Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Metal-free Aerobic C-H Oxidation of Cyclic Enones

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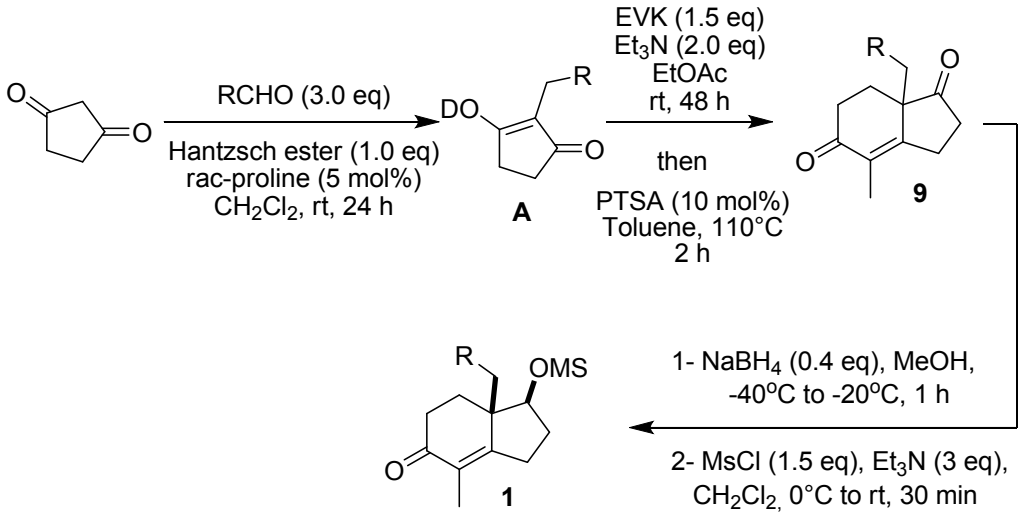
I) Experimental Section

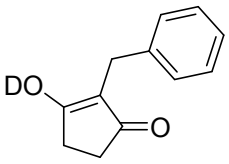
All reactions were carried out under a nitrogen or argon atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. Dry tetrahydrofuran (THF), diethyl ether (Et_2O), methylene chloride (CH_2Cl_2), and toluene were obtained by distillation (from CaH_2 for CH_2Cl_2, sodium/benzophenone for THF, from sodium for toluene and, from sodium benzophenone for Et_2O). Methanol (MeOH), N,N'-dimethylformamide (DMF) and dimethylsulfoxide (DMSO) were purchased in anhydrous form and used without further purification. Ethyl acetate (EtOAc), diethyl ether (Et_2O), methylene chloride (CH_2Cl_2), and cyclohexane were purchased at ACS grade quality and used without further purification, unless otherwise stated. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Yields refer to chromatographically and spectroscopically (^1H NMR and ^{13}C NMR) homogeneous materials, unless otherwise stated. Reactions were monitored by thin-layer chromatography (TLC) carried out on Merck silica gel plates with QF-254 indicator and an ethanolic solution of ammonium molybdate or potassium permanganate and heat as developing agents. Merck silica gel (60, particle size 0.040-0.063 mm) was used for flash column chromatography. NMR spectra were recorded on Bruker Advance DMX -300 or -200 instruments and calibrated using residual undeuterated solvent as an internal reference (7.26 ppm and 77.00 ppm for ^1H and ^{13}C NMR in $CDCl_3$; 7.16 ppm and 128.06 ppm for ^1H and ^{13}C NMR in C_6D_6). The following abbreviations were used to describe the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, pent = pentet, hex = hexet, br = broad. IR spectra were recorded on a PerkinElmer Spectrum 100 FT-IR-spectrometer with only major peaks being reported. High-resolution mass spectra (HRMS) were recorded on an LCT Premier XE benchtop orthogonal acceleration time-of-flight (TOF) mass spectrometer (Waters Micromass).

Synthesis of mesylates 1a-h:



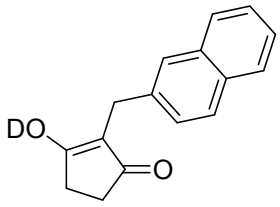
● ***General procedure A for the synthesis of known alkylated cyclopentanediones:***

The alkylated cyclopentanediones were prepared according to a slightly modified procedure from Ramachary:[1] To a stirred solution of cyclopentanedione (1.0 eq), aldehyde (3.0 eq) and Hantzsch ester (1.0 eq) in CH_2Cl_2 (0.3 M) at rt was added proline (5 mol%). The resulting mixture was stirred for 24 h before being concentrated *in vacuo.* The crude reaction mixture was then triturated with a mixture of EtOAc/Et_2O (1/4). The resulting suspension was filtered, washed with Et_2O and dried *in vacuo* to afford the desired pure alkyl cyclopentadione.

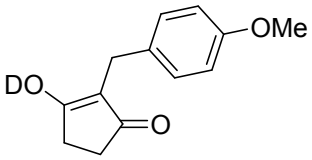


Aa:[1] According to the general procedure **A**, the reaction of 1,3-cyclopentanedione (200 mg, 2.0 mmol), benzaldehyde (620µL, 6.0 mmol), Hantzsch ester (517 mg, 2.0 mmol) and proline (12 mg, 0.1 mmol) in CH_2Cl_2 (6.7 mL) provided **Aa** (310 mg, 81%) as a white powder.

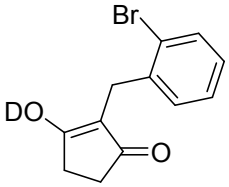
[1] D. B. Ramachary and M. Kishor, *Org. Biomol. Chem.*, 2008, **6**, 4176.



Ab:[1] According to the general procedure **A**, the reaction of 1,3-cyclopentanedione (1.2 g, 12.20 mmol), 2-naphtaldehyde (5.73 g, 36.60 mmol), Hantzsch ester (3.1 g, 12.20 mmol) and proline (70 mg, 0.61 mmol) in CH_2Cl_2 (41 mL) provided **Ab** (2.57 mg, 88%) as a white powder.

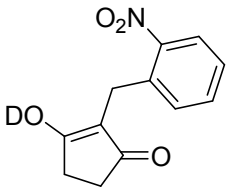


Ac:[2] According to the general procedure **A**, the reaction of 1,3-cyclopentanedione (589 mg, 6.0 mmol), anisaldehyde (2.19 mL, 18.0 mmol), Hantzsch ester (1.520 g, 6.0 mmol) and proline (36 mg, 0.3 mmol) in CH_2Cl_2 (20 mL) provided **Ac** (1.12 g, 85%) as a white powder . **IR** (film) ν_{max} 2909, 1563, 1509, 1433, 1355, 1324, 1260, 1242, 1178, 1030, 815, 665 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$ + 2 drops of MeOD) δ 7.08 (d, *J* = 8.4 Hz, 2H), 6.68 (d, *J* = 8.5 Hz, 2H), 3.66 (s, 3H), 3.32 (s, 2H), 2.38 (s, 4H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 157.5, 132.2, 129.2 (2C), 117.5, 113.4 (2C), 55.0, 30.2 (2C), 25.7.

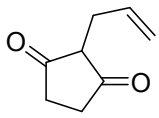


Ad:[2] According to the general procedure **A**, the reaction of 1,3-cyclopentanedione (589 mg, 6.0 mmol), *o*-bromobenzaldehyde (2.10 mL, 18 mmol), Hantzsch ester (1.52 g, 6.0 mmol) and proline (36 mg, 0.3 mmol) in CH_2Cl_2 (20 mL) provided **Ad** (1.24 g, 89%). **IR** (film) ν_{max} 2922, 1568, 1383, 1267, 1035, 744, 659 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$+ 2 drops of MeOD) δ 7.42 (d, *J* = 7.7 Hz, 1H), 7.04-7.17 (m, 1H), 6.83-7.02 (m, 2H), 3.49 (s, 2H), 2.45 (s, 4H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 197.2, 138.2, 132.2, 129.2, 127.3, 127.0, 124.4, 114.9, 30.3 (2C), 27.2.

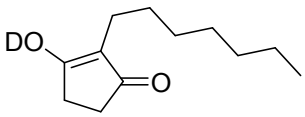
[2] K. Sudheendran, C. C. Malakar, J. Conrad, and U. Beifuss, *J. Org. Chem*., 2012, **77**, 10194.



Ae:[1] According to the general procedure **A**, the reaction of 1,3-cyclopentanedione (589 mg, 6.0 mmol), *o*-nitrobenzaldehyde (2.72 g, 18 mmol), Hantzsch ester (1.52 g, 6.0 mmol) and proline (36 mg, 0.3 mmol) in CH_2Cl_2 (20 mL) provided **Ae** (1.38 g, 77%). **^{1}H NMR** (300 MHz, $CDCl_3$+ 2 drops of MeOD) δ 7.68 (d, *J* = 8.1 Hz, 1H), 7.30 (m, 1H), 7.06-7.19 (m, 2H), 3.63 (s, 2H), 2.36 (s, 4H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 149.1, 134.1, 132.5, 130.7, 126.5, 124.0, 114.4, 30.0 (2C), 23.3.



Af: Triketone **Af** was synthesized according to known procedures.[3,4,5,6]



Ag:[1] According to the general procedure **A**, the reaction of 1,3-cyclopentanedione (980 mg, 10.0 mmol), heptanaldehyde (4.20 mL, 30.0 mmol), Hantzsch ester (2.53 g, 10.0 mmol) and proline (36 mg, 0.5 mmol) in CH_2Cl_2 (33 mL) provided **Ag** (1.37 g, 70%).

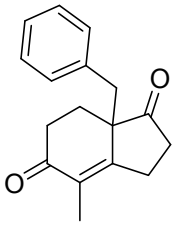
● ***General procedure B for the synthesis of enones:***

To a stirred solution of alkylated cyclopentanedione (1.0 eq) and Et_3N (2.0 eq) in EtOAc (0.2 M) at rt was added EVK (1.5 eq). The resulting mixture was stirred for 2 days

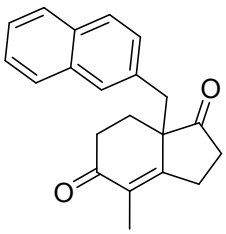
[3] P. K. Ruprah, J.-P. Cros, J. E. Pease, W. G. Whittingham and J. M. Williams, *Eur. J. Org. Chem.* 2002, 3145.
[4] E. Lacoste, E. Vaique, M. Berlande, I. Pianet, J. M. Vincent and Y. Landais, *Eur. J. Org. Chem.* 2007, 167.
[5] X.-M. Zhang, M. Wang, Y.-Q. Tu, C.-A. Fan, Y.-J. Jiang, S.-Y. Zhang and F.-M. Zhang, *Synlett* 2008, 2831.
[6] J. Xu, L. Trzoss, W. K. Chang and E. A. Theodorakis, *Angew. Chem. Int. Ed*. 2011, **50**, 3672.

before being concentrated *in vacuo*. When required, flash column chromatography of the crude was performed to afford the triketone. Otherwise, the next step was directly carried out.

To a stirred solution of triketone (1 eq) in toluene (0.1 M) at rt was added PTSA (10% mol). The resulting mixture was refluxed for 2 h before being cooled to rt and quenched with $NaHCO_3$ (sat. aq.). The resulting mixture was diluted with EtOAc, the layers were separated and the aqueous layer was back extracted with EtOAc. The combined organic layers were washed with brine, dried (Na_2SO_4) and concentrated *in vacuo*. Flash column chromatography (silica gel) of the crude afforded enones **9a-i**.

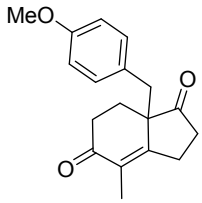


9a: According to the general procedure **B**, the reaction of alkylated cyclopentanedione **Aa** (305 mg, 1.62 mmol), triethylamine (0.45 mL, 3.24 mmol), EVK (0.32 mL, 3.24 mmol) in EtOAc (8.1 mL) gave triketone **Ba** (9.12 g, 93%) as a colorless oil (silica gel - cyclohexane: EtOAc, 75:25). $\mathbf{R_f}$ = 0.35 (silica gel, cyclohexane: EtOAc, 75:25). The reaction of the corresponding triketone (364 mg, 1.34 mmol), PTSA (26 mg, 0.13 mmol) in toluene (13.4 mL) provided enone **9a** (300 mg, 88%) as colorless oil (silica gel - cyclohexane: EtOAc, 65:35). $\mathbf{R_f}$ = 0.45 (silica gel, cyclohexane: EtOAc, 65:35); **IR** (film) ν 2926, 1730, 1664, 1450, 1311, 1114, 748, 705, cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.22-7.31 (m, 3H), 6.98-7.08 (m, 2H), 3.05 (d, *J* = 13.0 Hz, 1H), 2.98 (d, *J* = 13.0 Hz, 1H), 2.41-2.75 (m, 3H), 2.13-2.40 (m, 3H), 1.97 (ddt, *J* = 17.7, 9.9, 1.6 Hz, 1H), 1.82 (ddd~dt, *J* = 13.7, 6.1 Hz, 1H), 1.81 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 218.4, 197.6, 162.0, 135.7, 131.0, 129.5 (2C), 128.5 (2C), 127.3, 54.2, 42.8, 36.6, 32.6, 28.4, 25.6, 10.9; **HRMS** (EI): calcd for $C_{17}H_{18}O_2^+$ [M^+]: 254.1307, found 254.1324.

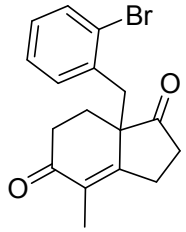


9b: According to the general procedure **B**, the reaction of alkylated cyclopentanedione **Ab** (2.57 g, 10.8 mmol), triethylamine (3.0 mL, 21.6 mmol), EVK (2.15 mL, 21.6 mmol) in EtOAc (54 mL) provided triketone **Bb** (2.85 g, 82%) as colorless oil (silica gel - cyclohexane: EtOAc, 75:25). $\mathbf{R_f}$ = 0.40 (silica gel, cyclohexane: EtOAc, 75:25). The reaction of the corresponding triketone (2.85 g, 8.8 mmol), PTSA (170 mg, 0.88 mmol) in toluene (88 mL) provided enone **9b** (2.59 g, 96%) as colorless oil (silica gel - cyclohexane: EtOAc, 80:20). $\mathbf{R_f}$ = 0.40 (silica gel, cyclohexane: EtOAc, 75:25); **IR** (film) ν 2926, 2857, 1735, 1644, 1501, 1350, 1138, 962, 825, 752, 480 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.63-7.84 (m, 3H), 7.33-7.55 (m, 3H), 7.12 (d, *J* = 8.4 Hz, 1H), 3.20 (d, *J* = 12.9 Hz, 1H), 3.11 (d, *J* = 12.9 Hz, 1H), 2.42-2.76 (m, 3H), 2.07-2.29 (m, 3H), 1.71 – 1.93 (m, 2H), 1.81 (s, 3H); **^{13}C NMR** (75 MHz,

$CDCl_3$) δ 218.5, 197.5, 162.1, 133.3, 133.1, 132.3, 131.0, 128.2, 128.0, 127.5 (2C), 126.3, 125.9, 54.3, 42.9, 36.6, 32.6, 28.6, 26.8, 25.7, 10.8; **HRMS** (EI): calcd for $C_{21}H_{20}O_2^+$ [M^+]: 304.1463, found 304.1456.

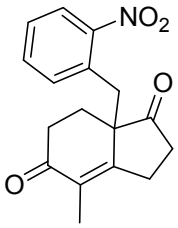


9c: According to the general procedure **B**, the reaction of alkylated cyclopentanedione **Ac** (1.12 g, 5.1 mmol), triethylamine (1.43 mL, 10.2 mmol), EVK (0.76 mL, 7.7 mmol) in EtOAc (25.5 mL) provided triketone **Bc** (1.53 g, 99%) as colorless oil (silica gel chromatography - cyclohexane: EtOAc, 75:25). $\mathbf{R_f}$ = 0.30 (silica gel, cyclohexane: EtOAc, 75:25). The reaction of the corresponding triketone (261 g, 0.86 mmol), PTSA (17 mg, 0.09 mmol) in toluene (8.6 mL) provided enone **9c** (244 mg, 99%) as colorless oil (silica gel - cyclohexane: EtOAc, 75:25). $\mathbf{R_f}$ = 0.3 (silica gel, cyclohexane: EtOAc, 75:25); **IR** (film) ν 2926, 2845, 1730, 1659, 1607, 1513, 1446, 1300, 1251, 1110, 1031, 964, 835, 746, 492 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.85 (d, *J* = 8.6 Hz, 2H), 6.69 (d, *J* = 8.6 Hz, 2H), 3.67 (s, 3H), 2.90 (d, *J* = 13.2 Hz, 1H), 2.82 (d, *J* = 13.2 Hz, 1H), 2.42 – 2.67 (m, 2H), 2.34 (dd, *J* = 18.4, 4.6 Hz, 1H), 2.12 – 2.22 (m, 2H), 1.87 – 2.11 (m, 2H), 1.71 (s, 3H), 1.68 (ddd~dt, *J* = 13.8, 6.0 Hz, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 218.2, 197.3, 162.1, 158.5, 130.5, 130.3, 127.3, 113.5, 54.9, 54.0, 41.7, 36.3, 32.3, 27.9, 25.3, 10.6; **HRMS** (ESI): calcd for $C_{18}H_{21}O_3$ $[M+H]^+$: 285.1491, found 285.1476.

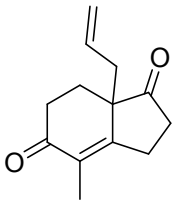


9d: According to the general procedure **B**, the reaction of alkylated cyclopentanedione **Ad** (405 mg, 1.52 mmol), triethylamine (0.42 mL, 3.04 mmol), EVK (0.23 mL, 2.28 mmol) in EtOAc (7.6 mL) provided triketone **Bd** (348 mg, 65%) as colorless oil (silica gel - cyclohexane: EtOAc, 75:25). $\mathbf{R_f}$ = 0.35 (silica gel, cyclohexane: EtOAc, 75:25). The reaction of the corresponding triketone (980 mg, 2.80 mmol), PTSA (54 mg, 0.28 mmol) in toluene (28 mL) provided enone **9d** (926 mg, 99%) as colorless oil (silica gel - cyclohexane: EtOAc, 75:25). $\mathbf{R_f}$ = 0.3 (silica gel, cyclohexane: EtOAc, 75:25); **IR** (film) ν 2921, 2848, 1738, 1662, 1653, 1439, 1348, 1115, 1024, 753, 573, 448 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.9 Hz, 1H), 7.15 (t, *J* = 6.8 Hz, 1H), 6.97 – 7.08 (m, 2H), 3.45 (d, *J* = 13.3 Hz, 1H), 2.92 (d, *J* = 13.3 Hz, 1H), 2.51 – 2.73 (m, 2H), 2.39 (ddd, *J* = 18.4, 5.6, 1.5 Hz, 1H), 2.11 – 2.31

(m, 3H), 1.85 – 2.03 (m, 1H), 1.72 (ddd~dt, J = 13.9, 5.7 Hz, 1H), 1.70 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 218.0, 197.2, 160.3, 135.5, 133.0, 131.7, 131.4, 128.8, 127.3, 125.2, 53.6, 40.4, 36.8, 32.5, 28.5, 25.5, 10.8; **MS** (EI): 332 and 334; **HRMS** (EI): calcd for $C_{17}H_{17}O_2Br^+$ [M^+]: 332.0412, found 332.0407.

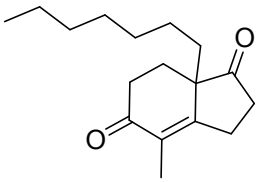


9e: According to the general procedure **B**, the reaction of alkylated cyclopentanedione **Ae** (1.24 g, 5.33 mmol), triethylamine (1.49 mL, 10.70 mmol), EVK (0.80 mL, 8.00 mmol) in EtOAc (26.7 mL) provided triketone **Be** (1.45 g, 66%) as colorless oil (Silica gel chromatography - cyclohexane: EtOAc, 65:35). $\mathbf{R_f}$ = 0.65 (silica gel, cyclohexane: EtOAc, 5:5). The reaction of the corresponding triketone (1.45 g, 4.60 mmol), PTSA (88 mg, 0.46 mmol) in toluene (46 mL) provided enone **9e** (1.11 g, 76%) as a colorless oil (silica gel - cyclohexane: EtOAc / 75:25). $\mathbf{R_f}$ = 0.55 (silica gel, cyclohexane: EtOAc, 5:5); **IR** (film) ν 2926, 2865, 1737, 1660, 1522, 1446, 1358, 1288, 1132, 1110, 959, 852, 786, 715, 495 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.99 (dd, J = 8.0, 1.5 Hz, 1H), 7.63 (td, J = 7.4, 1.5 Hz, 1H), 7.51 (td, J = 8.0, 1.5 Hz, 1H), 7.34 (dd, J = 7.4, 1.5 Hz, 1H), 3.93 (d, J = 13.5 Hz, 1H), 3.18 (d, J = 13.5 Hz, 1H), 2.78 – 3.01 (m, 1H), 2.26 – 2.73 (m, 5H), 2.18 (ddd, J = 13.9, 4.8, 2.3 Hz, 1H), 1.84 (s, J = 1.0 Hz, 3H), 1.68 – 1.89 (ddd~dt, J = 13.7, 6.8 Hz, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 217.2, 196.8, 160.2, 149.3, 133.2, 133.0, 131.9, 130.8, 128.6, 125.4, 52.9, 36.6 (2C), 32.3, 27.3, 25.3, 11.0; **HRMS** (EI): calcd for $C_{17}H_{17}NO_4^+$ [M^+]: 299.1158, found 299.1162.

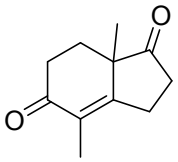


9f: To a stirred solution of 2-allylcyclopentane-1,3-dione (853mg, 6.2 mmol) and EVK (1.23 mL, 12.4 mmol) in H_2O (12.4 mL) at rt was added AcOH (180 µL, 3.1 mmol). The resulting mixture was refluxed for 4 h before being cooled down to rt and extracted with EtOAc (3 x 25

mL). The combined organic layers were then washed with $NaHCO_3$ (2 x 20 mL, sat. aq.), dried (Na_2SO_4) and concentrated *in vacuo*. Purification (silica gel, cyclohexane:EtOAc from 90:10 to 70:30) afforded triketone **Bf** (1.03 g, 75%) as colorless oil. $\mathbf{R_f}$ = 0.20 (silica gel, cyclohexane: EtOAc, 8:2). The reaction of the corresponding triketone (810 mg, 3.6 mmol), PTSA (69 mg, 0.36 mmol) in toluene (36 mL) provided enone **9f** (661 mg, 90%) as a colorless oil (silica gel - cyclohexane: EtOAc / 75:25). $\mathbf{R_f}$ = 0.25 (silica gel, cyclohexane: EtOAc, 8:2); **IR** (film) ν 2949, 2921, 2870, 1739, 1649, 1436, 1354, 1316, 1160, 1113, 968, 921, 577, 491 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 5.55 – 5.75 (m, 1H), 4.97 – 5.14 (m, 2H), 2.25 – 2.93 (m, 8H), 2.12 (ddd, *J* = 13.6, 5.4, 1.8 Hz, 1H), 1.72 (s, 3H), 1.69 (ddd~dt, *J* = 13.9, 5.8 Hz, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 216.4, 197.6, 161.7, 131.9, 130.3, 119.2, 52.5, 39.2, 35.6, 32.1, 26.4, 24.7, 10.6; **HRMS** (EI): calcd for $C_{13}H_{16}O_2^+$ [M^+]: 204.1150, found 204.1142.



9g: According to the general procedure **B**, the reaction of alkylated cyclopentanedione **Ag** (209 mg, 1.06 mmol), triethylamine (0.30 mL, 2.12 mmol), EVK (0.16 mL, 1.59 mmol) in EtOAc (5.3 mL) provided triketone **Bg** (260 mg, 88%) as a colorless oil (silica gel – cyclohexane: EtOAc / 65:35). $\mathbf{R_f}$ = 0.40 (silica gel, cyclohexane: EtOAc, 75:25). The reaction of the corresponding triketone (260 mg, 0.93 mmol), PTSA (18 mg, 0.09 mmol) in toluene (9.3 mL) provided enone **9g** (224 mg, 92%) as a colorless oil (silica gel - cyclohexane: EtOAc / 75:25). $\mathbf{R_f}$ = 0.40 (silica gel, cyclohexane: EtOAc, 75:25); **IR** (film) ν 2926, 2855, 1740, 1663, 1651, 1457, 1377, 1356, 1154, 1114, 959, 573, 495 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 2.44 – 2.87 (m, 3H), 2.14 – 2.41 (m, 3H), 1.97 – 2.13 (m, 1H), 1.62 (s, 3H), 1.40 – 1.68 (m, 3H), 1.10 (s, 10H), 0.71 (t, *J* = 6.3 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 218.0, 197.2, 160.3, 135.5, 133.0, 131.7, 131.4, 128.8, 127.3, 125.2, 53.6, 40.4, 36.8, 32.5, 28.5, 25.5, 10.8; **HRMS** (EI): calcd for $C_{17}H_{26}O_2^+$ [M^+]: 262.1933, found 262.1939.

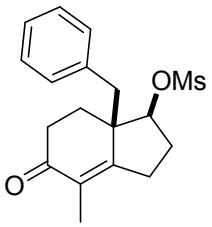


9h:[7] According to the general procedure **C**, the reaction of the corresponding triketone (9.09 g, 46.4 mmol), PTSA (890 mg, 4.6 mmol) in toluene (460 mL) provided diketone **9h** (8.26 g, 97%) as colorless oil (silica gel chromatography - cyclohexane: EtOAc, 60:40).

● ***General procedure for the synthesis of mesylates 1a-i:***

To a stirred solution of diketone **9a-i** (1 eq) in MeOH (0.1M) at -40^{o}C was added $NaBH_4$ (0.5 eq). The resulting mixture was stirred for 1 h to -20 ^{o}C and subsequently concentrated *in vacuo*. The crude was diluted with CH_2Cl_2 and treated with HCl (1N, aq. sol.). The layers were separated and aqueous layer was re-extracted with CH_2Cl_2. The combined organic layers were then washed with brine, dried (Na_2SO_4) and concentrated *in vacuo* leading to the corresponding alcohol as colorless oil which was used directly without further purification.

To a stirred solution of the crude alcohol and Et_3N (3 eq) in CH_2Cl_2 (0.1 M) at rt was added methanesulfonyl chloride (1.5 eq). The resulting mixture was stirred for 30 min before it was quenched with $NaHCO_3$ (sat. aq.). The layers were separated and the aqueous layer was re-extracted with CH_2Cl_2. The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. Flash column chromatography (silica gel) of the crude afforded mesylate **1a-i**.

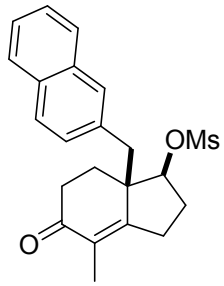


1a: According to the general procedure, the reaction of diketone **9a** (294 mg, 1.16 mmol), $NaBH_4$ (22 mg, 0.56 mmol) in MeOH (11.6 mL) provided the crude alcohol.

The reaction of the crude alcohol, Et_3N (0.49 mL, 3.48 mmol) and MsCl (0.14 mL, 1.74 mmol) in CH_2Cl_2 (11.6 mL) provided mesylate **1a** (360 mg, 93% over two steps) as a slightly yellow amorphous powder (silica gel – CH_2Cl_2: EtOAc, 95:5). $\mathbf{R_f}$ = 0.35 (silica gel,

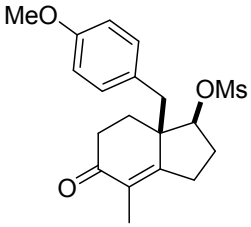
[7] S. G. Davies, A. J. Russell, R. L. Sheppard, A. D. Smith and J. E. Thomson, *Org. Biomol. Chem.* 2007, **5**, 3190

cyclohexane: EtOAc, 7:3); **IR** (film) ν 2927, 1653, 1331, 1173, 940, 843, 703 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.97 – 7.22 (m, 5H), 4.60 (dd, *J* = 10.4, 8.2 Hz, 1H), 2.96 (s, 3H), 2.94 (d, *J* = 13.7 Hz, 1H), 2.83 (d, *J* = 13.7 Hz, 1H), 2.02 – 2.50 (m, 6H), 1.74 – 1.98 (m, 2H), 1.64 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 196.9, 160.5, 137.1, 131.5, 130.0 (2C), 127.8 (2C), 126.5, 88.1, 48.7, 37.9, 37.5, 32.7, 32.4, 27.2, 26.1, 10.6; **HRMS** (EI): calcd for $C_{18}H_{22}O_4S^+$ [M^+]: 334.1239, found 334.1226.



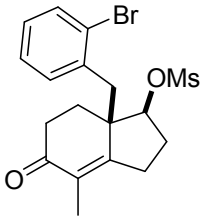
1b: According to the general procedure, the reaction of diketone **9b** (2.5 g, 8.21 mmol), $NaBH_4$ (156 mg, 4.11 mmol) in MeOH (82 mL) provided the crude alcohol.

The reaction of the crude alcohol, Et_3N (3.45 mL, 24.63 mmol) and MsCl (1.0 mL, 12.32 mmol) in CH_2Cl_2 (82 mL) provided mesylate **1b** (3.0 g, 95% over two steps) as a slightly yellow amorphous powder (silica gel– CH_2Cl_2: EtOAc, 95:5). $\mathbf{R_f}$ = 0.35 (silica gel, cyclohexane: EtOAc, 65:35); **IR** (film) ν 2928, 1656, 1351, 1331, 1174, 941, 846, 754, 734 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.64 – 7.80 (m, 3H), 7.56 (s, 1H), 7.35 – 7.47 (m, 2H), 7.21 (d, *J* = 8.4 Hz, 1H), 4.66 (dd, *J* = 13.7, 10.1 Hz, 1H), 3.15 (d, *J* = 13.7 Hz, 1H), 3.06 (d, *J* = 13.7 Hz, 1H), 3.00 (s, 3H), 2.03 – 2.44 (m, 6H), 1.89 (ddd~dt, *J* = 12.9, 6.9 Hz, 1H), 1.72 (s, 3H), 1.63 – 1.79 (m, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 197.3, 161.1, 135.2, 133.2, 132.2, 132.0, 129.1, 128.6, 127.7, 127.6, 127.5, 126.3, 125.8, 88.5, 49.3, 38.4, 38.0, 33.3, 32.9, 27.8, 26.6, 11.0; **HRMS** (ESI): calcd for $C_{22}H_{25}O_4S^+$ [M + H^+]: 385.1474, found 385.1480.



1c: According to the general procedure, the reaction of diketone **9c** (240 mg, 0.84 mmol), $NaBH_4$ (16 mg, 0.42 mmol) in MeOH (8.4 mL) provided the crude alcohol.

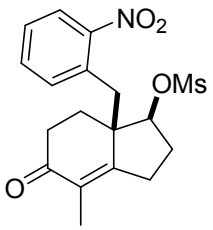
The reaction of the crude alcohol, Et_3N (0.35 mL, 2.52 mmol) and MsCl (98 μL, 1.26 mmol) in CH_2Cl_2 (8 mL) provided mesylate **1c** (269 mg, 88% over two steps) as a light yellow amorphous powder (silica gel – CH_2Cl_2: EtOAc, 9:1). $\mathbf{R_f}$ = 0.3 (silica gel, cyclohexane: EtOAc, 65:35); **IR** (film) ν_{max} 2921, 2854, 1652, 1512, 1330, 1245, 1172, 1018, 941, 833, 525 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.96 (d, *J* = 8.6 Hz, 2H), 6.70 (d, *J* = 8.7 Hz, 2H), 4.61 (dd, *J* = 10.4, 8.3 Hz, 1H), 3.69 (s, 3H), 3.00 (s, 3H), 2.91 (d, *J* = 13.8 Hz, 1H), 2.81 (d, *J* = 13.8 Hz, 1H), 1.98 – 2.39 (m, 6H), 1.84 (ddd~dt, *J* = 13.0, 6.4 Hz, 1H), 1.68 – 1.80 (m, 1H), 1.66 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 197.1, 160.9, 158.3, 131.6, 131.0 (2C), 129.0, 113.3 (2C), 88.3, 54.9, 48.8, 38.1, 36.8, 32.9, 32.5, 27.4, 26.3, 10.7; **HRMS** (ESI): calcd for $C_{19}H_{24}O_5S^+$ [M + H^+]: 365.1423, found 365.1421.



1d: According to the general procedure, the reaction of diketone **9d** (278 mg, 0.83 mmol), $NaBH_4$ (16 mg, 0.42 mmol) in MeOH (8.3 mL) provided the crude alcohol.

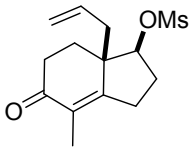
The reaction of the crude alcohol, Et_3N (0.35 mL, 2.52 mmol) and MsCl (98 μL, 1.26 mmol) in CH_2Cl_2 (8.3 mL) provided mesylate **1d** (310 mg, 90% over two steps) as a white amorphous powder (silica gel – CH_2Cl_2: EtOAc, 95:5). $\mathbf{R_f}$ = 0.3 (silica gel, cyclohexane: EtOAc, 65:35); **IR** (film) ν 2925, 2855, 1694, 1674, 1638, 1451, 1178, 1099, 1072, 824 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.7 Hz, 1H), 6.90 – 7.16 (m, 3H), 4.62 (dd, *J* = 10.3, 8.0 Hz, 1H), 3.37 (d, *J* = 13.9 Hz, 1H), 3.02 (s, 3H), 2.83 (d, *J* = 13.9 Hz, 1H), 1.97 – 2.58 (m, 6H), 1.65 – 1.88 (m, 2H), 1.62 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 196.8, 158.8, 136.8, 133.0, 132.6, 132.3, 128.4, 126.8, 125.4, 88.1, 48.9, 38.2, 35.9, 32.4, 32.1, 27.1, 25.9,

10.8; **HRMS** (ESI): calcd for $C_{18}H_{22}O_4SBr^+$ [M + H^+]: 413.0422 and 415.0402, found 413.0418 and 415.0412.



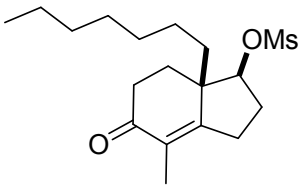
1e: According to the general procedure, the reaction of diketone **9e** (1.11 g, 3.7 mmol), $NaBH_4$ (70 mg, 1.85 mmol) in MeOH (37 mL) provided the crude alcohol.

The reaction of the crude alcohol, Et_3N (1.50 mL, 11.1 mmol) and MsCl (433 µL, 5.6 mmol) in CH_2Cl_2 (37 mL) provided mesylate **1e** (1.25 g, 90% over two steps) as a light yellow amorphous powder (silica gel – CH_2Cl_2: EtOAc / 95:5). $\mathbf{R_f}$ = 0.3 (silica gel, cyclohexane: EtOAc, 6:4); **IR** (film) ν 3375, 2936, 1659, 1531, 1350, 1176, 940, 846, 739 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.48 (td, *J* = 7.4, 1.0 Hz, 1H), 7.38 (m, 2H), 4.68 (dd, *J* = 10.7, 8.0 Hz, 1H), 3.55 (d, *J* = 14.0 Hz, 1H), 3.39 (d, *J* = 14.0 Hz, 1H), 3.10 (s, 3H), 2.40 (m, 3H), 2.20 – 2.29 (m, 1H), 2.16 (dd, *J* = 18.2, 5.6 Hz, 1H), 1.89 (m, 2H), 1.71 (dd, *J* = 18.6, 6.0 Hz, 1H), 1.64 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 196.6, 158.9, 150.6, 133.8, 133.4, 132.5, 131.9, 128.4, 125.1, 87.6, 48.9, 38.4, 33.2, 32.6, 32.5, 27.3, 26.1, 11.1; **HRMS** (ESI): calcd for $C_{18}H_{22}NO_6S^+$ [M + H^+]: 380.1168, found 380.1167.



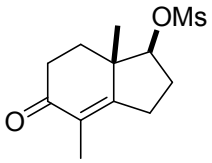
1f: According to the general procedure, the reaction of diketone **9f** (408 mg, 2.0 mmol), $NaBH_4$ (38 mg, 1.0 mmol) in MeOH (20 mL) provided the crude alcohol.

The reaction of the crude alcohol, Et_3N (0.84 mL, 6.0 mmol) and MsCl (232 µL, 3.0 mmol) in CH_2Cl_2 (20 mL) provided mesylate **1f** (448 mg, 79% over two steps) as a white amorphous powder (silica gel – CH_2Cl_2: EtOAc / 9:1). $\mathbf{R_f}$ = 0.4 (silica gel, cyclohexane: EtOAc, 6:4); **IR** (film) ν 2933, 1655, 1352, 1331, 1174, 1015, 964, 928, 844, 757 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 5.71 – 5.91 (m, 1H), 4.93 – 5.11 (m, 2H), 4.60 (dd, *J* = 10.1, 7.9 Hz, 1H), 2.99 (s, 3H), 2.37 – 2.64 (m, 4H), 1.99 – 2.37 (m, 5H), 1.78 (ddd~dt, *J* = 13.6, 5.7 Hz, 1H), 1.62 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 197.5, 161.8, 134.4, 130.5, 117.9, 87.9, 47.4, 38.1, 36.7, 32.5, 32.1, 27.4, 25.8, 10.6; **HRMS** (ESI): calcd for $C_{14}H_{21}O_4S^+$ [M + H^+]: 285.1161, found 285.1160.



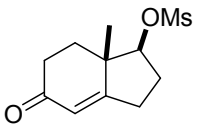
1g: According to the general procedure, the reaction of diketone **9g** (224 mg, 0.85 mmol), $NaBH_4$ (16 mg, 0.43 mmol) in MeOH (8.5 mL) provided an intermediate crude alcohol.

The reaction of the crude alcohol, Et_3N (0.47 mL, 3.4 mmol) and MsCl (100 μL, 1.28 mmol) in CH_2Cl_2 (8.5 mL) provided mesylate **1g** (266 mg, 91% over two steps) as a white amorphous powder (silica gel – CH_2Cl_2: EtOAc / 95:05). $\mathbf{R_f}$ = 0.3 (silica gel, cyclohexane: EtOAc, 8:2); **IR** (film) ν 2925, 2856, 1658, 1354, 1331, 1175, 1010, 968, 931, 845, 734 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 4.57 (dd, *J* = 10.1, 7.8 Hz, 1H), 2.97 (s, 3H), 2.19 – 2.64 (m, 6H), 2.10 (m, 1H), 1.73 (ddd~dt, *J* = 13.1, 5.7 Hz, 1H), 1.59 (s, 3H), 1.35 – 1.51 (m, 2H), 1.17 (s, 10H), 0.78 (t, *J* = 6.6 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 197.6, 163.1, 129.8, 88.1, 46.9, 38.0, 32.9, 32.3, 31.8, 31.5, 30.3, 28.8, 27.6, 25.9, 25.8, 22.3, 13.8, 10.6; **HRMS** (ESI): calcd for $C_{18}H_{31}O_4S^+$ [M + H^+]: 343.1943, found 343.1944.



1h: According to the general procedure, the reaction of diketone **9h** (8.03 g, 45.1 mmol), $NaBH_4$ (853 mg, 22.6 mmol) in MeOH (450 mL) provided the crude alcohol.

The reaction of the crude alcohol, Et_3N (18.9 mL, 135.3 mmol) and MsCl (5.24 mL, 67.7 mmol) in CH_2Cl_2 (450 mL) provided mesylate **1h** (9.15 g, 79% over two steps) as a white amorphous powder (silica gel – CH_2Cl_2: EtOAc / 90:10). $\mathbf{R_f}$ = 0.40 (silica gel, cyclohexane: EtOAc, 6:4); **IR** (film) ν 2933, 1651, 1331, 1173, 966, 890, 862 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 4.62 (dd, *J* = 10.3, 7.5 Hz, 1H), 3.05 (s, 3H), 2.27 – 2.75 (m, 5H), 2.07 – 2.23 (m, 2H), 1.87 (ddd~dt, *J* = 13.5, 5.7 Hz, 1H), 1.66 (s, 3H), 1.19 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 197.6, 163.0, 129.9, 87.2, 44.5, 38.3, 33.5, 32.8, 27.2, 25.3, 16.4, 10.7; **HRMS** (ESI): calcd for $C_{12}H_{19}O_4S^+$ [M + H^+]: 259.1004, found 259.1014.



1i: According to the general procedure, the reaction of diketone **9i** (300 mg, 1.827 mmol), $NaBH_4$ (34.6 mg, 0.913 mmol) in MeOH (18 mL) provided the crude alcohol.

The reaction of the crude alcohol, Et_3N (0.76 mL, 5.48 mmol) and MsCl (0.212 mL, 2.741 mmol) in CH_2Cl_2 (18 mL) provided mesylate **1i** (355 mg, 80% over two steps) as a white amorphous powder (silica gel – CH_2Cl_2: EtOAc / 90:10). $\mathbf{R_f}$ = 0.40 (silica gel, cyclohexane: EtOAc, 6:4); **IR** (film) ν 2934, 1643, 1334, 1169, 1039, 962, 778, 523 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 5.67 (s, 1H), 4.52 (dd, *J* = 10.1, 7.8 Hz, 1H), 2.95 (s, 3H), 2.68 (ddt, *J* = 19.5, 12.0, 2.5 Hz, 1H), 2.15 – 2.43 (m, 4H), 1.95 – 2.10 (m, 2H), 1.77 (ddd~dt, *J* = 13.5, 5.5 Hz, 1H), 1.10 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 197.6, 170.4, 123.6, 86.6, 44.4, 37.9, 33.3, 32.5, 26.5, 25.8, 15.9; **MS** (SCI): 244 $[M]^+$

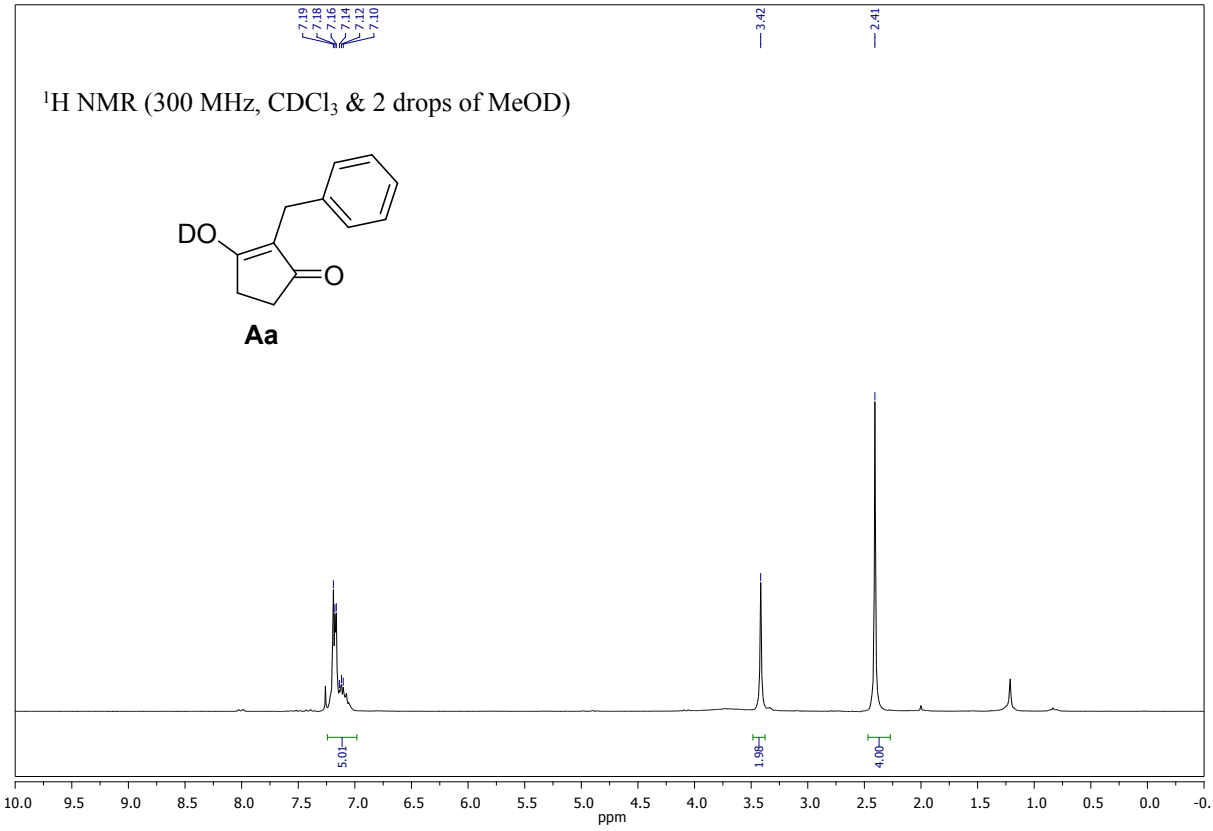
II) Abbreviations

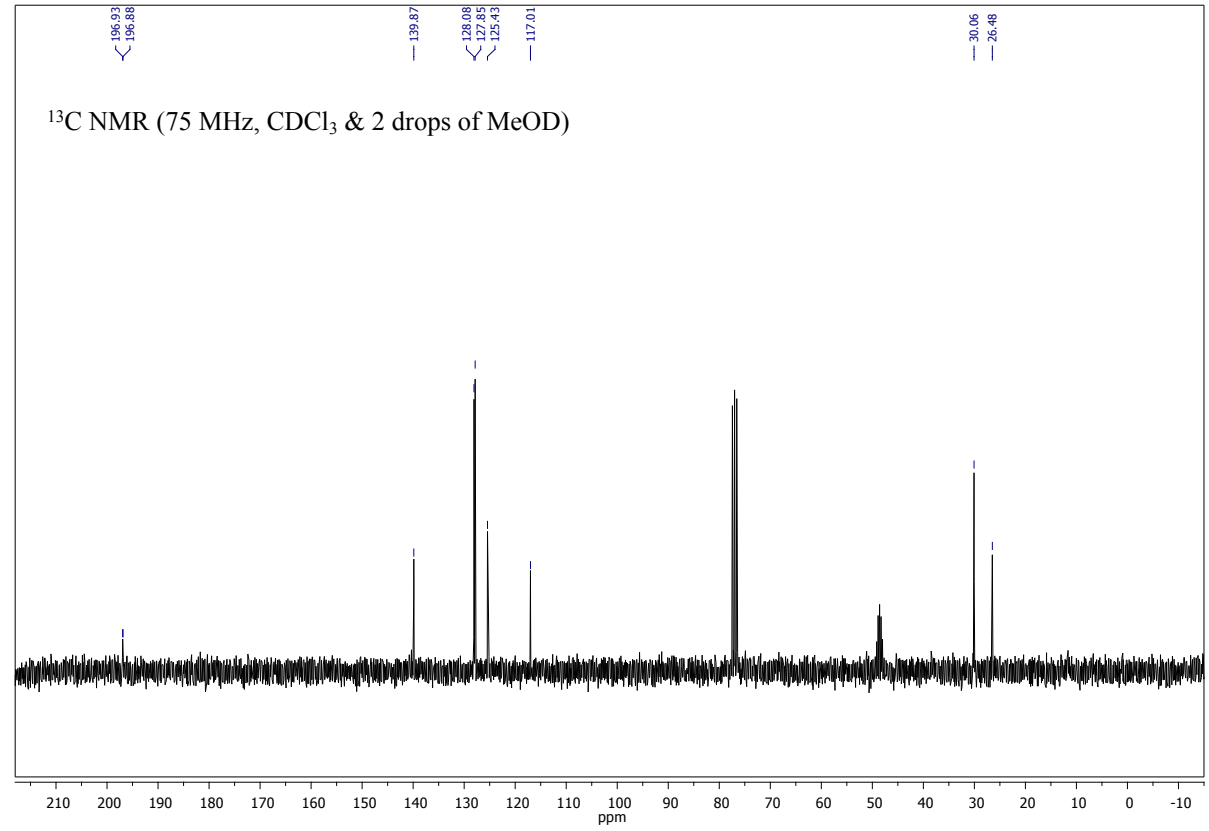
PTSA = *p*-toluenesulonic acid.

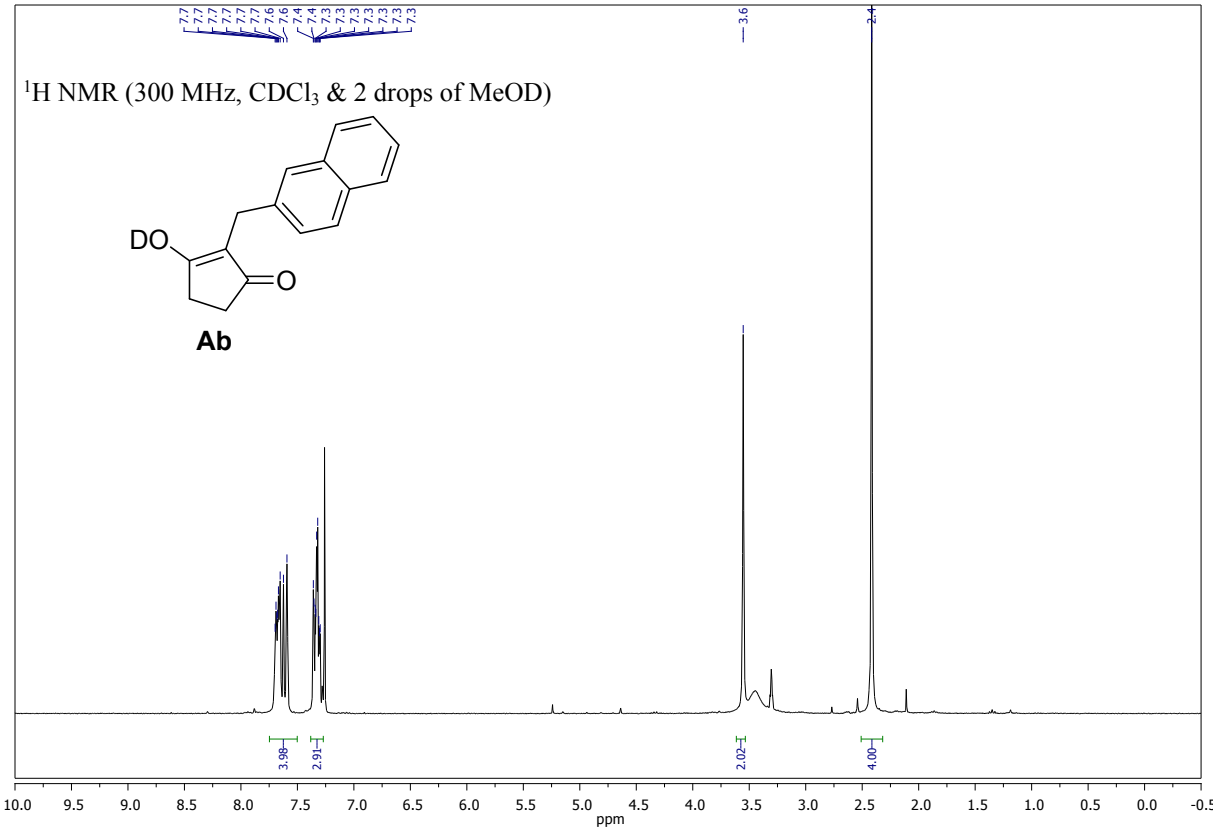
DBU = 1,8-Diazabicyclo[5.4.0]undec-7-ene.

EVK = Ethyl vinyl ketone

III) ^{1}H and 13C NMR Spectra



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[1]H NMR (300 MHz, CDCl3 & 2 drops of MeOD)
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2.91
2.02
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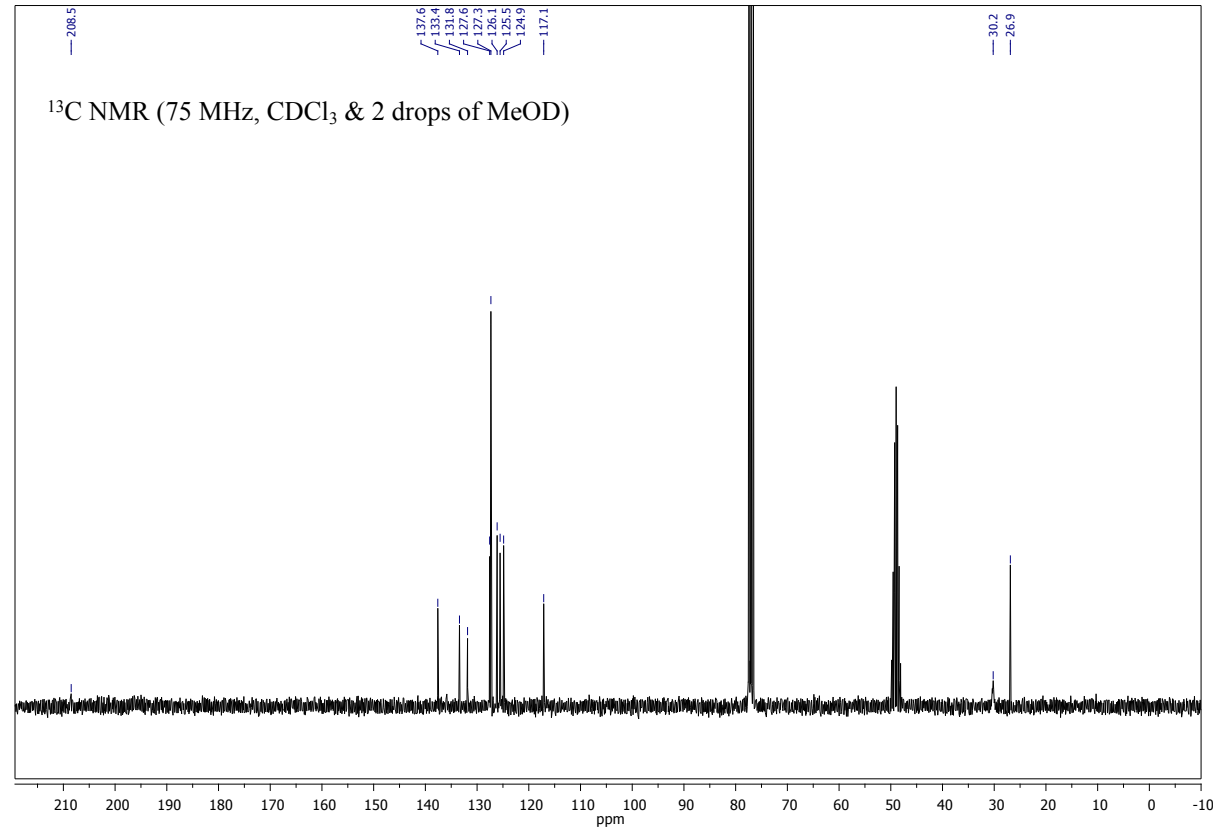
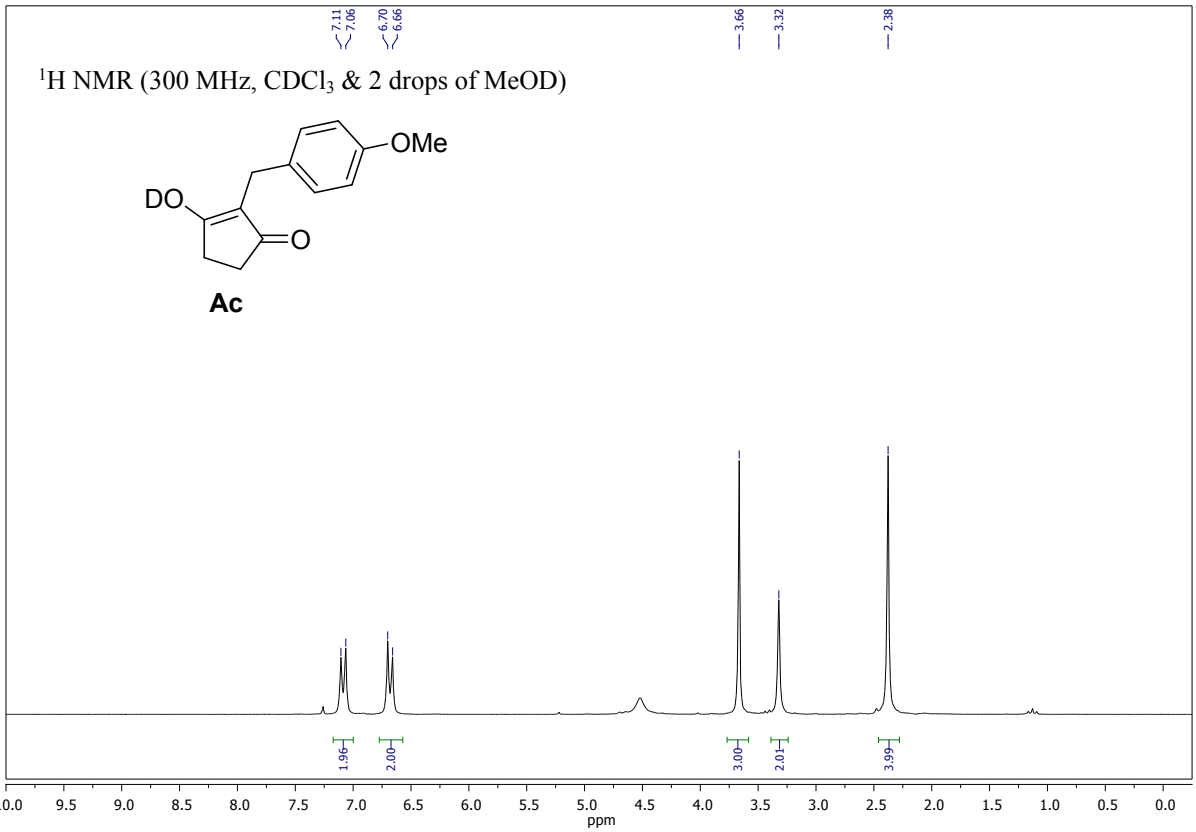
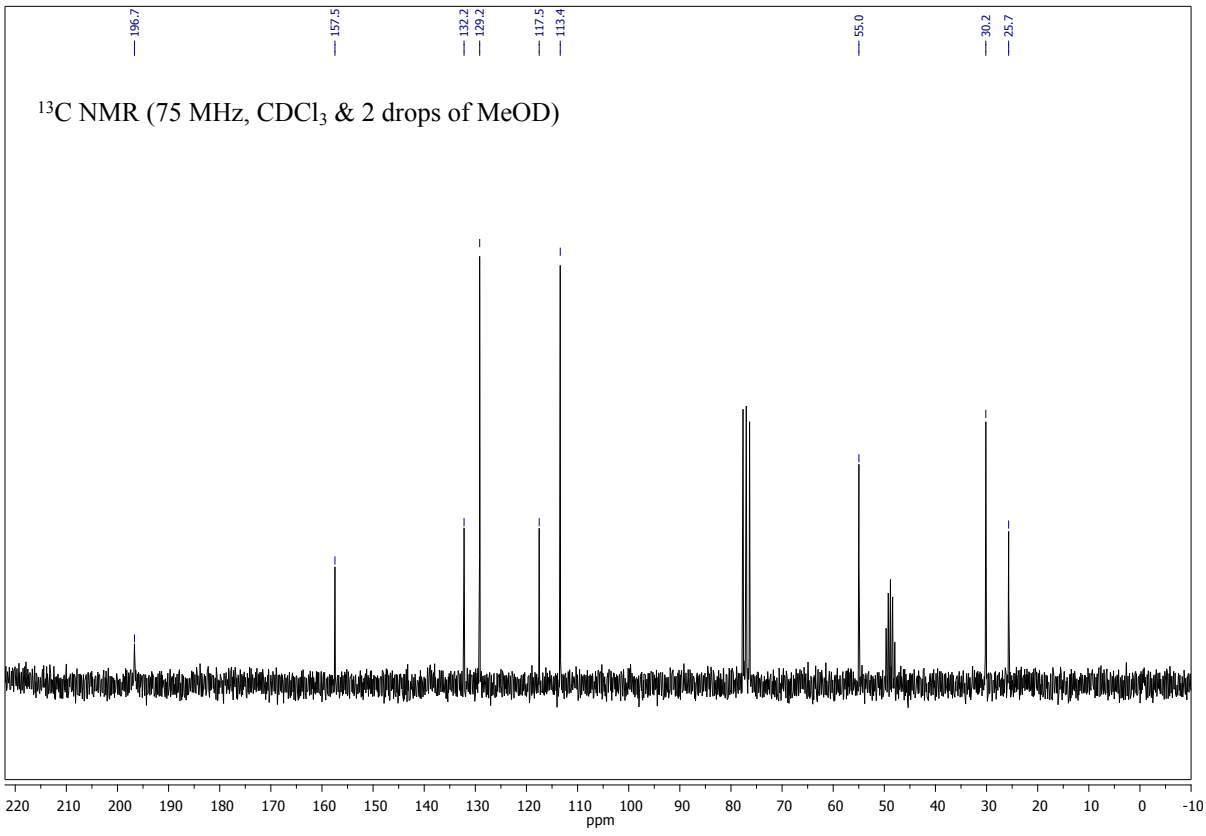
0.0
ppm


208.5
137.6
133.4
131.8
127.6
127.3
126.1
125.5
124.9
117.1
30.2
26.9
[13]C NMR (75 MHz, CDCl3 & 2 drops of MeOD)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

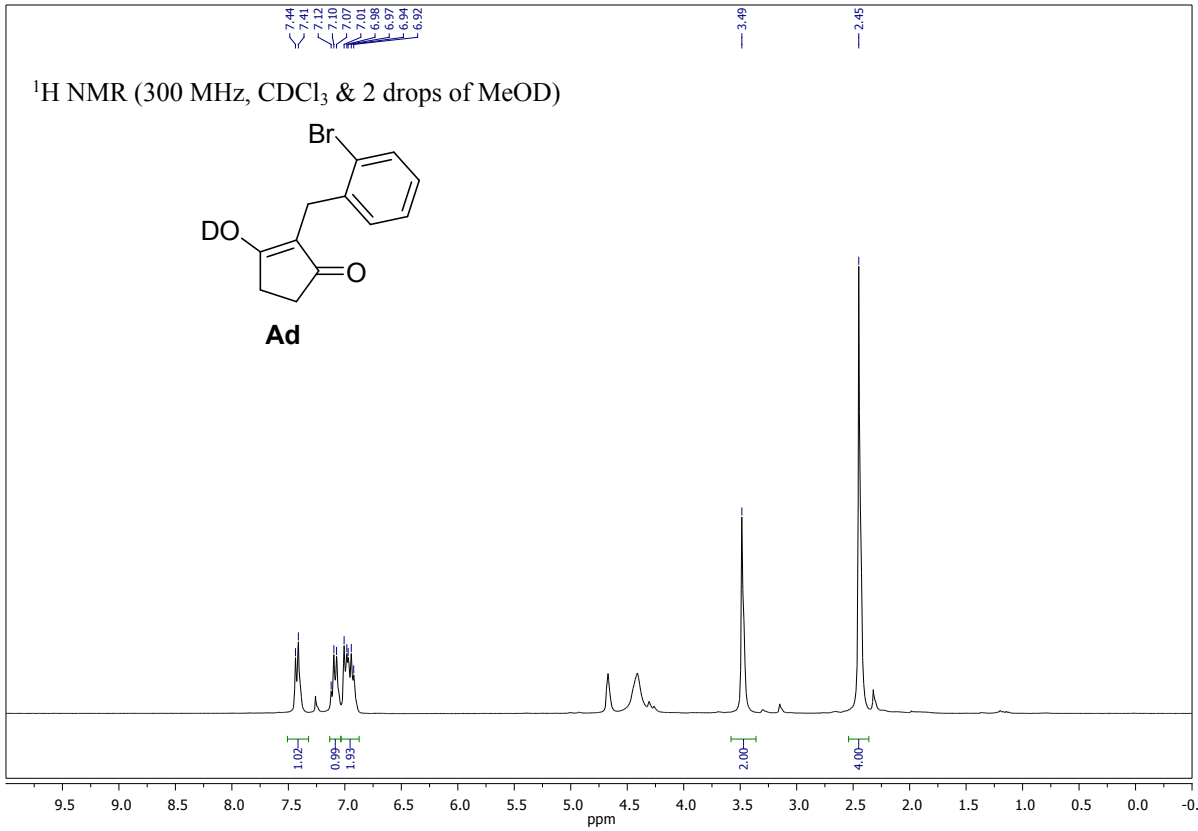


^{1}H NMR (300 MHz, $CDCl_3$ & 2 drops of MeOD)

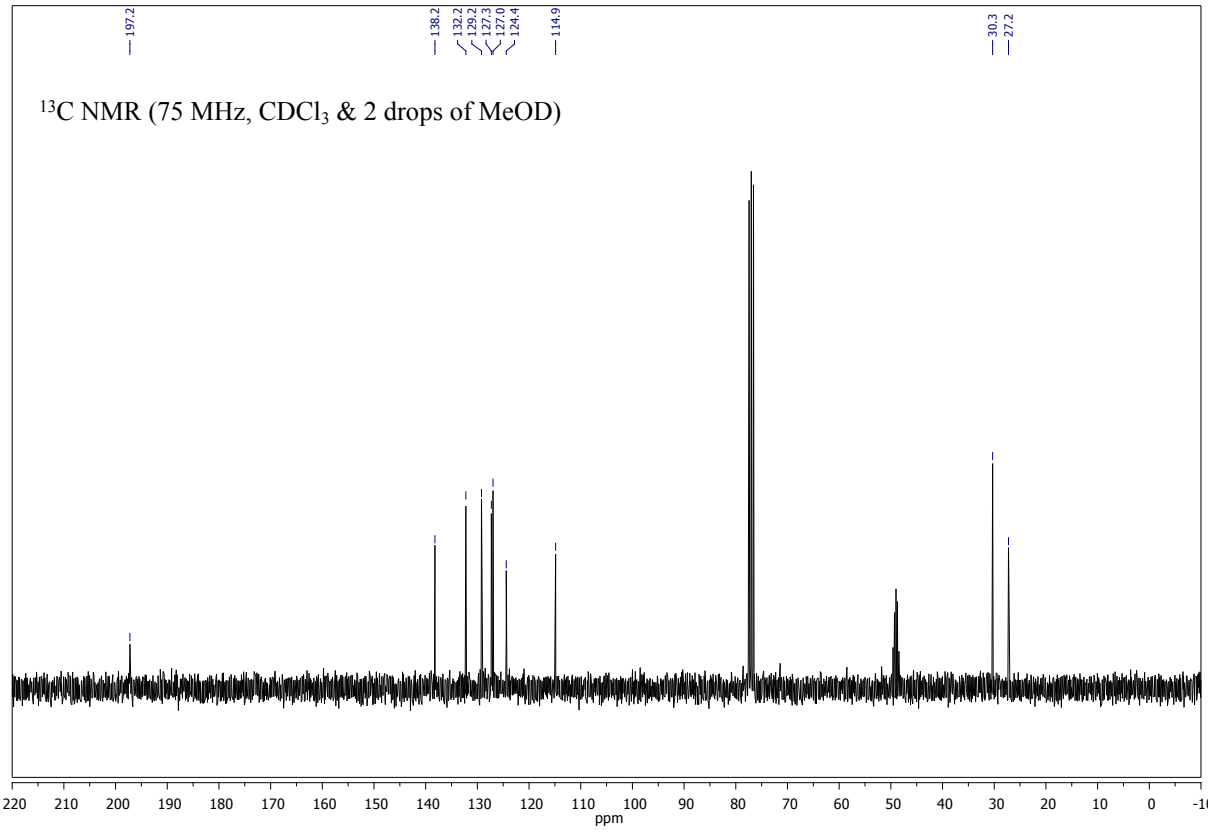
Ac



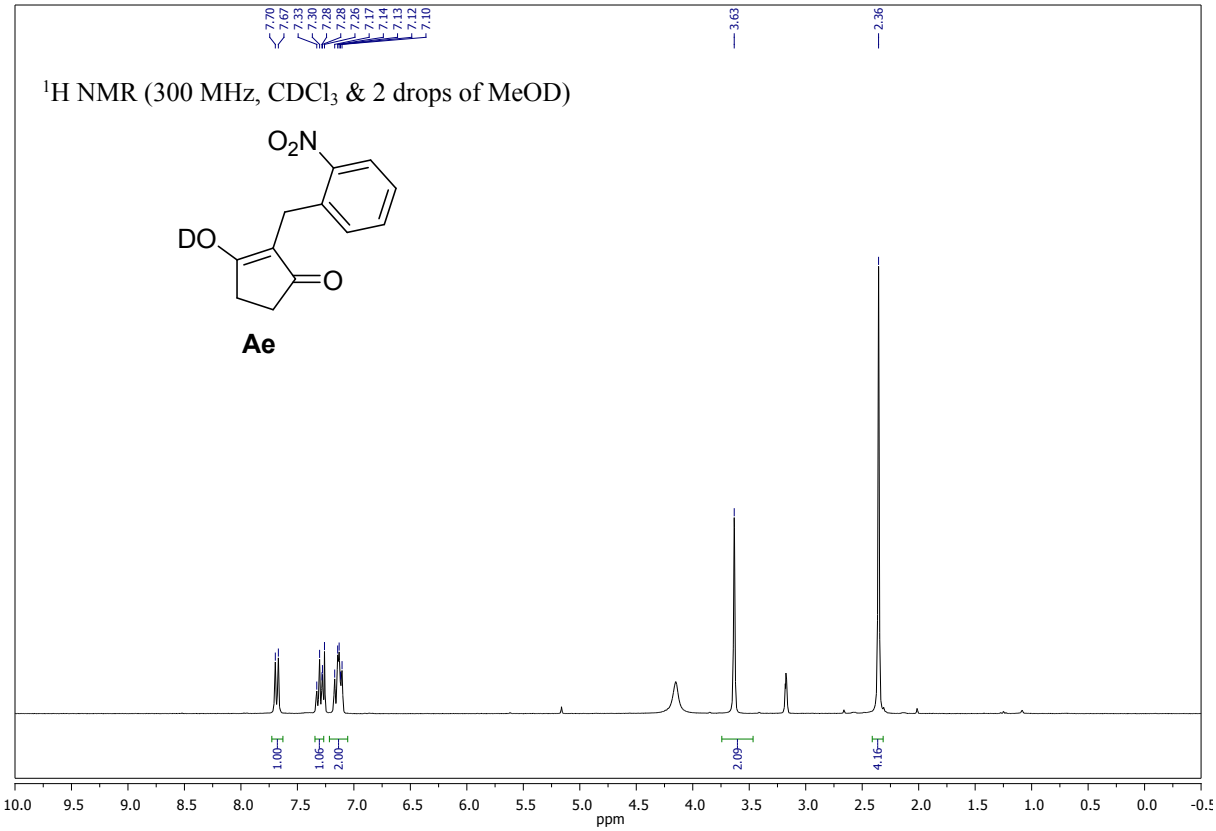
^{13}C NMR (75 MHz, $CDCl_3$ & 2 drops of MeOD)

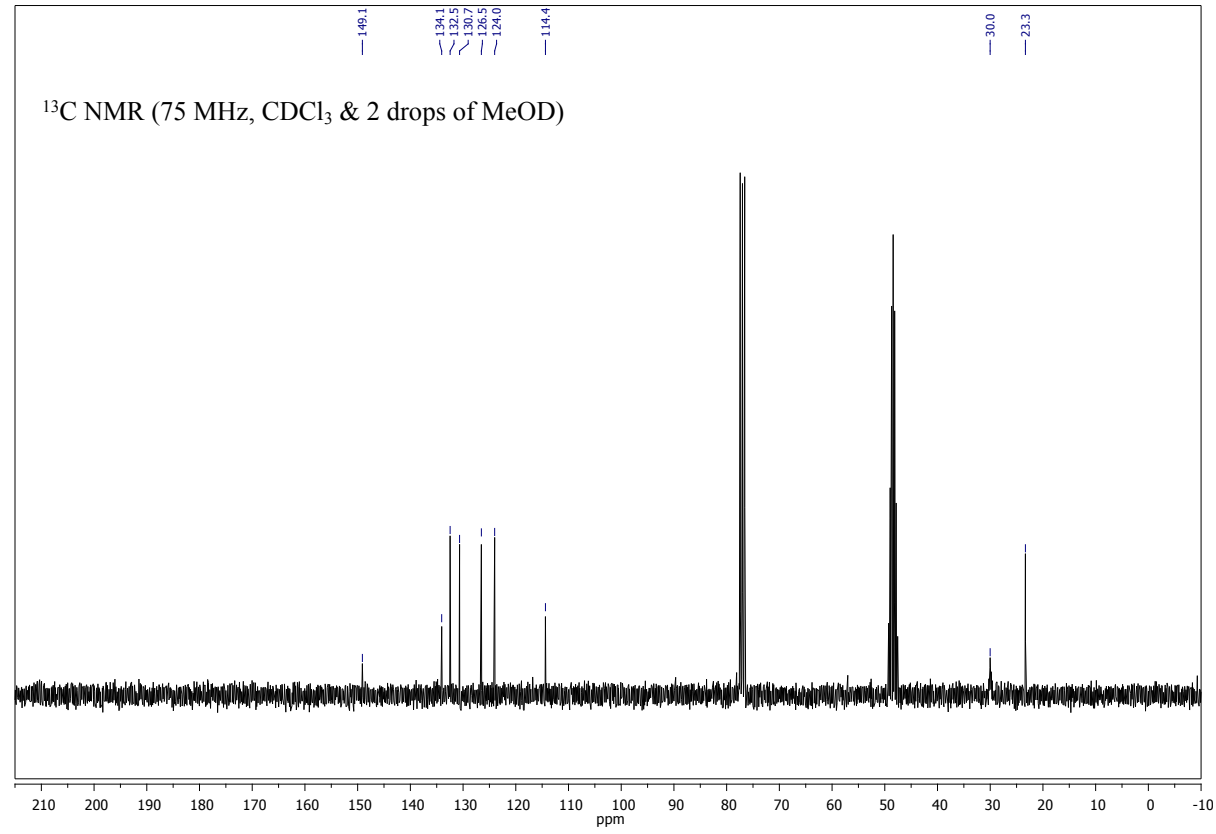


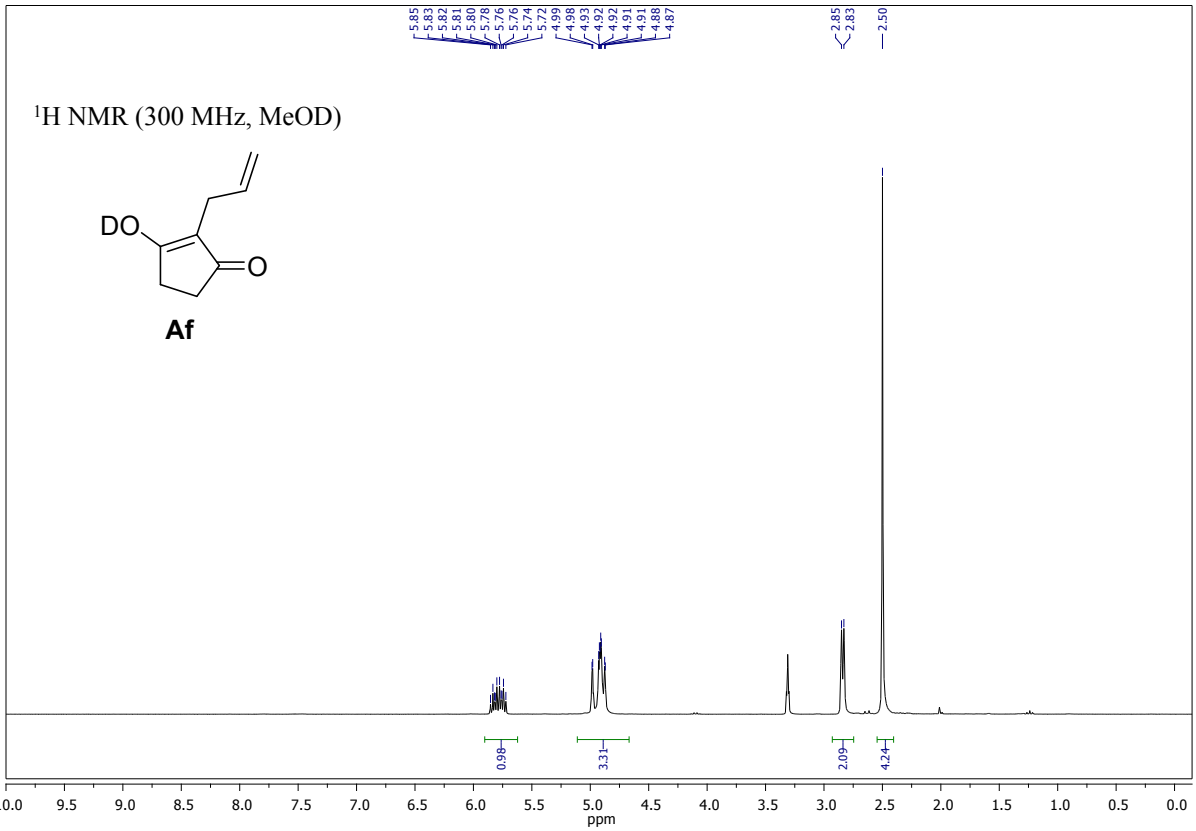
^{1}H NMR (300 MHz, $CDCl_3$ & 2 drops of MeOD)



^{13}C NMR (75 MHz, $CDCl_3$ & 2 drops of MeOD)

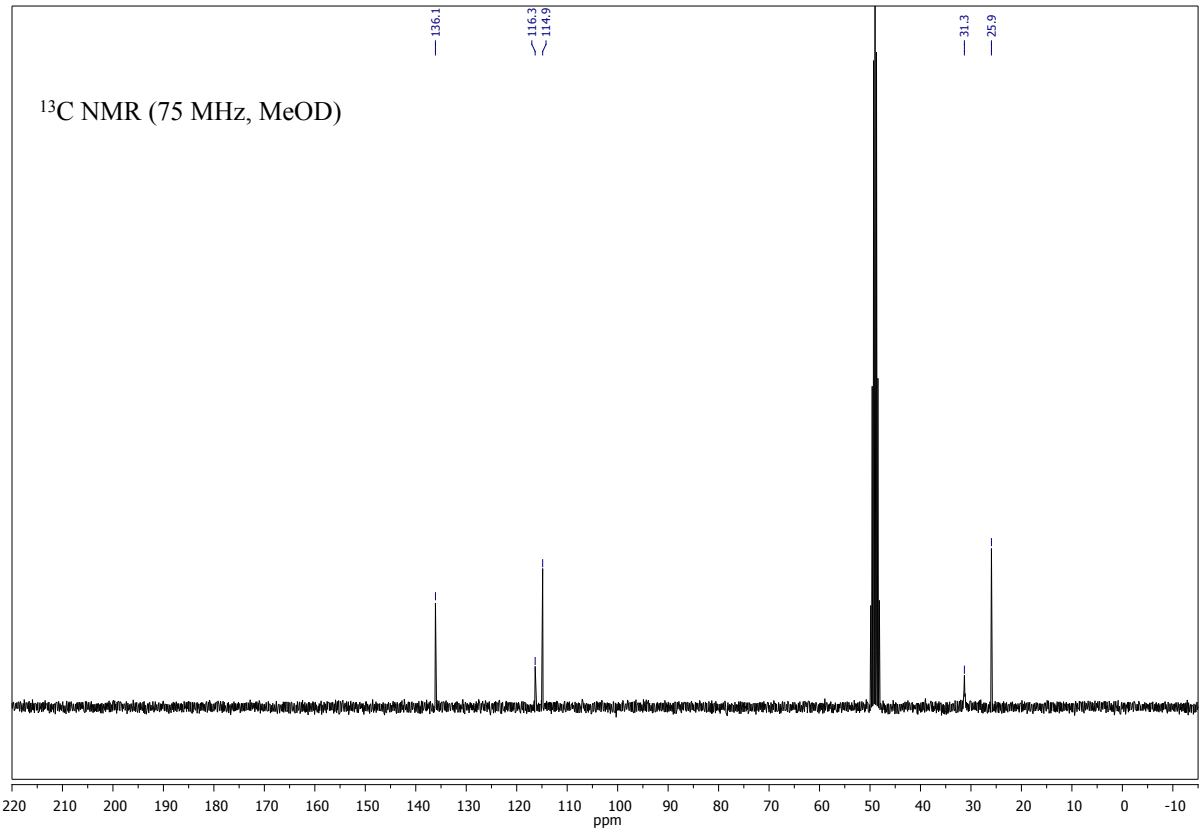

7.70
7.67
7.33
7.30
7.28
7.28
7.26
7.17
7.14
7.13
7.12
7.10
3.63
2.36
^{1}H NMR (300 MHz, $CDCl_3$ & 2 drops of MeOD)
O_2N
DO
O
Ae
1.00
1.06
2.00
2.09
4.16
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


149.1
134.1
132.5
130.7
126.5
124.0
114.4
30.0
23.3
^{13}C NMR (75 MHz, $CDCl_3$ & 2 drops of MeOD)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm



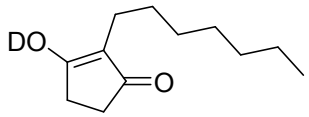
^{1}H NMR (300 MHz, MeOD)

Af



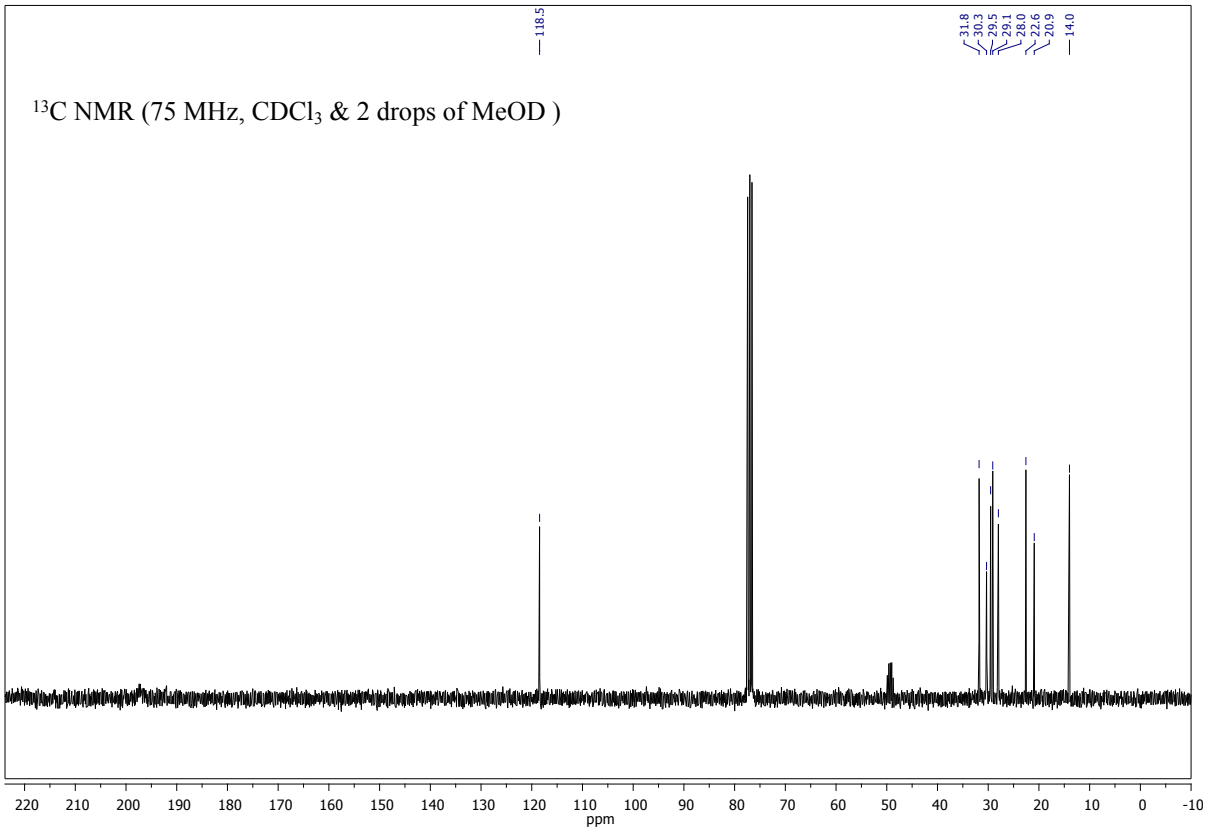
^{13}C NMR (75 MHz, MeOD)

^{1}H NMR (300 MHz, $CDCl_3$ & 2 drops of MeOD)

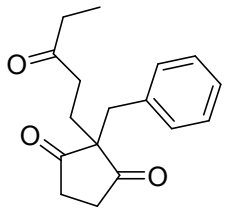


Ag

^{13}C NMR (75 MHz, $CDCl_3$ & 2 drops of MeOD)

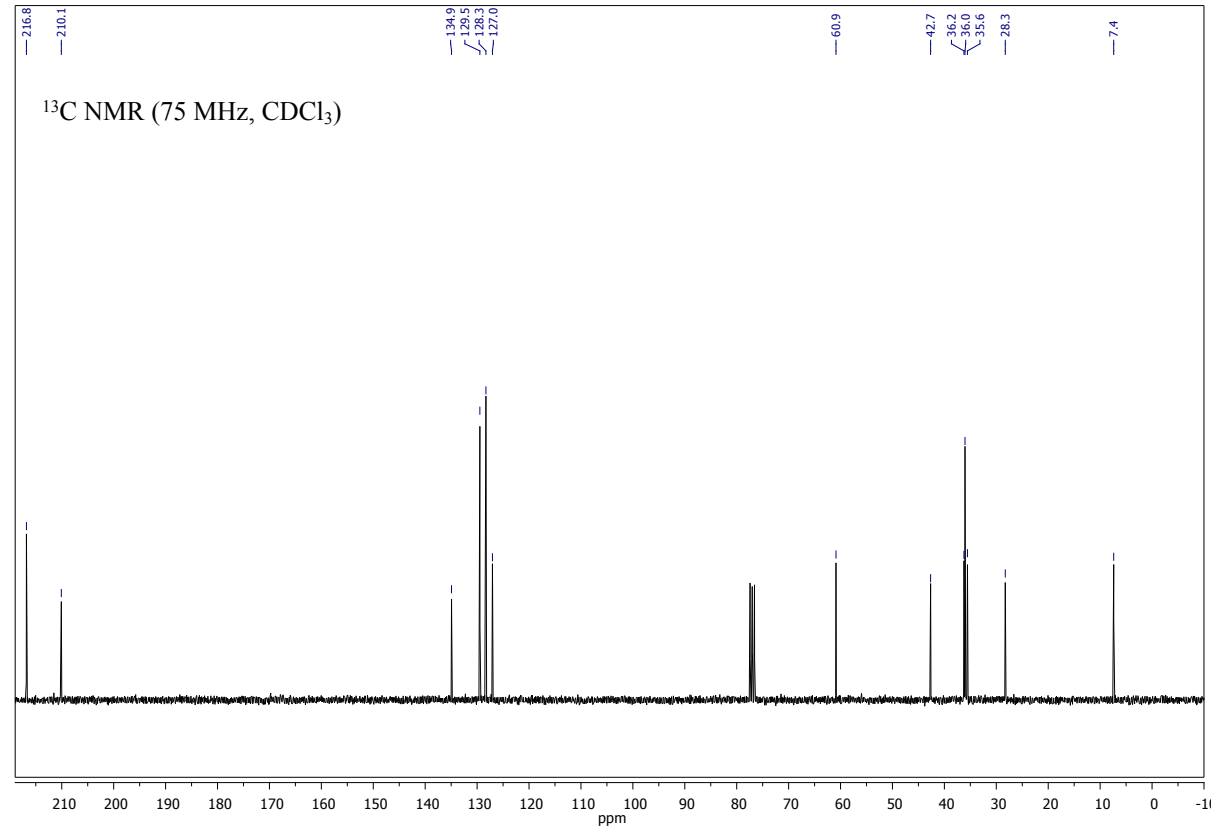


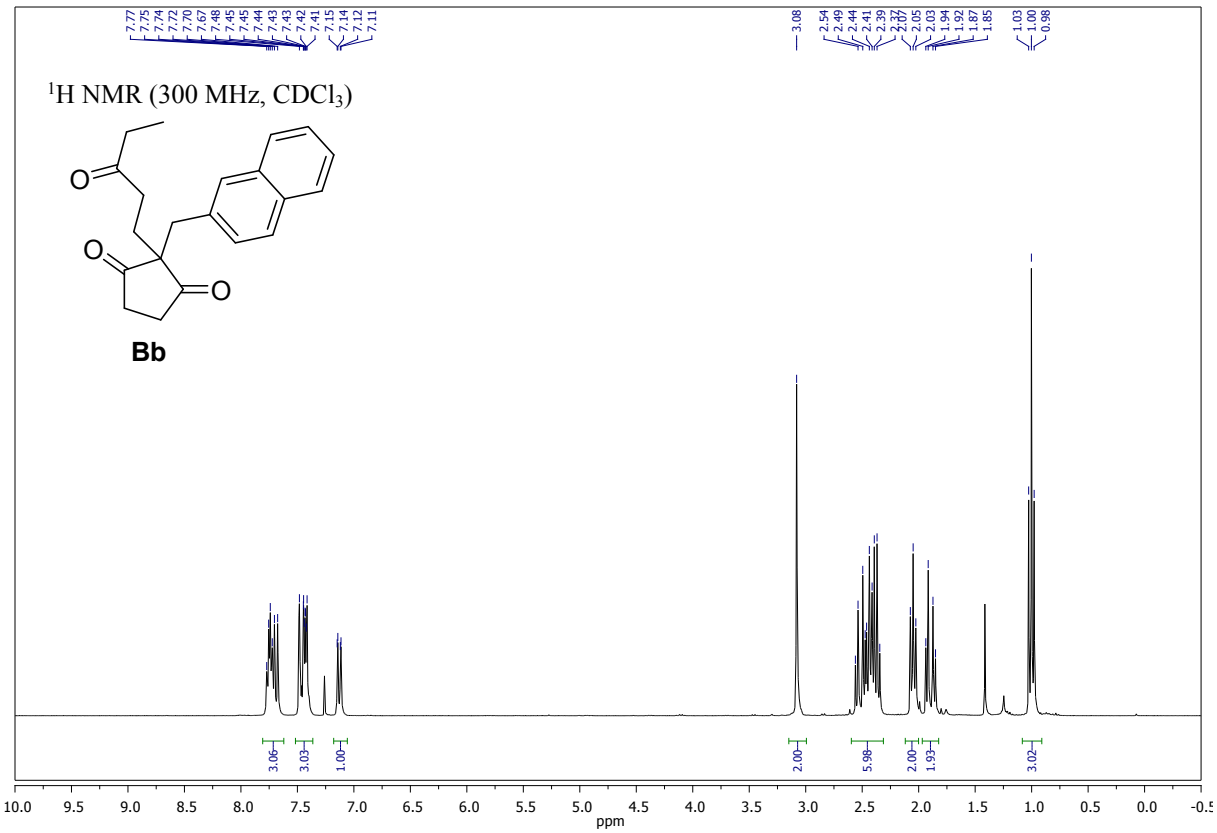
^{1}H NMR (300 MHz, $CDCl_3$)

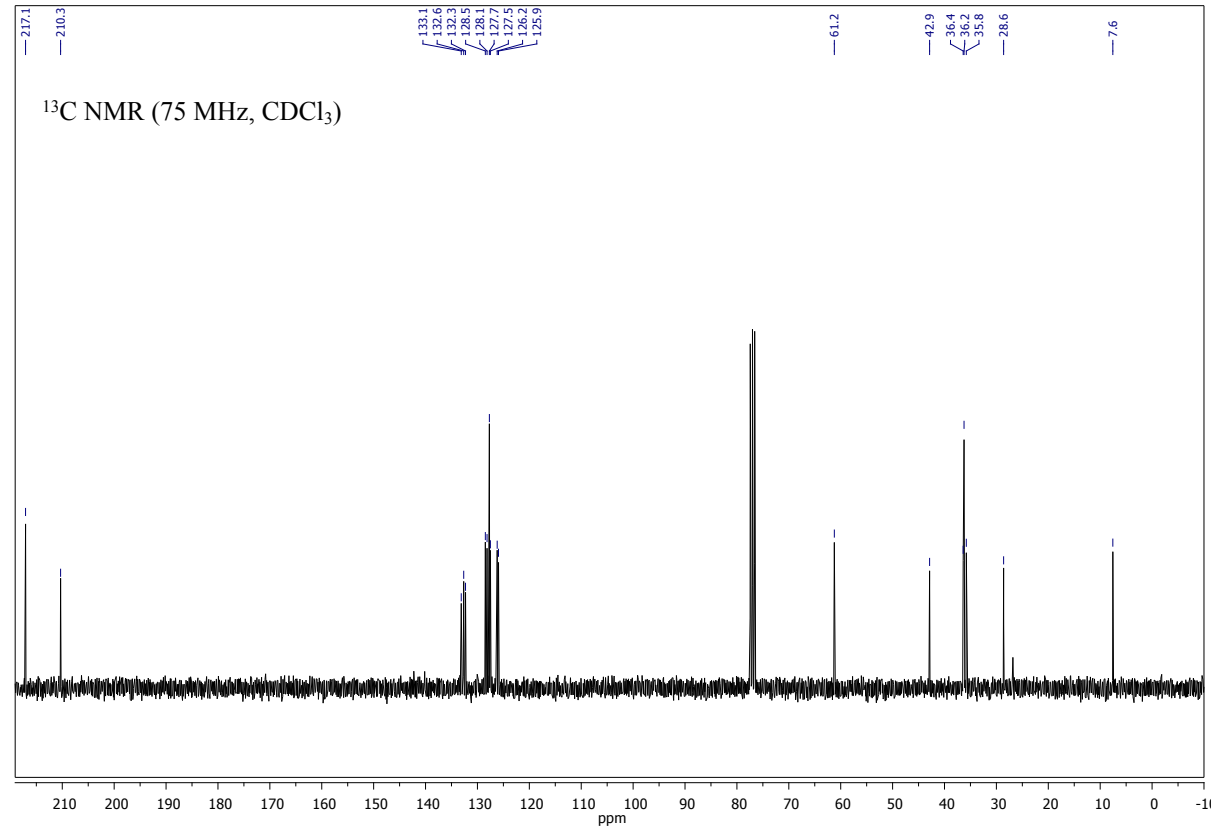


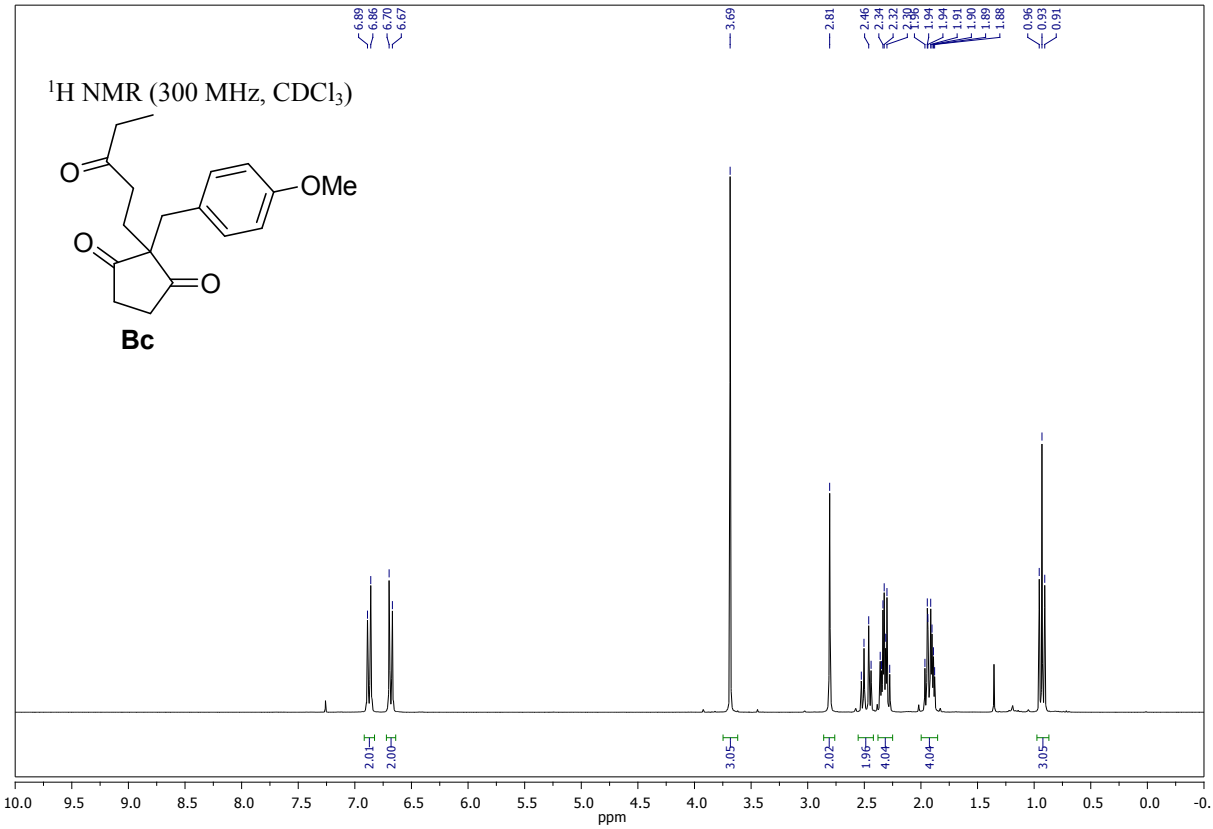
Ba

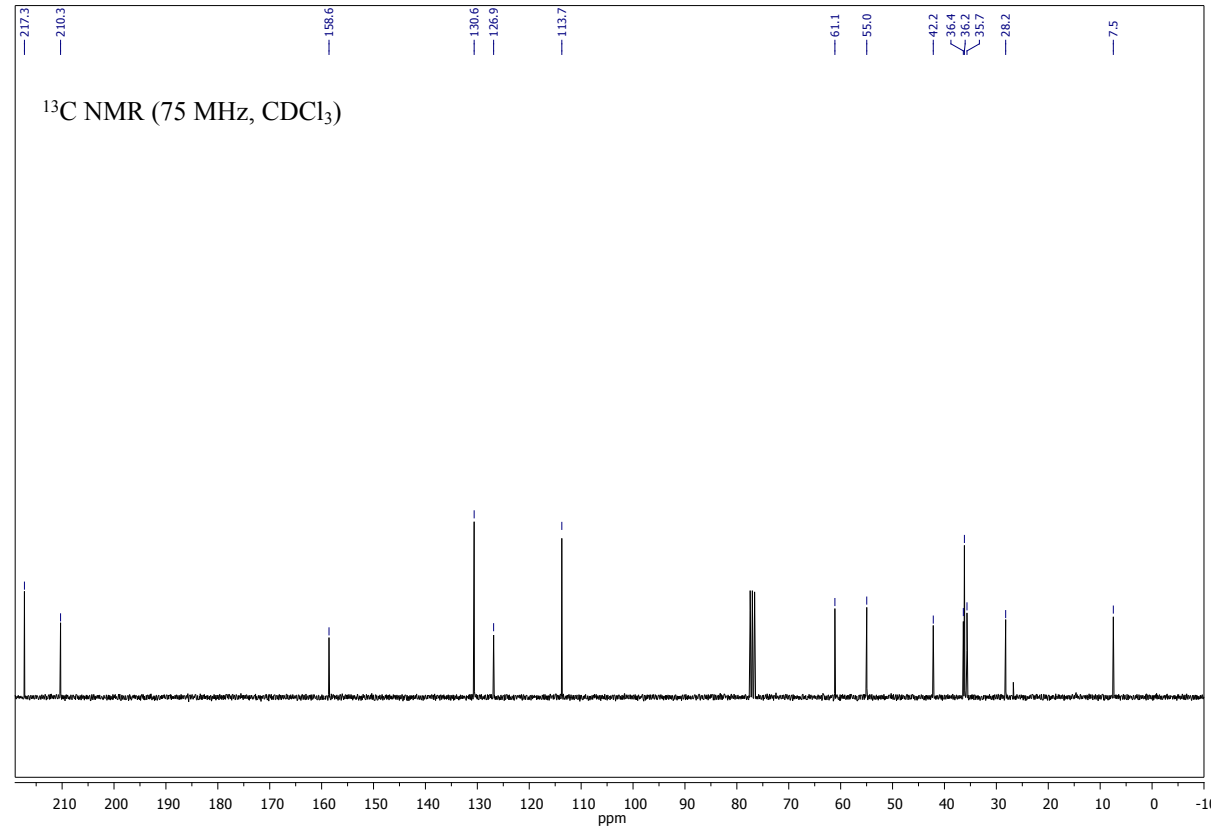
^{13}C NMR (75 MHz, $CDCl_3$)



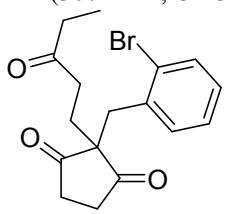

7.77
7.75
7.74
7.72
7.70
7.67
7.48
7.45
7.45
7.44
7.43
7.43
7.42
7.41
7.15
7.14
7.12
7.11
3.08
2.54
2.49
2.44
2.41
2.39
2.07
2.05
2.03
1.94
1.92
1.87
1.85
1.03
1.00
0.98
1H NMR (300 MHz, CDCl3)
O
O
O
Bb
3.06
3.03
1.00
2.00
5.98
2.00
1.93
3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


217.1
210.3
133.1
132.6
132.3
128.5
128.1
127.7
127.5
126.2
125.9
61.2
42.9
36.4
36.2
35.8
28.6
7.6
13C NMR (75 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


6.89
6.86
6.70
6.67
3.69
2.81
2.46
2.34
2.32
2.30
1.98
1.94
1.94
1.91
1.90
1.89
1.88
0.96
0.93
0.91
^{1}H NMR (300 MHz, $CDCl_3$)
O
OMe
O
O
Bc
2.01
2.00
3.05
2.02
1.96
4.04
4.04
3.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

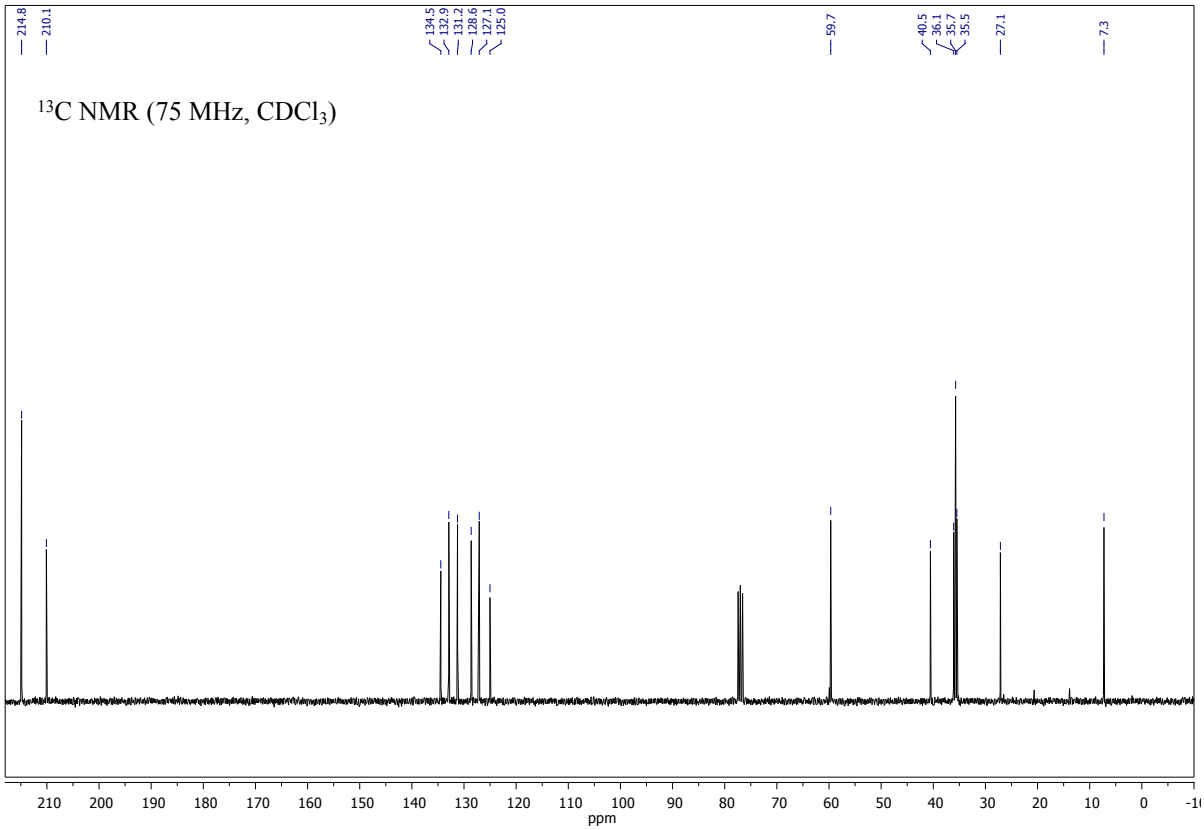

217.3
210.3
158.6
130.6
126.9
113.7
61.1
55.0
42.2
36.4
36.2
35.7
28.2
7.5
^{13}C NMR (75 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

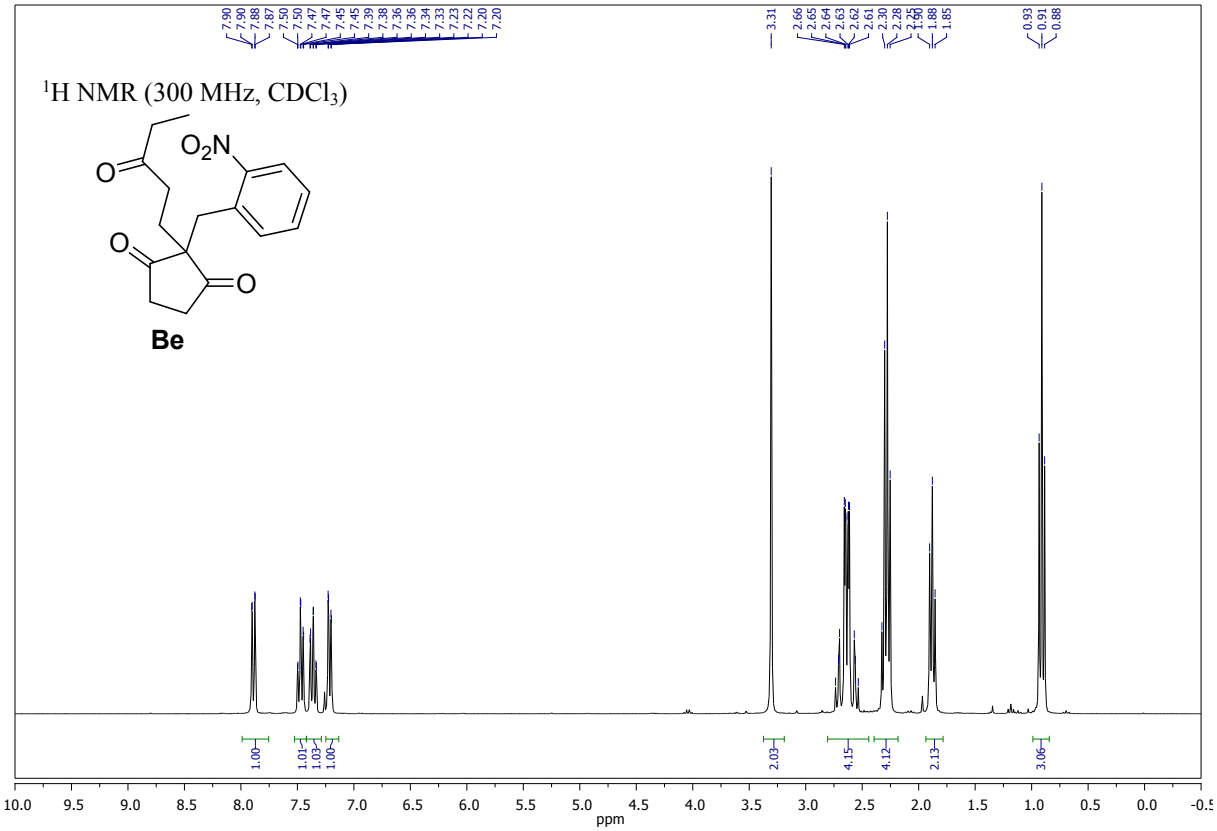
^{1}H NMR (300 MHz, $CDCl_3$)



Bd

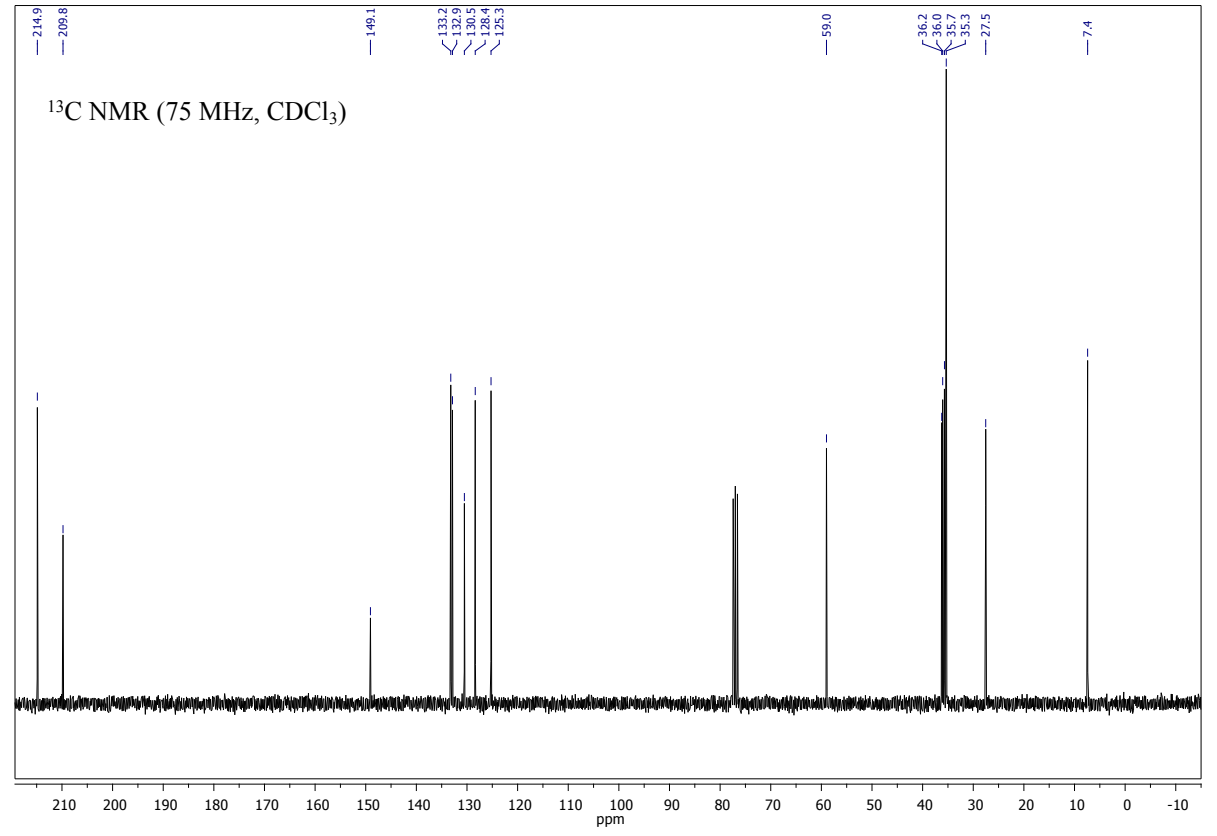
^{13}C NMR (75 MHz, $CDCl_3$)



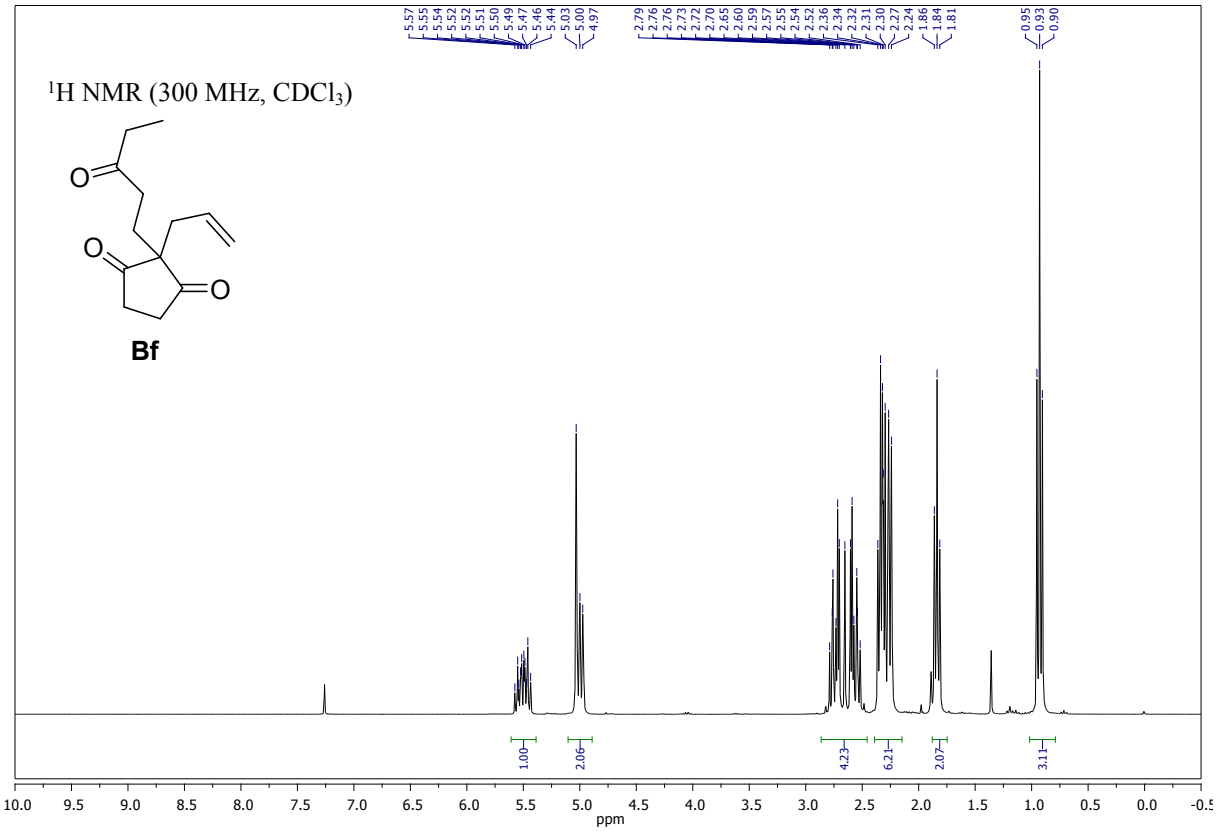


^{1}H NMR (300 MHz, $CDCl_3$)

Be

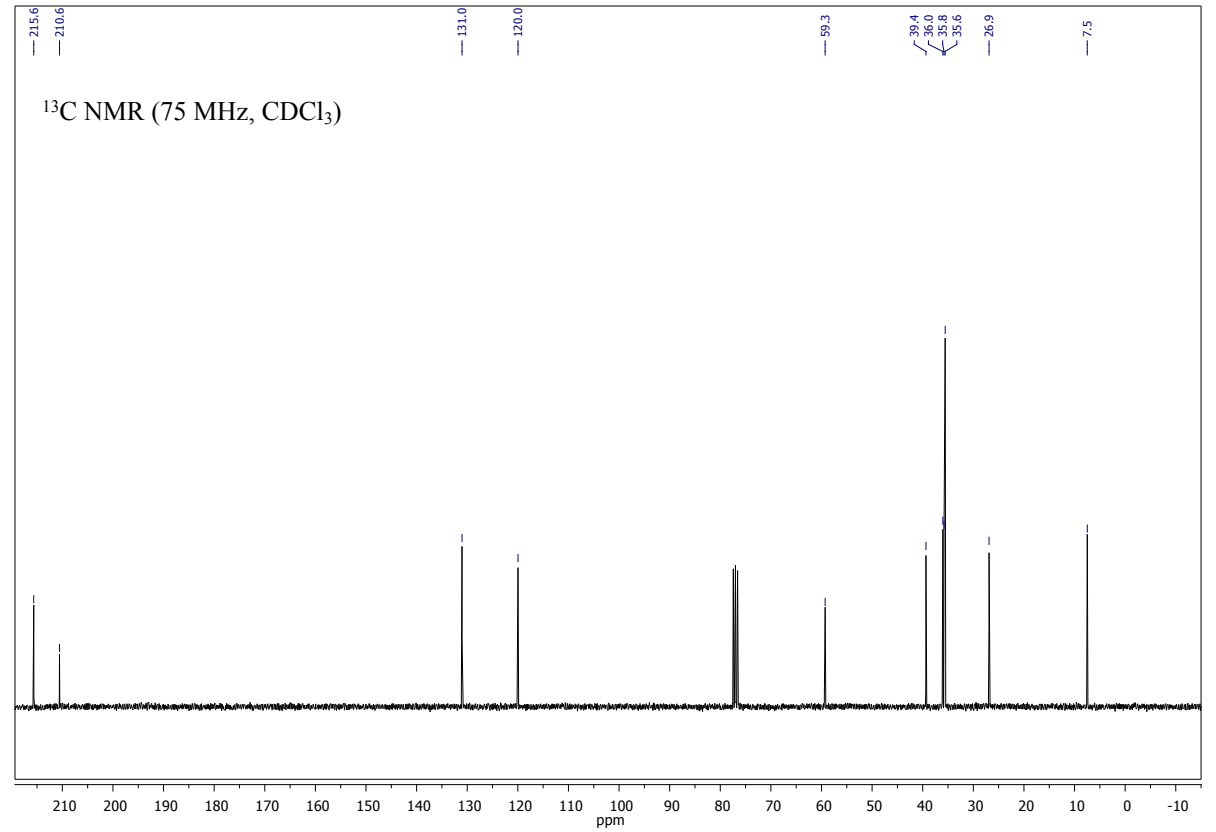


^{13}C NMR (75 MHz, $CDCl_3$)



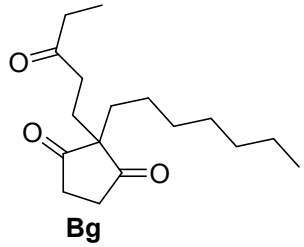
^{1}H NMR (300 MHz, $CDCl_3$)

Bf



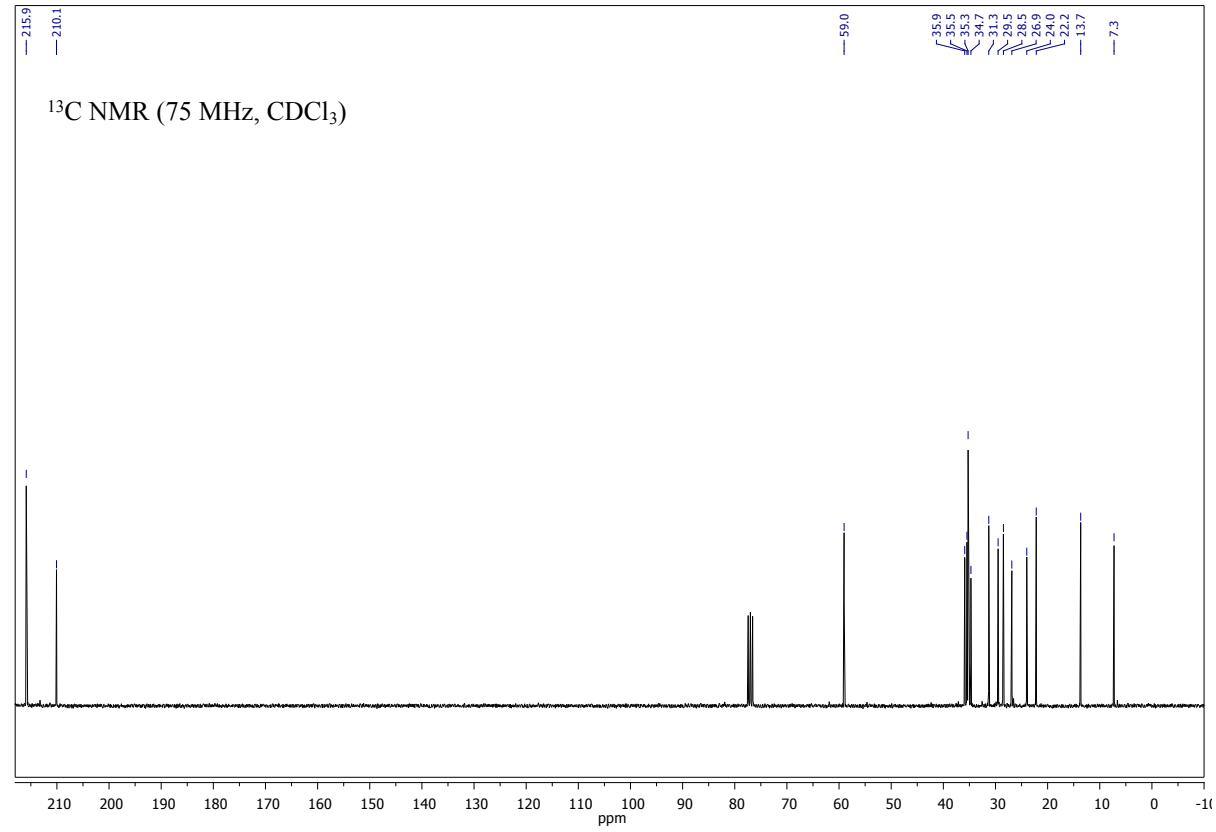
^{13}C NMR (75 MHz, $CDCl_3$)

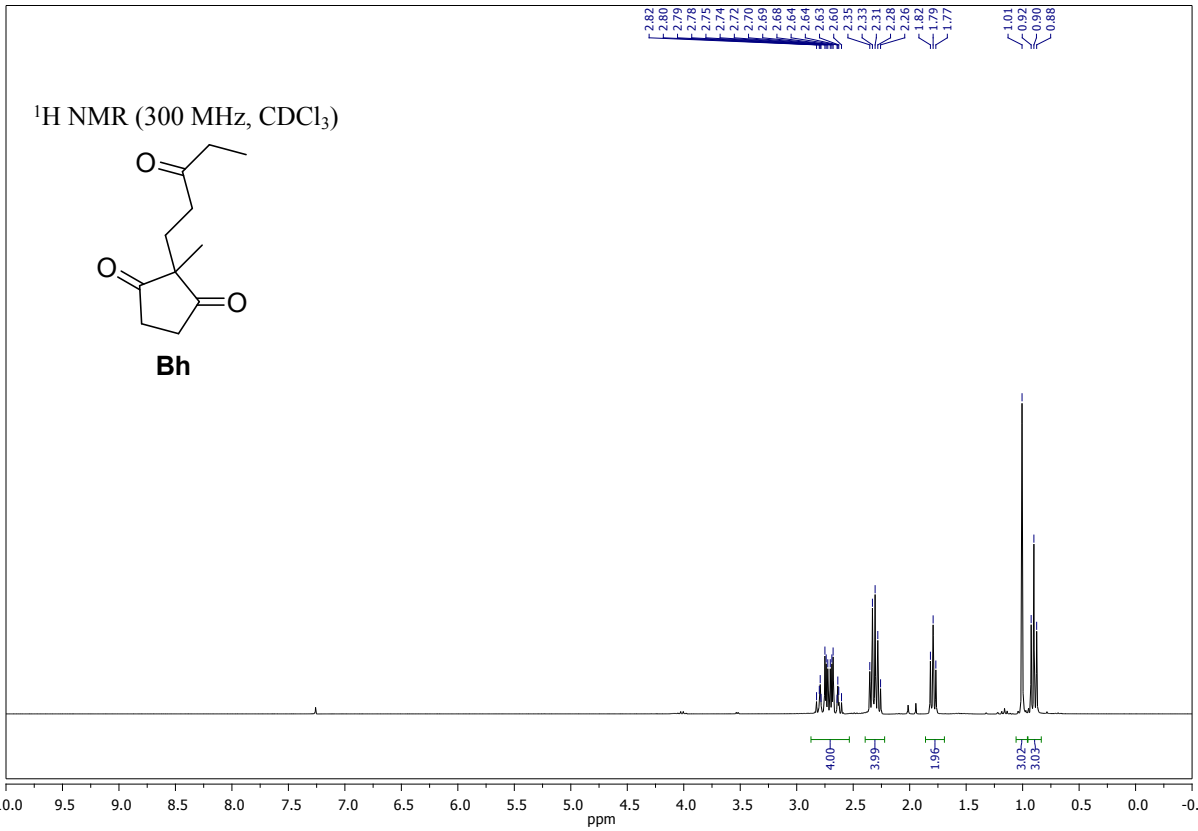
^{1}H NMR (300 MHz, $CDCl_3$)



Bg

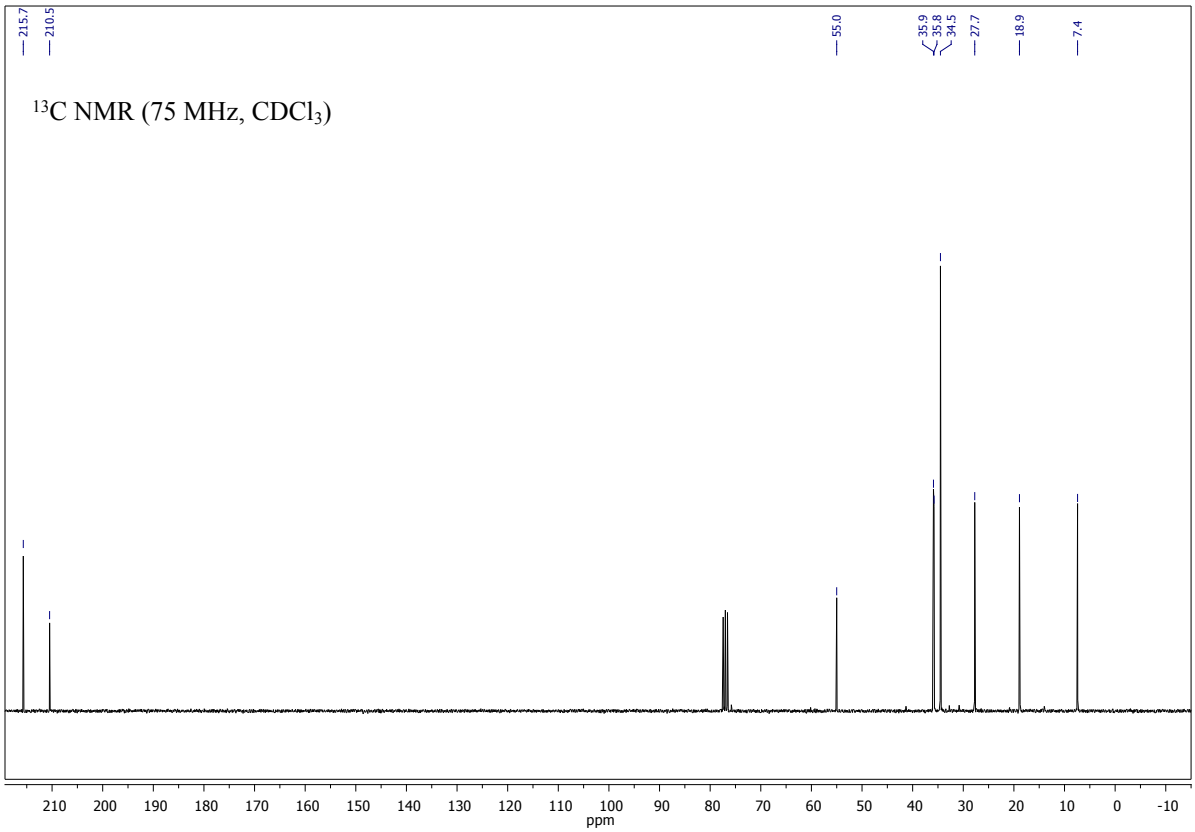
^{13}C NMR (75 MHz, $CDCl_3$)





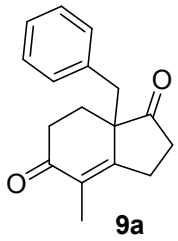
^{1}H NMR (300 MHz, $CDCl_3$)

Bh



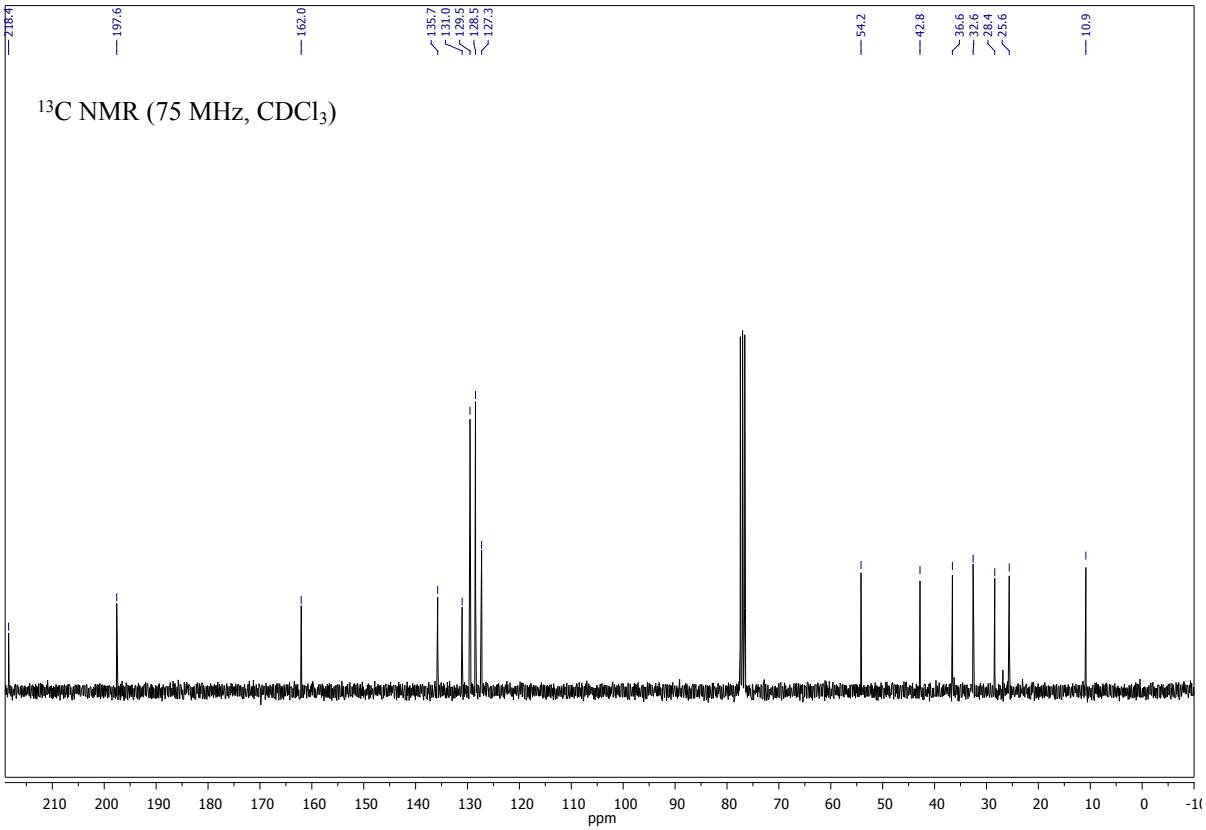
^{13}C NMR (75 MHz, $CDCl_3$)

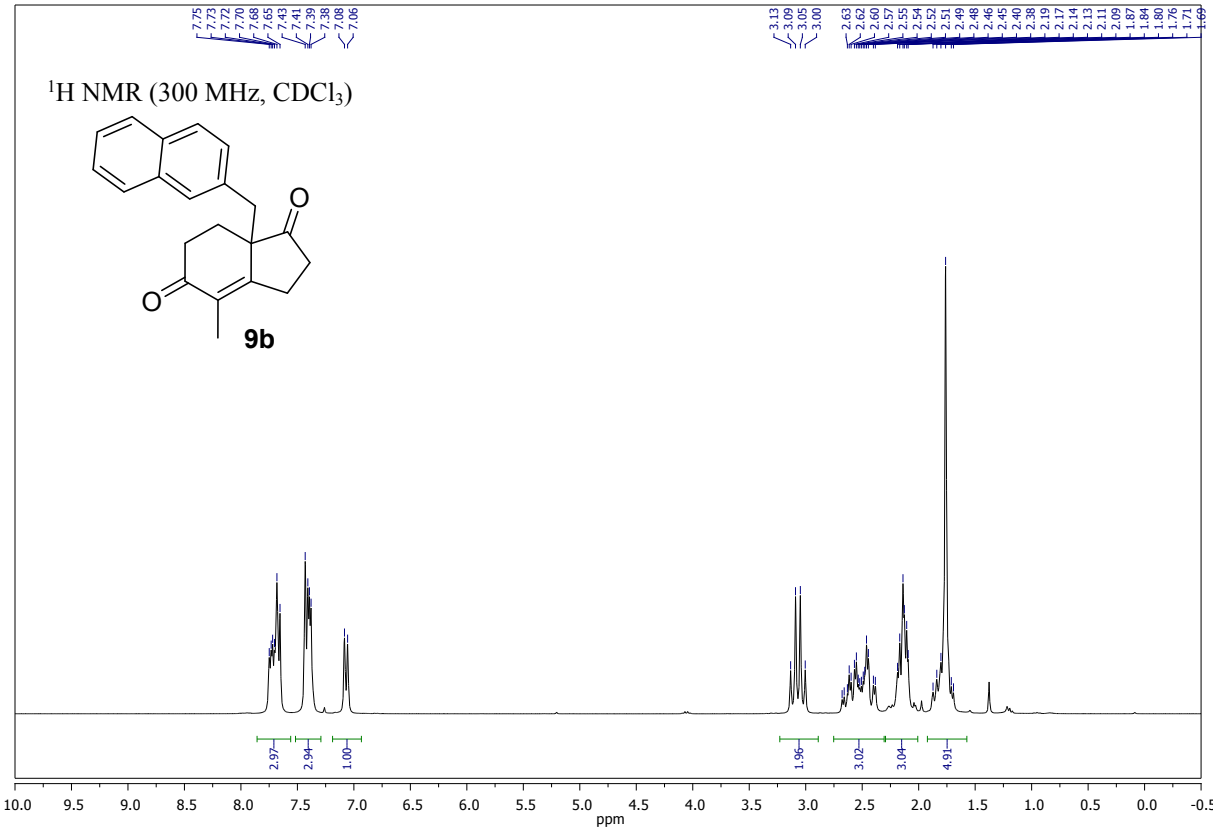
^{1}H NMR (300 MHz, $CDCl_3$)



9a

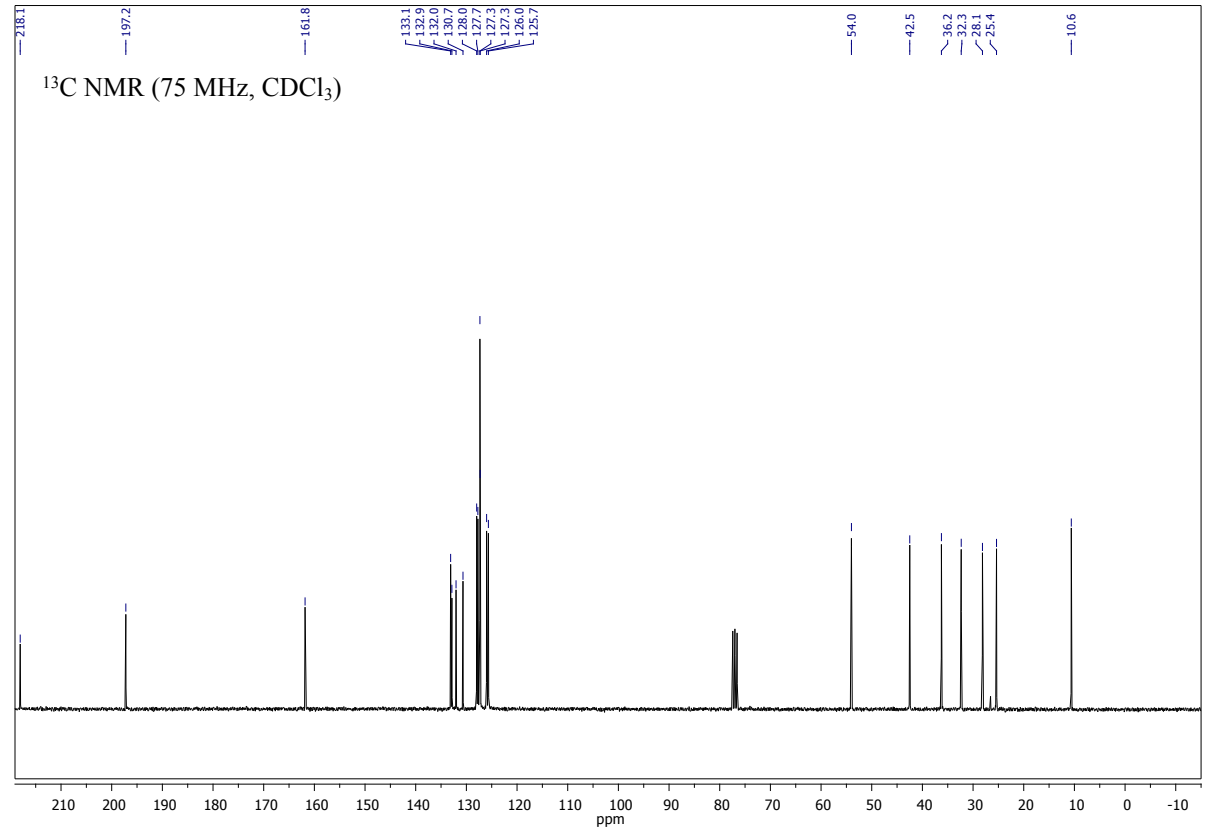
^{13}C NMR (75 MHz, $CDCl_3$)



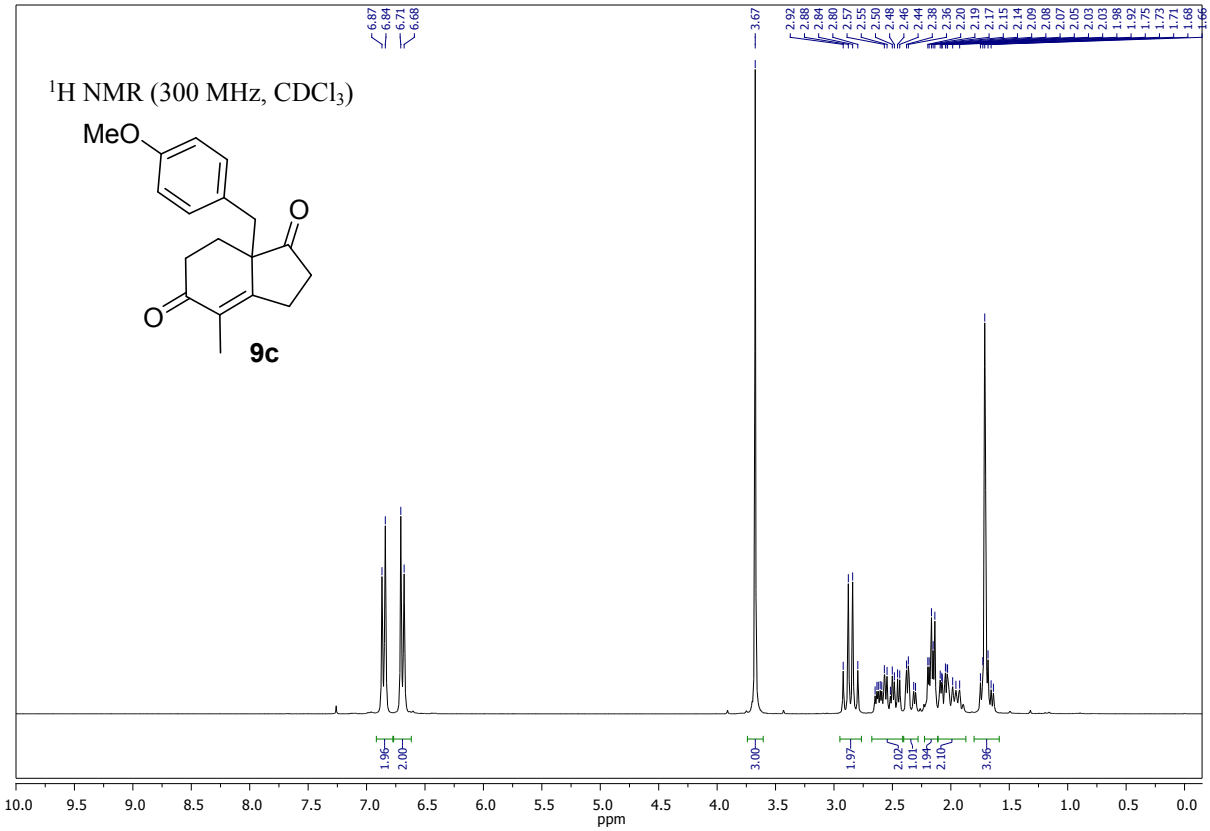


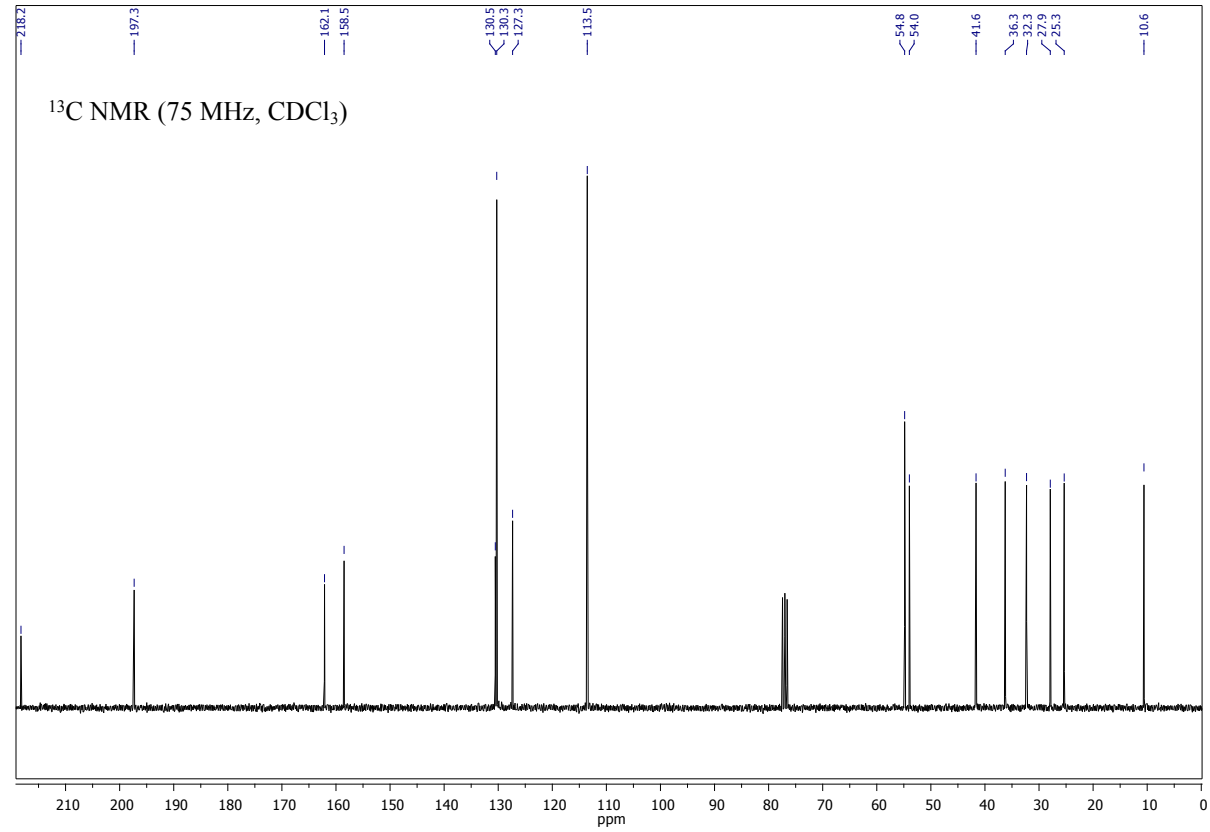
^{1}H NMR (300 MHz, $CDCl_3$)

9b

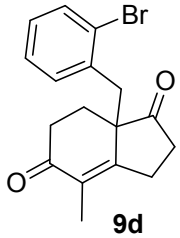


^{13}C NMR (75 MHz, $CDCl_3$)


^{1}H NMR (300 MHz, $CDCl_3$)
MeO
O
O
9c
6.87
6.84
6.71
6.68
3.67
1.96
2.00
3.00
1.97
2.02
1.01
1.94
2.10
3.96
ppm

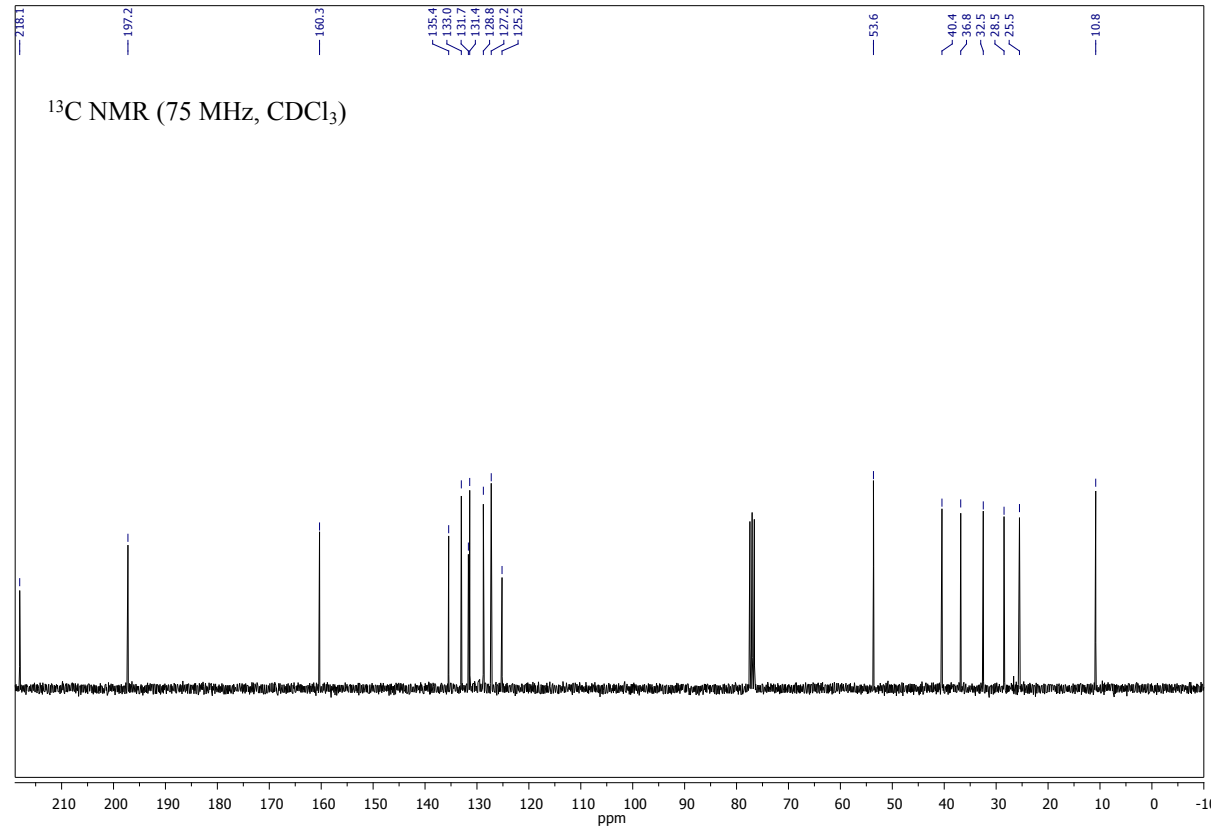

^{13}C NMR (75 MHz, $CDCl_3$)
218.2
197.3
162.1
158.5
130.5
130.3
127.3
113.5
54.8
54.0
41.6
36.3
32.3
27.9
25.3
10.6
ppm

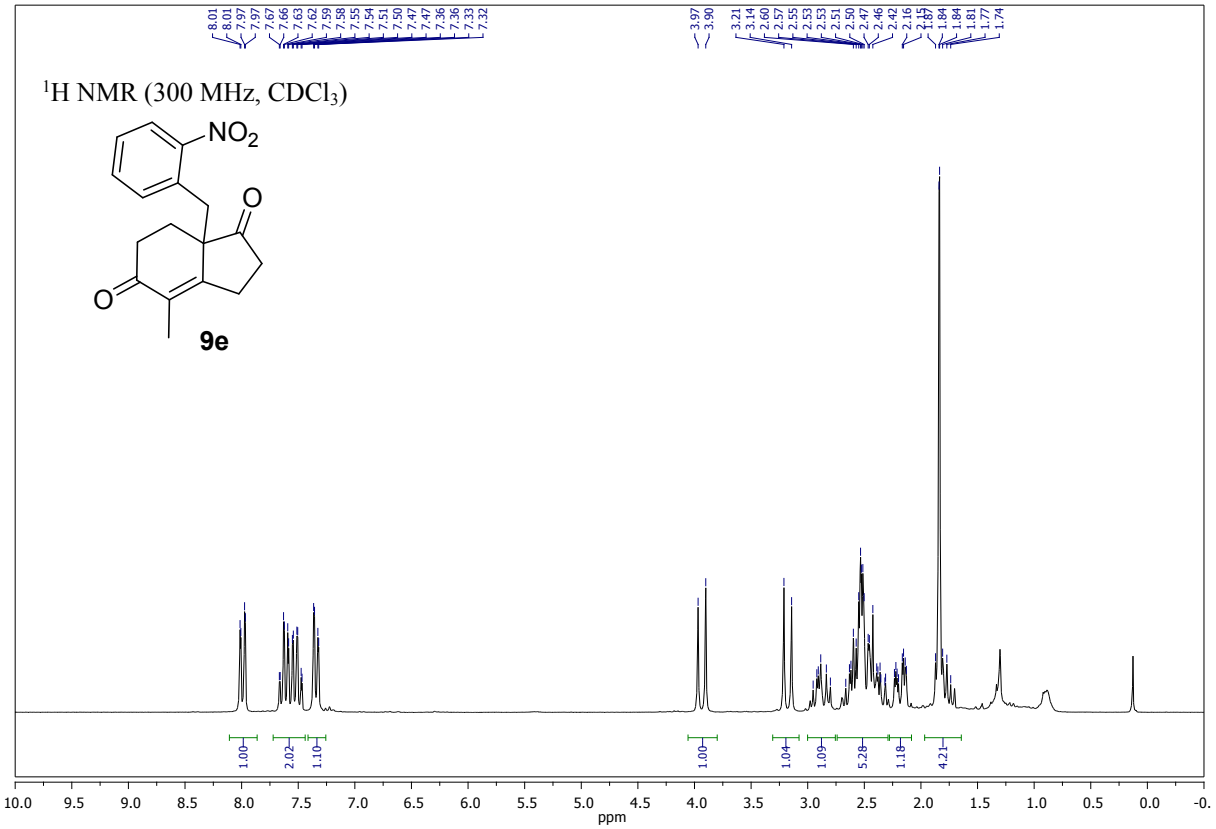
^{1}H NMR (300 MHz, $CDCl_3$)

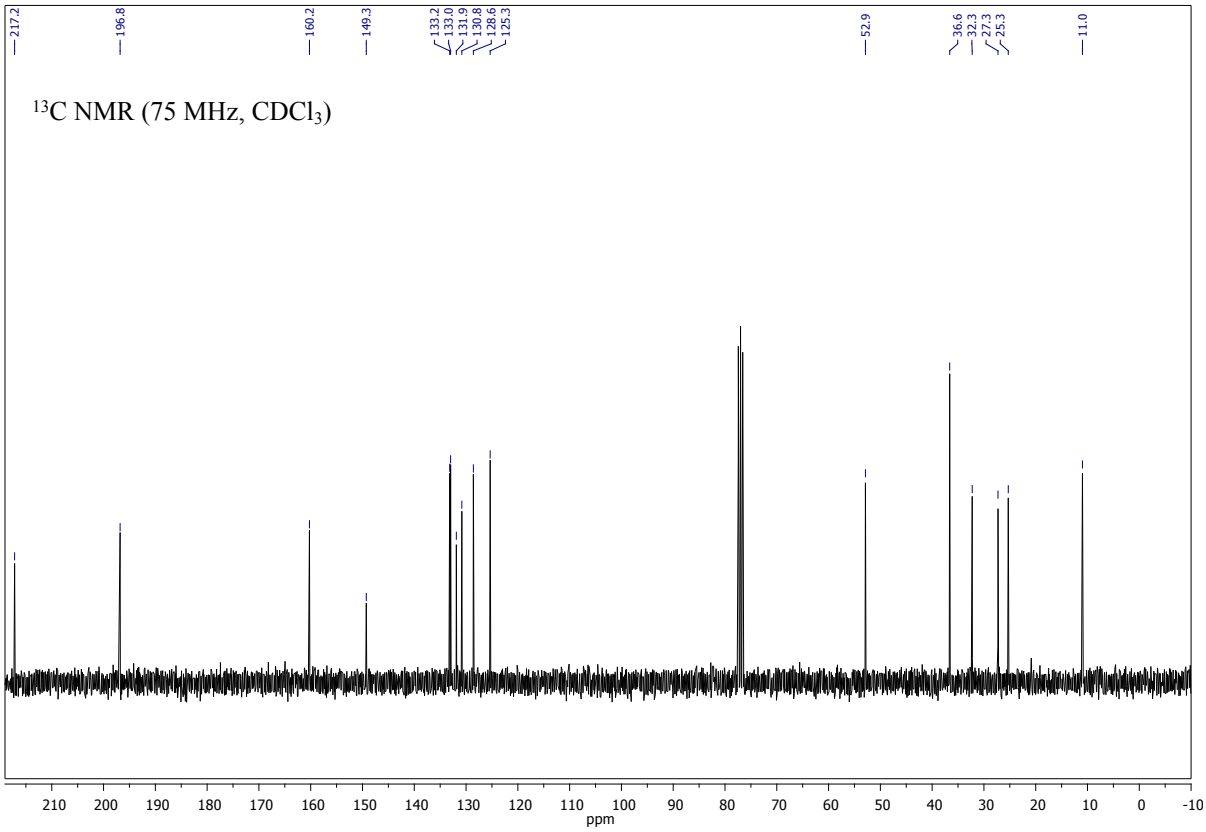


9d

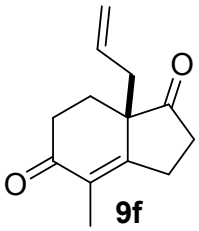
^{13}C NMR (75 MHz, $CDCl_3$)




8.01
8.01
7.97
7.97
7.97
7.67
7.66
7.63
7.62
7.59
7.58
7.55
7.54
7.51
7.50
7.47
7.47
7.36
7.36
7.33
7.32
3.97
3.90
3.21
3.14
2.60
2.57
2.55
2.53
2.53
2.51
2.50
2.47
2.46
2.42
2.16
1.87
1.84
1.84
1.81
1.77
1.74
1H NMR (300 MHz, CDCl3)
NO2
O
O
9e
1.00
2.02
1.10
1.00
1.04
1.09
5.28
1.18
4.21
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
ppm

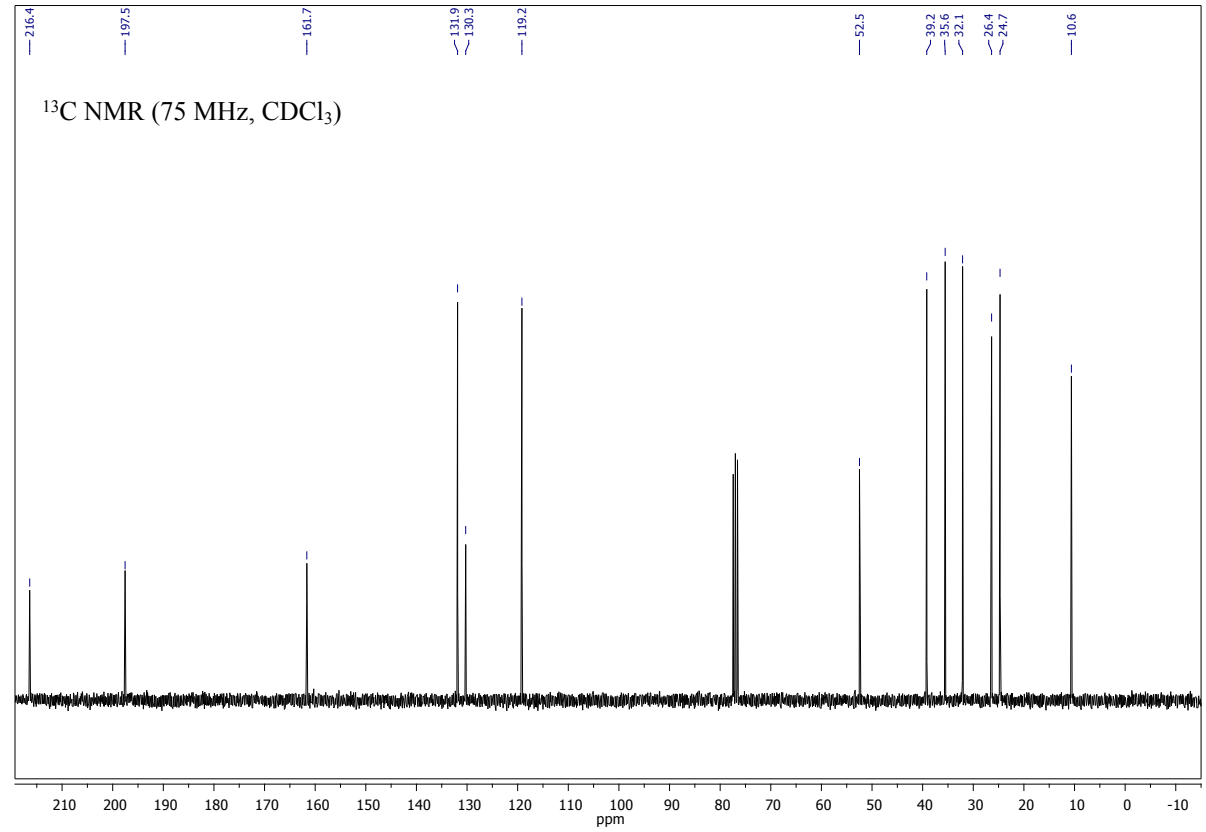

217.2
196.8
160.2
149.3
133.2
133.0
131.9
130.8
128.6
125.3
52.9
36.6
32.3
27.3
25.3
11.0
13C NMR (75 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

^{1}H NMR (300 MHz, $CDCl_3$)

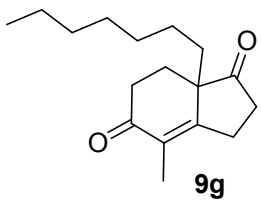


9f

^{13}C NMR (75 MHz, $CDCl_3$)

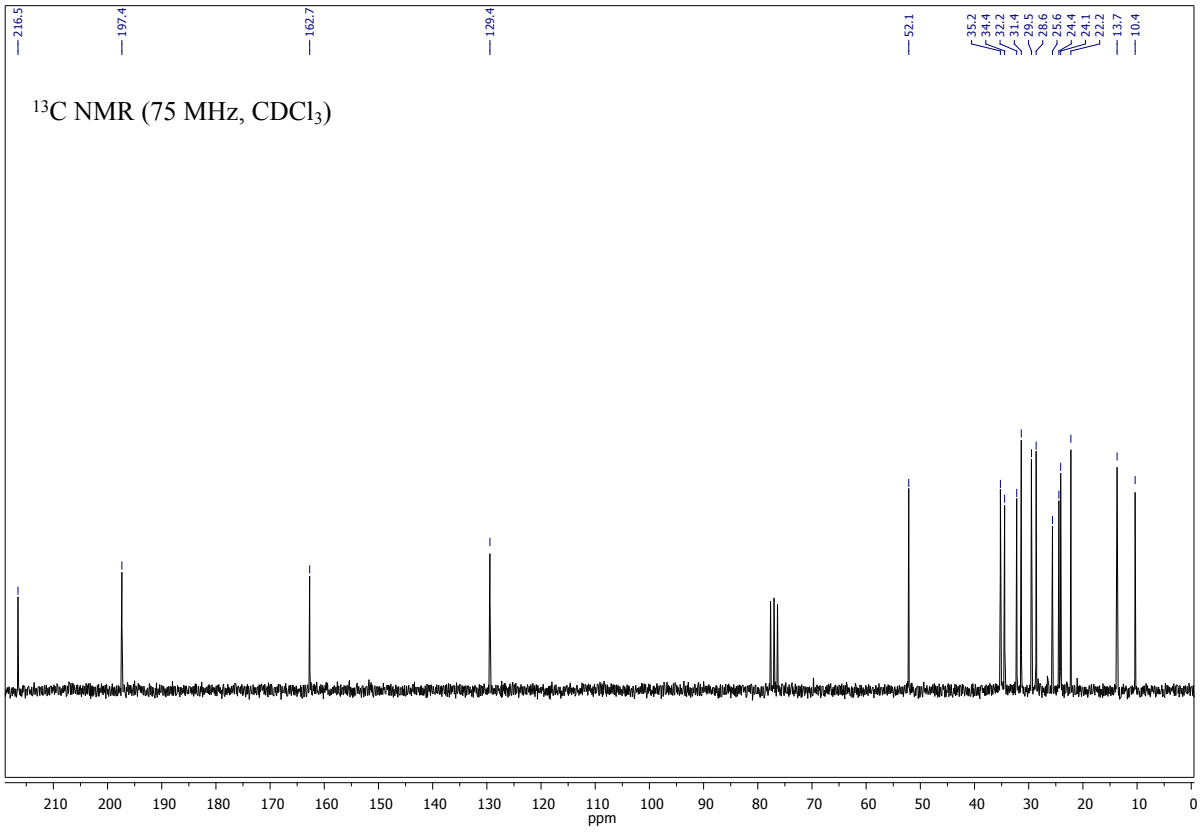


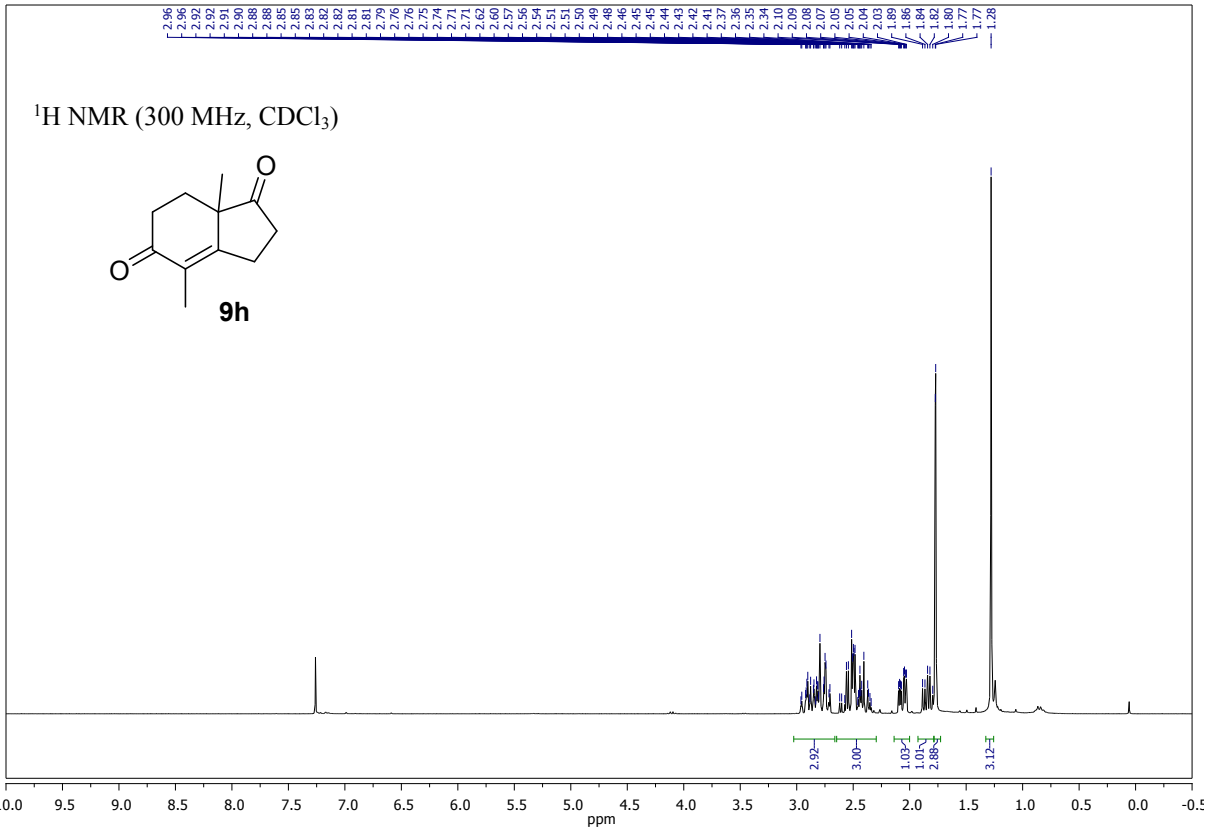
^{1}H NMR (300 MHz, $CDCl_3$)

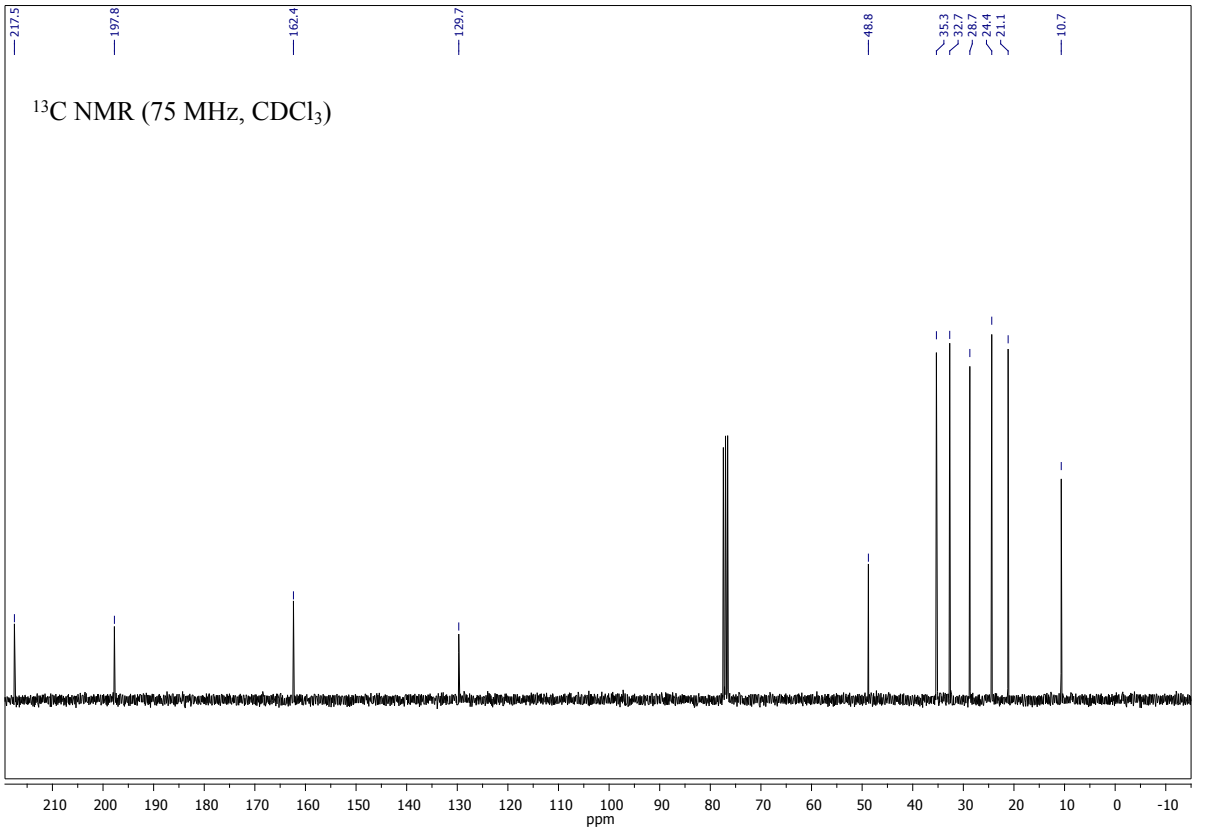


9g

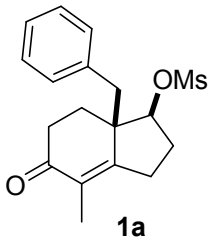
^{13}C NMR (75 MHz, $CDCl_3$)




2.96 2.96 2.92 2.92 2.91 2.90 2.88 2.88 2.85 2.85 2.83 2.82 2.82 2.81 2.81 2.79 2.76 2.76 2.75 2.74 2.71 2.71 2.62 2.60 2.57 2.56 2.54 2.51 2.51 2.50 2.49 2.48 2.46 2.45 2.45 2.44 2.43 2.42 2.41 2.37 2.36 2.35 2.34 2.10 2.09 2.08 2.07 2.05 2.05 2.04 2.03 1.89 1.86 1.84 1.82 1.80 1.77 1.77 1.28
1H NMR (300 MHz, CDCl3)
O
O
9h
2.92
3.00
1.03
1.01
2.88
3.12
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

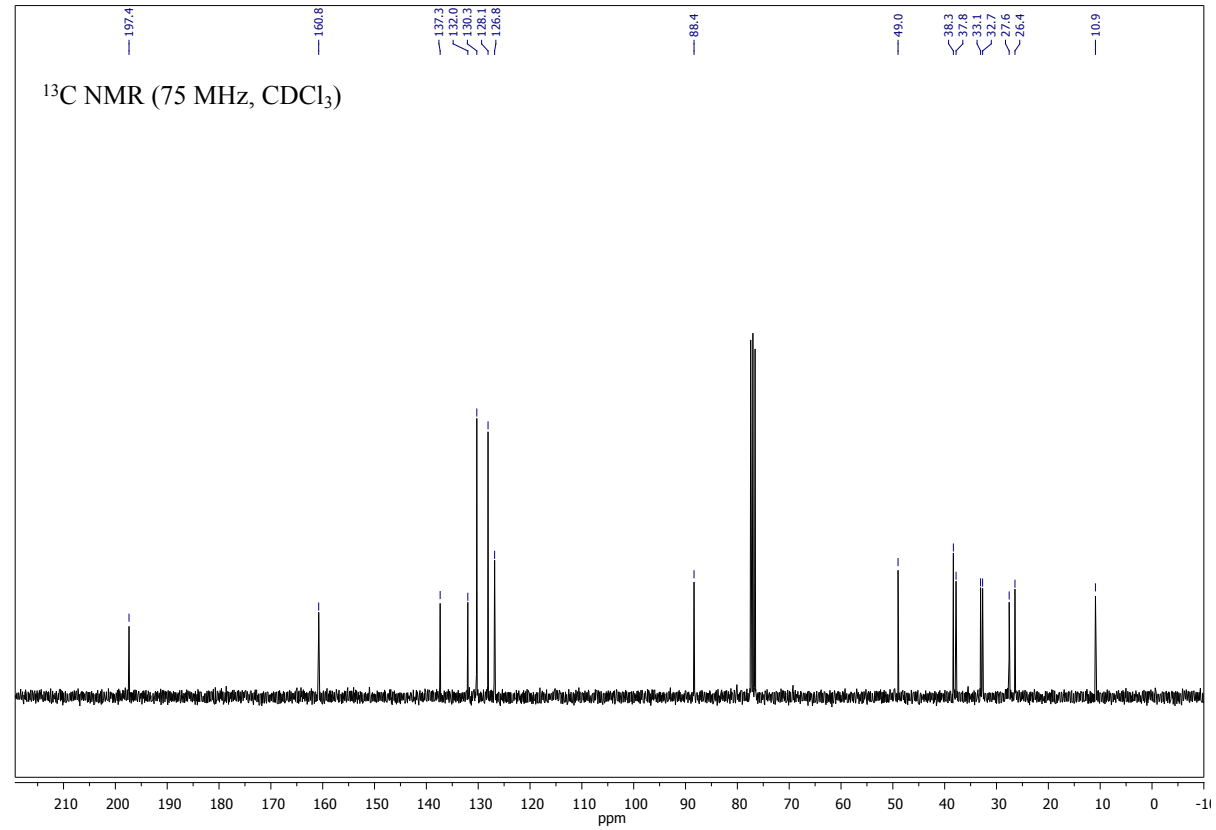

217.5
197.8
162.4
129.7
48.8
35.3
32.7
28.7
24.4
21.1
10.7
13C NMR (75 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

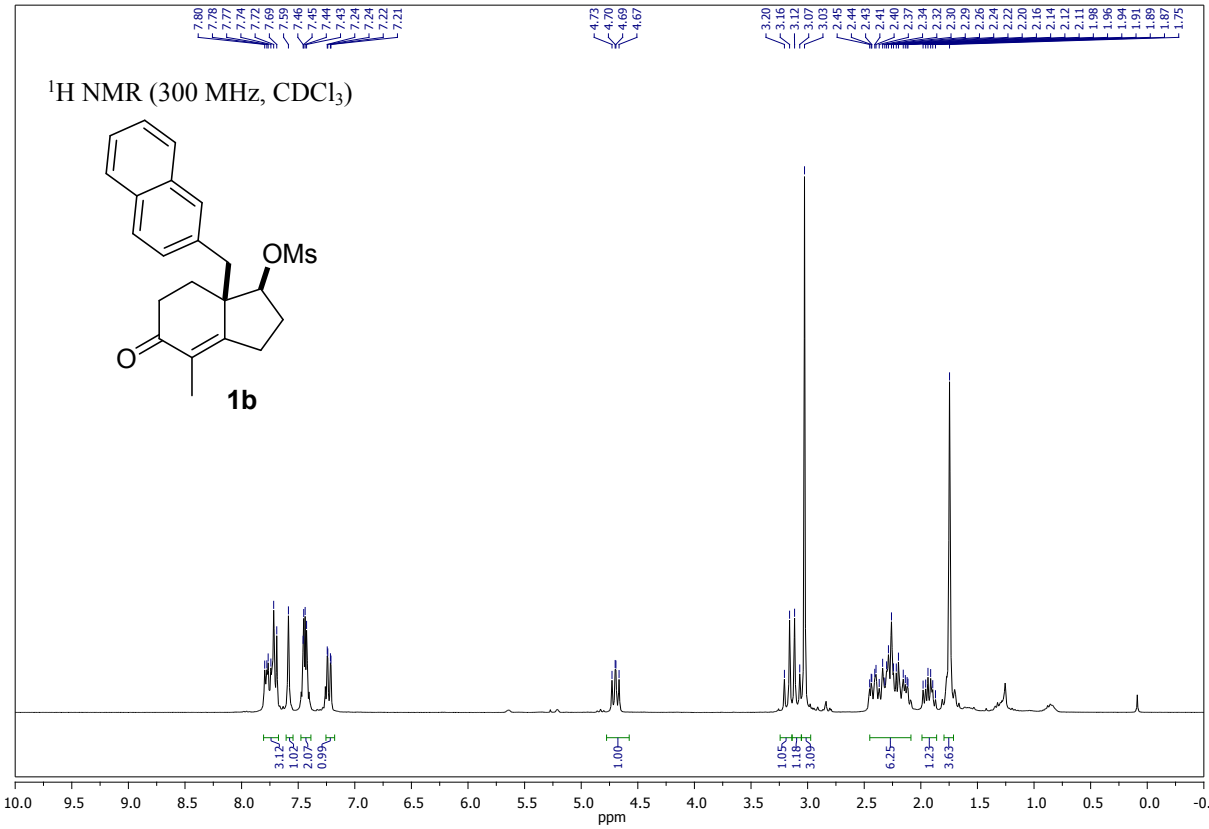
^{1}H NMR (300 MHz, $CDCl_3$)

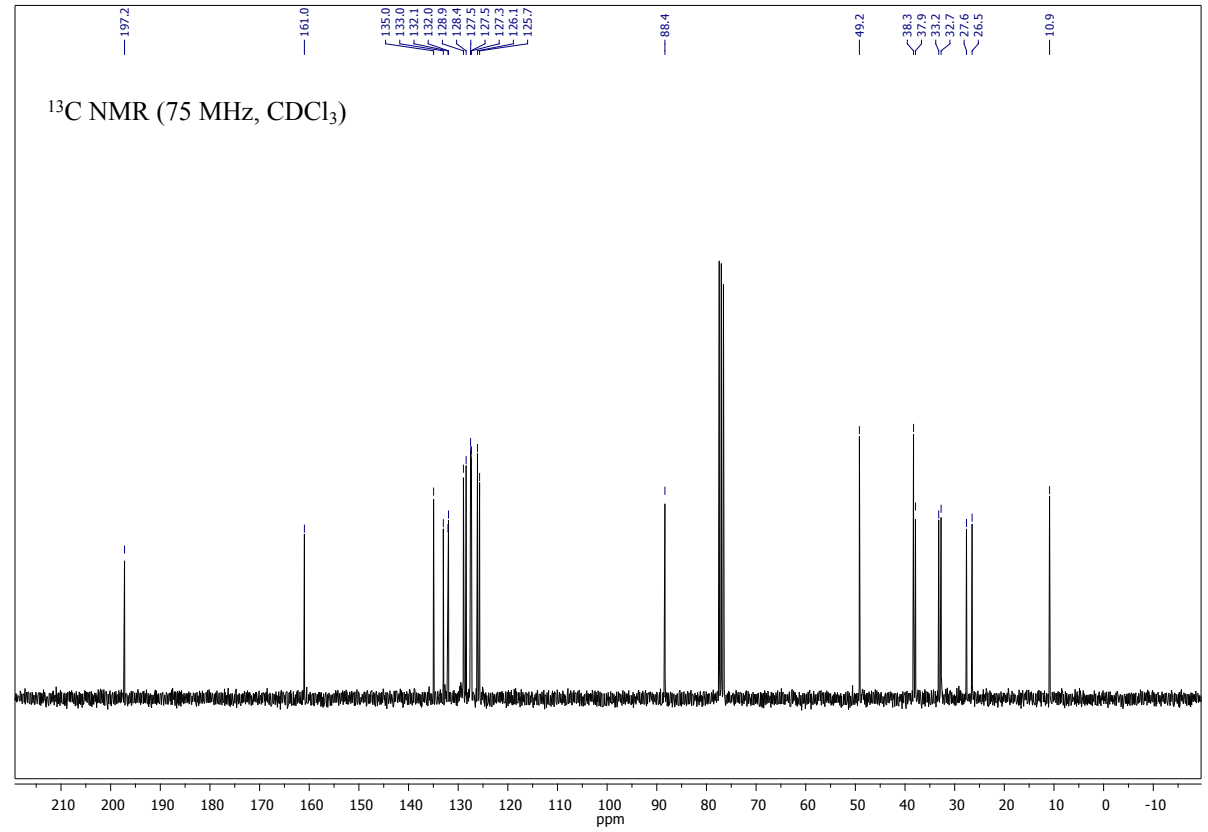


1a

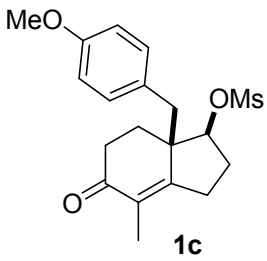
^{13}C NMR (75 MHz, $CDCl_3$)




7.80 7.78 7.77 7.74 7.72 7.69 7.59 7.46 7.45 7.44 7.43 7.24 7.24 7.22 7.21
4.73 4.70 4.69 4.67
3.20 3.16 3.12 3.07 3.03
2.45 2.44 2.43 2.41 2.40 2.37 2.34 2.32 2.30 2.29 2.26 2.24 2.22 2.20 2.16 2.14 2.12 2.11 1.98 1.96 1.94 1.91 1.89 1.87 1.75
1H NMR (300 MHz, CDCl3)
OMs
O
1b
3.12 1.02 2.07 0.99
1.00
1.05 1.18 3.09
6.25
1.23
3.63
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
ppm

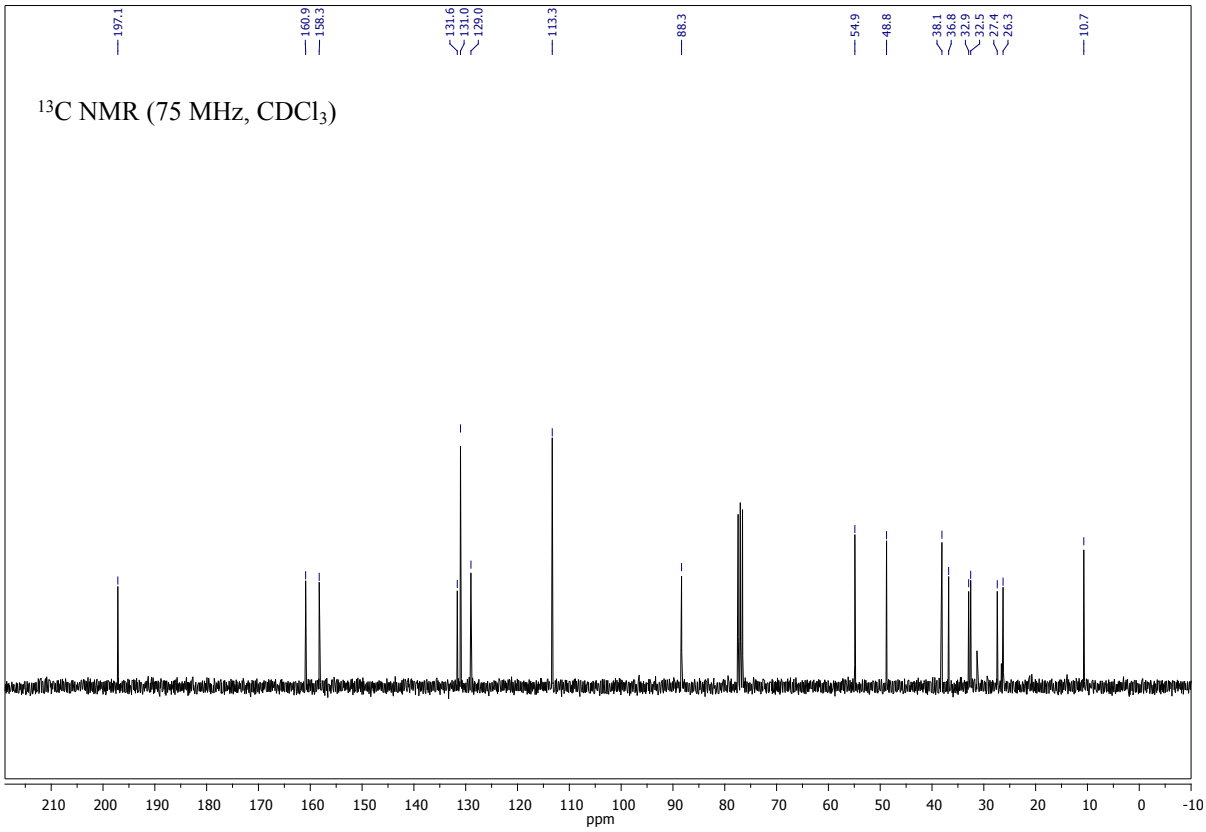

197.2
161.0
135.0 133.0 132.1 132.0 128.9 128.4 127.5 127.5 127.3 126.1 125.7
88.4
49.2
38.3 37.9 33.2 32.7 27.6 26.5
10.9
13C NMR (75 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

^{1}H NMR (300 MHz, $CDCl_3$)

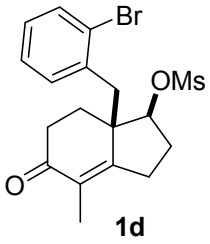


1c

^{13}C NMR (75 MHz, $CDCl_3$)

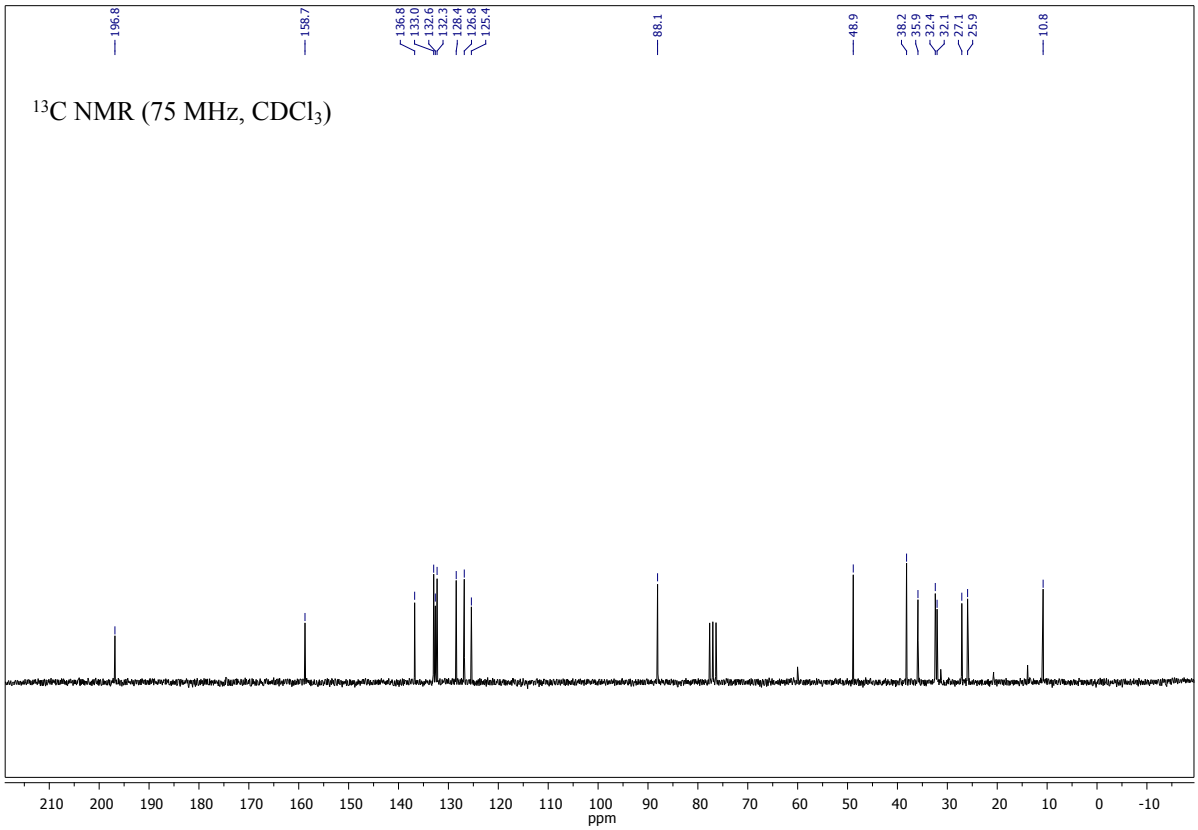


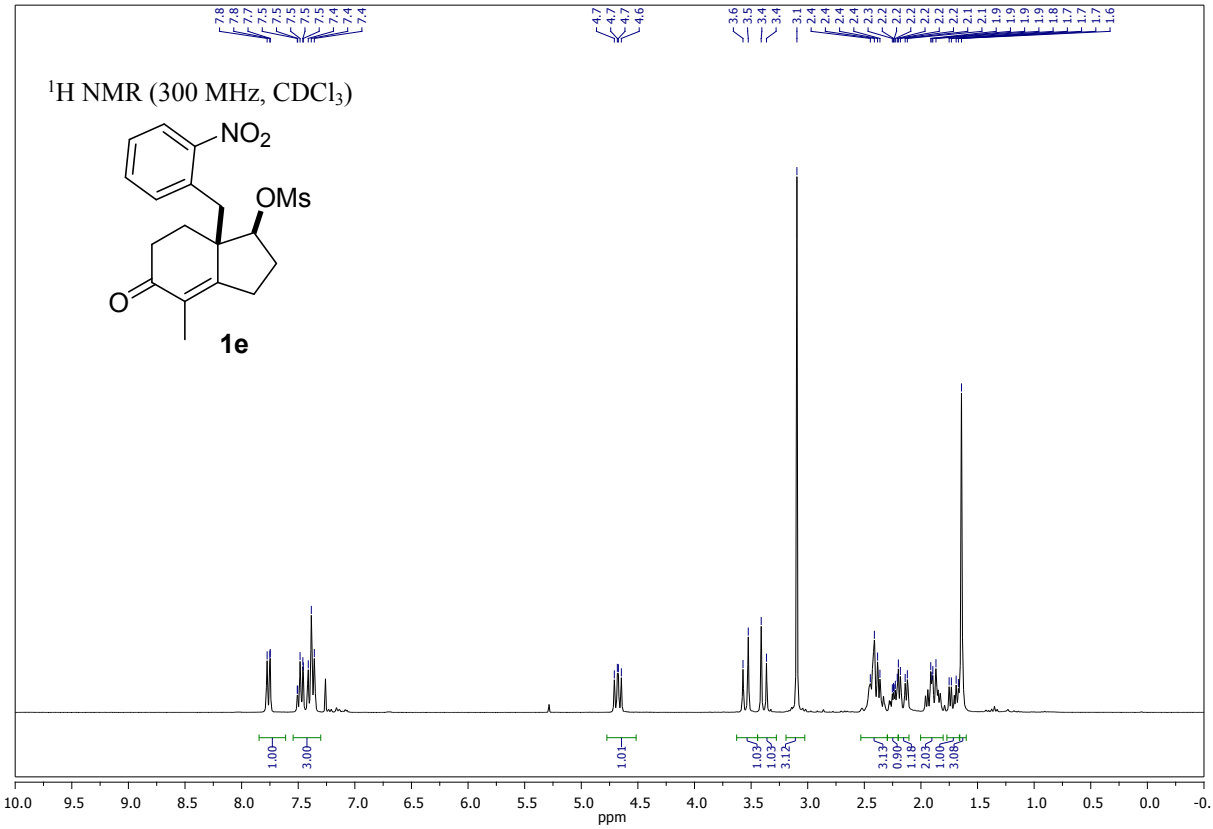
^{1}H NMR (300 MHz, $CDCl_3$)

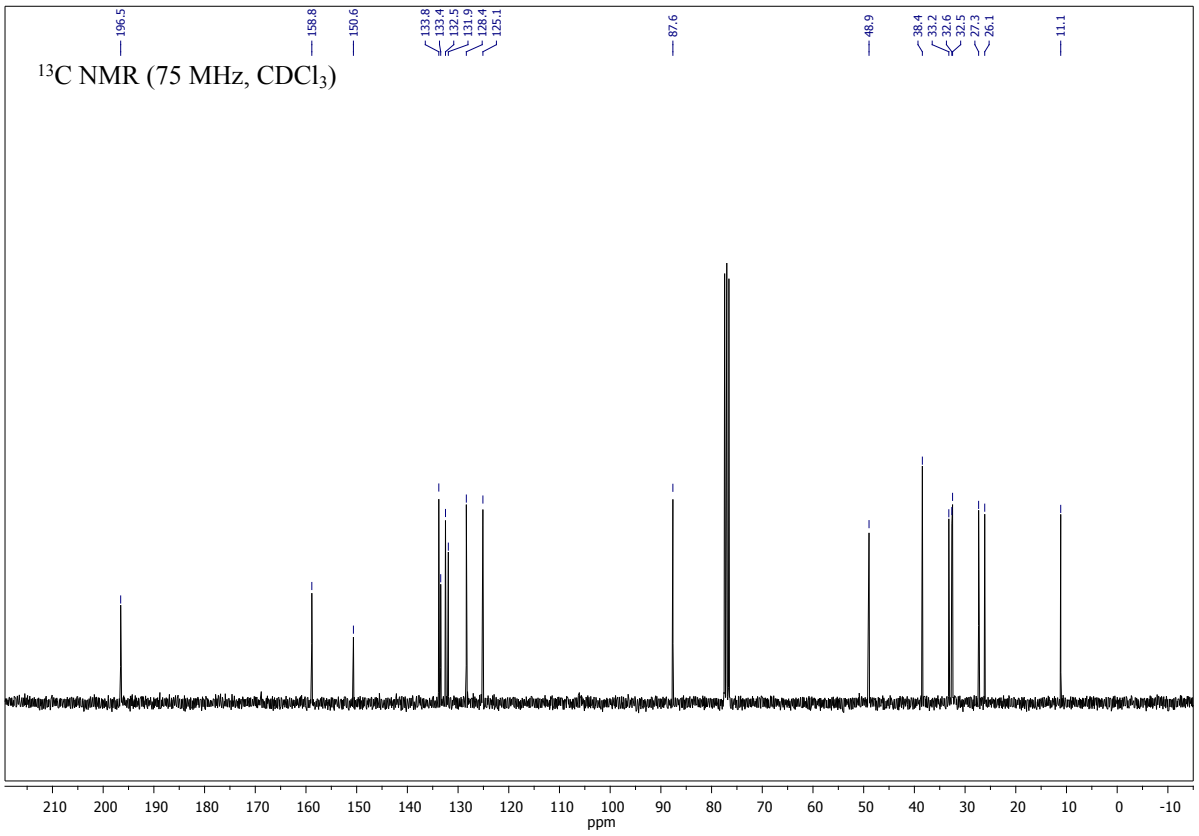


1d

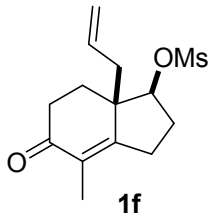
^{13}C NMR (75 MHz, $CDCl_3$)




^{1}H NMR (300 MHz, $CDCl_3$)
NO_2
OMs
O
1e
ppm

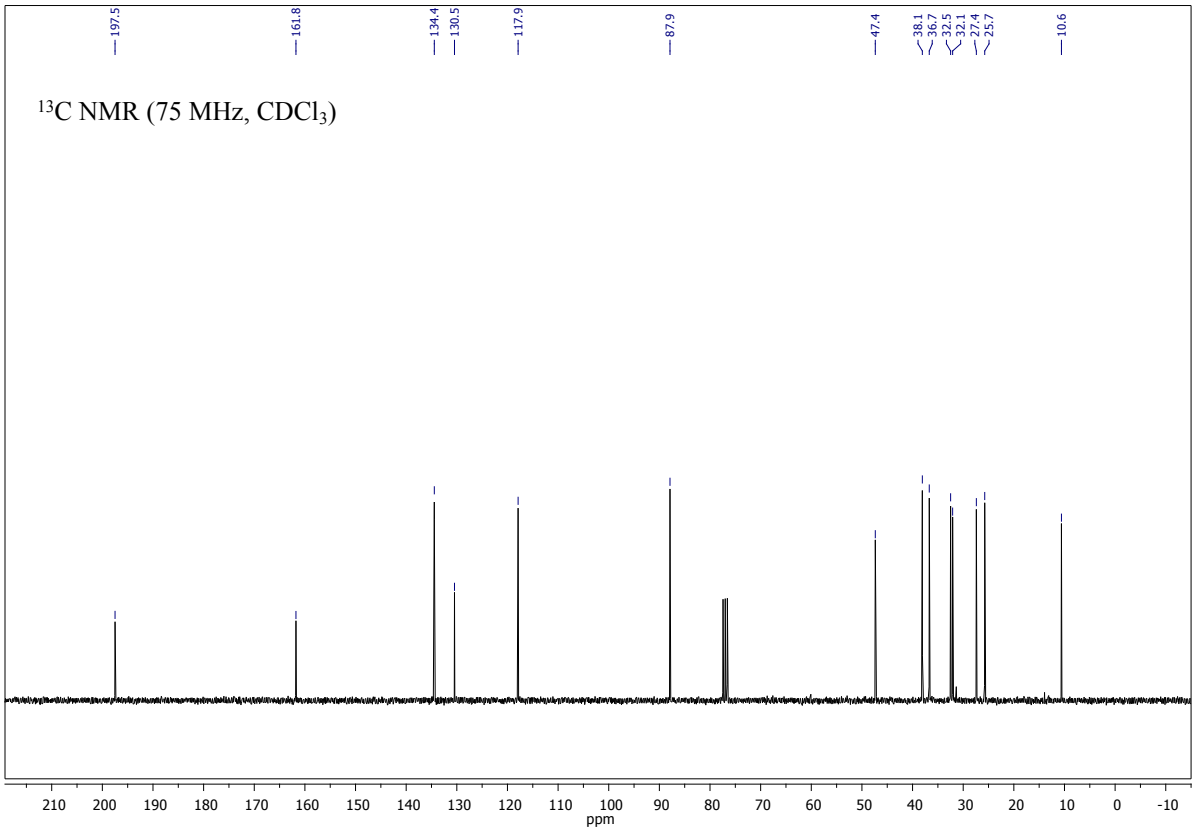

^{13}C NMR (75 MHz, $CDCl_3$)
ppm

^{1}H NMR (300 MHz, $CDCl_3$)

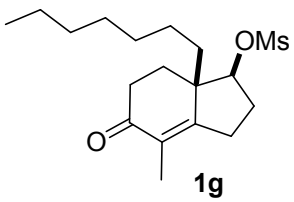


1f

^{13}C NMR (75 MHz, $CDCl_3$)

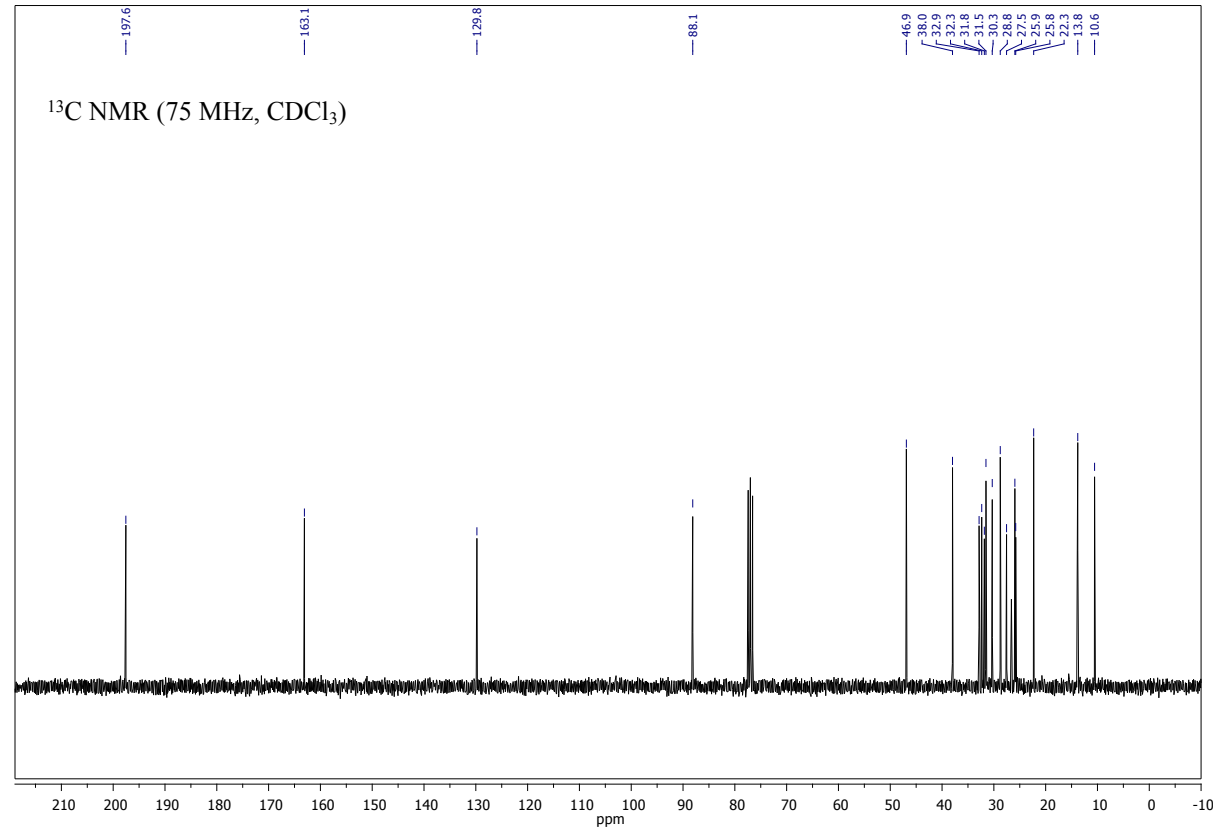


^{1}H NMR (300 MHz, $CDCl_3$)

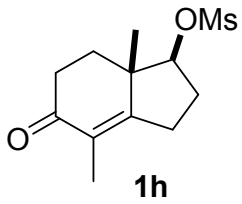


1g

^{13}C NMR (75 MHz, $CDCl_3$)

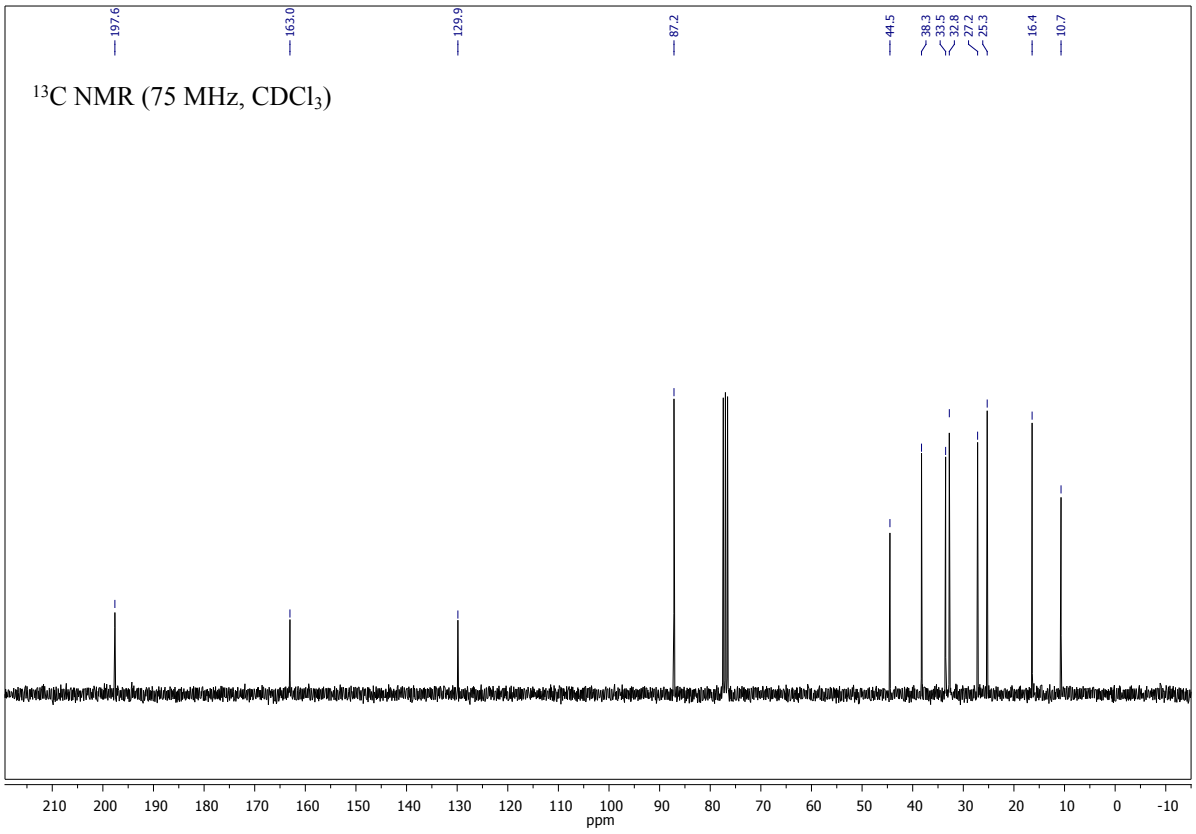


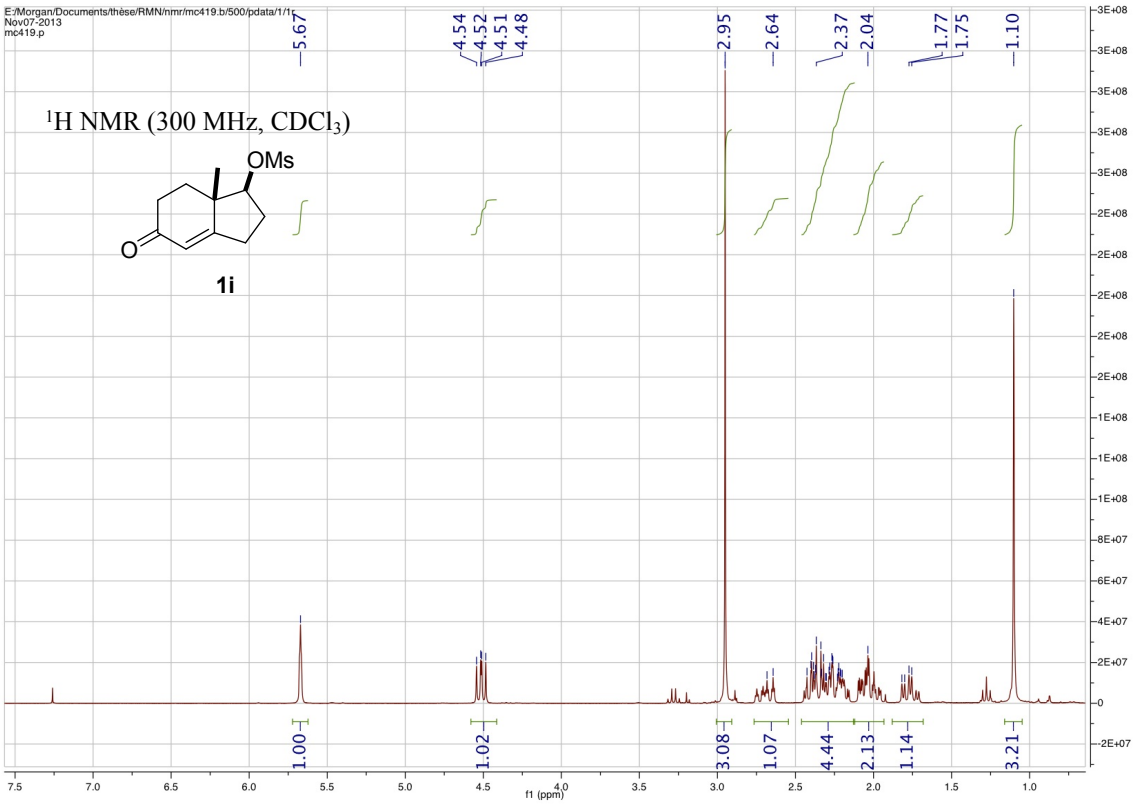
^{1}H NMR (300 MHz, $CDCl_3$)



1h

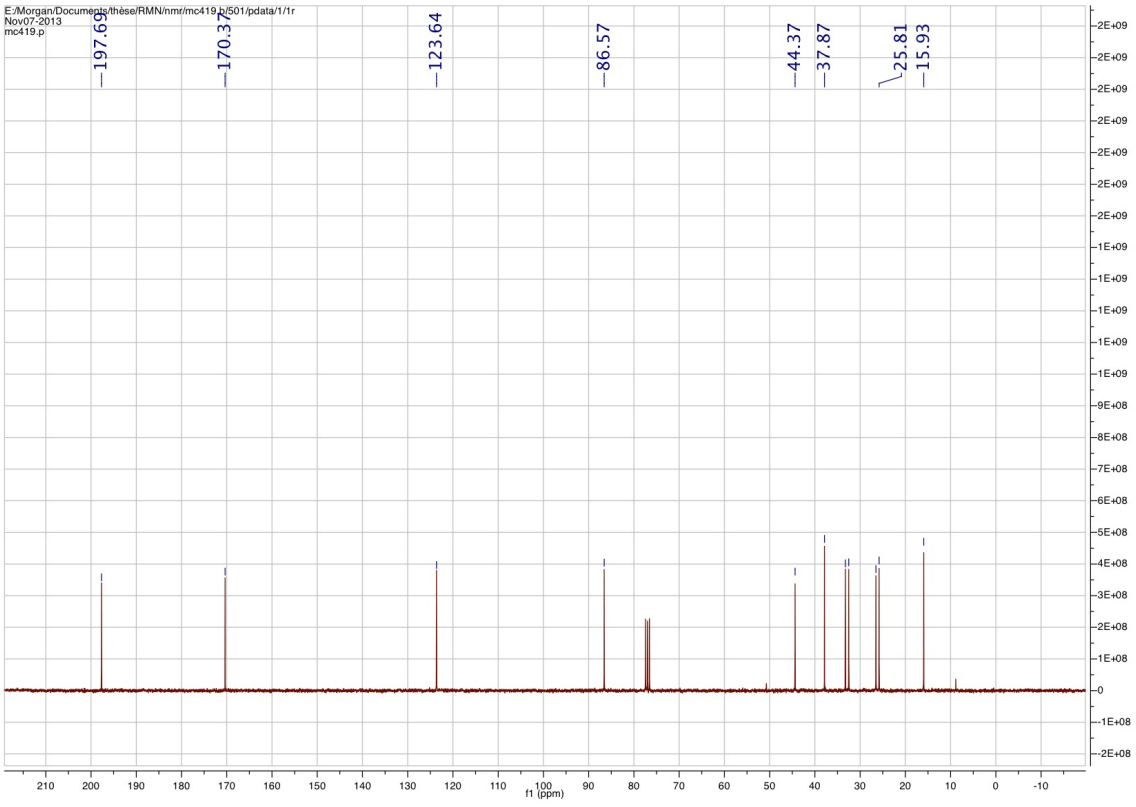
^{13}C NMR (75 MHz, $CDCl_3$)

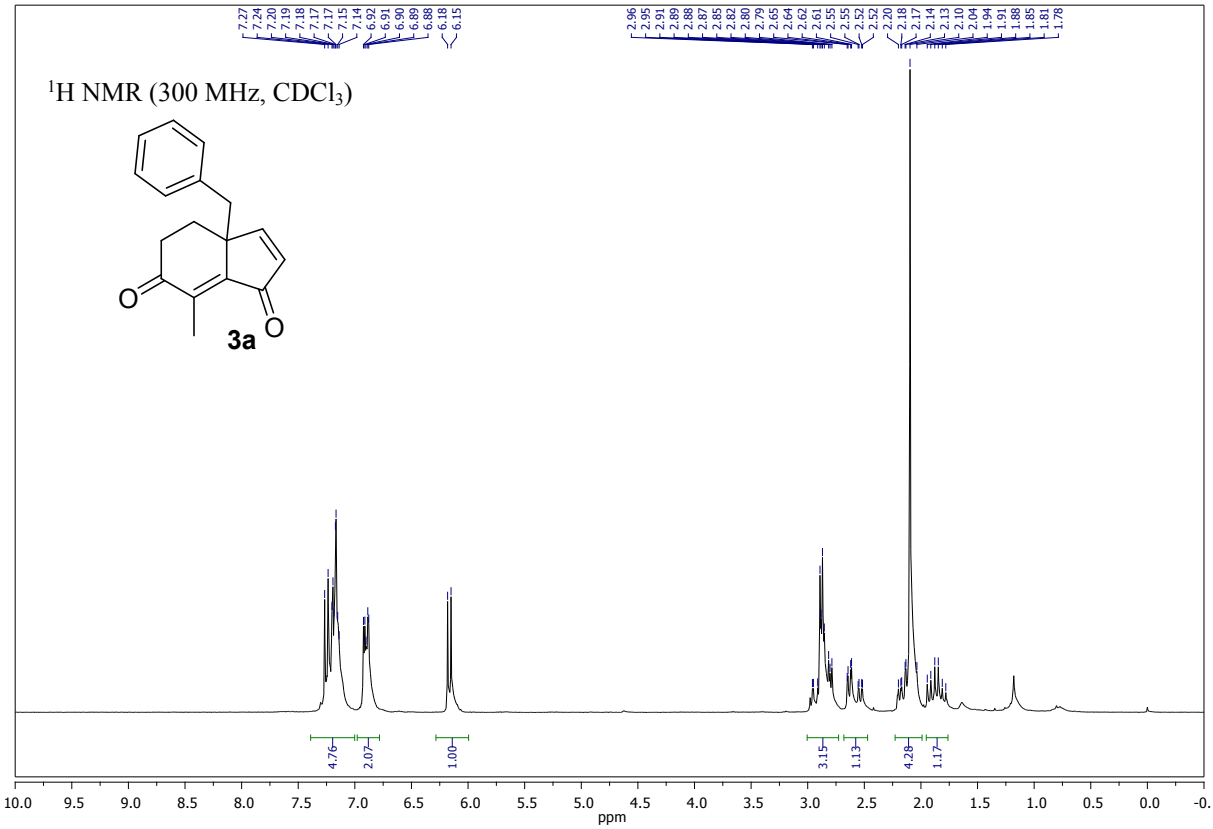


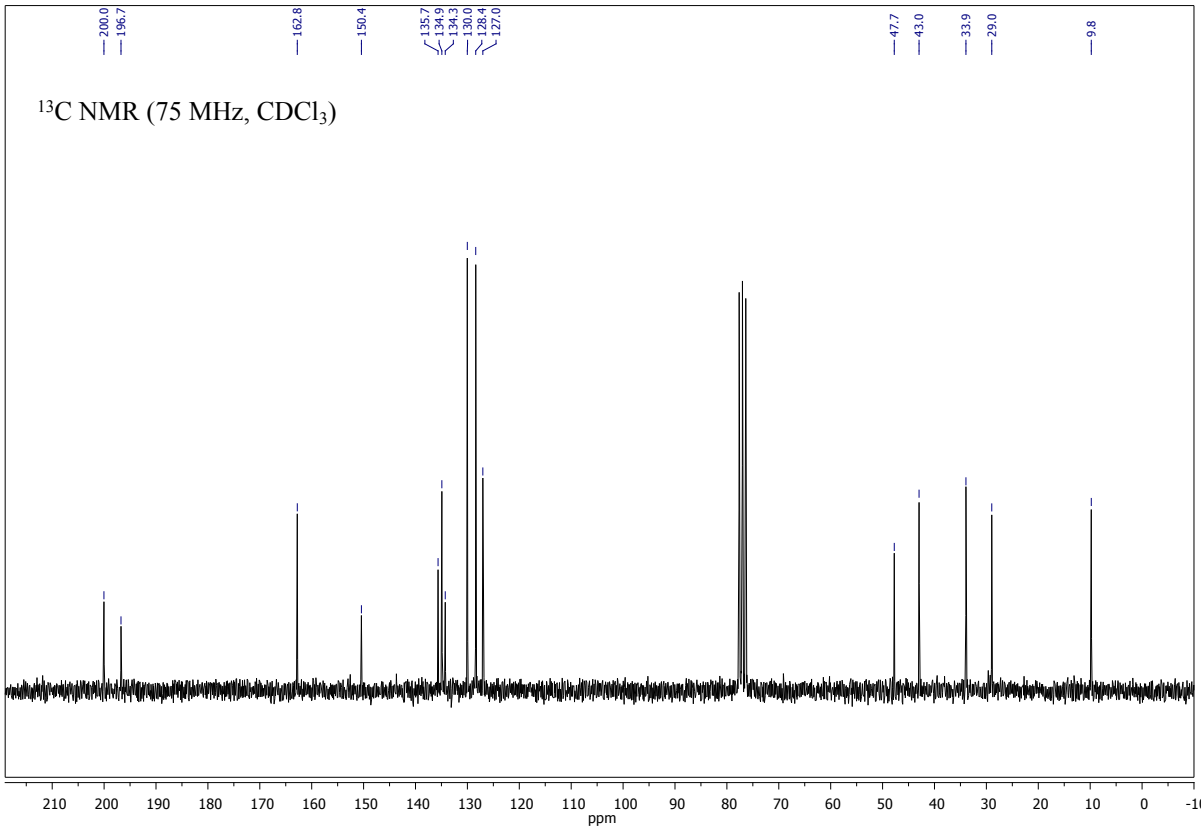


^{1}H NMR (300 MHz, $CDCl_3$)

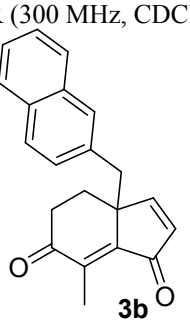
1i




^{1}H NMR (300 MHz, $CDCl_3$)
O
O
3a
ppm

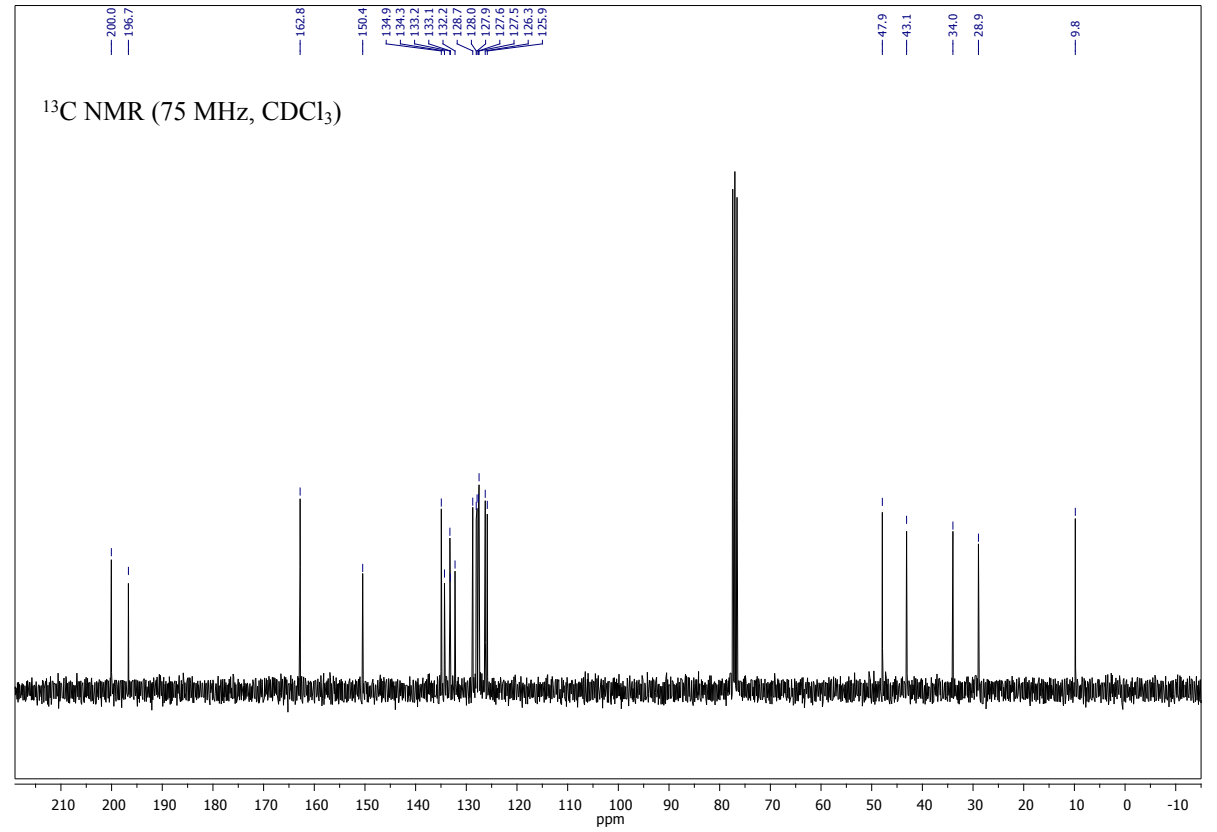

^{13}C NMR (75 MHz, $CDCl_3$)
ppm

^{1}H NMR (300 MHz, $CDCl_3$)

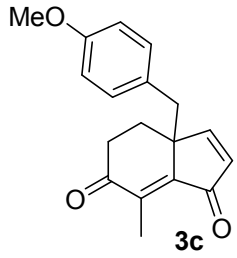


3b

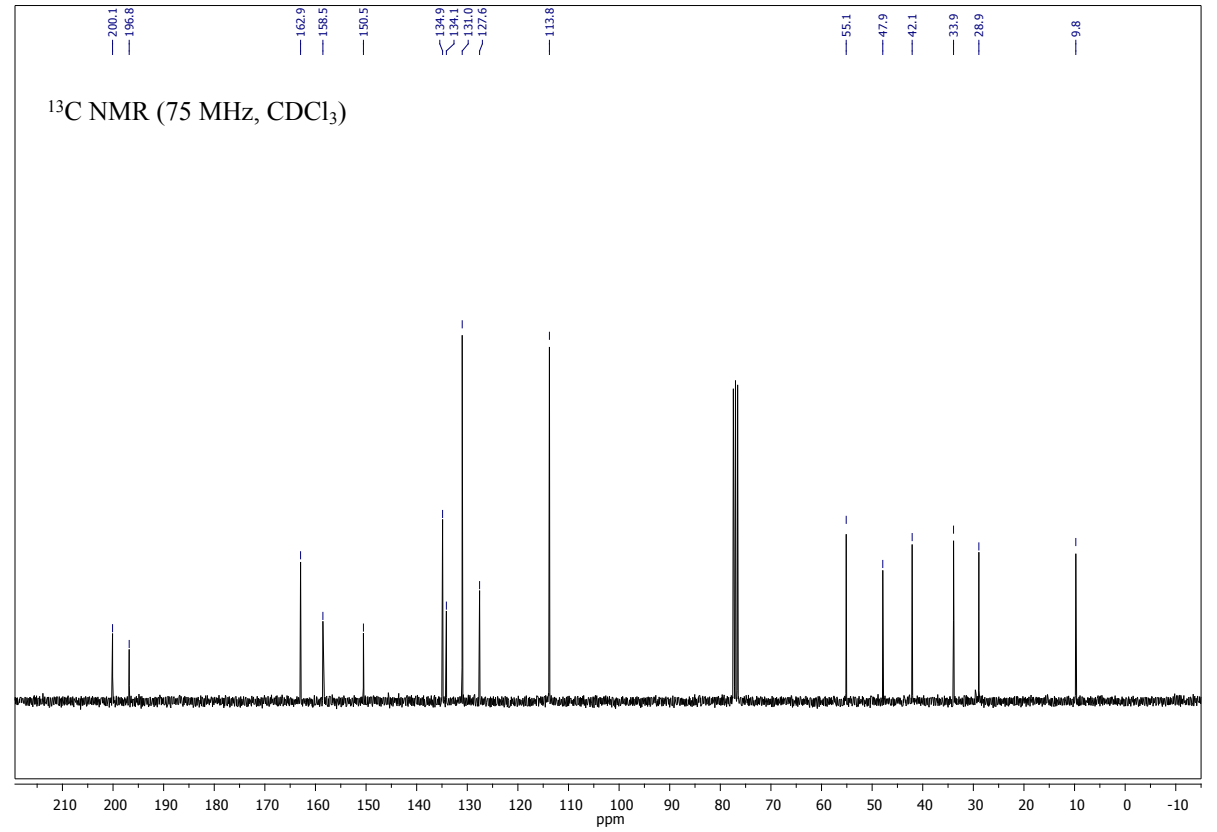
^{13}C NMR (75 MHz, $CDCl_3$)

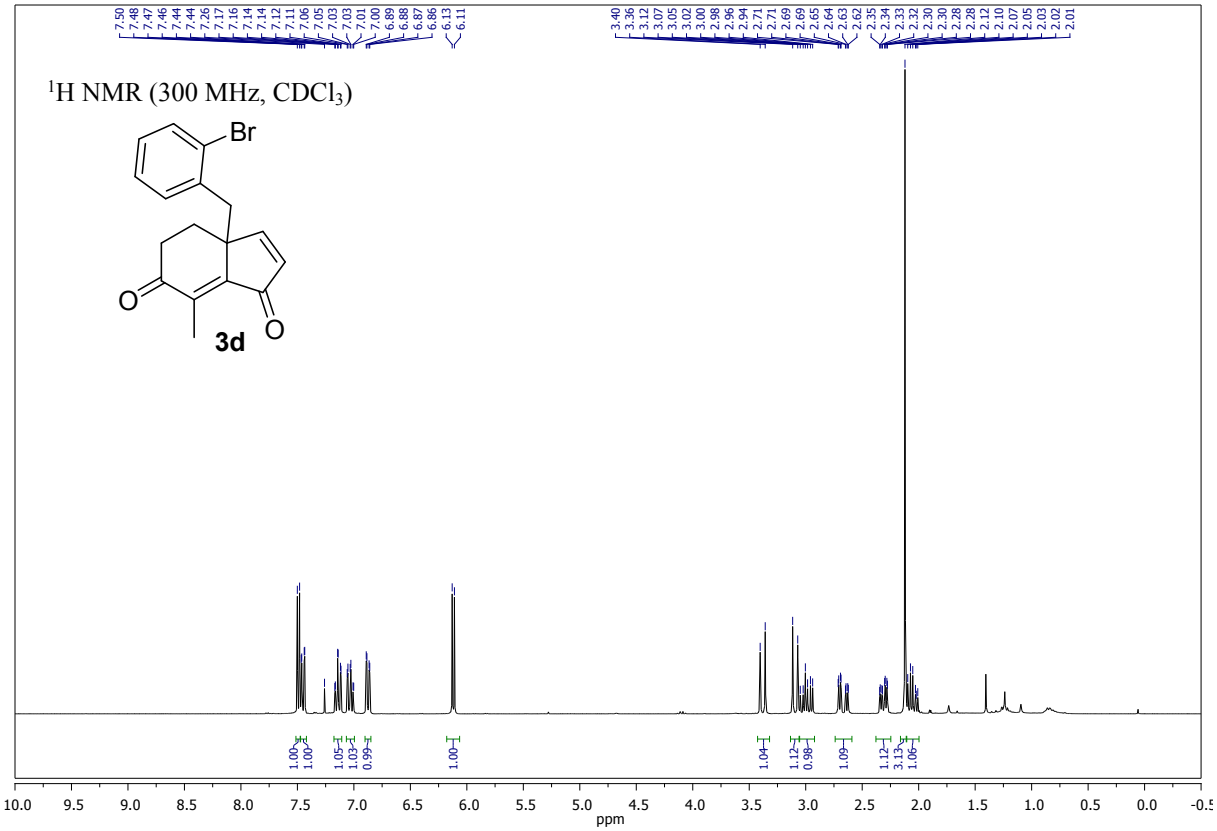


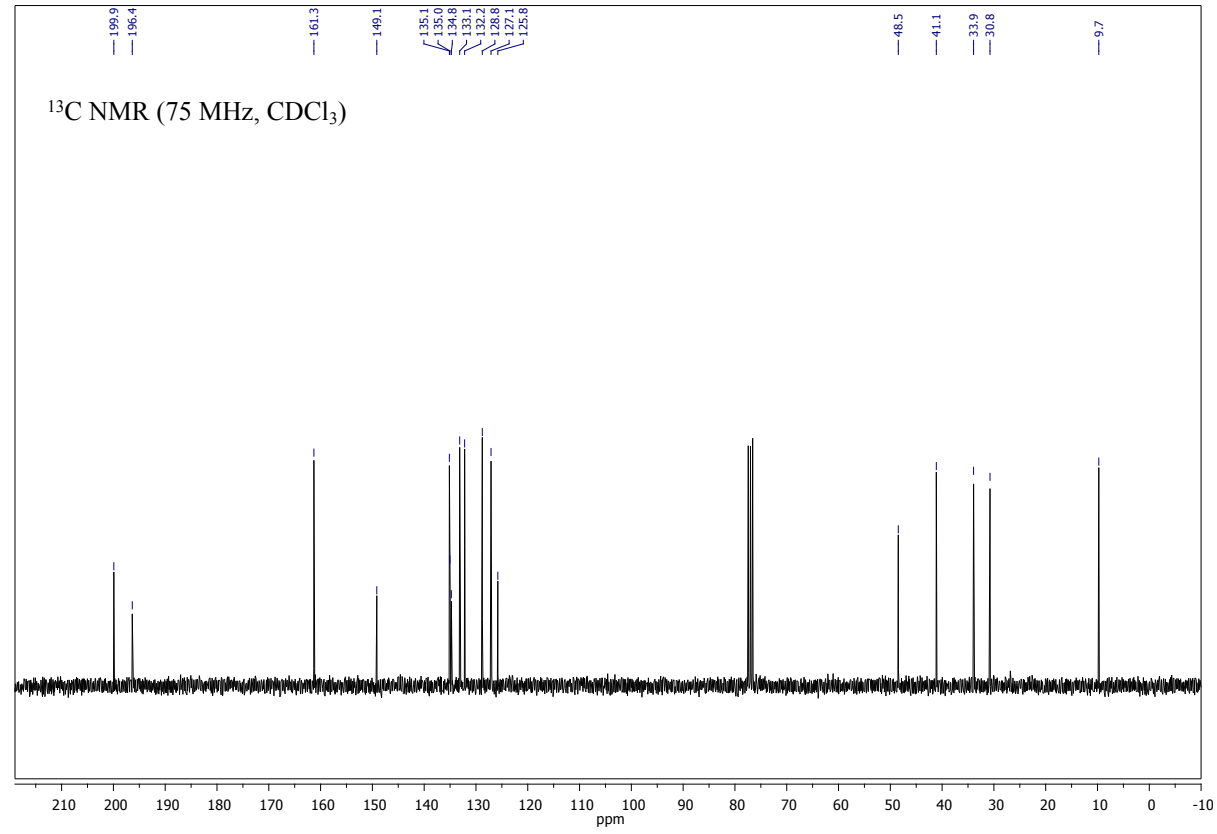
^{1}H NMR (300 MHz, $CDCl_3$)

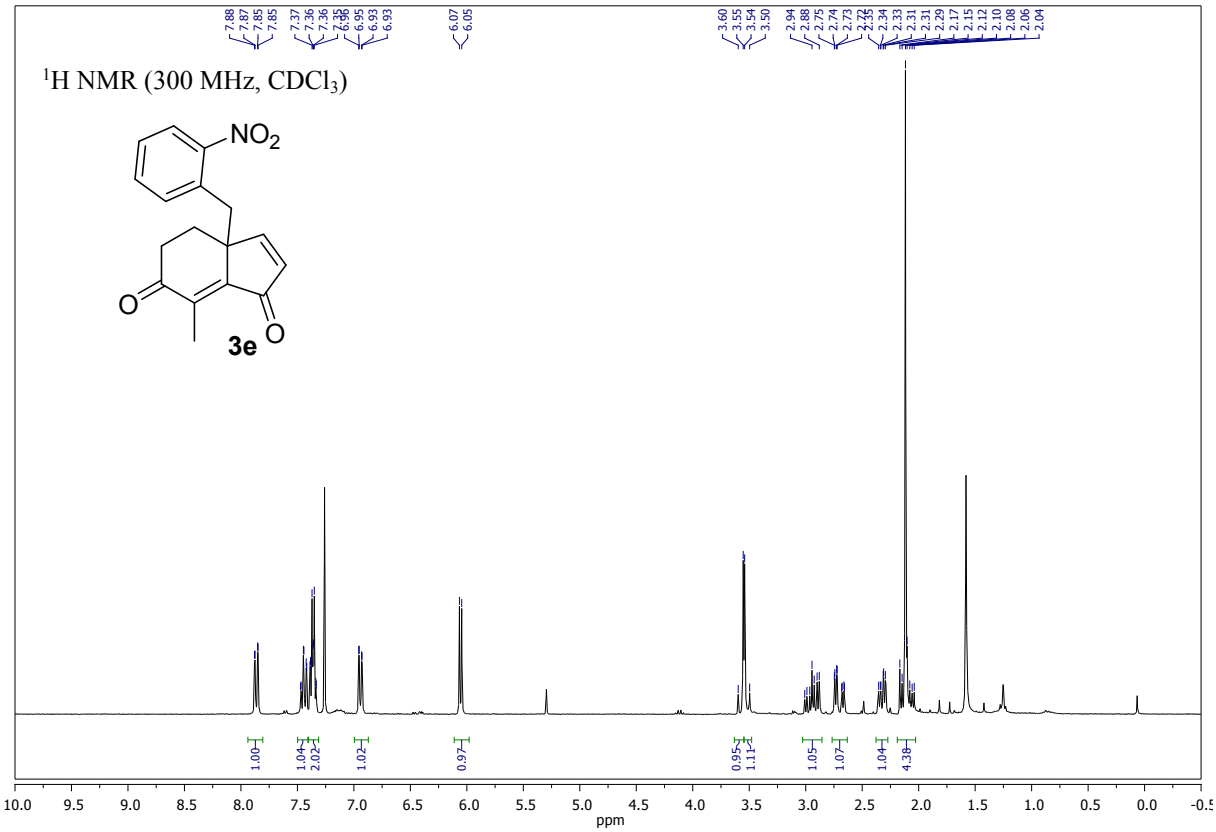


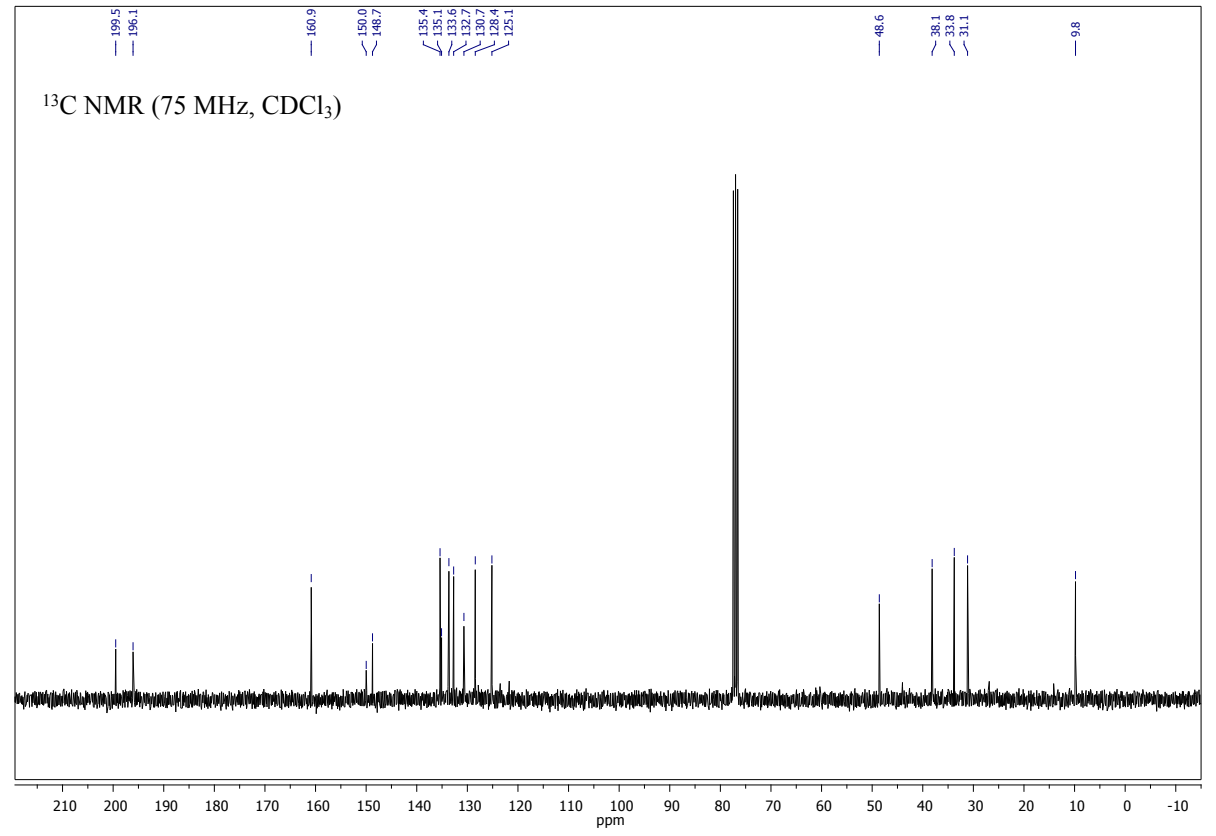
^{13}C NMR (75 MHz, $CDCl_3$)

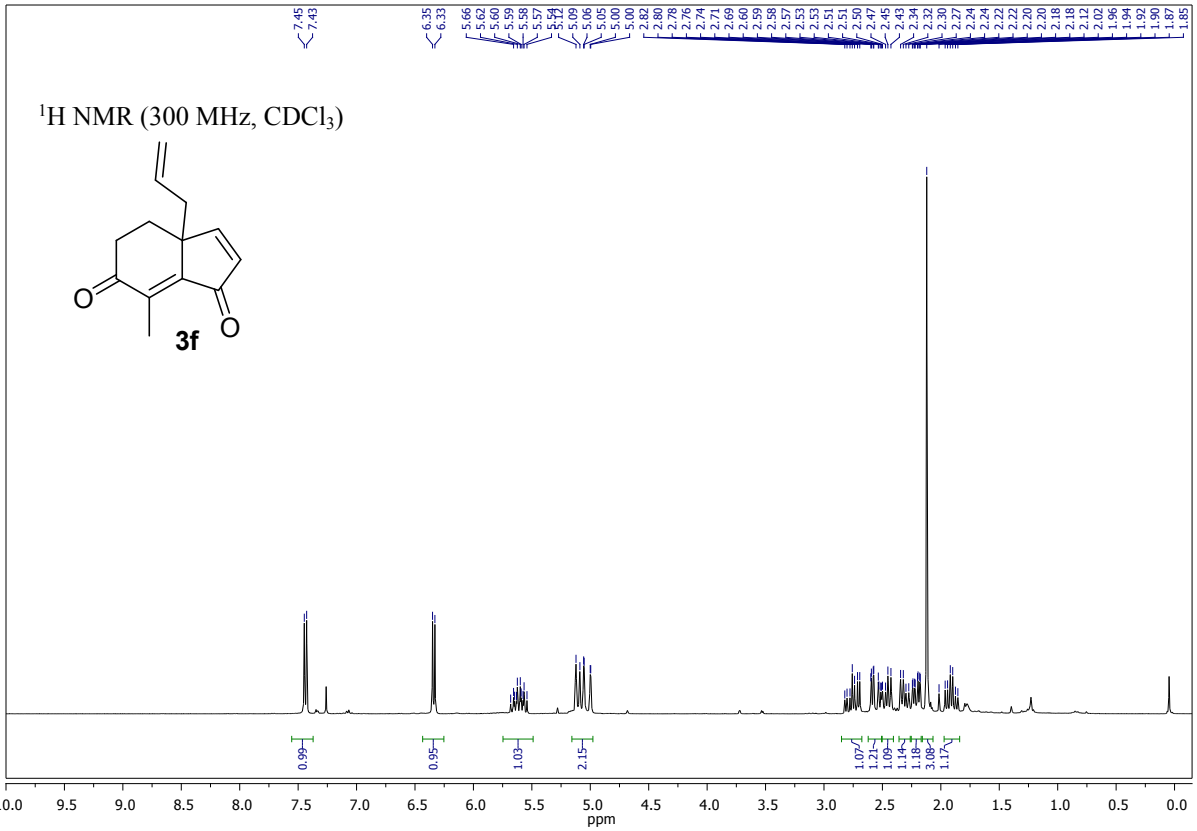



7.50 7.48 7.47 7.46 7.44 7.44 7.26 7.17 7.16 7.14 7.14 7.12 7.11 7.06 7.05 7.03 7.03 7.01 7.00 6.89 6.88 6.87 6.86 6.13 6.11
3.40 3.36 3.12 3.07 3.05 3.02 3.00 2.98 2.96 2.94 2.71 2.71 2.69 2.69 2.65 2.64 2.63 2.62 2.35 2.34 2.33 2.32 2.30 2.30 2.28 2.28 2.12 2.10 2.07 2.05 2.03 2.02 2.01
1H NMR (300 MHz, CDCl3)
Br
O
O
3d
1.00 1.00 1.05 1.03 0.99 1.00 1.04 1.12 0.98 1.09 1.12 3.13 1.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


199.9 196.4 161.3 149.1 135.1 135.0 134.8 133.1 132.2 128.8 127.1 125.8 48.5 41.1 33.9 30.8 9.7
13C NMR (75 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

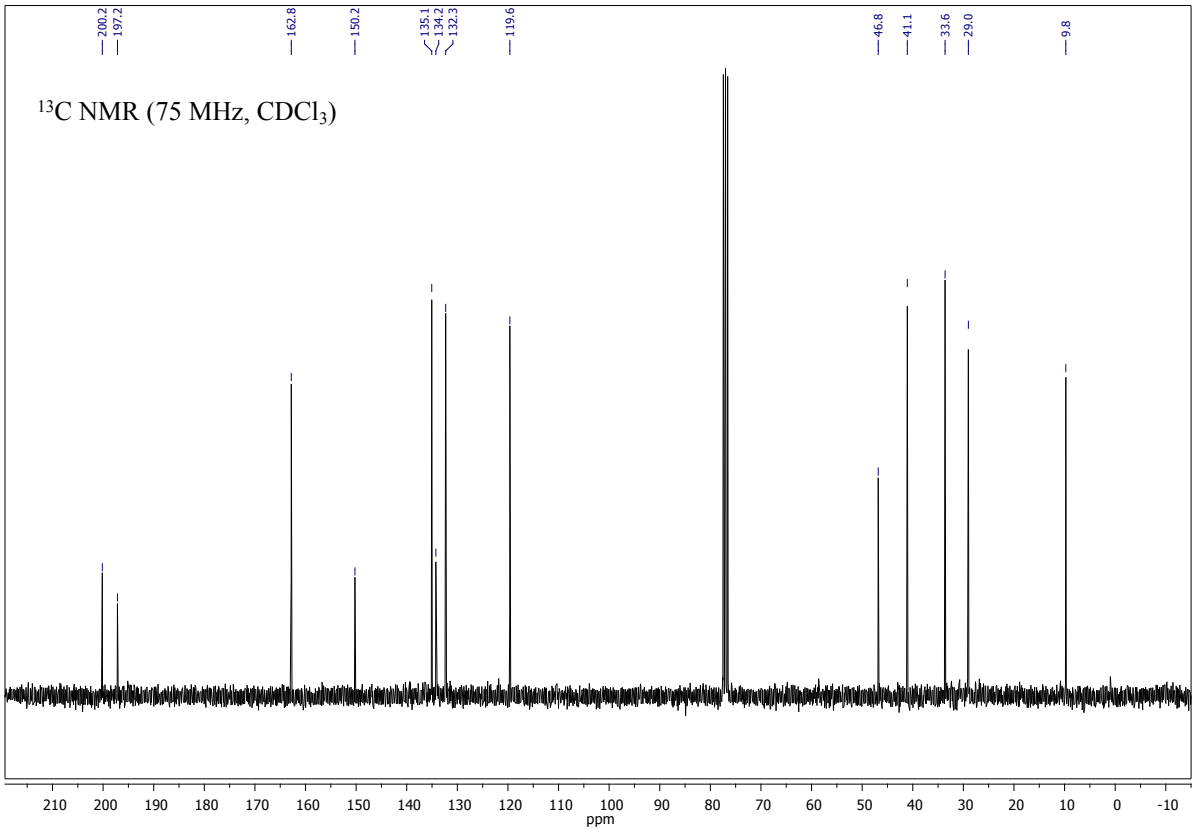

7.88
7.87
7.85
7.85
7.37
7.36
7.36
7.35
6.95
6.93
6.93
6.07
6.05
3.60
3.55
3.54
3.50
2.94
2.88
2.75
2.74
2.73
2.72
2.35
2.34
2.33
2.31
2.31
2.29
2.17
2.15
2.12
2.10
2.08
2.06
2.04
1H NMR (300 MHz, CDCl3)
NO2
O
O
3e
1.00
1.04
2.02
1.02
0.97
0.95
1.11
1.05
1.07
1.04
4.38
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


199.5
196.1
160.9
150.0
148.7
135.4
135.1
133.6
132.7
130.7
128.4
125.1
48.6
38.1
33.8
31.1
9.8
13C NMR (75 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

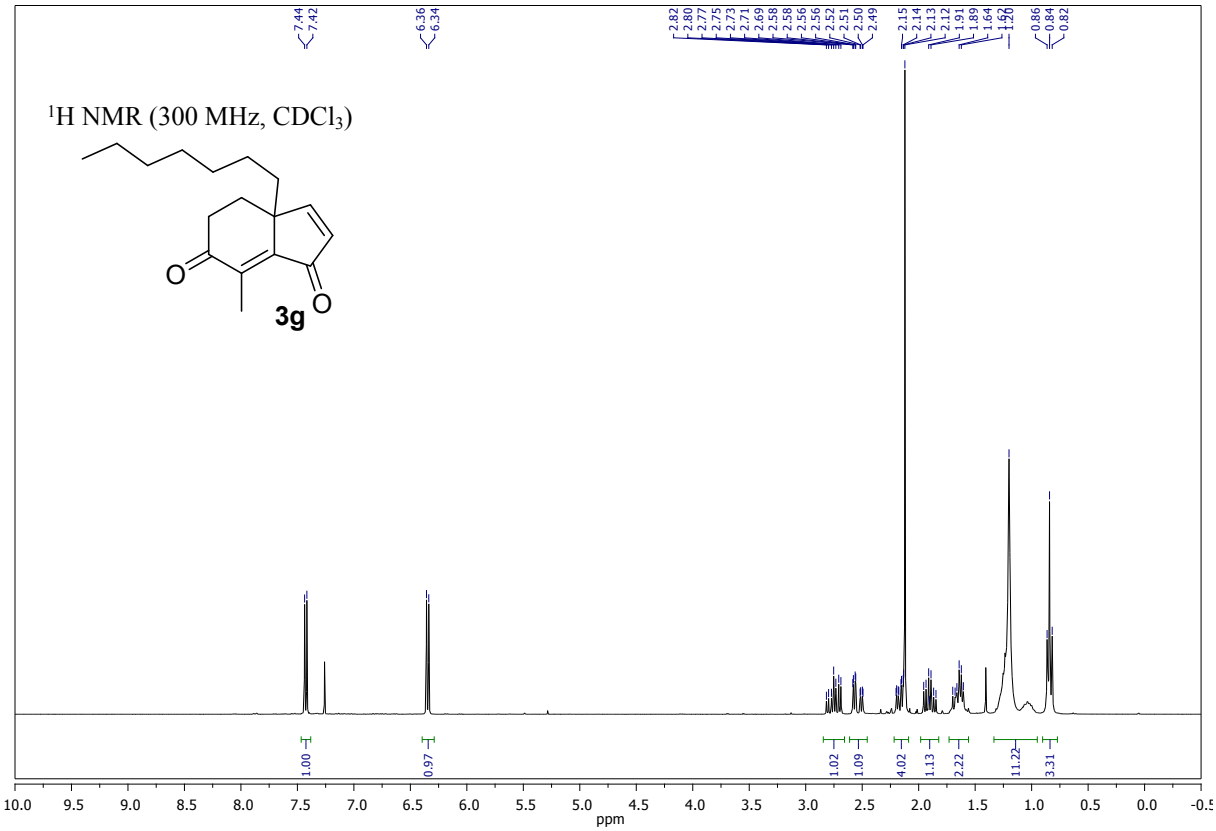


^{1}H NMR (300 MHz, $CDCl_3$)

3f

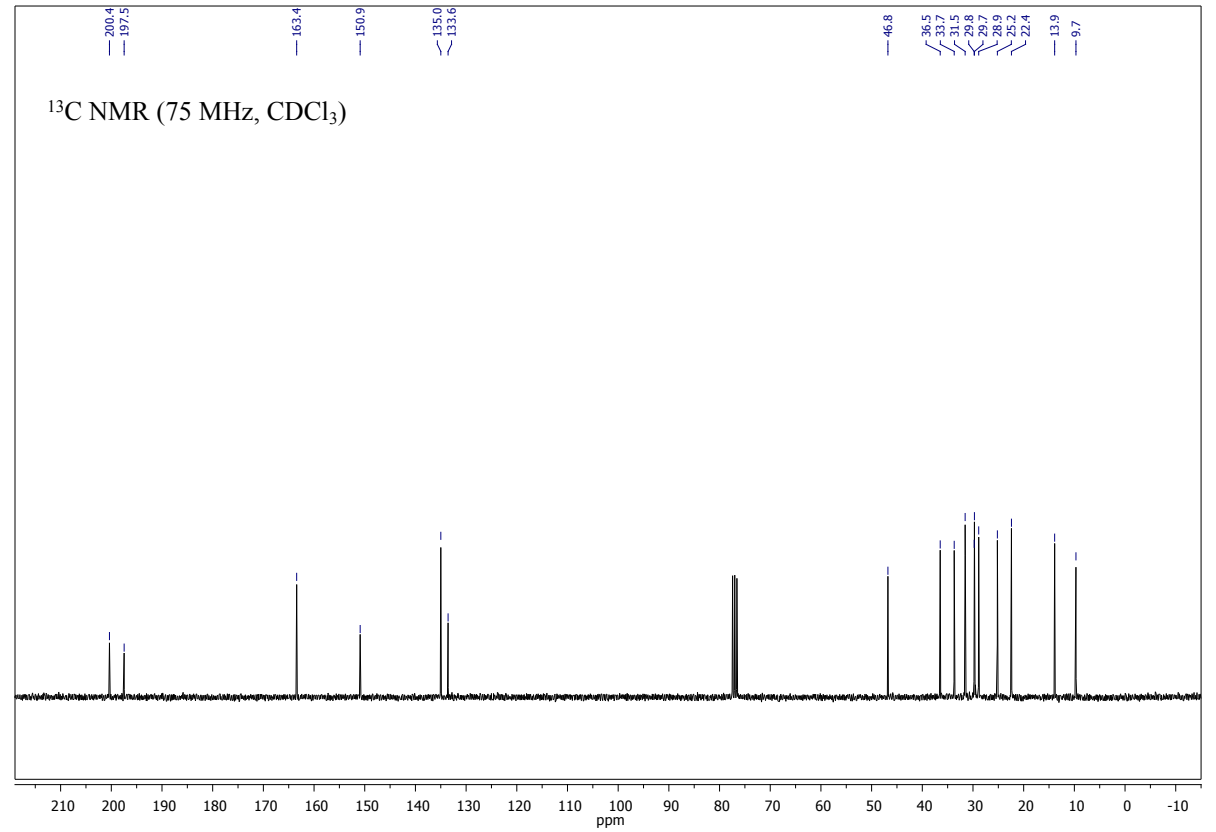


^{13}C NMR (75 MHz, $CDCl_3$)



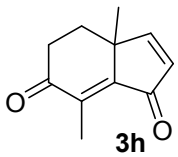
^{1}H NMR (300 MHz, $CDCl_3$)

3g



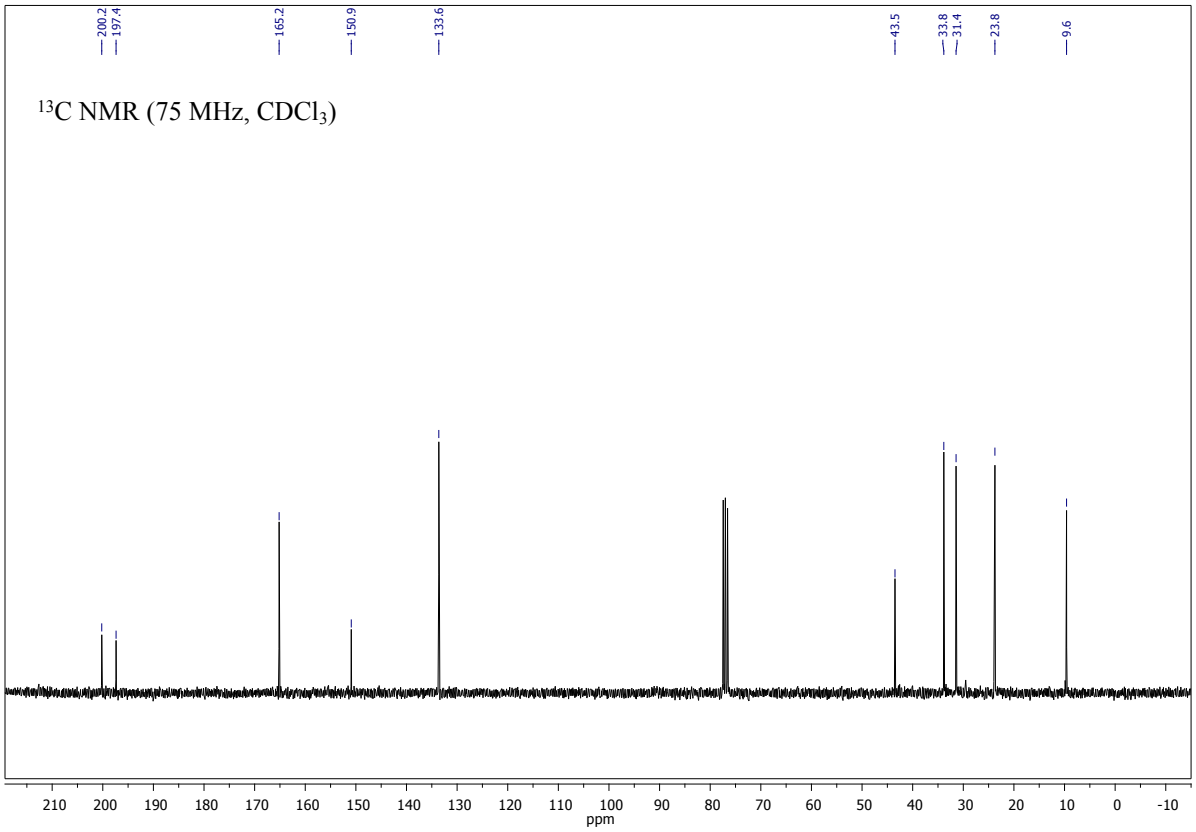
^{13}C NMR (75 MHz, $CDCl_3$)

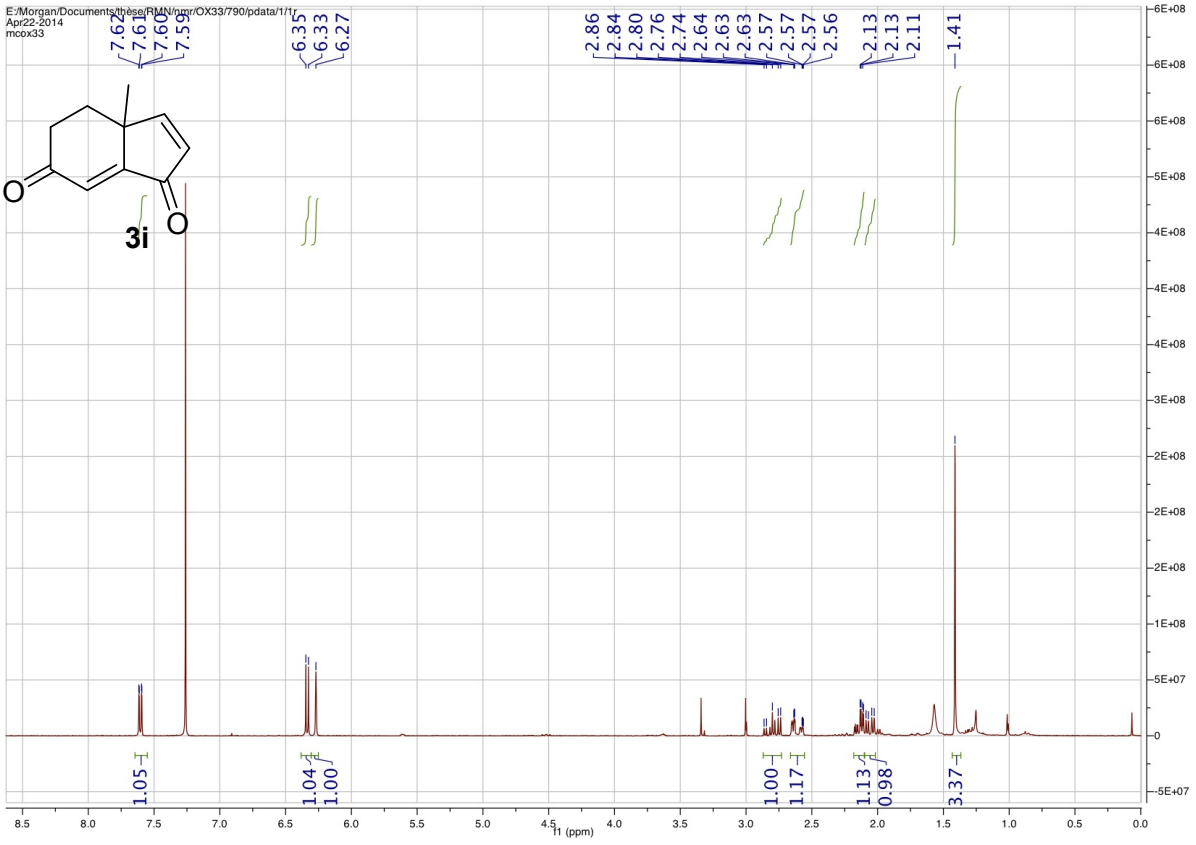
^{1}H NMR (300 MHz, $CDCl_3$)



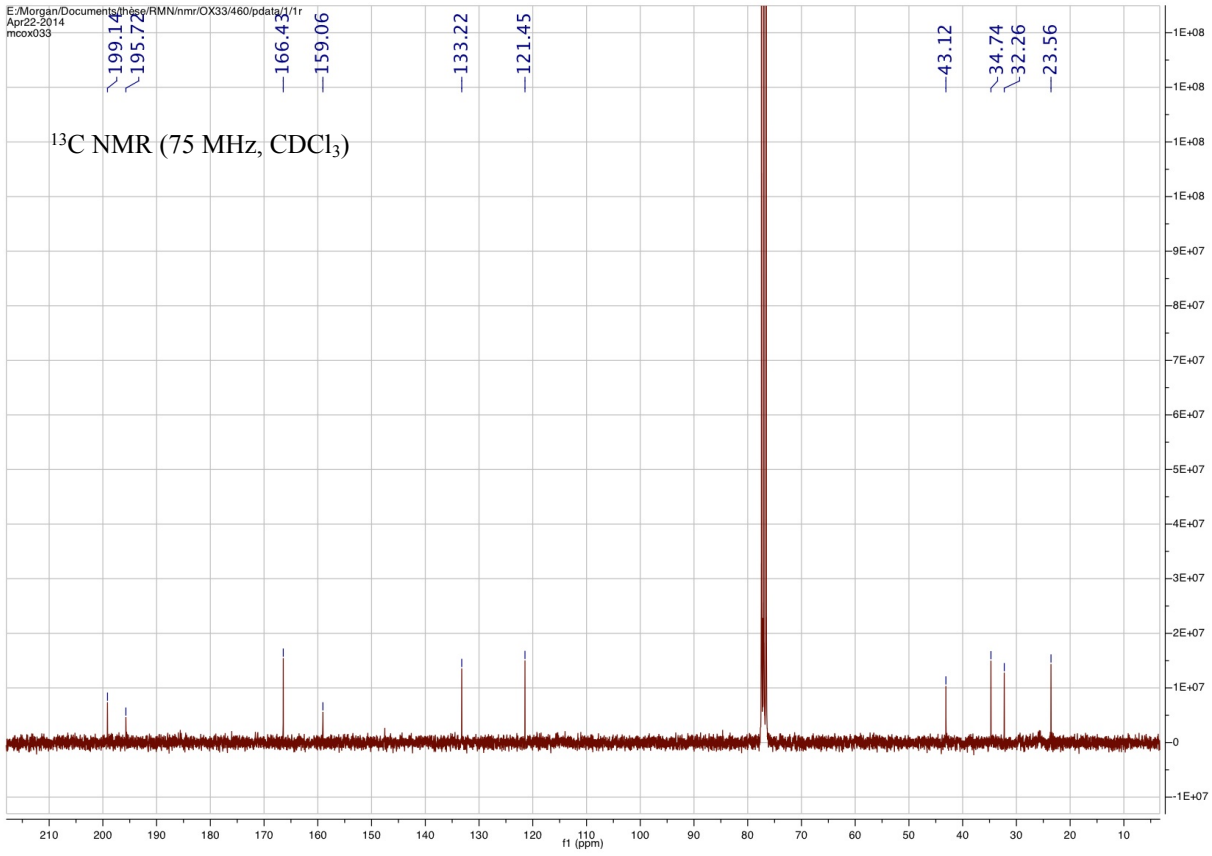
3h

^{13}C NMR (75 MHz, $CDCl_3$)



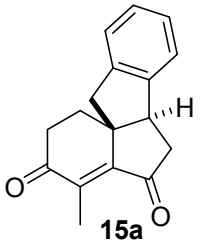


3i



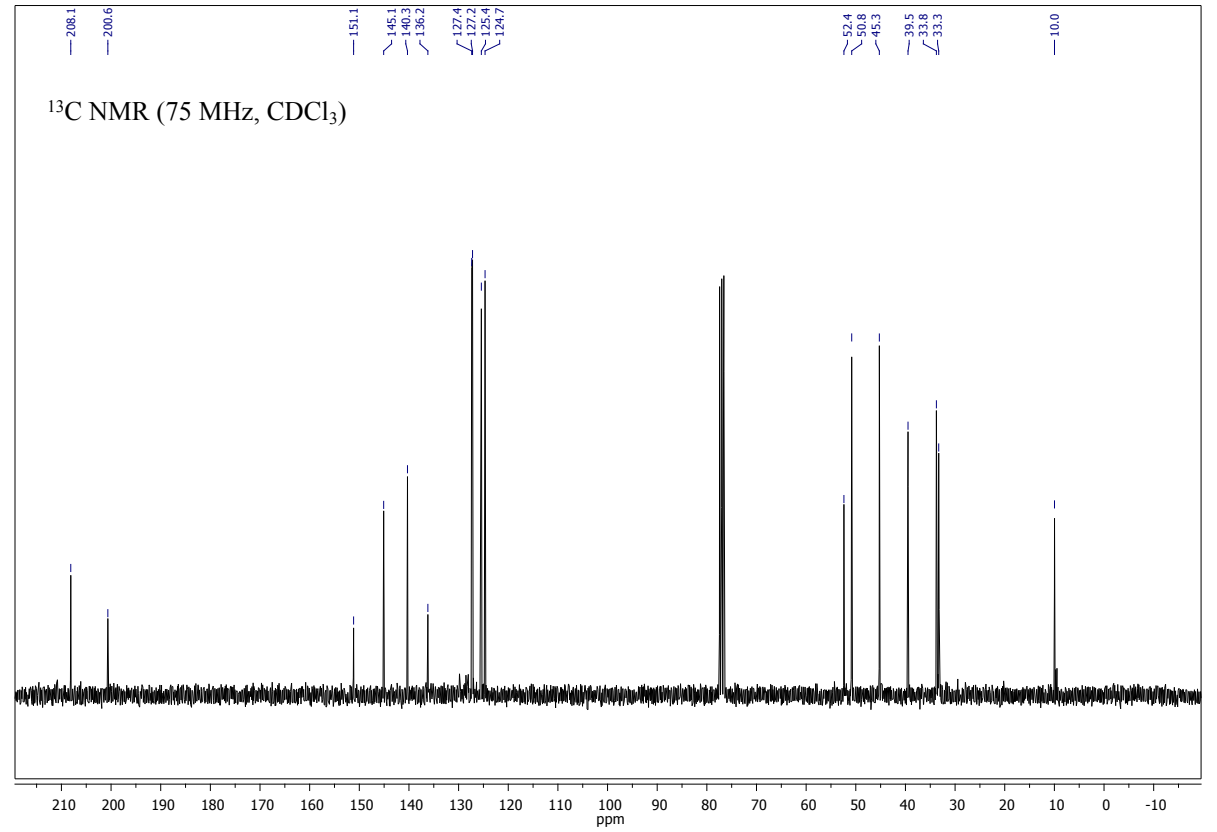
^{13}C NMR (75 MHz, $CDCl_3$)

^{1}H NMR (300 MHz, $CDCl_3$)

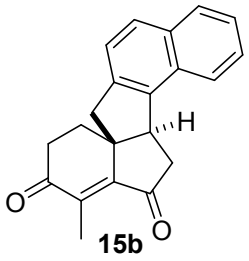


15a

^{13}C NMR (75 MHz, $CDCl_3$)

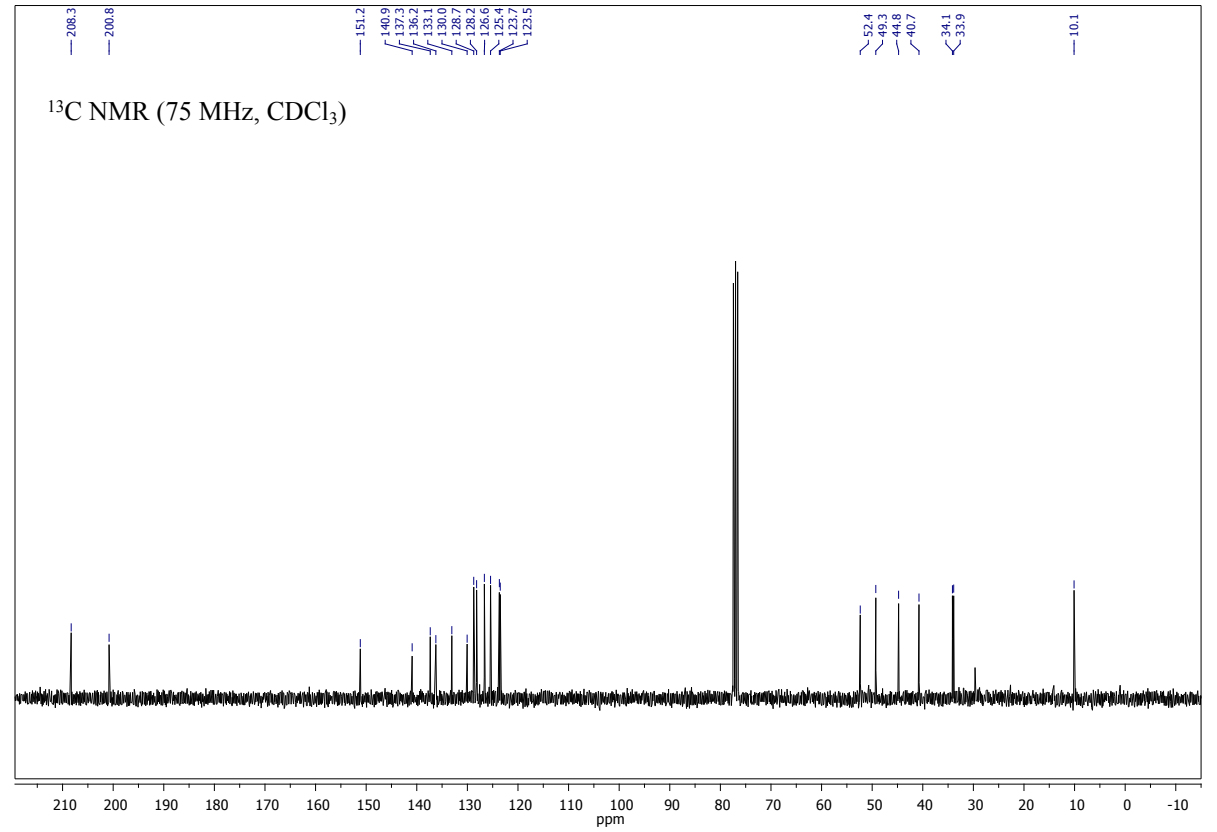


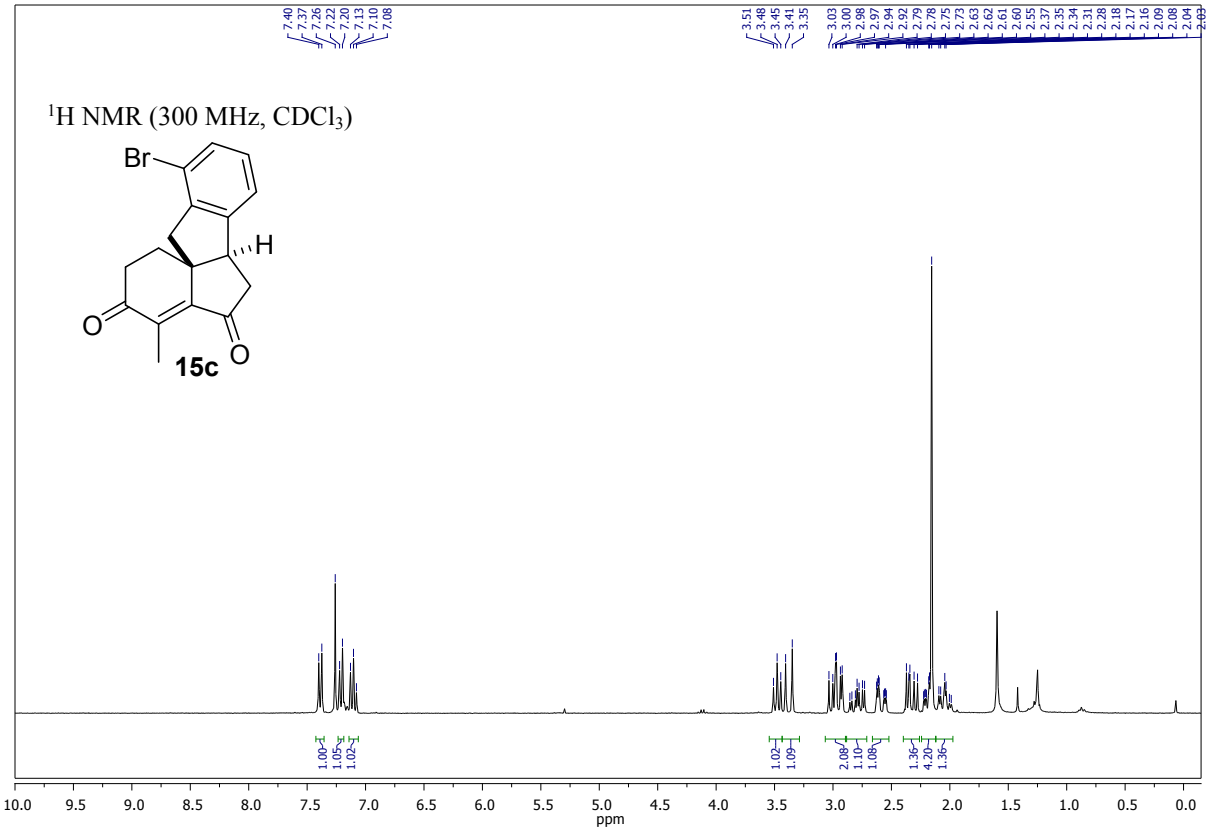
^{1}H NMR (300 MHz, $CDCl_3$)

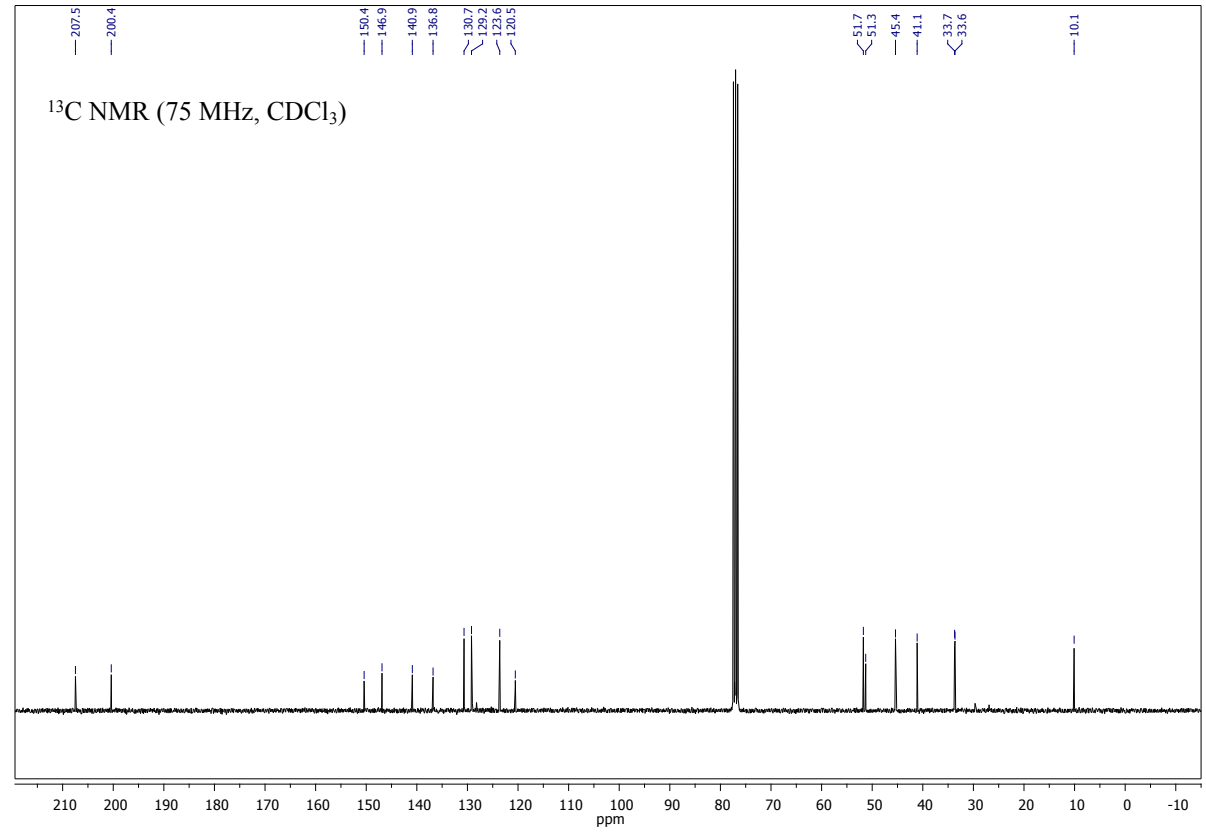


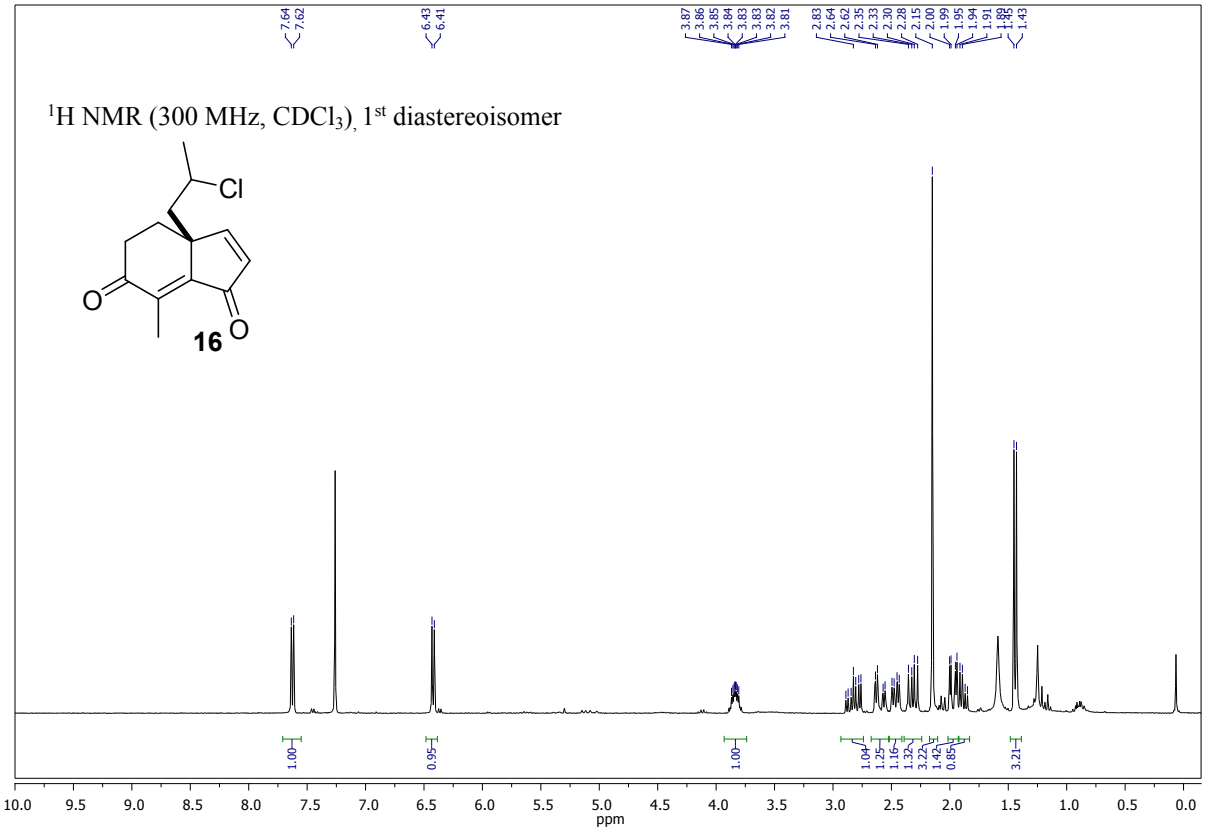
15b

^{13}C NMR (75 MHz, $CDCl_3$)

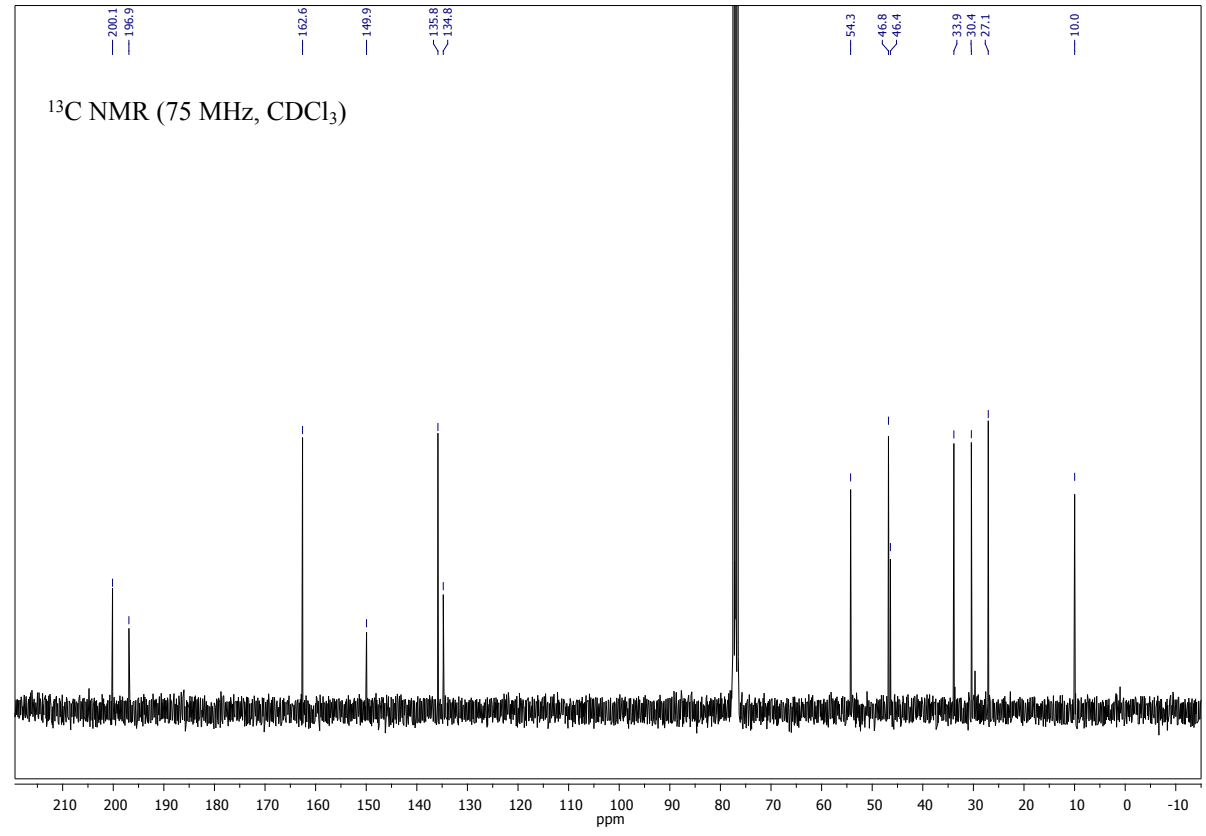



^{1}H NMR (300 MHz, $CDCl_3$)
Br
H
O
O
15c
ppm

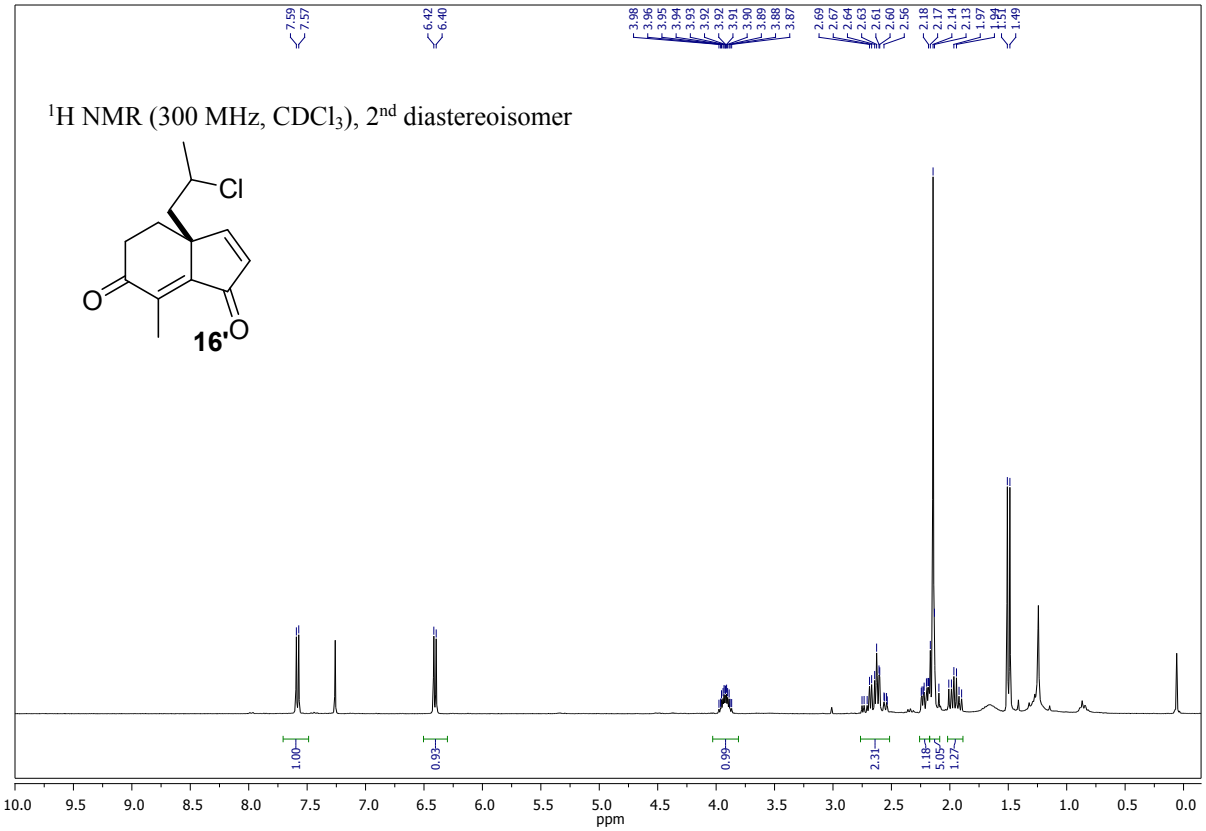

^{13}C NMR (75 MHz, $CDCl_3$)
ppm

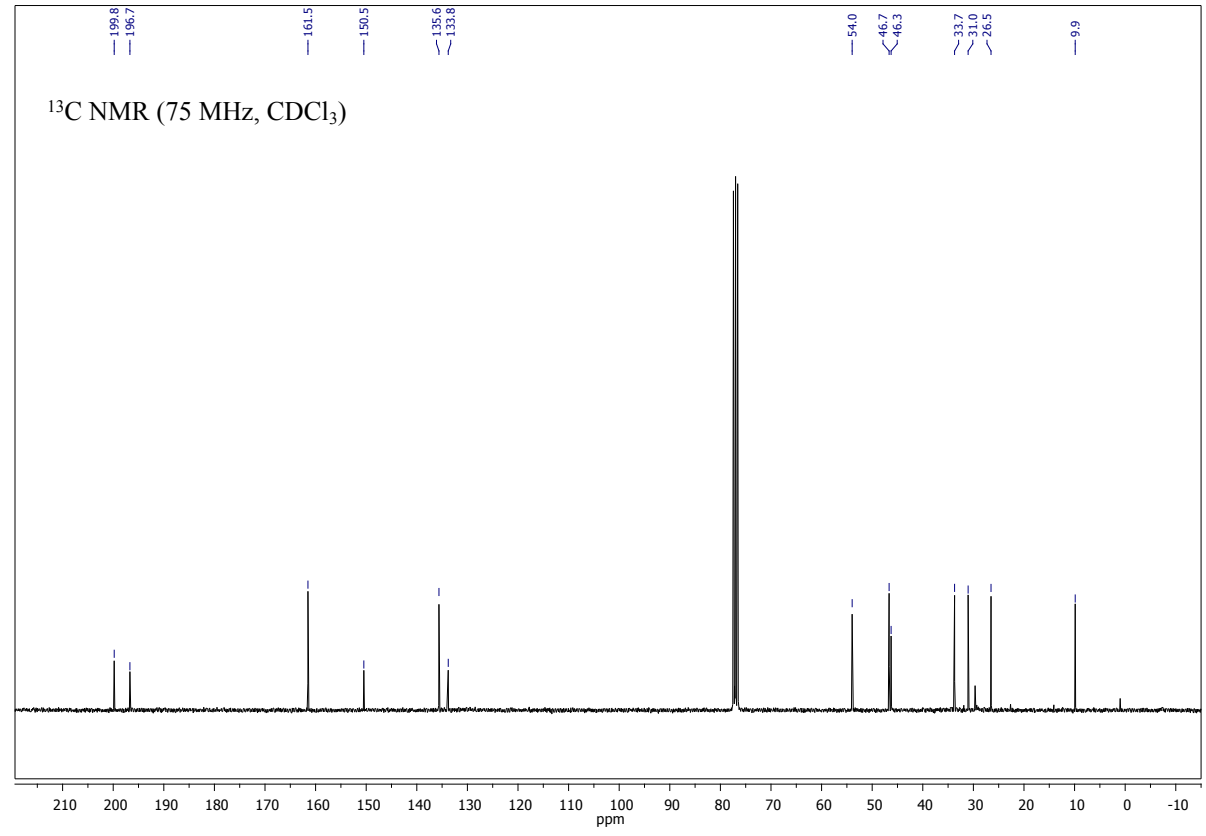


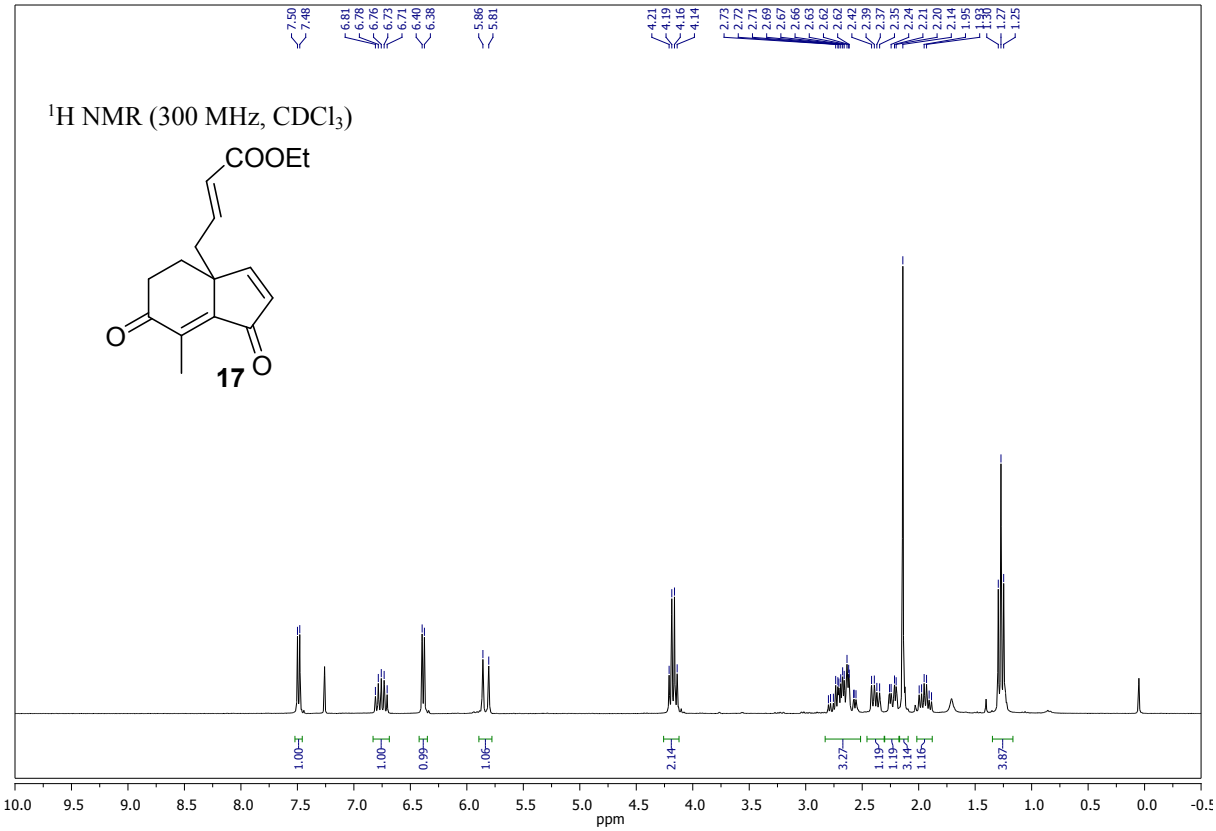
^{1}H NMR (300 MHz, $CDCl_3$), 1st diastereoisomer



^{13}C NMR (75 MHz, $CDCl_3$)

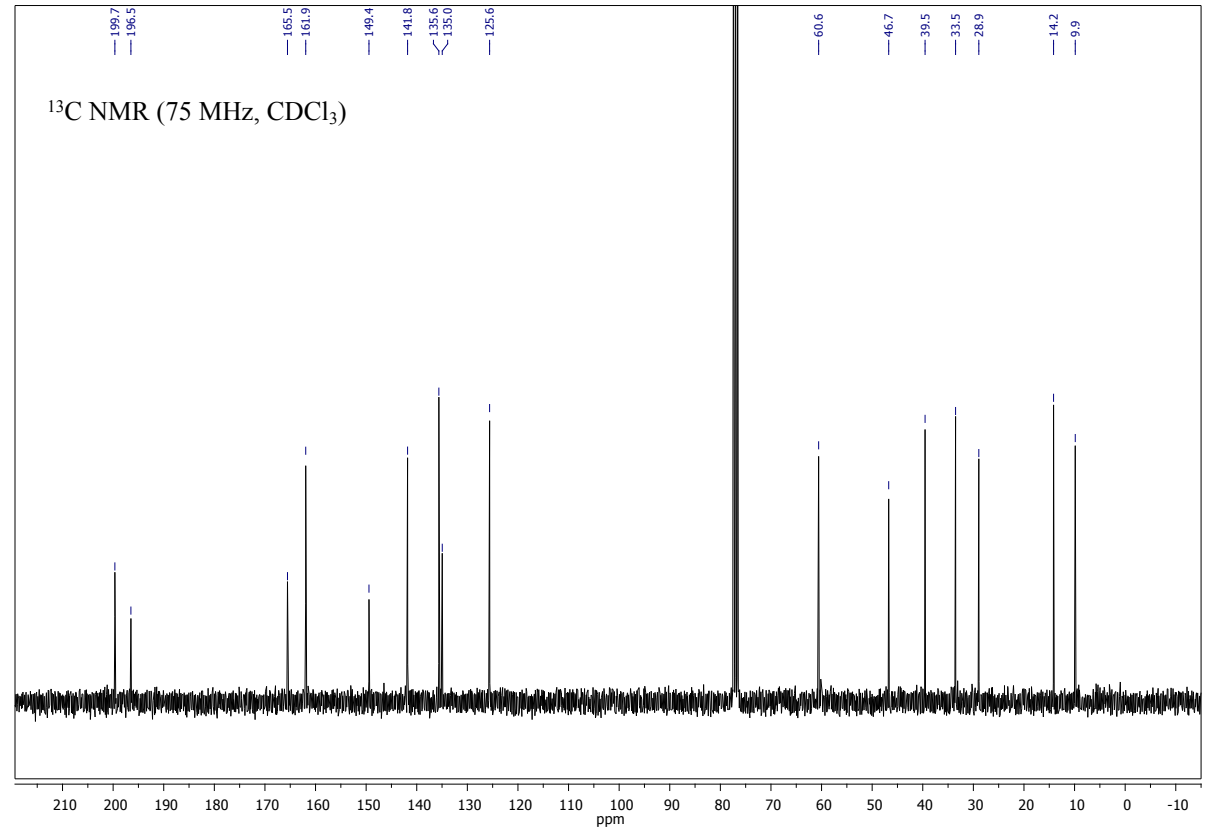

7.59
7.57
6.42
6.40
3.98
3.96
3.95
3.94
3.93
3.92
3.92
3.91
3.90
3.89
3.88
3.87
2.69
2.67
2.64
2.63
2.61
2.60
2.56
2.18
2.17
2.14
2.13
1.97
1.54
1.51
1.49
1H NMR (300 MHz, CDCl3), 2nd diastereoisomer
Cl
O
O
16'
1.00
0.93
0.99
2.31
1.18
5.05
1.27
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


199.8
196.7
161.5
150.5
135.6
133.8
54.0
46.7
46.3
33.7
31.0
26.5
9.9
13C NMR (75 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm



^{1}H NMR (300 MHz, $CDCl_3$)

17



^{13}C NMR (75 MHz, $CDCl_3$)