Phosphine-Catalyzed Annulation Reactions of 2-Butynoate and α-Keto Esters: Synthesis of Cyclopentene Derivatives

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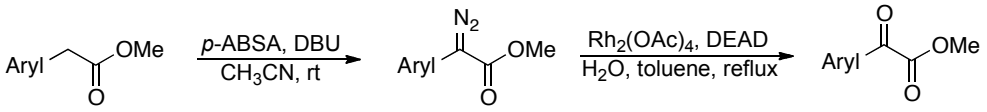
Supporting Information

I. General Procedures

Proton NMR spectra were recorded on 400 or 500 MHz spectrometers. Proton chemical shifts (δ) were reported in parts per million (ppm) downfield of tetramethylsilane, using residual protonated solvent as internal standard ($CDCl_3$, δ 7.26 ppm). Spectral data are reported as follows: chemical shift (multiplicity [singlet (s), doublet (d), doublet of doublets (dd), triplet (t), and multiplet (m), apparent quartet (app. q)], coupling constants [Hz], integration). Carbon NMR spectra were recorded on a 500 (126) MHz spectrometer with complete proton decoupling. Carbon chemical shifts (δ) were reported in parts per million (ppm) downfield of tetramethylsilane, using residual protonated solvent as an internal standard ($CDCl_3$, δ 77.2 ppm). Infrared spectra (thin film and attenuated total reflectance (ATR-IR)) were obtained on a Nicolet 6700 FT-IR spectrometer; υmax (cm^{-1}) are partially reported. Analytical thin-layer chromatography (TLC) was performed using Silica Gel 60 Å F254 pre-coated plates (250 μm thickness). TLC R_f values are reported and visualization was accomplished by irradiation with a UV lamp and/or staining with $KMnO_4$ solution. Flash column chromatography was performed using Silica Gel 60 Å (32-63 micron). High resolution mass spectrometry (HRMS) was performed at the Mass Spectrometry Facility of the University of Illinois (Urbana-Champaign, IL). The method of ionization is given in parentheses. Solvents were purified using a Seca Solvent Purification System by GlassContour. Methyl benzoylformate was purchased from TCI and used as received.

Abbreviations: *p*-ABSA = 4-Acetamidobenzenesulfonyl azide; DEAD = Diethyl azodicarboxylate; DBU = 1,8-Diazabicycloundec-7-ene; 4 Å M.S. = 4 Å molecular sieves; rt = room temperature.

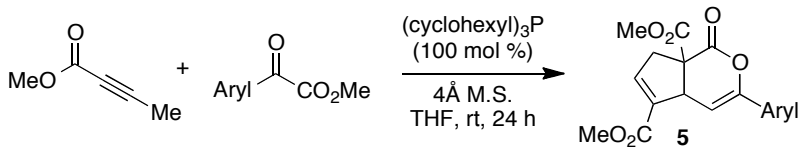
II. Synthesis of Aroylformate Esters



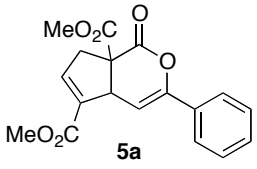
General Procedure for Aroylformate Esters:[1,2] To a 25 mL round bottom flask containing a stir bar, methyl arylacetate (2.9 mmol, 1.0 equiv) and *p*-ABSA (826 mg, 3.4 mmol, 1.2 equiv) in anhydrous CH_3CN (10 mL), was added DBU (0.6 mL, 4.0 mmol, 1.4 equiv). The resulting mixture was stirred at rt overnight. The reaction mixture was diluted with distilled water (10 mL), followed by extraction with diethyl ether (3 x 10 mL), and was then washed with saturated aqueous NH_4Cl solution (3 x 10 mL) and saturated aqueous NaCl solution (3 x 10 mL). The combined organic extracts were dried over $MgSO_4$, filtered and concentrated on a rotary evaporator. The crude material was purified by flash chromatography to afford pure diazoesters that were carried forward to the next step.

To a 100 mL round bottom flask containing a solution of toluene (15 mL), H_2O (23 mL, 1.3 mmol, 1.1 equiv) and DEAD (0.20 mL, 1.3 mmol, 1.1 equiv) was added $Rh_2(OAc)_4$ (5.0 mg, 0.01 mmol, 0.01 equiv). The resulting mixture was heated to reflux. Next, aryl diazoacetate (1.2 mmol, 1.0 equiv) was added as solution in toluene (10 mL) over 1 h *via* a syringe pump. After stirring for an additional 3 h, the reaction mixture was cooled to rt and the organic layer was extracted. The aqueous layer was extracted with ethyl acetate (20 mL) and the combined organic layers were concentrated in vacuo. The crude product was purified by flash chromatography on silica gel eluting with 15% ethyl acetate/hexanes to give the desired product. ^{1}H-NMR spectra of aryl formate esters matched data previously reported in the literature.[3,4]

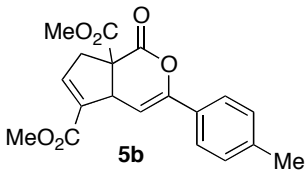
III. Preparation of Bicyclic Compounds (5)



General Procedure for 5: An oven-dried 1 dram glass vial charged with a stir bar and methyl aroylformate (0.10 mmol, 1.0 equiv.) was taken into the glove box where methyl 2-butynoate (29 mg, 3.0 mmol, 3 equiv.) and THF (1.0 mL) were added, followed by 4 Å M.S. (~150 mg, granular) and tricyclohexylphosphine (28 mg, 0.10 mmol, 1.0 equiv.) The vial was capped tightly with a Teflon-lined cap and allowed to stir at rt over 24 h. The reaction mixture was concentrated under a stream of nitrogen. The crude residue was dissolved in ethyl acetate (1 mL) and molecular sieves were decanted off, and subsequently washed with ethyl acetate (3 x 0.5 mL). The combined ethyl acetate mixtures were washed with 1 M $NaHSO_4$ (1 x 2 mL) followed by saturated aqueous NaCl solution (1 x 2 mL). The organic layer was collected and concentrated. The residue was purified by silica gel chromatography eluting with 10% ethyl acetate/hexanes to give desired product.

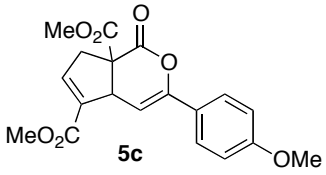


5a 21 mg, 66% yield. **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 7.68 – 7.61 (m, 2H), 7.43 – 7.33 (m, 3H), 6.76 (app q, J = 2.5 Hz, 1H), 6.04 (d, J = 5.0 Hz, 1H), 4.48 – 4.11 (m, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 3.54 – 3.46 (m, 1H), 3.42 – 3.32 (m, 1H); **^{13}C-NMR** (126 MHz, $CDCl_3$) δ 170.4, 167.0, 163.7, 148.2, 141.1, 135.3, 132.0, 129.5, 128.7, 124.9, 98.4, 57.2, 53.8, 52.0, 47.7, 41.5; **IR** (FT-RT, cm^{-1}) 3091, 2956, 1707, 1433, 1236, 1156, 1093, 1006; **TLC** R_f = 0.34 (30% ethyl acetate/hexanes); **HRMS** (ESI) *m/z* calc'd for $[C_{18}H_{16}O_6H]^+$ 329.1025, found 329.1021.

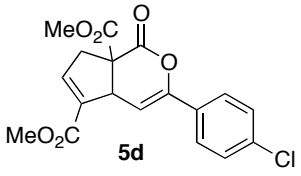


5b 18 mg, 53% yield. **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 7.53 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 7.9 Hz, 2H), 6.75 (app q, J = 2.5 Hz, 1H), 5.97 (d, J = 5.0 Hz, 1H), 4.30 – 4.21 (m, 1H), 3.78 (s, 3H), 3.77 (s, 3H), 3.53 – 3.45 (m, 1H), 3.42 – 3.31 (m, 1H), 2.36 (s, 3H); **^{13}C-NMR** (126 MHz, $CDCl_3$) δ 170.4, 167.0, 163.8, 148.3, 141.0, 139.6, 135.5, 129.3, 129.2, 124.9, 97.5, 57.2, 53.8, 52.0, 47.7, 41.5, 21.4; **IR** (FT-RT, cm^-

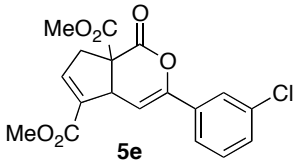
[1]) 3093, 2955, 1759, 1437, 1243, 1150; **TLC** R_f = 0.38 (30% ethyl acetate/hexanes); **HRMS** (ESI) *m/z* calc'd for $[C_{19}H_{18}O_6H]^+$ 343.1182, found 343.1181.



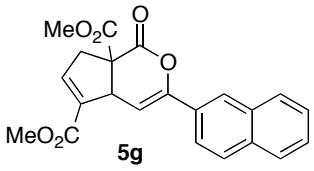
5c 8.7 mg, 24% yield. **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.9 Hz, 2H), 6.89 (d, *J* = 8.9 Hz, 2H), 6.77 – 6.71 (m, 1H), 5.89 (d, *J* = 5.1 Hz, 1H), 4.28 – 4.21 (m, 1H), 3.83 (s, 3H), 3.78 (s, 3H), 3.77 (s, 3H), 3.53 – 3.44 (m, 1H), 3.40 – 3.31 (m, 1H); **^{13}C-NMR** (126 MHz, $CDCl_3$) δ 170.5, 167.1, 163.8, 160.6, 148.0, 140.9, 135.5, 126.4, 124.6, 114.0, 96.5, 57.2, 55.5, 53.8, 52.0, 47.7, 41.5; **IR** (FT-RT, cm^{-1}) 3081, 2955, 1715, 1608, 1513, 1435, 1244, 1152, 10289; **TLC** R_f = 0.28 (30% ethyl acetate/hexanes); **HRMS** (ESI) *m/z* calc'd for $[C_{19}H_{18}O_7H]^+$ 359.1131, found 359.1127.



5d 19 mg, 54% yield. **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.6 Hz, 2H), 7.35 (d, *J* = 8.6 Hz, 2H), 6.76 (app q, *J* = 2.5 Hz, 1H), 6.04 (d, *J* = 5.1 Hz, 1H), 4.32 – 4.23 (m, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 3.55 – 3.44 (m, 1H), 3.43 – 3.34 (m, 1H); **^{13}C-NMR** (126 MHz, $CDCl_3$) δ 170.2, 166.7, 163.7, 147.3, 141.1, 135.4, 135.2, 130.5, 128.9, 126.2, 98.8, 57.1, 53.9, 52.1, 47.7, 41.5; **IR** (FT-RT, cm^{-1}) 3100, 2966, 1711, 1439, 1235, 1115,1007; **TLC** R_f = 0.33 (30% ethyl acetate/hexanes); **HRMS** (ESI) *m/z* calc'd for $[C_{18}H_{15}ClO_6H]^+$ 363.0635, found 363.0634.

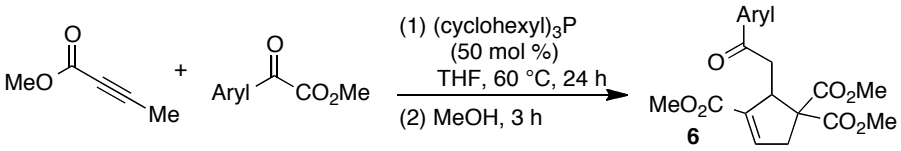


5e 20 mg, 56% yield. **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.57 – 7.49 (m, 1H), 7.38 – 7.27 (m, 2H), 6.76 (app q, 2.5 Hz, 1H), 6.08 (d, *J* = 5.1 Hz, 1H), 4.30 – 4.24 (m, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 3.53 – 3.46 (m, 1H) 3.43 – 3.34 (m, 1H); **^{13}C-NMR** (126 MHz, $CDCl_3$) δ 170.2, 166.6, 163.6, 147.0, 141.2, 135.1, 134.8, 133.8, 129.9, 129.5, 125.1, 123.1, 99.6, 57.2, 53.9, 52.1, 47.7, 41.5; **IR** (FT-RT, cm^{-1}) 3100, 2972, 1702, 1438, 1210, 1089; **TLC** R_f = 0.33 (30% ethyl acetate/hexanes); **HRMS** (ESI) *m/z* calc'd for $[C_{18}H_{15}ClO_6H]^+$ 363.0635, found 363.0641.

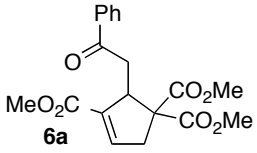


5g 26 mg, 68% yield. **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.94 – 7.86 (m, 1H), 7.86 – 7.80 (m, 2H), 7.68 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.62 – 7.46 (m, 2H), 6.79 (app q, *J* = 2.5 Hz, 1H), 6.19 (d, *J* = 5.0 Hz, 1H), 4.38 – 4.27 (m, 1H), 3.80 (s, 3H), 3.80 (s, 3H), 3.59 – 3.49 (m, 1H), 3.47 – 3.37 (m, 1H); **^{13}C-NMR** (126 MHz, $CDCl_3$) δ 170.4, 167.0, 163.8, 148.2, 141.1, 135.4, 133.7, 133.2, 129.0, 128.8, 128.4, 127.8, 127.0, 126.8, 124.5, 122.2, 98.9, 57.3, 53.9, 52.1, 47.8, 41.5; **IR** (FT-RT, cm^{-1}) 3067, 2954, 1713, 1435, 1243, 1097; **TLC** R_f = 0.34 (30% ethyl acetate/hexanes); **HRMS** (ESI) *m/z* calc'd for $[C_{22}H_{18}O_6H]^+$ 379.1182, found 379.1174.

IV. Preparation of Monocyclic Compounds (6)

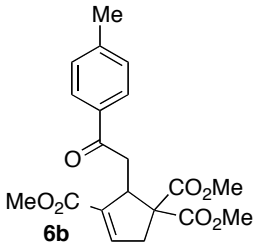


General Procedure for 6: An oven-dried 1 dram glass vial charged with a stir bar and methyl aroylformate (0.10 mmol, 1.0 equiv.) was taken into the glove box where methyl 2-butynoate (29 mg, 3.0 mmol, 3.0 equiv.) and THF (1.0 mL) were added, followed by tricyclohexylphosphine (14 mg, 0.050 mmol, 0.50 equiv.) The vial was capped tightly with a Teflon-lined cap and stirred at 60 °C over 24 h. MeOH (1.0 mL) was added and the reaction was left to stir for 3 h. The reaction mixture was concentrated in vacuo and the residue was purified by silica gel chromatography eluting with 10% ethyl acetate/hexanes to give the desired product.



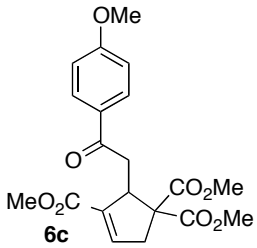
6a 24 mg, 67% yield. **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.6 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 6.83 – 6.66 (m, 1H), 4.65 – 4.47 (m, 1H), 3.77 (s, 3H), 3.69 (s, 3H), 3.51 (s, 3H), 3.44 – 3.24 (m, 3H), 3.12 (dd, *J* =

18.8, 3.1 Hz, 1H); **^{13}C-NMR** (126 MHz, $CDCl_3$) δ 197.9, 171.7, 170.5, 164.2, 140.7, 137.1, 137.1, 133.0, 128.7, 128.2, 63.4, 53.2, 52.7, 51.6, 45.9, 40.2, 38.5; **IR** (FT-RT, cm^{-1}) 3068, 2961, 1708, 1433, 1233, 1155, 1065; **TLC** R_f = 0.25 (30% ethyl acetate/hexanes); **HRMS** (ESI) *m/z* calc'd for $[C_{19}H_{20}O_7H]^+$ 361.1287, found 361.1290.



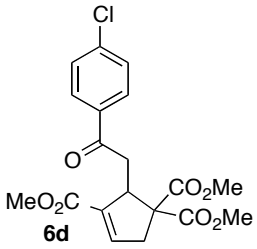
6b

24 mg, 63% yield. **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 6.77 – 6.71 (m, 1H), 4.59 – 4.49 (m, 1H), 3.76 (s, 3H), 3.69 (s, 3H), 3.50 (s, 3H), 3.44 – 3.16 (m, 3H), 3.11 (dd, *J* = 18.9, 3.2 Hz, 1H), 2.40 (s, 3H); **^{13}C-NMR** (126 MHz, $CDCl_3$) δ 197.5, 171.8 170.5, 164.2, 143.9, 140.8, 137.1, 134.4, 129.4, 128.3, 63.3, 53.3, 52.9, 51.7, 45.7, 40.2, 38.3, 21.8; **IR** (FT-RT, cm^{-1}) 3033, 2960, 1708, 1608, 1433, 1236, 1063; **TLC** R_f = 0.24 (30% ethyl acetate/hexanes); **HRMS** (ESI) *m/z* calc'd for $[C_{20}H_{22}O_7H]^+$ 375.1444, found 375.1437.



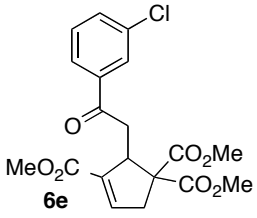
6c

11 mg, 28% yield. **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.9 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.78 – 6.68 (m, 1H), 4.57 – 4.49 (m, 1H), 3.86 (s, 3H), 3.76 (s, 3H), 3.69 (s, 3H), 3.50 (s, 3H), 3.44 – 3.35 (m, 1H), 3.29 (dd, *J* = 17.2, 8.6 Hz, 1H), 3.22 (dd, *J* = 17.2, 3.9 Hz, 1H), 3.10 (dd, *J* = 18.9, 3.2 Hz, 1H); **^{13}C-NMR** (126 MHz, $CDCl_3$) δ 196.4, 171.8, 170.5, 164.3, 163.5, 140.8, 137.2, 130.4, 130.0, 113.9, 63.3, 55.6, 53.3, 52.9, 51.7, 45.8, 40.1, 38.1; **IR** (FT-RT, cm^{-1}) 3003, 2953, 1715, 1599, 1511, 1435, 1243, 1166, 1110,1025; **TLC** R_f = 0.15 (30% ethyl acetate/hexanes); **HRMS** (ESI) *m/z* calc'd for $[C_{20}H_{22}O_8H]^+$ 391.1393, found 391.1388.



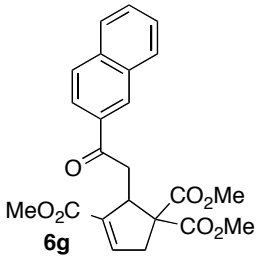
6d

27 mg, 68% yield. **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.1 Hz, 2H), 7.43 (d, *J* = 8.1 Hz, 2H), 6.82 – 6.69 (m, 1H), 4.59 – 4.43 (m, 1H), 3.77 (s, 3H), 3.70 (s, 3H), 3.52 (s, 3H), 3.42 – 3.24 (m, 3H), 3.13 (dd, *J* = 18.8, 3.1 Hz, 1H); **^{13}C-NMR** (126 MHz, $CDCl_3$) δ 196.8, 171.6, 170.5 164.2, 140.9, 139.5, 136.8, 135.1, 129.6, 129.0, 63.1, 53.3, 52.9, 51.8, 45.8, 40.2, 38.5; **IR** (FT-RT, cm^{-1}) 3097, 2954, 1716, 1685, 1589, 1432, 1279, 1155, 1062; **TLC** R_f = 0.28 (30% ethyl acetate/hexanes); **HRMS** (ESI) *m/z* calc'd for $[C_{19}H_{19}ClO_7H]^+$ 395.0898, found 395.0898.



6e

25 mg, 62% yield. **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.52 (d, *J* = 8.1 Hz, 1H), 7.39 (t, *J* = 7.9 Hz, 1H), 6.79 – 6.70 (m, 1H), 4.57 – 4.44 (m, 1H), 3.77 (s, 3H), 3.70 (s, 3H), 3.54 (s, 3H), 3.43 – 3.26 (m, 3H), 3.13 (dd, *J* = 18.8, 3.1 Hz, 1H); **^{13}C-NMR** (126 MHz, $CDCl_3$) δ 196.8, 171.6, 170.5, 164.2, 141.0, 138.3, 136.7, 135.0, 133.1, 130.1, 128.3, 126.3, 63.1, 53.4, 52.9, 51.7, 45.7, 40.2, 38.6; **IR** (FT-RT, cm^{-1}) 3095, 2953, 1726, 1440, 1245, 1203, 1114, 1065; **TLC** R_f = 0.26 (30% ethyl acetate/hexanes); **HRMS** (ESI) *m/z* calc'd for $[C_{19}H_{19}ClO_7H]^+$ 395.0898, found 395.0899.



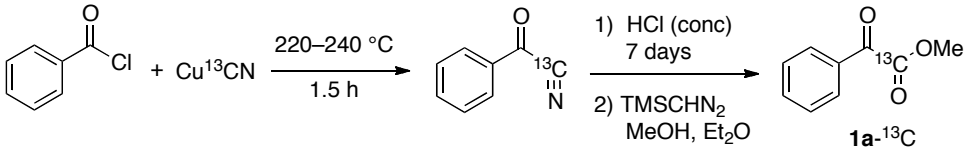
6g

27 mg, 65% yield. **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.02 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.99 – 7.94 (m, 1H), 7.88 (t, *J* = 8.7 Hz, 2H), 7.62 – 7.57 (m, 1H), 7.57 – 7.52 (m, 1H), 6.82 – 6.73 (m, 1H), 4.66 – 4.58 (m, 1H), 3.78 (s, 3H), 3.71 (s, 3H), 3.51 (s, 3H), 3.50 – 3.39 (m, 3H), 3.14 (dd, *J* = 18.8, 3.1 Hz, 1H); **^{13}C-NMR** (126 MHz, $CDCl_3$) δ 197.9, 171.8, 170.6, 164.3, 140.9, 137.1, 135.7, 134.1, 132.7, 129.9,

129.8, 128.6, 128.5, 127.9, 126.9, 124.0, 63.3, 53.4, 52.9, 51.8, 45.9, 40.3, 38.5; **IR** (FT-RT, cm^{-1}) 3022, 2959, 1730, 1708, 1628, 1434, 1252, 1157, 1065; **TLC** R_f = 0.26 (30% ethyl acetate/hexanes); **HRMS** (ESI) *m/z* calc'd for $[C_{23}H_{22}O_7H]^+$ 411.1444, found 411.1447.

V. Mechanistic Studies

Synthesis of ^{13}C-labeled methyl benzoylformate (1a-^{13}C)

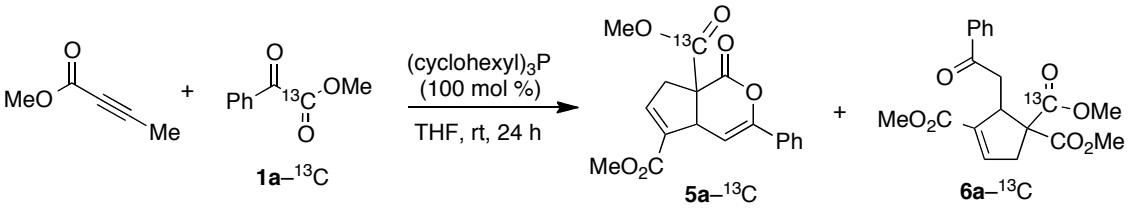


To an oven dried 15 mL round bottom flask charged with a stir bar and ^{13}C-labeled cuprous cyanide (371 mg, 4.1 mmol) that had been heated under reduced pressure at 110 ºC for 3 h, was added freshly distilled benzoyl chloride (0.48 mL, 4.1 mmol). The flask was shaken to moisten all the cuprous cyanide and was placed in an oil bath that was preheated to 150 ºC. The reaction mixture was stirred and the temperature of the bath was raised to 220–230 ºC and maintained between these limits for 1.5 h. The flask was allowed to cool to rt and extracted with diethyl ether (5 x 2 mL). Evaporation of diethyl ether under reduced pressure left brown crude material that was used directly in the next step.

To a 50 mL round bottom flask containing ^{13}C-labeled benzoyl cyanide and a stir bar was added concentrated HCl (5 mL) and the mixture was stirred at rt for 7 days. The heterogeneous reaction mixture was poured onto 20 mL of ice-cold water and extracted with diethyl ether (3 x 10 mL). The ether extracts were dried over $MgSO_4$, filtered and partially concentrated under a stream of nitrogen to about 10 mL of solvent and the crude mixture was cooled to 0 ºC. TMS diazomethane (2 M in hexanes) (3.0 mL, 6.2 mmol) was added to the reaction flask followed by MeOH (1.0 mL) and stirred for 1.5 h at 0 ºC. Upon completion, the reaction mixture was quenched by addition of silica gel, then concentrated on the rotary evaporator. The crude was dry loaded onto a silica column and

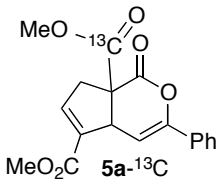
eluted with 5% EtOAc/hexanes to afford the desired product as a pale yellow oil (187 mg, 28% overall yield).[5] ^{1}H-NMR and IR spectra matched previously reported data.[5]

^{13}C-label tracking experiment in cycloaddition products

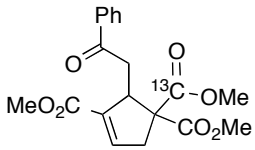


1a–^{13}C **5a**–^{13}C **6a**–^{13}C

An oven-dried 1 dram glass vial charged with a stir bar, 2,3-dimethylnaphthalene (16 mg, 1.0 equiv, 0.10 mmol) as an internal standard and methyl benzoylformate **1a**-^{13}C (17 mg, 0.10 mmol, 1.0 equiv.) was taken into the glove box where methyl 2-butynoate (29 mg, 3.0 mmol, 3.0 equiv.) and THF (1.0 mL) were added, followed by tricyclohexylphosphine (28 mg, 0.10 mmol, 0.10 equiv.) The vial was capped tightly with a Teflon-lined cap and stirred at rt over 24 h. ^{1}H-NMR analysis of the crude reaction mixture revealed 49% NMR yield of **5a**-^{13}C and 25% NMR yield of **6a**-^{13}C. No scrambling of the ^{13}C–label was observed for both products.



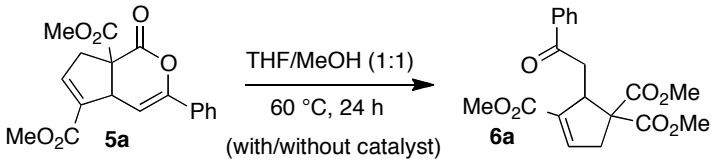
5a-^{13}C **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 7.67 – 7.63 (m, 2H), 7.47 – 7.32 (m, 3H), 6.76 (app q, J = 2.4 Hz, 1H), 6.04 (d, J = 5.0 Hz, 1H), 4.33 – 4.21 (m, 1H), 3.79 (d, J = 3.9 Hz, 3H), 3.78 (s, 3H), 3.53 – 3.47 (m, 1H), 3.44 – 3.35 (m, 1H); **^{13}C-NMR** (126 MHz, $CDCl_3$) δ 170.4, 167.0, 163.7, 148.2, 141.0 (d, J_{C-C} = 2.2 Hz), 135.4 (d, J_{C-C} = 2.6 Hz), 132.0, 129.5, 128.7, 125.0, 98.4, 57.2 (d, J_{C-C} = 59.6 Hz), 53.8 (d, J_{C-C} = 2.8 Hz), 52.1, 47.7, 41.6; **IR** (FT-RT, cm^{-1}) 3090, 2955, 1701, 1432, 1223, 1150, 1092; **TLC** R_f = 0.33 (30% ethyl acetate/hexanes); **HRMS** (ESI) *m/z* calc'd for $[C_{17}{}^{13}CH_{16}O_6H]^+$ 330.1059, found 330.1056.



6a-^{13}C

^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.94 (d, J = 7.9 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.7 Hz, 2H), 6.79 – 6.70 (m, 1H), 4.61 – 4.47 (m, 1H), 3.77 (d, J_{C-H} = 3.8 Hz, 3H), 3.69 (s, 3H), 3.51 (s, 3H), 3.44 – 3.24 (m, 3H), 3.18 – 3.05 (m, 1H); **^{13}C-NMR** (126 MHz, $CDCl_3$) δ 198.0, 171.7, 170.6, 164.2, 140.9, 137.0, 136.8, 133.1, 128.7, 128.2, 63.2 (d, J_{C-C} = 58.1 Hz), 53.3 (d, J_{C-C} = 2.8 Hz), 52.9, 51.8, 45.7, 40.2 (d, J_{C-C} = 1.4 Hz), 38.5 (d, J_{C-C} = 2.7 Hz); **IR** (FT-RT, cm^{-1}) 3005, 2953, 1697, 1434, 1243, 1148; **TLC** R_f = 0.23 (30% ethyl acetate/hexanes); **HRMS** (ESI) *m/z* calc'd for $[C_{18}{}^{13}CH_{20}O_7H]^+$ 362.1321, found 362.1320.

Methanolysis of bicyclo 5a to monocyclo 6a.



Without catalyst: To an oven-dried 1 dram glass vial containing a stir bar and bicyclo **5a** (16 mg, 0.050 mmol, 1.0 equiv.) was added THF/MeOH (1 mL, 1:1). The vial was capped tightly with a Teflon-lined cap and stirred at 60 ºC over 24 h. ^{1}H-NMR analysis of the crude reaction mixture revealed no reaction of the starting material.

With catalyst: An oven-dried 1 dram glass vial containing a stir bar, 2,3-dimethylnaphthalene (7.8 mg, 0.050 mmol, 1.0 equiv,) as an internal standard and bicyclo **5a** (16 mg, 0.050 mmol, 1.0 equiv.) was taken into the glove box where THF (0.50 mL) was added, followed by tricyclohexylphosphine (14 mg, 0.050 mmol, 0.10 equiv.) The vial was capped tightly with a septum fitted cap. In the fume hood, MeOH (0.50 mL) was added via syringe and the cap was quickly replaced with Teflon-lined cap and stirred at 60 ºC over 24 h. ^{1}H-NMR analysis of the crude reaction mixture revealed quantitative conversion to monocyclo **6a**.

VI. X-ray Structure Report for 5a (racemate)

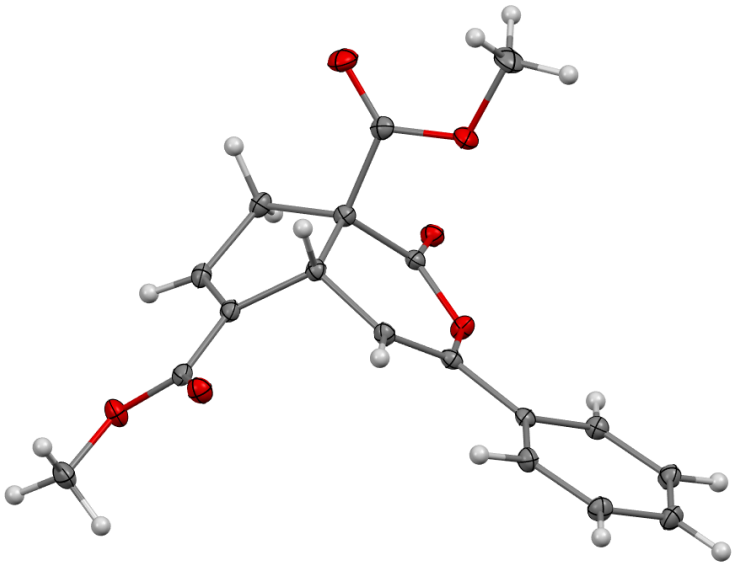


Figure S1. ORTEP of the X-ray crystal structure of bicyclo **5a**.

Table S1. Crystal data and structure refinement for **5a**.

Identification code	12054	
Empirical formula	C18 H16 O6	
Formula weight	328.31	
Temperature	93(2) K	
Wavelength	1.54187 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.2090(2) Å	a= 72.370(5)°.
	b = 11.5382(2) Å	b= 89.090(6) °.
	c = 15.2590(11) Å	g = 66.272(5) °.
Volume	1556.57(14) $Å^3$	
Z	4	
Density (calculated)	1.401 Mg/m^3	
Absorption coefficient	0.887 mm^{-1}	
F(000)	688	
Crystal size	0.15 x 0.15 x 0.05 mm^3	
Theta range for data collection	7.21 to 68.19°.	

Index ranges	-12<=h<=12, -13<=k<=13, -18<=l<=18
Reflections collected	47179
Independent reflections	5473 [R(int) = 0.0923]
Completeness to theta = 68.19°	96.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9570 and 0.8784
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5473 / 0 / 437
Goodness-of-fit on F^2	1.075
Final R indices [I>2sigma(I)]	R1 = 0.0377, wR2 = 0.0991
R indices (all data)	R1 = 0.0410, wR2 = 0.1027
Largest diff. peak and hole	0.279 and -0.248 e.Å^{-3}

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **5a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	4987(1)	1364(1)	1010(1)	22(1)
C(1)	4786(1)	1476(1)	1860(1)	20(1)
O(2)	5730(1)	710(1)	2482(1)	25(1)
C(2)	3426(1)	2560(1)	2018(1)	21(1)
C(9)	3862(1)	3630(2)	2137(1)	26(1)
O(3)	3549(1)	4124(1)	2738(1)	39(1)
O(4)	4608(1)	3970(1)	1450(1)	37(1)
C(10)	5037(2)	5028(2)	1454(2)	45(1)
C(3)	2836(2)	1923(2)	2884(1)	26(1)
C(4)	1582(1)	1810(2)	2488(1)	25(1)
C(5)	1200(1)	2515(1)	1596(1)	20(1)
C(11)	-106(1)	2764(1)	1028(1)	20(1)
O(5)	-589(1)	3632(1)	288(1)	25(1)
O(6)	-689(1)	1915(1)	1434(1)	28(1)
C(12)	-1979(2)	2094(2)	931(1)	32(1)
C(6)	2168(1)	3212(1)	1208(1)	20(1)
C(7)	2674(1)	3066(1)	304(1)	20(1)

C(8)	3970(1)	2214(1)	227(1)	19(1)
C(21)	4592(1)	1993(1)	-620(1)	20(1)
C(22)	6015(2)	1069(2)	-573(1)	24(1)
C(23)	6605(2)	892(2)	-1375(1)	27(1)
C(24)	5792(2)	1619(2)	-2230(1)	27(1)
C(25)	4383(2)	2533(2)	-2286(1)	27(1)
C(26)	3784(2)	2722(2)	-1490(1)	23(1)
O(101)	10782(1)	864(1)	4530(1)	21(1)
C(101)	9774(1)	1596(1)	4804(1)	18(1)
O(102)	9894(1)	1472(1)	5712(1)	20(1)
C(102)	8418(1)	2650(1)	4160(1)	19(1)
C(109)	8808(1)	3768(1)	3578(1)	21(1)
O(103)	8438(1)	4344(1)	2766(1)	33(1)
O(104)	9592(1)	4048(1)	4110(1)	28(1)
C(110)	9980(2)	5143(2)	3649(1)	36(1)
C(103)	7927(1)	1989(2)	3564(1)	22(1)
C(104)	6673(1)	1815(1)	4000(1)	21(1)
C(105)	6212(1)	2491(1)	4594(1)	20(1)
C(111)	4903(1)	2653(1)	5057(1)	20(1)
O(105)	4334(1)	3504(1)	5420(1)	26(1)
O(106)	4407(1)	1754(1)	5023(1)	27(1)
C(112)	3100(2)	1859(2)	5444(1)	31(1)
C(106)	7098(1)	3250(1)	4673(1)	18(1)
C(107)	7529(1)	3132(1)	5644(1)	20(1)
C(108)	8820(1)	2315(1)	6103(1)	18(1)
C(121)	9393(1)	2162(1)	7034(1)	18(1)
C(122)	10854(1)	1370(1)	7366(1)	20(1)
C(123)	11415(2)	1316(2)	8206(1)	24(1)
C(124)	10534(2)	2020(2)	8737(1)	25(1)
C(125)	9077(2)	2790(2)	8420(1)	24(1)
C(126)	8510(1)	2859(1)	7580(1)	21(1)

Table S3. Bond lengths [Å] and angles [°] for **5a**.

O(1)-C(1)	1.3459(16)	C(22)-H(22)	0.9500
O(1)-C(8)	1.4066(16)	C(23)-C(24)	1.381(2)
C(1)-O(2)	1.2027(16)	C(23)-H(23)	0.9500
C(1)-C(2)	1.5242(18)	C(24)-C(25)	1.384(2)
C(2)-C(9)	1.529(2)	C(24)-H(24)	0.9500
C(2)-C(3)	1.547(2)	C(25)-C(26)	1.387(2)
C(2)-C(6)	1.5654(18)	C(25)-H(25)	0.9500
C(9)-O(3)	1.1946(18)	C(26)-H(26)	0.9500
C(9)-O(4)	1.341(2)	O(101)-C(101)	1.2034(16)
O(4)-C(10)	1.4544(19)	C(101)-O(102)	1.3501(16)
C(10)-H(10A)	0.9800	C(101)-C(102)	1.5252(18)
C(10)-H(10B)	0.9800	O(102)-C(108)	1.4066(15)
C(10)-H(10C)	0.9800	C(102)-C(109)	1.523(2)
C(3)-C(4)	1.492(2)	C(102)-C(103)	1.5494(18)
C(3)-H(3A)	0.9900	C(102)-C(106)	1.5660(17)
C(3)-H(3B)	0.9900	C(109)-O(103)	1.1961(17)
C(4)-C(5)	1.326(2)	C(109)-O(104)	1.3386(17)
C(4)-H(4)	0.9500	O(104)-C(110)	1.4505(19)
C(5)-C(11)	1.4790(18)	C(110)-H(11A)	0.9800
C(5)-C(6)	1.5189(19)	C(110)-H(11B)	0.9800
C(11)-O(5)	1.2066(17)	C(110)-H(11C)	0.9800
C(11)-O(6)	1.3383(17)	C(103)-C(104)	1.4895(19)
O(6)-C(12)	1.4424(17)	C(103)-H(10D)	0.9900
C(12)-H(12A)	0.9800	C(103)-H(10E)	0.9900
C(12)-H(12B)	0.9800	C(104)-C(105)	1.3306(19)
C(12)-H(12C)	0.9800	C(104)-H(104)	0.9500
C(6)-C(7)	1.4990(18)	C(105)-C(111)	1.4731(19)
C(6)-H(6)	1.0000	C(105)-C(106)	1.5183(18)
C(7)-C(8)	1.3225(19)	C(111)-O(105)	1.2117(17)
C(7)-H(7)	0.9500	C(111)-O(106)	1.3381(17)
C(8)-C(21)	1.4775(19)	O(106)-C(112)	1.4475(17)
C(21)-C(26)	1.3974(19)	C(112)-H(11D)	0.9800
C(21)-C(22)	1.4002(19)	C(112)-H(11E)	0.9800
C(22)-C(23)	1.390(2)	C(112)-H(11F)	0.9800

C(106)-C(107)	1.5015(18)	C(122)-H(122)	0.9500
C(106)-H(106)	1.0000	C(123)-C(124)	1.383(2)
C(107)-C(108)	1.3222(19)	C(123)-H(123)	0.9500
C(107)-H(107)	0.9500	C(124)-C(125)	1.390(2)
C(108)-C(121)	1.4770(18)	C(124)-H(124)	0.9500
C(121)-C(126)	1.3967(19)	C(125)-C(126)	1.3830(19)
C(121)-C(122)	1.4007(19)	C(125)-H(125)	0.9500
C(122)-C(123)	1.3872(19)	C(126)-H(126)	0.9500

C(1)-O(1)-C(8)	122.71(10)	C(5)-C(4)-H(4)	123.8
O(2)-C(1)-O(1)	117.51(12)	C(3)-C(4)-H(4)	123.8
O(2)-C(1)-C(2)	121.55(12)	C(4)-C(5)-C(11)	126.11(13)
O(1)-C(1)-C(2)	120.92(11)	C(4)-C(5)-C(6)	112.64(12)
C(1)-C(2)-C(9)	106.45(11)	C(11)-C(5)-C(6)	120.91(12)
C(1)-C(2)-C(3)	108.75(12)	O(5)-C(11)-O(6)	124.06(12)
C(9)-C(2)-C(3)	112.46(12)	O(5)-C(11)-C(5)	124.06(13)
C(1)-C(2)-C(6)	113.99(11)	O(6)-C(11)-C(5)	111.88(12)
C(9)-C(2)-C(6)	109.64(12)	C(11)-O(6)-C(12)	115.68(11)
C(3)-C(2)-C(6)	105.69(11)	O(6)-C(12)-H(12A)	109.5
O(3)-C(9)-O(4)	124.69(15)	O(6)-C(12)-H(12B)	109.5
O(3)-C(9)-C(2)	125.16(15)	H(12A)-C(12)-H(12B)	109.5
O(4)-C(9)-C(2)	110.12(12)	O(6)-C(12)-H(12C)	109.5
C(9)-O(4)-C(10)	115.99(13)	H(12A)-C(12)-H(12C)	109.5
O(4)-C(10)-H(10A)	109.5	H(12B)-C(12)-H(12C)	109.5
O(4)-C(10)-H(10B)	109.5	C(7)-C(6)-C(5)	114.90(11)
H(10A)-C(10)-H(10B)	109.5	C(7)-C(6)-C(2)	113.20(11)
O(4)-C(10)-H(10C)	109.5	C(5)-C(6)-C(2)	101.96(11)
H(10A)-C(10)-H(10C)	109.5	C(7)-C(6)-H(6)	108.8
H(10B)-C(10)-H(10C)	109.5	C(5)-C(6)-H(6)	108.8
C(4)-C(3)-C(2)	103.47(11)	C(2)-C(6)-H(6)	108.8
C(4)-C(3)-H(3A)	111.1	C(8)-C(7)-C(6)	123.79(12)
C(2)-C(3)-H(3A)	111.1	C(8)-C(7)-H(7)	118.1
C(4)-C(3)-H(3B)	111.1	C(6)-C(7)-H(7)	118.1
C(2)-C(3)-H(3B)	111.1	C(7)-C(8)-O(1)	121.37(12)
H(3A)-C(3)-H(3B)	109.0	C(7)-C(8)-C(21)	128.68(12)
C(5)-C(4)-C(3)	112.44(13)	O(1)-C(8)-C(21)	109.95(11)

C(26)-C(21)-C(22)	118.35(13)	H(11A)-C(110)-H(11C)	109.5
C(26)-C(21)-C(8)	120.70(12)	H(11B)-C(110)-H(11C)	109.5
C(22)-C(21)-C(8)	120.94(12)	C(104)-C(103)-C(102)	103.54(10)
C(23)-C(22)-C(21)	120.61(14)	C(104)-C(103)-H(10D)	111.1
C(23)-C(22)-H(22)	119.7	C(102)-C(103)-H(10D)	111.1
C(21)-C(22)-H(22)	119.7	C(104)-C(103)-H(10E)	111.1
C(24)-C(23)-C(22)	120.37(14)	C(102)-C(103)-H(10E)	111.1
C(24)-C(23)-H(23)	119.8	H(10D)-C(103)-H(10E)	109.0
C(22)-C(23)-H(23)	119.8	C(105)-C(104)-C(103)	112.62(12)
C(23)-C(24)-C(25)	119.57(13)	C(105)-C(104)-H(104)	123.7
C(23)-C(24)-H(24)	120.2	C(103)-C(104)-H(104)	123.7
C(25)-C(24)-H(24)	120.2	C(104)-C(105)-C(111)	126.05(13)
C(24)-C(25)-C(26)	120.56(14)	C(104)-C(105)-C(106)	112.28(12)
C(24)-C(25)-H(25)	119.7	C(111)-C(105)-C(106)	121.30(12)
C(26)-C(25)-H(25)	119.7	O(105)-C(111)-O(106)	123.88(12)
C(25)-C(26)-C(21)	120.53(13)	O(105)-C(111)-C(105)	124.14(13)
C(25)-C(26)-H(26)	119.7	O(106)-C(111)-C(105)	111.98(12)
C(21)-C(26)-H(26)	119.7	C(111)-O(106)-C(112)	115.71(11)
O(101)-C(101)-O(102)	117.39(12)	O(106)-C(112)-H(11D)	109.5
O(101)-C(101)-C(102)	122.09(12)	O(106)-C(112)-H(11E)	109.5
O(102)-C(101)-C(102)	120.51(11)	H(11D)-C(112)-H(11E)	109.5
C(101)-O(102)-C(108)	122.61(10)	O(106)-C(112)-H(11F)	109.5
C(109)-C(102)-C(101)	106.73(10)	H(11D)-C(112)-H(11F)	109.5
C(109)-C(102)-C(103)	112.59(11)	H(11E)-C(112)-H(11F)	109.5
C(101)-C(102)-C(103)	108.79(11)	C(107)-C(106)-C(105)	115.23(11)
C(109)-C(102)-C(106)	109.19(11)	C(107)-C(106)-C(102)	113.06(10)
C(101)-C(102)-C(106)	114.19(11)	C(105)-C(106)-C(102)	102.11(10)
C(103)-C(102)-C(106)	105.48(10)	C(107)-C(106)-H(106)	108.7
O(103)-C(109)-O(104)	124.48(14)	C(105)-C(106)-H(106)	108.7
O(103)-C(109)-C(102)	125.26(13)	C(102)-C(106)-H(106)	108.7
O(104)-C(109)-C(102)	110.23(11)	C(108)-C(107)-C(106)	123.38(12)
C(109)-O(104)-C(110)	115.97(12)	C(108)-C(107)-H(107)	118.3
O(104)-C(110)-H(11A)	109.5	C(106)-C(107)-H(107)	118.3
O(104)-C(110)-H(11B)	109.5	C(107)-C(108)-O(102)	121.62(12)
H(11A)-C(110)-H(11B)	109.5	C(107)-C(108)-C(121)	128.34(12)
O(104)-C(110)-H(11C)	109.5	O(102)-C(108)-C(121)	109.99(11)

C(126)-C(121)-C(122)	118.66(12)	C(123)-C(124)-C(125)	119.54(13)
C(126)-C(121)-C(108)	120.78(12)	C(123)-C(124)-H(124)	120.2
C(122)-C(121)-C(108)	120.48(12)	C(125)-C(124)-H(124)	120.2
C(123)-C(122)-C(121)	120.41(12)	C(126)-C(125)-C(124)	120.46(13)
C(123)-C(122)-H(122)	119.8	C(126)-C(125)-H(125)	119.8
C(121)-C(122)-H(122)	119.8	C(124)-C(125)-H(125)	119.8
C(124)-C(123)-C(122)	120.41(13)	C(125)-C(126)-C(121)	120.49(12)
C(124)-C(123)-H(123)	119.8	C(125)-C(126)-H(126)	119.8
C(122)-C(123)-H(123)	119.8	C(121)-C(126)-H(126)	119.8

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **5a**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	20(1)	23(1)	18(1)	-7(1)	-1(1)	-4(1)
C(1)	20(1)	21(1)	20(1)	-8(1)	2(1)	-11(1)
O(2)	22(1)	26(1)	22(1)	-9(1)	-3(1)	-4(1)
C(2)	18(1)	24(1)	21(1)	-10(1)	1(1)	-7(1)
C(9)	19(1)	21(1)	32(1)	-12(1)	-6(1)	-2(1)
O(3)	50(1)	28(1)	34(1)	-18(1)	-6(1)	-6(1)
O(4)	31(1)	35(1)	62(1)	-30(1)	15(1)	-22(1)
C(10)	31(1)	33(1)	85(2)	-30(1)	6(1)	-18(1)
C(3)	23(1)	35(1)	18(1)	-9(1)	2(1)	-8(1)
C(4)	21(1)	31(1)	21(1)	-9(1)	7(1)	-10(1)
C(5)	17(1)	22(1)	22(1)	-9(1)	4(1)	-7(1)
C(11)	18(1)	23(1)	22(1)	-11(1)	7(1)	-8(1)
O(5)	23(1)	27(1)	24(1)	-5(1)	-1(1)	-11(1)
O(6)	24(1)	33(1)	28(1)	-6(1)	2(1)	-18(1)
C(12)	25(1)	39(1)	37(1)	-11(1)	2(1)	-20(1)
C(6)	16(1)	22(1)	22(1)	-8(1)	0(1)	-7(1)
C(7)	18(1)	23(1)	18(1)	-4(1)	0(1)	-11(1)

C(8)	20(1)	19(1)	17(1)	-3(1)	-1(1)	-10(1)
C(21)	22(1)	20(1)	21(1)	-7(1)	3(1)	-12(1)
C(22)	24(1)	23(1)	23(1)	-7(1)	2(1)	-9(1)
C(23)	26(1)	28(1)	30(1)	-12(1)	9(1)	-11(1)
C(24)	34(1)	32(1)	24(1)	-13(1)	11(1)	-20(1)
C(25)	31(1)	34(1)	21(1)	-8(1)	3(1)	-18(1)
C(26)	23(1)	26(1)	22(1)	-6(1)	2(1)	-13(1)
O(101)	19(1)	22(1)	20(1)	-7(1)	4(1)	-8(1)
C(101)	20(1)	18(1)	17(1)	-5(1)	3(1)	-11(1)
O(102)	19(1)	20(1)	18(1)	-7(1)	1(1)	-4(1)
C(102)	19(1)	19(1)	18(1)	-6(1)	2(1)	-8(1)
C(109)	18(1)	20(1)	22(1)	-5(1)	2(1)	-5(1)
O(103)	43(1)	29(1)	22(1)	2(1)	-2(1)	-16(1)
O(104)	33(1)	26(1)	28(1)	-2(1)	0(1)	-20(1)
C(110)	40(1)	28(1)	41(1)	-1(1)	3(1)	-22(1)
C(103)	22(1)	22(1)	20(1)	-8(1)	0(1)	-7(1)
C(104)	20(1)	21(1)	22(1)	-7(1)	-4(1)	-8(1)
C(105)	18(1)	20(1)	19(1)	-4(1)	-3(1)	-7(1)
C(111)	18(1)	22(1)	19(1)	-3(1)	-3(1)	-8(1)
O(105)	24(1)	28(1)	28(1)	-12(1)	6(1)	-11(1)
O(106)	24(1)	31(1)	34(1)	-12(1)	5(1)	-17(1)
C(112)	24(1)	38(1)	36(1)	-8(1)	5(1)	-19(1)
C(106)	16(1)	17(1)	19(1)	-5(1)	1(1)	-6(1)
C(107)	18(1)	22(1)	21(1)	-10(1)	4(1)	-10(1)
C(108)	19(1)	17(1)	20(1)	-7(1)	5(1)	-9(1)
C(121)	21(1)	16(1)	18(1)	-4(1)	2(1)	-11(1)
C(122)	20(1)	20(1)	21(1)	-7(1)	3(1)	-8(1)
C(123)	20(1)	25(1)	23(1)	-6(1)	-1(1)	-7(1)
C(124)	27(1)	30(1)	20(1)	-9(1)	-1(1)	-12(1)
C(125)	24(1)	27(1)	23(1)	-11(1)	5(1)	-10(1)
C(126)	18(1)	22(1)	23(1)	-8(1)	2(1)	-8(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **5a**.

	x	y	z	U(eq)
H(10A)	4177	5845	1407	68
H(10B)	5570	5200	927	68
H(10C)	5654	4750	2032	68
H(3A)	3572	1032	3254	32
H(3B)	2527	2502	3280	32
H(4)	1111	1291	2836	30
H(12A)	-2622	3049	692	48
H(12B)	-2469	1614	1347	48
H(12C)	-1721	1741	414	48
H(6)	1642	4186	1130	24
H(7)	2025	3618	-246	24
H(22)	6581	558	12	28
H(23)	7574	268	-1334	33
H(24)	6196	1492	-2777	33
H(25)	3823	3036	-2873	33
H(26)	2816	3351	-1538	28
H(11A)	10576	4926	3162	54
H(11B)	10524	5283	4100	54
H(11C)	9103	5960	3372	54
H(10D)	7637	2575	2911	26
H(10E)	8704	1116	3590	26
H(104)	6249	1280	3868	25
H(11D)	3292	1658	6113	47
H(11E)	2774	1221	5330	47
H(11F)	2351	2770	5174	47
H(106)	6539	4218	4313	22
H(107)	6837	3671	5943	23
H(122)	11464	867	7013	25
H(123)	12412	793	8419	28
H(124)	10920	1978	9314	30
H(125)	8468	3272	8784	29
H(126)	7512	3384	7372	25

VII. References

[1] Chan, W. W.; Yeung, S. H.; Zhou, Z.; Chan, A. S.; Yu, W. Y. *Org. Lett.* **2010**, *12*, 604–607.
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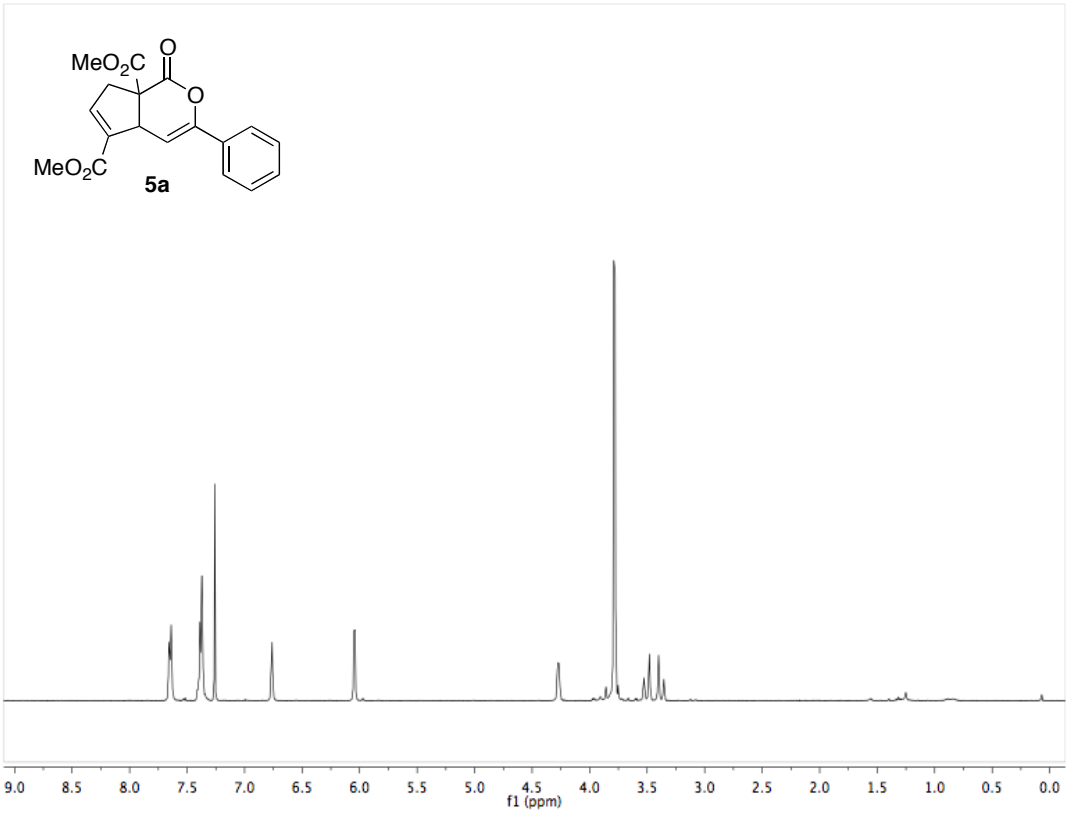
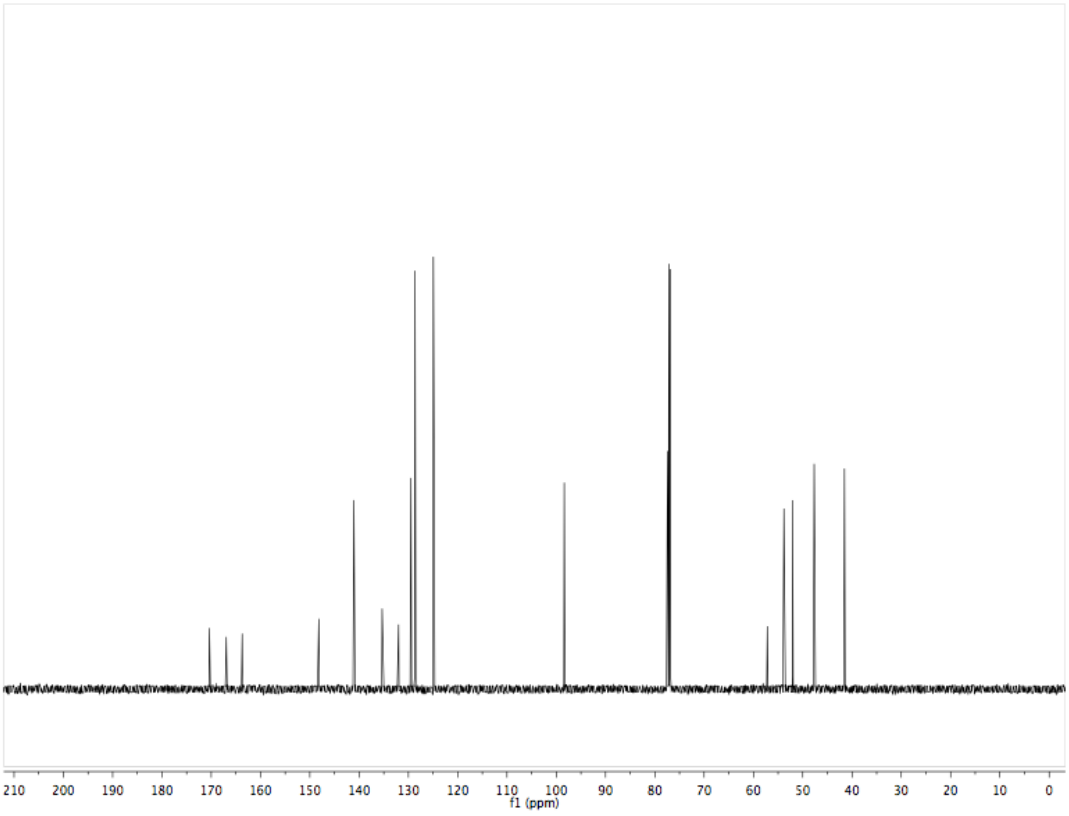
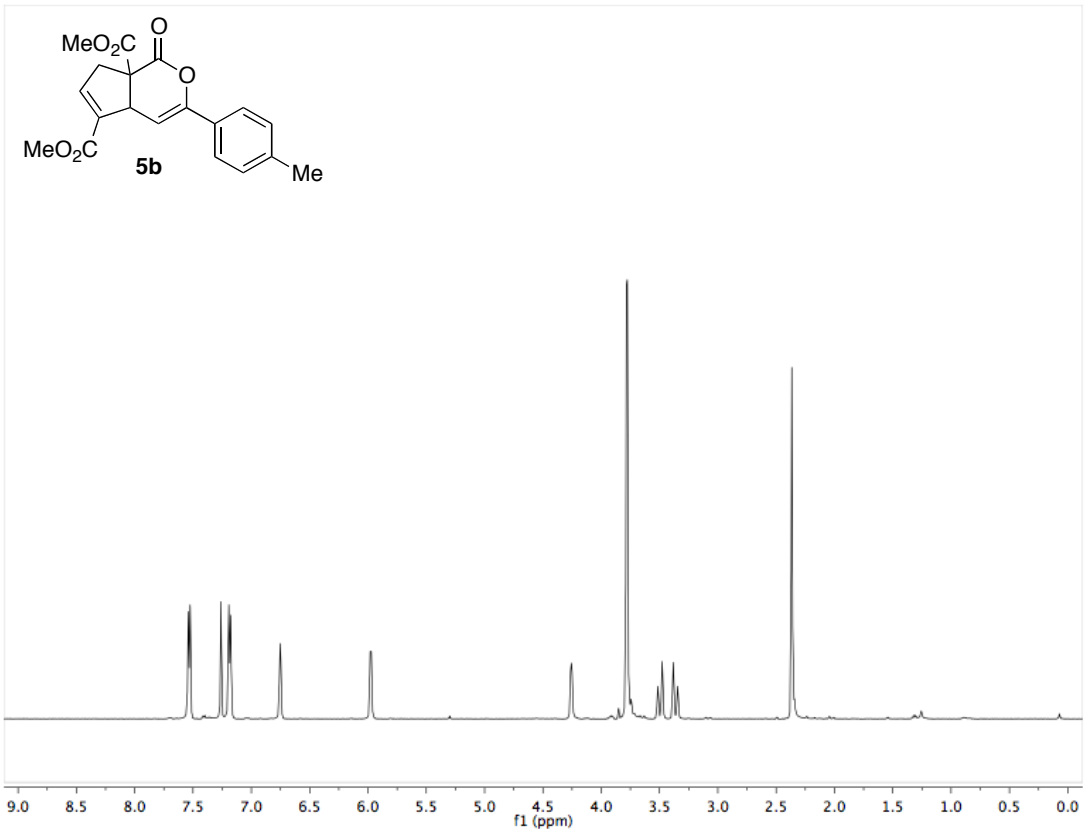
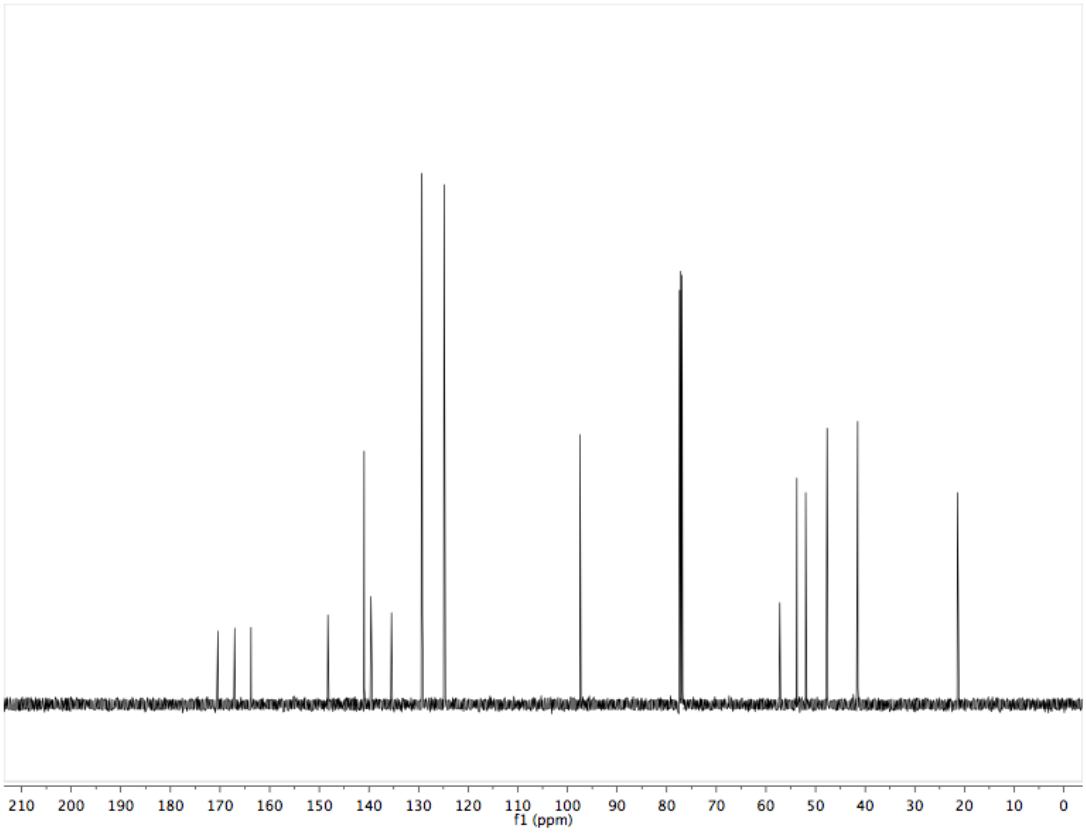
[5] Breau, L.; Kayser, M. M. *J. Label Compd. Radiopharm.* **1988**, *25*, 301–312.

VIII. ^{1}H-NMR and ^{13}C-NMR Spectra






MeO2C
O
O
MeO2C
Me
5b
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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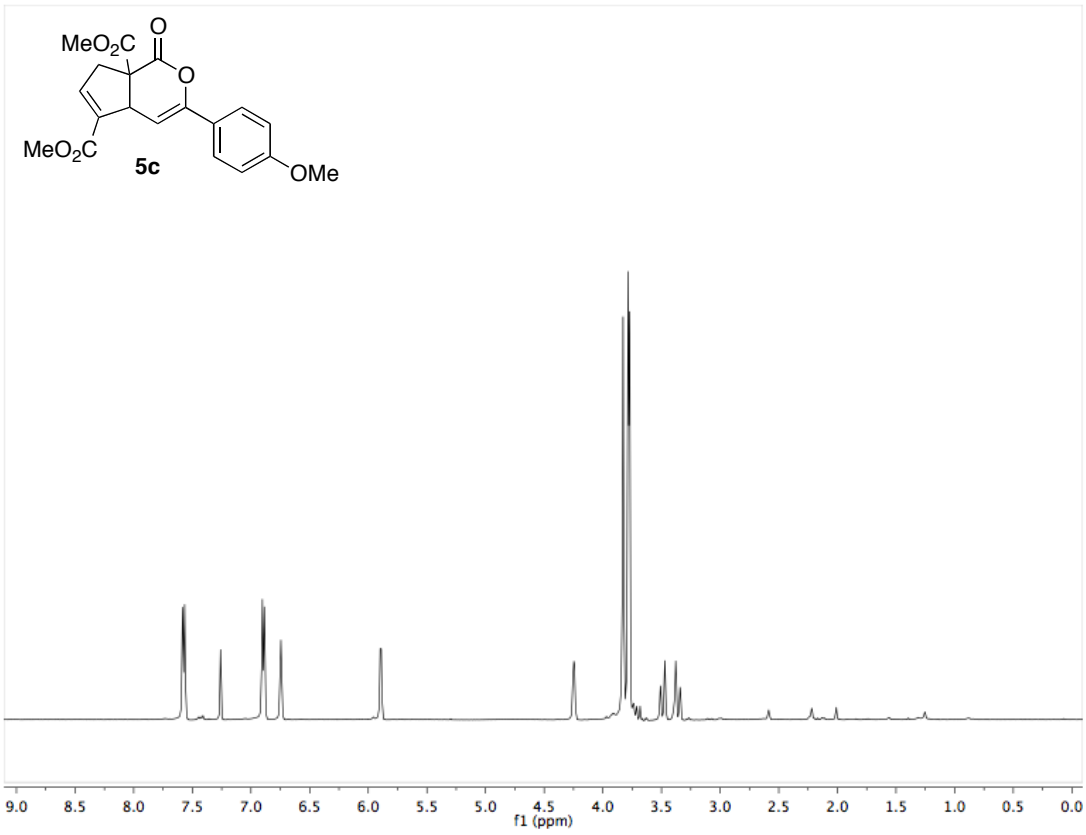
f1 (ppm)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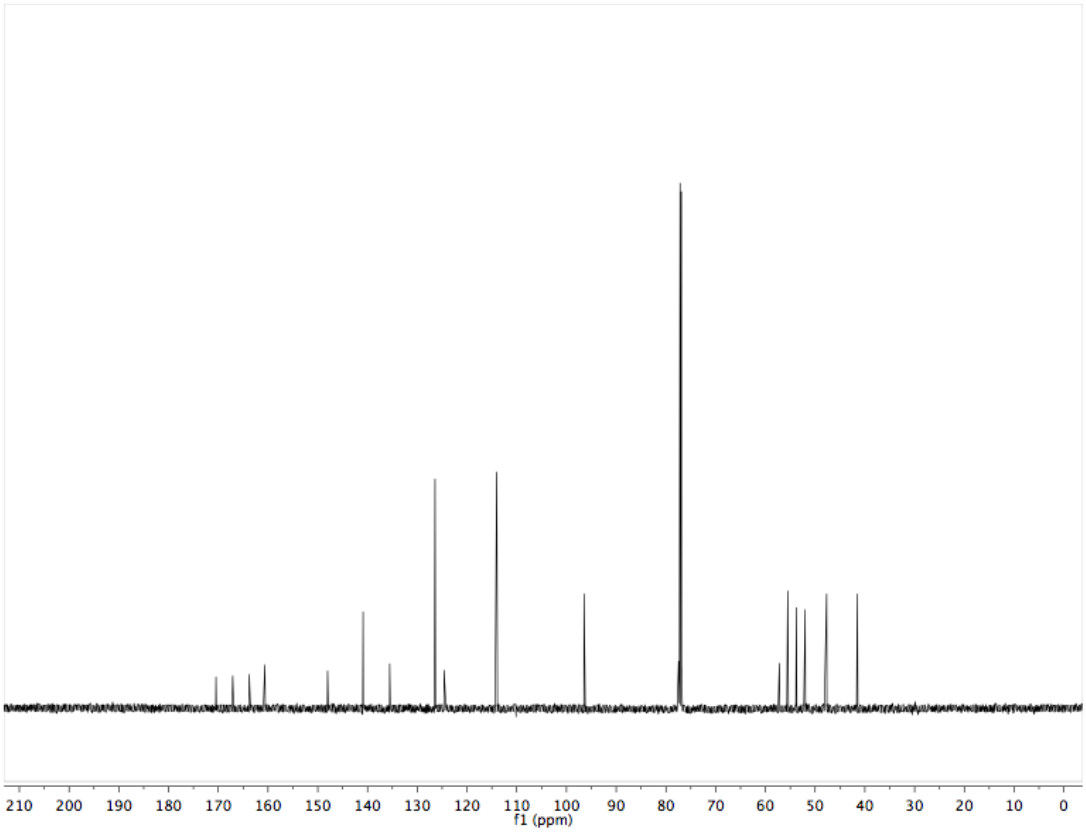
O
O
MeO2C
OMe
5c
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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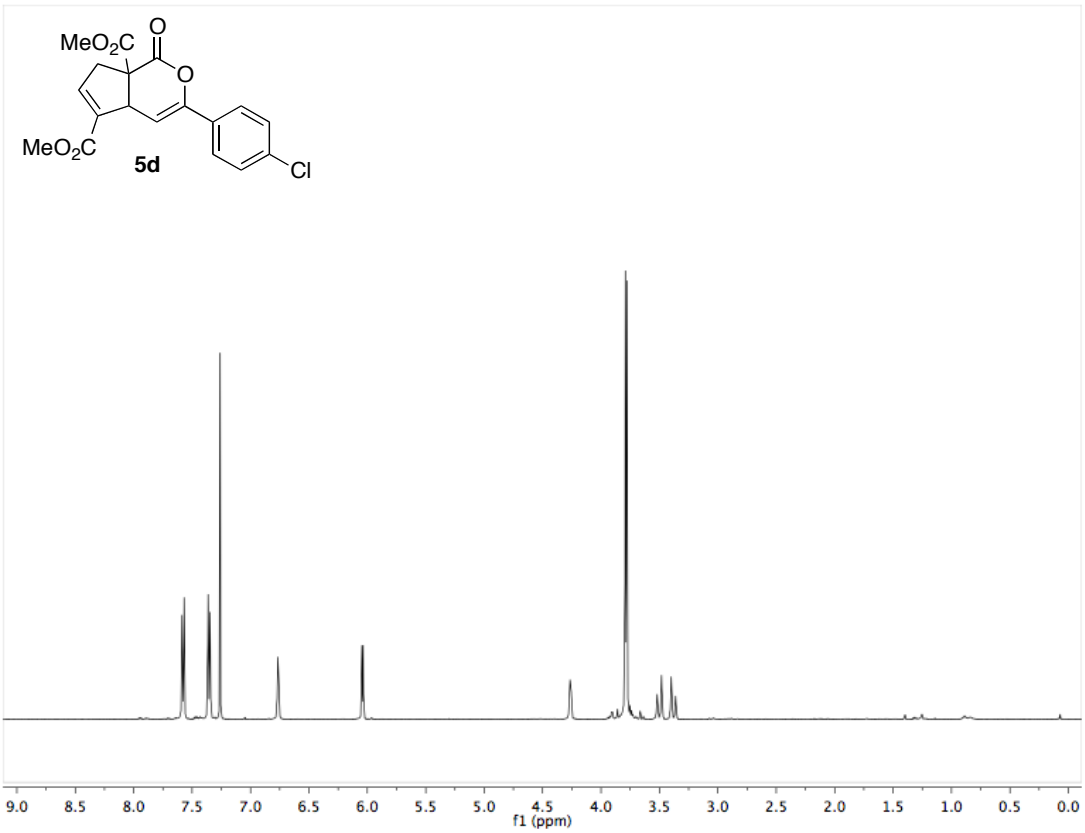
f1 (ppm)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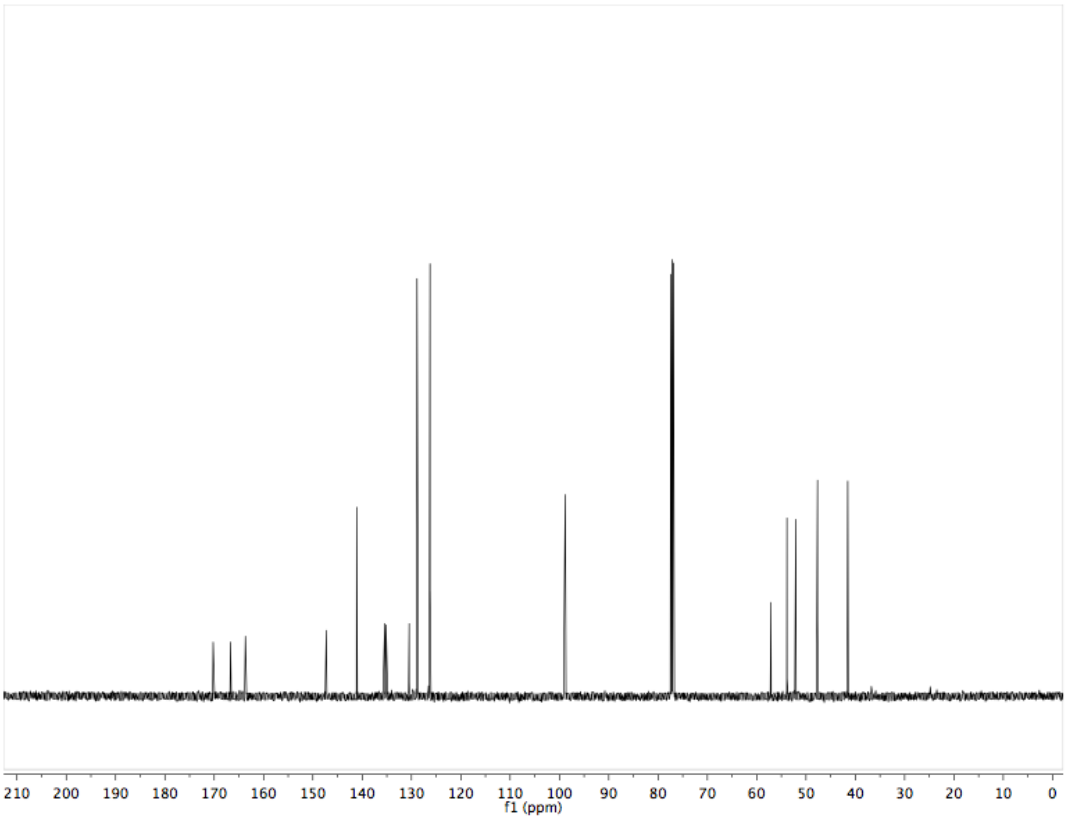
O
O
MeO2C
Cl
5d
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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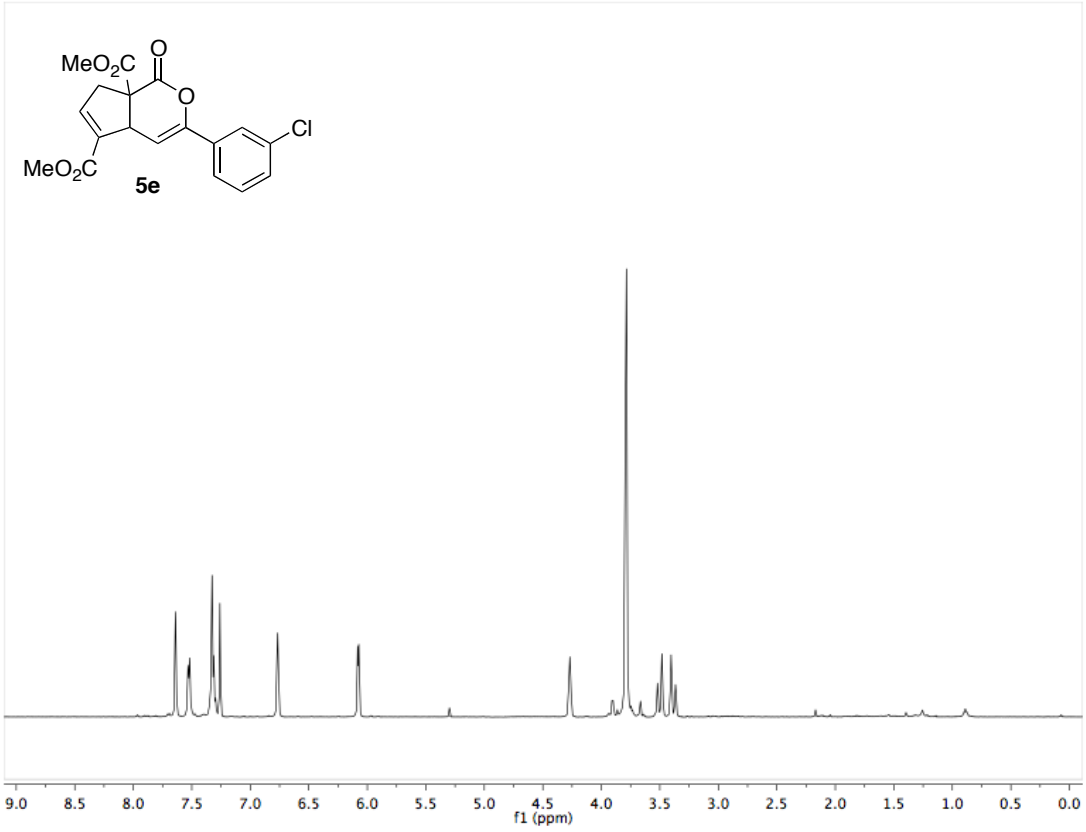
f1 (ppm)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O
O
Cl
MeO2C
5e
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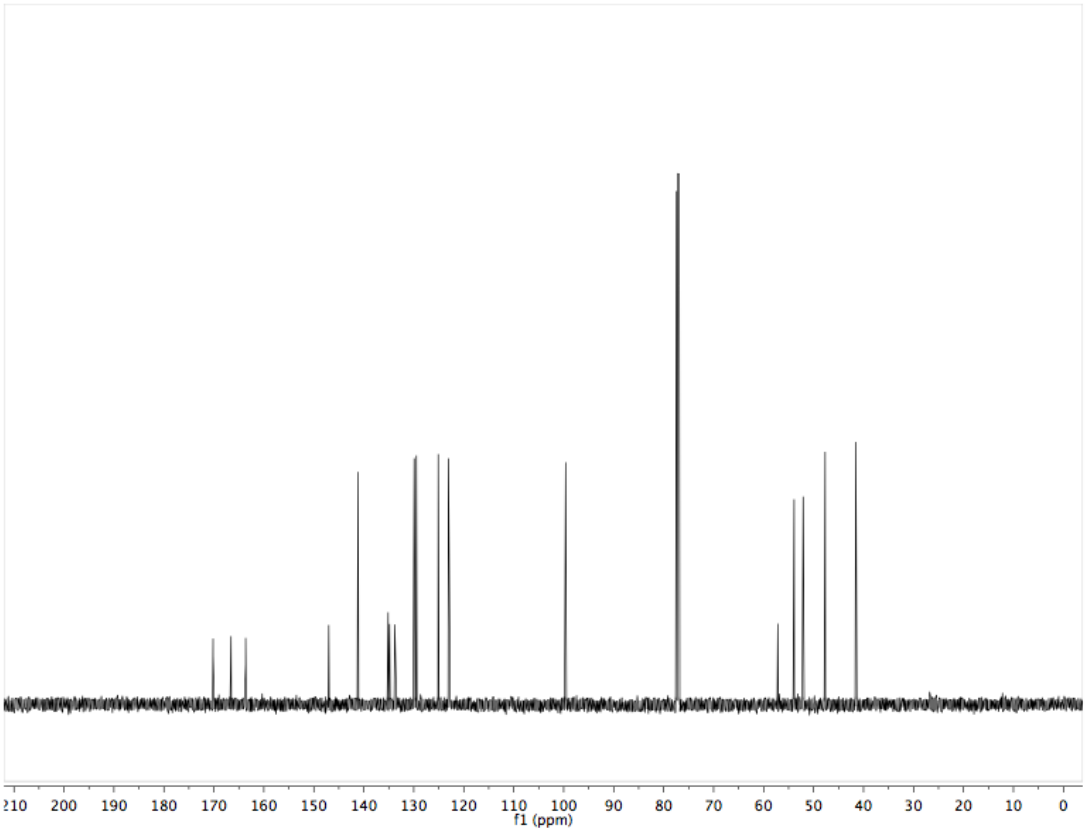
f1 (ppm)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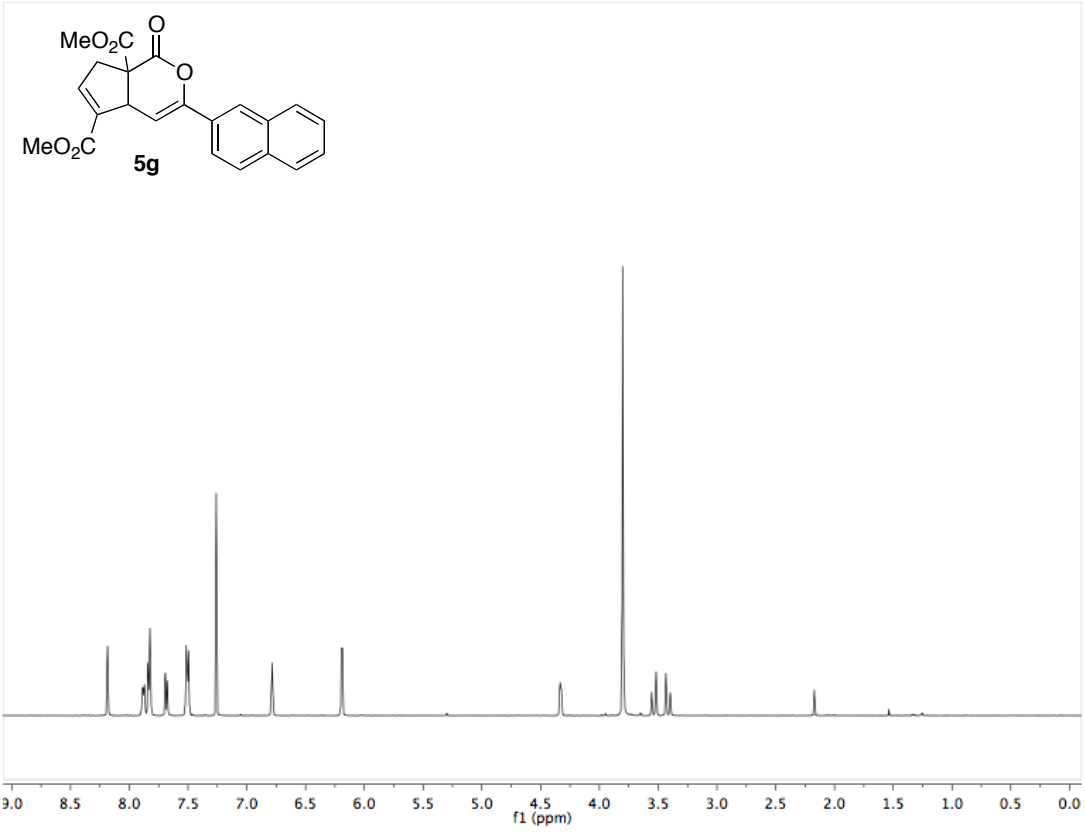
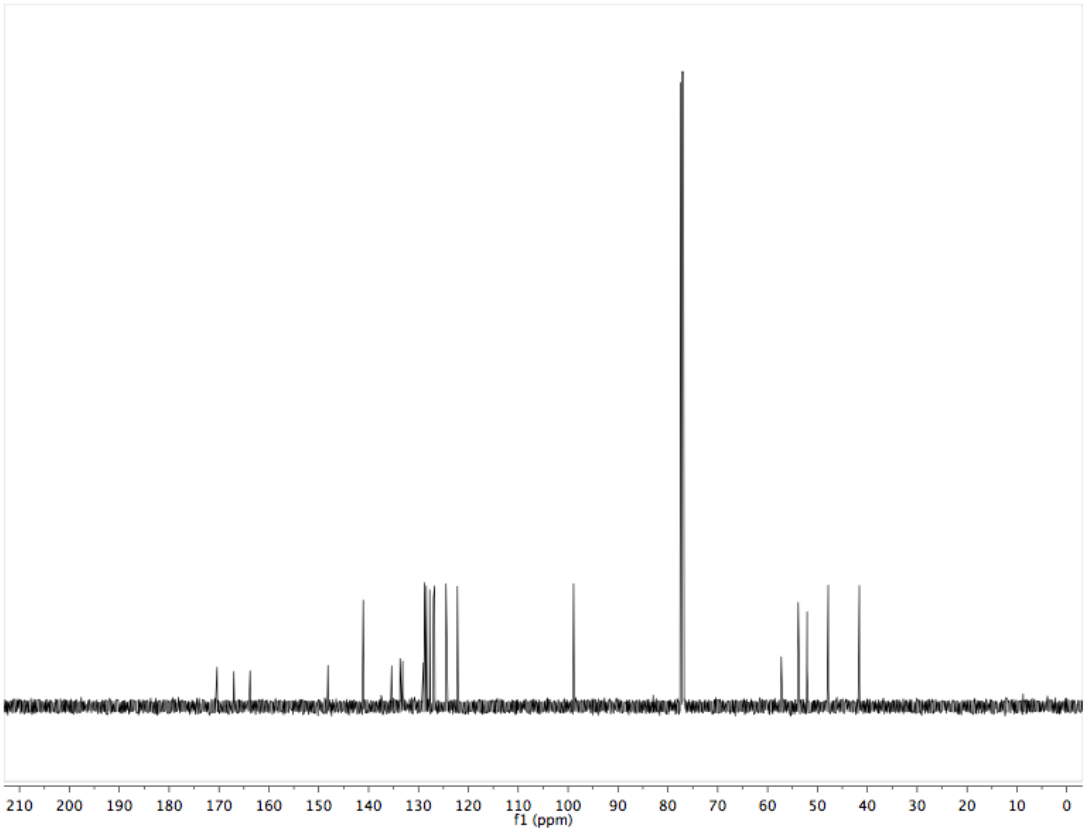
f1 (ppm)


MeO2C
O
O
MeO2C
5g
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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200
190
180
170
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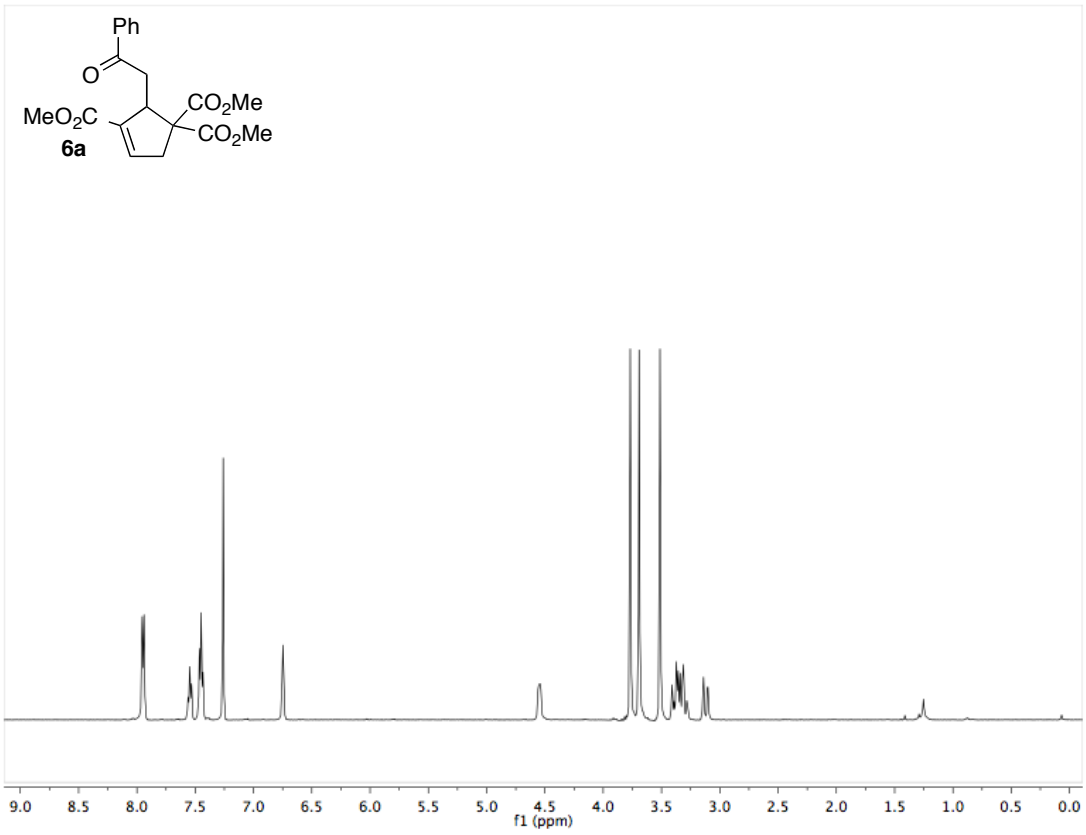
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Ph
O
MeO2C
CO2Me
CO2Me
6a
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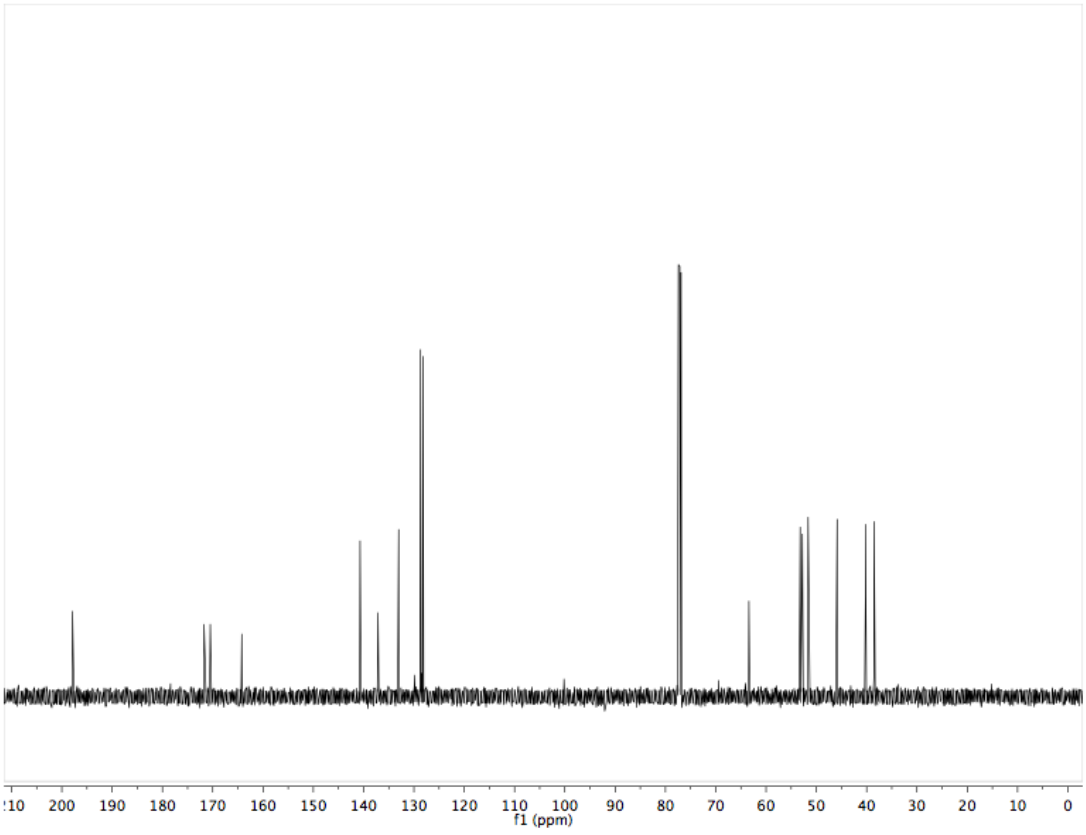
f1 (ppm)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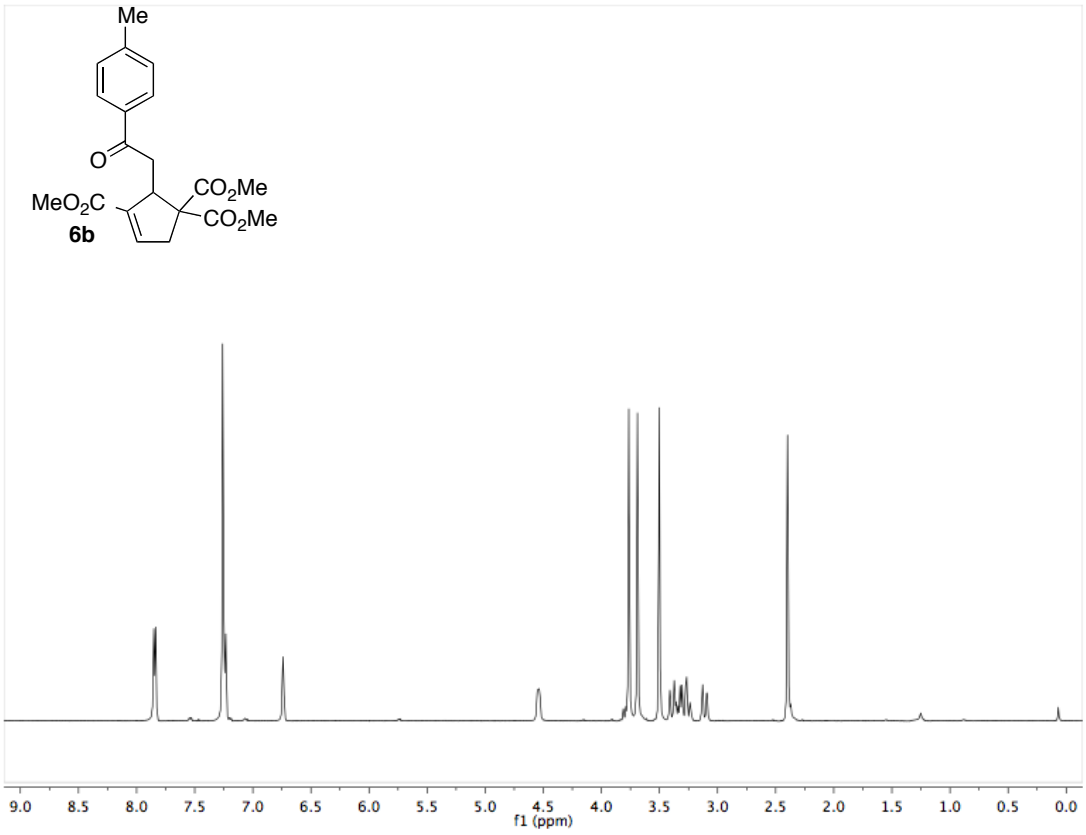
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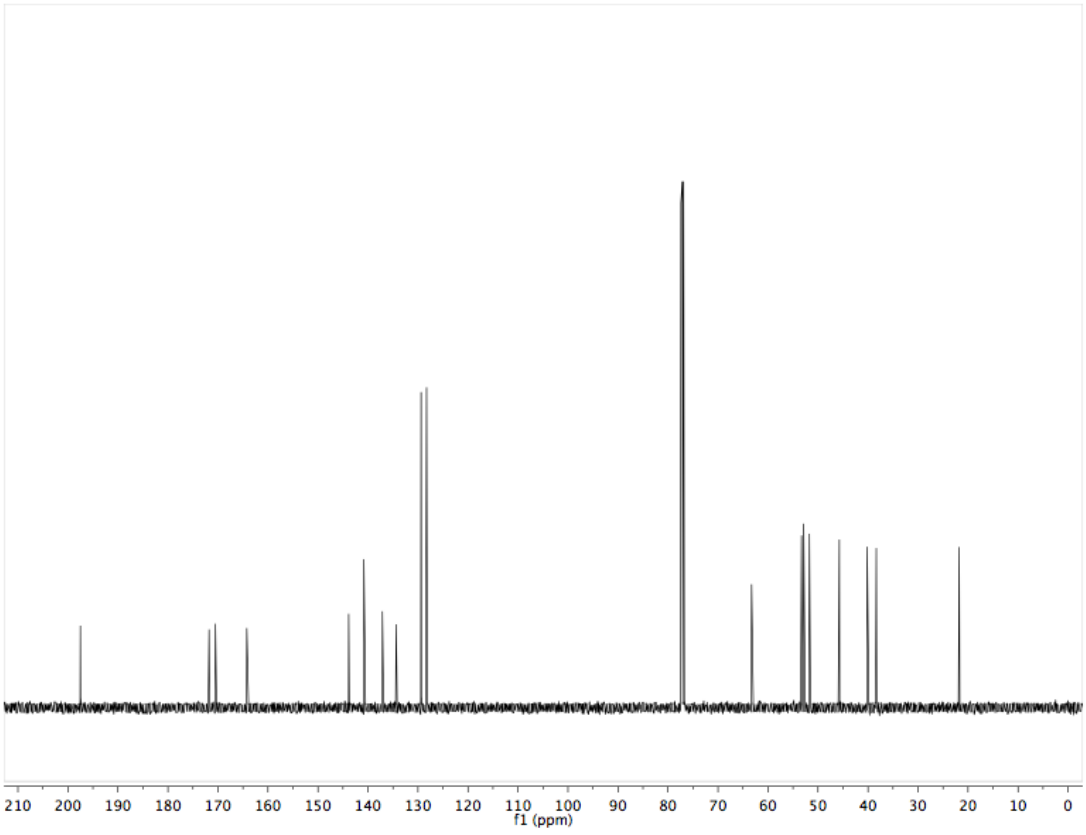
O
MeO2C
CO2Me
CO2Me
6b
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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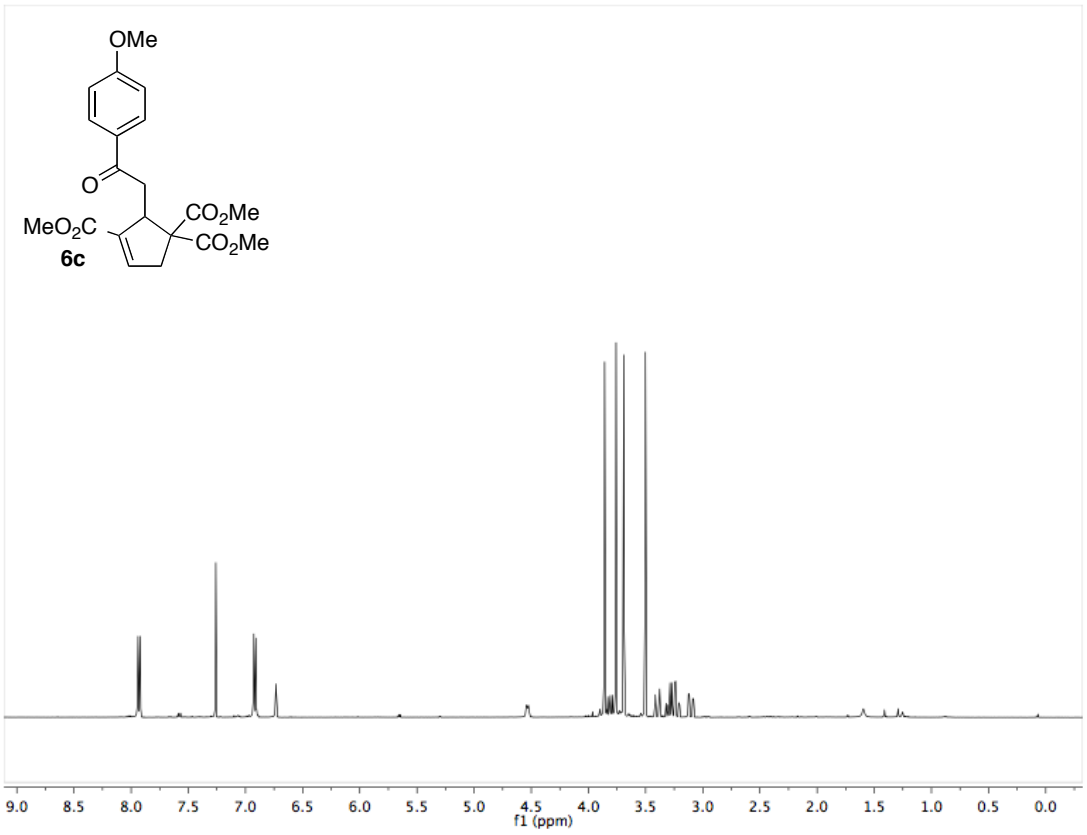
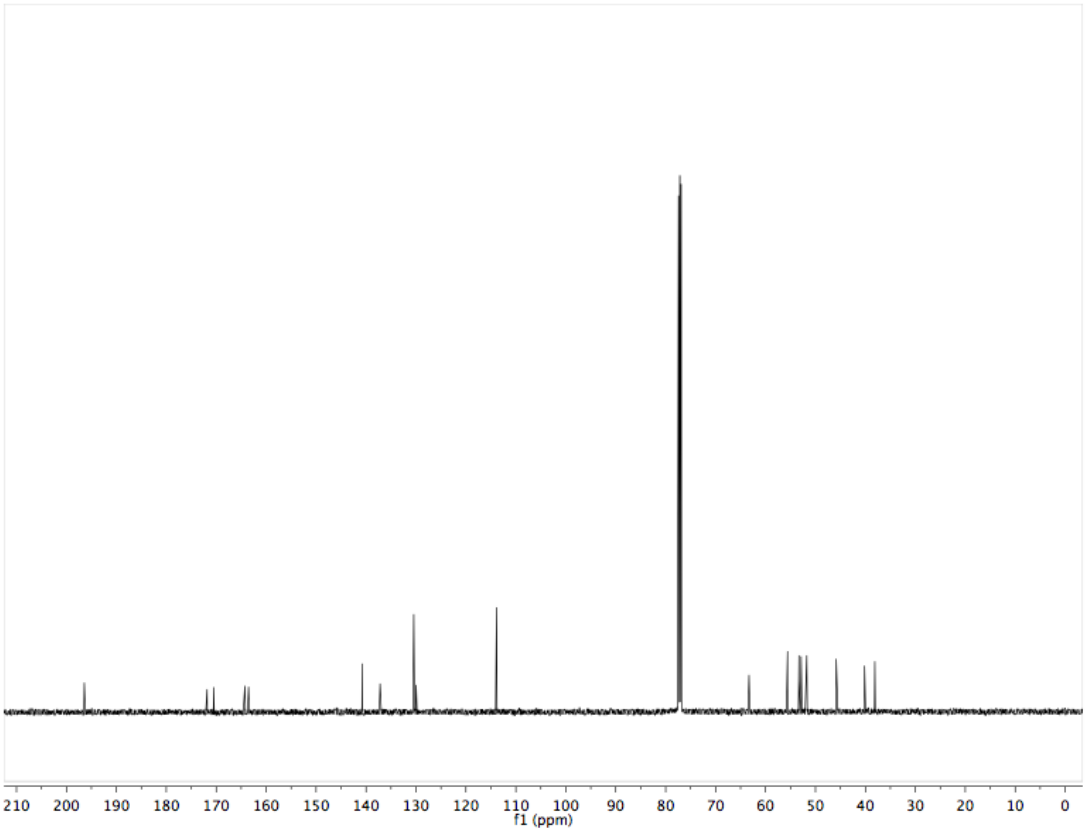
f1 (ppm)


OMe
O
MeO2C
CO2Me
CO2Me
6c
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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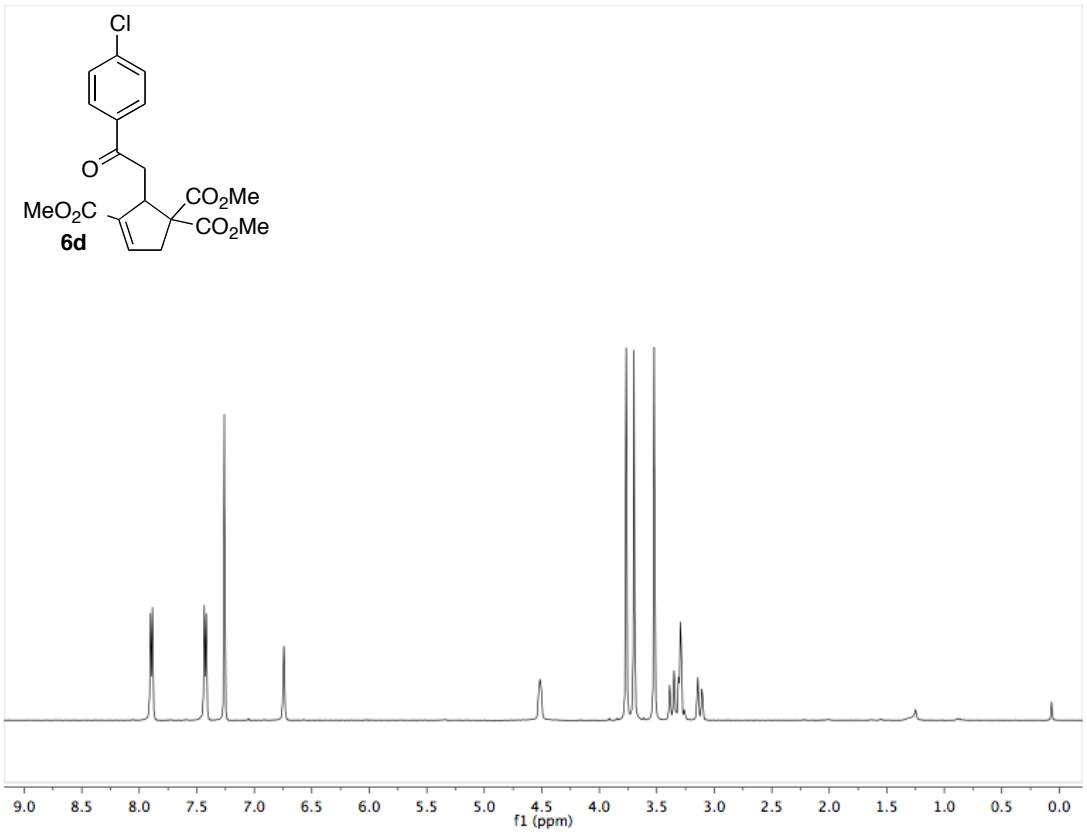
f1 (ppm)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MeO2C
CO2Me
CO2Me
6d
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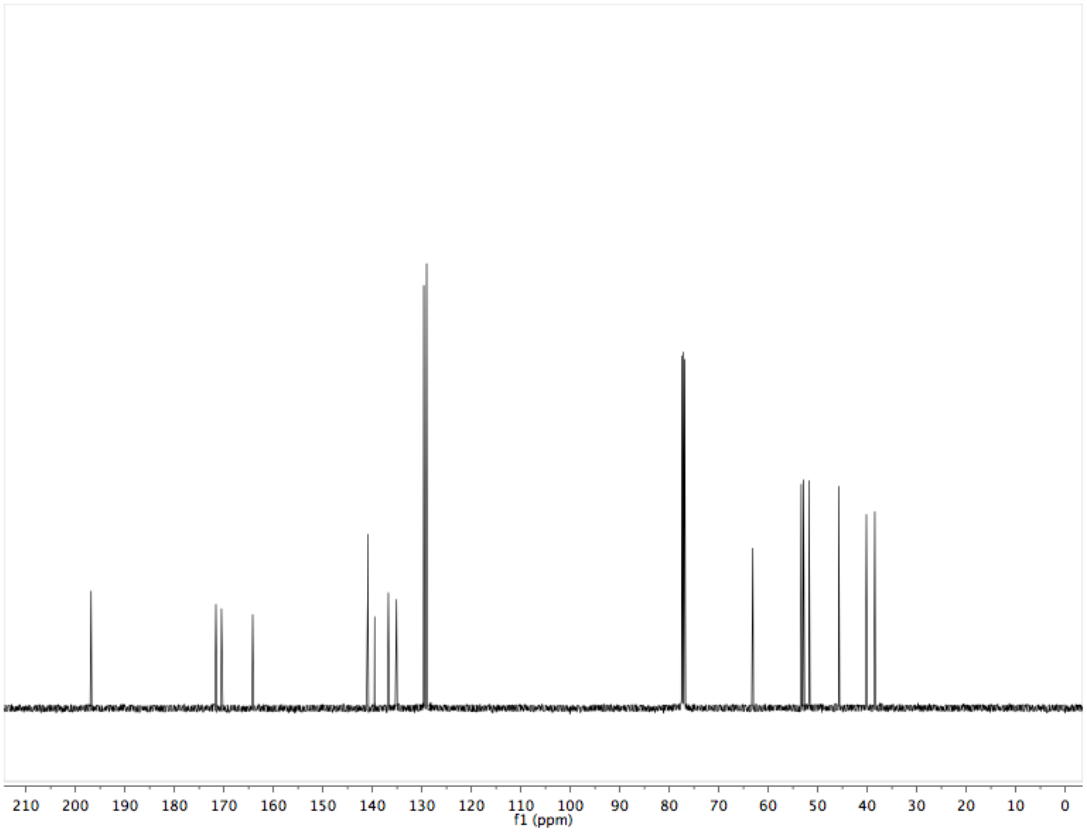
f1 (ppm)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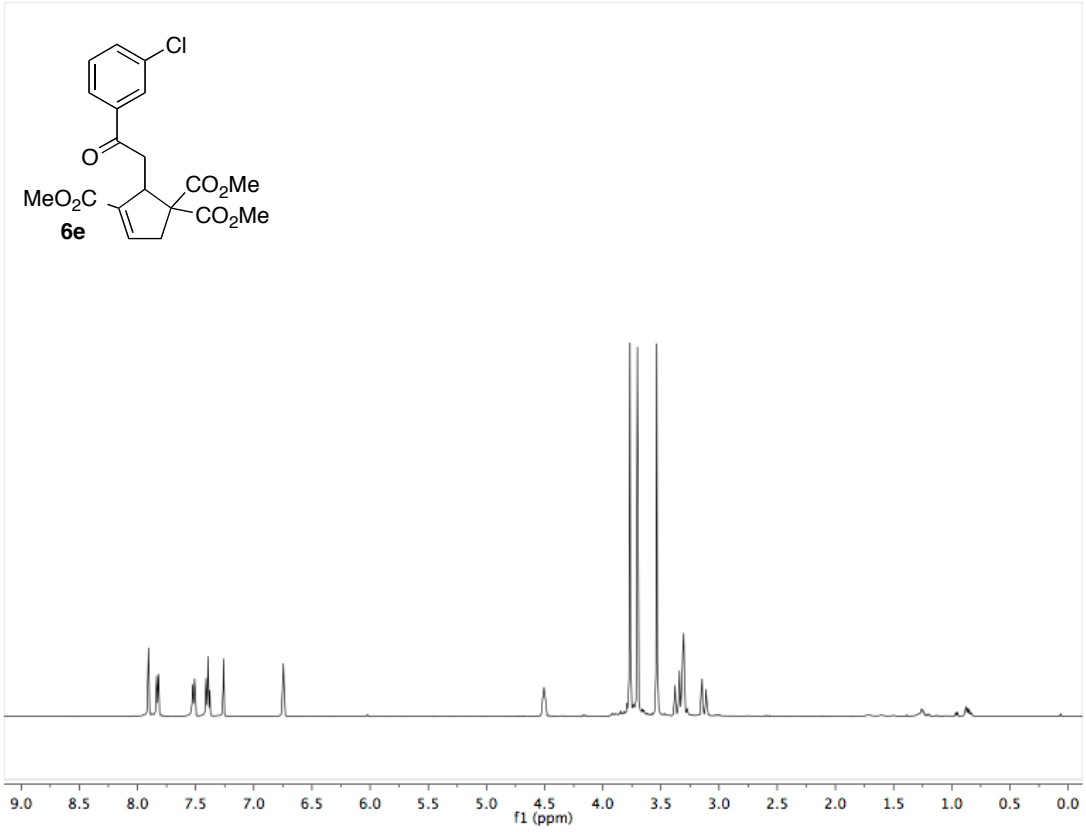
f1 (ppm)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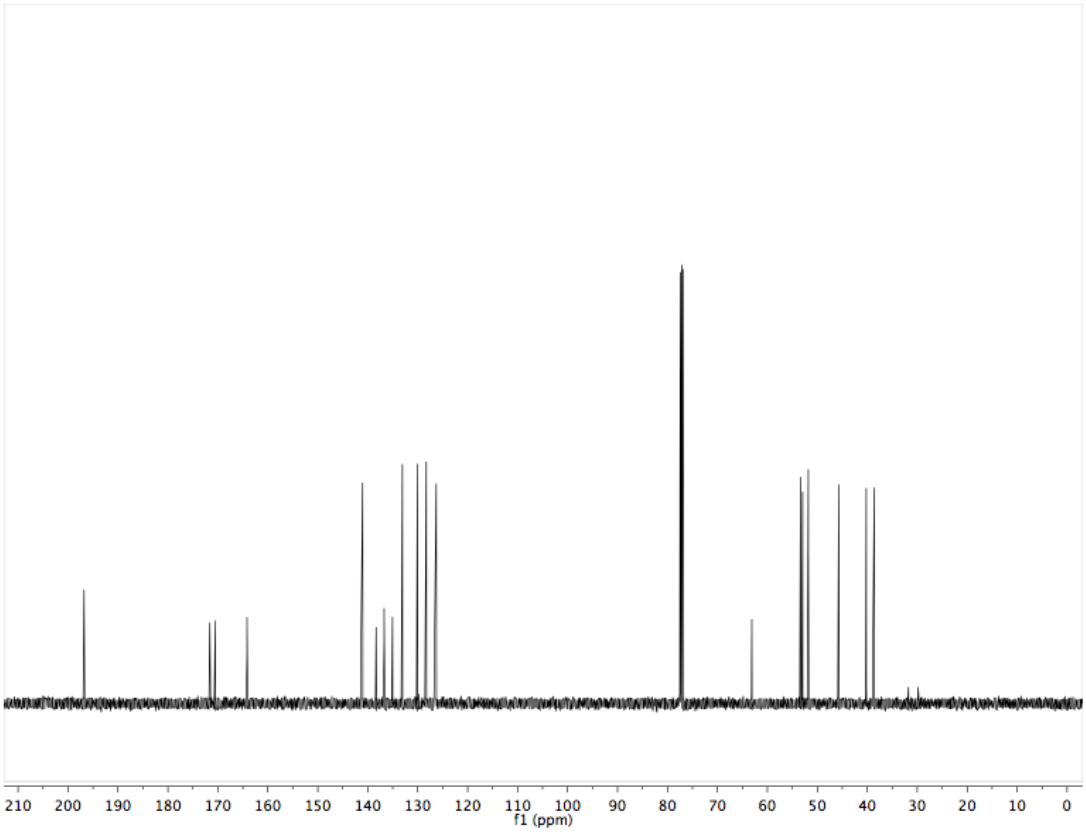
O
MeO2C
CO2Me
CO2Me
6e
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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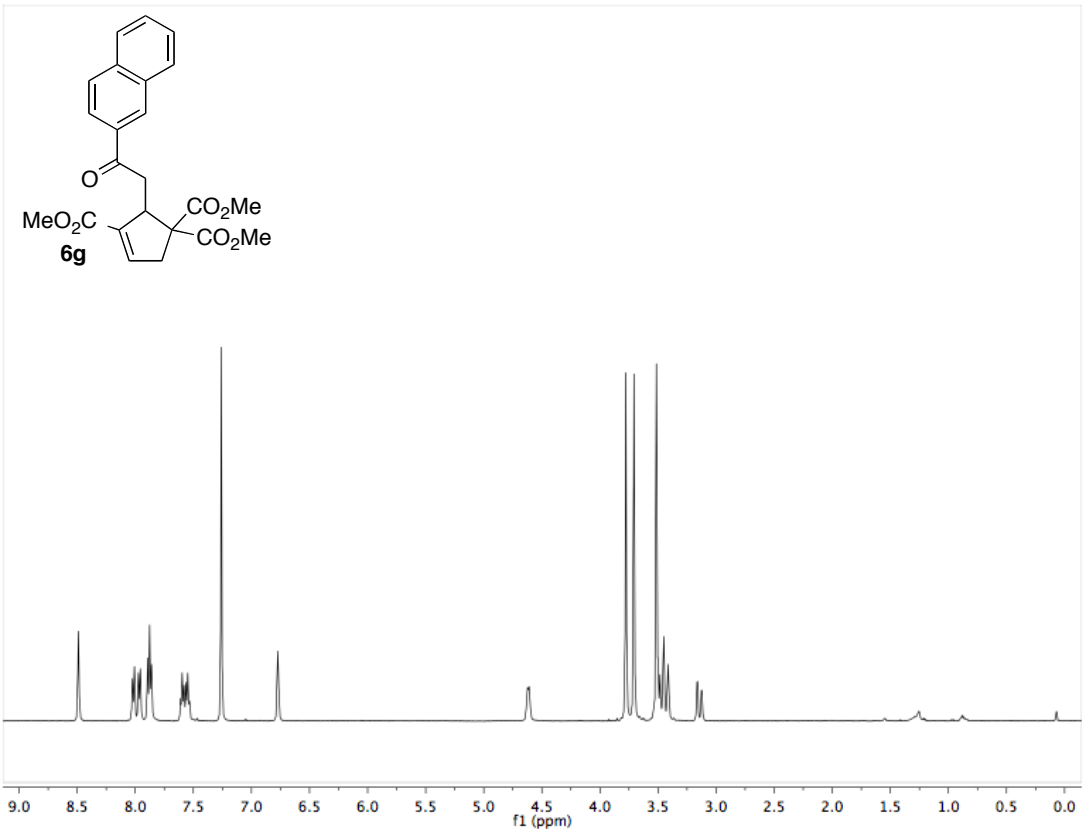
f1 (ppm)


O
MeO2C
CO2Me
CO2Me
6g
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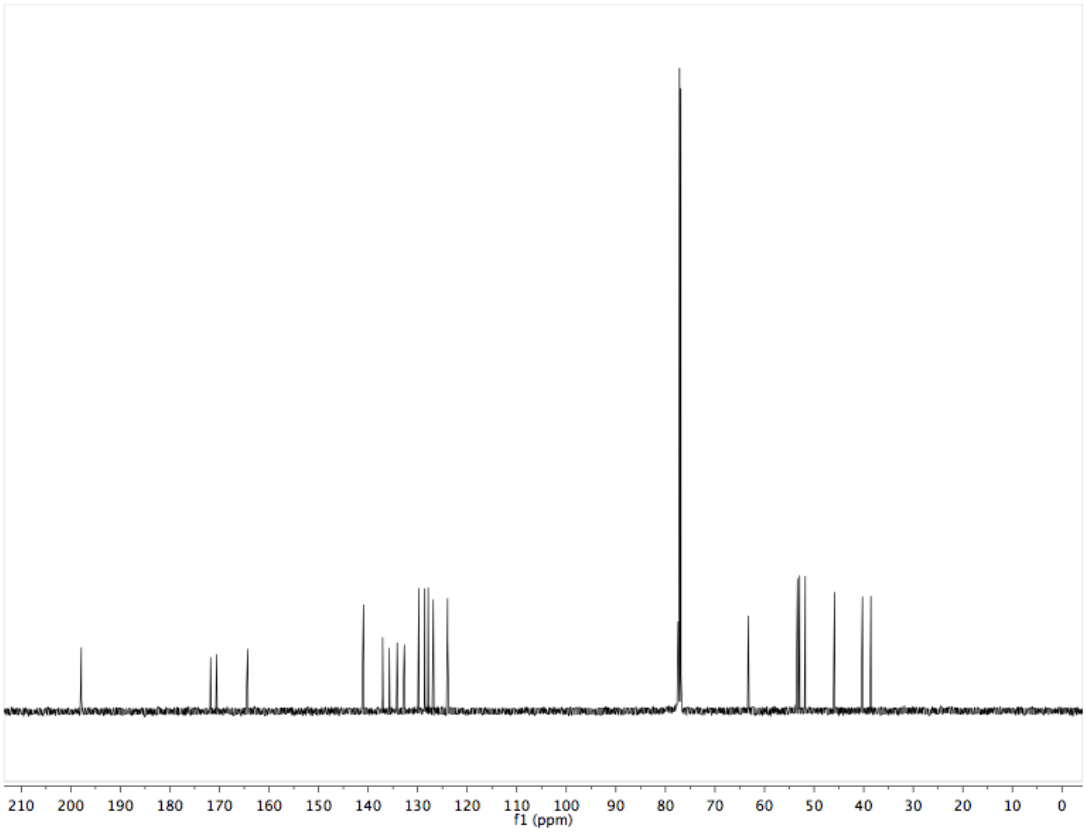
f1 (ppm)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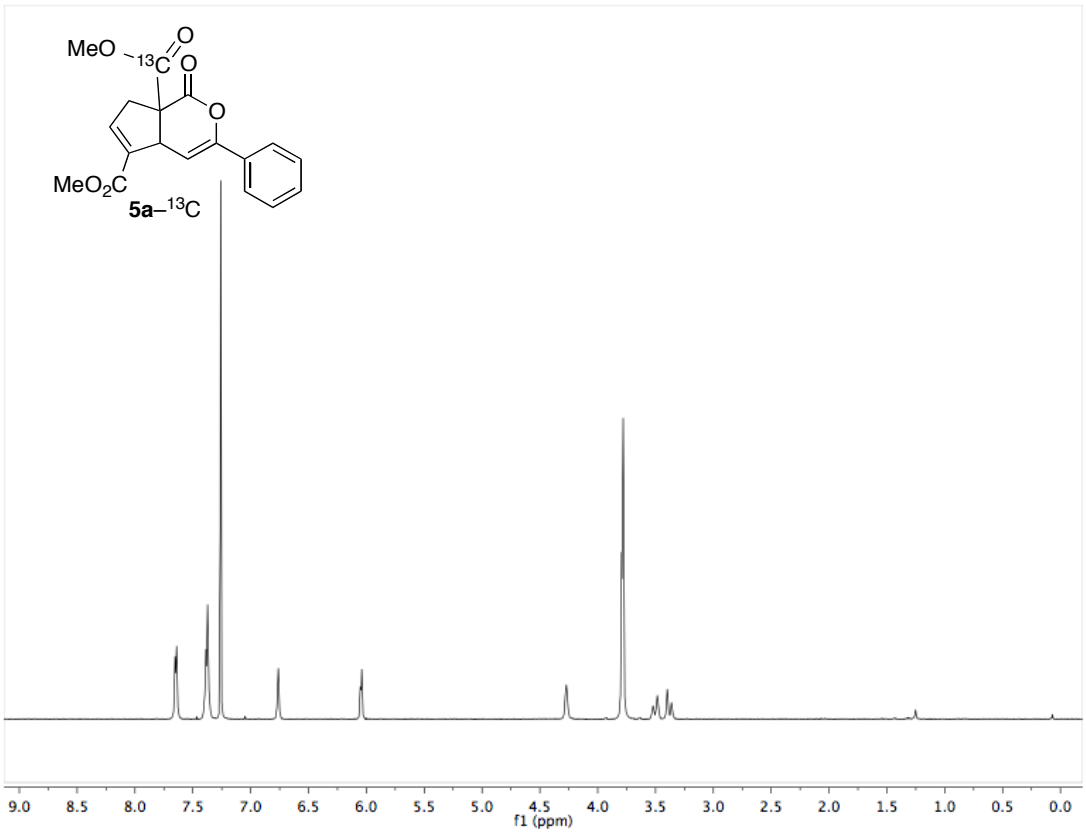
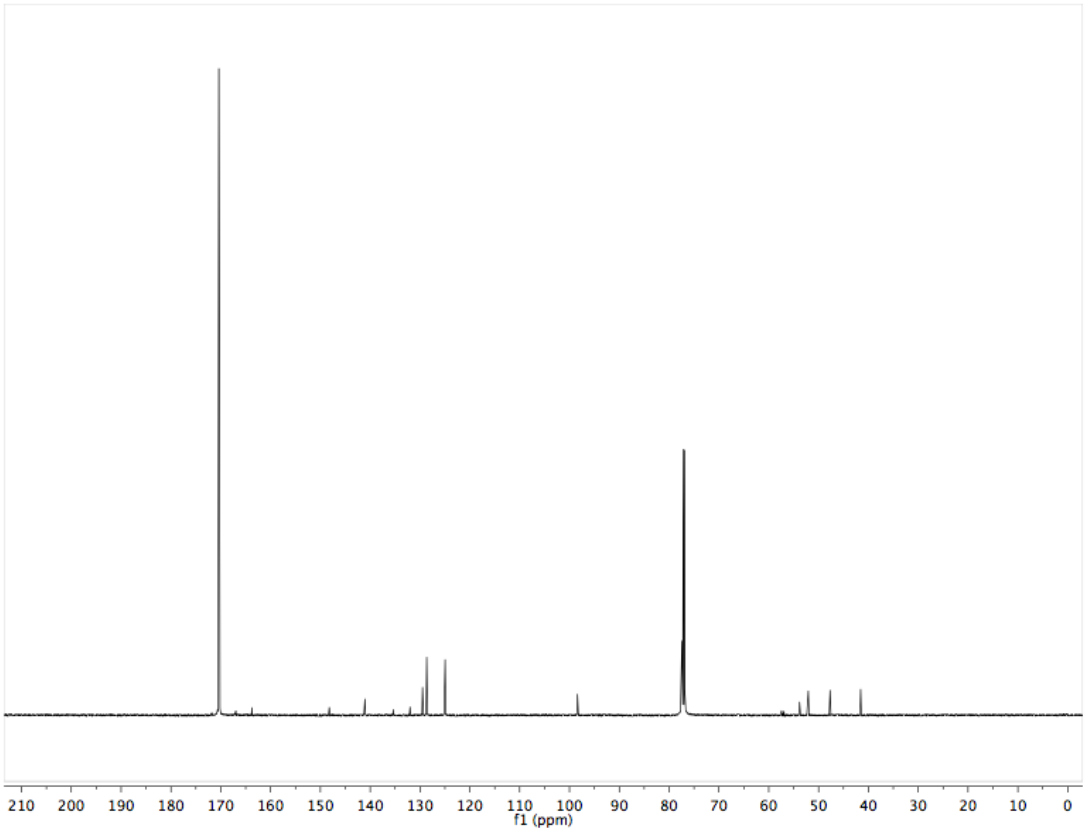
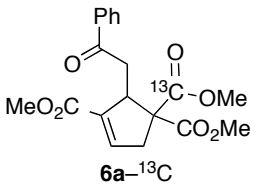
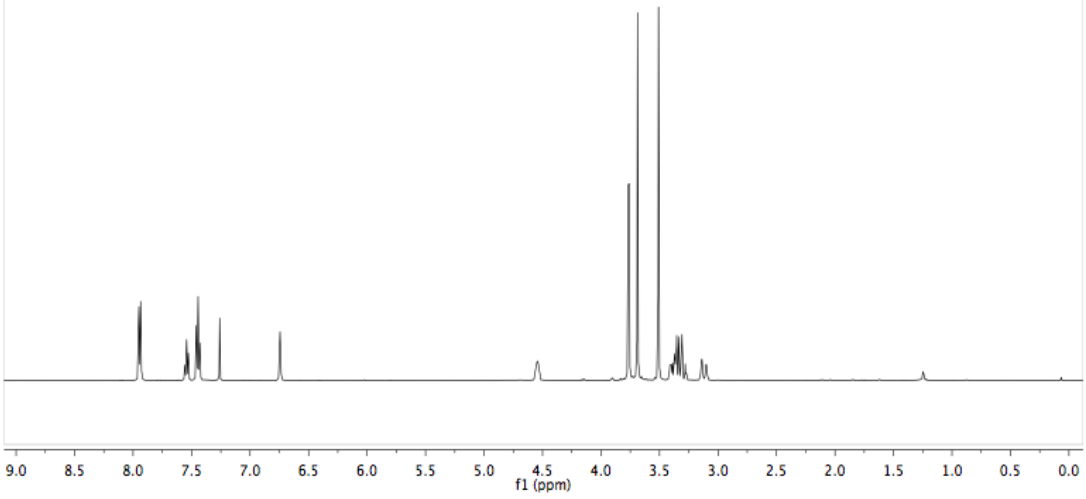
f1 (ppm)

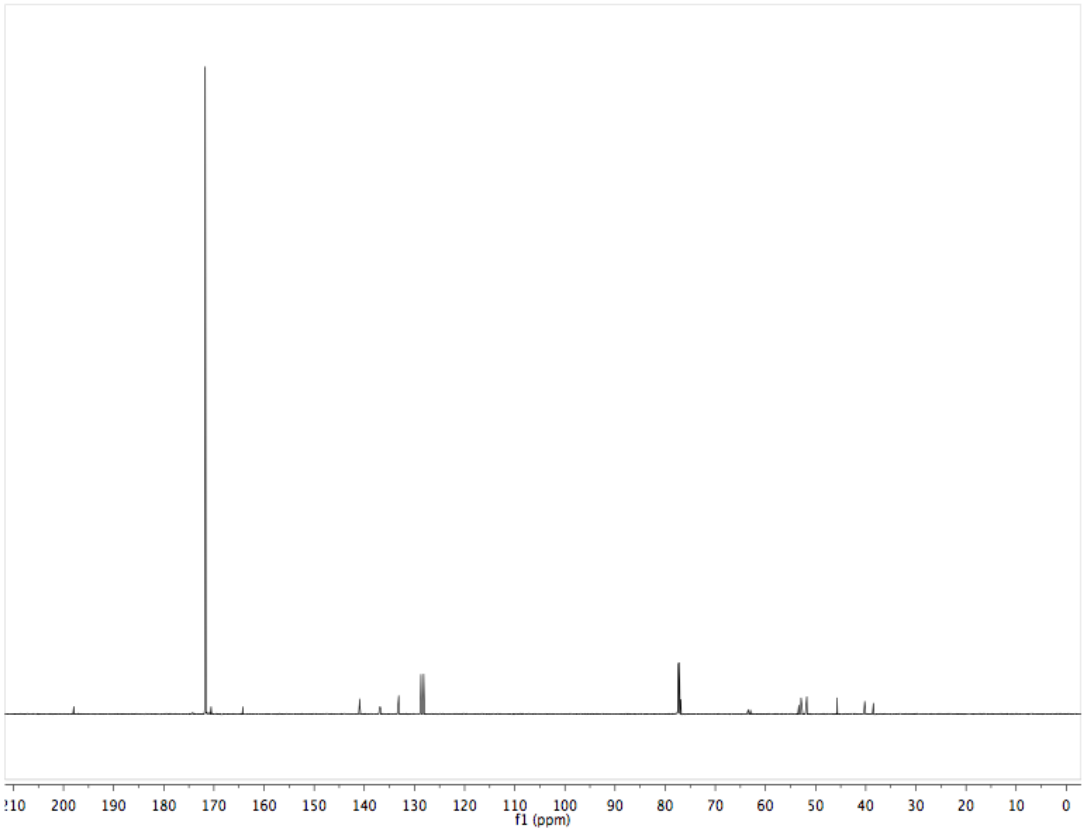

MeO
13C
O
O
O
MeO2C
5a–13C
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ph
O
O
^{13}C
OMe
MeO_2C
CO_2Me

6a–^{13}C


9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)