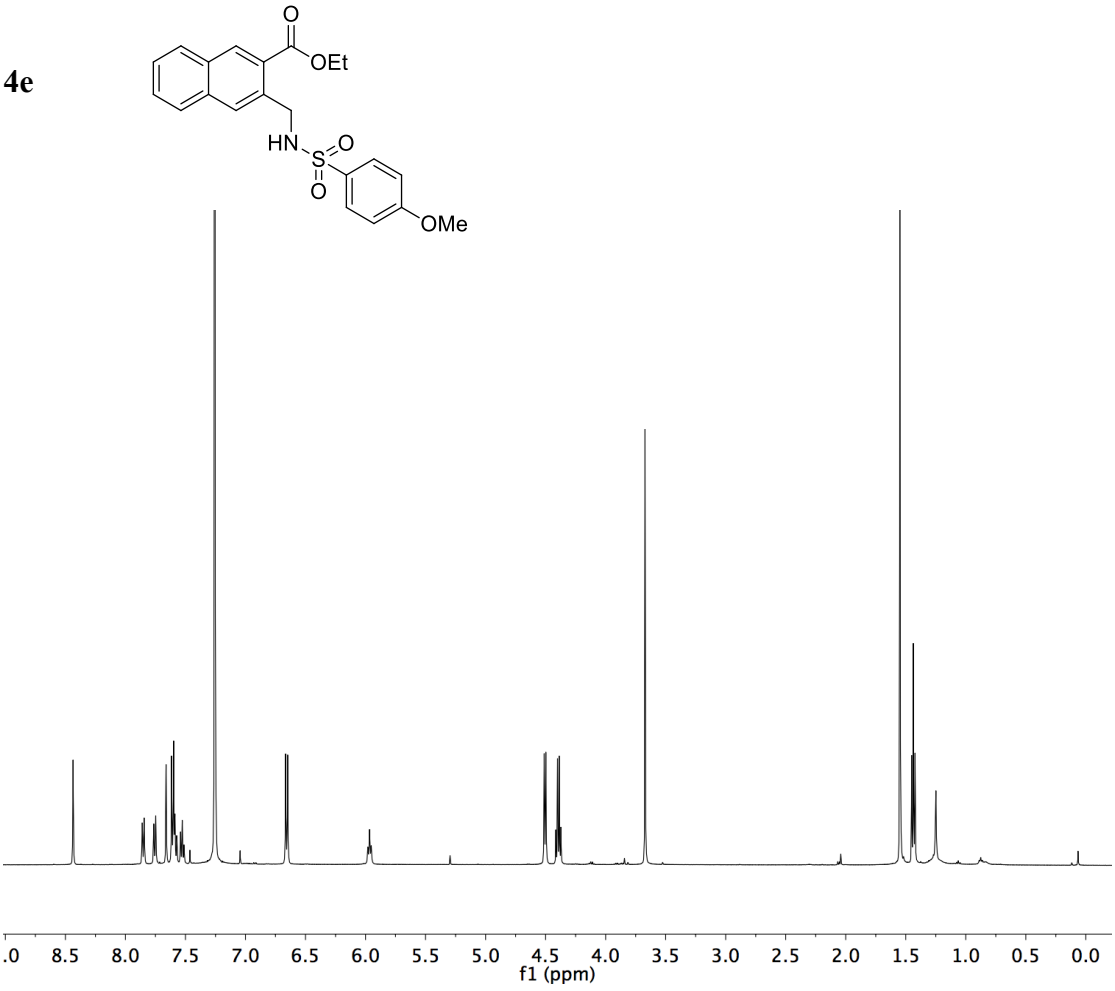
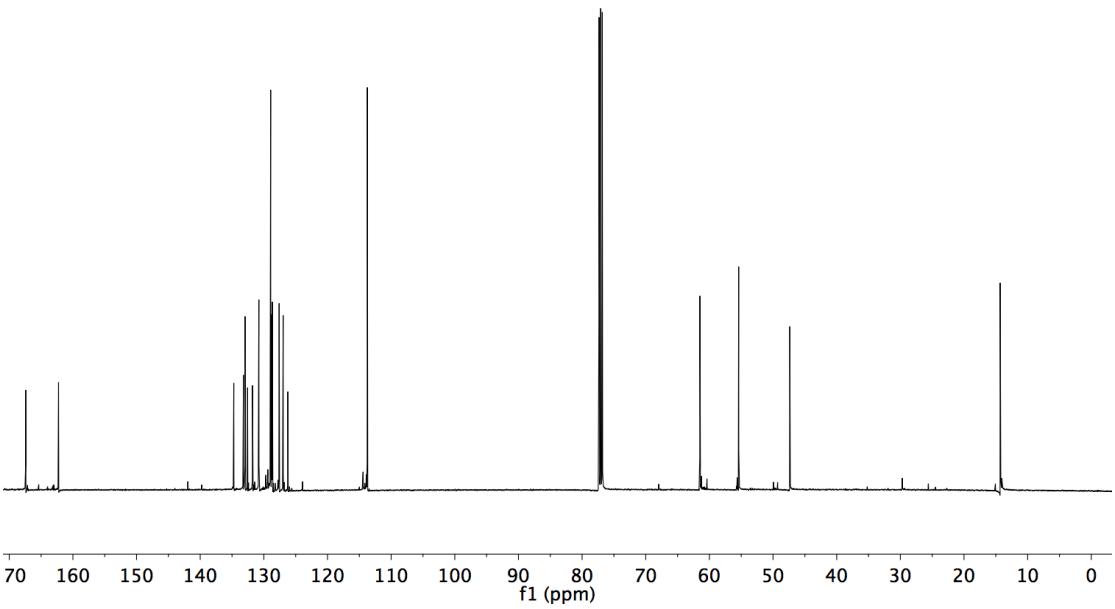
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

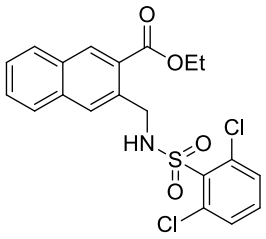

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

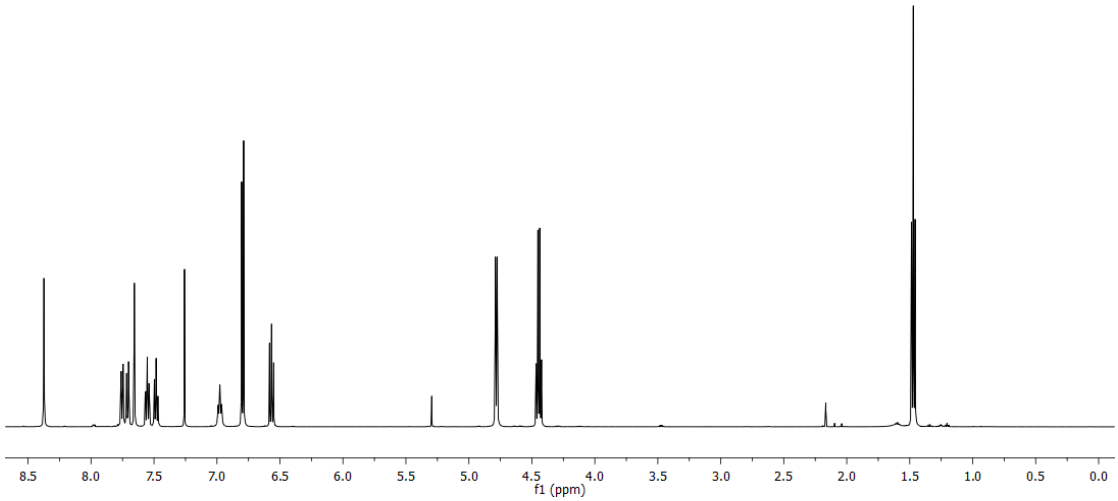
4e

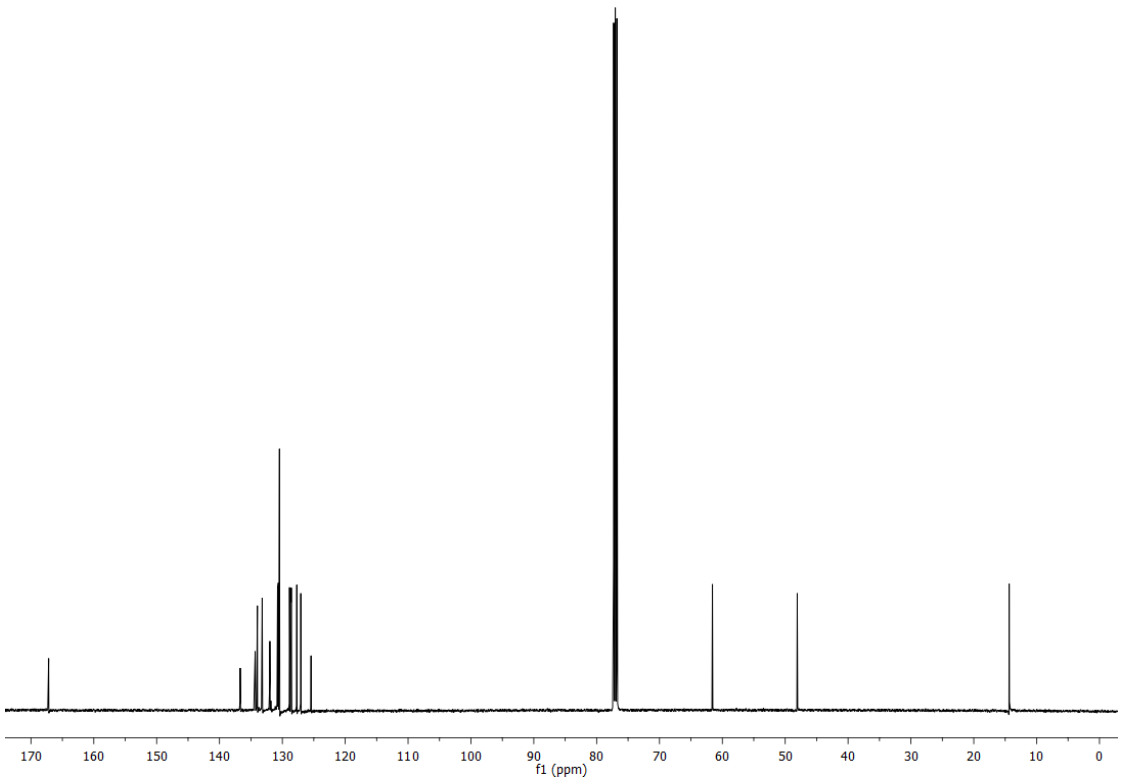

O
OEt
HN
S
O
O
OMe
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


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

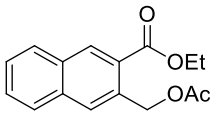
4f

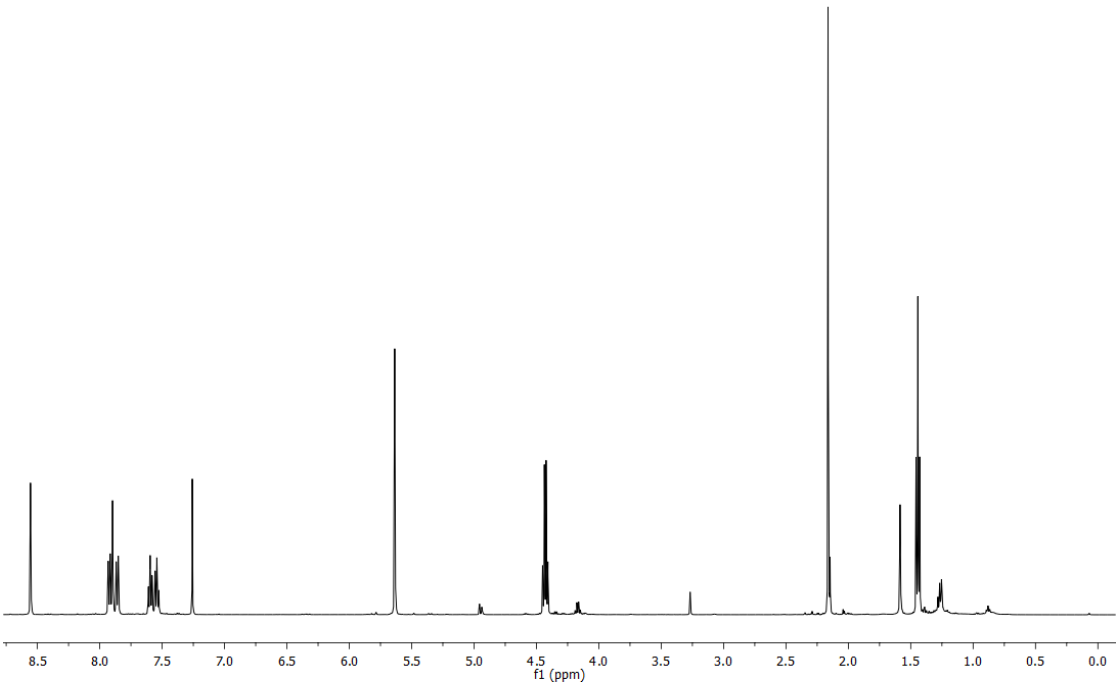

O
OEt
HN
S
O
O
Cl
Cl

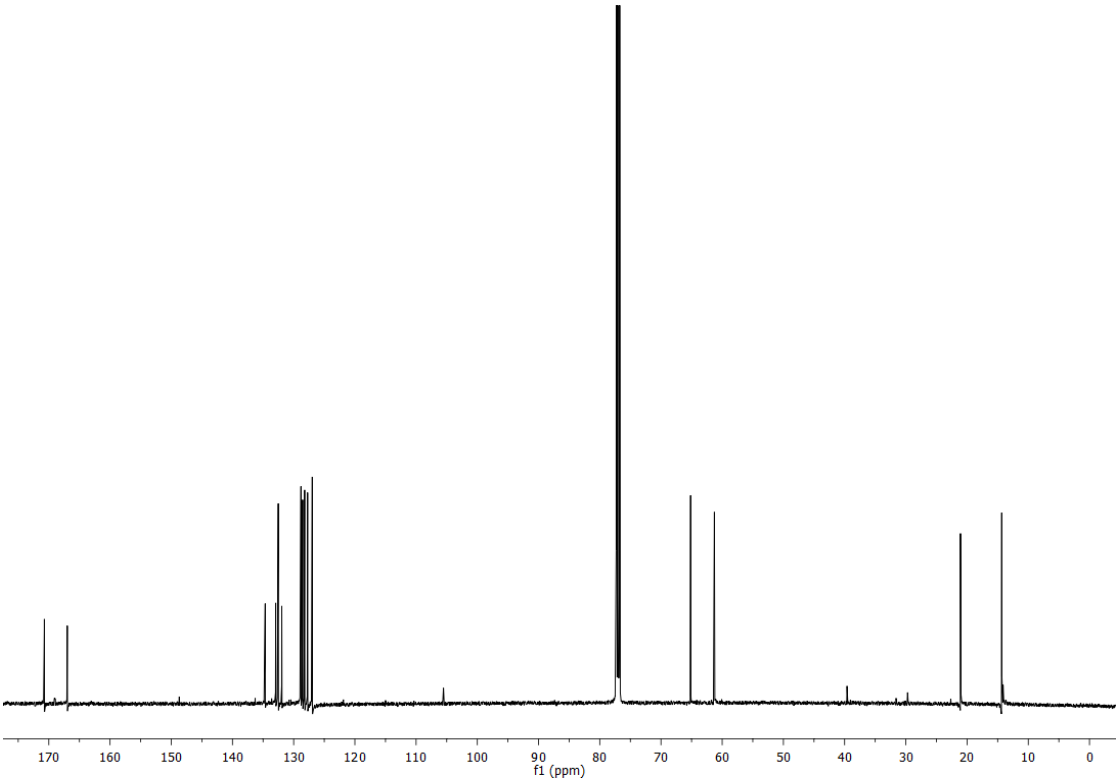

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


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

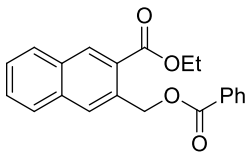
4g

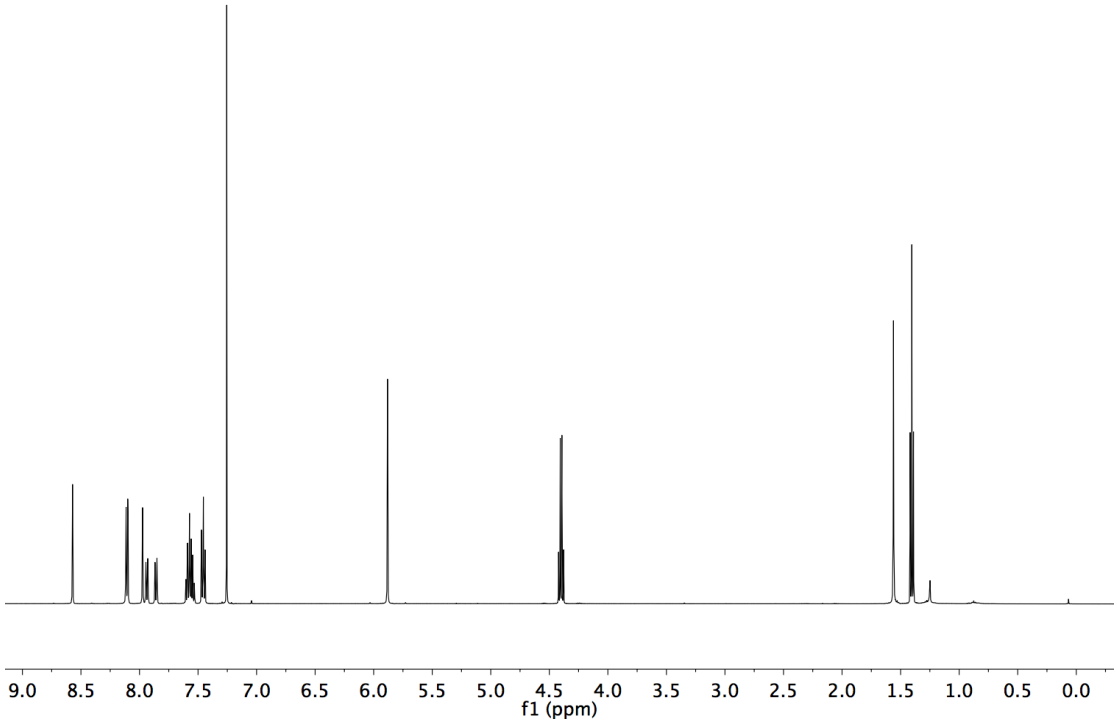

O
OEt
OAc

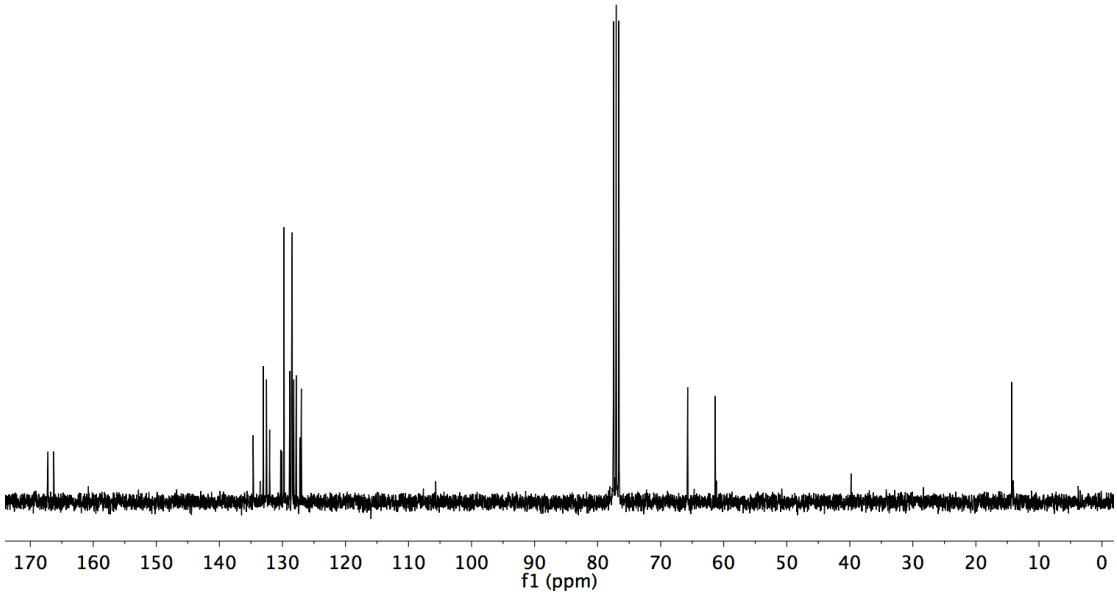

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


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

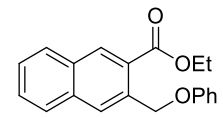
4h

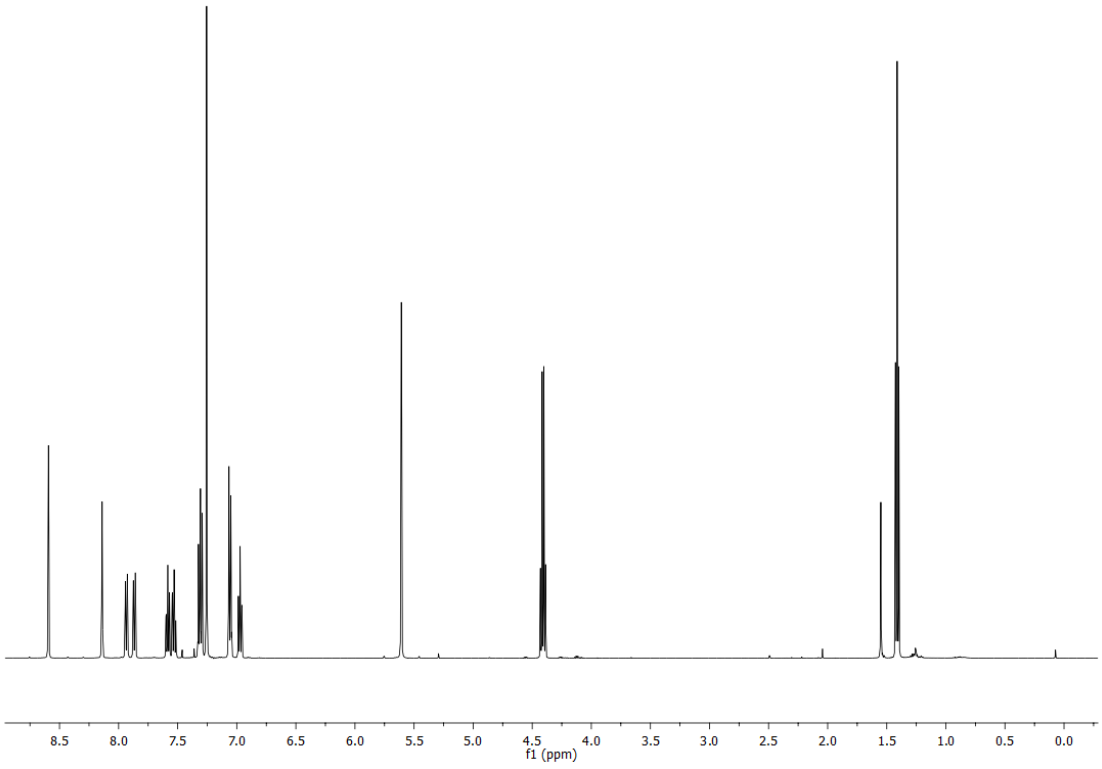

O
OEt
O
Ph
O

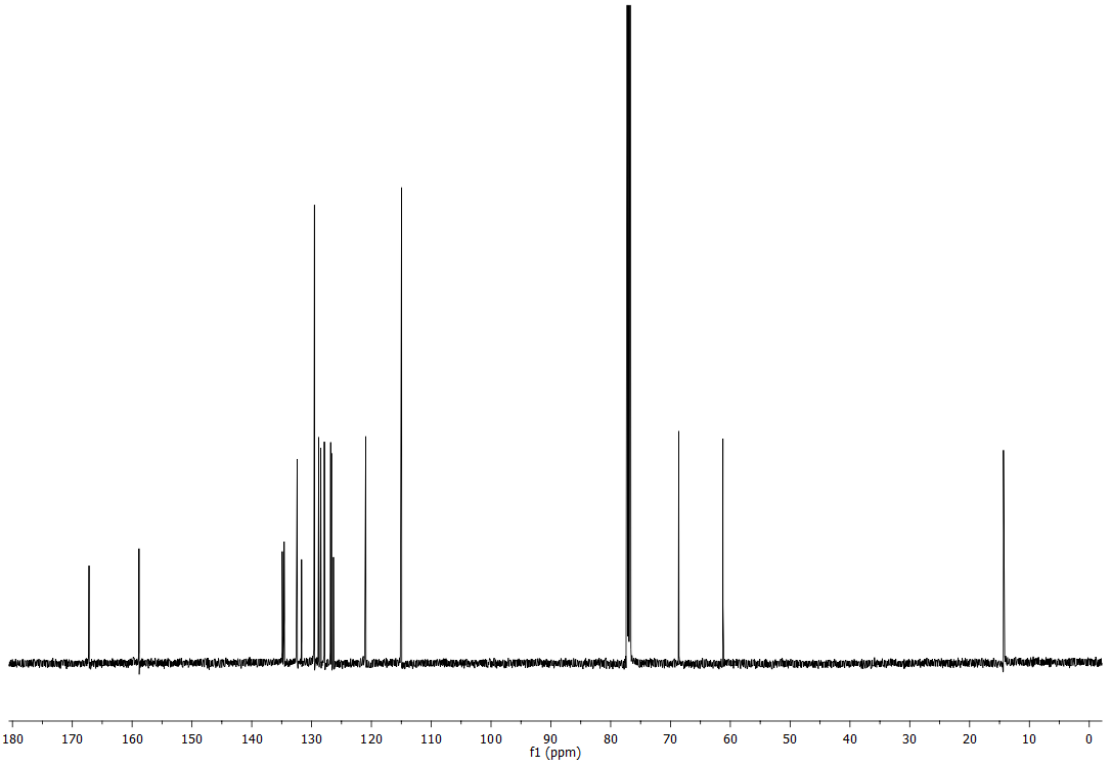

9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


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

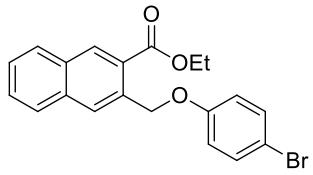
4i

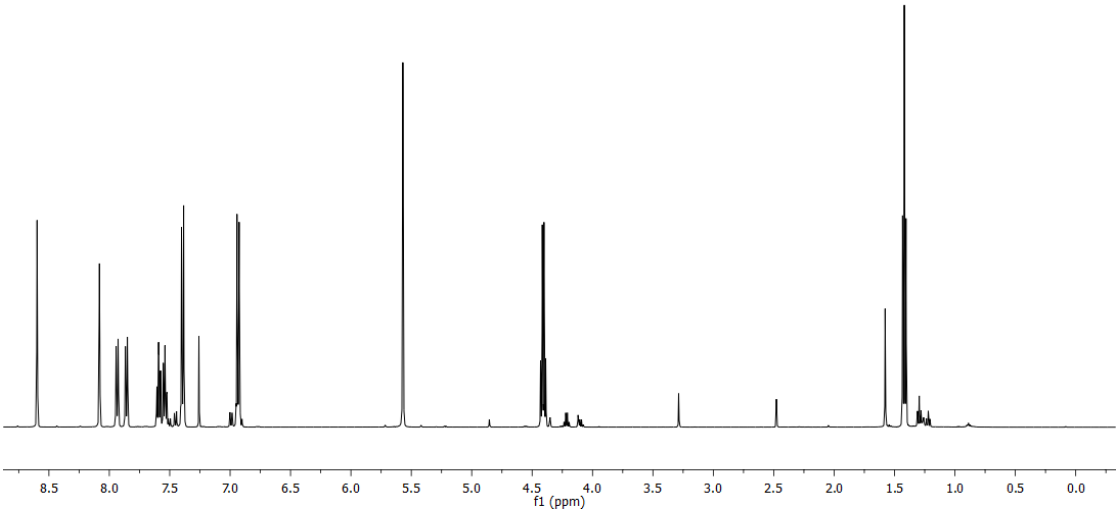

O
OEt
OPh

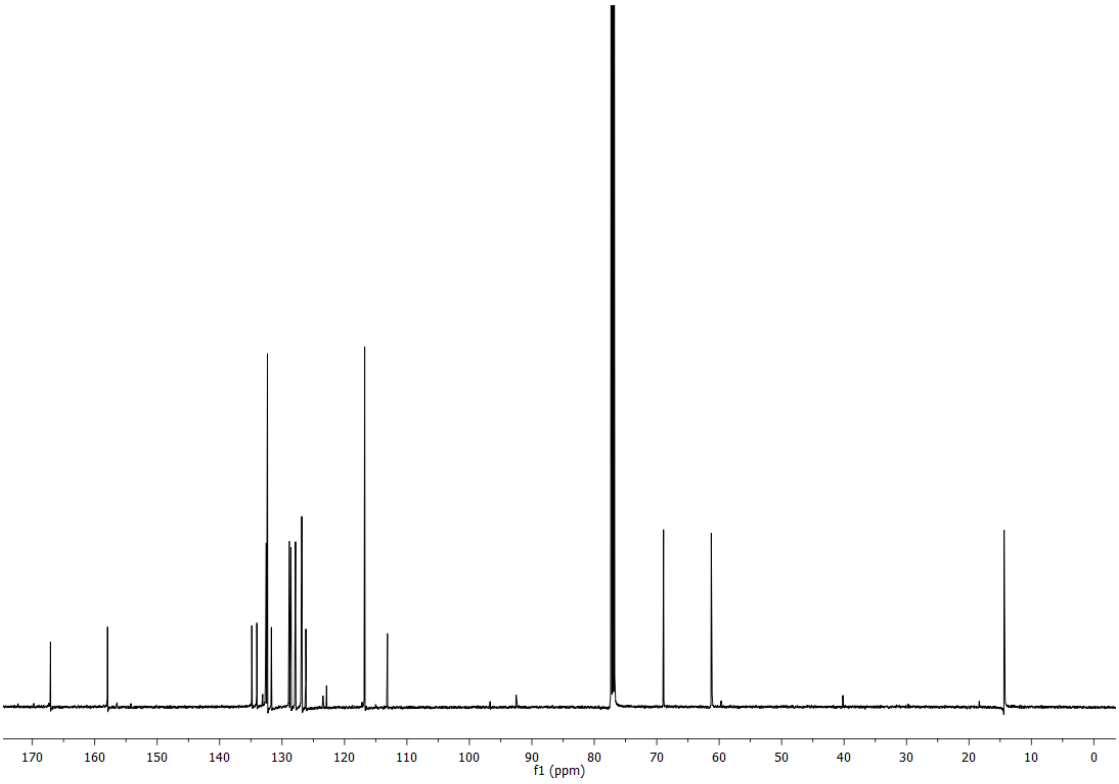

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


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

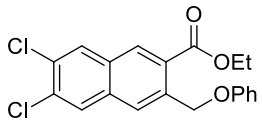
4j

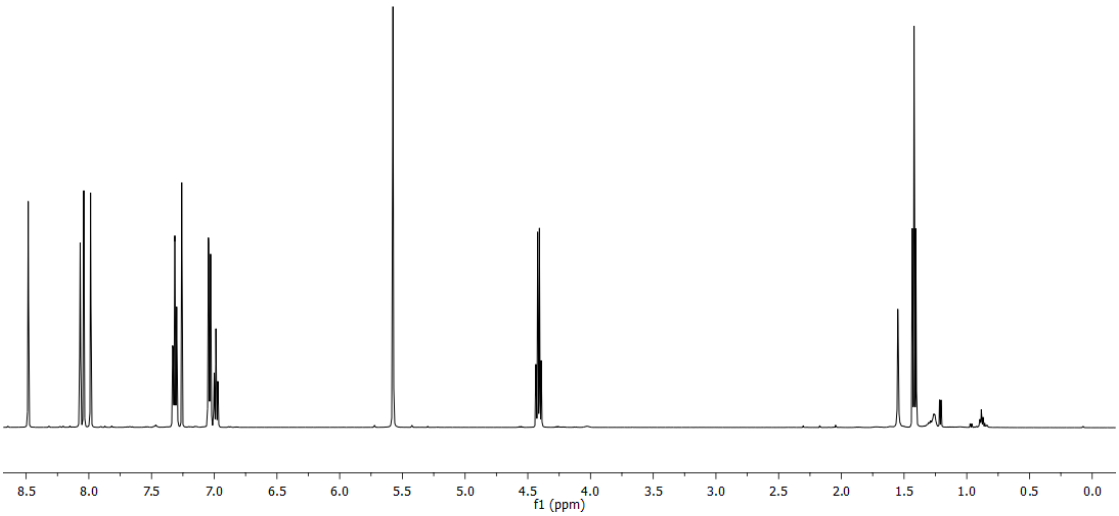

O
OEt
O
Br

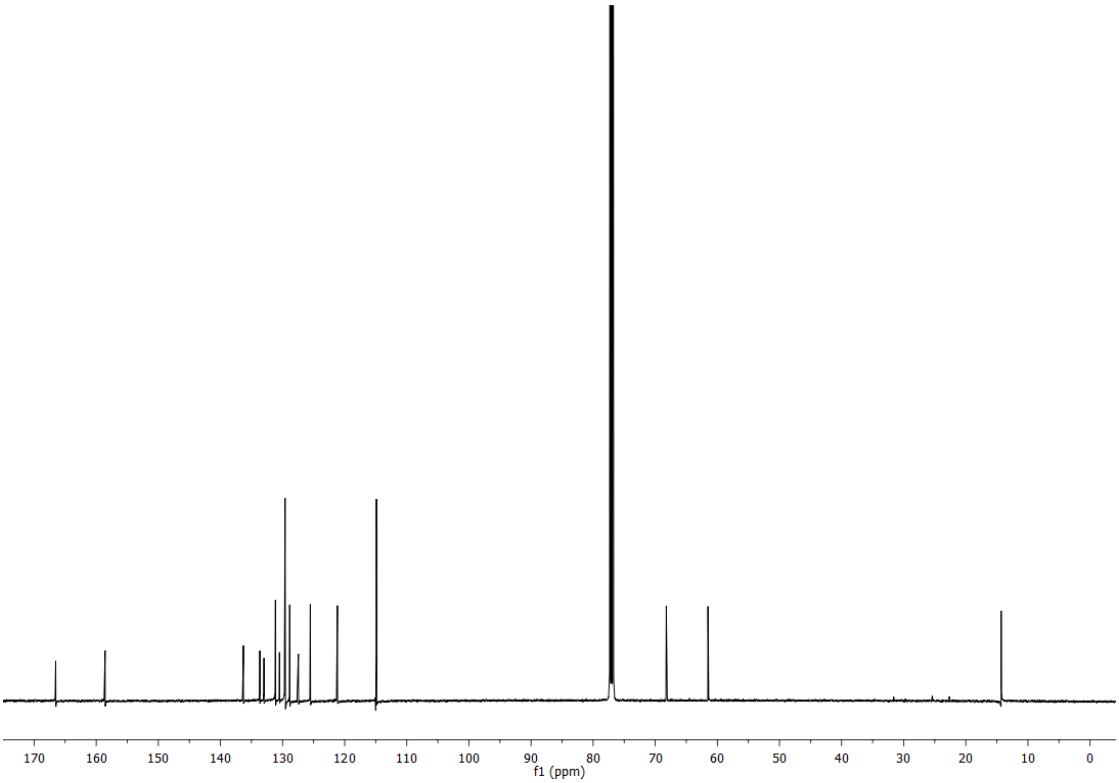

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


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

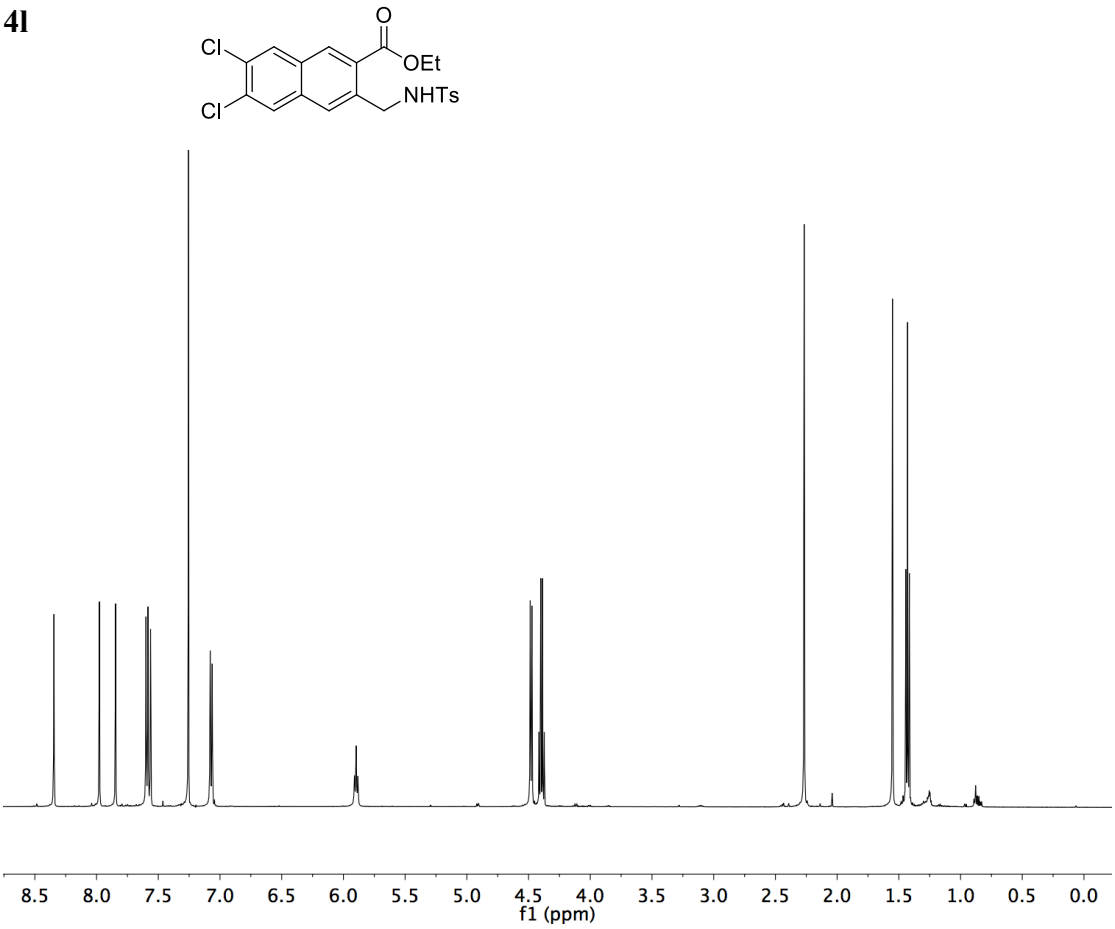
4k

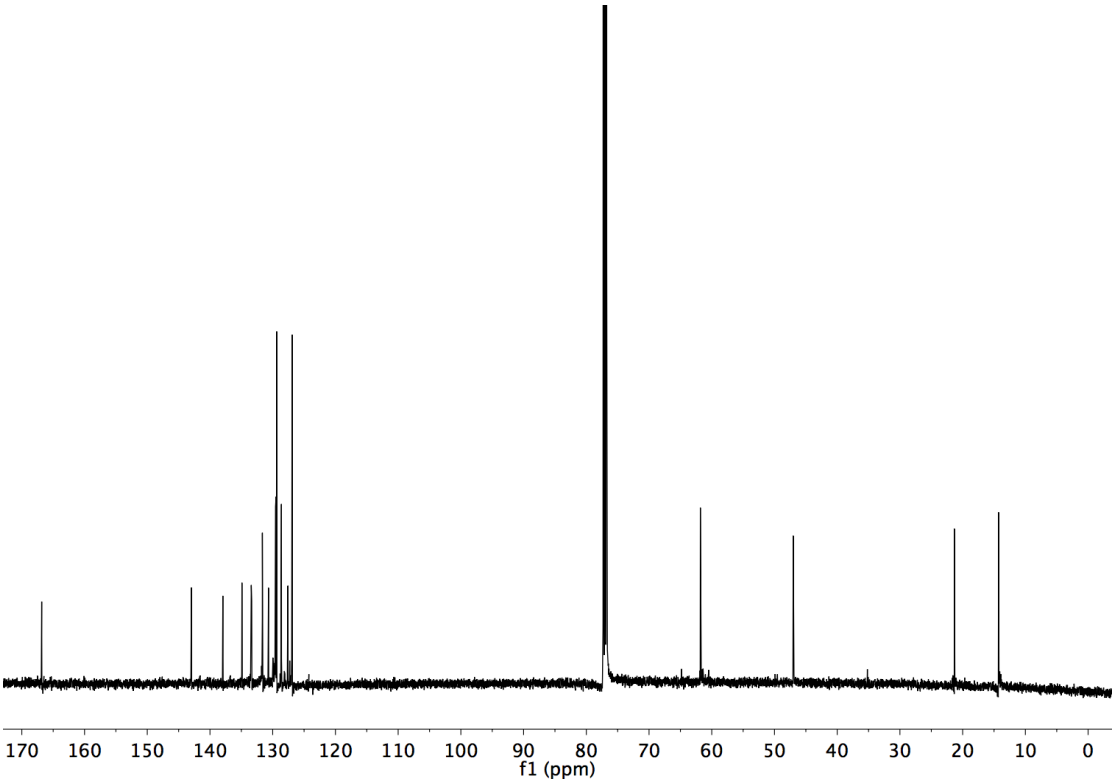

O
Cl
OEt
OPh
Cl


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)

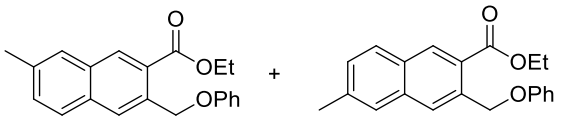

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

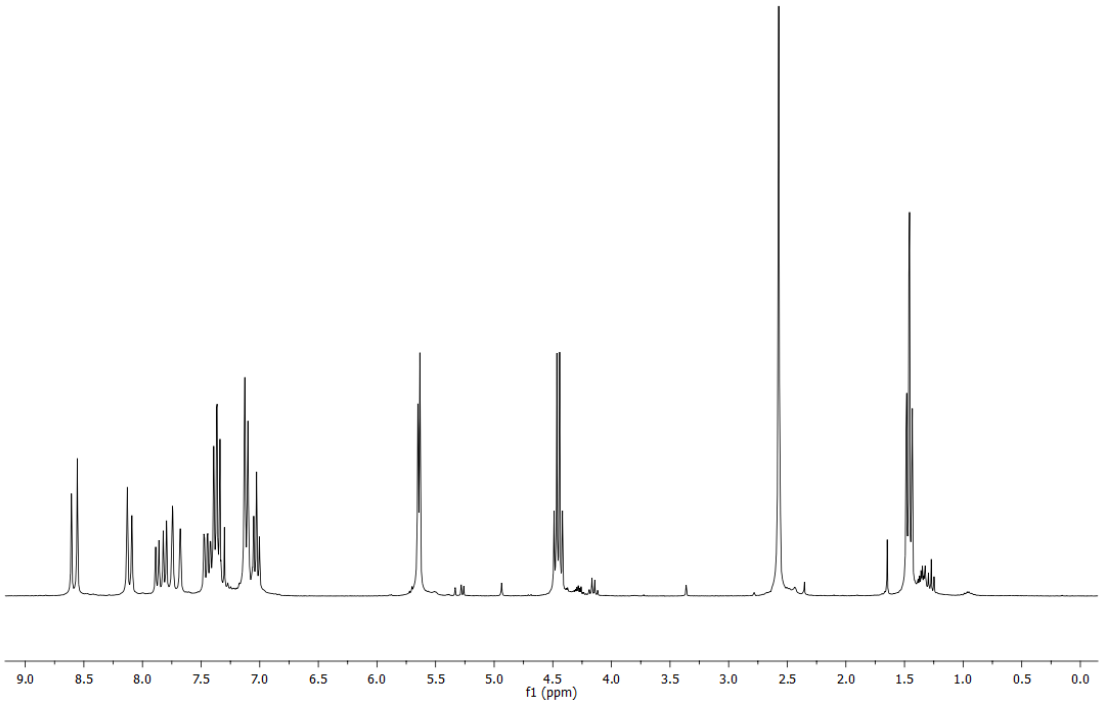
4l

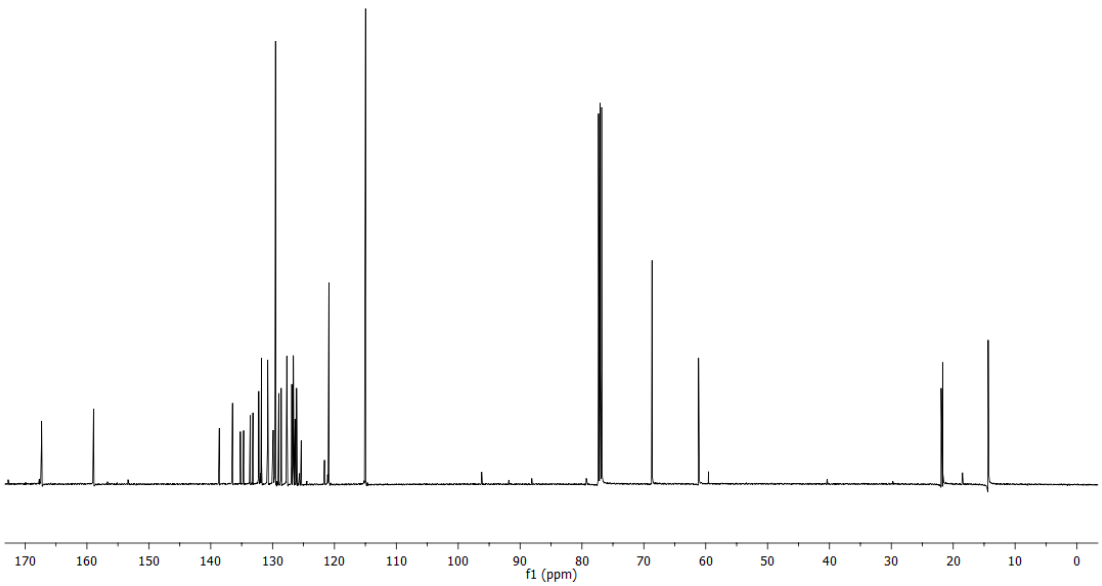

Cl
Cl
O
OEt
NHTs
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


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

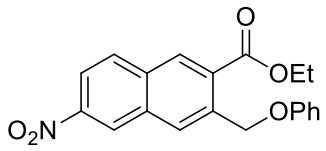
4m and **4m'**

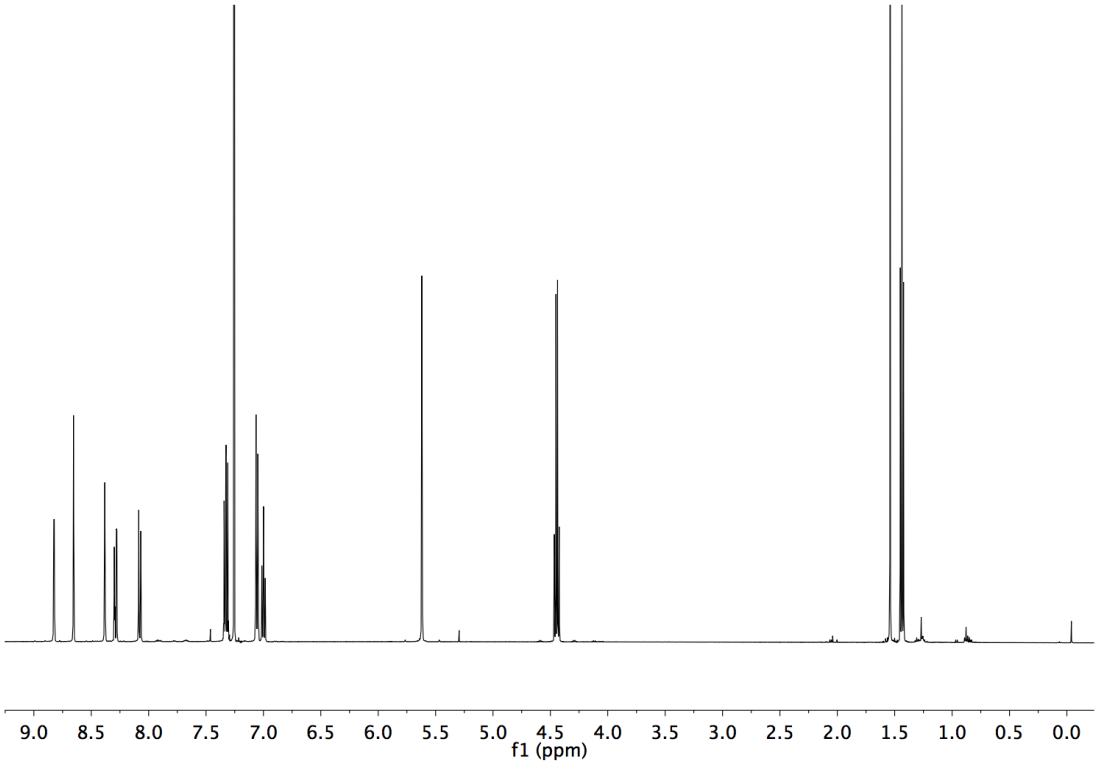

O
OEt
OPh
+
O
OEt
OPh

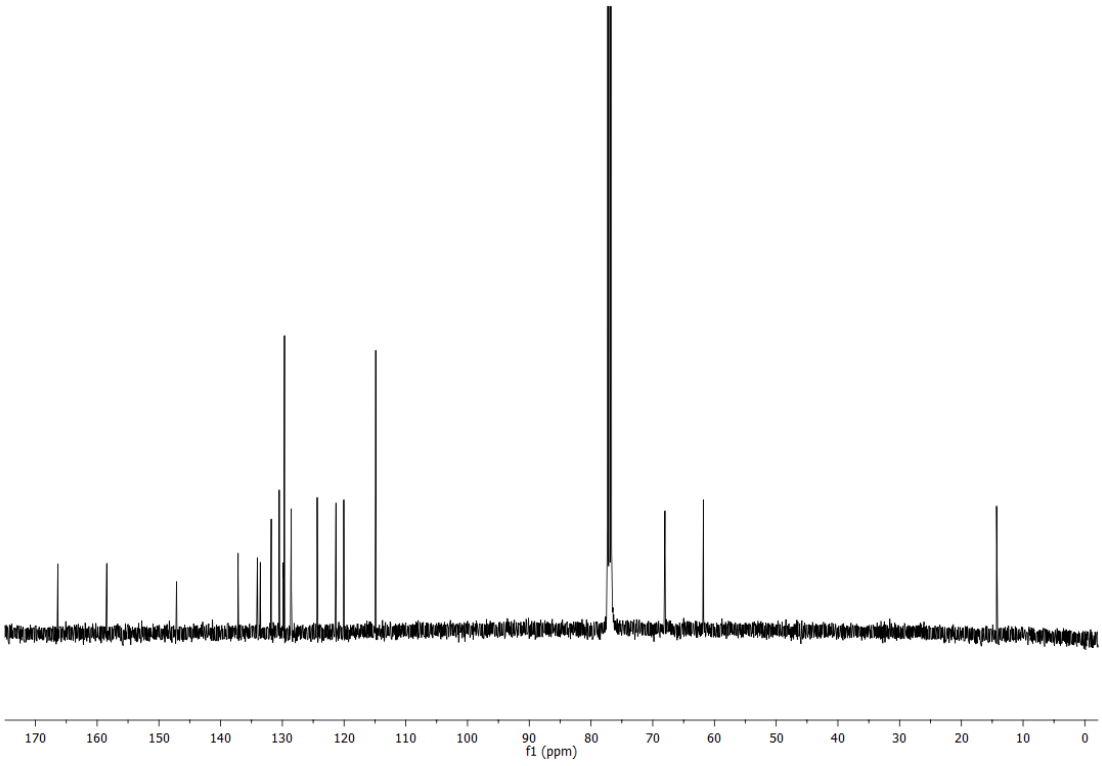

9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


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

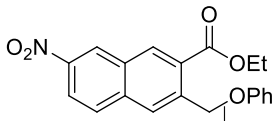
4n

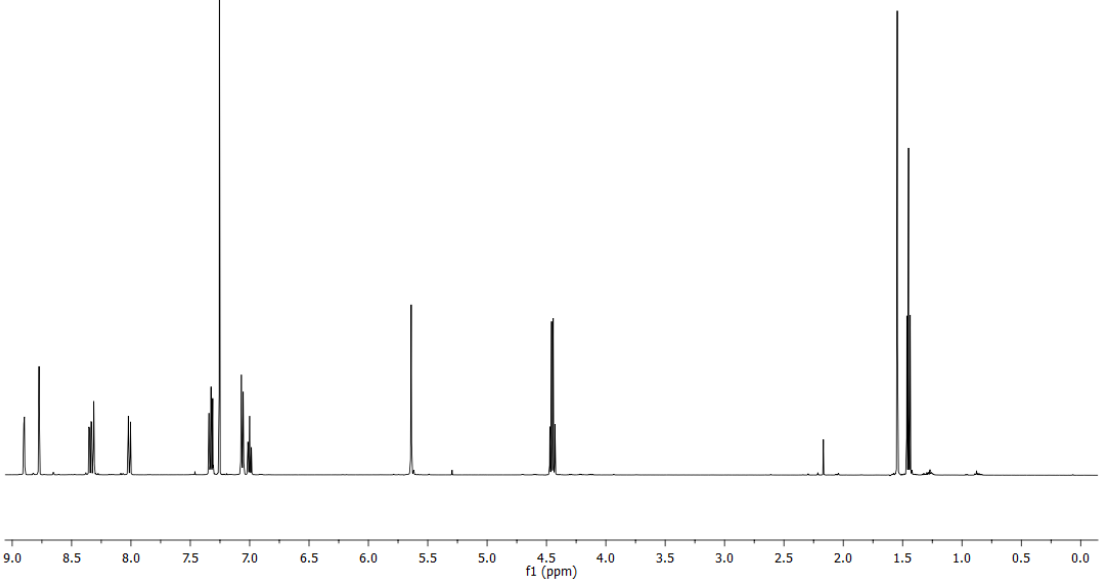

O
OEt
OPh
O2N

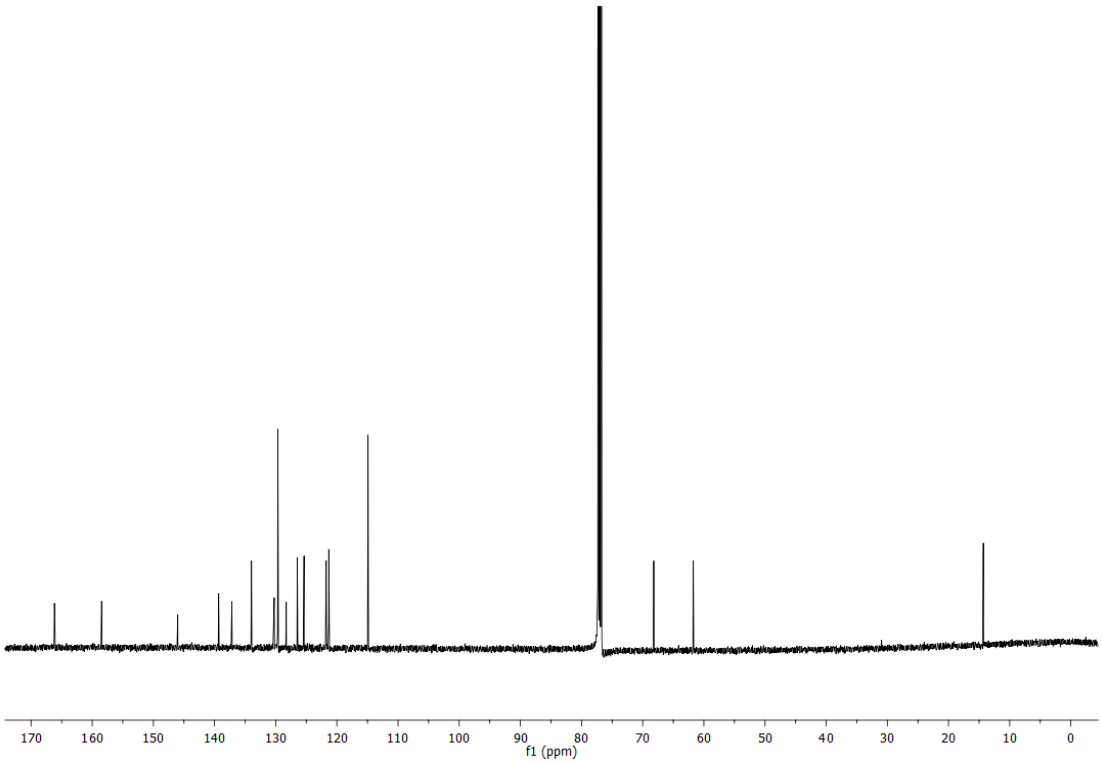

9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


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

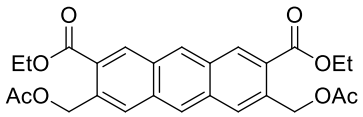
4n’


O
O2N
OEt
OPh

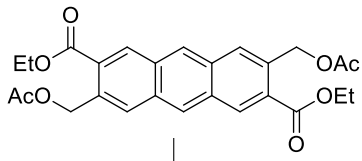

9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

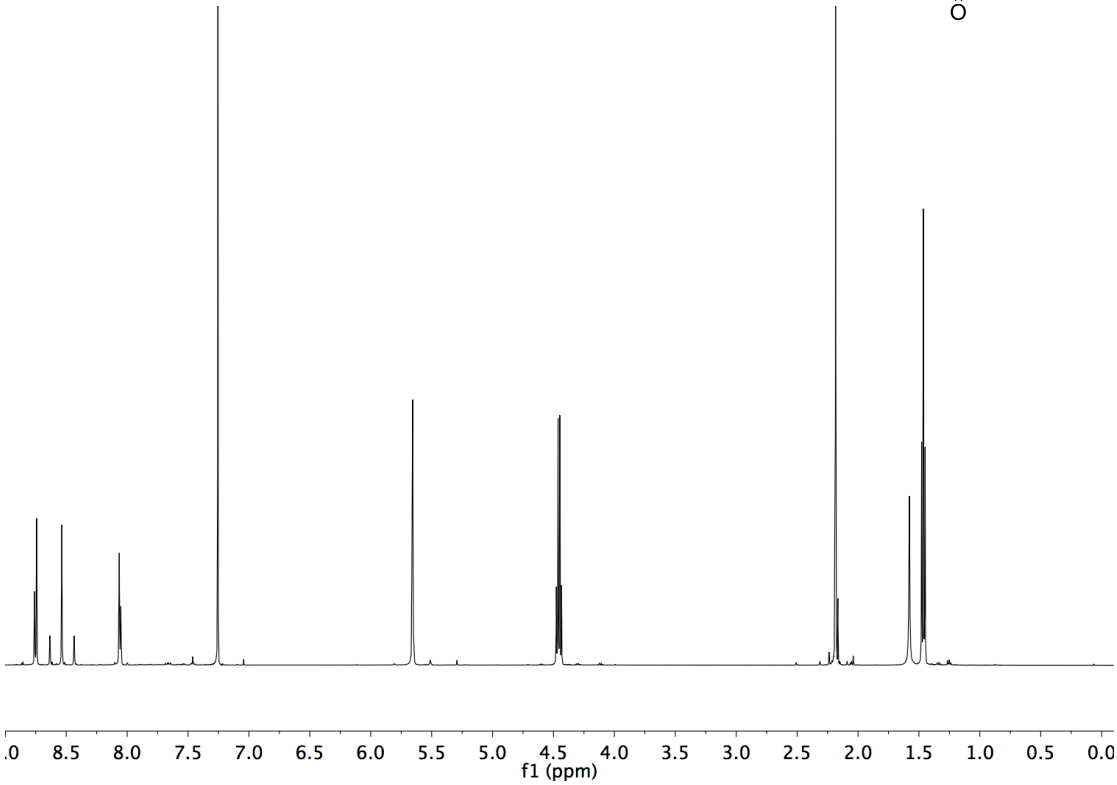

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

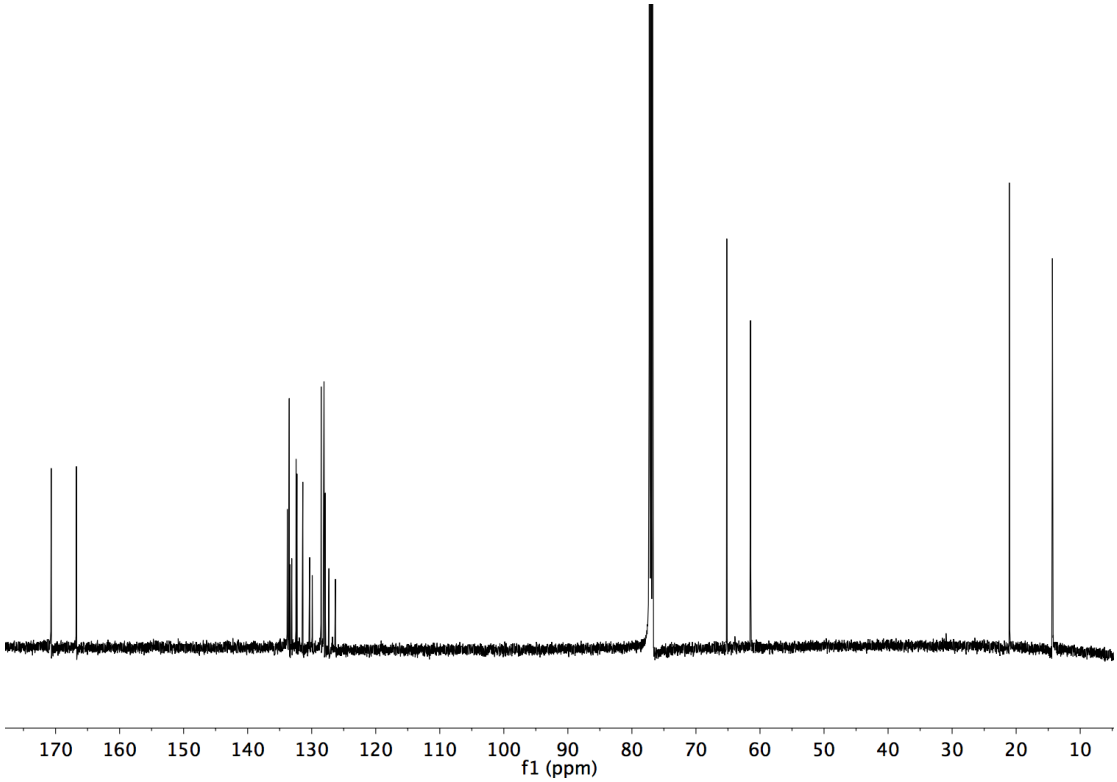
4o & 4o'


O
O
EtO
OEt
AcO
OAc

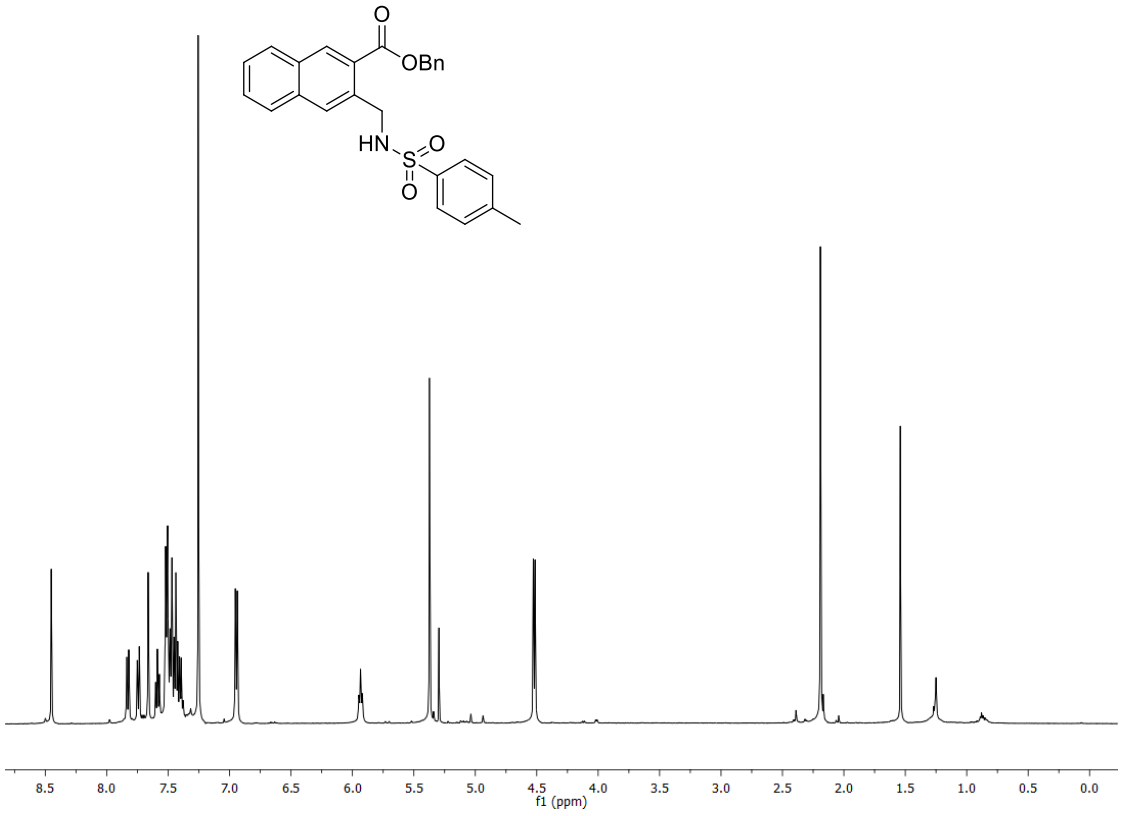
+

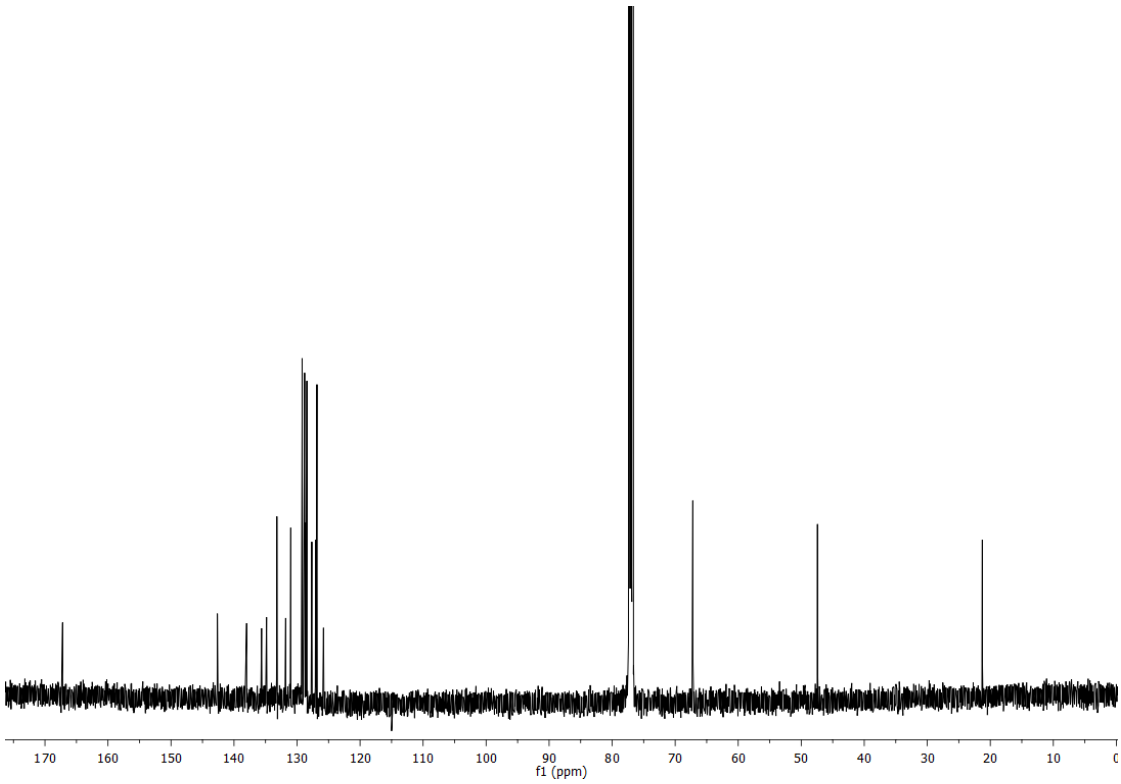

O
EtO
OAc
AcO
OEt
O


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)

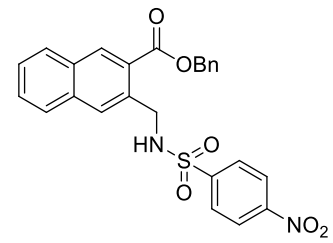

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

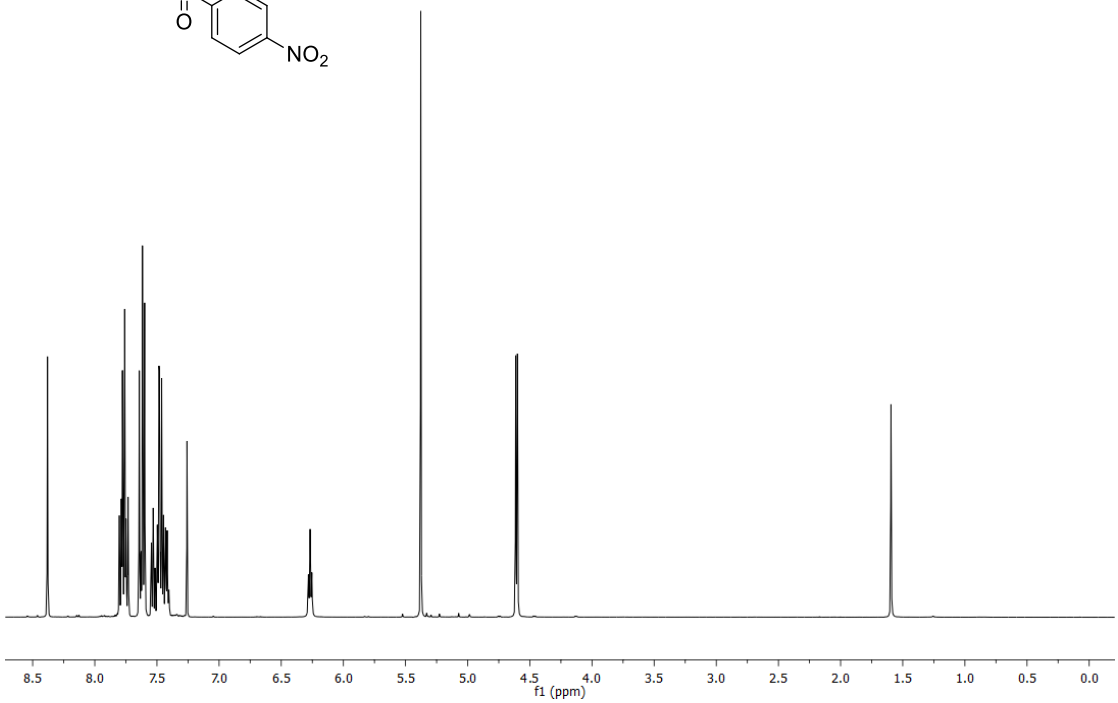
4p

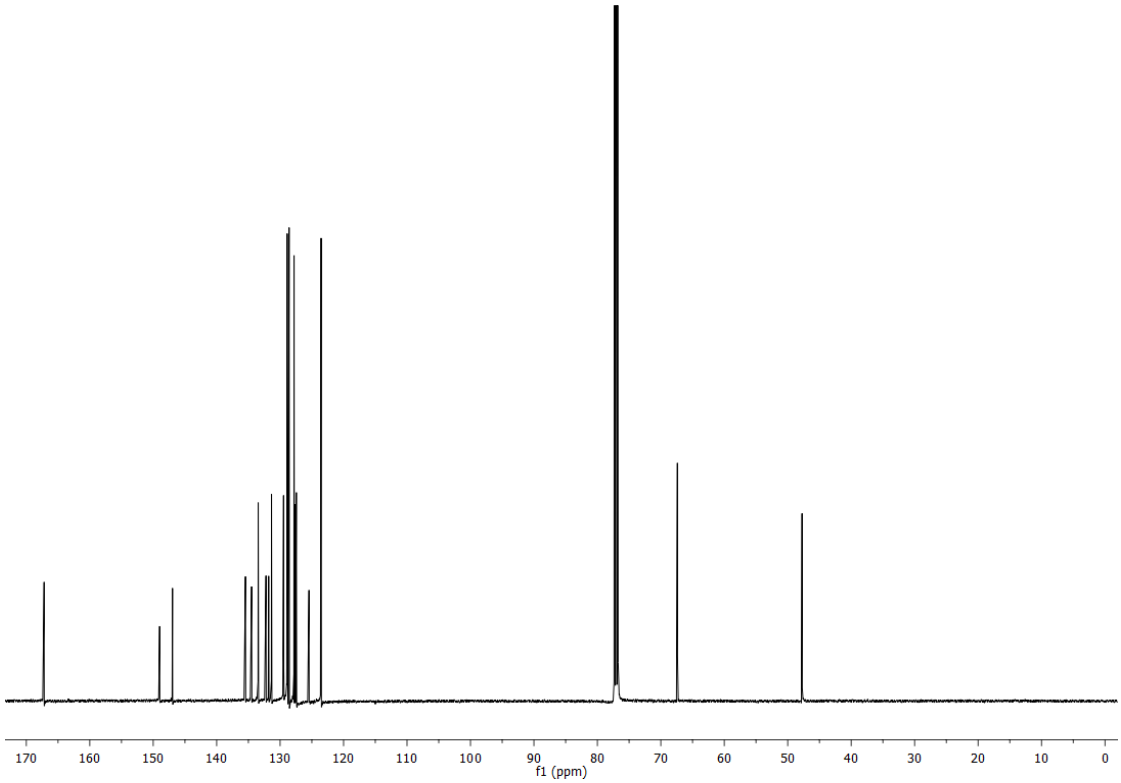

O
OBn
HN
S
O
O
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


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

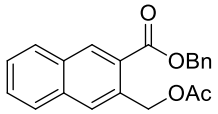
4q


O
OBn
HN
S
O
O
NO2

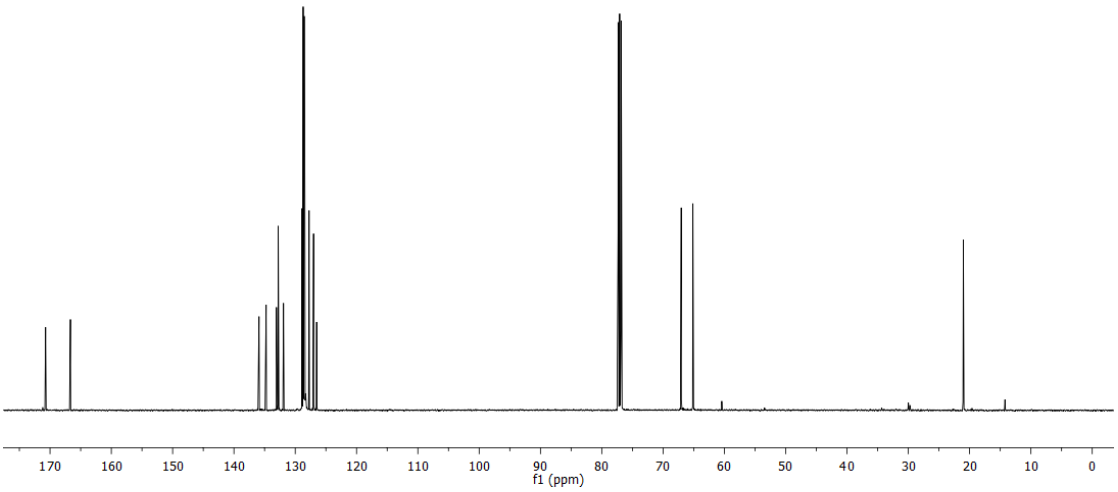

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


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

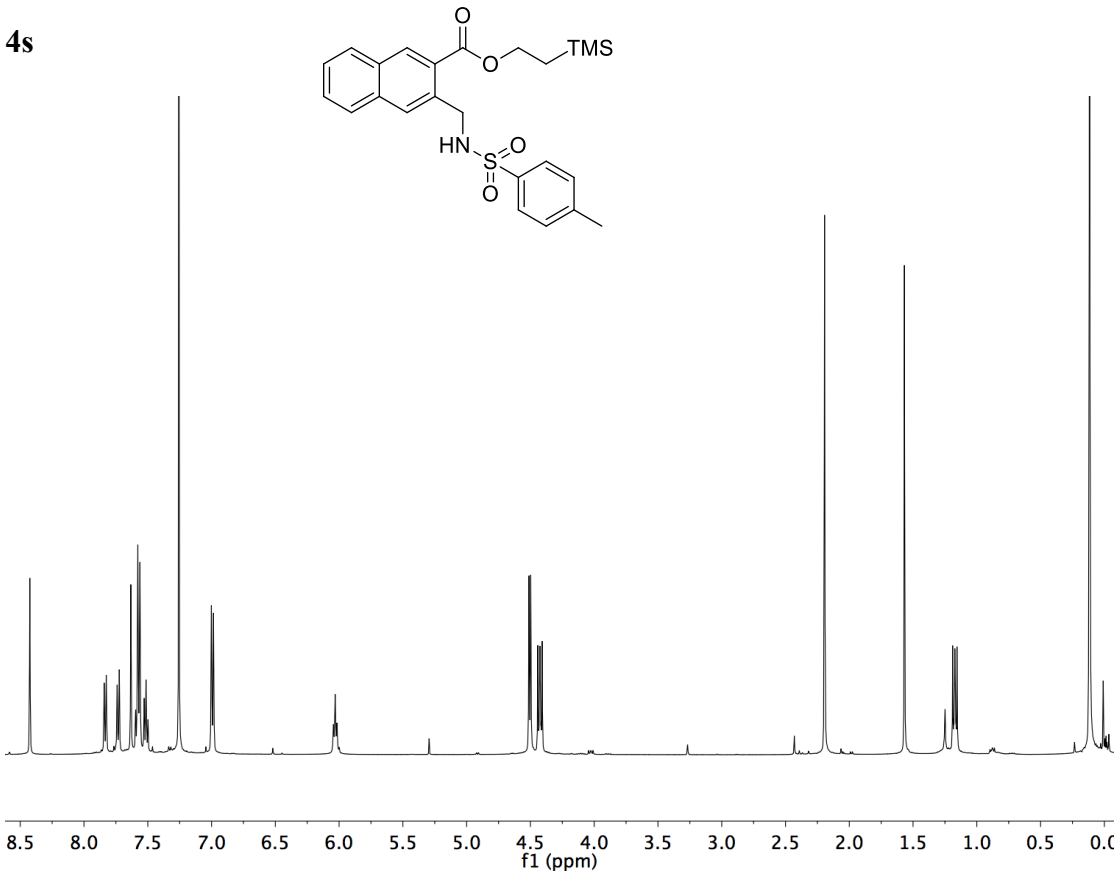
4r

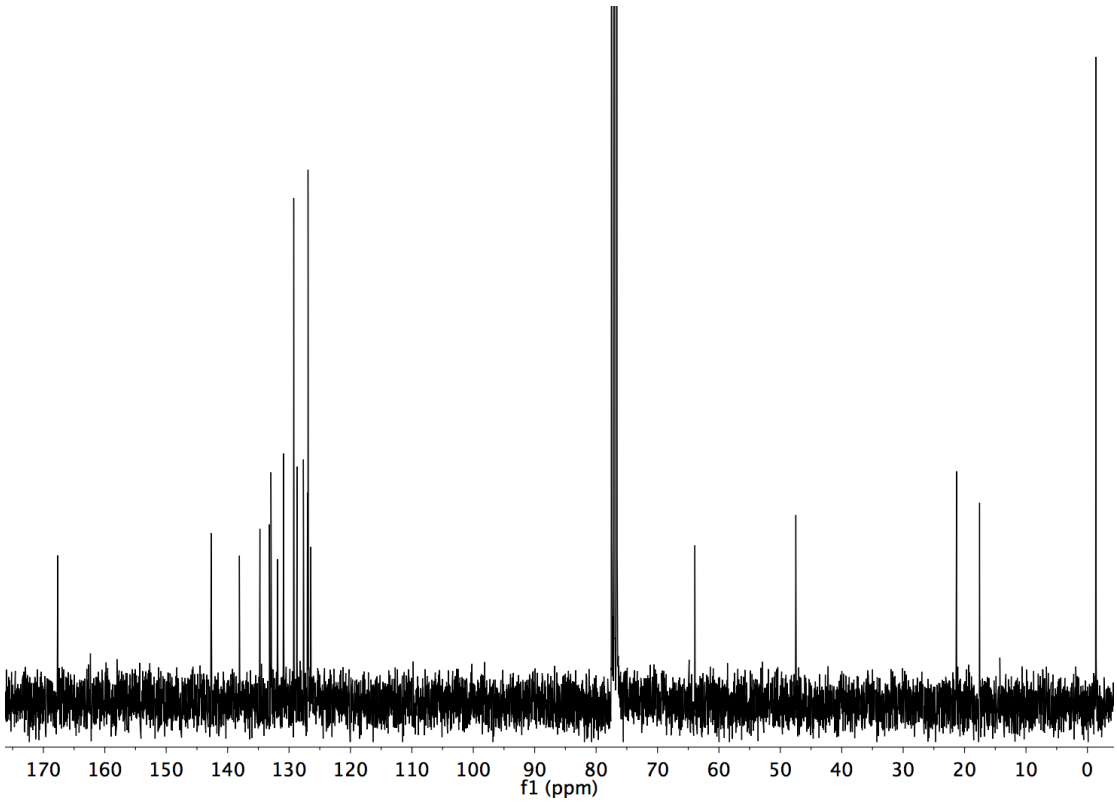

O
OBn
OAc

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)

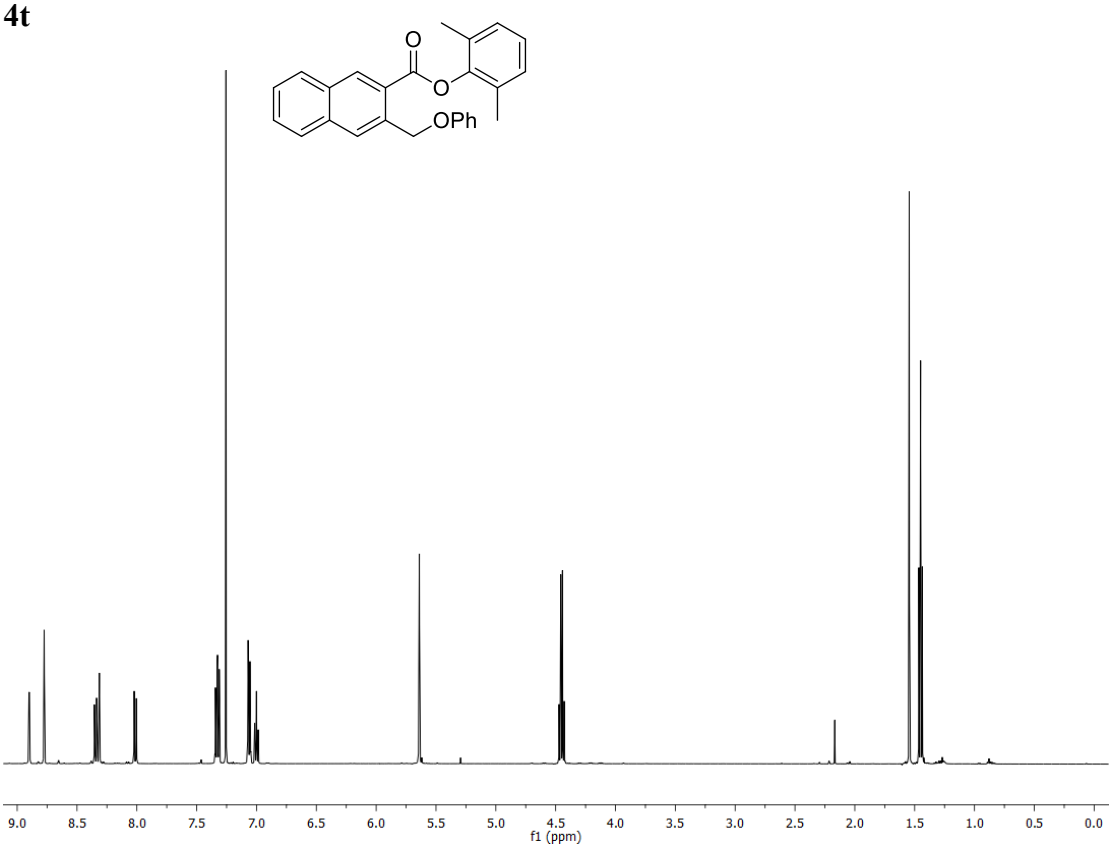

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

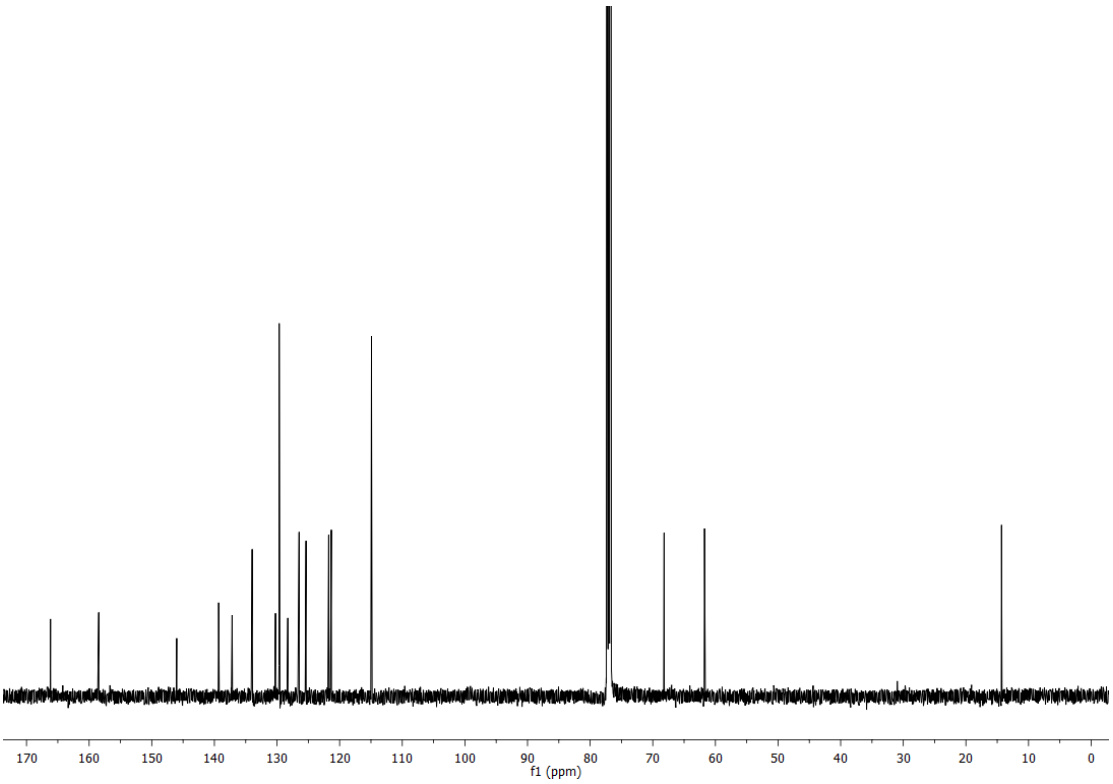
4s


O
O
TMS
HN
S
O
O
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
f1 (ppm)

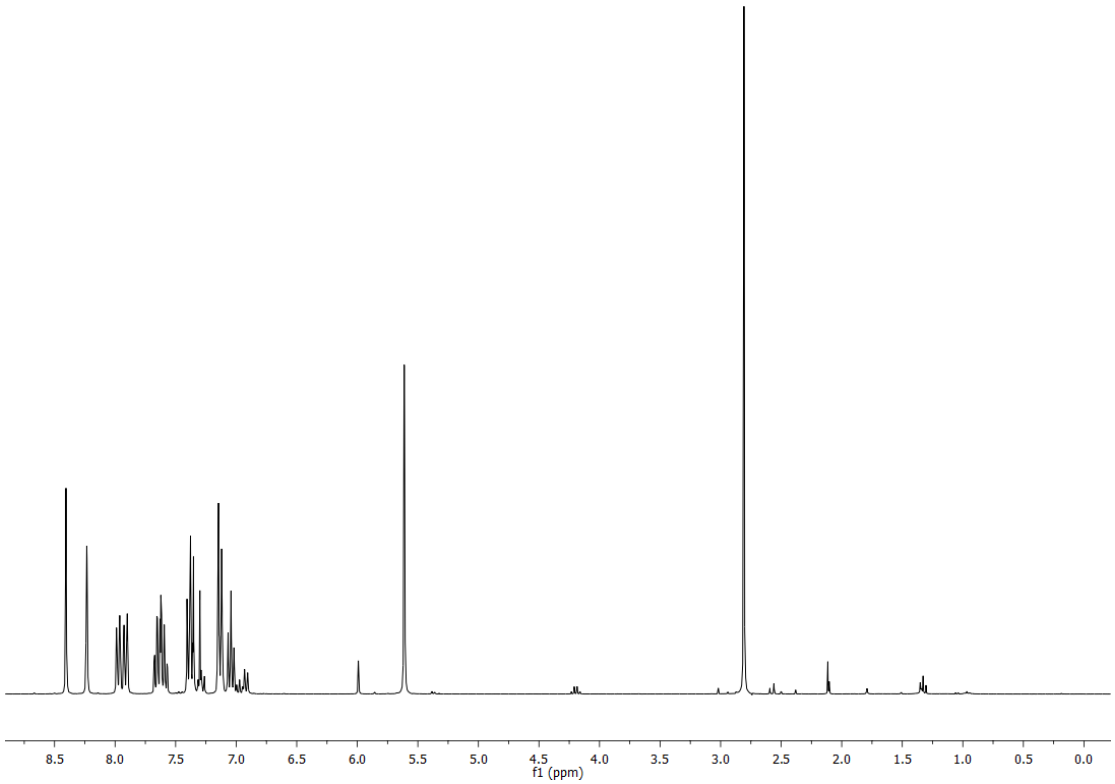

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

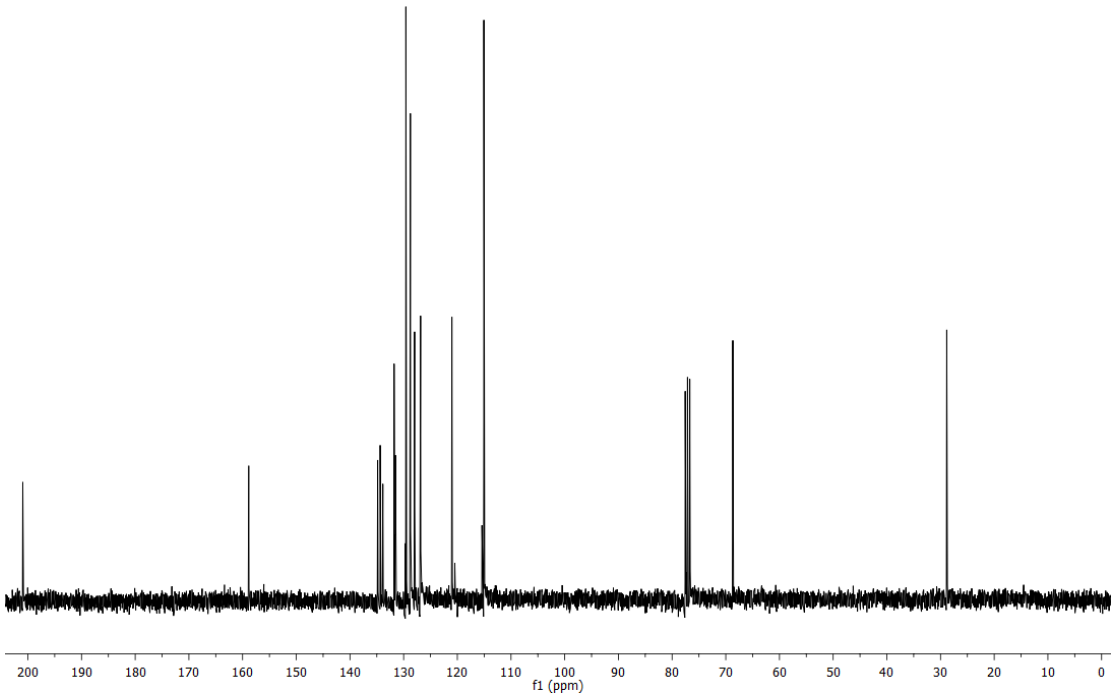
4t


O
O
OPh
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)

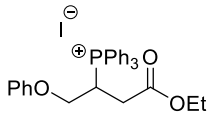

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

4u


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)

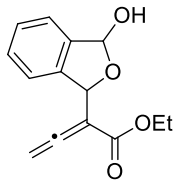

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

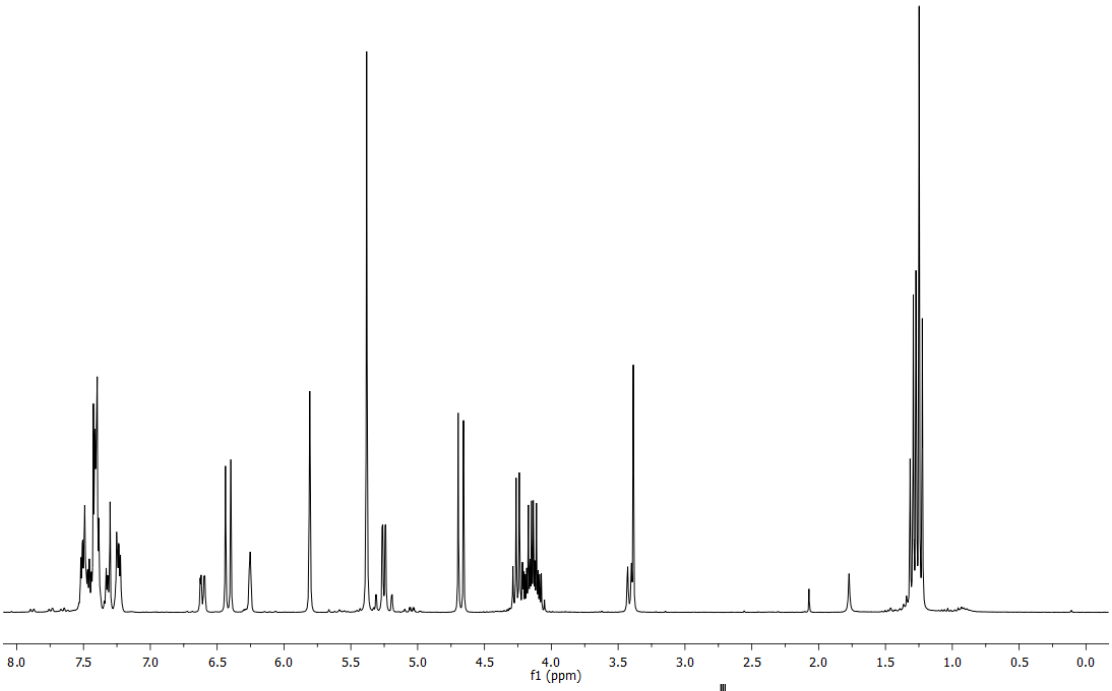
5

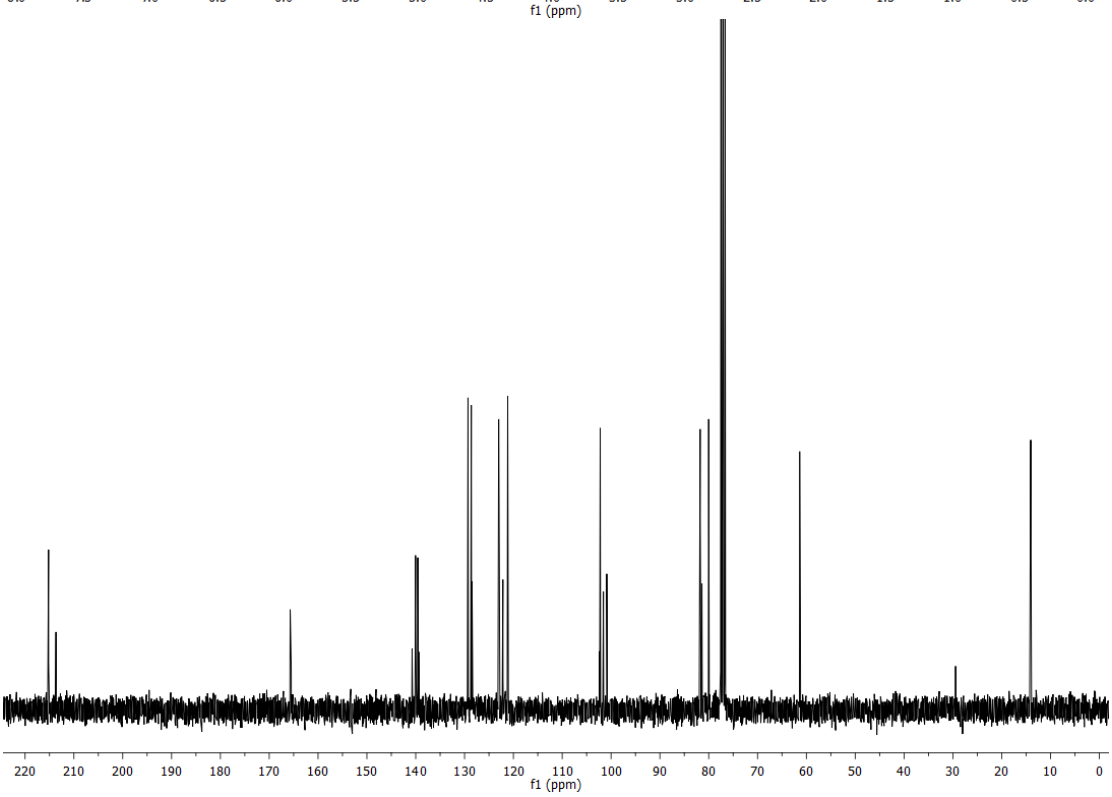

I
PPh3
O
PhO
OEt

39 37 35 33 31 29 27 25 23
f1 (ppm)
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)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

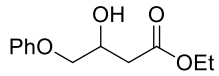
6

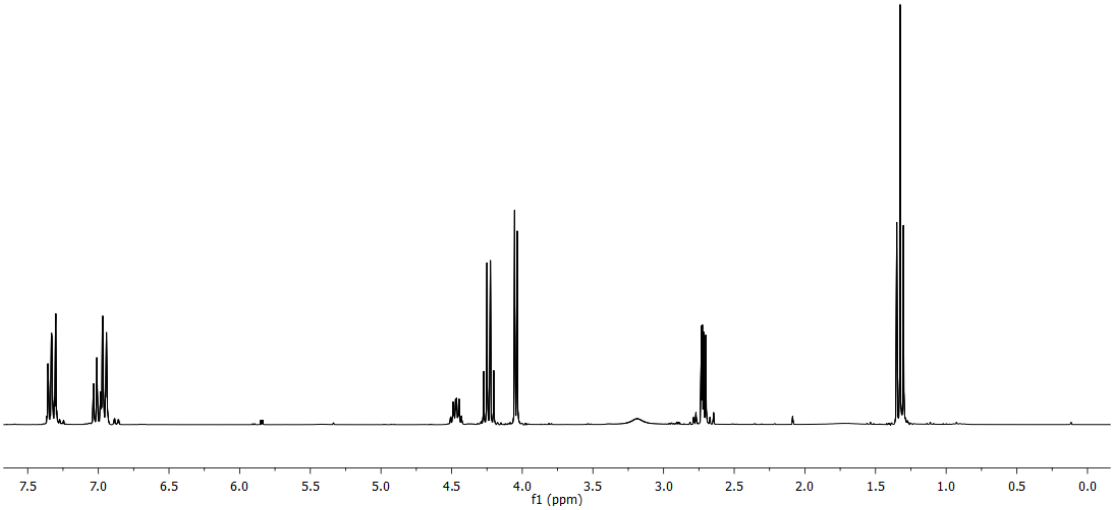

OH
O
OEt
O

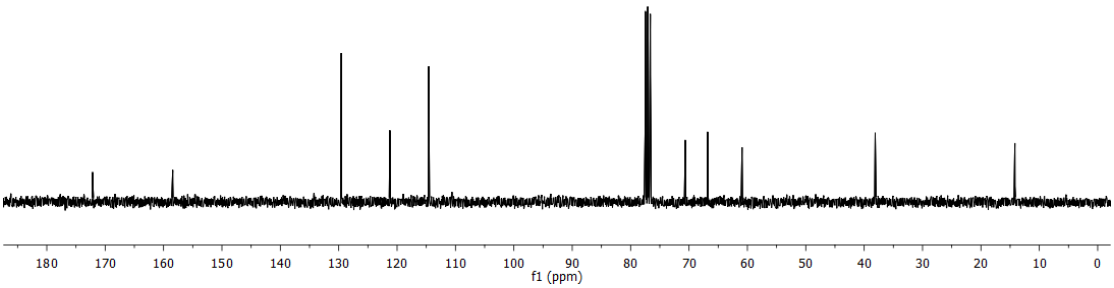

8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

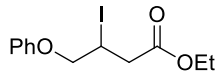
S3

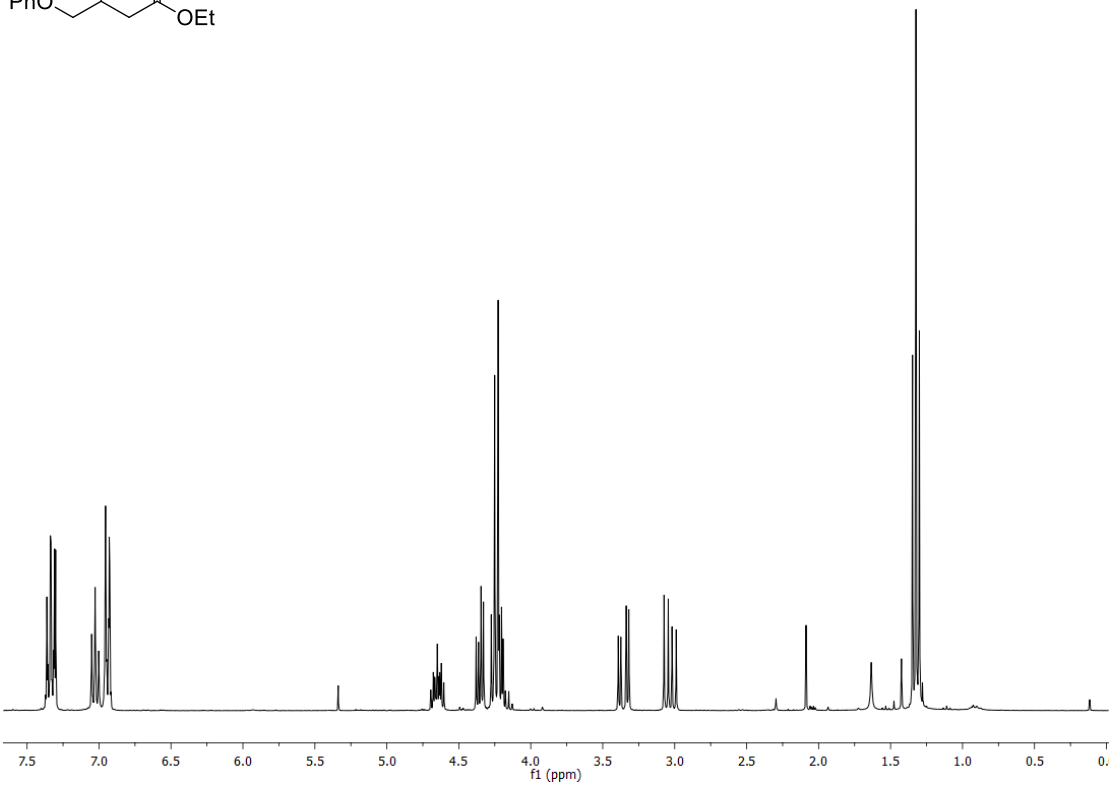

OH
O
PhO
OEt

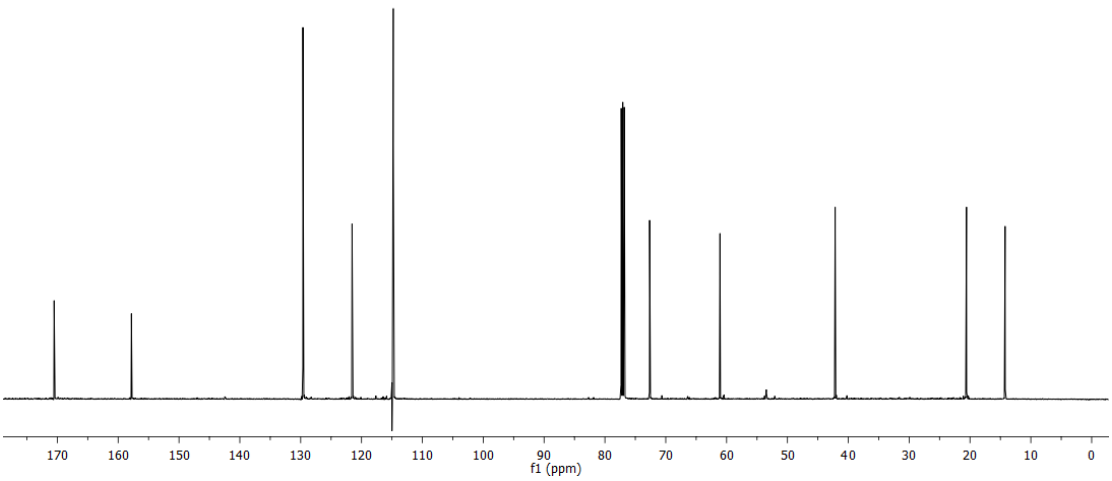

7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


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

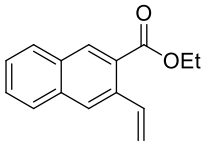
S4

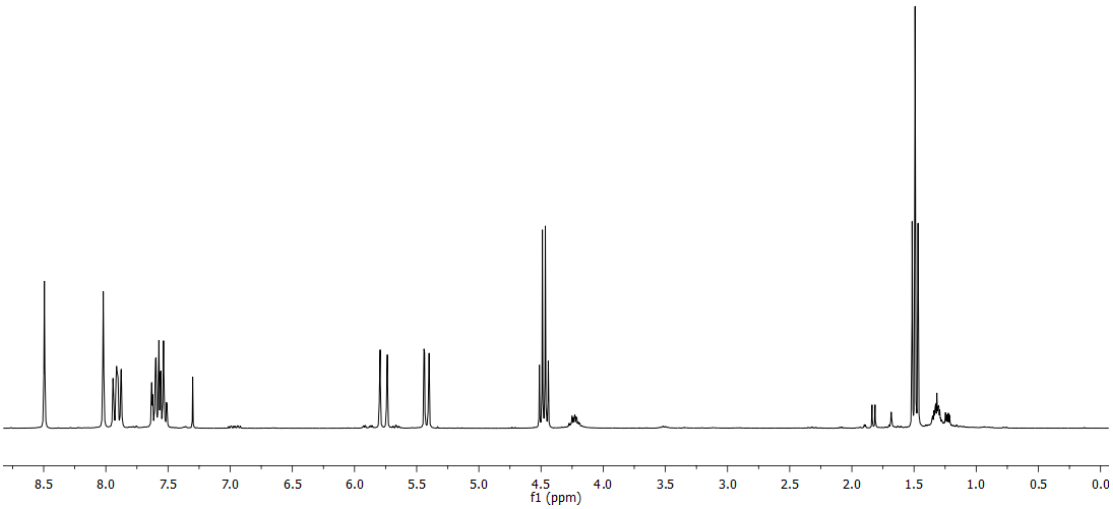

I
O
PhO
OEt

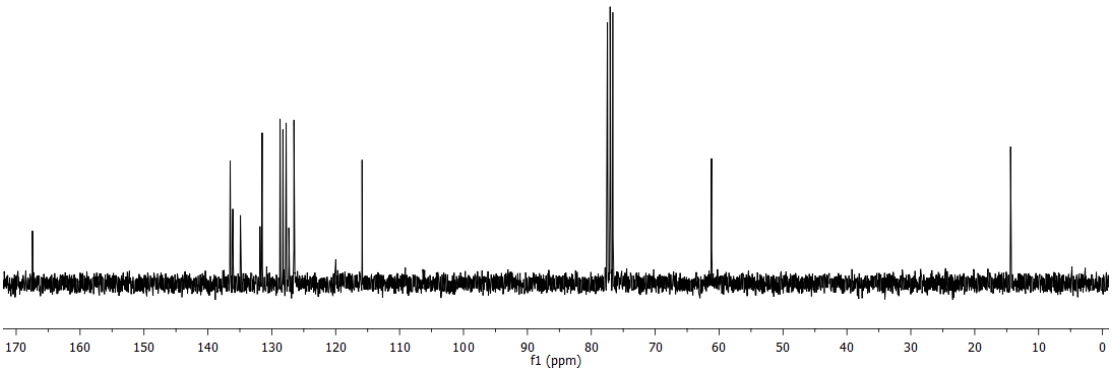

7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


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

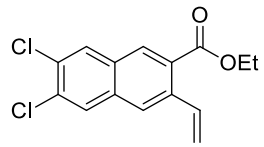
7

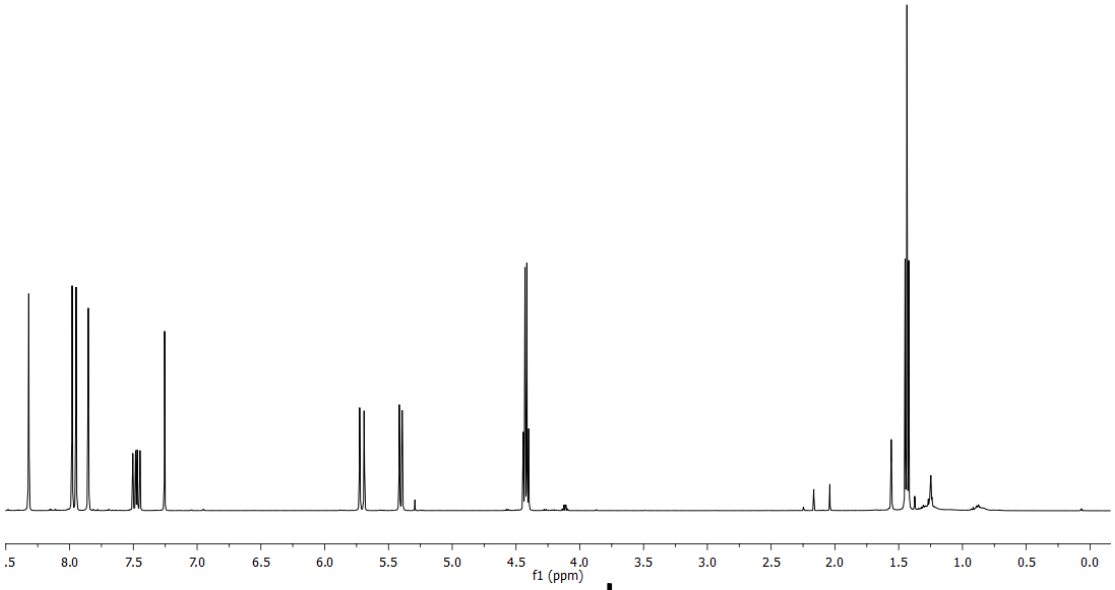

O
OEt

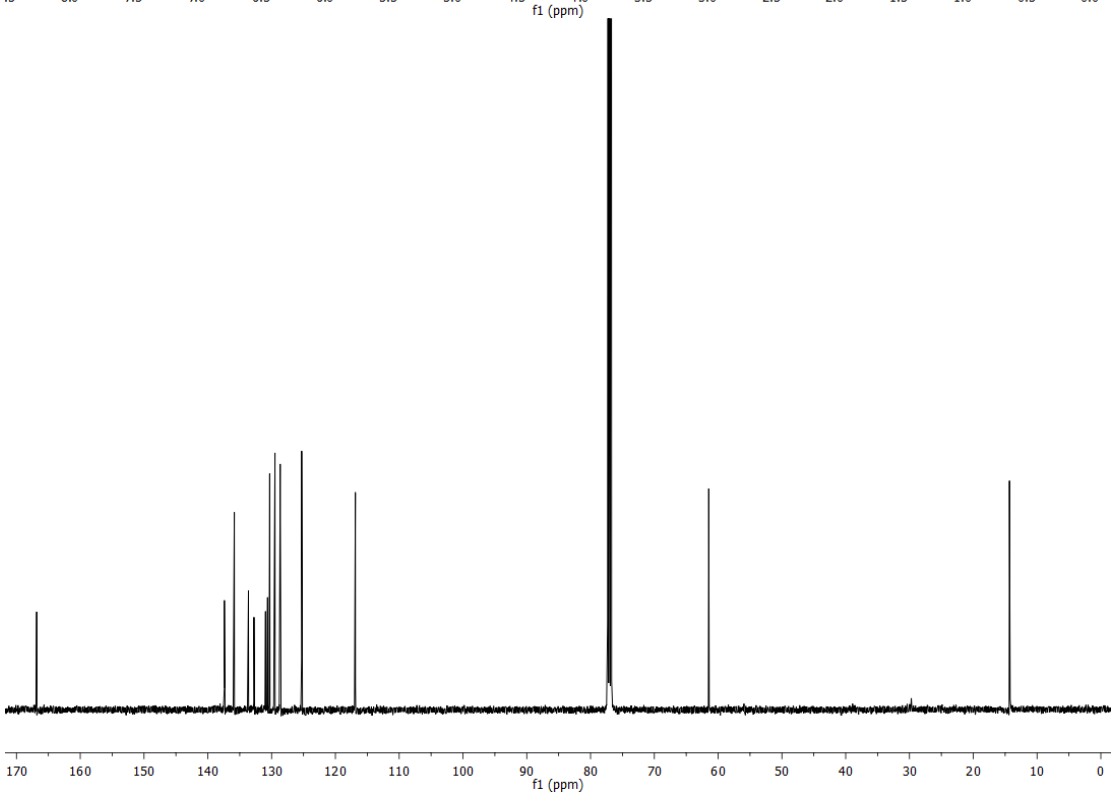

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


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

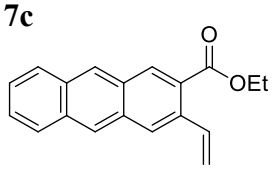
7b

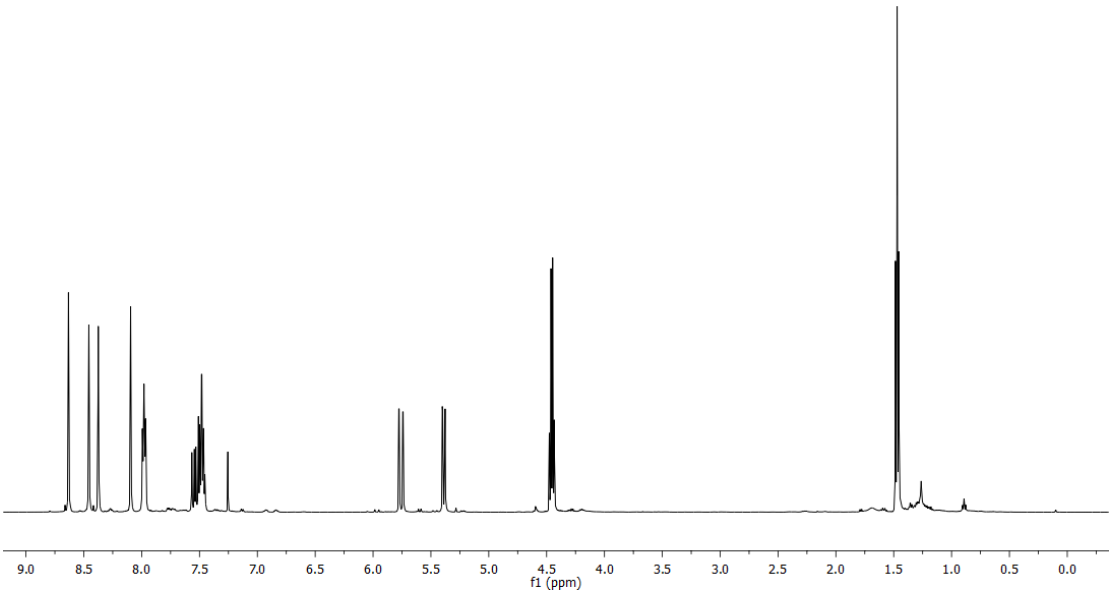

O
Cl
OEt
Cl

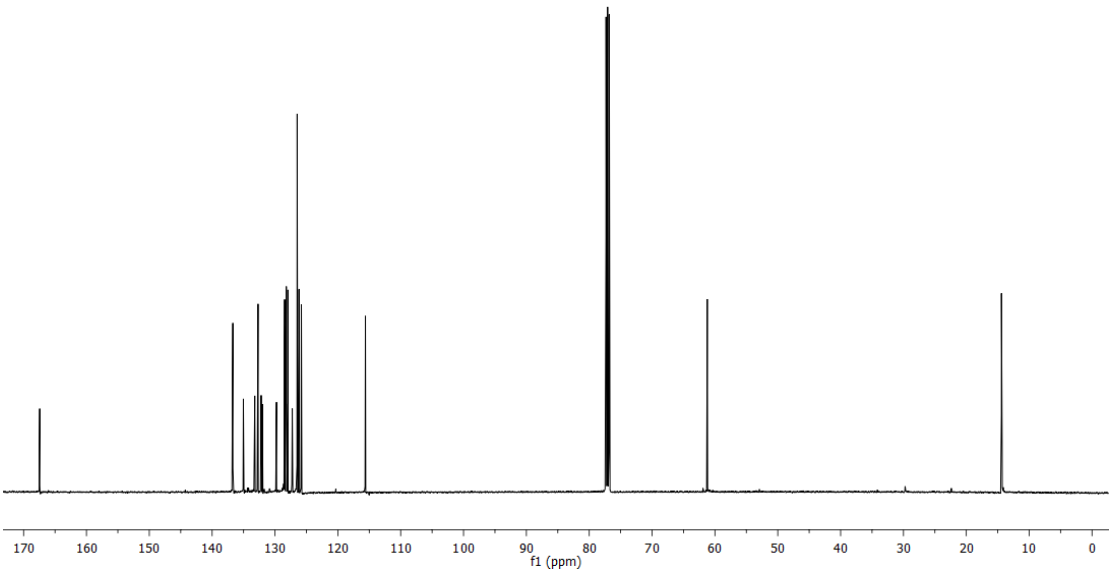

.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


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

7c


O
OEt


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)


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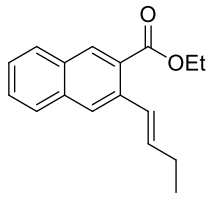
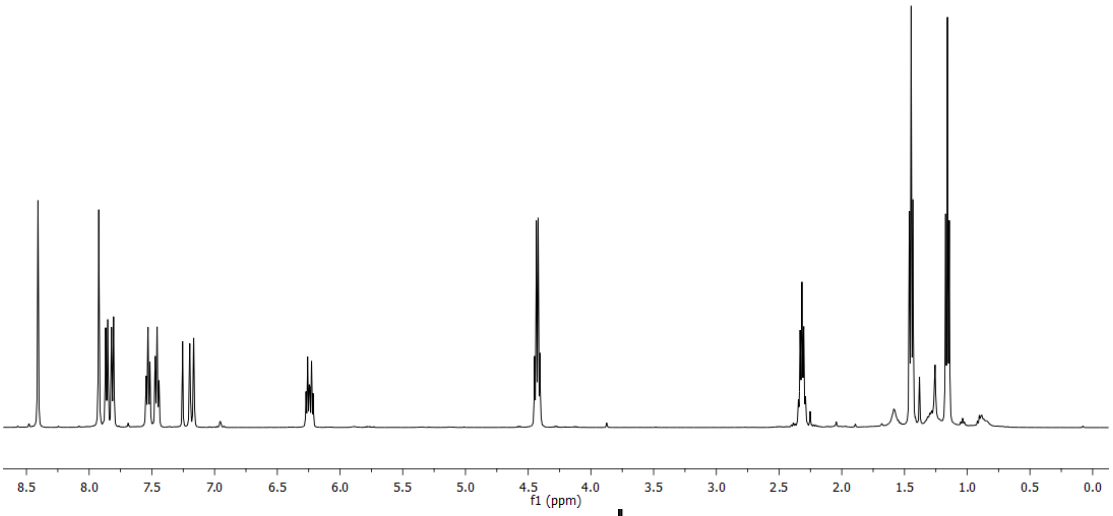
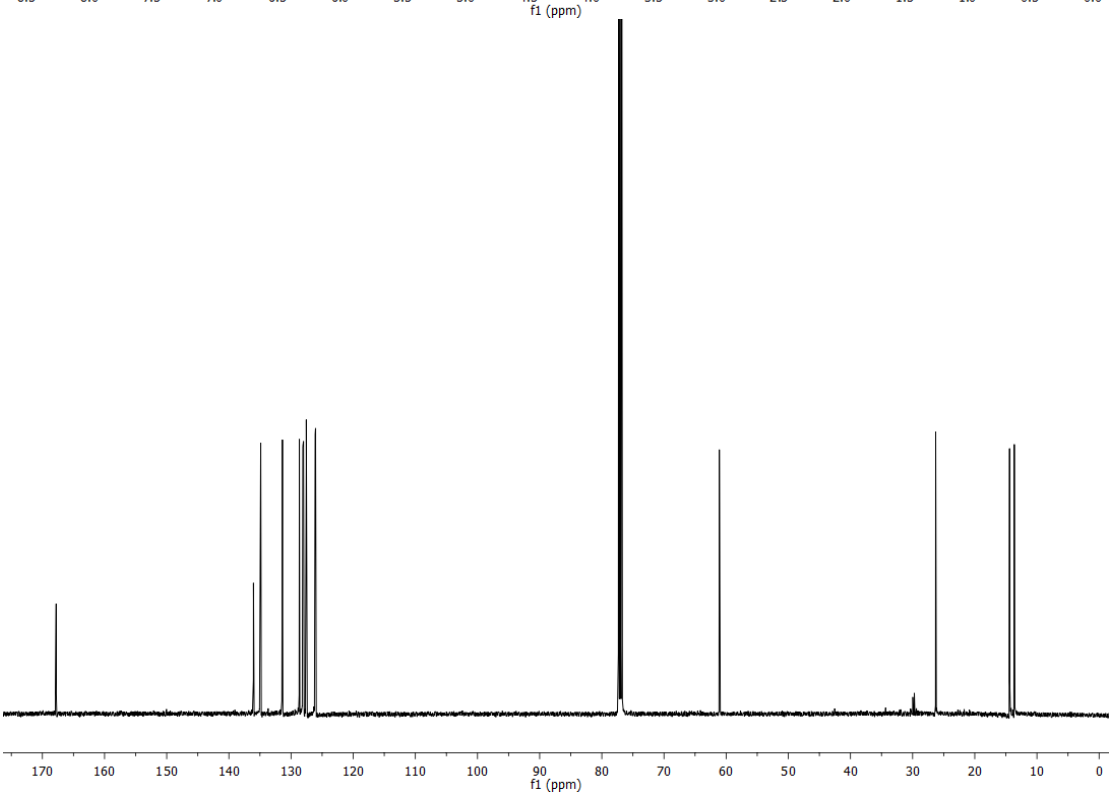
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

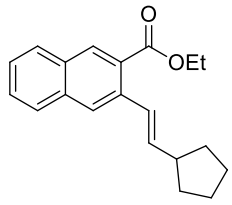
7d


O
OEt

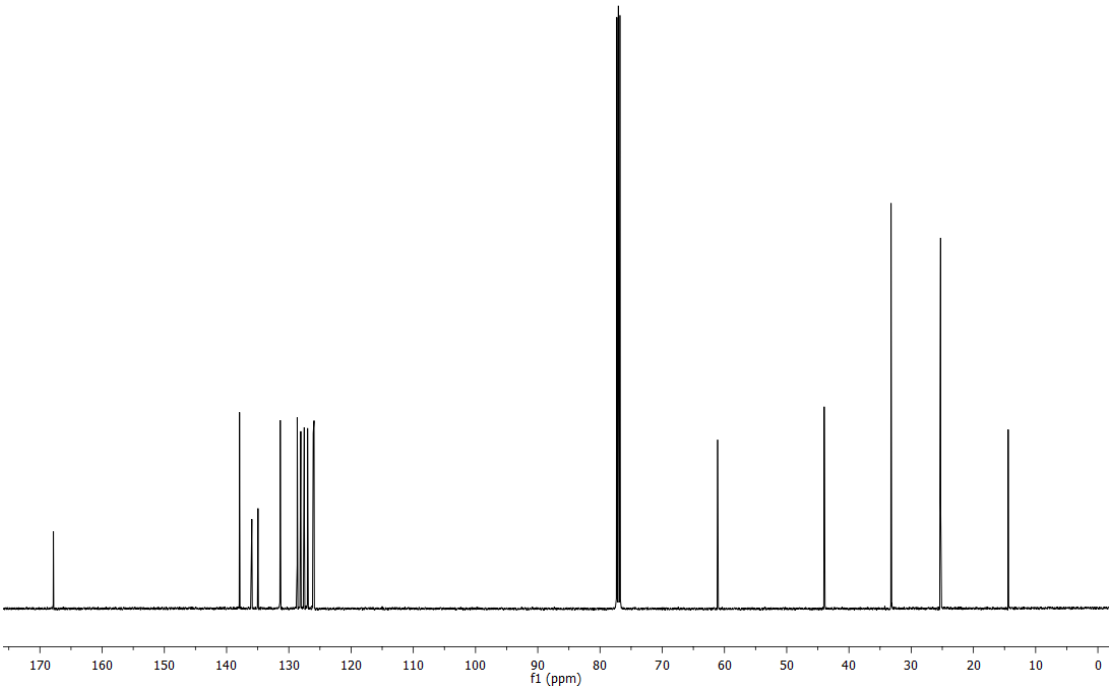

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


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

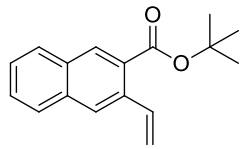
7e


O
OEt

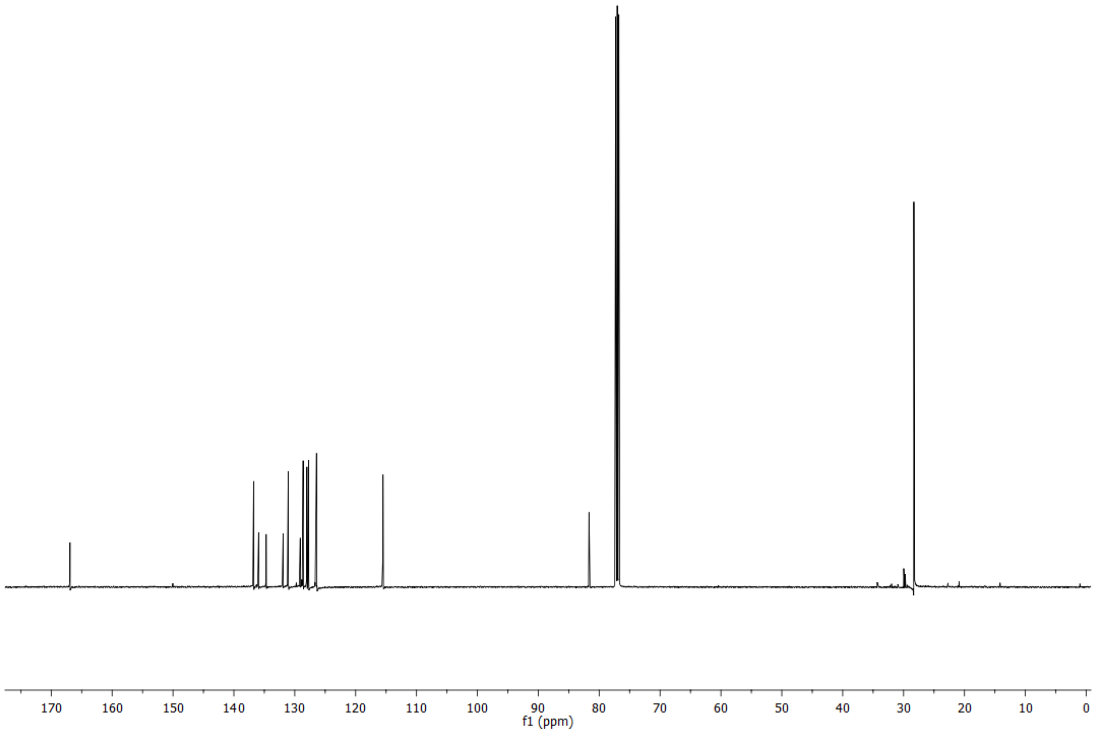
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


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

7f


O
O

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
f1 (ppm)


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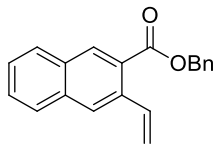
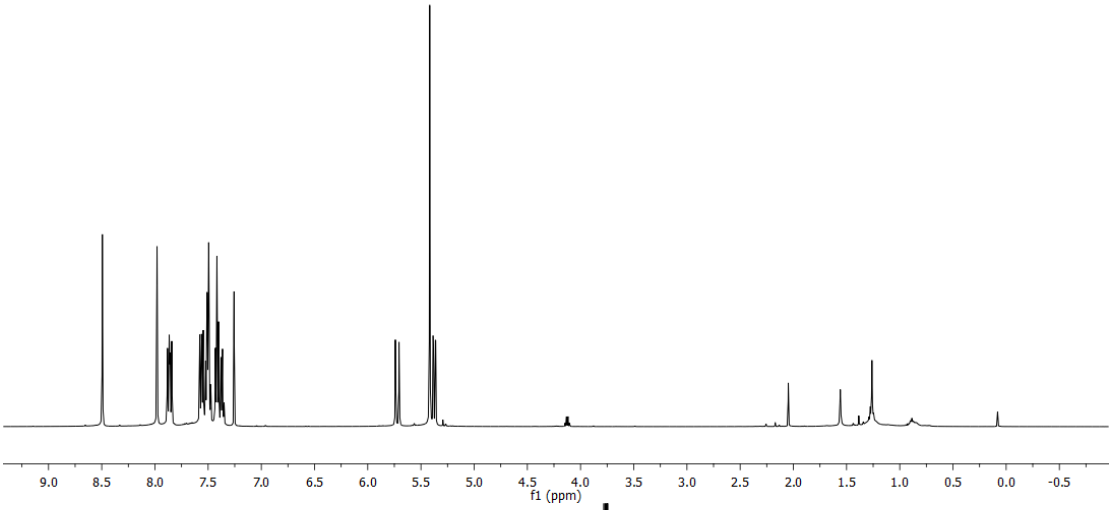
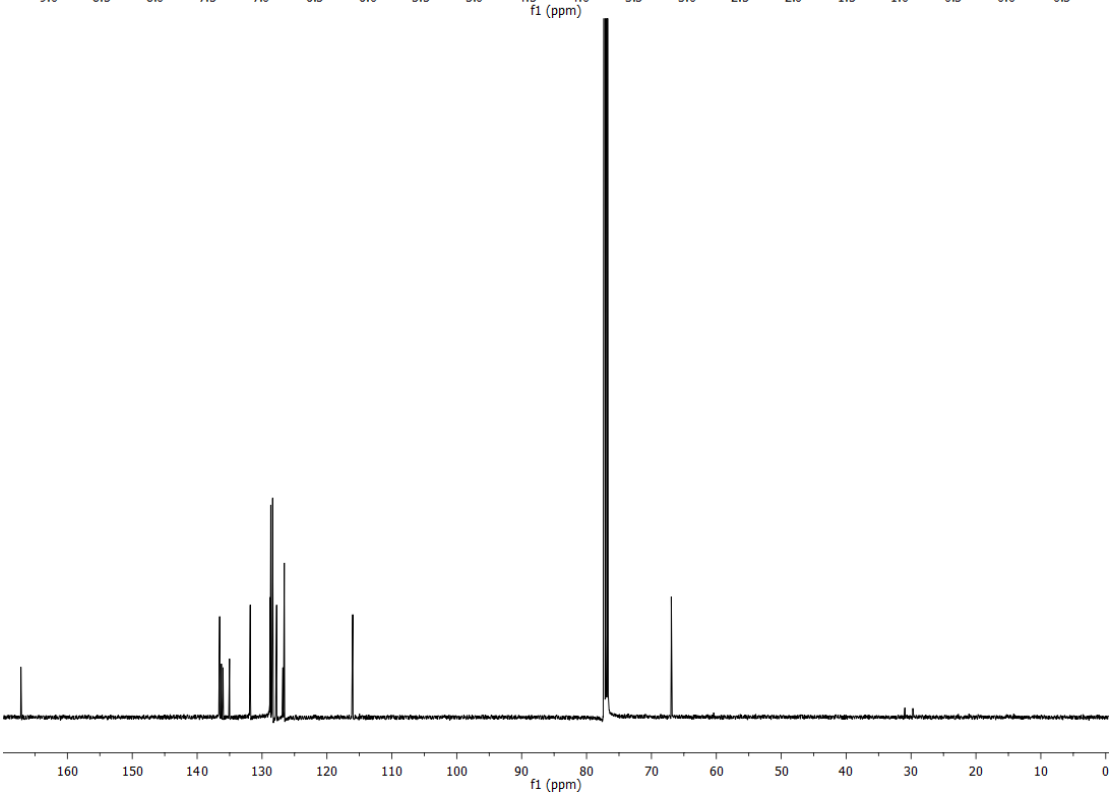
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

7g

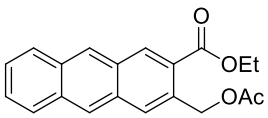

O
OBn

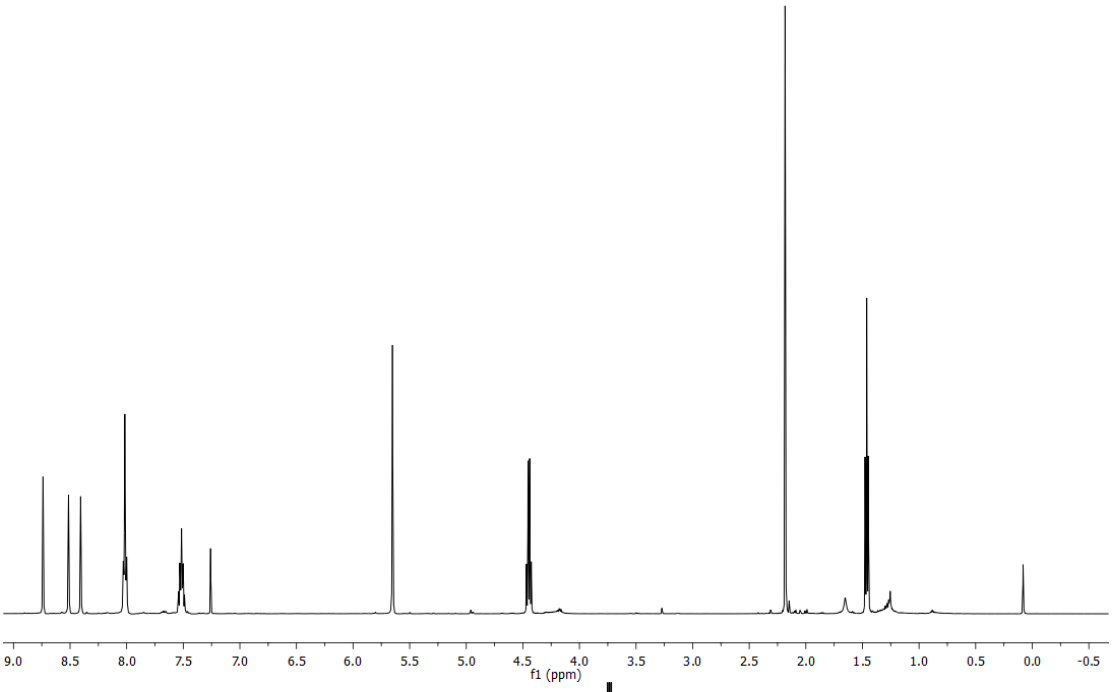

9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

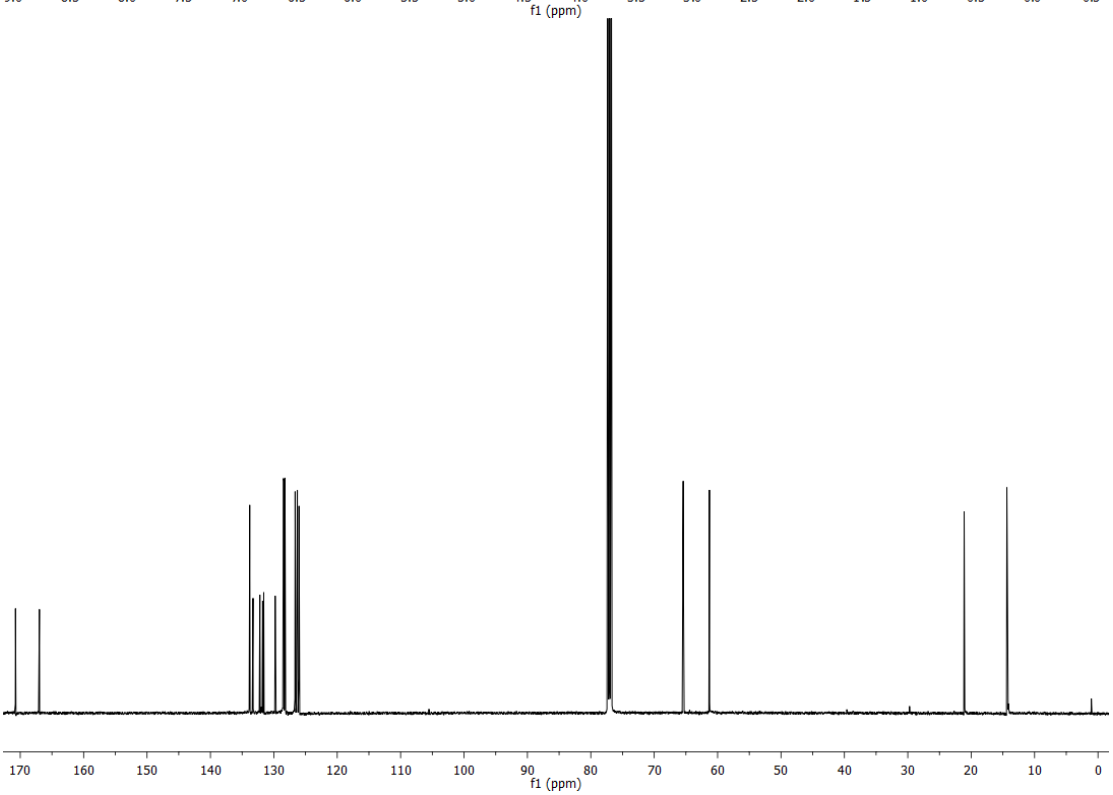

160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

9

9


O
OEt
OAc


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
-0.5
f1 (ppm)


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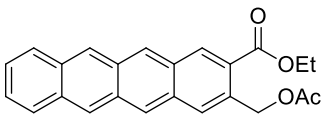
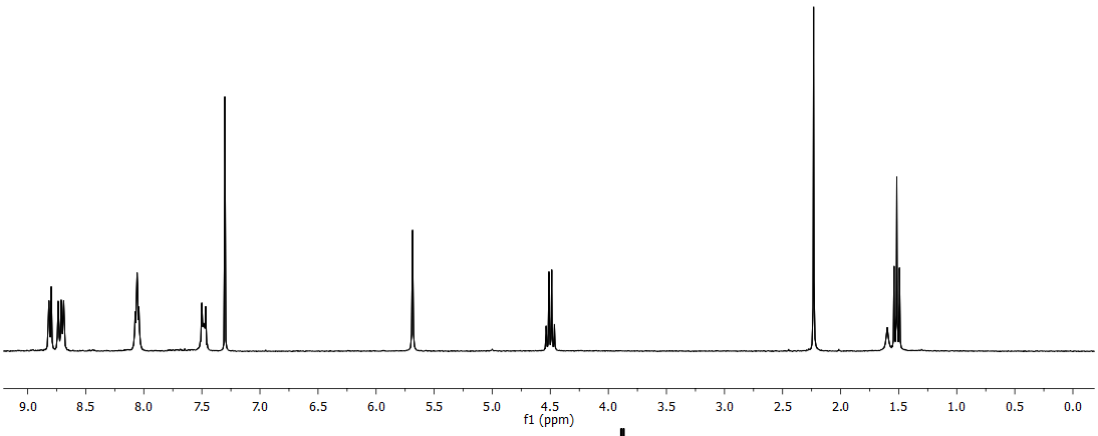
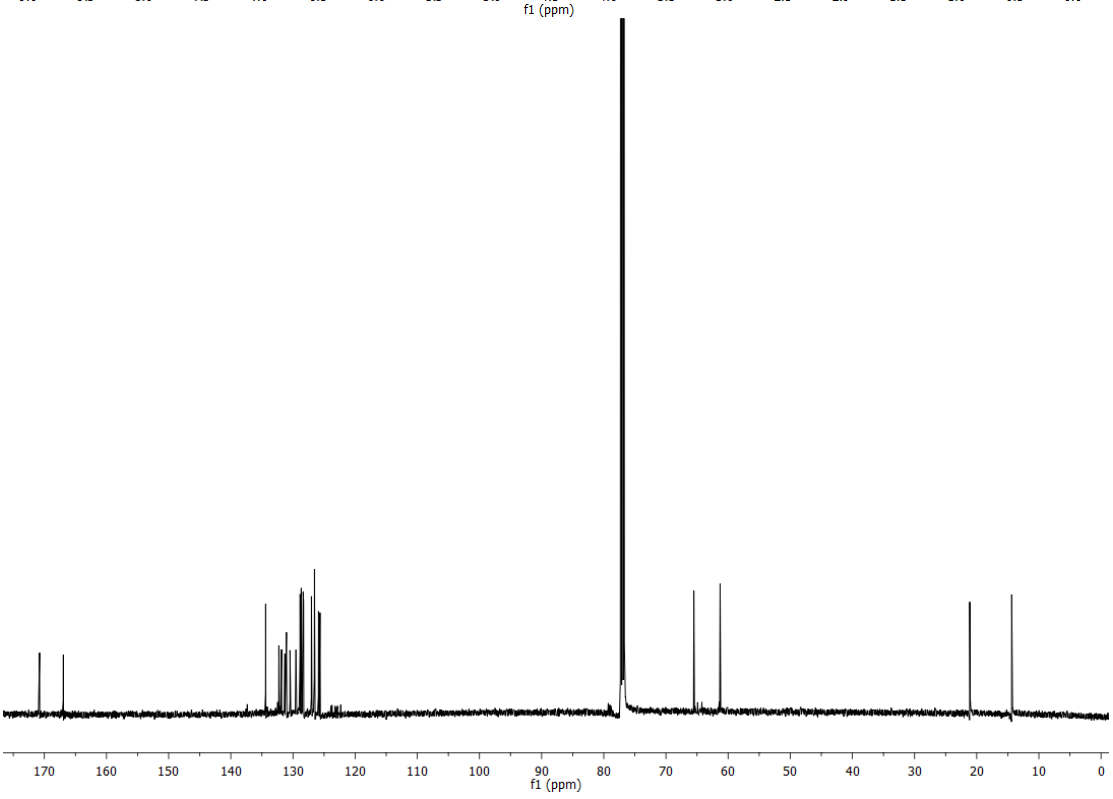
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

11


O
OEt
OAc


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)


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