Supporting Information

Multicatalytic Dearomatization of Phenols into Epoxyquinols via a Photooxygenation Process

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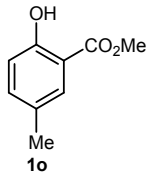
1. General

^{1}H NMR and ^{13}C spectra were recorded on a BRUKER AC300 (300 MHz for ^{1}H and 75 MHz for ^{13}C) at room temperature on samples dissolved in $CDCl_3$. Chemical shifts (δ) are given in parts per million and coupling constants are given as absolute values expressed in Hertz. High-resolution mass spectrometry (HRMS) analyses were recorded on a XEVO G2-XS QTOF (Waters). Infrared spectra were recorded with a Bruker Tensor 27 FT ATR spectrometer. Melting points were determined on a Stuart melting point SMP3 apparatus. Thin-layer chromatography (TLC) was carried out on aluminium sheets precoated with silica gel 60 F_{254} (Merck). Column chromatography separations were performed using Merck Kieselgel 60 (0.040-0.060 mm). The phenols **1a-n** were prepared according to literature procedure.[S1] Compound **3** has been characterized in our previous work.[S1]

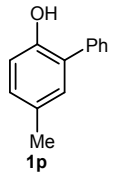
2. Preparation of 1o-q

❖ methyl 2-hydroxy-5-methylbenzoate, *1o*



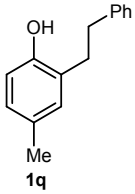
The ester **1o** was prepared according to the procedure reported by the group of A. M. Harned.[S2] Colourless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.56 (s, 1H), 7.63 (d, J = 2.0 Hz, 1H), 7.26 (dd, J = 8.5, 2.0 Hz, 1H), 6.88 (d, J = 8.5 Hz, 1H), 3.94 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.7, 159.6, 136.8, 129.7, 128.5, 117.5, 112.1, 52.3, 20.5; IR (ATR, cm^{-1}) 3169, 2953, 1674, 1489, 1439, 1389, 1331, 1291, 1089, 826, 794; 537; HRMS (ESI) Calcd for $C_9H_9O_3$ $[M-H]^-$: 165.0552, Found: 165.0547.

❖ 5-methyl-[1,1'-biphenyl]-2-ol, *1p*



The phenol **1p** was prepared according to a modified procedure reported by X. Zhang, X. Fan and coll.[S3] The reaction mixture was stirred for 4h under our experimental conditions. White solid; m.p. 68°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49-7.37 (m, 5H), 7.08-7.06 (m, 2H), 6.89 (d, J = 8.8 Hz, 1H), 5.04 (s, 1H), 2.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.3, 137.4, 130.8, 130.1, 129.8, 129.4 (2C), 129.2 (2C), 128.0, 127.9, 115.8, 20.6; IR (ATR, cm^{-1}) 3503, 1508, 1487, 1444, 1397, 1330, 1245, 1127, 817, 757, 698, 581, 537; HRMS (ESI) Calcd for $C_{13}H_{11}O$ $[M-H]^-$: 183.0810, Found: 183.0804.

❖ 4-methyl-2-phenethylphenol, *1q*

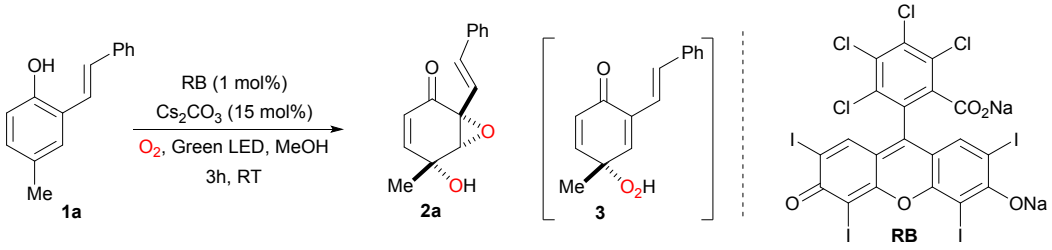


To a suspension of $Pd(OH)_2$ (40 mg) in ethyl acetate (27 mL) was added phenol **1a** (210 mg, 1 mmol). The reaction mixture was stirred for 5h under H_2 atmosphere. The reaction mixture was then filtered over a pad of celite and concentrated under reduced pressure. No further purification was required

(yield = 96%). Colourless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33-7.19 (m, 5H), 6.93-6.88 (m, 2H), 6.68 (d, J = 8.0 Hz, 1H), 4.42 (s, 1H), 2.93-2.88 (m; 4H), 2.27 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.4, 142.2, 131.0, 130.2, 128.6 (2C), 128.5 (2C), 127.8 (2C), 126.1, 115.4, 36.5, 32.6, 20.6; IR (ATR, cm^{-1}) 3398, 2921, 2859, 1503, 1258, 1104, 810, 749, 699; HRMS (ESI) Calcd for $C_{15}H_{15}O$ [M-H]$^-$: 211.1123, Found: 211.1116.

3. Influence of experimental parameters on the photooxygenation

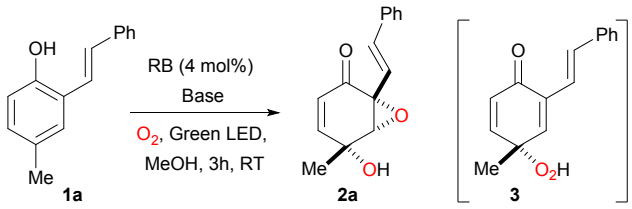
❖ Control experiments



Entry	RB	Base	Light	O_2	Yield [%][a]
1	✗	✓	✓	✓	n.r.
2	✓	✗	✓	✓	28 (**3**)
3	✓	✓	✗	✓	n.r.
4	✓	✓	✓	✗	n.r.
5	✓	✓	✓	✓	65 (**2a**)

[a] Determined by ^{1}H NMR on the crude using methyl phenyl sulfone (0.125 mmol, 19.5 mg) as an internal standard. n.r. : no reaction.

❖ **Base screening**



Entry[a]	Base loading	Yield **2a** (%)[b]
1	1 equiv. Cs_2CO_3	-[c]
2	50 mol% Cs_2CO_3	-[c]
3	15 mol% Cs_2CO_3	53
4	5 mol% Cs_2CO_3	19[d]
5	no Cs_2CO_3	28 (**3**)[e]
6	15 mol% Et_3N	n.r.
7	15 mol% Na_2CO_3	30
8	15 mol% AcONa	5[f]

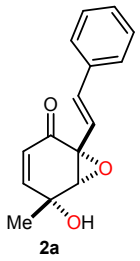
[a] Reaction conditions unless otherwise noted: **1a** (0.25 mmol), RB (0.01 mmol), base, O_2, green LED, MeOH (5 mL), 3h, rt; n.r.: no reaction. [b] Yields were determined by ^{1}H NMR using an internal standard. [c] Complex reaction mixture was obtained. [d] 12% of **3** was also observed. [e] compound **2a** was not detected. [f] 16% of **3** was also observed.

4. Photooxygenation procedure and characterization data

4.1 General experimental procedure for the photooxygenation

To a Schlenk flask was added 2-alkenylphenol **1** (0.25 mmol), cesium carbonate (12.2 mg, 37.5 µmol, 15 mol%), Rose Bengal (2.5 mg, 2.5 µmol, 1 mol%) and MeOH (5 mL) to give a purple solution. The reaction medium was gently bubbled with dioxygen throughout the reaction time and the homogeneous solution was irradiated with two green LED (2 x 1 W). The distance from the light source to the irradiation Schlenk vessel was 5 cm without the use of any filters. The reaction was stirred for 3 hours at which point methanol was removed under reduced pressure. The crude was quickly purified by chromatography on silica gel to give the desired product (dichloromethane/diethyl ether). [In the case of **1q**, the photooxygenation step was followed by addition of PPh_3 (65.5 mg, 0.25 mmol). The reaction mixture was stirred for 1h at room temperature and the solvent was then removed under reduced pressure prior to purification]

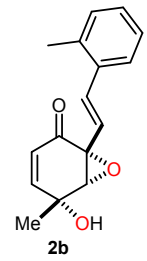
4.2 Characterization data of 2a-q, 2'q



2a

5-hydroxy-5-methyl-1-[(E)-2-phenylethenyl]-7-oxabicyclo[4.1.0]hept-3-en-2-one, *2a*

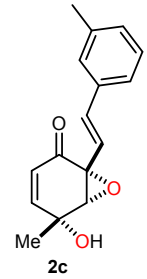
Colourless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34-7.30 (m, 2H), 7.25-7.13 (m, 3H), 6.61 (app. s, 2H), 6.37 (dd, J = 10.5, 2.8 Hz, 1H), 5.79 (d, J = 10.5 Hz, 1H), 3.53 (d, J = 2.8 Hz, 1H), 2.76 (bs, 1H), 1.40 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.3, 149.3, 135.8, 133.1, 128.8 (2C), 128.5, 126.9 (2C), 124.3, 119.5, 68.8, 68.6, 60.6, 25.4; IR (ATR, cm^{-1}) 3405, 2979, 1679, 1148, 966, 693, 520; HRMS (ESI) Calcd for $C_{15}H_{15}O_3$ $[M+H]^+$: 243.1021, Found: 243.1014.



2b

5-hydroxy-5-methyl-1-[(E)-2-(2-methylphenyl)ethenyl]-7-oxabicyclo[4.1.0]hept-3-en-2-one, *2b*

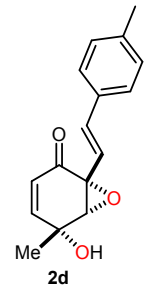
White solid; m.p. 88-90°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55-7.46 (m, 1H), 7.22-7.13 (m, 3H), 6.97 (d, J = 16.0 Hz, 1H), 6.59 (d, J = 16.0 Hz, 1H), 6.49 (dd, J = 10.5, 2.8 Hz, 1H), 5.90 (d, J = 10.5 Hz, 1H), 3.62 (d, J = 2.8 Hz, 1H), 2.82 (bs, 1H), 2.35 (s, 3H), 1.52 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.4, 149.2, 135.9, 134.9, 130.8, 130.5, 128.4, 126.3, 125.9, 124.3, 120.8, 69.0, 68.8, 60.8, 25.4, 19.9; IR (ATR, cm^{-1}) 3401, 2986, 2935, 1667, 1151, 971, 860, 745, 539; HRMS (ESI) Calcd for $C_{16}H_{15}O_3$ $[M-H]^-$: 255.1021, Found: 255.1033.



2c

5-hydroxy-5-methyl-1-[(E)-2-(3-methylphenyl)ethenyl]-7-oxabicyclo[4.1.0]hept-3-en-2-one, *2c*

Viscous oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26-7.20 (m, 3H), 7.12-7.08 (m, 1H), 6.70 (app. s, 2H), 6.49 (dd, J = 10.5, 2.8 Hz, 1H), 5.90 (d, J = 10.5 Hz, 1H), 3.64 (d, J = 2.8 Hz, 1H), 2.77 (bs, 1H), 2.35 (s, 3H), 1.51 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.3, 149.2, 138.3, 135.7, 133.2, 129.3, 128.7, 127.6, 124.3, 124.2, 119.3, 68.8, 68.6, 60.6, 25.4, 21.5; IR (ATR, cm^{-1}) 3407, 2978, 2925, 1679, 1635, 1148, 967, 821, 693, 557; HRMS (ESI) Calcd for $C_{16}H_{15}O_3$ $[M-H]^-$: 255.1021, Found: 255.1027.

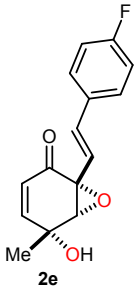


2d

5-hydroxy-5-methyl-1-[(E)-2-(4-methylphenyl)ethenyl]-7-oxabicyclo[4.1.0]hept-3-en-2-one, *2d*

Viscous oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 6.70 (d, J = 16.2 Hz, 1H), 6.64 (d, J = 16.2 Hz, 1H), 6.48 (dd, J = 10.5, 2.8 Hz, 1H), 5.89 (d, J = 10.5 Hz, 1H), 3.64 (d, J = 2.8 Hz, 1H), 2.76 (bs, 1H), 2.34 (s, 3H), 1.50 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.4, 149.2, 138.5, 133.0 (2C), 129.5 (2C), 126.9 (2C), 124.3, 118.3, 68.8, 68.6,

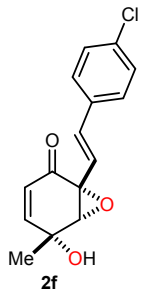
60.7, 25.4, 21.4; IR (ATR, cm^{-1}) 3365, 2977, 2923, 1702, 1682, 1152, 966, 890, 584, 542; HRMS (ESI) Calcd for $C_{16}H_{15}O_3$ $[M-H]^-$: 255.1021, Found: 255.1026.



2e

1-[(E)-2-(4-fluorophenyl)ethenyl]-5-hydroxy-5-methyl-7-oxabicyclo[4.1.0]hept-3-en-2-one, *2e*

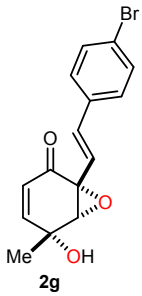
Viscous oil; ^1H NMR (300 MHz, $CDCl_3$) δ 7.41-7.37 (m, 2H), 7.04-6.95 (m, 2H), 6.69 (d, J = 16.2 Hz, 1H), 6.61 (d, J = 16.2 Hz, 1H), 6.48 (dd, J = 10.5, 2.8 Hz, 1H), 5.90 (d, J = 10.5 Hz, 1H), 3.62 (d, J = 2.8 Hz, 1H), 2.69 (bs, 1H), 1.50 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.2, 162.9 (d, J = 248 Hz), 149.3, 132.0 (d, J = 3 Hz), 131.9, 128.6 (d, J = 8 Hz, 2C), 124.3, 119.3 (d, J = 2 Hz), 115.8 (d, J = 22 Hz, 2C), 68.8, 68.7, 60.6, 25.4; IR (ATR, cm^{-1}) 3454, 2971, 1685, 1385, 1153, 941, 804, 536; HRMS (ESI) Calcd for $C_{15}H_{14}O_3F$ $[M+H]^+$: 261.0927, Found: 261.0936.



2f

1-[(E)-2-(4-chlorophenyl)ethenyl]-5-hydroxy-5-methyl-7-oxabicyclo[4.1.0]hept-3-en-2-one, *2f*

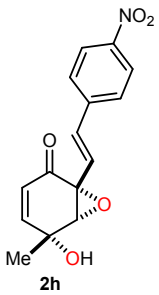
Yellow solid; m.p. 114-116°C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.35 (d, J = 8.8 Hz, 2H), 7.30 (d, J = 8.8 Hz, 2H), 6.68 (app. s, 2H), 6.49 (dd, J = 10.5, 2.8 Hz, 1H), 5.90 (d, J = 10.5 Hz, 1H), 3.63 (d, J = 2.8 Hz, 1H), 2.81 (bs, 1H), 1.51 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.1, 149.3, 134.3, 134.2, 131.9, 129.0 (2C), 128.1 (2C), 124.2, 120.3, 68.8, 68.7, 60.5, 25.4; IR (ATR, cm^{-1}) 3451, 2972, 1686, 1153, 1084, 806, 731, 499; HRMS (ESI) Calcd for $C_{15}H_{14}O_3Cl$ $[M+H]^+$: 277.0631, Found: 277.0643.



2g

1-[(E)-2-(4-bromophenyl)ethenyl]-5-hydroxy-5-methyl-7-oxabicyclo[4.1.0]hept-3-en-2-one, *2g*

Yellow solid; m.p. 128-130°C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.45 (d, J = 8.5 Hz, 2H), 7. 28 (d, J = 8.5 Hz, 2H), 6.71 (d, J = 16.2 Hz, 1H), 6.64 (d, J = 16.2 Hz, 1H), 6.50 (dd, J = 10.5, 2.8 Hz, 1H), 5.90 (d, J = 10.5 Hz, 1H), 3.63 (d, J = 2.8 Hz, 1H), 2.87 (bs, 1H), 1.51 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.1, 149.4, 134.7, 131.9 (2C), 131.8, 128.4 (2C), 124.2, 122.4, 120.5, 68.7, 68.6, 60.5, 25.4; IR (ATR, cm^{-1}) 3453, 2970, 1685, 1153, 804, 727, 537; HRMS (ESI) Calcd for $C_{15}H_{14}O_3Br$ $[M+H]^+$: 321.0126, Found: 321.0121.

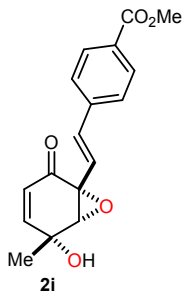


2h

5-hydroxy-5-methyl-1-[(E)-2-(4-nitrophenyl)ethenyl]-7-oxabicyclo[4.1.0]hept-3-en-2-one, *2h*

Yellow solid; m.p. 149-151°C; ^1H NMR (300 MHz, $CDCl_3$) δ 8.24-8.12 (m, 2H), 7.63-7.48 (m, 2H), 6.88 (d, J = 16.2 Hz, 1H), 6.77 (d, J = 16.2 Hz, 1H), 6.52 (dd, J = 10.5, 2.8 Hz, 1H), 5.91 (d, J = 10.5 Hz, 1H), 3.63 (d, J = 2.8 Hz,

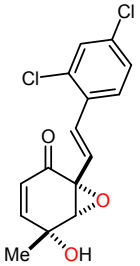
1H), 2.79 (bs, 1H), 1.51 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.8, 149.6, 147.5, 142.1, 130.7, 127.5 (2C), 125.0, 124.2 (2C), 124.1, 69.0, 68.7, 60.4, 25.4; IR (ATR, cm^{-1}) 3472, 2978, 2933, 1683, 1595, 1508, 1338, 1153, 972, 863, 688, 541; HRMS (ESI) Calcd for $C_{15}H_{12}O_5N$ $[M-H]^-$: 286.0715, Found: 286.0722.



2i

methyl 4-{(E)-2-[5-hydroxy-5-methyl-2-oxo-7-oxabicyclo[4.1.0]hept-3-en-1-yl]ethenyl}benzoate, *2i*

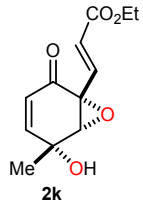
Yellow solid; m.p. 148-150°C; ^{1}H NMR (300 MHz, $CDCl_3$) 8.02-7.94 (m, 2H), 7.50-7.43 (m, 2H), 6.82 (d, J = 16.2 Hz, 1H), 6.73 (d, J = 16.2 Hz, 1H), 6.49 (dd, J = 10.5, 2.8 Hz, 1H), 5.89 (d, J = 10.5 Hz, 1H), 3.90 (s, 3H), 3.62 (d, J = 2.8 Hz, 1H), 2.91 (bs, 1H), 1.50 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.1, 166.9, 149.5, 140.2, 132.0, 130.1 (2C), 129.8, 126.8 (2C), 124.2, 122.5, 68.8, 68.7, 60.4, 52.3, 25.5; IR (ATR, cm^{-1}) 3449, 2973, 2950, 1707, 1683, 1606, 1274, 1150, 1110, 1082, 966, 855, 694, 537; HRMS (ESI) Calcd for $C_{17}H_{17}O_5$ $[M+H]^+$: 301.1076, Found: 301.1079.



2j

1-[(E)-2-(2,4-dichlorophenyl)ethenyl]-5-hydroxy-5-methyl-7-oxabicyclo[4.1.0]hept-3-en-2-one, *2j*

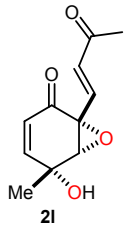
Yellow solid; m.p. 120-122°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (d, J = 8.5 Hz, 1H), 7.36 (d, J = 2.1 Hz, 1H), 7.21 (dd, J = 8.5, 2.1 Hz, 1H), 7.03 (d, J = 16.1 Hz, 1H), 6.70 (d, J = 16.1 Hz, 1H), 6.50 (dd, J = 10.5, 2.8 Hz, 1H), 5.90 (d, J = 10.5 Hz, 1H), 3.64 (d, J = 2.8 Hz, 1H), 2.83 (bs, 1H), 1.51 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.0, 149.5, 134.5, 134.1, 132.6, 129.7, 128.2, 128.0, 127.5, 124.2, 123.1, 69.0, 68.8, 60.5, 25.4; IR (ATR, cm^{-1}) 3388, 2974, 2931, 1683, 1665, 1137, 964, 861, 542; HRMS (ESI) Calcd for $C_{15}H_{11}O_3Cl_2$ $[M-H]^-$: 309.0085, Found: 309.0090.



2k

ethyl (3E)-4-[5-hydroxy-5-methyl-2-oxo-7-oxabicyclo[4.1.0]hept-3-en-1-yl]but-3-enoate, *2k*

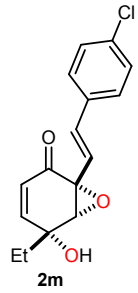
White solid; m.p. 113-115°C; ^{1}H NMR (300 MHz, $CDCl_3$) 7.32 (d, J = 15.8 Hz, 1H), 6.50 (dd, J = 10.5, 2.8 Hz, 1H), 6.16 (d, J = 15.8 Hz, 1H), 5.88 (d, J = 10.5 Hz, 1H), 4.22 (q, J = 7.1 Hz, 2H), 3.53 (d, J = 2.8 Hz, 1H), 2.92 (bs, 1H), 1.48 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.8, 165.6, 149.7, 138.1, 124.5, 124.0, 68.9, 68.6, 61.0, 59.7, 25.4, 14.3; IR (ATR, cm^{-1}) 3443, 2971, 1678, 1255, 1190, 1155, 975, 825, 691, 585; HRMS (ESI) Calcd for $C_{12}H_{14}O_5Na$ $[M+Na]^+$: 261.0739, Found: 261.0749.



2l

5-hydroxy-5-methyl-1-[(1E)-4-oxopent-1-en-1-yl]-7-oxabicyclo[4.1.0]hept-3-en-2-one, *2l*

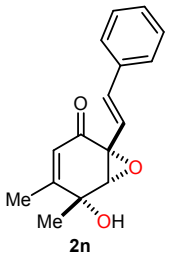
Colourless oil; ^{1}H NMR (300 MHz, $CDCl_3$) 7.19 (d, J = 16.1 Hz, 1H), 6.51 (dd, J = 10.5, 2.8 Hz, 1H), 6.35 (d, J = 16.1 Hz, 1H), 5.90 (d, J = 10.5 Hz, 1H), 3.55 (d, J = 2.8 Hz, 1H), 2.75 (bs, 1H), 2.33 (s, 3H), 1.49 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.7, 191.9, 149.8, 136.7, 132.1, 124.0, 69.0, 68.7, 59.7, 27.6, 25.4; IR (ATR, cm^{-1}) 3385, 2977, 2928, 1679, 1634, 1151, 976, 822, 570; HRMS (ESI) Calcd for $C_{11}H_{12}O_4Na$ $[M+Na]^+$: 231.0633, Found: 231.0641.



2m

1-[(1E)-3-(4-chlorophenyl)prop-1-en-1-yl]-5-ethyl-5-hydroxy-7-oxabicyclo[4.1.0]hept-3-en-2-onene, *2m*

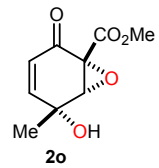
Colourless oil; ^{1}H NMR (300 MHz, $CDCl_3$) 7.39-7.25 (m, 4H), 6.68 (app. s, 2H), 6.40 (dd, J = 10.5, 2.8 Hz, 1H), 6.00 (d, J = 10.5 Hz, 1H), 3.55 (d, J = 2.8 Hz, 1H), 2.85 (bs, 1H), 1.86 (q, J = 7.6 Hz, 2H), 0.90 (t, J = 7.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.4, 147.9, 134.3, 134.2, 131.9, 128.9 (2C), 128.1 (2C), 125.7, 120.2, 71.9, 68.1, 60.4, 31.4, 7.7; IR (ATR, cm^{-1}) 3408, 2971, 2937, 1683, 1090, 1013, 971, 810, 734, 541; HRMS (ESI) Calcd for $C_{16}H_{14}O_3Cl$ $[M-H]^-$: 289.0631, Found: 289.0638.



2n

5-hydroxy-4,5-dimethyl-1-[(1E)-3-phenylprop-1-en-1-yl]-7-oxabicyclo[4.1.0]hept-3-en-2-one, *2n*

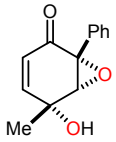
Yellow solid; m.p. 49-51°C; ^{1}H NMR (300 MHz, $CDCl_3$) 7.45-7.41 (m, 2H), 7.36-7.24 (m, 3H), 6.73 (app. s, 2H), 5.81 (q, J = 1.4 Hz, 1H), 3.66 (s, 1H), 2.59 (bs, 1H), 2.03 (d, J = 1.4 Hz, 3H), 1.50 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.8, 159.8, 135.9, 132.9, 128.8 (2C), 128.5, 127.0 (2C), 122.6, 119.6, 70.8, 69.4, 61.3, 25.0, 18.2; IR (ATR, cm^{-1}) 3405, 2980, 2925, 1669, 1629, 1152, 965, 866, 693, 534; HRMS (ESI) Calcd for $C_{16}H_{17}O_3$ $[M+H]^+$: 257.1178, Found: 257.1177.



2o

methyl 5-hydroxy-5-methyl-2-oxo-7-oxabicyclo[4.1.0]hept-3-ene-1-carboxylate, *2o*

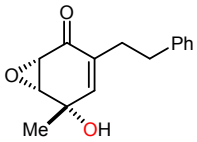
Colourless oil; ^{1}H NMR (300 MHz, $CDCl_3$) 6.51 (dd, J = 10.6, 2.7 Hz, 1H), 5.89 (d, J = 10.6 Hz, 1H), 3.86 (s, 3H), 3.74 (d, J = 2.7 Hz, 1H), 2.68 (s, 1H), 1.53 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 187.8, 165.1, 149.9, 123.9, 67.8, 63.2, 59.0, 53.3, 25.4; IR (ATR, cm^{-1}) 3473, 2960, 1748, 1665, 1443, 1238, 1027, 944, 823, 779, 590; HRMS (ESI) Calcd for $C_9H_{10}O_5Na$ $[M+Na]^+$: 221.0426, Found: 221.0417.



2p

5-hydroxy-5-methyl-1-phenyl-7-oxabicyclo[4.1.0]hept-3-en-2-one, *2p*

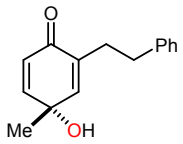
Colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) 7.43-7.34 (m, 5H), 6.52 (dd, J = 10.5, 2.8 Hz, 1H), 5.97 (d, J = 10.5 Hz, 1H), 3.58 (d, J = 2.8 Hz, 1H), 2.57 (s, 1H), 1.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.3, 148.9, 132.6, 128.9, 128.5 (2C), 127.4 (2C), 124.8, 68.5, 67.5, 62.6, 25.6; IR (ATR, cm^{-1}) 3401, 2978, 1682, 1497, 1447, 1087, 939, 817, 761, 592, 556; HRMS (ESI) Calcd for $C_{13}H_{12}O_3Na$ $[M+Na]^+$: 239.0684, Found: 239.0690.



2q

5-hydroxy-5-methyl-3-(2-phenylethyl)-7-oxabicyclo[4.1.0]hept-3-en-2-one, *2q*

Colourless oil; ^{1}H NMR (300 MHz, $CDCl_3$) 7.30-7.25 (m, 2H), 7.21-7.11 (m, 3H), 5.97-5.96 (m, 1H), 3.58 (dd, J = 3.9, 2.8 Hz, 1H), 3.52 (d, J = 3.9 Hz, 1H), 2.75-2.69 (m, 2H), 2.60-2.50 (m, 1H), 2.45-2.38 (m, 1H), 2.23 (s, 1H), 1.35 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.7, 145.5, 140.9, 133.4, 128.9 (2C), 128.5 (2C), 126.3, 68.6, 58.9, 54.7, 34.4, 31.4, 25.5; IR (ATR, cm^{-1}) 3409, 2925, 1677, 1495, 1452, 1085, 883, 672, 591; HRMS (ESI) Calcd for $C_{15}H_{16}O_3Na$ $[M+Na]^+$: 267.0997, Found: 267.0999.



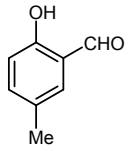
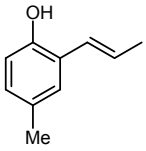
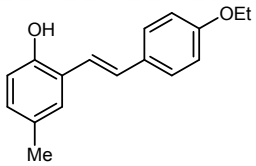
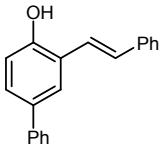
2'q

4-hydroxy-4-methyl-2-(2-phenylethyl)cyclohexa-2,5-dien-1-one, *2'q*

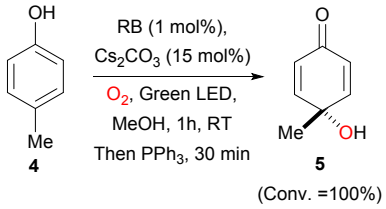
Colourless oil; ^{1}H NMR (300 MHz, $CDCl_3$) 7.29-7.25 (m, 2H), 7.20-7.13 (m, 3H), 6.81 (dd, J = 10.0, 3.1 Hz, 1H), 6.40-6.38 (m, 1H), 6.11 (d, J = 10.0 Hz, 1H), 2.81-2.76 (m, 2H), 2.60-2.54 (m, 2H), 1.83 (s, 1H), 1.35 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.5, 151.6, 147.8, 141.5, 136.5, 128.8 (2C), 128.4 (2C), 127.4, 126.2, 67.5, 34.5, 31.2, 26.9; IR (ATR, cm^{-1}) 3381, 2925, 1665, 1633, 1494, 1451, 1123, 1049, 833, 749, 700; HRMS (ESI) Calcd for $C_{15}H_{16}O_2Na$ $[M+Na]^+$: 251.1048, Found: 251.1051.

4.3 Substrate limitations

The general procedure for the photooxygenation process applied to the following phenolic substrates failed to give the desired products.

			
Complex reaction mixture was observed by ^{1}H NMR of the crude	*Decomposition of the substrate observed by ^{1}H NMR of the crude*	*Decomposition of the substrate observed by ^{1}H NMR of the crude*	*Decomposition of the substrate observed by ^{1}H NMR of the crude*

The photooxygenation of *para*-cresol did not afford the desired epoxyquinol as depicted below:

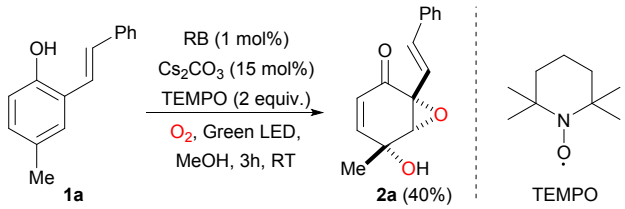


NMR data are in agreement with those reported in the literature.[S4]

5. Control experiments

➢ Reaction in the presence of TEMPO

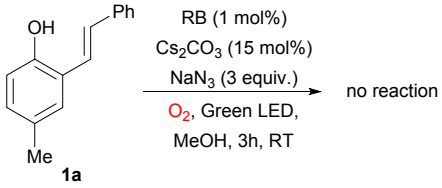
Similar levels of yields were obtained for the photooxygenation of **1a** without or with two equivalents of TEMPO. This experiment confirms that a mechanism involving radical intermediates is not the main pathway by which **2a** is formed.



Experimental procedure: To a Schlenk flask was added 2-alkenylphenol **1a** (0.25 mmol), cesium carbonate (12.2 mg, 37.5 µmol, 15 mol%), Rose Bengal (2.5 mg, 2.5 µmol, 1 mol%), TEMPO (78 mg, 0.5 mmol) and MeOH (5 mL) to give a purple solution. The reaction medium was gently bubbled with dioxygen throughout the reaction time and the homogeneous solution was irradiated with two green LED (2 x 1 W). The distance from the light source to the irradiation Schlenk vessel was 5 cm without the use of any filters. The reaction was stirred for 3 hours at which point methanol was removed under reduced pressure. The crude was quickly purified by chromatography on silica gel to give the desired product **2a** (pentane/diethyl ether, 95/5) in 40% yield.

➢ Reaction in the presence of sodium azide

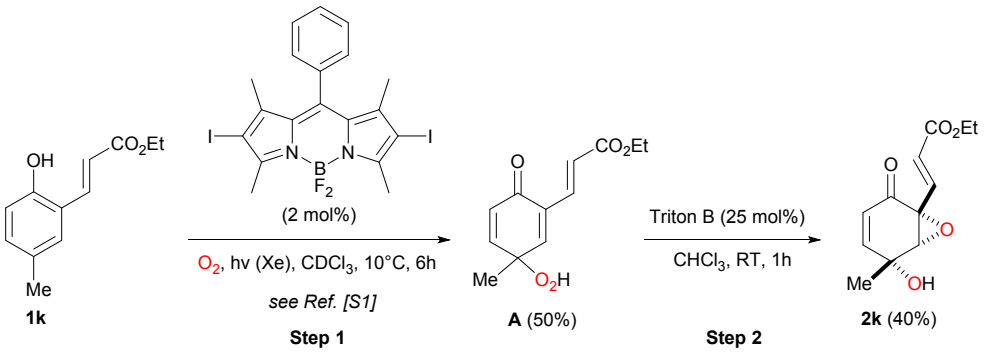
No reaction occurred in the presence of 3 equivalents of sodium azide which is a quencher of singlet oxygen. This experiment confirms that a mechanism involving singlet oxygen is the main pathway by which **2a** is formed.



Experimental procedure: To a Schlenk flask was added 2-alkenylphenol **1a** (0.25 mmol), cesium carbonate (12.2 mg, 37.5 µmol, 15 mol%), Rose Bengal (2.5 mg, 2.5 µmol, 1 mol%), sodium azide (49 mg, 0.75 mmol) and MeOH (5 mL) to give a purple solution. The reaction medium was gently bubbled with dioxygen throughout the reaction time and the homogeneous solution was irradiated with two green LED (2 x 1 W). The distance from the light source to the irradiation Schlenk vessel was 5 cm without the use of any filters. The reaction was stirred for 3 hours at which point methanol was removed under reduced pressure. The crude was analyzed by ^{1}H NMR and only the starting material **1a** was detected.

➢ Two step reaction

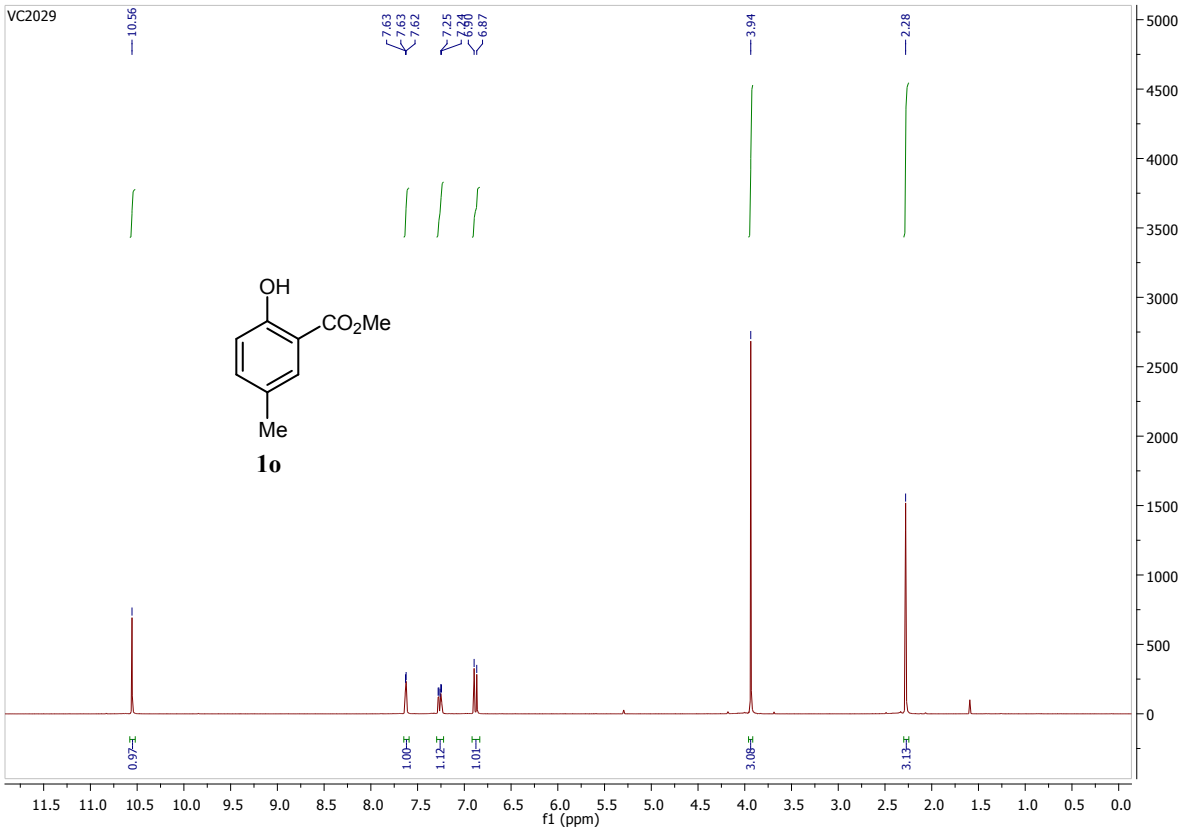
A two-step procedure was performed to confirm the relative stereochemistry of the epoxyquinols **2**. To this aim, the phenol **1k** was transformed into the hydroperoxide **A** through a reported procedure which uses a catalytic amount of a BODIPY photosensitizer.[S1] Based on a reported procedure known to form *cis*-epoxyquinols,[S5] the hydroperoxide **A** underwent a base-catalyzed epoxidation reaction to form the compound **2k** which exhibits identical NMR data to those observed for the product obtained by photooxygenation of phenol **1k** using the rose bengal/cesium carbonate multicatalytic system.

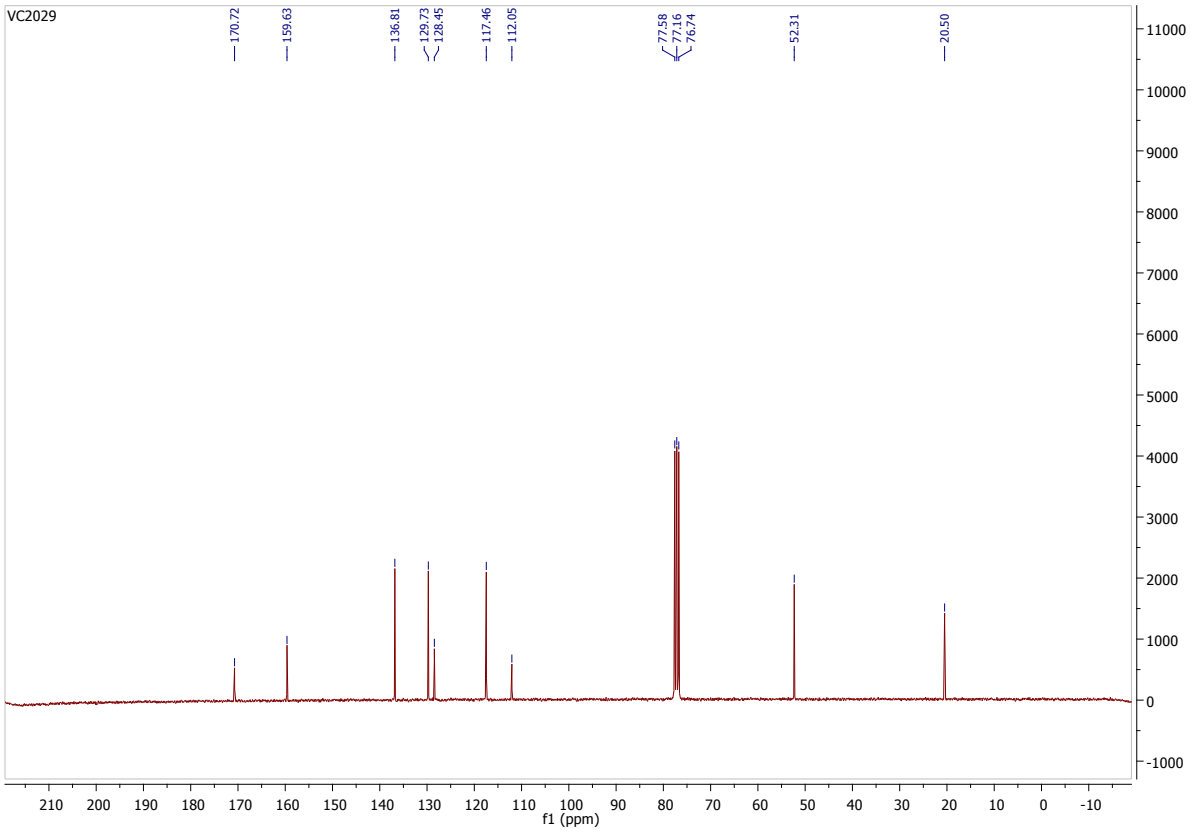


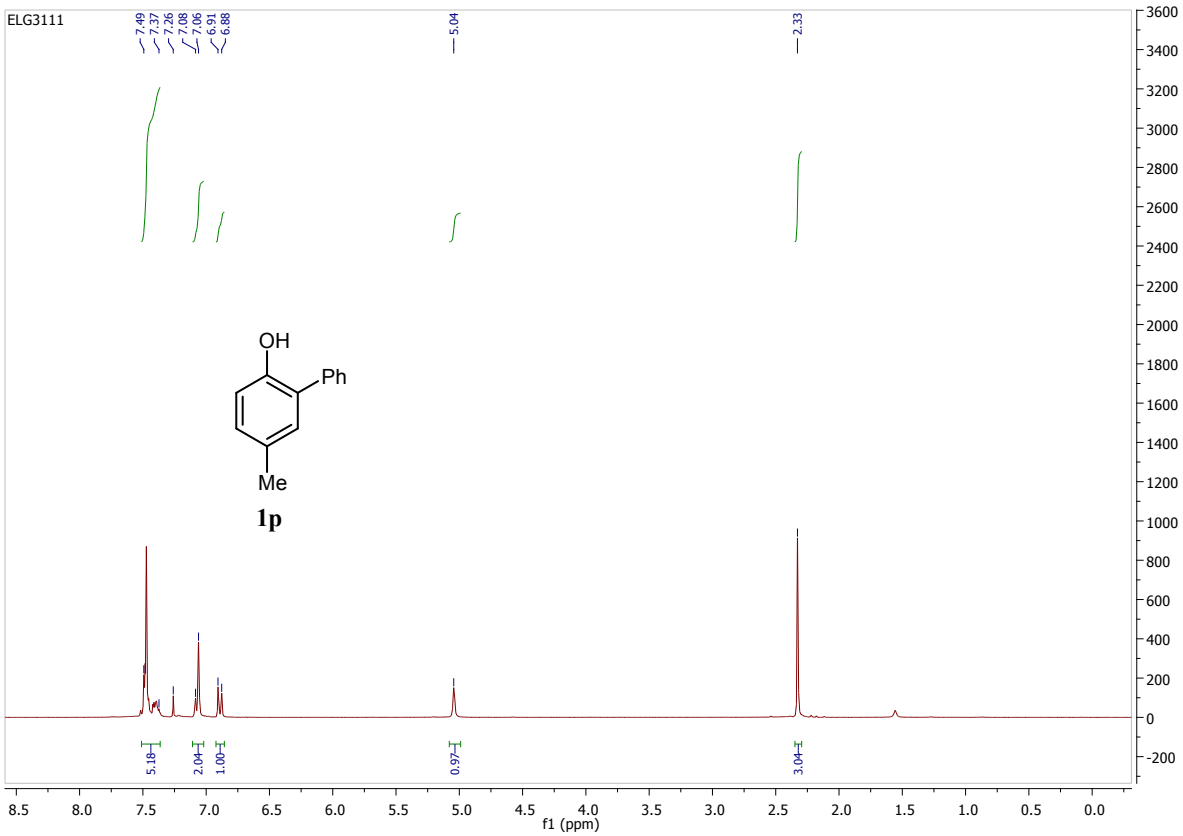
Experimental procedure (step 1): To a Schlenk flask was added 2-alkenylphenol **1k** (206 mg, 1 mmol), photosensitizer (2 mol%, 0.02 mmol, 11.2 mg) and $CDCl_3$ (9.6 mL) to give a pink red solution. The flask was placed into a crystallizing dish with water (10°C). The reaction medium was gently bubbled with dioxygen throughout the reaction time (6h) and the homogeneous solution was irradiated with a Xenon lamp (12 V, 35 W). The distance from the light source to the irradiation Schlenk vessel was 10 cm without the use of any filters. The solvent was removed in vacuo and the crude was quickly purified by chromatography on a pad of silica gel (pentane/EtOAc, 6/4) to give the desired compound **A** in 50% yield which turned out to be rather unstable. NMR data are in agreement with those reported in the literature.[S1]

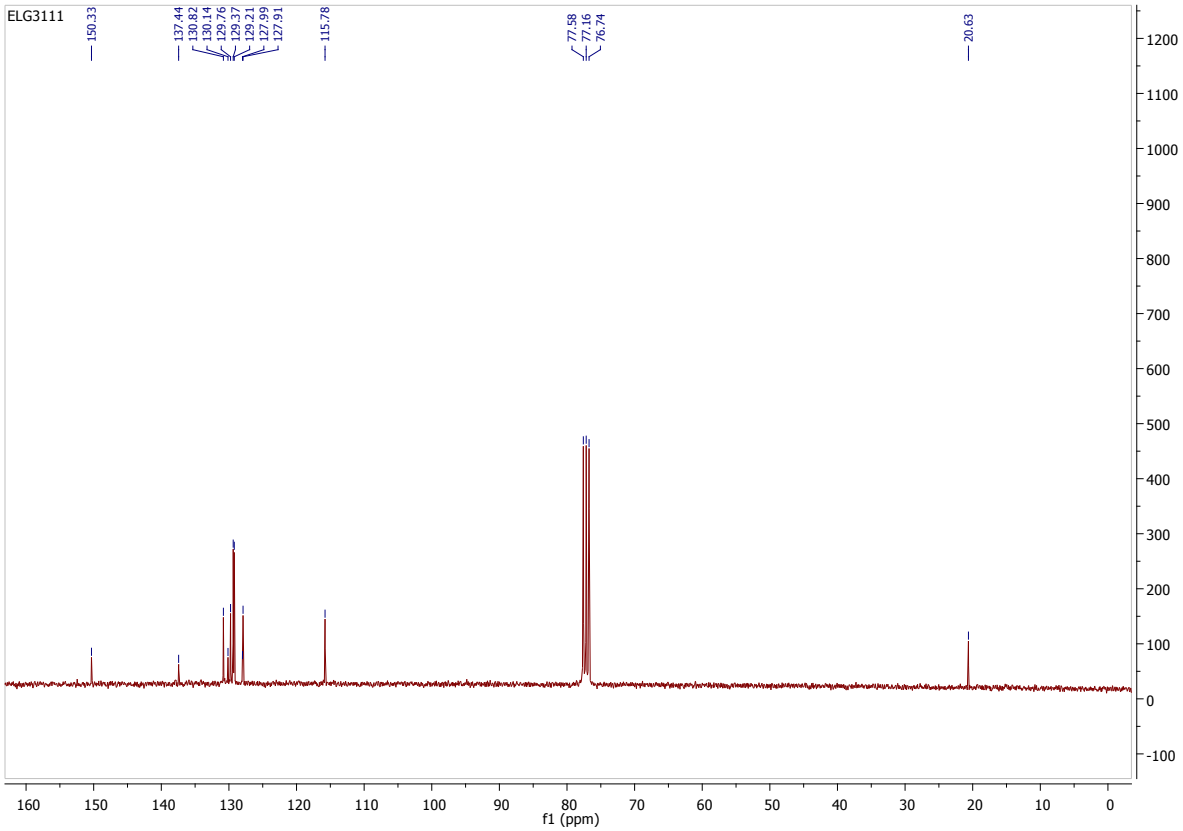
Experimental procedure (step 2): To a solution of *para*-peroxyquinol **A** (50 mg, 0.21 mmol) in chloroform (4.8 mL) was added a 40% solution of Triton B in MeOH (24 µL, 0.052 mmol, 0.25 equiv.), and the resulting mixture was stirred at room temperature. After 1 hour, the solvent was removed in vacuo and the crude was purified by chromatography on silica gel (pentane/EtOAc, 1/1) to afford **2k** in 40% yield.

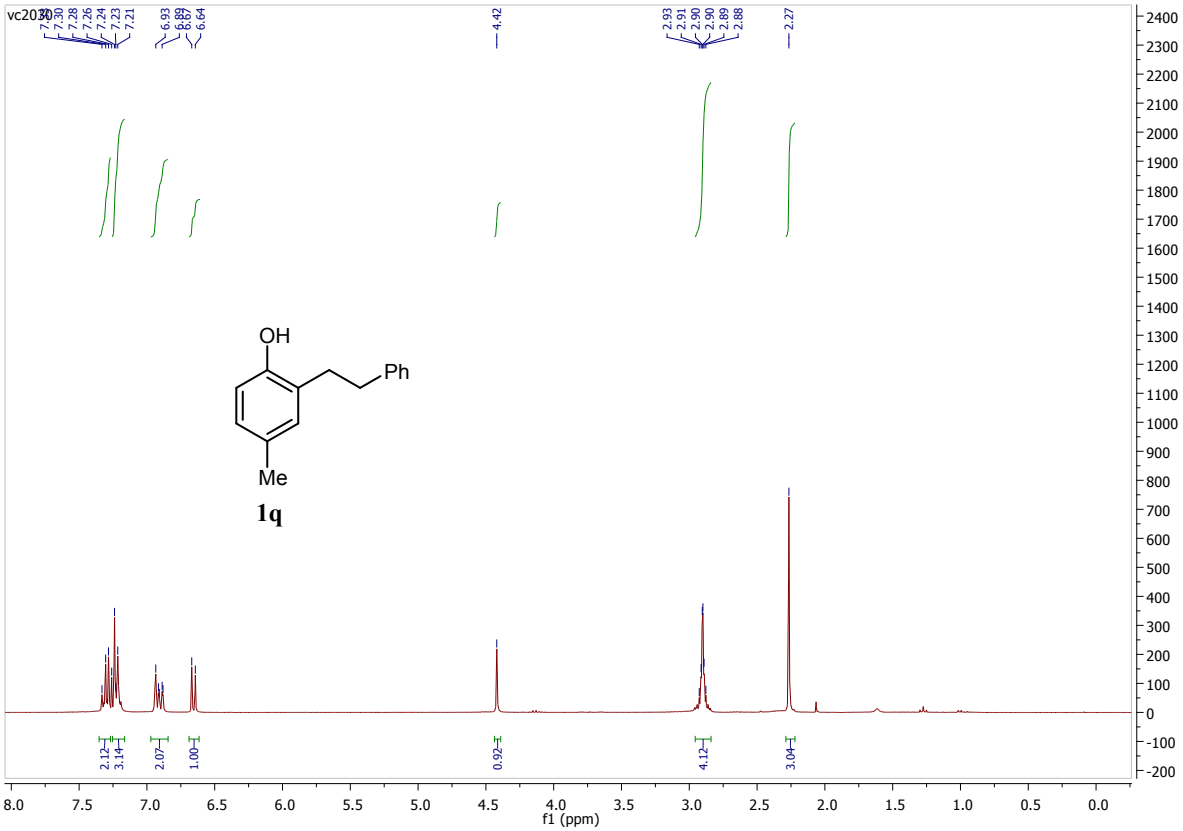
6. ^{1}H and ^{13}C NMR spectra






ELG3111
7.49
7.37
7.36
7.08
7.06
6.91
6.88
5.04
2.33
OH
Ph
Me
1p
5.18
2.04
1.00
0.97
3.04
f1 (ppm)


ELG3111
150.33
137.44
130.82
130.14
129.76
129.37
129.21
127.99
127.91
115.78
77.58
77.16
76.74
20.63
f1 (ppm)


vc2030
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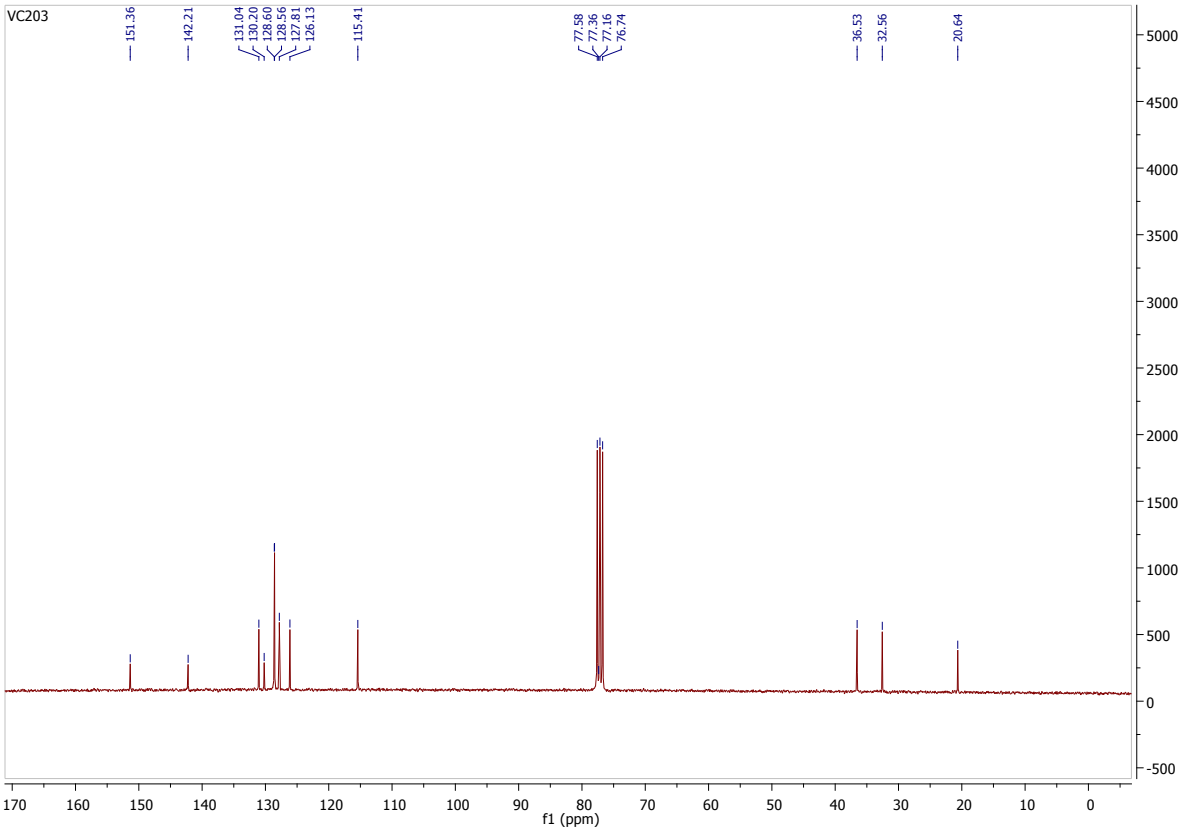
7.26
7.24
7.23
7.21
6.93
6.89
6.87
6.64
4.42
2.93
2.91
2.90
2.90
2.89
2.88
2.27
OH
Ph
Me
1q
2.12
3.14
2.07
1.00
0.92
4.12
3.04
f1 (ppm)


VC203
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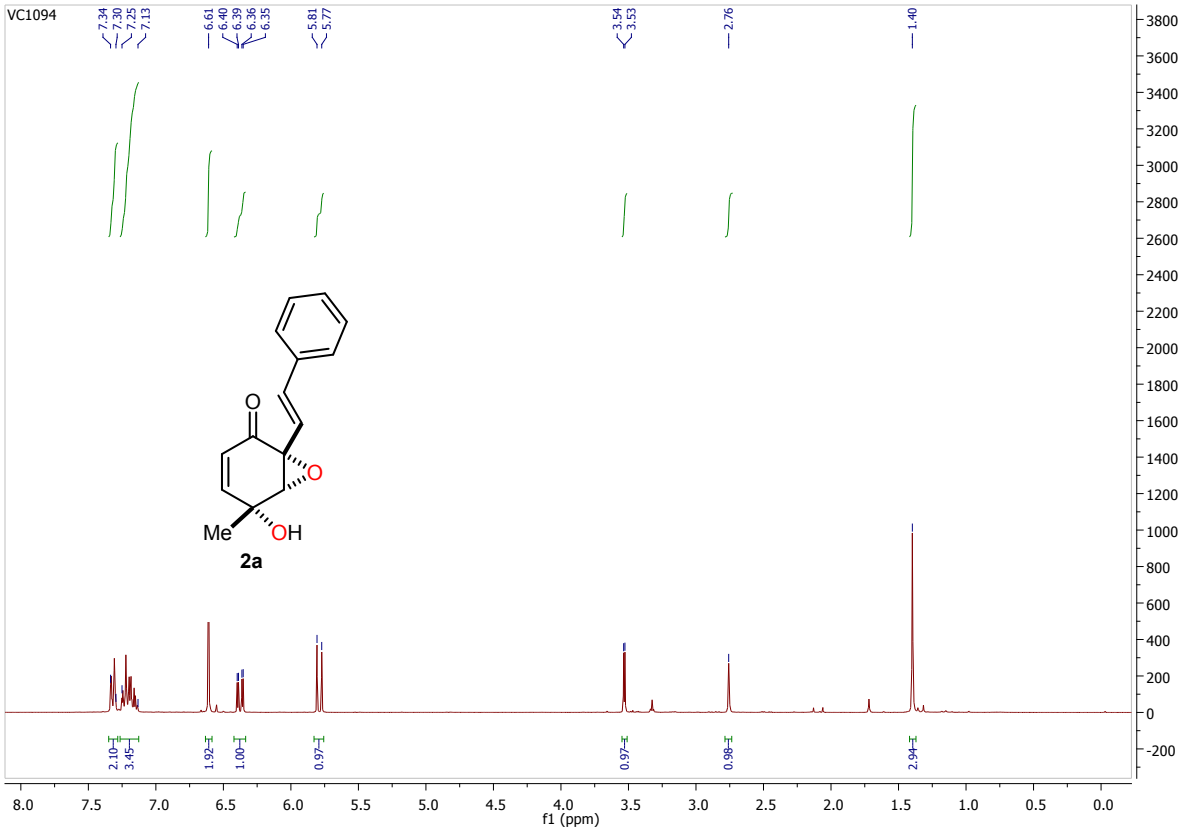
131.04
130.20
128.60
128.56
127.81
126.13
115.41
77.58
77.36
77.16
76.74
36.53
32.56
20.64
f1 (ppm)


VC1094
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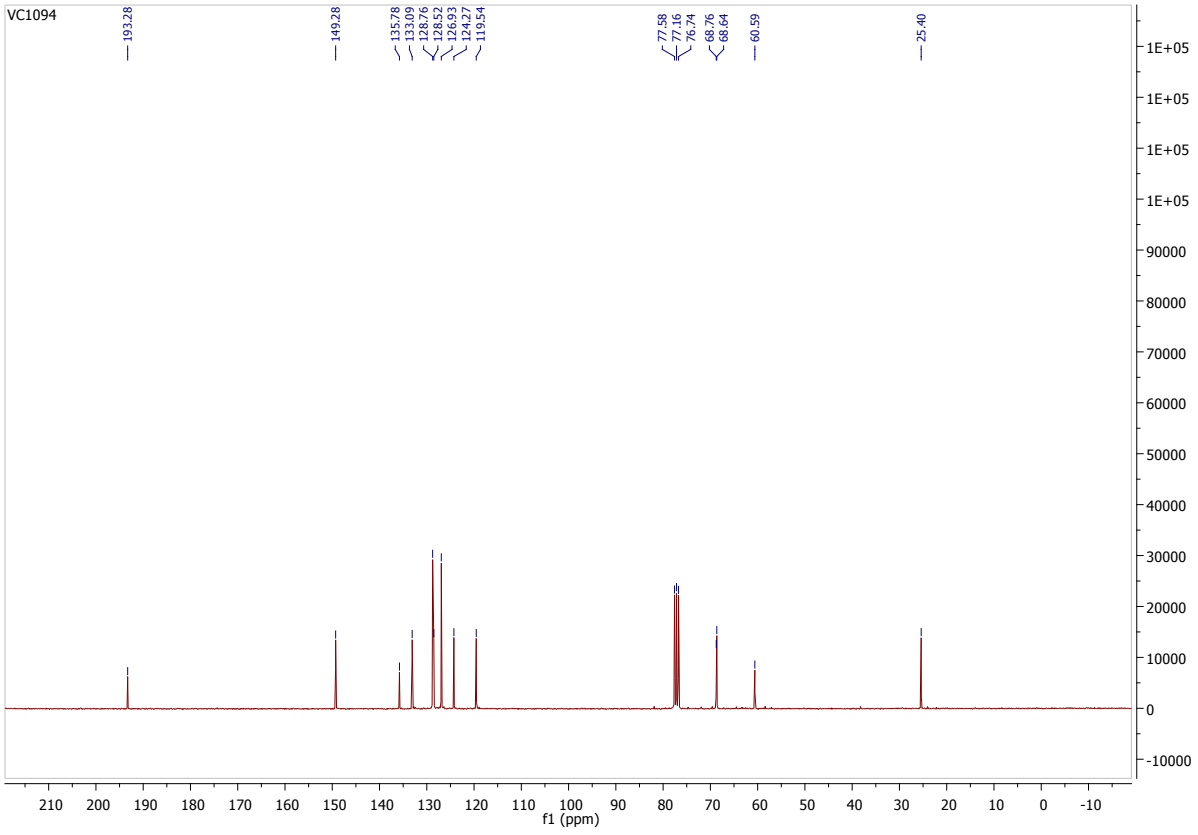
7.30
7.25
7.13
6.61
6.40
6.39
6.36
6.35
5.81
5.77
3.54
3.53
2.76
1.40
O
O
Me
OH
2a
2.10
3.45
1.92
1.00
0.97
0.97
0.98
2.94
f1 (ppm)


VC1094
193.28
149.28
135.78
133.09
128.76
128.52
126.93
124.27
119.54
77.58
77.16
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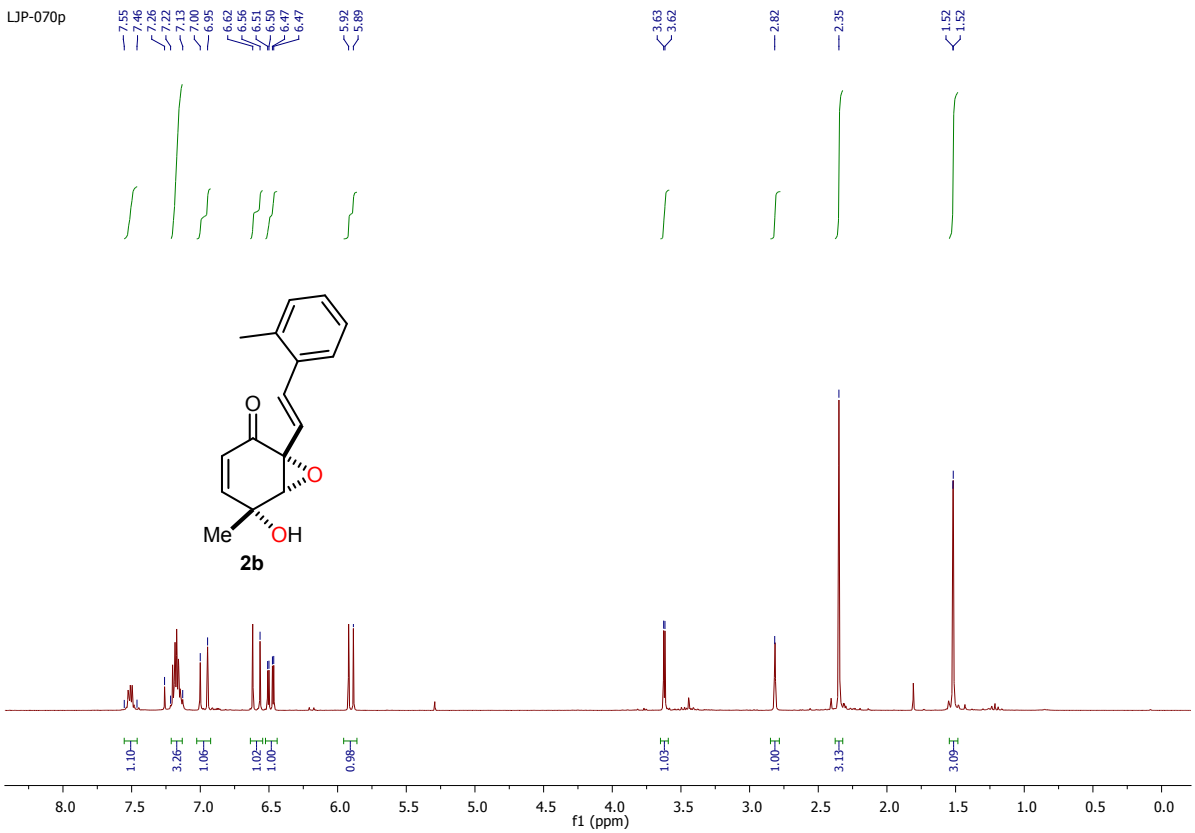
68.76
68.64
60.59
25.40
f1 (ppm)


LJP-070p
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7.46
7.26
7.22
7.13
7.00
6.95
6.62
6.56
6.51
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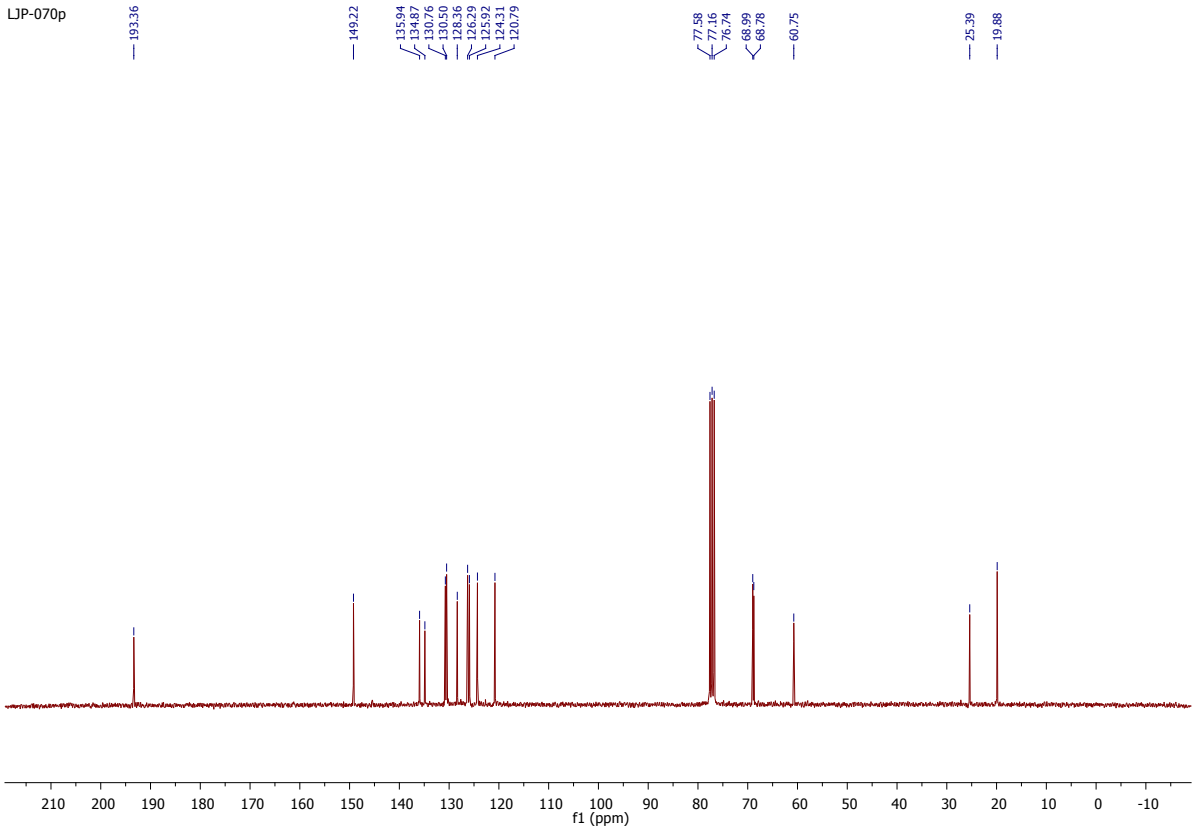
6.47
6.47
5.92
5.89
3.63
3.62
2.82
2.35
1.52
1.52
O
O
Me
OH
2b
1.10
3.26
1.06
1.02
1.00
0.98
1.03
1.00
3.13
3.09
f1 (ppm)


LJP-070p
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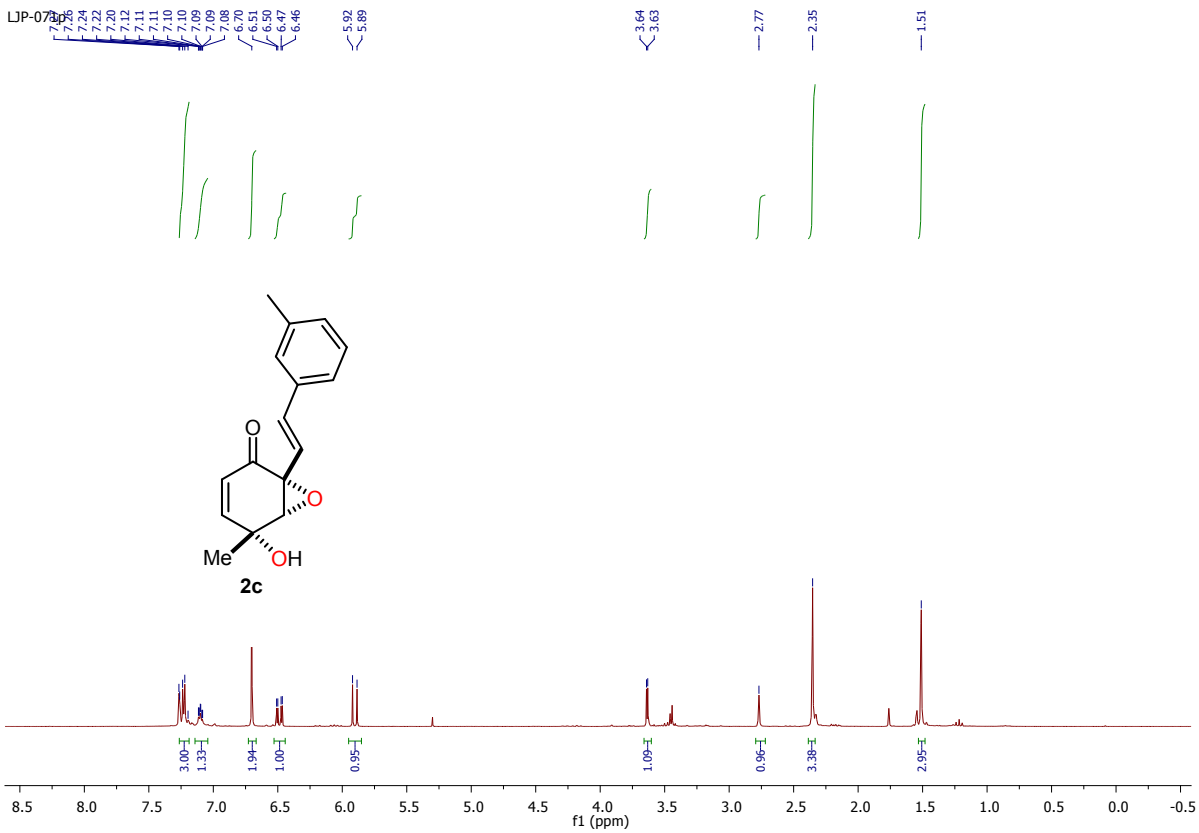
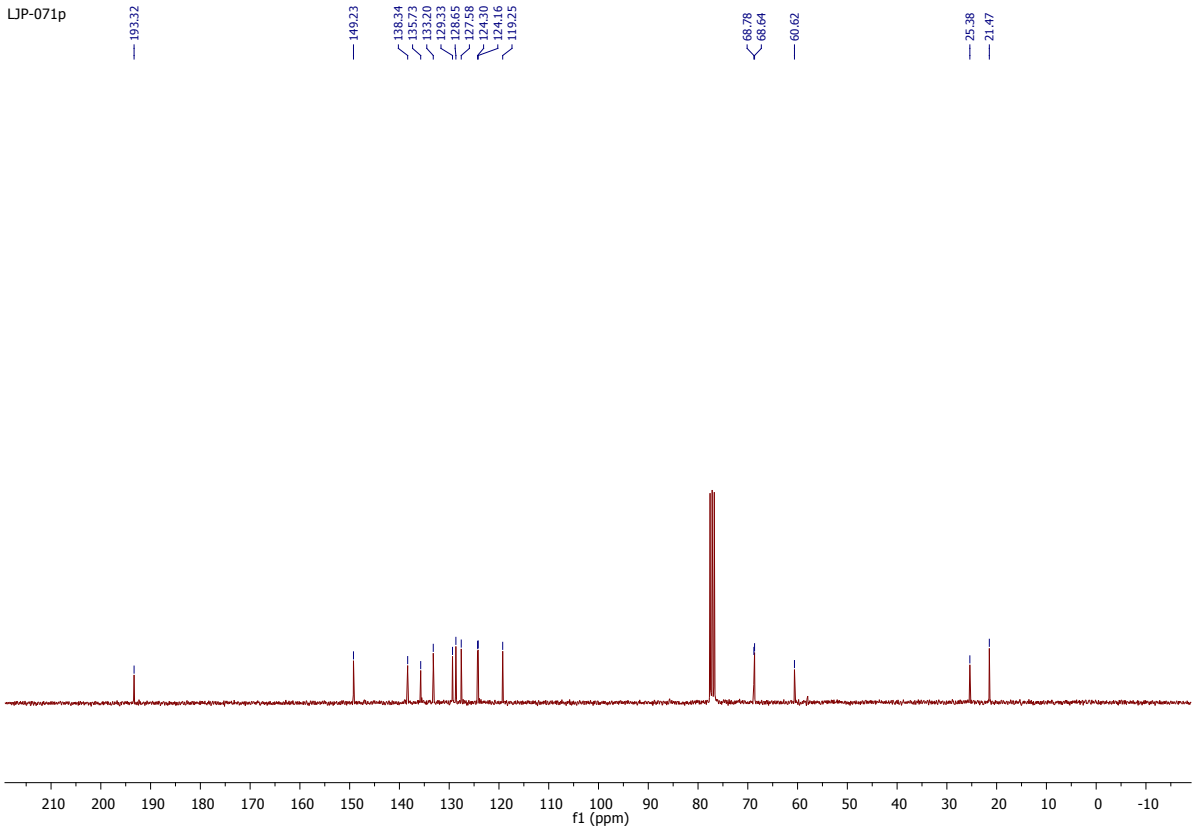
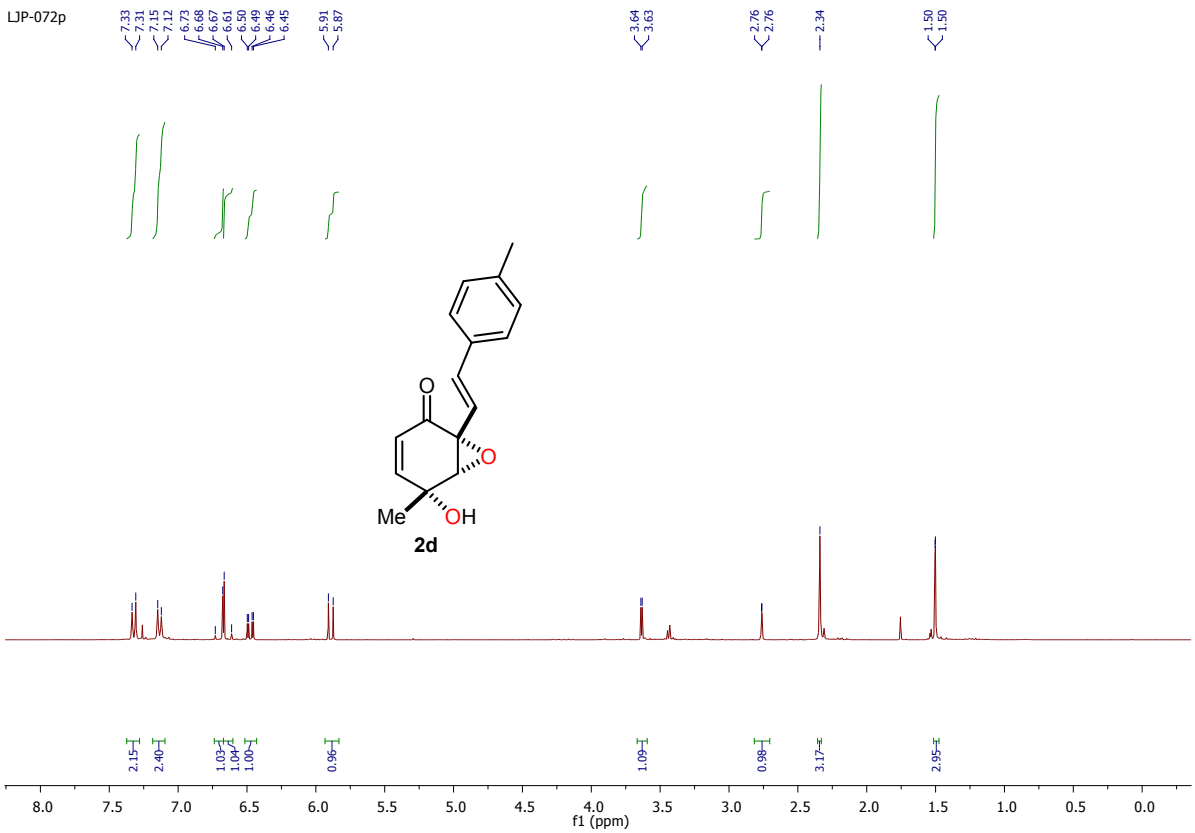
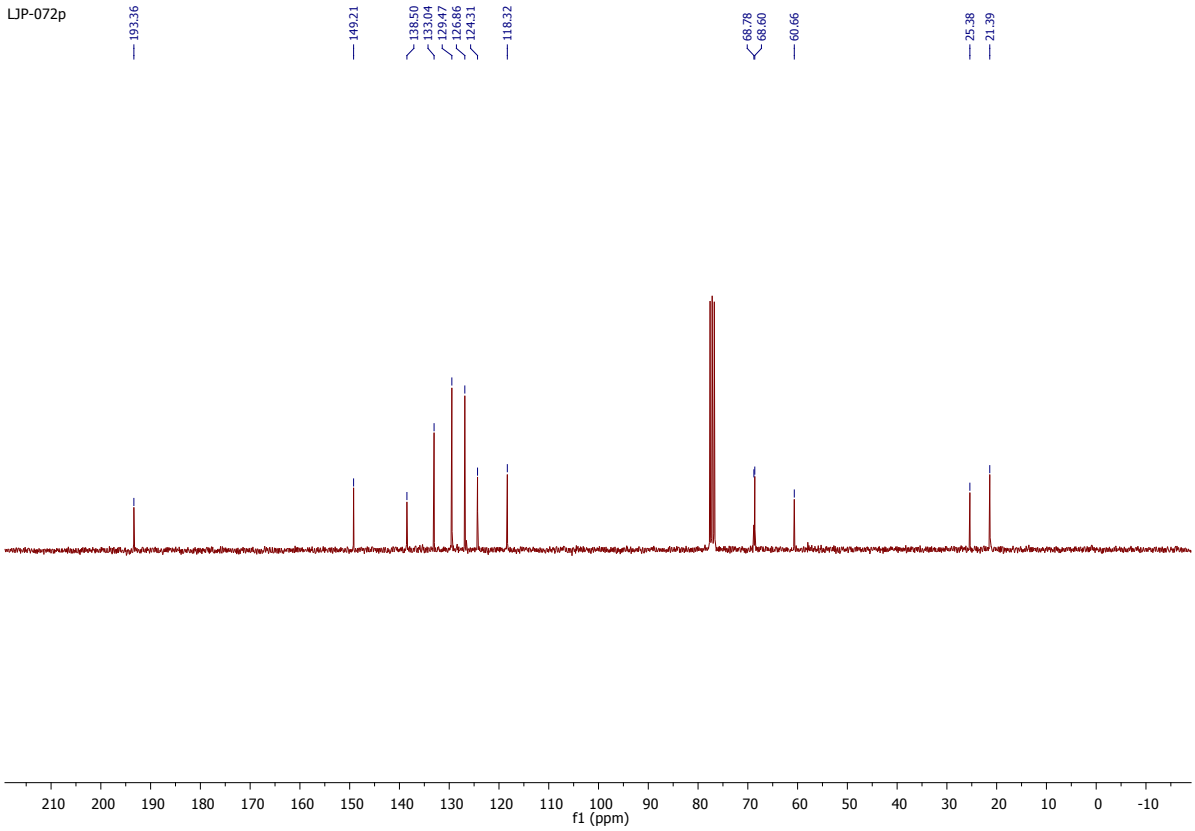
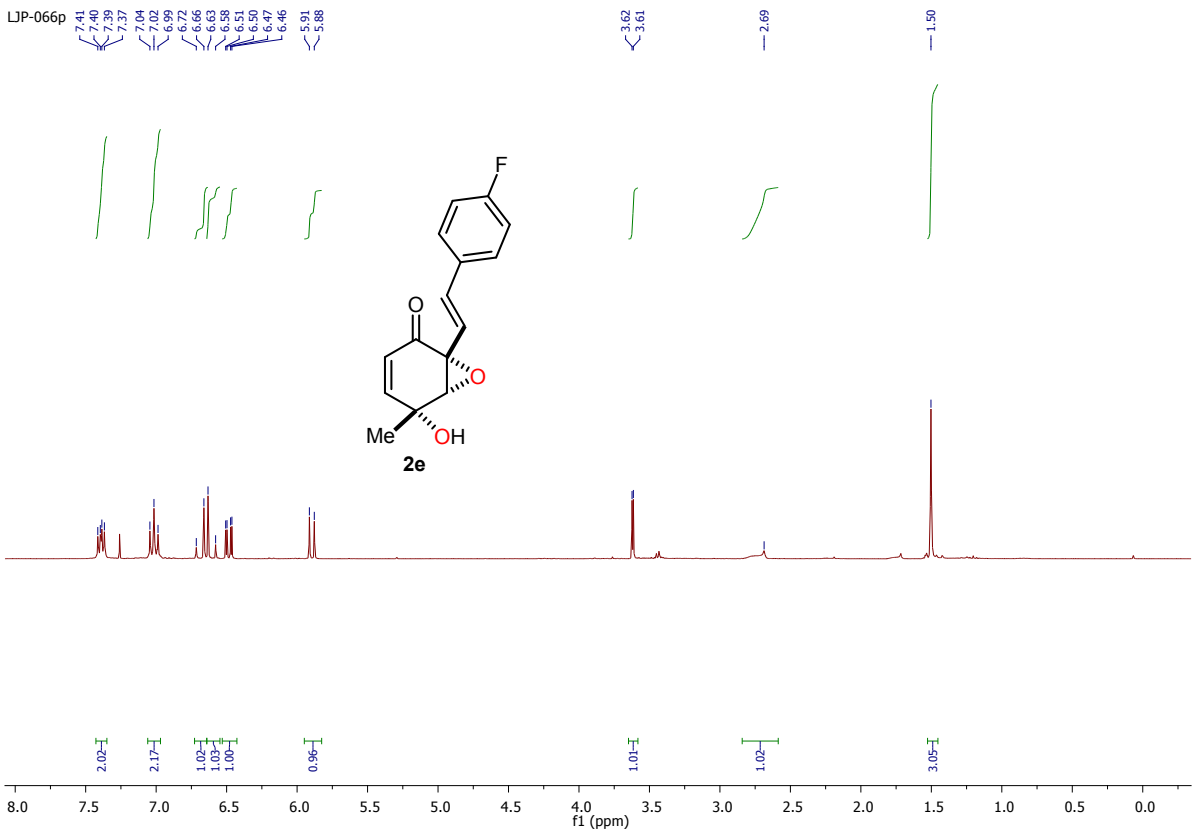
149.22
135.94
134.87
130.76
130.50
128.36
126.29
125.92
124.31
120.79
77.58
77.16
76.74
68.99
68.78
60.75
25.39
19.88
f1 (ppm)

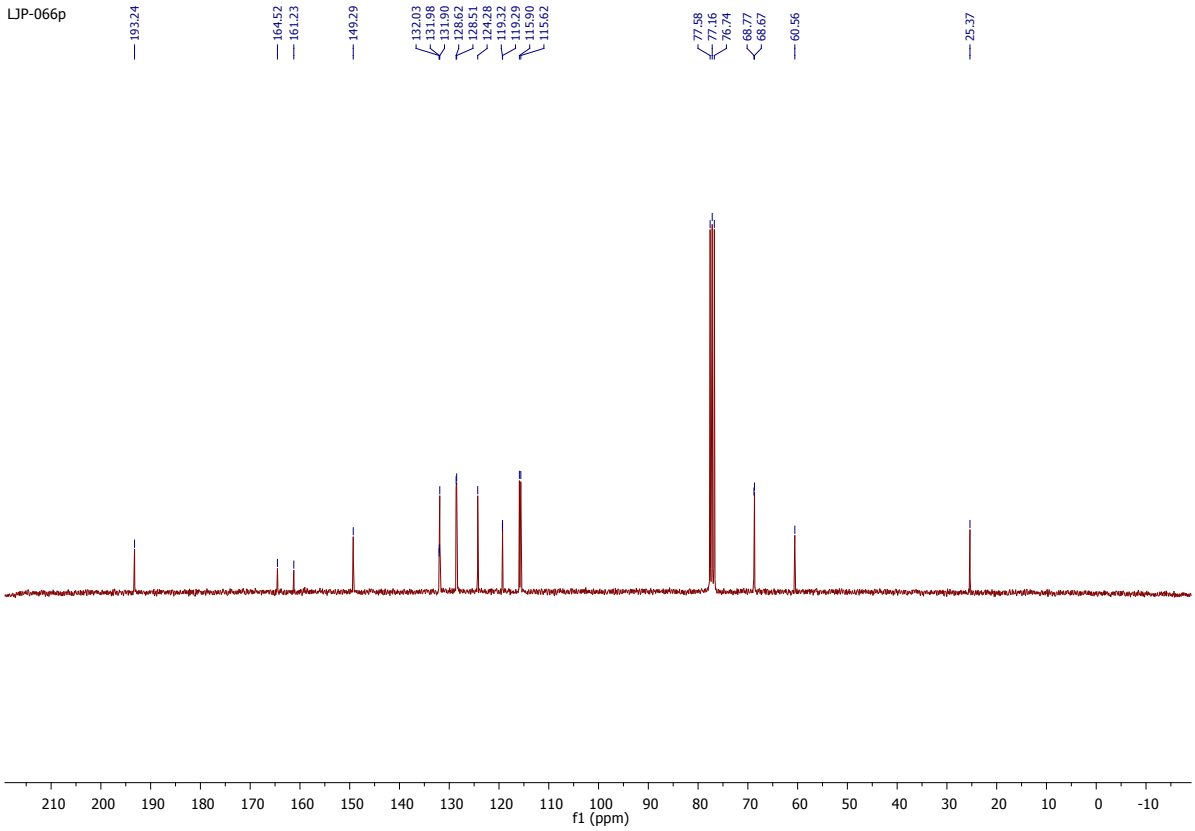

LJP-071p
7.26
7.24
7.22
7.20
7.12
7.11
7.11
7.10
7.10
7.09
7.09
7.08
6.70
6.51
6.50
6.47
6.46
5.92
5.89
3.64
3.63
2.77
2.35
1.51
O
O
Me
OH
2c
3.00
1.33
1.94
1.00
0.95
1.09
0.96
3.38
2.95
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

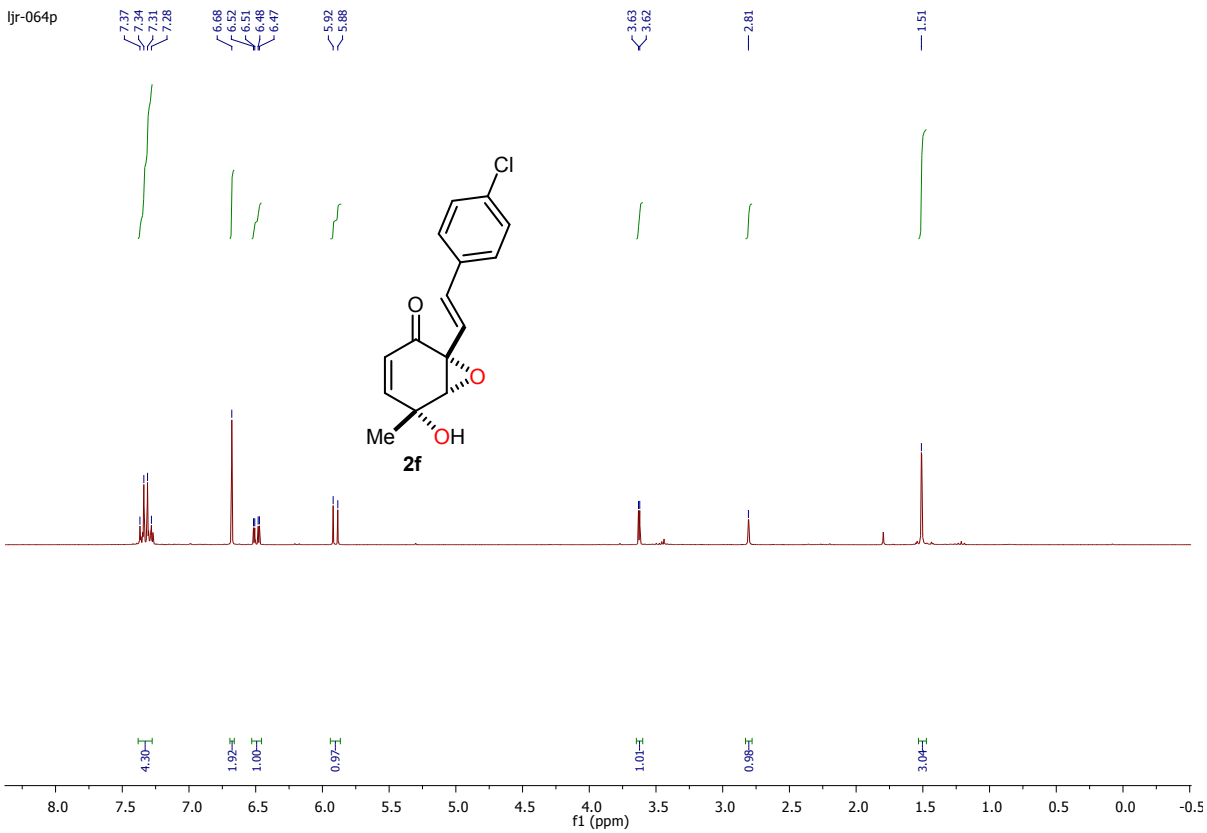

LJP-071p
193.32
149.23
138.34
135.73
133.20
129.33
128.65
127.58
124.30
124.16
119.25
68.78
68.64
60.62
25.38
21.47
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

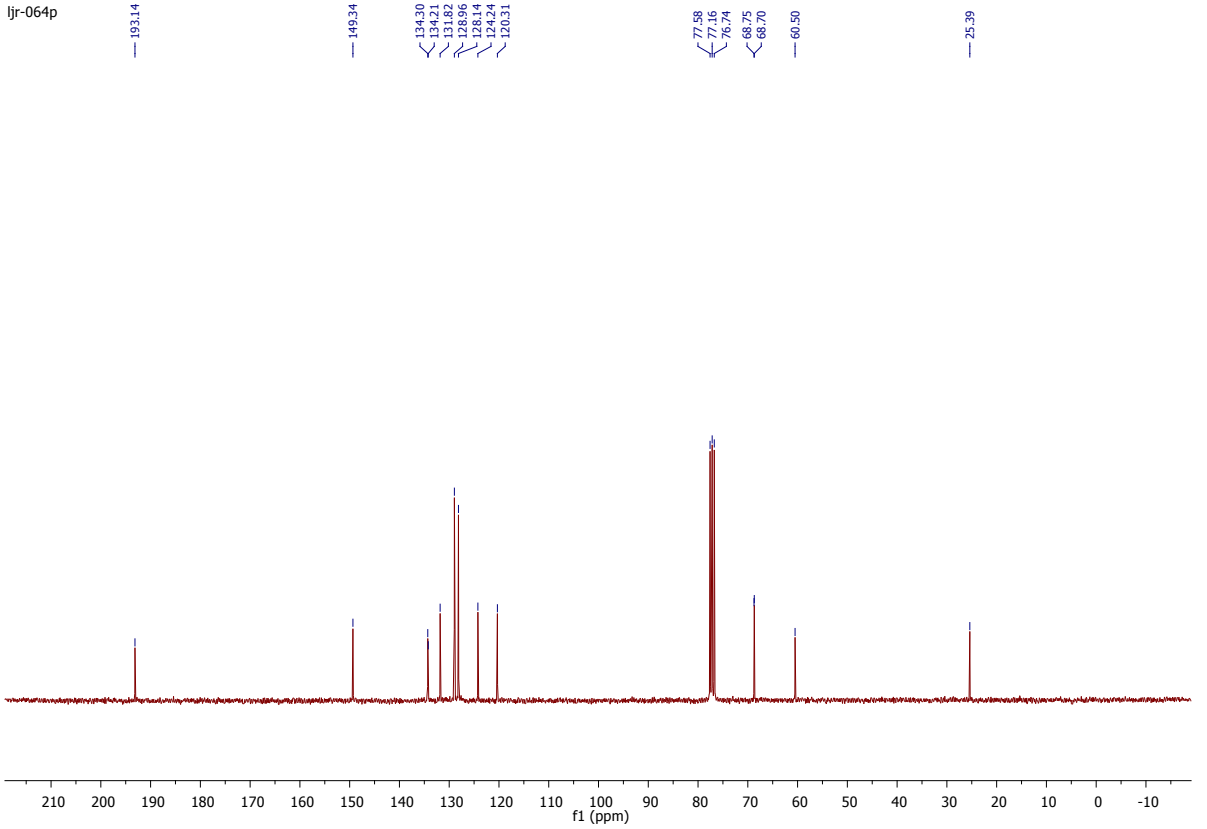

LJP-072p
7.33
7.31
7.15
7.12
6.73
6.68
6.67
6.61
6.50
6.49
6.46
6.45
5.91
5.87
3.64
3.63
2.76
2.76
2.34
1.50
1.50
O
O
Me
OH
2d
2.15
2.40
1.03
1.04
1.00
0.96
1.09
0.98
3.17
2.95
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

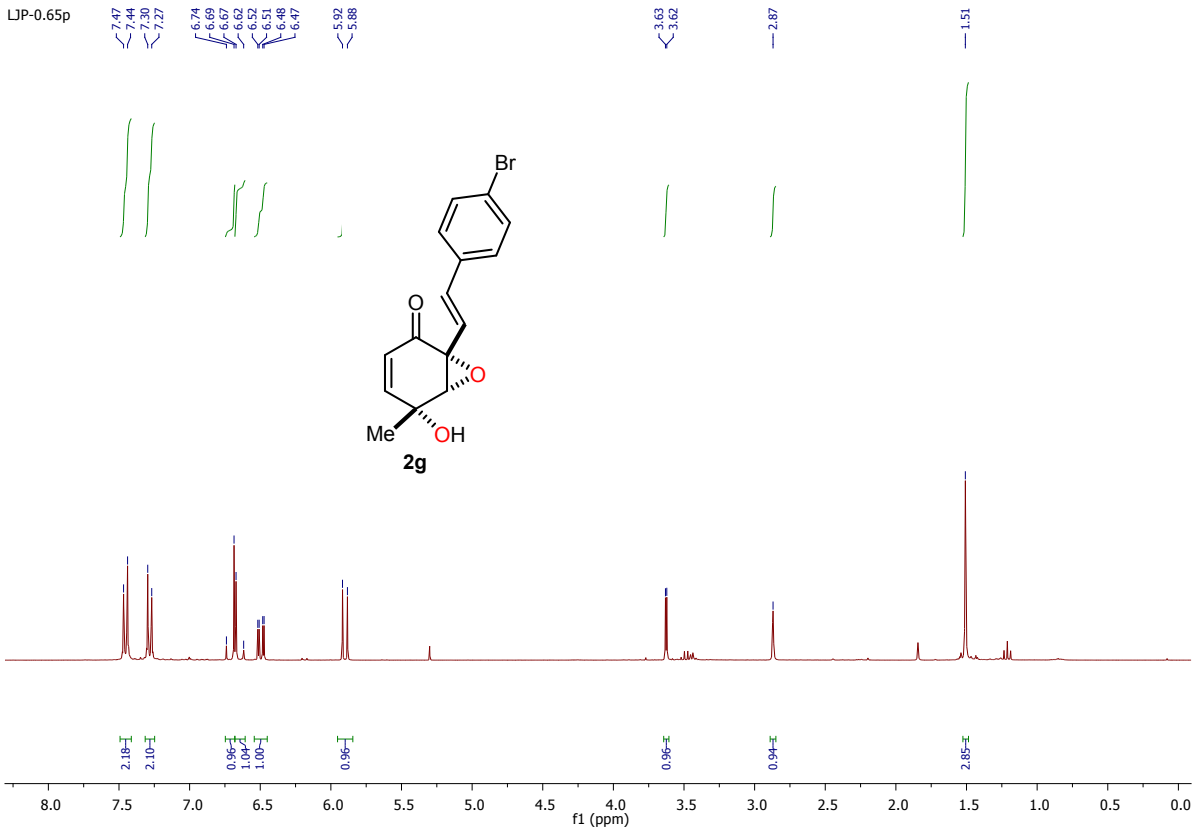

LJP-072p
193.36
149.21
138.50
133.04
129.47
126.86
124.31
118.32
68.78
68.60
60.66
25.38
21.39
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

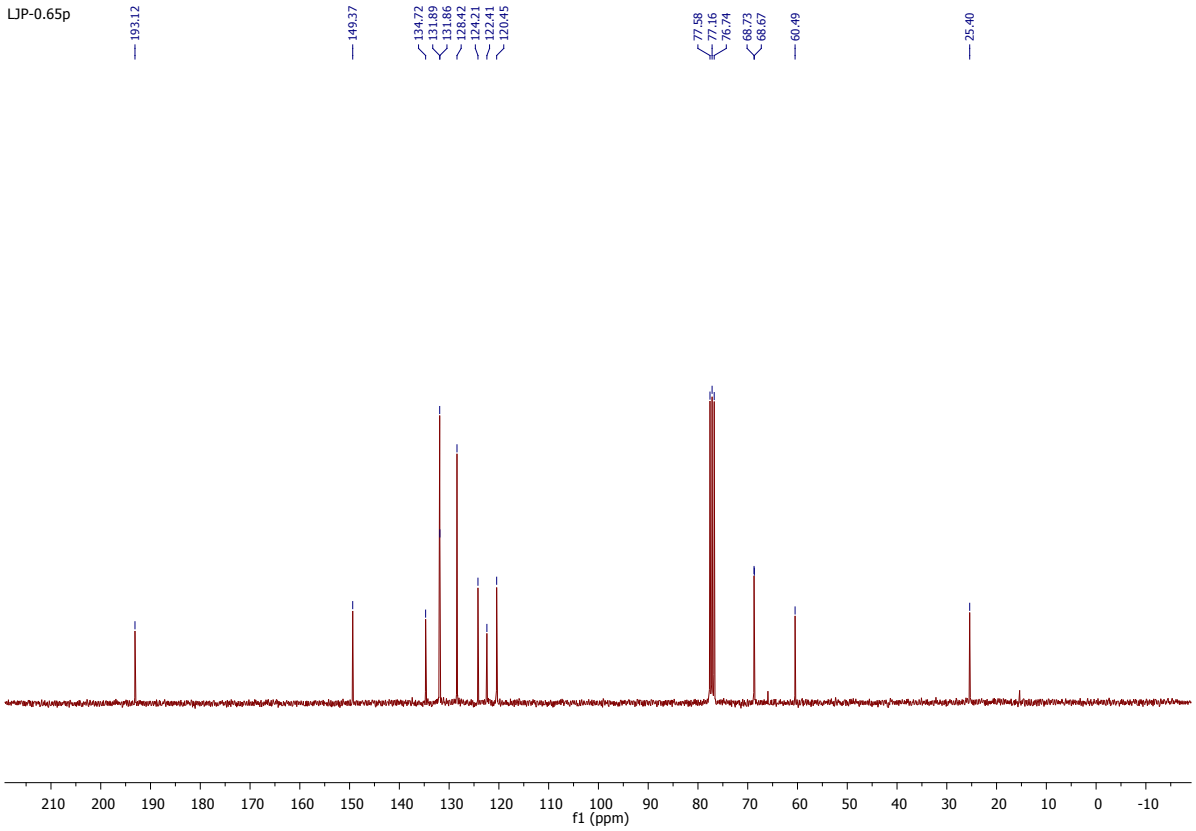

LJP-066p
7.41
7.40
7.39
7.37
7.04
7.02
6.99
6.72
6.66
6.63
6.58
6.51
6.50
6.47
6.46
5.91
5.88
3.62
3.61
2.69
1.50
F
O
O
Me
OH
2e
2.02
2.17
1.02
1.03
1.00
0.96
1.01
1.02
3.05
f1 (ppm)

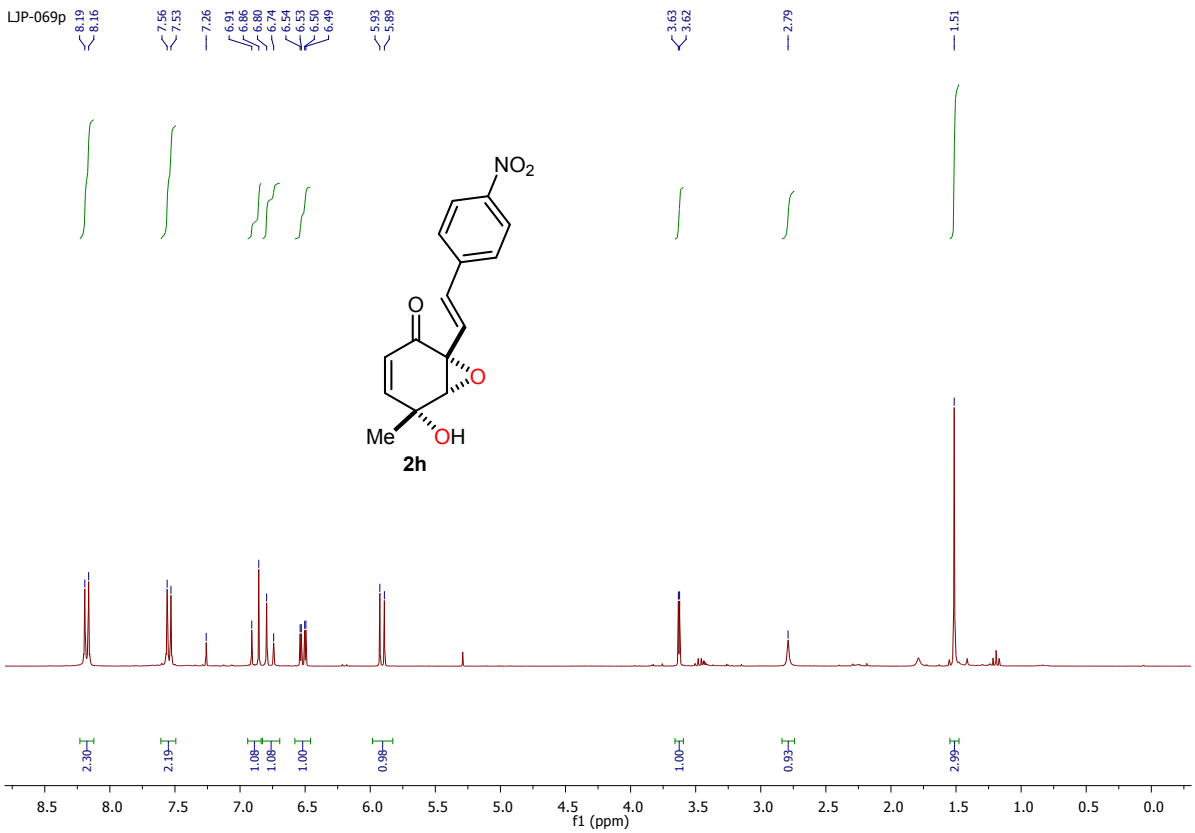

LJP-066p
193.24
164.52
161.23
149.29
132.03
131.98
131.90
128.62
128.51
124.28
119.32
119.29
115.90
115.62
77.58
77.16
76.74
68.77
68.67
60.56
25.37
f1 (ppm)

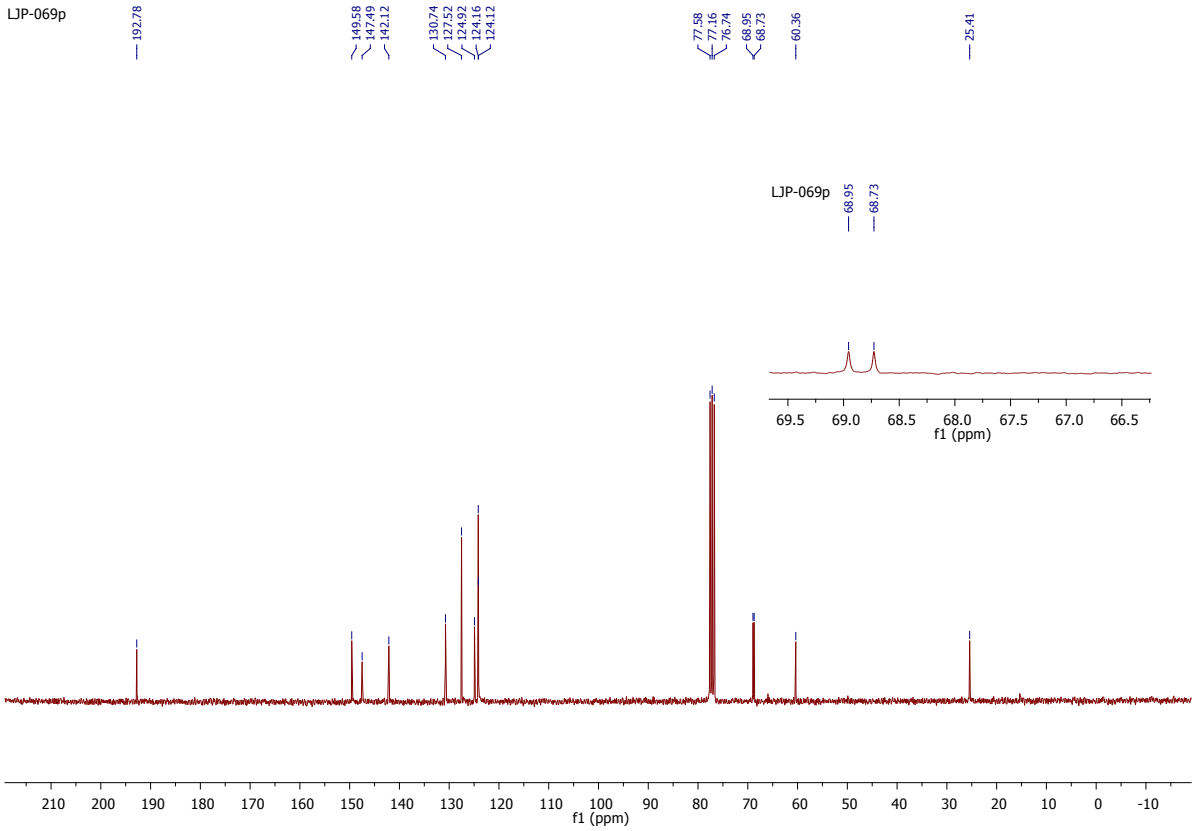

ljr-064p
7.37
7.34
7.31
7.28
6.68
6.52
6.51
6.48
6.47
5.92
5.88
3.63
3.62
2.81
1.51
Cl
O
O
Me
OH
2f
4.30
1.92
1.00
0.97
1.01
0.98
3.04
f1 (ppm)


ljr-064p
193.14
149.34
134.30
134.21
131.82
128.96
128.14
124.24
120.31
77.58
77.16
76.74
68.75
68.70
60.50
25.39
f1 (ppm)

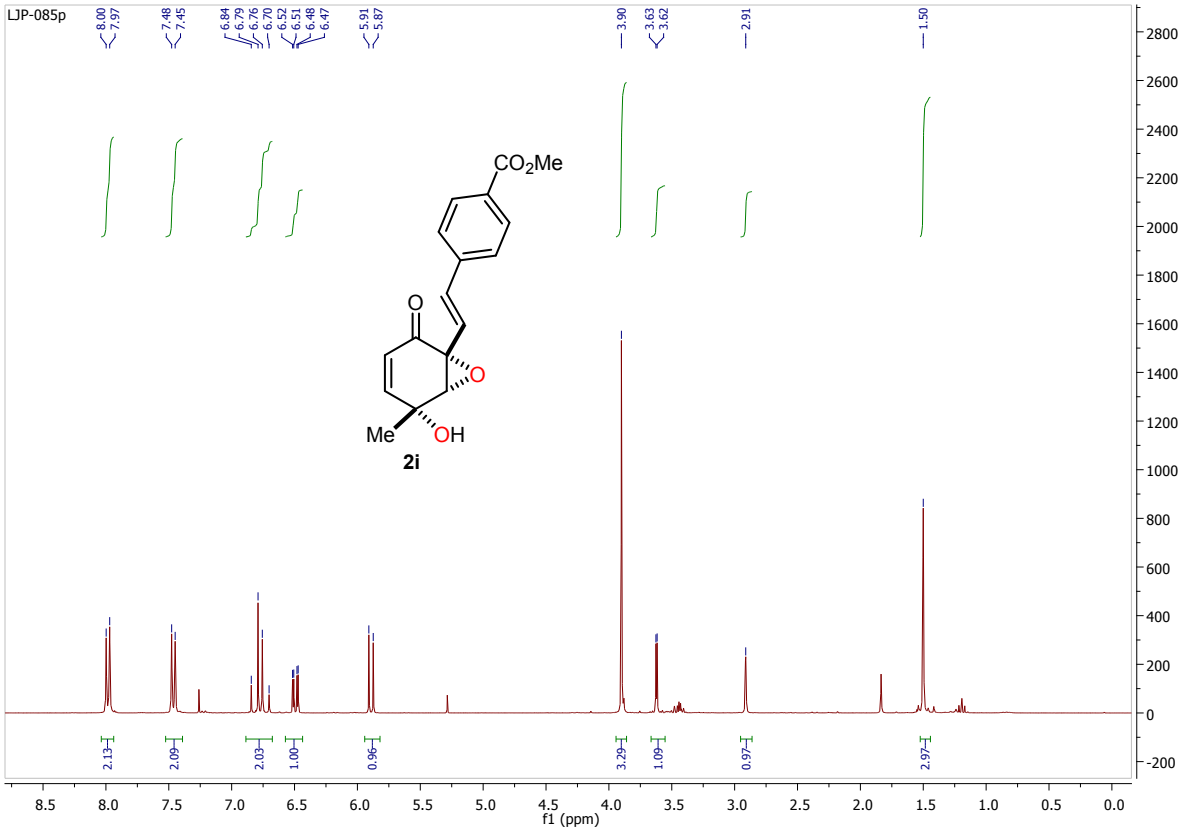

LJP-0.65p
7.47
7.44
7.30
7.27
6.74
6.69
6.67
6.62
6.52
6.51
6.48
6.47
5.92
5.88
3.63
3.62
2.87
1.51
Br
O
O
Me
OH
2g
2.18
2.10
0.96
1.04
1.00
0.96
0.96
0.94
2.85
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

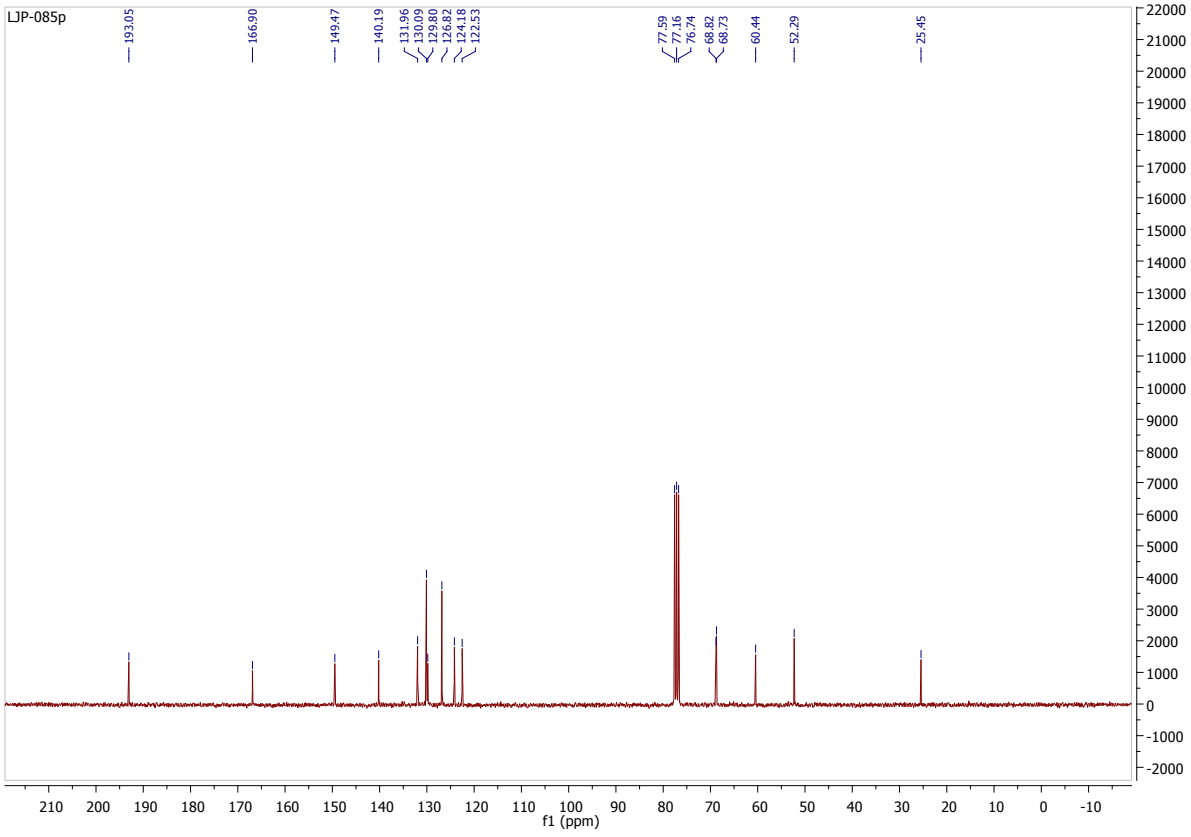

LJP-0.65p
193.12
149.37
134.72
131.89
131.86
128.42
124.21
122.41
120.45
77.58
77.16
76.74
68.73
68.67
60.49
25.40
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

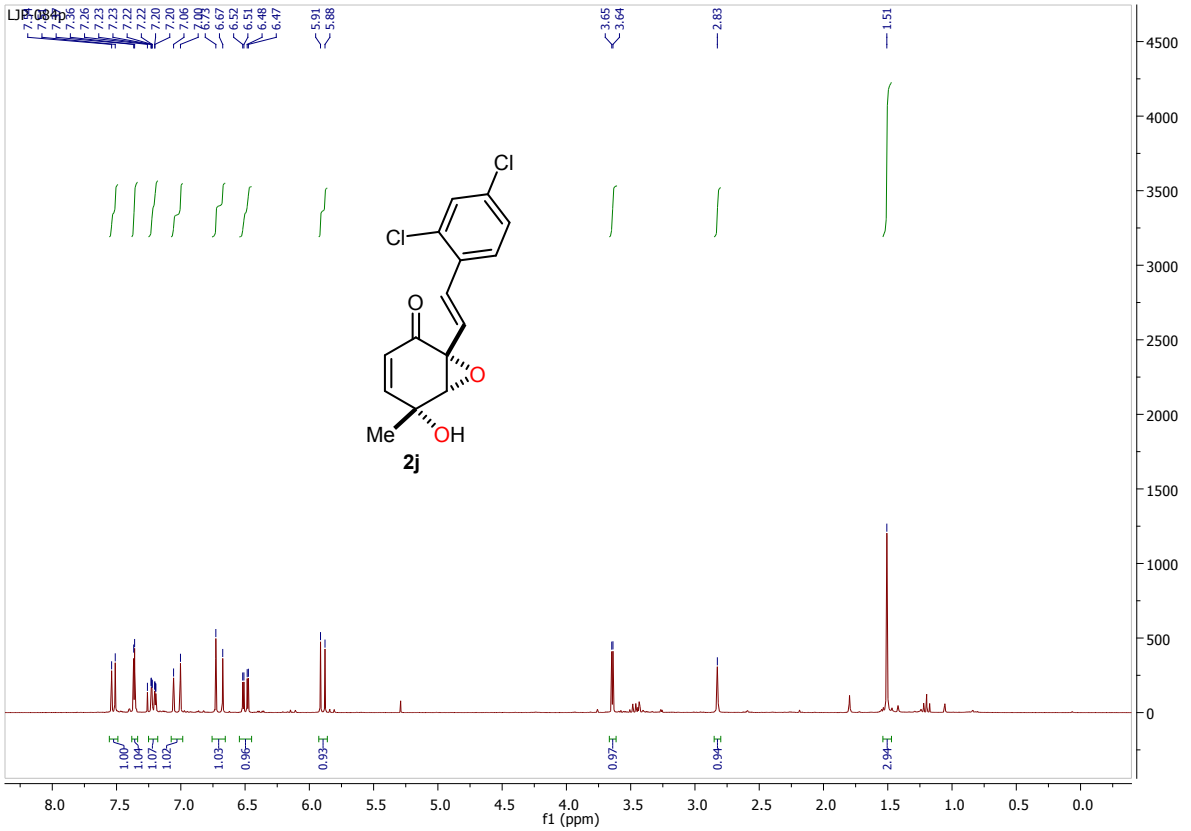

LJP-069p
8.19
8.16
7.56
7.53
7.26
6.91
6.86
6.80
6.74
6.54
6.53
6.50
6.49
5.93
5.89
3.63
3.62
2.79
1.51
NO2
O
O
Me
OH
2h
2.30
2.19
1.08
1.08
1.00
0.98
1.00
0.93
2.99
f1 (ppm)

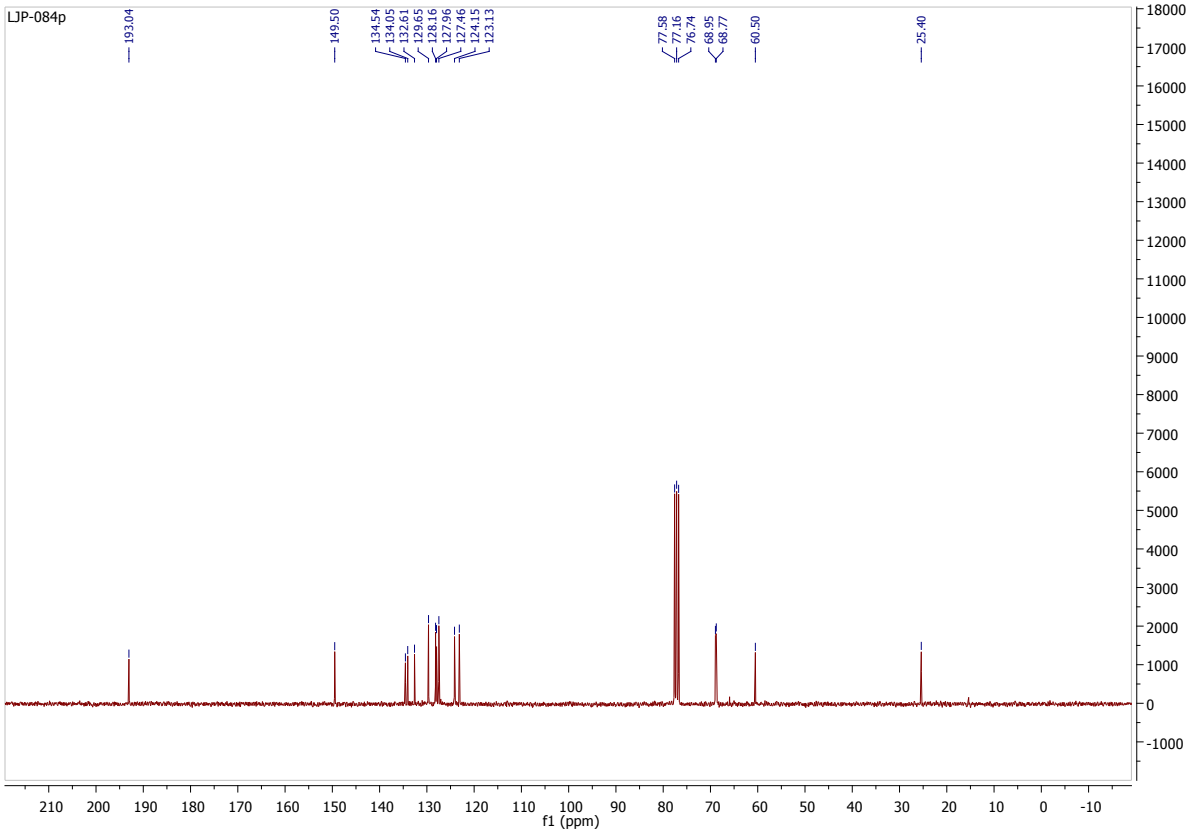

LJP-069p
192.78
149.58
147.49
142.12
130.74
127.52
124.92
124.16
124.12
77.58
77.16
76.74
68.95
68.73
60.36
25.41
f1 (ppm)

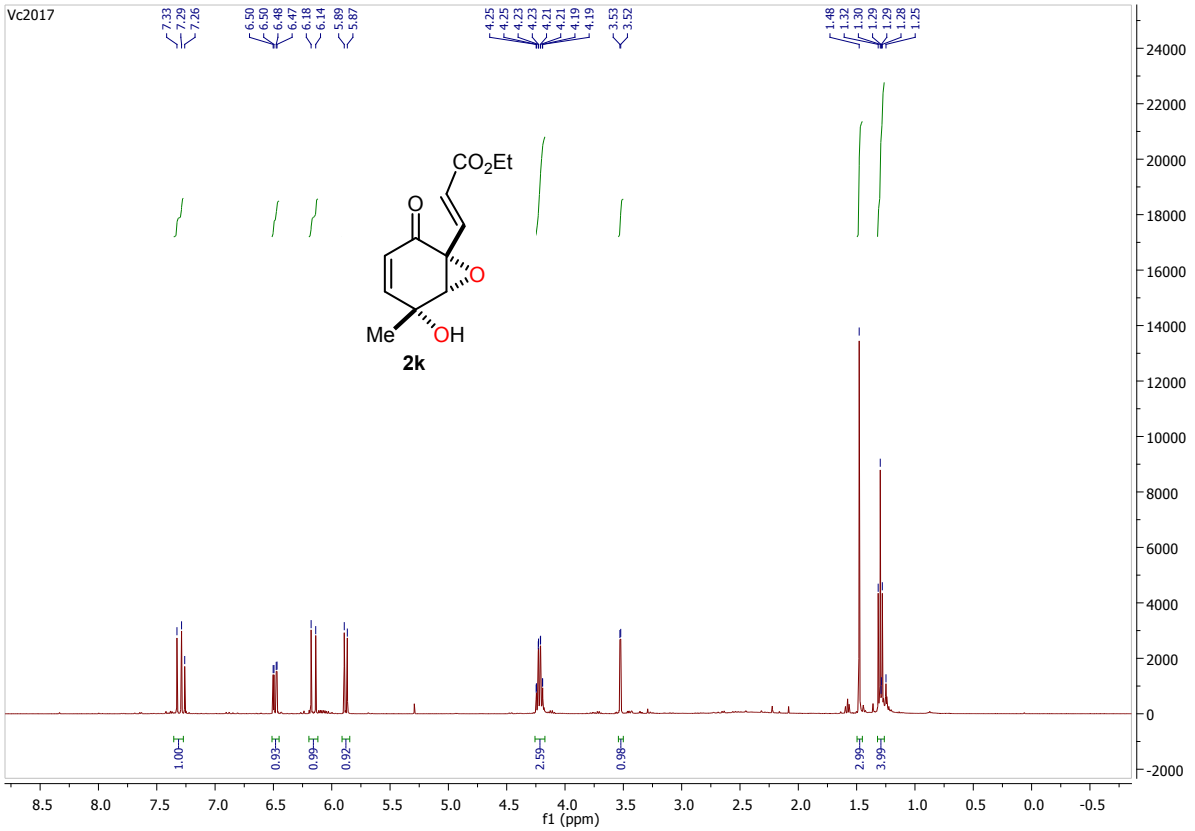
LJP-069p
68.95
68.73
f1 (ppm)

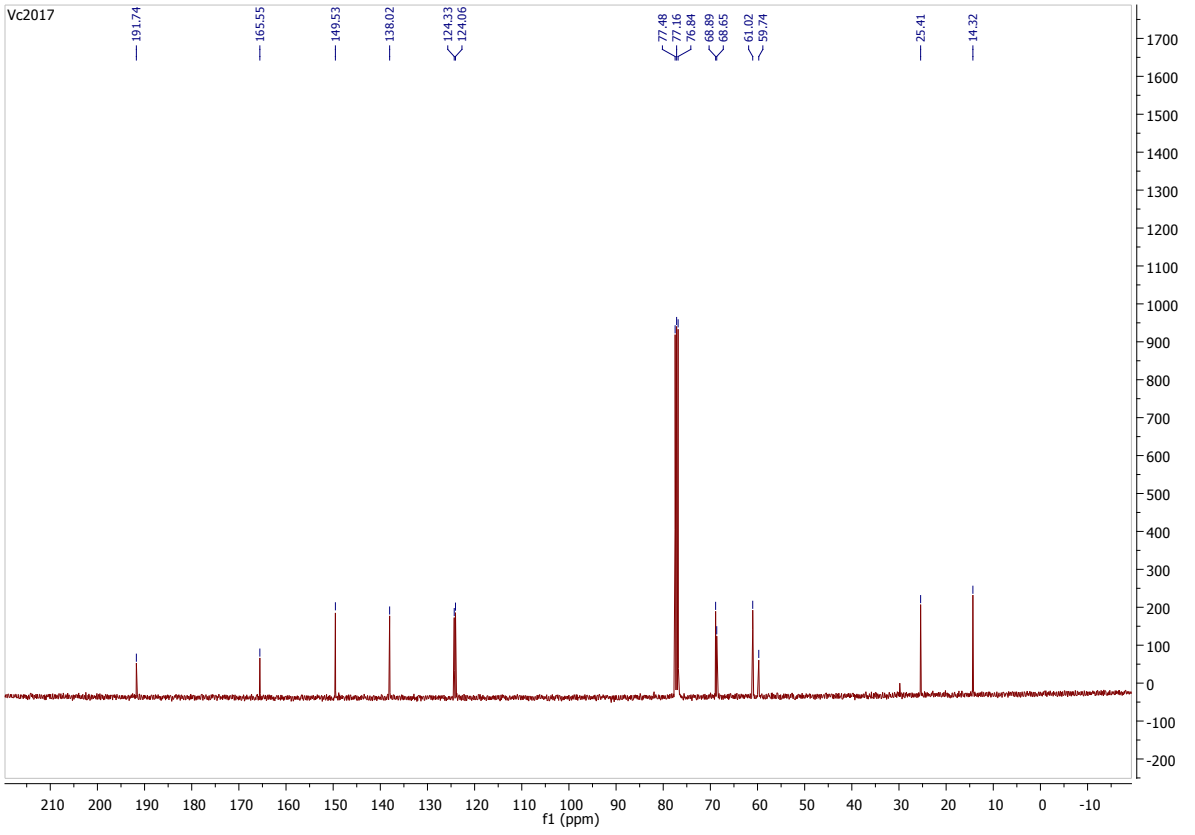

LJP-085p
8.00
7.97
7.48
7.45
6.84
6.79
6.76
6.70
6.52
6.51
6.48
6.47
5.91
5.87
3.90
3.63
3.62
2.91
1.50
CO2Me
O
O
Me
OH
2i
2.13
2.09
2.03
1.00
0.96
3.29
1.09
0.97
2.97
f1 (ppm)

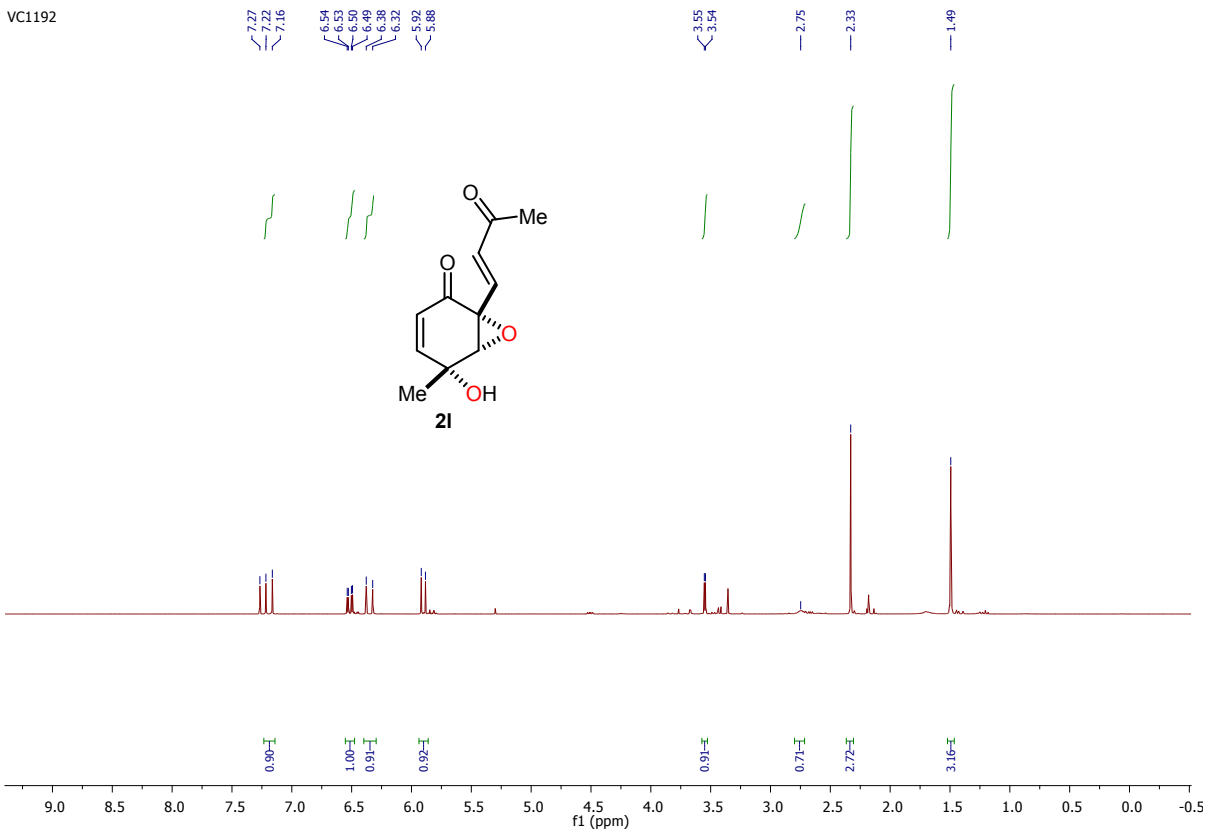

LJP-085p
193.05
166.90
149.47
140.19
131.96
130.09
129.80
126.82
124.18
122.53
77.59
77.16
76.74
68.82
68.73
60.44
52.29
25.45
f1 (ppm)

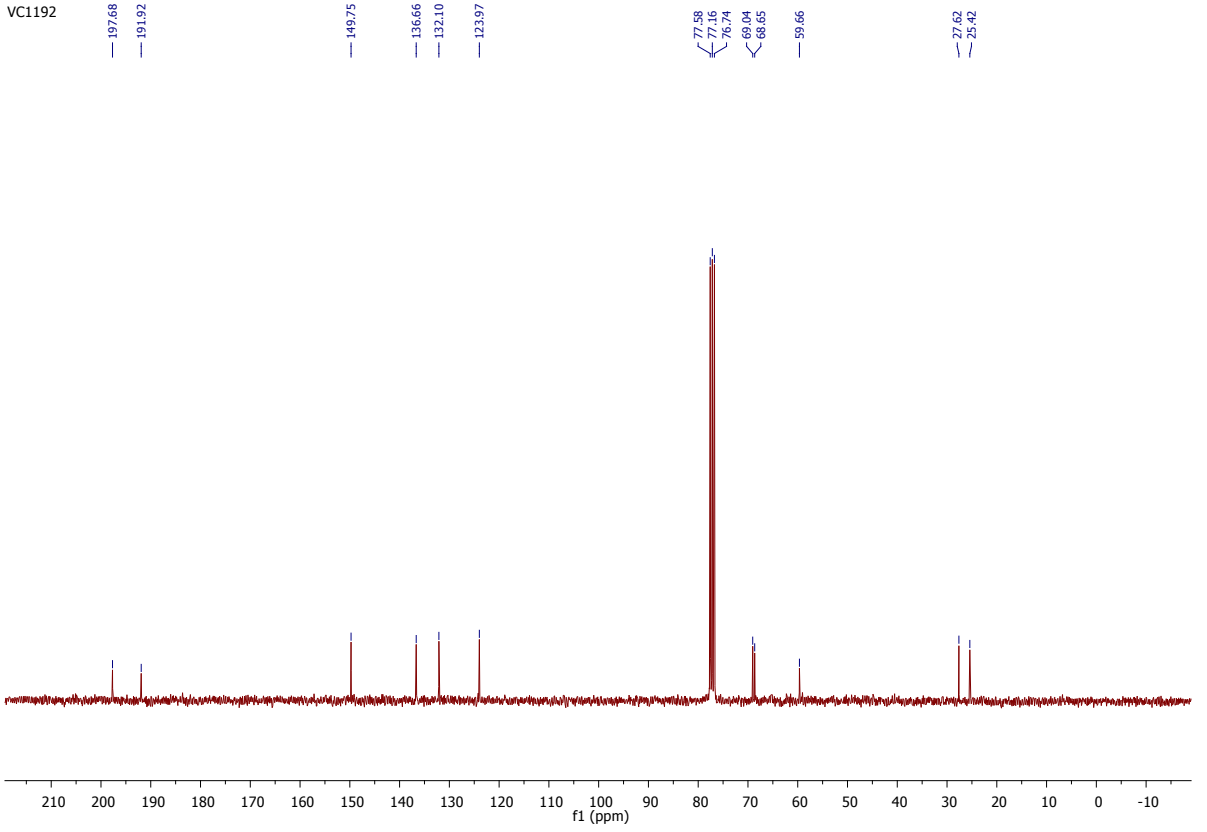

LJP-084p
7.36
7.26
7.23
7.22
7.20
7.06
6.70
6.67
6.52
6.51
6.48
6.47
5.91
5.88
3.65
3.64
2.83
1.51
Cl
Cl
O
O
Me
OH
2j
1.00
1.04
1.07
1.02
1.03
0.96
0.93
0.97
0.94
2.94
f1 (ppm)

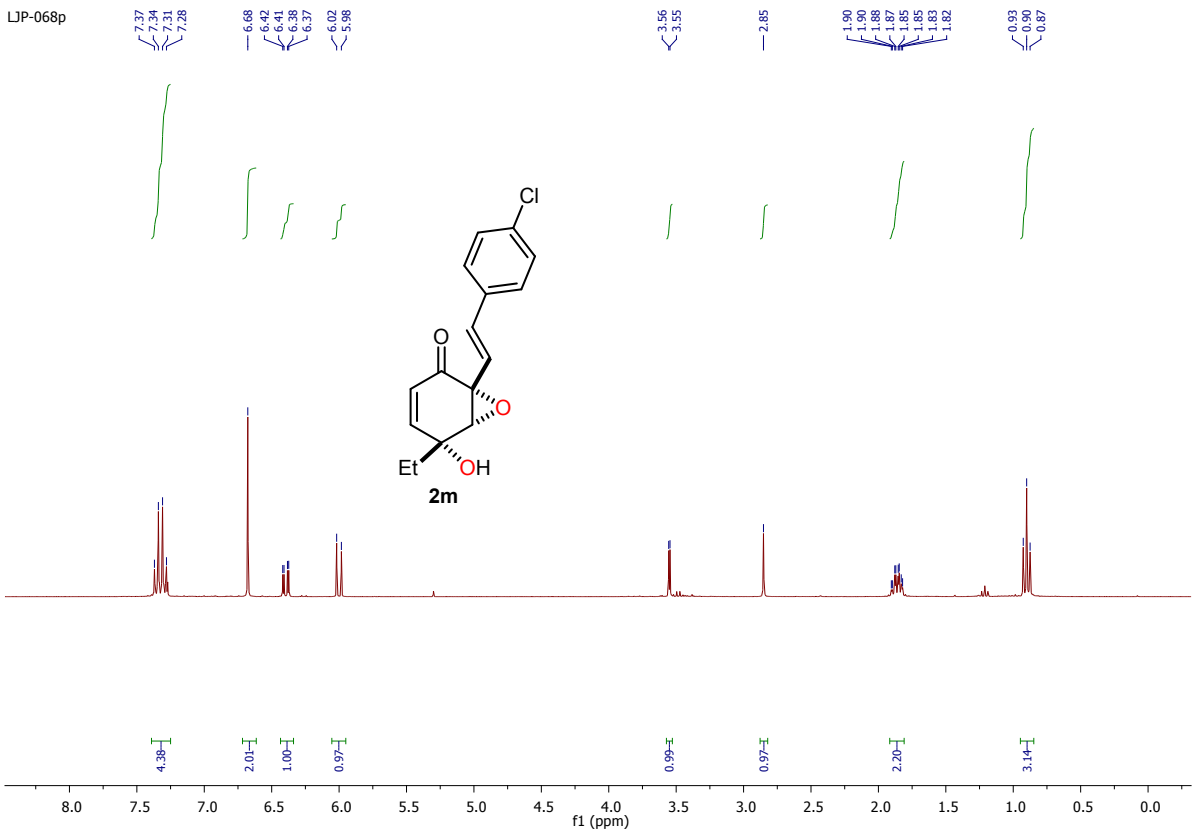

LJP-084p
193.04
149.50
134.54
134.05
132.61
129.65
128.16
127.96
127.46
124.15
123.13
77.58
77.16
76.74
68.95
68.77
60.50
25.40
f1 (ppm)

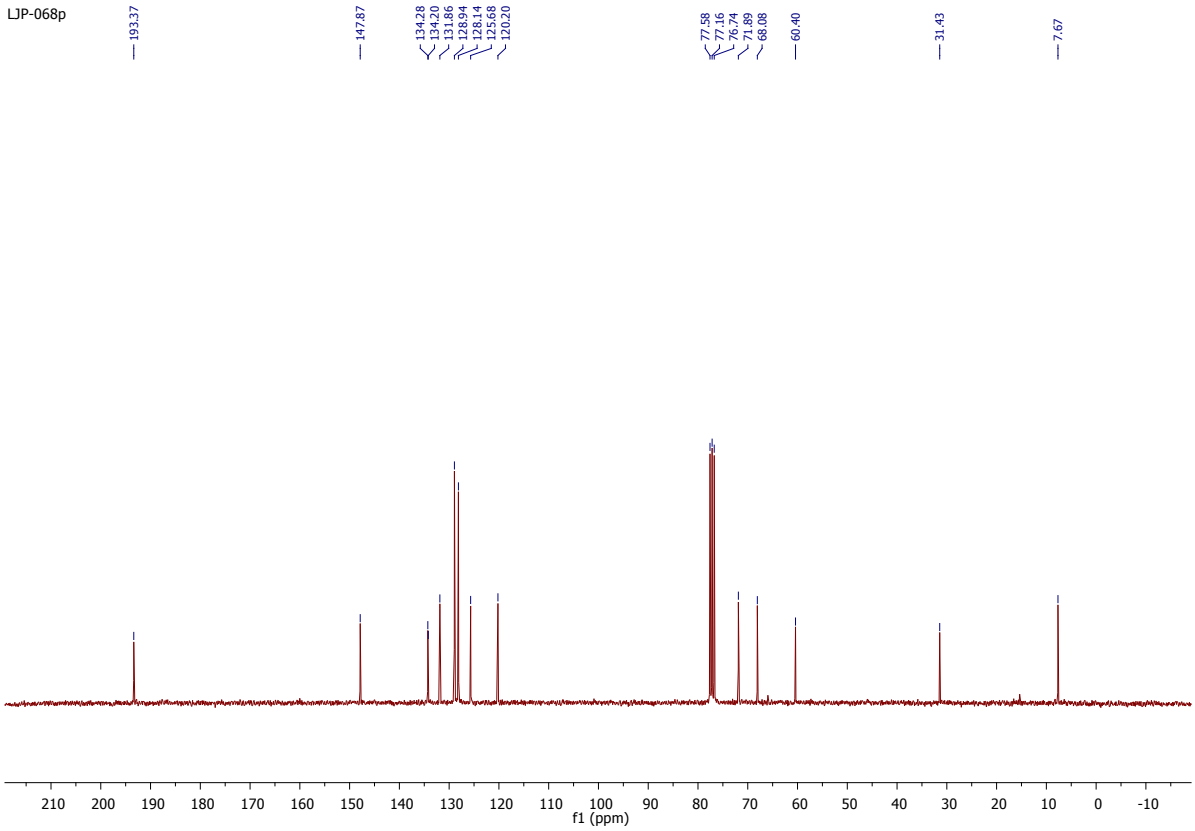

Vc2017
7.33
7.29
7.26
6.50
6.50
6.48
6.47
6.18
6.14
5.89
5.87
4.25
4.25
4.23
4.23
4.21
4.21
4.19
4.19
3.53
3.52
1.48
1.32
1.30
1.29
1.29
1.28
1.25
CO2Et
O
O
Me
OH
2k
1.00
0.93
0.99
0.92
2.59
0.98
2.99
3.99
f1 (ppm)

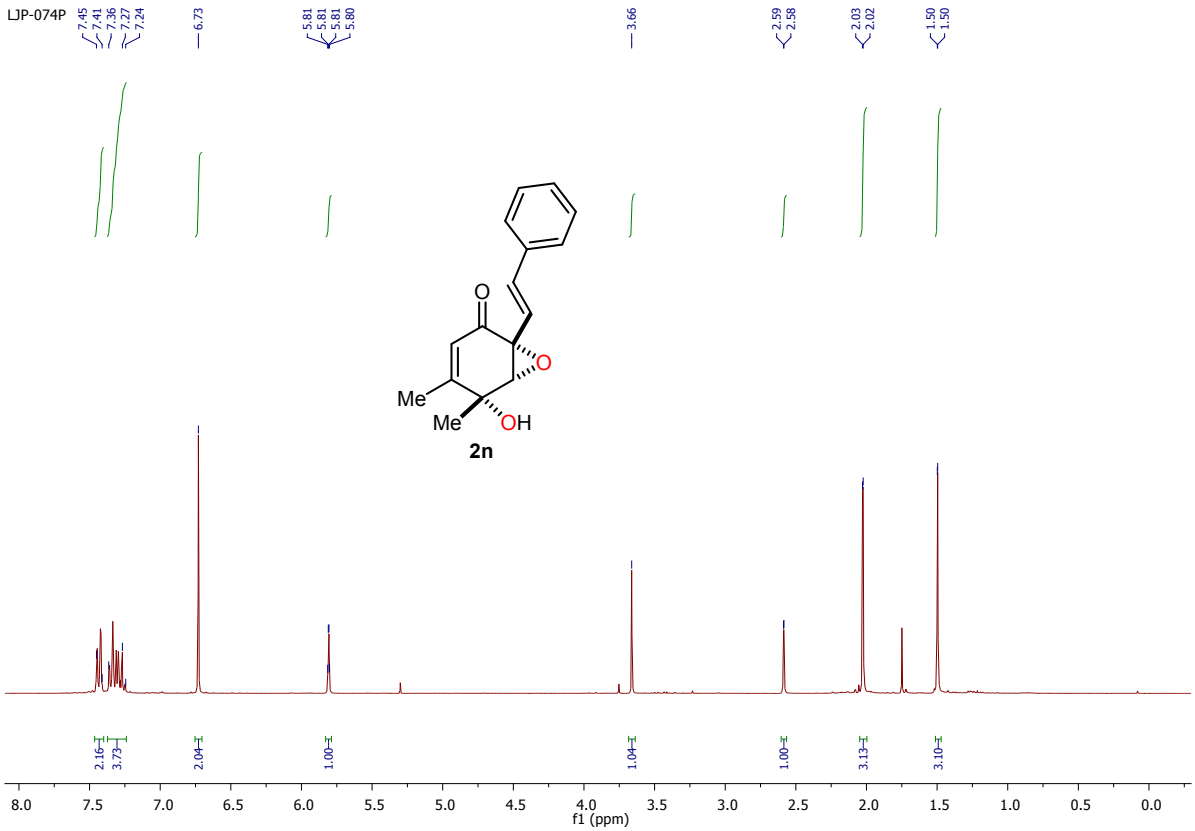

Vc2017
191.74
165.55
149.53
138.02
124.33
124.06
77.48
77.16
76.84
68.89
68.65
61.02
59.74
25.41
14.32
f1 (ppm)

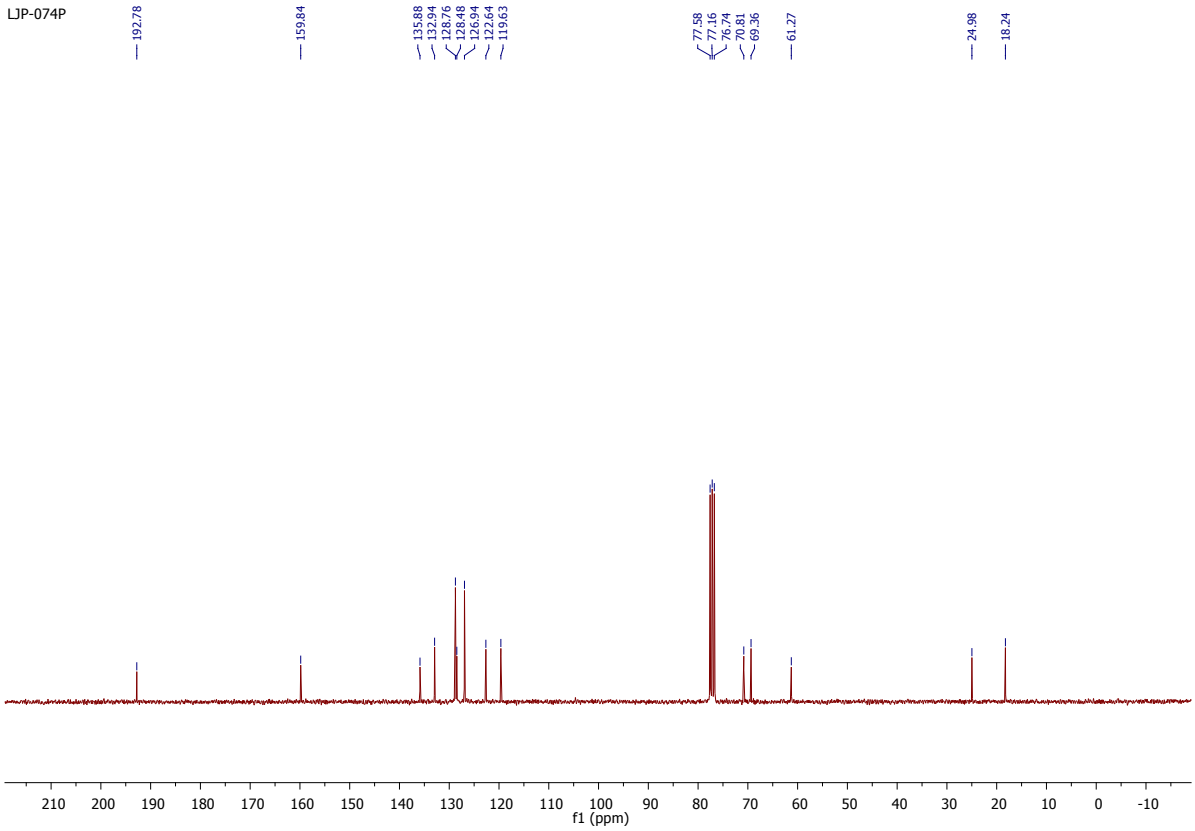

VC1192
7.27
7.22
7.16
6.54
6.53
6.50
6.49
6.38
6.32
5.92
5.88
3.55
3.54
2.75
2.33
1.49
O
Me
O
O
Me
OH
2l
0.90
1.00
0.91
0.92
0.91
0.71
2.72
3.16
f1 (ppm)

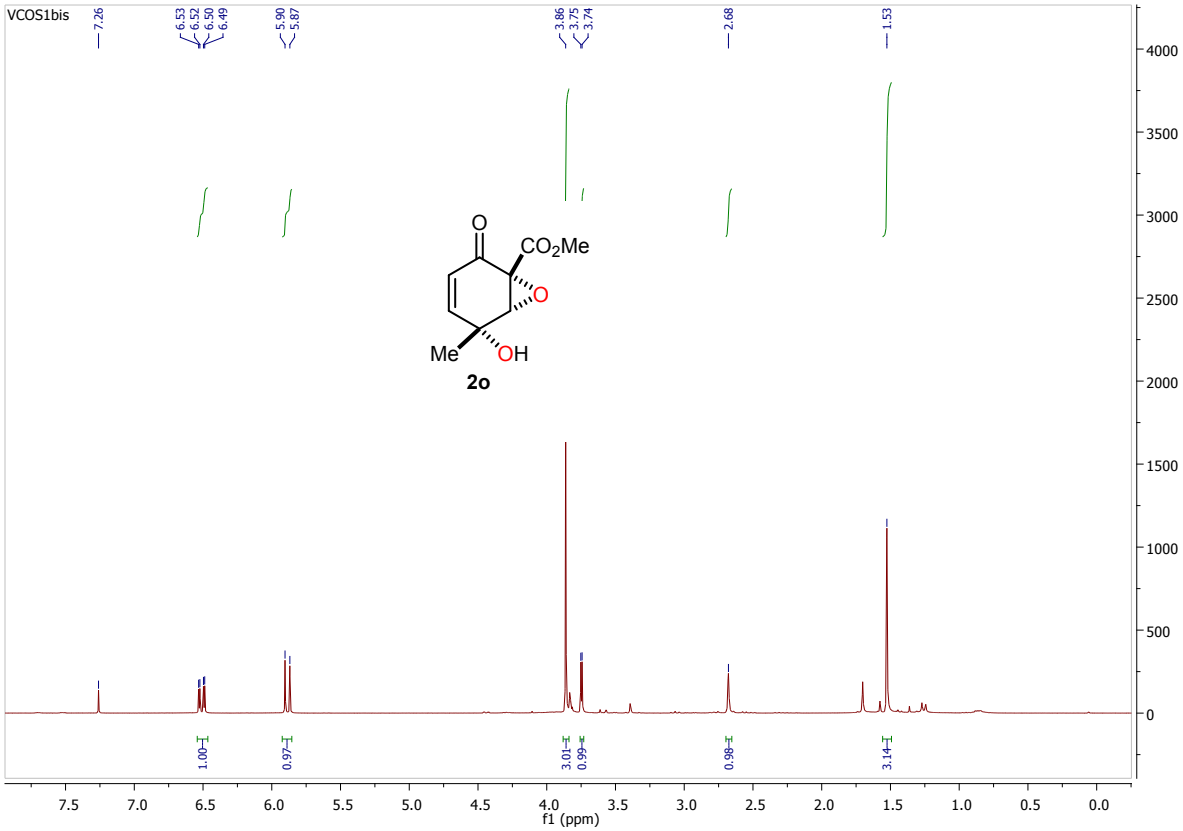

VC1192
197.68
191.92
149.75
136.66
132.10
123.97
77.58
77.16
76.74
69.04
68.65
59.66
27.62
25.42
f1 (ppm)

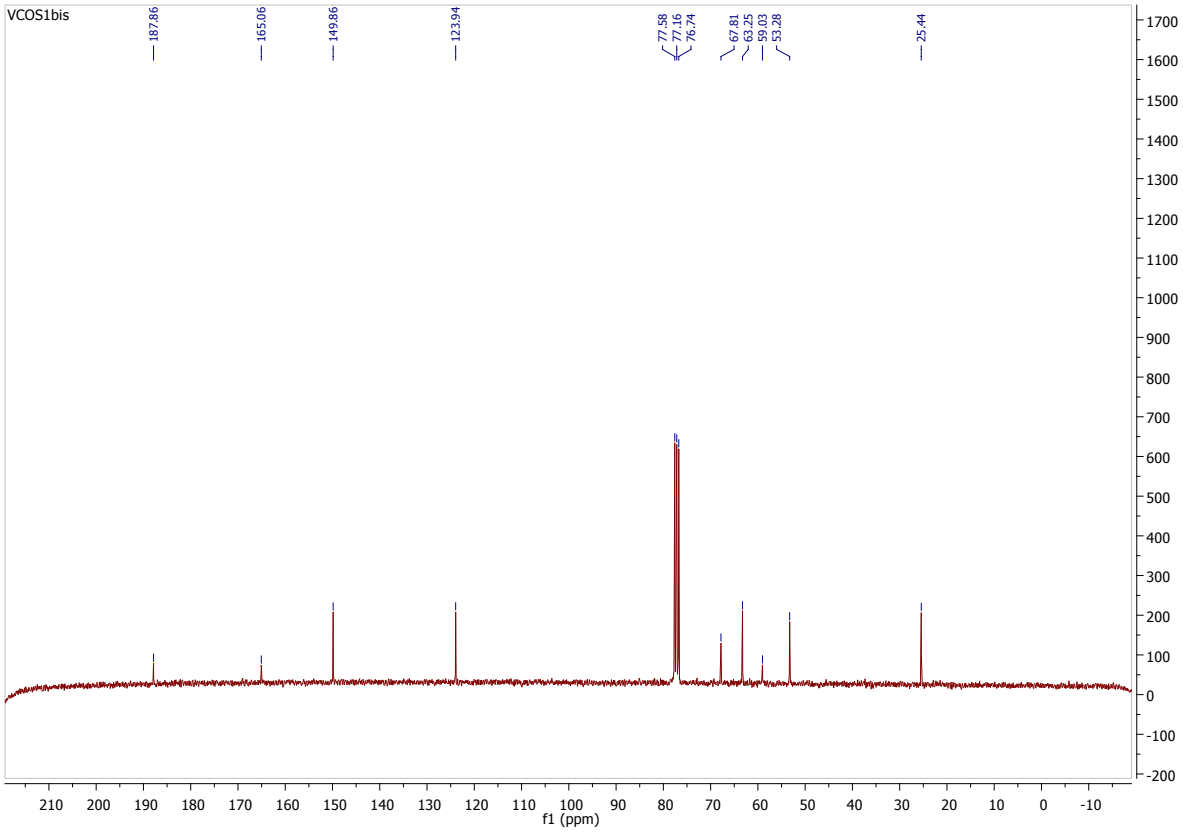

LJP-068p
7.37
7.34
7.31
7.28
6.68
6.42
6.41
6.38
6.37
6.02
5.98
3.56
3.55
2.85
1.90
1.90
1.88
1.87
1.85
1.85
1.83
1.82
0.93
0.90
0.87
Cl
O
O
Et
OH
2m
4.38
2.01
1.00
0.97
0.99
0.97
2.20
3.14
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

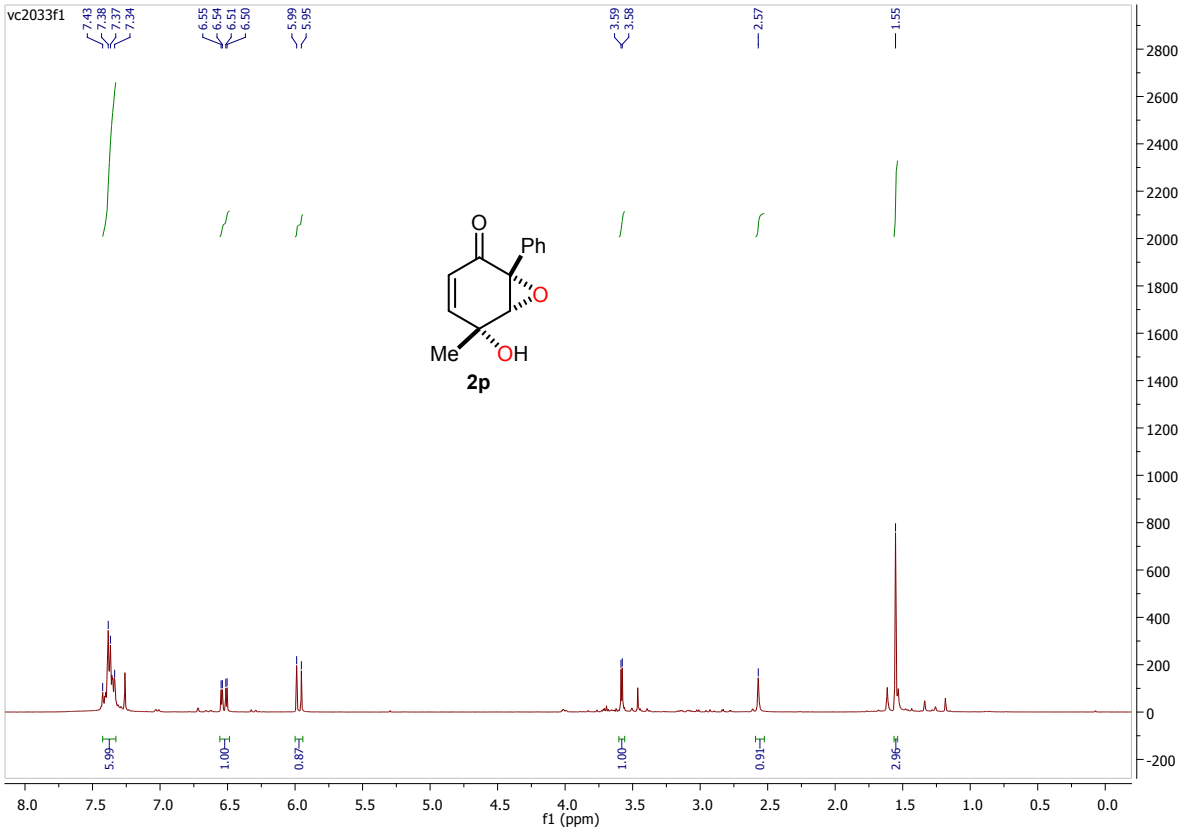

LJP-068p
193.37
147.87
134.28
134.20
131.86
128.94
128.14
125.68
120.20
77.58
77.16
76.74
71.89
68.08
60.40
31.43
7.67
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

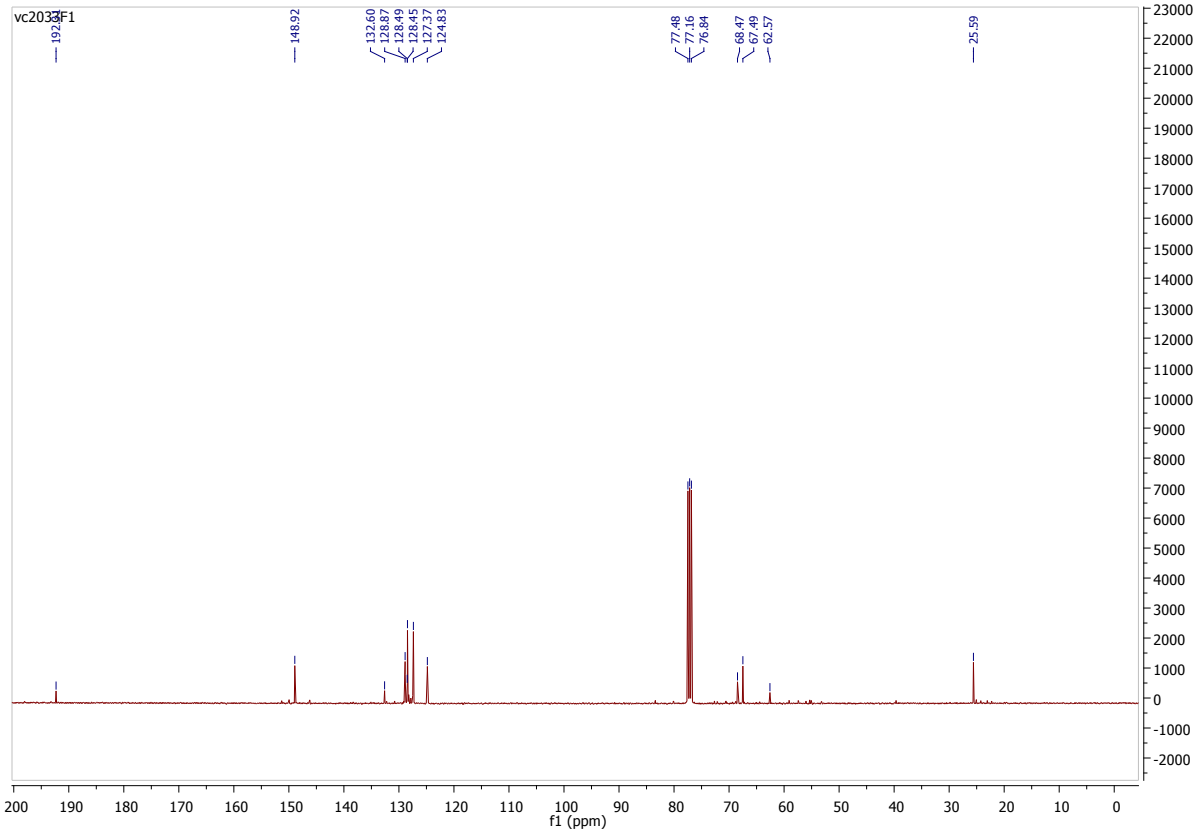

LJP-074P
7.45
7.41
7.36
7.27
7.24
6.73
5.81
5.81
5.81
5.80
3.66
2.59
2.58
2.03
2.02
1.50
1.50
O
O
Me
Me
OH
2n
2.16
3.73
2.04
1.00
1.04
1.00
3.13
3.10
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

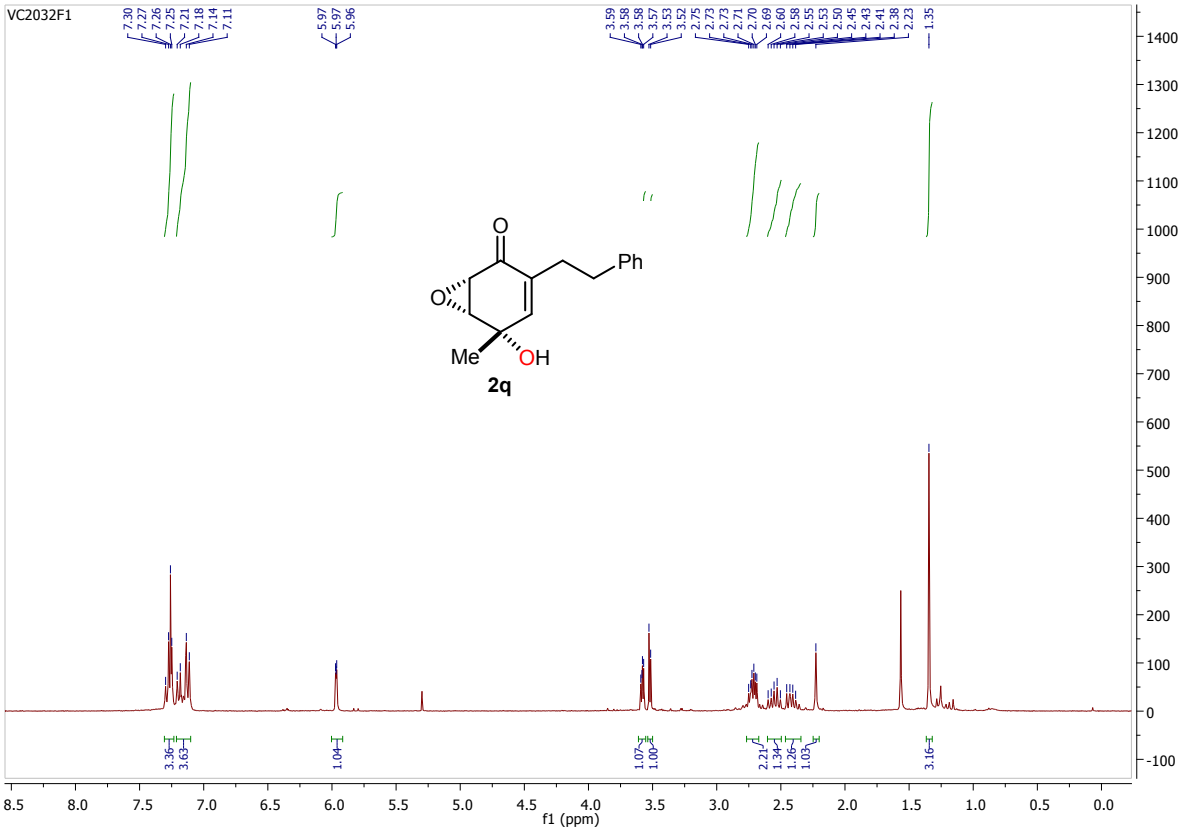

LJP-074P
192.78
159.84
135.88
132.94
128.76
128.48
126.94
122.64
119.63
77.58
77.16
76.74
70.81
69.36
61.27
24.98
18.24
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

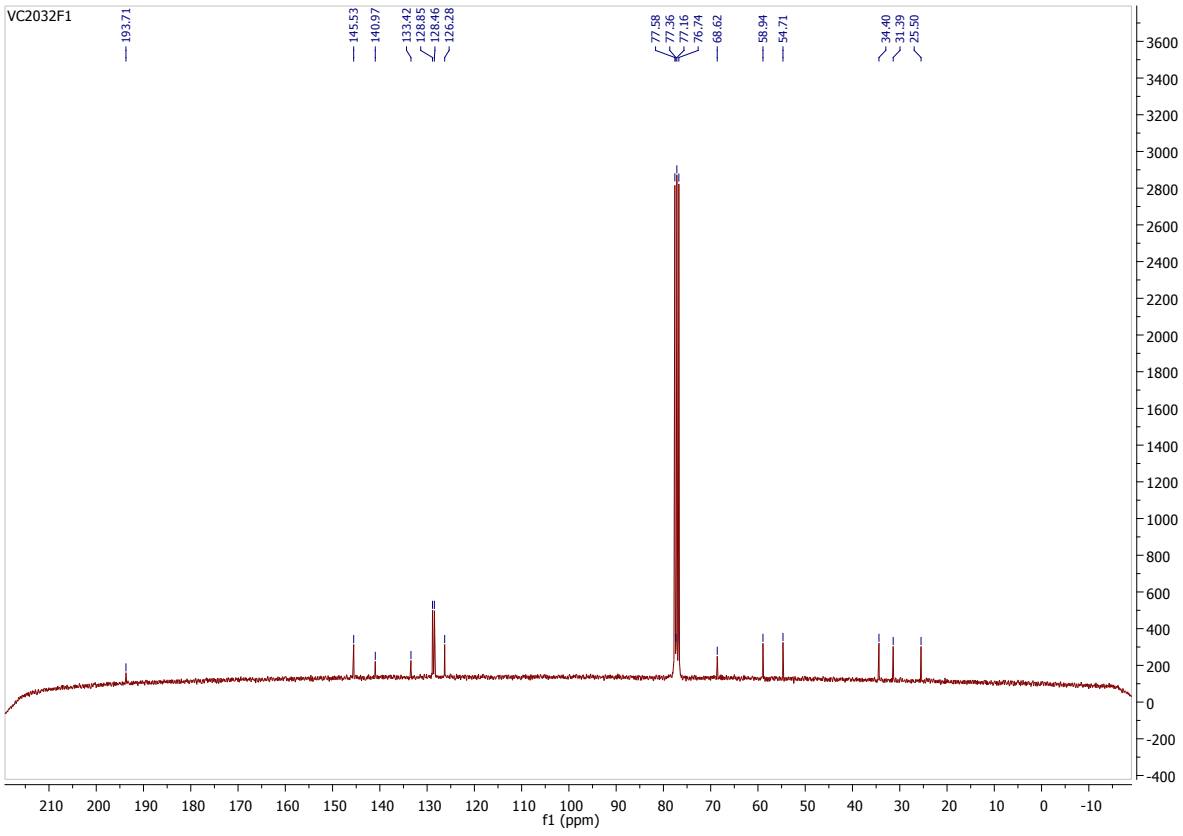

VCOS1bis
7.26
6.53
6.52
6.50
6.49
5.90
5.87
3.86
3.75
3.74
2.68
1.53
O
CO2Me
O
Me
OH
2o
1.00
0.97
3.01
0.99
0.98
3.14
f1 (ppm)

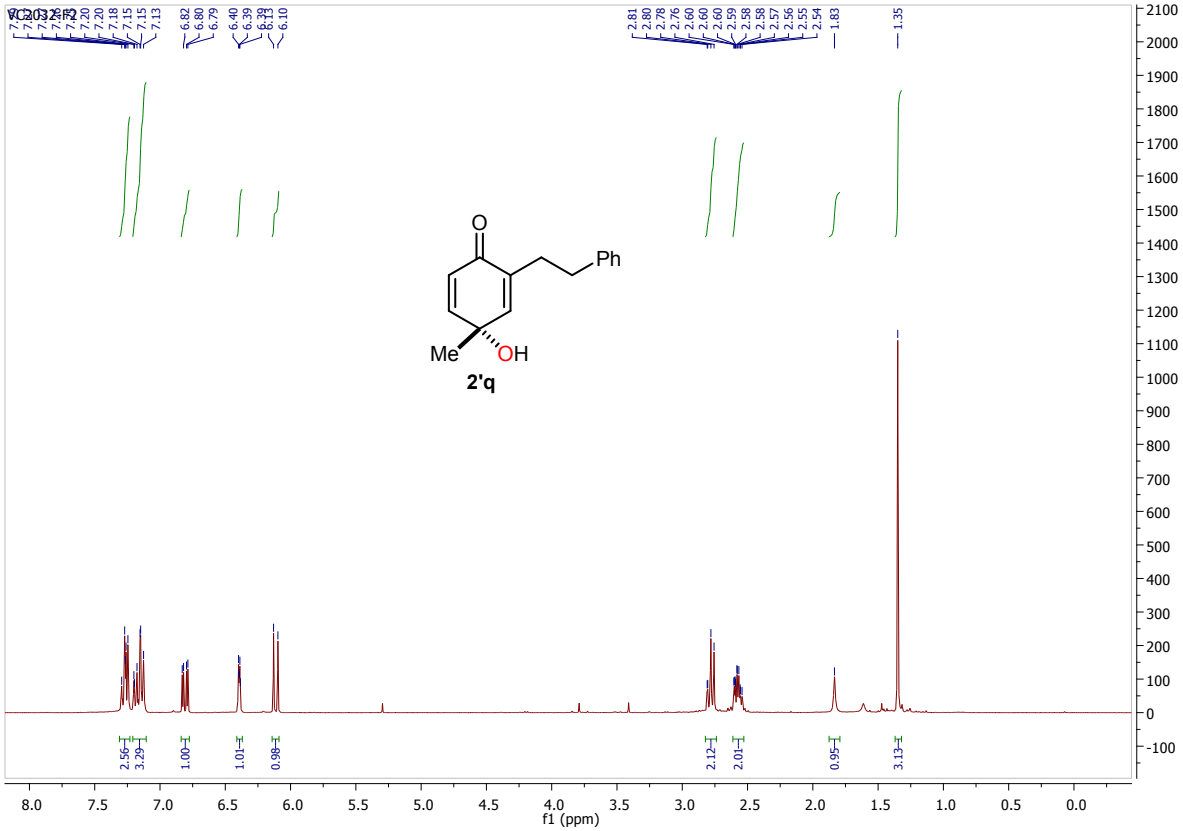

VCOS1bis
187.86
165.06
149.86
123.94
77.58
77.16
76.74
67.81
63.25
59.03
53.28
25.44
f1 (ppm)

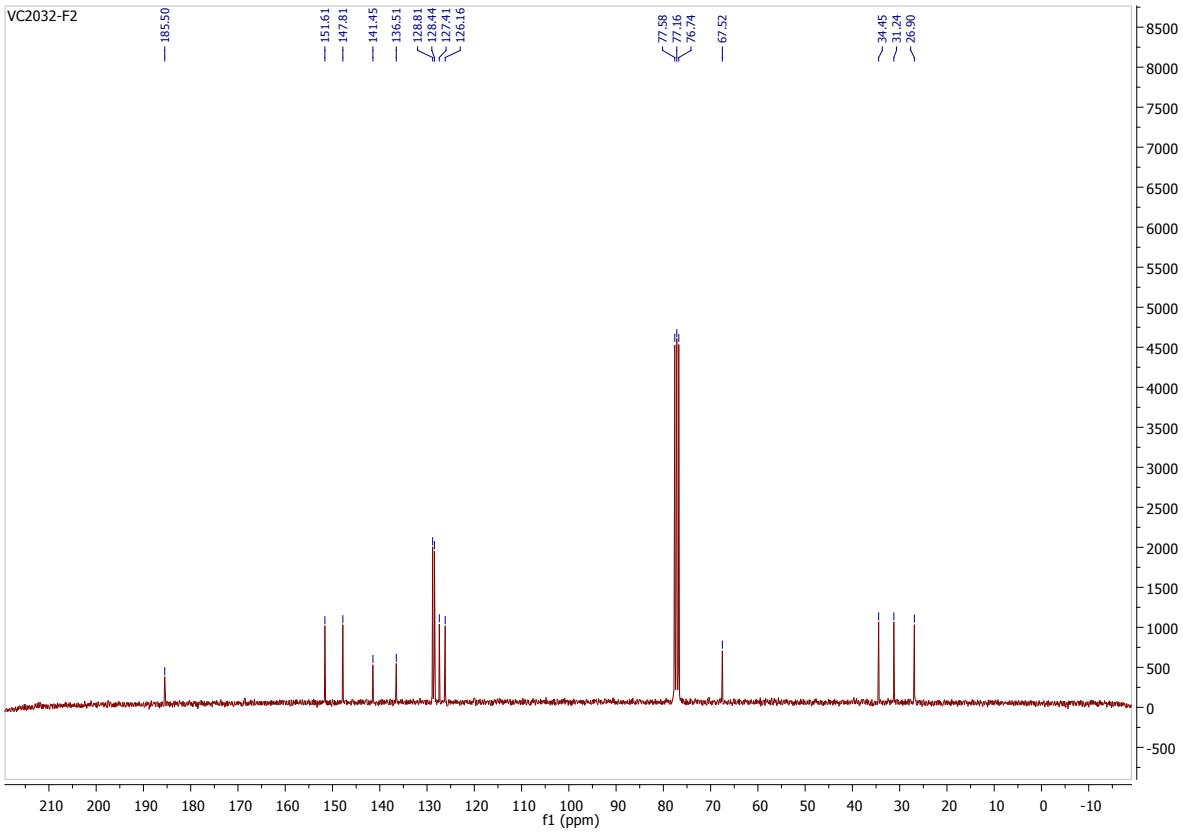

vc2033f1
7.43
7.38
7.37
7.34
6.55
6.54
6.51
6.50
5.99
5.95
3.59
3.58
2.57
1.55
O
Ph
O
Me
OH
2p
5.99
1.00
0.87
1.00
0.91
2.96
f1 (ppm)


vc2033F1
192.38
148.92
132.60
128.87
128.49
128.45
127.37
124.83
77.48
77.16
76.84
68.47
67.49
62.57
25.59
f1 (ppm)

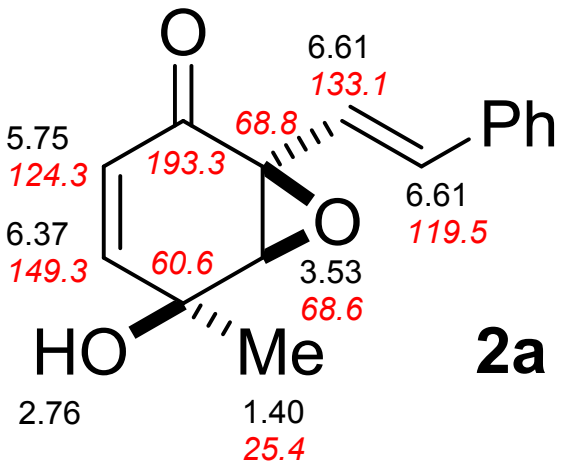

VC2032F1
7.30
7.27
7.26
7.25
7.21
7.18
7.14
7.11
5.97
5.97
5.96
3.59
3.58
3.58
3.57
3.53
3.52
2.75
2.73
2.73
2.71
2.70
2.69
2.60
2.58
2.55
2.53
2.50
2.45
2.43
2.41
2.38
2.23
1.35
O
Ph
O
Me
OH
2q
3.36
3.63
1.04
1.07
1.00
2.21
1.34
1.26
1.03
3.16
f1 (ppm)

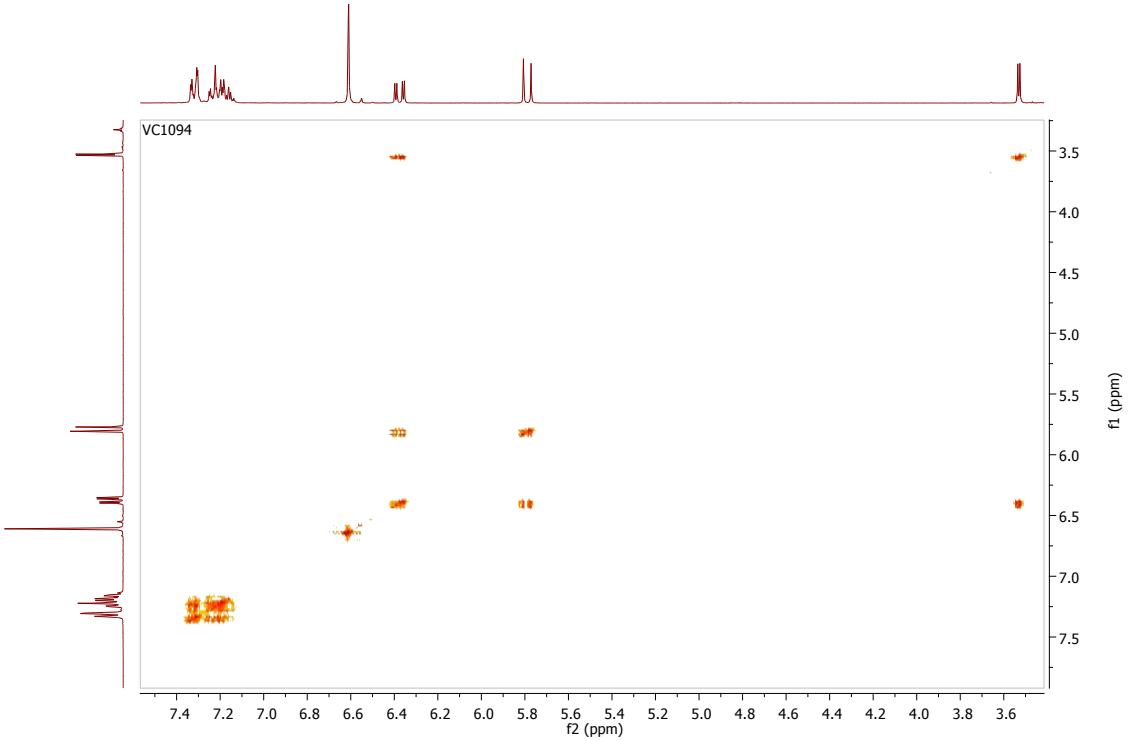

VC2032F1
193.71
145.53
140.97
133.42
128.85
128.46
126.28
77.58
77.36
77.16
76.74
68.62
58.94
54.71
34.40
31.39
25.50
f1 (ppm)


VC2032-F2
O
Ph
Me
OH
2'q
f1 (ppm)

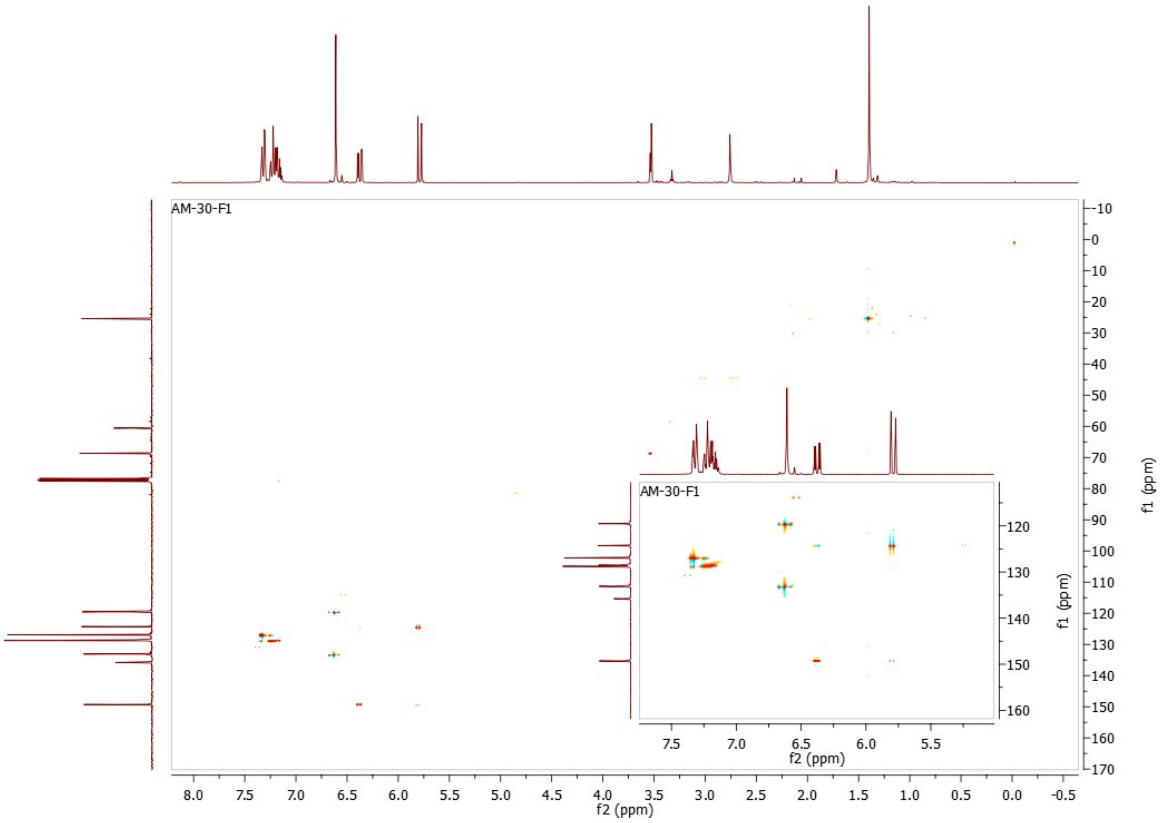

VC2032-F2
f1 (ppm)

7. Full characterization (2D NMR spectra) of 2a

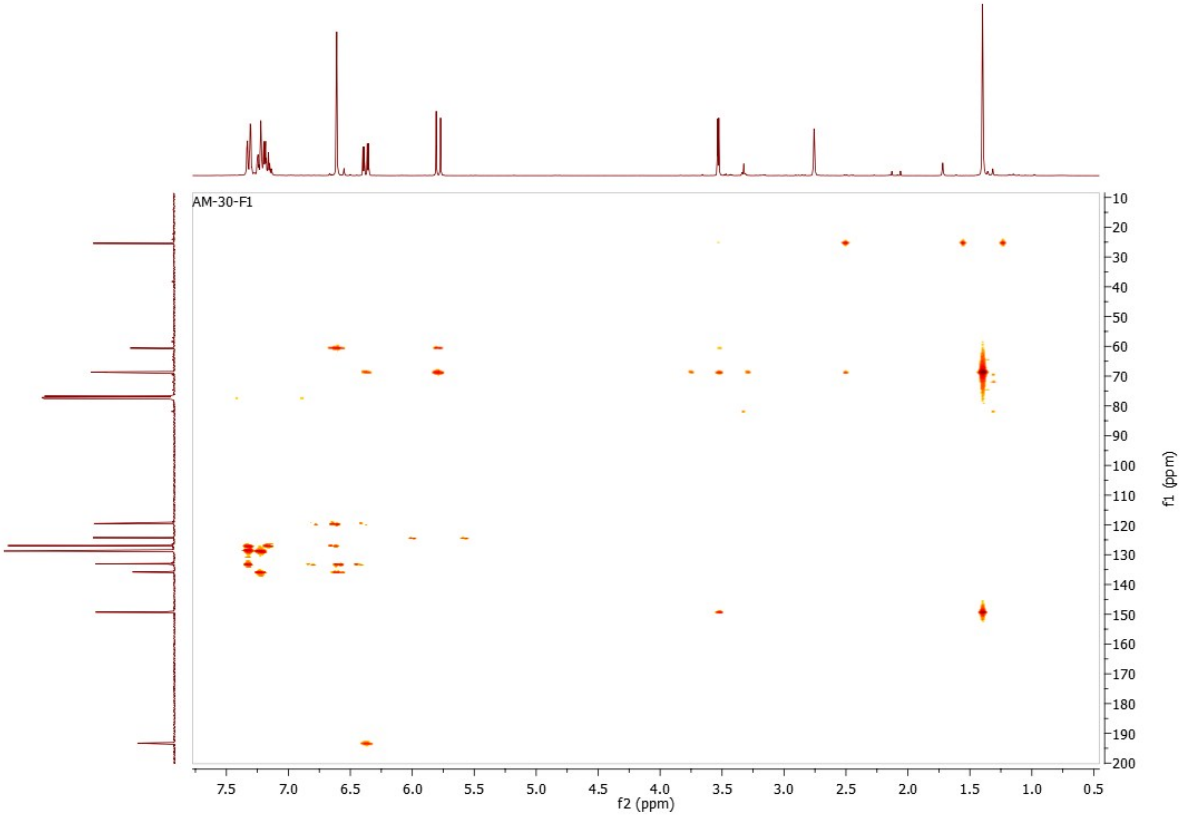




COSY of 2a



HMQC of 2a



HMBC of 2a

8. References

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