Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

Rh-catalyzed Reagent-Free Ring Expansion of Cyclobutenones and Benzocyclobutenones

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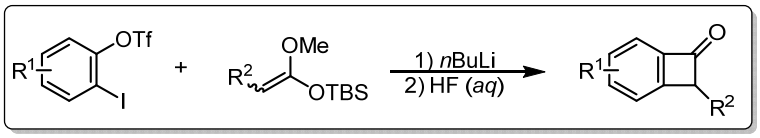
1. General Information

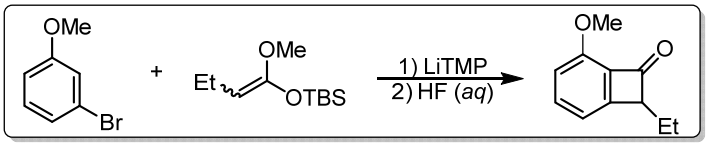
Unless noted otherwise, all solvents were dried by filtration through a Pure-Solv MD-5 Solvent Purification System (Innovative Technology). 1, 4-dioxane, THF and dibutyl ether were distilled freshly over sodium. Ethylbenzene, benzene, toluene and acetonitrile were distilled freshly over sodium hydride. For all rhodium catalyzed reactions, solvents were freeze-pump-thawed using standard technique right after fresh distillation and stored in a nitrogen-filled glovebox respectively. All other solvents and reagents were purchased and used as received. Reaction temperatures were reported as the temperatures of the bath surrounding the flasks or vials. For all rhodium catalyzed reactions, reactants were weighted under air and transferred under nitrogen into a nitrogen-filled glovebox with standard techniques. Vials for rhodium catalyzed reactions (15 x 45 mm 1 dram (4mL) / 17 x 60 mm 3 dram (7.5mL) with PTFE lined cap attached) were purchased from Qorpak and flame-dried right before setting up the reaction. High-resolution mass spectra (HRSM) were obtained on a Karatos MS9 and are reported as m/z (relative intensity). Accurate masses are reported for the molecular ion $[M+Na]^+$, $[M+H]^+$, $[M-H]^-$ or [M]. Infrared spectra were recorded on a Nicolet iS5 using neat thin film technique. Analytical thin-layer chromatography (TLC) was carried out using 0.2 mm commercial silica gel plates (silica gel 60, F254, EMD chemical). Nuclear magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded with a Varian Gemini (400 MHz, ^{1}H at 400 MHz, ^{13}C at 100 MHz). Unless otherwise noted, all spectrums were acquired in $CDCl_3$. Chemical shifts are reported in parts per million (ppm, δ), and are referenced to residual solvent ($CDCl_3$, δ=7.26 ppm (^{1}H) and 77.16 ppm(^{13}C)). Coupling constants were reported in Hertz (Hz). Data for ^{1}H NMR spectra were reorted as follows: chemical shift (ppm, referenced to protium; s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, dd = doublet of doublets, td = triplet of doublets, ddd = doublet of doublet of doublets, m = multiplet, coupling constant (Hz), and integration). Brsm=based on recovered starting material; COD=1,5-cyclooctadiene; dppp = 1,3-bis(diphenylphosphino)propane; dppb = 1,4-bis(diphenylphosphino)butane; NMR = nuclear magnetic resonance; HPLC = High Performance Liquid Chromatography. Compounds **1c**[1], **1k**[2] and **1l**[3] can be synthesized from known procedures.

2. Experimental Procedure and Characterization Data

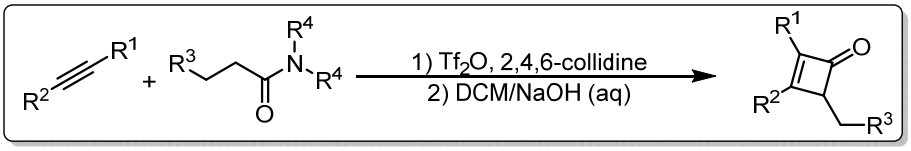
General schemes for substrate synthesis



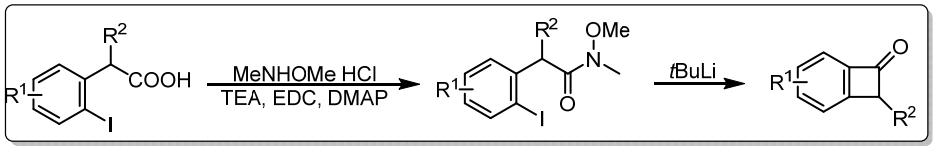
Scheme 1. Synthesis of benzocyclobutenones via [2+2] with ketene silyl acetal and 2-iodophenyl triflate as benzyne precursor.[1]



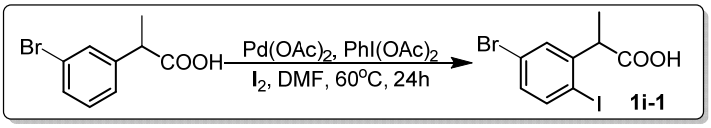
Scheme 2. Synthesis of benzocyclobutenones via [2+2] with ketene silyl acetal and 3-bromoanisole as benzyne precursor.[2]



Scheme 3. Synthesis of cyclobutenones via [2+2] with alkynes and N,N-dialkylamide.[4]

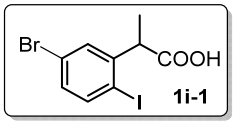


Scheme 4. Synthesis of benzocyclobutenones via a weinreb amid formation—ring closure sequence.[5]



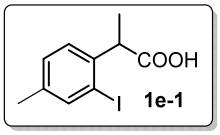
General procedure A

A similar procedure[5a] was applied: In a 20 mL vial, 2-(3-bromophenyl)propanoic acid[6] (1 mmol, 1 *equiv*, 229 mg), $Pd(OAc)_2$ (0.1 mmol, 0.1 *equiv*, 22.5 mg), $PhI(OAc)_2$ (0.75 mmol, 0.75 *equiv*, 242 mg) and I_2 (0.75 mmol, 0.75 *equiv*, 190.4 mg) were dissolved in 6 mL anhydrous DMF under air. The vial was sealed with Teflon lined cap, wrapped with aluminum foil to keep dark and stirred in a preheated pie-block at 60°C for 24h. Then the reaction mixture was filtered through a pad of celite, and to the filtrate was added 6 M HCl (*aq*, 5 mL) and was extracted with ethyl acetate (10 mL × 3) The combined organic extract was washed with saturated sodium thiosulfate aqueous solution (20 mL) and brine (20 mL) and dried over sodium sulfate. Then the solution was filtered, concentrated under vacuum and purified by column chromatography on silica gel to obtain 247.9 mg **1i-1** as a yellow solid in 73% yield.



2-(5-bromo-2-iodophenyl)propanoic acid

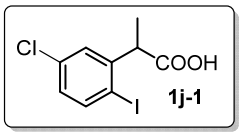
1i-1: $\mathbf{R_f}$ = 0.2 (Hexane : EtOAc : HOAc = 2 : 1 : 0.05). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.4 Hz, 1H), 7.45 (d, *J* = 2.4 Hz, 1H), 7.10 (dd, *J* = 8.4, 2.4 Hz, 1H), 4.12 (q, *J* = 7.2 Hz, 1H), 1.50 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.14 (s), 144.71 (s), 140.88 (s), 132.16 (s), 130.76 (s), 123.00 (s), 99.03 (s), 49.35 (s), 17.89 (s). **IR:** ν 2981.09, 2930.33, 1706.69, 1456.96, 1412.96, 1378.99, 1223.18, 1094.55, 1007.50, 881.12, 807.76 cm^{-1}. **HRMS** calcd. for $C_9H_8O_2BrINa^+$ $[M+Na]^+$: 376.8645, Found: 376.8643. **Mp(°C):** 120-123.



2-(2-iodo-4-methylphenyl)propanoic acid

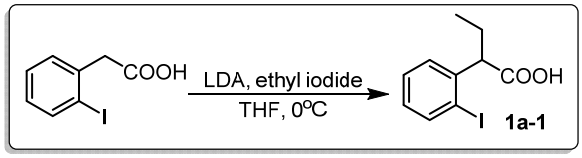
1e-1 was obtained as a white solid (291 mg) in quantitive yield following a similar procedure as *General procedure A* from 2-(p-tolyl)propanoic acid[8] (1 mmol, 1 *equiv*, 164 mg), $Pd(OAc)_2$ (0.1 mmol, 0.1 *equiv*, 22.5 mg), $PhI(OAc)_2$ (0.75 mmol, 0.75 *equiv*, 242 mg) and I_2 (0.75 mmol, 0.75 *equiv*, 190.4

mg): $\mathbf{R_f}$ = 0.4 (Hexane : EtOAc : HOAc = 2 : 1 : 0.05). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.1 Hz, 1H), 7.13 (d, *J* = 1.8 Hz, 1H), 6.79 (ddd, *J* = 8.0, 2.1, 0.5 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 1H), 2.30 (s, 1H), 1.47 (d, *J* = 7.2 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.87 (s), 142.49 (s), 139.42 (s), 138.78 (s), 130.08 (s), 128.34 (s), 96.98 (s), 49.25 (s), 21.02 (s), 17.95 (s). **IR:** ν 2979.56, 2936.41, 1706.74, 1467.80, 1412.82, 1291.21, 1238.16, 1215.49, 1009.39, 808.18 cm^{-1}. **HRMS** calcd. for $C_{10}H_{11}O_2INa^+$ $[M+Na]^+$: 312.9696, Found: 312.9697. **Mp(°C):** 98-100.



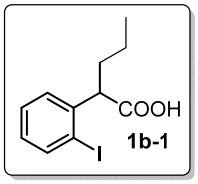
2-(5-chloro-2-iodophenyl)propanoic acid

1j-1 was obtained as a colorless oil (219.3 mg) in 95% yield following a similar procedure as *General procedure A* from 2-(3-chlorophenyl)propanoic acid[7] (1 mmol, 1 *equiv*, 184 mg), $Pd(OAc)_2$ (0.1 mmol, 0.1 *equiv*, 22.5 mg), $PhI(OAc)_2$ (0.75 mmol, 0.75 *equiv*, 242 mg) and I_2 (0.75 mmol, 0.75 *equiv*, 190.4 mg): $\mathbf{R_f}$ = 0.35 (Hexane : EtOAc : HOAc = 2 : 1 : 0.05). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.5 Hz, 1H), 7.30 (d, *J* = 2.5 Hz, 1H), 6.95 (dd, *J* = 8.5, 2.5 Hz, 1H), 4.12 (q, *J* = 7.2 Hz, 1H), 1.48 (d, *J* = 7.2 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.47 (s), 144.38 (s), 140.59 (s), 135.04 (s), 129.25 (s), 127.92 (s), 98.10 (s), 49.41 (s), 17.88 (s). **IR:** ν 2981.77, 1707.10, 1457.98, 1413.24, 1382.25, 1222.55, 1104.38, 1011.04, 882.05, 809.96 cm^{-1}. **HRMS** calcd. for $C_9H_8O_2ClINa^+$ $[M+Na]^+$: 332.9150, Found: 332.9147.



General procedure B

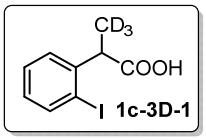
2-iodo-phenylacetic acid (8 mmol, 1 *equiv*, 2.1 g) in THF (8 mL) was slowly added into freshly prepared LDA (16 mmol, 2 *equiv*, in 24 mL THF) at 0°C and stirred at the same temperature. After one hour, ethyl iodide (40 mmol, 5 *equiv*, 3.2 mL) was added dropwise. The reaction was slowly warmed up to RT and kept stirring for 2 hours. Then 0.5 M NH_4OAc (*aq*, 10 mL) was added to quench the reaction followed by adding 6 M HCl (*aq*, 5 mL). The mixture was extracted with ethyl acetate (20 mL × 3), and the combined organic extract was washed with saturated sodium thiosulfate aqueous solution (30 mL) and brine (30 mL) and dried over sodium sulfate. Then the solution was filtered, concentrated under vacuum and purified by column chromatography on silica gel to obtain 2.23 g **1a-1** as a white solid in 96% yield. All data match the literature reported ones[9].



2-(2-iodophenyl)pentanoic acid

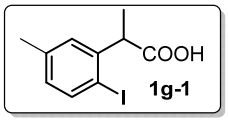
1b-1 was obtained as a brown oil (1.9574 g) in 80% yield following a similar procedure as *General procedure B* from 2-iodo-phenylacetic acid (8 mmol, 1 *equiv*, 2.1 g), LDA (16 mmol, 2 *equiv*) and *n*propyl iodide (40 mmol, 5 *equiv*, 6.8 g, 3.9 mL): $\mathbf{R_f}$ = 0.8 (Hexane : EtOAc = 1 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 12.42 (s, 1H), 7.92 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.44 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.39 – 7.34

(m, 1H), 6.99 (td, *J* = 7.8, 1.6 Hz, 1H), 4.21 (t, *J* = 7.5 Hz, 1H), 2.11 (dddd, *J* = 13.4, 9.7, 7.6, 5.7 Hz, 1H), 1.84 (dddd, *J* = 13.4, 9.7, 7.3, 5.9 Hz, 1H), 1.52 – 1.30 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 180.29 (s), 141.53 (s), 139.86 (s), 129.13 (s), 128.76 (s), 128.04 (s), 102.13 (s), 54.76 (s), 35.47 (s), 20.64 (s), 14.13 (s). **IR:** ν 2958.94, 2872.05, 1708.45, 1465.80, 1435.13, 1412.04, 1273.82, 1211.69, 1010.57, 930.78, 742.99 cm^{-1}. **HRMS** calcd. for $C_{11}H_{13}O_2INa^+$ $[M+Na]^+$: 326.9852, Found: 326.9852.



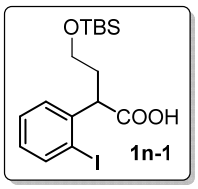
2-(2-iodophenyl)propanoic-3,3,3-d3 acid

1c-3D-1 was obtained as a white solid (245.1 mg) in 94% yield following a similar procedure as *General procedure B* from 2-iodo-phenylacetic acid (2.67 mmol, 1 *equiv*, 700 mg), LDA (5.88 mmol, 2.2 *equiv*) and iodomethane-d_3 (9.35 mmol, 3.5 *equiv*, 1.36 g, 582 μL): $\mathbf{R_f}$ = 0.5 (Hexane : EtOAc : HOAc = 2 : 1 : 0.05). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 – 7.84 (m, 1H), 7.37 – 7.32 (m, 2H), 6.96 (ddd, *J* = 8.0, 6.2, 2.8 Hz, 1H), 4.16 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 180.14 (s), 142.77 (s), 139.76 (s), 129.01 (s), 128.74 (s), 127.62 (s), 101.15 (s), 49.33 (s). **IR:** ν 3060.16, 1706.18, 1467.01, 1435.17, 1413.80, 1287.58, 1227.12, 1012.13, 911.79, 788.49, 753.75, 646.22 cm^{-1}. **HRMS** calcd. for $C_9H_7D_3O_2I^+$ $[M+H]^+$: 279.9914, Found: 279.9920. **Mp(°C):** 117-118.



2-(2-iodo-5-methylphenyl)propanoic acid

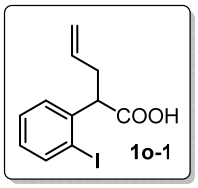
1g-1 was obtained as a white solid (229.6 mg) in 95% yield following a similar procedure as *General procedure B* from 2-(2-iodo-5-methylphenyl)acetic acid[5a] (0.83 mmol, 1 *equiv*, 230 mg), LDA (2.49 mmol, 3 *equiv*) and methyl iodide (4.15 mmol, 5 *equiv*, 589 mg, 258 μL): $\mathbf{R_f}$ = 0.5 (Hexane : EtOAc : HOAc = 2 : 1 : 0.05). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.1 Hz, 1H), 7.13 (s, 1H), 6.81 – 6.77 (m, 1H), 4.15 (q, *J* = 7.2 Hz, 1H), 2.30 (s, 3H), 1.47 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 180.07 (s), 142.49 (s), 139.42 (s), 138.78 (s), 130.08 (s), 128.35 (s), 96.99 (s), 49.28 (s), 21.03 (s), 17.95 (s). **IR:** ν 2979.51, 2933.33, 2360.01, 2341.30, 1707.02, 1468.07, 1413.39, 1238.26, 1215.59, 1009.44, 808.29 cm^{-1}. **HRMS** calcd. for $C_{10}H_{11}O_2INa^+$ $[M+Na]^+$: 312.9696, Found: 312.9700. **Mp(°C):** 100-103.



4-((tert-butyldimethylsilyl)oxy)-2-(2-iodophenyl)butanoic acid

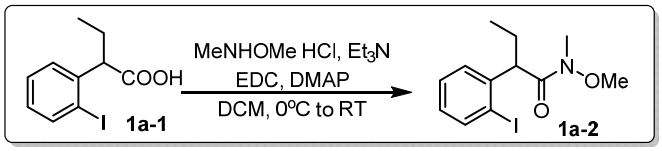
1n-1 was obtained as a brown oil (1.441 g) in 45% yield following a similar procedure as *General procedure B* from 2-iodo-phenylacetic acid (7.63 mmol, 1 *equiv*, 2 g), LDA (16.79 mmol, 2.2 *equiv*) and tert-butyl(2-iodoethoxy)dimethylsilane[10] (30.52 mmol, 4 *equiv*, 8.74 g), and buffer solution (pH = 4.00) was used to quench the reaction instead of 0.5 M NH_4OAc (*aq*) : $\mathbf{R_f}$ = 0.75 (Hexane : EtOAc : = 1 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 – 7.84 (m, 1H), 7.36 – 7.28 (m, 1H), 6.95 (ddd, *J* = 8.1, 6.6, 2.3 Hz, 1H), 4.30 (dd, *J* = 8.3, 5.9 Hz, 1H), 3.72 – 3.59 (m, 1H), 2.36 – 2.23 (m, 1H), 2.00 – 1.87 (m, 1H), 0.89 (s, 2H), 0.04 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.37 (s), 141.43 (s), 139.90 (s), 128.98 (s), 128.57 (s), 128.19 (s), 101.48 (s), 60.58 (s), 51.60 (s), 35.73 (s), 25.93 (s), 18.24 (s), -5.39

(s), -5.49 (s). **IR:** ν 2954.27, 2928.04, 2856.45, 1707.42, 1467.72, 1255.21, 1103.97, 1010.67, 834.84, 776.03, 742.66 cm^{-1}. **HRMS** calcd. for $C_{16}H_{26}O_3SiI^+$ $[M+H]^+$: 421.0696, Found: 421.0709.



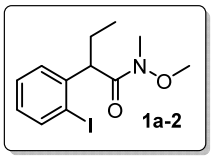
2-(2-iodophenyl)pent-4-enoic acid

1o-1 was obtained as a yellow oil (892.9 mg) in 97% yield following a similar procedure as *General procedure B* from 2-iodo-phenylacetic acid (3.05 mmol, 1 *equiv*, 800 mg), LDA (6.72 mmol, 2.2 *equiv*) and allyl bromide (12.21 mmol, 4 *equiv*, 1.48 g, 1.06 mL): $\mathbf{R_f}$ = 0.37 (Hexane : EtOAc : = 2 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.95 (s, 1H), 7.86 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.37 – 7.29 (m, 2H), 6.95 (ddd, *J* = 8.0, 6.9, 2.1 Hz, 1H), 5.76 (ddt, *J* = 17.0, 10.2, 6.8 Hz, 1H), 5.08 (dq, *J* = 17.1, 1.4 Hz, 1H), 5.02 (dd, *J* = 10.2, 1.5 Hz, 1H), 4.20 (t, *J* = 7.5 Hz, 1H), 2.76 (ddd, *J* = 14.6, 7.9, 6.9 Hz, 1H), 2.52 (dt, *J* = 14.2, 6.9 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.10 (s), 140.76 (s), 139.87 (s), 134.34 (s), 129.18 (s), 128.68 (s), 128.07 (s), 117.52 (d, *J* = 34.7 Hz), 101.85 (s), 54.68 (s), 37.06 (s). **IR:** ν 3077.58, 1708.22, 1466.35, 1435.74, 1415.93, 1250.27, 1207.65, 1010.68, 916.99, 742.49 cm^{-1}. **HRMS** calcd. for $C_{11}H_{12}O_2I^+$ $[M+H]^+$: 302.9882, Found: 302.9877.



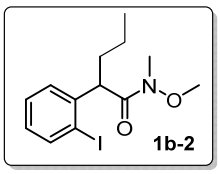
General procedure C

To a solution of **1a-1** (3.45 mmol, 1 *equiv*, 1 g) and MeNHOMe·HCl (4.59 mmol, 1.33 *equiv*, 448 mg) in DCM (40 mL) was added triethylamine (5.87 mmol, 1.7 *equiv*, 0.82 mL) at 0 °C. EDC (4.14 mmol, 1.2 *equiv*, 794 mg) and DMAP (0.35 mmol, 0.1 *equiv*, 43 mg) were then added directly as solid. The reaction mixture was gradually warmed to RT overnight and directly concentrated under vacuum. The resulting Weinreb amide was purified via silica gel chromatography to afford **1a-2** (913 mg**)** as a colorless oil in 79% yield.



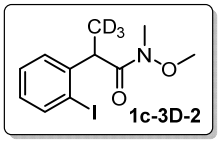
2-(2-iodophenyl)-*N*-methoxy-*N*-methylbutanamide

1a-2: $\mathbf{R_f}$ = 0.3 (Hexane : EtOAc = 5 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.35 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.28 (dt, *J* = 7.8, 1.4 Hz, 1H), 6.90 (ddd, *J* = 7.9, 7.2, 1.8 Hz, 1H), 4.24 (s, 1H), 3.47 (s, 3H), 3.16 (s, 3H), 2.06 – 1.93 (m, 1H), 1.72 – 1.60 (m, 1H), 0.96 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.12 (s), 143.26 (s), 139.52 (s), 128.69 (s), 128.39 (s), 127.73 (s), 101.92 (s), 61.38 (s), 53.19 (s), 32.36 (s), 27.26 (s), 12.37 (s). **IR:** ν 2963.98, 2933.21, 2873.61, 1661.15, 1464.92, 1435.61, 1411.40, 1380.93, 1173.89, 1009.11, 753.45 cm^{-1}. **HRMS** calcd. for $C_{12}H_{16}INO_2Na^+$ $[M+Na]^+$: 356.0118, Found: 356.0117.



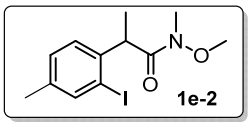
2-(2-iodophenyl)-*N*-methoxy- *N* -methylpentanamide

1b-2 was obtained as a light yellow oil (900.7 mg) in 79% yield following a similar procedure as *General procedure C* from **1b-1** (3.29 mmol, 1 *equiv*, 1 g), MeNHOMe·HCl (4.37 mmol, 1.33 *equiv*, 426.2 mg), triethylamine (5.59 mmol, 1.7 *equiv*, 565.7 mg, 779.2 μL), EDC (3.95 mmol, 1.2 *equiv*, 756 mg) and DMAP (0.33 mmol, 0.1 *equiv*, 40.3 mg): $\mathbf{R_f}$ = 0.35 (Hexane : EtOAc = 5 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.33 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.23 (td, *J* = 7.6, 1.2 Hz, 1H), 6.85 (td, *J* = 7.8, 1.7 Hz, 1H), 4.30 (s, 1H), 3.43 (s, 3H), 3.11 (s, 3H), 2.00 – 1.89 (m, 1H), 1.57 – 1.47 (m, 1H), 1.47 – 1.34 (m, 1H), 1.30 – 1.16 (m, 1H), 0.89 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.08 (s), 143.38 (s), 139.50 (s), 128.67 (s), 128.36 (s), 127.78 (s), 101.69 (s), 61.39 (s), 51.35 (s), 36.22 (s), 32.33 (s), 20.95 (s), 14.17 (s). **IR:** ν 2957.77, 2933.46, 2871.27, 1663.36, 1585.14, 1465.33, 1435.87, 1410.99, 1380.95, 1175.61, 1108.31, 1009.55, 992.28, 755.45 cm^{-1}. **HRMS** calcd. for $C_{13}H_{18}O_2NINa^+$ $[M+Na]^+$: 370.0274, Found: 370.0274.



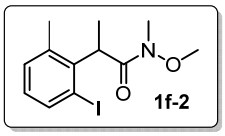
2-(2-iodophenyl)-*N*-methoxy-*N*-methylpropanamide-3,3,3-d_3

1c-3D-2 was obtained as a light yellow oil (585.7 mg) in 85% yield following a similar procedure as *General procedure C* from **1c-3D-1** (2.15 mmol, 1 *equiv*, 600 mg), MeNHOMe·HCl (2.86 mmol, 1.7 *equiv*, 357 mg), triethylamine (3.66 mmol, 1.7 *equiv*, 370 mg, 511 μL), EDC (2.58 mmol, 1.2 *equiv*, 493.9 mg) and DMAP (0.22 mmol, 0.1 *equiv*, 27 mg): $\mathbf{R_f}$ = 0.2 (Hexane : EtOAc = 5 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 – 7.80 (m, 1H), 7.29 – 7.25 (m, 2H), 6.88 (ddd, *J* = 7.9, 5.5, 3.5 Hz, 1H), 4.34 (s, 1H), 3.36 (s, 3H), 3.13 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.97 (s), 144.82 (s), 139.56 (s), 128.83 (s), 128.39 (s), 127.26 (s), 100.82 (s), 61.14 (s), 46.80 (s), 32.46 (s), 17.57 (dt, *J* = 39.7, 19.7 Hz). **IR:** ν 3058.40, 2966.02, 2934.84, 2229.66, 1664.91, 1466.06, 1412.56, 1380.03, 1276.33, 1239.01, 1175.20, 1115.12, 1091.97, 1050.62, 1012.59, 963.55, 761.01, 740.46, 643.33 cm^{-1}. **HRMS** calcd. for $C_{11}H_{11}D_3O_2NINa^+$ $[M+Na]^+$: 345.0150, Found: 345.0147.



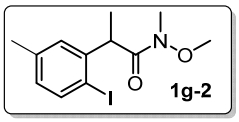
2-(2-iodo-4-methylphenyl)-*N*-methoxy-*N*-methylpropanamide

1e-2 was obtained as a colorless oil (351.5 mg) in 66% yield following a similar procedure as *General procedure C* from **1e-1** (1.61 mmol, 1 *equiv*, 467.6 mg), MeNHOMe·HCl (2.42 mmol, 1.5 *equiv*, 236 mg), triethylamine (2.74 mmol, 1.7 *equiv*, 276.7 mg, 381 μL), EDC (1.93 mmol, 1.2 *equiv*,369.5 mg) and DMAP (0.161 mmol, 0.1 *equiv*, 20 mg): $\mathbf{R_f}$ = 0.3 (Hexane : EtOAc = 5 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.1 Hz, 1H), 7.11 (d, *J* = 1.6 Hz, 1H), 6.73 (ddd, *J* = 8.0, 2.1, 0.5 Hz, 1H), 4.35 (s, 1H), 3.39 (s, 3H), 3.16 (s, 3H), 2.26 (s, 3H), 1.33 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.03 (s), 144.48 (s), 139.20 (s), 138.90 (s), 129.49 (s), 127.88 (s), 96.75 (s), 61.17 (s), 46.74 (s), 32.44 (s), 20.94 (s), 18.42 (s). **IR:** ν 2971.08, 2930.47, 1664.91, 1468.89, 1413.18, 1374.67, 1174.23, 1008.94, 994.93, 807.87, 453.81 cm^{-1}. **HRMS** calcd. for $C_{12}H_{16}O_2NINa^+$ $[M+Na]^+$: 356.0118, Found: 356.0120.



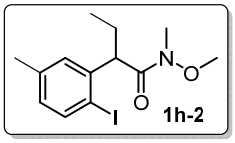
2-(2-iodo-6-methylphenyl)-*N*-methoxy-*N*-methylpropanamide

1f-2 was obtained as a light yellow oil (150.4 mg) in 82% yield over two steps. First, *General procedure B* was applied with 2-(2-iodo-6-methylphenyl)acetic acid[5a] (2.54 mmol, 1 *equiv*, 700 mg), LDA (8.88 mmol, 3.5 *equiv*) and methyl iodide (12.7 mmol, 5 *equiv*, 1.8 g, 791 μL) and gave 693.2 mg 2-(2-iodo-6-methylphenyl)propanoic acid with inseparable unknown impurity. Second, *General procedure C* was applied with 150 mg out of previous 693.2 mg product, MeNHOMe·HCl (0.78 mmol, 1.5 *equiv*, 76.1 mg), triethylamine (0.78 mmol, 1.5 *equiv*, 78.8 mg, 109 μL), EDC (0.93 mmol, 1.8 *equiv*, 178 mg) and DMAP (0.05 mmol, 0.1 *equiv*, 6.1 mg) and gave **1f-2**: $\mathbf{R_f}$ = 0.67 (Hexane : EtOAc : HOAc = 2 : 1 : 0.05). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.9 Hz, 1H), 7.03 (d, *J* = 7.5 Hz, 1H), 6.72 (t, *J* = 7.7 Hz, 1H), 4.42 (d, *J* = 5.9 Hz, 1H), 3.09 (s, 3H), 2.91 (s, 3H), 2.26 (s, 3H), 1.32 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.08 (s), 142.68 (s), 138.11 (s), 137.31 (s), 131.90 (s), 127.94 (s), 60.21 (s), 49.61 (s), 32.76 (s), 20.46 (s), 14.77 (s). **IR:** ν 2975.15, 2932.82, 1664.75, 1557.11, 1458.57, 1443.99, 1410.92, 1372.64, 1174.31, 1122.90, 1063.58, 1000.87, 839.42, 771.03, 622.82 cm^{-1}. **HRMS** calcd. for $C_{12}H_{16}O_2NINa^+$ $[M+Na]^+$: 356.0118, Found: 356.0118.



2-(2-iodo-5-methylphenyl)-*N*-methoxy-*N*-methylpropanamide

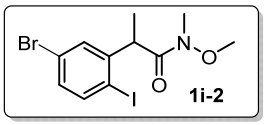
1g-2 was obtained as a yellow oil (175.3 mg) in 85% yield following a similar procedure as *General procedure C* from **1g-1** (0.62 mmol, 1 *equiv*, 180 mg), MeNHOMe·HCl (0.93 mmol, 1.5 *equiv*, 90.7 mg), triethylamine (0.93 mmol, 1.5 *equiv*, 93.9 mg, 129 μL), EDC (0.93 mmol, 1.5 *equiv*, 178 mg) and DMAP (0.062 mmol, 0.1 *equiv*, 7.6 mg): $\mathbf{R_f}$ = 0.7 (Hexane : EtOAc : HOAc = 2 : 1 : 0.05). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.1 Hz, 1H), 7.09 (dd, *J* = 12.3, 4.7 Hz, 1H), 6.74 (dd, *J* = 8.1, 2.2 Hz, 1H), 4.35 (s, 1H), 3.40 (s, 3H), 3.16 (s, 3H), 2.26 (s, 3H), 1.33 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.01 (s), 144.47 (s), 139.20 (s), 138.87 (s), 129.49 (s), 127.87 (s), 96.77 (s), 61.16 (s), 46.72 (s), 32.44 (s), 20.94 (s), 18.43 (s). **IR:** ν 2971.80, 2931.31, 2869.21, 1664.01, 1469.01, 1413.37, 1375.28, 1284.52, 1174.71, 1117.36, 1074.72, 1009.08, 995.08, 808.40, 783.13, 454.01 cm^{-1}. **HRMS** calcd. for $C_{12}H_{16}O_2NINa^+$ $[M+Na]^+$: 356.0118, Found: 356.0117.



2-(2-iodo-5-methylphenyl)-*N*-methoxy-*N*-methylbutanamide

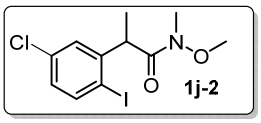
1h-2 was obtained as a light yellow oil (201.2 mg) in 77% yield over two steps. First, *General procedure B* was applied with 2-(2-iodo-5-methylphenyl)acetic acid[5a] (0.93 mmol, 1 *equiv*, 258 mg), LDA (2.8 mmol, 3 *equiv*) and ethyl iodide (4.67 mmol, 5 *equiv*, 663 mg, 342 μL) and gave 245.1 mg 2-(2-iodo-5-methylphenyl)butanoic acid with inseparable unknown impurity. Second, *General procedure C* was applied with 200 mg out of previous 245.1 mg, MeNHOMe·HCl (0.99 mmol, 1.5 *equiv*, 96.6 mg), triethylamine (0.99 mmol, 1.5 *equiv*, 100 mg, 138 μL), EDC (1.18 mmol, 1.8 *equiv*, 226.3 mg) and DMAP (0.07 mmol, 0.1 *equiv*, 8.6 mg) and gave **1h-2**: $\mathbf{R_f}$ = 0.65 (Hexane : EtOAc : HOAc = 2 : 1 : 0.05). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.1 Hz, 1H), 7.11 (d, *J* = 1.8 Hz, 1H), 6.69 (dd, *J* = 8.1, 1.9 Hz, 1H), 4.16 (s, 1H), 3.43 (s, 3H), 3.12 (s, 3H), 2.21 (s, 3H), 1.94 (ddt, *J* = 15.7,

14.6, 7.5 Hz, 1H), 1.66 – 1.53 (m, 1H), 0.91 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.15 (s), 142.91 (s), 139.15 (s), 138.72 (s), 129.51 (s), 128.33 (s), 97.93 (s), 61.39 (s), 52.96 (s), 32.32 (s), 27.32 (s), 20.97 (s), 12.40 (s). **IR:** ν 2963.87, 2932.54, 2872.82, 1662.70, 1466.92, 1414.45, 1379.58, 1175.10, 1117.77, 1008.63, 807.06, 451.99 cm^{-1}. **HRMS** calcd. for $C_{13}H_{18}O_2NINa^+$ $[M+Na]^+$: 370.0274, Found: 370.0272.



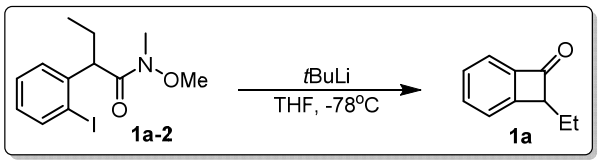
2-(5-bromo-2-iodophenyl)-*N*-methoxy-*N*-methylpropanamide

1i-2 was obtained as a white solid (136 mg) in 60% yield following a similar procedure as *General procedure C* from **1i-1** (0.59 mmol, 1 *equiv*, 200 mg), MeNHOMe·HCl (0.78 mmol, 1.33 *equiv*, 76.1 mg), triethylamine (0.1 mmol, 1.7 *equiv*, 101 mg, 139 μL), EDC (0.71 mmol, 1.2 *equiv*, 135.9 mg) and DMAP (0.06 mmol, 0.1 *equiv*, 7.3 mg): $\mathbf{R_f}$ = 0.36 (Hexane : EtOAc = 5 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.4 Hz, 1H), 7.44 (d, *J* = 2.4 Hz, 1H), 7.05 (dd, *J* = 8.4, 2.4 Hz, 1H), 4.33 (d, *J* = 6.4 Hz, 1H), 3.45 (s, 3H), 3.17 (s, 3H), 1.34 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.14 (s), 146.88 (s), 140.69 (s), 131.59 (s), 130.27 (s), 123.15 (s), 98.62 (s), 61.31 (s), 46.78 (s), 32.49 (s), 18.33 (s). **IR:** ν 2972.66, 2932.30, 1662.87, 1458.07, 1413.84, 1383.80, 1370.18, 1186.30, 1090.13, 1008.65, 986.48, 807.23, 451.47 cm^{-1}. **HRMS** calcd. for $C_{11}H_{13}O_2NBrINa^+$ $[M+Na]^+$: 419.9067, Found: 419.9063. **Mp(°C):** 107-108.



2-(5-chloro-2-iodophenyl)-*N*-methoxy-*N*-methylpropanamide

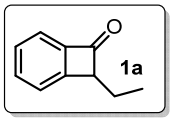
1j-2 was obtained as a white solid (159.1 mg) in 94% yield following a similar procedure as *General procedure C* from **1j-1** (0.48 mmol, 1 *equiv*, 150 mg), MeNHOMe·HCl (0.73 mmol, 1.5 *equiv*, 72.1 mg), triethylamine (0.73 mmol, 1.5 *equiv*, 73.7 mg, 102 μL), EDC (0.58 mmol, 1.2 *equiv*, 111 mg) and DMAP (0.05 mmol, 0.1 *equiv*, 6 mg): $\mathbf{R_f}$ = 0.65 (Hexane : EtOAc : HOAc = 2 : 1 : 0.05). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.4 Hz, 1H), 7.29 (d, *J* = 2.5 Hz, 1H), 6.90 (dd, *J* = 8.4, 2.5 Hz, 1H), 4.33 (d, *J* = 6.3 Hz, 1H), 3.44 (s, 3H), 3.16 (s, 3H), 1.33 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.15 (s), 146.57 (s), 140.39 (s), 135.16 (s), 128.65 (s), 127.43 (s), 97.68 (s), 61.31 (s), 46.79 (s), 32.48 (s), 18.30 (s). **IR:** ν 2972.70, 2932.76, 1663.55, 1458.36, 1413.65, 1375.76, 1235.22, 1188.67, 1100.80, 1071.71, 1011.66, 988.03, 850.48, 809.25 cm^{-1}. **HRMS** calcd. for $C_{11}H_{13}O_2NIClNa^+$ $[M+Na]^+$: 375.9572, Found: 375.9568. **Mp(°C):** 84-86.



General procedure D

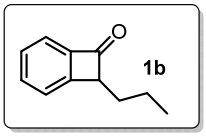
A modified procedure was used[5b]: **1a-2** (7.5 mmol, 1 *equiv*, 2.5 g) was dissolved in THF (80 mL) in a flame-dried flask and cooled to -78 °C. *t*BuLi (1.15 M in pentane, 15 mmol, 2 *equiv*, 13.0 mL) was added over one minute. The solution was stirred at -78 °C for four hours. Then saturated NH_4Cl aqueous solution (5 mL) was added to quench the reaction, and the mixture was extracted with ethyl

acetate (30 mL × 3), washed with brine and dried over sodium sulfate. Then the solution was filtered, concentrated under vacuum and purified by column chromatography on silica gel to afford 1.03 g **1a** as a light yellow oil in 94% yield.



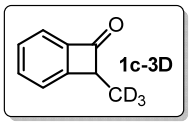
8-ethylbicyclo[4.2.0]octa-1,3,5-trien-7-one

1a: $\mathbf{R_f}$ = 0.5 (Hexane : DCM = 1 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 – 7.48 (m, 2H), 7.44 – 7.39 (m, 1H), 7.36 (d, *J* = 7.6 Hz, 1H), 4.20 (t, *J* = 7.0 Hz, 1H), 2.01 – 1.74 (m, 2H), 1.05 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 192.99 (s), 156.47 (s), 146.72 (s), 135.00 (s), 128.97 (s), 123.32 (s), 120.74 (s), 66.33 (s), 23.40 (s), 11.60 (s). **IR:** ν 2963.51, 2928.60, 1763.93, 1583.17, 1461.81, 1142.96, 973.93, 953.17, 900.25, 757.32 cm^{-1}. **HRMS** calcd. for $C_{10}H_{10}ONa^+$ $[M+Na]^+$: 169.0624, Found: 169.0622.



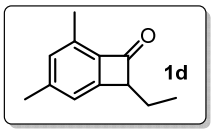
8-propylbicyclo[4.2.0]octa-1,3,5-trien-7-one

1b was obtained as a light yellow oil (270.1 mg) in 84% yield following a similar procedure as *General procedure D* from **1b-2** (2 mmol, 1 *equiv*, 694.4 mg) and *t*BuLi (1.15 M in pentane, 4 mmol, 2 *equiv*, 3.48 mL): $\mathbf{R_f}$ = 0.55 (Hexane : EtOAc = 10 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 (ddd, *J* = 4.9, 1.9, 1.1 Hz, 1H), 7.39 – 7.32 (m, 1H), 7.31 – 7.27 (m, 1H), 4.18 (dd, *J* = 7.7, 6.7 Hz, 1H), 1.89 – 1.79 (m, 1H), 1.75 – 1.64 (m, 1H), 1.52 – 1.40 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 192.92 (s), 156.63 (s), 146.60 (s), 134.98 (s), 128.91 (s), 123.30 (s), 120.68 (s), 64.83 (s), 32.43 (s), 20.63 (s), 13.99 (s). **IR:** ν 2958.61, 2930.05, 2872.74, 1768.48, 1582.82, 1462.29, 1143.18, 1092.88, 940.50, 768.84, 754.31, 740.36 cm^{-1}. **HRMS** calcd. for $C_{11}H_{12}ONa^+$ $[M+Na]^+$: 183.0780, Found: 183.0778.



8-(methyl-d_3)bicyclo[4.2.0]octa-1,3,5-trien-7-one

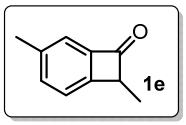
1c-3D was obtained as a colorless oil (133.9 mg) in 64% yield following a similar procedure as *General procedure D* from **1c-3D-2** (1.55 mmol, 1 *equiv*, 500 mg) and *t*BuLi (1.7 M in pentane, 3.88 mmol, 2.5 *equiv*, 2.28 mL): $\mathbf{R_f}$ = 0.5 (Hexane : EtOAc = 5 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 – 7.49 (m, 2H), 7.44 – 7.39 (m, 1H), 7.38 – 7.34 (m, 1H), 4.26 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.24 (s), 157.49 (s), 146.19 (s), 135.17 (s), 129.01 (s), 122.74 (s), 120.97 (s), 59.37 (s), 14.30 (dt, *J* = 39.5, 19.8 Hz). **IR:** ν 2926.03, 2854.72, 1771.20, 1665.49, 1582.86, 1462.32, 1378.30, 1277.79, 1177.72, 1143.36, 1085.90, 762.60, 736.17 cm^{-1}. **HRMS** calcd. for $C_9H_5D_3ONa^+$ $[M+Na]^+$: 158.0656, Found: 158.0653.



8-ethyl-3,5-dimethylbicyclo[4.2.0]octa-1,3,5-trien-7-one

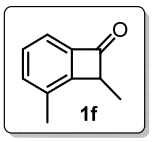
1d was was obtained as a colorless oil (330 mg) in 43% yield over three steps. First, *General procedure B* was applied with 2-(2-iodo-3,5-dimethylphenyl)acetic acid[1] (4.39 mmol, 1 *equiv*, 1.27 g), LDA (10.1

mmol, 2.3 *equiv*) and ethyl iodide (18.2 mmol, 4.1 *equiv*, 2.84 g, 1.46 mL) and gave 1.1089 g of 2-(2-iodo-3,5-dimethylphenyl)butanoic acid with inseparable impurity. Second, *General procedure C* was applied with all of the previous 1.1089 g product, MeNHOMe·HCl (5.24 mmol, 1.5 *equiv*, 511 mg), triethylamine (5.24 mmol, 1.5 *equiv*, 529 mg, 730 μL), EDC (5.24 mmol, 1.5 *equiv*, 1 g) and DMAP (0.349 mmol, 0.1 *equiv*, 42.6 mg) and gave 953 mg 2-(2-iodo-3,5-dimethylphenyl)-N-methoxy-N-methylbutanamide with inseparable impurity. Third, *General procedure D* was applied with all of the previous 953 mg product and *t*BuLi (1.7 M in pentane, 5.8 mmol, 2.2 *equiv*, 3.41 mL) and gave **1d**: $\mathbf{R_f}$ = 0.74 (Hexane : EtOAc = 5 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.02 (s, 1H), 6.86 (s, 1H), 3.93 (t, *J* = 7.0 Hz, 1H), 2.26 (d, *J* = 17.6 Hz, 6H), 1.86 – 1.58 (m, 2H), 0.94 (q, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 192.25 (s), 156.35 (s), 146.16 (s), 142.81 (s), 133.30 (s), 131.04 (s), 120.79 (s), 65.22 (s), 23.37 (s), 22.37 (s), 17.55 (s), 11.62 (s). **IR:** ν 2961.36, 2923.78, 1753.19, 1586.73, 1461.09, 1377.57, 1245.41, 1131.90, 892.82, 853.37 cm^{-1}. **HRMS** calcd. for $C_{12}H_{14}O$: 174.1045, Found: 174.1044.



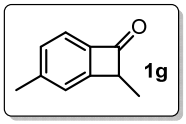
4,8-dimethylbicyclo[4.2.0]octa-1,3,5-trien-7-one

1e was obtained as a colorless oil (46.9 mg) in 43% yield following a similar procedure as *General procedure D* from **1e-2** (0.75 mmol, 1 *equiv*, 250 mg) and *t*BuLi (1.7 M in pentane, 1.88 mmol, 2.5 *equiv*, 1.1 mL): $\mathbf{R_f}$ = 0.68 (Hexane : EtOAc = 5 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (s, 1H), 7.26 – 7.21 (m, 2H), 4.20 (q, *J* = 7.2 Hz, 1H), 2.45 (s, 3H), 1.43 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 192.59 (s), 157.78 (s), 146.62 (s), 143.43 (s), 130.33 (s), 123.13 (s), 120.84 (s), 58.82 (s), 22.73 (s), 15.12 (s). **IR:** ν 2961.63, 2924.61, 1768.81, 1752.19, 1593.16, 1451.92, 1324.85, 1112.93, 902.50, 819.35 cm^{-1}. **HRMS** calcd. for $C_{10}H_{10}ONa^+$ $[M+Na]^+$: 169.0624, Found: 169.0624.



2,8-dimethylbicyclo[4.2.0]octa-1,3,5-trien-7-one

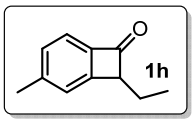
1f was obtained as a colorless oil (145.3 mg) in 66% yield following a similar procedure as *General procedure D* from **1f-2** (1.5 mmol, 1 *equiv*, 500 mg) and *t*BuLi (1.15 M in pentane, 3 mmol, 2 *equiv*, 2.6 mL): $\mathbf{R_f}$ = 0.17 (Hexane : Ether = 30 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 – 7.23 (m, 2H), 7.14 – 7.11 (m, 1H), 4.21 (q, *J* = 7.2 Hz, 1H), 2.34 (s, 3H), 1.43 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.12 (s), 156.06 (s), 145.70 (s), 136.04 (s), 133.78 (s), 129.48 (s), 118.14 (s), 58.67 (s), 17.33 (s), 14.52 (s). **IR:** ν 2962.92, 2926.30, 1799.84, 1765.21, 1585.49, 1481.15, 1452.89, 1211.70, 1169.34, 1041.58, 935.89, 864.02, 774.11, 744.48 cm^{-1}. **HRMS** calcd. for $C_{10}H_{10}ONa^+$ $[M+Na]^+$: 169.0624, Found: 169.0622.



3,8-dimethylbicyclo[4.2.0]octa-1,3,5-trien-7-one

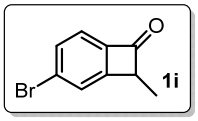
1g was obtained as a light yellow oil (181.5 mg) in 72% yield following a similar procedure as *General procedure D* from **1g-2** (1.72 mmol, 1 *equiv*, 573 mg) and *t*BuLi (1.15 M in pentane, 3.44 mmol, 2 *equiv*, 3.0 mL): $\mathbf{R_f}$ = 0.55 (Hexane : EtOAc = 5 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 (s, 1H), 7.15 (s, 2H), 4.12 (q, *J* = 7.2 Hz, 1H), 2.37 (s, 3H), 1.36 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ

192.36 (s), 157.70 (s), 146.59 (s), 143.38 (s), 130.30 (s), 123.12 (s), 120.70 (s), 58.77 (s), 22.65 (s), 15.06 (s). **IR:** ν 2963.42, 2925.88, 2868.74, 1808.60, 1769.15, 1752.44, 1593.52, 1452.04, 1325.05, 1170.09, 1113.29, 902.89, 819.95, 791.42, 681.00 cm^{-1}. **HRMS** calcd. for $C_{10}H_{11}O^+$ $[M+H]^+$: 147.0810, Found: 147.0812.



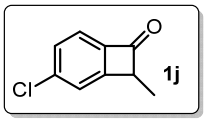
8-ethyl-3-methylbicyclo[4.2.0]octa-1,3,5-trien-7-one

1h was obtained as a light yellow oil (199.4 mg) in 86% yield following a similar procedure as *General procedure D* from **1h-2** (1.44 mmol, 1 *equiv*, 500 mg) and *t*BuLi (1.7 M in pentane, 2.88 mmol, 2 *equiv*, 1.7 mL): $\mathbf{R_f}$ = 0.65 (Hexane : EtOAc = 5 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 (s, 1H), 7.17 (d, *J* = 1.1 Hz, 2H), 4.09 – 4.04 (m, 1H), 1.92 – 1.81 (m, 1H), 1.79 – 1.66 (m, 1H), 0.99 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 192.18 (s), 156.67 (s), 146.37 (s), 143.97 (s), 130.25 (s), 123.73 (s), 120.48 (s), 65.59 (s), 23.40 (s), 22.66 (s), 11.60 (s). **IR:** ν 2963.35, 2925.89, 1758.10, 1592.80, 1459.91, 1318.09, 1112.28, 885.49, 814.87 cm^{-1}. **HRMS** calcd. for $C_{11}H_{12}ONa^+$ $[M+Na]^+$: 183.0780, Found: 183.0781.



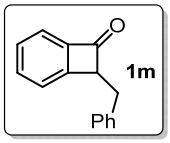
3-bromo-8-methylbicyclo[4.2.0]octa-1,3,5-trien-7-one

1i was obtained as a light yellow oil (42.1 mg) in 42% yield following a similar procedure as *General procedure D* from **1i-2** (0.47 mmol, 1 *equiv*, 186.7 mg) and *t*BuLi (1.7 M in pentane, 0.61 mmol, 1.3 *equiv*, 0.36 mL): $\mathbf{R_f}$ = 0.8 (Hexane : EtOAc = 5 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (dt, *J* = 1.6, 0.8 Hz, 1H), 7.57 (ddd, *J* = 8.0, 1.5, 0.9 Hz, 1H), 7.22 (dd, *J* = 8.0, 0.7 Hz, 1H), 4.27 (q, *J* = 7.3 Hz, 1H), 1.45 (d, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 191.38 (s), 158.58 (s), 144.75 (s), 132.92 (s), 130.01 (s), 126.58 (s), 122.50 (s), 59.75 (s), 14.96 (s). **IR:** ν 2925.07, 2851.59, 1807.78, 1764.11, 1572.21, 1318.58, 1108.76, 1042.86, 901.24, 823.05 cm^{-1}. **HRMS** calcd. for $C_9H_8OBr^+$ $[M+H]^+$: 210.9759, Found: 210.9760.



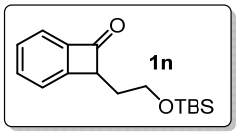
3-chloro-8-methylbicyclo[4.2.0]octa-1,3,5-trien-7-one

1j was obtained as a light yellow oil (156.2 mg) in 85% yield following a similar procedure as *General procedure D* from **1j-2** (1.1 mmol, 1 *equiv*, 390 mg) and *t*BuLi (1.7 M in pentane, 2.21 mmol, 2 *equiv*, 1.3 mL): $\mathbf{R_f}$ = 0.6 (Hexane : EtOAc = 5 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 – 7.48 (m, 1H), 7.39 (ddd, *J* = 8.0, 1.5, 0.9 Hz, 1H), 7.28 (dd, *J* = 8.1, 0.5 Hz, 1H), 4.25 (q, *J* = 7.3 Hz, 1H), 1.44 (d, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 191.06 (s), 158.49 (s), 144.30 (s), 141.18 (s), 130.13 (s), 123.54 (s), 122.42 (s), 59.46 (s), 14.86 – 11.10 (m). **IR:** ν 2966.30, 2927.74, 1812.71, 1764.71, 1579.02, 1317.70, 1170.87, 1111.41, 1056.91, 903.68, 826.57, 814.50, 782.05, 677.72 cm^{-1}. **HRMS** calcd. for $C_9H_7OClNa^+$ $[M+Na]^+$: 189.0078, Found: 189.0077.



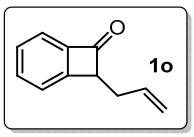
8-benzylbicyclo[4.2.0]octa-1,3,5-trien-7-one

1m was obtained as a pink oil (990.6 mg) in 68% yield over three steps. First, *General procedure B* was applied with 2-iodo-phenylacetic acid (7.63 mmol, 1 *equiv*, 2 g), LDA (16.79 mmol, 2.2 *equiv*) and benzyl bromide (30.52 mmol, 4 *equiv*, 5.2 g, 3.63 mL) and gave 2.52 g 2-(2-iodophenyl)-3-phenylpropanoic acid with inseparable impurity. Second, *General procedure C* was applied with 2.4 g of the previous 2.5 g product, MeNHOMe·HCl (10.22 mmol, 1.5 *equiv*, 1 g), triethylamine (10.22 mmol, 1.5 *equiv*, 1.03 g, 1.42 mL), EDC (12.27 mmol, 1.8 *equiv*, 2.4 g) and DMAP (0.68 mmol, 0.1 *equiv*, 83 mg) and gave 2.76 g 2-(2-iodophenyl)-*N*-methoxy-*N*-methyl-3-phenylpropanamide with inseparable impurity. Third, *General procedure D* was applied with 2.6 g of the previous 2.76 g product and *t*BuLi (1.6 M in pentane, 13.16 mmol, 2 *equiv*, 8.22 mL) and gave **1m**: $\mathbf{R_f}$ = 0.58 (Hexane : EtOAc = 5 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.42 (m, 1H), 7.41 – 7.28 (m, 4H), 7.26 – 7.18 (m, 4H), 4.49 (dd, *J* = 9.6, 5.6 Hz, 1H), 3.34 (dd, *J* = 14.0, 5.6 Hz, 1H), 2.93 (dd, *J* = 14.0, 9.6 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 191.64 (s), 155.99 (s), 146.63 (s), 138.74 (s), 135.07 (s), 129.30 (s), 128.94 (s), 128.54 (s), 126.46 (s), 123.86 (s), 121.00 (s), 65.96 (s), 36.52 (s). **IR:** ν 3062.67, 3027.13, 2915.94, 1764.38, 1583.10, 1495.83, 1276.77, 1142.53, 755.19, 700.88 cm^{-1}. **HRMS** calcd. for $C_{15}H_{13}O^+$ $[M+H]^+$: 209.0966, Found: 209.0965.



8-(2-((tert-butyldimethylsilyl)oxy)ethyl)bicyclo[4.2.0]octa-1,3,5-trien-7-one

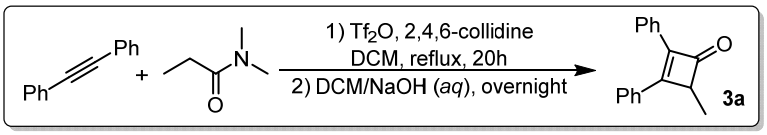
1n was obtained as a light yellow oil (478.4 mg) in 64% yield over two steps. First, *General procedure C* was applied with **1n-1** (3.09 mmol, 1 *equiv*, 1.3 g), MeNHOMe·HCl (4.64 mmol, 1.5 *equiv*, 453 mg), triethylamine (4.64 mmol, 1.5 *equiv*, 470 mg, 647 μL), EDC (5.57 mmol, 1.8 *equiv*, 1.07 g) and DMAP (0.31 mmol, 0.1 *equiv*, 38 mg) and gave 1.15 g 4-((tert-butyldimethylsilyl)oxy)-2-(2-iodophenyl)-*N*-methoxy-*N*-methylbutanamide with inseparable impurity. Second, *General procedure D* was applied with 1 g of the previous 1.15 g product and *t*BuLi (1.6 M in pentane, 4.32 mmol, 2 *equiv*, 2.7 mL) and gave **1n**: $\mathbf{R_f}$ = 0.60 (Hexane : EtOAc = 5 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 – 7.48 (m, 2H), 7.44 – 7.39 (m, 1H), 7.37 – 7.33 (m, 1H), 4.35 (dd, *J* = 7.7, 6.6 Hz, 1H), 3.83 – 3.78 (m, 2H), 2.18 – 2.08 (m, 1H), 2.02 – 1.93 (m, 1H), 0.89 (s, 9H), 0.04 (d, *J* = 4.0 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 192.61 (s), 156.12 (s), 146.73 (s), 135.00 (s), 128.94 (s), 123.60 (s), 120.75 (s), 62.15 (s), 60.99 (s), 33.31 (s), 25.92 (s), 18.31 (s), -5.39 (s). **IR:** ν 2935.75, 2928.85, 2856.88, 1770.20, 1583.27, 1462.91, 1255.52, 1097.65, 834.96, 775.88 cm^{-1}. **HRMS** calcd. for $C_{16}H_{25}O_2Si^+$ $[M+H]^+$: 277.1624, Found: 277.1618.



8-allylbicyclo[4.2.0]octa-1,3,5-trien-7-one

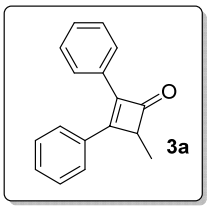
1o was obtained as a colorless oil (279.8 mg) in 73% yield over two steps. First, *General procedure C* was applied with **1o-1** (2.65 mmol, 1 *equiv*, 800 mg), MeNHOMe·HCl (4.5 mmol, 1.7 *equiv*, 439 mg), triethylamine (4.5 mmol, 1.7 *equiv*, 455 mg, 627 μL), EDC (3.18 mmol, 1.2 *equiv*, 610 mg) and DMAP (0.27 mmol, 0.1 *equiv*, 32 mg) and gave 769.4 mg 2-(2-iodophenyl)-*N*-methoxy-*N*-methylpent-4-enamide with inseparable impurity. Second, *General procedure D* was applied with 700 mg of the previous 769.4 mg product and *t*BuLi (1.6 M in pentane, 4.46 mmol, 2.2 *equiv*, 2.8 mL) and gave **1o**: $\mathbf{R_f}$ = 0.68 (Hexane : EtOAc = 5 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 2H), 7.44 – 7.37 (m, 1H), 7.36 – 7.33 (m, 1H), 5.87 (dddd, *J* = 17.3, 10.2, 7.5, 6.1 Hz, 1H), 5.16 – 5.06 (m, 2H), 4.29 (dd, *J*

= 8.8, 5.8 Hz, 1H), 2.74 – 2.65 (m, 1H), 2.49 – 2.40 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ191.88 (s), 156.11 (s), 146.70 (s), 135.12 (s), 134.75 (s), 129.22 (s), 123.57 (s), 120.92 (s), 116.97 (s), 63.91 (s), 34.55 (s). **IR:** ν 3075.82, 2908.35, 1767.25, 1640.63, 1583.00, 1462.42, 1142.72, 913.80, 763.83, 743.59 cm^{-1}. **HRMS** calcd. for $C_{11}H_{11}O^+$ $[M+H]^+$: 159.0810, Found: 159.0808.



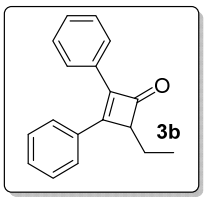
General procedure E

A modified procedure[3] was used: diphenylacetylene (8 mmol, 1 *equiv*, 1.43 g), *N, N*-dimethylpropionamide (10 mmol, 1.25 *equiv*, 1.01 g, 1.1 mL) and 2, 4, 6-collidine (12 mmol, 1.5 *equiv*, 1.45 g, 1.6 mL) were dissolved in 60 mL DCM in a flame-dried flask and the solution was heated to reflux. Triflic anhydride (12 mmol, 1.5 *equiv*, 3.4 g, 2 mL) in 40 mL DCM was added into the refluxing reaction solution over 20h. Then the solution was directly concentrated under vacuum to evaporate all the solvent. DCM (40 mL) and water (40 mL) were added to the same flask and form a heterogeneous mixture and NaOH (200 mg) was added to hydrolyze the [2+2] product, after which the reaction solution was stirred at RT overnight. The reaction mixture was then extracted with DCM (30 mL × 3), washed with brine, and dried over sodium sulfate. Then the solution was filtered, concentrated under vacuum and purified by column chromatography on silica gel to afford 1.21 g **3a** as a white solid in 64% yield.



4-methyl-2,3-diphenylcyclobut-2-en-1-one

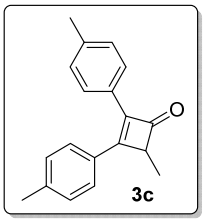
3a: **R_f** = 0.4 (Hexane : EtOAc = 5 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 – 7.67 (m, 4H), 7.47 – 7.42 (m, 3H), 7.40 – 7.30 (m, 3H), 4.04 (q, *J* = 6.9 Hz, 1H), 1.40 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 192.67 (s), 167.17 (s), 140.08 (s), 131.67 (s), 131.33 (s), 129.72 (s), 128.97 (s), 128.87 (s), 128.81 (s), 128.67 (s), 127.60 (s), 56.52 (s), 13.45 (s). **IR:** ν 3058.28, 2961.68, 2924.63, 1753.86, 1622.03, 1598.04, 1498.55, 1484.63, 1444.55, 1373.17, 1348.16, 1313.94, 1180.12, 1140.37, 1076.17, 1058.39, 956.45, 869.94, 763.06, 738.61, 691.18, 655.44 cm^{-1}. **HRMS** calcd. for $C_{17}H_{14}O$: 234.1045, Found: 234.1048. **Mp(°C):** 83-85.



4-ethyl-2,3-diphenylcyclobut-2-en-1-one

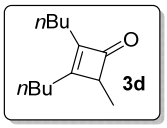
3b was obtained as a yellow solid (371 mg) in 38% yield following a similar procedure as *General procedure E* from diphenylacetylene (4 mmol, 1 *equiv*, 713 mg), *N, N*-diethylbutyramide (5 mmol, 1.25 *equiv*, 716 mg), 2, 4, 6-collidine (6 mmol, 1.5 *equiv*, 727 mg, 793 μL) and Triflic anhydride (6 mmol, 1.5 *equiv*, 1.7 g, 1 mL) and NaOH (1 g) was used for hydrolysis: **R_f** = 0.3 (Hexane : EtOAc = 20 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.66 (m, 4H), 7.47 – 7.41 (m, 3H), 7.40 – 7.30 (m, 3H), 4.04 (dd, *J* = 6.9, 4.1 Hz, 1H), 1.97 (dqd, *J* = 15.0, 7.5, 4.1 Hz, 1H), 1.86 – 1.73 (m, 1H), 0.96 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 192.44 (s), 166.07 (s), 141.24 (s), 132.14 (s), 131.21 (s), 129.63 (s), 128.93 (s), 128.83 (s), 128.65 (s), 128.49 (s), 127.58 (s), 62.61 (s), 21.00 (s), 10.69 (s). **IR:** ν 3058.85, 2962.65, 2929.31, 2874.97, 1748.44, 1621.68, 1598.10, 1484.99, 1444.32, 1349.71, 1140.80, 1078.42, 759.26, 690.47 cm^{-1}. **HRMS** calcd. for $C_{18}H_{16}O$: 248.1201, Found: 248.1199. **Mp(°C):** 69-71.



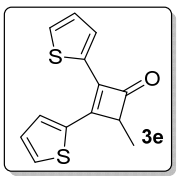
4-methyl-2,3-di-p-tolylcyclobut-2-en-1-one

3c was obtained as a yellow solid (143.8 mg) in 55% yield following a similar procedure as *General procedure E* from 1,2-di-p-tolylethyne[11] (1 mmol, 1 *equiv*, 206 mg), *N, N*-dimethylpropionamide (1.25 mmol, 1.25 *equiv*, 126 mg, 137 µL), 2, 4, 6-collidine (1.5 mmol, 1.5 *equiv*, 182 mg, 198 µL) and Triflic anhydride (1.5 mmol, 1.5 *equiv*, 423 mg, 252 µL) and NaOH (100 mg) was used for hydrolysis: $\mathbf{R_f}$ = 0.5 (Hexane : EtOAc = 5 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 (t, *J* = 8.8 Hz, 4H), 7.25 (d, *J* = 7.9 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 3.99 (q, *J* = 6.9 Hz, 1H), 2.40 (s, 3H), 2.36 (s, 3H), 1.38 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 192.85 (s), 166.49 (s), 141.93 (s), 139.23 (s), 138.71 (s), 129.67 (s), 129.30 (s), 129.07 (s), 128.86 (s), 127.51 (s), 127.08 (s), 56.27 (s), 21.73 (s), 21.50 (s), 13.49 (s). **IR:** ν 3027.84, 2960.44, 2922.81, 1751.52, 1605.77, 1499.62, 1451.18, 1345.23, 1309.79, 1182.57, 1140.67, 1057.27, 812.58, 533.99 cm^{-1}. **HRMS** calcd. for $C_{19}H_{18}O$: 262.1358, Found: 262.1365. **Mp(°C):** 105-108.



2,3-dibutyl-4-methylcyclobut-2-en-1-one

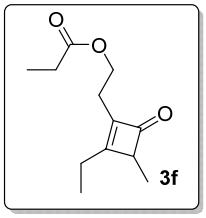
3d was obtained as a pale yellow oil (169.9 mg) in 44% yield following a similar procedure as *General procedure E* from dec-5-yne (2 mmol, 1 *equiv*, 277 mg, 359 µL), *N, N*-dimethylpropionamide (4 mmol, 2 *equiv*, 405 mg, 440 µL), 2, 4, 6-collidine (4.8 mmol, 2.4 *equiv*, 582 mg, 634 µL) and Triflic anhydride (4.8 mmol, 2.4 *equiv*, 1.35 g, 808 µL) and NaOH (100 mg) was used for hydrolysis: $\mathbf{R_f}$ = 0.7 (Hexane : EtOAc = 5 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.41 – 3.34 (m, 1H), 2.58 – 2.37 (m, 2H), 2.04 (t, *J* = 7.6 Hz, 2H), 1.65 – 1.23 (m, 10H), 1.15 (d, *J* = 6.9 Hz, 3H), 0.95 (t, *J* = 7.3 Hz, 3H), 0.89 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.04 (s), 177.94 (s), 146.12 (s), 55.96 (s), 29.53 (s), 28.29 (s), 27.87 (s), 22.93 (s), 22.83 (s), 22.57 (s), 13.76 (s), 13.74 (s), 13.55 (s). **IR:** ν 2958.48, 2931.22, 2872.81, 1756.47, 1633.98, 1456.76, 1377.84, 1342.35, 1179.07, 1103.39, 1048.99, 927.18, cm^{-1}. **HRMS** calcd. for $C_{13}H_{22}O$: 194.1671, Found: 194.1670.



4-methyl-2,3-di(thiophen-2-yl)cyclobut-2-en-1-one

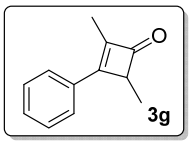
3e was obtained as a yellow oil (143.8 mg) in 50% yield following a similar procedure as *General procedure E* from 1,2-di(thiophen-2-yl)ethyne[11] (1 mmol, 1 *equiv*, 190 mg), *N,*

N-dimethylpropionamide (2 mmol, 2 *equiv*, 202 mg, 220 μL), 2, 4, 6-collidine (2.4 mmol, 2.4 *equiv*, 291 mg, 317 μL) and Triflic anhydride (2.4 mmol, 2.4 *equiv*, 677 mg, 404 μL) and NaOH (100 mg) was used for hydrolysis: $\mathbf{R_f}$ = 0.3 (Hexane : Ether = 10 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 – 7.77 (m, 1H), 7.72 (d, *J* = 5.0 Hz, 1H), 7.65 (dd, *J* = 3.7, 1.0 Hz, 1H), 7.40 (d, *J* = 5.0 Hz, 1H), 7.26 – 7.22 (m, 1H), 7.12 (dd, *J* = 4.9, 3.8 Hz, 1H), 4.00 (q, *J* = 6.9 Hz, 1H), 1.46 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.53 (s), 154.07 (s), 134.63 (s), 132.48 (s), 132.08 (s), 130.59 (s), 130.23 (s), 128.68 (s), 128.61 (s), 127.52 (s), 126.63 (s), 58.09 (s), 13.76 (s). **IR:** ν 3103.41, 2962.41, 2923.99, 1749.37, 1597.40, 1520.98, 1427.62, 1408.24, 1365.73, 1320.04, 1300.94, 1231.56, 1123.85, 1082.98, 1053.44, 858.46, 836.19, 707.25 cm^{-1}. **HRMS** calcd. for $C_{13}H_{10}OS_2$: 246.0173, Found: 246.0176.



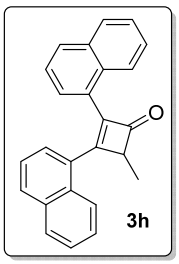
2-(2-ethyl-3-methyl-4-oxocyclobut-1-en-1-yl)ethyl propionate

3f was obtained as a colorless oil (122.2 mg) in 19% yield following a similar procedure as *General procedure E* from hex-3-yn-1-ol (3 mmol, 1 *equiv*, 294 mg, 328 μL), *N, N*-dimethylpropionamide (12 mmol, 4 *equiv*, 1.21 g, 1.32 mL), 2, 4, 6-collidine (14.4 mmol, 4.8 *equiv*, 1.74 g, 1.90 mL) and Triflic anhydride (14.4 mmol, 4.8 *equiv*, 4.06 g, 2.42 mL) and NaOH (300 mg) was used for hydrolysis: $\mathbf{R_f}$ = 0.45 (Hexane : EtOAc = 5 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.15 (t, *J* = 6.8 Hz, 2H), 3.41 (q, *J* = 6.9 Hz, 1H), 2.64 – 2.42 (m, 2H), 2.40 (t, *J* = 6.8 Hz, 2H), 2.30 (q, *J* = 7.6 Hz, 2H), 1.18 (t, *J* = 7.6 Hz, 3H), 1.15 (d, *J* = 6.9 Hz, 3H), 1.11 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.99 (s), 181.18 (s), 174.26 (s), 140.92 (s), 61.54 (s), 56.17 (s), 27.49 (s), 23.03 (s), 21.79 (s), 13.39 (s), 10.73 (s), 9.03 (s). **IR:** ν 2968.08, 2925.64, 1755.99, 1741.66, 1638.74, 1462.18, 1349.90, 1274.52, 1182.16, 1083.80, 1026.82, cm^{-1}. **HRMS** calcd. for $C_{12}H_{19}O_3^+$ $[M+H]^+$: 211.1334, Found: 211.1336.



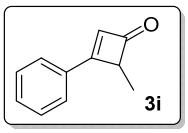
2,4-dimethyl-3-phenylcyclobut-2-en-1-one

3g was obtained as a light yellow oil (286.1 mg) in 83% yield following a similar procedure as *General procedure E* from prop-1-yn-1-ylbenzene (2 mmol, 1 *equiv*, 232 mg, 250 μL), *N, N*-dimethylpropionamide (4 mmol, 2 *equiv*, 405 mg, 440 μL), 2, 4, 6-collidine (4.8 mmol, 2.4 *equiv*, 582 mg, 634 μL) and Triflic anhydride (4.8 mmol, 2.4 *equiv*, 1.35 g, 808 μL) and NaOH (100 mg) was used for hydrolysis: $\mathbf{R_f}$ = 0.4 (Hexane : EtOAc = 5 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 – 7.57 (m, 2H), 7.53 – 7.44 (m, 3H), 3.90 – 3.82 (m, 1H), 2.00 (d, *J* = 2.1 Hz, 2H), 1.36 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 194.71 (s), 168.96 (s), 139.47 (s), 132.07 (s), 130.76 (s), 129.01 (s), 55.18 (s), 13.72 (s), 9.12 (s). **IR:** ν 2961.37, 2924.84, 2868.51, 1746.95, 1615.98, 1448.78, 1376.19, 1342.83, 1311.81, 1201.78, 1043.62, 1009.12, 960.01, 911.24, 775.94, 752.32, 692.83 cm^{-1}. **HRMS** calcd. for $C_{12}H_{12}O$: 172.0888, Found: 172.0887.



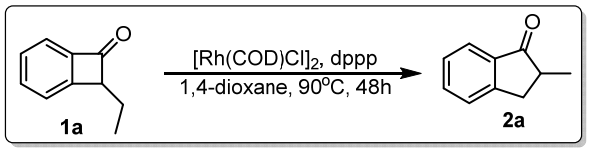
4-methyl-2,3-di(naphthalen-1-yl)cyclobut-2-en-1-one

3h was obtained as a sticky yellow oil (248.5 mg) in 74% yield following a similar procedure as *General procedure E* from 1,2-di(naphthalen-1-yl)ethyne[11] (1 mmol, 1 *equiv*, 278 mg), *N, N*-dimethylpropionamide (2 mmol, 2 *equiv*, 202 mg, 220 µL), 2, 4, 6-collidine (2.4 mmol, 2.4 *equiv*, 291 mg, 317 µL) and Triflic anhydride (2.4 mmol, 2.4 *equiv*, 677 mg, 404 µL) and NaOH (100 mg) was used for hydrolysis: $\mathbf{R_f}$ = 0.6 (Hexane : EtOAc = 5 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.2 Hz, 1H), 7.82 (t, *J* = 8.7 Hz, 4H), 7.76 (d, *J* = 8.5 Hz, 1H), 7.64 (d, *J* = 7.2 Hz, 1H), 7.57 (dd, *J* = 7.0, 1.2 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 1H), 7.38 (dd, *J* = 14.3, 6.8 Hz, 3H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.18 – 7.12 (m, 1H), 4.55 (q, *J* = 6.9 Hz, 1H), 1.47 (dd, *J* = 7.0, 0.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 192.79 (s), 170.07 (s), 142.51 (s), 133.73 (s), 133.64 (s), 131.84 (s), 130.40 (s), 130.20 (s), 129.52 (s), 129.41 (s), 128.70 (s), 128.53 (s), 128.38 (s), 127.56 (s), 127.49 (s), 126.84 (s), 126.39 (s), 126.26 (s), 126.03 (s), 125.76 (s), 125.46 (s), 125.31 (s), 125.18 (s), 58.76 (s), 13.58 (s). **IR:** ν 3049.08, 2960.51, 2923.67, 1749.90, 1605.43, 1586.85, 1509.34, 1450.53, 1318.37, 1251.72, 1144.72, 800.73, 775.80 cm^{-1}. **HRMS** calcd. for $C_{25}H_{18}O$: 334.1358, Found: 334.1361.



4-methyl-3-phenylcyclobut-2-en-1-one

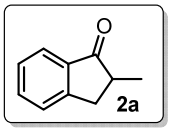
3i was obtained as a yellow oil (67.6 mg) in 5% yield following a similar procedure as *General procedure E* from phenylacetylene (9 mmol, 1 *equiv*, 919 mg), *N, N*-dimethylpropionamide (11.25 mmol, 1.25 *equiv*, 1.14 g, 1.24 mL), 2, 4, 6-collidine (13.5 mmol, 1.5 *equiv*, 1.64 g, 1.78 mL) and Triflic anhydride (13.5 mmol, 1.5 *equiv*, 3.81 g, 2.27 mL) and NaOH (100 mg) was used for hydrolysis: $\mathbf{R_f}$ = 0.47 (Hexane : EtOAc = 5 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 – 7.60 (m, 2H), 7.53 – 7.48 (m, 3H), 6.34 (s, 1H), 3.92 (q, *J* = 7.0 Hz, 1H), 1.42 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 192.38 (s), 176.37 (s), 131.86 (s), 130.81 (s), 129.03 (s), 128.80 (s), 128.13 (s), 55.75 (s), 13.70 (s). **IR:** ν 3061.30, 2962.76, 2926.32, 2868.35, 1754.78, 1601.94, 1560.52, 1487.24, 1449.52, 1264.50, 1076.47, 1052.61, 1017.49, 853.51, 767.75, 695.27 cm^{-1}. **HRMS** calcd. for $C_{11}H_{10}O$: 158.0732, Found: 158.0735.



General procedure F

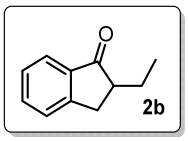
To a flame-dried 8 mL vial equipped with a stir-bar was added **1a** (0.2 mmol, 1 *equiv*, 29.2 mg), $[Rh(COD)Cl]_2$ (0.01 mmol, 0.05 *equiv*, 4.9 mg) and dppp (0.024 mmol, 0.12 *equiv*, 9.9 mg). The vial was then transferred into a nitrogen-filled glovebox. 1, 4-dioxane (2 mL) was added, and the vial was sealed and stirred in a pre-heated pie-block at 90°C for 48h. The reaction solution was concentrated

under vacuum and directed purified via column chromatography on silica gel to afford 27.1 mg **2a** as a colorless oil in 93% yield.



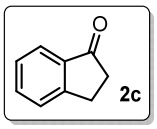
2-methyl-2,3-dihydro-1H-inden-1-one

2a: $\mathbf{R_f}$ = 0.5 (Hexane : EtOAc = 5 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 7.7, 0.5 Hz, 1H), 7.59 – 7.54 (m, 1H), 7.45 – 7.41 (m, 1H), 7.37 – 7.32 (m, 1H), 3.38 (dd, *J* = 17.9, 8.9 Hz, 1H), 2.75 – 2.65 (m, 2H), 1.29 (d, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 209.50 (s), 153.46 (s), 136.32 (s), 134.66 (s), 127.33 (s), 126.51 (s), 123.96 (s), 41.96 (s), 34.94 (s), 16.27 (s). **IR:** ν 2962.84, 2927.85, 2871.42, 1711.60, 1608.79, 1464.10, 1326.94, 1292.80, 1236.68, 1204.10, 1150.15, 965.39, 786.66, 740.80, 719.91 cm^{-1}. **HRMS** calcd. for $C_{10}H_{10}O$: 146.0732, Found: 146.0735.



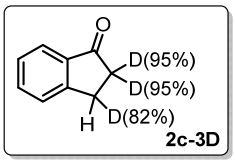
2-ethyl-2,3-dihydro-1H-inden-1-one

2b was obtained as a colorless oil (22.8 mg) in 71% yield (80% brsm) following a similar procedure as *General procedure F* from **1b** (0.2 mmol, 1 *equiv*, 32.0 mg), $[Rh(COD)Cl]_2$ (0.01 mmol, 0.05 *equiv*, 4.9 mg) and dppp (0.024 mmol, 0.12 *equiv*, 9.9 mg): $\mathbf{R_f}$ = 0.6 (Hexane : EtOAc = 5 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 – 7.73 (m, 1H), 7.58 (td, *J* = 7.5, 1.2 Hz, 1H), 7.48 – 7.44 (m, 1H), 7.38 – 7.33 (m, 1H), 3.32 (dd, *J* = 17.2, 7.9 Hz, 1H), 2.82 (dd, *J* = 17.2, 3.9 Hz, 1H), 2.62 (ddd, *J* = 12.5, 8.4, 4.2 Hz, 1H), 1.98 (dqd, *J* = 13.7, 7.5, 4.5 Hz, 1H), 1.54 (ddq, *J* = 14.6, 9.1, 7.3 Hz, 1H), 1.01 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 209.01 (s), 153.83 (s), 136.93 (s), 134.62 (s), 127.28 (s), 126.54 (s), 123.82 (s), 48.75 (s), 32.32 (s), 24.47 (s), 11.62 (s). **IR:** ν 2960.77, 2926.27, 2854.73, 1713.10, 1609.67, 1463.60, 1327.00, 1277.19, 1203.77, 748.90, 718.34 cm^{-1}. **HRMS** calcd. for $C_{11}H_{12}ONa^+$ $[M+Na]^+$: 183.0780, Found: 183.0779.



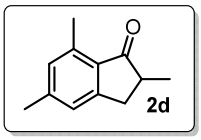
2,3-dihydro-1H-inden-1-one

2c was obtained as a colorless oil (19.2 mg) in 73% yield following a similar procedure as *General procedure F* from **1c** (0.2 mmol, 1 *equiv*, 26.4 mg), $[Rh(COD)Cl]_2$ (0.01 mmol, 0.05 *equiv*, 4.9 mg) and dppp (0.024 mmol, 0.12 *equiv*, 9.9 mg) under 110°C instead of 90°C: $\mathbf{R_f}$ = 0.33 (Hexane : EtOAc = 5 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 7.7, 0.4 Hz, 1H), 7.59 – 7.54 (m, 1H), 7.48 – 7.44 (m, 1H), 7.37 – 7.32 (m, 1H), 3.16 – 3.10 (m, 2H), 2.70 – 2.65 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 207.08 (s), 155.14 (s), 137.05 (s), 134.57 (s), 127.25 (s), 126.67 (s), 123.69 (s), 36.20 (s), 25.79 (s). **IR:** ν 3071.57, 2925.33, 2858.92, 1712.03, 1610.49, 1463.10, 1439.52, 1326.57, 1277.70, 1243.58, 1203.04, 1150.09, 1087.80, 1033.49, 827.34, 758.20, 568.84, 463.90 cm^{-1}. **HRMS** calcd. for $C_9H_8ONa^+$ $[M+Na]^+$: 155.0467, Found: 155.0465.



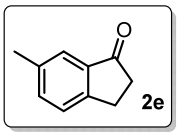
2,3-dihydro-1H-inden-1-one-2,2,3-d_3

2c-3D was obtained as a colorless oil (12.3 mg) in 30% yield following a similar procedure as *General procedure F* from **1c-3D** (0.3 mmol, 1 *equiv*, 40.4 mg), $[Rh(COD)Cl]_2$ (0.015 mmol, 0.05 *equiv*, 7.4 mg) and dppp (0.036 mmol, 0.12 *equiv*, 14.9 mg) under 110°C instead of 90°C: $\mathbf{R_f}$ = 0.4 (Hexane : EtOAc = 5 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.7 Hz, 1H), 7.59 (td, *J* = 7.5, 1.2 Hz, 1H), 7.48 (dd, *J* = 7.7, 0.8 Hz, 1H), 7.40 – 7.34 (m, 1H), 3.16 – 3.10 (m, 1.18H), 2.72 – 2.65 (m, 0.11H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 207.17 (s), 155.13 (s), 137.14 (s), 134.57 (s), 127.27 (s), 126.70 (s), 123.70 (s), 35.90 (s), 35.70 (s), 35.50 (s), 35.30 (s), 25.62 (s), 25.51 (s), 25.31 (s), 25.11 (s). **HRMS** calcd. for $C_9H_5D_3O$: 135.0763, Found: 135.0768.



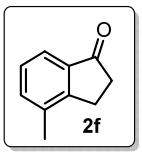
2,5,7-trimethyl-2,3-dihydro-1H-inden-1-one

2d was obtained as a colorless oil (15.0 mg) in 85% yield following a similar procedure as *General procedure F* from **1d** (0.1 mmol, 1 *equiv*, 17.6 mg), $[Rh(COD)Cl]_2$ (0.005 mmol, 0.05 *equiv*, 2.5 mg) and dppp (0.012 mmol, 0.12 *equiv*, 5.0 mg) under 150°C instead of 90°C: $\mathbf{R_f}$ = 0.6 (Hexane : EtOAc = 5 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.05 (s, 1H), 6.91 (s, 1H), 3.32 – 3.24 (m, 1H), 2.69 – 2.60 (m, 2H), 2.59 (s, 3H), 2.38 (s, 3H), 1.28 (d, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 209.78 (s), 154.65 (s), 144.97 (s), 138.72 (s), 131.51 (s), 130.33 (s), 124.21 (s), 42.36 (s), 34.42 (s), 21.81 (s), 18.17 (s), 16.51 (s). **IR:** ν 2962.12, 2926.20, 2870.97, 1701.50, 1610.30, 1456.66, 1374.94, 1327.44, 1254.25, 1234.53, 1196.34, 1150.32, 1035.01, 934.30, 847.82, 668.94 cm^{-1}. **HRMS** calcd. for $C_{12}H_{15}O^+$ $[M+H]^+$: 175.1123, Found: 175.1120.



6-methyl-2,3-dihydro-1H-inden-1-one

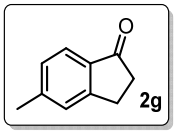
2e was obtained as a white solid (24.5 mg) in 84% yield following a similar procedure as *General procedure F* from **1e** (0.2 mmol, 1 *equiv*, 29.2 mg), $[Rh(COD)Cl]_2$ (0.01 mmol, 0.05 *equiv*, 4.9 mg) and dppp (0.024 mmol, 0.12 *equiv*, 9.9 mg): $\mathbf{R_f}$ = 0.2 (Hexane : EtOAc = 5 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.8 Hz, 1H), 7.26 – 7.23 (m, 1H), 7.15 (dd, *J* = 7.9, 0.6 Hz, 1H), 3.09 – 3.03 (m, 2H), 2.67 – 2.62 (m, 2H), 2.41 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 206.61 (s), 155.70 (s), 145.72 (s), 134.80 (s), 128.52 (s), 126.99 (s), 123.48 (s), 36.36 (s), 25.61 (s), 22.03 (s). **IR:** ν 2952.73, 2920.23, 2864.03, 1699.36, 1608.69, 1584.84, 1443.37, 1326.67, 1237.97, 1030.21, 830.93, 811.41, 568.44 cm^{-1}. **HRMS** calcd. for $C_{10}H_{10}ONa^+$ $[M+Na]^+$: 169.0624, Found: 169.0622. **Mp(°C):** 71-73.



4-methyl-2,3-dihydro-1H-inden-1-one

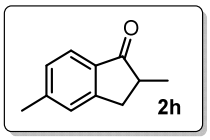
2f was obtained as a white solid (21.3 mg) in 73% yield (825 brsm) following a similar procedure as *General procedure F* from **1f** (0.2 mmol, 1 *equiv*, 29.2 mg), $[Rh(COD)Cl]_2$ (0.01 mmol, 0.05 *equiv*, 4.9 mg) and dppp (0.024 mmol, 0.12 *equiv*, 9.9 mg) under 110°C instead of 90°C: $\mathbf{R_f}$ = 0.5 (Hexane : EtOAc = 5 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 7.6, 0.5 Hz, 1H), 7.40 (d, *J* = 7.3 Hz, 1H), 7.29 (t, *J* = 7.5 Hz, 1H), 3.04 – 2.99 (m, 2H), 2.71 – 2.67 (m, 2H), 2.36 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 207.48 (s), 154.18 (s), 136.82 (s), 135.86 (s), 134.99 (s), 127.46 (s), 121.05 (s), 36.17 (s),

24.64 (s), 17.74 (s). **IR:** ν 2929.38, 2854.95, 1701.84, 1603.19, 1591.39, 1479.82, 1445.87, 1404.09, 1378.34, 1329.91, 1286.37, 1267.39, 1046.30, 907.60, 791.10, 781.28, 733.06, 632.93, 548.81, 439.70 cm^{-1}. **HRMS** calcd. for $C_{10}H_{10}ONa^+$ $[M+Na]^+$: 169.0624, Found: 169.0621. **Mp(°C):** 97-99.



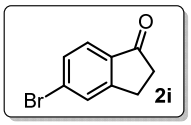
5-methyl-2,3-dihydro-1H-inden-1-one

2g was obtained as a white solid (27.6 mg) in 94% yield following a similar procedure as *General procedure F* from **1g** (0.2 mmol, 1 *equiv*, 29.4 mg), $[Rh(COD)Cl]_2$ (0.01 mmol, 0.05 *equiv*, 4.9 mg) and dppp (0.024 mmol, 0.12 *equiv*, 9.9 mg): $\mathbf{R_f}$ = 0.4 (Hexane : EtOAc = 5 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.8 Hz, 1H), 7.26 – 7.23 (m, 1H), 7.17 – 7.13 (m, 1H), 3.09 – 3.04 (m, 2H), 2.67 – 2.62 (m, 2H), 2.41 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 206.62 (s), 155.70 (s), 145.73 (s), 134.80 (s), 128.53 (s), 126.98 (s), 123.48 (s), 36.36 (s), 25.61 (s), 22.03 (s). **IR:** ν 2952.47, 2919.57, 1699.44, 1608.33, 1443.21, 1326.36, 1277.39, 1237.71, 1030.26, 892.59, 811.19, 568.19 cm^{-1}. **HRMS** calcd. for $C_{10}H_{10}ONa^+$ $[M+Na]^+$: 169.0624, Found: 169.0622. **Mp(°C):** 71-73.



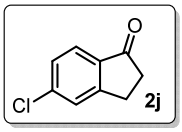
2,5-dimethyl-2,3-dihydro-1H-inden-1-one

2h was obtained as a colorless oil (28.3 mg) in 87% yield (94% brsm) following a similar procedure as *General procedure F* from **1h** (0.2 mmol, 1 *equiv*, 32.2 mg), $[Rh(COD)Cl]_2$ (0.01 mmol, 0.05 *equiv*, 4.9 mg) and dppp (0.024 mmol, 0.12 *equiv*, 9.9 mg): $\mathbf{R_f}$ = 0.55 (Hexane : EtOAc = 5 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.8 Hz, 1H), 7.22 (s, 1H), 7.16 (dd, *J* = 7.8, 0.5 Hz, 1H), 3.37 – 3.27 (m, 1H), 2.72 – 2.61 (m, 2H), 2.41 (s, 3H), 1.28 (d, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 209.03 (s), 153.98 (s), 145.80 (s), 134.02 (s), 128.60 (s), 126.84 (s), 123.79 (s), 42.07 (s), 34.79 (s), 22.05 (s), 16.41 (s). **IR:** ν 2962.55, 2928.91, 2871.09, 1707.88, 1609.67, 1456.28, 1437.07, 1371.59, 1326.57, 1277.46, 1236.42, 1203.32, 1109.41, 1038.26, 963.92, 883.87, 825.95, 766.49, 669.60, 544.62 cm^{-1}. **HRMS** calcd. for $C_{11}H_{12}ONa^+$ $[M+Na]^+$: 183.0780, Found: 183.0780.



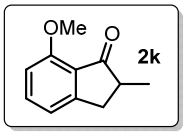
5-bromo-2,3-dihydro-1H-inden-1-one

2i was obtained as a white solid (17.9 mg) in 42% yield (53% brsm) following a similar procedure as *General procedure F* from **1i** (0.2 mmol, 1 *equiv*, 42.2 mg), $[Rh(COD)Cl]_2$ (0.01 mmol, 0.05 *equiv*, 4.9 mg) and dppp (0.024 mmol, 0.12 *equiv*, 9.9 mg) under 130°C instead of 90°C: $\mathbf{R_f}$ = 0.18 (Hexane : Ether = 5 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 0.8 Hz, 1H), 7.61 (d, *J* = 8.2 Hz, 1H), 7.53 – 7.49 (m, 1H), 3.16 – 3.11 (m, 2H), 2.72 – 2.67 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 205.60 (s), 156.66 (s), 135.90 (s), 130.94 (s), 129.95 (s), 124.93 (s), 36.14 (s), 25.51 (s). **IR:** ν 1707.09, 1592.61, 1570.88, 1435.13, 1318.22, 1266.27, 1197.08, 1168.26, 1052.16, 1031.60, 857.12, 836.35, 812.64 cm^{-1}. **HRMS** calcd. for $C_9H_8OBr^+$ $[M+H]^+$: 210.9759, Found: 210.9754. **Mp(°C):** 119-123.



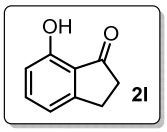
5-chloro-2,3-dihydro-1H-inden-1-one

2j was obtained as a white solid (18.7 mg) in 57% yield (86% brsm) following a similar procedure as *General procedure F* from **1j** (0.2 mmol, 1 *equiv*, 33.2 mg), $[Rh(COD)Cl]_2$ (0.01 mmol, 0.05 *equiv*, 4.9 mg) and dppp (0.024 mmol, 0.12 *equiv*, 9.9 mg) under 110°C instead of 90°C: $\mathbf{R_f}$ = 0.5 (Hexane : EtOAc = 5 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 – 7.65 (m, 1H), 7.46 (dd, *J* = 1.6, 0.6 Hz, 1H), 7.36 – 7.31 (m, 1H), 3.15 – 3.10 (m, 2H), 2.72 – 2.68 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 205.37 (s), 156.51 (s), 141.09 (s), 135.52 (s), 128.09 (s), 126.84 (s), 124.80 (s), 36.23 (s), 25.55 (s). **IR:** ν 2919.22, 1705.64, 1600.45, 1577.75, 1435.07, 1418.78, 1405.52, 1319.55, 1289.31, 1267.55, 1200.71, 1061.54, 1030.38, 871.21, 826.86, 799.90 cm^{-1}. **HRMS** calcd. for $C_9H_7OClNa^+$ $[M+Na]^+$: 189.0078, Found: 189.0099. **Mp(°C):** 93-95.



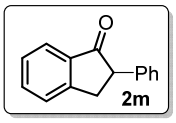
7-methoxy-2-methyl-2,3-dihydro-1H-inden-1-one

2k was obtained as a light yellow oil (10.9 mg) in 31% yield (74% brsm) following a similar procedure as *General procedure F* from 8-ethyl-5-methoxybicyclo[4.2.0]octa-1,3,5-trien-7-one (**1k**)[2] (0.2 mmol, 1 *equiv*, 35.2 mg), $[Rh(COD)Cl]_2$ (0.01 mmol, 0.05 *equiv*, 4.9 mg) and dppp (0.024 mmol, 0.12 *equiv*, 9.9 mg) under 150°C instead of 90°C: $\mathbf{R_f}$ = 0.2 (Hexane : EtOAc = 5 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 8.1, 7.6 Hz, 1H), 6.96 (ddd, *J* = 7.5, 1.6, 0.8 Hz, 1H), 6.76 (d, *J* = 8.2 Hz, 1H), 3.93 (s, 3H), 3.31 (dd, *J* = 18.0, 8.7 Hz, 1H), 2.71 – 2.60 (m, 2H), 1.27 (d, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 207.23 (s), 158.18 (s), 156.14 (s), 136.34 (s), 124.34 (s), 118.28 (s), 108.81 (s), 55.71 (s), 42.18 (s), 34.67 (s), 16.77 (s). **IR:** ν 2960.29, 2925.69, 2851.97, 1704.86, 1597.17, 1480.54, 1291.51, 1272.74, 1225.60, 1199.07, 1066.36, 969.21, 796.72, 776.45 cm^{-1}. **HRMS** calcd. for $C_{11}H_{12}O_2Na^+$ $[M+Na]^+$: 199.0730, Found: 199.0726.



7-hydroxy-2,3-dihydro-1H-inden-1-one

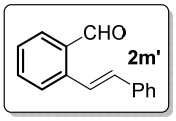
2l was obtained as a colorless oil (14.4 mg) in 48% yield (56% brsm) following a similar procedure as *General procedure F* from 5-hydroxy-8-methylbicyclo[4.2.0]octa-1,3,5-trien-7-one (**1l**)[3] (0.2 mmol, 1 *equiv*, 29.6 mg), $[Rh(COD)Cl]_2$ (0.01 mmol, 0.05 *equiv*, 4.9 mg) and dppp (0.024 mmol, 0.12 *equiv*, 9.9 mg): $\mathbf{R_f}$ = 0.65 (Hexane : EtOAc = 3 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.05 (s, 1H), 7.48 – 7.43 (m, 1H), 6.93 (ddd, *J* = 7.5, 1.6, 0.9 Hz, 1H), 6.74 (dd, *J* = 8.2, 0.7 Hz, 1H), 3.12 – 3.07 (m, 2H), 2.73 – 2.68 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.07 (s), 157.45 (s), 155.22 (s), 137.58 (s), 122.64 (s), 117.39 (s), 113.41 (s), 35.95 (s), 25.83 (s). **IR:** ν 3363.04, 2924.23, 1679.02, 1617.23, 1598.71, 1465.87, 1327.55, 1293.28, 1176.27, 1059.42, 829.66, 780.32, 646.51 cm^{-1}. **HRMS** calcd. for $C_9H_8O_2Na^+$ $[M+Na]^+$: 171.0417, Found: 171.0409.



2-phenyl-2,3-dihydro-1H-inden-1-one

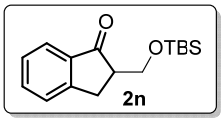
2m was obtained as a colorless oil (12.0 mg) in 29% yield following a similar procedure as *General procedure F* from **1m** (0.2 mmol, 1 *equiv*, 41.5 mg), $[Rh(COD)Cl]_2$ (0.01 mmol, 0.05 *equiv*, 4.9 mg) and dppp (0.024 mmol, 0.12 *equiv*, 9.9 mg) under 110°C instead of 90°C: $\mathbf{R_f}$ = 0. 5 (Hexane : EtOAc = 5 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 – 7.80 (m, 1H), 7.68 – 7.63 (m, 1H), 7.56 – 7.51 (m, 1H),

7.45 – 7.40 (m, 1H), 7.35 – 7.29 (m, 2H), 7.28 – 7.22 (m, 1H), 7.21 – 7.16 (m, 2H), 3.90 (dd, *J* = 8.3, 4.1 Hz, 1H), 3.70 (dd, *J* = 17.6, 8.2 Hz, 1H), 3.28 (dd, *J* = 17.4, 4.0 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 205.99 (s), 153.68 (s), 139.69 (s), 136.23 (s), 135.02 (s), 128.84 (s), 127.85 (s), 127.74 (s), 127.02 (s), 126.43 (s), 124.54 (s), 53.40 (s), 35.84 (s). **IR:** ν 3317.23, 2923.84, 1712.87, 1606.79, 1494.42, 1464.03, 1453.06, 1297.25, 1213.56, 1032.18, 759.84, 699.13 cm^{-1}. **HRMS** calcd. for $C_{15}H_{13}O^+$ $[M+H]^+$: 209.0966, Found: 209.0963.



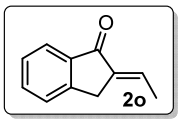
(E)-2-styrylbenzaldehyde

2m' was obtained as a colorless oil (19.3 mg) in 48% yield together with **2m** from the same reaction : $\mathbf{R_f}$ = 0.6 (Hexane : EtOAc = 5 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.33 (s, 1H), 8.05 (d, *J* = 16.2 Hz, 1H), 7.85 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.62 – 7.54 (m, 3H), 7.44 (td, *J* = 7.5, 1.1 Hz, 1H), 7.42 – 7.35 (m, 2H), 7.33 – 7.28 (m, 1H), 7.06 (d, *J* = 16.2 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 192.18 (s), 139.44 (s), 136.36 (s), 133.49 (s), 133.22 (s), 132.41 (s), 131.82 (s), 128.26 (s), 127.80 (s), 127.11 (s), 126.67 (s), 126.45 (s), 124.26 (s). **IR:** ν 3060.53, 3024.91, 2739.06, 1693.42, 1595.27, 1495.38, 1476.52, 1448.15, 1287.96, 1195.93, 963.49, 761.37, 719.83, 690.76 cm^{-1}. **HRMS** calcd. for $C_{15}H_{12}O$: 208.0888, Found: 208.0887.



2-(((tert-butyldimethylsilyl)oxy)methyl)-2,3-dihydro-1H-inden-1-one

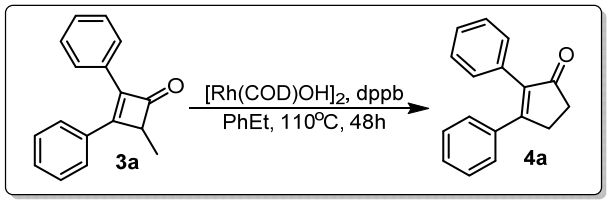
2n was obtained as a colorless oil (34.9 mg) in 63% yield following a similar procedure as *General procedure F* from **1n** (0.2 mmol, 1 *equiv*, 55.1 mg), $[Rh(COD)Cl]_2$ (0.01 mmol, 0.05 *equiv*, 4.9 mg) and dppp (0.024 mmol, 0.12 *equiv*, 9.9 mg) under 110°C instead of 90°C: $\mathbf{R_f}$ = 0.63 (Hexane : EtOAc = 5 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 7.7, 0.4 Hz, 1H), 7.60 – 7.55 (m, 1H), 7.49 – 7.45 (m, 1H), 7.37 – 7.31 (m, 1H), 3.98 (qd, *J* = 9.8, 4.7 Hz, 2H), 3.29 – 3.13 (m, 2H), 2.81 (ddt, *J* = 7.8, 5.3, 3.9 Hz, 1H), 0.74 (s, 9H), -0.00 (d, *J* = 17.3 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 207.30 (s), 154.75 (s), 137.26 (s), 134.60 (s), 127.05 (s), 126.46 (s), 123.56 (s), 62.91 (s), 49.92 (s), 30.02 (s), 25.63 (s), 18.06 (s), -5.52 (s), -5.59 (s). **IR:** ν 2953.84, 2928.38, 2864.64, 1715.48, 1610.30, 1464.40, 1255.08, 1113.41, 1041.33, 982.48, 836.85, 777.34 cm^{-1}. **HRMS** calcd. for $C_{16}H_{25}O_2Si^+$ $[M+H]^+$: 277.1624, Found: 277.1624.



(*E*)-2-ethylidene-2,3-dihydro-1H-inden-1-one

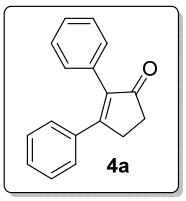
2o was obtained as a light yellow oil (8.8 mg) in 28% yield following a similar procedure as *General procedure F* from **1o** (0.2 mmol, 1 *equiv*, 31.7 mg), $[Rh(COD)Cl]_2$ (0.01 mmol, 0.05 *equiv*, 4.9 mg) and dppp (0.024 mmol, 0.12 *equiv*, 9.9 mg) under 130°C instead of 90°C: $\mathbf{R_f}$ = 0.42 (Hexane : EtOAc = 5 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 7.7, 0.4 Hz, 1H), 7.59 (td, *J* = 7.5, 1.2 Hz, 1H), 7.53 – 7.49 (m, 1H), 7.43 – 7.37 (m, 1H), 6.96 (qt, *J* = 7.1, 2.2 Hz, 1H), 3.67 (s, 2H), 1.98 (dt, *J* = 7.2, 1.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.21 (s), 149.25 (s), 138.86 (s), 137.46 (s), 134.37 (s), 133.09 (s), 127.43 (s), 126.29 (s), 124.34 (s), 29.81 (s), 15.39 (s). **IR:** ν 2916.74, 1704.21, 1653.50, 1609.37, 1466.10, 1322.50, 1295.10, 1265.72, 1093.16, 900.78, 735.64 cm^{-1}. **HRMS** calcd. for

$C_{11}H_{11}O^+$ $[M+H]^+$: 159.0810, Found: 159.0809.



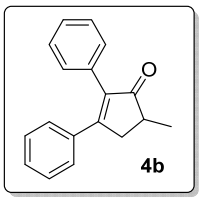
General procedure G

To a flame-dried 8 mL vial equipped with stir-bar was added **3a** (0.2 mmol, 1 *equiv*, 44.0 mg), $[Rh(COD)OH]_2$ (0.01 mmol, 0.05 *equiv*, 4.6 mg) and dppb (0.024 mmol, 0.12 *equiv*, 10.2 mg). The vial was then transferred into a nitrogen-filled glovebox. Ethyl benzene (2 mL) was added, and the vial was sealed and stirred at a pre-heated pie-block at 110°C for 48h. The reaction solution was directly loaded on column chromatography on silica gel to afford 41.6 mg **4a** as a light yellow solid in 95% yield.



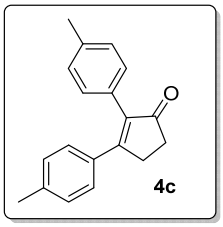
2,3-diphenylcyclopent-2-en-1-one

4a: $\mathbf{R_f}$ = 0.3 (Hexane : EtOAc = 5 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.24 (m, 8H), 7.22 – 7.18 (m, 2H), 3.07 – 3.02 (m, 2H), 2.72 – 2.67 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 207.58 (s), 168.02 (s), 139.92 (s), 135.71 (s), 132.32 (s), 129.83 (s), 129.46 (s), 128.47 (s), 128.43 (s), 128.08 (s), 127.84 (s), 34.82 (s), 29.55 (s). **IR:** ν 3054.61, 2922.45, 2853.07, 1698.62, 1622.18, 1593.79, 1490.10, 1444.57, 1351.34, 1296.90, 1222.06, 1159.90, 1081.10, 1042.48, 932.29, 760.43, 696.88, 637.69, 574.02, 558.79, 485.60 cm^{-1}. **HRMS** calcd. for $C_{17}H_{14}ONa^+$ $[M+Na]^+$: 257.0937, Found: 257.0937. All data match the literature reported ones[12].



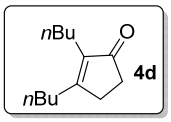
5-methyl-2,3-diphenylcyclopent-2-en-1-one

4b was obtained as a light yellow oil (28.9 mg) in 58% yield (80% brsm) following a similar procedure as *General procedure G* from **3b** (0.2 mmol, 1 *equiv*, 49.7 mg), $[Rh(COD)OH]_2$ (0.01 mmol, 0.05 *equiv*, 4.6 mg) and dppb (0.024 mmol, 0.12 *equiv*, 10.2 mg): $\mathbf{R_f}$ = 0.5 (Hexane : EtOAc = 5 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.23 (m, 8H), 7.22 – 7.19 (m, 2H), 3.28 (dd, *J* = 17.9, 6.8 Hz, 1H), 2.74 – 2.61 (m, 2H), 1.34 (d, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 209.98 (s), 166.11 (s), 138.58 (s), 135.69 (s), 132.43 (s), 129.75 (s), 129.48 (s), 128.40 (s), 128.38 (s), 128.11 (s), 127.76 (s), 40.15 (s), 38.65 (s), 16.81 (s). **IR:** ν 3054.35, 2963.07, 2928.36, 2870.42, 1697.71, 1620.58, 1488.96, 1443.83, 1350.59, 1158.15, 760.99, 735.74, 695.94 cm^{-1}. **HRMS** calcd. for $C_{18}H_{16}O$: 248.1201, Found: 248.1195.



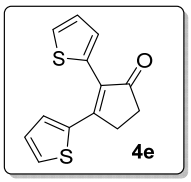
2,3-di-p-tolylcyclopent-2-en-1-one

4c was obtained as a light red solid (46.4 mg) in 88% yield (91% brsm) following a similar procedure as *General procedure G* from **3c** (0.2 mmol, 1 *equiv*, 52.5 mg), $[Rh(COD)OH]_2$ (0.01 mmol, 0.05 *equiv*, 4.6 mg) and dppb (0.024 mmol, 0.12 *equiv*, 10.2 mg): $\mathbf{R_f}$ = 0.4 (Hexane : EtOAc = 5 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 – 7.23 (m, 2H), 7.16 – 7.06 (m, 6H), 3.03 – 2.99 (m, 2H), 2.69 – 2.65 (m, 2H), 2.34 (s, 3H), 2.32 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 207.85 (s), 167.42 (s), 140.12 (s), 139.25 (s), 137.48 (s), 132.88 (s), 129.56 (s), 129.26 (s), 129.23 (s), 129.09 (s), 128.04 (s), 34.71 (s), 29.35 (s), 21.41 (s), 21.35 (s). **IR:** ν 3026.38, 2920.23, 1696.85, 1606.79, 1504.47, 1439.89, 1348.46, 1294.93, 1158.25, 1043.48, 928.07, 813.09, 721.84, 614.58, 497.90 cm^{-1}. **HRMS** calcd. for $C_{19}H_{18}O$: 262.1358, Found: 262.1358. **Mp(°C):** 119-121.



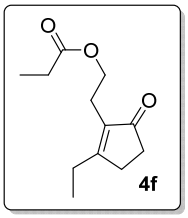
2,3-dibutylcyclopent-2-en-1-one

4d was obtained as a light yellow oil (29.9 mg) in 78% yield (87% brsm) following a similar procedure as *General procedure G* from **3d** (0.2 mmol, 1 *equiv*, 38.9 mg), $[Rh(COD)OH]_2$ (0.01 mmol, 0.05 *equiv*, 4.6 mg) and dppb (0.024 mmol, 0.12 *equiv*, 10.2 mg): $\mathbf{R_f}$ = 0.5 (Hexane : EtOAc = 5 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.48 – 2.43 (m, 2H), 2.41 – 2.35 (m, 2H), 2.34 – 2.30 (m, 2H), 2.13 (t, *J* = 7.1 Hz, 2H), 1.53 – 1.43 (m, 2H), 1.39 – 1.21 (m, 6H), 0.92 (t, *J* = 7.3 Hz, 3H), 0.86 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.46 (s), 174.36 (s), 140.68 (s), 34.49 (s), 31.16 (s), 31.06 (s), 29.90 (s), 29.21 (s), 23.11 (s), 23.04 (s), 23.02 (s), 14.15 (s), 14.12 (s). **IR:** ν 2956.97, 2931.09, 2860.61, 1699.54, 1639.82, 1474.96, 1367.72, 1209.36, 1169.79, 1085.42, 1041.88 cm^{-1}. **HRMS** calcd. for $C_{13}H_{22}ONa^+$ $[M+Na]^+$: 217.1563, Found: 217.1564.



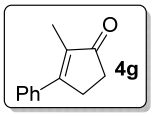
2,3-di(thiophen-2-yl)cyclopent-2-en-1-one\

4e was obtained as a brown solid (34.1 mg) in 68% yield (84% brsm) following a similar procedure as *General procedure G* from **3e** (0.2 mmol, 1 *equiv*, 49.3 mg), $[Rh(COD)OH]_2$ (0.01 mmol, 0.05 *equiv*, 4.6 mg) and dppb (0.024 mmol, 0.12 *equiv*, 10.2 mg): $\mathbf{R_f}$ = 0.5 (Hexane : EtOAc = 3 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.47 (dd, *J* = 2.6, 1.1 Hz, 1H), 7.46 – 7.45 (m, 1H), 7.14 (dd, *J* = 5.1, 3.5 Hz, 1H), 7.11 (dd, *J* = 3.5, 1.2 Hz, 1H), 7.06 (dd, *J* = 4.9, 3.9 Hz, 1H), 3.17 – 3.12 (m, 2H), 2.73 – 2.68 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 206.07 (s), 161.84 (s), 137.94 (s), 131.83 (s), 131.51 (s), 131.18 (s), 129.93 (s), 128.46 (s), 127.76 (s), 127.49 (s), 127.34 (s), 34.03 (s), 29.21 (s). **IR:** ν 3099.23, 2920.00, 1693.45, 1604.78, 1523.29, 1430.93, 1416.86, 1366.56, 1322.72, 1292.66, 1201.57, 1121.39, 847.93, 704.63 cm^{-1}. **HRMS** calcd. for $C_{13}H_{10}OS_2$: 246.0173, Found: 246.0172. **Mp(°C):** turned black at 133.



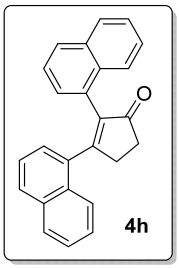
2-(2-ethyl-5-oxocyclopent-1-en-1-yl)ethyl propionate

4f was obtained as a brown oil (29.0 mg) in 69% yield following a similar procedure as *General procedure G* from **3f** (0.2 mmol, 1 *equiv*, 42.1 mg), $[Rh(COD)OH]_2$ (0.01 mmol, 0.05 *equiv*, 4.6 mg) and dppb (0.024 mmol, 0.12 *equiv*, 10.2 mg): $\mathbf{R_f}$ = 0.15 (Hexane : EtOAc = 5 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.08 – 4.02 (m, 2H), 2.53 – 2.41 (m, 6H), 2.37 – 2.32 (m, 2H), 2.29 – 2.21 (m, 2H), 1.15 – 1.05 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 209.38 (s), 177.51 (s), 174.31 (s), 135.55 (s), 62.38 (s), 34.05 (s), 28.67 (s), 27.48 (s), 24.24 (s), 22.71 (s), 12.00 (s), 9.01 (s). **IR:** ν 2973.96, 2940.36, 1737.50, 1698.78, 1643.74, 1462.97, 1381.01, 1352.88, 1274.57, 1182.33, 1080.49, 1018.39 cm^{-1}. **HRMS** calcd. for $C_{12}H_{18}O_3Na^+$ $[M+Na]^+$: 233.1148, Found: 233.1150.



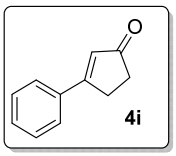
2-methyl-3-phenylcyclopent-2-en-1-one

4g was obtained as a light yellow oil (25.9 mg) in 78% yield following a similar procedure as *General procedure G* from **3g** (0.2 mmol, 1 *equiv*, 33.4 mg), $[Rh(COD)OH]_2$ (0.01 mmol, 0.05 *equiv*, 4.6 mg) and dppb (0.024 mmol, 0.12 *equiv*, 10.2 mg): $\mathbf{R_f}$ = 0.4 (Hexane : EtOAc = 5 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.48 (m, 2H), 7.47 – 7.37 (m, 3H), 2.93 – 2.87 (m, 2H), 2.55 – 2.50 (m, 2H), 1.94 (t, *J* = 2.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 209.85 (s), 166.58 (s), 136.49 (s), 136.37 (s), 129.45 (s), 128.59 (s), 127.53 (s), 33.99 (s), 29.23 (s), 9.91 (s). **IR:** ν 2921.10, 2856.01, 1697.94, 1624.49, 1494.99, 1445.39, 1378.54, 1346.23, 1300.09, 1225.19, 1098.74, 1075.98, 1056.95, 842.96, 762.84, 696.28, 607.67 cm^{-1}. **HRMS** calcd. for $C_{12}H_{12}ONa^+$ $[M+Na]^+$: 195.0780, Found: 195.0777.



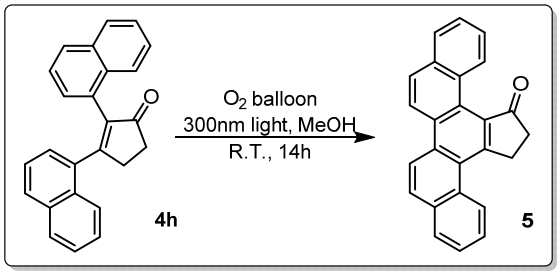
2,3-di(naphthalen-1-yl)cyclopent-2-en-1-one

4h was obtained as a yellow solid (59.0 mg) in 88% yield following a similar procedure as *General procedure G* from **3h** (0.2 mmol, 1 *equiv*, 66.9 mg), $[Rh(COD)OH]_2$ (0.01 mmol, 0.05 *equiv*, 4.6 mg) and dppb (0.024 mmol, 0.12 *equiv*, 10.2 mg): $\mathbf{R_f}$ = 0.2 (Hexane : EtOAc = 5 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.9 Hz, 1H), 7.75 – 7.66 (m, 4H), 7.60 (d, *J* = 8.2 Hz, 1H), 7.37 (ddd, *J* = 8.3, 4.3, 2.1 Hz, 3H), 7.32 – 7.26 (m, 2H), 7.25 – 7.22 (m, 1H), 7.15 (dd, *J* = 8.2, 7.1 Hz, 1H), 7.04 (dd, *J* = 7.1, 1.3 Hz, 1H), 3.28 (qdd, *J* = 19.0, 6.3, 3.4 Hz, 2H), 3.02 – 2.87 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 207.44 (s), 173.16 (s), 143.48 (s), 135.03 (s), 133.44 (s), 133.31 (s), 131.40 (s), 129.79 (s), 129.58 (s), 128.82 (s), 128.44 (s), 128.36 (s), 128.28 (s), 127.46 (s), 126.20 (s), 125.99 (s), 125.76 (s), 125.59 (s), 125.47 (s), 125.06 (s), 124.93 (s), 124.56 (s), 35.33 (s), 33.15 (s). **IR:** ν 3055.68, 2925.19, 1701.37, 1506.86, 1435.46, 1329.35, 1207.15, 1152.73, 1103.57, 799.21, 775.45, 733.71 cm^{-1}. **HRMS** calcd. for $C_{25}H_{18}O$: 334.1358, Found: 334.1357. **Mp(°C):** 206-208.



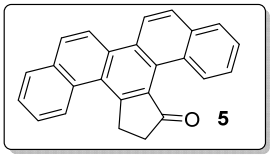
3-phenylcyclopent-2-en-1-one

4i was obtained as a light yellow oil (6.0 mg) in 19% yield following a similar procedure as *General procedure G* from **3i** (0.2 mmol, 1 *equiv*, 31.4 mg), $[Rh(COD)OH]_2$ (0.01 mmol, 0.05 *equiv*, 4.6 mg) and dppb (0.024 mmol, 0.12 *equiv*, 10.2 mg): $\mathbf{R_f}$ = 0.18 (Hexane : EtOAc = 5 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ7.68 – 7.64 (m, 2H), 7.49 – 7.43 (m, 3H), 6.58 (t, *J* = 1.8 Hz, 1H), 3.08 – 3.04 (m, 2H), 2.62 – 2.58 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 209.38 (s), 173.96 (s), 134.05 (s), 131.24 (s), 128.91 (s), 127.50 (s), 126.80 (s), 35.28 (s), 28.64 (s). **IR:** ν 2921.38, 1683.44, 1601.38, 1570.43, 1447.73, 1332.25, 1274.26, 1194.12, 878.14, 861.98, 760.69, 690.74 cm^{-1}. **HRMS** calcd. for $C_{11}H_{11}O^+$ $[M+H]^+$: 159.0810, Found: 159.0808.



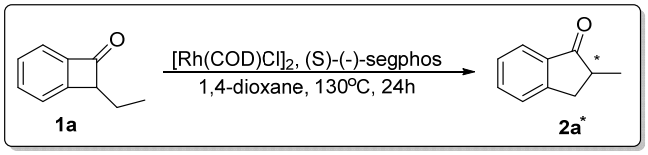
Synthesis of compound 5

A modified procedure was applied[13]: **4h** (0.073 mmol, 1 *equiv*, 24.4 mg) was dissolved in 4 mL MeOH in a quartz flask equipped with a magnetic stir-bar and an oxygen balloon. The flask was irradiated at 300 nm wavelength in a Rayonet reactor equipped with 8 lamps. After stirring at RT for 14 h, white precipitate was formed, and the reaction mixture was directly concentrated under vacuum to afford 17.1 mg **5** as a light yellow solid in 70% yield.



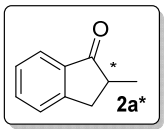
14,15-dihydro-13H-cyclopenta[s]picen-13-one

5: $\mathbf{R_f}$ = 0.4 (Hexane : EtOAc = 3 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.87 – 8.81 (m, 1H), 8.74 (d, *J* = 8.3 Hz, 1H), 8.52 (dd, *J* = 18.4, 9.2 Hz, 2H), 8.04 – 7.91 (m, 4H), 7.76 – 7.62 (m, 4H), 3.85 – 3.78 (m, 2H), 2.90 – 2.82 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.02 (s), 156.15 (s), 133.63 (s), 132.99 (s), 132.91 (s), 131.97 (s), 131.26 (s), 130.99 (s), 130.71 (s), 129.28 (s), 128.87 (s), 128.54 (s), 128.14 (s), 127.44 (s), 127.34 (s), 126.98 (s), 126.70 (s), 126.52 (s), 126.36 (s), 124.90 (s), 121.72 (s), 120.61 (s), 36.65 (s), 30.60 (s). **IR:** ν 2923.51, 2852.19, 1692.83, 1514.63, 1462.41, 1332.22, 1275.37, 1259.53, 1130.44, 1069.50, 1029.04, 907.23, 801.86, 743.30 cm^{-1}. **HRMS** calcd. for $C_{25}H_{16}ONa^+$ $[M+Na]^+$: 355.1093, Found: 355.1093. **Mp(°C):** 215-218.



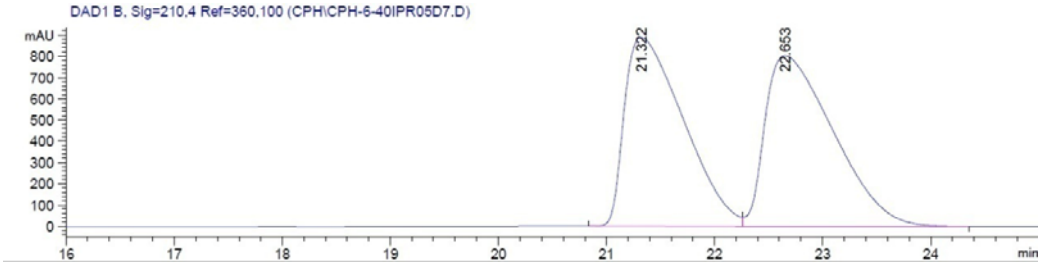
General Procedure H

To a flame-dried 4 mL vial equipped with stir-bar was added **1a** (0.1 mmol, 1 *equiv*, 14.6 mg), $[Rh(COD)Cl]_2$ (0.005 mmol, 0.05 *equiv*, 2.5 mg) and (S)-(-)-segphos (0.012 mmol, 0.12 *equiv*, 7.3 mg) and was transferred into a nitrogen-filled glovebox via standard glovebox technique. 1, 4-dioxane (1 mL) was added, and the vial was sealed and stirred in a pre-heated pie-block at 130°C for 24h. The reaction solution was concentrated under vacuum and directed purified via column chromatography on silica gel to afford 4.5 mg of **2a** as colorless oil in 31% yield. After that, all the product was dissolved in 1 mL of MeOH, and *ee* value was measured by HPLC to be 49%.



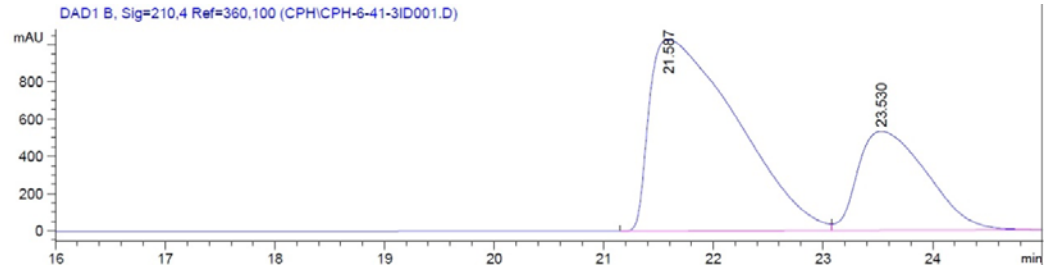
Chiral HPLC (Chiralpak ID, hexane : isopropanol = 99.5 : 0.5, 1 mL/min, 210.4 nm) : t_{minor} = 17.71 min, t_{major} = 18.67 min.

Racemic spectrum

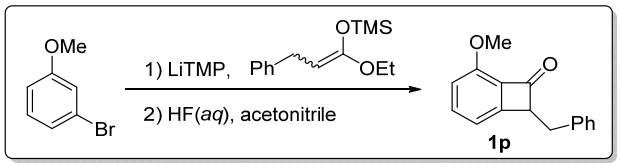


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.322	BV	0.6133	3.36338e4	889.09198	48.7937
2	22.653	VB	0.7026	3.52968e4	803.31305	51.2063

Enantiomeric spectrum

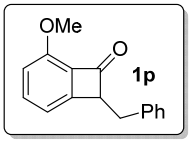


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.587	BV	0.7941	5.69334e4	1031.17004	71.0036
2	23.530	VB	0.7333	2.32504e4	532.60626	28.9964



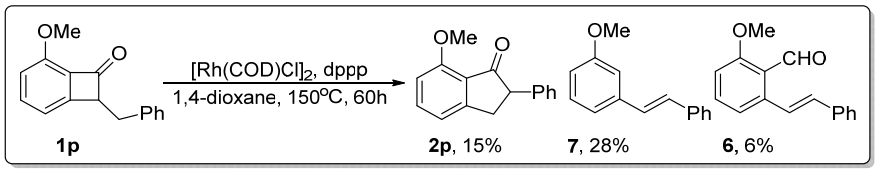
Preparation of 1p

A modified procedure[2] was applied: To a 50 mL flamed-dried flask equipped with a stir bar and a nitrogen-filled ballon were added 2,2,6,6-tetramethylpiperidine (7.5 mmol, 1.5 *equiv*, 1.06 g, 1.28 mL) and THF (20 mL). After cooled to 0°C with an ice-water bath, *n*-BuLi (2.5M in hexane, 1.2 *equiv*, 3 mL) was added dropwise and the rection was stirred at 0°C for 0.5h. To a 100 mL flame-dried flask equipped with a stir bar and a nitrogen-filled balloon were added THF (20 mL), 3-bromoanisole (5 mmol, 1 *equiv*, 935.2 mg, 633 μL) and ((1-ethoxy-3-phenylprop-1-en-1-yl)oxy)trimethylsilane[14] (8.5 mmol, 1.5 *equiv*, 2.13 g) and was cooled to –78 °C with an acetone-dry ice bath before *in situ* generated lithium tetramethylpiperidide was added dropwise. The reaction was then monitored and aqueous NH_4Cl was added upon disappearance of the benzyne precursor. After warming to RT, the reaction mixture was extracted with ethyl acetate (30 mL × 3), washed with brine and concentrated under reduced pressure. Acetonitrile (30 mL) was added to the concentrated reaction system and cooled to 0°C with an ice-water bath followed by slow addition of hydrofluoric acid (27.6 M in H_2O, 50 mmol, 10 *equiv*, 1.8 mL). The reaction was then heated to 40 °C for overnight before water (100 mL) was added. The mixture was extracted with ethyl acetate (30 mL × 3), washed with brine and dried over Na_2SO_4. The combined organic extract was concentrated under reduced pressure and purified by column chromatography on silica gel to afford **1p** (357.4 mg) as light yellow oil in 30% yield.



8-benzyl-5-methoxybicyclo[4.2.0]octa-1,3,5-trien-7-one

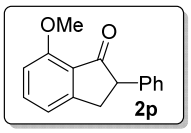
1p: $\mathbf{R_f}$ = 0.58 (Hexane : EtOAc = 10 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 3H), 7.25 – 7.20 (m, 3H), 6.78 (d, *J* = 8.4 Hz, 1H), 6.70 (d, *J* = 7.1 Hz, 1H), 4.41 (dd, *J* = 9.7, 5.5 Hz, 1H), 4.09 (s, 3H), 3.33 (dd, *J* = 14.0, 5.4 Hz, 1H), 2.93 (dd, *J* = 14.0, 9.7 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 187.73 (s), 155.36 (s), 153.72 (s), 138.71 (s), 137.56 (s), 131.01 (s), 128.97 (s), 128.48 (s), 126.43 (s), 116.24 (s), 115.17 (s), 64.66 (s), 59.75 (s), 36.45 (s). **IR:** ν 3063.02,, 3027.27, 2981.30, 2938.46, 2846.34, 1762.46, 1604.21, 1573.57, 1495.66, 1483.37, 1453.88, 1435.06, 1278.22, 1123.27, 1095.60, 1018.40, 791.83, 707.73 cm^{-1}. **HRMS** calcd. for $C_{16}H_{14}O_2Na^+$ $[M+Na]^+$: 261.0886, Found: 261.0885.



Ring Expansion of 1p

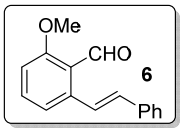
To a flame-dried 4 mL vial equipped with a stir-bar was added **1p** (0.1 mmol, 1 *equiv*, 23.8 mg), $[Rh(COD)Cl]_2$ (0.005 mmol, 0.05 *equiv*, 2.5 mg) and dppp (0.012 mmol, 0.12 *equiv*, 5.0 mg). The vial was then transferred into a nitrogen-filled glovebox. 1, 4-dioxane (1 mL) was added, and the vial was sealed and stirred in a pre-heated pie-block at 150°C for 60h. The reaction solution was concentrated

under vacuum and purified by preparative TCL on silica gel to afford 3.5 mg of **2p** as colorless oil in 15% yield, 5.9 mg of **6** as light yellow solid in 28% yield and 1.5 mg of **7** as a light yellow solid in 6% yield.



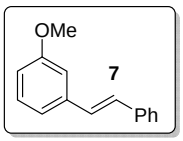
7-methoxy-2-phenyl-2,3-dihydro-1H-inden-1-one

2p: $\mathbf{R_f}$ = 0.08 (Hexane : EtOAc = 10 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 8.1, 7.6 Hz, 1H), 7.33 – 7.17 (m, 5H), 7.06 (dd, *J* = 7.5, 0.7 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 3.95 (s, 3H), 3.87 (dd, *J* = 8.4, 3.9 Hz, 1H), 3.62 (dd, *J* = 17.5, 8.4 Hz, 1H), 3.20 (dd, *J* = 17.5, 3.9 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 203.49 (s), 158.57 (s), 156.25 (s), 140.00 (s), 136.70 (s), 128.67 (s), 127.82 (s), 126.82 (s), 124.33 (s), 118.08 (s), 109.18 (s), 55.74 (s), 53.58 (s), 35.47 (s). **IR:** ν 2926.28, 1708.68, 1595.50, 1479.99, 1292.71, 1279.45, 1229.67, 1197.63, 1084.91, 1066.59, 1008.14, 997.42, 776.06, 704.77 cm^{-1}. **HRMS** calcd. for $C_{16}H_{14}O_2Na^+$ $[M+Na]^+$: 261.0886, Found: 261.0886.



(*E*)-2-methoxy-6-styrylbenzaldehyde

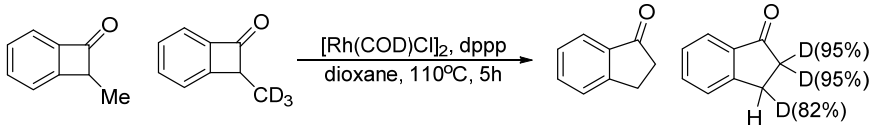
6: $\mathbf{R_f}$ = 0.33 (Hexane : EtOAc = 10 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.69 (d, *J* = 0.6 Hz, 1H), 8.08 (d, *J* = 16.2 Hz, 1H), 7.59 – 7.54 (m, 2H), 7.53 – 7.47 (m, 1H), 7.39 – 7.33 (m, 2H), 7.32 – 7.26 (m, 2H), 7.04 (d, *J* = 16.2 Hz, 1H), 6.92 (dd, *J* = 8.3, 0.6 Hz, 1H), 3.93 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 192.34 (s), 162.93 (s), 140.51 (s), 137.23 (s), 134.56 (s), 132.64 (s), 128.62 (s), 127.94 (s), 127.12 (s), 126.99 (s), 122.03 (s), 119.26 (s), 110.14 (s), 55.90 (s). **HRMS** calcd. for $C_{16}H_{14}O_2Na^+$ $[M+Na]^+$: 261.0886, Found: 261.0884. All data match the literature reported ones[15].



(*E*)-1-methoxy-3-styrylbenzene

7: $\mathbf{R_f}$ = 0.64 (Hexane : EtOAc = 10 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 – 7.50 (m, 2H), 7.39 – 7.34 (m, 2H), 7.31 – 7.24 (m, 2H), 7.14 – 7.11 (m, 1H), 7.10 (d, *J* = 1.7 Hz, 2H), 7.07 – 7.05 (m, 1H), 6.83 (ddd, *J* = 8.2, 2.6, 0.9 Hz, 1H), 3.86 (s, 3H). **IR:** ν 3058.09, 3026.28, 2936.37, 2833.73, 1598.78, 1580.23, 1495.67, 1451.96, 1272.75, 1255.73, 1153.90, 1047.66, 959.42, 775.13, 749.48, 692.52 cm^{-1}. **HRMS** calcd. for $C_{15}H_{14}O$: 210.1045, Found: 210.1045. All data match the literature reported ones[16].

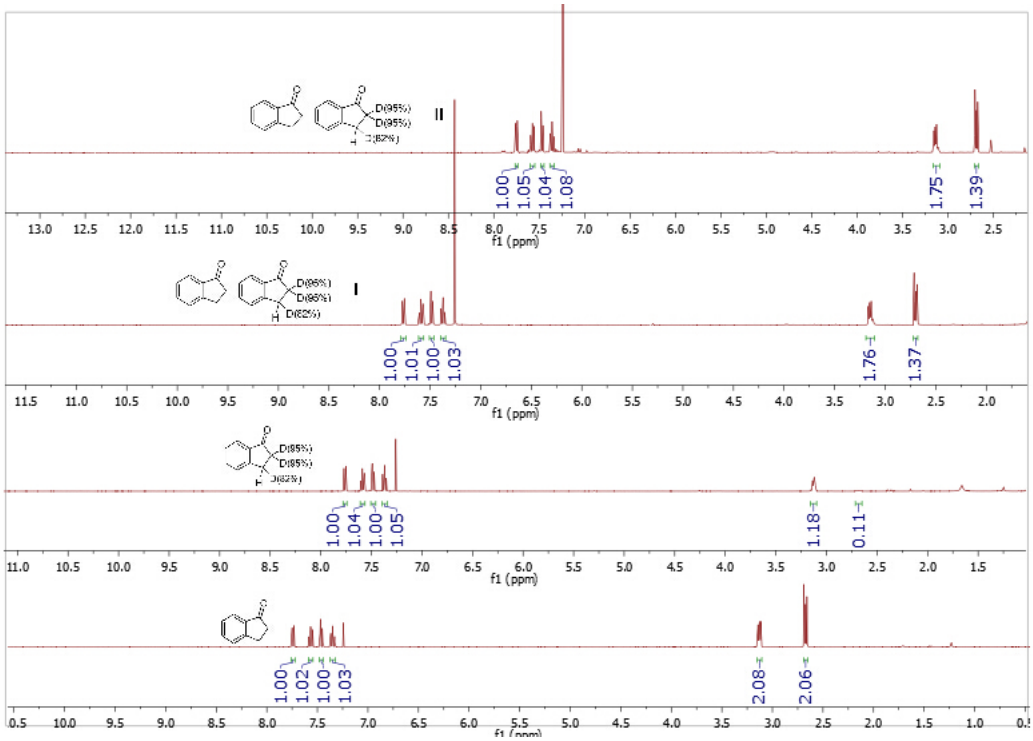
3. Calculation of KIE



1c **1c-3D** **2c** **2c-3D**

Two same reactions were run in parallel. The average of the results was used to calculate the KIE. To a flame-dried 8 mL vial equipped with stir-bar was added **1c** (0.144 mmol, 1 *equiv*, 19.4 mg), **1c-3D** (0.144 mmol, 1 *equiv*, 19.6 mg), $[Rh(COD)Cl]_2$ (0.0144 mmol, 0.1 *equiv*, 7.1 mg) and dppp (0.0343 mmol, 0.24 *equiv*, 14.16 mg). The vial was then transferred into a nitrogen-filled glovebox. 1,

4-dioxane (2.9 mL) was added, and the vial was sealed and stirred in a pre-heated pie-block at 110°C for 5 h. The reaction solution was concentrated under vacuum and purified by column chromatography on silica gel to afford 2.6 mg mixture of **2c** and **2c-3D**. The ^{1}H spectrum (marked as **I**) of the mixture was taken. Another reaction was set up with **1c** (0.156 mmol, 1 *equiv*, 21.1 mg), **1c-3D** (0.156 mmol, 1 *equiv*, 20.6 mg), $[Rh(COD)Cl]_2$ (0.0156 mmol, 0.1 *equiv*, 7.7 mg) and dppp (0.0374 mmol, 0.24 *equiv*, 15.43 mg) in 1,4-dioxane (3.1 mL), and 5 mg mixture of **2c** and **2c-3D** was obtained. The ^{1}H spectrum of the mixture (marked as **II**) was taken. The spectrum of **I**, **II**, **2c** and **2c-3D** were displayed below.



$$S_1 = \frac{M_{2i} \times S_{1,2i} + M_{2f} \times S_{1,2f}}{M_{2i} + M_{2f}}, S_2 = \frac{M_{2i} \times S_{2,2i} + M_{2f} \times S_{2,2f}}{M_{2i} + M_{2f}}$$

$$KIE = \frac{M_{2i}}{M_{2f}} = \frac{S_{1,2f} - S_1}{S_1 - S_{1,2i}} = \frac{S_{2,2f} - S_2}{S_2 - S_{2,2i}}$$

$$S_{1,2i} = 2.08, S_{2,2i} = 2.06, S_{1,2f} = 1.18, S_{2,2f} = 0.11$$

$$S_{1,\mathrm{I}} = 1.76, S_{2,\mathrm{I}} = 1.37, S_{1,\mathrm{II}} = 1.75, S_{2,\mathrm{II}} = 1.39$$

With this information, we can calculate that

$$KIE_{1,\mathrm{I}} = \frac{1.18 - 1.76}{1.76 - 2.08} = 1.81, KIE_{2,\mathrm{I}} = \frac{0.11 - 1.37}{1.37 - 2.06} = 1.83, KIE_{\mathrm{I}} = (KIE_{1,\mathrm{I}} + KIE_{2,\mathrm{I}})/2 = 1.82$$

$$KIE_{1,\mathrm{II}} = \frac{1.18 - 1.75}{1.75 - 2.08} = 1.73, KIE_{2,\mathrm{II}} = \frac{0.11 - 1.39}{1.39 - 2.06} = 1.91, KIE_{\mathrm{II}} = (KIE_{1,\mathrm{II}} + KIE_{2,\mathrm{II}})/2 = 1.82$$

$$ave(KIE) = (KIE_{\mathrm{I}} + KIE_{\mathrm{II}})/2 = 1.82$$

4. References

(1) For a concise synthesis via [2+2] with ketene silyl acetal and 2-Iodophenyl triflate as benzyne precursor, see: X.-F. Fu, Y. Xiang, Z.-X. Yu, *Chem. Eur. J.* 2015, **21**, 4242.

(2) For a recent report on [2+2] with ketene silyl acetal and 3-bromoanisole as benzyne precursor, see: P.-H. Chen, N. A. Savage, G. Dong, *Tetrahedron*, 2014, **70**, 4135.

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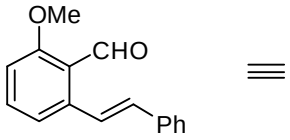
(15) I. R. Girling, D. A. Widdowson, *J. Chem. Soc., Perkin Trans. 1*, 1988, 1317.
(16) J.-Y. Yu, R. Shimizu, R. Kuwano, *Angew. Chem. Int. Ed.* 2010, **49**, 6396.

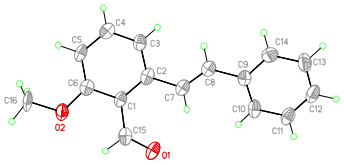
5. X-Ray Data

X-Ray data for **6**.

View of **6** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level.



≡



Crystal data and structure refinement for **6**.

Empirical formula	C16 H14 O2	
Formula weight	238.27	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 6.4697(18) Å	α= 90°.
	b = 8.331(2) Å	β= 97.669(13)°.
	c = 23.081(5) Å	γ = 90°.
Volume	1232.9(5) $Å^3$	
Z	4	
Density (calculated)	1.284 Mg/m^3	

Absorption coefficient	0.084 mm^{-1}
F(000)	504
Crystal size	0.13 x 0.06 x 0.06 mm
Theta range for data collection	0.890 to 25.228°.
Index ranges	-7<=h<=7, -9<=k<=9, -26<=l<=27
Reflections collected	16388
Independent reflections	2297 [R(int) = 0.1432]
Completeness to theta = 25.242°	100.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00 and 0.855
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2297 / 0 / 166
Goodness-of-fit on F^2	1.096
Final R indices [I>2sigma(I)]	R1 = 0.0848, wR2 = 0.1897
R indices (all data)	R1 = 0.1775, wR2 = 0.2369
Extinction coefficient	6.0(^{13})x10^{-5}
Largest diff. peak and hole	0.320 and -0.347 e.$Å^{-3}$

X-Ray data for **5**.

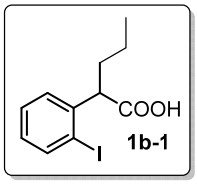
View of **5** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level.

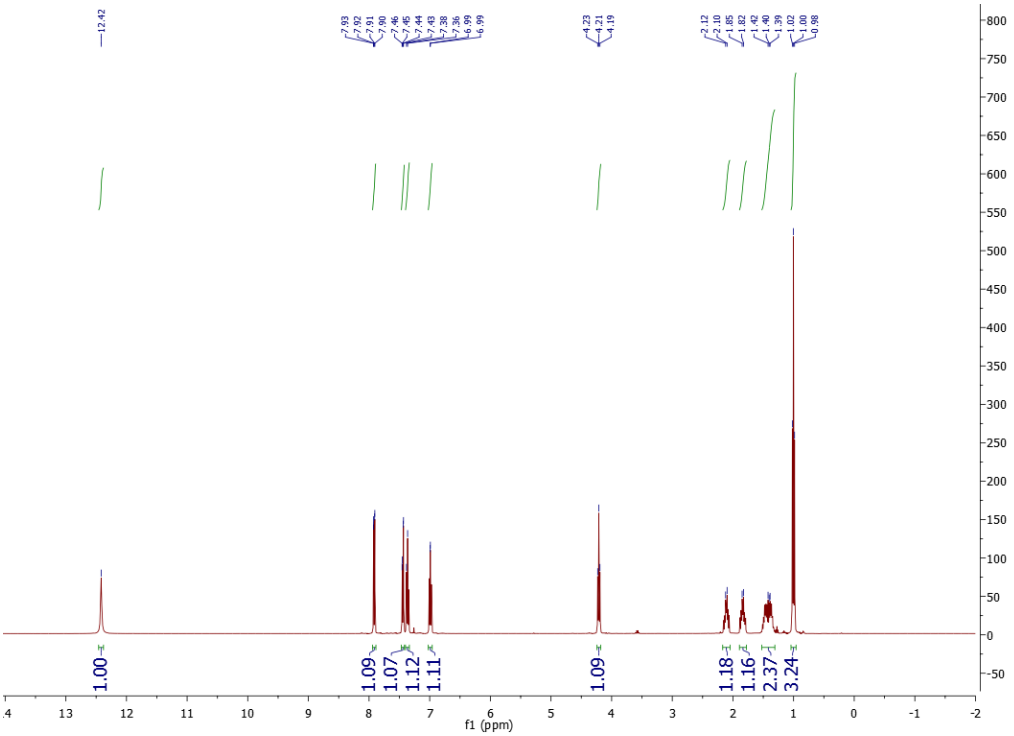
Crystal data and structure refinement for **5**.

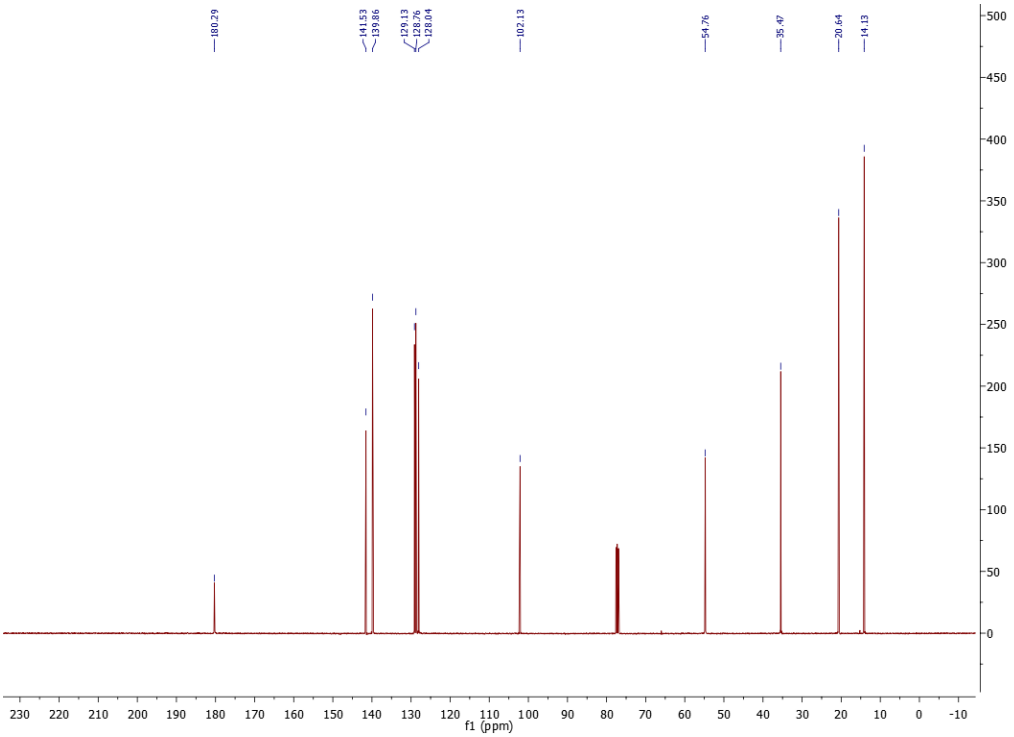
Empirical formula	C25 H16 O	
Formula weight	332.38	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P 21	
Unit cell dimensions	a = ^{13}.561(3) Å	α= 90°.
	b = 7.4573(17) Å	β= 106.496(12)°.
	c = 19.172(4) Å	γ = 90°.
Volume	1584.9(6) $Å^3$	

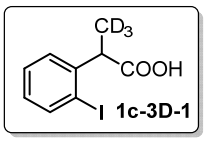
Z	4
Density (calculated)	1.393 Mg/m^3
Absorption coefficient	0.083 mm^{-1}
F(000)	696
Crystal size	0.460 x 0.300 x 0.060 mm
Theta range for data collection	1.837 to 27.496°.
Index ranges	-15<=h<=15, -9<=k<=9, -24<=l<=24
Reflections collected	22727
Independent reflections	7246 [R(int) = 0.0314]
Completeness to theta = 25.242°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00 and 0.870
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7246 / 1 / 501
Goodness-of-fit on F^2	1.005
Final R indices [I>2sigma(I)]	R1 = 0.0388, wR2 = 0.0997
R indices (all data)	R1 = 0.0416, wR2 = 0.1025
Absolute structure parameter	1.1(5)
Extinction coefficient	n/a
Largest diff. peak and hole	0.203 and -0.188 $e.Å^{-3}$

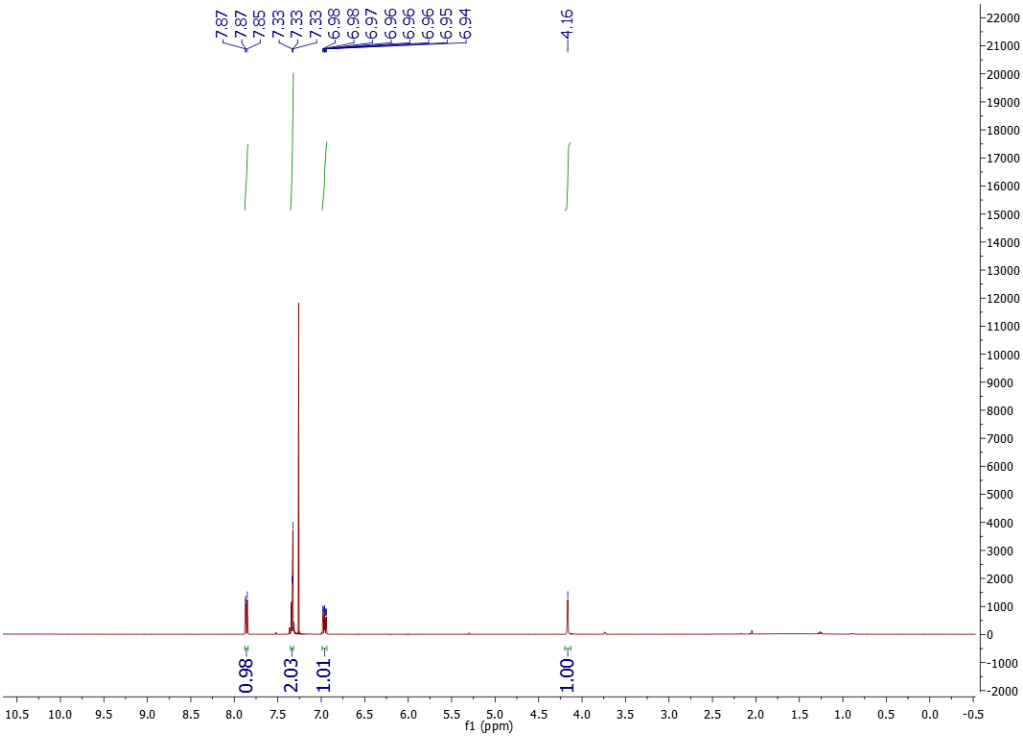
6. Spectra for all new compounds








CD3
COOH
I
1c-3D-1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7.87
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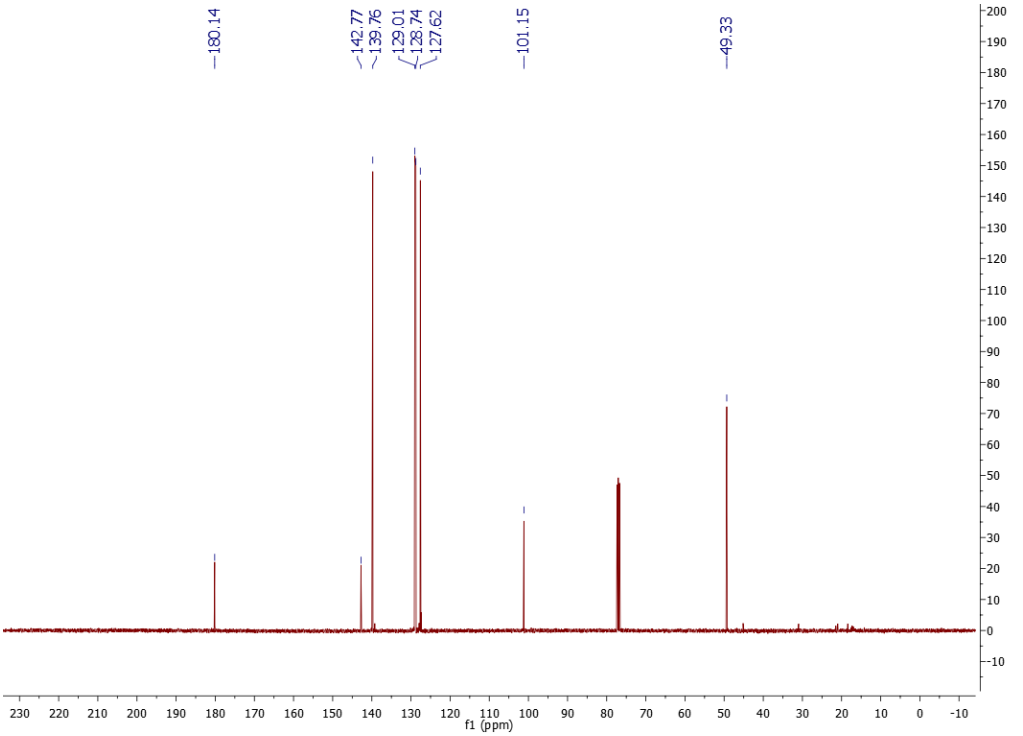
7.33
7.33
7.33
6.98
6.98
6.97
6.96
6.96
6.96
6.95
6.94
4.16
0.98
2.03
1.01
1.00
f1 (ppm)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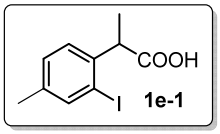
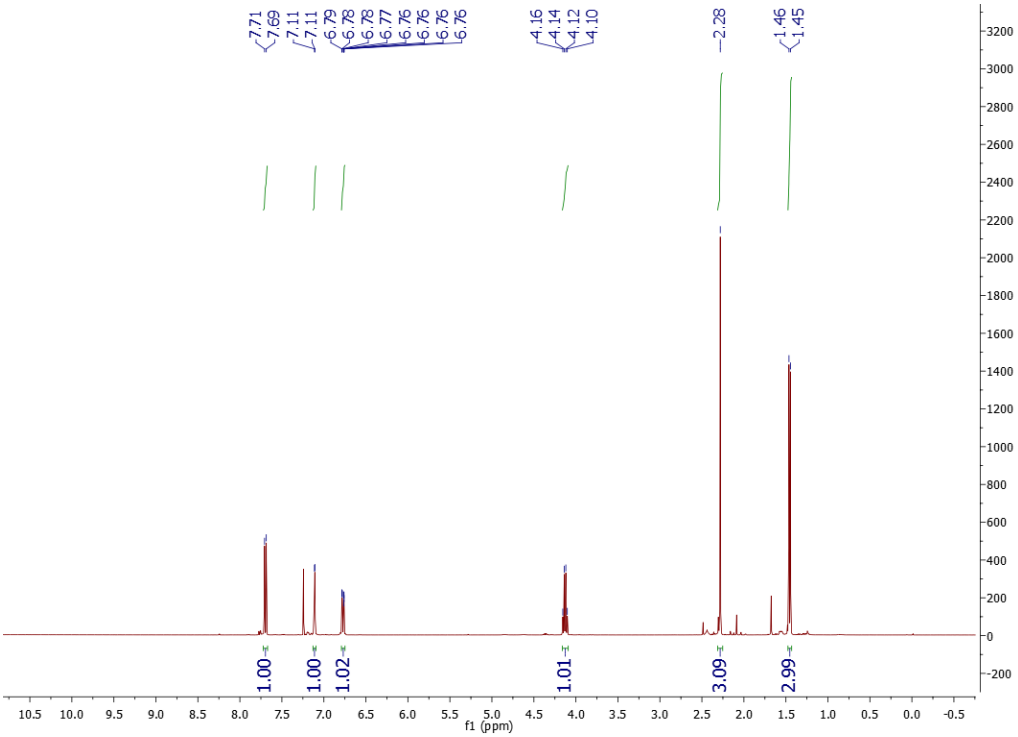
f1 (ppm)


COOH
I
1e-1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6.77
6.76
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6.76
6.76
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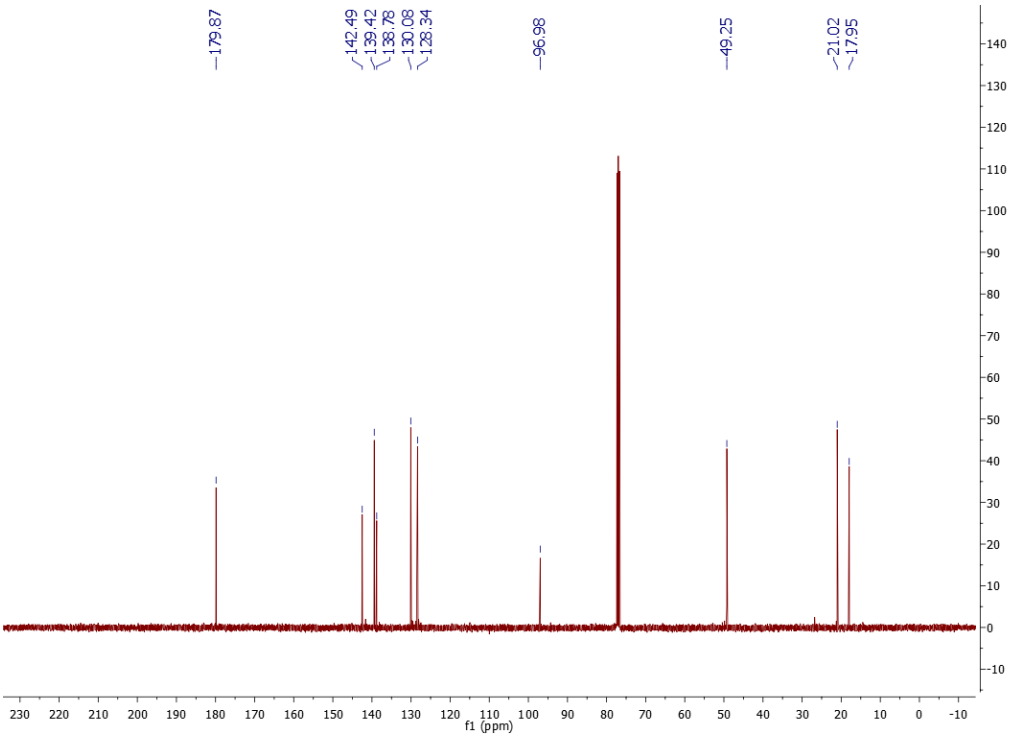
1.02
1.01
3.09
2.99
f1 (ppm)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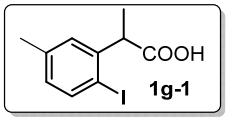
f1 (ppm)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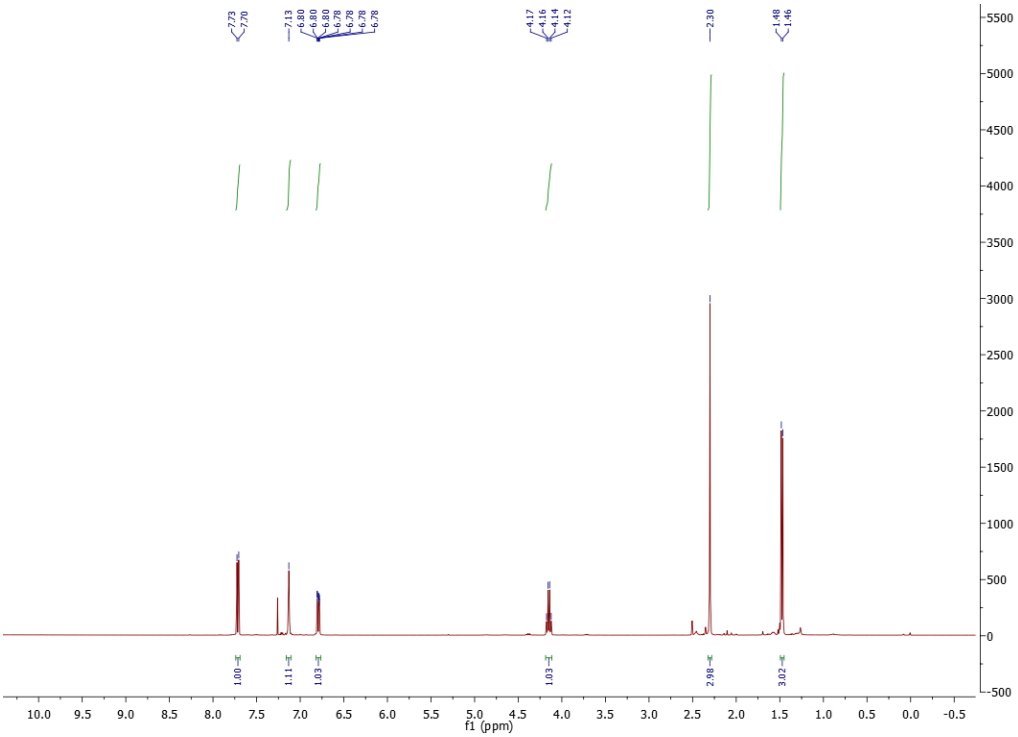
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6.78
6.78
6.78
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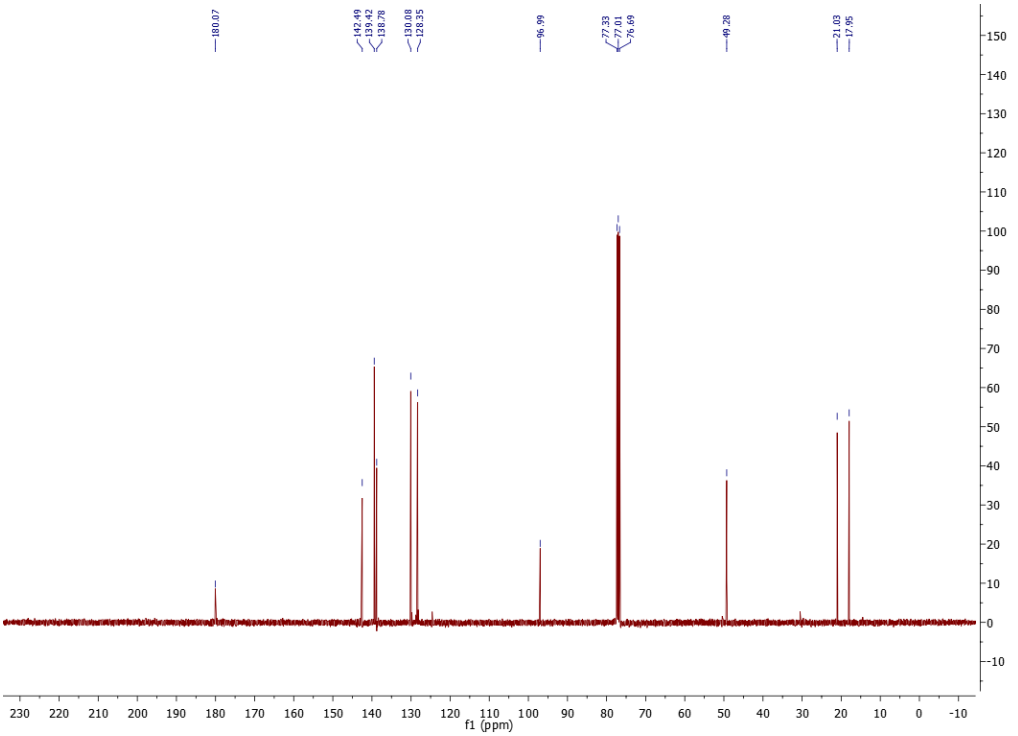
4.16
4.14
4.12
2.30
1.48
1.46
1.00
1.11
1.03
1.03
2.98
3.02
f1 (ppm)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142.49
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128.35
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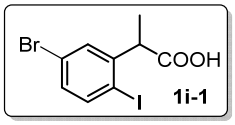
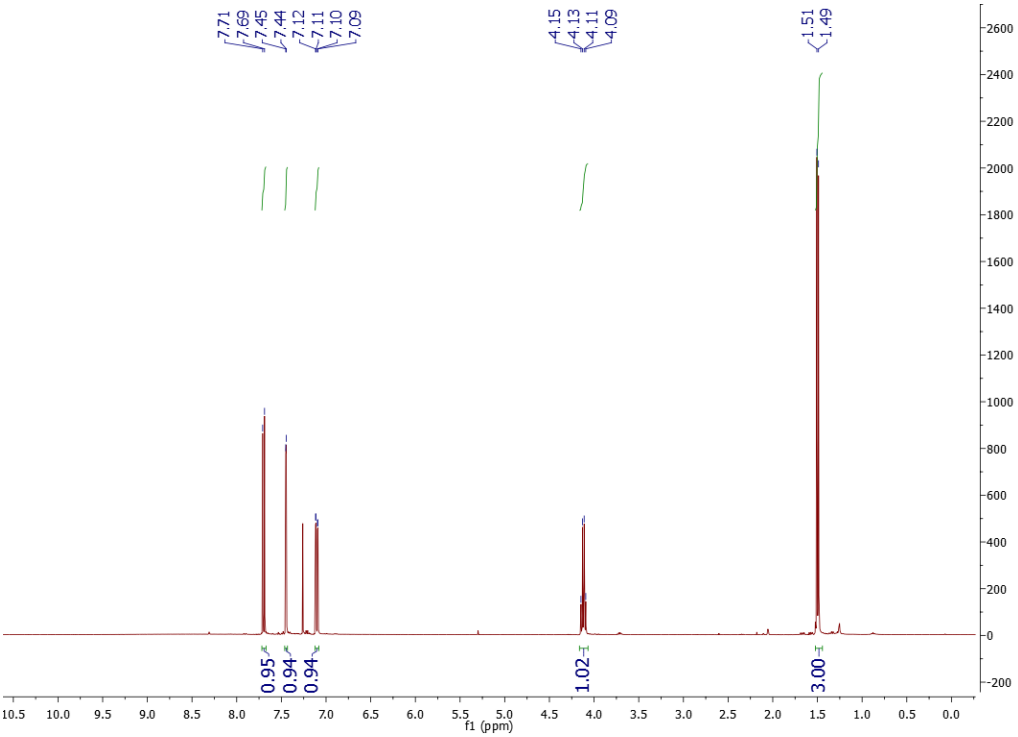
77.33
77.01
76.69
49.28
21.03
17.95
f1 (ppm)


Br
COOH
I
1i-1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7.69
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7.44
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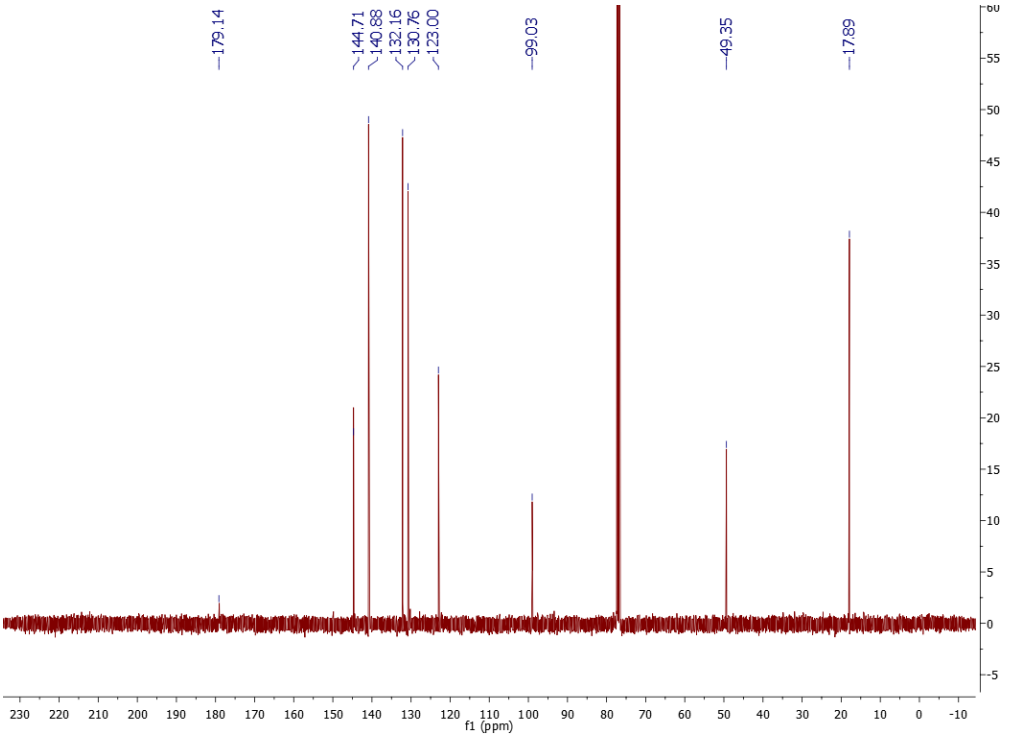
7.11
7.10
7.09
4.15
4.13
4.11
4.09
1.51
1.49
0.95
0.94
0.94
1.02
3.00
f1 (ppm)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144.71
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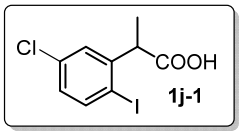
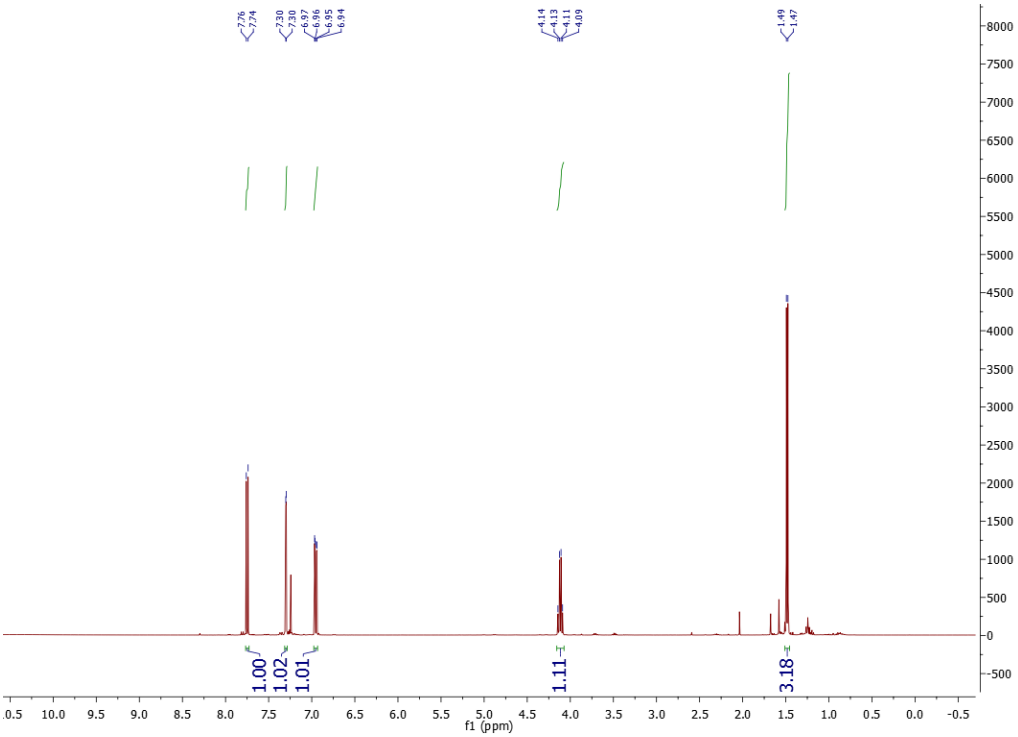
132.16
130.76
123.00
99.03
49.35
17.89
f1 (ppm)


Cl
COOH
I
1j-1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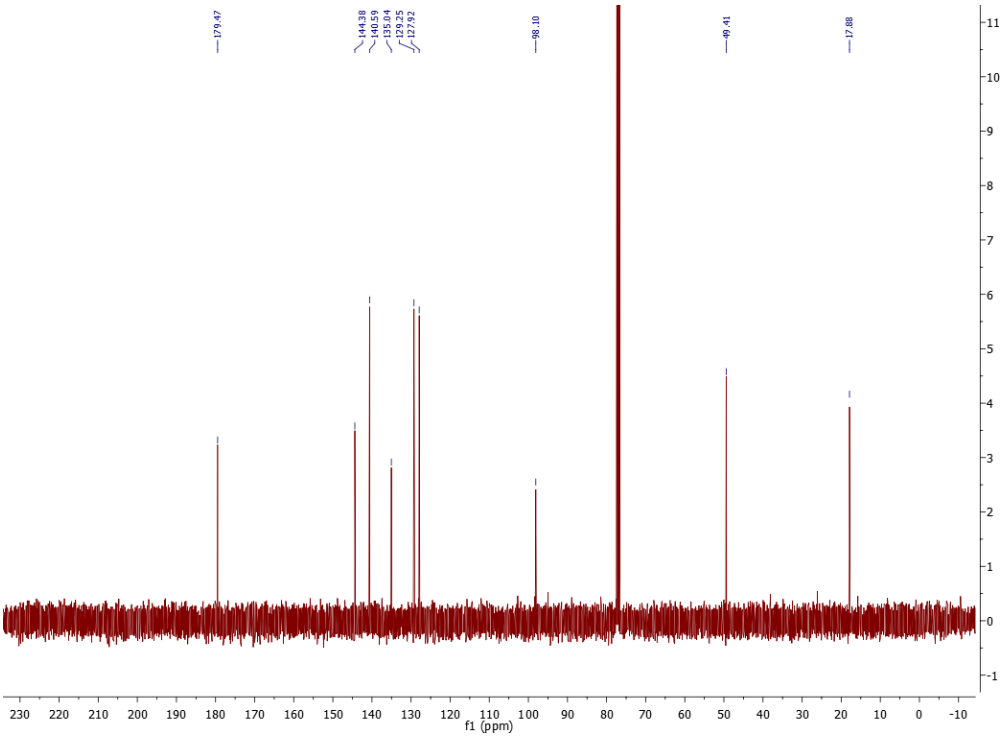
7.74
7.30
7.30
6.97
6.96
6.95
6.94
4.14
4.13
4.11
4.09
1.49
1.47
1.00
1.02
1.01
1.11
3.18
f1 (ppm)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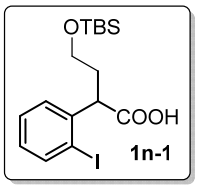
88.10
49.41
17.88
f1 (ppm)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COOH
I
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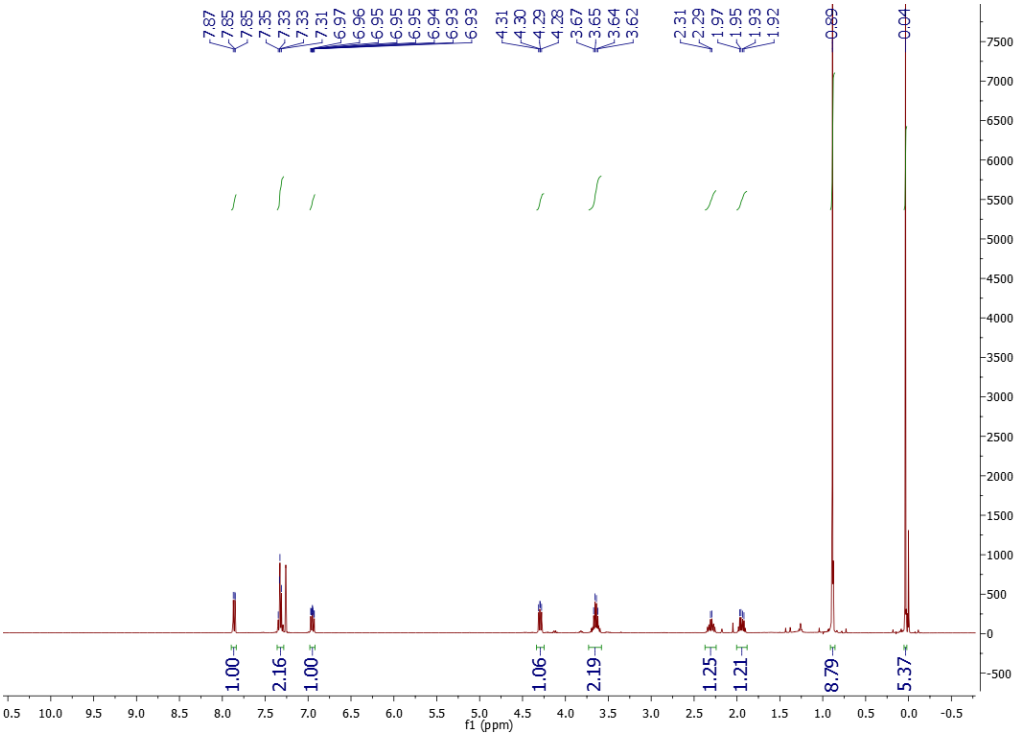
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7.85
7.35
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7.33
7.31
6.97
6.96
6.95
6.95
6.95
6.94
6.93
6.93
4.31
4.30
4.29
4.28
3.67
3.65
3.64
3.62
2.31
2.29
1.97
1.95
1.93
1.92
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0.04
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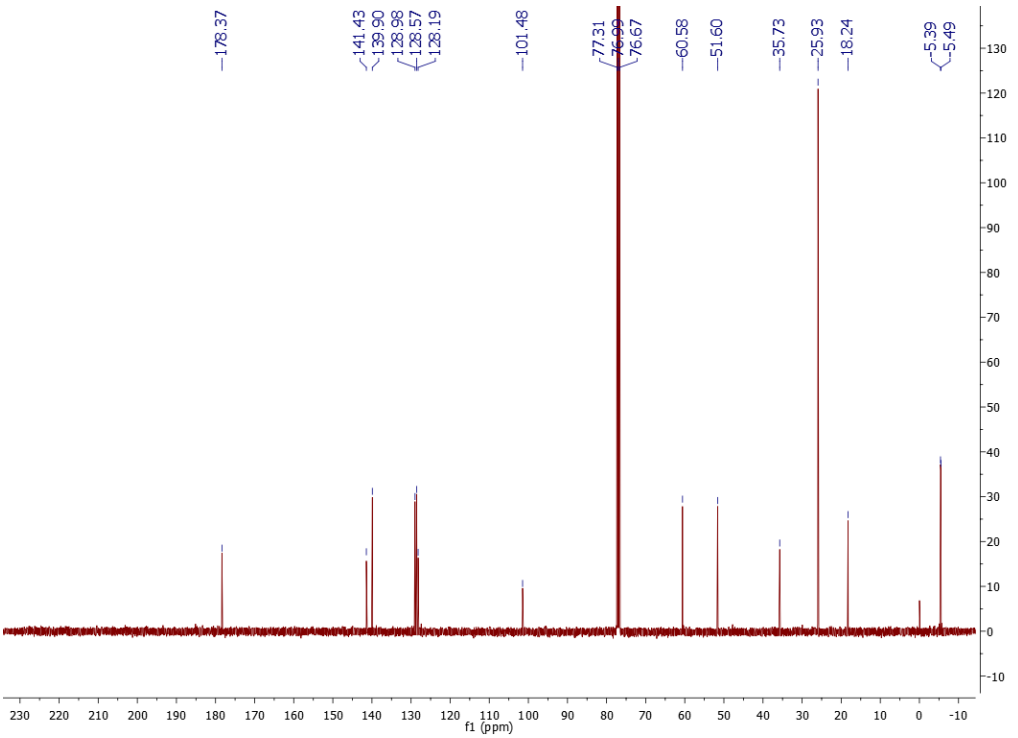
2.16
1.00
1.06
2.19
1.25
1.21
8.79
5.37
f1 (ppm)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141.43
139.90
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128.19
101.48
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76.67
60.58
51.60
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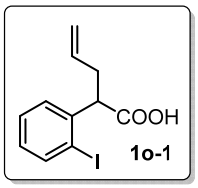
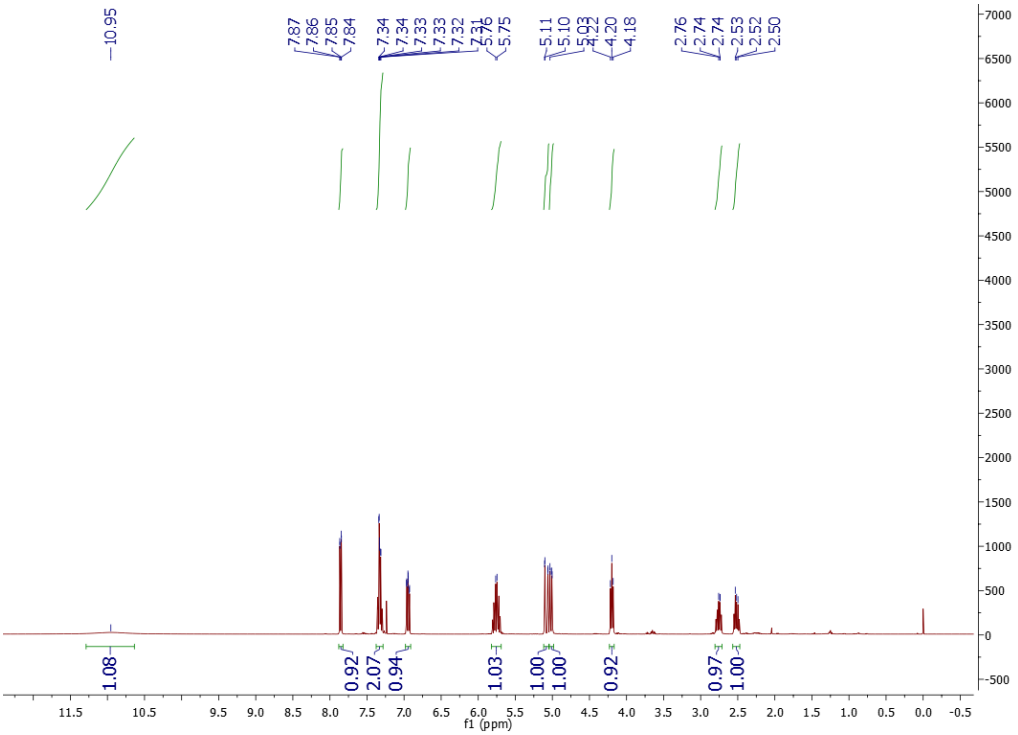
25.93
18.24
-5.39
-5.49
f1 (ppm)


COOH
I
1o-1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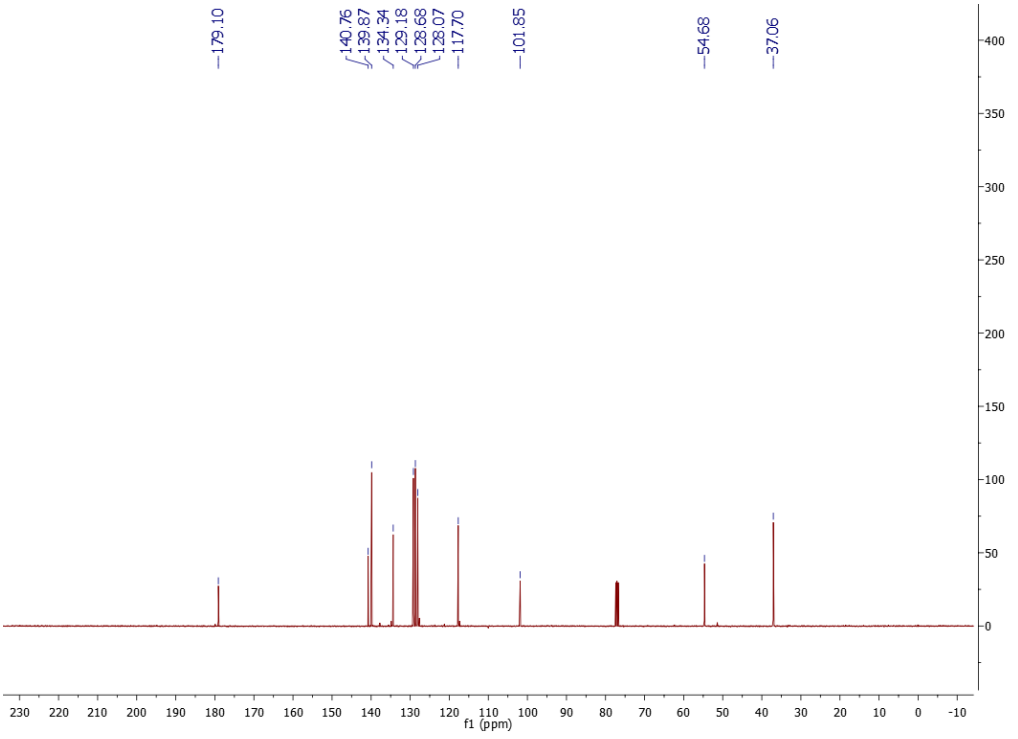
7.86
7.85
7.84
7.34
7.34
7.33
7.33
7.32
7.31
5.76
5.75
5.11
5.10
5.03
4.22
4.20
4.18
2.76
2.74
2.74
2.53
2.52
2.50
1.08
0.92
2.07
0.94
1.03
1.00
1.00
0.92
0.97
1.00
f1 (ppm)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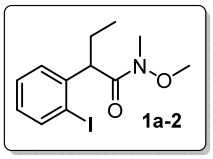
129.18
128.68
128.07
117.70
101.85
54.68
37.06
f1 (ppm)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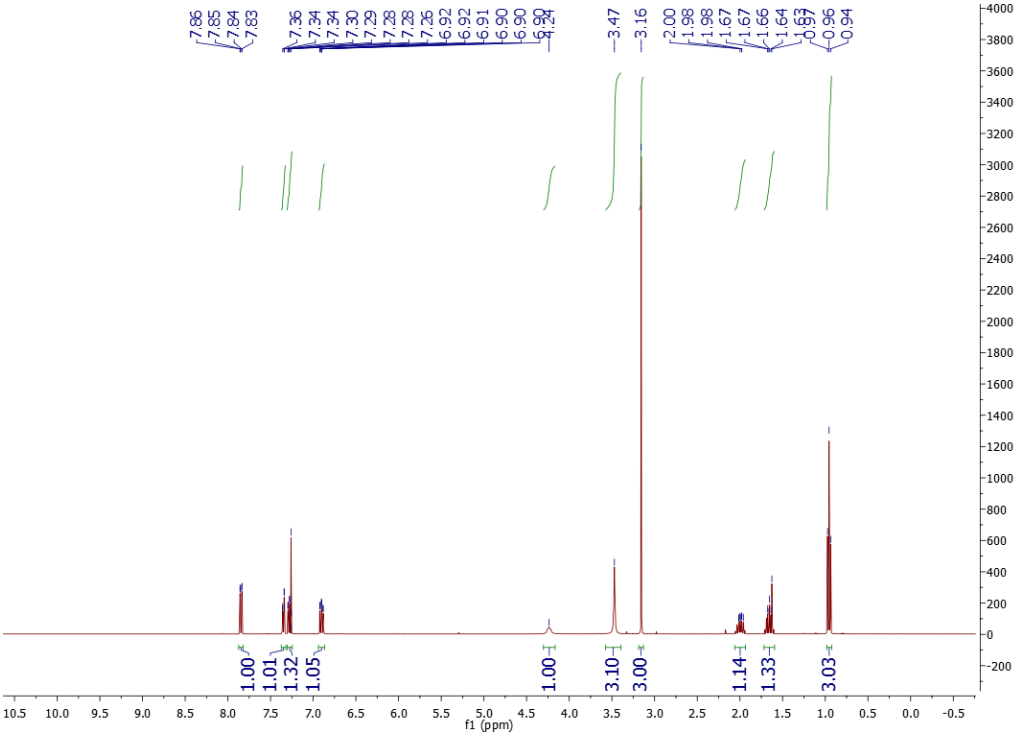
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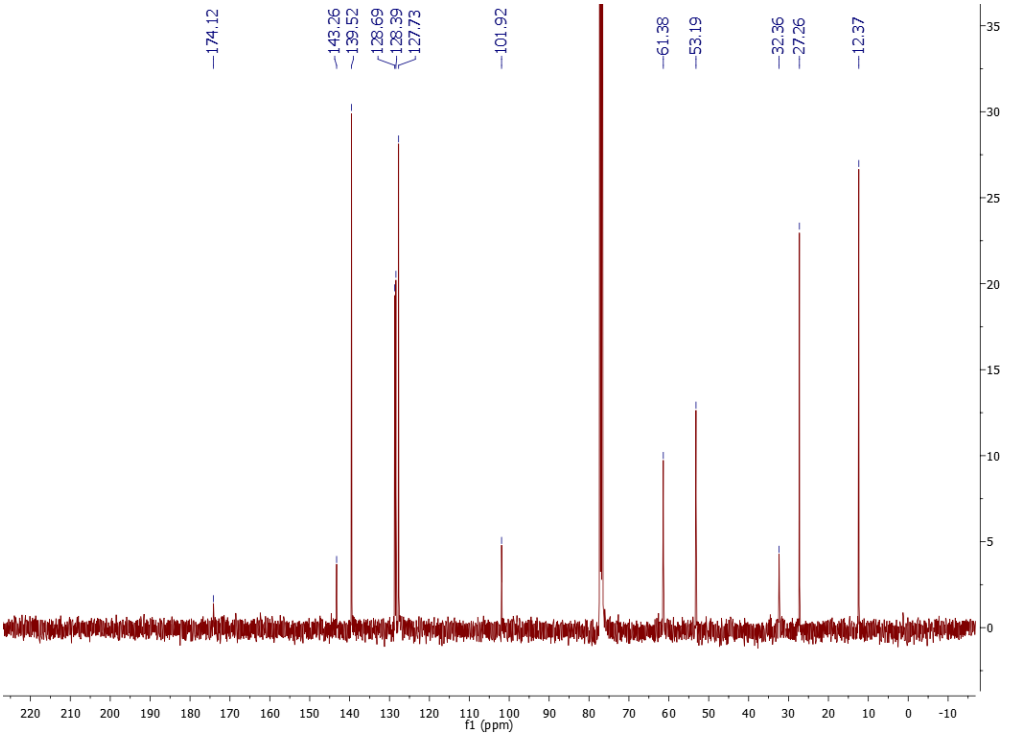
7.83
7.36
7.34
7.34
7.30
7.29
7.28
7.26
6.92
6.91
6.90
6.90
6.90
4.24
3.47
3.16
2.00
1.98
1.98
1.67
1.67
1.66
1.64
1.63
0.97
0.96
0.94
1.00
1.01
1.32
1.05
1.00
3.10
3.00
1.14
1.33
3.03
f1 (ppm)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143.26
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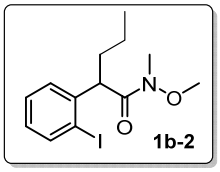
128.39
127.73
101.92
61.38
53.19
32.36
27.26
12.37
f1 (ppm)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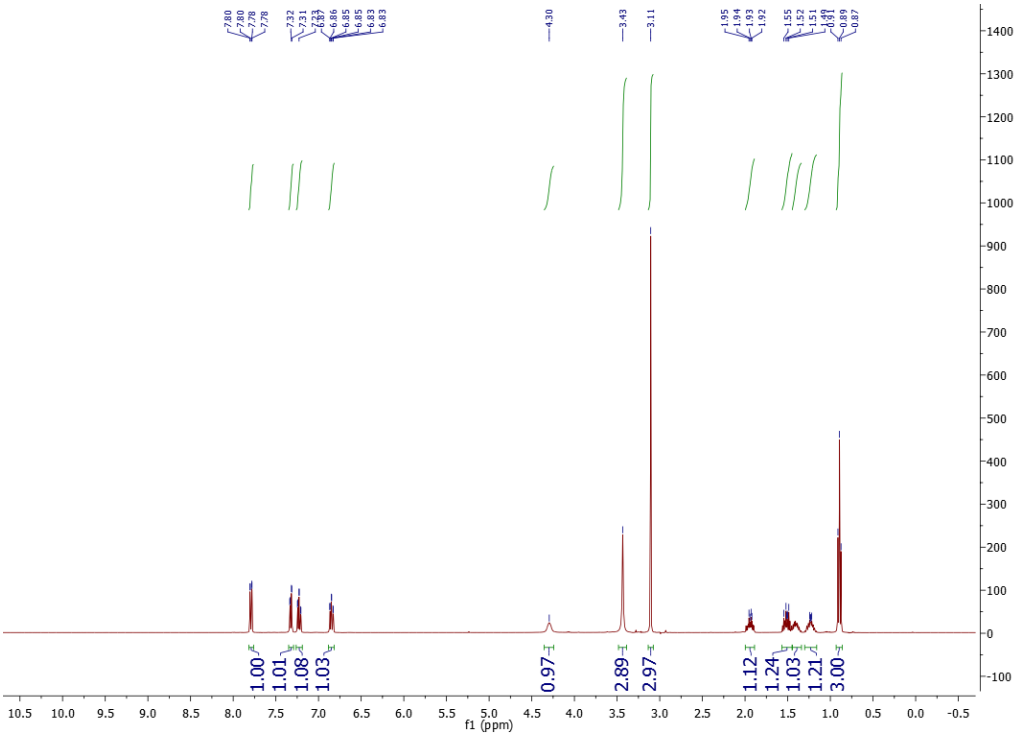
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7.78
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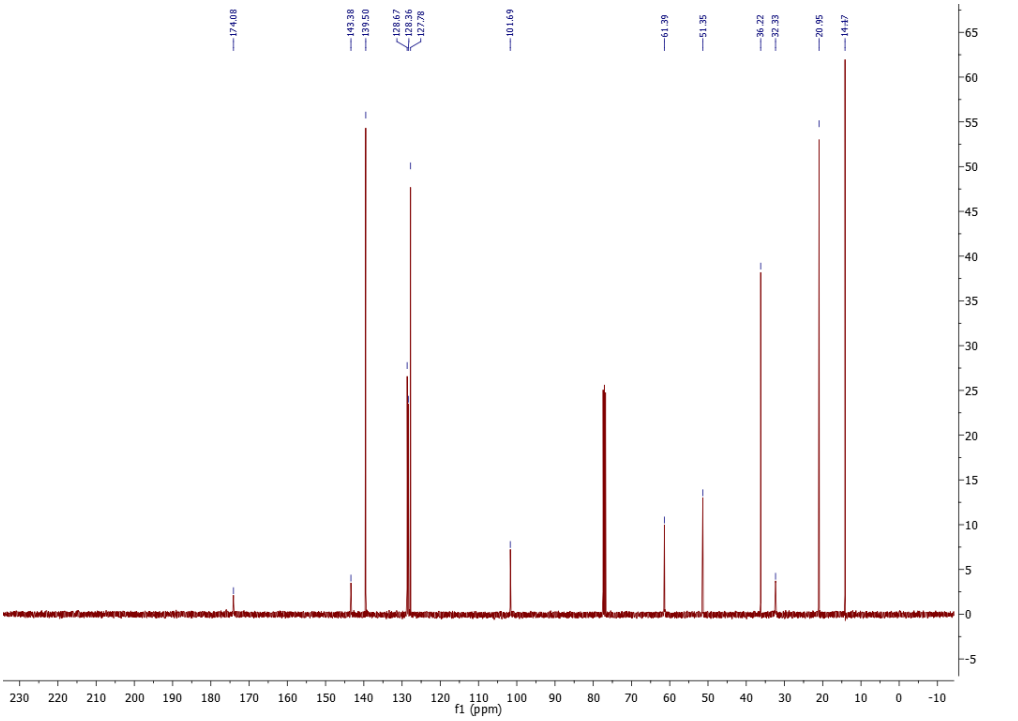
7.31
7.23
7.23
6.86
6.85
6.85
6.83
6.83
4.30
3.43
3.11
1.95
1.94
1.93
1.92
1.55
1.52
1.51
1.41
0.91
0.89
0.87
1.00
1.01
1.08
1.03
0.97
2.89
2.97
1.12
1.24
1.03
1.21
3.00
f1 (ppm)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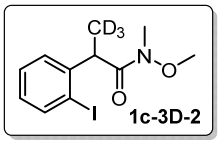
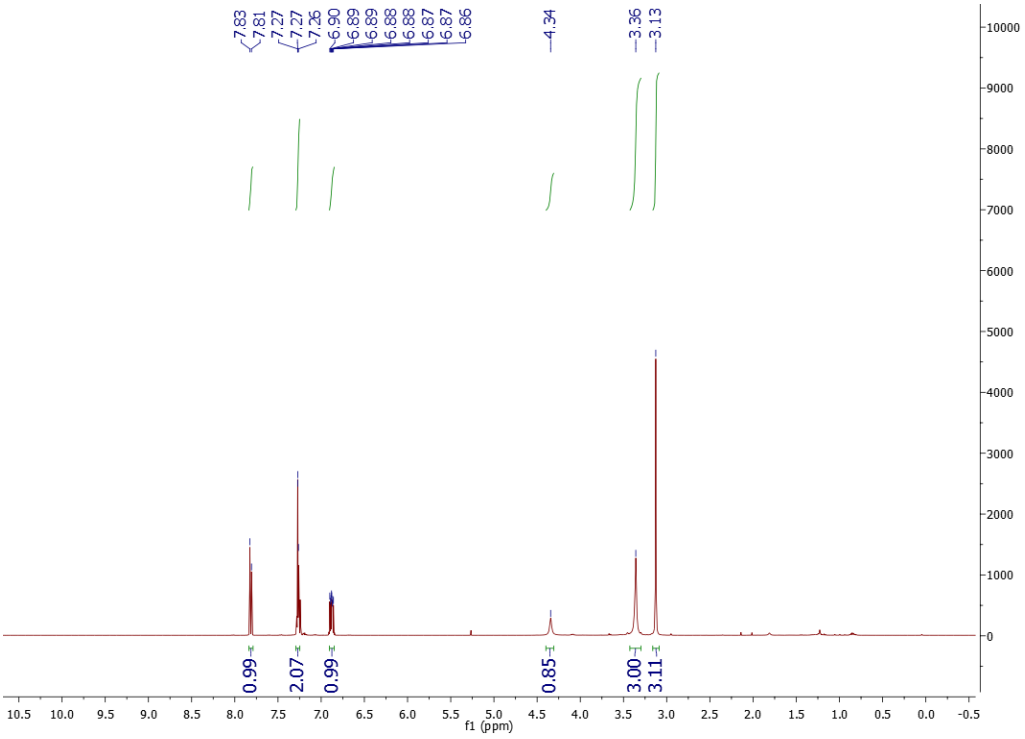
127.78
101.69
61.39
51.35
36.22
32.33
20.95
14.47
f1 (ppm)


CD3
N
O
O
I
1c-3D-2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7.27
7.26
6.90
6.89
6.89
6.88
6.88
6.87
6.87
6.86
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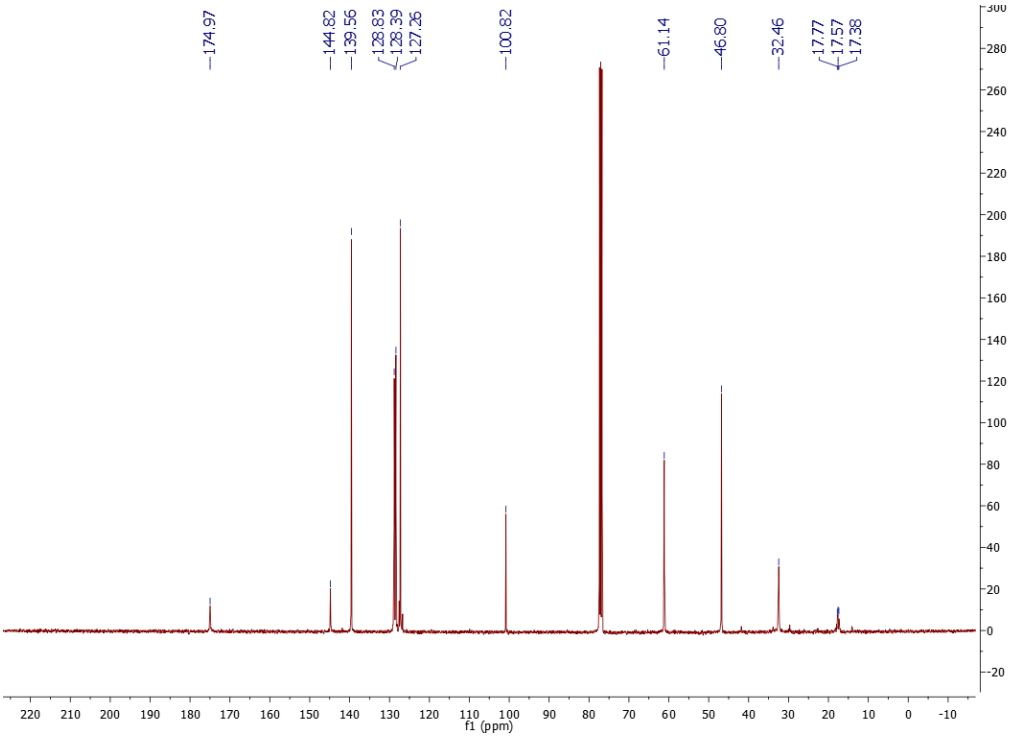
3.36
3.13
0.99
2.07
0.99
0.85
3.00
3.11
f1 (ppm)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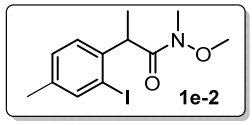
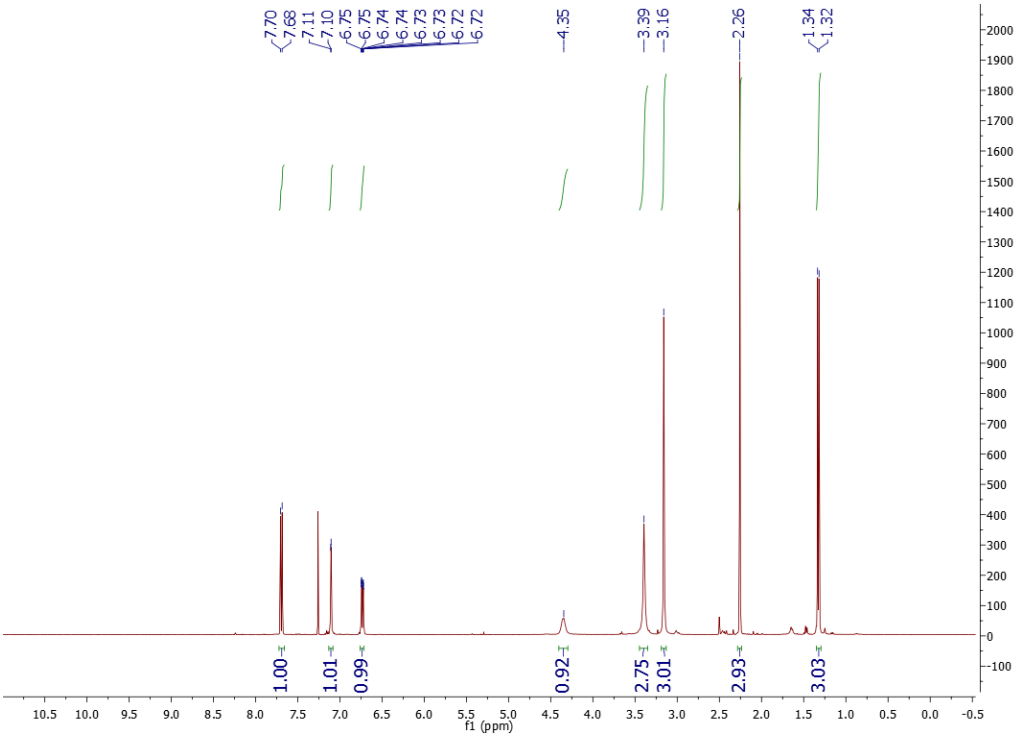
32.46
17.77
17.57
17.38
f1 (ppm)


1e-2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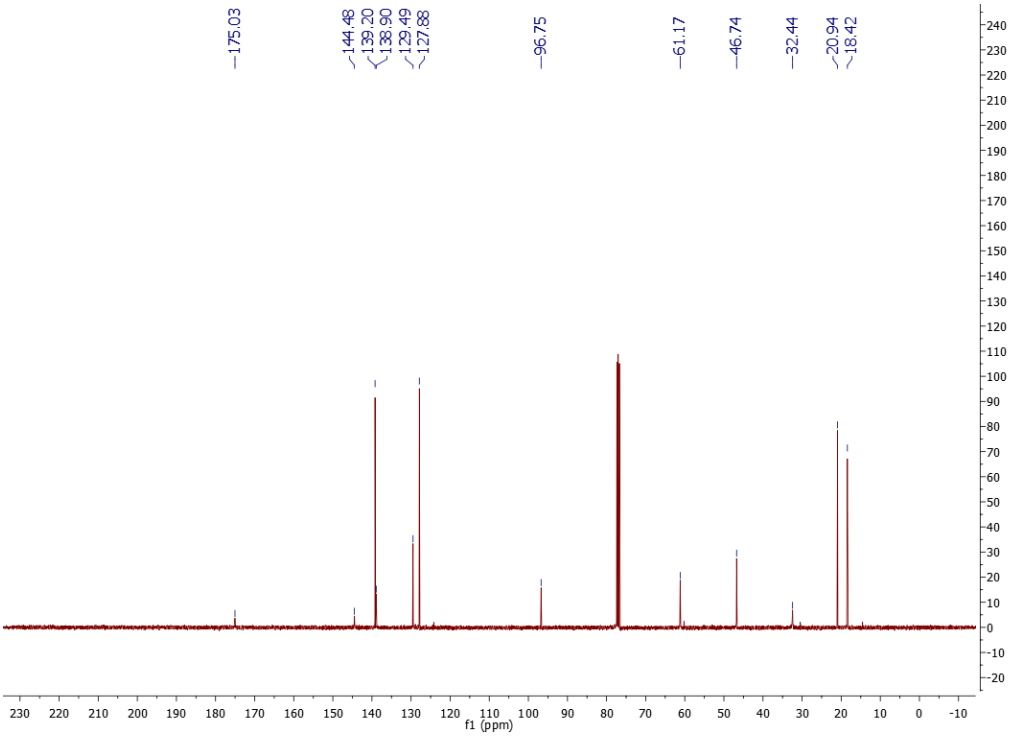
6.75
6.74
6.74
6.73
6.73
6.72
6.72
4.35
3.39
3.16
2.26
1.34
1.32
1.00
1.01
0.99
0.92
2.75
3.01
2.93
3.03
f1 (ppm)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61.17
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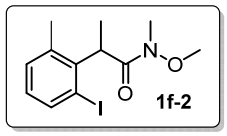
32.44
20.94
18.42
f1 (ppm)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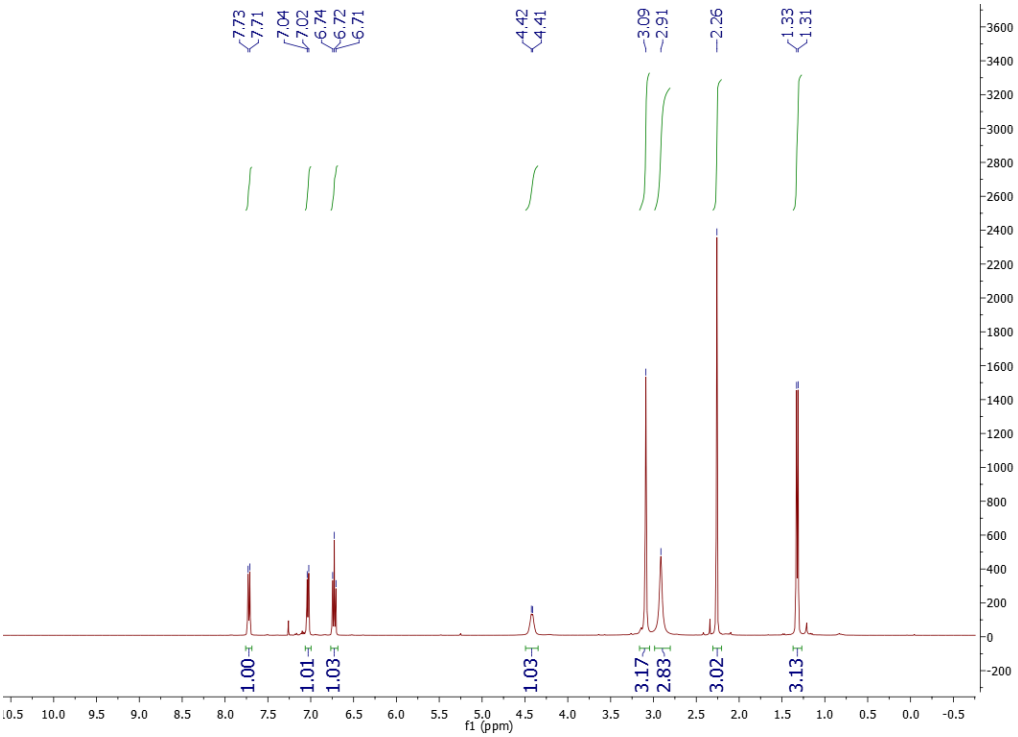
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6.71
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4.41
3.09
2.91
2.26
1.33
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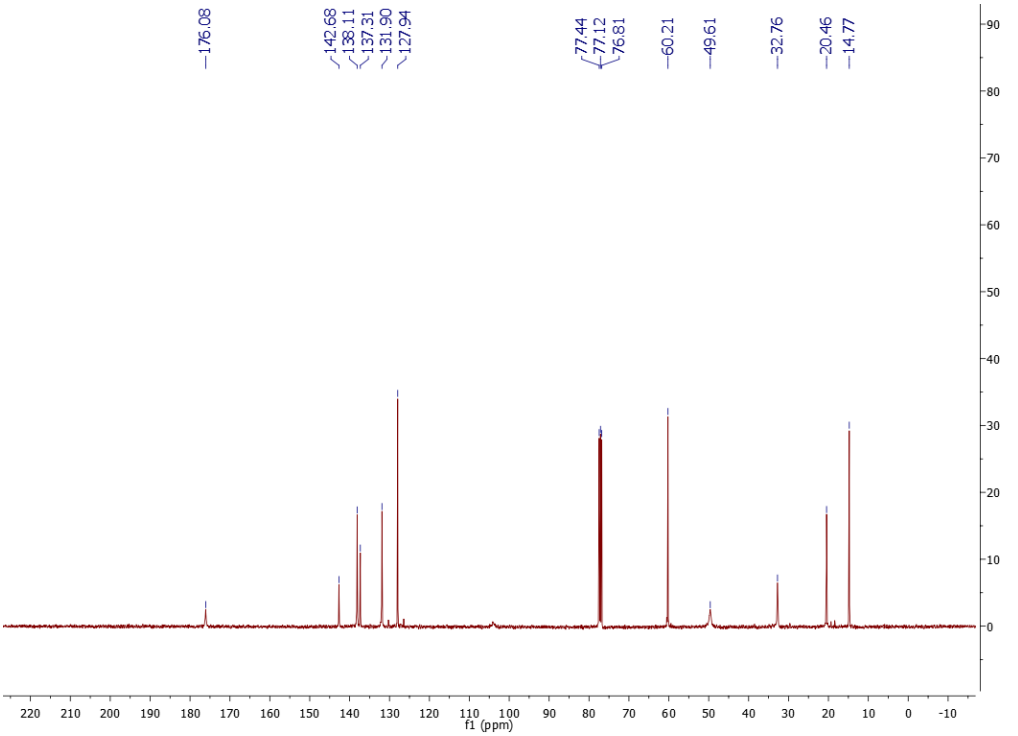
1.00
1.01
1.03
1.03
3.17
2.83
3.02
3.13
f1 (ppm)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131.90
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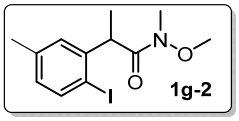
77.44
77.12
76.81
60.21
49.61
32.76
20.46
14.77
f1 (ppm)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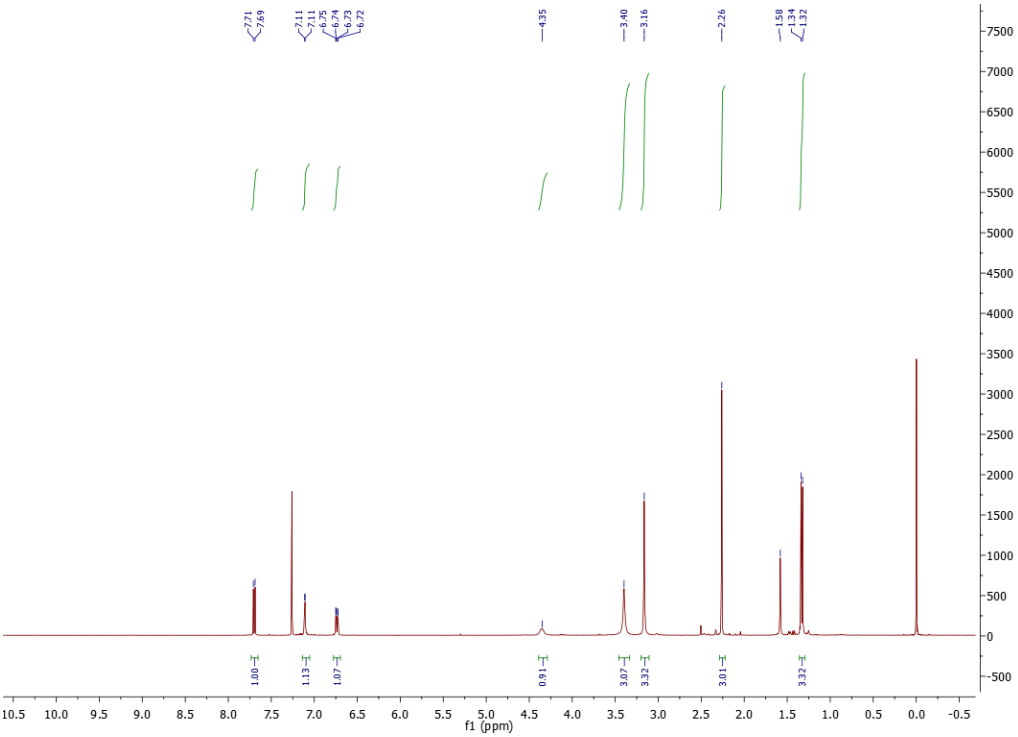
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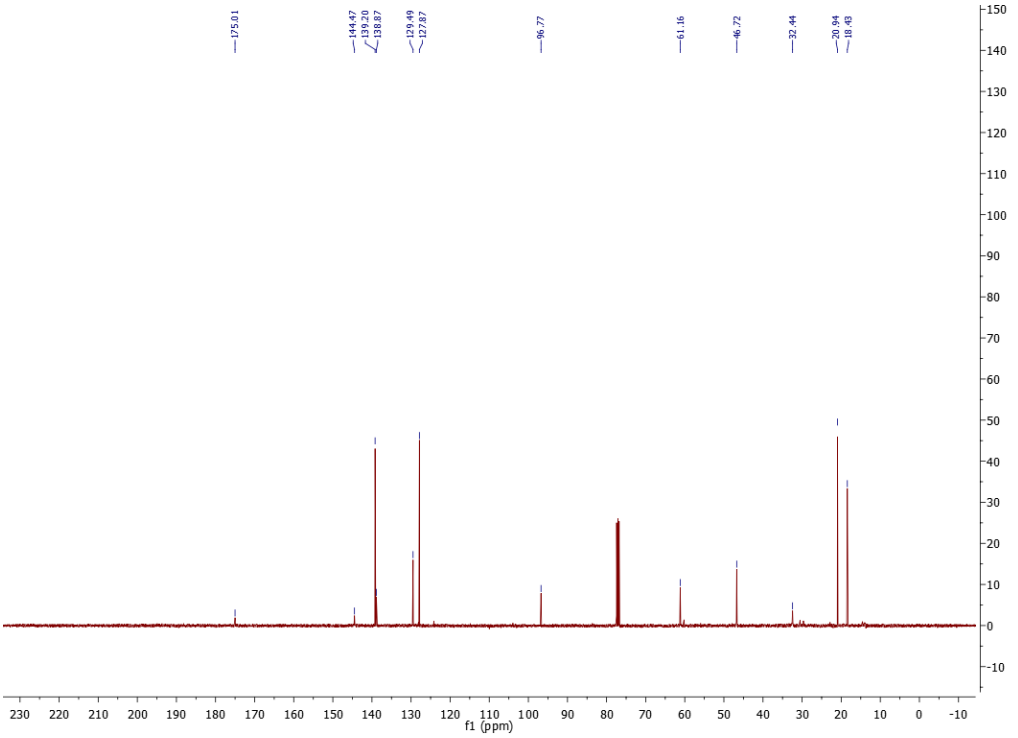
7.11
6.75
6.74
6.73
6.72
4.35
3.40
3.16
2.26
1.58
1.34
1.32
1.00
1.13
1.07
0.91
3.07
3.32
3.01
3.32
f1 (ppm)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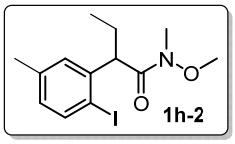
127.87
96.77
61.16
46.72
32.44
20.94
18.43
f1 (ppm)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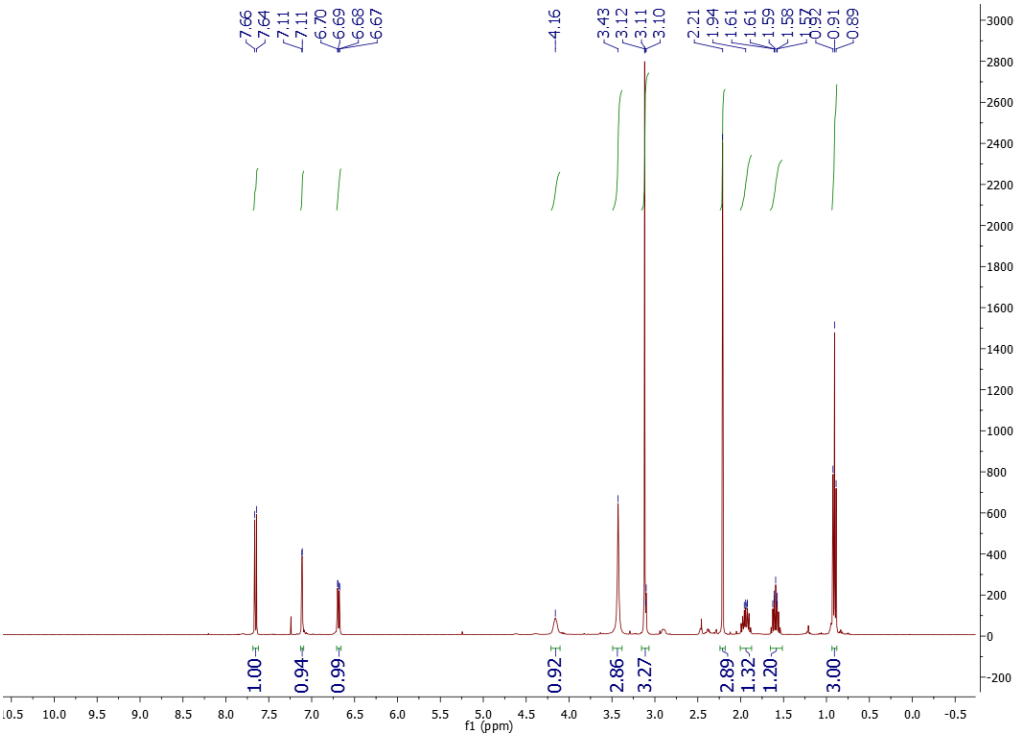
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6.69
6.68
6.67
4.16
3.43
3.12
3.11
3.10
2.21
1.94
1.61
1.61
1.59
1.58
1.57
0.92
0.91
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0.99
0.92
2.86
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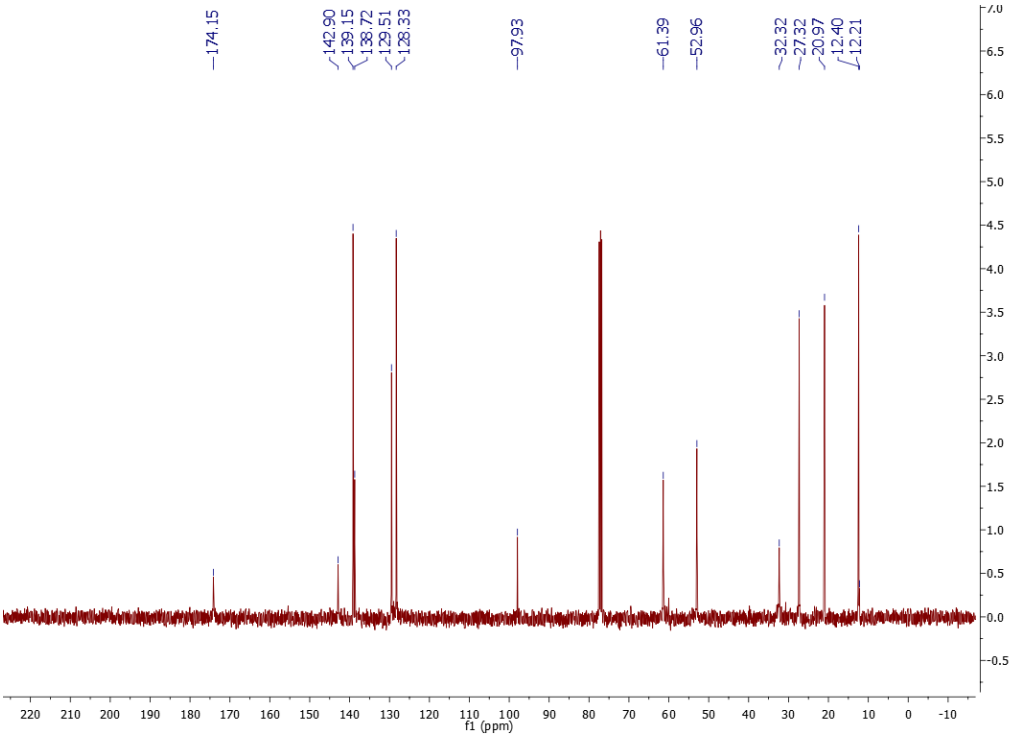
2.89
1.32
1.20
3.00
f1 (ppm)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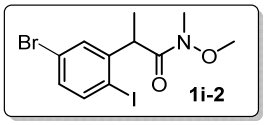
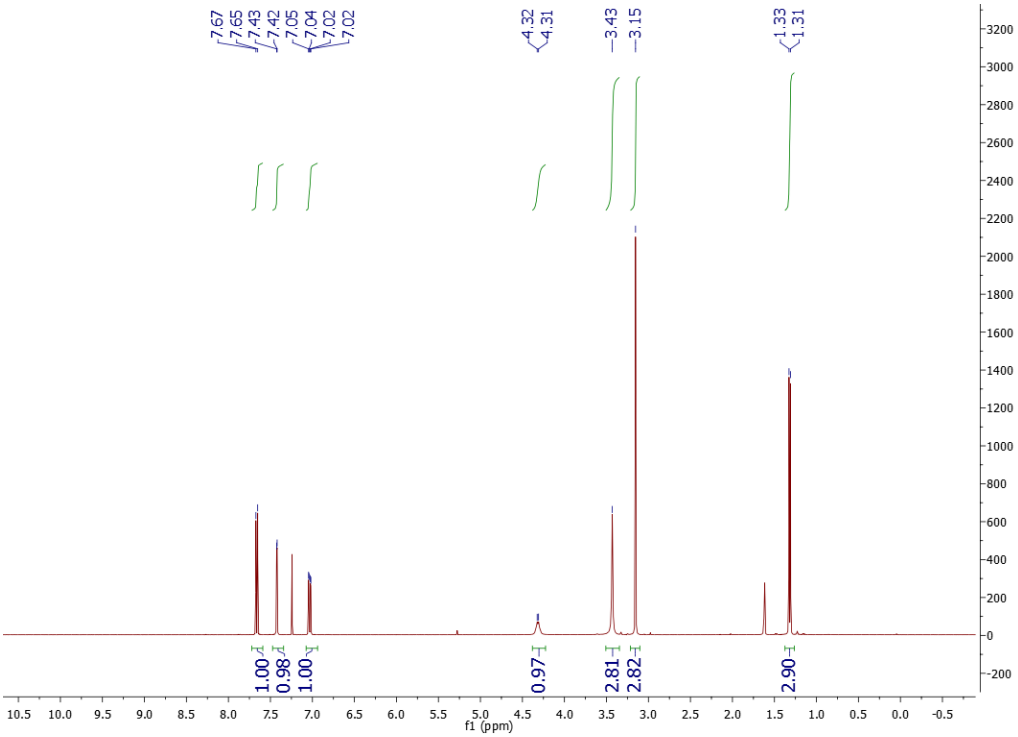
97.93
61.39
52.96
32.32
27.32
20.97
12.40
12.21
f1 (ppm)


Br
N
O
O
I
1i-2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7.04
7.02
7.02
4.32
4.31
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3.15
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1.31
1.00
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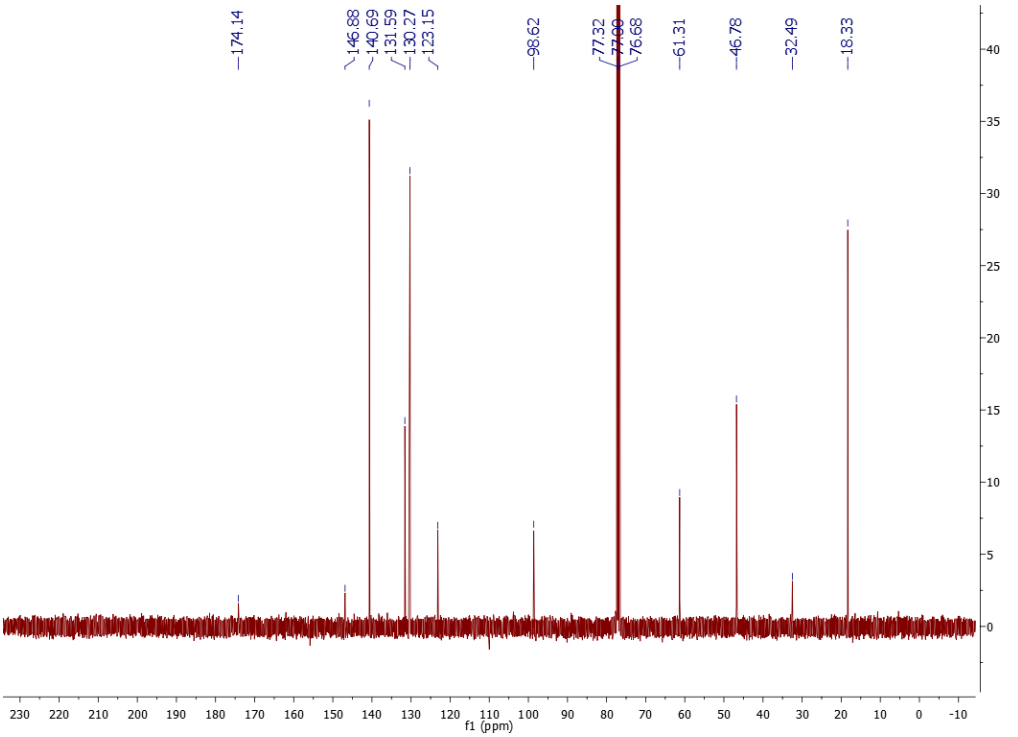
1.00
0.97
2.81
2.82
2.90
f1 (ppm)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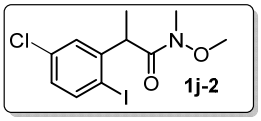
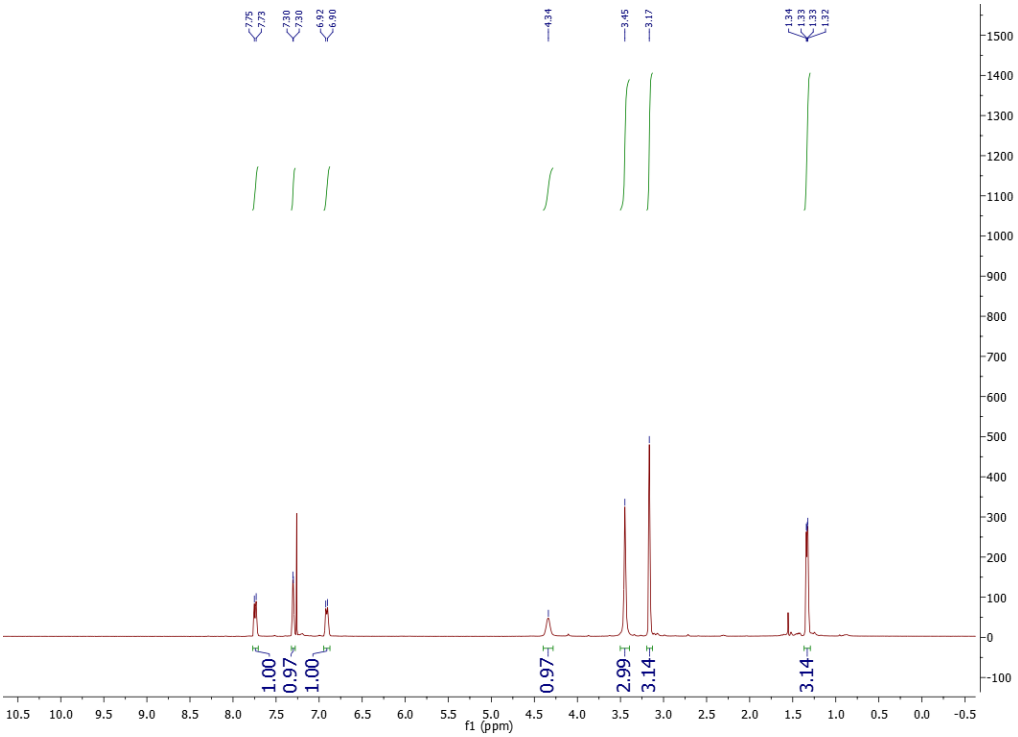
98.62
77.32
77.00
76.68
61.31
46.78
32.49
18.33
f1 (ppm)


Cl
N
O
O
I
1j-2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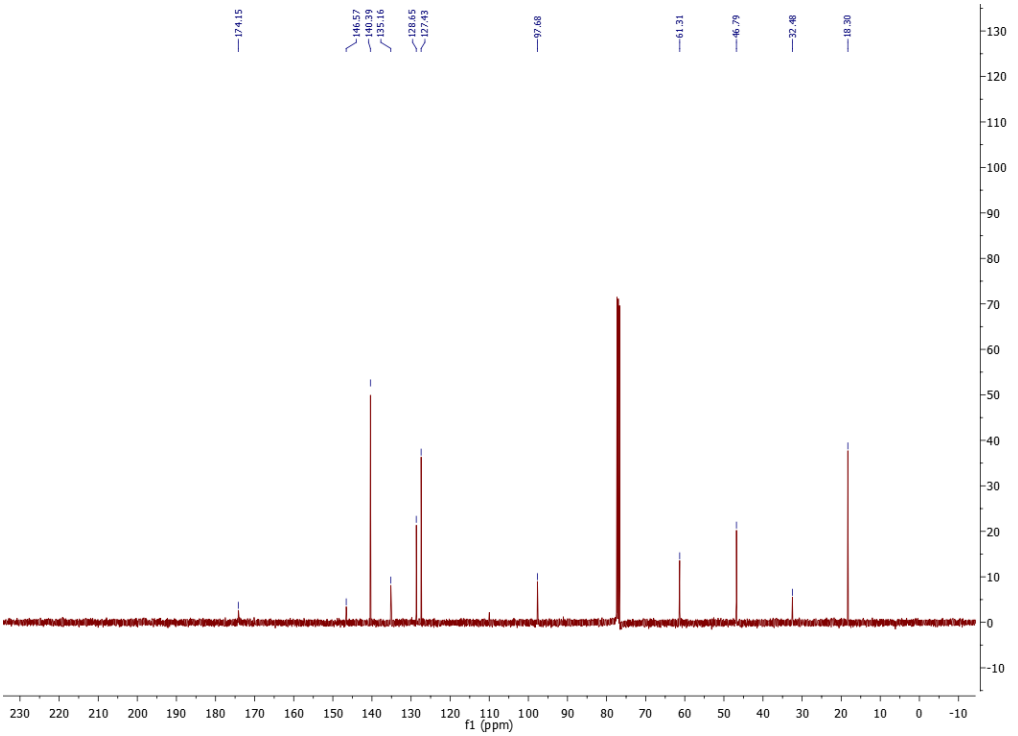
6.90
4.34
3.45
3.17
1.34
1.33
1.33
1.32
1.00
0.97
1.00
0.97
2.99
3.14
3.14
f1 (ppm)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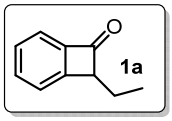
18.30
f1 (ppm)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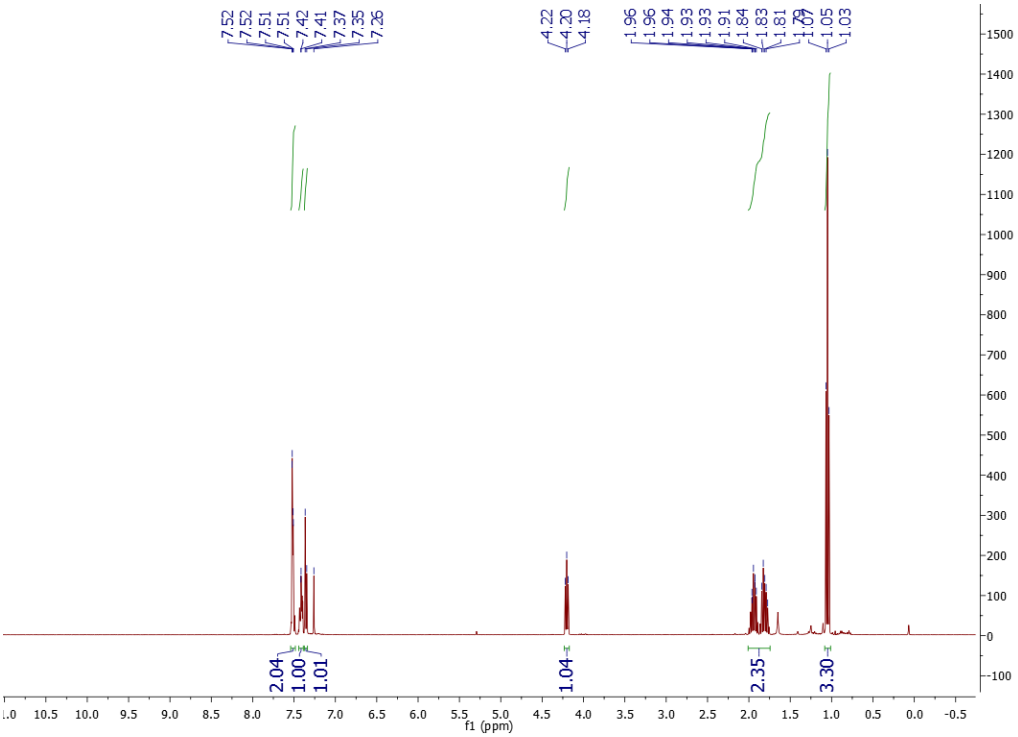
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4.18
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1.94
1.93
1.93
1.91
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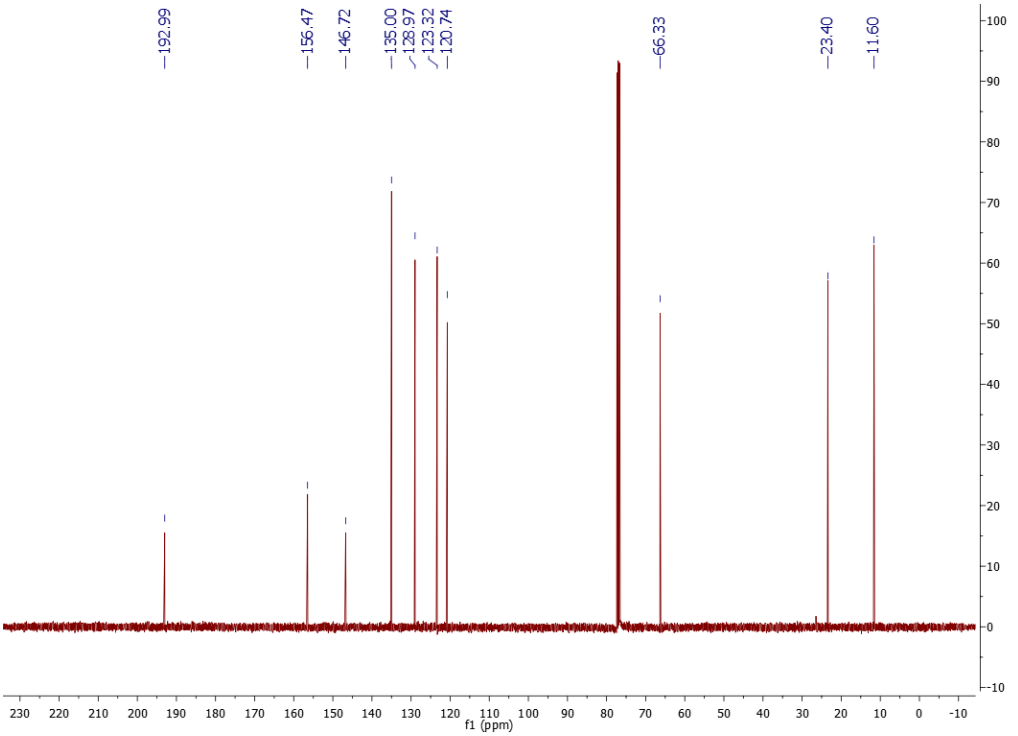
1.04
2.35
3.30
f1 (ppm)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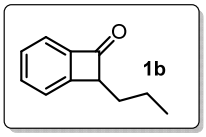
11.60
f1 (ppm)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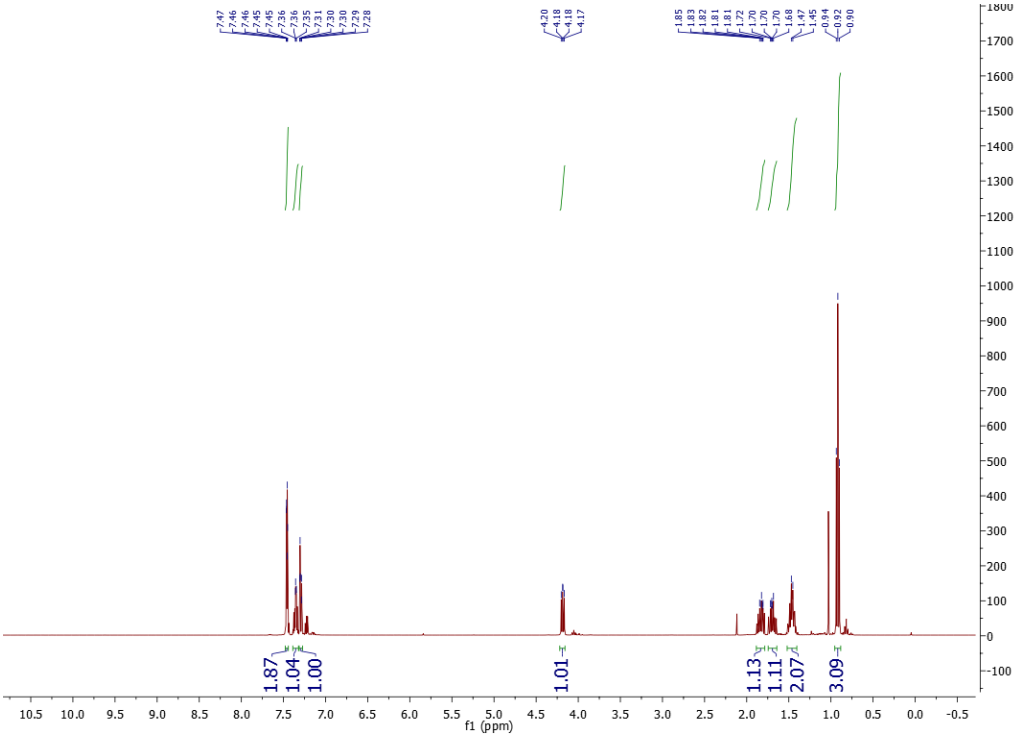
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4.18
4.17
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1.83
1.82
1.81
1.81
1.72
1.70
1.70
1.70
1.68
1.47
1.45
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1.01
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1.11
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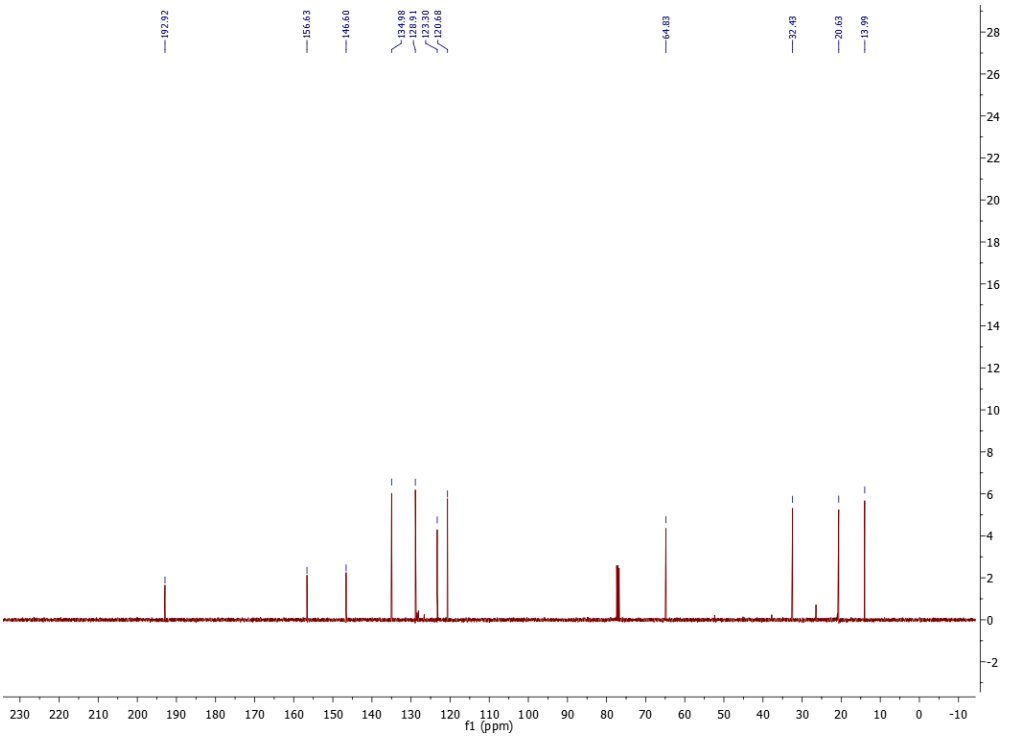
3.09
f1 (ppm)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64.83
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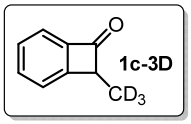
20.63
13.99
f1 (ppm)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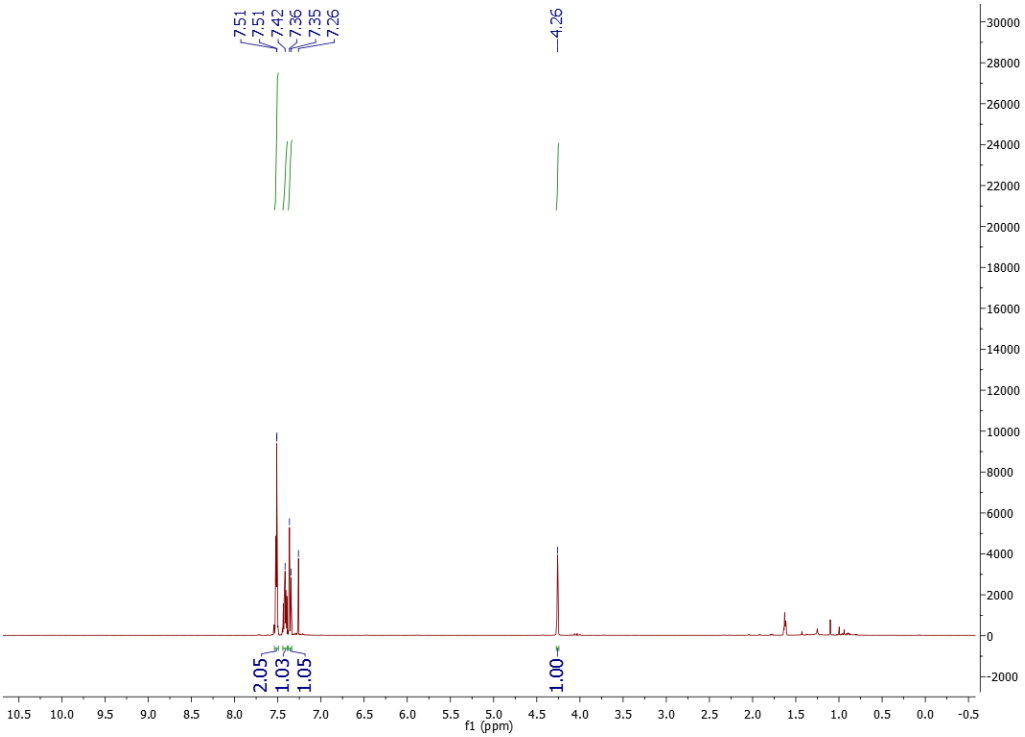
CD3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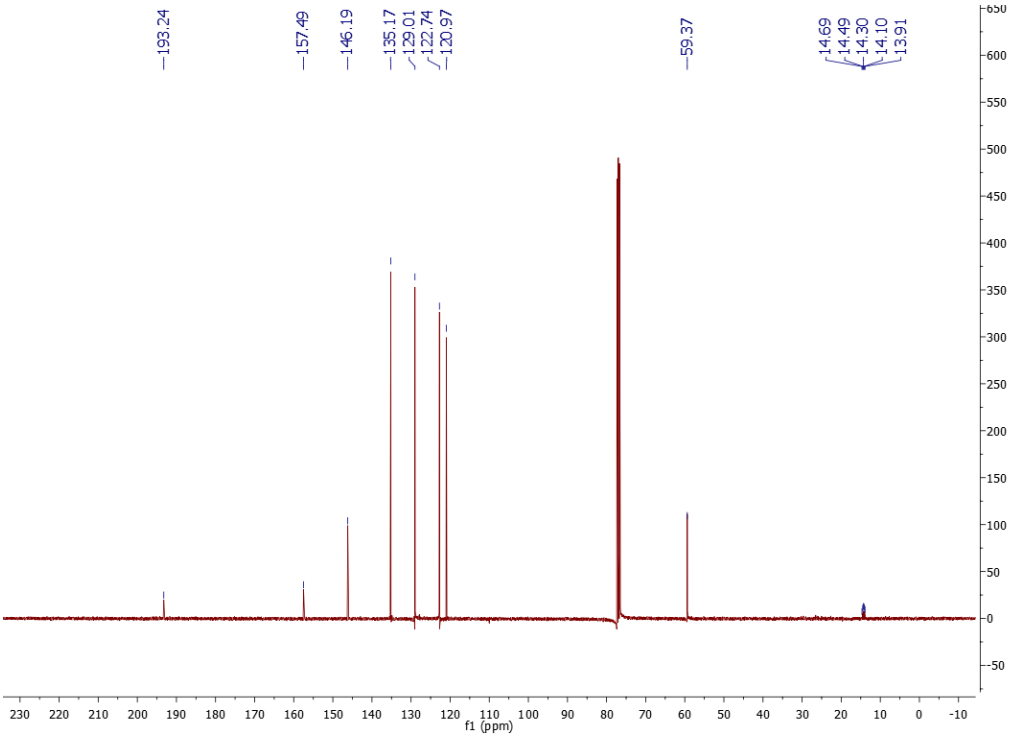
4.26
2.05
1.03
1.05
1.00
f1 (ppm)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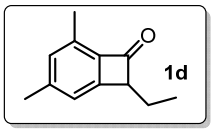
f1 (ppm)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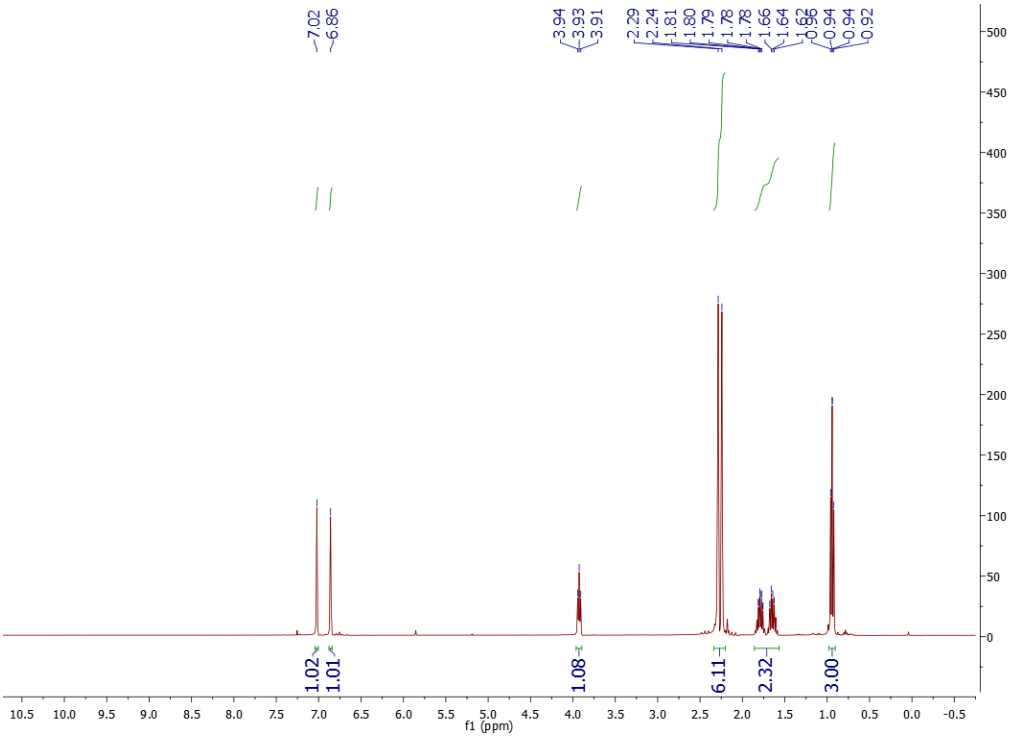
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2.24
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1.78
1.78
1.66
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0.94
0.92
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1.01
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6.11
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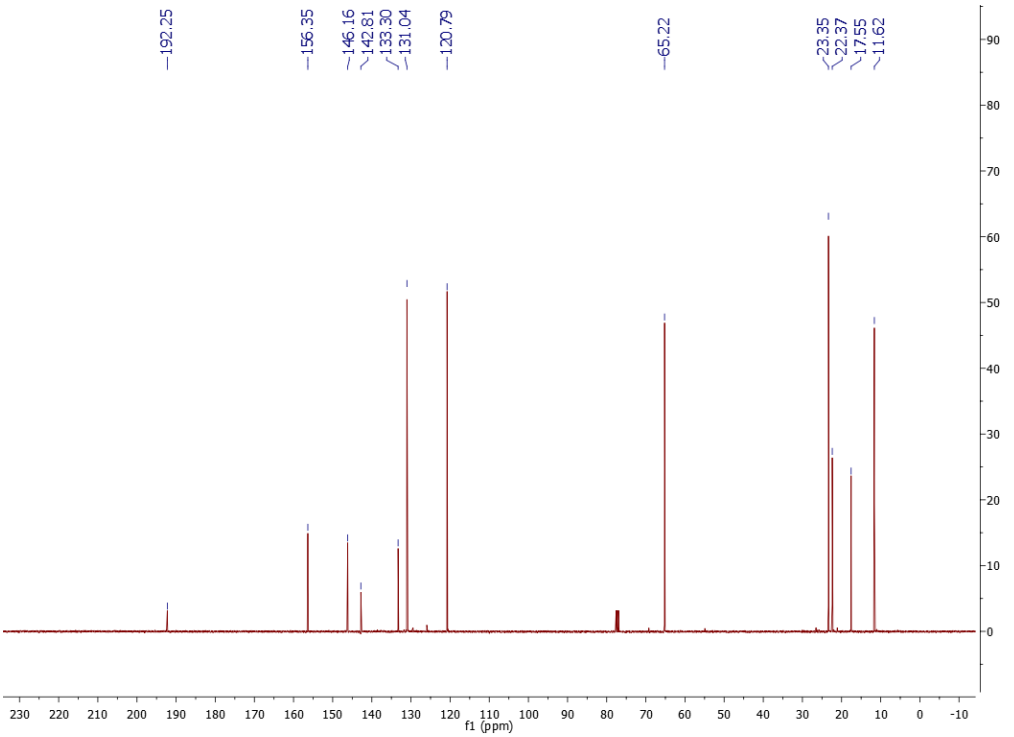
3.00
f1 (ppm)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65.22
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22.37
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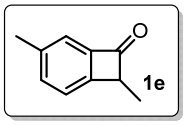
11.62
f1 (ppm)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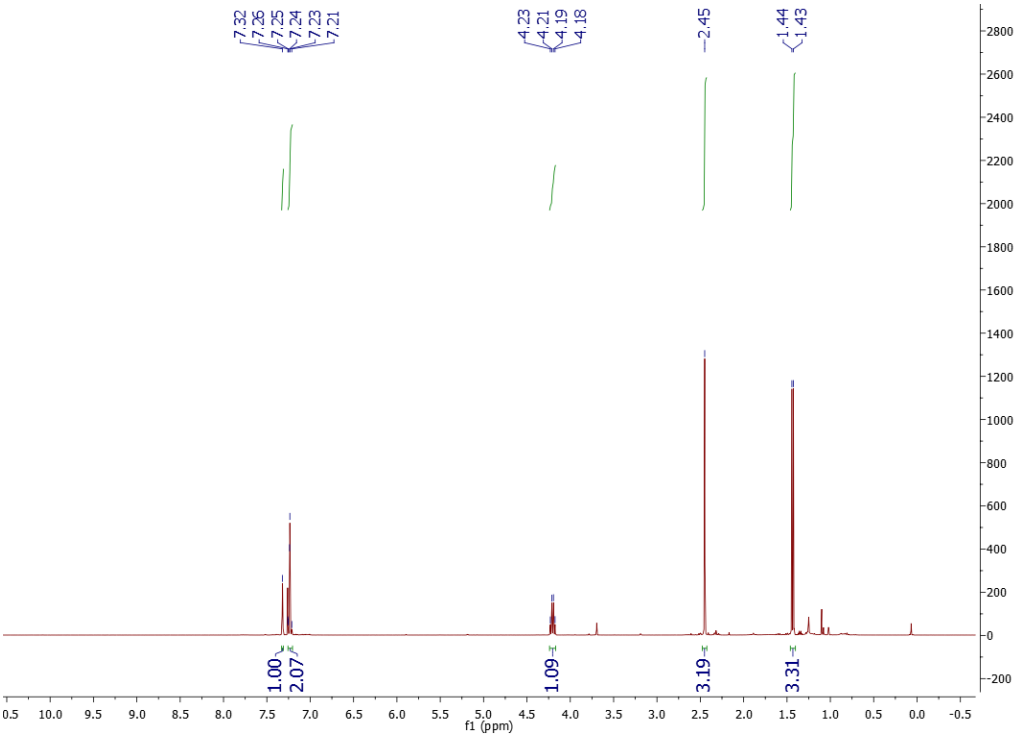
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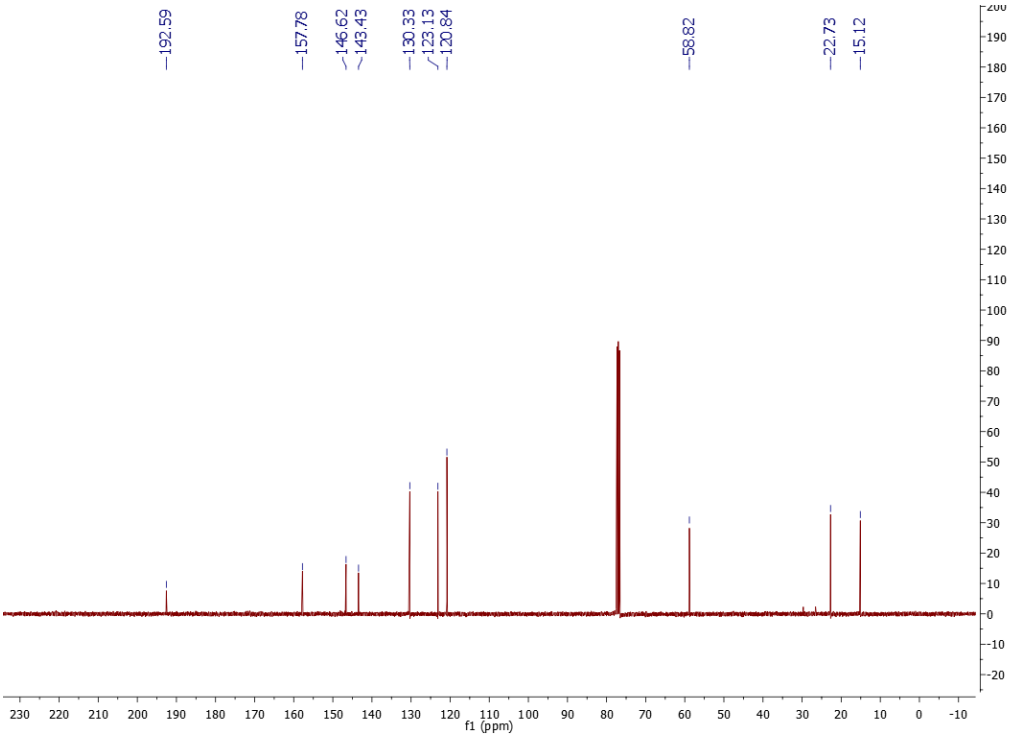
1.09
3.19
3.31
f1 (ppm)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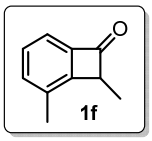
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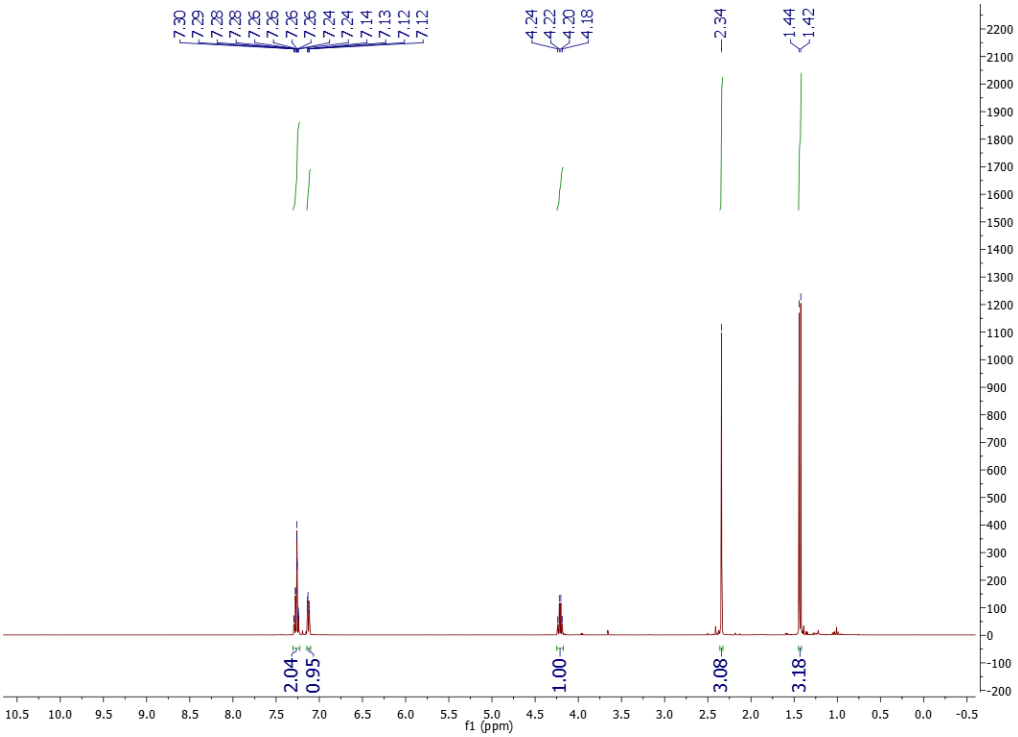
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7.12
4.24
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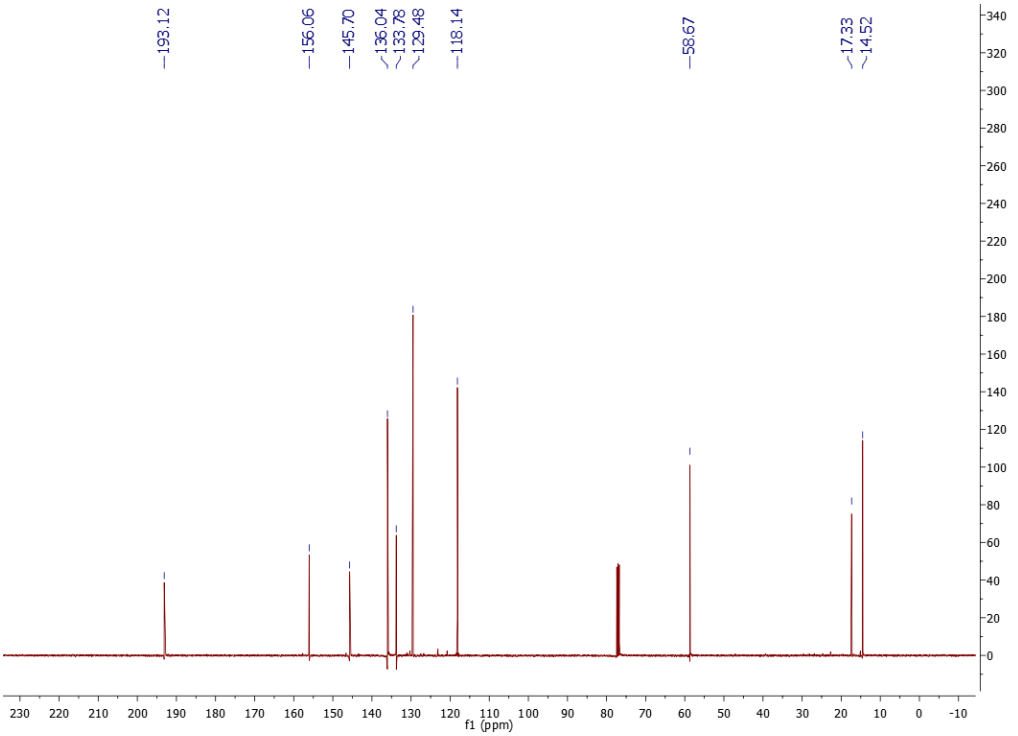
3.18
f1 (ppm)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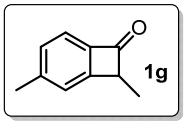
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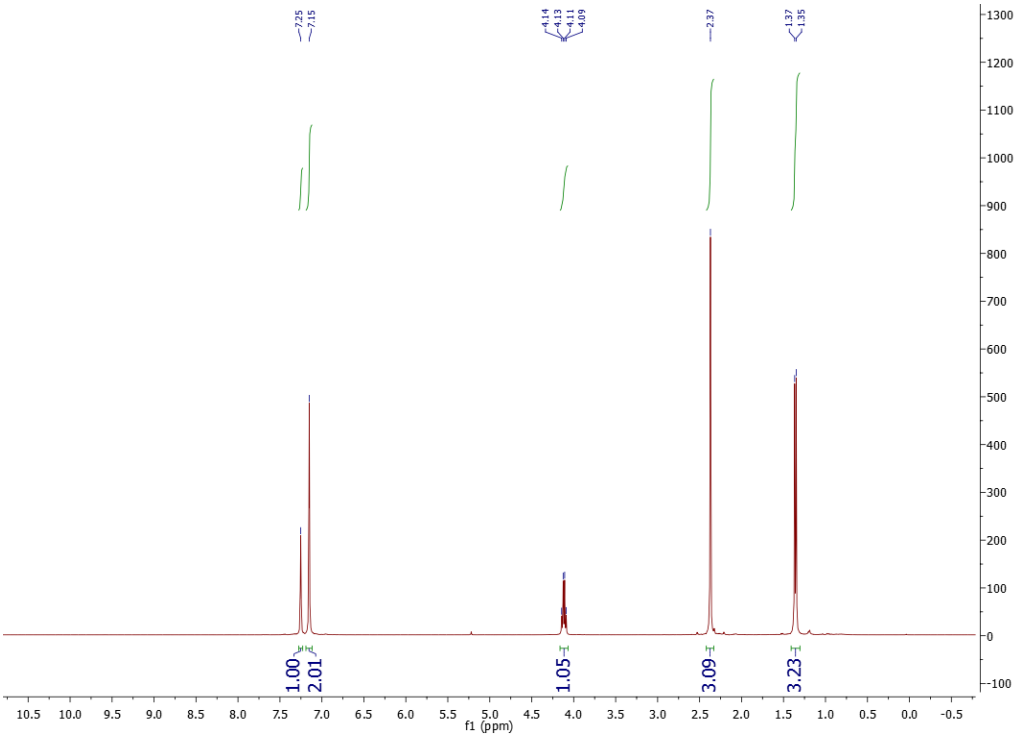
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1.00
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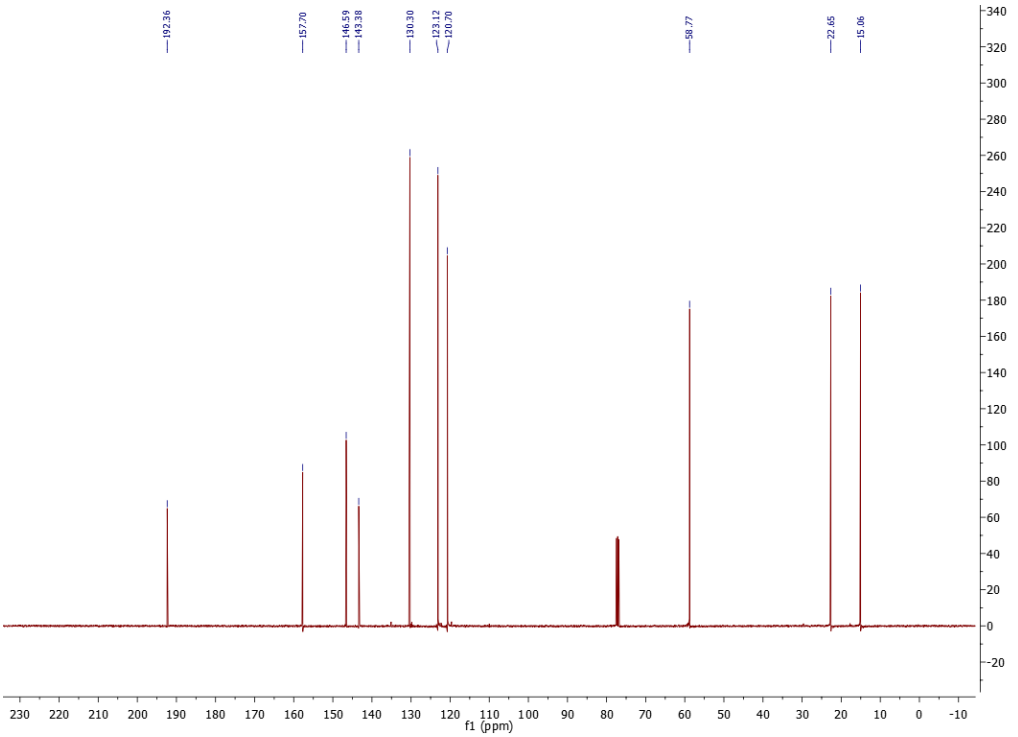
1.05
3.09
3.23
f1 (ppm)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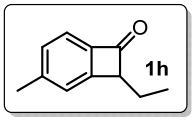
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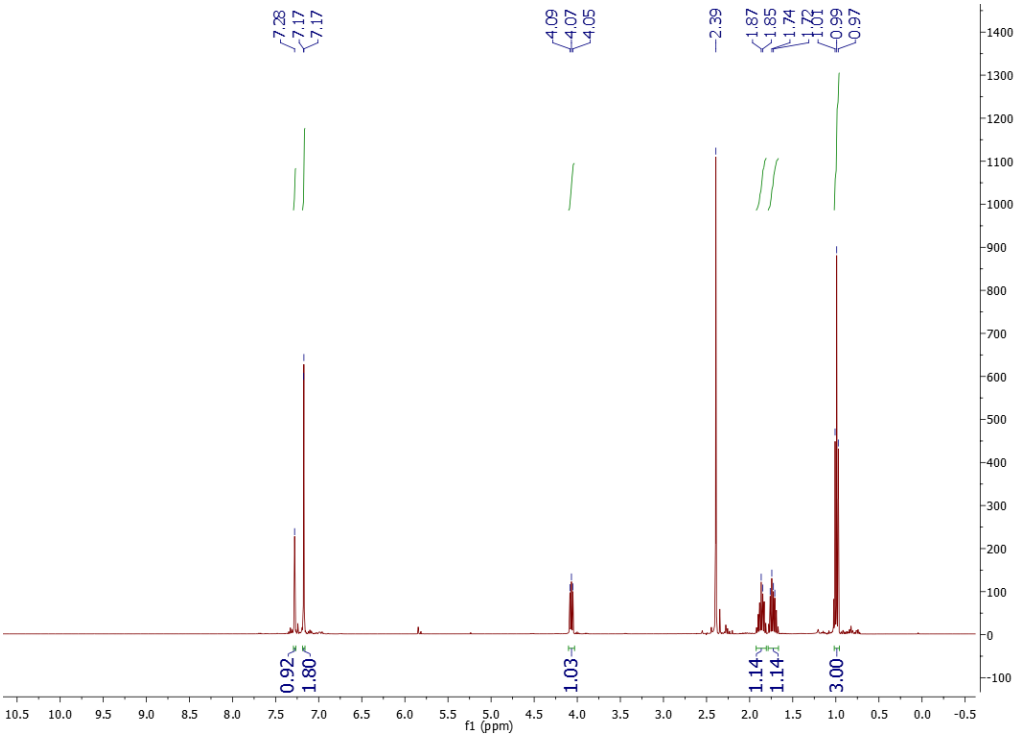
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1.80
1.03
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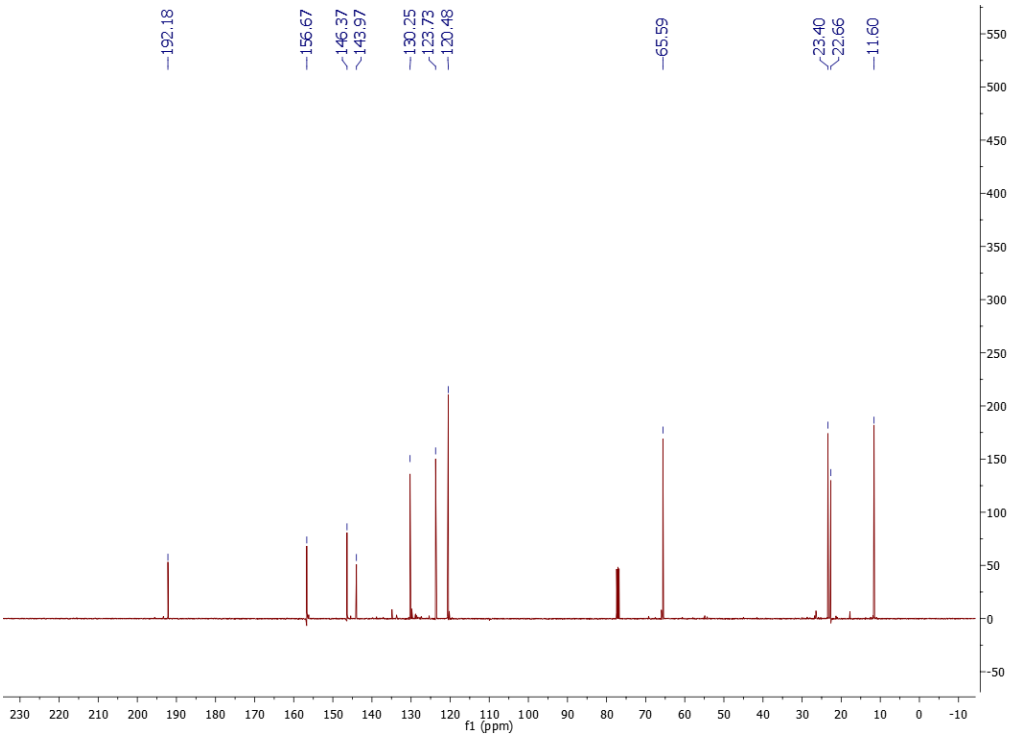
1.14
3.00
f1 (ppm)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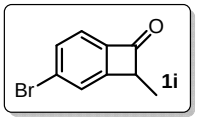
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Br
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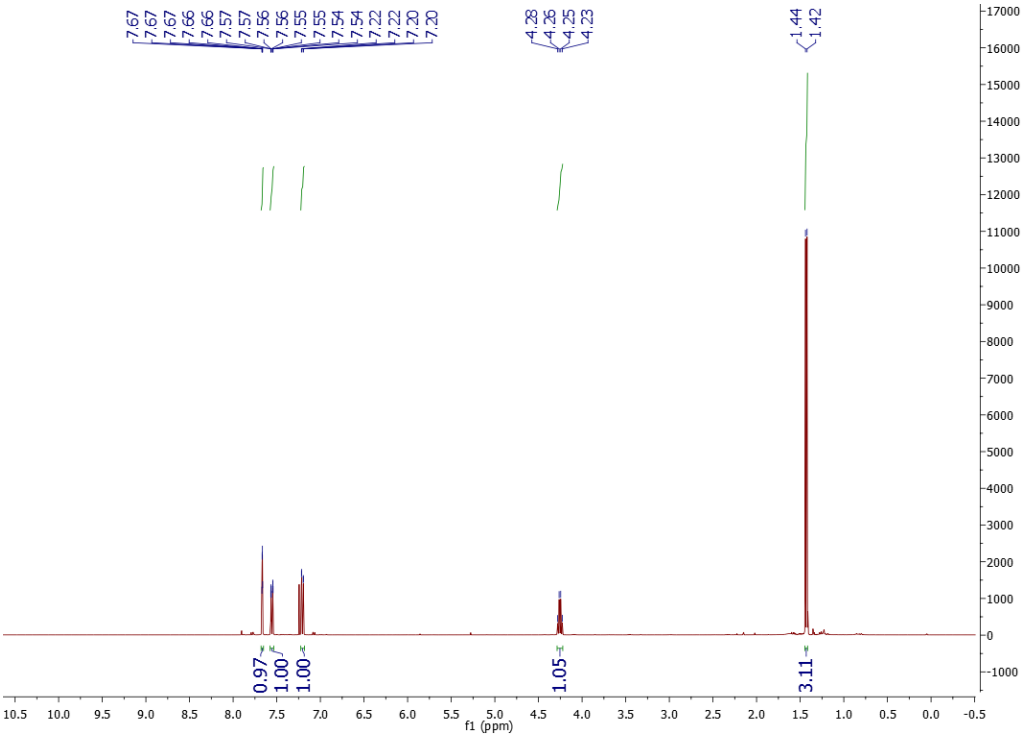
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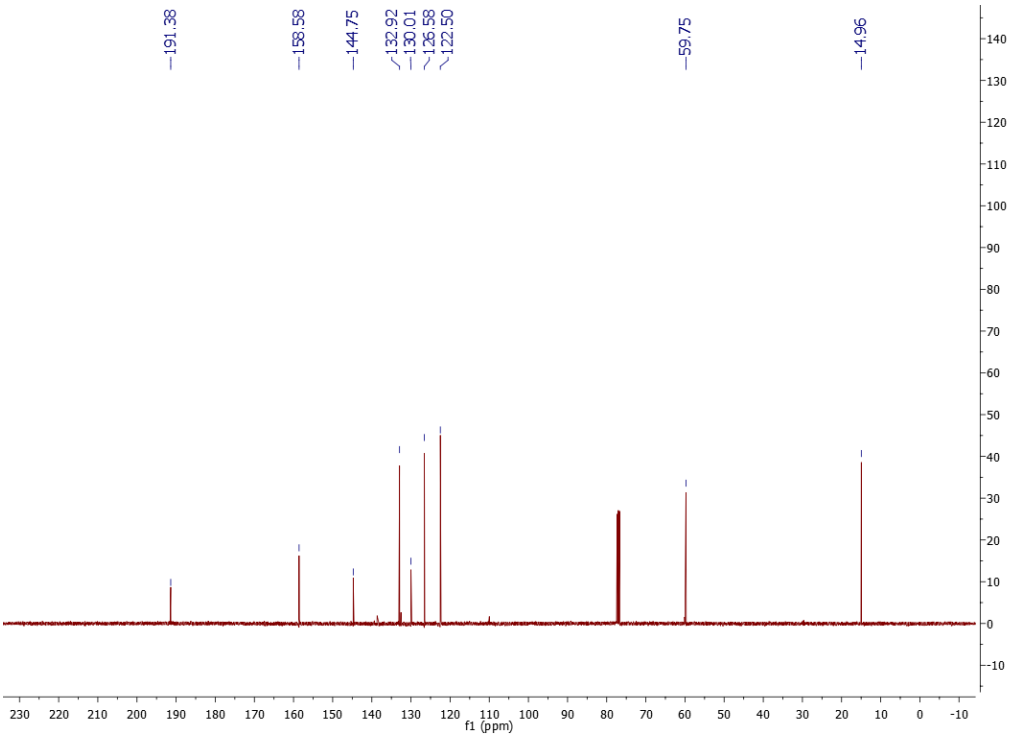
3.11
f1 (ppm)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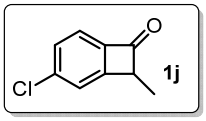
f1 (ppm)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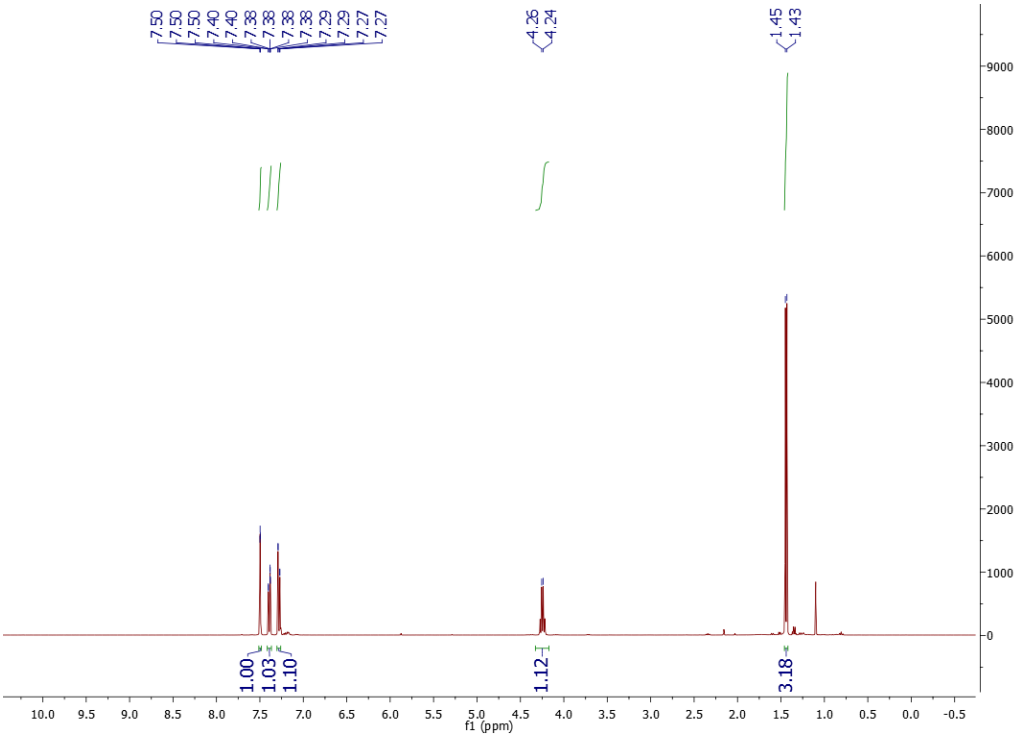
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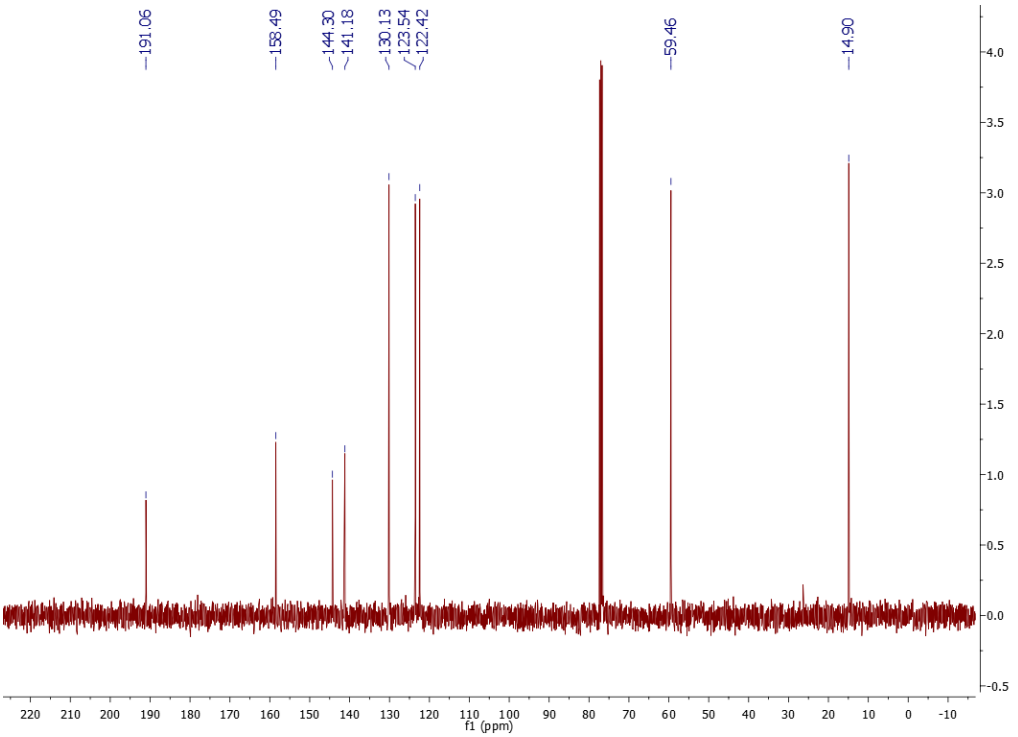
f1 (ppm)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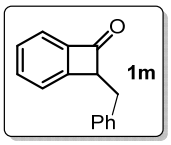
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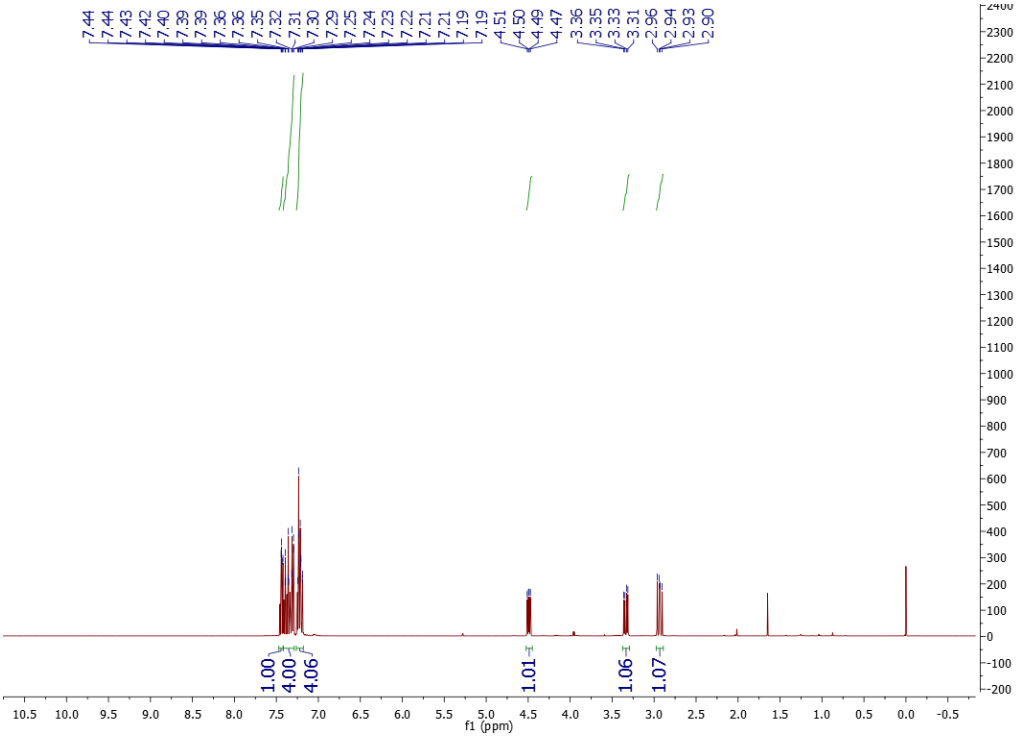
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3.33
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4.00
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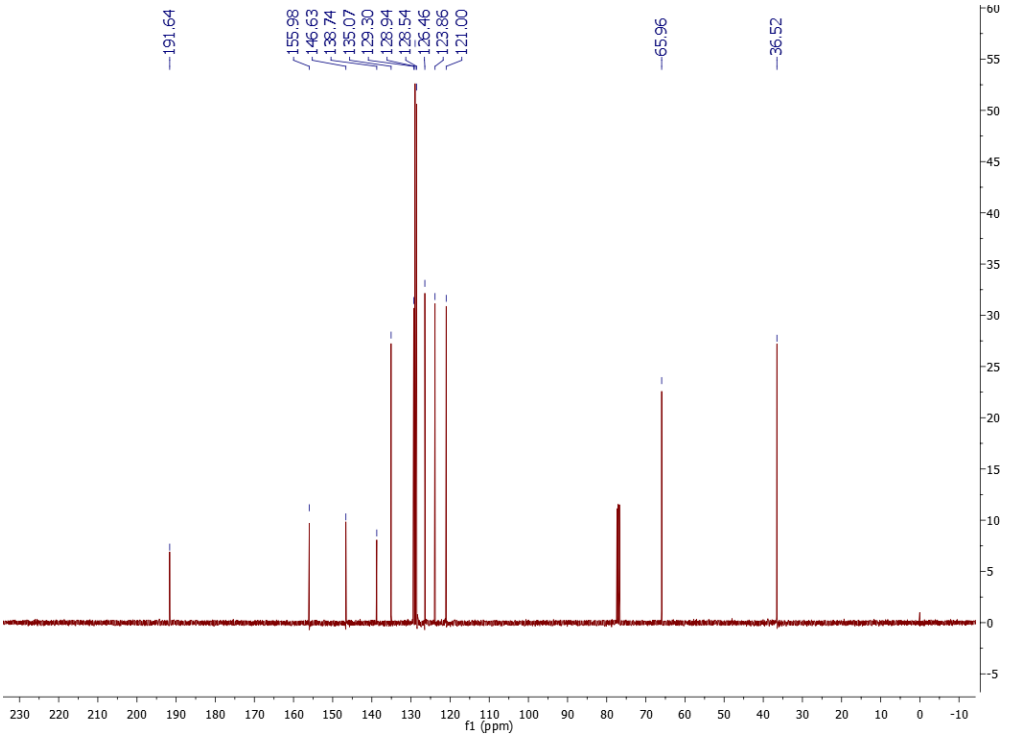
1.07
f1 (ppm)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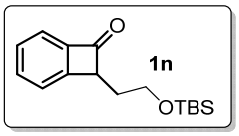
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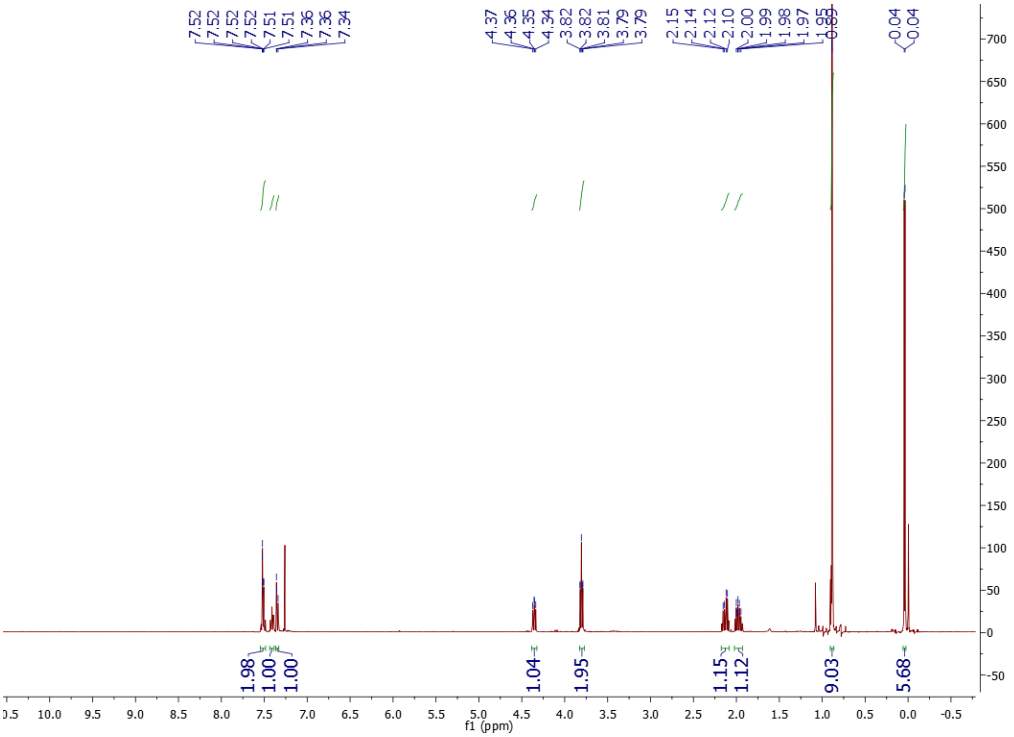
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3.81
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3.79
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2.14
2.12
2.10
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1.98
1.97
1.95
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1.04
1.95
1.15
1.12
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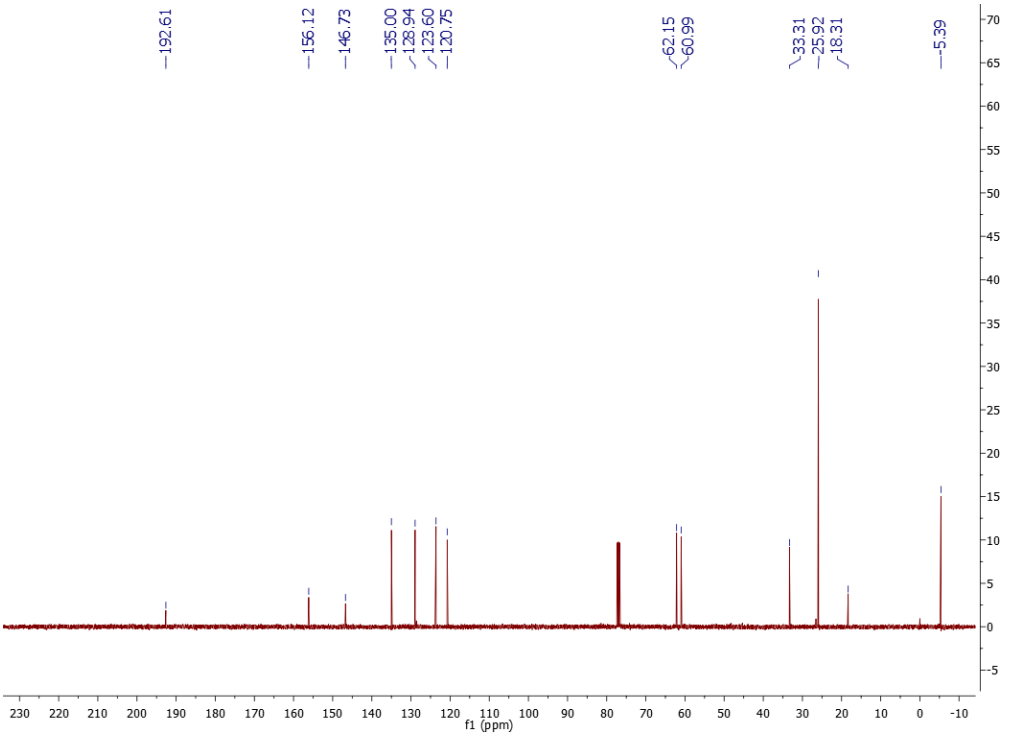
f1 (ppm)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25.92
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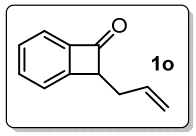
f1 (ppm)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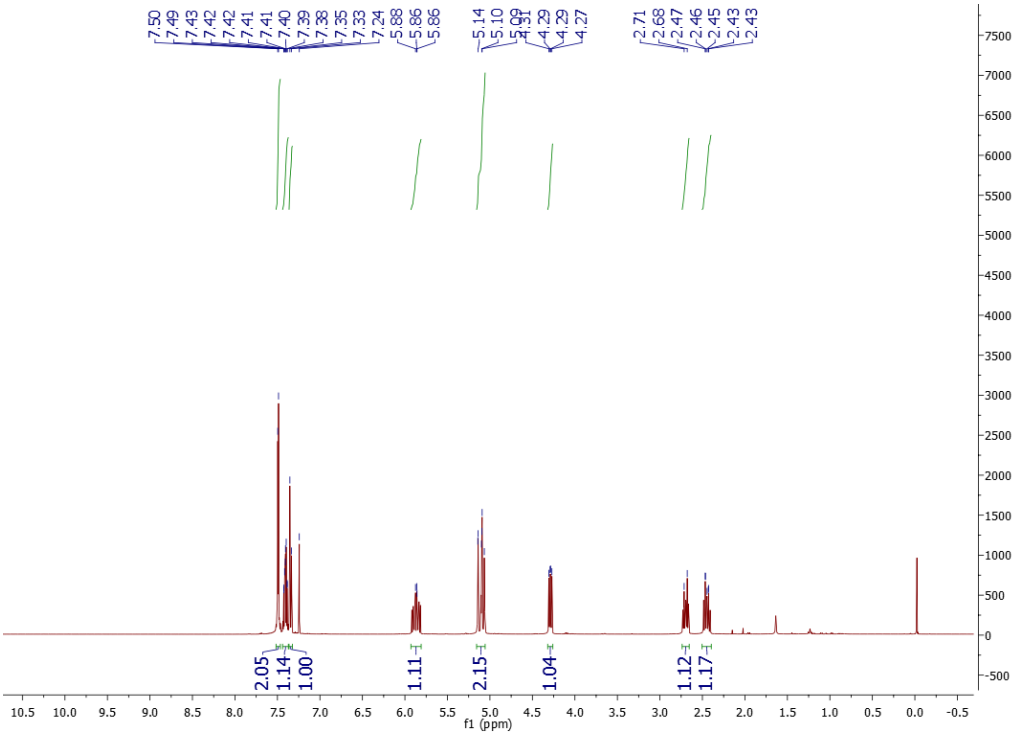
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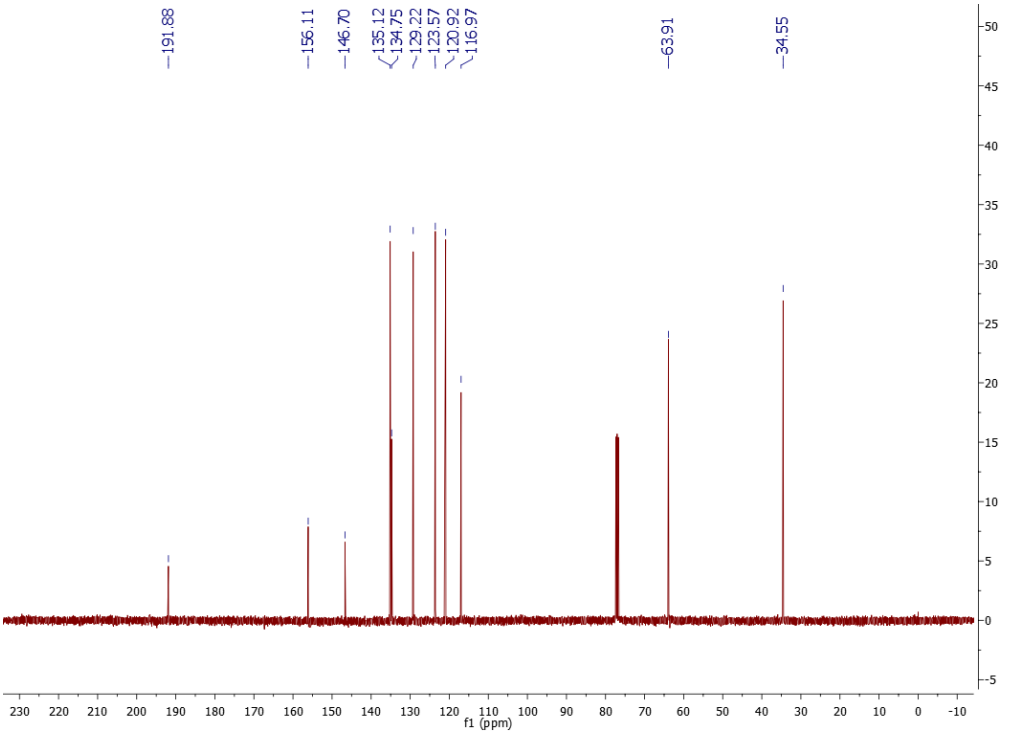
1.04
1.12
1.17
f1 (ppm)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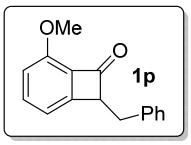
63.91
34.55
f1 (ppm)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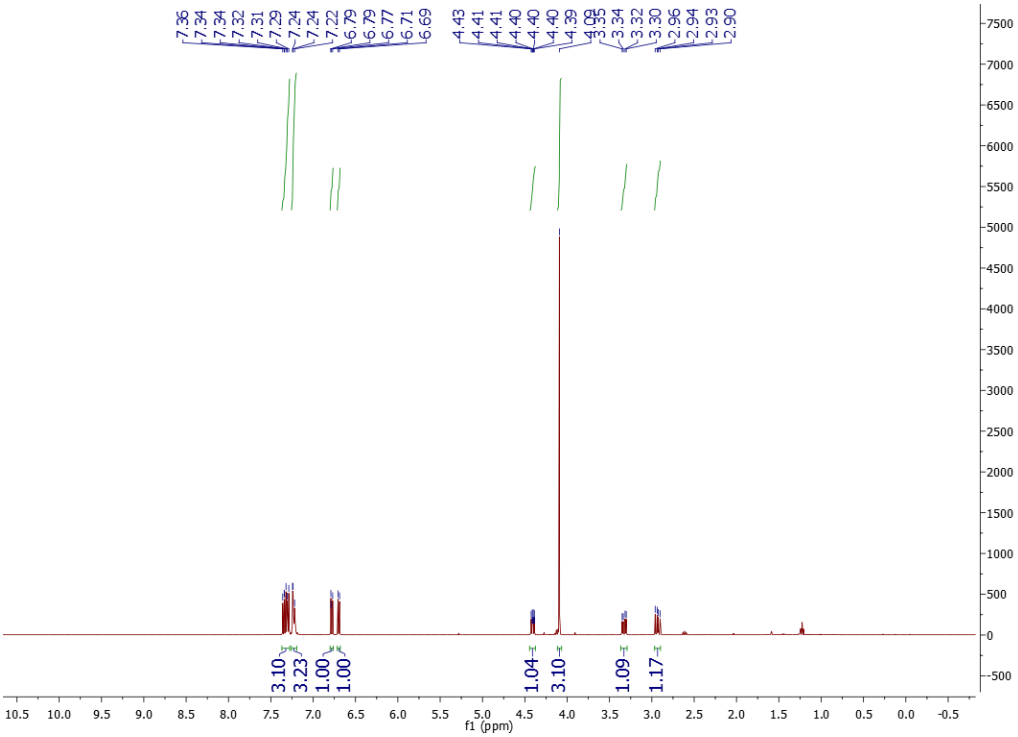
1p
Ph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6.69
4.43
4.41
4.41
4.40
4.40
4.40
4.39
4.09
3.95
3.34
3.32
3.30
2.96
2.94
2.93
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3.23
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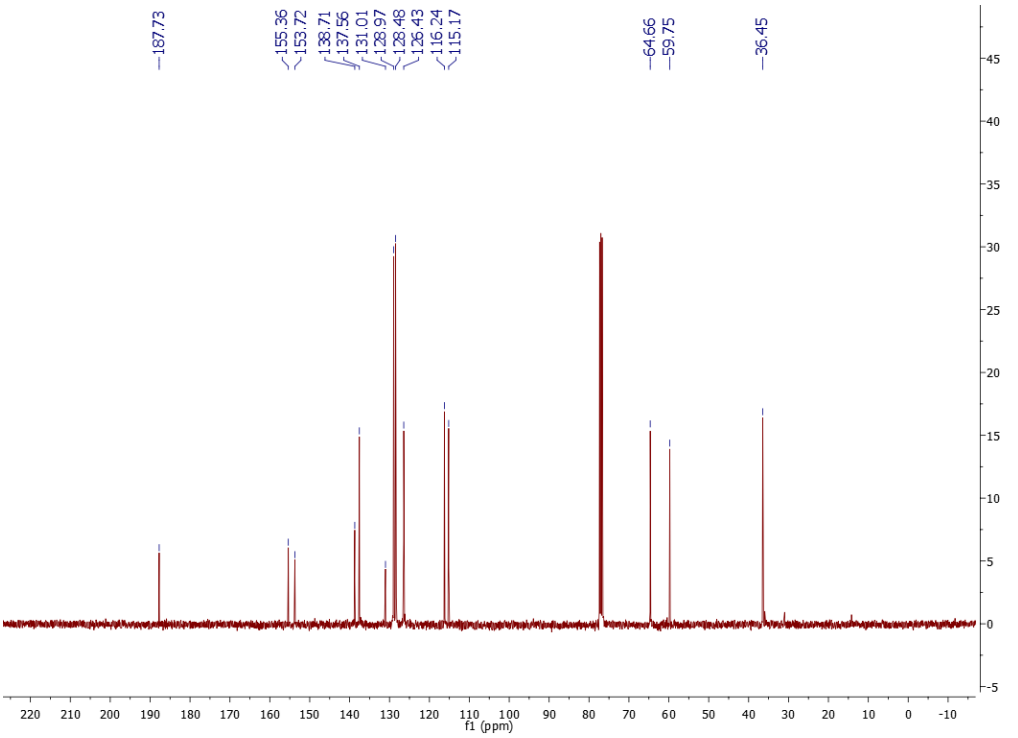
1.00
1.04
3.10
1.09
1.17
f1 (ppm)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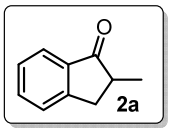
128.48
126.43
116.24
115.17
64.66
59.75
36.45
f1 (ppm)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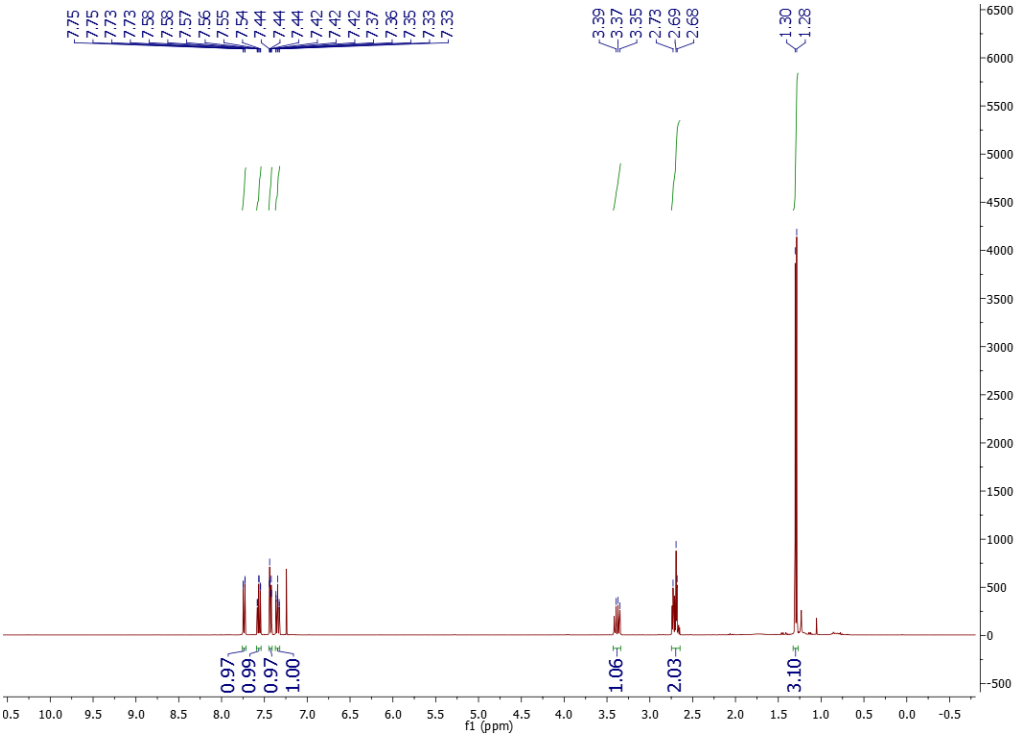
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7.56
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7.35
7.33
7.33
3.39
3.37
3.35
2.73
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2.68
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0.97
1.00
1.06
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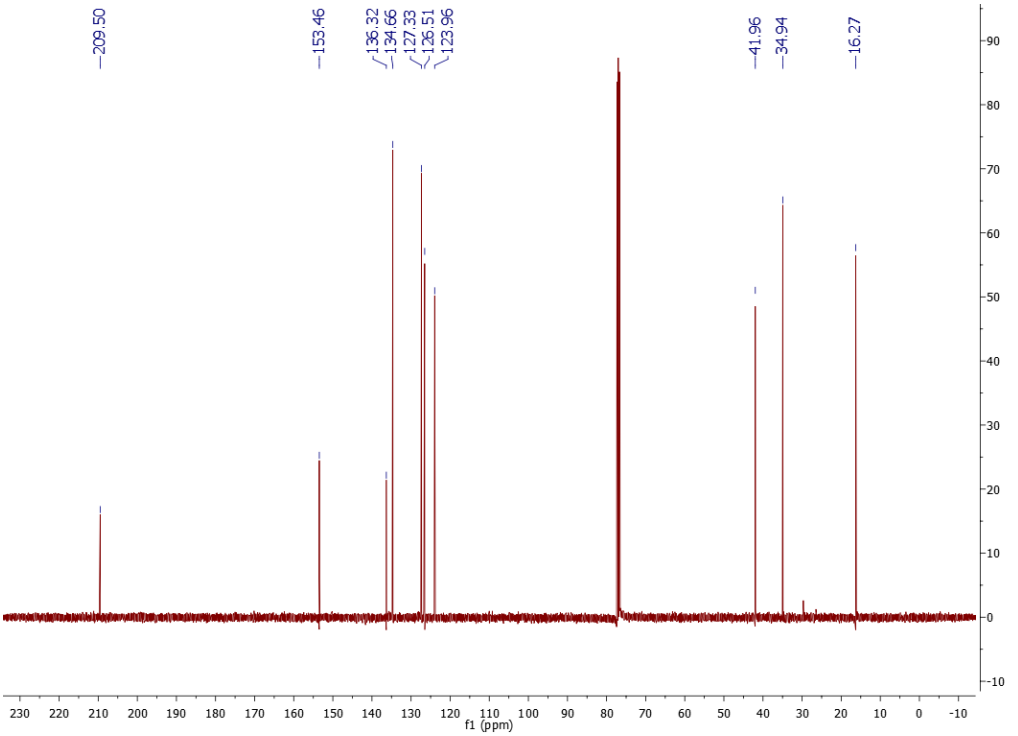
3.10
f1 (ppm)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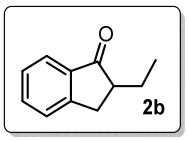
34.94
16.27
f1 (ppm)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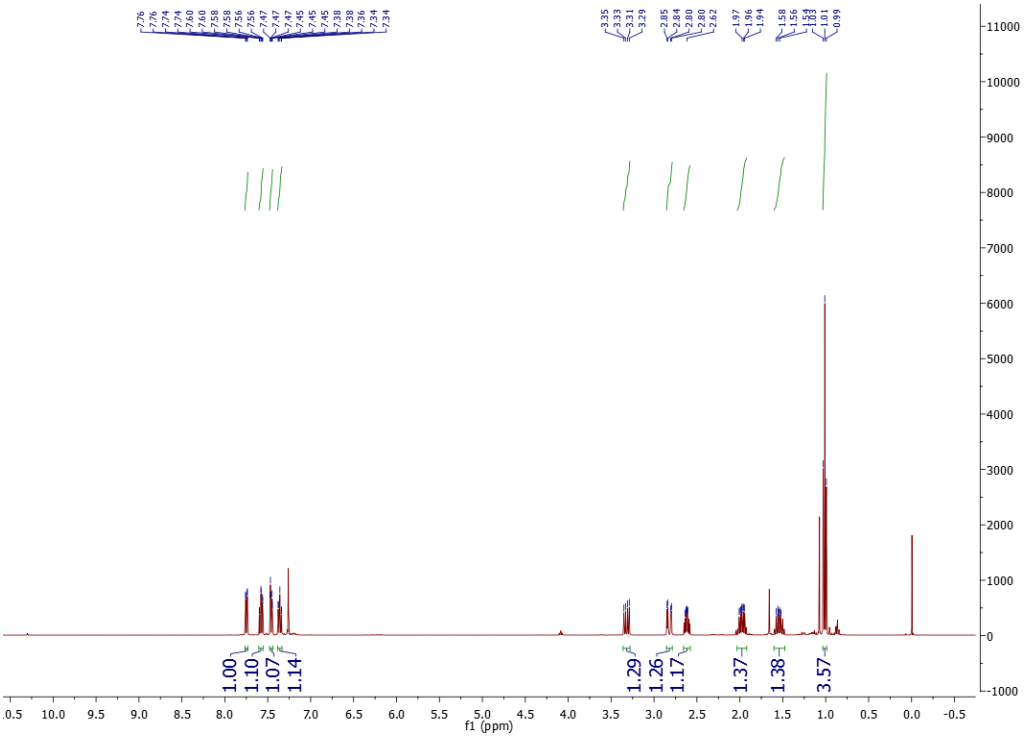
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7.47
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7.45
7.45
7.45
7.38
7.38
7.36
7.34
7.34
3.35
3.33
3.33
3.31
3.29
2.85
2.84
2.80
2.80
2.62
1.97
1.96
1.94
1.58
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1.04
1.03
1.01
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1.00
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1.26
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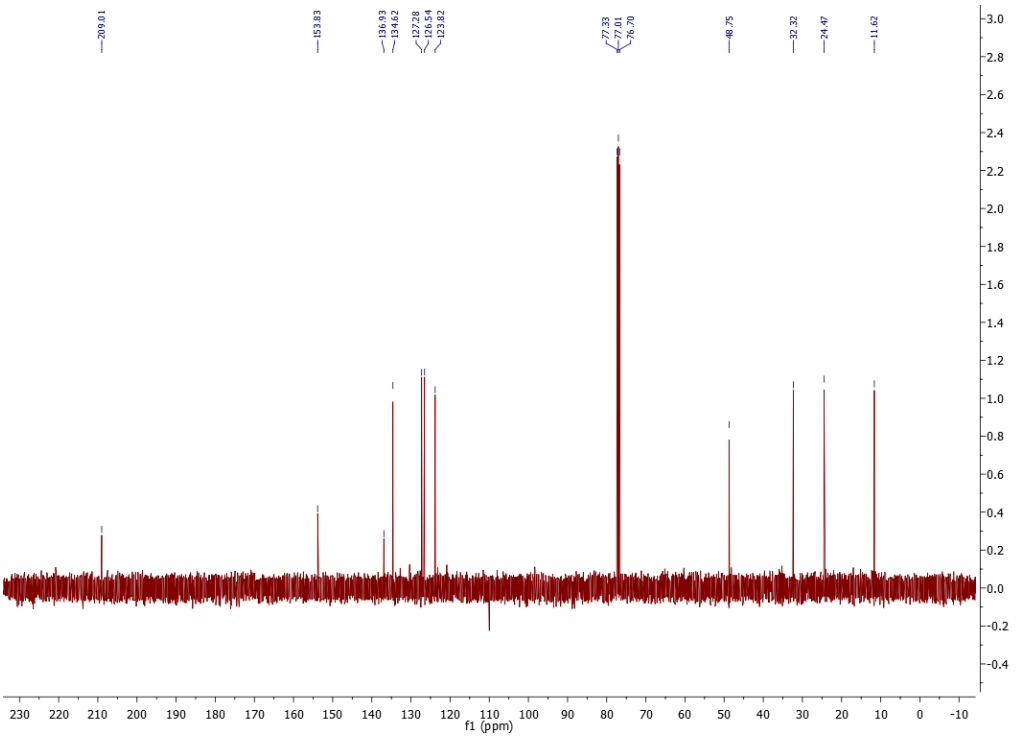
1.37
1.38
3.57
f1 (ppm)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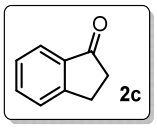
76.70
48.75
32.32
24.47
11.62
f1 (ppm)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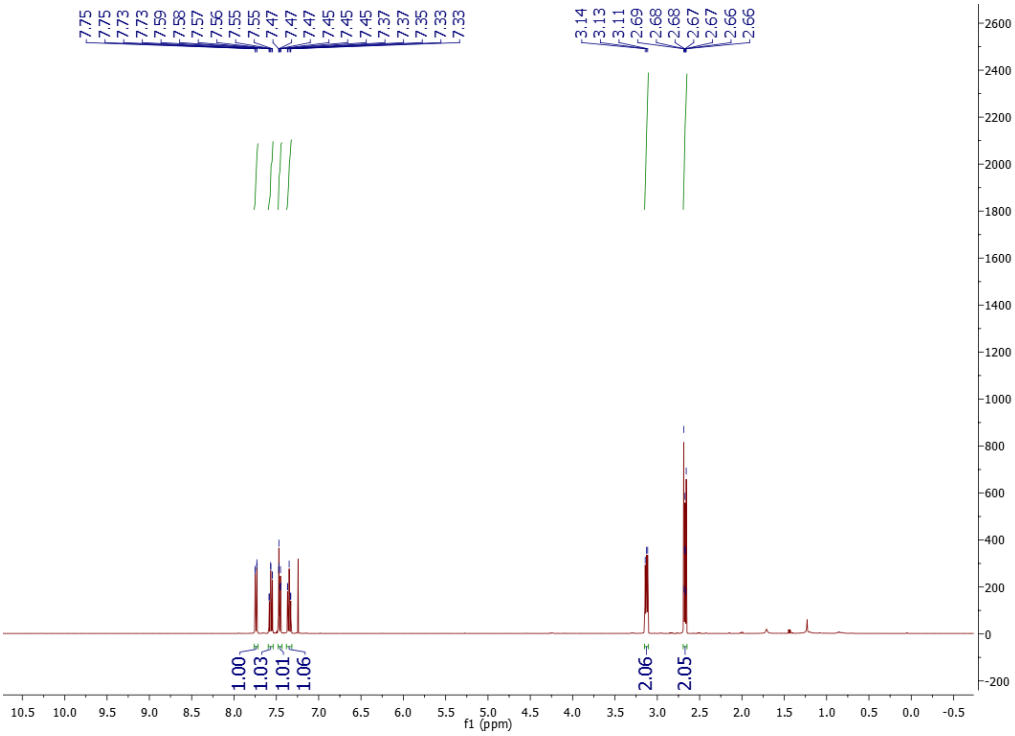
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7.47
7.45
7.45
7.45
7.37
7.37
7.35
7.33
7.33
3.14
3.13
3.11
2.69
2.68
2.68
2.67
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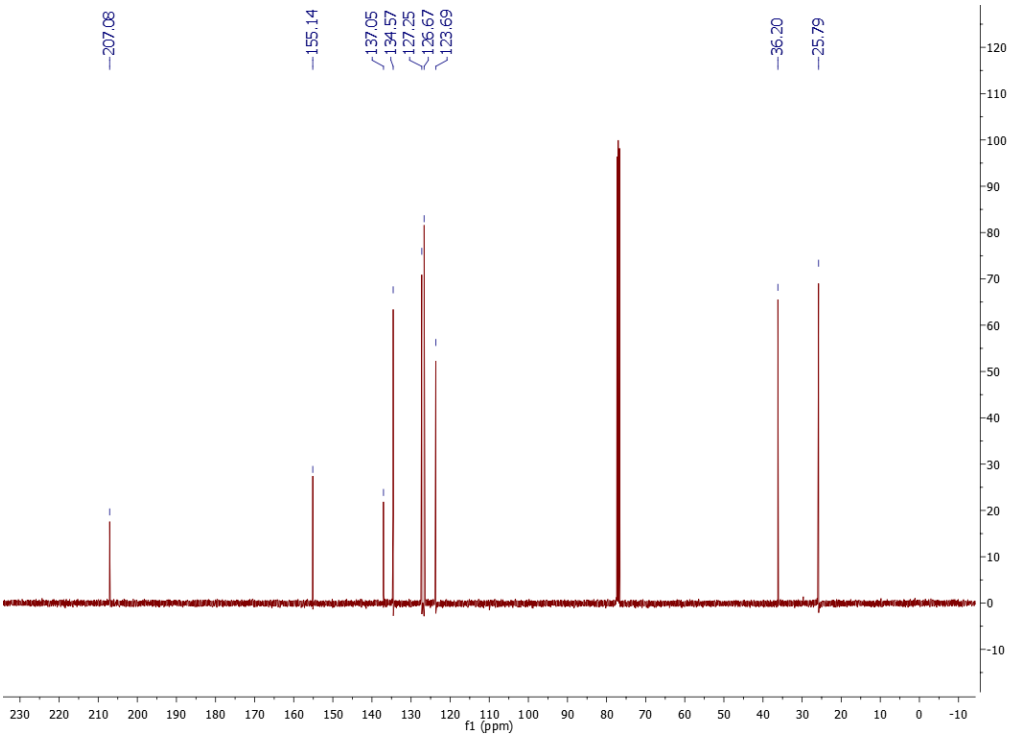
1.01
1.06
2.06
2.05
f1 (ppm)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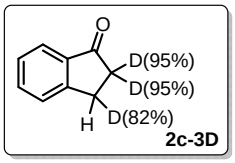
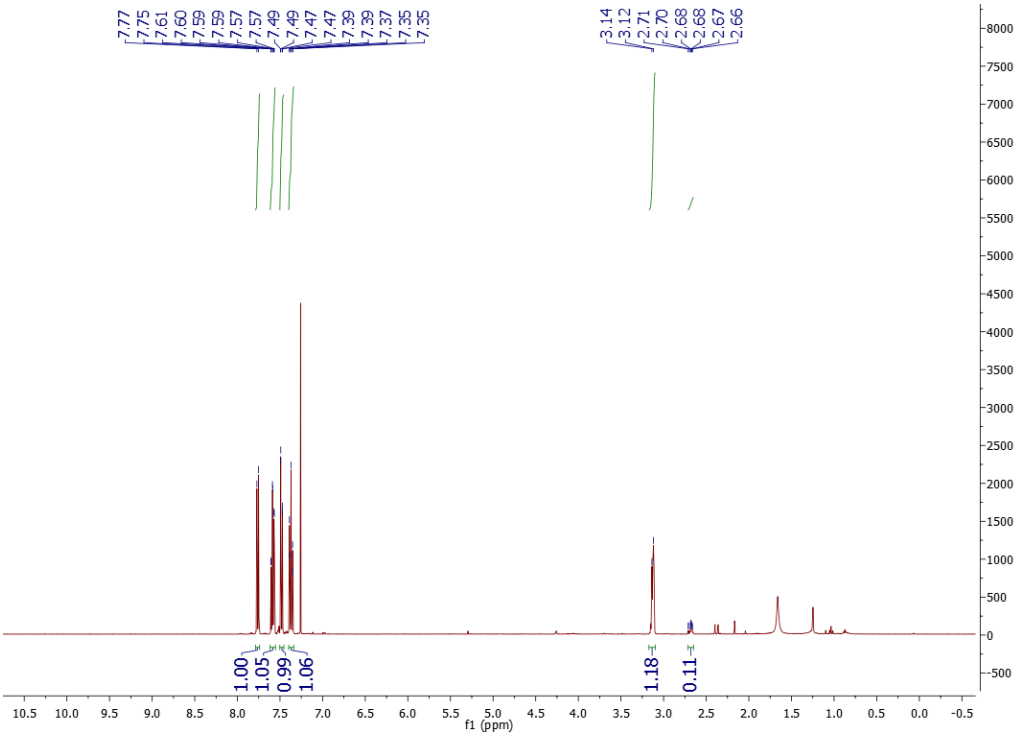
126.67
123.69
36.20
25.79
f1 (ppm)


O
D(95%)
D(95%)
H
D(82%)
2c-3D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7.57
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7.49
7.47
7.47
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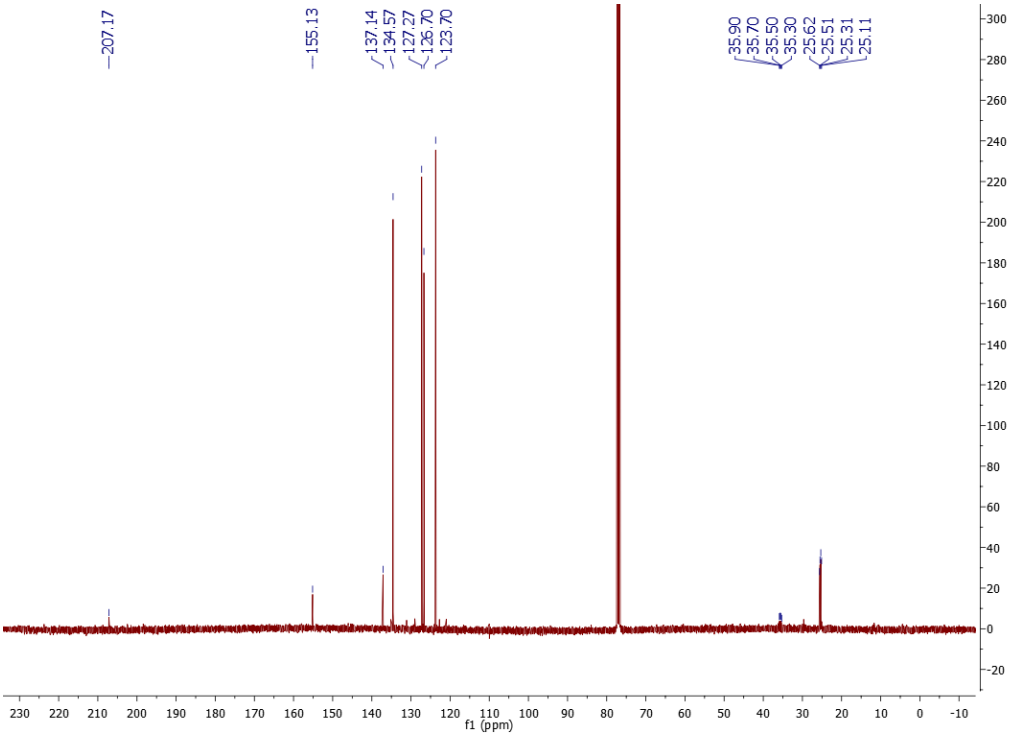
7.37
7.35
7.35
3.14
3.12
2.71
2.70
2.68
2.68
2.67
2.66
1.00
1.05
0.99
1.06
1.18
0.11
f1 (ppm)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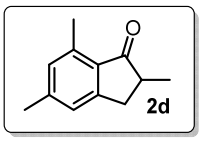
35.50
35.30
25.62
25.51
25.31
25.11
f1 (ppm)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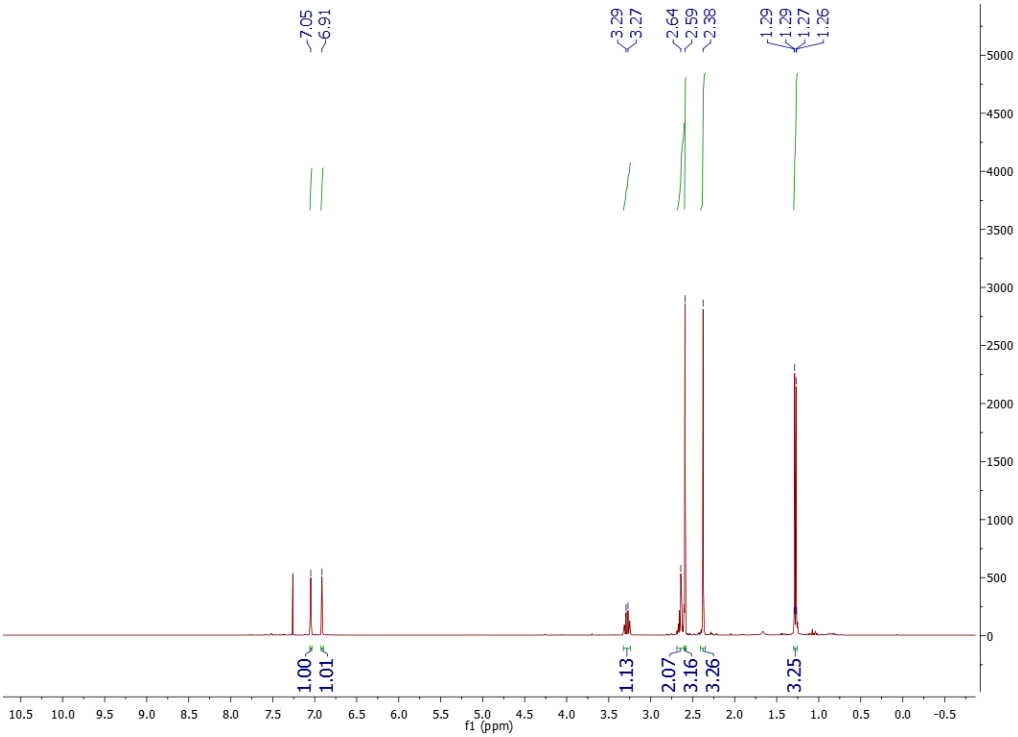
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1.29
1.27
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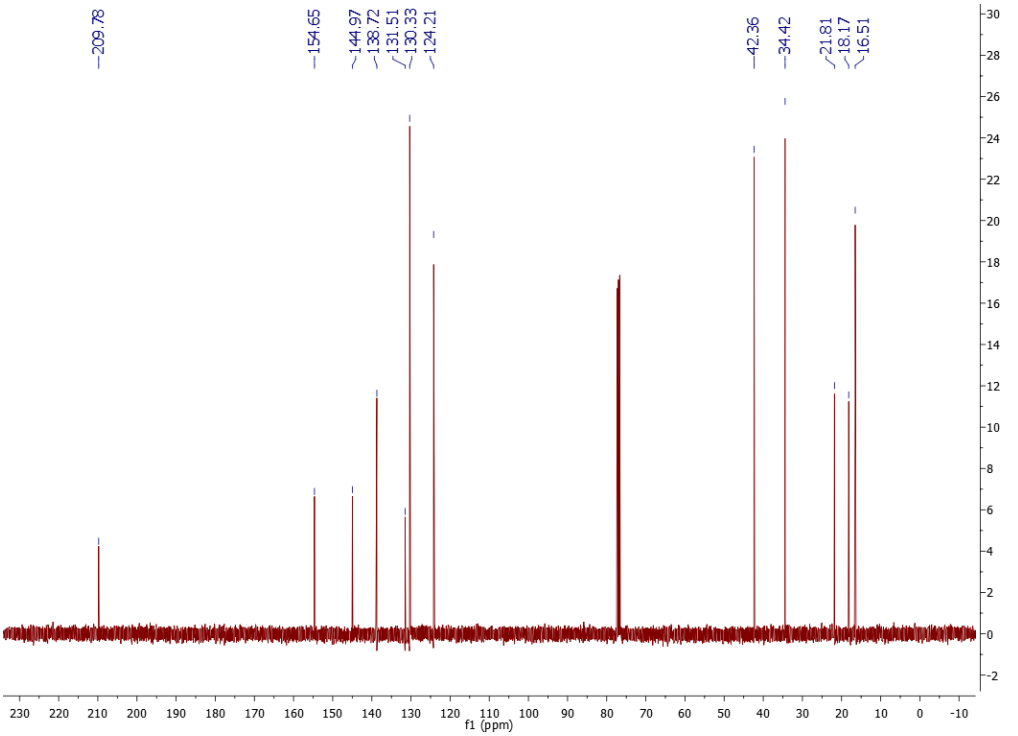
2.07
3.16
3.26
3.25
f1 (ppm)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124.21
42.36
34.42
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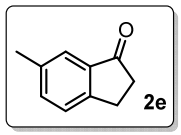
18.17
16.51
f1 (ppm)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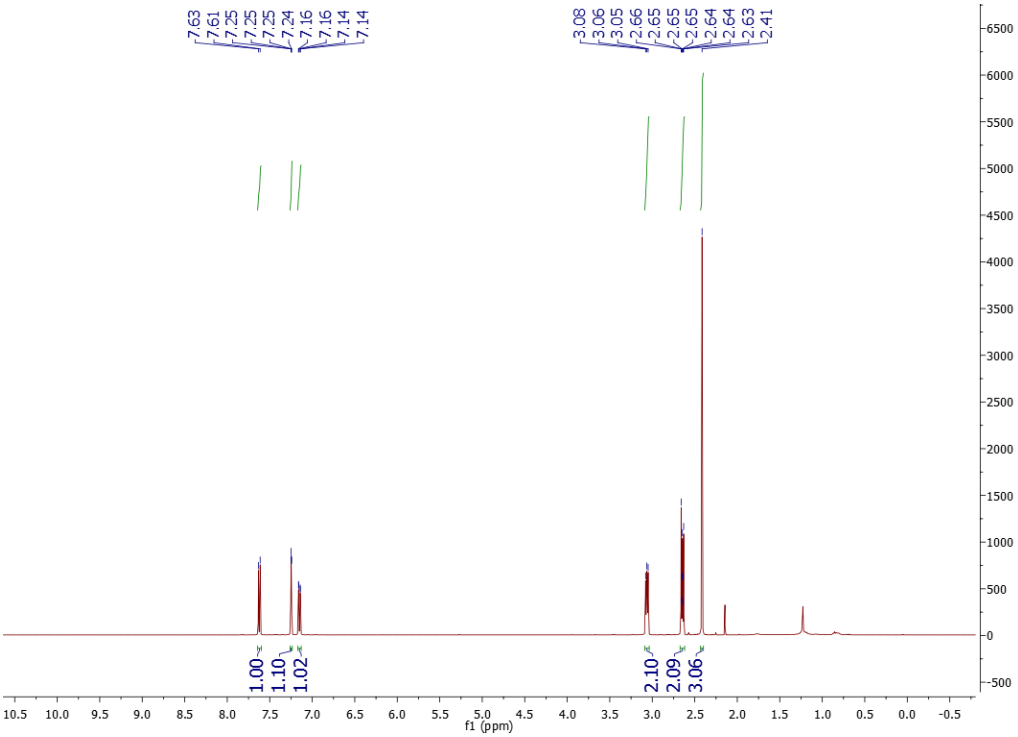
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7.25
7.24
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7.16
7.14
7.14
3.08
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3.05
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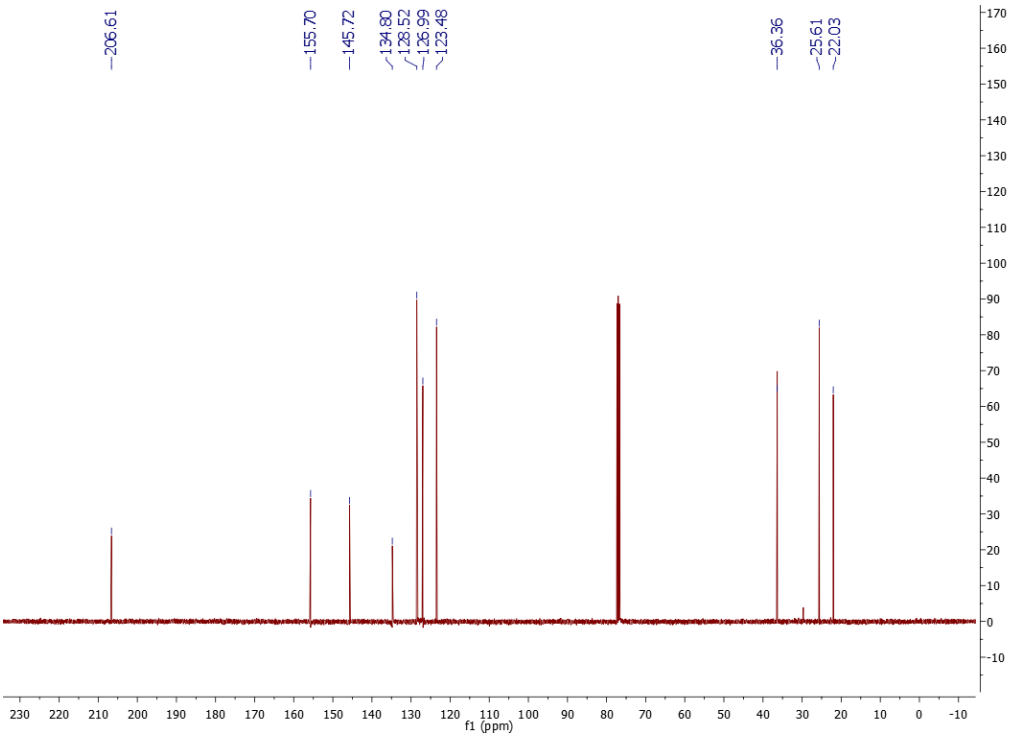
1.02
2.10
2.09
3.06
f1 (ppm)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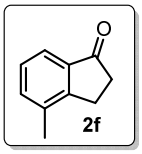
25.61
22.03
f1 (ppm)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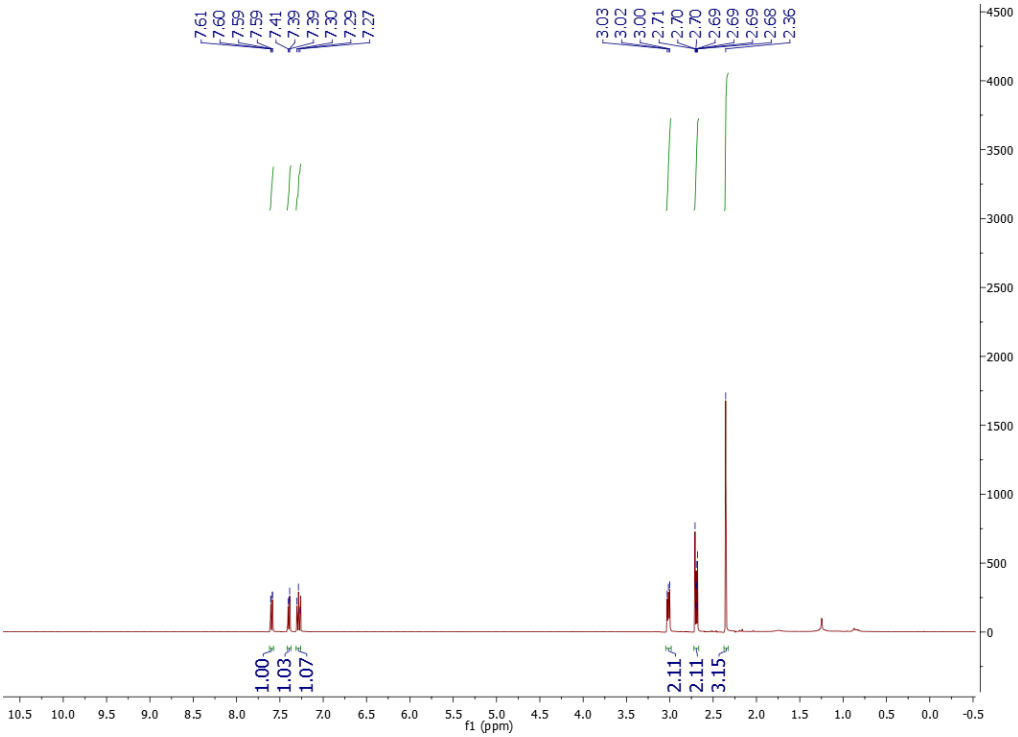
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7.27
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2.70
2.70
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2.69
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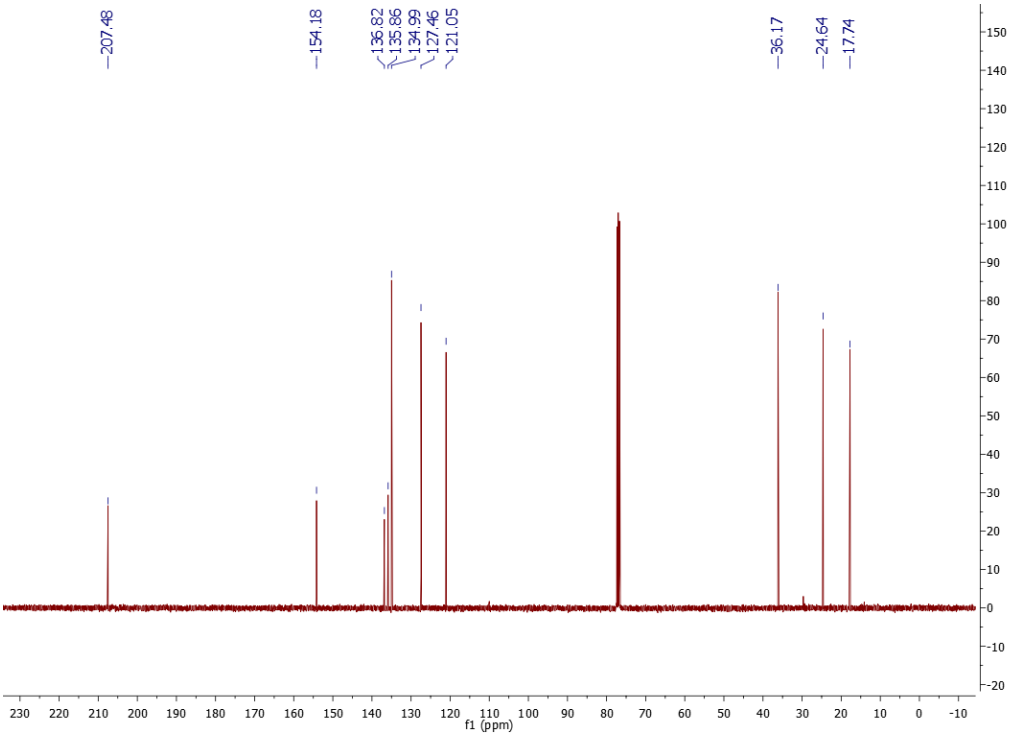
1.03
1.07
2.11
2.11
3.15
f1 (ppm)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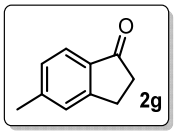
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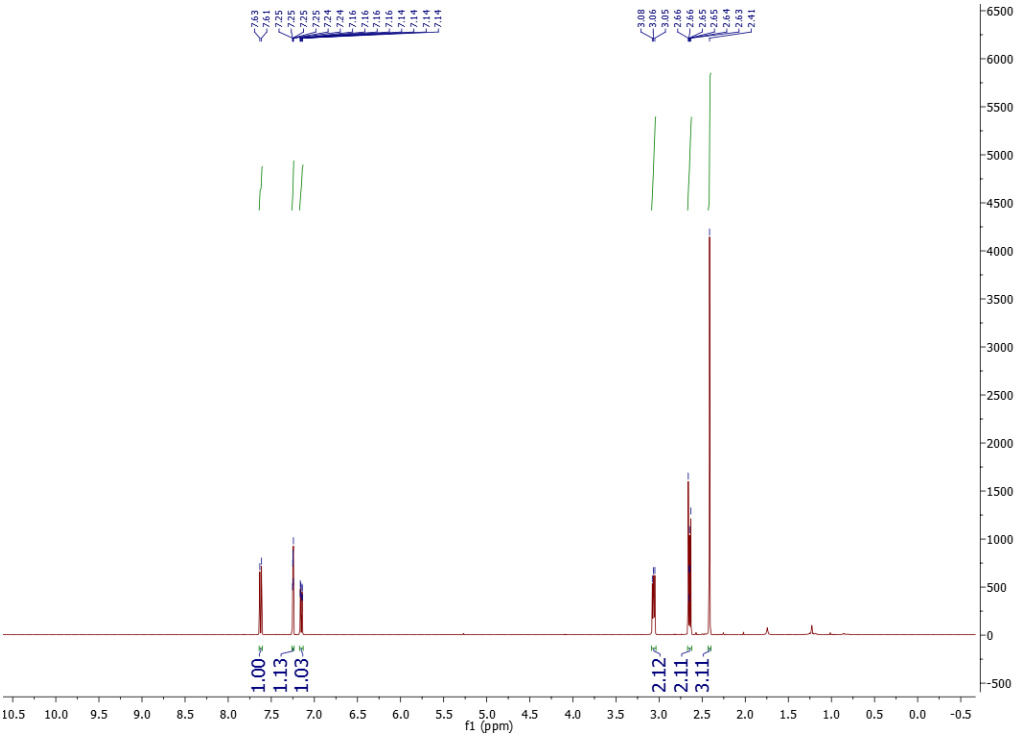
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7.14
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2.12
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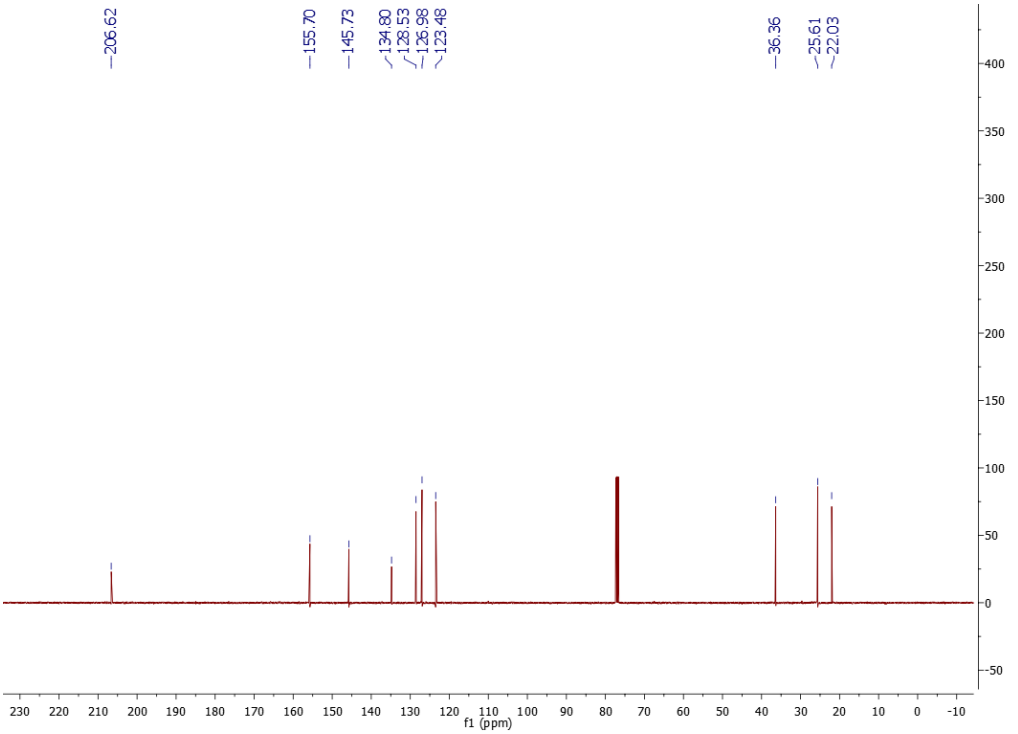
3.11
f1 (ppm)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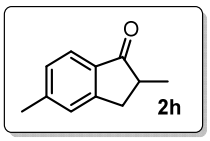
25.61
22.03
f1 (ppm)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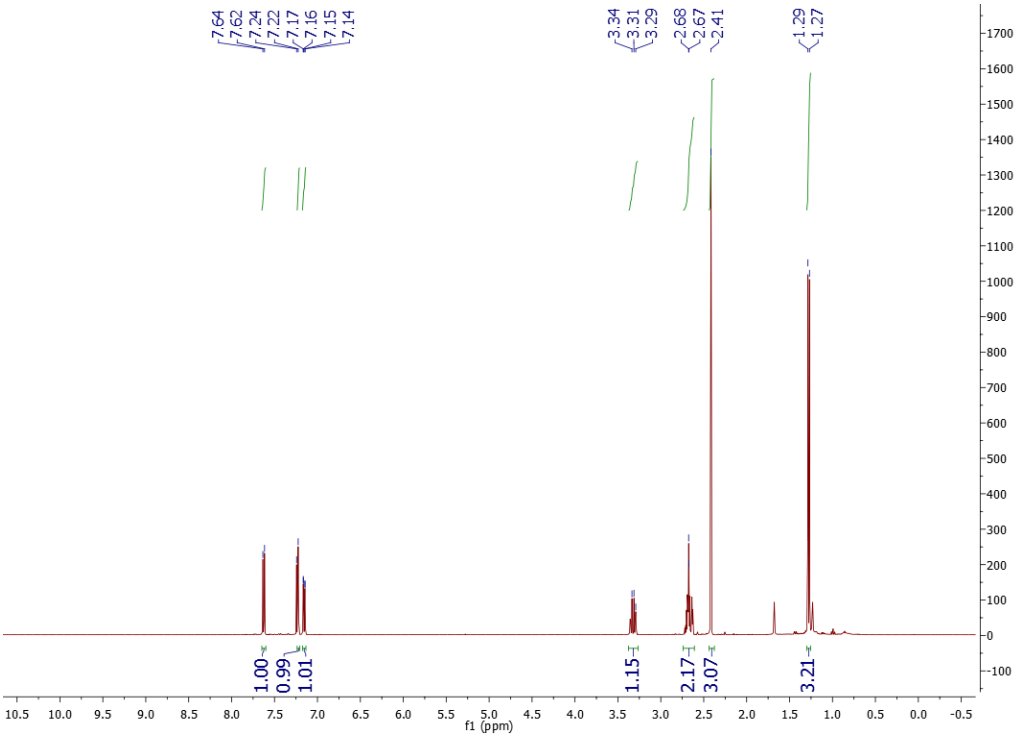
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7.15
7.14
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3.31
3.29
2.68
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2.41
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1.27
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1.01
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2.17
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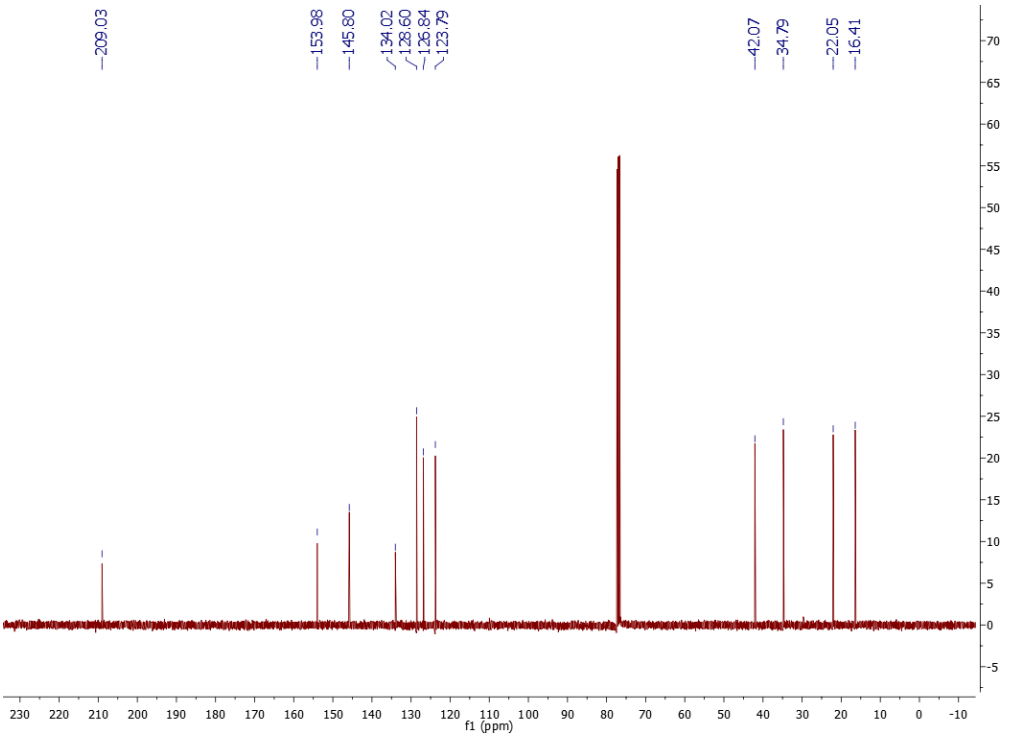
3.21
f1 (ppm)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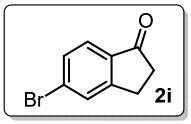
f1 (ppm)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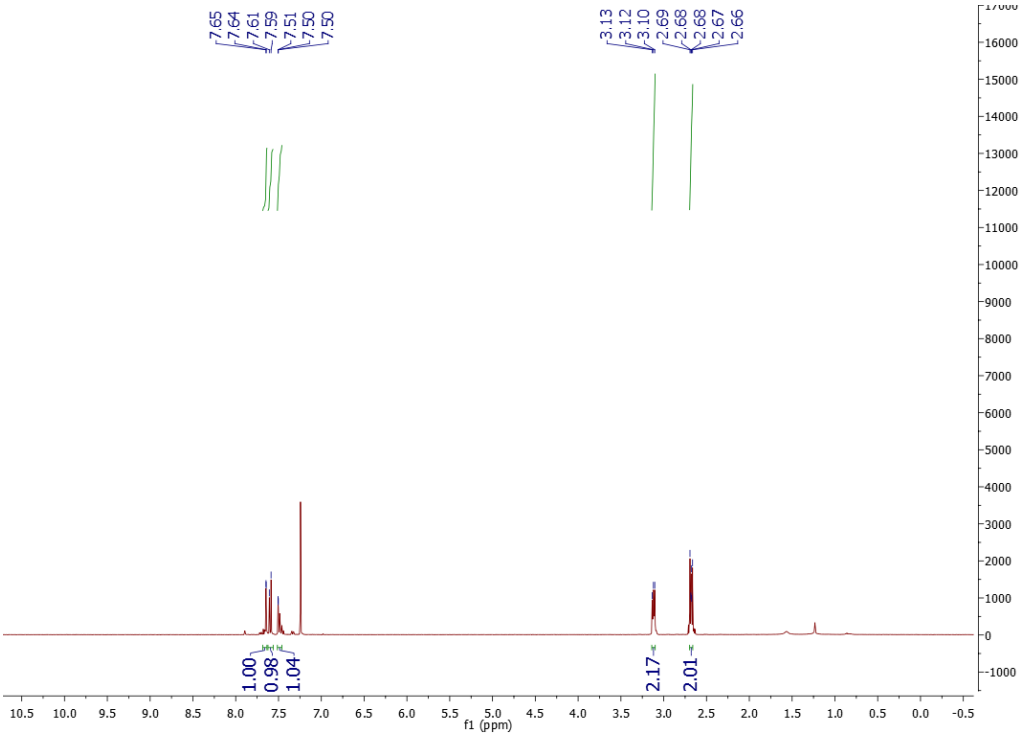
Br
2i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3.12
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2.68
2.67
2.66
1.00
0.98
1.04
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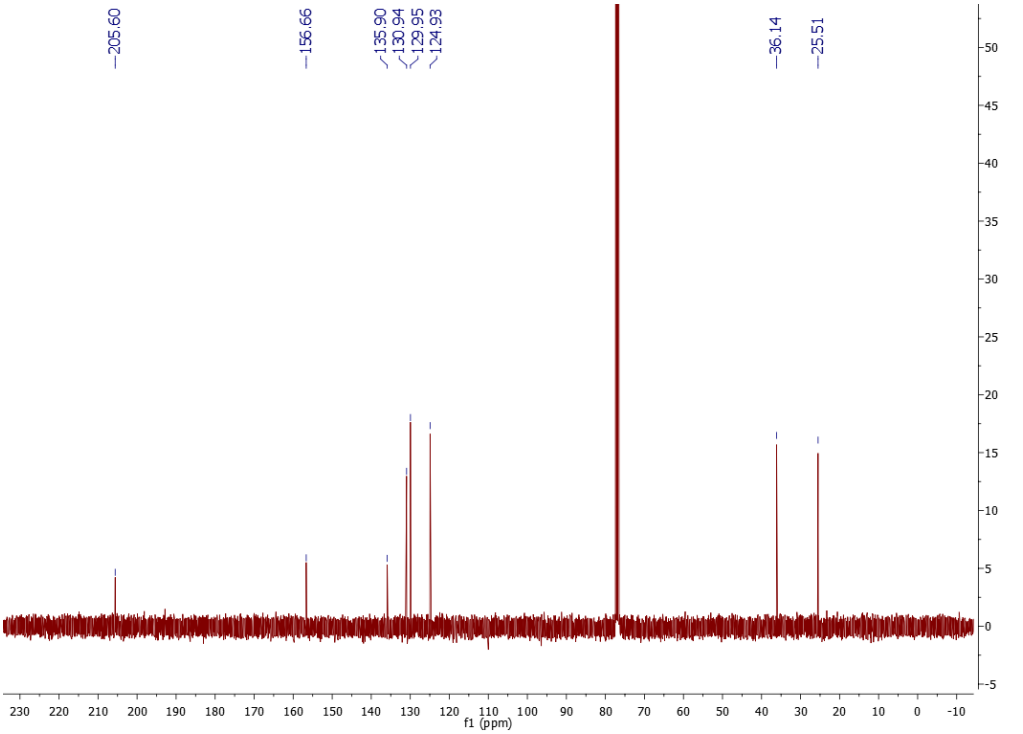
2.01
f1 (ppm)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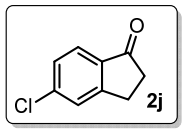
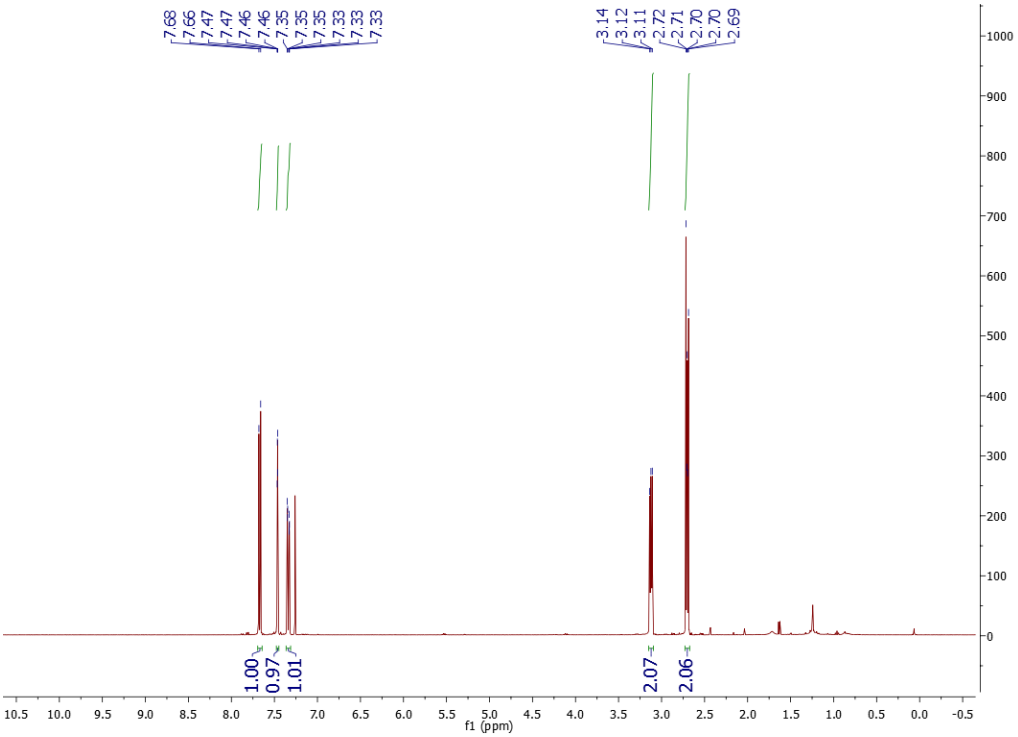

O
Cl
2j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3.12
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2.70
2.69
1.00
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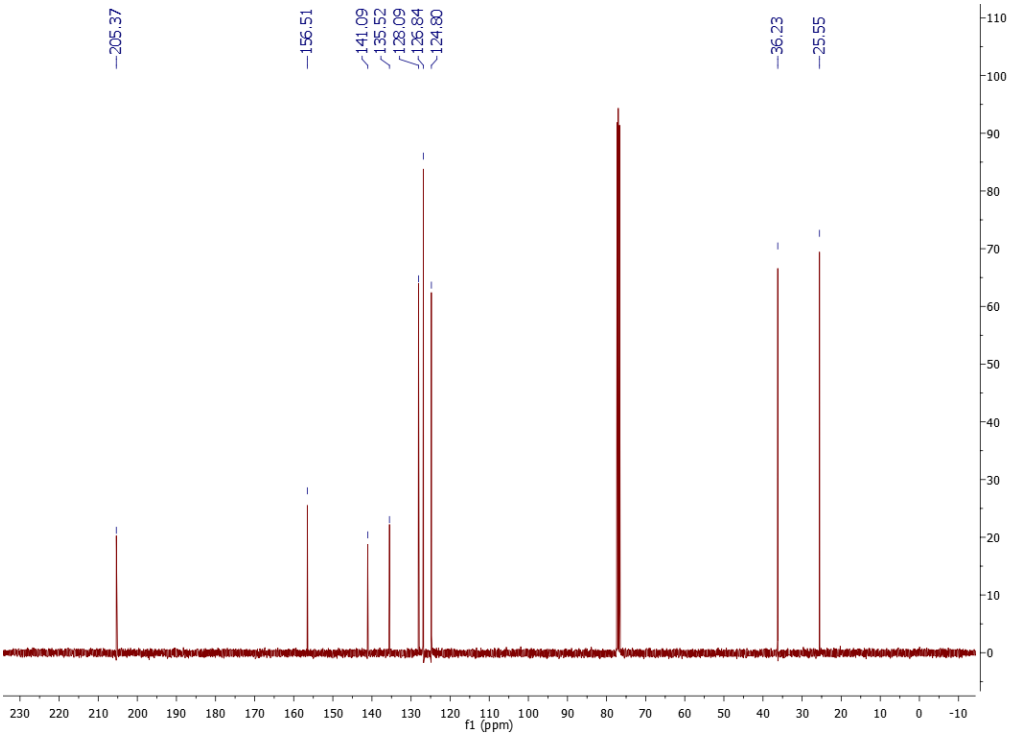
1.01
2.07
2.06
f1 (ppm)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124.80
36.23
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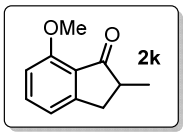
f1 (ppm)


OMe
O
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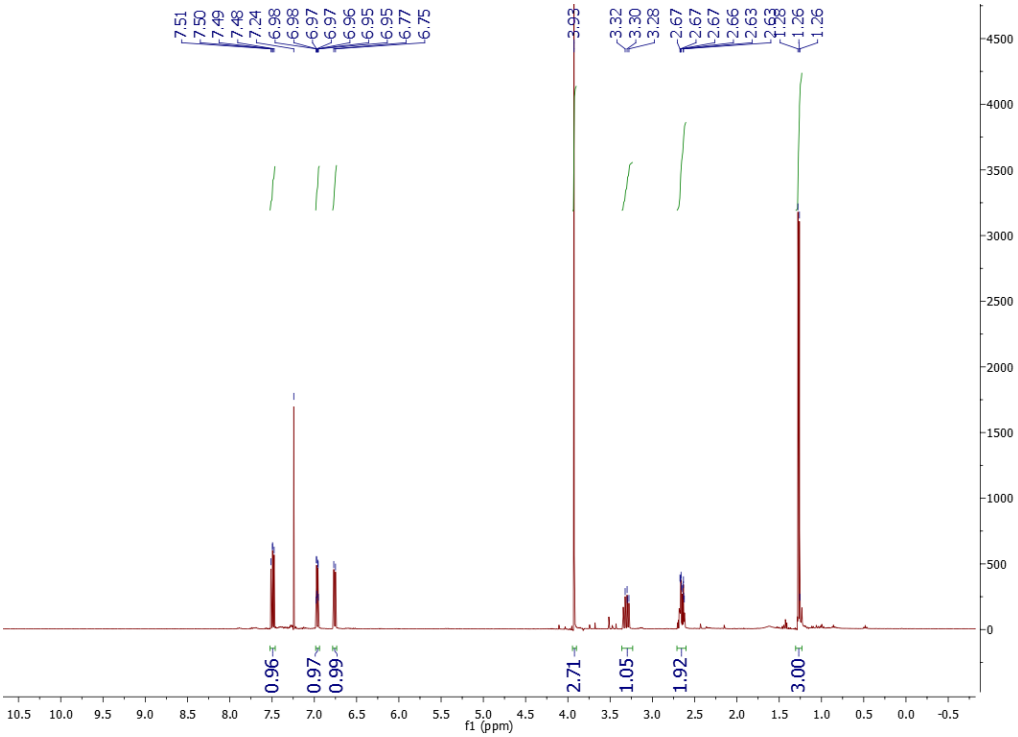
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3.28
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2.66
2.63
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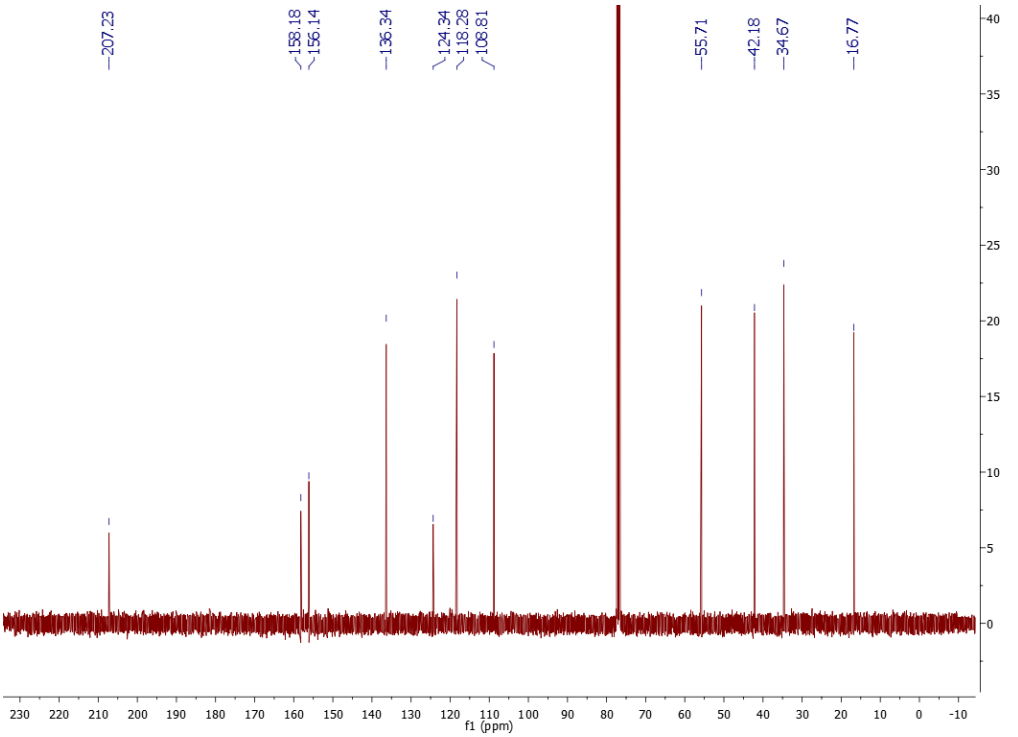
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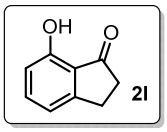
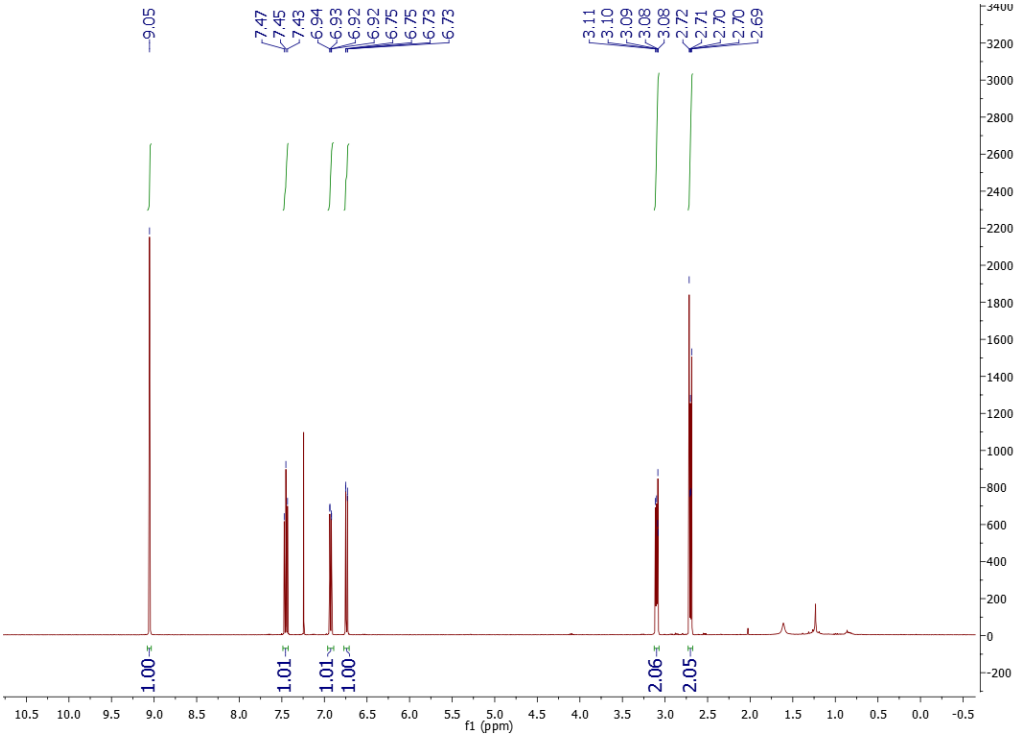
42.18
34.67
16.77
f1 (ppm)


OH
O
2l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6.92
6.92
6.75
6.75
6.73
6.73
3.11
3.10
3.09
3.08
3.08
2.72
2.71
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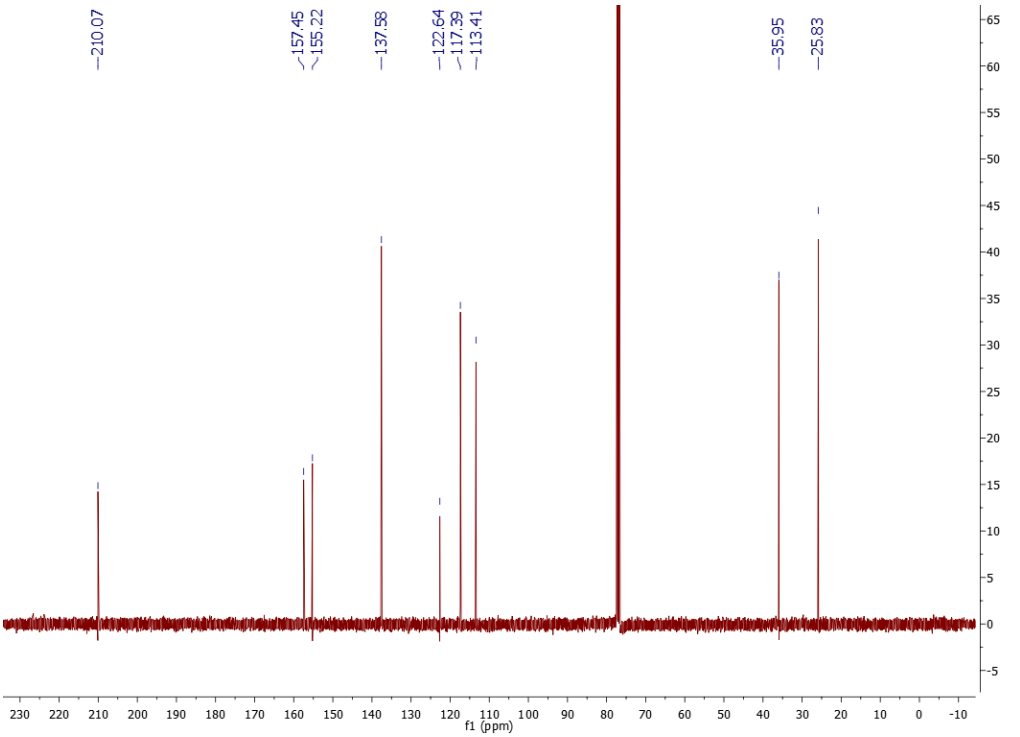
2.70
2.69
1.00
1.01
1.01
1.00
2.06
2.05
f1 (ppm)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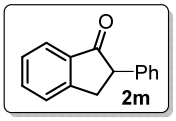
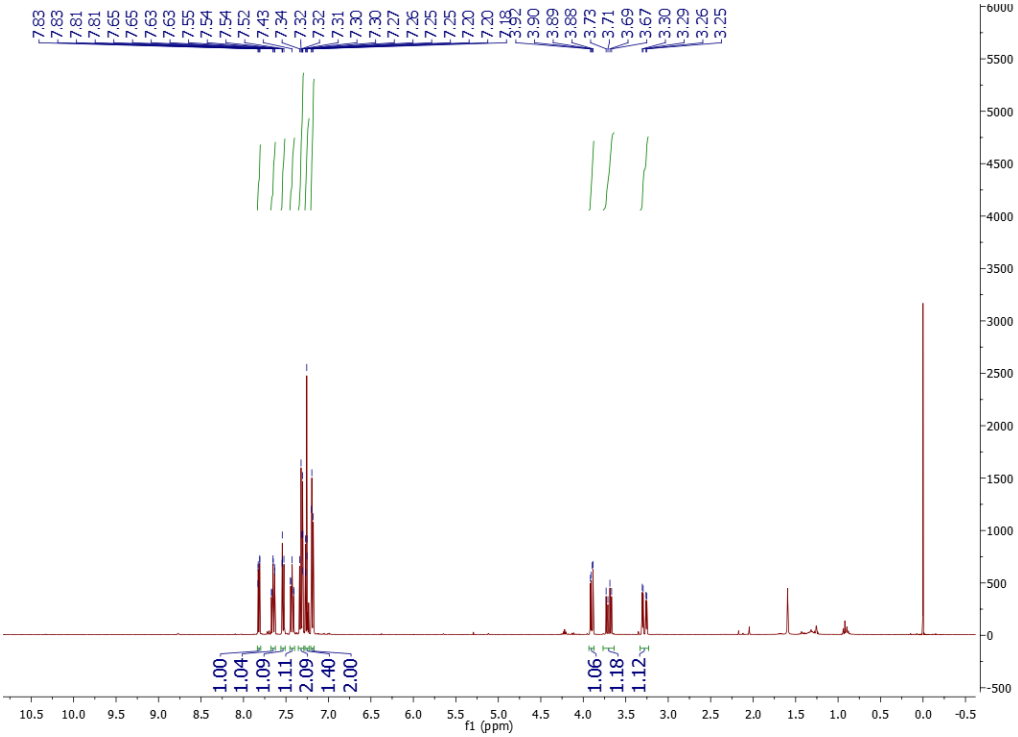
122.64
117.39
113.41
35.95
25.83
f1 (ppm)


O
Ph
2m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7.54
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7.43
7.34
7.32
7.32
7.31
7.30
7.30
7.27
7.26
7.25
7.25
7.20
7.20
7.18
3.92
3.90
3.89
3.88
3.73
3.71
3.69
3.67
3.30
3.29
3.26
3.25
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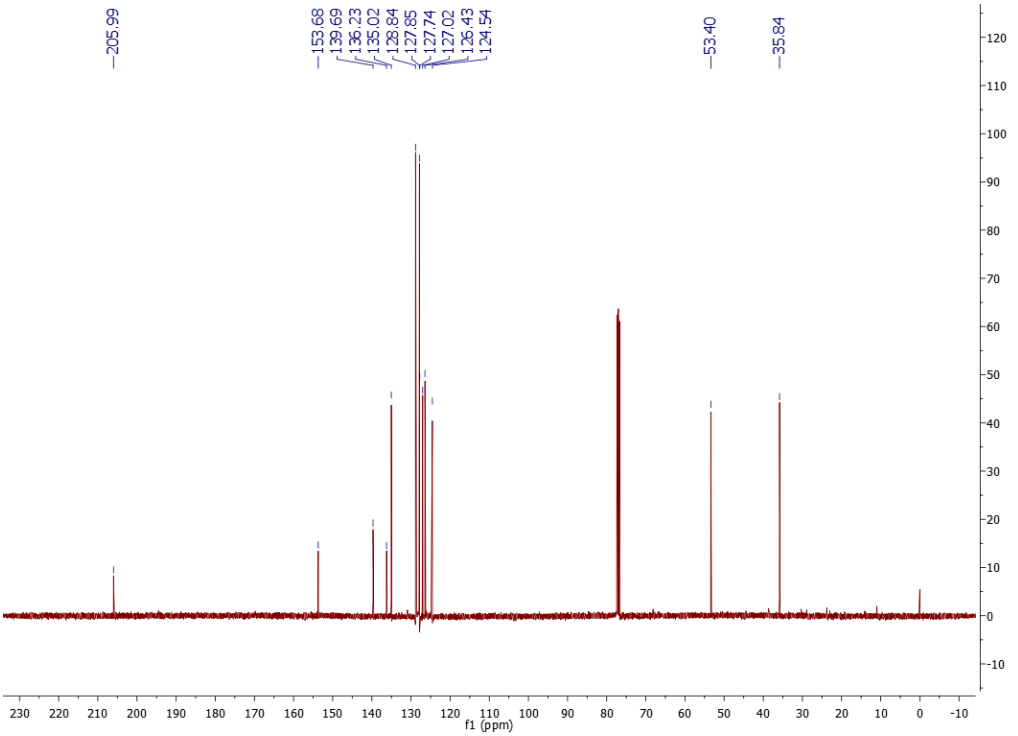
2.00
1.06
1.18
1.12
f1 (ppm)


205.99
153.68
139.69
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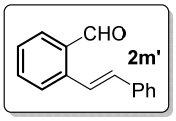
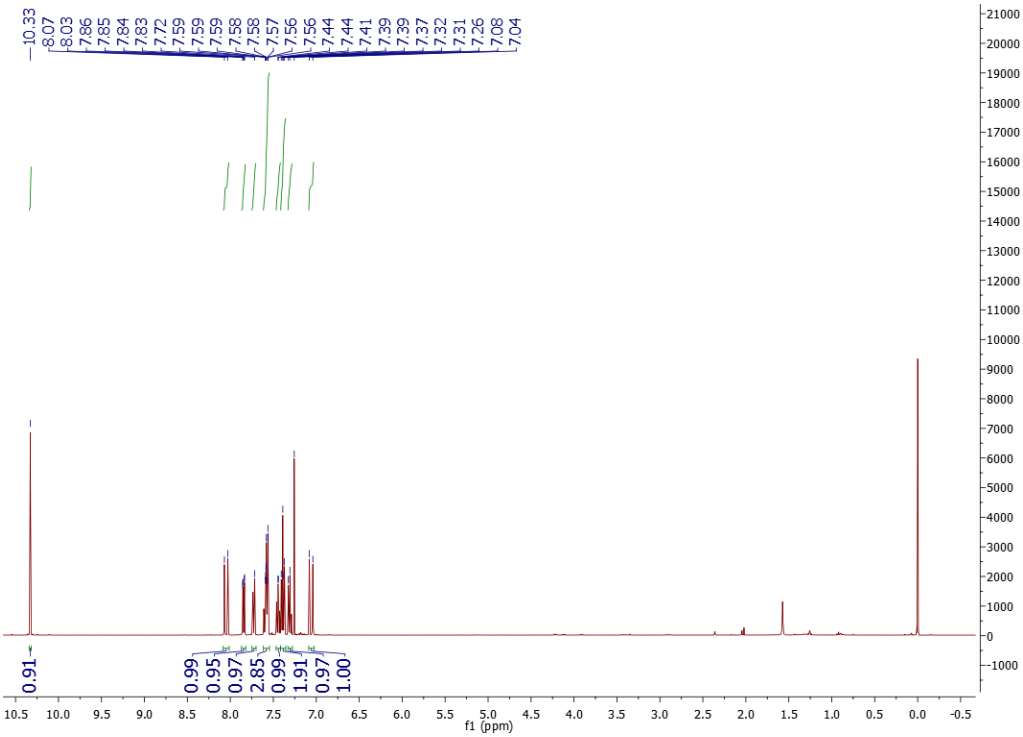
128.84
127.85
127.74
127.02
126.43
124.54
53.40
35.84
f1 (ppm)


CHO
2m'
Ph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8.03
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7.85
7.84
7.83
7.72
7.59
7.59
7.59
7.58
7.58
7.57
7.56
7.56
7.44
7.44
7.41
7.39
7.39
7.37
7.32
7.31
7.26
7.08
7.04
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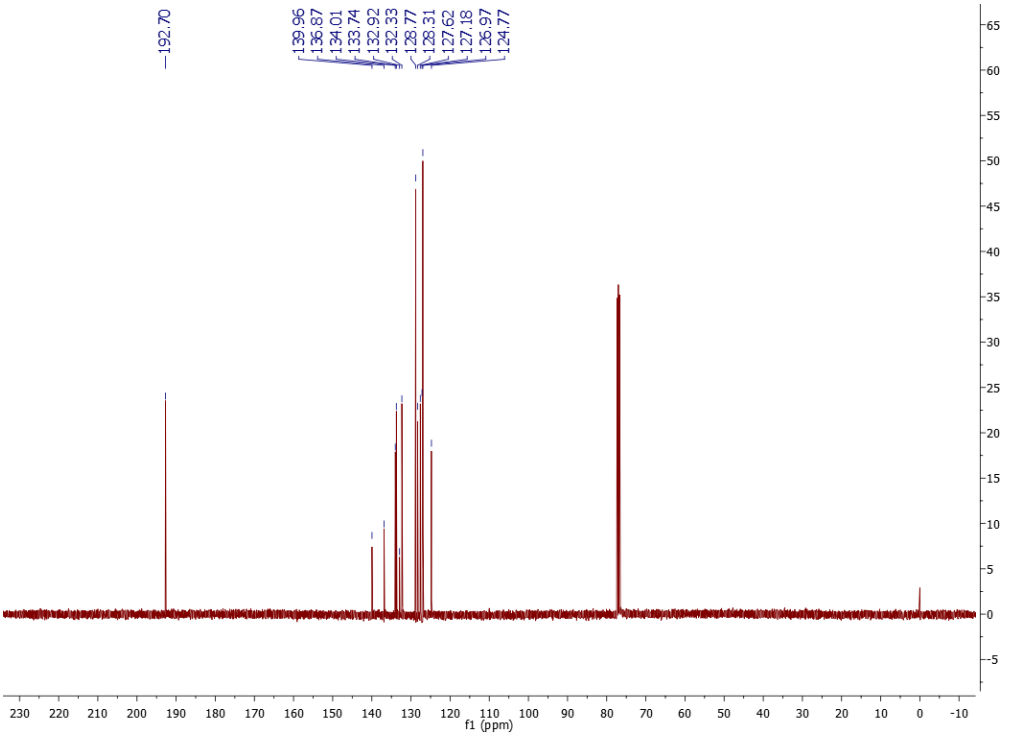
0.99
0.95
0.97
2.85
0.99
1.91
0.97
1.00
f1 (ppm)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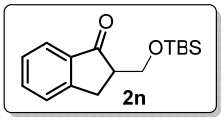
127.62
127.18
126.97
124.77
f1 (ppm)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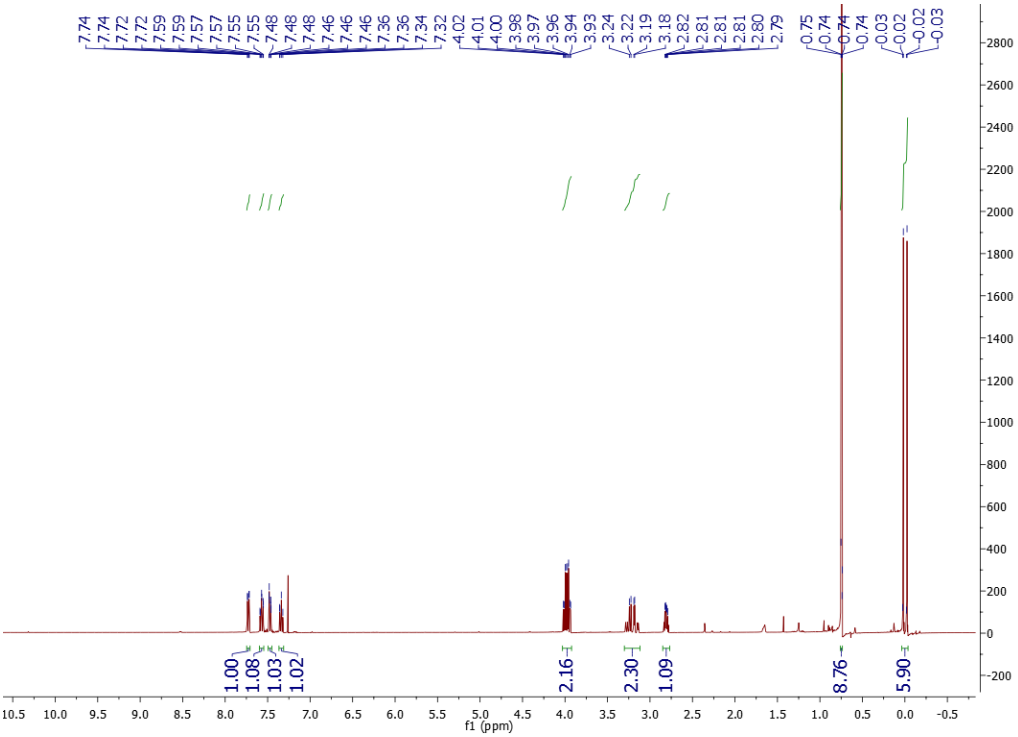
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7.55
7.48
7.48
7.48
7.46
7.46
7.46
7.36
7.36
7.34
7.32
4.02
4.01
4.00
3.98
3.97
3.96
3.94
3.93
3.24
3.22
3.19
3.18
2.82
2.81
2.81
2.81
2.80
2.79
0.75
0.74
0.74
0.74
0.03
0.02
-0.02
-0.03
1.00
1.08
1.03
1.02
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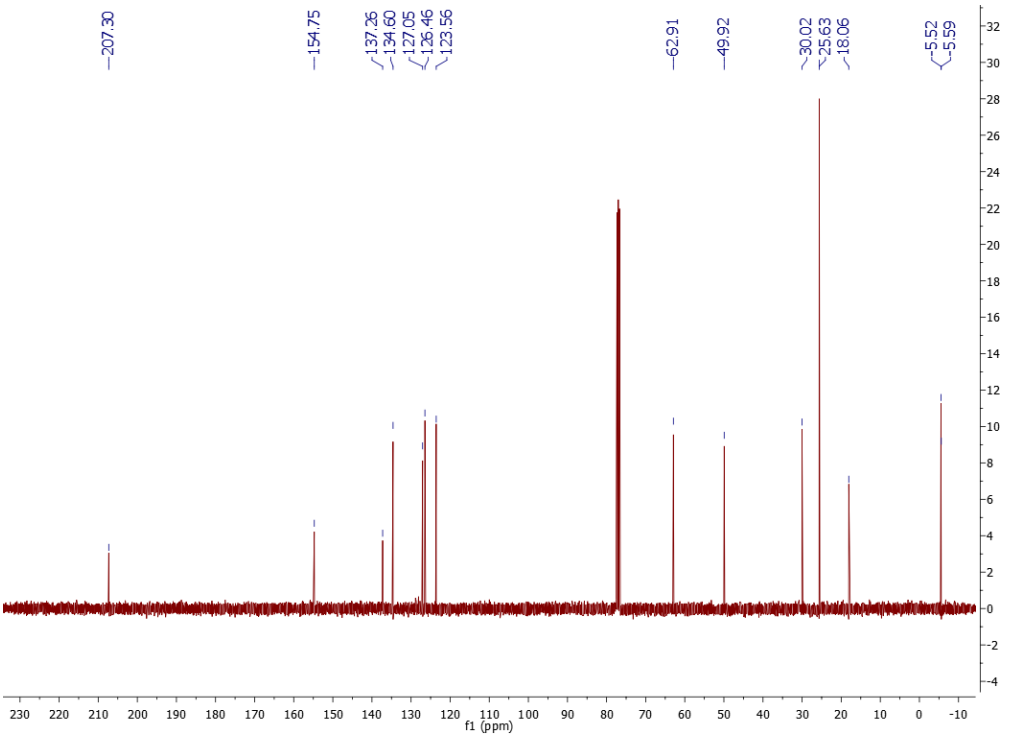
2.30
1.09
8.76
5.90
f1 (ppm)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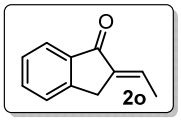
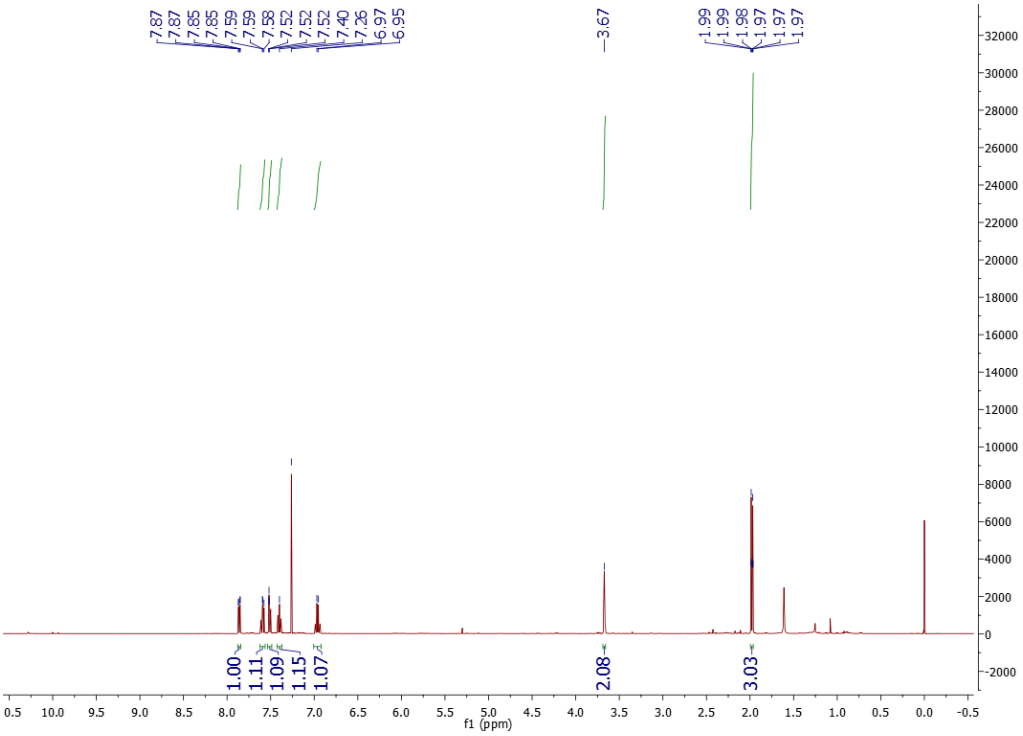
62.91
49.92
30.02
25.63
18.06
-5.52
-5.59
f1 (ppm)


O
2o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7.52
7.52
7.52
7.40
7.26
6.97
6.95
3.67
1.99
1.99
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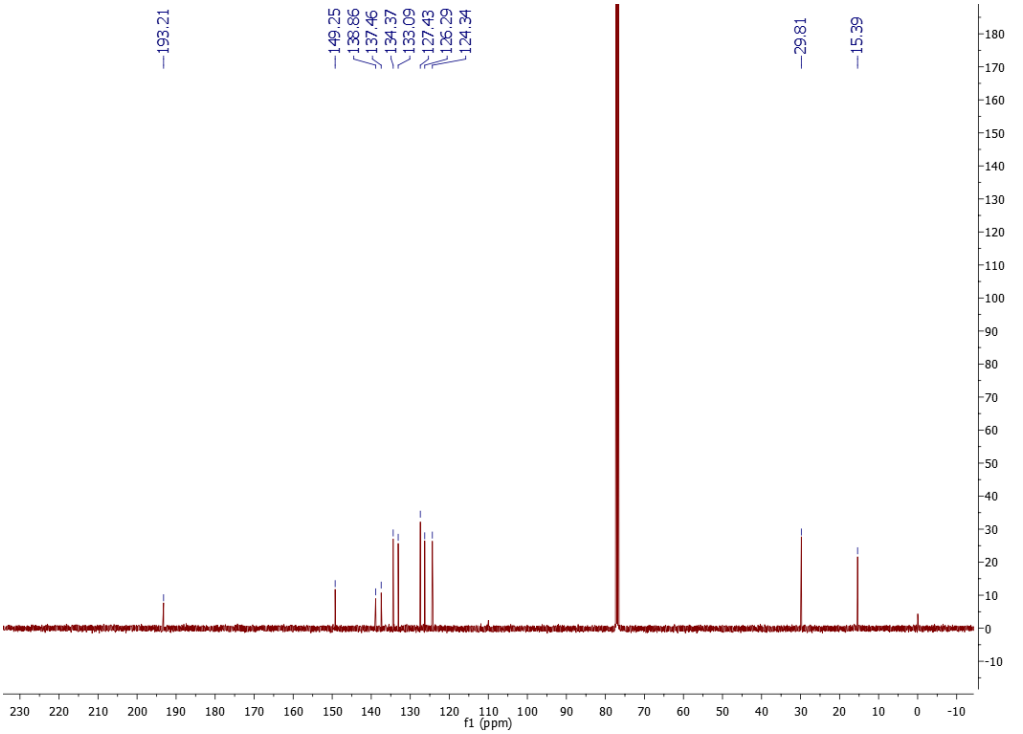
1.15
1.07
2.08
3.03
f1 (ppm)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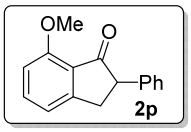
15.39
f1 (ppm)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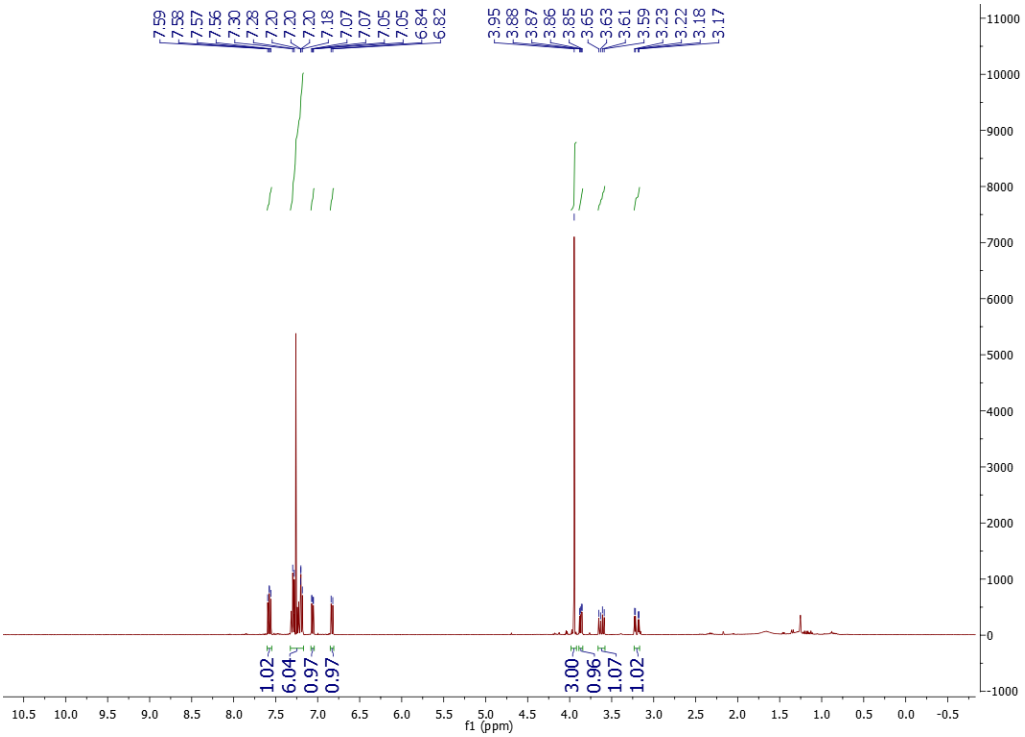
O
Ph
2p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7.18
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7.07
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7.05
6.84
6.82
3.95
3.88
3.87
3.86
3.85
3.65
3.63
3.61
3.59
3.23
3.22
3.18
3.17
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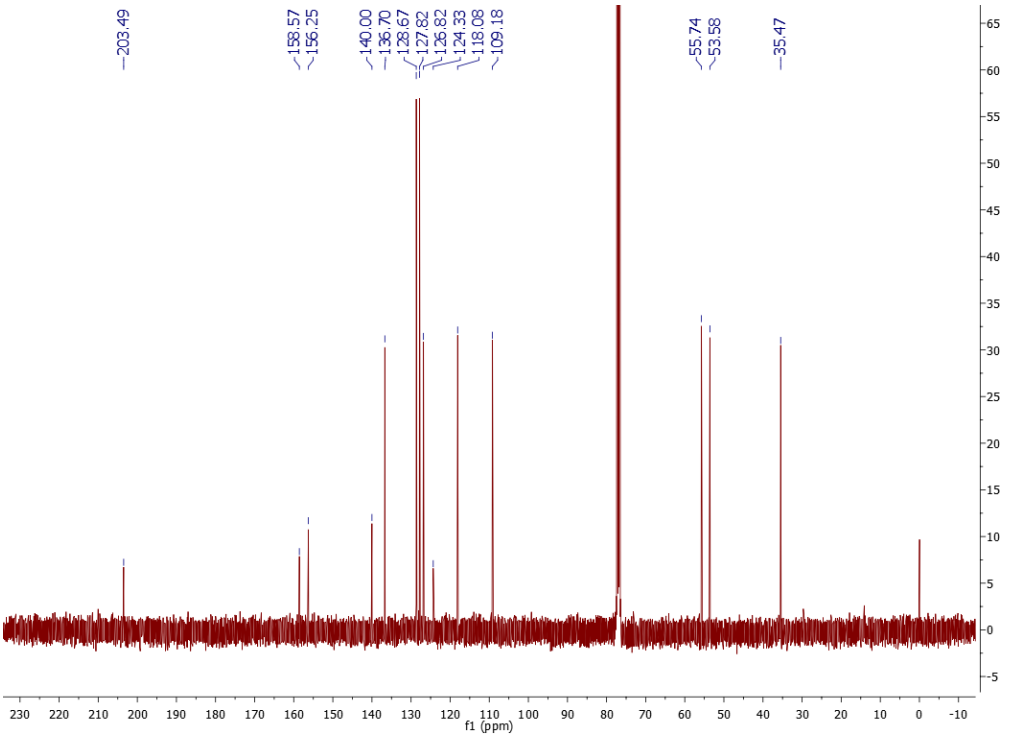
0.97
0.97
3.00
0.96
1.07
1.02
f1 (ppm)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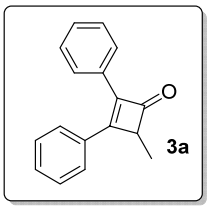
118.08
109.18
55.74
53.58
35.47
f1 (ppm)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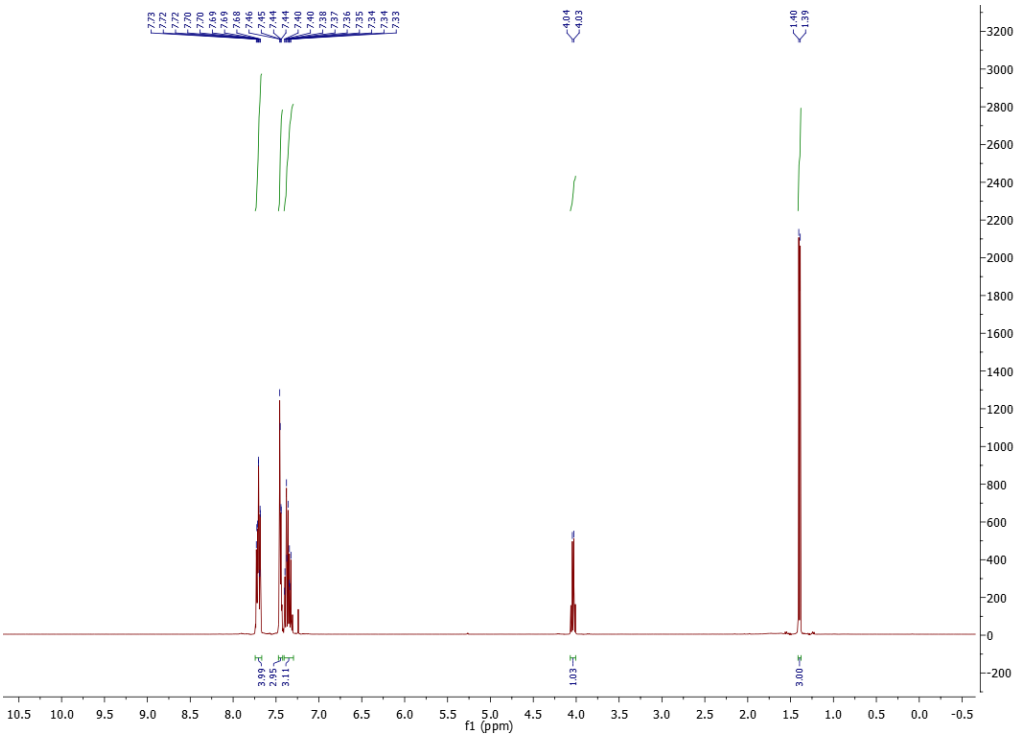
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7.44
7.40
7.40
7.38
7.37
7.36
7.35
7.34
7.34
7.33
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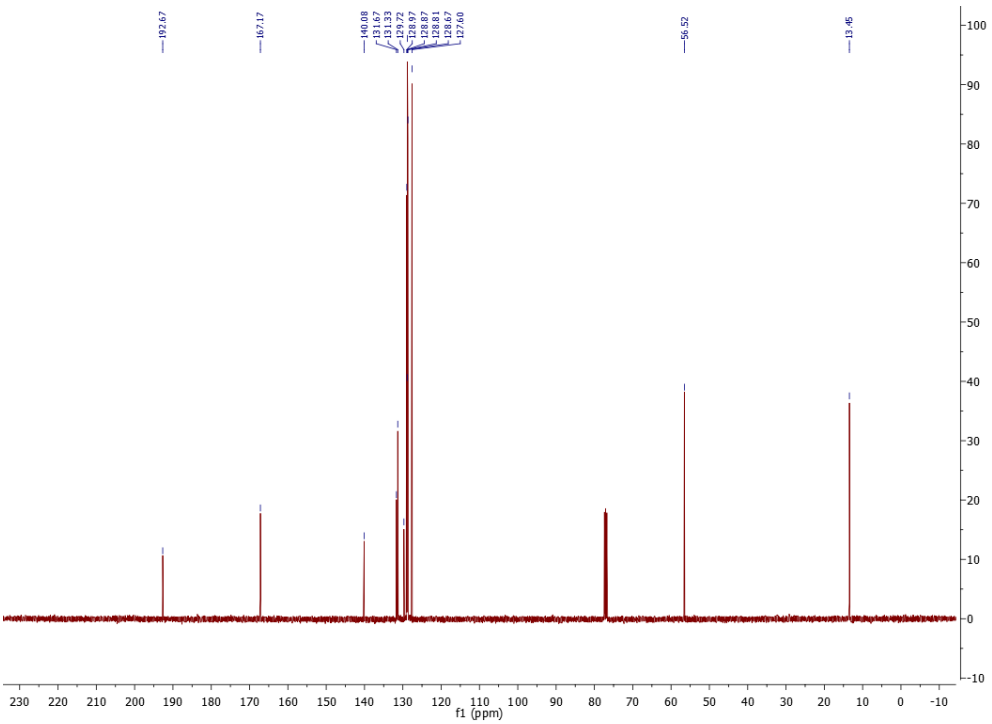
4.03
1.40
1.39
3.99
2.95
3.11
1.03
3.00
f1 (ppm)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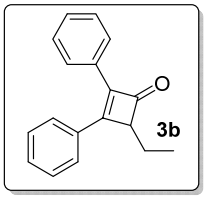
128.87
128.81
128.67
127.60
56.52
13.46
f1 (ppm)


O
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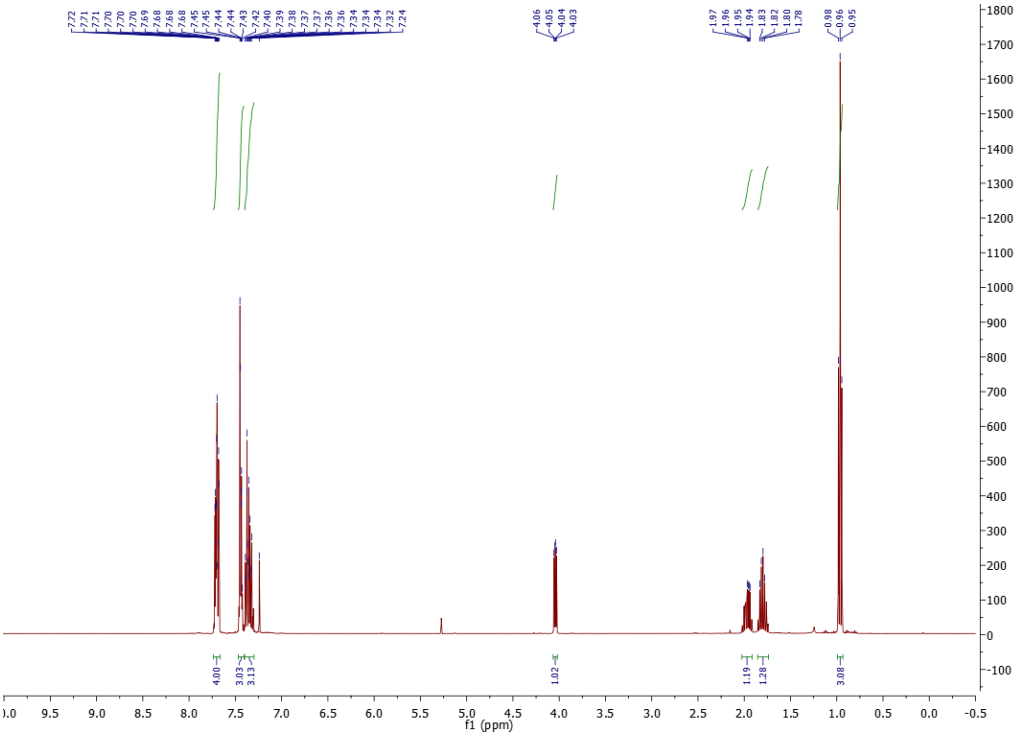
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7.68
7.45
7.45
7.44
7.44
7.43
7.42
7.40
7.39
7.38
7.37
7.37
7.36
7.36
7.34
7.34
7.34
7.32
7.24
4.06
4.05
4.04
4.03
1.97
1.96
1.95
1.94
1.83
1.82
1.80
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0.95
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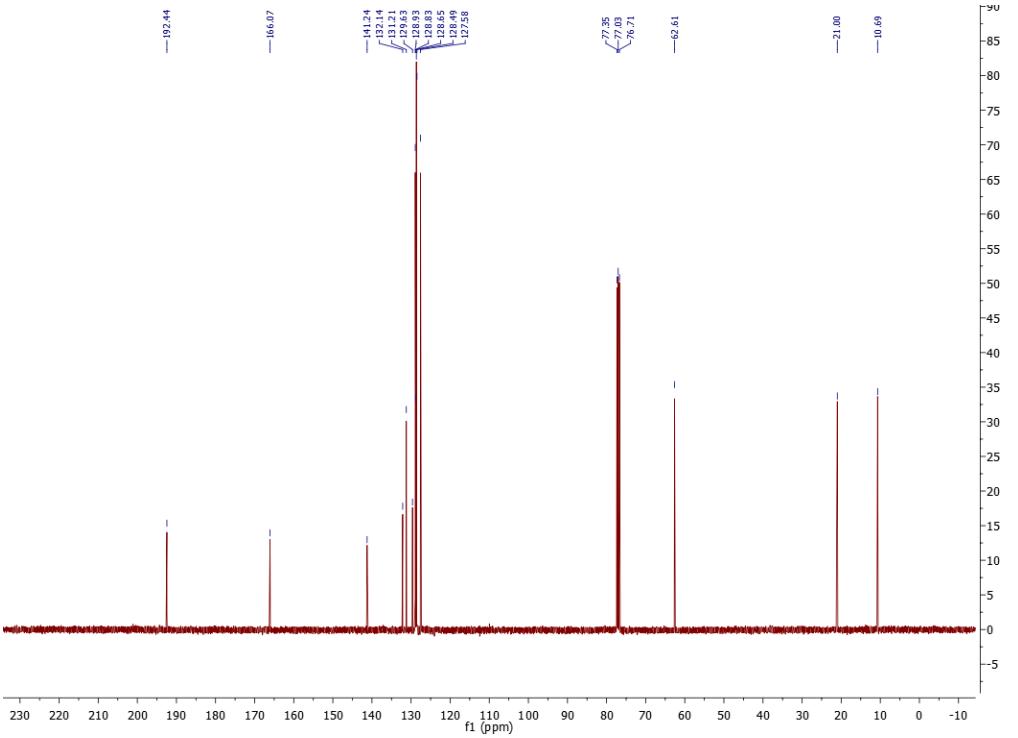
3.13
1.02
1.19
1.28
3.08
f1 (ppm)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62.61
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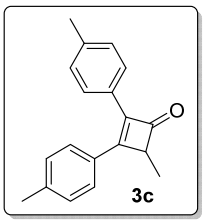
10.69
f1 (ppm)


O
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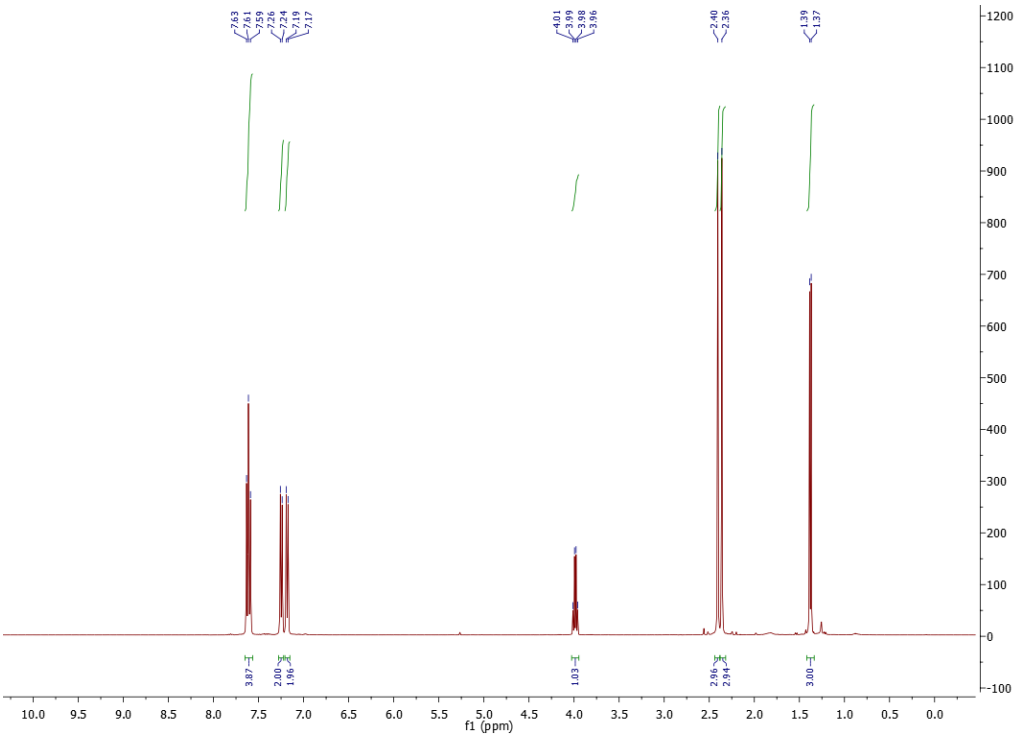
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7.17
4.01
3.99
3.98
3.96
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2.36
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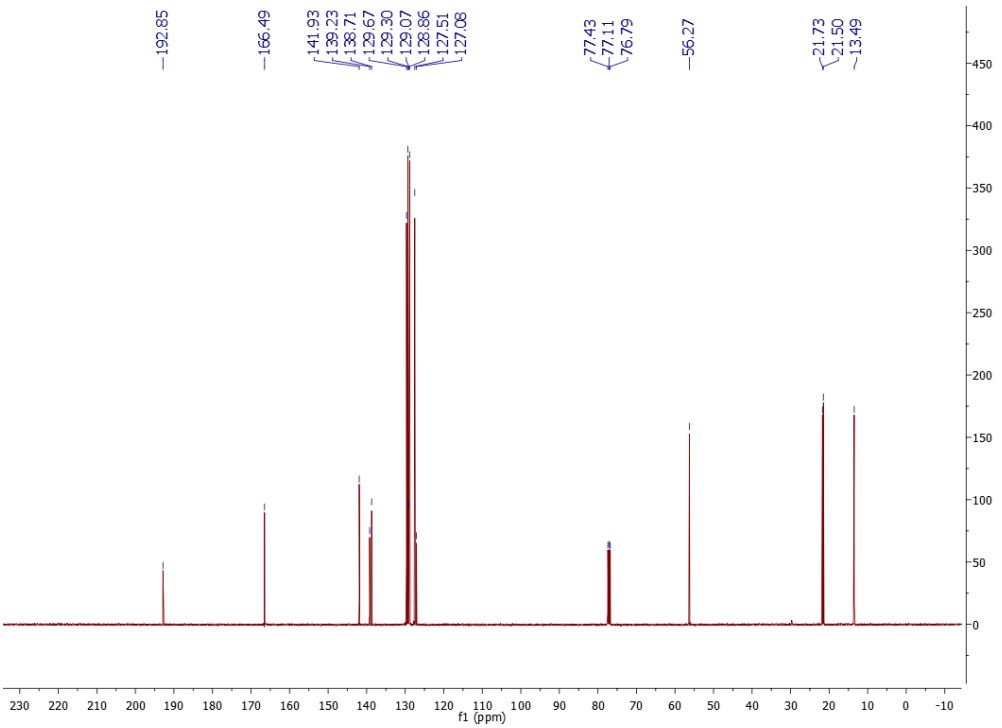
1.37
3.87
2.00
1.96
1.03
2.96
2.94
3.00
f1 (ppm)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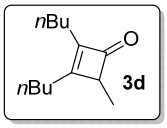
56.27
21.73
21.50
13.49
f1 (ppm)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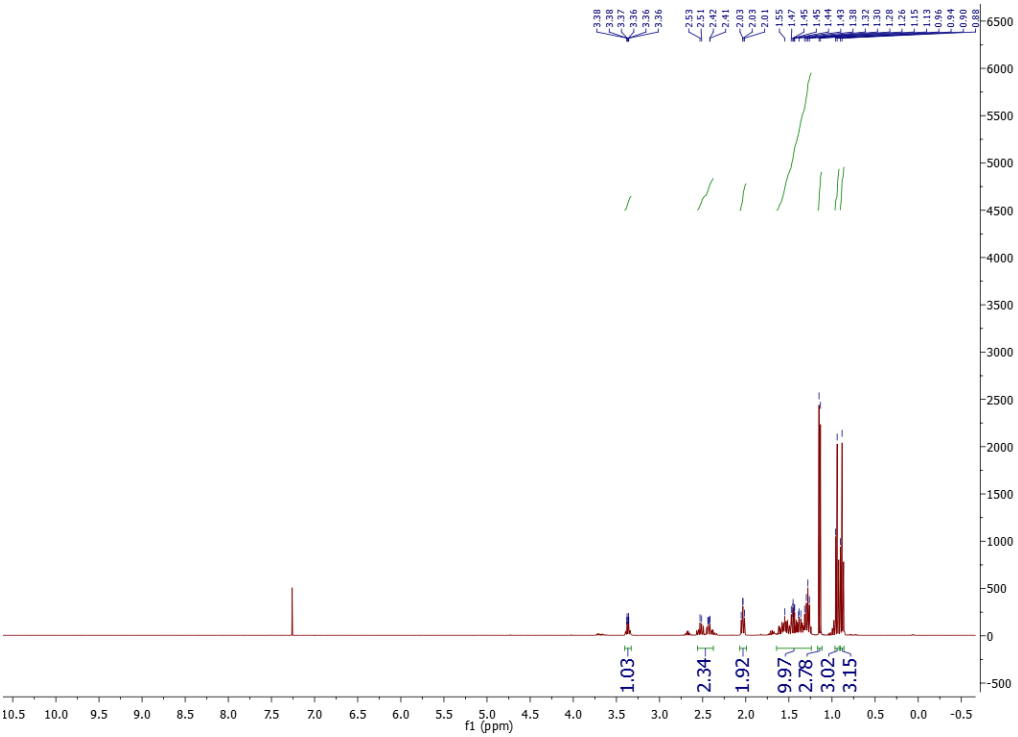
O
nBu
3d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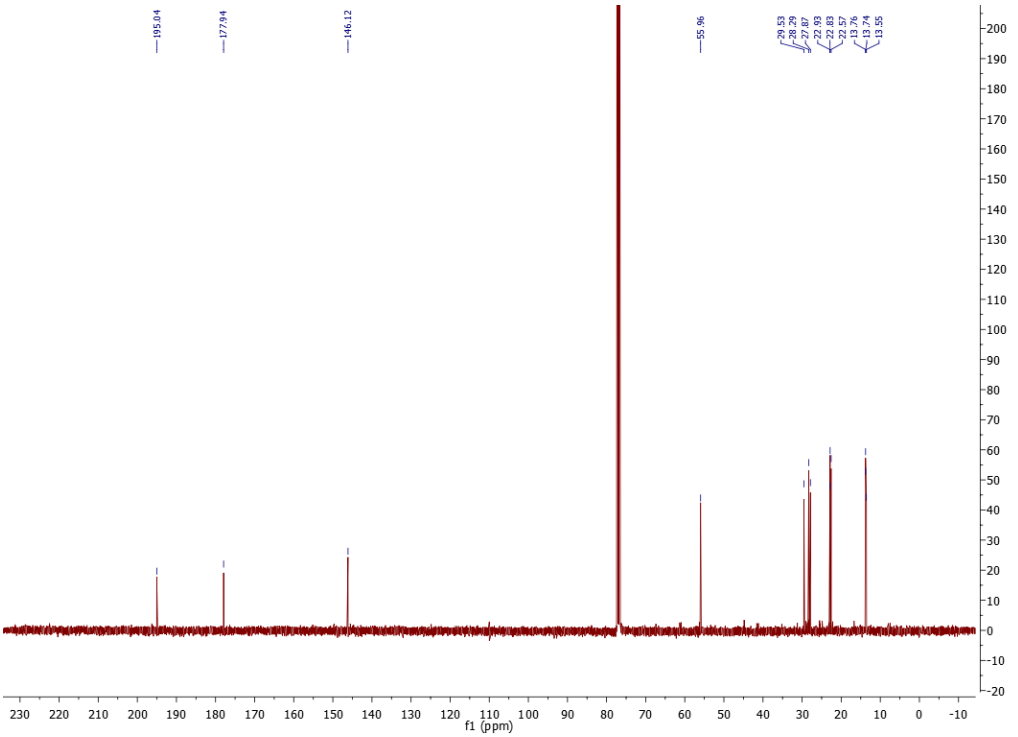
3.15
f1 (ppm)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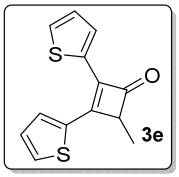
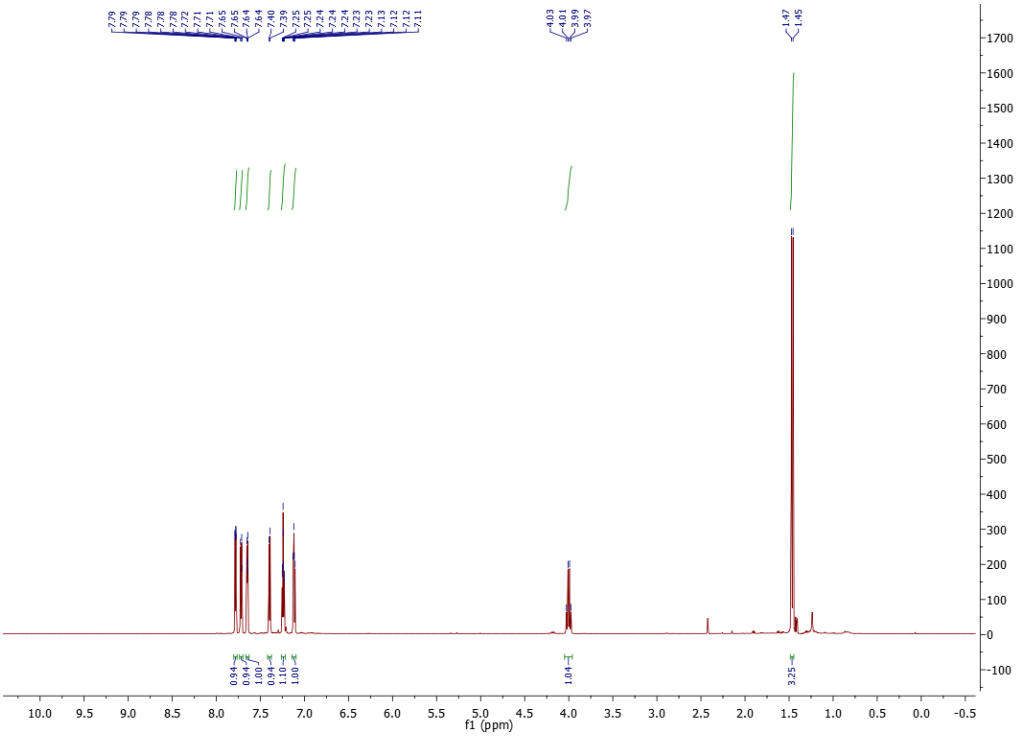
13.36
13.74
13.55
f1 (ppm)


S
O
S
3e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7.23
7.13
7.12
7.12
7.11
4.03
4.01
3.99
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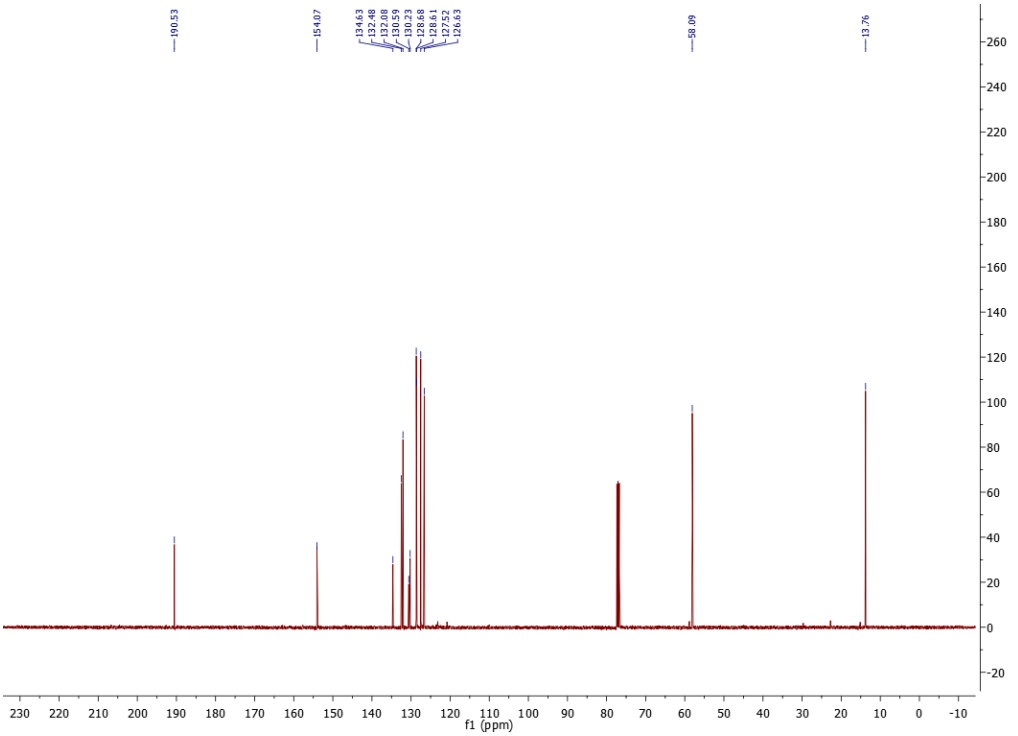
0.94
1.00
0.94
1.10
1.00
1.04
3.25
f1 (ppm)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130.59
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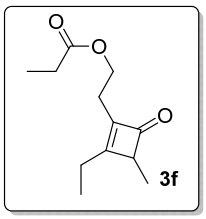
128.68
128.61
127.52
126.63
58.09
13.76
f1 (ppm)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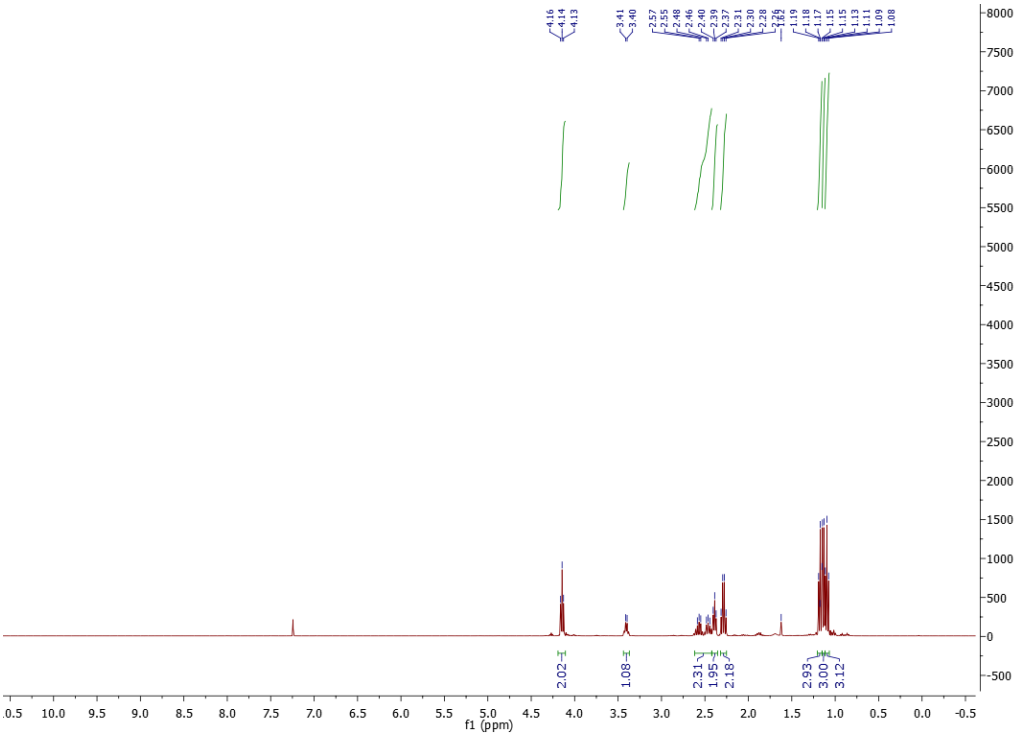
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2.39
2.37
2.31
2.30
2.28
1.19
1.18
1.17
1.15
1.13
1.11
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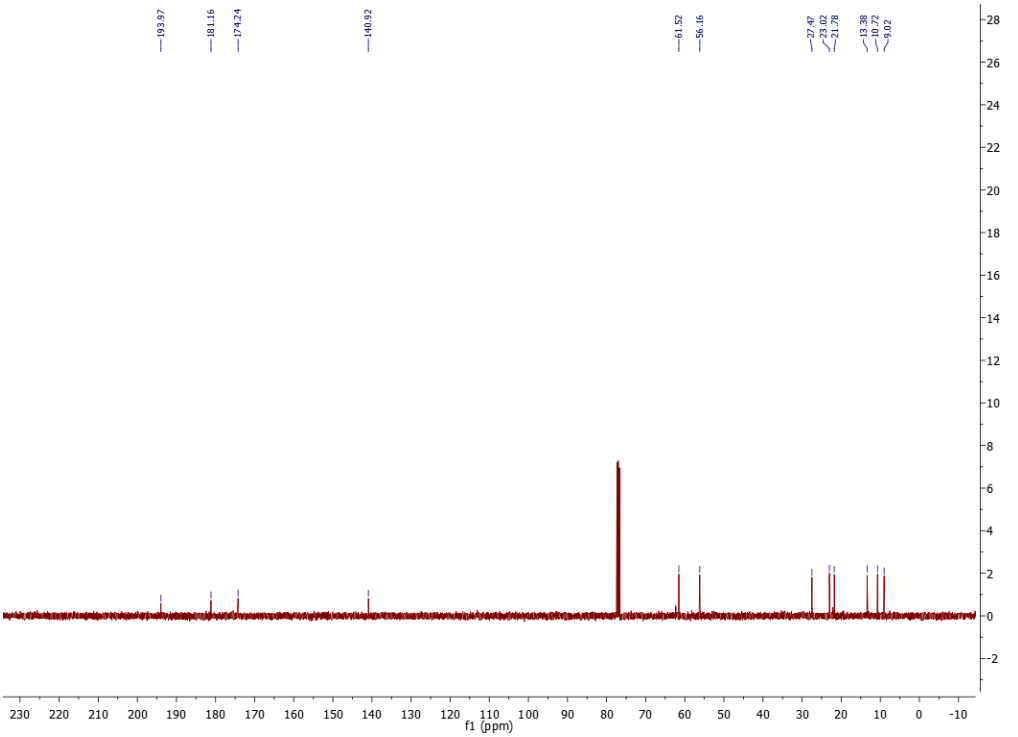
2.02
1.08
2.31
1.95
2.18
2.93
3.00
3.12
f1 (ppm)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23.02
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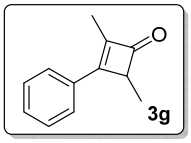
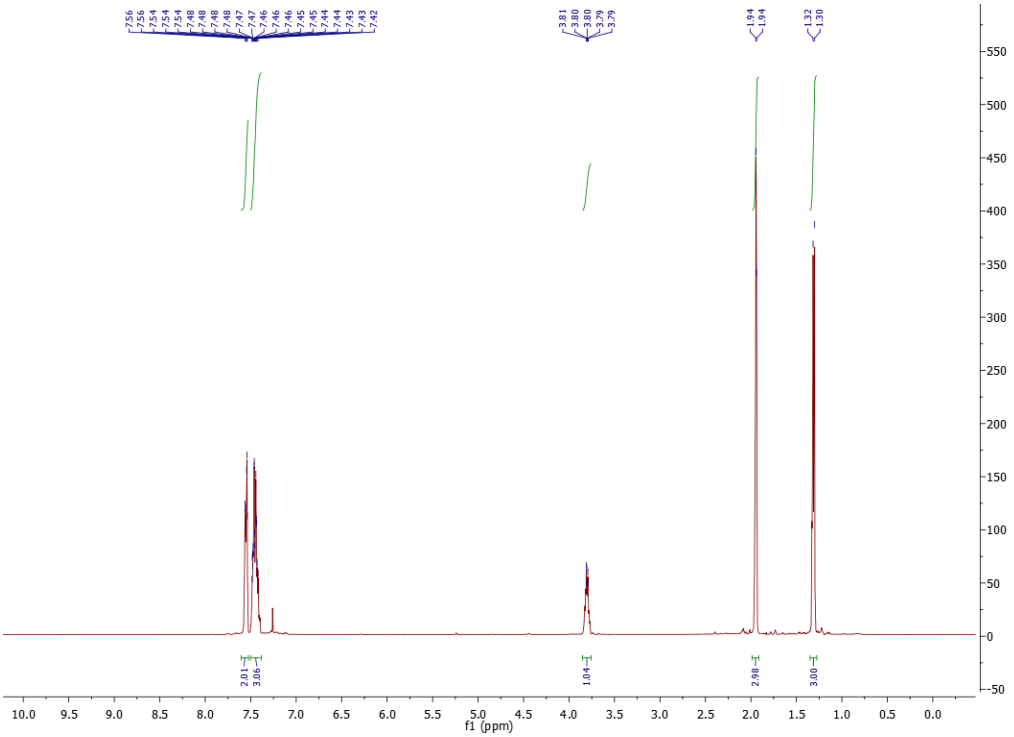
f1 (ppm)


O
3g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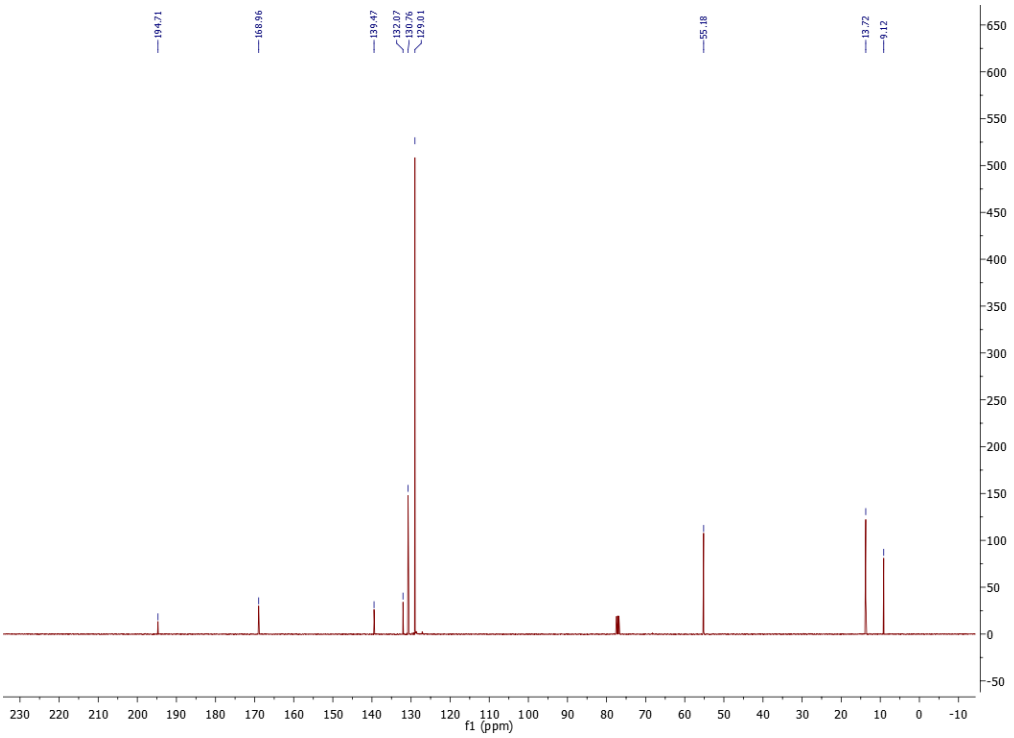
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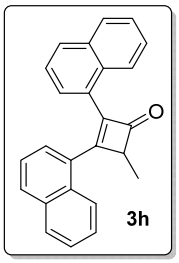
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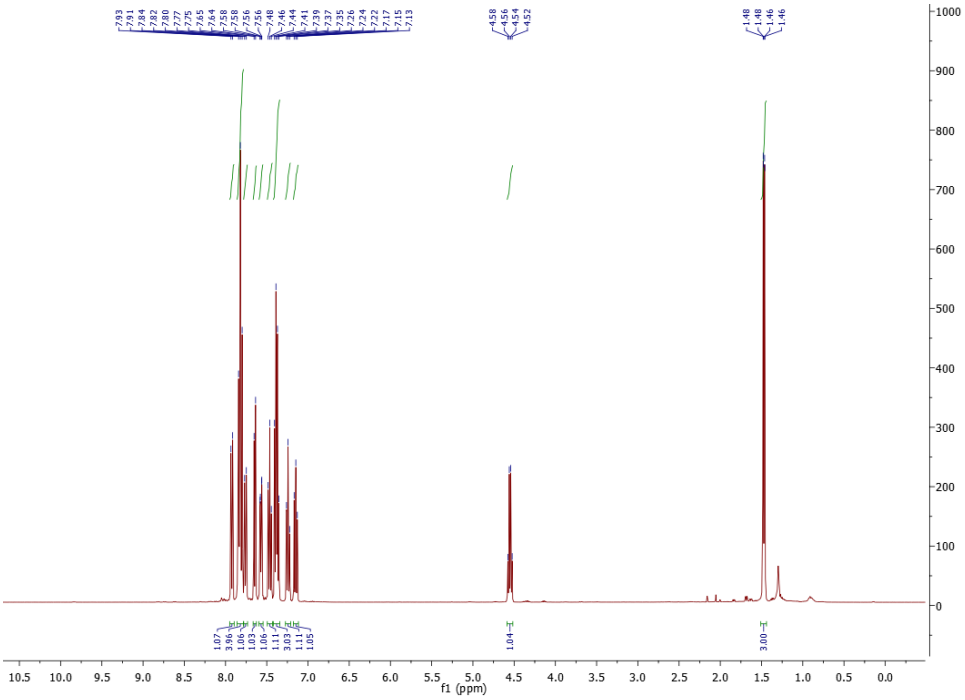
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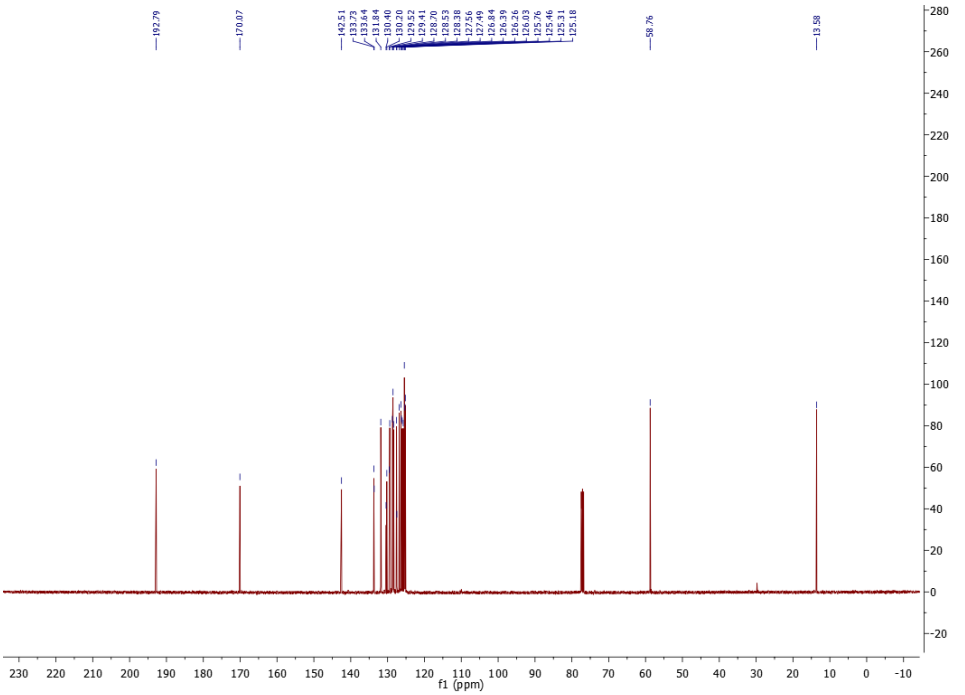
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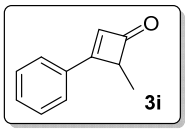
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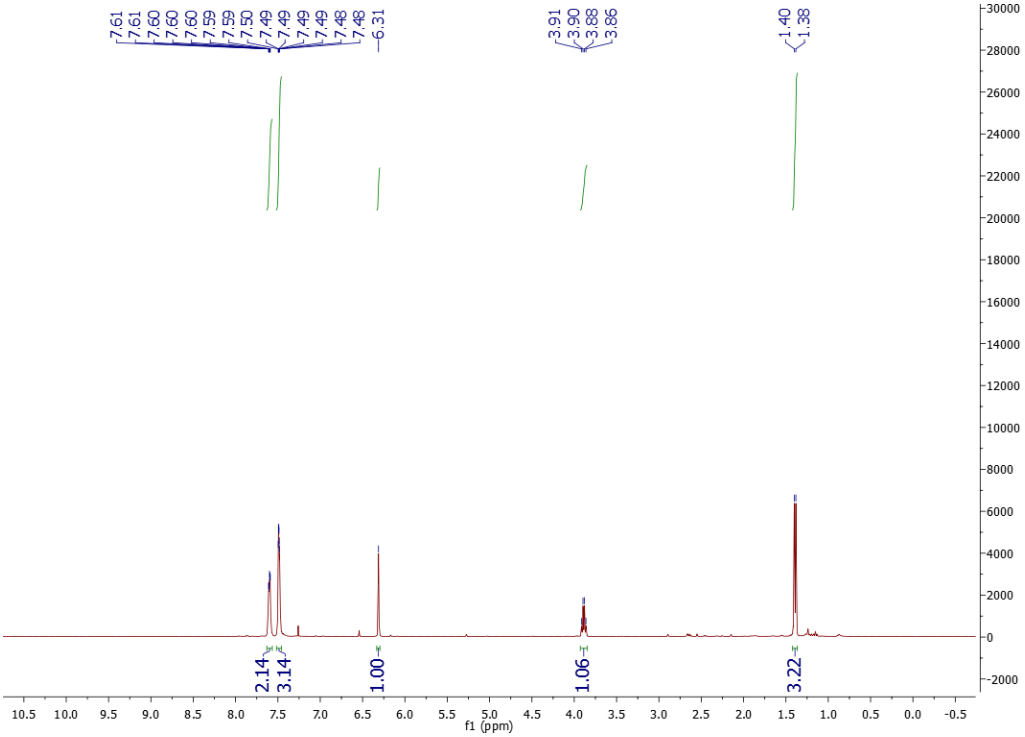
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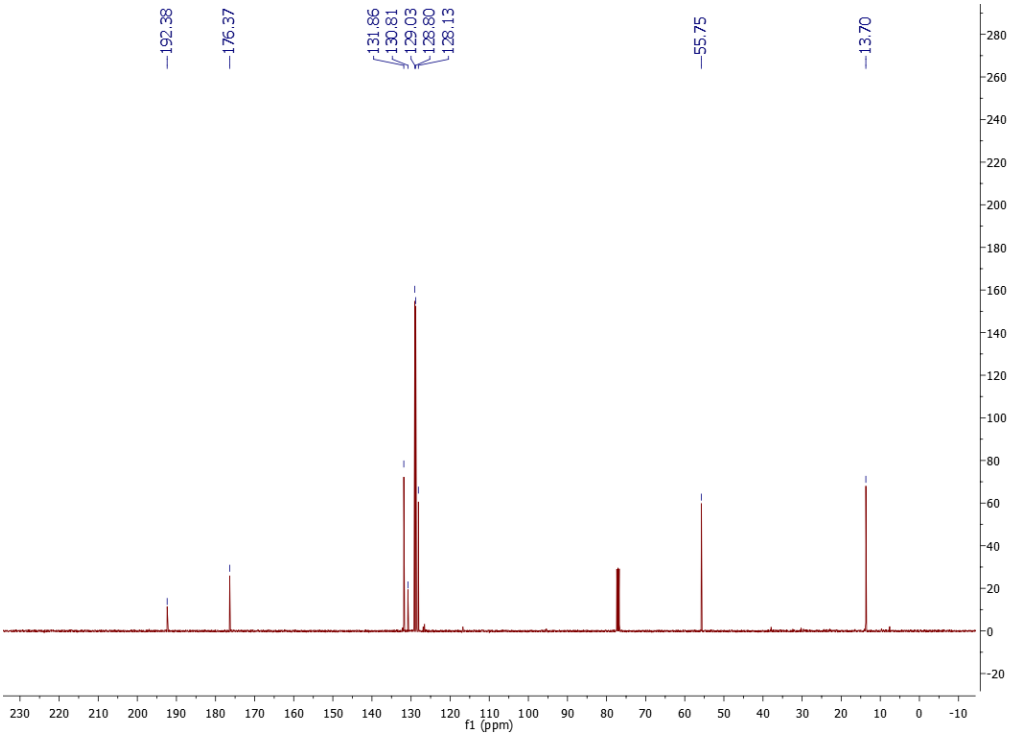
f1 (ppm)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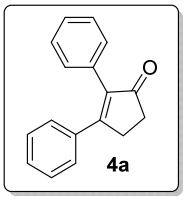
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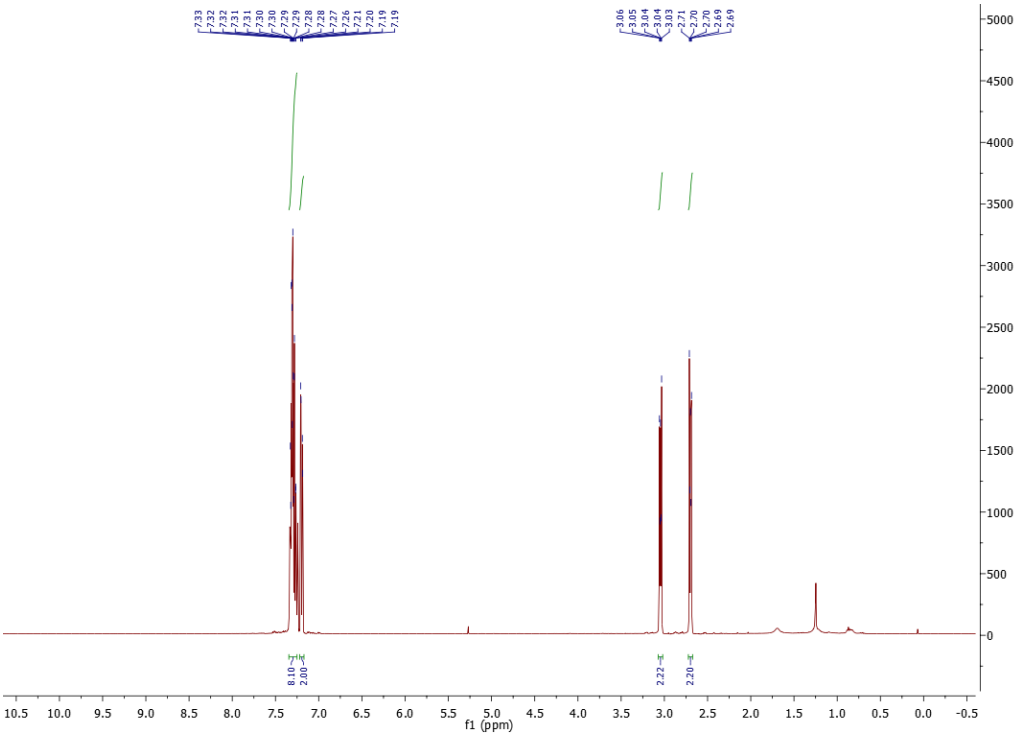
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3.04
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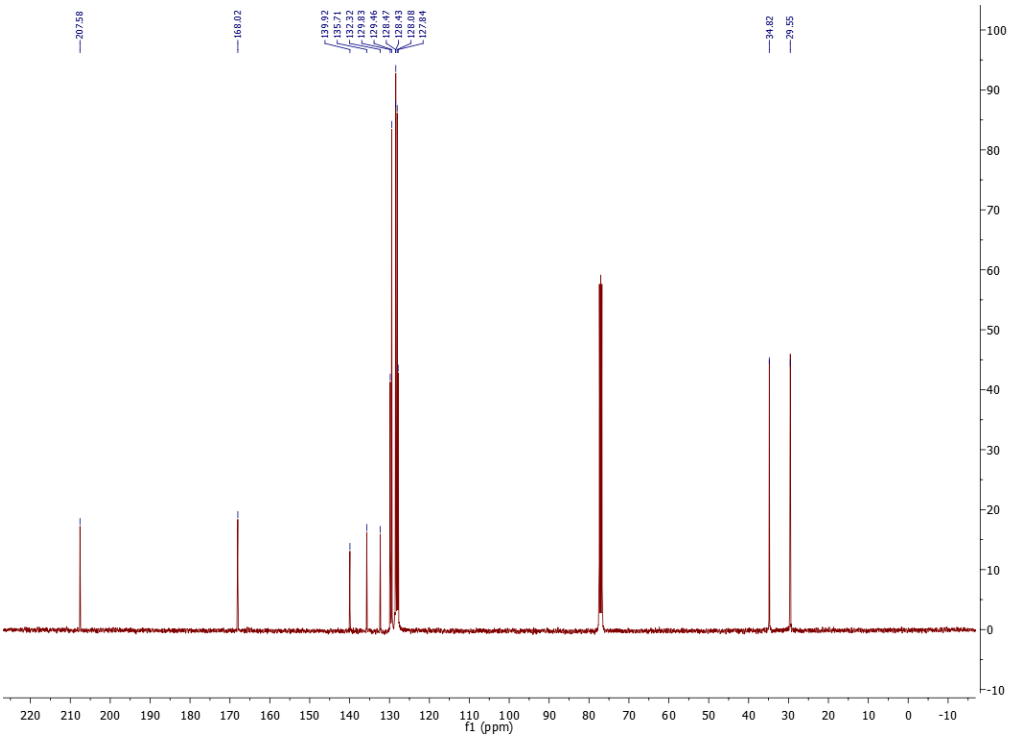
f1 (ppm)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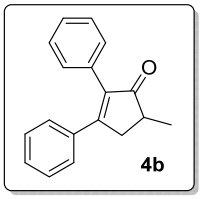
f1 (ppm)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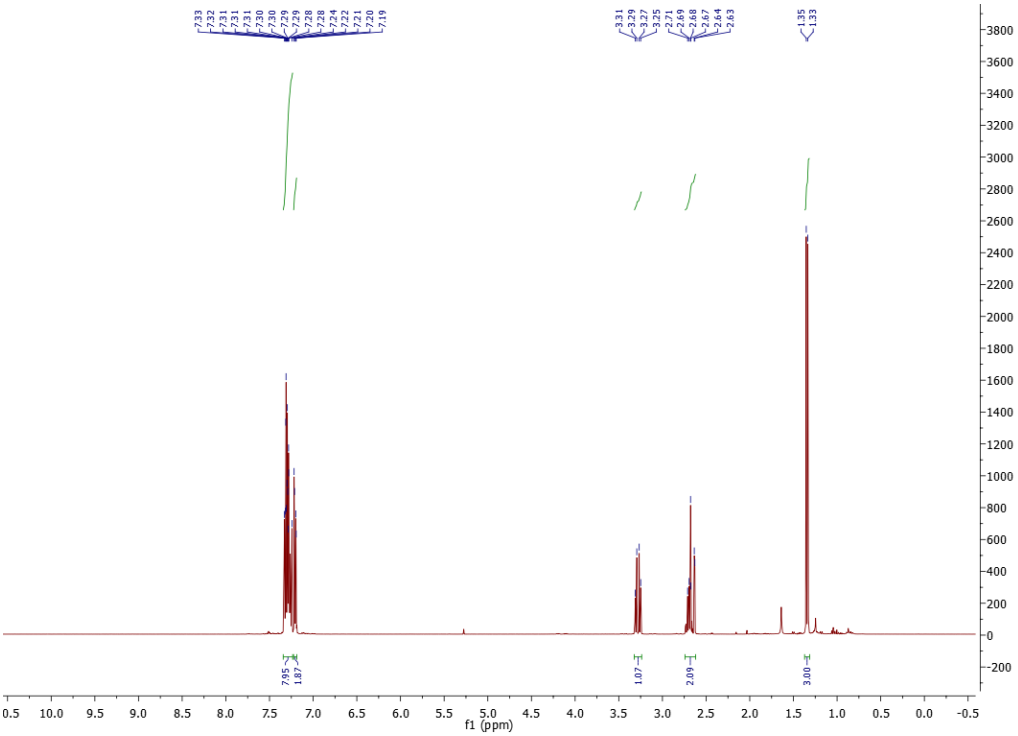
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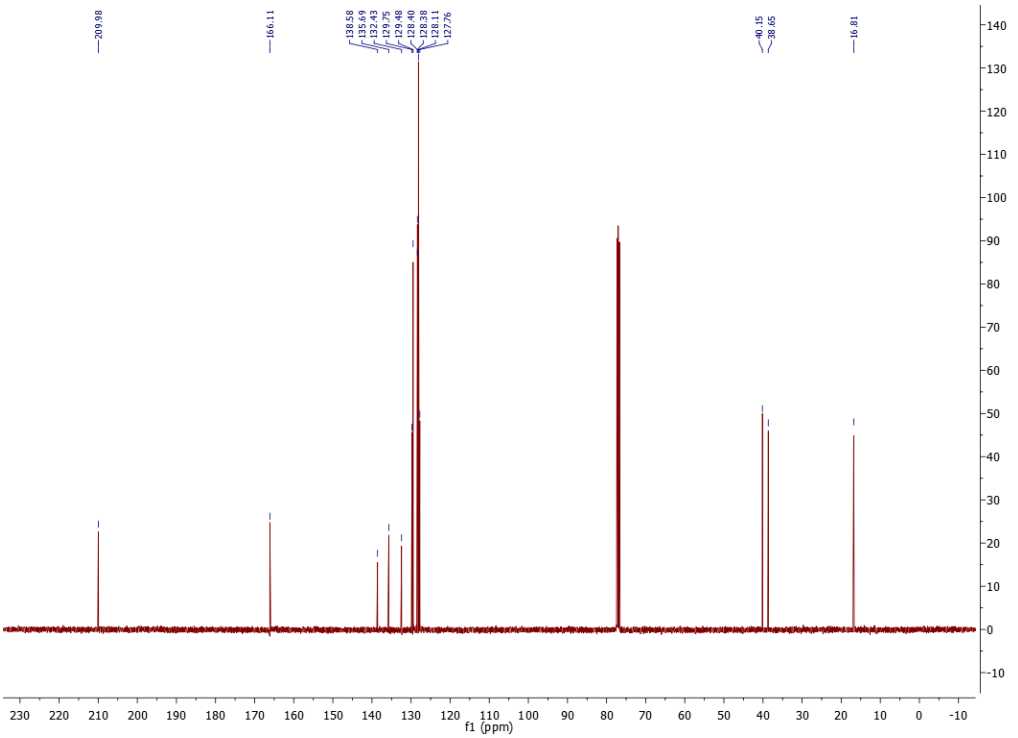
3.00
f1 (ppm)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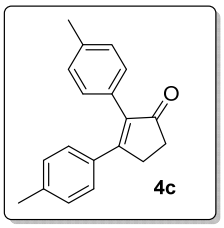
f1 (ppm)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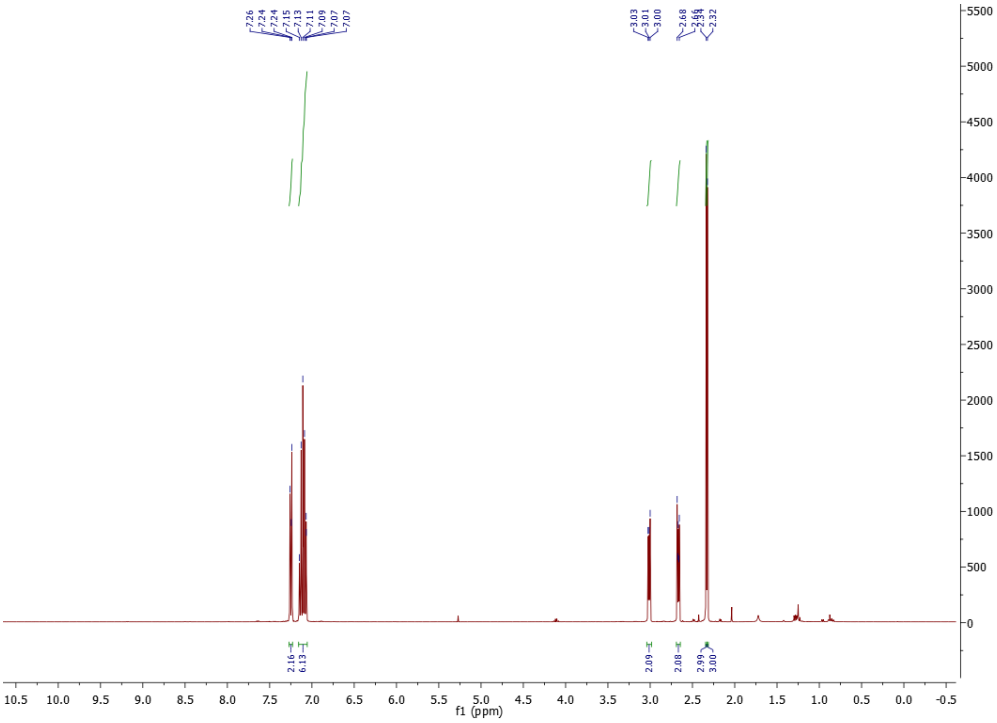
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7.07
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2.09
2.08
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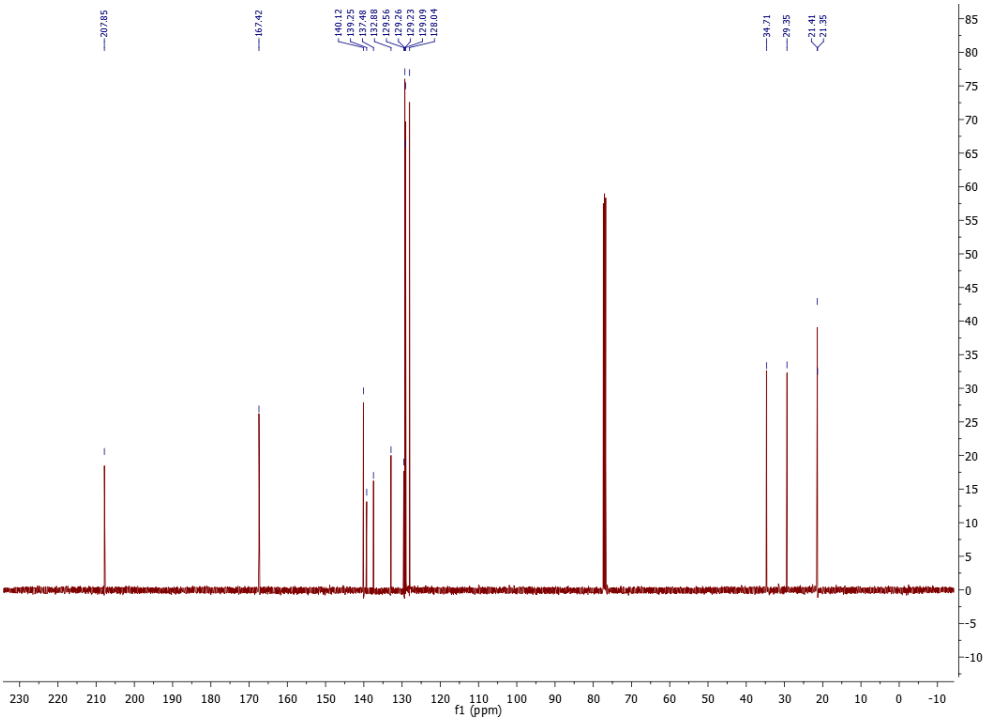
3.00
f1 (ppm)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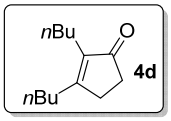
21.35
f1 (ppm)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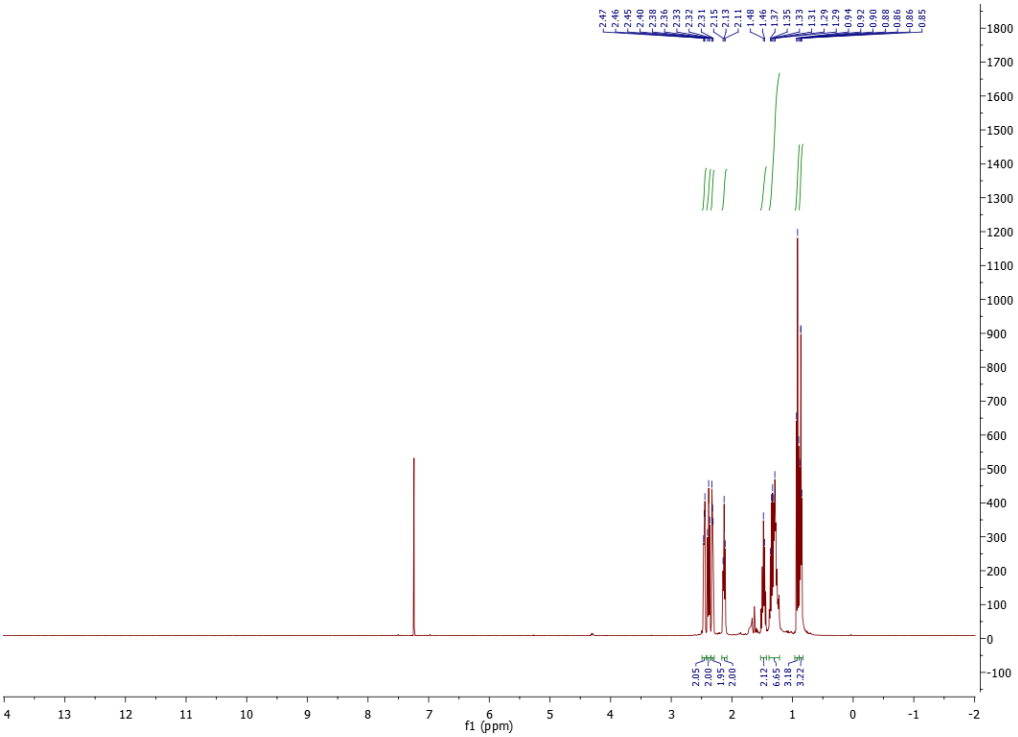
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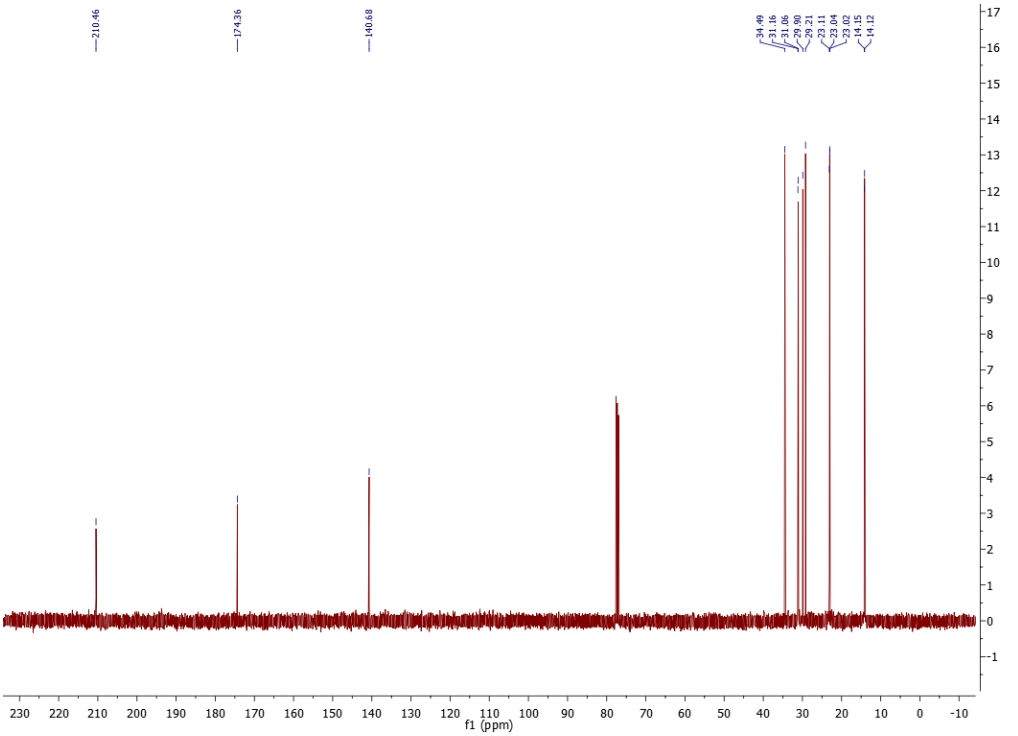
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23.04
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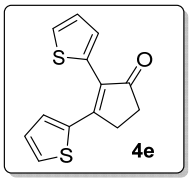
14.12
f1 (ppm)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S
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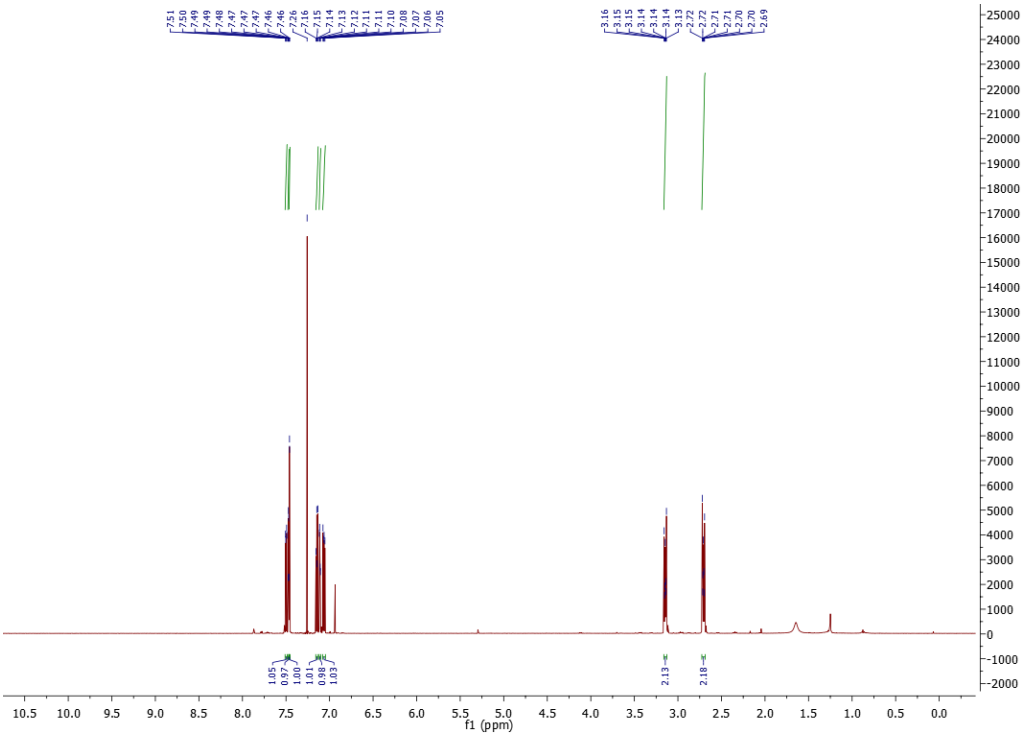
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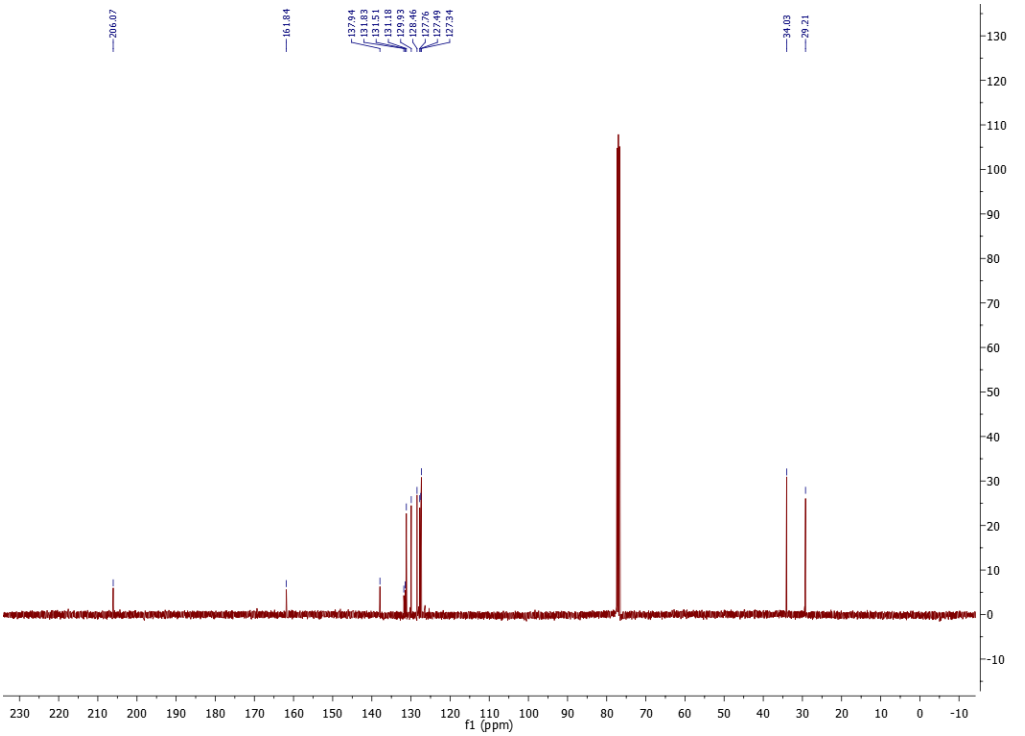
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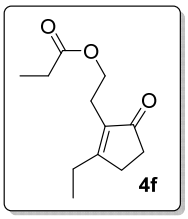
f1 (ppm)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O
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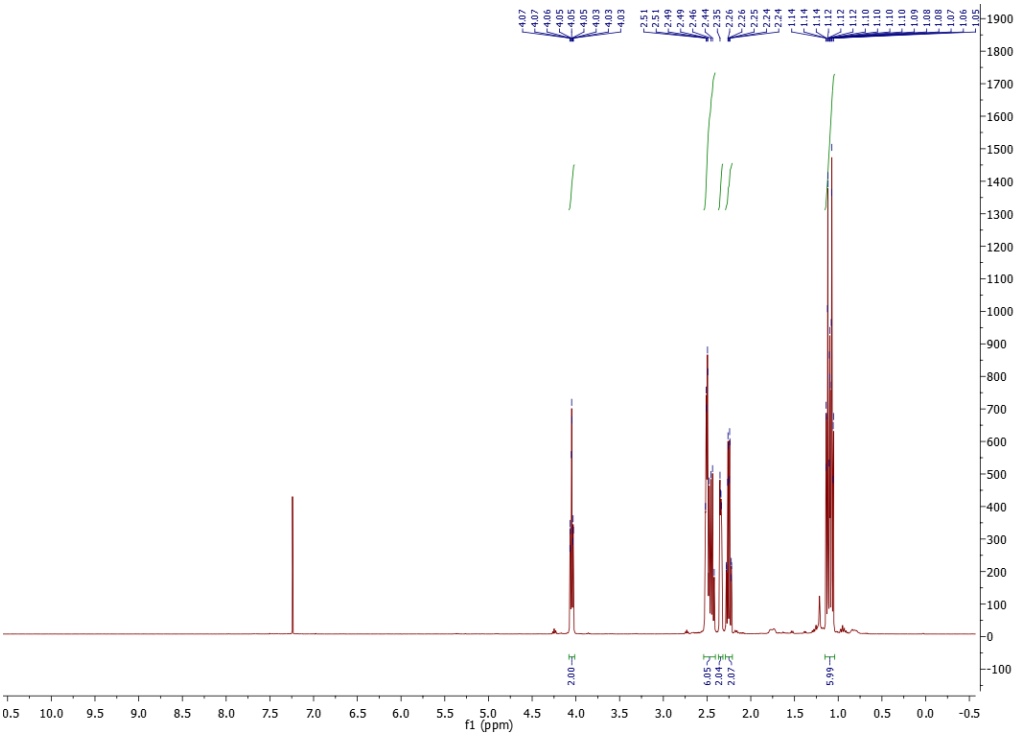
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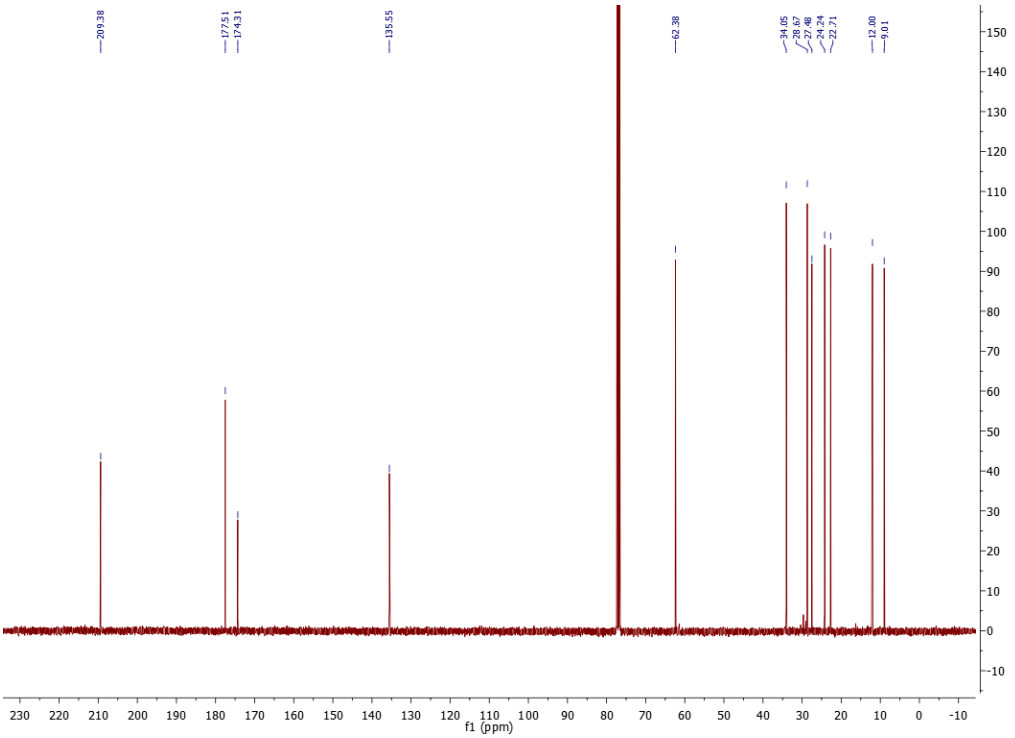
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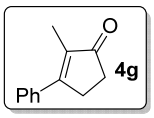
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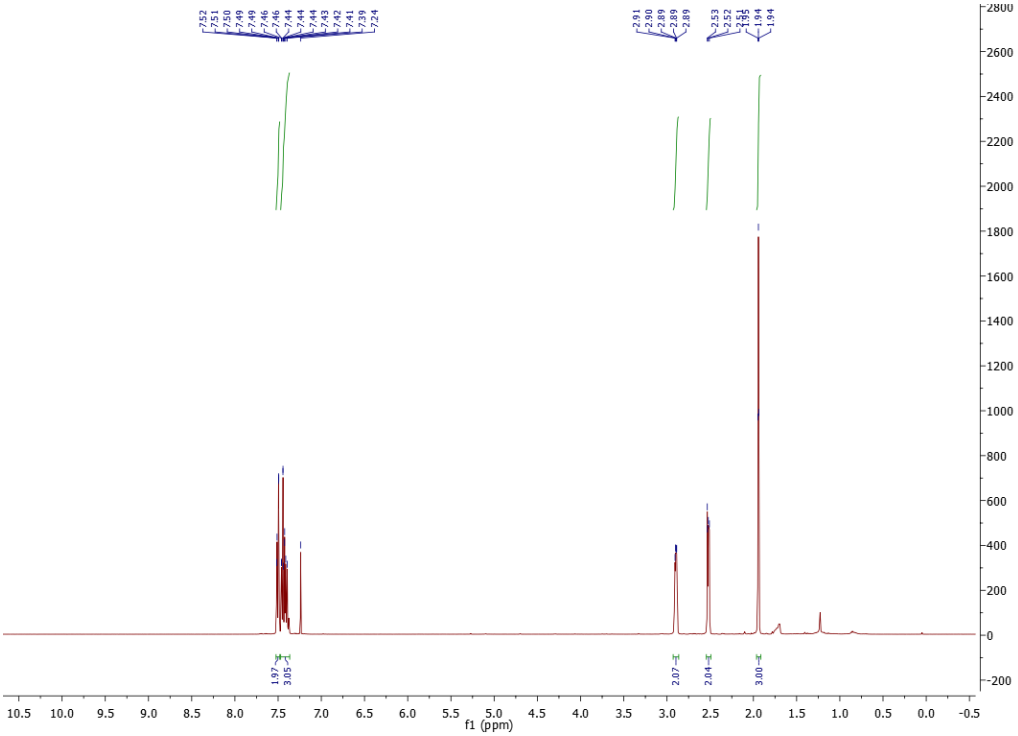
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3.00
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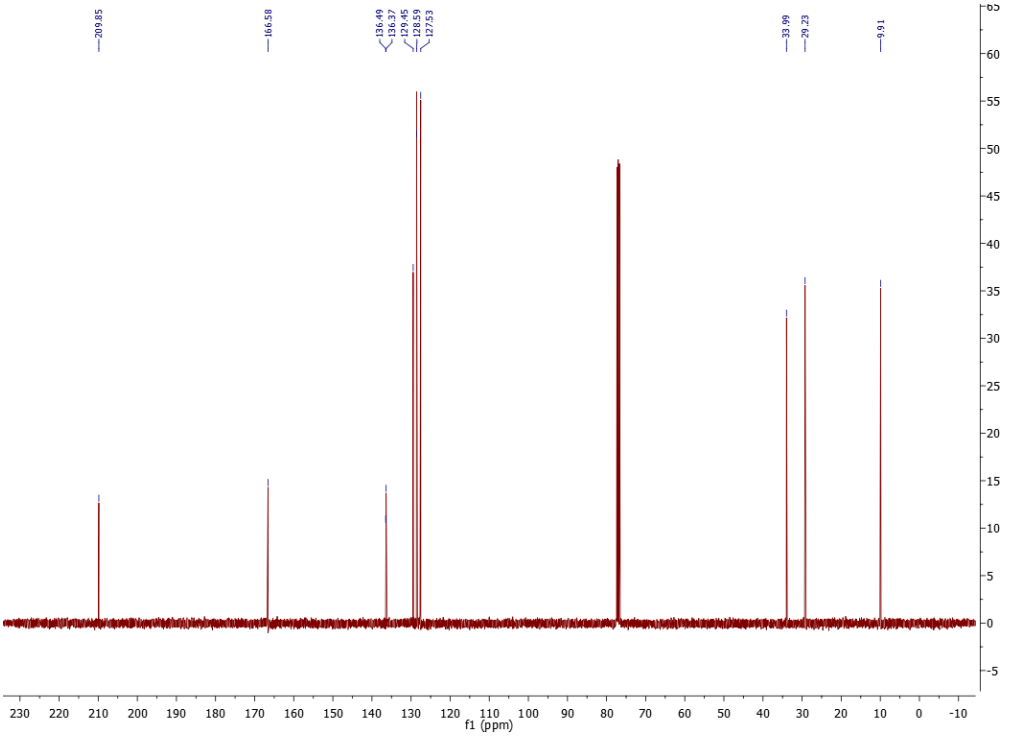
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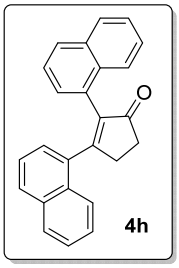
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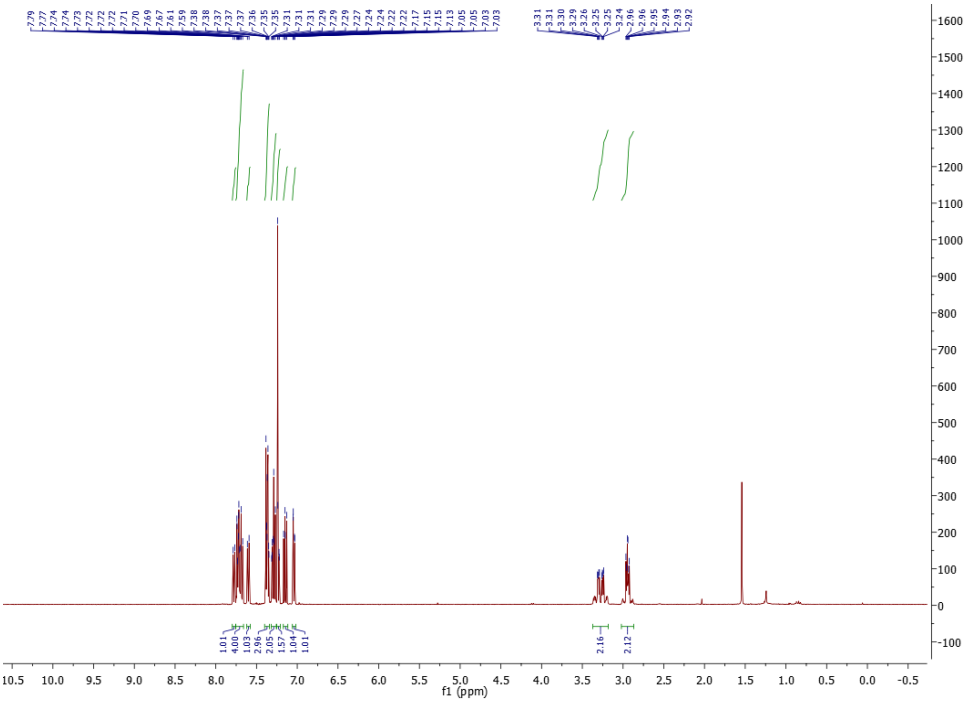
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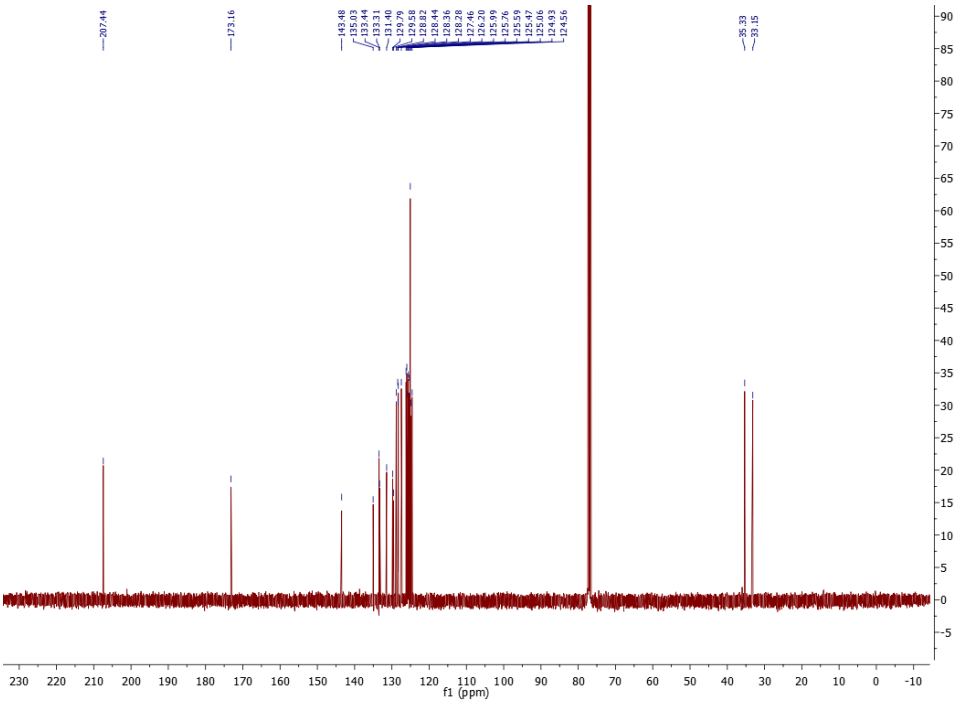
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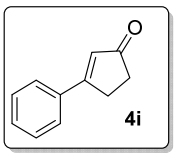
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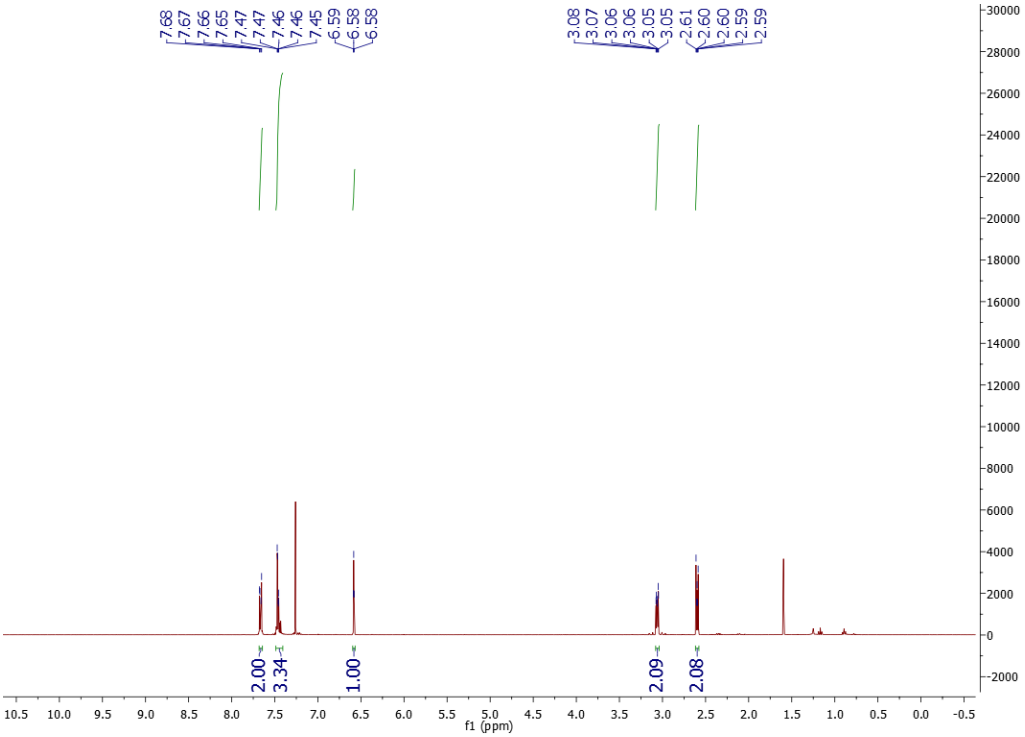
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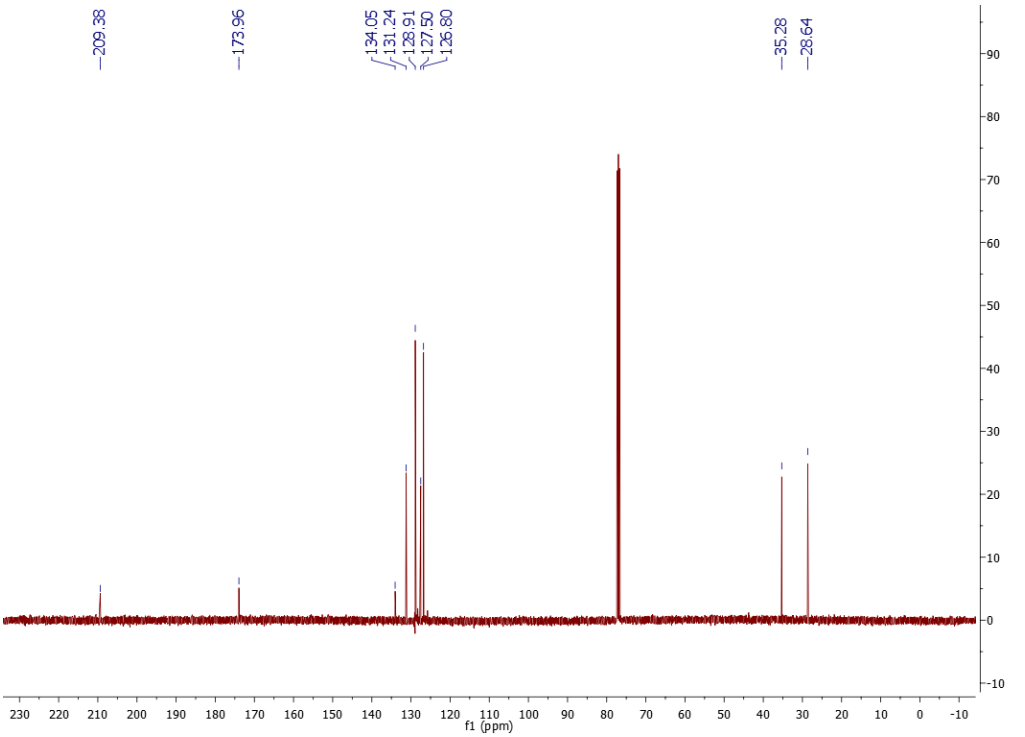
2.08
f1 (ppm)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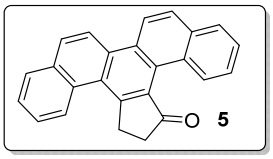
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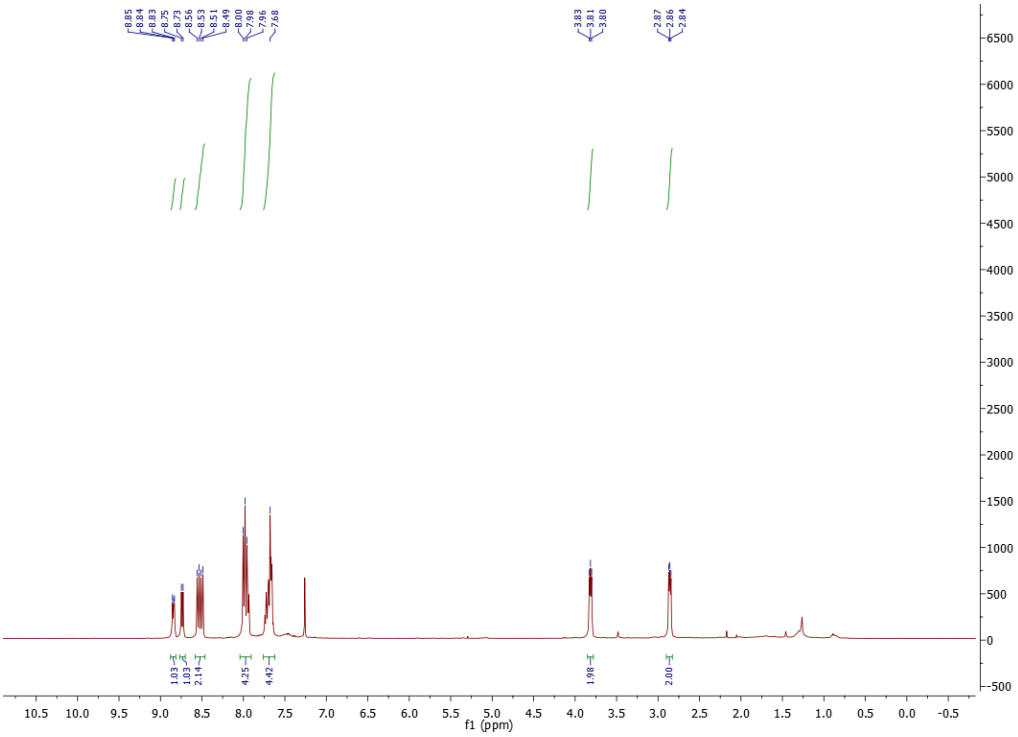
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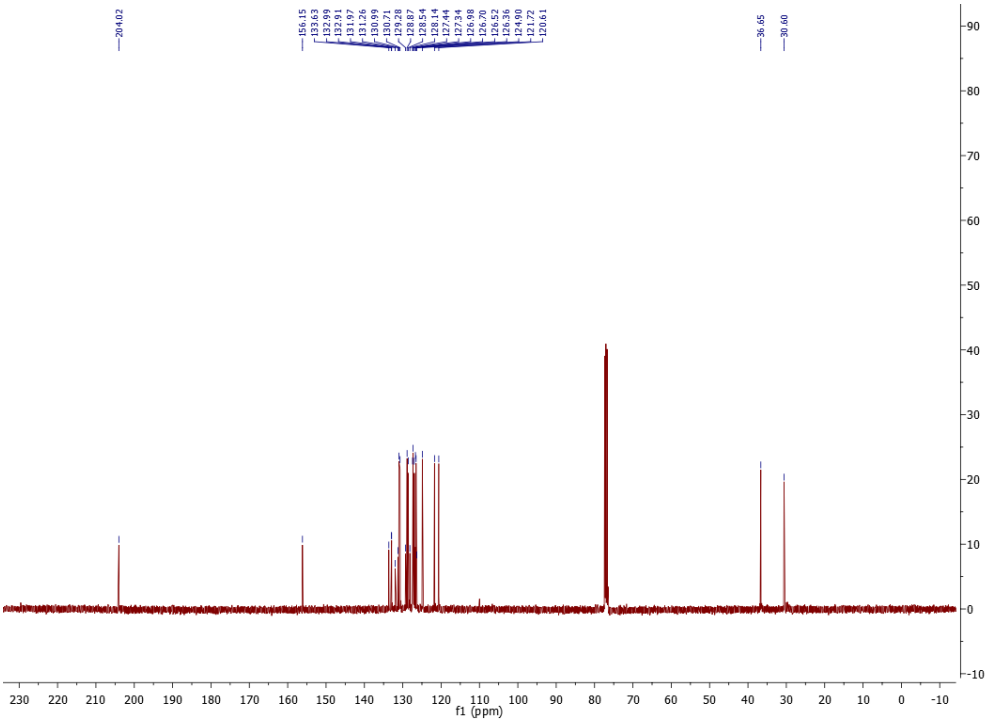
2.00
f1 (ppm)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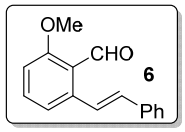
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CHO
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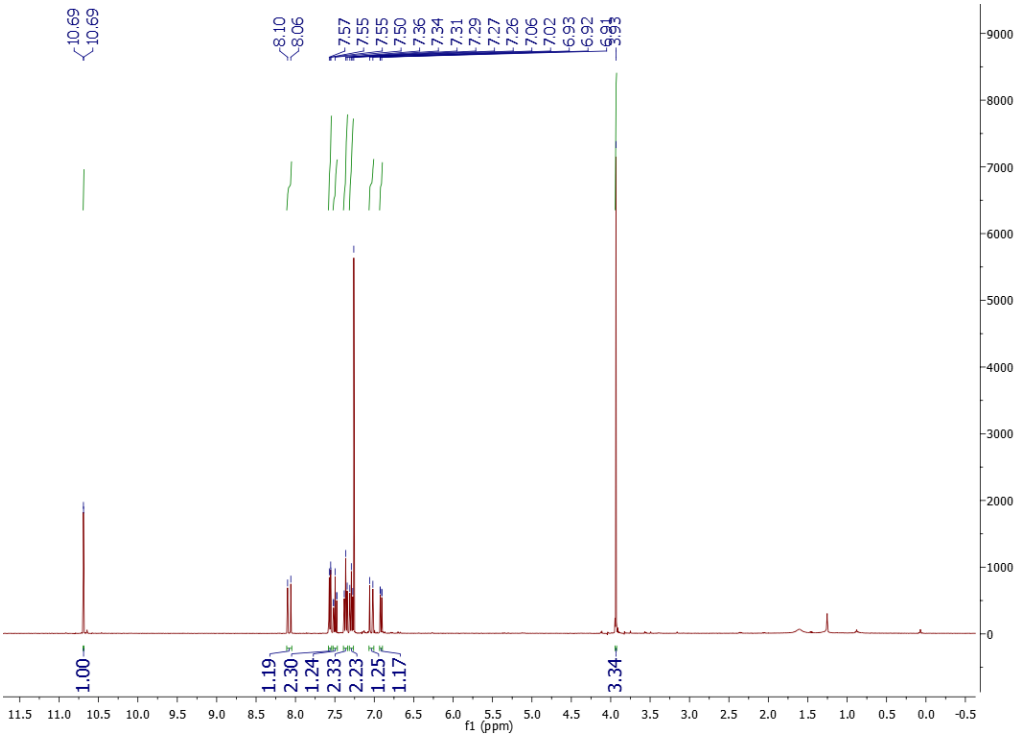
Ph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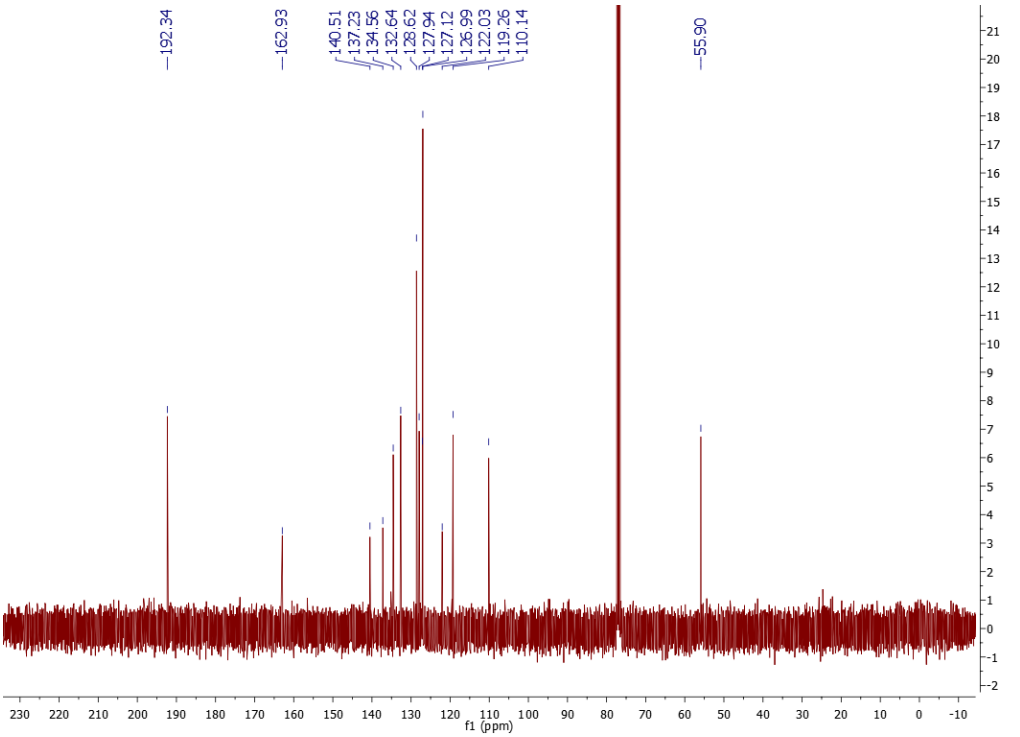
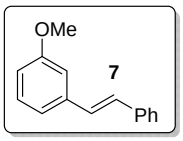
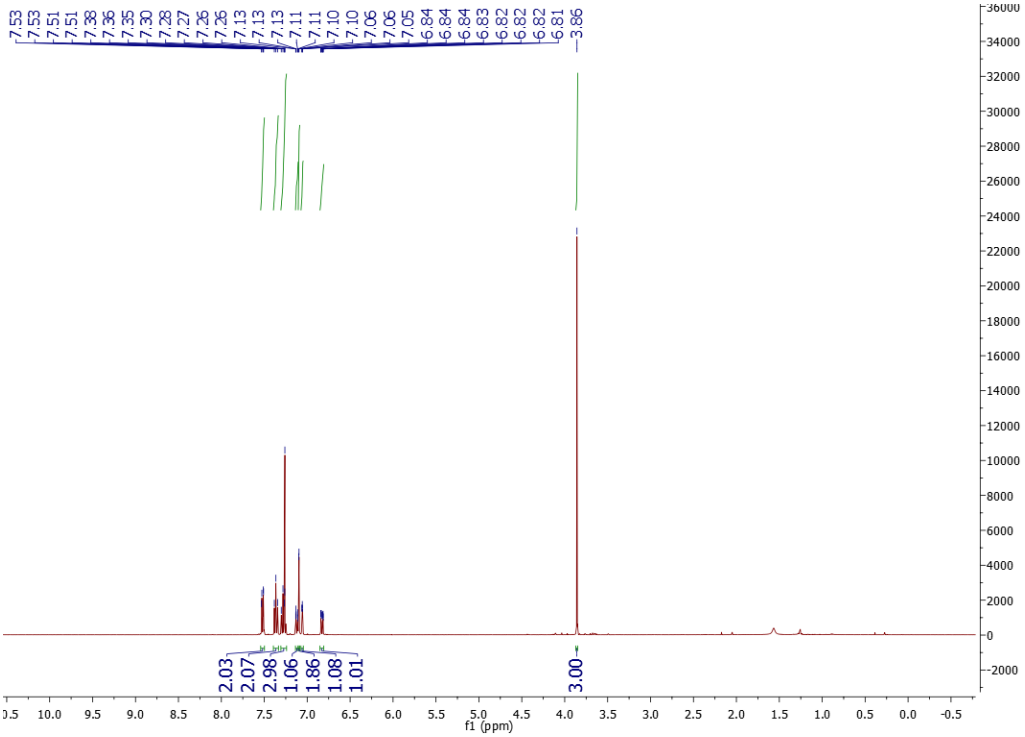
2.33
2.23
1.25
1.17
3.34
f1 (ppm)


192.34
162.93
140.51
137.23
134.56
132.64
128.62
127.94
127.12
126.99
122.03
119.26
110.14
55.90
f1 (ppm)


OMe
7
Ph


7.53
7.53
7.51
7.51
7.38
7.36
7.35
7.30
7.28
7.27
7.26
7.26
7.13
7.13
7.13
7.11
7.11
7.10
7.10
7.06
7.06
7.05
6.84
6.84
6.84
6.83
6.82
6.82
6.82
6.81
3.86
2.03
2.07
2.98
1.06
1.86
1.08
1.01
3.00
f1 (ppm)