Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supplementary Information Section:

Optimizing the Lifetimes of Phenoxonium Cations Derived from Vitamin E *via* Structural Modifications

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CONTENTS

1. Synthesis of Modified Forms of Vitamin E

1.1. Experimental Section

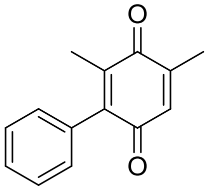
NMR spectra were recorded on Bruker AVANCE 400 NMR instrument and were calibrated using residual non deuterated solvent as an internal reference ($CHCl_3$ @ 7.26 ppm ^{1}H-NMR, 77.0 ppm ^{13}C-NMR). The following abbreviations were used to explain the multiplicities: s = singlet, brs = broad singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet. Melting points were uncorrected. High-resolution mass spectra (HRMS) were obtained with JEOL MS-700P mass spectrometer, Finnigan MAT 95 XP mass spectrometer (Thermo Electron Corporation), and Q-Tof Premier. Flash column chromatography was performed using Merck silica gel 60 with distilled hexane, and preparative thin-layer chromatography (PTLC) was bought from CEMS MARKETING PTE LTD, PTLC plate (20 cm × 20 cm) was coated with 10 µm, 60 Ǻ particles, 500 µm coating thickness.

1.2. Compound Characterization and Synthetic Steps

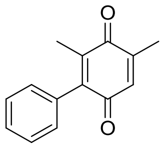
Arylation of 2,6-dimethylcyclohexa-2,5-diene-1,4-dione.[S1]

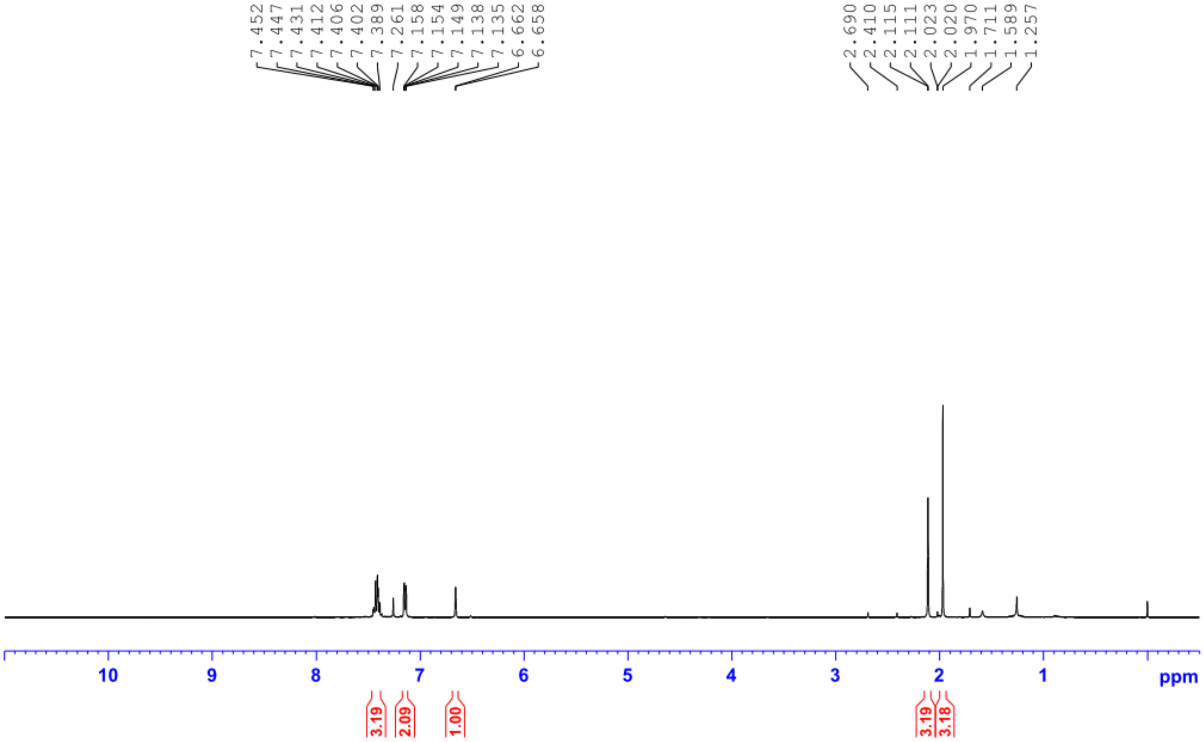
To a solution of 2,6-dimethylclohexa-2,5-diene-1,4-dione (4.0 mmol) in trifluorotoluene (20 ml) was added the corresponding boronic acid (6.0 mmol), water (20 ml), silver nitrate (0.8 mmol), and potassium persulfate (12.0 mmol). The solution was then stirred vigorously at room temperature and monitored by thin-layer chromatography of the organic layer. Upon consumption of quinone (6–24 h), the reaction was diluted with dichloromethane (48 ml) and washed with 5% sodium bicarbonate. The layers were separated, and the aqueous layer was extracted with dichloromethane (3×64 ml), dried over $MgSO_4$, and evaporated *in vacuo*. Purification was performed by silica gel chromatography to give the arylation product in 60–85% yield. (The reaction needed 48 hours to complete because trimethylphenyl boronic acid is a very bulky acid).

3,5-dimethyl-2-phenylcyclohexa-2,5-diene-1,4-dione



79%; Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.97 (s, 6H), 2.11 (d, 3H, J = 1.6 Hz), 6.66 (d, 1H, J = 1.6 Hz), 7.13–7.16 (m, 2H), 7.39–7.45 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.0, 15.9, 128.1, 128.5, 129.5, 132.9, 133.2, 141.6, 143.7, 145.5, 186.7, 188.6; m.p. 66–69 °C (EtOAc); ESI-HRMS: *m/z* calcd for $C_{14}H_{23}O_2$ $[M+H]^+$: 223.1698; found: 223.1691.

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6.658
2.690
2.410
2.115
2.111
2.023
2.020
1.970
1.711
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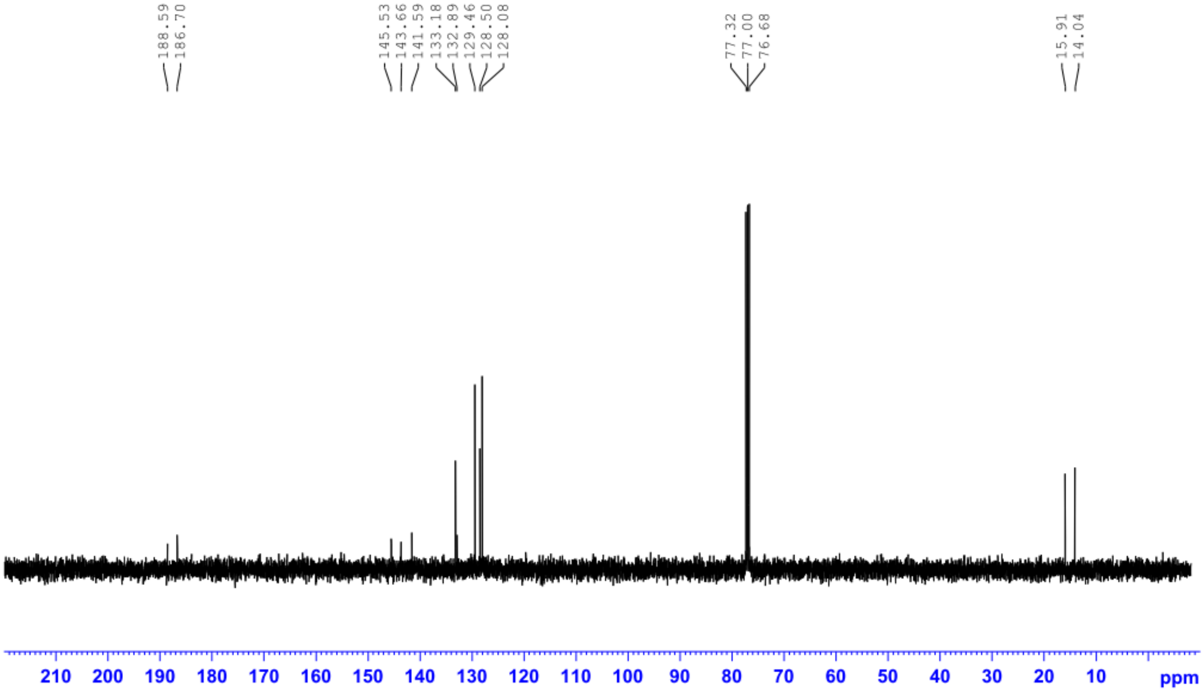
1.00
3.19
3.18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14.04
210
200
190
180
170
160
150
140
130
120
110
100
90
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50
40
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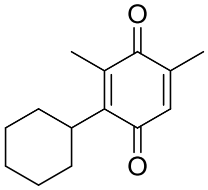
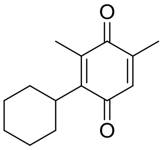
10
ppm

2-cyclohexyl-3,5-dimethylcyclohexa-2,5-diene-1,4-dione



75%; Yellow liquid; ^{1}H NMR (400 MHz, CDCl$_3$) δ: 1.28–1.30 (m, 3H), 1.50–1.54 (m, 2H), 1.69–1.71 (m, 1H), 1.78–1.86 (m, 2H), 1.88–1.95 (m, 2H), 1.99 (d, 3H, *J* = 1.6 Hz), 2.07 (s, 3H), 2.67–2.75 (m, 1H), 6.44 (d, 1H, *J* = 1.6 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ: 12.1, 15.6, 25.8, 26.9, 29.9, 39.9, 134.0, 140.4, 144.3, 147.7, 187.8, 188.6; ESI-HRMS: *m/z* calcd for $C_{14}H_{19}O_2$ $[M+H]^+$: 219.1385; found: 219.1385.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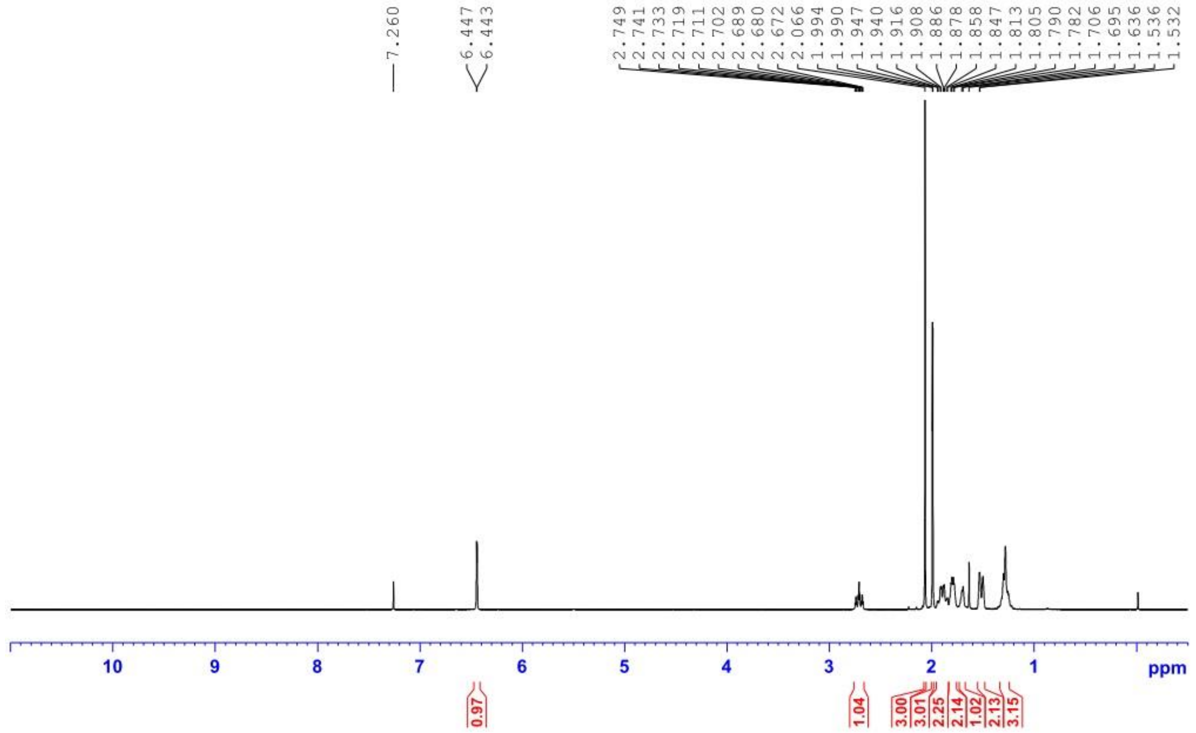
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1.636
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1.532
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9
8
7
6
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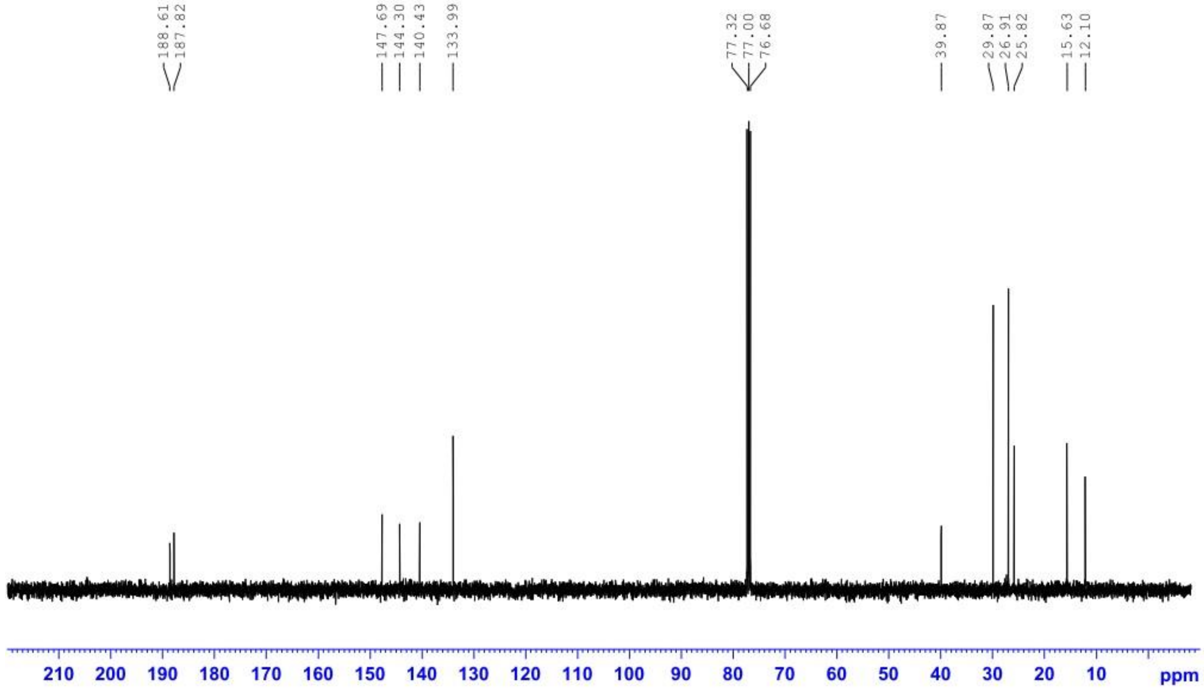
1.02
2.13
3.15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150
140
130
120
110
100
90
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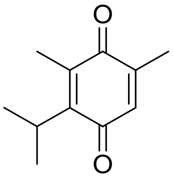
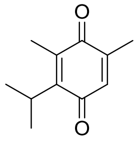
3,5-dimethyl-2-(propan-2-yl)cyclohexa-2,5-diene-1,4-dione



85%; Yellow liquid; ^{1}H NMR (400 MHz, CDCl$_3$) δ: 1.25 (s, 3H), 1.27 (s, 3H), 2.00 (s, 3H), 2.06 (s, 3H), 3.07–3.14 (m, 1H), 6.46 (s, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ: 11.9, 15.7, 20.4, 28.6, 134.0, 140.1, 144.4, 148.6, 187.6, 188.6; ESI-HRMS: *m/z* calcd for $C_{11}H_{15}O_2$ $[M+H]^+$: 179.1072; found: 179.1073.



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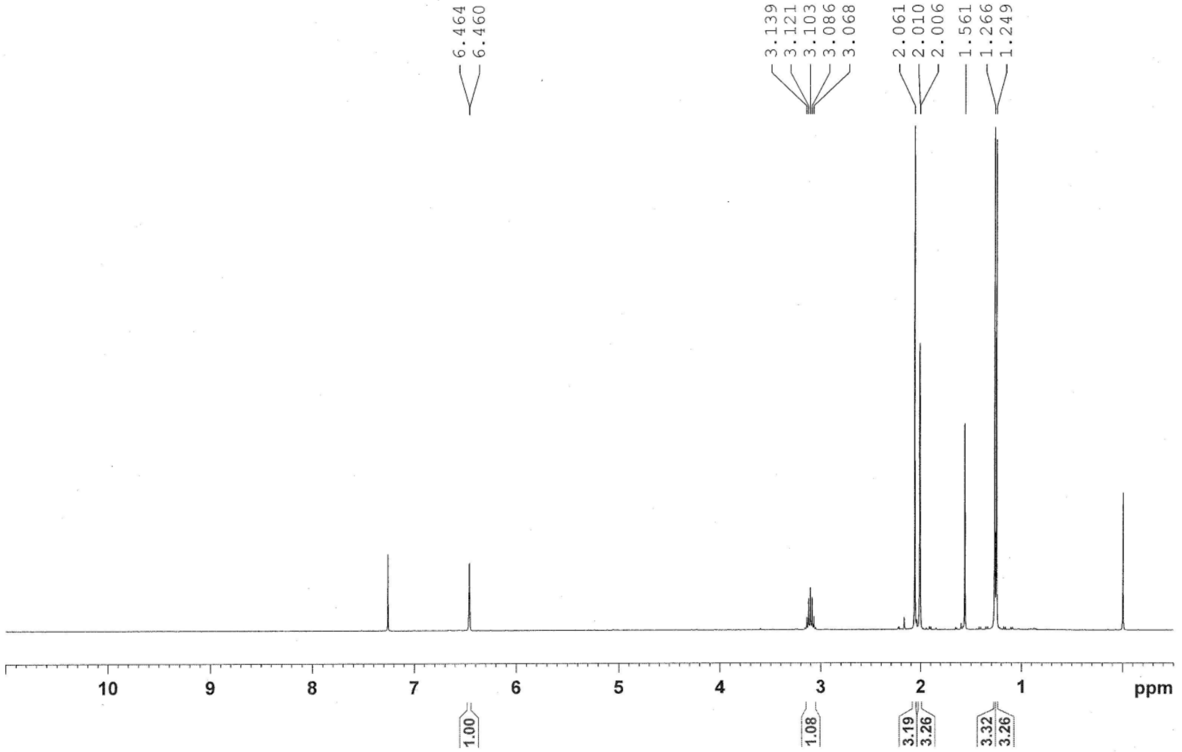

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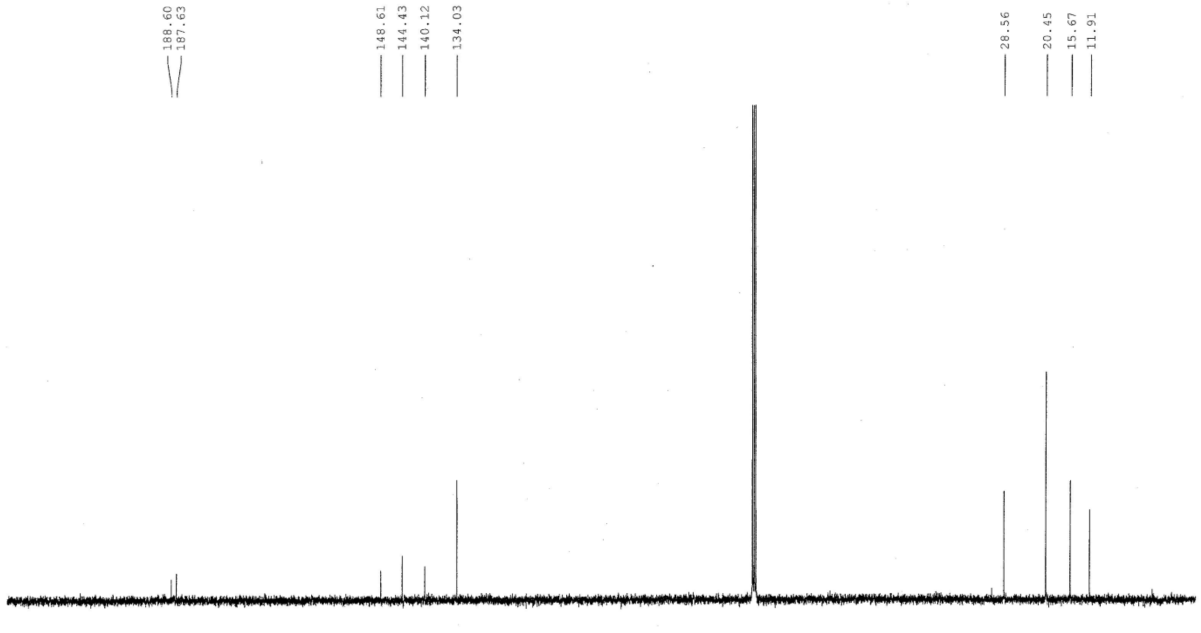
3.26



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160
150
140
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120
110
100
90
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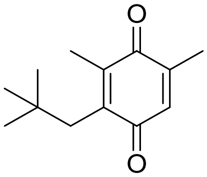
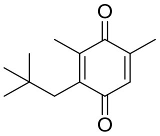
ppm

2-(2,2-dimethyl propyl)-3,5-dimethylcyclohexa-2,5-diene-1,4-dione



82%; Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.89 (s, 9H), 2.03(s, 3H), 2.04 (s, 3H), 2.49 (s, 2H), 6.55 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.2, 15.8, 30.4, 34.2, 38.2, 133.4, 142.5, 143.5, 145.0, 187.8, 188.3; m.p. 54–56 °C (EtOAc); ESI-HRMS: *m/z* calcd for $C_{13}H_{19}O_2$ $[M+H]^+$: 207.1385; found: 207.1382.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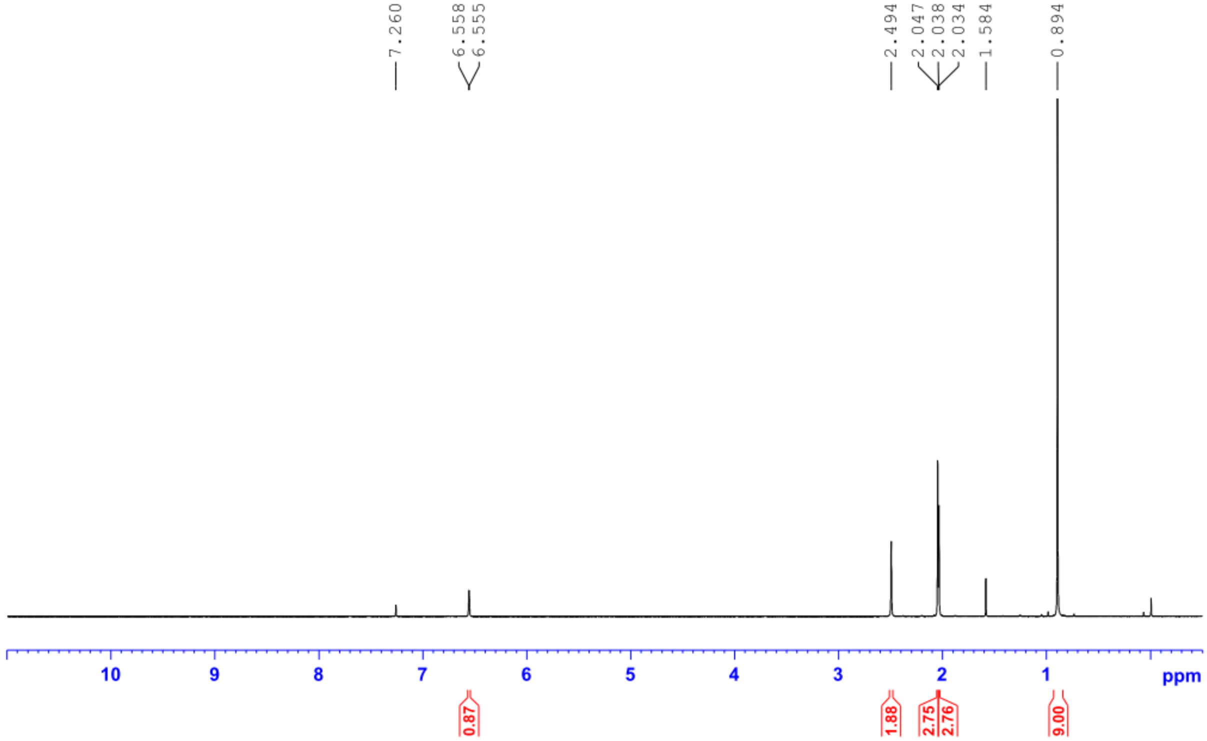
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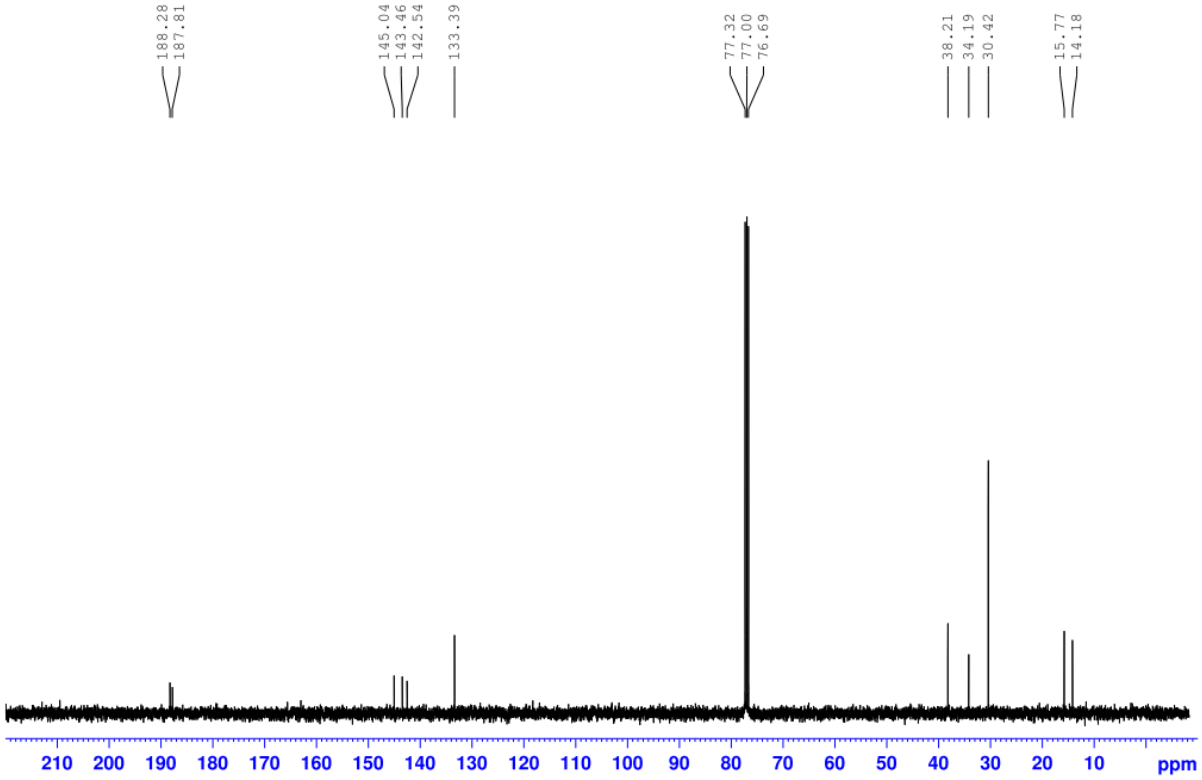
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14.18
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170
160
150
140
130
120
110
100
90
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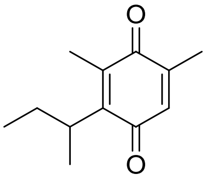
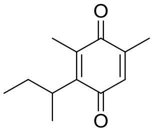
ppm

2-(butan-2-yl)-3,5-dimethylcyclohexa-2,5-diene-1,4-dione



82%; Yellow liquid; ^{1}H NMR (400 MHz, CDCl$_3$) δ: 0.82 (t, 3H, *J* = 7.6 Hz), 1.23 (d, 3H, *J* = 7.2 Hz), 1.61–1.68 (m, 1H), 1.73–1.80 (m, 1H), 2.01 (d, 3H, *J* = 0.8 Hz), 2.05(s, 3H), 2.82–2.88 (m, 1H), 6.46 (d, 1H, *J* =1.2 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ: 12.1, 12.8, 15.7, 18.6, 27.9, 36.1, 134.0, 141.1, 144.5, 147.7, 187.7, 188.4; ESI-HRMS: *m/z* calcd for $C_{12}H_{17}O_2$ [M+H]$^+$: 193.1229; found: 193.1229.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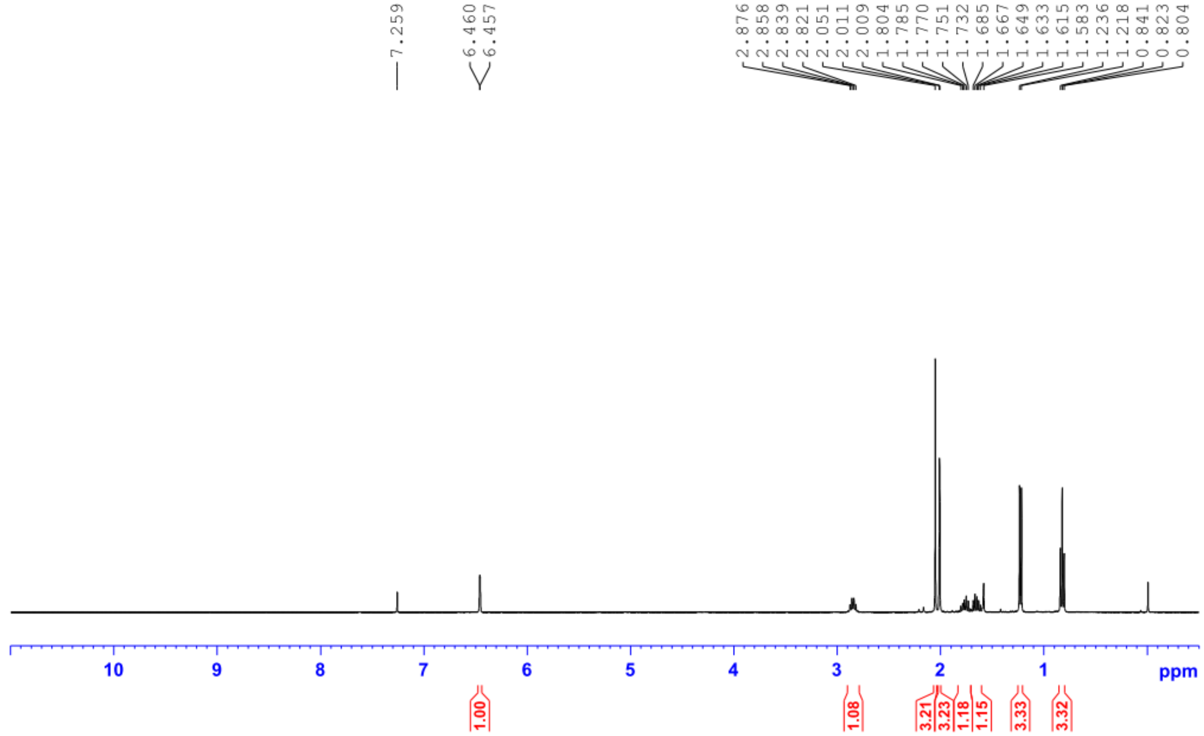
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1.751
1.732
1.685
1.667
1.649
1.633
1.615
1.583
1.236
1.218
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0.804
10
9
8
7
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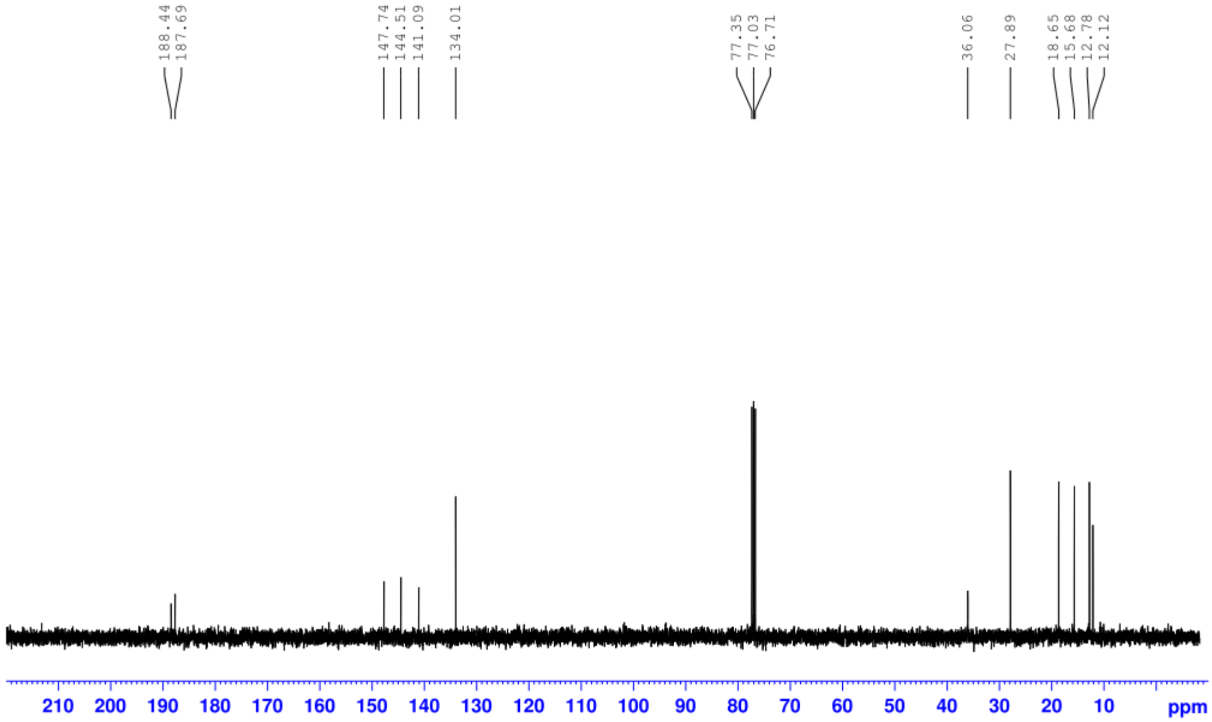
3.32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12.12
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200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
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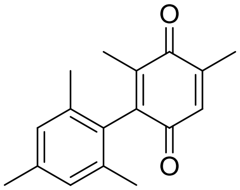
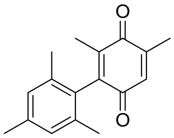
20
10
ppm

3,5-dimethyl-2-(2,4,6-trimethylphenyl)cyclohexa-2,5-diene-1,4-dione



60%; Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ:1.78 (s, 3H), 2.00 (s, 6H), 2.12 (s, 3H), 2.31 (s, 3H), 6.67 (s,1H), 6.92 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.1, 15.9, 19.7, 21.1, 128.2, 129.7, 133.4, 135.0, 137.9, 142.8, 144.1, 145.6, 186.4, 188.2; m.p. 58–60 °C (EtOAc); ESI-HRMS: *m/z* calcd for $C_{17}H_{19}O_2$ $[M+H]^+$: 255.1385; found: 255.1382.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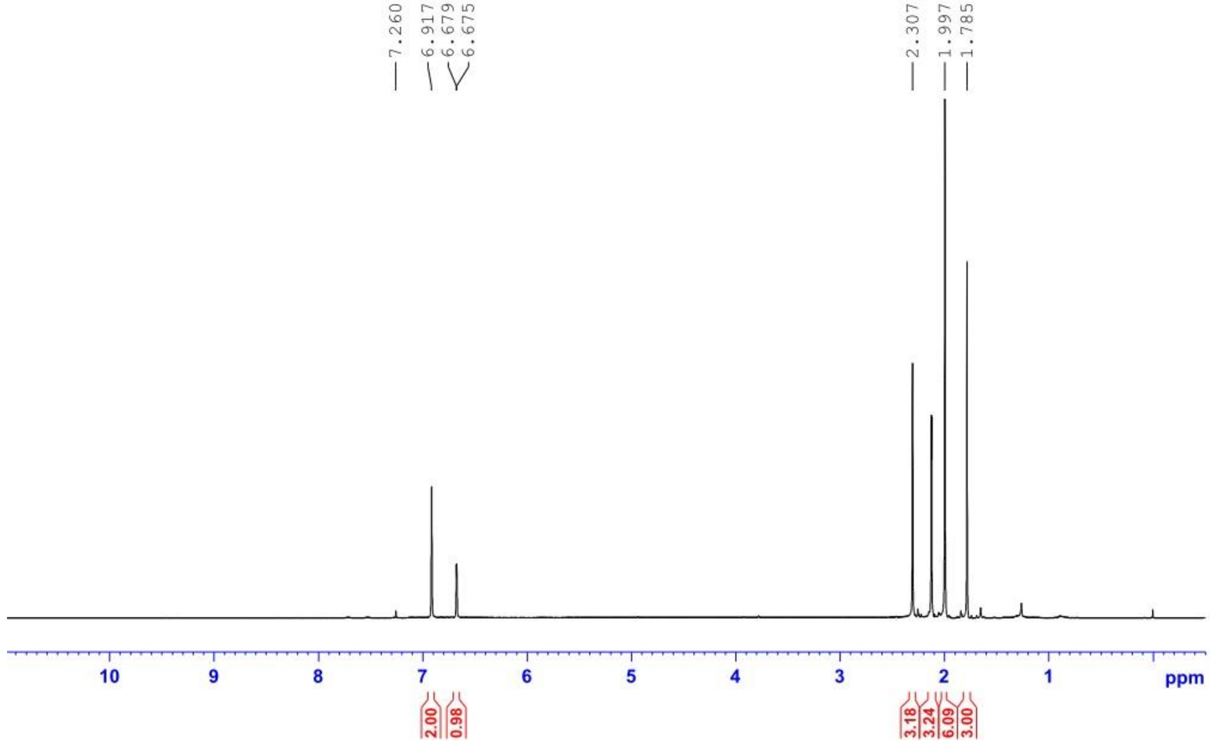
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10
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8
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5
4
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ppm
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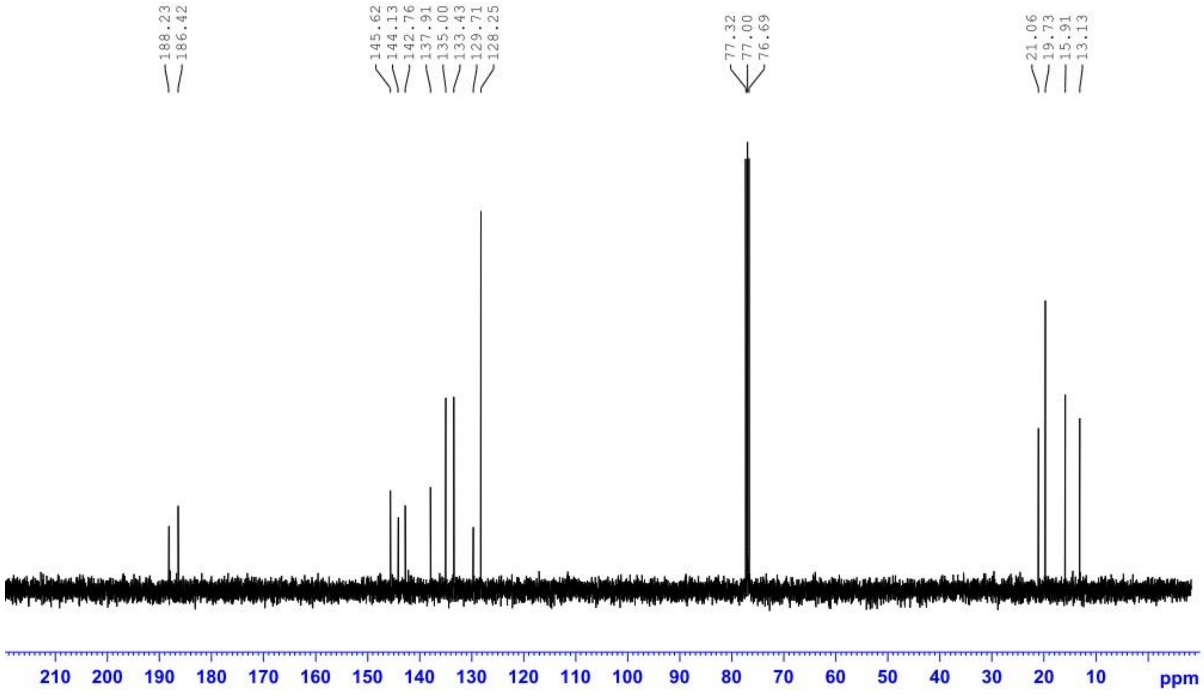
6.09
3.00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128.25
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76.69
21.06
19.73
15.91
13.13
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200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

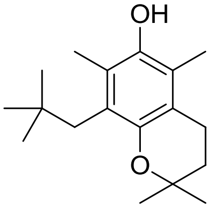
General procedure to synthesize hydroquinones from benzoquinones[S2]

To a solution of benzoquinone (2.2 mmol) in acetic acid (6.0 ml), zinc powder (4 eq, 589 mg) was added. The mixture was then sonicated for 30 minutes. Upon consumption of quinone, the reaction mixture was filtered and the residue was washed with ethyl acetate. The combined filtrates were concentrated *in vacuo*, affording the pure reduction product in quantitative yield.

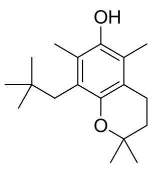
General procedure to synthesize different substituted 3,4-dihydro-2H-1-benzopyran-6-ol[S3]

A solution of hydroquinone and 2-methylbut-3-en-2-ol in 1:1 mole ratio in minimum amount of trifluoroacetic acid was stirred at room temperature under inert atmosphere, and completion of reaction was monitored by thin-layer chromatography. The solvent was removed under reduced pressure, and the residue was dissolved in hexane. The organic layer was neutralized with saturated sodium bicarbonate, then washed with saturated sodium chloride, dried over anhydrous $NaSO_4$, and concentrated *in vacuo*. Purification was performed by silica gel chromatography to yield pure product in (56–72%).

8-(2,2-dimethylpropyl)-2,2,5,7-tetramethyl-3,4-dihydro-2H-1-benzopyran-6-ol



68%; White solid; ^{1}H NMR (400MHz, $CDCl_3$) δ: 0.93 (s, 9H), 1.28 (s, 6H), 1.74 (t, 2H, J = 6.8 Hz), 2.13 (s, 3H), 2.19 (s, 3H), 2.63 (s, 2H), 2.63 (t, 2H, J = 7.5 Hz), 4.19 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 11.4, 13.9, 21.2, 26.7, 30.5, 33.2, 34.1, 38.1, 72.5, 116.8, 118.9, 122.2, 125.1, 144.8, 146.5; m.p. 84–86 °C (EtOAc); ESI-HRMS: *m/z* calcd for $C_{18}H_{29}O_2$ $[M+H]^+$: 277.2168; found: 277.2168.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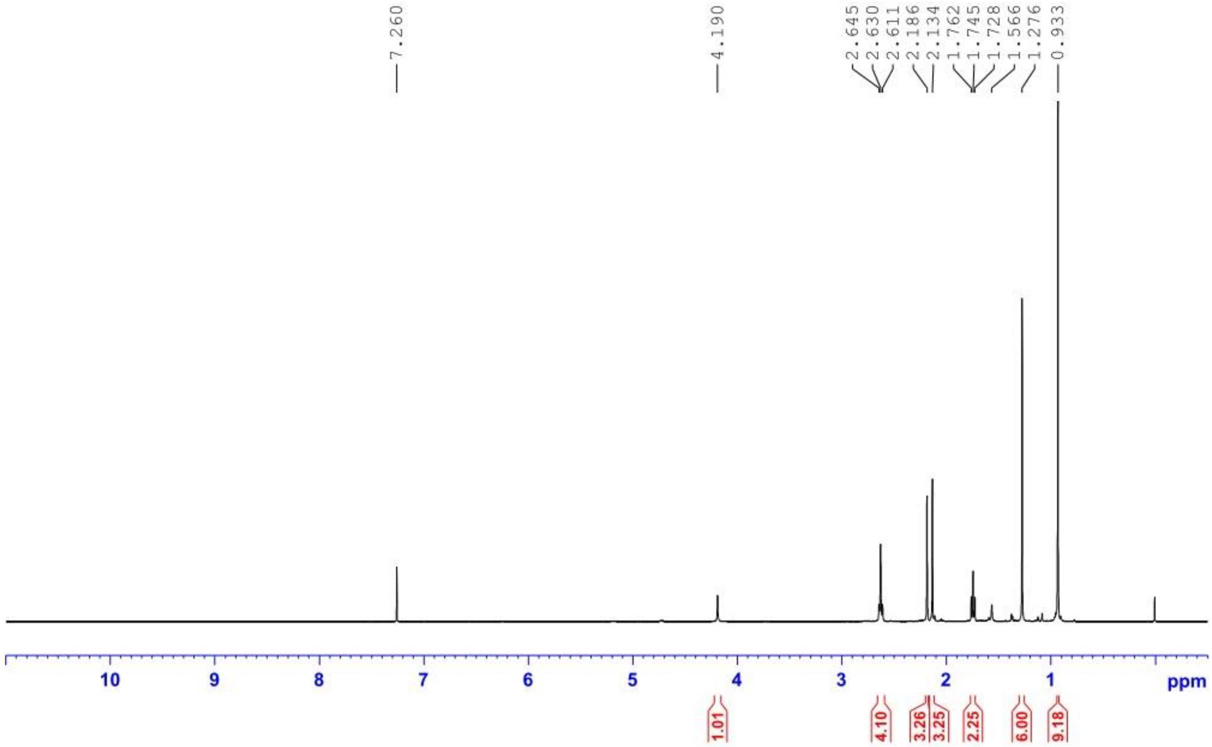
O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2.186
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1.728
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10
9
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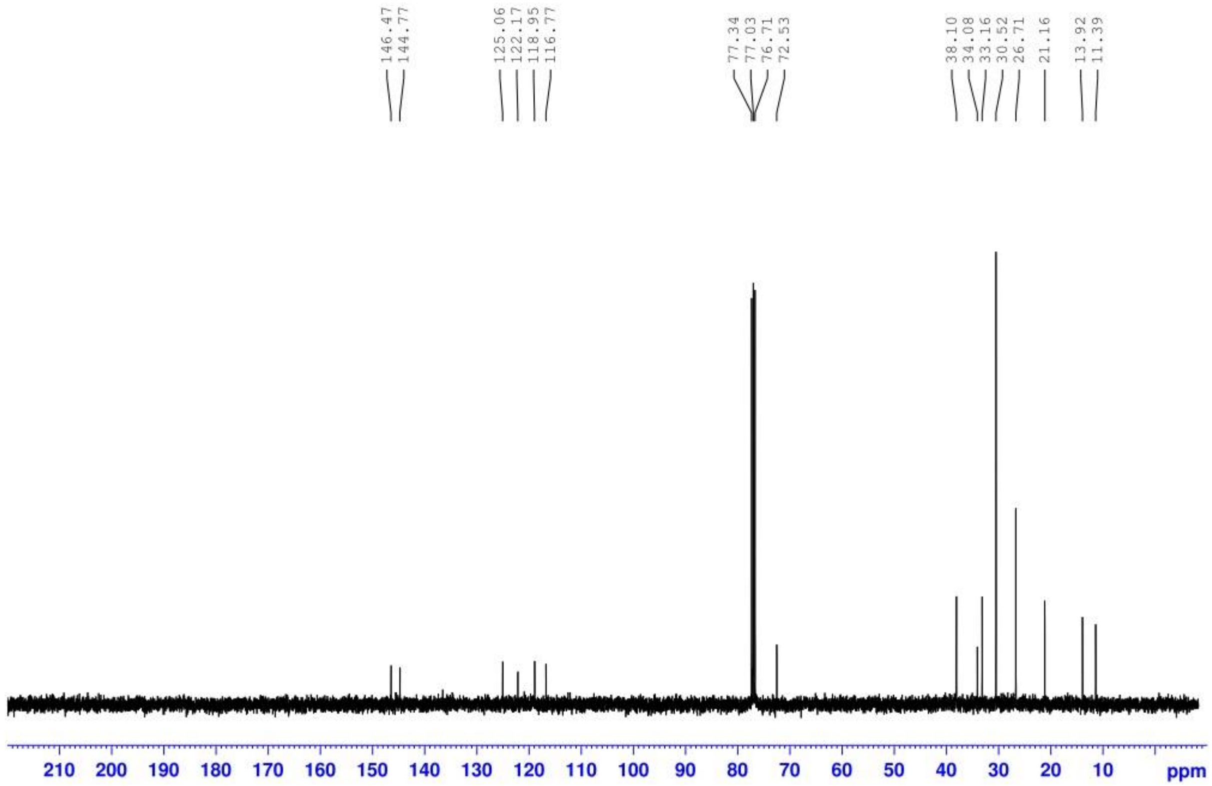
2.25
6.00
9.18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77.03
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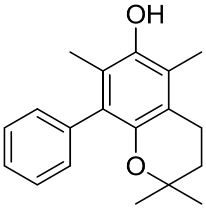
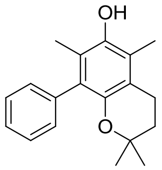
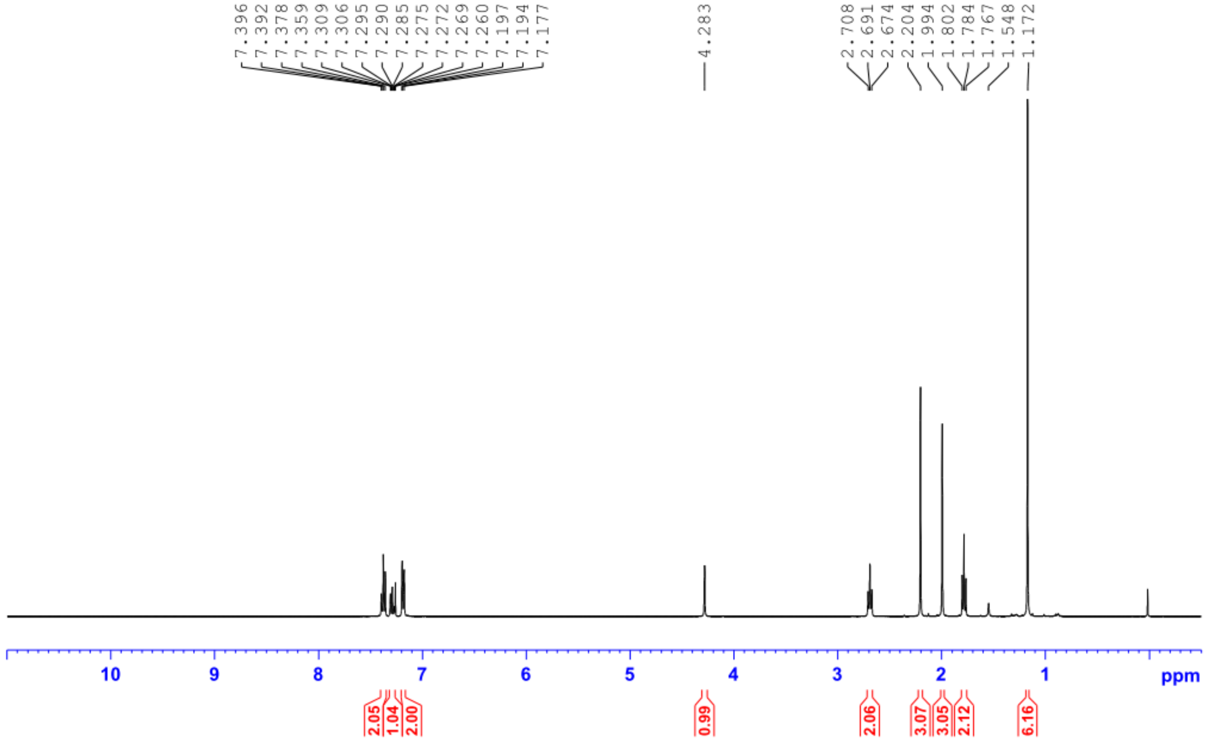
26.71
21.16
13.92
11.39
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

2,2,5,7-tetramethyl-8-phenyl-3,4-dihydro-2H-1-benzopyran-6-ol



60%; White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.17 (s, 6H), 1.78 (t, 2H, *J* = 7.2 Hz), 1.99 (s, 3H), 2.20 (s, 3H), 2.69 (t, 2H, *J* = 6.8 Hz), 4.28 (s, 1H), 7.18–7.19 (d, 2H, *J* = 6.8 Hz), 7.20–7.31 (m, 1H), 7.36–7.40 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 11.5, 13.5, 21.2, 26.4, 32.9, 72.5, 118.0, 120.5, 120.9, 126.1, 127.5, 128.9, 130.6, 138.0, 144.9, 145.0; m.p. 88–90 °C (EtOAc); ESI-HRMS: *m/z* calcd for $C_{19}H_{23}O_2$ $[M+H]^+$: 283.1698; found: 283.1696.


OH
O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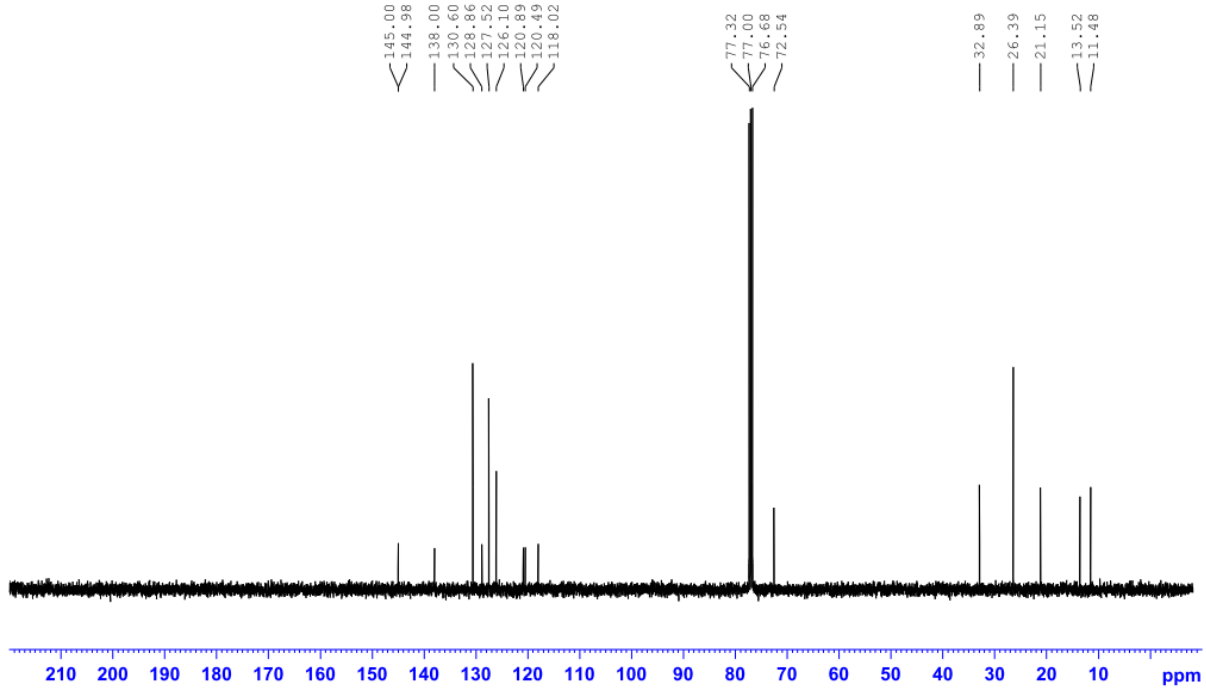
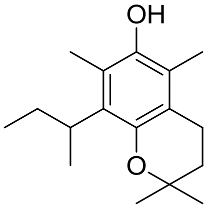
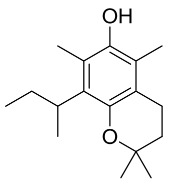
7.392
7.378
7.359
7.309
7.306
7.295
7.290
7.285
7.275
7.272
7.269
7.260
7.197
7.194
7.177
4.283
2.708
2.691
2.674
2.204
1.994
1.802
1.784
1.767
1.548
1.172
10
9
8
7
6
5
4
3
2
1
ppm
2.05
1.04
2.00
0.99
2.06
3.07
3.05
2.12
6.16

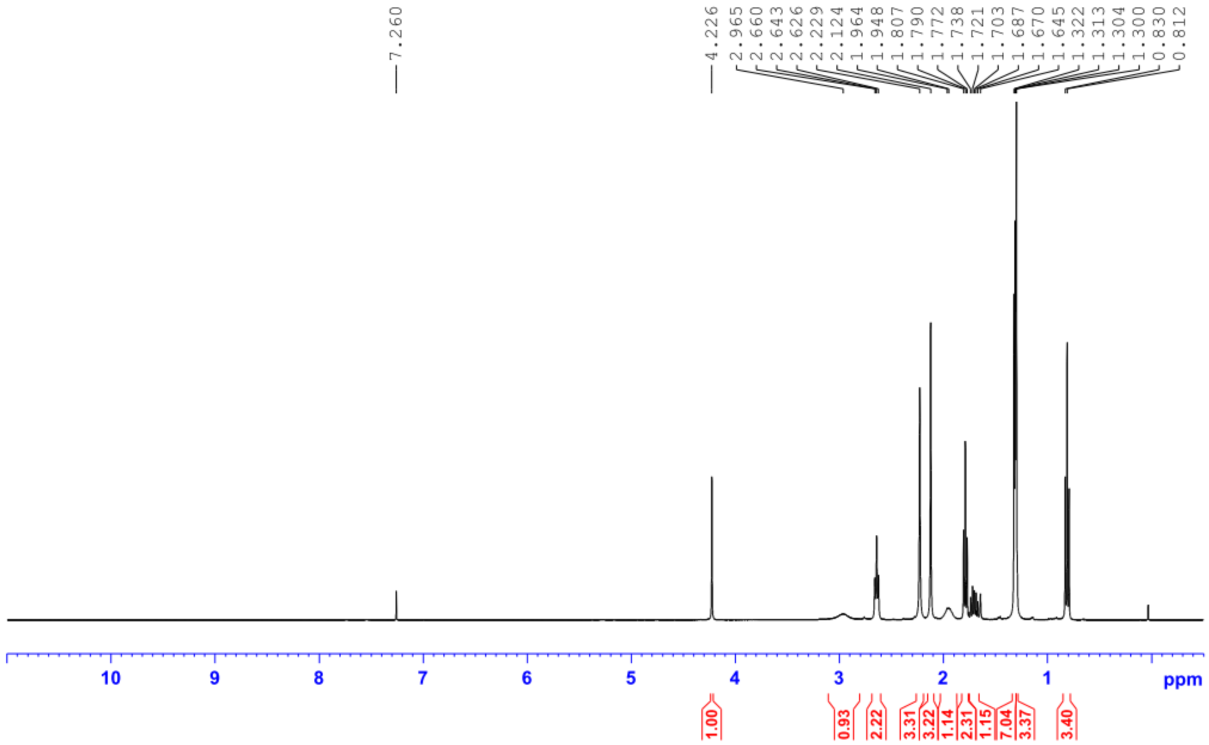

145.00
144.98
138.00
130.60
128.86
127.52
126.10
120.89
120.49
118.02
77.32
77.00
76.68
72.54
32.89
26.39
21.15
13.52
11.48
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

8-(butan-2-yl)-2,2,5,7-tetramethyl-3,4-dihydro-2H-1-benzopyran-6-ol



70%; White solid; ^{1}H NMR (400 MHz, CDCl$_3$) δ: 0.79 (t, 3H, *J* = 7.6 Hz), 1.28 (s, 6H), 1.29 (d, 3H, *J* = 2.4 Hz),1.64–1.71 (m, 1H), 1.77 (t, 2H, *J* = 7.2Hz), 1.93–1.94 (m, 1H), 2.10 (s, 3H), 2.21 (s, 3H), 2.62 (t, 3H, *J* = 6.8 Hz), 2.94 (s, 1H), 4.18 (s, 1H) ; ^{13}C NMR (100 MHz, CDCl$_3$) δ: 11.4, 12.4, 13.1, 18.8, 21.2, 26.3, 26.5, 27.9, 32.9, 36.5, 72.0, 117.3, 118.9, 120.9, 130.9, 144.5, 146.6; m.p. 47–49 °C (EtOAc); ESI-HRMS: *m/z* calcd for $C_{17}H_{27}O_2$ $[M+H]^+$: 263.2011; found: 263.2009.


OH
O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4.226
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2.660
2.643
2.626
2.229
2.124
1.964
1.948
1.807
1.790
1.772
1.738
1.721
1.703
1.687
1.670
1.645
1.322
1.313
1.304
1.300
0.830
0.812
10
9
8
7
6
5
4
3
2
1
ppm
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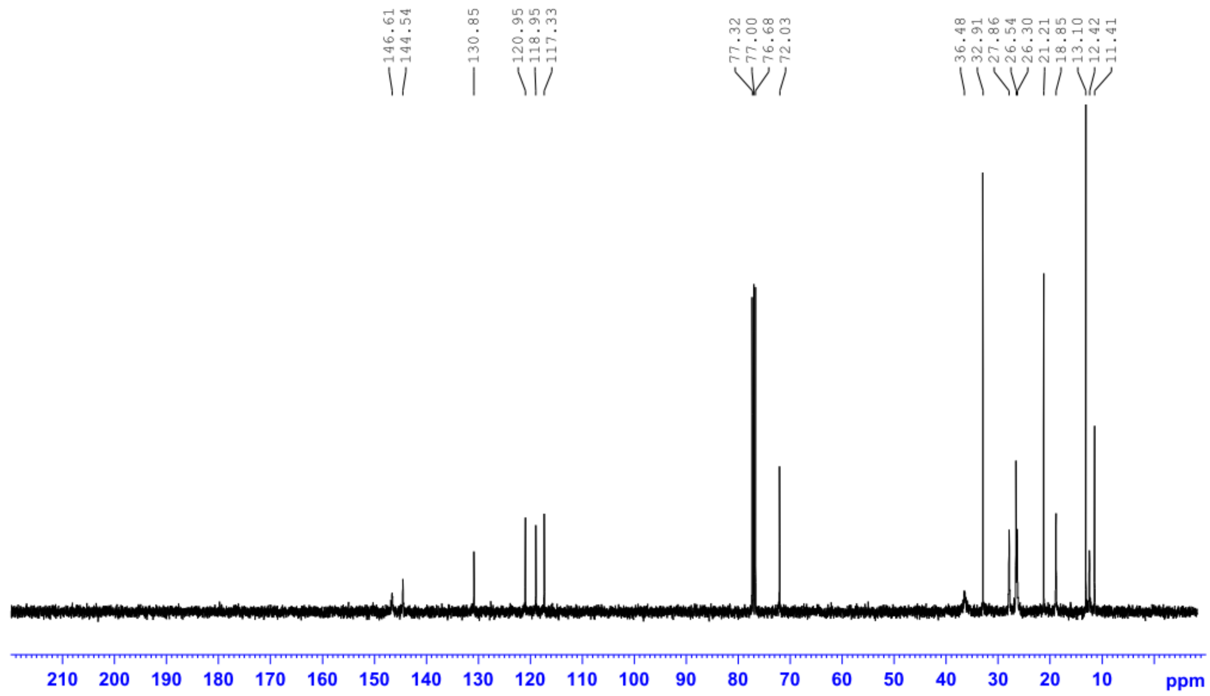
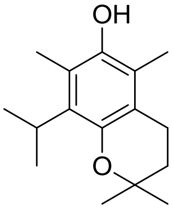
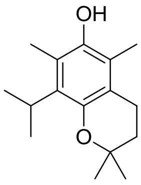
0.93
2.22
3.31
3.22
1.14
2.31
1.15
7.04
3.37
3.40

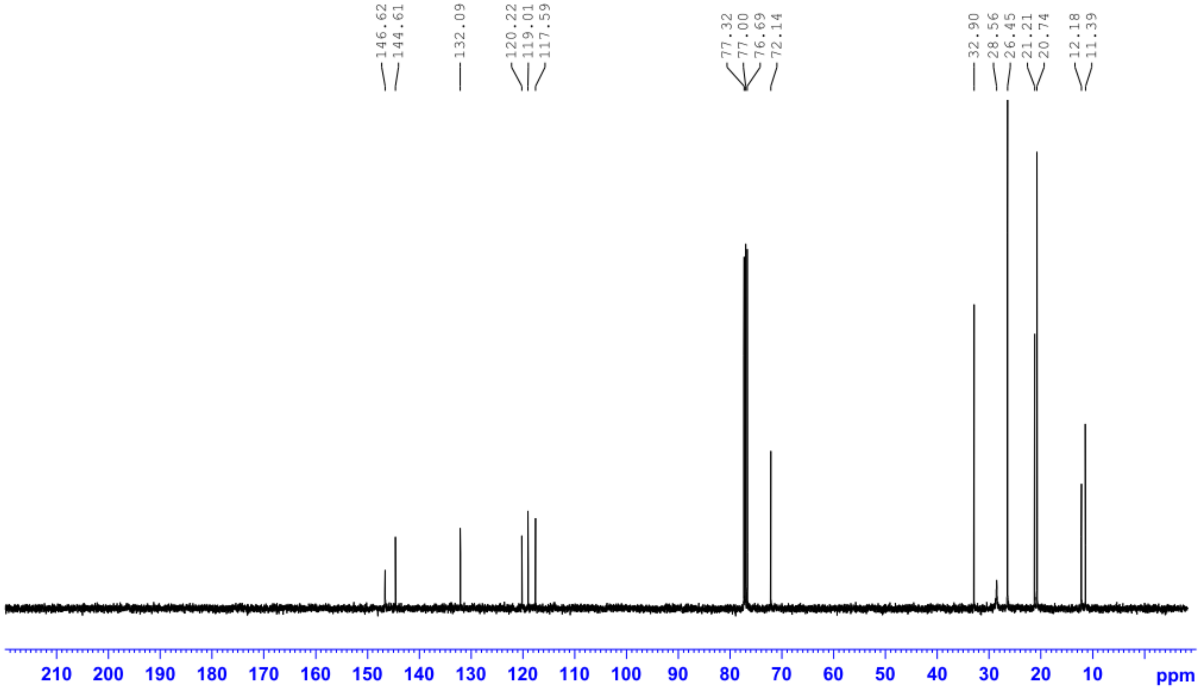

146.61
144.54
130.85
120.95
118.95
117.33
77.32
77.00
76.68
72.03
36.48
32.91
27.86
26.54
26.30
21.21
18.85
13.10
12.42
11.41
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

2,2,5,7-tetramethyl-8-(propan-2-yl)-3,4-dihydro-2H-1-benzopyran-6-ol



72%; White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.31 (s, 6H), 1.32 (s, 3H), 1.34 (s, 3H), 1.79 (t, 2H , *J* = 6.8 Hz), 2.11 (s, 3H), 2.23 (s, 3H), 2.64 (t, 2H, *J* = 6.8 Hz), 3.29 (s, 1H), 4.19 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 11.4, 12.2, 20.7, 21.2, 26.4, 28.6, 32.9, 72.1, 117.6, 119.0, 120.2, 132.1, 144.6, 146.6; m.p. 66–69 °C (EtOAc); ESI-HRMS: *m/z* calcd for $C_{16}H_{25}O_2$ $[M+H]^+$: 249.1855; found: 249.1858.


OH
O


146.62
144.61
132.09
120.22
119.01
117.59
77.32
77.00
76.69
72.14
32.90
28.56
26.45
21.21
20.74
12.18
11.39
210
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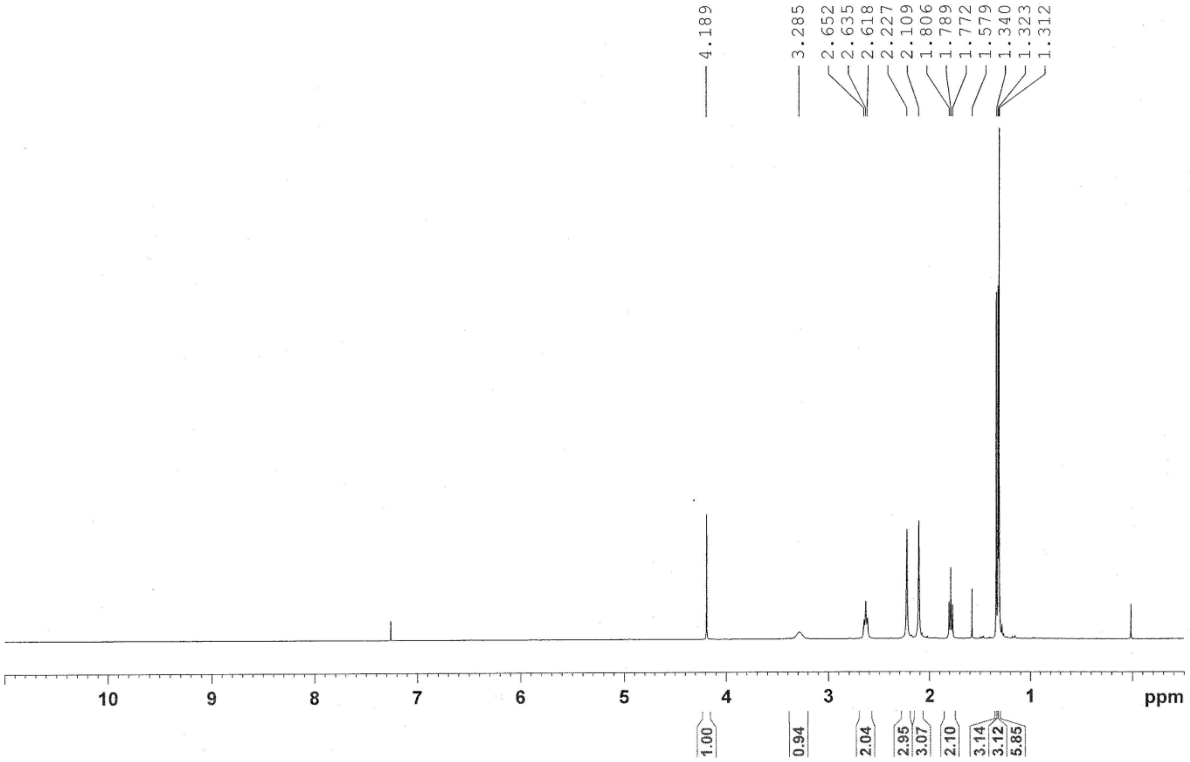
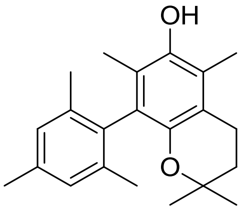
40
30
20
10
ppm

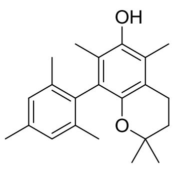

4.189
3.285
2.652
2.635
2.618
2.227
2.109
1.806
1.789
1.772
1.579
1.340
1.323
1.312
10
9
8
7
6
5
4
3
2
1
ppm
1.00
0.94
2.04
2.95
3.07
2.10
3.14
3.12
5.85

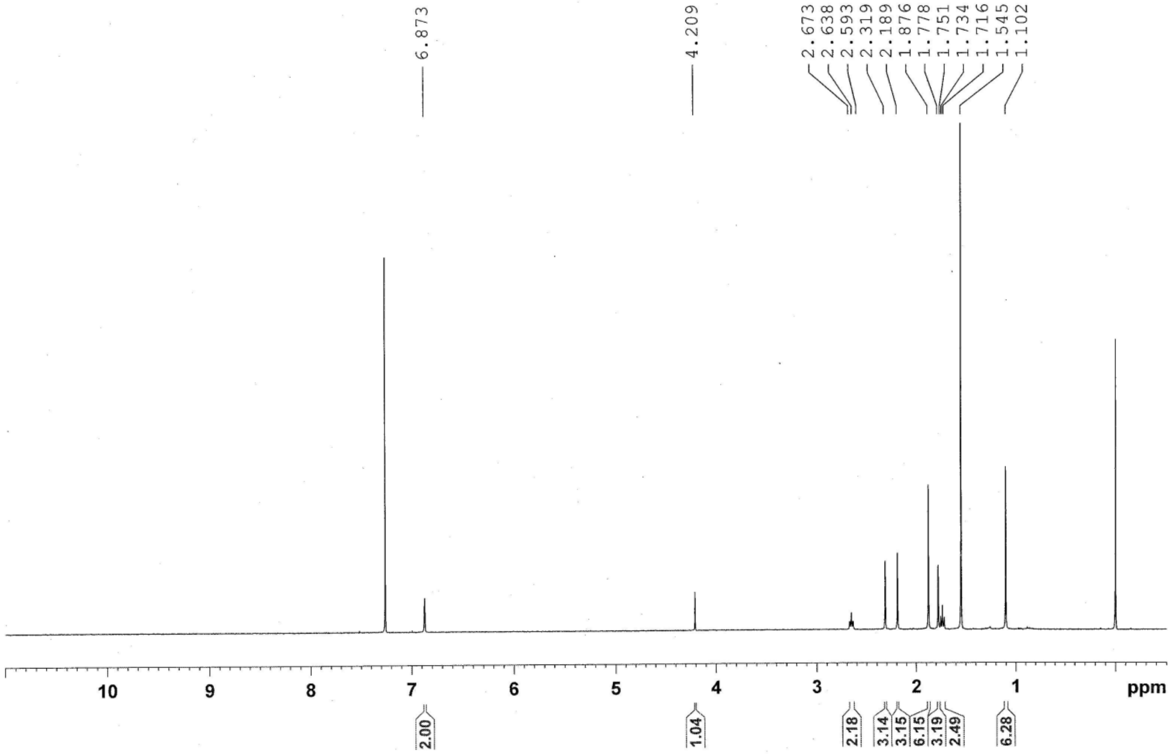
2,2,5,7-tetramethyl-8-(2,4,6-trimethylphenyl)-3,4-dihydro-2H-1-benzopyran-6-ol[17]



Trimethylphenyl dimethyl hydroquinone (1.2 mmol, 307 mg) and *p*-toluenesulfonic acid ($TsOH·H_2O$) (0.15 eq, 0.18 mmol, 34.7 mg) were added to a two-necked flask, then dry toluene (5 ml) was added under nitrogen. After stirring for five minutes, 2-methyl-but-3-en-2-ol (1.2 eq, 0.15 ml) was injected dropwise into the flask by syringe. The reaction was then stirred for 48 hours at 100 °C. After cooling, ethyl acetate was added to dilute the solution. The organic layer was washed with sodium bicarbonate and water, and dried with $MgSO_4$. After the solvent was removed, the residue was separated by column chromatography (hexane:EtOAc = 99:1) to give the white solid in 12% yield.

12%; White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.10 (s, 6H), 1.73 (t, 2H, *J* = 7.2 Hz), 1.78 (s, 3H), 1.88 (s, 6H), 2.19 (s, 3H), 2.32 (s, 3H), 2.64 (t, 2H, *J* = 7.21 Hz), 4.21 (s, 1H), 6.87 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 11.5, 12.3, 20.0, 21.1, 21.2, 26.5, 33.0, 72.0, 117.5, 120.1, 120.2, 126.9, 127.4, 134.8, 135.4, 136.2, 144.7, 144.8; m.p. 84–86 °C (EtOAc); ESI-HRMS: *m/z* calcd for $C_{22}H_{28}O_2Na$ $[M+Na]^+$: 347.1987; found: 347.1992.


OH
O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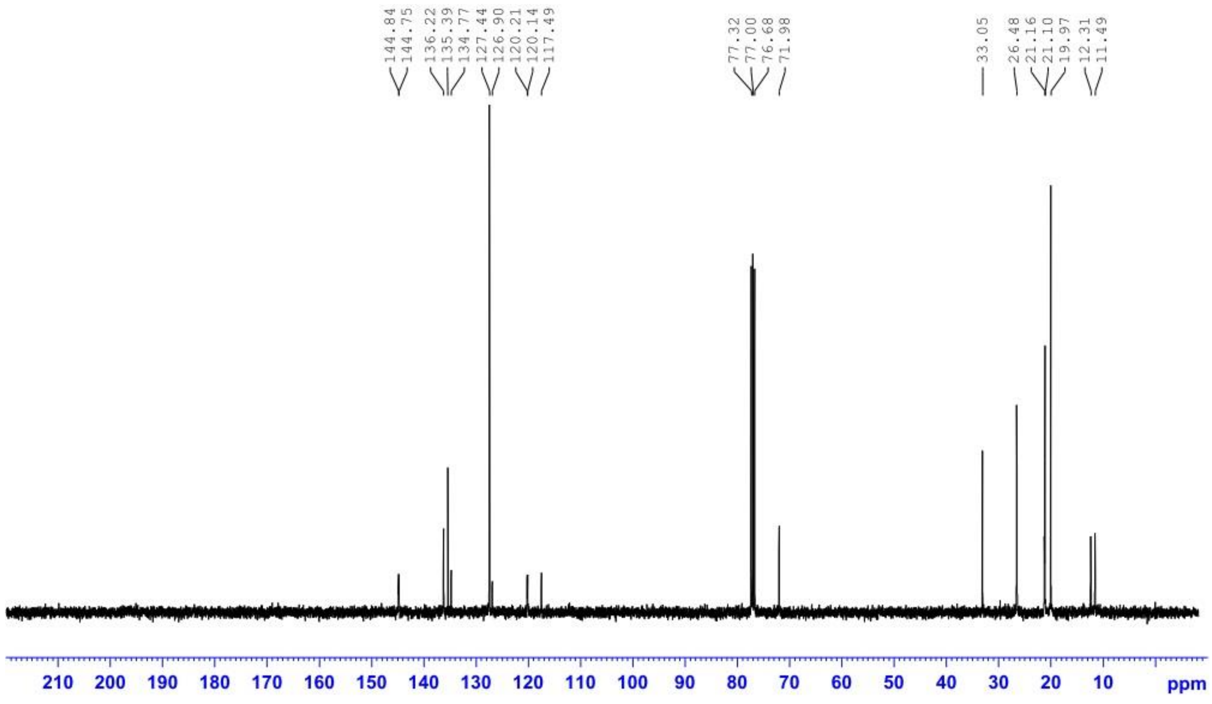
2.673
2.638
2.593
2.319
2.189
1.876
1.778
1.751
1.734
1.716
1.545
1.102
10
9
8
7
6
5
4
3
2
1
ppm
2.00
1.04
2.18
3.14
3.15
6.15
3.19
2.49
6.28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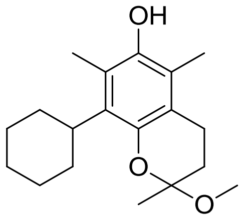
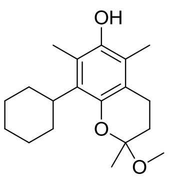
144.75
136.22
135.39
134.77
127.44
126.90
120.21
120.14
117.49
77.32
77.00
76.68
71.98
33.05
26.48
21.16
21.10
19.97
12.31
11.49
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

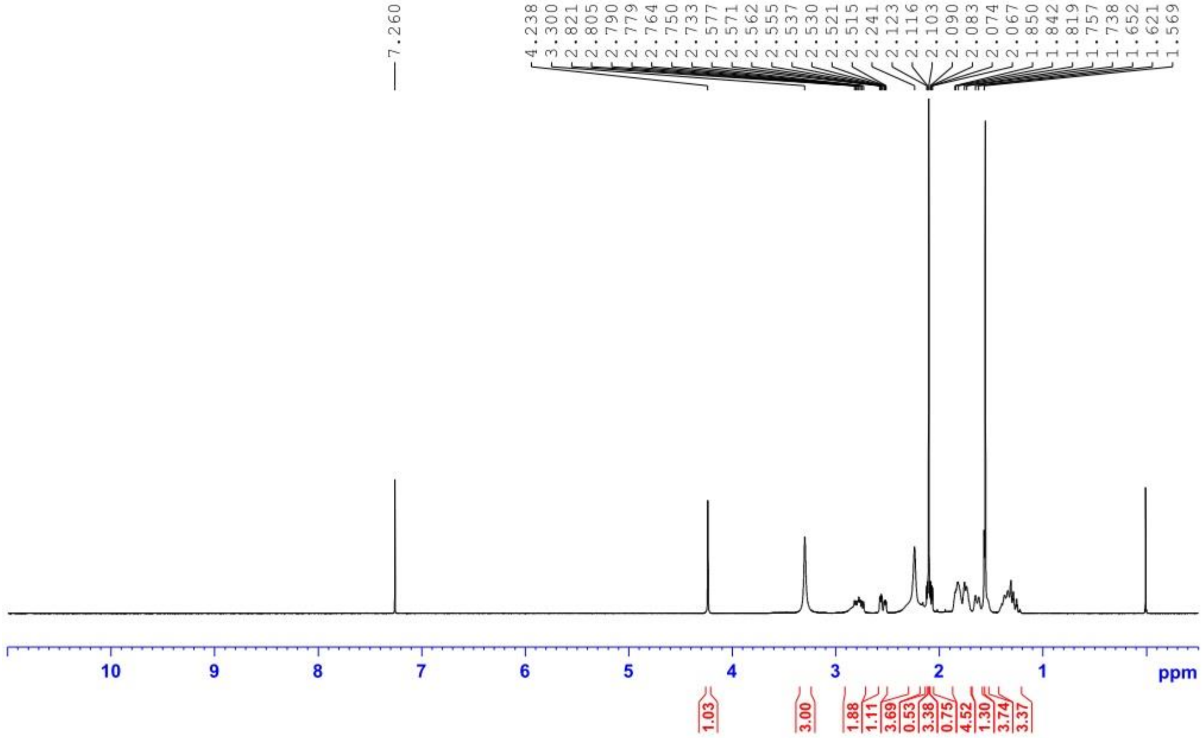
8-cyclohexyl-2-methoxy-2,5,7-trimethyl-3,4-dihydro-2H-1-benzopyran-6-ol[17]



Cyclohexyldimethylhydroquinone (441 mg, 2.0 mmol) was added to a round-bottomed flask, and methanol (10 ml) was injected under nitrogen. After methyl vinyl ketone (0.32 ml, 2.0 mmol) was added, conc. sulfuric acid (2 drops) was added quickly. The solution was stirred for five minutes and trimethyl orthoformate (0.33 ml, 3 mmol) was added, then the solution was stirred for 48 hours at room temperature. After the solvent was removed, ethyl acetate and water were added. The organic layer was washed with sodium bicarbonate and brine, dried with Na_2SO_4. The residue was purified by chromatography (hexane:EtOAc = 4:1) to give the white solid product (50%).

50%; White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.28–1.37 (m, 3H), 1.56 (s, 3H), 1.56–1.57 (m, 1H), 1.62–1.65 (m, 1H), 1.74–1.85 (m, 5H), 2.07–2.12 (m, 2H), 2.10 (s, 3H), 2.24 (s, 3H), 2.52–2.58 (m, 1H), 2.73–2.82 (m, 2H), 3.30 (s, 3H), 4.24 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 11.4, 12.3, 20.2, 23.0, 26.6, 27.7, 27.8, 30.2, 30.4, 31.8, 40.7, 49.7, 97.4, 118.8, 119.0, 120.5, 130.9, 145.3; m.p. 136–138 °C (EtOAc); ESI-HRMS: *m/z* calcd for $C_{19}H_{23}O_2$ $[M+H]^+$: 283.1698; found: 283.1696.


OH
O
O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2.790
2.779
2.764
2.750
2.733
2.577
2.571
2.562
2.555
2.537
2.530
2.521
2.515
2.241
2.123
2.116
2.103
2.090
2.083
2.074
2.067
1.850
1.842
1.819
1.757
1.738
1.652
1.621
1.569
10
9
8
7
6
5
4
3
2
1
ppm
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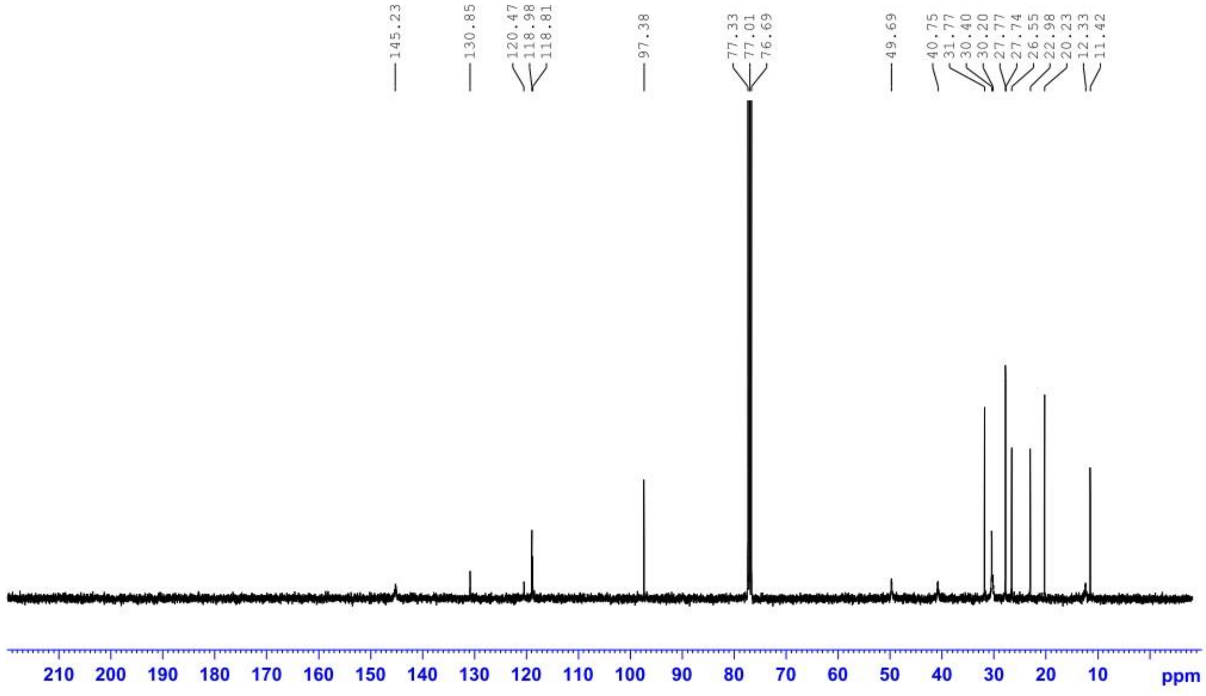
1.88
1.11
3.69
0.53
3.38
0.75
4.52
1.30
3.74
3.37


145.23
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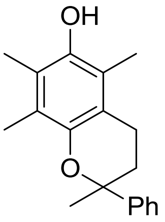
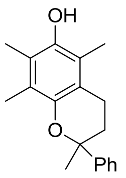
118.98
118.81
97.38
77.33
77.01
76.69
49.69
40.75
31.77
30.40
30.20
27.77
27.74
26.55
22.98
20.23
12.33
11.42
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

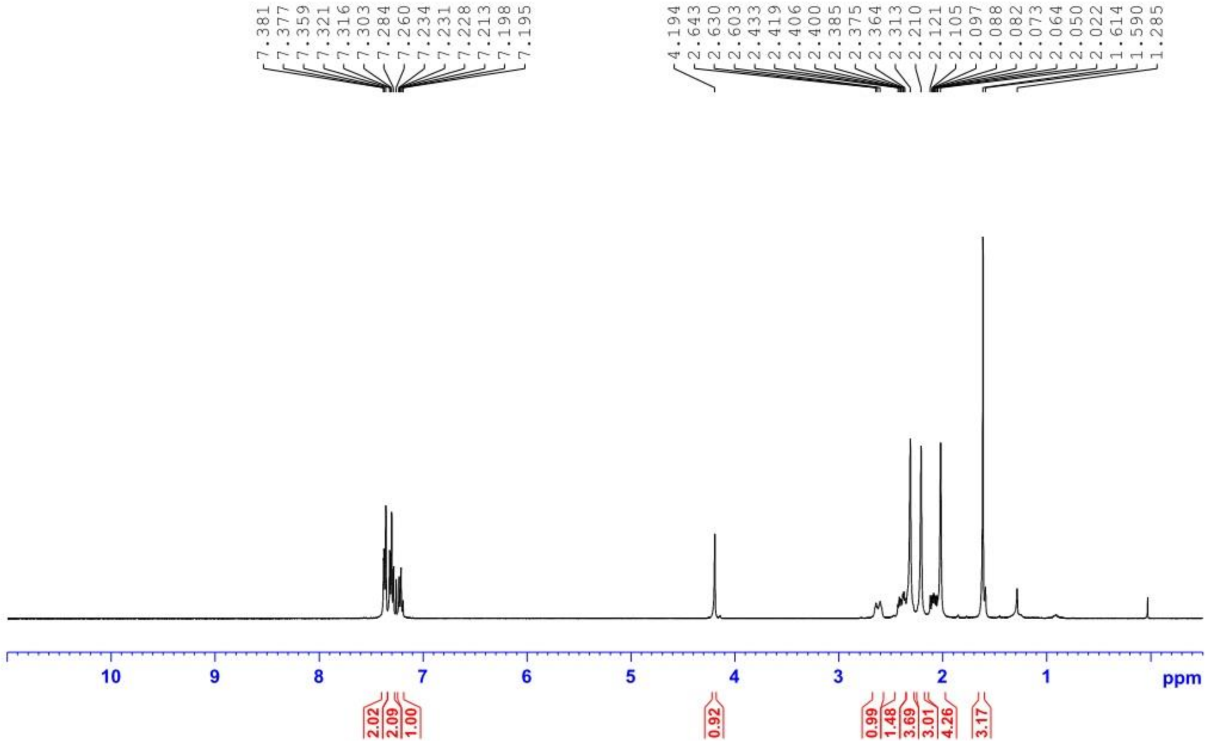
2,5,7,8-tetramethyl-2-phenyl-3,4-dihydro-2H-1-benzopyran-6-ol[17]



Trimethyl hydroquinone (1.2 mmol, 183 mg) and *p*-toluenesulfonic acid (TsOH·H_2O) (0.152 eq, 0.18 mmol, 34.7 mg) were added to a two-necked flask, and dry toluene (5 mml) was added under nitrogen. After stirring for five minutes, 2-phenyl-but-3-en-2-ol (1.2 eq, 213 mg) was injected dropwise into the flask by syringe. Then it was stirred for 18 hours at 100 °C. After cooling, ethyl acetate was added to dilute the solution, and the organic layer was washed with sodium bicarbonate and water, and dried with $MgSO_4$. The solvent was removed, the residue was separated by column chromatography (hexane:EtOAc = 49:1) to give the white solid in 45% yield.

45%; White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.61 (s, 3H), 2.02 (s, 3H), 2.05–2.12 (m, 1H), 2.21 (s, 3H), 2.31 (s, 3H), 2.36–2.43 (m, 2H), 2.60–2.64 (m, 1H), 4.19 (s, 1H), 7.20–7.23 (m, 1H), 7.28–7.32 (m, 2H), 7.36–7.38 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 11.2, 11.9, 12.2, 21.0, 30.1, 32.8, 76.9, 117.5, 118.4, 121.1, 122.2, 124.8, 126.5, 128.3, 144.8, 145.6, 146.2; m.p. 77–79 °C (EtOAc); ESI-HRMS: *m/z* calcd for $C_{19}H_{29}O_3$ $[M+H]^+$: 305.2117; found: 305.2114.


OH
O
Ph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7.303
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7.231
7.228
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2.643
2.630
2.603
2.433
2.419
2.406
2.400
2.385
2.375
2.364
2.313
2.210
2.121
2.105
2.097
2.088
2.082
2.073
2.064
2.050
2.022
1.614
1.590
1.285
10
9
8
7
6
5
4
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2
1
ppm
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2.09
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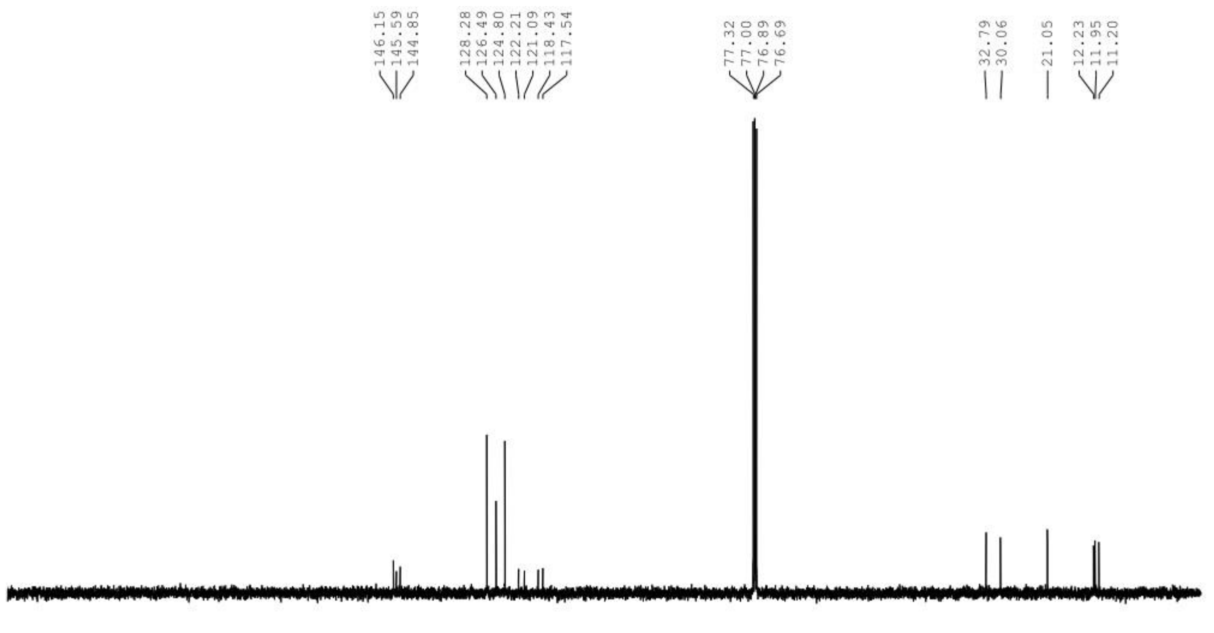
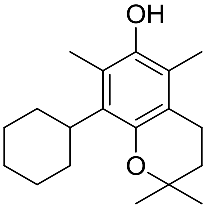
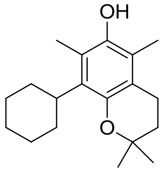
0.99
1.48
3.69
3.01
4.26
3.17

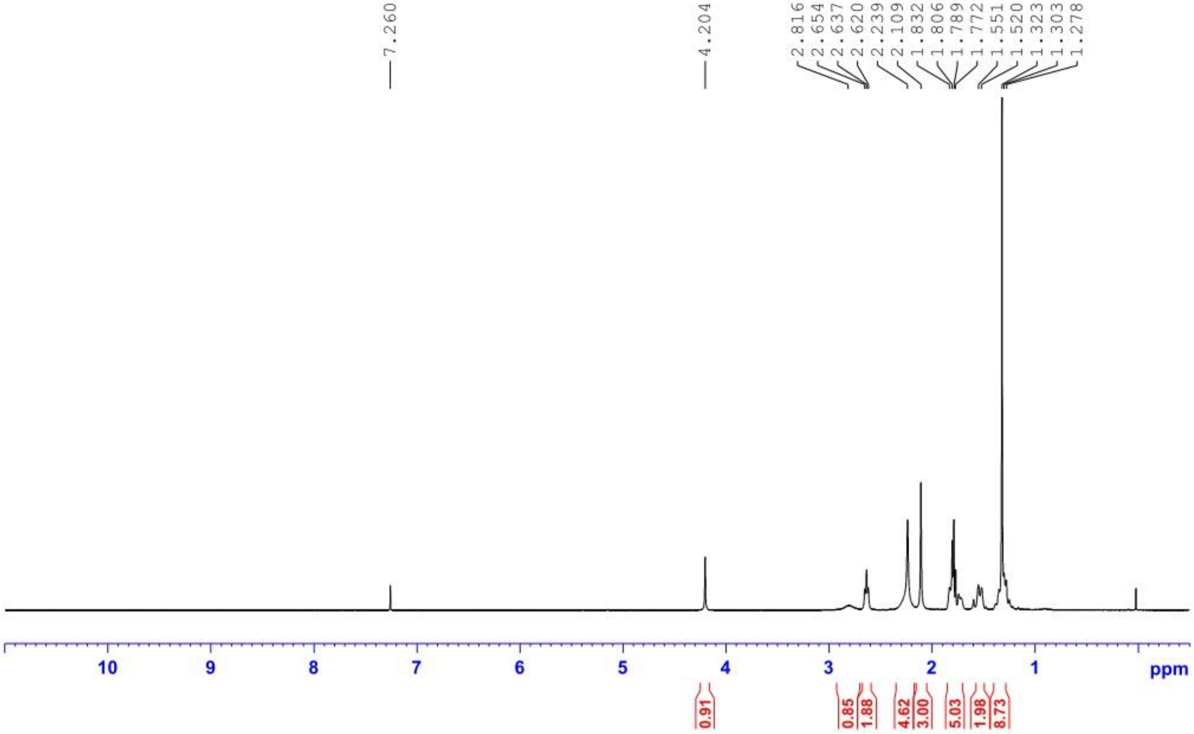

146.15
145.59
144.85
128.28
126.49
124.80
122.21
121.09
118.43
117.54
77.32
77.00
76.89
76.69
32.79
30.06
21.05
12.23
11.95
11.20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

8-cyclohexyl-2,2,5,7-tetramethyl-3,4-dihydro-2H-1-benzopyran-6-ol



56%; White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.28–1.32 (m, 9H), 1.52–1.55 (m, 2H), 1.77–1.83 (m, 5H), 2.11(s, 3H), 2.24 (brs, 5H), 2.64 (t, 2H, *J* = 6.8 Hz), 2.82 (brs, 1H), 4.20 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 11.4, 12.3, 21.3, 26.4, 26.5, 27.7, 29.8, 32.9, 40.5, 72.2, 117.6, 119.1, 120.4, 131.4, 144.7, 146.7; m.p. 85–88 °C (EtOAc); ESI-HRMS: *m/z* calcd for $C_{19}H_{29}O_2$ $[M+H]^+$: 289.2168; found: 289.2163.


OH
O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2.109
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1.806
1.789
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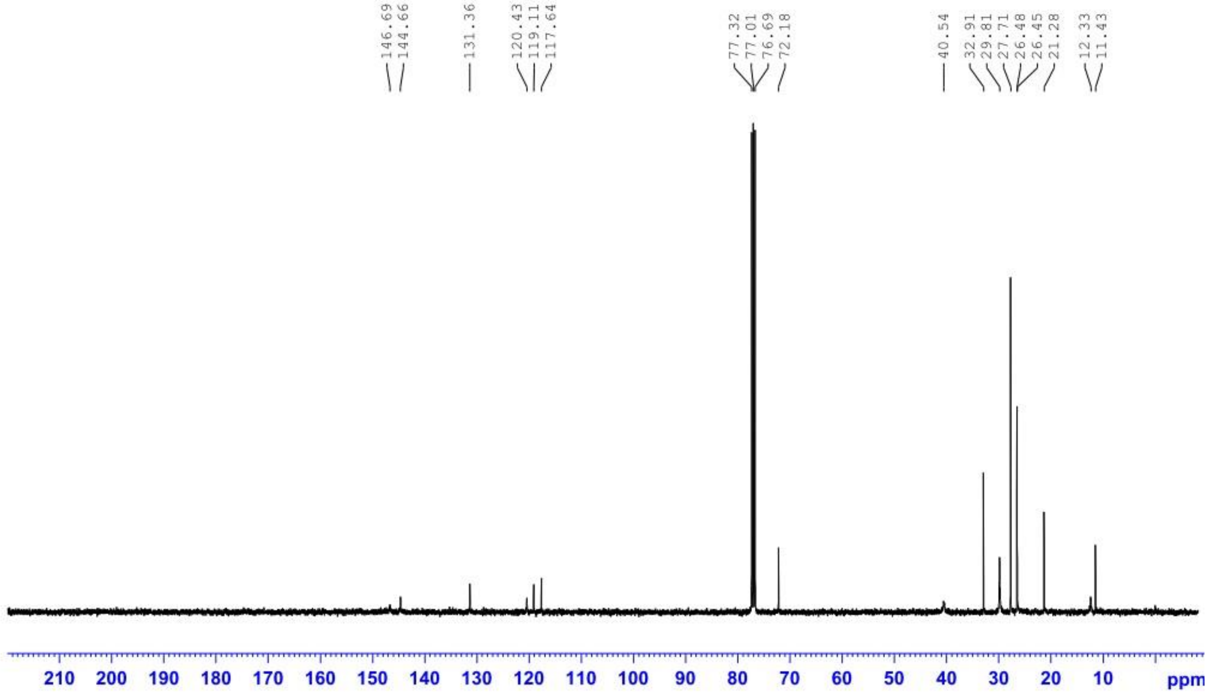
1.551
1.520
1.323
1.303
1.278
10
9
8
7
6
5
4
3
2
1
ppm
0.91
0.85
1.88
4.62
3.00
5.03
1.98
8.73


146.69
144.66
131.36
120.43
119.11
117.64
77.32
77.01
76.69
72.18
40.54
32.91
29.81
27.71
26.48
26.45
21.28
12.33
11.43
210
200
190
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170
160
150
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130
120
110
100
90
80
70
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40
30
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10
ppm

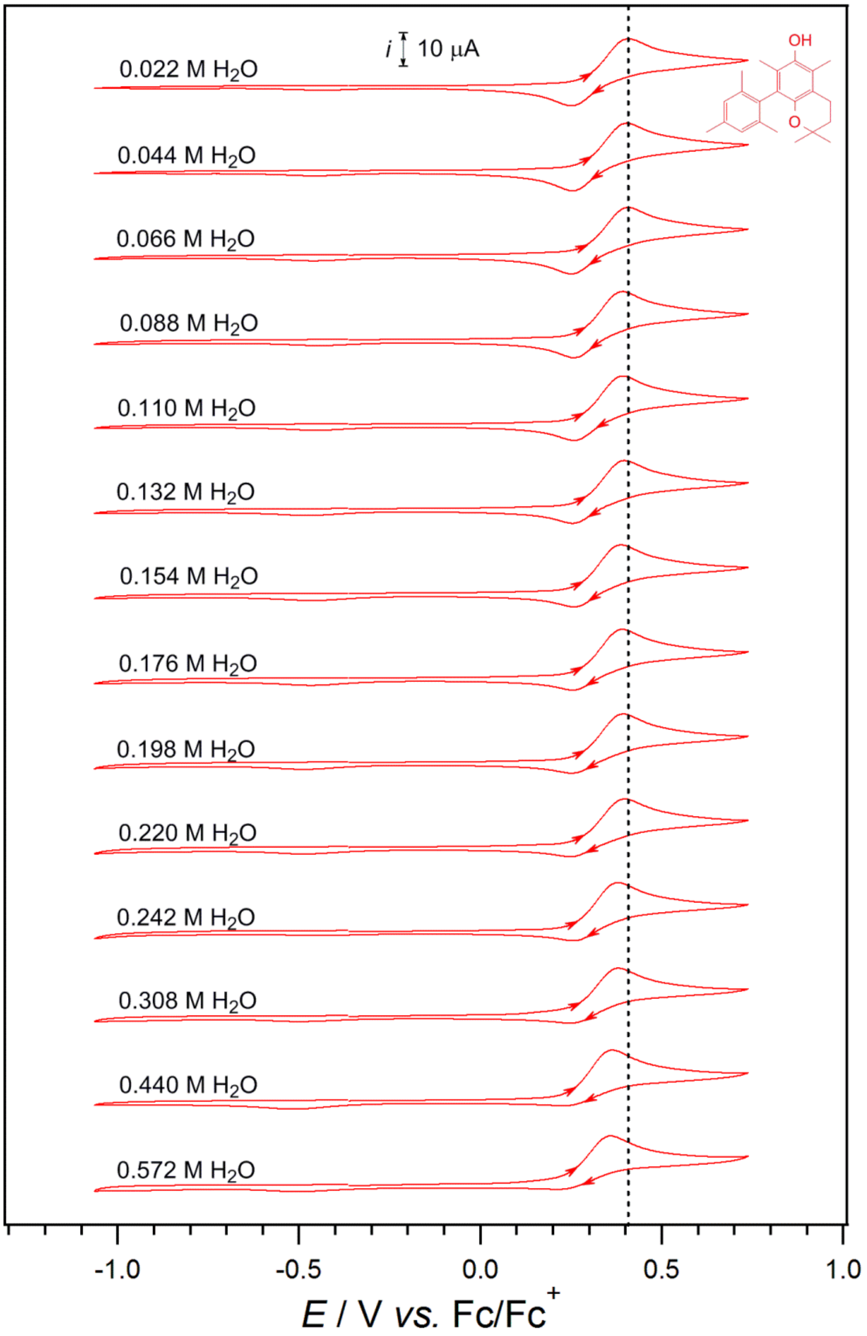


Figure S1. CVs of 2 mM of R_3 2,4,6-trimethylphenyl substituted compound in CH_3CN containing 0.2 M Bu_4NPF_6 at a 1 mm diameter circular planar Pt electrode at 22 ± 2 ^{o}C at a scan rate of 0.1 V s^{-1} at the specified concentration of water.

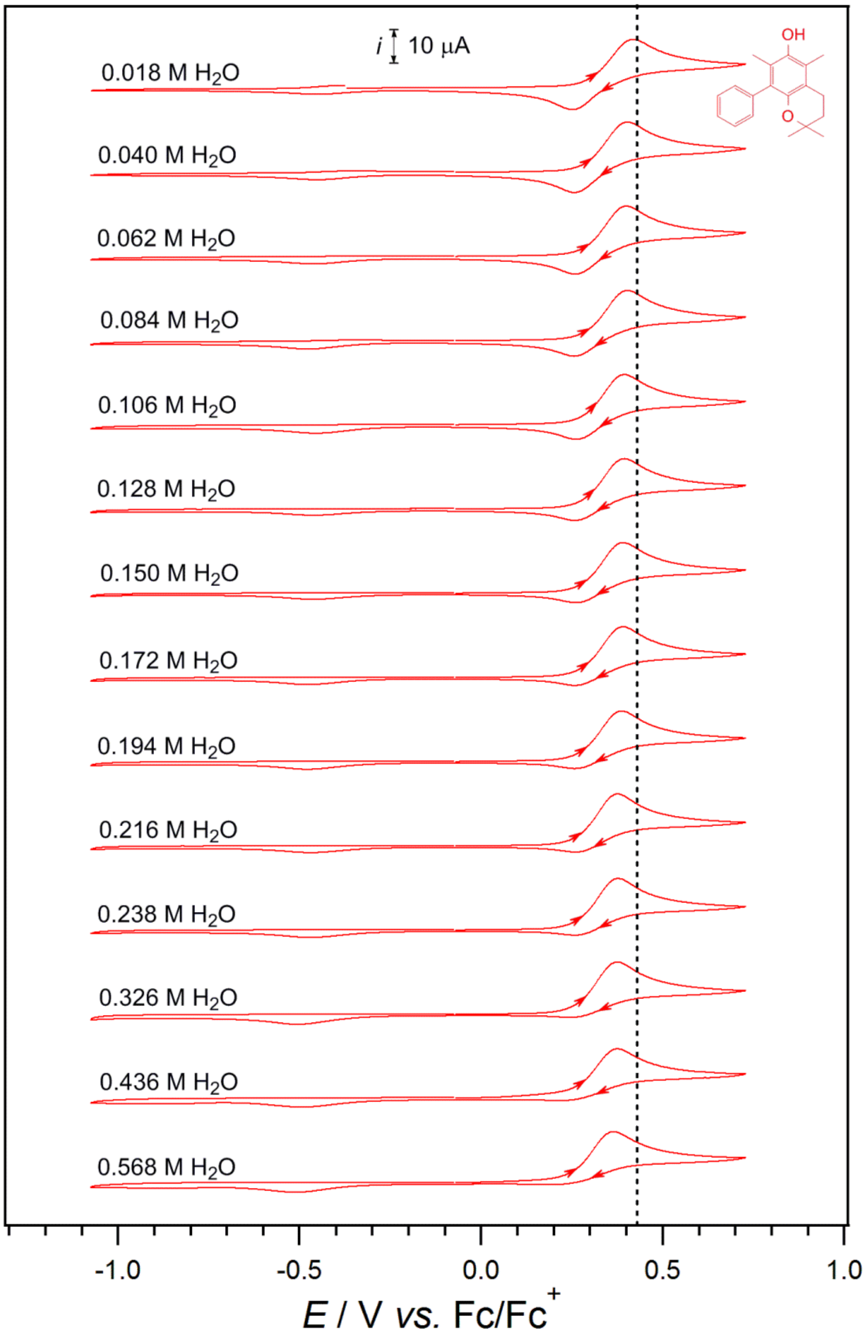


Figure S2. CVs of 2 mM of R_3 phenyl substituted compound in CH_3CN containing 0.2 M Bu_4NPF_6 at a 1 mm diameter circular planar Pt electrode at 22 ± 2 ^{o}C at a scan rate of 0.1 V s^{-1} at the specified concentration of water.

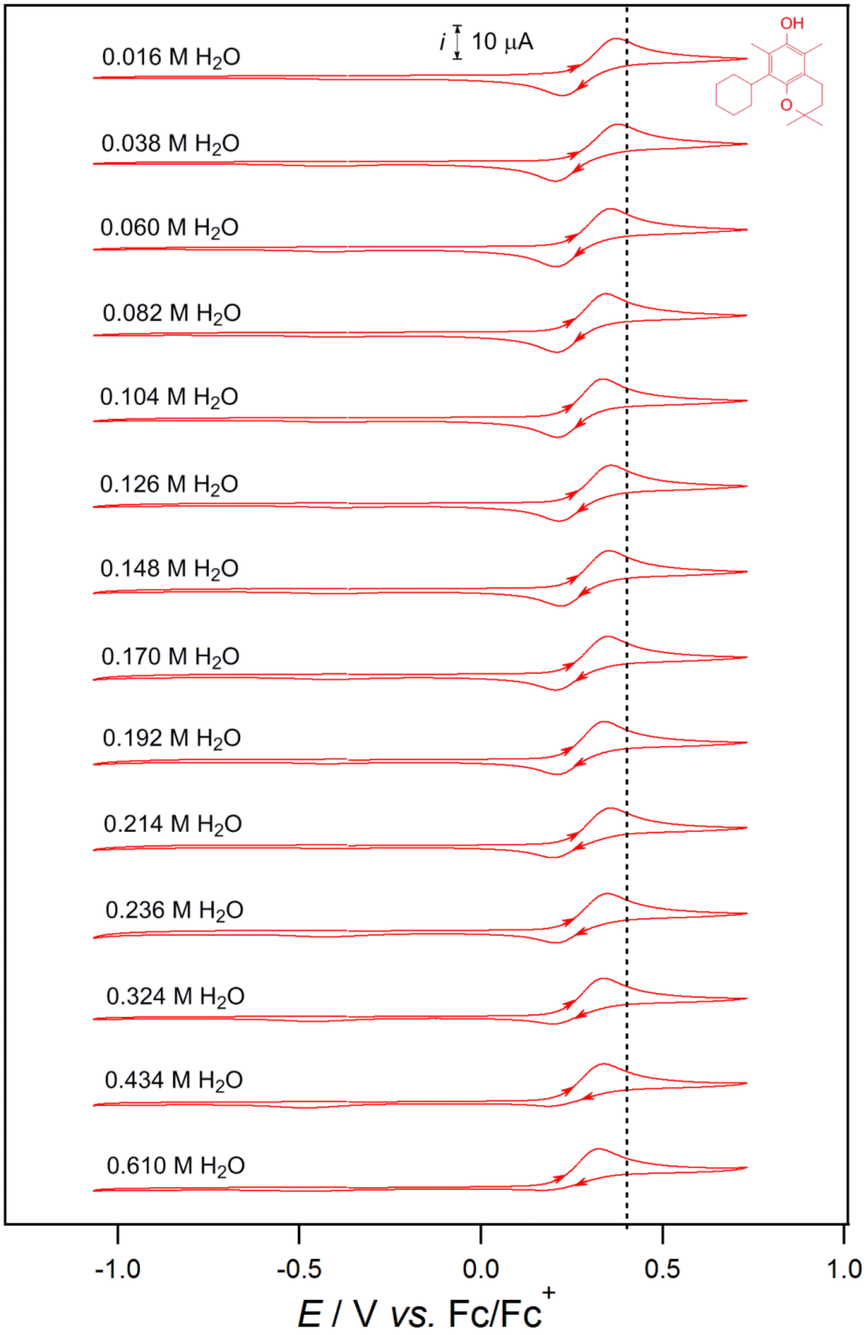


Figure S3. CVs of 2 mM of R_3 cyclohexyl substituted compound in CH_3CN containing 0.2 M Bu_4NPF_6 at a 1 mm diameter circular planar Pt electrode at 22 ± 2 °C at a scan rate of 0.1 V s^{-1} at the specified concentration of water.

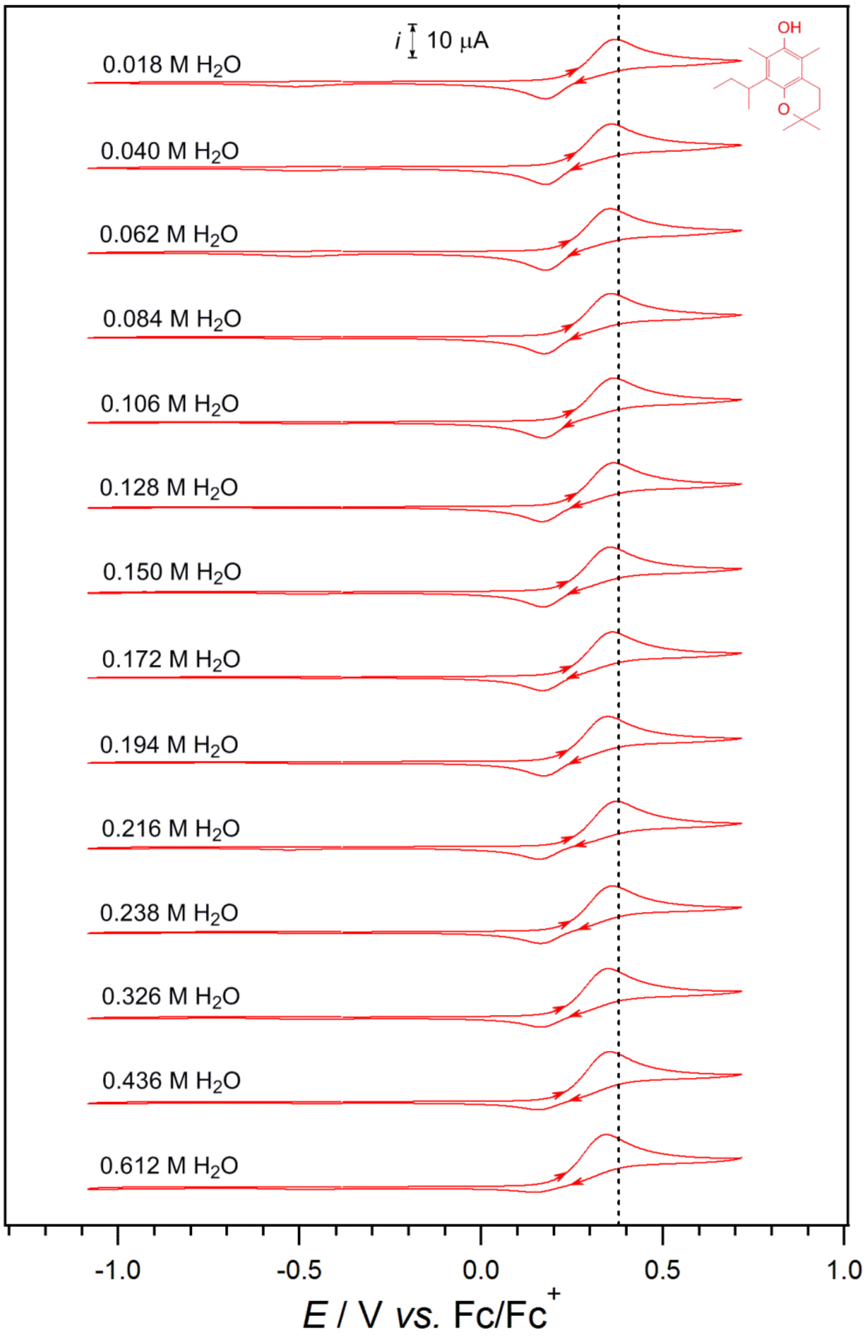


Figure S4. CVs of 2 mM of R_3 *sec*-butyl substituted compound in CH_3CN containing 0.2 M Bu_4NPF_6 at a 1 mm diameter circular planar Pt electrode at 22 ± 2 °C at a scan rate of 0.1 V s^{-1} at the specified concentration of water.

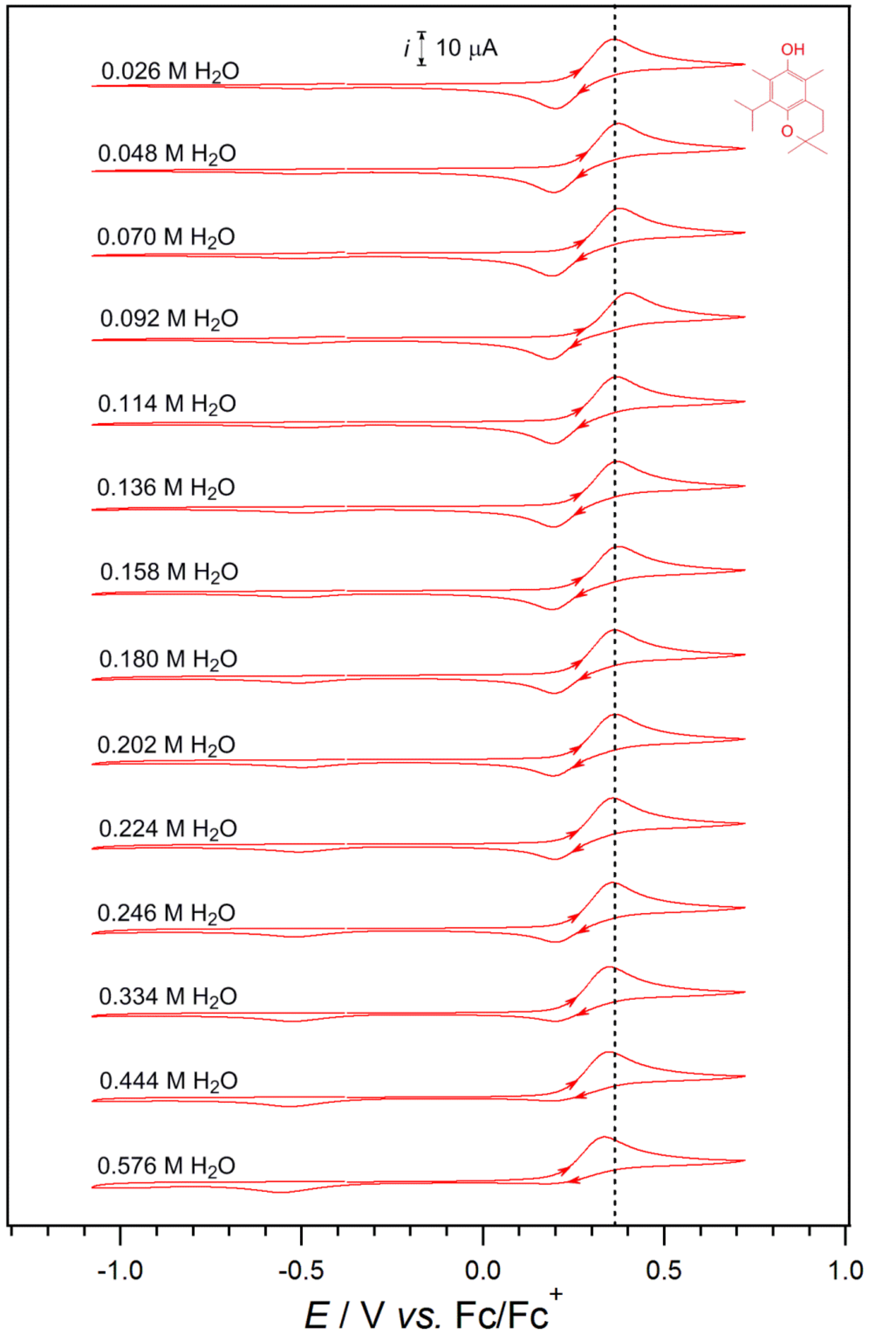


Figure S5. CVs of 2 mM of R_3 isopropyl substituted compound in CH_3CN containing 0.2 M Bu_4NPF_6 at a 1 mm diameter circular planar Pt electrode at 22 ± 2 ^{o}C at a scan rate of 0.1 V s^{-1} at the specified concentration of water.

3. Computational Studies

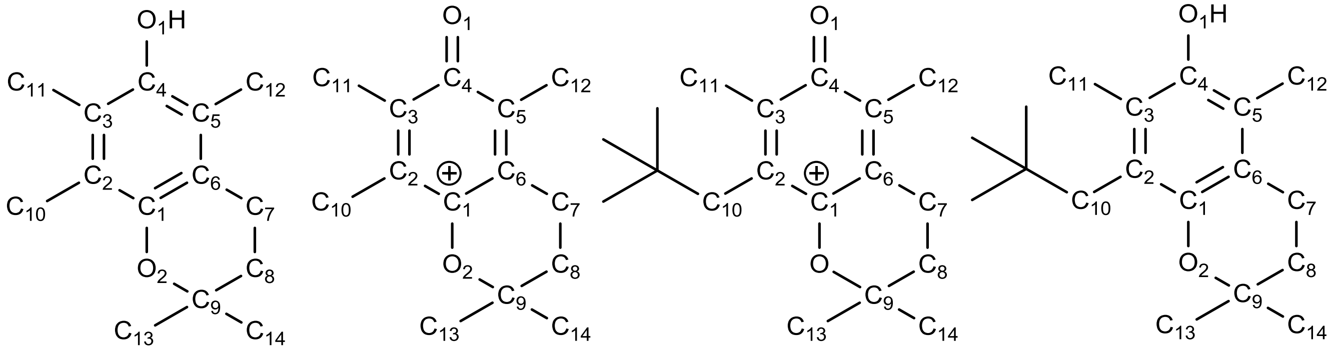
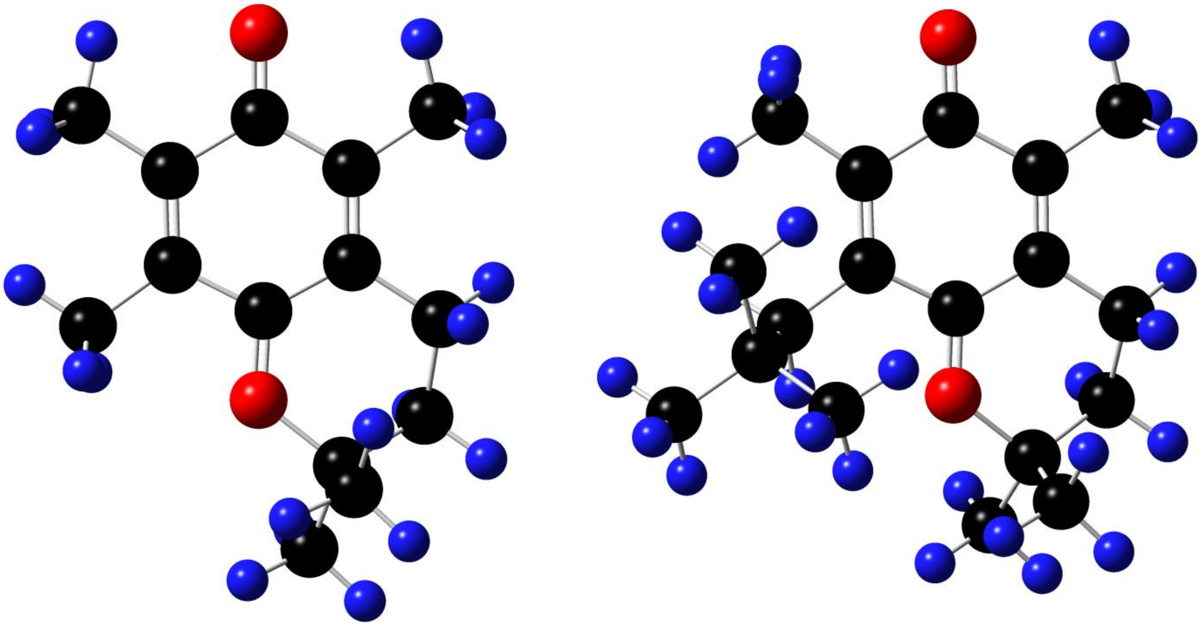


Figure S6. Numbering system for atoms in density functional theory calculations.



$(CH_3)\alpha$-TO$^+$

$(CH_3)\alpha$-TO$^+$(Np)

Figure S7. Density functional theory B3LYP/6-311+G(2df,p) optimized structures of the diamagnetic cations

Table S1. Calculated (B3LYP/6-311+G(2df,p)) bond lengths and energies (gaseous and solution phase) for the α-tocopherol model compound [(CH_3)α-TOH)] and its neopentyl derivative [(CH_3)-αTOH(Np)] and their associated diamagnetic cationic forms, (CH_3)α-TO+ and (CH_3)-αTO^+(Np).

Bond	Bond Length / Å							
	(CH_3)α-TOH		(CH_3)-αTOH(Np)		(CH_3)α-TO^+		(CH_3)-αTO^+(Np)	
	Gas	CH_3CN	Gas	CH_3CN	Gas	CH_3CN	Gas	CH_3CN
C_1–O_2	1.37726	1.37746	1.37630	1.37558	1.28499	1.28052	1.28403	1.27935
C_4–O_1	1.37950	1.38135	1.37993	1.38234	1.21056	1.21491	1.21134	1.21538
C_9–O_2	1.44333	1.45069	1.44571	1.45147	1.51975	1.51976	1.52089	1.52460
C_1–C_2	1.40232	1.40282	1.40930	1.41091	1.45676	1.45890	1.46491	1.46753
C_2–C_3	1.39760	1.39948	1.40324	1.40422	1.35464	1.35148	1.35913	1.35583
C_3–C_4	1.39692	1.39730	1.40221	1.40312	1.50042	1.49782	1.49939	1.49805
C_4–C_5	1.39474	1.39624	1.38990	1.39086	1.50521	1.50201	1.50044	1.49670
C_5–C_6	1.40389	1.40410	1.40134	1.40253	1.35427	1.35206	1.35237	1.35051
C_1–C_6	1.39720	1.39889	1.39610	1.39681	1.44826	1.44769	1.45303	1.45178
C_6–C_7	1.51383	1.51392	1.51107	1.51130	1.50726	1.50394	1.50667	1.50287
C_7–C_8	1.52690	1.52659	1.52543	1.52532	1.52690	1.52583	1.52580	1.52526
C_8–C_9	1.52985	1.52859	1.52859	1.52766	1.52085	1.51982	1.51950	1.51894
C_2–C_{10}	1.50699	1.50782	1.51689	1.51738	1.50134	1.49916	1.51159	1.51024
C_3–C_{11}	1.50731	1.50829	1.51100	1.51121	1.49382	1.49495	1.49044	1.49161
C_5–C_{12}	1.51047	1.51051	1.50725	1.50803	1.48971	1.49004	1.49015	1.49074
C_9–C_{13}	1.53243	1.53134	1.53301	1.53203	1.52293	1.52237	1.52287	1.52153
C_9–C_{14}	1.52422	1.52365	1.52484	1.52431	1.51771	1.51747	1.51845	1.51795
Energy / hartrees	-696.226614	-696.233328	-853.523478	-853.529546	-695.358120	-695.424351	-852.656778	-852.721333
ZPE / hartrees	0.310284	0.309934	0.423576	0.422933	0.299181	0.298922	0.412232	0.412188
Total Energy / hartrees	-695.919774	-695.926834	-853.104604	-853.111307	-695.062260	-695.128747	-852.249122	-852.313720

Table S2. Calculated (B3LYP/6-31G(d)) Mulliken (default) charges (gaseous and solution phase) for the α-tocopherol model compound [(CH_3)α-TOH)] and its neopentyl derivative [(CH_3)-αTOH(Np)] and their associated diamagnetic cationic forms, (CH_3)α-TO+ and (CH_3)-αTO^+(Np).

Bond	Charge							
	(CH_3)α-TOH		(CH_3)-αTOH(Np)		(CH_3)α-TO^+		(CH_3)-αTO^+(Np)	
	Gas	CH_3CN	Gas	CH_3CN	Gas	CH_3CN	Gas	CH_3CN
H	0.411	0.411	0.412	0.412	-	-	-	-
O_1	-0.665	-0.666	-0.665	-0.667	-0.385	-0.388	-0.387	-0.390
O_2	-0.574	-0.576	-0.578	-0.579	-0.455	-0.452	-0.457	-0.455
C_1	0.270	0.272	0.275	0.276	0.376	0.376	0.372	0.372
C_2	0.049	0.049	0.041	0.041	0.060	0.059	0.082	0.083
C_3	0.098	0.099	0.102	0.102	0.086	0.086	0.049	0.048
C_4	0.205	0.205	0.206	0.206	0.390	0.389	0.394	0.392
C_5	0.095	0.095	0.084	0.084	0.062	0.063	0.059	0.061
C_6	0.081	0.080	0.075	0.074	0.093	0.094	0.094	0.094
C_7	-0.371	-0.372	-0.362	-0.362	-0.370	-0.371	-0.370	-0.369
C_8	-0.275	-0.275	-0.278	-0.278	-0.308	-0.308	-0.309	-0.310
C_9	0.310	0.309	0.313	0.312	0.248	0.246	0.251	0.248
C_{10}	-0.532	-0.531	-0.351	-0.352	-0.522	-0.521	-0.359	-0.360
C_{11}	-0.535	-0.536	-0.591	-0.590	-0.557	-0.557	-0.524	-0.522
C_{12}	-0.592	-0.591	-0.534	-0.534	-0.551	-0.550	-0.550	-0.551
C_{13}	-0.457	-0.457	-0.460	-0.459	-0.465	-0.463	-0.466	-0.465
C_{14}	-0.456	-0.456	-0.458	-0.459	-0.463	-0.461	-0.463	-0.460
Residual Atoms	2.937	2.941	2.766	2.768	3.748	3.723	3.585	3.583
Total	-0.001	0.001	-0.003	-0.005	0.987	0.965	1.001	0.999

Table S3. Calculated (B3LYP/6-31G(d)) charges from natural bond orbital (NBO) analysis (gaseous and solution phase) for the α-tocopherol model compound [(CH_3)α-TOH)] and its neopentyl derivative [(CH_3)-αTOH(Np)] and their associated diamagnetic cationic forms, (CH_3)α-TO+ and (CH_3)-αTO$^+$(Np).

Bond	Charge							
	(CH_3)α-TOH		(CH_3)-αTOH(Np)		(CH_3)α-TO$^+$		(CH_3)-αTO$^+$(Np)	
	Gas	CH_3CN	Gas	CH_3CN	Gas	CH_3CN	Gas	CH_3CN
H	0.411	0.490	0.491	0.491	-	-	-	-
O_1	-0.665	-0.707	-0.707	-0.708	-0.427	-0.427	-0.434	-0.434
O_2	-0.574	-0.563	-0.563	-0.564	-0.431	-0.430	-0.431	-0.430
C_1	0.270	0.304	0.311	0.311	0.559	0.561	0.566	0.568
C_2	0.049	-0.049	-0.057	-0.057	-0.065	-0.064	-0.062	-0.061
C_3	0.098	-0.062	-0.086	-0.086	0.033	0.031	0.035	0.032
C_4	0.205	0.321	0.319	0.319	0.516	0.514	0.514	0.512
C_5	0.095	-0.090	-0.058	-0.058	0.064	0.063	0.061	0.060
C_6	0.081	-0.088	-0.086	-0.086	-0.103	-0.103	-0.103	-0.102
C_7	-0.371	-0.472	-0.470	-0.470	-0.487	-0.486	-0.485	-0.484
C_8	-0.275	-0.474	-0.475	-0.475	-0.493	-0.493	-0.492	-0.493
C_9	0.310	0.287	0.289	0.288	0.283	0.283	0.284	0.285
C_{10}	-0.532	-0.692	-0.468	-0.468	-0.706	-0.706	-0.484	-0.484
C_{11}	-0.535	-0.693	-0.707	-0.707	-0.726	-0.725	-0.713	-0.712
C_{12}	-0.592	-0.709	-0.693	-0.693	-0.727	-0.726	-0.727	-0.726
C_{13}	-0.457	-0.696	-0.696	-0.696	-0.704	-0.702	-0.702	-0.700
C_{14}	-0.456	-0.679	-0.679	-0.679	-0.697	-0.696	-0.696	-0.695
Residual Atoms	2.937	4.571	4.328	4.342	5.110	5.104	4.873	4.859
Total	-0.001	-0.001	-0.007	0.004	0.999	0.998	1.004	0.995

4. Additional References

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