

Supplementary Information

Synthesis of highly strained bicyclic[3.*n*.1]alkenes by metal-catalyzed Conia-ene reaction

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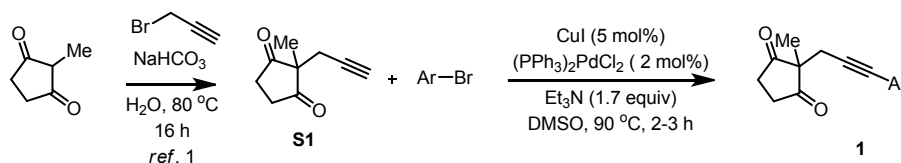
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1. General details

General information: Unless otherwise noted, all reagents were used as received from commercial suppliers. Silver and gold catalysts were obtained from Sigma-Aldrich and used without further purification. All reactions were performed under nitrogen atmosphere and in a flame-dried or oven-dried glassware with magnetic stirring. Dichloroethane (DCE) was dried in the presence of calcium chloride and distilled prior to use. Reactions were monitored using thin-layer chromatography (SiO₂). TLC plates were visualized with UV light (254 nm), iodine treatment or using *p*-anisaldehyde stain. Column chromatography was carried out using silica gel (60-120 mesh & 100-200 mesh) packed in glass columns. NMR spectra were recorded at 300, 400, 500 MHz (H) and at 75, 101, 126 MHz (C), respectively. Chemical shifts (δ) are reported in ppm, using the residual solvent peak in CDCl₃ (H: δ = 7.26 and C: δ = 77.0 ppm) as internal standard, and coupling constants (*J*) are given in Hz. HRMS were recorded using ESI-TOF techniques.

2. Experimental procedures and analytical data

a. General procedure for the synthesis of Substrates:



General procedure:

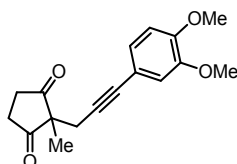
Step 1:

To a vigorously stirred suspension of 2-methyl-1,3-cyclopentanone (1 equiv) in water (1 M) was gradually added powdered NaHCO_3 (1 equiv). After the frothing had settled, propargyl bromide (2 equiv.) was added and the reaction mixture was stirred at 80°C for 16 hr. Later, The reaction mixture was extracted with CH_2Cl_2 (2 times) and the combined organic solvent was washed with 5% aqueous NaHCO_3 , dried (Na_2SO_4), filtered, and concentrated *in vacuo* to give pale yellow solid. Recrystallization of crude material in ether-pentane gave of pure compound **S1** in 85% yield.

Step 2:

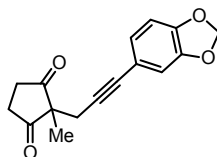
To a solution of 2-methyl-2-propargyl-1,3-cyclopentanedione (**S1**)¹ (10.0 mmol) in anhydrous DMSO (0.5 M, 20 mL) was added Pd(PPh₃)₂Cl₂ (0.2 mmol), CuI (0.5 mmol), Et₃N (17 mmol) and arylbromide (11 mmol). The mixture was stirred at 90 °C for 2 hours. The reaction was cooled to room temperature, water (50 mL) was added, and the mixture was extracted with diethyl ether (50 mL). The combined organic solvent was washed with 10% aqueous HCl (3 × 20 mL), dried (Na₂SO₄), filtered, and concentrated *in vacuo*. The mixture was purified by column chromatography (EtOAc/hexane) to give *alkynone* **1**. Compounds **1a-d**, **1g**, **3a** were prepared according to a previously reported procedure.²

2-(3-(3,4-Dimethoxyphenyl)prop-2-yn-1-yl)-2-methylcyclopentane-1,3-dione (**1e**):



Prepared according to the general procedure as described above in 96% yield. It was purified by flash chromatography (20% EtOAc/hexanes) to afford a white solid; mp = 92 – 94 °C; ¹H NMR (300 MHz, CDCl₃) δ 6.96 (dd, *J* = 8.3, 1.6 Hz, 1H), 6.86 (d, *J* = 1.5 Hz, 1H), 6.81 (d, *J* = 8.3 Hz, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 2.88 (s, 4H), 2.70 (s, 2H), 1.21 (s, 3H); ¹³C NMR (75 MHz, CDCl₃+DMSO) δ 205.4, 148.9, 148.0, 124.3, 115.4, 113.8, 110.6, 82.2, 81.9, 55.3, 35.3, 25.2, 18.3; IR (neat): ν_{max} 3473, 2970, 2839, 1766, 1727, 1606, 1511, 1248, 1032, 834, 773 cm⁻¹; HRMS (ESI) calcd for C₁₇H₁₉O₄ [M+H]⁺: 287.1278; found: 287.1288.

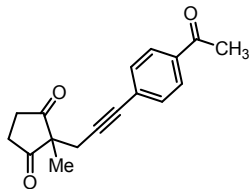
2-(3-(Benzo[d][1,3]dioxol-5-yl)prop-2-yn-1-yl)-2-methylcyclopentane-1,3-dione (**1f**):



Prepared according to the general procedure as described above in 91% yield. It was purified by flash chromatography (15% EtOAc/hexanes) to afford yellow oil; ¹H NMR (300 MHz, CDCl₃) δ 6.82 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.74 (d, *J* = 1.4 Hz, 1H), 6.68 (d, *J* = 8.0 Hz, 1H), 5.93 (s, 2H), 2.81 (s, 4H), 2.63 (s, 2H), 1.14 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 215.5, 147.8, 147.3, 126.1, 115.7, 111.5, 108.3, 101.2, 82.7, 82.2, 55.4, 35.9, 25.9, 18.8; IR (neat):

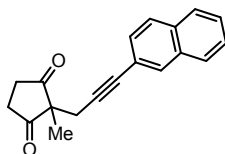
$\nu_{\max}$ 3056, 2965, 1766, 1726 1566, 1263, 1045, 1065, 985, 822, 655 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{15}\text{O}_4$ $[\text{M}+\text{H}]^+$: 271.0965; found: 271.0979.

2-(3-(4-Acetylphenyl)prop-2-yn-1-yl)-2-methylcyclopentane-1,3-dione (1h):



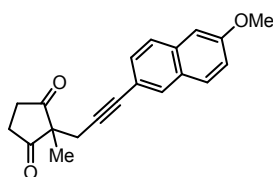
Prepared according to the general procedure as described above in 95% yield. It was purified by flash chromatography (20% EtOAc/hexanes) to afford a white solid; mp = 85 – 87 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.85 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 8.3 Hz, 2H), 2.83 (dd, J = 4.8, 1.5 Hz, 4H), 2.71 (s, 2H), 2.57 (s, 3H), 1.18 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 215.0, 197.1, 136.3, 131.7, 128.6, 127.4, 87.6, 82.1, 55.3, 35.8, 26.5, 25.5, 19.2; IR (neat): $\nu_{\max}$ 2929, 1766, 1753. 1726, 1407, 1356, 1267, 1220, 1052, 959, 823, 773 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{17}\text{O}_3$ $[\text{M}+\text{H}]^+$: 269.1172; found: 269.1187.

2-Methyl-2-(3-(naphthalen-2-yl)prop-2-yn-1-yl)cyclopentane-1,3-dione (2k):



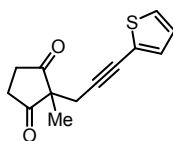
Prepared according to the general procedure as described above in 92% yield. It was purified by flash chromatography (10% EtOAc/hexanes) to afford a white solid; mp = 104 – 106 °C; ^1H NMR (300 MHz, CDCl_3) δ 8.18 (d, J = 8.3 Hz, 1H), 7.80 (t, J = 8.2 Hz, 2H), 7.62 – 7.53 (m, 2H), 7.53 – 7.46 (m, 1H), 7.37 (dd, J = 8.0, 7.3 Hz, 1H), 2.86 (s, 2H), 2.82 (s, 4H), 1.23 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 215.5, 133.3, 133.0, 130.5, 128.7, 128.2, 126.8, 126.4, 125.8, 125.0, 120.1, 88.9, 80.8, 55.6, 35.8, 25.9, 19.1; IR (neat): $\nu_{\max}$ 3215, 2913, 1766, 1724, 1416, 1315, 1219, 1070, 962, 772 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{16}\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 299.1043; found: 299.1063.

2-(3-(6-Methoxynaphthalen-2-yl)prop-2-yn-1-yl)-2-methylcyclopentane-1,3-dione (2l):



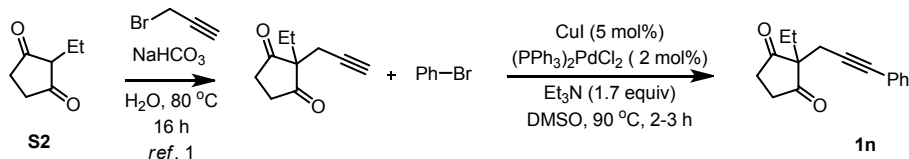
Prepared according to the general procedure as described above in 96% yield. It was purified by flash chromatography (15% EtOAc/hexanes) to afford a white solid; mp = 98 – 100 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.76 (s, 1H), 7.63 (dd, J = 8.7, 8.7 Hz, 2H), 7.32 (dd, J = 8.5, 1.5 Hz, 1H), 7.14 (dd, J = 8.9, 2.5 Hz, 1H), 7.07 (d, J = 2.3 Hz, 1H), 3.90 (s, 3H), 2.86 (s, 2H), 2.85 (s, 2H), 2.72 (s, 2H), 1.19 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 215.6, 158.3, 134.1, 131.3, 129.2, 128.9, 128.3, 126.8, 119.4, 117.4, 105.8, 83.5, 83.4, 55.5, 55.3, 36.0, 29.7, 26.1, 18.9; IR (neat): ν_{max} 3024, 2958, 1768, 1721, 1521, 1043, 988, 842 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{19}\text{O}_3$ $[\text{M}+\text{H}]^+$: 307.1329 ; found: 307.1337.

2-Methyl-2-(3-(thiophen-2-yl)prop-2-yn-1-yl)cyclopentane-1,3-dione (2m):



Prepared according to the general procedure as described above in 86% yield. It was purified by flash chromatography (10% EtOAc/hexanes) to afford a brown oil; ^1H NMR (300 MHz, CDCl_3) δ 7.18 (dd, J = 5.2, 0.9 Hz, 1H), 7.08 (d, J = 3.5 Hz, 1H), 6.90 (dd, J = 5.1, 3.7 Hz, 1H), 2.81 (s, 4H), 2.68 (s, 2H), 1.15 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 215.3, 131.8, 126.8, 122.4, 88.0, 76.0, 55.3, 35.8, 26.0, 18.9; IR (neat): ν_{max} 3106, 1768, 1727, 1451, 1192, 1075, 992, 773, 707 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{13}\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$: 233.0631; found: 233.0644.

2-Ethyl-2-(3-phenylprop-2-yn-1-yl)cyclopentane-1,3-dione (1n):



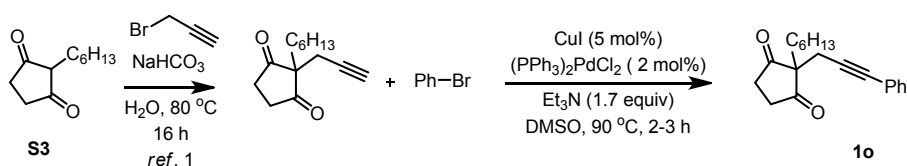
Procedure for the synthesis of **S2**³:

A solution of acetaldehyde (3.0 eq), 1,3-cyclopentanone (1.0 eq) and Hantzsch ester (1.0 eq) in CH_2Cl_2 (0.3M) was added *L*-Proline (0.50 mmol, 5 mol%) and the reaction mixture was stirred at rt for 1 h. After evaporation of the solvent completely, the crude reaction mixture was subjected to silica gel column chromatography (hexane–ethyl acetate) with or without aqueous work-up to afford product **S2** in 75% yield.

Compound **1n** was prepared according to the general procedure as described above in 85% yield. It was purified by flash chromatography (10% EtOAc/hexanes) to afford a yellow

solid; mp = 95 – 96°C; ^1H NMR (300 MHz, CDCl_3) δ 7.36 – 7.21 (m, 5H), 2.91 – 2.68 (m, 4H), 2.67 (s, 2H), 1.74 (q, J = 7.5 Hz, 2H), 0.81 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 216.1, 131.5, 128.2, 122.5, 84.0, 82.7, 60.3, 36.8, 28.0, 24.8, 9.1; IR (neat): ν_{max} 3472, 2923, 1724, 1417, 1206, 1084, 963, 758, 715, 692 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{17}\text{O}_2$ $[\text{M}+\text{H}]^+$: 241.1223; found: 241.1210.

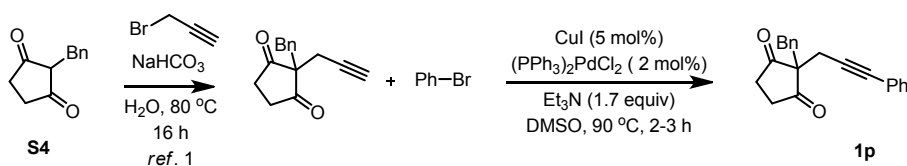
2-Hexyl-2-(3-phenylprop-2-yn-1-yl)cyclopentane-1,3-dione (**1o**):



Procedure for the synthesis of **S3** was similar to the literature³.

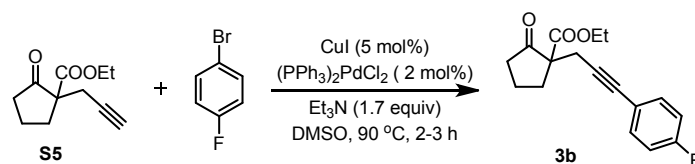
Compound **1o** was prepared according to the general procedure as described above in 82% yield. It was purified by flash chromatography (5% EtOAc/hexanes) to afford a yellow oil; ^1H NMR (300 MHz, CDCl_3) δ 7.28 – 7.13 (m, 5H), 2.81 – 2.61 (m, 4H), 2.59 (s, 2H), 1.60 (dd, J = 9.7, 6.5 Hz, 2H), 1.28 – 0.95 (m, 8H), 0.78 (t, J = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 216.3, 131.5, 128.2, 122.5, 83.9, 82.7, 59.9, 36.8, 35.1, 31.2, 29.4, 25.3, 24.7, 22.3, 13.9; IR (neat): ν_{max} 3011, 2968, 1727, 1426, 1106, 1084, 963, 916, 755, 692, 616 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{24}\text{NaO}_2$ $[\text{M}+\text{Na}]^+$: 319.1669; found: 319.1686.

2-Benzyl-2-(3-phenylprop-2-yn-1-yl)cyclopentane-1,3-dione (**1p**):

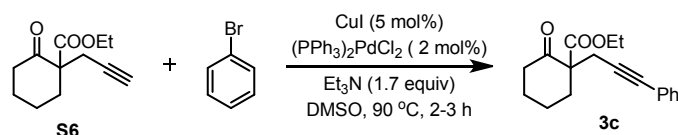


Procedure for the synthesis of **S4** was similar to the literature³.

Compound **1p** was prepared according to the general procedure as described above in 89% yield. It was purified by flash chromatography (10% EtOAc/hexanes) to afford a white solid; mp = 116 – 118 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.32 – 7.18 (m, 8H), 7.07 – 7.03 (m, 2H), 3.00 (s, 2H), 2.81 (s, 2H), 2.58 (dd, J = 19.3, 6.8 Hz, 2H), 2.06 (dd, J = 19.3, 6.8 Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 216.4, 135.0, 131.6, 129.7, 128.7, 128.3, 127.4, 122.5, 83.8, 82.9, 61.7, 41.6, 37.1, 25.7; IR (neat): ν_{max} 3032, 2918, 1727, 1492, 1219, 1079, 991, 917, 771, 702 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{19}\text{O}_2$ $[\text{M}+\text{H}]^+$: 303.1380; found: 303.1391.

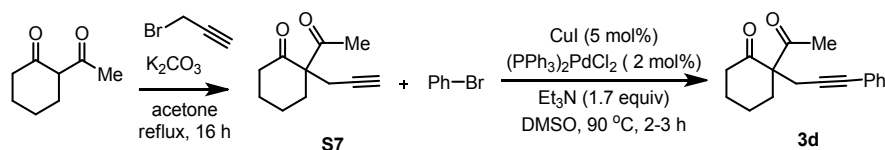
Ethyl 1-(3-(4-fluorophenyl)prop-2-yn-1-yl)-2-oxocyclopentanecarboxylate (3b):

Prepared according to the general procedure as described above from ethyl 2-oxo-1-(prop-2-yn-1-yl)cyclopentanecarboxylate (**S5**)⁴ in 83% yield. It was purified by flash chromatography (10% EtOAc/hexanes) to afford a yellow oil; ¹H NMR (300 MHz, CDCl₃) δ 7.33 (dd, *J* = 8.6, 5.5 Hz, 2H), 6.96 (dd, *J* = 8.7, 8.7 Hz, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 2.93 (s, 2H), 2.63 – 2.43 (m, 2H), 2.33 (ddd, *J* = 27.0, 15.6, 8.4 Hz, 2H), 2.22 – 1.98 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 213.8, 170.4, 162.3 (d, *J*_{C-F} = 249.0 Hz), 133.5 (d, *J*_{C-F} = 8.2 Hz), 119.2 (d, *J*_{C-F} = 3.2 Hz), 115.5 (d, *J*_{C-F} = 22.0 Hz), 85.0, 81.7, 61.8, 59.1, 38.4, 32.8, 24.1, 19.9, 14.1; IR (neat): ν_{max} 2977, 1754, 1728, 1501, 1225, 1154, 1095, 838, 772 cm⁻¹; HRMS (ESI) calcd for C₁₇H₁₈O₃F [M+H]⁺: 289.1234; found: 289.1249.

Ethyl 2-oxo-1-(3-phenylprop-2-yn-1-yl)cyclohexanecarboxylate (3c):

Prepared according to the general procedure as described above from ethyl 2-oxo-1-(prop-2-yn-1-yl)cyclohexanecarboxylate (**S6**)⁴ in 87% yield. It was purified by flash chromatography (10% EtOAc/hexanes) to afford a colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.42 – 7.36 (m, 2H), 7.32 – 7.26 (m, 3H), 4.26 (dq, *J* = 7.1, 1.7 Hz, 2H), 3.02 (d, *J* = 17.0 Hz, 1H), 2.80 – 2.73 (m, 1H), 2.77 (d, *J* = 17.0 Hz, 1H), 2.56 – 2.42 (m, 2H), 2.15 – 2.03 (m, 1H), 1.92 – 1.79 (m, 2H), 1.76 – 1.62 (m, 2H), 1.34 – 1.25 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 206.1, 170.4, 131.5, 128.1, 127.8, 123.4, 85.0, 83.4, 61.6, 60.3, 40.8, 35.5, 27.4, 25.6, 22.4, 14.1; IR (neat): ν_{max} 2936, 2859, 1736, 1717, 1366, 1279, 1232, 1072, 895, 770, 696 cm⁻¹; HRMS (ESI) calcd for C₁₈H₂₁O₃ [M+H]⁺: 285.1485; found: 285.1501.

2-Acetyl-2-(3-phenylprop-2-yn-1-yl)cyclohexanone (**3d**):

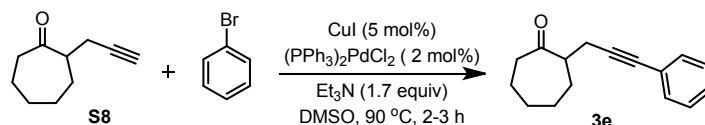


Procedure for the synthesis of **S7**⁵:

A solution of 2-acetylcyclohexanone (1.0 eq) and K_2CO_3 (4.0 eq) in acetone (0.3M) was added propargyl bromide (80% solution w/w in toluene, 1.6 eq) at room temperature. The mixture was refluxed for 16 h, then was cooled at room temperature, diluted with ether and filtered to remove most of the potassium carbonate. Filtrate was evaporated under reduced pressure, the residue was purified by flash chromatography (hexane–ethyl acetate) to afford **S7** in 82% yield.

Compound **3d** was prepared according to the general procedure as described above in 91% yield. It was purified by flash chromatography (10% EtOAc/hexanes) to afford a colorless oil; 1H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.25 (m, 2H), 7.23 – 7.16 (m, 3H), 3.01 (d, J = 17.5 Hz, 1H), 2.72 (ddd, J = 13.9, 6.2, 3.6 Hz, 1H), 2.65 (d, J = 17.5 Hz, 1H), 2.44 (dt, J = 14.1, 3.8 Hz, 1H), 2.23 (ddd, J = 14.1, 12.5, 5.9 Hz, 1H), 2.14 (s, 3H), 2.01 – 1.92 (m, 1H), 1.79 – 1.70 (m, 1H), 1.70 – 1.47 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.3, 204.9, 131.6, 128.2, 128.0, 123.1, 84.6, 84.1, 66.9, 41.5, 34.4, 27.2, 26.5, 25.3, 22.3; IR (neat): ν_{max} 2932, 2857, 1713, 1496, 1446, 1226, 1047, 885, 757, 696 cm^{-1} ; HRMS (ESI) calcd for $C_{17}H_{19}O_2$ $[M+H]^+$: 255.1380; found: 255.1366.

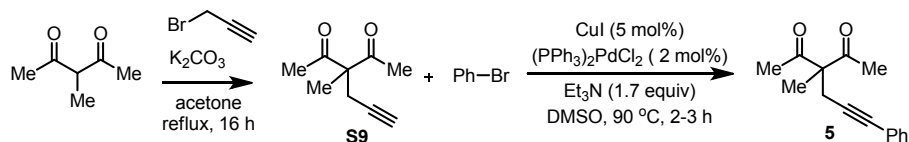
2-(3-Phenylprop-2-yn-1-yl)cycloheptanone (**3e**):



Prepared according to the general procedure as described above from 2-(prop-2-yn-1-yl)cycloheptanone (**S8**)⁶ in 75% yield. It was purified by flash chromatography (10% EtOAc/hexanes) to afford a colorless oil; 1H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 2H), 7.23 – 7.17 (m, 3H), 2.78 – 2.70 (m, 1H), 2.66 (dd, J = 17.0, 5.0 Hz, 1H), 2.50 (dt, J = 15.9, 4.9 Hz, 1H), 2.47 – 2.38 (m, 2H), 2.08 – 1.96 (m, 1H), 1.88 – 1.79 (m, 2H), 1.79 – 1.74 (m, 1H), 1.66 – 1.47 (m, 2H), 1.48 – 1.42 (m, 1H), 1.34 – 1.21 (m, 1H); ^{13}C NMR (101 MHz,

CDCl₃) δ 214.2, 131.5, 128.1, 127.6, 123.6, 88.1, 81.6, 51.0, 43.3, 30.4, 29.4, 28.9, 24.0, 21.9; IR (neat): ν_{max} 2927, 2854, 1701, 1490, 1219, 1160, 1025, 935, 771, 692 cm⁻¹; HRMS (ESI) calcd for C₁₆H₁₈ONa [M+Na]⁺: 249.1250; found: 249.1244.

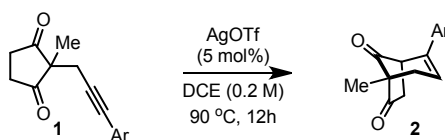
3-Methyl-3-(3-phenylprop-2-yn-1-yl)pentane-2,4-dione (**5**):



Procedure for the synthesis of **S9** was similar to the literature⁵.

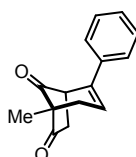
Compound **5** was prepared according to the general procedure as described above in 81% yield. It was purified by flash chromatography (10% EtOAc/hexanes) to afford a colorless oil; ¹H NMR (300 MHz, CDCl₃) δ 7.34 – 7.23 (m, 2H), 7.23 – 7.16 (m, 3H), 2.89 (s, 2H), 2.12 (s, 6H), 1.46 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 205.5, 131.5, 128.2, 128.0, 122.9, 84.8, 83.8, 66.3, 26.5, 25.3, 18.6; IR (neat): ν_{max} 3012, 2926, 1701, 1455, 1357, 1299, 1219, 1053, 998, 816, 772, 684 cm⁻¹; HRMS (ESI) calcd for C₁₅H₁₆O₂K [M+K]⁺: 267.0782; found: 267.0795.

b. General procedure for 6-endo-dig cyclization of alkynones:



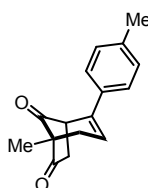
To a solution of alkynone **1** (1 equiv) in DCE (0.2M) was added AgOTf (5 mol%) and the reaction mixture was stirred at 90 °C for 4 hours. The solvent was evaporated and the residue was purified by flash column chromatography using EtOAc/hexanes mixture gave product **2**.

5-Methyl-2-phenylbicyclo[3.2.1]oct-2-ene-6,8-dione (**2a**) :



Prepared according to the general procedure as described above in 96% yield. It was purified by flash chromatography (10% EtOAc/hexanes) to afford a white solid; mp = 125–127 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.38 – 7.30 (m, 5H), 5.89 (t, *J* = 3.4 Hz, 1H), 3.63 (d, *J* = 6.9 Hz, 1H), 3.10 (d, *J* = 18.3 Hz, 1H), 2.91 (dd, *J* = 18.3, 6.9 Hz, 1H), 2.84 (dd, *J* = 17.8, 3.9 Hz, 1H), 2.76 (dd, *J* = 17.8, 2.9 Hz, 1H), 1.21 (s, 3H); ¹³C NMR (CDCl₃, 75MHz) δ 213.3, 211.2, 144.9, 138.0, 128.7, 128.6, 125.4, 121.1, 57.2, 50.1, 48.4, 45.8, 12.4; IR (neat): ν_{max} 3474, 2974, 1776, 1732, 1628, 1315, 1241, 1072, 997, 912, 842, 773 cm⁻¹; HRMS (ESI) calcd for C₁₅H₁₄O₂Na [M+Na]⁺: 249.0886; found: 249.0898.

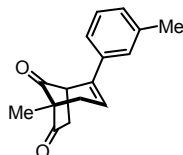
5-Methyl-2-(*p*-tolyl)bicyclo[3.2.1]oct-2-ene-6,8-dione (**2b**):



Prepared according to the general procedure as described above in 90% yield. It was purified by flash chromatography (10 % EtOAc/hexanes) to afford a white solid; mp = 110–112 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.23 (d, *J* = 8.3 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 5.84 (t, *J* = 3.4 Hz, 1H), 3.61 (d, *J* = 6.8 Hz, 1H), 3.08 (d, *J* = 18.2 Hz, 1H), 2.89 (dd, *J* = 18.3, 6.8 Hz, 1H), 2.84 (dd, *J* = 14.7, 5.4 Hz, 1H), 2.72 (d, *J* = 17.8, 2.9 Hz, 1H), 2.35 (s, 3H), 1.20 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 213.5, 211.4, 144.8, 138.2, 135.1, 129.4, 125., 120.2, 57.2, 50.8, 48.4, 45.9, 21.1, 12.4; IR (neat): ν_{max} 3041, 2926, 2854, 1773, 1735, 1693, 1596, 1456,

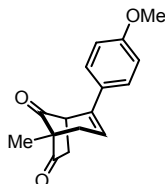
1162, 1044, 909, 795 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{17}\text{O}_2$ $[\text{M}+\text{H}]^+$: 241.1223; found: 241.1231.

5-Methyl-2-(*o*-tolyl)bicyclo[3.2.1]oct-2-ene-6,8-dione (2c):

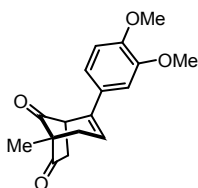


Prepared according to the general procedure as described above in 92% yield. It was purified by flash chromatography (10% EtOAc/hexanes) to afford a yellow solid; mp = 147–149 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.23 (d, J = 7.4 Hz, 1H), 7.16 – 7.10 (m, 3H), 5.86 (t, J = 3.4 Hz, 1H), 3.62 (d, J = 6.9 Hz, 1H), 3.09 (d, J = 18.3 Hz, 1H), 2.90 (dd, J = 18.2, 6.8 Hz, 1H), 2.84 (dd, J = 17.7, 3.8 Hz, 1H), 2.73 (dd, J = 17.8, 2.9 Hz, 1H), 2.36 (s, 3H), 1.20 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 213.4, 211.4, 145.1, 138.4, 138.0, 129.0, 128.7, 126.2, 122.6, 120.9, 57.2, 50.2, 48.5, 45.9, 21.5, 12.4; IR (neat): ν_{max} 3124, 2826, 2654, 1773, 1733, 1652, 1583, 1406, 1162, 1044, 909, 855, 795 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{17}\text{O}_2$ $[\text{M}+\text{H}]^+$: 241.1223; found: 241.1229.

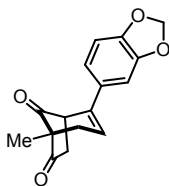
2-(4-Methoxyphenyl)-5-methylbicyclo[3.2.1]oct-2-ene-6,8-dione (2d):



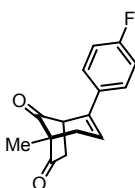
Prepared according to the general procedure as described above in 94% yield. It was purified by flash chromatography (15% EtOAc/hexanes) to afford a white solid; mp = 135 – 137 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.21 (d, J = 7.9 Hz, 2H), 6.81 (d, J = 8.8 Hz, 2H), 5.72 (t, J = 3.4 Hz, 1H), 3.75 (s, 3H), 3.53 (d, J = 6.7 Hz, 1H), 3.01 (d, J = 18.2 Hz, 1H), 2.83 (dd, J = 18.2, 6.9 Hz, 1H), 2.77 (dd, J = 13.8, 3.9 Hz, 1H), 2.65 (dd, J = 17.7, 3.0 Hz, 1H), 1.13 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 213.5, 211.4, 159.6, 144.4, 130.4, 126.6, 119.2, 114.1, 57.2, 55.3, 50.1, 48.4, 45.9, 12.4; IR (neat): ν_{max} 3061, 3972, 1776, 1732, 1612, 1485, 1453, 1373, 1159, 1070, 991, 761 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{16}\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 279.0992; found: 279.1003.

2-(3,4-Dimethoxyphenyl)-5-methylbicyclo[3.2.1]oct-2-ene-6,8-dione (2e):

Prepared according to the general procedure as described above in 93% yield. It was purified by flash chromatography (20% EtOAc/hexanes) to afford a yellow solid; mp = 142 – 144 °C; ^1H NMR (500 MHz, CDCl_3) δ 6.88(dd, J = 8.3, 2.2 Hz, 1H), 6.85 – 6.82 (m, 2H), 5.78 (t, J = 3.4 Hz, 1H), 3.88 (s, 3H), 3.88 (s, 3H), 3.60 (d, J = 6.9 Hz, 1H), 3.06 (d, J = 18.2 Hz, 1H), 2.89 (dd, J = 18.3, 6.9 Hz, 1H), 2.82 (dd, J = 17.7, 4.0 Hz, 1H), 2.72 (dd, J = 17.7, 2.9 Hz, 1H), 1.19 (s, 3H); ^{13}C NMR (CDCl_3 , 75MHz) δ 213.5, 211.3, 149.3, 149.1, 144.7, 130.9, 119.5, 118.1, 111.1, 108.9, 57.2, 55.9, 50.2, 48.5, 45.8, 12.4; IR (neat): ν_{max} 3068, 2987, 1772, 1731, 1611, 1433, 1035, 986, 855, 612 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{18}\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$: 309.1097; found: 309.1108.

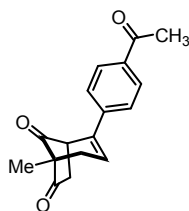
2-(Benzo[d][1,3]dioxol-5-yl)-5-methylbicyclo[3.2.1]oct-2-ene-6,8-dione (2f):

Prepared according to the general procedure as described above in 89% yield. It was purified by flash chromatography (15% EtOAc/hexanes) to afford a white solid; mp = 137 – 139 °C; ^1H NMR (300 MHz, CDCl_3) δ 6.80 (d, J = 1.8 Hz, 1H), 6.78 (d, J = 1.6 Hz, 1H), 6.77 (s, 1H), 5.96 (s, 2H), 5.75 (t, J = 3.4 Hz, 1H), 3.54 (d, J = 6.7 Hz, 1H), 3.05 (d, J = 18.2 Hz, 1H), 2.88 (dd, J = 17.0, 5.5 Hz, 1H), 2.81 (dd, J = 18.3, 3.3 Hz, 1H), 2.69 (dd, J = 17.7, 3.0 Hz, 1H), 1.18 (s, 3H); ^{13}C NMR (CDCl_3 , 75MHz) δ 213.2, 211.2, 148.1, 147.7, 144.5, 132.3, 119.9, 119.1, 108.3, 106.0, 101.3, 57.2, 50.1, 48.6, 45.7, 12.3; IR (neat): ν_{max} 3125, 2862, 1776, 1731, 1658, 1426, 1264, 1053, 992, 884, 775, 662 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{15}\text{O}_4$ $[\text{M}+\text{H}]^+$: 271.0965; found: 271.0975.

2-(4-Fluorophenyl)-5-methylbicyclo[3.2.1]oct-2-ene-6,8-dione (2g):

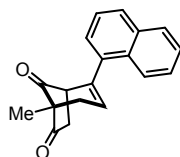
Prepared according to the general procedure as described above in 87% yield. It was purified by flash chromatography (10% EtOAc/hexanes) to afford a white solid; mp = 145 – 147 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.30 (dd, J = 8.7, 5.2, 2.6 Hz, 2H), 7.00 (t, J = 8.6 Hz, 1H), 5.83 (t, J = 3.4 Hz, 1H), 3.57 (d, J = 6.9 Hz, 1H), 3.07 (d, J = 18.3 Hz, 1H), 2.90 (dd, J = 18.3, 6.9 Hz, 1H), 2.84 (dd, J = 17.8, 3.9 Hz, 1H), 2.72 (dd, J = 17.8, 2.9 Hz, 1H), 1.20 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 213.1, 211.0, 162.6 (d, $J_{\text{C-F}}$ = 248.4 Hz), 143.9, 134.1 (d, $J_{\text{C-F}}$ = 2.9 Hz), 127.7 (d, $J_{\text{C-F}}$ = 8.1 Hz), 121.0, 115.7 (d, $J_{\text{C-F}}$ = 21.6 Hz), 57.1, 50.1, 48.5, 45.7, 12.4; IR (neat): ν_{max} 3026, 2826, 2754, 1763, 1736, 1623, 1496, 1456, 1162, 1044, 909, 844, 795, 698 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{14}\text{FO}_2$ $[\text{M}+\text{H}]^+$: 271.0972; found: 271.0975.

2-(4-Acetylphenyl)-5-methylbicyclo[3.2.1]oct-2-ene-6,8-dione (2h):



Prepared according to the general procedure as described above in 90% yield. It was purified by flash chromatography (20% EtOAc/hexanes) to afford a white solid; mp = 140 – 142 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.94 (d, J = 8.5 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 6.02 (t, J = 3.4 Hz, 1H), 3.64 (d, J = 6.7 Hz, 1H), 3.10 (d, J = 18.2 Hz, 1H), 2.94 (dd, J = 18.2, 6.8 Hz, 1H), 2.88 (dd, J = 14.2, 4.0 Hz, 1H), 2.76 (dd, J = 18.2, 3.0 Hz, 1H), 2.60 (s, 3H), 1.22 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 212.7, 210.7, 197.3, 144.0, 142.3, 136.6, 128.9, 125.6, 123.5, 57.1, 50.1, 48.1, 45.8, 26.6, 12.3; IR (neat): ν_{max} 2925, 2853, 1775, 1731, 1680, 1602, 1407, 1356, 1269, 1052, 959, 823, 772; HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{17}\text{O}_3$ $[\text{M}+\text{H}]^+$: 269.1172; found: 269.1184.

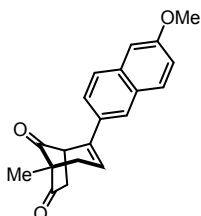
5-Methyl-2-(naphthalen-1-yl)bicyclo[3.2.1]oct-2-ene-6,8-dione (2k):



Prepared according to the general procedure as described above in 83% yield. It was purified by flash chromatography (10% EtOAc/hexanes) to afford a colorless oil; ^1H NMR (300 MHz, CDCl_3) δ 7.94 – 7.85 (m, 2H), 7.83 (d, J = 8.3 Hz, 1H), 7.62 – 7.48 (m, 2H), 7.44 (dd, J = 8.2, 7.0 Hz, 1H), 7.33 (dd, J = 7.0, 1.1 Hz, 1H), 5.71 (t, J = 3.2 Hz, 1H), 3.49 (d, J = 6.9 Hz, 1H), 3.14 (d, J = 18.5 Hz, 1H), 2.87 (d, J = 3.0 Hz, 2H), 2.78 (d, J = 18.5, 6.9 Hz, 1H), 1.27

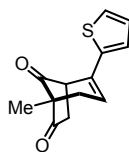
(s, 3H); ^{13}C NMR (CDCl_3 , 75MHz): δ 213.5, 211.7, 146.4, 137.4, 133.8, 130.6, 128.7, 128.6, 126.8, 126.2, 125.8, 125.3, 125.3, 124.4, 57.1, 50.9, 49.8, 46.1, 12.5; IR (neat): ν_{max} 3072, 2956, 1772, 1738, 1654, 1452, 1258, 1046, 998, 845, 772 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{17}\text{O}_2$ $[\text{M}+\text{H}]^+$: 277.1223; found: 277.1235.

2-(6-Methoxynaphthalen-2-yl)-5-methylbicyclo[3.2.1]oct-2-ene-6,8-dione (2l):

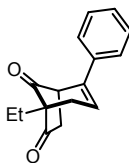


Prepared according to the general procedure as described above in 89% yield. It was purified by flash chromatography (15% EtOAc/hexanes) to afford a white solid; mp = 190 – 192 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.72 (d, J = 5.6 Hz, 1H), 7.70 (d, J = 5.3 Hz, 1H), 7.68 (d, J = 1.3 Hz, 1H), 7.44 (dd, J = 8.6, 1.9 Hz, 1H), 7.16 (d, J = 8.9, 2.5 Hz, 1H), 7.11 (d, J = 2.4 Hz, 1H), 5.98 (t, J = 3.4 Hz, 1H), 3.92 (s, 3H), 3.77 (d, J = 6.8 Hz, 1H), 3.14 (d, J = 18.3 Hz, 1H), 2.96 (dd, J = 18.3, 6.9 Hz, 1H), 2.89 (dd, J = 17.8, 4.0 Hz, 1H), 2.78 (dd, J = 17.8, 3.0 Hz, 1H), 1.23 (s, 3H); ^{13}C NMR (75MHz, CDCl_3): δ 213.6, 211.7, 146.3, 137.3, 133.8, 130.6, 128.7, 128.6, 126.8, 126.2, 125.8, 125.4, 125.3, 124.4, 57.2, 50.9, 49.9, 46.2, 12.9; IR (neat): ν_{max} 3026, 2986, 1774, 1726, 1698, 1236, 1056, 996, 862, 754, 625 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{19}\text{O}_3$ $[\text{M}+\text{H}]^+$: 307.1329; found: 307.1345.

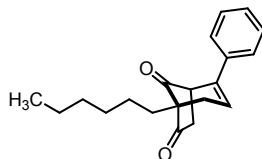
5-Methyl-2-(thiophen-2-yl)bicyclo[3.2.1]oct-2-ene-6,8-dione (2m):



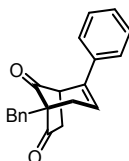
Prepared according to the general procedure as described above in 55% yield. It was purified by flash chromatography (10% EtOAc/hexanes) to afford a yellow solid; mp = 102 – 104 $^{\circ}\text{C}$; ^1H NMR (300 MHz, CDCl_3) δ 7.22 (dd, J = 4.5, 1.7 Hz, 1H), 7.03-6.97 (m, 2H), 5.91 (t, J = 3.5 Hz, 1H), 3.65 (d, J = 6.8 Hz, 1H), 3.08 (d, J = 18.3 Hz, 1H), 2.89 (dd, J = 18.3, 6.8 Hz, 1H), 2.84 (dd, J = 17.9, 4.0 Hz, 1H), 2.73 (dd, J = 18.1, 3.1 Hz, 1H), 1.19 (s, 3H); ^{13}C NMR (CDCl_3 , 75MHz): δ 212.6, 210.9, 141.6, 138.7, 127.6, 125.3, 123.3, 119.2, 56.9, 49.9, 48.5, 45.6, 12.4; IR (neat): ν_{max} 2927, 1775, 1731, 1349, 1220, 1050, 773, 703 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{13}\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$: 233.0631; found: 233.0639.

5-Ethyl-2-phenylbicyclo[3.2.1]oct-2-ene-6,8-dione (2n):

Prepared according to the general procedure as described above in 91% yield. It was purified by flash chromatography (10% EtOAc/hexanes) to afford a white solid; mp = 131 – 133 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.34 – 7.17 (m, 5H), 5.79 (t, J = 3.4 Hz, 1H), 3.53 (d, J = 6.8 Hz, 1H), 3.02 (d, J = 18.1 Hz, 1H), 2.76 (dd, J = 18.0, 6.8 Hz, 1H), 2.69 (ddd, J = 23.2, 17.8, 3.0 Hz, 2H), 1.82 – 1.58 (m, 2H), 0.80 (t, J = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 213.5, 211.5, 144.9, 138.0, 128.7, 128.2, 125.4, 121.1, 61.7, 50.8, 48.6, 44.9, 21.3, 9.1; IR (neat): ν_{max} 2988, 1766, 1723, 1617, 1348, 1206, 1084, 963, 916, 758, 692 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{16}\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 263.1043; found: 263.1031.

5-Hexyl-2-phenylbicyclo[3.2.1]oct-2-ene-6,8-dione (2o):

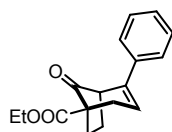
Prepared according to the general procedure as described above in 92% yield. It was purified by flash chromatography (5% EtOAc/hexanes) to afford a light yellow oil; ^1H NMR (500 MHz, CDCl_3) δ 7.31 – 7.19 (m, 5H), 5.78 (t, J = 3.4 Hz, 1H), 3.53 (d, J = 6.8 Hz, 1H), 3.01 (d, J = 18.0 Hz, 1H), 2.76 (dd, J = 18.0, 6.9 Hz, 1H), 2.72 (dd, J = 17.8, 3.8 Hz, 1H), 2.66 (dd, J = 17.7, 2.9 Hz, 1H), 1.72 – 1.56 (m, 2H), 1.28 – 1.14 (m, 7H), 1.12 – 1.01 (m, 1H), 0.80 (t, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 213.6, 211.6, 144.9, 137.9, 128.7, 128.1, 125.4, 121.0, 61.1, 50.6, 48.6, 45.2, 31.4, 29.8, 28.5, 24.6, 22.5, 14.0; IR (neat): ν_{max} 3012, 2928, 2865, 1776, 1728, 1596, 1275, 1077, 974, 848, 762, 693 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{24}\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 319.1669; found: 319.1659.

5-Benzyl-2-phenylbicyclo[3.2.1]oct-2-ene-6,8-dione (2p):

Prepared according to the general procedure as described above in 89% yield. It was purified by flash chromatography (10% EtOAc/hexanes) to afford a yellow solid. mp = 110 – 112 °C;

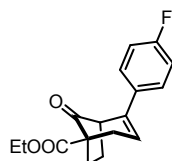
^1H NMR (400 MHz, CDCl_3) δ 7.43 – 7.30 (m, 7H), 7.30 – 7.23 (m, 2H), 7.24 – 7.14 (m, 1H), 5.89 (t, $J = 3.4$ Hz, 1H), 3.58 (d, $J = 6.8$ Hz, 1H), 3.19 (d, $J = 14.0$ Hz, 1H), 3.07 (d, $J = 5.4$ Hz, 1H), 3.03 (s, 1H), 2.93 – 2.79 (m, 2H), 2.65 (dd, $J = 17.9, 6.9$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 212.8, 210.7, 145.0, 137.8, 136.6, 130.6, 128.7, 128.2, 128.1, 126.5, 125.3, 120.9, 62.3, 50.5, 48.5, 45.2, 33.8; IR (neat): ν_{max} 3033, 2917, 1726, 1719, 1650, 1462, 1211, 1043, 991, 884, 771, 688 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{19}\text{O}_2$ $[\text{M}+\text{H}]^+$: 303.138; found: 303.1392.

Ethyl 8-oxo-4-phenylbicyclo[3.2.1]oct-3-ene-1-carboxylate (4a):



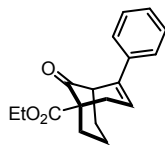
Prepared according to the general procedure as described above in 91% yield. It was purified by flash chromatography (10 % EtOAc/hexanes) to afford a colorless oil; ^1H NMR (500 MHz, CDCl_3) δ 7.28 – 7.18 (m, 5H), 5.86 (dd, $J = 4.3, 2.9$ Hz, 1H), 4.21 – 4.16 (q, $J = 7.1$ Hz, 2H), 3.32 (dt, $J = 18.0, 2.5$ Hz, 1H), 3.10 – 3.07 (m, 1H), 2.75 (dd, $J = 18.0, 4.4$ Hz, 1H), 2.72 – 2.66 (m, 1H), 2.28 – 2.18 (m, 2H), 2.16 – 2.09 (m, 1H), 1.26 – 1.22 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 210.5, 171.1, 142.9, 138.7, 128.5, 127.7, 125.4, 120.9, 61.4, 55.5, 48.9, 43.2, 30.9, 29.0, 14.2; IR (neat): ν_{max} 3011, 2964, 1722, 1713, 1615, 1598, 1453, 1206, 1025, 958, 845, 772, 692 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{19}\text{O}_3$ $[\text{M}+\text{H}]^+$: 271.1329; found: 271.1335.

Ethyl 4-(4-fluorophenyl)-8-oxobicyclo[3.2.1]oct-3-ene-1-carboxylate (4b):



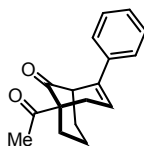
Prepared according to the general procedure as described above in 89% yield. It was purified by flash chromatography (10% EtOAc/hexanes) to afford a colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.25 – 7.18 (m, 2H), 6.97 – 6.91 (m, 2H), 5.80 (dd, $J = 4.3, 2.9$ Hz, 1H), 4.18 (q, $J = 7.1$ Hz, 2H), 3.31 (dt, $J = 18.0, 2.4$ Hz, 1H), 3.02 (d, $J = 5.0$ Hz, 1H), 2.74 (dd, $J = 18.0, 4.4$ Hz, 1H), 2.73 – 2.65 (m, 1H), 2.29 – 2.08 (m, 3H), 1.24 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 210.3, 171.0, 162.3 (d, $J_{\text{C-F}} = 247.2$ Hz), 142.0, 134.8 (d, $J_{\text{C-F}} = 2.9$ Hz), 127.1 (d, $J_{\text{C-F}} = 8.0$ Hz), 120.8, 115.4 (d, $J_{\text{C-F}} = 21.5$ Hz), 61.4, 55.4, 49.0, 43.1, 30.9, 28.9, 14.2; IR (neat): ν_{max} 2998, 1714, 1706, 1624, 1568, 1233, 1146, 1056, 996, 865, 765, 654 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{18}\text{O}_3\text{F}$ $[\text{M}+\text{H}]^+$: 289.1234; found: 289.1238.

Ethyl 9-oxo-4-phenylbicyclo[3.3.1]non-3-ene-1-carboxylate(4c):



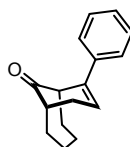
Prepared according to the general procedure as described above in 86% yield. It was purified by flash chromatography (10% EtOAc/hexanes) to afford a colorless oil; ^1H NMR (500 MHz, CDCl_3) δ 7.31 – 7.23 (m, 4H), 7.22 – 7.17 (m, 1H), 6.22 (t, $J = 3.8$ Hz, 1H), 4.19 (q, $J = 7.1$ Hz, 2H), 3.48 (dd, $J = 19.2, 3.0$ Hz, 1H), 3.41 (t, $J = 2.8$ Hz, 1H), 2.61 (dd, $J = 19.3, 3.9$ Hz, 1H), 2.42 – 2.31 (m, 1H), 2.01 – 1.89 (m, 4H), 1.68 – 1.58 (m, 1H), 1.24 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 209.8, 171.9, 138.7, 136.2, 128.6, 127.6, 125.6, 124.5, 61.4, 57.5, 49.7, 39.0, 38.3, 32.4, 17.5, 14.1; IR (neat): ν_{max} 3125, 2984, 1758, 1712, 1635, 1433, 1268, 1086, 964, 831, 734, 667 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{21}\text{O}_3$ $[\text{M}+\text{H}]^+$: 285.1485; found: 285.1484.

5-Acetyl-2-phenylbicyclo[3.3.1]non-2-en-9-one (4d):



Prepared according to the general procedure as described above in 91% yield. It was purified by flash chromatography (10% EtOAc/hexanes) to afford a colorless oil; ^1H NMR (500 MHz, CDCl_3) δ 7.33 – 7.23 (m, 4H), 7.23 – 7.17 (m, 1H), 6.25 (t, $J = 3.7$ Hz, 1H), 3.40 (t, $J = 3.0$ Hz, 1H), 3.26 (dd, $J = 19.5, 2.8$ Hz, 1H), 2.48 (dd, $J = 19.4, 3.9$ Hz, 1H), 2.23 (s, 3H), 2.21 – 2.11 (m, 1H), 2.02 – 1.87 (m, 4H), 1.69 – 1.60 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 212.4, 207.7, 138.5, 136.6, 128.6, 127.7, 125.6, 124.4, 61.5, 50.4, 38.7, 37.1, 32.6, 27.9, 17.5; IR (neat): ν_{max} 3043, 2684, 1724, 1721, 1621, 1589, 1255, 1066, 992, 822, 785 732, 655, cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{19}\text{O}_2$ $[\text{M}+\text{H}]^+$: 255.138; found: 255.1366.

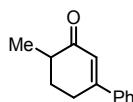
7-Phenylbicyclo[4.3.1]dec-7-en-10-one (4e) :



Prepared according to the general procedure as described above in 64% yield. It was purified by flash chromatography (10% EtOAc/hexanes) to afford a colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.38 – 7.26 (m, 5H), 6.01 (d, $J = 5.9$ Hz, 1H), 3.55 (d, $J = 3.3$ Hz, 1H), 2.87 – 2.79 (m, 1H), 2.72 – 2.63 (m, 1H), 2.42 (ddd, $J = 17.9, 5.9, 1.6$ Hz, 1H), 2.25 – 2.15 (m, 1H), 1.84

– 1.71 (m, 2H), 1.63 – 1.54 (m, 1H), 1.41 (tt, $J = 12.9, 4.1$ Hz, 1H), 1.34 (dddd, $J = 12.7, 8.7, 6.4, 2.8$ Hz, 2H), 1.09 (dd, $J = 26.0, 12.8$ Hz, 1H); ^{13}C NMR (CDCl_3 , 75MHz) δ 215.2, 139.9, 139.8, 128.5, 127.4, 126.3, 124.8, 50.9, 46.1, 34.2, 30.9, 29.4, 26.8, 26.0; IR (neat): ν_{max} 3068, 2935, 1722, 1654, 1499, 1208, 1056, 992, 773, 664 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{19}\text{O}$ $[\text{M}+\text{H}]^+$: 227.143; found: 227.1435.

4-Methyl-5,6-dihydro-[1,1'-biphenyl]-3(4H)-one (6):



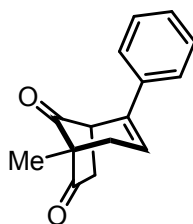
Prepared according to the general procedure as described above in 89% yield. It was purified by flash chromatography (10% EtOAc/hexanes) to afford a colorless oil; ^1H NMR (300 MHz, CDCl_3) δ 7.59 – 7.49 (m, 2H), 7.45 – 7.36 (m, 3H), 6.41 (t, $J = 1.3$ Hz, 1H), 2.88 – 2.71 (m, 2H), 2.52 – 2.38 (m, 1H), 2.23 (dq, $J = 13.5, 4.5$ Hz, 1H), 1.93 – 1.78 (m, 1H), 1.21 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 202.3, 158.6, 138.6, 129.8, 128.7, 126.0, 124.8, 40.7, 30.8, 27.6, 15.1; IR (neat): ν_{max} 2926, 1666, 1602, 1559 1218, 1035, 772, 669 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{14}\text{ONa}$ $[\text{M}+\text{Na}]^+$: 209.0937; found: 209.0943.

References:

1. Prepared according to: P. T. Lansbury, A. K. Serelis, J. E. Hengeveld, D. G. Hangauer Jr, *Tetrahedron*, **1980**, *36*, 2701–2710.
2. (a) B. M. Partridge, J. S. González, and H. W. Lam, *Angew. Chem., Int. Ed.*, **2014**, *53*, 6523–6527; (b) S. Zhu, Q. Zhang, K. Chen and H. Jiang, *Angew. Chem., Int. Ed.*, **2015**, DOI: 10.1002/anie.201504964.
3. D. B. Ramachary, M. Kishor, *Org. Biomol. Chem.*, **2008**, *6*, 4176–4187.
4. F. Barabé, G. v. Bétournay, G. Bellavance, L. Barriault, *Org. Lett.*, **2009**, *11*, 4236–4238.
5. A. Bacchi, M. Costa, N. Della Ca', B. Gabriele, G. Salerno, S. Cassoni, *J. Org. Chem.*, **2005**, *70*, 4971–4979.
6. A. Arcadi, E. Rossi, *Tetrahedron*, **1998**, *54*, 15253–15272.

3. X-ray crystallographic data

Compound 2a



Crystallographic data

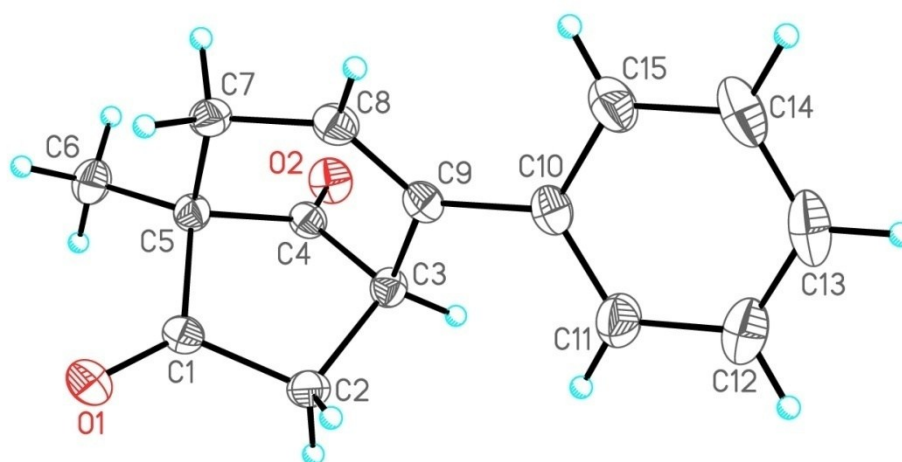


Figure caption: ORTEP diagram of compound **2a** with the atom-numbering. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius.

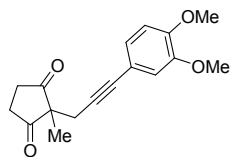
Crystal data for compound 2a: C₁₅H₁₄O₂, $M = 226.26$, colorless plate, 0.49 x 0.38 x 0.10 mm³, monoclinic, space group $P2_1/n$, $a = 12.4961(8)$, $b = 6.0394(4)$, $c = 16.0699(10)$ Å, $\alpha = 90$, $\beta = 104.082(1)^\circ$, $\gamma = 90$, $V = 1176.33(13)$ Å³, $Z = 4$, $D_c = 1.278$ g/cm³, $F_{000} = 480$, CCD area detector, MoK α radiation, $\lambda = 0.71073$ Å, $T = 293(2)$ K, $2\theta_{\max} = 56.6$, 13090 reflections collected, 2830 unique ($R_{\text{int}} = 0.021$), Final $GooF = 1.399$, $R1 = 0.0443$, $wR2 = 0.1270$, R indices based on 2535 reflections with $I > 2\sigma(I)$ (refinement on F^2), 155 parameters, $\mu = 0.084$ mm⁻¹. CCDC 1412029 contains supplementary crystallographic data for the structure. This data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0) 1223 336 033; email: deposit@ccdc.cam.ac.uk.

Data collection and Structure solution: X-ray data for compound **2a** were collected at room temperature using the Bruker Smart Apex CCD diffractometer with graphite monochromated MoK α radiation ($\lambda=0.71073\text{\AA}$) with ω -scan method.¹ Preliminary lattice parameters and orientation matrices were obtained from four sets of frames. Unit cell dimensions were determined using 7257 reflections. Integration and scaling of intensity data were accomplished using SAINT program.¹ The structures were solved by Direct Methods using SHELXS97² and refinement was carried out by full-matrix least-squares technique using SHELXL-2014/7.² Anisotropic displacement parameters were included for all non-hydrogen atoms. All H atoms were positioned geometrically and treated as riding on their parent C atoms, with C-H distances of 0.93--0.97 $\text{\AA}$, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}$ for methyl atoms.

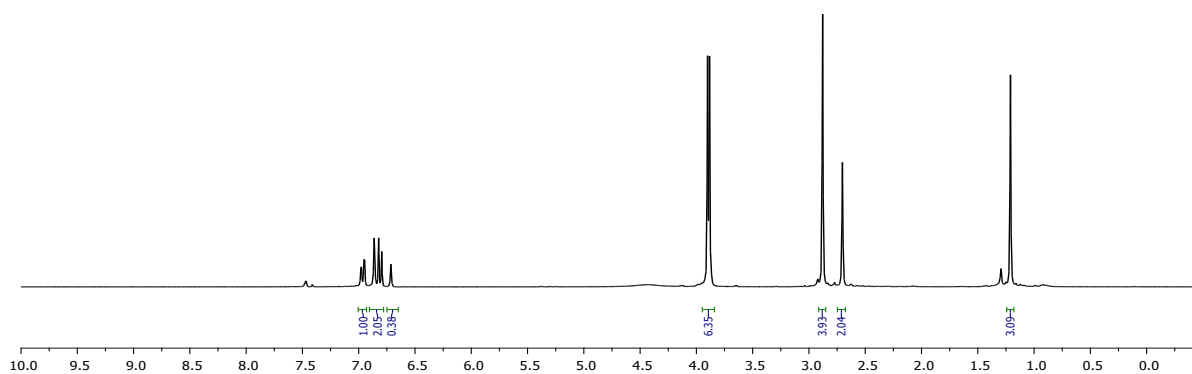
1. SMART & SAINT. Software Reference manuals. Versions 6.28a & 5.625, Bruker Analytical X-ray Systems Inc., Madison, Wisconsin, U.S.A., 2001.
2. Sheldrick, G. M. SHELXS97 and SHELXL-2014/7, Programs for crystal structure solution and refinement; University of Gottingen: Germany, 2014.

4. ^1H NMR, ^{13}C NMR spectra:

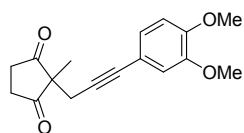
2-(3-(3,4-Dimethoxyphenyl)prop-2-yn-1-yl)-2-methylcyclopentane-1,3-dione (1e):



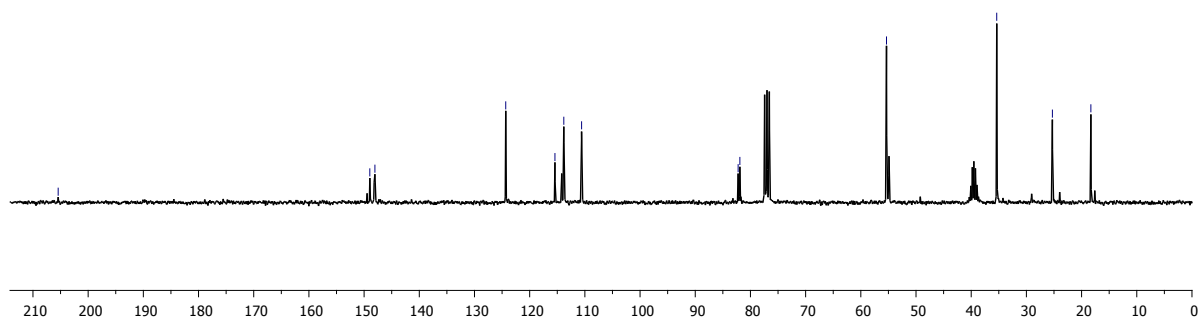
(^1H NMR, CDCl_3 , 300MHz)



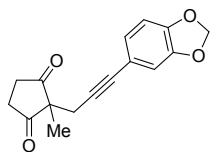
— 205.43 — 148.97 — 148.04 — 124.34 — 115.42 — 113.82 — 110.59 — 82.23 — 81.91 — 55.35 — 35.38 — 25.29 — 18.32



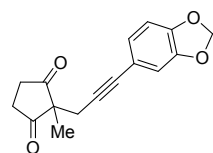
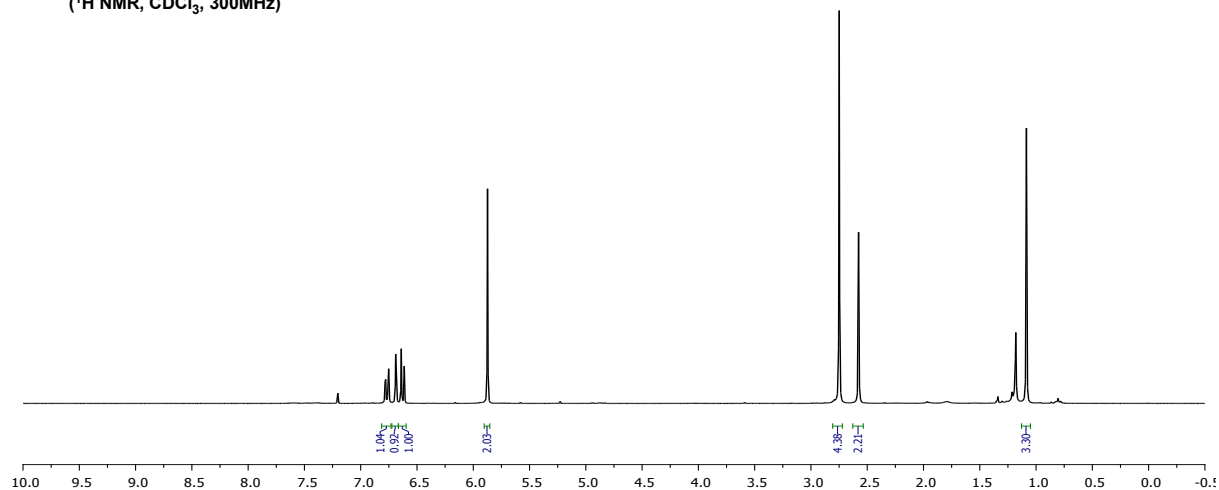
(^{13}C NMR, CDCl_3 +DMSO, 75MHz)



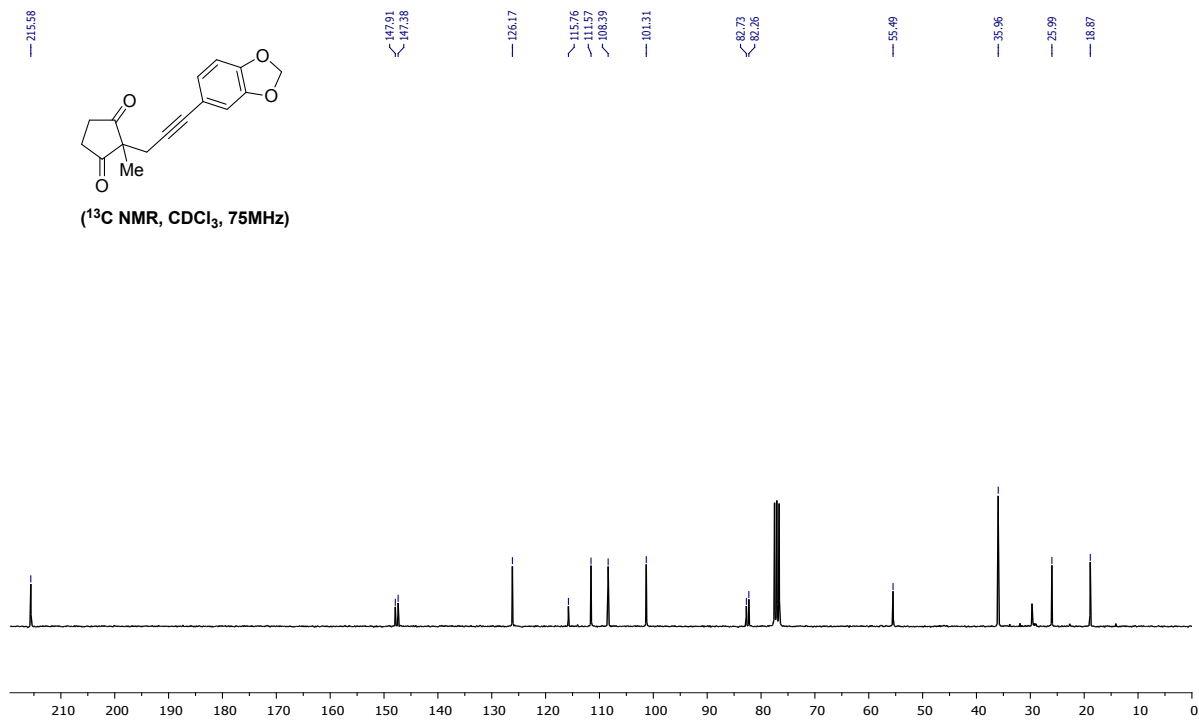
2-(3-(Benzo[d][1,3]dioxol-5-yl)prop-2-yn-1-yl)-2-methylcyclopentane-1,3-dione (1f):



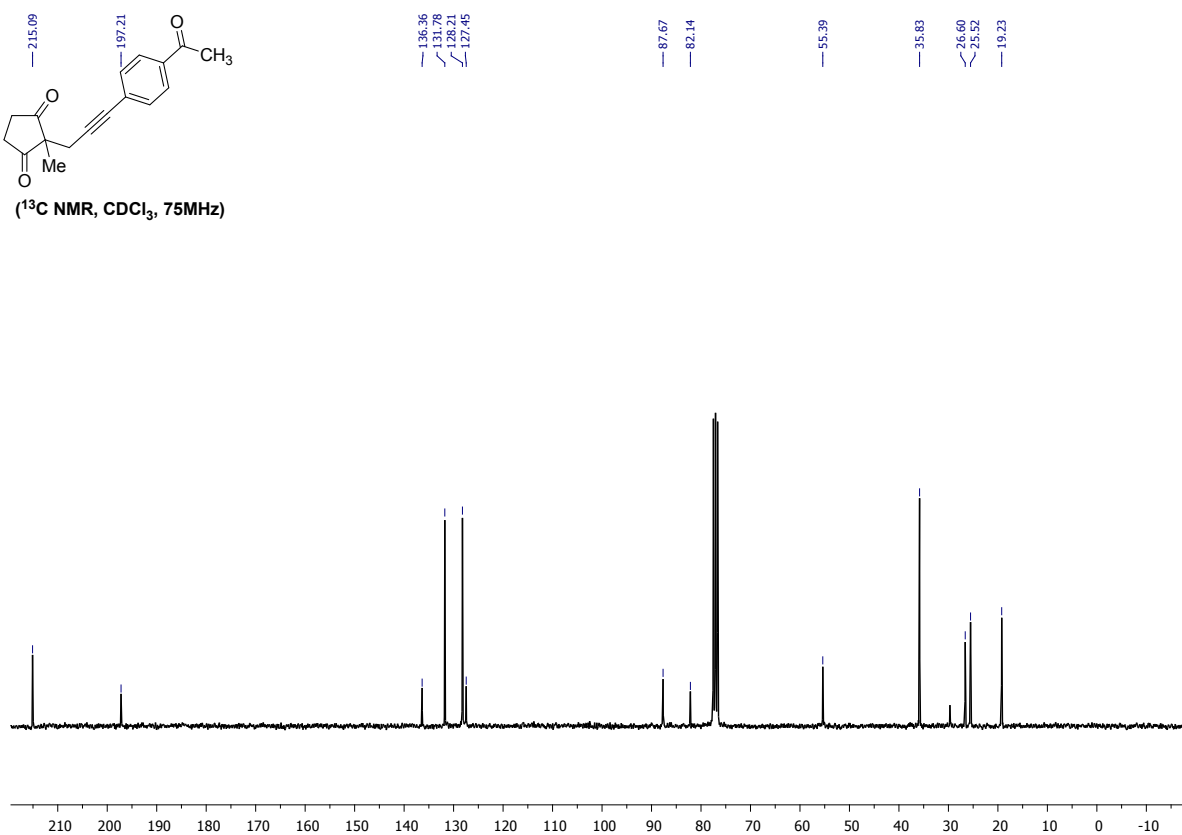
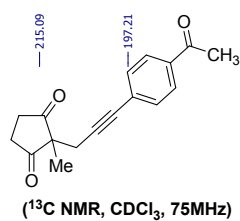
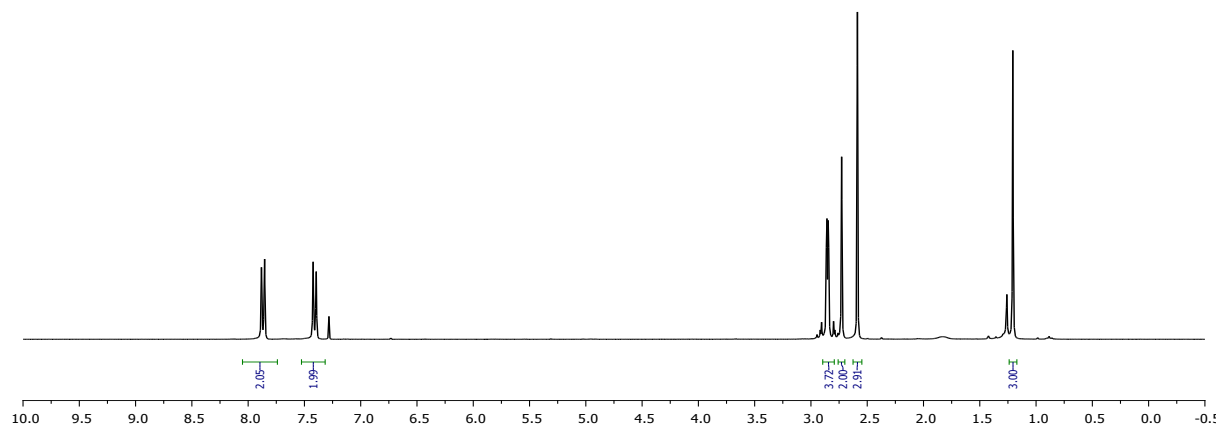
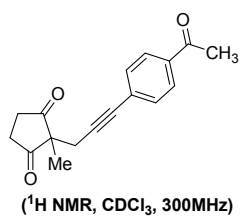
(¹H NMR, CDCl₃, 300MHz)



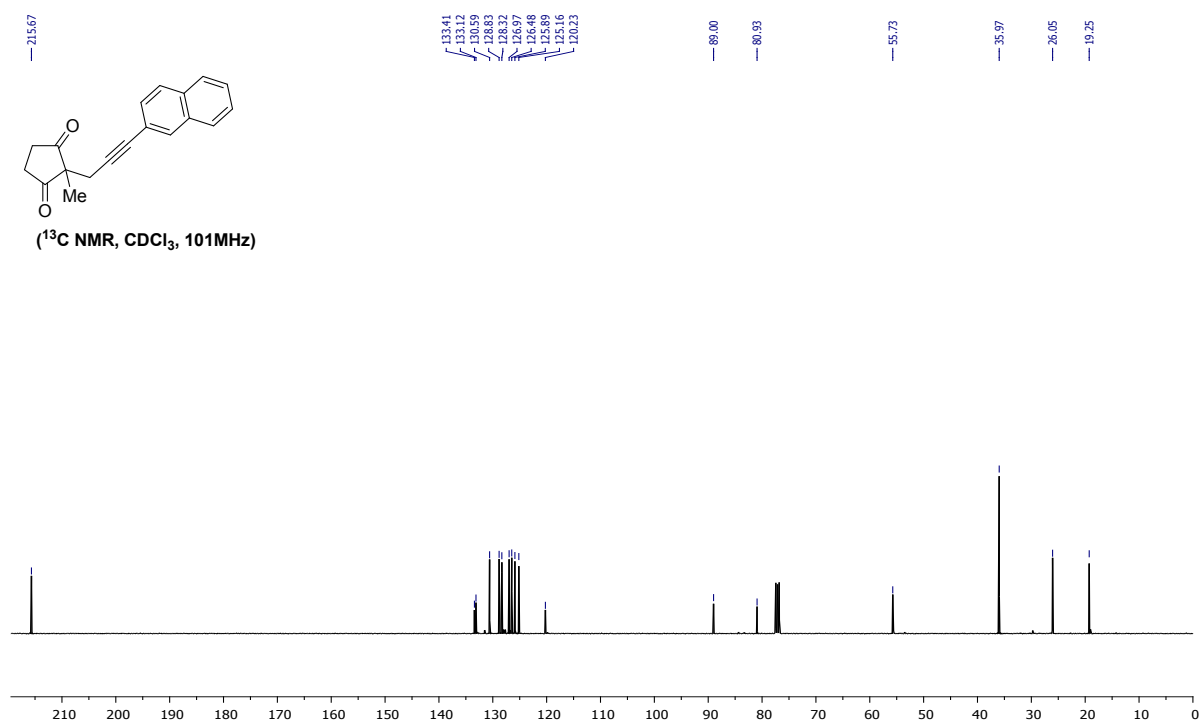
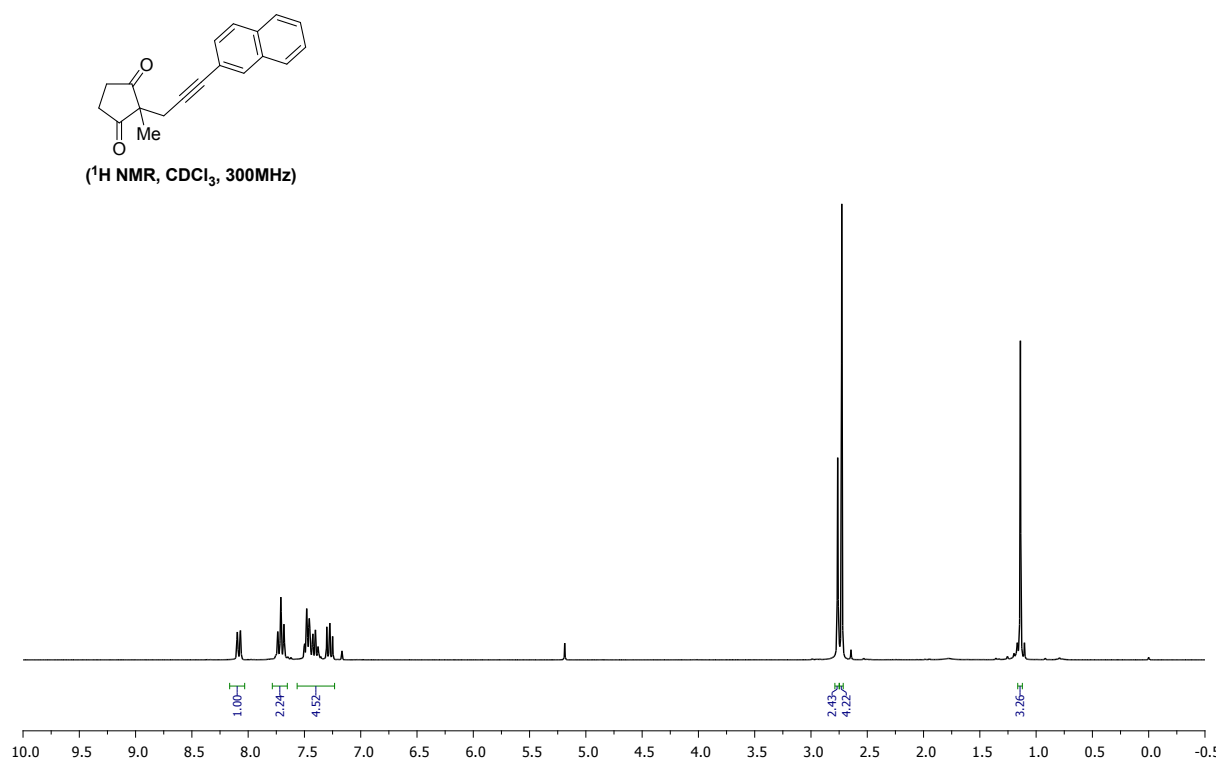
(¹³C NMR, CDCl₃, 75MHz)



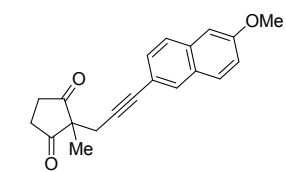
2-(3-(4-Acetylphenyl)prop-2-yn-1-yl)-2-methylcyclopentane-1,3-dione (1h):



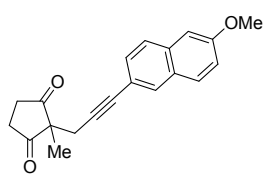
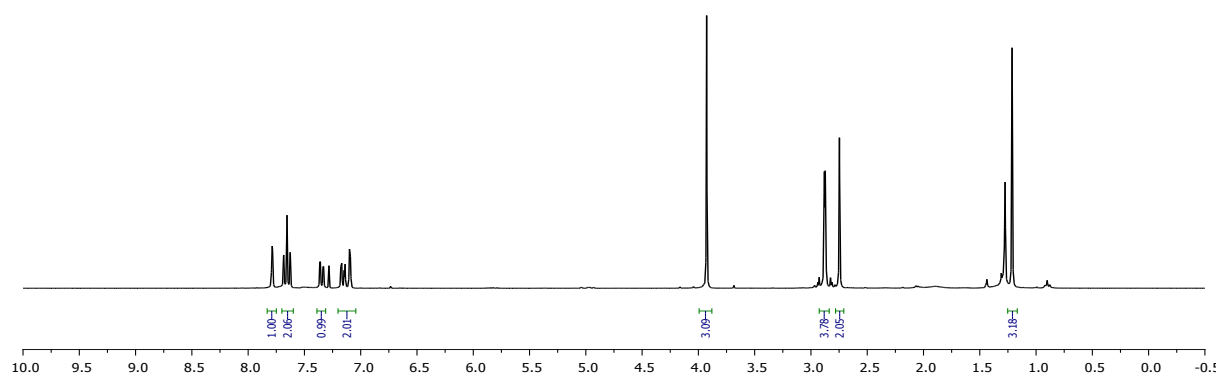
2-Methyl-2-(3-(naphthalen-2-yl)prop-2-yn-1-yl)cyclopentane-1,3-dione (1k):



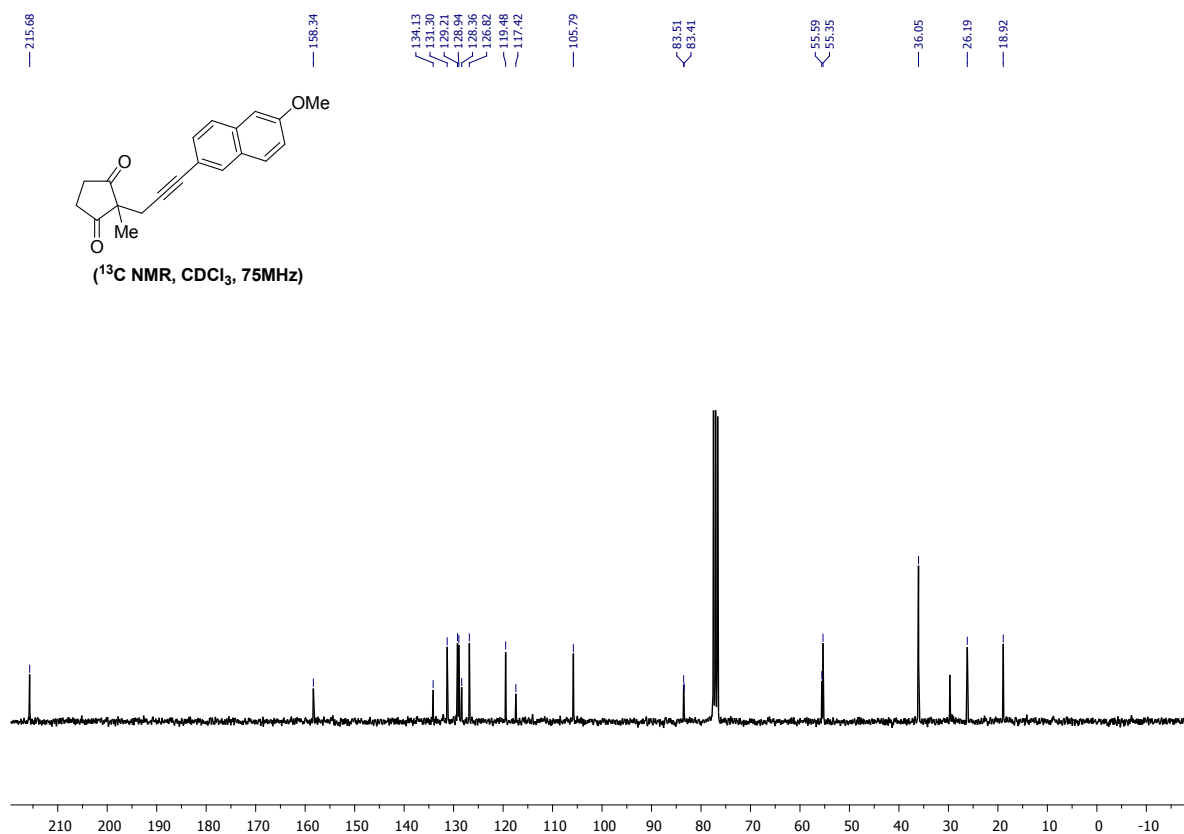
2-(3-(6-Methoxynaphthalen-2-yl)prop-2-yn-1-yl)-2-methylcyclopentane-1,3-dione (11):



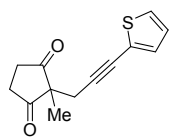
(^1H NMR, CDCl_3 , 300MHz)



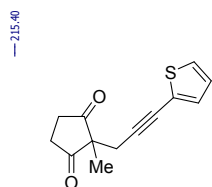
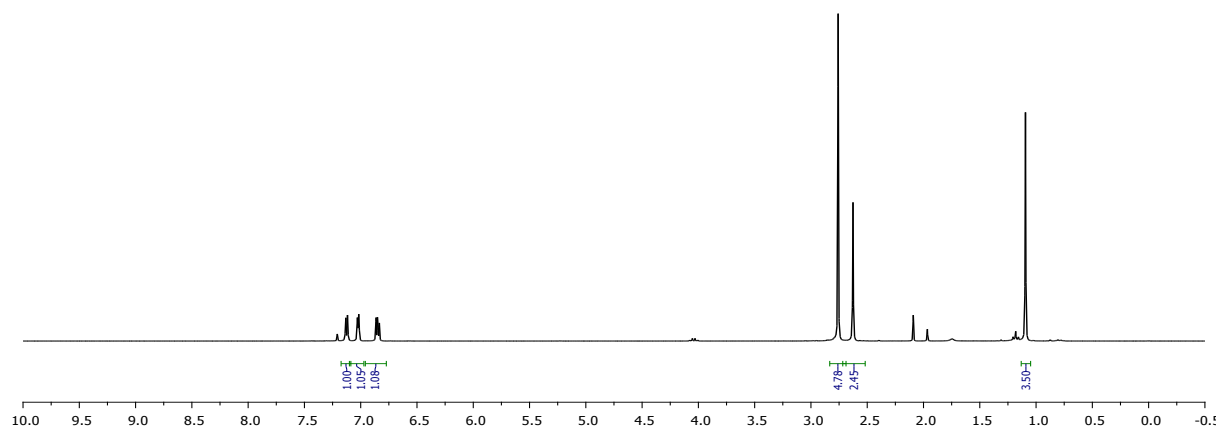
(^{13}C NMR, CDCl_3 , 75MHz)



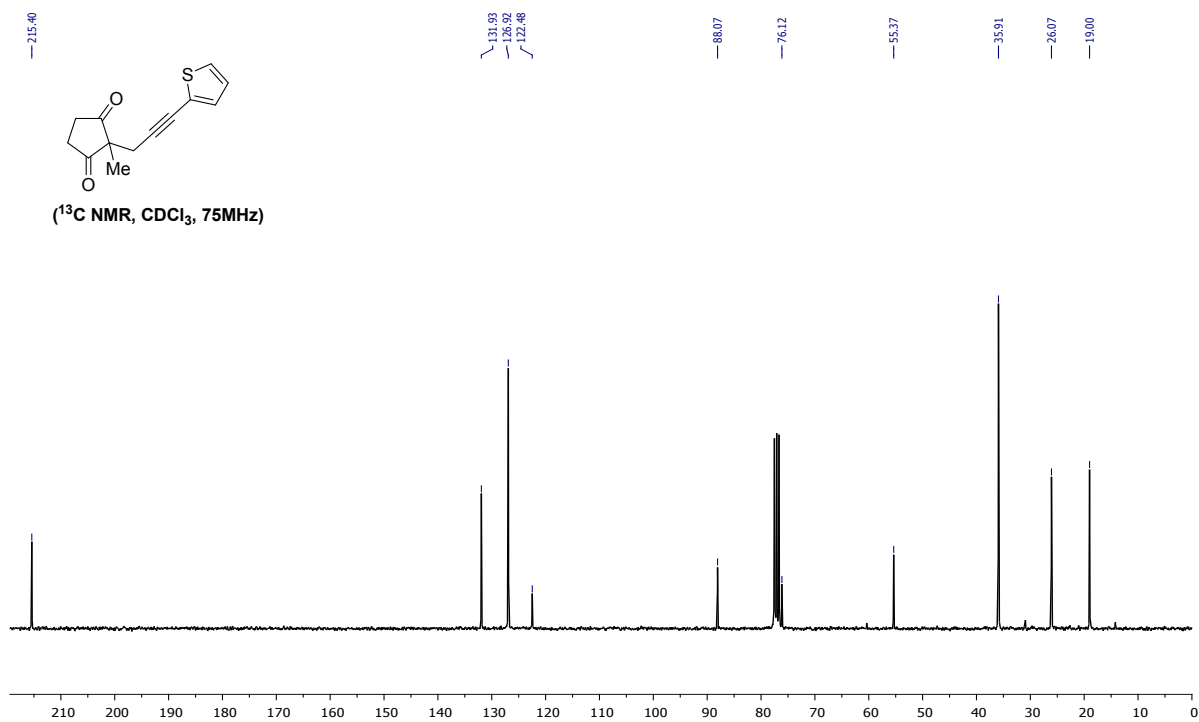
2-Methyl-2-(3-(thiophen-2-yl)prop-2-yn-1-yl)cyclopentane-1,3-dione (1m):



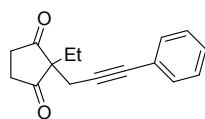
(^1H NMR, CDCl_3 , 300MHz)



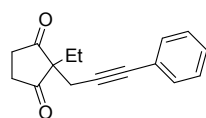
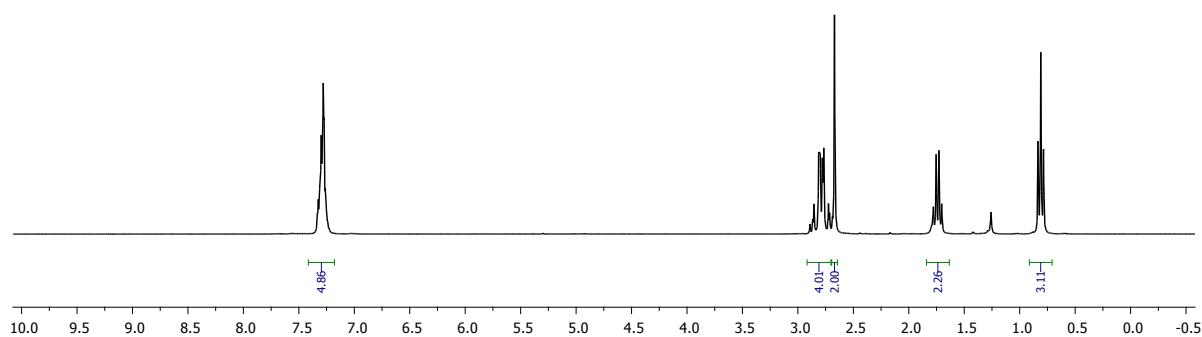
(^{13}C NMR, CDCl_3 , 75MHz)



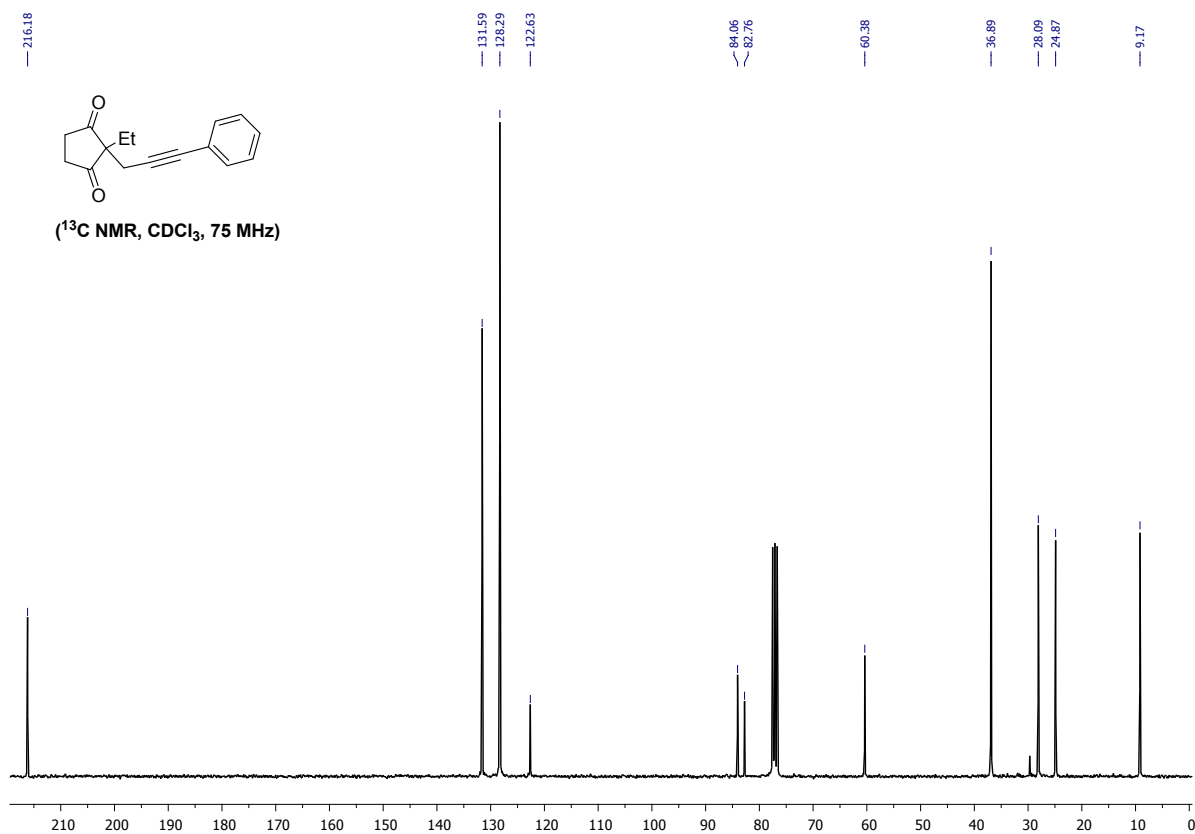
2-Ethyl-2-(3-phenylprop-2-yn-1-yl)cyclopentane-1,3-dione (1n):



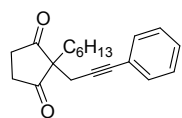
(¹H NMR, CDCl₃, 300 MHz)



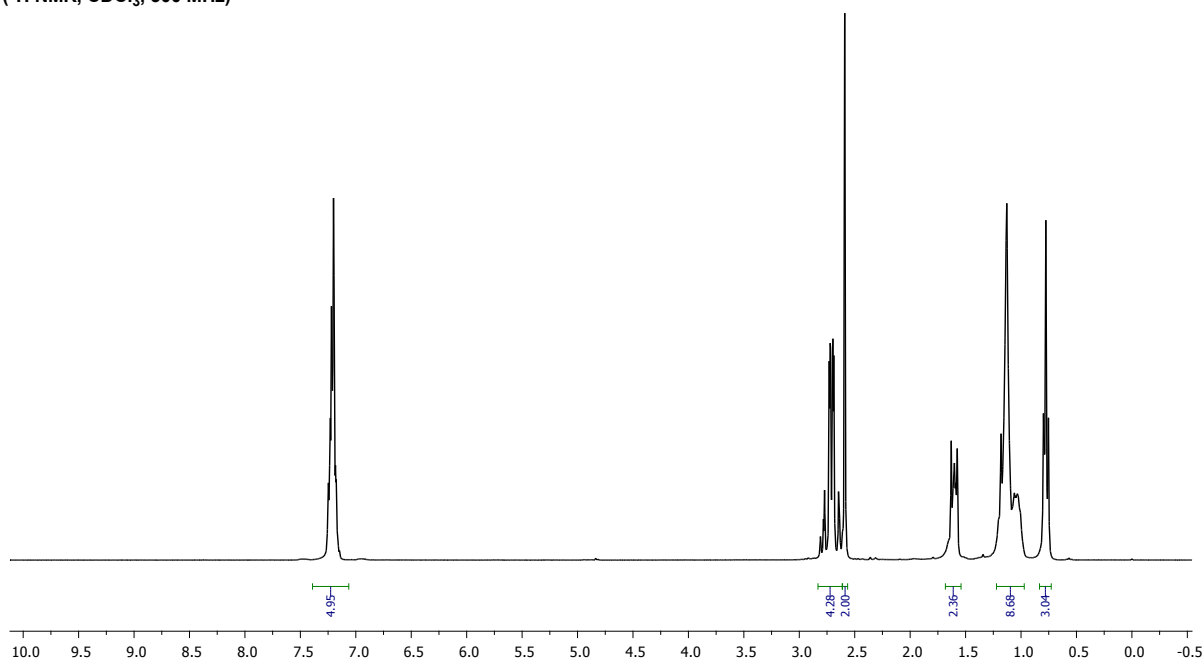
(¹³C NMR, CDCl₃, 75 MHz)



2-Hexyl-2-(3-phenylprop-2-ynyl)cyclopentane-1,3-dione (1o) :



(^1H NMR, CDCl_3 , 300 MHz)



— 216.39

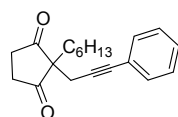
131.58
128.29
122.61

84.01
82.77

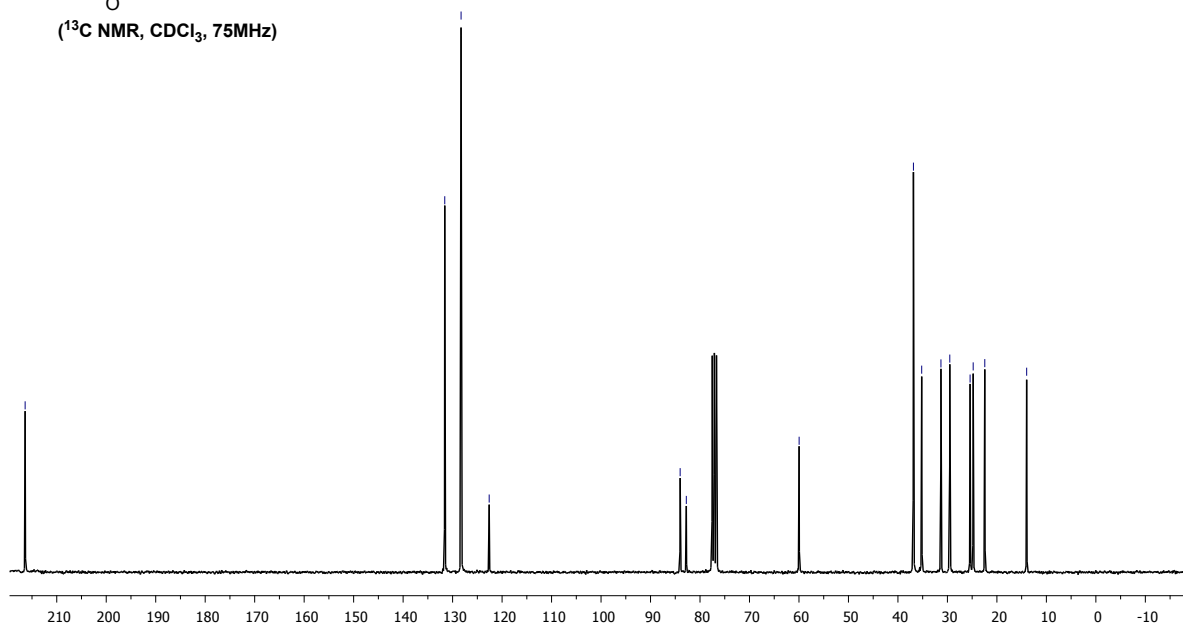
— 59.97

36.87
35.20
34.11
33.52
25.42
24.79
22.45

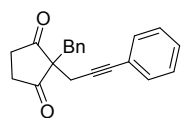
— 13.98



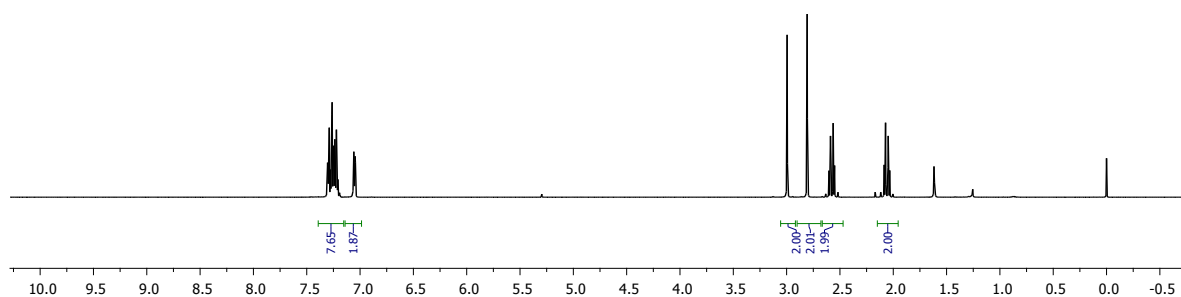
(^{13}C NMR, CDCl_3 , 75MHz)



2-Benzyl-2-(3-phenylprop-2-ynyl)cyclopentane-1,3-dione (1p) :



(^1H NMR, CDCl_3 , 500 MHz)



216.44

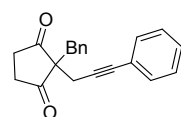
135.04
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129.73
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128.30
127.40
122.55

83.85
82.95

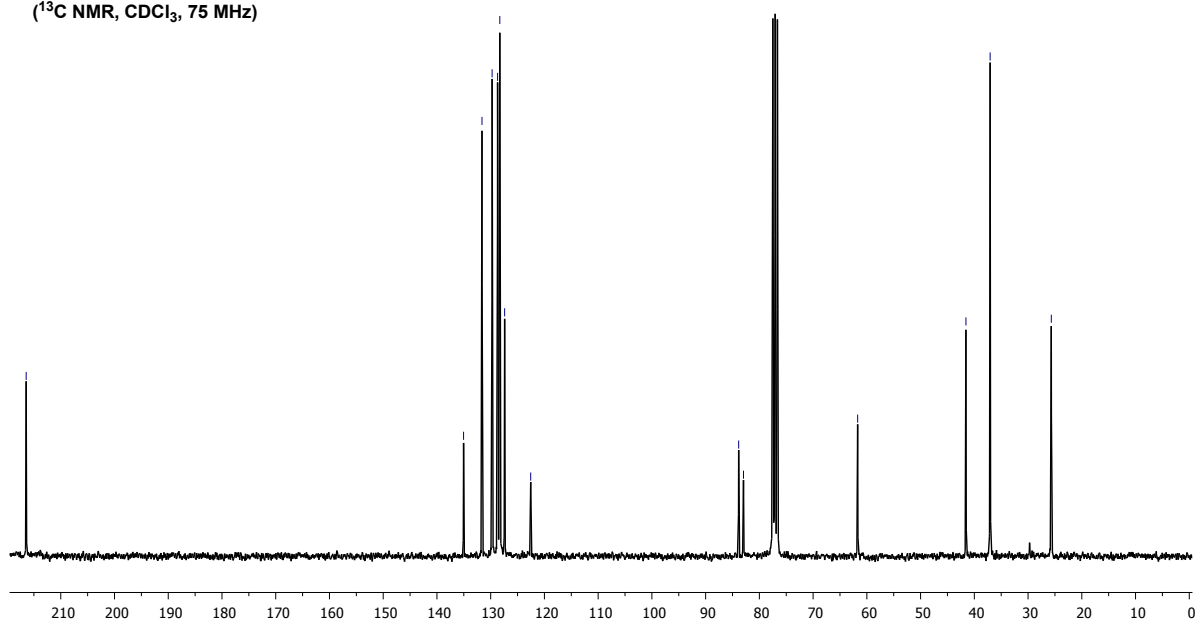
61.71

41.56
37.06

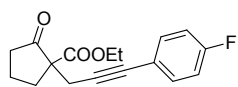
25.68



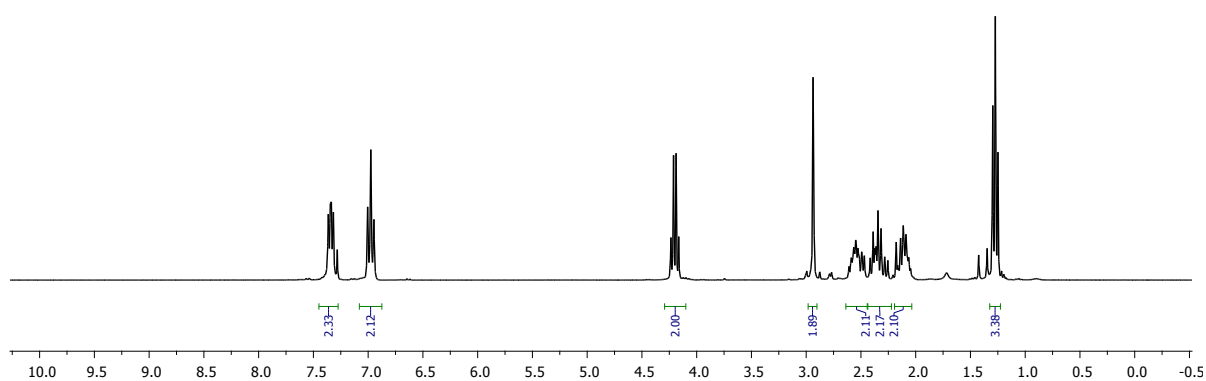
(^{13}C NMR, CDCl_3 , 75 MHz)



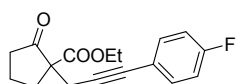
Ethyl 1-(3-(4-fluorophenyl)prop-2-ynyl)-2-oxocyclopentanecarboxylate (3b) :



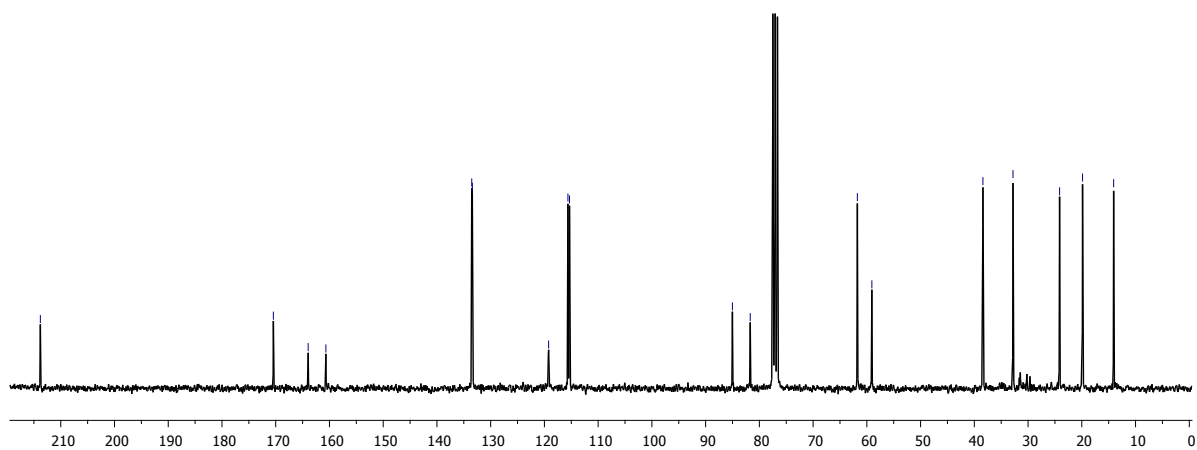
(^1H NMR, CDCl_3 , 300 MHz)



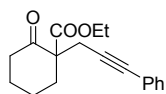
213.80, 170.44, 163.96, 160.66, 133.52, 133.41, 119.21, 115.63, 115.33, 85.02, 81.70, 61.77, 59.07, 38.40, 32.80, 24.13, 19.86, 14.08



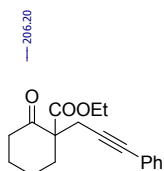
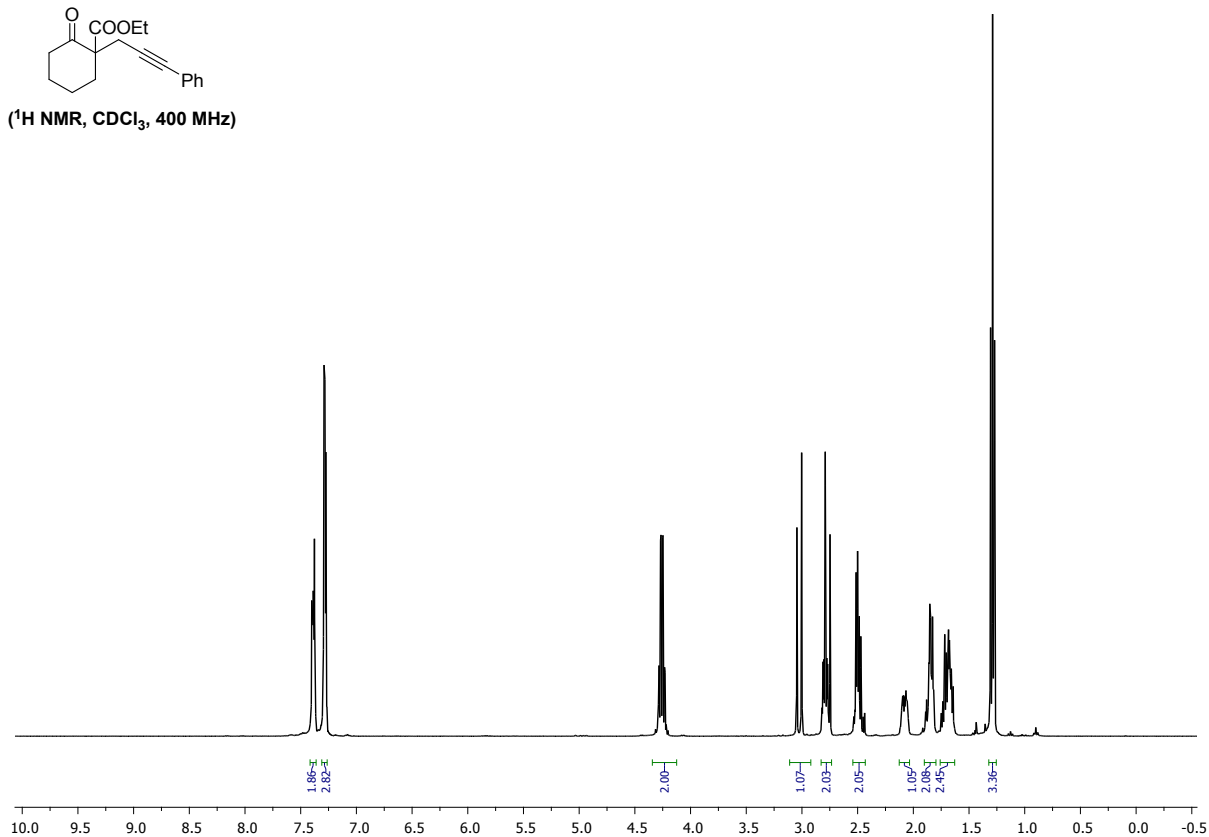
(^{13}C NMR, CDCl_3 , 75 MHz)



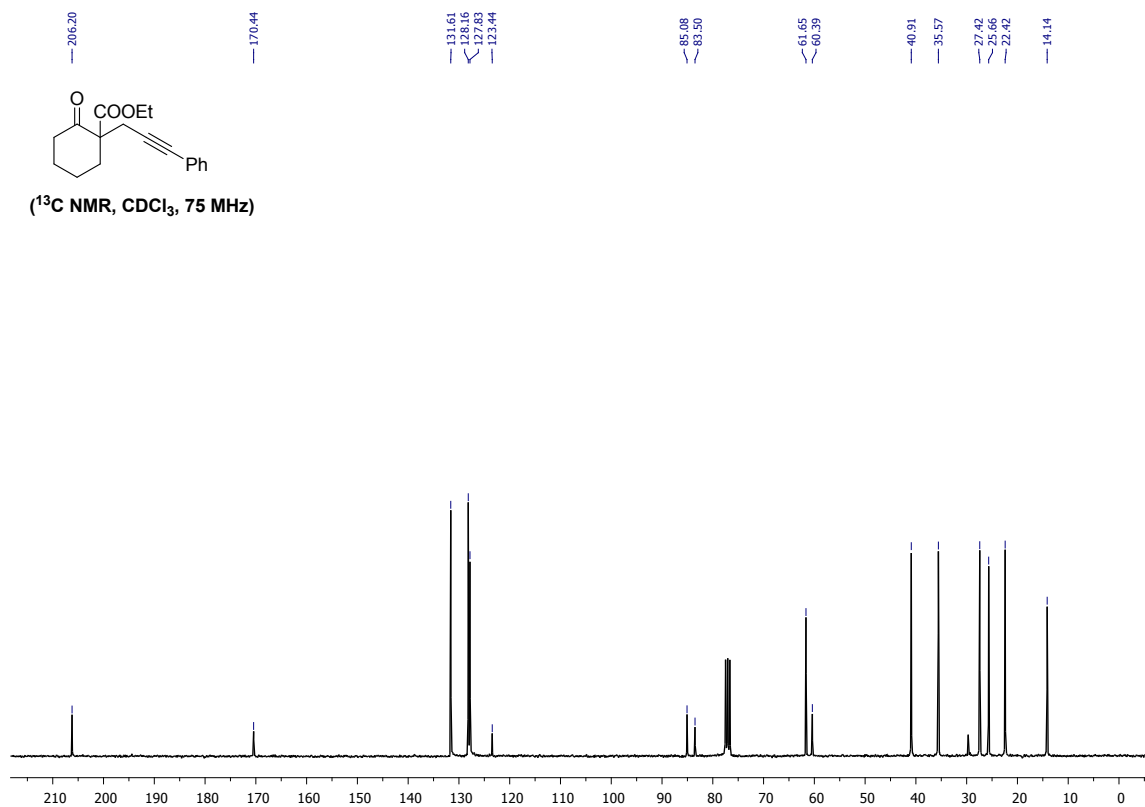
Ethyl 2-oxo-1-(3-phenylprop-2-ynyl)cyclohexanecarboxylate (3c) :



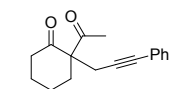
(¹H NMR, CDCl₃, 400 MHz)



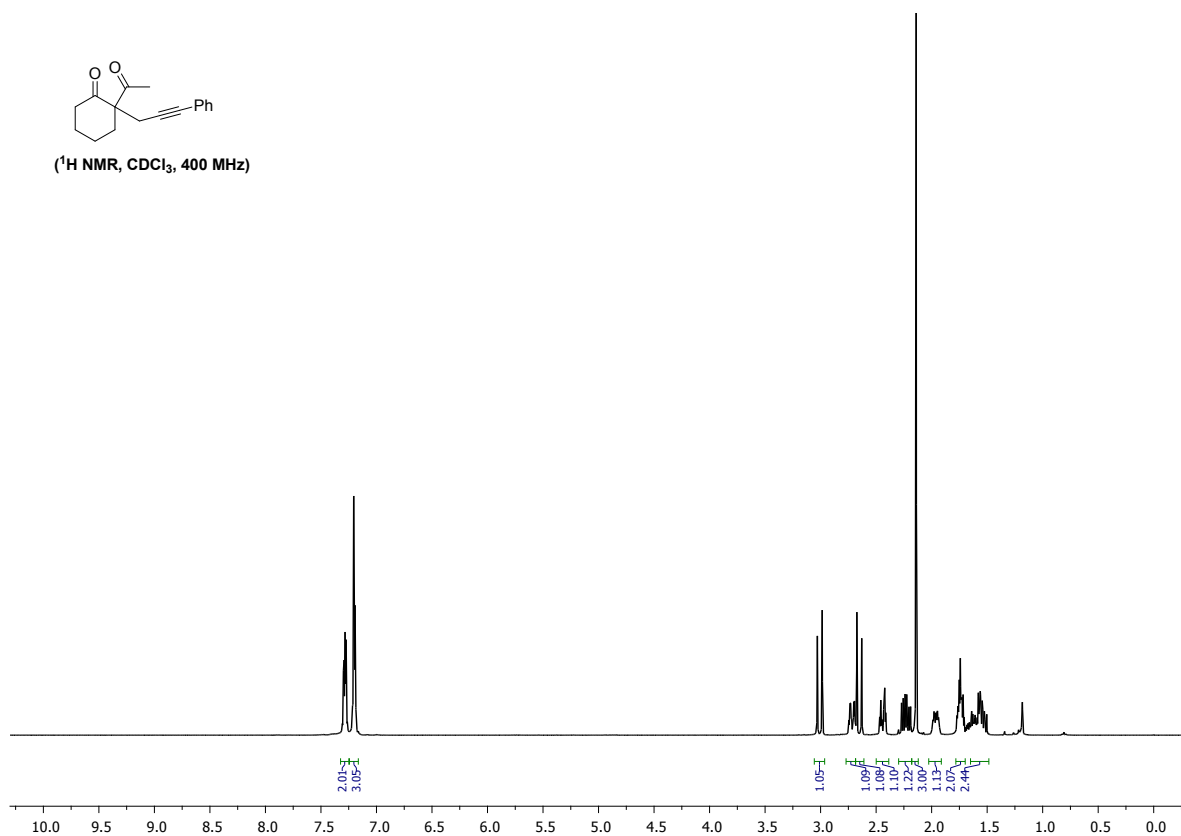
(¹³C NMR, CDCl₃, 75 MHz)



2-Acetyl-2-(3-phenylprop-2-ynyl)cyclohexanone (3d):



(¹H NMR, CDCl₃, 400 MHz)



208.31
204.90

131.61
128.92
128.02
123.11

84.63
84.06

66.89

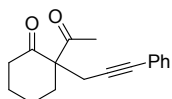
41.52

34.39

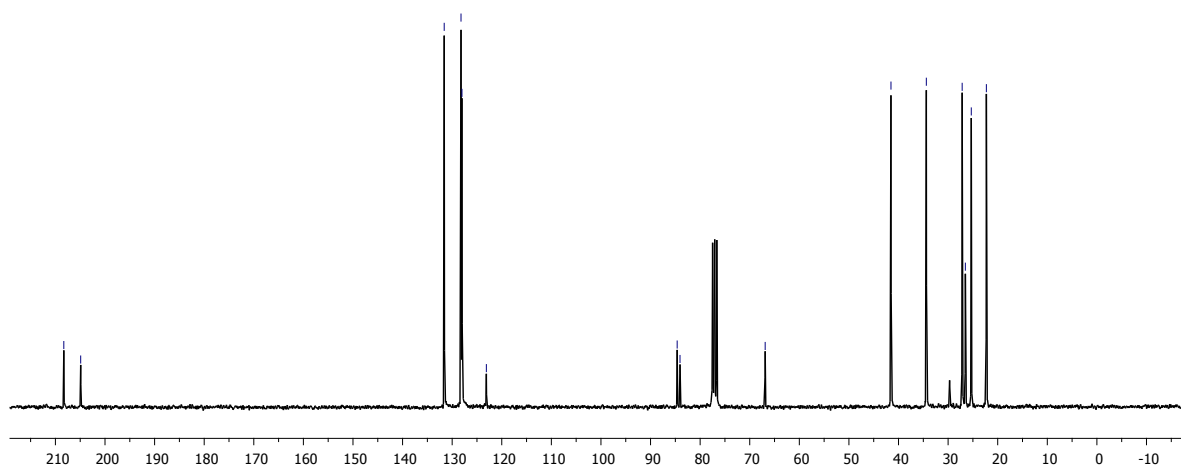
27.17

25.33

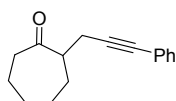
22.29



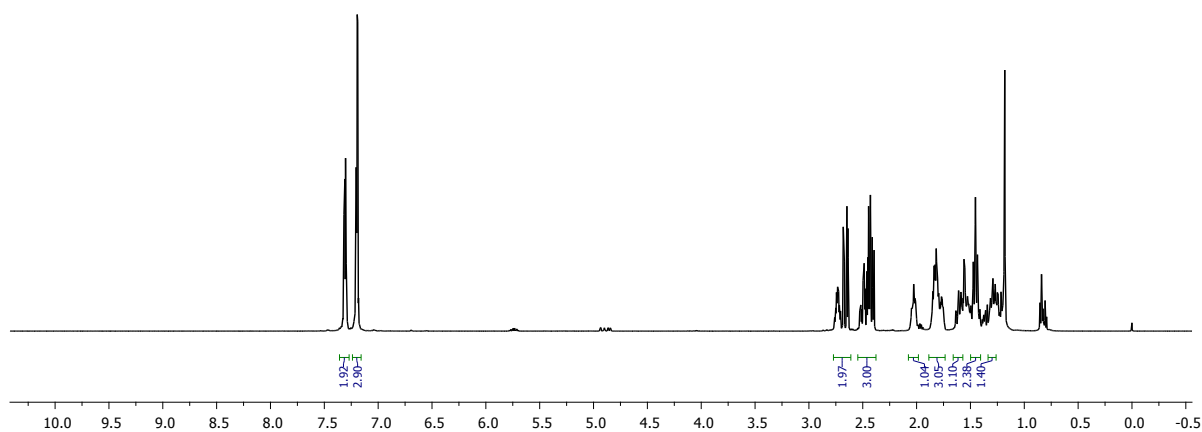
(¹³C NMR, CDCl₃, 75 MHz)



2-(3-Phenylprop-2-ynyl)cycloheptanone (3e):



(¹H NMR, CDCl₃, 500 MHz)



214.33

131.62
128.22
127.72
123.74

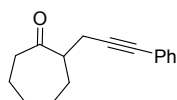
88.23

81.69

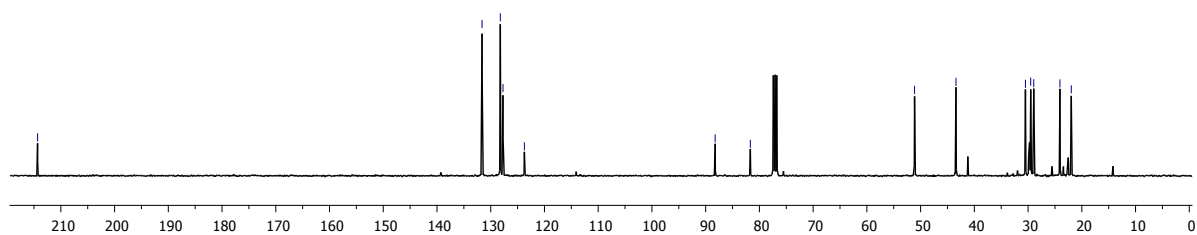
51.13

43.42

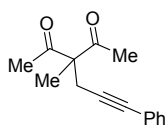
30.49
29.51
28.95
24.67
21.96



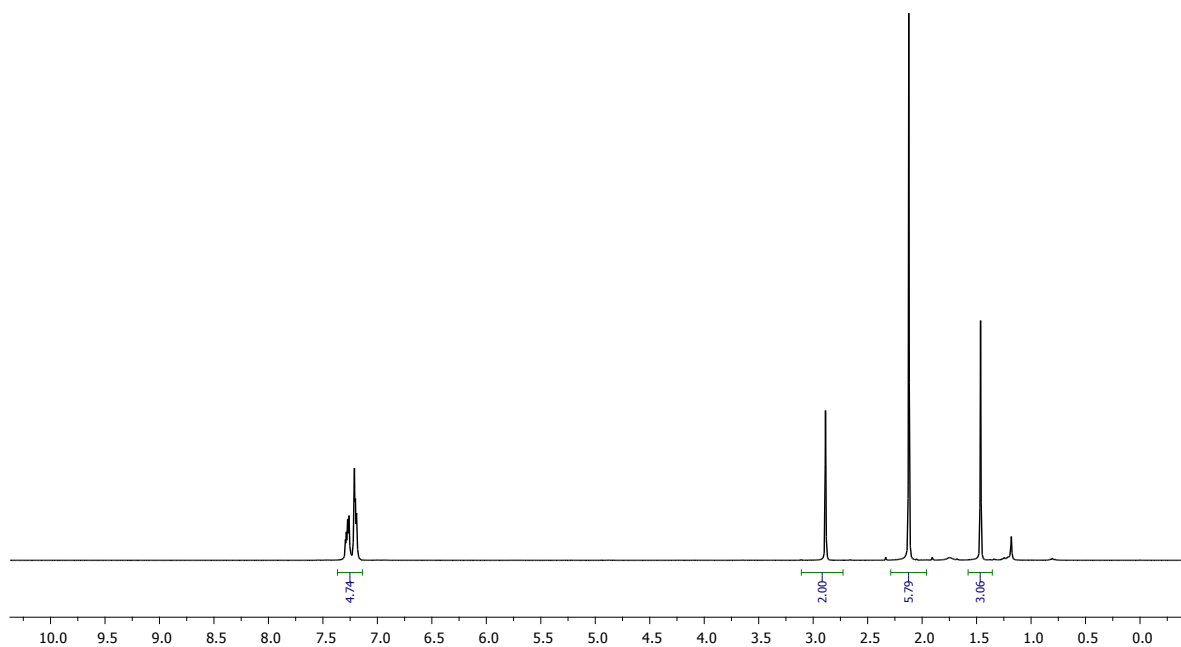
(¹³C NMR, CDCl₃, 101 MHz)



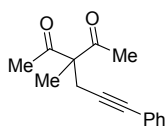
3-Methyl-3-(3-phenylprop-2-ynyl)pentane-2,4-dione(5) :



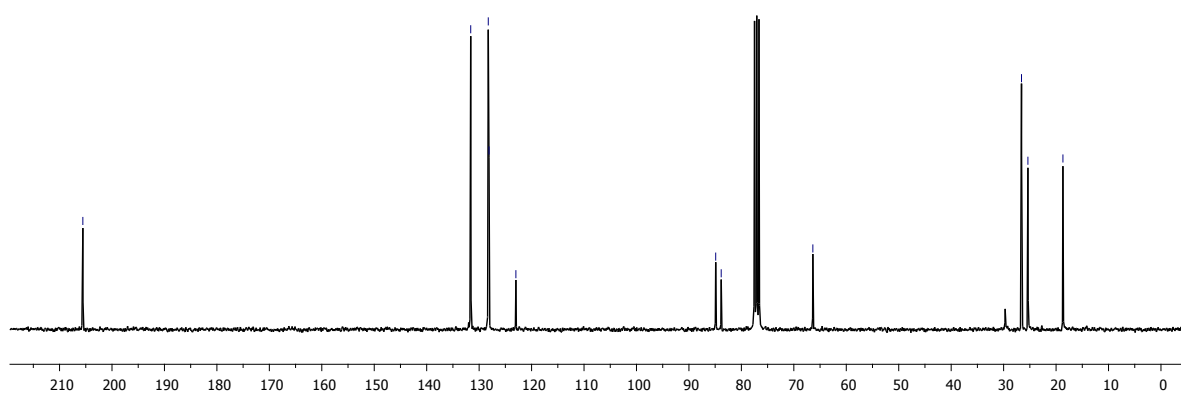
(¹H NMR, CDCl₃, 300 MHz)



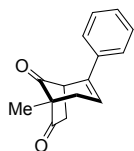
205.56
131.61
128.26
128.12
122.99
84.90
83.85
66.37
26.59
25.37
18.69



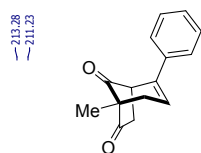
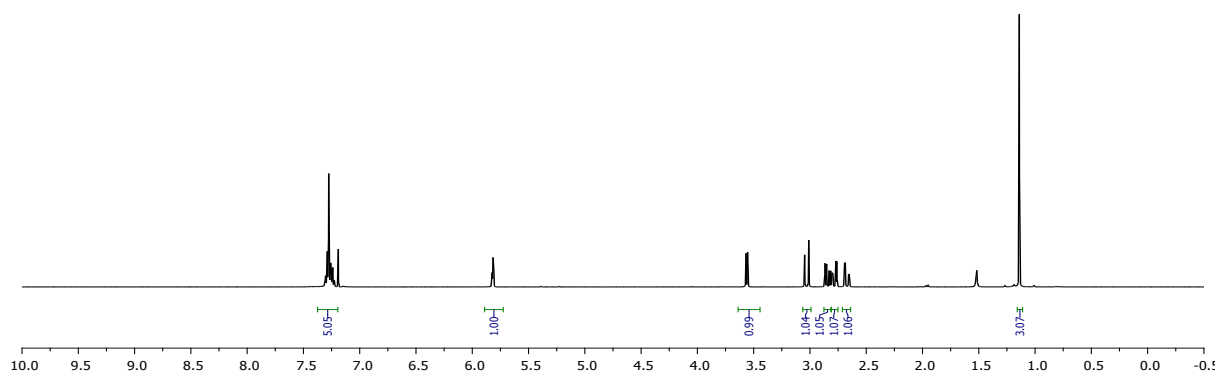
(¹³C NMR, CDCl₃, 75 MHz)



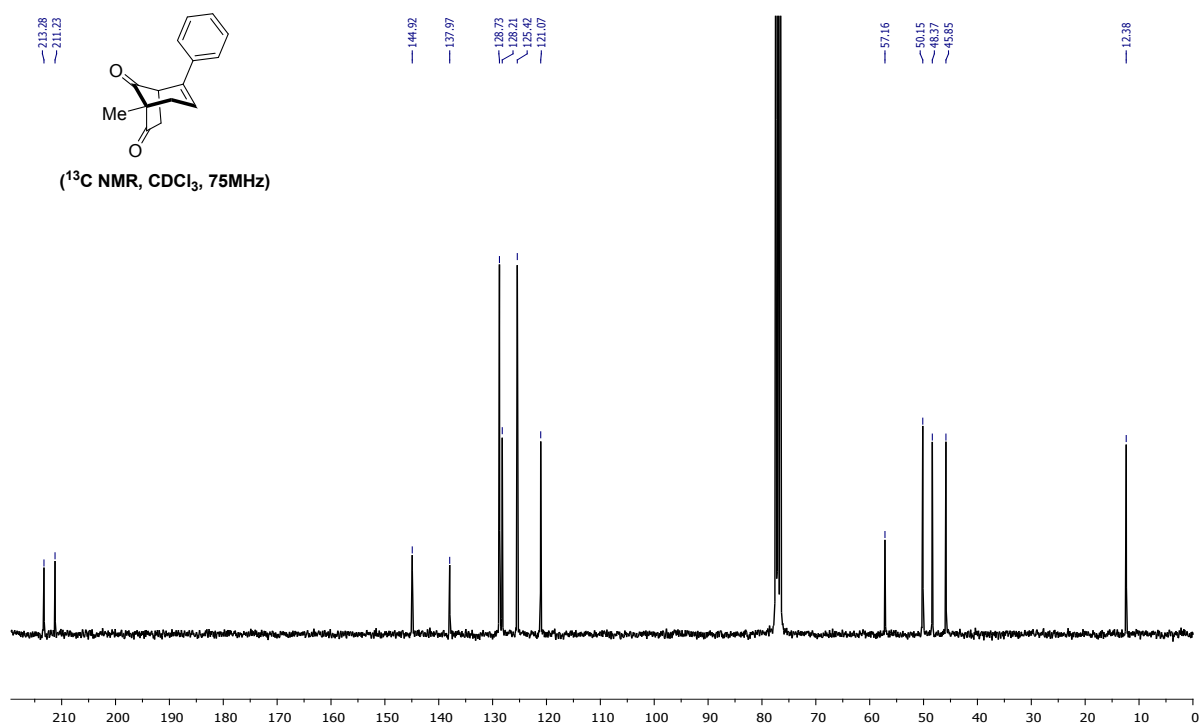
5-Methyl-2-phenylbicyclo[3.2.1]oct-2-ene-6,8-dione (2a):



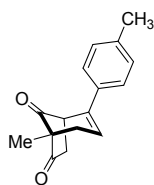
(¹H NMR, CDCl₃, 500MHz)



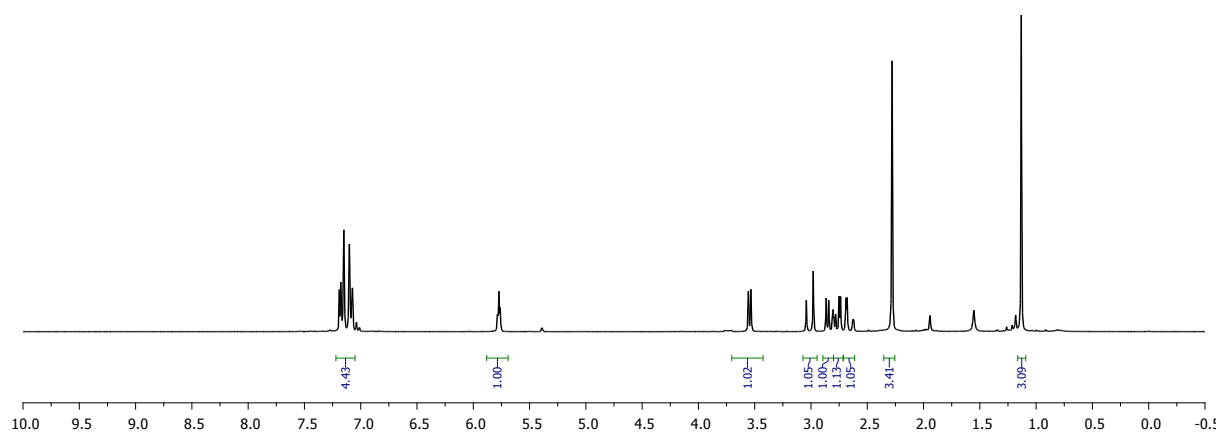
(¹³C NMR, CDCl₃, 75MHz)



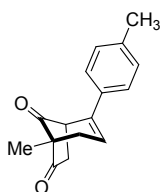
5-Methyl-2-(*p*-tolyl)bicyclo[3.2.1]oct-2-ene-6,8-dione(2b):



(¹H NMR, CDCl₃, 300MHz)



213.52
211.43



(¹³C NMR, CDCl₃, 126MHz)

144.84

138.22

135.13

129.44

125.35

120.15

57.24

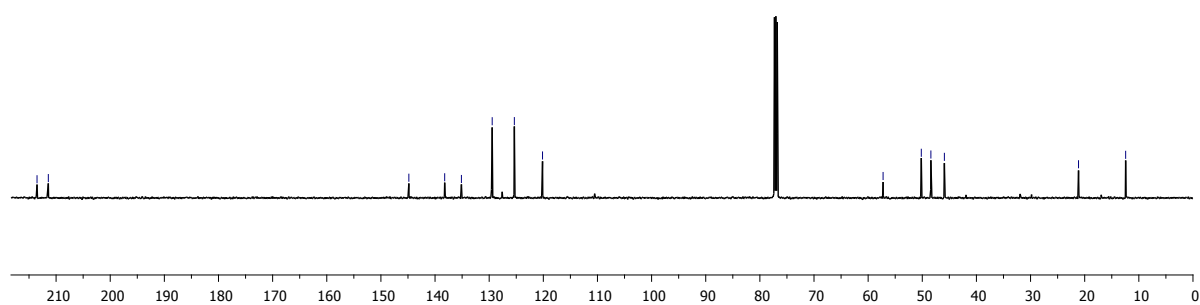
50.18

48.41

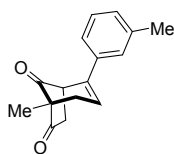
45.92

21.14

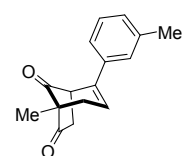
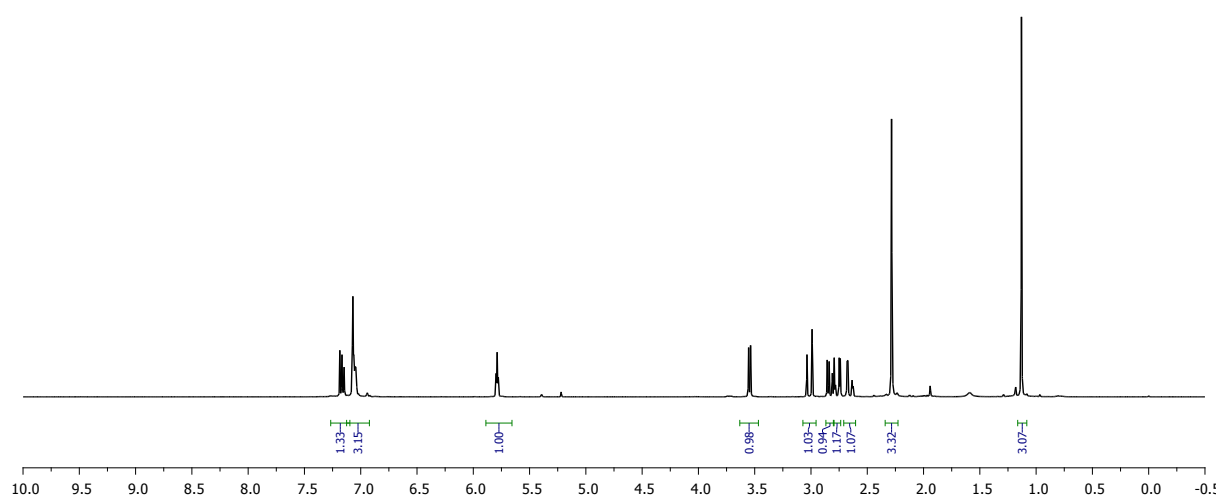
12.43



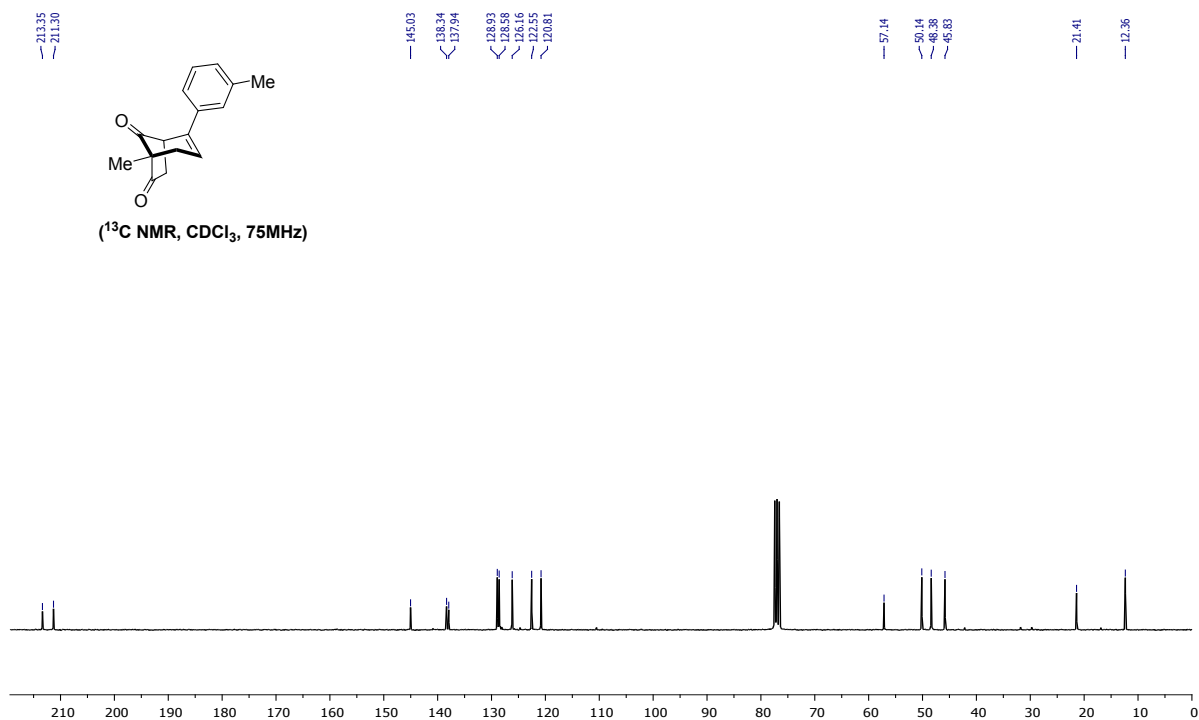
5-Methyl-2-(*m*-tolyl)bicyclo[3.2.1]oct-2-ene-6,8-dione (2c):



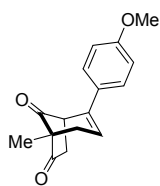
(¹H NMR, CDCl₃, 400MHz)



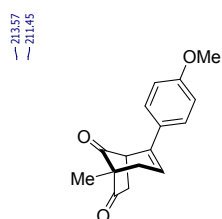
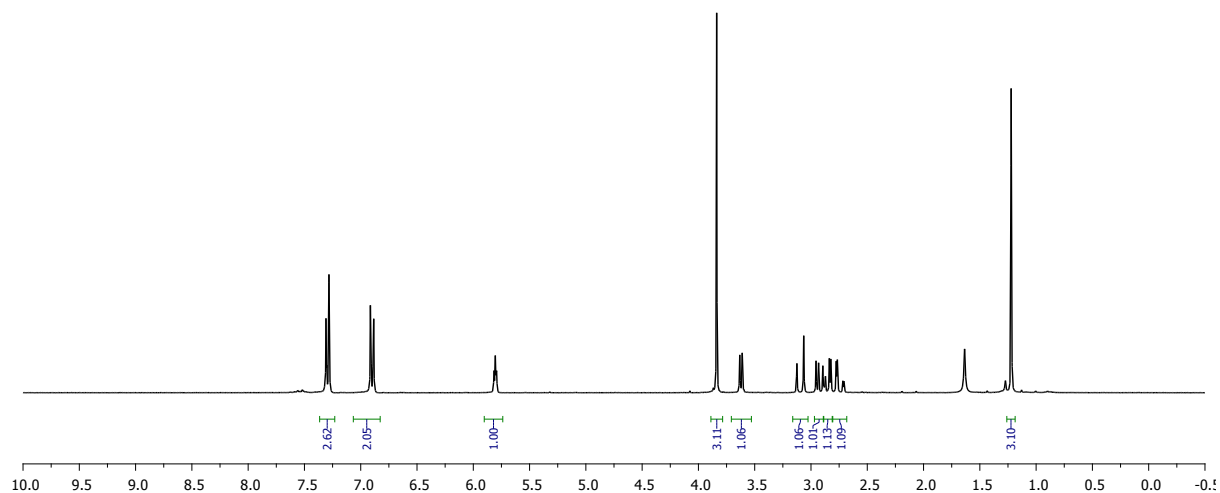
(¹³C NMR, CDCl₃, 75MHz)



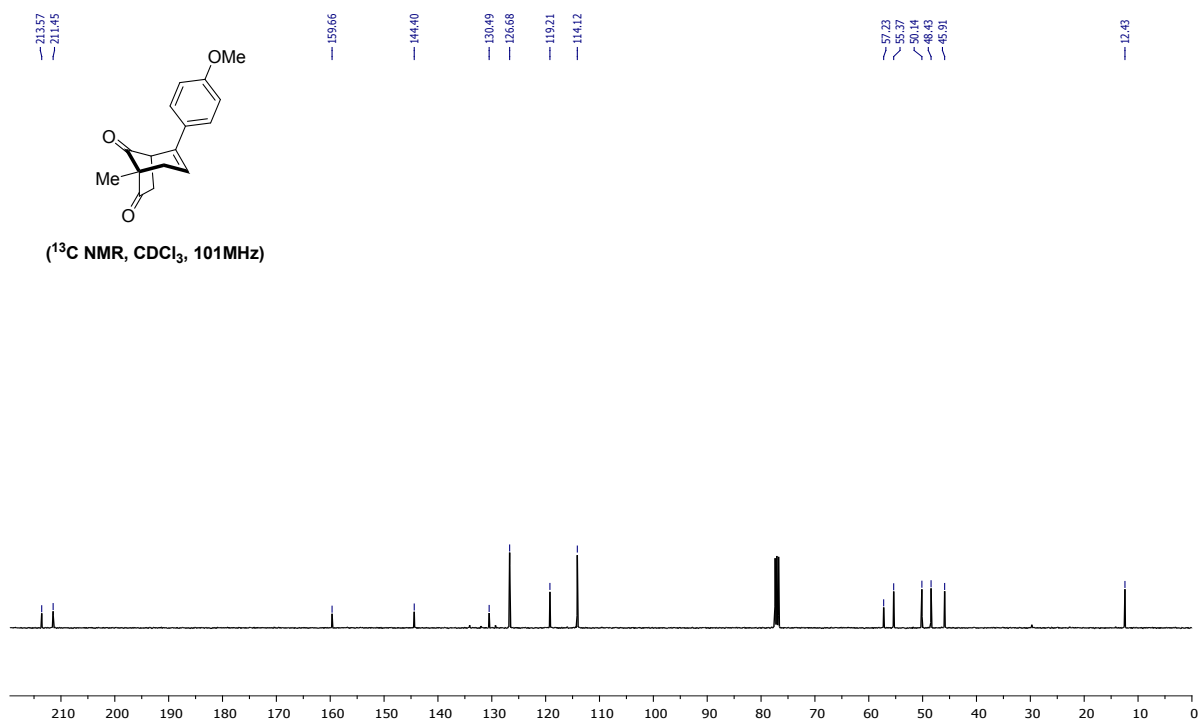
2-(4-Methoxyphenyl)-5-methylbicyclo[3.2.1]oct-2-ene-6,8-dione (2d):



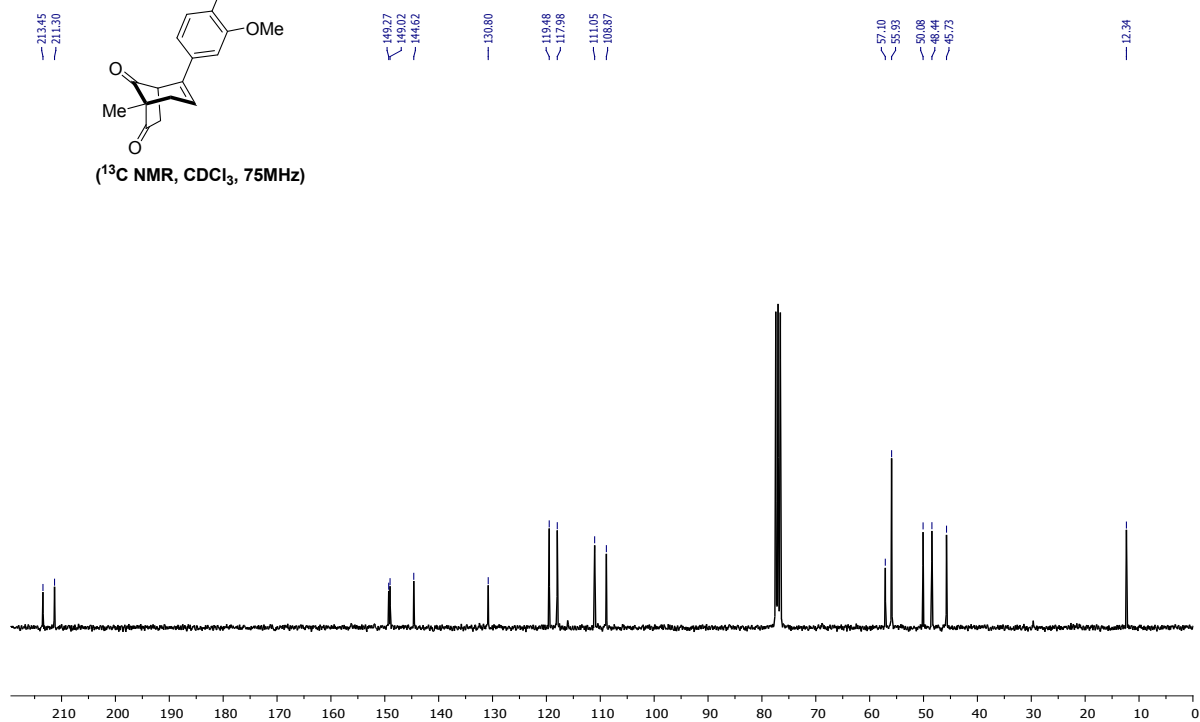
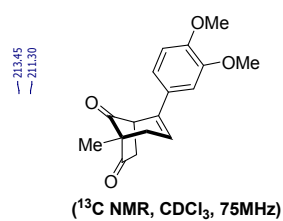
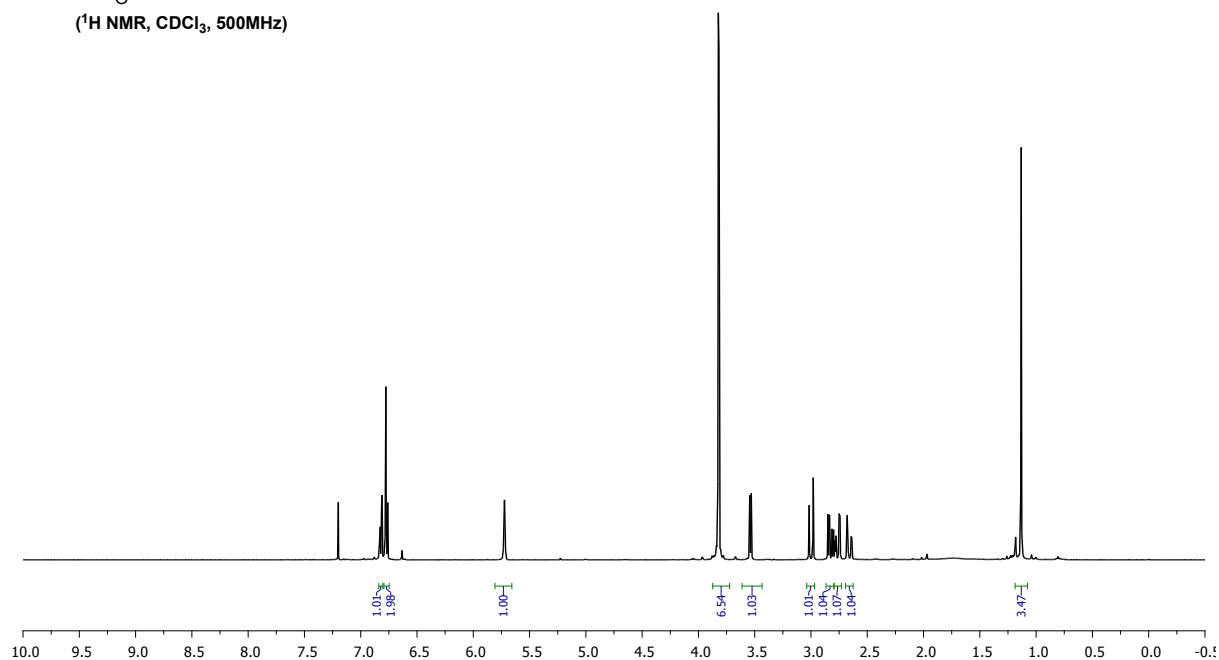
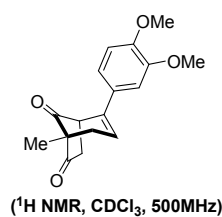
(¹H NMR, CDCl₃, 300MHz)



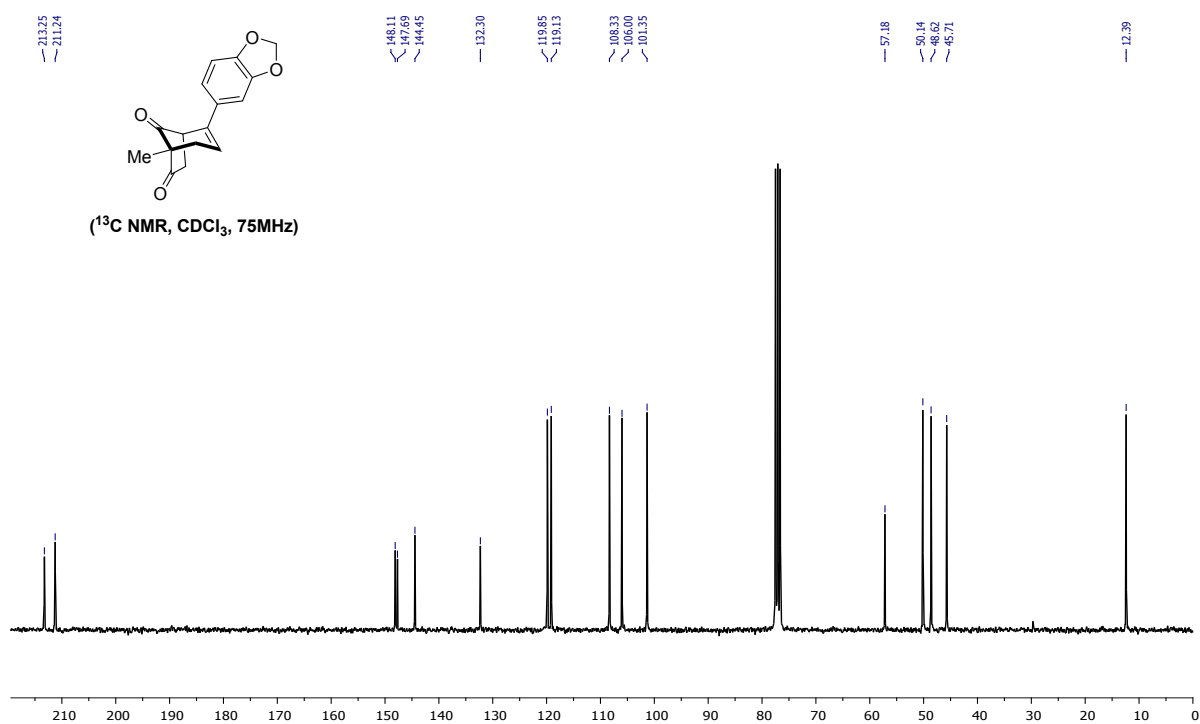
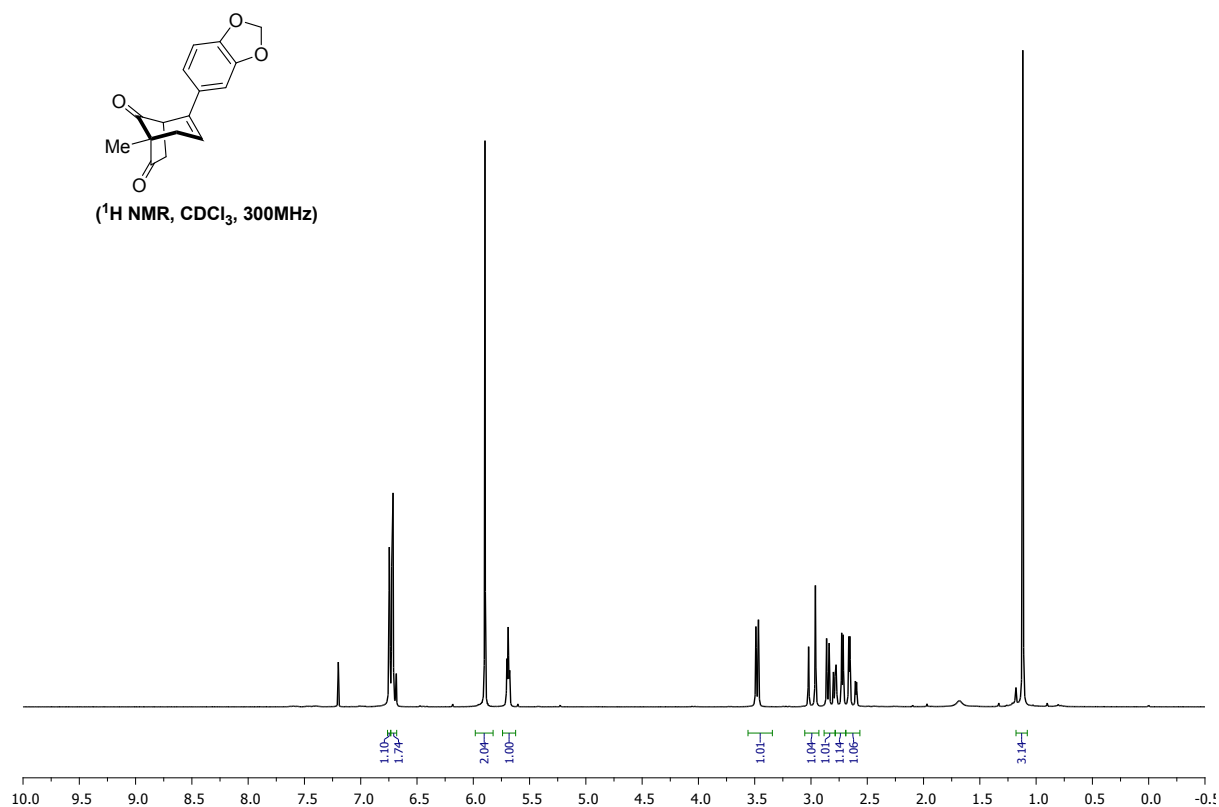
(¹³C NMR, CDCl₃, 101MHz)



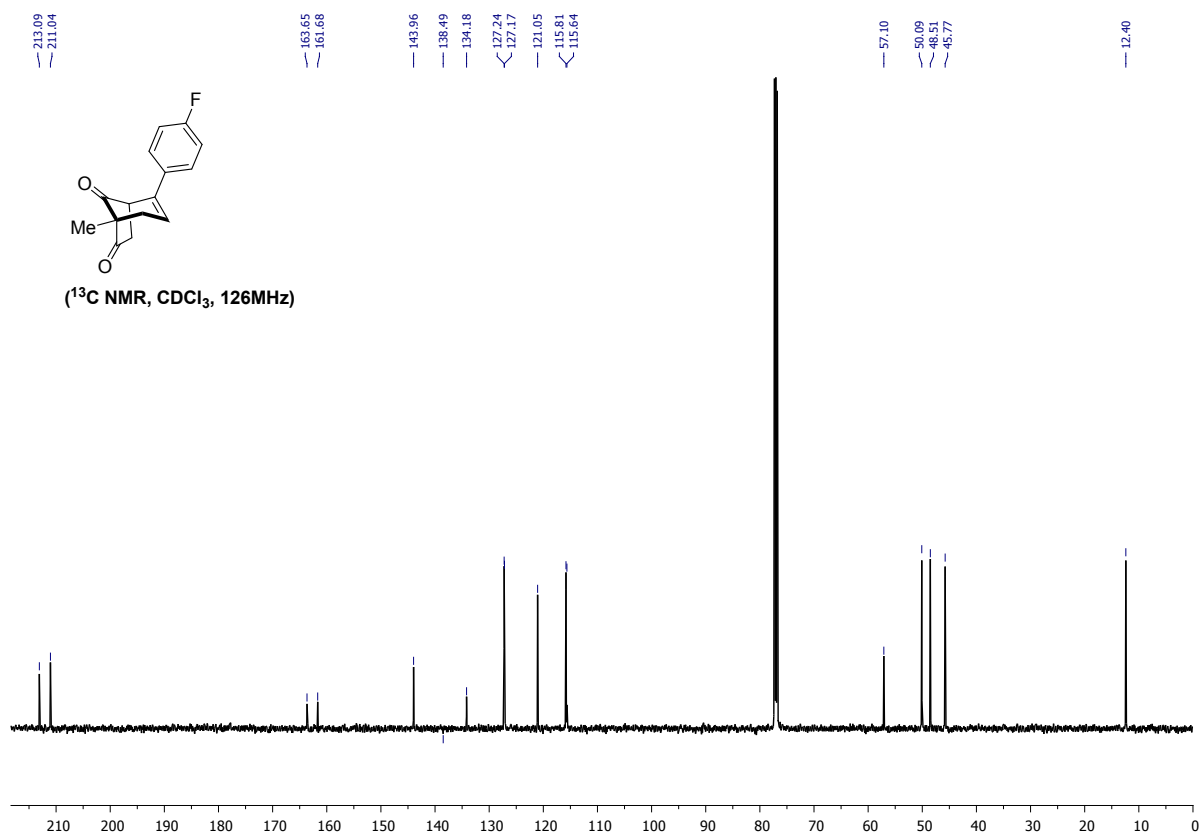
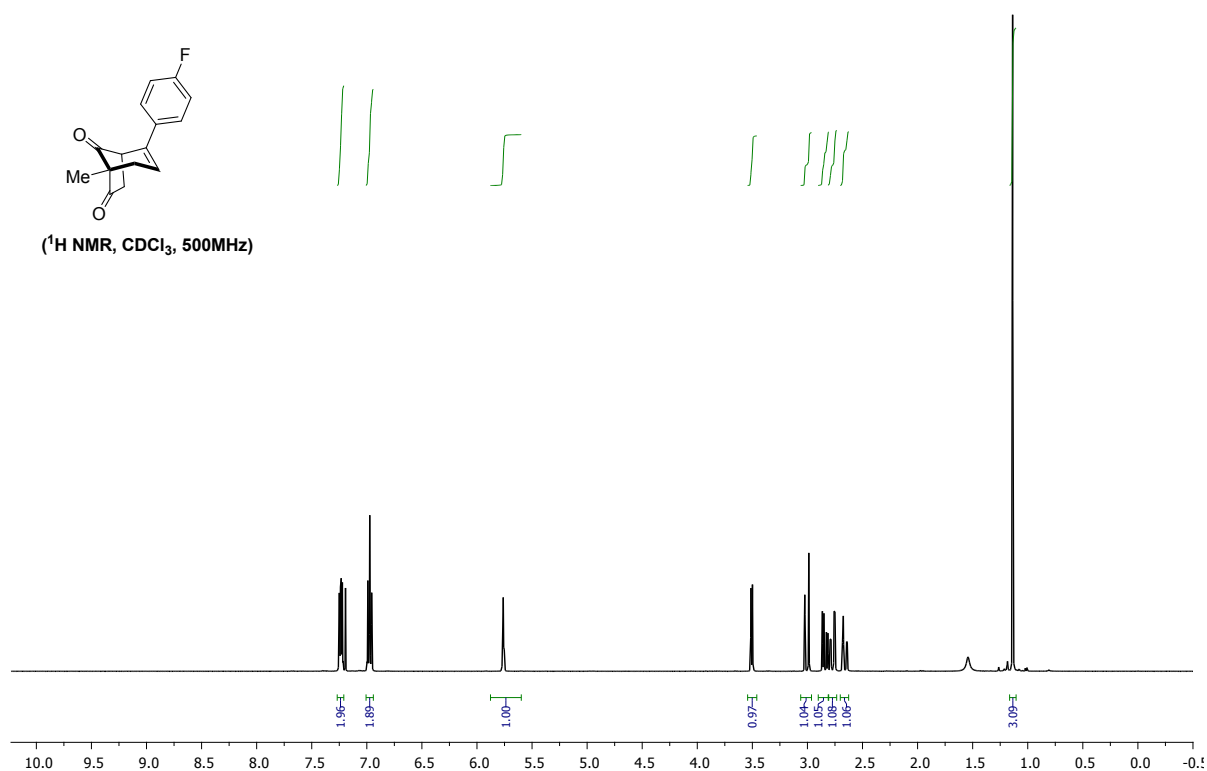
2-(3,4-Dimethoxyphenyl)-5-methylbicyclo[3.2.1]oct-2-ene-6,8-dione (2e):



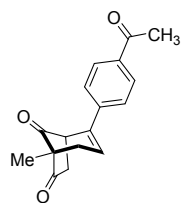
2-(Benzo[d][1,3]dioxol-5-yl)-5-methylbicyclo[3.2.1]oct-2-ene-6,8-dione (2f):



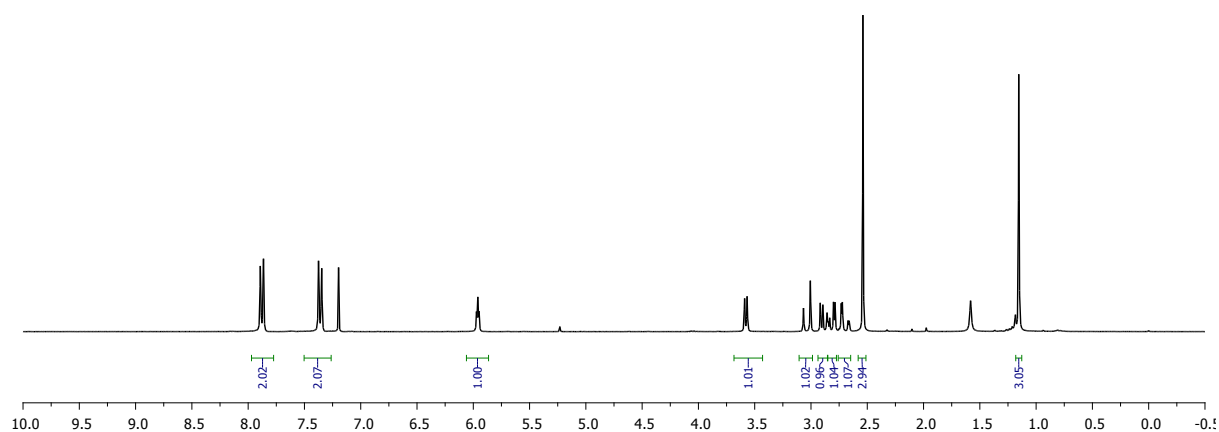
2-(4-Fluorophenyl)-5-methylbicyclo[3.2.1]oct-2-ene-6,8-dione (2g) :



2-(4-Acetylphenyl)-5-methylbicyclo[3.2.1]oct-2-ene-6,8-dione (2h):



(¹H NMR, CDCl₃, 300MHz)



212.74
210.68

197.29

144.04
142.28

136.63

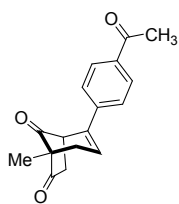
128.88
125.55
123.53

57.08

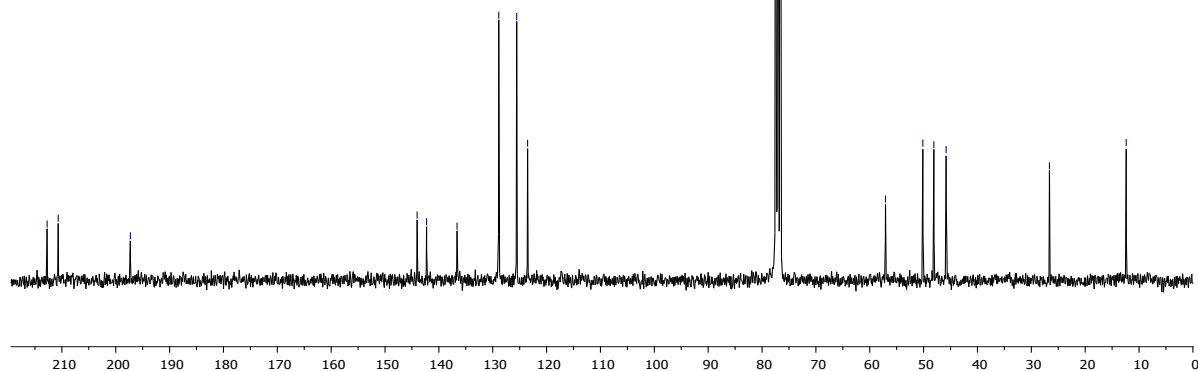
50.14
48.09
45.82

26.63

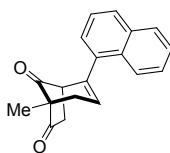
12.39



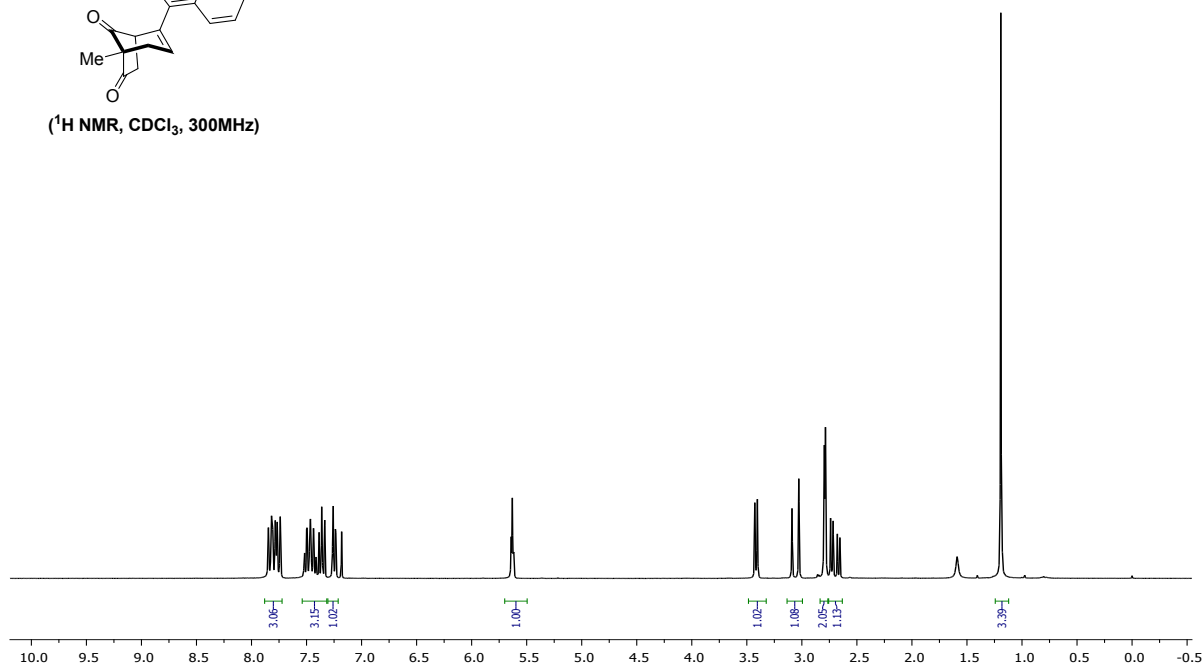
(¹³C NMR, CDCl₃, 75MHz)



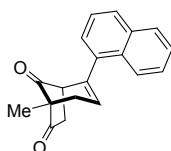
5-Methyl-2-(naphthalen-1-yl)bicyclo[3.2.1]oct-2-ene-6,8-dione (2k):



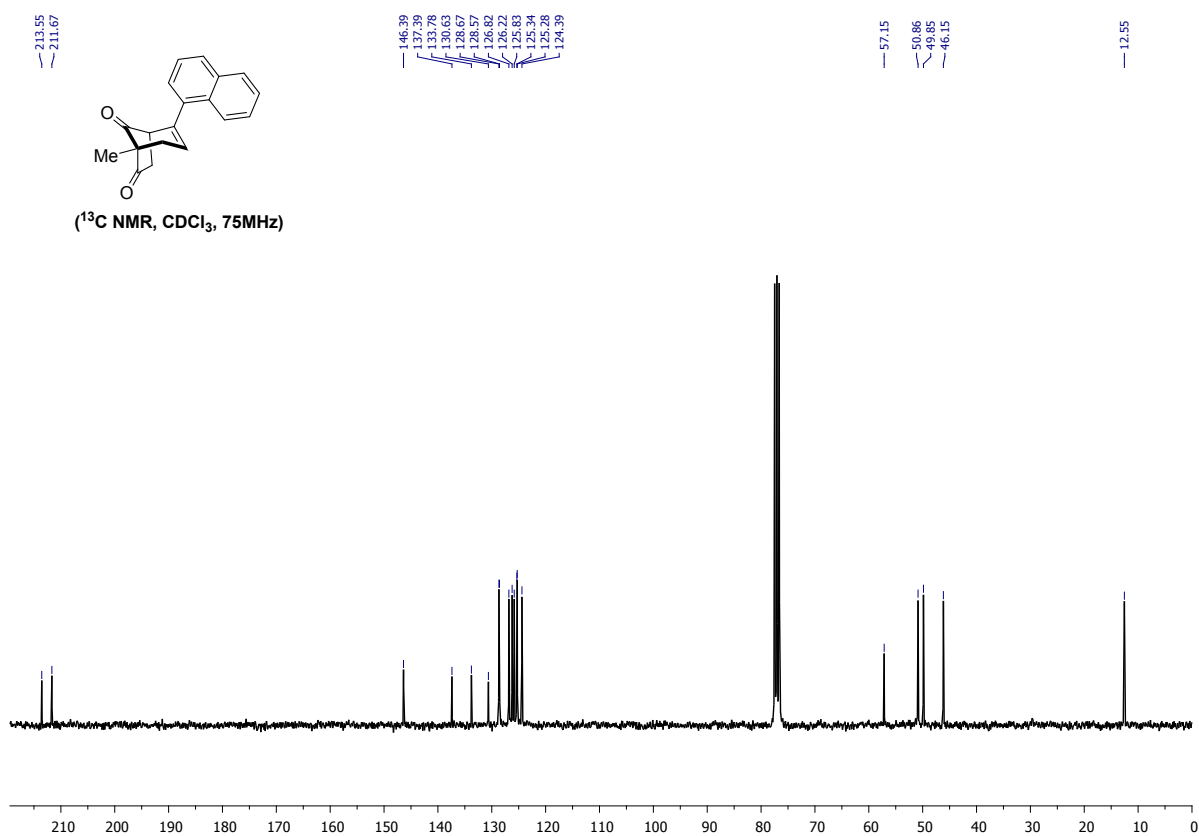
(¹H NMR, CDCl₃, 300MHz)



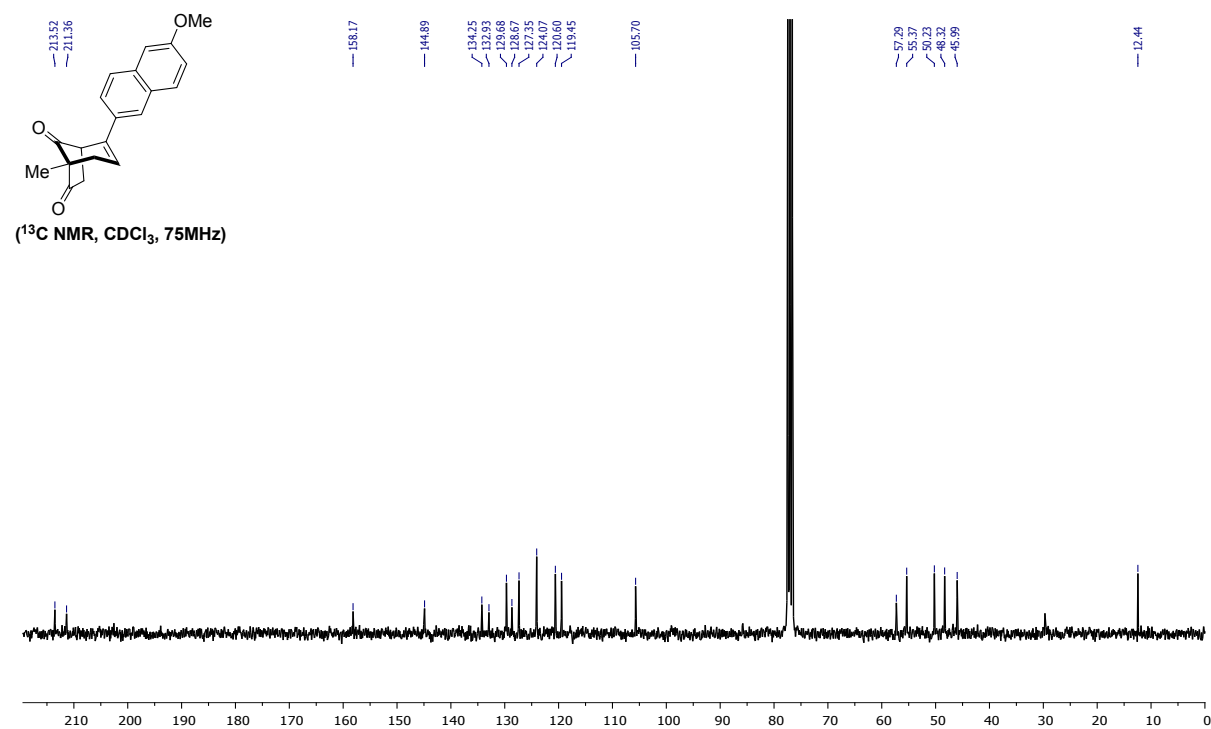
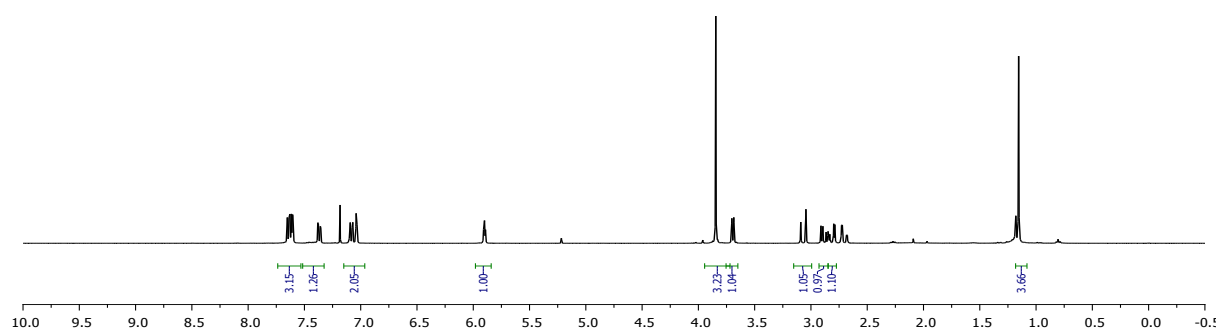
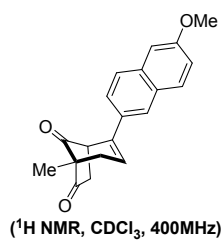
213.55
211.67



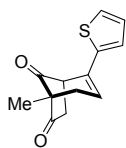
(¹³C NMR, CDCl₃, 75MHz)



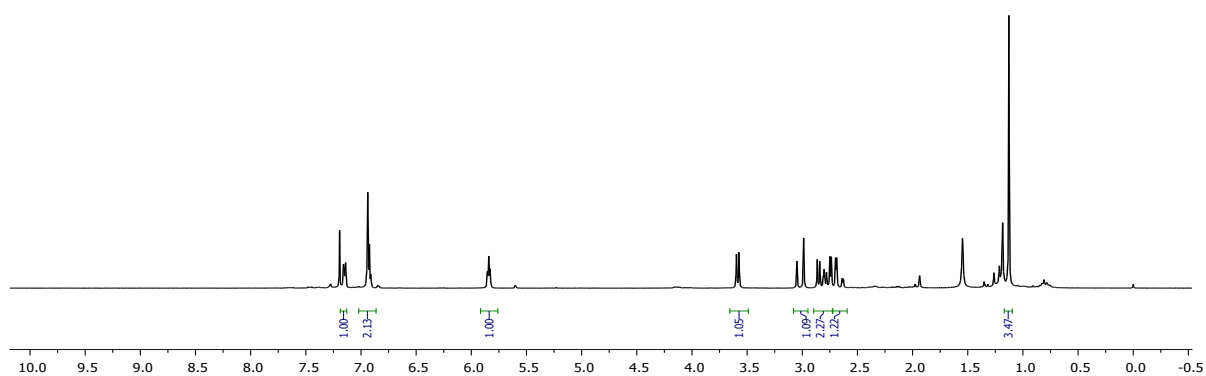
2-(6-Methoxynaphthalen-2-yl)-5-methylbicyclo[3.2.1]oct-2-ene-6,8-dione (2l):



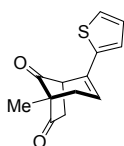
5-Methyl-2-(thiophen-2-yl)bicyclo[3.2.1]oct-2-ene-6,8-dione (2m):



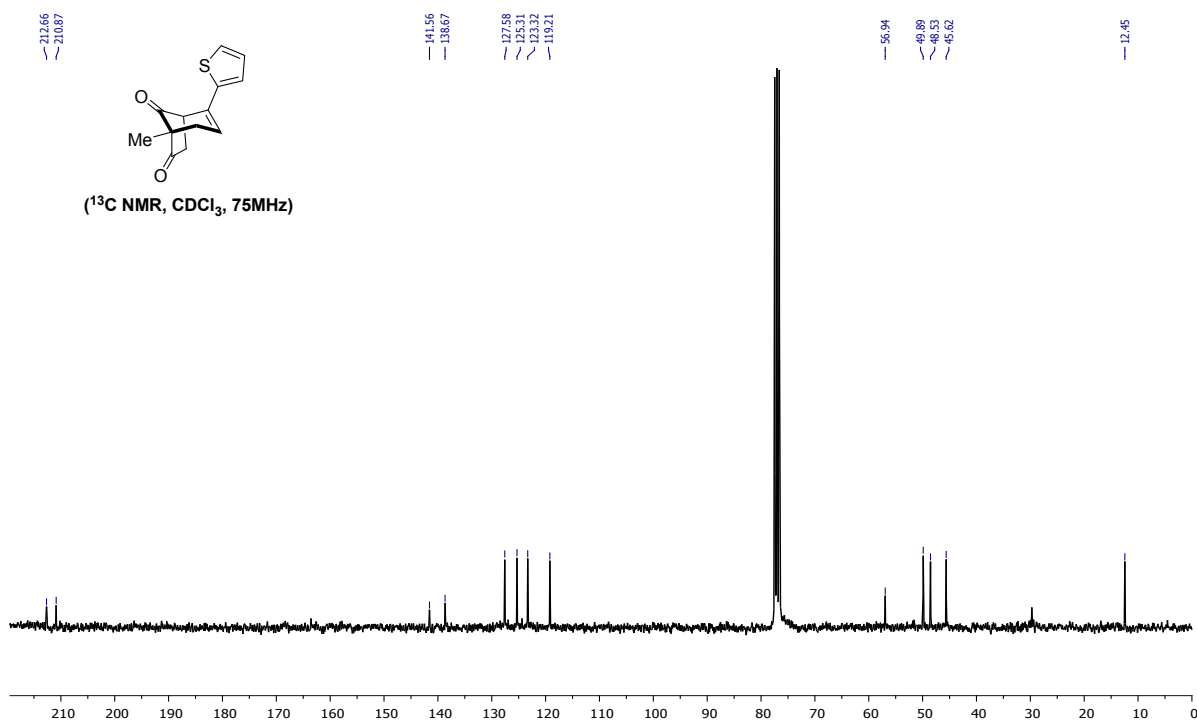
(¹H NMR, CDCl₃, 300MHz)



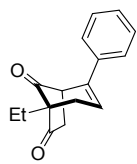
212.66
210.87



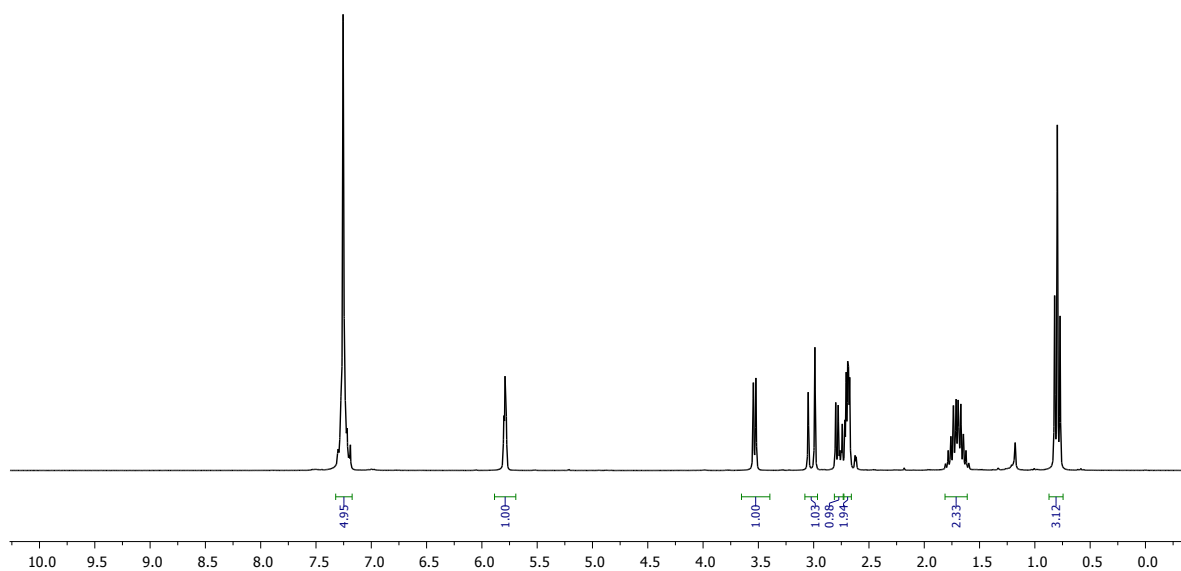
(¹³C NMR, CDCl₃, 75MHz)



5-Ethyl-2-phenylbicyclo[3.2.1]oct-2-ene-6,8-dione (2n) :



(¹H NMR, CDCl₃, 300 MHz)



213.54
211.55

144.98

138.04

128.75

128.22

125.45

121.11

61.72

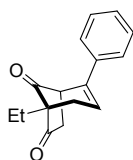
50.81

48.65

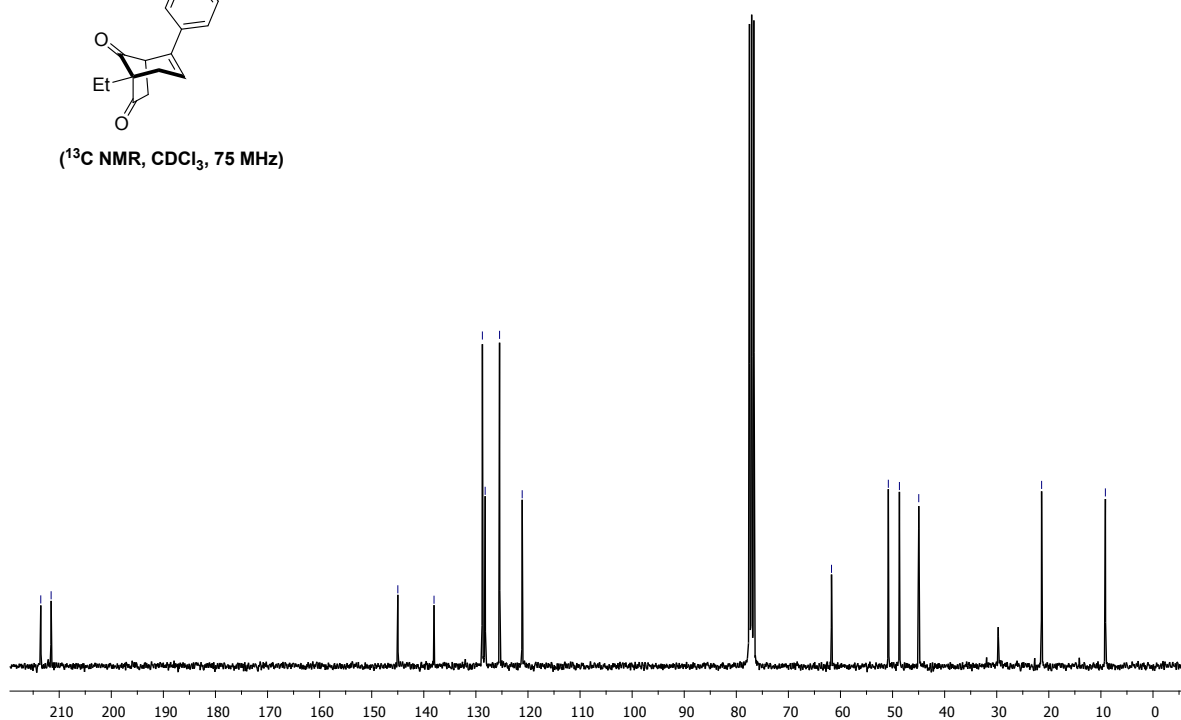
44.97

21.38

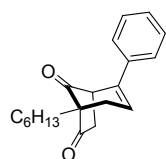
9.14



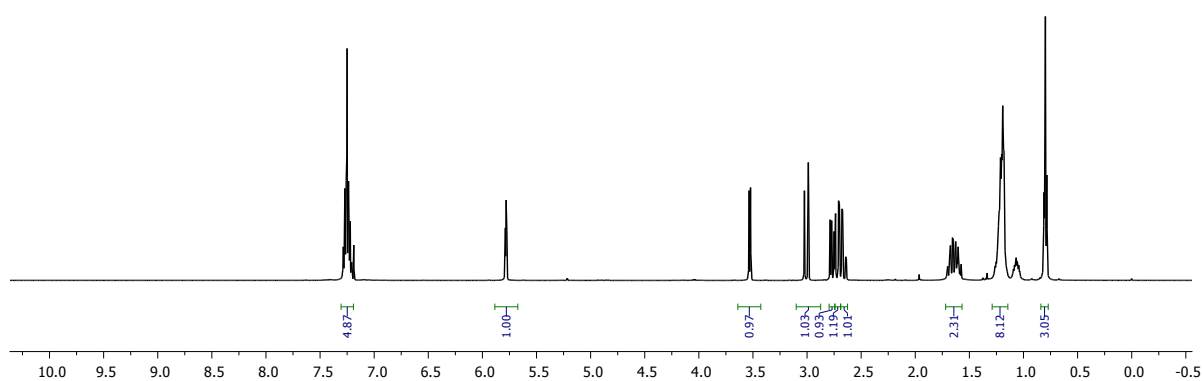
(¹³C NMR, CDCl₃, 75 MHz)



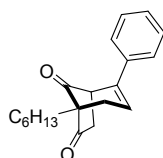
5-Hexyl-2-phenylbicyclo[3.2.1]oct-2-ene-6,8-dione(2o) :



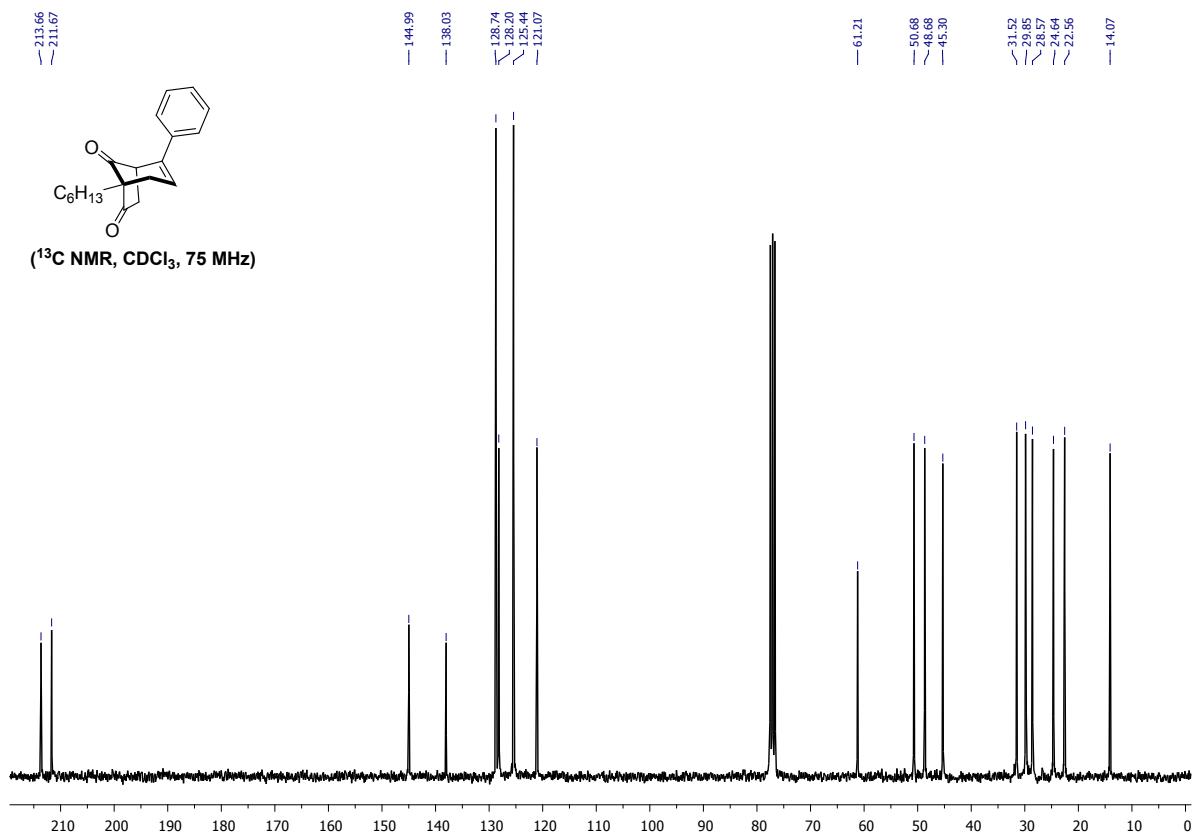
(¹H NMR, CDCl₃, 500 MHz)



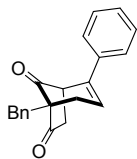
213.66
211.67



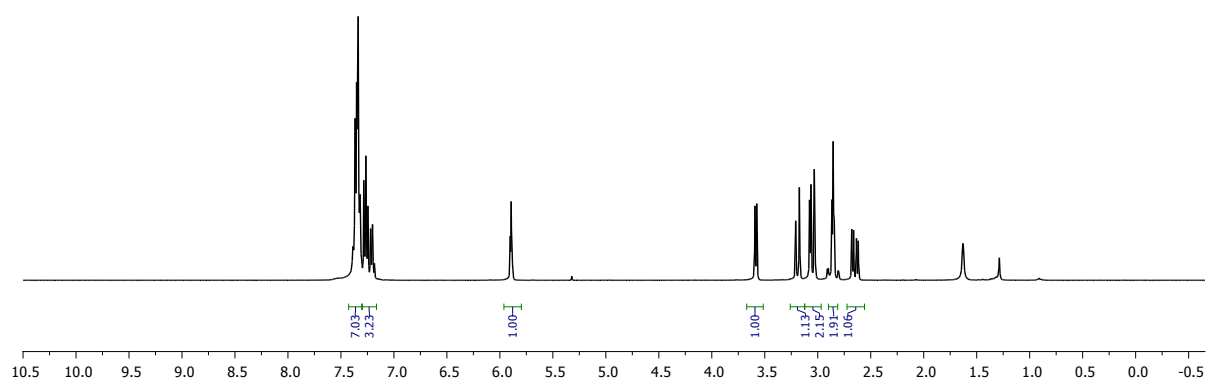
(¹³C NMR, CDCl₃, 75 MHz)



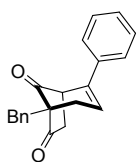
5-Benzyl-2-phenylbicyclo[3.2.1]oct-2-ene-6,8-dione(2p) :



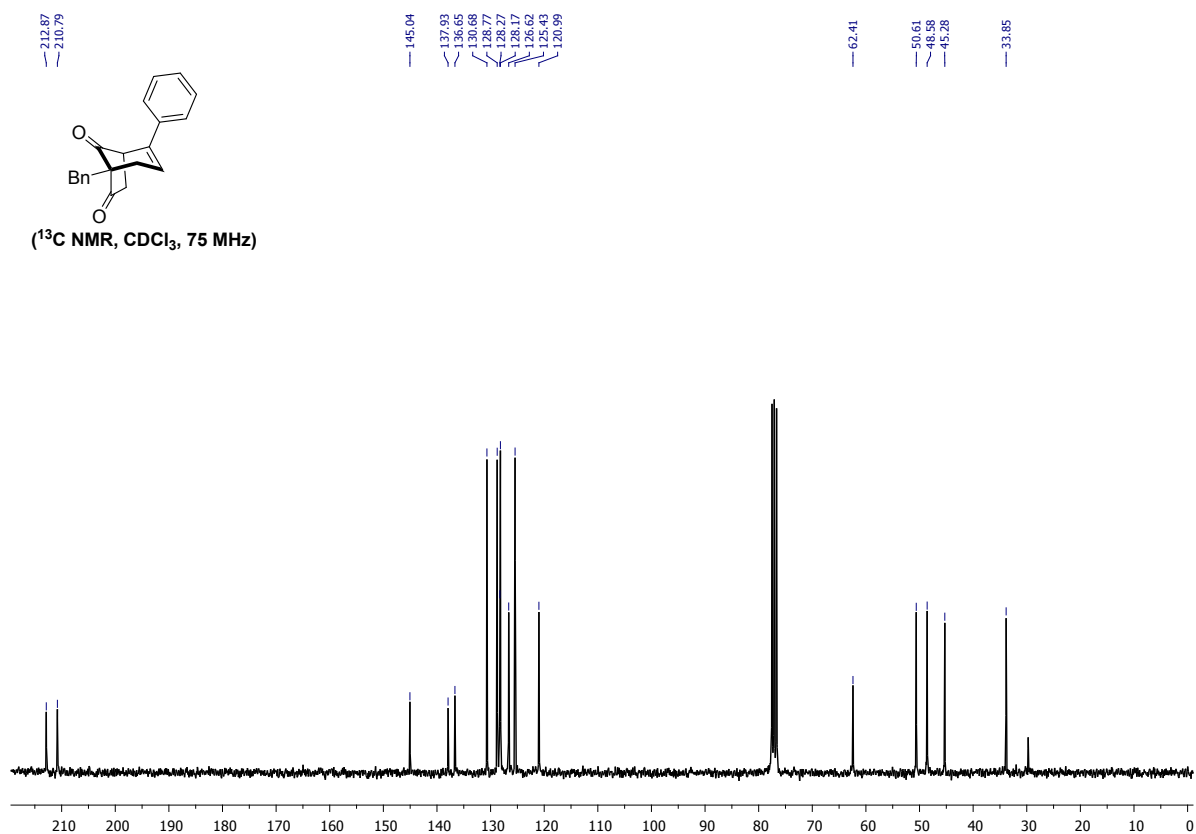
(^1H NMR, CDCl_3 , 400 MHz)



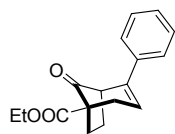
212.87
210.79



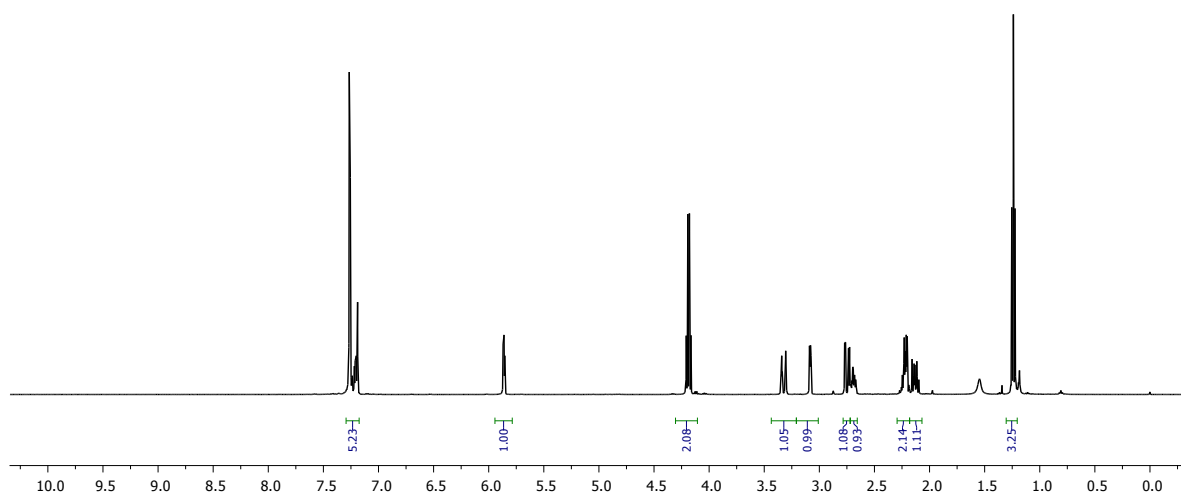
(^{13}C NMR, CDCl_3 , 75 MHz)



Ethyl 8-oxo-4-phenylbicyclo[3.2.1]oct-3-ene-1-carboxylate (4a) :



(¹H NMR, CDCl₃, 500 MHz)



— 210.58

— 171.17

— 142.98

— 138.74

— 128.61

— 127.76

— 125.49

— 120.97

— 61.46

— 55.58

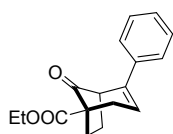
— 49.00

— 43.23

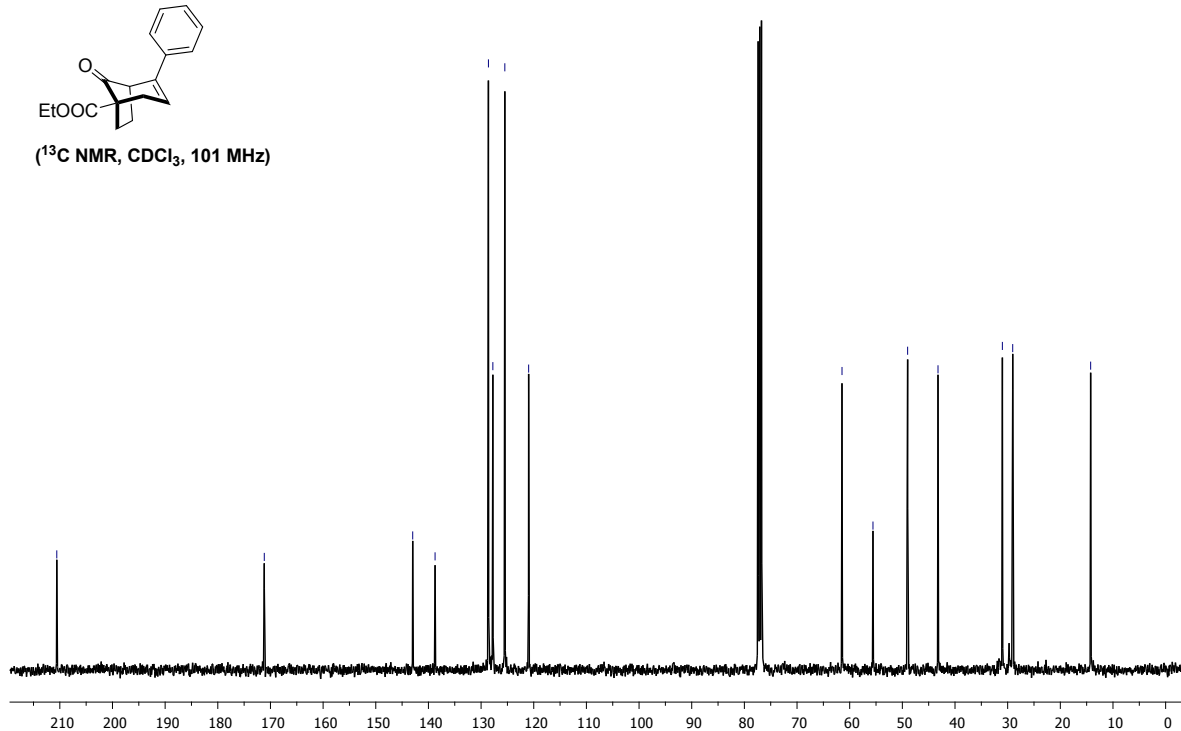
— 31.01

— 23.04

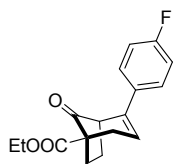
— 14.24



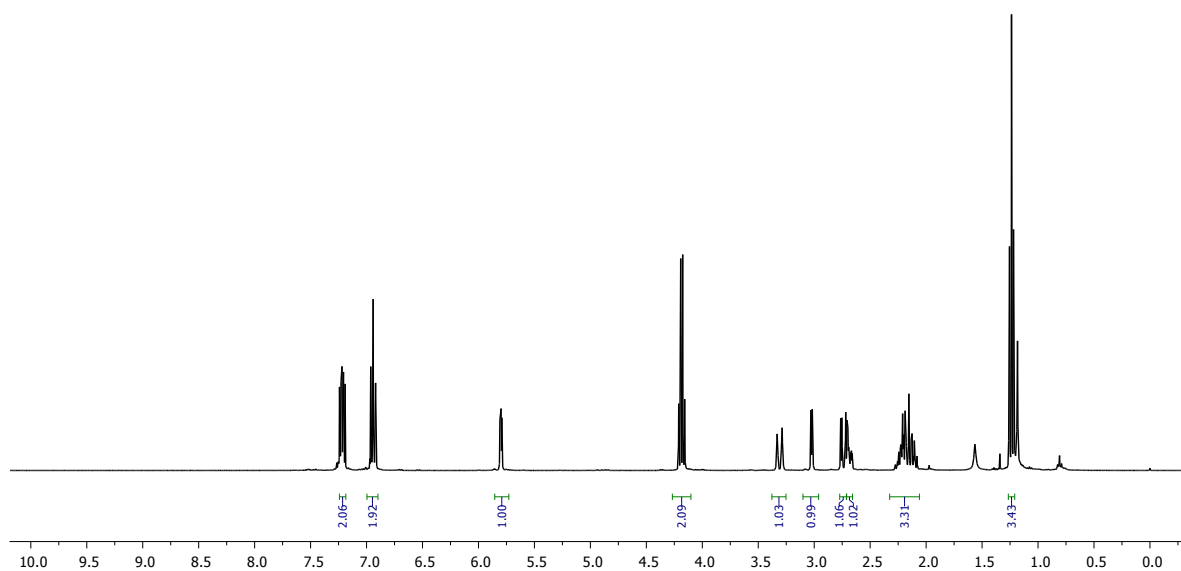
(¹³C NMR, CDCl₃, 101 MHz)



Ethyl 4-(4-fluorophenyl)-8-oxobicyclo[3.2.1]oct-3-ene-1-carboxylate (4b) :



(^1H NMR, CDCl_3 , 400 MHz)



210.32

171.07
169.08
163.63
161.17

142.02
134.91

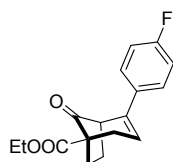
127.21
127.13
120.88
115.59
115.38

61.50
56.20
55.47

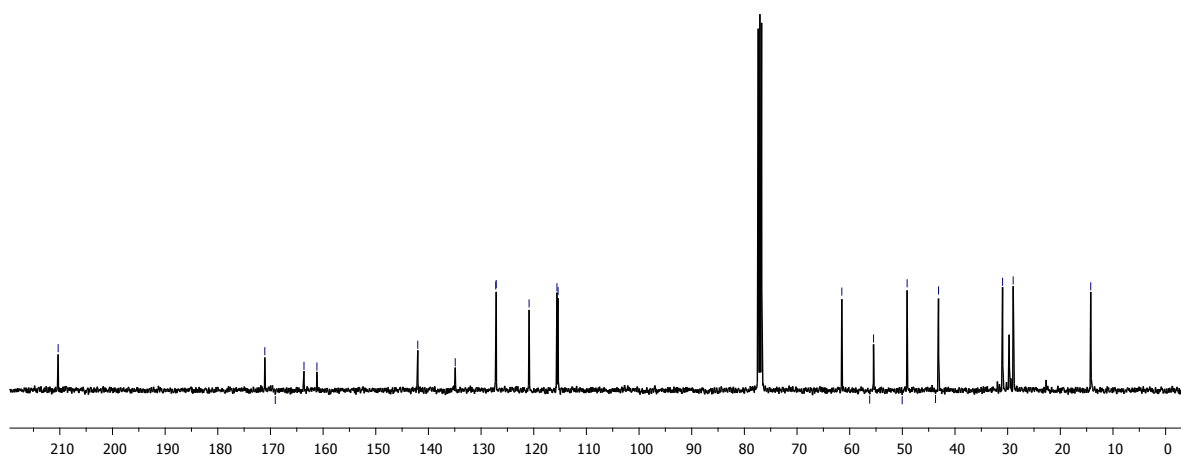
50.03
49.09
43.70
43.13

30.97
28.96

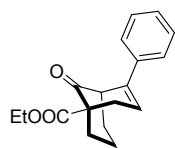
14.23



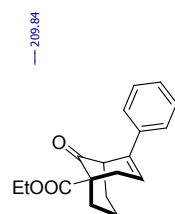
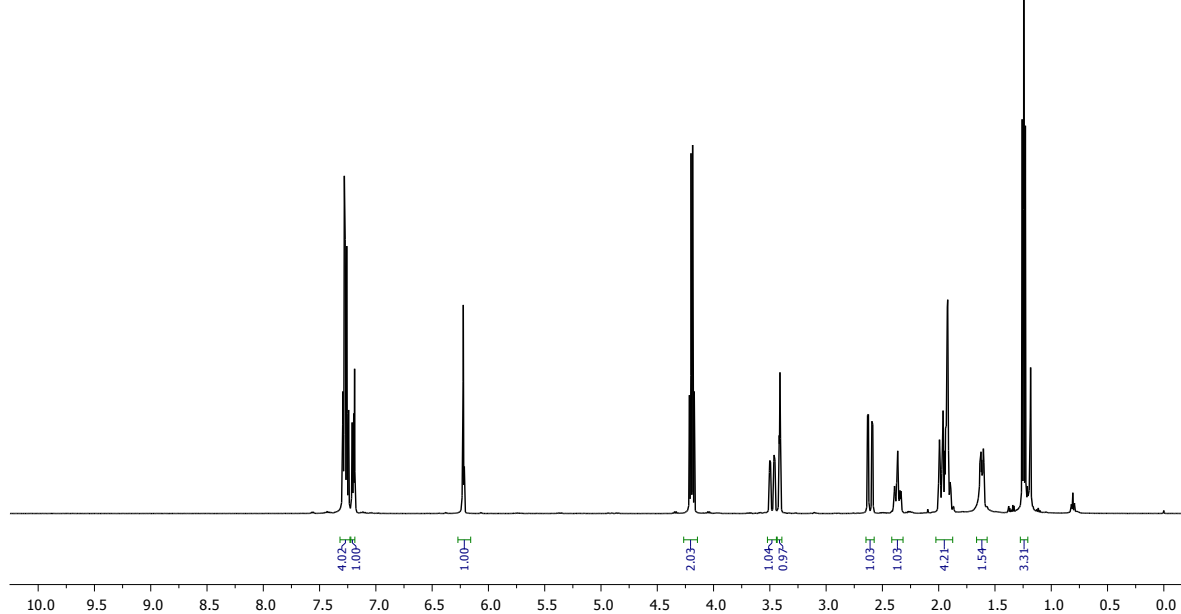
(^{13}C NMR, CDCl_3 , 101MHz)



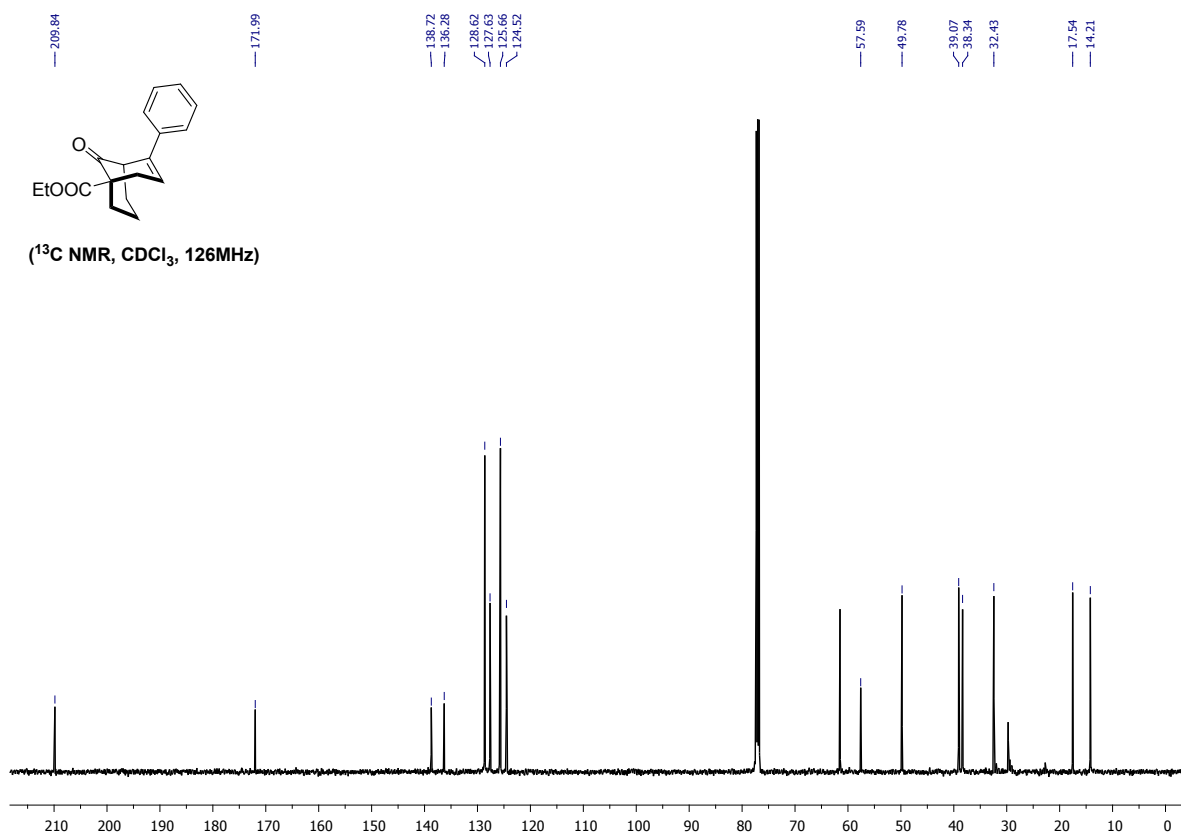
Ethyl 9-oxo-4-phenylbicyclo[3.3.1]non-3-ene-1-carboxylate (4c) :



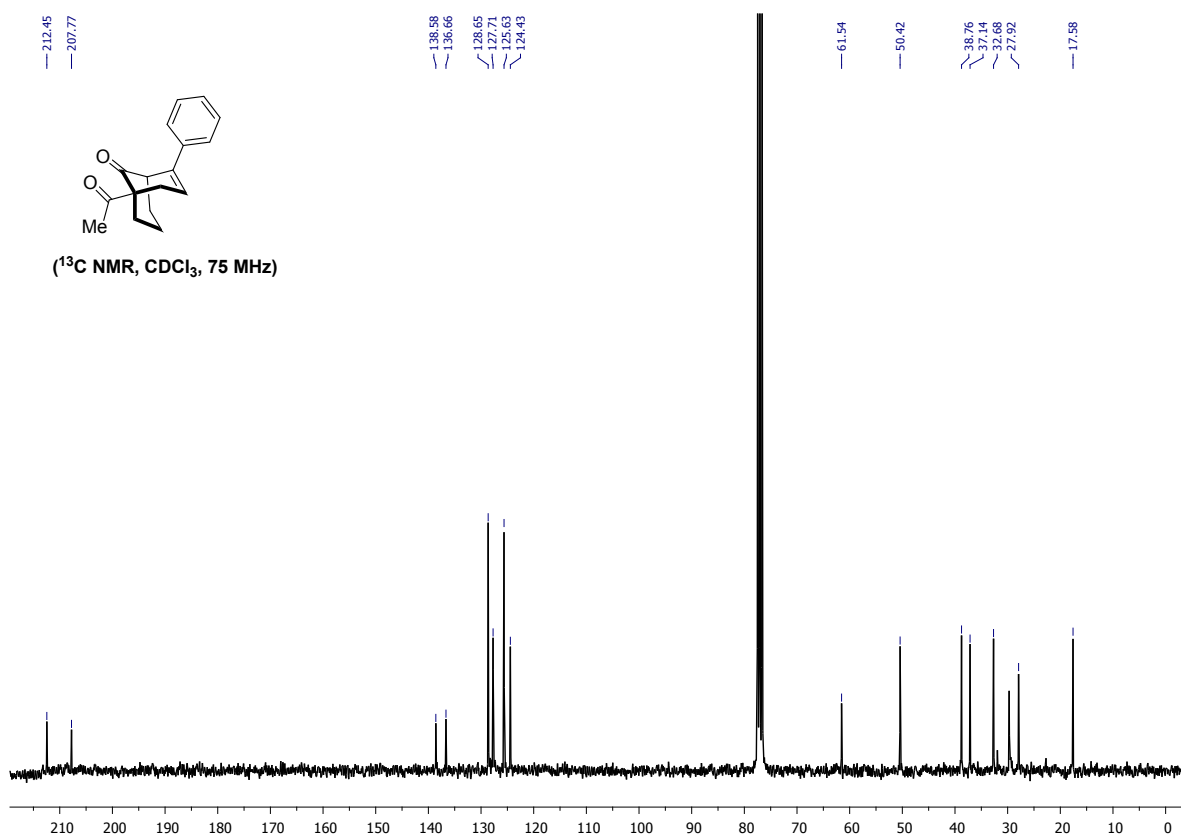
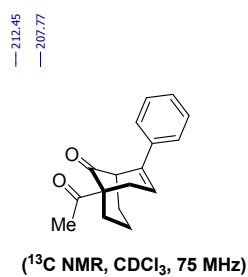
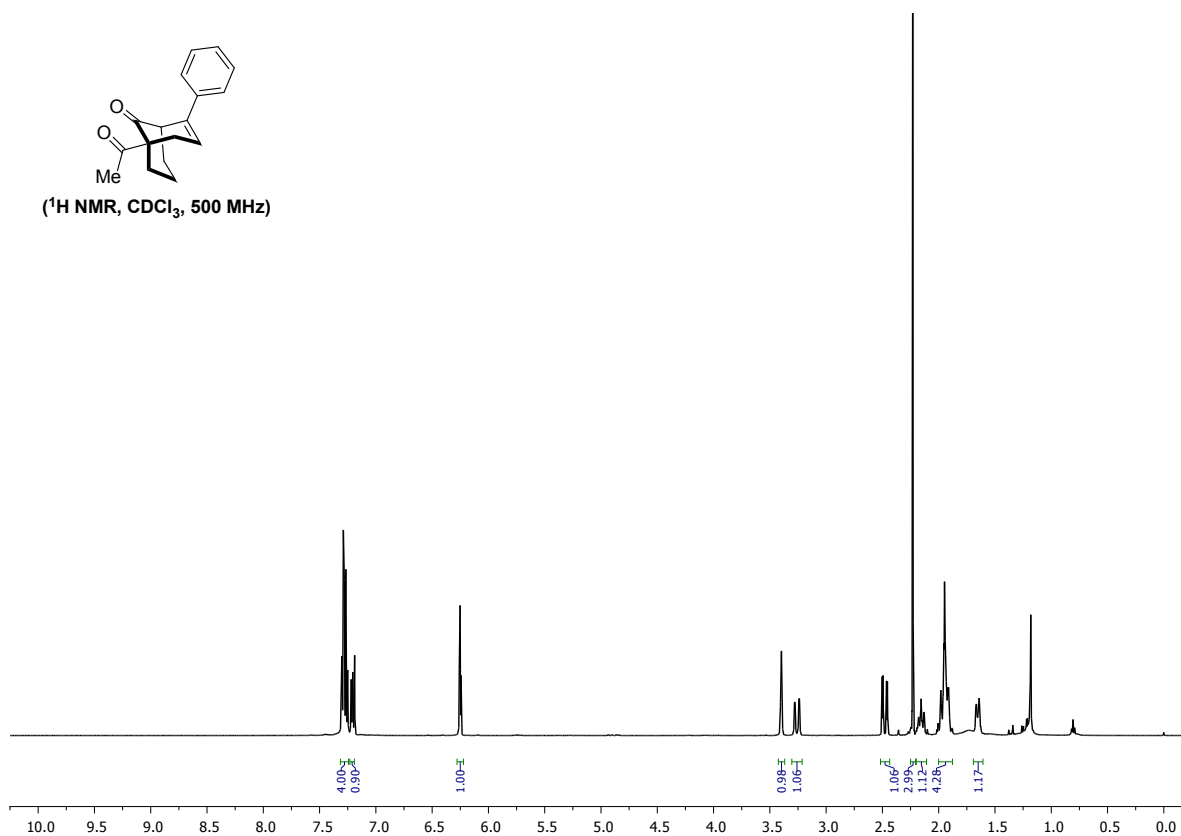
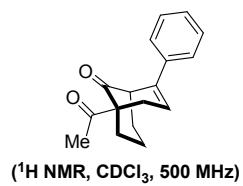
(^1H NMR, CDCl_3 , 500 MHz)



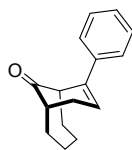
(^{13}C NMR, CDCl_3 , 126MHz)



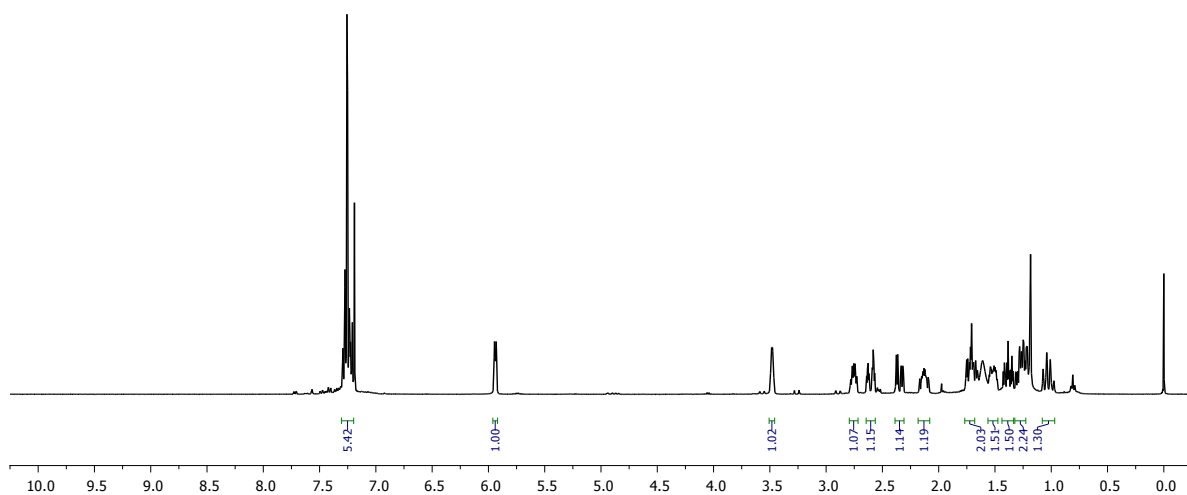
5-Acetyl-2-phenylbicyclo[3.3.1]non-2-en-9-one (4d) :



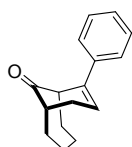
7-phenylbicyclo[4.3.1]dec-7-en-10-one (4e) :



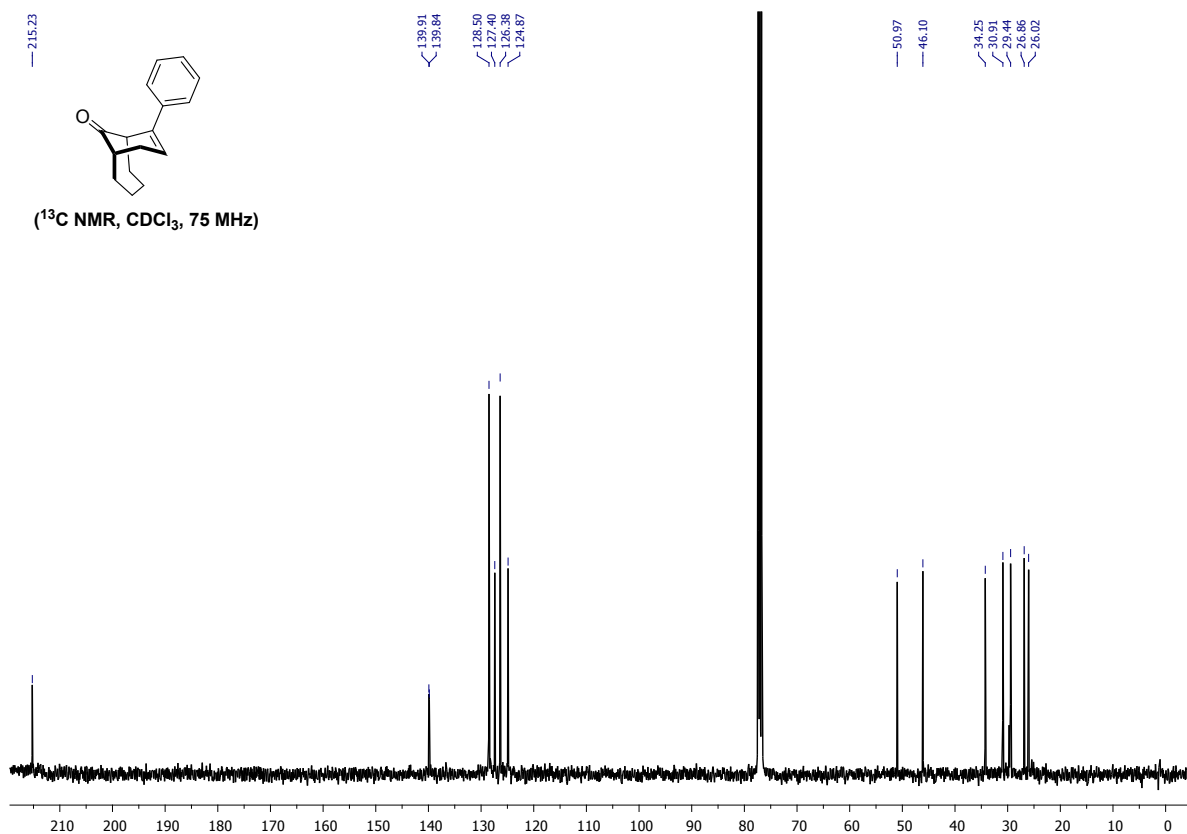
(¹H NMR, CDCl₃, 400 MHz)



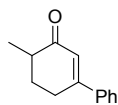
— 215.23



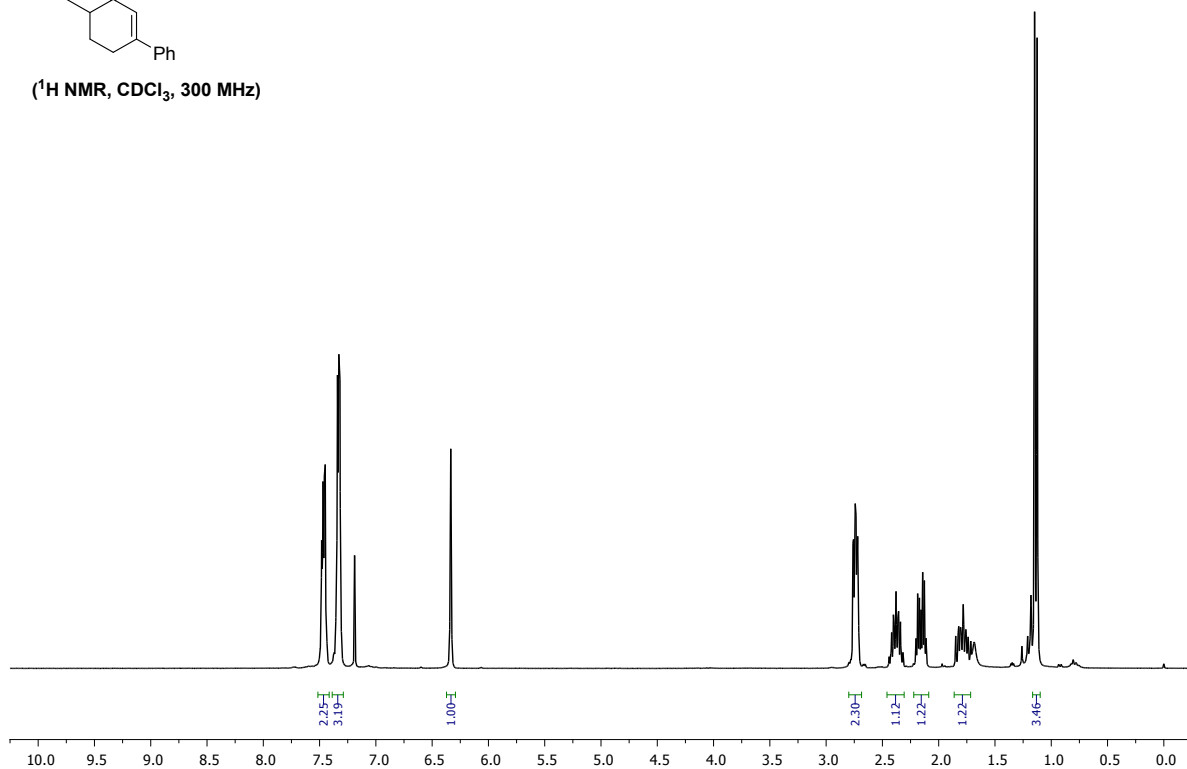
(¹³C NMR, CDCl₃, 75 MHz)



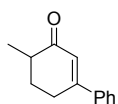
6-Methyl-3-phenylcyclohex-2-enone (6):



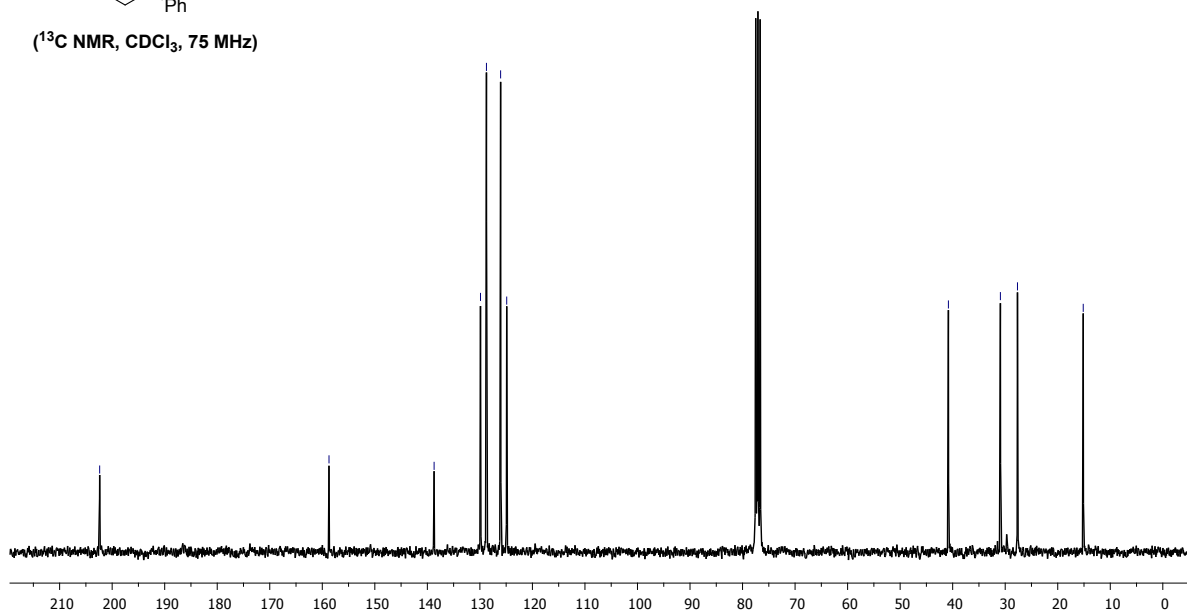
(¹H NMR, CDCl₃, 300 MHz)



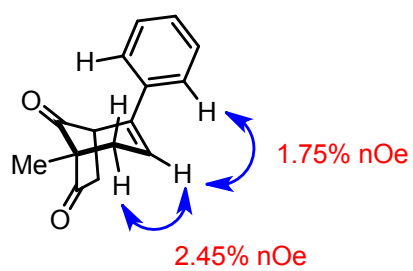
202.38
158.72
138.71
129.88
128.75
126.05
124.89
40.81
30.92
27.66
15.15



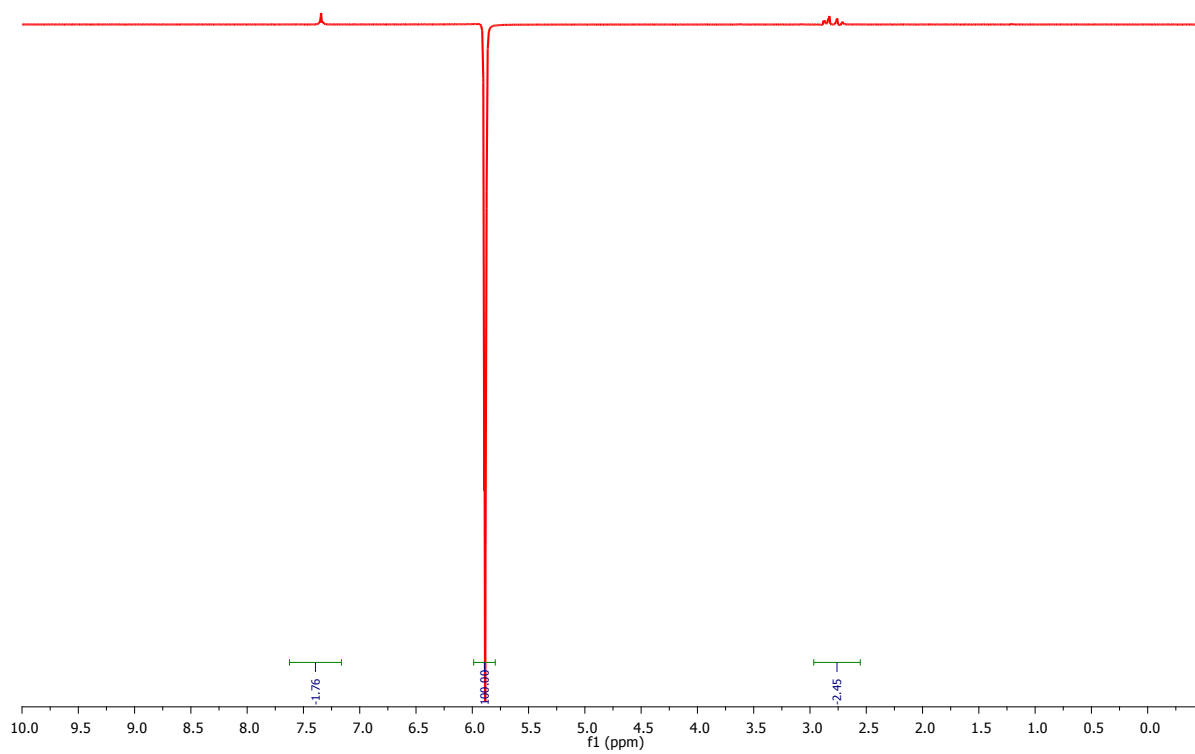
(¹³C NMR, CDCl₃, 75 MHz)



nOe interactions of compound 2a:



compound **2a**



2D COSEY NMR of compound 2a:

