

Supporting Information

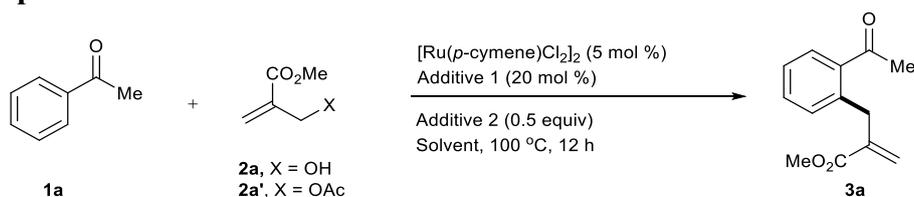
Ruthenium-catalyzed site-selective C-H allylation of aryl ketones using Morita-Baylis-Hillman alcohols: access to α -benzyl acrylates

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General Information. [Ru(*p*-cymene)Cl₂]₂ (97%), AgSbF₆ (98%), Ag₂O (99%), AgOTf (>99.99%), AgNTf₂ (99.9%), Cu(OAc)₂ (98%), Cu(OAc)₂·H₂O (98%), Zn(OAc)₂ (>98%), PdCl₂ (99.99%), K₂CO₃ (>99.5%), NaH (60% dispersion in mineral oil), *N,N*-dimethylacetamide (DMA) (>99.5%), 2,2,2-trifluoroethanol (TFE) (>99%), 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) (>99%), benzyl amine, benzyl mercaptan and aryl ketones of Sigma-Aldrich, BLD Pharm and TCI chemicals were used as received. Ethanol, 1,4-dioxane, dichloromethane and 1,2-dichloroethane were dried prior to use as per the standard procedure. Silica gel-G/GF254 plates (Merck) were used for TLC analysis with a mixture of hexane and EtOAc as the eluent. Column chromatography was carried out using Rankem silica gel (60-120 mesh). Bruker Avance III 400 and 500 MHz NMR spectrometers were used to record (¹H, ¹³C, ¹⁹F, COSY, NOESY, HSQC and HMBC) spectra using CDCl₃ as the solvent and tetramethylsilane (TMS) as an internal standard. Chemical shifts (δ) and spin-spin coupling constant (*J*) are reported in parts per million and hertz (Hz), respectively, and to describe peak patterns following abbreviations were used when appropriate: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets and m = multiplet. Structural assignments of **4a-c**, (±)-**5**, (±)-**6** and (±)-**6'** were made from COSY, NOESY HSQC and HMBC experiments. Mestre nova software was used for the spectral analysis. Q-Tof ESI-MS instrument (model HAB273) was used for recording HRMS data. Infrared spectra were recorded on Perkin Elmer FT-IR instrument.

Table S1. Optimization of Reaction Conditions^a



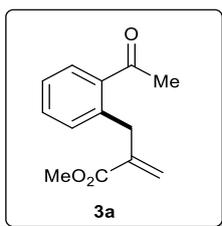
entry	additive 1	additive 2	solvent	yield of 3a ^b (%)
1	AgSbF ₆	Cu(OAc) ₂	DCE	73
2	AgSbF₆	Cu(OAc)₂·H₂O	DCE	85
3	AgSbF ₆	Zn(OAc) ₂	DCE	57
4	AgOTf	Cu(OAc) ₂ ·H ₂ O	DCE	66
5	AgNTf ₂	Cu(OAc) ₂ ·H ₂ O	DCE	73
6	AgSbF ₆	Cu(OAc) ₂ ·H ₂ O	DCM	67
7	AgSbF ₆	Cu(OAc) ₂ ·H ₂ O	1,4-Dioxane	75
8	AgSbF ₆	Cu(OAc) ₂ ·H ₂ O	TFE	62

9	AgSbF ₆	Cu(OAc) ₂ ·H ₂ O	HFIP	70
10	AgSbF ₆	Cu(OAc) ₂ ·H ₂ O	CH ₃ CN	n.d.
11	-	Cu(OAc) ₂ ·H ₂ O	DCE	n.d.
12	AgSbF ₆	-	DCE	n.d.
13 ^c	AgSbF ₆	-	DCE	n.d.
14 ^c	AgSbF ₆	Cu(OAc) ₂ ·H ₂ O	DCE	68
15 ^d	AgSbF ₆	Cu(OAc) ₂ ·H ₂ O	DCE	n.d.
16 ^e	AgSbF ₆	Cu(OAc) ₂ ·H ₂ O	DCE	n.d.
17 ^f	AgSbF ₆	Cu(OAc) ₂ ·H ₂ O	DCE	71
18 ^g	AgSbF ₆	Cu(OAc) ₂ ·H ₂ O	DCE	55
19 ^h	AgSbF ₆	Cu(OAc) ₂ ·H ₂ O	DCE	67
20 ⁱ	AgSbF ₆	Cu(OAc) ₂ ·H ₂ O	DCE	40

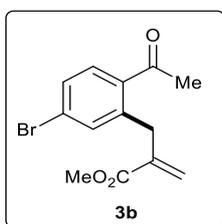
^aReaction conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), [Ru(*p*-cymene)Cl₂]₂ (5 mol %), additive 1 (20 mol %), additive 2 (1 equiv), solvent (1 mL), 100 °C, 12 h. ^bIsolated yield. ^cMethyl 2-(acetoxymethyl)acrylate **2a'** was used in place of **2a**. ^dIn absence of [Ru(*p*-cymene)Cl₂]₂. ^e[CoCp*(CO)I₂] (5 mol %) was used instead of [Ru(*p*-cymene)Cl₂]₂. ^fCu(OAc)₂·H₂O (2 equiv) was used. ^gCu(OAc)₂·H₂O (0.5 equiv) was used. ^hAt 120 °C. ⁱAt 60 °C. n.d. = not detected. DCE = 1,2-Dichloroethane. DCM = Dichloromethane. TFE = 2,2,2-Trifluoroethanol. HFIP = 1,1,1,3,3,3-Hexafluoro-isopropanol.

General Procedure for the Ru-Catalyzed C-H Allylation of Aryl Ketones using Morita-Baylis-Hillman Alcohols

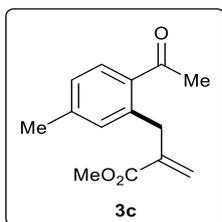
Aryl ketone **1** (0.1 mmol, 1.0 equiv), MBH alcohol **2a** (0.15 mmol, 1.5 equiv), [Ru(*p*-cymene)Cl₂]₂ (0.005 mmol, 3.06 mg, 0.05 equiv), AgSbF₆ (0.02 mmol, 6.87 mg, 0.2 equiv) and Cu(OAc)₂·H₂O (0.1 mmol, 20 mg, 1.0 equiv) were stirred in 1,2-dichloroethane (DCE) (1 mL, 0.1 M) at 100 °C (in a pre-heated oil bath) in a sealed tube for 12 h. After completion (monitored by TLC), the reaction mixture was diluted with EtOAc (5 mL) and passed through a short celite pad. Evaporation of the solvent gave a residue that was purified on silica gel column chromatography using n-hexane and EtOAc as an eluent to afford **3**.



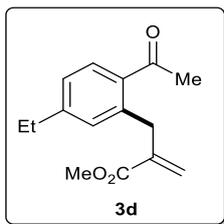
Methyl 2-(2-acetylbenzyl)acrylate 3a. Analytical TLC on silica gel, 1:10 EtOAc/hexane $R_f = 0.55$; colorless liquid; yield 85% (18.6 mg); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.68 (d, $J = 7.5$ Hz, 1H), 7.42 (t, $J = 7.5$ Hz, 1H), 7.32 (t, $J = 7.5$ Hz, 1H), 7.25 (d, $J = 7.4$ Hz, 1H), 6.19 (s, 1H), 5.26 (s, 1H), 3.92 (s, 2H), 3.74 (s, 3H), 2.56 (s, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 201.9, 167.5, 140.2, 138.4, 138.3, 131.9, 131.6, 129.4, 126.7, 126.0, 52.0, 35.7, 29.7; FT-IR (neat) 2953, 1723, 1676, 1609, 1436, 1264, 1259, 1144, 1065 cm^{-1} ; HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{13}\text{H}_{14}\text{NaO}_3$ 241.0835; Found 241.0837.



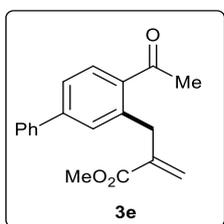
Methyl 2-(2-acetyl-5-bromobenzyl)acrylate 3b. Analytical TLC on silica gel, 1:10 EtOAc/hexane $R_f = 0.48$; light yellow liquid; yield 71% (21 mg); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.53 (d, $J = 8.5$ Hz, 1H), 7.44 (d, $J = 8.5$ Hz, 1H), 7.41 (s, 1H), 6.22 (s, 1H), 5.33 (s, 1H), 3.88 (s, 2H), 3.74 (s, 3H), 2.54 (s, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 200.8, 167.2, 140.9, 139.5, 137.0, 134.7, 130.8, 129.8, 126.6, 126.2, 52.1, 35.4, 29.7; FT-IR (neat) 2945, 1718, 1679, 1604, 1433, 1267, 1257, 1145, 1057 cm^{-1} ; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{14}\text{O}_3\text{Br}$ 297.0121; Found 297.0110.



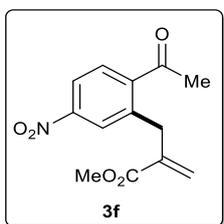
Methyl 2-(2-acetyl-5-methylbenzyl)acrylate 3c. Analytical TLC on silica gel, 1:10 EtOAc/hexane $R_f = 0.52$; colorless liquid; yield 86% (20 mg); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.62 (d, $J = 8.0$ Hz, 1H), 7.10 (d, $J = 8.0$ Hz, 1H), 7.04 (s, 1H), 6.16 (s, 1H), 5.22 (s, 1H), 3.90 (s, 2H), 3.74 (s, 3H), 2.53 (s, 3H), 2.36 (s, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 201.1, 167.6, 142.3, 140.4, 138.9, 135.2, 132.8, 130.0, 127.3, 125.7, 52.0, 35.8, 29.5, 21.5; FT-IR (neat) 2952, 2924, 1719, 1682, 1609, 1436, 1267, 1257, 1144, 1057 cm^{-1} ; HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{14}\text{H}_{16}\text{NaO}_3$ 255.0992; Found 255.0993.



Methyl 2-(2-acetyl-5-ethylbenzyl)acrylate 3d. Analytical TLC on silica gel, 1:10 EtOAc/hexane $R_f = 0.42$; colorless liquid; yield 81% (20 mg); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.65 (d, $J = 8.0$ Hz, 1H), 7.13 (d, $J = 8.0$ Hz, 1H), 7.07 (s, 1H), 6.16 (s, 1H), 5.21 (s, 1H), 3.92 (s, 2H), 3.75 (s, 3H), 2.66 (q, $J = 7.5$ Hz, 2H), 2.54 (s, 3H), 1.23 (t, $J = 7.5$ Hz, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 201.1, 167.7, 148.5, 140.4, 138.9, 135.4, 131.7, 130.2, 126.0, 125.7, 52.0, 35.9, 29.5, 28.8, 15.3; FT-IR (neat) 2966, 1721, 1683, 1608, 1436, 1256, 1200, 1146 cm^{-1} ; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{19}\text{O}_3$ 247.1329; Found 247.1330.

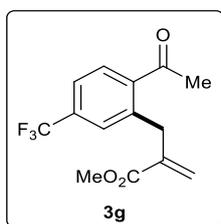


Methyl 2-((4-acetyl-[1,1'-biphenyl]-3-yl)methyl)acrylate 3e. Analytical TLC on silica gel, 1:10 EtOAc/hexane $R_f = 0.50$; colorless liquid; yield 69% (20 mg); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.79 (d, $J = 8.0$ Hz, 1H), 7.59 (d, $J = 7.5$ Hz, 2H), 7.54 (d, $J = 8.0$ Hz, 1H), 7.49-7.44 (m, 3H), 7.39 (t, $J = 7.5$ Hz, 1H), 6.20 (s, 1H), 5.31 (s, 1H), 4.01 (s, 2H), 3.76 (s, 3H), 2.60 (s, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 201.2, 167.6, 144.4, 140.2, 139.9, 139.3, 136.7, 130.7, 130.4, 129.1, 128.3, 127.3, 126.0, 125.2, 52.1, 35.9, 29.7; FT-IR (neat) 2967, 1724, 1683, 1605, 1436, 1256, 1203, 1147 cm^{-1} ; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{19}\text{O}_3$ 295.1329; Found 295.1322.

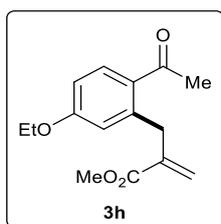


Methyl 2-(2-acetyl-5-nitrobenzyl)acrylate 3f. Analytical TLC on silica gel, 1:10 EtOAc/hexane $R_f = 0.34$; yellow liquid; yield 66% (17.4 mg); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.15-8.13 (m, 2H), 7.71 (d, $J = 8.0$ Hz, 1H), 6.30 (s, 1H), 5.51 (s, 1H), 3.92 (s, 2H), 3.72 (s, 3H), 2.62 (s, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 201.4, 166.8, 148.9, 144.4, 140.1, 138.6, 129.1, 127.7, 126.1, 121.7, 52.2, 35.4, 30.3; FT-IR (neat) 2976, 1718, 1679, 1604, 1433,

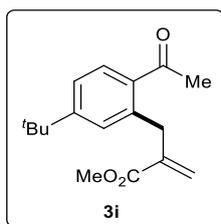
1256, 1204, 1156 cm^{-1} ; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{14}\text{NO}_5$ 264.0866; Found 264.0858.



Methyl 2-(2-acetyl-5-(trifluoromethyl)benzyl)acrylate 3g. Analytical TLC on silica gel, 1:10 EtOAc/hexane $R_f = 0.44$; colorless liquid; yield 70% (20 mg); ^1H NMR (500 MHz, CDCl_3) δ 7.70 (d, $J = 8.0$ Hz, 1H), 7.56 (d, $J = 8.0$ Hz, 1H), 7.52 (s, 1H), 6.24 (s, 1H), 5.37 (s, 1H), 3.92 (s, 2H), 3.74 (s, 3H), 2.59 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 201.6, 167.1, 141.9, 139.3, 139.0, 133.1 ($J_{\text{C-F}} = 32.2$ Hz), 128.9, 128.4 ($J_{\text{C-F}} = 3.5$ Hz), 127.0, 123.6 ($J_{\text{C-F}} = 3.6$ Hz), 122.6 ($J_{\text{C-F}} = 270.8$ Hz), 52.2, 35.4, 30.0; ^{19}F NMR (470 MHz, CDCl_3) δ -63.08; FT-IR (neat) 2918, 1721, 1697, 1438, 1331, 1254, 1130, 1092 cm^{-1} ; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{14}\text{O}_3\text{F}_3$ 287.0890; Found 287.0890.

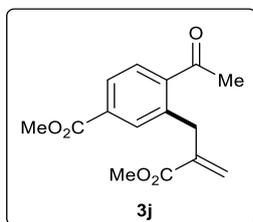


Methyl 2-(2-acetyl-5-ethoxybenzyl)acrylate 3h. Analytical TLC on silica gel, 1:10 EtOAc/hexane $R_f = 0.35$; colorless liquid; yield 82% (21.5 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.74 (d, $J = 8.8$ Hz, 1H), 6.79-6.76 (m, 1H), 6.74-6.73 (m, 1H), 6.16 (s, 1H), 5.23 (s, 1H), 4.06 (q, $J = 7.2$ Hz, 2H), 3.95 (s, 2H), 3.74 (s, 3H), 2.51 (s, 3H), 1.41 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 199.3, 167.6, 161.6, 142.1, 140.1, 132.8, 129.9, 125.6, 118.1, 111.7, 63.7, 52.0, 36.3, 29.1, 14.7; FT-IR (neat) 2926, 1720, 1676, 1602, 1566, 1436, 1249, 1140, 1065 cm^{-1} ; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{19}\text{O}_4$ 263.1278; Found 263.1278.



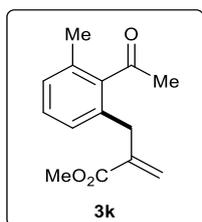
Methyl 2-(2-acetyl-5-(tert-butyl)benzyl)acrylate 3i. Analytical TLC on silica gel, 1:10 EtOAc/hexane $R_f = 0.50$; colorless liquid; yield 71% (19.5 mg); ^1H NMR (500 MHz, CDCl_3) δ 7.67 (d, $J = 8.5$ Hz, 1H), 7.32 (d, $J = 8.0$ Hz, 1H), 7.26 (s, 1H), 6.16 (s, 1H),

5.20 (s, 1H), 3.95 (s, 2H), 3.75 (s, 3H), 2.54 (s, 3H), 1.32 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 201.1, 167.7, 155.3, 140.6, 138.6, 135.1, 129.9, 129.4, 125.5, 123.5, 52.0, 36.1, 35.0, 31.2, 29.5; FT-IR (neat) 2955, 1721, 1681, 1604, 1433, 1277, 1257, 1143, 1054 cm^{-1} ; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{23}\text{O}_3$ 275.1642; Found 275.1644.



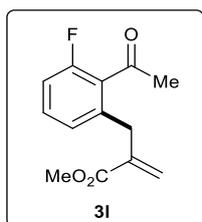
Methyl 4-acetyl-3-(2-(methoxycarbonyl)allyl)benzoate 3j. Analytical

TLC on silica gel, 1:10 EtOAc/hexane $R_f = 0.43$; colorless liquid; yield 78% (21.5 mg); ^1H NMR (500 MHz, CDCl_3) δ 7.95 (d, $J = 8.0$ Hz, 1H), 7.92 (s, 1H), 7.66 (d, $J = 7.5$ Hz, 1H), 6.22 (s, 1H), 5.31 (s, 1H), 3.93 (s, 3H), 3.90 (s, 2H), 3.73 (s, 3H), 2.58 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 202.0, 167.2, 166.3, 142.5, 139.6, 138.3, 132.7, 132.4, 128.6, 127.8, 126.6, 52.6, 52.1, 35.4, 30.1; FT-IR (neat) 2936, 1734, 1690, 1460, 1253, 1238, 1145, 1096 cm^{-1} ; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{17}\text{O}_5$ 277.1071; Found 277.1081.



Methyl 2-(2-acetyl-3-methylbenzyl)acrylate 3k. Analytical TLC on silica

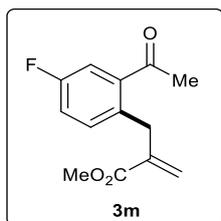
gel, 1:10 EtOAc/hexane $R_f = 0.46$; colorless liquid; yield 77% (18 mg); ^1H NMR (500 MHz, CDCl_3) δ 7.20 (t, $J = 8.0$ Hz, 1H), 7.06 (d, $J = 7.5$ Hz, 1H), 7.00 (d, $J = 8.0$ Hz, 1H), 6.28 (s, 1H), 5.38 (s, 1H), 3.74 (s, 3H), 3.54 (s, 2H), 2.48 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 208.2, 167.3, 142.9, 139.4, 133.3, 132.7, 128.9, 128.8, 127.5, 127.4, 52.1, 35.1, 32.6, 19.4; FT-IR (neat) 2952, 1720, 1681, 1604, 1436, 1265, 1257, 1146, 1057 cm^{-1} ; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{17}\text{O}_3$ 233.1172; Found 233.1172.



Methyl 2-(2-acetyl-3-fluorobenzyl)acrylate 3l. Analytical TLC on silica gel,

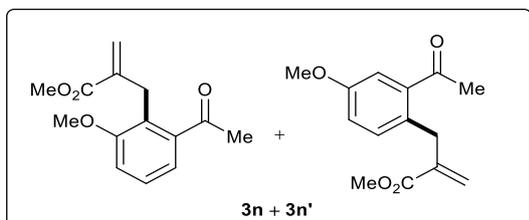
1:10 EtOAc/hexane $R_f = 0.47$; colorless liquid; yield 80% (19 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.33-7.27 (m, 1H), 7.02 (d, $J = 7.6$ Hz, 1H), 6.98 (t, $J = 9.6$ Hz, 1H), 6.24-6.23 (m,

1H), 5.41-5.40 (m, 1H), 3.72 (s, 3H), 3.69 (s, 2H), 2.54 (d, $J = 3.2$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 201.5, 167.1, 159.2 ($J_{\text{C-F}} = 245.7$ Hz), 139.4, 138.7 ($J_{\text{C-F}} = 33.7$ Hz), 131.2 ($J_{\text{C-F}} = 91.2$ Hz), 129.2 ($J_{\text{C-F}} = 165.0$ Hz), 127.1, 126.5 ($J_{\text{C-F}} = 27.5$ Hz), 114.1 ($J_{\text{C-F}} = 22.5$ Hz), 52.1, 34.8, 32.7; ^{19}F NMR (470 MHz, CDCl_3) δ -114.53; FT-IR (neat) 2927, 1721, 1696, 1438, 1322, 1254, 1130, 1094 cm^{-1} ; HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{13}\text{H}_{13}\text{NaO}_3\text{F}$ 259.0741; Found 259.0736.



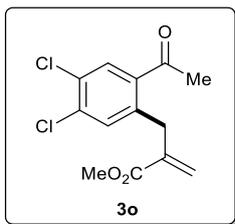
Methyl 2-(2-acetyl-4-fluorobenzyl)acrylate 3m. Analytical TLC on silica

gel, 1:10 EtOAc/hexane $R_f = 0.53$; colorless liquid; yield 81% (19 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.45 (d, $J = 8.0$ Hz, 1H), 7.35-7.30 (m, 1H), 7.19 (t, $J = 8.4$ Hz, 1H), 6.16 (s, 1H), 5.14 (s, 1H), 3.90 (s, 2H), 3.77 (s, 3H), 2.56 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 201.0, 167.3, 160.7 ($J_{\text{C-F}} = 246.1$ Hz), 140.9 ($J_{\text{C-F}} = 34.0$ Hz), 138.7, 128.1 ($J_{\text{C-F}} = 87.0$ Hz), 125.2 ($J_{\text{C-F}} = 162.0$ Hz), 125.1, 124.6 ($J_{\text{C-F}} = 34.0$ Hz), 118.5 ($J_{\text{C-F}} = 236.0$ Hz), 52.1, 29.9, 27.5; ^{19}F NMR (376 MHz, CDCl_3) δ -115.18; FT-IR (neat) 2918, 1720, 1695, 1436, 1331, 1254, 1130, 1092 cm^{-1} ; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{14}\text{O}_3\text{F}$ 237.0921; Found 237.0912.

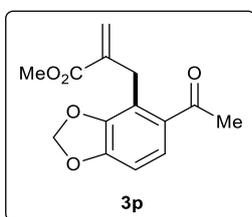


Methyl 2-(2-acetyl-4-methoxybenzyl)acrylate

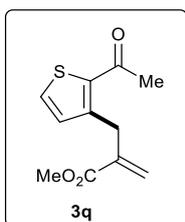
3n+3n'. Analytical TLC on silica gel, 1:10 EtOAc/hexane $R_f = 0.45$; colorless liquid; yield 79% (19.6 mg); a 1.16:1 mixture of regioisomers; ^1H NMR (500 MHz, CDCl_3) δ 7.29 (t, $J = 8.0$ Hz, 1H, major), 7.19 (d, $J = 8.0$ Hz, 1H, major), 7.17-7.15 (m, 1.79H, major + minor), 6.99 (d, $J = 8.5$ Hz, 1H, major), 6.96-6.94 (m, 0.86 H, minor), 6.15 (s, 0.86 H, minor), 6.08 (s, 1H, major), 5.24 (s, 0.86 H, minor), 5.02 (s, 1H, major), 3.82-3.81 (m, 6.31 H, major + minor), 3.79 (s, 3H, major), 3.77 (s, 3H, major), 3.73 (s, 2.58 H, minor), 2.53-2.52 (m, 5.59 H, major + minor); ^{13}C NMR (125 MHz, CDCl_3) δ 202.5, 201.7, 167.8, 167.6, 158.4, 158.0, 141.0, 140.5, 139.5, 139.4, 133.0, 130.0, 127.6, 126.1, 125.7, 124.2, 120.5, 116.5, 115.2, 113.4, 56.0, 55.6, 52.0, 34.8, 30.2, 29.7, 28.1; FT-IR (neat) 2951, 1716, 1687, 1631, 1436, 1267, 1219, 1135, 1048 cm^{-1} ; HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{14}\text{H}_{16}\text{NaO}_4$ 271.0941; Found 271.0942.



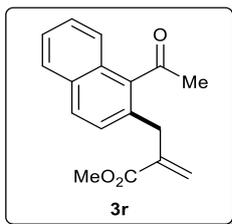
Methyl 2-(2-acetyl-4,5-dichlorobenzyl)acrylate 3o. Analytical TLC on silica gel, 1:10 EtOAc/hexane $R_f = 0.39$; colorless liquid; yield 74% (21 mg); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.73 (s, 1H), 7.35 (s, 1H), 6.24 (s, 1H), 5.38 (s, 1H), 3.86 (s, 2H), 3.74 (s, 3H), 2.55 (s, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 199.6, 167.0, 139.1, 138.8, 137.7, 135.8, 133.4, 131.1, 130.7, 126.9, 52.2, 35.0, 29.7; FT-IR (neat) 2954, 1721, 1666, 1593, 1448, 1268, 1207, 1139, 1056 cm^{-1} ; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{13}\text{O}_3\text{Cl}_2$ 287.0236; Found 287.0236.



Methyl 2-((5-acetylbenzo[d][1,3]dioxol-4-yl)methyl)acrylate 3p. Analytical TLC on silica gel, 1:10 EtOAc/hexane $R_f = 0.45$; colorless liquid; yield 81% (21 mg); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.39 (d, $J = 8.0$ Hz, 1H), 6.75 (d, $J = 8.5$ Hz, 1H), 6.11 (s, 1H), 6.00 (s, 2H), 5.12 (s, 1H), 3.92 (s, 2H), 3.78 (s, 3H), 2.50 (s, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 199.0, 167.6, 150.0, 147.9, 138.7, 132.1, 126.1, 124.3, 120.8, 106.1, 101.8, 52.1, 29.1, 28.7; FT-IR (neat) 2952, 1717, 1675, 1598, 1450, 1261, 1207, 1139, 1056 cm^{-1} ; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{15}\text{O}_5$ 263.0914; Found 263.0912.

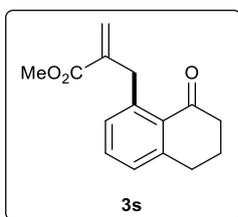


Methyl 2-((2-acetylthiophen-3-yl)methyl)acrylate 3q. Analytical TLC on silica gel, 1:10 EtOAc/hexane $R_f = 0.44$; colorless liquid; yield 80% (18 mg); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.42 (d, $J = 5.0$ Hz, 1H), 6.98 (d, $J = 5.0$ Hz, 1H), 6.22 (s, 1H), 5.48 (s, 1H), 4.04 (s, 2H), 3.75 (s, 3H), 2.53 (s, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 191.0, 167.5, 145.7, 138.7, 136.6, 132.2, 129.9, 126.6, 52.1, 32.2, 29.8; FT-IR (neat) 2924, 1719, 1679, 1604, 1438, 1267, 1207, 1125, 1071 cm^{-1} ; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{11}\text{H}_{13}\text{O}_3\text{S}$ 225.0580; Found 225.0582.



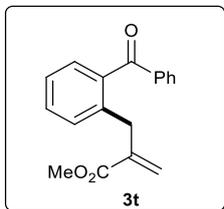
Methyl 2-((1-acetylnaphthalen-2-yl)methyl)acrylate 3r.

Analytical TLC on silica gel, 1:10 EtOAc/hexane $R_f = 0.52$; colorless liquid; yield 81% (22 mg); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.86-7.83 (m, 1H), 7.79 (d, $J = 8.4$ Hz, 1H), 7.64-7.62 (m, 1H), 7.53-7.46 (m, 2H), 7.28 (d, $J = 8.4$ Hz, 1H), 6.32-6.31 (m, 1H), 5.41-5.40 (m, 1H), 3.75 (s, 3H), 3.72 (s, 2H), 2.66 (s, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 208.0, 167.2, 139.6, 139.2, 132.3, 130.8, 129.2, 129.1, 128.5, 127.7, 127.6, 127.1, 126.1, 124.4, 52.2, 35.3, 33.4; FT-IR (neat) 2968, 1723, 1685, 1605, 1437, 1253, 1203, 1148 cm^{-1} ; HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{17}\text{H}_{16}\text{NaO}_3$ 271.0992; Found 271.0990.



Methyl 2-((8-oxo-5,6,7,8-tetrahydronaphthalen-1-yl)methyl)acrylate

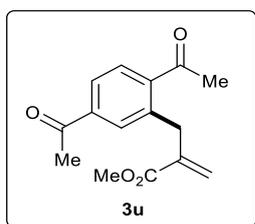
3s. Analytical TLC on silica gel, 1:10 EtOAc/hexane $R_f = 0.42$; colorless liquid; yield 67% (16.4 mg); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.36 (t, $J = 7.5$ Hz, 1H), 7.15 (d, $J = 7.5$ Hz, 1H), 7.08 (d, $J = 7.5$ Hz, 1H), 6.13 (s, 1H), 5.14 (s, 1H), 4.06 (s, 2H), 3.77 (s, 3H), 2.97 (t, $J = 6.0$ Hz, 2H), 2.62 (t, $J = 6.2$ Hz, 2H), 2.08 (p, $J = 6.5$ Hz, 2H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 199.7, 168.0, 146.3, 141.3, 140.6, 132.5, 131.2, 130.5, 127.9, 125.0, 52.1, 41.0, 36.9, 31.2, 23.0; FT-IR (neat) 2956, 1717, 1688, 1631, 1436, 1269, 1220, 1135, 1049 cm^{-1} ; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{17}\text{O}_3$ 245.1172; Found 245.1170.



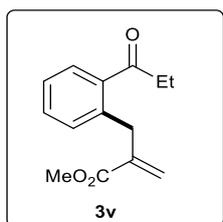
Methyl 2-((2-benzoylbenzyl)acrylate 3t.

Analytical TLC on silica gel, 1:10 EtOAc/hexane $R_f = 0.40$; colorless liquid; yield 82% (23 mg); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.78 (d, $J = 7.5$ Hz, 2H), 7.58 (t, $J = 8.0$ Hz, 1H), 7.46-7.42 (m, 3H), 7.34-7.27 (m, 3H), 6.17 (s, 1H), 5.37 (s, 1H), 3.75 (s, 2H), 3.64 (s, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 198.3, 167.3, 139.6, 138.9, 138.0, 137.8, 133.3, 131.0, 130.6, 130.4, 129.1, 128.5, 127.2, 126.0, 52.0, 35.2;

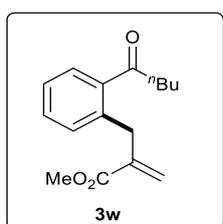
FT-IR (neat) 2951, 1722, 1664, 1597, 1448, 1266, 1203, 1139, 940 cm^{-1} ; HRMS (ESI-TOF) m/z : $[M+H]^+$ calcd for $\text{C}_{18}\text{H}_{17}\text{O}_3$ 281.1172; Found 281.1173.



Methyl 2-(2,5-diacetylbenzyl)acrylate 3u. Analytical TLC on silica gel, 1:10 EtOAc/hexane $R_f = 0.53$; colorless liquid; yield 78% (20.3 mg); ^1H NMR (500 MHz, CDCl_3) δ 7.86 (d, $J = 8.0$ Hz, 1H), 7.83 (s, 1H), 7.68 (d, $J = 8.0$ Hz, 1H), 6.22 (s, 1H), 5.33 (s, 1H), 3.91 (s, 2H), 3.73 (s, 3H), 2.60 (s, 3H), 2.58 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 201.9, 197.5, 167.2, 142.6, 139.6, 138.8, 138.5, 131.4, 128.9, 126.7, 126.5, 52.1, 35.5, 30.1, 26.9; FT-IR (neat) 2953, 1719, 1688, 1632, 1437, 1356, 1257, 1201, 1145 cm^{-1} ; HRMS (ESI-TOF) m/z : $[M+H]^+$ calcd for $\text{C}_{15}\text{H}_{17}\text{O}_4$ 261.1121; Found 261.1120.

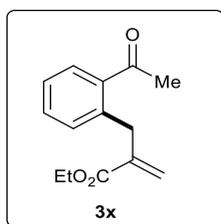


Methyl 2-(2-propionylbenzyl)acrylate 3v. Analytical TLC on silica gel, 1:10 EtOAc/hexane $R_f = 0.55$; colorless liquid; yield 68% (15.8 mg); ^1H NMR (500 MHz, CDCl_3) δ 7.60 (d, $J = 8.0$ Hz, 1H), 7.40 (t, $J = 7.5$ Hz, 1H), 7.30 (t, $J = 7.5$ Hz, 1H), 7.25 (d, $J = 8.0$ Hz, 1H), 6.19 (s, 1H), 5.27 (s, 1H), 3.86 (s, 2H), 3.73 (s, 3H), 2.90 (q, $J = 7.5$ Hz, 2H), 1.17 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 205.3, 167.5, 140.2, 138.9, 137.9, 131.7, 131.1, 128.3, 126.6, 126.2, 52.0, 35.6, 35.0, 8.4; FT-IR (neat) 2966, 1720, 1683, 1608, 1436, 1256, 1200, 1142 cm^{-1} ; HRMS (ESI-TOF) m/z : $[M+H]^+$ calcd for $\text{C}_{14}\text{H}_{17}\text{O}_3$ 233.1172; Found 233.1163.

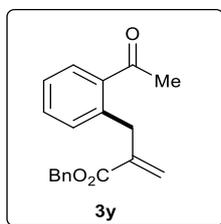


Methyl 2-(2-pentanoylbenzyl)acrylate 3w. Analytical TLC on silica gel, 1:10 EtOAc/hexane $R_f = 0.58$; colorless liquid; yield 65% (17 mg); ^1H NMR (500 MHz, CDCl_3) δ 7.60 (d, $J = 7.5$ Hz, 1H), 7.39 (t, $J = 7.5$ Hz, 1H), 7.30 (t, $J = 7.5$ Hz, 1H), 7.24 (d, $J = 8.0$ Hz, 1H), 6.19 (s, 1H), 5.26 (s, 1H), 3.85 (s, 2H), 3.73 (s, 3H), 2.86 (t, $J = 7.5$ Hz, 2H),

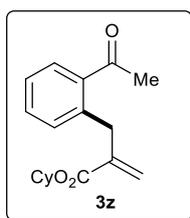
1.68-1.62 (m, 2H), 1.41-1.33 (m, 2H), 0.93 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 205.0, 167.5, 140.1, 139.1, 137.9, 131.7, 131.1, 128.4, 126.6, 126.3, 52.0, 41.7, 35.5, 26.5, 22.5, 14.0; FT-IR (neat) 2955, 1724, 1662, 1597, 1448, 1267, 1203, 1139, 941 cm^{-1} ; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{21}\text{O}_3$ 261.1485; Found 261.1478.



Ethyl 2-(2-acetylbenzyl)acrylate 3x. Analytical TLC on silica gel, 1:10 EtOAc/hexane $R_f = 0.44$; colorless liquid; yield 82% (19 mg); ^1H NMR (500 MHz, CDCl_3) δ 7.67 (d, $J = 7.5$ Hz, 1H), 7.41 (t, $J = 7.5$ Hz, 1H), 7.31 (t, $J = 8.0$ Hz, 1H), 7.25 (d, $J = 7.5$ Hz, 1H), 6.19 (s, 1H), 5.25 (s, 1H), 4.20 (q, $J = 7.0$ Hz, 2H), 3.92 (s, 2H), 2.56 (s, 3H), 1.26 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 201.9, 167.1, 140.5, 138.5, 138.4, 131.9, 131.6, 129.3, 126.6, 125.8, 60.9, 35.7, 29.7, 14.3; FT-IR (neat) 2954, 1722, 1681, 1604, 1436, 1267, 1204, 1146, 1047 cm^{-1} ; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{17}\text{O}_3$ 233.1172; Found 233.1172.

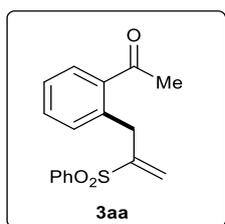


Benzyl 2-(2-acetylbenzyl)acrylate 3y. Analytical TLC on silica gel, 1:10 EtOAc/hexane $R_f = 0.46$; colorless liquid; yield 77% (18 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.68-7.66 (m, 1H), 7.42-7.24 (m, 8H), 6.26-6.25 (m, 1H), 5.32-5.31 (m, 1H), 5.17 (s, 2H), 3.94 (s, 2H), 2.52 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 201.9, 166.9, 140.1, 138.5, 138.3, 136.1, 131.8, 131.6, 129.3, 128.6, 128.2, 128.1, 126.6, 126.5, 66.6, 35.7, 29.7; FT-IR (neat) 2951, 1724, 1684, 1603, 1448, 1266, 1203, 1141, 1040 cm^{-1} ; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{19}\text{O}_3$ 295.1329; Found 295.1314.

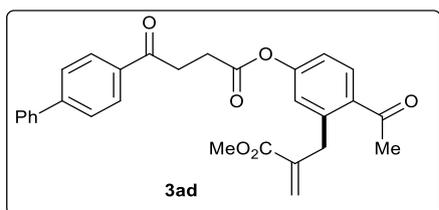


Cyclohexyl 2-(2-acetylbenzyl)acrylate 3z. Analytical TLC on silica gel, 1:10 EtOAc/hexane $R_f = 0.51$; colorless liquid; yield 72% (20.6 mg); ^1H NMR (400 MHz, CDCl_3)

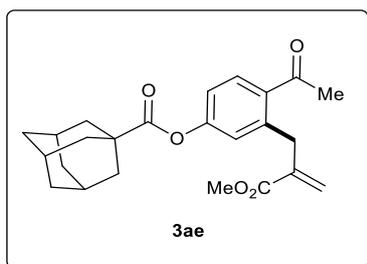
δ 7.66 (d, J = 8.0 Hz, 1H), 7.41 (t, J = 7.6 Hz, 1H), 7.30 (t, J = 7.6 Hz, 1H), 7.27-7.26 (m, 1H), 6.20-6.19 (m, 1H), 5.27-5.26 (m, 1H), 4.84-4.78 (m, 1H), 3.92 (s, 2H), 2.56 (s, 3H), 1.83-1.78 (m, 2H), 1.70-1.64 (m, 2H), 1.54-1.47 (m, 1H), 1.45-1.34 (m, 4H), 1.32-1.25 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 202.0, 166.5, 140.8, 138.7, 138.4, 131.7, 131.5, 129.2, 126.5, 125.8, 73.0, 35.8, 31.6, 29.8, 25.6, 23.7; FT-IR (neat) 2946, 1719, 1685, 1630, 1436, 1269, 1220, 1135, 1044 cm^{-1} ; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{23}\text{O}_3$ 287.1642; Found 287.1644.



1-(2-(2-(Phenylsulfonyl)allyl)phenyl)ethan-1-one 3aa. Analytical TLC on silica gel, 1:10 EtOAc/hexane R_f = 0.55; yellow solid; yield 89% (28 mg); ^1H NMR (500 MHz, CDCl_3) δ 7.84 (d, J = 7.5 Hz, 2H), 7.64-7.60 (m, 2H), 7.52 (t, J = 7.5 Hz, 2H), 7.38 (t, J = 6.5 Hz, 1H), 7.31 (t, J = 7.0 Hz, 1H), 7.15 (d, J = 8.0 Hz, 1H), 6.34 (s, 1H), 5.30 (s, 1H), 3.87 (s, 2H), 2.40 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 200.8, 150.3, 139.0, 137.8, 135.6, 133.5, 132.5, 132.0, 129.7, 129.1, 128.3, 127.4, 125.0, 34.0, 29.2; FT-IR (neat) 3065, 1683, 1573, 1446, 1357, 1303, 1254, 1131, 1080 cm^{-1} ; HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{17}\text{H}_{16}\text{NaO}_3\text{S}$ 323.0712; Found 323.0710.

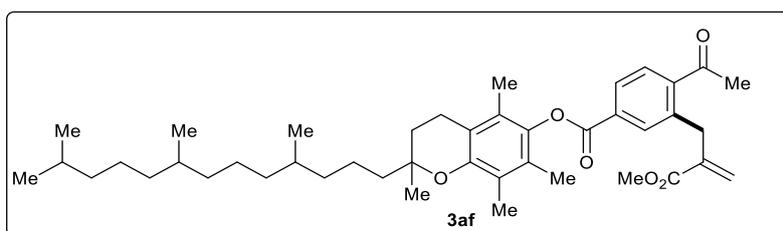


4-Acetyl-3-(2-(methoxycarbonyl)allyl)phenyl 4-([1,1'-biphenyl]-4-yl)-4-oxobutanoate 3ad. Analytical TLC on silica gel, 1:5 EtOAc/hexane R_f = 0.34; sticky brown solid; yield 65% (30.6 mg); ^1H NMR (500 MHz, CDCl_3) δ 8.07 (d, J = 8.0 Hz, 2H), 7.73 (d, J = 8.5 Hz, 1H), 7.70 (d, J = 8.5 Hz, 2H), 7.62 (d, J = 7.5 Hz, 2H), 7.48 (t, J = 7.5 Hz, 2H), 7.41 (t, J = 7.0 Hz, 1H), 7.12 (d, J = 9.5 Hz, 1H), 7.03 (s, 1H), 6.21 (s, 1H), 5.32 (s, 1H), 3.93 (s, 2H), 3.74 (s, 3H), 3.46 (t, J = 6.5 Hz, 2H), 3.04 (t, J = 6.5 Hz, 2H), 2.56 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 200.6, 197.5, 171.2, 167.4, 153.0, 146.3, 141.1, 139.9, 139.6, 135.5, 135.2, 131.1, 129.1, 128.8, 128.5, 127.5, 127.4, 126.4, 124.8, 119.8, 52.1, 35.7, 33.5, 29.7, 28.7; FT-IR (neat) 2925, 1761, 1716, 1683, 1603, 1438, 1356, 1254, 1132, 1056 cm^{-1} ; HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{29}\text{H}_{26}\text{NaO}_6$ 493.1622; Found 493.1610.



4-Acetyl-3-(2-(methoxycarbonyl)allyl)phenyl adamantane-1-

carboxylate 3ae. Analytical TLC on silica gel, 1:10 EtOAc/hexane $R_f = 0.35$; colorless liquid; yield 68% (27 mg); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.72 (d, $J = 8.5$ Hz, 1H), 7.04-7.02 (m, 1H), 6.94 (s, 1H), 6.20 (s, 1H), 5.28 (s, 1H), 3.92 (s, 2H), 3.74 (s, 3H), 2.55 (s, 3H), 2.09 (s, 3H), 2.05 (s, 6H), 1.80-1.74 (m, 6H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 200.5, 175.8, 167.4, 153.4, 141.0, 139.7, 135.3, 131.1, 126.3, 125.0, 119.8, 52.1, 41.3, 38.8, 36.5, 35.7, 29.7, 28.0; FT-IR (neat) 2908, 1751, 1721, 1687, 1604, 1577, 1259, 1205, 1042 cm^{-1} ; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{24}\text{H}_{29}\text{O}_5$ 397.2010; Found 397.2009.



2,5,7,8-Tetramethyl-2-(4,8,12

-trimethyltridecyl)chroman-6-yl 4-acetyl-3-(2-(methoxycarbonyl)allyl)benzoate 3af.

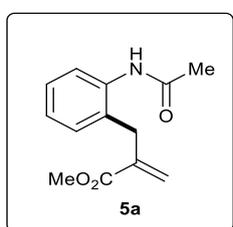
Analytical TLC on silica gel, 1:10 EtOAc/hexane $R_f = 0.41$; colorless liquid; yield 62% (42 mg); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.17 (d, $J = 8.0$ Hz, 1H), 8.12 (s, 1H), 7.73 (d, $J = 8.0$ Hz, 1H), 6.25 (s, 1H), 5.38 (s, 1H), 3.95 (s, 2H), 3.74 (s, 3H), 2.62 (s, 3H), 2.12 (s, 3H), 2.04 (s, 3H), 2.00 (s, 3H), 1.87-1.78 (m, 2H), 1.55-1.50 (m, 2H), 1.42-1.37 (m, 4H), 1.30-1.21 (dm, 12H), 1.16-1.05 (m, 8H), 0.87-0.84 (m, 12H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 202.0, 167.2, 164.4, 149.7, 143.0, 140.6, 139.5, 138.5, 134.8, 133.2, 131.9, 128.8, 128.4, 126.9, 126.8, 125.1, 123.4, 117.7, 75.3, 52.1, 39.5, 37.5, 35.4, 32.9, 30.1, 28.1, 24.96, 24.95, 24.6, 22.9, 22.8, 21.2, 20.8, 19.9, 19.8, 13.2, 12.4, 12.0; FT-IR (neat) 2926, 2867, 1733, 1696, 1460, 1238, 1148, 1099 cm^{-1} ; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{43}\text{H}_{63}\text{O}_6$ 675.4619; Found 675.4619.

Scale-up Synthesis of 3a. Acetophenone **1a** (2 mmol, 240 mg, 1.0 equiv), MBH alcohol **2a** (3 mmol, 348 mg, 1.5 equiv), $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$ (0.1 mmol, 61.2 mg, 0.05 equiv), AgSbF_6 (0.4 mmol, 137 mg, 0.2 equiv) and $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (2 mmol, 400 mg, 1.0 equiv) were stirred in 1,2-dichloroethane (DCE) (4 mL, 0.5 M) at 100 °C (in a pre-heated oil bath) in a sealed tube for

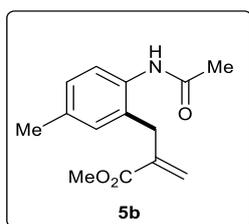
12 h. The work up and purification have been performed as described in the general procedure to furnish **3a** in 72% (314 mg) yield.

General Procedure for the Synthesis of **5**

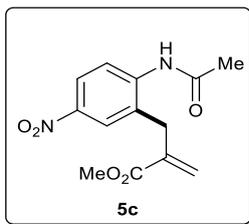
Acetanilide **4** (0.1 mmol, 1.0 equiv), MBH alcohol **2a** (0.15 mmol, 1.5 equiv), [Ru(*p*-cymene)Cl₂]₂ (0.005 mmol, 3.06 mg, 0.05 equiv), AgSbF₆ (0.02 mmol, 6.87 mg, 0.2 equiv) and Cu(OAc)₂·H₂O (0.1 mmol, 20 mg, 1.0 equiv) were stirred in 1,2-dichloroethane (DCE) (1 mL, 0.1 M) at 100 °C (in a pre-heated oil bath) in a sealed tube for 12 h. After completion (monitored by TLC), the reaction mixture was diluted with EtOAc (5 mL) and passed through a short celite pad. Evaporation of the solvent gave a residue that was purified on silica gel column chromatography using *n*-hexane and EtOAc as an eluent to afford **5**.



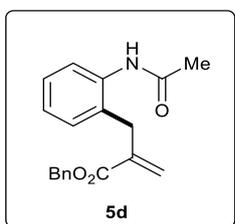
Methyl 2-(2-acetamidobenzyl)acrylate 5a. Analytical TLC on silica gel, 3:7 EtOAc/hexane $R_f = 0.55$; brown sticky solid; yield 60% (14 mg); ¹H NMR (500 MHz, CDCl₃) δ 8.78 (bs, 1H), 7.81 (d, $J = 8.1$ Hz, 1H), 7.23 (t, $J = 7.7$ Hz, 1H), 7.18 (d, $J = 7.1$ Hz, 1H), 7.08 (t, $J = 7.4$ Hz, 1H), 6.23 (s, 1H), 5.80 (s, 1H), 3.76 (s, 3H), 3.57 (s, 2H), 2.23 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 169.0, 168.7, 139.2, 135.7, 130.3, 127.7, 127.6, 125.2, 124.6, 52.6, 33.9, 24.4; FT-IR (neat) 3284, 2924, 1720, 1665, 1522, 1438, 1372, 1294, 1206, 1142 cm⁻¹; HRMS (ESI-TOF) m/z : [M+H]⁺ calcd for C₁₃H₁₆NO₃ 234.1125; Found 234.1128.



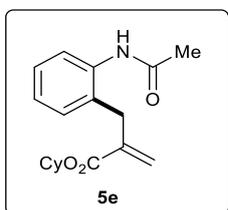
Methyl 2-(2-acetamido-5-methylbenzyl)acrylate 5b. Analytical TLC on silica gel, 3:7 EtOAc/hexane $R_f = 0.60$; brown sticky liquid; yield 55% (13.6 mg); ¹H NMR (400 MHz, CDCl₃) δ 8.61 (bs, 1H), 7.63 (d, $J = 8.4$ Hz, 1H), 7.03 (d, $J = 8.4$ Hz, 1H), 6.98 (s, 1H), 6.22 (s, 1H), 5.80 (s, 1H), 3.76 (s, 3H), 3.52 (s, 2H), 2.28 (s, 3H), 2.21 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 169.0, 168.7, 139.4, 135.0, 133.1, 130.7, 130.4, 128.3, 127.5, 124.8, 52.6, 33.9, 24.3, 21.0; FT-IR (neat) 3283, 2924, 1720, 1665, 1522, 1438, 1371, 1296, 1206, 1142 cm⁻¹; HRMS (ESI-TOF) m/z : [M+H]⁺ calcd for C₁₄H₁₈NO₃ 248.1281; Found 248.1279.



Methyl 2-(2-acetamido-5-nitrobenzyl)acrylate 5c. Analytical TLC on silica gel, 3:7 EtOAc/hexane $R_f = 0.45$; light yellow liquid; yield 50% (14 mg); ^1H NMR (400 MHz, CDCl_3) δ 9.15 (bs, 1H), 8.80 (s, 1H), 7.90 (d, $J = 10.0$ Hz, 1H), 7.32 (d, $J = 8.4$ Hz, 1H), 6.32 (s, 1H), 5.92 (s, 1H), 3.78 (s, 3H), 3.64 (s, 2H), 2.27 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 169.2, 168.7, 147.4, 138.0, 136.9, 136.8, 130.9, 129.0, 119.5, 119.4, 53.0, 33.9, 24.4; FT-IR (neat) 3283, 2934, 1720, 1677, 1522, 1437, 1296, 1202, 1148 cm^{-1} ; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{15}\text{N}_2\text{O}_5$ 279.0975; Found 279.0969.



Benzyl 2-(2-acetamidobenzyl)acrylate 5d. Analytical TLC on silica gel, 3:7 EtOAc/hexane $R_f = 0.50$; colorless liquid; yield 62% (19.2 mg); ^1H NMR (500 MHz, CDCl_3) δ 8.60 (bs, 1H), 7.81 (d, $J = 8.0$ Hz, 1H), 7.38-7.32 (m, 5H), 7.25 (t, $J = 8.0$ Hz, 1H), 7.18 (d, $J = 7.5$ Hz, 1H), 7.09 (t, $J = 7.5$ Hz, 1H), 6.30 (s, 1H), 5.81 (s, 1H), 5.18 (s, 2H), 3.59 (s, 2H), 2.18 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 169.0, 168.1, 139.3, 135.7, 135.5, 130.3, 128.8, 128.6, 128.3, 128.0, 127.6, 125.3, 124.6, 67.4, 33.8, 24.4; FT-IR (neat) 3280, 2926, 1720, 1665, 1522, 1438, 1375, 1306, 1142 cm^{-1} ; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{20}\text{NO}_3$ 310.1438; Found 310.1437.



Cyclohexyl 2-(2-acetamidobenzyl)acrylate 5e. Analytical TLC on silica gel, 3:7 EtOAc/hexane $R_f = 0.50$; colorless liquid; yield 66% (20 mg); ^1H NMR (500 MHz, CDCl_3) δ 8.87 (bs, 1H), 7.83 (d, $J = 8.0$ Hz, 1H), 7.23 (t, $J = 7.5$ Hz, 1H), 7.18 (d, $J = 7.5$ Hz, 1H), 7.08 (t, $J = 7.5$ Hz, 1H), 6.22 (s, 1H), 5.77 (s, 1H), 4.84-4.81 (m, 1H), 3.56 (s, 2H), 2.23 (s, 3H), 1.85-1.80 (m, 2H), 1.74-1.69 (m, 3H), 1.50-1.32 (m, 5H); ^{13}C NMR (125 MHz, CDCl_3) δ 169.0, 167.8, 140.0, 135.8, 130.4, 130.3, 127.5, 127.1, 125.1, 124.4, 74.0, 33.8, 31.5, 25.4,

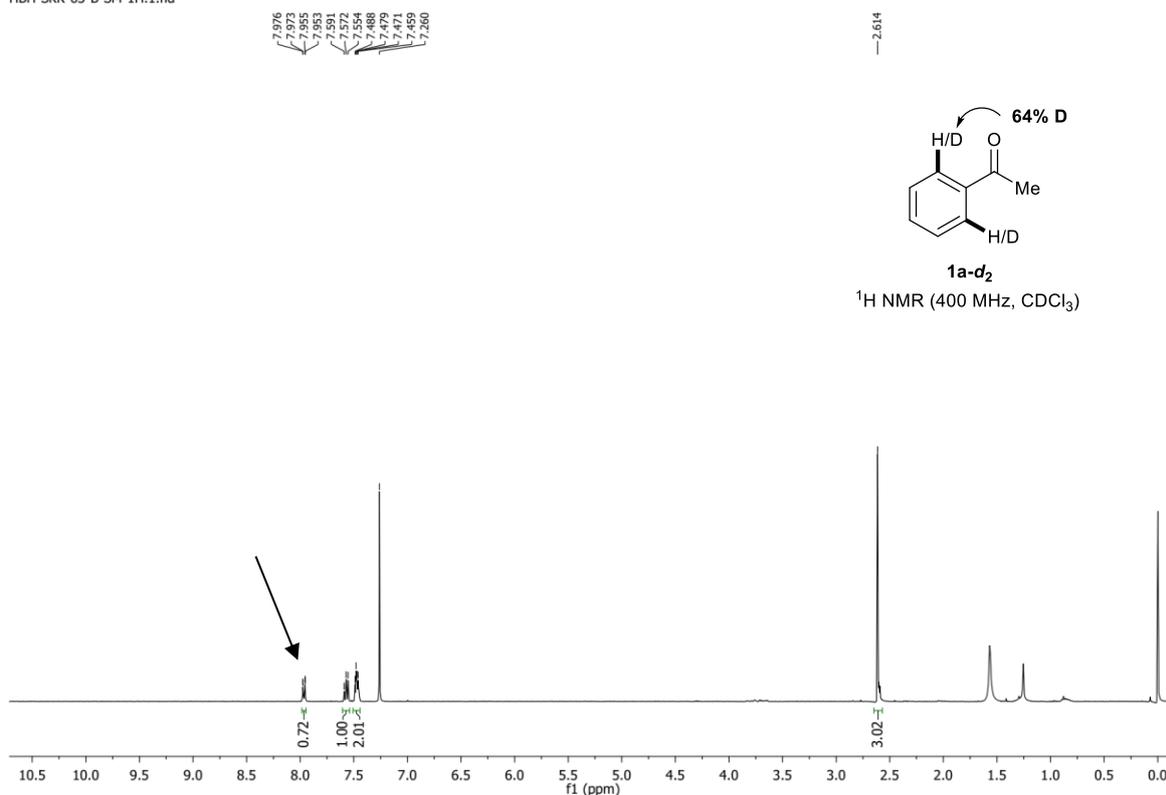
24.4, 23.7; FT-IR (neat) 3284, 2928, 1718, 1667, 1524, 1438, 1371, 1301, 1208, 1145 cm^{-1} ; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{20}\text{NO}_3$ 302.1751; Found 302.1749.

Preliminary Mechanistic Investigations

H/D Exchange Experiments

H/D Exchange Experiment of 1a with D₂O in Absence of 2a. Acetophenone **1a** (0.1 mmol, 12 mg, 1.0 equiv), $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$ (0.005 mmol, 3 mg, 0.05 equiv), AgSbF_6 (0.02 mmol, 6.87 mg, 0.2 equiv), $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (0.1 mmol, 20 mg, 1.0 equiv) and D_2O (1 mmol, 18 μL , 10.0 equiv) were stirred in 1,2-dichloroethane (DCE) (1 mL, 0.1 M) at 100 $^\circ\text{C}$ (in a pre-heated oil bath) in a sealed tube for 2 h. The reaction mixture was diluted with EtOAc (5 mL) and passed through a short celite pad. Evaporation of the solvent gave a residue that was purified on silica gel column chromatography using n-hexane and EtOAc as an eluent to afford **1a-d₂**. The deuterium incorporation of **1a-d₂** was calculated based on its 400 MHz ^1H NMR spectrum (See the following ^1H NMR spectrum).

HBH-SKK-63-B-SM-1H.1.fid

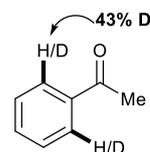


H/D Exchange Experiment of 1a with D₂O in Presence of 2a. Acetophenone **1a** (0.1 mmol, 12 mg, 1.0 equiv), MBH alcohol **2a** (0.15 mmol, 17.4 mg, 1.5 equiv), [Ru(*p*-cymene)Cl₂]₂ (0.005 mmol, 3 mg, 0.05 equiv), AgSbF₆ (0.02 mmol, 6.87 mg, 0.2 equiv), Cu(OAc)₂·H₂O (0.1 mmol, 20 mg, 1.0 equiv) and D₂O (1 mmol, 18 μL, 10.0 equiv) were stirred in 1,2-dichloroethane (DCE) (1 mL, 0.1 M) at 100 °C (in a pre-heated oil bath) in a sealed tube for 6 h. The reaction mixture was diluted with EtOAc (5 mL) and passed through a short celite pad. Evaporation of the solvent gave a residue that was purified on silica gel column chromatography using n-hexane and EtOAc as an eluent to afford **3a-d** and **1a-d₂**. The deuterium incorporation of **3a-d** and **1a-d₂** was calculated based on their respective 400 MHz ¹H NMR spectrum (See the following ¹H NMR spectrums).

HBH-SKK-63-A-SM-1H.1.fid

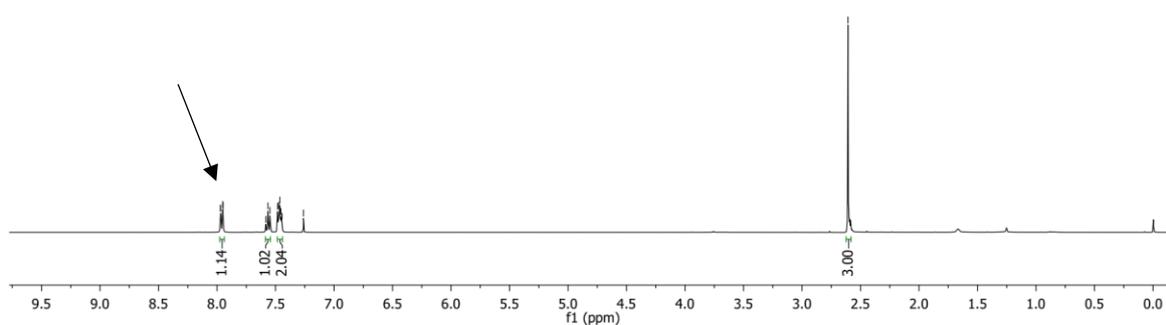


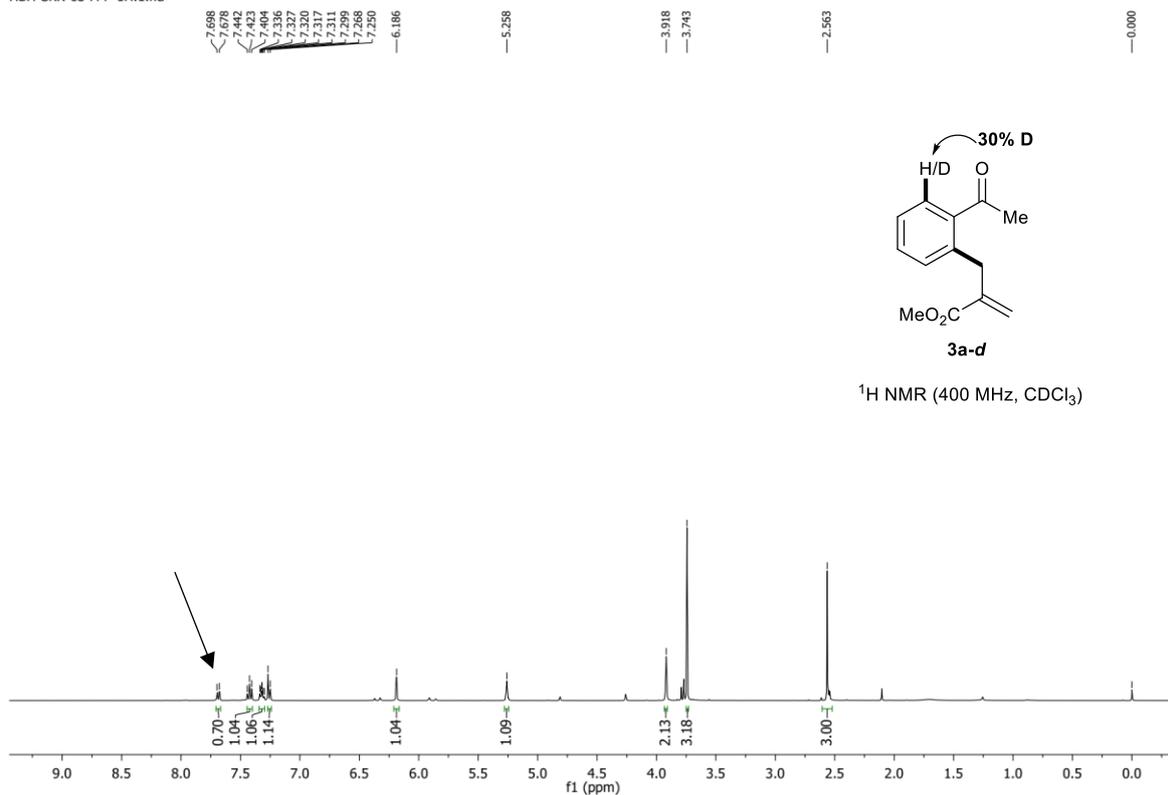
—2.607



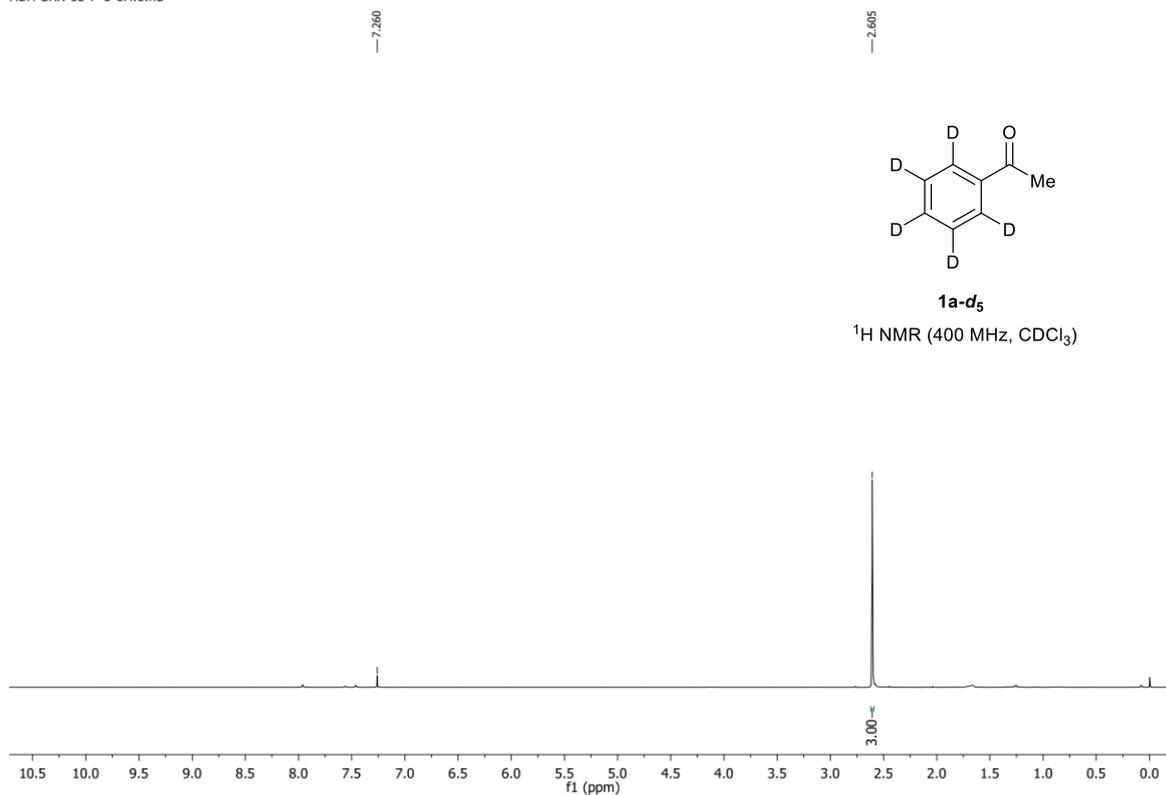
recovered
1a-d₂

¹H NMR (400 MHz, CDCl₃)



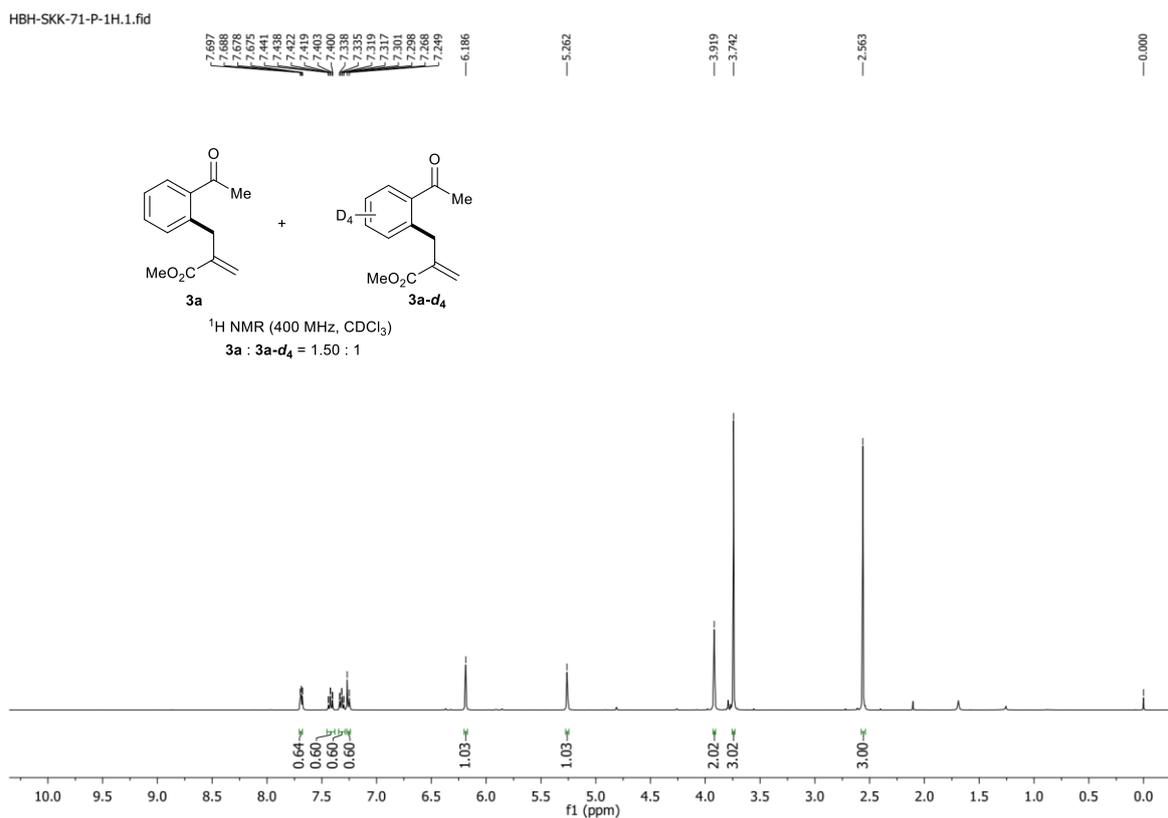


Preparation of 1-(phenyl-*d*₅)ethan-1-one **1a-d₅.**¹ To a stirred solution benzene-*d*₆ (11.8 mmol, 1 mL) and AlCl₃ (14.7 mmol, 1.9 g) in CS₂ (4 mL) at 0 °C under N₂ atmosphere, acetyl chloride (14.7 mmol, 1 mL) in CS₂ (4 mL) was added. The resulting mixture allowed to stir at room temperature for 5 h and then at 50 °C for 3 h. The reaction mixture was then cooled to room temperature and poured into ice-cold water and extracted using CH₂Cl₂ (3 x 15 mL). The organic layer was washed with aqueous Na₂CO₃ (20 mL) and water (10 mL). Drying (Na₂SO₄) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using n-hexane and ethyl acetate as eluent to provide [*D*₅]-acetophenone **1a-d**₅ in 78% (1.1 g) yield.



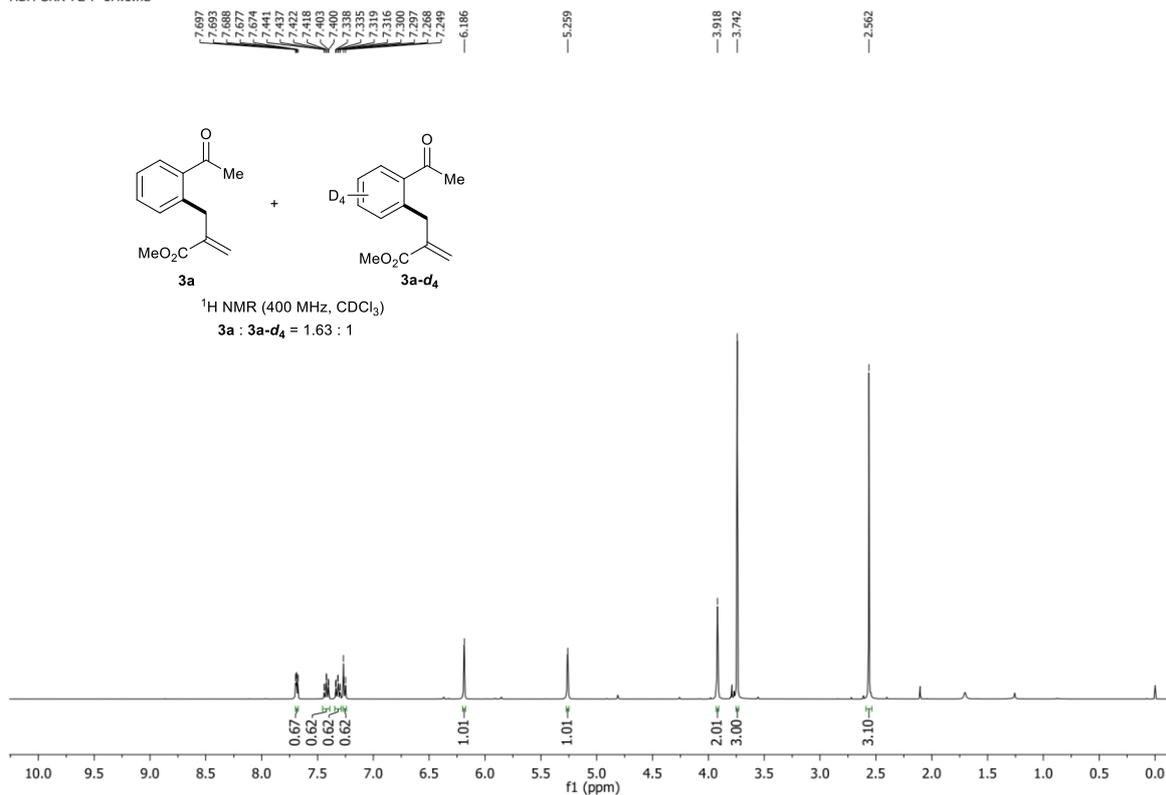
Kinetic Isotope Effect Experiments

Parallel Experiment: Acetophenone **1a** (0.1 mmol, 12 mg, 1.0 equiv) or **1a-d₅** (0.1 mmol, 12.5 mg, 1.0 equiv), MBH alcohol **2a** (0.15 mmol, 17.4 mg, 1.5 equiv), [Ru(*p*-cymene)Cl₂]₂ (0.005 mmol, 3 mg, 0.05 equiv), AgSbF₆ (0.02 mmol, 6.87 mg, 0.2 equiv) and Cu(OAc)₂·H₂O (0.1 mmol, 20 mg, 1.0 equiv) were stirred in 1,2-dichloroethane (DCE) (1 mL, 0.1 M) at 100 °C (in a pre-heated oil bath) in a sealed tube for 2 h. Both the reaction mixtures were combined and passed through a short celite pad using EtOAc (5 mL). The solvent was removed under reduced pressure and the purification was performed as described in the general procedure to afford a mixture **3a** and **3a-d₄**. The KIE value was determined to be $k_H/k_D = 1.50$ on the basis of ¹H NMR analysis.



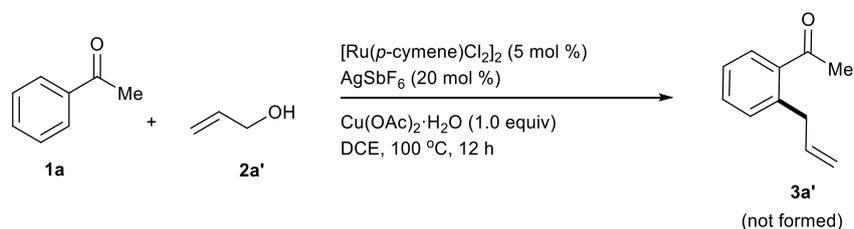
Competitive Experiment: Acetophenone **1a** (0.1 mmol, 12 mg, 1.0 equiv), 1-(phenyl-*d*₅)ethan-1-one **1a-d₅** (0.1 mmol, 12.5 mg, 1.0 equiv), MBH alcohol **2a** (0.15 mmol, 17.4 mg, 1.5 equiv), [Ru(*p*-cymene)Cl₂]₂ (0.005 mmol, 3 mg, 0.05 equiv), AgSbF₆ (0.02 mmol, 6.87 mg, 0.2 equiv) and Cu(OAc)₂·H₂O (0.1 mmol, 20 mg, 1.0 equiv) were stirred in 1,2-dichloroethane (DCE) (1 mL, 0.1 M) at 100 °C (in a pre-heated oil bath) in a sealed tube for 2 h. The reaction mixture was diluted with EtOAc (5 mL) and passed through a short celite pad. The solvent was removed under reduced pressure and the purification was carried out as described in the general procedure to afford a mixture of **3a** and **3a-d₄**. The KIE value was determined to be $k_H/k_D = 1.63$ on the basis of ¹H NMR analysis.

HBH-SKK-72-P-1H.1.fid



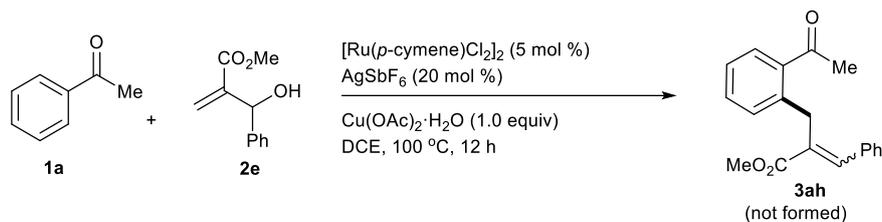
Control Experiment (1)

Acetophenone **1a** (0.1 mmol, 12 mg, 1.0 equiv), prop-2-en-1-ol **2a'** (0.15 mmol, 8.7 mg, 1.5 equiv), [Ru(*p*-cymene)Cl₂]₂ (0.005 mmol, 3 mg, 0.05 equiv), AgSbF₆ (0.02 mmol, 6.87 mg, 0.2 equiv) and Cu(OAc)₂·H₂O (0.1 mmol, 20 mg, 1.0 equiv) were stirred in 1,2-dichloroethane (DCE) (1 mL, 0.1 M) at 100 °C (in a pre-heated oil bath) in a sealed tube for 12 h. The corresponding allylated product **3a'** was not formed.



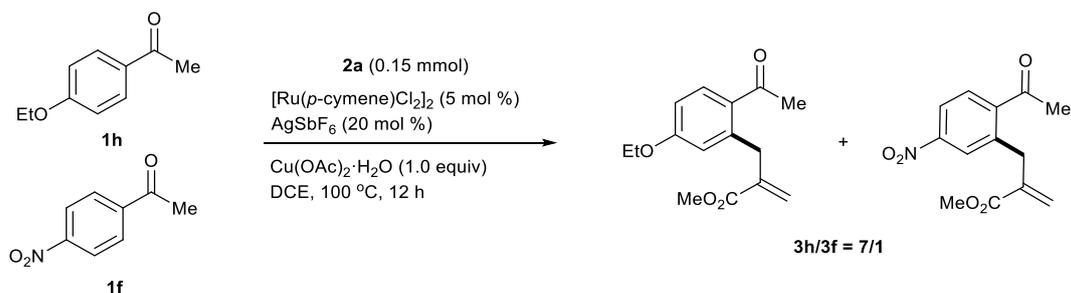
Control Experiment (2)

Acetophenone **1a** (0.1 mmol, 12 mg, 1.0 equiv), methyl 2-(hydroxy(phenyl)methyl)acrylate **2e** (0.15 mmol, 28.8 mg, 1.5 equiv), [Ru(*p*-cymene)Cl₂]₂ (0.005 mmol, 3 mg, 0.05 equiv), AgSbF₆ (0.02 mmol, 6.87 mg, 0.2 equiv) and Cu(OAc)₂·H₂O (0.1 mmol, 20 mg, 1.0 equiv) were stirred in 1,2-dichloroethane (DCE) (1 mL, 0.1 M) at 100 °C (in a pre-heated oil bath) in a sealed tube for 12 h. The corresponding allylated product **3ah** was not formed.



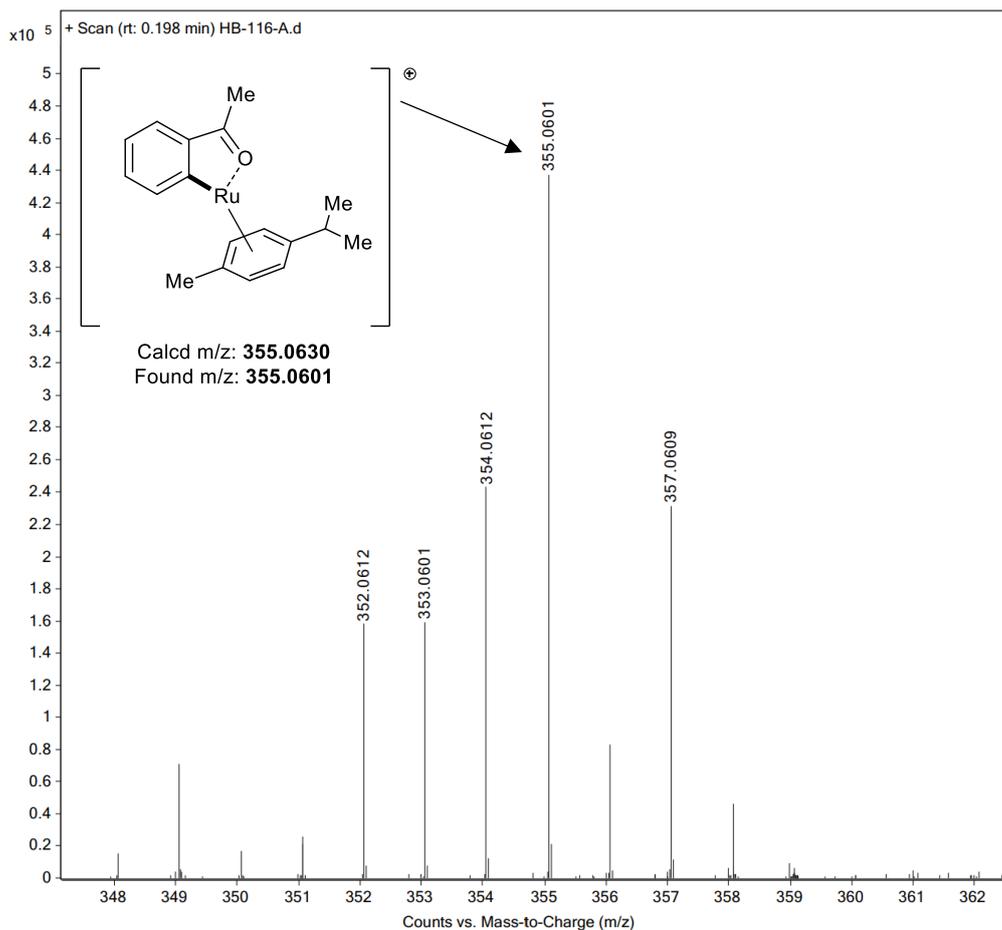
Intermolecular Competition Experiment

Aryl ketones **1h** (0.1 mmol, 16.4 mg, 1.0 equiv) and **1f** (0.1 mmol, 16.5 mg, 1.0 equiv), MBH alcohol **2e** (0.15 mmol, 17.4 mg, 1.5 equiv), [Ru(*p*-cymene)Cl₂]₂ (0.01 mmol, 3 mg, 0.05 equiv), AgSbF₆ (0.04 mmol, 6.87 mg, 0.2 equiv) and Cu(OAc)₂·H₂O (0.2 mmol, 20 mg, 1.0 equiv) were stirred in 1,2-dichloroethane (DCE) (1 mL, 0.1 M) at 100 °C (in a pre-heated oil bath) in a sealed tube for 12 h. The reaction mixture was diluted with EtOAc (5 mL) and passed through a short celite pad. Evaporation of the solvent gave a mixture of **3h** and **3f** in 7:1 ratio, calculated from 400 MHz ¹H NMR spectroscopy.



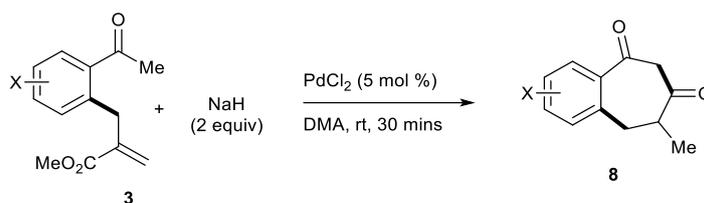
Detection of Intermediate B

Acetophenone **1a** (0.1 mmol, 12 mg, 1.0 equiv), [Ru(*p*-cymene)Cl₂]₂ (0.005 mmol, 3.06 mg, 0.05 equiv), AgSbF₆ (0.02 mmol, 6.87 mg, 0.2 equiv) and Cu(OAc)₂·H₂O (0.1 mmol, 20 mg, 1.0 equiv) were stirred in 1,2-dichloroethane (DCE) (1 mL, 0.1 M) at 100 °C (in a pre-heated oil bath) in a sealed tube for 3 h. The resultant mixture was analysed using HRMS analysis. HRMS (ESI) *m/z* [M]⁺ calcd for C₁₈H₂₁ORu (Intermediate **B**) 355.0630; Found 355.0601.



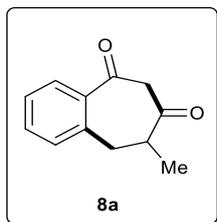
Post-synthetic Transformations

Synthesis of **8**.²



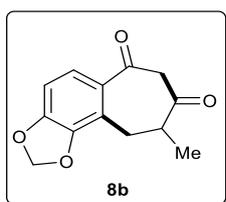
PdCl₂ (0.01 mmol, 1.8 mg, 5 mol %) and sodium hydride (0.4 mmol, 16 mg, 2.0 equiv, 60% dispersion in oil) were stirred in *N,N*-dimethylacetamide (DMA) (1.0 mL, 0.2 M) at room temperature under N₂ for 5 min. Compound **3** (0.2 mmol, 1.0 equiv) in DMA (0.5 mL) was then added and the reaction mixture was stirred at room temperature for 30 mins. After completion (monitored by TLC), saturated aqueous NH₄Cl (5 mL) was added. The resulting mixture was extracted with EtOAc (2 x 10 mL), and the combined organic extracts were washed with water (10 mL) and brine (10 mL). Drying (Na₂SO₄) and evaporation of the solvent

gave a residue that was purified on silica gel column chromatography using n-hexane and EtOAc as an eluent to afford **8**.



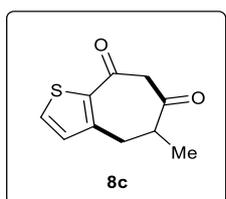
8-Methyl-8,9-dihydro-5H-benzo[7]annulene-5,7(6H)-dione **8a.**

Analytical TLC on silica gel, 1:5 EtOAc/hexane $R_f = 0.60$; yellow liquid; yield 85% (32 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.91 (d, $J = 7.6$ Hz, 1H), 7.49 (t, $J = 7.2$ Hz, 1H), 7.36 (t, $J = 6.8$ Hz, 1H), 7.23 (d, $J = 7.6$ Hz, 1H), 4.09 (d, $J = 14.4$ Hz, 1H), 4.00 (d, $J = 14.4$ Hz, 1H), 3.40 (dd, $J = 15.2, 4.0$ Hz, 1H), 3.18 (dd, $J = 15.6, 8.4$ Hz, 1H), 2.82-2.73 (m, 1H), 1.19 (d, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 206.0, 192.5, 140.3, 136.2, 133.8, 131.4, 130.2, 127.8, 58.6, 46.2, 38.5, 16.2; FT-IR (neat) 2922, 1715, 1676, 1604, 1438, 1241, 1207, 1121, 1081 cm^{-1} ; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{12}\text{H}_{13}\text{O}_2$ 189.0910; Found 189.0904.



9-Methyl-9,10-dihydro-6H-cyclohepta[3,4]benzo[1,2-d][1,3]dioxole-6,8(7H)-dione **8b.**

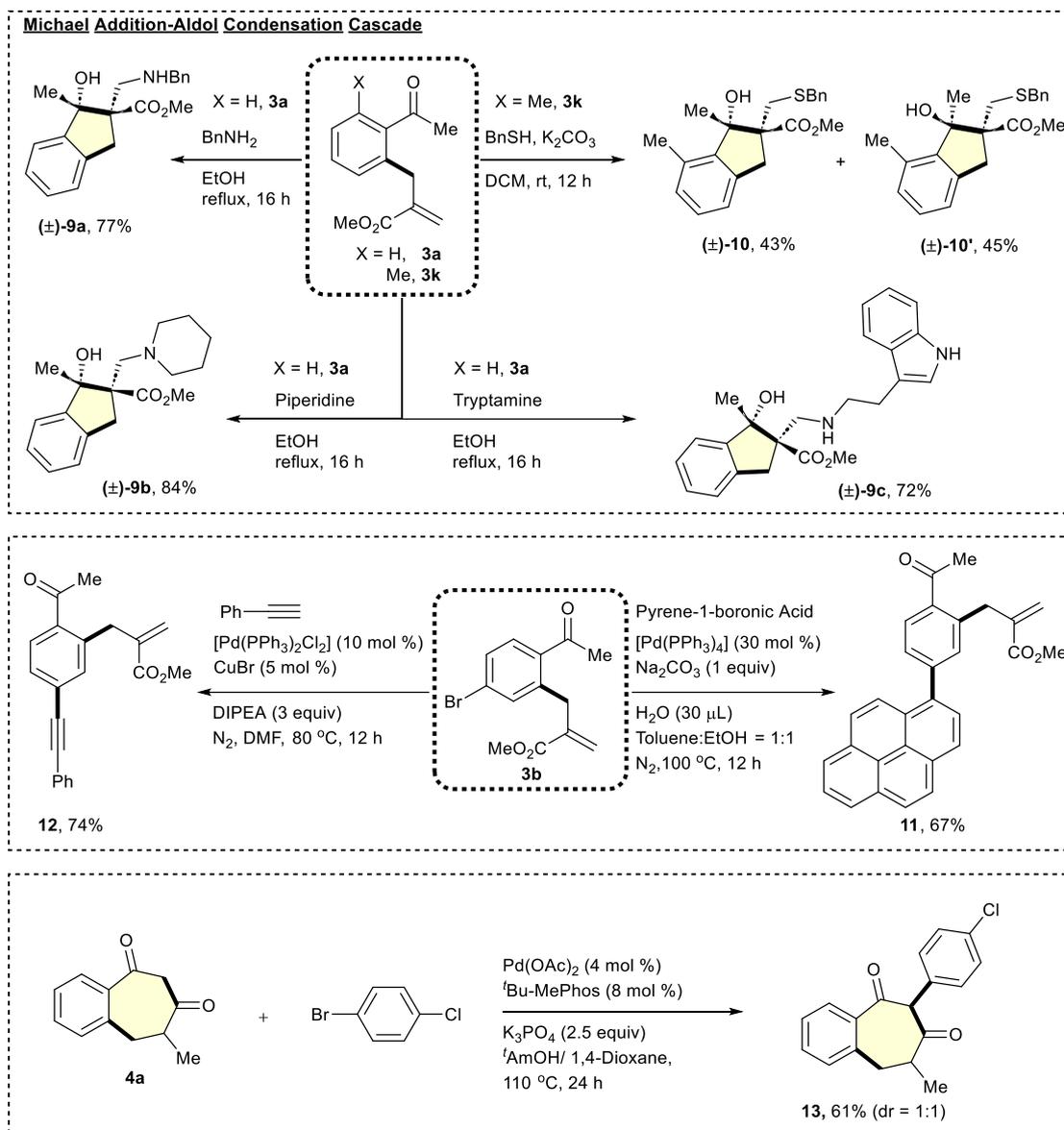
Analytical TLC on silica gel, 1:5 EtOAc/hexane $R_f = 0.51$; yellow liquid; yield 81% (37.6 mg); ^1H NMR (500 MHz, CDCl_3) δ 7.62 (d, $J = 8.0$ Hz, 1H), 6.79 (d, $J = 8.5$ Hz, 1H), 6.07 (s, 2H), 4.08 (d, $J = 14.0$ Hz, 1H), 3.97 (d, $J = 13.5$ Hz, 1H), 3.34 (d, $J = 16$ Hz, 1H), 3.10 (dd, $J = 15.5, 8.5$ Hz, 1H), 2.76-2.72 (m, 1H), 1.22 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 205.9, 190.1, 151.4, 146.6, 130.7, 126.5, 121.8, 107.7, 102.0, 58.6, 45.5, 29.4, 16.4; FT-IR (neat) 2922, 1715, 1672, 1622, 1455, 1349, 1279, 1053 cm^{-1} ; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{13}\text{O}_4$ 233.0808; Found 233.0809.



5-Methyl-4,5-dihydro-6H-cyclohepta[b]thiophene-6,8(7H)-dione **8c.**

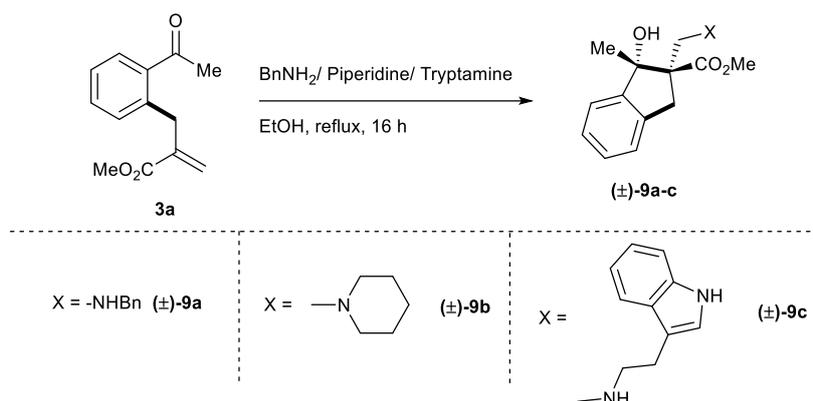
Analytical TLC on silica gel, 1:5 EtOAc/hexane $R_f = 0.47$; yellow liquid; yield 77% (30 mg); ^1H NMR (500 MHz, CDCl_3) δ 7.64 (d, $J = 5.0$ Hz, 1H), 6.99 (d, $J = 5.0$ Hz, 1H), 4.13 (d, $J = 13.0$ Hz, 1H), 3.99 (d, $J = 13.0$ Hz, 1H), 3.37 (dd, $J = 15.5, 3.0$ Hz, 1H), 3.15 (dd, $J = 15.5, 8.5$

Hz, 1H), 2.77-2.70 (m, 1H), 1.22 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 205.4, 183.2, 147.8, 139.5, 134.5, 131.6, 58.4, 44.9, 33.4, 17.4; FT-IR (neat) 2925, 1709, 1651, 1457, 1417, 1289, 1242, 1172 cm^{-1} ; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{10}\text{H}_{11}\text{O}_2\text{S}$ 195.0474; Found 195.0475.

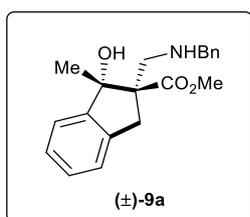


Scheme S1 Post synthetic transformations.

Synthesis of 9.

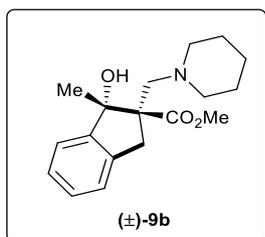


Compound **3a** (0.2 mmol, 43.6 mg, 1.0 equiv) and benzyl amine/ piperidine/ tryptamine (0.4 mmol, 2.0 equiv) were dissolved in EtOH (5 mL, 0.04 M) and refluxed in a pre-heated oil-bath for 16 h. After completion (monitored by TLC), the solvent was evaporated and the residue was purified on silica gel column chromatography using n-hexane and EtOAc as an eluent to afford **(±)-9a-c**.



Methyl-2-((benzylamino)methyl)-1-hydroxy-1-methyl-2,3-dihydro-

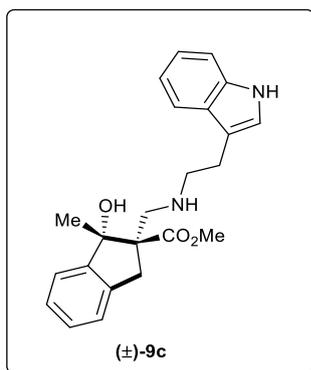
1H-indene-2-carboxylate (**±-9a**). Analytical TLC on silica gel, 1:20 EtOAc/hexane $R_f = 0.50$; colorless liquid; yield 77% (50 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.40 (d, $J = 7.6$ Hz, 1H), 7.29-7.17 (m, 7H), 7.11 (d, $J = 7.6$ Hz, 1H), 3.77 (s, 3H), 3.69-3.58 (m, 3H), 3.11 (d, $J = 12.4$ Hz, 1H), 2.81 (d, $J = 12.0$ Hz, 1H), 2.63 (d, $J = 16.4$ Hz, 1H), 1.36 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.9, 148.3, 138.9, 137.2, 128.6, 128.0, 127.9, 127.5, 127.3, 124.5, 123.2, 84.9, 59.9, 54.1, 53.7, 52.2, 38.2, 27.6; FT-IR (neat) 3330, 2949, 2840, 1719, 1454, 1231, 1203, 1123, 1094 cm^{-1} ; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{24}\text{O}_3\text{N}$ 326.1751; Found 326.1751.



Methyl-1-hydroxy-1-methyl-2-(piperidin-1-ylmethyl)-2,3-dihydro-

1H-indene-2-carboxylate (**±-9b**). Analytical TLC on silica gel, 1:20 EtOAc/hexane $R_f = 0.53$;

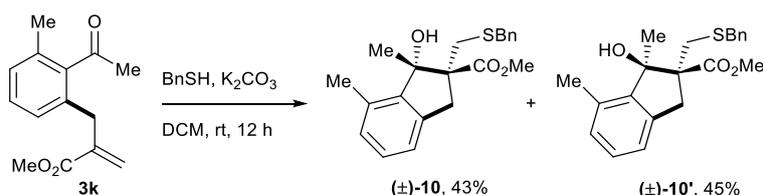
brown liquid; yield 84% (51 mg); ^1H NMR (500 MHz, CDCl_3) δ 7.36 (d, $J = 7.5$ Hz, 1H), 7.23 (t, $J = 7.5$ Hz, 1H), 7.19 (t, $J = 8.0$ Hz, 1H), 7.13 (d, $J = 7.0$ Hz, 1H), 3.77 (s, 3H), 3.32 (d, $J = 16.0$ Hz, 1H), 2.86 (d, $J = 16.0$ Hz, 1H), 2.75-2.68 (m, 2H), 2.42-2.36 (m, 2H), 2.27-2.22 (m, 2H), 1.50-1.41 (m, 4H), 1.37 (s, 3H), 1.34-1.30 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 175.3, 148.7, 137.4, 127.8, 127.3, 124.8, 122.7, 84.0, 63.5, 59.9, 56.1, 51.9, 37.4, 27.0, 26.3, 23.8; FT-IR (neat) 3451, 2933, 2853, 1723, 1441, 1351, 1275, 1234, 1199, 1039 cm^{-1} ; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{26}\text{O}_3\text{N}$ 304.1907; Found 304.1892.



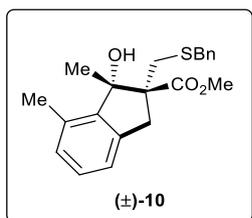
Methyl-2-(((2-(1H-indol-3-yl)ethyl)amino)methyl)-1-hydroxy-1-

methyl-2,3-dihydro-1H-indene-2-carboxylate (±)-9c. Analytical TLC on silica gel, 1:20 EtOAc/hexane $R_f = 0.36$; brown liquid; yield 72% (54.5 mg); ^1H NMR (500 MHz, CDCl_3) δ 8.07 (bs, 1H), 7.53 (d, $J = 7.5$ Hz, 1H), 7.40 (d, $J = 7.5$ Hz, 1H), 7.34 (d, $J = 8.0$ Hz, 1H), 7.28 (t, $J = 7.5$ Hz, 1H), 7.23-7.17 (m, 2H), 7.11-7.08 (m, 2H), 6.86 (s, 1H), 3.64 (s, 3H), 3.56 (d, $J = 16.0$ Hz, 1H), 3.12 (d, $J = 12.0$ Hz, 1H), 2.87 (t, $J = 6.5$ Hz, 2H), 2.80-2.75 (m, 3H), 2.56 (d, $J = 16.5$ Hz, 1H), 1.33 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 174.8, 148.7, 137.2, 136.5, 127.8, 127.5, 127.4, 124.5, 123.2, 122.3, 122.1, 119.4, 118.8, 113.4, 111.3, 84.8, 59.8, 54.7, 52.0, 49.6, 38.3, 27.5, 25.3; FT-IR (neat) 3318, 2925, 2848, 1718, 1457, 1434, 1339, 1231, 1207, 1096 cm^{-1} ; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{27}\text{O}_3\text{N}_2$ 379.2016; Found 379.201.

Synthesis of 10 and 10'.

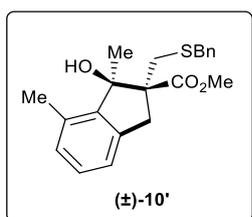


Compound **3k** (0.2 mmol, 46.5 mg, 1.0 equiv), benzyl mercaptan (0.4 mmol, 50 mg, 2.0 equiv) and K_2CO_3 (0.2 mmol, 27.6 mg, 1.0 equiv) were stirred in dichloromethane (DCM) (5 mL, 0.04 M) at room temperature for 12 h. After completion (monitored by TLC), the reaction was quenched with water (5 mL) and extracted with EtOAc (2 x 10 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using n-hexane and EtOAc as an eluent to afford a separable mixture of diastereomers (\pm)-**10** and (\pm)-**10'** in 43% and 45% yields, respectively.



Methyl-2-((benzylthio)methyl)-1-hydroxy-1,7-dimethyl-2,3-dihydro-

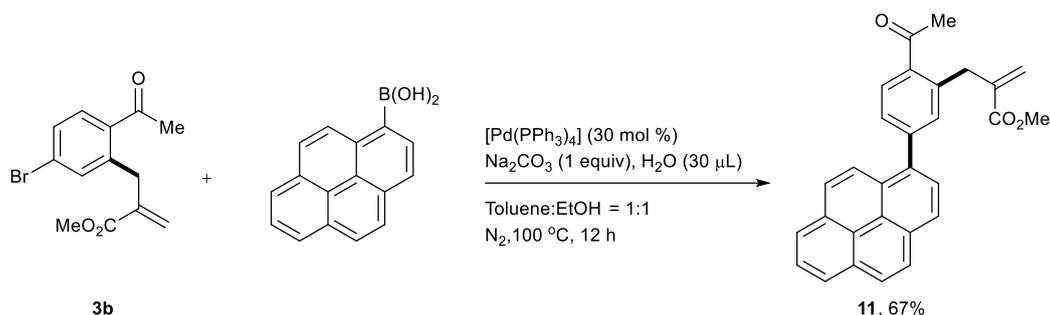
1H-indene-2-carboxylate (\pm)-**10**. Analytical TLC on silica gel, 1:50 EtOAc/hexane R_f = 0.52; colorless liquid; yield 43% (30.6 mg); 1H NMR (500 MHz, $CDCl_3$) δ 7.28-7.19 (m, 5H), 7.11 (t, J = 7.5 Hz, 1H), 6.97 (t, J = 7.5 Hz, 2H), 3.76 (s, 3H), 3.67-3.60 (m, 2H), 3.36 (d, J = 16.5 Hz, 1H), 3.14 (d, J = 12.5 Hz, 1H), 3.05 (d, J = 16.5 Hz, 1H), 2.60 (d, J = 13.0 Hz, 1H), 2.43 (s, 3H), 2.28 (s, 1H), 1.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.3, 141.6, 138.3, 137.9, 134.8, 129.9, 129.0, 128.6, 128.2, 127.1, 122.9, 85.3, 64.2, 52.2, 37.8, 35.8, 35.5, 24.9, 17.8; FT-IR (neat) 3503, 2927, 1725, 1453, 1272, 1223, 1175, 1029 cm^{-1} ; HRMS (ESI-TOF) m/z : $[M+Na]^+$ calcd for $C_{21}H_{24}NaO_3S$ 379.1338; Found 379.1334.



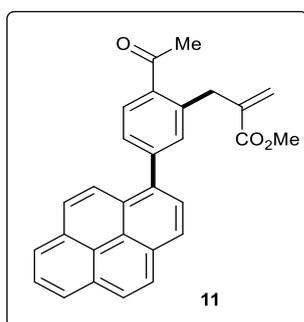
Methyl-2-((benzylthio)methyl)-1-hydroxy-1,7-dimethyl-2,3-dihydro-

1H-indene-2-carboxylate (\pm)-**10'**. Analytical TLC on silica gel, 1:50 EtOAc/hexane R_f = 0.58; colorless liquid; yield 45% (32 mg); 1H NMR (400 MHz, $CDCl_3$) δ 7.31-7.30 (m, 4H), 7.25-7.22 (m, 1H), 7.09 (t, J = 7.6 Hz, 1H), 6.96 (t, J = 6.8 Hz, 2H), 3.72 (s, 2H), 3.66-3.65 (m, 4H), 3.44 (d, J = 16.0 Hz, 1H), 3.05 (d, J = 12.4 Hz, 1H), 2.83 (d, J = 16.0 Hz, 1H), 2.70 (d, J = 12.4 Hz, 1H), 2.46 (s, 3H), 1.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.3, 143.8, 138.6, 138.3, 134.7, 130.3, 129.1, 128.6, 128.3, 127.2, 122.4, 85.3, 63.1, 52.4, 38.9, 38.1, 35.3, 22.3, 18.5; FT-IR (neat) 3457, 2951, 1599, 1454, 1305, 1199, 1071 cm^{-1} ; HRMS (ESI-TOF) m/z : $[M+Na]^+$ calcd for $C_{21}H_{24}O_3SNa$ 379.1338; Found 379.1335.

Synthesis of 11.

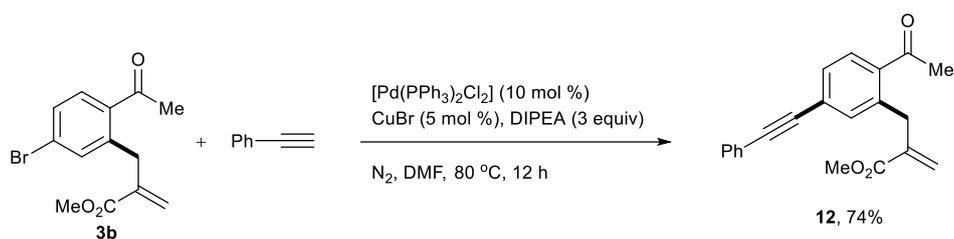


Compound **3b** (0.2 mmol, 40 mg, 1.0 equiv), pyren-1-ylboronic acid (0.2 mmol, 49 mg, 1.0 equiv), $Pd(PPh_3)_4$ (0.006 mmol, 7 mg, 30 mol %), Na_2CO_3 (0.2 mmol, 22 mg, 1.0 equiv) and H_2O (50 μ L) were stirred in toluene/EtOH (1:1, 2 mL) at 100 $^\circ$ C in an oil bath for 12 h under N_2 atmosphere. After completion (monitored by TLC), the reaction mixture was cooled to room temperature and passed through a short pad of celite using dichloromethane (10 mL). Evaporation of the solvent gave a residue that was purified on silica gel column chromatography using n-hexane and EtOAc as an eluent to afford **11** in 67% yield.

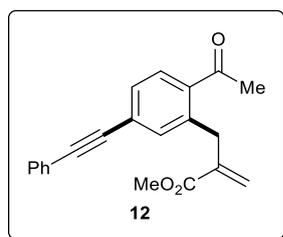


Methyl 2-(2-(2-(5-(methylacetyl)benzyl)pyren-1-yl)benzyl)acrylate 11. Analytical TLC on silica gel, 1:50 EtOAc/hexane R_f = 0.60; brown liquid; yield 67% (56 mg); 1H NMR (500 MHz, $CDCl_3$) δ 8.24-8.21 (m, 2H), 8.18 (d, J = 7.5 Hz, 1H), 8.11-8.10 (m, 3H), 8.06-8.02 (m, 2H), 7.95 (d, J = 7.5 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.60 (d, J = 7.5 Hz, 1H), 7.55 (s, 1H), 6.25 (s, 1H), 5.43 (s, 1H), 4.08 (s, 2H), 3.78 (s, 3H), 2.69 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.6, 167.5, 144.7, 140.1, 138.9, 136.8, 136.3, 134.1, 131.6, 131.2, 131.0, 129.8, 128.8, 128.5, 128.0, 127.9, 127.5, 127.4, 126.3, 126.2, 125.5, 125.2, 125.1, 125.0, 124.9, 124.8, 52.1, 35.9, 29.8; FT-IR (neat) 2924, 1718, 1683, 1602, 1435, 1251, 1198, 1147, 959 cm^{-1} ; HRMS (ESI-TOF) m/z : $[M+H]^+$ calcd for $C_{29}H_{23}O_3$ 419.1642; Found 419.1642.

Synthesis of 12.



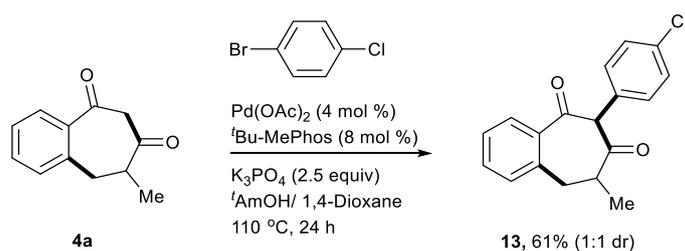
Compound **3b** (0.2 mmol, 40 mg, 1.0 equiv), phenylacetylene (0.6 mmol, 61.3 mg, 3.0 equiv), $Pd(PPh_3)_2Cl_2$ (0.02 mmol, 14 mg, 10 mol %), CuBr (0.01 mmol, 1.4 mg, 5 mol %) and DIPEA (0.6 mmol, 77.6 mg, 3.0 equiv) were stirred in DMF (1 mL, 0.2 M) at 80 °C for 4 h under N_2 atmosphere. After completion (monitored by TLC), the reaction mixture was cooled to room temperature and diluted with EtOAc (10 mL). The organic phase was washed with brine (1 x 10 mL) and ice-cold water (2 x 10 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using n-hexane and EtOAc as an eluent to afford **12** in 74% yield.



Methyl 2-(2-(phenylethynyl)-5-(methylacetyl)phenyl)acrylate **12**.

Analytical TLC on silica gel, 1:50 EtOAc/hexane $R_f = 0.52$; brown liquid; yield 74% (47 mg); 1H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, $J = 8.0$ Hz, 1H), 7.55-7.53 (m, 2H), 7.48-7.46 (m, 1H), 7.42-7.41 (m, 1H), 7.37-7.35 (m, 3H), 6.23-6.22 (m, 1H), 5.31-5.30 (m, 1H), 3.92 (s, 2H), 3.76 (s, 3H), 2.57 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.0, 167.4, 139.8, 138.9, 137.5, 134.8, 131.9, 129.7, 129.5, 128.9, 128.6, 126.8, 126.3, 122.8, 92.0, 88.6, 52.1, 35.5, 29.7; FT-IR (neat) 2951, 2210, 1719, 1685, 1603, 1437, 1251, 1121, 1038 cm^{-1} ; HRMS (ESI-TOF) m/z : $[M+H]^+$ calcd for $C_{21}H_{19}O_3$ 319.1329; Found 319.1331.

Synthesis of 13.³



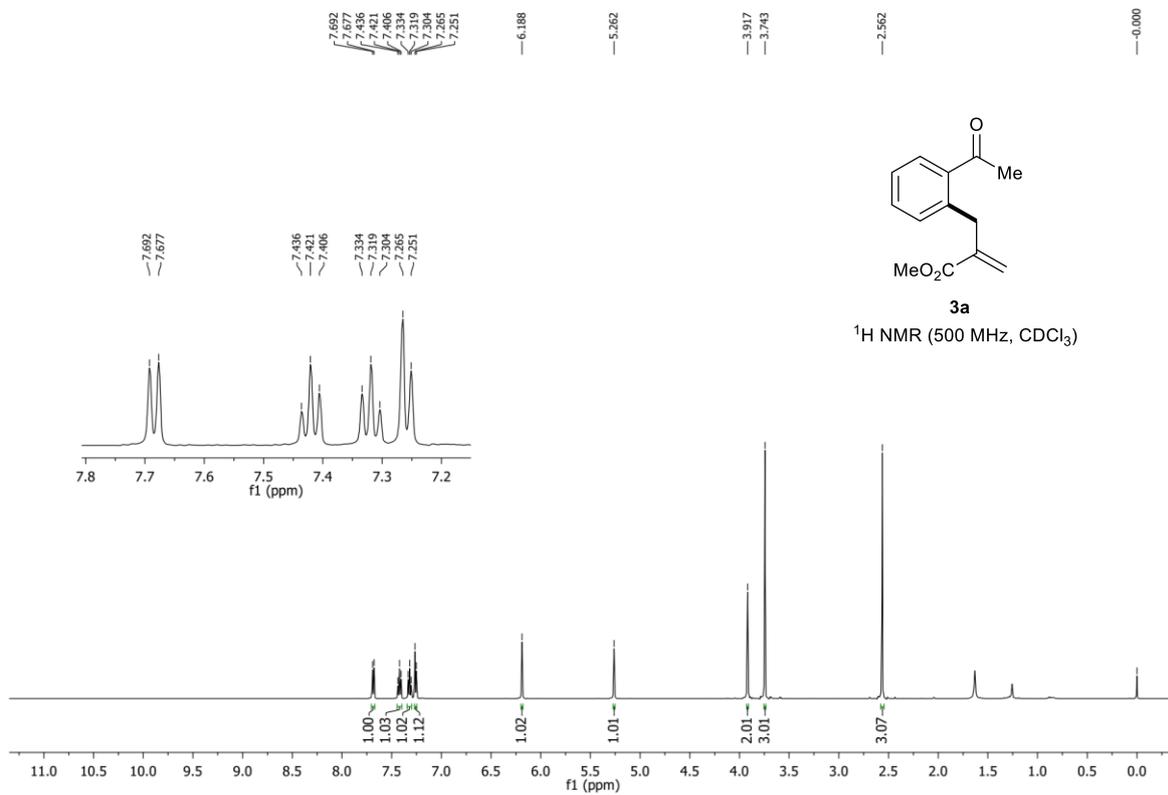
To a stirred solution of 8-methyl-8,9-dihydro-5*H*-benzo[7]annulene-5,7(6*H*)-dione **4a** (0.13 mmol, 25 mg, 1.0 equiv) and 1-bromo-4-chlorobenzene (0.16 mmol, 30 mg, 1.2 equiv) in *t*-AmOH/1,4-dioxane (0.5 mL (2:3)), K₃PO₄ (0.33 mmol, 70 mg, 2.5 equiv), *t*Bu-MePhos (0.008 mmol, 4 mg, 8 mol %) and Pd(OAc)₂ (0.004 mmol, 2 mg, 4 mol %) were added under N₂ atmosphere. The resulting mixture was stirred at 110 °C for 24 h. After completion (monitored by TLC), the reaction mixture was quenched with 10% HCl (5 mL) and was extracted with ethyl acetate (3 x 10 mL). Drying (Na₂SO₄) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using n-hexane and EtOAc as an eluent to afford **13** in 61% yield (23.7 mg). Analytical TLC on silica gel, 1:5 EtOAc/hexane R_f = 0.45; yellow liquid; a 1:1 mixture of diastereomers; ¹H NMR (500 MHz, CDCl₃) δ 7.93 (d, *J* = 7.5 Hz, 2H), 7.54-7.50 (m, 2H), 7.41-7.35 (m, 6H), 7.32-7.28 (m, 2H), 7.25-7.23 (m, 4H), 5.66 (s, 1H), 5.61 (s, 1H), 4.05-4.01 (m, 1H), 3.55-3.50 (m, 1H), 3.16-3.08 (m, 2H), 3.02-2.98 (m, 1H), 2.88-2.81 (m, 1H), 1.32 (d, *J* = 7.5 Hz, 3H), 1.13 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 205.1, 204.6, 193.1, 192.9, 140.5, 138.9, 136.7, 136.6, 134.02, 133.98, 133.9, 133.7, 132.3, 132.2, 132.0, 131.8, 131.4, 131.1, 130.7, 130.6, 128.51, 128.46, 128.0, 127.9, 70.6, 69.0, 47.2, 46.4, 39.1, 37.6, 17.6, 14.6; FT-IR (neat) 2957, 2920, 1722, 1681, 1597, 1493, 1460, 1298, 1213, 1016 cm⁻¹; HRMS (ESI-TOF) *m/z*: [M+H]⁺ calcd for C₁₈H₁₆ClO₂ 299.0833; Found 299.0833.

References

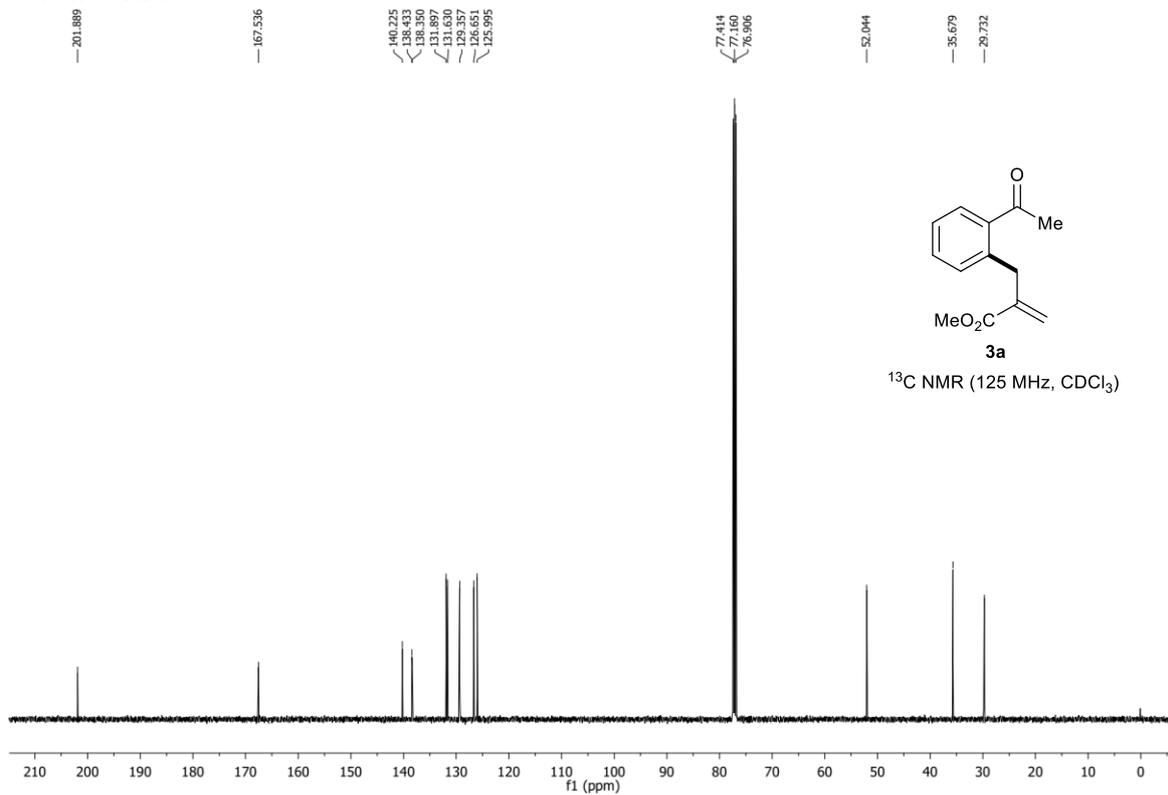
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2. Y. Liu, Y. Mao, Y. Hu, J. Gui, L. Wang, W. Wang and S. Zhang, *Adv. Synth. Catal.*, 2019, **361**, 1554.
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NMR (¹H, ¹³C, ¹⁹F, COSY, NOESY, HSQC and HMBC) Spectra

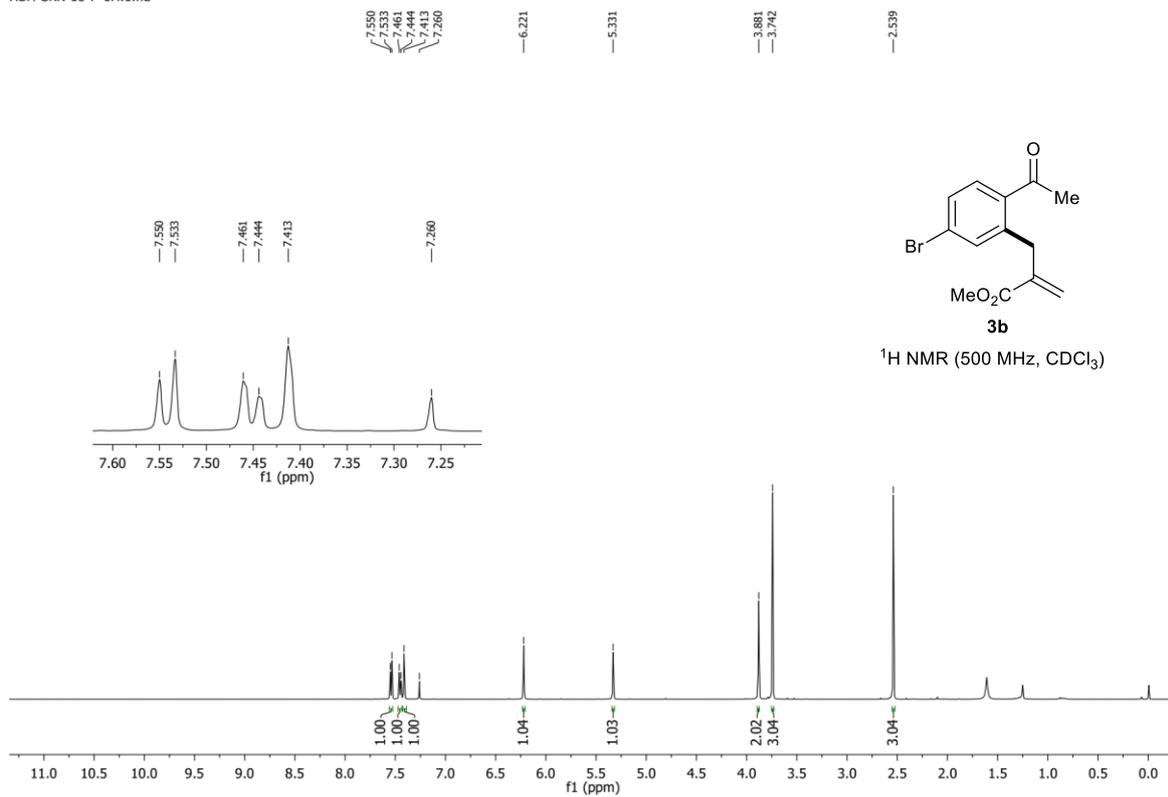
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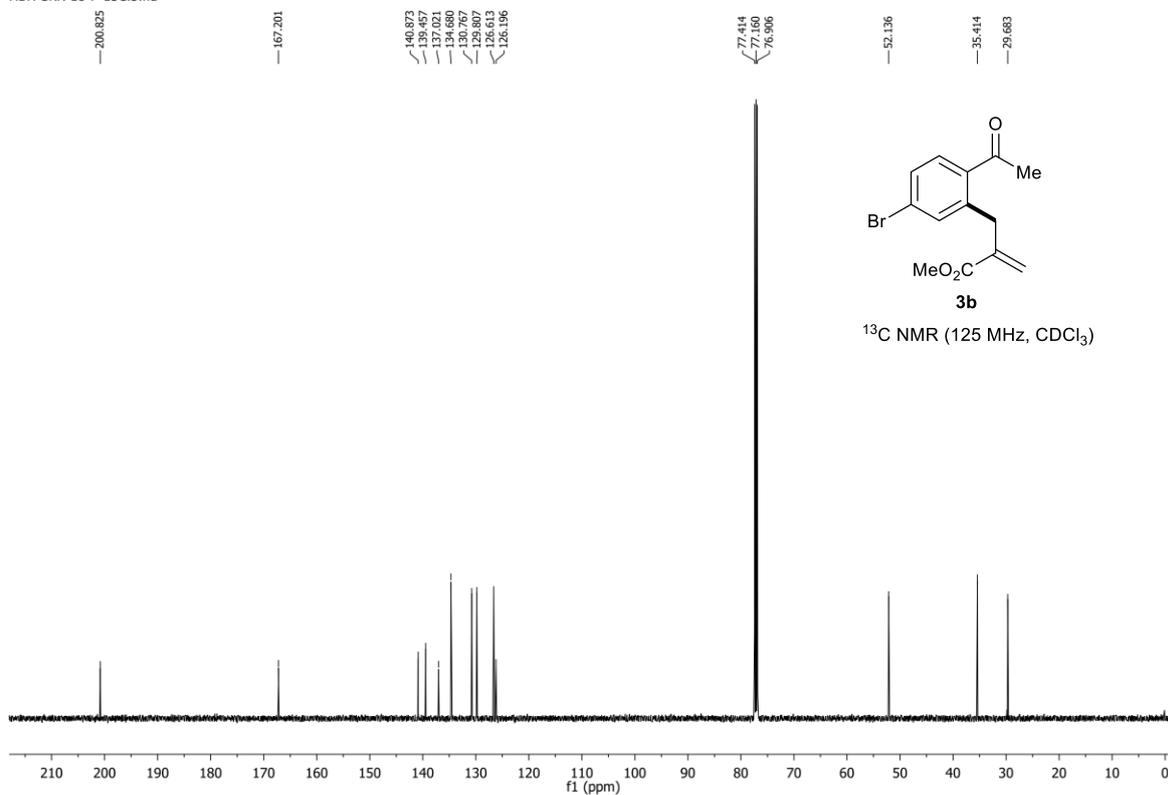
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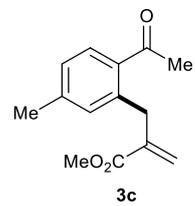
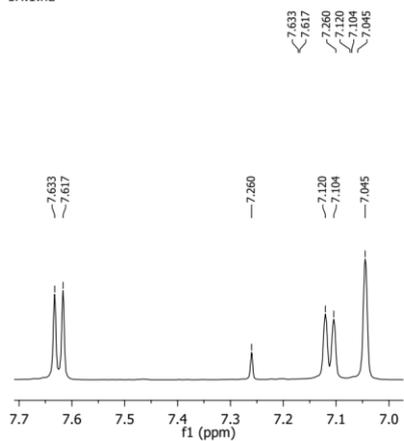
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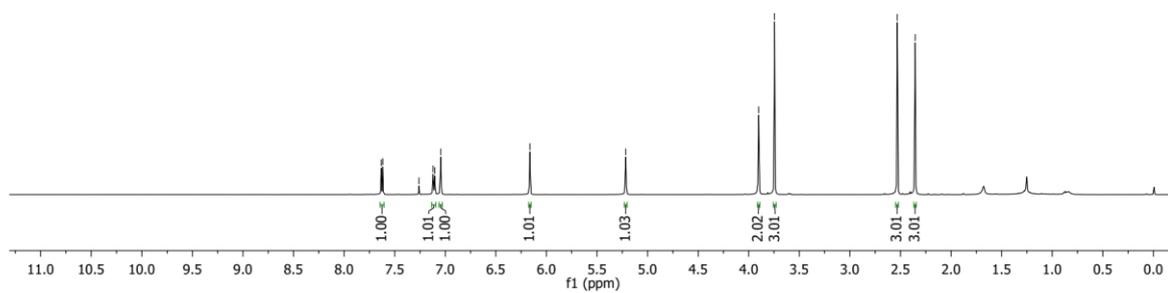
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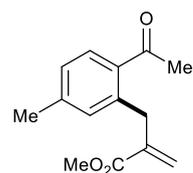
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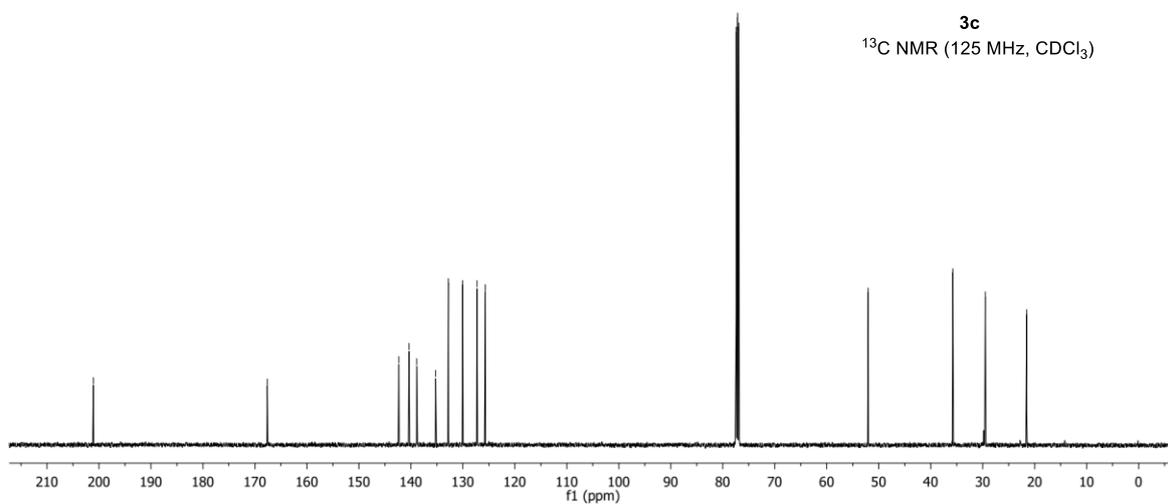
¹H NMR (500 MHz, CDCl₃)



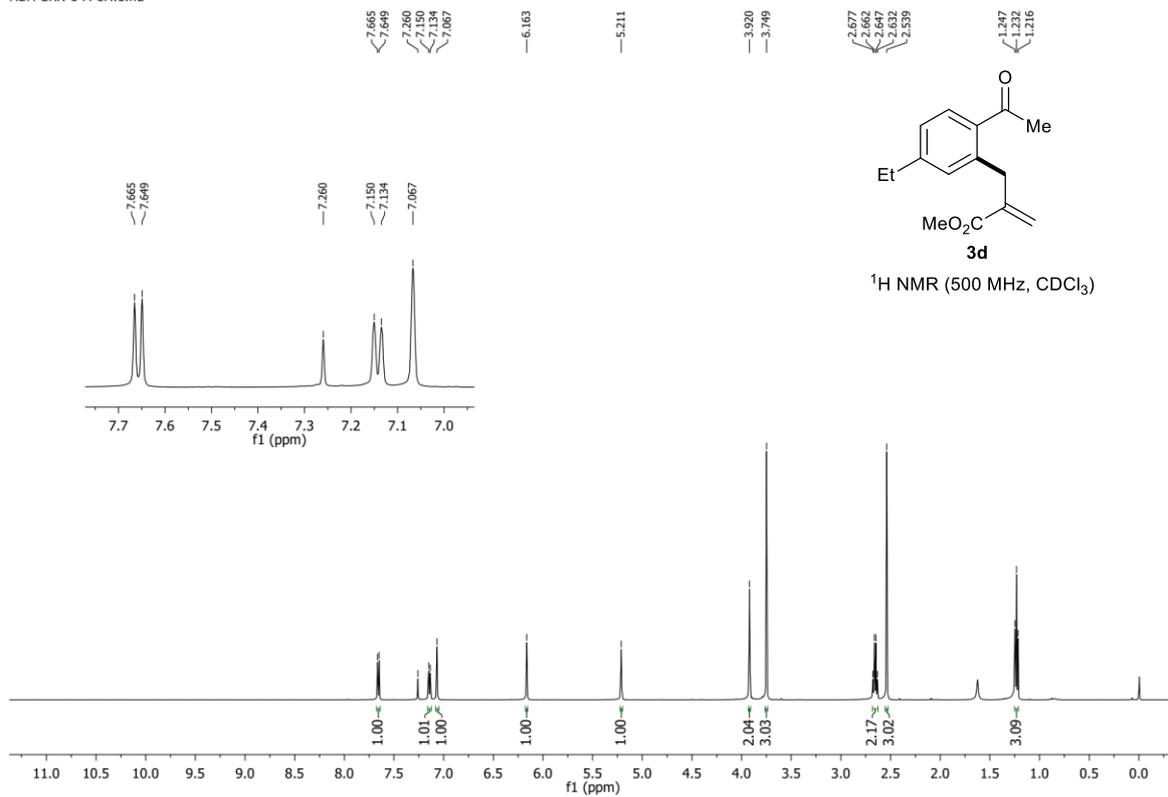
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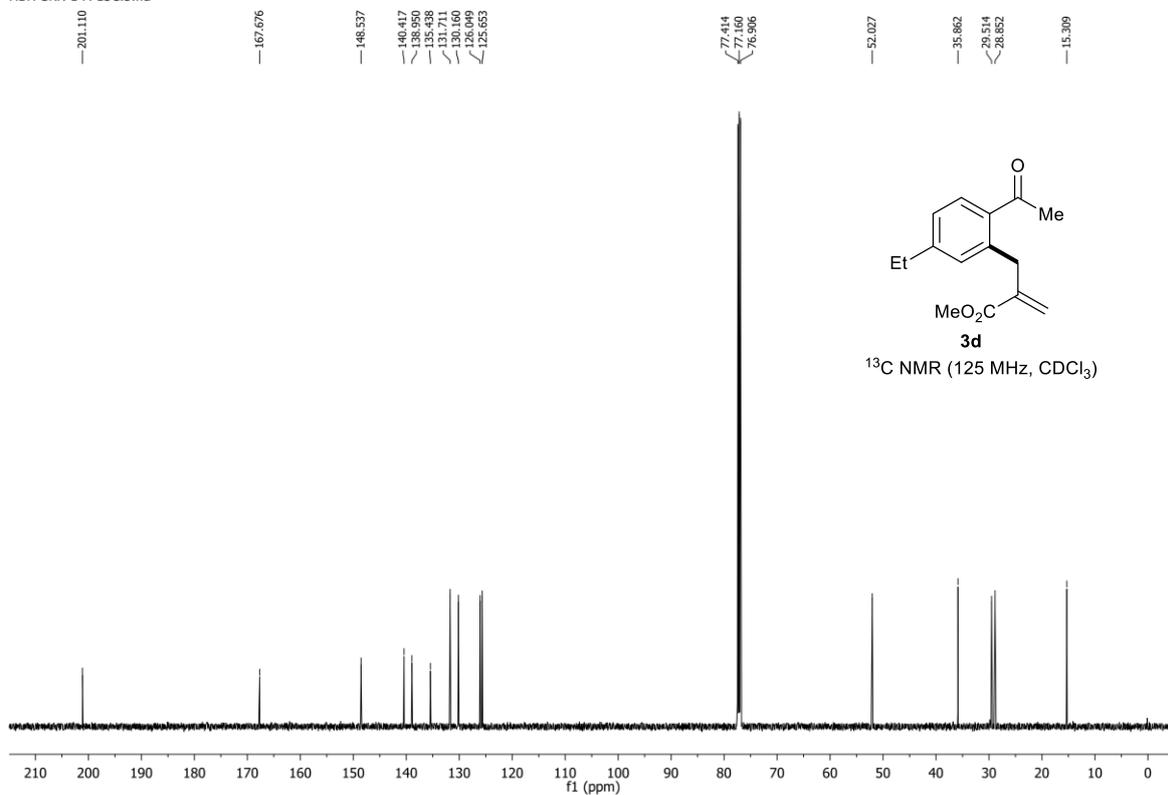
¹³C NMR (125 MHz, CDCl₃)



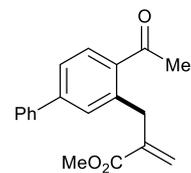
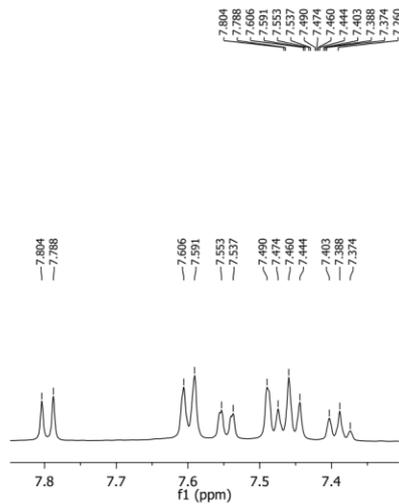
HBH-SKK-1-A-1H.1.fid



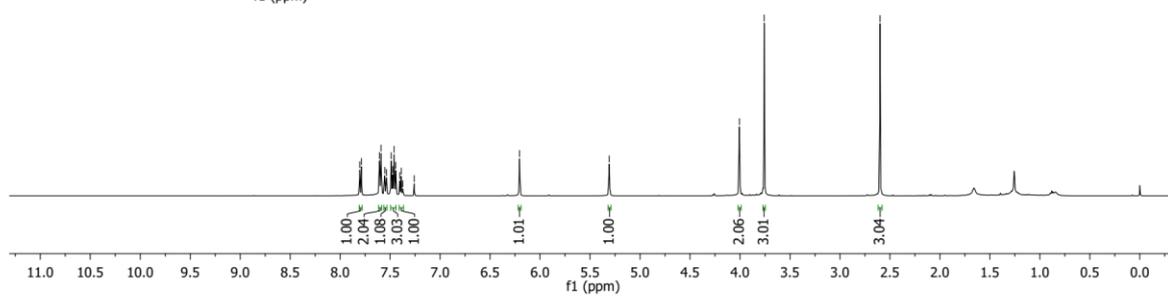
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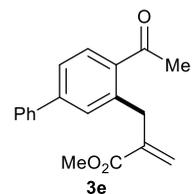
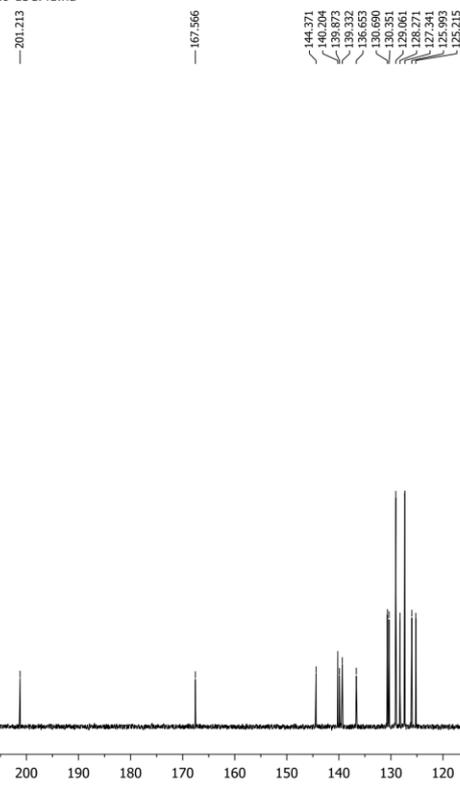
HBH-SKK-26-1H.39.fid



3e
¹H NMR (500 MHz, CDCl₃)

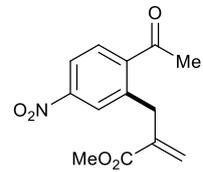
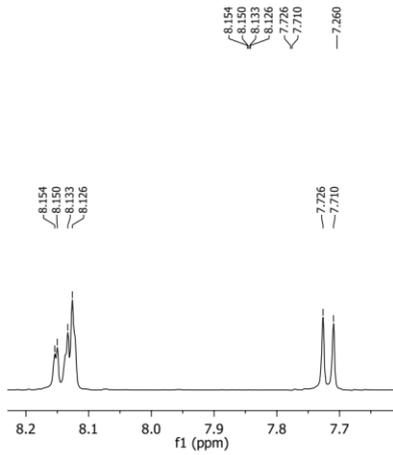


HBH-SKK-26-13C.41.fid

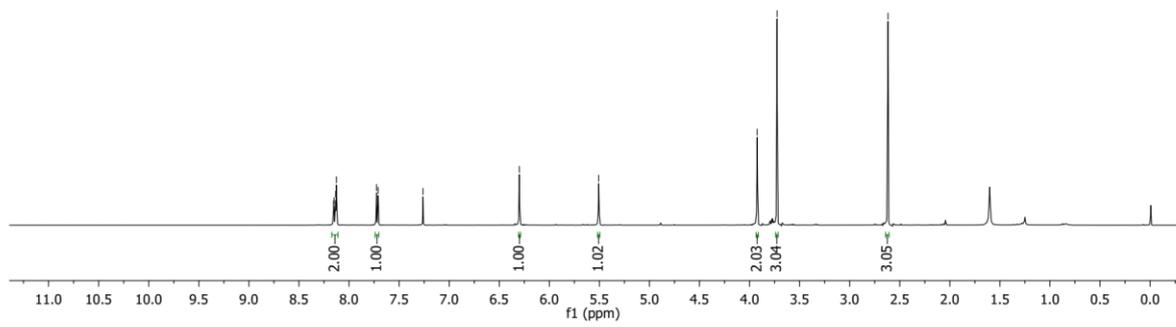


3e
¹³C NMR (125 MHz, CDCl₃)

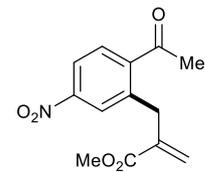
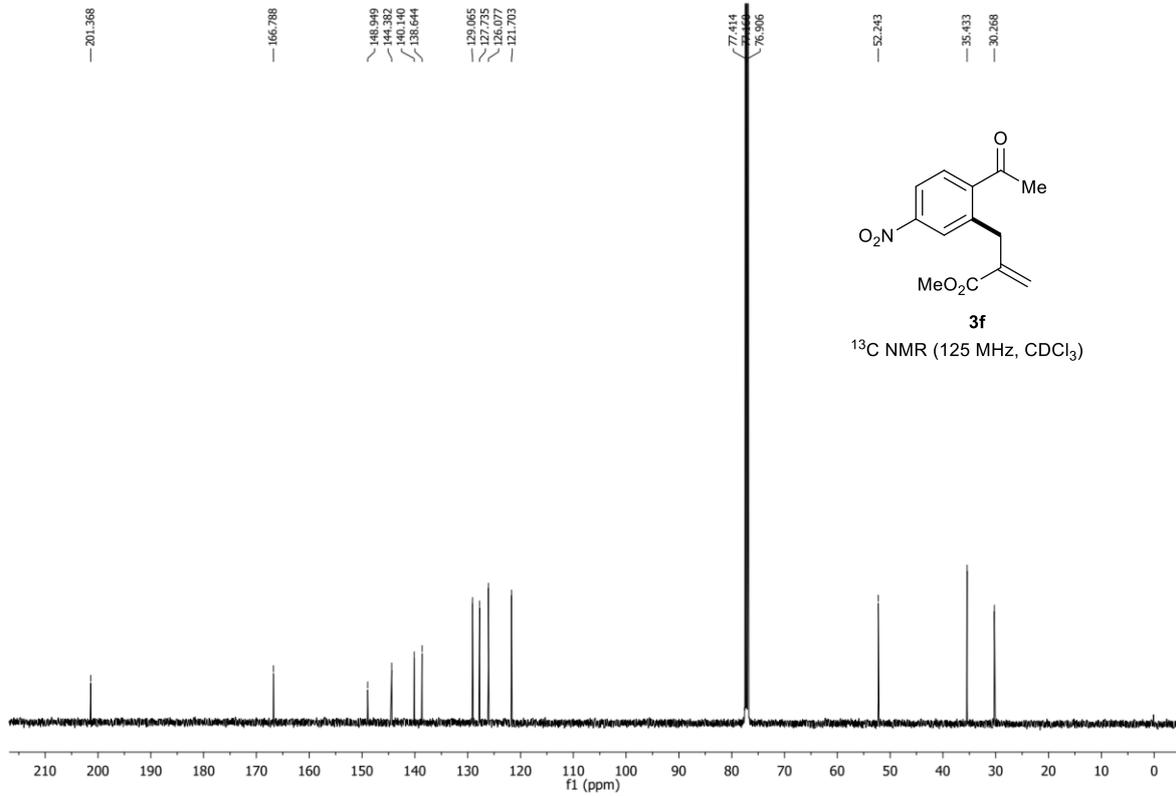
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3f
¹H NMR (500 MHz, CDCl₃)

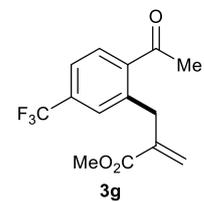
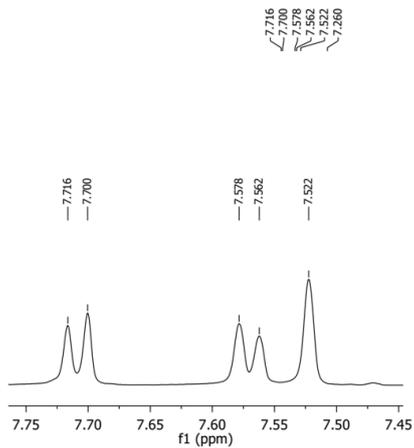


HBH-SKK-30-P-13C.3.fid

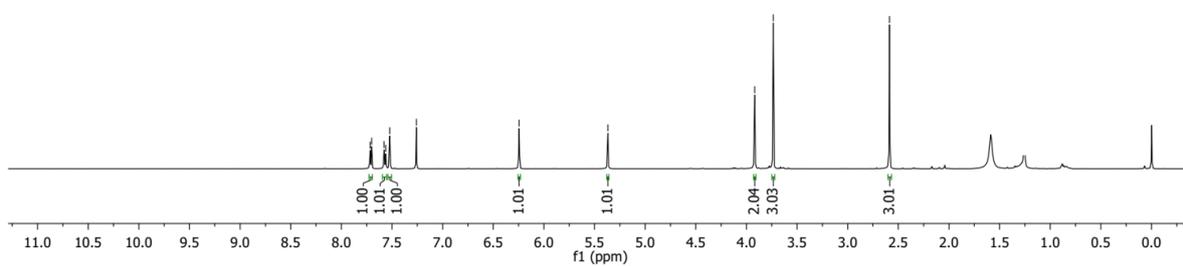


3f
¹³C NMR (125 MHz, CDCl₃)

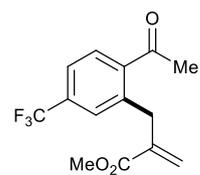
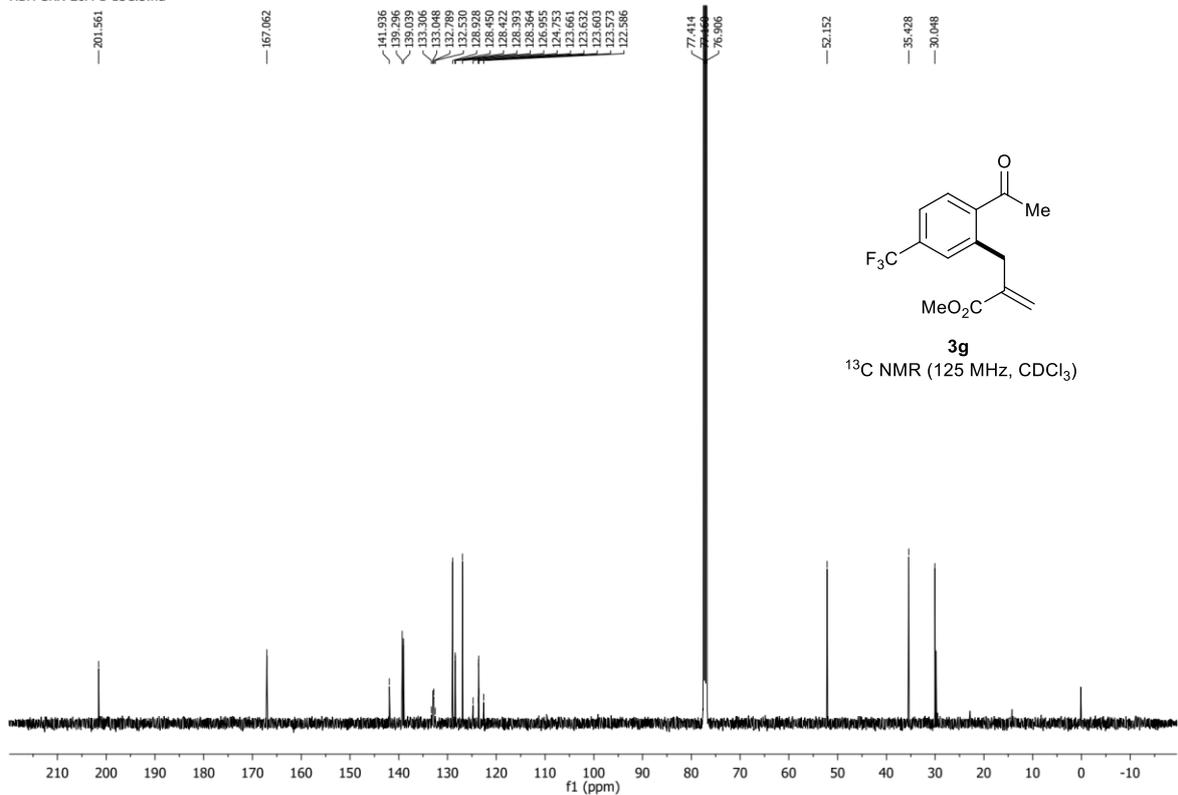
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¹H NMR (500 MHz, CDCl₃)

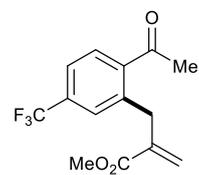


HBH-SKK-20A-1-13C.3.fid



¹³C NMR (125 MHz, CDCl₃)

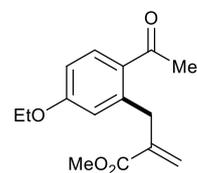
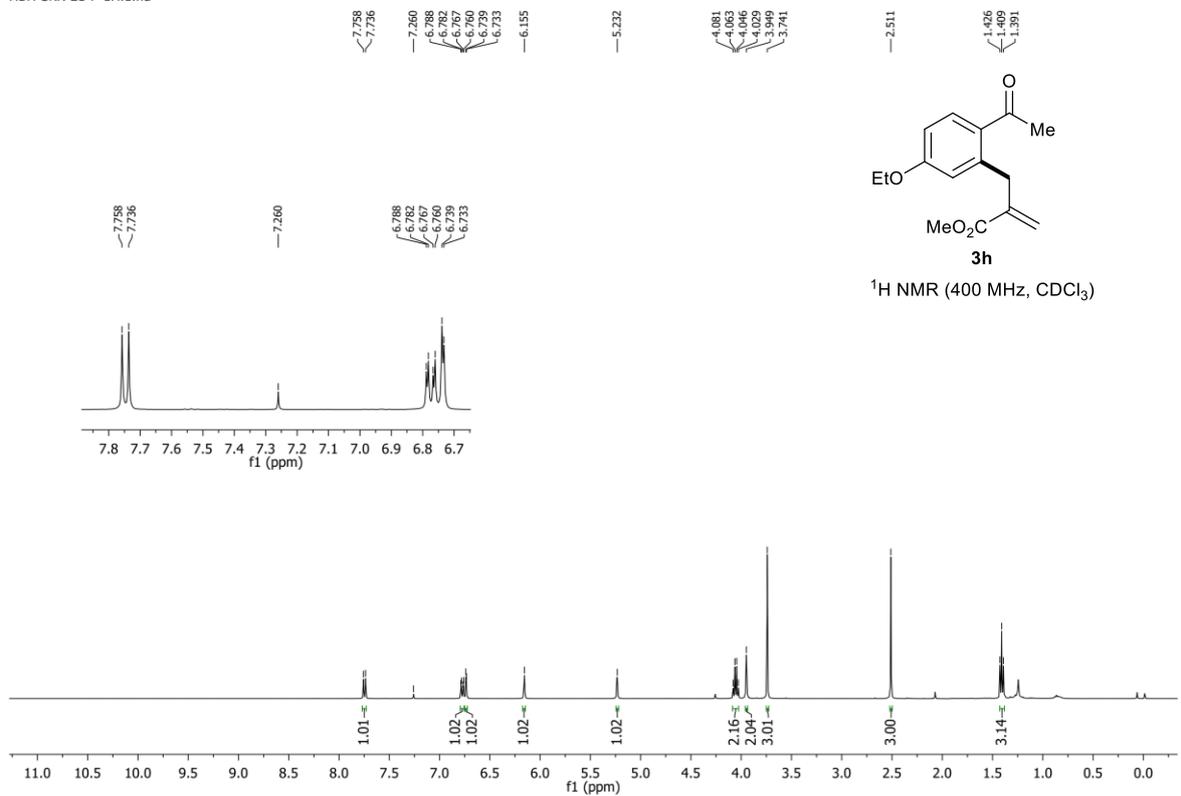
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3g

¹⁹F NMR (470 MHz, CDCl₃)

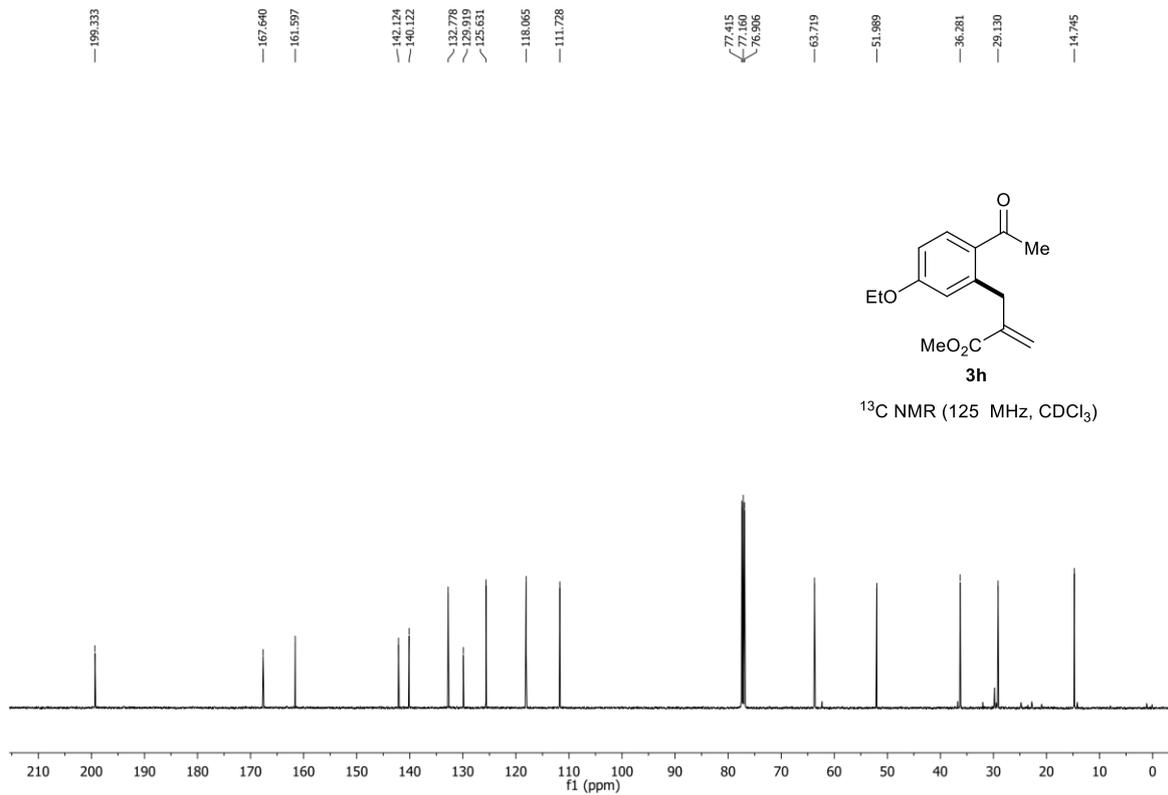
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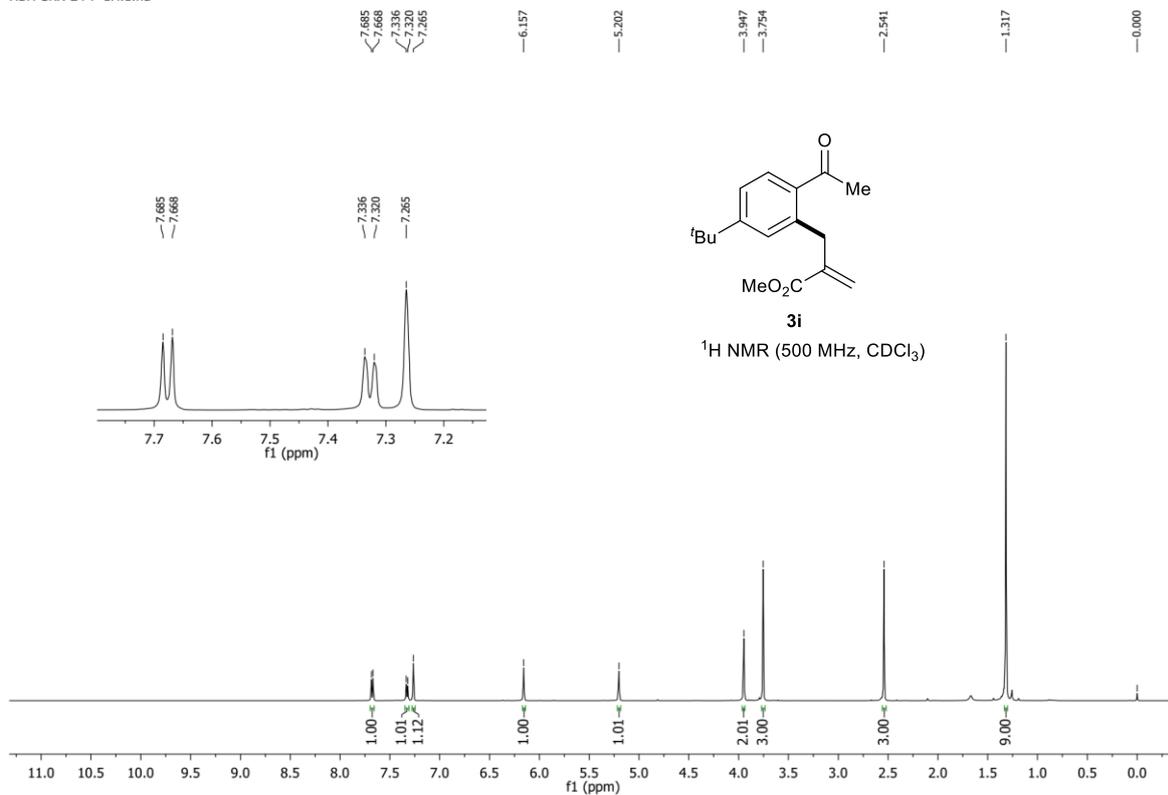
3h

¹H NMR (400 MHz, CDCl₃)

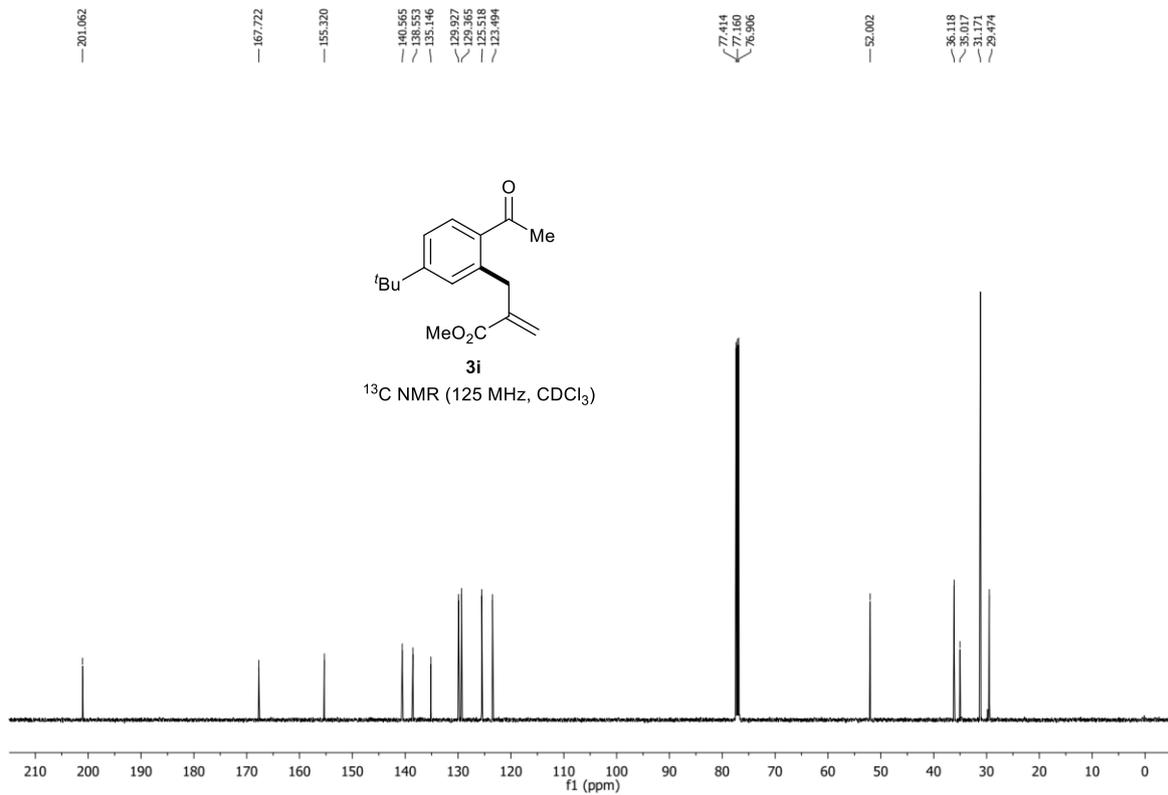
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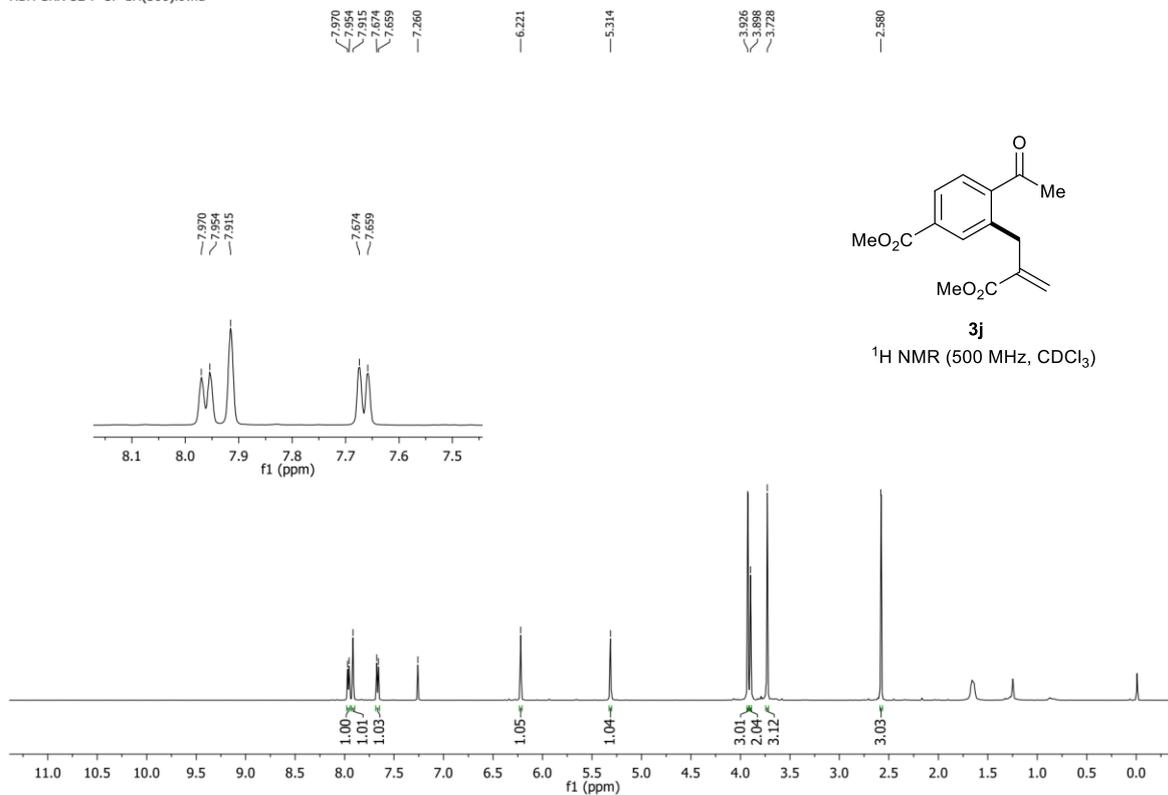
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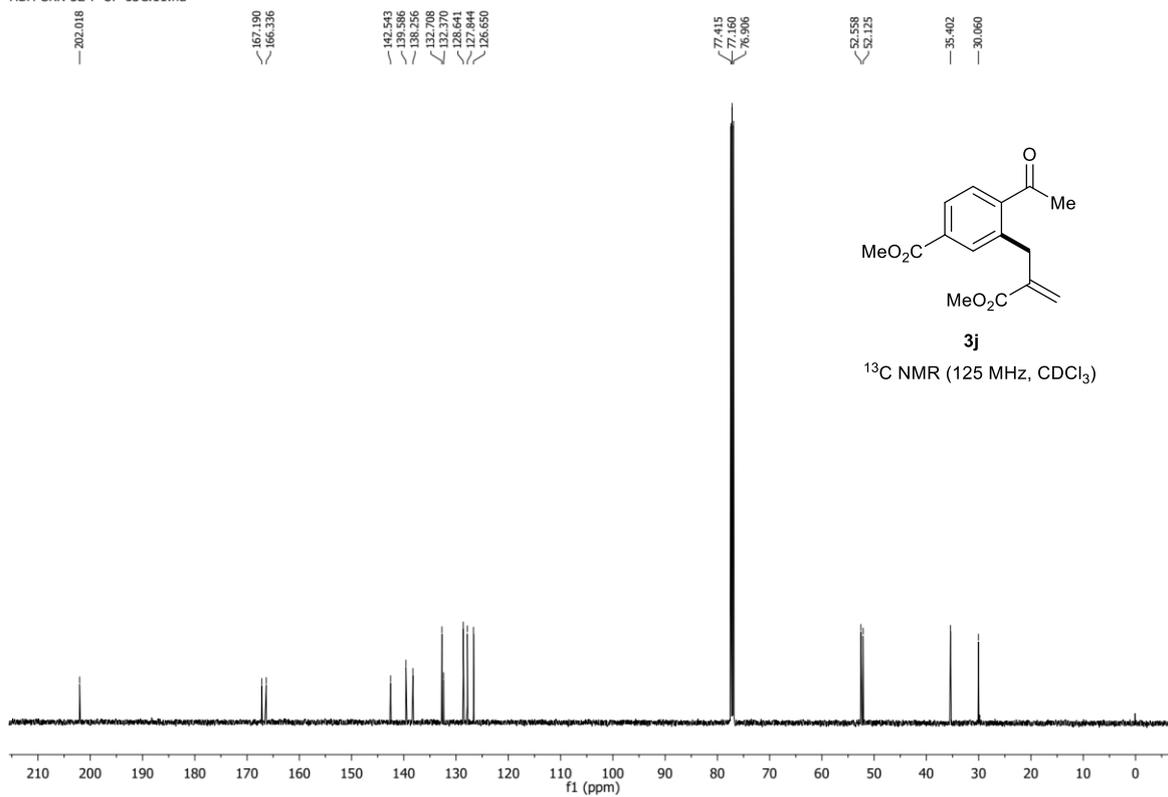
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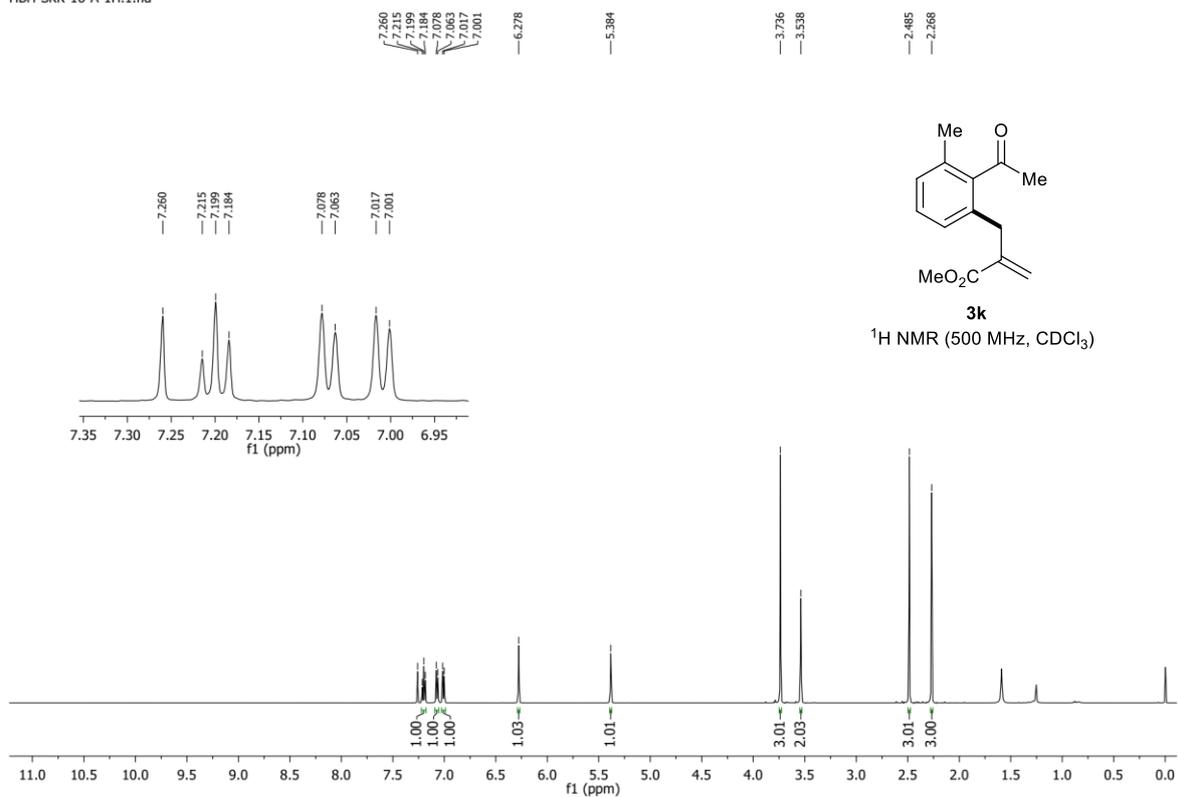
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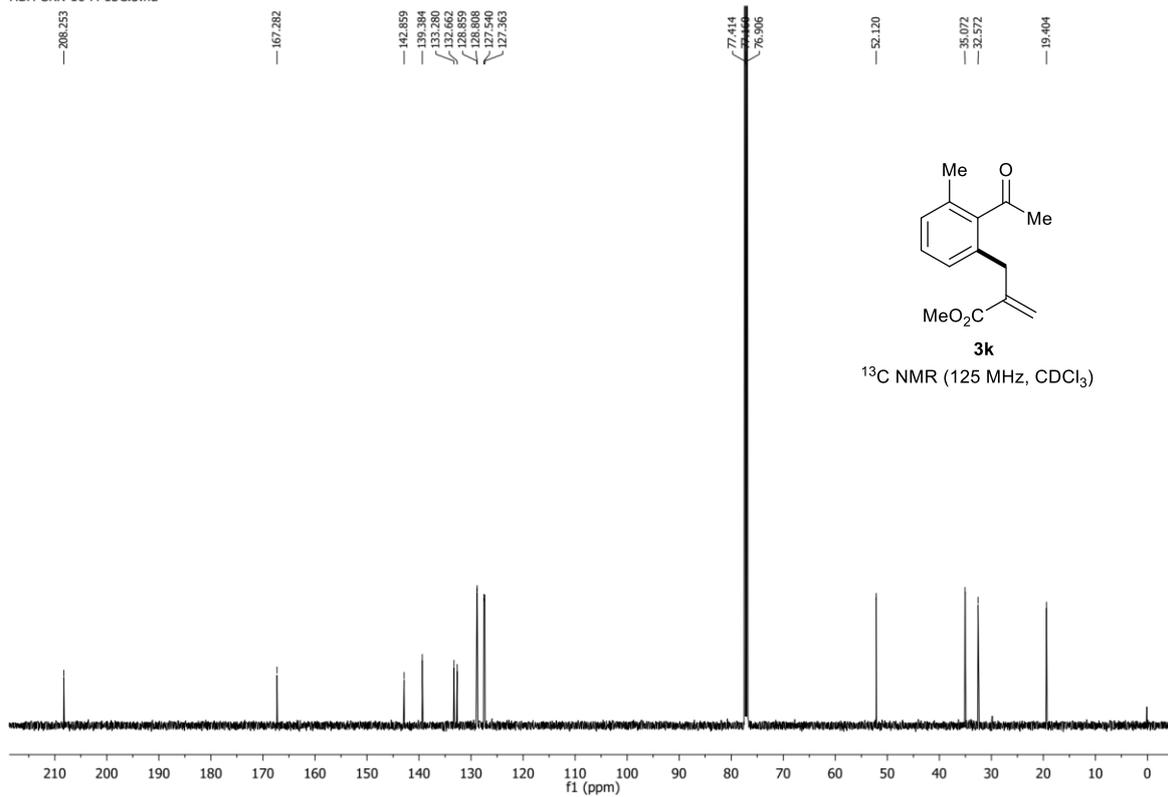
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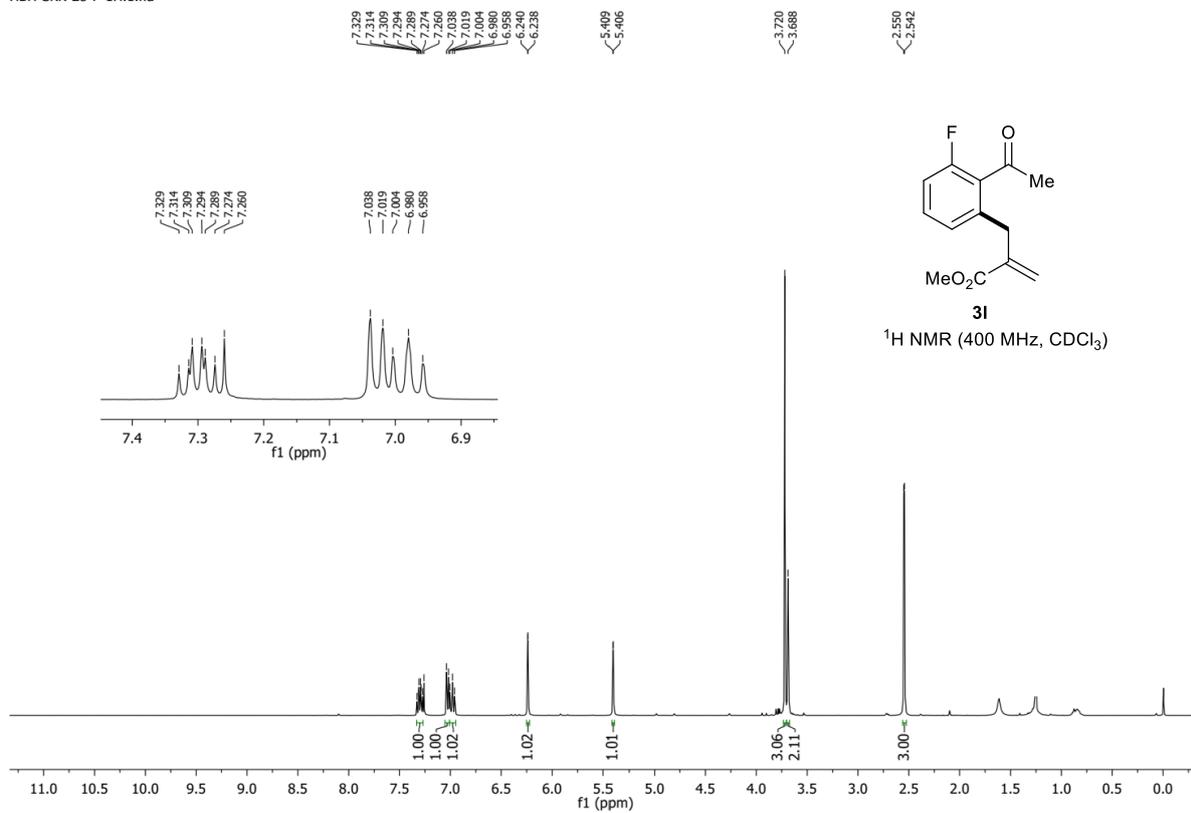
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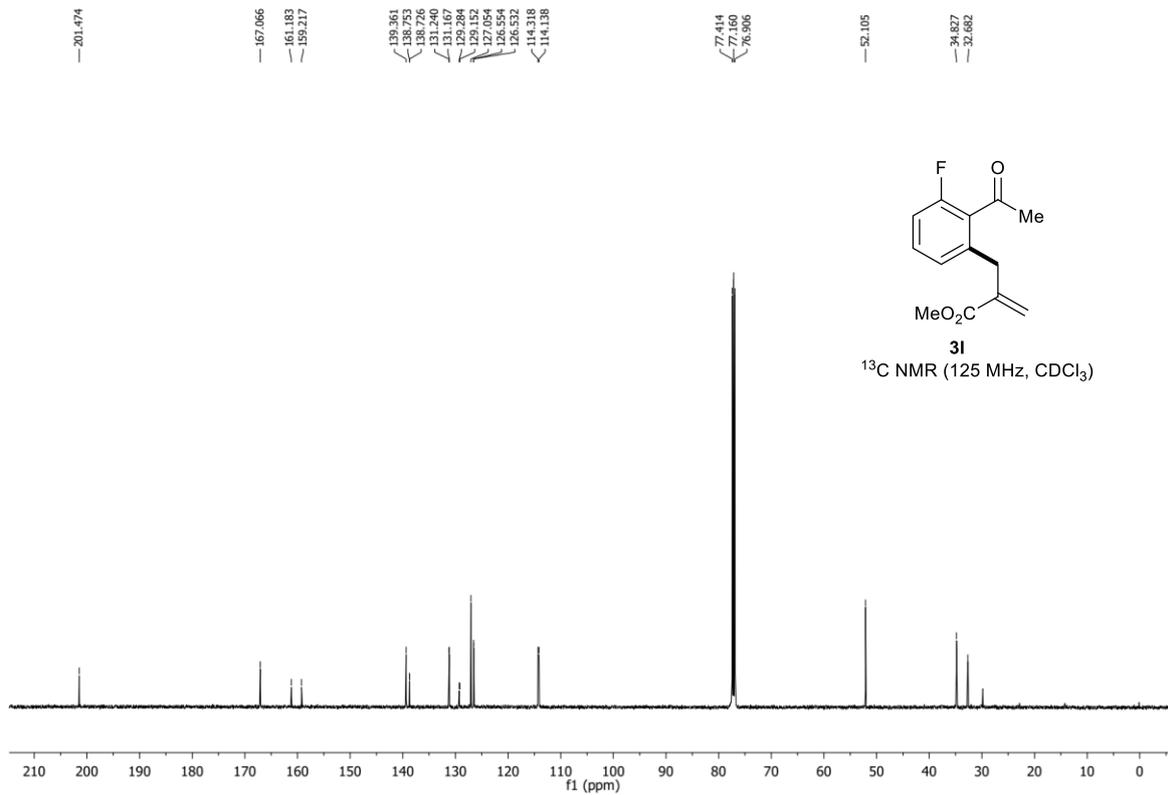
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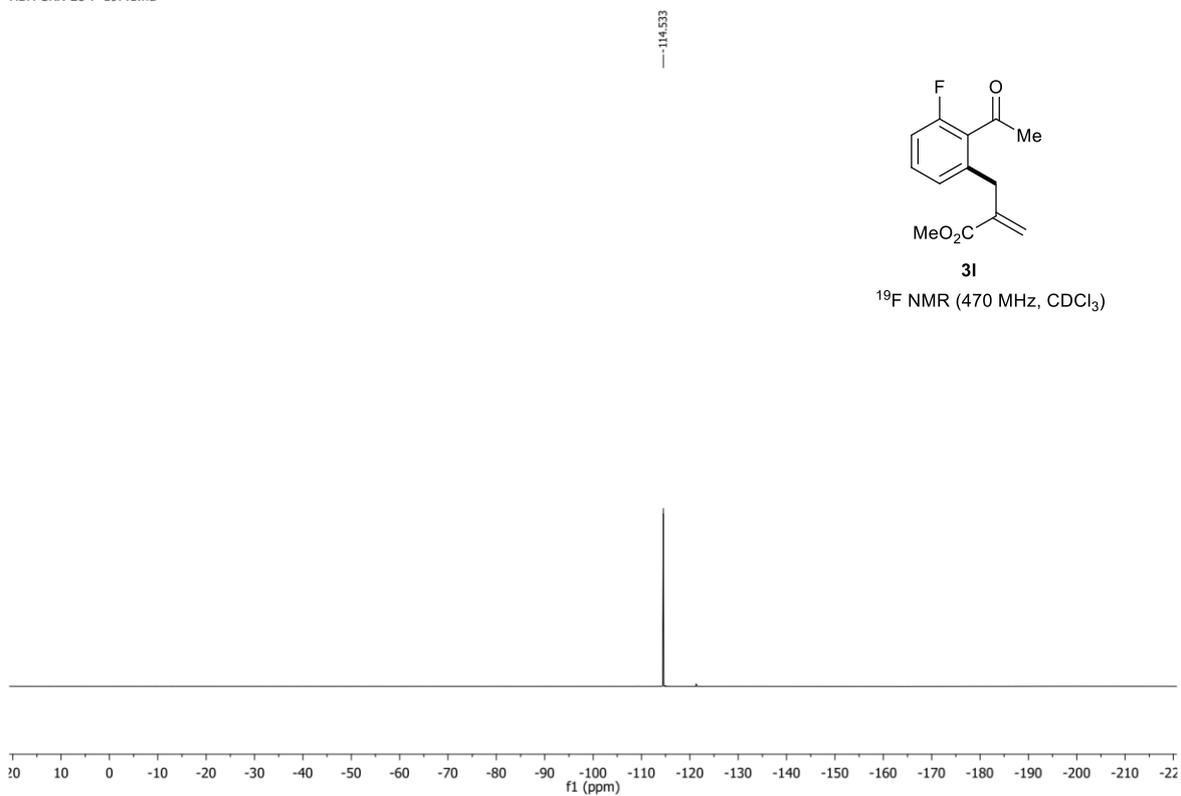
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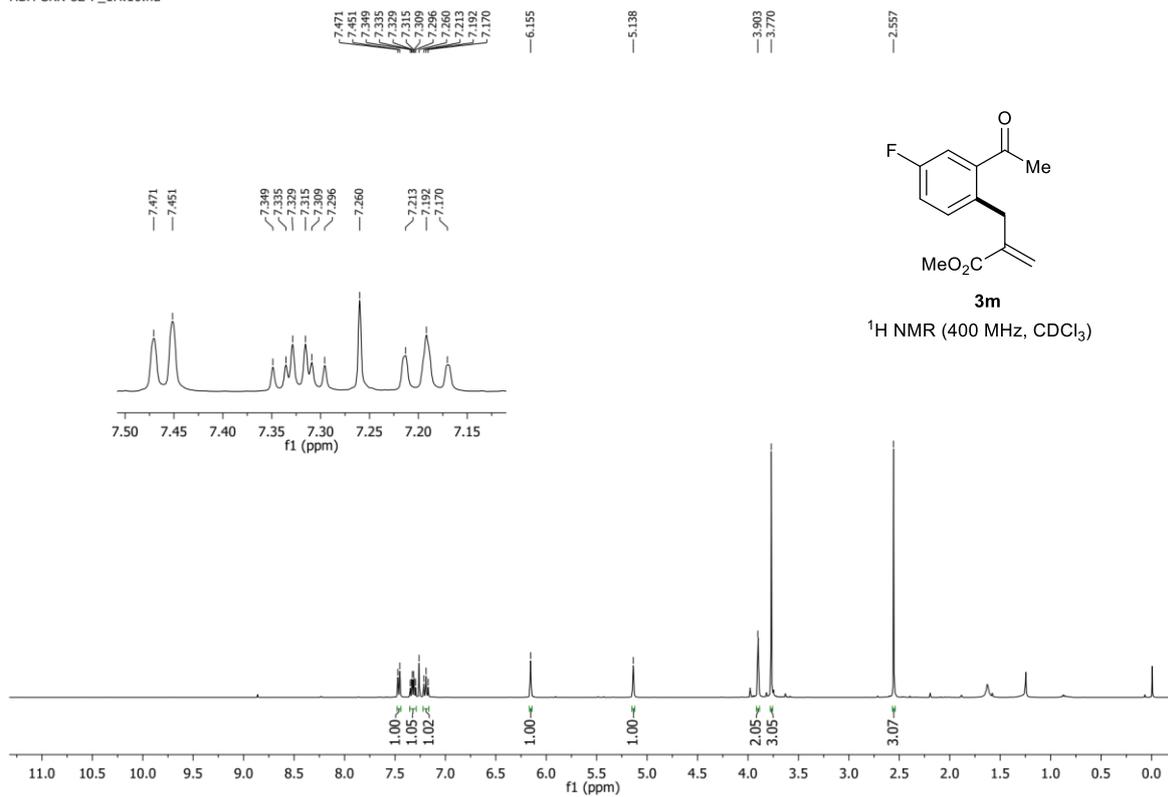
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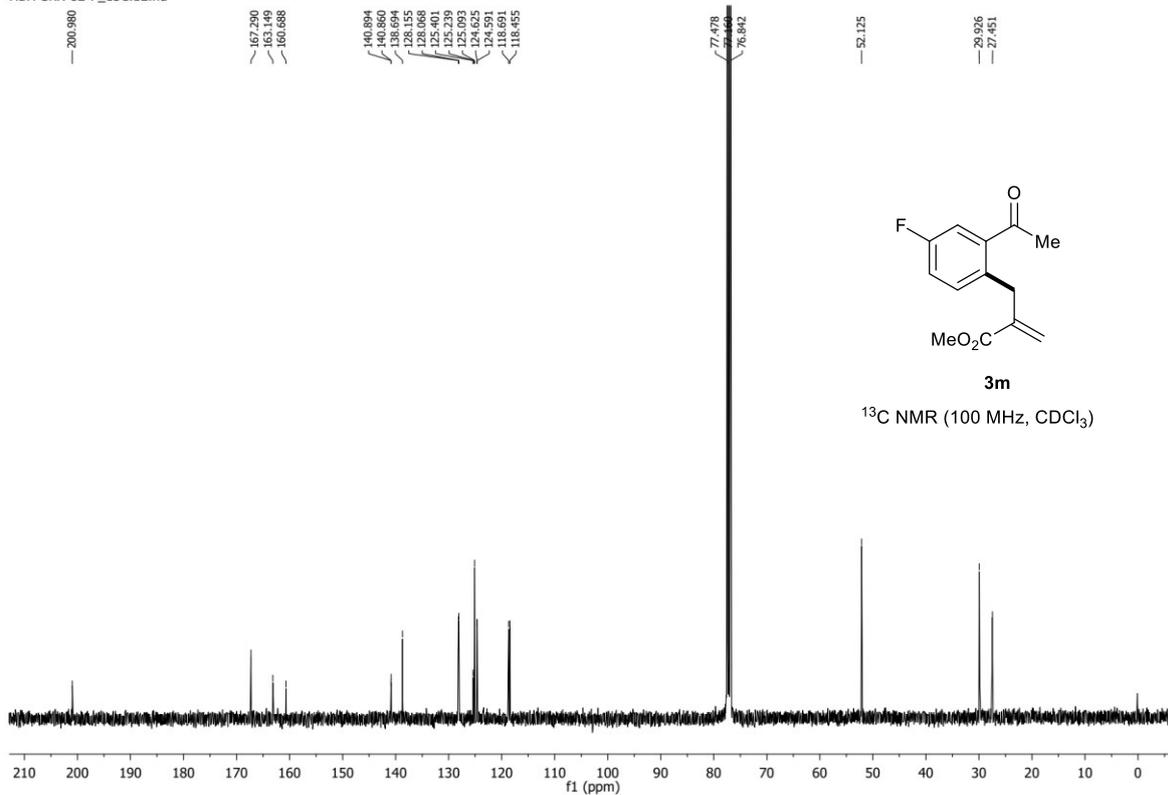
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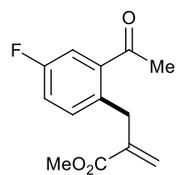
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HBH-SKK-82-P_13C.12.fid

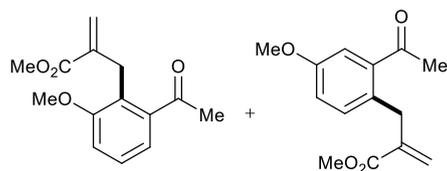
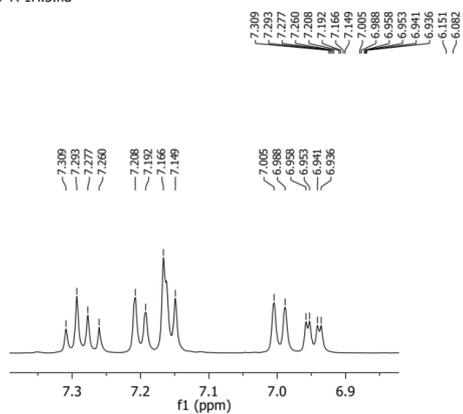
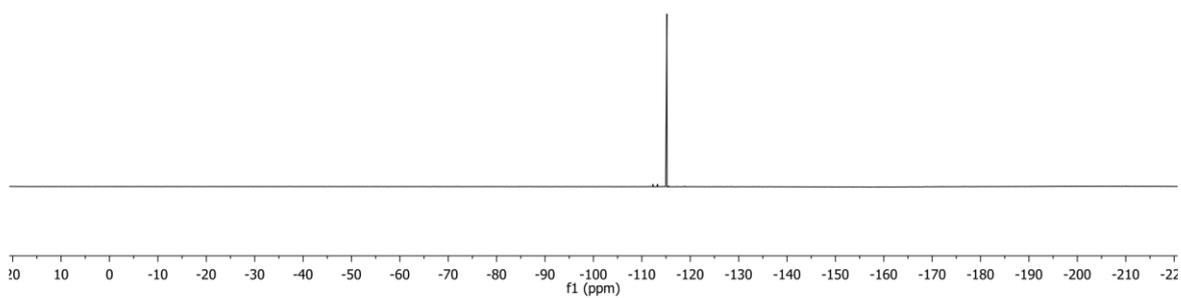


-115.177



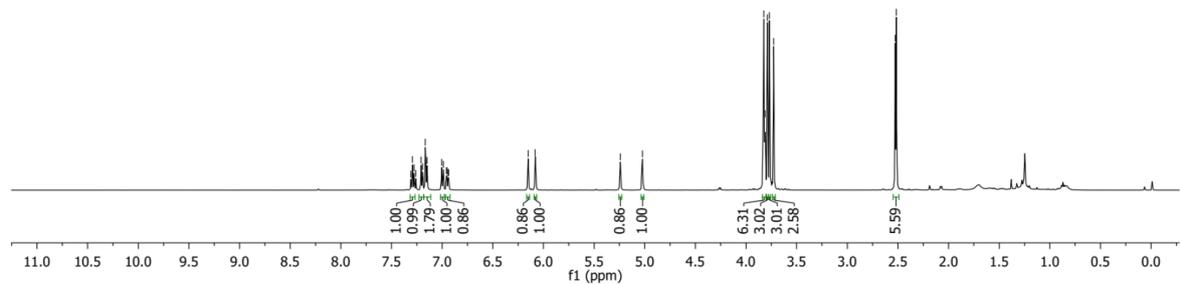
3m

¹⁹F NMR (376 MHz, CDCl₃)

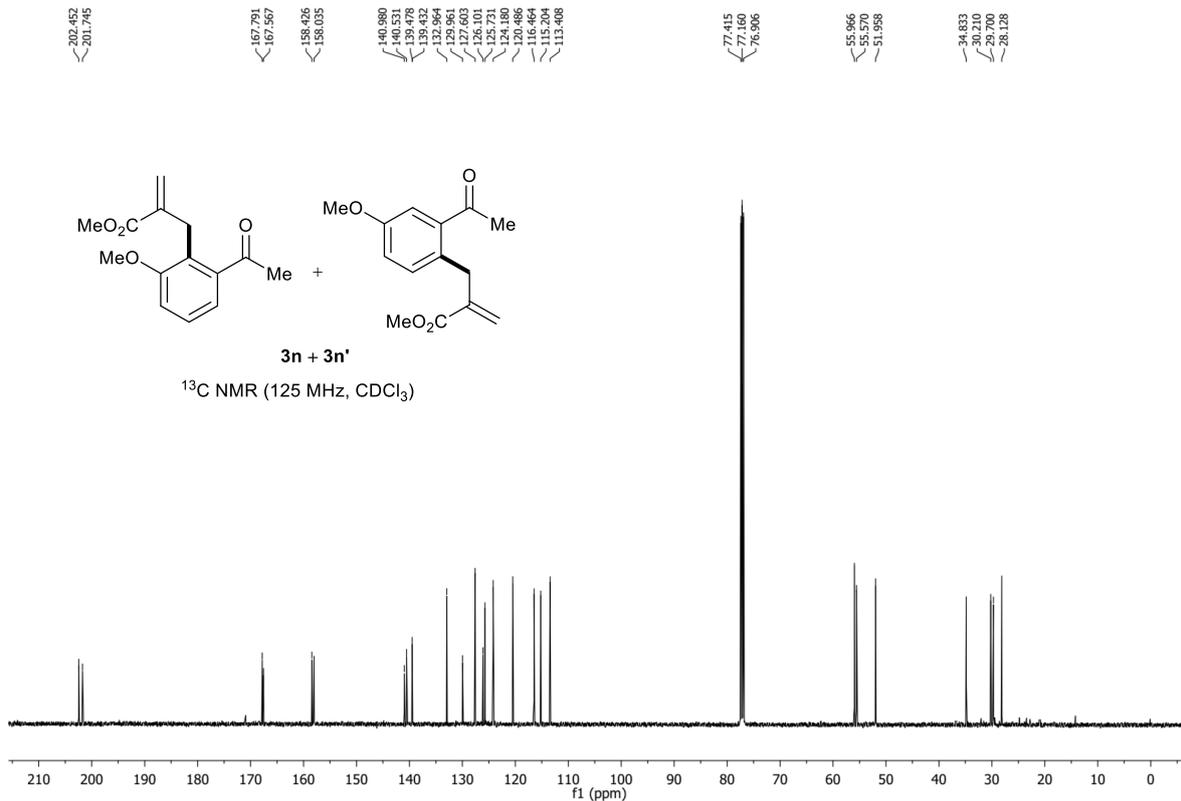


3n + 3n'

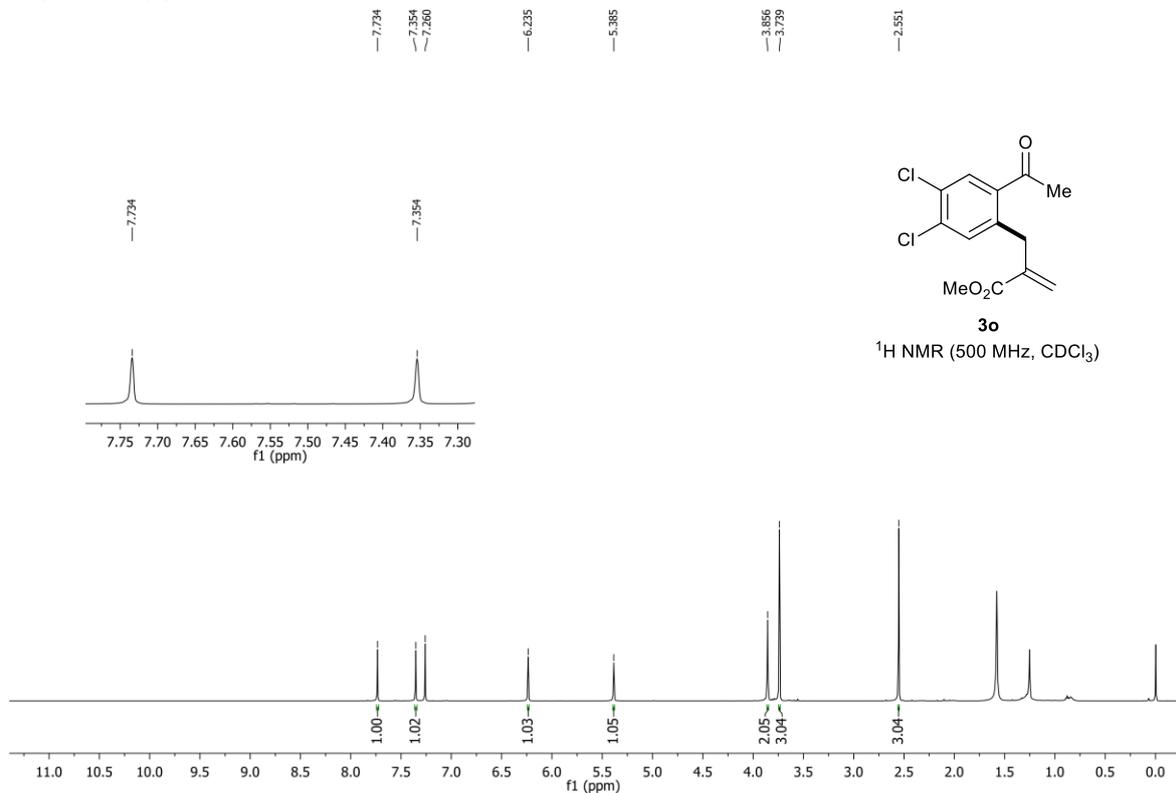
¹H NMR (500 MHz, CDCl₃)



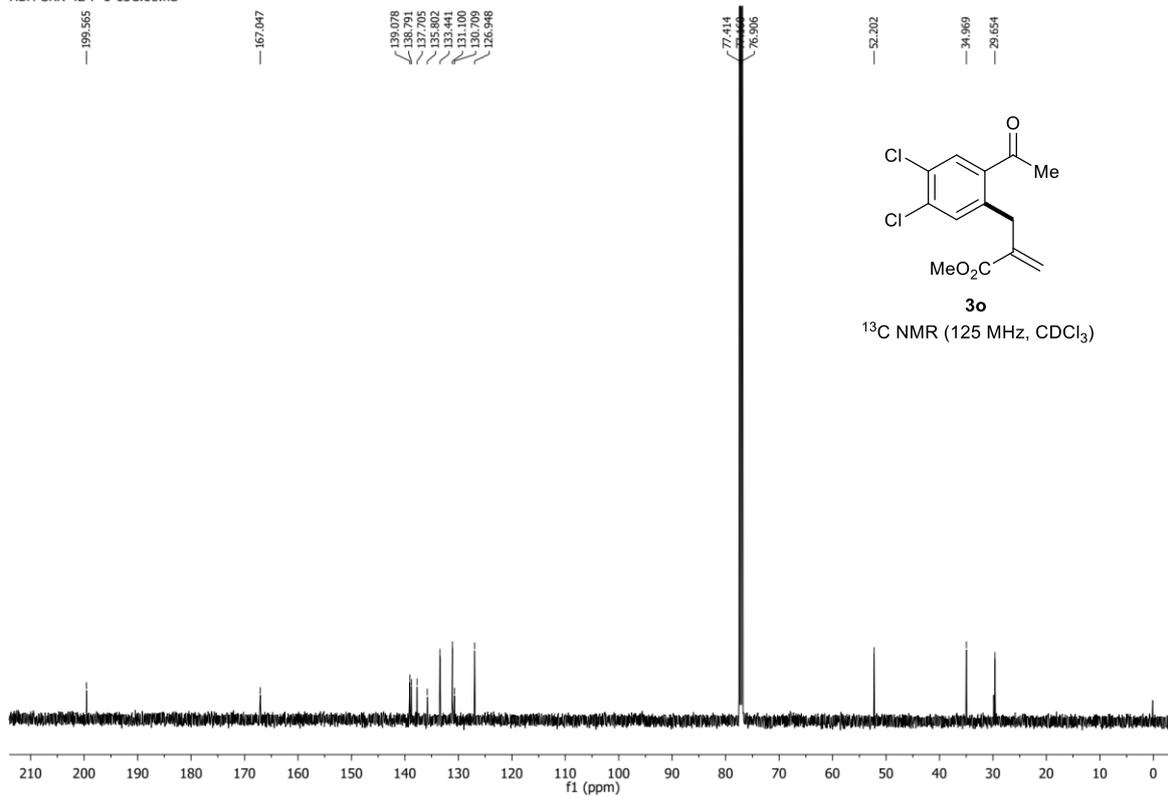
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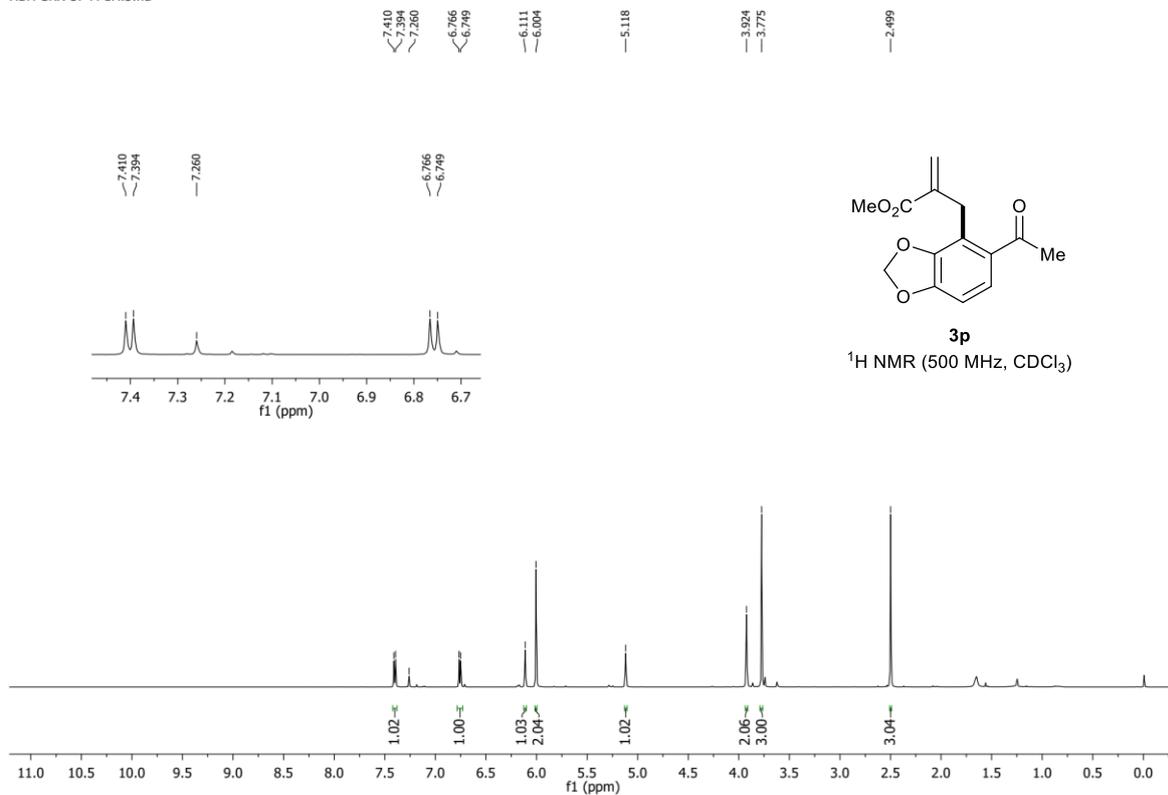
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HBH-SKK-42-P-1-13C.18.fid

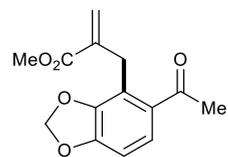


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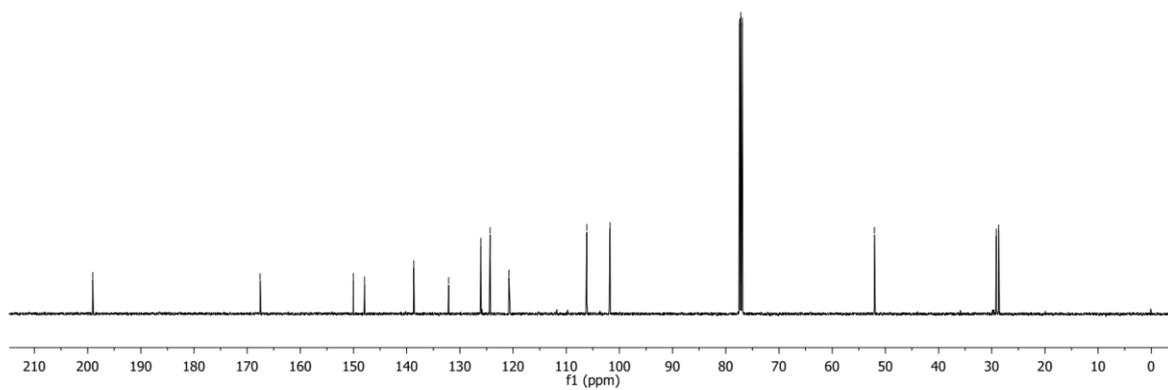
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199.011
167.554
150.050
147.930
138.679
132.110
126.078
124.318
120.774
106.137
101.772
77.414
77.160
76.966
52.051
29.141
28.709



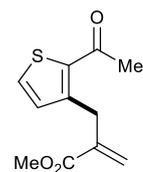
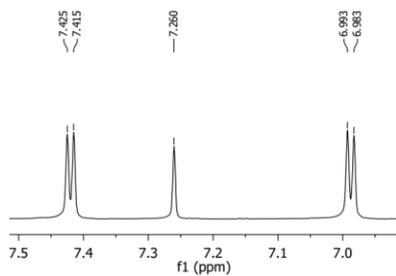
3p

¹³C NMR (125 MHz, CDCl₃)



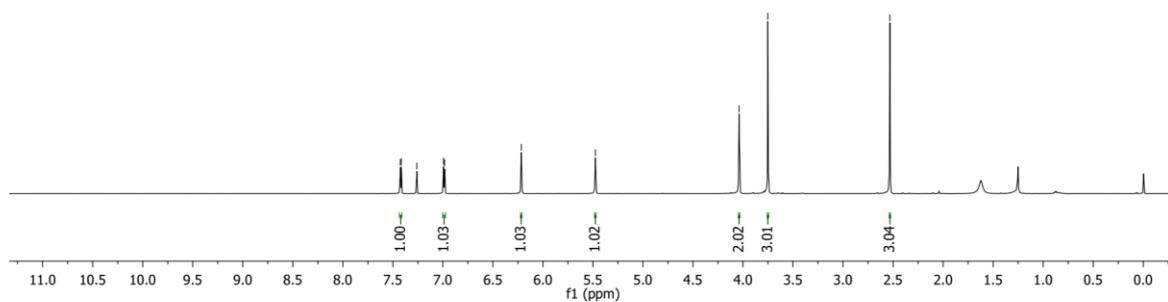
HBH-SKK-23-A-1-1H.1.fid

7.425
7.415
7.260
6.993
6.983
6.215
5.475
4.039
3.751
2.533

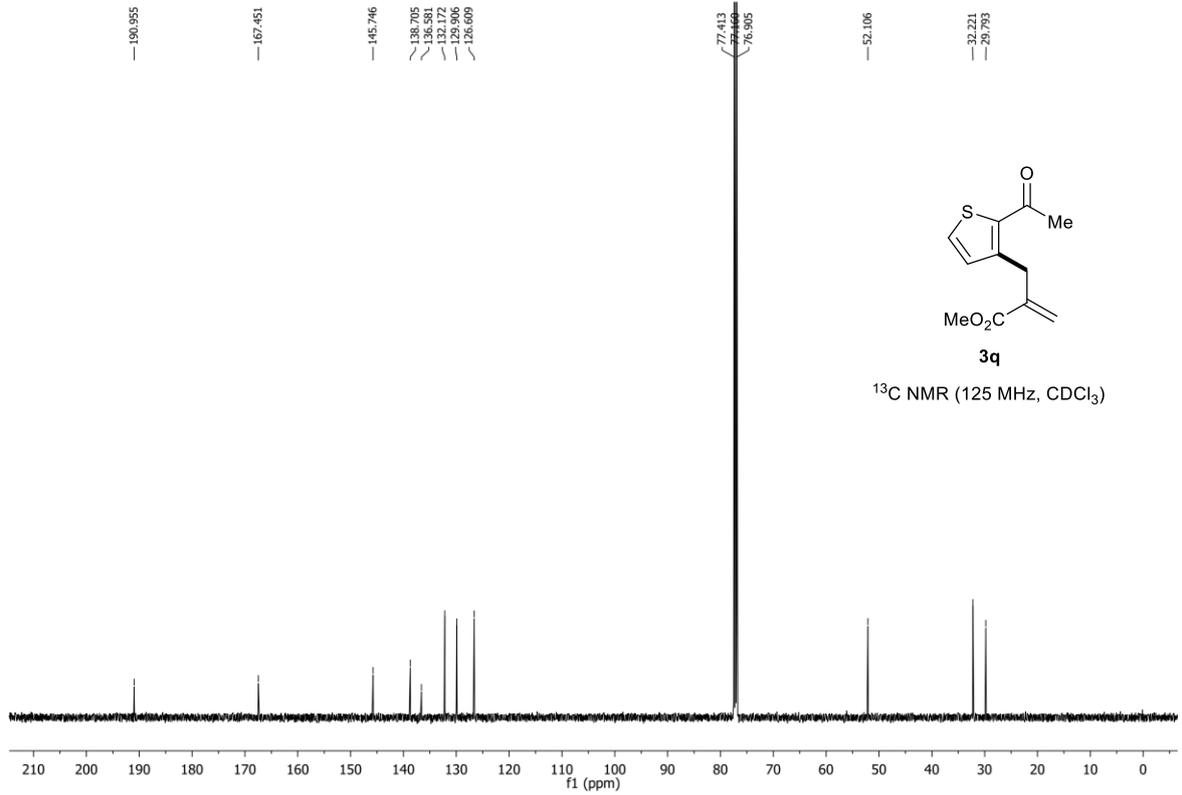


3q

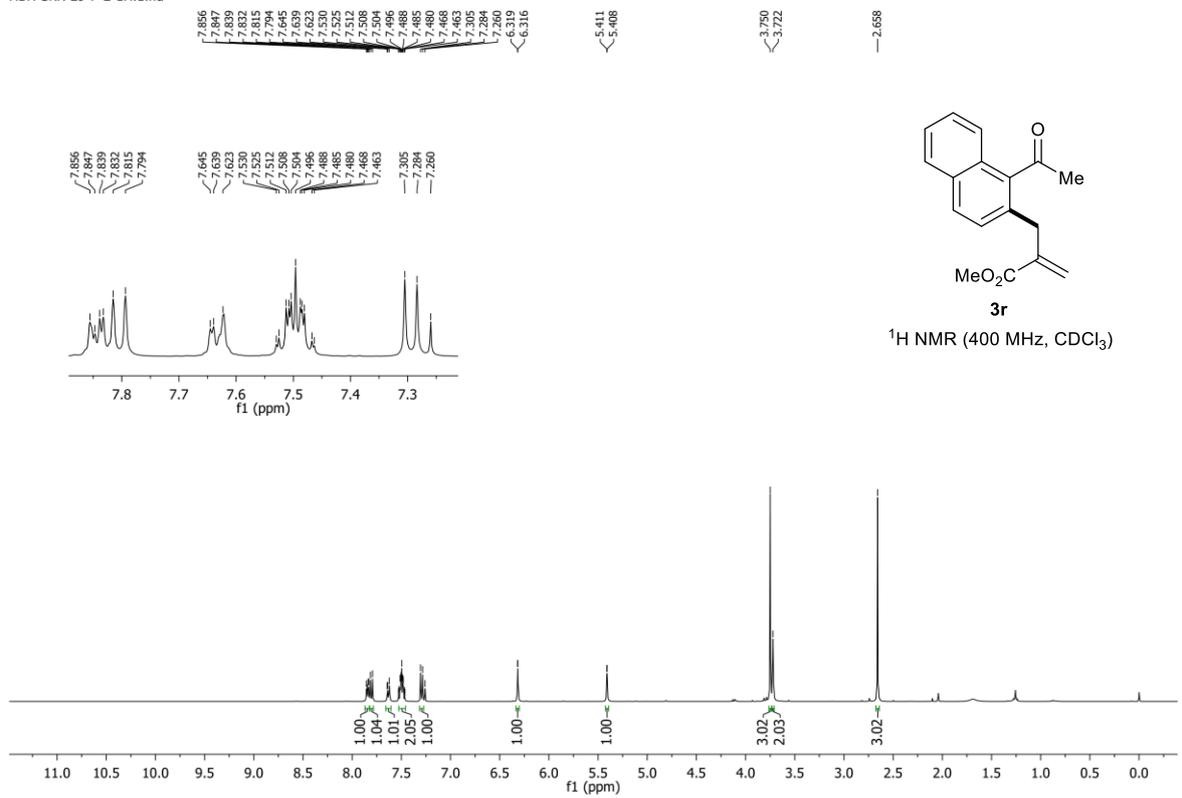
¹H NMR (500 MHz, CDCl₃)



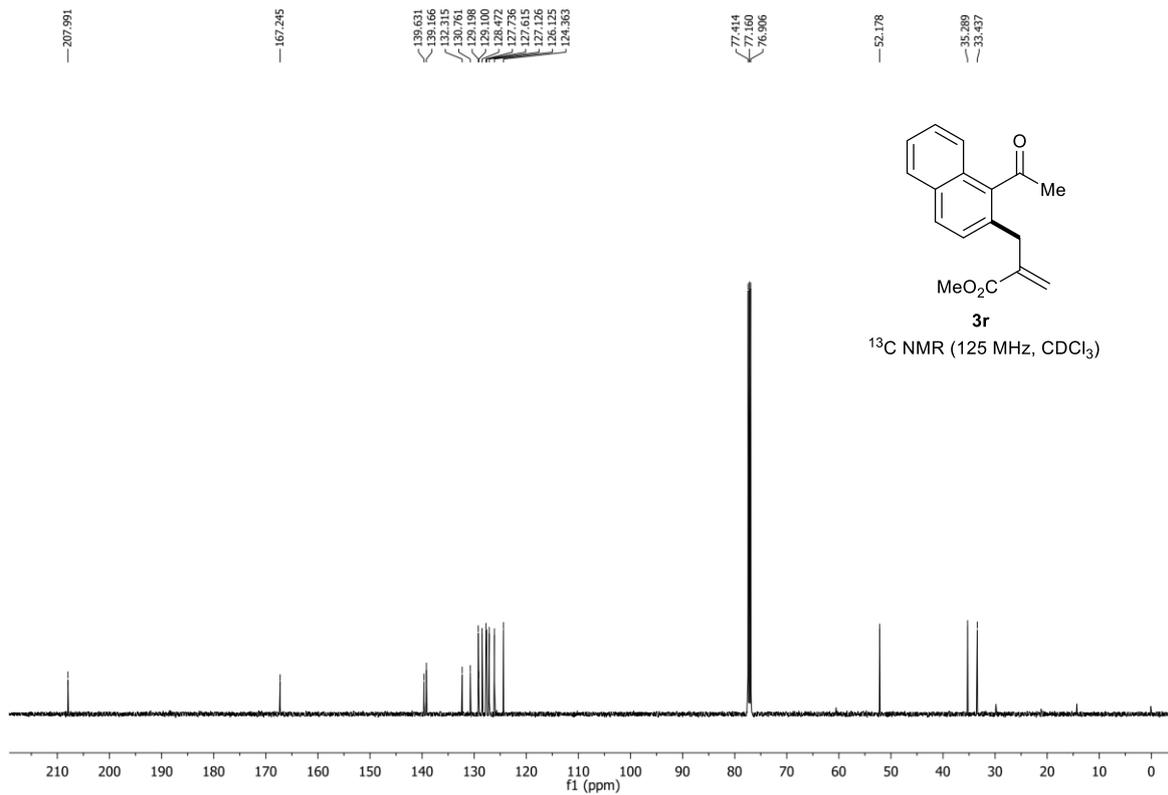
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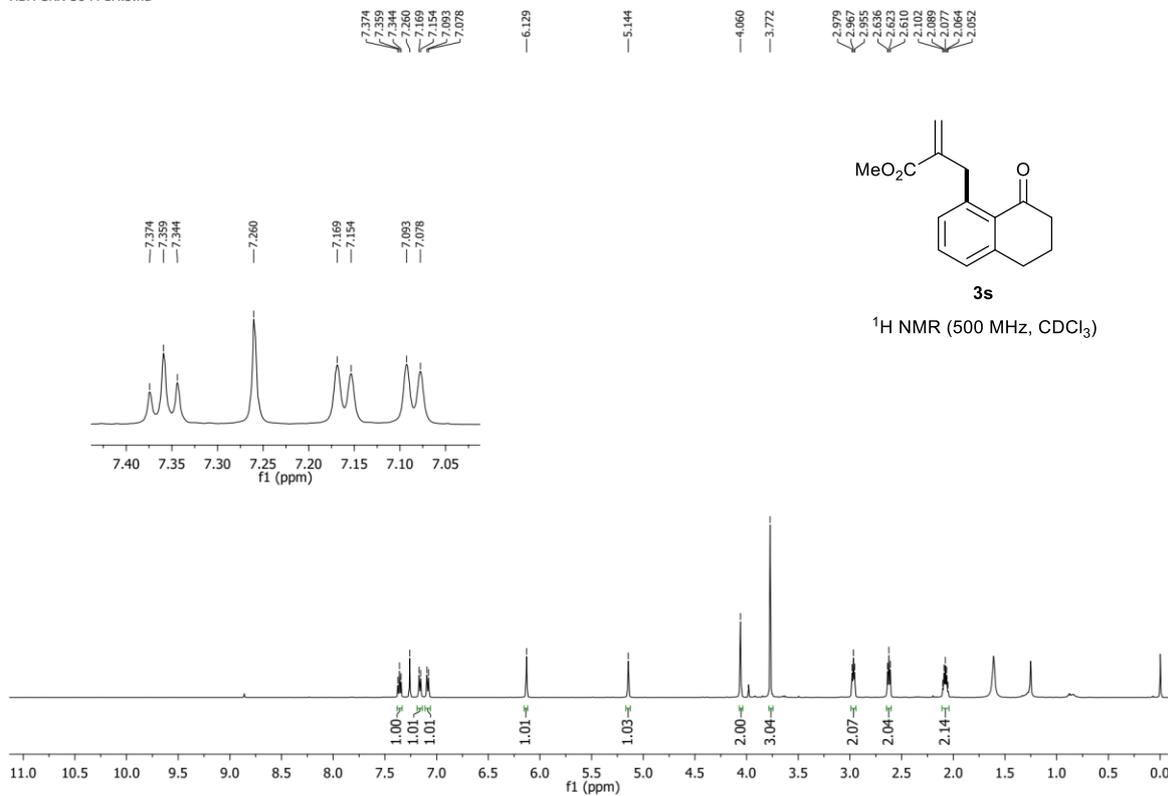
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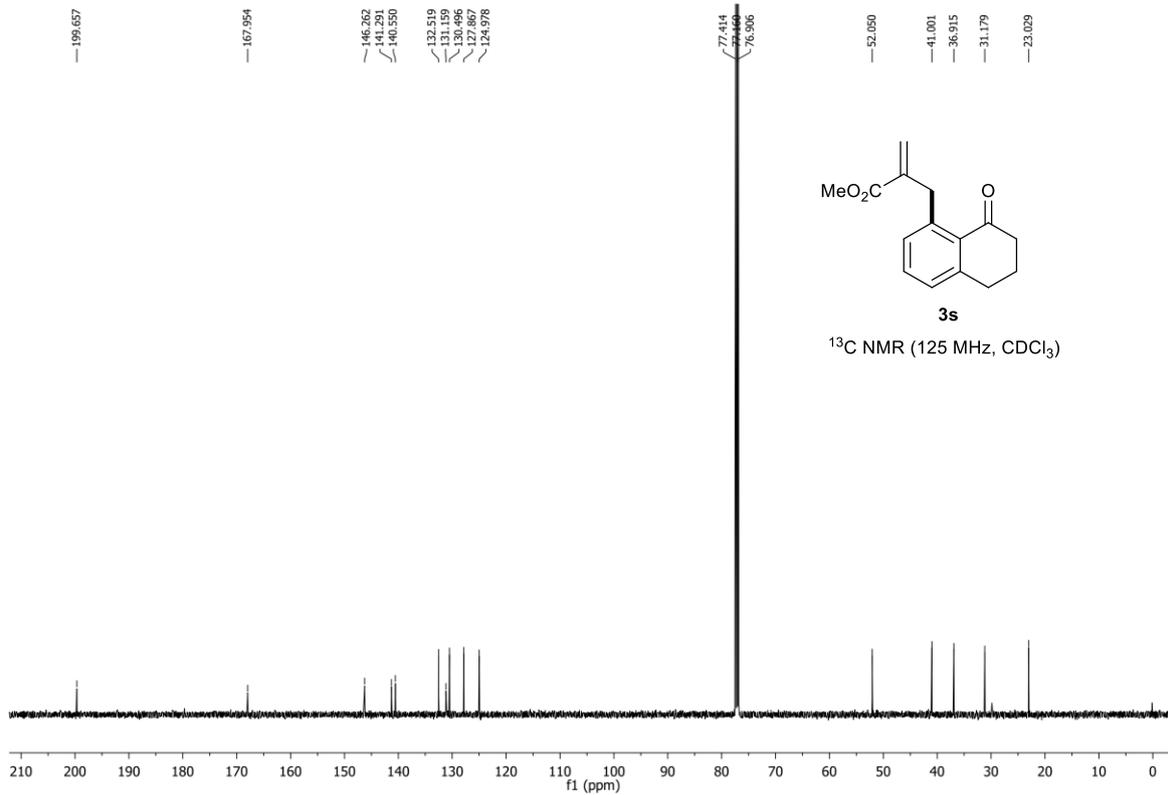
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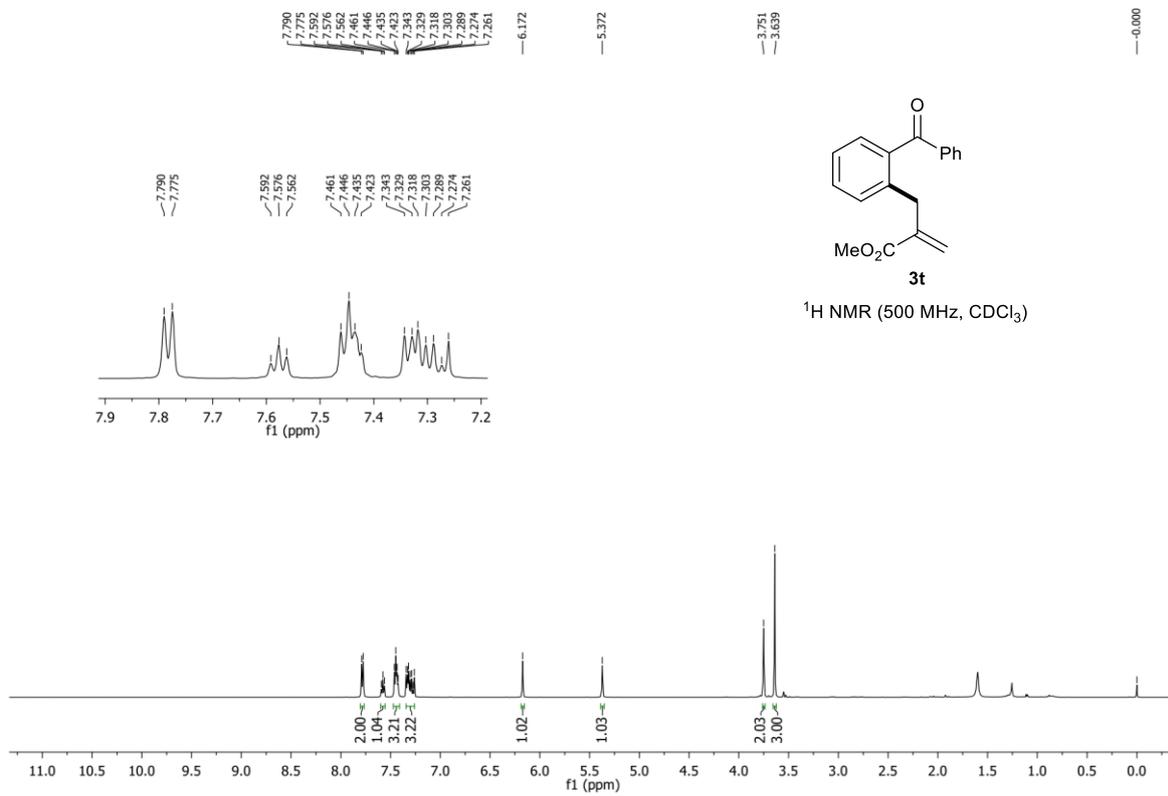
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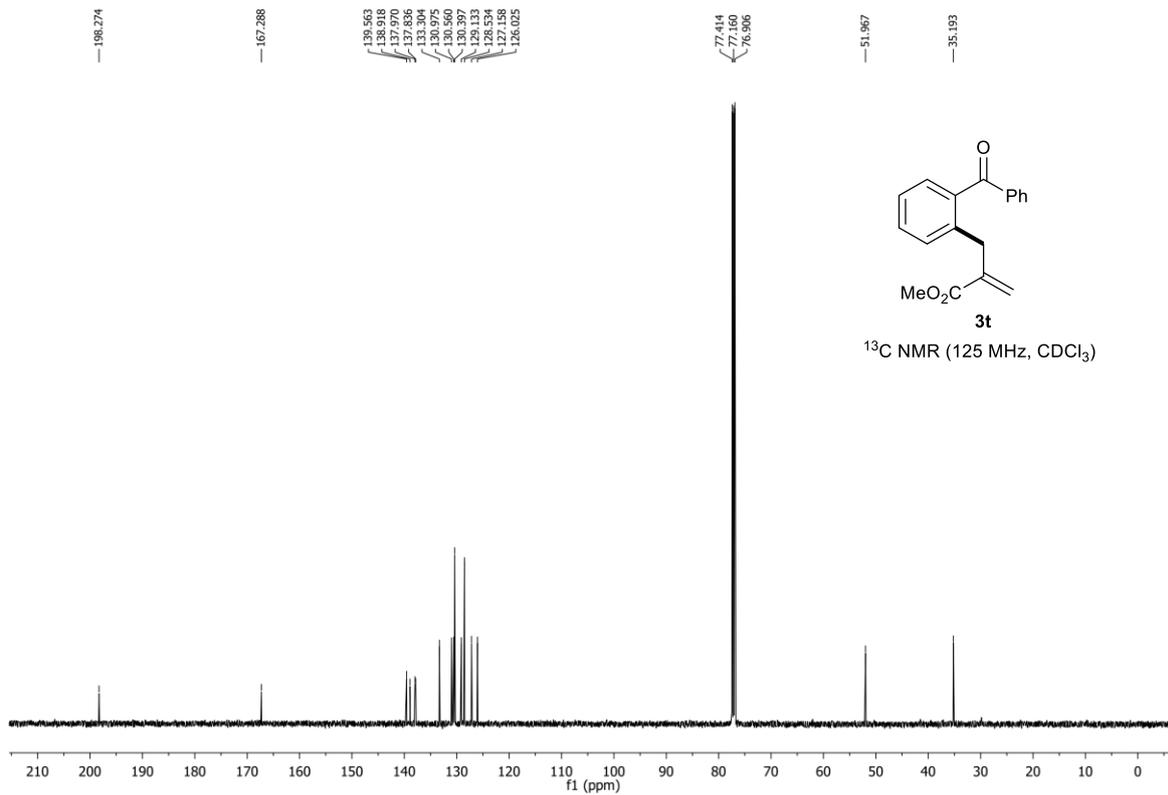
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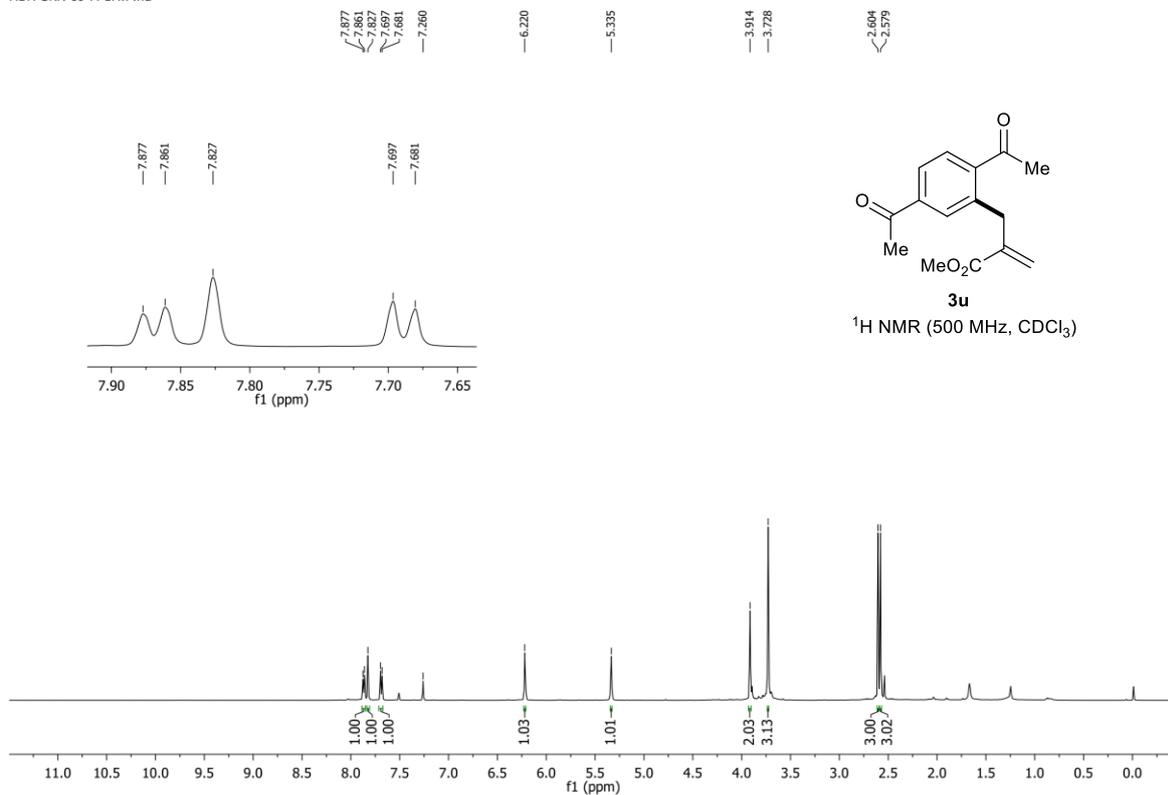
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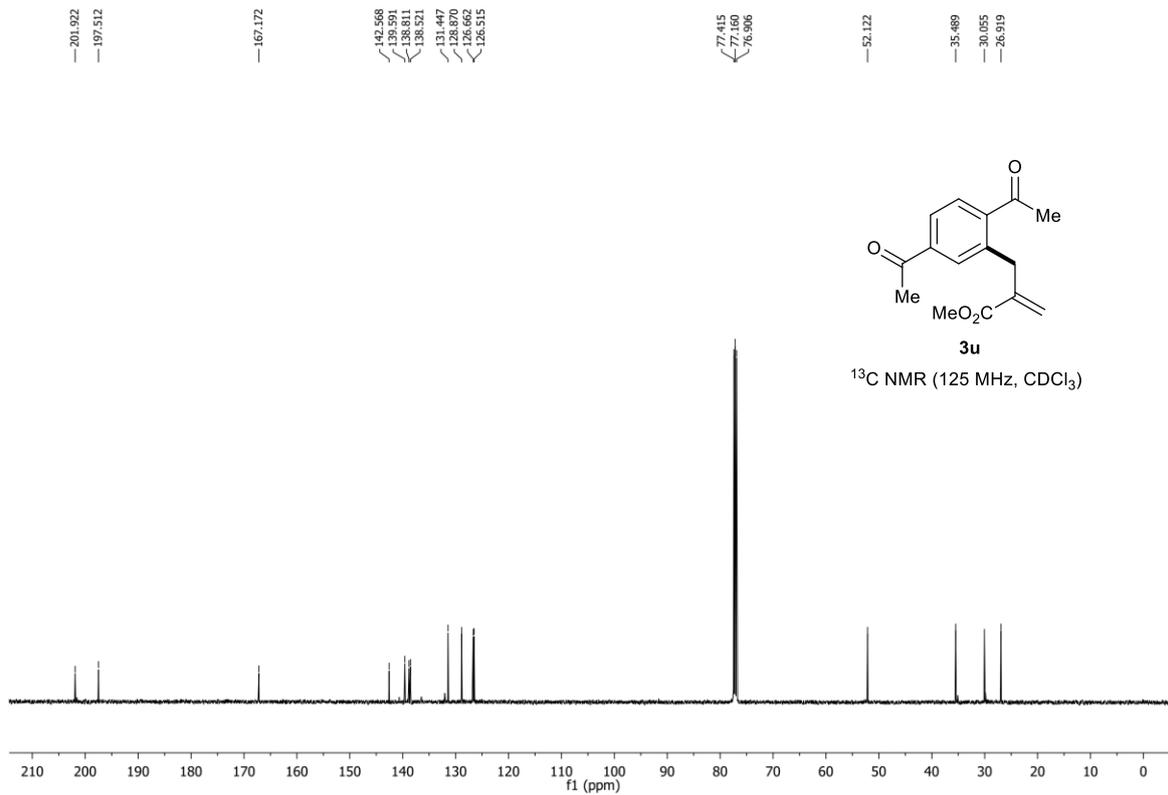
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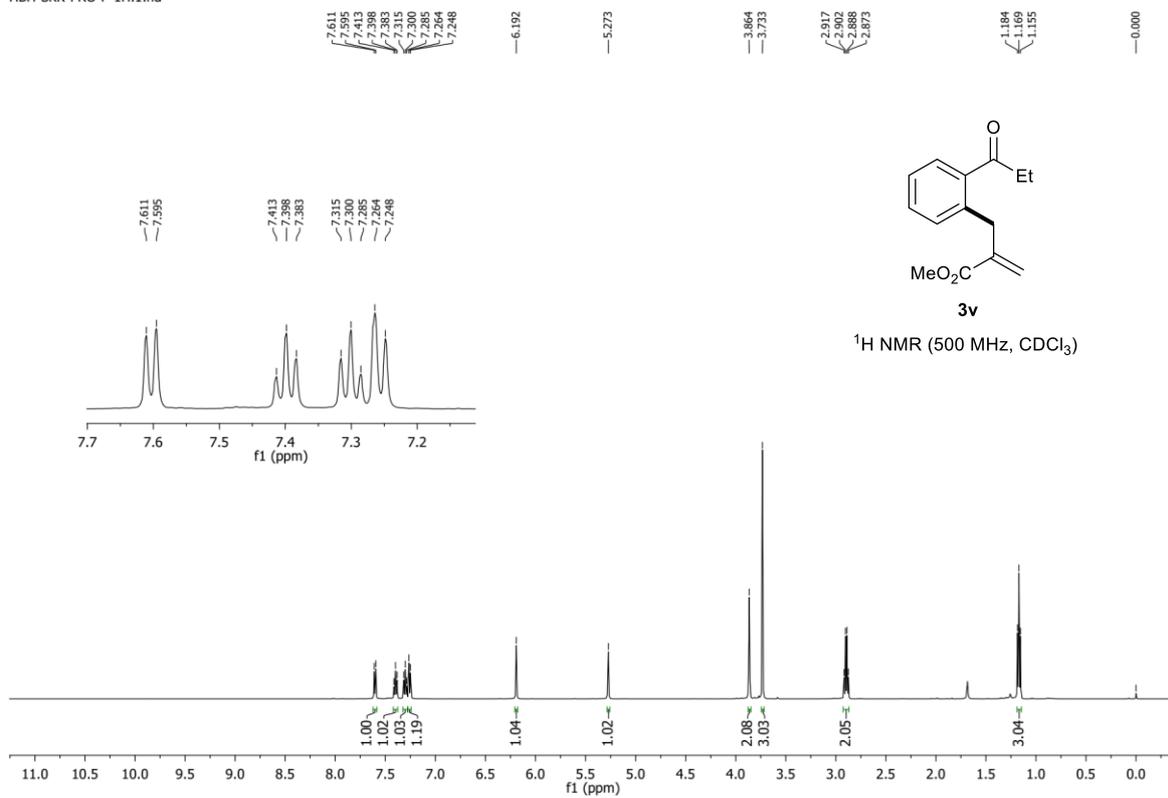
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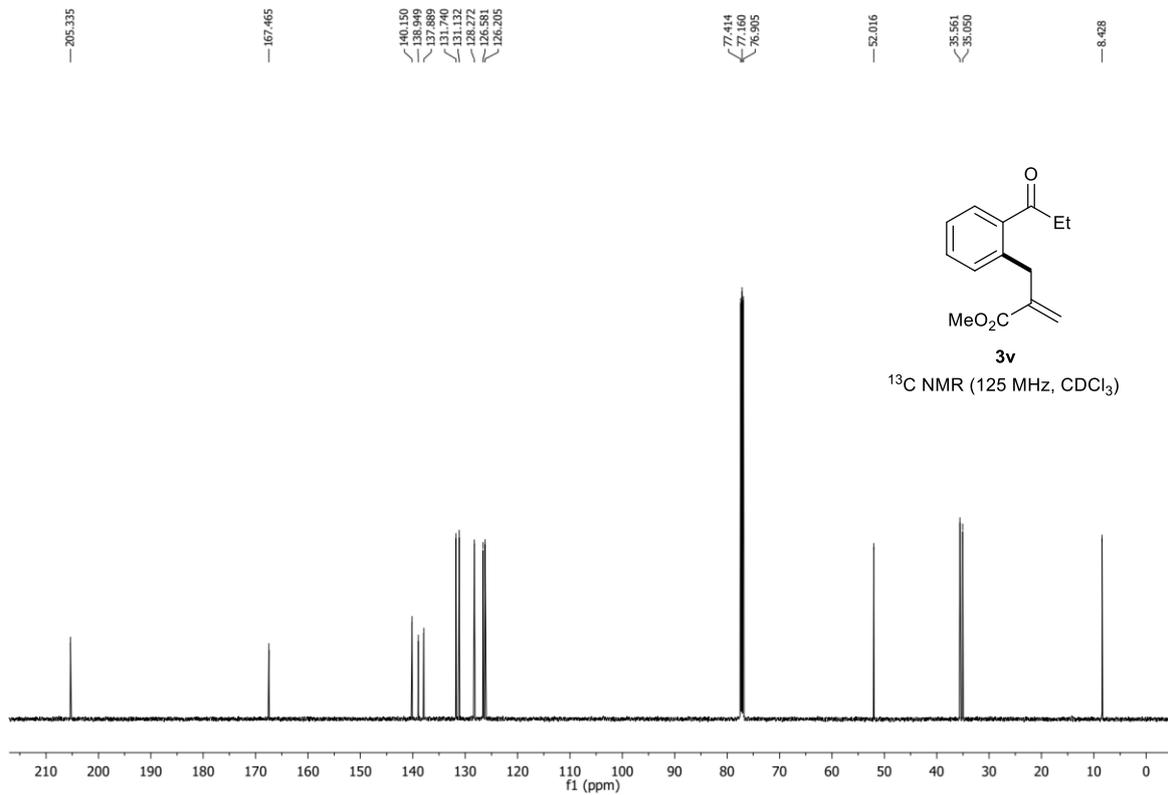
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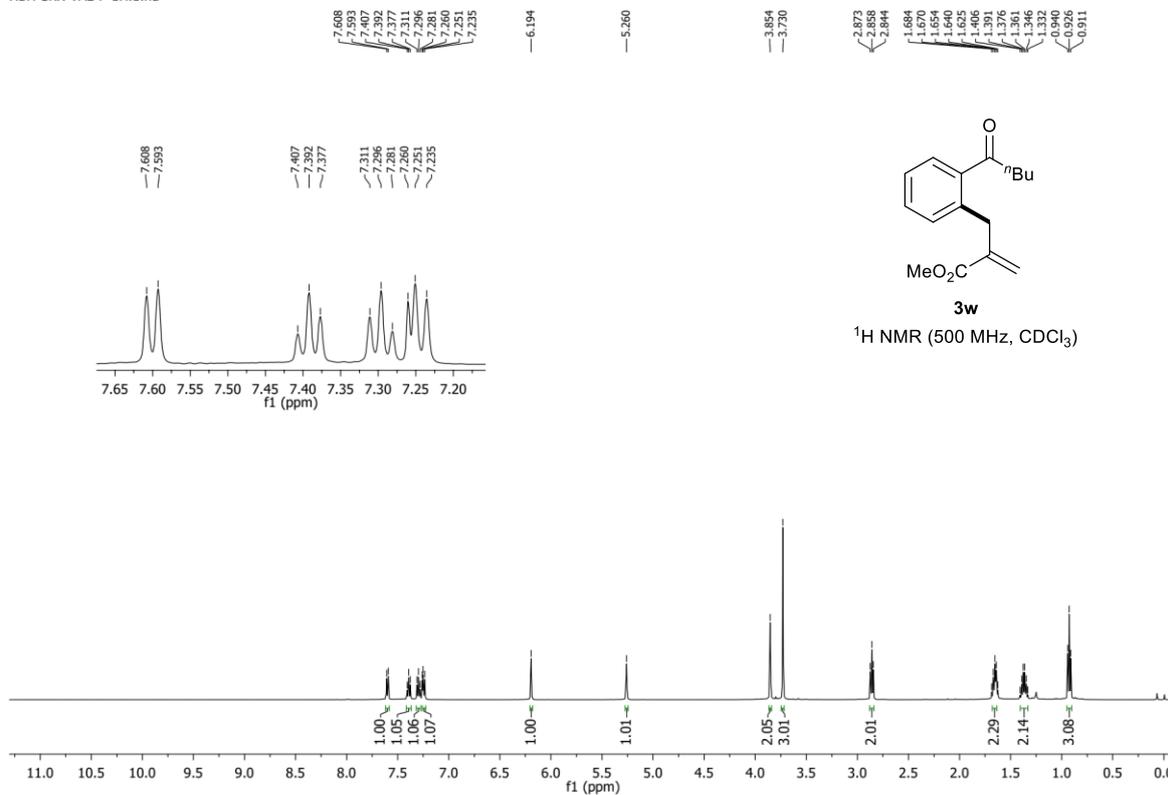
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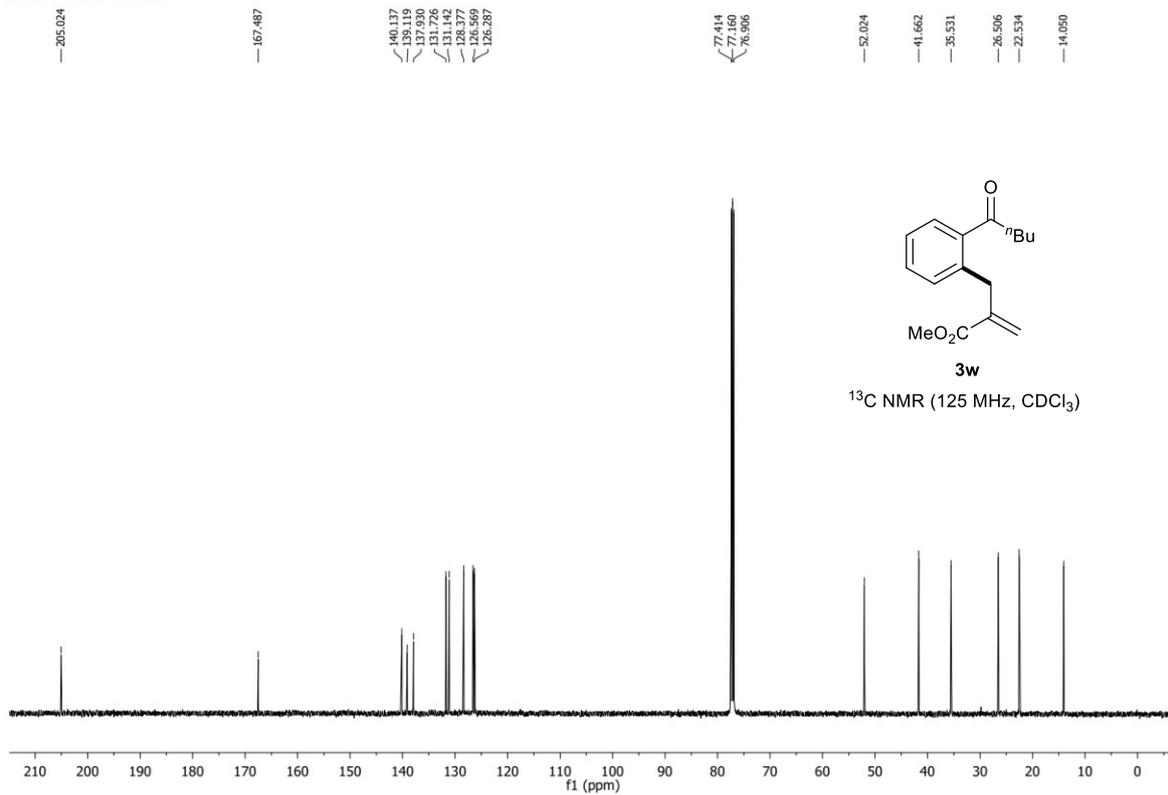
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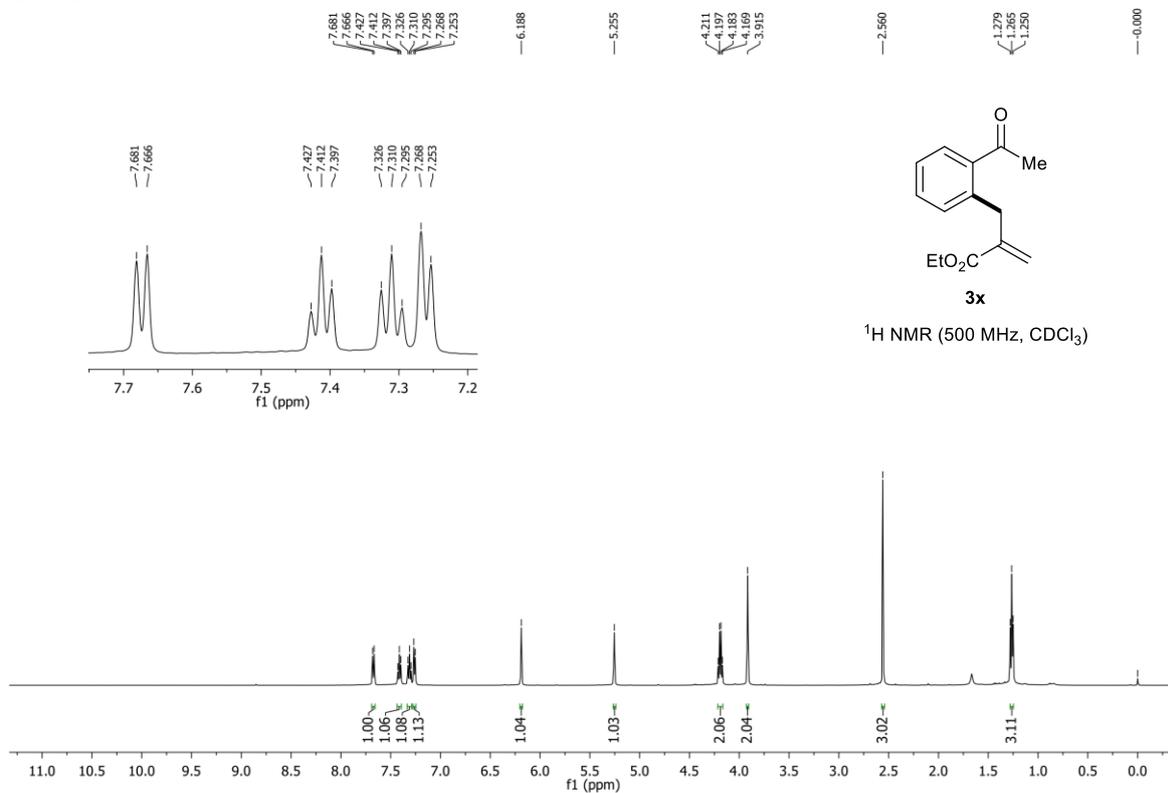
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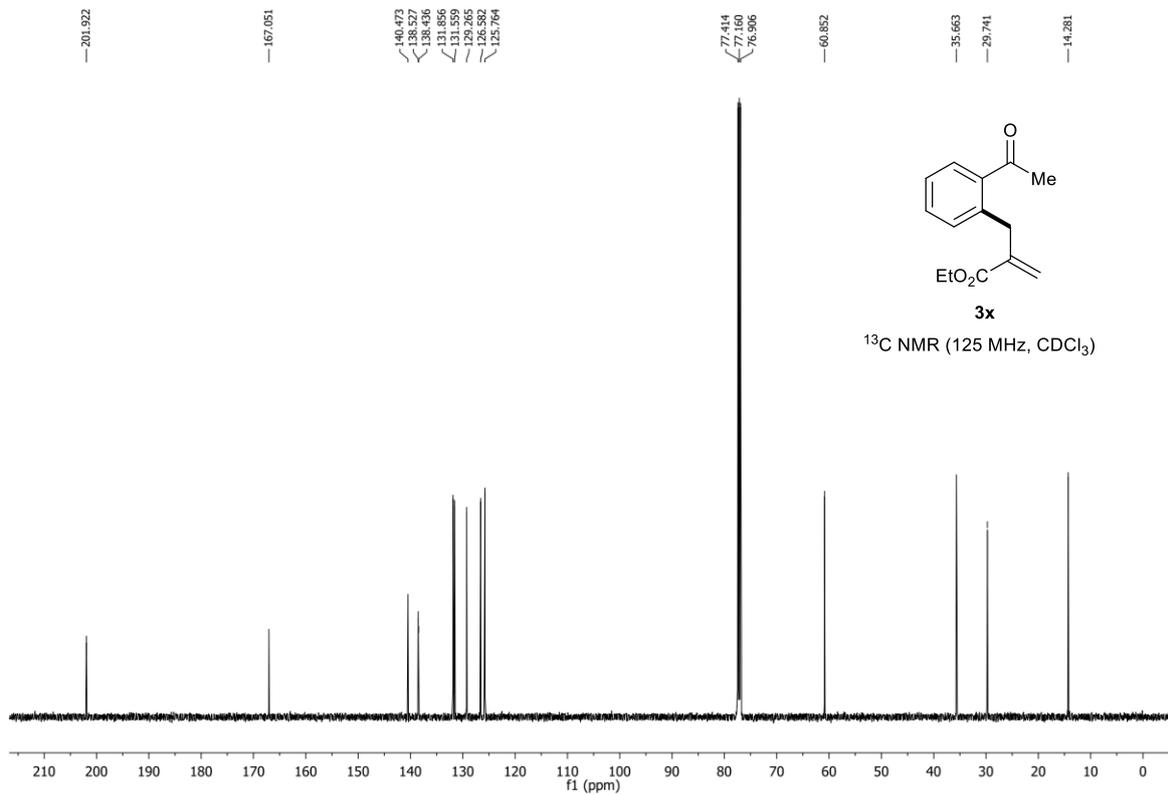
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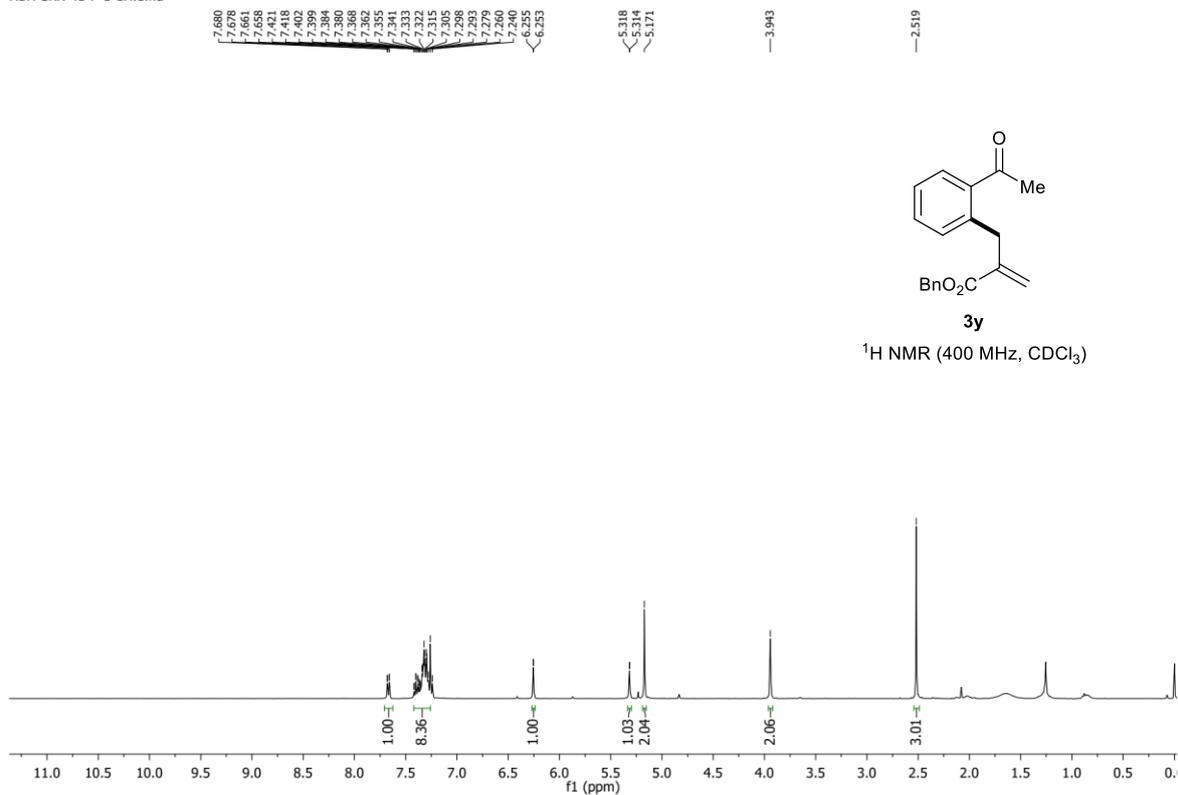
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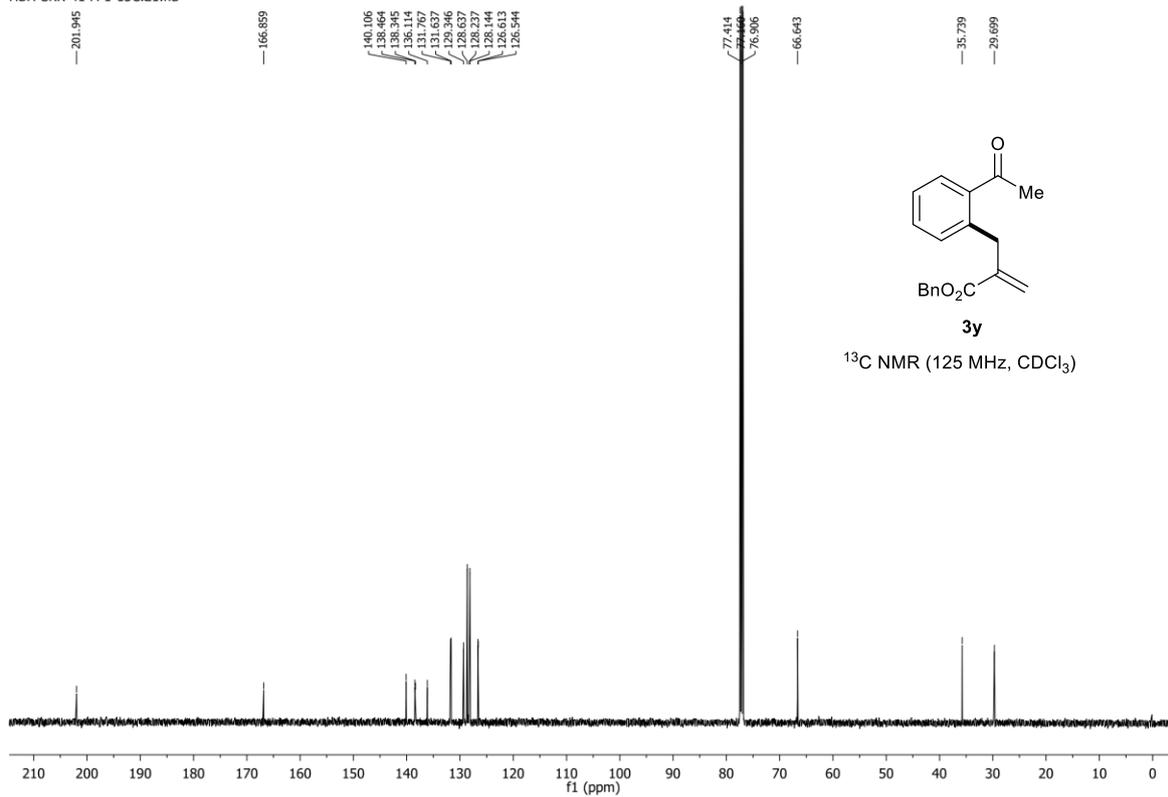
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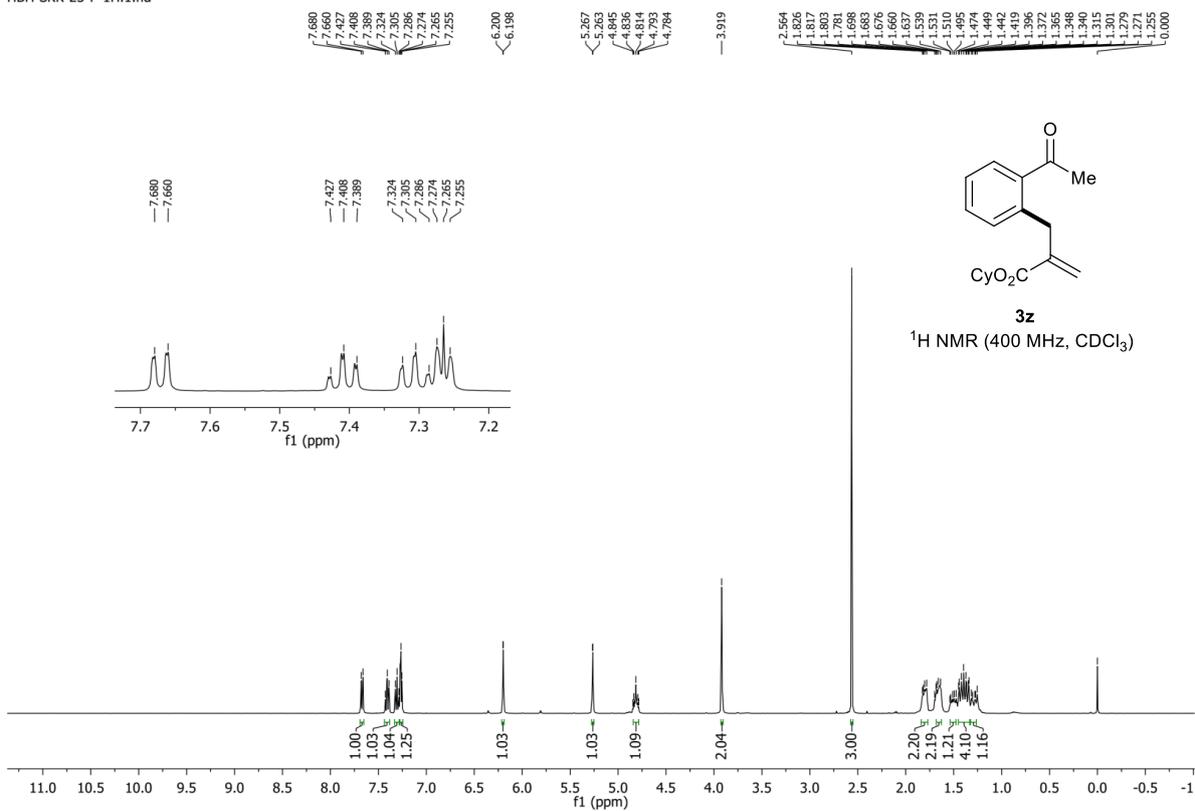
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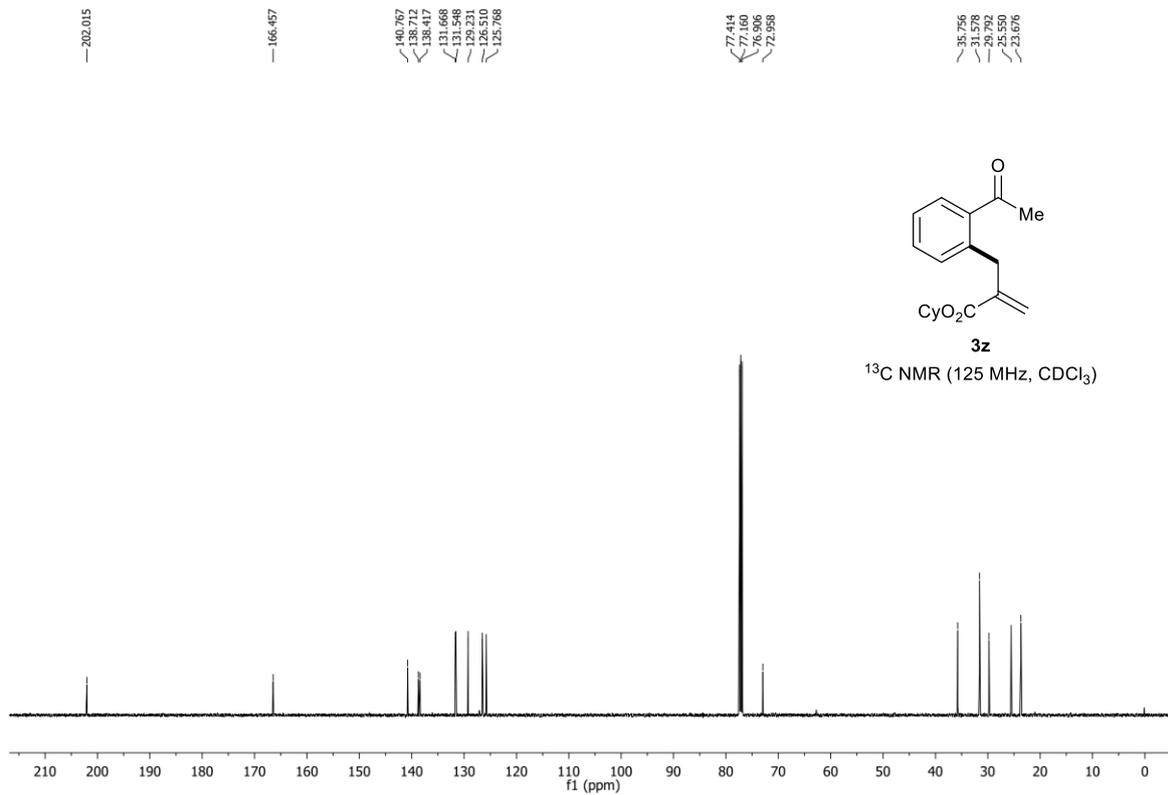
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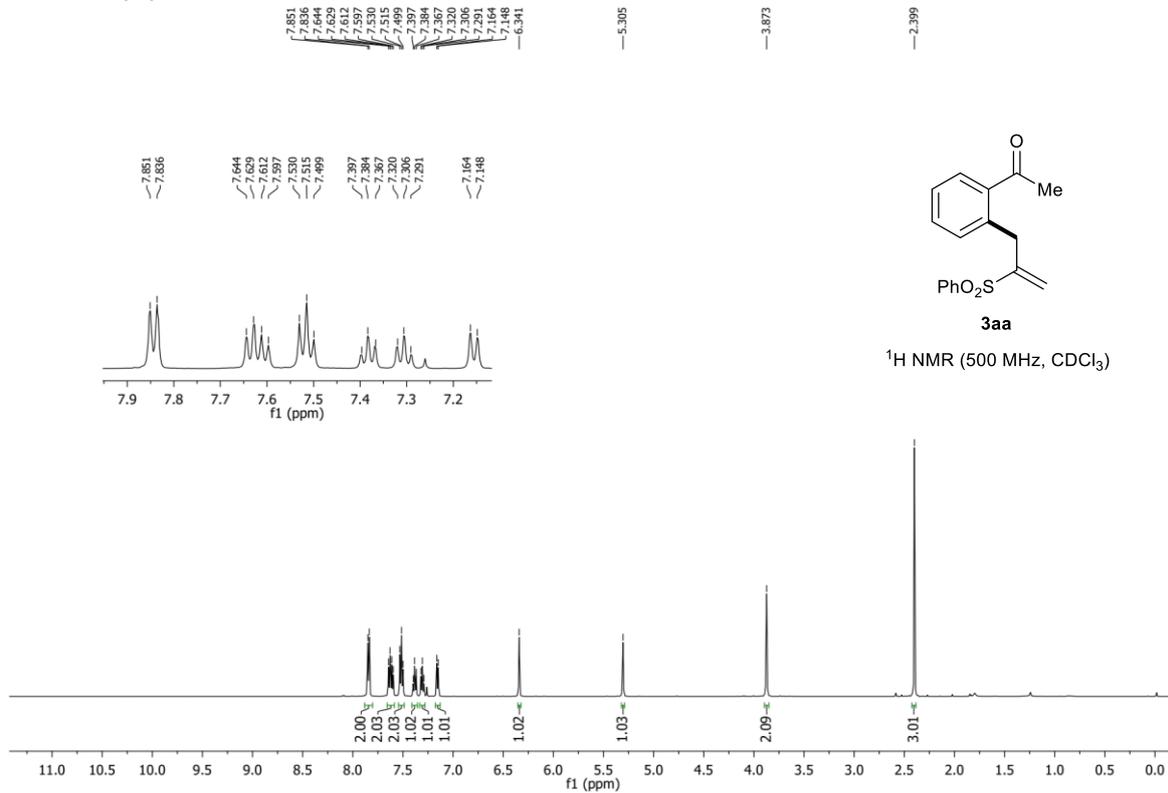
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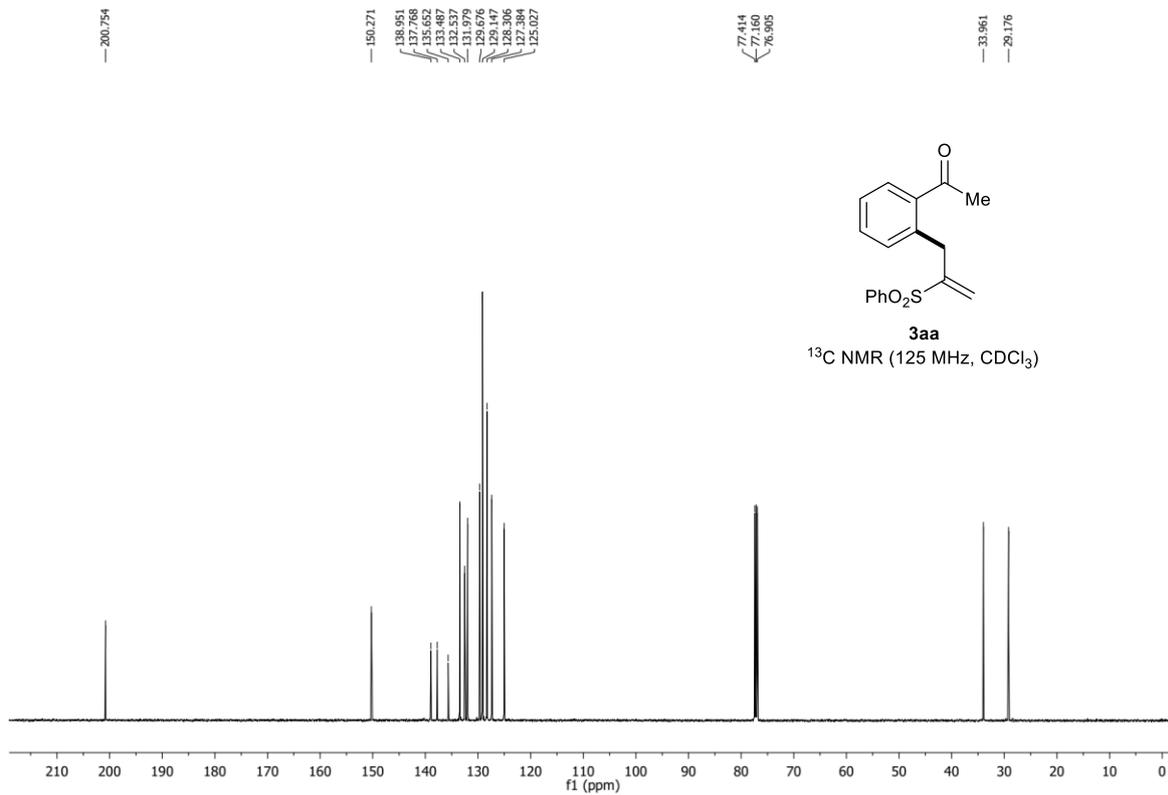
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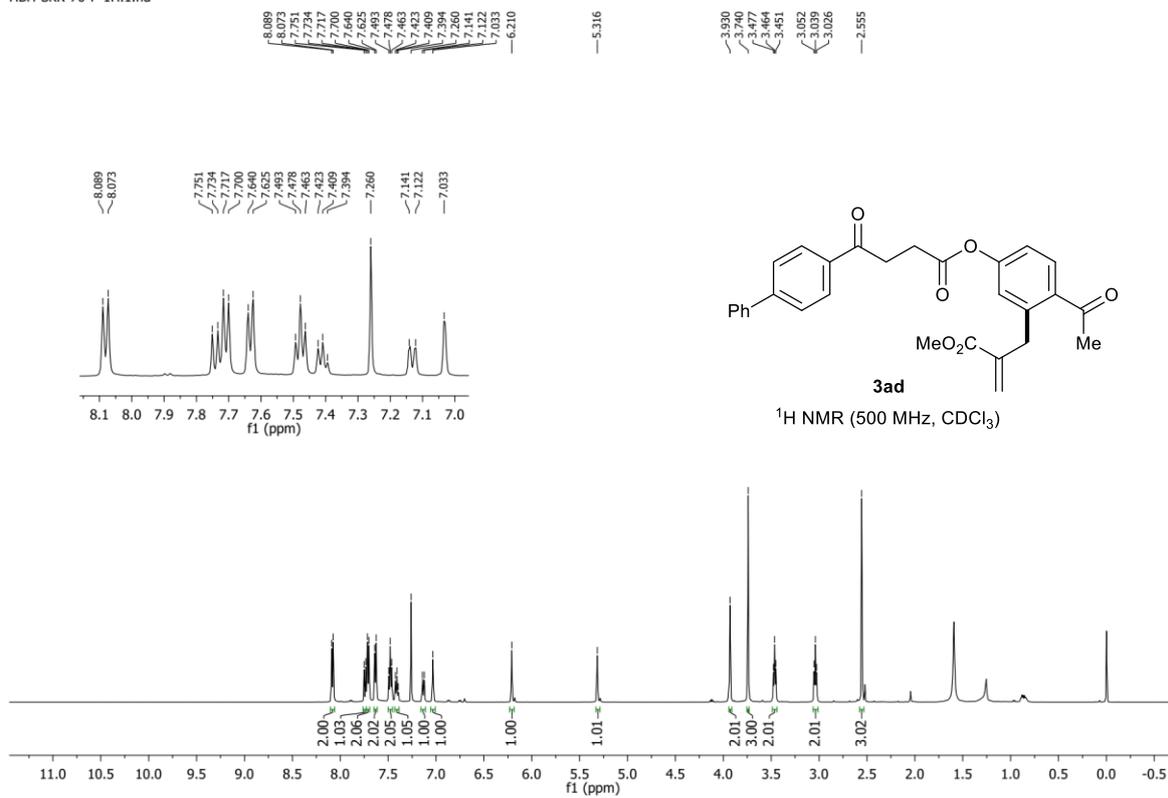
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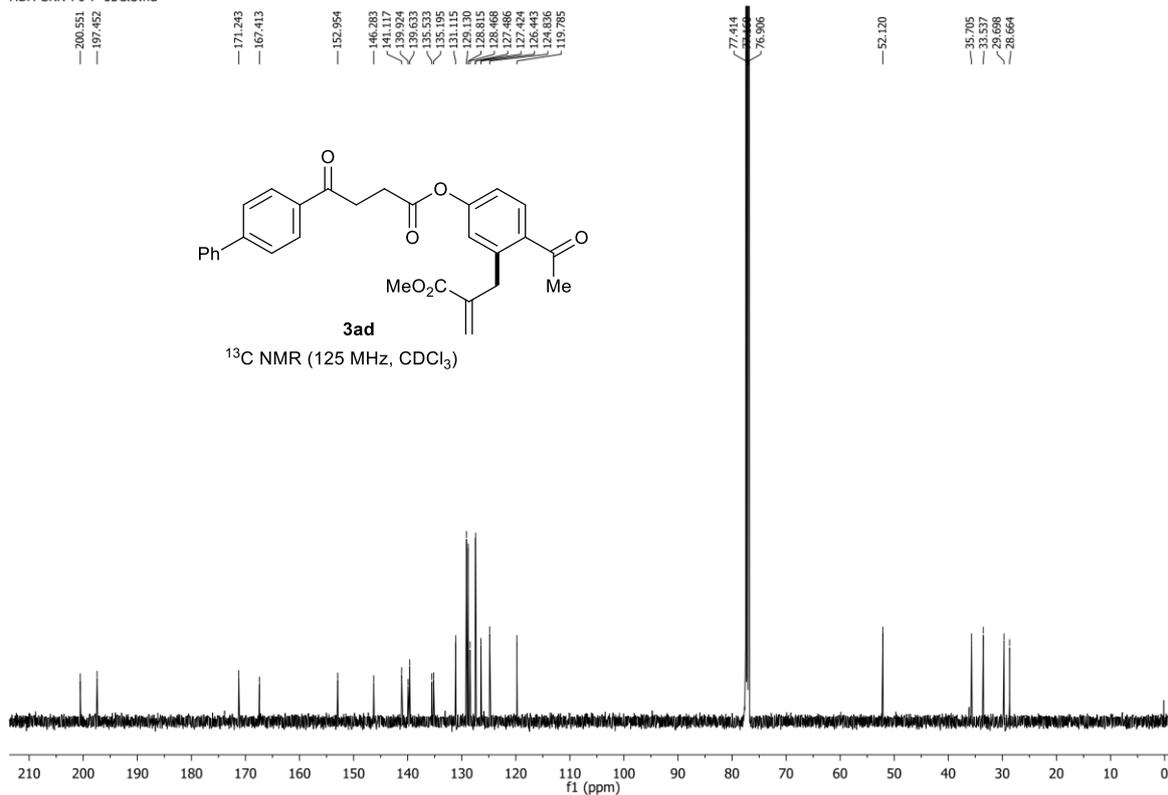
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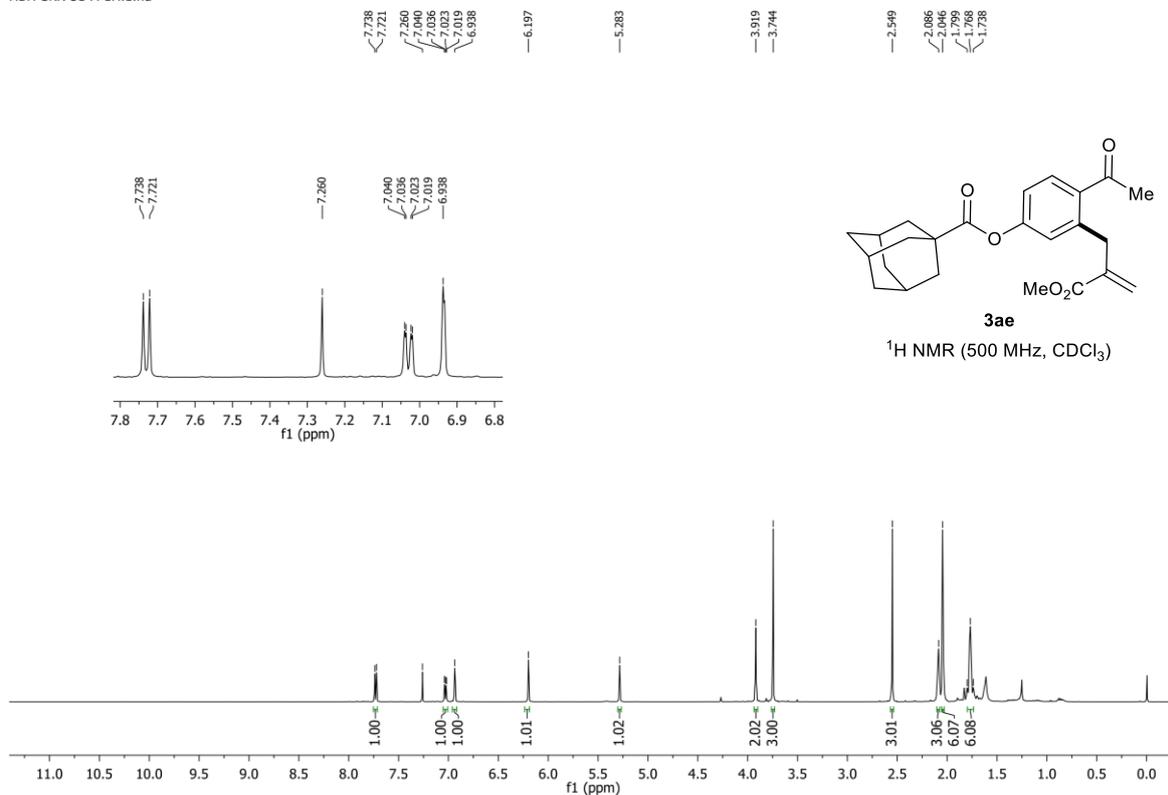
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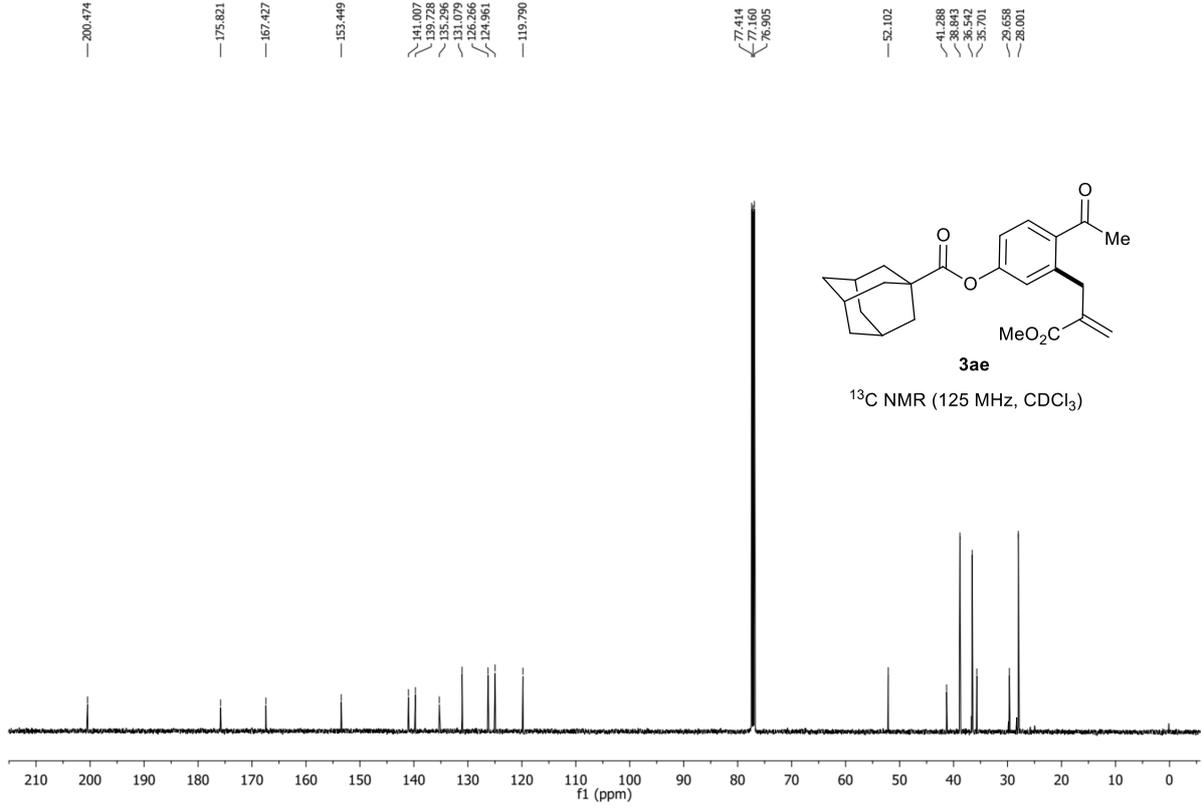
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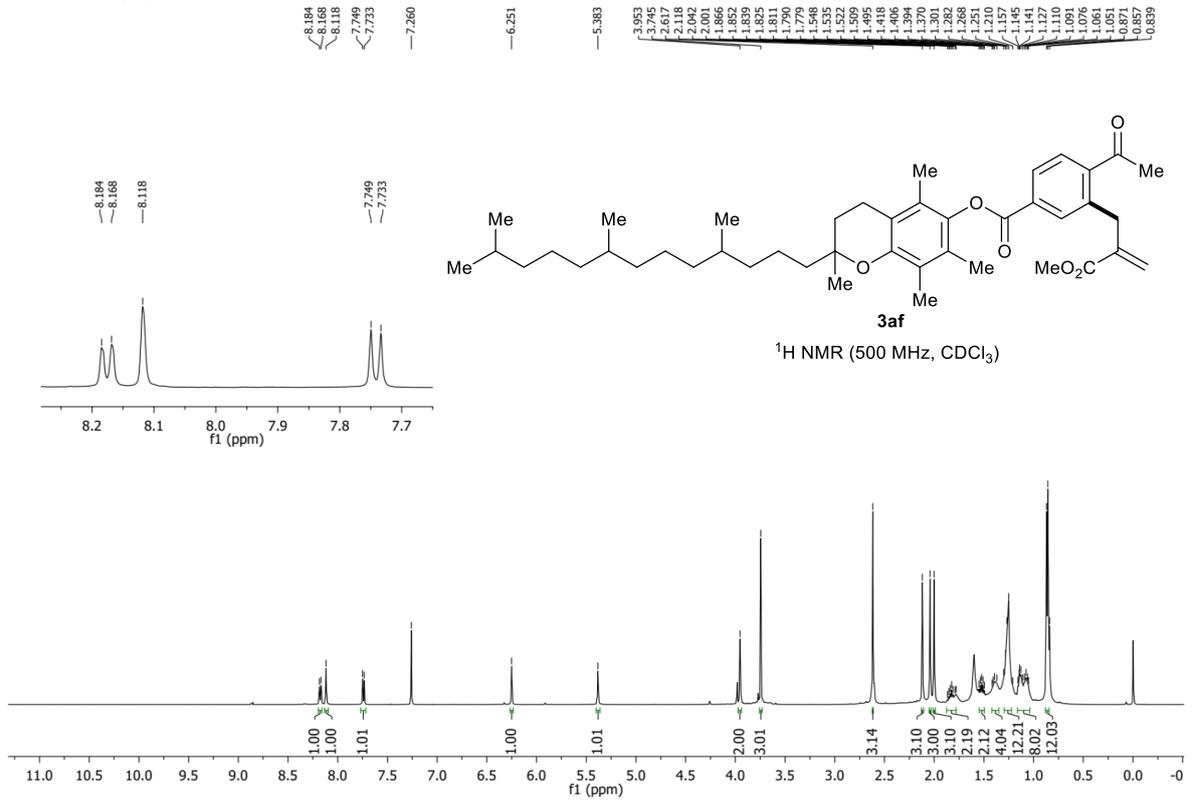
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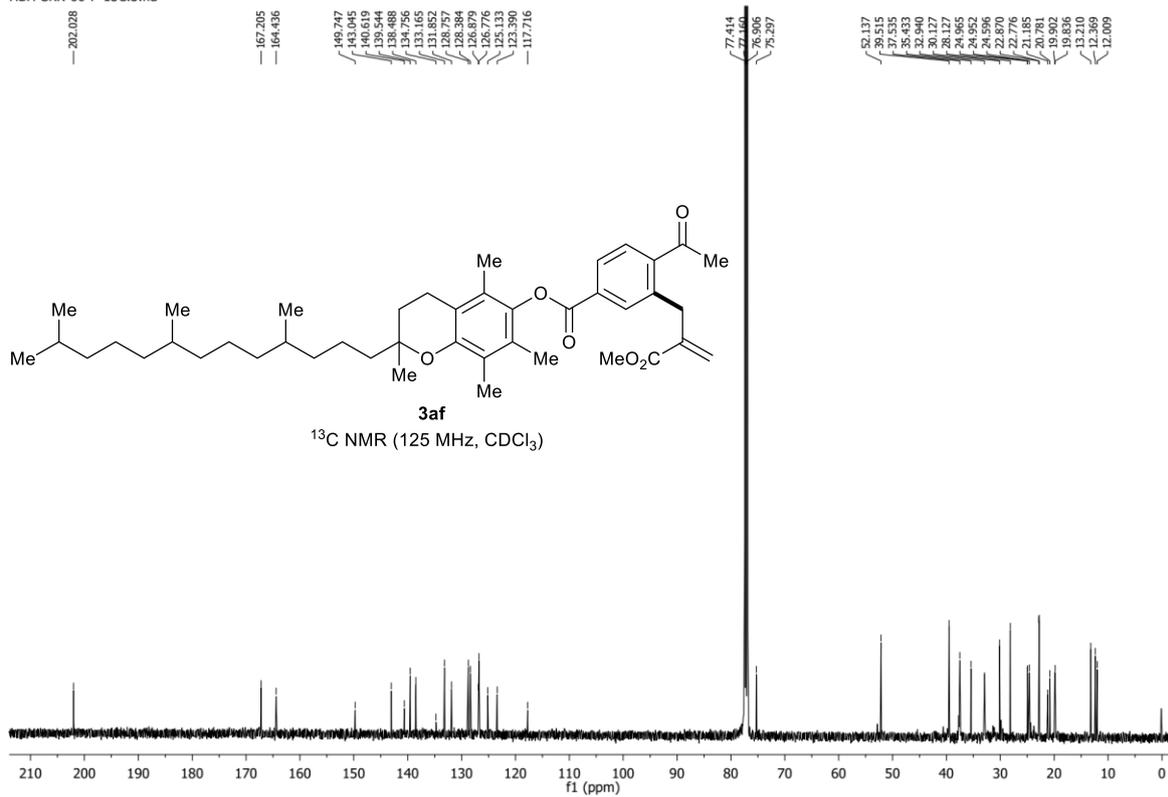
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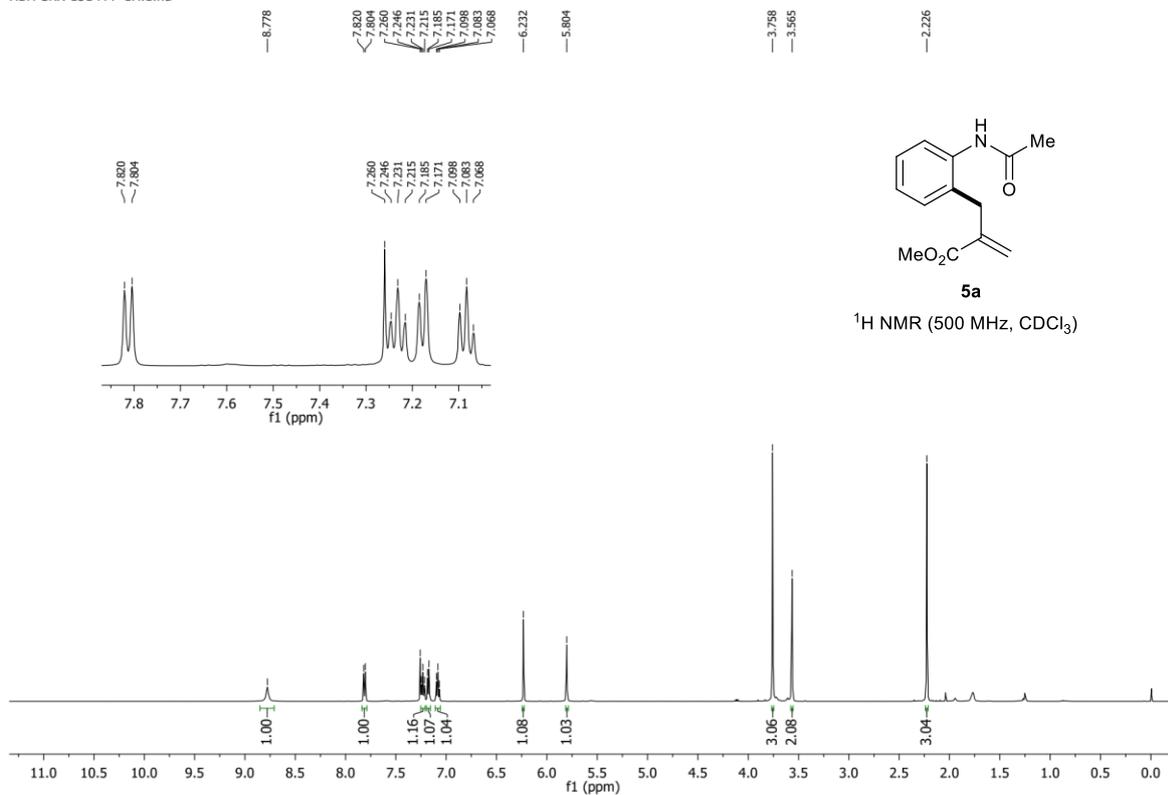
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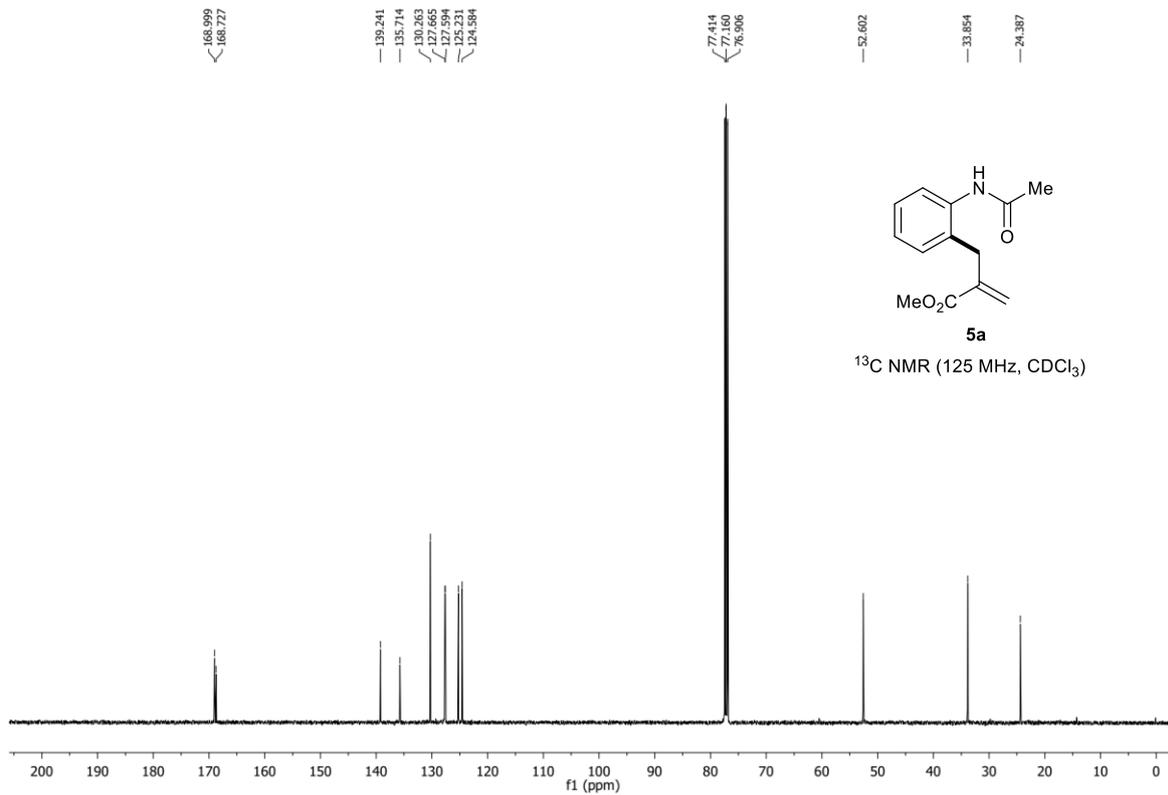
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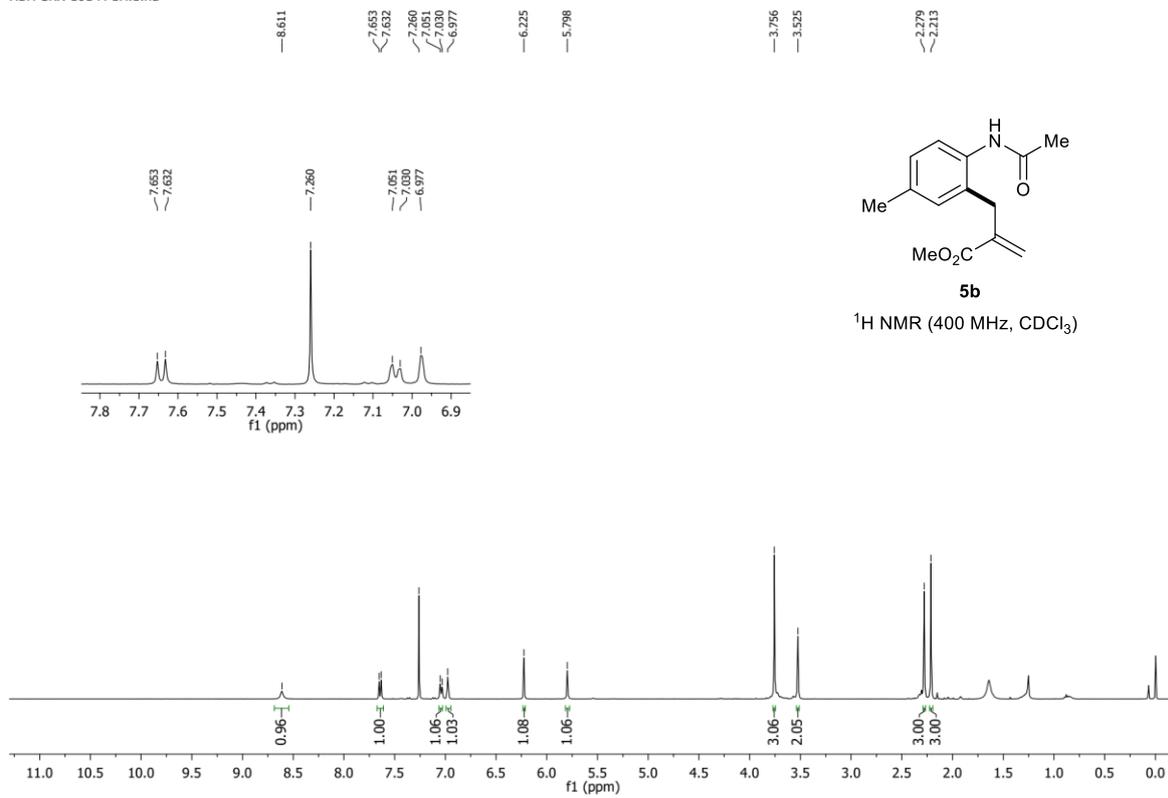
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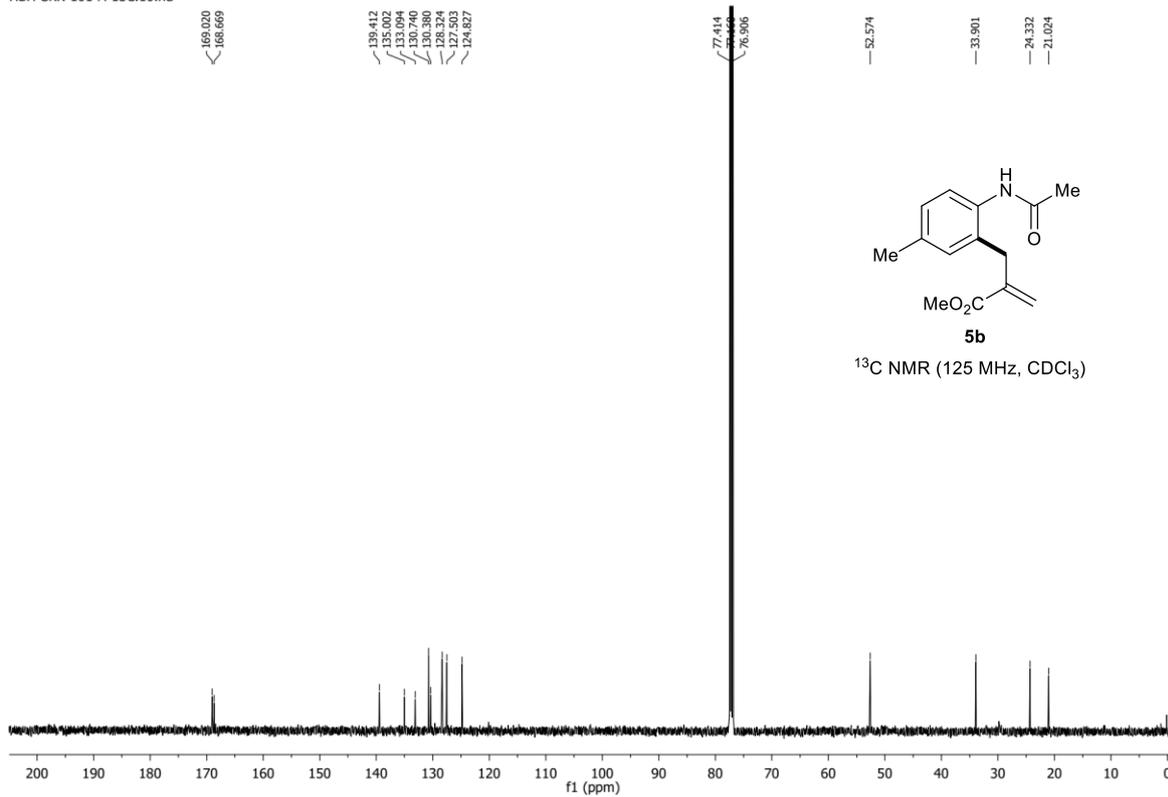
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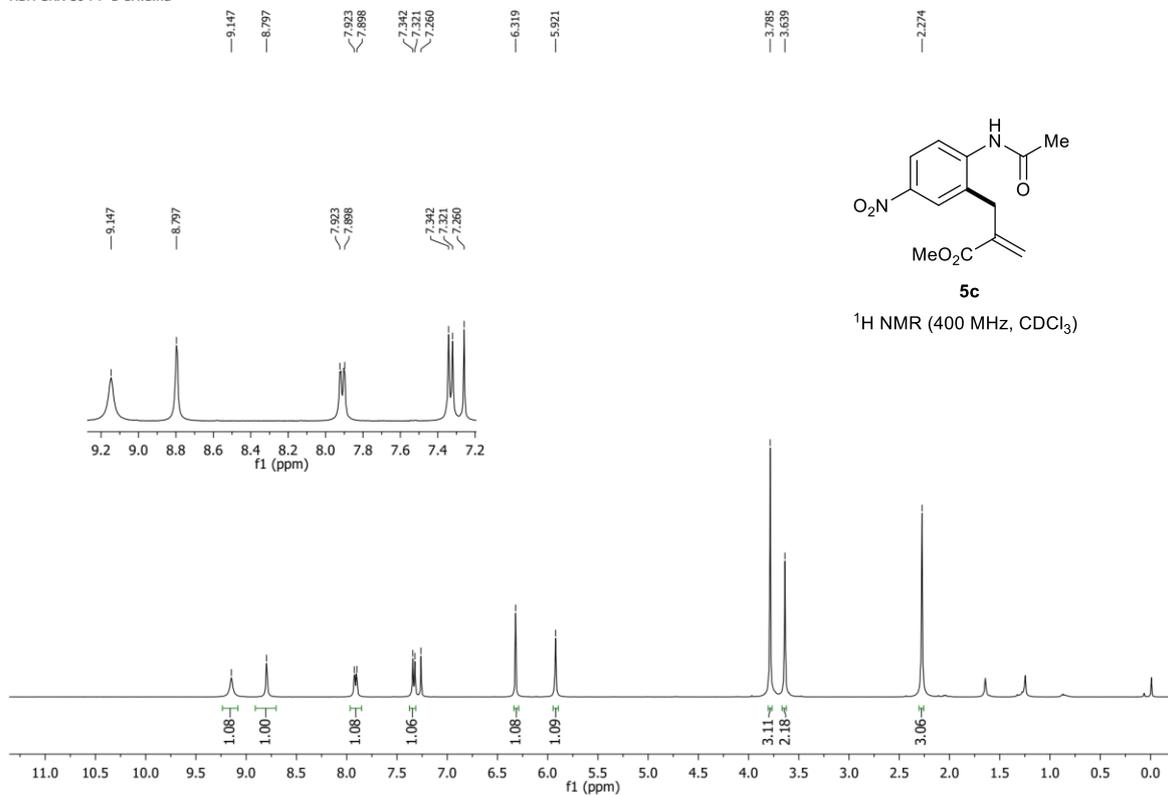
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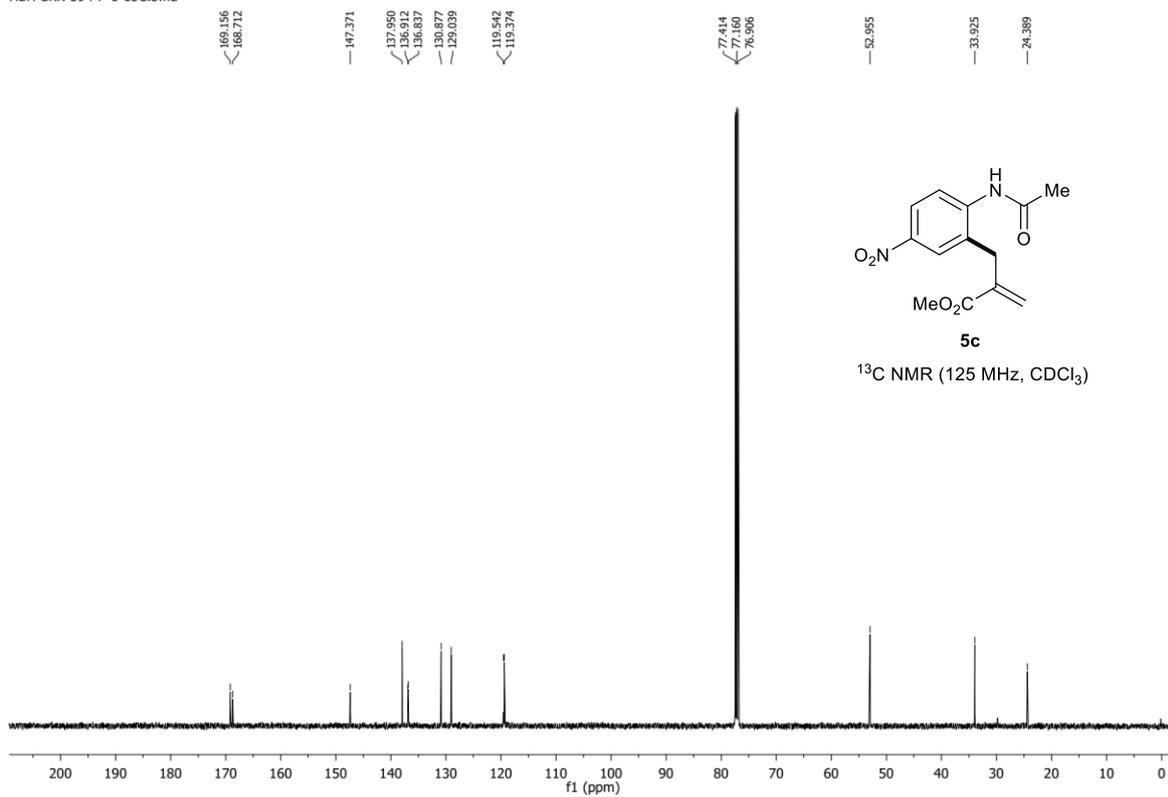
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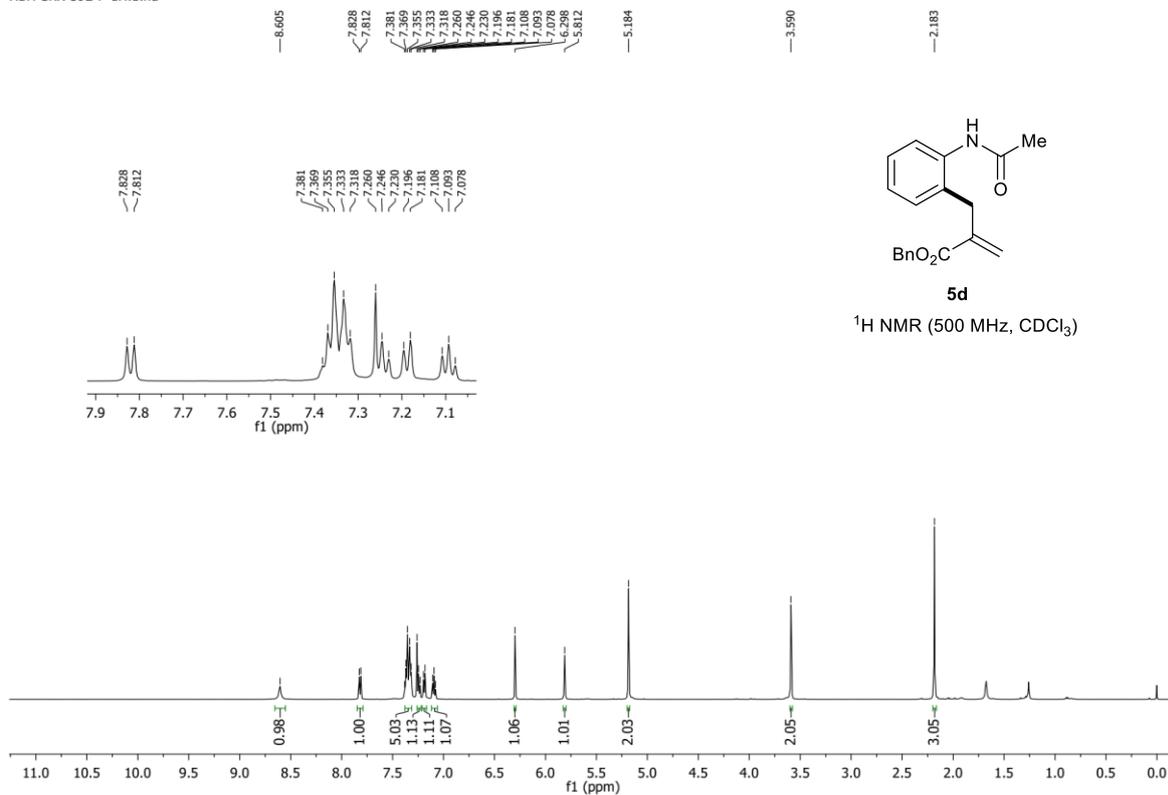
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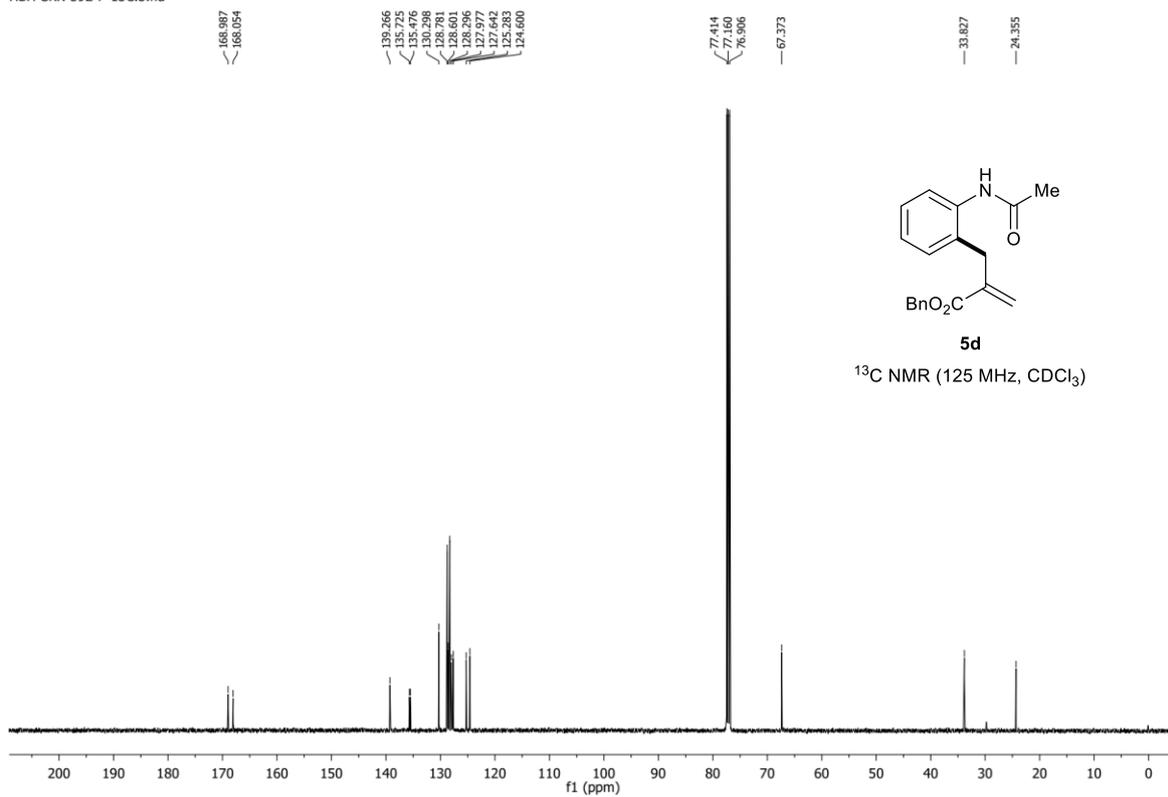
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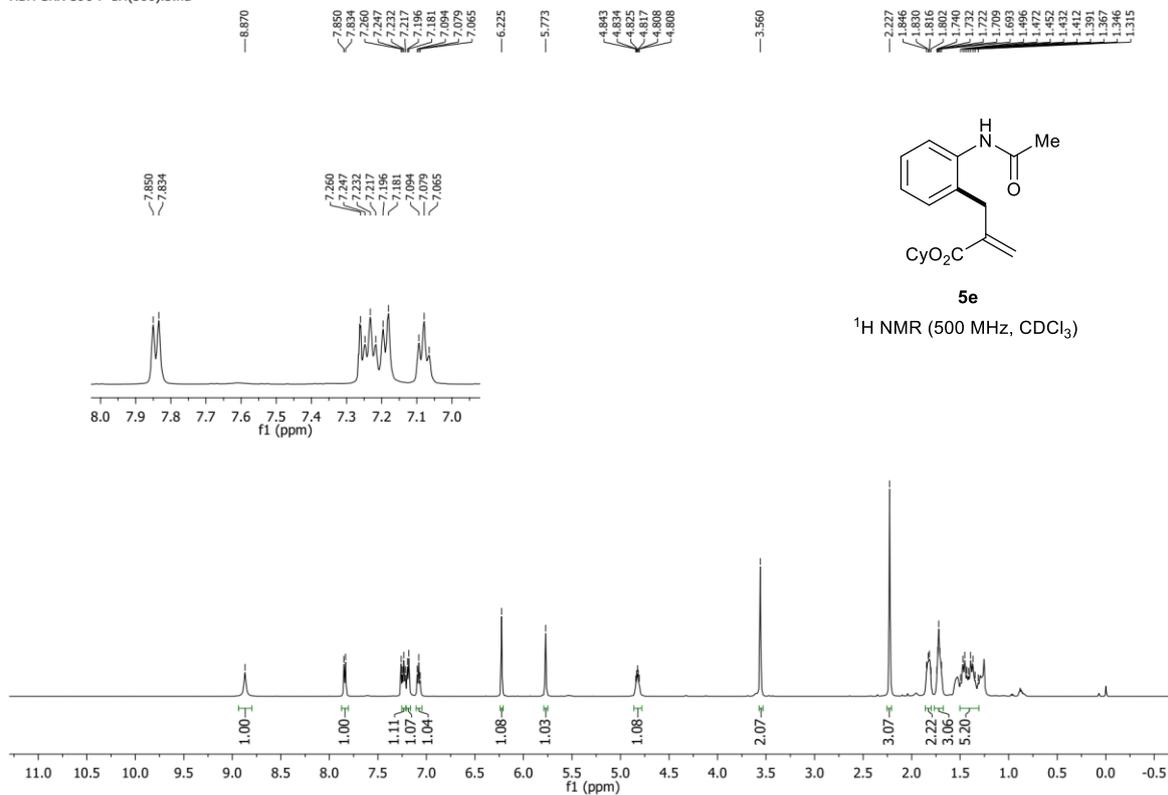
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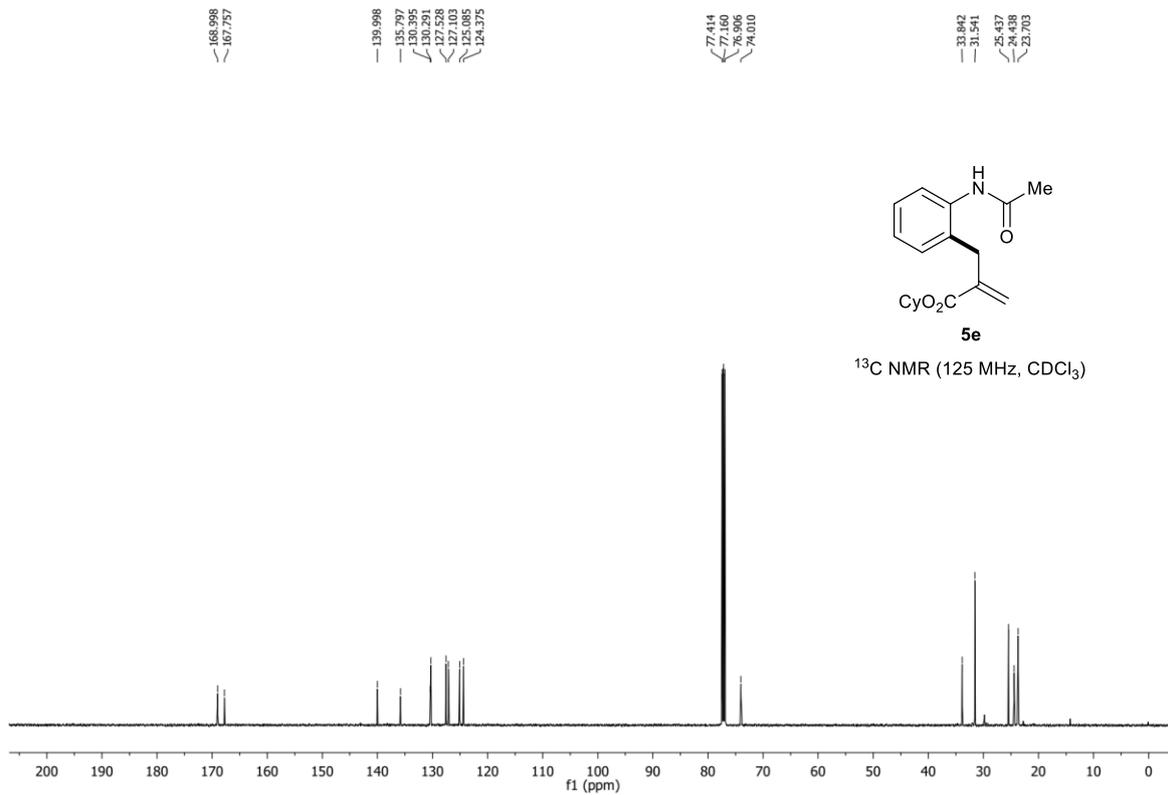
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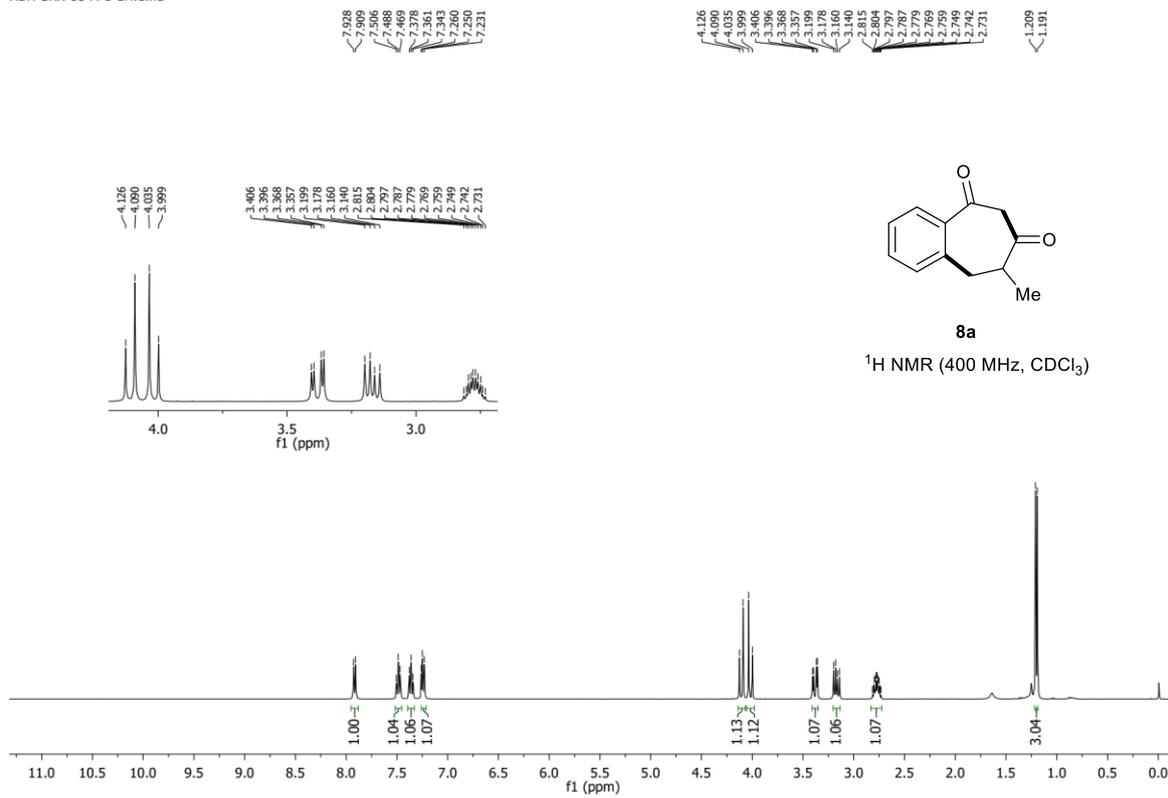
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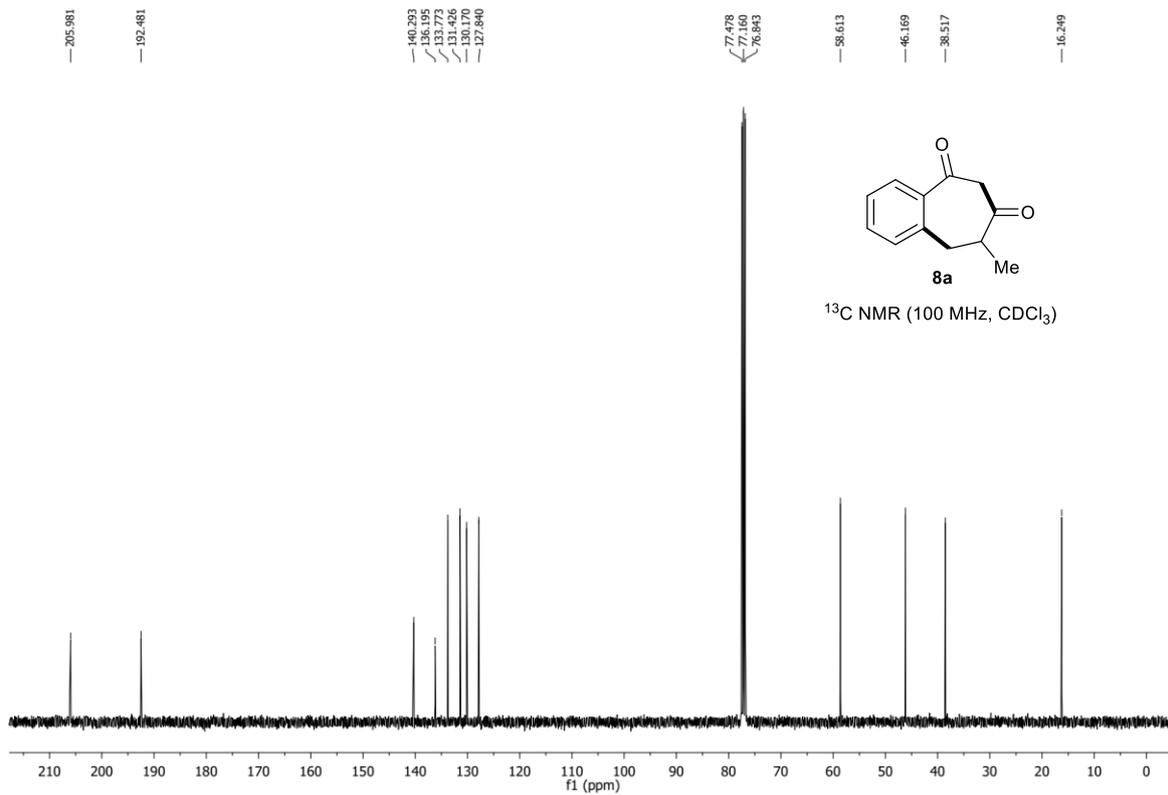
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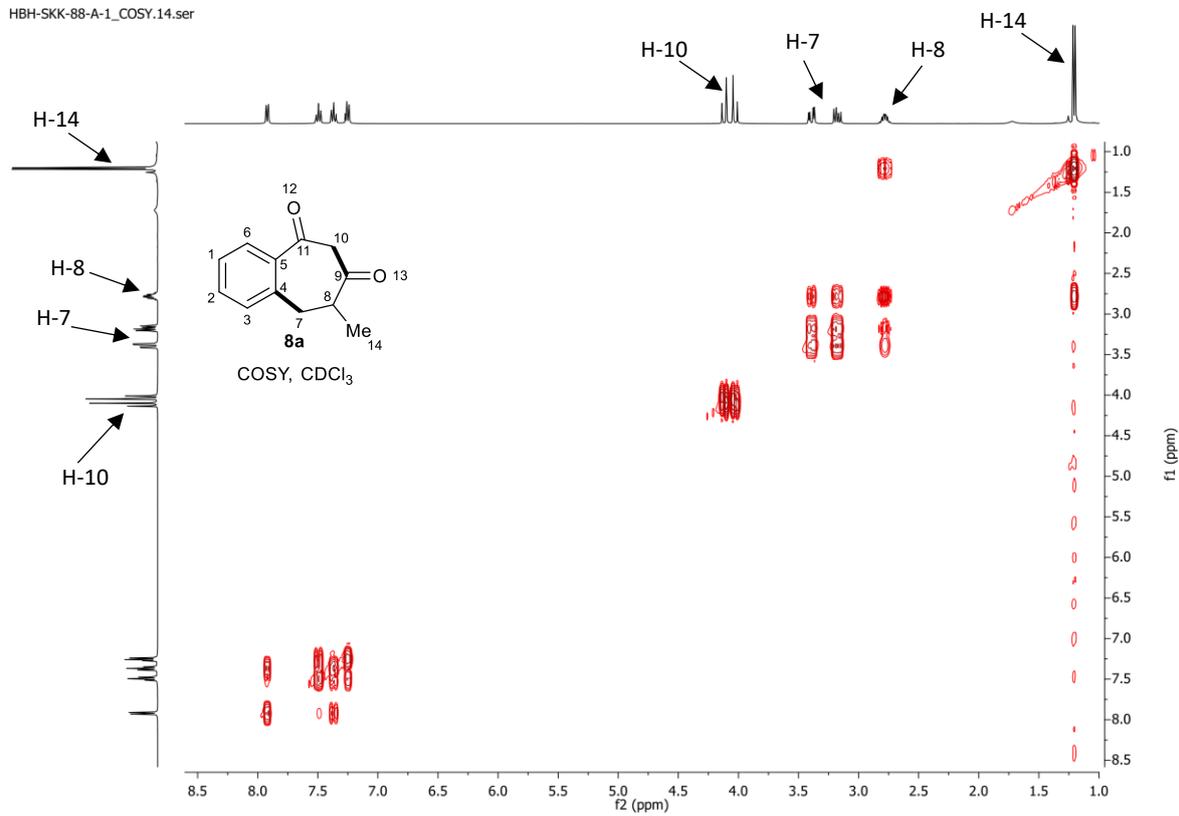
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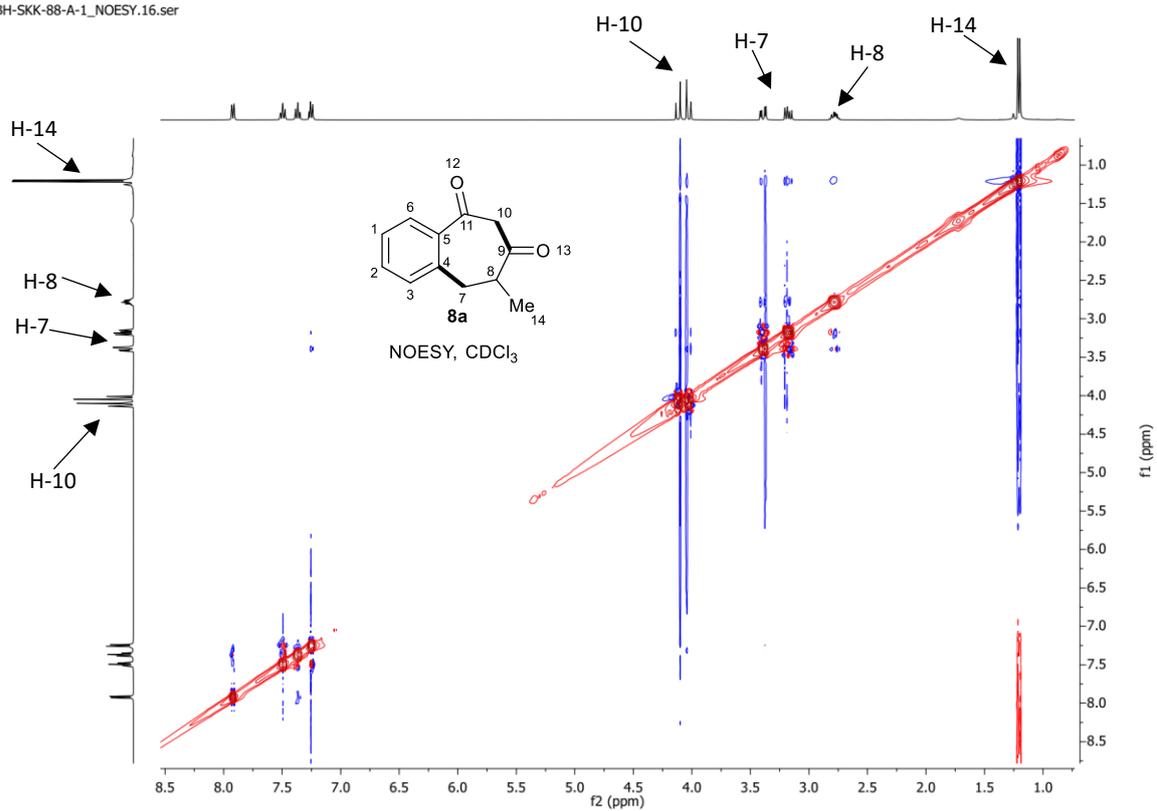
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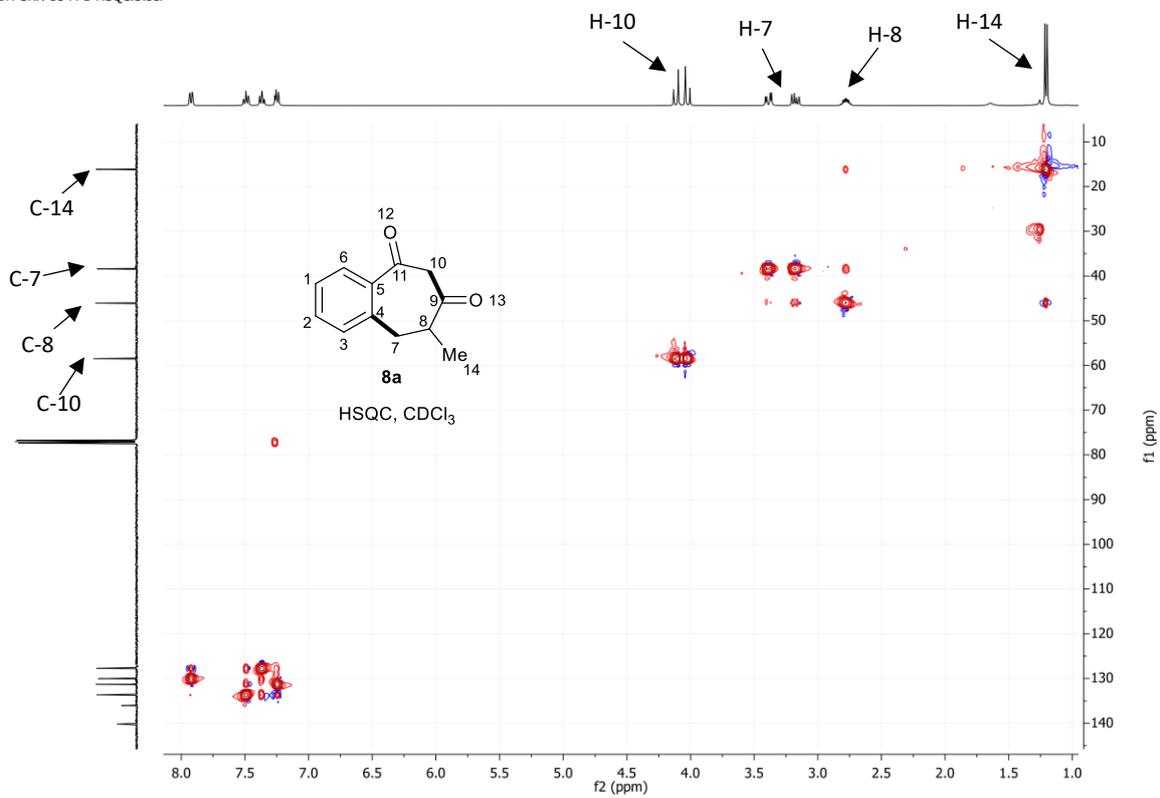
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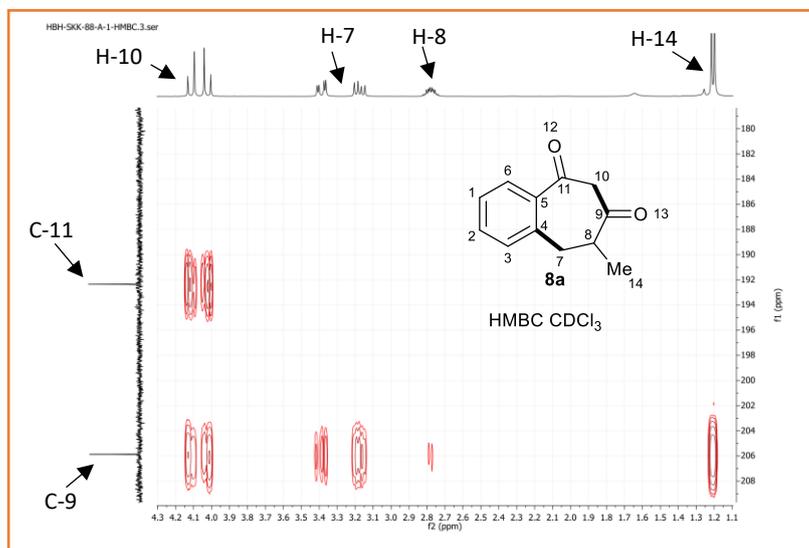
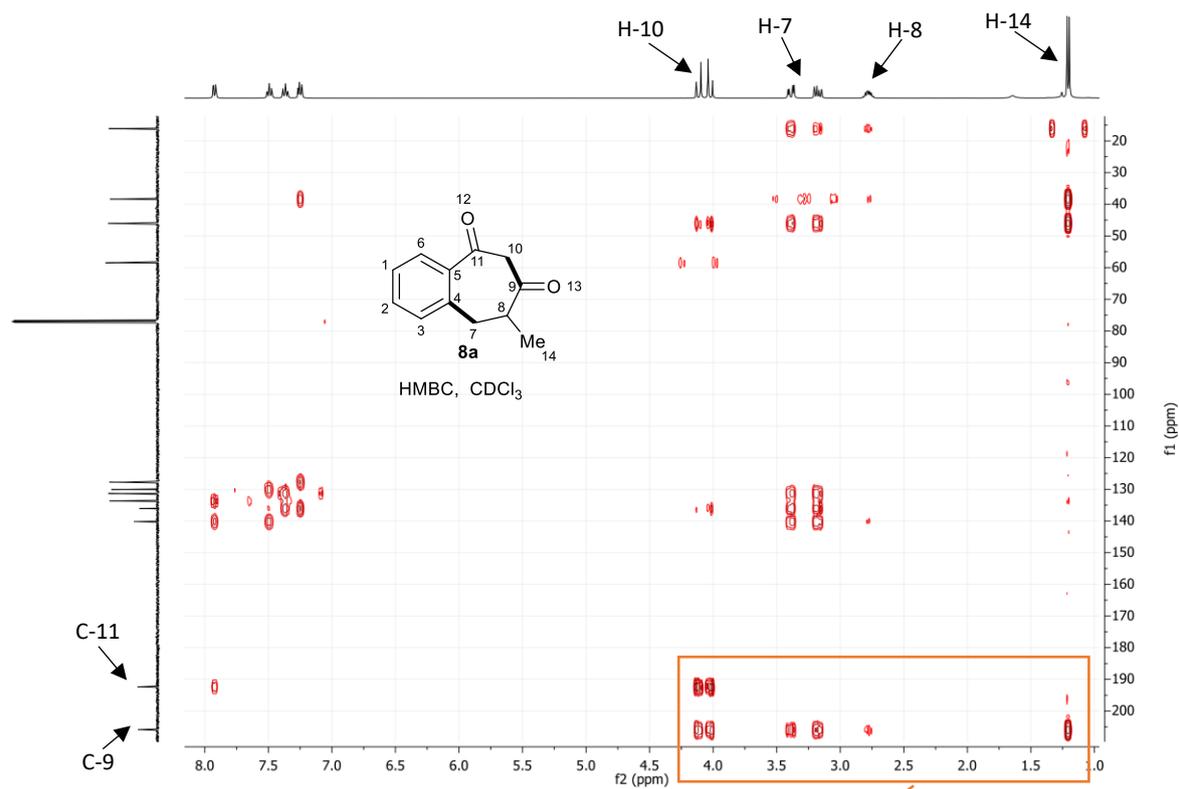


HBH-SKK-88-A-1_NOESY.16.ser

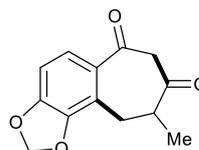
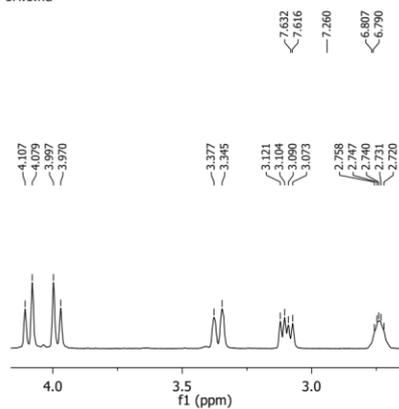


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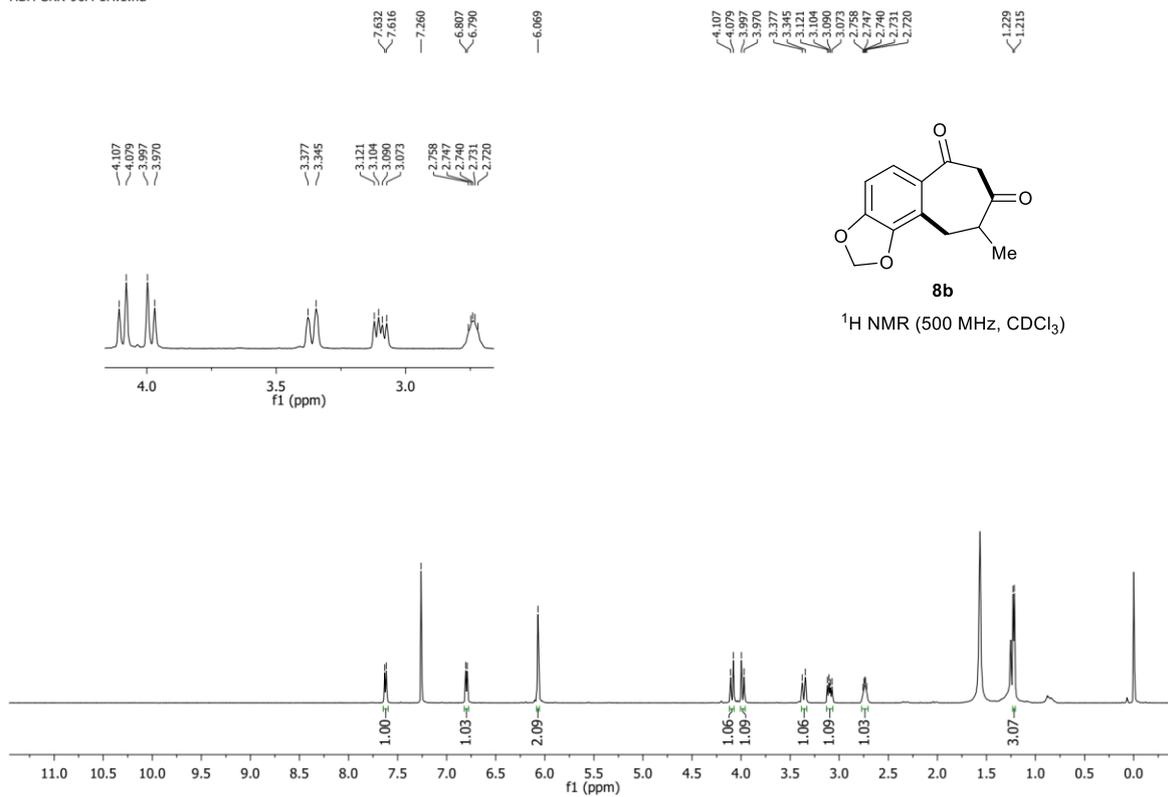


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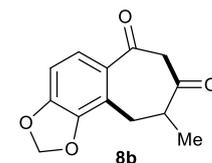
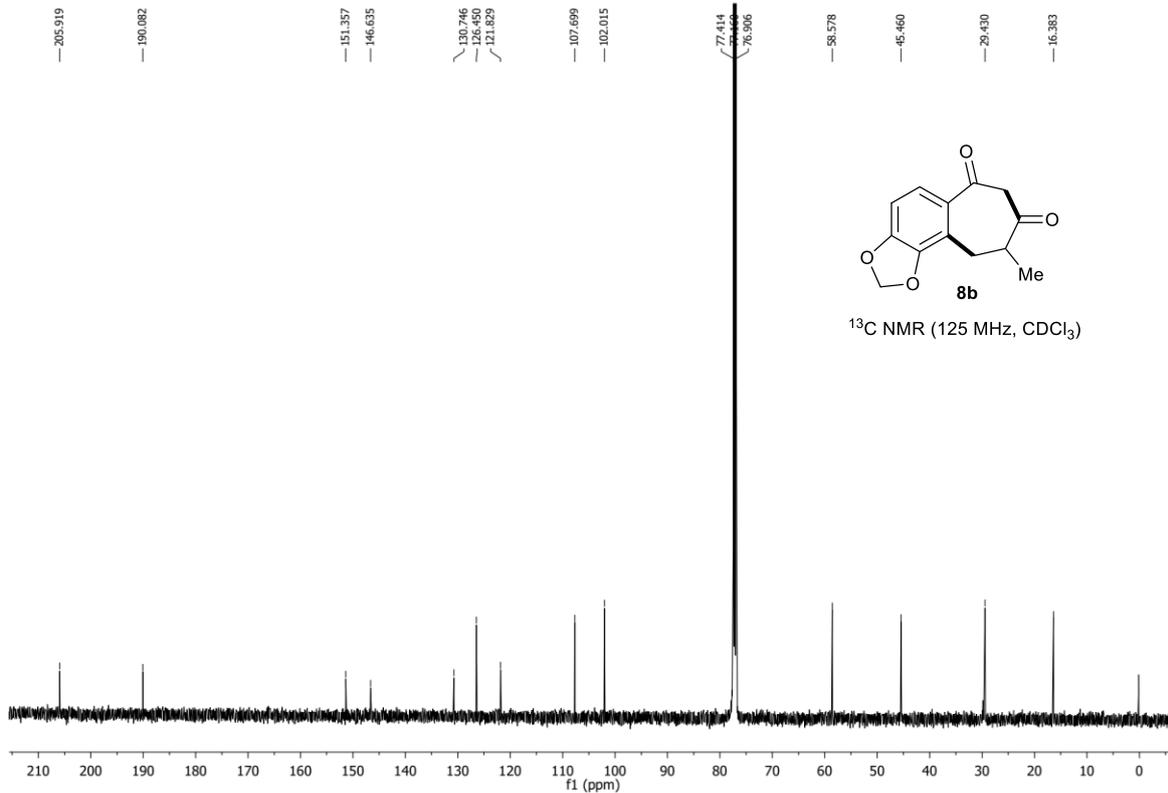


8b

¹H NMR (500 MHz, CDCl₃)



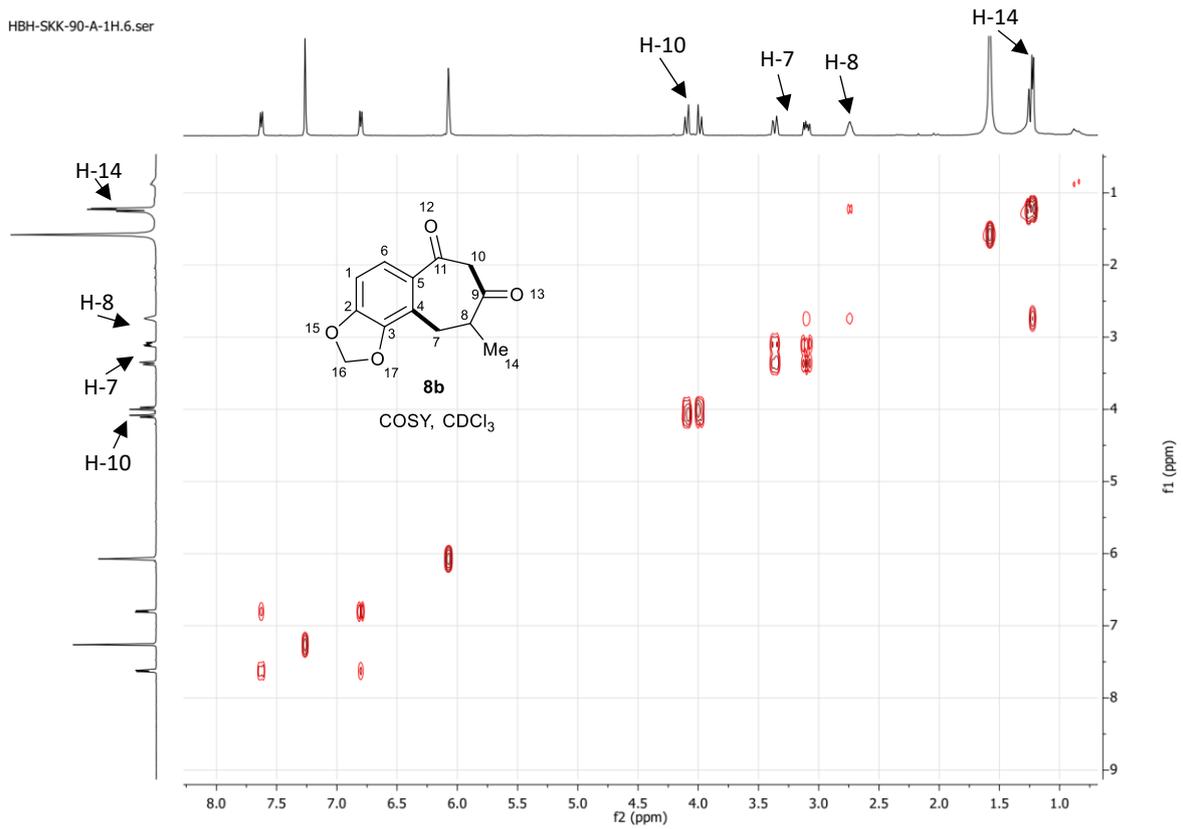
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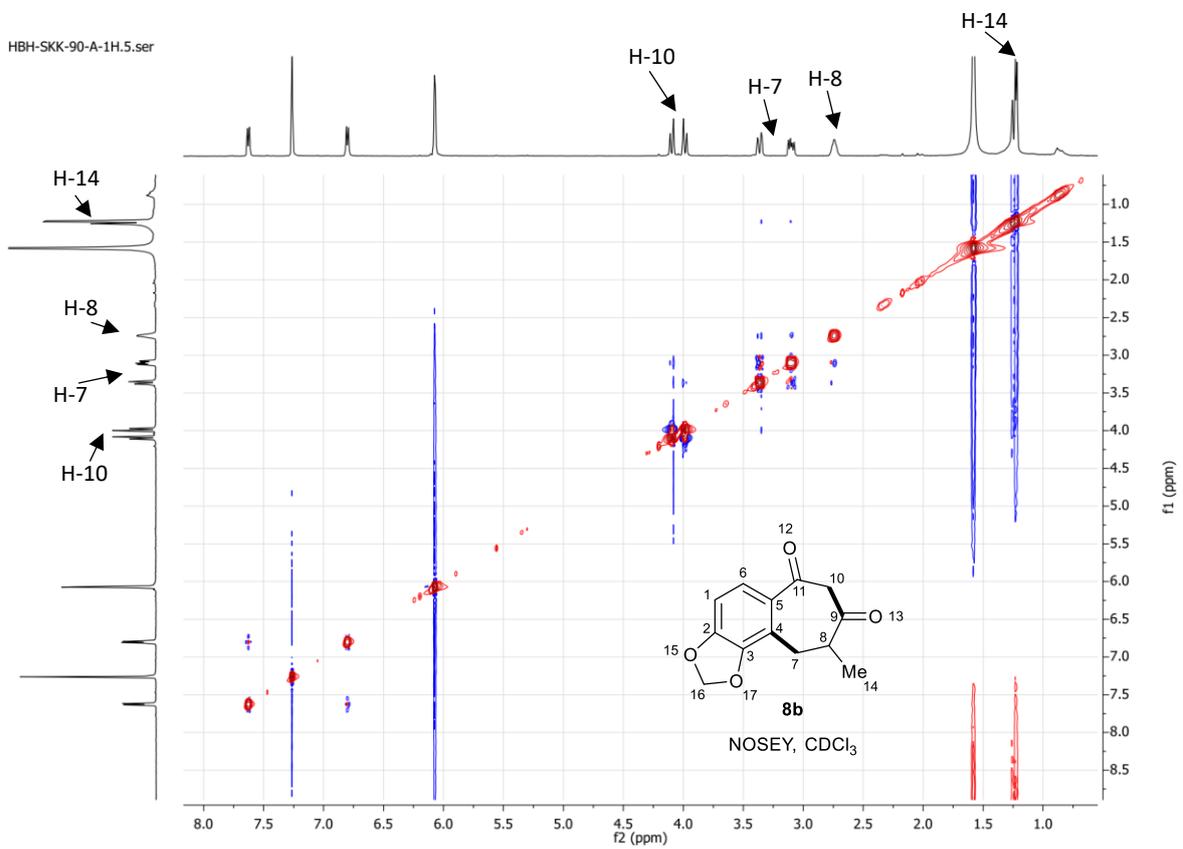
8b

¹³C NMR (125 MHz, CDCl₃)

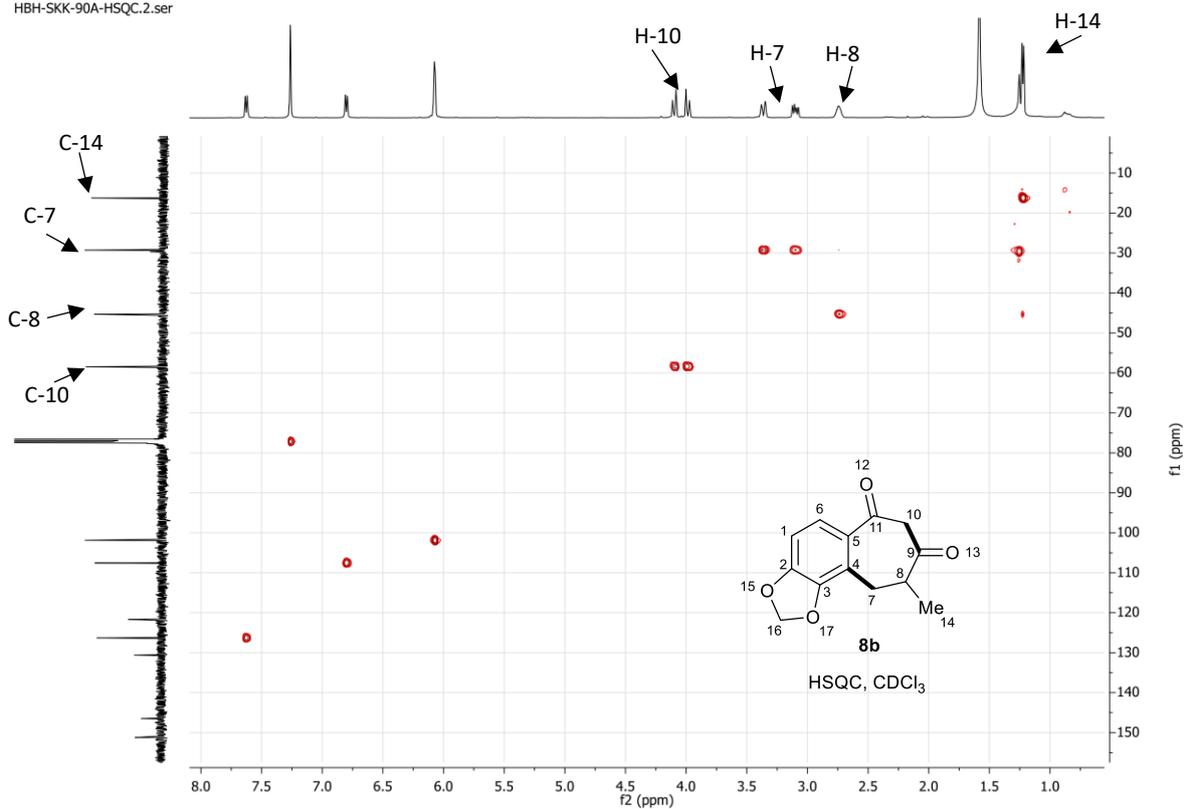
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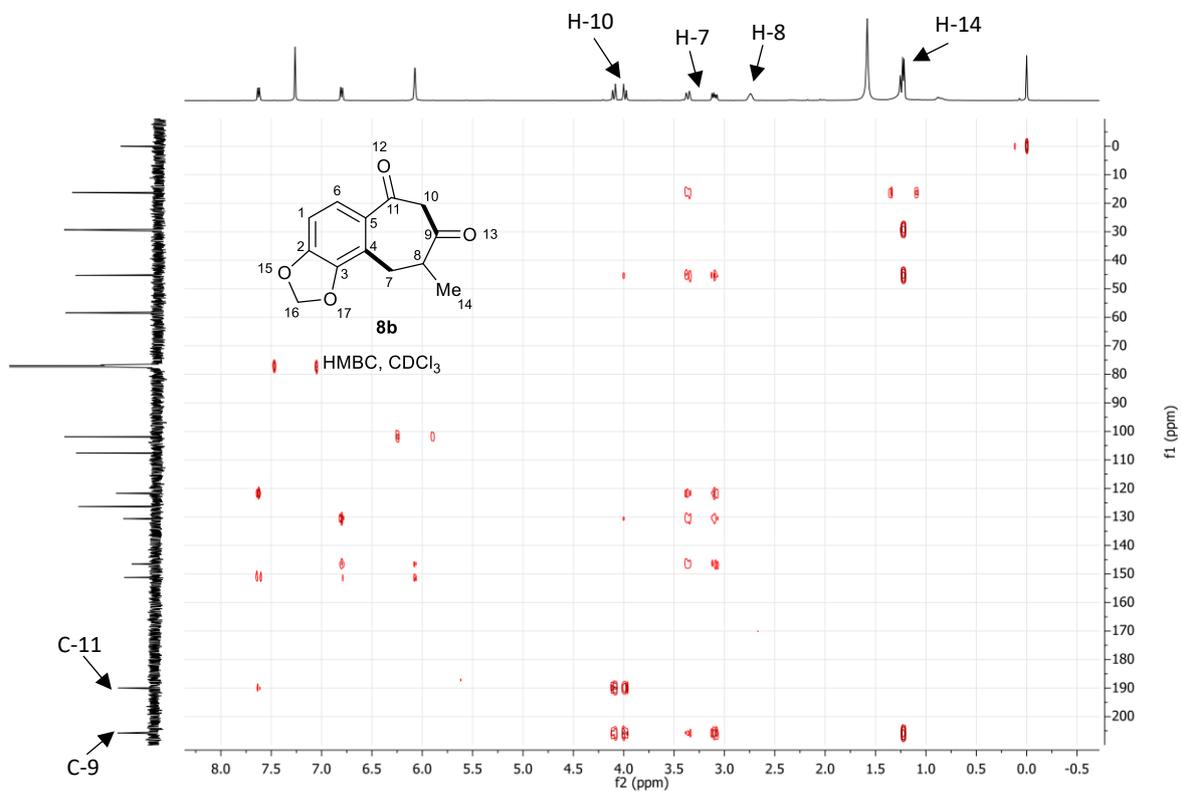
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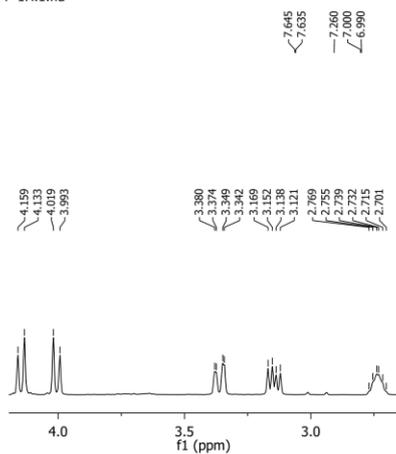
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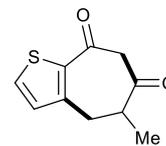
HBH-SKK-90A-HMBC.4.ser



HBH-SKK-93-P-1H.1.fid

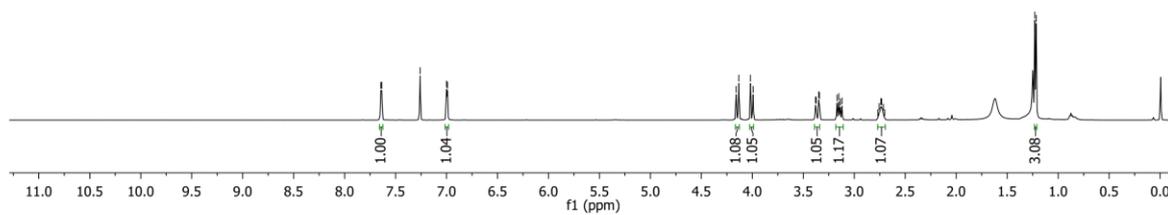


4.159
4.133
4.019
3.993
3.380
3.374
3.349
3.342
3.159
3.152
3.138
3.121
2.769
2.755
2.739
2.732
2.715
2.701

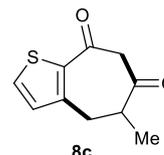
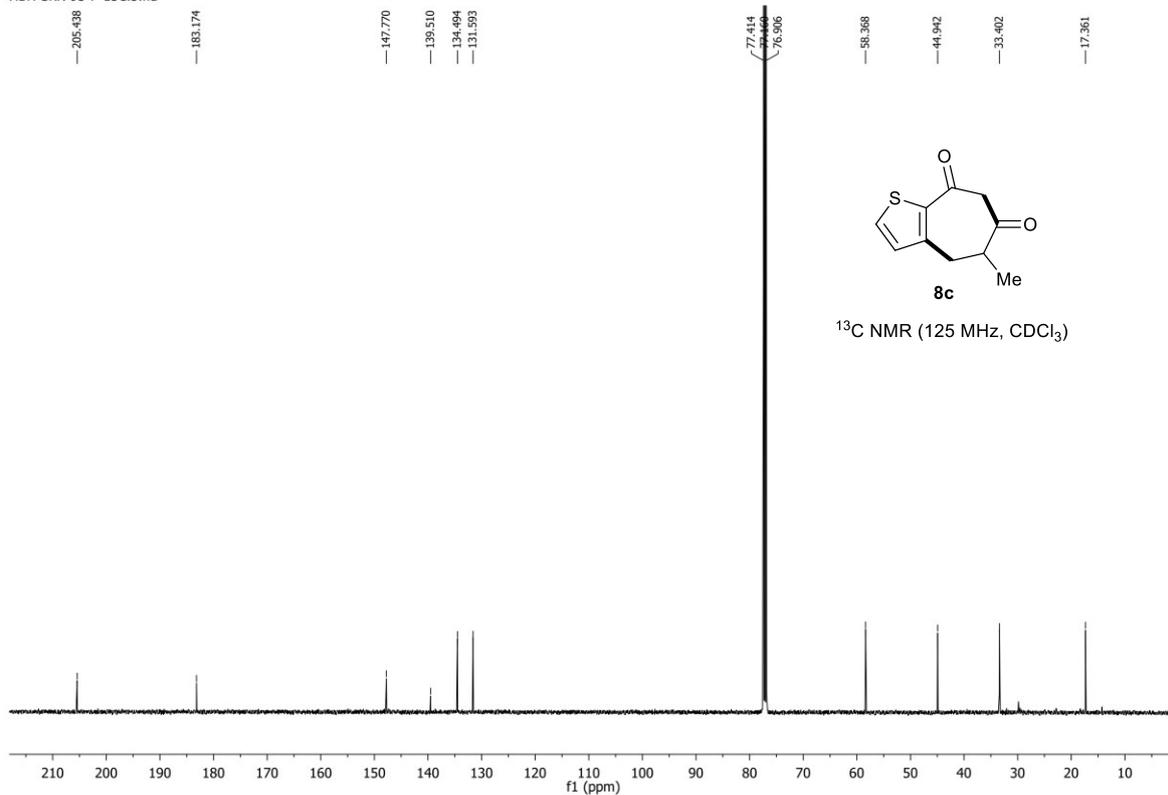


8c

¹H NMR (500 MHz, CDCl₃)



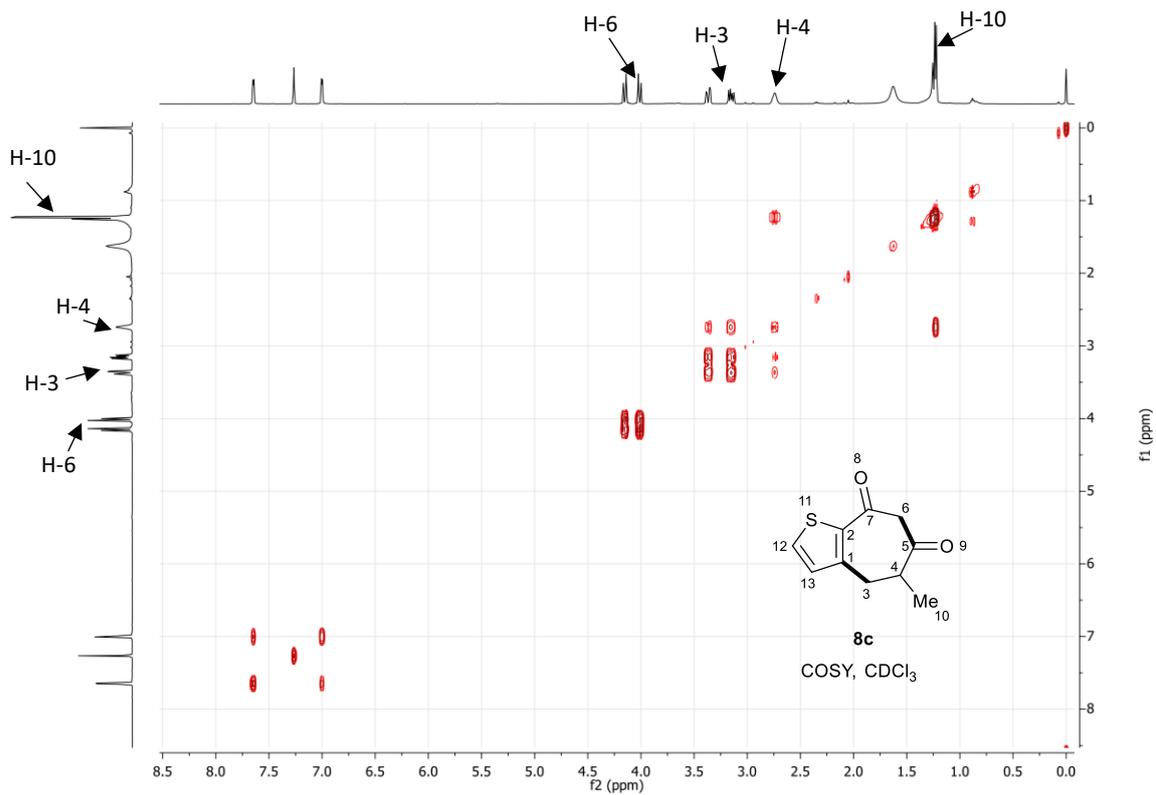
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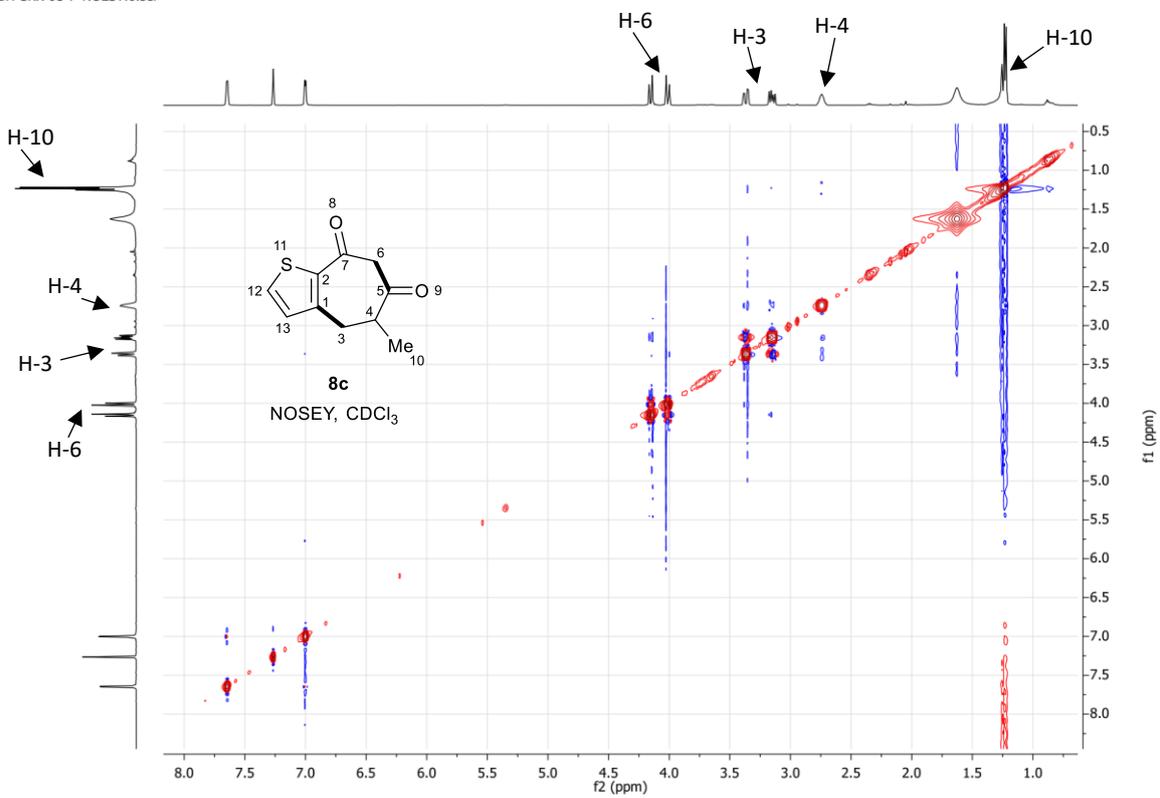
8c

¹³C NMR (125 MHz, CDCl₃)

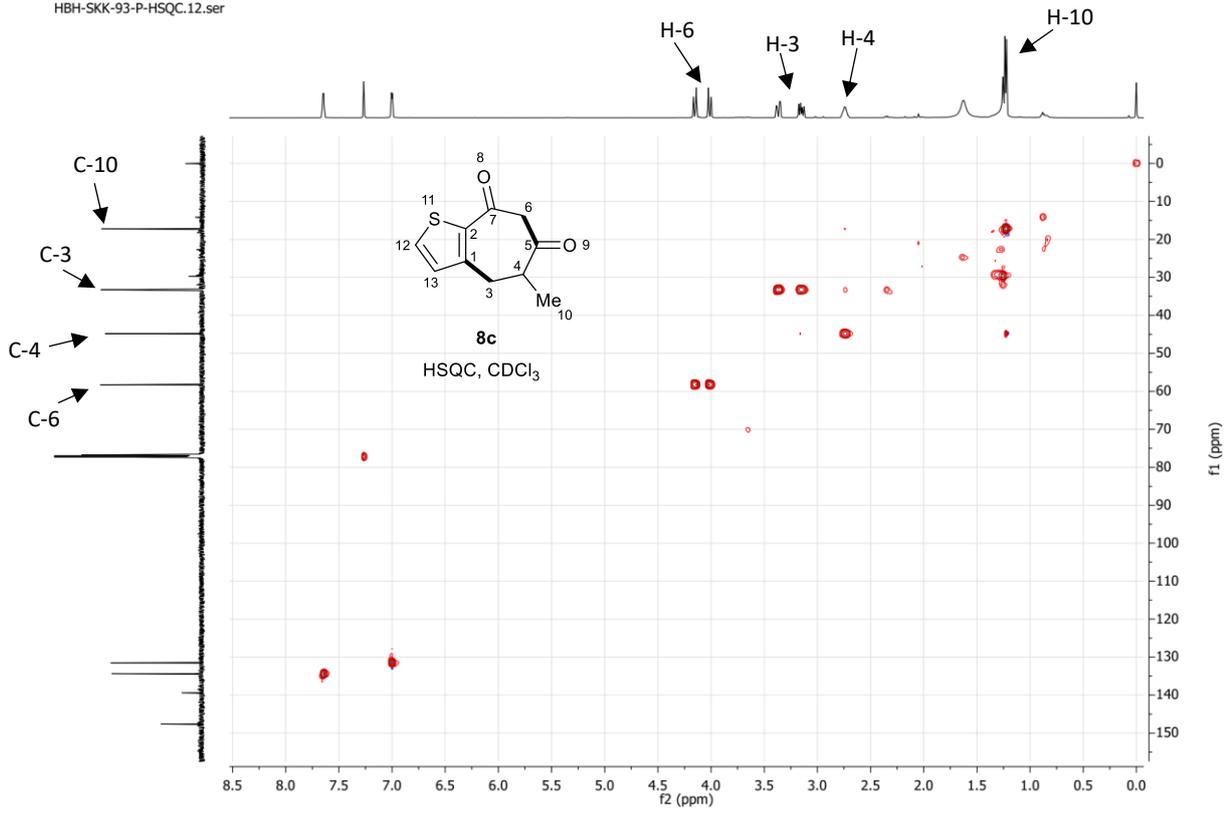
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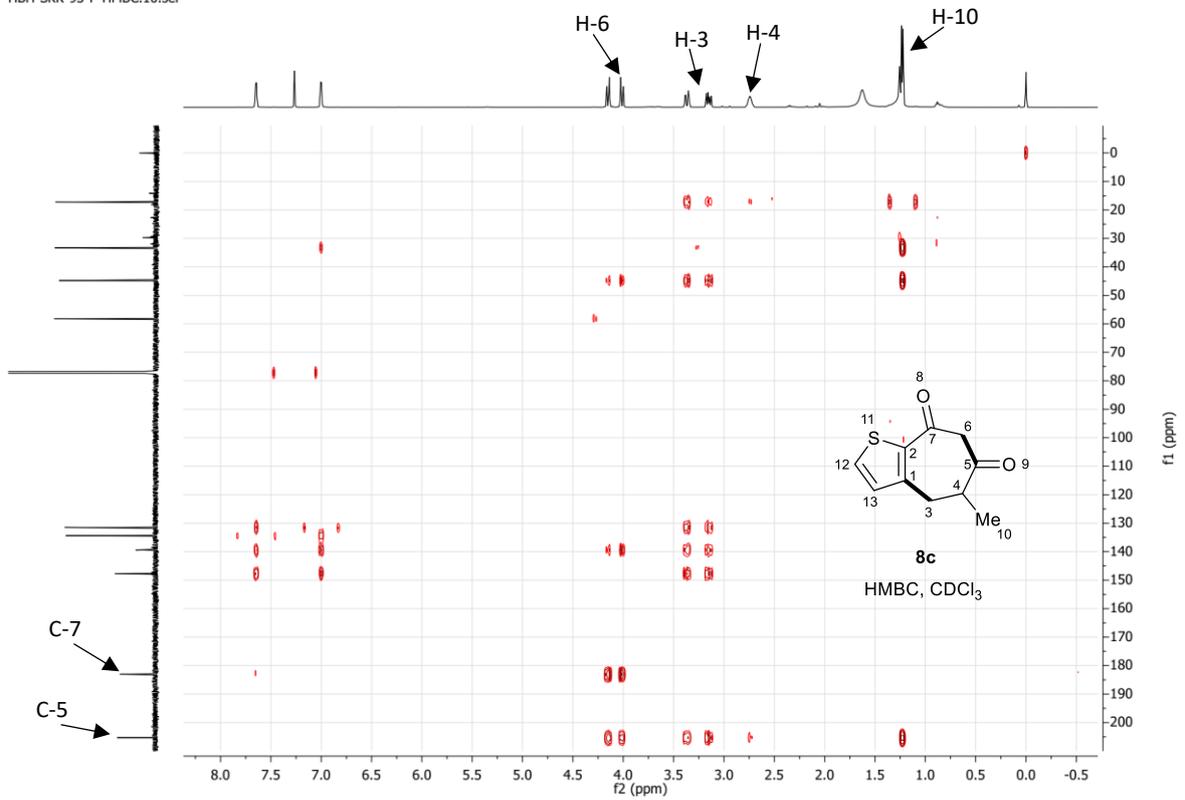
HBH-SKK-93-P-NOESY.6.ser



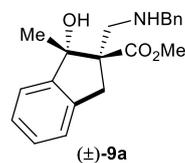
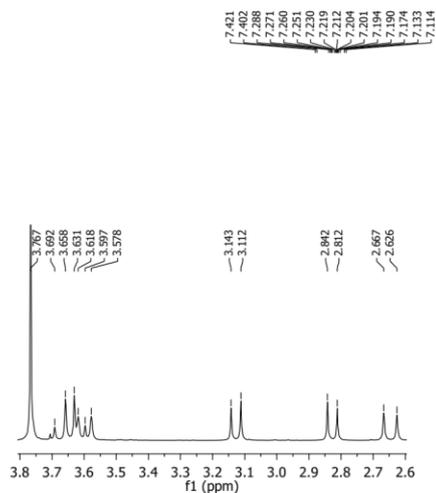
HBH-SKK-93-P-HSQC.12.ser



HBH-SKK-93-P-HMBC.10.ser

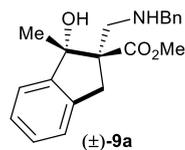
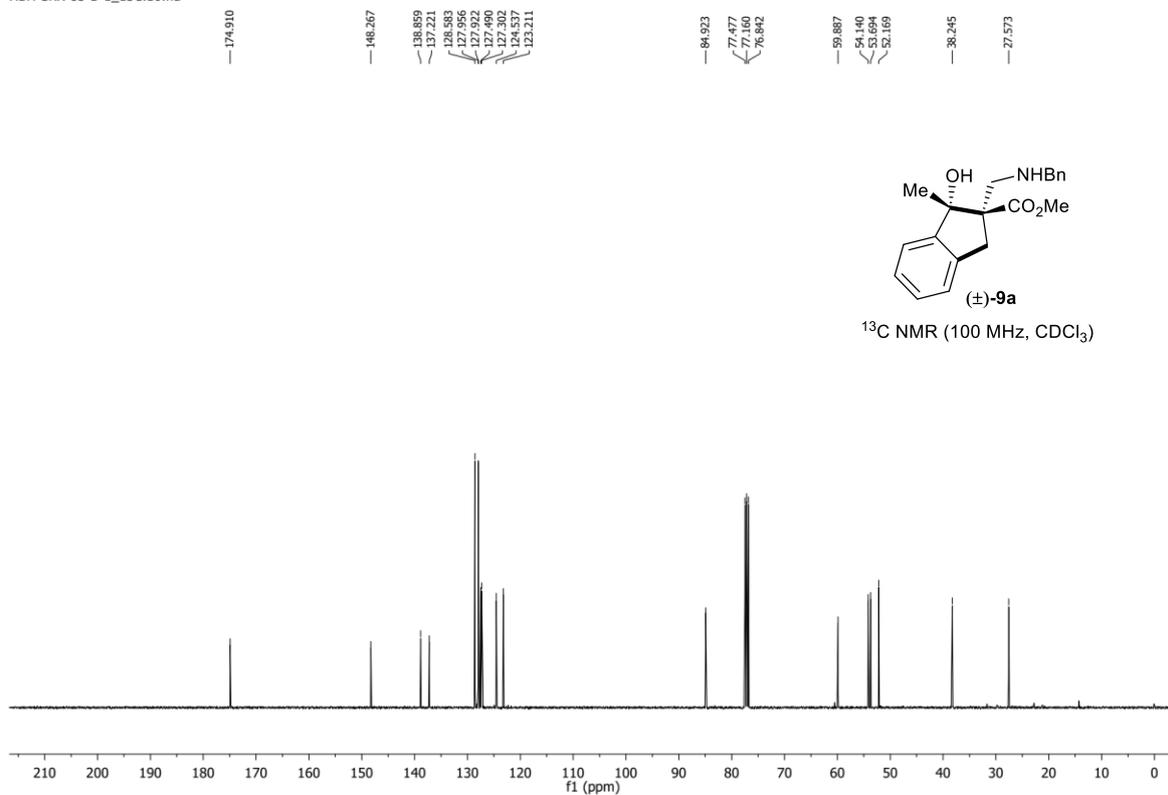


HBH-SKK-85-B-1-1H.1.fid



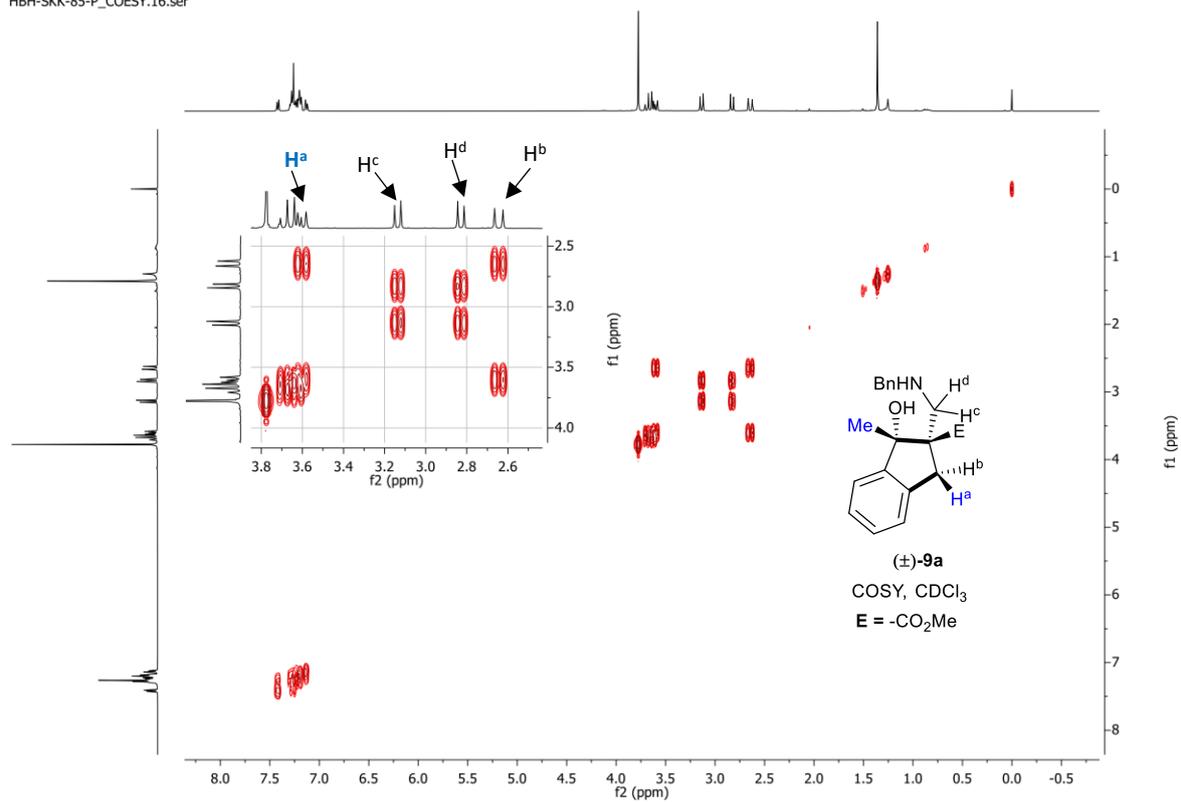
¹H NMR (400 MHz, CDCl₃)

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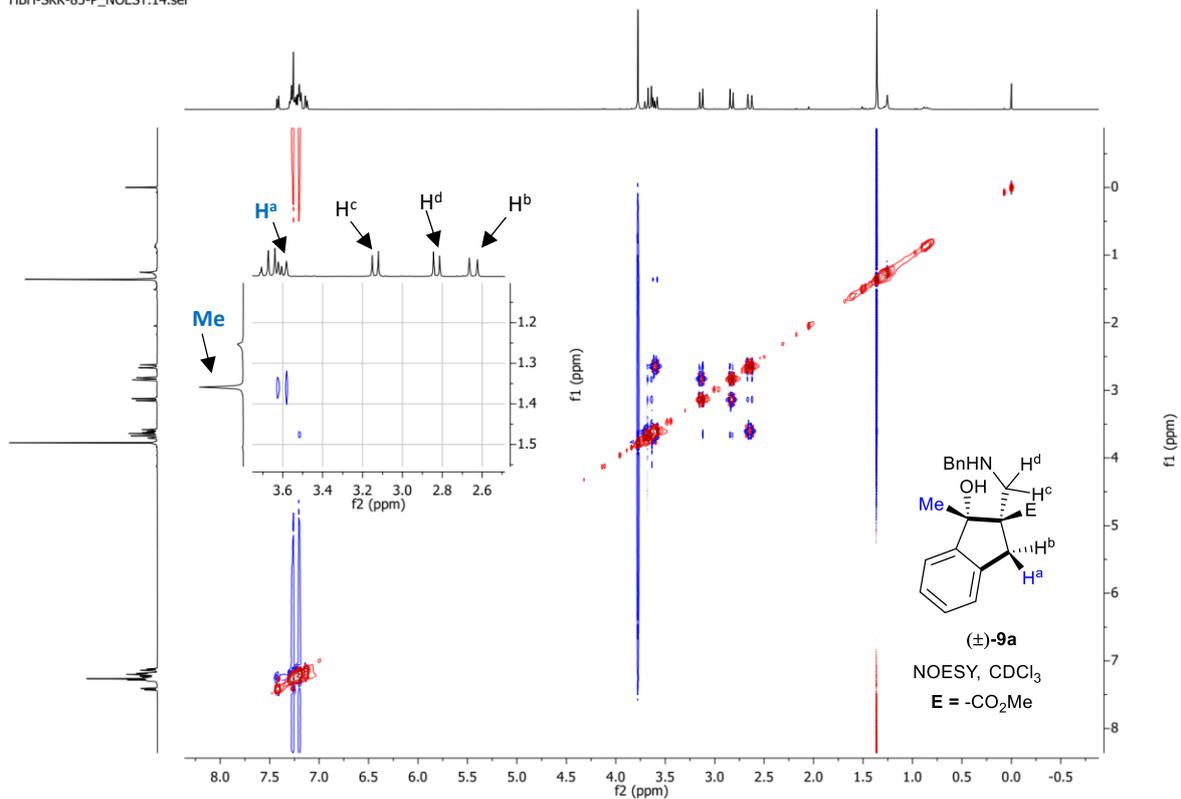


¹³C NMR (100 MHz, CDCl₃)

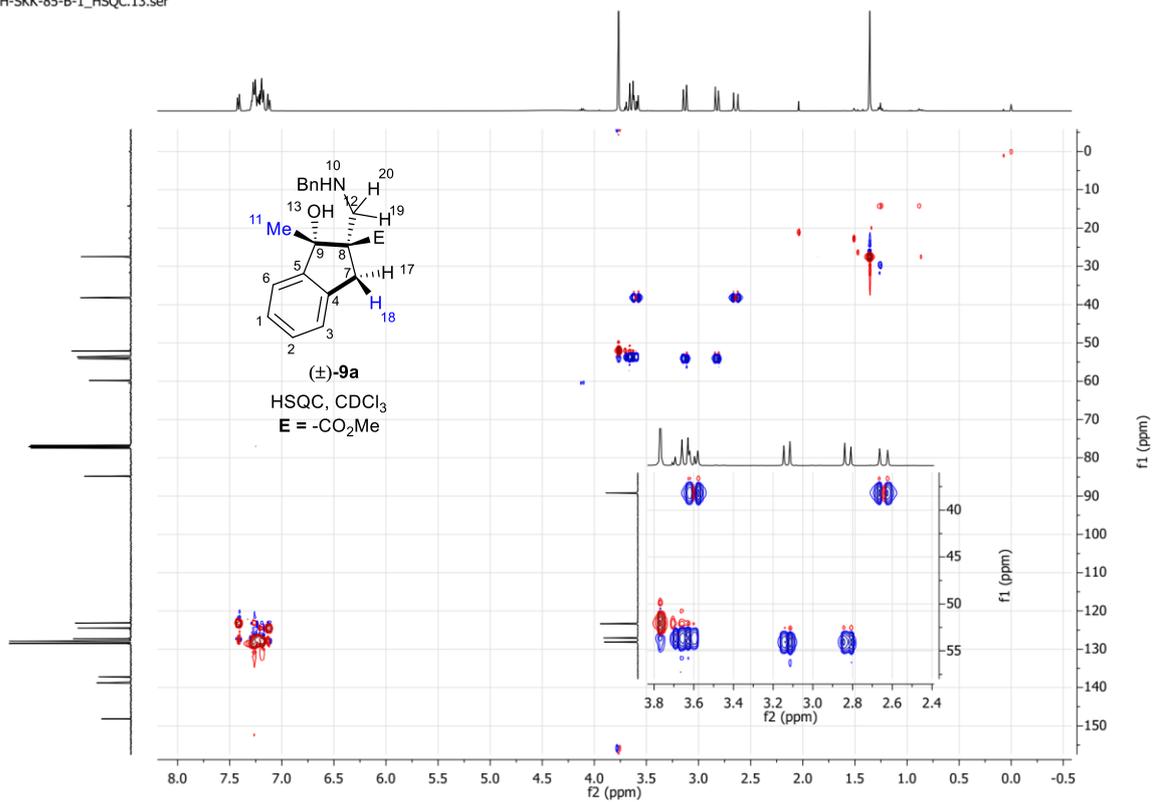
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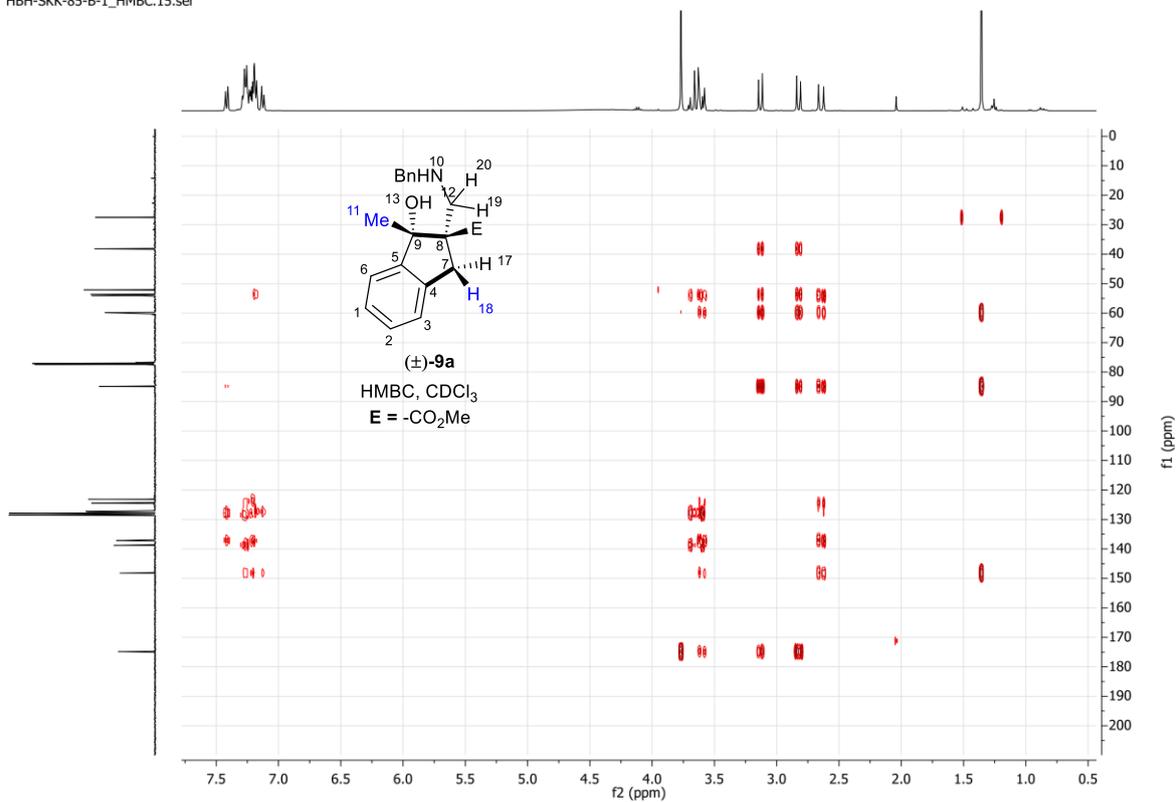
HBH-SKK-85-P_NOESY.14.ser



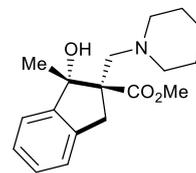
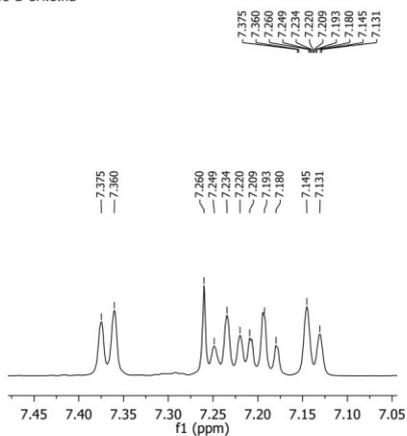
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HBH-SKK-85-B-1_HMBC.15.ser

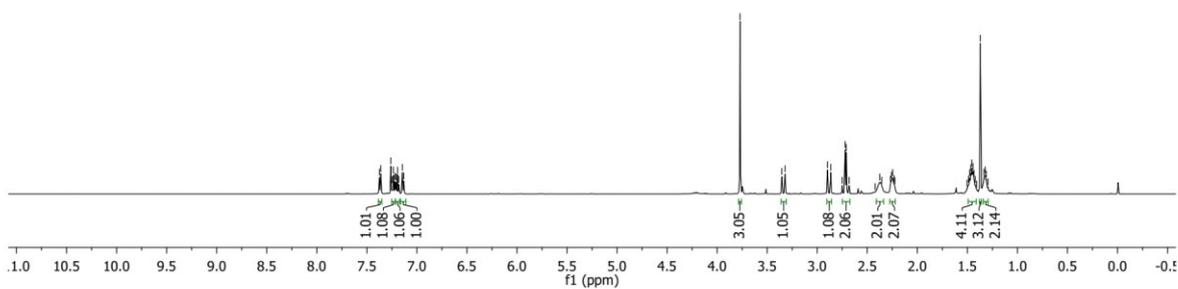


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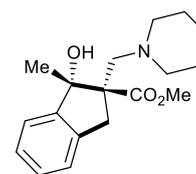
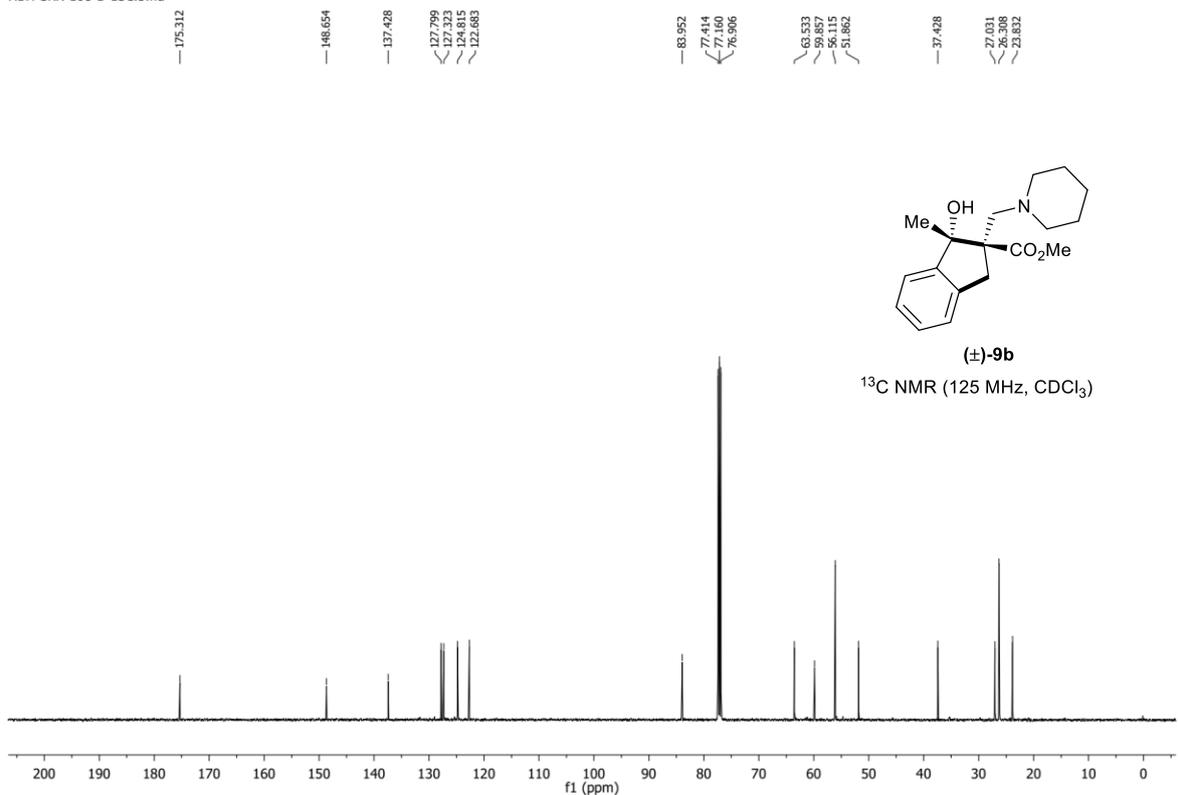


(±)-9b

¹H NMR (500 MHz, CDCl₃)



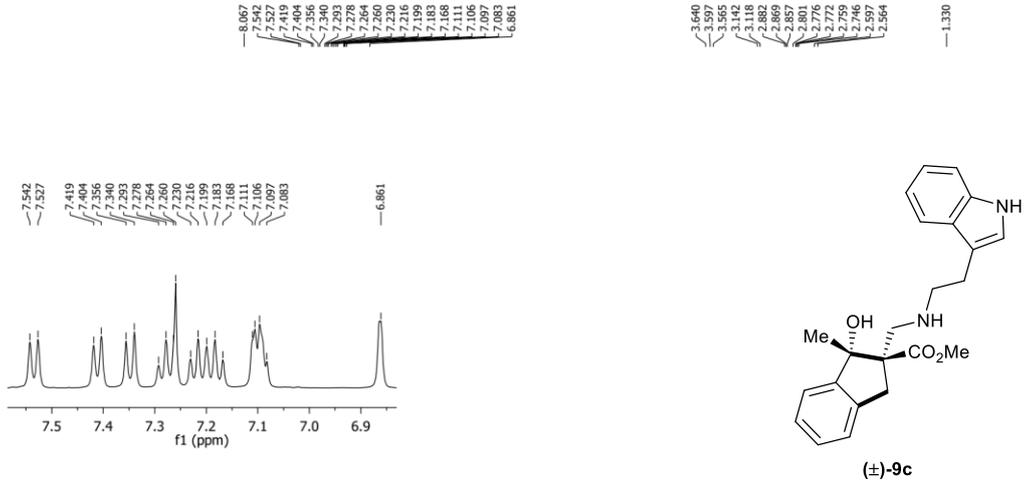
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(±)-9b

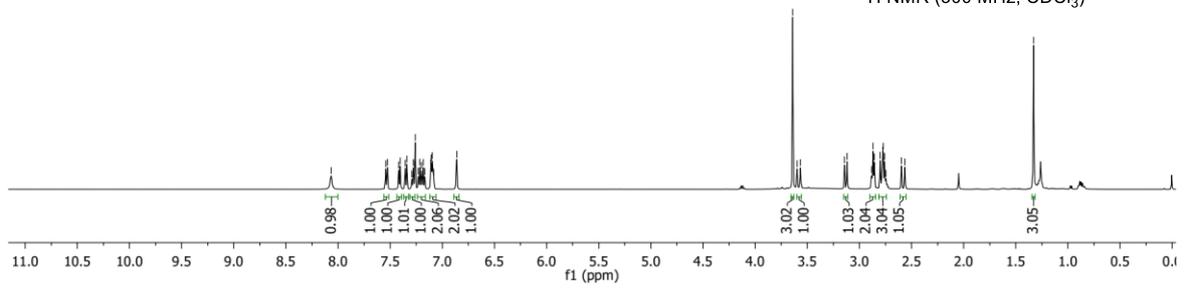
¹³C NMR (125 MHz, CDCl₃)

HBH-SKK-118-UP-1-1H.1.fid



(±)-9c

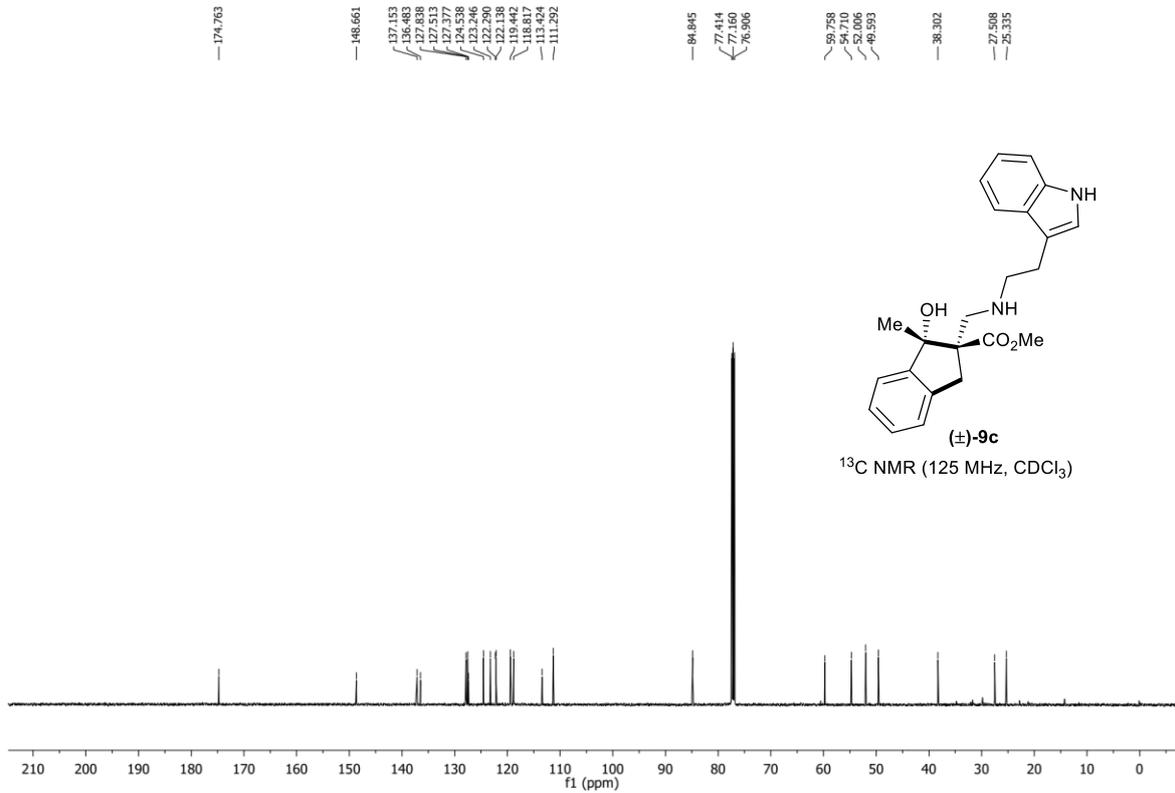
¹H NMR (500 MHz, CDCl₃)



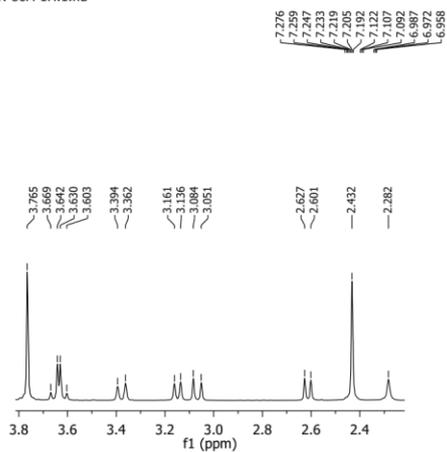
(±)-9c

¹³C NMR (125 MHz, CDCl₃)

HBH-SKK-118-UP-1-13C.6.fid



HBH-SKK-86A-1H.1.fid

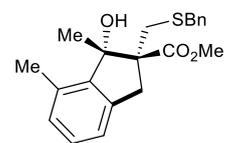


7.276
7.259
7.247
7.233
7.219
7.205
7.192
7.172
7.107
7.092
6.987
6.972
6.958

3.765
3.669
3.642
3.630
3.603
3.394
3.362
3.161
3.136
3.084
3.051
2.627
2.601
2.432
2.282

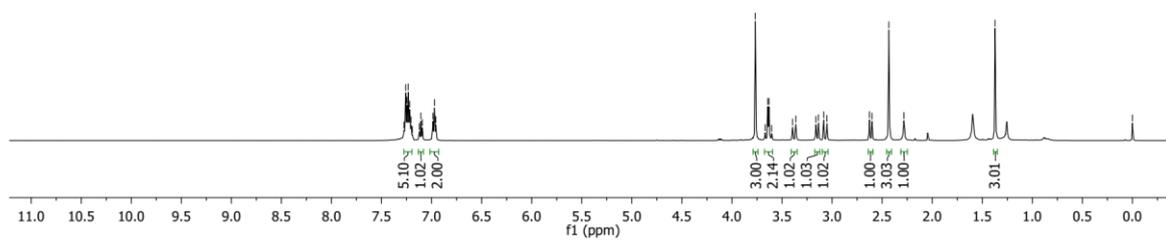
1.372

0.000



(±)-10

¹H NMR (500 MHz, CDCl₃)



HBH-SKK-86A-13C.3.fid

174.346

141.648
138.322
137.859
134.835
129.949
128.878
128.749
127.144
122.901

85.278

77.414
77.160
76.906

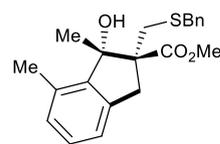
64.166

52.216

37.839
37.581
35.539

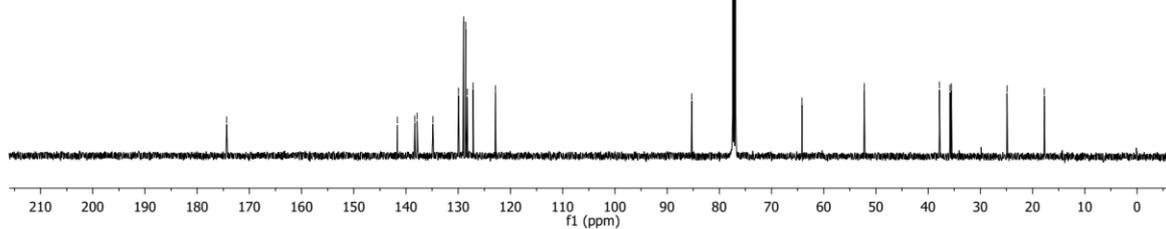
24.888

17.753

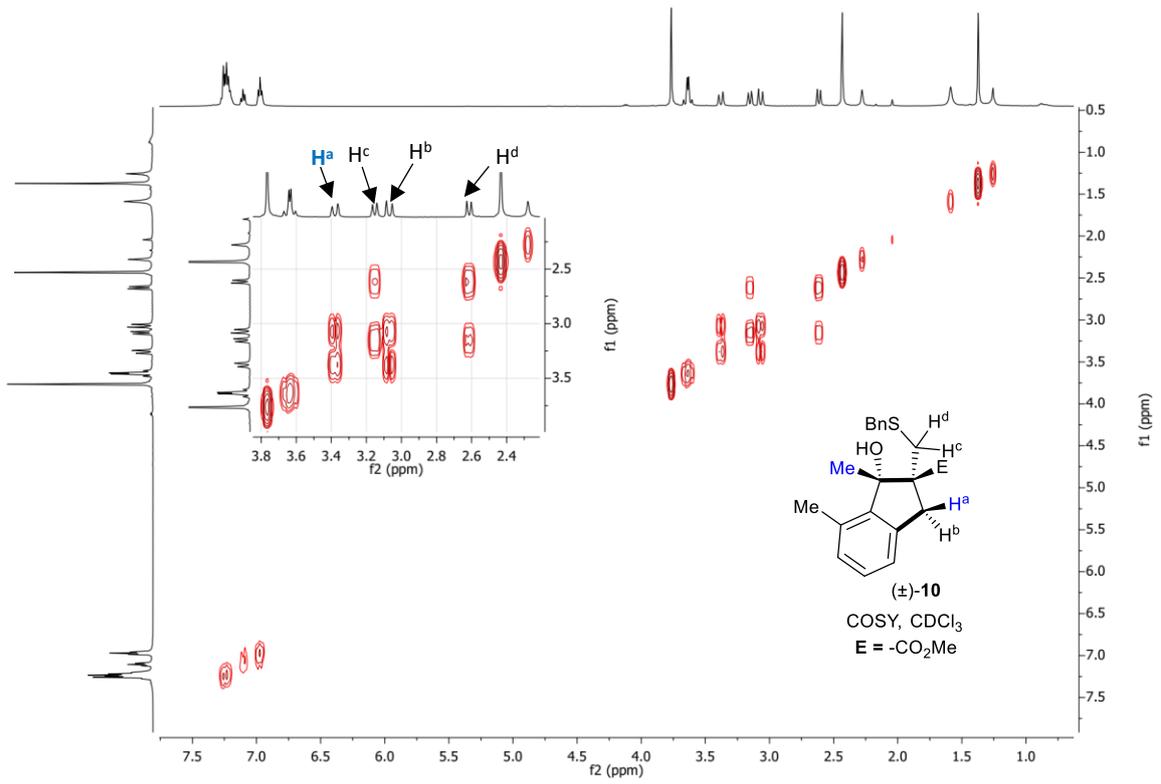


(±)-10

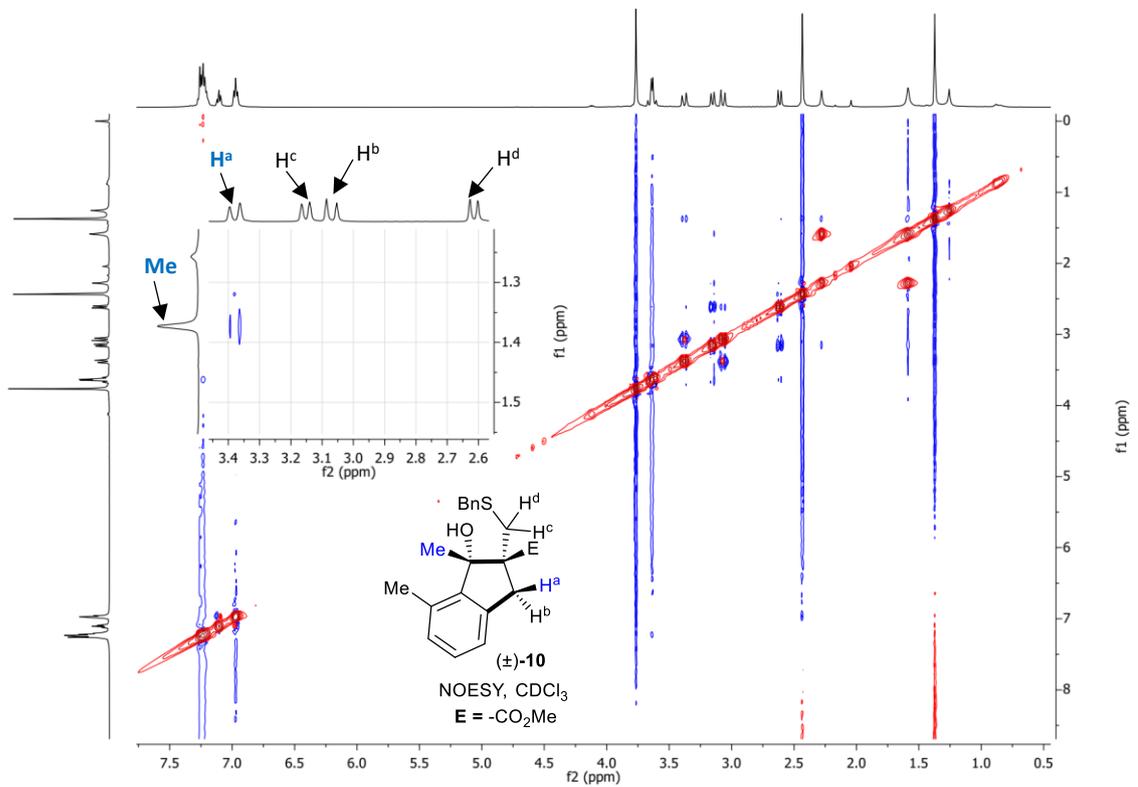
¹³C NMR (125 MHz, CDCl₃)



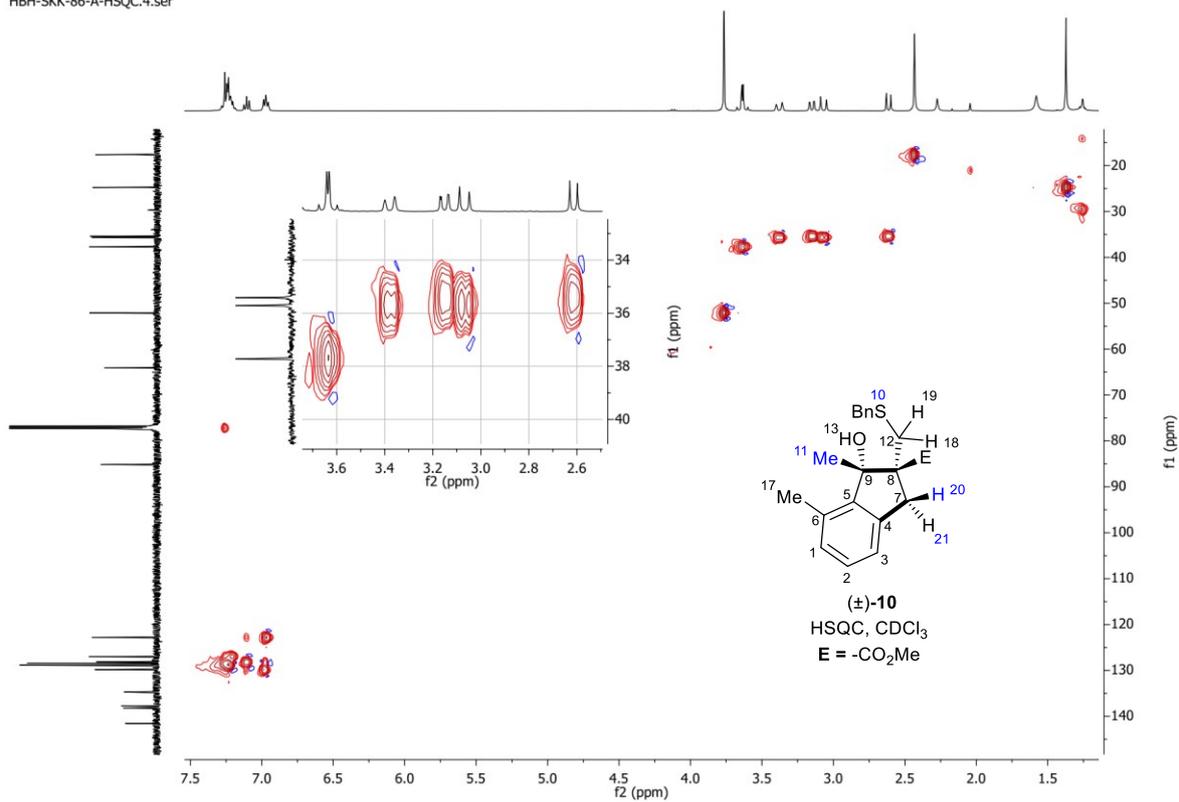
HBH-SKK-86-A-COSY.6.ser



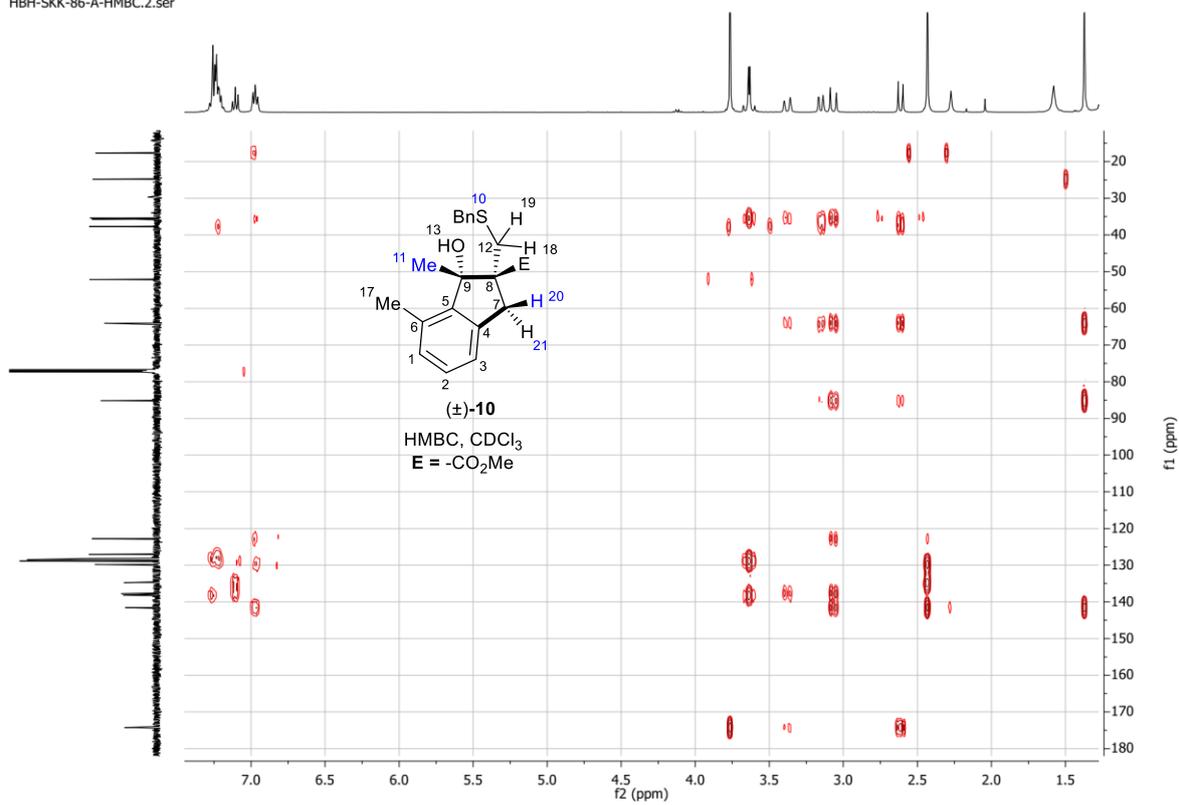
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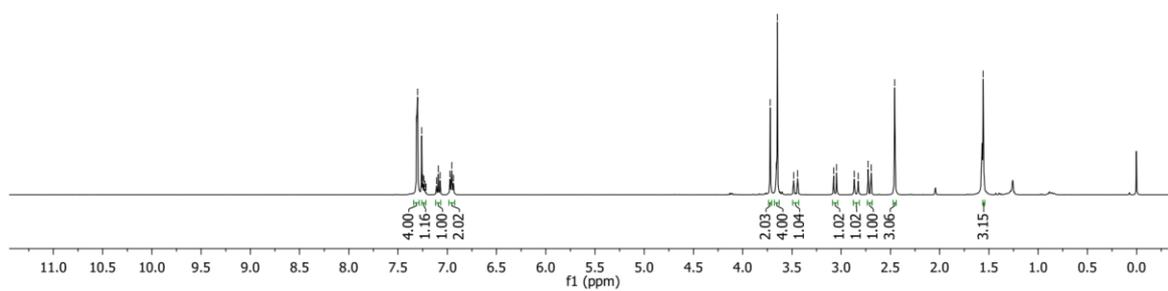
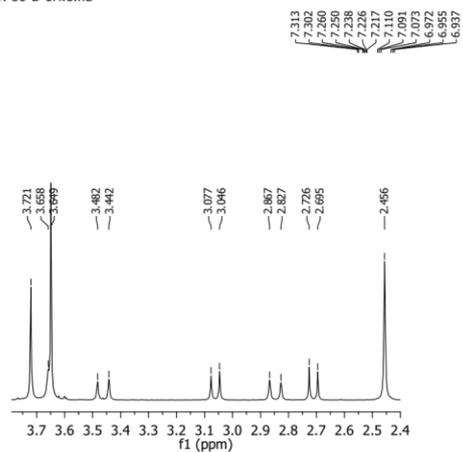
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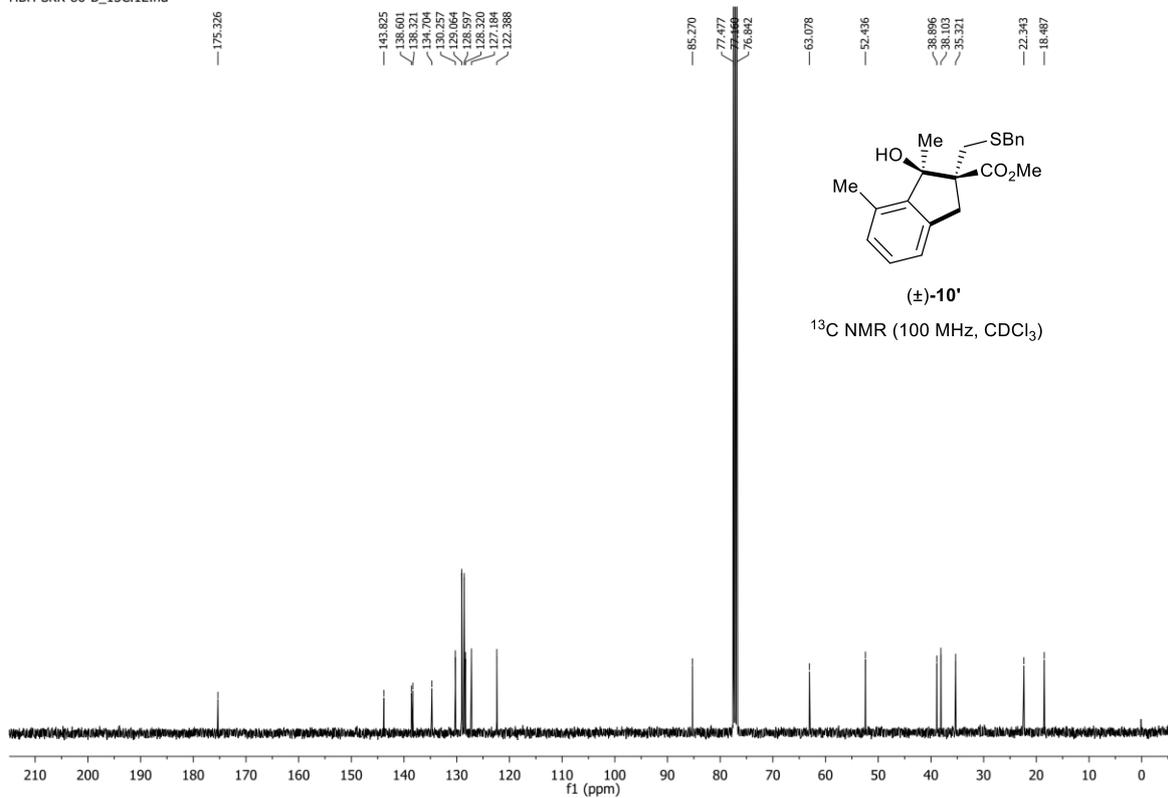
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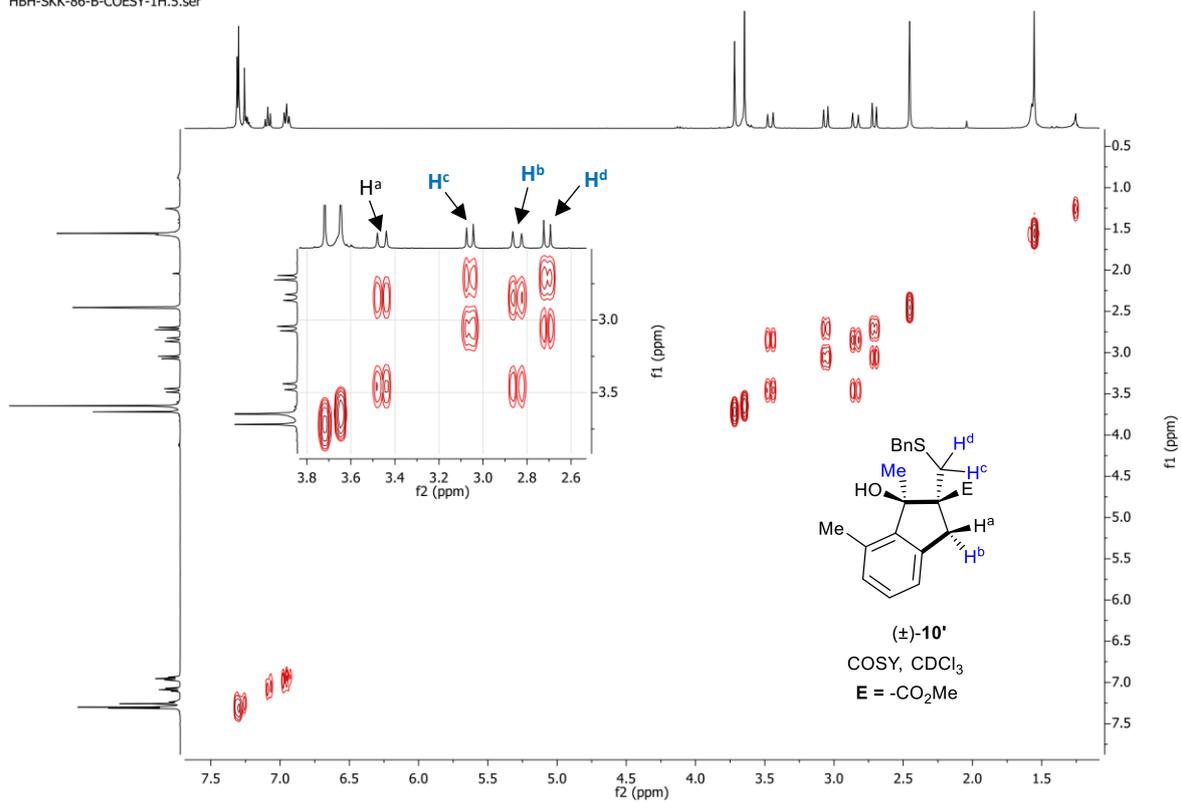
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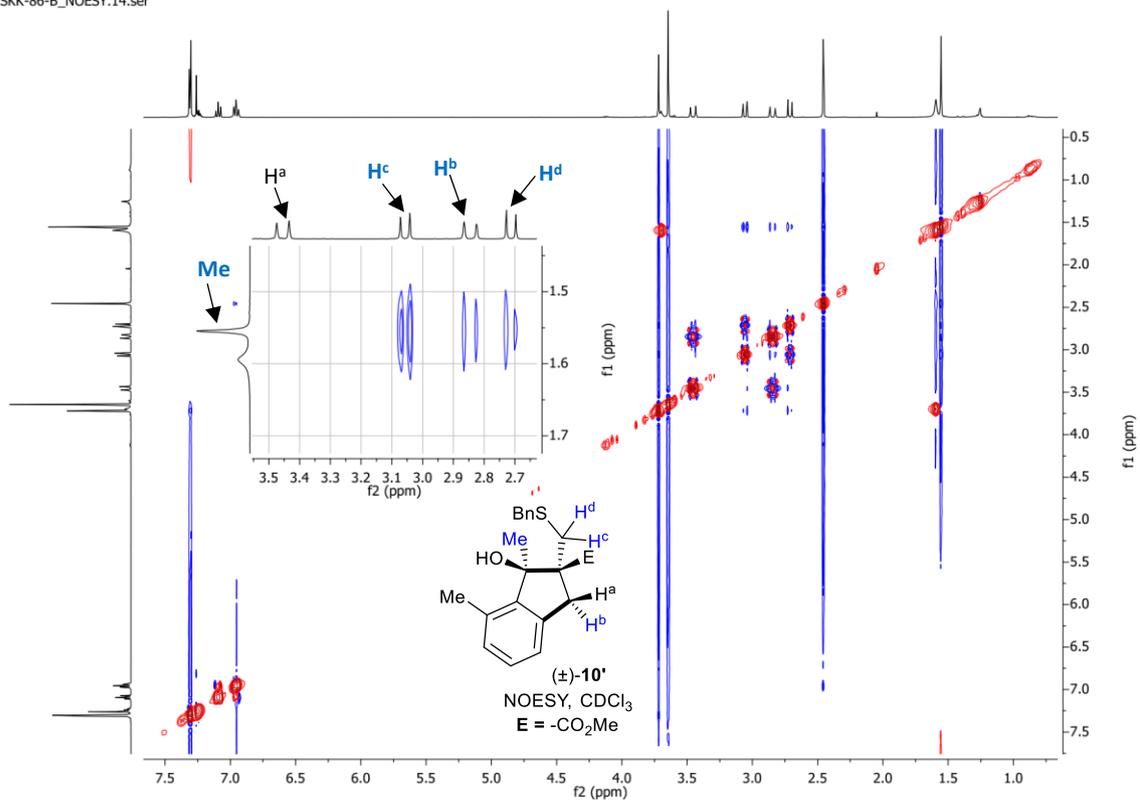
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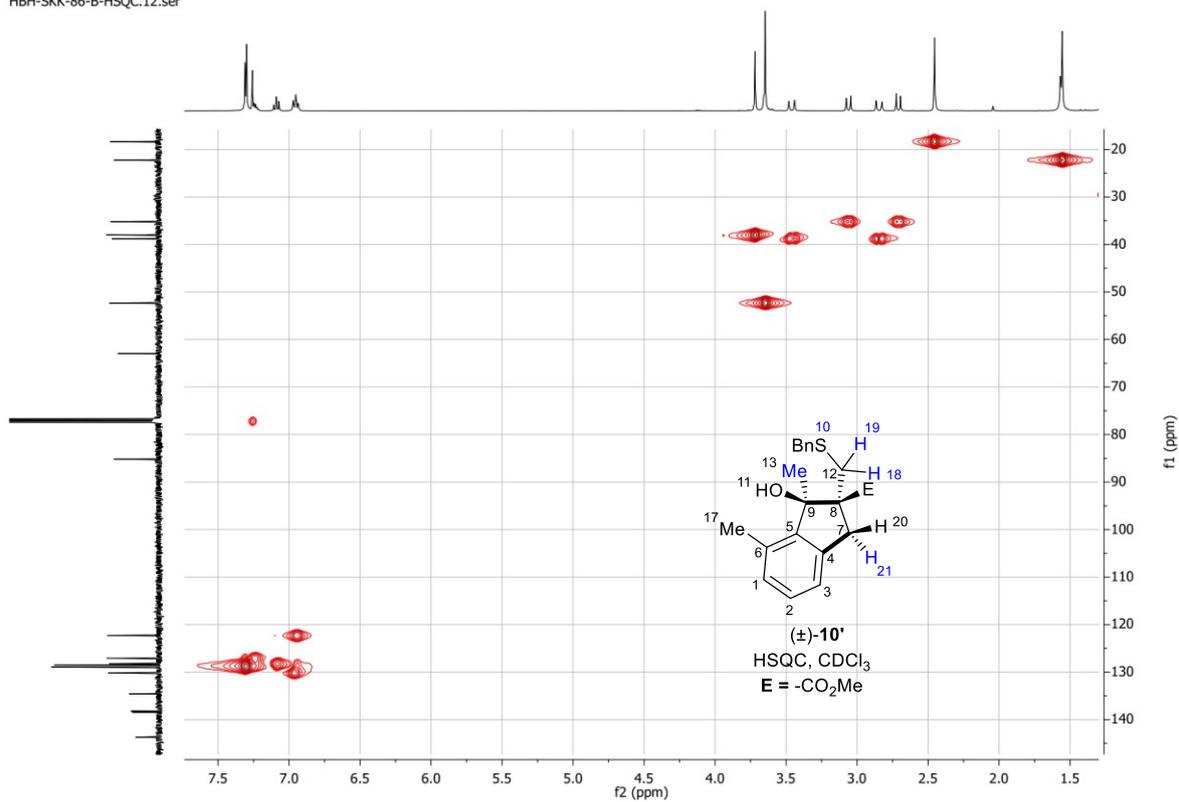
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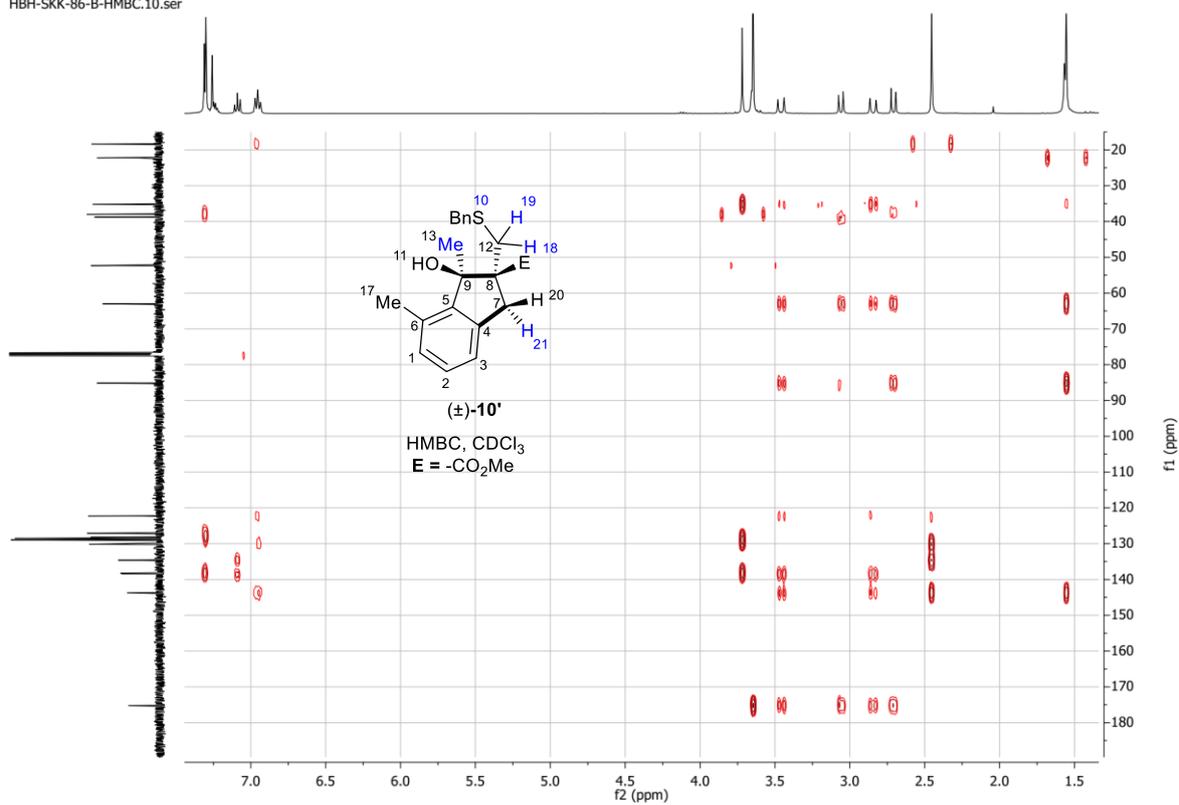
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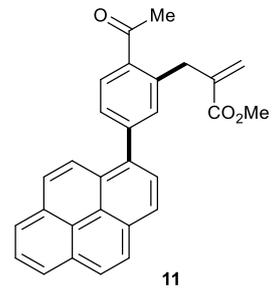
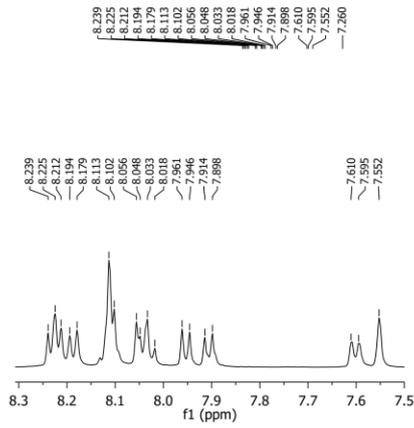
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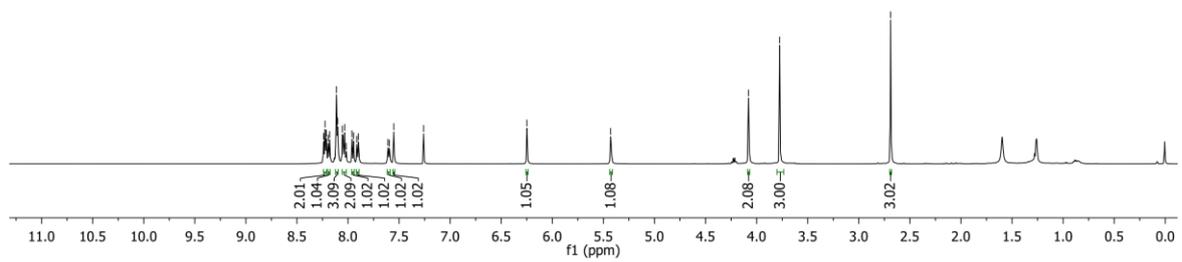
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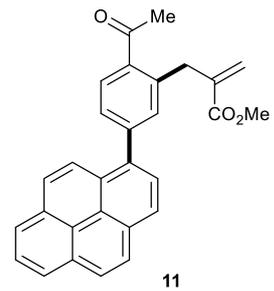
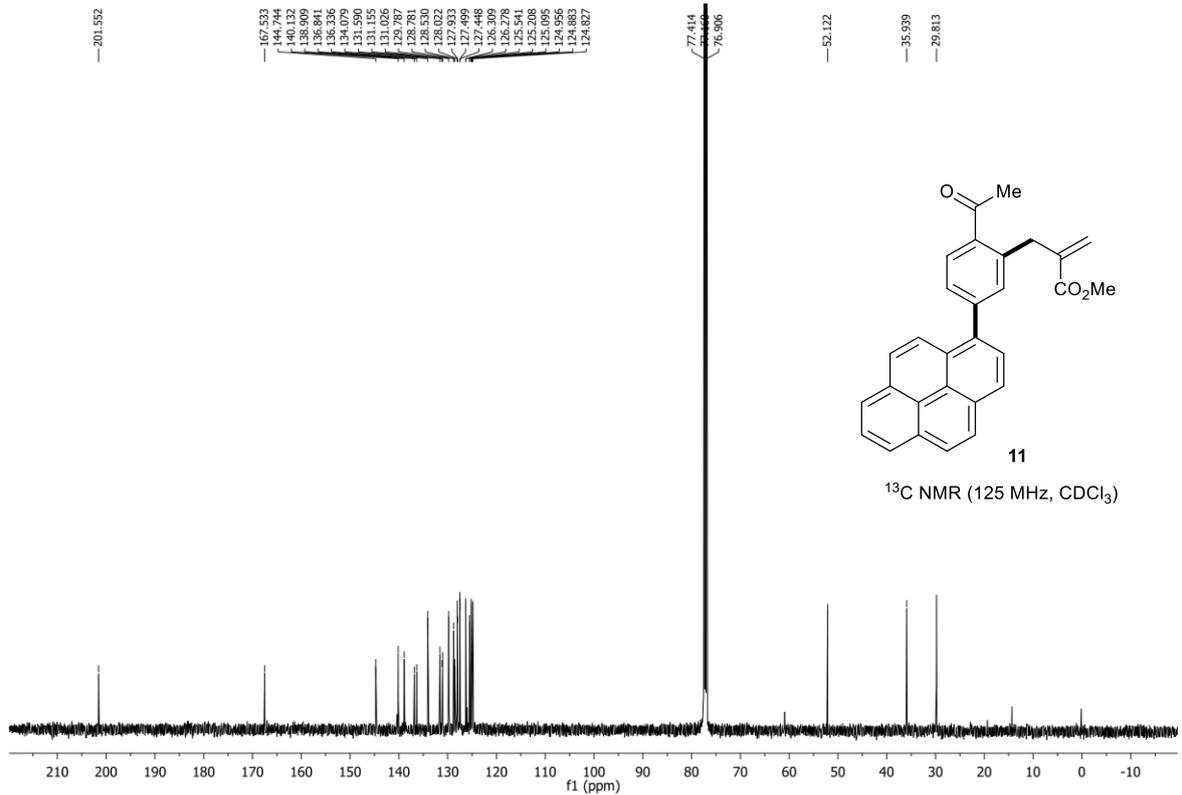
HBH-387-C-1-1H.1.fid



¹H NMR (500 MHz, CDCl₃)

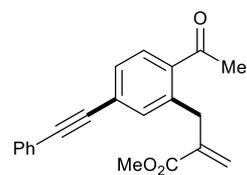
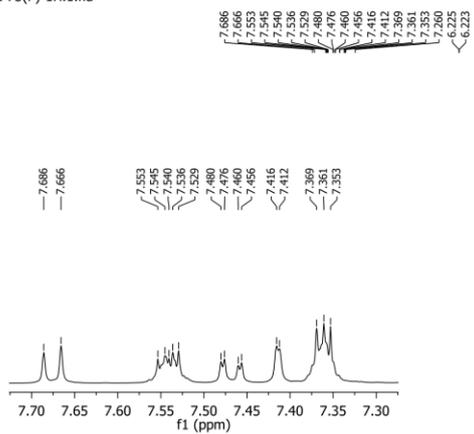


HBH-387-C-1-13C.3.fid



¹³C NMR (125 MHz, CDCl₃)

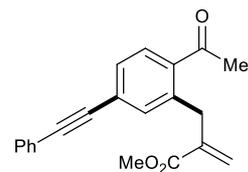
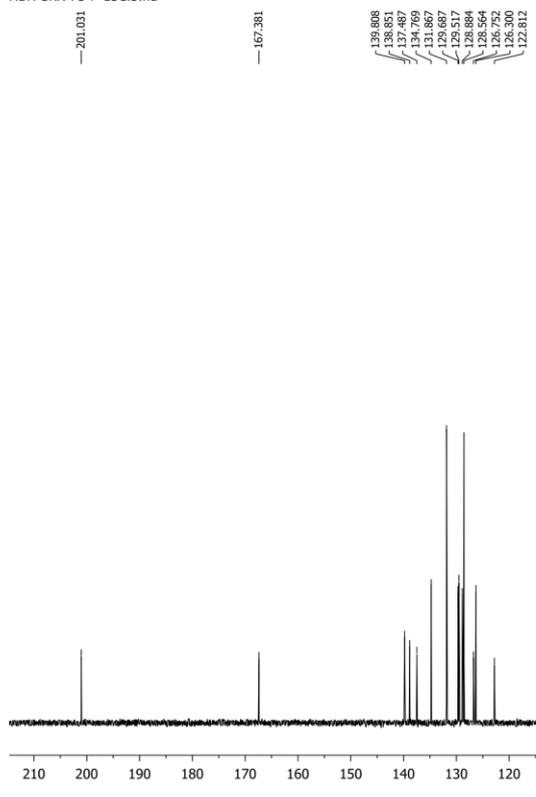
BHB-SKK-73(P)-1H.1.fid



12

¹H NMR (400 MHz, CDCl₃)

HBH-SKK-73-P-13C.3.fid



12

¹³C NMR (125 MHz, CDCl₃)

