Electronic Supplementary Material (ESI) for ChemComm.


**Supporting Information**

# Oxidative Heck Desymmetrisation of 2,2-Disubstituted Cyclopentene-1,3-diones

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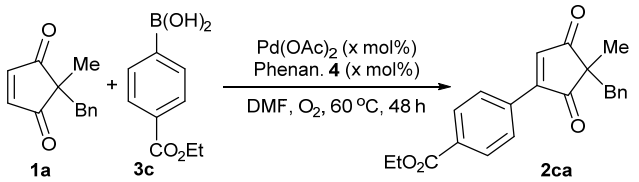
## General Experimental Section

$^{1}$H NMR spectra were recorded on Bruker AV 300 and AV 400 spectrometers at 300 and 400 MHz respectively and referenced to residual solvent. $^{13}$C NMR spectra were recorded using the same spectrometers at 75 and 100 MHz respectively. Chemical shifts ($\delta$ in ppm) were referenced to tetramethylsilane (TMS) or to residual solvent peaks ($CDCl_3$ at $\delta_H$ 7.26, $\delta_C$ at 77.00 ppm, $(CD_3)_2CO$ at $\delta_H$ 2.05 ppm, $\delta_C$ at 29.84 ppm or $C_6D_6$ at $\delta_H$ 7.16 ppm, $\delta_C$ at 128.06 ppm). *J* values are given in Hz and s, d, dd, t, q, qn and m abbreviations correspond to singlet, doublet, doublet of doublet, triplet, quartet, quintet and multiplet. Mass spectra were obtained at the EPSRC UK National Mass Spectrometry Facility at Swansea University. Infrared spectra were obtained on Perkin-Elmer Spectrum 100 FT-IR Universal ATR Sampling Accessory, deposited neat or as a chloroform solution to a diamond/ZnSe plate. Flash column chromatography was carried out using Matrix silica gel 60 from Fisher Chemicals and TLC was performed using Merck silica gel 60 F254 pre-coated sheets and visualised by UV (254 nm) or stained by the use of aqueous acidic KMnO4 or aqueous acidic ceric ammonium molybdate as appropriate. Enantiomer separation was achieved by chiral stationary phase HPLC with an Agilent Technologies 1120 Compact LC with either CHIRALPAK IA or IB column as appropriate. Alternatively, where specified, enantiomeric ratios were calculated using chiral shift reagent (*S*)-(+)-1-(9-anthryl)-2,2,2-trifluoroethanol, purchased from Sigma-Aldrich. Optical rotation was measured on a Bellingham and Stanley ADP410 polarimeter. Petrol ether refers to petroleum ether (40–60 $^{o}$C). Anhydrous DMF and DMA were purchased from Sigma-Aldrich and Fluorochem respectively and used without further purification. All arylboronic acids were purchased from Sigma-Aldrich, Fluorochem or Acros, and better results are achieved if they are heated under vacuum with a heat gun prior to the oxidative Heck reaction. The oxidative Heck reactions were carried out in dried glassware, using anhydrous DMF and $Pd(OAc)_2$ from Johnson Matthey.

**Further optimisation for electron withdrawing arylboronic acids**

Optimisation studies for electron withdrawing boronic acids found portionwise addition of the catalyst and ligand was found to be optimal (Table S1, Entry 4). These conditions were then used for the boronic acid screen.




| Entry[a] | 1st portion x (mol%) | 2nd portion x (mol%) | Time of 2nd portion | Yield (%)[b] |
|---|---|---|---|---|
| 1 | 5 | - | - | 25 |
| 2 | 10 | - | - | 35 |
| 3 | 5 | 5 | 24 | 57 |
| 4[c] | 5 | 5 | 24 | 65 |

[a]2 equiv. of **3c**. [b]Isolated yields. [c]70 °C.

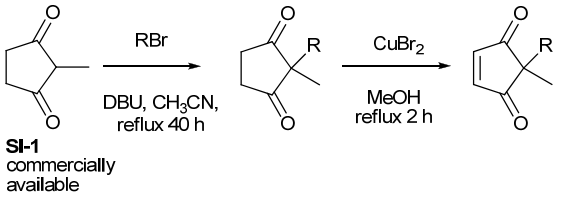
**Table S1** Further optimisation – catalyst loading

## Experimental Procedures

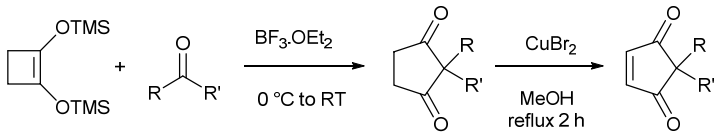
### Synthesis of 2,2-Disubstituted Cyclopentene-1,3-dione Starting Materials:

Substrate **1n** was purchased from Sigma-Aldrich. Substrates **1a**, **1b**, **1d**, **1h** and **1i** were synthesised according to literature known procedures.[1, 2] Precursors to substrates **1f, 1g, 1m** and **1o** were synthesised using a procedure adapted from literature;[3] synthetic routes are provided to these compounds.

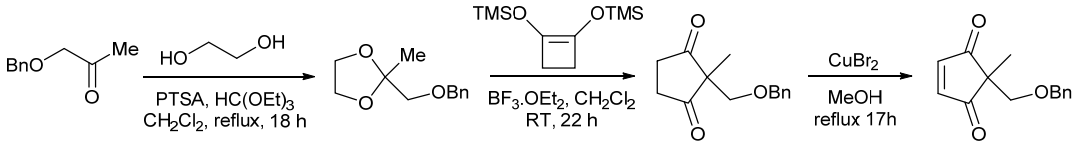
Substrates **1a** and **1b** were synthesised according to the following general procedure:




Substrates **1d** and **1h** were synthesised according to the following general procedure:

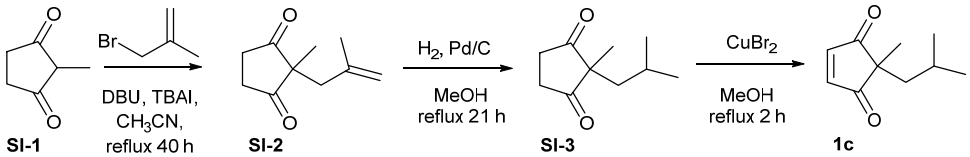



Substrate **1i** was synthesised according to the following procedure:

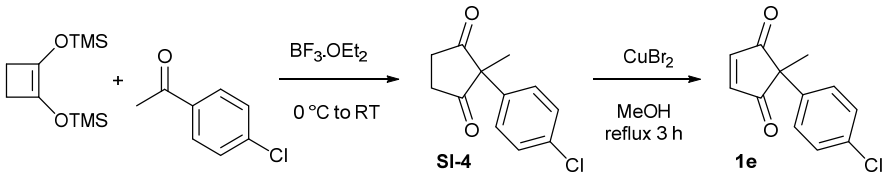



The following substrates have no literature precedence and their synthetic routes are given below:

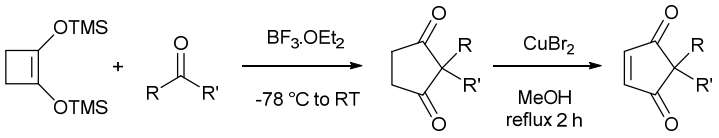
Synthetic route for **1c**:



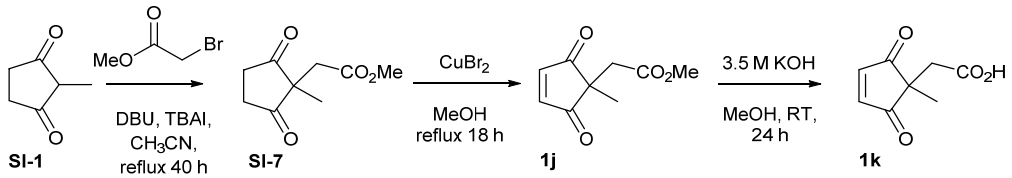
Synthetic route for **1e** (adapted from literature known procedures for similar substrates):[1]



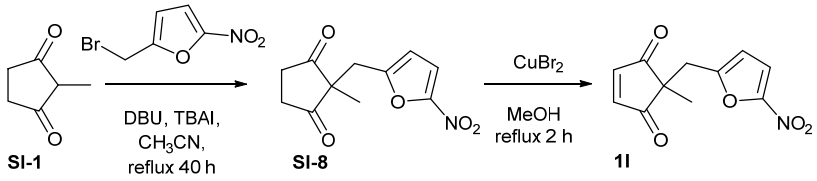

Synthetic route for **1f, 1g** and **1o** (step 1 adapted from literature known procedure for similar substrates):[3]



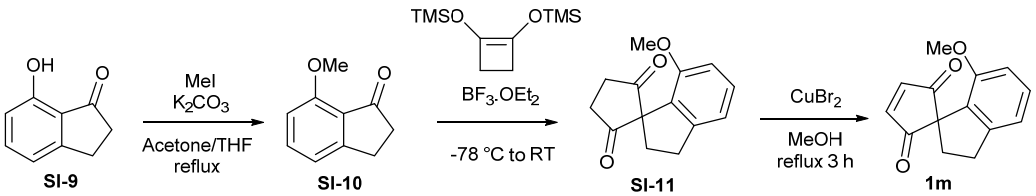

Synthetic route for **1j** and **1k**:



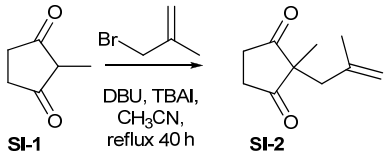

Synthetic route for **1l**:




Synthetic route for **1m:**[3]



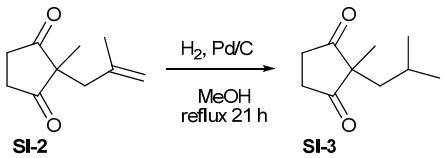
**2-Methyl-2-(2-methylprop-1-ene)cyclopentane-1,3-dione (SI-2)**[4]




2-Methylcyclopentane-1,3-dione **SI-1** (2.82 g, 25.1 mmol, 1 equiv.) was added to anhydrous $CH_3CN$ (150 mL) before DBU (4.5 mL, 39.5 mmol, 1.6 equiv.) was added dropwise at 0 °C. After the solution was warmed to room temperature 3-bromo-2-methylprop-1-ene (5.0 g, 37.0 mmol, 1.5 equiv.) was added and the reaction mixture refluxed for 41.5 h. The reaction mixture was quenched with $H_2O$ and the aqueous layer was washed with EtOAc until the organic layer was colourless. The combined organic layers were dried with $MgSO_4$ before solvent was removed under pressure. The resulting residue was purified by silica gel column chromatography (petroleum ether/EtOAc 20:1) to yield 2-methyl-2-(2-methylprop-1-ene)cyclopentane-1,3-dione **SI-2** (1.71 g, 10.4 mmol, 42%) as a colourless liquid.

$R_f$ = 0.40 (5:1, petroleum ether/EtOAc); $\nu_{max}/cm^{-1}$ 3022, 2974, 2928, 1765, 1721, 1645, 1452, 1420, 1373, 1326, 1217, 1153, 1069, 1034, 993, 904, 749, 667; $^1H$ NMR (300 MHz, $CDCl_3$) δ 4.78 (p, *J* = 1.5 Hz, 1H, C=C<u>H</u>H), 4.54 (dt, *J* = 1.5, 0.9 Hz, 1H, C=CH<u>H</u>), 2.86 – 2.60 (m, 4H, $CH_2CH_2$), 2.40 (d, *J* = 0.9 Hz, 2H, $CCH_2$), 1.64 - 1.58 (m, 3H, $CH_3$), 1.11 (s, 3H, $CH_3$); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 216.7 (C), 140.7 (C), 115.0 ($CH_2$), 56.8 (C), 43.7 ($CH_2$), 35.5 ($CH_2$), 24.0 ($CH_3$), 20.6 ($CH_3$); HRMS (APCI) *m/z calc*. for $C_{10}H_{15}O_2$: 167.1067 $[M+H]^+$; found: 167.1064.

**2-Methyl-2-(2-methylpropane)cyclopentane-1,3-dione (SI-3)**

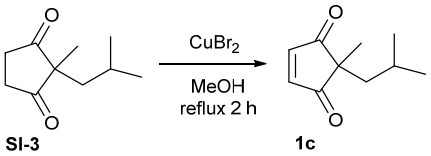



2-Methyl-2-(2-methylprop-1-ene)cyclopentane-1,3-dione **SI-2** (586 mg, 3.57 mmol, 1 equiv.) and Pd (10%)/C (100 mg, 0.94 mmol, 0.26 equiv.) was added to MeOH (15 mL) and set to stir. $H_2$ was then introduced into the system and the reaction left to stir for 21 h. The Pd (10%)/C was then filtered off through a plug of celite and the solvent removed under reduced pressure. The resulting residue was purified by silica gel chromatography (petroleum ether/EtOAc 30:1→10:1) to yield 2-methyl-2-(2-methylpropane)cyclopentane-1,3-dione **SI-3**

(404 mg, 2.43 mmol, 56%) as a colourless liquid. The product was slightly impure but was taken forward to the next step without further purification.

$R_f$ = 0.32 (petroleum ether/EtOAc 5:1); $\nu_{max}$/cm$^{-1}$ 2959, 2873, 1765, 1719, 1453, 1422, 1389, 1372, 1308, 1273, 1236, 1157, 1121, 1060, 1022, 994, 917, 843, 781, 734; $^1$H NMR (400 MHz, $CDCl_3$) δ 2.83 – 2.63 (m, 4H, $CH_2CH_2$), 1.59 (d, *J* = 7.1 Hz, 2H, C<u>H</u>$_2$CH), 1.57-1.43 (m, 1H, CH), 1.03 (s, 3H, $CH_3$), 0.69 (d, *J* = 6.5 Hz, 6H, C<u>H</u>$_3$(CH)C<u>H</u>$_3$); $^{13}$C NMR (100MHz, $CDCl_3$) δ 216.4 (C), 56.3 (C), 44.3 ($CH_2$), 34.9 ($CH_2$), 25.0 (CH), 23.5 ($CH_3$), 21.5 ($CH_3$); HRMS (APCI) *m/z calc*. for $C_{10}H_{17}O_2$: 169.1223 $[M+H]^+$; found: 169.1220.

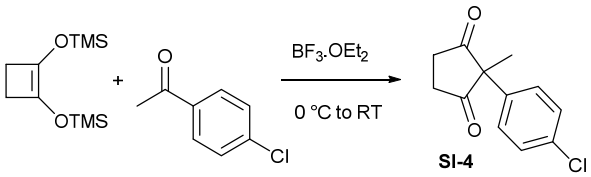
**2-Isobutyl-2-methylcyclopent-4-ene-1,3-dione (1c)**




2-Methyl-2-(2-methylpropane)cyclopentane-1,3-dione **SI-3** (302.5 mg, 1.82 mmol, 1 equiv.) was added to a solution of $CuBr_2$ (883 mg, 3.95 mmol, 2.2 equiv.) in anhydrous MeOH (1.4 mL). The resulting reaction mixture was refluxed for 2 h before being quenched with cold $H_2O$ and 1 M HCl. $Et_2O$ was added to the solution. The aqueous layer was washed with $Et_2O$ until the organic layer was colourless. The combined organic layers were washed with brine (15 mL) and dried over $Na_2SO_4$ before solvent was removed under reduced pressure. The resulting residue was purified by silica gel column chromatography (hexane/EtOAc, 10:1) to yield 2-isobutyl-2-methylcyclopent-4-ene-1,3-dione **1c** (119.6 mg, 0.73 mmol, 40%) as a yellow oil.

$R_f$ = 0.34 (petroleum ether/EtOAc 5:1); $\nu_{max}$/cm$^{-1}$ 2961, 2931, 2873, 1699, 1568, 1454, 1431, 1390, 1374, 1323, 1310, 1255, 1143, 1064, 1034, 854, 785, 734, 699, 661; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.24 (s, 2H, CH=CH), 1.64 (d, *J*= 6.6 Hz, 2H, $CH_2$), 1.41 (nonet, *J* = 6.6 Hz, 1H, $CH_2CH$), 1.10 (s, 3H, $CH_3$), 0.72 (d, *J* = 6.6 Hz, 6H, C<u>H</u>$_3$CHC<u>H</u>$_3$); $^{13}$C NMR (75.5 MHz, $CDCl_3$) δ 207.9 (C), 148.1 (CH), 50.3 (C), 43.5 ($CH_2$), 25.3 (CH), 23.8 ($CH_3$), 21.3 ($CH_3$); HRMS (APCI) *m/z calc*. for $C_{10}H_{15}O_2$: 167.1067 $[M+H]^+$; found: 167.1064.

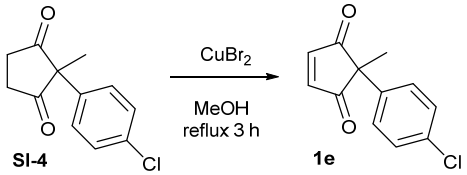
**2-(4-Chlorophenyl)-2-methylcyclopentane-1,3-dione (SI-4)**




4'-Chloroacetophenone (0.310 g, 2.00 mmol, 1 equiv.) and 1,2-bis(trimethylsiloxy)cyclobutene (0.77 mL, 3.00 mmol, 1.5 equiv.) were added to dichloromethane (5.1 mL), followed by $BF_3.OEt_2$ (0.37 mL, 3.00 mmol, 1.5 equiv.) at 0 °C. The solution was warmed to room temperature and stirred for 16 h under an inert atmosphere. Water (10 mL) was added and the reaction left to stir for 30 min. The organic layer was separated and the aqueous layer was washed with dichloromethane (3 × 15 mL). The combined organic layer was washed with brine, dried over $MgSO_4$ and the solvent evaporated *in vacuo*. The residue was purified by silica gel column chromatography (10:1 hexane:EtOAc) to yield 2-(4-chlorophenyl)-2-methylcyclopentane-1,3-dione **SI-4** as a colourless oil, (0.1994 g, 0.90 mmol, 45%).

$R_f$ = 0.48 (2:1 hexane/EtOAc); $\nu_{max}/cm^{-1}$ 2976, 2930, 1765, 1721, 1491, 1260, 1095, 1013, 990, 828; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.16 (d, *J* = 8.8 Hz, 2H, Ar-H), 3.11 – 2.58 (m, 4H, $H_2C$-$CH_2$), 1.42 (s, 3H, $CH_3$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 212.7 (C), 135.3 (C), 134.2 (C), 129.4 (CH), 127.8 (CH), 61.0 (C), 35.2 ($CH_2$), 20.1 ($CH_3$); HRMS (APCI) *m/z calc*. For $C_{12}H_{12}O_2Cl$: 223.0520 $[M+H]^+$; found: 223.0520.

**2-(4-Chlorophenyl)-2-methylcyclopent-4-ene-1,3-dione (1e)**

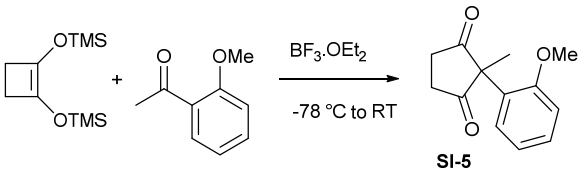



2-(4-Chlorophenyl)-2-methylcyclopentane-1,3-dione (**SI-4**) (188.5 mg, 0.846 mmol, 1 equiv.) was added to a solution of $CuBr_2$ (420.8 mg, 1.88 mmol, 2.2 equiv.) in anhydrous MeOH (7 mL). The resulting reaction mixture was refluxed for 3 h before being quenched with cold $H_2O$ and 1 M HCl. $Et_2O$ was added to the solution. The aqueous layer was washed with $Et_2O$ until the organic layer was colourless. The combined organic layers were washed

with brine (15 mL) and dried over $Na_2SO_4$ before solvent was removed under reduced pressure. The resulting residue was purified by silica gel column chromatography (hexane/EtOAc, 7:1→5:1) to yield 2-(4-chlorophenyl)-2-methylcyclopent-4-ene-1,3-dione **1e** (107.4 mg, 0.487 mmol, 58%) as a yellow oil.

$R_f$ = 0.13 (2:1 hexane/EtOAc); $\nu_{max}/cm^{-1}$ 3072, 2973, 1699, 1492, 1095, 1012, 833, 805, 728; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.34 (s, 2H, alkene-H), 7.31 – 7.27 (m, 2H, Ar-H), 7.25 – 7.21 (m, 2H, Ar-H), 1.54 (s, 3H, $CH_3$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 204.5 (C), 148.3 (CH), 135.2 (C), 133.9 (C), 129.0 (CH), 127.9 (CH), 53.8 (C), 20.1 ($CH_3$); HRMS (APCI) *m/z calc*. For $C_{12}H_{10}O_2Cl$: 221.0364 $[M+H]^+$; found: 221.0365.

**2-(2-Methoxyphenyl)-2-methylcyclopentane-1,3-dione (SI-5)**[5]



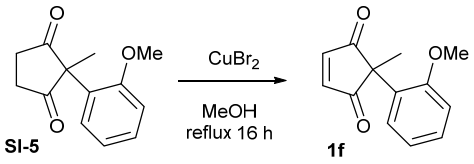
**SI-5**

2'-Methoxyacetophenone (310 mg, 2.03 mmol, 1 equiv.) and $BF_3.OEt_2$ (0.51 mL, 4.13 mmol, 2.0 equiv.) were added to dichloromethane (20 mL) at -78 °C and the solution stirred for 30 min. 1,2-bis(trimethylsiloxy)cyclobutene (0.91 mL, 3.54 mmol, 1.8 equiv.) was added and the solution was warmed to room temperature and stirred for 18 h under an inert atmosphere. Additional portions of 1,2-bis(trimethylsiloxy)cyclobutene (0.51 mL, 1.99 mmol, 1.0 equiv.) and $BF_3.OEt_2$ (0.26 mL, 2.11 mmol, 1.1 equiv.) were added at -78 °C and the solution allowed to warm to room temperature and stirred for a further 5 h. Water (10 mL) was added and the reaction left to stir for 1 h. The organic layers were separated and the aqueous layer was washed with dichloromethane (3 × 20 mL). The combined organic layers were washed with brine, dried over $MgSO_4$ and the solvent evaporated *in vacuo*. The residue was purified by silica gel column chromatography (10:1→2:1 hexane:EtOAc) to yield 2-(2-methoxyphenyl)-2-methylcyclopentane-1,3-dione **SI-5** as a colourless amorphous solid (148.5 mg, 0.680 mmol, 34%).

$R_f$ = 0.35 (2:1 hexane/EtOAc); $\nu_{max}/cm^{-1}$ 2941, 1714, 1490, 1459, 1259, 1243, 1188, 1021, 761; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 7.6, 1.6 Hz, 1H, Ar-H), 7.30 (ddd, *J* = 8.1, 7.6, 1.6 Hz, 1H, Ar-H), 7.04 (td, *J* = 7.6, 1.1 Hz, 1H, Ar-H), 6.81 (dd, *J* = 8.1, 1.1 Hz, 1H, Ar-H), 3.70 (s, 3H, $OCH_3$), 3.04 – 2.84 (m, 4H, $H_2C$-$CH_2$), 1.49 (s, 3H, $CH_3$); $^{13}C$ NMR (101

MHz, $CDCl_3$) δ 215.3 (C), 154.6 (C), 129.3 (CH), 128.1 (CH), 127.8 (C), 121.5 (CH), 110.7 (CH), 57.8 (C), 55.2 ($CH_3$), 35.0 ($CH_2$), 17.7 ($CH_3$); HRMS (APCI) *m/z calc*. For $C_{13}H_{15}O_3$: 219.1016 $[M+H]^+$; found: 219.1017.

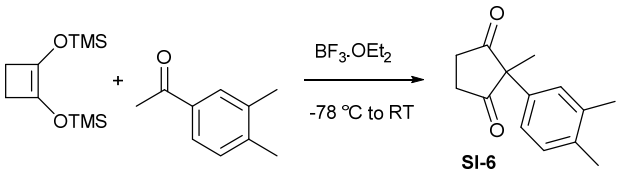
**2-(2-Methoxyphenyl)-2-methylcyclopent-4-ene-1,3-dione (1f)**




2-(2-Methoxyphenyl)-2-methylcyclopentane-1,3-dione (**SI-5**) (143.0 mg, 0.655 mmol, 1 equiv.) was added to a solution of $CuBr_2$ (324.8 mg, 1.454 mmol, 2.2 equiv.) in anhydrous MeOH (7 mL). The resulting reaction mixture was refluxed for 16 h before being quenched with cold $H_2O$ and 1 M HCl. $Et_2O$ was added to the solution. The aqueous layer was washed with $Et_2O$ until the organic layer was colourless. The combined organic layers were washed with brine (15 mL) and dried over $Na_2SO_4$ before solvent was removed under reduced pressure. The resulting residue was purified by silica gel column chromatography (hexane/EtOAc, 7:1→5:1) to yield 2-(2-methoxyphenyl)-2-methylcyclopent-4-ene-1,3-dione **1f** (112.7 mg, 0.5212 mmol, 80%) as a yellow solid.

M.p. 105-107 °C; $R_f$ = 0.25 (2:1 hexane/EtOAc); $\nu_{max}/cm^{-1}$ 2972, 1697, 1493, 1457, 1264, 1245, 1036, 1017, 845, 746; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 7.6, 1.6 Hz, 1H, Ar-H), 7.29 (ddd, *J* = 8.2, 7.6, 1.6 Hz, 1H, Ar-H), 7.20 (s, 2H, alkene-H), 7.03 (td, *J* = 7.6, 1.2 Hz, 1H, Ar-H), 6.76 (dd, *J* = 8.2, 1.2 Hz, 1H, Ar-H), 3.58 (s, 3H, $OCH_3$), 1.55 (s, 3H, $CH_3$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 206.7 (C), 156.0 (C), 145.0 (CH), 129.5 (CH), 129.1 (CH), 125.4 (C), 121.4 (CH), 110.7 (CH), 55.0 ($CH_3$), 53.3 (C), 18.9 ($CH_3$); HRMS (NSI) *m/z calc*. For $C_{13}H_{13}O_3$: 217.0859 $[M+H]^+$; found: 217.0862.

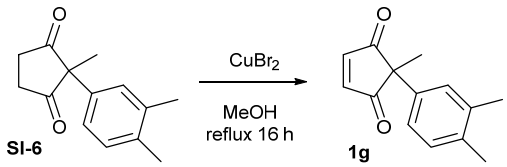
**2-(3,4-Dimethylphenyl)-2-methylcyclopentane-1,3-dione (SI-6)**




3',4'-Dimethylacetophenone (1.00 g, 6.75 mmol, 1 equiv.) was added to dichloromethane (70 mL) at -78 °C followed by $BF_3.OEt_2$ (1.66 mL, 13.46 mmol, 2.0 equiv.) and the solution stirred for 30 min. 1,2-Bis(trimethylsiloxy)cyclobutene (3.12 mL, 12.15 mmol, 1.8 equiv.) was then added, the solution was warmed to room temperature and stirred for 18 h under an inert atmosphere. $BF_3.OEt_2$ (2 mL) was added followed by $Na_2CO_3$ (20 mL), water (20 mL) and chloroform (20 mL). The organic layer was separated and the aqueous layer was washed with chloroform (3 × 25 mL). The combined organic layers were washed with brine, dried over $MgSO_4$ and the solvent evaporated *in vacuo*. The residue was purified by silica gel column chromatography (10:1 hexane:EtOAc) to yield 2-(3,4-dimethylphenyl)-2-methylcyclopentane-1,3-dione **SI-6** (982 mg, 4.54 mmol, 67%).

M.p. 70-72 °C; $R_f$ = 0.24 (2:1 hexane/EtOAc); $\nu_{max}/cm^{-1}$ 2977, 2931, 1759, 1716, 1608, 1500, 1447, 1417, 1267, 1120, 1076, 1022, 991, 818, 715; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.09 (d, *J* = 7.9 Hz, 1H, Ar-H), 6.97 – 6.87 (m, 2H, Ar-H), 3.03 – 2.58 (m, 4H, $H_2C$-$CH_2$), 2.22 (s, 3H, $CH_3$), 2.21 (s, 3H, $CH_3$), 1.39 (s, 3H, $CH_3$); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 213.1 (C), 137.7 (C), 136.6 (C), 134.3 (C), 130.4 (CH), 127.3 (CH), 123.6 (CH), 61.9 (C), 35.2 ($CH_2$), 19.8 ($CH_3$), 19.5 ($CH_3$), 19.2 ($CH_3$); HRMS (APCI) *m/z calc*. For $C_{14}H_{17}O_2$: 217.1223 $[M+H]^+$; found: 217.1223.

**2-(3,4-Dimethylphenyl)-2-methylcyclopent-4-ene-1,3-dione (1g)**

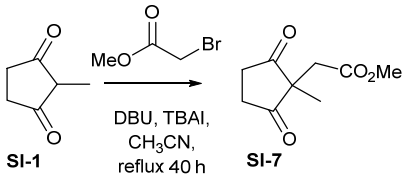



2-(3,4-Dimethylphenyl)-2-methylcyclopentane-1,3-dione **SI-6** (982.2 mg, 4.541 mmol, 1 equiv.) was added to a solution of $CuBr_2$ (2.26 g, 10.12 mmol, 2.2 equiv.) in anhydrous MeOH (51 mL). The resulting reaction mixture was refluxed for 1 h before being quenched

with cold $H_2O$ and 1 M HCl. $Et_2O$ was added to the solution. The aqueous layer was washed with $Et_2O$ until the organic layer was colourless. The combined organic layers were washed with brine (15 mL) and dried over $MgSO_4$ before solvent was removed under reduced pressure. The resulting residue was purified by silica gel column chromatography (hexane/EtOAc 10:1) to yield 2-(3,4-dimethylphenyl)-2-methylcyclopent-4-ene-1,3-dione **1g** (728.1 mg, 3.398 mmol, 75%) as a yellow crystalline solid.

M.p. 73-74 °C; $R_f$ = 0.32 (2:1 hexane/EtOAc); $\nu_{max}/cm^{-1}$ 3058, 2973, 1740, 1697, 1608, 1503, 1444, 1330, 1253, 1047, 874, 815, 711; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.33 (s, 2H, alkene-H), 7.08 (d, *J* = 7.7 Hz, 1H, Ar-H), 7.04 – 6.96 (m, 2H, Ar-H), 2.22 (s, 3H, $CH_3$), 2.21 (s, 3H, $CH_3$), 1.55 (s, 3H, $CH_3$); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 205.2 (C), 148.3 (CH), 137.1 (C), 136.3 (C), 134.2 (C), 130.0 (CH), 127.5 (CH), 123.7 (CH), 54.3 (C), 19.9 ($CH_3$), 19.4 ($CH_3$), 19.3 ($CH_3$); HRMS (APCI) *m/z calc*. For $C_{14}H_{18}O_2N$: 232.1332 $[M+NH_4]^+$; found: 232.1327.

**Methyl 2-(1-methyl-2,5-dioxocyclopentyl)acetate[6] (SI-7)**



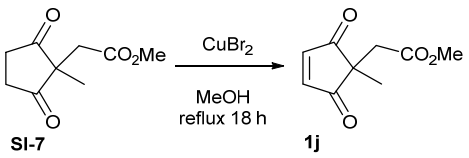

Synthesis adapted from literature procedure for similar substrates[1]

To a suspension of 2-methylcyclopentane-1,3-dione **SI-1** (1.47 g, 13.1 mmol, 1 equiv.) and TBAI (482.1 mg, 1.31 mmol, 0.1 equiv.) in anhydrous $CH_3CN$ (70 mL), DBU (2.3 mL, 15.6 mmol, 1.3 equiv.) was added dropwise at 0 °C. After the solution was warmed to room temperature, methylbromoacetate (1.9 mL, 20.0 mmol, 1.7 equiv.) was added and the reaction was refluxed for 40 h. The reaction was quenched with $H_2O$. The aqueous layer was washed with EtOAc until the organic layer was colourless. The combined organic layers were dried over $MgSO_4$ before the solvent was removed with reduced pressure. The resulting residue was purified by silica gel column chromatography (petrol ether/EtOAc, 10:1→2:1) to obtain methyl 2-(1-methyl-2,5-dioxocyclopentyl)acetate **SI-7** (620 mg, 3.37 mmol, 28%) as a white crystalline solid.

M.p. 94 – 96 °C; $R_f$ = 0.2 (3:1 petrol ether:EtOAc); $\nu_{max}/cm^{-1}$ 2958, 1762, 1712, 1408, 1398, 1213, 1153, 1075, 997, 799; $^1$H NMR (300 MHz, $CDCl_3$) δ 3.55 (s, 3H, $OCH_3$), 2.89 (s, 2H,

$CH_2$), 2.83 (s, 4H, $CH_2CH_2$), 1.04 (s, 3H, $CH_3$); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 215.9 (C), 171.9 (C), 52.7 (C), 52.2 ($CH_3$), 39.8 ($CH_2$), 34.6 ($CH_2$), 19.8 ($CH_3$).

**Methyl 2-(1-methyl-2,5-dioxocyclopent-3-en-1-yl)acetate[1] (1j)**

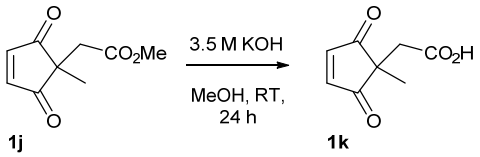



SI-7 1j

To a flask containing $CuBr_2$ (580.9 mg, 2.60 mmol, 2.6 equiv.), methyl 2-(1-methyl-2,5-dioxocyclopentyl)acetate **SI-7** (194.4 mg, 1.10 mmol, 1 equiv.) dissolved in anhydrous MeOH (12 mL) was added. The reaction was left to reflux for 18 h. The reaction was quenched with $H_2O$ and acidified with HCl (2 mL, 1M). The aqueous layer was extracted with $Et_2O$ until the organic layer was colourless. The combined organic layers were washed with brine and dried over $MgSO_4$ before solvent was removed under reduced pressure. The resulting residue was purified by silica gel column chromatography (petrol ether/EtOAc, 15:1→5:1) to obtain methyl 2-(1-methyl-2,5-dioxocyclopent-3-en-1-yl)acetate **1j** (140.7 mg, 0.77 mmol, 70%) as a yellow crystalline solid.

M.p. 73-74 °C; $R_f$ = 0.5 (3:1 petrol ether:EtOAc); $\nu_{max}$/ $cm^{-1}$ 3070, 2955, 1729, 1698, 1403, 1207, 1187, 1006, 862, 701; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.27 (s, 2H, HC=CH), 3.55 (s, 3H, $CH_3$), 2.86 (s, 2H, $CH_2$), 1.14 (s, 3H, $CH_3$); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 205.7 (C), 170.8 (C), 147.5 (CH), 52.0 ($CH_3$), 47.7 (C), 37.4 ($CH_2$), 20.5 ($CH_3$).

**2-(1-Methyl-2,5-dioxocyclopent-3-en-1-yl)acetic acid (1g)**

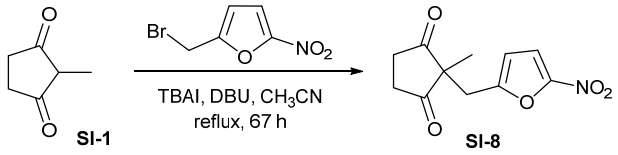



Synthesis adapted from literature procedure for ester hydrolysis[7]

(1-Methyl-2,5-dioxo-cyclopent-3-enyl)-acetic acid methyl ester **1j** (121.8 mg, 0.67 mmol, 1 equiv.) was dissolved in anhydrous MeOH (40 mL) and KOH (0.9 mL, 3.5M) was added drop-wise before the reaction was left to stir at RT for 23 h. The reaction was concentrated under reduced pressure and the resulting crude was dissolved in $Et_2O$. $H_2O$ was added and the aqueous layer was acidified with conc. HCl. The aqueous layer was extracted with $Et_2O$ until organic layer was colourless. The combined organic layers were dried over $MgSO_4$ and solvent was removed with reduced pressure. The reaction was repeated a further 2 times on 0.27 mmol scale of **1j**. The resulting crudes were combined and purified with silica gel column chromatography (hexane/EtOAc, 2:1 with 1% acetic acid) to obtain 2-(1-methyl-2,5-dioxocyclopent-3-en-1-yl)acetic acid **1k** (19.4 mg, 0.12 mmol, 9%) as a yellow crystalline solid.

M.p. 125-127 °C; $R_f$ = 0.1 (1:1 petrol ether:EtOAc); $\nu_{max}$/ $cm^{-1}$ 2956, 2854, 1725, 1705, 1606, 1439, 1354, 1209, 1011, 754; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.25 (s, 2H, HC=CH), 2.89 (s, 2H, $CH_2$), 1.15 (s, 3H, $CH_3$); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 205.4 (C), 174.8 (C), 147.5 (CH), 47.6 (C), 37.0 ($CH_2$), 20.7 ($CH_3$); HRMS (NSP) *m/z calc*. For $C_8H_7O_4$: 167.0350 $[M-H]^-$; found: 167.0352.

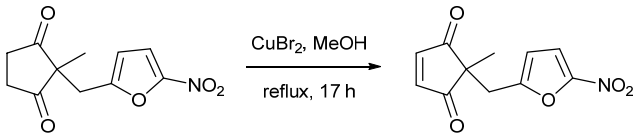
**2-Methyl-2-((5-nitrofuran-2-yl)methyl)cyclopentane-1,3-dione (SI-8)**




To a suspension of 2-methylcyclopentane-1,3-dione **SI-1** (364.9 mg, 3.25 mmol, 1 equiv) and TBAI (122.9 mg, 0.33 mmol, 1 equiv.) in anhydrous $CH_3CN$ (17.5 mL), DBU (0.6 mL, 3.90 mmol, 1.2 equiv.) was added dropwise at 0 °C. After the solution was warmed to room temperature, 2-(bromomethyl)-5-nitrofuran (929.1 mg, 4.51 mmol, 1.7 equiv.) was added and the reaction was refluxed for 67 h. The reaction was quenched with $H_2O$. The aqueous layer was washed with EtOAc until the organic layer was colourless. The combined organic layers were dried over $MgSO_4$ before the solvent was removed with reduced pressure. The resulting residue was purified by silica gel column chromatography (petrol ether/ EtOAc, gradient 10:1→2:1) to yield 2-methyl-2-((5-nitrofuran-2-yl)methyl)cyclopentane-1,3-dione **SI-8** (214.2 mg, 0.90 mmol, 28%) as a yellow amorphous solid.

$R_f$ = 0.2 (2:1 petrol ether: EtOAc); $\nu_{max}/cm^{-1}$ 3133, 2930, 2360, 1723, 1528, 1493, 1452, 1381, 1354, 811, 730; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.17 (d, *J* = 3.7 Hz, 1H, HetAr-H), 6.28 (d, *J* = 3.7 Hz, 1H, HetAr-H), 3.17 (s, 2H, $CH_2$), 2.98 – 2.83 (m, 4H, $H_2C$-$CH_2$), 1.25 (s, 3H, $CH_3$); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 214.8 (C), 154.7 (C), 148.2 (C), 112.9 (CH), 110.7 (CH), 54.9 (C), 34.8 ($CH_2$), 32.1 ($CH_2$), 21.3 ($CH_3$); HRMS (APCI) *m/z calc*. For $C_{11}H_{12}O_5N$: 238.0710 $[M+H]^+$; found: 238.0710.

**2-Methyl-2-(methyl-5-nitrofuran)-1,3-cyclopentene-1,3-dione (1l)**

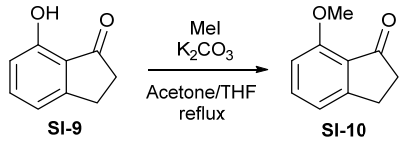



**SI-8** **1l**

To a solution of $CuBr_2$ (234.5 mg, 1.05 mmol, 2.4 equiv.) in MeOH (12 mL), 2-methyl-2-(5-nitro-furan-2-methyl)-cyclopentane-1,3-dione **SI-8** (101.3 mg, 0.43 mmol, 1 equiv.) was added. The reaction was heated at reflux for 17 h. The reaction was quenched with $H_2O$ and acidified with HCl (2 mL, 1M). The aqueous layer was extracted with $Et_2O$ until the organic layer was colourless. The combined organic layers were washed with brine and dried over $MgSO_4$ before solvent was removed under reduced pressure. The resulting residue was purified by silica gel column chromatography (petrol ether/EtOAc, gradient 15:1→5:1) to yield 2-methyl-2-(methyl-5-nitrofuran)-1,3-cyclopentene-1,3-dione **1l** (70.8 mg, 0.30 mmol, 75%) as a yellow crystalline solid.

M.p. = 100-103 °C; $R_f$ = 0.4 (2:1 petrol ether/EtOAc); $\nu_{max}/cm^{-1}$ 3147, 3068, 2360, 2341, 1700, 1571, 1488, 1352, 1237, 841, 770; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.25 (s, 2H, HC=CH), 7.14 (d, *J* = 3.6 Hz, 1H, HetAr-H), 6.25 (d, *J* = 3.6 Hz, 1H, HetAr-H), 3.10 (s, 2H, $CH_2$), 1.29 (s, 3H, $CH_3$); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 205.0 (C), 154.0 (C), 148.2 (CH), 147.9 (C), 112.2 (CH), 111.9 (CH), 49.8 (C), 32.1 ($CH_2$), 19.5 ($CH_3$); HRMS (APCI) *m/z calc*. For $C_{11}H_{10}O_5N$: 236.0553 $[M+H]^+$; found: 236.0553.

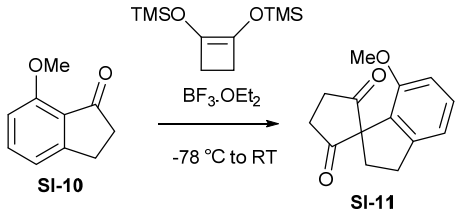
**7-Methoxy-2,3-dihydro-1H-inden-1-one (SI-10)**[8]




7-Hydroxy-1-indanone **SI-9** (0.508 g, 3.41 mmol, 1 equiv.), $K_2CO_3$ (0.950 g, 6.88 mmol, 2.0 equiv.), methyl iodide (0.25 mL, 4.02 mmol, 1.2 equiv.) were added to acetone (50 mL) and tetrahydrofuran (30 mL) and refluxed for 20 h. Upon completion, brine (50 mL) and dichloromethane (50 mL) were added and the phases separated. The aqueous phase was washed with dichloromethane (4 × 50 mL) and the organic layers combined, dried over $MgSO_4$, filtered and the solvent evaporated *in vacuo* to yield 7-methoxy-2,3-dihydro-1H-inden-1-one **SI-10** as colourless crystals (0.553 g, 3.41 mmol, 100%).

M.p. 99-100 °C; $R_f$ = 0.36 (1.5:1 EtOAc/hexane); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 8.2, 7.6 Hz, 1H, Ar-H), 7.01 (dd, *J* = 7.6, 0.8 Hz, 1H, Ar-H), 6.78 (dd, *J* = 8.2, 0.8 Hz, 1H, Ar-H), 3.95 (s, 3H, $CH_3$), 3.15 – 3.01 (m, 2H, $CH_2$), 2.70 – 2.63 (m, 2H, $CH_2$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 204.7 (C), 158.2 (C), 157.9 (C), 136.3 (CH), 125.2 (C), 118.4 (CH), 108.8 (CH), 55.7 ($CH_3$) , 36.8 ($CH_2$), 25.5 ($CH_2$); HRMS (APCI) *m/z calc*. For $C_{10}H_{11}O_2$: 163.0754 $[M+H]^+$; found: 163.0750.

**7'-Methoxy-2',3'-dihydrospiro[cyclopentane-1,1'-indene]-2,5-dione (SI-11)**

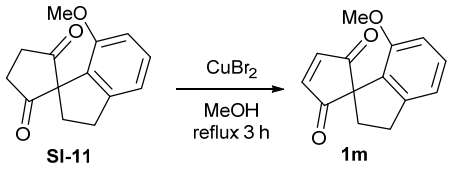



7-Methoxy-2,3-dihydro-1H-inden-1-one **SI-10** (0.481 g, 2.96 mmol, 1 equiv.), was added to dichloromethane (29 mL) at -78 °C followed by $BF_3$.$OEt_2$ (0.75 mL, 6.08 mmol, 2.1 equiv.) and the solution stirred for 45 min. 1,2-Bis(trimethylsiloxy)cyclobutene (1.35 mL, 5.24 mmol, 1.8 equiv.) was then added, the solution was warmed to room temperature and stirred for 18 h under an inert atmosphere. Upon completion, $BF_3$.$OEt_2$ (1 mL) was added followed by $Na_2CO_3$ (20 mL), water (20 mL) and chloroform (20 mL). The organic layer was

separated and the aqueous layer was washed with chloroform (3 × 20 mL). The combined organic layers were washed with brine, dried over $MgSO_4$ and the solvent evaporated *in vacuo*. The residue was purified by silica gel column chromatography (5:1→1:1 hexane:EtOAc) to yield 7'-methoxy-2',3'-dihydrospiro[cyclopentane-1,1'-indene]-2,5-dione **SI-11** as a white crystalline solid (158.1 mg, 0.688 mmol, 23%).

M.p. 104-105 °C; $R_f$ = 0.57 (1.5:1 EtOAc/hexane); $\nu_{max}/cm^{-1}$ 2938, 2839, 1715, 1601, 1586, 1477, 1440, 1268, 1173, 1074, 777; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.20 (dd, *J* = 8.1, 7.6 Hz, 1H, Ar-H), 6.89 (dd, *J* = 7.6, 0.9 Hz, 1H, Ar-H), 6.67 – 6.57 (m, 1H, Ar-H), 3.72 (s, 3H, $CH_3$), 3.18 (t, *J* = 7.4 Hz, 2H, $CH_2$), 3.12 – 2.95 (m, 2H, $CH_2$), 2.91 – 2.74 (m, 2H, $CH_2$), 2.39 – 2.29 (m, 2H, $CH_2$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 215.6 (C), 154.2 (C), 147.7 (C), 130.3 (C), 130.2 (CH), 117.6 (CH), 108.5 (CH), 65.9 (C), 55.3 ($CH_3$), 36.5 ($CH_2$), 35.5 ($CH_2$), 32.5 ($CH_2$); HRMS (NSI) *m/z calc*. For $C_{14}H_{15}O_3$: 231.1016 $[M+H]^+$; found: 231.1019.

**7'-Methoxy-2',3'-dihydrospiro[cyclopentane-1,1'-inden]-3-ene-2,5-dione (1m)**[9]

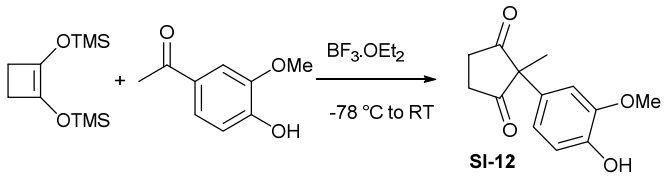



7'-Methoxy-2',3'-dihydrospiro[cyclopentane-1,1'-indene]-2,5-dione **SI-11** (158.1 mg, 0.6879 mmol, 1 equiv.) was added to a solution of $CuBr_2$ (0.342 g, 1.53 mmol, 2.2 equiv.) in anhydrous MeOH (8 mL). The resulting reaction mixture was refluxed for 3 h before being quenched with cold $H_2O$ and 1 M $HCl{\cdot}Et_2O$ was added to the solution. The aqueous layer was washed with $Et_2O$ until the organic layer was colourless. The combined organic layers were washed with brine (15 mL) and dried over $MgSO_4$ before solvent was removed under reduced pressure. The resulting residue was purified by silica gel column chromatography (hexane/EtOAc 5:1→3:1) to yield 7'-methoxy-2',3'-dihydrospiro[cyclopentane-1,1'-inden]-3-ene-2,5-dione **1m** (123.7 mg, 0.5425 mmol, 79%) as a yellow crystalline solid.

M.p. 101-103 °C; $R_f$ = 0.26 (1:1 EtOAc/hexane); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.32 (s, 2H, alkene-H), 7.21 (dd, *J* = 8.2, 7.6 Hz, 1H, Ar-H), 6.90 (dd, *J* = 7.6, 0.9 Hz, 1H, Ar-H), 6.59 (dd, *J* = 8.2, 0.9 Hz, 1H, Ar-H), 3.62 (s, 3H, $CH_3$), 3.18 (t, *J* = 7.5 Hz, 2H, $CH_2$), 2.32 (t, *J* = 7.5 Hz, 2H, $CH_2$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 206.0 (C), 155.1 (C), 148.3 (C), 147.9

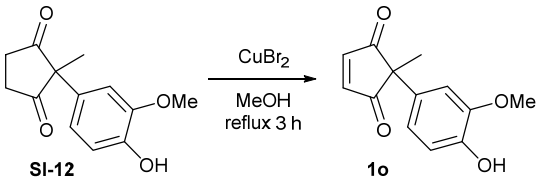
(CH), 130.4 (CH), 127.5 (C), 117.4 (CH), 108.4 (CH), 61.2 (C), 55.2 ($CH_3$), 34.1 ($CH_2$), 32.2 ($CH_2$); HRMS (NSI) *m/z calc*. For $C_{14}H_{13}O_3$: 229.0859 $[M+H]^+$; found: 229.0862.

**2-(4-Hydroxy-3-methoxyphenyl)-2-methylcyclopentane-1,3-dione (SI-12)**




4'-Hydroxy-3'-methoxyacetophenone (1.0044 g, 6.044 mmol, 1 equiv.), was added to dichloromethane (60 mL) at -78 °C followed by $BF_3.OEt_2$ (1.85 mL, 15.00 mmol, 2.5 equiv.) and the solution stirred for 30 min. 1,2-Bis(trimethylsiloxy)cyclobutene (2.79 mL, 10.9 mmol, 1.8 equiv.) was then added, the solution was warmed to room temperature and stirred for 16 h under an inert atmosphere. $BF_3.OEt_2$ (1.5 mL) was added followed by $Na_2CO_3$ (20 mL), water (20 mL) and chloroform (20 mL). The organic layer was separated and the aqueous layer was washed with chloroform (3 × 20 mL). The combined organic layers were washed with brine, dried over $MgSO_4$ and the solvent evaporated *in vacuo*. The residue was purified by silica gel column chromatography (5:1→1:1 hexane:EtOAc). Pure product **SI-12** could not be purified due to coelution with 4'-hydroxy-3'-methoxyacetophenone. Therefore the mixture was used for the following step to synthesise 2-(4-hydroxy-3-methoxyphenyl)-2-methylcyclopent-4-ene-1,3-dione **1o.**

**2-(4-Hydroxy-3-methoxyphenyl)-2-methylcyclopent-4-ene-1,3-dione (1o)**



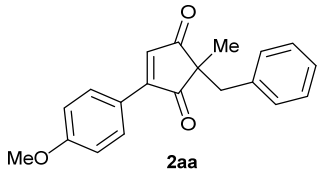

A crude mixture of 2-(4-hydroxy-3-methoxyphenyl)-2-methylcyclopentane-1,3-dione **SI-12** from the previous step (0.455 g, 1.94 mmol, 1 equiv.) was added to a solution of $CuBr_2$ (0.964 g, 4.32 mmol, 2.2 equiv.) in anhydrous MeOH (22 mL). The resulting reaction mixture was refluxed for 16 h before being quenched with cold $H_2O$ and 1 M HCl. $Et_2O$ was

added to the solution. The aqueous layer was washed with $Et_2O$ until the organic layer was colourless. The combined organic layers were washed with brine (15 mL) and dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. The resulting residue was purified by silica gel column chromatography (hexane/EtOAc, 5:1→3:1) followed by recrystallisation to yield 2-(4-hydroxy-3-methoxyphenyl)-2-methylcyclopent-4-ene-1,3-dione **1o** (98.5 mg, 0.4242 mmol, 13% over two steps) as a yellow crystalline solid.

M.p. 131-132 °C; $R_f$ = 0.22 (1:1 hexane/EtOAc); $\nu_{max}/cm^{-1}$ 3320, 2941, 1693, 1598, 1516, 1524, 1257, 1240, 1135, 1030, 858, 836, 779; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.32 (s, 2H, alkene-H), 6.87 – 6.81 (m, 2H, Ar-H), 6.74 (dd, *J* = 8.4, 2.1 Hz, 1H, Ar-H), 5.57 (s, 1H, O<u>H</u>), 3.88 (s, 3H, $CH_3$), 1.54 (s, 3H, $CH_3$); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 205.1 (C), 148.1 (CH), 146.7 (C), 145.3 (C), 128.5 (C), 119.4 (CH), 114.5 (CH), 109.0 (CH), 55.9 ($CH_3$), 53.9 (C), 20.1 ($CH_3$); HRMS (APCI) *m/z calc*. For $C_{13}H_{13}O_4$: 233.0808 $[M+H]^+$; found: 233.0812.

**Oxidative Heck Reactions:**

**2-Benzyl-4-(4-methoxyphenyl)-2-methylcyclopent-4-ene-1,3-dione (2aa)**




**2aa**

Racemic procedure:

$Pd(OAc)_2$ (2.9 mg, 12.9 µmol, 0.05 equiv.) and 1,10-phenanthroline **4** (2.5 mg, 13.8 µmol, 0.05 equiv.) were dissolved in DMF (1.5 mL). After stirring at room temperature for 30 min, 2-benzyl-2-methylcyclopent-4-ene-1,3-dione **1a** (50.0 mg, 0.25 mmol, 1 equiv.) and 4-methoxyphenyl boronic acid **3a** (76.7 mg, 0.50 mmol, 2 equiv., dehydrated to form the boroxine by heating with a heat gun under vacuum) were added and washed in with DMF (1.0 mL). The solution was left to stir at 70 °C under an oxygen atmosphere (balloon) for 60 h. On completion, hexane and ethyl acetate were added and the resulting solution was washed with brine (15 mL). The aqueous phase was washed twice with hexane (5 mL) and ethyl acetate (2.5 mL). The combined organic phase was washed with brine (10 mL), dried over sodium sulfate and the solvent removed under reduced pressure. The residue was purified by flash column chromatography (petroleum ether/EtOAc 15:1) to yield the target molecule **2aa** (59.4 mg, 0.193 mmol, 77%) as yellow crystals.

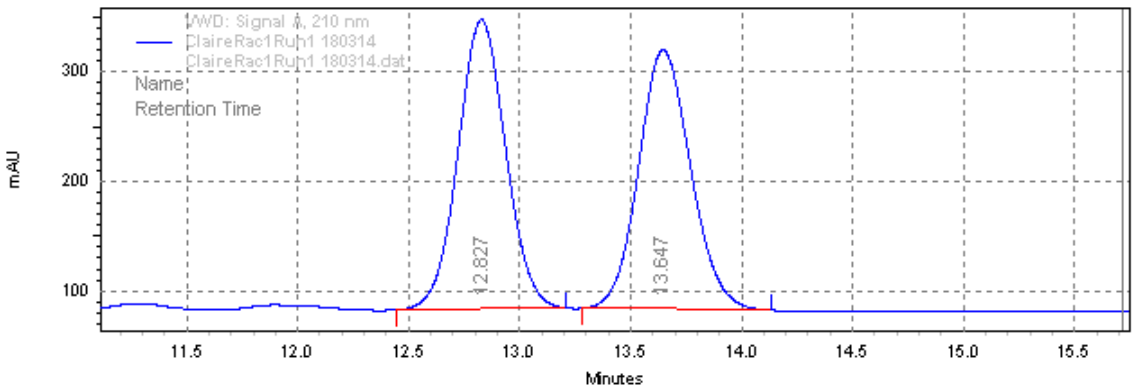
M.p. 89 - 91 °C; $R_f = 0.36$ (5:1 petroleum ether/EtOAc); $\nu_{max}/cm^{-1}$ 3069, 2972, 2937, 2846, 1731, 1712, 1684, 1604, 1585, 1563, 1509, 1453, 1422, 1372, 1267, 1181, 1025; $^1$H-NMR (300 MHz, $CDCl_3$) δ 7.75 (d, $J = 9.0$ Hz, 2H, Ar-H), 7.11 - 7.06 (m, 3H, Ar-H), 6.99 - 6.96 (m, 3H, Ar-H + =CH), 6.91 (d, $J = 9.0$ Hz, 2H, Ar-H), 3.84 (s, 3H, $OCH_3$), 3.04 (s, 2H, $CH_2$), 1.32 (s, 3H, $CH_3$); $^{13}$C-NMR (75 MHz, $CDCl_3$) δ 207.1 (C), 205.6 (C), 162.4 (C), 156.1 (C), 138.8 (CH), 136.0 (C), 131.1 (CH), 129.8 (CH), 128.3 (CH), 127.0 (CH), 121.5 (C), 114.4 (CH), 55.5 ($CH_3$), 54.0 (C), 41.6 ($CH_2$), 19.8 ($CH_3$); HRMS (APCI) *m/z calc*. for $C_{20}H_{18}O_3H$: 307.1329 $[M+H]^+$; found: 307.1331.

Enantioselective procedure:

(*S*)-4-*Tert*-Butyl-2-(2-pyridyl)oxazoline **6a** (2.3 mg, 11.3 μmol, 0.11 equiv.) was added to a dried flask which was subsequently purged with $N_2$. DMA (0.5 mL), followed by $Pd(OAc)_2$ (2.2 mg, 9.8 μmol, 0.10 equiv.) were added and the solution was left to stir at room temperature for 1 h. 2-Benzyl-2-methylcyclopent-4-ene-1,3-dione **1a** (20.6 mg, 0.103 mmol, 1 equiv.), was added to the solution followed by DMA (0.5 mL) and 4-methoxyphenyl boronic acid **3a** (32.5 mg, 0.24 mmol, 2.4 equiv.) which was freshly dehydrated under vacuum with a heat gun to form the boroxine. The reaction was left to stir at 50 °C for 95 h under an $O_2$ atmosphere (balloon) and with an air condenser. On completion, 2:1 EtOAc:$Et_2O$ was added to the reaction solution before being washed with $H_2O$ and brine. The aqueous layer was extracted with 2:1 EtOAc:$Et_2O$ until the organic layer was colourless. The combined organic layers were washed with brine, dried over $MgSO_4$ and solvent was removed *via* reduced pressure. The resulting crude was purified by silica gel column chromatography (hexane/EtOAc, 20:1) to yield (*S*)-2-benzyl-4-(4-methoxyphenyl)-2-methylcyclopent-4-ene-1,3-dione **2aa** (25.6 mg, 0.0836 mmol, 81%) as yellow crystals (65:35 er).

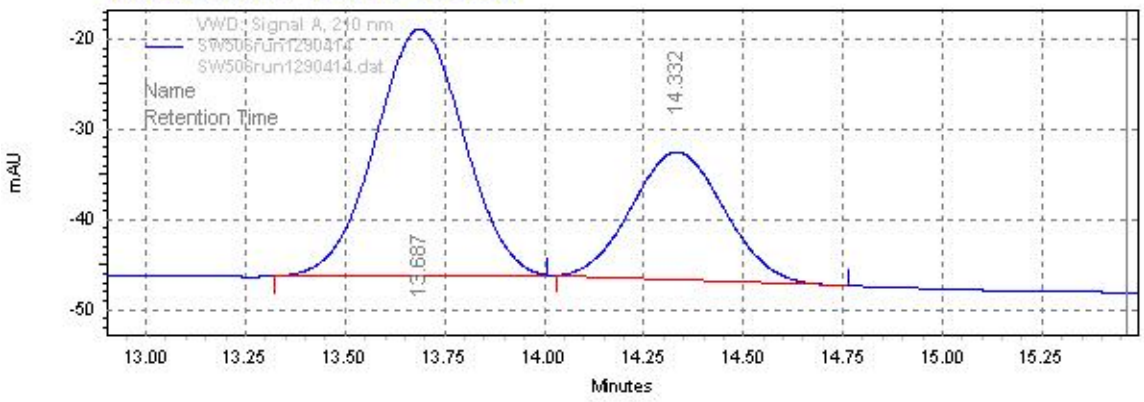
See racemic procedure above for characterisation.

$[\alpha]_D^{22}$ = +54.0 (*c* 1.00, $CHCl_3$); 65:35 er; HPLC (CHIRALPAK IA, hexane/2-propanol: 99/1, flow rate: 1.0 mL $min^{-1}$, detection UV 210 nm, 25 °C) $t_R$ of major isomer: 13.7 min, $t_R$ of minor isomer: 14.3 min.




**VWD: Signal A, 210 nm Results**

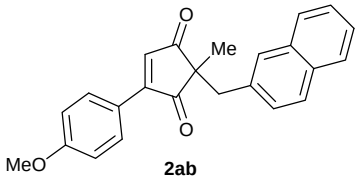
| Retention Time | Area | Area % | Height | Height % |
|---|---|---|---|---|
| 12.827 | 66241476 | 50.57 | 4423825 | 52.77 |
| 13.647 | 64742384 | 49.43 | 3959541 | 47.23 |




**VWD: Signal A, 210 nm Results**

| Retention Time | Area | Area % | Height | Height % |
|---|---|---|---|---|
| 13.687 | 7073473 | 64.88 | 458540 | 65.91 |
| 14.332 | 3828251 | 35.12 | 237121 | 34.09 |

**4-(4-Methoxyphenyl)-2-methyl-2-(naphthalen-2-ylmethyl)cyclopent-4-ene-1,3-dione (2ab)**

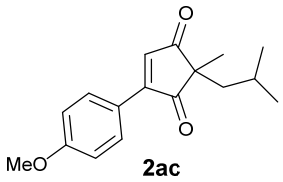


**2ab**

4-Methoxyphenyl boronic acid **3a** (31.1 mg, 0.205 mmol, 2 equiv.) was heated (heat gun) under vacuum in the reaction flask in order to dehydrate it to the arylboroxine before a $N_2$ environment was introduced. 2-Methyl-2-(naphthalen-2-ylmethyl)cyclopent-4-ene-1,3-dione **1b** (25.7 mg, 0.103 mmol, 1 equiv.), 1-10-phenanthroline **4** (1.0 mg, 5.3 μmol, 0.05 equiv.) and $Pd(OAc)_2$ (1.2 mg, 5.3 μmol, 0.05 equiv.) were added in order, with a $N_2$ environment re-introduced after each addition. Anhydrous DMF (1 mL) was added before the solution was stirred at 70 °C under an $O_2$ atmosphere (balloon) for 67 h. On completion, $Et_2O$ and EtOAc were added to the reaction solution before being washed with water (10 mL) and brine (10 mL). The aqueous layer was washed with diethyl ether (5 mL) and ethyl acetate (2.5 mL) until the organic layer was colourless. The combined organic layers were washed with brine (15 mL) and dried with $Na_2SO_4$ before solvent was removed under reduced pressure. The crude was purified by flash column chromatography (petroleum ether/ethyl acetate 20:1) to yield 4-(4-methoxyphenyl)-2-methyl-2-(naphthalen-2-ylmethyl)cyclopent-4-ene-1,3-dione **2ab** (32.1 mg, 92.9 μmol, 76%) as a yellow solid.

M.p. 91-95 °C; $R_f$ = 0.31 (5:1 petroleum ether/EtOAc); $\nu_{max}$/cm$^{-1}$ 2928, 2842, 1736, 1690, 1603, 1583, 1564, 1506, 1453, 1371, 1325, 1309, 1294, 1257, 1178, 1109, 1052, 1027, 897, 864, 836, 822, 750; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.78 – 7.63 (m, 4H, Ar-H), 7.58 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.46 (s, 1H, Ar-H), 7.39 – 7.33 (m, 2H, Ar-H), 7.10 (dd, *J* = 8.4, 1.7 Hz, 1H, Ar-H), 6.92 (s, 1H, C=CH), 6.86 (d, *J* = 9.0 Hz, 2H, Ar-H), 3.81 (s, 3H, $OCH_3$), 3.21 (s, 2H, $CH_2$), 1.37 (s, 3H, $CH_3$); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 207.0 (C), 205.4 (C), 162.2 (C), 156.0 (C), 138.7 (CH), 133.5 (C), 133.2 (C), 132.3 (C), 131.0 (CH), 128.6 (CH), 127.9 (CH), 127.9 (CH), 127.7 (CH), 127.5 (CH), 125.9 (CH), 125.6 (CH), 121.4 (C), 114.3 (CH), 55.4 ($CH_3$), 54.0 (C), 41.4 ($CH_2$), 20.0 ($CH_3$); HRMS (ESI) *m/z calc*. for $C_{24}H_{21}O_3$: 357.1485 $[M+H]^+$; found: 357.1482.

**2-Isobutyl-4-(4-methoxyphenyl)-2-methylcyclopentene-1,3-dione (2ac)**

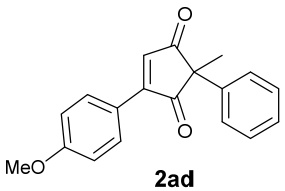


**2ac**

4-Methoxyphenyl boronic acid **3a** (36.1 mg, 0.24 mmol, 2.4 equiv.) was added to dried glassware and dehydrated to the boroxine under vacuum with a heat gun, then an $N_2$ atmosphere was introduced. 2-Isobutyl-2-methyl-cyclopentene-1,3-dione **1c** (16.8 mg, 0.1 mmol, 1 equiv.), 1,10-phenanthroline **4** (1.1 mg, 6.1 μmol, 0.06 equiv.) and $Pd(OAc)_2$ (1.3 mg, 5.8 μmol, 0.06 equiv.) were added sequentially, with an $N_2$ environment reintroduced after each addition. DMF (1 mL) was added, the reaction was left to stir at 70 °C for 70 h under an $O_2$ atmosphere (balloon). On completion, 2:1 EtOAc:$Et_2O$ was added to the reaction solution before being washed with $H_2O$ and brine. The aqueous layer was extracted with 2:1 EtOAc:$Et_2O$ until the organic layer was colourless. The combined organic layers were washed with brine and dried over $Na_2SO_4$ and solvent was removed *via* reduced pressure. The resulting crude was purified by silica gel column chromatography (petrol ether/EtOAc, 12:1) to yield 2-isobutyl-4-(4-methoxyphenyl)-2-methylcyclopentene-1,3-dione **2ac** (16.0 mg, 0.06 mmol, 56%) as a yellow amorphous solid.

$R_f$ = 0.3 (10:1 petroleum ether:EtOAc); $\nu_{max}/cm^{-1}$ 3058, 2958, 2930, 1732, 1689, 1602, 1581, 1505, 1460, 1310, 1239, 1182, 1135, 1043, 1020, 836; $^1$H NMR (300 MHz, $CDCl_3$) δ 8.01 (d, *J* = 9.0 Hz, 2H, Ar-H), 7.27 (s, 1H, alkene-H), 7.01 (d, *J* = 9.0 Hz, 2H, Ar-H), 3.89 (s, 3H, $OCH_3$), 1.76 – 1.70 (m, 2H, $CH_2$), 1.58 – 1.43 (m, 1H, C<u>H</u>$(CH_3)_2$), 1.21 (s, 3H, $CH_3$), 0.80 (d, *J* = 6.6 Hz, 3H, $CH_3$), 0.75 (d, *J* = 6.6 Hz, 3H, $CH_3$); $^{13}$C NMR (300 MHz, $CDCl_3$) δ 207.7 (C), 206.4 (C), 162.4 (C), 155.2 (C), 137.9 (CH), 131.2 (CH), 121.7 (C), 114.5 (CH), 55.5 ($CH_3$), 51.9 (C), 44.2 ($CH_2$), 25.4 (CH), 24.0 ($CH_3$), 23.9 ($CH_3$), 21.7 ($CH_3$); HRMS (NSI) *m/z* calc. for $C_{17}H_{21}O_3$: 273.1485 $[M+H]^+$; found: 273.1488.

**4-(4-Methoxyphenyl)-2-methyl-2-phenylcyclopentene-1,3-dione (2ad)**




**2ad**

Racemic procedure:

4-Methoxyphenyl boronic acid **3a** (36.7 mg, 0.24 mmol, 2.4 equiv.) was added to dried glassware and dehydrated to the boroxine under vacuum with a heat gun, then an $N_2$ atmosphere was introduced. 2-Methyl-2-phenylcyclopentene-1,3-dione **1d** (18.7 mg, 0.1 mmol, 1 equiv.), 1,10-phenanthroline **4** (1.1 mg, 6.1 μmol, 0.06 equiv.) and $Pd(OAc)_2$ (1.2 mg, 5.5 μmol, 0.055 equiv.) were added sequentially, with an $N_2$ environment being reintroduced after each addition. DMF (1.1 mL) was added, the reaction was left to stir at 70 °C for 70 h under an $O_2$ atmosphere (balloon). On completion, 2:1 EtOAc:$Et_2O$ was added to the reaction solution before being washed with $H_2O$ and brine. The aqueous layer was extracted with 2:1 EtOAc:$Et_2O$ until the organic layer was colourless. The combined organic layers were washed with brine and dried over $Na_2SO_4$ and solvent was removed *via* reduced pressure. The resulting crude was purified by silica gel column chromatography (hexane/EtOAc 12:1) to yield 4-(4-methoxyphenyl)-2-methyl-2-phenylcyclopentene-1,3-dione **2ad** (23.0 mg, 0.077 mmol, 79%) as a yellow crystalline solid.

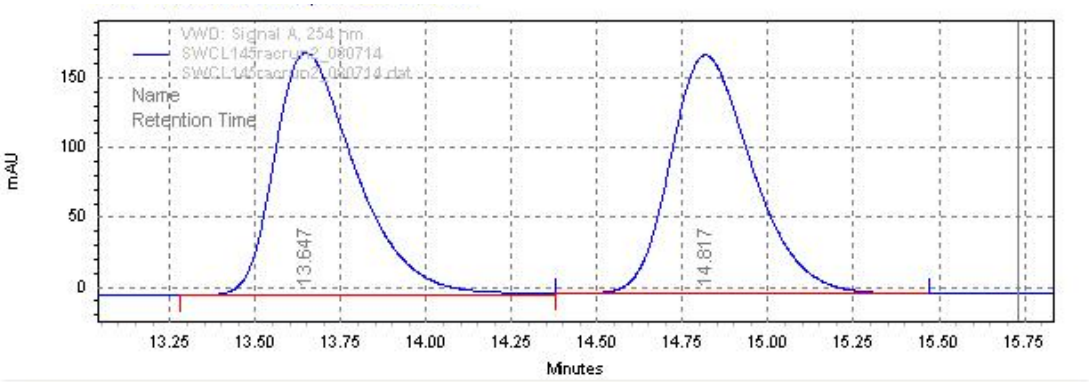
M.p. 105-106 °C; $R_f$ = 0.1 (10:1 petrol ether:EtOAc); $\nu_{max}/cm^{-1}$ 2969, 1736, 1695, 1603, 1508, 1444, 1257, 1180, 1046, 837, 698; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.93 (d, *J* = 9.1 Hz, 2H, Ar-H), 7.31 – 7.13 (m, 6H, Ar-H and alkene-H), 6.91 (d, *J* = 9.1 Hz, 2H, Ar-H), 3.79 (s, 3H, $OCH_3$), 1.56 (s, 3H, $CH_3$); $^{13}C$ NMR (300 MHz, $CDCl_3$) δ 204.6 (C), 203.3 (C), 162.6 (C), 155.5 (C), 137.9 (CH), 137.7 (C), 131.3 (CH), 128.8 (CH), 127.6 (CH), 126.4 (CH), 121.5 (C), 114.5 (CH), 56.1 (C), 55.5 ($CH_3$), 19.9 ($CH_3$); HRMS (APCI) *m/z* calc. for $C_{19}H_{17}O_3$: 293.1177 $[M+H]^+$; found: 293.1178.

Enantioselective procedure:

(*S*)-4- *Tert* -Butyl-2-(2-pyridyl)oxazoline **6a** (2.3 mg, 11.3 μmol, 0.11 equiv.) was added to a dried flask, purged with $N_2$. DMA (0.4 mL), followed by $Pd(OAc)_2$ (2.3 mg, 10.2 μmol, 0.10 equiv.) were added and the solution was left to stir at room temperature for 1 h. 2-Methyl-2-phenylcyclopentene-1,3-dione **1d** (18.8 mg, 0.101 mmol, 1 equiv.), was added to the solution followed by DMA (0.6 mL) and 4-methoxyphenyl boronic acid **3a** (32.4 mg, 0.24 mmol, 2.4 equiv.) which was freshly dehydrated under vacuum with a heat gun to form the boroxine. The reaction was left to stir at 50 °C for 95 h under an $O_2$ atmosphere (balloon) and with an air condenser. On completion, 2:1 EtOAc:$Et_2O$ was added to the reaction solution before being washed with $H_2O$ and brine. The aqueous layer was extracted with 2:1 EtOAc:$Et_2O$ until the organic layer was colourless. The combined organic layers were washed with brine and dried over $MgSO_4$ and solvent was removed *via* reduced pressure. The resulting crude was purified by silica gel column chromatography (hexane/EtOAc 20:1→15:1) to yield (*S*)-4-(4-methoxyphenyl)-2-methyl-2-phenylcyclopentene-1,3-dione **2ad** (27.5 mg, 0.094 mmol, 93%) as a yellow oil (83:17 er).

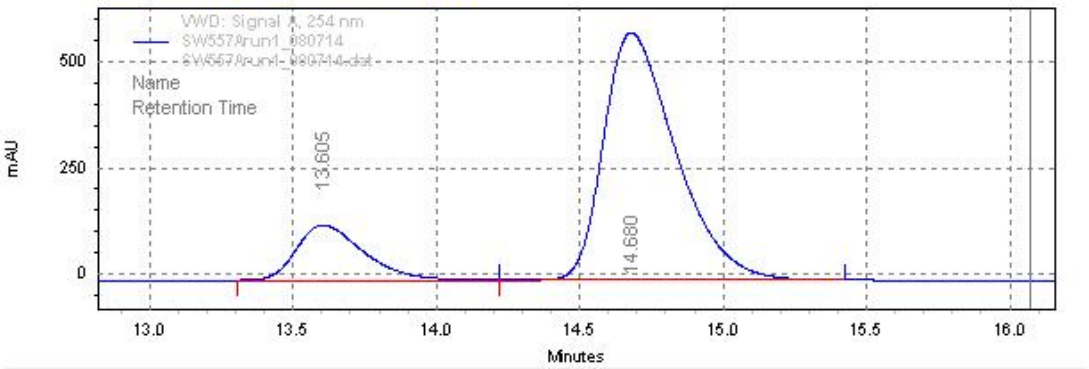
See racemic procedure above for characterisation.

$[\alpha]_D^{28}$ = +77.8 (*c* 0.18, $CHCl_3$); 83:17 er; HPLC (CHIRALPAK IB, hexane/2-propanol: 99/1, flow rate: 1.0 mL $min^{-1}$, detection UV 254 nm) $t_R$ of major isomer: 14.7 min, $t_R$ of minor isomer: 13.6 min.




**VWD: Signal A,**
**254 nm Results**

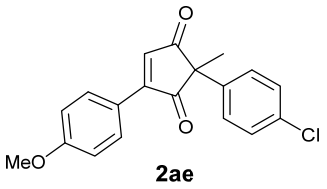
| Retention Time | Area | Area % | Height | Height % |
|---|---|---|---|---|
| 13.647 | 48356060 | 50.06 | 2915702 | 50.37 |
| 14.817 | 48235074 | 49.94 | 2873310 | 49.63 |




**VWD: Signal A,**
**254 nm Results**

| Retention Time | Area | Area % | Height | Height % |
|---|---|---|---|---|
| 13.605 | 35338979 | 17.20 | 2170867 | 18.22 |
| 14.680 | 170095100 | 82.80 | 9742169 | 81.78 |

**2-(4-Chlorophenyl)-4-(4-methoxyphenyl)-2-methylcyclopent-4-ene-1,3-dione (2ae)**




**2ae**

Racemic procedure:

4-Methoxyphenyl boronic acid **3a** (18.2 mg, 0.120 mmol, 2.4 equiv.) was added to dried glassware and dehydrated to the boroxine under vacuum with a heat gun, then an $N_2$ atmosphere was introduced. 2-(4-Chlorophenyl)-2-methylcyclopent-4-ene-1,3-dione **1e** (11.0 mg, 0.0499 mmol, 1 equiv.), 1,10-phenanthroline **4** (0.6 mg, 3.3 μmol, 0.067 equiv.) and $Pd(OAc)_2$ (0.6 mg, 2.7 μmol, 0.054 equiv.) were added sequentially, with an $N_2$ environment being reintroduced after each addition. DMF (0.5 mL) was added, the reaction was left to stir at 70 °C for 70 h under an $O_2$ atmosphere (balloon). On completion, 2:1 EtOAc:$Et_2O$ was added to the reaction solution before being washed with $H_2O$ and brine. The aqueous layer was extracted with 2:1 EtOAc:$Et_2O$ until the organic layer was colourless. The combined organic layers were washed with brine and dried over $MgSO_4$ and solvent was removed *via* reduced pressure. The resulting crude was purified by silica gel column chromatography (hexane/EtOAc gradient 10:1) to yield 2-(4-chlorophenyl)-4-(4-methoxyphenyl)-2-methylcyclopent-4-ene-1,3-dione **2ae** (15.5 mg, 0.0474 mmol, 95%) as a yellow oil.

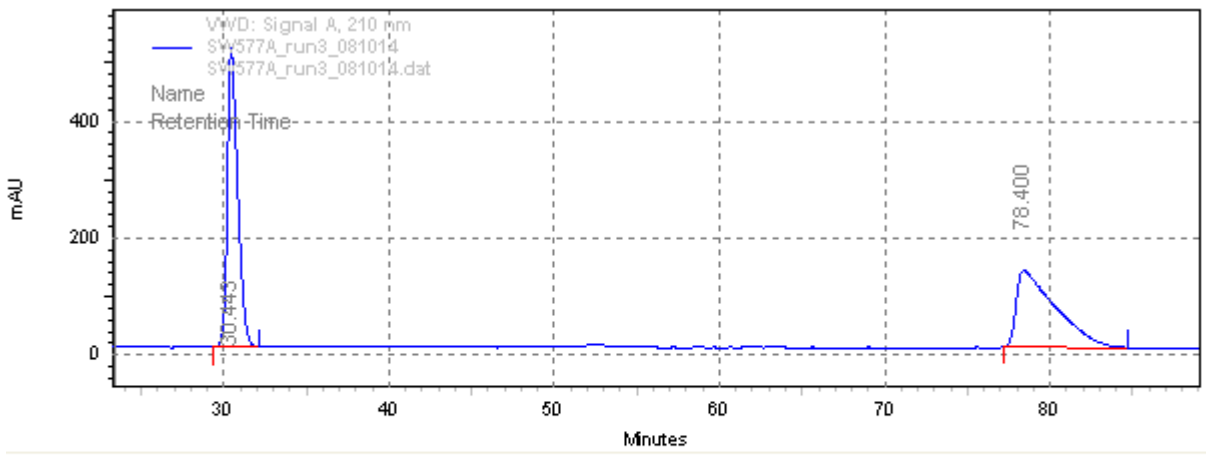
$R_f$ = 0.13 (2:1 hexane:EtOAc); $\nu_{max}/cm^{-1}$ 2933, 2839, 1737, 1689, 1601, 1575, 1506, 1492, 1253, 1177, 1095, 1046, 1026, 836, 808; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.9 Hz, 2H, Ar-H), 7.34 – 7.19 (m, 5H, Ar-H and alkene-H), 6.96 (d, *J* = 8.9 Hz, 2H, Ar-H), 3.84 (s, 3H, $CH_3$), 1.58 (s, 3H, $CH_3$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 204.3 (C), 202.9 (C), 162.8 (C), 155.4 (C), 137.8 (CH), 136.2 (C), 133.7 (C), 131.4 (CH), 128.9 (CH), 128.0 (CH), 121.4 (C), 114.6 (CH), 55.5 (C and $CH_3$), 20.3 ($CH_3$); HRMS (NSI) *m/z* calc. for $C_{19}H_{16}O_3Cl$: 327.0782 $[M+H]^+$; found: 327.0786.

Enantioselective procedure:

(*S*)-4-(*Tert*-Butyl)-2-[4-(trifluoromethyl)pyridin-2-yl]-4,5-dihydrooxazole **6b** (3.0 mg, 11.0 μmol, 0.11 equiv.) was added to a dried flask, purged with $N_2$. DMA (0.4 mL), followed by $Pd(OAc)_2$ (2.4 mg, 10.7 μmol, 0.11 equiv.) were added and the solution was left to stir at room temperature for 1 h. 2-(4-Chlorophenyl)-2-methylcyclopent-4-ene-1,3-dione **1e** (22.0 mg, 0.0997 mmol, 1 equiv.), was added to the solution followed by DMA (0.6 mL) and 4-methoxyphenyl boronic acid **3a** (32.3 mg, 0.241 mmol, 2.4 equiv.) which was freshly dehydrated under vacuum with a heat gun to form the boroxine. The reaction was left to stir at 50 °C for 95 h under an $O_2$ atmosphere (balloon) and with an air condenser. On completion, 2:1 EtOAc:$Et_2O$ was added to the reaction solution before being washed with $H_2O$ and brine. The aqueous layer was extracted with 2:1 EtOAc:$Et_2O$ until the organic layer was colourless. The combined organic layers were washed with brine and dried over $MgSO_4$ and solvent was removed *via* reduced pressure. The resulting crude was purified by silica gel column chromatography (hexane/EtOAc 10:1) to yield (*S*)-2-(4-chlorophenyl)-4-(4-methoxyphenyl)-2-methylcyclopent-4-ene-1,3-dione **2ae** (29.2 mg, 0.0893 mmol, 90%) as a yellow oil (80:20 er).

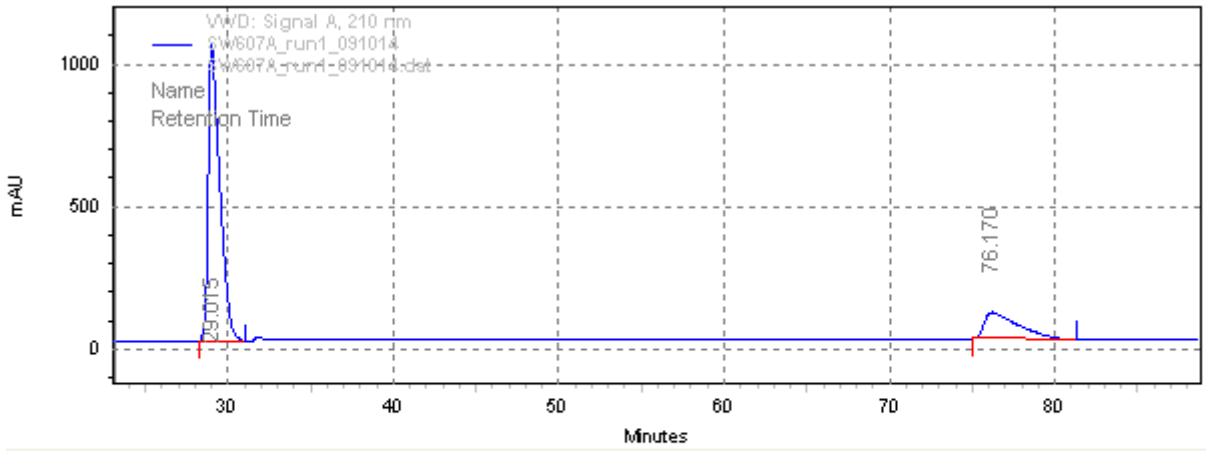
See racemic procedure above for characterisation.

$[\alpha]_D^{25}$ = +86.0 (*c* 1.00, $CHCl_3$); 80:20 er; HPLC (CHIRALPAK IA, hexane/2-propanol: 99/1, flow rate: 1.0 mL $min^{-1}$, detection UV 210 nm, 25 °C) $t_R$ of major isomer: 29.0 min, $t_R$ of minor isomer: 76.2 min.




**VWD: Signal A, 210 nm Results**

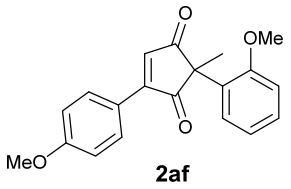
| Retention Time | Area | Area % | Height | Height % |
|---|---|---|---|---|
| 30.443 | 368036250 | 50.28 | 8602387 | 79.68 |
| 78.400 | 363906806 | 49.72 | 2194144 | 20.32 |




**VWD: Signal A, 210 nm Results**

| Retention Time | Area | Area % | Height | Height % |
|---|---|---|---|---|
| 29.015 | 847120840 | 79.82 | 17456077 | 91.91 |
| 76.170 | 214234541 | 20.18 | 1536984 | 8.09 |

**2-(2-Methoxyphenyl)-4-(4-methoxyphenyl)-2-methylcyclopent-4-ene-1,3-dione (2af)**




**2af**

Racemic procedure:

4-Methoxyphenyl boronic acid **3a** (18.3 mg, 0.120 mmol, 2.4 equiv.) was added to dried glassware and dehydrated to the boroxine under vacuum with a heat gun, then an $N_2$ atmosphere was introduced. 2-(2-Methoxyphenyl)-2-methylcyclopent-4-ene-1,3-dione **1f** (10.9 mg, 0.0504 mmol, 1 equiv.), 1,10-phenanthroline **4** (0.6 mg, 3.3 μmol, 0.058 equiv.) and $Pd(OAc)_2$ (0.6 mg, 2.7 μmol, 0.053 equiv.) were added sequentially, with an $N_2$ environment being reintroduced after each addition. DMF (0.5 mL) was added, the reaction was left to stir at 70 °C for 70 h under an $O_2$ atmosphere (balloon). On completion, 2:1 EtOAc:$Et_2O$ was added to the reaction solution before being washed with $H_2O$ and brine. The aqueous layer was extracted with 2:1 EtOAc:$Et_2O$ until the organic layer was colourless. The combined organic layers were washed with brine and dried over $MgSO_4$ and solvent was removed *via* reduced pressure. The resulting crude was purified by silica gel column chromatography (hexane/EtOAc, 20:1→5:1) to yield 2-(2-methoxyphenyl)-4-(4-methoxyphenyl)-2-methylcyclopent-4-ene-1,3-dione **2af** (14.5 mg, 0.0450 mmol, 89%) as a yellow oil.

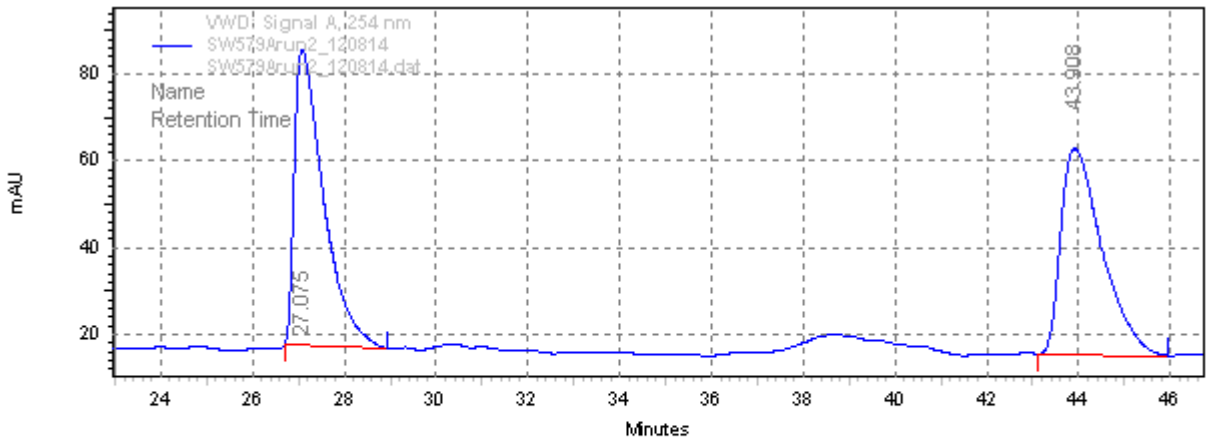
$R_f$ = 0.31 (2:1 hexane:EtOAc); $\nu_{max}/cm^{-1}$ 2978, 2939, 1733, 1687, 1601, 1585, 1508, 1491, 1251, 1176, 1040, 1014, 835, 773; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 9.0 Hz, 2H, Ar-H), 7.41 (dd, *J* = 7.7, 1.6 Hz, 1H, Ar-H), 7.31 – 7.26 (m, 1H, Ar-H), 7.20 (s, 1H, alkene-H), 7.07 – 7.02 (m, 1H, Ar-H), 7.01 (d, *J* = 9.0 Hz, 2H, Ar-H), 6.77 (dd, *J* = 8.2, 1.1 Hz, 1H, Ar-H), 3.88 (s, 3H, $CH_3$), 3.54 (s, 3H, $CH_3$), 1.63 (s, 3H, $CH_3$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 206.1 (C), 205.3 (C), 162.2 (C), 156.2 (C), 153.0 (C), 134.9 (CH), 131.0 (CH), 129.3 (CH), 129.1 (CH), 126.2 (C), 122.2 (C), 121.3 (CH), 114.5 (CH), 110.9 (CH), 55.4 ($CH_3$), 55.3 ($CH_3$), 54.8 (C), 19.4 ($CH_3$); HRMS (NSI) *m/z* calc. for $C_{20}H_{19}O_4$: 323.1278 $[M+H]^+$; found: 323.1276.

Enantioselective procedure:

(*S*)-4-*Tert*-Butyl-2-(2-pyridyl)oxazoline **6a** (2.2 mg, 10.8 μmol, 0.11 equiv.) was added to a dried flask, purged with $N_2$. DMA (0.8 mL), followed by $Pd(OAc)_2$ (2.3 mg, 10.2 μmol, 0.10 equiv.) were added and the solution was left to stir at room temperature for 1 h. 2-(2-Methoxyphenyl)-2-methylcyclopent-4-ene-1,3-dione **1f** (21.4 mg, 0.0990 mmol, 1 equiv.), was added to the solution followed by DMA (0.2 mL) and 4-methoxyphenyl boronic acid **3a** (32.8 mg, 0.245 mmol, 2.5 equiv.) which was freshly dehydrated under vacuum with a heat gun to form the boroxine. The reaction was left to stir at 50 °C for 95 h under an $O_2$ atmosphere (balloon) and with an air condenser. On completion, 2:1 EtOAc:$Et_2O$ was added to the reaction solution before being washed with $H_2O$ and brine. The aqueous layer was extracted with 2:1 EtOAc:$Et_2O$ until the organic layer was colourless. The combined organic layers were washed with brine and dried over $MgSO_4$ and solvent was removed *via* reduced pressure. The resulting crude was purified by silica gel column chromatography (hexane/EtOAc, 15:1→7:1) to yield (*S*)-2-(2-methoxyphenyl)-4-(4-methoxyphenyl)-2-methylcyclopent-4-ene-1,3-dione **2af** (27.1 mg, 0.0841 mmol, 85%) as a yellow oil (78:22) er.

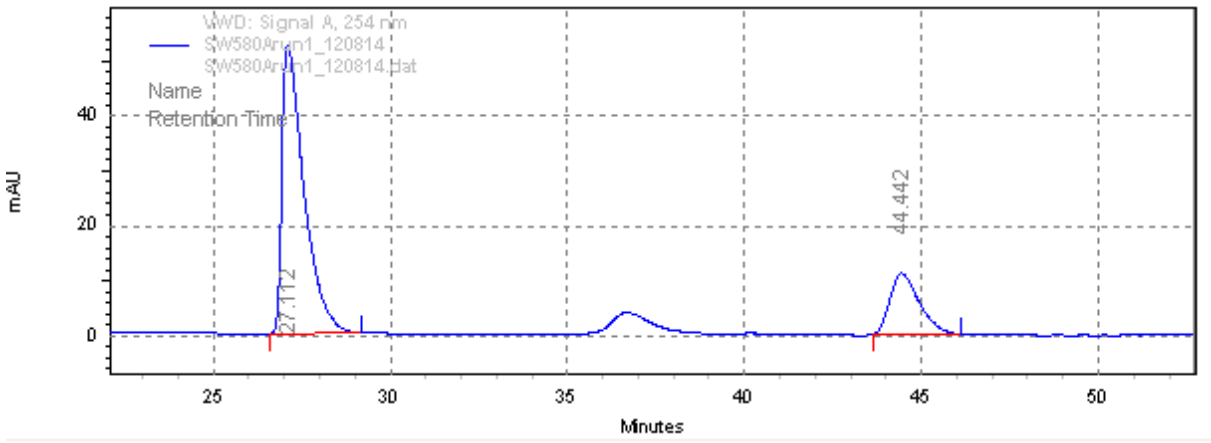
See racemic procedure for characterisation.

$[\alpha]_D^{24}$ = -56.0 (*c* 1.00, $CHCl_3$); 78:22 er; HPLC (CHIRALPAK IB, hexane/2-propanol: 99/1, flow rate: 1.0 mL $min^{-1}$, detection UV 254 nm, 25 °C) $t_R$ of major isomer: 27.1 min, $t_R$ of minor isomer: 44.4 min.




**VWD: Signal A, 254 nm Results**

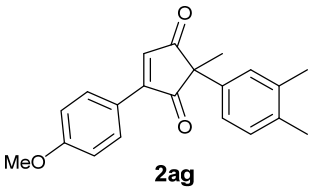
| Retention Time | Area | Area % | Height | Height % |
|---|---|---|---|---|
| 27.075 | 50347435 | 50.21 | 1139289 | 58.92 |
| 43.908 | 49926816 | 49.79 | 794298 | 41.08 |




**VWD: Signal A, 254 nm Results**

| Retention Time | Area | Area % | Height | Height % |
|---|---|---|---|---|
| 27.112 | 38264978 | 78.31 | 882509 | 82.65 |
| 44.442 | 10596134 | 21.69 | 185305 | 17.35 |

**2-(3,4-Dimethylphenyl)-4-(4-methoxyphenyl)-2-methylcyclopent-4-ene-1,3-dione (2ag)**




**2ag**

Racemic procedure:

4-Methoxyphenyl boronic acid **3a** (36.7 mg, 0.242 mmol, 2.4 equiv.) was added to dried glassware and dehydrated to the boroxine under vacuum with a heat gun, then an $N_2$ atmosphere was introduced. 2-(3,4-Dimethylphenyl)-2-methylcyclopent-4-ene-1,3-dione **1g** (21.3 mg, 0.0994 mmol, 1 equiv.), 1,10-phenanthroline **4** (1.2 mg, 6.7 μmol, 0.067 equiv.) and $Pd(OAc)_2$ (1.1 mg, 4.9 μmol, 0.049 equiv.) were added sequentially, with an $N_2$ environment being reintroduced after each addition. DMF (1.0 mL) was added and the reaction was left to stir at 70 °C for 70 h under an $O_2$ atmosphere (balloon). On completion, 2:1 EtOAc:$Et_2O$ was added to the reaction solution before being washed with $H_2O$ and brine. The aqueous layer was extracted with 2:1 EtOAc:$Et_2O$ until the organic layer was colourless. The combined organic layers were washed with brine and dried over $MgSO_4$ and solvent was removed *via* reduced pressure. The resulting crude was purified by silica gel column chromatography (hexane/EtOAc gradient 15:1) to yield 2-(3,4-dimethylphenyl)-4-(4-methoxyphenyl)-2-methylcyclopent-4-ene-1,3-dione **2ag** (29.0 mg, 0.0905 mmol, 91%) as a yellow oil.

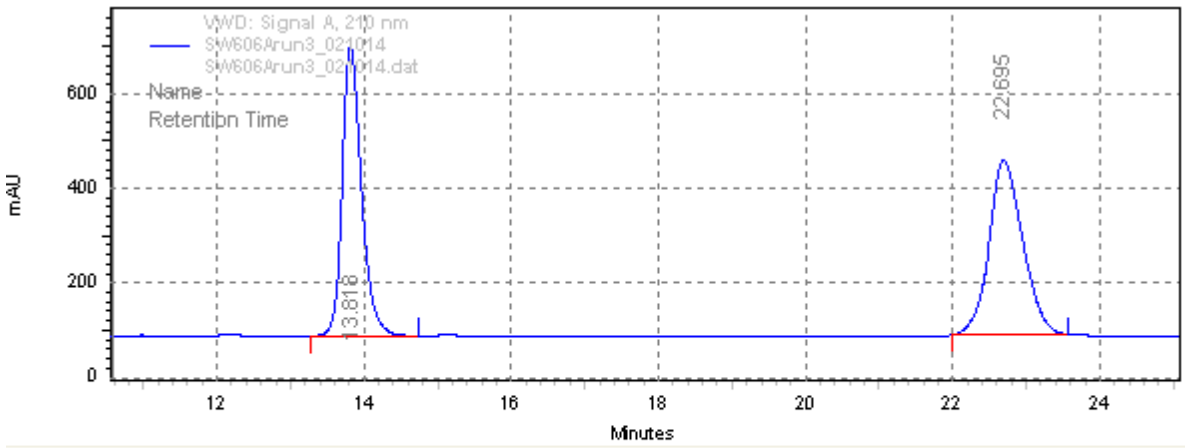
$R_f$ = 0.31 (2:1 hexane:EtOAc); $\nu_{max}/cm^{-1}$ 2925, 2838, 1731, 1680, 1601, 1577, 1505, 1238, 1185, 1103, 1049, 847; $^1H$ NMR (300 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.9 Hz, 2H, Ar-H), 7.34 (s, 1H, alkene-H), 7.12 – 7.05 (m, 3H, Ar-H), 6.99 (d, *J* = 8.9 Hz, 2H, Ar-H), 3.88 (s, 3H, $CH_3$), 2.23 (s, 3H, $CH_3$), 2.21 (s, 3H, $CH_3$), 1.62 (s, 3H, $CH_3$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 204.8 (C), 203.6 (C), 162.5 (C), 155.4 (C), 137.9 (CH), 137.0 (C), 136.1 (C), 135.2 (C), 131.3 (CH), 130.0 (CH), 127.5 (CH), 123.8 (CH), 121.6 (C), 114.5 (CH), 55.9 (C), 55.4 ($CH_3$), 19.9 ($CH_3$), 19.6 ($CH_3$), 19.3 ($CH_3$); HRMS (NSI) *m/z* calc. for $C_{21}H_{21}O_3$: 321.1485 $[M+H]^+$; found: 321.1491.

Enantioselective procedure:

(*S*)-4-Tert-Butyl-2-(2-pyridyl)oxazoline **6a** (2.4 mg, 11.8 μmol, 0.12 equiv.) was added to a dried flask, purged with $N_2$. DMA (0.8 mL), followed by $Pd(OAc)_2$ (2.3 mg, 10.2 μmol, 0.10 equiv.) were added and the solution was left to stir at room temperature for 1 h. 2-(3,4-Dimethylphenyl)-2-methylcyclopent-4-ene-1,3-dione **1g** (21.4 mg, 0.0999 mmol, 1 equiv.), was added to the solution followed by DMA (0.2 mL) and 4-methoxyphenyl boronic acid **3a** (32.1 mg, 0.240 mmol, 2.4 equiv.) which was freshly dehydrated under vacuum with a heat gun to form the boroxine. The reaction was left to stir at 50 °C for 95 h under an $O_2$ atmosphere (balloon) and with an air condenser. On completion, 2:1 EtOAc:$Et_2O$ was added to the reaction solution before being washed with $H_2O$ and brine. The aqueous layer was extracted with 2:1 EtOAc:$Et_2O$ until the organic layer was colourless. The combined organic layers were washed with brine and dried over $MgSO_4$ and solvent was removed *via* reduced pressure. The resulting crude was purified by silica gel column chromatography (hexane/EtOAc 15:1) to yield (*S*)-2-(3,4-dimethylphenyl)-4-(4-methoxyphenyl)-2-methylcyclopent-4-ene-1,3-dione **2ag** (32.0 mg, 0.0999 mmol, 100%) as a yellow oil (80:20 er).

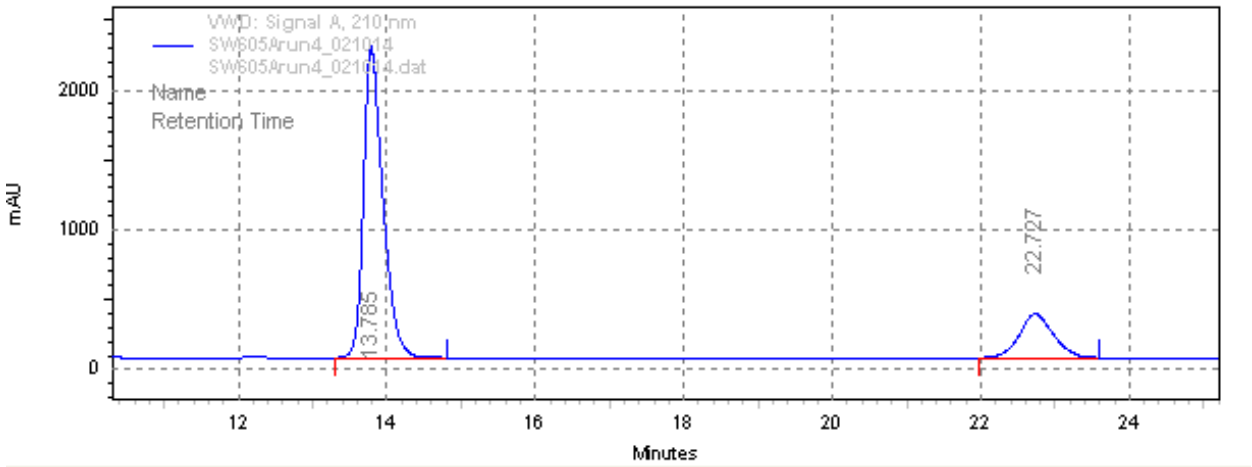
See racemic procedure for characterisation.

$[\alpha]_D^{24}$ = +122.0 (*c* 1.00, $CHCl_3$); 80:20 er; HPLC (CHIRALPAK IA, hexane/2-propanol: 95/5, flow rate: 1.0 mL $min^{-1}$, detection UV 210 nm, 25 °C) $t_R$ of major isomer: 13.8 min, $t_R$ of minor isomer: 22.7 min.




**VWD: Signal A, 210 nm Results**

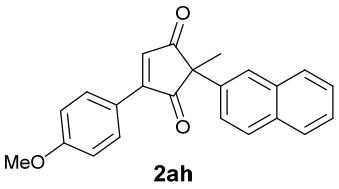
| Retention Time | Area | Area % | Height | Height % |
|---|---|---|---|---|
| 13.818 | 186581899 | 48.74 | 10293325 | 62.43 |
| 22.695 | 196229670 | 51.26 | 6195540 | 37.57 |




**VWD: Signal A, 210 nm Results**

| Retention Time | Area | Area % | Height | Height % |
|---|---|---|---|---|
| 13.785 | 685046108 | 80.37 | 37299761 | 87.64 |
| 22.727 | 167308107 | 19.63 | 5260784 | 12.36 |

**4-(4-Methoxyphenyl)-2-methyl-2-(naphthalen-2-yl)cyclopent-4-ene-1,3-dione (2ah)**




**2ah**

Racemic procedure:

4-Methoxyphenyl boronic acid **3a** (36.3 mg, 0.24 mmol, 2.4 equiv.) was added to dried glassware and dehydrated to the boroxine under vacuum with a heat gun, then an $N_2$ atmosphere was introduced. 2-Methyl-2-(naphthalen-2-yl)cyclopentane-1,3-dione (23.6 mg, 0.10 mmol, 1 equiv.) **1h**, 1,10-phenanthroline **4** (1.0 mg, 5.6 μmol, 0.056 equiv.) and $Pd(OAc)_2$ (1.1 mg, 4.9 μmol, 0.049 equiv.) were added sequentially, with an $N_2$ environment being reintroduced after each addition. DMF (1 mL) was added and the reaction was left to stir at 70 °C for 70 h under an $O_2$ atmosphere (balloon). On completion, 2:1 EtOAc:$Et_2O$ was added to the reaction solution before being washed with $H_2O$ and brine. The aqueous layer was extracted with 2:1 EtOAc:$Et_2O$ until the organic layer was colourless. The combined organic layers were washed with brine and dried over $MgSO_4$ and solvent was removed *via* reduced pressure. The resulting crude was purified by silica gel column chromatography (hexane/EtOAc 20:1→10:1) to yield 4-(4-methoxyphenyl)-2-methyl-2-(naphthalen-2-yl)cyclopent-4-ene-1,3-dione **2ah** (31.1 mg, 0.091 mmol, 91%) as a yellow crystalline solid.

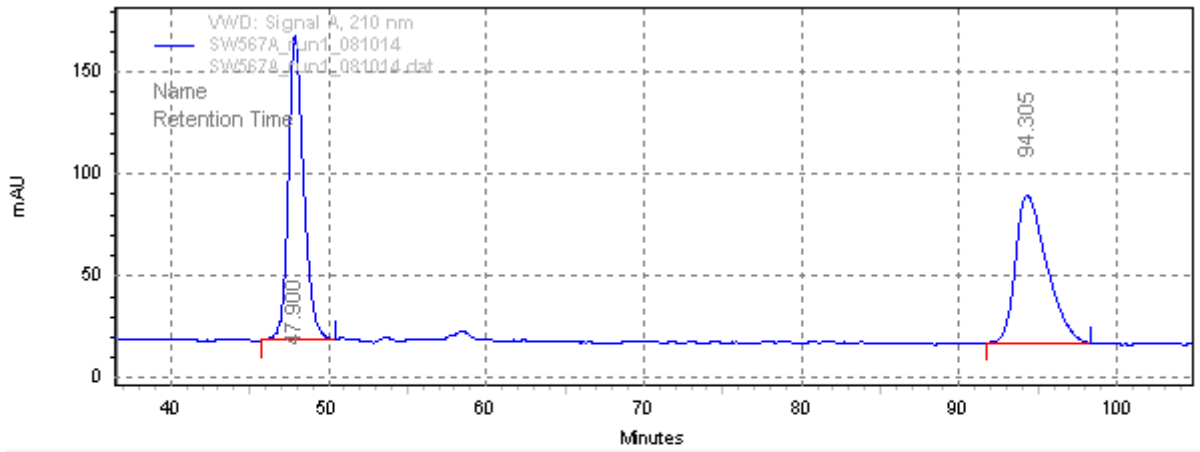
M.p. 144-146 °C; $R_f$ = 0.38 (2:1 hexane:EtOAc); $\nu_{max}/cm^{-1}$ 3057, 2997, 1733, 1683, 1599, 1580, 1506, 1457, 1435, 1329, 1312, 1239, 1185, 1099, 1045, 902, 881, 838, 824; $^1$H NMR (300 MHz, $CDCl_3$) δ 8.04 (d, *J* = 9.0 Hz, 2H, Ar-H), 7.87 – 7.73 (m, 4H, Ar-H), 7.55 – 7.42 (m, 3H, Ar-H), 7.39 (s, 1H, alkene-H), 7.00 (d, *J* = 9.0 Hz, 2H, Ar-H), 3.87 (s, 3H, $OCH_3$), 1.75 (s, 3H, $CH_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 204.5 (C), 203.2 (C), 162.6 (C), 155.4 (C), 137.9 (CH), 135.1 (C), 133.2 (C), 132.5 (C), 131.4 (CH), 128.6 (CH), 128.1 (CH), 127.5 (CH), 126.29 (CH), 126.26 (CH), 125.7 (CH), 124.1 (CH), 121.5 (C), 114.6 (CH), 56.3 (C), 55.5 ($CH_3$), 20.0 ($CH_3$); HRMS (APCI) *m/z* calc. for $C_{23}H_{19}O_3$: 343.1329 $[M+H]^+$; found: 343.1330.

Enantioselective procedure:

(*S*)-4-(*Tert*-Butyl)-2-[4-(trifluoromethyl)pyridin-2-yl]-4,5-dihydrooxazole **6b** (3.0 mg, 11.0 μmol, 0.11 equiv.) was added to a dried flask, purged with $N_2$. DMA (0.4 mL), followed by $Pd(OAc)_2$ (2.4 mg, 10.7 μmol, 0.11 equiv.) were added and the solution was left to stir at room temperature for 1 h. 2-Methyl-2-(naphthalen-2-yl)cyclopent-4-ene-1,3-dione **1h** (23.7 mg, 0.1003 mmol, 1 equiv.), was added to the solution followed by DMA (0.6 mL) and 4-methoxyphenyl boronic acid **3a** (32.6 mg, 0.244 mmol, 2.4 equiv.) which was freshly dehydrated under vacuum with a heat gun to form the boroxine. The reaction was left to stir at 50 °C for 95 h under an $O_2$ atmosphere (balloon) and with an air condenser. On completion, 2:1 EtOAc:$Et_2O$ was added to the reaction solution before being washed with $H_2O$ and brine. The aqueous layer was extracted with 2:1 EtOAc:$Et_2O$ until the organic layer was colourless. The combined organic layers were washed with brine and dried over $MgSO_4$ and solvent was removed *via* reduced pressure. The resulting crude was purified by silica gel column chromatography (hexane/EtOAc, 25:1) to yield (*S*)-4-(4-methoxyphenyl)-2-methyl-2-(naphthalen-2-yl)cyclopent-4-ene-1,3-dione **2ah** (34.2 mg, 0.100 mmol, 100%) as a yellow solid (90:10 er).

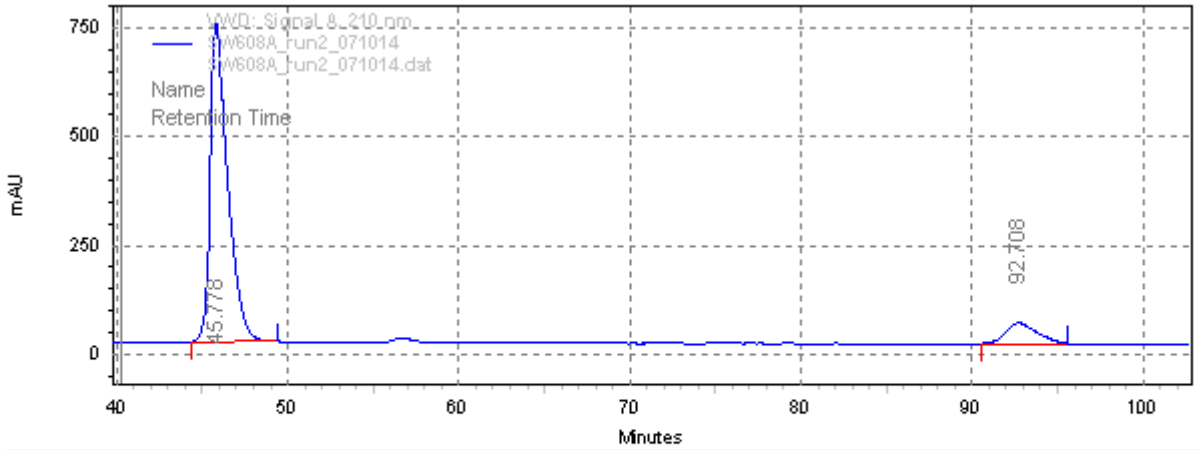
See racemic procedure above for characterisation.

$[\alpha]_D^{25}$ = +133.3 (*c* 0.12, $CHCl_3$); 90:10 er; HPLC (CHIRALPAK IA, hexane/2-propanol: 99/1, flow rate: 1.0 mL $min^{-1}$, detection UV 210 nm, 25 °C) $t_R$ of major isomer: 45.8 min, $t_R$ of minor isomer: 92.7 min.




**VWD: Signal A, 210 nm Results**

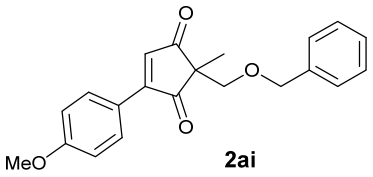
| Retention Time | Area | Area % | Height | Height % |
|---|---|---|---|---|
| 47.900 | 168392572 | 50.15 | 2503773 | 67.42 |
| 94.305 | 167386735 | 49.85 | 1210129 | 32.58 |




**VWD: Signal A, 210 nm Results**

| Retention Time | Area | Area % | Height | Height % |
|---|---|---|---|---|
| 45.778 | 890351112 | 89.73 | 12340211 | 93.89 |
| 92.708 | 101864324 | 10.27 | 802627 | 6.11 |

**2-Benzyloxymethyl-4-(4-methoxyphenyl)-2-methylcyclopentene-1,3-dione (2ai)**

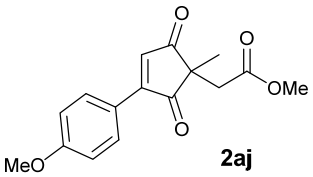



**2ai**

4-Methoxyphenyl boronic acid **3a** (39.6 mg, 0.26 mmol, 2.6 equiv.) was added to dried glassware and dehydrated to the boroxine under vacuum with a heat gun, then an $N_2$ atmosphere was introduced. 2-Benzyloxymethyl-2-methyl-cyclopentene-1,3-dione **1i** (24.0 mg, 0.10 mmol, 1 equiv.), 1,10-phenanthroline **4** (1.1 mg, 6.1 μmol, 0.06 equiv.) and $Pd(OAc)_2$ (1.3 mg, 5.8 μmol, 0.06 equiv.) were added sequentially, with an $N_2$ environment being reintroduced after each addition. DMF (1 mL) was added, the reaction was left to stir at 70 °C for 70 h under an $O_2$ atmosphere (balloon). On completion, 2:1 EtOAc:$Et_2O$ was added to the reaction solution before being washed with $H_2O$ and brine. The aqueous layer was extracted with 2:1 EtOAc:$Et_2O$ until the organic layer was colourless. The combined organic layers were washed with brine and dried over $Na_2SO_4$ and solvent was removed *via* reduced pressure. The resulting crude was purified by silica gel column chromatography (hexane/EtOAc, gradient 10:1→7:1) to yield 2-benzyloxymethyl-4-(4-methoxyphenyl)-2-methylcyclopentene-1,3-dione **2ai** (21.2 mg, 0.063 mmol, 63%) as a yellow amorphous solid.

$R_f$ = 0.1 (10:1 petrol ether:EtOAc); $\nu_{max}/cm^{-1}$ 3054, 2930, 2862, 1740, 1690, 1061, 1584, 1509, 1452, 1209, 1184, 1111, 1026, 743, 697; $^1H$ NMR (300 MHz, $CDCl_3$) δ 8.01 (d, $J$ = 9.0 Hz, 2H, Ar-H), 7.33 (s, 1H, alkene-H), 7.30–7.20 (m, 3H, Ar-H), 7.16-7.10 (m, 2H, Ar-H), 7.00 (d, $J$ = 9.0 Hz, 2H, Ar-H), 4.39 (s, 2H, O$\underline{CH_2}$($C_6H_5$)), 3.88 (s, 3H, $OCH_3$), 3.68 (s, 2H, $CH_2$), 1.10 (s, 3H, $CH_3$); $^{13}C$ NMR (300 MHz, $CDCl_3$) δ 205.9 (C), 204.5 (C), 162.3 (C), 156.2 (C), 139.1 (CH), 137.5 (C), 131.2 (CH), 128.3 (CH), 127.5 (CH), 127.2 (CH), 121.8 (C), 114.4 (CH), 73.3 ($CH_2$), 72.2 ($CH_2$), 55.4 ($CH_3$), 52.8 (C), 15.4 ($CH_3$); HRMS (APCI) *m/z* calc. for $C_{21}H_{21}O_4$: 337.1434 $[M+H]^+$; found: 337.1440.

**3-(4-Methoxyphenyl)-1-methyl-2,5-dioxocyclopent-3-enylacetic acid methyl ester (2aj)**

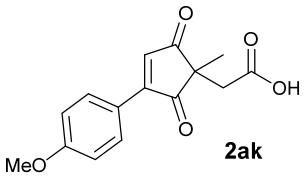



**2aj**

4-Methoxyphenyl boronic acid **3a** (36.6 mg, 0.24 mmol, 2.4 equiv.) was added to dried glassware and dehydrated to the boroxine under vacuum with a heat gun, then an $N_2$ atmosphere was introduced. Methyl 2-(1-methyl-2,5-dioxocyclopent-3-en-1-yl)acetate **1j** (18.3 mg, 0.1 mmol, 1 equiv.), 1,10-phenanthroline **4** (1.0 mg, 5.5 μmol, 0.055 equiv.) and $Pd(OAc)_2$ (1.2 mg, 5.5 μmol, 0.055 equiv.) were added sequentially, with an $N_2$ environment being reintroduced after each addition. DMF (1 mL) was added, the reaction was left to stir at 70 °C for 72 h under an $O_2$ atmosphere (balloon). On completion, 2:1 EtOAc:$Et_2O$ was added to the reaction solution before being washed with $H_2O$ and brine. The aqueous layer was extracted with 2:1 EtOAc:$Et_2O$ until the organic layer was colourless. The combined organic layers were washed with brine and dried over $Na_2SO_4$ and solvent was removed *via* reduced pressure. The resulting crude was purified by silica gel column chromatography (petrol ether/EtOAc 20:1→5:1) to yield 3-(4-methoxyphenyl)-1-methyl-2,5-dioxocyclopent-3-enylacetic acid methyl ester **2aj** (26.0 mg, 0.094 mmol, 94%) as a yellow amorphous solid.

$R_f$ = 0.2 (2:1 petrol ether:EtOAc); $\nu_{max}/cm^{-1}$ 2954, 1736, 1689, 1604, 1579, 1506, 1461, 1332, 1262, 1206, 1185, 1157, 1201, 1057, 1029, 863, 843; $^1H$ NMR (300 MHz, $CDCl_3$) δ 8.00 (d, *J* = 9.0 Hz, 2H, Ar-H), 7.27 (s, 1H, alkene-H), 6.99 (d, *J* = 9.0 Hz, 2H, Ar-H), 3.87 (s, 3H, $OCH_3$), 3.56 (s, 3H, $OCH_3$), 2.91 (s, 2H, $CH_2$), 1.24 (s, 3H, $CH_3$); $^{13}C$ NMR (300 MHz, $CDCl_3$) δ 205.5 (C), 204.1 (C), 170.9 (C), 162.4 (C), 154.9 (C), 137.1 (CH), 131.2 (CH), 122.0 (C), 114.4 (CH), 55.5 (C), 51.9 ($CH_3$), 49.4 ($CH_3$), 37.8 ($CH_2$), 21.1 ($CH_3$); HRMS (NSI) *m/z* calc. for $C_{16}H_{17}O_5$: 289.1071 $[M+H]^+$; found: 289.1072.

**2-(3-(4-Methoxyphenyl)-1-methyl-2,5-dioxocyclopent-3-en-1-yl)acetic acid (2ak)**

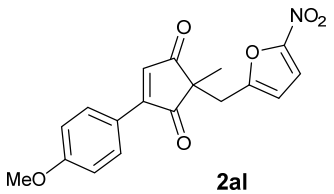



**2ak**

4-Methoxyphenyl boronic acid **3a** (24.3 mg, 0.16 mmol, 2.7 equiv.) was added to dried glassware and dehydrated to the boroxine under vacuum with a heat gun, then an $N_2$ atmosphere was introduced. 2-(1-Methyl-2,5-dioxocyclopent-3-en-1-yl)acetic acid **1k** (10.9 mg, 0.06 mmol, 1 equiv.), 1,10-phenanthroline **4** (0.6 mg, 0.003 μmol, 0.055 equiv.) and $Pd(OAc)_2$ (0.7 mg, 3.0 μmol, 0.05 equiv.) were added sequentially, with an $N_2$ environment being reintroduced after each addition. DMF (1.2 mL) was added, the reaction was left to stir at 70 °C for 64 h under an $O_2$ atmosphere (balloon). On completion, 2:1 EtOAc:$Et_2O$ was added to the reaction solution before being washed with $H_2O$ and brine. The aqueous layer was acidified with dilute HCl (2 mL) before being extracted with 2:1 EtOAc:$Et_2O$ until the organic layer was colourless. The combined organic layers were washed with brine and dried over $Na_2SO_4$ and solvent was removed *via* reduced pressure. The resulting crude was purified by silica gel column chromatography (hexane/EtOAc, 5:1→2:1) to yield 2-(3-(4-methoxyphenyl)-1-methyl-2,5-dioxocyclopent-3-en-1-yl)acetic acid **2ak** (13.7 mg, 0.049 mmol, 83%) as a yellow crystalline solid.

M.p. 128-130 °C; $R_f$ = 0.3 (2:1 petrol ether:EtOAc); $\nu_{max}/cm^{-1}$ 3067, 2933, 1738, 1693, 1602, 1589, 1508, 1241, 1116, 836; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.9 Hz, 2H, Ar-H), 7.23 (s, 1H, alkene-H), 6.98 (d, *J* = 8.9 Hz, 2H, Ar-H), 3.87 (s, 3H, $OCH_3$), 2.91 (s, 2H, $CH_2$), 1.22 (s, 3H, $CH_3$); $^{13}C$ NMR (400 MHz, $CDCl_3$) δ 205.1 (C), 203.9 (C), 174.9 (C), 162.4 (C), 154.8 (C), 137.0 (CH), 131.2 (CH), 121.8 (C), 114.5 (CH), 55.5 ($CH_3$), 49.2 (C), 37.3 ($CH_2$), 21.3 ($CH_3$); HRMS (APCI) *m/z* calc. for $C_{15}H_{15}O_5$: 275.0914$[M+H]^+$; found: 275.0915.

**4-(4-Methoxyphenyl)-2-methyl-2-((5-nitrofuran-2-yl)methyl)cyclopent-4-ene-1,3-dione (2al)**

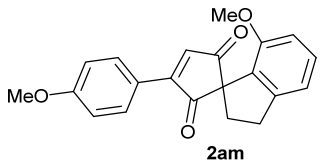



**2al**

4-Methoxyphenyl boronic acid **3a** (36.9 mg, 0.26 mmol, 2.6 equiv.) was added to dried glassware and dehydrated to the boroxine under vacuum with a heat gun, then an $N_2$ atmosphere was introduced. 2-Methyl-2-(methyl-5-nitrofuran)-1,3-cyclopentene-1,3-dione **1l** (23.6 mg, 0.1 mmol, 1 equiv.), 1,10-phenanthroline **4** (1.0 mg, 5.5 μmol, 0.055 equiv.) and $Pd(OAc)_2$ (1.1 mg, 5.0 μmol, 0.05 equiv.) were added sequentially, with an $N_2$ environment being reintroduced after each addition. DMF (1.1 mL) was added, the reaction was left to stir at 70 °C for 70 h under an $O_2$ atmosphere (balloon). On completion, 2:1 EtOAc:$Et_2O$ was added to the reaction solution before being washed with $H_2O$ and brine. The aqueous layer was extracted with 2:1 EtOAc:$Et_2O$ until the organic layer was colourless. The combined organic layers were washed with brine and dried over $Na_2SO_4$ and solvent was removed *via* reduced pressure. The resulting crude was purified by silica gel column chromatography (hexane/EtOAc, 6:1→4:1) to yield 4-(4-methoxyphenyl)-2-methyl-2-((5-nitrofuran-2-yl)methyl)cyclopent-4-ene-1,3-dione **2al** (23.8 mg, 0.081 mmol, 70%) as a yellow amorphous solid.

$R_f$ = 0.4 (2:1 petrol ether:EtOAc); $\nu_{max}/cm^{-1}$ 2927, 2360, 2341, 1696, 1604, 1508, 1455, 1356, 1258, 1179, 1116, 1031, 750; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 9.0 Hz, 2H, Ar-H), 7.17 (s, 1H, alkene-H), 7.09 (d, *J* = 3.6 Hz, 1H, HetAr-H), 6.98 (d, *J* = 9.0 Hz, 2H, Ar-H), 6.25 (d, *J* = 3.6 Hz, 1H, HetAr-H), 3.87 (s, 3H, $OCH_3$), 3.14 (s, 2H, $CH_2$), 1.34 (s, 3H, $CH_3$); $^{13}$C NMR (400 MHz, $CDCl_3$) δ 204.9 (C), 203.3 (C), 162.8 (C), 155.7 (C), 154.5 (C), 148.1 (C), 137.4 (CH), 131.3 (CH), 121.1 (C), 114.6 (CH), 112.2 (CH), 111.8 (CH), 55.5 ($CH_3$), 51.4 (C), 32.9 ($CH_2$), 19.8 ($CH_3$); HRMS (APCI) *m/z* calc. for $C_{18}H_{16}O_6N$: 342.0972 $[M+H]^+$; found: 342.0969.

**7'-Methoxy-3-(4-methoxyphenyl)-2',3'-dihydrospiro[cyclopentane-1,1'-inden]-3-ene-2,5-dione (2am)**

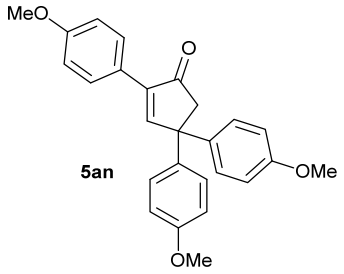



**2am**

4-Methoxyphenyl boronic acid **3a** (18.2 mg, 0.120 mmol, 2.4 equiv.) was added to dried glassware and dehydrated to the boroxine under vacuum with a heat gun, then an $N_2$ atmosphere was introduced. 7'-Methoxy-2',3'-dihydrospiro[cyclopentane-1,1'-inden]-3-ene-2,5-dione **1m** (11.5 mg, 0.0504 mmol, 1 equiv.), 1,10-phenanthroline **4** (0.6 mg, 3.3 μmol, 0.066 equiv.) and $Pd(OAc)_2$ (0.6 mg, 2.7 μmol, 0.053 equiv.) were added sequentially, with an $N_2$ environment being reintroduced after each addition. DMF (0.5 mL) was added and the reaction was left to stir at 70 °C for 70 h under an $O_2$ atmosphere (balloon). On completion, 2:1 EtOAc:$Et_2O$ was added to the reaction solution before being washed with $H_2O$ and brine. The aqueous layer was extracted with 2:1 EtOAc:$Et_2O$ until the organic layer was colourless. The combined organic layers were washed with brine and dried over $MgSO_4$ and solvent was removed *via* reduced pressure. The resulting crude was purified by silica gel column chromatography (hexane/EtOAc, 15:1→7:1) to yield 7'-methoxy-3-(4-methoxyphenyl)-2',3'-dihydrospiro[cyclopentane-1,1'-inden]-3-ene-2,5-dione **2am** (13.8 mg, 0.0413 mmol, 82%) as a yellow solid.

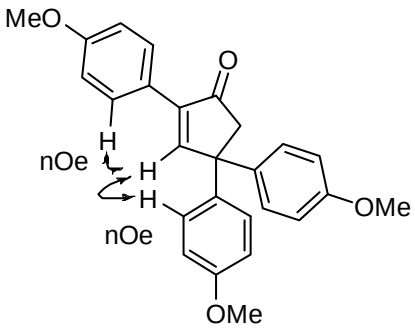
M. p. 147-149 °C; $R_f$ = 0.31 (1:1 hexane:EtOAc); $\nu_{max}/cm^{-1}$ 2933, 2843, 1737, 1686, 1601, 1580, 1506, 1262, 1202, 1178, 1078, 778; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 9.0 Hz, 2H, Ar-H), 7.31 (s, 1H, alkene-H), 7.21 (dd, *J* = 8.2, 7.6 Hz, 1H, Ar-H), 7.01 (d, *J* = 9.0 Hz, 2H, Ar-H), 6.91 (dd, *J* = 7.6, 0.9 Hz, 1H, Ar-H), 6.59 (dd, *J* = 8.2, 0.9 Hz, 1H, Ar-H), 3.88 (s, 3H, $CH_3$), 3.57 (s, 3H, $CH_3$), 3.35 – 3.08 (m, 2H, $CH_2$), 2.49 – 2.29 (m, 2H, $CH_2$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 205.5 (C), 204.4 (C), 162.2 (C), 155.5 (C), 155.2 (C), 148.2 (C), 137.7 (CH), 131.1 (CH), 130.2 (CH), 128.3 (C), 122.2 (C), 117.4 (CH), 114.5 (CH), 108.5 (CH), 62.9 (C), 55.4 ($CH_3$), 55.3 ($CH_3$), 34.4 ($CH_2$), 32.3 ($CH_2$); HRMS (NSI) *m/z* calc. for $C_{21}H_{19}O_4$: 335.1278 $[M+H]^+$; found: 335.1281.

**2,4,4-Tris-(4-methoxyphenyl)-cyclopent-2-enone (5an)**

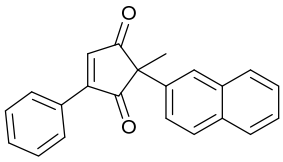



4-Methoxyphenyl boronic acid **3a** (36.5 mg, 0.24 mmol, 2.4 equiv.) was added to dried glassware and dehydrated to the boroxine under vacuum with a heat gun, then an $N_2$ atmosphere was introduced. Cyclopentene-1,3-dione **1n** (9.6 mg, 0.1 mmol, 1 equiv.), 1,10-phenanthroline **4** (1.0 mg, 5.5 μmol, 0.055 equiv.) and $Pd(OAc)_2$ (1.2 mg, 5.5 μmol, 0.055 equiv.) were added sequentially, with an $N_2$ environment being reintroduced after each addition. DMF (1.1 mL) was added, the reaction was left to stir at 70 °C for 68 h under an $O_2$ atmosphere (balloon). On completion, 2:1 EtOAc:$Et_2O$ was added to the reaction solution before being washed with $H_2O$ and brine. The aqueous layer was extracted with 2:1 EtOAc:$Et_2O$ until the organic layer was colourless. The combined organic layers were washed with brine and dried over $Na_2SO_4$ and solvent was removed *via* reduced pressure. The resulting crude was purified by silica gel column chromatography (hexane/EtOAc, gradient 15:1→5:1) to yield 2,4,4-*tris*-(4-methoxyphenyl)-cyclopent-2-enone **5an** (6.1 mg, 0.15 μmol, 19% with respect to boroxine) as a yellow amorphous solid.

$\nu_{max}/cm^{-1}$ 2957, 2836, 2360, 1703, 1606, 1509, 1463, 1250, 1179, 731; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H, alkene-H), 7.78 (d, $J$ = 9.0 Hz, 2H, Ar-H), 7.15 (d, $J$ = 9.0 Hz, 4H, Ar-H), 6.96 (d, $J$ = 9.0 Hz, 2H, Ar-H), 6.89 (d, $J$ = 9.0 Hz, 4H, Ar-H), 3.87 (s, 3H, $OCH_3$), 3.83 (s, 6H, 2 × $OCH_3$), 3.32 (s, 2H, $CH_2$); $^{13}C$ NMR (400 MHz, $CDCl_3$) δ 207.0 (C), 161.4 (CH), 160.0 (C), 158.3 (C), 139.1 (C), 137.8 (C), 128.7 (CH), 128.4 (CH), 123.6 (C), 114.0 (CH), 113.9 (CH), 55.3 (2 × $CH_3$), 53.2 ($CH_2$), 52.4 (C); HRMS (NSI) *m/z* calc. for $C_{26}H_{25}O_4$: 401.1747 $[M+H]^+$; found: 401.1747.



**2-Methyl-2-(naphthalen-2-yl)-4-phenylcyclopent-4-ene-1,3-dione (2bh)**



**2bh**

Racemic procedure:

Phenyl boronic acid **3b** (27.0 mg, 0.222 mmol, 2.2 equiv.) was heated (heat gun) under vacuum in the reaction flask to convert it to the boroxine before an $N_2$ environment was introduced. 2-Methyl-2-(naphthalen-2-yl)cyclopent-4-ene-1,3-dione **1h** (23.9 mg, 0.101 mmol, 1 equiv.), 1,10-phenanthroline **4** (1.0 mg, 5.6 μmol, 0.05 equiv.) and $Pd(OAc)_2$ (1.1 mg, 4.9 μmol, 0.05 equiv.) were then added in order, with a $N_2$ environment being re-introduced after each addition. Anhydrous DMF (1 mL) was then added before the solution was stirred at 70 °C in an $O_2$ environment (balloon) for 72 h. On completion, diethyl ether and ethyl acetate were added to the reaction solution before being washed with water (10 mL) and brine (10 mL). The aqueous layer was washed with $Et_2O$ (5 mL) and EtOAc (2.5 mL) until the organic layer was colourless. The combined organic layers were washed with brine (15 mL) and dried with $Na_2SO_4$ before solvent was removed under reduced pressure. The crude was purified by silica-gel column chromatography (hexane/ethyl acetate 20:1), to yield 2-methyl-2-(naphthalen-2-yl)-4-phenylcyclopent-4-ene-1,3-dione **2bh** (26.4 mg, 0.0845 mmol, 84%) as a yellow solid.

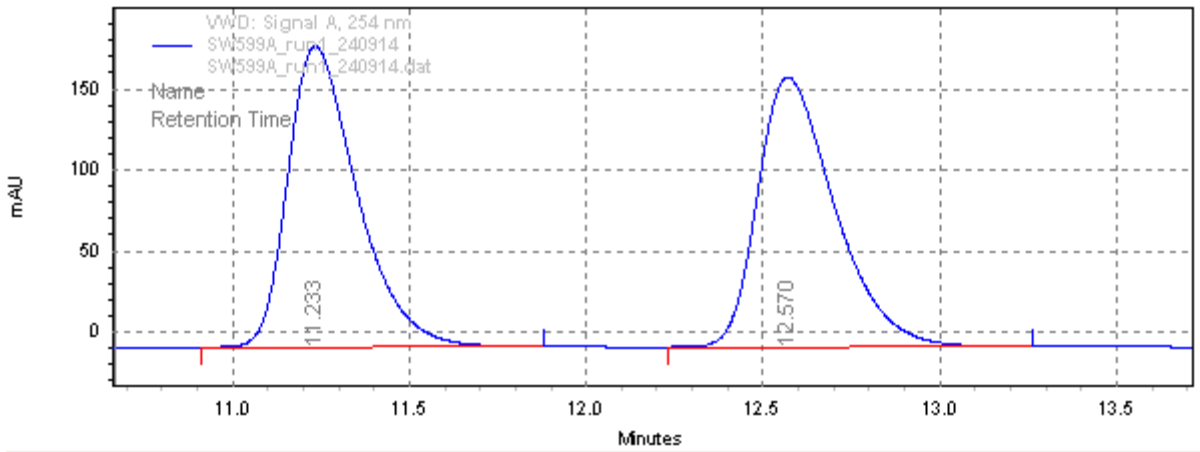
M. p. 108-110 °C; $R_f$ = 0.74 (1:1 hexane:EtOAc); $\nu_{max}/cm^{-1}$ 3054, 1737, 1691, 1596, 1506, 1446, 1246, 1104, 1050, 922, 808, 762; $^1H$ NMR (300 MHz, $CDCl_3$) δ 8.08 – 7.94 (m, 2H, Ar-H), 7.89 – 7.73 (m, 4H, Ar-H), 7.59 – 7.40 (m, 7H, Ar-H and alkene-H), 1.76 (s, 3H, $CH_3$); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 204.0 (C), 203.4 (C), 156.3 (C), 140.4 (CH), 134.8 (C), 133.2 (C), 132.5 (C), 131.8 (CH), 129.4 (CH), 129.01 (CH), 128.97 (C), 128.7 (CH), 128.1 (CH), 127.5 (CH), 126.4 (CH × 2), 125.7 (CH), 124.1 (CH), 56.3 (C), 20.0 ($CH_3$); HRMS (NSI) *m/z* calc. for $C_{22}H_{17}O_2$: 313.1223 $[M+H]^+$; found: 313.1227.

Enantioselective procedure:

(*S*)-4-Tert-Butyl-2-(2-pyridyl)oxazoline **6a** (2.4 mg, 11.8 μmol, 0.12 equiv.) was added to a dried flask, purged with $N_2$. DMA (0.8 mL), followed by $Pd(OAc)_2$ (2.3 mg, 10.2 μmol, 0.10 equiv.) were added and the solution was left to stir at room temperature for 1 h. 2-Methyl-2-(naphthalen-2-yl)cyclopent-4-ene-1,3-dione **1h** (23.6 mg, 0.0999 mmol, 1 equiv.), was added to the solution followed by DMA (0.2 mL) and phenyl boronic acid **3b** (24.7 mg, 0.24 mmol, 2.4 equiv.) which was freshly dehydrated under vacuum with a heat gun to form the boroxine. The reaction was left to stir at 50 °C for 95 h under an $O_2$ atmosphere (balloon) and with an air condenser. On completion, 2:1 EtOAc:$Et_2O$ was added to the reaction solution before being washed with $H_2O$ and brine. The aqueous layer was extracted with 2:1 EtOAc:$Et_2O$ until the organic layer was colourless. The combined organic layers were washed with brine and dried over $MgSO_4$ and solvent was removed *via* reduced pressure. The resulting crude was purified by silica gel column chromatography (hexane / EtOAc, 20:1) to yield (*S*)-2-methyl-2-(naphthalen-2-yl)-4-phenylcyclopent-4-ene-1,3-dione **2bh** (30.4 mg, 0.097 mmol, 97%) as a yellow solid (74:26 er).

See racemic procedure for characterisation.

$[\alpha]_D^{23}$ = +74.0 (*c* 1.00, $CHCl_3$); 74:26 er; HPLC (CHIRALPAK IB, hexane/2-propanol: 99/1, flow rate: 1.0 mL $min^{-1}$, detection UV 254 nm, 25 °C) $t_R$ of major isomer: 12.8 min, $t_R$ of minor isomer: 11.5 min.




**VWD: Signal A, 254 nm Results**

| Retention Time | Area | Area % | Height | Height % |
|---|---|---|---|---|
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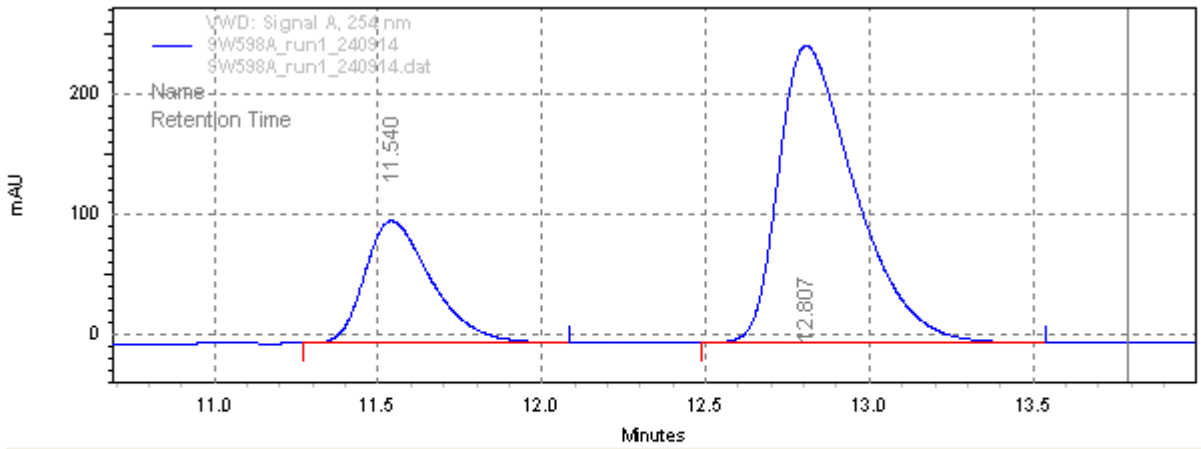
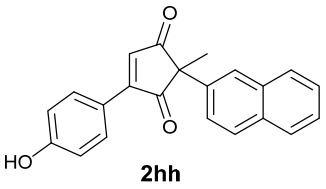
| 12.570 | 42333898 | 49.93 | 2791206 | 47.26 |




**VWD: Signal A, 254 nm Results**

| Retention Time | Area | Area % | Height | Height % |
|---|---|---|---|---|
| 11.540 | 24260799 | 26.32 | 1714583 | 29.15 |
| 12.807 | 67904196 | 73.68 | 4167749 | 70.85 |

**4-(4-Hydroxyphenyl)-2-methyl-2-(naphthalen-2-yl)cyclopent-4-ene-1,3-dione (2hh)**




**2hh**

Racemic procedure:

4-Hydroxyphenyl boronic acid **3h** (30.7 mg, 0.223 mmol, 2.2 equiv.) was added to dried glassware and dehydrated to the boroxine under vacuum with a heat gun, then an $N_2$ atmosphere was introduced. 2-Methyl-2-(naphthalen-2-yl)cyclopentane-1,3-dione **1h** (23.7 mg, 0.100 mmol, 1 equiv.), 1,10-phenanthroline **4** (1.2 mg, 6.6 μmol, 0.066 equiv.) and $Pd(OAc)_2$ (1.2 mg, 5.3 μmol, 0.053 equiv.) were added sequentially, with an $N_2$ environment being reintroduced after each addition. DMF (1 mL) was added and the reaction was left to stir at 70 °C under an $O_2$ atmosphere (balloon). After 20 h, additional portions of 1,10-phenanthroline **4** (1.2 mg, 6.6 μmol, 0.066 equiv.), $Pd(OAc)_2$ (1.2 mg, 5.3 μmol, 0.053 equiv.) and DMF (0.1 mL) were added and the reaction was left to stir for a further 48 h. On completion, 2:1 EtOAc:$Et_2O$ was added to the reaction solution before being washed with $H_2O$ and brine. The aqueous layer was extracted with 2:1 EtOAc:$Et_2O$ until the organic layer was colourless. The combined organic layers were washed with brine and dried over $MgSO_4$ and solvent was removed *via* reduced pressure. The resulting crude was purified by silica gel column chromatography (hexane/EtOAc 15:1→2:1) to yield 4-(4-hydroxyphenyl)-2-methyl-2-(naphthalen-2-yl)cyclopent-4-ene-1,3-dione **2hh** (28.3 mg, 0.086 mmol, 86%) as an orange solid.

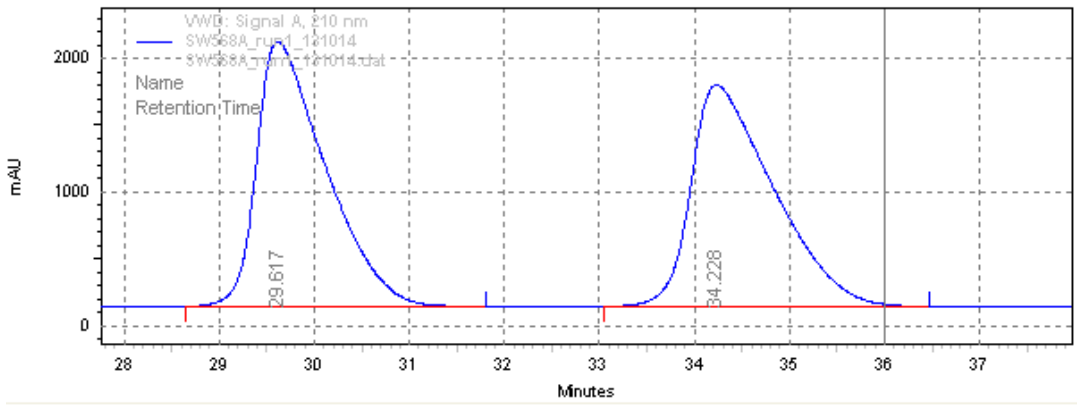
M.p. 159-161 °C; $R_f$ = 0.26 (1:1 hexane:EtOAc); $\nu_{max}/cm^{-1}$ 3380, 3052, 2984, 1733, 1683, 1605, 1568, 1580, 1510, 1434, 1236, 1179, 1102, 840, 816, 743; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.83 – 7.75 (m, 4H, Ar-H), 7.53 – 7.42 (m, 3H, Ar-H), 7.37 (s, 1H, alkene-H), 6.89 (d, *J* = 8.8 Hz, 2H, Ar-H), 6.38 (s, 1H, O<u>H</u>), 1.76 (s, 3H, $CH_3$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 204.6 (C), 203.9 (C), 159.4 (C), 155.8 (C), 137.8 (CH), 134.9 (C), 133.2 (C), 132.5 (C), 131.7 (CH), 128.7 (CH), 128.1 (CH), 127.5 (CH), 126.36 (CH), 126.34 (CH), 125.7 (CH), 124.1 (CH), 121.4 (C), 116.2 (CH), 56.4 (C), 19.8 ($CH_3$); HRMS (NSI) *m/z* calc. for $C_{22}H_{17}O_3$: 329.1172 $[M+H]^+$; found: 329.1175.

Enantioselective procedure:

(*S*)-4-(Tert-Butyl)-2-[4-(trifluoromethyl)pyridin-2-yl]-4,5-dihydrooxazole **6b** (3.0 mg, 11.0 μmol, 0.11 equiv.) was added to a dried flask, purged with $N_2$. DMA (0.4 mL), followed by $Pd(OAc)_2$ (2.4 mg, 10.7 μmol, 0.11 equiv.) were added and the solution was left to stir at room temperature for 1 h. 2-Methyl-2-(naphthalen-2-yl)cyclopent-4-ene-1,3-dione **1h** (23.7 mg, 0.1003 mmol, 1 equiv.), was added to the solution followed by DMA (0.6 mL) and 4-hydroxyphenyl boronic acid **3h** (29.2 mg, 0.244 mmol, 2.4 equiv.) which was freshly dehydrated under vacuum with a heat gun to form the boroxine. The reaction was left to stir at 50 °C for 95 h under an $O_2$ atmosphere (balloon) and with an air condenser. On completion, 2:1 EtOAc:$Et_2O$ was added to the reaction solution before being washed with $H_2O$ and brine. The aqueous layer was extracted with 2:1 EtOAc:$Et_2O$ until the organic layer was colourless. The combined organic layers were washed with brine and dried over $MgSO_4$ and solvent was removed *via* reduced pressure. The resulting crude was purified by silica gel column chromatography (hexane/EtOAc, 10:1→2:1) to yield (*S*)-4-(4-hydroxyphenyl)-2-methyl-2-(naphthalen-2-yl)cyclopent-4-ene-1,3-dione **2hh** (33.6 mg, 0.100 mmol, 100%) as a yellow solid (83:17 er).

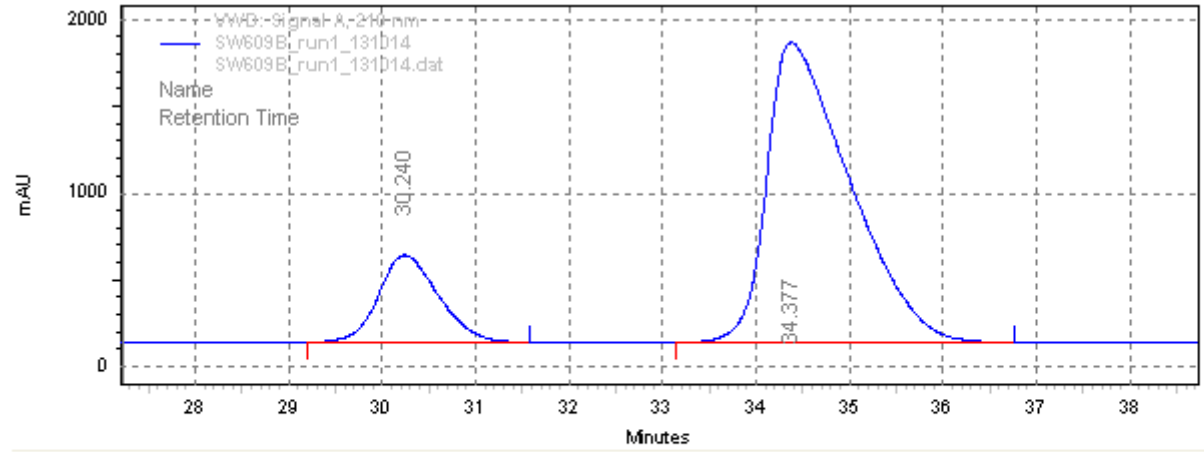
See racemic procedure above for characterisation.

$[\alpha]_D^{22}$ = +122.0 (*c* 1.00, $CHCl_3$); 83:17 er; HPLC (CHIRALPAK IA, hexane/2-propanol: 90/10, flow rate: 1.0 mL $min^{-1}$, detection UV 210 nm, 25 °C) $t_R$ of major isomer: 34.4 min, $t_R$ of minor isomer: 30.2 min.




**VWD: Signal A, 210 nm Results**

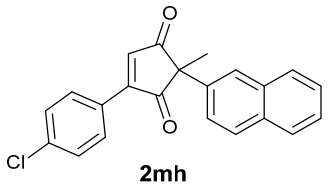
| Retention Time | Area | Area % | Height | Height % |
|---|---|---|---|---|
| 29.617 | 1676787643 | 50.00 | 33240353 | 54.46 |
| 34.228 | 1676497371 | 50.00 | 27794072 | 45.54 |




**VWD: Signal A, 210 nm Results**

| Retention Time | Area | Area % | Height | Height % |
|---|---|---|---|---|
| 30.240 | 375245307 | 17.34 | 8413332 | 22.49 |
| 34.377 | 1788967092 | 82.66 | 28987796 | 77.51 |

**4-(4-Chlorophenyl)-2-methyl-2-(naphthalen-2-yl)cyclopent-4-ene-1,3-dione (2mh)**




**2mh**

Racemic procedure:

4-Chlorophenyl boronic acid **3m** (34.6 mg, 0.221 mmol, 2.2 equiv.) was heated (heat gun) under vacuum in the reaction flask to convert it to the boroxine before an $N_2$ environment was introduced. 2-Methyl-2-(naphthalen-2-yl)cyclopent-4-ene-1,3-dione **1h** (23.8 mg, 0.101 mmol, 1 equiv.), 1,10-phenanthroline **4** (1.0 mg, 5.6 μmol, 0.06 equiv.) and $Pd(OAc)_2$ (1.1 mg, 4.9 μmol, 0.05 equiv.) were then added in order, with a $N_2$ environment being re-introduced after each addition. Anhydrous DMF (1 mL) was then added before the solution was stirred at 70 °C in an $O_2$ environment (balloon) for 72 h. On completion, diethyl ether and ethyl acetate were added to the reaction solution before being washed with water (10 mL) and brine (10 mL). The aqueous layer was washed with $Et_2O$ (5 mL) and EtOAc (2.5 mL) until the organic layer was colourless. The combined organic layers were washed with brine (15 mL) and dried with $MgSO_4$ before solvent was removed under reduced pressure. The crude was purified by silica-gel column chromatography (hexane/ethyl acetate 50:1), to yield 4-(4-chlorophenyl)-2-methyl-2-(naphthalen-2-yl)cyclopent-4-ene-1,3-dione **2mh** (27.7 mg, 0.0799 mmol, 79%) as a yellow solid.

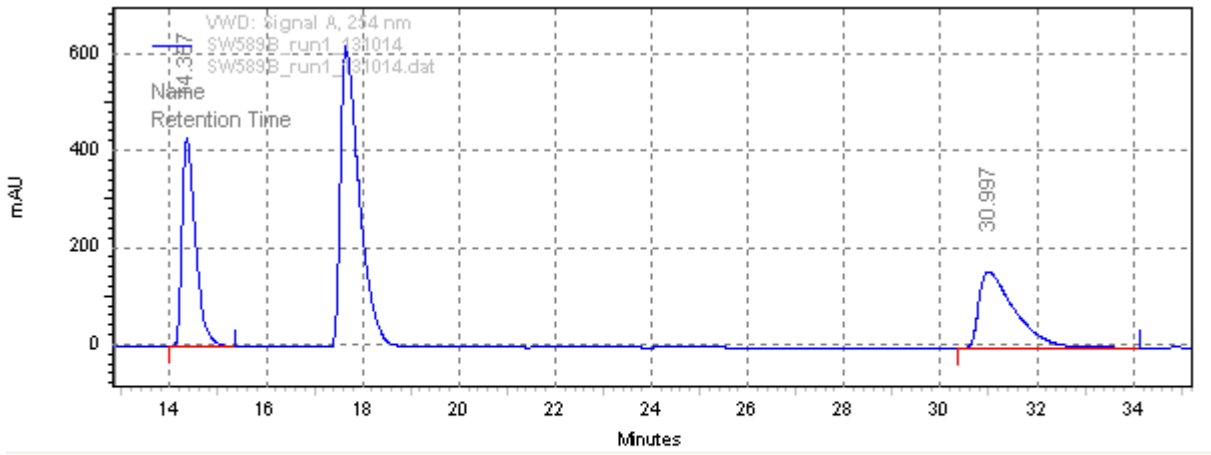
M. p. 130-135 °C; Yellow solid; $R_f$ = 0.87 (2:1 hexane:EtOAc); $\nu_{max}/cm^{-1}$ 3051, 1738, 1689, 1589, 1558, 1484, 1314, 1244, 1092, 1014, 826, 749; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.6 Hz, 2H, Ar-H), 7.86 – 7.73 (m, 4H, Ar-H), 7.56 – 7.39 (m, 6H, Ar-H and alkene-H), 1.75 (s, 3H, $CH_3$); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 203.8 (C), 203.1 (C), 154.9 (C), 140.3 (CH), 138.2 (C), 134.6 (C), 133.2 (C), 132.5 (C), 130.6 (CH), 129.4 (CH), 128.8 (CH), 128.1 (CH), 127.5 (CH), 127.4 (C), 126.4 (CH × 2), 125.6 (CH), 124.0 (CH), 56.3 (C), 20.1 ($CH_3$); HRMS (APCI) *m/z* calc. for $C_{22}H_{16}O_2Cl$: 347.0833 $[M+H]^+$; found: 347.0830.

Enantioselective procedure:

(*S*)-4-(Tert-Butyl)-2-[4-(trifluoromethyl)pyridin-2-yl]-4,5-dihydrooxazole **6b** (3.1 mg, 11.0 μmol, 0.11 equiv.) was added to a dried flask, purged with $N_2$. DMA (0.4 mL), followed by $Pd(OAc)_2$ (2.4 mg, 10.7 μmol, 0.11 equiv.) were added and the solution was left to stir at room temperature for 1 h. 2-Methyl-2-(naphthalen-2-yl)cyclopent-4-ene-1,3-dione **1h** (23.7 mg, 0.1003 mmol, 1 equiv.), was added to the solution followed by DMA (0.6 mL) and 4-chlorophenyl boronic acid **3m** (33.6 mg, 0.243 mmol, 2.4 equiv.) which was freshly dehydrated under vacuum with a heat gun to form the boroxine. The reaction was left to stir at 50 °C for 95 h under an $O_2$ atmosphere (balloon) and with an air condenser. On completion, 2:1 EtOAc:$Et_2O$ was added to the reaction solution before being washed with $H_2O$ and brine. The aqueous layer was extracted with 2:1 EtOAc:$Et_2O$ until the organic layer was colourless. The combined organic layers were washed with brine and dried over $MgSO_4$ and solvent was removed *via* reduced pressure. The resulting crude was purified by silica gel column chromatography (hexane/EtOAc 50:1) to yield (*S*)-4-(4-chlorophenyl)-2-methyl-2-(naphthalen-2-yl)cyclopent-4-ene-1,3-dione **2mh** (29.7 mg, 0.0856 mmol, 85%) as a yellow solid (94:6 er).

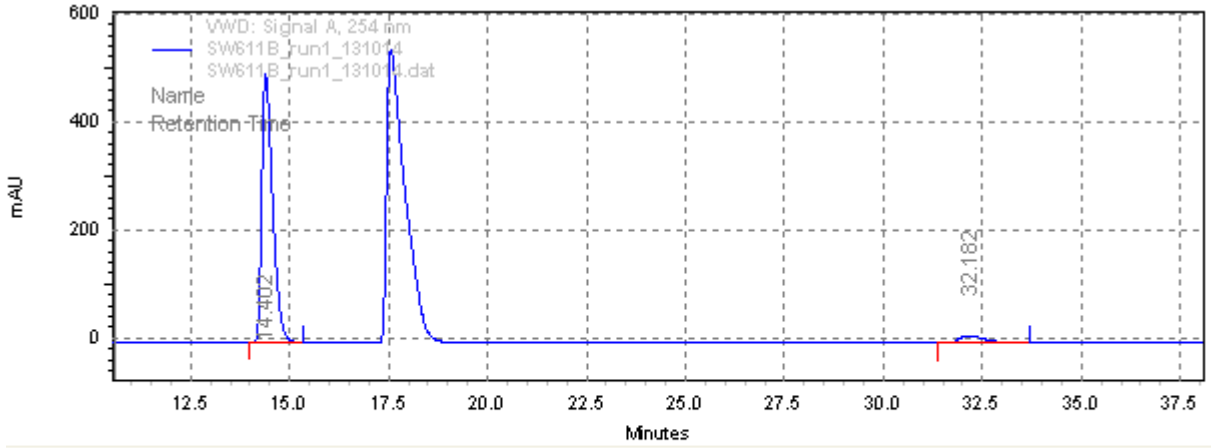
See racemic procedure for characterisation.

$[\alpha]_D^{23}$ = +56.8 (*c* 0.35, $CHCl_3$); 94:6 er; HPLC (CHIRALPAK IB, hexane/2-propanol: 99/1, flow rate: 1.0 mL $min^{-1}$, detection UV 254 nm, 25 °C) $t_R$ of major isomer: 14.4 min, $t_R$ of minor isomer: 32.2 min.




**VWD: Signal A, 254 nm Results**

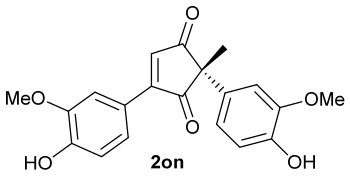
| Retention Time | Area | Area % | Height | Height % |
|---|---|---|---|---|
| 14.357 | 137807233 | 50.46 | 7240160 | 73.33 |
| 30.997 | 135267797 | 49.54 | 2633611 | 26.67 |




**VWD: Signal A, 254 nm Results**

| Retention Time | Area | Area % | Height | Height % |
|---|---|---|---|---|
| 14.402 | 157246667 | 93.98 | 8325327 | 97.41 |
| 32.182 | 10068139 | 6.02 | 221416 | 2.59 |

**2,4-Bis(4-hydroxy-3-methoxyphenyl)-2-methylcyclopent-4-ene-1,3-dione (2on)[1]**



**2on**

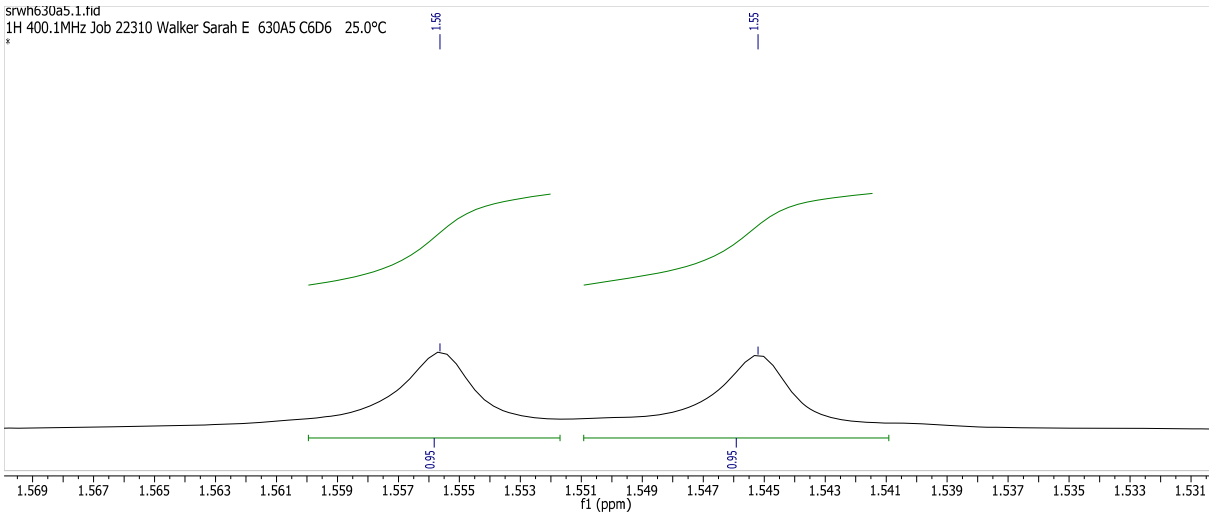
(*S*)-4-(Tert-Butyl)-2-[4-(trifluoromethyl)pyridin-2-yl]-4,5-dihydrooxazole **6b** (1.5 mg, 5.5 μmol, 0.055 equiv.) was added to a dried flask, purged with $N_2$. DMA (0.5 mL), followed by $Pd(OAc)_2$ (1.1 mg, 4.9 μmol, 0.049 equiv.) were added and the solution was left to stir at room temperature for 1 h. 2-(4-Hydroxy-3-methoxyphenyl)-2-methylcyclopent-4-ene-1,3-dione **1o** (23.2 mg, 0.0999 mmol, 1 equiv.), was added to the solution followed by DMA (0.5 mL) and 4-hydroxy-3-methoxyphenyl boronic acid pinacol ester **7n** (62.5 mg, 0.250 mmol, 2.5 equiv.) and the reaction was left to stir at 50 °C under an $O_2$ atmosphere (balloon) and with an air condenser. Additional portions of both (*S*)-4-(Tert-Butyl)-2-[4-(trifluoromethyl)pyridin-2-yl]-4,5-dihydrooxazole **6b** (1.5 mg, 5.5 μmol, 0.055 equiv.) and $Pd(OAc)_2$ (1.1 mg, 4.9 μmol, 0.049 equiv.) were added after 24 and 48 h. After a further 24 h, EtOAc was added to the reaction solution before being washed with $H_2O$ and brine. The aqueous layer was extracted with EtOAc until the organic layer was colourless. The combined organic layers were washed with brine and dried over $MgSO_4$ and solvent was removed *via* reduced pressure. The resulting crude was purified by silica gel column chromatography (hexane/EtOAc 2:1) to yield 2,4-bis(4-hydroxy-3-methoxyphenyl)-2-methylcyclopent-4-ene-1,3-dione [(+)-preussidone)] **2on** (28.1 mg, 0.0793 mmol, 79%) as a red oil (85:15 er).

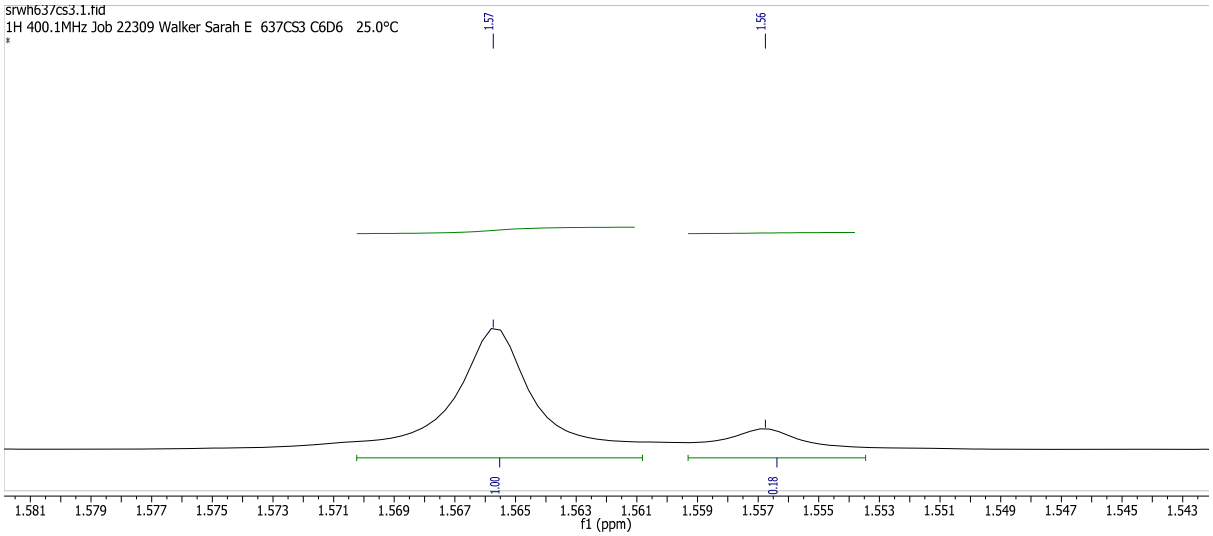
Red oil; $R_f$ = 0.27 (2:1 EtOAc:hexane); $\nu_{max}/cm^{-1}$ 3411, 2937, 1735, 1687, 1573, 1508, 1449, 1424, 1246, 1204, 1127, 1028, 908, 727; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.70 (d, *J* = 2.0 Hz, 1H, Ar-H), 7.59 (dd, *J* = 8.4, 2.0 Hz, 1H, Ar-H), 7.33 (s, 1H, alkene-H), 7.02 (d, *J* = 8.4 Hz, 1H, Ar-H), 6.90 (d, *J* = 2.0 Hz, 1H, Ar-H), 6.85 (d, *J* = 8.3 Hz, 1H, Ar-H), 6.80 (dd, *J* = 8.3, 2.0 Hz, 1H, Ar-H), 6.15 (s, 1H, O<u>H</u>), 5.65 (s, 1H, OH), 3.96 (s, 3H, $CH_3$), 3.87 (s, 3H, $CH_3$), 1.61 (s, 3H, $CH_3$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 204.8 (C), 203.4 (C), 155.2 (C), 149.3 (C), 146.67 (C), 146.65 (C), 145.2 (C), 137.8 (CH), 129.5 (C), 124.1 (CH), 121.3 (C), 119.5 (CH),

[1] $^1H$ and $^{13}C$ NMR spectra also obtained using acetone-$d_6$ as reference and data corresponds with literature data from Cichewicz *et al., J. Nat. Prod.,* 2012, **75**, 1819-1823. Spectra obtained using $CDCl_3$ and acetone-$d_6$ are included.

115.1 (CH), 114.4 (CH), 111.6 (CH), 109.1 (CH), 56.1 ($CH_3$), 55.9 ($CH_3$), 55.7 (C), 20.2 ($CH_3$); HRMS (APCI) *m/z* calc. for $C_{20}H_{19}O_6$: 355.1176 $[M+H]^+$ found: 355.1181.

$[\alpha]_D^{20}$ = +78.0 (*c* 1.00, $CHCl_3$); 85:15 er determined by high resolution $^1H$ NMR spectroscopy (400 MHz, $CDCl_3$) in the presence of 5.0 equivalents (*S*)-(+)-1-(9-anthryl)-2,2,2-trifluoroethanol.

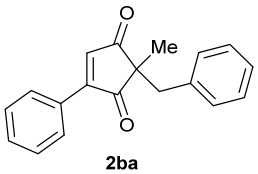


**Boronic acid screen**

Note that there are slightly different procedures for the following arylboronic acid/arylboroxine screen. The original procedure paid less attention to moisture-free conditions (e.g. procedure for **2fa**) as it was found to proceed well for selected arylboronic acids. For other arylboronic acids, a second slightly modified procedure pays more attention to keeping the reaction moisture-free (e.g. procedure for **2da**).

**2-Benzyl-2-methyl-4-phenylcyclopent-4-ene-1,3-dione (2ba)**



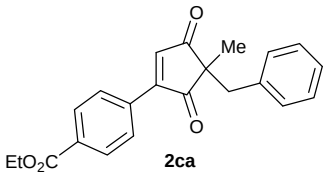

**2ba**

$Pd(OAc)_2$ (1.2 mg, 5.3 µmol, 0.05 equiv.) and 1,10-phenanthroline **4** (1.0 mg, 5.3 µmol, 0.05 equiv.) were stirred at room temperature for 45 min. 2-Benzyl-2-methylcyclopent-4-ene-1,3-dione **1a** (20.3 mg, 0.101 mmol, 1 equiv.) and phenyl boroxine **3b** (24.1 mg, 0.198 mmol, 2 equiv. based on equiv. of Ph) were added and washed in with DMF (0.8 mL). The solution was left to stir at 70 °C under an oxygen atmosphere (balloon) for 19 h. A second portion of $Pd(OAc)_2$ (1.2 mg, 5.3 µmol, 0.05 equiv.) and 1,10-phenanthroline **4** (1.0 mg, 5.3 µmol, 0.05 equiv.) were added and the reaction was allowed to continue stirring at 70 °C under an oxygen atmosphere for 24 h. On completion, hexane and ethyl acetate were added and the resulting solution was washed with brine (15 mL). The aqueous phase was washed twice with hexane (5 mL) and ethyl acetate (2.5 mL). The combined organic phase was washed with brine (10 mL), dried over sodium sulfate and the solvent removed under reduced pressure. The crude mixture was purified by flash column chromatography (petroleum ether/EtOAc 20:1, $R_f = 0.39$) to yield the target molecule **2ba** (19.0 mg, 68.7 µmol, 68%) as yellow crystals.

M.p. 91 - 93 °C; $R_f = 0.39$ (20:1 petroleum ether/EtOAc); $\nu_{max}/cm^{-1}$ 3062, 3028, 2920, 1739, 1692, 1599, 1588, 1570, 1493, 1449, 1374, 1329, 1304, 1286, 1251, 915, 792; $^1$H-NMR (300 MHz, $CDCl_3$) δ 7.69-7.66 (m, 2H, Ar-H), 7.44-7.37 (m, 3H, Ar-H), 7.14-7.07 (m, 3H, Ar-H), 7.04 (s, 1H, alkene=H), 6.99-6.96 (m, 2H, Ar-H), 3.06 (s, 2H, $CH_2$), 1.34 (s, 3H, $CH_3$); $^{13}$C-NMR (75 MHz, $CDCl_3$) δ 206.5 (C), 205.7 (C), 157.2 (C), 141.2 (CH), 135.9 (C), 131.5 (CH), 129.8 (CH), 129.1 (CH), 129.0 (C), 128.9 (CH), 128.4 (CH), 127.1 (CH),

54.0 (C), 41.6 ($CH_2$), 19.7 ($CH_3$); HRMS (APCI) *m/z calc*. for $C_{19}H_{17}O_2$: 277.1223 $[M+H]^+$; found: 277.1221.

**Ethyl 4-(4-benzyl-4-methyl-3,5-dioxocyclopent-1-en-1-yl)benzoate (2ca)**

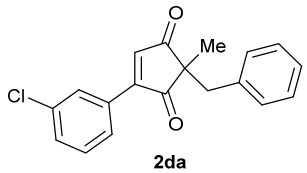


**2ca**

$Pd(OAc)_2$ (1.2 mg, 5.3 µmol, 0.05 equiv.) and 1,10-phenanthroline **4** (0.9 mg, 4.9 µmol, 0.05 equiv.) were stirred at room temperature for 30 min. 2-Benzyl-2-methylcyclopent-4-ene-1,3-dione **1a** (20.2 mg, 0.101 mmol, 1 equiv.) and 4-ethoxycarbonylphenyl boronic acid **3c** (39.2 mg, 0.203 mmol, 2 equiv., heated under vacuum with a heat gun to dehydrate to the arylboroxine) were added and washed in with DMF (0.8 mL). The solution was left to stir at 70 °C under an oxygen atmosphere (balloon) for 19 h. A second portion of $Pd(OAc)_2$ (1.2 mg, 5.3 µmol, 0.05 equiv.) and 1,10-phenanthroline **4** (1.0 mg, 5.3 µmol, 0.05 equiv.) were added and the reaction was allowed to continue stirring at 70 °C under an oxygen atmosphere for an additional 23 h. On completion, hexane and ethyl acetate were added and the resulting solution was washed with brine (15 mL). The aqueous phase was washed twice with hexane (5 mL) and ethyl acetate (2.5 mL). The combined organic phase was washed with brine (10 mL), dried over sodium sulfate and the solvent removed under reduced pressure. The crude was purified by flash column chromatography (petroleum ether/EtOAc 20:1) to yield the target molecule **2ca** (23.0 mg, 65.8 µmol, 65%) as yellow crystals.

M.p. 88 - 91 °C; $R_f = 0.33$ (10:1 petroleum ether/EtOAc); $\nu_{max}/cm^{-1}$ 3074, 2978, 2919, 1736, 1706, 1700, 1589, 1563, 1497, 1453, 1413, 1380, 1367, 1324, 1280, 1242, 1127, 1111, 1055, 1022, 867, 702; $^1H$ NMR (300 MHz, $CDCl_3$) δ 8.04 (d, 2H, $J = 8.4$ Hz, Ar-H), 7.70 (d, 2H, $J = 8.4$ Hz, Ar-H), 7.14-7.07 (m, 4H, Ar-H and alkene-H), 6.97-6.94 (m, 2H, Ar-H), 4.38 (q, 2H, $J = 7.0$ Hz, $OCH_2$), 3.07 (s, 2H, $CH_2$), 1.39 (t, 3H, $J = 7.0$ Hz, $CH_2C\underline{H}_3$), 1.34 (s, 3H, $CH_3$); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 206.0 (C), 205.5 (C), 165.8 (C), 156.2 (C), 142.4 (CH), 135.7 (C), 132.9 (C), 132.7 (C), 129.9 (CH), 129.7 (CH), 128.9 (CH), 128.5 (CH), 127.2 (CH), 61.5 ($CH_2$), 54.1 (C), 41.9 ($CH_2$), 19.5 ($CH_3$), 14.4 ($CH_3$); HRMS (ESI) *m/z calc*. for $C_{22}H_{21}O_4$: 349.1434 $[M+H]^+$; found: 349.1436.

**2-Benzyl-4-(3-chlorophenyl)-2-methylcyclopent-4-ene-1,3-dione (2da)**

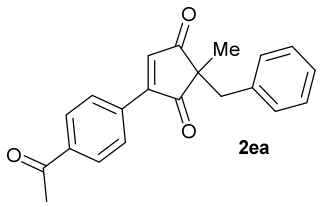


**2da**

3-Chlorophenyl boronic acid **3d** (34.2 mg, 0.219 mmol, 2.2 equiv.) was heated (heat gun) under vacuum in the reaction flask to convert it to the boroxine before an $N_2$ environment was introduced. 2-Benzyl-2-methylcyclopent-4-ene-1,3-dione **1a** (20.5 mg, 0.102 mmol, 1 equiv.), 1,10-phenanthroline **4** (1.0 mg, 5.3 μmol, 0.05 equiv.) and $Pd(OAc)_2$ (1.2 mg, 5.3 μmol, 0.05 equiv.) were then added in order, with a $N_2$ environment being re-introduced after each addition. Anhydrous DMF (1 mL) was then added before the solution was stirred at 70 °C in an $O_2$ environment (balloon) for 25 h. A second portion of $Pd(OAc)_2$ (1.2 mg, 5.3 μmol, 0.05 equiv.) and 1,10-phenanthroline (1.0 mg, 5.3 μmol, 0.05 equiv.) were added before the reaction was continued for a further 20 h. On completion, diethyl ether and ethyl acetate were added to the reaction solution before being washed with water (10 mL) and brine (10 mL). The aqueous layer was washed with $Et_2O$ (5 mL) and EtOAc (2.5 mL) until the organic layer was colourless. The combined organic layers were washed with brine (15 mL) and dried with $Na_2SO_4$ before solvent was removed under reduced pressure. The crude was purified by silica-gel column chromatography (petroleum ether/EtOAc 50:1), to yield 2-benzyl-4-(3-chlorophenyl)-2-methylcyclopent-4-ene-1,3-dione **2da** (19.0 mg, 61.1 μmol, 61%) as yellow crystals.

M.p. 108-109 °C; $R_f$ = 0.43 (30:1 petroleum ether/EtOAc); $\nu_{max}$/cm$^{-1}$ 3078, 3028, 2973, 2917, 1734, 1692, 1595, 1582, 1561, 1493, 1477, 1453, 1435, 1414, 1371, 1318, 1299, 1241, 1147, 1115, 1054, 892, 808, 795, 771, 725, 700; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.67 (t, 1H, *J* = 1.8 Hz, Ar-H), 7.54 (dt, 1H, *J* = 7.5, 1.5 Hz, Ar-H), 7.41 (ddd, 1H, *J* = 8.1, 1.8, 1.2 Hz, Ar-H), 7.36-7.31 (m, 1H, Ar-H), 7.16-7.08 (m, 3H, Ar-H), 7.03 (s, 1H, alkene-H), 6.97-6.94 (m, 2H, Ar-H), 3.06 (s, 2H, $CH_2$), 1.34 (s, 3H, $CH_3$); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 205.9 (C), 205.4 (C), 155.8 (C), 141.9 (CH), 135.8 (C), 135.0 (C), 131.4 (CH), 130.7 (C), 130.2 (CH), 129.7 (CH), 129.0 (CH), 128.5 (CH), 127.23 (CH), 127.16 (CH), 54.1 (C), 41.7 ($CH_2$), 19.6 ($CH_3$); HRMS (APCI) *m/z calc*. for $C_{19}H_{16}O_2Cl$: 311.0833 $[M+H]^+$; found: 311.0833.

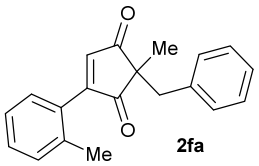
**4-(4-Acetylphenyl)-2-benzyl-2-methylcyclopent-4-ene-1,3-dione (2ea)**




4-Acetylphenyl boronic acid **3e** (36.3 mg, 0.221 mmol, 2.2 equiv.) was heated (heat gun) under vacuum to convert it to the boroxine before a $N_2$ environment was introduced. 2-Benzyl-2-methylcyclopent-4-ene-1,3-dione **1a** (19.9 mg, 0.0995 mmol, 1 equiv.), 1,10-phenanthroline **4** (1.2 mg, 6.7 μmol, 0.07 equiv.) and $Pd(OAc)_2$ (1.3 mg, 5.8 μmol, 0.06 equiv.) were added in order, with a $N_2$ environment being re-introduced after each addition. Anhydrous DMF (1 mL) was then added before the resulting solution was allowed to stir at 70 °C in an $O_2$ environment (balloon) for 24 h. The reaction was removed from the heat for further addition of 1,10-phenanthroline **4** (1.2 mg, 6.7 μmol, 0.07 equiv.) and $Pd(OAc)_2$ (1.3 mg, 5.8 μmol, 0.06 equiv.) and left to stir at 70 °C under an $O_2$ atmosphere for a further 17 h. On completion, 2:1 EtOAc:$Et_2O$ was added to the reaction solution before being washed with $H_2O$ and brine. The aqueous layer was extracted with 2:1 EtOAc:$Et_2O$ until the organic layer was colourless. The combined organic layers were washed with brine and dried over $MgSO_4$ and solvent was removed *via* reduced pressure. The resulting crude was purified by silica gel column chromatography (hexane:EtOAc, gradient 25:1 to 10:1) to yield **2ea** (17.3 mg, 53.4 μmol, 54%) as a yellow oil.

$R_f$ = 0.24 (1:1 hexane:EtOAc); $\nu_{max}$/cm$^{-1}$ 3084, 2921, 1737, 1689, 1593, 1555, 1454, 1356, 1262, 1237, 1017, 958, 837, 757, 701; $^1$H NMR (300 MHz, $CDCl_3$) δ 8.00 – 7.92 (m, 2H, Ar-H), 7.78 – 7.69 (m, 2H, Ar-H), 7.16 – 7.04 (m, 4H, Ar-H and =CH), 7.00 – 6.91 (m, 2H, Ar-H), 3.07 (s, 2H, $CH_2$), 2.61 (s, 3H, $CH_3$), 1.35 (s, 3H, $CH_3$); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 205.9 (C), 205.3 (C), 197.2 (C), 155.9 (C), 142.3 (CH), 138.6 (C), 135.6 (C), 133.0 (C), 129.6 (CH), 129.1 (CH), 128.5 (CH), 128.4 (CH), 127.1 (CH), 54.0 (C), 41.7 ($CH_2$), 26.7 ($CH_3$), 19.3 ($CH_3$); HRMS (NSI) *m/z calc*. for $C_{21}H_{19}O_3$: 319.1329 $[M+H]^+$; found: 319.1333.

**2-Benzyl-2-methyl-4-(*o*-tolyl)cyclopent-4-ene-1,3-dione (2fa)**

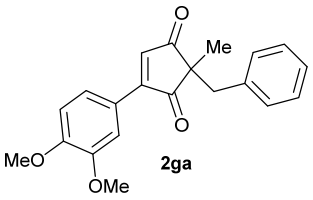


**2fa**

$Pd(OAc)_2$ (1.2 mg, 5.3 µmol, 0.05 equiv.) and 1,10-phenanthroline **4** (1.0 mg, 5.3 µmol, 0.06 eq) were stirred at room temperature for 30 min. 2-Benzyl-2-methylcyclopent-4-ene-1,3-dione **1a** (20.4 mg, 0.102 mmol, 1 equiv.) and *o*-tolyl boronic acid **3f** (27.6 mg, 0.203 mmol, 2 equiv.) were added and washed in with DMF (0.8 mL). The solution was left to stir at 70 °C under an oxygen atmosphere for 27 h. A second portion of $Pd(OAc)_2$ (1.2 mg, 5.3 µmol, 0.05 equiv.) and 1,10-phenanthroline **4** (1.0 mg, 5.3 µmol, 0.05 equiv.) were added and washed in with DMF (0.3 mL). The solution was left to stir at 70 °C under an oxygen atmosphere (balloon) for 22 h. On completion, hexane and ethyl acetate were added and the resulting solution was washed with brine (15 mL). The aqueous phase was washed twice with hexane (5 mL) and ethyl acetate (2.5 mL). The combined organic phase was washed with brine (10 mL), dried over sodium sulfate and the solvent removed under reduced pressure. The residue was purified by flash column chromatography (petroleum ether/EtOAc 20:1) to yield the target molecule **2fa** (18.9 mg, 65.1 µmol, 64%) as yellow oil.

$R_f = 0.51$ (10:1 petroleum ether/EtOAc); $\nu_{max}/cm^{-1}$ 3064, 3030, 2967, 2928, 1746, 1696, 1605, 1586, 1496, 1451, 1373, 1329, 1303, 1237, 1203, 1120, 1071, 1055, 1042, 1031, 902, 859, 790, 750, 726, 700; H NMR (300 MHz, $CDCl_3$) δ 7.32-7.27 (m, 1H, Ar-H), 7.22-7.13 (m, 5H, Ar-H), 6.99-6.96 (m, 3H, Ar-H), 6.88 (s, 1H, =CH), 3.10 (d, 1H, $J$ = 13.2 Hz, C<u>H</u>HBn), 3.05 (d, 1H, $J$ = 13.2 Hz, CH<u>H</u>Bn), 1.90 (s, 3H, $CH_3$), 1.36 (s, 3H, $CH_3$); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 206.4 (C), 206.12 (C), 160.1 (C), 145.9 (CH), 136.6 (C), 135.9 (C), 130.9 (CH), 130.2 (CH), 129.9 (CH), 129.4 (CH), 128.8 (C), 128.5 (CH), 127.2 (CH), 125.8 (CH), 52.9 (C), 41.6 ($CH_2$), 20.3 ($CH_3$), 19.8 ($CH_3$); HRMS (APCI) *m/z calc*. for $C_{20}H_{19}O_2$: 291.1380 $[M+H]^+$; found: 291.1377.

**2-Benzyl-4-(3,4-dimethoxyphenyl)-2-methylcyclopent-4-ene-1,3-dione (2ga)**

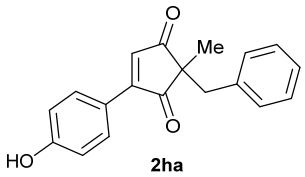


**2ga**

Reaction vessels were flame dried and the DMF freshly distilled over 4 Å molecular sieves using short path distillation apparatus. $Pd(OAc)_2$ (1.2 mg, 5.3 µmol, 0.05 equiv.) and 1,10-phenanthroline **4** (1.0 mg, 5.3 µmol, 0.05 equiv.) were stirred at room temperature for 30 min. 2-Benzyl-2-methylcyclopent-4-ene-1,3-dione **1a** (20.2 mg, 0.101 mmol, 1 equiv.) and 3,4-dimethoxyphenyl boroxine **3g** (36.8 mg, 0.202 mmol, 2 equiv., heated under vacuum with heat gun to dehydrate to the boroxine) were added and washed in with DMF (0.8 mL). The solution was left to stir at 70 °C under an oxygen atmosphere (balloon) for 20 h. A second portion of $Pd(OAc)_2$ (1.2 mg, 5.3 µmol, 0.05 equiv.) and 1,10-phenanthroline **4** (1.0 mg, 5.3 µmol, 0.05 equiv.) were added. The solution was left to stir at 70 °C under an oxygen atmosphere for a further 21 h. Upon completion, hexane and ethyl acetate were added and the resulting solution was washed with brine (15 mL). The aqueous phase was washed twice with diethyl ether (5 mL) and ethyl acetate (2.5 mL). The combined organic phase was washed with brine (10 mL), dried over sodium sulfate and the solvent removed under reduced pressure. The residue was purified by flash column chromatography (petroleum ether/EtOAc 5:1 → 2:1, $R_f = 0.62$) to yield the target molecule **2ga** (30.3 mg, 90.2 µmol, 89%) as yellow crystals.

M.p. 103 - 105 °C; $R_f = 0.62$ (5:1 petroleum ether/EtOAc); $\nu_{max}/cm^{-1}$ 3078, 2930, 2835, 1732, 1682, 1597, 1588, 1567, 1507, 1464, 1454, 1440, 1423, 1378, 1334, 1288, 1247, 1217, 1190, 1141, 1116, 1058, 1021, 867, 814, 763, 750, 719, 701; $^1$H-NMR (300 MHz, $CDCl_3$) δ 7.43 (dd, 1H, *J* = 8.7, 2.1 Hz, Ar-H), 7.31 (d, 1H, *J* = 2.1 Hz, Ar-H), 7.14-7.07 (m, 3H, Ar-H), 6.99-6.96 (m, 3H, Ar-H + =CH), 6.87 (d, 1H, *J* = 8.7 Hz, Ar-H), 3.91 (s, 3H, $OCH_3$), 3.90 (s, 3H, $OCH_3$), 3.04 (s, 2H, $CH_2$), 1.32 (s, 3H, $CH_3$); $^{13}$C-NMR (75 MHz, $CDCl_3$) δ 207.1 (C), 205.4 (C), 156.1 (C), 152.1 (C), 149.1 (C), 139.0 (CH), 136.0 (C), 129.8 (CH), 128.4 (CH), 127.0 (CH), 123.4 (CH), 121.8 (C), 111.6 (CH), 111.2 (CH), 56.12 ($CH_3$), 56.10 ($CH_3$), 54.2 (C), 41.6 ($CH_2$), 19.9 ($CH_3$); HRMS (APCI) *m/z calc*. for $C_{21}H_{21}O_4$: 337.1434 $[M+H]^+$; found: 337.1433.

**2-Benzyl-4-(4-hydroxyphenyl)-2-methylcyclopent-4-ene-1,3-dione (2ha)**

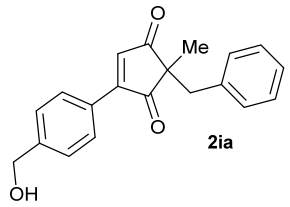


**2ha**

4-Hydroxyphenyl boronic acid **3h** (27.5 mg, 0.227 mmol, 2.3 equiv.) was heated (heat gun) under vacuum to convert it to the boroxine before a $N_2$ environment was introduced. 2-Benzyl-2-methylcyclopent-4-ene-1,3-dione **1a** (20.4 mg, 0.102 mmol, 1 equiv.), 1,10-phenanthroline **4** (1.0 mg, 5.3 μmol, 0.05 equiv.) and $Pd(OAc)_2$ (1.2 mg, 5.3 μmol, 0.05 equiv.) were added in order, with a $N_2$ environment being re-introduced after each addition. Anhydrous DMF (1 mL) was then added before the resulting solution was allowed to stir at 70 °C in an $O_2$ environment (balloon) for 67 h. On completion, diethyl ether and ethyl acetate were added to the reaction solution before being washed with water (10 mL) and brine (10 mL). The aqueous layer was washed with $Et_2O$ (5 mL) and EtOAc (2.5 mL) until the organic layer was colourless. The combined organic layers were washed with brine (15 mL) and dried with $Na_2SO_4$ before solvent was removed under reduced pressure. The crude was purified by flash column chromatography (petroleum ether/ethyl acetate 5:1) to yield 2-benzyl-4-(4-hydroxyphenyl)-2-methylcyclopent-4-ene-1,3-dione **2ha** (17.3 mg, 59.2 μmol, 69%) as yellow crystals.

M,p. 133-135 °C; $R_f$ = 0.29 (3:1, petroleum ether, EtOAc); $\nu_{max}$/cm$^{-1}$ 3270, 2929, 1738, 1679, 1604, 1585, 1569, 1508, 1451, 1370, 1321, 1284, 1203, 1174, 1110, 1072, 1050, 1029, 910, 861, 840, 754, 731, 700; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.14-7.05 (m, 3H, Ar-H), 6.98-6.95 (m, 3H, Ar-H and alkene-H), 6.87 (d, *J* = 8.8 Hz, 2H, Ar-H), 5.96 (br s, 1H, OH), 3.05 (s, 2H, $CH_2$), 1.33 (s, 3H. $CH_3$); $^{13}$ C NMR (75.5MHz, $CDCl_3$) δ 207.1 (C), 206.1 (C), 159.0 (C), 156.4 (C), 138.7 (CH), 135.9 (C), 131.4 (CH), 129.8 (CH), 128.4 (CH), 127.1 (CH), 121.6 (C), 116.0 (CH), 54.1 (C), 41.6 ($CH_2$), 19.8 ($CH_3$); HRMS (APCI) *m/z calc*. for $C_{19}H_{17}O_3$: 293.1172 $[M+H]^+$; found: 293.1175.

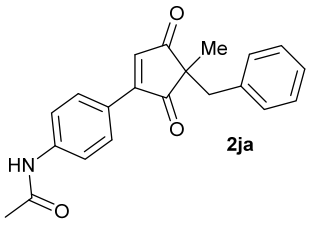
**2-Benzyl-4-(4-(hydroxymethyl)phenyl)-2-methylcyclopent-4-ene-1,3-dione (2ia)**




4-Hydroxymethylphenyl boronic acid **3i** (33.3 mg, 0.219 mmol, 2.2 equiv.) was heated (heat gun) under vacuum to convert it to the boroxine before a $N_2$ environment was introduced. 2-Benzyl-2-methylcyclopent-4-ene-1,3-dione **1a** (20.3 mg, 0.101 mmol, 1 equiv.), 1,10-phenanthroline **4** (1.2 mg, 6.7 μmol, 0.07 equiv.) and $Pd(OAc)_2$ (1.3 mg, 5.8 μmol, 0.06 equiv.) were added in order, with a $N_2$ environment being re-introduced after each addition. Anhydrous DMF (1 mL) was then added before the resulting solution was allowed to stir at 70 °C in an $O_2$ environment (balloon). Additional portions of 1,10-phenanthroline **4** (1.2 mg, 6.7 μmol, 0.07 equiv.) and $Pd(OAc)_2$ (1.2 mg, 5.3 μmol, 0.053 equiv.) were added after 18 h, 21 h and 24 h and the reaction was left to stir at 70 °C under an $O_2$ atmosphere for a further 16 h. On completion, 2:1 EtOAc:$Et_2O$ was added to the reaction solution before being washed with $H_2O$ and brine. The aqueous layer was extracted with 2:1 EtOAc:$Et_2O$ until the organic layer was colourless. The combined organic layers were washed with brine and dried over $MgSO_4$ and solvent was removed *via* reduced pressure. The resulting crude was purified by silica gel column chromatography (hexane:EtOAc, 1:1) to yield **2ia** (23.5 mg, 76.7 μmol, 76%) as a yellow oil.

$R_f$ = 0.44 (1:1 hexane:EtOAc); $\nu_{max}/cm^{-1}$ 3415, 3029, 2926, 1739, 1691, 1604, 1585, 1562, 1451, 1205, 1047, 828, 753, 701; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.72 – 7.63 (m, 2H, Ar-H), 7.46 – 7.34 (m, 2H, Ar-H), 7.14 – 7.05 (m, 3H, Ar-H), 7.02 (s, 1H, =CH), 7.00 – 6.91 (m, 2H, Ar-H), 4.72 (s, 2H, $CH_2$), 3.05 (s, 2H, $CH_2$), 1.33 (s, 3H, $CH_3$); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 206.4 (C), 205.6 (C), 156.7 (C), 144.4 (C), 140.8 (CH), 135.7 (C), 129.6 (CH), 129.2 (CH), 128.3 (CH), 128.1 (C), 126.96 (CH), 126.95 (CH), 64.7 ($CH_2$), 53.9 (C), 41.6 ($CH_2$), 19.5 ($CH_3$); HRMS (NSI) *m/z calc*. for $C_{20}H_{19}O_3$: 307.1329 $[M+H]^+$; found: 307.1332.

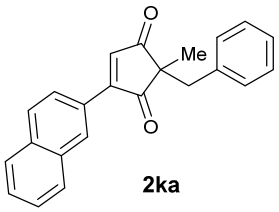
***N*-(4-(4-benzyl-4-methyl-3,5-dioxocyclopent-1-en-1-yl)phenyl)acetamide (2ja)**




4-Acetamidophenyl boronic acid **3j** (39.4 mg, 0.220 mmol, 2.2 equiv.) was heated (heat gun) under vacuum to convert it to the boroxine before a $N_2$ environment was introduced. 2-Benzyl-2-methylcyclopent-4-ene-1,3-dione **1a** 20.1 mg, 0.100 mmol, 1 equiv.), 1,10-phenanthroline **4** (1.2 mg, 6.7 μmol, 0.07 equiv.) and $Pd(OAc)_2$ (1.3 mg, 5.8 μmol, 0.06 equiv.) were added in order, with a $N_2$ environment being re-introduced after each addition. Anhydrous DMF (1 mL) was then added before the resulting solution was allowed to stir at 70 °C in an $O_2$ environment (balloon) for 28 h. The reaction was removed from the heat for further addition of 1,10-phenanthroline **4** (1.2 mg, 6.7 μmol, 0.07 equiv.) and $Pd(OAc)_2$ (1.3 mg, 5.8 μmol, 0.058 equiv.) and left to stir at 70 °C under an $O_2$ atmosphere for a further 17 h. On completion, 2:1 EtOAc:$Et_2O$ was added to the reaction solution before being washed with $H_2O$ and brine. The aqueous layer was extracted with 2:1 EtOAc:$Et_2O$ until the organic layer was colourless. The combined organic layers were washed with brine and dried over $MgSO_4$ and solvent was removed *via* reduced pressure. The resulting crude was purified by silica gel column chromatography (hexane:EtOAc, gradient 5:1 to 1:3) to yield **2ja** (28.3 mg, 84.8 μmol, 84%) as a yellow oil.

$R_f$ = 0.31 (1:1 hexane:EtOAc); $\nu_{max}/cm^{-1}$ 3307, 2964, 1739, 1688, 1662, 1592, 1507, 1452, 1410, 1317, 1258, 1184, 1051, 844, 753, 700; H NMR (300 MHz, $CDCl_3$) δ 7.81 – 7.63 (m, 3H, Ar-H and NH), 7.62 – 7.51 (m, 2H, Ar-H), 7.17 – 7.02 (m, 3H, Ar-H), 6.99 (s, 1H, =CH), 6.98 – 6.87 (m, 2H, Ar-H), 3.04 (s, 2H, $CH_2Ph$), 2.18 (s, 3H, $CH_3$), 1.32 (s, 3H, $CH_3$); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 206.7 (C), 205.5 (C), 168.6 (C), 155.8 (C), 140.8 (C), 139.6 (CH), 135.7 (C), 130.1 (CH), 129.6 (CH), 128.2 (CH), 126.3 (CH), 124.4 (C), 119.4 (CH), 53.9 (C), 41.5 ($CH_2$), 24.7 ($CH_3$), 19.5 ($CH_3$); HRMS (NSI) *m/z calc*. for $C_{21}H_{20}NO_3$: 334.1438 $[M+H]^+$; found: 334.1442.

**2-Benzyl-2-methyl-4-(naphthalen-2-yl)cyclopent-4-ene-1,3-dione (2ka)**

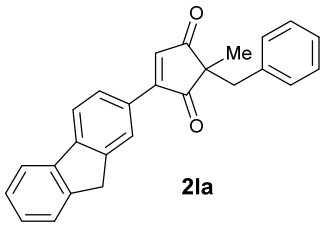



**2ka**

2-Naphthaleneboronic acid **3k** (44.0 mg, 0.24 mmol, 2.4 equiv.) was added to dried glassware and dehydrated to the boroxine under vacuum with a heat gun, then an $N_2$ atmosphere was introduced. 2-Benzyl-2-methylcyclopent-4-ene-1,3-dione **1a** (20.1 mg, 0.1 mmol, 1 equiv.), 1,10-phenanthroline **4** (1.1 mg, 6.1 μmol, 0.06 equiv.) and $Pd(OAc)_2$ (1.2 mg, 5.5 μmol, 0.055 equiv.) were added sequentially, with an $N_2$ environment being reintroduced after each addition. DMF (1 mL) was added, the reaction was left to stir at 70 °C for 28 h under an $O_2$ atmosphere (balloon). The reaction was removed from the heat for further addition of 1,10-phenanthroline **4** (1.1 mg, 6.1 μmol, 0.06 equiv.) and $Pd(OAc)_2$ (1.2 mg, 5.5 μmol, 0.055 equiv.) and left to stir at 70 °C under an $O_2$ atmosphere for a further 17 h. On completion, 2:1 EtOAc:$Et_2O$ was added to the reaction solution before being washed with $H_2O$ and brine. The aqueous layer was extracted with 2:1 EtOAc:$Et_2O$ until the organic layer was colourless. The combined organic layers were washed with brine and dried over $Na_2SO_4$ and solvent was removed *via* reduced pressure. The resulting crude was purified by silica gel column chromatography (petrol ether:EtOAc, gradient 15:1 to 10:1) to yield 2-benzyl-2-methyl-4-(naphthalen-2-yl)cyclopent-4-ene-1,3-dione **2ka** (32.6 mg, 0.066 mmol, 66%) as a yellow crystalline solid.

M.p. 126 – 128 °C; $R_f$ = 0.4 (5:1 petrol ether:EtOAc); $\nu_{max}/cm^{-1}$ 3059, 2917, 1736, 1687, 1560, 1581, 1564, 1454, 1370, 1560, 1247, 1143, 900, 867, 823, 750, 699; $^1$H NMR (300 MHz, $CDCl_3$) δ 8.51 – 8.47 (m, 1H, Ar-H), 7.97 – 7.90 (m, 1H, Ar-H), 7.86 – 7.79 (m, 2H, Ar-H), 7.63 – 7.50 (m, 3H, Ar-H), 7.18 (s, 1H, C=CH), 7.15 – 6.97 (m, 5H, Ar-H), 3.12 (d, *J* = 12.9 Hz, 1H, C<u>H</u>HPh), 3.07 (d, *J* = 12.9 Hz, 1H, CH<u>H</u>Ph), 1.38 (s, 3H, $CH_3$); $^{13}$C NMR (300 MHz, $CDCl_3$) δ 206.7 (C), 205.5 (C), 156.5 (C), 140.9 (CH), 135.8 (C), 134.4 (C), 132.9 (C), 130.5 (CH), 129.7 (CH), 129.4 (CH), 128.6 (CH), 128.3 (CH), 128.1 (CH), 127.7 (CH), 127.0 (CH), 126.8 (CH), 126.2 (C), 124.9 (CH), 54.1 (C), 41.6 ($CH_2$), 19.7 ($CH_3$); HRMS (NSI) *m/z* calc. for $C_{23}H_{19}O_2$: 327.1380 $[M+H]^+$; found: 327.1383.

**2-Benzyl-4-(2-fluorenyl)-2-methylcyclopentene-1,3-dione (2la)**

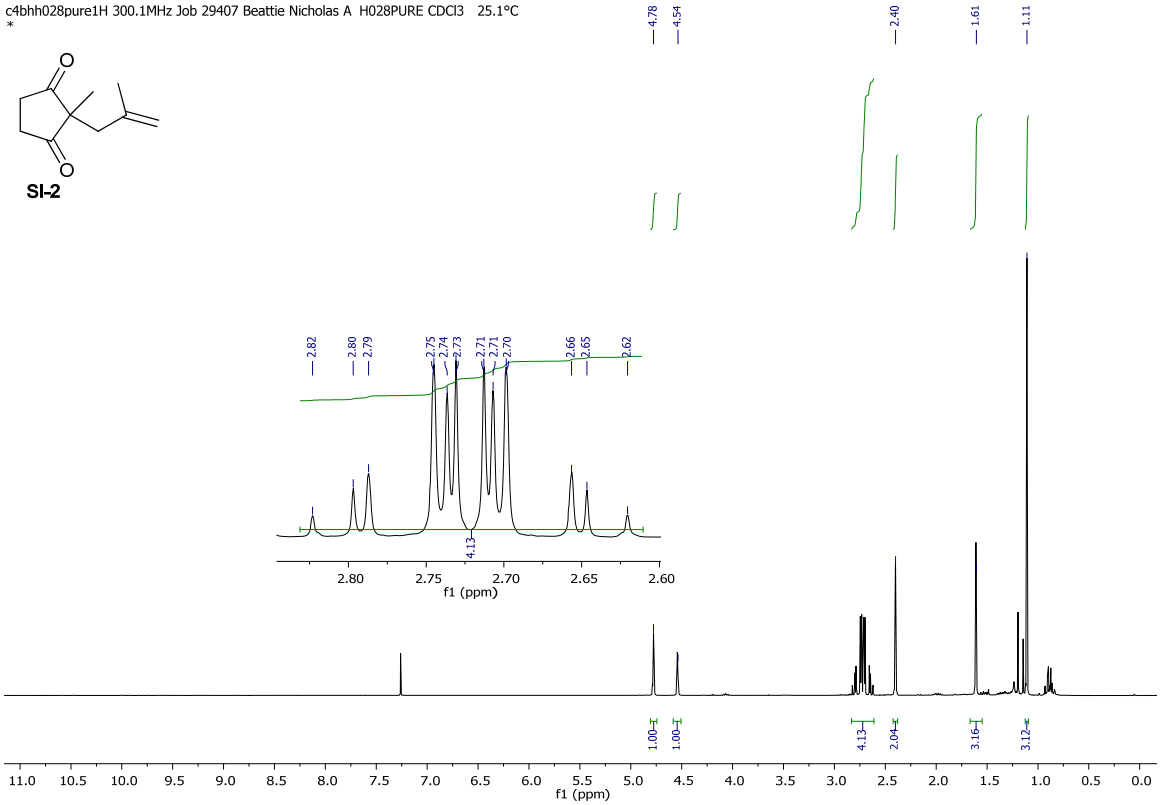


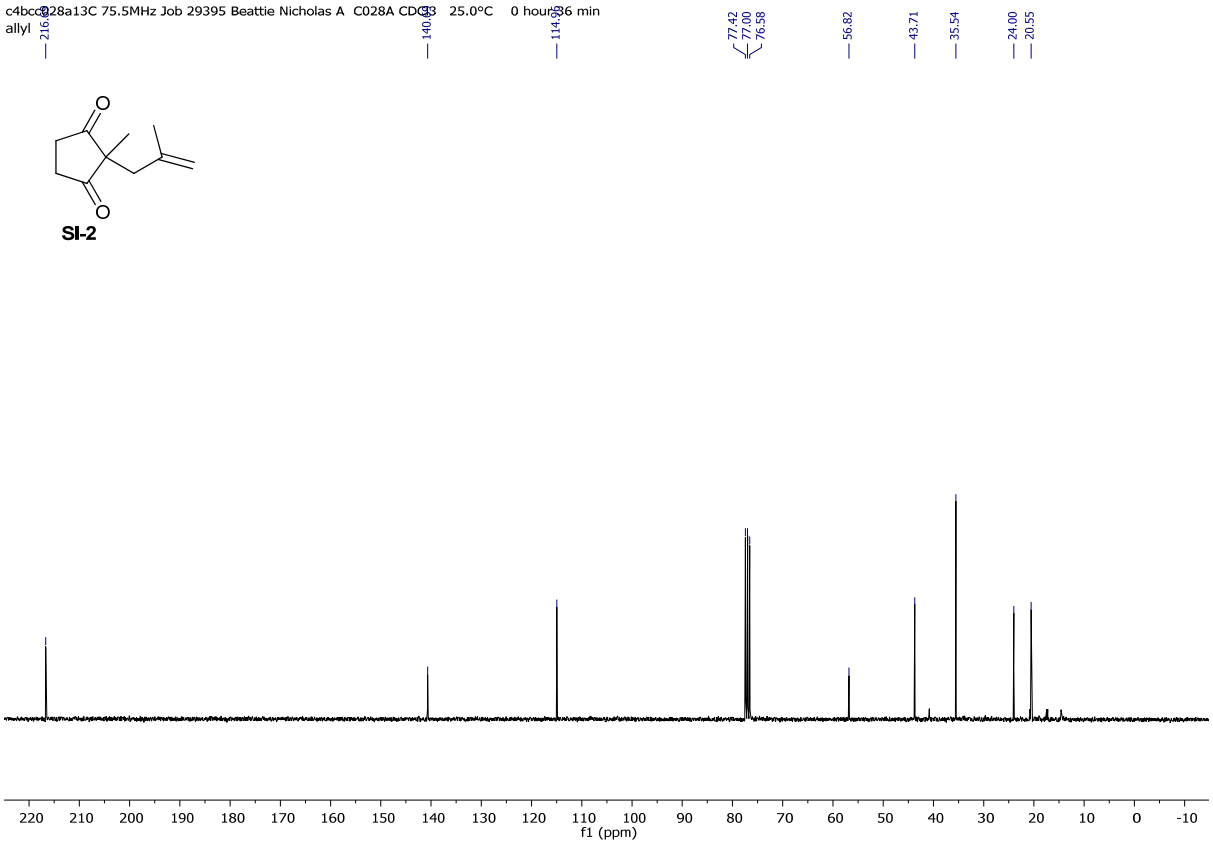

**2la**

2-Fluoreneboronic acid **3l** (50.6 mg, 0.24 mmol, 2.4 equiv.) was added to dried glassware and dehydrated to the boroxine under vacuum with a heat gun, then an $N_2$ atmosphere was introduced. 2-Benzyl-2-methylcyclopent-4-ene-1,3-dione **1a** (20.1 mg, 0.1 mmol, 1 equiv.), 1,10-phenanthroline **4** (1.1 mg, 6.1 μmol, 0.06 equiv.) and $Pd(OAc)_2$ (1.3 mg, 5.7 μmol, 0.06 equiv.) were added sequentially, with an $N_2$ environment being reintroduced after each addition. DMF (1 mL) was added, the reaction was left to stir at 70 °C for 23 h under an $O_2$ atmosphere (balloon). The reaction was removed from the heat for further addition of 1,10-phenanthroline **4** (1.1 mg, 6.1 μmol, 0.06 equiv.) and $Pd(OAc)_2$ (1.2 mg, 5.5 μmol, 0.055 equiv.) and DMF (0.2 mL) and left to stir at 70 °C under an $O_2$ atmosphere for a further 24 h. On completion, 2:1 EtOAc:$Et_2O$ was added to the reaction solution before being washed with $H_2O$ and brine. The aqueous layer was extracted with 2:1 EtOAc:$Et_2O$ until the organic layer was colourless. The combined organic layers were washed with brine and dried over $Na_2SO_4$ and solvent was removed *via* reduced pressure. The resulting crude was purified by silica gel column chromatography (petrol ether:EtOAc, gradient 20:1 to 15:1) to yield 2-benzyl-2-methyl-4-fluorenecyclopent-4-ene-1,3-dione **2la** (26.1 mg, 0.072 mmol, 72%) as a yellow crystalline solid.

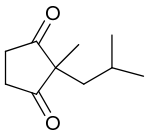
M.p. 156 – 158 °C; $R_f$ = 0.7 (5:1 petrol ether:EtOAc); $\nu_{max}/cm^{-1}$ 3080, 2972, 2920, 1730, 1688, 1609, 1583, 1453, 1323, 1233, 1223, 1100, 1058, 840, 757, 757, 735; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.97-7.95 (m, 1H, Ar-H), 7.84 – 7.71 (m, 3H, Ar-H), 7.60 – 7.54 (m, 1H, Ar-H), 7.45 – 7.31 (m, 2H, Ar-H), 7.17 – 7.03 (m, 4H, Ar-H + C=CH), 7.03 – 6.98 (m, 2H, Ar-H), 3.94 (s, 2H, $CH_2$), 3.11 (d, *J* = 13.8 Hz, 1H, C<u>H</u>HPh), 3.06 (d, *J* = 13.8 Hz, 1H, CH<u>H</u>Ph), 1.36 (s, 3H, $CH_3$); $^{13}$C NMR (300 MHz, $CDCl_3$) δ 206.8 (C), 205.5 (C), 157.0 (C), 145.0 (C), 144.1 (C), 143.5 (C), 140.6 (C), 140.1 (CH), 135.9 (C), 129.7 (CH), 128.3 (CH), 128.1 (CH), 128.0 (CH), 127.2 (C), 127.1 (CH), 126.9 (CH), 125.7 (CH), 125.2 (CH), 120.7 (CH), 120.1 (CH), 54.1 (C), 41.5 ($CH_2$), 36.9 ($CH_2$), 19.7 ($CH_3$); HRMS (NSI) *m/z* calc. for $C_{26}H_{21}O_2$: 365.1536 $[M+H]^+$; found: 365.1539.

# $^{1}$H-NMR and $^{13}$C-NMR Spectra of Synthesised Compounds



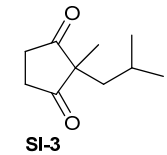
c4bhc34a1H 400.1MHz Job 20145 Beattie Nicholas A C34A CDCl3 21.9°C
*



SI-3

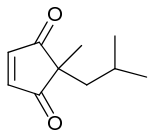



c4bcc34a13C 100.6MHz Job 20148 Beattie Nicholas A C34A CDCl3 25.9°C 0 hour 14 min
*



SI-3

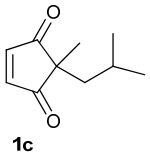
c4bhh035a1H 300.1MHz Job 29771 Beattie Nicholas A H035A CDCl3 25.1°C
hydroged allyl SM



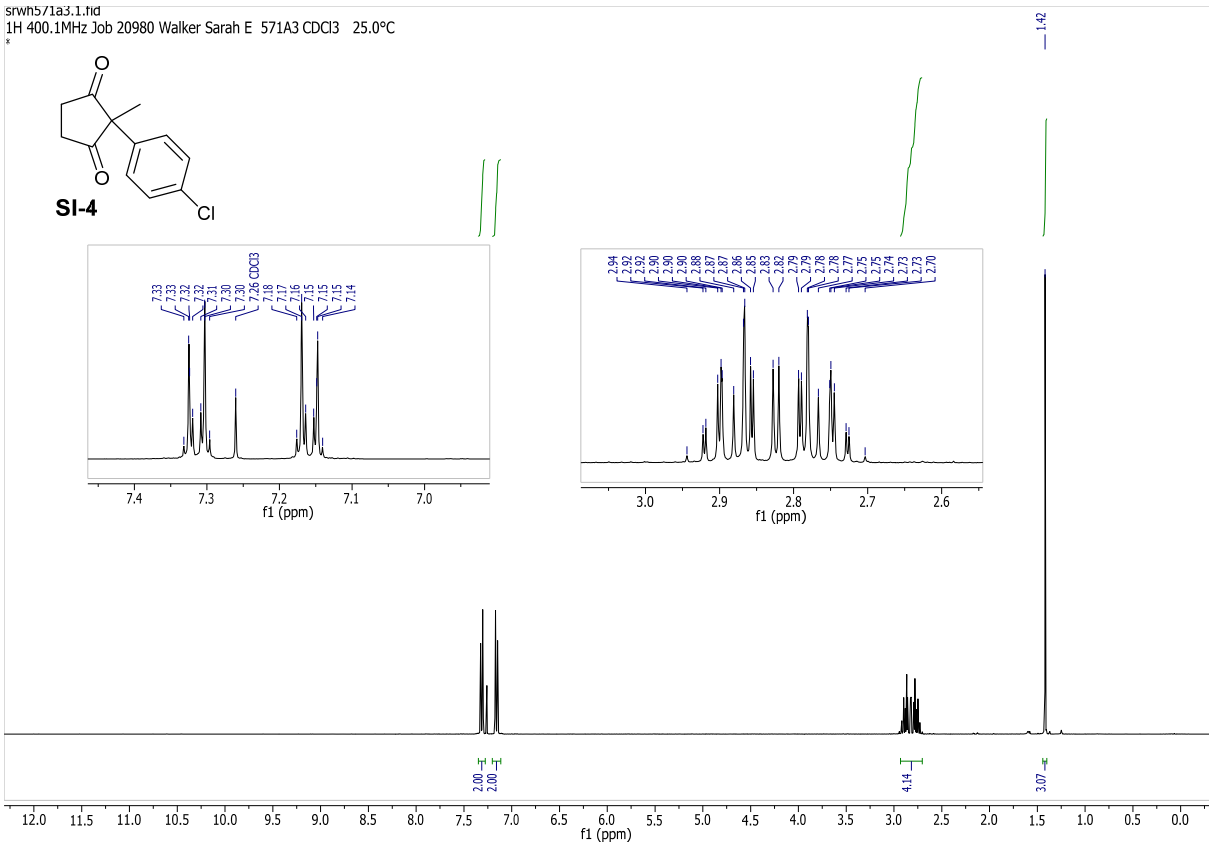
1c

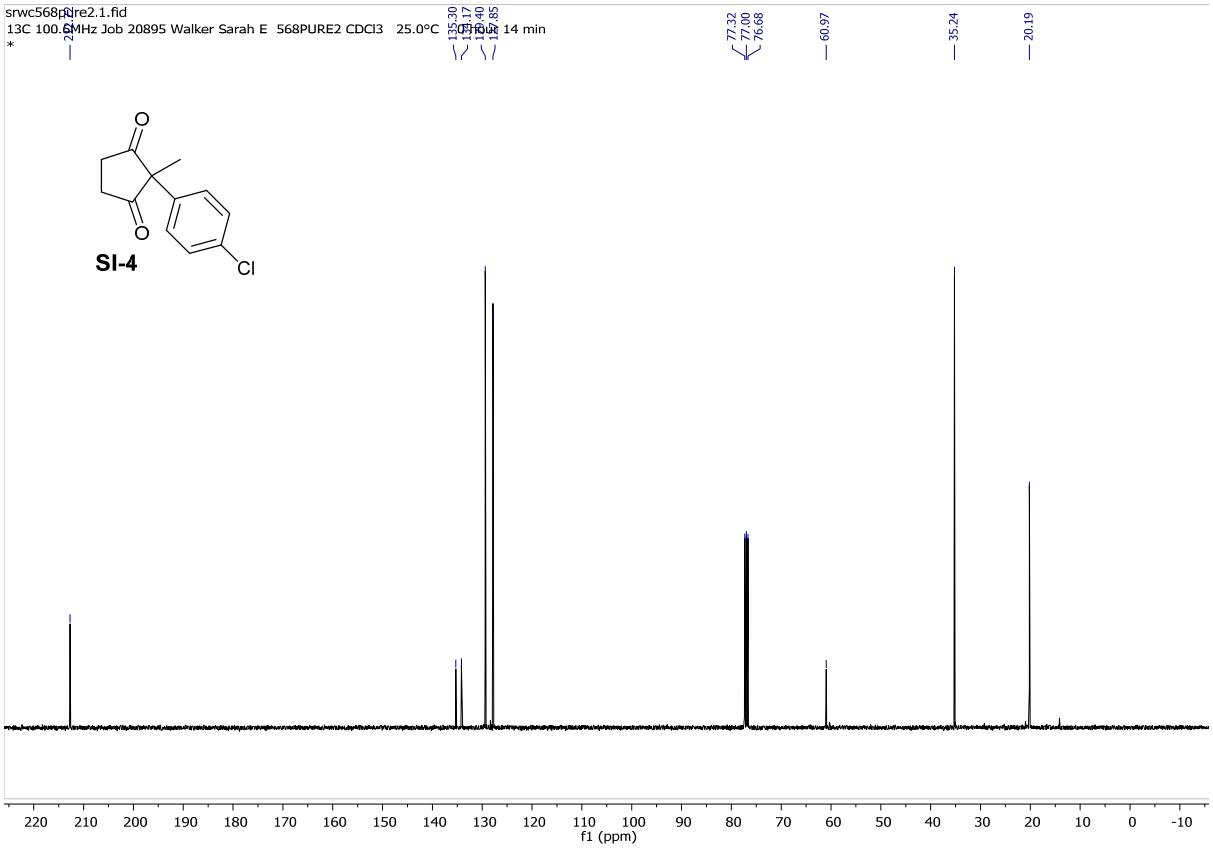


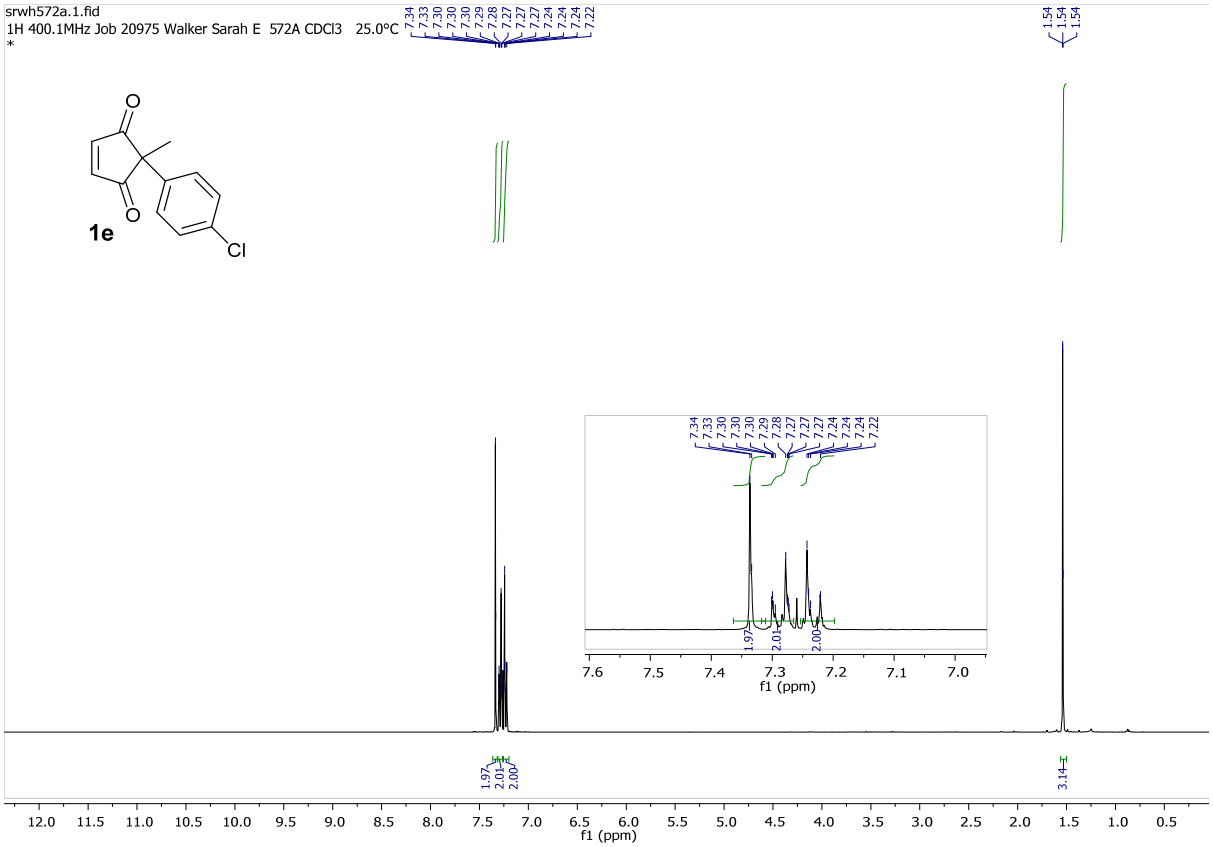

c4bcc035a13C 75.5MHz Job 29794 Beattie Nicholas A C035A CDCl3 25.0°C 0 hour 18 min
*

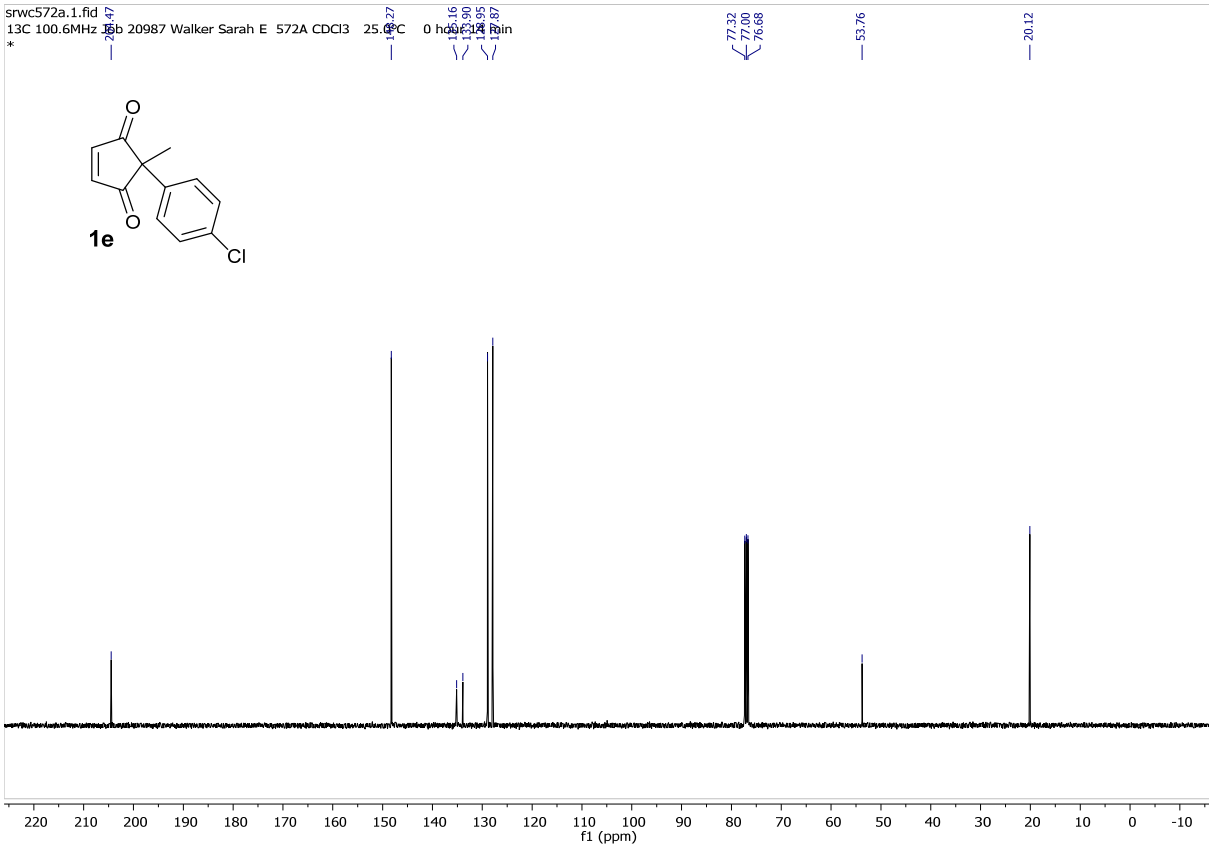


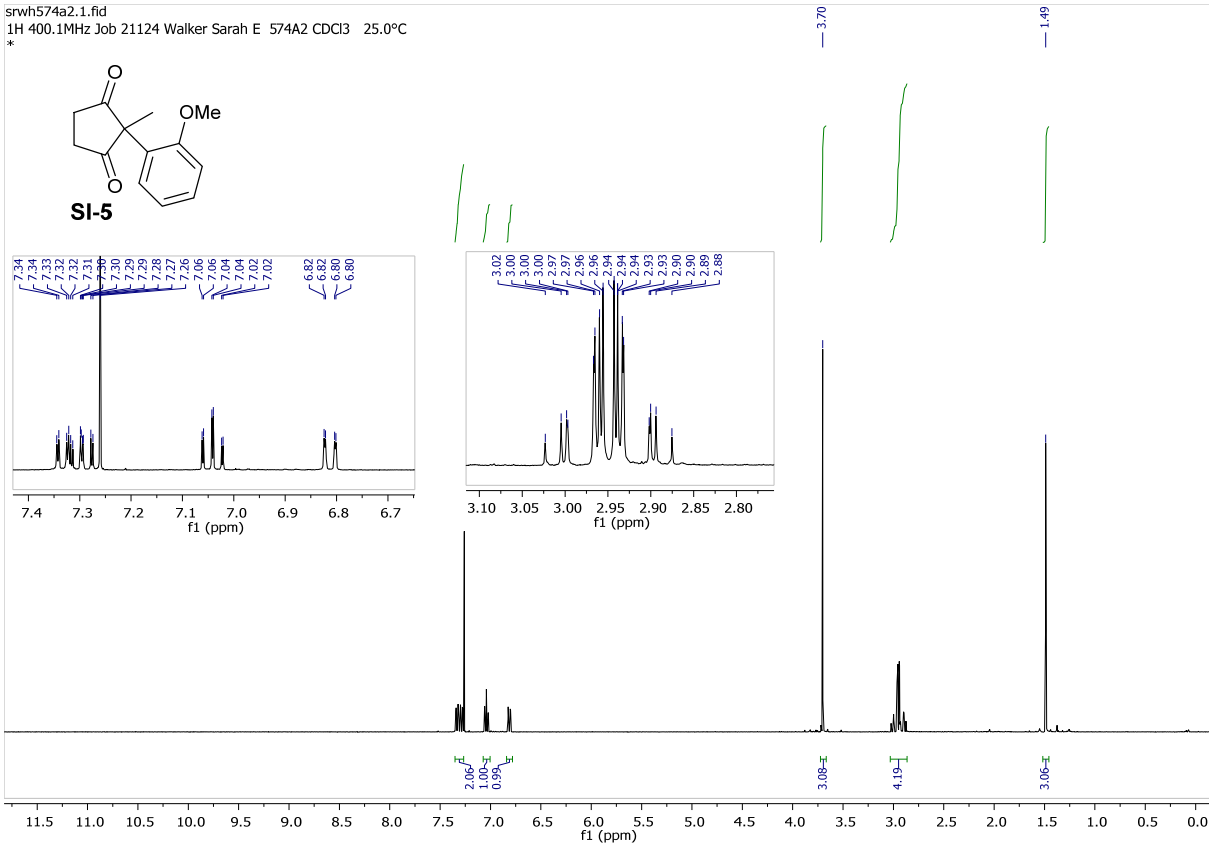
1c

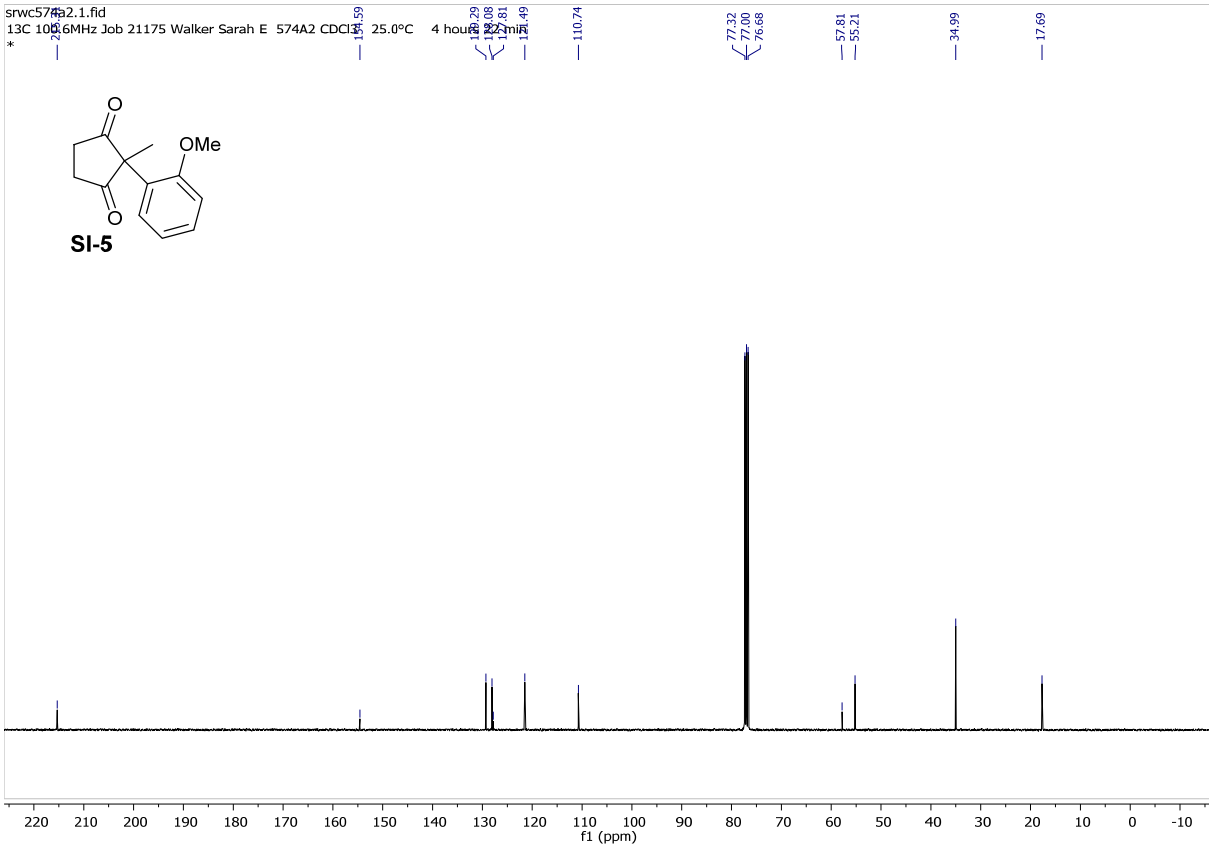

srwh571a3.1.fid
1H 400.1MHz Job 20980 Walker Sarah E 571A3 CDCl3 25.0°C
SI-4
Cl
f1 (ppm)

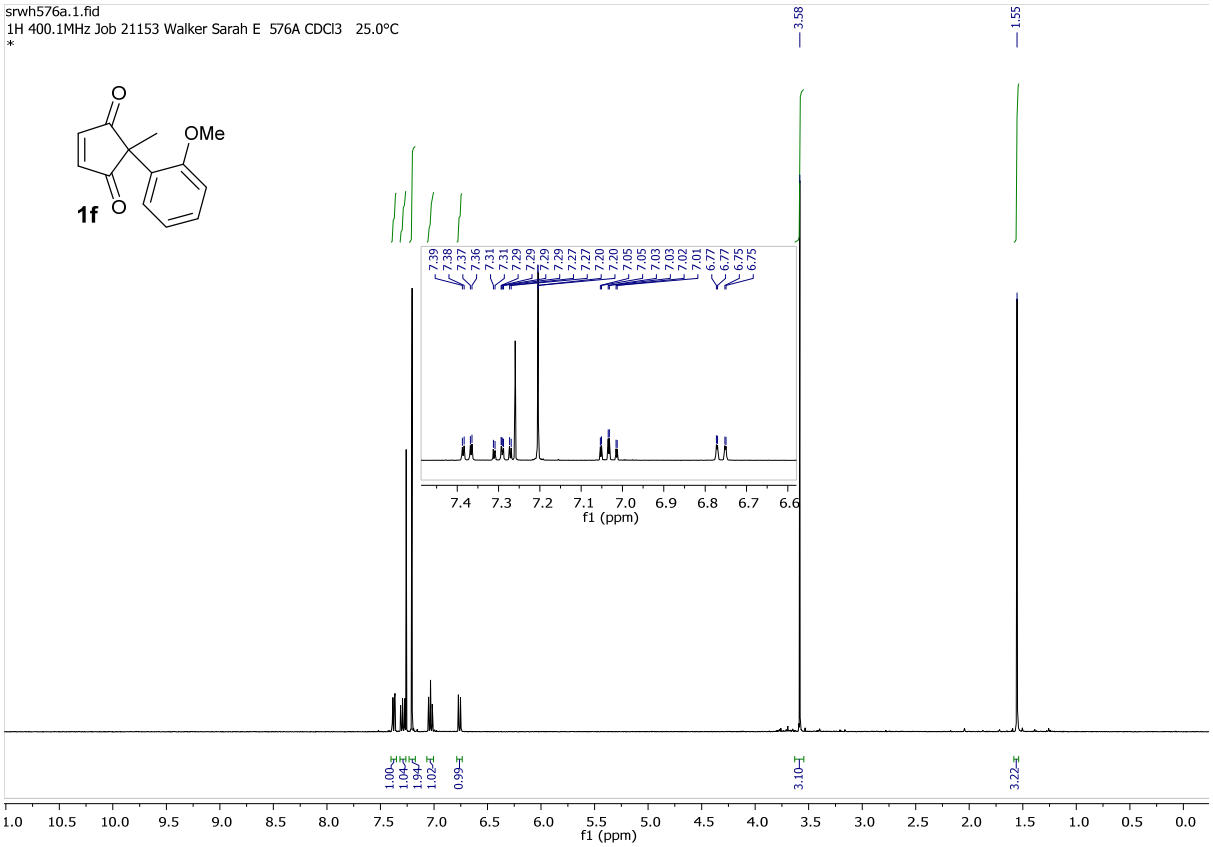

srwc568pure2.1.fid
13C 100.6MHz Job 20895 Walker Sarah E 568PURE2 CDCl3 25.0°C
SI-4
Cl
f1 (ppm)

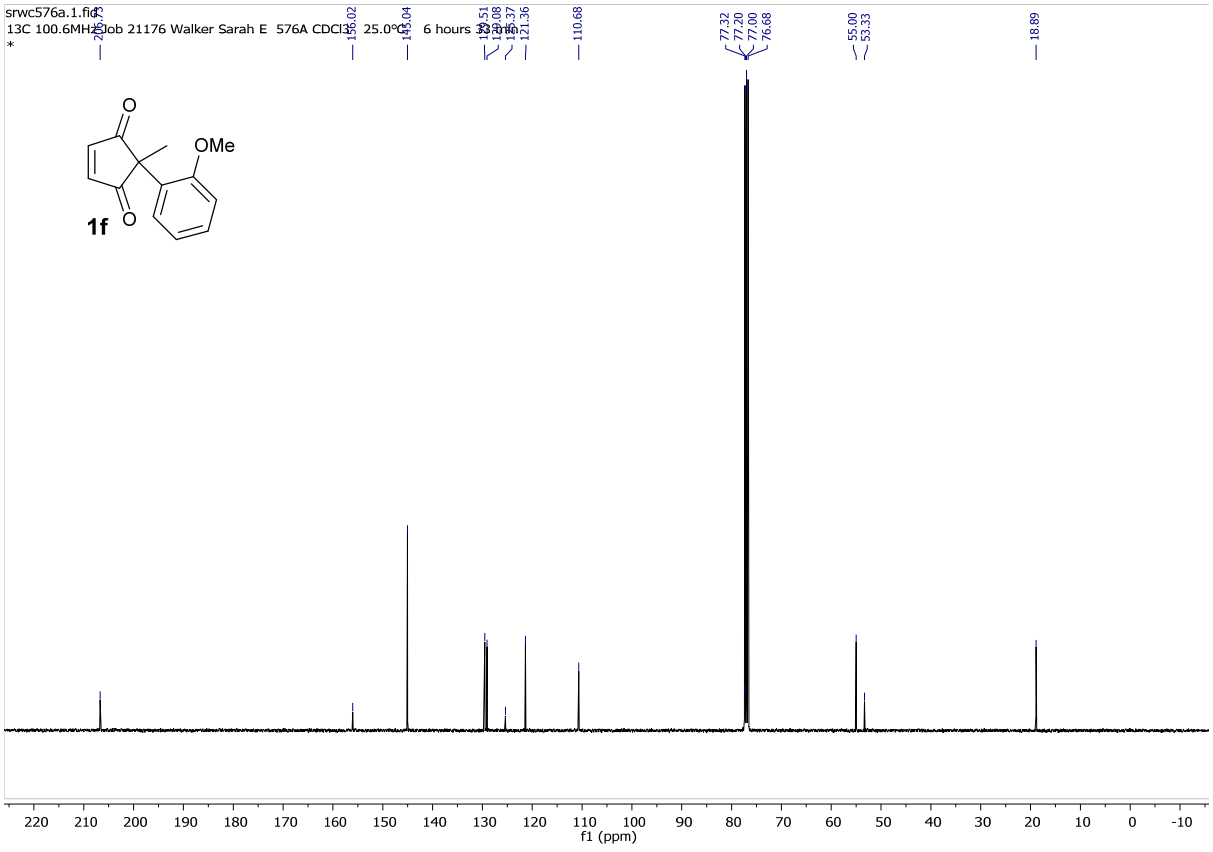

srwh572a.1.fid
1H 400.1MHz Job 20975 Walker Sarah E 572A CDCl3 25.0°C
*
1e
Cl
f1 (ppm)

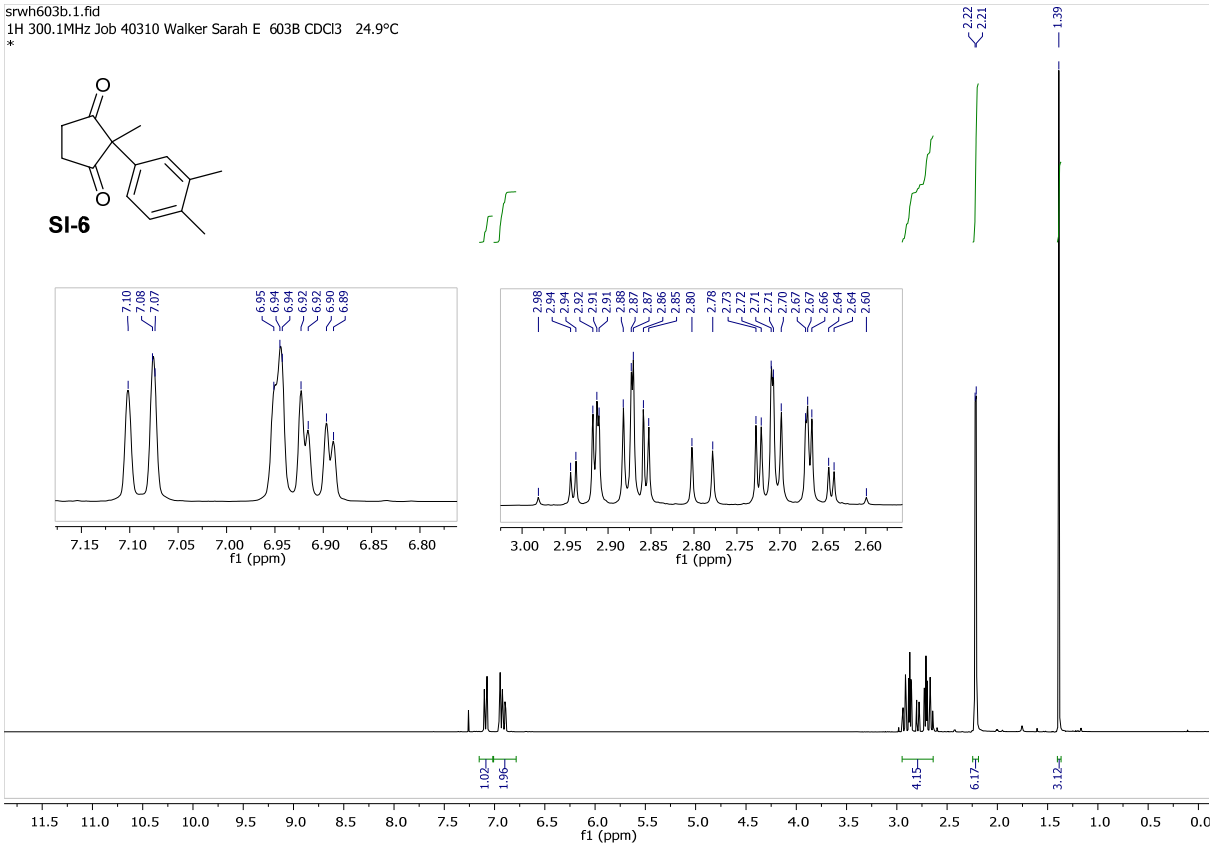

srwc572a.1.fid
13C 100.6MHz Job 20987 Walker Sarah E 572A CDCl3 25.0°C
*
1e
Cl
f1 (ppm)

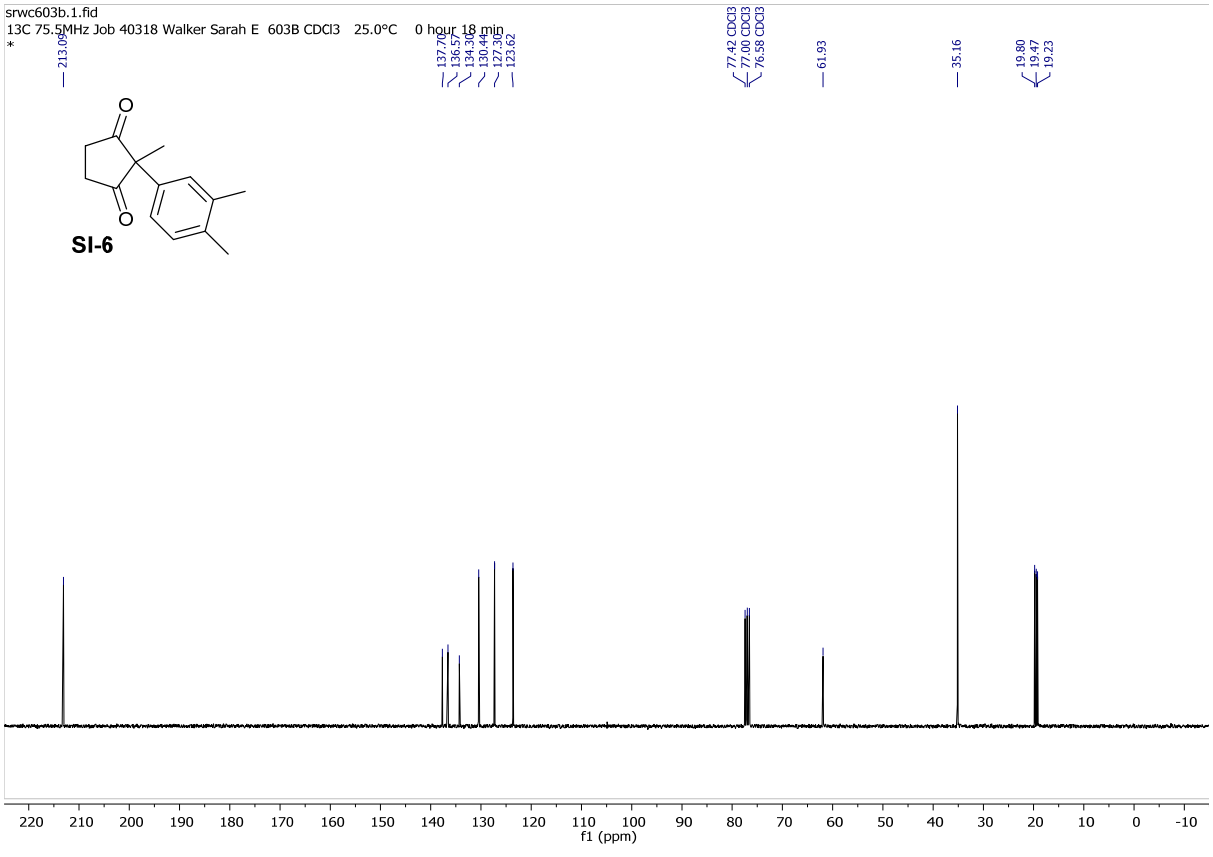

srwh574a2.1.fid
1H 400.1MHz Job 21124 Walker Sarah E 574A2 CDCl3 25.0°C
*
OMe
O
O
SI-5
3.70
1.49
f1 (ppm)

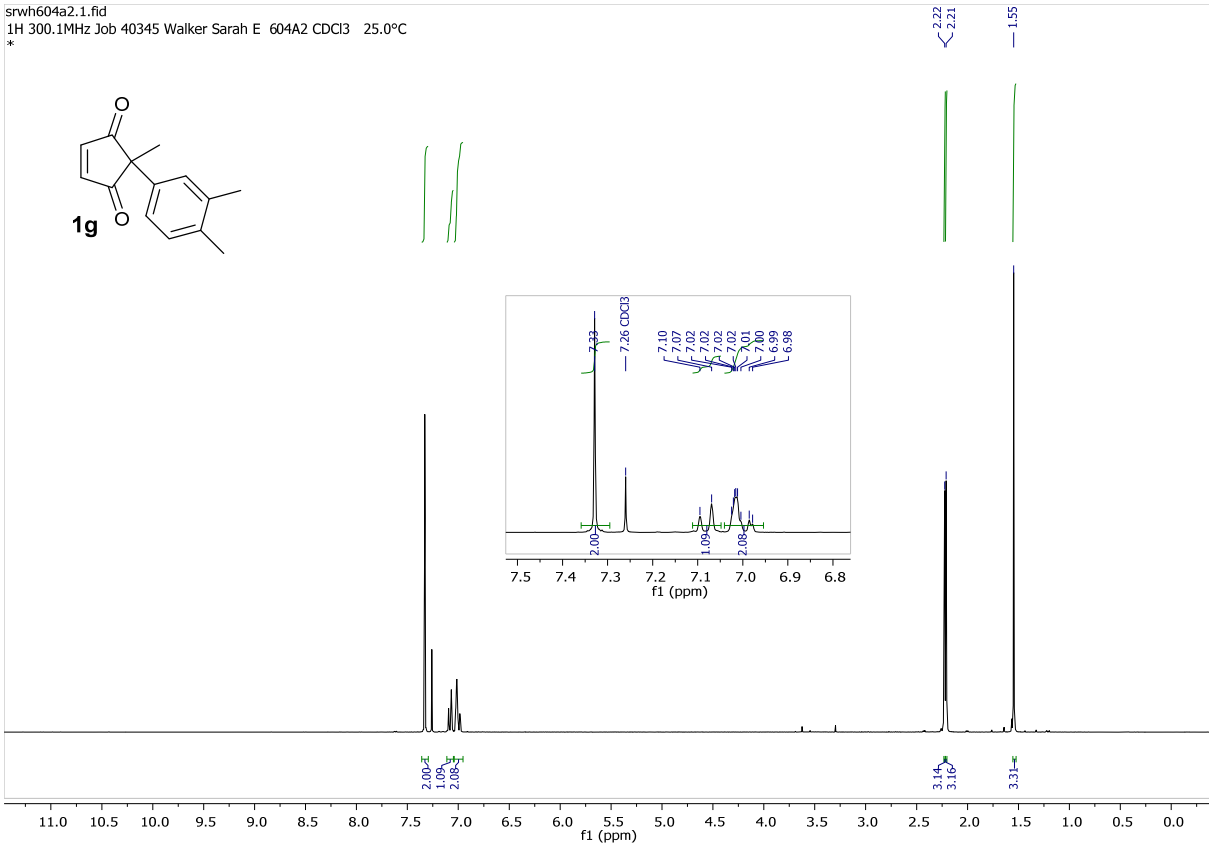

srwc574a2.1.fid
13C 100.6MHz Job 21175 Walker Sarah E 574A2 CDCl3 25.0°C 4 hours 32 min
*
OMe
O
O
SI-5
f1 (ppm)

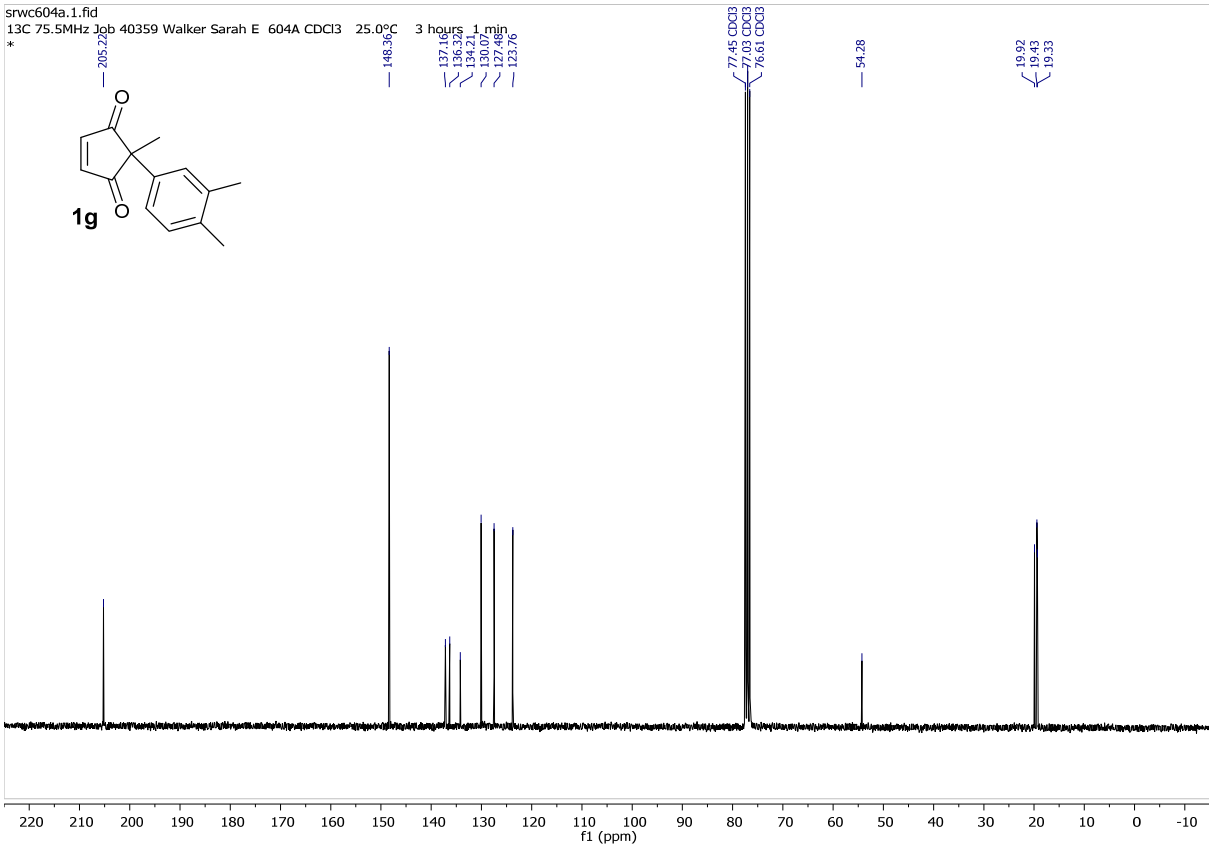

srwh576a.1.fid
1H 400.1MHz Job 21153 Walker Sarah E 576A CDCl3 25.0°C
*
OMe
1f
3.58
1.55
7.39
7.38
7.37
7.36
7.31
7.31
7.29
7.29
7.29
7.29
7.27
7.27
7.20
7.20
7.05
7.05
7.03
7.03
7.02
7.01
6.77
6.77
6.75
6.75
7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6
f1 (ppm)
1.00
1.04
1.94
1.02
0.99
3.10
3.22
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


srwc576a.1.fid
13C 100.6MHz Job 21176 Walker Sarah E 576A CDCl3 25.0°C 6 hours
*
205.42
155.02
143.04
130.51
129.08
128.37
121.36
110.68
77.32
77.20
77.00
76.68
55.00
53.33
18.89
OMe
1f
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

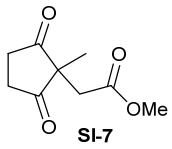

srwh603b.1.fid
1H 300.1MHz Job 40310 Walker Sarah E 603B CDCl3 24.9°C
*
SI-6
7.10
7.08
7.07
6.95
6.94
6.94
6.92
6.92
6.90
6.89
2.98
2.94
2.94
2.92
2.91
2.91
2.88
2.87
2.87
2.86
2.85
2.80
2.78
2.73
2.72
2.71
2.71
2.70
2.67
2.67
2.66
2.64
2.64
2.60
2.22
2.21
1.39
1.02
1.96
4.15
6.17
3.12
f1 (ppm)


srwc603b.1.fid
13C 75.5MHz Job 40318 Walker Sarah E 603B CDCl3 25.0°C 0 hour 18 min
*
SI-6
213.09
137.70
136.57
134.30
130.44
127.30
123.62
77.42 CDCl3
77.00 CDCl3
76.58 CDCl3
61.93
35.16
19.80
19.47
19.23
f1 (ppm)


srwh604a2.1.fid
1H 300.1MHz Job 40345 Walker Sarah E 604A2 CDCl3 25.0°C
*
1g
2.22
2.21
1.55
7.33
7.26 CDCl3
7.10
7.07
7.02
7.02
7.02
7.02
7.01
7.00
6.99
6.98
2.00
1.09
2.08
7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8
f1 (ppm)
2.00
1.09
2.08
3.14
3.16
3.31
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


srwc604a.1.fid
13C 75.5MHz Job 40359 Walker Sarah E 604A CDCl3 25.0°C 3 hours 1 min
*
1g
205.22
148.36
137.16
136.32
134.21
130.07
127.48
123.76
77.45 CDCl3
77.03 CDCl3
76.61 CDCl3
54.28
19.92
19.43
19.33
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

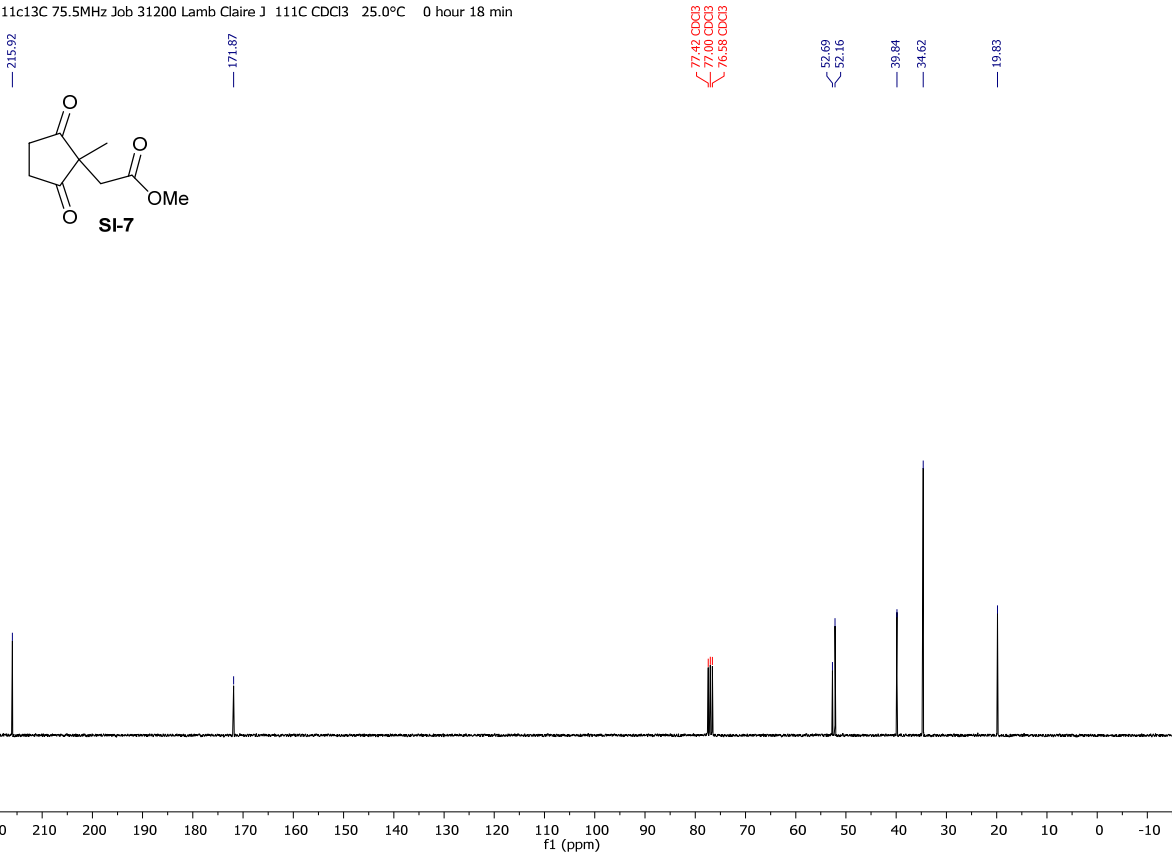
c5lh111c1H 300.1MHz Job 31158 Lamb Claire J 111C CDCl3 25.1°C
*



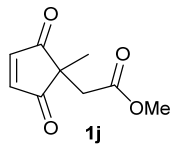

**SI-7**




c5lc111c13C 75.5MHz Job 31200 Lamb Claire J 111C CDCl3 25.0°C 0 hour 18 min
*



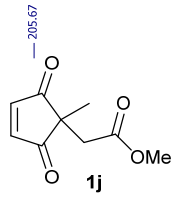
c5lh113c1H 300.1MHz Job 31159 Lamb Claire J 113C CDCl3 25.1°C
*




**1j**

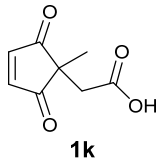



c5lc113c13C 75.5MHz Job 31201 Lamb Claire J 113C CDCl3 25.0°C 0 hour 54 min
*




**1j**

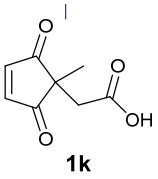
c5lhacid12181H 300.1MHz Job 35920 Lamb Claire J ACID1218 CDCl3 25.0°C
Acid combined - fraction 12-18



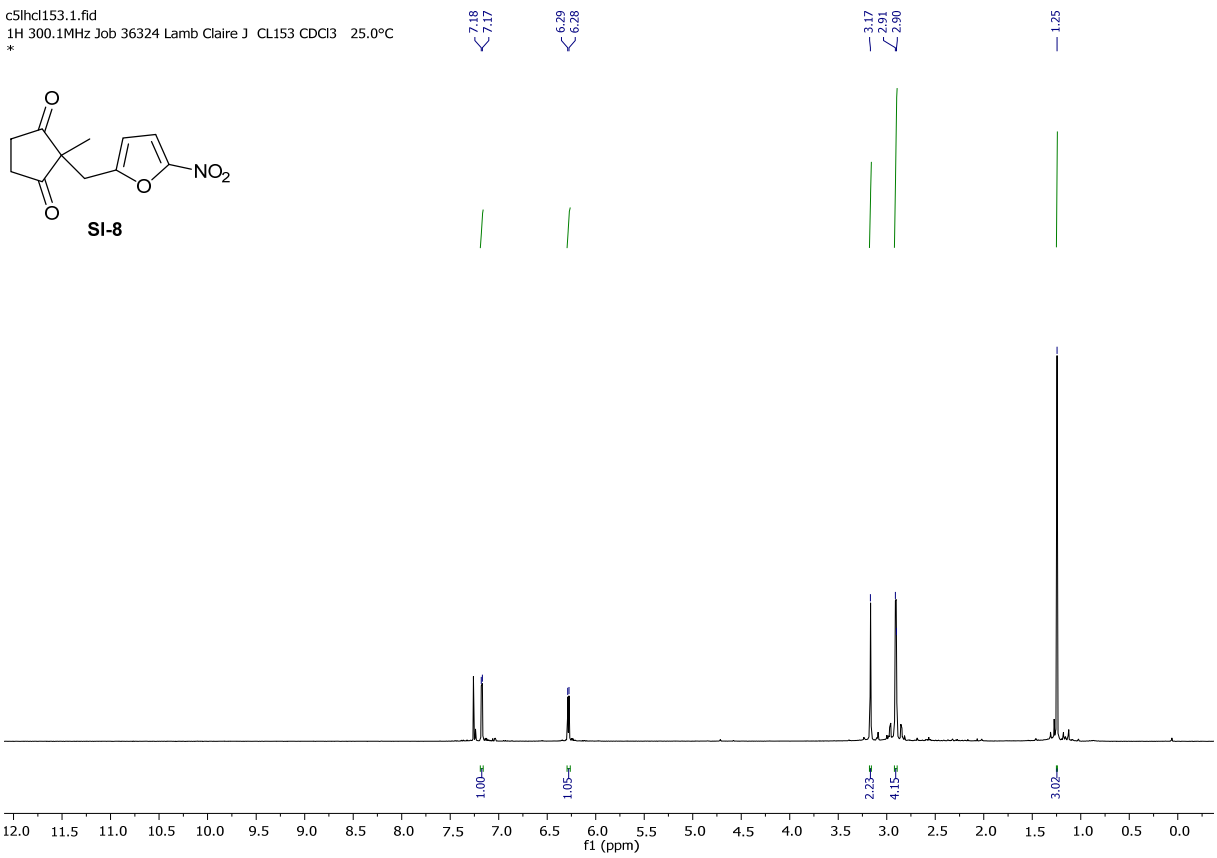
**1k**

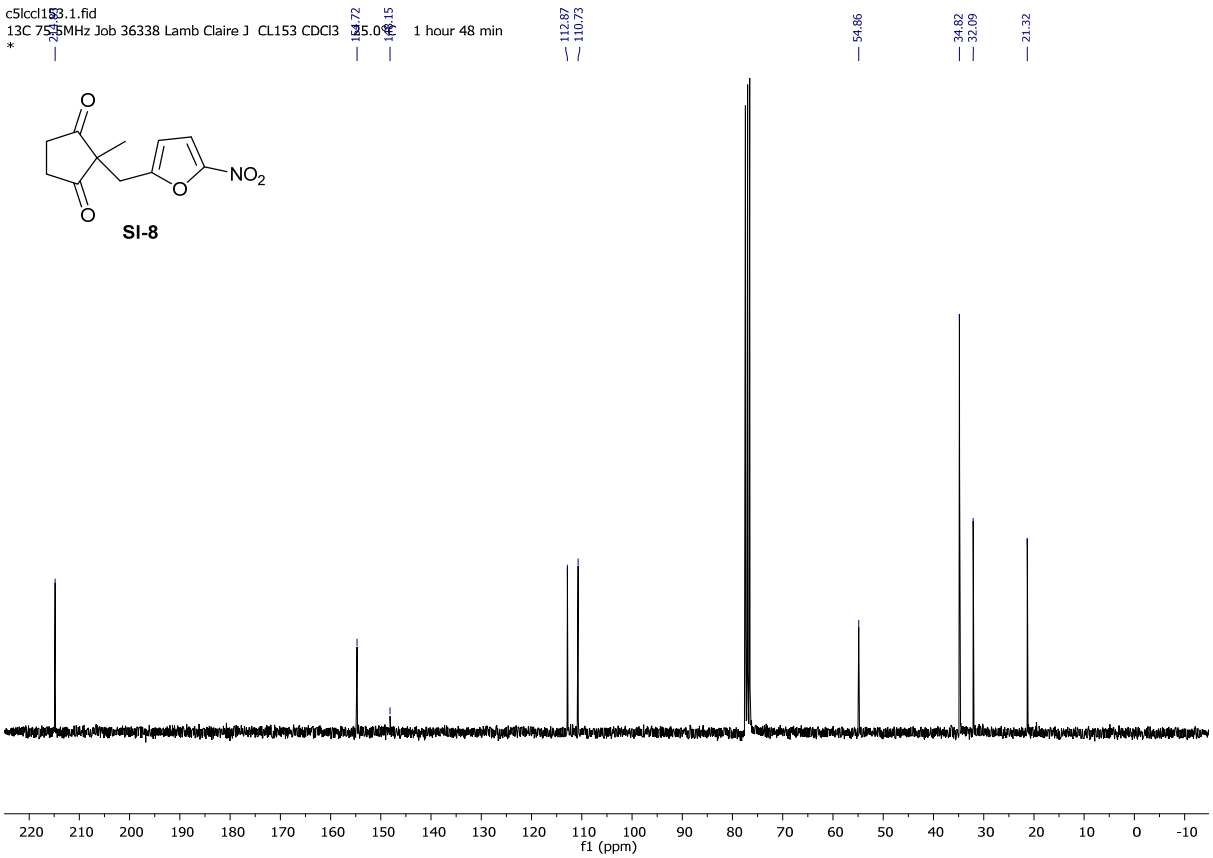



c5lc127gpr13C 75.5MHz Job 31996 Lamb Claire J 127GPR CDCl3 25.0°C 3 hours 1 min
Good - precipitate

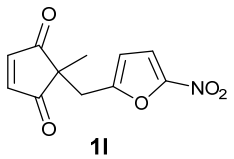


**1k**


c5lhcl153.1.fid
1H 300.1MHz Job 36324 Lamb Claire J CL153 CDCl3 25.0°C
*
7.18
7.17
6.29
6.28
3.17
2.91
2.90
1.25
O
O
O
NO2
SI-8
1.00
1.05
2.23
4.15
3.02
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


c5lccl153.1.fid
13C 75.5MHz Job 36338 Lamb Claire J CL153 CDCl3 25.0°C 1 hour 48 min
*
154.72
144.15
112.87
110.73
54.86
34.82
32.09
21.32
O
O
O
NO2
SI-8
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

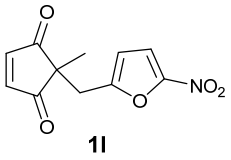
c5lh155p.1.fid
1H 300.1MHz Job 35035 Lamb Claire J 155P CDCl3 24.9°C
*



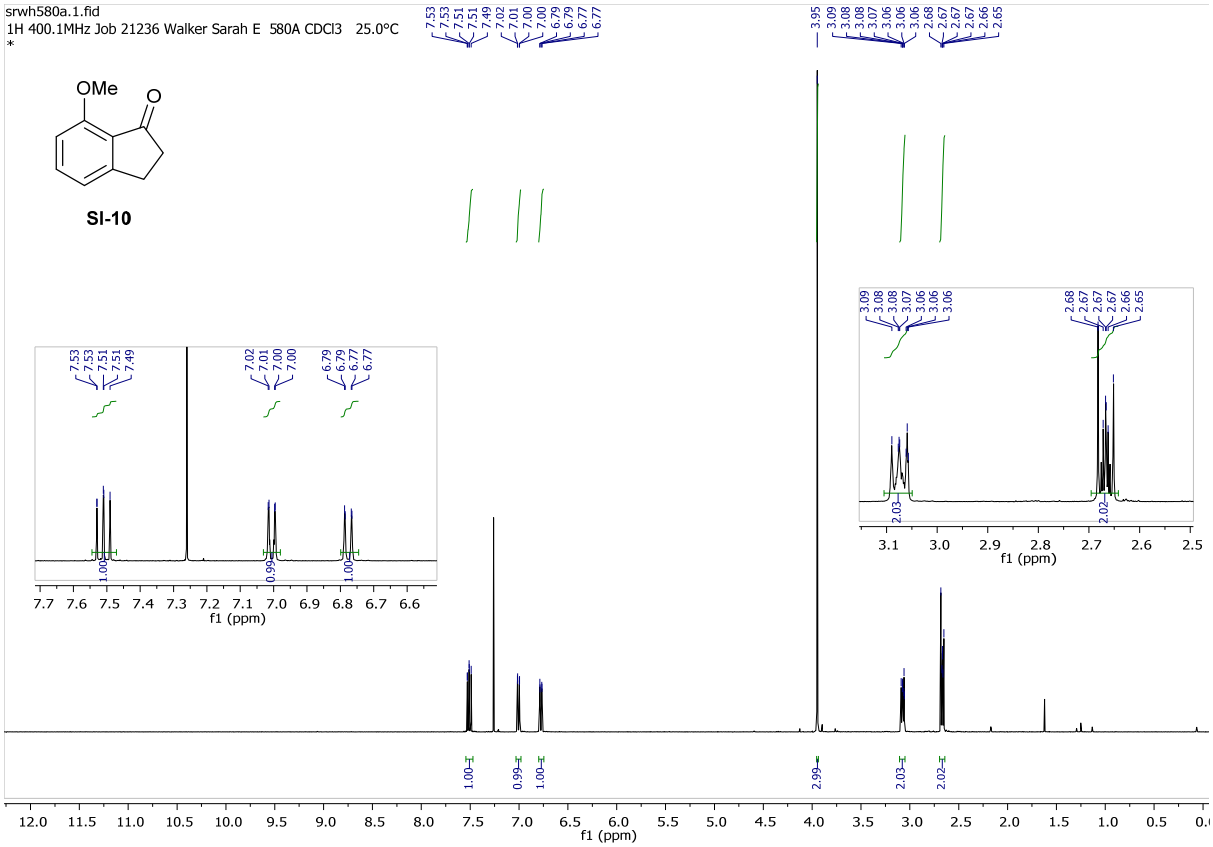
1l

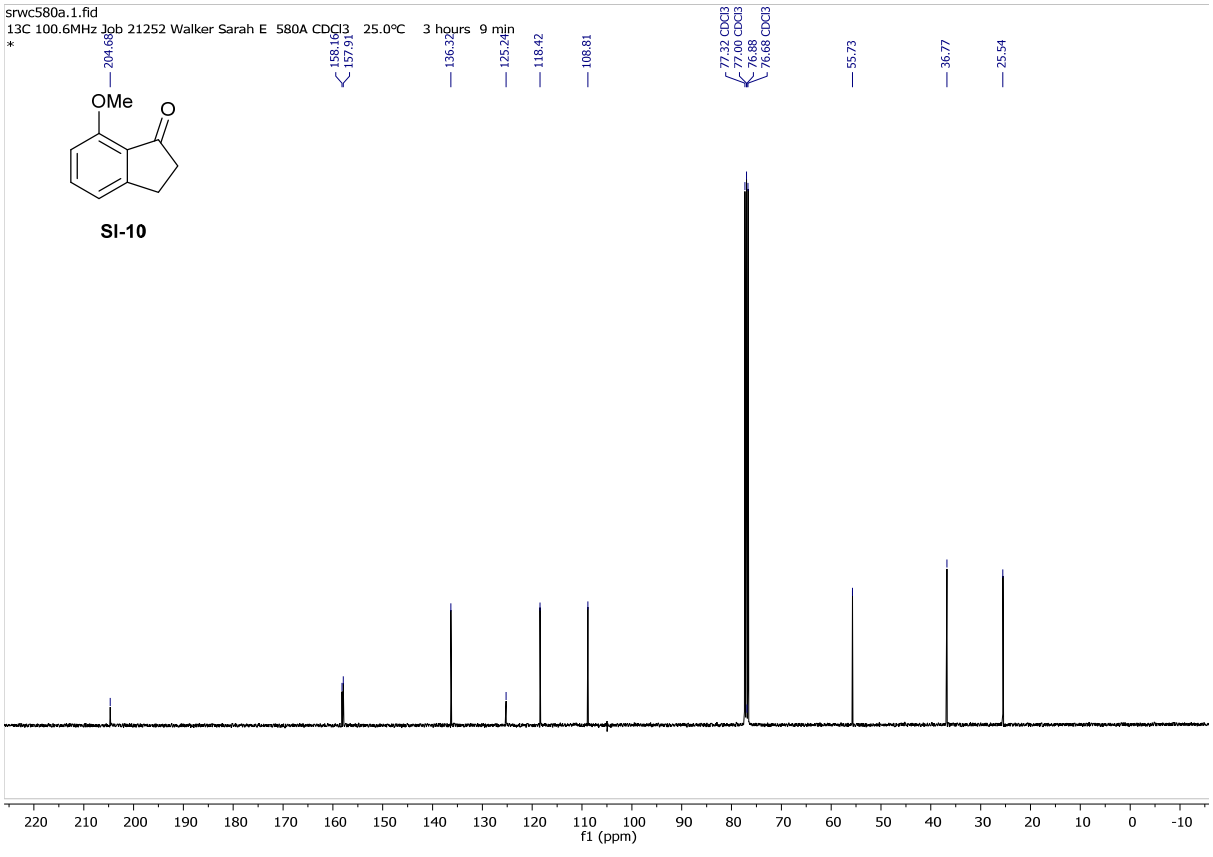


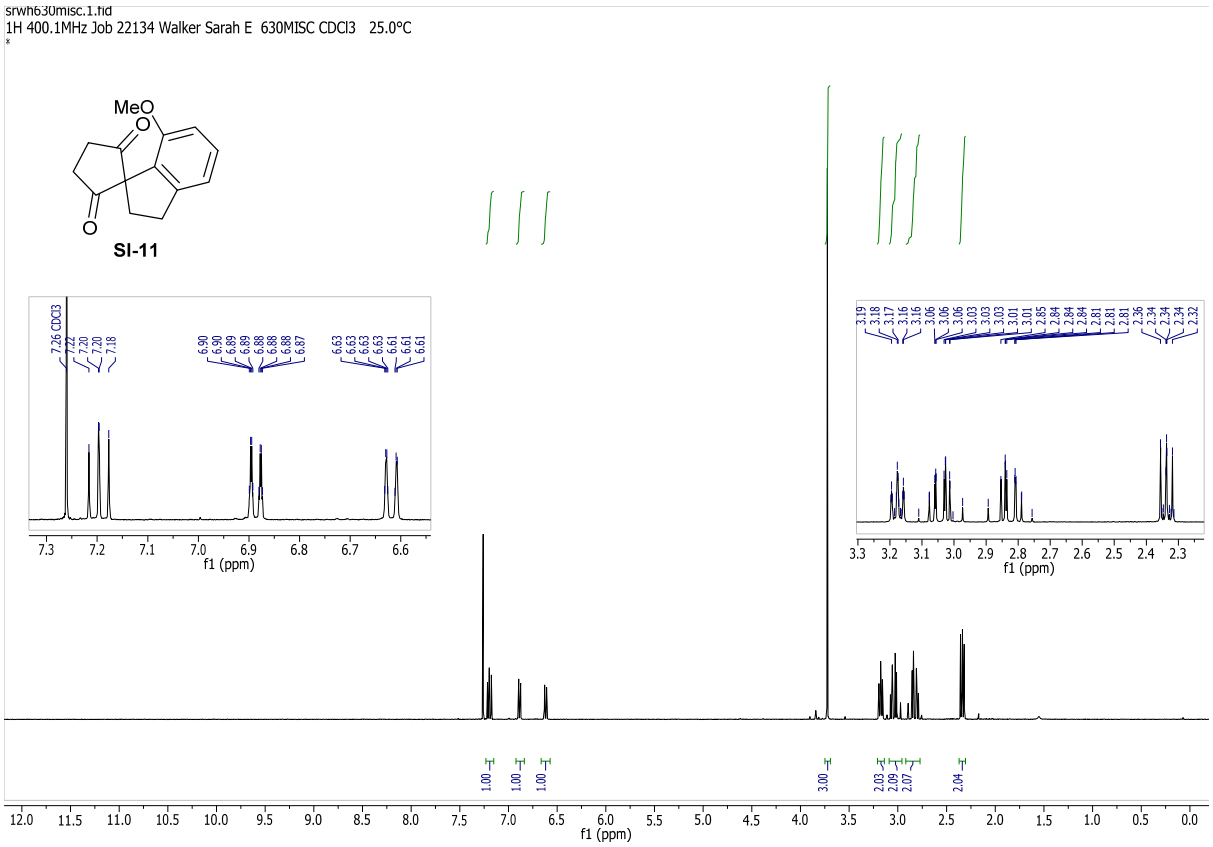

c5lc155prod.1.fid
13C 75.5MHz Job 35450 Lamb Claire J 155PROD CDCl3 25.0°C 3 hours 1 min
*

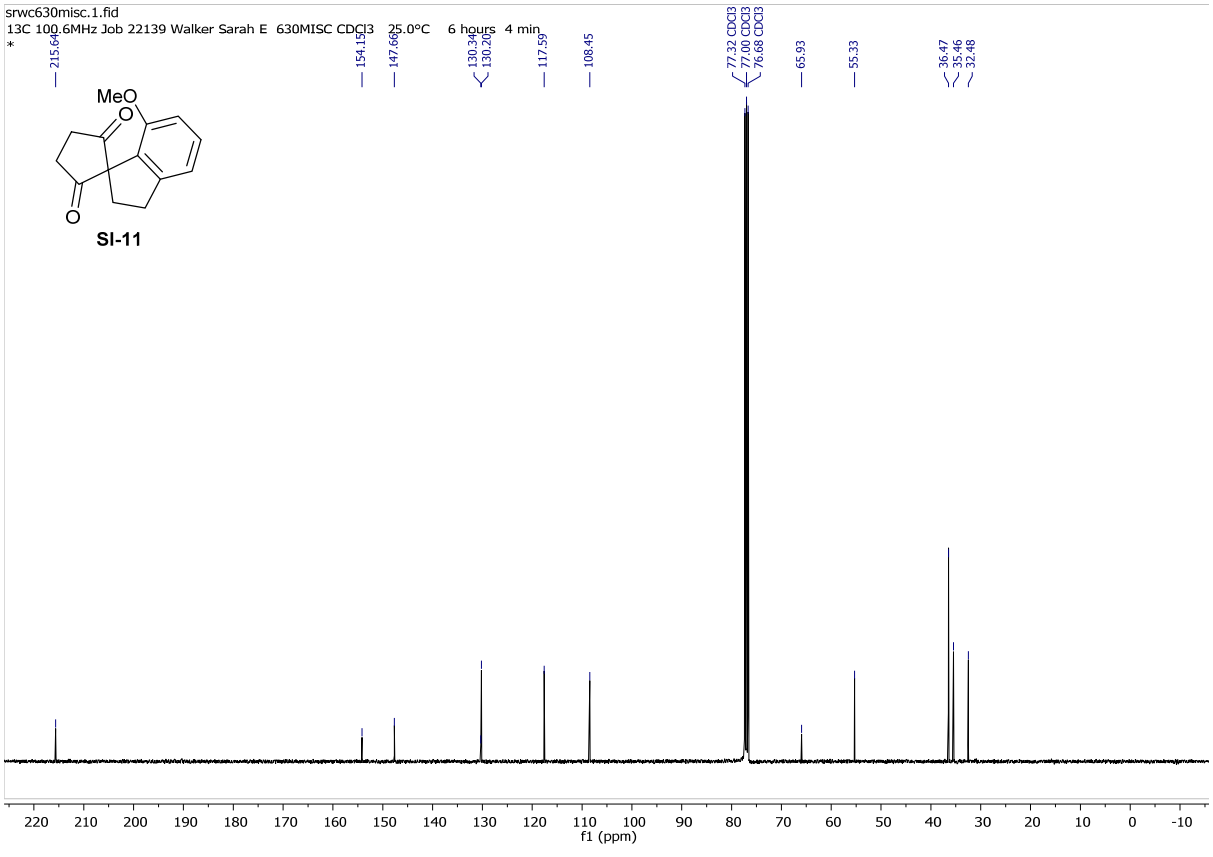


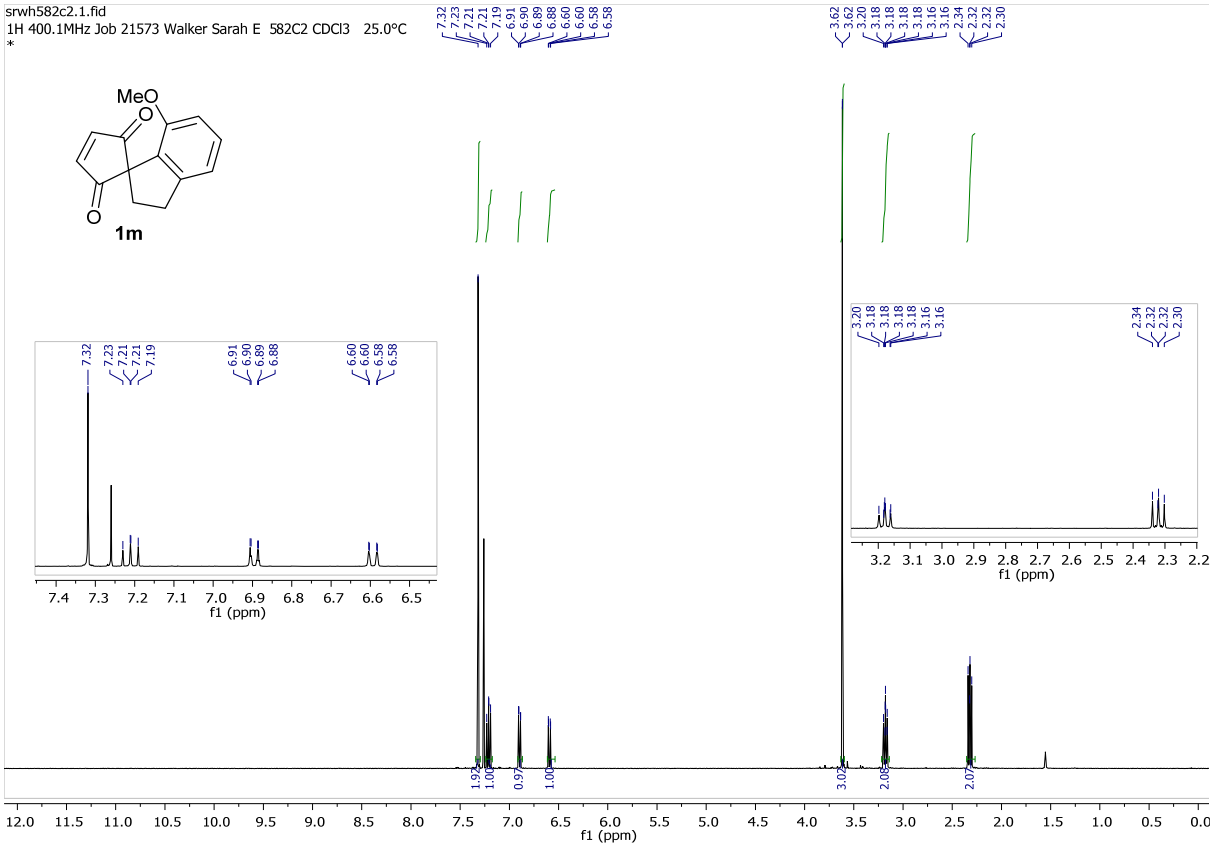
1l

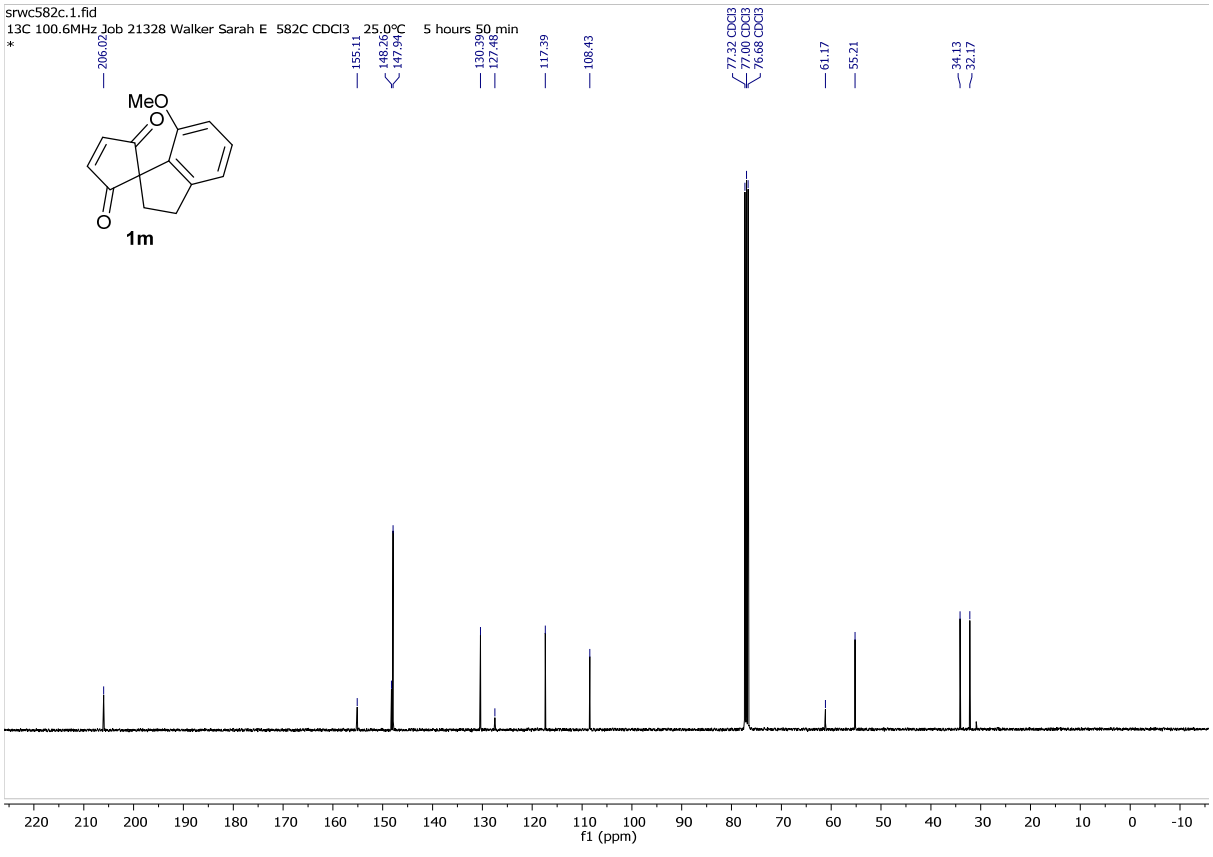

srwh580a.1.fid
1H 400.1MHz Job 21236 Walker Sarah E 580A CDCl3 25.0°C
*
OMe
O
SI-10
f1 (ppm)

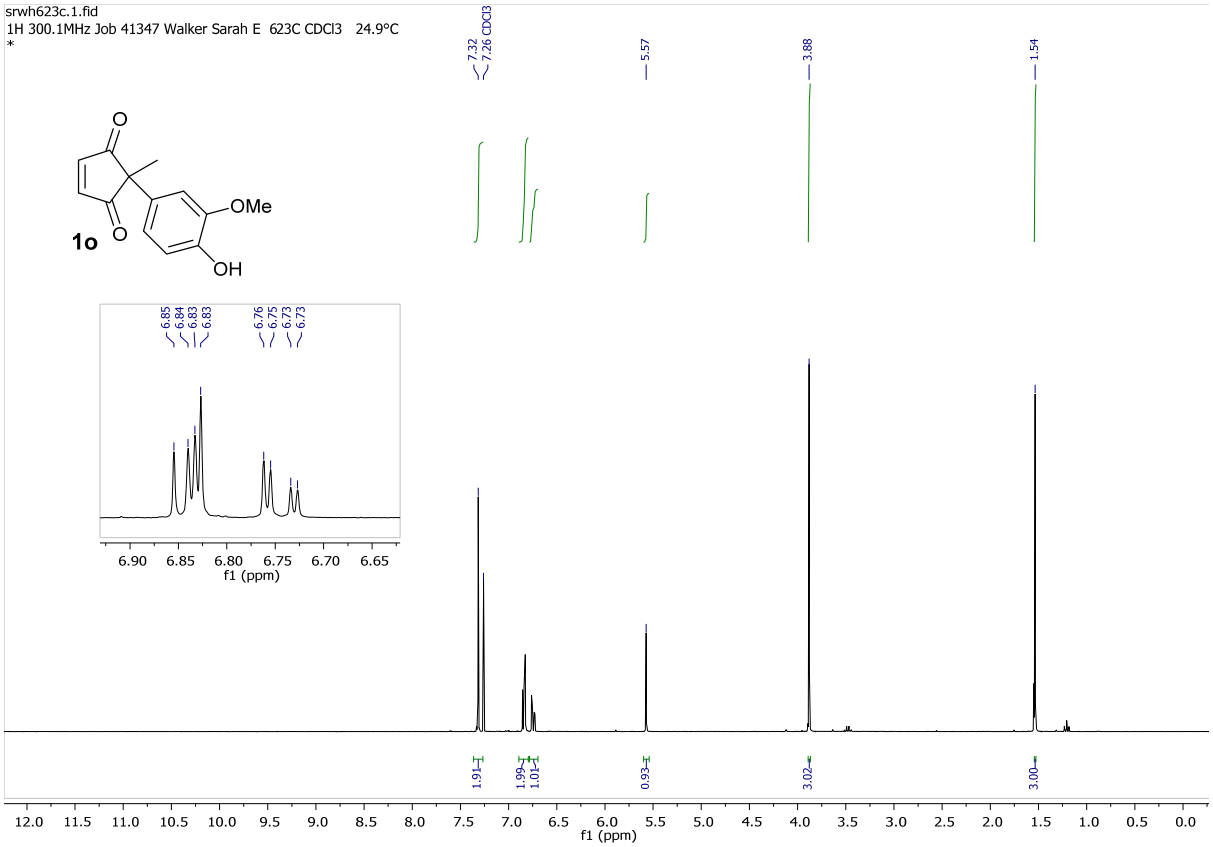

srwc580a.1.fid
13C 100.6MHz Job 21252 Walker Sarah E 580A CDCl3 25.0°C 3 hours 9 min
*
OMe
O
SI-10
f1 (ppm)

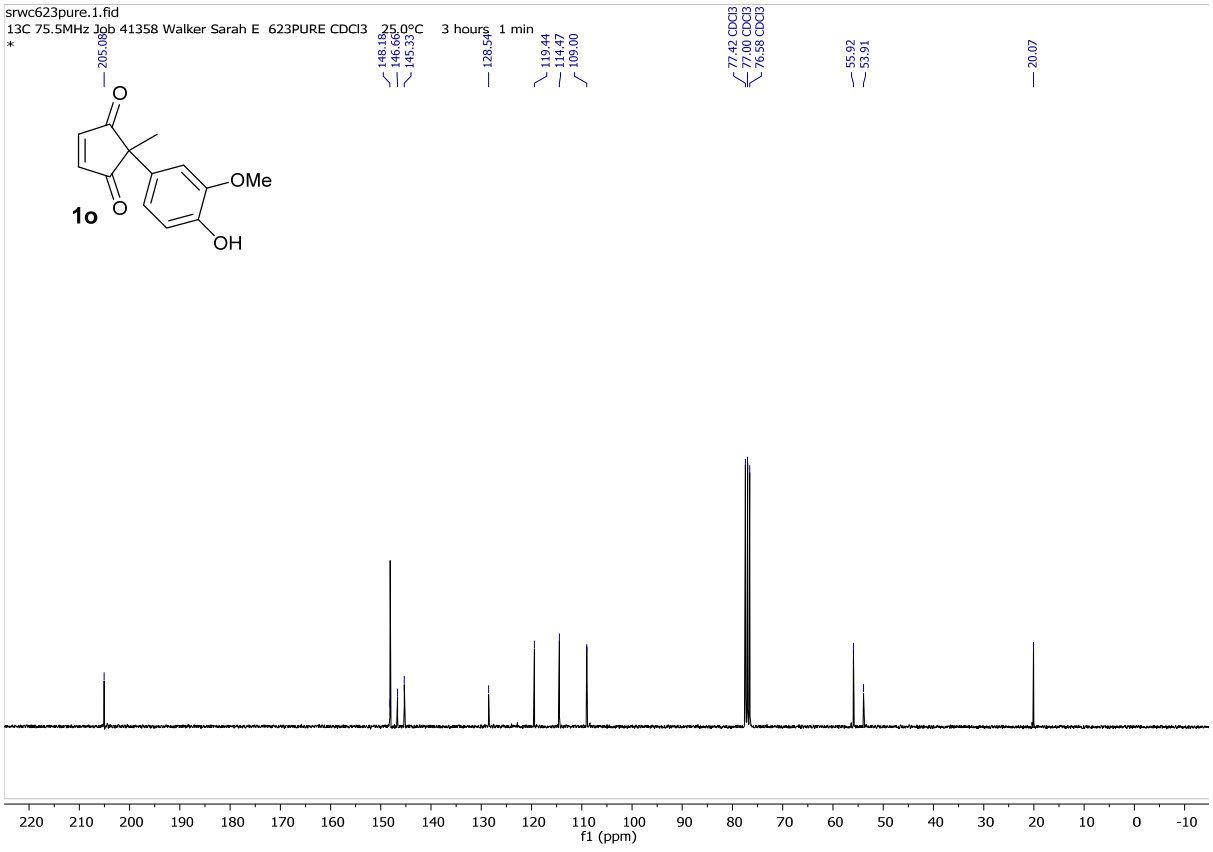

srwh630misc.1.fid
1H 400.1MHz Job 22134 Walker Sarah E 630MISC CDCl3 25.0°C
MeO
O
O
SI-11
f1 (ppm)

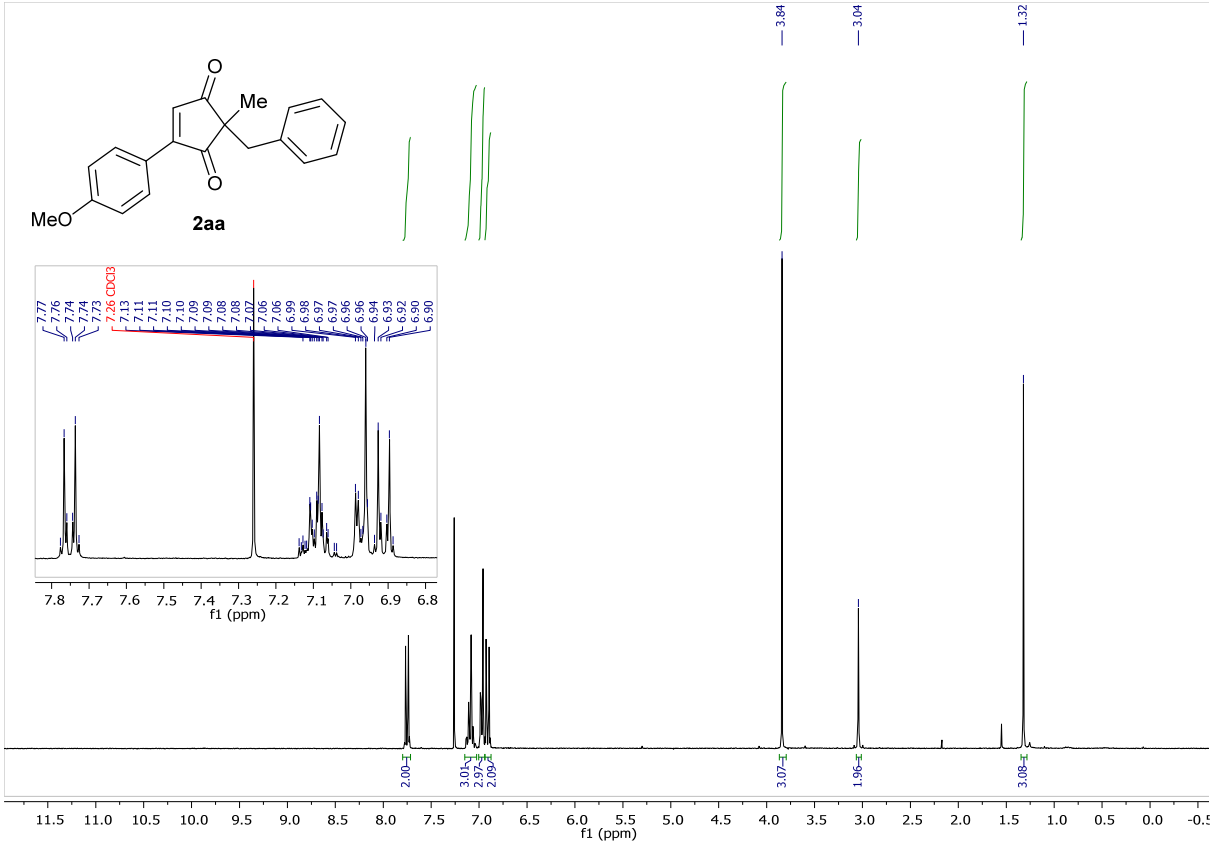

srwc630misc.1.fid
13C 100.6MHz Job 22139 Walker Sarah E 630MISC CDCl3 25.0°C 6 hours 4 min
MeO
O
O
SI-11
f1 (ppm)

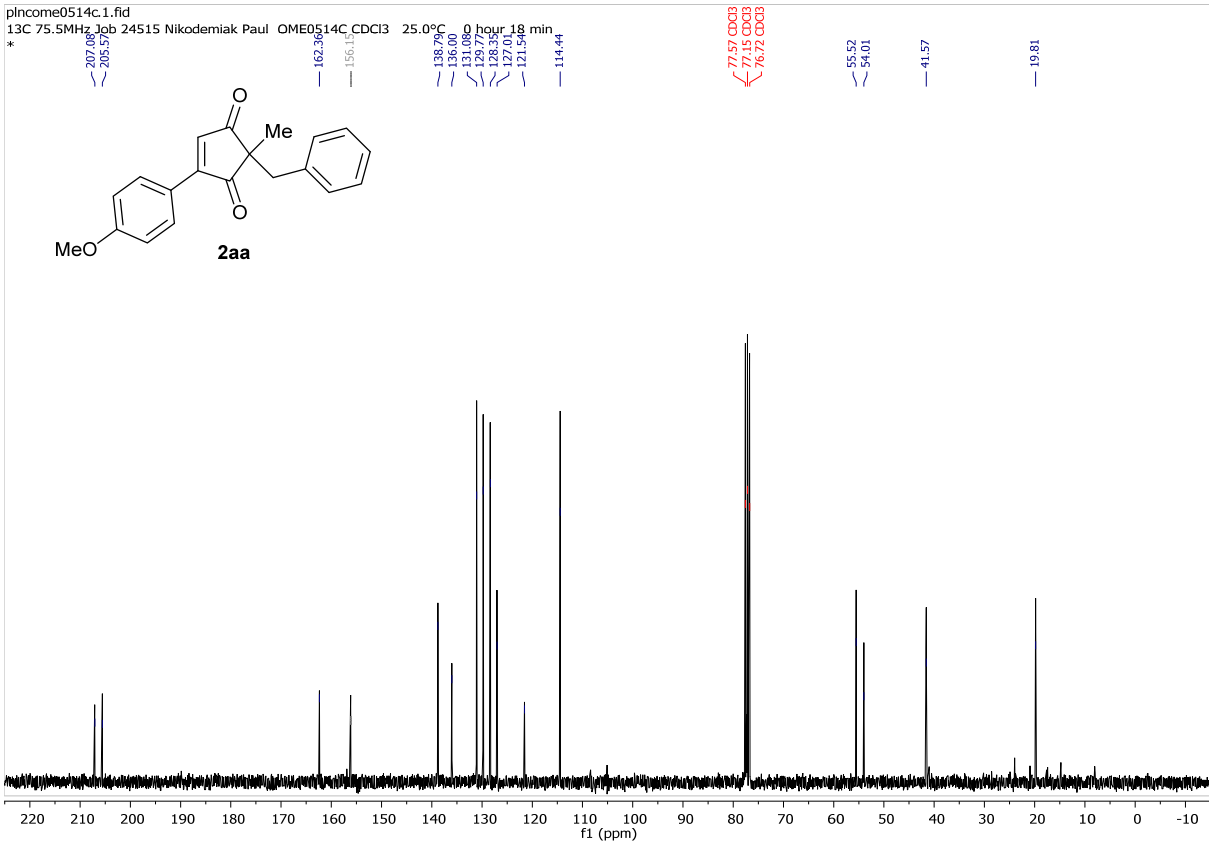

srwh582c2.1.fid
1H 400.1MHz Job 21573 Walker Sarah E 582C2 CDCl3 25.0°C
*
MeO
O
O
1m
f1 (ppm)

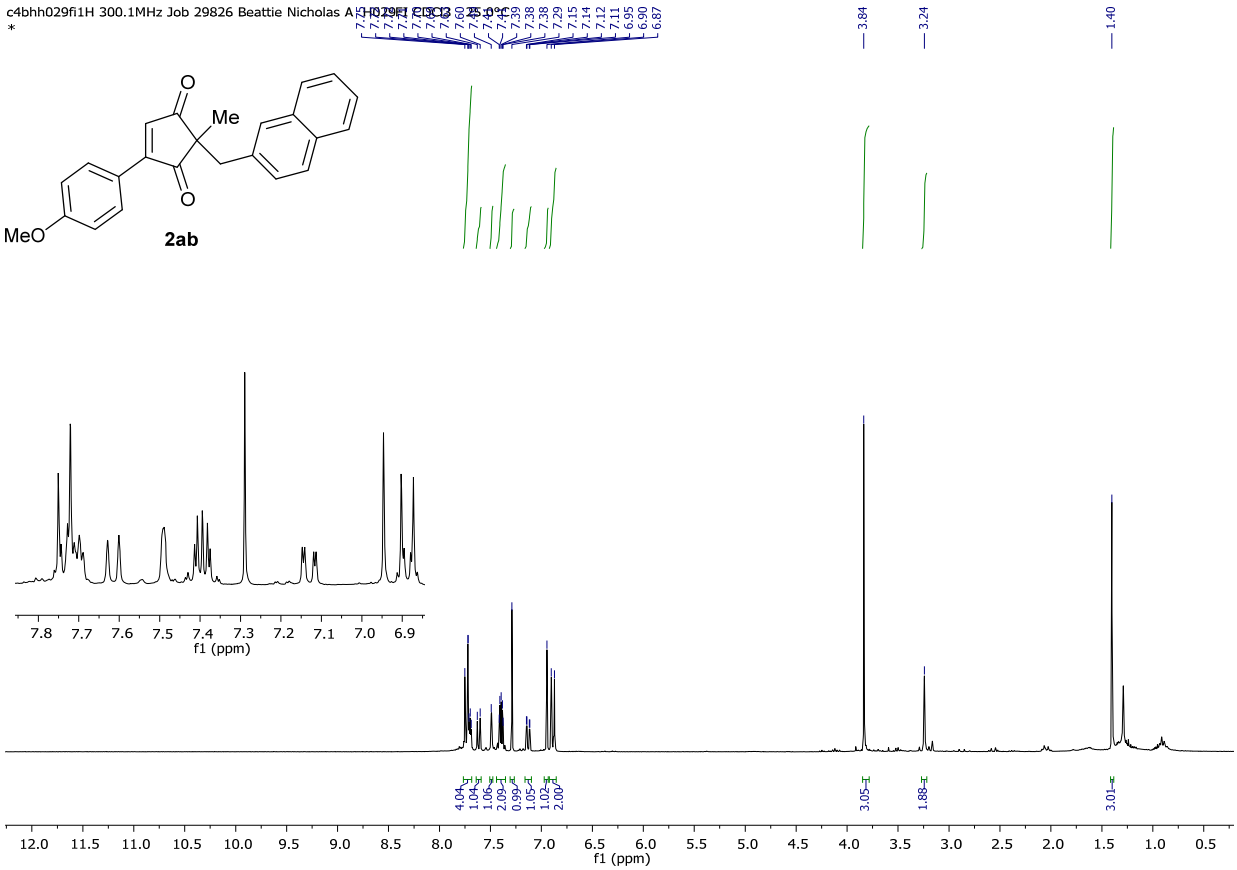

srwc582c.1.fid
13C 100.6MHz Job 21328 Walker Sarah E 582C CDCl3 25.0°C 5 hours 50 min
*
MeO
O
O
1m
f1 (ppm)

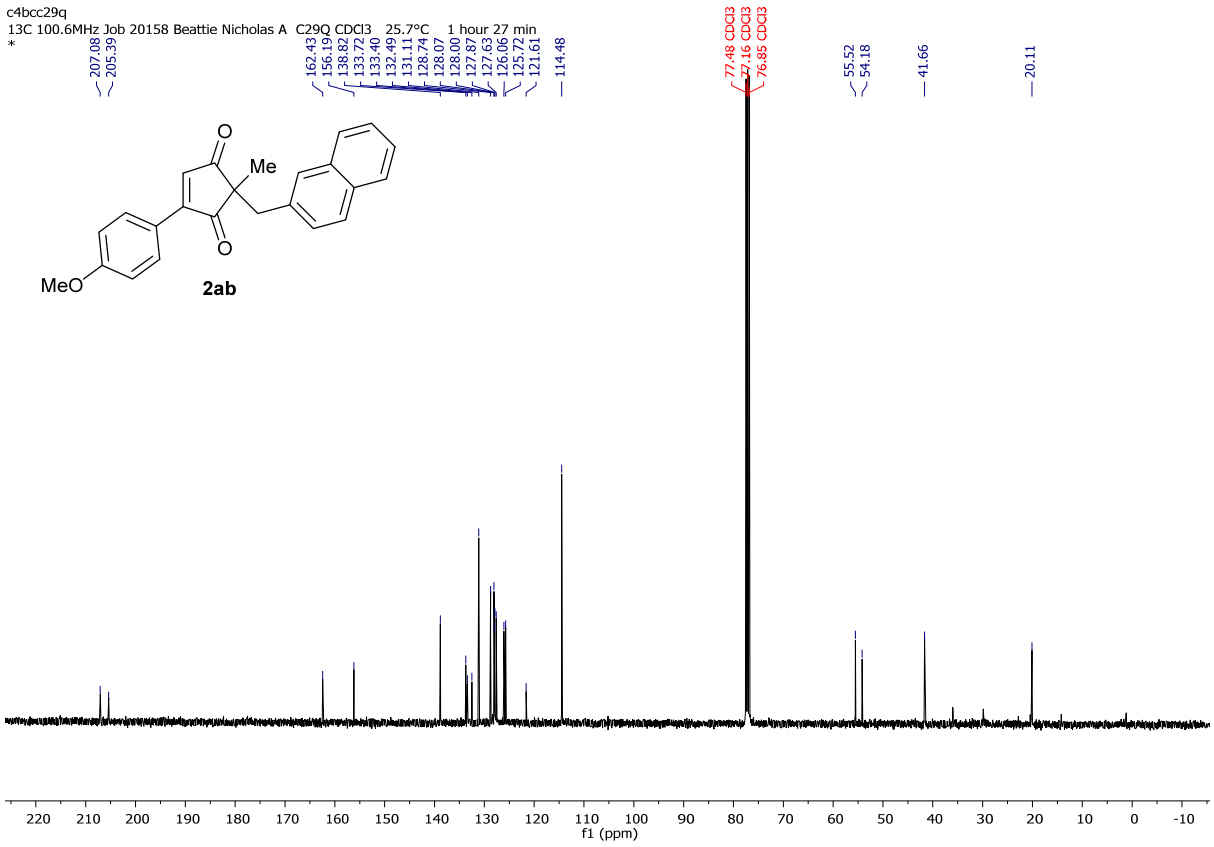

srwh623c.1.fid
1H 300.1MHz Job 41347 Walker Sarah E 623C CDCl3 24.9°C
*
7.32
7.26 CDCl3
5.57
3.88
1.54
O
O
OMe
OH
1o
6.85
6.84
6.83
6.83
6.76
6.75
6.73
6.73
6.90 6.85 6.80 6.75 6.70 6.65
f1 (ppm)
1.91
1.99
1.01
0.93
3.02
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


srwc623pure.1.fid
13C 75.5MHz Job 41358 Walker Sarah E 623PURE CDCl3 25.0°C 3 hours 1 min
*
205.08
148.18
146.66
145.33
128.54
119.44
114.47
109.00
77.42 CDCl3
77.00 CDCl3
76.58 CDCl3
55.92
53.91
20.07
O
O
OMe
OH
1o
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

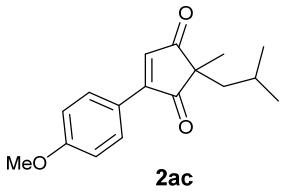

Me
O
O
MeO
2aa
3.84
3.04
1.32
7.77
7.76
7.74
7.74
7.73
7.26 CDCl3
7.13
7.11
7.11
7.10
7.10
7.09
7.09
7.08
7.08
7.07
7.06
7.06
6.99
6.98
6.97
6.97
6.96
6.96
6.94
6.93
6.92
6.90
6.90
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8
f1 (ppm)
2.00
3.01
2.97
2.09
3.07
1.96
3.08
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


plncome0514c.1.fid
13C 75.5MHz Job 24515 Nikodemiak Paul OME0514C CDCl3 25.0°C 0 hour 18 min
*
207.08
205.57
162.36
156.15
138.79
136.00
131.08
129.77
128.35
127.01
121.54
114.44
77.57 CDCl3
77.15 CDCl3
76.72 CDCl3
55.52
54.01
41.57
19.81
Me
O
O
MeO
2aa
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


c4bhh029fi1H 300.1MHz Job 29826 Beattie Nicholas A
*
3.84
3.24
1.40
Me
MeO
2ab
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9
f1 (ppm)
4.04
1.04
1.06
2.09
0.99
1.05
1.02
2.00
3.05
1.88
3.01
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


c4bcc29q
13C 100.6MHz Job 20158 Beattie Nicholas A C29Q CDCl3 25.7°C 1 hour 27 min
*
207.08
205.39
162.43
156.19
138.82
133.72
133.40
132.49
131.11
128.74
128.07
128.00
127.87
127.63
126.06
125.72
121.61
114.48
77.48 CDCl3
77.16 CDCl3
76.85 CDCl3
55.52
54.18
41.66
20.11
Me
MeO
2ab
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

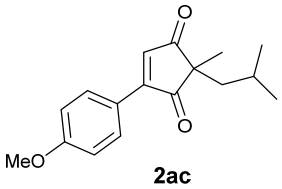
c5lh100cl1H 300.1MHz Job 33831 Lamb Claire J 100CL CDCl3 25.0°C
*



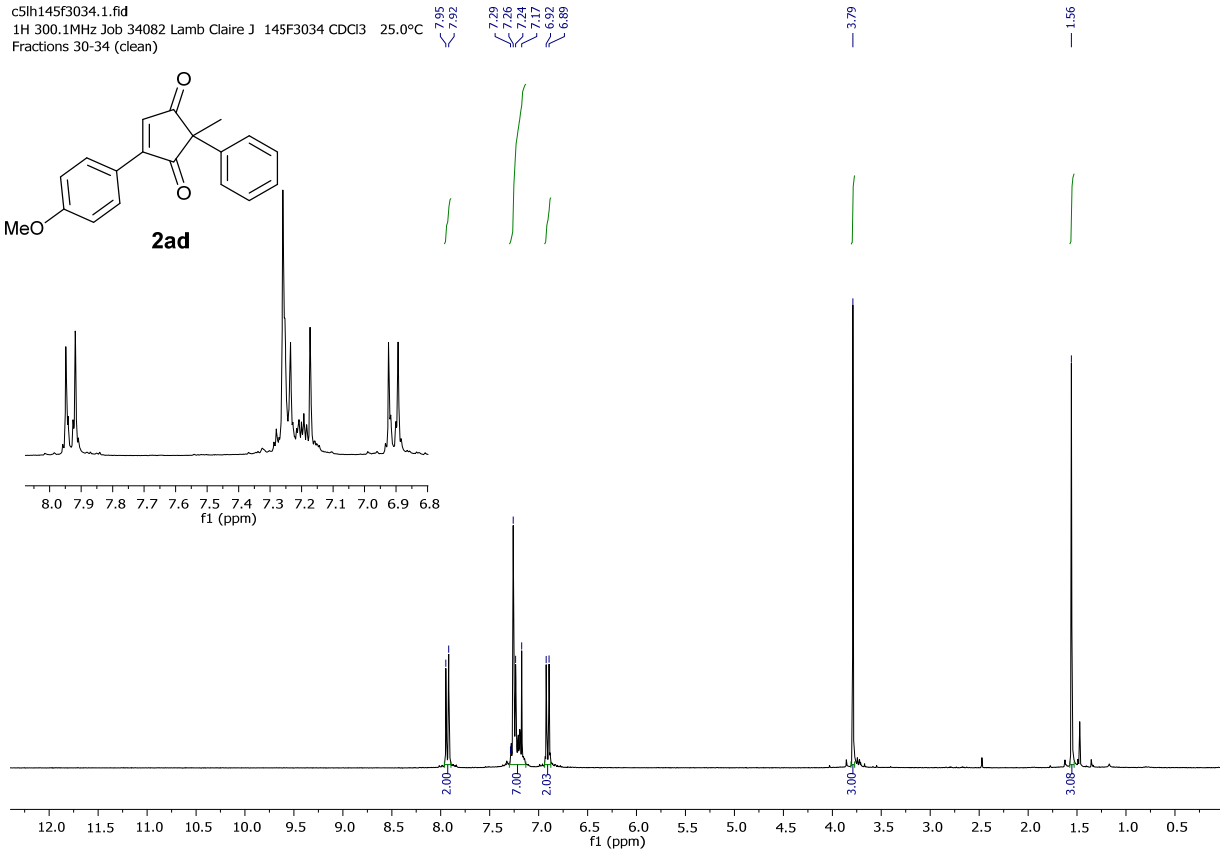

**2ac**

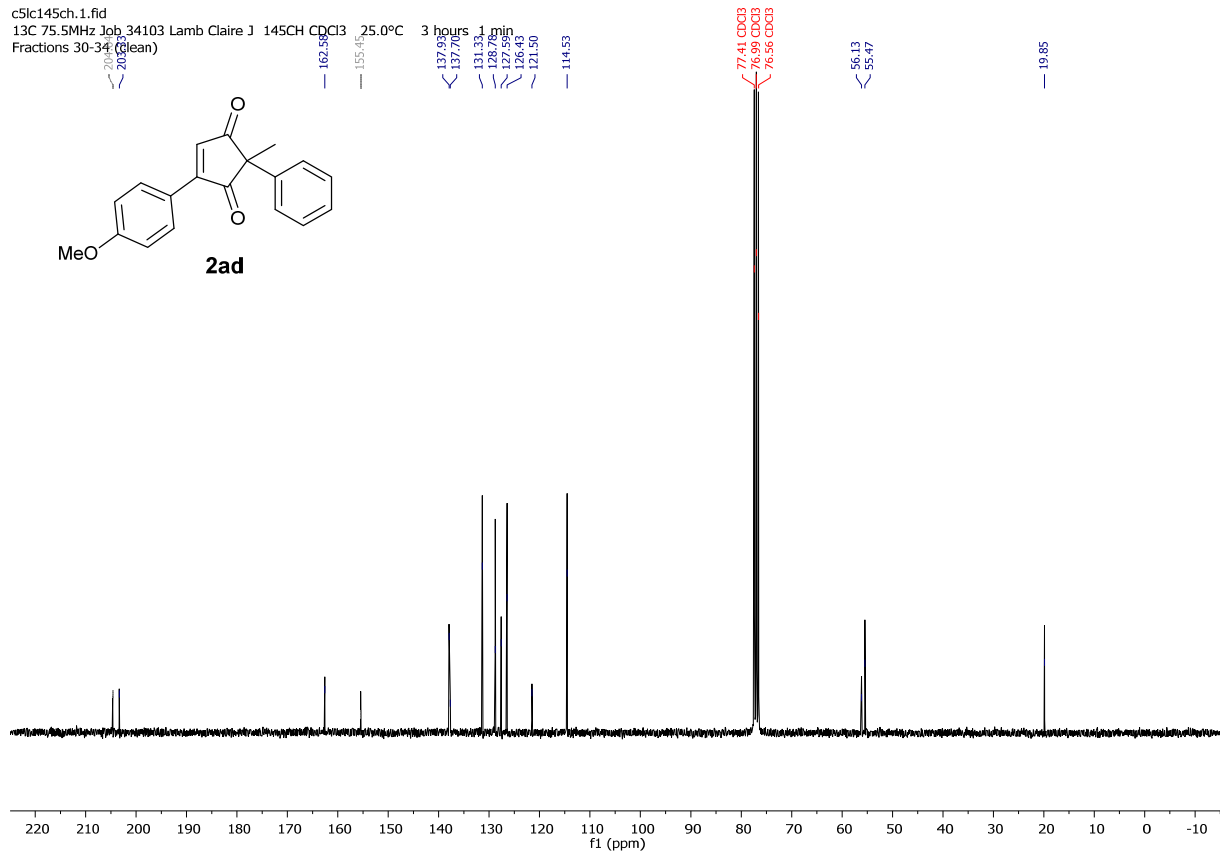


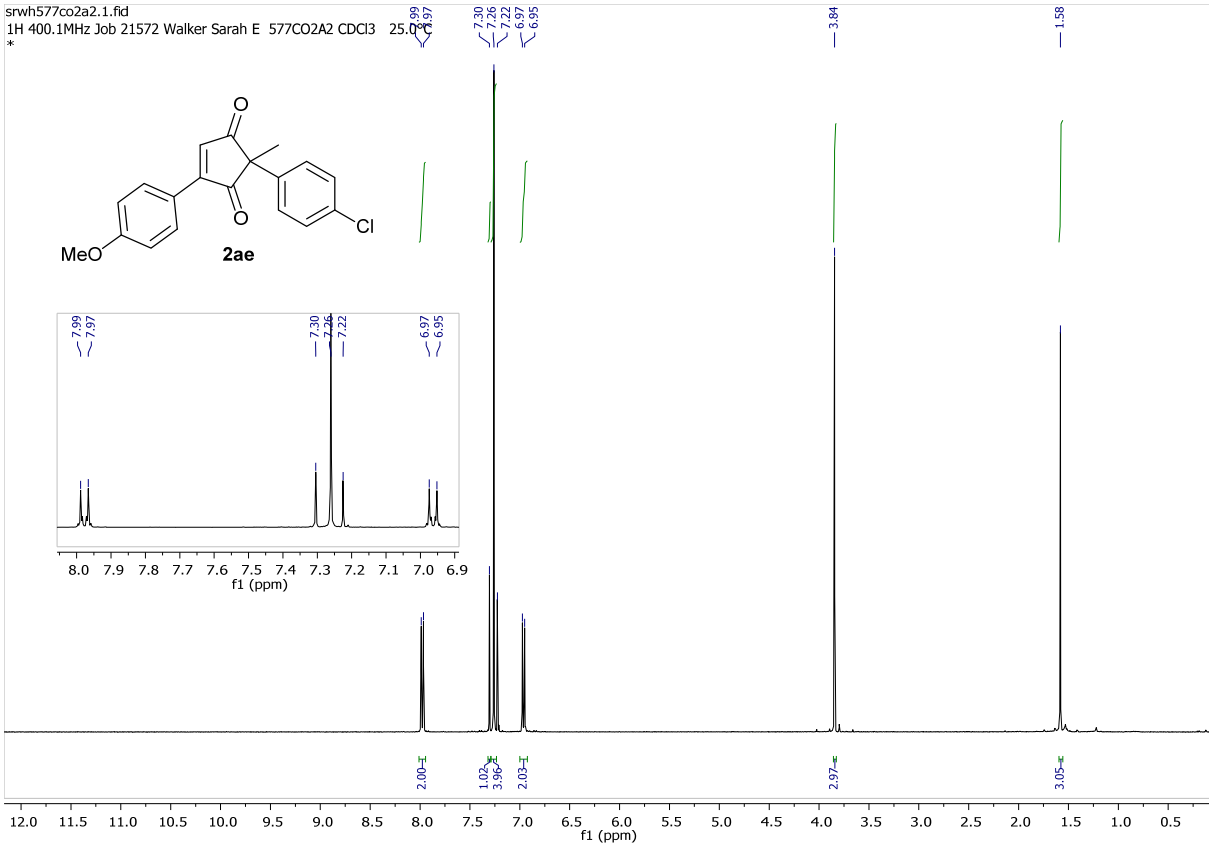

c5lccl157.1.fid
13C 100.6MHz Job 20544 Lamb Claire J CL157 CDCl3 25.0°C 4 hours 31 min
*

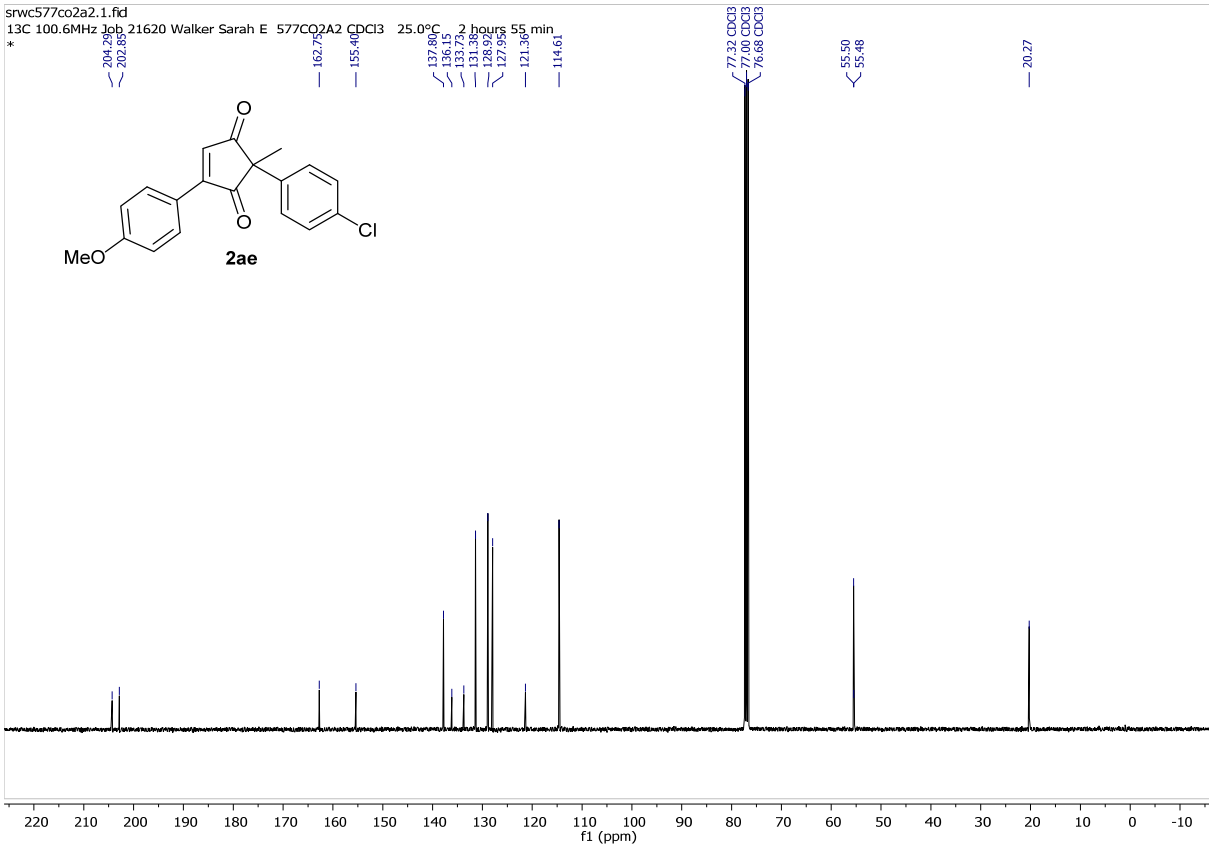


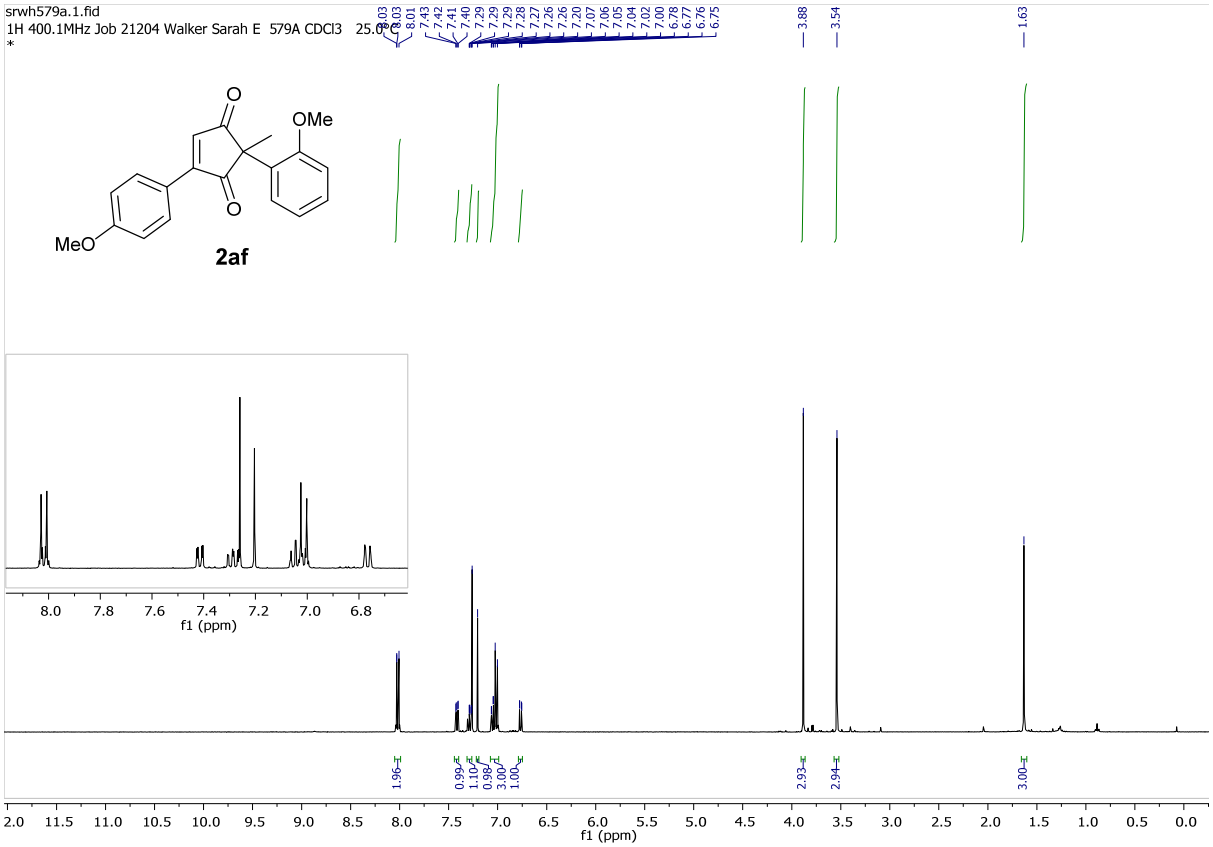

**2ac**

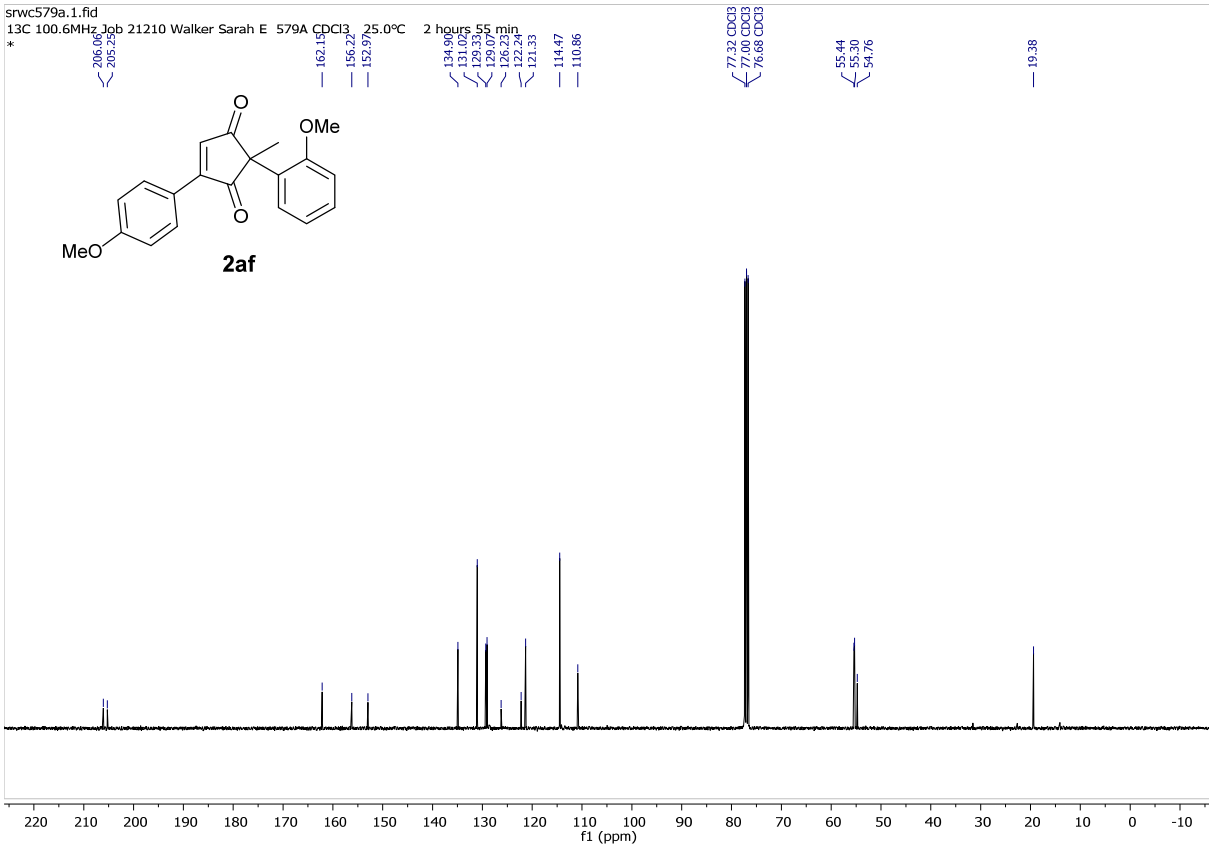

c5lh145f3034.1.fid
1H 300.1MHz Job 34082 Lamb Claire J 145F3034 CDCl3 25.0°C
Fractions 30-34 (clean)
7.95
7.92
7.29
7.26
7.24
7.17
6.92
6.89
3.79
1.56
MeO
2ad
2.00
7.00
2.03
3.00
3.08
f1 (ppm)

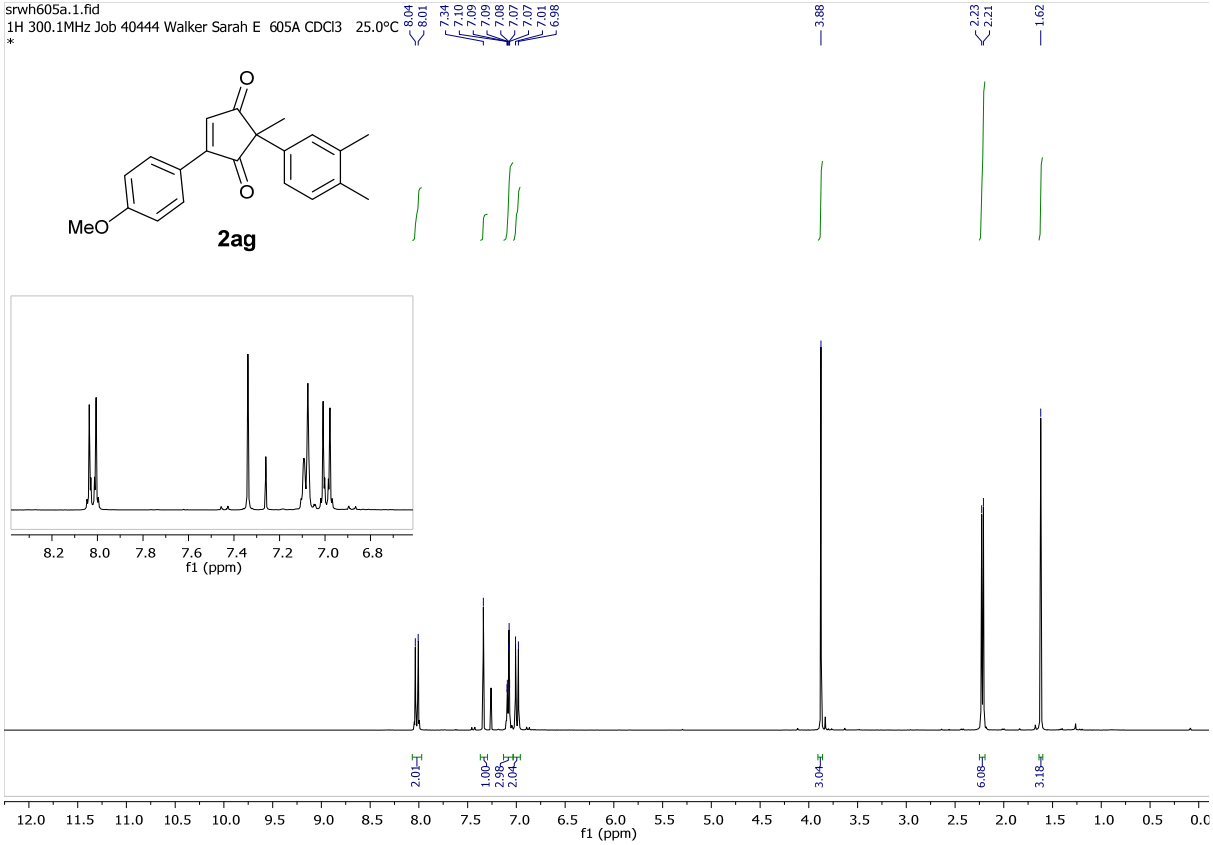

c5lc145ch.1.fid
13C 75.5MHz Job 34103 Lamb Claire J 145CH CDCl3 25.0°C 3 hours 1 min
Fractions 30-34 (clean)
162.56
155.45
137.93
137.70
131.33
128.78
127.55
126.43
121.50
114.53
77.41 CDCl3
76.99 CDCl3
76.56 CDCl3
56.13
55.47
19.85
MeO
2ad
f1 (ppm)

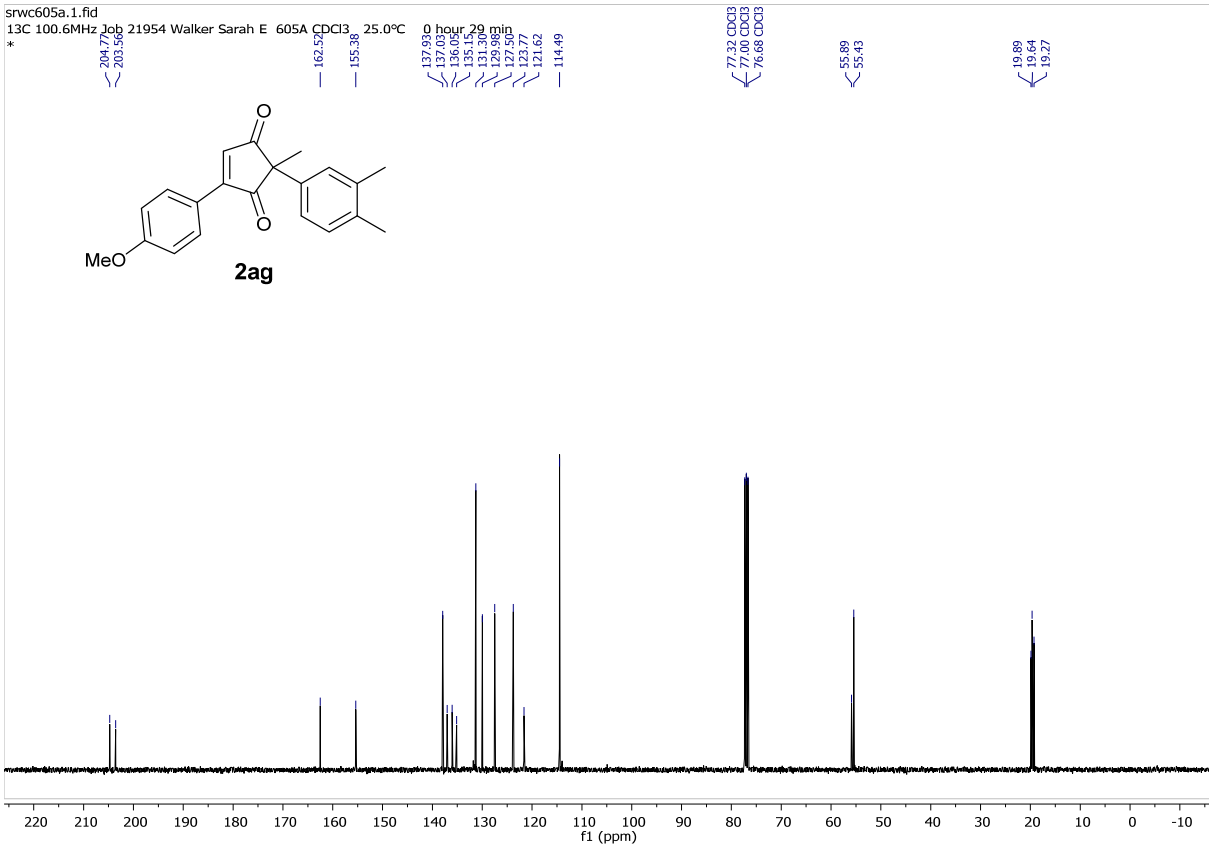

srwh577co2a2.1.fid
1H 400.1MHz Job 21572 Walker Sarah E 577CO2A2 CDCl3 25.0°C
*
7.99
7.97
7.30
7.26
7.22
6.97
6.95
3.84
1.58
O
O
Cl
MeO
2ae
2.00
1.02
3.96
2.03
2.97
3.05
f1 (ppm)

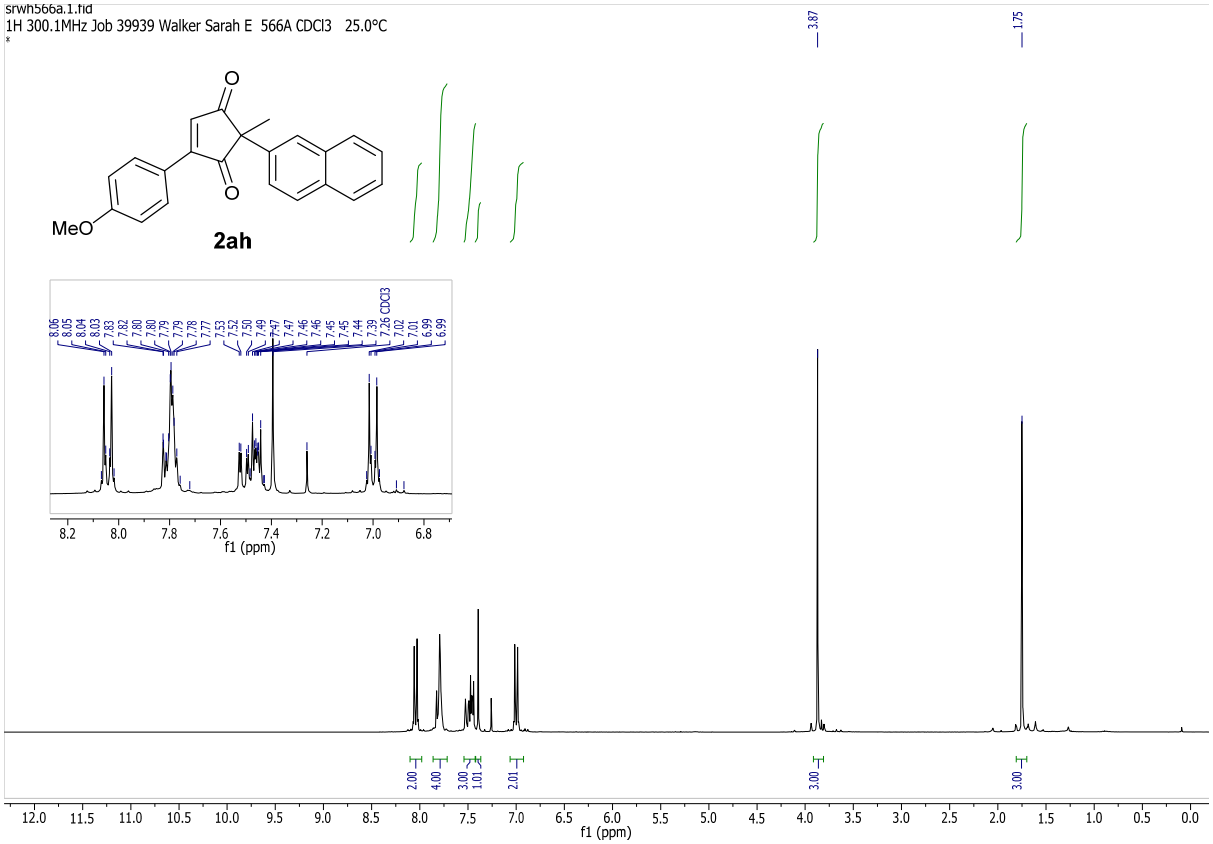

srwc577co2a2.1.fid
13C 100.6MHz Job 21620 Walker Sarah E 577CO2A2 CDCl3 25.0°C 2 hours 55 min
*
204.29
202.85
162.75
155.40
137.80
136.15
133.73
131.38
128.92
127.95
121.36
114.61
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
55.50
55.48
20.27
O
O
Cl
MeO
2ae
f1 (ppm)

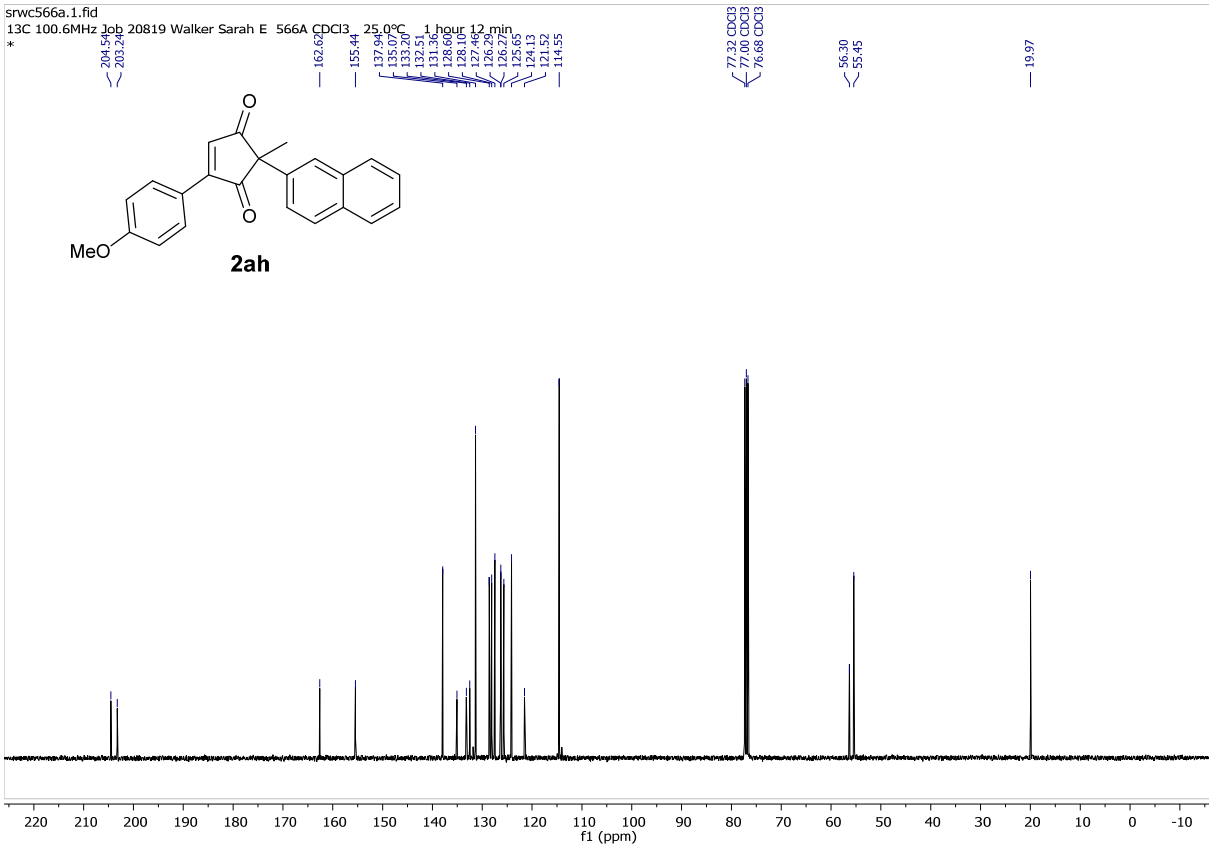

srwh579a.1.fid
1H 400.1MHz Job 21204 Walker Sarah E 579A CDCl3 25.0°C
*
OMe
MeO
2af
f1 (ppm)


srwc579a.1.fid
13C 100.6MHz Job 21210 Walker Sarah E 579A CDCl3 25.0°C 2 hours 55 min
*
OMe
MeO
2af
f1 (ppm)

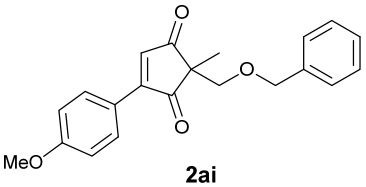

srwh605a.1.fid
1H 300.1MHz Job 40444 Walker Sarah E 605A CDCl3 25.0°C
*
8.04
8.01
7.34
7.10
7.09
7.09
7.08
7.07
7.07
7.01
6.98
3.88
2.23
2.21
1.62
MeO
2ag
f1 (ppm)
2.01
1.00
2.98
2.04
3.04
6.08
3.18


srwc605a.1.fid
13C 100.6MHz Job 21954 Walker Sarah E 605A CDCl3 25.0°C 0 hour 29 min
*
204.77
203.56
162.52
155.38
137.93
137.03
136.05
135.15
131.30
129.98
127.50
123.77
121.62
114.49
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
55.89
55.43
19.89
19.64
19.27
MeO
2ag
f1 (ppm)


srwh566a.1.fid
1H 300.1MHz Job 39939 Walker Sarah E 566A CDCl3 25.0°C
MeO
2ah
f1 (ppm)


srwc566a.1.fid
13C 100.6MHz Job 20819 Walker Sarah E 566A CDCl3 25.0°C 1 hour 12 min
MeO
2ah
f1 (ppm)

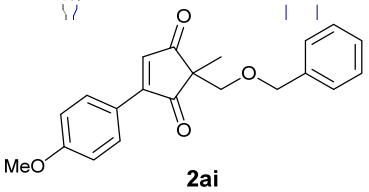
c5lh141prod1H 300.1MHz Job 33137 Lamb Claire J 141PROD CDCl3 25.1°C
Product after recolumn



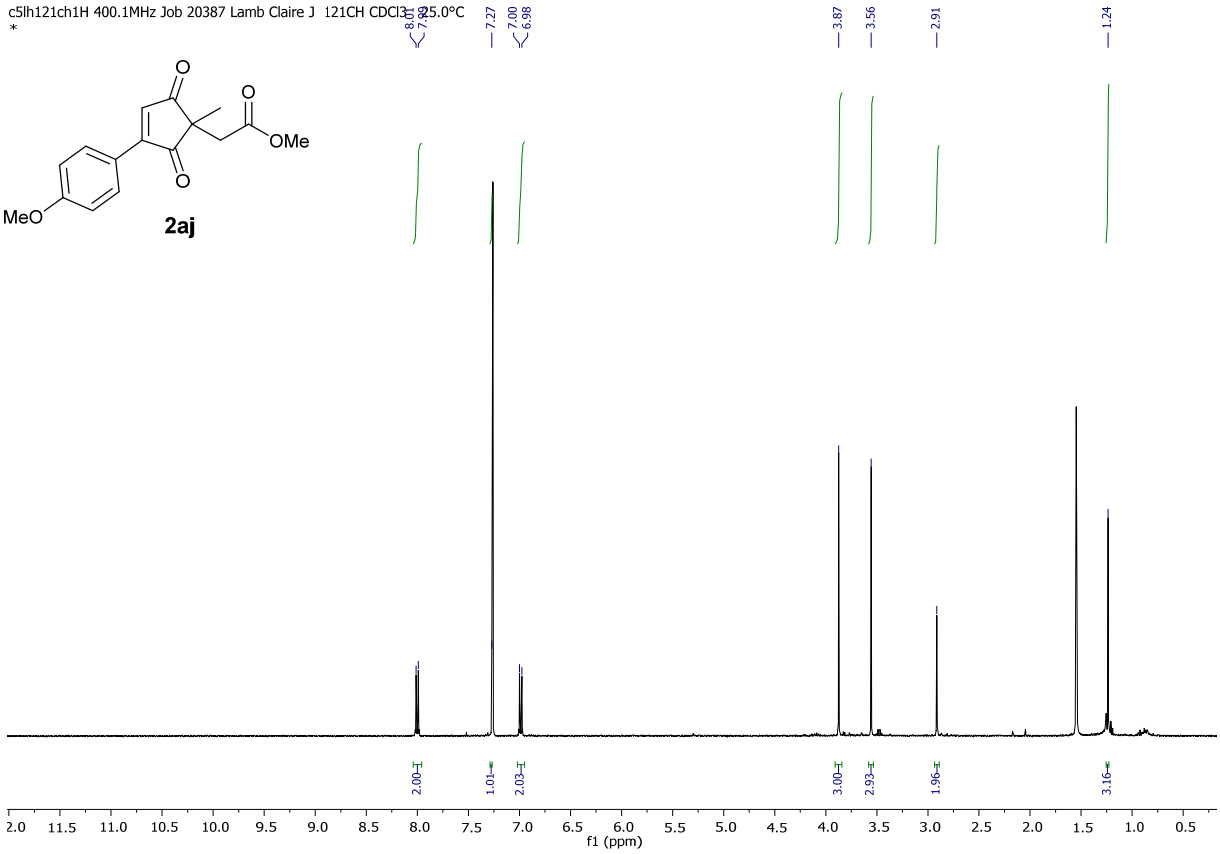

**2ai**

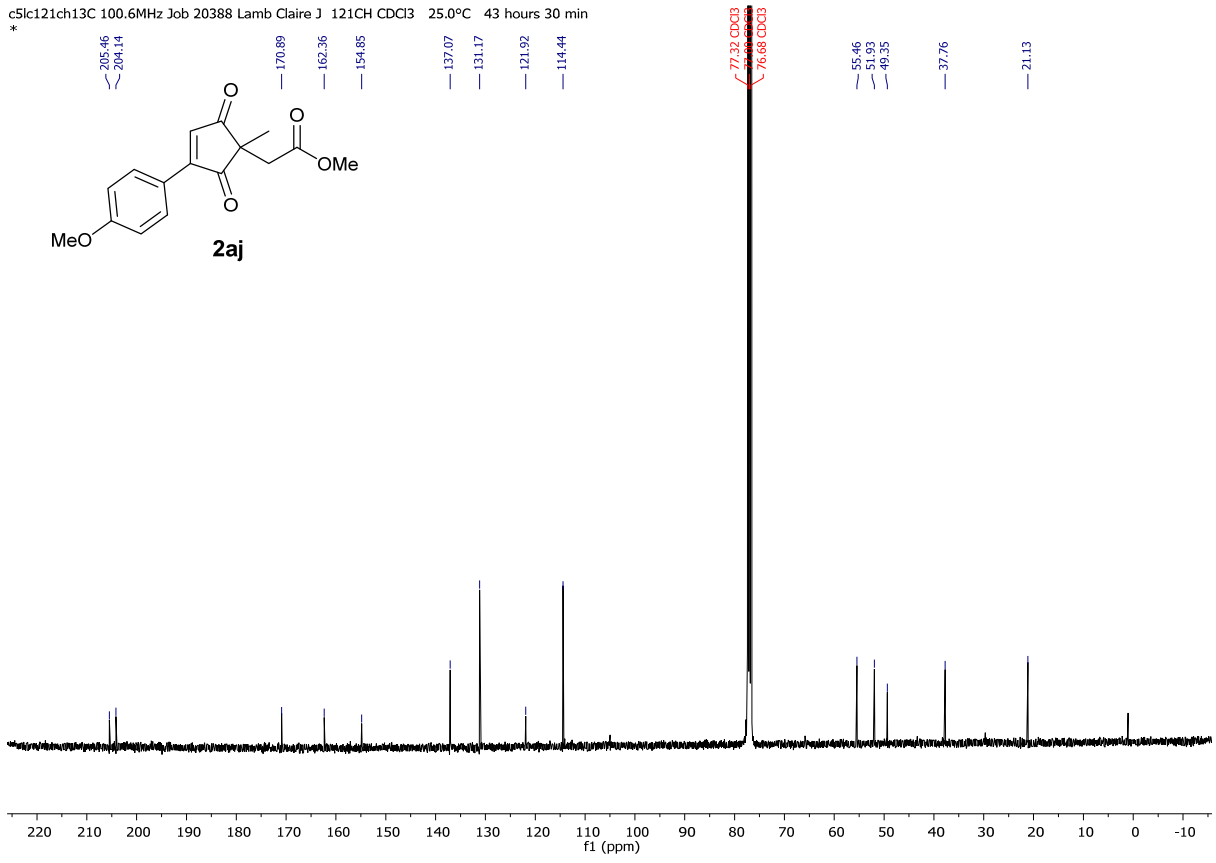


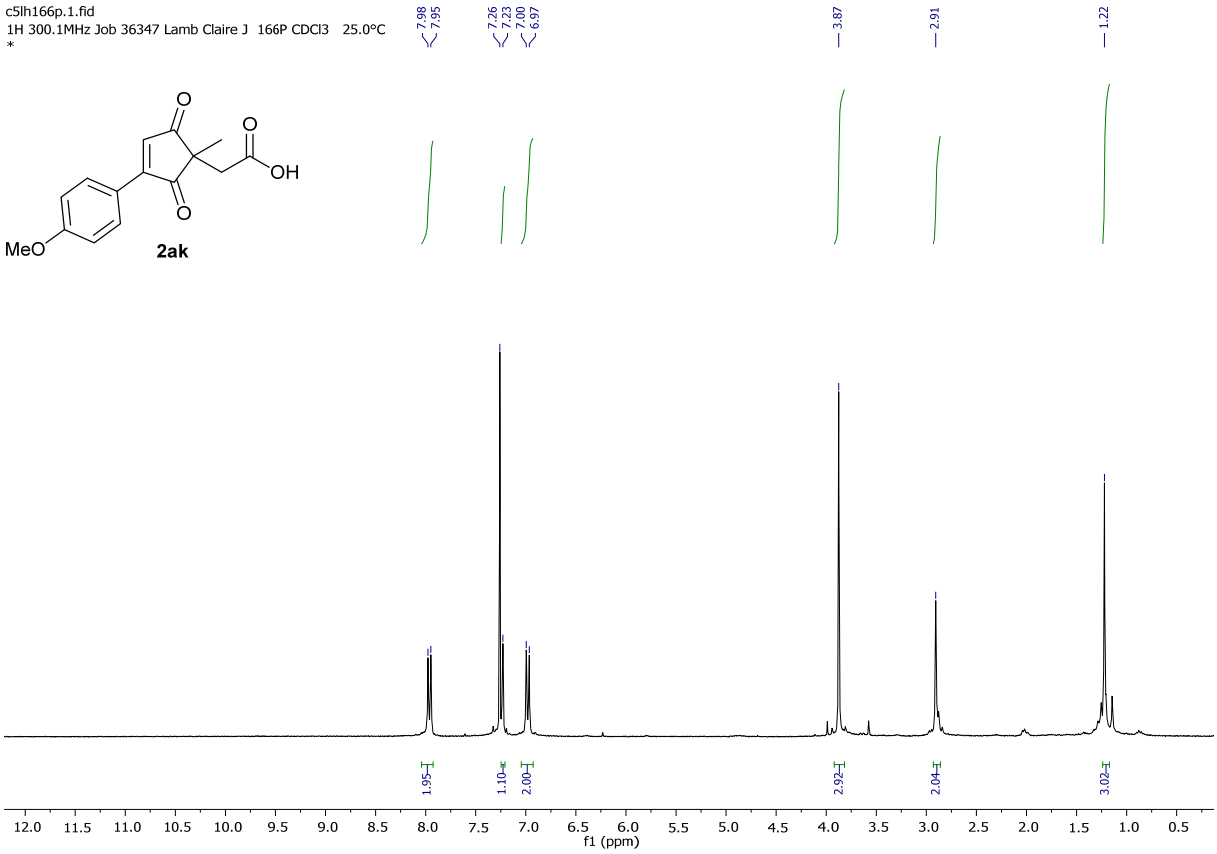

c5lc141prod13C 75.5MHz Job 33162 Lamb Claire J 141PROD CDCl3 25.0°C 3 hours 1 min
product after recolumn

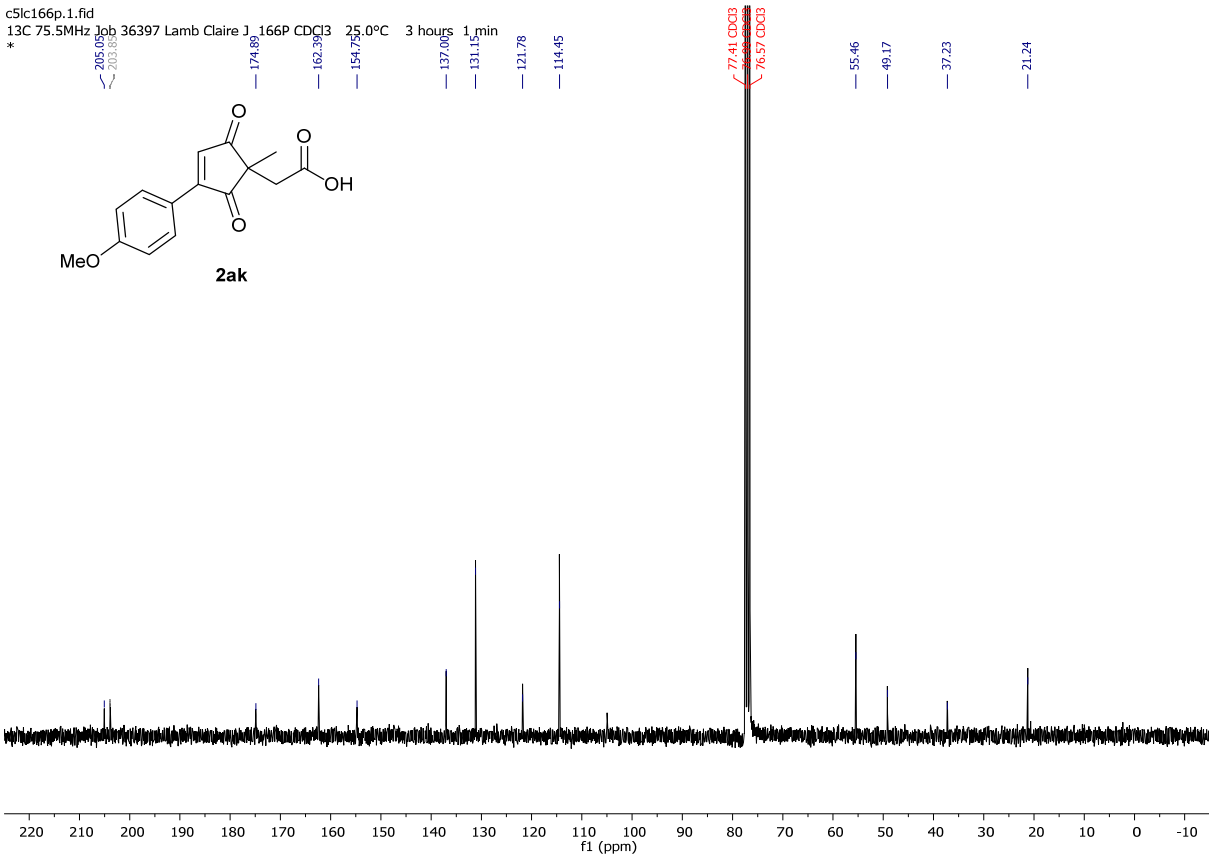



**2ai**

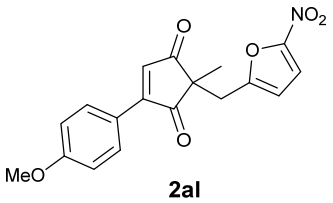

c5lh121ch1H 400.1MHz Job 20387 Lamb Claire J 121CH CDCl3 25.0°C
*
8.01
7.99
7.27
7.00
6.98
3.87
3.56
2.91
1.24
O
O
OMe
O
MeO
2aj
2.00
1.01
2.03
3.00
2.93
1.96
3.16
f1 (ppm)


c5lc121ch13C 100.6MHz Job 20388 Lamb Claire J 121CH CDCl3 25.0°C 43 hours 30 min
*
205.46
204.14
170.89
162.36
154.85
137.07
131.17
121.92
114.44
77.32 CDCl3
76.68 CDCl3
55.46
51.93
49.35
37.76
21.13
O
O
OMe
O
MeO
2aj
f1 (ppm)


c5lh166p.1.fid
1H 300.1MHz Job 36347 Lamb Claire J 166P CDCl3 25.0°C
*
7.98
7.95
7.26
7.23
7.00
6.97
3.87
2.91
1.22
O
O
OH
O
MeO
2ak
1.95
1.10
2.00
2.92
2.04
3.02
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


c5lc166p.1.fid
13C 75.5MHz Job 36397 Lamb Claire J 166P CDCl3 25.0°C 3 hours 1 min
*
205.05
203.85
174.89
162.39
154.75
137.05
131.15
121.78
114.45
77.41 CDCl3
76.57 CDCl3
55.46
49.17
37.23
21.24
O
O
OH
O
MeO
2ak
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

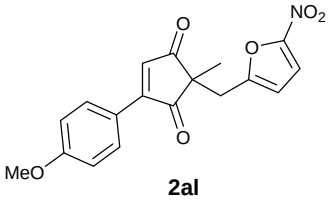
c5lh157f38a.1.fid
1H 300.1MHz Job 35445 Lamb Claire J 157F38A CDCl3 24.8°C
FRactions 38-60



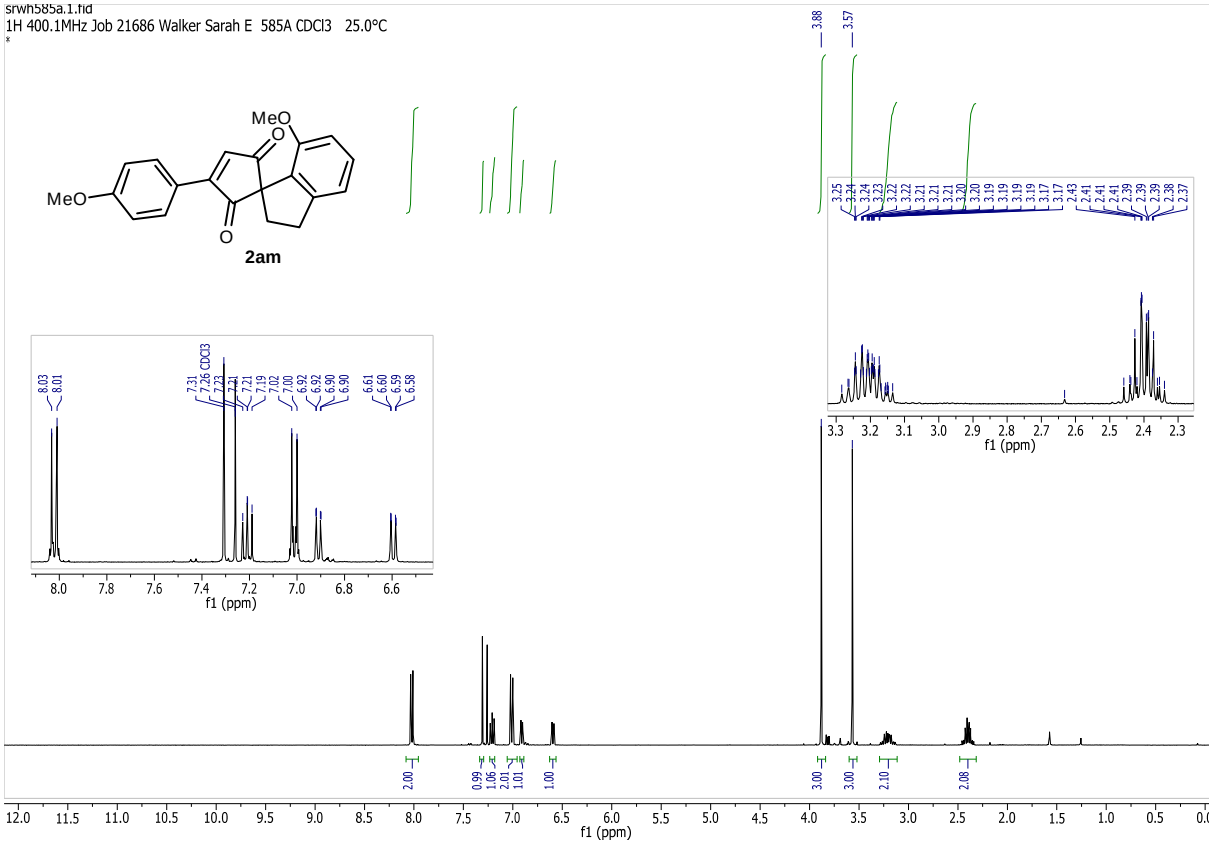

**2al**

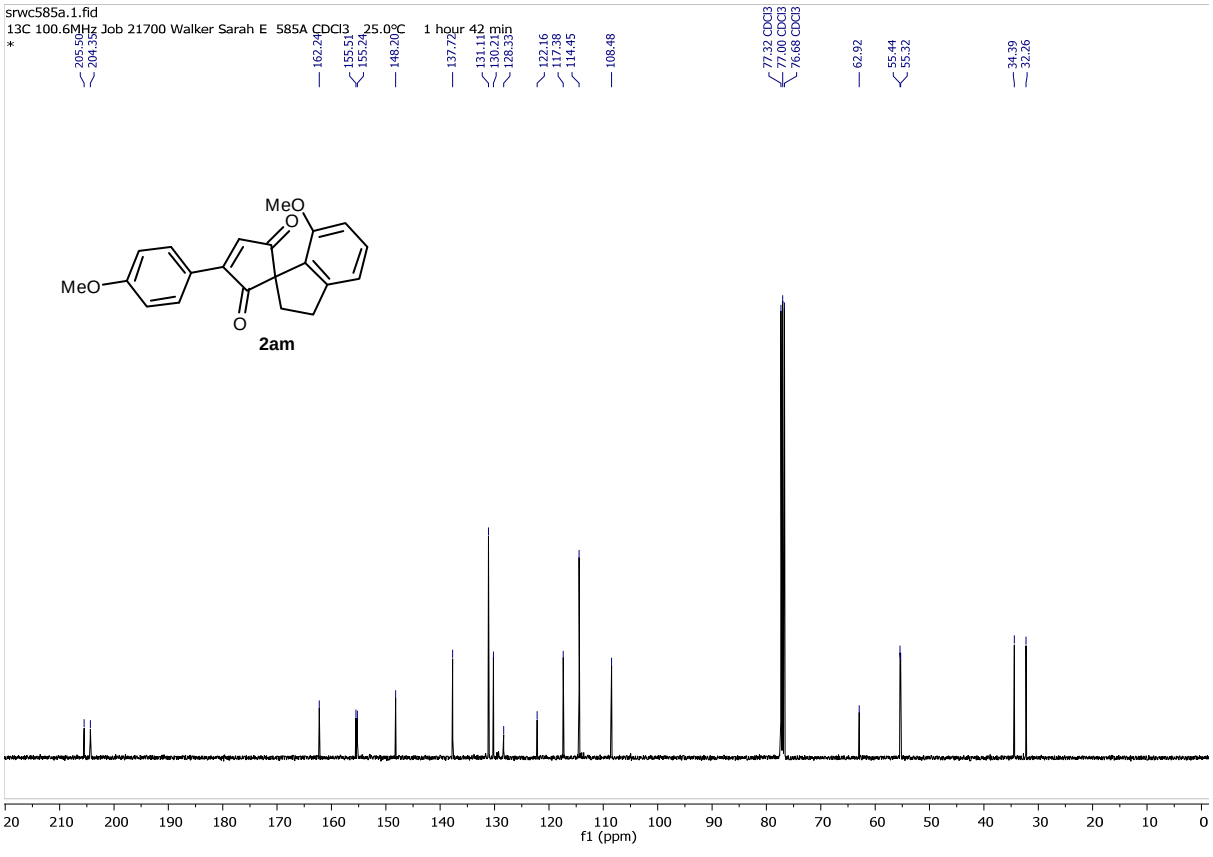


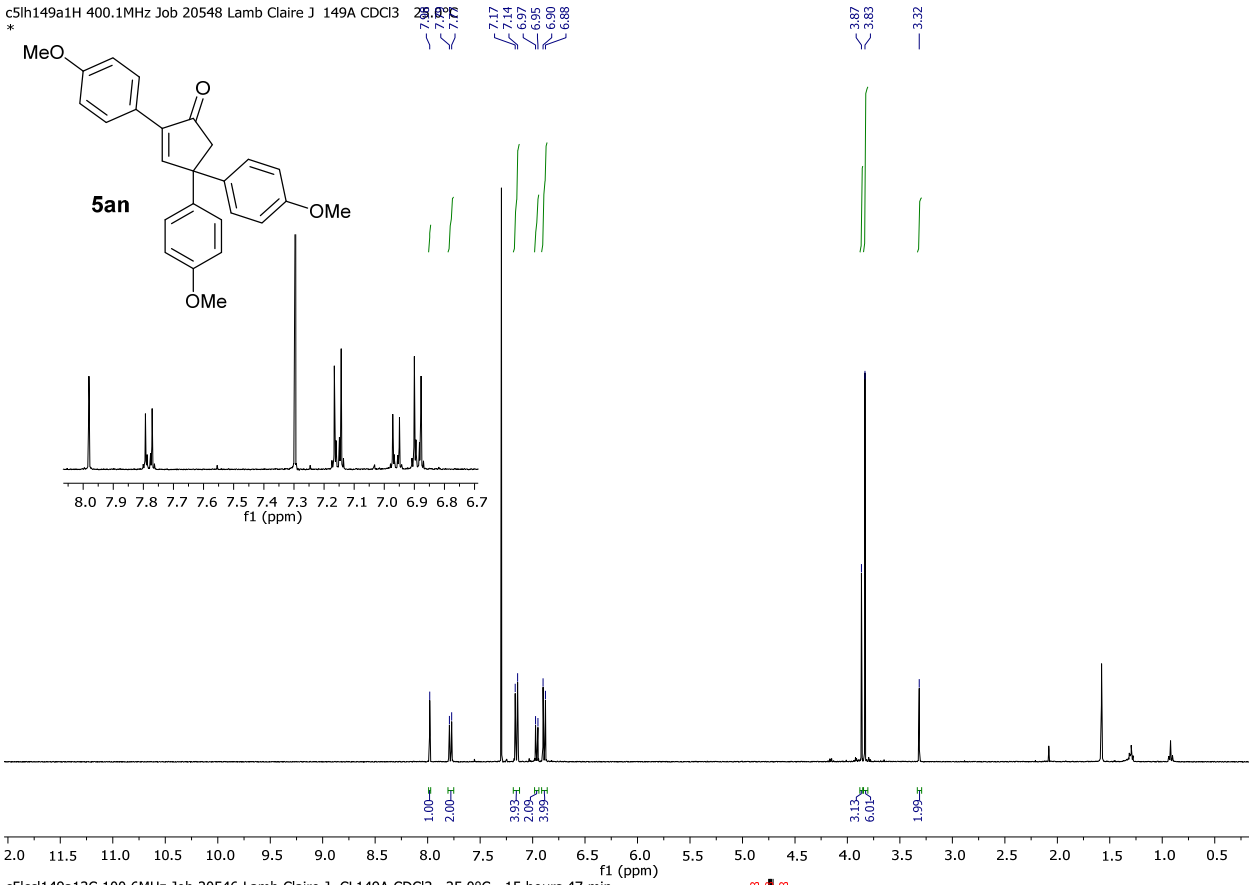

c5lccl157.1.fid
13C 100.6MHz Job 20544 Lamb Claire J CL157 CDCl3 25.0°C 4 hours 51 min
*

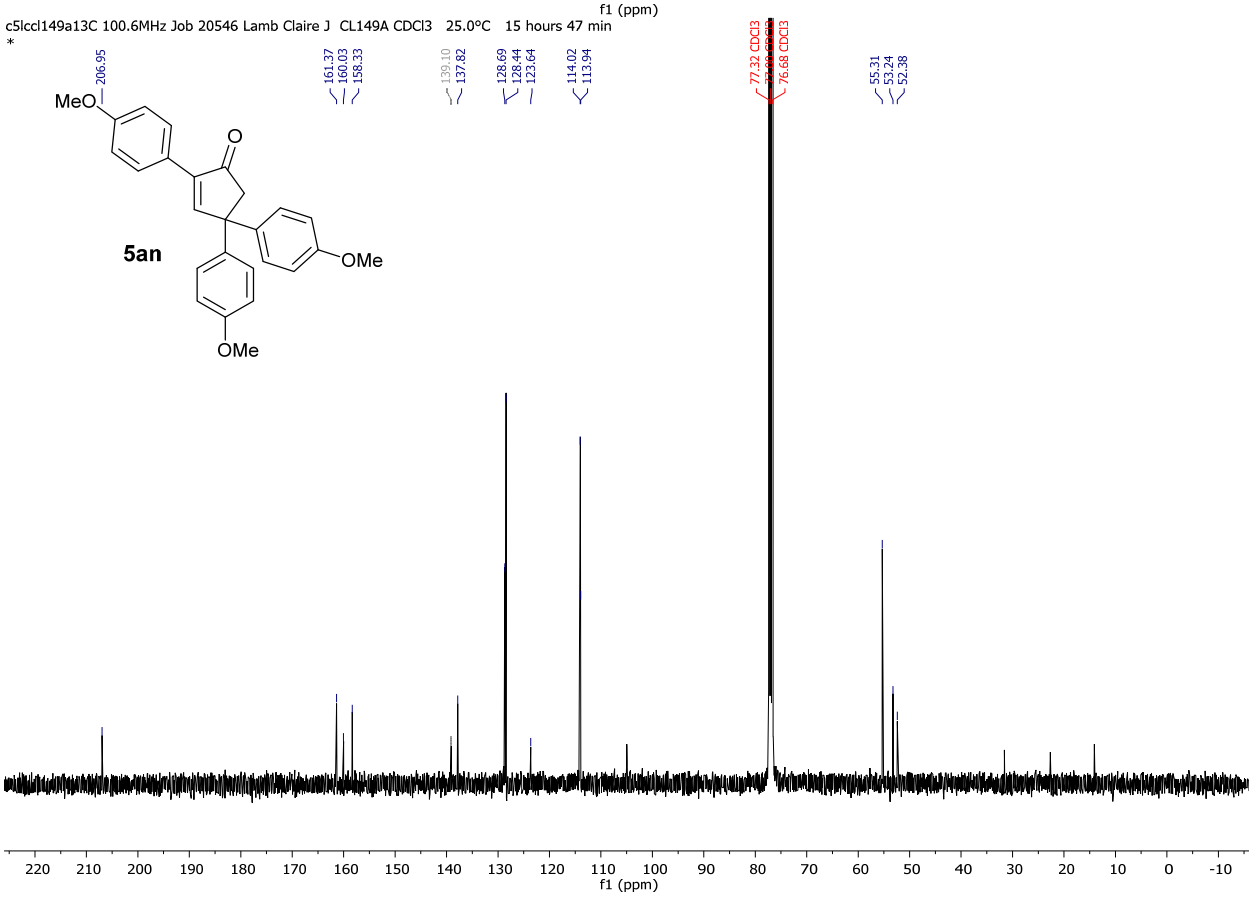


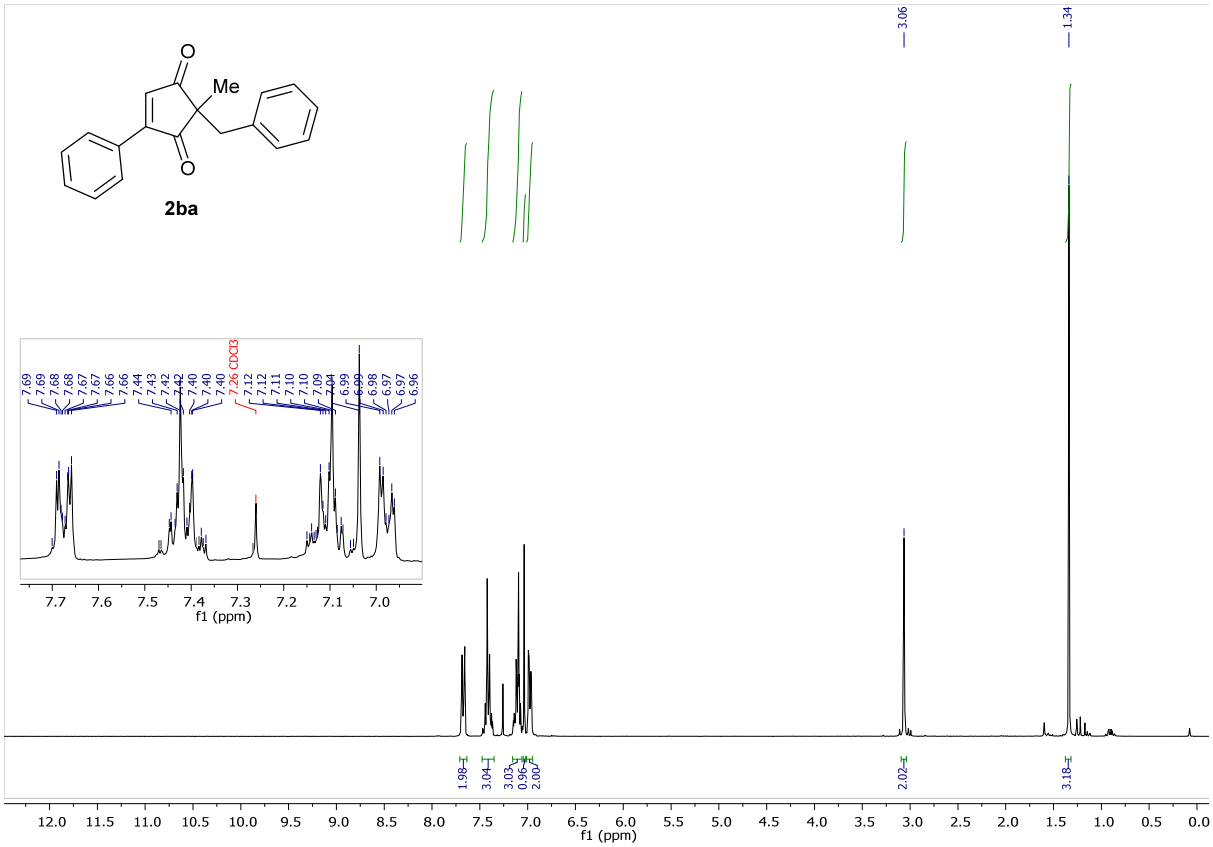

**2al**

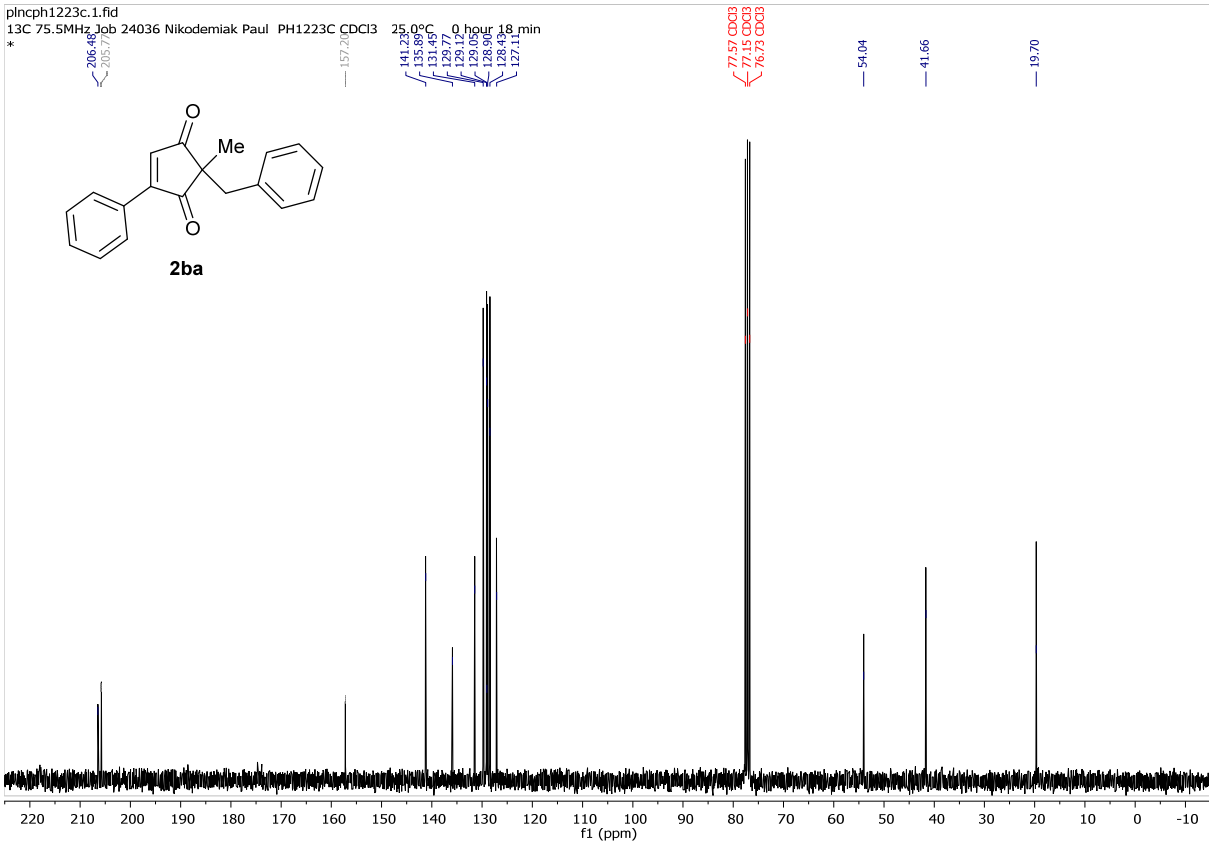

srwh585a.1.fid
1H 400.1MHz Job 21686 Walker Sarah E 585A CDCl3 25.0°C
MeO
O
MeO
O
2am
f1 (ppm)

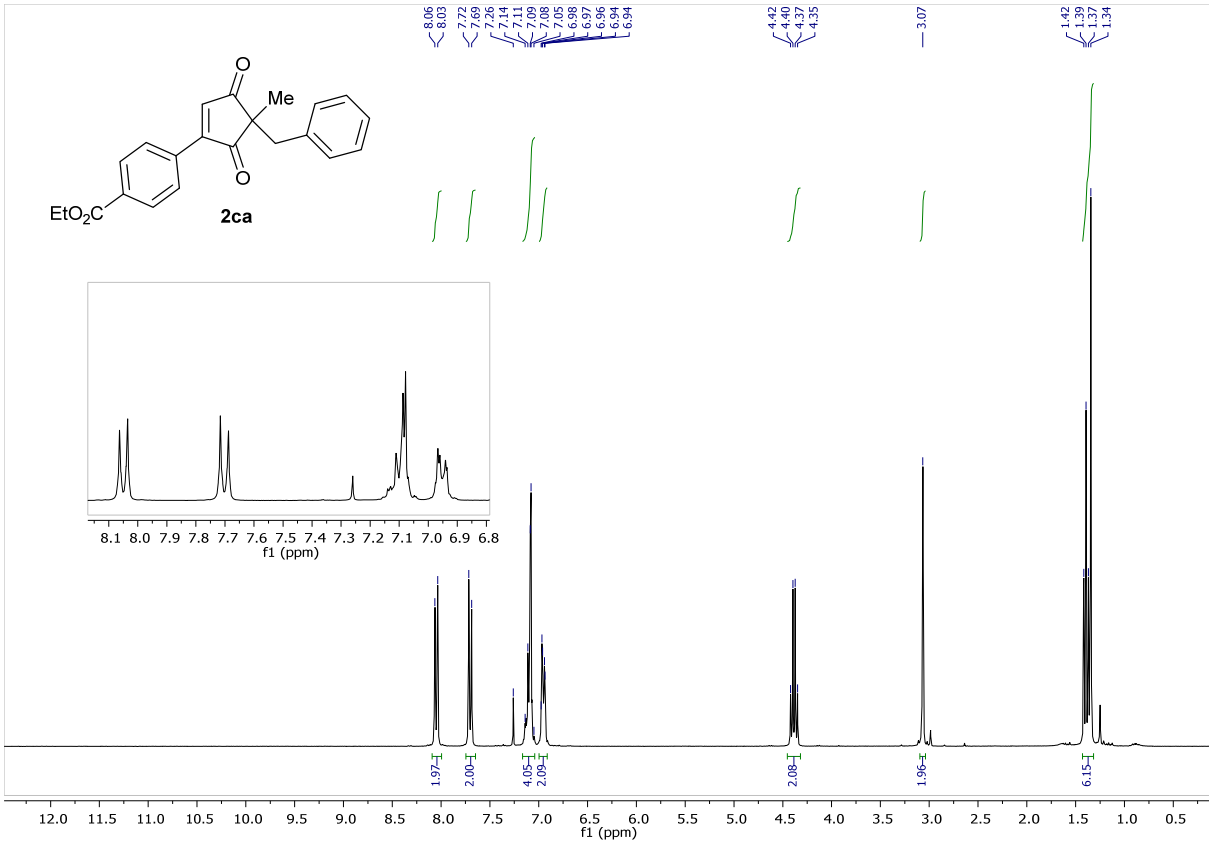

srwc585a.1.fid
13C 100.6MHz Job 21700 Walker Sarah E 585A CDCl3 25.0°C 1 hour 42 min
MeO
O
MeO
O
2am
f1 (ppm)

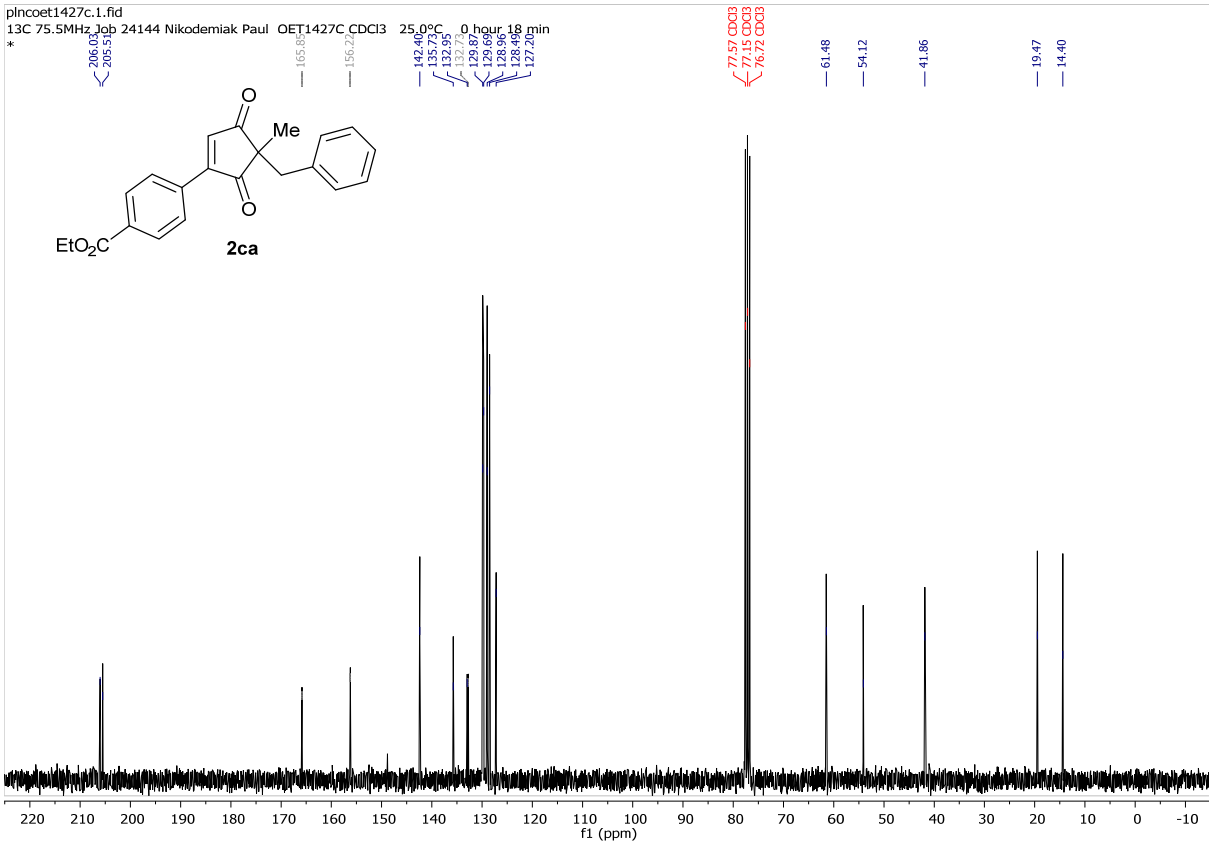

c5lh149a1H 400.1MHz Job 20548 Lamb Claire J 149A CDCl3
MeO
O
OMe
OMe
5an
f1 (ppm)

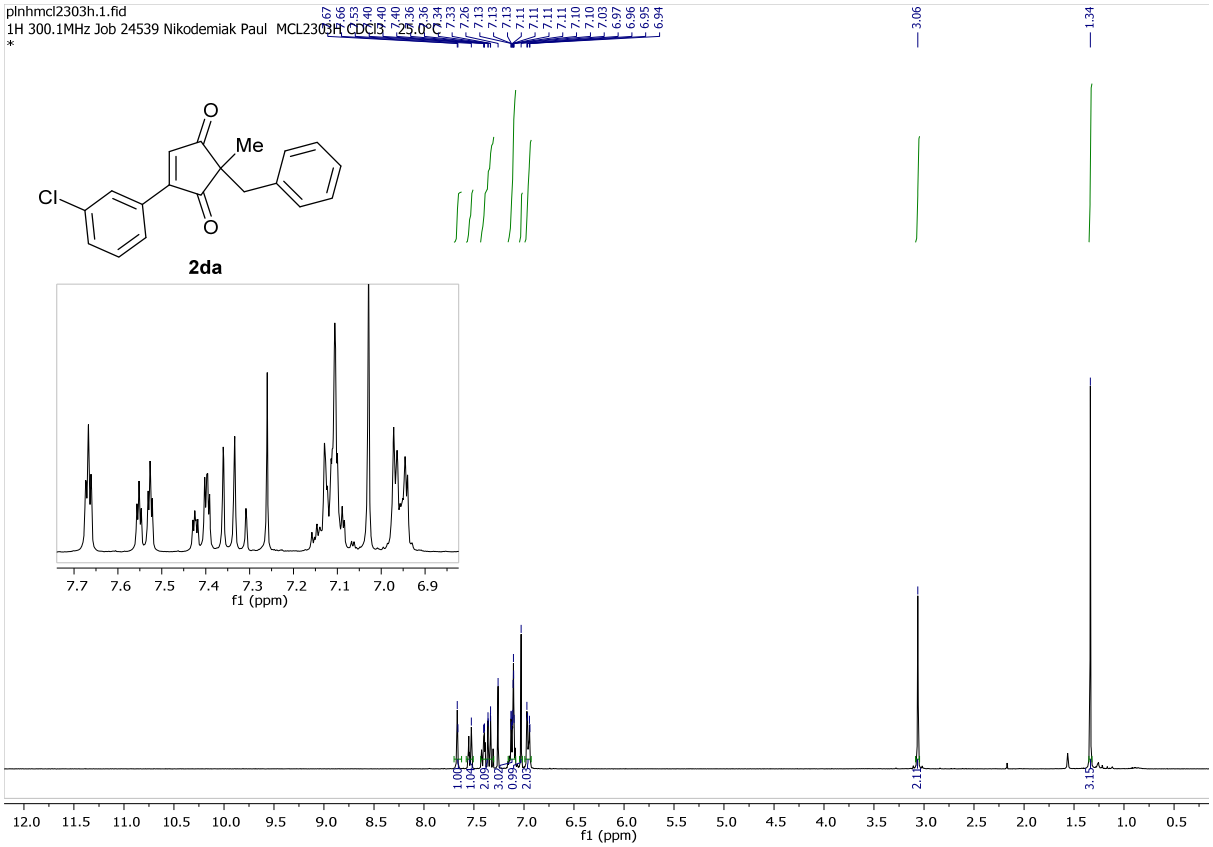

c5lccl149a13C 100.6MHz Job 20546 Lamb Claire J CL149A CDCl3 25.0°C 15 hours 47 min
MeO
O
OMe
OMe
5an
77.32 CDCl3
76.68 CDCl3
f1 (ppm)

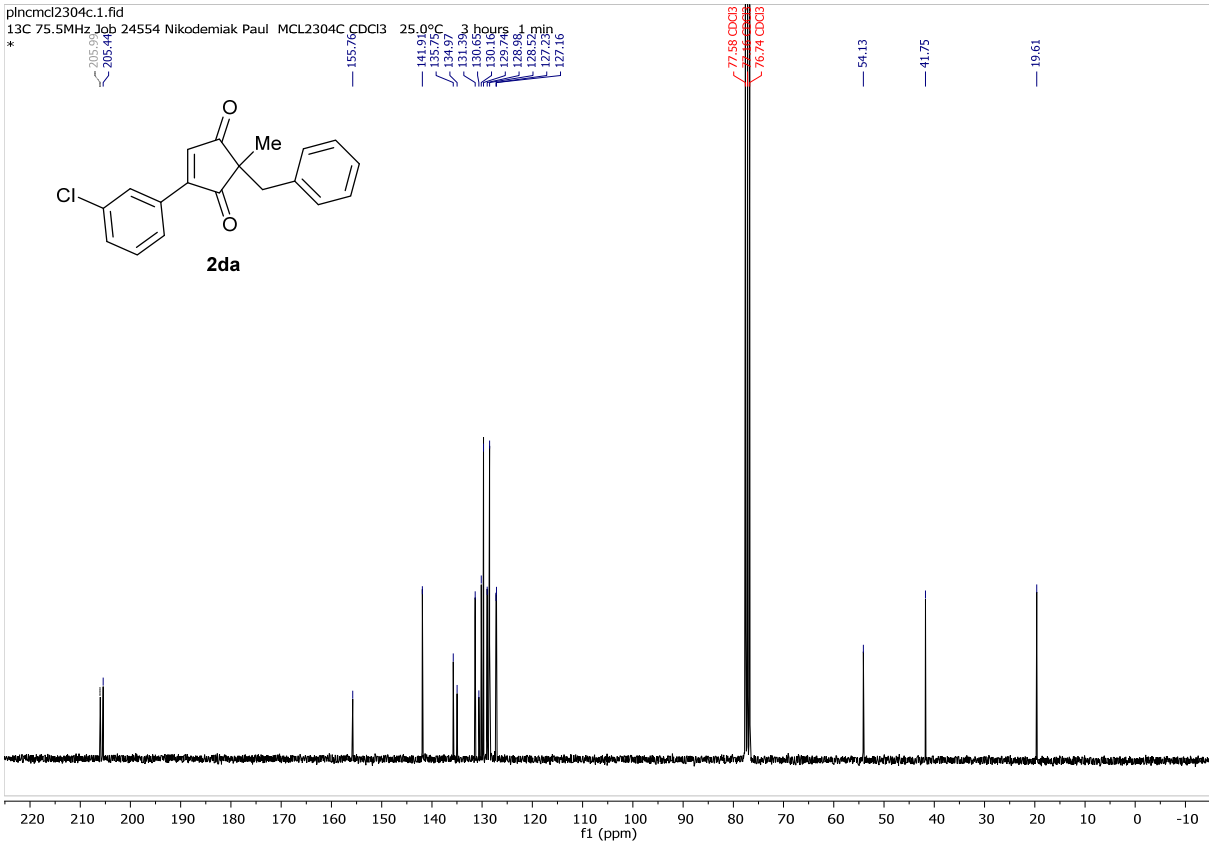

Me
2ba
3.06
1.34
7.69
7.69
7.68
7.68
7.67
7.67
7.66
7.66
7.44
7.43
7.42
7.42
7.40
7.40
7.40
7.26 CDCl3
7.12
7.12
7.11
7.10
7.10
7.09
7.04
6.99
6.99
6.98
6.97
6.97
6.96
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0
f1 (ppm)
1.98
3.04
3.03
0.96
2.00
2.02
3.18
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

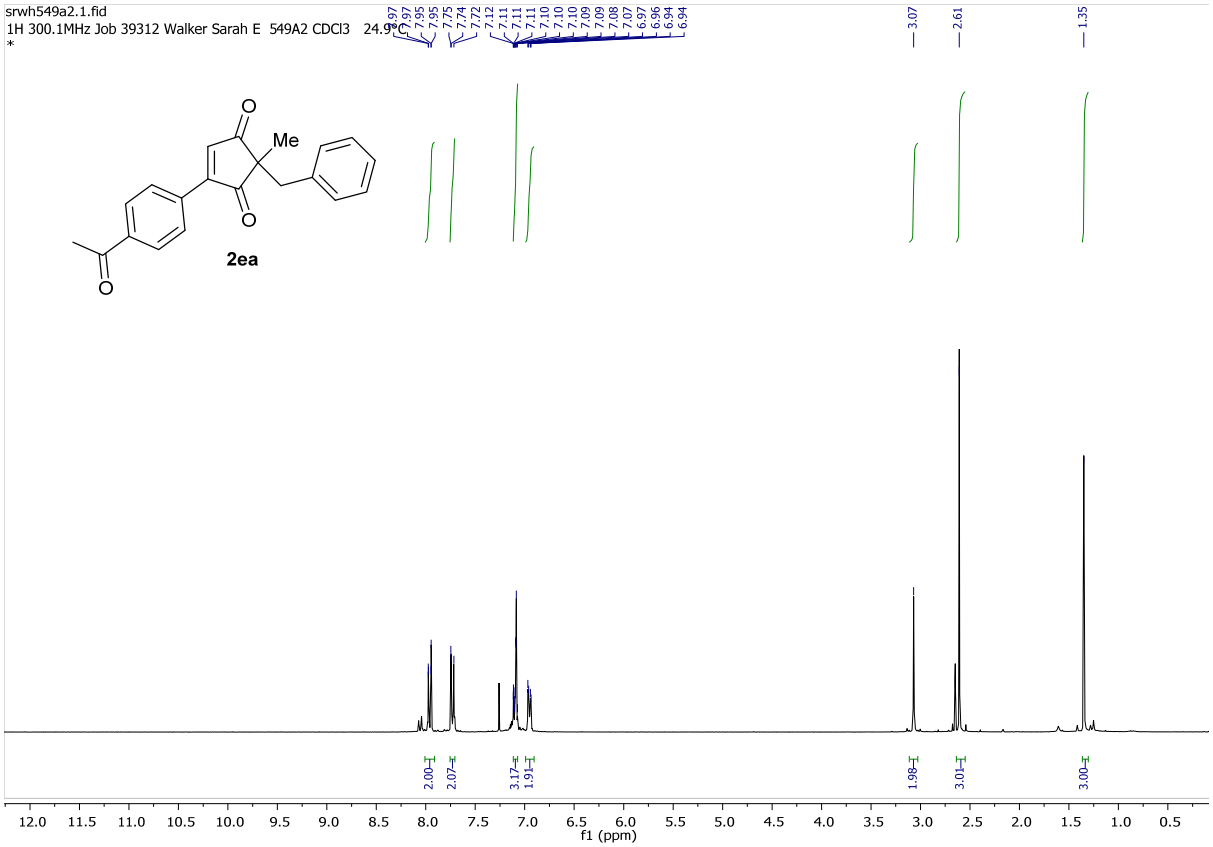

plncph1223c.1.fid
13C 75.5MHz Job 24036 Nikodemiak Paul PH1223C CDCl3 25.0°C 0 hour 18 min
*
206.48
205.77
157.20
141.23
135.89
131.45
129.77
129.12
129.05
128.90
128.43
127.11
77.57 CDCl3
77.15 CDCl3
76.73 CDCl3
54.04
41.66
19.70
Me
2ba
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

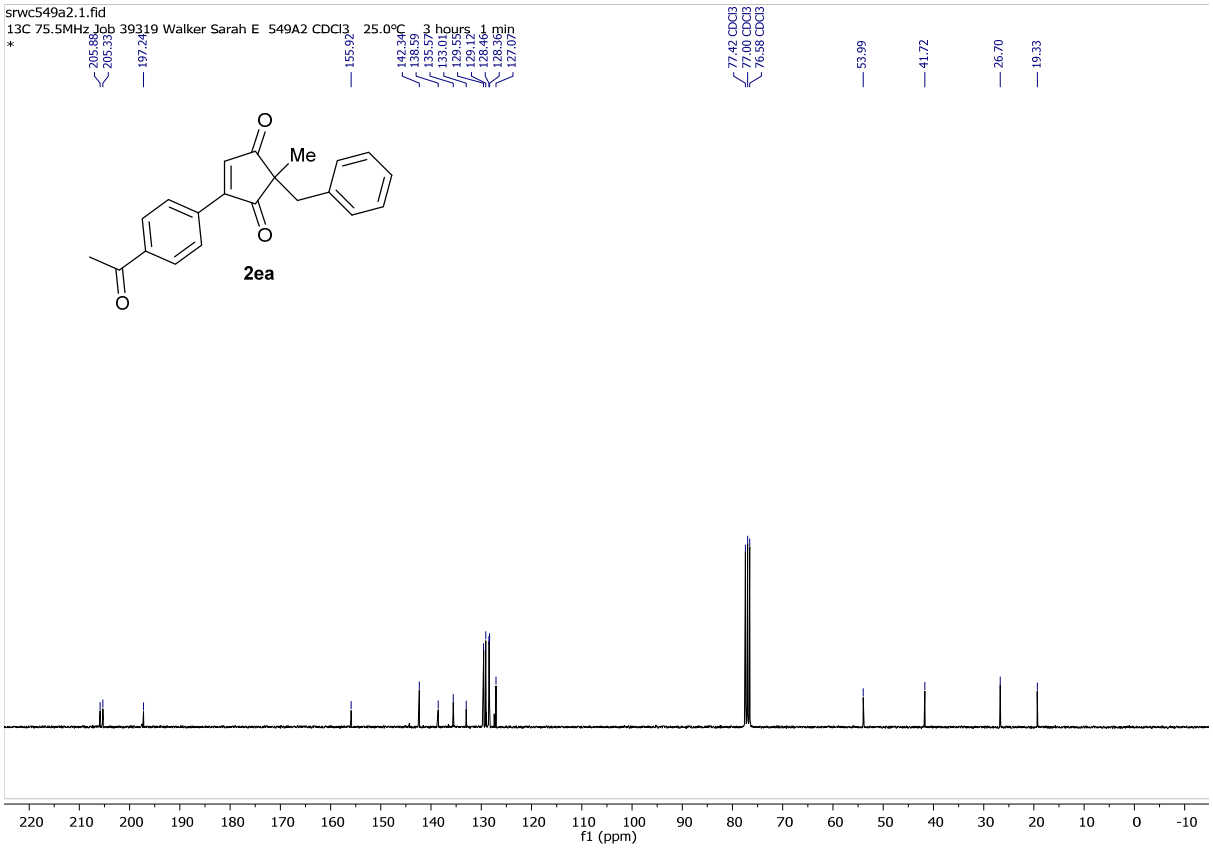

8.06
8.03
7.72
7.69
7.26
7.14
7.11
7.09
7.08
7.05
6.98
6.97
6.96
6.94
6.94
4.42
4.40
4.37
4.35
3.07
1.42
1.39
1.37
1.34
Me
O
O
EtO2C
2ca
8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8
f1 (ppm)
1.97
2.00
4.05
2.09
2.08
1.96
6.15
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

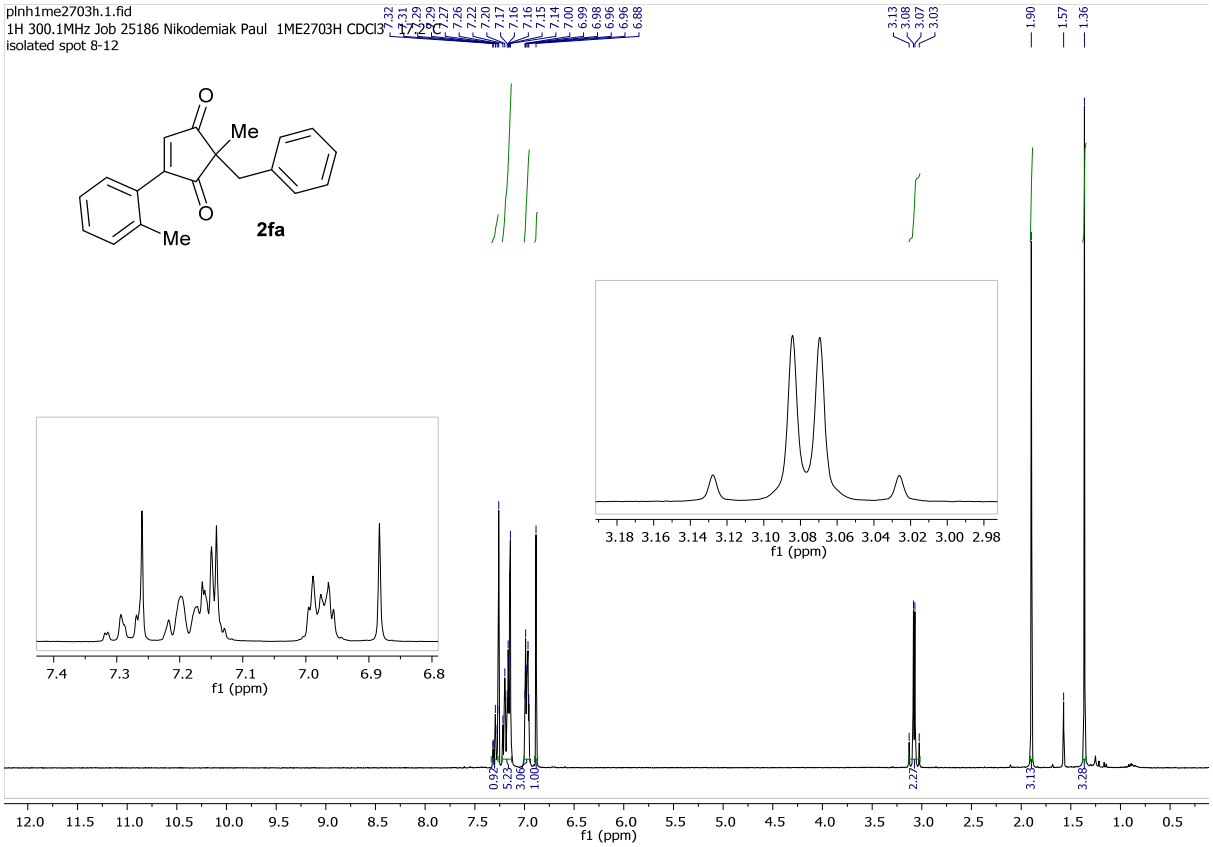

plncoet1427c.1.fid
13C 75.5MHz Job 24144 Nikodemiak Paul OET1427C CDCl3 25.0°C 0 hour 18 min
*
206.03
205.51
165.87
156.22
142.46
135.73
132.95
132.77
129.87
129.69
128.96
128.49
127.20
77.57 CDCl3
77.15 CDCl3
76.72 CDCl3
61.48
54.12
41.86
19.47
14.40
Me
O
O
EtO2C
2ca
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

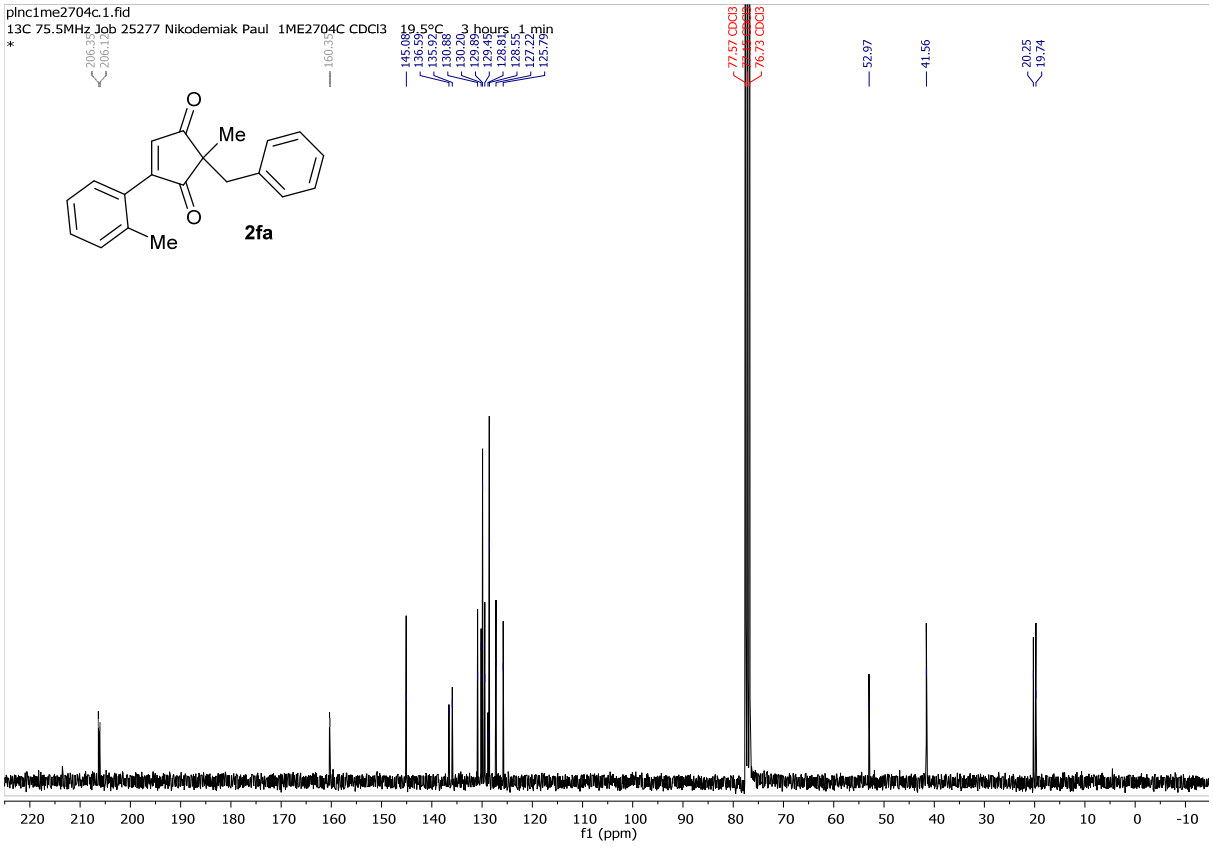

plnhmcl2303h.1.fid
1H 300.1MHz Job 24539 Nikodemiak Paul MCL2303H CDCl3 25.0°C
*
Me
Cl
O
O
2da
f1 (ppm)

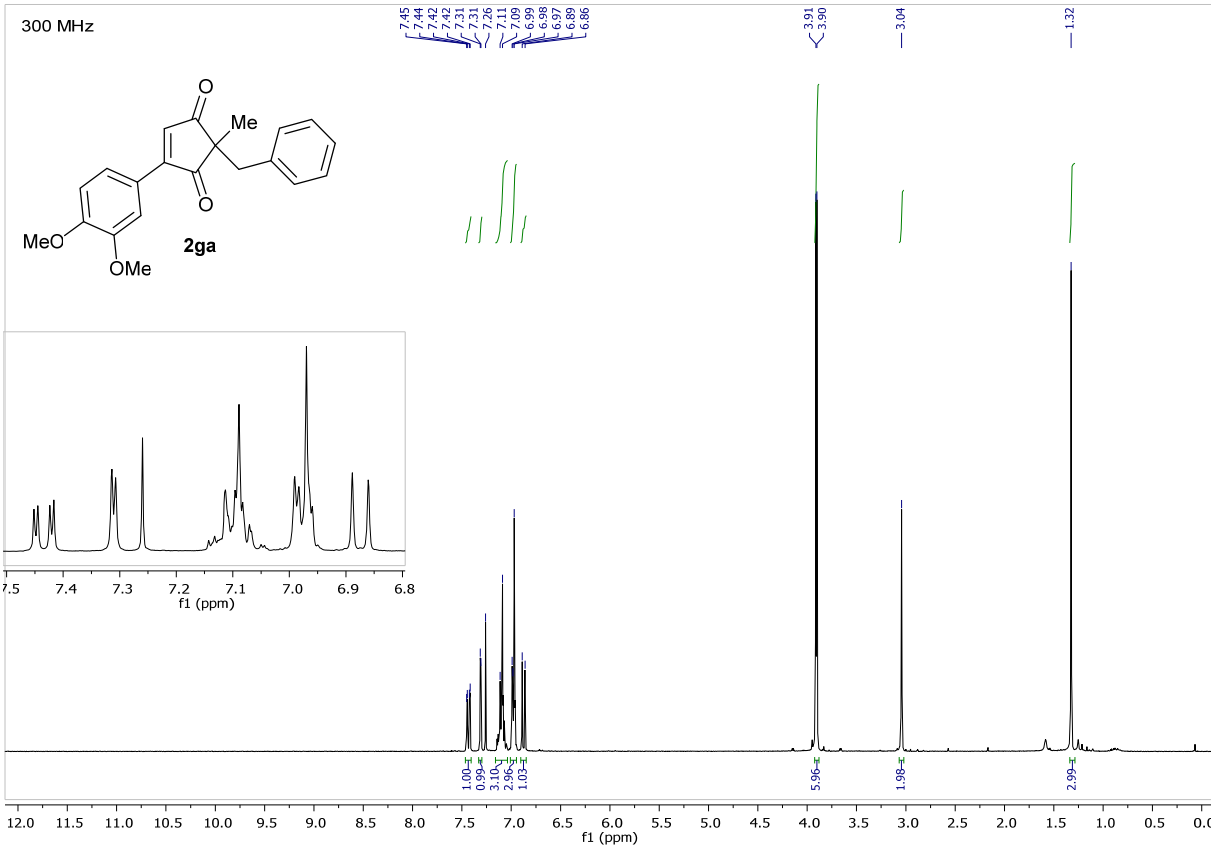

plncmcl2304c.1.fid
13C 75.5MHz Job 24554 Nikodemiak Paul MCL2304C CDCl3 25.0°C 3 hours 1 min
*
Me
Cl
O
O
2da
f1 (ppm)

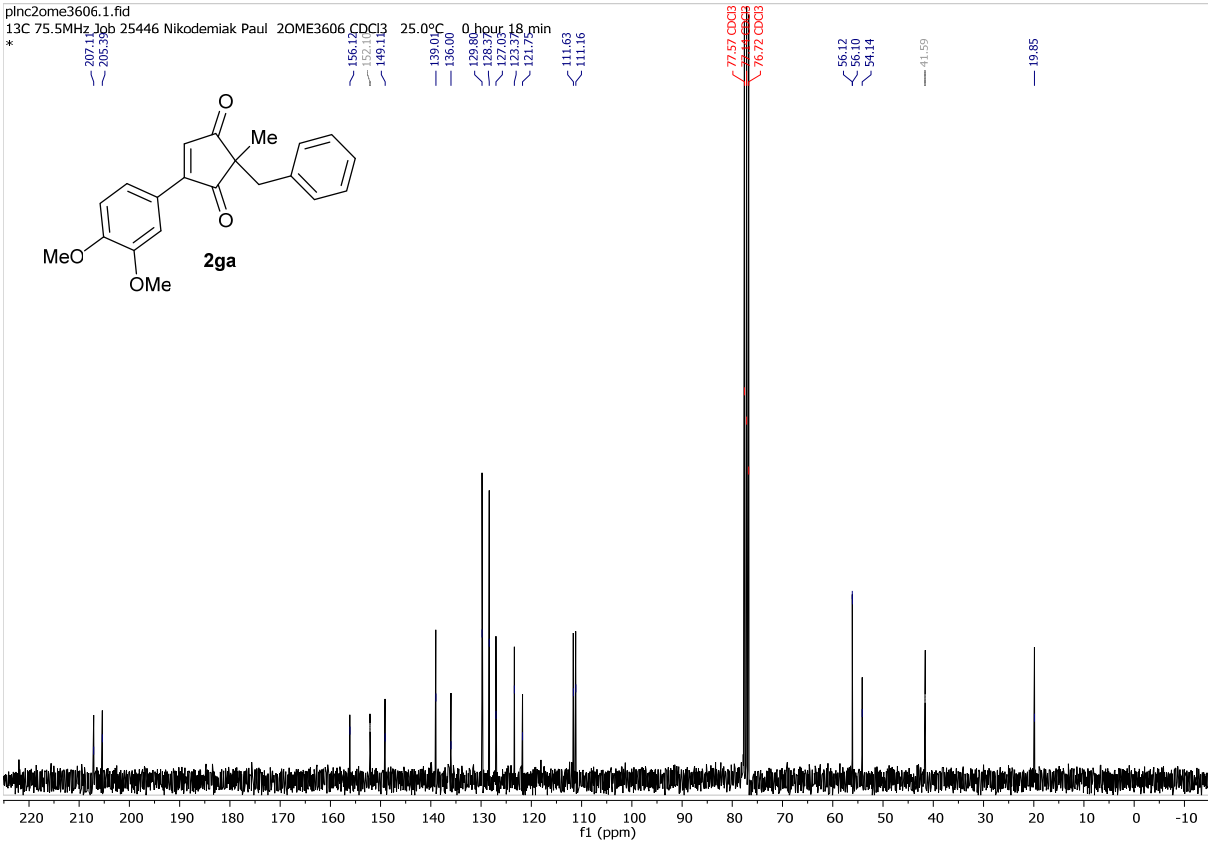

srwh549a2.1.fid
1H 300.1MHz Job 39312 Walker Sarah E 549A2 CDCl3 24.9°C
*
Me
2ea
f1 (ppm)

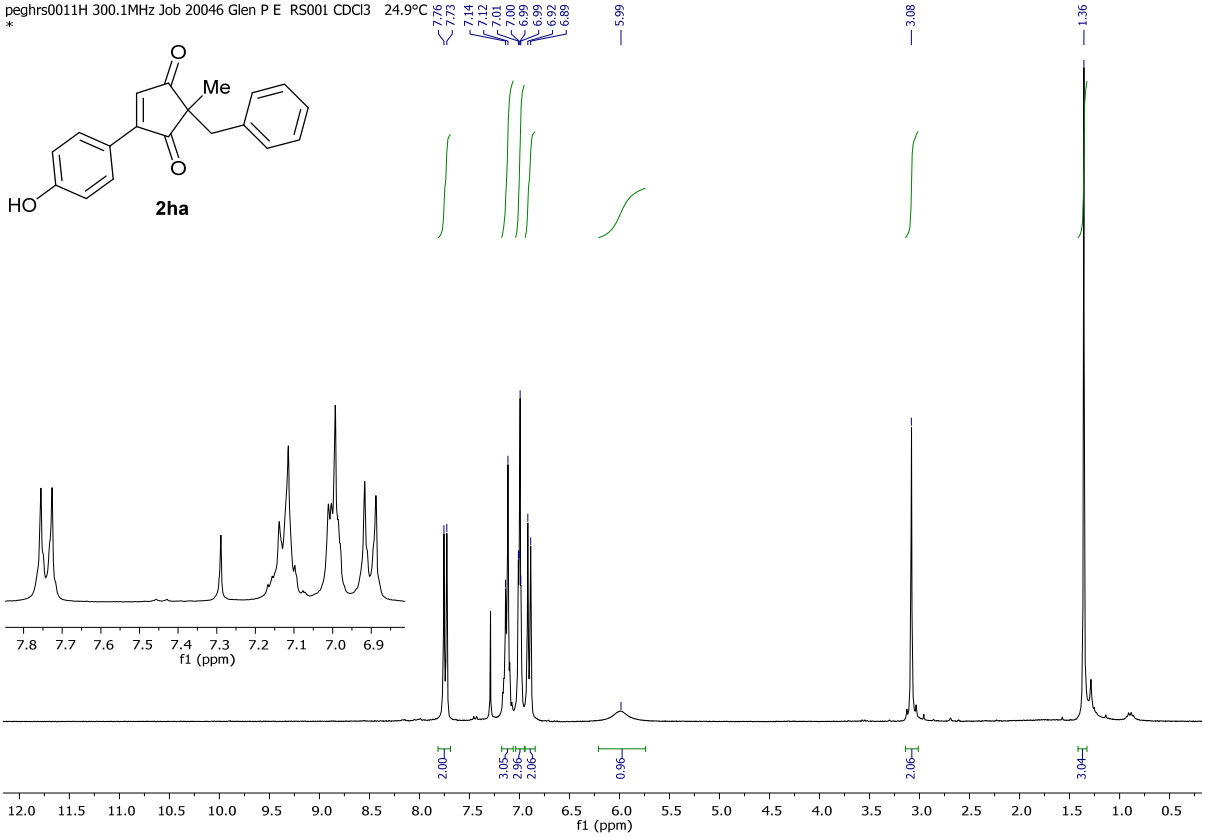

srwc549a2.1.fid
13C 75.5MHz Job 39319 Walker Sarah E 549A2 CDCl3 25.0°C 3 hours 1 min
*
Me
2ea
f1 (ppm)

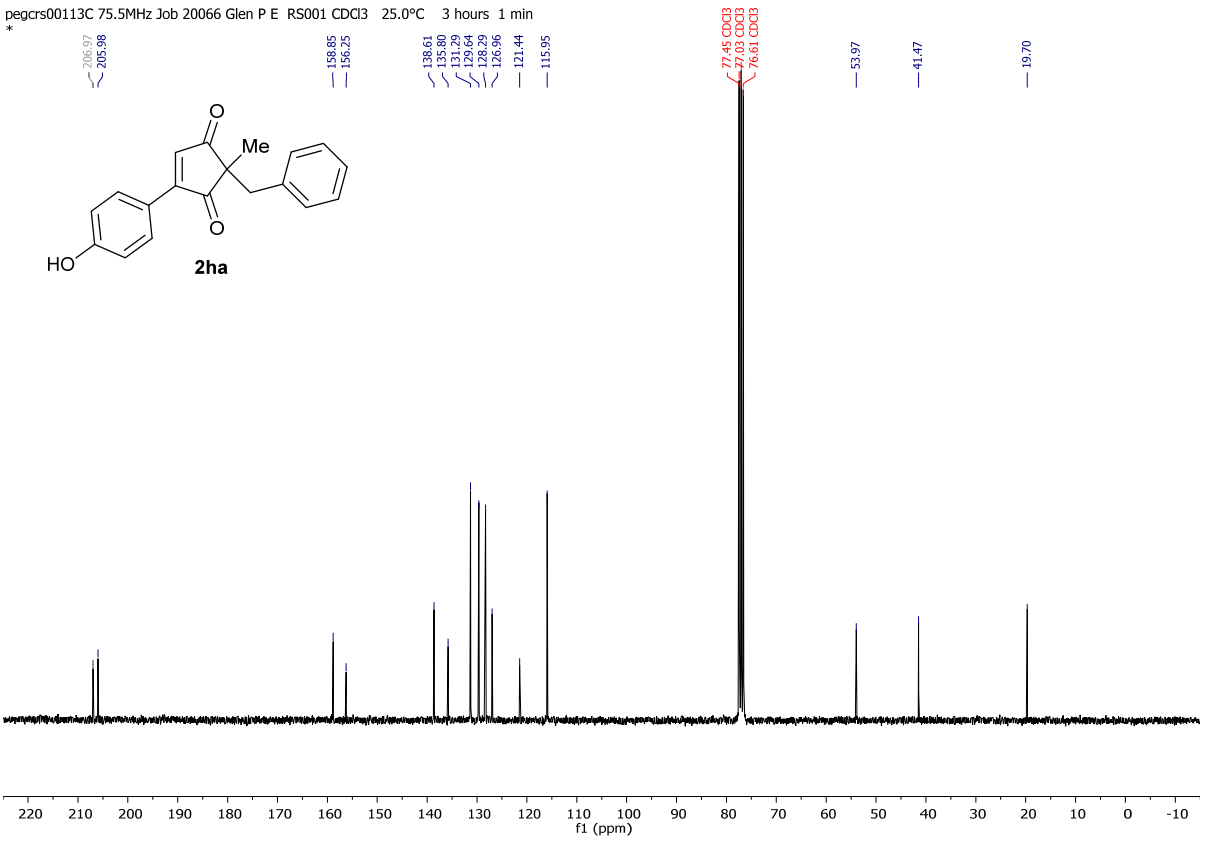

plnh1me2703h.1.fid
1H 300.1MHz Job 25186 Nikodemiak Paul 1ME2703H CDCl3 17.2°C
isolated spot 8-12
Me
Me
2fa
f1 (ppm)

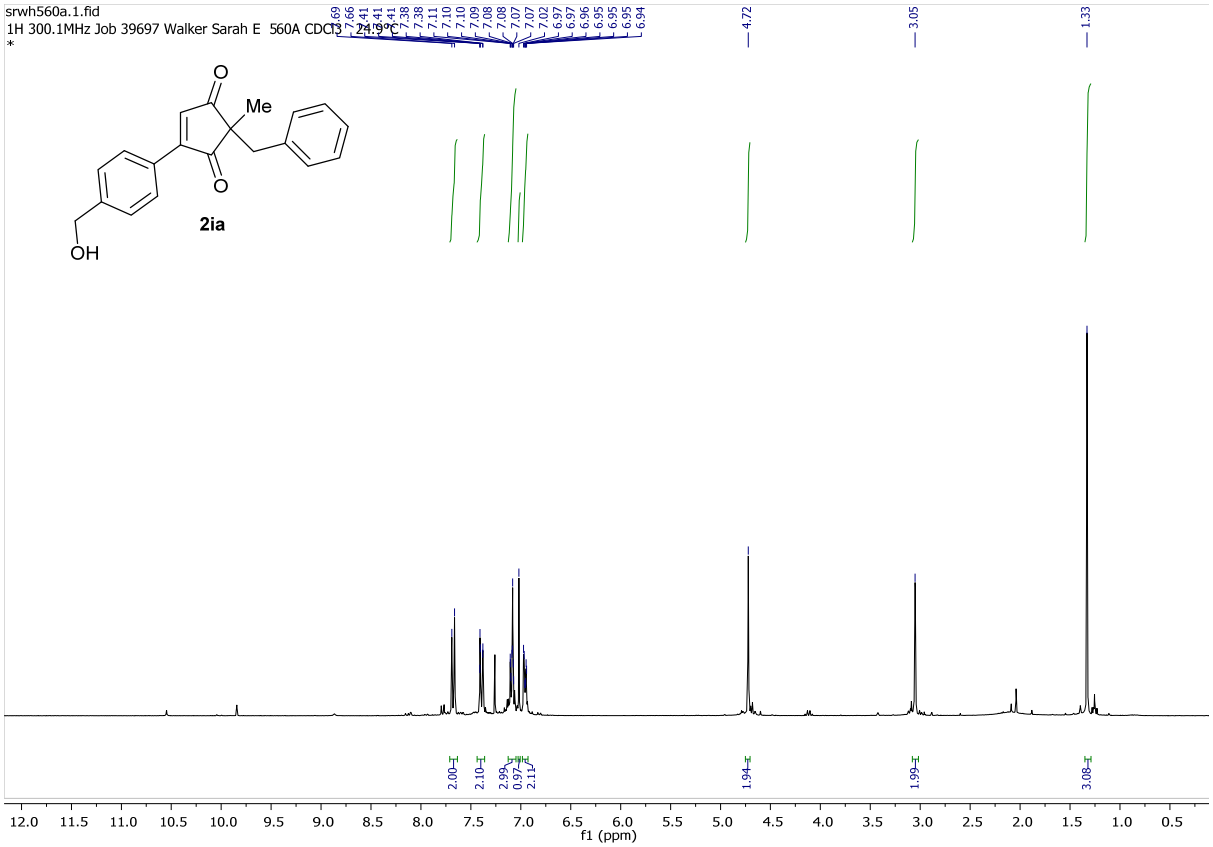

plnc1me2704c.1.fid
13C 75.5MHz Job 25277 Nikodemiak Paul 1ME2704C CDCl3 19.5°C 3 hours 1 min
*
Me
Me
2fa
f1 (ppm)

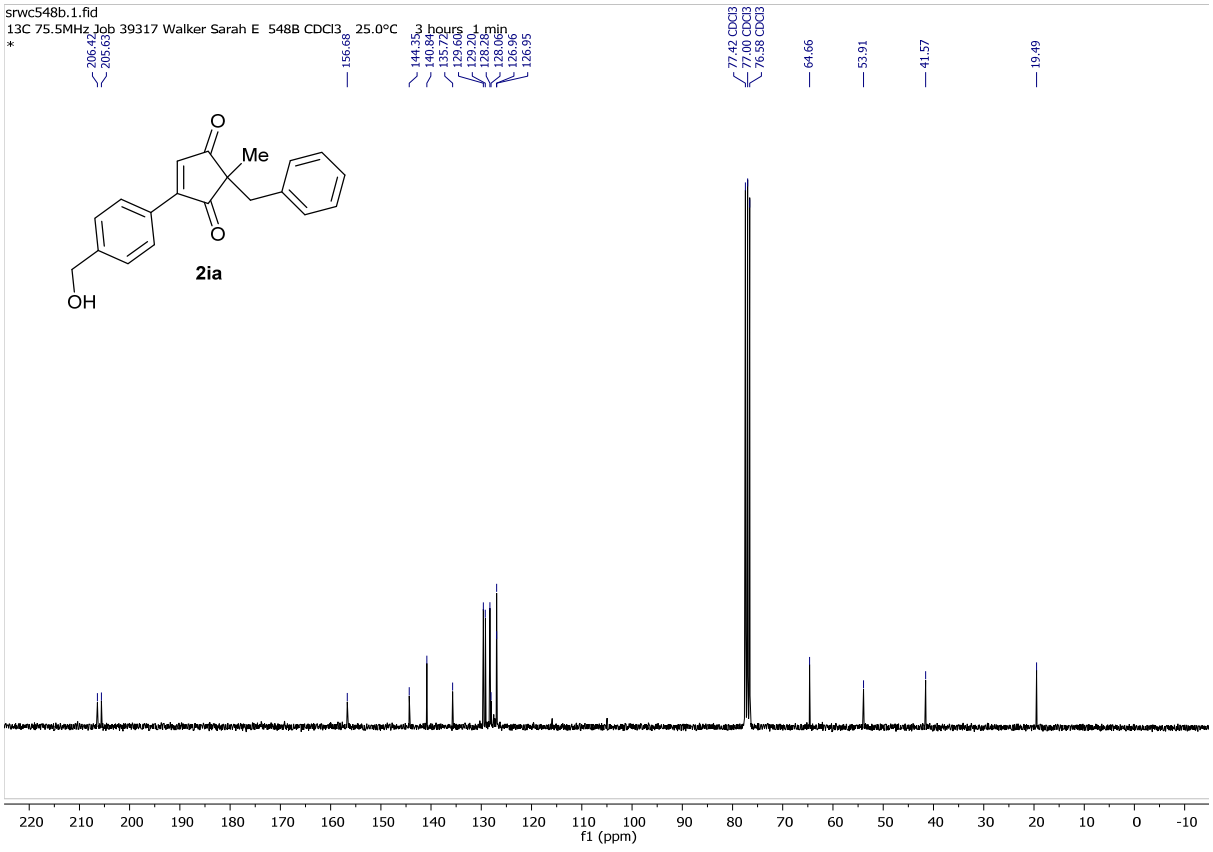

300 MHz
Me
O
O
MeO
OMe
2ga
f1 (ppm)

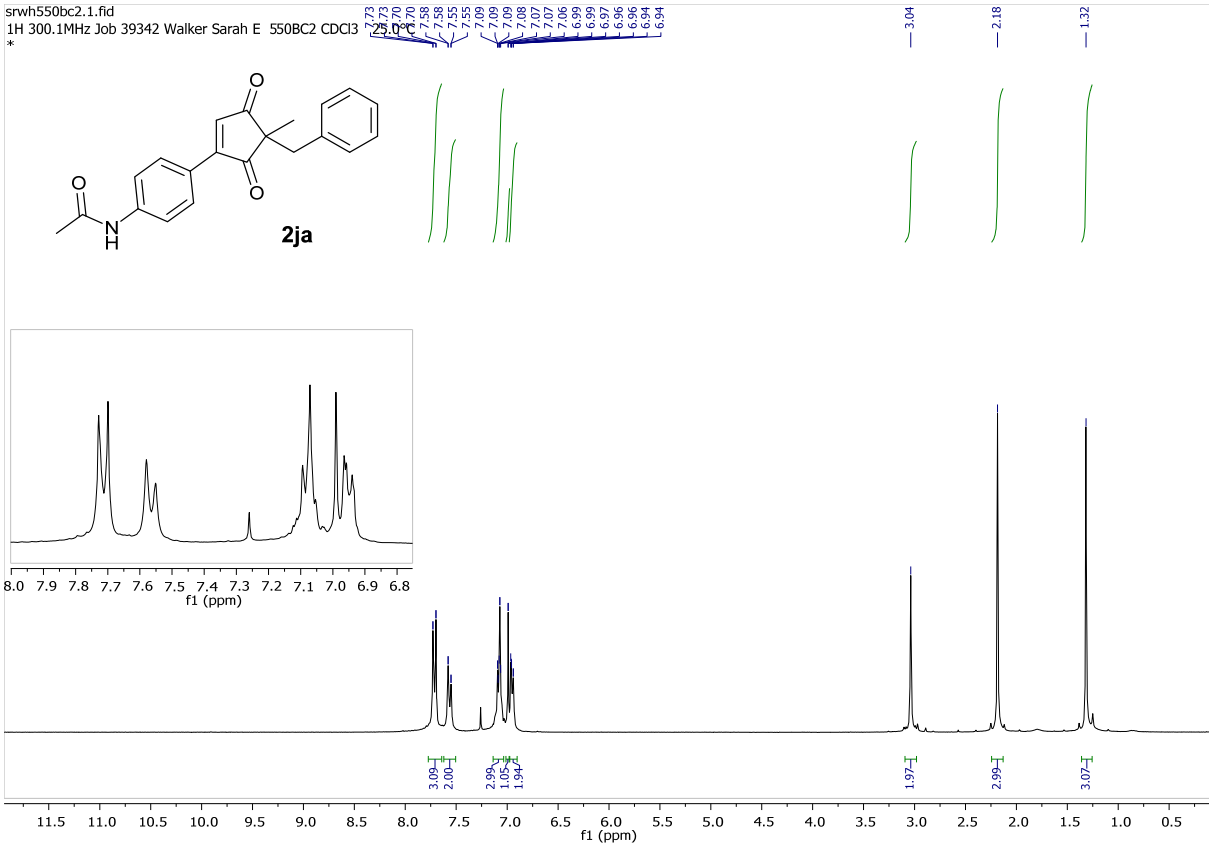

plnc2ome3606.1.fid
13C 75.5MHz Job 25446 Nikodemiak Paul 2OME3606 CDCl3 25.0°C 0 hour 18 min
*
Me
O
O
MeO
OMe
2ga
f1 (ppm)

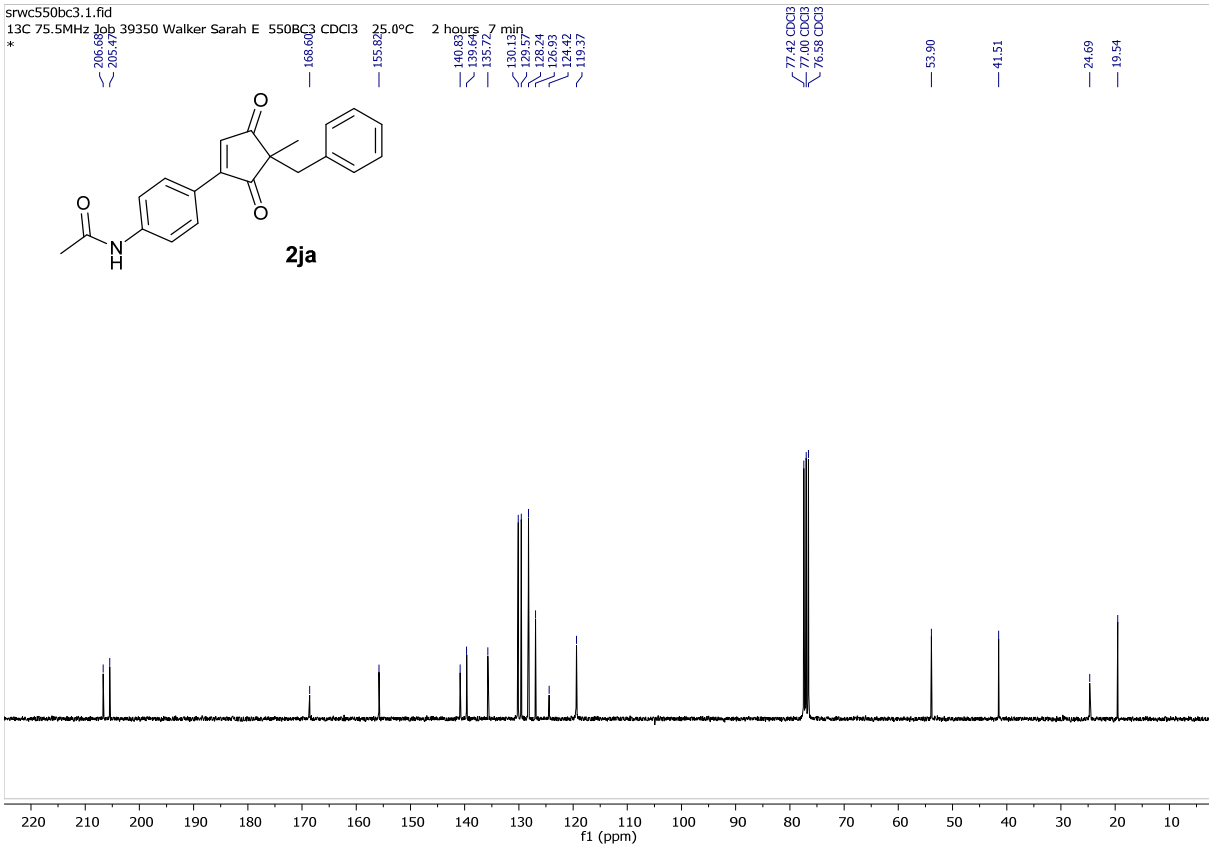

peghrs0011H 300.1MHz Job 20046 Glen P E RS001 CDCl3 24.9°C
*
Me
O
O
HO
2ha
7.76
7.73
7.14
7.12
7.01
7.00
6.99
6.99
6.92
6.89
5.99
3.08
1.36
2.00
3.05
2.96
2.06
0.96
2.06
3.04
f1 (ppm)

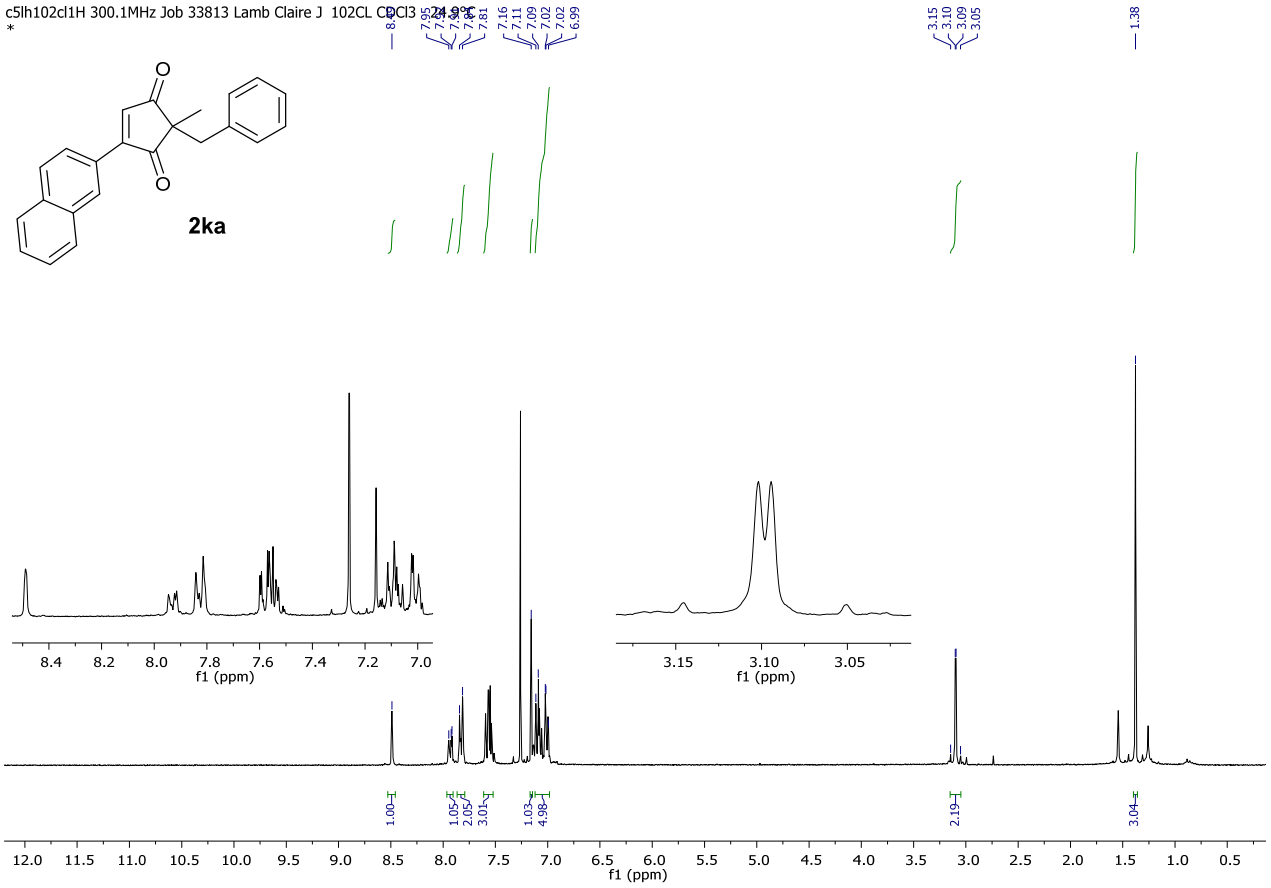

pegcrs00113C 75.5MHz Job 20066 Glen P E RS001 CDCl3 25.0°C 3 hours 1 min
*
Me
O
O
HO
2ha
206.97
205.98
158.85
156.25
138.61
135.80
133.29
130.64
128.29
126.96
121.44
115.95
77.45 CDCl3
77.03 CDCl3
76.61 CDCl3
53.97
41.47
19.70
f1 (ppm)

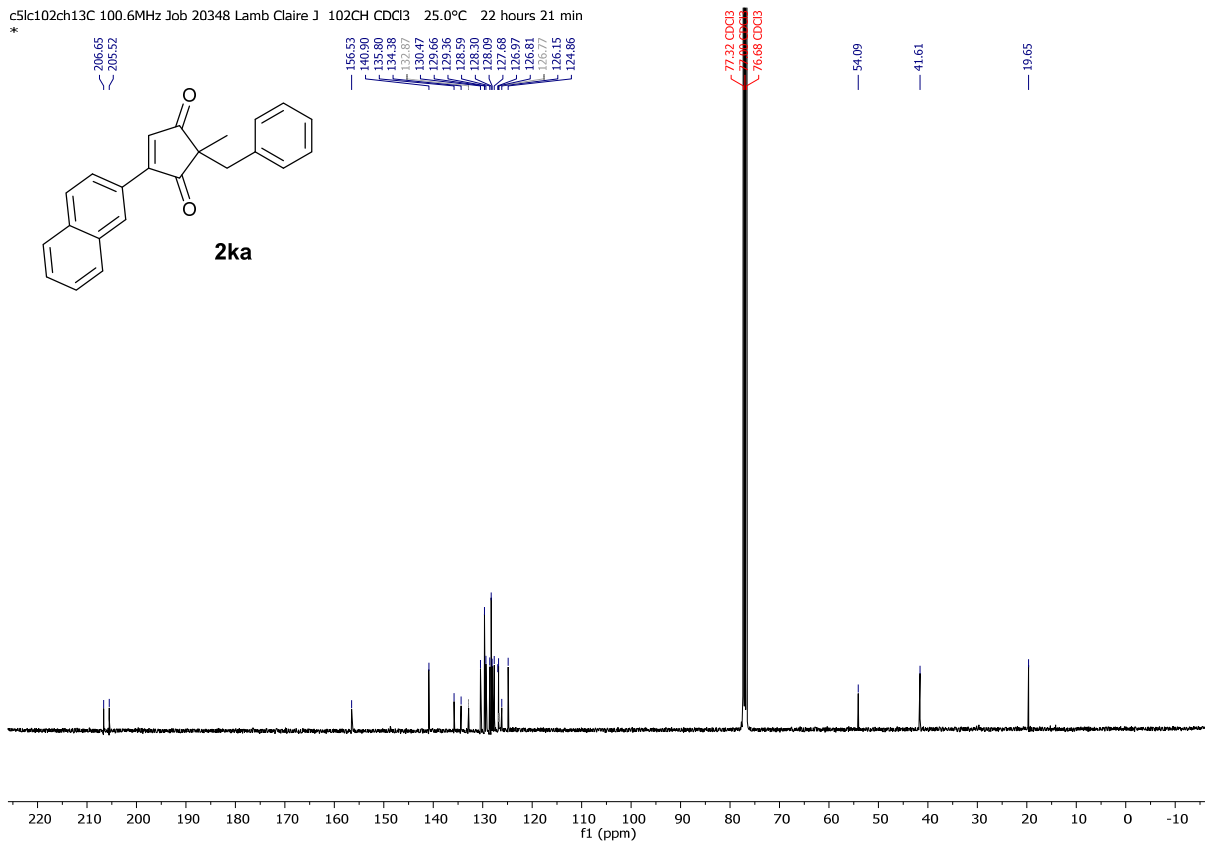

srwh560a.1.fid
1H 300.1MHz Job 39697 Walker Sarah E 560A CDCl3 24.9°C
*
Me
2ia
OH
f1 (ppm)

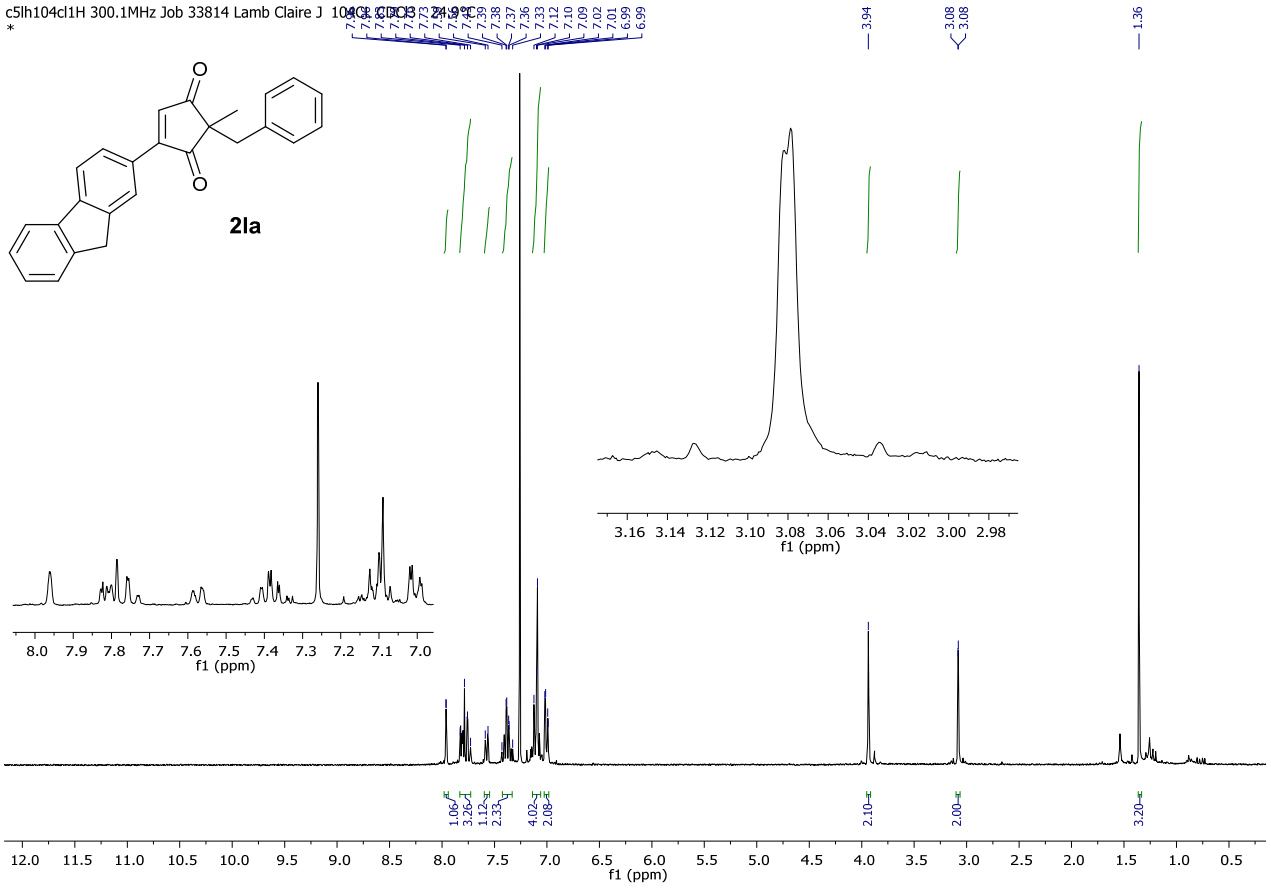

srwc548b.1.fid
13C 75.5MHz Job 39317 Walker Sarah E 548B CDCl3 25.0°C 3 hours 1 min
*
Me
2ia
OH
f1 (ppm)

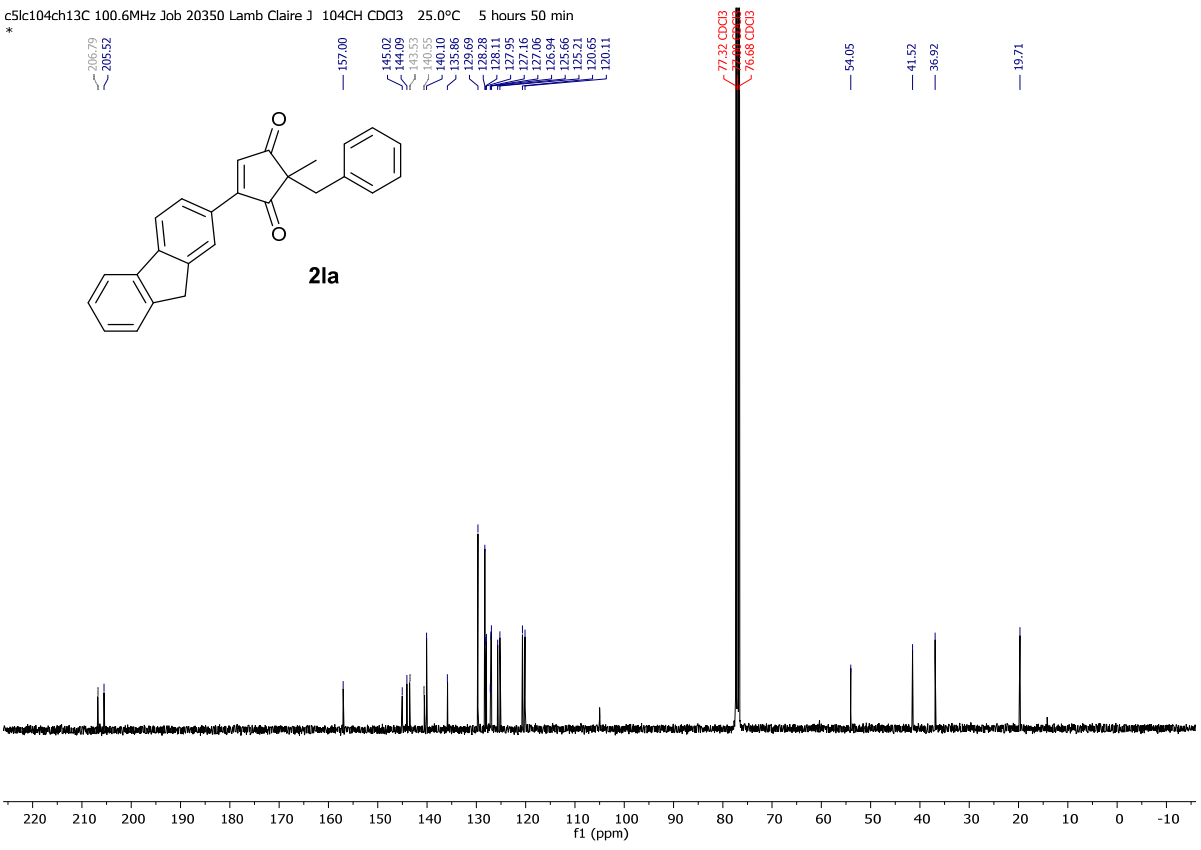

srwh550bc2.1.fid
1H 300.1MHz Job 39342 Walker Sarah E 550BC2 CDCl3 25.0°C
*
7.73 7.73 7.70 7.70 7.58 7.58 7.55 7.55 7.09 7.09 7.08 7.07 7.07 7.06 6.99 6.99 6.97 6.96 6.96 6.94 6.94
3.04
2.18
1.32
2ja
8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8
f1 (ppm)
3.09 2.00 2.99 1.05 1.94 1.97 2.99 3.07
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

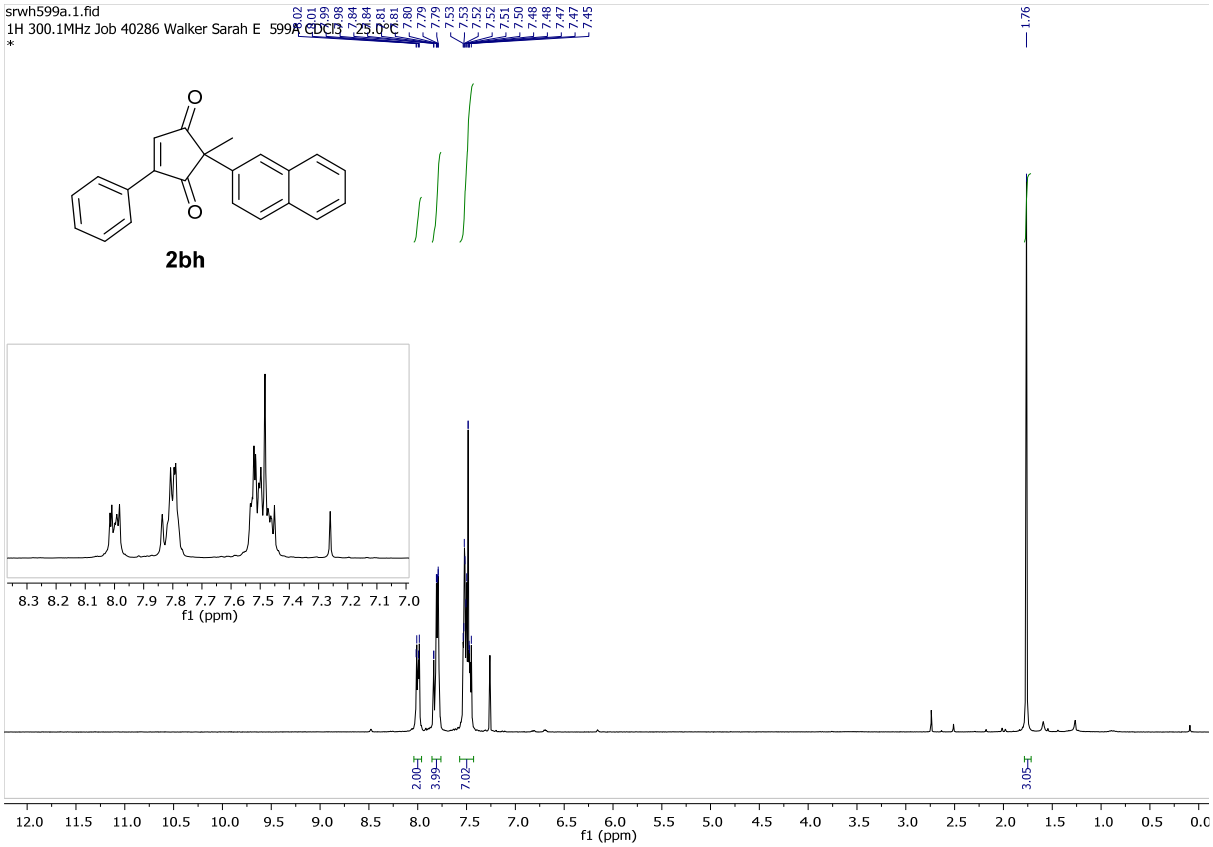

srwc550bc3.1.fid
13C 75.5MHz Job 39350 Walker Sarah E 550BC3 CDCl3 25.0°C 2 hours 7 min
*
206.68 205.47 168.60 155.82 140.83 139.64 135.72 130.13 129.57 128.24 126.93 124.42 119.37
77.42 CDCl3 77.00 CDCl3 76.58 CDCl3
53.90
41.51
24.69
19.54
2ja
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

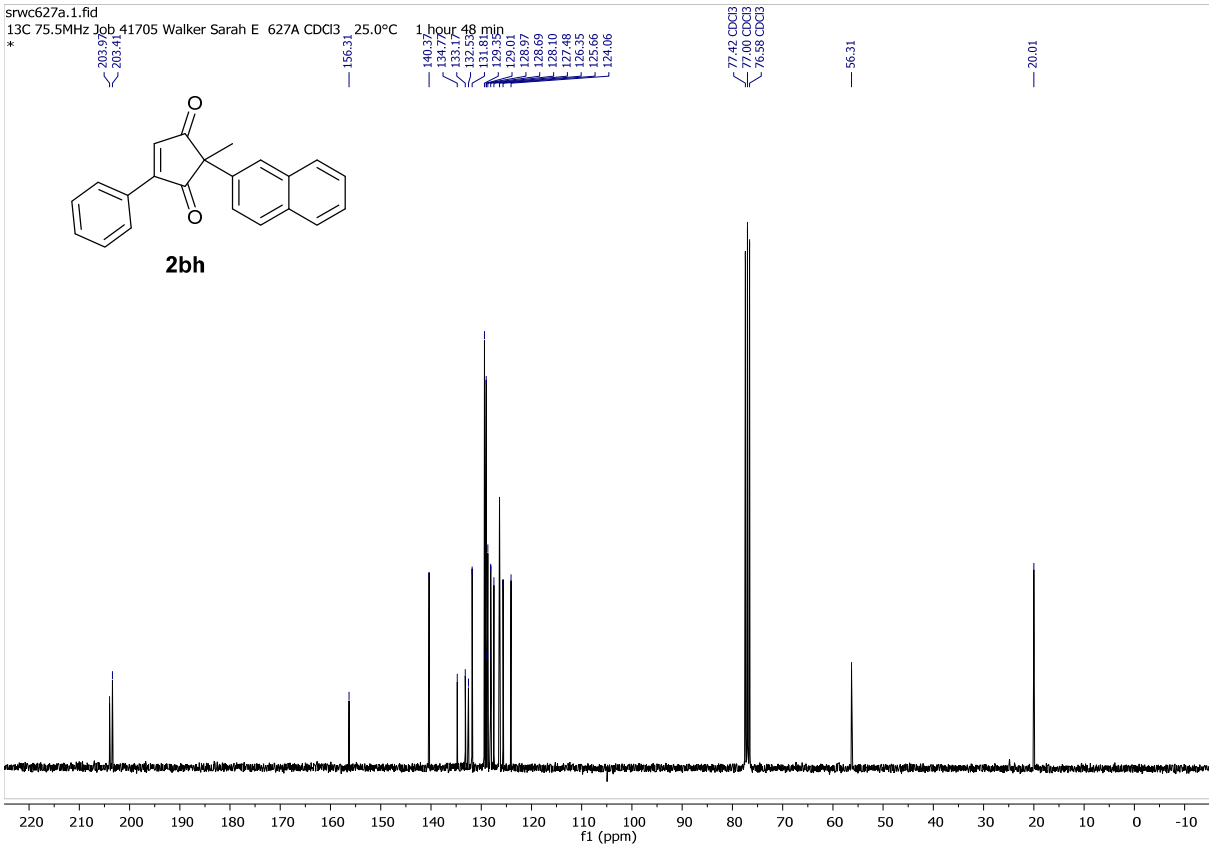

c5lh102cl1H 300.1MHz Job 33813 Lamb Claire J 102CL CDCl3 24.9°C
*
2ka
f1 (ppm)

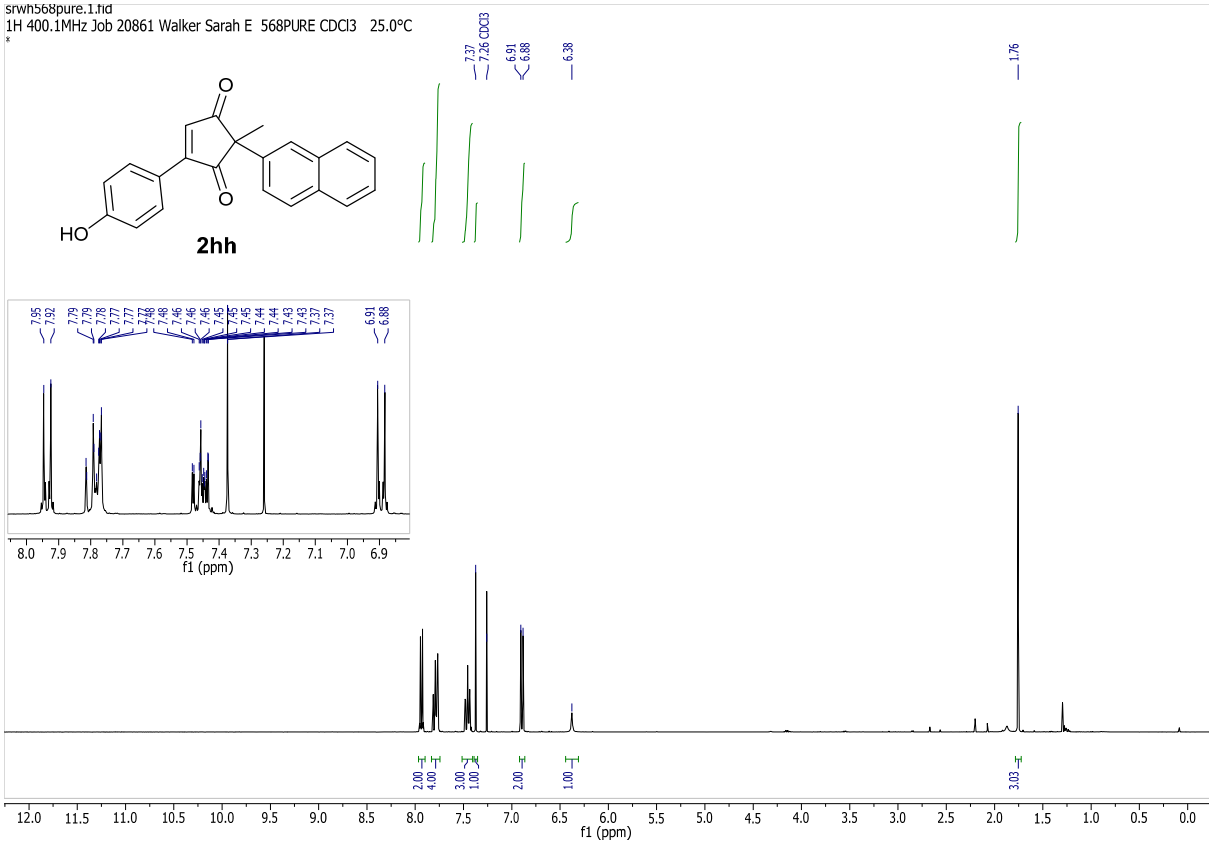

c5lc102ch13C 100.6MHz Job 20348 Lamb Claire J 102CH CDCl3 25.0°C 22 hours 21 min
*
2ka
f1 (ppm)

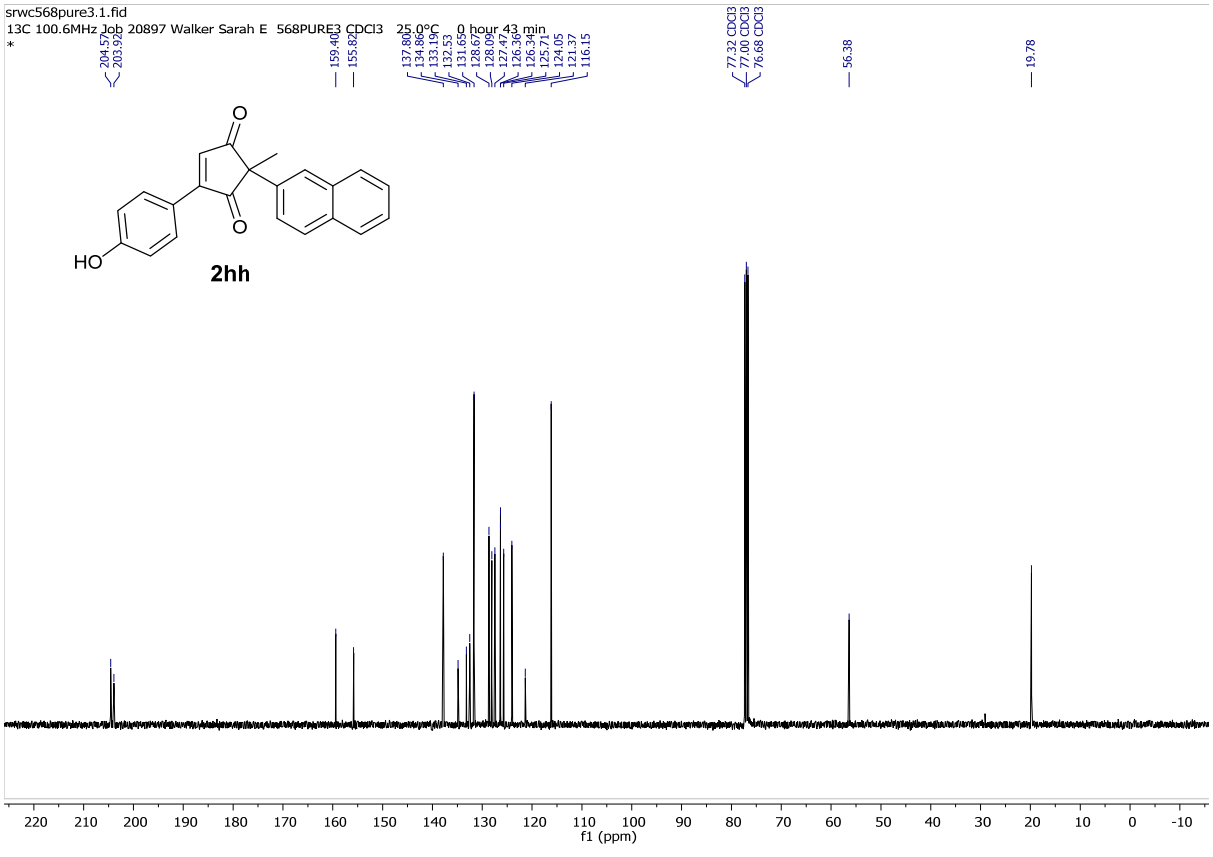

c5lh104cl1H 300.1MHz Job 33814 Lamb Claire J
2la
f1 (ppm)

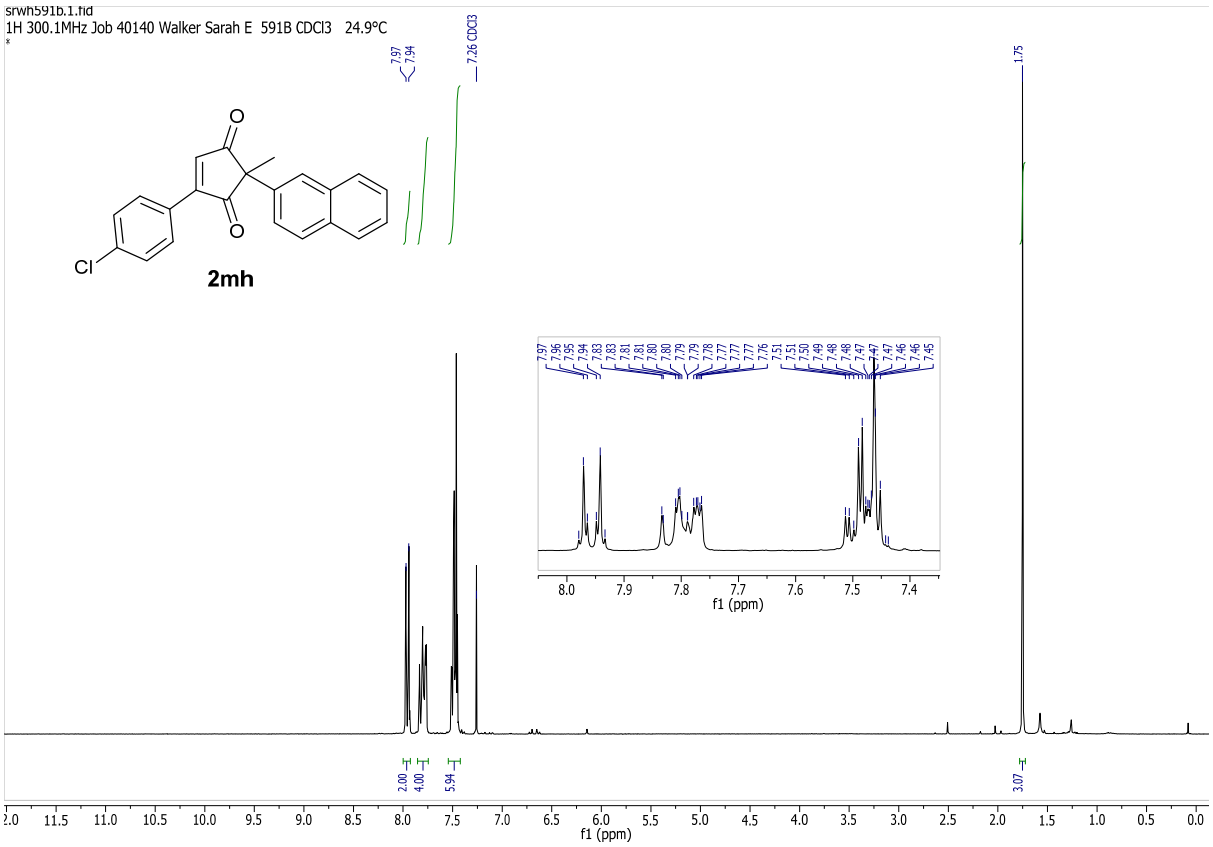

c5lc104ch13C 100.6MHz Job 20350 Lamb Claire J 104CH CDCl3 25.0°C 5 hours 50 min
2la
f1 (ppm)

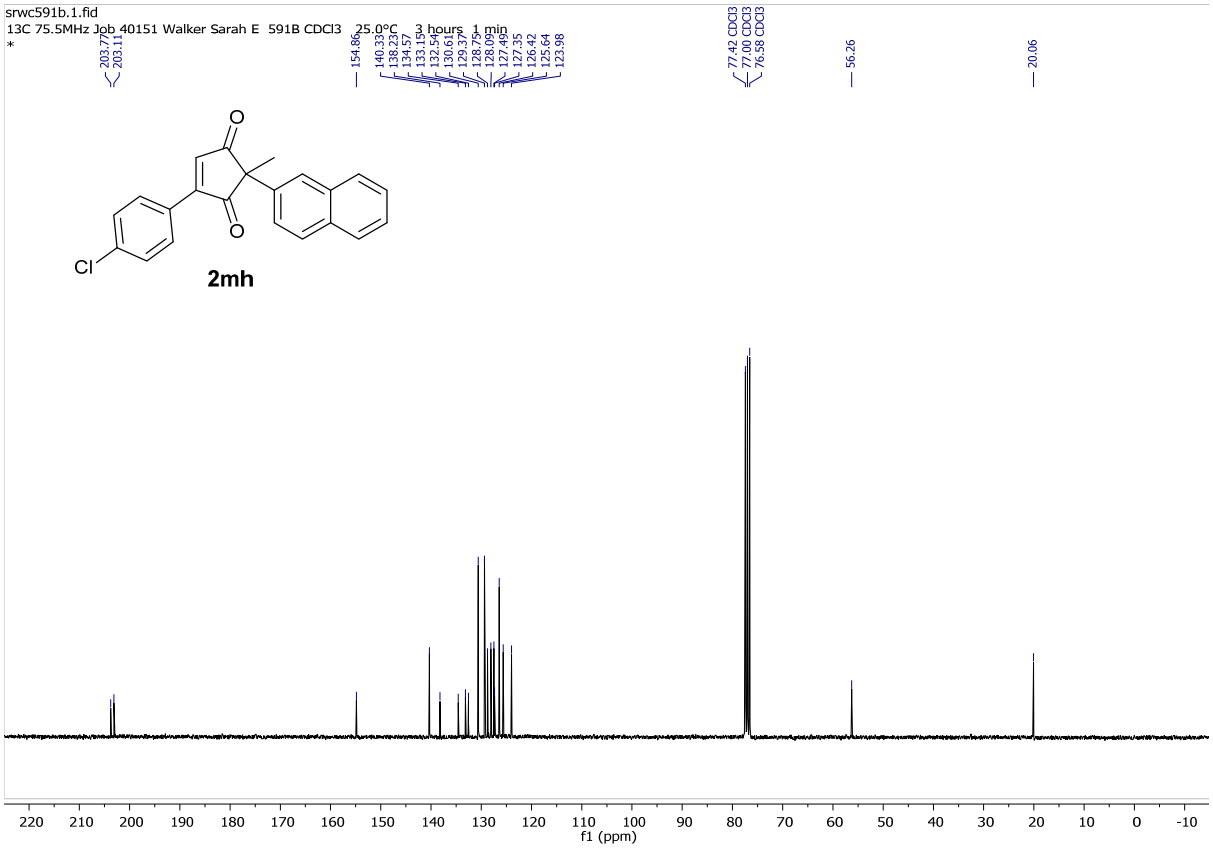

srwh599a.1.fid
1H 300.1MHz Job 40286 Walker Sarah E 599A CDCl3 25.0°C
*
2bh
f1 (ppm)


srwc627a.1.fid
13C 75.5MHz Job 41705 Walker Sarah E 627A CDCl3 25.0°C 1 hour 48 min
*
2bh
f1 (ppm)

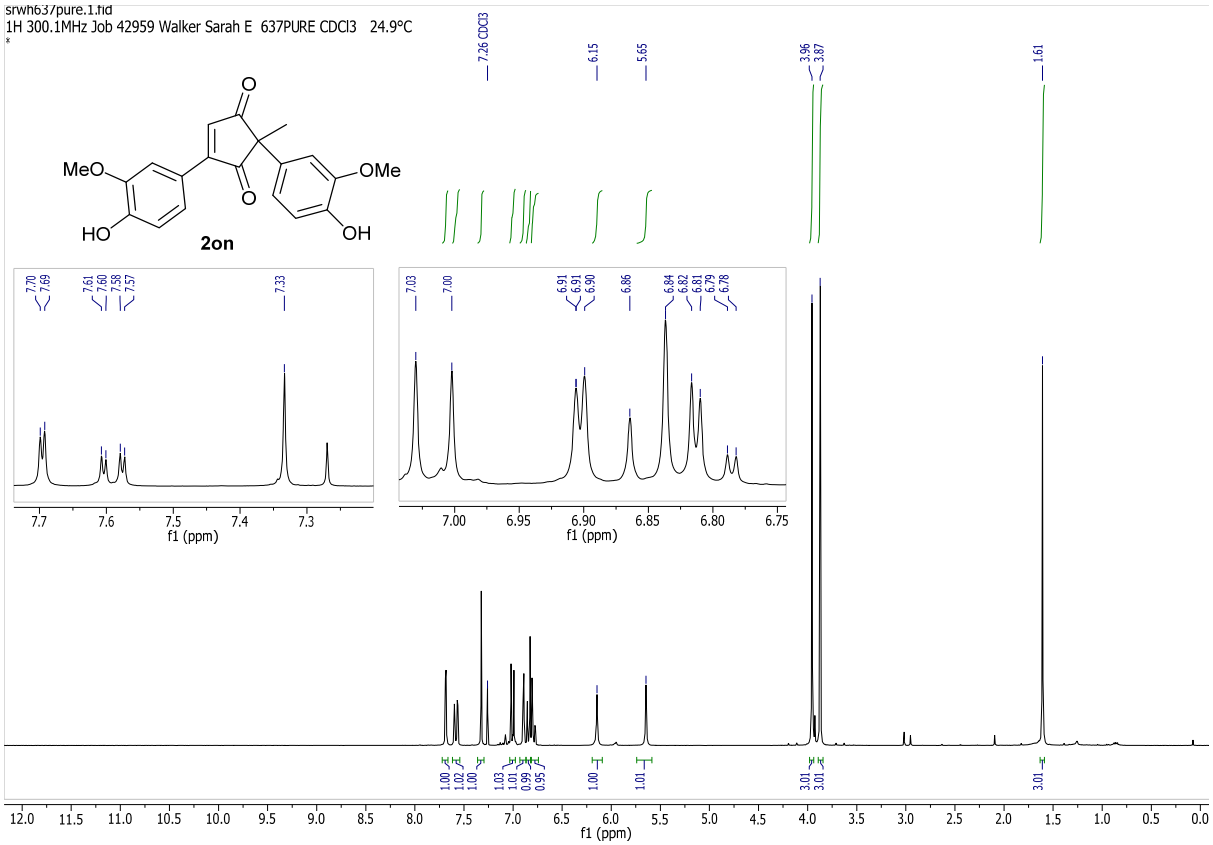

srwh568pure.1.fid
1H 400.1MHz Job 20861 Walker Sarah E 568PURE CDCl3 25.0°C
2hh
f1 (ppm)

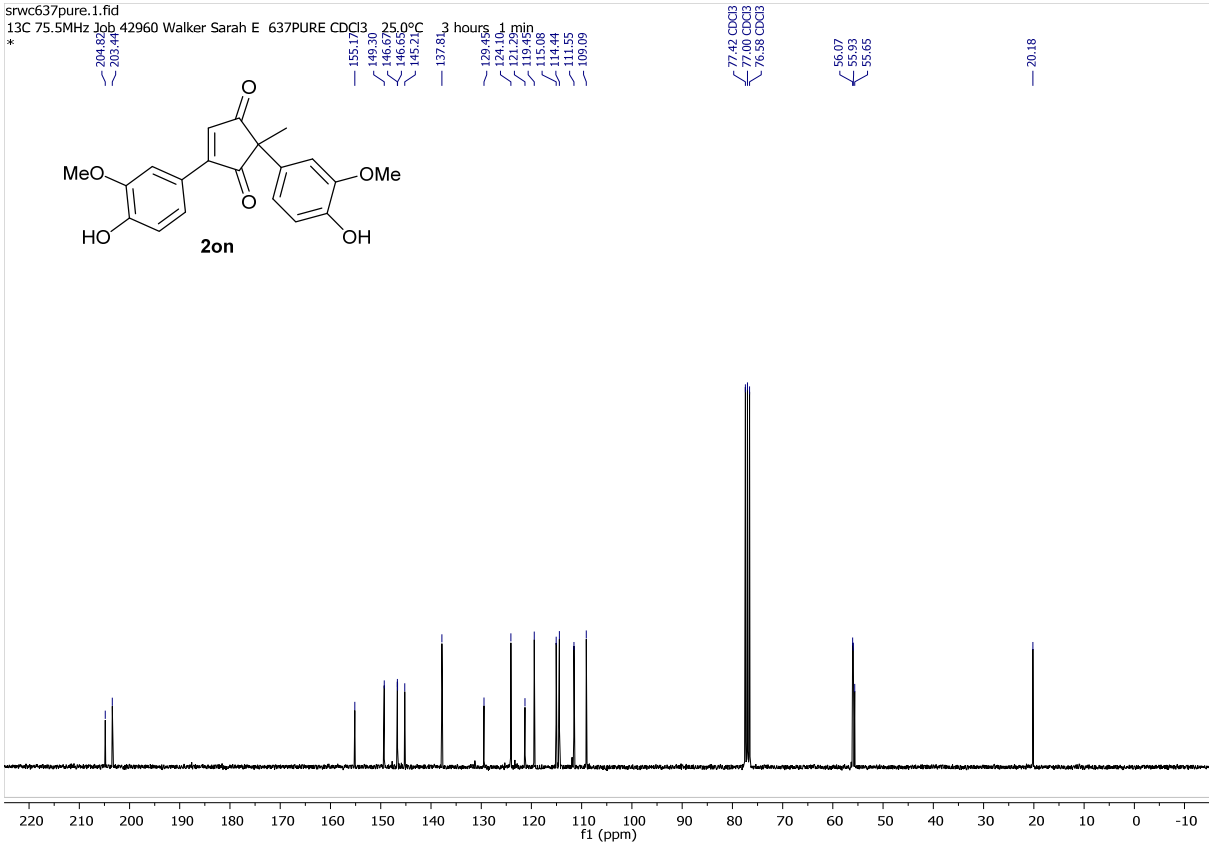

srwc568pure3.1.fid
13C 100.6MHz Job 20897 Walker Sarah E 568PURE3 CDCl3 25.0°C 0 hour 43 min
2hh
f1 (ppm)


srwh591b.1.fid
1H 300.1MHz Job 40140 Walker Sarah E 591B CDCl3 24.9°C
7.97
7.94
7.26 CDCl3
1.75
O
O
Cl
2mh
2.00
4.00
5.94
3.07
f1 (ppm)

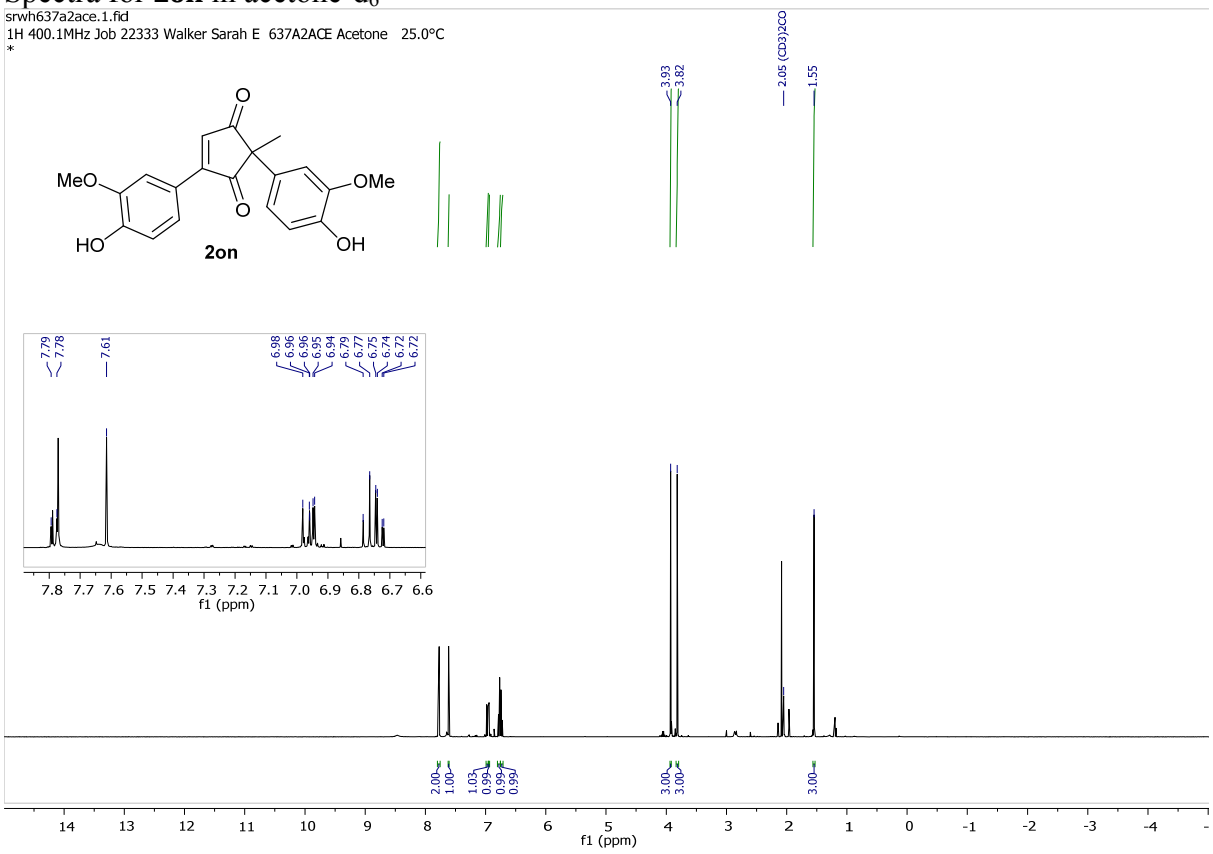

srwc591b.1.fid
13C 75.5MHz Job 40151 Walker Sarah E 591B CDCl3 25.0°C 3 hours 1 min
203.77
203.11
154.86
140.33
138.23
134.57
133.15
132.54
130.61
129.37
128.75
128.09
127.49
127.35
126.42
125.64
123.98
77.42 CDCl3
77.00 CDCl3
76.58 CDCl3
56.26
20.06
O
O
Cl
2mh
f1 (ppm)

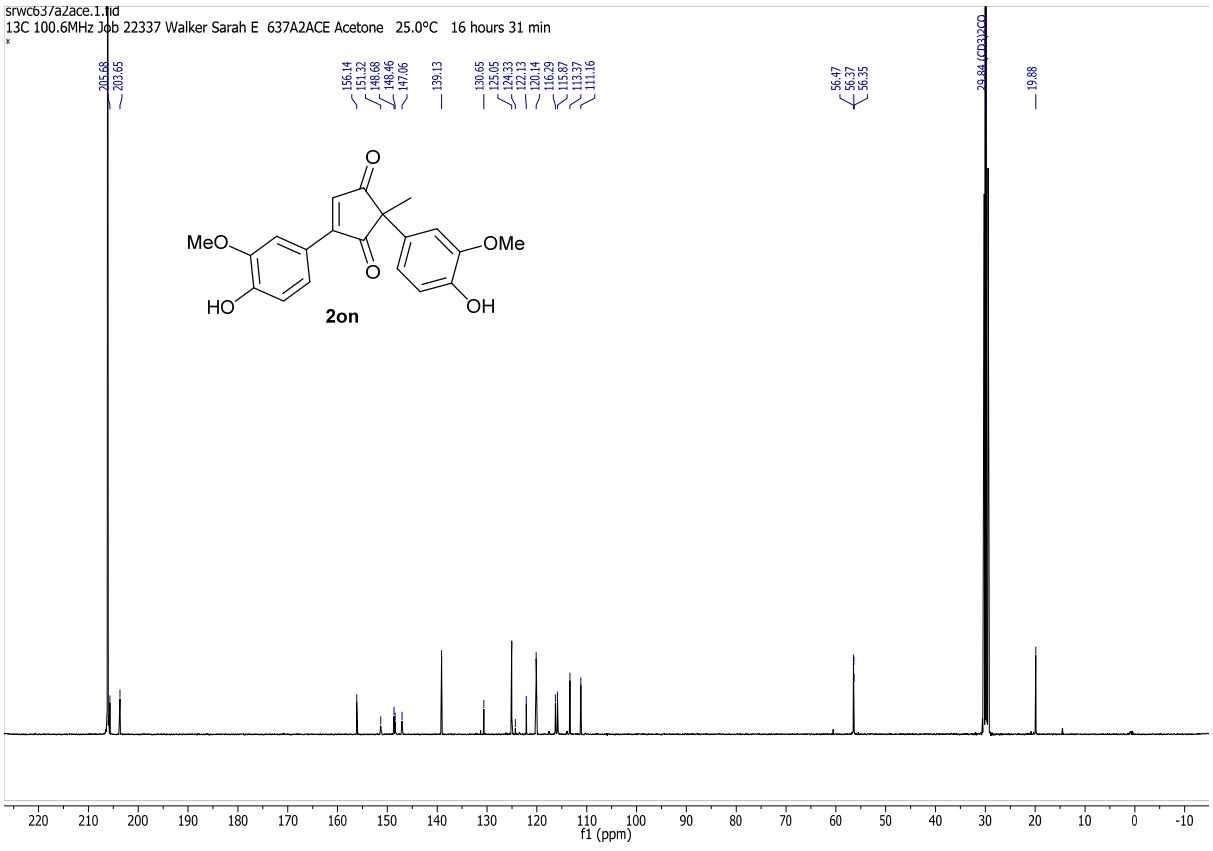
Spectra for **2on** in $CDCl_3$



Spectra for **2on** in acetone-$d_6$



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