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Supporting Information

An Iron-Catalyzed Bond-Making/Bond-Breaking Cascade Merges Cycloisomerization and Cross-Coupling Chemistry

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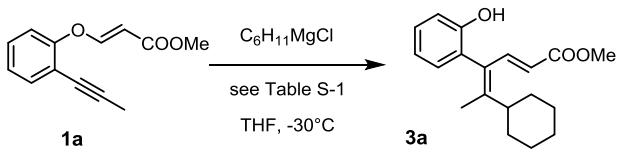
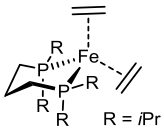
Table S-1. Optimization of the Reaction Conditions

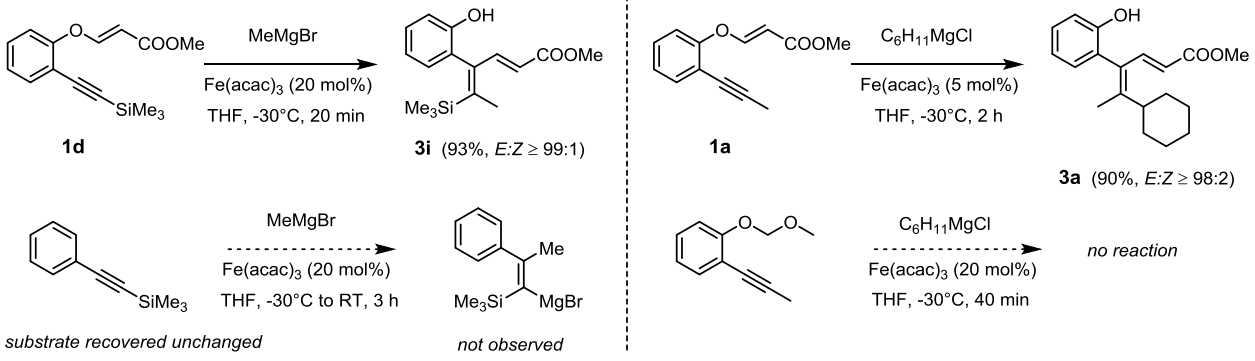


1a 3a

Entry	Precatalyst	Loading (mol%)	Additive (mol%)	t (min)	Conversion (%, NMR)	Yield	*E:Z*
1	$Fe(acac)_3$	20	---	20	100	86%	97:3
2	$Fe(acac)_3$	20	tmeda (20)	10	96	91%	97:3
3	$Fe(acac)_3$	20	dppe (20)	80	100	82%	97:3
4	$Fe(acac)_3$	10	---	50	100	91%	97:3
5	$Fe(acac)_3$	5	---	60	93	84%	98:2
6	$Fe(acac)_3$	5	---	120	100	90%	98:2
7	$Fe(acac)_3$	1	---	1140	93	55%	98:2
8	$FeBr_2$	20	---	600	100	nd	98:2
9	 R = *i*Pr	20	---	120	100	nd	95:5

Control Experiments

A series of control experiments proved that simple arylalkynes do not undergo carbometalation under the chosen conditions even if the mixture is allowed to reach room temperature. The examples shown in Scheme S-1 are representative.



Scheme S-1. Representative control experiments that provide additional evidence that the observed reaction cascade is not trigged by an ordinary iron catalyzed carbometalation of the alkyne unit.

Even if the flanking alkene in substrates of type **1** provides assistance,[1] a triggering carbometalation of **1d** would almost certainly afford the opposite regiochemical pattern to what is experimentally observed due to the directing effect of the silyl group.[2] Furthermore, it is unlikely that the tethering O-atom in substrates of type **1** exerts a critical role by coordination to the catalyst and/or Grignard reagent, because the MOM-derivative analogous to substrate **1a** also failed to undergo carbometalation under otherwise identical conditions.

Supplementary Crystallographic Information

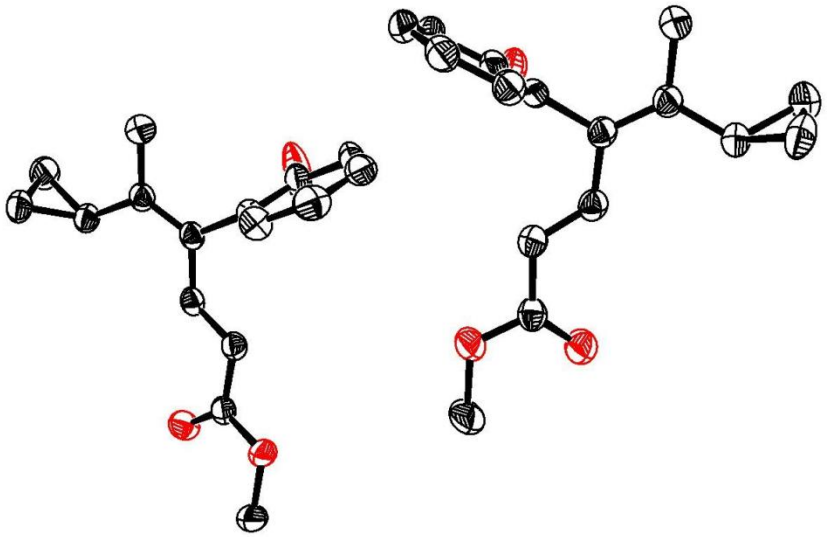


Figure S-1. Structure of compound **3c** in the solid state

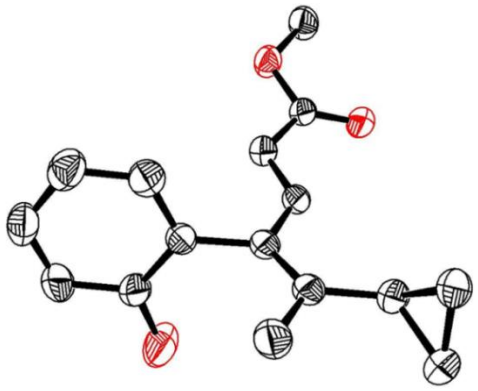


Figure S-2. Structure of one of the two independent molecules of compound **3c** in the unit cell.

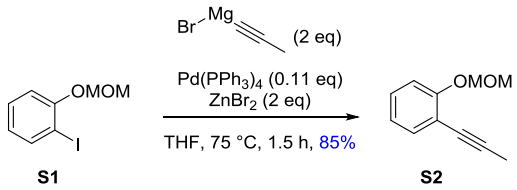
[1] For evidence that alkenes can facilitate iron catalyzed processes without taking part in the net reaction, see: S. Gülak, A. Jacobi von Wangelin, *Angew. Chem. Int. Ed*. **2012**, *51*, 1357-1361;

[2] For the regiochemical course of a carbometalation of trimethyl(phenylethynyl)silane, see: M. Yamaguchi, T. Sotokawa, M. Hirama, *Chem. Commun*. **1997**, 743-744.

X-ray Crystal Structure Analysis of Compound 3c: $C_{16}H_{18}O_3$, M_r = 258.30 $g \cdot mol^{-1}$, colorless plate, crystal size 0.58 x 0.52 x 0.52 mm, triclinic, space group $P\bar{1}$, a = 7.7944(3) Å, b = 10.4981(4) Å, c = 18.9565(7) Å, α = 101.4730(10)°, β = 94.4570(10)°, γ = 111.5750(10)°, V = 1394.14(9) Å^3, T = 200 K, Z = 4, D_{calc} = 1.231 g·cm^3, λ = 1.54178 Å, μ(*Cu-K*$_\alpha$) = 0.678 mm^{-1}, Empirical absorption correction (T_{min} = 0.66, T_{max} = 0.78), Bruker AXS X8 Proteum diffractometer, 2.411 < θ < 67.493°, 32194 measured reflections, 4816 independent reflections, 4688 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.036 [$I > 2\sigma(I)$], wR_2 = 0.092, 349 parameters, H atoms riding, S = 1.045, residual electron density 0.2 / -0.2 e Å^{-3}. **CCDC-1478953**.

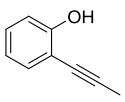
General. All reactions were carried out under Ar in glassware dried with a heat gun under vacuum (Schlenk line). The solvents were purified by distillation over the indicated drying agents and were transferred under Ar: THF, Et_2O (Mg/anthracene), CH_2Cl_2, toluene (Na/K), MeOH (Mg, stored over MS 3Å); DMF, CH_3CN , NEt_3 and pyridine were dried by an adsorption solvent purification system based on molecular sieves. Thin layer chromatography (TLC): Macherey-Nagel precoated plates (POLYGRAM® SIL/UV254); Flash chromatography: Merck silica gel 60 (40–63 μm or 15–40 μm (fine)) with predistilled or HPLC grade solvents. NMR: Spectra were recorded on Bruker DPX 300, AV 400 or AV 500 spectrometers in $CDCl_3$; chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δ_C = 77.0 ppm; residual $CHCl_3$ in $CDCl_3$: δ_H = 7.26 ppm). IR: Spectrum One (Perkin-Elmer) spectrometer, wavenumbers (ν) in cm^{-1}. MS (EI): Finnigan MAT 8200 (70 eV), ESI-MS: ESQ3000 (Bruker), accurate mass determinations: Bruker APEX III FT-MS (7 T magnet) or Mat 95 (Finnigan). Unless stated otherwise, all commercially available compounds (Alfa Aesar, Sigma-Aldrich) were used as received. $Fe(acac)_3$ (> 99.9%) was purchased from Sigma-Aldrich. The Grignard reagents were commercially available compounds (Alfa Aesar, Sigma-Aldrich); they were titrated prior to use according to a literature procedure.[3]

Preparation of the Substrates



Compound S2. 1-Propynylmagnesium bromide (0.5 M in THF, 15.1 mmol, 30.3 mL) was added dropwise to a solution of dried $ZnBr_2$ (prepared according to ref. 4, 15.1 mmol, 3.4 g) in THF (90 mL) at room temperature, resulting in the immediate formation of a white precipitate. The suspension was stirred for 15 min before it was filtrated under argon. The filtrate was added to a solution of **S1** (7.6 mmol, 2 g)[5] and $Pd(PPh_3)_4$ (0.8 mmol, 963 mg. 11 mol%) in THF (20 mL) and the resulting mixture was stirred for 1.5 h at 75°C. After reaching room temperature, the mixture was filtered through a pad of silica, rinsing with *tert*-butyl methyl ether. The combined filtrates were evaporated and the residue was purified by flash chromatography (hexane/EtOAc, 20/1) to give the title compound as a pale yellow oil (1.14 g, 85%).[6] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (dd, J = 7.6, 1.8 Hz, 1H), 7.26 – 7.18 (m, 1H), 7.09 (dd, J = 8.3, 1.2 Hz, 1H), 6.94 (td, J = 7.5, 1.2 Hz, 1H), 5.24 (s, 2H), 3.53 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.7, 133.6, 128.8, 121.8, 115.4, 114.6, 95.1, 89.8, 75.8, 56.1, 4.7; IR (neat) 3072, 3029, 2996, 2956, 2915, 2848, 2826, 1596, 1574, 1489, 1440, 1404, 1378, 1310, 1261, 1229, 1196, 1151, 1112, 1078, 1044, 989, 966, 920, 793, 751, 686, 644, 568, 542, 481, 443 cm^{-1}; MS (EI) *m/z* (%): 45 (100), 51 (7), 63 (5), 77 (15), 91 (7), 103 (8), 115 (19), 31 (49), 145 (52), 161 (13), 176 (28); HRMS (APPIpos): calcd for $C_{11}H_{12}O_2$: 176.08318; found: 176.08326.

Compound S3. The MOM ether **S2** (8.0 mmol, 1.4 g) was dissolved in MeOH (16 mL) and HCl (36% w/w, 19.0 mmol, 1.6 mL) was added dropwise. The resulting yellow solution was stirred for 6 h at room temperature, the acid was neutralized with saturated $NaHCO_3$, the aqueous layer was extracted with EtOAc and the combined organic phases were dried over Na_2SO_4. Evaporation of the solvent followed by purification of the residue by flash chromatography (hexane/Et_2O



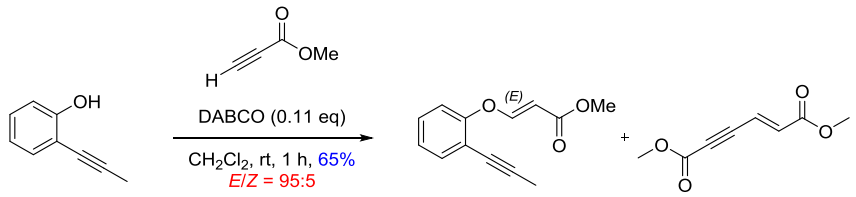
[3] Krasovskiy, A.; Knochel, P. *Synthesis* **2006**, 890.

[4] Jensen, A. E,; Kneisel, F.; Knochel, P. *Org. Synth.* **2002**, *79*, 35.

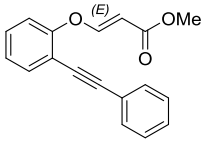
[5] Liu, J.; Liu, Y. *Org. Lett.* **2012**, *14*, 4742.

[6] Compound **1b** was synthesized using a modified Negishi procedure: Hoffmeister, L.; Persich, P.; Fürstner, A. *Chem. Eur. J.* **2014**, *20*, 1396.

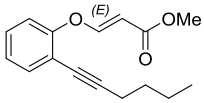
20:1) gave the title compound as a volatile yellow oil (936 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (dd, J = 7.7, 1.7 Hz, 1H), 7.23 – 7.19 (m, 1H), 6.94 (dd, J = 8.2, 0.9 Hz, 2H), 6.85 (td, J = 7.4, 1.1 Hz, 1H), 5.86 (s, 1H), 2.13 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 131.4, 129.6, 120.1, 114.3, 110.1, 93.3, 73.8, 4.5. The data are in agreement with those previously reported in the literature.[7]



Compound 1a. DABCO (0.8 mmol, 84 mg, 11 mol%) was added in one portion to a mixture of phenol **S3** (6.8 mmol, 894 mg) and methyl propiolate (6.8 mmol, 0.6 mL) in CH_2Cl_2 (40 mL) at 0 °C. The mixture was stirred at ambient temperature for 1 h before the solvent was removed *in vacuo*. The brown residue (*E*:*Z* = 95:5, NMR) was purified by flash chromatography (hexane/EtOAc, 20:1) to afford a pure fraction of *E*-**1a** (yellow oil, 956 mg, 65%) and a second fraction containing a mixture of *E*-**1a** and the *trans* enyne **S4** resulting from the homo-coupling of the alkyne.[8] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, J = 12.3 Hz, 1H), 7.42 (dd, J = 7.7, 1.7 Hz, 1H), 7.27 (td, J = 7.7, 1.7 Hz, 1H), 7.12 (td, J = 7.6, 1.2 Hz, 1H), 7.03 (dd, J = 8.1, 1.2 Hz, 1H), 5.49 (d, J = 12.3 Hz, 1H), 3.72 (s, 3H), 2.06 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.6, 160.0, 155.9, 133.8, 129.0, 125.1, 118.8, 116.2, 101.3, 92.0, 74.2, 51.2, 4.5; IR (neat) 3078, 2995, 2951, 2917, 2847, 2241, 1711, 1646, 1629, 1600, 1570, 1487, 1436, 1320, 1291, 1255, 1193, 1117, 1098, 1043, 936, 830, 804, 754, 681, 615, 604, 568, 515, 471 cm^{-1}; MS (EI) *m/z* (%): 39 (7), 51 (13), 64 (18), 77 (20), 89 (15), 102 (10), 115 (28), 128 (70), 145 (14), 157 (34), 173 (16), 185 (100), 201 (17), 216 (34); HRMS (APPIpos): calcd for $C_{13}H_{12}O_3$: 216.07810; found: 216.07823.



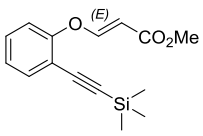
1b (*E*/*Z* = 97:3)



1c (*E*/*Z* = 96:4)

Compounds **1b** and **1c** are known compounds and were prepared according to a literature procedure.[5]

Compound 1d.[9] Prepared analogously as a pale orange oil (188 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 12.2 Hz, 1H), 7.49 (d, J = 7.7 Hz, 1H), 7.33 (t, J = 7.8 Hz, 1H), 7.15 (t, J = 7.6 Hz, 1H), 7.05 (d, J = 8.2 Hz, 1H), 5.52 (d, J = 12.3 Hz, 1H), 3.72 (s, 3H), 0.23 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 159.9, 156.4, 134.0, 130.0, 125.1, 118.9, 115.3, 101.3, 101.1, 99.1, 51.3, –0.3 (3C); IR (neat) 3079, 2955, 2900, 2845, 2162, 1715, 1646, 1632, 1599, 1571, 1483, 1444, 1320, 1285, 1235, 1190, 1165, 1116, 1046, 945, 864, 836, 788, 755, 719, 701, 642, 616, 577, 539, 516, 471, 429 cm^{-1}; MS (EI) *m/z* (%): 43 (6), 53 (5), 59 (24), 73 (12), 89 (100), 107 (13), 115 (24), 129 (7), 143 (7), 159 (13), 175 (6), 185 (17), 201 (25), 211 (10), 231 (8), 244 (13), 259 (78); HRMS (ESIpos): calcd for $C_{15}H_{18}O_3SiNa$: 297.09174; found: 297.09171.

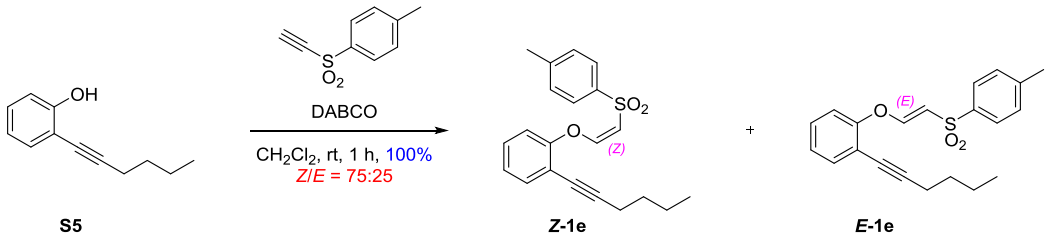


[7] Yoneda, E.; Sugioka, T.; Hirao, K.; Zhang, S.-W.; Takahashi, S. *J. Chem. Soc., Perkin Trans. 1* **1998**, 477.

[8] For the addition of phenol to methyl propiolate, see ref 1 and the following: Fan, M.-J., Li, G.-Q.; Li, L.-H.; Yang, S.-D.; Liang, Y.-M. *Synthesis* **2006**, 2286.

[9] Kimura, M.; Ezoe, A.; Mori, M.; Tamaru, Y. *J. Am. Chem. Soc.* **2005**, *127*, 201.

Compound 1f.[10] Prepared analogously as a white solid, 308 mg, 81%). m.p. = 75 – 77 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 13.8 Hz, 1H), 7.56 – 7.51 (m, 1H), 7.43 – 7.39 (m, 2H), 7.35 – 7.32 (m, 1H), 4.63 (d, J = 13.8 Hz, 1H), 3.68 (s, 3H), 3.14 (s, 3H), 2.37 (t, J = 7.0 Hz, 2H), 1.55 – 1.48 (m, 2H), 1.45 – 1.36 (m, 2H), 0.90 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 142.4, 135.5, 134.0, 131.2, 130.0, 129.4, 124.0, 99.3, 97.2, 76.8, 51.3, 41.2, 30.4, 21.9, 19.1, 13.5; IR (neat) 3023, 2956, 2933, 2873, 2232, 1711, 1625, 1597, 1567, 1487, 1436, 1360, 1321, 1290, 1254, 1234, 1191, 1165, 1128, 1095, 1041, 958, 900, 871, 855, 832, 789, 753, 699, 666, 607, 597, 552, 528, 516, 481, 411 cm^{-1}; MS (EI) *m/z* (%): 41 (4), 59 (11), 77 (7), 91 (3), 127 (18), 142 (9), 154 (66), 167 (42), 182 (95), 196 (73), 214 (43), 224 (40), 256 (100), 276 (26), 304 (17); HRMS (ESIpos): calcd for $C_{17}H_{21}NO_4SNa$: 358.10835; found: 358.10864.

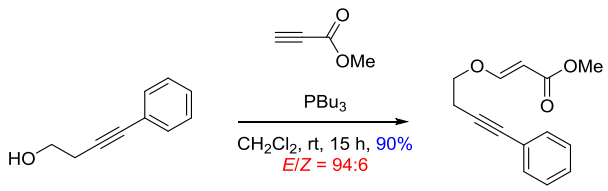


Compound 1e. DABCO (0.18 mmol, 19.9 mg, 10 mol%) was added in one portion to a mixture of phenol **S5** (1.77 mmol, 309 mg)[5] and ethynyl *p*-tolyl sulfone (1.77 mmol, 319.6 mg) in CH_2Cl_2 (10 mL) at 0 °C. The mixture was stirred for 1 h at ambient temperature and the solvent was evaporated. The brown residue (*Z*:*E* = 75:25, NMR) was purified by flash chromatography (hexane/EtOAc, 9:1 then 8:2) to afford *E*-**1e** (pale yellow oil, 177 mg, 28%) and a second fraction containing the *Z*-**1e** (pale yellow oil, 451 mg, 72%).

Spectral data of *E*-**1e:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.76 (m, 3H), 7.42 (dd, J = 7.7, 1.6 Hz, 1H), 7.31 (d, J = 8.2 Hz, 2H), 7.27 (dd, J = 7.5, 1.6 Hz, 1H), 7.15 (td, J = 7.6, 1.0 Hz, 1H), 7.03 (dd, J = 8.2, 0.8 Hz, 1H), 5.90 (d, J = 11.9 Hz, 1H), 2.43 (s, 3H), 2.34 (t, J = 7.0 Hz, 2H), 1.56 – 1.49 (m, 2H), 1.47 – 1.38 (m, 2H), 0.91 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 155.3, 143.8, 139.2, 133.8, 129.7 (2C), 129.1, 127.1 (2C), 125.8, 119.3, 116.4, 111.3, 97.2, 74.7, 30.5, 21.9, 21.6, 19.2, 13.6; IR (neat) 3065, 2957, 2931, 2872, 2233, 1631, 1615, 1598, 1569, 1485, 1445, 1313, 1302, 1259, 1219, 1200, 1137, 1102, 1082, 1036, 1018, 944, 888, 863, 802, 760, 705, 662, 619, 606, 579, 559, 537 cm^{-1}.

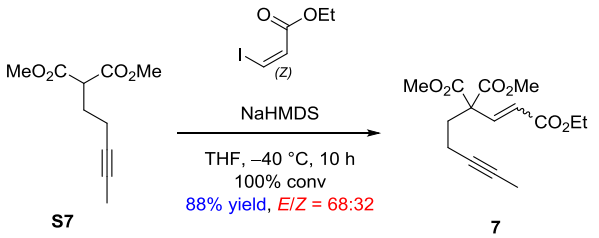
Spectral data of *Z*-**1e:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.3 Hz, 2H), 7.39 (dd, J = 7.6, 1.7 Hz, 1H), 7.30 (d, J = 8.0 Hz, 2H), 7.23 (td, J = 7.8, 1.8 Hz, 1H), 7.12 (td, J = 7.6, 1.2 Hz, 1H), 6.95 (dd, J = 8.1, 1.3 Hz, 1H), 6.81 (d, J = 6.4 Hz, 1H), 5.78 (d, J = 6.5 Hz, 1H), 2.42 (s, 3H), 2.27 (t, J = 7.0 Hz, 2H), 1.52 – 1.44 (m, 2H), 1.43 – 1.35 (m, 2H), 0.91 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 152.8, 143.8, 139.7, 133.8, 129.3 (2C), 128.9, 127.7 (2C), 125.5, 118.9, 115.8, 110.6, 97.3, 74.6, 30.4, 22.0, 21.6, 19.2, 13.6; IR (neat) 3076, 3028, 2957, 2931, 2871, 1627, 1597, 1569, 1486, 1444, 1402, 1380, 1316, 1302, 1291, 1259, 1240, 1202, 1183, 1141, 1115, 1083, 1067, 1040, 1019, 944, 884, 814, 754, 708, 665, 644, 580, 552, 525, 514, 466 cm^{-1}; HRMS (ESIpos): calcd for $C_{21}H_{22}O_3SNa$: 377.11819; found: 377.11870.

[10] Shen, Z.; Lu, X. *Adv. Synth. Catal.* **2009**, *351*, 3107.



S6 **4**

Compound 4.[11] Methyl propiolate (2.19 mmol, 0.20 mL) was added dropwise to a stirred solution of alcohol **S6** (2.19 mmol, 320 mg)[12] and freshly distilled tributylphosphine (0.4 mmol, 0.1 mL, 18 mol%) in CH_2Cl_2 (10 mL) at room temperature, resulting in a color change to dark brown. The mixture was stirred for 16 h before the solvent was removed under vacuum. The residue was purified by flash chromatography on silica (hexane/EtOAc, 9:1) to afford the title compound as a colorless solid (453 mg, 90%); m.p. = 44 – 46 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 12.7 Hz, 1H), 7.38 – 7.35 (m, 2H), 7.27 – 7.22 (m, 3H), 5.23 (d, J = 12.6 Hz, 1H), 3.99 (t, J = 6.8 Hz, 2H), 3.66 (s, 3H), 2.79 (t, J = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 162.1, 131.6 (2C), 128.2 (2C), 128.0, 123.0, 96.7, 84.7, 82.4, 69.0, 51.1, 20.2; IR (neat) 2949, 1705, 1641, 1623, 1572, 1490, 1464, 1436, 1389, 1332, 1287, 1238, 1207, 1189, 1127, 1047, 988, 968, 952, 917, 823, 755, 691, 602, 576, 561, 527, 502, 456, 420 cm^{-1}; MS (EI) *m/z* (%): 51 (7), 63 (6), 77 (13), 91 (15), 102 (11), 115 (30), 128 (100), 141 (8), 159 (3), 171 (18), 187 (1), 199 (7), 215 (1), 229 (21); HRMS (ESIpos): calcd for $C_{14}H_{14}O_3Na$: 253.08351; found: 253.08351.



S7 **7**

Compound 7.[13] A solution of NaHMDS (2.98 mmol, 547 mg) in THF (10 mL) was added dropwise at –78 °C to a solution of **S7** (2.74 mmol, 543 mg) [14] in THF (10 mL). The mixture was stirred for 30 min at –78 °C before (*Z*)-iodo acrylate (3.01 mmol, 0.39 mL) was added dropwise. The resulting yellow solution was warmed to –40 °C and stirring was continued for 10 h at this temperature. The reaction was quenched with saturated aqueous NH_4Cl at –40 °C and the resulting mixture allowed to reach room temperature before it was diluted with water and EtOAc. The aqueous phase was extracted with EtOAc and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The crude material (*E*:*Z* = 68:32, NMR) was purified by flash chromatography (hexane/EtOAc, 9:1) to afford the title compound as a separable mixture of the two isomers (colorless oil, 710 mg, 88% combined yield). Spectral data of *E*-**7**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 16.4 Hz, 1H), 5.92 (d, J = 16.4 Hz, 1H), 4.21 (q, J = 7.1 Hz, 2H), 3.76 (s, 6H), 2.33 – 2.29 (m, 2H), 2.12 – 2.07 (m, 2H), 1.75 (t, J = 2.5 Hz, 3H), 1.30 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3 (2C), 165.6, 142.8, 123.4, 77.3, 76.8, 60.8, 59.0, 53.1 (2C), 34.7, 14.4, 14.2, 3.4; IR (neat) 2981, 2956, 2921, 2849, 1735, 1651, 1436, 1392, 1368, 1252, 1226, 1192, 1085, 1071, 1034, 981,

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[11] (a) Inanaga, J.; Baba, Y.; Hanamoto, T. *Chem. Lett.* **1993**, *22*, 241. (b) O'Rourke, N. F.; Davies, K. A.; Wulff, J. E. *J. Org. Chem.* **2012**, *77*, 8634.

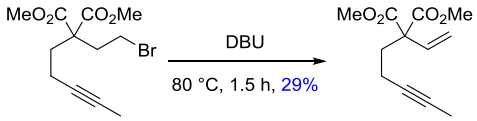
[12] Panteleev, J.; Huang, R. Y.; Lui, E. K. J.; Lautens, M. *Org. Lett.* **2011**, *13*, 5314.

[13] Prepared by using a modified procedure: Esteban, J.; Costa, A. M.; Gómez, À.; Vilarrasa, J. *Org. Lett.* **2008**, *10*, 65.

[14] Hog, D. T.; Huber, F. M. E.; Jiménez-Osés, G.; Mayer, P.; Houk, K. N.; Trauner, D. *Chem. Eur. J.* **2015**, *21*, 13646.

939, 915, 864, 830, 793, 709, 594, 537, 488, 427 cm^{-1}; MS (ESIpos) *m/z* = 297 ([M+H]), 314 ([M+NH_4]), 319 ([M+Na]), 615 ([2M+Na]); HRMS (ESIpos): calcd for $C_{15}H_{20}O_6Na$: 319.11521; found: 319.11526.

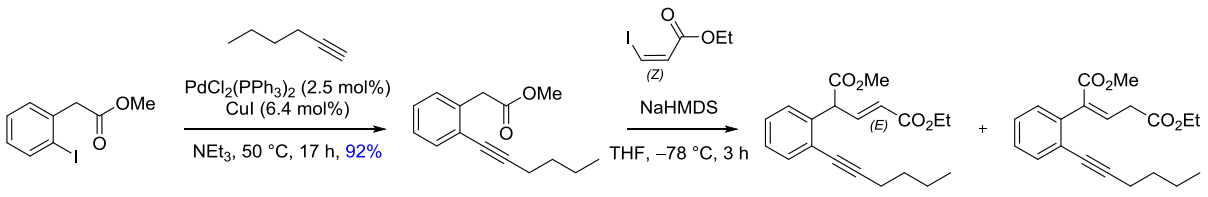
Spectral data of *Z*-**7**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 (d, *J* = 12.3 Hz, 1H), 6.00 (d, *J* = 12.2 Hz, 1H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.72 (s, 6H), 2.51 – 2.47 (m, 2H), 2.13 – 2.07 (m, 2H), 1.73 (t, *J* = 2.5 Hz, 3H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6 (2C), 165.2, 143.4, 121.8, 77.7, 76.5, 60.5, 58.8, 53.0 (2C), 34.7, 14.9, 14.1, 3.4.



S8 **10**

Compound S8. A solution of malonate **S7** (1.51 mmol, 300 mg) in DMF (1 mL) was added dropwise to a suspension of NaH (1.75 mmol, 42 mg) in DMF (1 mL) at 0 °C. The resulting mixture was stirred at room temperature for 15 min. The solution was cooled to 0 °C before 1,2-dibromoethane (1.62 mmol, 0.14 mL) was added. The mixture was stirred at ambient temperature for 15 h before the reaction was carefully quenched with saturated aqueous NH_4Cl. The aqueous phase was extracted with methyl *tert*-butyl ether and the combined organic extracts were washed with brine, dried over Na_2SO_4, filtered, and concentrated. The crude material was purified by flash chromatography (hexanes/EtOAc, 20:1) to afford the title compound as a colorless oil (247 mg, 53% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.73 (s, 6H), 3.32 (app. t, *J* = 8.0 Hz, 2H), 2.50 (app. t, *J* = 8.6 Hz, 2H), 2.12 (app. s, 4H), 1.76 (app. s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7 (2C), 77.2, 76.6, 57.2, 52.7 (2C), 36.1, 32.2, 26.9, 14.2, 3.5; IR (neat) 2954, 2920, 2858, 2845, 1732, 1435, 1348, 1260, 1217, 1200, 1180, 1088, 1064, 1038, 1012, 968, 887, 796, 740, 662, 576, 554, 519, 450, 418 cm^{-1}; MS (ESIpos) *m/z* = 305 ([M+H]), 322 ([M+NH_4]), 327 ([M+Na]), 631 ([2M+Na]); HRMS (ESIpos): calcd for $C_{12}H_{17}O_4BrNa$: 327.02025; found: 327.02026.

Compound 10. A mixture of bromide **S8** (0.73 mmol, 221 mg) and DBU (3.65 mmol, 0.55 mL) was stirred at 80 °C for 1.5 h. The mixture was cooled to room temperature, the reaction was quenched with saturated aqueous NH_4Cl and the aqueous phase extracted with methyl *tert*-butyl ether. The combined extracts were washed with brine, dried over Na_2SO_4, filtered, and concentrated. The crude material was purified by flash chromatography (hexanes/EtOAc, 15:1) to afford the title compound as a colorless oil (47 mg, 29%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.30 (dd, *J* = 17.9, 10.9 Hz, 1H), 5.32 (d, *J* = 10.9 Hz, 1H), 5.18 (d, *J* = 17.8 Hz, 1H), 3.73 (s, 6H), 2.30 – 2.26 (m, 2H), 2.12 – 2.06 (m, 2H), 1.75 (t, *J* = 2.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4 (2C), 133.9, 117.3, 77.8, 76.2, 59.3, 52.7 (2C), 34.2, 14.2, 3.5; IR (neat) 2954, 2921, 2854, 1733, 1635, 1435, 1281, 1258, 1225, 1197, 1084, 994, 932, 812, 785, 704, 654, 420 cm^{-1}; MS (EI) *m/z* (%): 39 (12), 53 (36), 68 (25), 79 (21), 91 (24), 98 (49), 105 (67), 126 (93), 133 (28), 149 (6), 158 (100), 165 (31), 193 (7), 224 (4); HRMS (ESIpos): calcd for $C_{12}H_{16}O_4Na$: 247.09408; found: 247.09416.

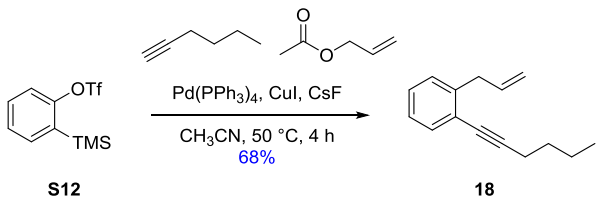


S9 **S10** **15** **S11**

Compound S10. 1-Hexyne (7.41 mmol, 0.85 mL), $PdCl_2(PPh_3)_2$ (0.17 mmol, 117.1 mg) and CuI (0.43 mmol, 81.8 mg) were successively added to a solution of **S9** (6.74 mmol, 1.86 g)[15] in freshly distilled NEt_3 (67 mL). The resulting yellow solution was stirred at 50 °C for 17 h. After reaching room temperature, EtOAc was added and the suspension was filtered through a pad of Celite. Evaporation of the filtrate gave a brown residue which was purified by flash chromatography (hexane/EtOAc, 40:1) to afford the title compound as a yellow oil (1.43 g, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 6.8 Hz, 1H), 7.29 – 7.22 (m, 3H), 3.86 (s, 2H), 3.74 (s, 3H), 2.48 (t, J = 7.0 Hz, 2H), 1.67 – 1.60 (m, 2H), 1.57 – 1.48 (m, 2H), 1.00 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 135.9, 132.0, 129.5, 127.6, 126.9, 124.3, 95.1, 78.5, 51.9, 39.7, 30.7, 21.9, 19.1, 13.6; IR (neat) 3066, 3025, 2955, 2932, 2872, 1737, 1601, 1487, 1450, 1434, 1412, 1379, 1339, 1245, 1207, 1157, 1103, 1043, 1011, 949, 926, 897, 867, 824, 755, 687, 632, 581, 547, 513, 464 cm^{-1}; MS (EI) *m/z* (%): 91 (7), 102 (7), 115 (39), 129 (100), 141 (40), 155 (33), 171 (17), 188 (29), 201 (9), 215 (5), 230 (22); HRMS (APPIpos): calcd for $C_{15}H_{18}O_2$: 230.13013; found: 230.13029.

Compound 15. A solution of NaHMDS (0.47 mmol, 86.6 mg) in THF (2 mL) was added dropwise at −78 °C to a solution of **S10** (0.43 mmol, 100 mg) in THF (2 mL). The yellow mixture was stirred for 15 min at –78 °C before ethyl (*Z*)-iodo-acrylate (0.48 mmol, 61 μL) was slowly introduced and stirring was continued for 3 h at –78 °C. The reaction was quenched with saturated aqueous NH_4Cl at –78 °C and the mixture was allowed to reach room temperature before it was diluted with water and EtOAc. The aqueous phase was extracted with EtOAc and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography (hexane/EtOAc, 20:1) to afford compound **15** as a slightly colored oil (86 mg, 60%) and second fraction containing isomer **S11** as a colorless oil (18 mg, 13% yield). Spectral data of compound **15**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (dd, J = 7.4, 1.7 Hz, 1H), 7.36 (dd, J = 7.6, 1.5 Hz, 1H), 7.25 (td, J = 7.4, 1.6 Hz, 1H), 7.20 (td, J = 7.5, 1.5 Hz, 1H), 6.65 (dd, J = 11.3, 9.4 Hz, 1H), 6.06 (dd, J = 9.4, 1.1 Hz, 1H), 5.94 (dd, J = 11.3, 1.1 Hz, 1H), 4.18 (qd, J = 7.1, 5.2 Hz, 2H), 3.70 (s, 3H), 2.41 (t, J = 7.1 Hz, 2H), 1.63 – 1.55 (m, 2H), 1.51 – 1.41 (m, 2H), 1.28 (t, J = 7.2 Hz, 3H), 0.94 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 165.7, 144.3, 139.8, 132.7, 128.7, 128.1, 127.3, 123.6, 121.3, 95.7, 78.3, 60.2, 52.3, 48.6, 30.6, 22.1, 19.2, 14.2, 13.6; IR (neat) 2956, 2934, 2873, 1736, 1717, 1648, 1485, 1463, 1446, 1434, 1411, 1386, 1321, 1283, 1184, 1097, 1074, 1029, 926, 854, 824, 758 cm^{-1}; MS (EI) *m/z* (%): 29 (11), 41 (8), 59 (5), 76 (9), 128 (13), 141 (29), 153 (43), 165 (45), 181 (32), 199 (65), 207 (29), 223 (100), 239 (12), 250 (43), 285 (45), 296 (10), 328 (56); HRMS (ESIpos): calcd for $C_{20}H_{24}O_4Na$: 351.15668; found: 351.15661.

Spectral data of isomer **S11**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.43 (m, 1H), 7.30 – 7.24 (m, 3H), 7.14 – 7.12 (m, 1H), 4.15 (q, J = 7.1 Hz, 2H), 3.73 (s, 3H), 3.08 (d, J = 7.4 Hz, 2H), 2.34 (t, J = 6.9 Hz, 2H), 1.55 – 1.47 (m, 2H), 1.46 – 1.37 (m, 2H), 1.26 (t, J = 7.2 Hz, 3H), 0.92 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 166.8, 136.9, 136.2, 135.6, 132.0, 129.5, 127.8, 127.4, 124.1, 94.5, 78.7, 61.0, 52.1, 35.0, 30.7, 21.9, 19.1, 14.1, 13.6; IR (neat) 2959, 2933, 2873, 1737, 1722, 1435, 1372, 1326, 1251, 1179, 1046, 1028, 760, 734 cm^{-1}; MS (EI) *m/z* (%): 29 (16), 57 (11), 85 (14), 115 (20), 128 (19), 141 (30), 153 (70), 165 (100), 181 (45), 211 (53), 223 (27), 239 (61), 254 (25), 268 (73), 296 (14), 328 (46); HRMS (ESIpos): calcd for $C_{20}H_{24}O_4Na$: 351.15668; found: 351.15658.



S12 **18**

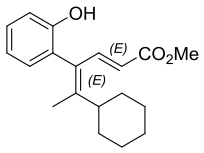
[15] Marchal, E.; Uriac, P.; Legouin, B.; Toupet, L.; van de Weghe, P. *Tetrahedron* **2007**, *63*, 9979.

Compound 18.[16] A vacuum-dried Schlenk tube containing $Pd(PPh_3)_4$ (32 μmol, 37.51 mg), CuI (40 μmol, 7.62 mg) and CsF (3.43 mmol, 521 mg) was purged with argon before freshly distilled CH_3CN (3 mL), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (1 mmol, 0.24 mL), allyl acetate (1.31 mmol, 0.14 mL) and 1-hexyne (1.11 mmol, 0.13 mL) were successively added. The resulting mixture was stirred at 50 °C for 4 h. For work-up, the mixture was filtered through a pad of Celite which was carefully rinsed with CH_2Cl_2. The combined filtrates were evaporated and the residue was purified by flash chromatography on silica (hexane) to afford the title compound as a colorless liquid (136 mg, 68%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 (d, J = 7.3 Hz, 1H), 7.24 – 7.11 (m, 3H), 6.00 (ddt, J = 16.9, 10.1, 6.7 Hz, 1H), 5.13 – 5.04 (m, 2H), 3.56 (d, J = 6.7 Hz, 2H), 2.46 (t, J = 6.9 Hz, 2H), 1.67 – 1.55 (m, 2H), 1.54 – 1.45 (m, 2H), 0.96 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.8, 136.8, 132.2, 128.6, 127.7, 125.9, 123.6, 115.7, 94.4, 79.1, 38.7, 30.9, 22.0, 19.2, 13.6. The data are in agreement with those previously reported in the literature.[17]

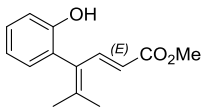
Products

General Procedure for Iron Catalyzed Reaction Cascade. $Fe(acac)_3$ (5-20 mol%) was added to a Schlenk tube containing a solution of the 1,6-enyne in THF (0.01 M) and the orange mixture was cooled to –30 °C. A solution of the Grignard reagent in THF or Et_2O (2 equiv) was added dropwise, resulting in an immediate color change to dark brown or dark green. Stirring was continued at –30 °C until TLC indicated complete consumption of the starting material. The reaction was then quenched with EtOH (1 mL). The mixture was concentrated, the residue suspended in CH_2Cl_2 and the mixture filtered through a pad of silica, eluting with hexane/EtOAc (1:1). The combined filtrates were evaporated and the residue was purified by flash chromatography to afford the desired product.

Compound 3a. Pale yellow oil (90% yield, $E/Z \geq$ 98:2, NMR). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 15.3 Hz, 1H), 7.24 – 7.20 (m, 1H), 6.94 – 6.87 (m, 3H), 5.33 (d, J = 15.3 Hz, 1H), 4.85 (s, 1H), 3.69 (s, 3H), 3.09 – 3.02 (m, 1H), 1.83 – 1.73 (m, 3H), 1.64 – 1.62 (m, 2H), 1.59 (s, 3H), 1.49 – 1.38 (m, 4H), 1.25 – 1.17 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 156.5, 152.4, 140.7, 130.4, 129.1, 127.0, 125.0, 120.7 (2C), 119.3, 115.3, 51.5, 41.4, 31.5, 31.1, 26.1, 25.9, 17.1; IR (neat) 3410, 2927, 2852, 1688, 1602, 1501, 1486, 1446, 1435, 1374, 1351, 1286, 1233, 1192, 1114, 1083, 1020, 972, 930, 909, 888, 863, 843, 828, 752, 730, 705, 621, 602, 550, 511, 491, 449, 412 cm^{-1}; MS (ESIpos) m/z = 301 ([M+H]), 323 ([M+Na]), 623 ([2M+Na]), 923 ([3M+Na]); HRMS (ESIpos): calcd for $C_{19}H_{24}O_3Na$: 323.16176; found: 323.16175.

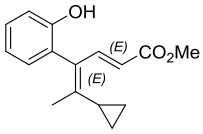


Compound 3b. White solid (93% yield). m.p. = 149 – 151 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 15.3 Hz, 1H), 7.25 – 7.20 (m, 1H), 6.95 – 6.88 (m, 3H), 5.32 (d, J = 15.3 Hz, 1H), 5.04 (s, 1H), 3.69 (s, 3H), 2.14 (s, 3H), 1.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 152.6, 147.4, 141.9, 130.5, 129.2, 128.3, 124.5, 120.7, 118.9, 115.4, 51.5, 23.6, 20.6; IR (neat) 3412, 2996, 2951, 1697, 1614, 1578, 1483, 1454, 1437, 1371, 1331, 1311, 1292, 1243, 1215, 1193, 1173, 1149, 1126, 1049, 1028, 1013, 971, 930, 876, 859, 823, 773, 763, 733, 682, 623, 606, 584, 542, 517, 485, 455, 444 cm^{-1}; MS (EI) m/z (%): 31 (7), 43 (15), 51 (13), 63 (12), 77 (32), 91 (29), 107 (12), 115 (34), 131 (61), 145 (33), 159 (100), 173 (51), 185 (87), 200 (13), 217 (40), 232 (87); HRMS (ESIpos): calcd for $C_{14}H_{16}O_3Na$: 255.09916; found: 255.09922.

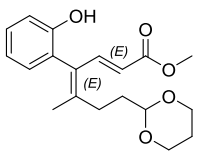


[16] Bhuvaneswari, S.; Jeganmohan, M.; Yang, M.-C.; Cheng, C.-H. *Chem. Commun.* **2008**, 2158.
[17] Jeganmohan, M.; Cheng, C.-H. *Org. Lett.* **2004**, *6*, 2821.

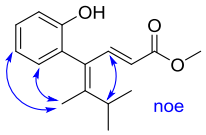
Compound 3c. Colorless solid (90% yield, *E*/*Z* = 99:1, NMR). m.p. = 86 – 88 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 15.3 Hz, 1H), 7.26 – 7.20 (m, 1H), 6.95 – 6.88 (m, 3H), 5.35 (d, *J* = 15.3 Hz, 1H), 5.00 (s, 1H), 3.69 (s, 3H), 2.28 (tt, *J* = 8.4, 5.2 Hz, 1H), 1.32 (s, 3H), 0.96 – 0.87 (m, 2H), 0.82 – 0.77 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 152.6, 151.4, 141.6, 130.4, 129.2, 128.4, 125.1, 120.7, 118.8, 115.4, 51.5, 15.7, 14.4, 6.7 (2C); IR (neat) 3391, 3085, 3009, 2949, 1688, 1600, 1580, 1486, 1447, 1435, 1289, 1249, 1231, 1192, 1167, 1129, 1096, 1051, 1033, 973, 917, 860, 840, 813, 755, 732, 681, 631, 604, 586, 549, 528, 481, 455, 431 cm^{-1}; MS (EI) *m/z* (%): 29 (100), 36 (34), 55 (14), 65 (12), 77 (30), 91 (26), 107 (32), 115 (32), 131 (33), 141 (21), 157 (32), 169 (50), 184 (68), 199 (37), 211 (12), 226 (6), 243 (10), 258 (43); HRMS (ESIpos): calcd for $C_{16}H_{19}O_3$: 259.13287; found: 259.13281.



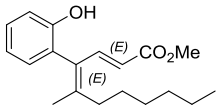
Compound 3d. Colorless oil (94% yield, *E*/*Z* = 99:1, NMR). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 15.4 Hz, 1H), 7.26 – 7.18 (m, 1H), 6.90 – 6.85 (m, 3H), 6.22 (s, 1H), 5.31 (d, *J* = 15.3 Hz, 1H), 4.69 (t, *J* = 3.9 Hz, 1H), 4.13 – 4.03 (m, 2H), 3.74 – 3.65 (m, 2H), 3.69 (s, 3H), 3.16 (ddd, *J* = 13.9, 9.5, 4.6 Hz, 1H), 2.20 (ddd, *J* = 11.4, 7.0, 4.3 Hz, 1H), 2.06 – 1.89 (m, 3H), 1.69 (s, 3H), 1.27 (app. d, *J* = 13.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 153.5, 150.3, 142.8, 129.8, 129.0 (2C), 124.5, 120.0, 118.8, 115.3, 102.2, 67.1, 67.0, 51.3, 32.7, 28.2, 25.2, 21.4; IR (neat) 3400, 2952, 2932, 2853, 1712, 1614, 1579, 1486, 1448, 1434, 1400, 1378, 1289, 1249, 1216, 1193, 1167, 1134, 1114, 1093, 1074, 1050, 1031, 999, 976, 948, 927, 886, 864, 829, 798, 753, 683, 666, 636, 604,508, 475, 437 cm^{-1}; MS (ESIpos) *m/z* = 333 ([M+H]), 355 ([M+Na]), 687 ([2M+Na]); HRMS (ESIpos): calcd for $C_{19}H_{24}O_5Na$: 355.15160; found: 355.15173.



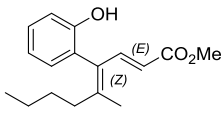
Compound 3e. Colorless oil (75% yield, *E*/*Z* = 96:4, NMR). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 15.3 Hz, 1H), 7.25 – 7.20 (m, 1H), 6.95 – 6.88 (m, 3H), 5.33 (d, *J* = 15.3 Hz, 1H), 4.85 (s, 1H), 3.69 (s, 3H), 3.48 (hept, *J* = 6.8 Hz, 1H), 1.57 (s, 3H), 1.14 (dd, *J* = 6.8, 5.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 156.8, 152.4, 140.6, 130.4, 129.1, 126.9, 125.0, 120.8, 119.4, 115.4, 51.5, 30.2, 21.3, 21.0, 15.6; IR (neat) 3401, 2966, 2872, 1689, 1602, 1486, 1447, 1435, 1362, 1285, 1193, 1167, 1129, 1098, 1052, 1032, 973, 910, 864, 839, 753, 731, 682, 647, 636, 605, 591, 554, 533, 496, 459, 442, 405 cm^{-1}; MS (EI) *m/z* (%): 43 (16), 55 (8), 65 (7), 77 (17), 91 (14), 115 (23), 131 (30), 145 (20), 157 (31), 175 (25), 185 (100), 201 (5), 217 (49), 229 (4), 245 (13), 260 (26); HRMS (ESIpos): calcd for $C_{16}H_{20}O_3Na$: 283.13046; found: 283.13072.



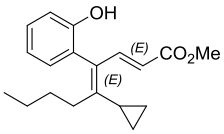
Compound 3f. In this case, the solution of the Grignard reagent was added over 30 min via syringe pump at –30°C; colorless oil (84% yield, *E*/*Z* = 97:3, NMR). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 15.2 Hz, 1H), 7.25 – 7.20 (m, 1H), 6.95 – 6.88 (m, 3H), 5.33 (d, *J* = 15.2 Hz, 1H), 4.88 (s, 1H), 3.69 (s, 3H), 2.58 – 2.43 (m, 2H), 1.67 (s, 3H), 1.59 – 1.51 (m, 2H), 1.40 – 1.31 (m, 6H), 0.94 – 0.82 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 151.8, 151.4, 140.7, 129.7, 128.5, 127.5, 124.0, 120.0, 118.4, 114.7, 50.8, 33.5, 30.9, 28.5, 28.3, 21.9, 20.9, 13.4; IR (neat) 3460, 2953, 2929, 2857, 1736, 1649, 1608, 1577, 1463, 1378, 1308, 1260, 1243, 1202, 1168, 1129, 1105, 1086, 1037, 1018, 987, 926, 901, 853, 752, 726, 676, 637, 619, 584, 558, 525, 464, 451 cm^{-1}.



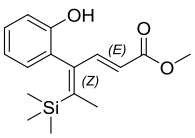
Compound 3g. Pale yellow oil (90% yield, *E*:*Z* > 99:1, NMR). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 15.4 Hz, 1H), 7.24 – 7.20 (m, 1H), 6.94 – 6.87 (m, 3H), 5.29 (d, *J* = 15.4 Hz, 1H), 4.98 (s, 1H), 3.68 (s, 3H), 2.12 (s, 3H), 1.96 (t, *J* = 7.9 Hz, 2H), 1.41 – 1.21 (m, 2H), 1.13 (sext, *J* = 6.9 Hz, 2H), 0.75 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 152.6, 151.8, 142.1, 130.7, 129.1, 128.1, 124.3, 120.6, 119.1, 115.3, 51.5, 36.7, 29.9, 22.5, 18.3, 13.7; IR (neat) 3399, 2955, 2929, 2871, 2860, 1713, 1692, 1608, 1486, 1448, 1436, 1377, 1309, 1284, 1225, 1195, 1170, 1132, 1107, 1073, 1037, 975, 925, 864, 828, 754, 731, 694, 681, 633, 609, 583, 549, 521 cm^{-1}; MS (EI) *m/z* (%): 41 (4), 55 (4), 77 (6), 91 (7), 107 (12), 131 (21), 145 (16), 157 (17), 171 (45), 185 (100), 199 (21), 217 (32), 231 (23), 243 (7), 259 (4), 274 (42); HRMS (ESIpos): calcd for $C_{17}H_{22}O_3Na$: 297.14611; found: 297.14600.



Compound 3h. Colorless oil (72% yield, *E*/*Z* > 99:1, NMR). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 15.4 Hz, 1H), 7.25 – 7.19 (m, 1H), 6.94 – 6.90 (m, 3H), 5.31 (d, *J* = 15.4 Hz, 1H), 4.86 (s, 1H), 3.68 (s, 3H), 2.06 (tt, *J* = 8.5, 5.4 Hz, 1H), 1.69 – 1.58 (m, 2H), 1.32 – 1.17 (m, 2H), 1.08 (sext, *J* = 7.2 Hz, 2H), 1.02 – 0.94 (m, 2H), 0.73 – 0.64 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 155.9, 152.5, 142.1, 130.7, 129.2, 129.2, 124.6, 120.6, 118.8, 115.3, 51.4, 30.9, 30.5, 22.7, 13.5, 13.0, 7.3, 7.0; IR (neat) 3399, 3083, 3008, 2954, 2931, 2871, 1689, 1604, 1578, 1485, 1447, 1435, 1282, 1230, 1192, 1166, 1132, 1105, 1073, 1032, 973, 917, 862, 842, 817, 753, 731, 665, 648, 612, 590, 571, 527, 483, 458, 446, 425 cm^{-1}; MS (ESIneg) *m/z*: 299 ([M-H]), 599 ([2M-H]); HRMS (ESIneg): calcd for $C_{19}H_{23}O_3$: 299.16527; found: 299.16531.

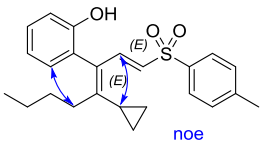


Compound 3i. Colorless oil (93% yield, *Z*:*E* > 99:1, NMR). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 15.4 Hz, 1H), 7.24 – 7.20 (m, 1H), 6.92 – 6.87 (m, 3H), 5.39 (d, *J* = 15.4 Hz, 1H), 5.03 (s, 1H), 3.69 (s, 3H), 2.16 (s, 3H), –0.18 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 153.8, 153.2, 140.8, 140.4, 131.2, 129.6, 126.5, 120.8, 120.3, 115.4, 51.6, 18.5, -1.2 (3C); IR (neat) 3411, 3062, 3030, 2952, 2896, 1716, 1693, 1608, 1575, 1485, 1447, 1436, 1281, 1247, 1193, 1169, 1135, 1096, 1075, 1036, 1019, 977, 920, 834, 753, 690, 655, 622, 591, 546, 502, 482, 431, 406 cm^{-1}; MS (EI) *m/z* (%): 45 (16), 59 (23), 73 (100), 89 (43), 115 (21), 128 (10), 141 (11), 157 (10), 171 (22), 185 (11), 201 (32), 215 (36), 231 (20), 243 (41), 258 (77), 275 (11), 290 (32); HRMS (ESIpos): calcd for $C_{16}H_{22}O_3SiNa$: 313.12304; found: 313.12324.

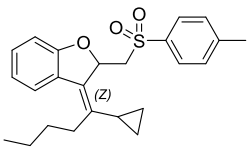


Compound 3j and 4j. The product was isolated as a yellow oil (74% yield, *E*/Z = 99:1, NMR) together with a second fraction consisting of the Michael adduct **4j** (yellow oil, 22% yield, *Z*/*E* (= 74:26.).

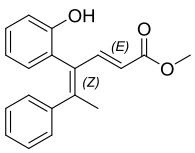
Spectral data of **3j**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 14.6 Hz, 1H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.19 (ddd, *J* = 8.0, 6.5, 2.8 Hz, 1H), 6.89 – 6.86 (m, 3H), 5.73 (d, *J* = 14.9 Hz, 1H), 2.40 (s, 3H), 2.05 (tt, *J* = 8.5, 5.4 Hz, 1H), 1.64 (t, *J* = 7.8 Hz, 2H), 1.29 – 1.15 (m, 2H), 1.11 – 1.00 (m, 4H), 0.76 – 0.65 (m, 2H), 0.67 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 152.4, 143.9, 139.5, 138.0, 130.7, 129.8 (2C), 129.4, 127.9, 127.5, 127.4 (2C), 123.8, 120.7, 115.6, 30.8, 30.6, 22.7, 21.6, 13.5, 13.2, 7.5, 7.2; MS (EI) *m/z* (%): 69 (52), 85 (41), 131 (42), 171 (38), 199 (96), 241 (100), 304 (8), 355 (18), 396 (18); HRMS (ESIpos): calcd for $C_{24}H_{28}O_3SNa$: 419.16522; found: 419.16514,



Spectral data of **4j**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 9.2 Hz, 1H), 7.10 – 7.03 (m, 1H), 6.89 – 6.84 (m, 1H), 6.57 (dd, *J* = 7.6, 3.8 Hz, 1H), 5.96 (d, *J* = 9.0 Hz, 1H), 3.59 (dd, *J* = 15.0, 1.4 Hz, 1H), 3.40 (dd, *J* = 15.0, 9.6 Hz, 1H), 2.47 (s, 3H), 2.05 – 1.97 (m, 1H), 1.95 – 1.80 (m, 1H), 1.40 – 1.23 (m, 5H), 0.95 – 0.90 (m, 3H), 0.78 – 0.68 (m, 2H), 0.57 – 0.51 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 144.6, 137.2, 135.9, 131.2, 129.6 (2C), 128.5, 128.4 (2C), 124.8, 123.5, 121.1, 110.7, 78.6, 60.9, 30.2, 27.1, 23.0, 21.6, 15.0, 13.9, 6.1, 5.6; IR (neat) 2959, 2931, 2872, 1724, 1635, 1598, 1460, 1386, 1364, 1320, 1302, 1290, 1262, 1231, 1201, 1140, 1083, 1019, 984, 950, 923, 850, 813, 747, 725, 661, 632, 601, 581, 541, 514, 463 cm^{-1}.



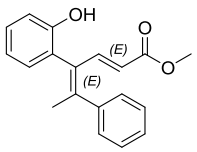
Compound 3k. The outcome of the reaction was found to be strongly time-dependent. Upon quenching of the cold reaction mixture after 10 min, ***E,Z*-3k** was obtained as the major product (95%, *Z*/*E* = 76:4); on prolonged stirring at –30°C, the *Z*/*E* decreases significantly (49:51 after 90 min) and variable amounts of the cyclized product **4k** were also detected.



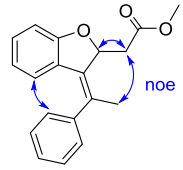
Spectral data of compound ***E,Z*-3k**: yellow solid; m.p. = 144 – 146 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 15.4 Hz, 1H), 7.14 – 6.98 (m, 6H), 6.80 (dd, *J* = 7.9, 2.0 Hz, 1H), 6.75 – 6.70 (m, 2H), 5.54 (d, *J* = 15.4 Hz, 1H), 4.98 (s, 1H), 3.73 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 152.7, 148.5, 142.4, 142.1, 131.6, 130.2, 129.0, 127.7 (2C), 127.5 (2C), 127.3, 124.8, 120.9, 120.4, 115.4, 51.6, 21.3; IR (neat) 3340, 3062, 3039, 2952, 2919, 2849, 1735, 1689, 1613, 1603, 1578, 1487,

1459, 1434, 1379, 1330, 1308, 1296, 1255, 1236, 1193, 1175, 1132, 1078, 1038, 1027, 1016, 991, 974, 943, 919, 867, 841, 792, 763, 752, 734, 700, 643, 594, 553, 535, 520, 507, 494, 463, 423 cm^{-1}; MS (EI) *m/z* (%): 31 (7), 51 (6), 63 (5), 77 (22), 91 (18), 103 (39), 115 (26), 131 (14), 165 (14), 178 (18), 191 (19), 202 (26), 221 (100), 234 (47), 247 (25), 262 (14), 279 (30), 294 (58); HRMS (APPIpos): calcd for $C_{19}H_{18}O_3$: 294.12505; found: 294.12524.

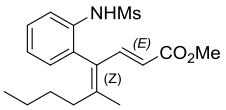
Spectral data of compound ***E,E*-3k**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 15.6 Hz, 1H), 7.46 – 7.36 (m, 3H), 7.32 – 7.26 (m, 3H), 7.06 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.00 (app. t, *J* = 6.3 Hz, 2H), 5.41 (d, *J* = 15.5 Hz, 1H), 4.93 (s, 1H), 3.62 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 152.5, 150.5, 143.6, 141.0, 130.5, 130.2, 129.5, 128.5 (2C), 128.5 (2C), 128.2, 124.2, 121.0, 120.1, 115.7, 51.4, 23.7; IR (neat) 3397, 3059, 3029, 2995, 2950, 2909, 2846, 1686, 1606, 1588, 1487, 1445, 1371, 1309, 1287, 1265, 1194, 1170, 1126, 1090, 1065, 1046, 1026, 1001, 985, 911, 866, 840, 797, 754, 731, 701, 647, 616, 599, 554, 542, 513, 484, 461, 418 cm^{-1}; MS (EI) *m/z* (%): 31 (10), 51 (9), 77 (30), 107 (46), 142 (31), 157 (13), 165 (21), 178 (23), 202 (46), 221 (100), 234 (100), 247 (56), 262 (32), 279 (31), 294 (94); HRMS (ESIpos): calcd for $C_{19}H_{18}O_3Na$: 317.11481; found : 317.11464.



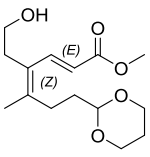
Spectral data of compound **4k**: yellow oil, 28% yield (*E*/*Z* > 99:1, NMR); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (app. t, *J* = 7.2 Hz, 2H), 7.37 (app. d, *J* = 7.3 Hz, 1H), 7.25 (d, *J* = 7.0 Hz, 2H), 7.03 (app. t, *J* = 7.3 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 6.52 (td, *J* = 7.8, 0.9 Hz, 1H), 6.20 (d, *J* = 7.8 Hz, 1H), 5.86 (dd, *J* = 8.9 Hz, 1H), 3.77 (s, 3H), 2.87 (dd, *J* = 16.0, 2.4 Hz, 1H), 2.71 (dd, *J* = 16.0, 9.8 Hz, 1H), 2.12 (d, *J* = 1.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 161.9, 142.6, 133.8, 129.5, 129.2, 129.0 (2C), 127.7 (2C), 127.4, 124.7, 123.6, 120.3, 110.6, 81.1, 52.0, 39.8, 23.3; IR (neat) 3076, 3053, 3021, 2951, 2852, 1737, 1602, 1586, 1491, 1461, 1437, 1405, 1369, 1334, 1273, 1245, 1222, 1164, 1120, 1107, 1072, 1024, 1011, 987, 888, 848, 803, 748, 702, 656, 610, 590, 538, 507, 444 cm^{-1}; MS (EI) *m/z* (%): 77 (5), 91 (5), 103 (17), 115 (12), 131 (4), 165 (8), 178 (12), 191 (12), 202 (12), 221 (100), 234 (19), 262 (3), 279 (31), 294 (57); HRMS (ESIpos): calcd for $C_{19}H_{18}O_3Na$: 317.11481; found: 317.11503.



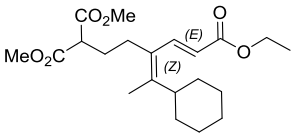
Compound 3l. Isolated as a mixture with unreacted starting material (68% brsm, *Z*/*E* = 90:10 NMR). An analytically pure sample of **3l** was obtained by preparative HPLC (150 mm YMC-Actus Triart C18, 5μm, 20 mm i.D., CH_3CN/H_2O = 70:30, 10 mL/min). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 15.4 Hz, 1H), 7.67 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.35 (td, *J* = 8.1, 1.6 Hz, 1H), 7.14 (td, *J* = 7.5, 1.1 Hz, 1H), 6.98 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.17 (s, 1H), 5.16 (d, *J* = 15.4 Hz, 1H), 3.70 (s, 3H), 2.93 (s, 3H), 2.15 (s, 3H), 1.88 (t, *J* = 7.9 Hz, 2H), 1.45 – 1.23 (m, 2H), 1.13 (h, *J* = 7.3 Hz, 2H), 0.75 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 152.4, 141.8, 134.7, 131.1, 129.2, 128.5, 127.8, 124.4, 119.3, 117.6, 51.6, 39.4, 36.8, 29.9, 22.6, 18.4, 13.7; IR (neat) 3276, 2955, 2931, 2871, 2861, 1713, 1614, 1579, 1492, 1451, 1434, 1394, 1335, 1308, 1280, 1192, 1158, 1132, 1112, 1071, 1042, 971, 913, 864, 817, 756 cm^{-1}; MS (EI) *m/z* (%): 130 (7), 156 (11), 170 (11), 184 (37), 212 (10), 216 (24), 271 (100), 351 (2); HRMS (ESIpos): calcd for $C_{18}H_{26}NO_4S$ $[M+H]^+$ 352.15779; found: 352.15771.



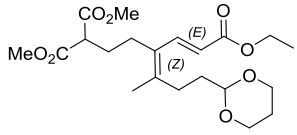
Compound 6. Colorless oil (81% yield, *Z*/*E* = 95:5, NMR). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 15.7 Hz, 1H), 5.87 (d, *J* = 15.7 Hz, 1H), 4.47 (t, *J* = 4.9 Hz, 1H), 4.07 (dd, *J* = 10.7, 5.0 Hz, 2H), 3.75 (s, 3H), 3.69 (td, *J* = 12.4, 2.6 Hz, 2H), 3.63 (t, *J* = 6.9 Hz, 2H), 2.59 (t, *J* = 7.0 Hz, 2H), 2.47 (t, *J* = 7.3 Hz, 2H), 2.10 – 1.99 (m, 1H), 1.93 (s, 3H), 1.75 (td, *J* = 7.3, 4.9 Hz, 3H), 1.30 (dt, *J* = 13.5, 1.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 148.2, 142.4, 127.2, 115.5, 101.4, 66.8 (2C), 61.2, 51.5, 33.5, 31.5, 29.0, 25.6, 20.7; IR (neat) 3449, 2954, 2931, 2852, 1702, 1612, 1461, 1434, 1403, 1378, 1303, 1285, 1262, 1193, 1178, 1133, 1101, 1077, 1038, 1000, 981, 948, 926, 883, 854, 809, 752, 666, 638, 583, 550, 469, 443 cm^{-1}; MS (ESIpos) *m/z* = 307 ([M+Na]), 591 ([2M+Na]); HRMS (ESIpos): calcd for $C_{15}H_{24}O_5Na$: 307.15159; found: 307.15130.



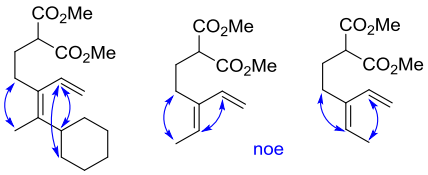
Compound 8. Colorless oil (70% yield *Z*/*E* = 99:1, NMR); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 15.6 Hz, 1H), 5.85 (d, *J* = 15.6 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.75 (s, 6H), 3.37 (t, *J* = 7.4 Hz, 1H), 2.87 – 2.82 (m, 1H), 2.28 – 2.24 (m, 2H), 1.94 – 1.88 (m, 2H), 1.76 (s, 3H), 1.76 – 1.67 (m, 3H), 1.45 (app. d, *J* = 7.8 Hz, 2H), 1.36 – 1.23 (m, 4H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.19 – 1.12 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 168.2, 151.8, 141.2 (2C), 128.2, 115.5, 60.2, 52.5 (2C), 51.4, 41.2, 31.0 (2C), 27.4, 26.5, 26.2 (2C), 26.0, 15.3, 14.3; IR (neat) 2929, 2853, 1734, 1706, 1610, 1436, 1365, 1290, 1254, 1223, 1185, 1150, 1094, 1036, 977, 931, 887, 861, 820, 793, 763, 741, 712, 697, 629, 590, 556, 512, 476, 461, 440 cm^{-1}; MS (EI) *m/z* (%): 55 (19), 67 (22), 91 (30), 105 (34), 145 (40), 174 (87), 192 (40), 202 (25), 248 (83), 269 (19), 297 (100), 306 (11), 334 (24), 380 (15); HRMS (ESIpos): calcd for $C_{21}H_{32}O_6Na$: 403.20911; found: 403.20923.



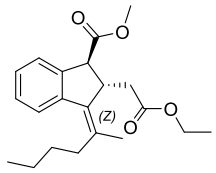
Compound 9. Colorless oil (63% yield, *Z*/*E* > 98:2, NMR); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 15.7 Hz, 1H), 5.84 (d, *J* = 15.6 Hz, 1H), 4.41 (t, *J* = 5.2 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 4.10 – 4.06 (m, 2H), 3.75 (s, 6H), 3.75 – 3.64 (m, 3H), 3.37 (t, *J* = 7.3 Hz, 1H), 2.41 (t, *J* = 7.4 Hz, 2H), 2.30 – 2.26 (m, 2H), 2.05 (qt, *J* = 12.6, 5.0 Hz, 1H), 1.96 – 1.90 (m, 2H), 1.86 (s, 3H), 1.72 – 1.67 (m, 2H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6 (2C), 167.9, 146.1, 141.6, 130.0, 115.9, 101.1, 66.8 (2C), 60.1, 52.6 (2C), 51.4, 33.7, 28.8, 27.4, 26.1, 25.7, 20.0, 14.3; IR (neat) 2956, 2851, 1733, 1706, 1614, 1461, 1435, 1402, 1378, 1366, 1344, 1289, 1256, 1228, 1182, 1146, 1100, 1077, 1041, 1002, 929, 884, 855, 797, 739, 638, 594, 490, 459 cm^{-1}; MS (EI) *m/z* (%): 59 (11), 79 (5), 87 (47), 100 (23), 113 (100), 131 (27), 145 (12), 158 (46), 178 (10), 204 (23), 226 (7), 259 (5), 290 (22), 325 (10), 367 (5), 412 (8); HRMS (ESIpos): calcd for $C_{21}H_{32}O_8Na$: 435.19894; found: 435.19885.



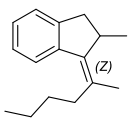
Compounds 12 and 14. Isolated as an inseparable mixture in the form of a colorless oil (combined yield 53%, 12:14 = 3.8:1, NMR). Characteristic data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.78 (dd, *J* = 17.3, 11.1 Hz, 1H), 5.15 (d, *J* = 17.7 Hz, 1H), 4.98 (d, *J* = 11.1 Hz, 1H), 3.74 (s, 6H), 3.38 (t, *J* = 7.4 Hz, 1H), 2.70 – 2.67 (m, 1H), 2.27 – 2.24 (m, 2H), 1.96 – 1.92 (m, 2H), 1.76 – 1.69 (m, 3H), 1.66 (s, 3H), 1.47 – 1.45 (m, 2H), 1.35 – 1.25 (m, 4H), 1.18 – 1.13 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.9 (2C), 141.5, 133.5, 129.1, 111.3, 52.4 (2C), 51.6, 40.7, 31.0 (2C), 27.7, 26.6 (2C), 26.2, 26.0, 14.4; IR (neat) 2928, 2852, 1735, 1620, 1436, 1345, 1280, 1257, 1236, 1222, 1200, 1153, 1088, 1056, 1041, 1020, 988, 890, 843, 803 cm^{-1}; MS (EI) *m/z* (%): 31 (7), 41 (21), 55 (31), 67 (27), 79 (50), 91 (42), 105 (51), 120 (34), 133 (67), 147 (100), 161 (49), 176 (81), 201 (6), 248 (6), 308 (12); HRMS (ESIpos): calcd for $C_{18}H_{28}O_4Na$: 331.18798; found: 331.18781.



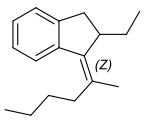
Compound 17. Colorless oil (67% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.8 Hz, 1H), 7.42 (d, *J* = 7.5 Hz, 1H), 7.26 (app. t, *J* = 7.9 Hz, 1H), 7.17 (app. t, *J* = 7.3 Hz, 1H), 4.15 – 4.07 (m, 2H), 3.83 – 3.80 (m, 1H), 3.80 (s, 1H), 3.67 (s, 3H), 2.63 (ddd, *J* = 13.4, 10.7, 5.1 Hz, 1H), 2.48 (dd, *J* = 15.8, 3.9 Hz, 1H), 2.21 (dd, *J* = 15.8, 11.5 Hz, 1H), 2.24 – 2.15 (m, 1H), 1.95 (s, 3H), 1.62 – 1.38 (m, 4H), 1.23 (t, *J* = 7.1 Hz, 3H), 0.97 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 172.3, 141.3, 140.2, 136.2, 133.6, 128.0, 126.7, 126.4, 124.6, 60.5, 53.4, 52.2, 43.1, 38.8, 34.7, 30.2, 22.9, 21.3, 14.2, 14.1; IR (neat) 2955, 2929, 2860, 1732, 1653, 1597, 1459, 1434, 1370, 1338, 1295, 1247, 1199, 1157, 1094, 1064, 1026, 944, 918, 887, 861, 755, 726 cm^{-1}; MS (ESIpos) *m/z*: 345 ([M+H]), 362 ([M+NH_4]), 367 ([M+Na]), 383 ([M+K]), 711 ([2M+Na]); HRMS (ESIpos): calcd for $C_{21}H_{28}O_4Na$: 367.18798; found: 367.18795.

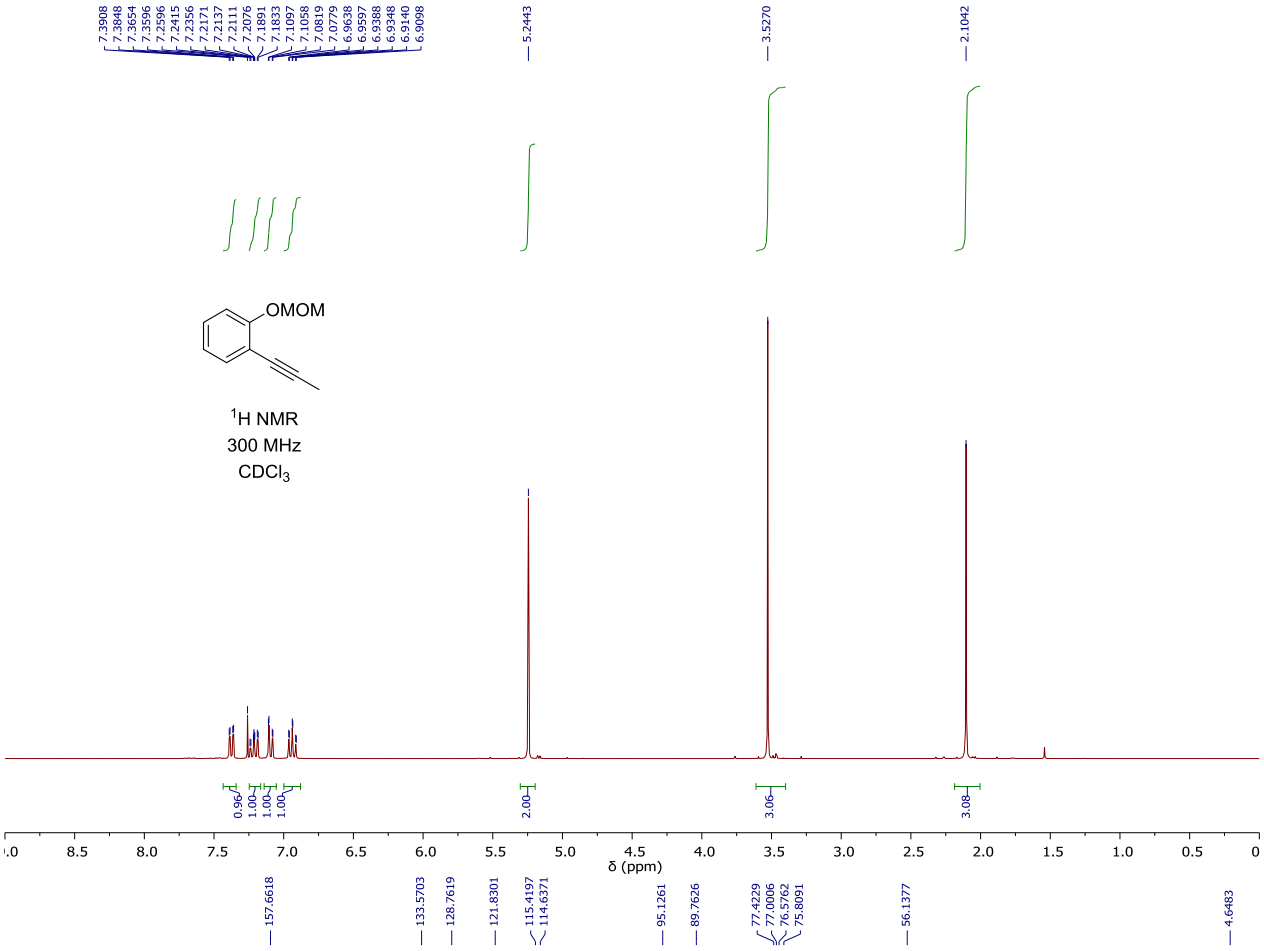


Compounds 20 and 21. The reaction was carried out with 1 equivalent of $Fe(acac)_3$, 2 equivalents of MeMgBr at –30 °C (50 min) and then at –15 °C (16 h); the crude product (quant.) was a mixture of **20** and **21** (69:31, NMR). Pure samples were obtained by preparative HPLC (150 mm YMC-Actus Triart C18, 5μm, 20 mm i.D., CH_3CN/H_2O = 90:10, 15 mL/min). During isolation, one has to be careful as both products are volatile in vacuum. Spectral data of compound **20**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 7.5 Hz, 1H), 7.24 (d, J = 6.6 Hz, 1H), 7.17 (td, J = 7.0, 1.0 Hz, 1H), 7.13 (td, J = 7.3, 1.2 Hz, 1H), 3.18 – 3.09 (m, 2H), 2.60 (ddd, J = 13.3, 10.6, 5.4 Hz, 1H), 2.44 (d, J = 14.8 Hz, 1H), 2.18 (ddd, J = 13.3, 10.3, 5.5 Hz, 1H), 1.89 (s, 3H), 1.63 – 1.38 (m, 4H), 1.01 – 0.96 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 140.8, 140.2, 130.9, 126.2, 126.1, 125.6, 124.5, 38.8, 37.4, 34.6, 30.4, 23.0, 20.9 (2C), 14.2; IR (neat) 3067, 3019, 2956, 2926, 2860, 1458, 1376, 766, 723 cm^{-1}; MS (EI) *m/z* (%): 115 (17), 128 (26), 129 (34), 130 (12), 143 (100), 157 (21), 158 (10), 171 (70), 214 (65); HRMS (APPIpos): calcd for C16H22: 214.17132; found: 214.17160.

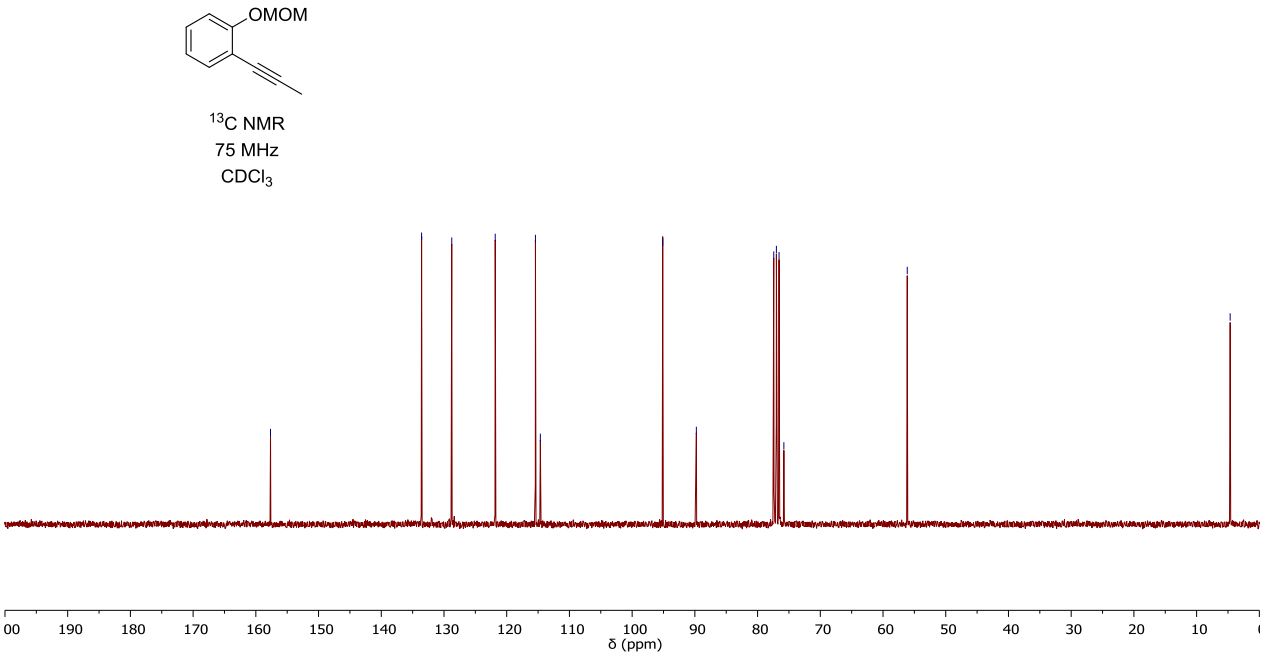


Spectral data of compound **21**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 7.4 Hz, 1H), 7.22 (d, J = 7.2 Hz, 1H), 7.16 (t, J = 7.2 Hz, 1H), 7.11 (td, J = 7.3, 1.2 Hz, 1H), 3.05 (dd, J = 15.8, 7.5 Hz, 1H), 2.94 (td, J = 8.3, 4.6 Hz, 1H), 2.63 (ddd, J = 13.3, 10.8, 5.2 Hz, 1H), 2.59 (d, J = 15.8 Hz, 1H), 2.15 (ddd, J = 13.3, 10.4, 5.4 Hz, 1H), 1.89 (s, 3H), 1.64 – 1.31 (m, 5H), 1.30 – 1.20 (m, 1H), 0.98 (t, J = 7.1 Hz, 3H), 0.87 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.8, 140.9, 139.8, 131.3, 126.1, 125.9, 125.3, 124.3, 44.5, 35.8, 34.7, 30.6, 28.0, 23.0, 21.3, 14.2, 11.8; IR (neat) 3065, 3018, 2957, 2927, 2871, 2858, 1649, 1599, 1459, 1377, 768, 734 cm^{-1}; MS (EI) *m/z* (%): 41 (10), 43 (12), 55 (12), 115 (20), 128 (28), 129 (35), 143 (100), 157 (14), 171 (11), 185 (21), 228 (26); HRMS (APPIpos): calcd for $C_{17}H_{24}$: 228.18713, found: 228.18725.

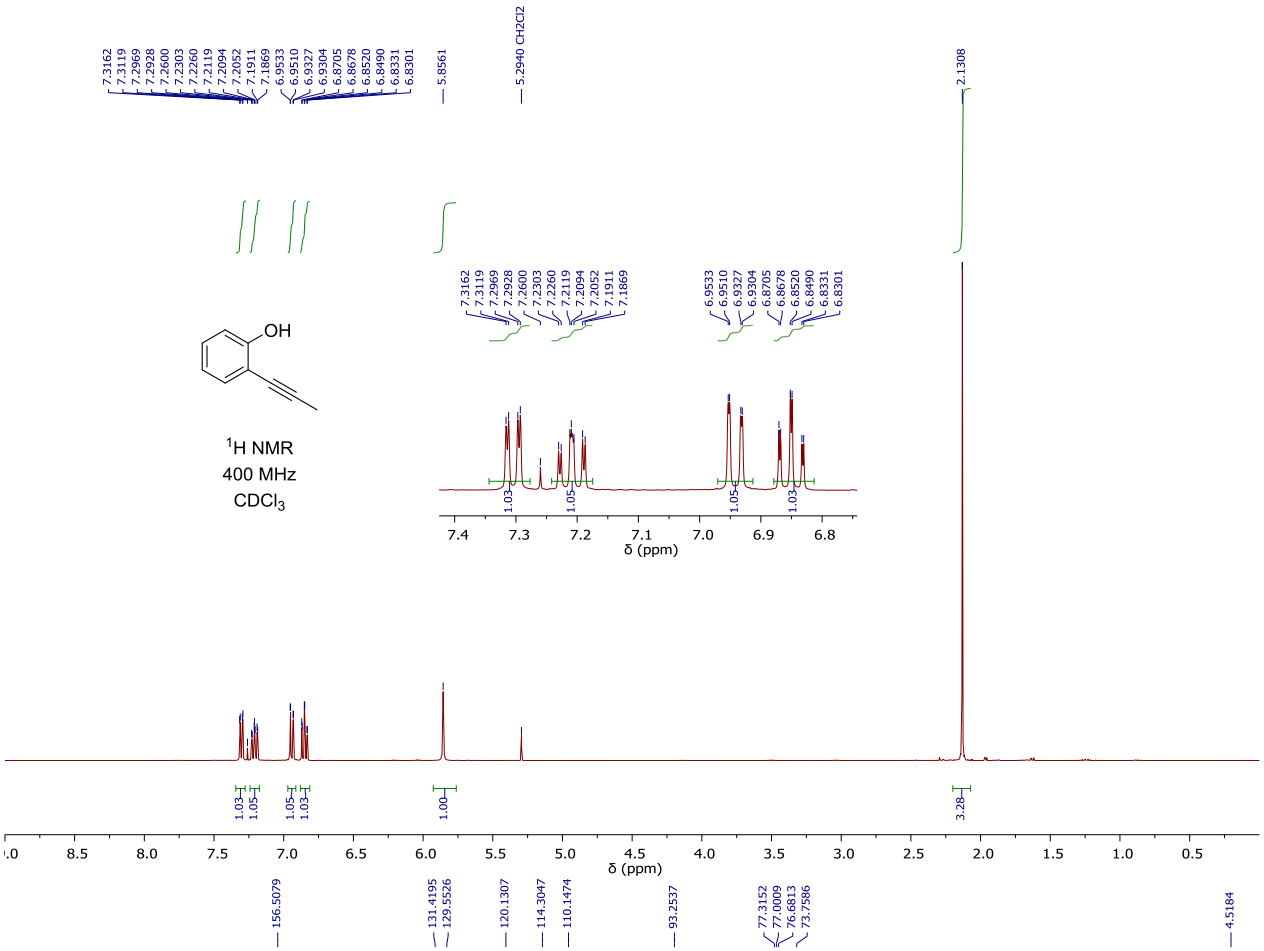


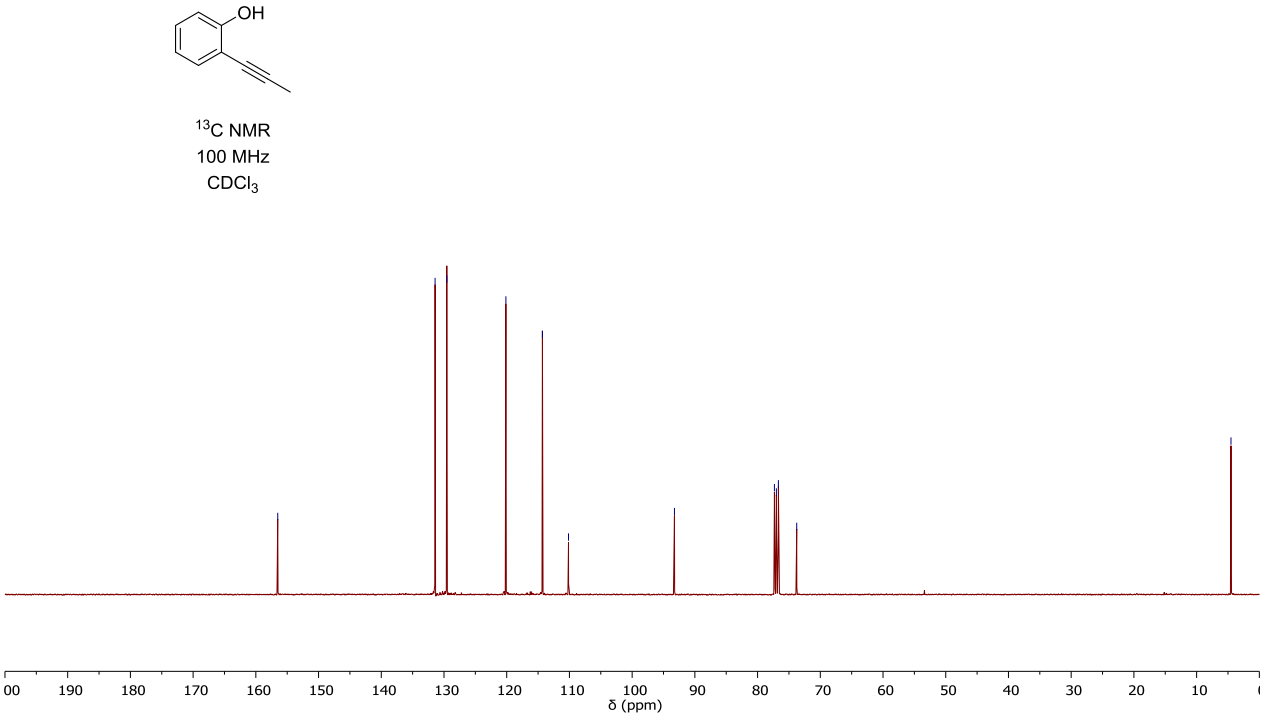


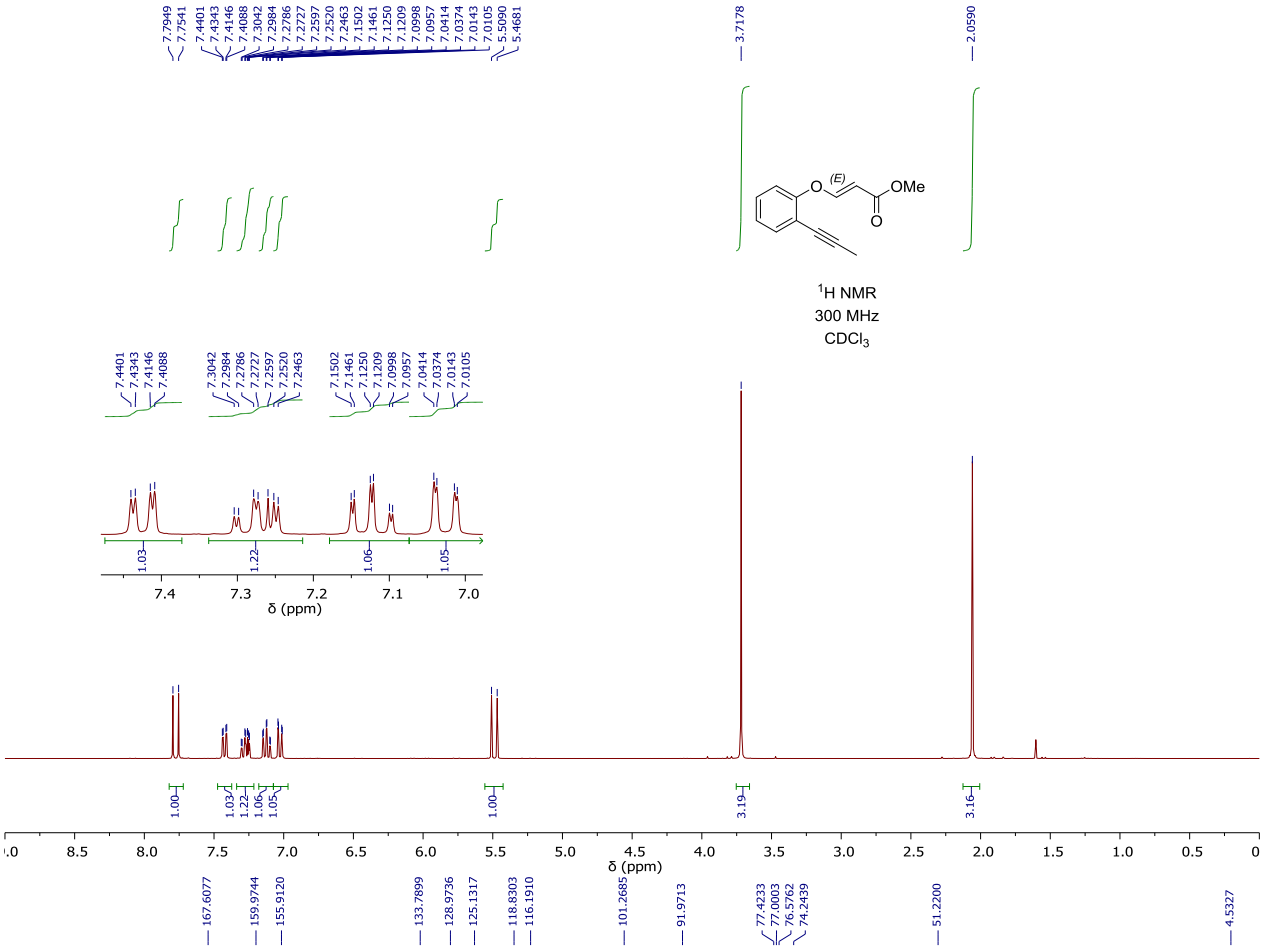
^{1}H NMR
300 MHz
$CDCl_3$



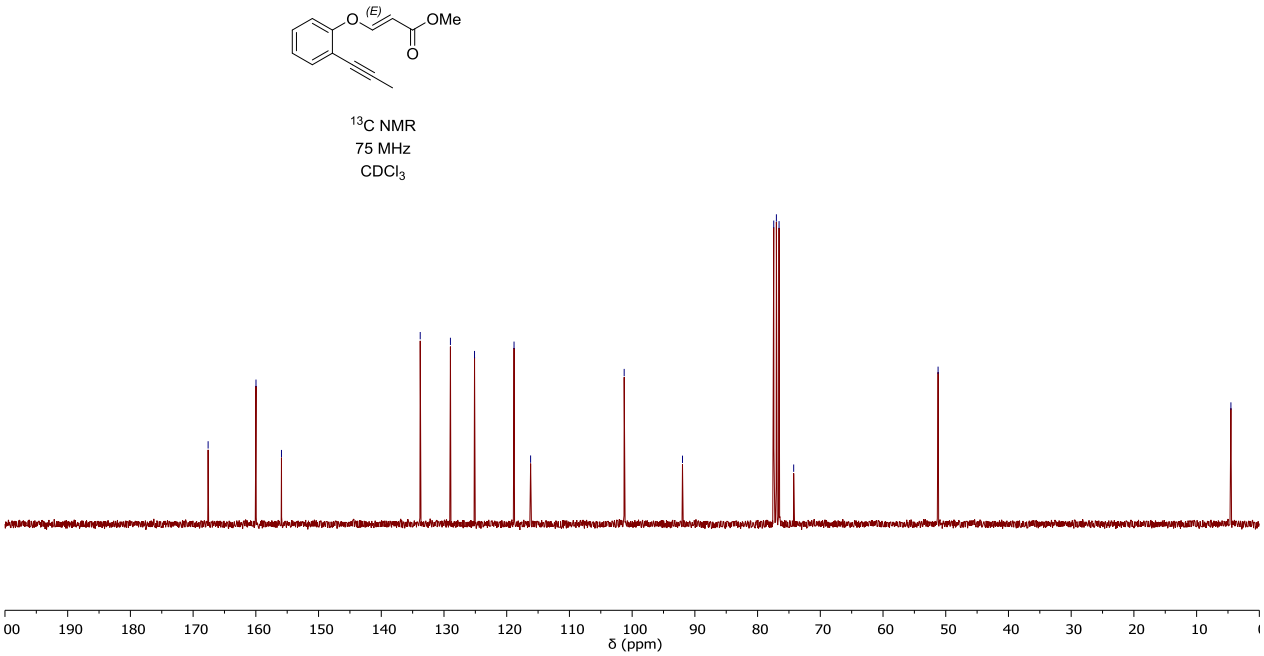
^{13}C NMR
75 MHz
$CDCl_3$


OH
^{1}H NMR
400 MHz
$CDCl_3$
δ (ppm)

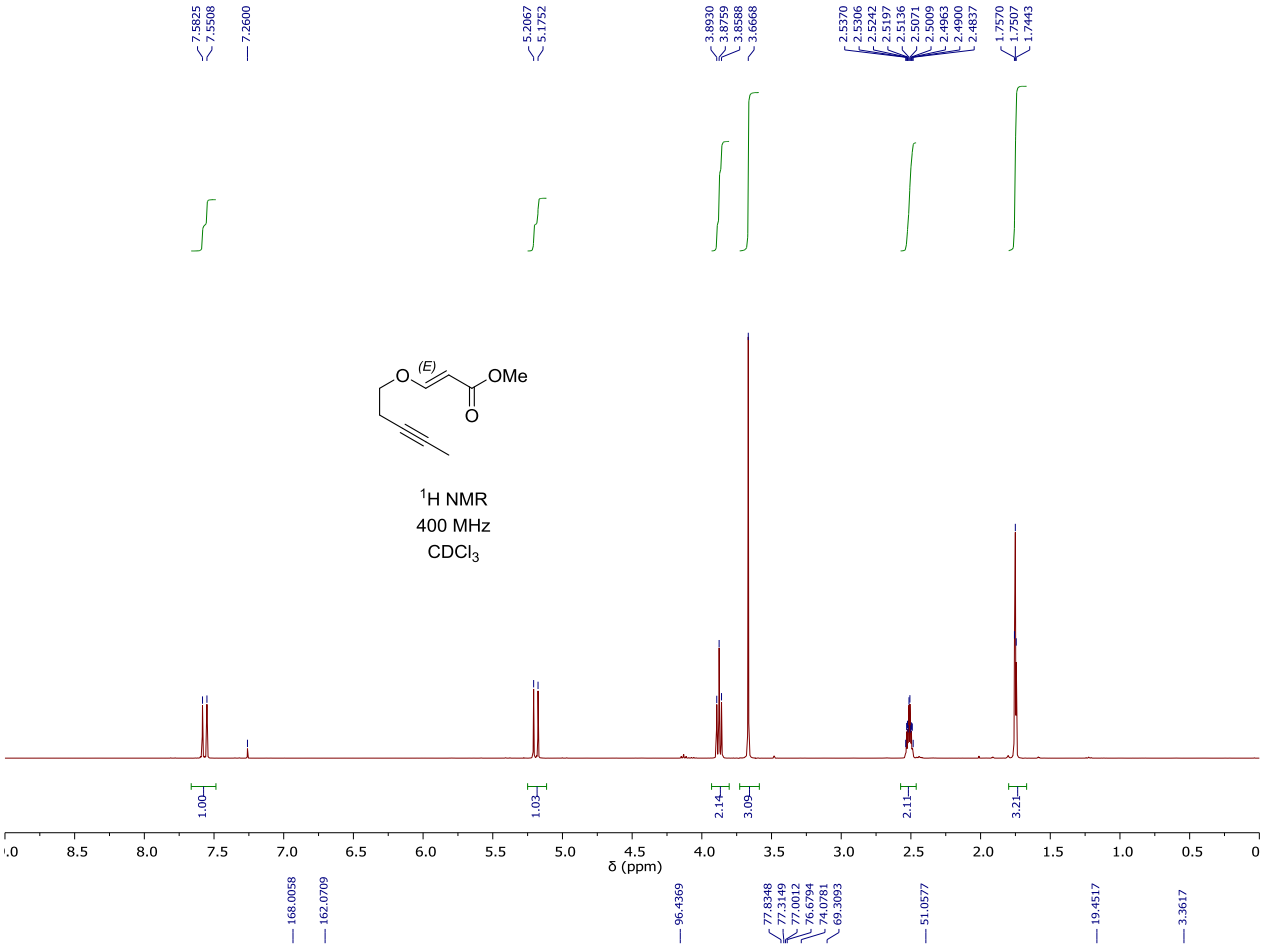

OH
^{13}C NMR
100 MHz
$CDCl_3$
δ (ppm)



^{1}H NMR
300 MHz
$CDCl_3$



^{13}C NMR
75 MHz
$CDCl_3$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7.2600
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3.8759
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3.6668
2.5370
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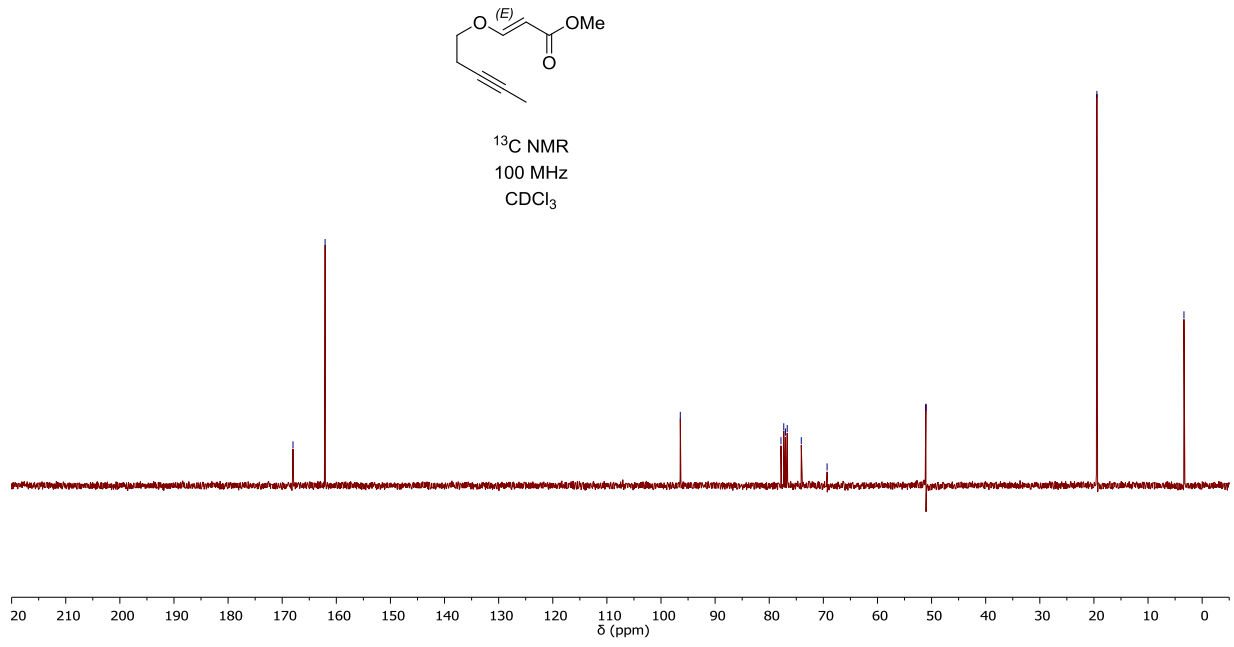
2.5242
2.5197
2.5136
2.5071
2.5009
2.4963
2.4900
2.4837
1.7570
1.7507
1.7443
(E)
O
OMe
O
1H NMR
400 MHz
CDCl3
1.00
1.03
2.14
3.09
2.11
3.21
δ (ppm)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77.3149
77.0012
76.6794
74.0781
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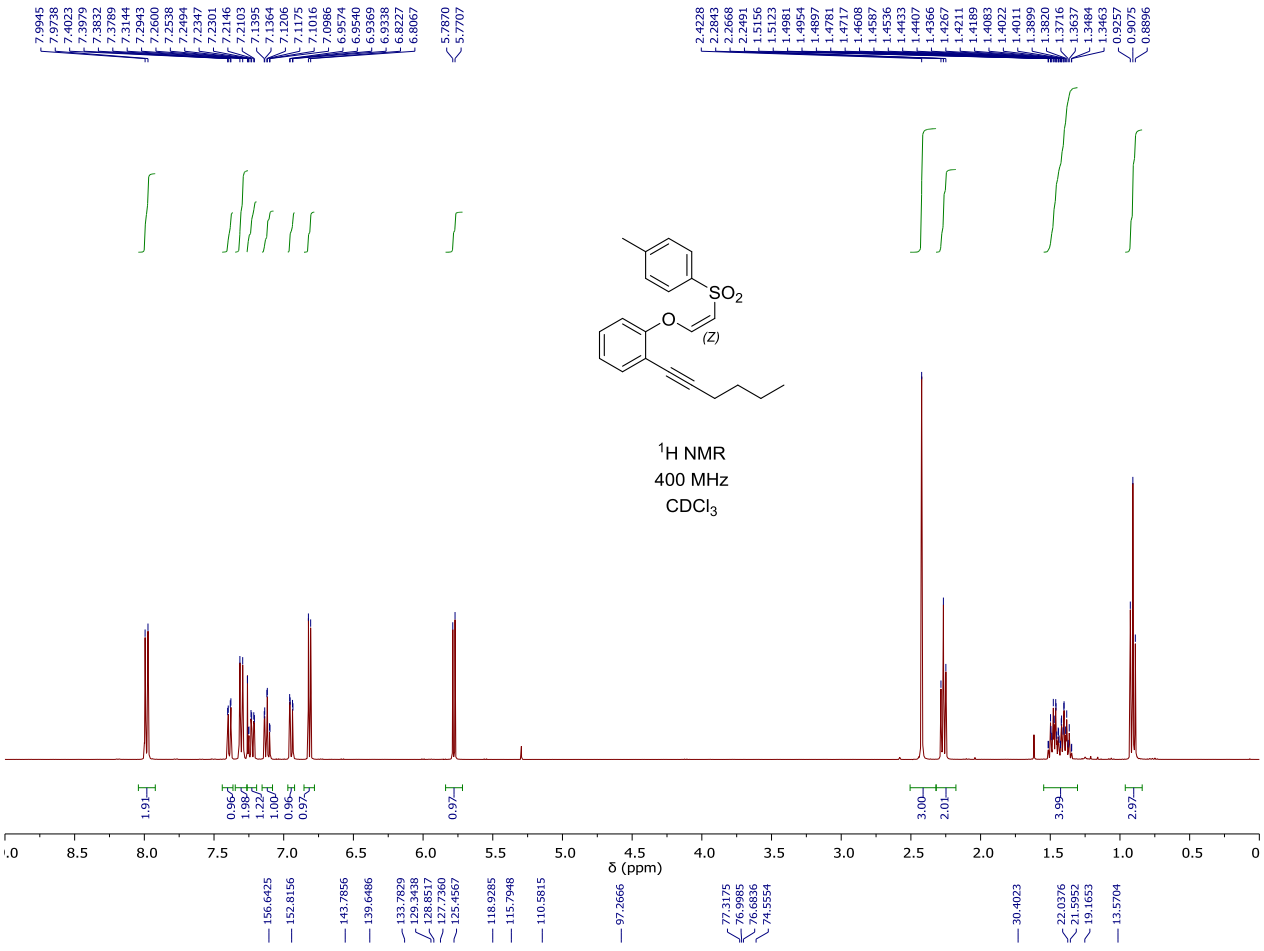
19.4517
3.3617
(E)
O
OMe
O
13C NMR
100 MHz
CDCl3
δ (ppm)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7.2347
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7.2146
7.2103
7.1395
7.1364
7.1206
7.1175
7.1016
7.0986
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1.3716
1.3637
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0.9075
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SO2
O
(Z)
1H NMR
400 MHz
CDCl3
1.91
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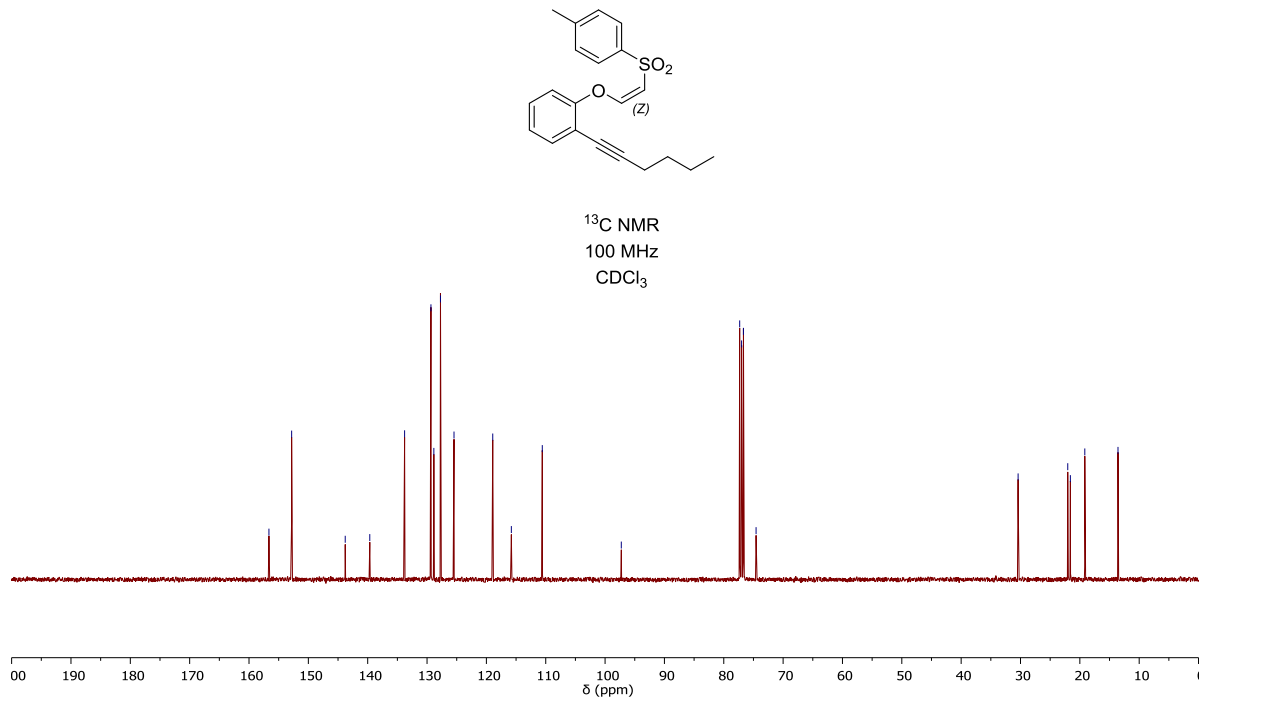
1.98
1.22
1.00
0.96
0.97
0.97
3.00
2.01
3.99
2.97
δ (ppm)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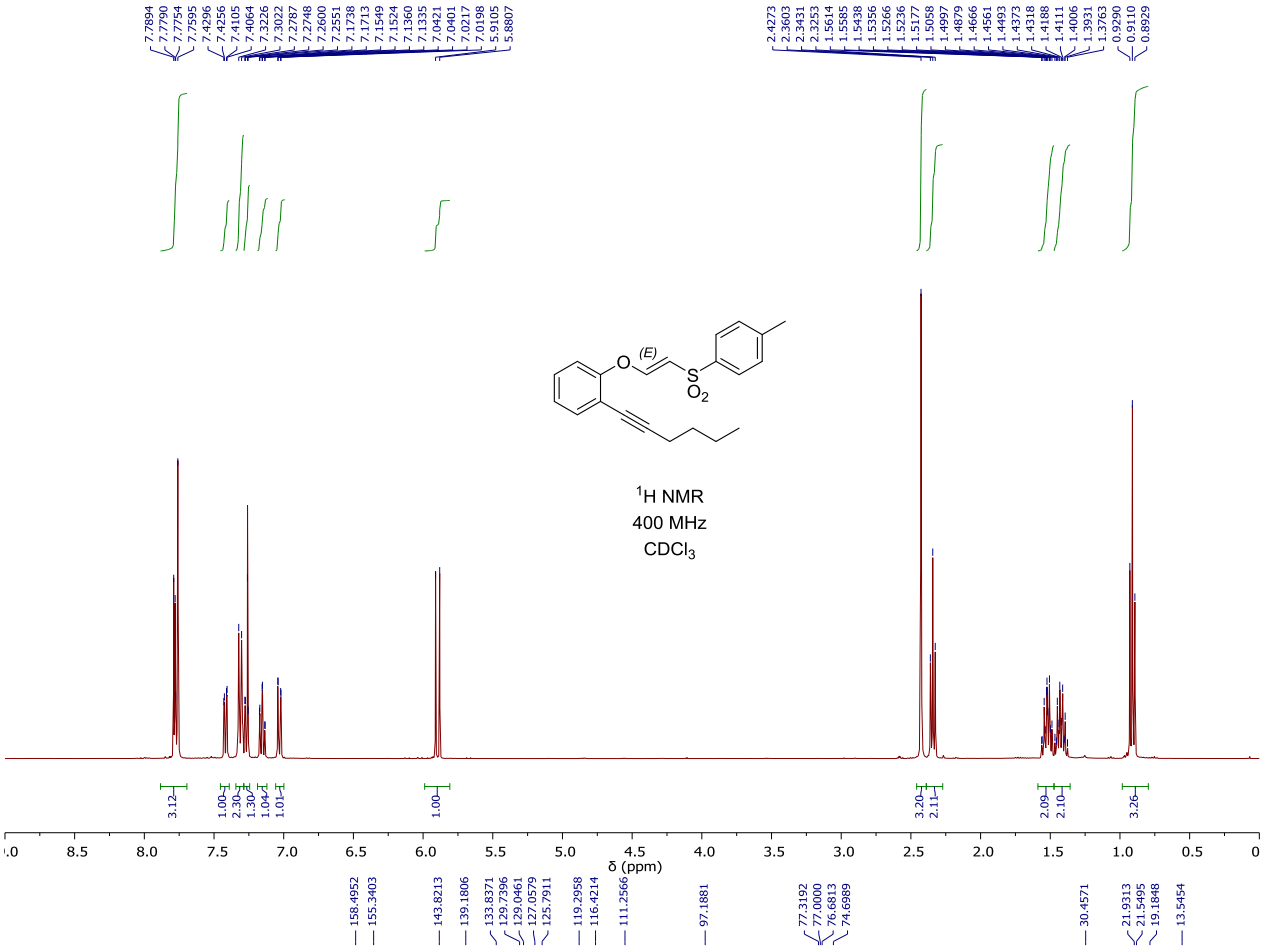
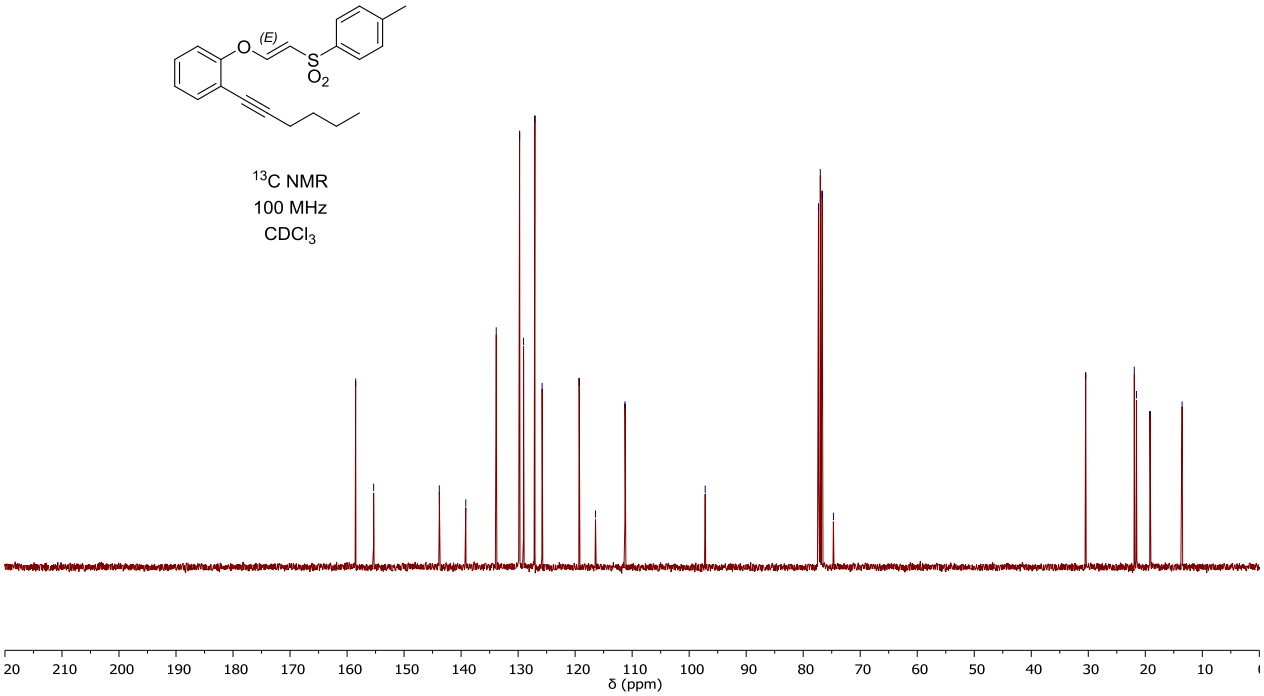
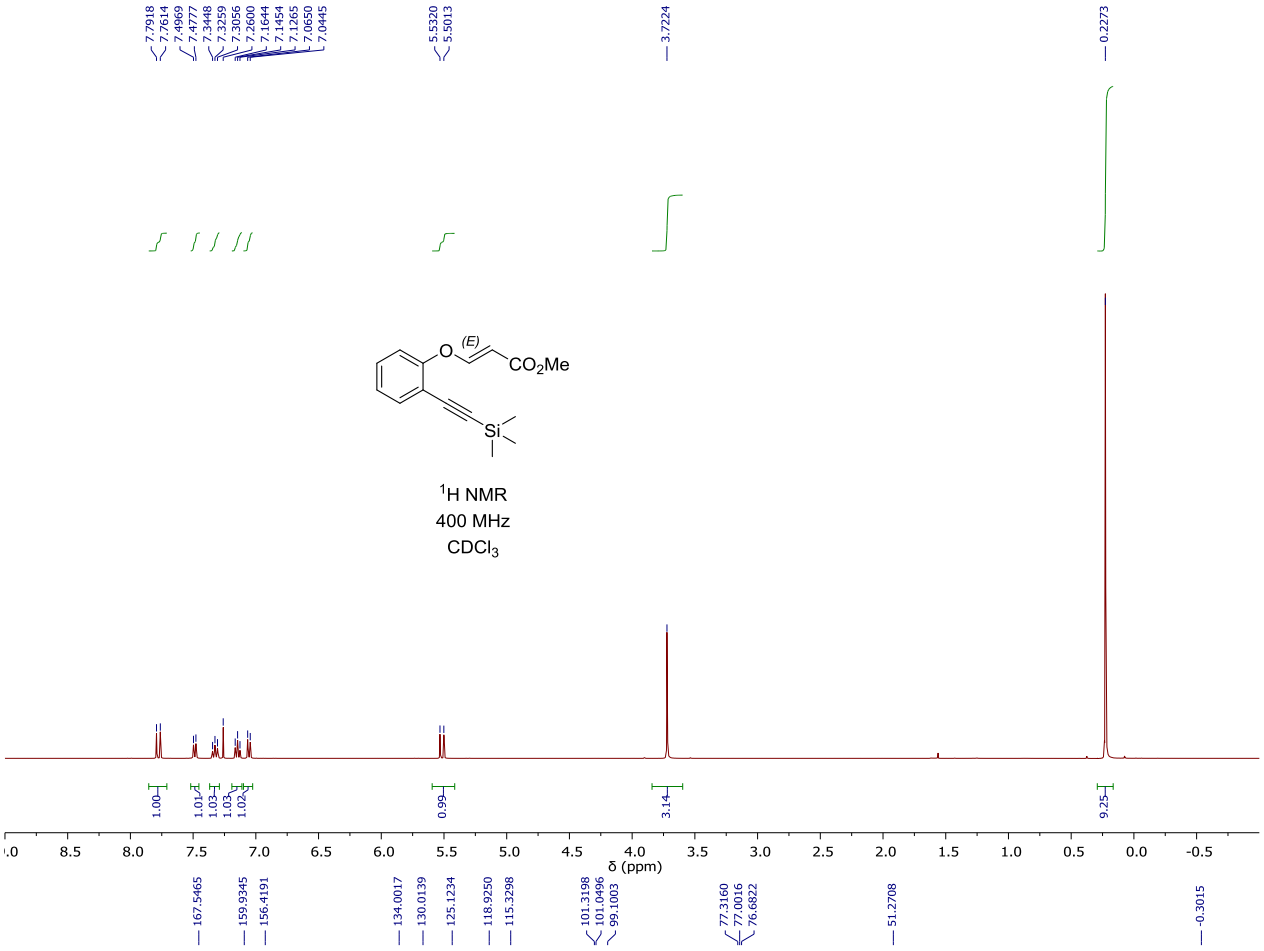
77.3175
76.9965
76.6836
74.5554
30.4023
22.0376
21.5952
19.1653
13.5704
SO2
O
(Z)
13C NMR
100 MHz
CDCl3
δ (ppm)



^{1}H NMR
400 MHz
$CDCl_3$



^{13}C NMR
100 MHz
$CDCl_3$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7.1265
7.0650
7.0445
5.5320
5.5013
3.7224
0.2273
(E)
O
CO2Me
Si
1H NMR
400 MHz
CDCl3
1.00
1.01
1.03
1.03
1.02
0.99
3.14
9.25
δ (ppm)
167.5465
159.9345
156.4191
134.0017
130.0139
125.1234
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99.1003
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77.0016
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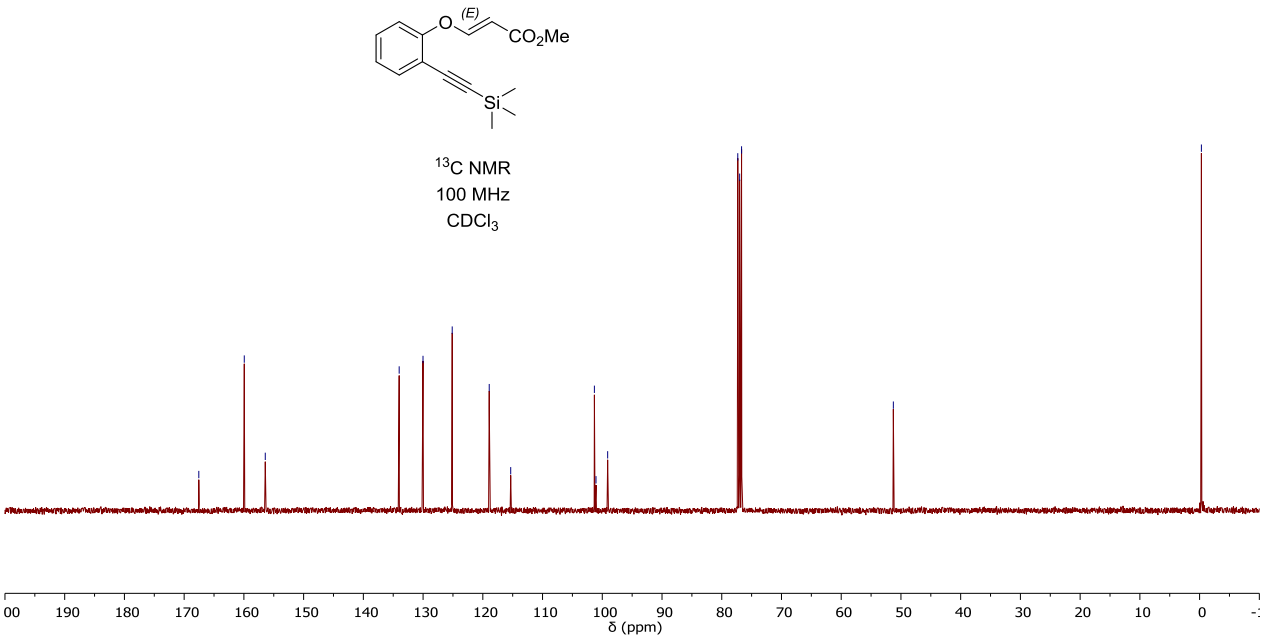
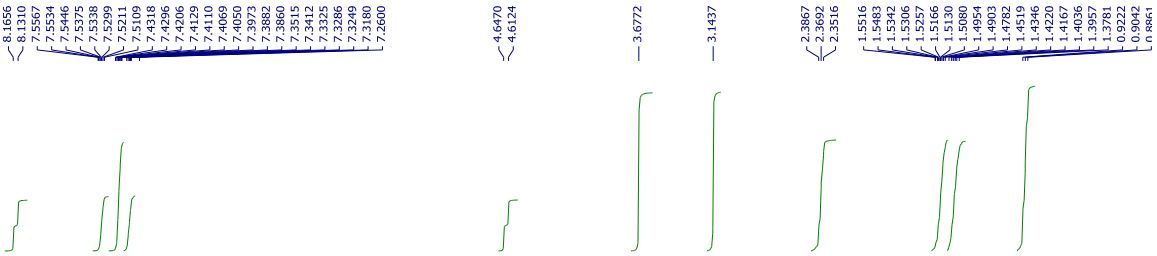
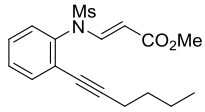
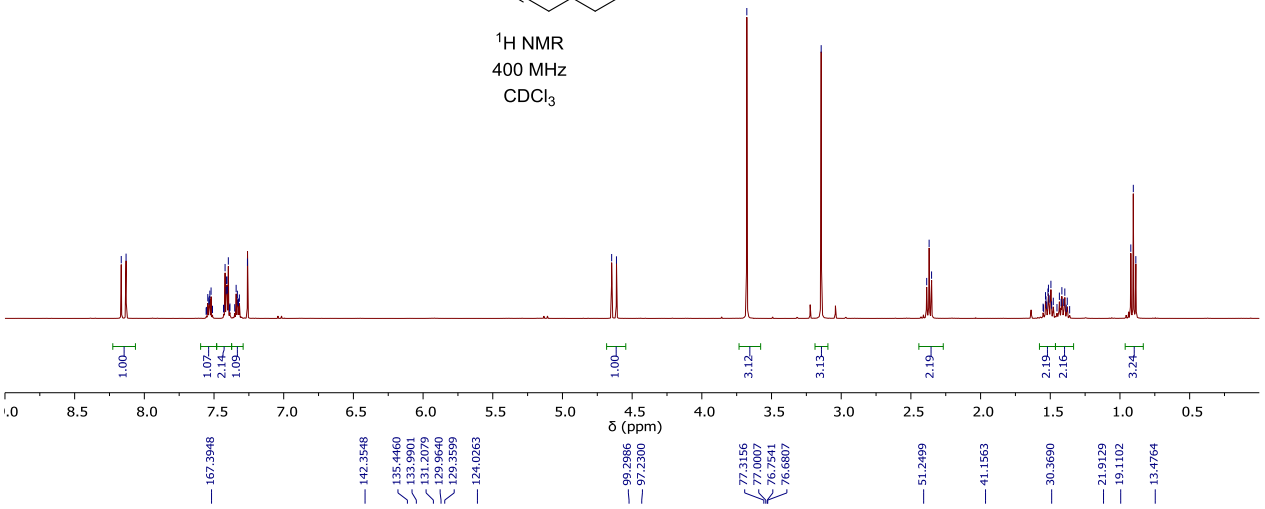
-0.3015

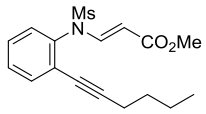

(E)
O
CO2Me
Si
13C NMR
100 MHz
CDCl3
δ (ppm)



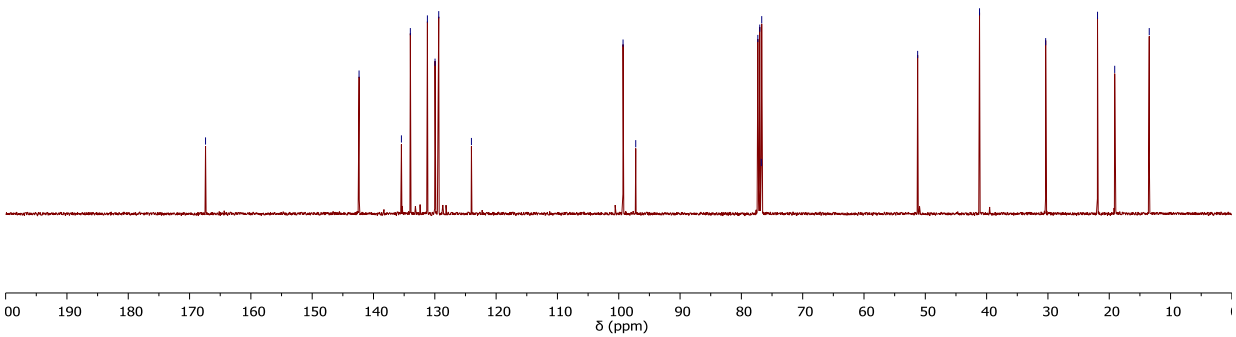


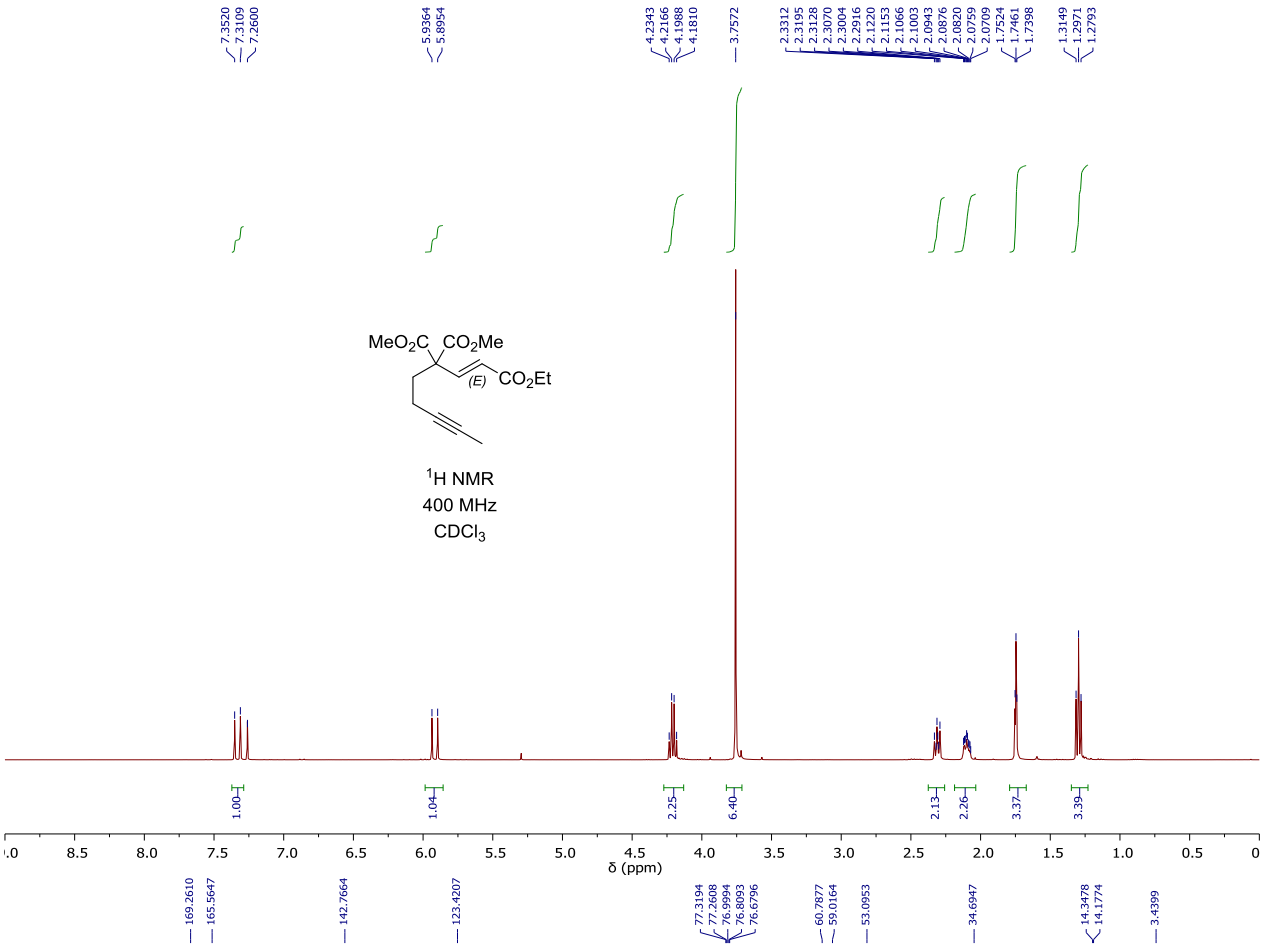
^{1}H NMR
400 MHz
$CDCl_3$





^{13}C NMR
100 MHz
$CDCl_3$

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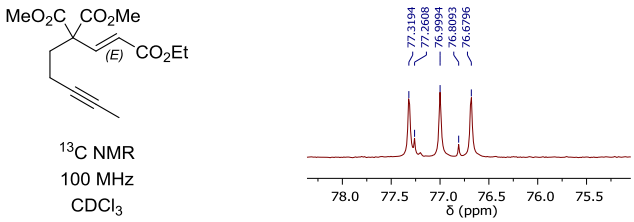
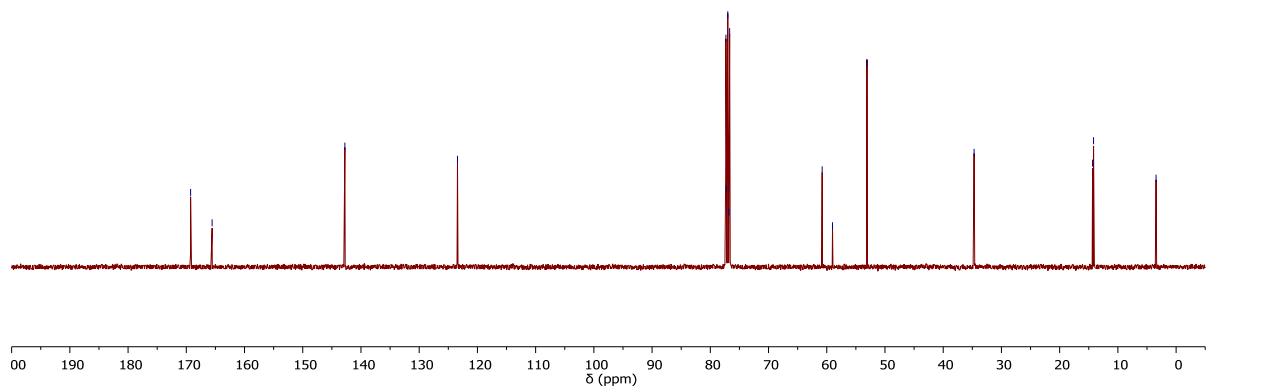
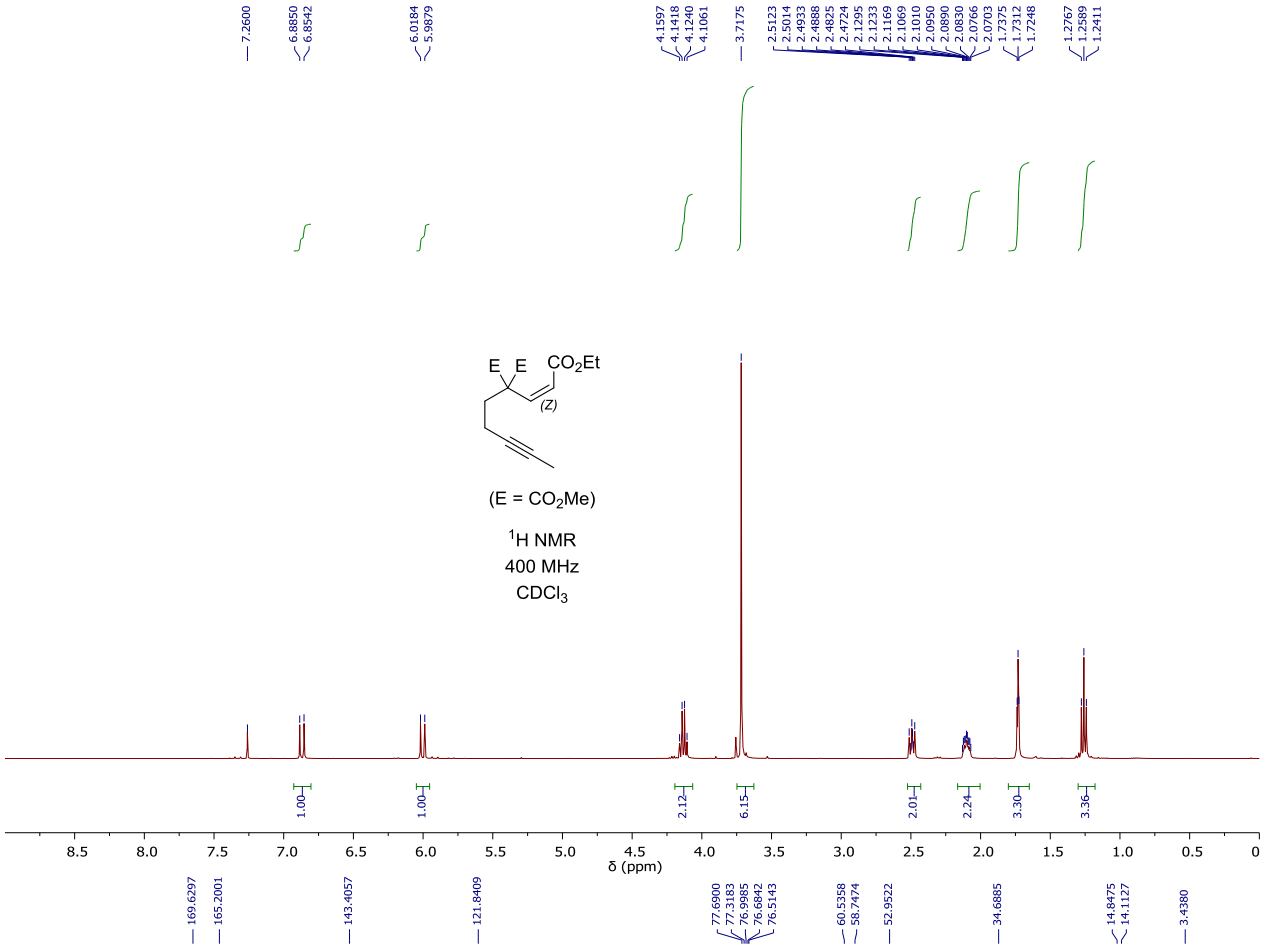
7.3109
7.2600
5.9364
5.8954
4.2343
4.2166
4.1988
4.1810
3.7572
2.3312
2.3195
2.3128
2.3070
2.3004
2.2916
2.1220
2.1153
2.1066
2.1003
2.0943
2.0876
2.0820
2.0759
2.0709
1.7524
1.7461
1.7398
1.3149
1.2971
1.2793
MeO2C CO2Me
(E) CO2Et
1H NMR
400 MHz
CDCl3
1.00
1.04
2.25
6.40
2.13
2.26
3.37
3.39
δ (ppm)

169.2610
165.5647
142.7664
123.4207
77.3194
77.2608
76.9994
76.8093
76.6796
60.7877
59.0164
53.0953
34.6947
14.3478
14.1774
3.4399


MeO2C CO2Me
(E) CO2Et
13C NMR
100 MHz
CDCl3
77.3194
77.2608
76.9994
76.8093
76.6796
78.0
77.5
77.0
76.5
76.0
75.5
δ (ppm)


δ (ppm)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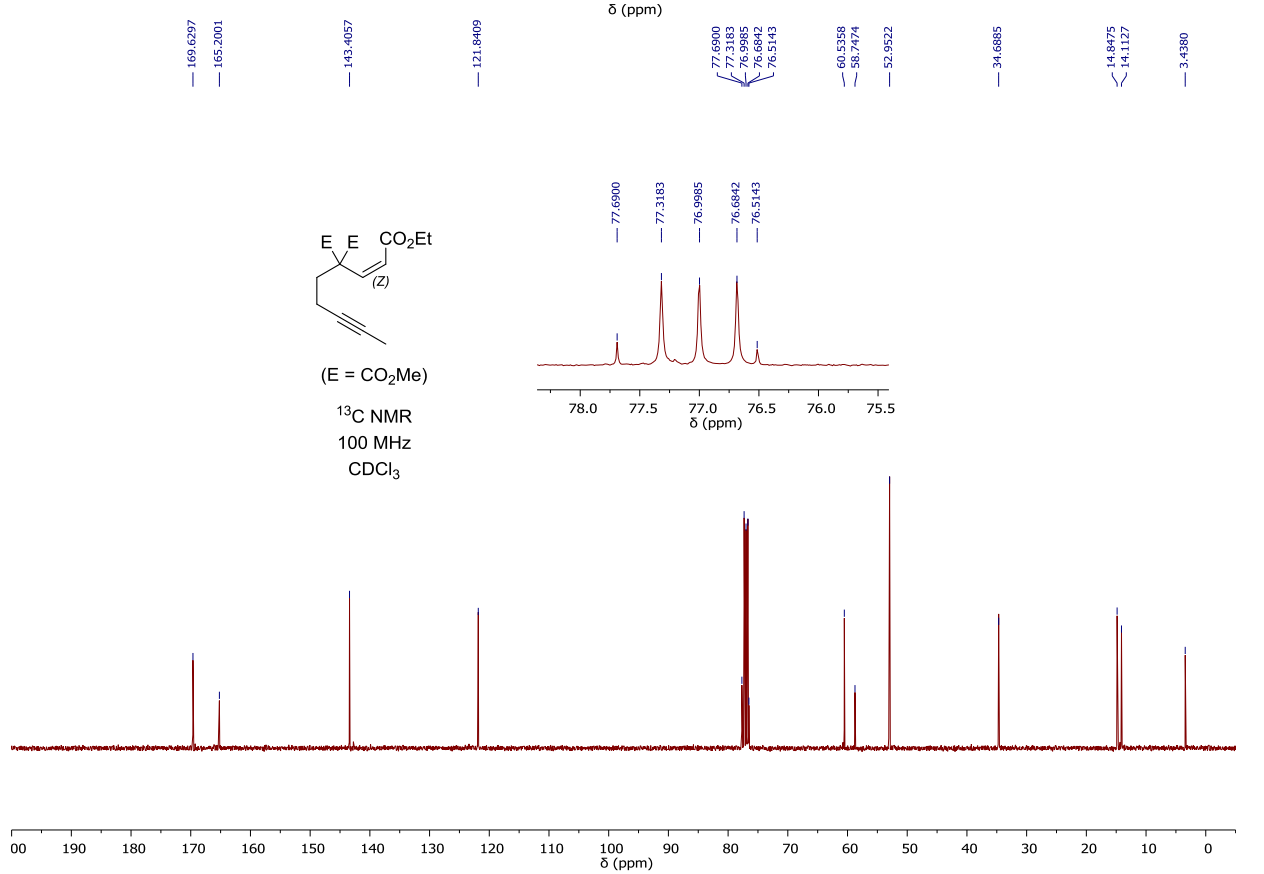
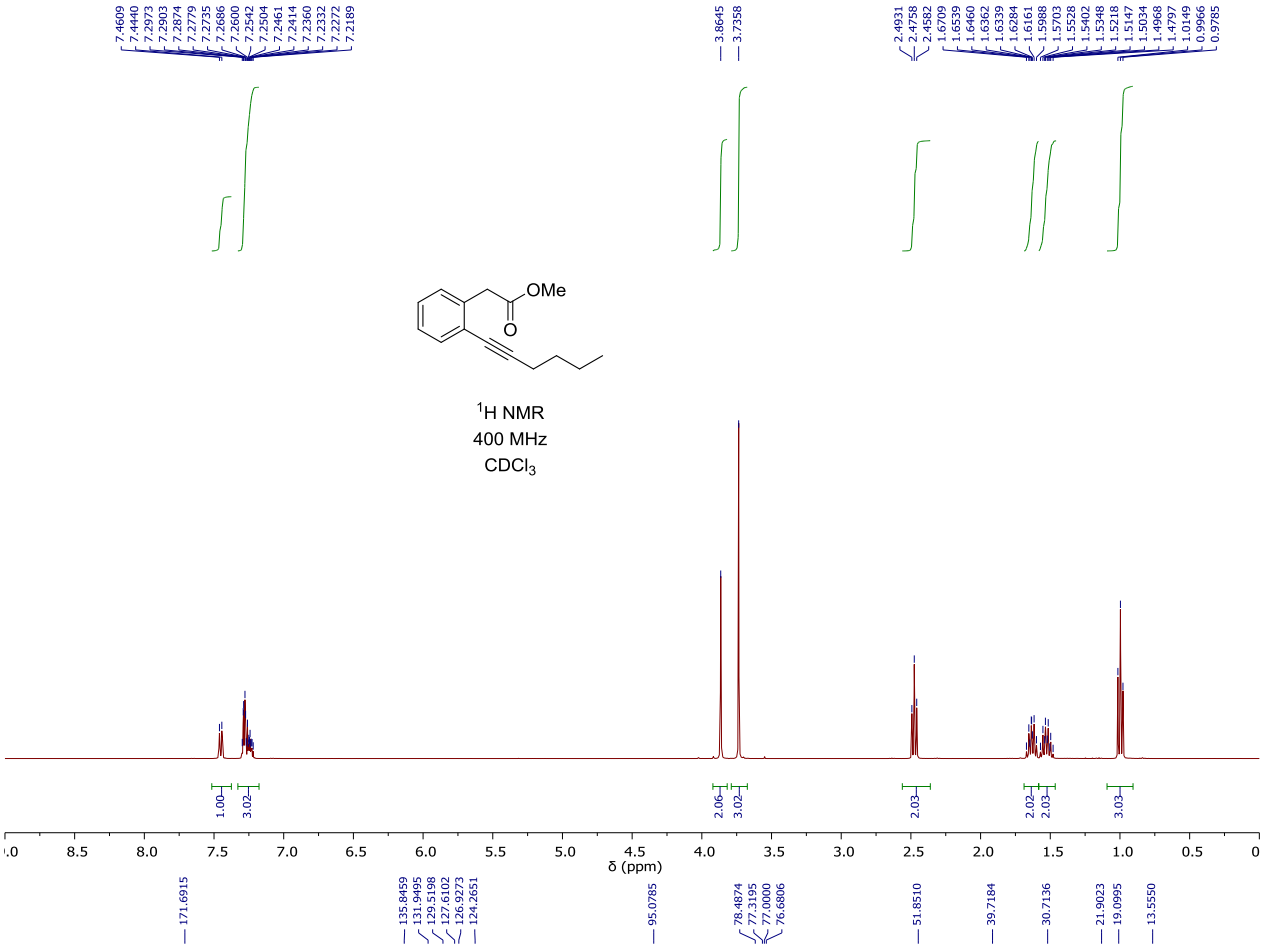
6.8850
6.8542
6.0184
5.9879
4.1597
4.1418
4.1240
4.1061
3.7175
2.5123
2.5014
2.4933
2.4888
2.4825
2.4724
2.1295
2.1233
2.1169
2.1069
2.1010
2.0950
2.0890
2.0830
2.0766
2.0703
1.7375
1.7312
1.7248
1.2767
1.2589
1.2411
E E CO2Et
(Z)
(E = CO2Me)
1H NMR
400 MHz
CDCl3
1.00
1.00
2.12
6.15
2.01
2.24
3.30
3.36
δ (ppm)


169.6297
165.2001
143.4057
121.8409
77.6900
77.3183
76.9985
76.6842
76.5143
60.5358
58.7474
52.9522
34.6885
14.8475
14.1127
3.4380
E E CO2Et
(Z)
(E = CO2Me)
13C NMR
100 MHz
CDCl3
δ (ppm)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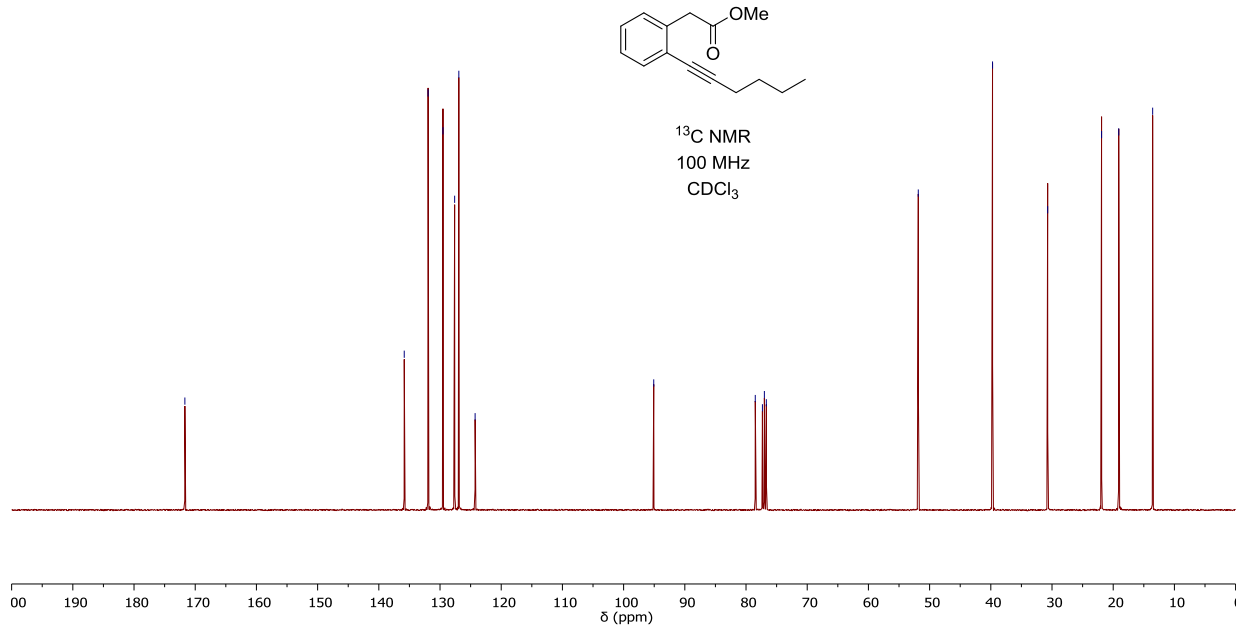
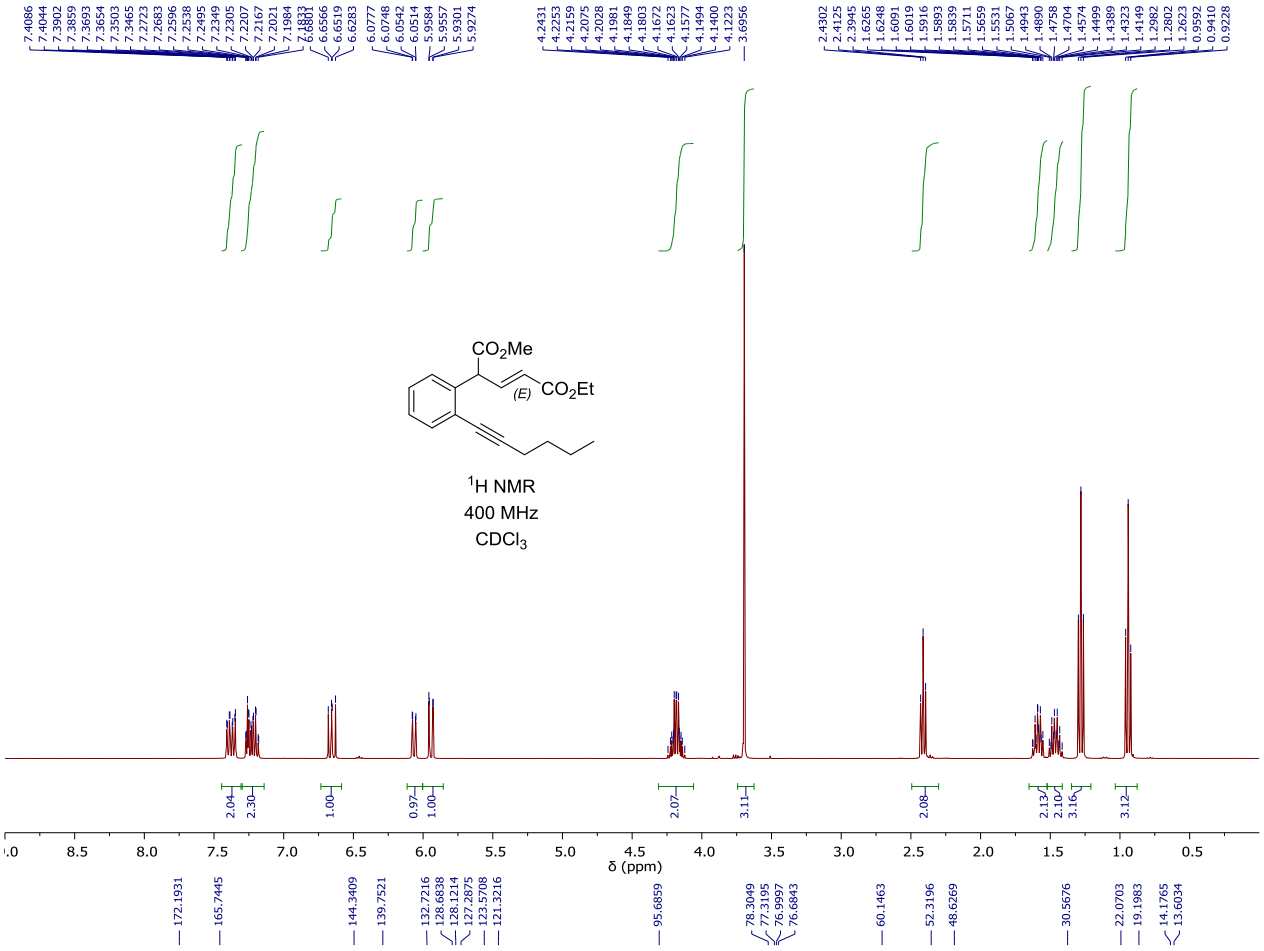
7.4440
7.2973
7.2903
7.2874
7.2779
7.2735
7.2686
7.2600
7.2542
7.2504
7.2461
7.2414
7.2360
7.2332
7.2272
7.2189
3.8645
3.7358
2.4931
2.4758
2.4582
1.6709
1.6539
1.6460
1.6362
1.6339
1.6284
1.6161
1.5988
1.5703
1.5528
1.5402
1.5348
1.5218
1.5147
1.5034
1.4968
1.4797
1.0149
0.9966
0.9785
OMe
O
1H NMR
400 MHz
CDCl3
1.00
3.02
2.06
3.02
2.03
2.02
2.03
3.03
δ (ppm)

171.6915
135.8459
131.9495
129.5198
127.6102
126.9273
124.2651
95.0785
78.4874
77.3195
77.0000
76.6806
51.8510
39.7184
30.7136
21.9023
19.0995
13.5550


OMe
O
13C NMR
100 MHz
CDCl3
δ (ppm)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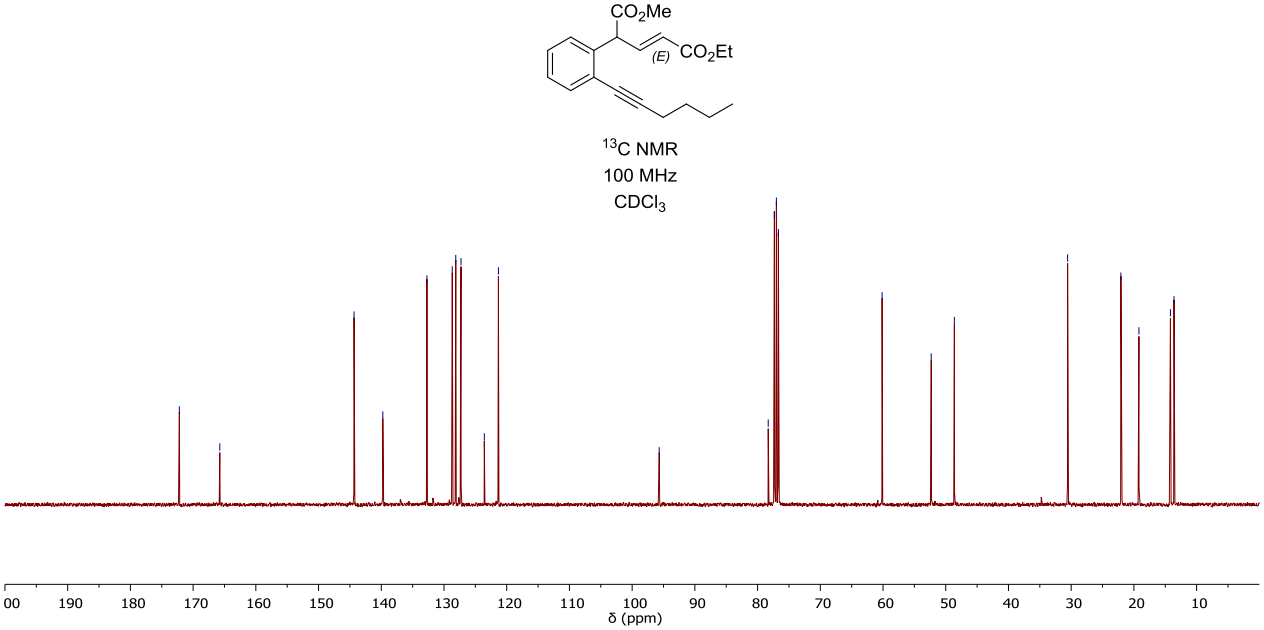
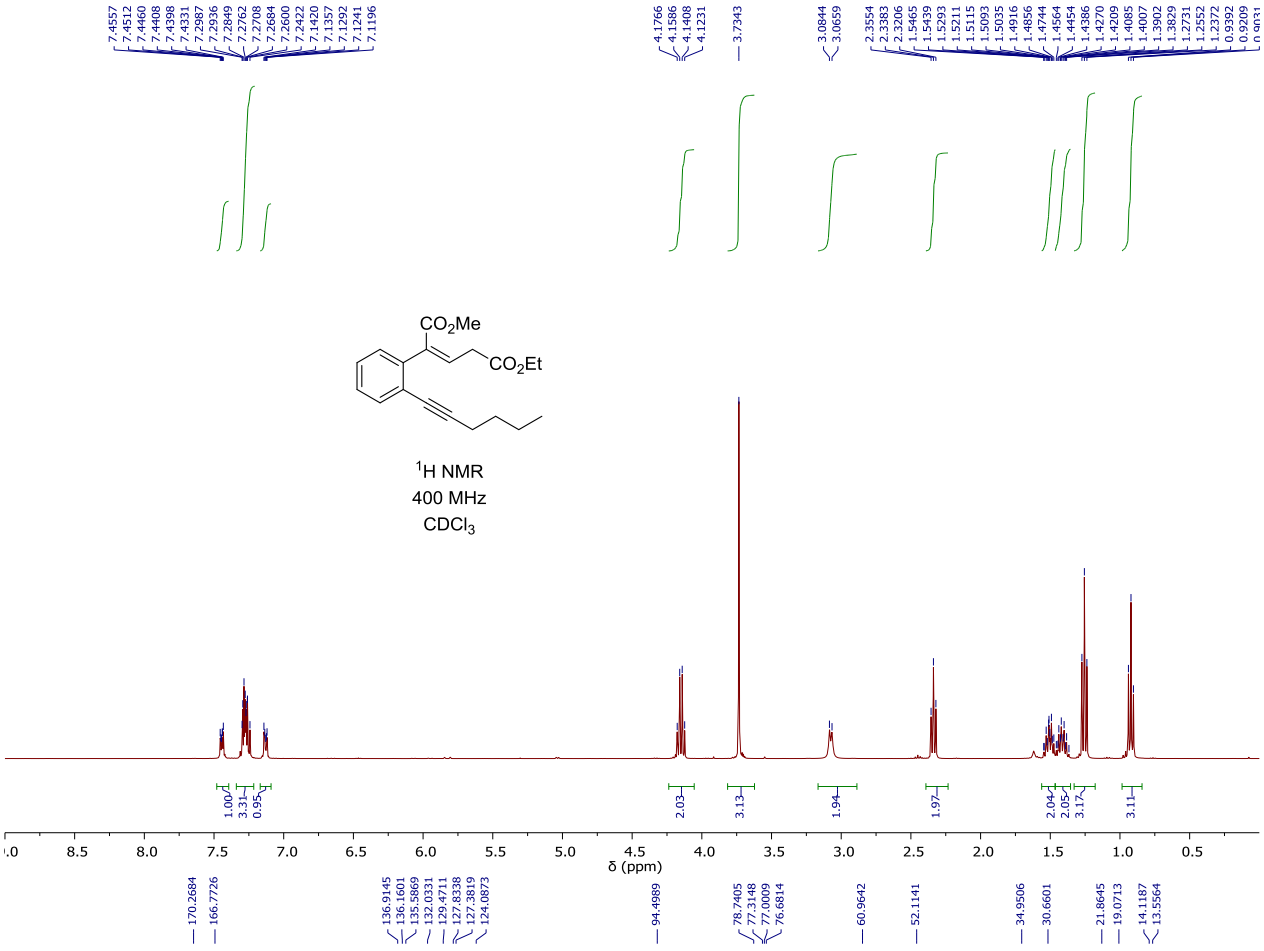
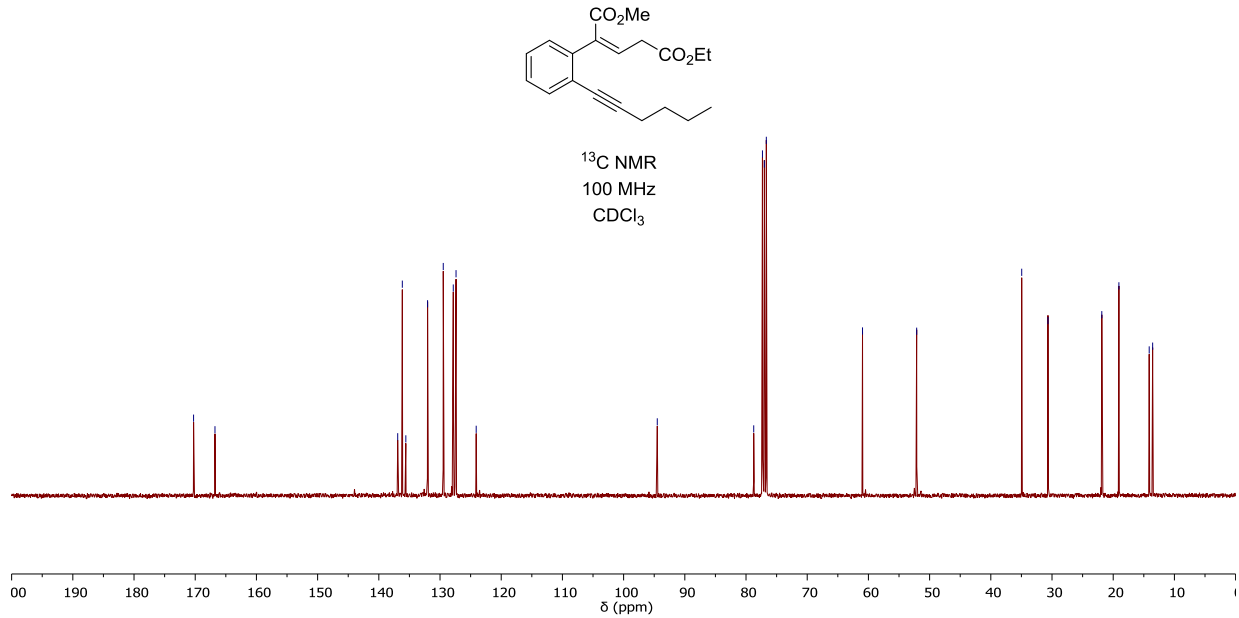
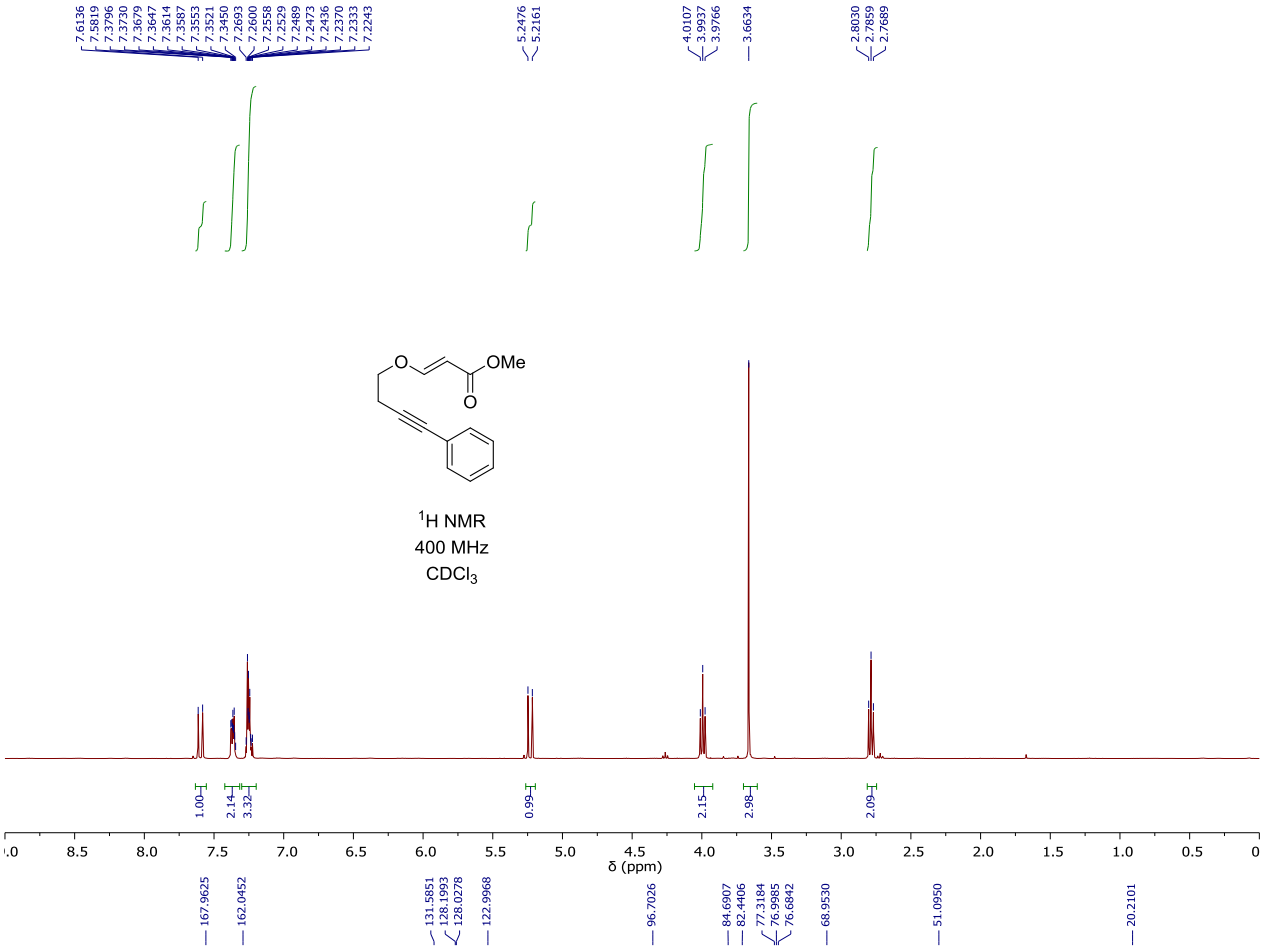
7.4044
7.3902
7.3859
7.3693
7.3654
7.3503
7.3465
7.2723
7.2683
7.2596
7.2538
7.2495
7.2349
7.2305
7.2207
7.2167
7.2021
7.1984
7.1833
6.6801
6.6566
6.6519
6.6283
6.0777
6.0748
6.0542
6.0514
5.9584
5.9557
5.9301
5.9274
4.2431
4.2253
4.2159
4.2075
4.2028
4.1981
4.1849
4.1803
4.1672
4.1623
4.1577
4.1494
4.1400
4.1223
3.6956
2.4302
2.4125
2.3945
1.6265
1.6248
1.6091
1.6019
1.5916
1.5893
1.5839
1.5711
1.5659
1.5531
1.5067
1.4943
1.4890
1.4758
1.4704
1.4574
1.4499
1.4389
1.4323
1.4149
1.2982
1.2802
1.2623
0.9592
0.9410
0.9228
CO2Me
(E) CO2Et
1H NMR
400 MHz
CDCl3
2.04
2.30
1.00
0.97
1.00
2.07
3.11
2.08
2.13
2.10
3.16
3.12
δ (ppm)


172.1931
165.7445
144.3409
139.7521
132.7216
128.6838
128.1214
127.2875
123.5708
121.3216
95.6859
78.3049
77.3195
76.9997
76.6843
60.1463
52.3196
48.6269
30.5676
22.0703
19.1983
14.1765
13.6034
CO2Me
(E) CO2Et
13C NMR
100 MHz
CDCl3
δ (ppm)


CO2Me
CO2Et
1H NMR
400 MHz
CDCl3
δ (ppm)


CO2Me
CO2Et
13C NMR
100 MHz
CDCl3
δ (ppm)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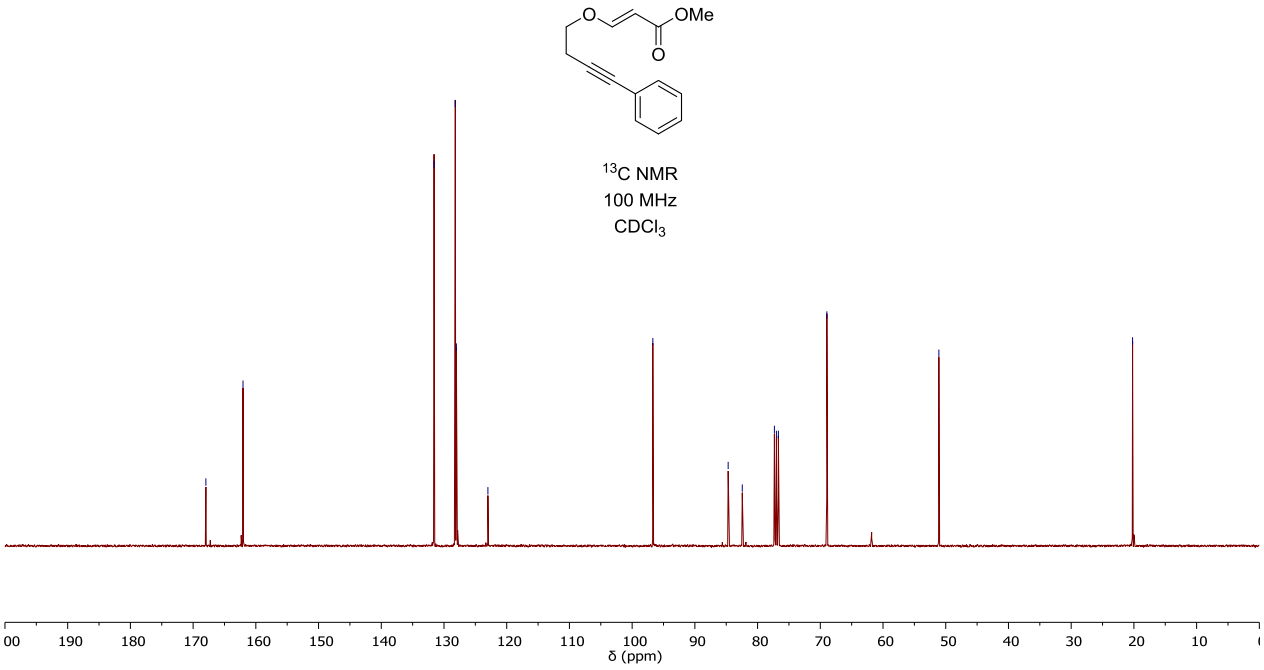
7.3796
7.3730
7.3679
7.3647
7.3614
7.3587
7.3553
7.3521
7.3450
7.2693
7.2600
7.2558
7.2529
7.2489
7.2473
7.2436
7.2370
7.2333
7.2243
5.2476
5.2161
4.0107
3.9937
3.9766
3.6634
2.8030
2.7859
2.7689
O
OMe
O
1H NMR
400 MHz
CDCl3
1.00
2.14
3.32
0.99
2.15
2.98
2.09
δ (ppm)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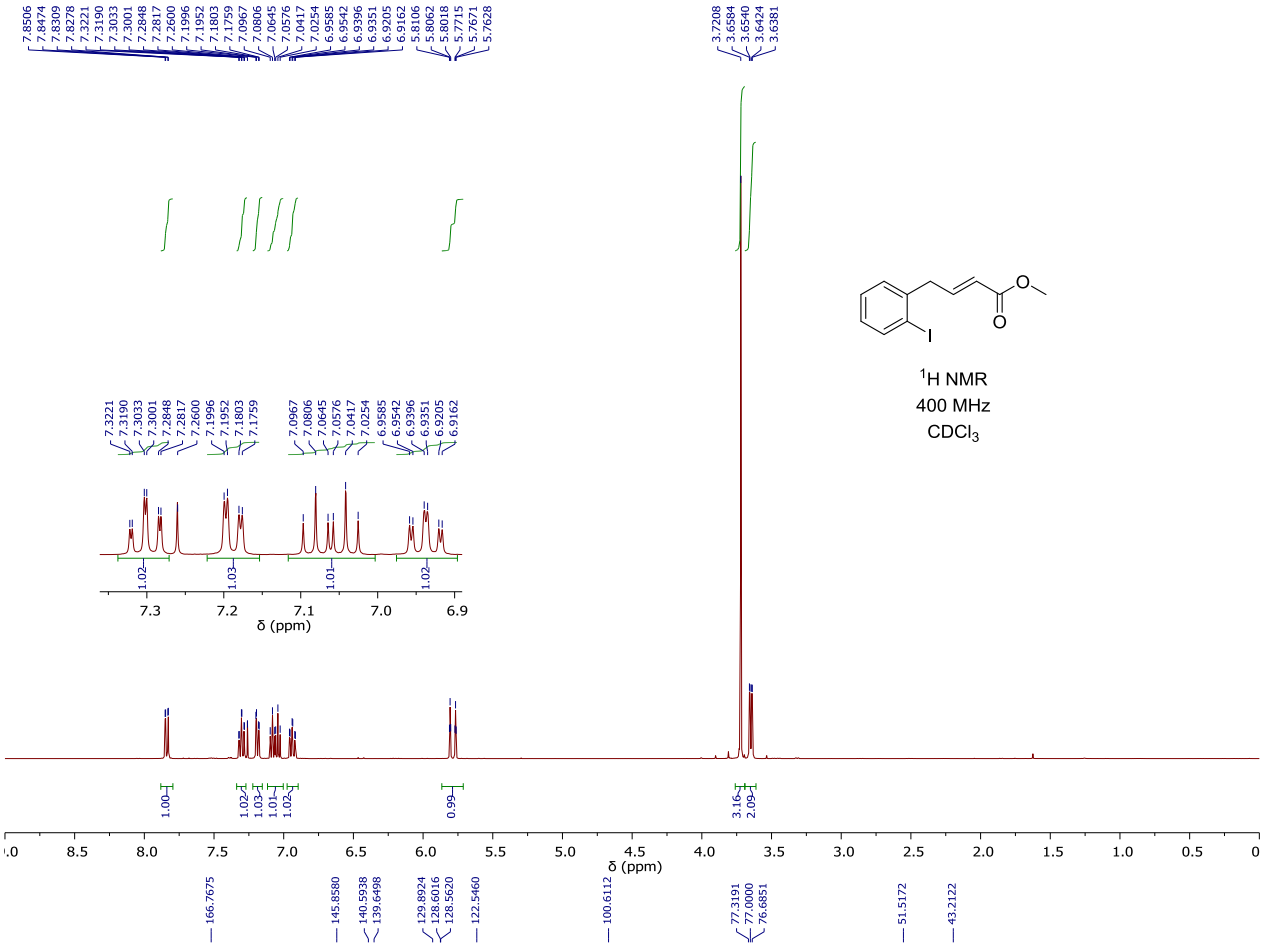
131.5851
128.1993
128.0278
122.9968
96.7026
84.6907
82.4406
77.3184
76.9985
76.6842
68.9530
51.0950
20.2101
O
OMe
O
13C NMR
100 MHz
CDCl3
δ (ppm)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7.8309
7.8278
7.3221
7.3190
7.3033
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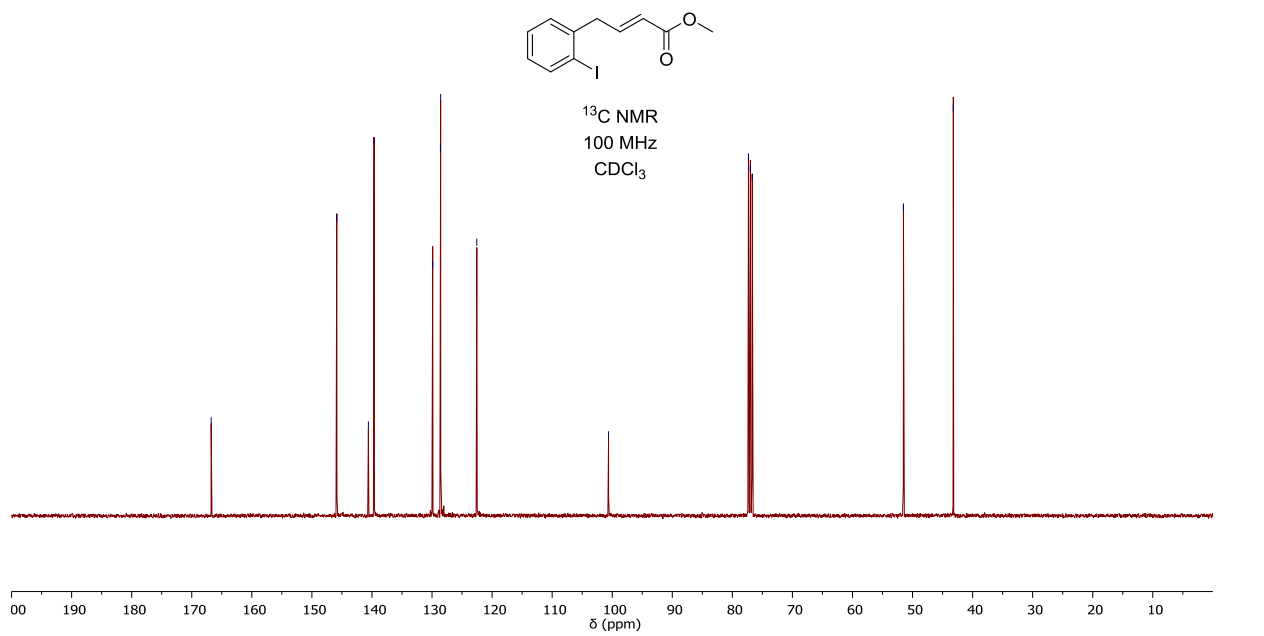
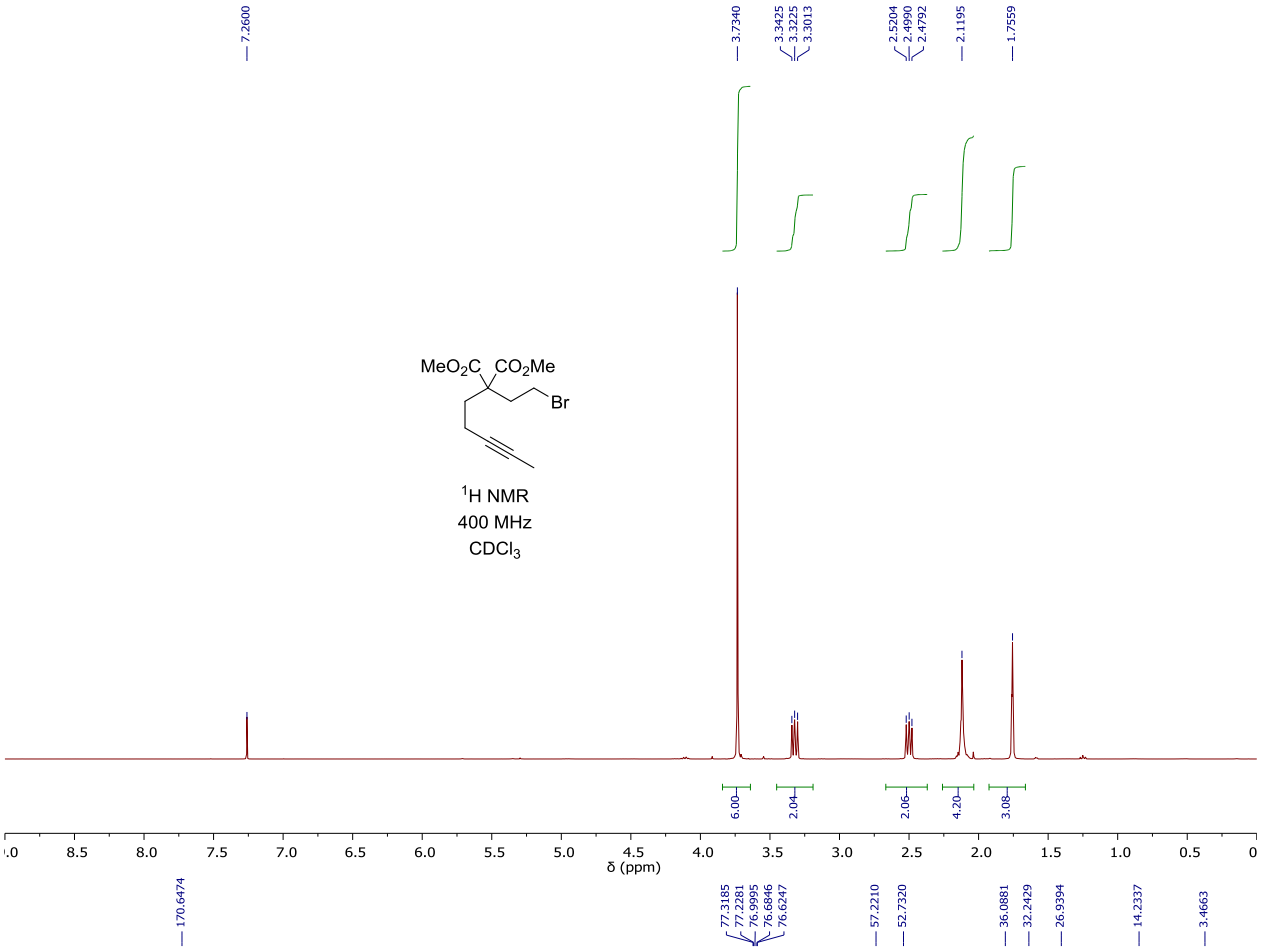
7.2848
7.2817
7.2600
7.1996
7.1952
7.1803
7.1759
7.0967
7.0806
7.0645
7.0576
7.0417
7.0254
6.9585
6.9542
6.9396
6.9351
6.9205
6.9162
5.8106
5.8062
5.8018
5.7715
5.7671
5.7628
3.7208
3.6584
3.6540
3.6424
3.6381
O
O
I
1H NMR
400 MHz
CDCl3
δ (ppm)


O
O
I
13C NMR
100 MHz
CDCl3
δ (ppm)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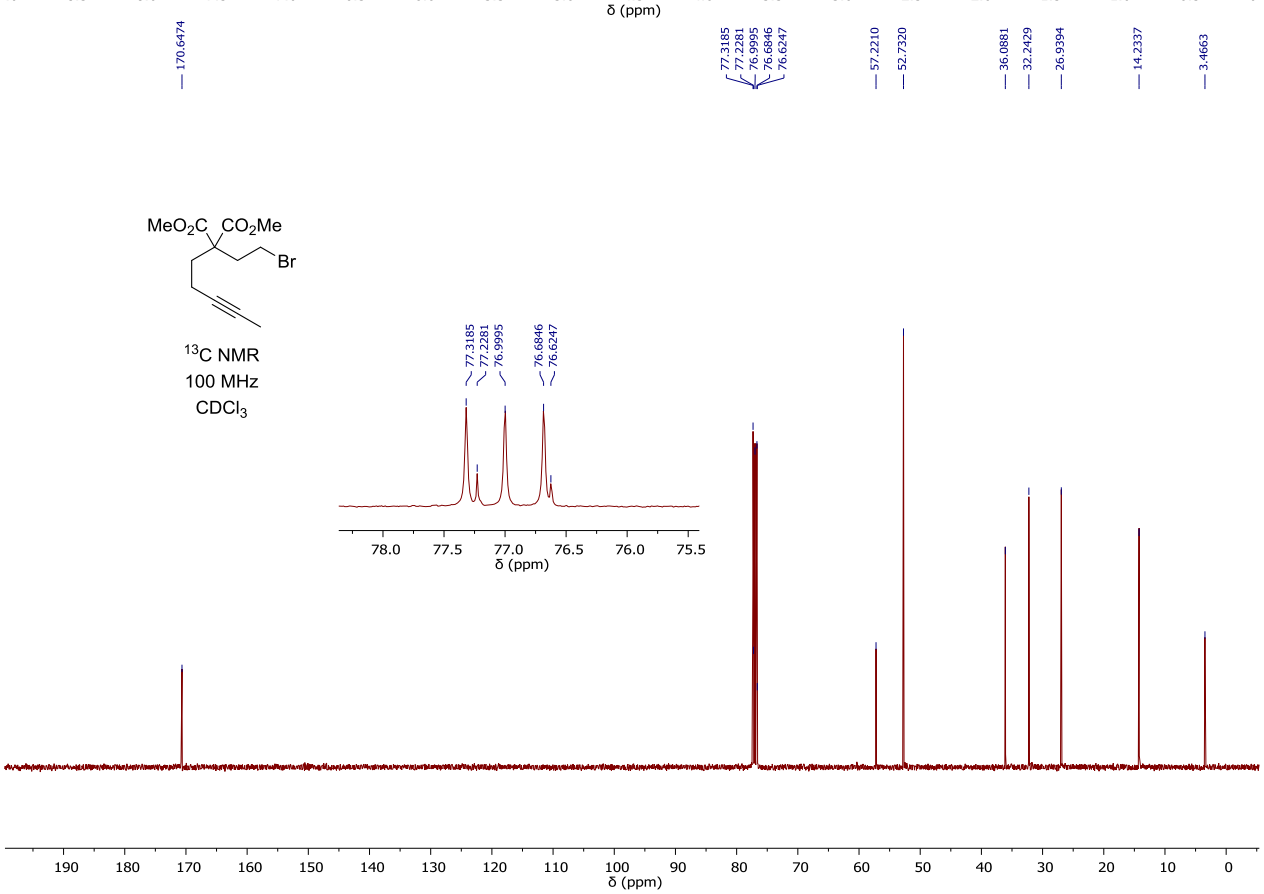
3.7340
3.3425
3.3225
3.3013
2.5204
2.4990
2.4792
2.1195
1.7559
MeO2C CO2Me
Br
1H NMR
400 MHz
CDCl3
6.00
2.04
2.06
4.20
3.08
δ (ppm)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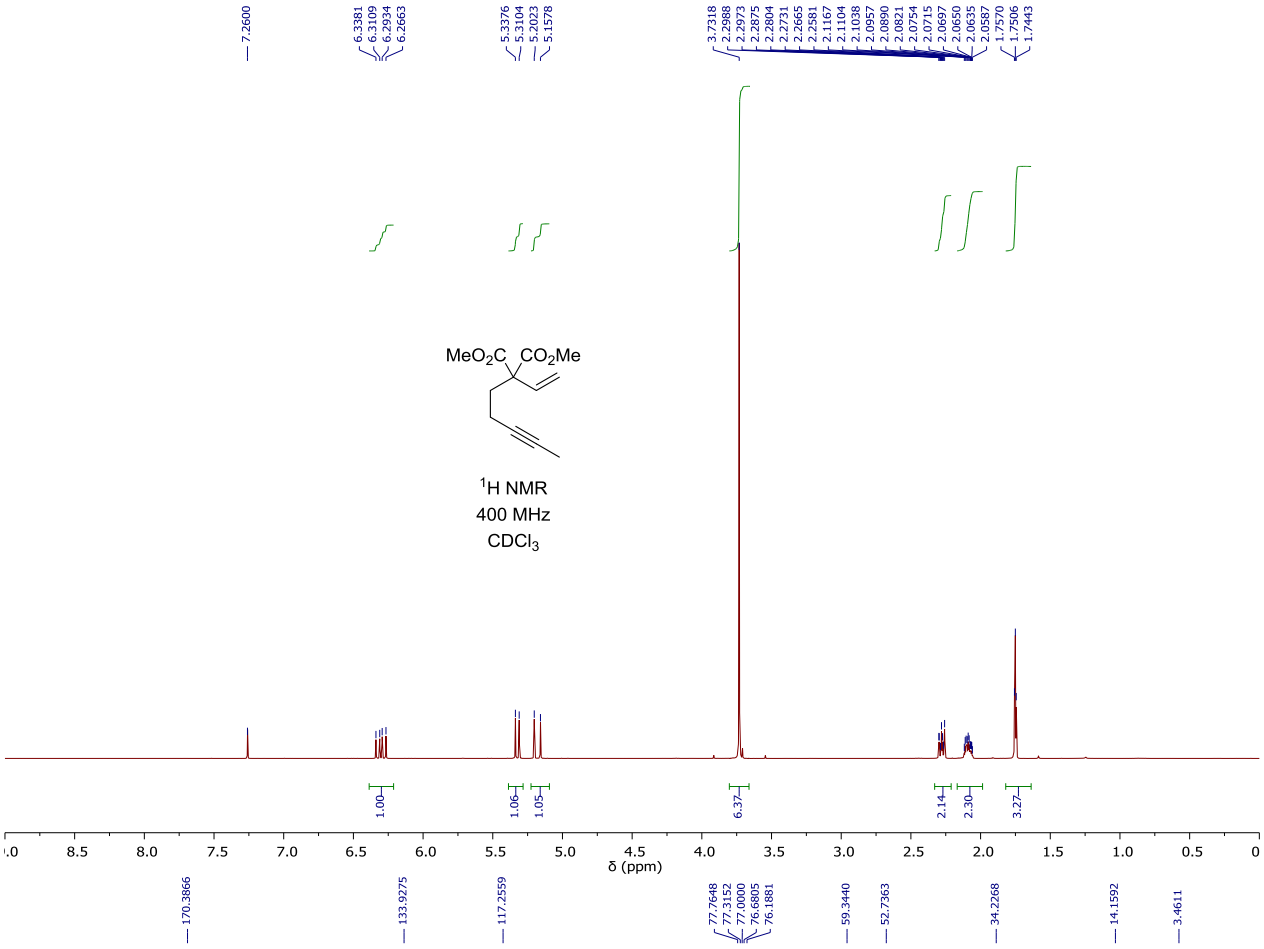
77.3185
77.2281
76.9995
76.6846
76.6247
57.2210
52.7320
36.0881
32.2429
26.9394
14.2337
3.4663
MeO2C CO2Me
Br
13C NMR
100 MHz
CDCl3
δ (ppm)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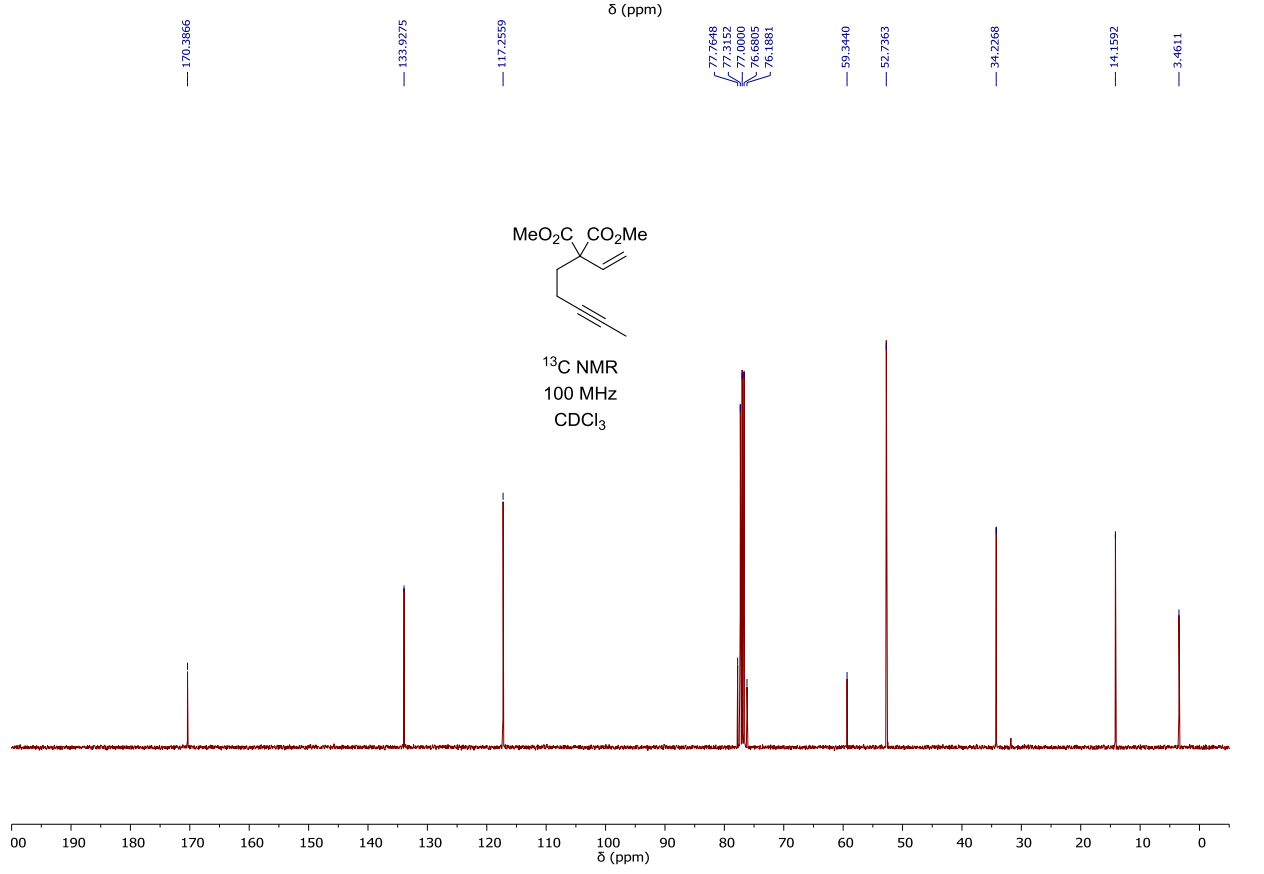
6.3109
6.2934
6.2663
5.3376
5.3104
5.2023
5.1578
3.7318
2.2988
2.2973
2.2875
2.2804
2.2731
2.2665
2.2581
2.1167
2.1104
2.1038
2.0957
2.0890
2.0821
2.0754
2.0715
2.0697
2.0650
2.0635
2.0587
1.7570
1.7506
1.7443
MeO2C CO2Me
1H NMR
400 MHz
CDCl3
1.00
1.06
1.05
6.37
2.14
2.30
3.27
δ (ppm)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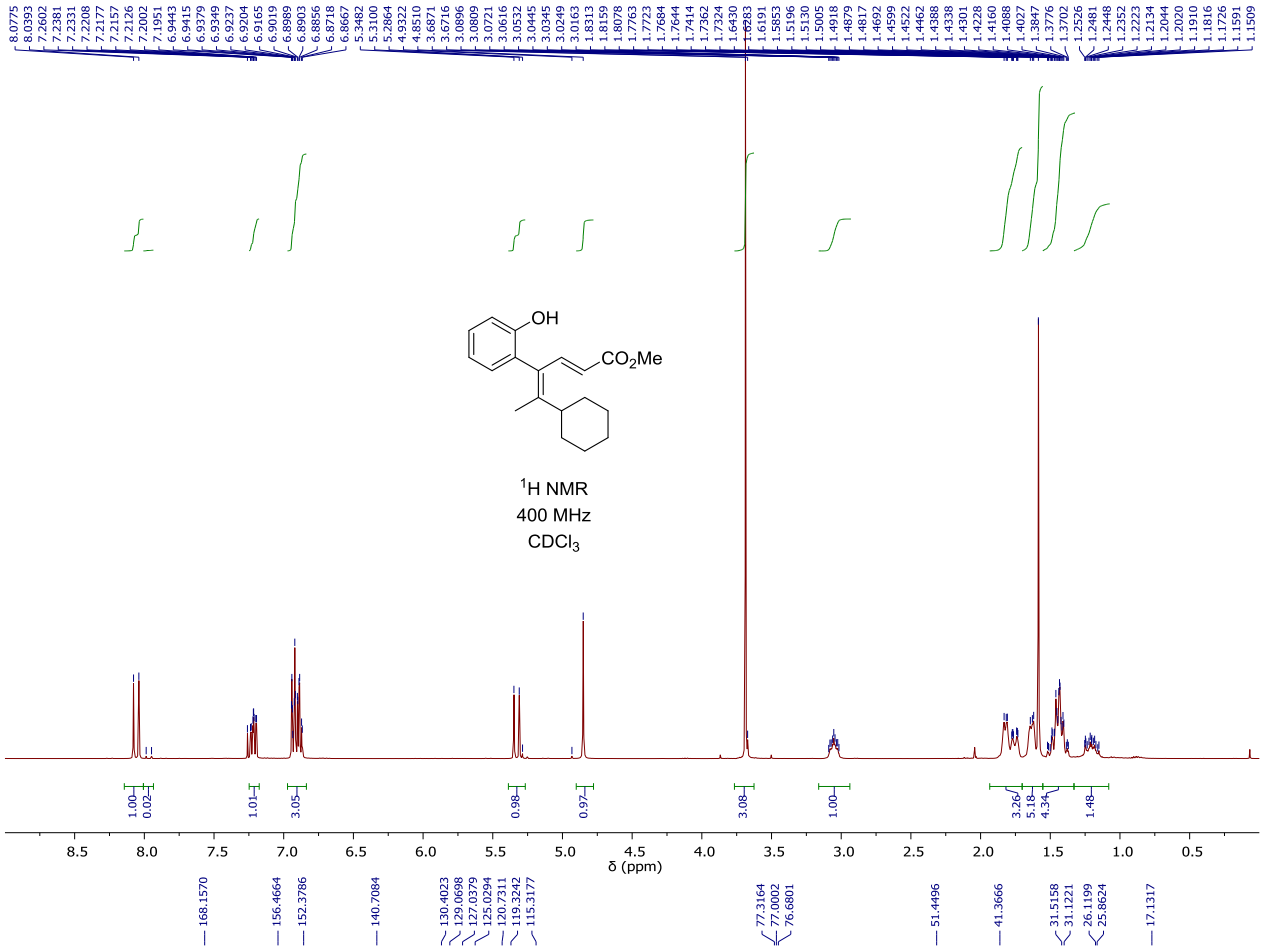
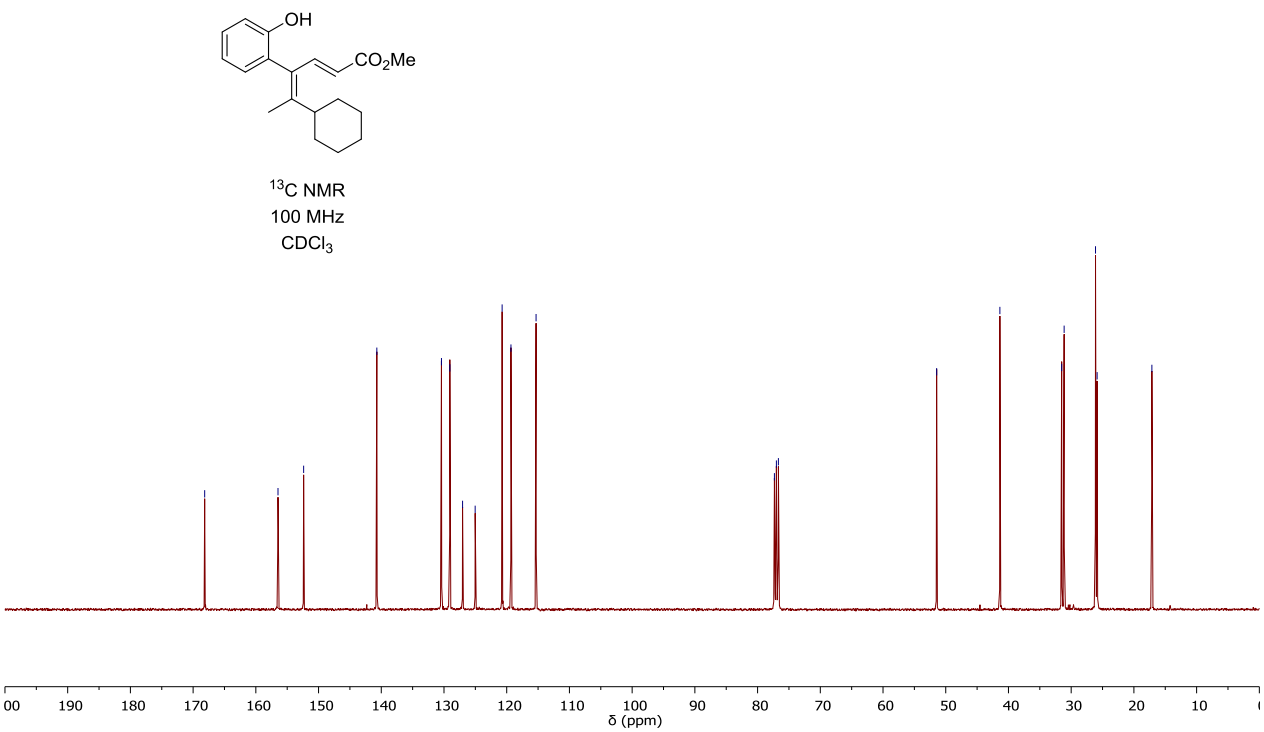
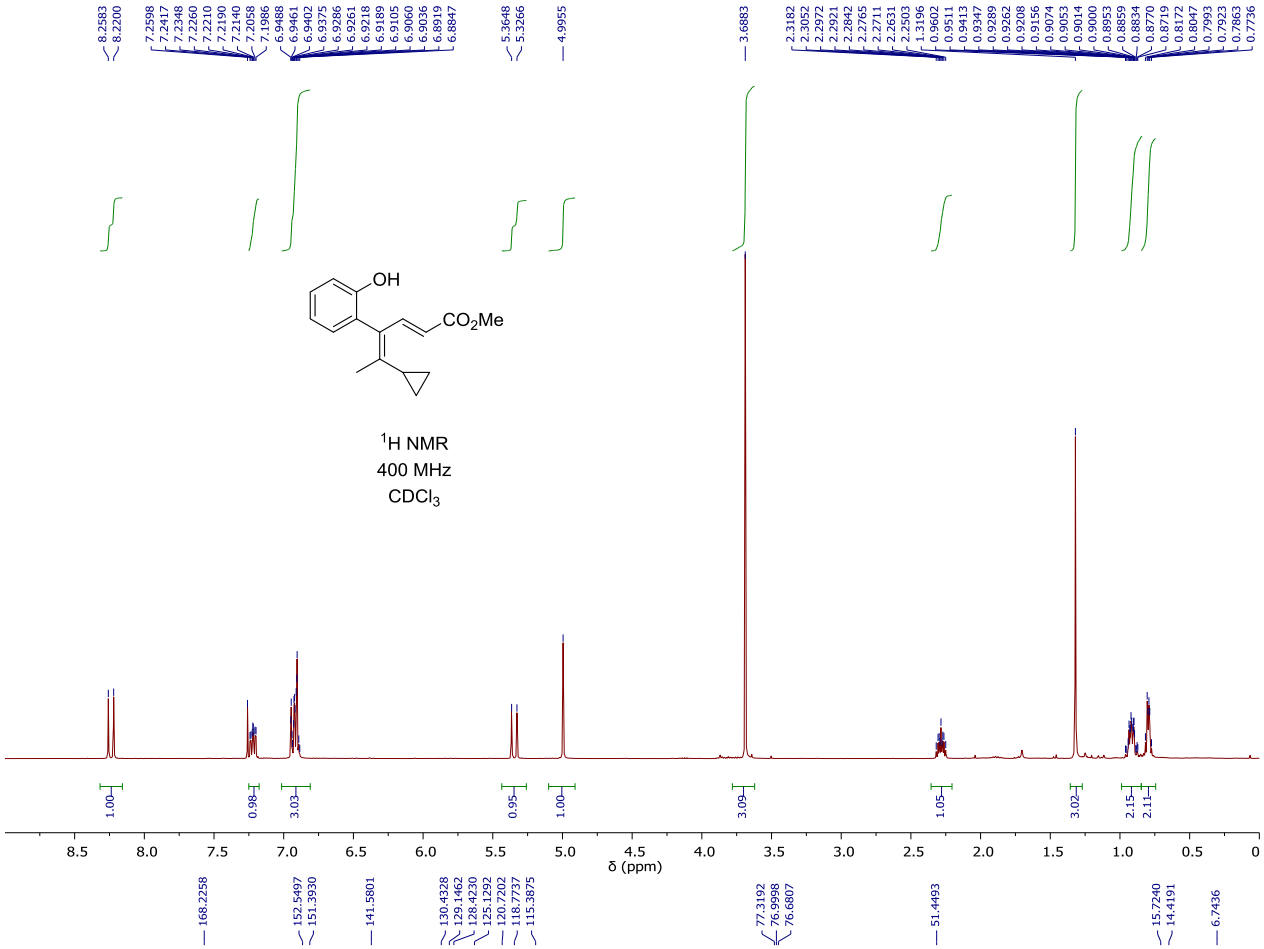
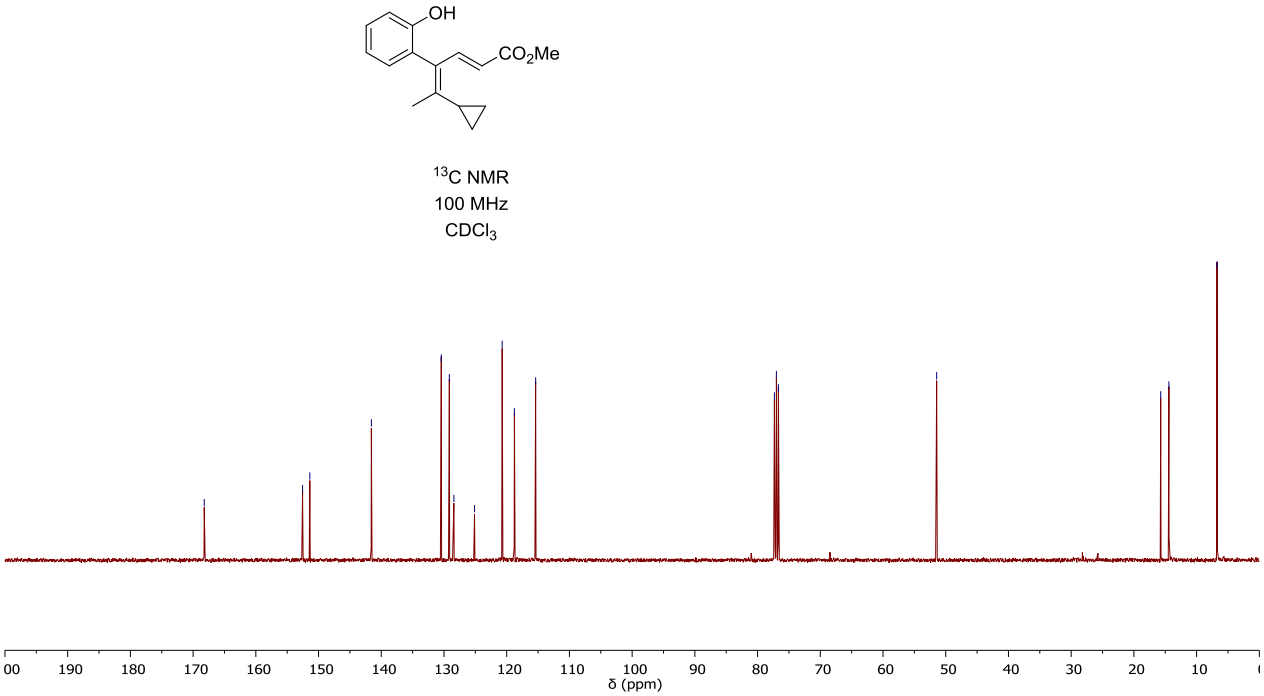
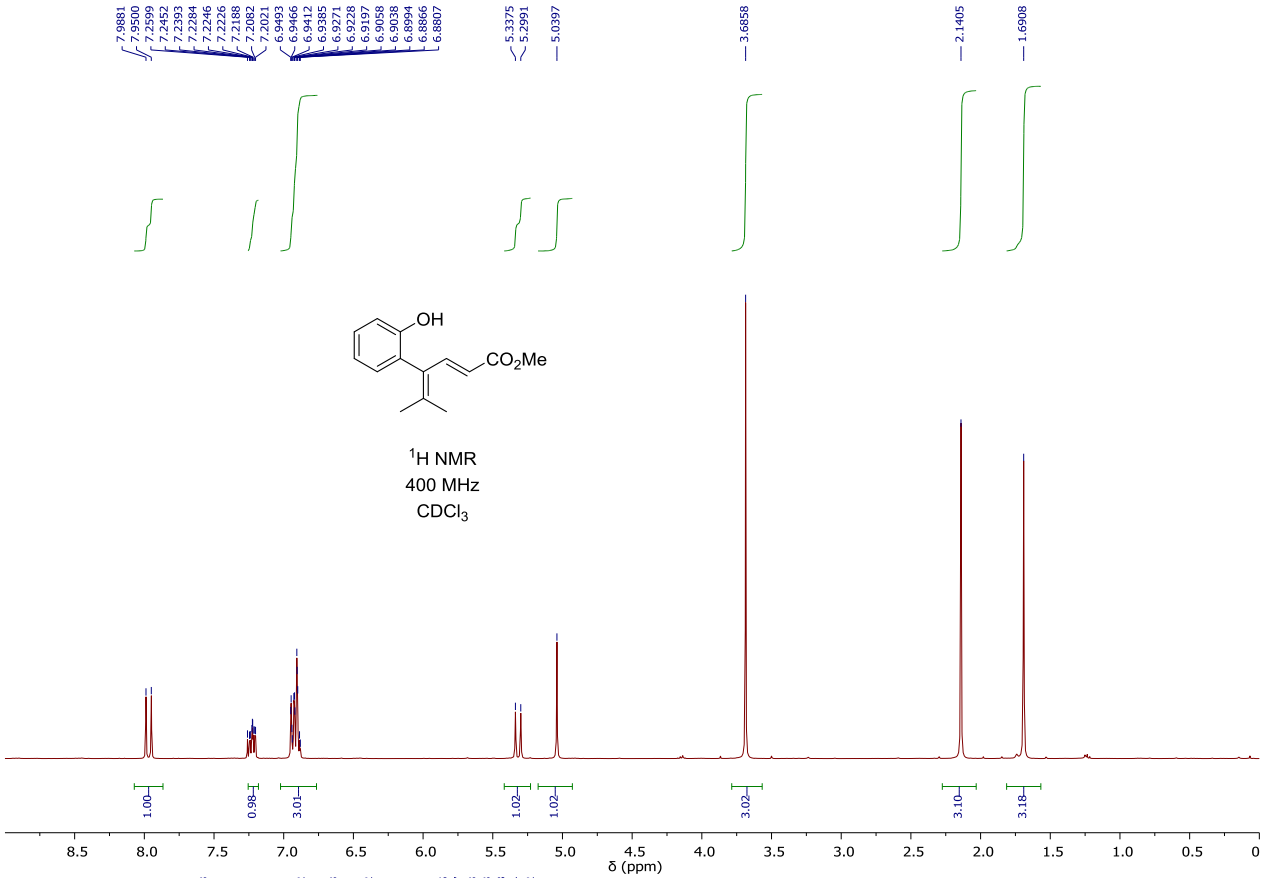
133.9275
117.2559
77.7648
77.3152
77.0000
76.6805
76.1881
59.3440
52.7363
34.2268
14.1592
3.4611
MeO2C CO2Me
13C NMR
100 MHz
CDCl3
δ (ppm)


OH
CO2Me
1H NMR
400 MHz
CDCl3
δ (ppm)

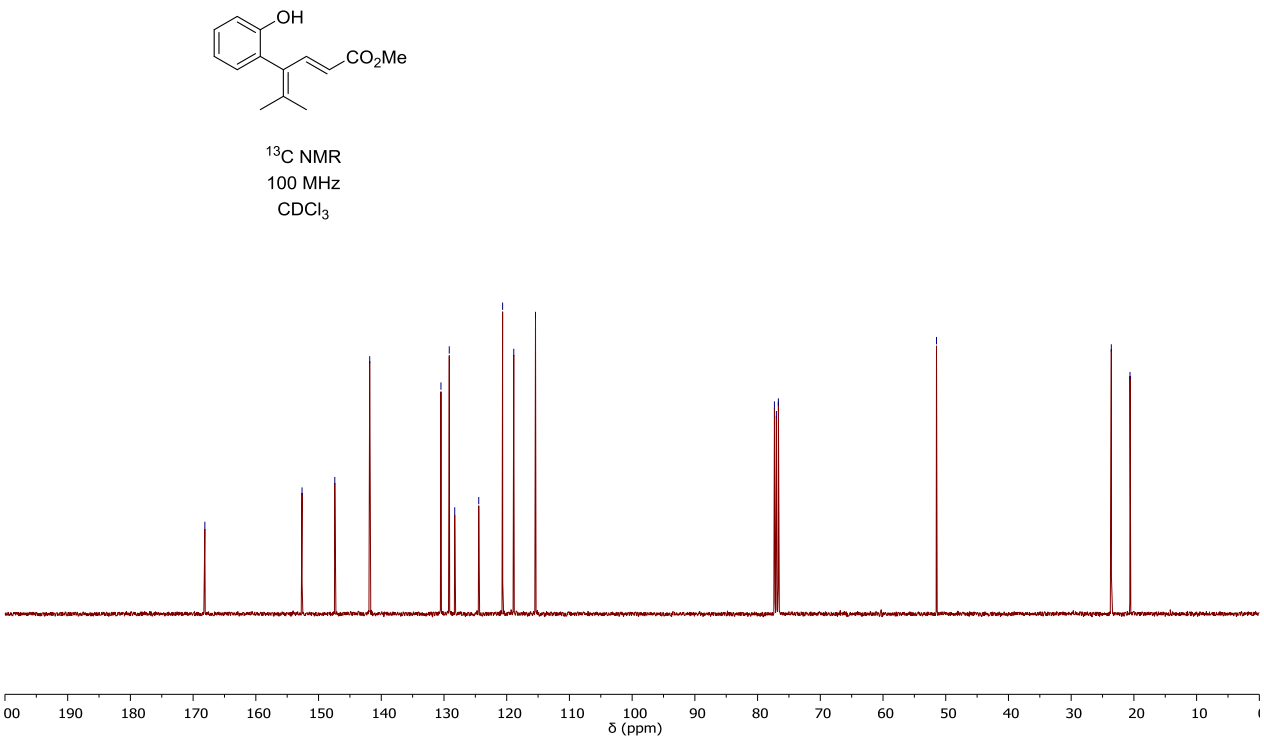

OH
CO2Me
13C NMR
100 MHz
CDCl3
δ (ppm)


OH
CO2Me
1H NMR
400 MHz
CDCl3
δ (ppm)

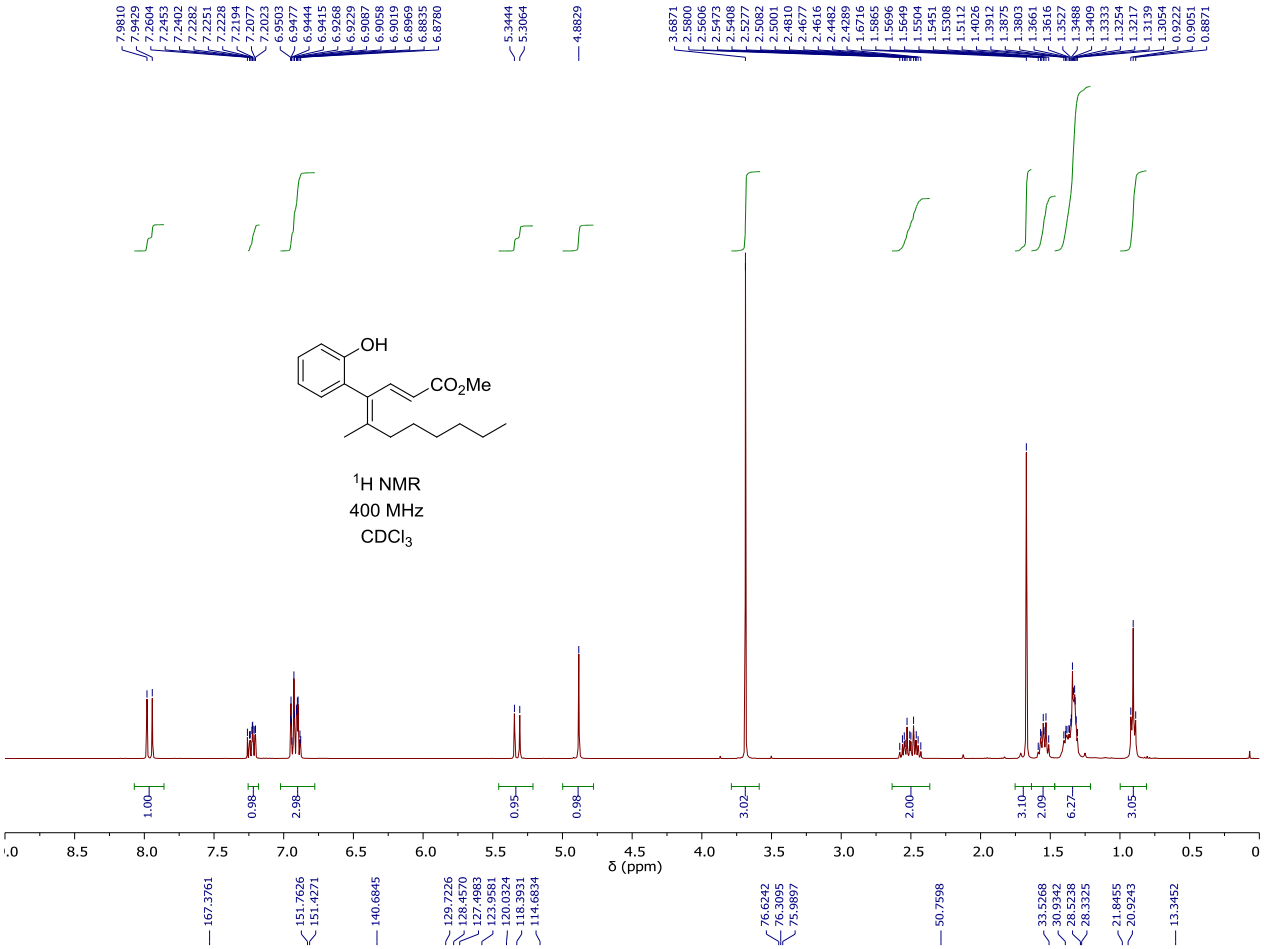

OH
CO2Me
13C NMR
100 MHz
CDCl3
δ (ppm)

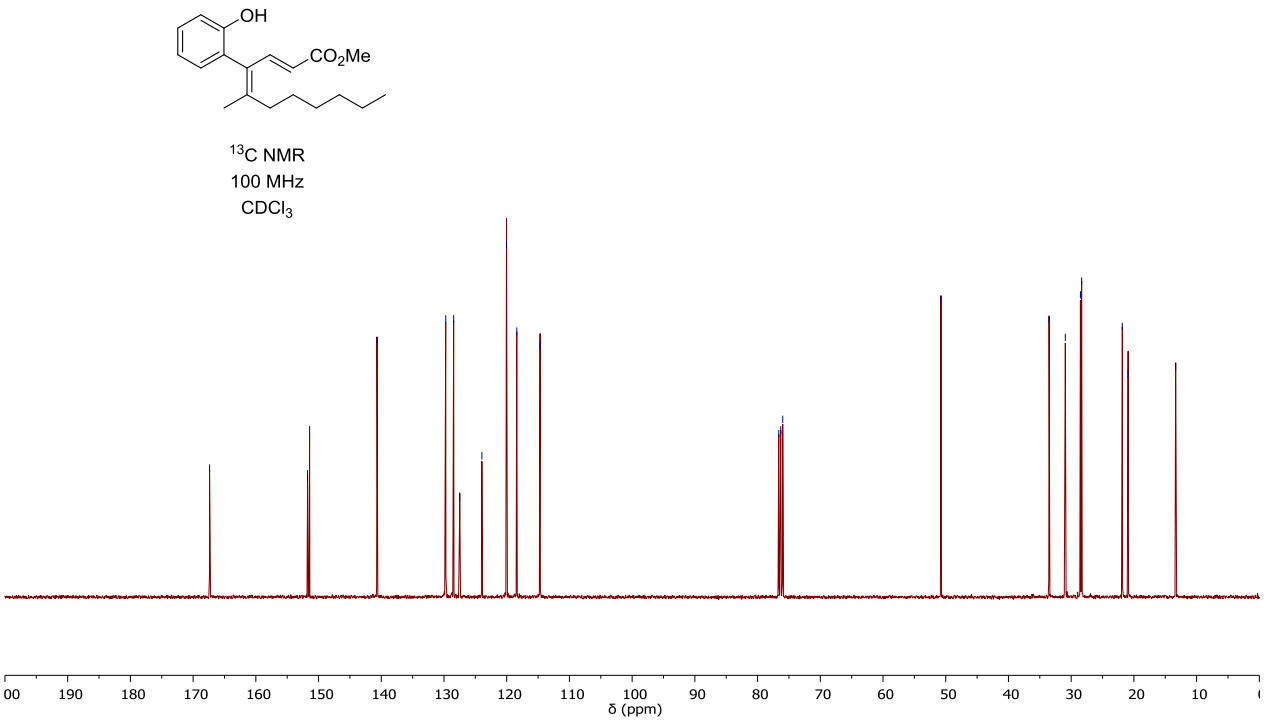


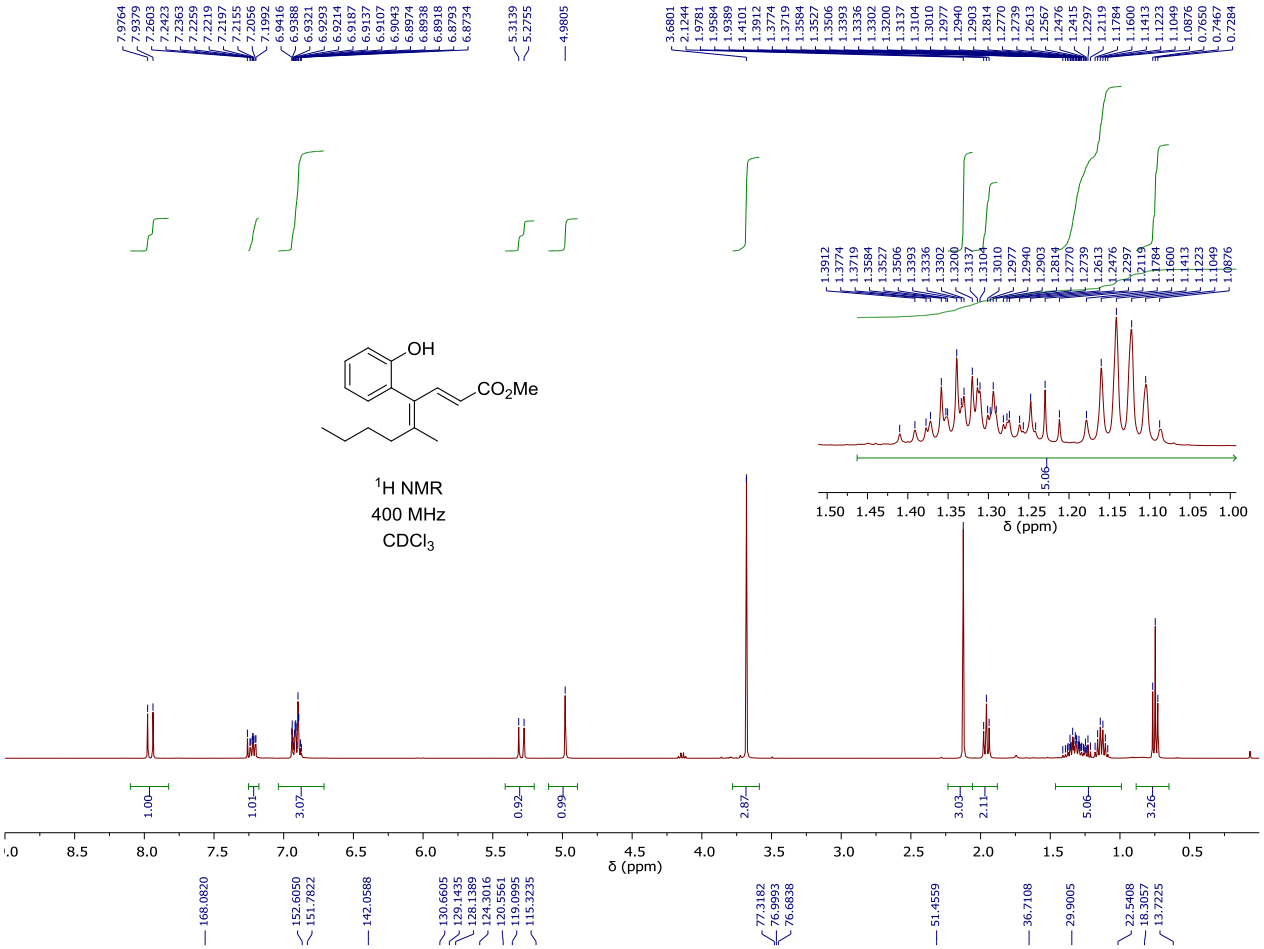
^{1}H NMR
400 MHz
$CDCl_3$

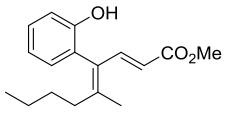


^{13}C NMR
100 MHz
$CDCl_3$

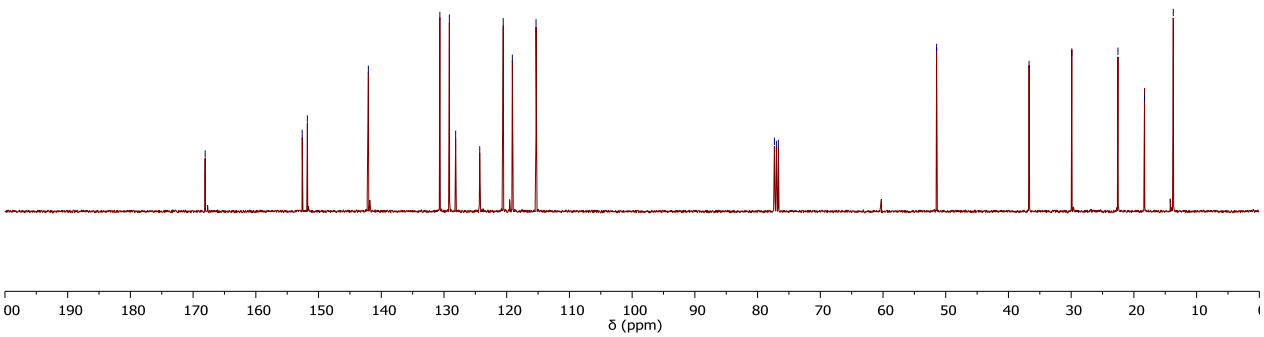

OH
CO2Me
1H NMR
400 MHz
CDCl3
δ (ppm)

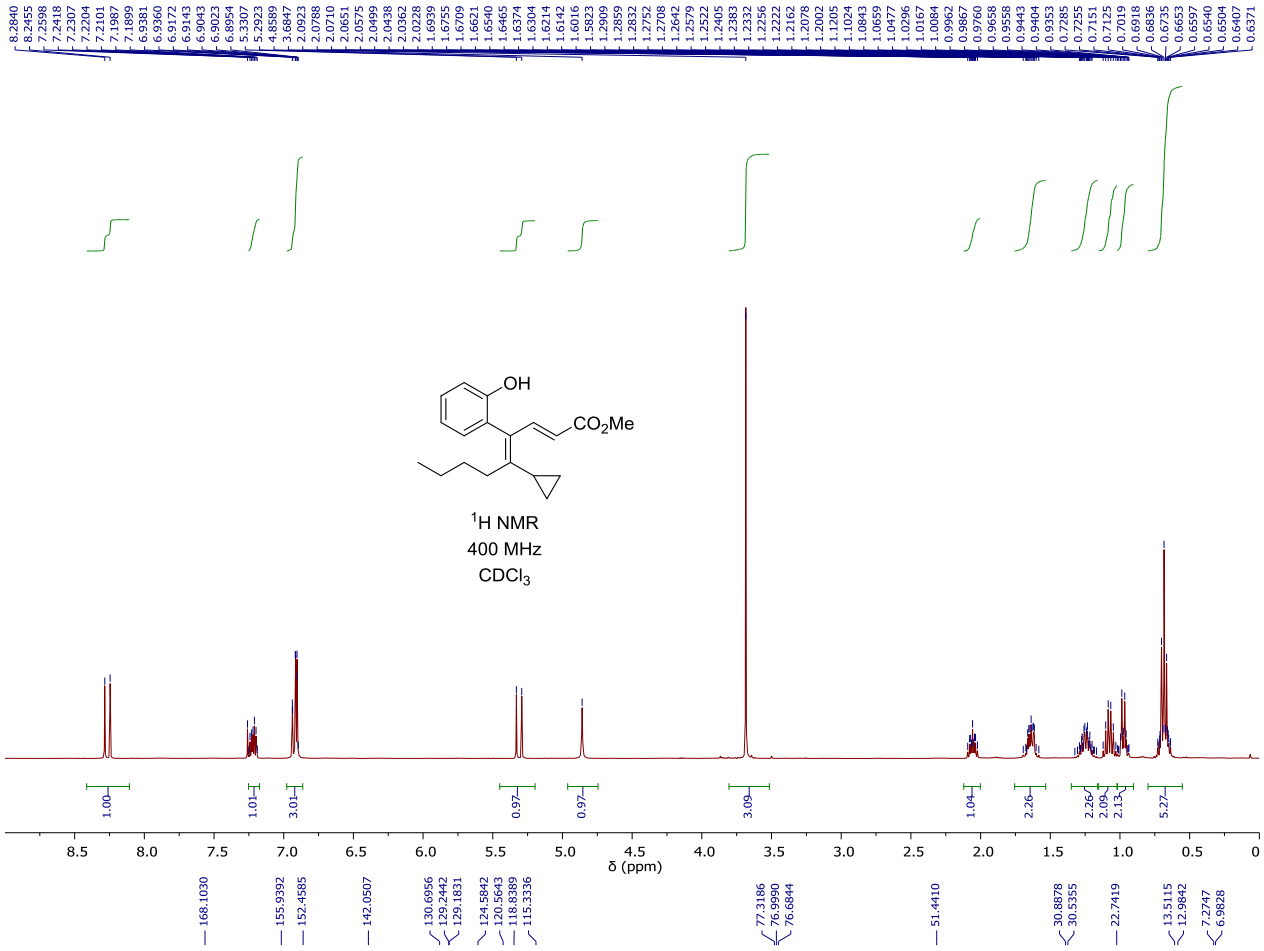

OH
CO2Me
13C NMR
100 MHz
CDCl3
δ (ppm)

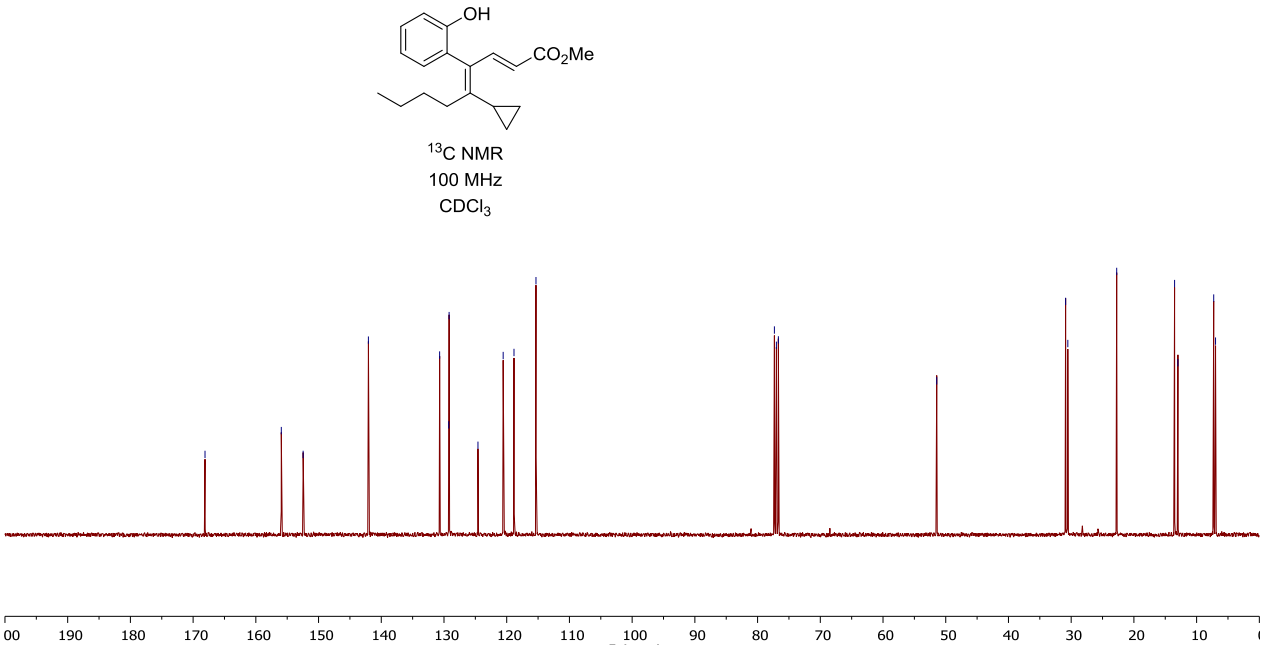


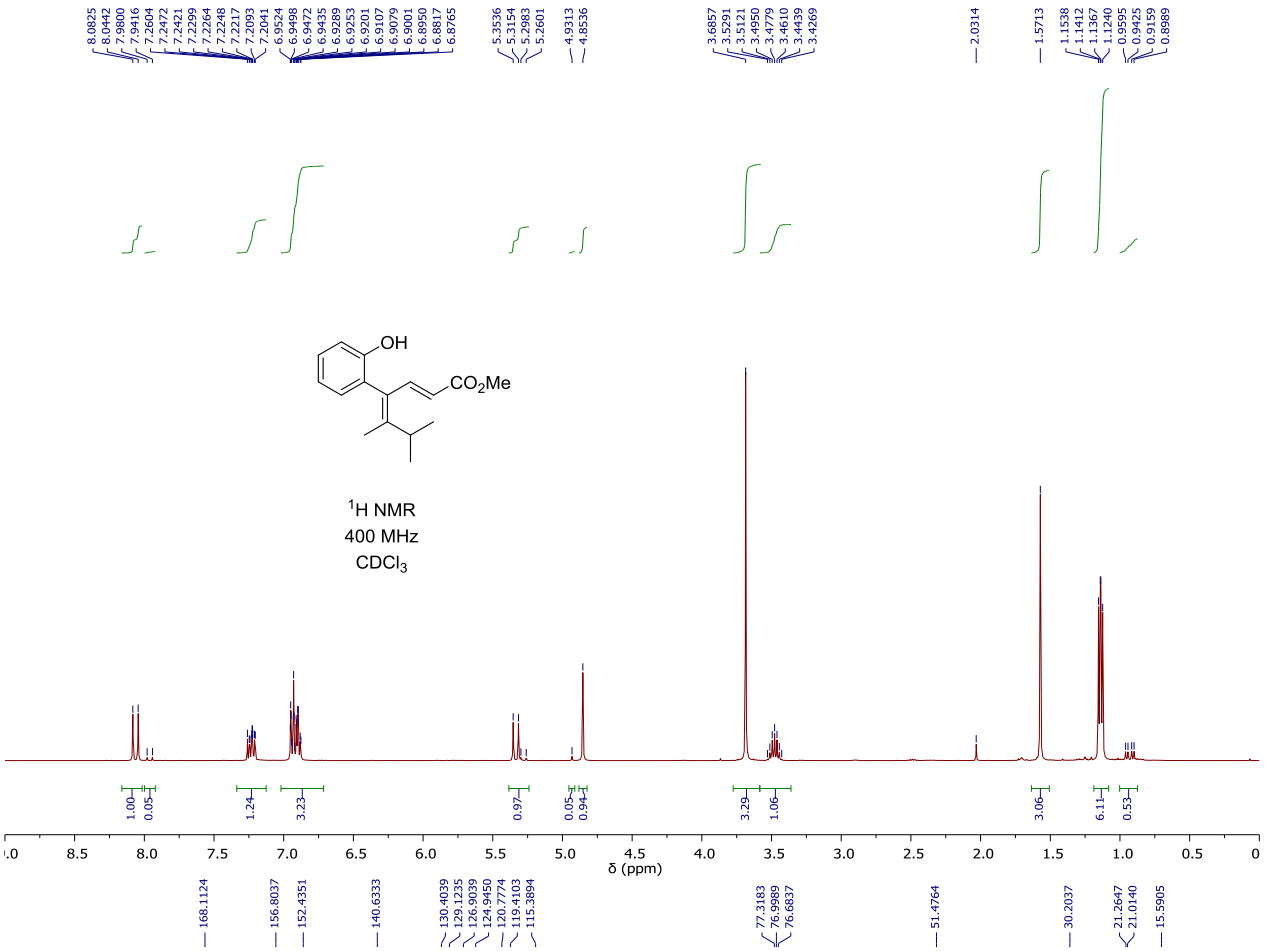


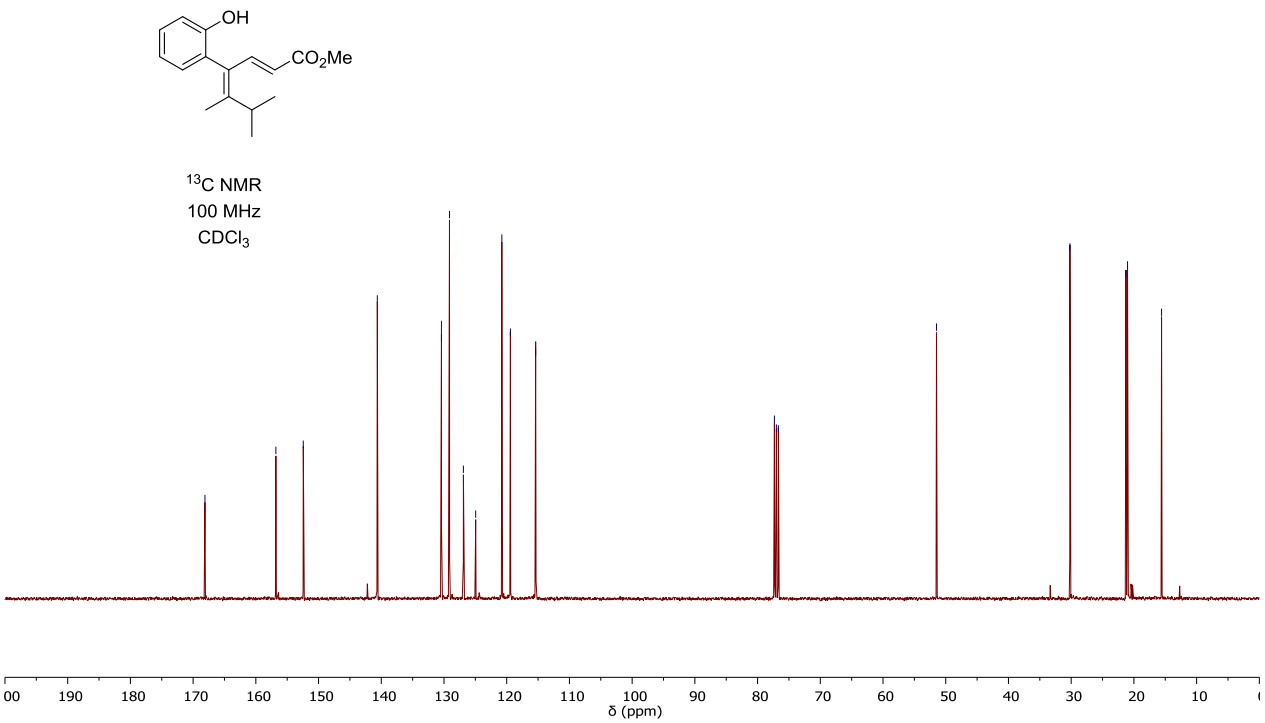
^{13}C NMR
100 MHz
$CDCl_3$

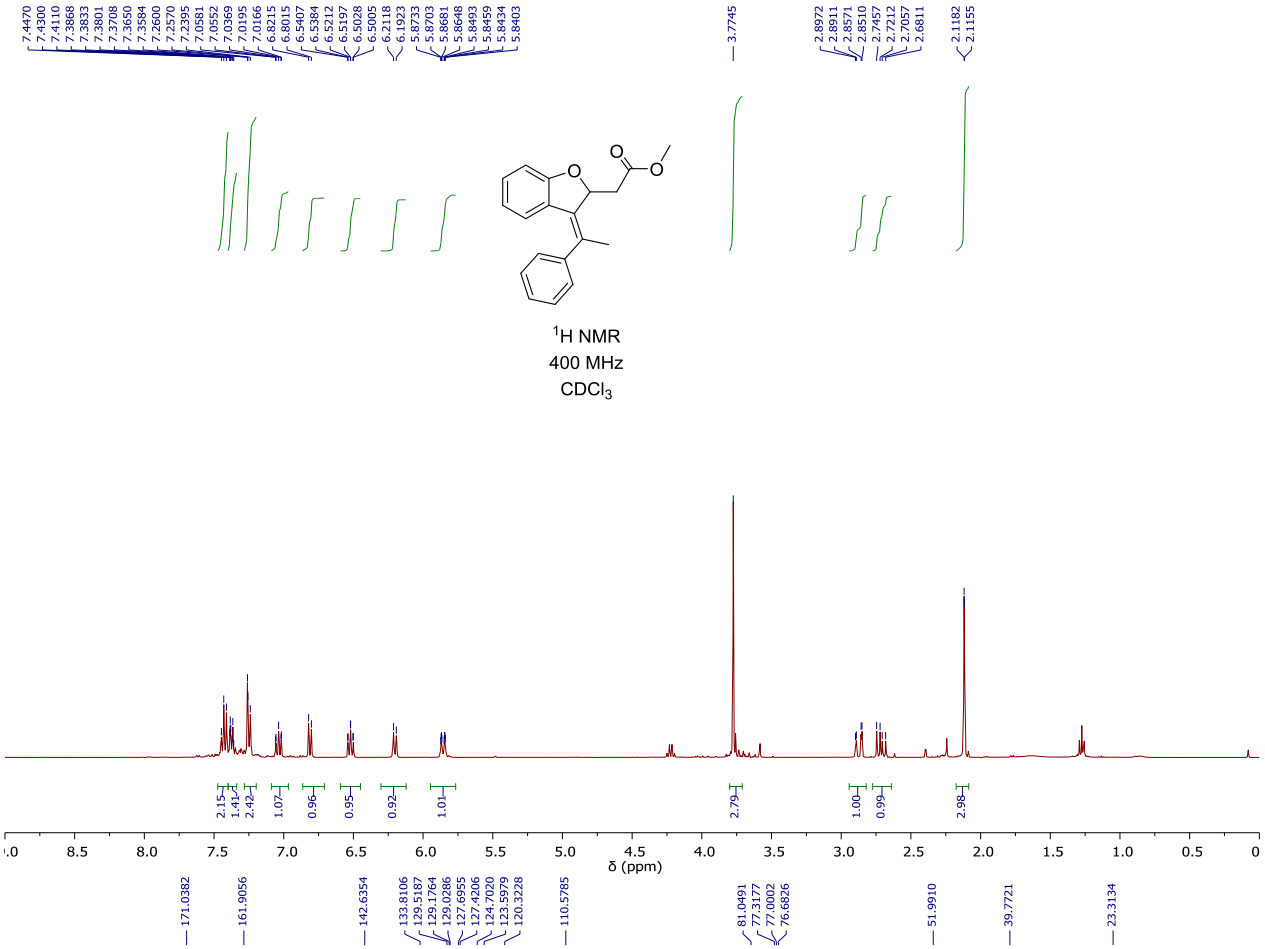



OH
CO2Me
1H NMR
400 MHz
CDCl3
δ (ppm)

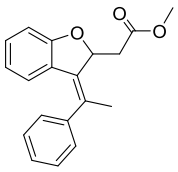

OH
CO2Me
13C NMR
100 MHz
CDCl3
δ (ppm)


OH
CO2Me
1H NMR
400 MHz
CDCl3
δ (ppm)

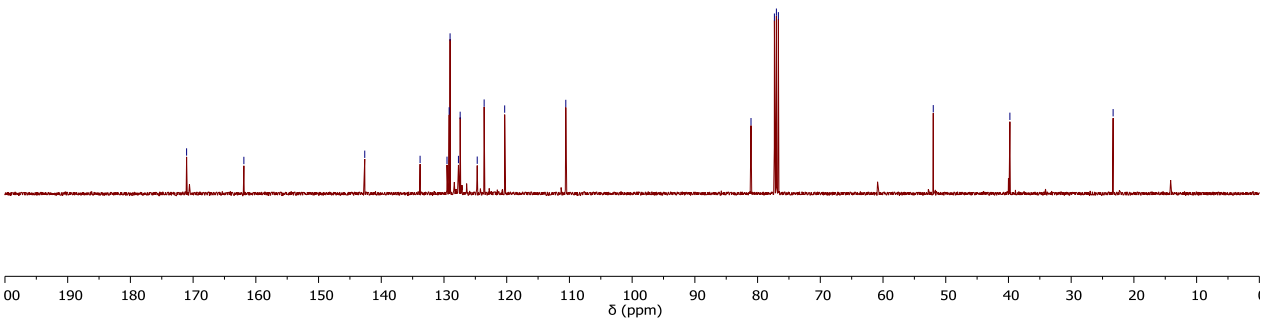

OH
CO2Me
13C NMR
100 MHz
CDCl3
δ (ppm)

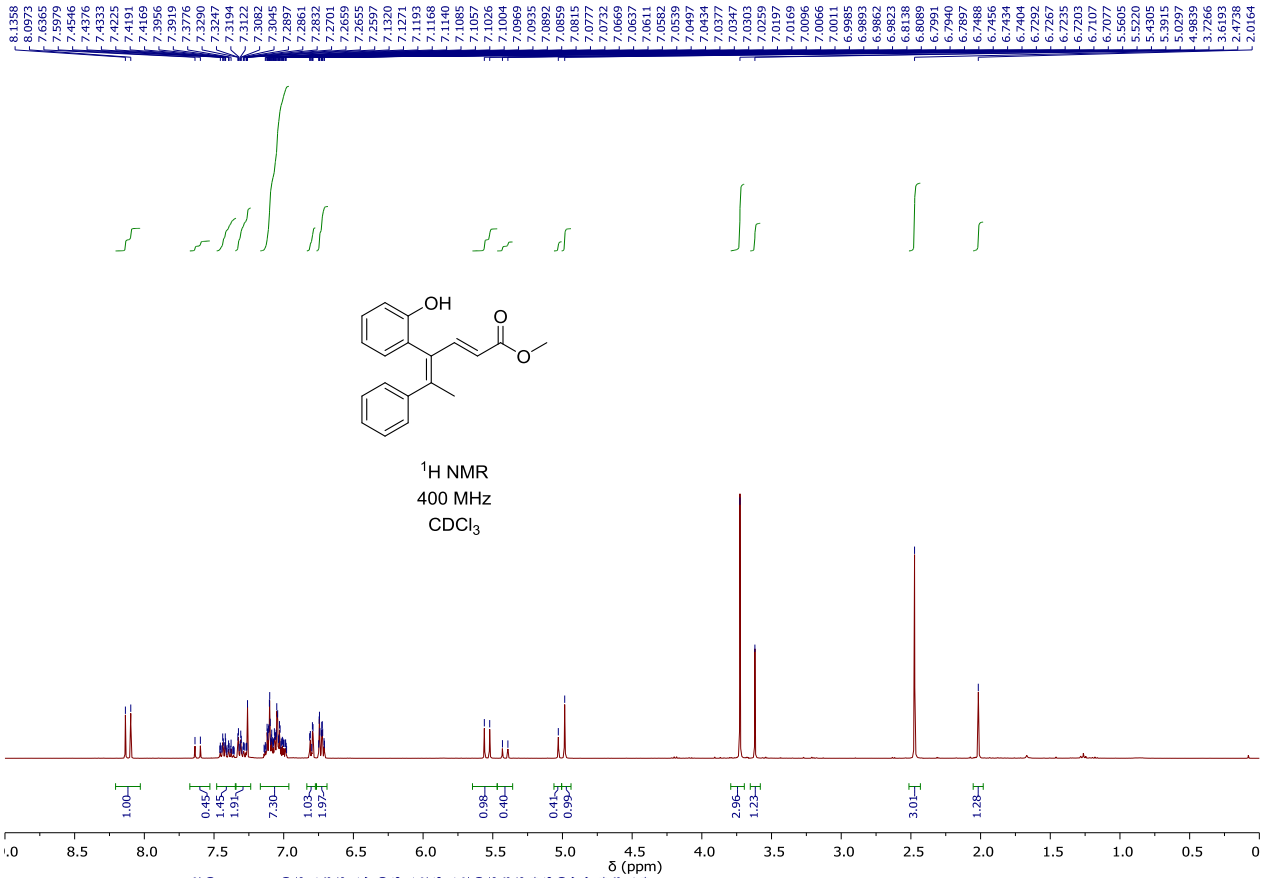


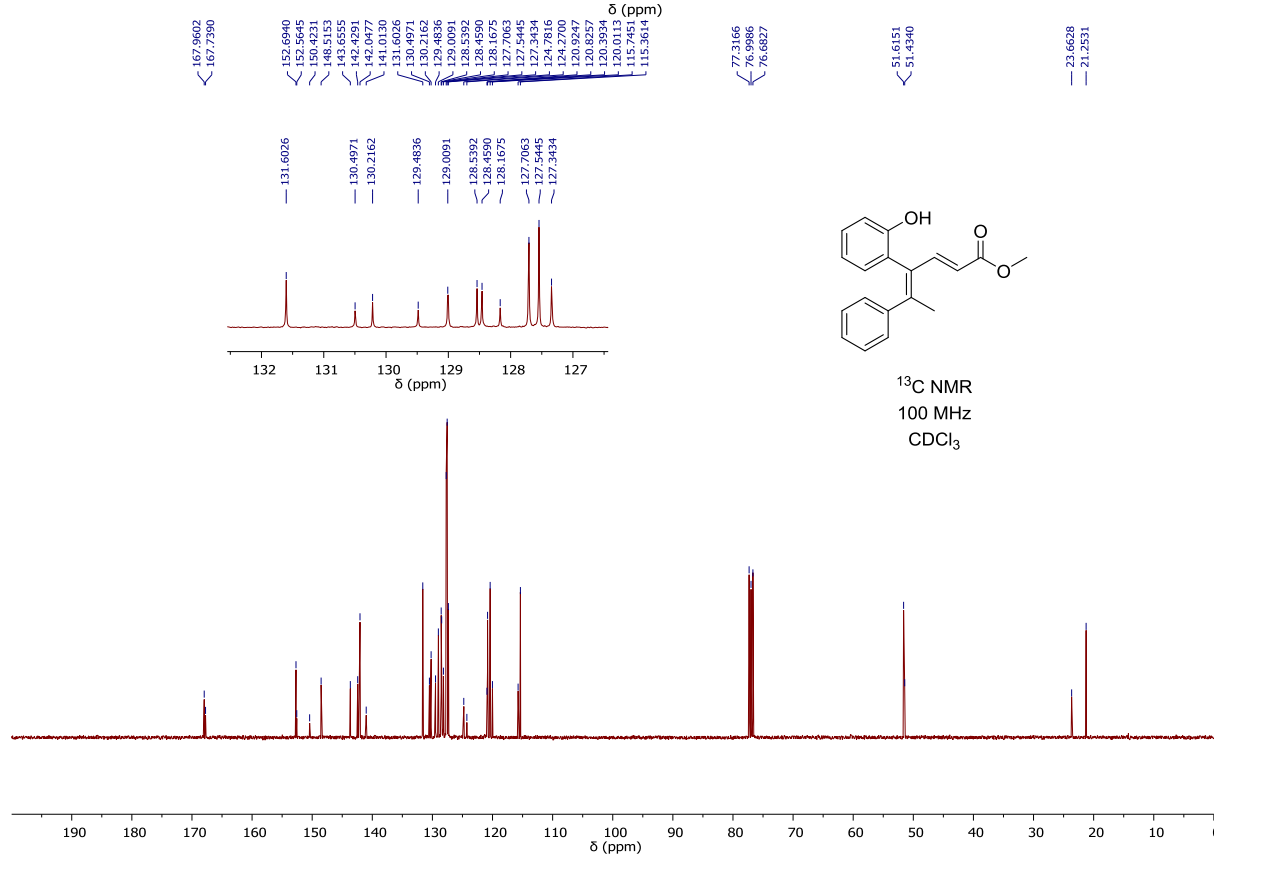
^{1}H NMR
400 MHz
$CDCl_3$

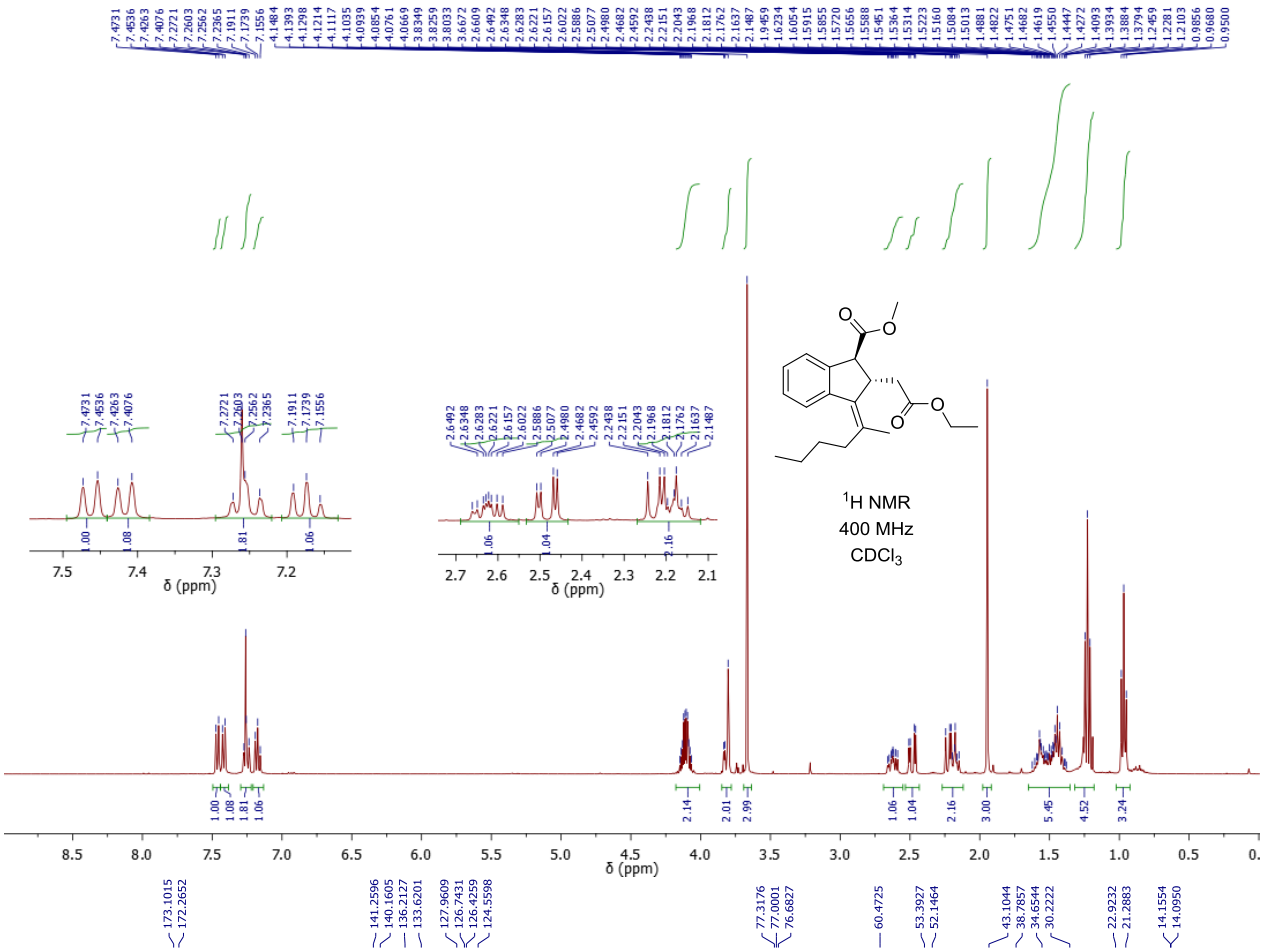


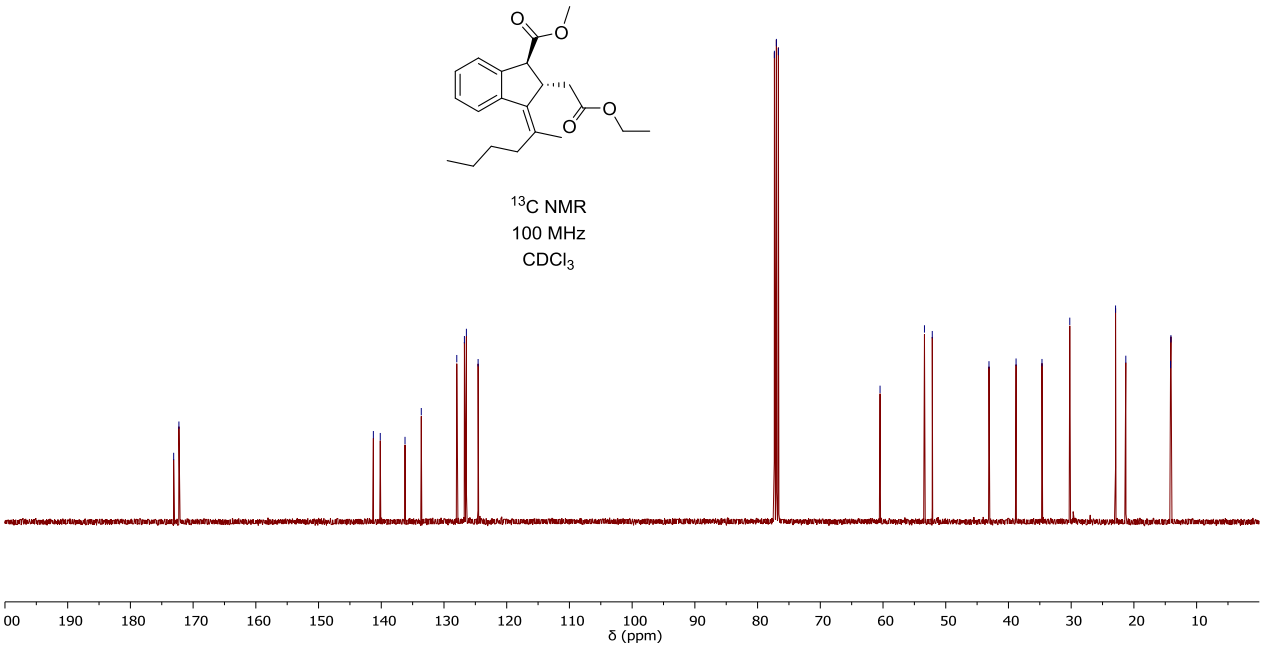
^{13}C NMR
100 MHz
$CDCl_3$

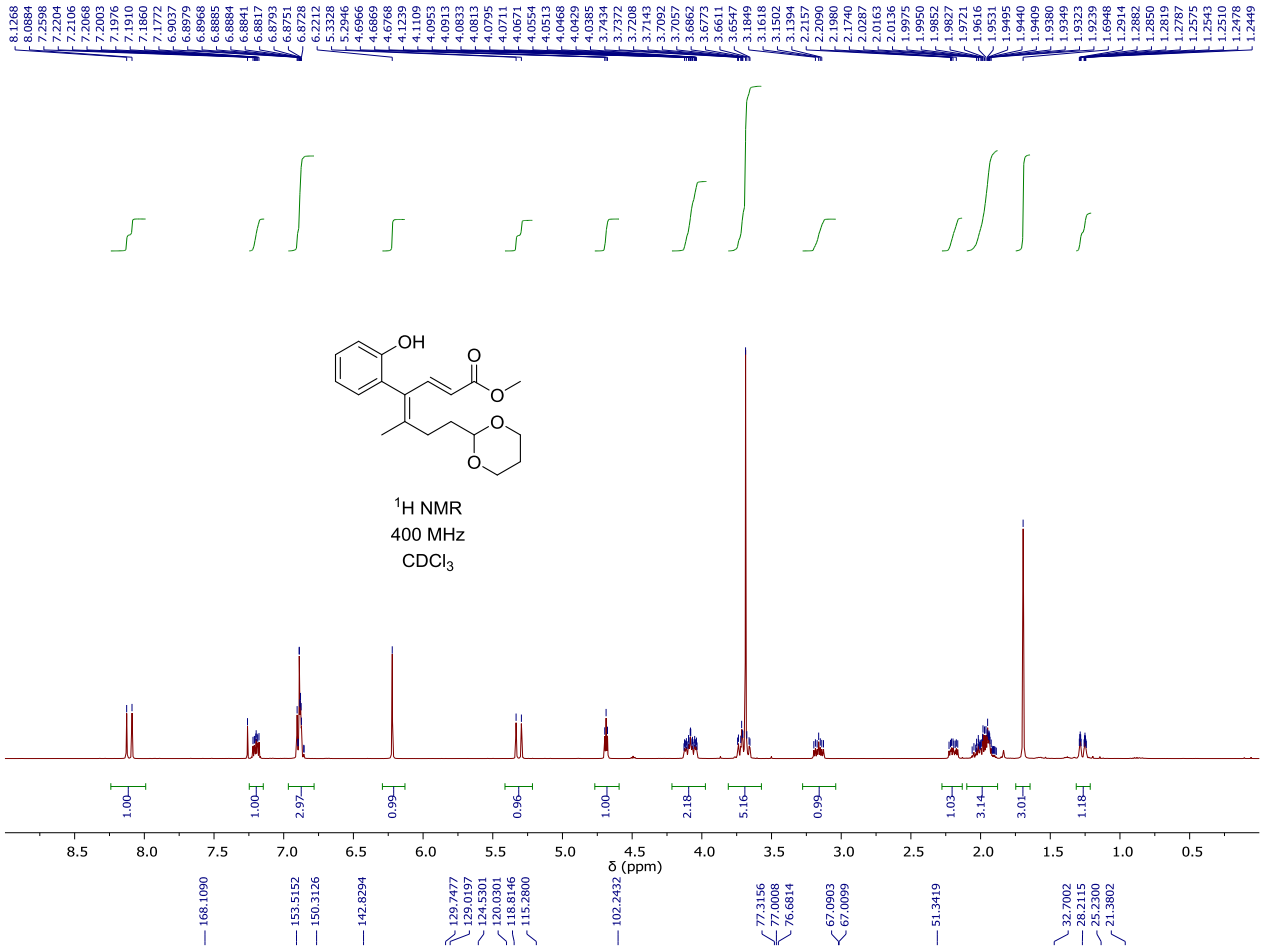


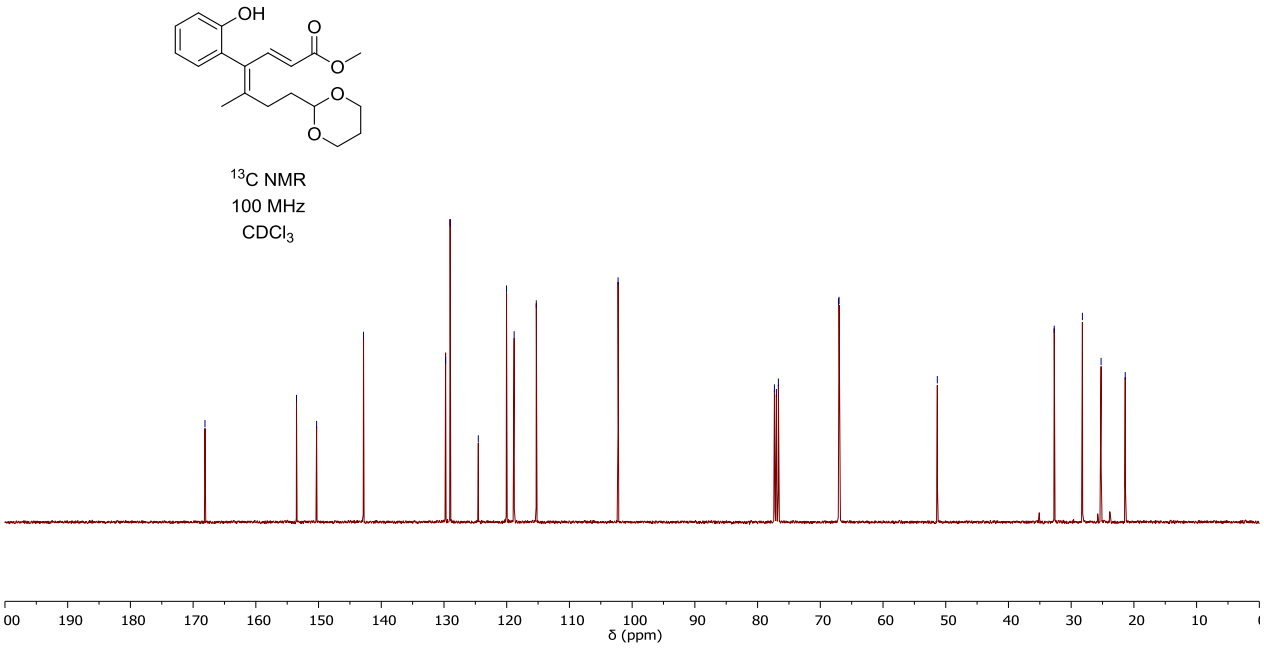

OH
O
O
^{1}H NMR
400 MHz
$CDCl_3$
δ (ppm)

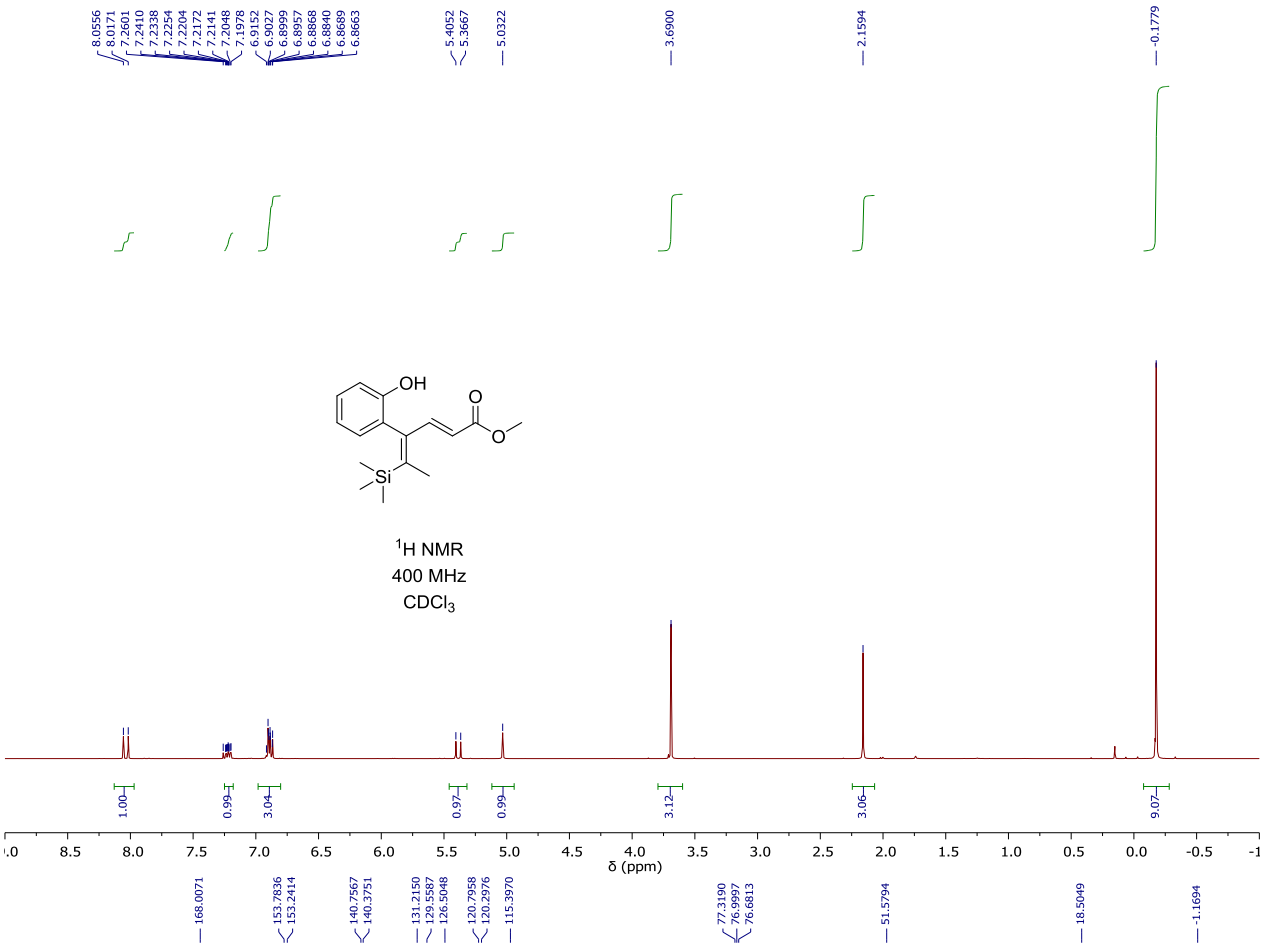

OH
O
O
^{13}C NMR
100 MHz
$CDCl_3$
δ (ppm)


^{1}H NMR
400 MHz
$CDCl_3$
δ (ppm)

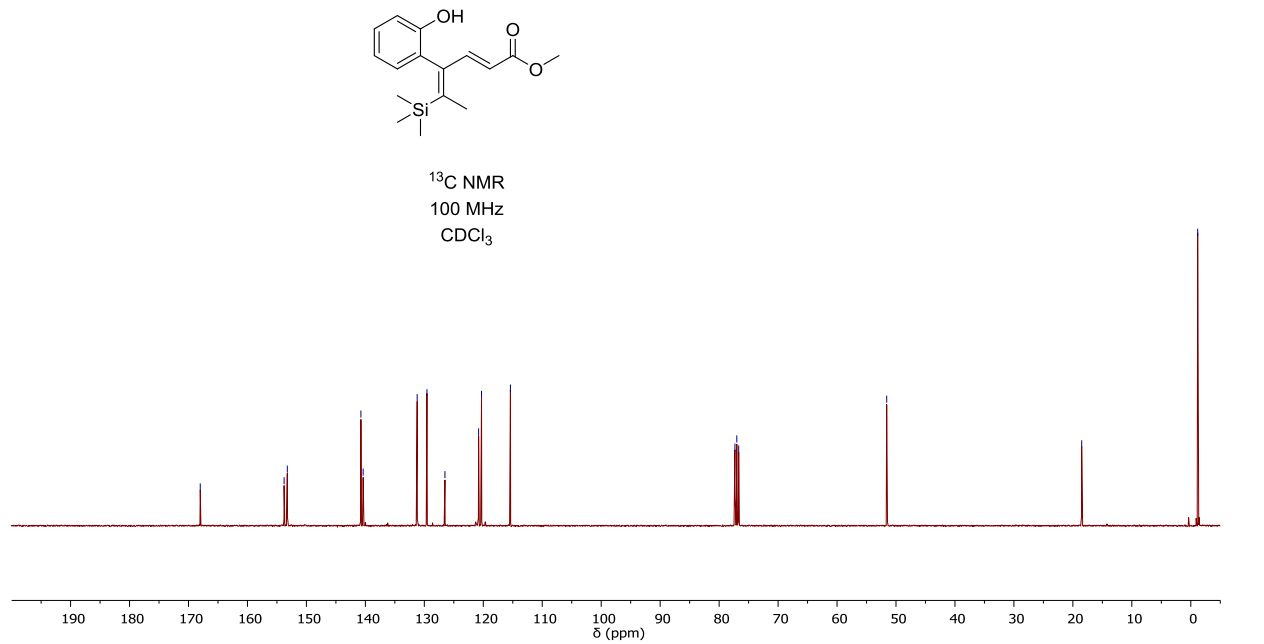

^{13}C NMR
100 MHz
$CDCl_3$
δ (ppm)


OH
O
O
O
O
^{1}H NMR
400 MHz
$CDCl_3$
δ (ppm)

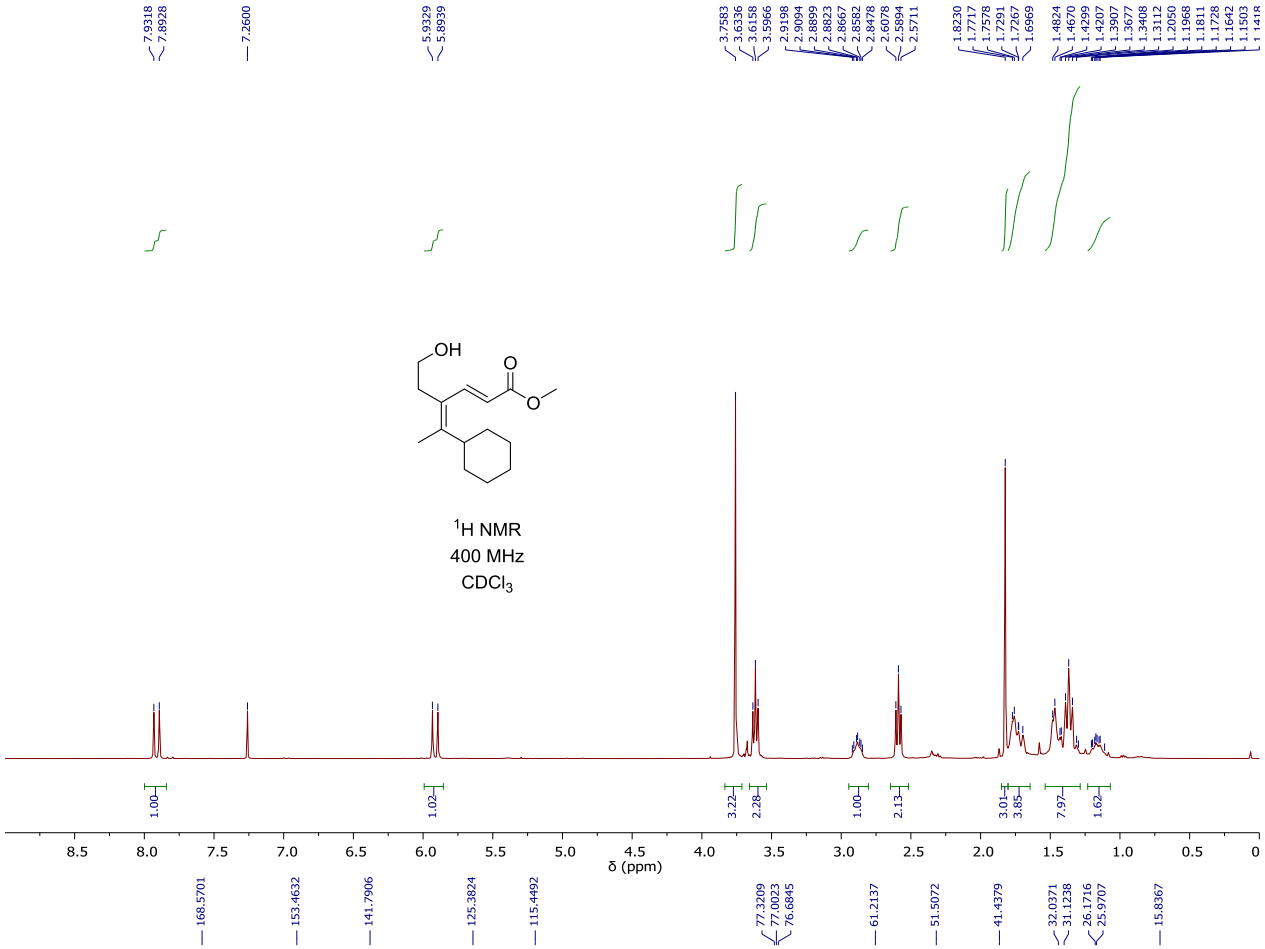

OH
O
O
O
O
^{13}C NMR
100 MHz
$CDCl_3$
δ (ppm)

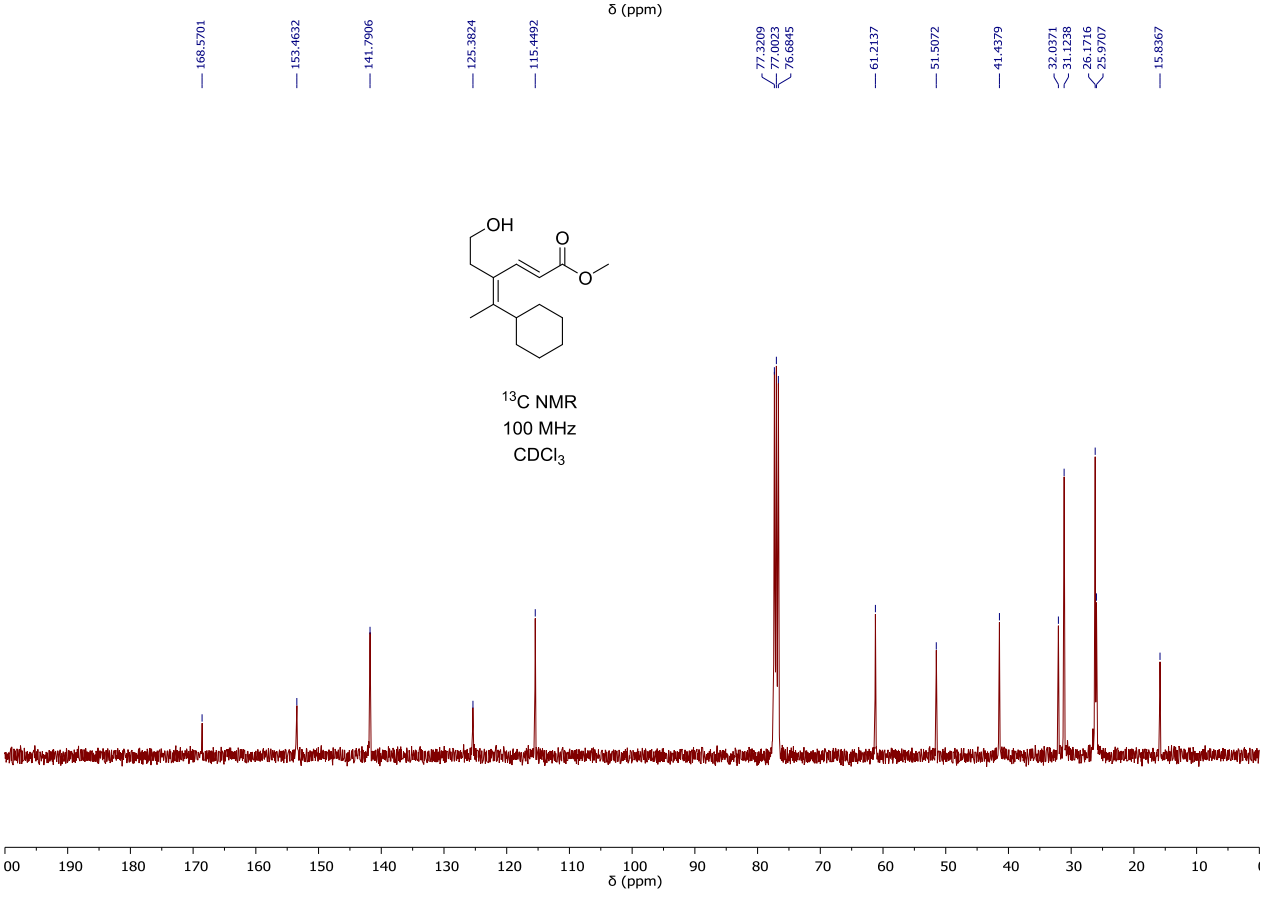


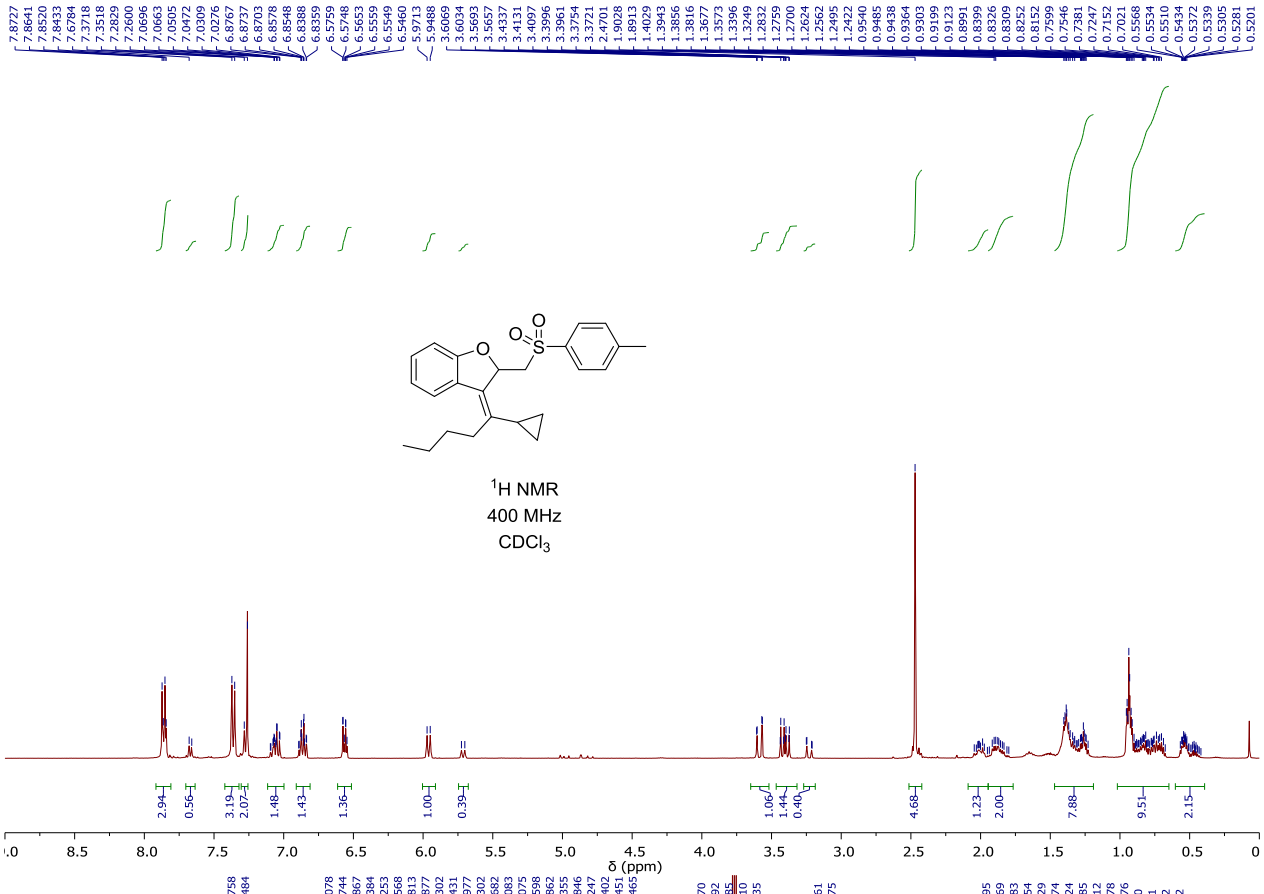
^{1}H NMR
400 MHz
$CDCl_3$

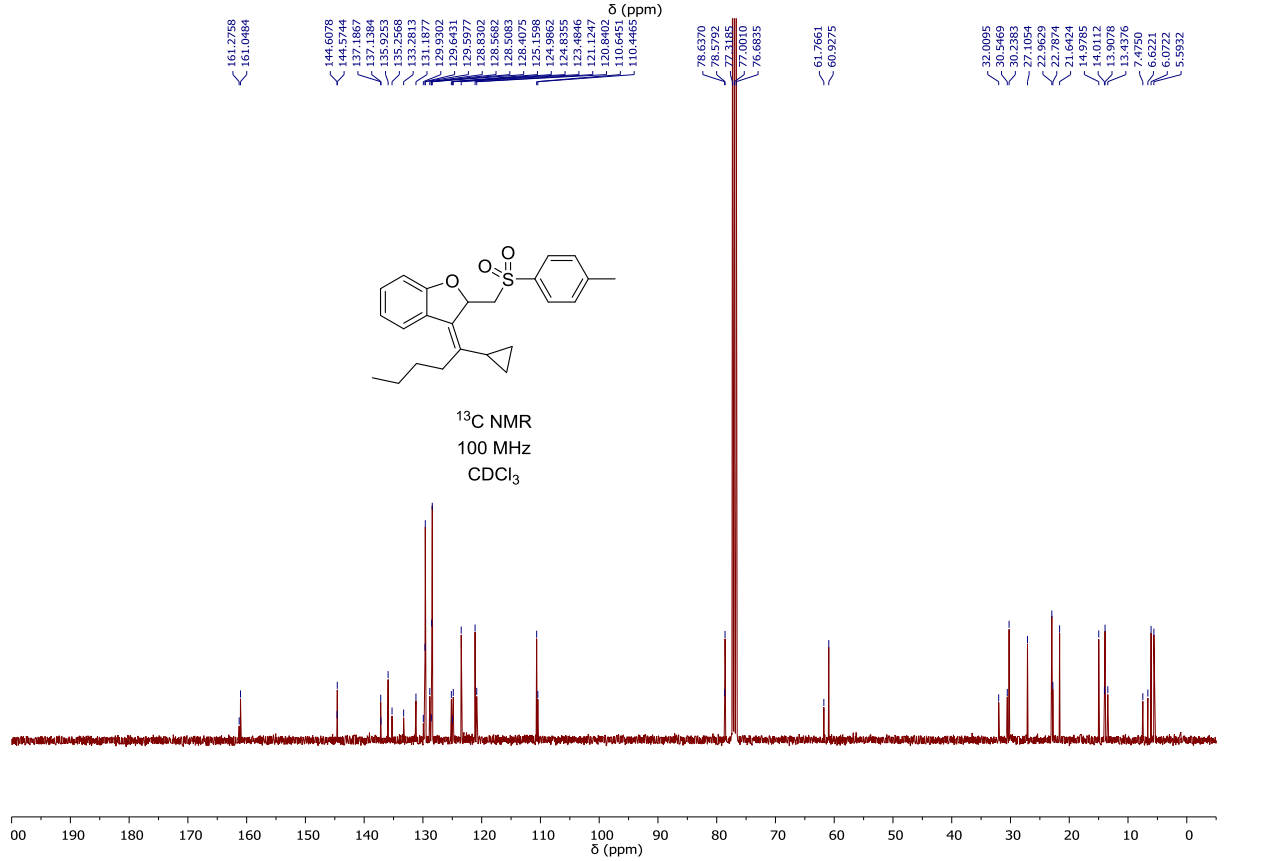


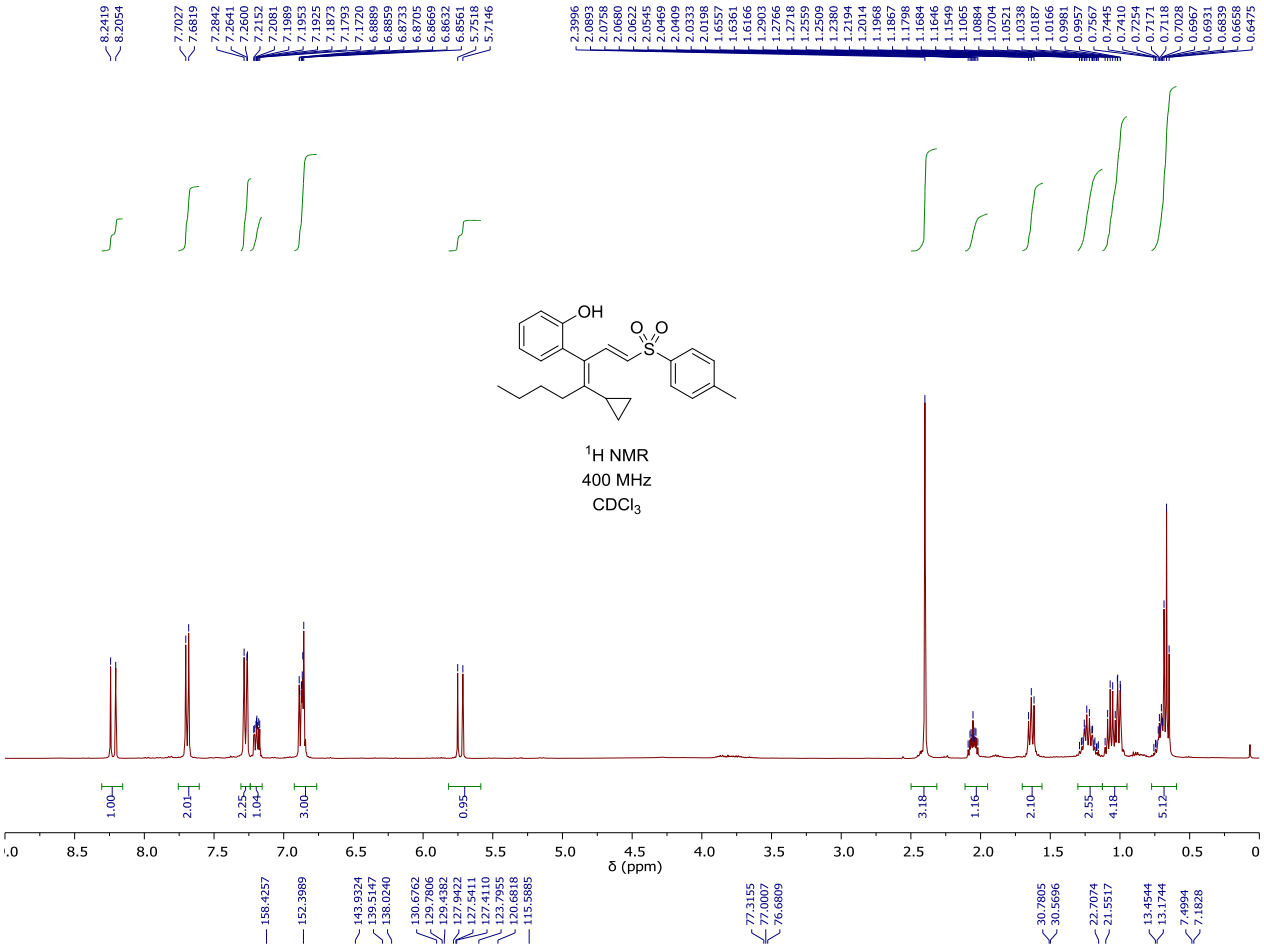
^{13}C NMR
100 MHz
$CDCl_3$

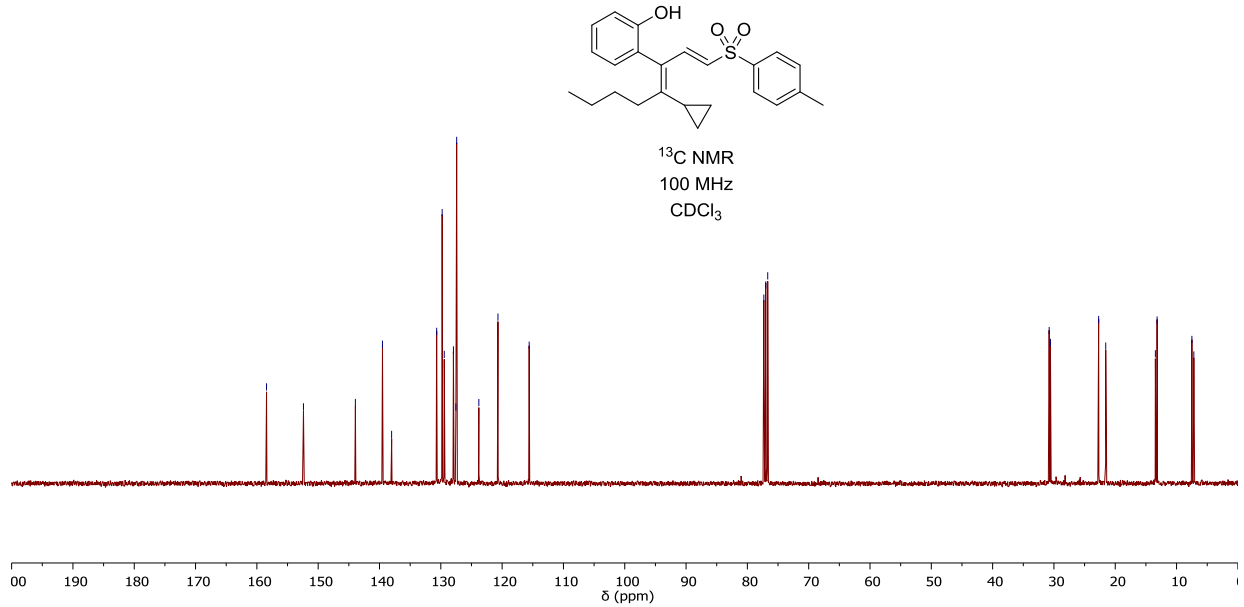

7.9318
7.8928
7.2600
5.9329
5.8939
3.7583
3.6336
3.6158
3.5966
2.9198
2.9094
2.8899
2.8823
2.8667
2.8582
2.8478
2.6078
2.5894
2.5711
1.8230
1.7717
1.7578
1.7291
1.7267
1.6969
1.4824
1.4670
1.4299
1.4207
1.3907
1.3677
1.3408
1.3112
1.2050
1.1968
1.1811
1.1728
1.1642
1.1503
OH
O
O
1H NMR
400 MHz
CDCl3
1.00
1.02
3.22
2.28
1.00
2.13
3.01
3.85
7.97
1.62
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
δ (ppm)

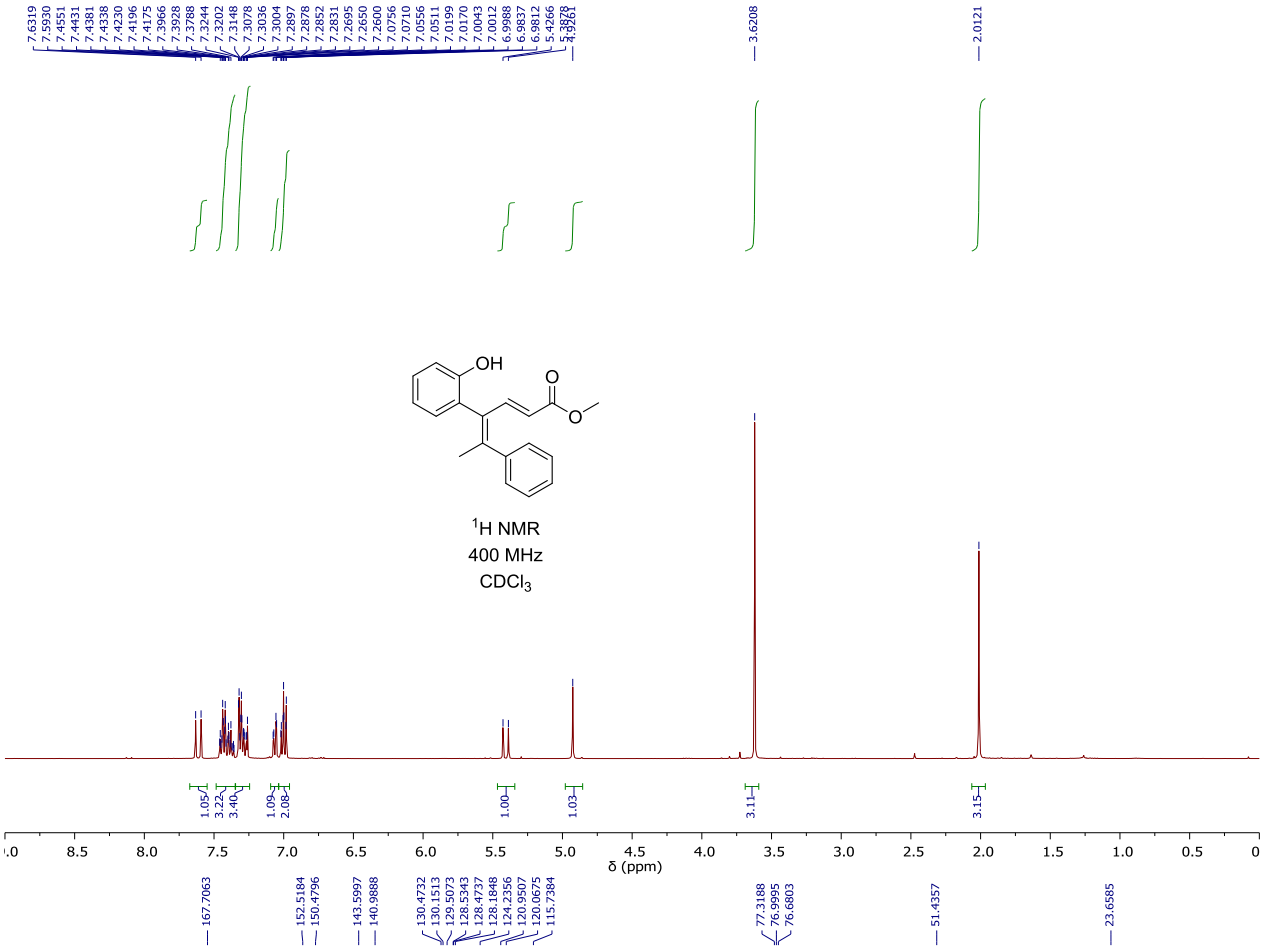

168.5701
153.4632
141.7906
125.3824
115.4492
77.3209
77.0023
76.6845
61.2137
51.5072
41.4379
32.0371
31.1238
26.1716
25.9707
15.8367
OH
O
O
13C NMR
100 MHz
CDCl3
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
δ (ppm)

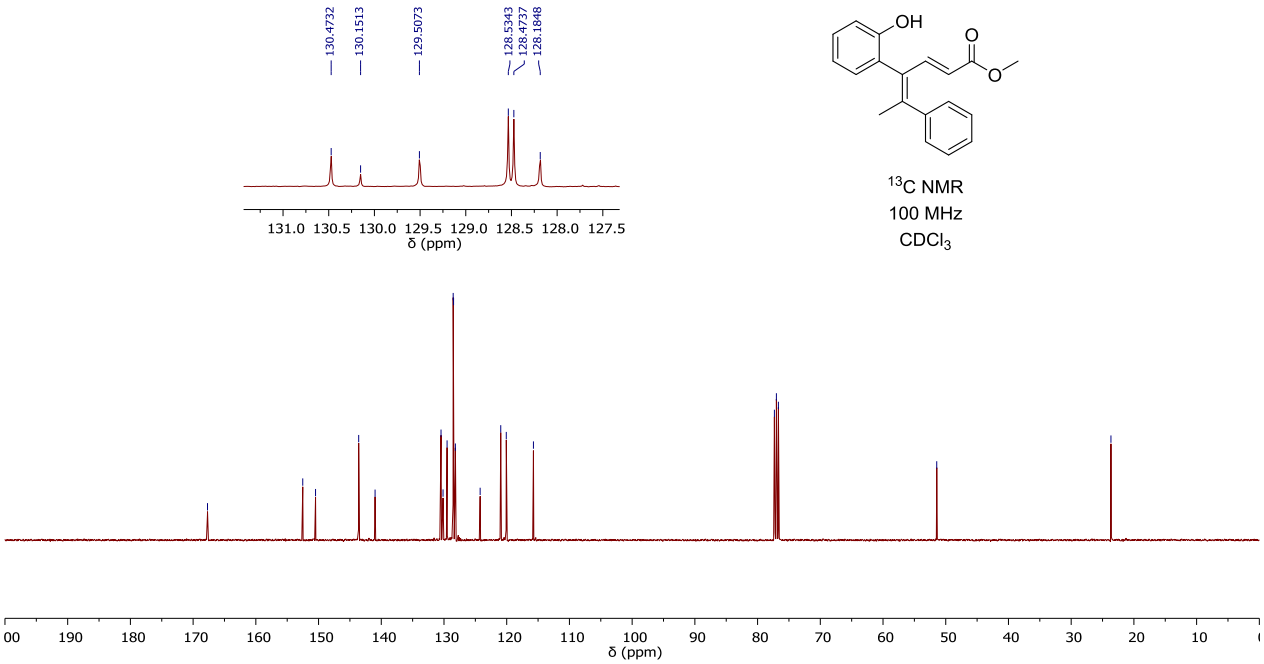

^{1}H NMR
400 MHz
$CDCl_3$
δ (ppm)

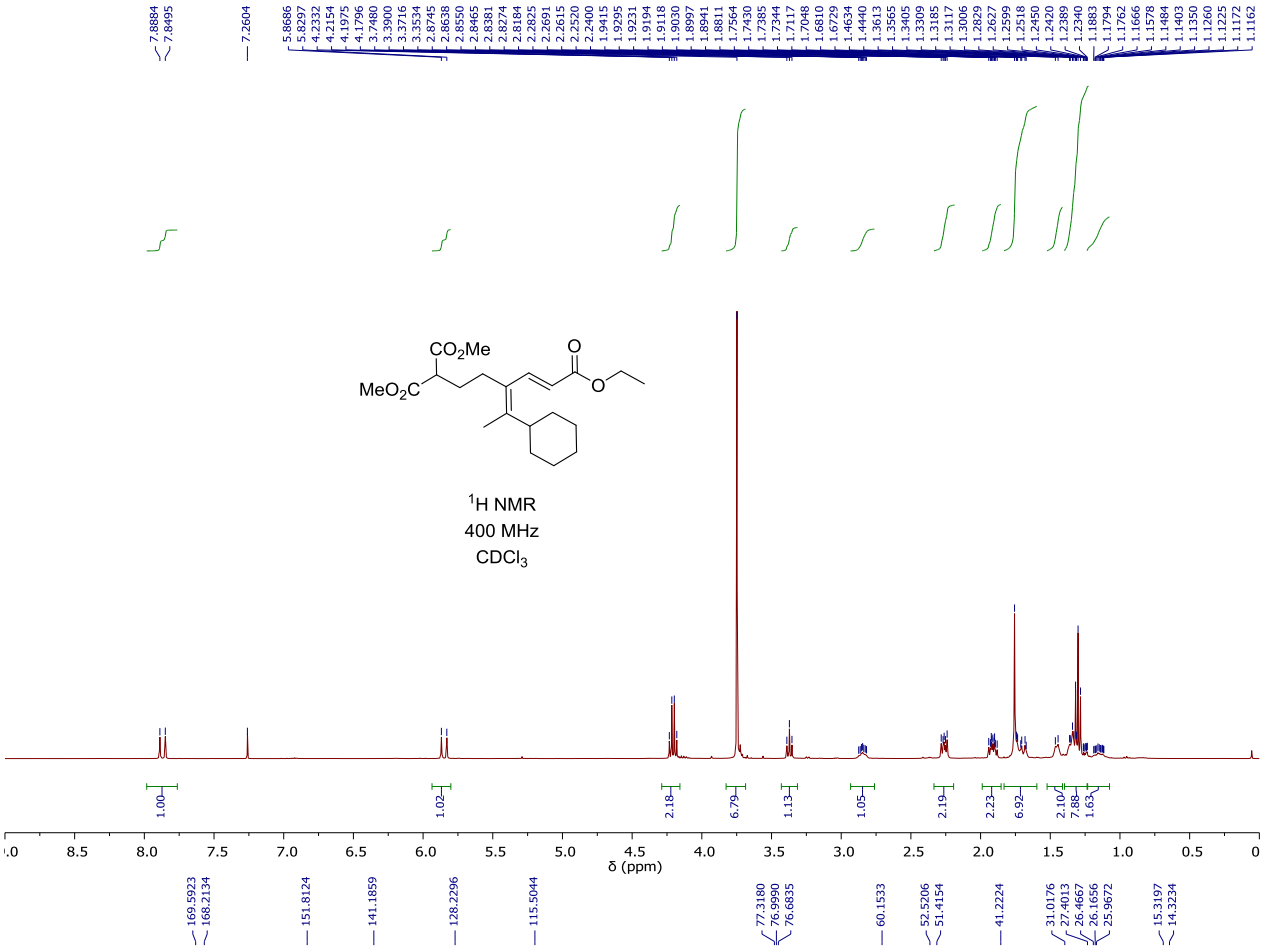

^{13}C NMR
100 MHz
$CDCl_3$
δ (ppm)

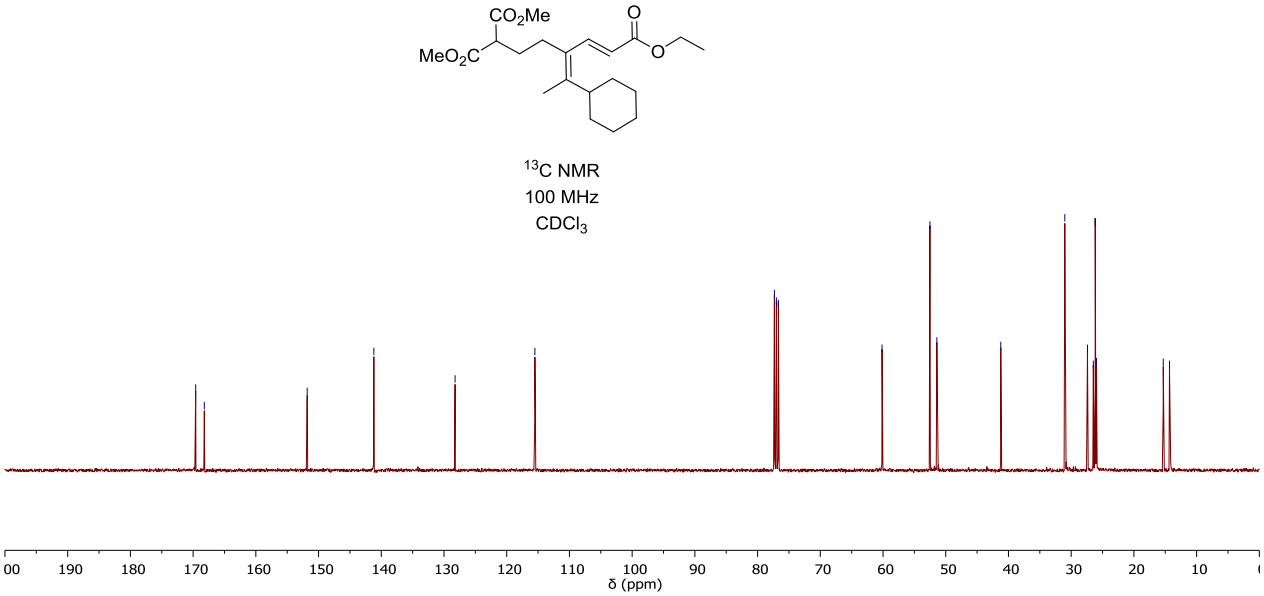

OH
O
O
S
^{1}H NMR
400 MHz
$CDCl_3$
δ (ppm)

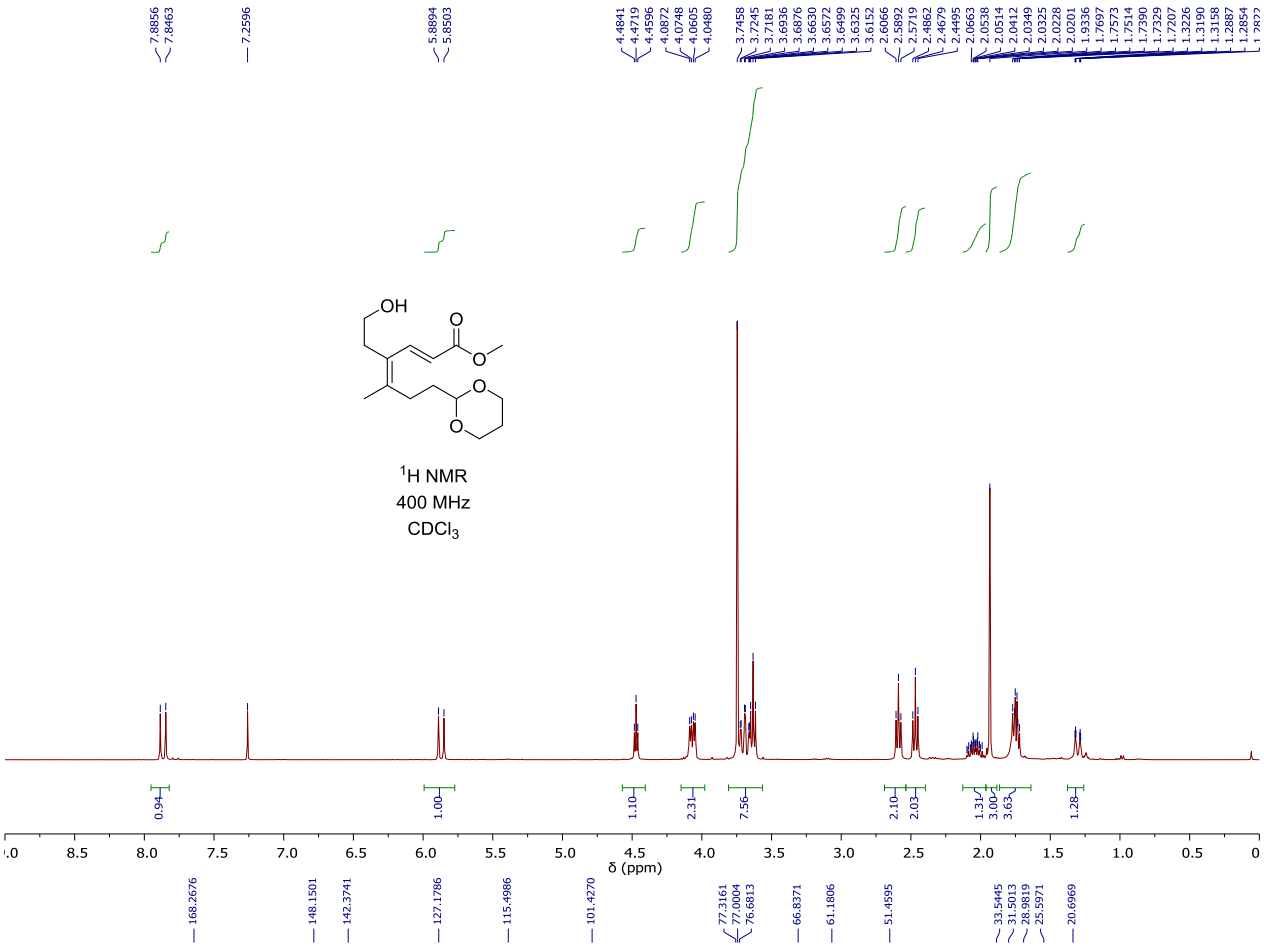

OH
O
O
S
^{13}C NMR
100 MHz
$CDCl_3$
δ (ppm)

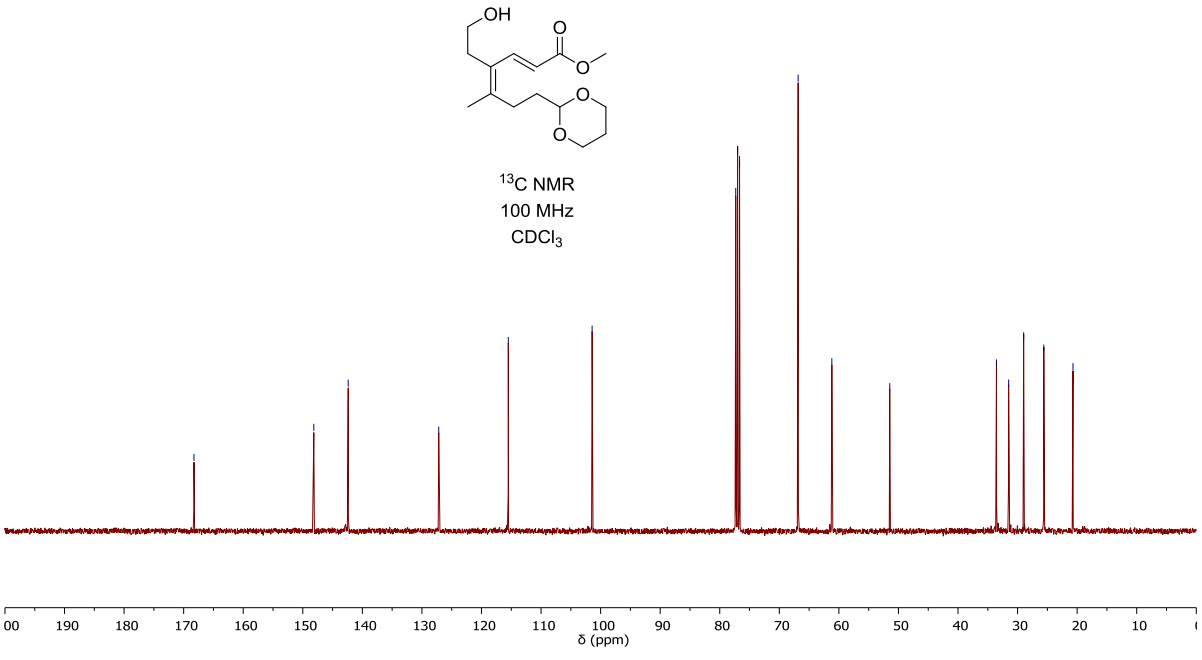

OH
O
O
^{1}H NMR
400 MHz
$CDCl_3$
δ (ppm)

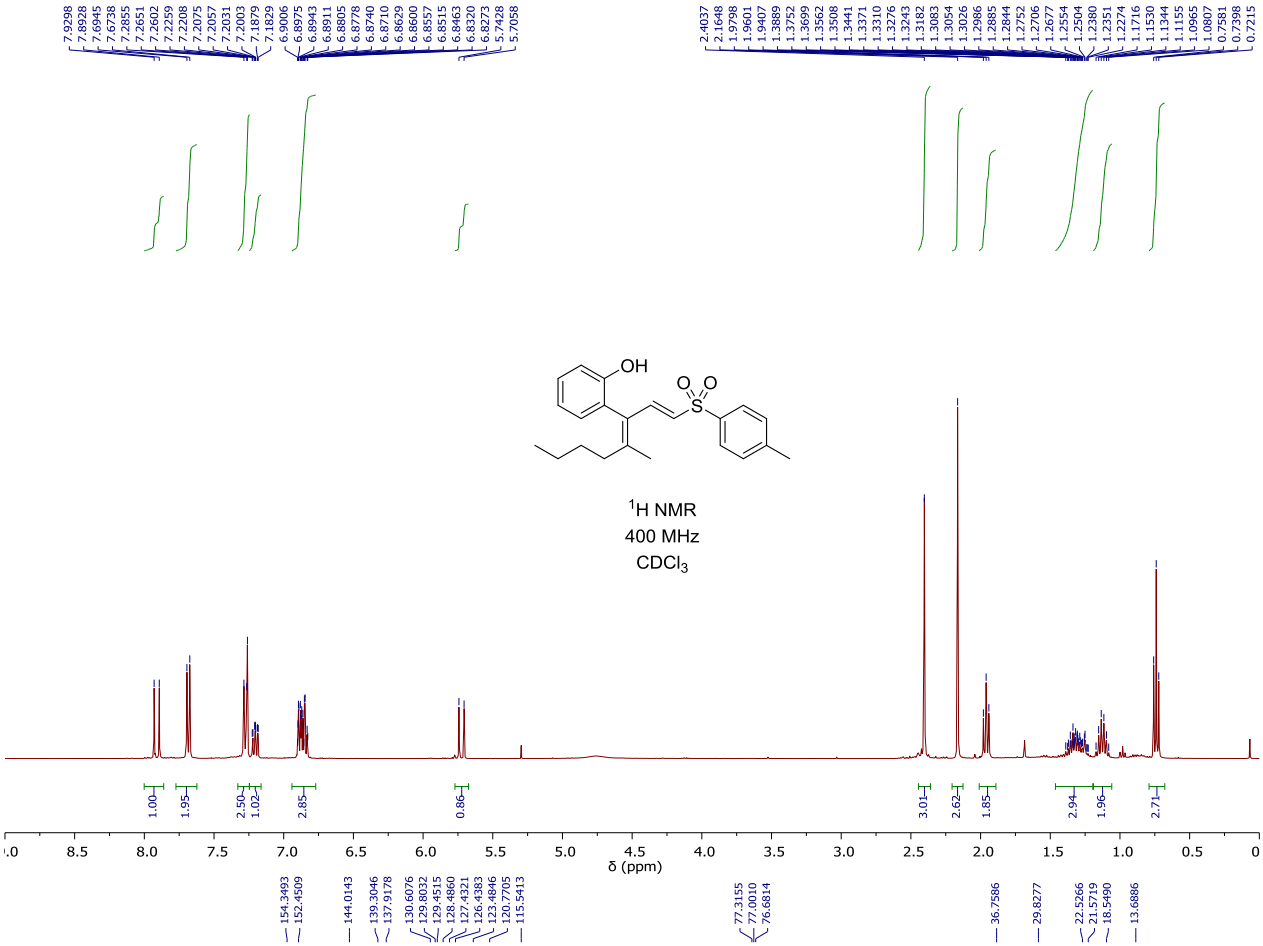

OH
O
O
^{13}C NMR
100 MHz
$CDCl_3$
δ (ppm)

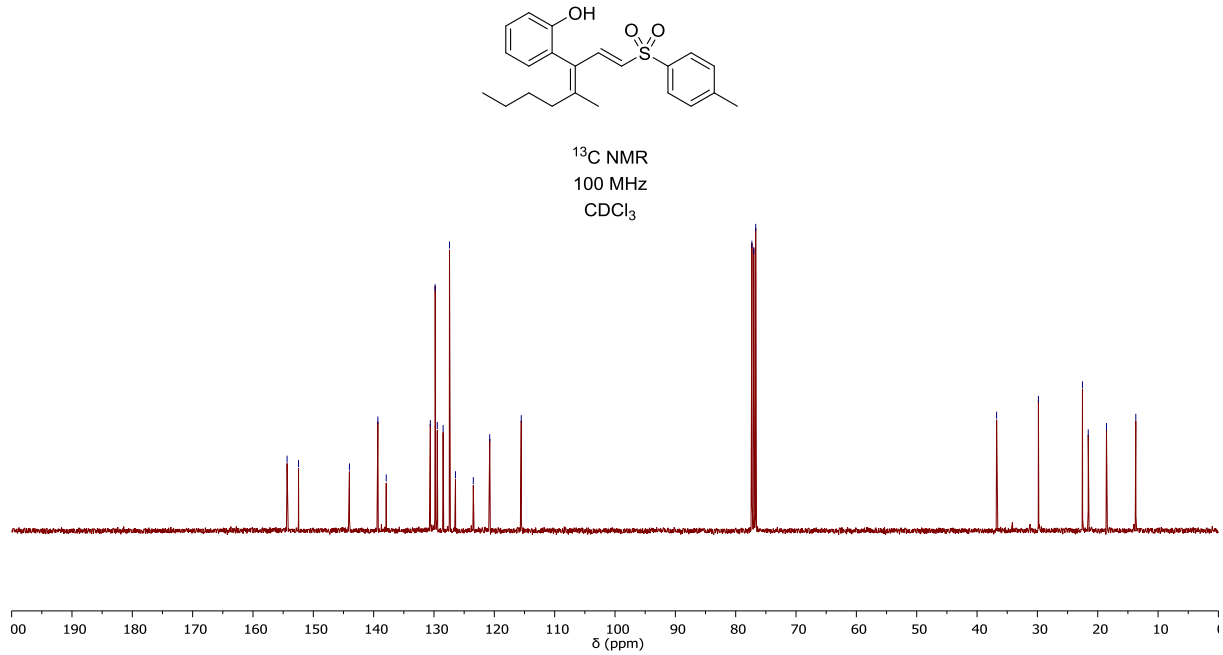

CO2Me
MeO2C
O
O
1H NMR
400 MHz
CDCl3
δ (ppm)

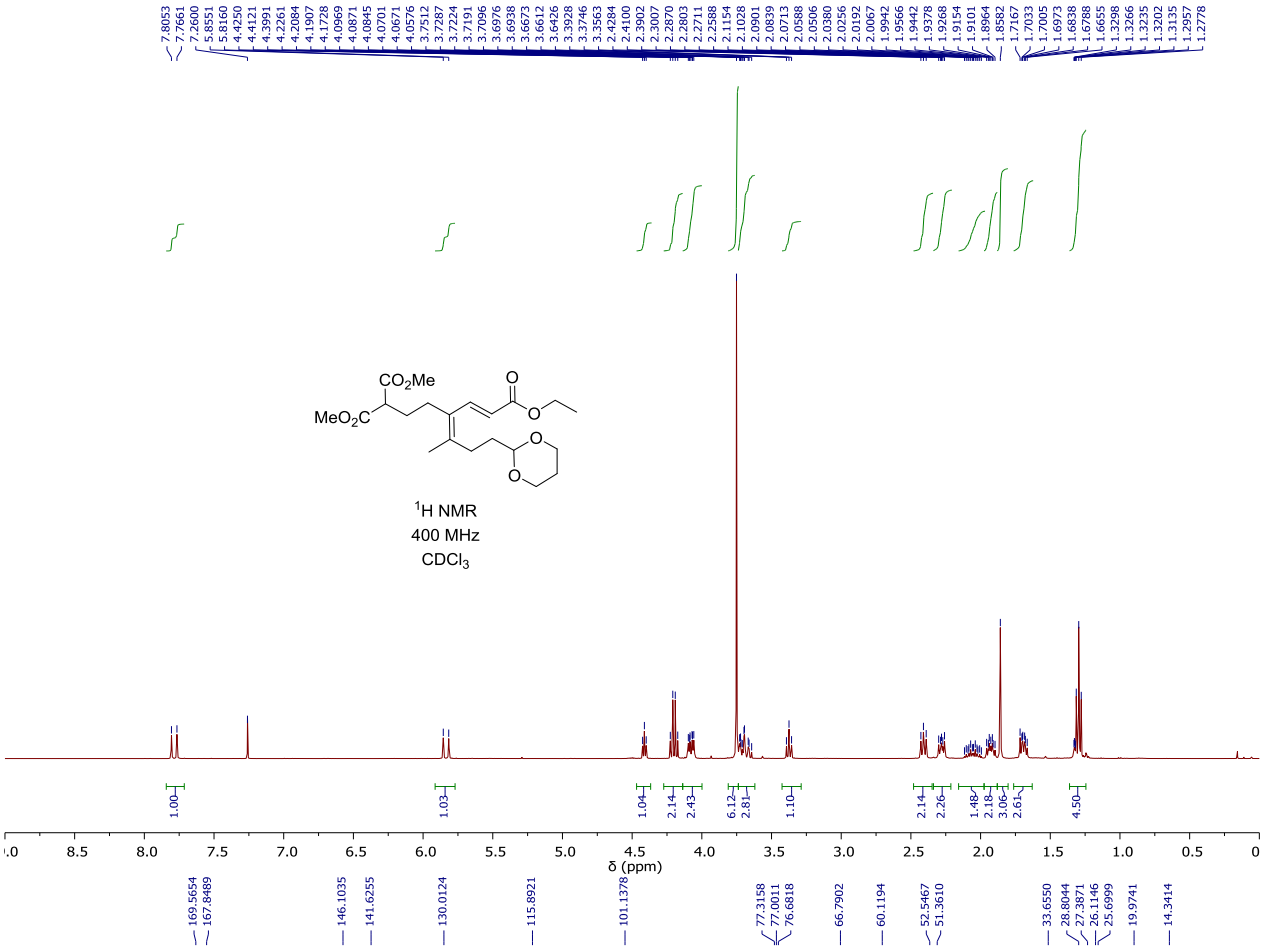

CO2Me
MeO2C
O
O
13C NMR
100 MHz
CDCl3
δ (ppm)

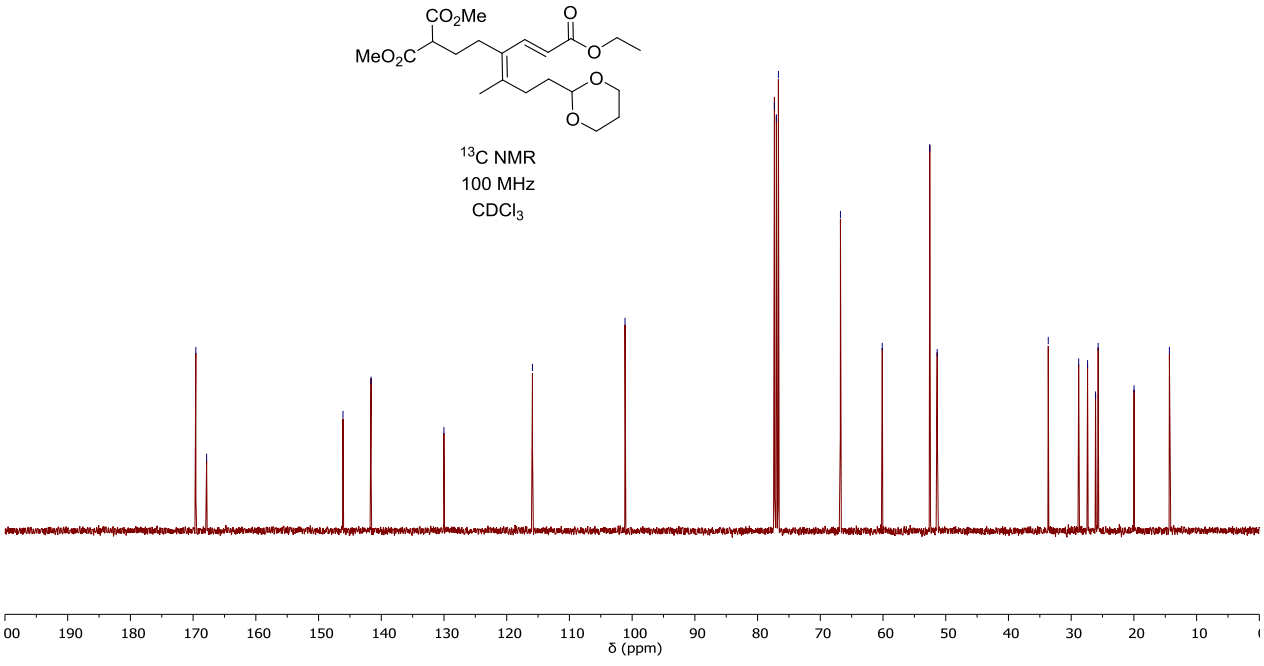

OH
O
O
O
O
^{1}H NMR
400 MHz
$CDCl_3$
δ (ppm)

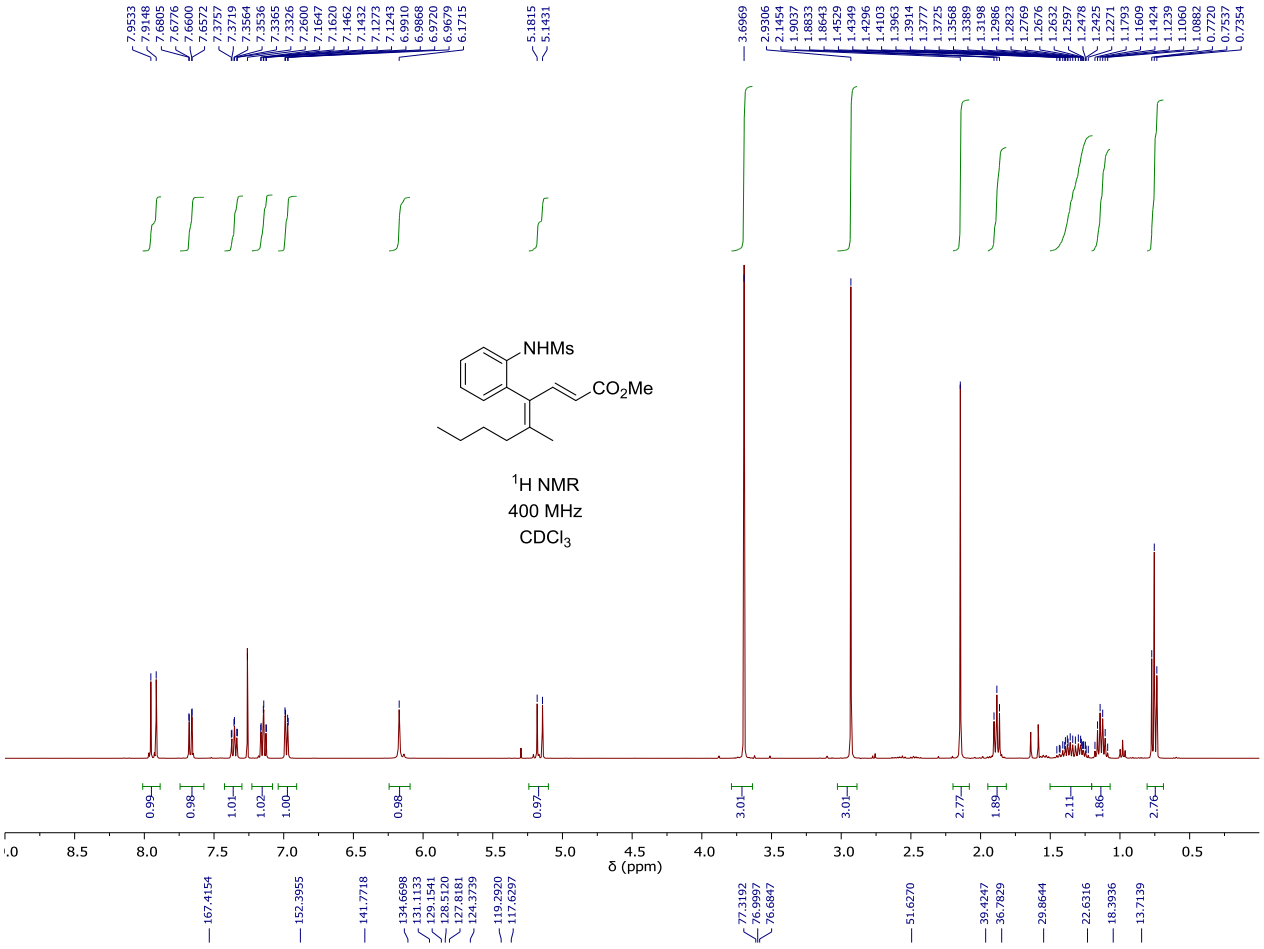

OH
O
O
O
O
^{13}C NMR
100 MHz
$CDCl_3$
δ (ppm)

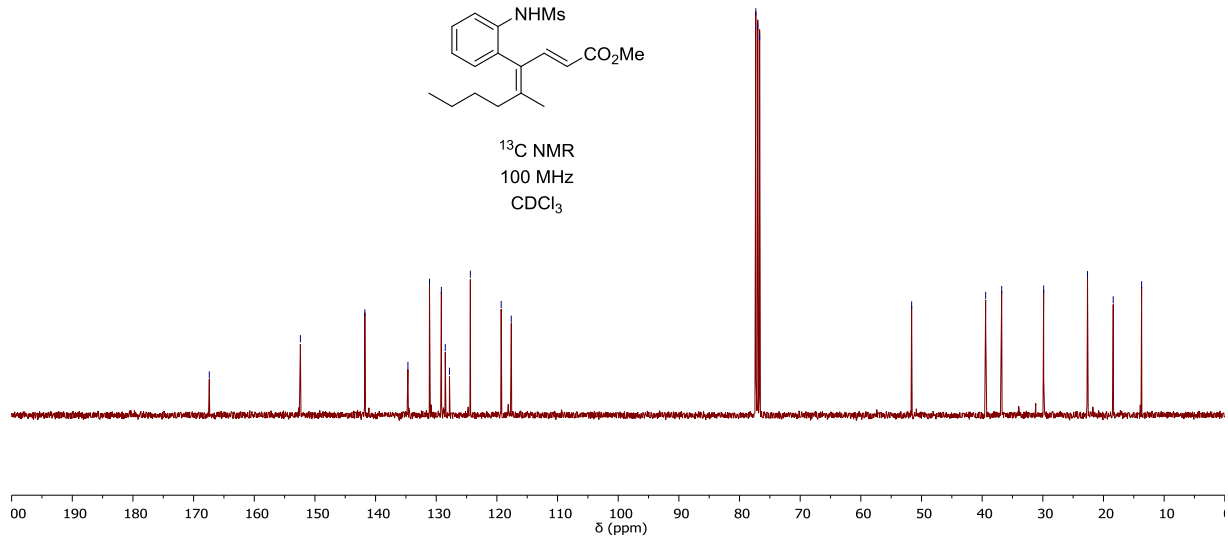

OH
O
O
S
^{1}H NMR
400 MHz
$CDCl_3$
δ (ppm)

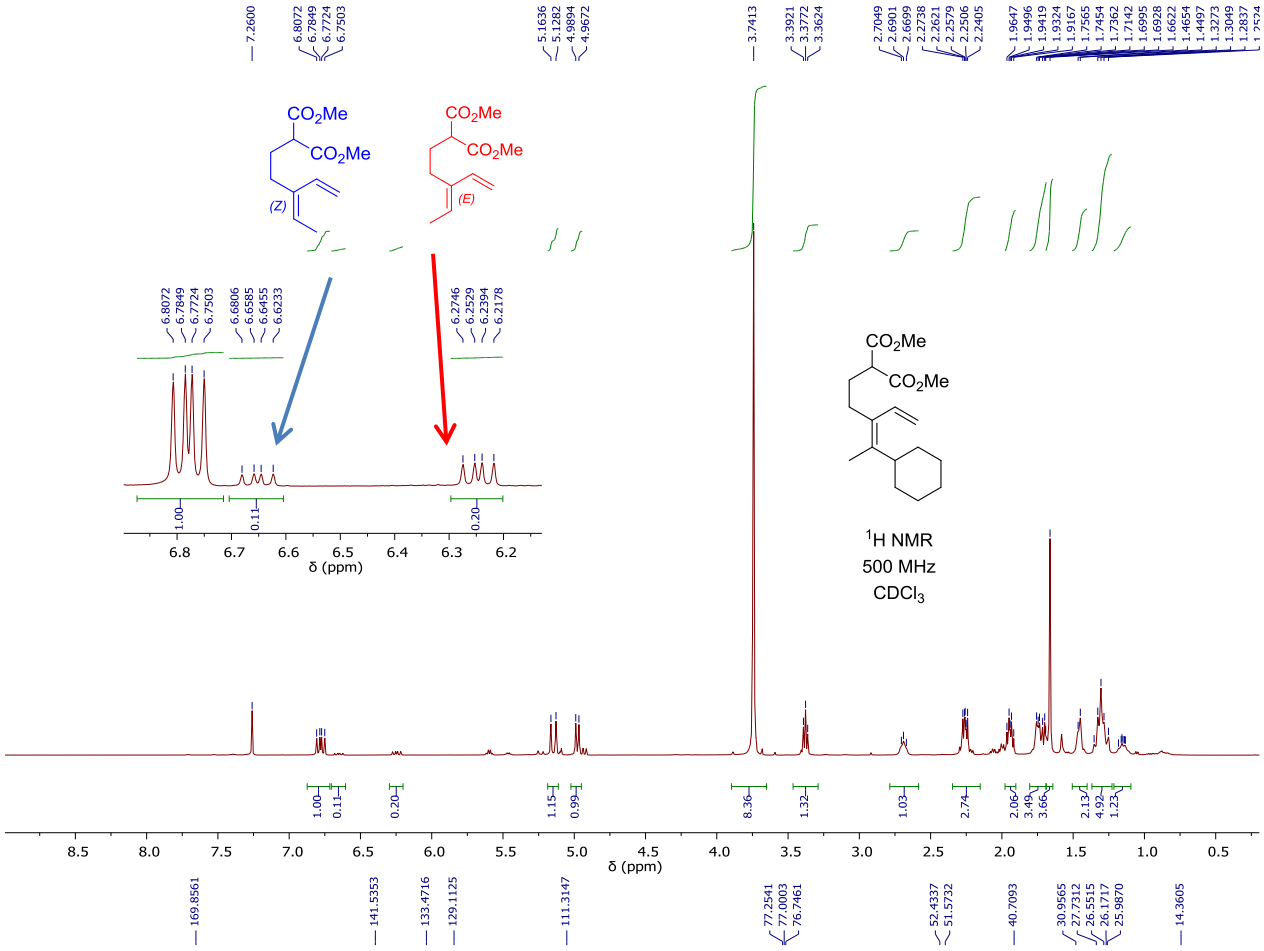

OH
O
O
S
^{13}C NMR
100 MHz
$CDCl_3$
δ (ppm)

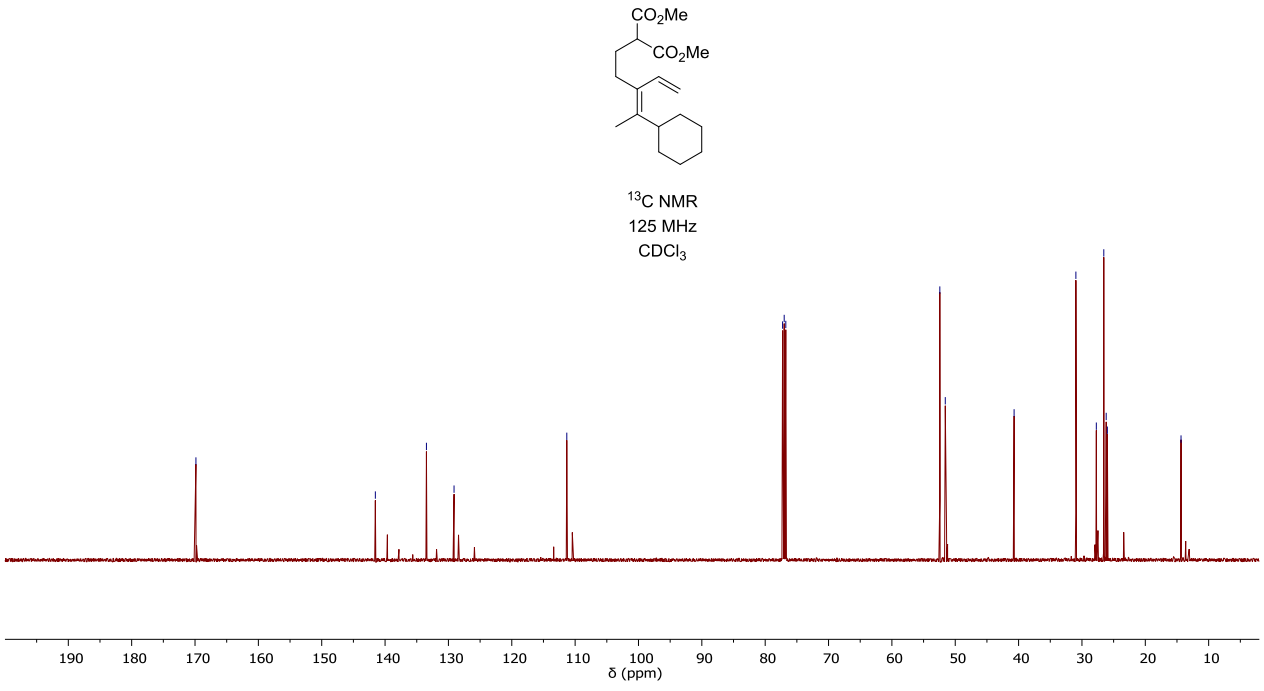

CO2Me
MeO2C
O
O
O
O
1H NMR
400 MHz
CDCl3
δ (ppm)

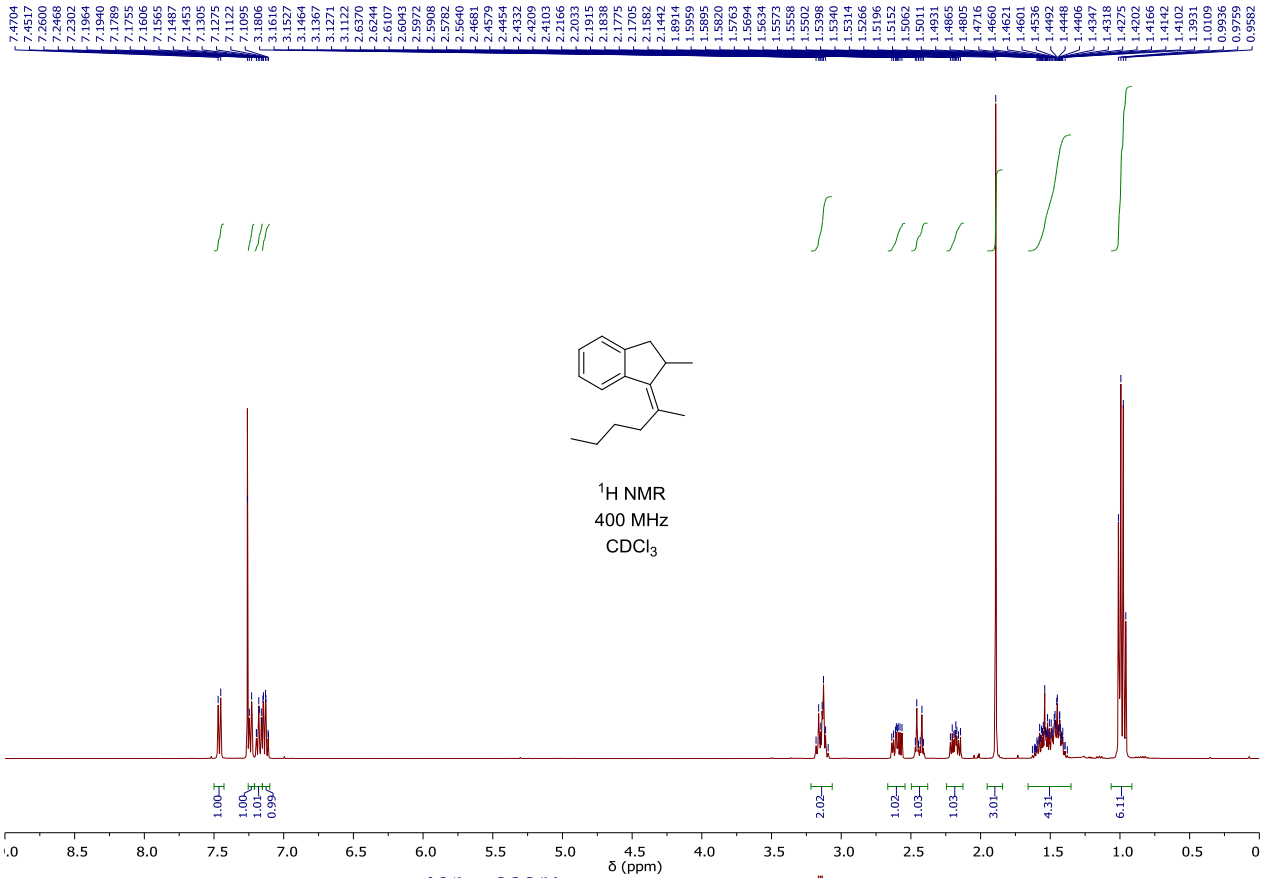

CO2Me
MeO2C
O
O
O
O
13C NMR
100 MHz
CDCl3
δ (ppm)

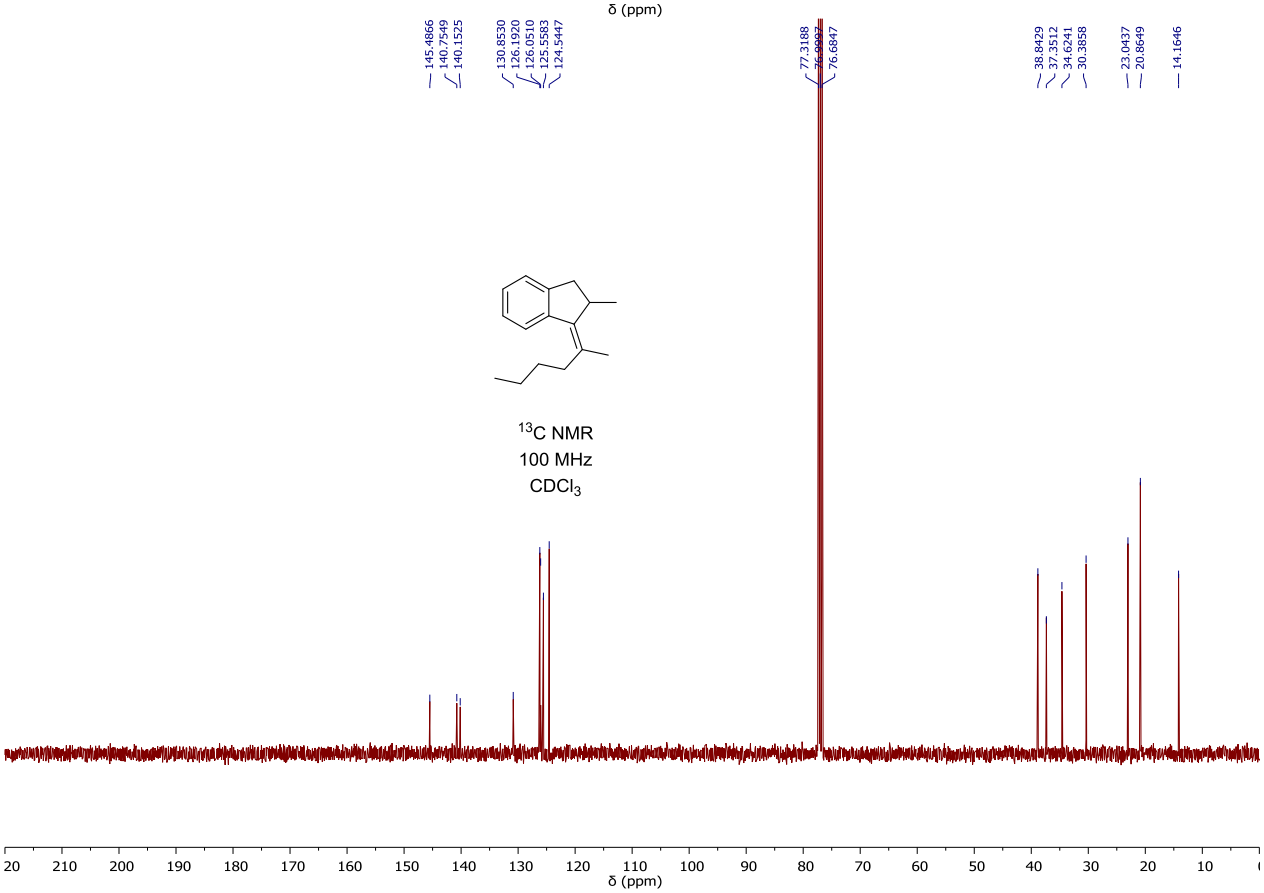

NHMs
CO2Me
1H NMR
400 MHz
CDCl3
δ (ppm)

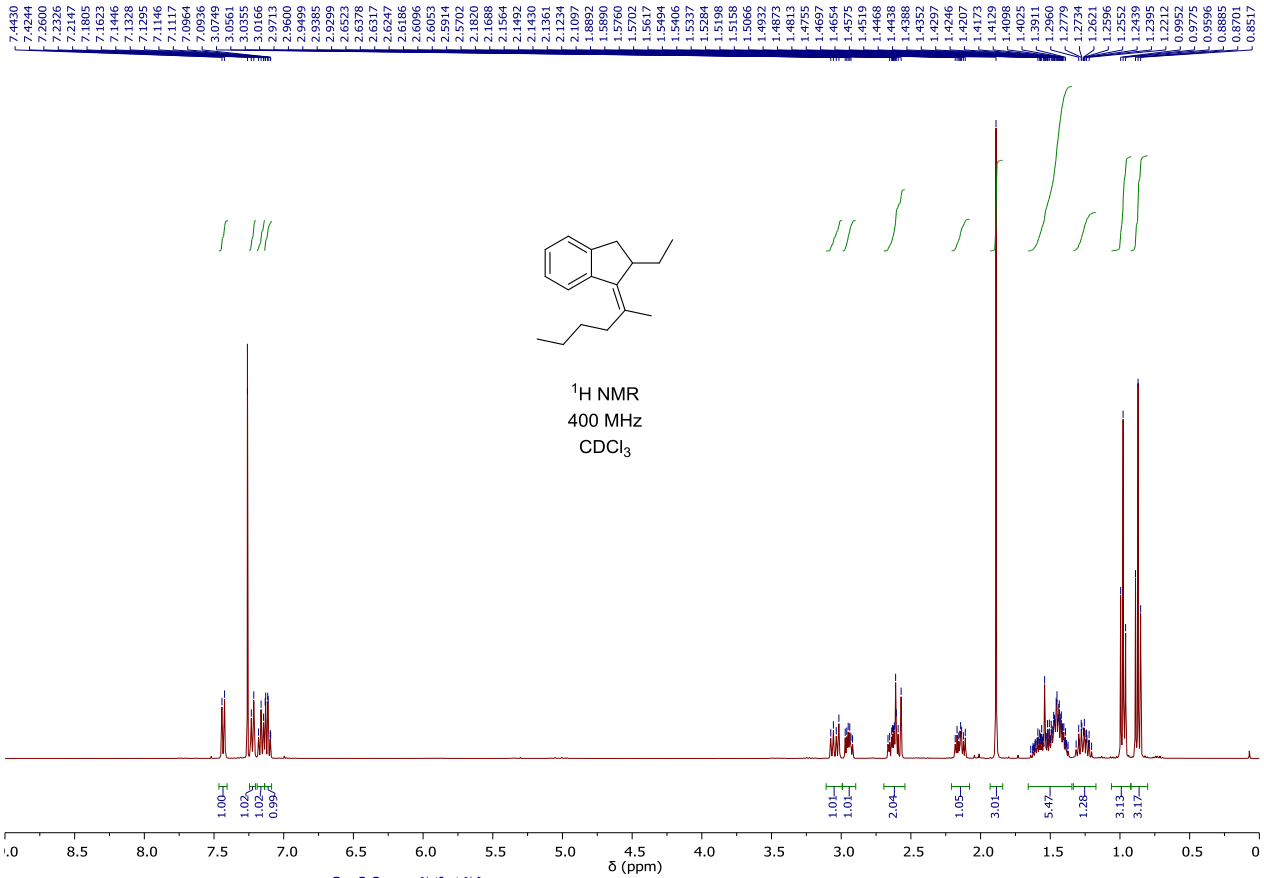

NHMs
CO2Me
13C NMR
100 MHz
CDCl3
δ (ppm)

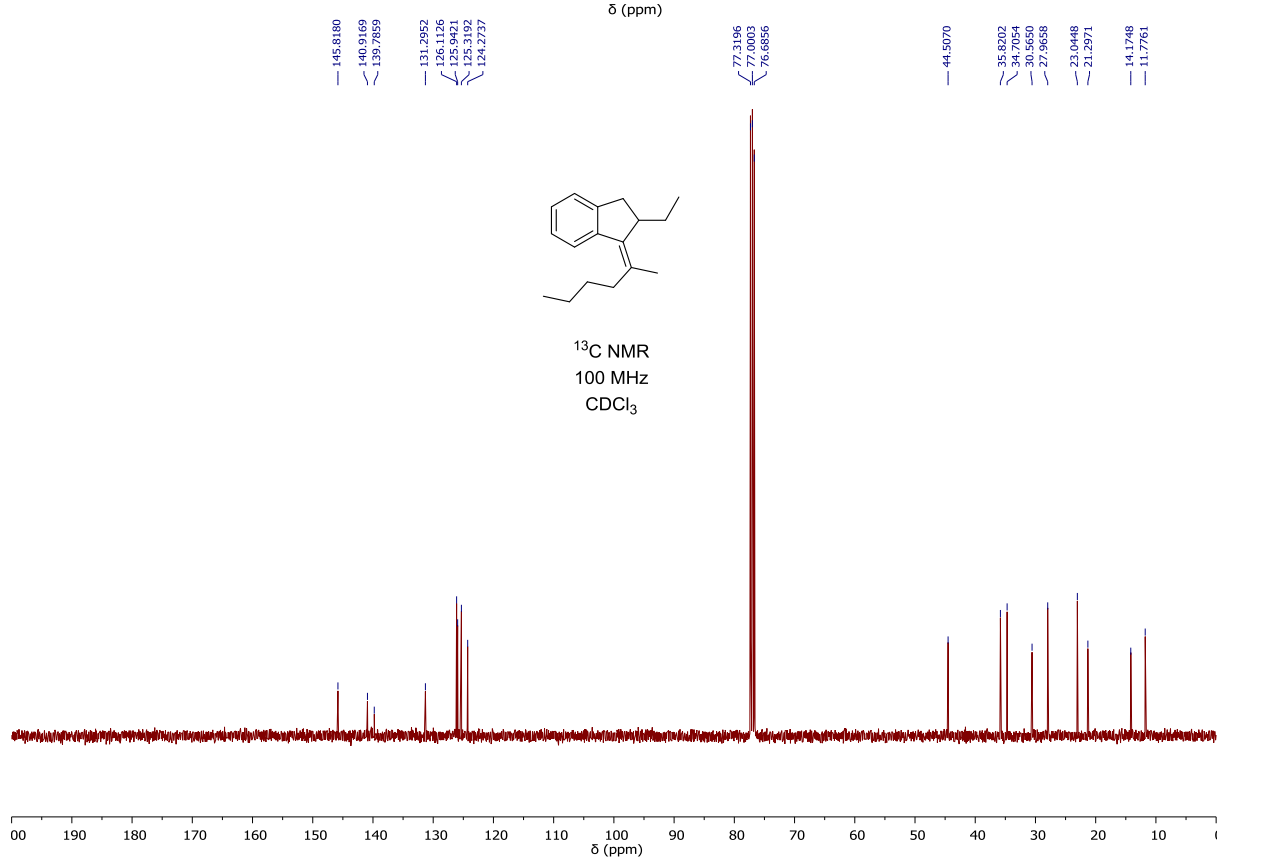

CO2Me
CO2Me
(Z)
CO2Me
CO2Me
(E)
δ (ppm)
CO2Me
CO2Me
1H NMR
500 MHz
CDCl3
δ (ppm)


CO2Me
CO2Me
13C NMR
125 MHz
CDCl3
δ (ppm)


^{1}H NMR
400 MHz
$CDCl_3$
δ (ppm)


^{13}C NMR
100 MHz
$CDCl_3$
δ (ppm)


^{1}H NMR
400 MHz
$CDCl_3$
δ (ppm)


^{13}C NMR
100 MHz
$CDCl_3$
δ (ppm)