Supporting Information for:

Cobalt-Catalyzed Enantioselective Desymmetrizing Reductive Cyclization of Alkynyl Cyclodiketones

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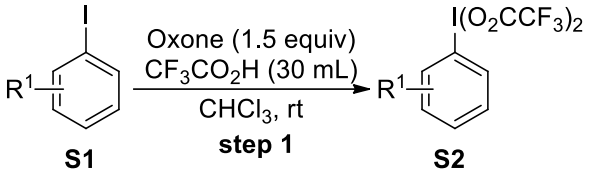
1. General information

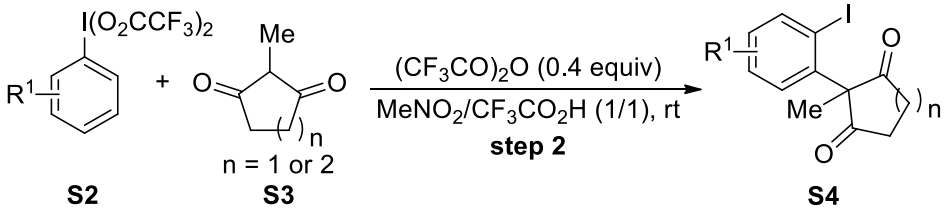
Reactions and manipulations involving organometallic or moisture sensitive compounds were carried out under dry nitrogen and glassware dried by heating gun for 5 min prior to use. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AVANCE III 400 MHz, 500 MHz, or 600 MHz using $CDCl_3$ as solvent with TMS as internal standard. Anhydrous 1,4-dioxane, THF, MTBE and toluene were freshly distilled over Na and benzophenone. Anhydrous DCM and DMF were freshly distilled over CaH_2. MeOH was freshly distilled with magnesium and iodine. Melting points were measured on a Büchi Melting Point B-545 apparatus and uncorrected. Commercial reagents were used as received without further purification unless otherwise noticed. HRMS were recorded on Thermo Scientific LTQ Orbitrap XL or Agilent 6210 TOF LC/MS mass spectrometer, and in the EI mode on Waters GCT Premier TOF MS. Optical rotations were determined using a Rudolph Autopol IV polarimeter. HPLC analyses were performed using Agilent 1260 chromatography. Chiralpak OJ-H column were purchased from Daicel Chemical Industries, LTD. Amylose-2, Cellulose-1 and Cellulose-2 columns were purchased from Phenomenex. Column chromatography was carried out using silica gel (200-300 mesh). Ligands **L1**-**L8** were purchased or prepared according to the literature procedures and used directly as received.[1]

2. Substrate synthesis

Substrates **1** were prepared according to the known procedures.

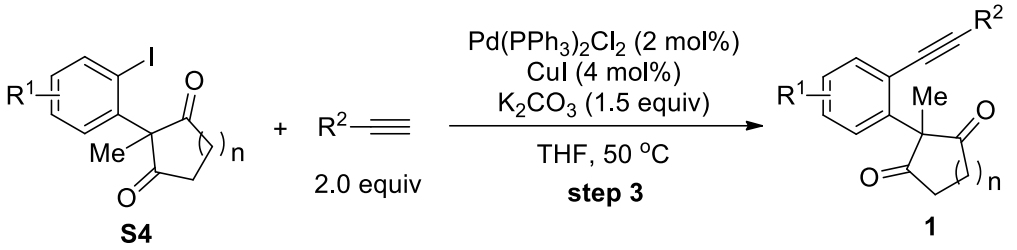


Step 1:[2]To a 100 mL flask was charged with Oxone (15 mmol, 1.5 equiv), CF_3CO_2H (30 mL), and $CHCl_3$ (30 mL). The corresponding aryl iodide (**S1**, 10 mmol) was then injected dropwise via syringe at room temperature. After stirring for 2 h at room temperature, the solvent was removed under vacuo. The residue was then dissolved in $CHCl_3$ (10 mL) and the inorganic salts were filtered. After concentration, the crude product **S2** was obtained and used in the next step without further purification.



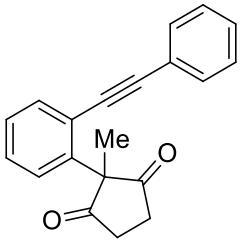
Step 2:[3] To a 100 mL flask was charged with $ArI(O_2CCF_3)_2$ (**S2**, 6.25 mmol), $MeNO_2$ (10 mL), CF_3CO_2H (10 mL), and $(CF_3CO)_2O$ (1.9 mmol, 260 μL). The mixture was stirred at room temperature for 15 min. Cyclic1,3-diketone (**S3**, 5.0 mmol) was then added and the resulting mixture was stirred at room temperature. When the reaction

was completed (monitored by TLC), the mixture was concentrated under reduced pressure. The residue was purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v), to afford compounds **S4**.

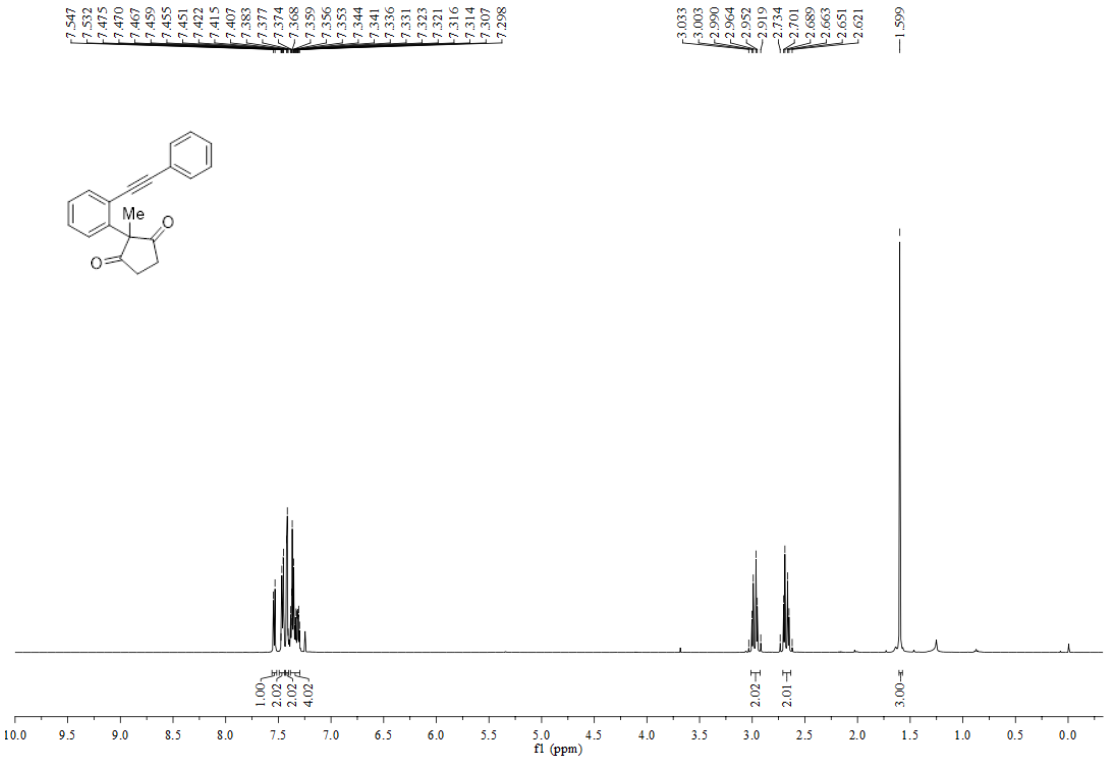


Step 3:[4] To a 100 mL flask was charged with $Pd(PPh_3)_2Cl_2$ (2 mol%, 0.1 mmol) CuI (4 mol%, 0.2 mmol), **S4** (1.0 equiv, 5 mmol), and K_2CO_3 (1.5 equiv, 7.5 mmol). A solution of alkynes (1.5 equiv, 7.5 mmol) in THF (10 mL) was then introduced via syringe under N_2 atmosphere. The resulting mixture was stirred at 60 °C. When **S4** was completely consumed (monitored by TLC), the mixture was concentrated under reduced pressure. The residue was then purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v), to give substrates **1**.

2-Methyl-2-(2-(phenylethynyl)phenyl)cyclopentane-1,3-dione (1a)



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); white solid, Mp = 151-152 °C; 73% yield (for the last step); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, J = 7.5 Hz, 1H), 7.49-7.44 (m, 2H), 7.41 (t, J = 3.5 Hz, 2H), 7.38-7.30 (m, 4H), 3.03-2.92 (m, 2H), 2.73-2.62 (m, 2H), 1.60 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 213.2, 140.7, 133.0, 131.4, 129.3, 128.9, 128.6, 128.1, 127.9, 121.9, 95.1, 89.7, 62.5, 35.4, 19.7. HRMS *m/z* (ESI+): Calculated for $C_{20}H_{17}O_2^+$ ($[M+H]^+$) 289.1223, found 289.1225.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7.356
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7.341
7.336
7.331
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7.321
7.316
7.314
7.307
7.298
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3.003
2.990
2.964
2.952
2.919
2.734
2.701
2.689
2.663
2.651
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O
O
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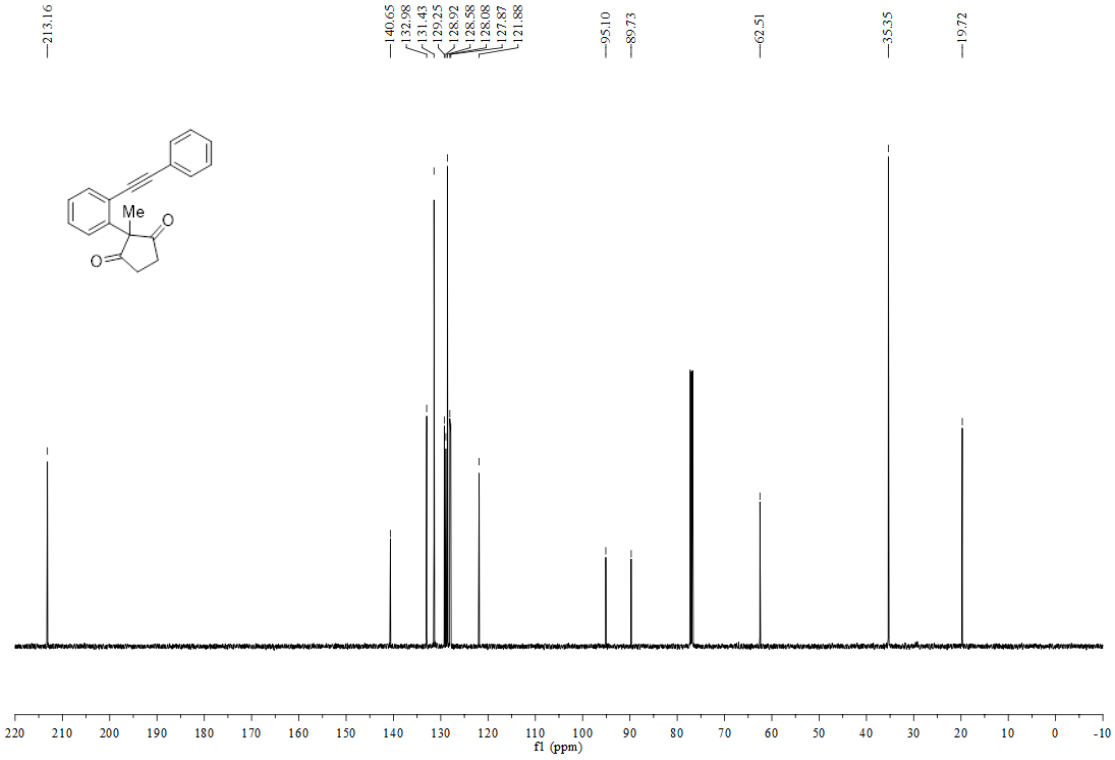
4.02
2.02
2.01
3.00
f1 (ppm)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121.88
95.10
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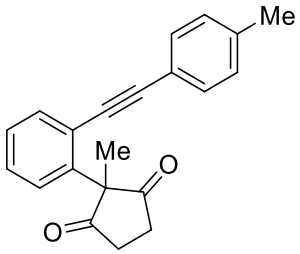
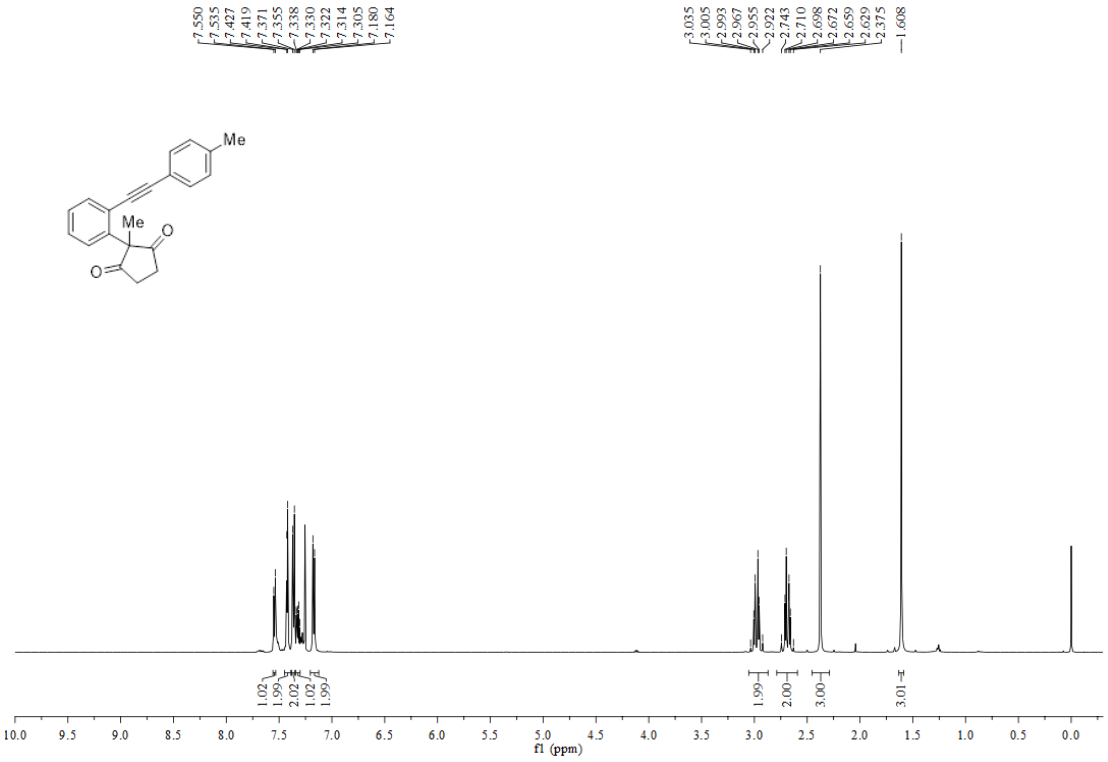
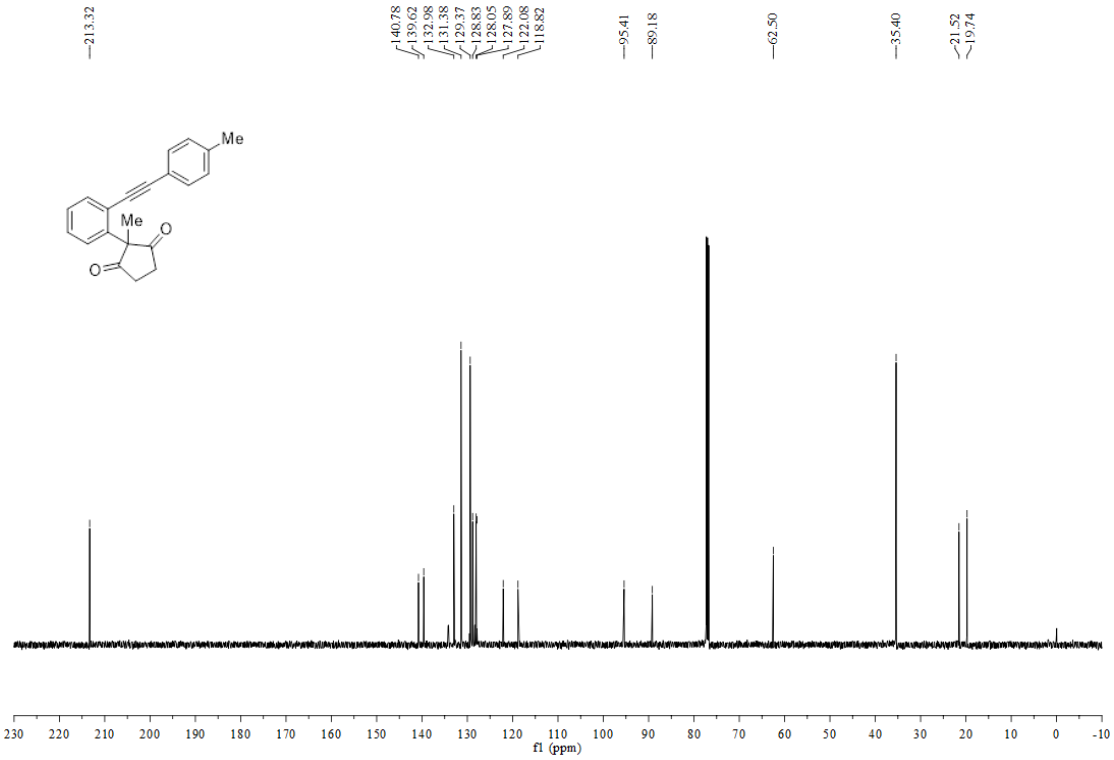
62.51
35.35
19.72
Me
O
O
f1 (ppm)

2-Methyl-2-(2-(p-tolylethynyl)phenyl)cyclopentane-1,3-dione (1b)

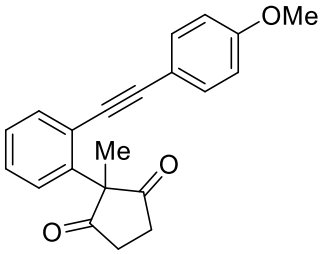


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow solid, Mp = 183-184 °C; 73% yield (for the last step); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, J = 7.5 Hz, 1H), 7.42 (d, J = 4.0 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.34-7.30 (m, 1H), 7.17 (d, J = 8.0 Hz, 2H), 3.04-2.92 (m, 2H), 2.74-2.63 (m, 2H), 2.38 (s, 3H), 1.61 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 213.3, 140.8, 139.6, 133.0, 131.4, 129.4, 128.8, 128.1, 127.9, 122.1, 118.8, 95.4, 89.2, 62.5, 35.4, 21.5, 19.7. HRMS m/z (ESI+): Calculated for $C_{21}H_{19}O_2^+$ ([M+H]$^+$) 303.1380, found 303.1382.

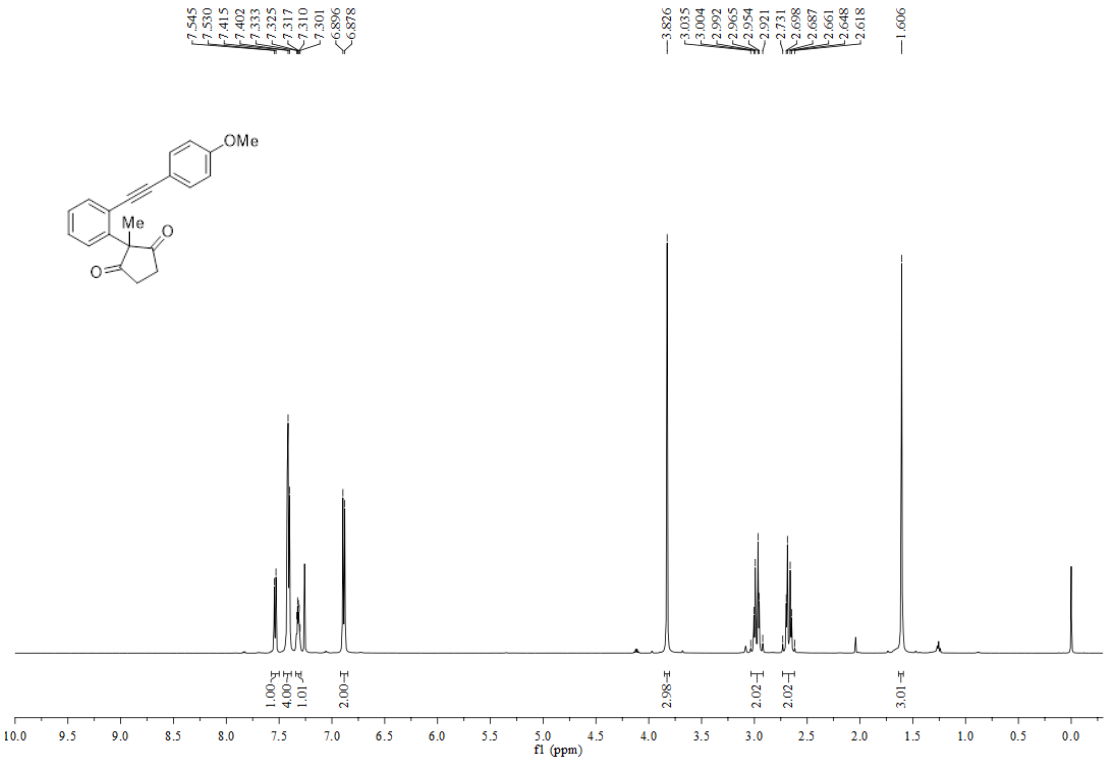




2-(2-((4-Methoxyphenyl)ethynyl)phenyl)-2-methylcyclopentane-1,3-dione (1c)



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); white solid, Mp = 179-180 °C; 81% yield (for the last step); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, J = 7.5 Hz, 1H), 7.41 (d, J = 6.5 Hz, 4H), 7.33-7.30 (m, 1H), 6.89 (d, J = 9.0 Hz, 2H), 3.83 (s, 3H), 3.04-2.92 (m, 2H), 2.73-2.62 (m, 2H), 1.61 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 213.3, 160.4, 140.9, 133.01, 132.99, 128.8, 128.0, 127.9, 122.2, 114.2, 113.9, 95.3, 88.6, 62.5, 55.3, 35.4, 19.7. HRMS *m*/*z* (ESI+): Calculated for $C_{21}H_{18}O_3Na^+$ ($[M+Na]^+$) 341.1148, found 341.1150.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3.004
2.992
2.965
2.954
2.921
2.731
2.698
2.687
2.661
2.648
2.618
1.606
OMe
Me
O
O
1.00
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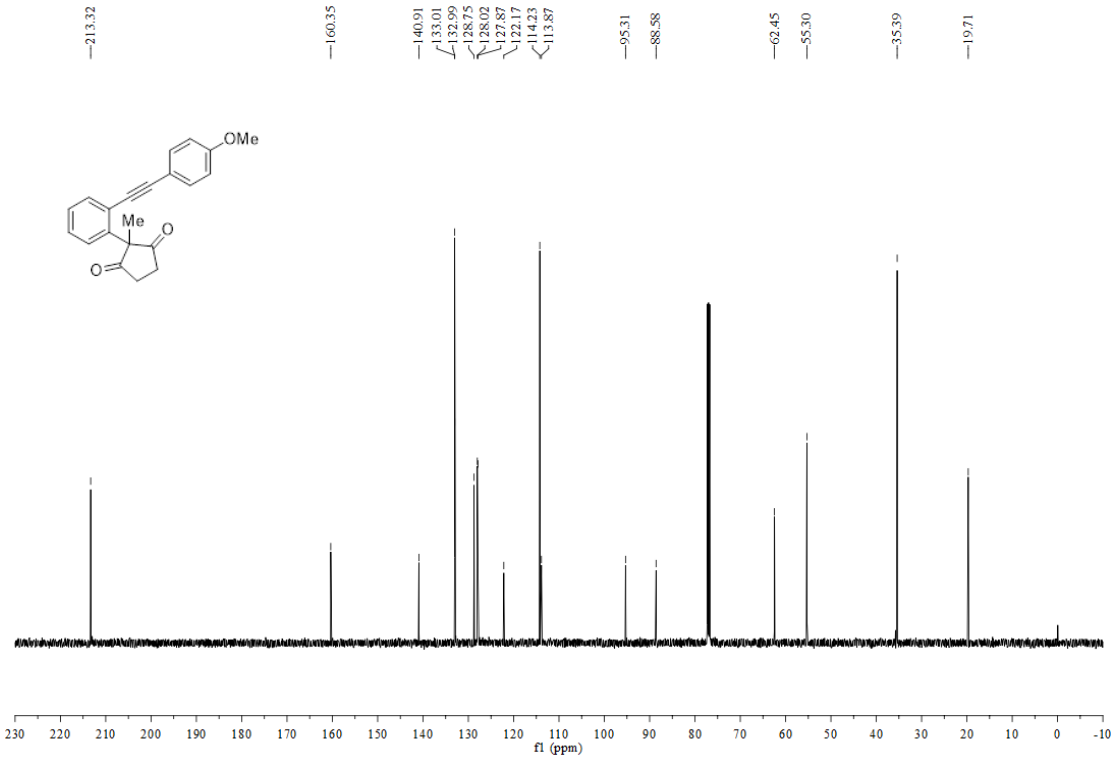
1.01
2.00
2.98
2.02
2.02
3.01
f1 (ppm)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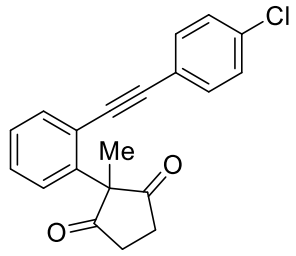
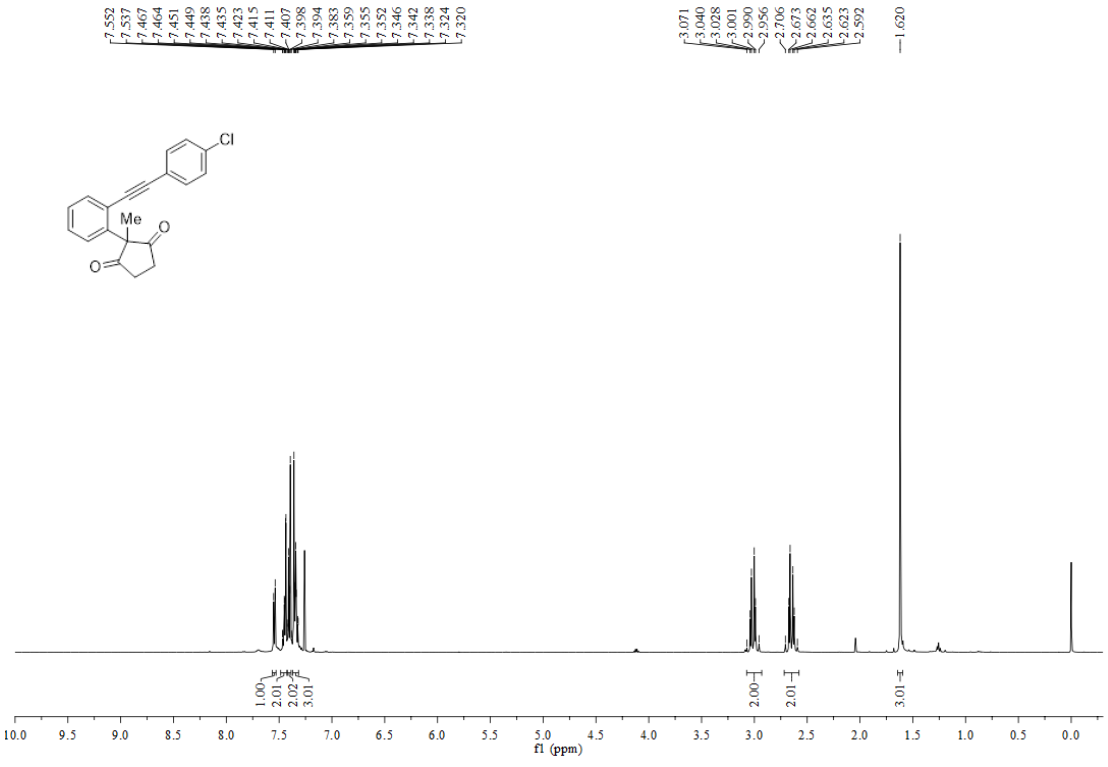
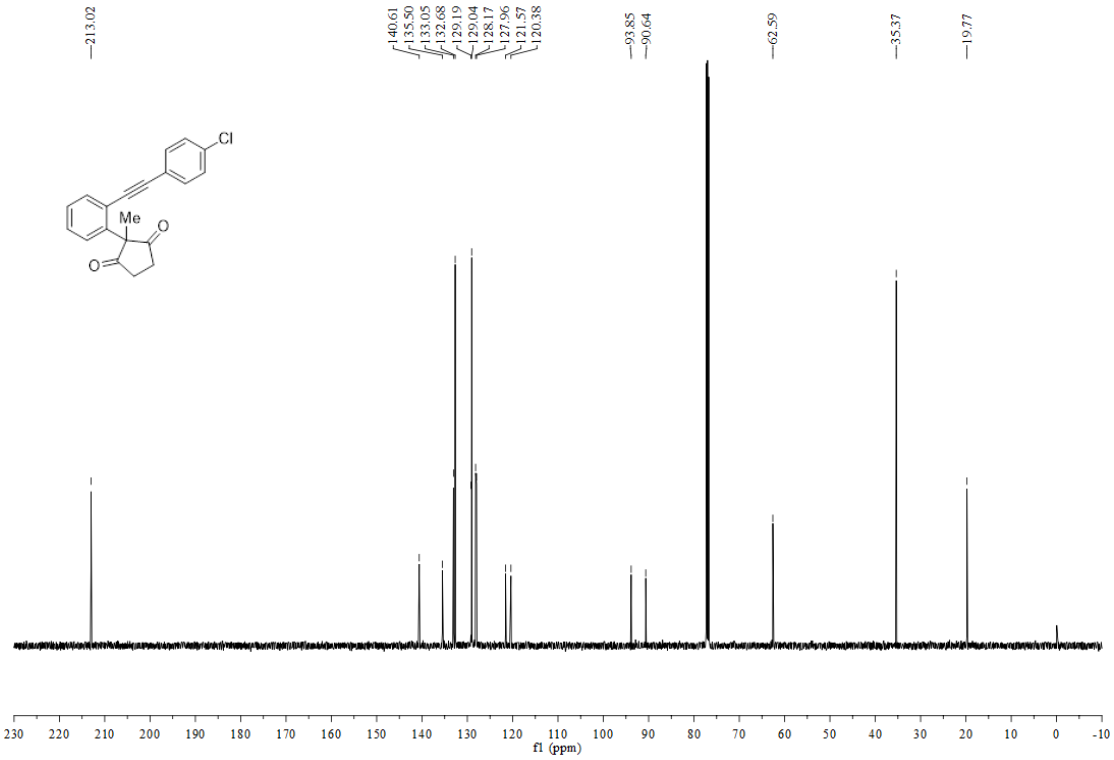
128.02
127.87
122.17
114.23
113.87
95.31
88.58
62.45
55.30
35.39
19.71
OMe
Me
O
O
f1 (ppm)

2-(2-((4-Chlorophenyl)ethynyl)phenyl)-2-methylcyclopentane-1,3-dione (1d)

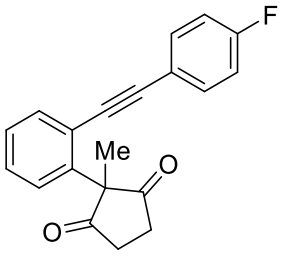


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); brown solid, Mp = 170-171 °C; 59% yield (for the last step); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, J = 7.5 Hz, 1H), 7.47-7.42 (m, 2H), 7.42-7.38 (m, 2H), 7.37-7.32 (m, 3H), 3.07-2.96 (m, 2H), 2.71-2.59 (m, 2H), 1.62 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 213.0, 140.6, 135.5, 133.1, 132.7, 129.2, 129.0, 128.2, 128.0, 121.6, 120.4, 93.9, 90.6, 62.6, 35.4, 19.8. HRMS m/z (ESI+): Calculated for $C_{20}H_{15}ClO_2Na^+$ ([M+Na]$^+$) 345.0653, found 345.0655.

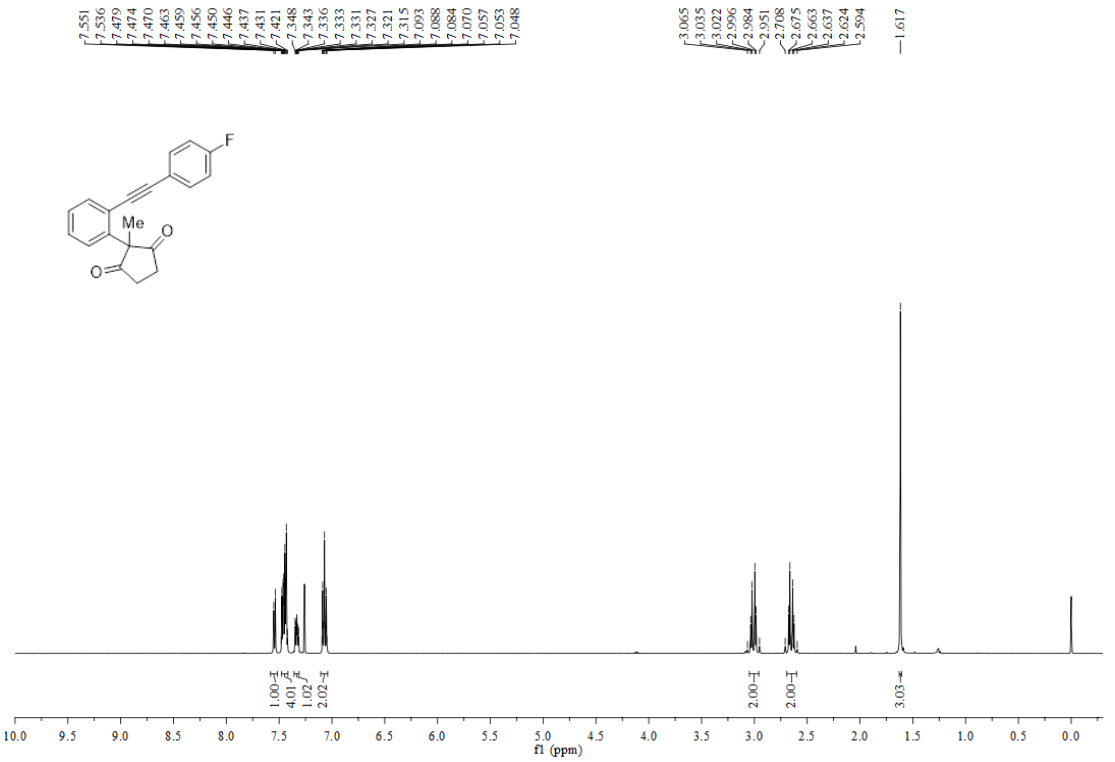




2-(2-((4-Fluorophenyl)ethynyl)phenyl)-2-methylcyclopentane-1,3-dione (1e)



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow solid, Mp = 170-171 °C; 68% yield (for the last step); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, J = 7.5 Hz, 1H), 7.48-7.42 (m, 4H), 7.35-7.32 (m, 1H), 7.09-7.05 (m, 2H), 3.07-2.95 (m, 2H), 2.71-2.59 (m, 2H), 1.62 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 213.1, 163.0 (d, J = 248.8 Hz), 140.7, 133.5 (d, J = 7.5 Hz), 133.1, 129.1, 128.1, 127.9, 121.7, 118.0 (d, J = 3.8 Hz), 116.0 (d, J = 22.5 Hz), 94.0, 89.5, 62.6, 35.4, 19.7. HRMS *m*/*z* (ESI+): Calculated for $C_{20}H_{15}FO_2Na^+$ ([M+Na]$^+$) 329.0948, found 329.0950.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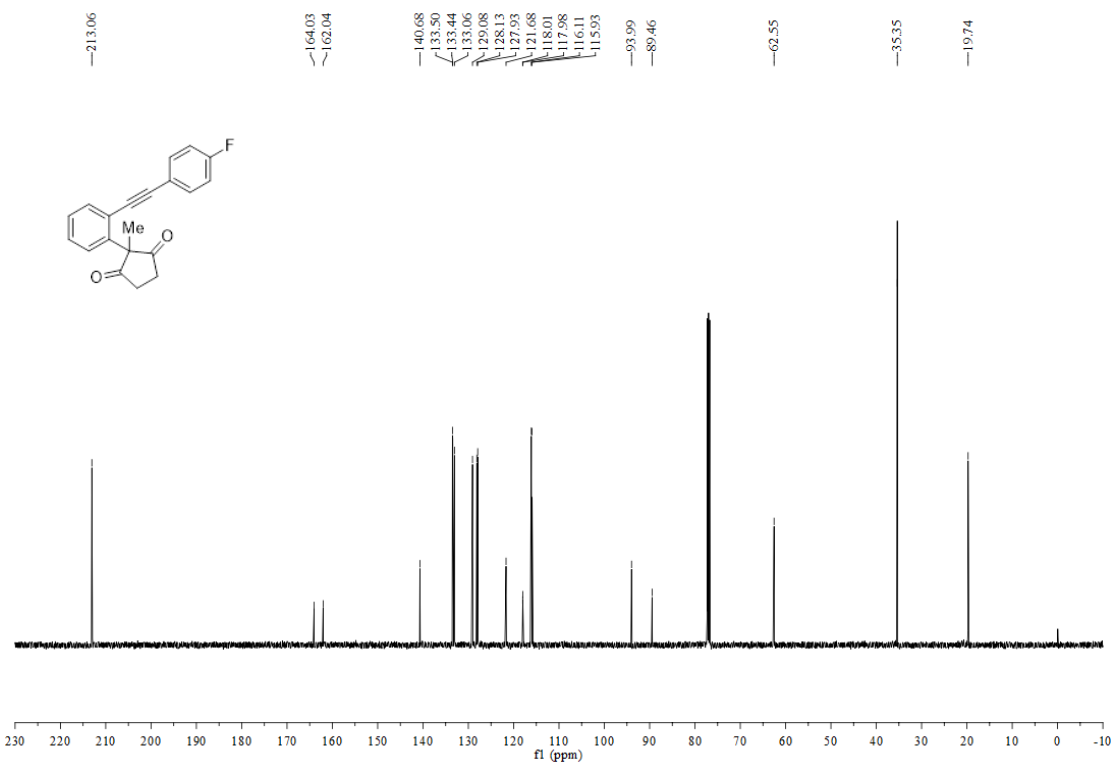
3.035
3.022
2.996
2.984
2.951
2.708
2.675
2.663
2.637
2.624
2.594
1.617
F
Me
O
O
1.00
4.01
1.02
2.02
2.00
2.00
3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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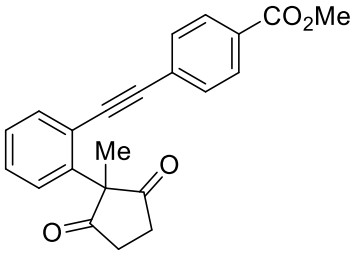
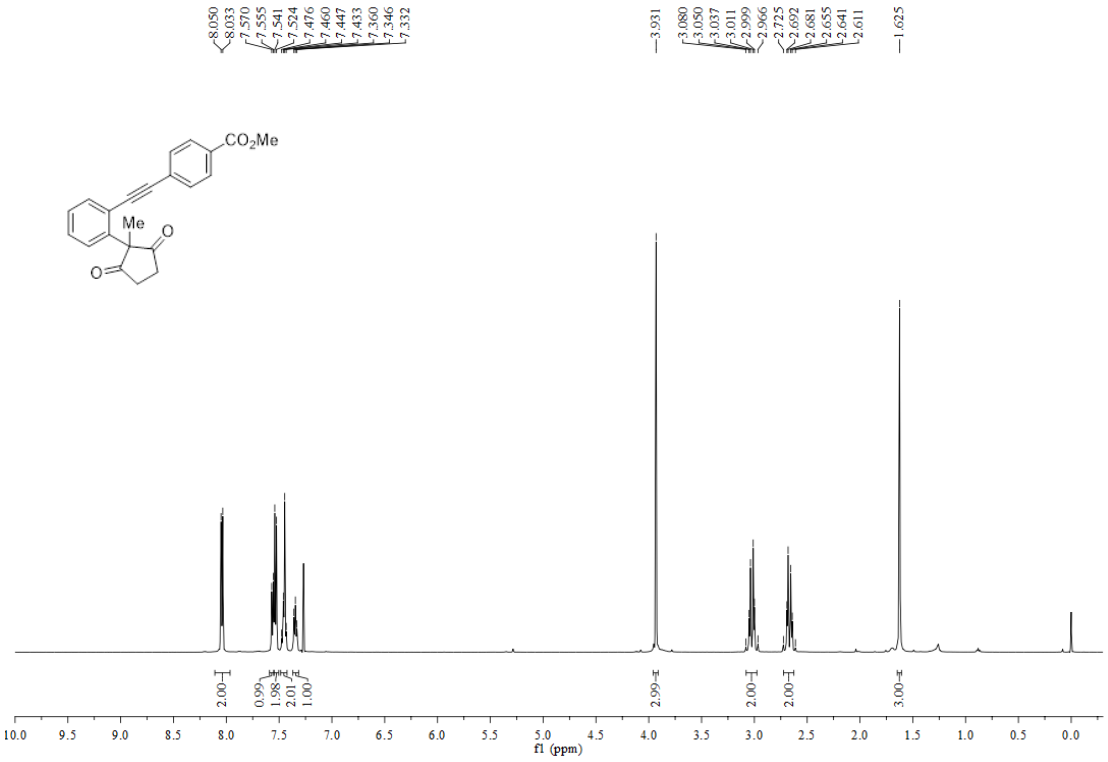
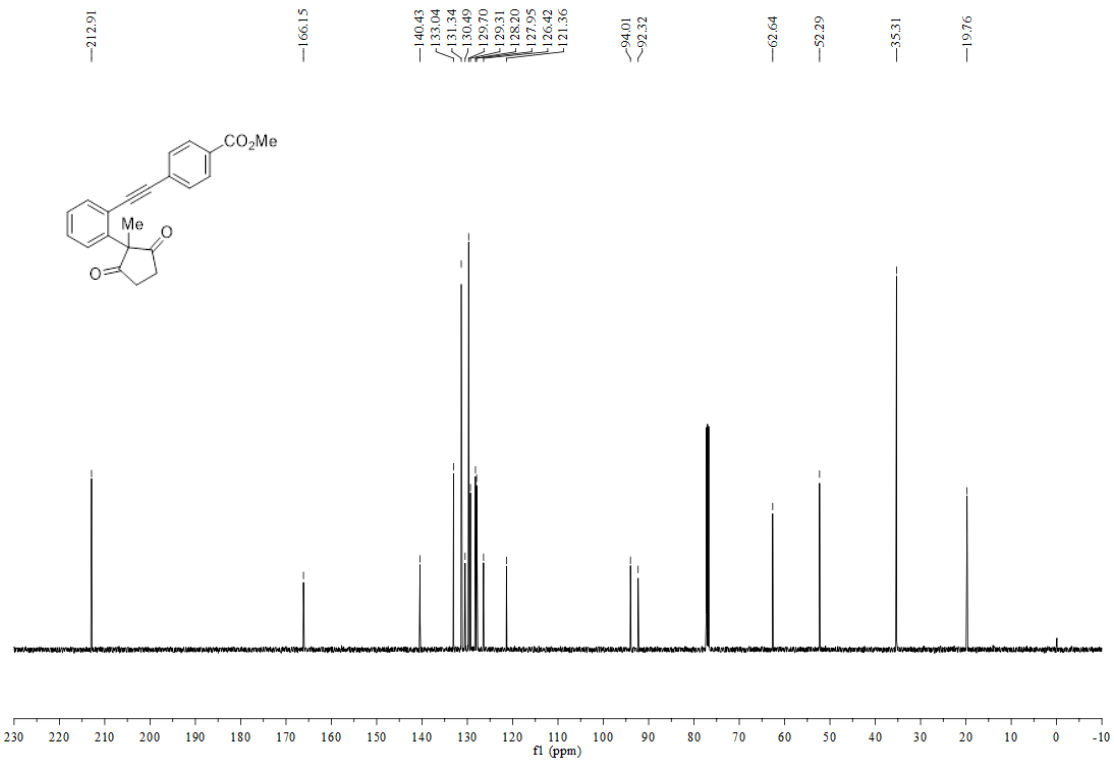
116.11
115.93
93.99
89.46
62.55
35.35
19.74
F
Me
O
O
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Methyl 4-((2-(1-methyl-2,5-dioxocyclopentyl)phenyl)ethynyl)benzoate (1f)

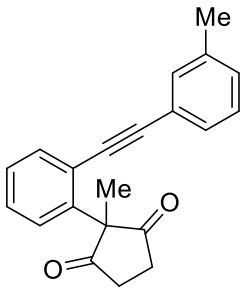


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow solid, Mp = 177-178 °C; 67% yield (for the last step); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, J = 8.5 Hz, 2H), 7.56 (d, J = 7.5 Hz, 1H), 7.53 (d, J = 8.5 Hz, 2H), 7.48-7.43 (m, 2H), 7.35 (t, J = 7.0 Hz, 1H), 3.93 (s, 3H), 3.08-2.97 (m, 2H), 2.73-2.61 (m, 2H), 1.63 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.9, 166.2, 140.4, 133.0, 131.3, 130.5, 129.7, 129.3, 128.2, 128.0, 126.4, 121.4, 94.0, 92.3, 62.6, 52.3, 35.3, 19.8. HRMS m/z (ESI+): Calculated for $C_{22}H_{19}O_4^+$ ([M+H]$^+$) 347.1278, found 347.1281.

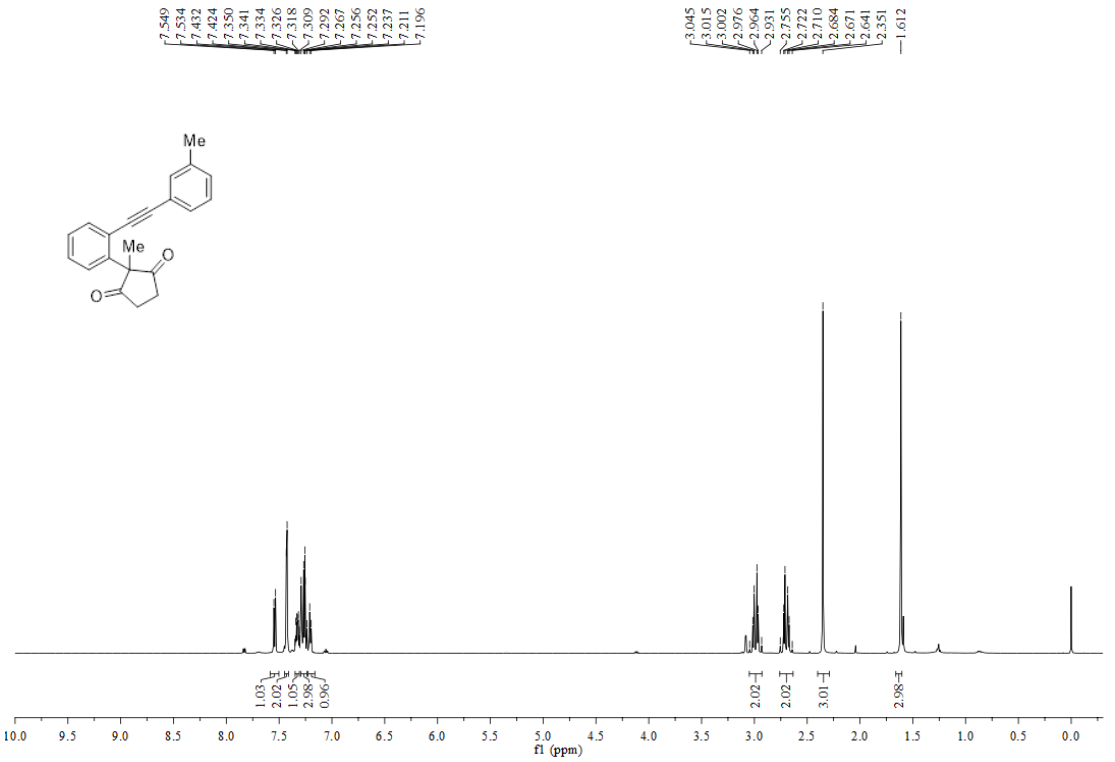




2-Methyl-2-(2-(m-tolylethynyl)phenyl)cyclopentane-1,3-dione (1g)



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow solid, Mp = 153-154 °C; 72% yield (for the last step); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, J = 7.5 Hz, 1H), 7.43 (d, J = 4.0 Hz, 2H), 7.35-7.31 (m, 1H), 7.30-7.23 (m, 3H), 7.20 (d, J = 7.5 Hz, 1H), 3.05-2.93 (m, 2H), 2.76-2.64 (m, 2H), 2.35 (s, 3H), 1.61 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 213.3, 140.7, 138.4, 133.0, 132.0, 130.2, 128.9, 128.54, 128.48, 128.1, 127.9, 122.0, 121.7, 95.4, 89.4, 62.5, 35.4, 21.2, 19.7. HRMS *m*/*z* (ESI+): Calculated for $C_{21}H_{19}O_2^+$ ($[M+H]^+$) 303.1380, found 303.1382.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7.252
7.237
7.211
7.196
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3.015
3.002
2.976
2.964
2.931
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2.722
2.710
2.684
2.671
2.641
2.351
1.612
Me
Me
O
O
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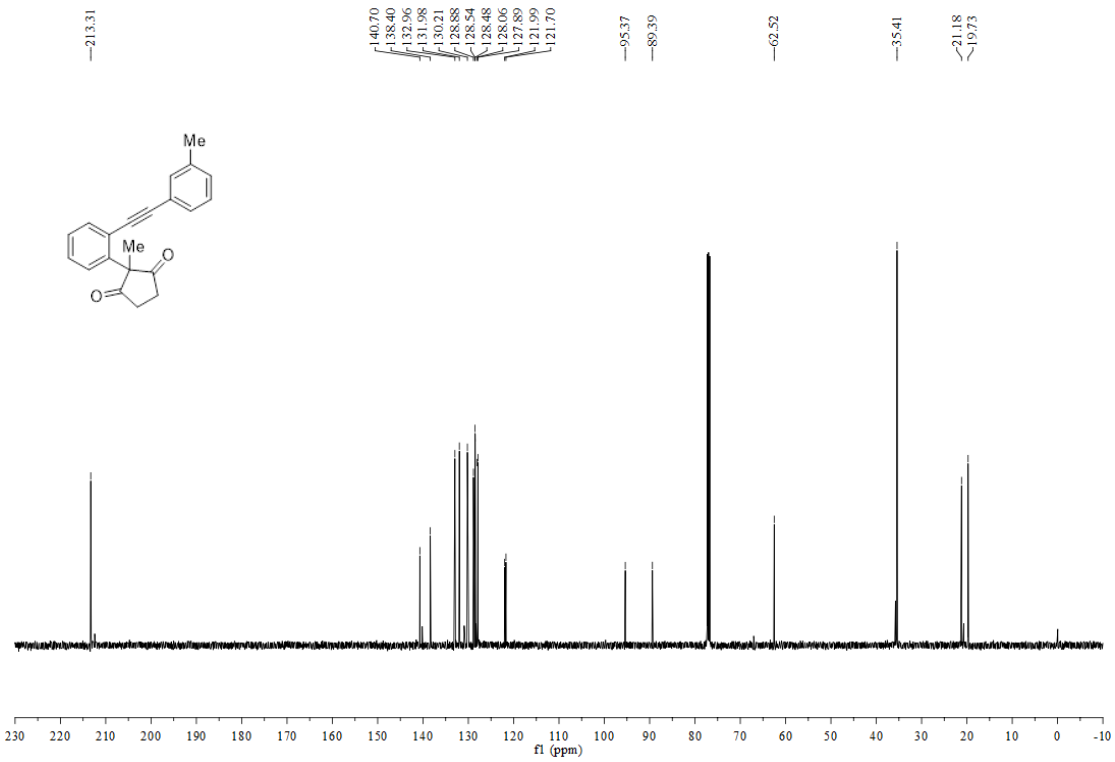
2.02
1.05
2.98
0.96
2.02
2.02
3.01
2.98
f1 (ppm)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132.96
131.98
130.21
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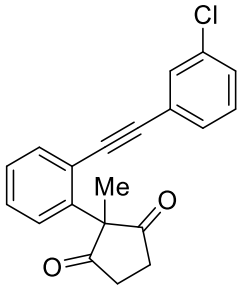
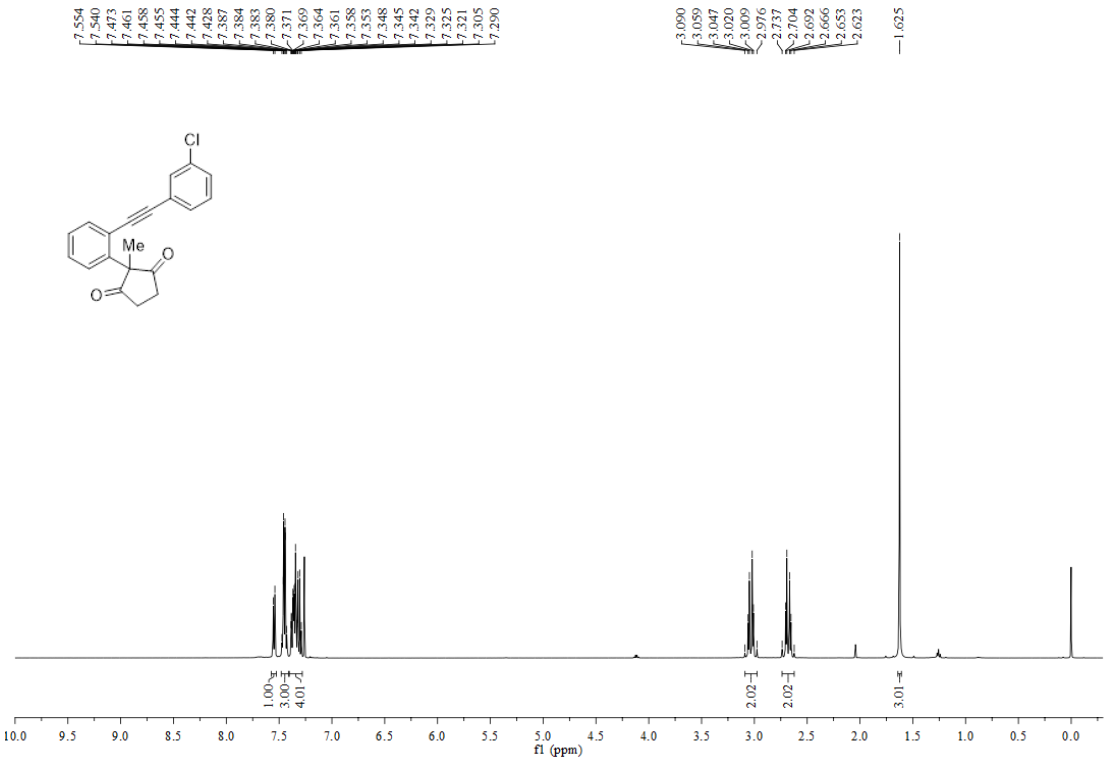
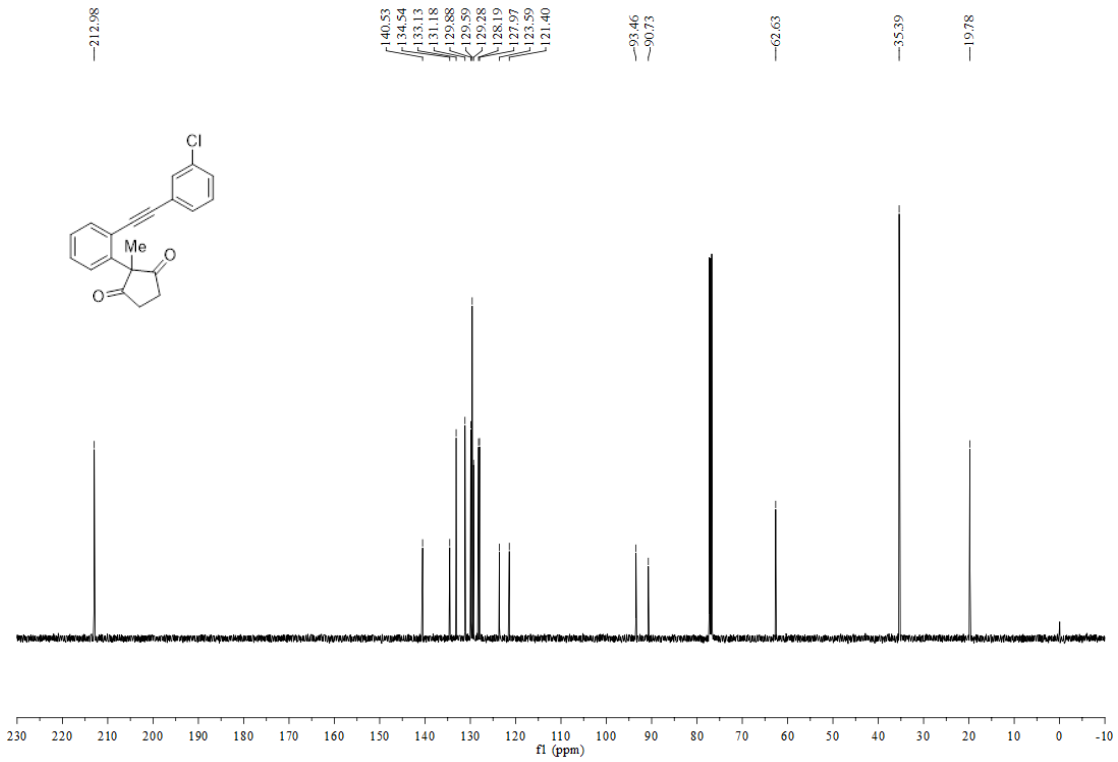
128.54
128.48
128.06
127.89
121.99
121.70
95.37
89.39
62.52
35.41
21.18
19.73
Me
Me
O
O
f1 (ppm)

2-(2-((3-Chlorophenyl)ethynyl)phenyl)-2-methylcyclopentane-1,3-dione (1h)

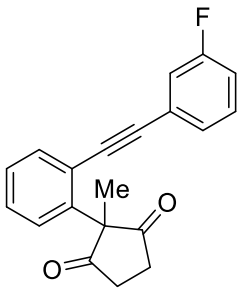


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow solid, Mp = 129-130 °C; 65% yield (for the last step); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, J = 7.0 Hz, 1H), 7.47-7.43 (m, 3H), 7.39-7.29 (m, 4H), 3.09-2.98 (m, 2H), 2.74-2.62 (m, 2H), 1.63 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 213.0, 140.5, 134.5, 133.1, 131.2, 129.9, 129.6, 129.3, 128.2, 128.0, 123.6, 121.4, 93.5, 90.7, 62.6, 35.4, 19.8. HRMS *m/z* (ESI+): Calculated for $C_{20}H_{15}ClO_2Na^+$ ([M+Na]$^+$) 345.0653, found 345.0653.

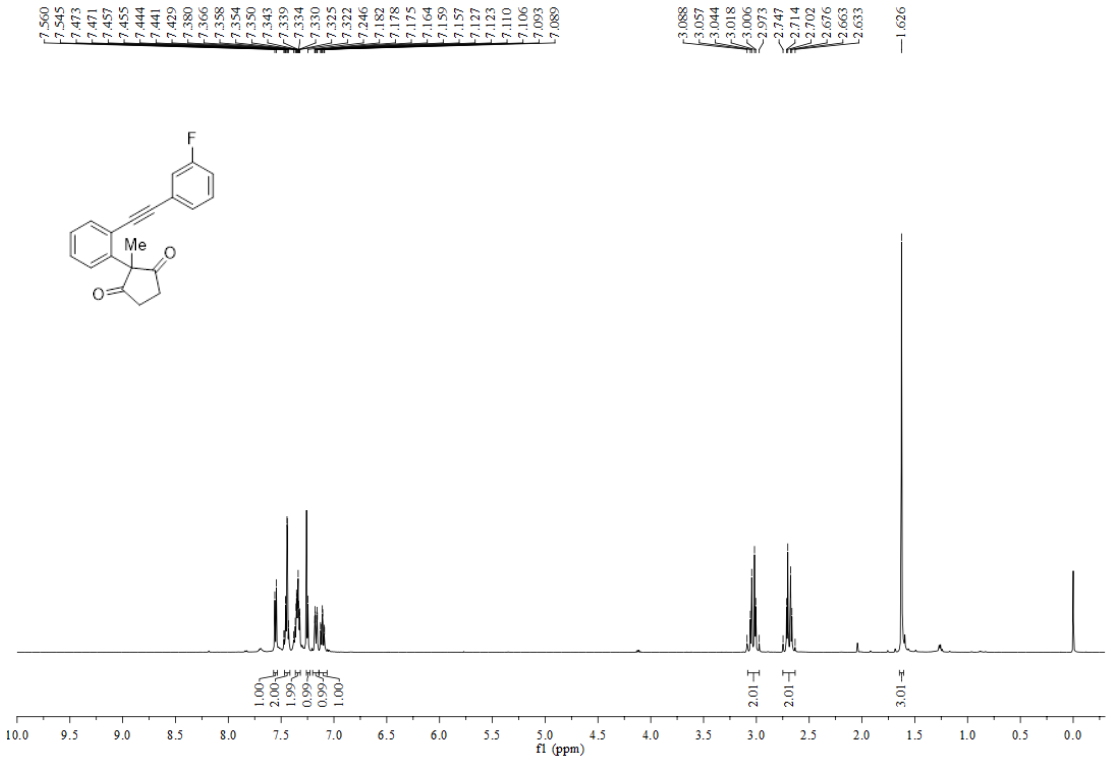


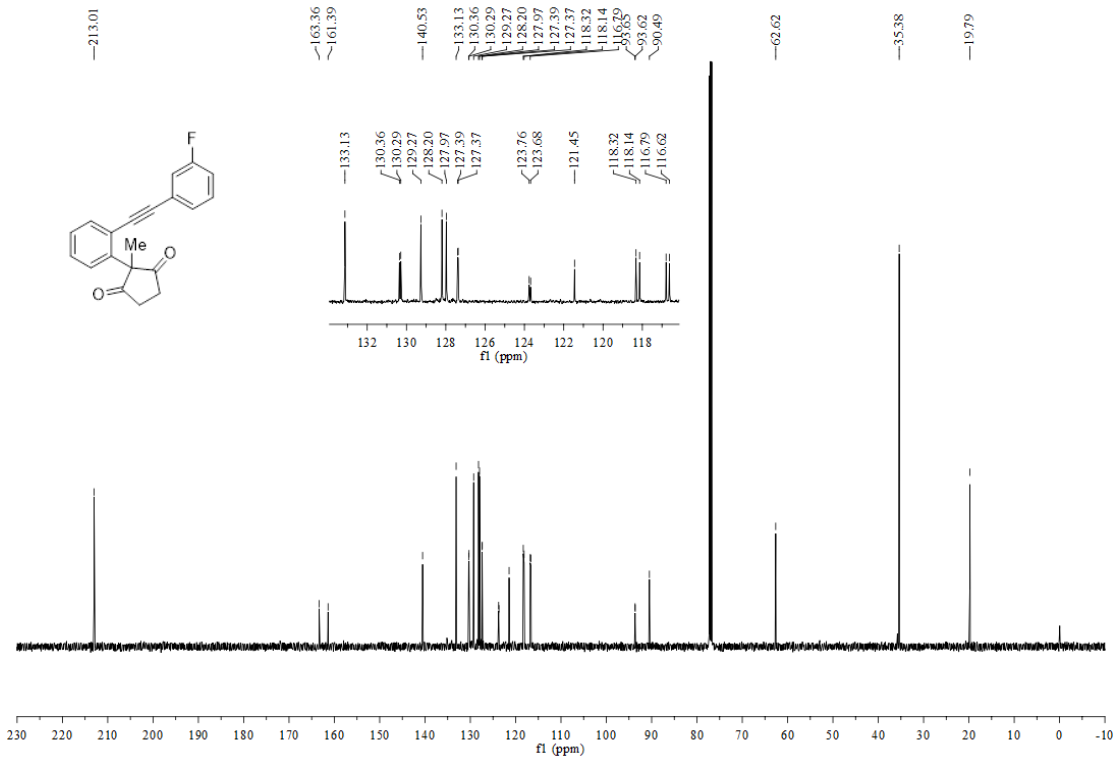


2-(2-((3-Fluorophenyl)ethynyl)phenyl)-2-methylcyclopentane-1,3-dione (1i)

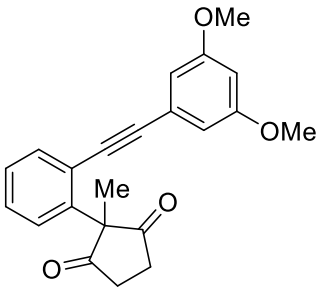


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow solid, Mp = 149-150 °C; 68% yield (for the last step); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, J = 7.5 Hz, 1H), 7.47-7.43 (m, 2H), 7.38-7.32 (m, 2H), 7.25 (s, 1H), 7.18-7.16 (m, 1H), 7.13-7.09 (m, 1H), 3.09-2.97 (m, 2H), 2.75-2.63 (m, 2H), 1.63 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 213.0, 162.4 (d, J = 246.3 Hz), 140.5, 133.1, 130.3 (d, J = 8.8 Hz), 129.3, 128.2, 128.0, 127.4 (d, J = 2.5 Hz), 123.7 (d, J = 10.0 Hz), 121.5, 118.2 (d, J = 22.5 Hz), 116.7 (d, J = 21.3 Hz), 93.6 (d, J = 3.8 Hz), 90.5, 62.6, 35.4, 19.8. HRMS m/z (ESI+): Calculated for $C_{20}H_{15}FO_2Na^+$ ([M+Na]$^+$) 329.0948, found 329.0949.

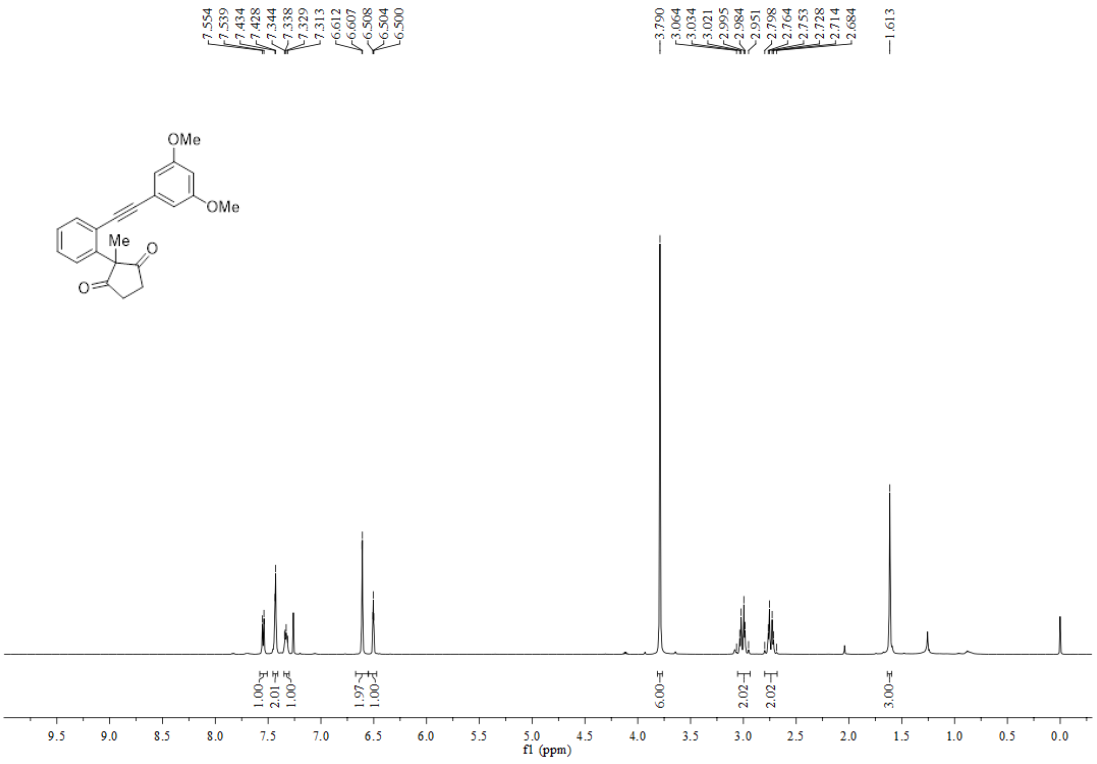

7.560
7.545
7.473
7.471
7.457
7.455
7.444
7.441
7.429
7.380
7.366
7.358
7.354
7.350
7.343
7.339
7.334
7.330
7.325
7.322
7.246
7.182
7.178
7.175
7.164
7.159
7.157
7.127
7.123
7.110
7.106
7.093
7.089
3.088
3.057
3.044
3.018
3.006
2.973
2.747
2.714
2.702
2.676
2.663
2.633
1.626
F
Me
O
O
1.00
2.00
1.99
0.99
0.99
1.00
2.01
2.01
3.01
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)

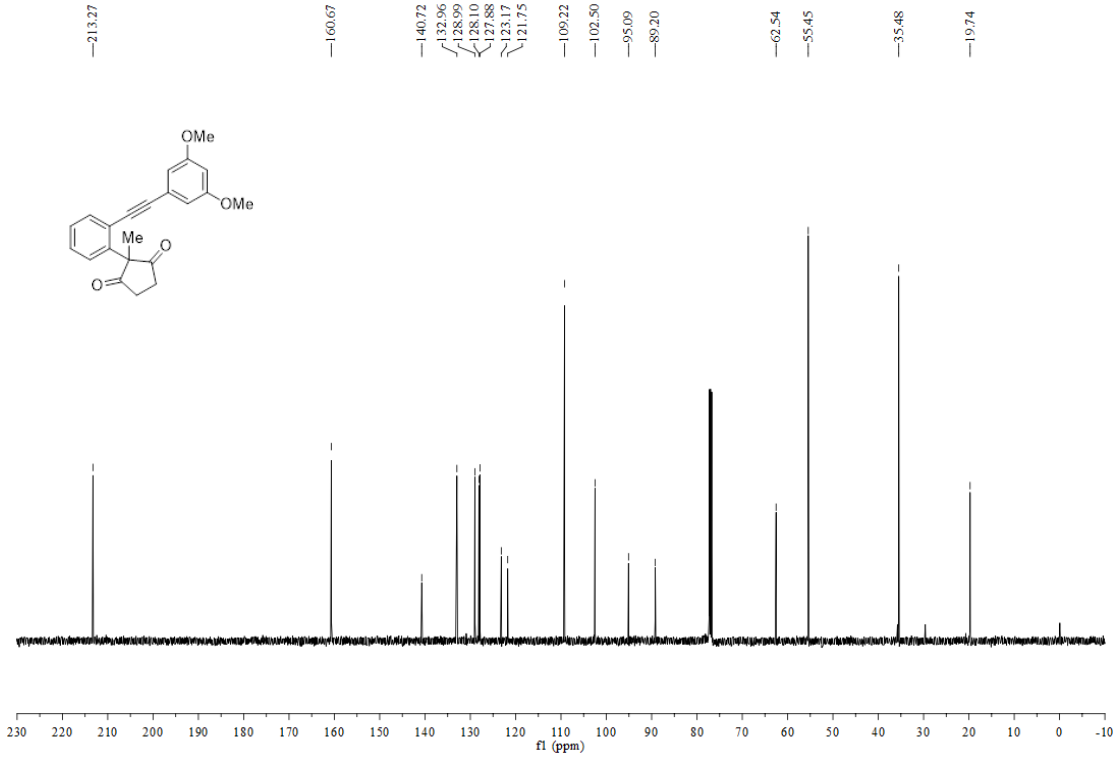

213.01
163.36
161.39
140.53
133.13
130.36
130.29
129.27
128.20
127.97
127.39
127.37
118.32
118.14
116.79
116.62
93.62
90.49
62.62
35.38
19.79
F
Me
O
O
133.13
130.36
130.29
129.27
128.20
127.97
127.39
127.37
123.76
123.68
121.45
118.32
118.14
116.79
116.62
132 130 128 126 124 122 120 118
f1 (ppm)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

2-(2-((3,5-Dimethoxyphenyl)ethynyl)phenyl)-2-methylcyclopentane-1,3-dione (1j)

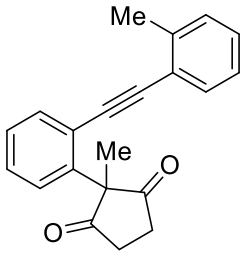


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow solid, Mp = 150-151 °C; 84% yield (for the last step); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, J = 7.5 Hz, 1H), 7.43 (d, J = 3.0 Hz, 2H), 7.35-7.32 (dd, J = 7.5, 3.0 Hz, 1H), 6.61 (d, J = 2.5 Hz, 2H), 6.50 (t, J = 2.0 Hz, 1H), 3.79 (s, 6H), 3.06-2.95 (m, 2H), 2.80-2.68 (m, 2H), 1.61 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 213.3, 160.7, 140.7, 133.0, 129.0, 128.1, 127.9, 123.2, 121.8, 109.2, 102.5, 95.1, 89.2, 62.5, 55.5, 35.5, 19.7. HRMS m/z (ESI+): Calculated for $C_{22}H_{20}O_4^+$ ([M+H]$^+$) 349.1434, found 349.1437.

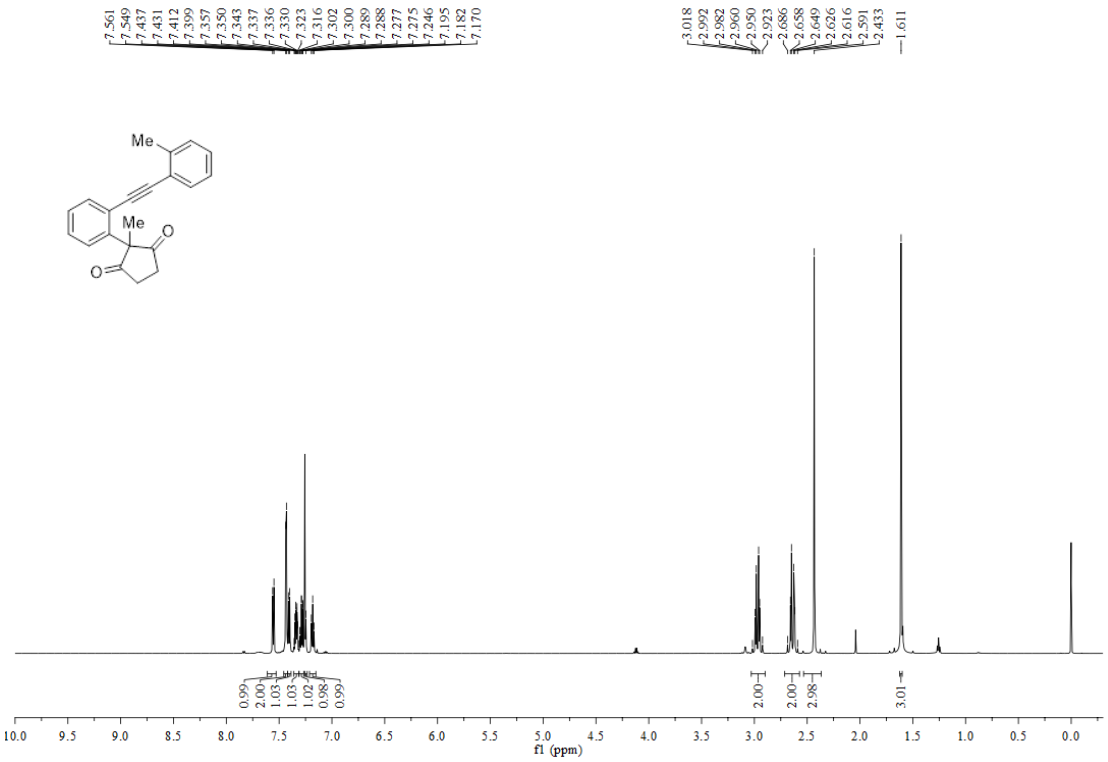


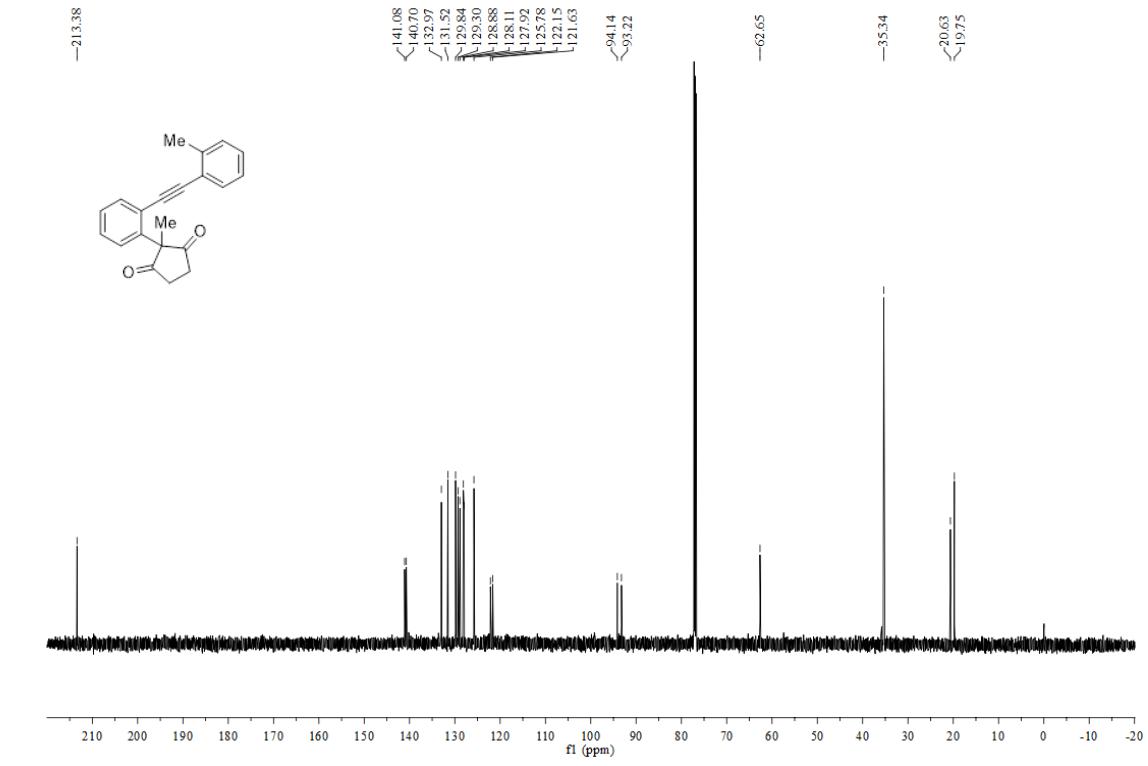


2-Methyl-2-(2-(o-tolylethynyl)phenyl)cyclopentane-1,3-dione (1k)

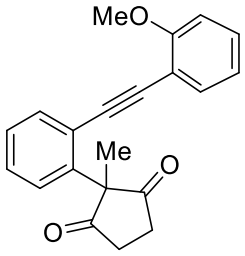


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow solid, Mp = 163-164 °C; 65 % yield (for the last step); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 (d, J = 7.2 Hz, 1H), 7.43 (d, J = 3.6 Hz, 2H), 7.40 (d, J = 7.8 Hz, 1H), 7.36-7.31 (m, 1H), 7.31-7.27 (m, 1H), 7.25 (s, 1H), 7.18 (t, J = 7.2 Hz, 1H), 3.02-2.92 (m, 2H), 2.69-2.59 (m, 2H), 2.43 (s, 3H), 1.61 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 213.4, 141.1, 140.7, 133.0, 131.5, 129.8, 129.3, 128.9, 128.1, 127.9, 125.8, 122.2, 121.6, 94.1, 93.2, 62.7, 35.3, 20.6, 19.8. HRMS *m/z* (ESI+): Calculated for $C_{21}H_{19}O_2^+$ ($[M+H]^+$) 303.1380, found 303.1382.

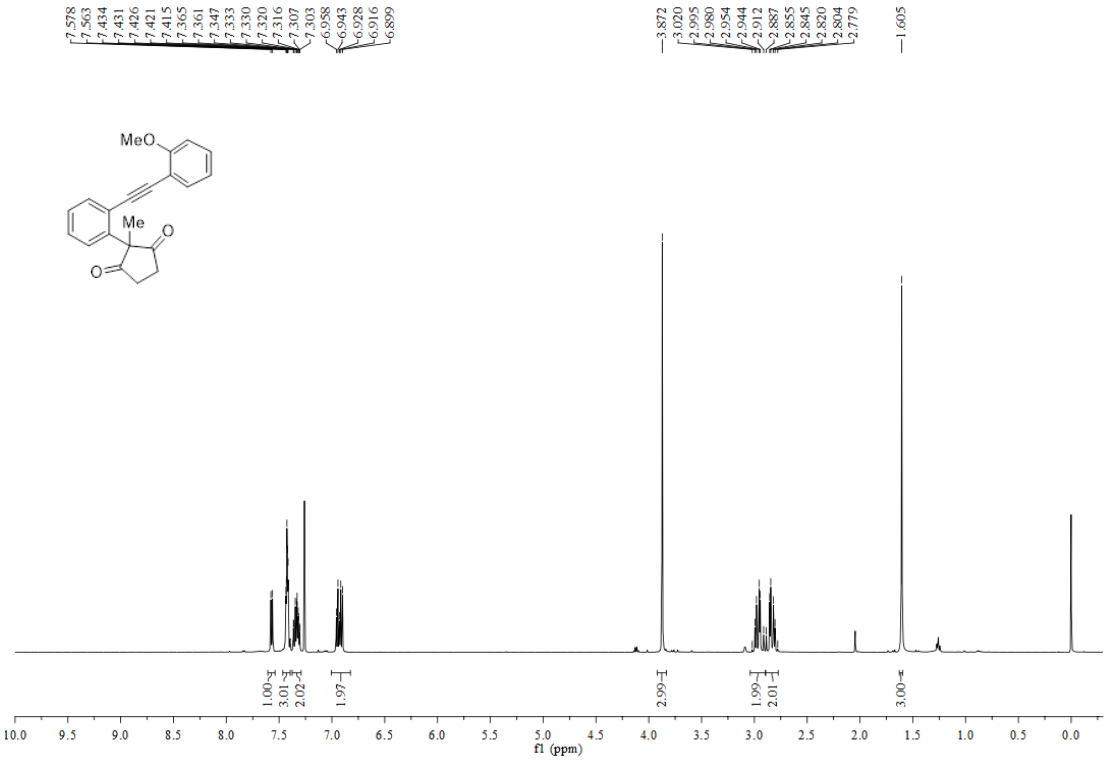

7.561
7.549
7.437
7.431
7.412
7.399
7.357
7.350
7.343
7.337
7.336
7.330
7.323
7.316
7.302
7.300
7.289
7.288
7.277
7.275
7.246
7.195
7.182
7.170
3.018
2.992
2.982
2.960
2.950
2.923
2.686
2.658
2.649
2.626
2.616
2.591
2.433
1.611
Me
Me
O
O
0.99
2.00
1.03
1.03
1.02
0.98
0.99
2.00
2.00
2.98
3.01
f1 (ppm)

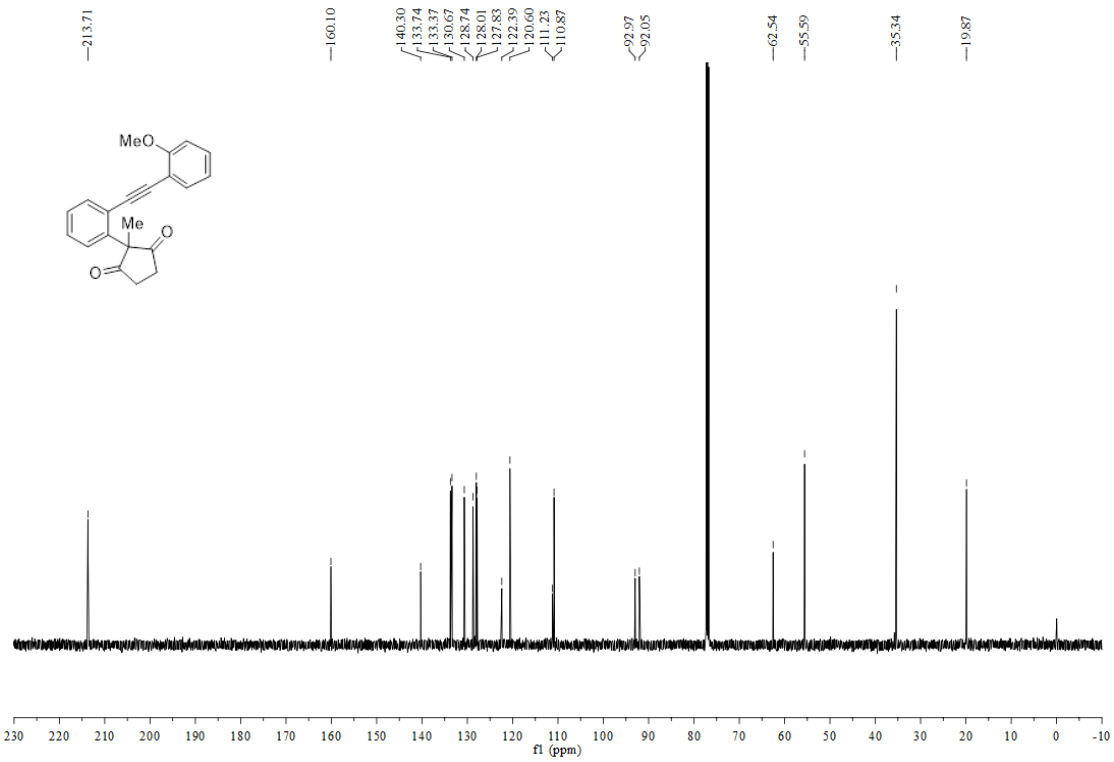

213.38
141.08
140.70
132.97
131.52
129.84
129.30
128.88
128.11
127.92
125.78
122.15
121.63
94.14
93.22
62.65
35.34
20.63
19.75
Me
Me
O
O
f1 (ppm)

2-(2-((2-Methoxyphenyl)ethynyl)phenyl)-2-methylcyclopentane-1,3-dione (1l)

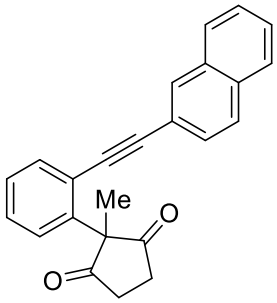


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); brown solid, Mp = 175-176 °C; 80% yield (for the last step); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, J = 7.5 Hz, 1H), 7.43-7.42 (m, 3H), 7.37-7.30 (m, 2H), 6.96-6.90 (m, 2H), 3.87 (s, 3H), 3.02-2.89 (m, 2H), 2.86-2.78 (m, 2H), 1.61 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 213.7, 160.1, 140.3, 133.7, 133.4, 130.7, 128.7, 128.0, 127.8, 122.4, 120.6, 111.2, 110.9, 93.0, 92.1, 62.5, 55.6, 35.3, 19.9. HRMS *m*/*z* (ESI+): Calculated for $C_{21}H_{19}O_3^+$ ([M+H]$^+$) 319.1329, found 319.1332.

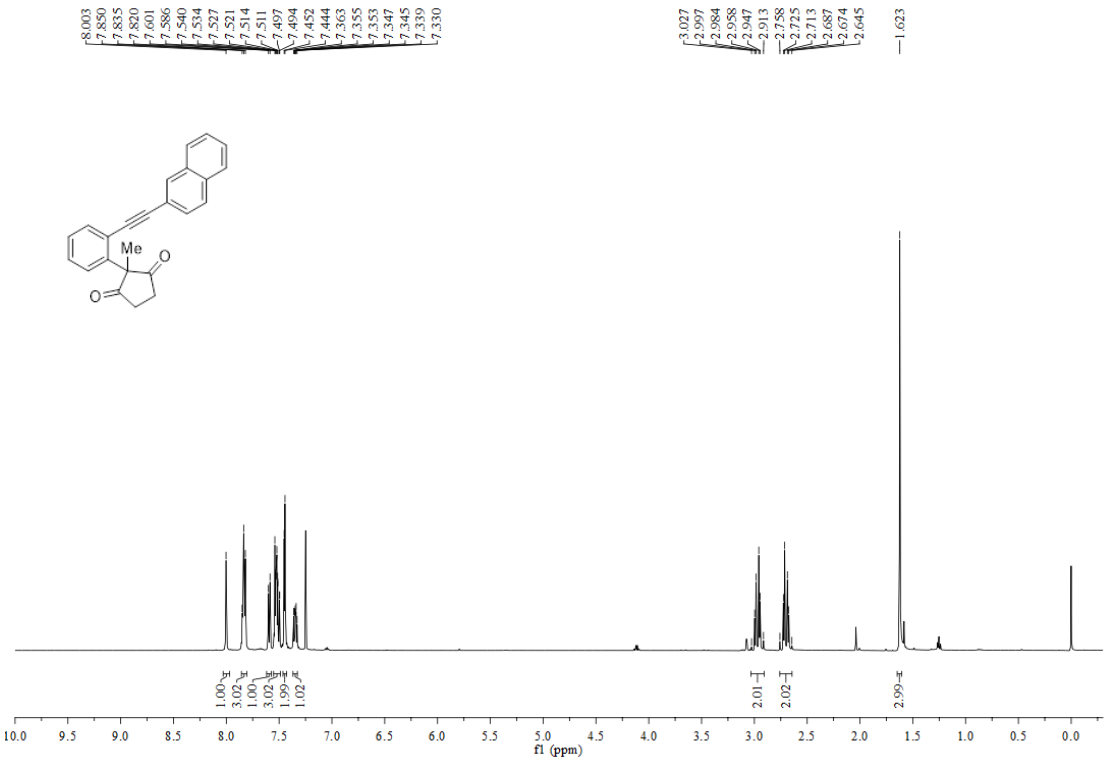


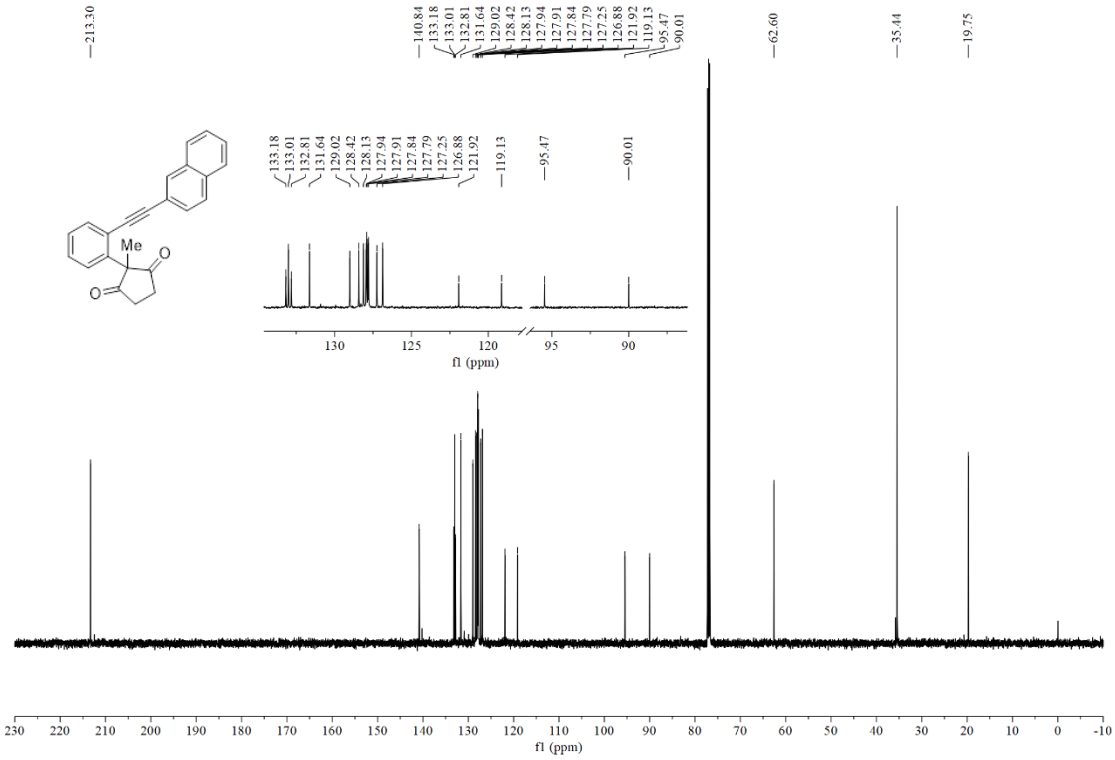


2-Methyl-2-(2-(naphthalen-2-ylethynyl)phenyl)cyclopentane-1,3-dione (1m)

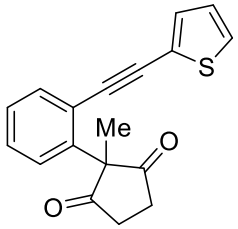


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow solid, Mp = 154-155 °C; 75% yield (for the last step); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.83 (t, J = 7.5 Hz, 3H), 7.59 (d, J = 7.5 Hz, 1H), 7.54-7.49 (m, 3H), 7.45 (d, J = 4.0 Hz, 2H), 7.36-7.33 (m, 1H), 3.03-2.91 (m, 2H), 2.76-2.64 (m, 2H), 1.62 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 213.3, 140.8, 133.2, 133.0, 132.8, 131.6, 129.0, 128.4, 128.1, 127.94, 127.91, 127.84, 127.79, 127.3, 126.9, 121.9, 119.1, 95.5, 90.0, 62.6, 35.4, 19.8. HRMS *m*/*z* (ESI+): Calculated for $C_{24}H_{19}O_2^+$ ([M+H]$^+$) 339.1380, found 339.1382.

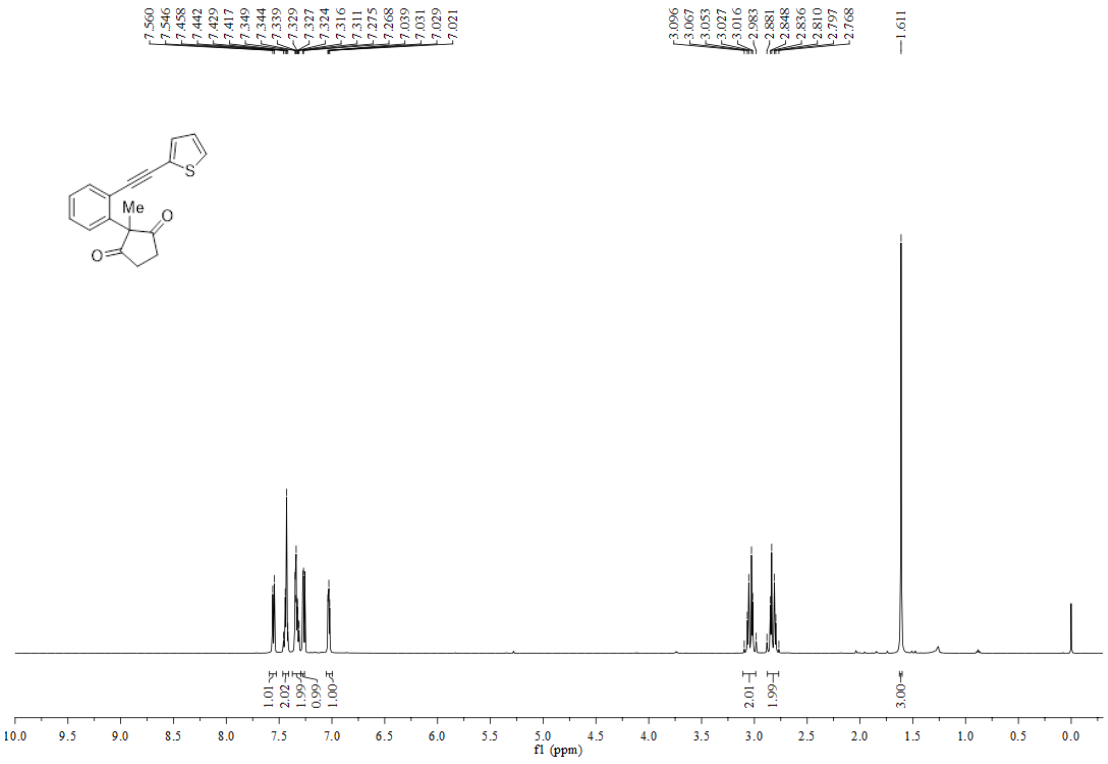

8.003
7.850
7.835
7.820
7.601
7.586
7.540
7.534
7.527
7.521
7.514
7.511
7.497
7.494
7.452
7.444
7.363
7.355
7.353
7.347
7.345
7.339
7.330
3.027
2.997
2.984
2.958
2.947
2.913
2.758
2.725
2.713
2.687
2.674
2.645
1.623
Me
O
O
1.00
3.02
1.00
3.02
1.99
1.02
2.01
2.02
2.99
f1 (ppm)

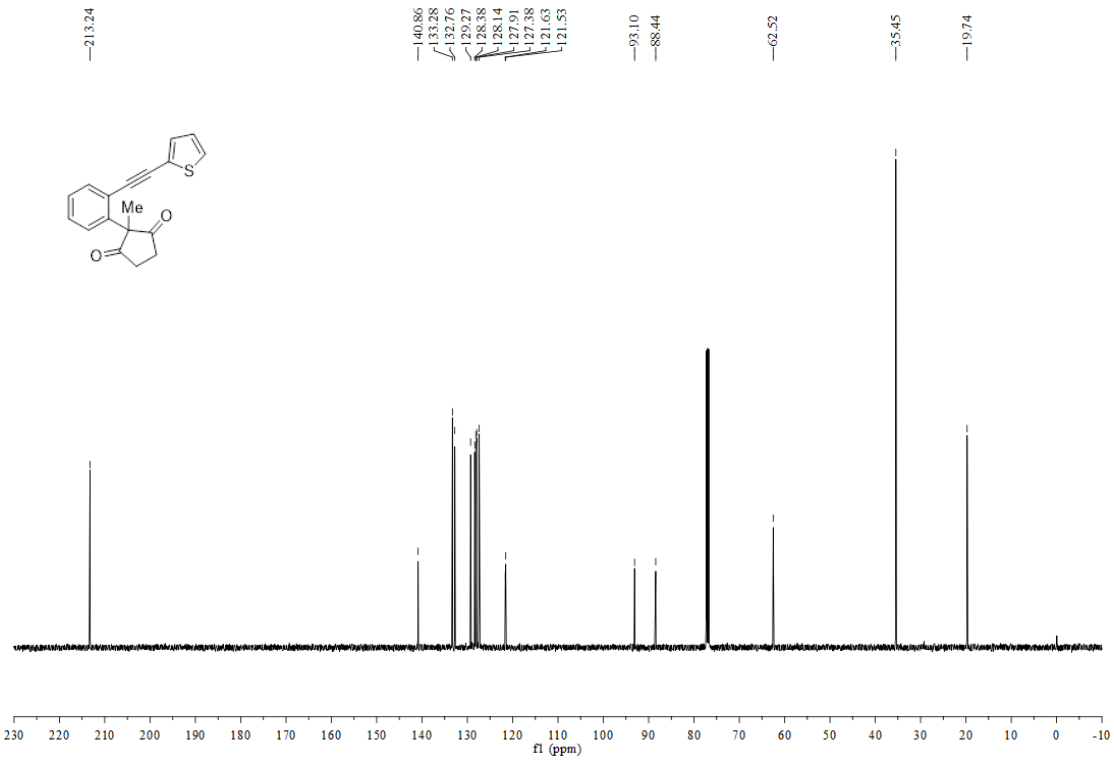

213.30
140.84
133.18
133.01
132.81
131.64
129.02
128.42
128.13
127.94
127.91
127.84
127.79
127.25
126.88
121.92
119.13
95.47
90.01
62.60
35.44
19.75
Me
O
O
f1 (ppm)

2-Methyl-2-(2-(thiophen-2-ylethynyl)phenyl)cyclopentane-1,3-dione (1n)

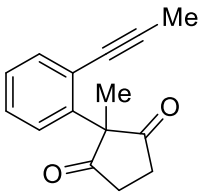


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); brown solid, Mp = 149-150 °C; 70% yield (for the last step); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.0 Hz, 1H), 7.46-7.41 (m, 2H), 7.35-7.31 (m, 2H), 7.27 (d, *J* = 3.5 Hz, 1H), 7.04-7.20 (m, 1H), 3.10-2.98 (m, 2H), 2.88-2.77 (m, 2H), 1.61 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) *δ* 213.2, 140.9, 133.3, 132.8, 129.3, 128.4, 128.1, 127.9, 127.4, 121.6, 121.5, 93.1, 88.4, 62.5, 35.5, 19.7. HRMS *m*/*z* (ESI+): Calculated for $C_{18}H_{15}O_2S^+$ ([M+H]$^+$) 295.0787, found 295.0787.

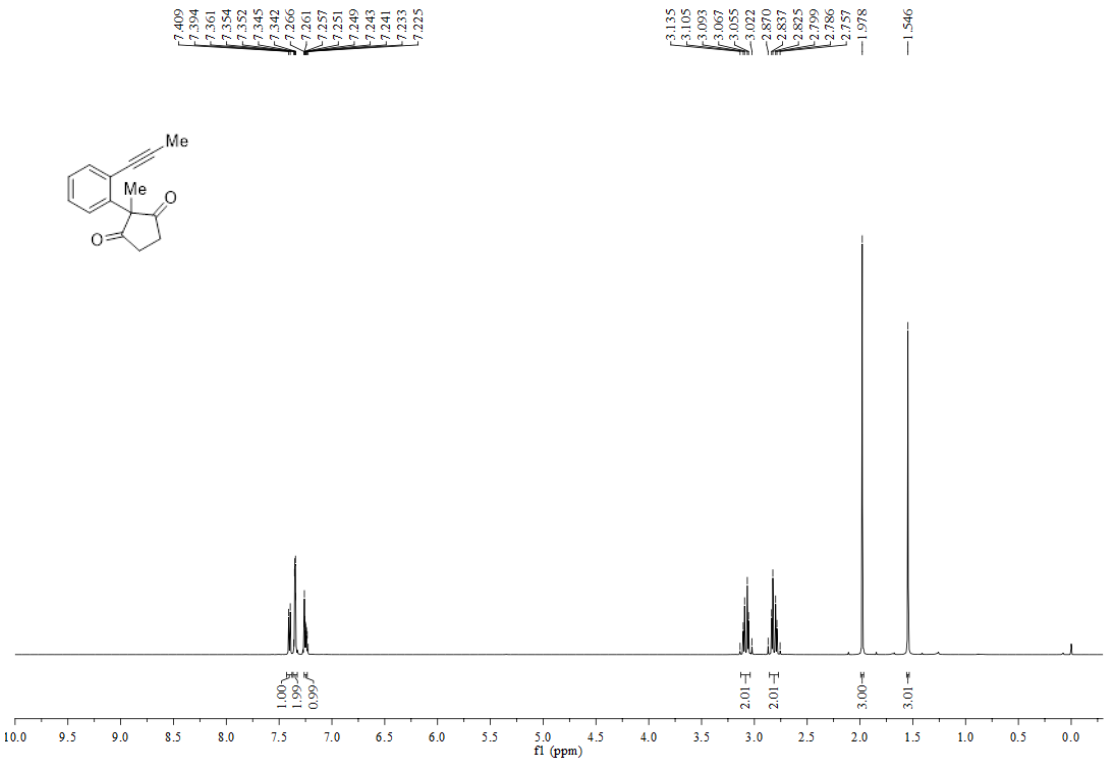


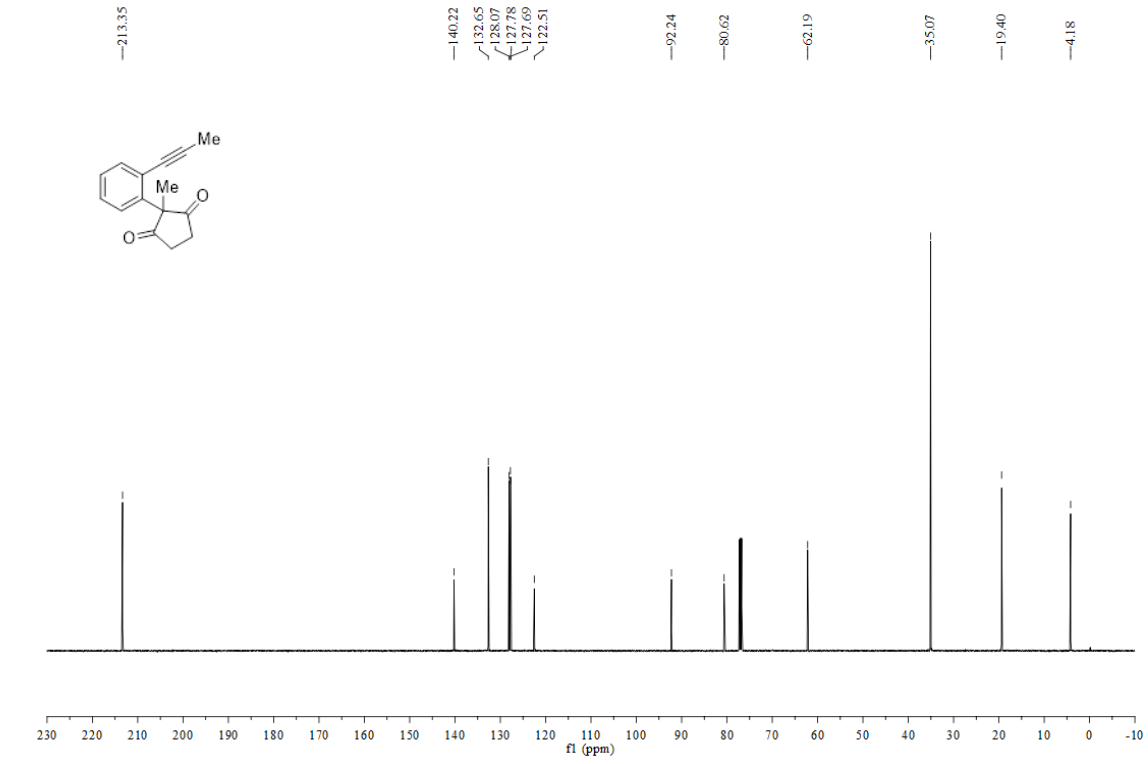


2-Methyl-2-(2-(prop-1-yn-1-yl)phenyl)cyclopentane-1,3-dione (1o)

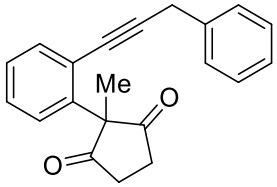


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); brown solid, Mp = 131-132 °C; 80% yield (for the last step); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, J = 7.5 Hz, 1H), 7.36-7.34 (m, 2H), 7.27-7.23 (m, 1H), 3.14-3.02 (m, 2H), 2.87-2.76 (m, 2H), 1.98 (s, 3H), 1.55 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 213.4, 140.2, 132.7, 128.1, 127.8, 127.7, 122.5, 92.2, 80.6, 62.2, 35.1, 19.4, 4.2. HRMS m/z (ESI+): Calculated for $C_{15}H_{14}O_2Na^+$ ([M+Na]$^+$) 249.0886, found 249.0888.

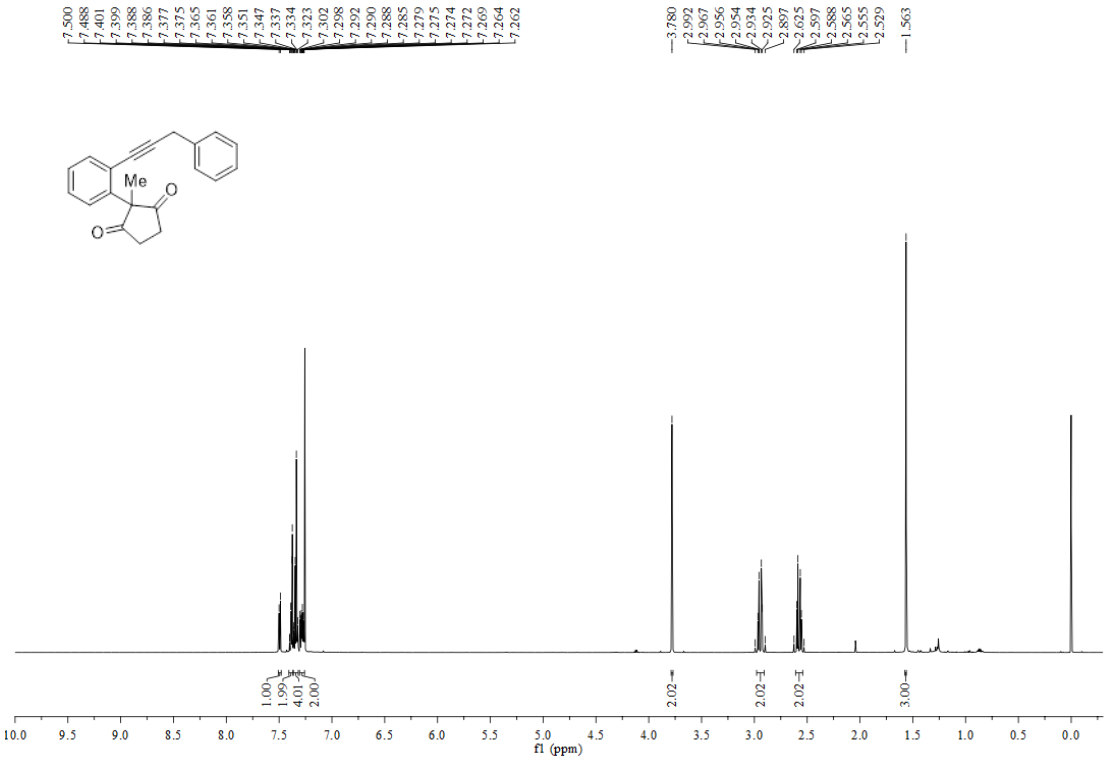

7.409
7.394
7.361
7.354
7.352
7.345
7.342
7.266
7.261
7.257
7.251
7.249
7.243
7.241
7.233
7.225
3.135
3.105
3.093
3.067
3.055
3.022
2.870
2.837
2.825
2.799
2.786
2.757
1.978
1.546
Me
Me
O
O
1.00
1.99
0.99
2.01
2.01
3.00
3.01
f1 (ppm)

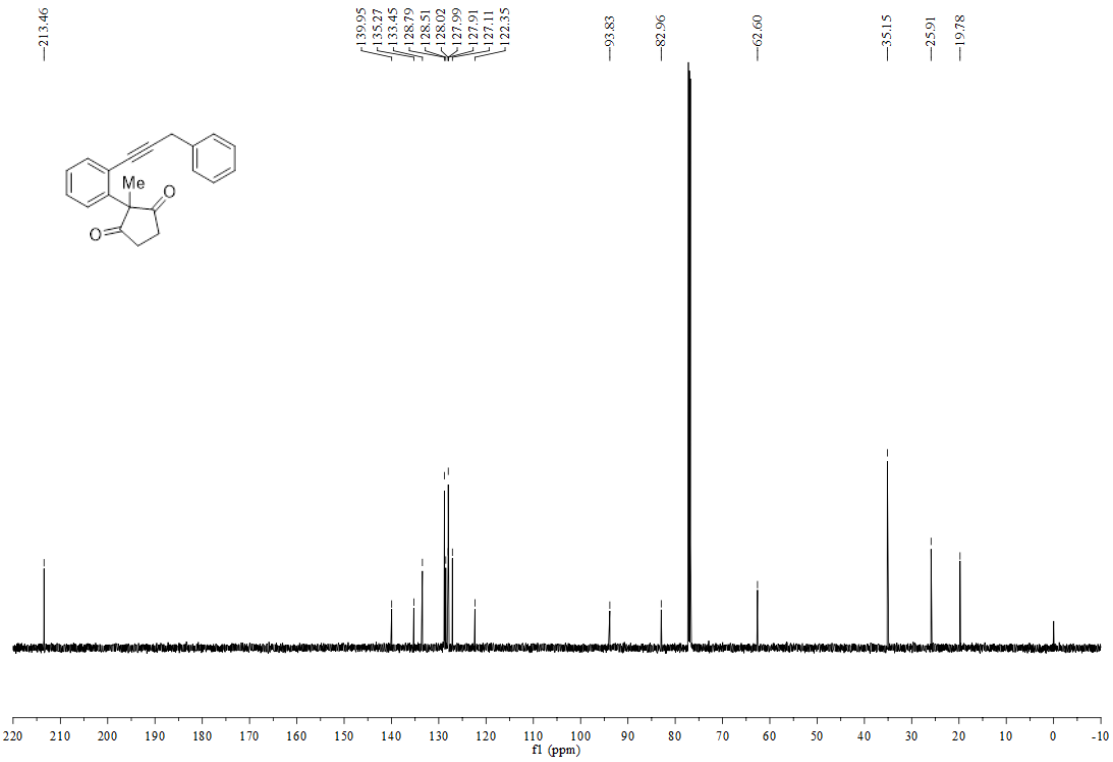

213.35
140.22
132.65
128.07
127.78
127.69
122.51
92.24
80.62
62.19
35.07
19.40
4.18
Me
Me
O
O
f1 (ppm)

***2-Methyl-2-(2-(3-phenylprop-1-yn-1-yl)phenyl)cyclopentane-1,3-dione* (*1p*)**

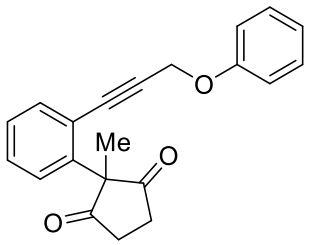


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); white solid, Mp = 119-120 °C; 68% yield (for the last step); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 (d, J = 7.2 Hz, 1H), 7.41-7.37 (m, 2H), 7.37-7.32 (m, 4H), 7.31-7.26 (m, 2H), 3.78 (s, 2H), 3.00-2.89 (m, 2H), 2.63-2.52 (m, 2H), 1.56 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 213.5, 140.0, 135.3, 133.5, 128.8, 128.5, 128.02, 127.99, 127.9, 127.1, 122.4, 93.8, 83.0, 62.6, 35.2, 25.9, 19.8. HRMS *m*/*z* (ESI+): Calculated for $C_{21}H_{18}NaO_2^+$ ([M+Na]$^+$) 325.1199, found 325.1197.

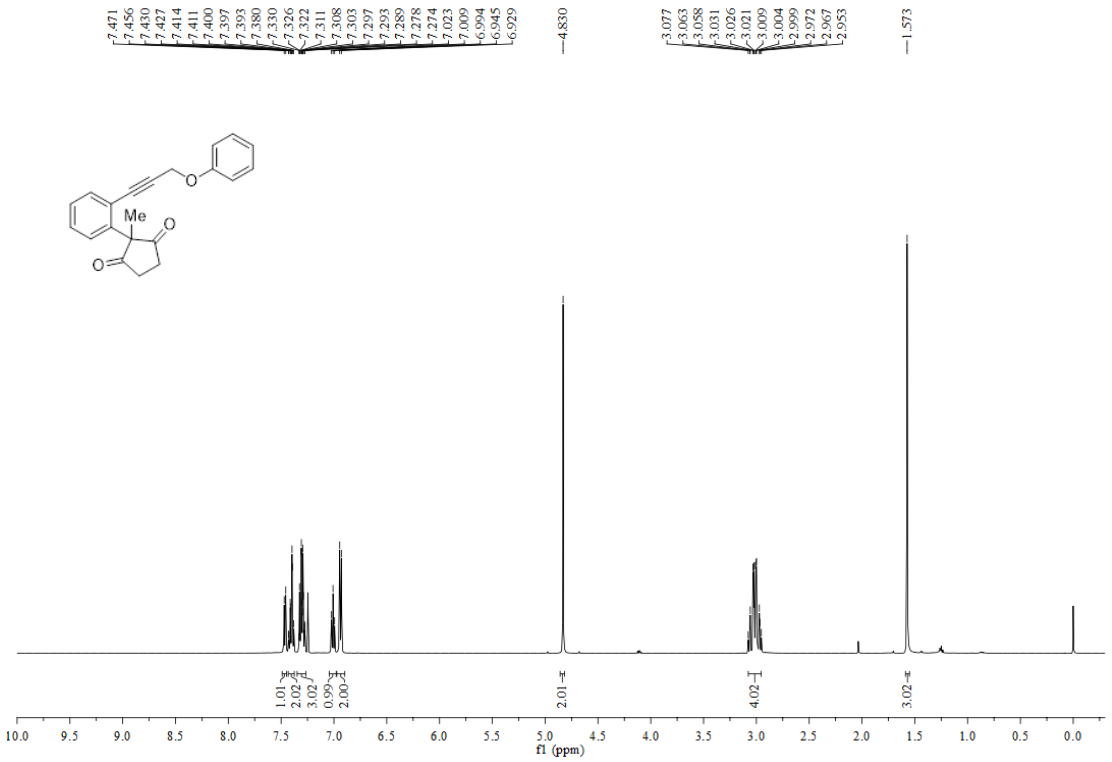


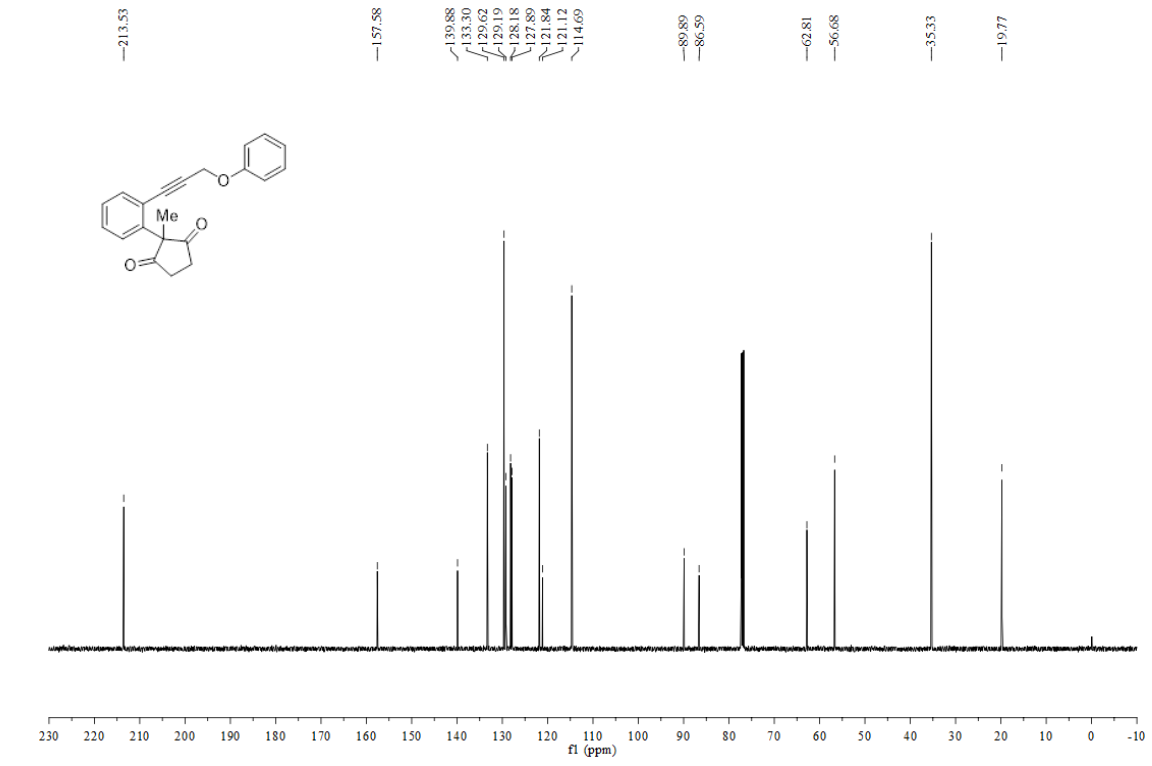


2-Methyl-2-(2-(3-phenoxyprop-1-yn-1-yl)phenyl)cyclopentane-1,3-dione (1q)

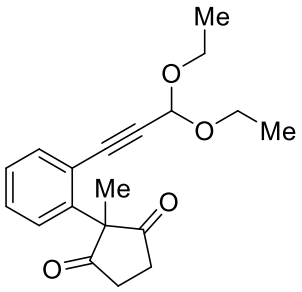


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow solid, Mp = 125-126 °C; 74% yield (for the last step); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, J = 7.5 Hz, 1H), 7.43-7.38 (m, 2H), 7.33-7.27 (m, 3H), 7.01 (t, J = 7.5 Hz, 1H), 6.94 (d, J = 8.0 Hz, 2H), 4.83 (s, 2H), 3.08-2.95 (m, 4H), 1.57 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 213.5, 157.6, 139.9, 133.3, 129.6, 129.2, 128.2, 127.9, 121.8, 121.1, 114.7, 89.9, 86.6, 62.8, 56.7, 35.3, 19.8. HRMS *m*/*z* (ESI+): Calculated for $C_{21}H_{18}NaO_3^+$ ([M+Na]$^+$) 341.1148, found 341.1146.

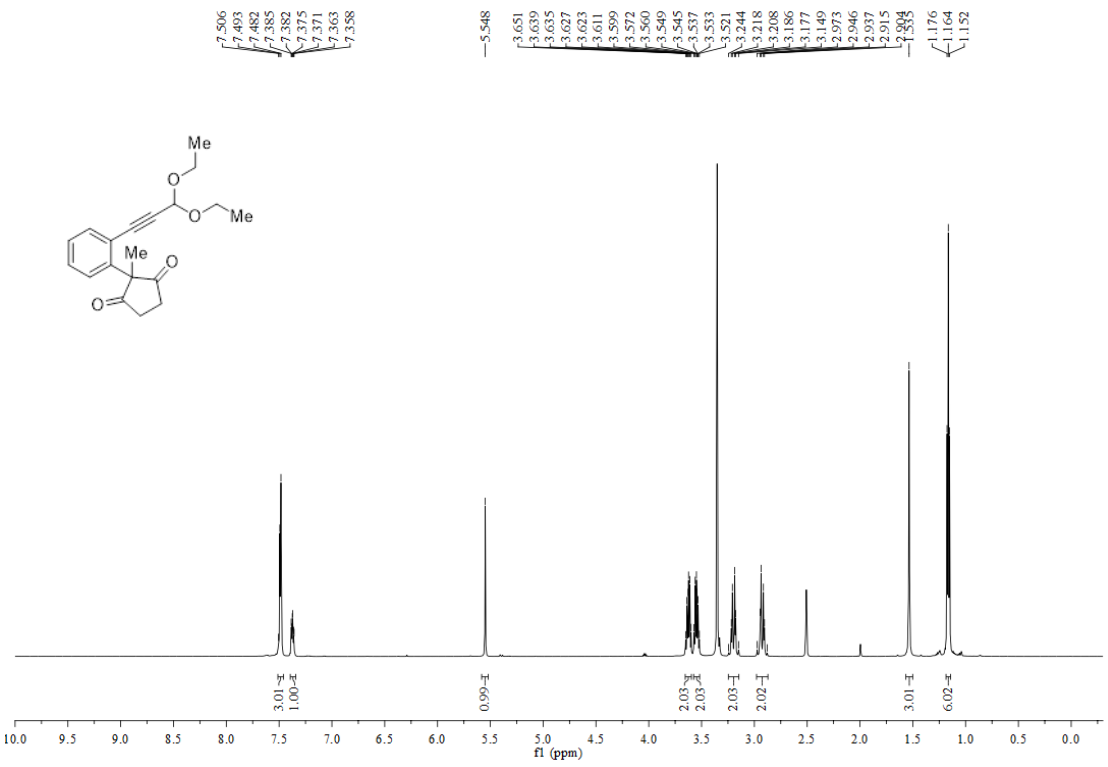

7.471
7.456
7.430
7.427
7.414
7.411
7.400
7.397
7.393
7.380
7.330
7.326
7.322
7.311
7.308
7.303
7.297
7.293
7.289
7.278
7.274
7.023
7.009
6.994
6.945
6.929
4.830
3.077
3.063
3.058
3.031
3.026
3.021
3.009
3.004
2.999
2.972
2.967
2.953
1.573
Me
O
O
O
1.01
2.02
3.02
0.99
2.00
2.01
4.02
3.02
10.0 9.5 9.0 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)

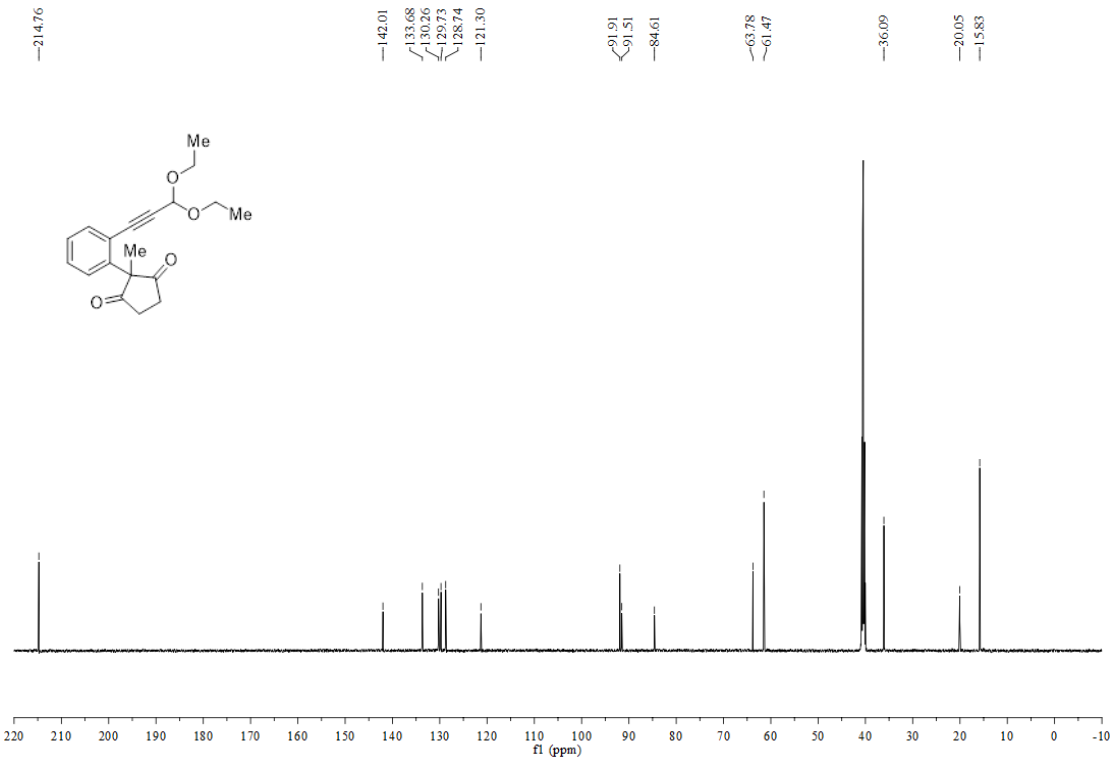

213.53
157.58
139.88
133.30
129.62
129.19
128.18
127.89
121.84
121.12
114.69
89.89
86.59
62.81
56.68
35.33
19.77
Me
O
O
O
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

2-(2-(3,3-Diethoxyprop-1-yn-1-yl)phenyl)-2-methylcyclopentane-1,3-dione (1r)

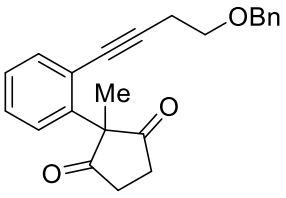


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); brown solid, Mp = 79-80 °C; 63% yield (for the last step); ^{1}H NMR (600 MHz, DMSO) δ 7.51-7.48 (m, 3H), 7.39-7.36 (m, 1H), 5.55 (s, 1H), 3.65-3.59 (m, 2H), 3.57-3.52 (m, 2H), 3.24-3.15 (m, 2H), 2.97-2.90 (m, 2H), 1.54 (s, 3H), 1.16 (t, J = 7.2 Hz, 6H). ^{13}C NMR (150 MHz, DMSO) δ 214.8, 142.0, 133.7, 130.3, 129.7, 128.7, 121.3, 91.9, 91.5, 84.6, 63.8, 61.5, 36.1, 20.1, 15.8. HRMS *m*/*z* (ESI+): Calculated for $C_{19}H_{22}NaO_4^+$ ([M+Na]$^+$) 337.1410, found 337.1408.

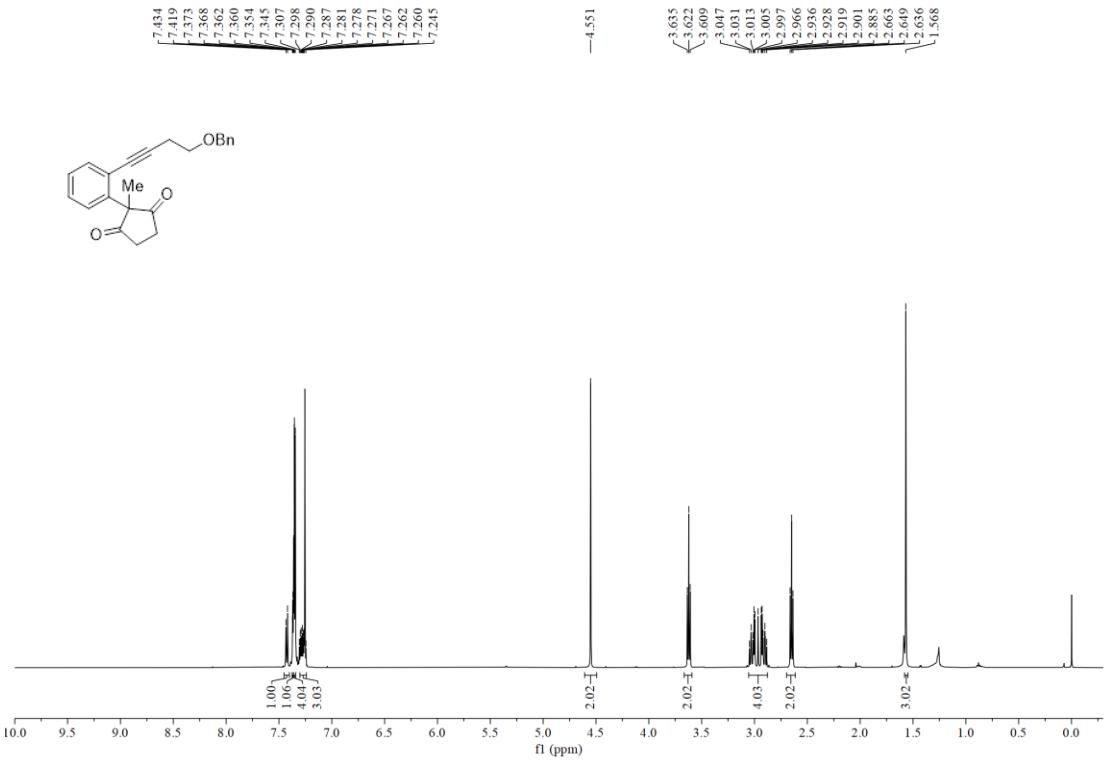




2-(2-(4-(Benzyloxy)but-1-yn-1-yl)phenyl)-2-methylcyclopentane-1,3-dione (1s)



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow oil; 70% yield (for the last step); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, J = 7.5 Hz, 1H), 7.37 (d, J = 2.5 Hz, 1H), 7.37-7.34 (m, 4H), 7.31-7.24 (m, 3H), 4.55 (s, 2H), 3.62 (t, J = 6.5 Hz, 2H), 3.05-2.89 (m, 4H), 2.65 (t, J = 6.5 Hz, 2H), 1.57 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 213.6, 140.1, 137.8, 133.4, 128.5, 128.0, 127.87, 127.85, 127.8, 122.4, 93.7, 82.1, 73.3, 68.0, 62.5, 35.4, 21.3, 19.8. HRMS *m*/*z* (ESI+): Calculated for $C_{23}H_{22}NaO_3^+$ ($[M+Na]^+$) 369.1461, found 369.1459.


7.434
7.419
7.373
7.368
7.362
7.360
7.354
7.345
7.307
7.298
7.290
7.287
7.281
7.278
7.271
7.267
7.262
7.260
7.245
4.551
3.635
3.622
3.609
3.047
3.031
3.013
3.005
2.997
2.966
2.936
2.928
2.919
2.901
2.885
2.663
2.649
2.636
1.568
OBn
Me
O
O
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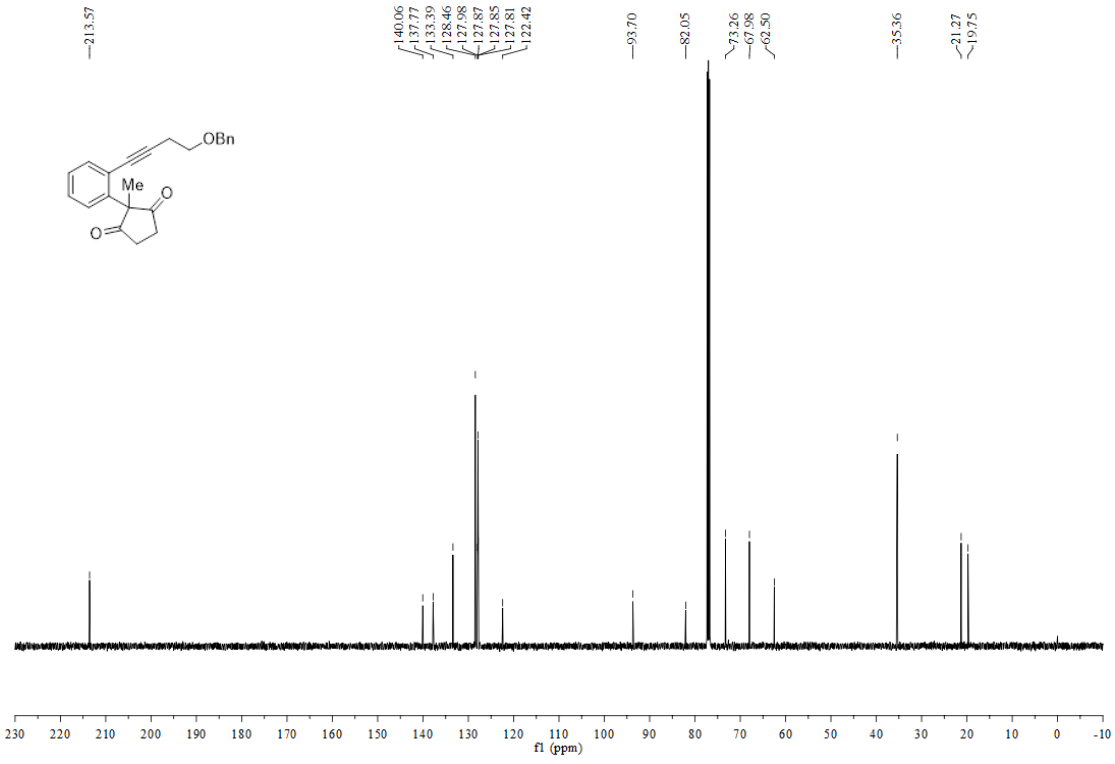
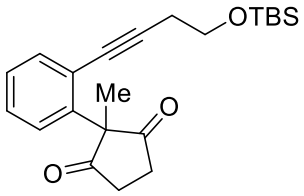
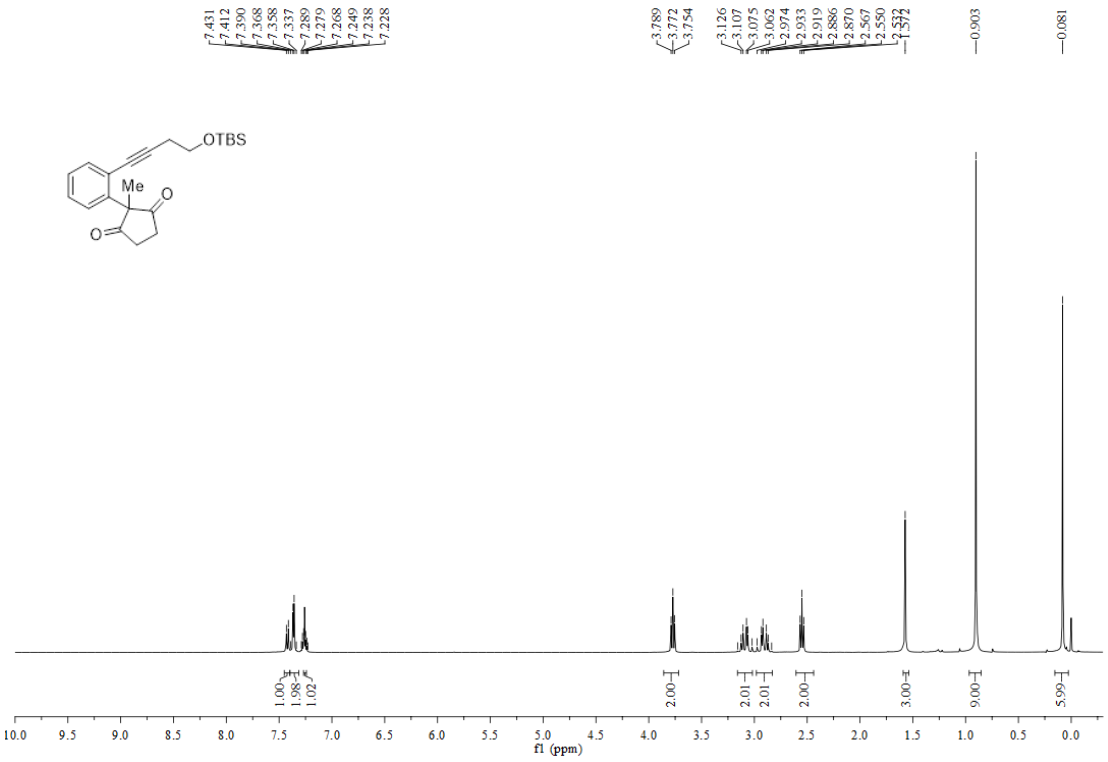
1.06
4.04
3.03
2.02
2.02
4.03
2.02
3.02
f1 (ppm)

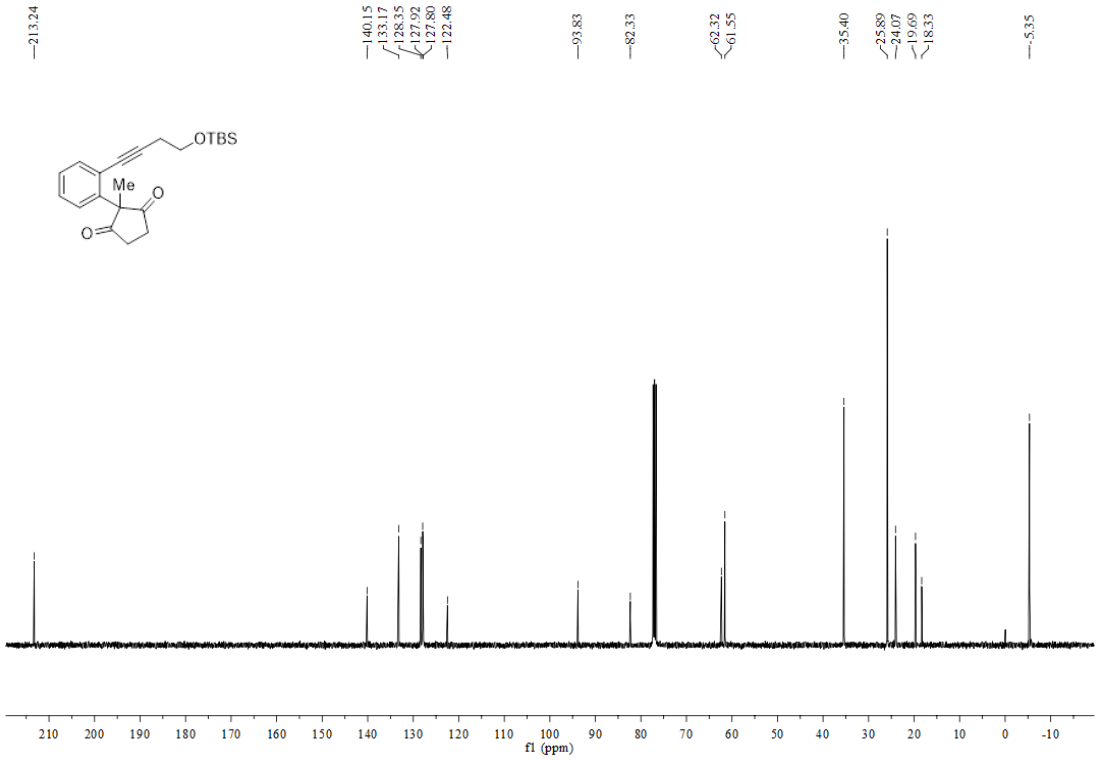

213.57
140.06
137.77
133.39
128.46
127.98
127.87
127.85
127.81
122.42
93.70
82.05
73.26
67.98
62.50
35.36
21.27
19.75
OBn
Me
O
O
f1 (ppm)

2-(2-(4-((tert-Butyldimethylsilyl)oxy)but-1-yn-1-yl)phenyl)-2-methylcyclopentane-1,3-dione (1t)

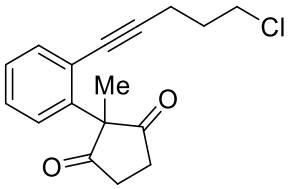


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); white solid, Mp = 100-101 °C; 88% yield (for the last step); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 7.6 Hz, 1H), 7.39-7.34 (m, 2H), 7.29-7.23 (m, 1H), 3.77 (t, J = 6.8 Hz, 2H), 3.13-3.06 (m, 2H), 2.97-2.87 (m, 2H), 2.55 (t, J = 6.8 Hz, 2H), 1.57 (s, 3H), 0.90 (s, 9H), 0.08 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.2, 140.2, 133.2, 128.4, 127.9, 127.8, 122.5, 93.8, 82.3, 62.3, 61.6, 35.4, 25.9, 24.1, 19.7, 18.3, -5.4. HRMS m/z (ESI+): Calculated for $C_{22}H_{30}NaO_3Si^+$ ([M+Na]$^+$) 393.1856, found 393.1854.

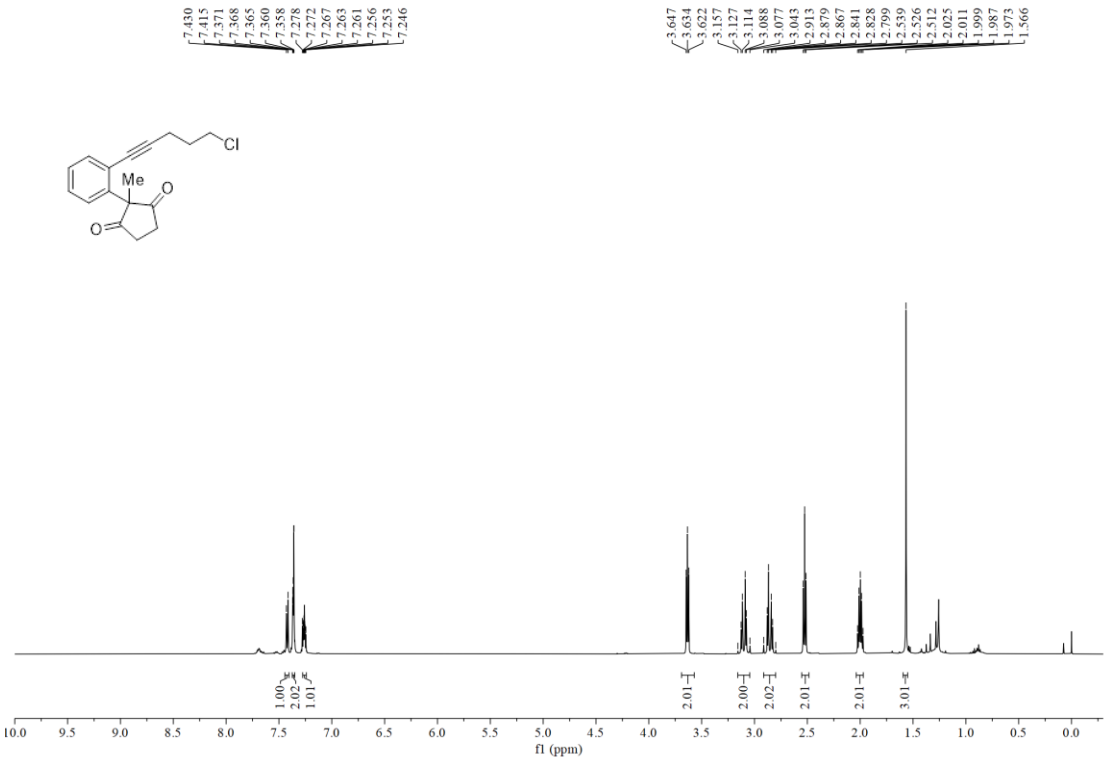


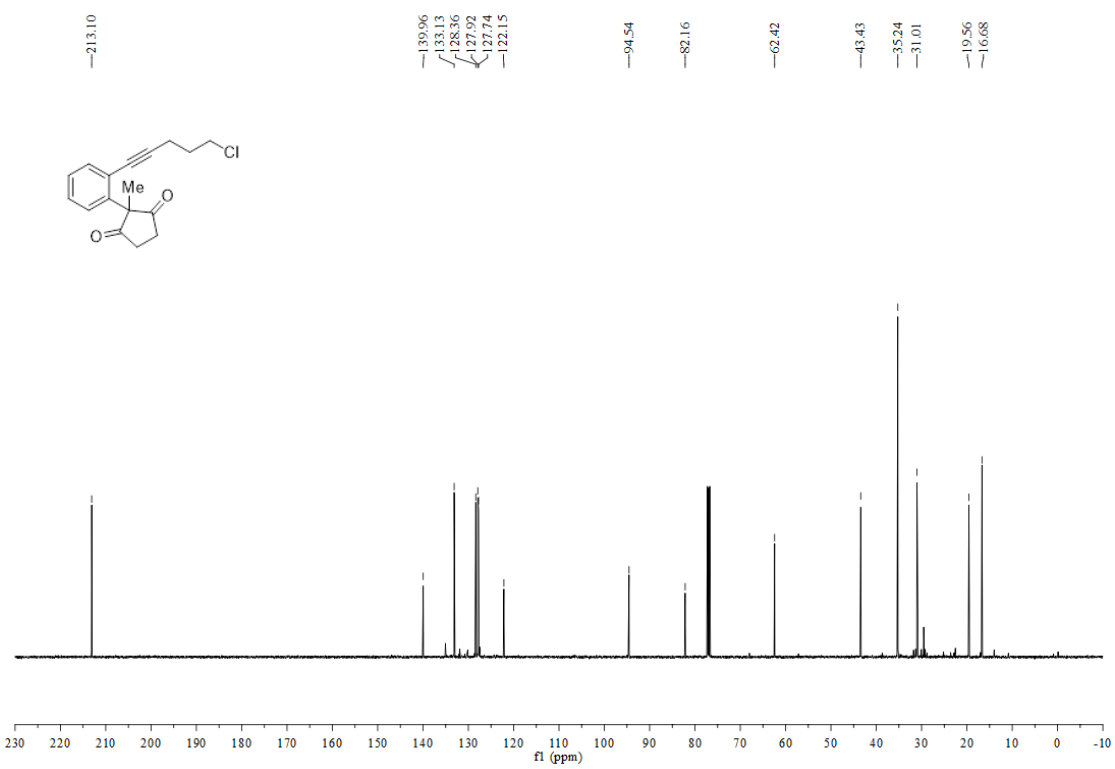


2-(2-(5-Chloropent-1-yn-1-yl)phenyl)-2-methylcyclopentane-1,3-dione (1u)

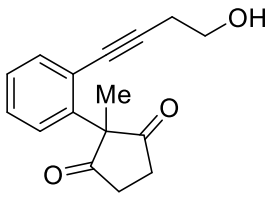


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow oil; 79% yield (for the last step); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, J = 7.0 Hz, 1H), 7.37-7.36 (m, 2H), 7.28-7.25 (m, 1H), 3.63 (t, J = 6.0 Hz, 2H), 3.16-3.04 (m, 2H), 2.91-2.80 (m, 2H), 2.53 (t, J = 6.5 Hz, 2H), 2.04-1.97 (m, 2H), 1.57 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 213.1, 140.0, 133.1, 128.4, 127.9, 127.7, 122.2, 94.5, 82.2, 62.4, 43.4, 35.2, 31.0, 19.6, 16.7. HRMS *m/z* (ESI+): Calculated for $C_{17}H_{17}ClNaO_2^+$ ([M+Na]$^+$) 311.0809, found 311.0808.

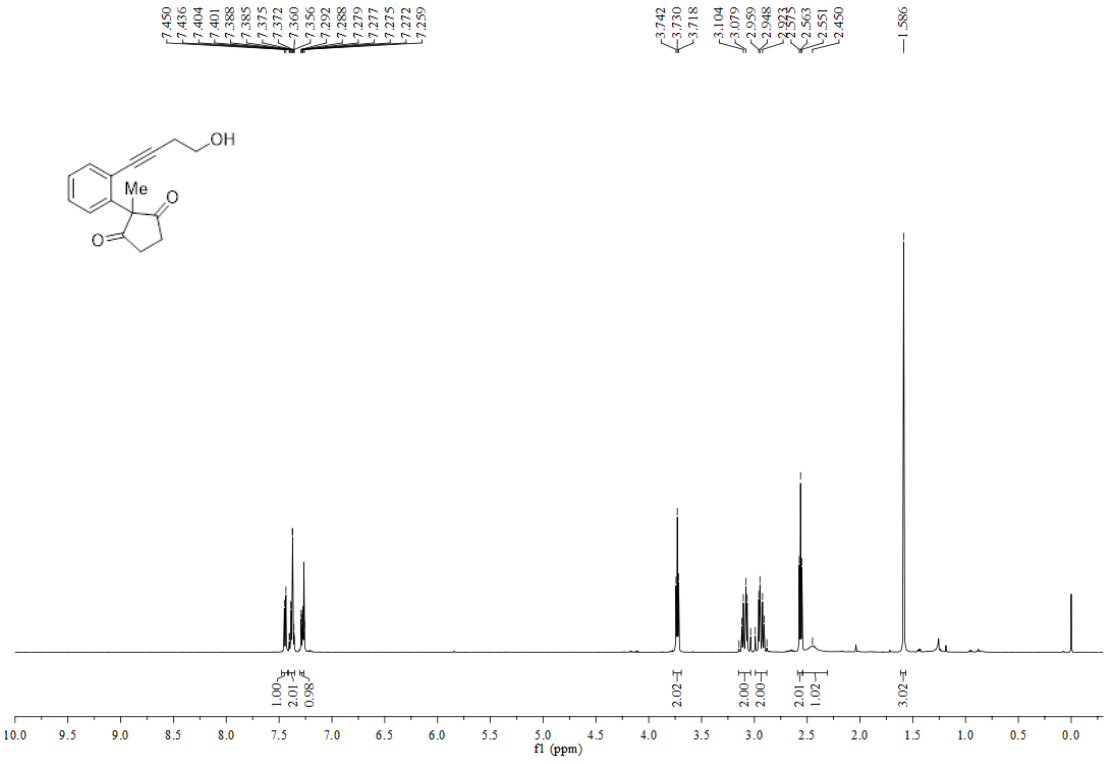

7.430
7.415
7.371
7.368
7.365
7.360
7.358
7.278
7.272
7.267
7.263
7.261
7.256
7.253
7.246
3.647
3.634
3.622
3.157
3.127
3.114
3.088
3.077
3.043
2.913
2.879
2.867
2.841
2.828
2.799
2.539
2.526
2.512
2.025
2.011
1.999
1.987
1.973
1.566
Cl
Me
O
O
1.00
2.02
1.01
2.01
2.00
2.02
2.01
2.01
3.01
10.0 9.5 9.0 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)

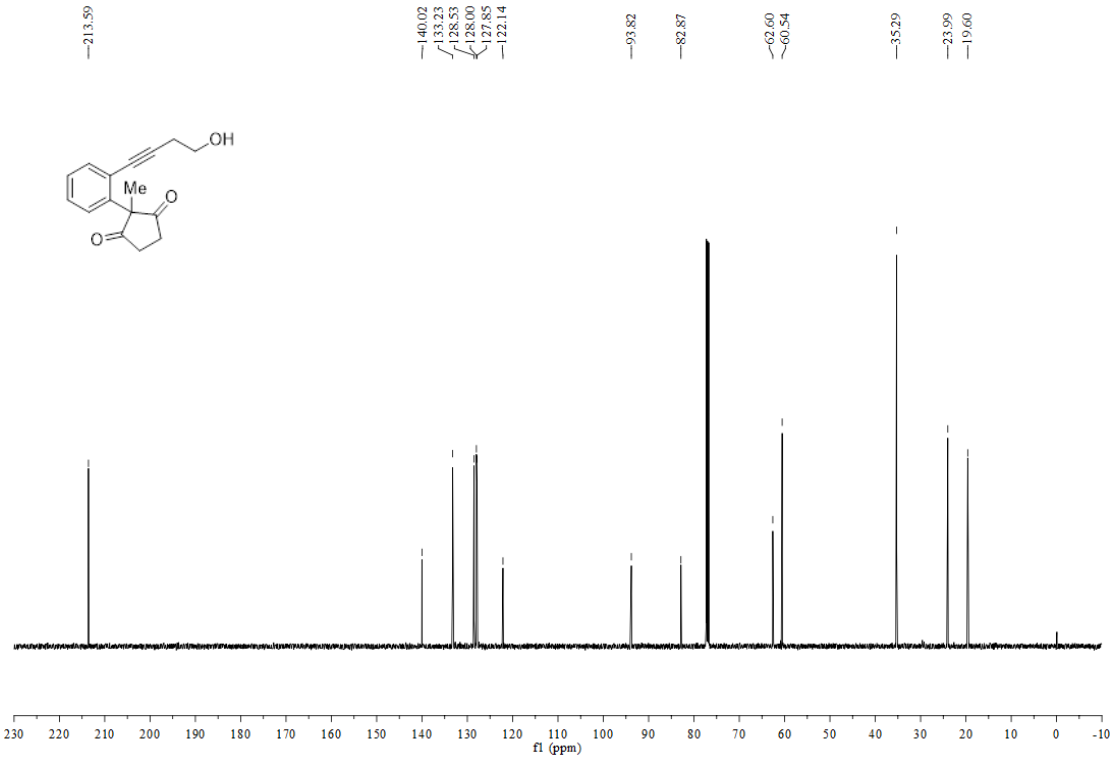

213.10
139.96
133.13
128.36
127.92
127.74
122.15
94.54
82.16
62.42
43.43
35.24
31.01
19.56
16.68
Cl
Me
O
O
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

2-(2-(4-Hydroxybut-1-yn-1-yl)phenyl)-2-methylcyclopentane-1,3-dione (1v)

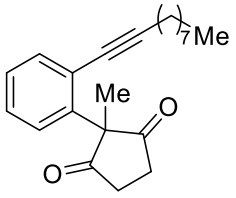


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); white solid, Mp = 155-156 °C; 69% yield (for the last step); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, J = 7.0 Hz, 1H), 7.40-7.36 (m, 2H), 7.29-7.26 (m, 1H), 3.73 (t, J = 6.0 Hz, 2H), 3.11-3.08 (m, 2H), 2.96-2.92 (m, 2H), 2.56 (t, J = 6.0 Hz, 2H), 2.45 (s, 1H), 1.59 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 213.6, 140.0, 133.2, 128.5, 128.0, 127.9, 122.1, 93.8, 82.9, 62.6, 60.5, 35.3, 24.0, 19.6. HRMS *m*/*z* (ESI+): Calculated for $C_{16}H_{16}O_3Na^+$ ([M+Na]$^+$) 279.0992, found 279.0992.

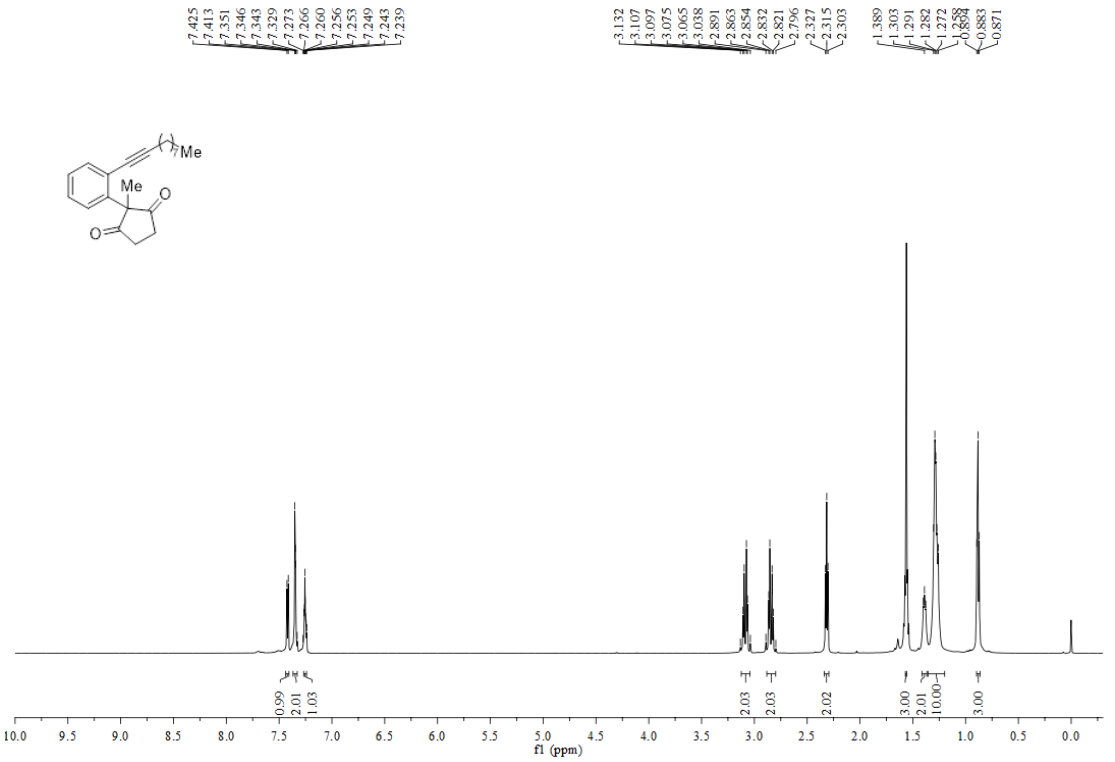


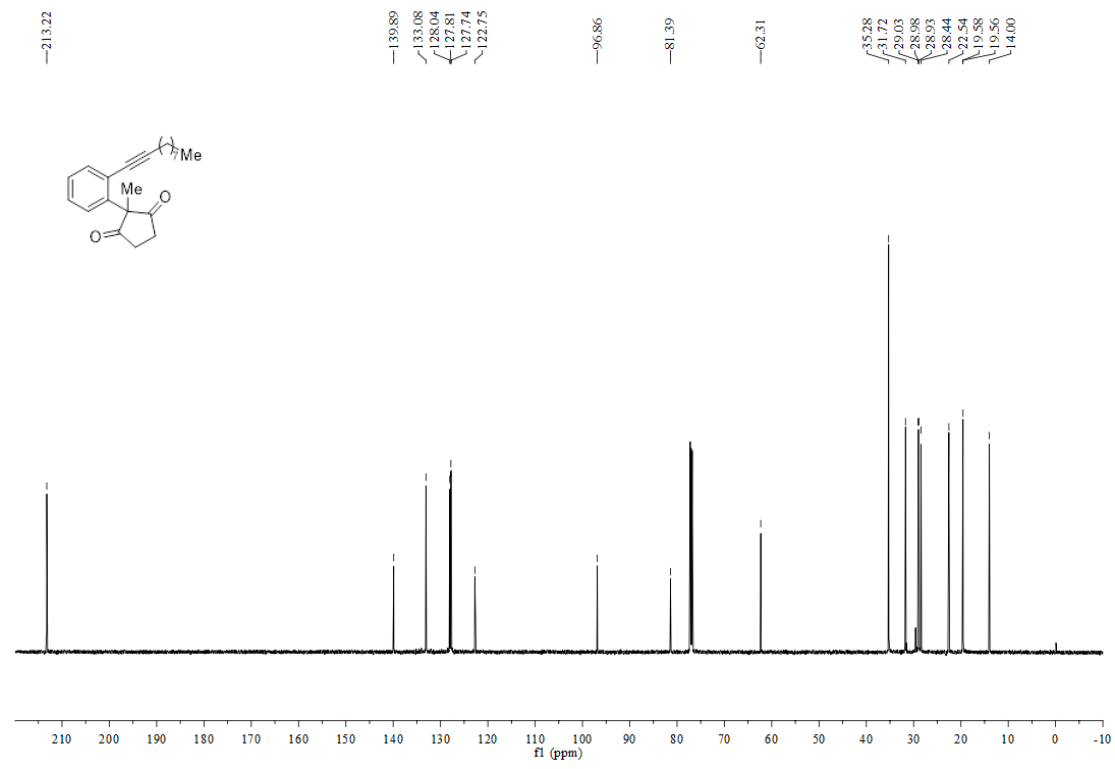


2-(2-(Dec-1-yn-1-yl)phenyl)-2-methylcyclopentane-1,3-dione (1w)

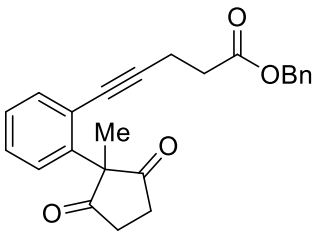


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); brown solid, Mp = 73-74 °C; 69% yield (for the last step); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (d, J = 7.2 Hz, 1H), 7.35-7.33 (m, 2H), 7.27-7.24 (m, 1H), 3.13-3.04 (m, 2H), 2.89-2.80 (m, 2H), 2.31 (t, J = 7.2 Hz, 2H), 1.56 (s, 3H), 1.39-1.35 (m, 2H), 1.34-1.26 (m, 10H), 0.88 (t, J = 6.6 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 213.2, 139.9, 133.1, 128.0, 127.8, 127.7, 122.8, 96.9, 81.4, 62.3, 35.3, 31.7, 29.03, 28.98, 28.9, 28.4, 22.5, 19.58, 19.56, 14.00. HRMS *m*/*z* (ESI+): Calculated for $C_{22}H_{29}O_2^+$ ($[M+H]^+$) 325.2162, found 325.2162.

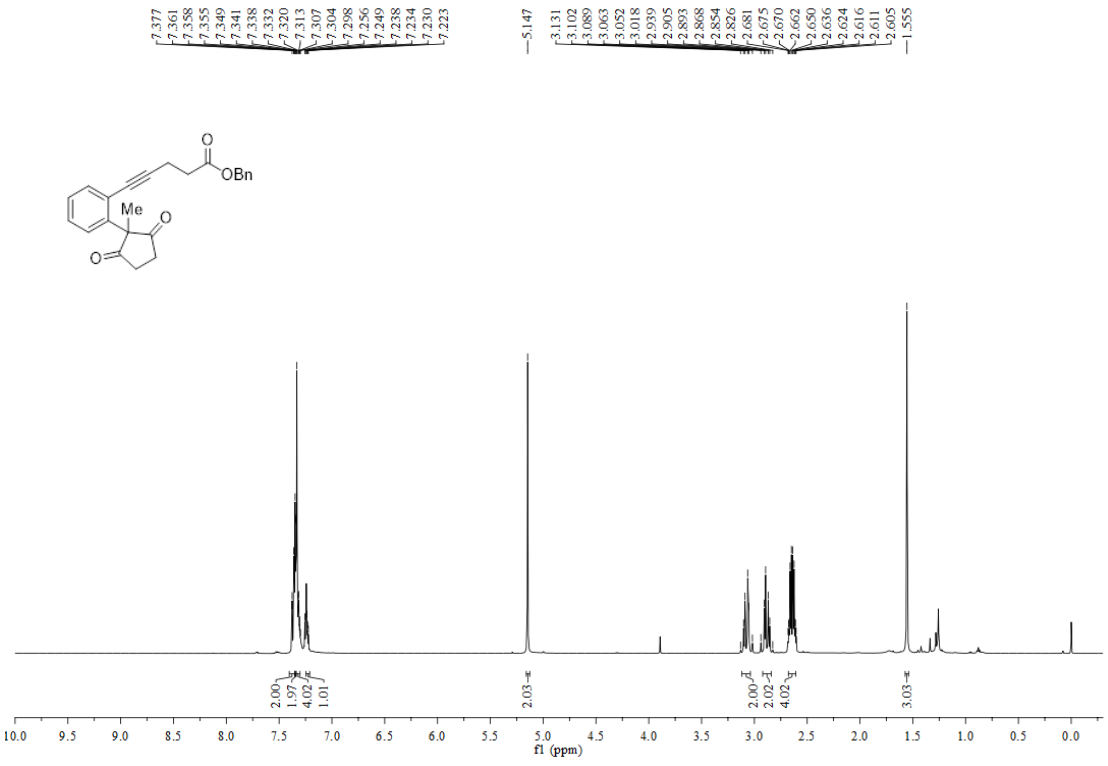

7.425
7.413
7.351
7.346
7.343
7.329
7.273
7.266
7.260
7.256
7.253
7.249
7.243
7.239
3.132
3.107
3.097
3.075
3.065
3.038
2.891
2.863
2.854
2.832
2.821
2.796
2.327
2.315
2.303
1.389
1.303
1.291
1.282
1.272
0.888
0.883
0.871
Me
Me
O
O
0.99
2.01
1.03
2.03
2.03
2.02
3.00
2.01
10.00
3.00
f1 (ppm)

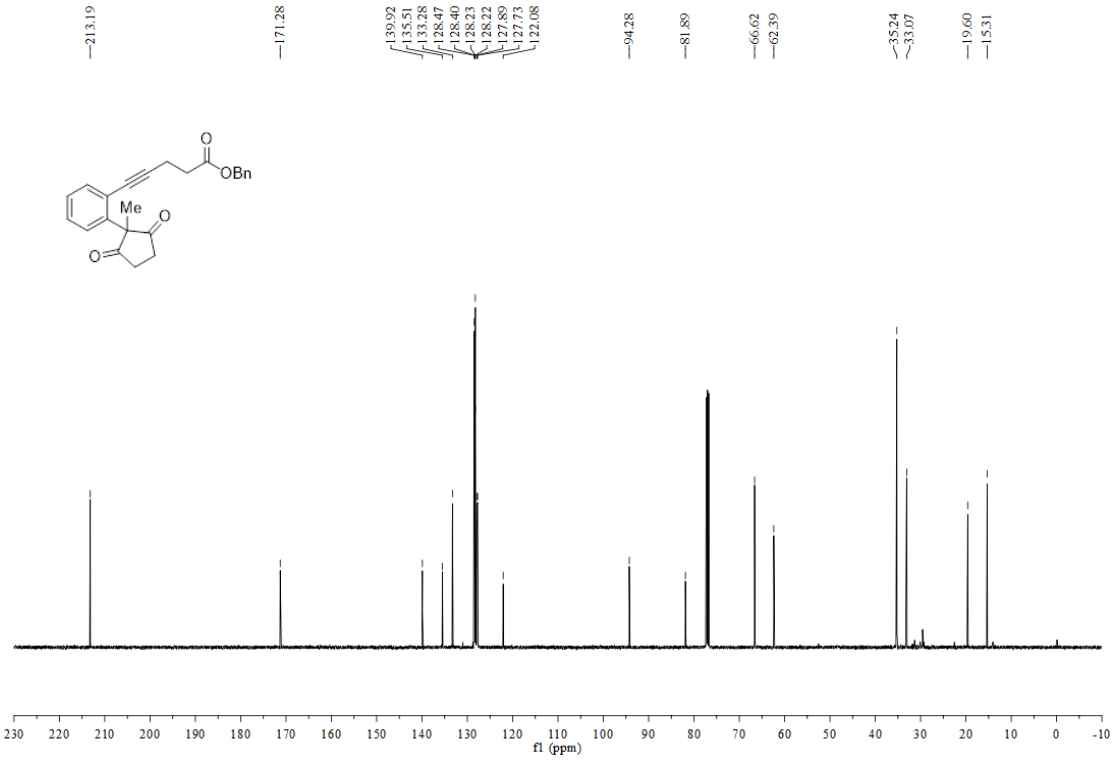

213.22
139.89
133.08
128.04
127.81
127.74
122.75
96.86
81.39
62.31
35.28
31.72
29.03
28.98
28.93
28.44
22.54
19.58
19.56
14.00
Me
Me
O
O
f1 (ppm)

Benzyl 5-(2-(1-methyl-2,5-dioxocyclopentyl)phenyl)pent-4-ynoate (1x)

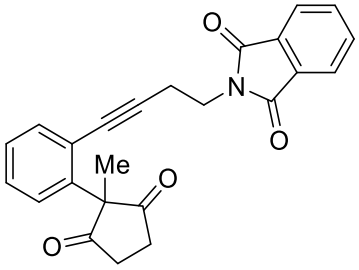


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow oil; 70% yield (for the last step); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.35 (m, 2H), 7.34-7.30 (m, 4H), 7.26-7.22 (m, 1H), 5.15 (s, 2H), 3.13-3.02 (m, 1H), 2.94-2.83 (m, 1H), 2.68-2.61 (m, 1H), 1.56 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 213.2, 171.3, 139.9, 135.5, 133.3, 128.5, 128.4, 128.23, 128.22, 127.9, 127.7, 122.1, 94.3, 81.9, 66.6, 62.4, 35.2, 33.1, 19.6, 15.3. HRMS *m*/*z* (ESI+): Calculated for $C_{24}H_{22}NaO_4^+$ ([M+Na]$^+$) 397.1410, found 397.1408.

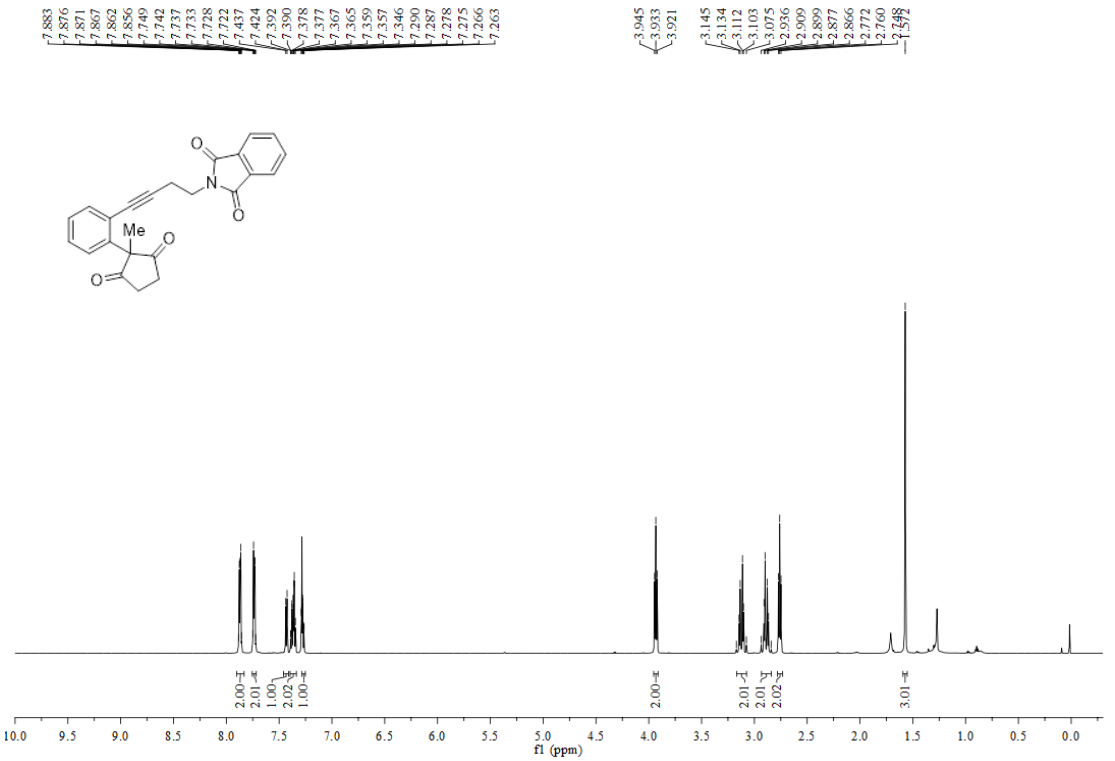


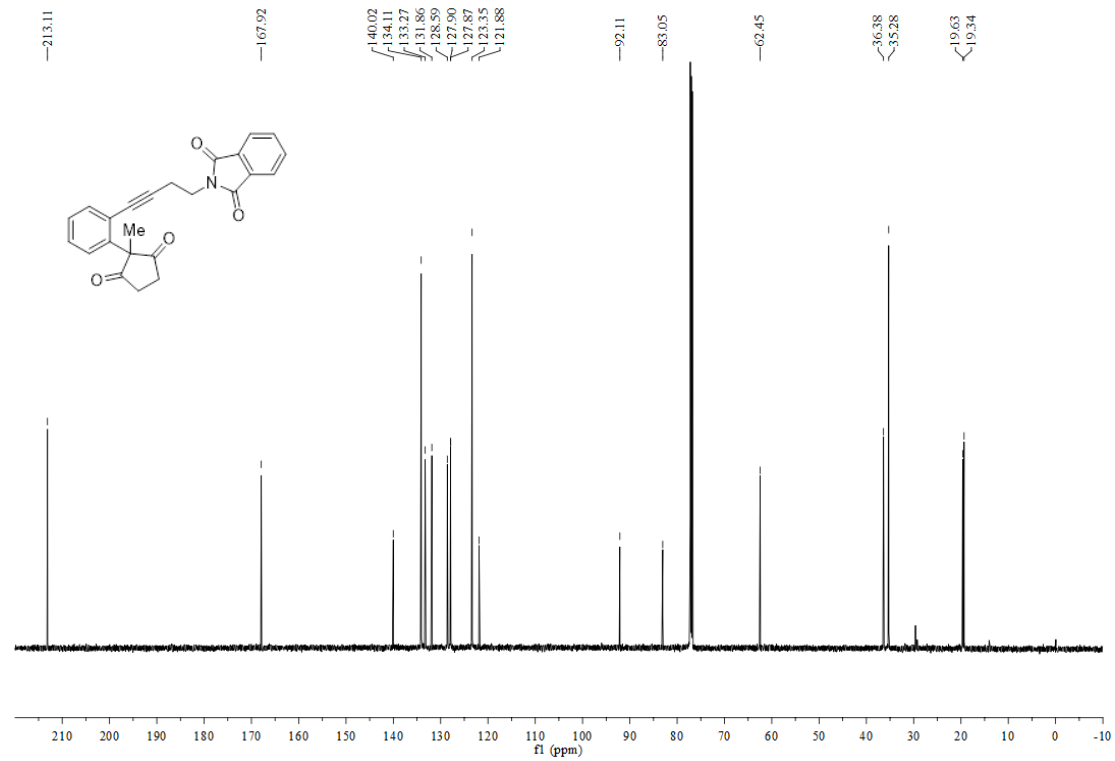


2-(4-(2-(1-Methyl-2,5-dioxocyclopentyl)phenyl)but-3-yn-1-yl)isoindoline-1,3-dione (1y)

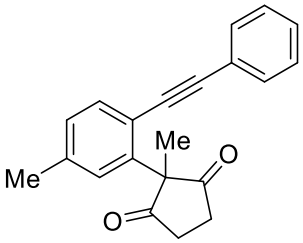


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); brown solid, Mp = 200-201 °C; 67% yield (for the last step); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88-7.86 (m, 2H), 7.75-7.72 (m, 2H), 7.43 (d, J = 7.8 Hz, 1H), 7.39-7.35 (m, 2H), 7.29-7.26 (m, 1H), 3.93 (t, J = 7.2 Hz, 2H), 3.15-3.08 (m, 2H), 2.94-2.87(m, 2H), 2.76 (t, J = 7.2 Hz, 2H), 1.57 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 213.1, 167.9, 140.0, 134.1, 133.3, 131.9, 128.6, 127.90, 127.87, 123.4, 121.9, 92.1, 83.1, 62.5, 36.4, 35.3, 19.6, 19.3. HRMS *m/z* (ESI+): Calculated for $C_{24}H_{19}NNaO_4^+$ ($[M+Na]^+$) 408.1206, found 408.1203.

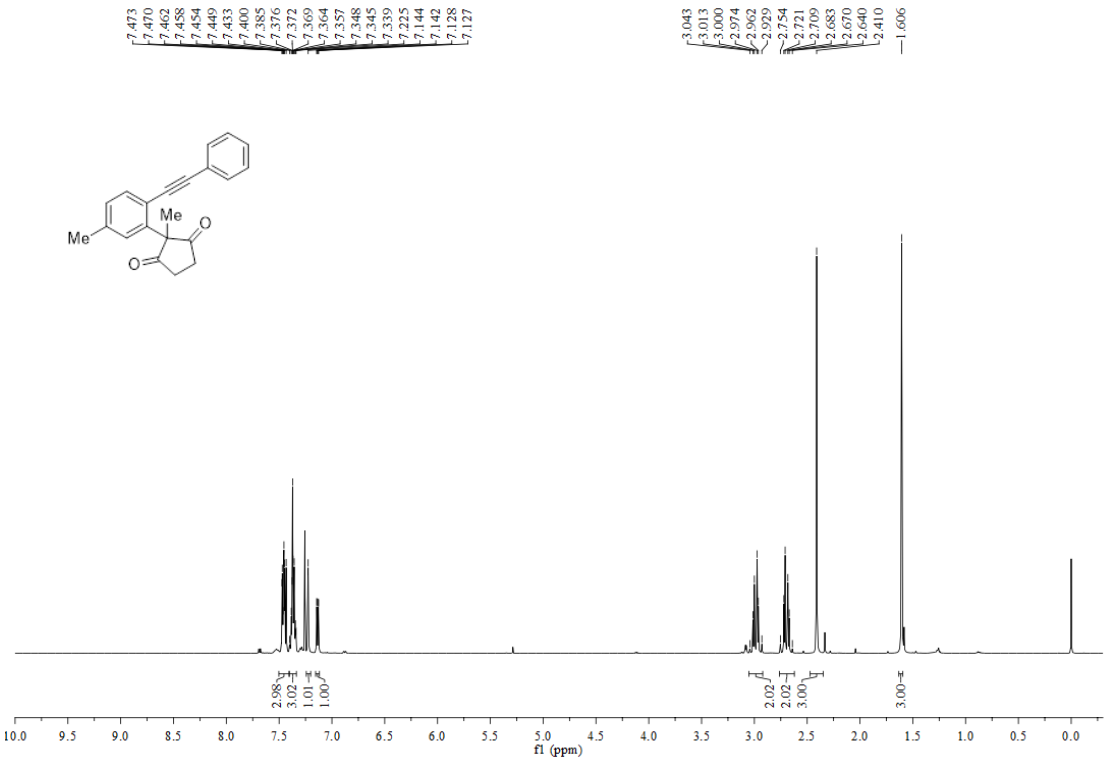

7.883
7.876
7.871
7.867
7.862
7.856
7.749
7.742
7.737
7.733
7.728
7.722
7.437
7.424
7.392
7.390
7.378
7.377
7.367
7.365
7.359
7.357
7.346
7.290
7.287
7.278
7.275
7.266
7.263
3.945
3.933
3.921
3.145
3.134
3.112
3.103
3.075
2.936
2.909
2.899
2.877
2.866
2.772
2.760
2.748
1.572
Me
O
N
2.00
2.01
1.00
2.02
1.00
2.00
2.01
2.01
2.02
3.01
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)

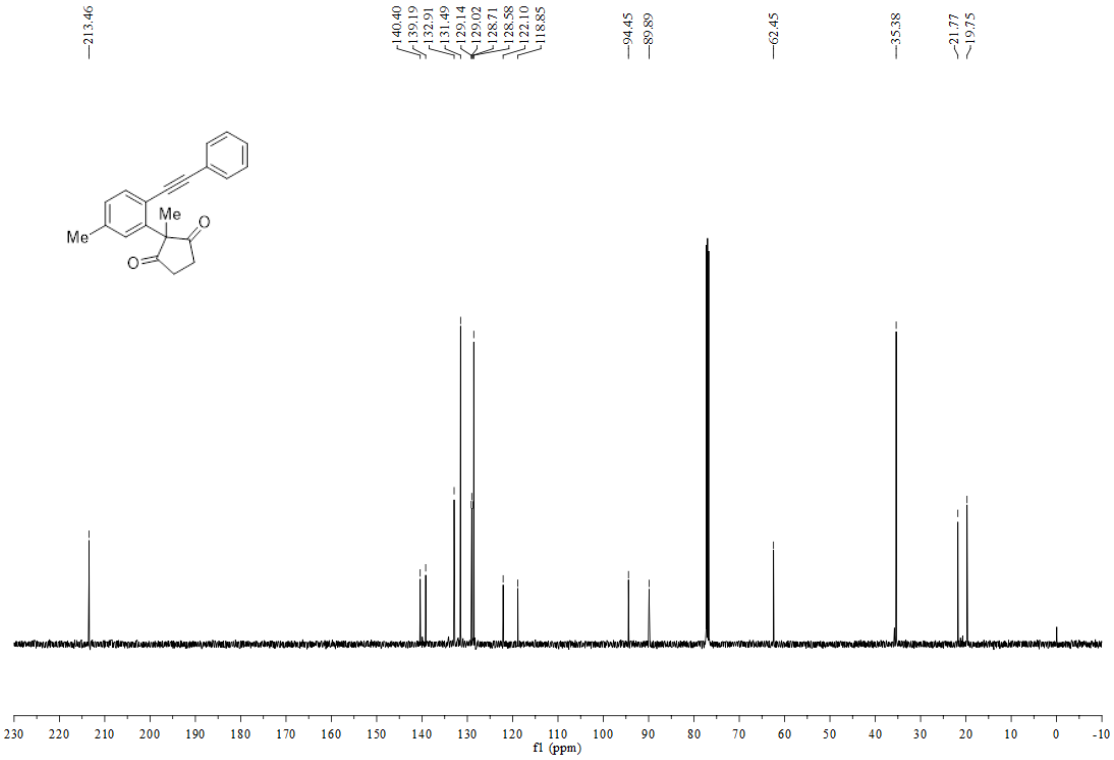

213.11
167.92
140.02
134.11
133.27
131.86
128.59
127.90
127.87
123.35
121.88
92.11
83.05
62.45
36.38
35.28
19.63
19.34
Me
O
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

2-Methyl-2-(5-methyl-2-(phenylethynyl)phenyl)cyclopentane-1,3-dione(1z)

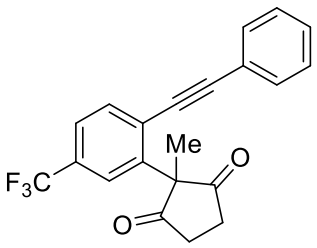


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow solid, Mp = 179-180 °C; 65% yield (for the last step); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47-7.43 (m, 3H), 7.40-7.34 (m, 3H), 7.23 (s, 1H), 7.14-7.13 (m, 1H), 3.04-2.93 (m, 2H), 2.75-2.64 (m, 2H), 2.41 (s, 3H), 1.61 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 213.5, 140.4, 139.2, 132.9, 131.5, 129.1, 129.0, 128.7, 128.6, 122.1, 118.9, 94.5, 89.9, 62.5, 35.4, 21.8, 19.8. HRMS *m/z* (ESI+): Calculated for $C_{21}H_{19}O_2^+$ ($[M+H]^+$) 303.1380, found 303.1382.

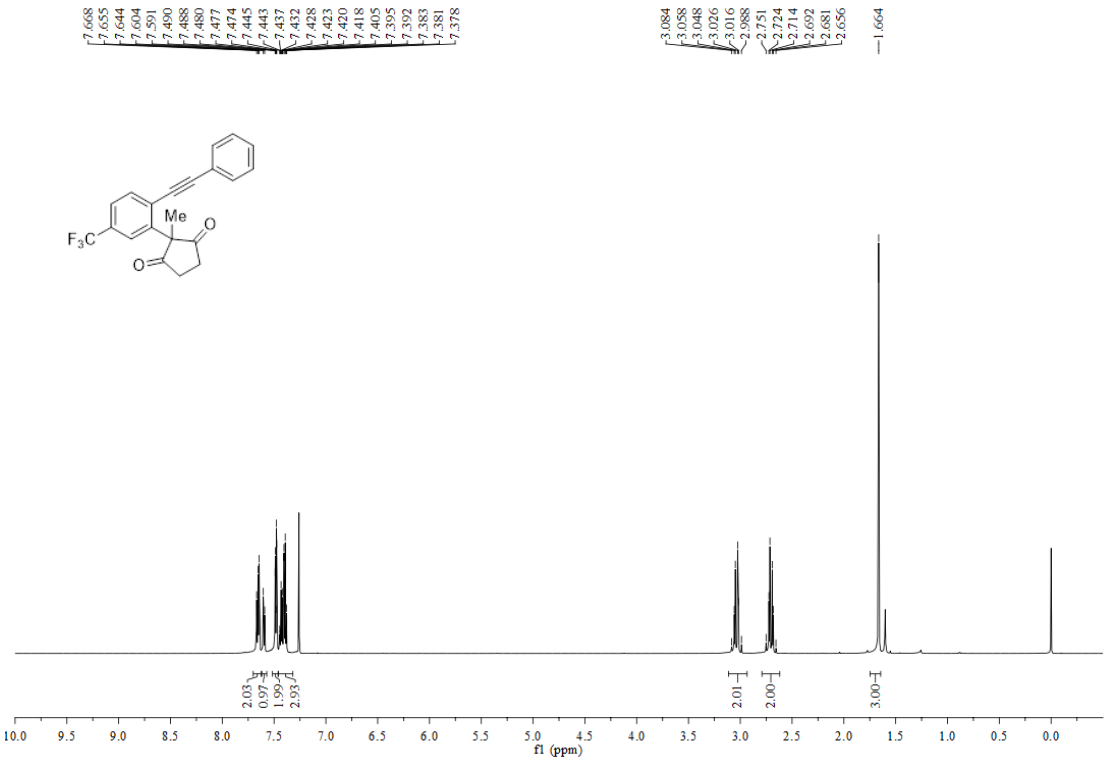


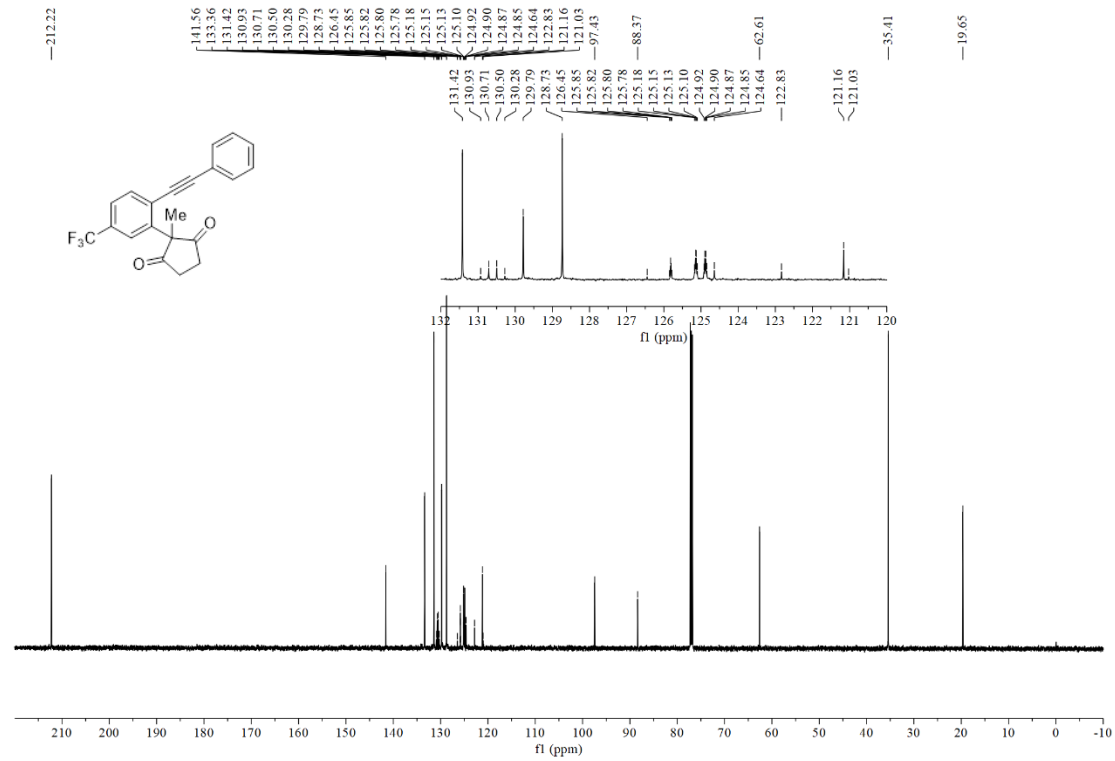


2-Methyl-2-(2-(phenylethynyl)-5-(trifluoromethyl)phenyl)cyclopentane-1,3-dione (1aa)

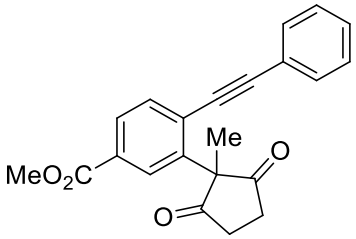


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); white solid, Mp = 164-165 °C; 75% yield (for the last step); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67-7.60 (m, 2H), 7.59 (d, J = 8.4 Hz, 1H), 7.49-7.47 (m, 2H), 7.45-7.38 (m, 3H), 3.08-2.99 (m, 2H), 2.75-2.66 (m, 2H), 1.66 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 212.2, 141.6, 133.4, 131.4, 130.6 (q, J = 33.0 Hz), 129.8, 128.7, 125.8 (q, J = 3.0 Hz), 125.1 (q, J = 4.5 Hz), 124.9 (q, J = 3.0 Hz), 123.7 (q, J = 271.5 Hz), 121.2, 97.4, 88.4, 62.6, 35.4, 19.7. HRMS (ESI) m/z Calculated for $C_{21}H_{15}F_3O_2Na^+$ ([M+Na]$^+$) 379.0916, found 379.0920.

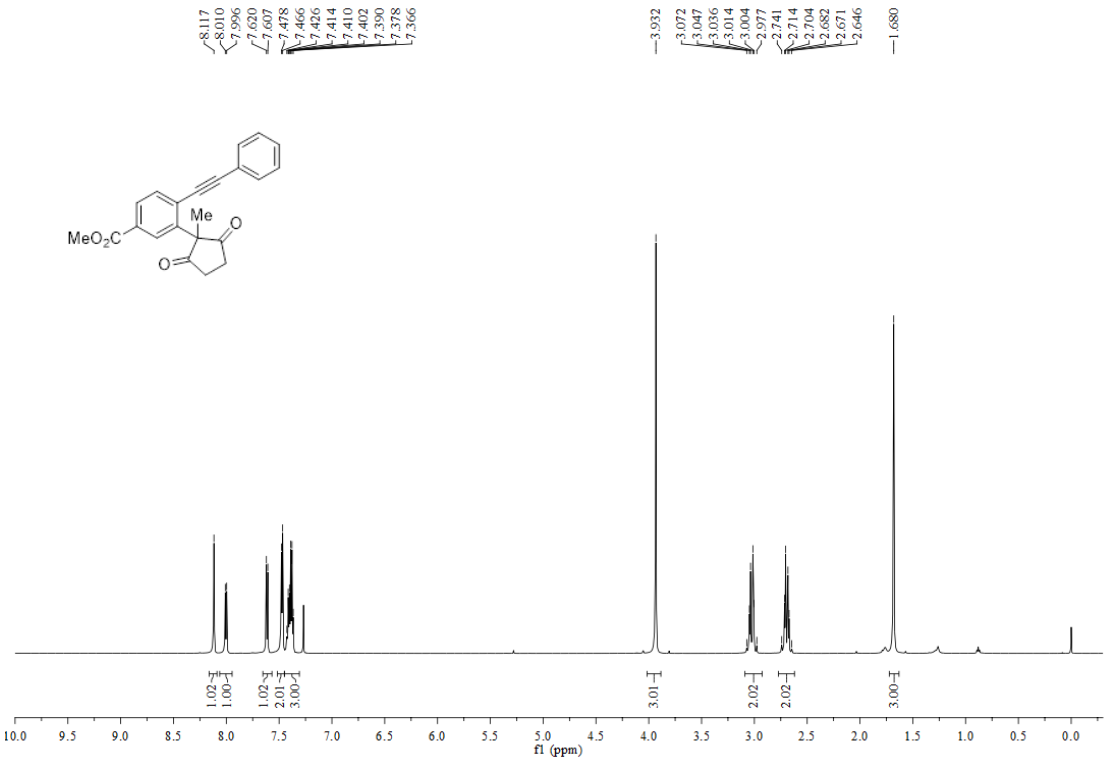

7.668
7.655
7.644
7.604
7.591
7.490
7.488
7.480
7.477
7.474
7.445
7.443
7.437
7.432
7.428
7.423
7.420
7.418
7.405
7.395
7.392
7.383
7.381
7.378
3.084
3.058
3.048
3.026
3.016
2.988
2.751
2.724
2.714
2.692
2.681
2.656
1.664
Me
O
O
F3C
2.03
0.97
1.99
2.93
2.01
2.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 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)

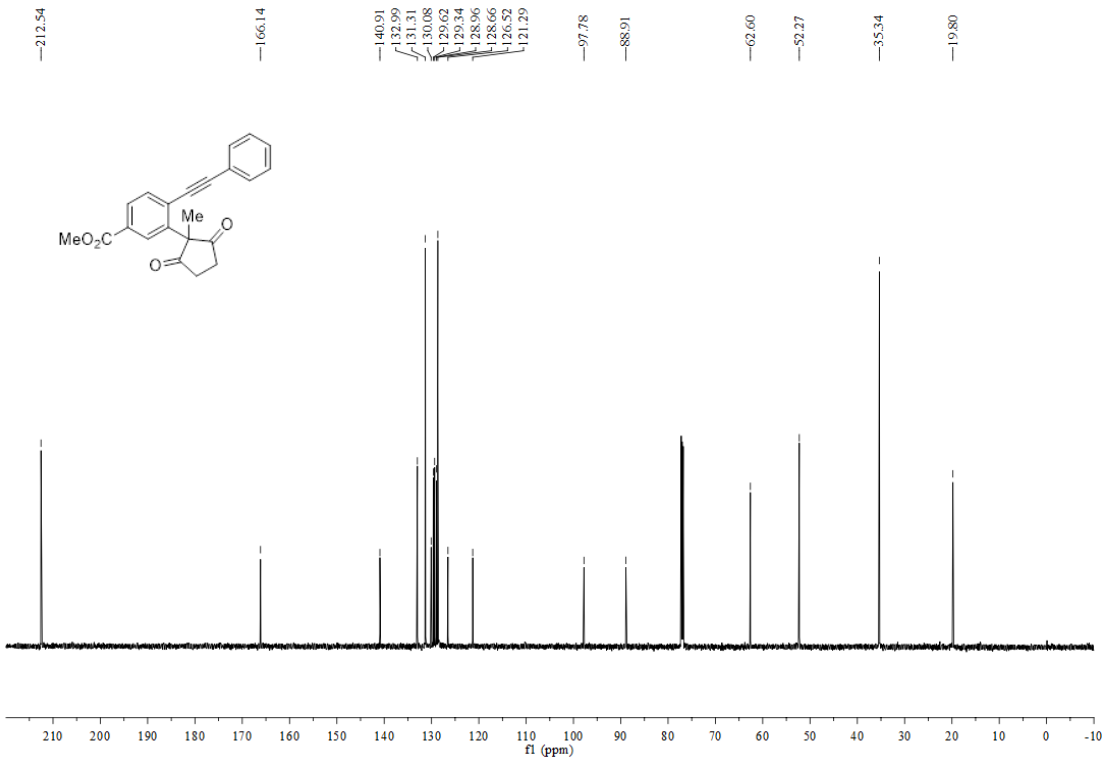

212.22
141.56
133.36
131.42
130.93
130.71
130.50
130.28
129.79
128.73
126.45
125.85
125.82
125.80
125.78
125.18
125.15
125.13
125.10
124.92
124.90
124.87
124.85
124.64
122.83
121.16
121.03
97.43
88.37
62.61
35.41
19.65
Me
O
O
F3C
132 131 130 129 128 127 126 125 124 123 122 121 120
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Methyl 3-(1-methyl-2,5-dioxocyclopentyl)-4-(phenylethynyl)benzoate (1ab)

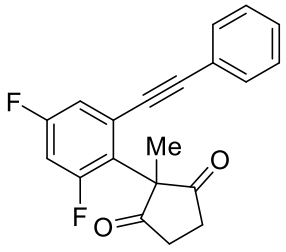


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); brown solid, Mp = 133-134 °C; 60% yield (for the last step); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (s, 1H), 8.00 (d, J = 8.4 Hz, 1H), 7.61 (d, J = 7.8 Hz, 1H), 7.47 (d, J = 7.2 Hz, 2H), 7.43-7.37 (m, 3H), 3.93 (s, 3H), 3.07-2.98 (m, 2H), 2.74-2.65 (m, 2H), 1.68 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 212.5, 166.1, 140.9, 133.0, 131.3, 130.1, 129.6, 129.3, 129.0, 128.7, 126.5, 121.3, 97.8, 88.9, 62.6, 52.3, 35.3, 19.8. HRMS *m*/*z* (ESI+): Calculated for $C_{22}H_{19}O_4^+$ ([M+H]$^+$) 347.1278, found 347.1281.

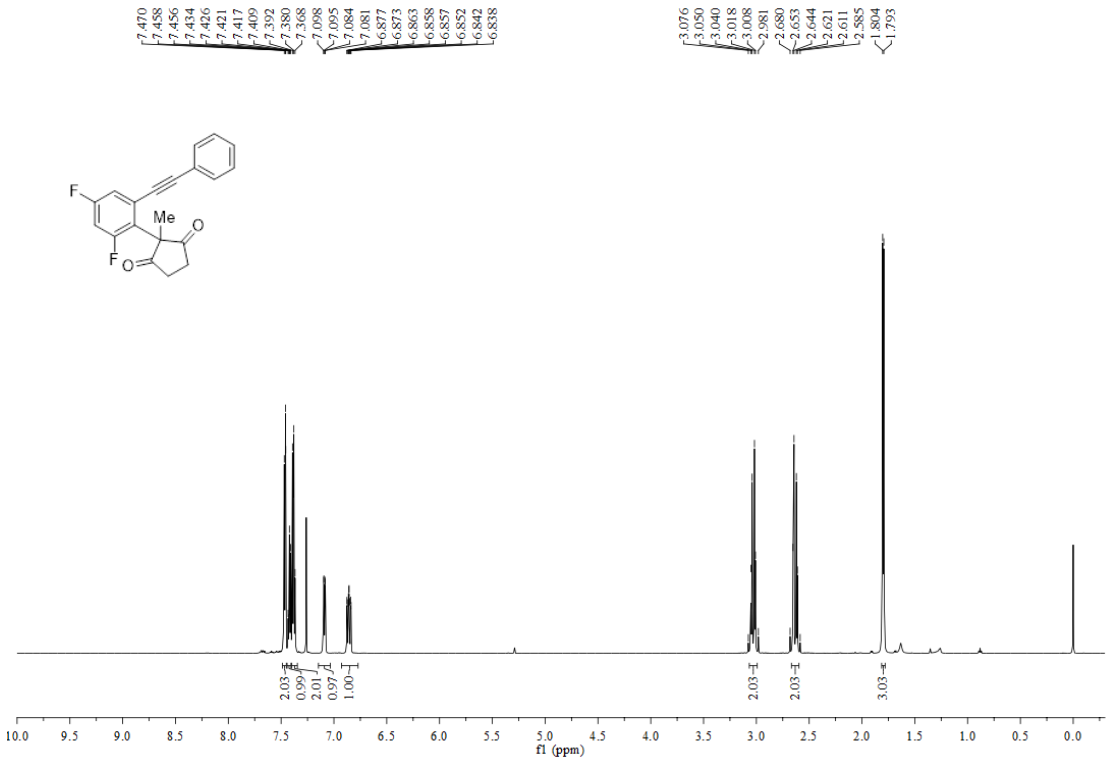


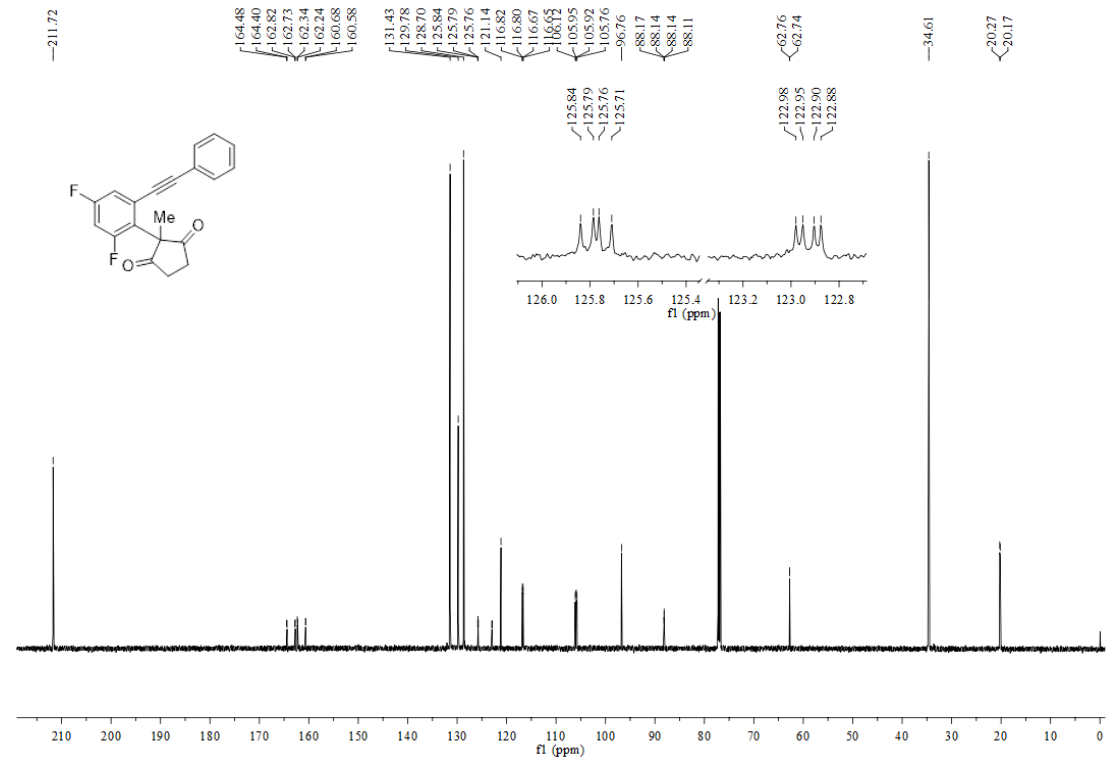


2-(2,4-Difluoro-6-(phenylethynyl)phenyl)-2-methylcyclopentane-1,3-dione (1ac)

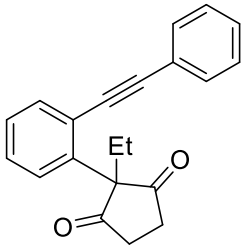


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow solid, Mp = 120-121 °C; 76% yield (for the last step); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47-7.46 (m, 2H), 7.43-7.41 (m, 1H), 7.38 (t, J = 7.2 Hz, 2H), 7.09 (dd, J = 8.4, 1.8 Hz, 1H), 6.88-6.84 (m, 1H), 3.08-2.98 (m, 2H), 2.68-2.59 (m, 2H), 1.80 (d, J = 6.6 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 211.7, 163.6 (dd, J = 249.0, 12.0 Hz), 161.5 (dd, J = 249.0, 15.0 Hz), 131.4, 129.8, 128.7, 125.8 (dd, J = 12.0, 7.5 Hz), 122.9 (dd, J = 11.4, 4.3 Hz), 121.1, 116.7 (dd, J = 22.5, 3.0 Hz), 105.9 (dd, J = 30.0, 24.0 Hz), 96.8, 88.1 (dd, J = 4.8, 3.8 Hz), 62.8 (d, J = 3.0 Hz), 34.6, 20.2 (d, J = 15.0 Hz). HRMS m/z (ESI+): Calculated for $C_{20}H_{15}F_2O_2^+$ ($[M+H]^+$) 325.1035, found 325.1034.

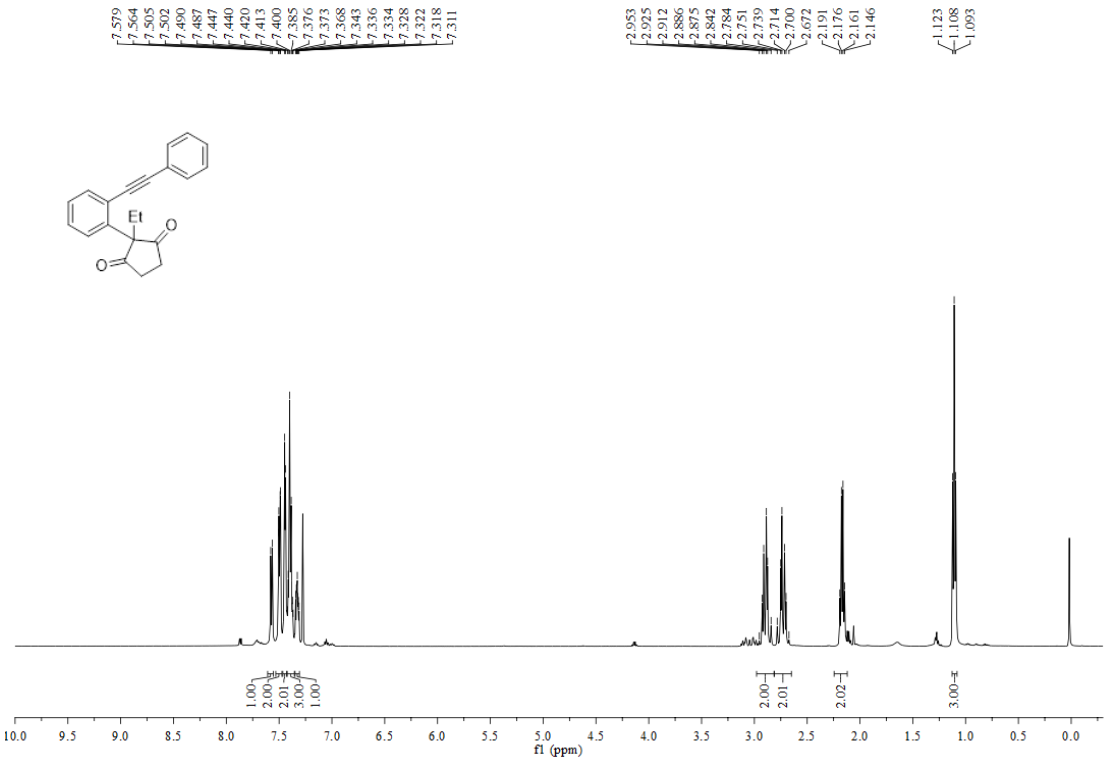

7.470
7.458
7.456
7.434
7.426
7.421
7.417
7.409
7.392
7.380
7.368
7.098
7.095
7.084
7.081
6.877
6.873
6.863
6.858
6.857
6.852
6.842
6.838
3.076
3.050
3.040
3.018
3.008
2.981
2.680
2.653
2.644
2.621
2.611
2.585
1.804
1.793
F
Me
O
F
O
2.03
0.99
2.01
0.97
1.00
2.03
2.03
3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 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)

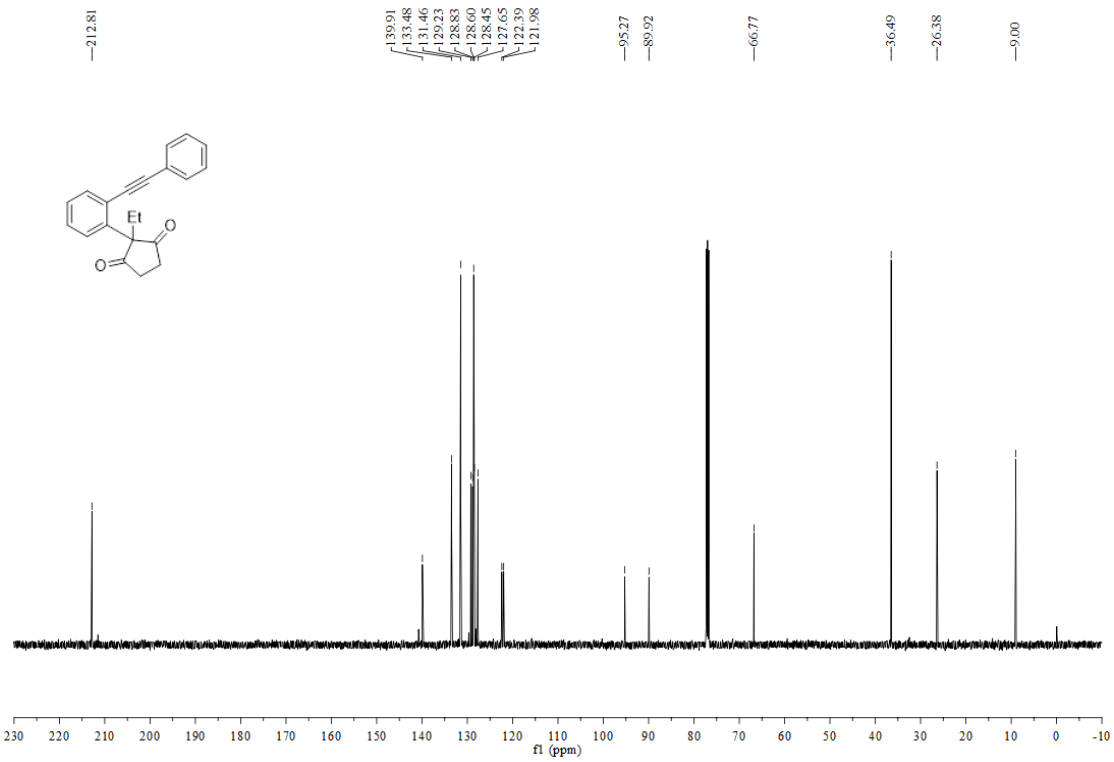

211.72
164.48
164.40
162.82
162.73
162.34
162.24
160.68
160.58
131.43
129.78
128.70
125.84
125.79
125.76
121.14
116.82
116.80
116.67
116.65
116.52
105.95
105.92
105.76
96.76
88.17
88.14
88.14
88.11
62.76
62.74
34.61
20.27
20.17
125.84
125.79
125.76
125.71
122.98
122.95
122.90
122.88
F
Me
O
F
O
126.0 125.8 125.6 125.4 123.2 123.0 122.8
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

2-Ethyl-2-(2-(phenylethynyl)phenyl)cyclopentane-1,3-dione (1ad)

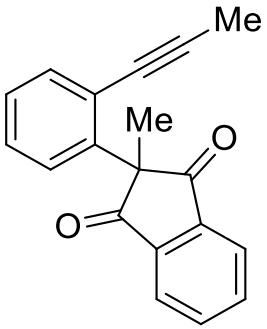


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow solid, Mp = 119-120 °C; 82% yield (for the last step); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, J = 7.5 Hz, 1H), 7.50 (dd, J = 7.5, 1.5 Hz, 2H), 7.44 (d, J = 3.5 Hz, 2H), 7.42-7.37 (m, 3H), 7.34-7.31 (m, 1H), 2.95-2.84 (m, 2H), 2.78-2.67 (m, 2H), 2.17 (q, J = 7.5 Hz, 2H), 1.11 (t, J = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.8, 139.9, 133.5, 131.4, 129.2, 128.8, 128.6, 128.5, 127.7, 122.4, 122.0, 95.3, 89.9, 66.8, 36.5, 26.4, 9.0. HRMS (ESI) m/z Calculated for $C_{21}H_{18}O_2Na^+$ ([M+Na]$^+$) 325.1199, found 325.1199.

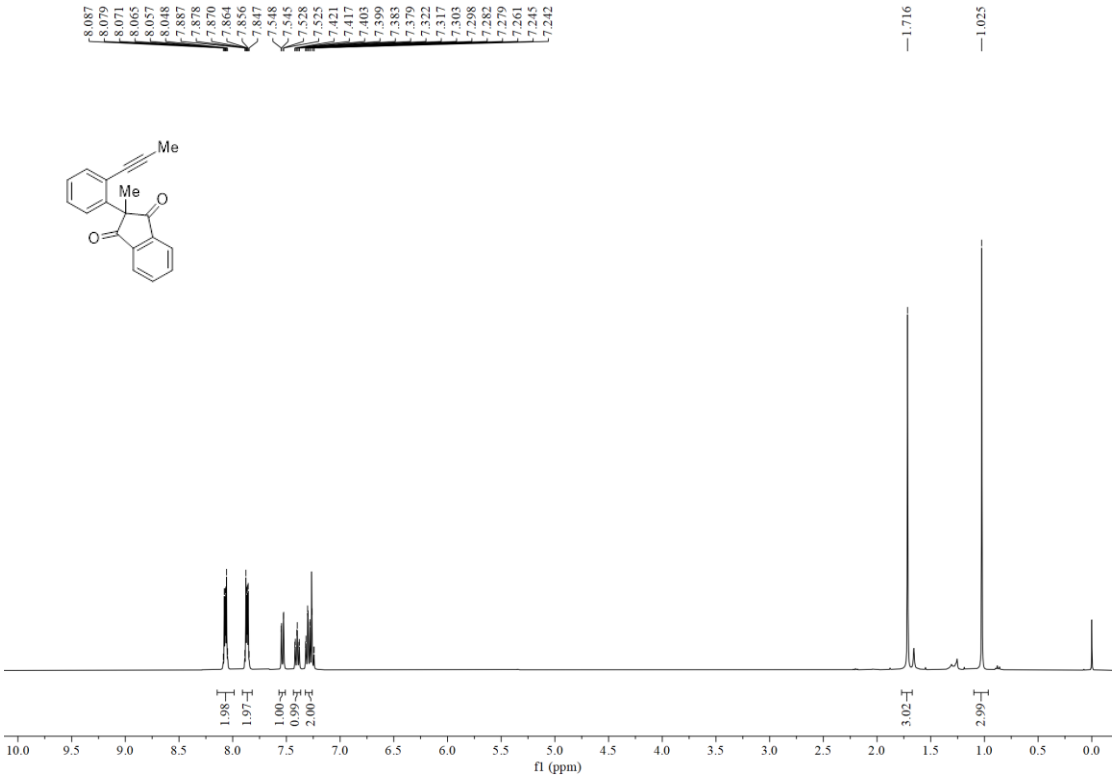


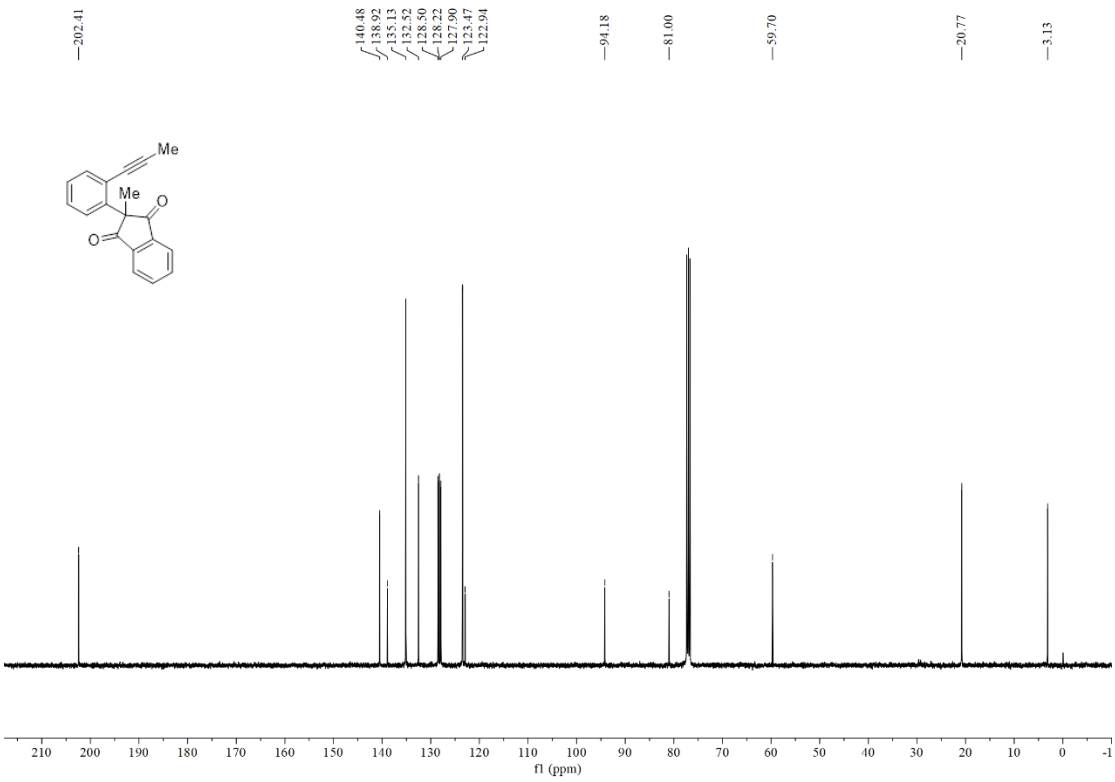


***2-Methyl-2-(2-(prop-1-yn-1-yl)phenyl)-1H-indene-1,3(2H)-dione* (*1ae*)**

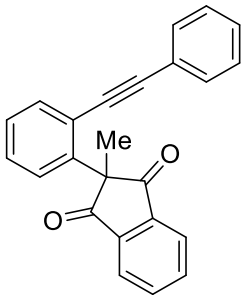


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow solid, Mp = 157-158 °C; 73% yield (for the last step); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09-8.05 (m, 2H), 7.89-7.85 (m, 2H), 7.55-7.53 (m, 1H), 7.42-7.38 (m, 1H), 7.32-7.24 (m, 2H), 1.72 (s, 3H), 1.03 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.4, 140.5, 138.9, 135.1, 132.5, 128.5, 128.2, 127.9, 123.5, 122.9, 94.2, 81.0, 59.7, 20.8, 3.1. HRMS *m*/*z* (ESI+): Calculated for $C_{19}H_{15}O_2^+$ ([M+H]$^+$) 275.1067, found 275.1062.

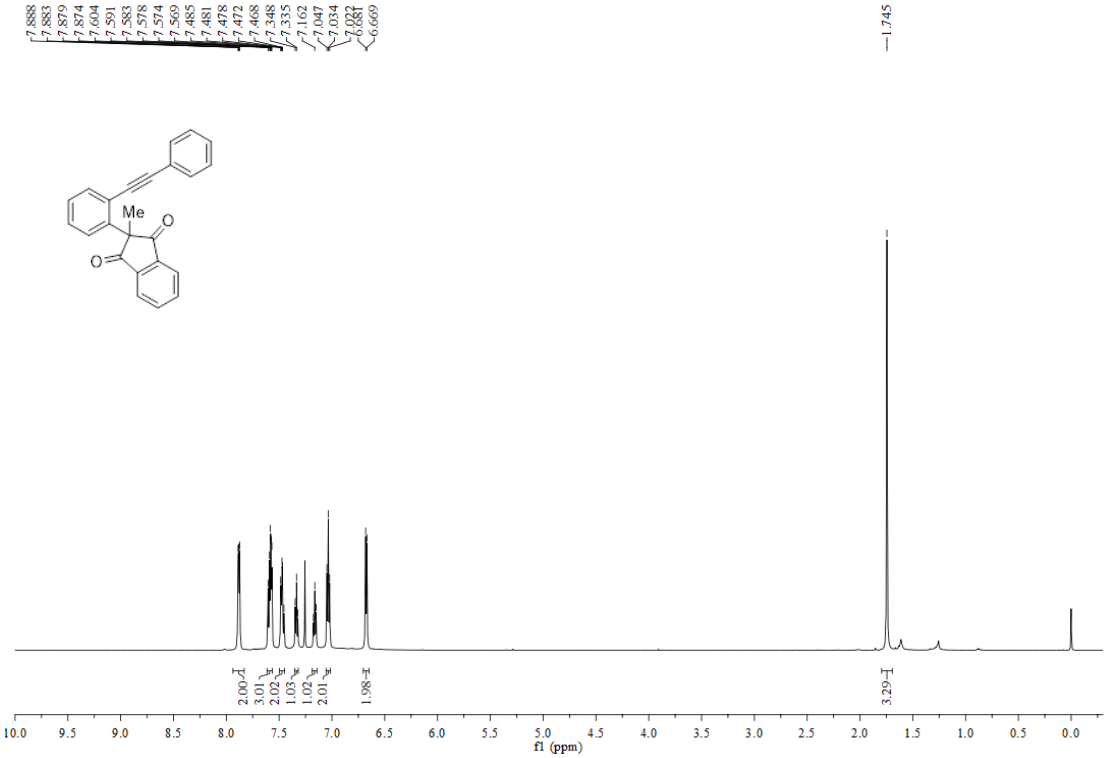

8.087
8.079
8.071
8.065
8.057
8.048
7.887
7.878
7.870
7.864
7.856
7.847
7.548
7.545
7.528
7.525
7.421
7.417
7.403
7.399
7.383
7.379
7.322
7.317
7.303
7.298
7.282
7.279
7.261
7.245
7.242
1.716
1.025
Me
Me
O
O
1.98
1.97
1.00
0.99
2.00
3.02
2.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

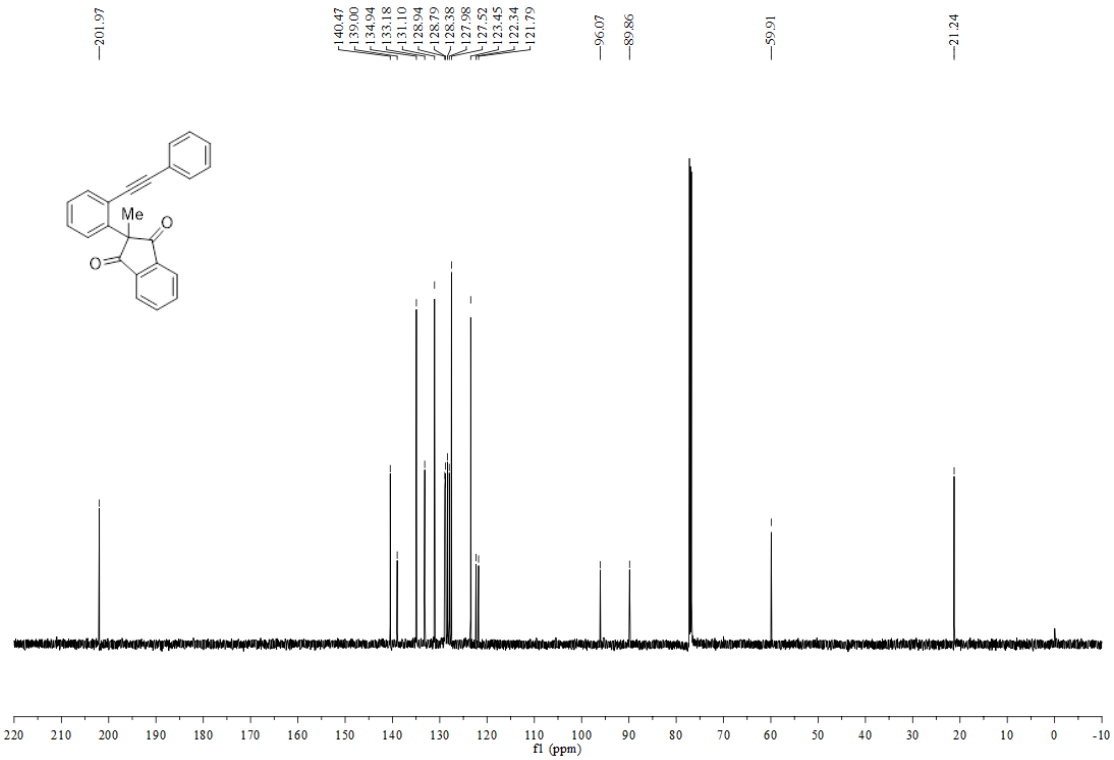

202.41
140.48
138.92
135.13
132.52
128.50
128.22
127.90
123.47
122.94
94.18
81.00
59.70
20.77
3.13
Me
Me
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

***2-Methyl-2-(2-(phenylethynyl)phenyl)-1H-indene-1,3(2H)-dione* (*1af*)**

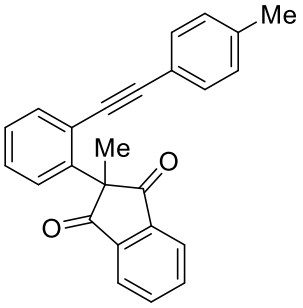


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow solid, Mp = 169-170 °C; 77% yield (for the last step); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (dd, J = 5.4, 3.0 Hz, 1H), 7.60-7.57 (m, 2H), 7.49-7.47 (m, 1H), 7.34 (t, J = 7.8 Hz, 1H), 7.16 (t, J = 7.8 Hz, 1H), 7.03 (t, J = 7.8 Hz, 1H), 6.67 (d, J = 7.2 Hz, 1H), 1.74 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 202.0, 140.5, 139.0, 134.9, 133.2, 131.1, 128.9, 128.8, 128.4, 128.0, 127.5, 123.5, 122.3, 121.8, 96.1, 89.9, 59.9, 21.2. HRMS *m*/*z* (ESI+): Calculated for $C_{24}H_{16}O_2Na^+$ ([M+Na]$^+$) 359.1043, found 359.1048.

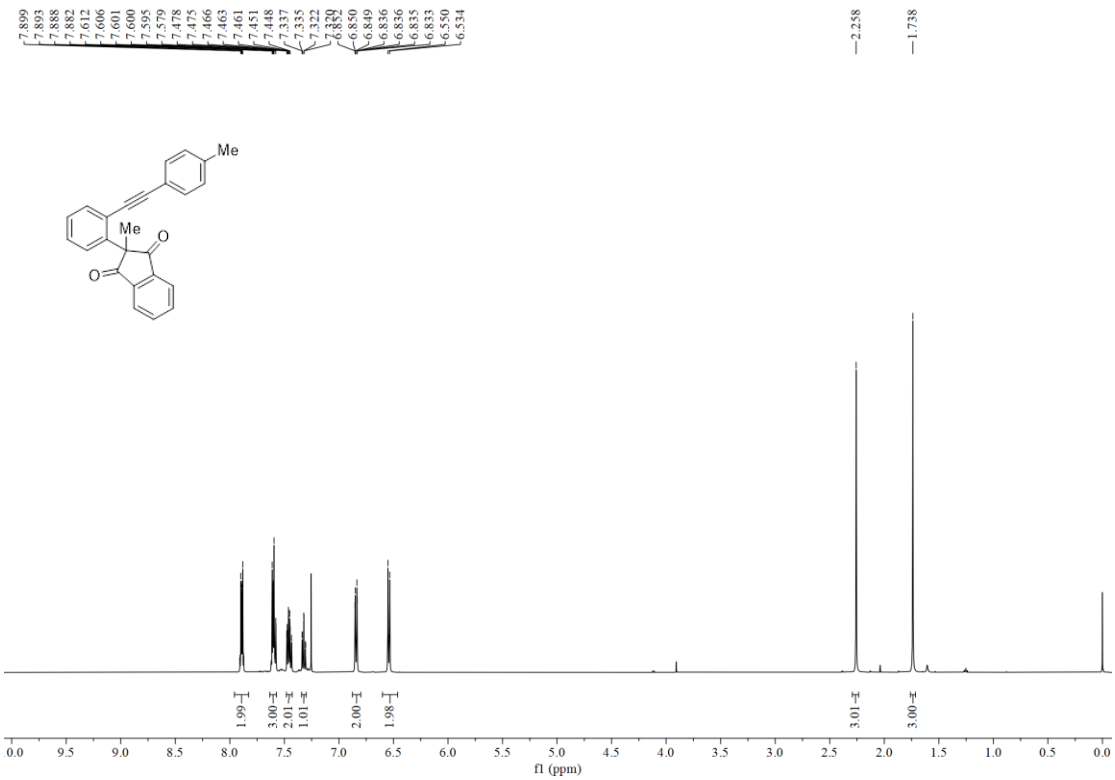


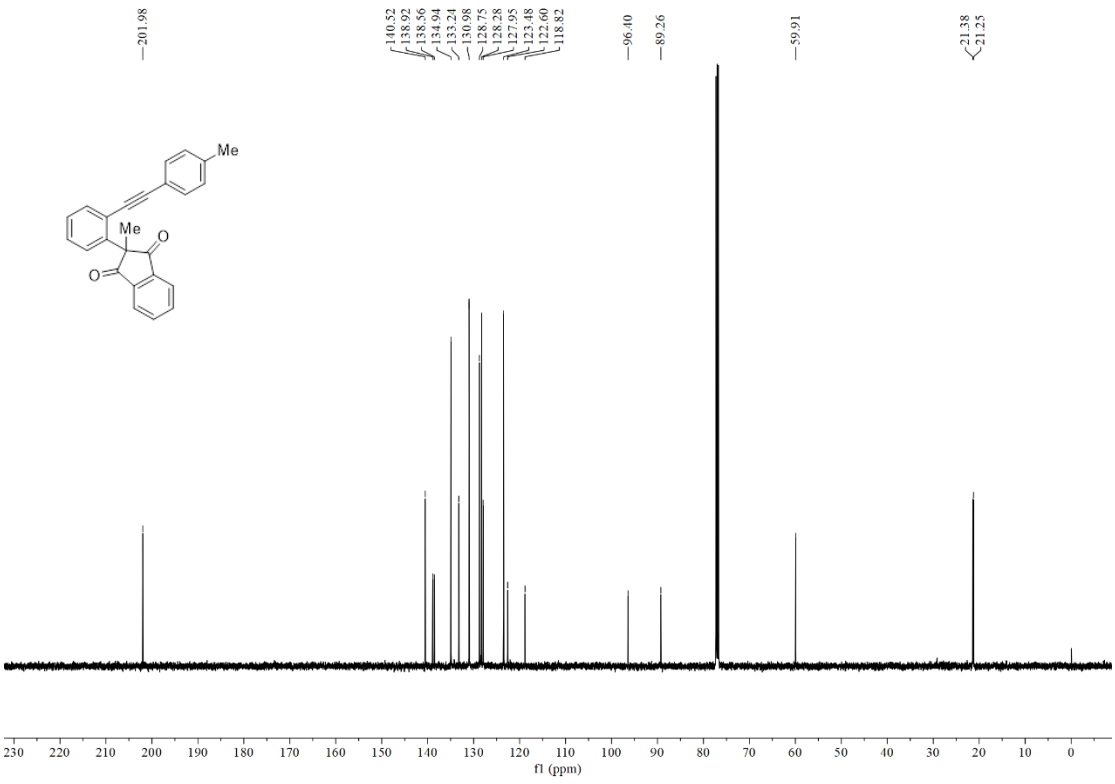


***2-Methyl-2-(2-(p-tolylethynyl)phenyl)-1H-indene-1,3(2H)-dione* (*1ag*)**

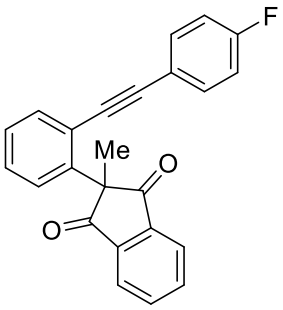


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow solid, Mp = 154-155 °C; 42% yield (for the last step); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90-7.88 (m, 2H), 7.61-7.58 (m, 3H), 7.48-7.45 (m, 2H), 7.34-7.32 (m, 1H), 6.85-6.83 (m, 2H), 6.54 (d, J = 8.0 Hz, 2H), 2.26 (s, 3H), 1.74 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.0, 140.5, 138.9, 138.6, 134.9, 133.2, 131.0, 128.8, 128.3, 127.9, 123.5, 122.6, 118.8, 96.4, 89.3, 59.9, 21.4, 21.3. HRMS *m*/*z* (ESI+): Calculated for $C_{25}H_{19}O_2^+$ ($[M+H]^+$) 351.1380, found 351.1374.

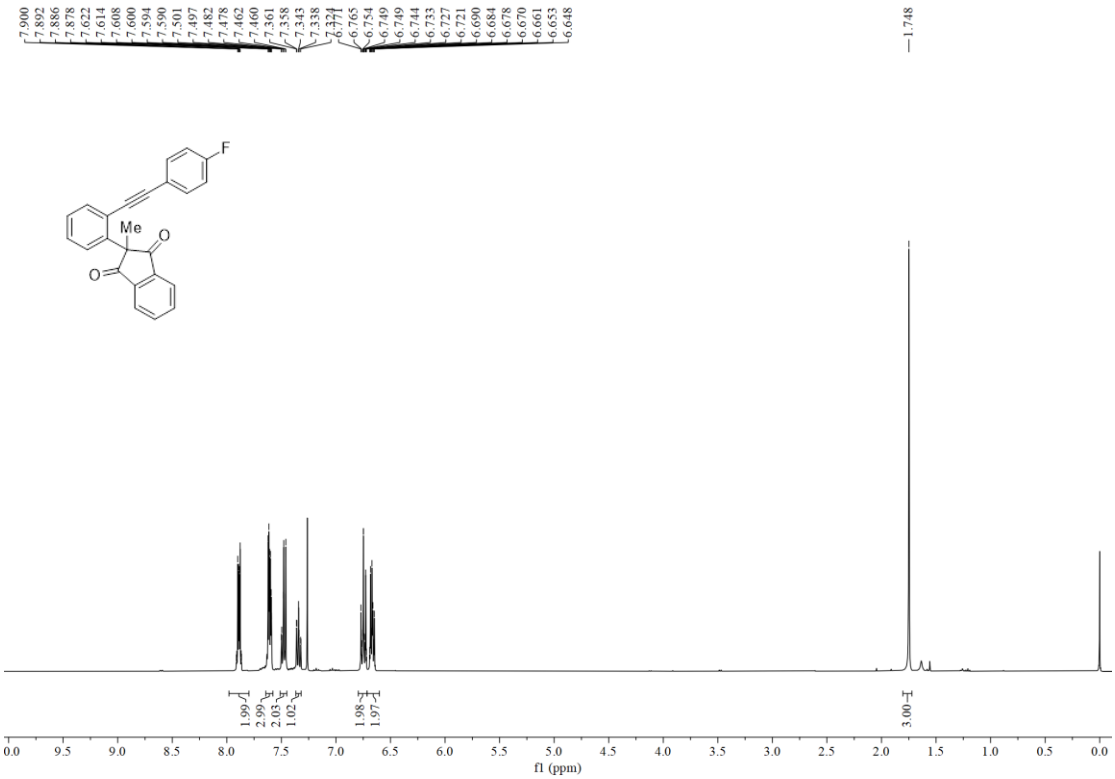

7.899
7.893
7.888
7.882
7.612
7.606
7.601
7.600
7.595
7.579
7.478
7.475
7.466
7.463
7.461
7.451
7.448
7.337
7.335
7.322
6.850
6.849
6.836
6.835
6.833
6.550
6.534
2.258
1.738
Me
Me
O
O
1.99
3.00
2.01
1.01
2.00
1.98
3.01
3.00
f1 (ppm)

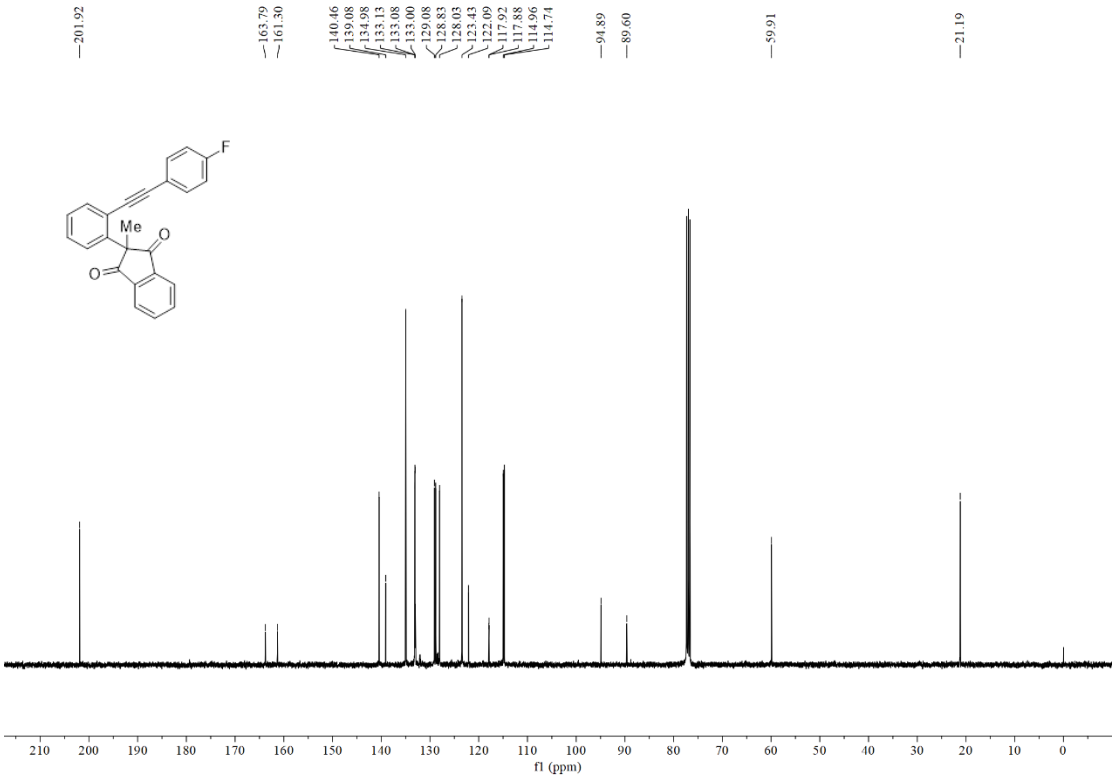

201.98
140.52
138.92
138.56
134.94
133.24
130.98
128.75
128.28
127.95
123.48
122.60
118.82
96.40
89.26
59.91
21.38
21.25
Me
Me
O
O
f1 (ppm)

***2-(2-((4-Fluorophenyl)ethynyl)phenyl)-2-methyl-1H-indene-1,3(2H)-dione* (*1ah*)**

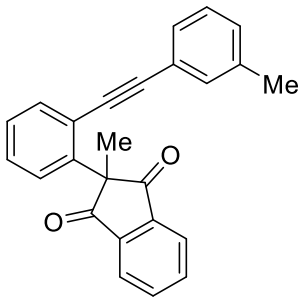


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow solid, Mp = 140-141 °C; 81% yield (for the last step); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90-7.88 (m, 2H), 7.62-7.59 (m, 3H), 7.50-7.46 (m, 2H), 7.36-7.32 (m, 1H), 6.80-6.72 (m, 2H), 6.69-6.65 (m, 2H), 1.75 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.9, 162.5 (d, J = 249.0 Hz), 140.5, 139.1, 135.0, 133.1, 133.0 (d, J = 8.0 Hz), 129.1, 128.8, 128.0, 123.4, 122.1, 117.9 (d, J = 4.0 Hz), 114.9 (d, J = 22.0 Hz), 94.9, 89.6, 59.9, 21.2. HRMS *m*/*z* (ESI+): Calculated for $C_{24}H_{15}FO_2^+$ ([M]$^+$) 354.1056, found 354.1061.

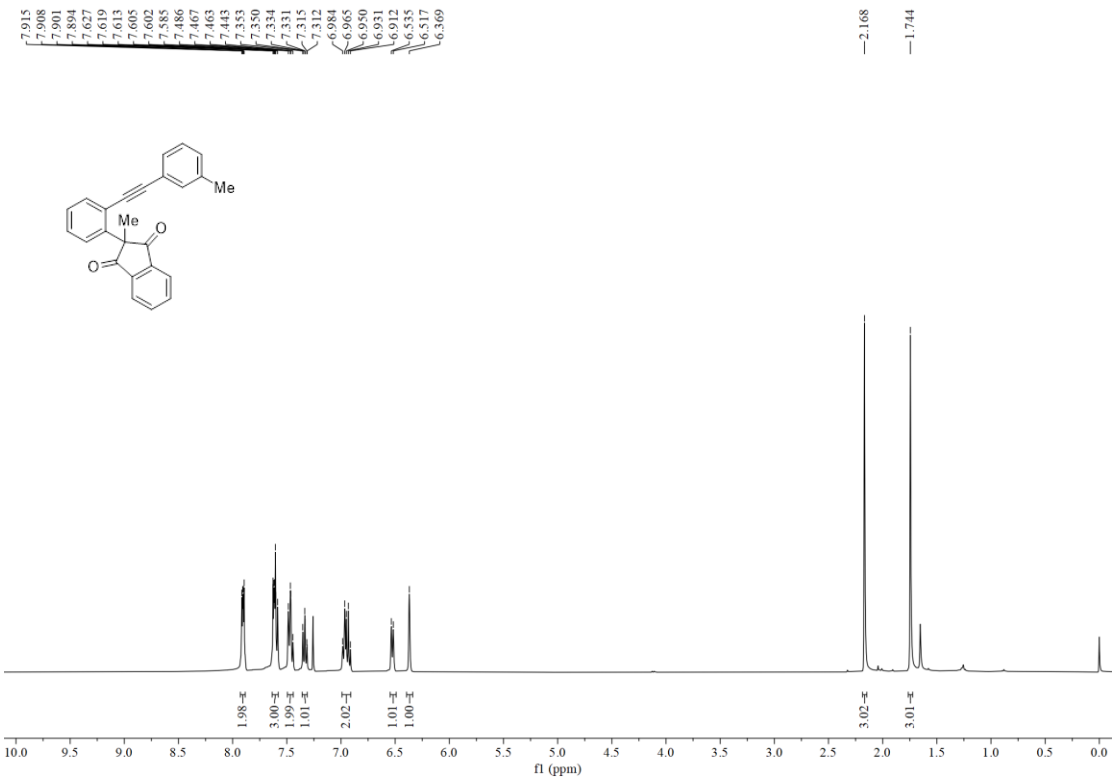


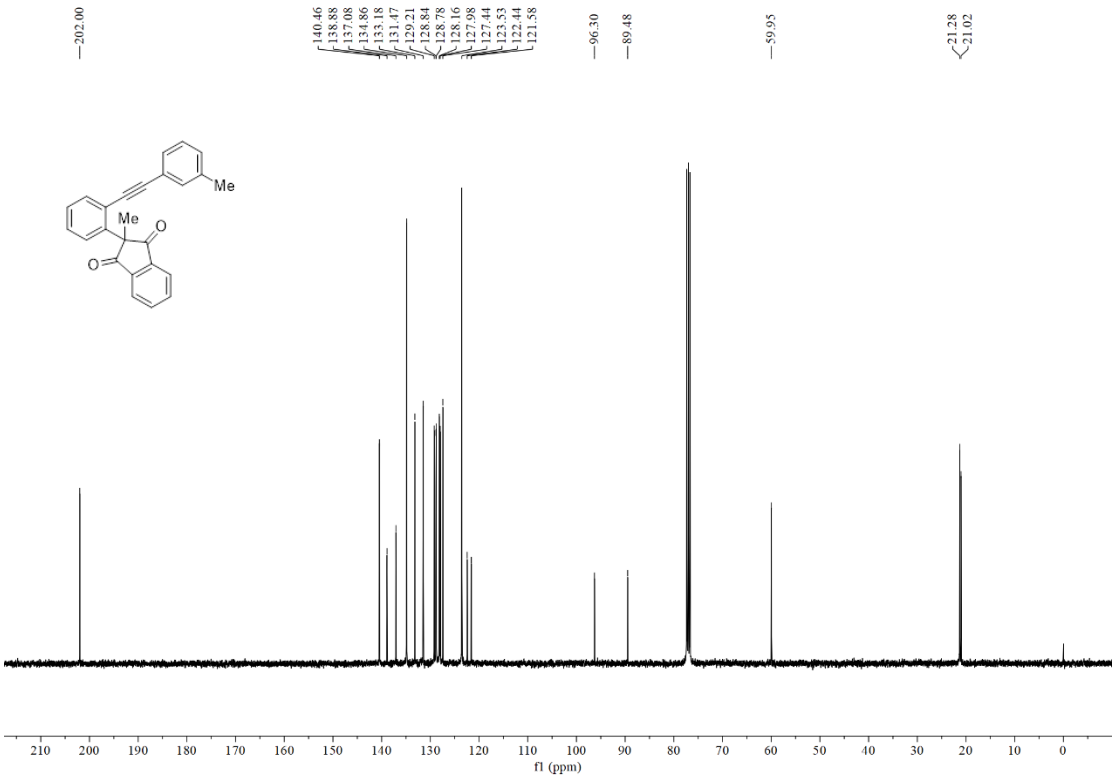


***2-Methyl-2-(2-(m-tolylethynyl)phenyl)-1H-indene-1,3(2H)-dione* (*1ai*)**

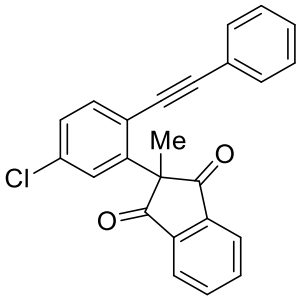


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow solid, Mp = 145-146 °C; 78% yield (for the last step); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92-7.89 (m, 2H), 7.63-7.59 (m, 3H), 7.49-7.44 (m, 2H), 7.35-7.31 (m, 1H), 6.98-6.91 (m, 2H), 6.53 (d, J = 7.2 Hz, 1H), 6.37 (s, 1H), 2.17 (s, 3H), 1.74 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.0, 140.5, 138.9, 137.1, 134.9, 133.2, 131.5, 129.2, 128.84, 128.78, 128.2, 128.0, 127.4, 123.5, 122.4, 121.6, 96.3, 89.5, 60.0, 21.3, 21.0. HRMS m/z (ESI+): Calculated for $C_{25}H_{19}O_2^+$ ([M+H]$^+$) 351.1380, found 351.1374.

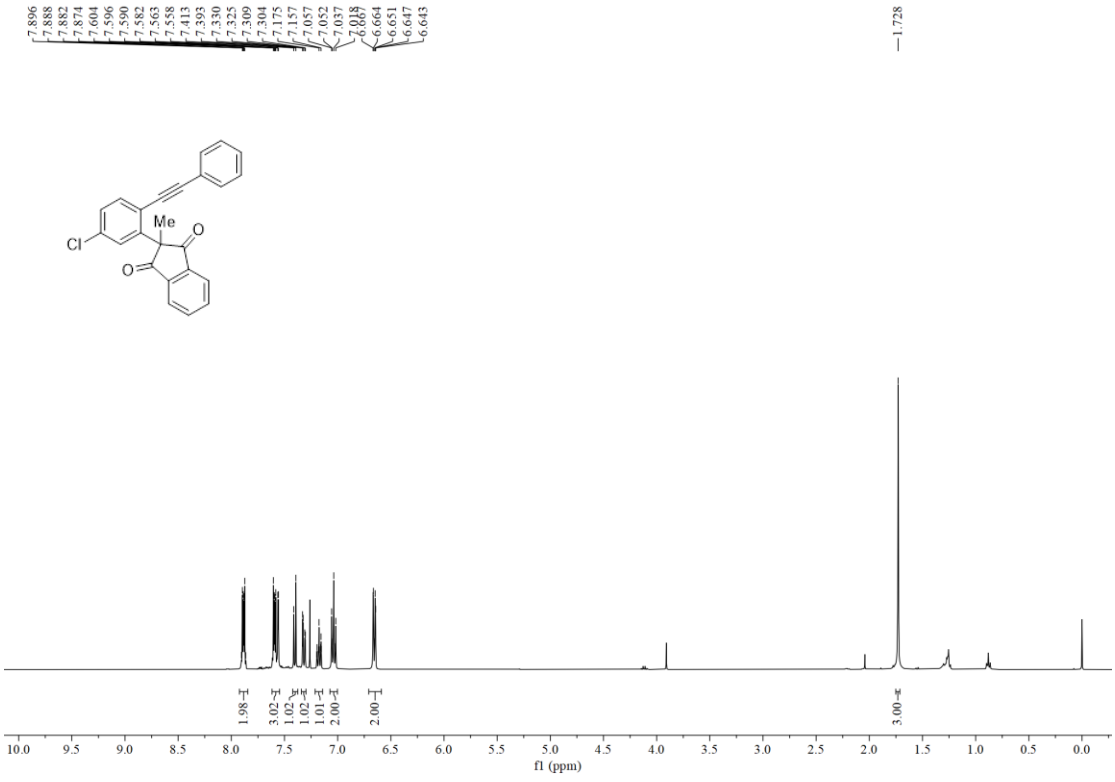

7.915
7.908
7.901
7.894
7.627
7.619
7.613
7.605
7.602
7.585
7.486
7.467
7.463
7.443
7.353
7.350
7.334
7.331
7.315
7.312
6.984
6.965
6.950
6.931
6.912
6.535
6.517
6.369
2.168
1.744
Me
Me
O
O
1.98
3.00
1.99
1.01
2.02
1.01
1.00
3.02
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

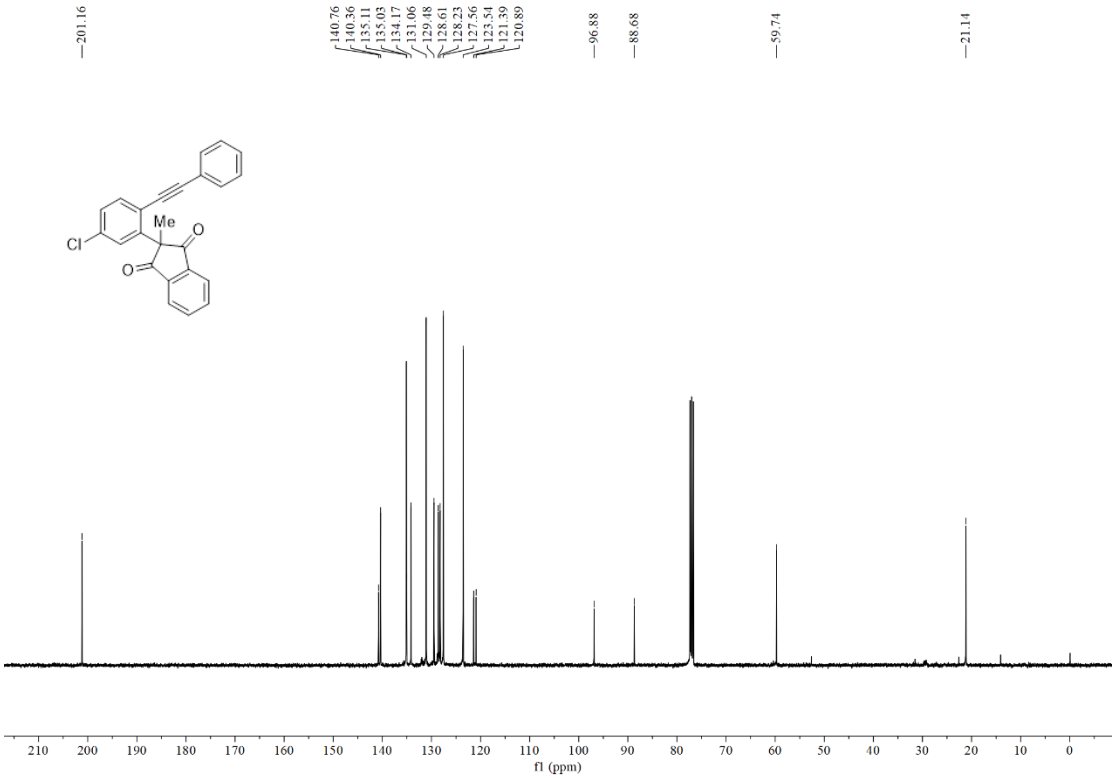

202.00
140.46
138.88
137.08
134.86
133.18
131.47
129.21
128.84
128.78
128.16
127.98
127.44
123.53
122.44
121.58
96.30
89.48
59.95
21.28
21.02
Me
Me
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

***2-(5-Chloro-2-(phenylethynyl)phenyl)-2-methyl-1H-indene-1,3(2H)-dione* (*1aj*)**

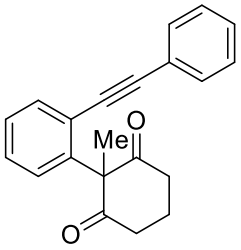


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow solid, Mp = 139-140 °C; 62% yield (for the last step); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90-7.87 (m, 2H), 7.60-7.56 (m, 3H), 7.40 (d, J = 8.0 Hz, 1H), 7.33-7.30 (m, 1H), 7.18-7.16 (m, 1H), 7.06-7.02 (m, 2H), 6.67-6.64 (m, 2H), 1.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.2, 140.8, 140.4, 135.1, 135.0, 134.2, 131.1, 129.5, 128.6, 128.2, 127.6, 123.5, 121.4, 120.9, 96.9, 88.7, 59.7, 21.1. HRMS *m/z* (ESI+): Calculated for $C_{24}H_{15}ClO_2^+$ ([M]$^+$) 370.0761, found 370.0767.

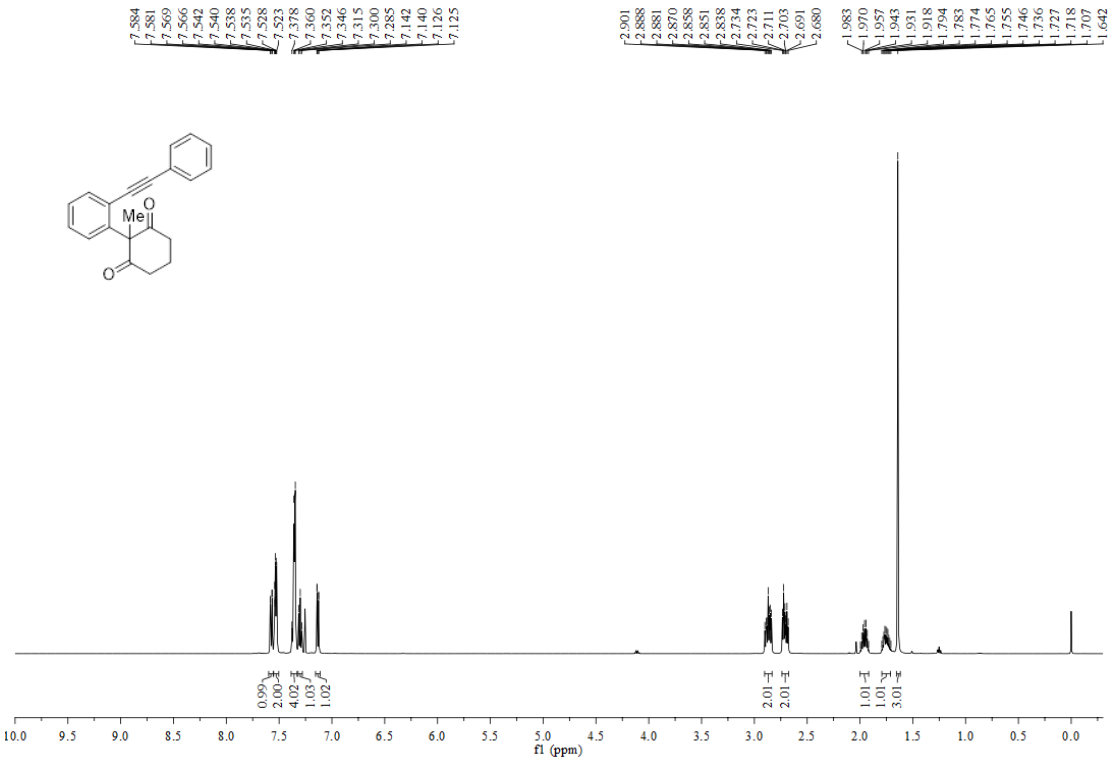


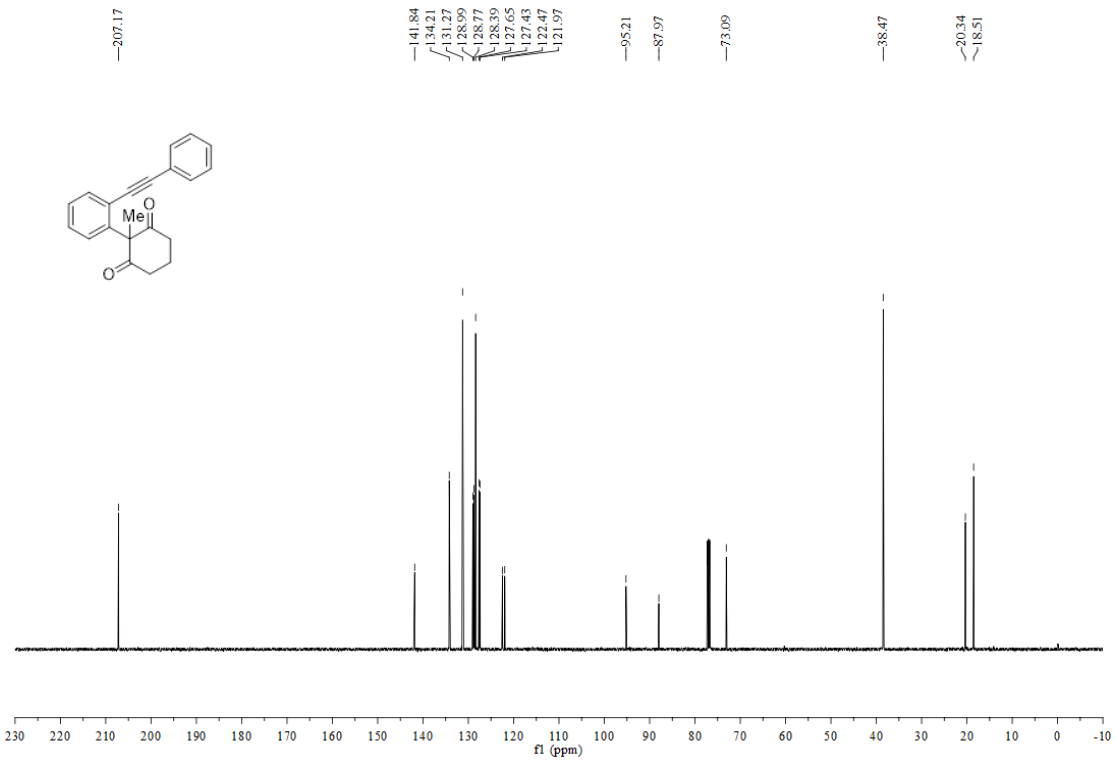


2-Methyl-2-(2-(phenylethynyl)phenyl)cyclohexane-1,3-dione (1ak)

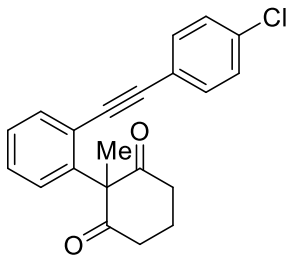


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow solid, Mp = 129-120 °C; 72% yield (for the last step); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (dd, J = 7.5, 1.5 Hz, 1H), 7.54-7.52 (m, 2H), 7.38-7.35 (m, 4H), 7.30 (t, J = 7.5 Hz, 1H), 7.13 (dd, J = 7.5, 1.0 Hz, 1H), 2.90-2.84 (m, 2H), 2.73-2.68 (m, 2H), 1.98-1.92 (m, 1H), 1.79-1.71 (m, 1H), 1.64 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.2, 141.8, 134.2, 131.3, 129.0, 128.8, 128.4, 127.7, 127.4, 122.5, 122.0, 95.2, 88.0, 73.1, 38.5, 20.3, 18.5. HRMS *m/z* (ESI+): Calculated for $C_{21}H_{19}O_2^+$ ($[M+H]^+$) 303.1380, found 303.1382.

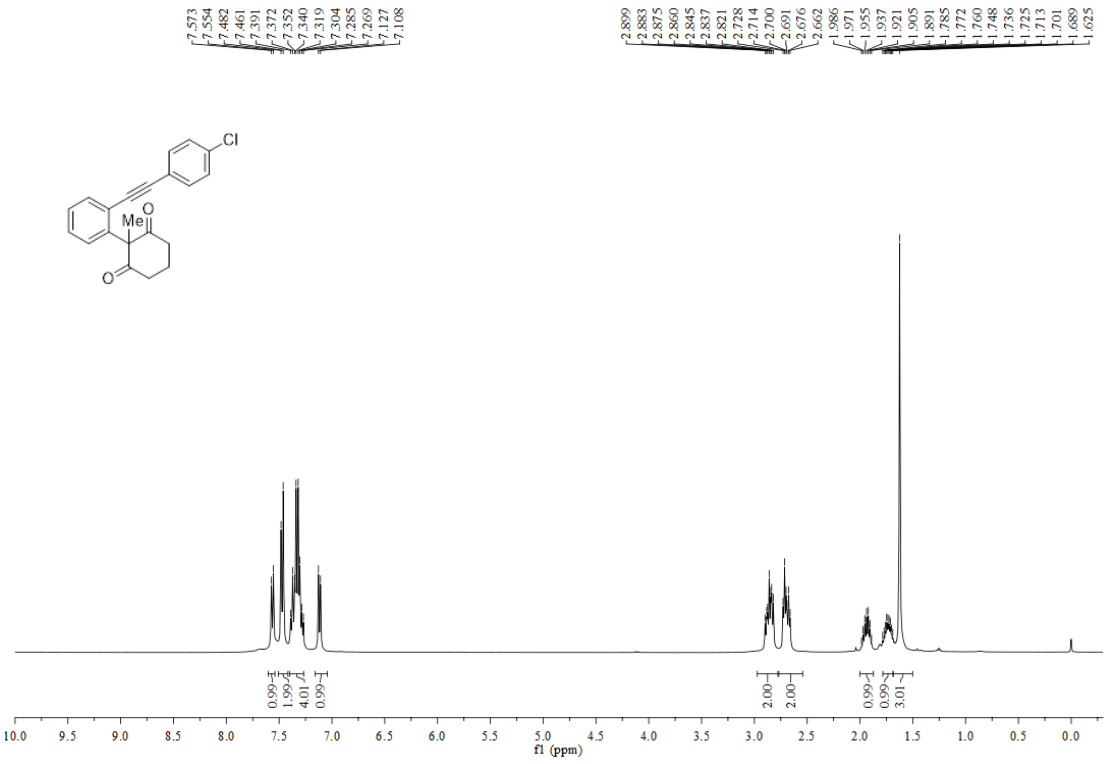

7.584
7.581
7.569
7.566
7.542
7.540
7.538
7.535
7.528
7.523
7.378
7.360
7.352
7.346
7.315
7.300
7.285
7.142
7.140
7.126
7.125
2.901
2.888
2.881
2.870
2.858
2.851
2.838
2.734
2.723
2.711
2.703
2.691
2.680
1.983
1.970
1.957
1.943
1.931
1.918
1.794
1.783
1.774
1.765
1.755
1.746
1.736
1.727
1.718
1.707
1.642
Me
O
O
0.99
2.00
4.02
1.03
1.02
2.01
2.01
1.01
1.01
3.01
f1 (ppm)

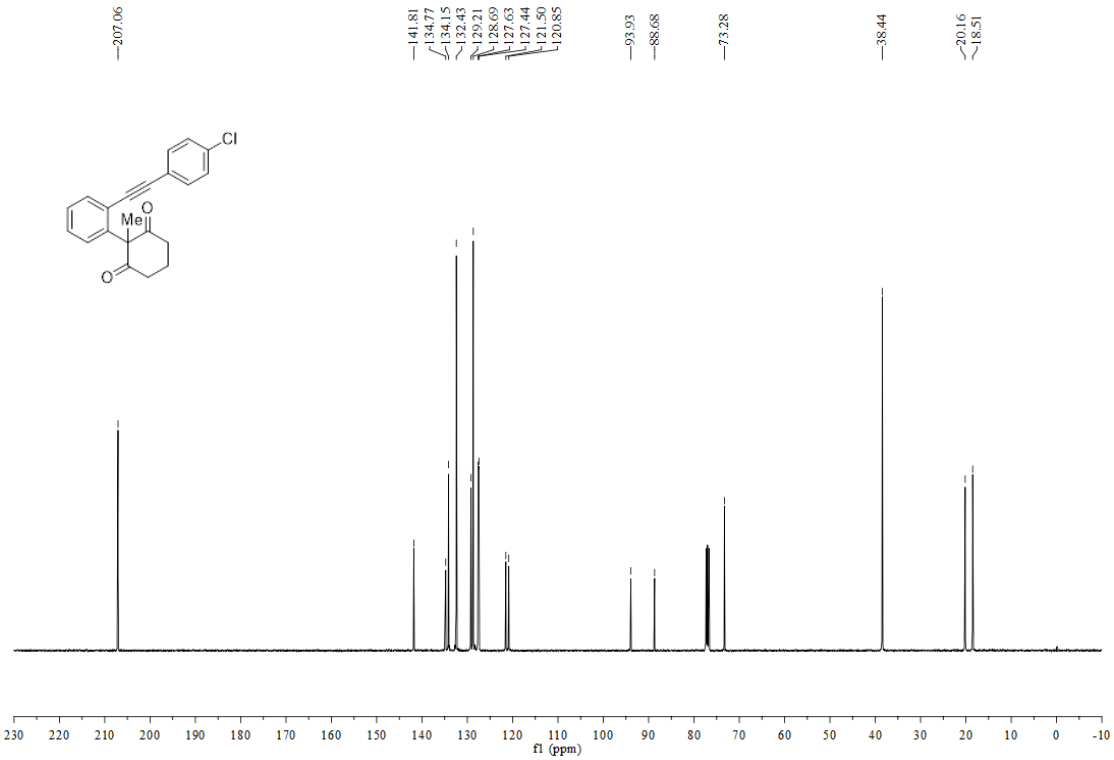

207.17
141.84
134.21
131.27
128.99
128.77
128.39
127.65
127.43
122.47
121.97
95.21
87.97
73.09
38.47
20.34
18.51
Me
O
O
f1 (ppm)

2-(2-((4-Chlorophenyl)ethynyl)phenyl)-2-methylcyclohexane-1,3-dione (1al)

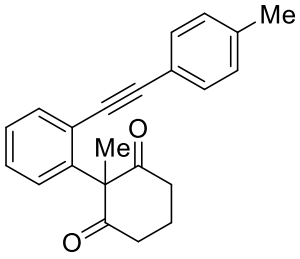


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow solid, Mp = 120-121 °C; 68% yield (for the last step); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 7.6 Hz, 1H), 7.47 (d, J = 7.6 Hz, 2H), 7.39-7.27 (m, 4H), 7.12 (d, J = 7.6 Hz, 1H), 2.90-2.82 (m, 2H), 2.73-2.66 (m, 2H), 1.99-1.89 (m, 1H), 1.79-1.69 (m, 1H), 1.63 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.1, 141.8, 134.8, 134.2, 132.4, 129.2, 128.7, 127.6, 127.4, 121.5, 120.9, 93.9, 88.7, 73.3, 38.4, 20.2, 18.5. HRMS m/z (ESI+): Calculated for $C_{21}H_{17}ClO_2Na^+$ ([M+Na]$^+$) 359.0809, found 359.0814.

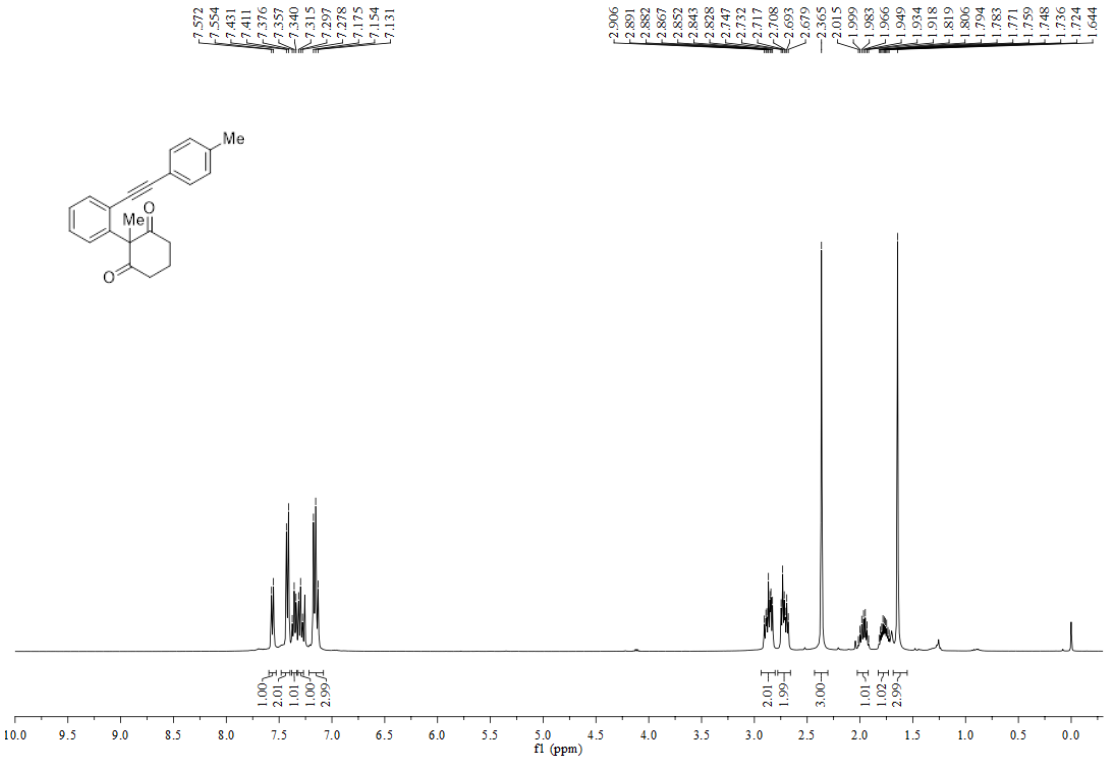




2-Methyl-2-(2-(p-tolylethynyl)phenyl)cyclohexane-1,3-dione (1am)



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow solid, Mp = 156-157 °C; 76% yield (for the last step); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 7.2 Hz, 1H), 7.42 (d, J = 8.0 Hz, 2H), 7.36 (t, J = 7.2 Hz, 1H), 7.30 (t, J = 7.2 Hz, 1H), 7.15 (t, J = 8.4 Hz, 3H), 2.91-2.83 (m, 2H), 2.75-2.68 (m, 2H), 2.36 (s, 3H), 2.02-1.92 (m, 1H), 1.81-1.72 (m, 1H), 1.64 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.4, 141.8, 139.0, 134.1, 131.2, 129.2, 128.8, 127.6, 127.4, 122.2, 119.4, 95.5, 87.5, 72.9, 38.4, 21.5, 20.5, 18.5. HRMS *m*/*z* (ESI+): Calculated for $C_{22}H_{20}O_2Na^+$ ($[M+Na]^+$) 339.1356, found 339.1357.


7.572
7.554
7.431
7.411
7.376
7.357
7.340
7.315
7.297
7.278
7.175
7.154
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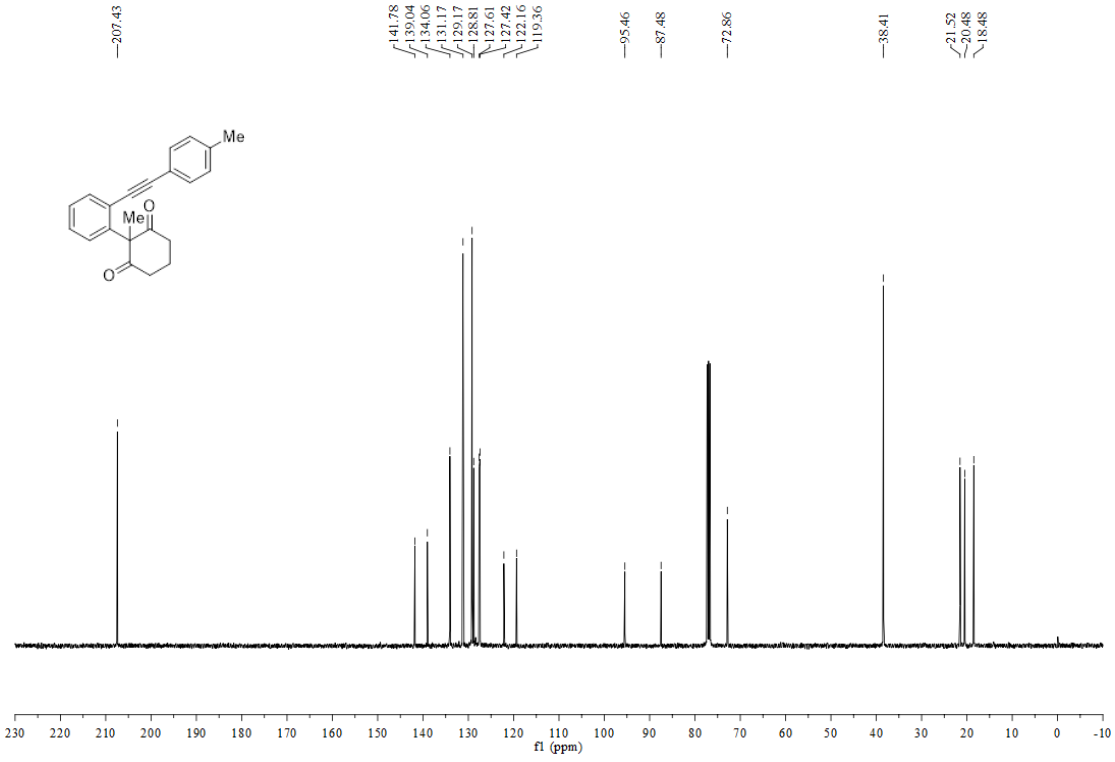
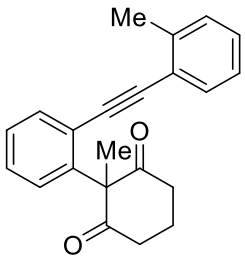
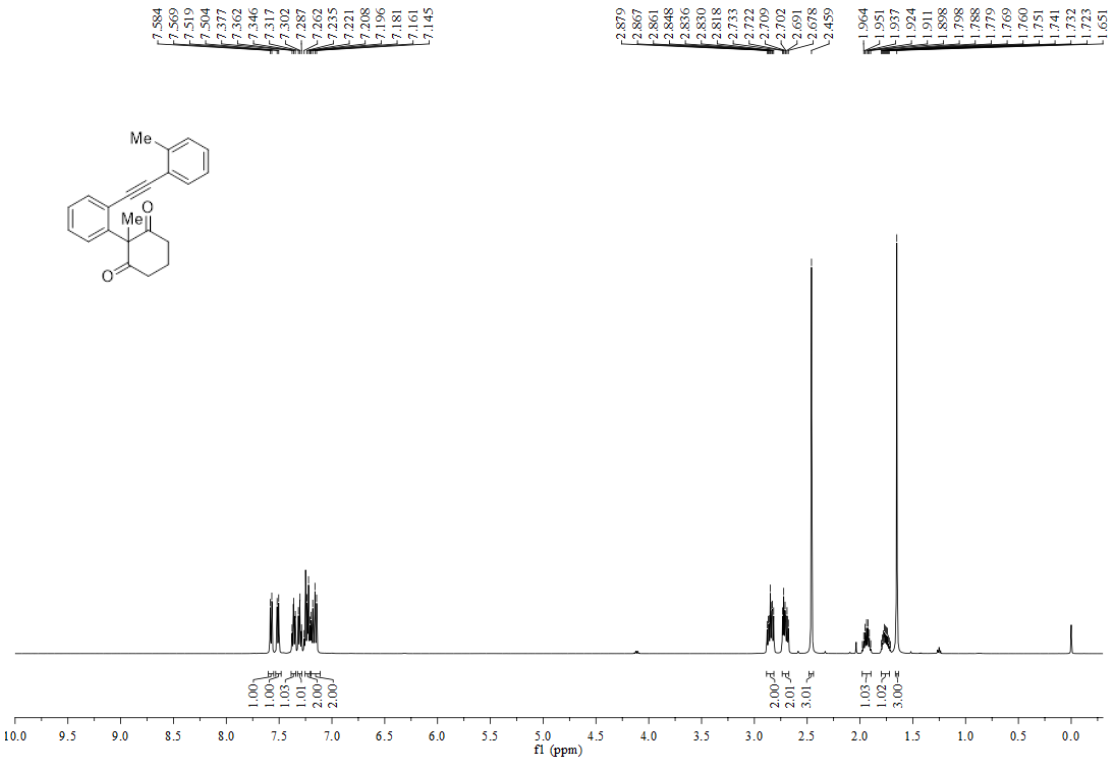
2.906
2.891
2.882
2.867
2.852
2.843
2.828
2.747
2.732
2.717
2.708
2.693
2.679
2.365
2.015
1.999
1.983
1.966
1.949
1.934
1.918
1.819
1.806
1.794
1.783
1.771
1.759
1.748
1.736
1.724
1.644
Me
O
Me
O
1.00
2.01
1.01
1.00
2.99
2.01
1.99
3.00
1.01
1.02
2.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

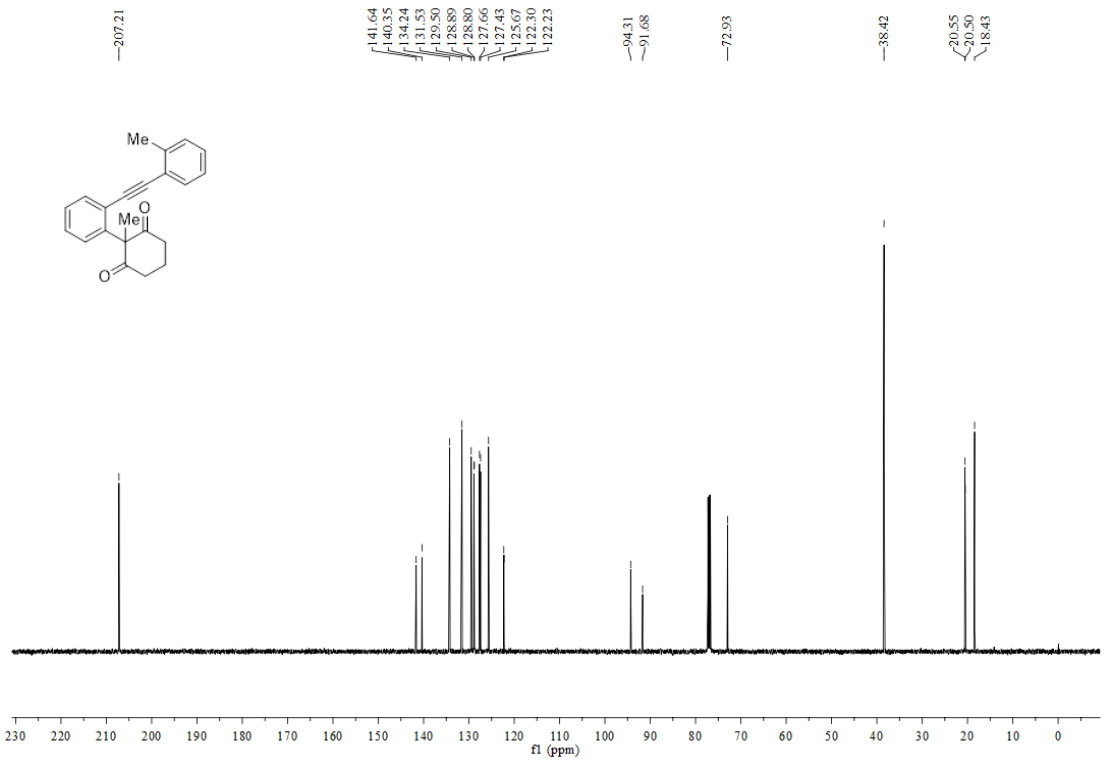

207.43
141.78
139.04
134.06
131.17
129.17
128.81
127.61
127.42
122.16
119.36
95.46
87.48
72.86
38.41
21.52
20.48
18.48
Me
O
Me
O
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

2-Methyl-2-(2-(o-tolylethynyl)phenyl)cyclohexane-1,3-dione (1an)

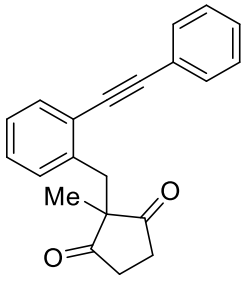


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow solid, Mp = 141-142 °C; 70% yield (for the last step); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, J = 7.5 Hz, 1H), 7.51 (d, J = 7.5 Hz, 1H), 7.36 (t, J = 7.5 Hz, 1H), 7.30 (t, J = 7.5 Hz, 1H), 7.26-7.20 (m, 2H), 7.18-7.15 (m, 2H), 2.88-2.82 (m, 2H), 2.73-2.68 (m, 2H), 2.46 (s, 3H), 1.96-1.90 (m, 1H), 1.80-1.72 (m, 1H), 1.65 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.2, 141.6, 140.4, 134.2, 131.5, 129.5, 128.9, 128.8, 127.7, 127.4, 125.7, 122.3, 122.2, 94.3, 91.7, 72.9, 38.4, 20.6, 20.5, 18.4. HRMS *m/z* (ESI+): Calculated for $C_{22}H_{20}O_2Na^+$ ([M+Na]$^+$) 339.13555, found 339.13577.

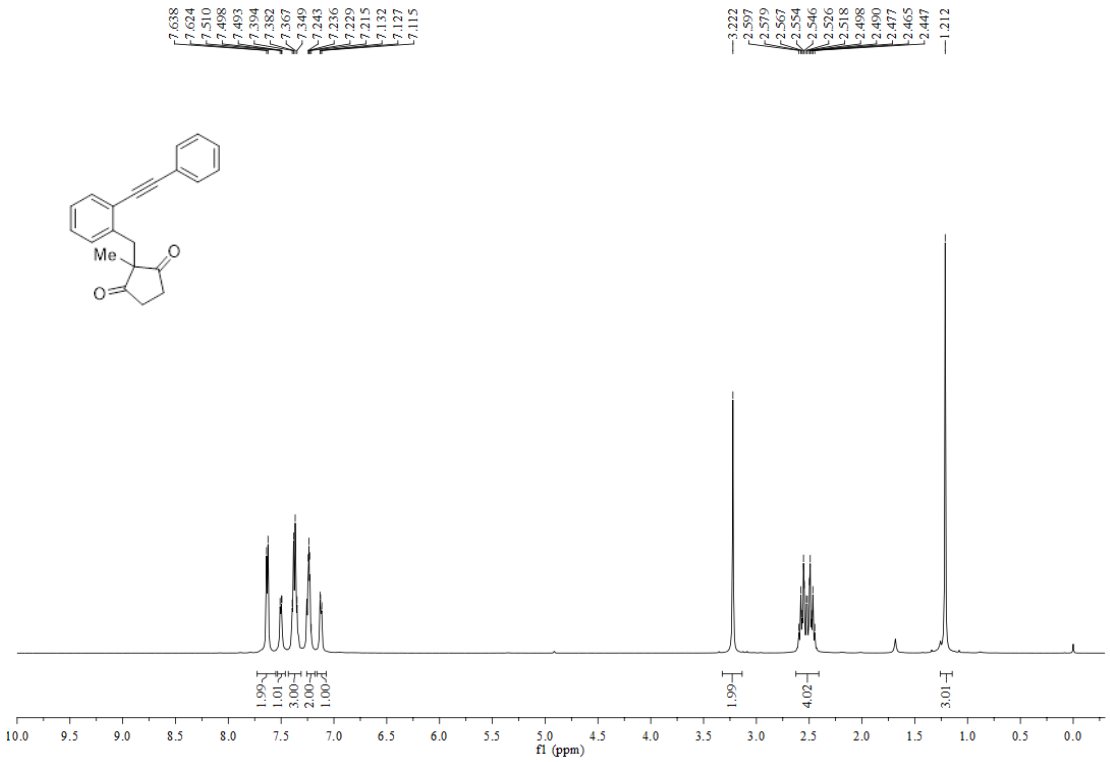


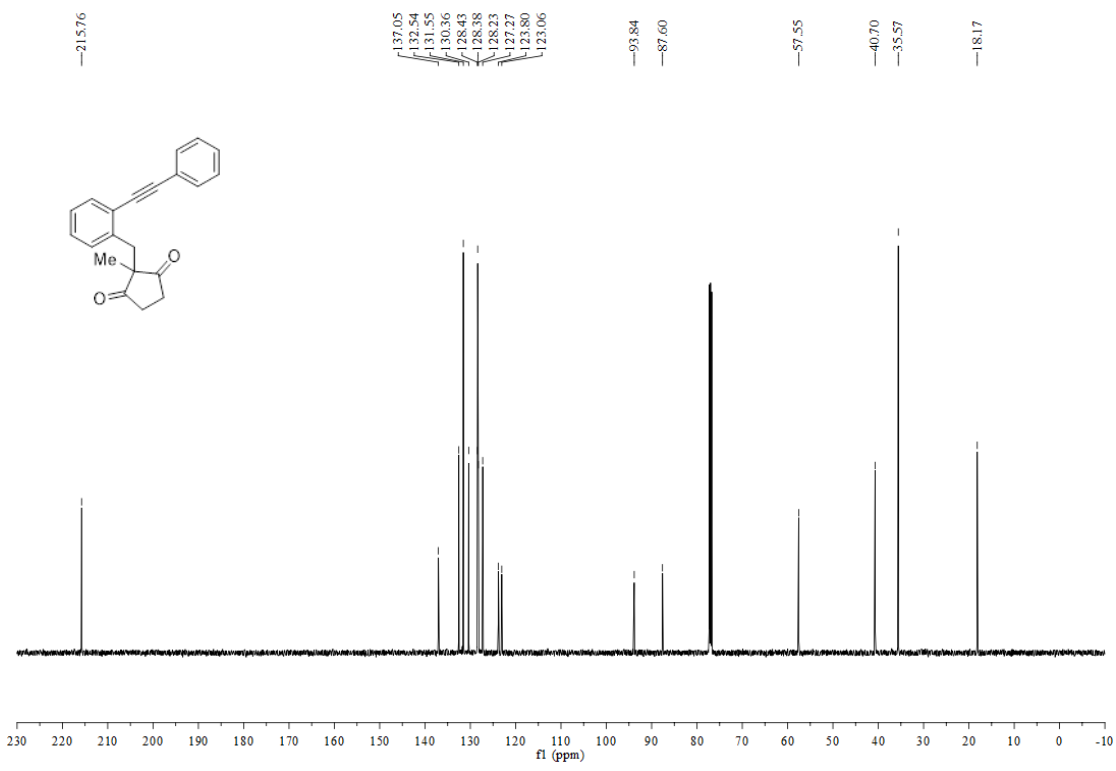


***2-Methyl-2-(2-(phenylethynyl)benzyl)cyclopentane-1,3-dione* (*1ao*)**

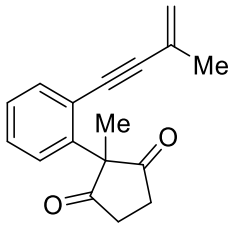


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow solid, Mp = 79-80 °C; 89% yield (for the last step); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, J = 7.0 Hz, 2H), 7.51-7.49 (m, 1H), 7.39-7.35 (m, 3H), 7.24-7.22 (m, 1H), 7.13-7.12 (m, 1H), 3.22 (s, 2H), 2.60-2.45 (m, 4H), 1.21 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 215.8, 137.1, 132.5, 131.6, 130.4, 128.43, 128.38, 128.2, 127.3, 123.8, 123.1, 93.8, 87.6, 57.6, 40.7, 35.6, 18.2. HRMS *m*/*z* (ESI+): Calculated for $C_{21}H_{19}O_2^+$ ([M+H]$^+$) 303.1380, found 303.1383.

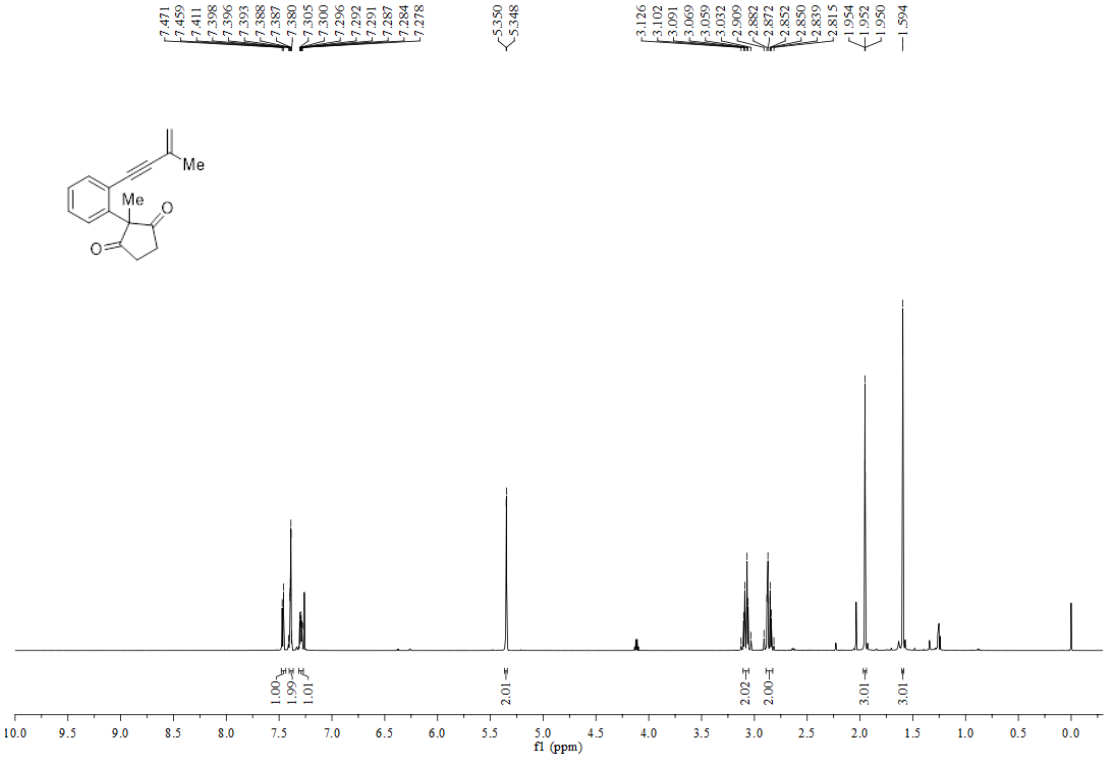

7.638
7.624
7.510
7.498
7.493
7.394
7.382
7.367
7.349
7.243
7.236
7.229
7.215
7.132
7.127
7.115
3.222
2.597
2.579
2.567
2.554
2.546
2.526
2.518
2.498
2.490
2.477
2.465
2.447
1.212
Me
O
O
1.99
1.01
3.00
2.00
1.00
1.99
4.02
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

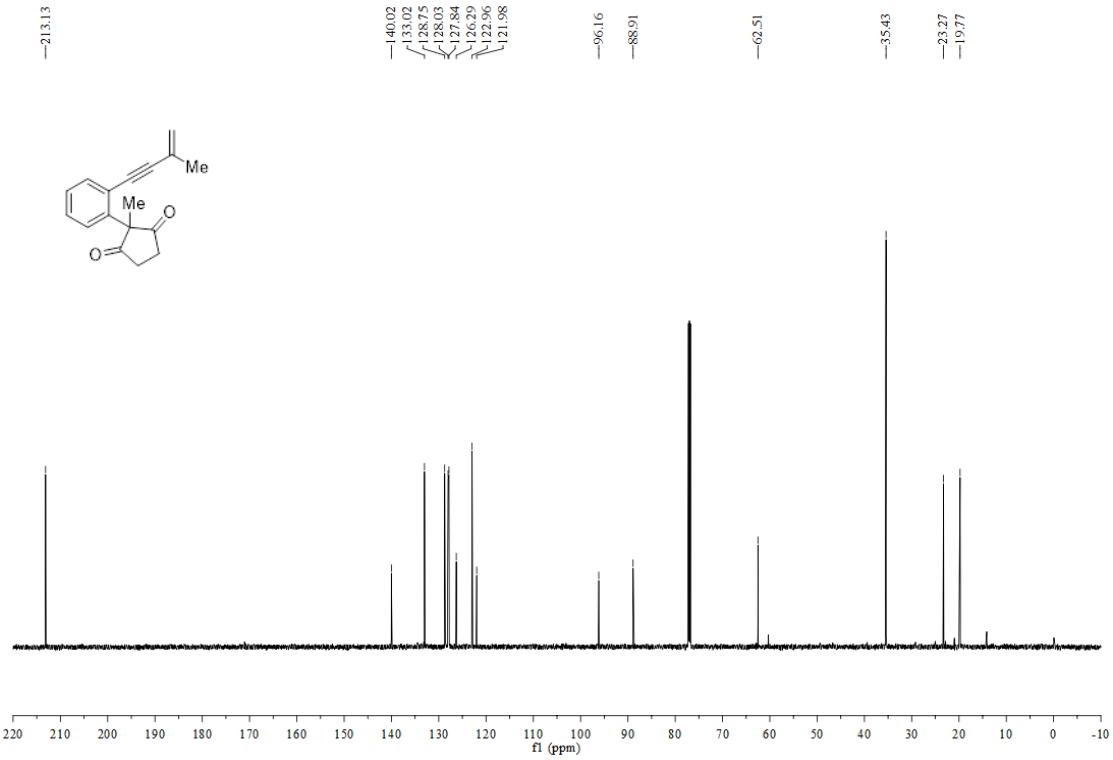

215.76
137.05
132.54
131.55
130.36
128.43
128.38
128.23
127.27
123.80
123.06
93.84
87.60
57.55
40.70
35.57
18.17
Me
O
O
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

2-Methyl-2-(2-(3-methylbut-3-en-1-yn-1-yl)phenyl)cyclopentane-1,3-dione (1ap)

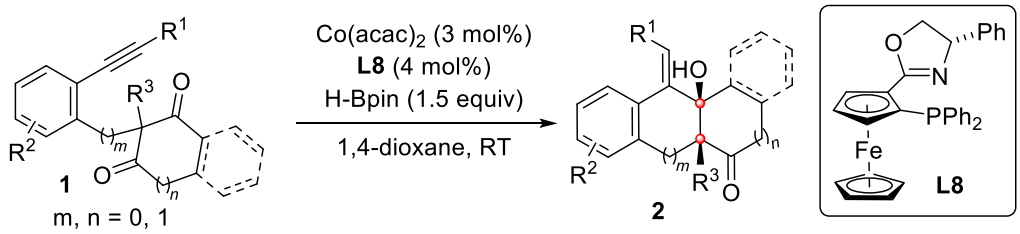


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow solid, Mp = 160-161 °C; 39% yield (for the last step); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, J = 7.2 Hz, 1H), 7.41-7.38 (m, 2H), 7.31-7.28 (m, 1H), 5.35 (d, J = 1.2 Hz, 2H), 3.13-3.03 (m, 2H), 2.91-2.82 (m, 2H), 1.95 (t, J = 1.2 Hz, 3H), 1.59 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 213.1, 140.0, 133.0, 128.8, 128.0 127.8, 126.3, 123.0, 122.0, 96.2, 88.9, 62.5, 35.4, 23.3, 19.8. HRMS m/z (ESI+): Calculated for $C_{17}H_{16}O_2Na^+$ ([M+Na]$^+$) 275.1043, found 275.1043.



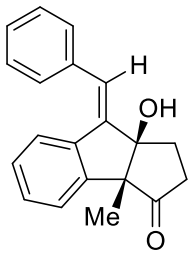


4. General procedure for enantioselective Co-catalyzed reductive cyclization

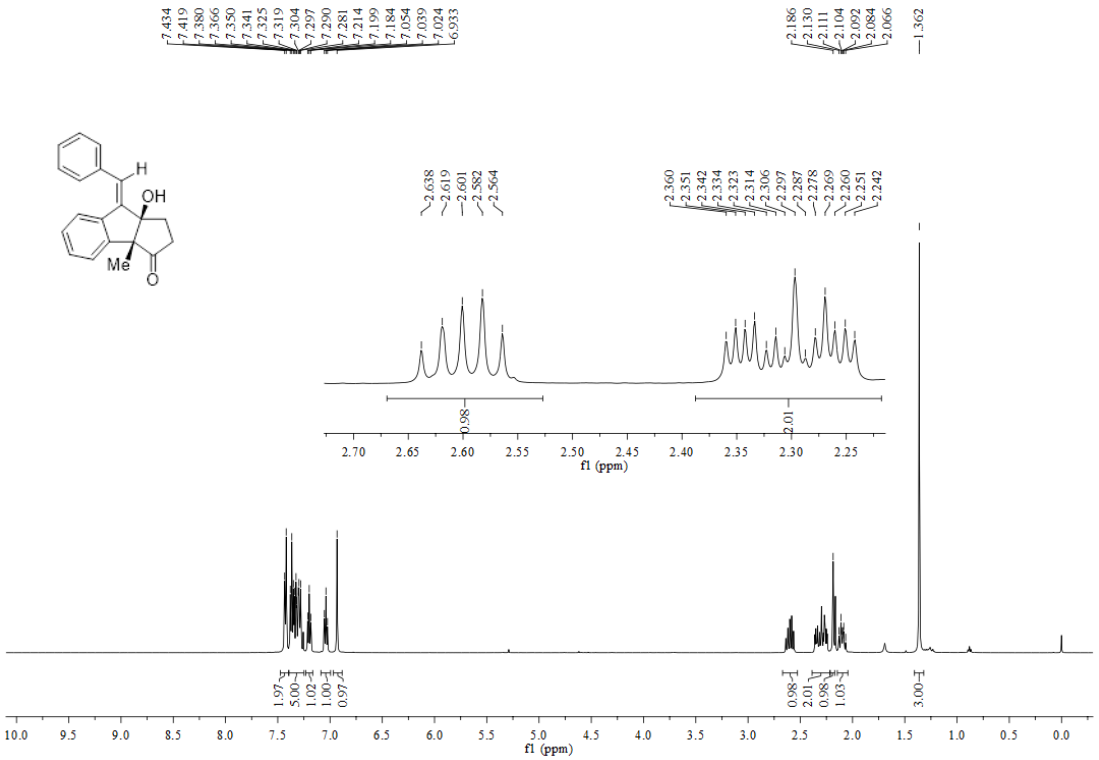


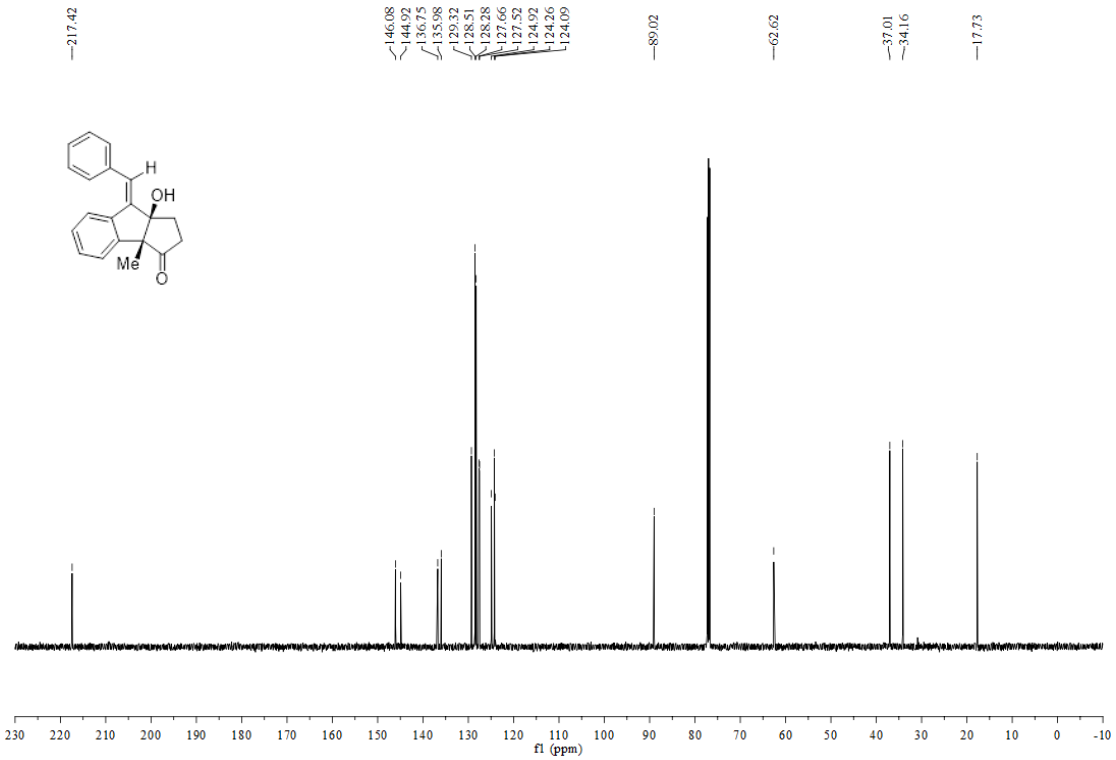
To a dried Schlenk tube were charged with $Co(acac)_2$ (3 mol%, 1.5 mg), **L8** (4 mol%, 4.2 mg), and **1** (0.2 mmol) under N_2 atmosphere. 1,4-Dioxane (1.0 mL) and HBpin (1.5 equiv, 44 μL) was then introduced via syringe. The resulting mixture was stirred at room temperature until **1** was completely consumed (monitored by TLC). The reaction mixture was then concentrated under reduced pressure and the crude was purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether (v/v = 1/5), to afford product **2**.

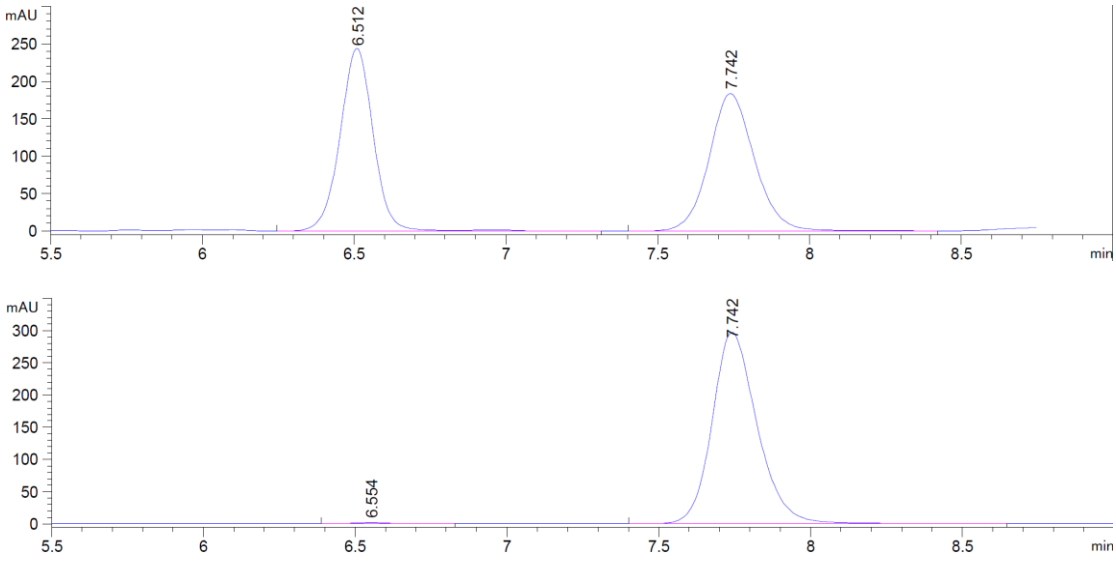
(3aR, 8aR)-8-((E)-Benzylidene)-8a-hydroxy-3a-methyl-1,3a,8,8a tetrahydrocyclo-penta[a]inden-3(2H)-one (2a)



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); white solid, Mp = 110-101 °C; 55 mg, 85% yield; $[\alpha]_D^{20}$ = -214.7 (*c* 1.0, CH_2Cl_2), 99% ee [Phenomenex Lux 5u Amylose-2 column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 80/20, 0.7 mL/min, 254 nm; t_{minor} = 6.6 min, t_{major} = 7.7 min]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, J = 7.5 Hz, 2H), 7.38-7.28 (m, 5H), 7.20 (t, J = 7.5 Hz, 1H), 7.04 (t, J = 7.5 Hz, 1H), 6.93 (s, 1H), 2.64-2.56 (m, 1H), 2.36-2.24 (m, 2H), 2.19 (s, 1H), 2.13-2.07 (m, 1H), 1.36 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 217.4, 146.1, 144.9, 136.8, 136.0, 129.3, 128.5, 128.3, 127.7, 127.5, 124.9, 124.3, 124.1, 89.0, 62.6, 37.0, 34.2, 17.7. HRMS *m*/*z* (ESI+): Calculated for $C_{20}H_{18}NaO_2^+$ ([M+Na]$^+$) 313.1199, found 313.1198.



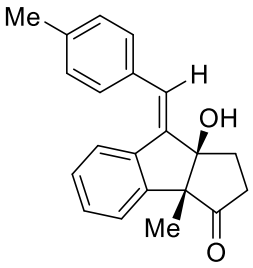




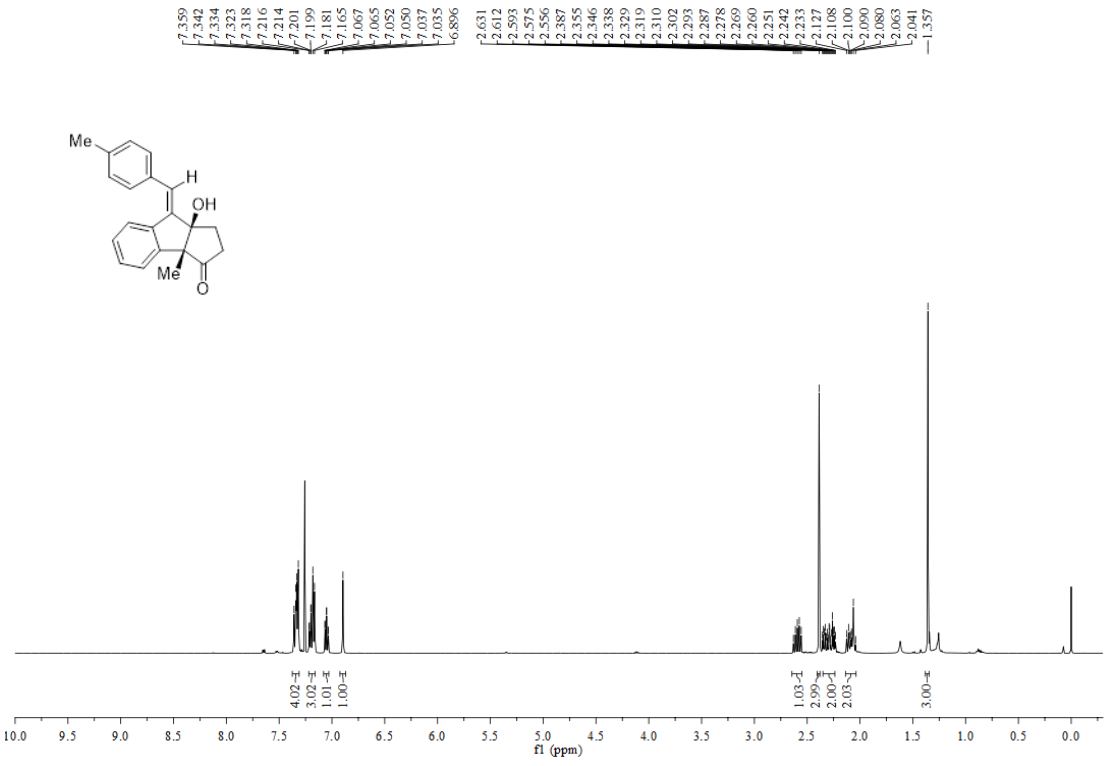
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

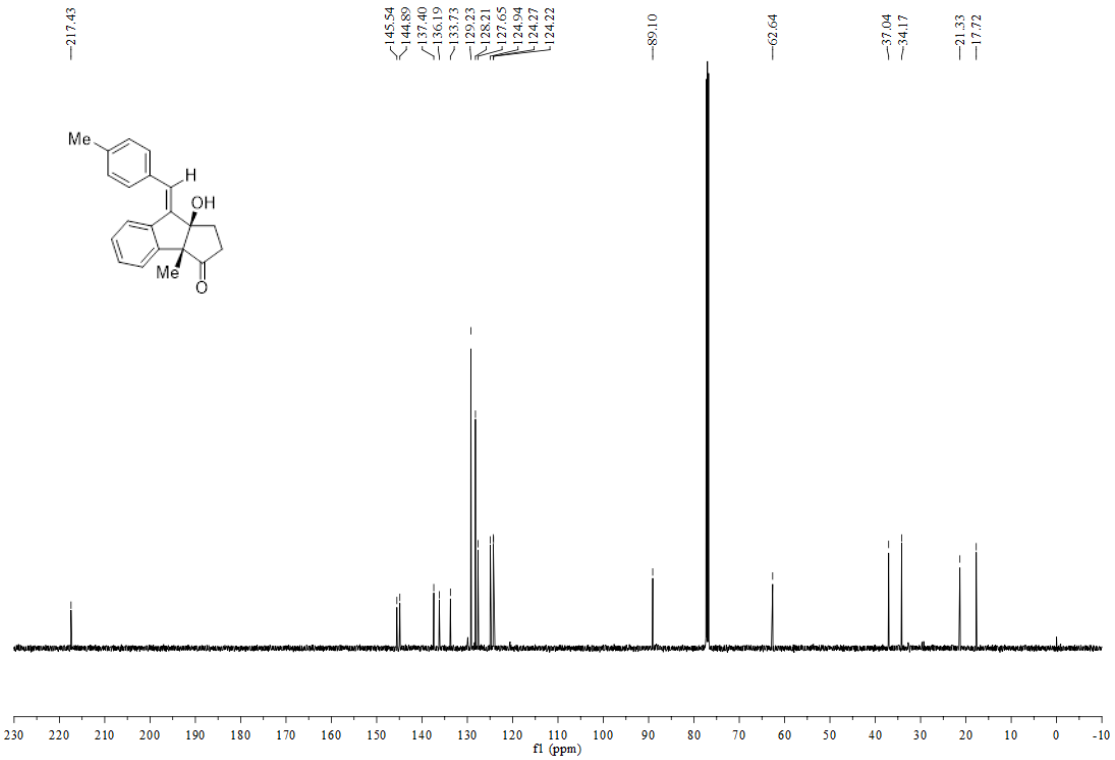
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.554	BB	0.1191	11.50782	1.50630	0.3752
2	7.742	BB	0.1559	3055.56152	297.41013	99.6248

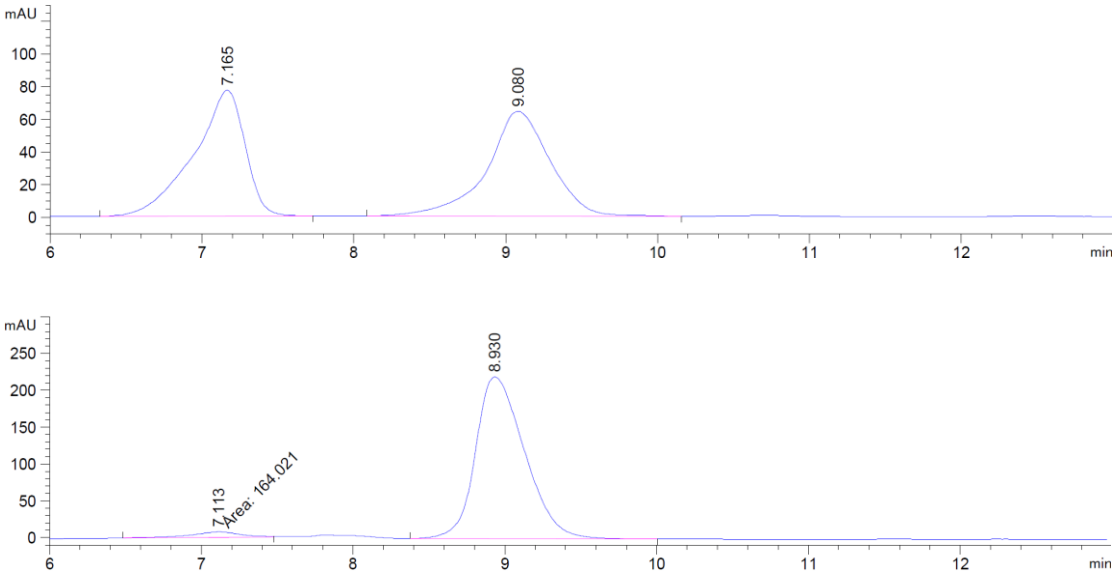
(3aR,8aR)-8a-Hydroxy-3a-methyl-8-((E)-4-methylbenzylidene)-1,3a,8,8a-tetra-hydrocyclopenta[a]inden-3(2H)-one (2b)



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); white solid, Mp = 114-115 °C; 32 mg, 52% yield; $[\alpha]_D^{20}$ = -210.4 (*c* 0.5, CH_2Cl_2), 93% ee [Phenomenex Lux 5u Amylose-2 column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 85/15, 0.7 mL/min, 254 nm; t_{minor} = 7.1 min, t_{major} = 8.9 min]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.32 (m, 4H), 7.22-7.16 (m, 3H), 7.07-7.03 (m, 1H), 6.90 (s, 1H), 2.63-2.56 (m, 1H), 2.39 (s, 3H), 2.36-2.23 (m, 2H), 2.13-2.04 (m, 2H), 1.36 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 217.4, 145.5, 144.9, 137.4, 136.2, 133.7, 129.2, 128.2, 127.7, 124.9, 124.3, 124.2, 89.1, 62.6, 37.0, 34.2, 21.3, 17.7. HRMS *m*/*z* (ESI+): Calculated for $C_{21}H_{20}O_2Na^+$ ([M+Na]$^+$) 327.1356, found 327.1355.



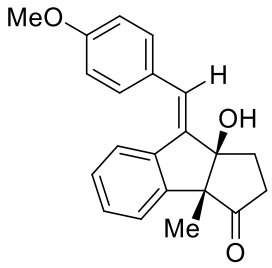




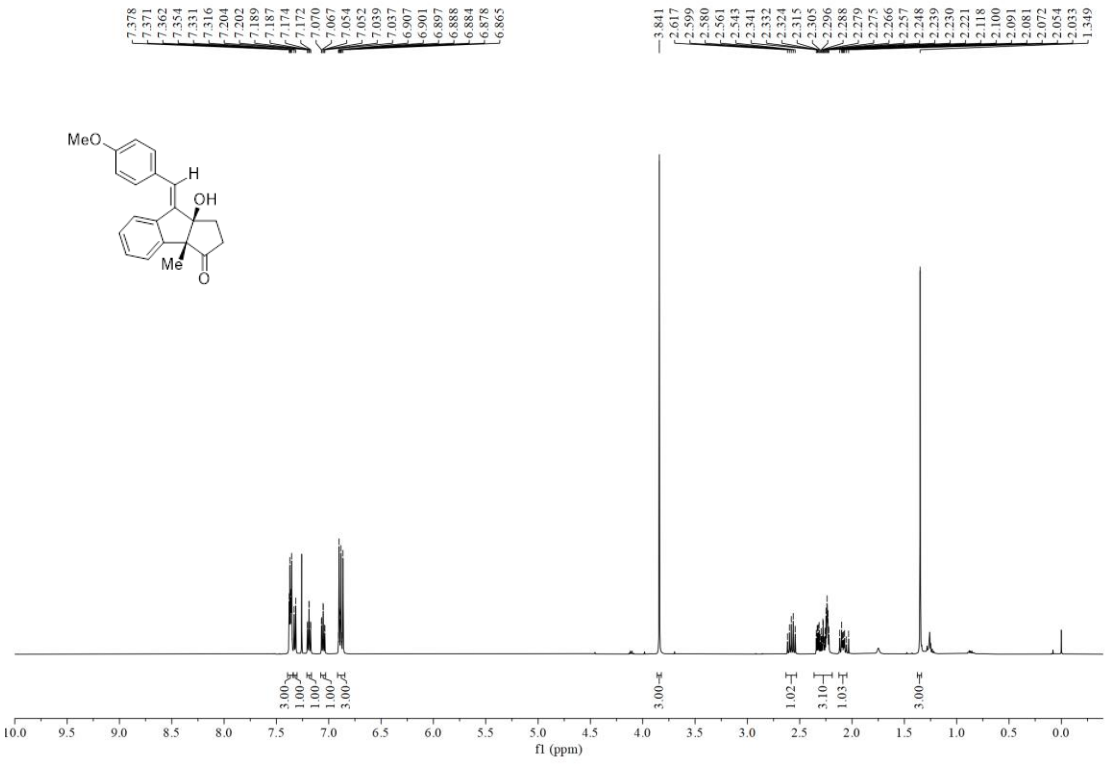
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

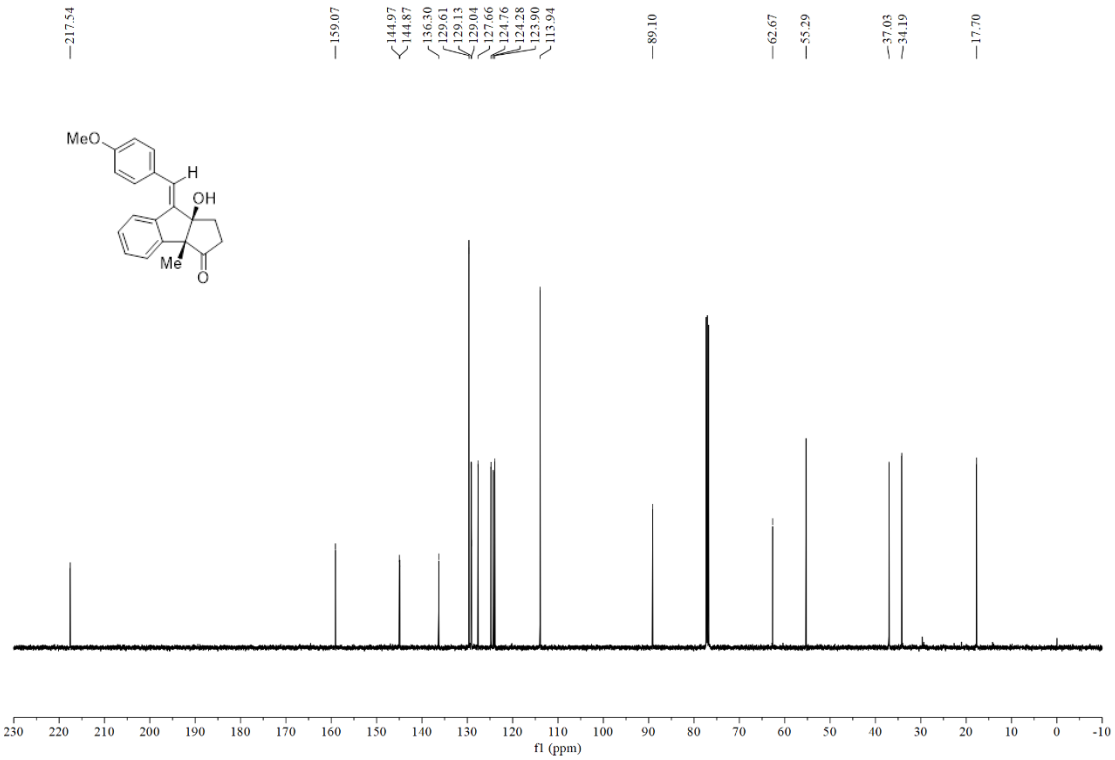
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.113	MM	0.3688	164.02098	7.41256	3.2176
2	8.930	BB	0.3480	4933.67285	219.72328	96.7824

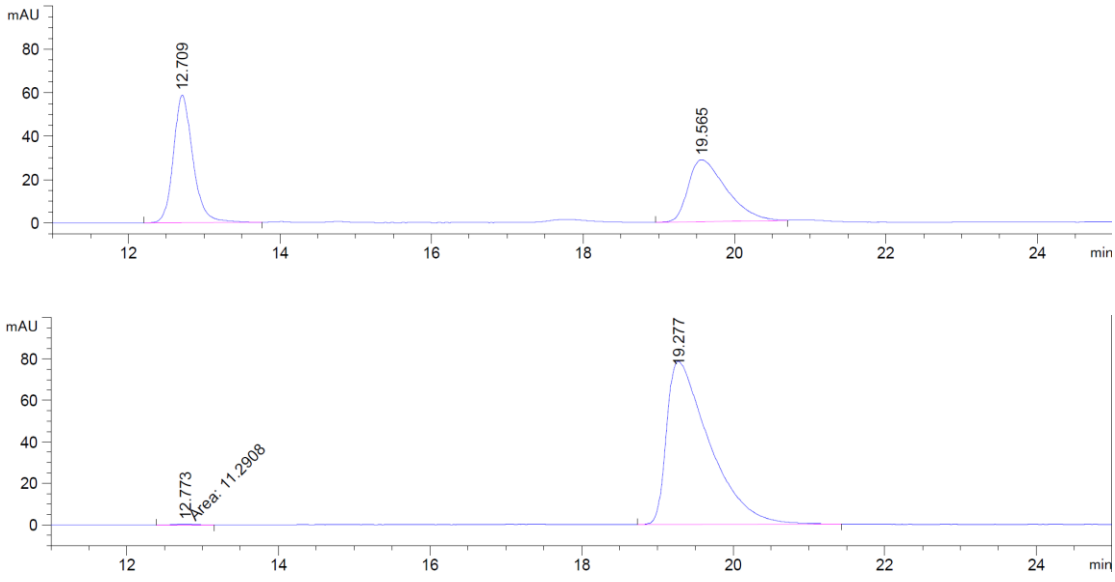
***(3aR,8aR)-8a-Hydroxy-8-((E)-4-methoxybenzylidene)-3a-methyl-1,3a,8,8a-tetra-hydrocyclopenta[a]inden-3(2H)-one* (*2c*)**



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); brown oil; 42 mg, 65% yield; $[\alpha]_D^{20}$ = -242.3 (*c* 0.5, CH_2Cl_2), 99% ee [Phenomenex Lux 5u Amylose-2 column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 90/10, 0.7 mL/min, 280 nm; t_{minor} = 12.8 min, t_{major} = 19.3 min]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 8.0, 4.0 Hz, 3H), 7.32 (d, *J* = 7.5 Hz, 1H), 7.20-7.17 (m, 1H), 7.07-7.04 (m, 1H), 6.91-6.87 (m, 3H), 3.84 (s, 3H), 2.62-2.54 (m, 1H), 2.34-2.22 (m, 3H), 2.12-2.03 (m, 1H), 1.35 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 217.5, 159.1, 145.0, 144.9, 136.3, 129.6, 129.1, 129.0, 127.7, 124.8, 124.3, 123.9, 113.9, 89.1, 62.7, 55.3, 37.0, 34.2, 17.7. Calculated for $C_{21}H_{20}O_3^+$ ([M]$^+$) 320.1407, found 320.1407.



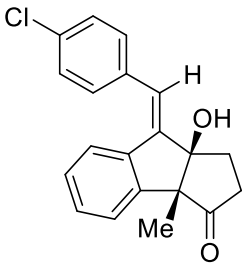




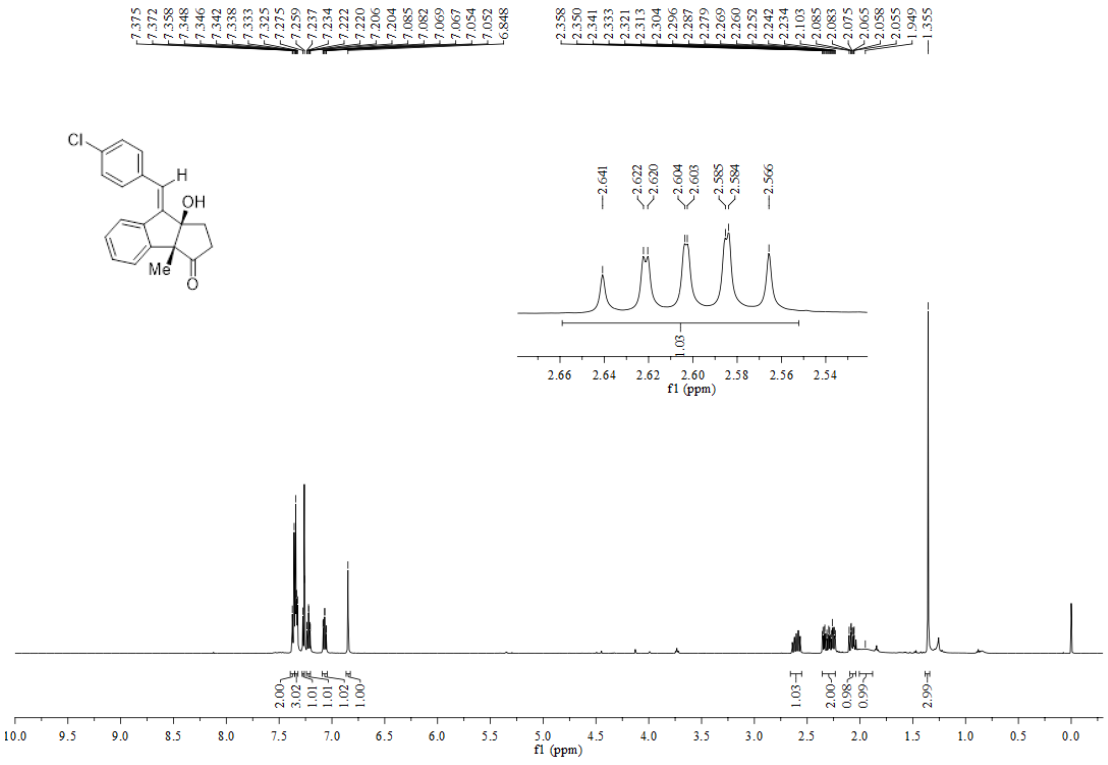
Signal 7: DAD1 G, Sig=280,4 Ref=360,100

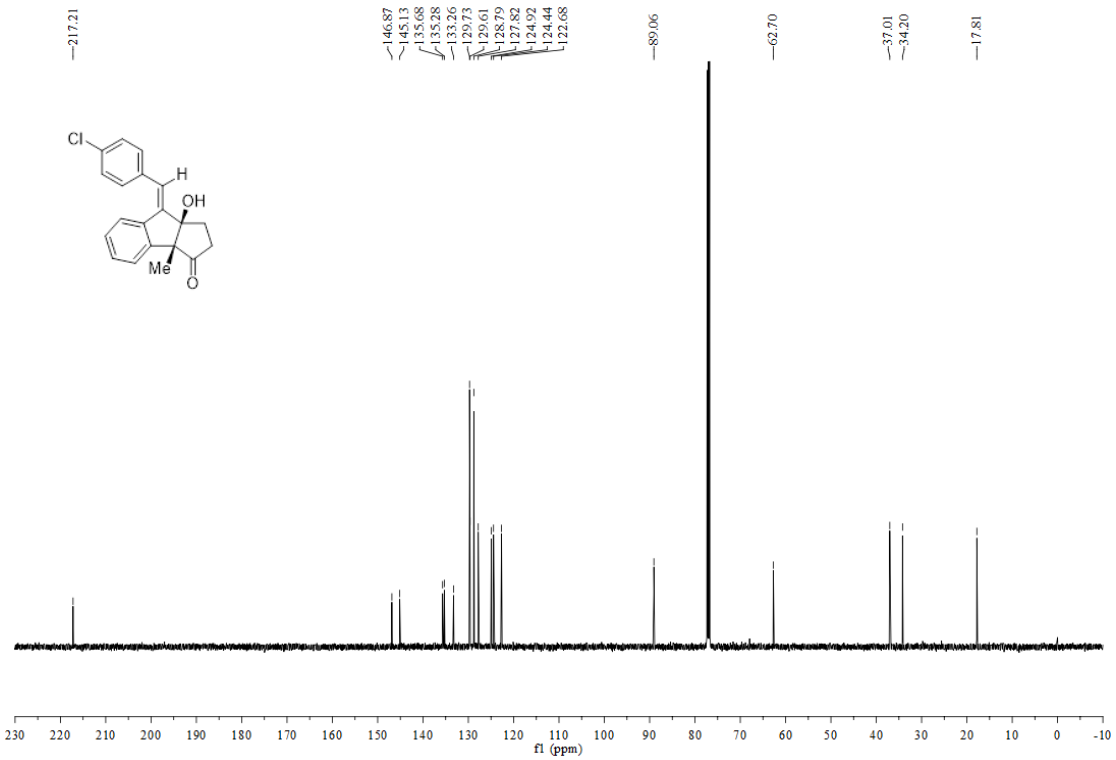
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.773	MM	0.3451	11.29077	5.45229e-1	0.3659
2	19.277	BB	0.5626	3074.20117	78.55772	99.6341

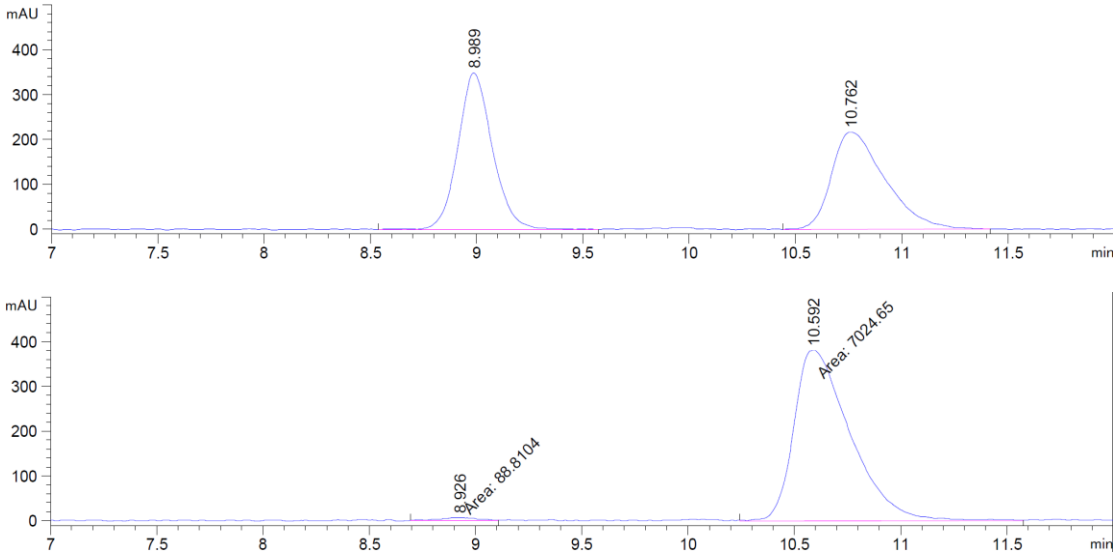
***(3aR,8aR)-8-((E)-4-Chlorobenzylidene)-8a-hydroxy-3a-methyl-1,3a,8,8a-tetrahydro-cyclopenta[a]inden-3(2H)-one* (*2d*)**



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); white solid, Mp = 95-96 °C; 48 mg, 75% yield; $[\alpha]_D^{20}$ = -246.35 (*c* 0.5, CH_2Cl_2), 98% ee [Phenomenex Lux 5u Amylose-2 column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 90/10, 0.7 mL/min, 254 nm; t_{minor} = 8.9 min, t_{major} = 10.6 min]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.35 (m, 2H), 7.34-7.33 (m, 3H), 7.27 (d, J = 8.0 Hz, 1H), 7.24-7.20 (m, 1H), 7.09-7.05 (m, 1H), 6.85 (s, 1H), 2.64-2.57 (m, 1H), 2.36-2.23 (m, 2H), 2.10-2.06 (m, 1H), 1.95 (s, 1H), 1.36 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 217.2, 146.9, 145.1, 135.7, 135.3, 133.3, 129.7, 129.6, 128.8, 127.8, 124.9, 124.4, 122.7, 89.1, 62.7, 37.0, 34.2, 17.8. HRMS *m*/*z* (ESI+): Calculated for $C_{20}H_{17}ClO_2Na^+$ ($[M+Na]^+$) 347.0809, found 347.0803.



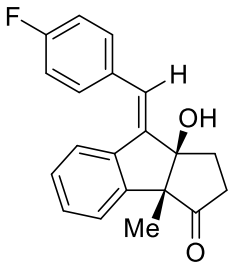




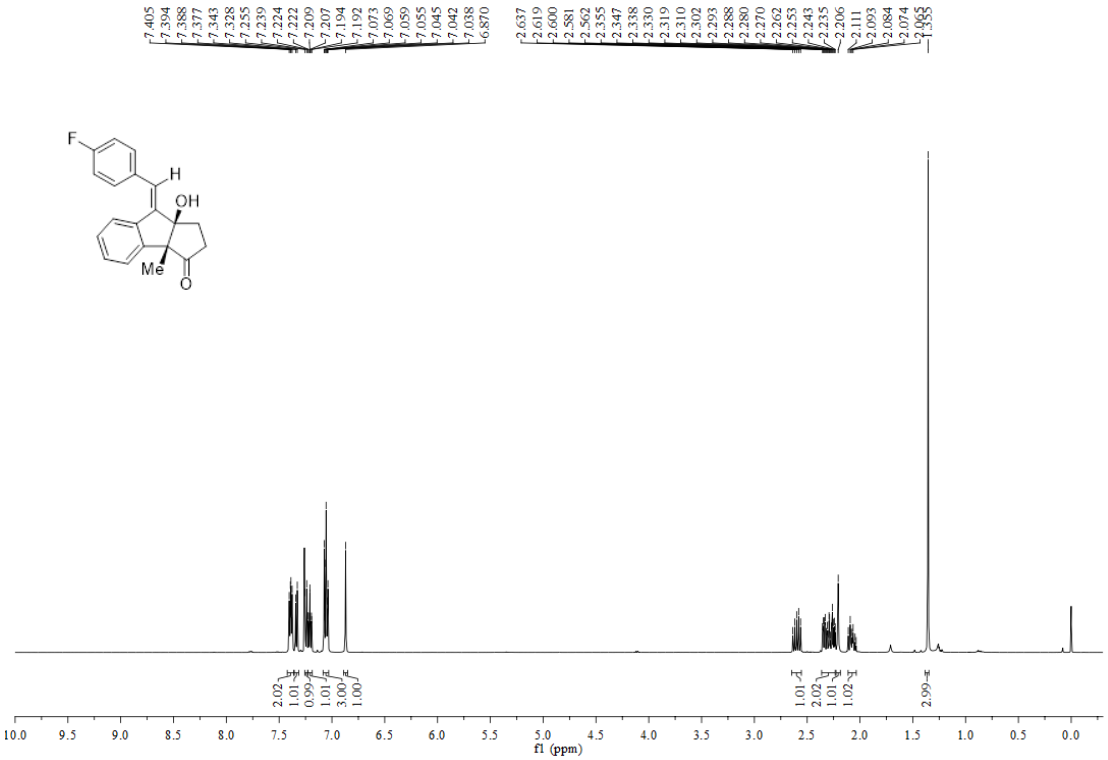
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

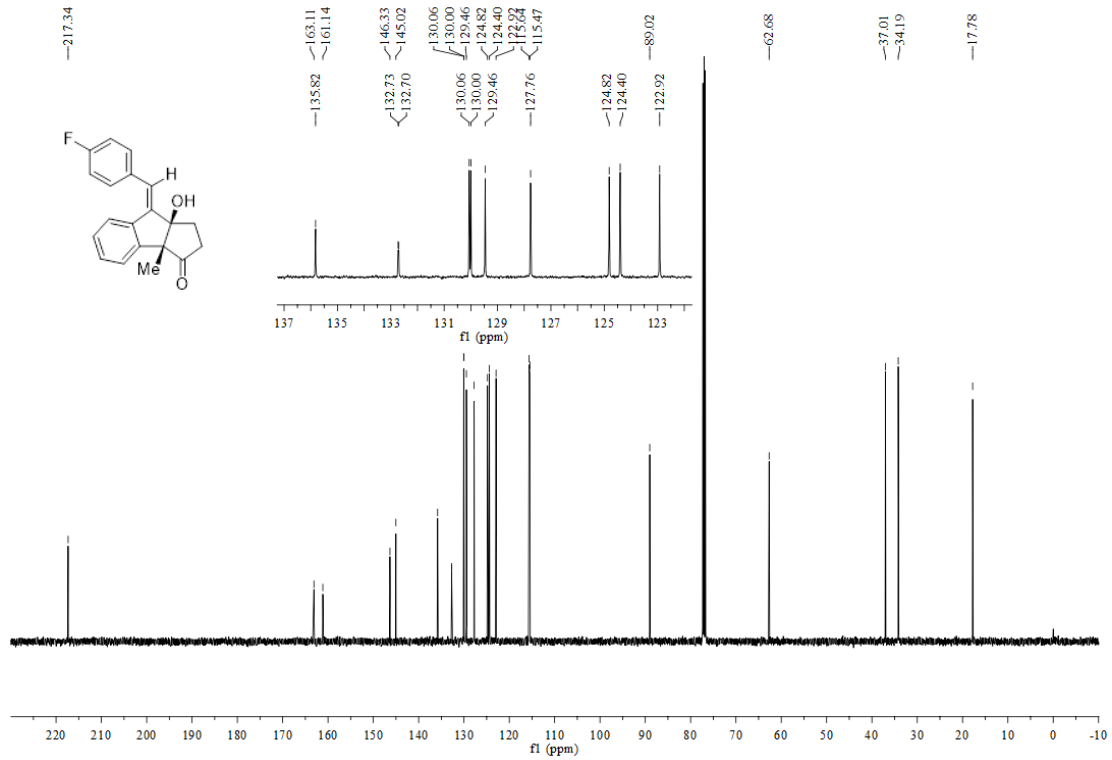
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.926	MM	0.2284	88.81040	6.47923	1.2485
2	10.592	MM	0.3076	7024.65186	380.59192	98.7515

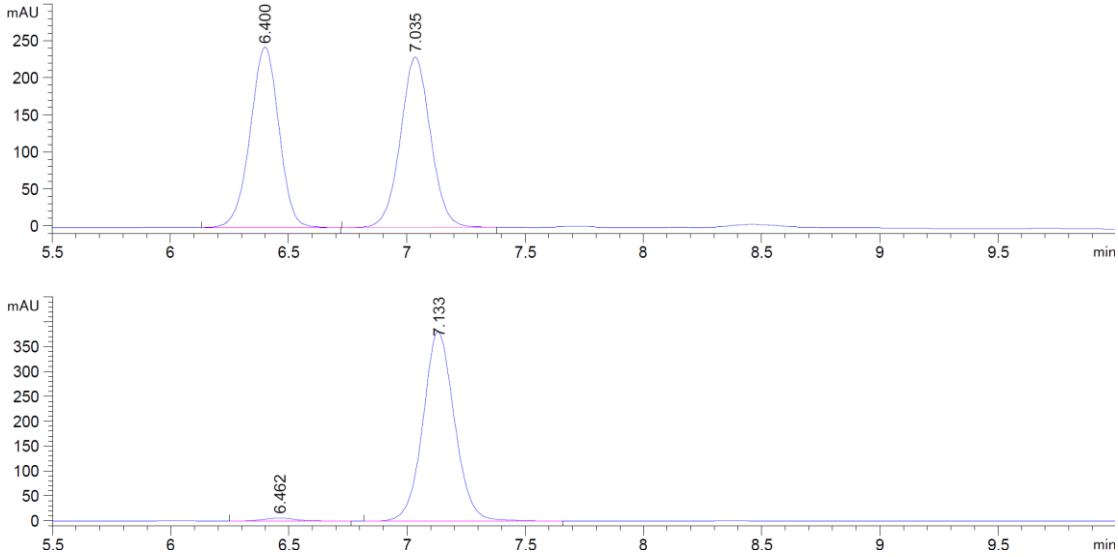
***(3aR,8aR)-8-((E)-4-Fluorobenzylidene)-8a-hydroxy-3a-methyl-1,3a,8,8a-tetra-hydro-cyclopenta[a]inden-3(2H)-one* (*2e*)**



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); white solid, Mp = 134-135 °C; 43 mg, 70% yield; $[\alpha]_D^{20}$ = -180.0 (*c* 1.0, CH_2Cl_2), 96% ee [Phenomenex Lux 5u Amylose-2 column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 95/05, 0.7 mL/min, 254 nm; t_{minor} = 6.5 min, t_{major} = 7.1 min]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (dd, J = 8.5, 5.5 Hz, 2H), 7.34 (d, J = 7.5 Hz, 1H), 7.25 (d, J = 8.0 Hz, 1H), 7.23-7.19 (m, 1H), 7.07-7.04 (m, 3H), 6.87 (s, 1H), 2.64-2.56 (m, 1H), 2.35-2.24 (m, 2H), 2.21 (s, 1H), 2.11-2.04 (m, 1H), 1.36 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 217.3, 162.1 (d, J = 246.3 Hz), 146.3, 145.0, 135.8, 132.7 (d, J = 3.8 Hz), 130.0 (d, J = 7.5 Hz), 129.5, 127.8, 124.8, 124.4, 122.9, 115.6 (d, J = 21.3 Hz). 89.0, 62.7, 37.0, 34.2, 17.8. HRMS *m*/*z* (ESI+): Calculated for $C_{20}H_{17}FO_2Na^+$ ($[M+Na]^+$) 331.1105, found 331.1104.



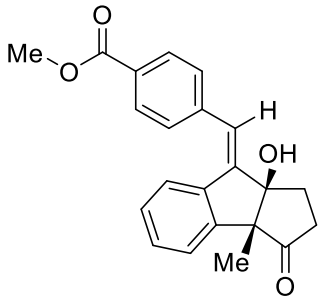




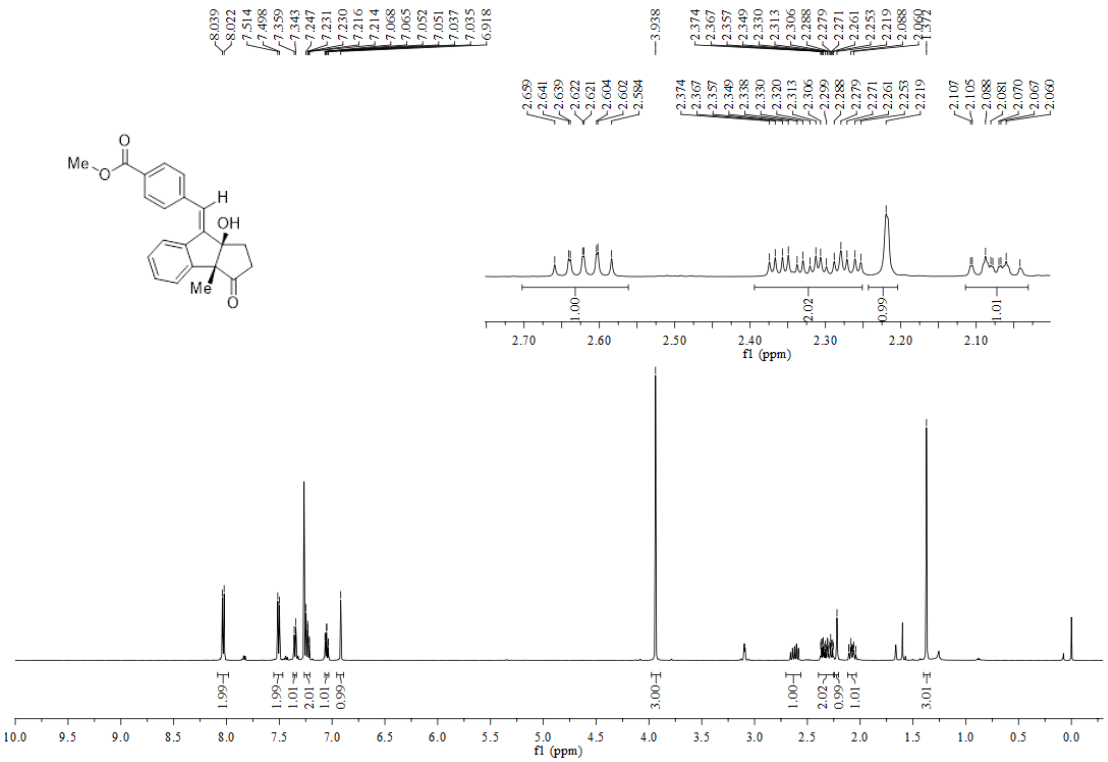
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

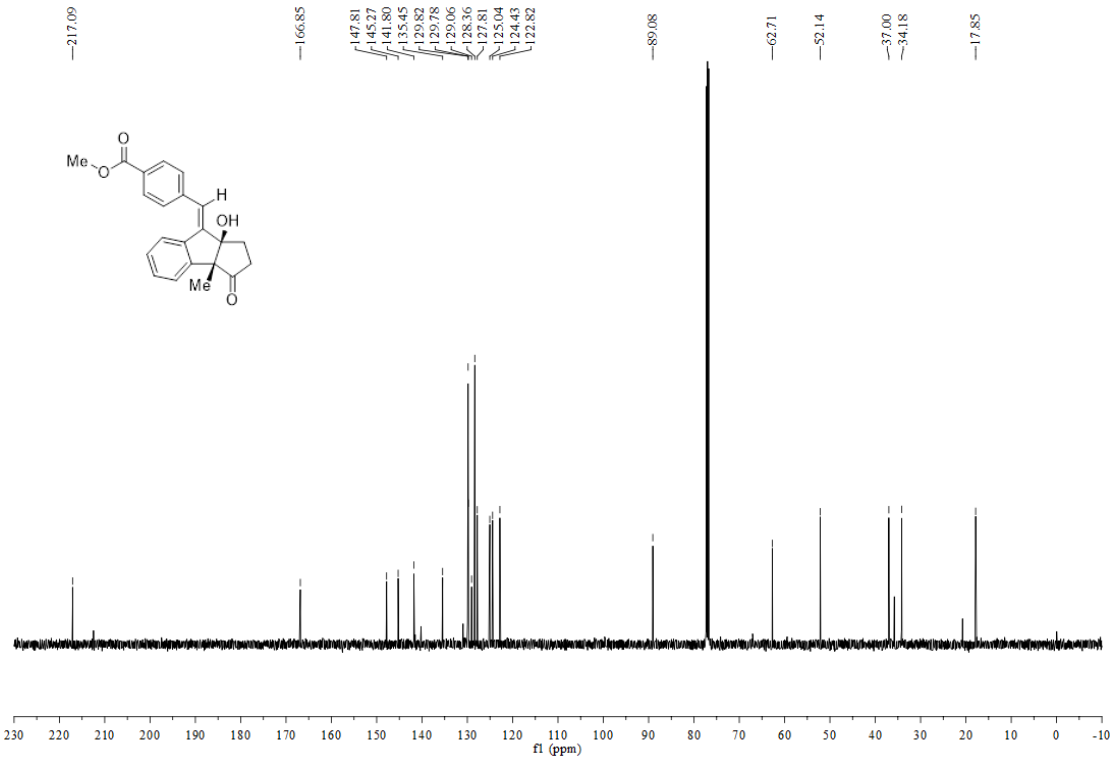
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.462	BB	0.1462	61.15265	6.24862	1.7041
2	7.133	BB	0.1421	3527.30322	380.62170	98.2959

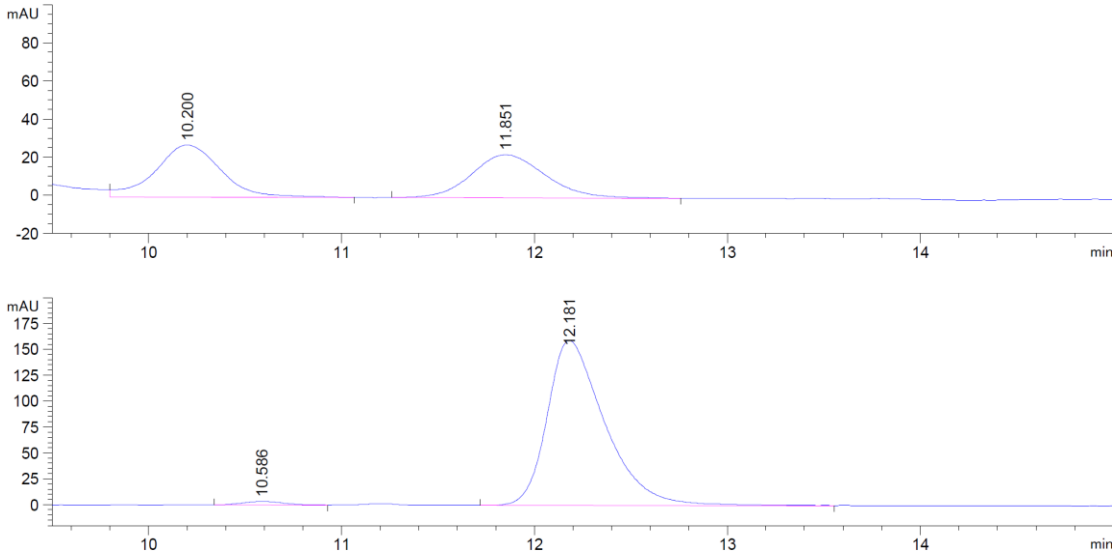
Methyl 4-((E)-((3aR,8aR)-8a-hydroxy-3a-methyl-3-oxo-2,3,3a,8a-tetrahydrocyclopenta[a]inden-8(1H)-ylidene)methyl)benzoate (2f)



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow oil; 62 mg, 89% yield; $[\alpha]_D^{20}$ = -127.8 (*c* 0.5, CH_2Cl_2), 97% ee [Phenomenex Lux 5u Amylose-2 column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 85/15, 0.7 mL/min, 254 nm; t_{minor} = 10.6 min, t_{major} = 12.2 min]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.26-7.21 (m, 2H), 7.07-7.04 (m, 1H), 6.92 (s, 1H), 3.94 (s, 3H), 2.66-2.58 (m, 1H), 2.37-2.25 (m, 2H), 2.22 (s, 1H), 2.11-2.06 (m, 1H), 1.37 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 217.1, 166.9, 147.8, 145.3, 141.8, 135.5, 129.82, 129.78, 129.1, 128.4, 127.8, 125.0, 124.4, 122.8, 89.1, 62.7, 52.1, 37.0, 34.2, 17.9. HRMS *m*/*z* (ESI+): Calculated for $C_{22}H_{20}O_4^+$ ([M]$^+$) 348.1356, found 348.1359.



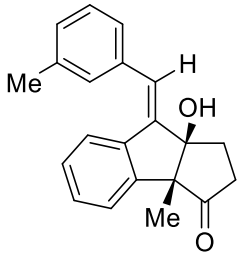




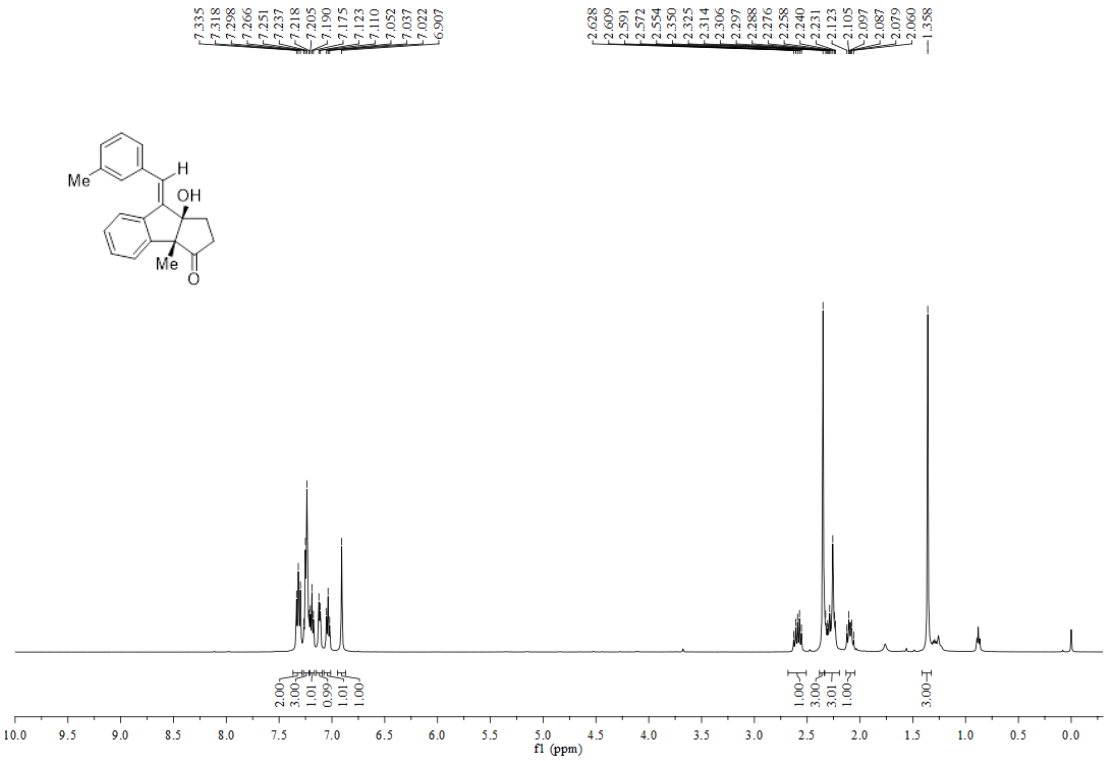
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

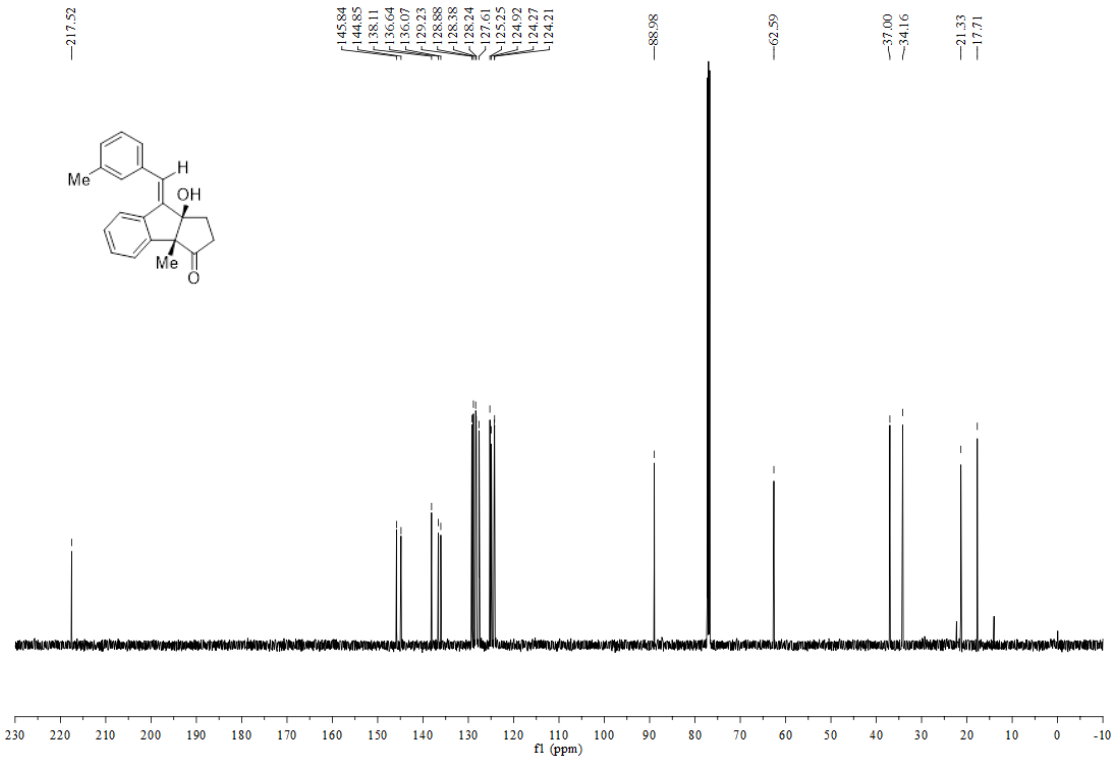
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.586	BB	0.1860	50.19617	3.40447	1.4967
2	12.181	BV R	0.3118	3303.52246	159.37894	98.5033

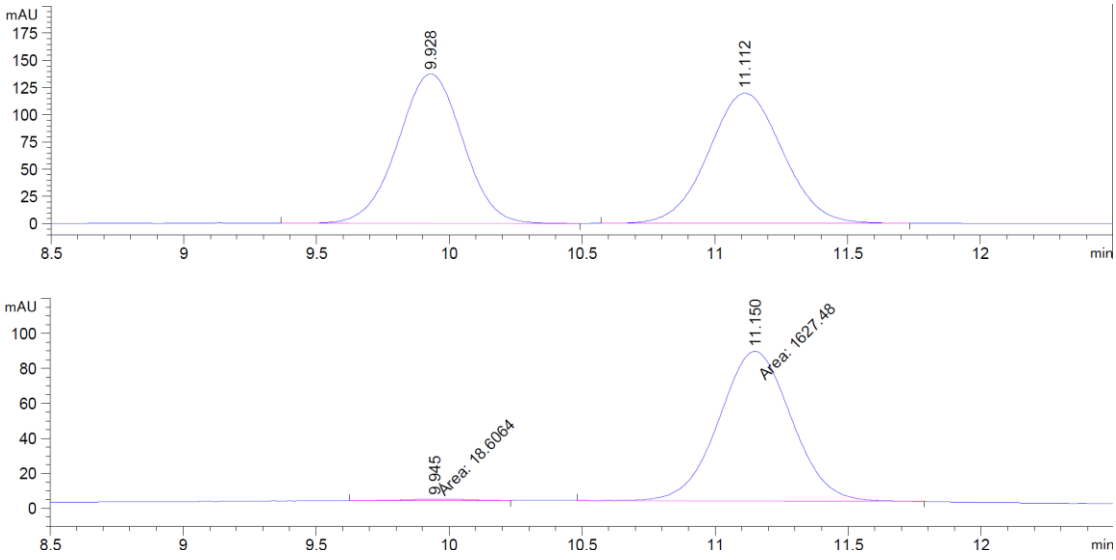
***(3aR,8aR)-8a-Hydroxy-3a-methyl-8-((E)-3-methylbenzylidene)-1,3a,8,8a-tetra-hydrocyclopenta[a]inden-3(2H)-one* (2g)**



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); brown solid, Mp = 97-98 °C; 43 mg, 71% yield; $[\alpha]_D^{20}$ = -209.1 (*c* 1.0, CH_2Cl_2), 98% ee [Phenomenex Lux 5u Cellulose-1 column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 85/15, 0.7 mL/min, 254 nm; t_{minor} = 9.9 min, t_{major} = 11.2 min]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34-7.27 (m, 2H), 7.25-7.21 (m, 3H), 7.19 (t, J = 7.5 Hz, 1H), 7.12 (d, J = 6.5 Hz, 1H), 7.04 (t, J = 7.5 Hz, 1H), 6.91 (s, 1H), 2.63-2.55 (m, 1H), 2.35 (s, 3H), 2.33-2.23 (m, 3H), 2.12-2.06 (m, 1H), 1.36 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 217.5, 145.8, 144.9, 138.1, 136.6, 136.1, 129.2, 128.9, 128.4, 128.2, 127.6, 125.3, 124.9, 124.3, 124.2, 89.0, 62.6, 37.0, 34.2, 21.3, 17.7. HRMS (ESI) *m*/*z* Calculated for $C_{21}H_{20}O_2Na^+$ ($[M+Na]^+$) 327.1356, found 327.1356.



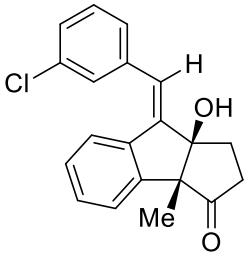




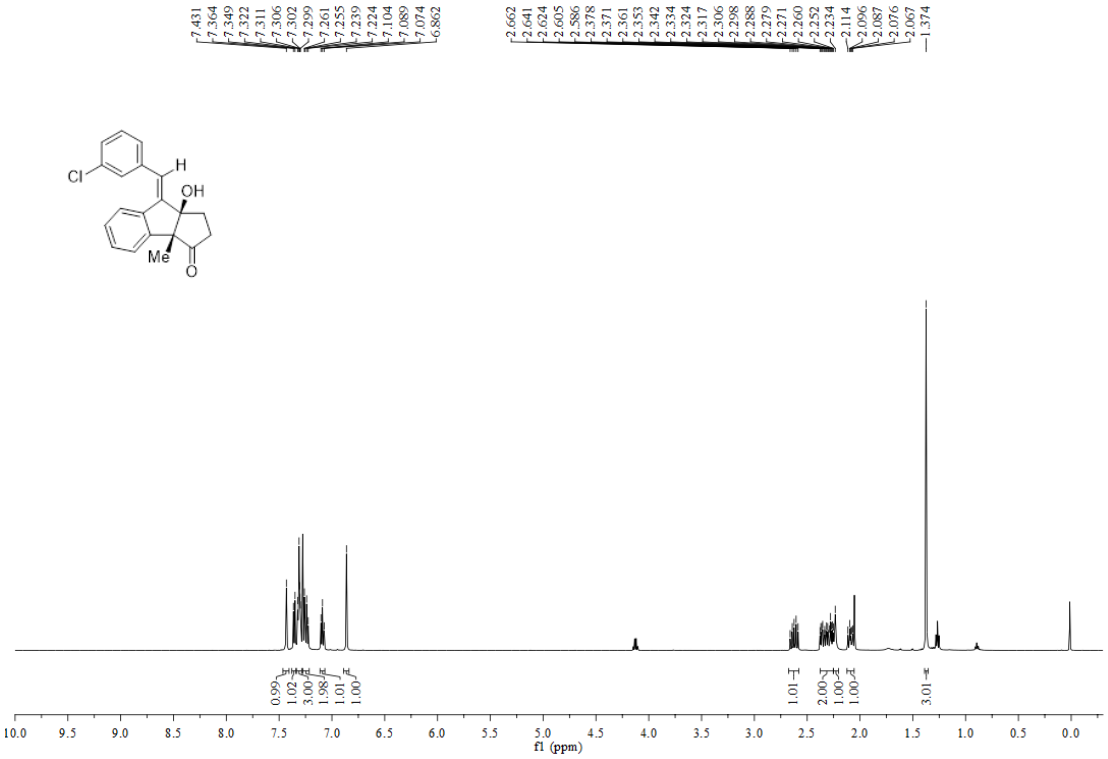
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

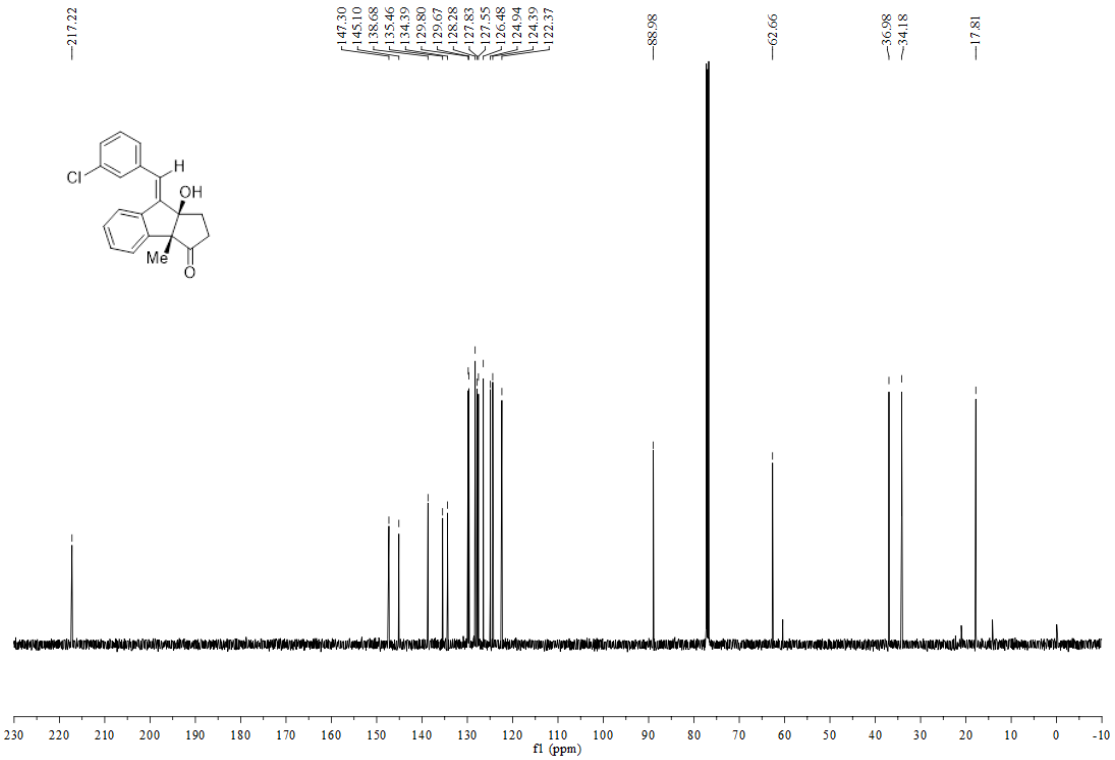
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.945	MM	0.3018	18.60638	1.02754	1.1303
2	11.150	MM	0.3178	1627.47791	85.35074	98.8697

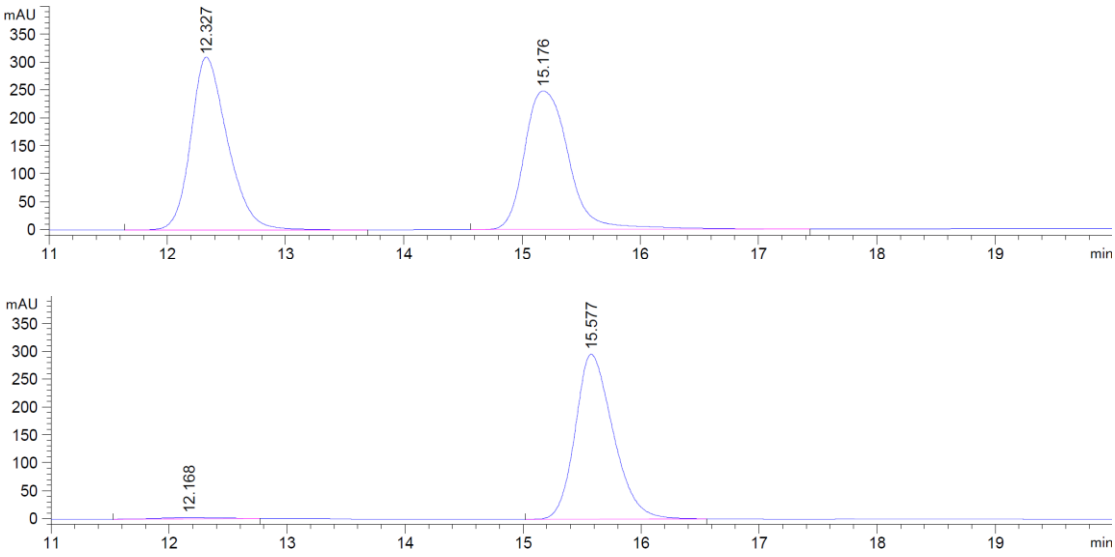
***(3aR,8aR)-8-((E)-3-Chlorobenzylidene)-8a-hydroxy-3a-methyl-1,3a,8,8a-tetrahydro-cyclopenta[a]inden-3(2H)-one* (*2h*)**



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); white solid, Mp = 149-150°C; 45 mg, 70% yield; $[\alpha]_D^{20}$ = -129.2 (*c* 0.5, CH_2Cl_2), 98% ee [Phenomenex Lux 5u Amylose-2 column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 85/15, 0.7 mL/min, 254 nm; t_{minor} = 12.2 min, t_{major} = 15.6 min]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.36 (d, J = 7.5 Hz, 1H), 7.32-7.30 (m, 3H), 7.26-7.22 (m, 2H), 7.09 (t, J = 7.5 Hz, 1H), 6.86 (s, 1H), 2.66-2.59 (m, 1H), 2.38-2.25 (m, 2H), 2.23 (s, 1H), 2.11-2.07 (m, 1H), 1.37 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 217.2, 147.3, 145.1, 138.7, 135.5, 134.4, 129.8, 129.7, 128.3, 127.8, 127.6, 126.5, 124.9, 124.4, 122.4, 89.0, 62.7, 37.0, 34.2, 17.8. HRMS *m*/*z* (ESI+): Calculated for $C_{20}H_{17}ClO_2^+$ ([M]$^+$) 324.0917, found 324.0914.



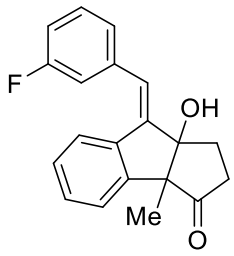




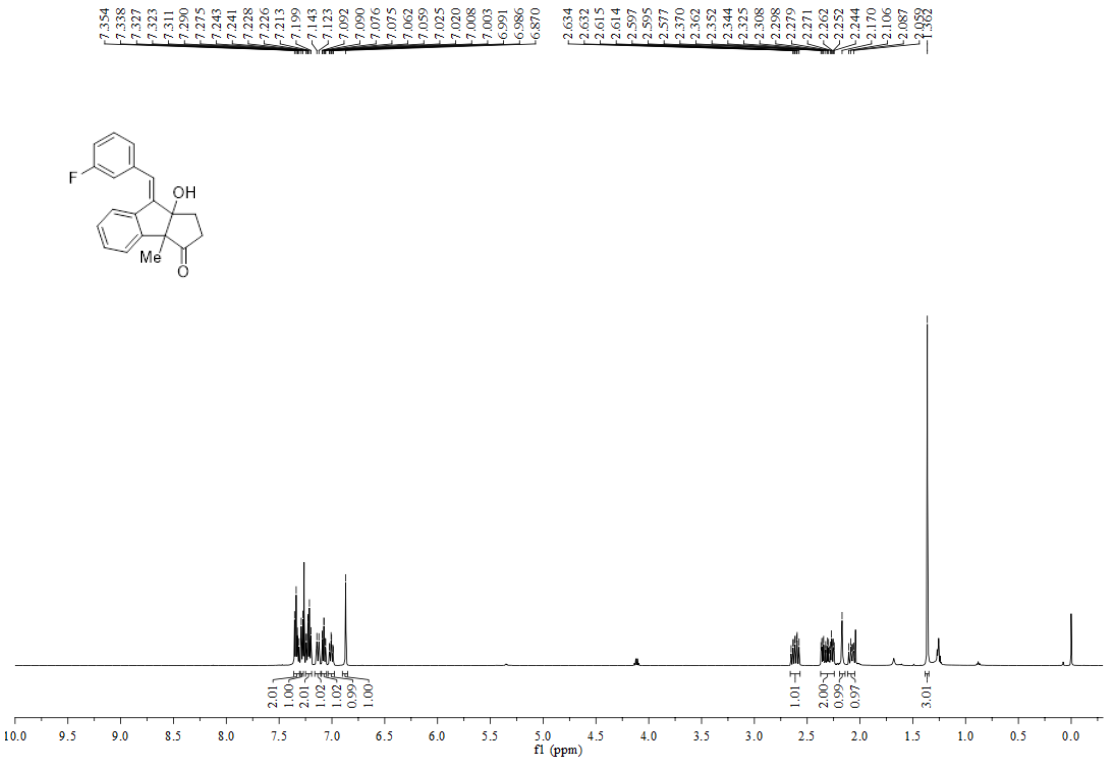
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

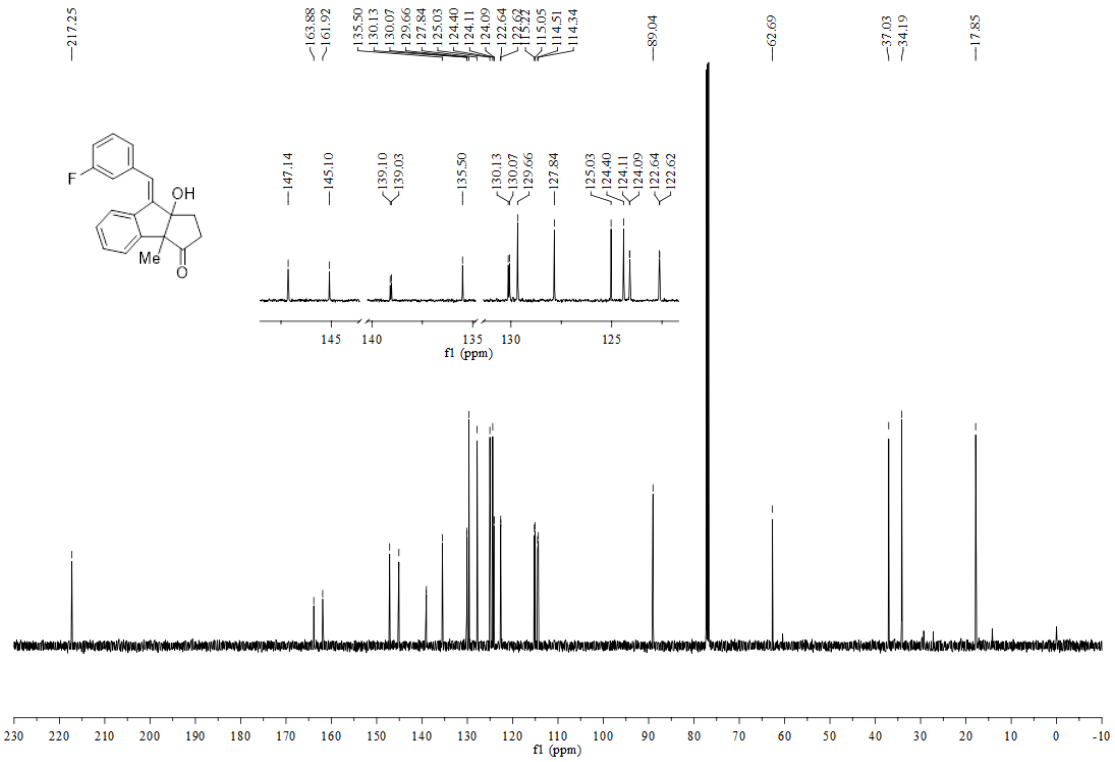
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.168	BB	0.4024	70.57710	2.46235	1.0587
2	15.577	BB	0.3381	6595.52393	295.89444	98.9413

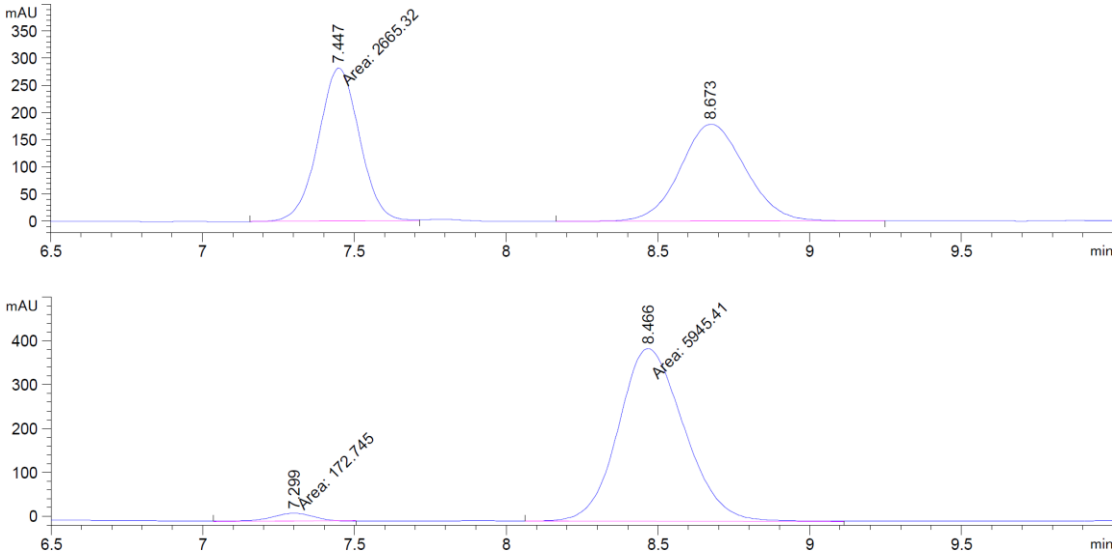
***(E)-8-(3-Fluorobenzylidene)-8a-hydroxy-3a-methyl-1,3a,8,8a-tetrahydrocyclopenta-[a]inden-3(2H)-one* (*2i*)**



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); white solid, Mp = 150-151°C; 36 mg, 58% yield; $[\alpha]_D^{20}$ = -195.9 (*c* 0.5, CH_2Cl_2), 94% ee [Phenomenex Lux 5u Amylose-2 column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 85/15, 0.7 mL/min, 254 nm; t_{minor} = 7.3 min, t_{major} = 8.5 min]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.31 (m, 2H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.24-7.20 (m, 2H), 7.13 (d, *J* = 10.0 Hz, 1H), 7.09-7.06 (m, 1H), 7.03-6.99 (m, 1H), 6.87 (s, 1H), 2.63-2.58 (m, 1H), 2.37-2.24 (m, 2H), 2.17 (s, 1H), 2.11-2.06 (m, 1H), 1.36 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 217.3, 162.9 (d, *J* = 245.0 Hz), 147.1, 145.1, 139.1 (d, *J* = 8.8 Hz), 135.5, 130.1 (d, *J* = 7.5 Hz), 129.7, 127.8, 125.0, 124.4, 124.1 (d, *J* = 2.5 Hz), 122.6 (d, *J* = 2.5 Hz), 115.1 (d, *J* = 21.3 Hz), 114.4 (d, *J* = 21.3 Hz), 89.0, 62.7, 37.0, 34.2, 17.9. HRMS (ESI) m/z Calculated for $C_{20}H_{17}FO_2Na^+$ ([M+Na]$^+$) 331.1105, found 331.1105.



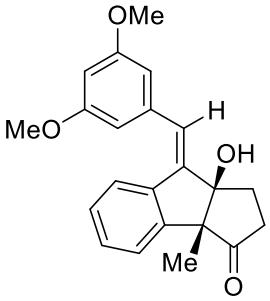




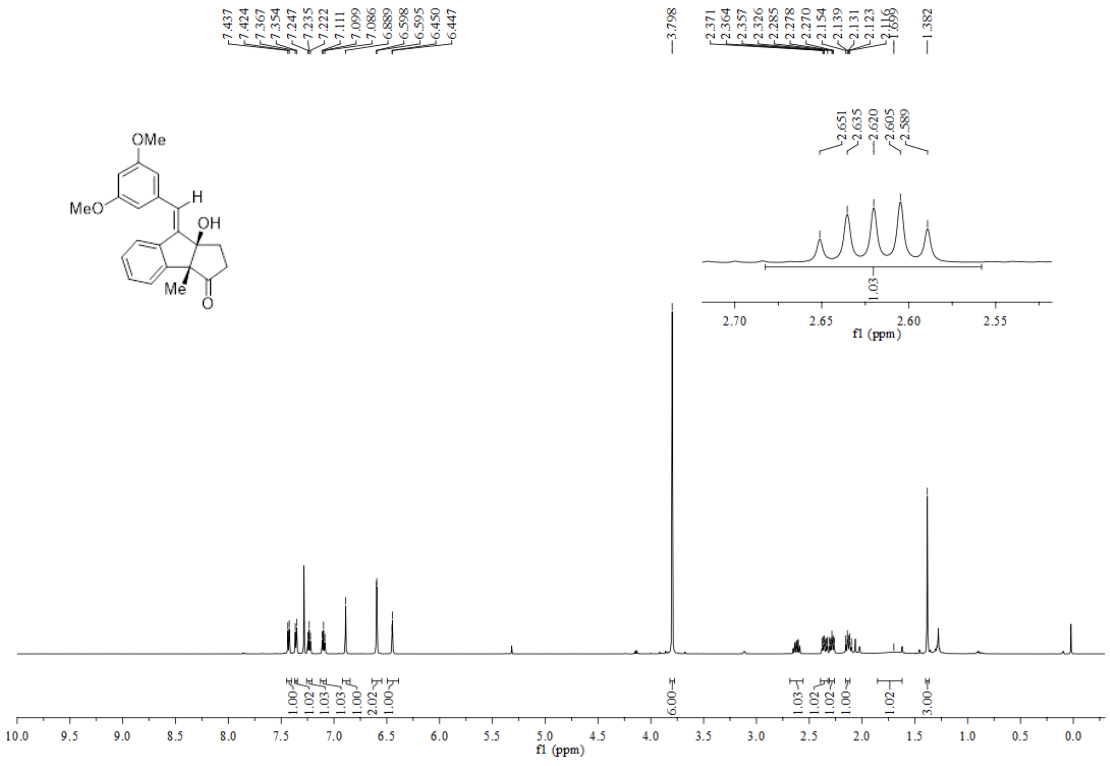
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

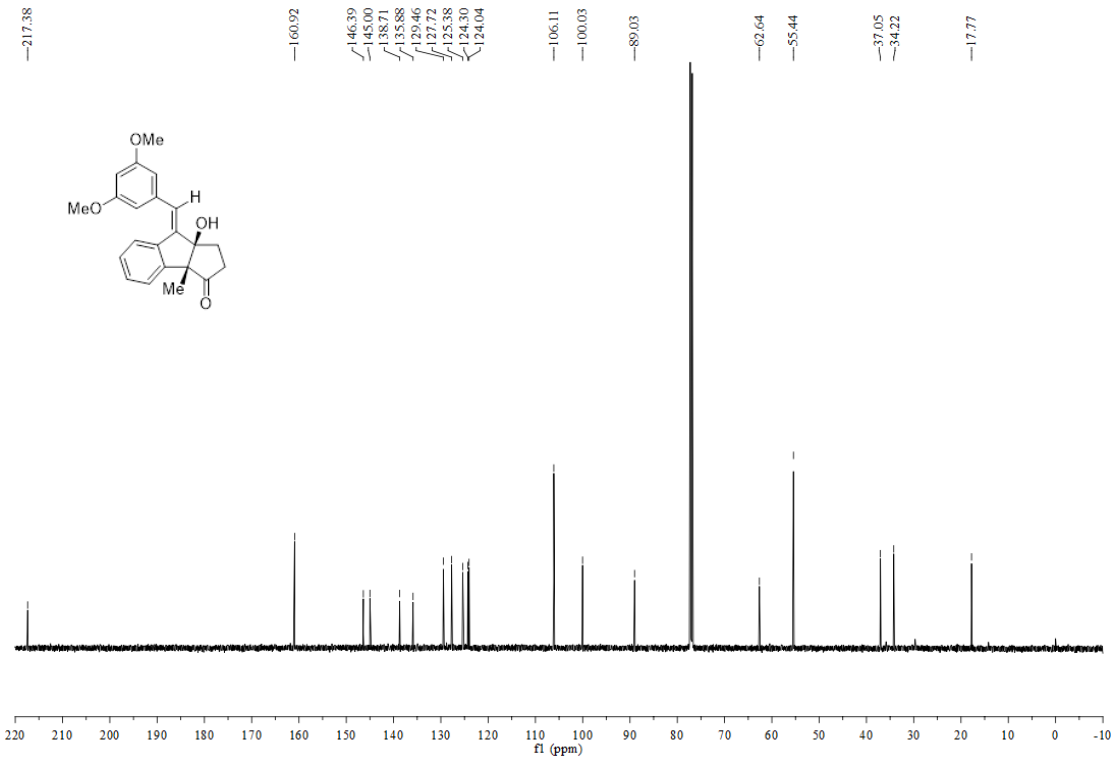
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.299	MM	0.1609	172.74529	17.88926	2.8235
2	8.466	MM	0.2516	5945.41016	393.82196	97.1765

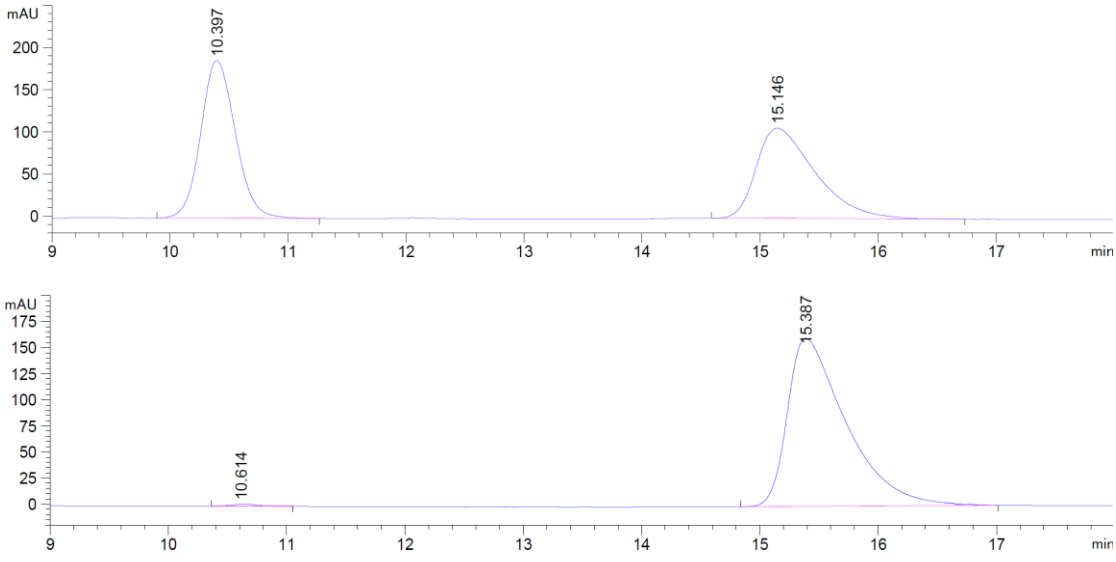
(3aR,8aR)-8-((E)-3,5-Dimethoxybenzylidene)-8a-hydroxy-3a-methyl-1,3a,8,8a-tetra-hydrocyclopenta[a]inden-3(2H)-one (2j)



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow oil; 55 mg, 79% yield; $[\alpha]_D^{20}$ = -147.8 (*c* 0.5, CH_2Cl_2), 99% ee [Phenomenex Lux 5u Amylose-2 column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 85/15, 0.7 mL/min, 254 nm; t_{minor} = 10.6 min, t_{major} = 15.4 min]; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.8 Hz, 1H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.23 (t, *J* = 7.2 Hz, 1H), 7.10 (t, *J* = 7.2 Hz, 1H), 6.89 (s, 1H), 6.60 (d, *J* = 2.4 Hz, 2H), 6.45 (d, *J* = 1.8 Hz, 1H), 3.80 (s, 6H), 2.65-2.59 (m, 1H), 2.37-2.33 (m, 1H), 2.29-2.27 (m, 1H), 2.15-2.12 (m, 1H), 1.70 (s, 1H), 1.38 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 217.4, 160.9, 146.4, 145.0, 138.7, 135.9, 129.5, 127.7, 125.4, 124.3, 124.0, 106.1, 100.0, 89.0, 62.6, 55.4, 37.1, 34.2, 17.8. HRMS *m*/*z* (ESI+): Calculated for $C_{22}H_{23}O_4^+$ ($[M+H]^+$) 351.1591, found 351.1594.



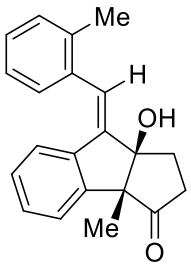




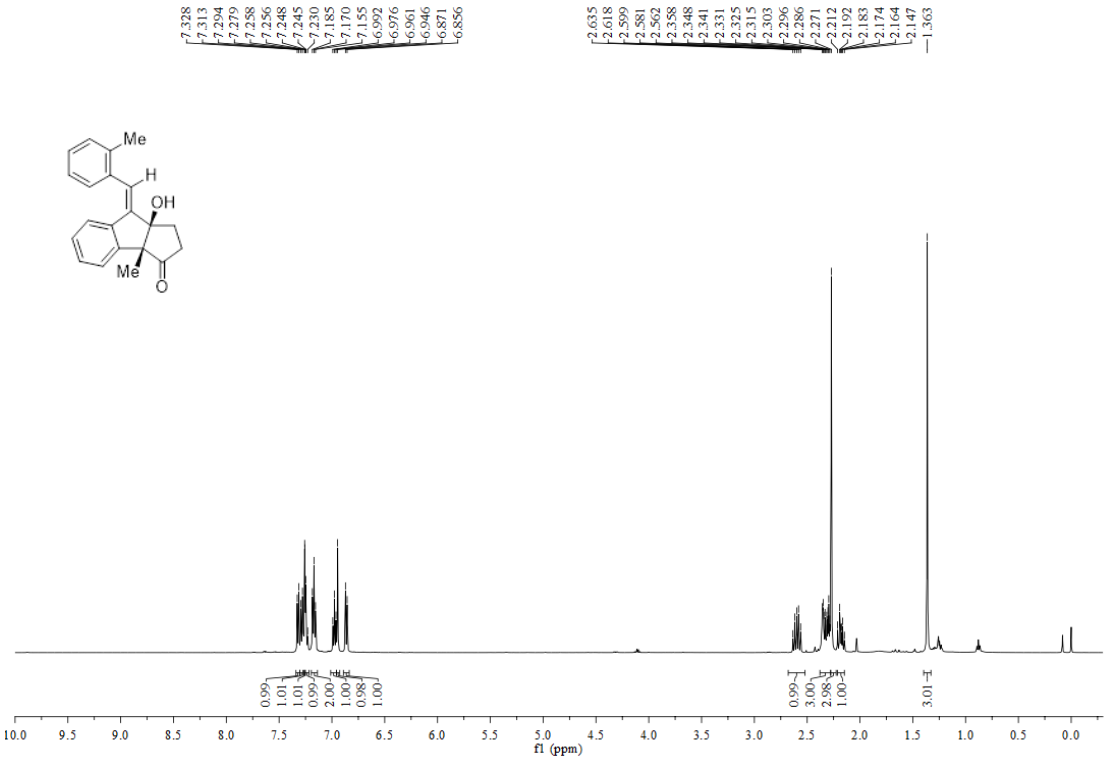
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

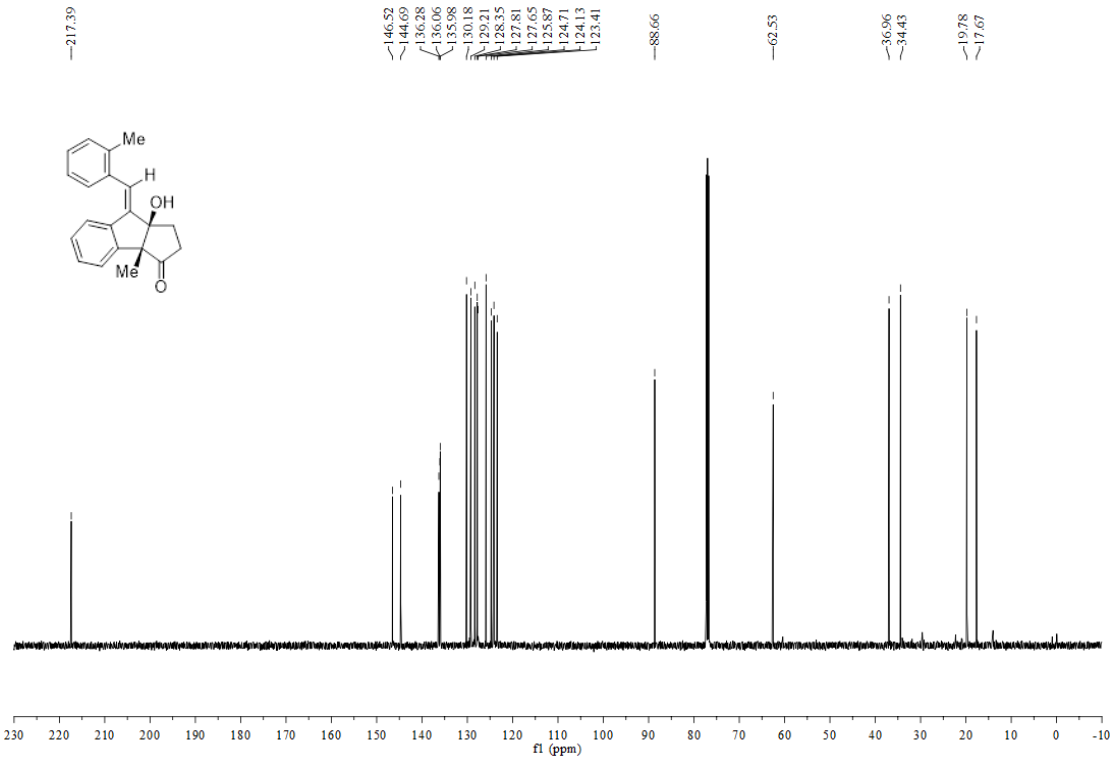
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.614	BB	0.2059	34.73489	2.04816	0.6240
2	15.387	BB	0.4830	5531.69629	160.92369	99.3760

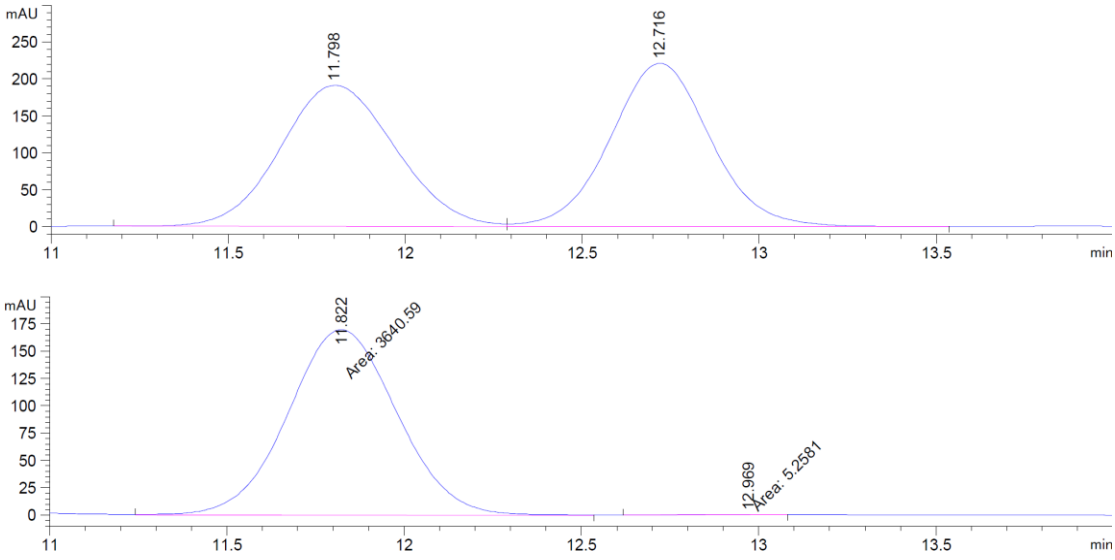
***(3aR,8aR)-8a-Hydroxy-3a-methyl-8-((E)-2-methylbenzylidene)-1,3a,8,8a-tetra-hydrocyclopenta[a]inden-3(2H)-one* (*2k*)**



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); brown oil; 50 mg, 82% yield; $[\alpha]_D^{20}$ = -202.4 (*c* 1.0, CH_2Cl_2), 99% ee [Phenomenex Lux 5u Cellulose-1 column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 85/15, 0.7 mL/min, 254 nm; t_{major} = 11.8 min, t_{minor} = 13.0 min]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, *J* = 7.5 Hz, 1H), 7.29 (d, *J* = 7.5 Hz, 1H), 7.26 (d, *J* = 1.0 Hz, 1H), 7.25-7.23 (m, 1H), 7.17 (t, *J* = 7.5 Hz, 2H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.95 (s, 1H), 6.86 (d, *J* = 7.5 Hz, 1H), 2.64-2.56 (m, 1H), 2.35-2.29 (m, 3H), 2.27 (s, 3H), 2.21-2.15 (m, 1H), 1.36 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 217.4, 146.5, 144.7, 136.3, 136.1, 136.0, 130.2, 129.2, 128.4, 127.8, 127.7, 125.9, 124.7, 124.1, 123.4, 88.7, 62.5, 37.0, 34.4, 19.8, 17.7. HRMS *m*/*z* (ESI+): Calculated for $C_{21}H_{20}O_2Na^+$ ([M+Na]$^+$) 327.1356, found 327.1355.



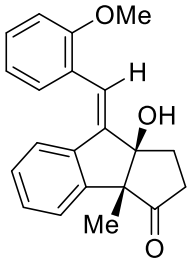




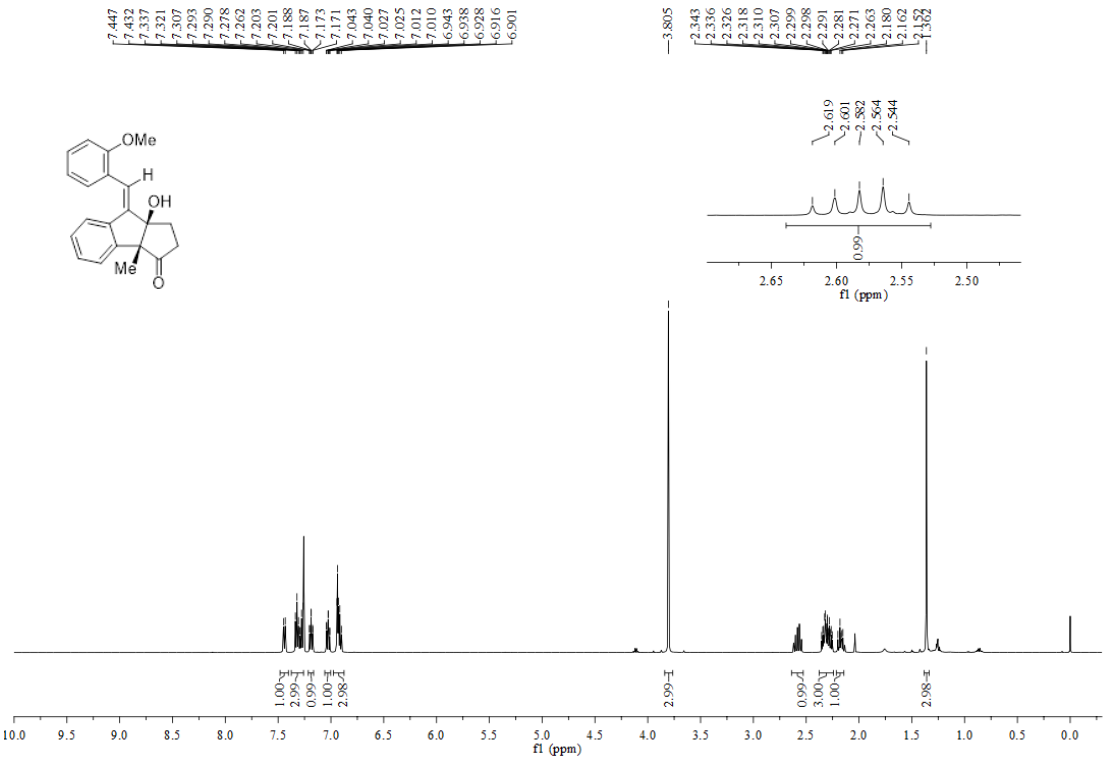
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

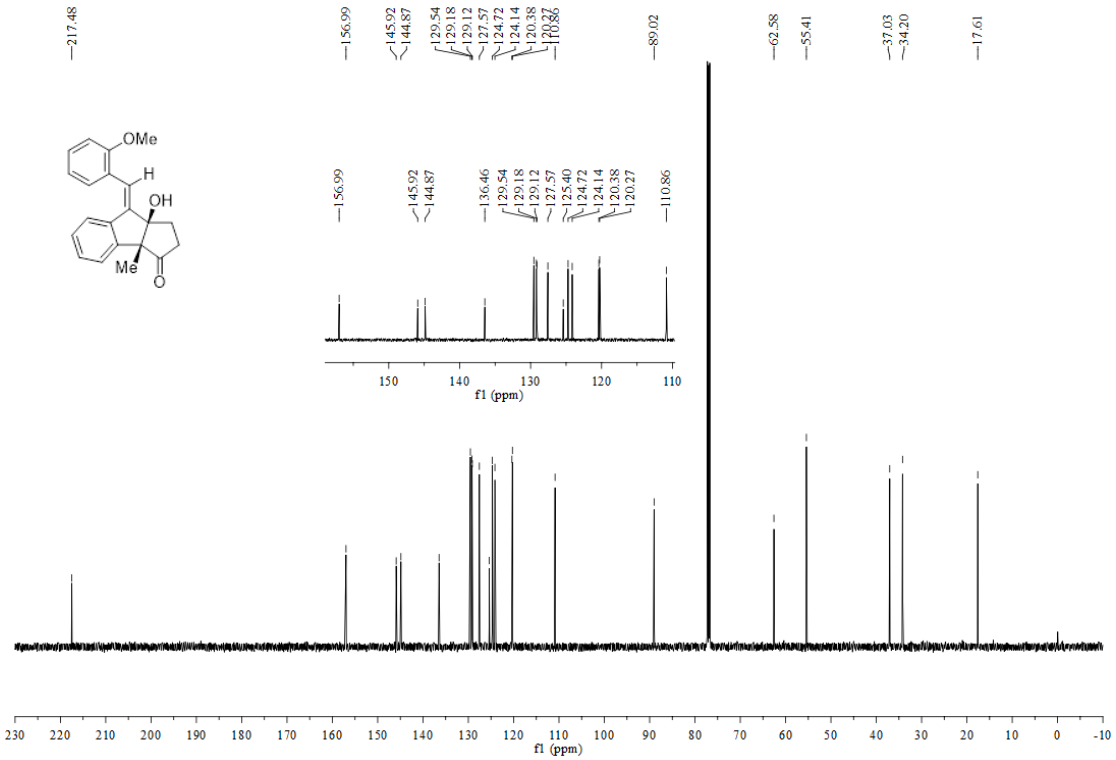
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.822	MM	0.3572	3640.58960	169.87329	99.8558
2	12.969	MM	0.3387	5.25810	2.58749e-1	0.1442

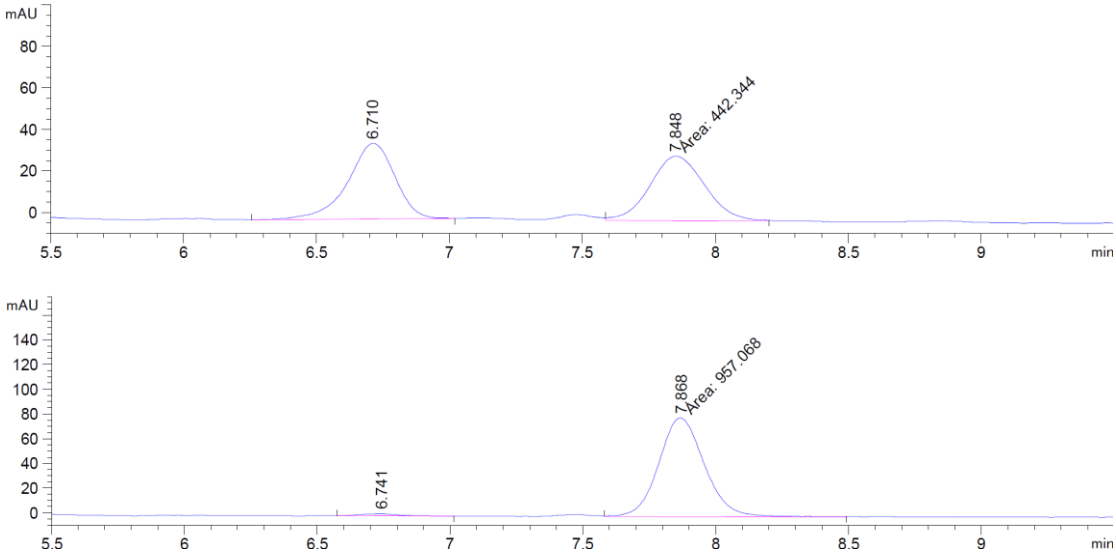
***(3aR,8aR)-8a-Hydroxy-8-((E)-2-methoxybenzylidene)-3a-methyl-1,3a,8,8a-tetra-hydrocyclopenta[a]inden-3(2H)-one* (*2l*)**



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:3 (v/v); yellow oil; 40 mg, 62% yield; $[\alpha]_D^{20}$ = -160.2 (*c* 0.5, CH_2Cl_2), 96% ee [Phenomenex Lux 5u Amylose-2 column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 85/15, 0.7 mL/min, 254 nm; t_{minor} = 6.7 min, t_{major} = 7.9 min]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, J = 7.5 Hz, 1H), 7.34-7.26 (m, 3H), 7.20-7.17 (m, 1H), 7.04-7.01 (m, 1H), 6.94-6.90 (m, 3H), 3.81 (s, 3H), 2.62-2.54 (m, 1H), 2.34-2.26 (m, 3H), 2.18-2.15 (m, 1H), 1.36 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 217.5, 157.0, 145.9, 144.9, 136.5, 129.5, 129.2, 129.1, 127.6, 125.4, 124.7, 124.1, 120.4, 120.3, 110.9, 89.0, 62.6, 55.4, 37.0, 34.2, 17.6. HRMS *m/z* (ESI+): Calculated for $C_{21}H_{20}O_3^+$ ([M]$^+$) 320.1407, found 320.1410.



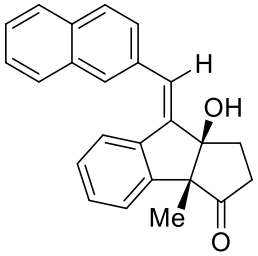




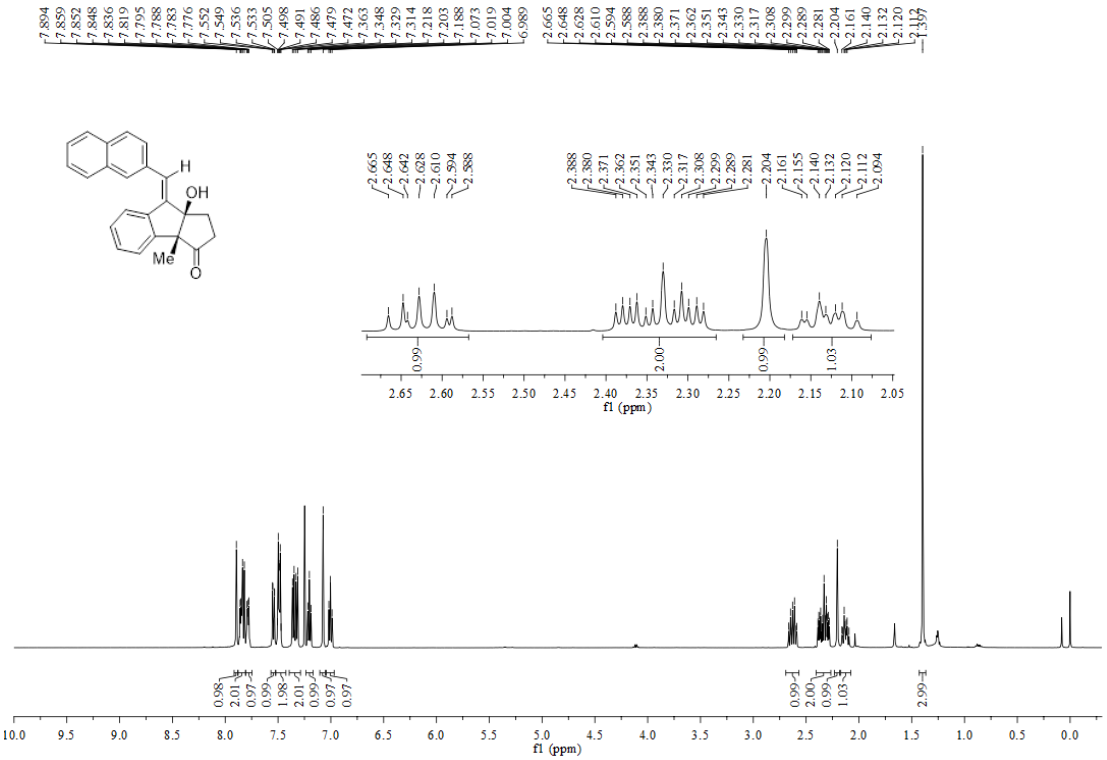
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

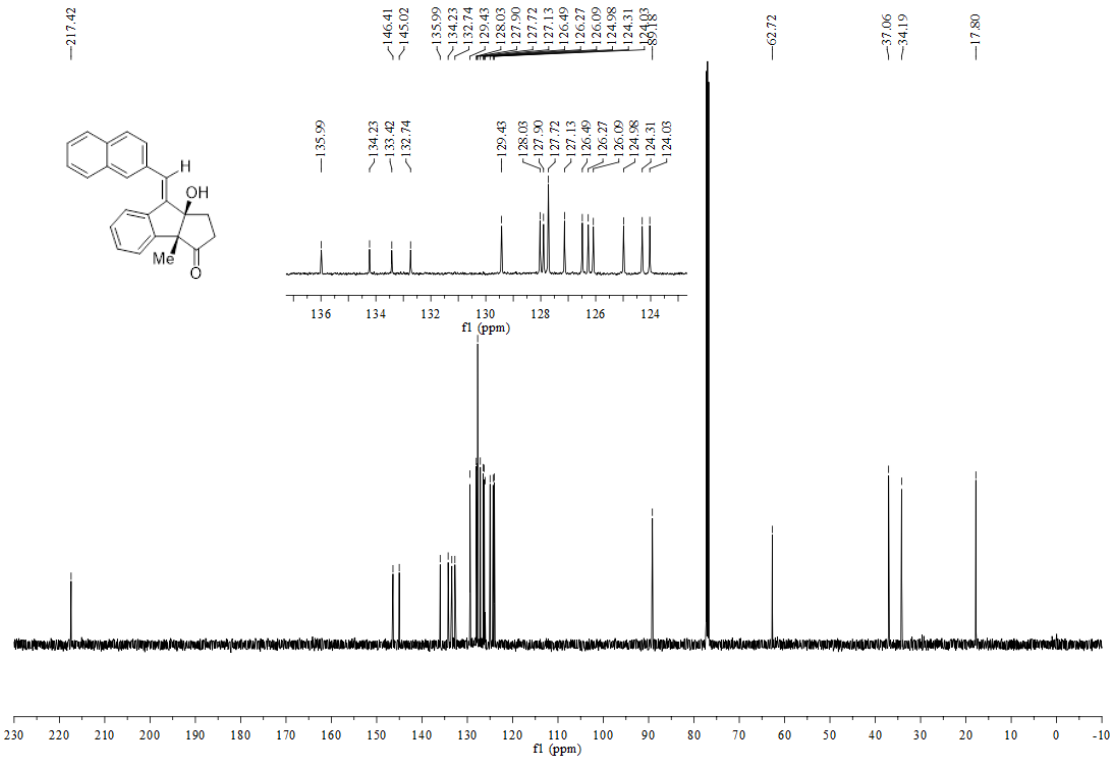
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.741	BB	0.1499	17.83801	1.68024	1.8297
2	7.868	MM	0.1992	957.06805	80.06898	98.1703

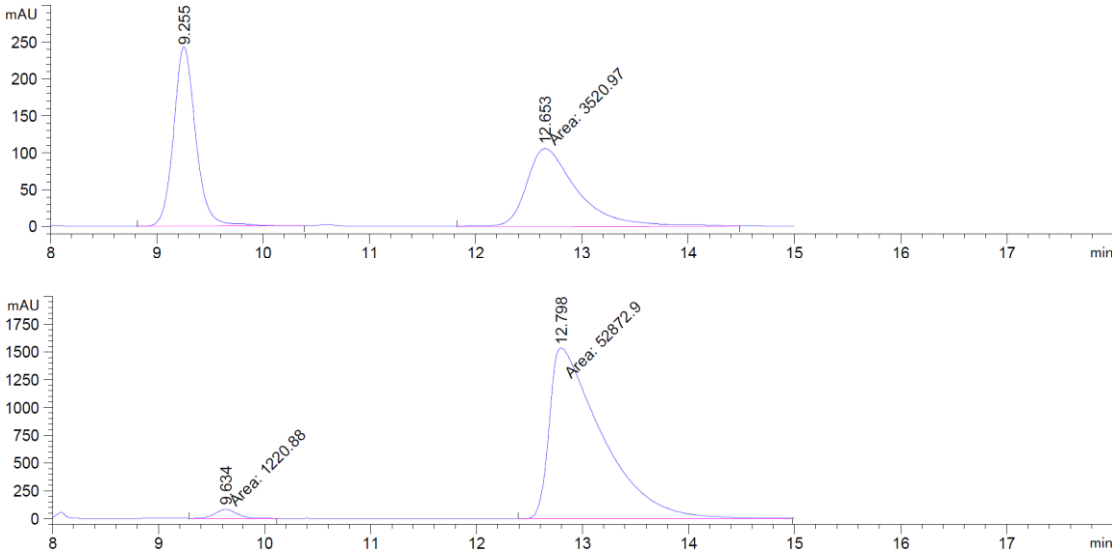
***(3aR,8aR,E)-8a-Hydroxy-3a-methyl-8-(naphthalen-2-ylmethylene)-1,3a,8,8a-tetrahydrocyclopenta[a]inden-3(2H)-one* (*2m*)**



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow solid, Mp = 130-131 °C; 50 mg, 74% yield; $[\alpha]_D^{20}$ = -212.2 (*c* 0.5, CH_2Cl_2), 95% ee [Phenomenex Lux 5u Amylose-2 column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 85/15, 0.7 mL/min, 280 nm; t_{minor} = 9.6 min, t_{major} = 12.8 min,]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.86-7.82 (m, 2H), 7.79 (dd, *J* = 6.0, 3.5 Hz, 1H), 7.54 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.51-7.47 (m, 2H), 7.34 (dd, *J* = 17.0, 7.5 Hz, 2H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.07 (s, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 2.67-2.59 (m, 1H), 2.39-2.28 (m, 2H), 2.20 (s, 1H), 2.16-2.09 (m, 1H), 1.40 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 217.4, 146.4, 145.0, 136.0, 134.2, 133.4, 132.7, 129.4, 128.0, 127.9, 127.7, 127.1, 126.5, 126.3, 126.1, 125.0, 124.3, 124.0, 89.2, 62.7, 37.1, 34.2, 17.8. HRMS *m*/*z* (ESI+): Calculated for $C_{24}H_{20}O_2^+$ ([M]$^+$) 340.1463, found 340.1461.



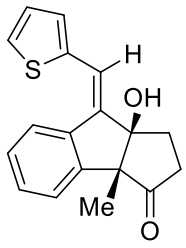




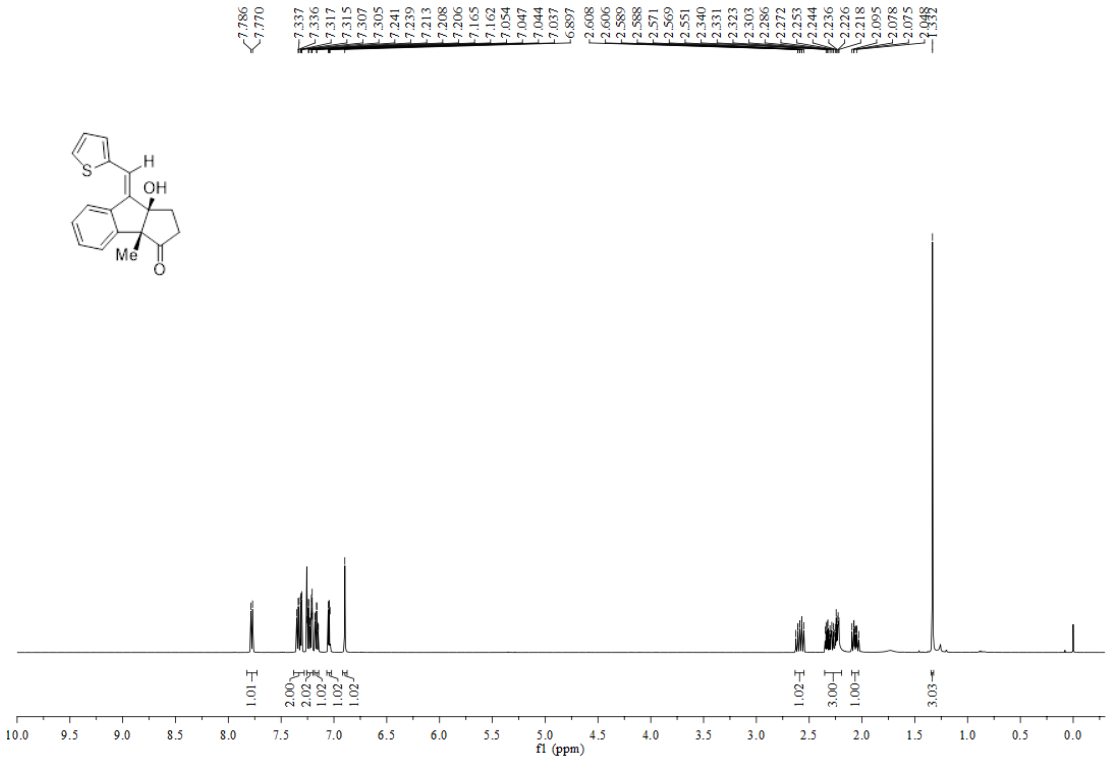
Signal 7: DAD1 G, Sig=280,4 Ref=360,100

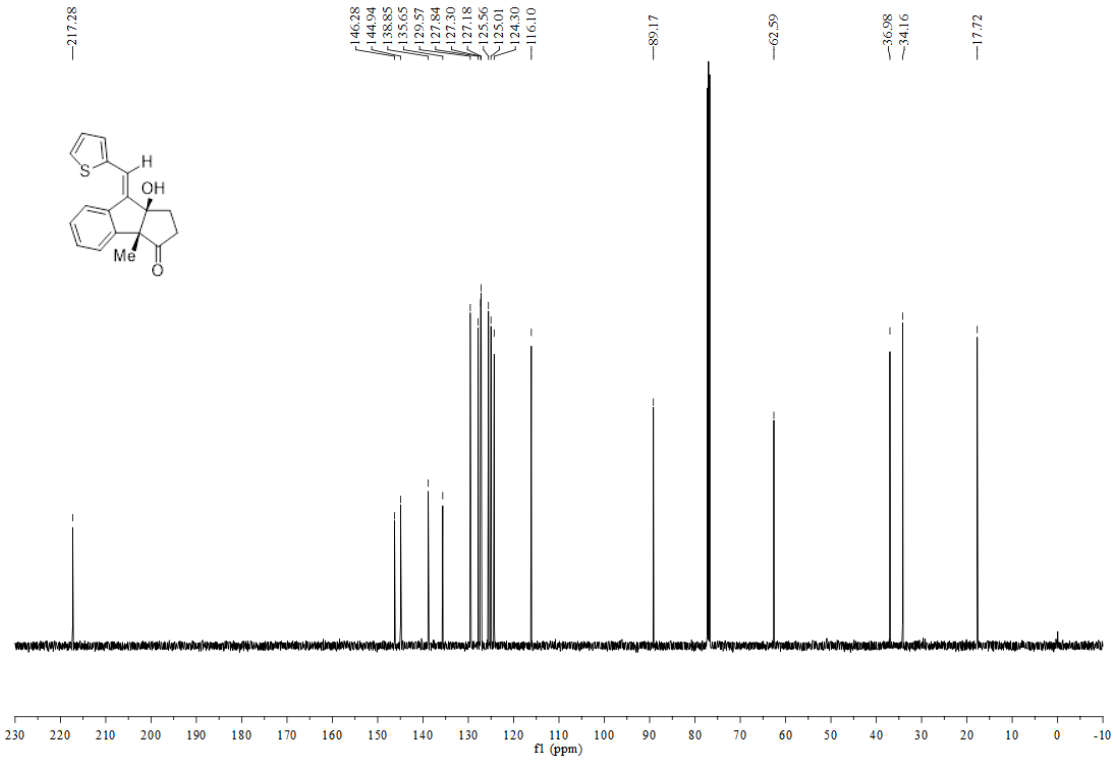
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.634	MM	0.2483	1220.88220	81.94859	2.2570
2	12.798	MM	0.5731	5.28729e4	1537.61206	97.7430

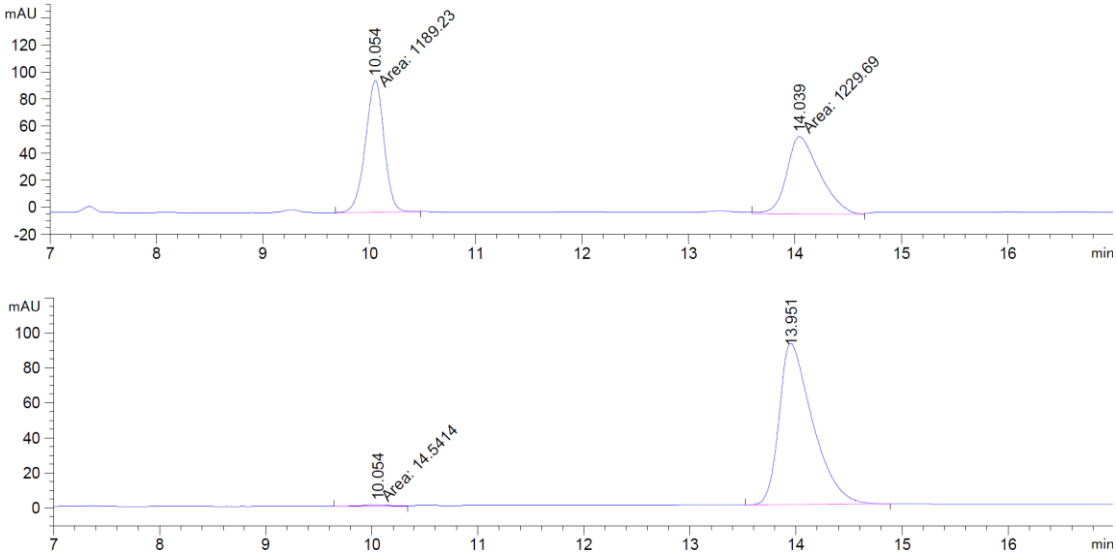
***(3aR,8aR,E)-8a-Hydroxy-3a-methyl-8-(thiophen-2-ylmethylene)-1,3a,8,8a-tetra-hydrocyclopenta[a]inden-3(2H)-one* (*2n*)**



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow solid, Mp = 158-159 °C; 30 mg, 51% yield; $[\alpha]_D^{20}$ = -330.4 (*c* 0.5, CH_2Cl_2), 98% ee [Phenomenex Lux 5u Amylose-2 column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 90/10, 0.7 mL/min, 254 nm; t_{minor} = 10.1 min, t_{major} = 14.0 min]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, J = 8.0 Hz, 1H), 7.34-7.31 (m, 2H), 7.24-7.21 (m, 2H), 7.17-7.16 (m, 1H), 7.05 (dd, J = 5.0, 3.5 Hz, 1H), 6.90 (s, 1H), 2.61-2.55 (m, 1H), 2.34-2.21 (m, 3H), 2.10-2.00 (m, 1H), 1.33 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 217.3, 146.3, 144.9, 138.9, 135.7, 129.6, 127.8, 127.3, 127.2, 125.6, 125.0, 124.3, 116.1, 89.2, 62.6, 37.0, 34.2, 17.7. Calculated for $C_{18}H_{16}O_2S^+$ ($[M]^+$) 296.0866, found 296.0866.



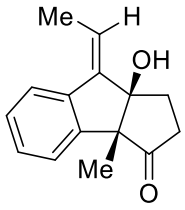




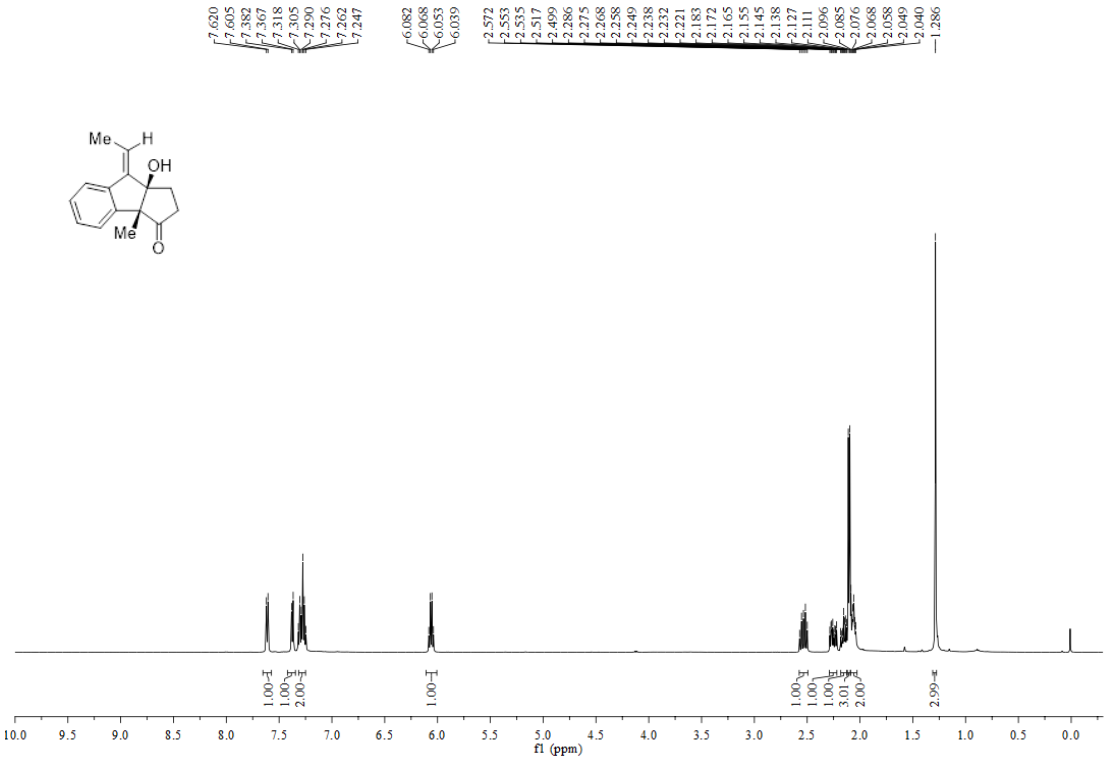
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

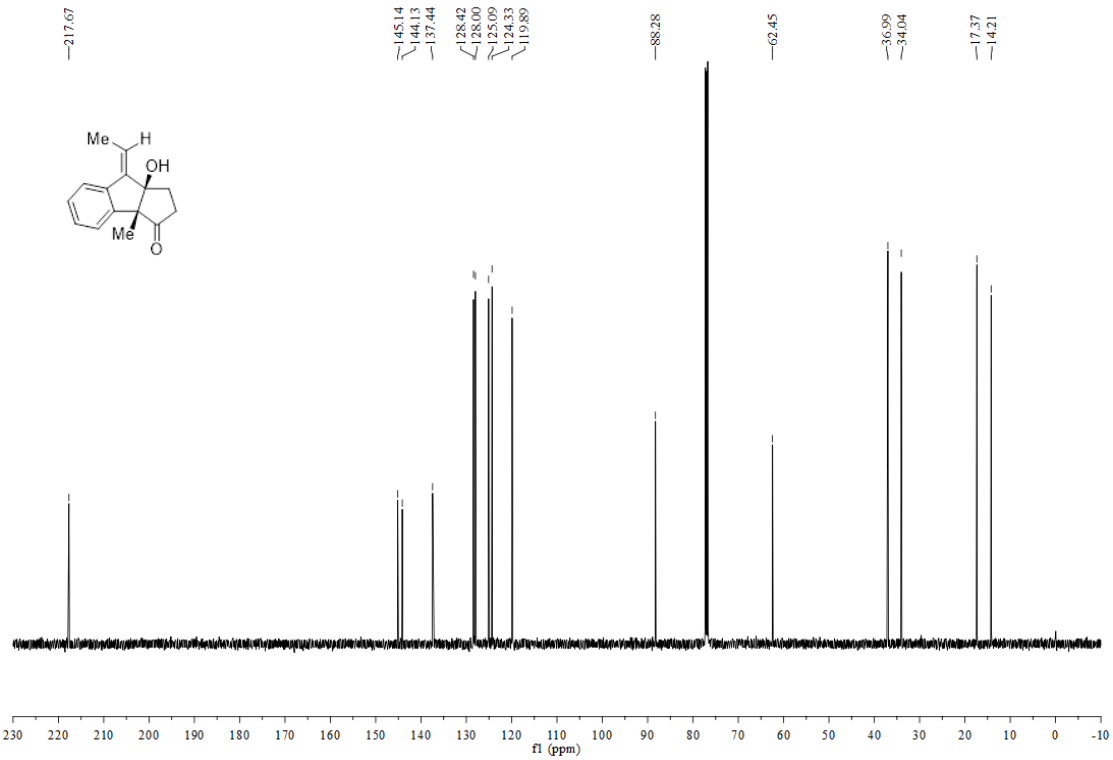
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.054	MM	0.2821	14.54141	8.59223e-1	0.7141
2	13.951	BB	0.3241	2021.80762	92.10149	99.2859

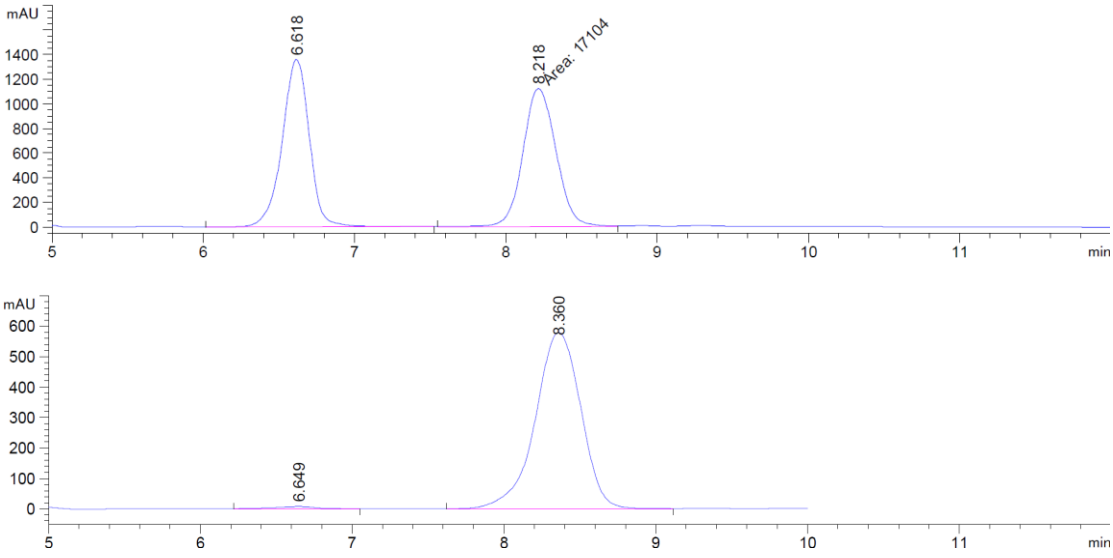
***(3aR,8aR,E)-8-Ethylidene-8a-hydroxy-3a-methyl-1,3a,8,8a-tetrahydrocyclopenta-[a]inden-3(2H)-one* (*2o*)**



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); white solid, Mp = 120-121 °C; 36 mg, 78% yield; $[\alpha]_D^{20}$ = -222.0 (*c* 0.5, CH_2Cl_2), 98% ee [Phenomenex Lux 5u Amylose-2 column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 80/20, 0.7 mL/min, 254 nm; t_{minor} = 6.6 min, t_{major} = 8.4 min]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, J = 7.5 Hz, 1H), 7.37 (d, J = 7.5 Hz, 1H), 7.32-7.25 (m, 2H), 6.06 (q, J = 7.0 Hz, 1H), 2.57-2.50 (m, 1H), 2.29-2.22 (m, 1H), 2.18-2.13 (m, 1H), 2.10 (d, J = 7.5 Hz, 3H), 2.09-2.04 (m, 2H), 1.29 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 217.7, 145.1, 144.1, 137.4, 128.4, 128.0, 125.1, 124.3, 119.9, 88.3, 62.5, 37.0, 34.0, 17.4, 14.2. HRMS *m*/*z* (ESI+): Calculated for $C_{15}H_{16}O_2Na^+$ ([M+Na]$^+$) 251.1043, found 251.1042.



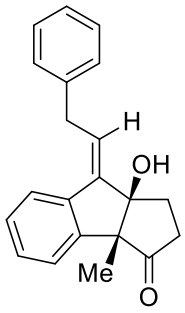




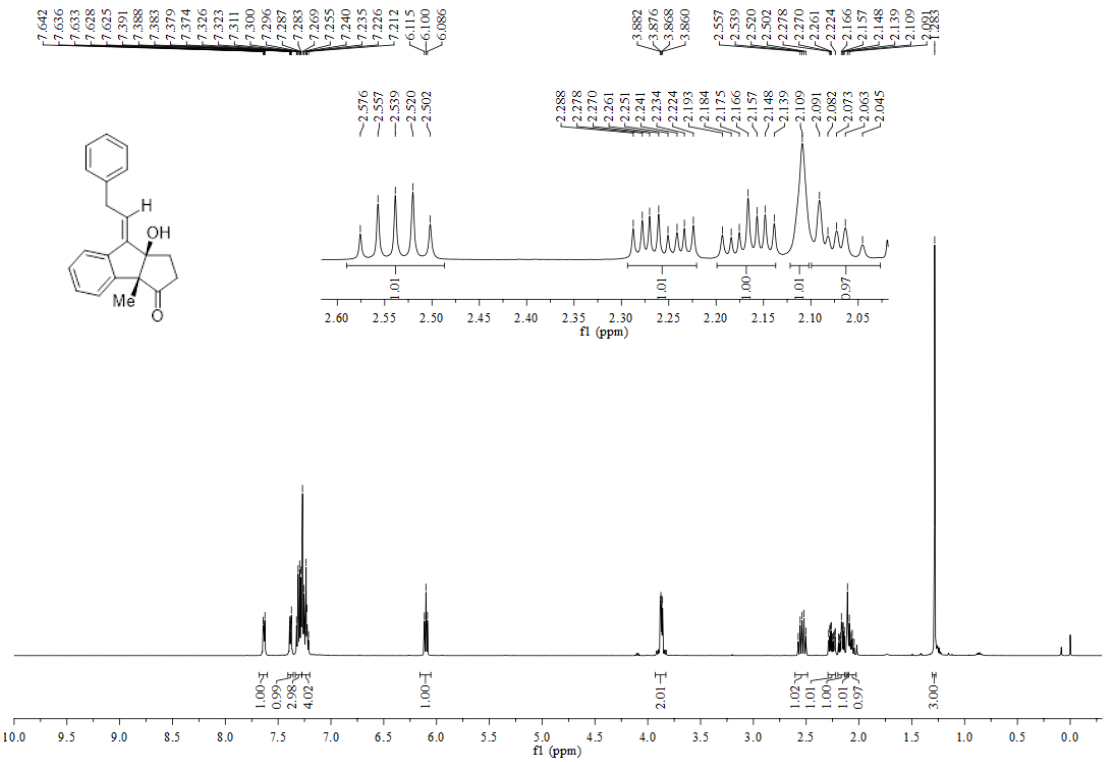
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

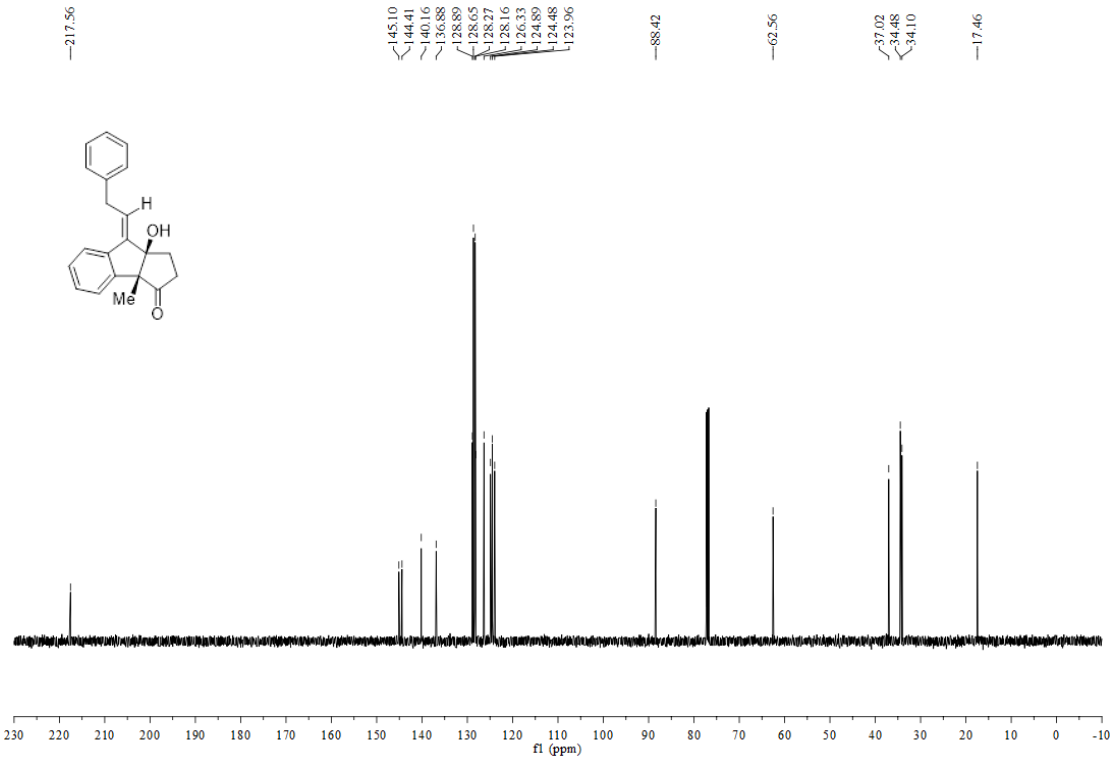
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.649	BB	0.2522	115.57787	6.73638	0.9513
2	8.360	BB	0.3268	1.20338e4	578.24561	99.0487

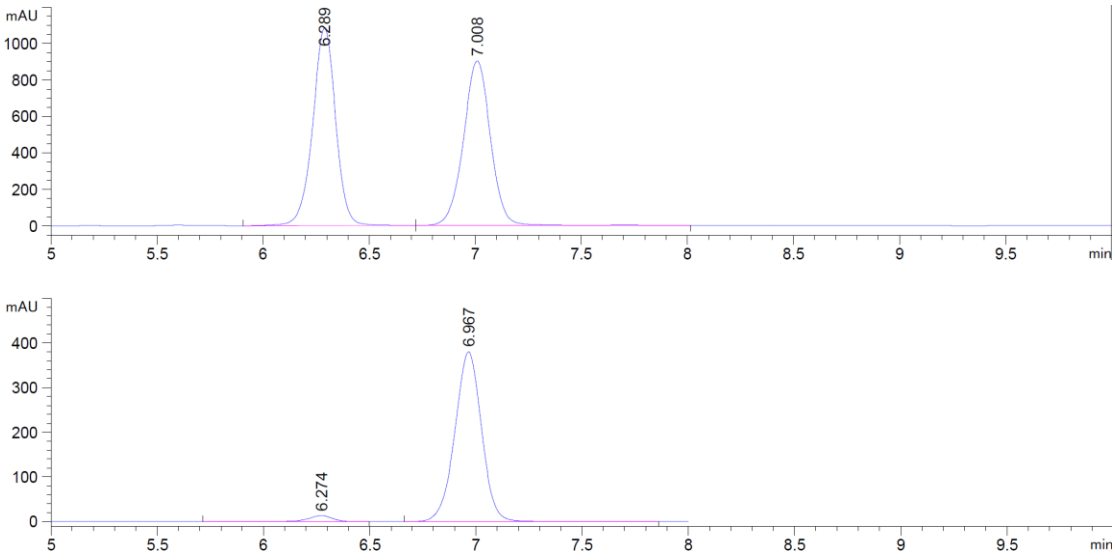
(3aR,8aR,E)-8a-Hydroxy-3a-methyl-8-(2-phenylethylidene)-1,3a,8,8a-tetrahydro-cyclopenta[a]inden-3(2H)-one (2p)



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow oil; 55 mg, 89% yield; $[\alpha]_D^{20}$ = -135.4 (*c* 0.5, CH_2Cl_2), 94% ee [Phenomenex Lux 5u Amylose-2 column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 80/20, 0.8 mL/min, 254 nm; t_{minor} = 6.3 min, t_{major} = 7.0 min]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64-7.63 (m, 1H), 7.39-7.37 (m, 1H), 7.33-7.28 (m, 3H), 7.27-7.21 (m, 4H), 6.10 (t, *J* = 7.5 Hz, 1H), 3.87 (dd, *J* = 8.0, 4.0 Hz, 2H), 2.58-2.50 (m, 1H), 2.29-2.22 (m, 1H), 2.19-2.14 (m, 1H), 2.11 (s, 1H), 2.09-2.05 (m, 1H), 1.28 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 217.6, 145.1, 144.4, 140.2, 136.9, 128.9, 128.7, 128.3, 128.2, 126.3, 124.9, 124.5, 124.0, 88.4, 62.6, 37.0, 34.5, 34.1, 17.5. HRMS *m*/*z* (ESI+): Calculated for $C_{21}H_{20}NaO_2^+$ ([M+Na]$^+$) 327.1356, found 327.1354.



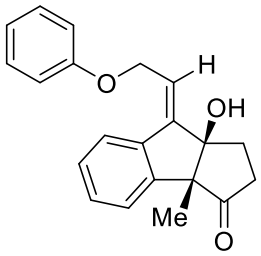




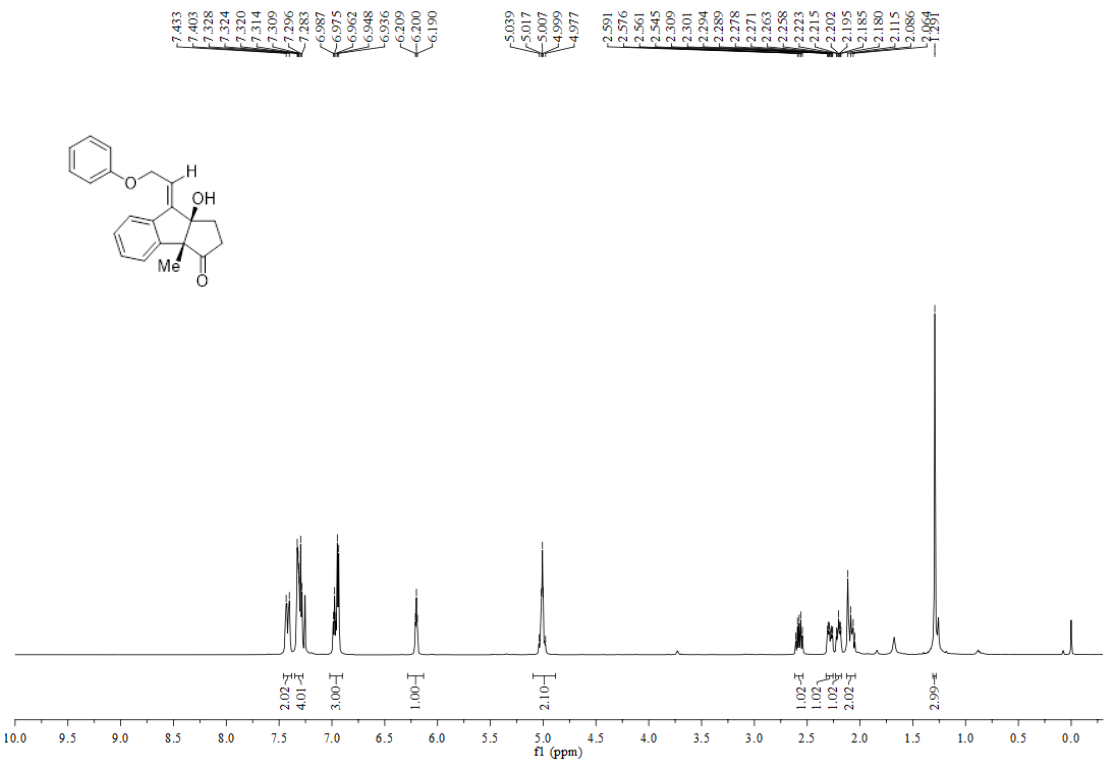
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

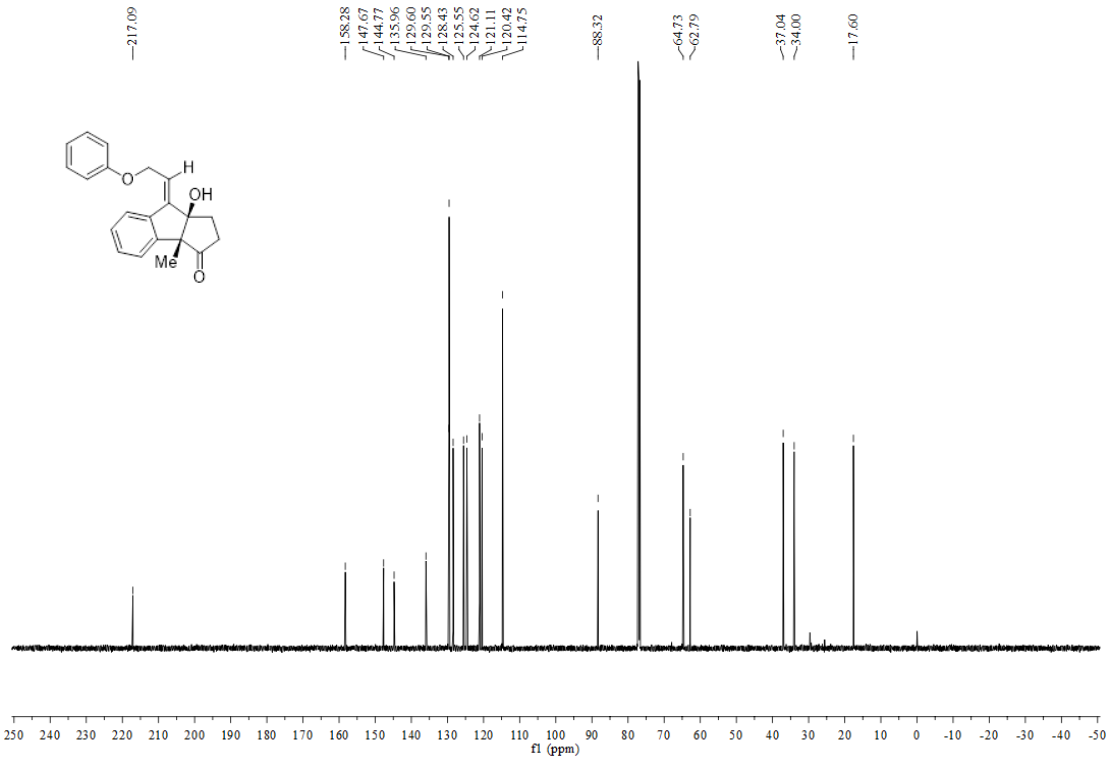
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.274	BB	0.1212	110.44466	13.53184	3.2180
2	6.967	BB	0.1339	3321.69019	380.47672	96.7820

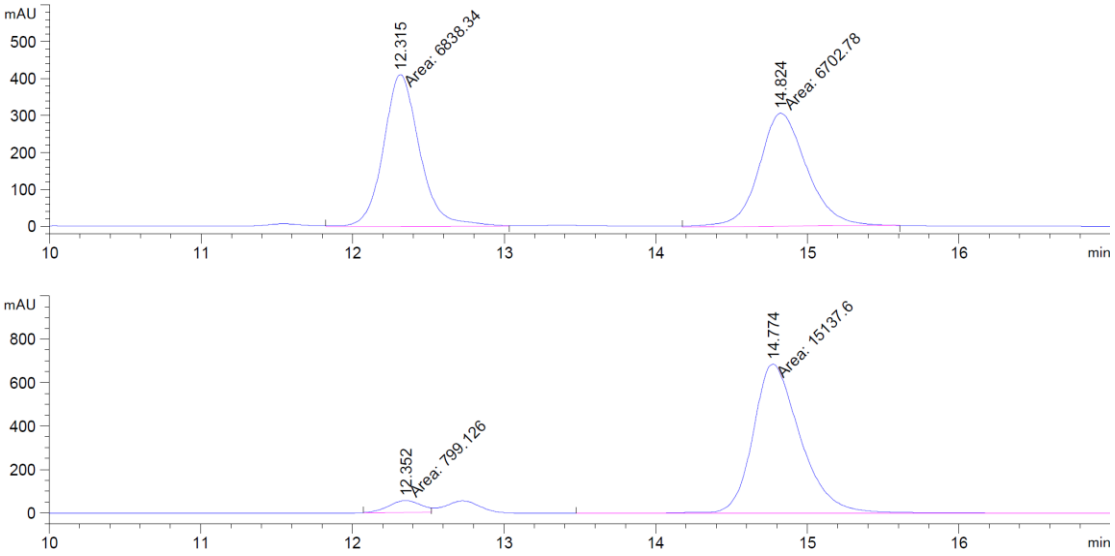
***(3aR,8aR,E)-8a-Hydroxy-3a-methyl-8-(2-phenoxyethylidene)-1,3a,8,8a-tetrahydro-cyclopenta[a]inden-3(2H)-one* (*2q*)**



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); white solid, Mp = 56-57 °C; 53 mg, 83% yield; $[\alpha]_D^{20}$ = -148.4 (*c* 0.5, CH_2Cl_2), 90% ee [Phenomenex Lux 5u Amylose-2 column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 90/10, 0.7 mL/min, 254 nm; t_{minor} = 12.4 min, t_{major} = 14.8 min]; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (d, *J* = 18.0 Hz, 2H), 7.33-7.28 (m, 4H), 6.99-6.94 (m, 3H), 6.20 (t, *J* = 6.0 Hz, 1H), 5.04-4.98 (m, 2H), 2.59-2.55 (m, 1H), 2.31-2.26 (m, 1H), 2.22-2.18 (m, 1H), 2.12-2.06 (m, 2H), 1.29 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 217.1, 158.3, 147.7, 144.8, 136.0, 129.60, 129.55, 128.4, 125.6, 124.6, 121.1, 120.4, 114.8, 88.3, 64.7, 62.8, 37.0, 34.0, 17.6. HRMS *m*/*z* (ESI+): Calculated for $C_{21}H_{20}NaO_3^+$ ([M+Na]$^+$) 343.1305, found 343.1303.



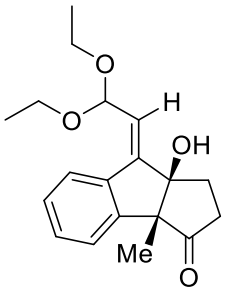




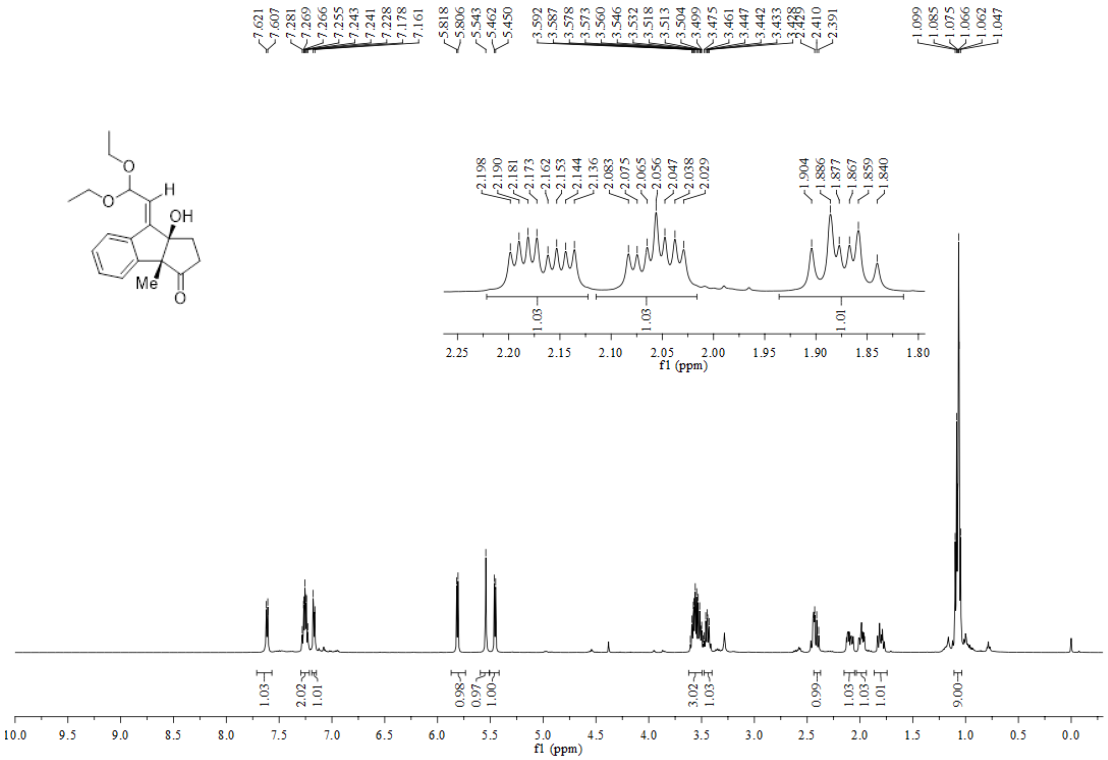
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

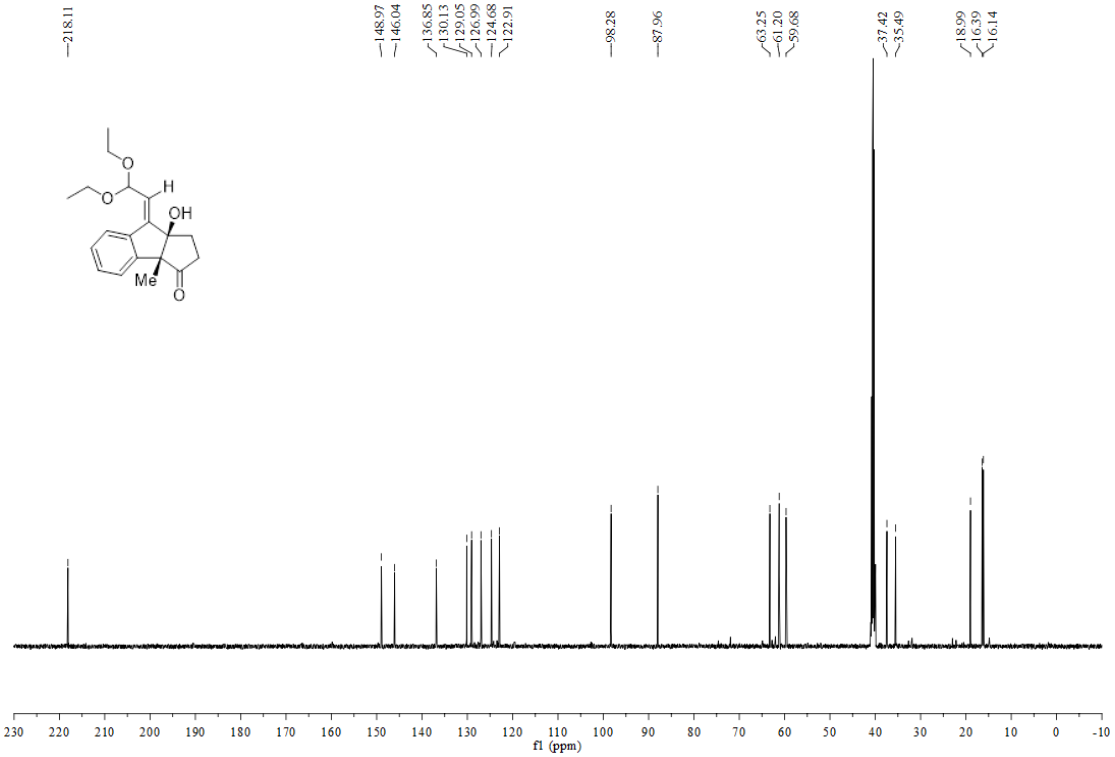
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.352	MM	0.2442	799.12573	54.53733	5.0144
2	14.774	MM	0.3668	1.51376e4	687.77661	94.9856

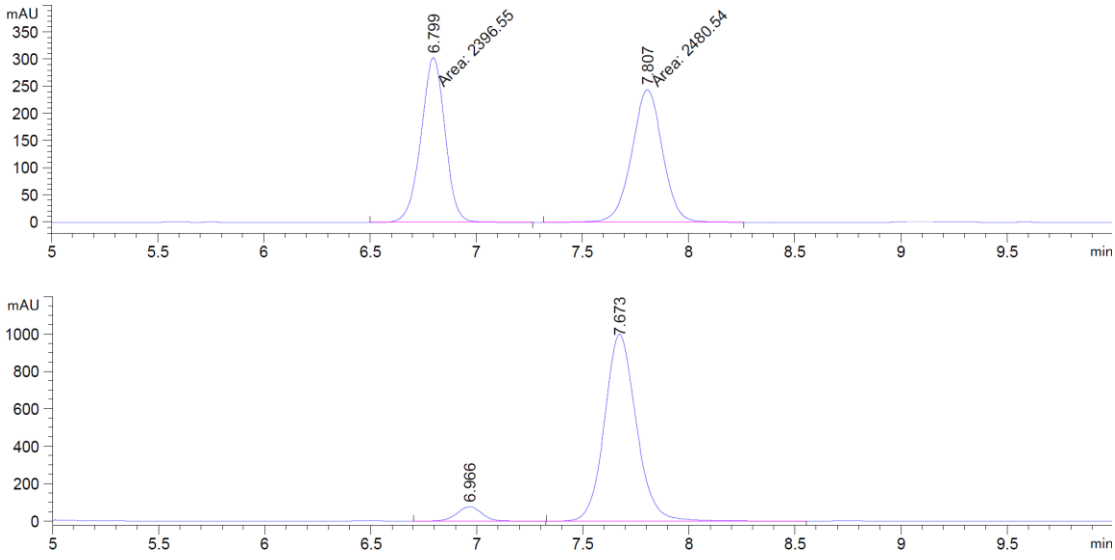
***(3aR,8aR,E)-8-(2,2-Diethoxyethylidene)-8a-hydroxy-3a-methyl-1,3a,8,8a-tetra-hydrocyclopenta[a]inden-3(2H)-one* (*2r*)**



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow oil; 54 mg, 85% yield; $[\alpha]_D^{20}$ = -61.2 (*c* 0.5, CH_2Cl_2), 89% ee [Phenomenex Lux 5u Amylose-2 column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 90/10, 0.7 mL/min, 254 nm; t_{minor} = 7.0 min, t_{major} = 7.7 min]; ^{1}H NMR (500 MHz, $(CD_3)_2SO$) δ 7.61 (d, J = 7.0 Hz, 1H), 7.28-7.23 (m, 2H), 7.17 (d, J = 8.5 Hz, 1H), 5.81 (d, J = 6.0 Hz, 1H), 5.54 (s, 1H), 5.46 (d, J = 6.0 Hz, 1H), 3.59-3.50 (m, 3H), 3.48-3.43 (m, 1H), 2.43-2.39 (m, 1H), 2.20-2.14 (m, 1H), 2.08-2.03 (m, 1H), 1.90-1.84 (m, 1H), 1.10-1.05 (m, 9H). ^{13}C NMR (125 MHz, $(CD_3)_2SO$) δ 218.1, 149.0, 146.0, 136.9, 130.1, 129.1, 127.0, 124.7, 122.9, 98.3, 88.0, 63.3, 61.2, 59.7, 37.4, 35.5, 19.0, 16.4, 16.1. HRMS *m*/*z* (ESI+): Calculated for $C_{19}H_{24}NaO_4^+$ ([M+Na]$^+$) 339.1567, found 339.1565.



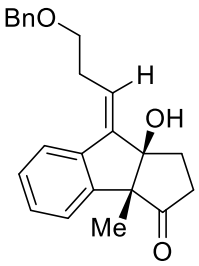




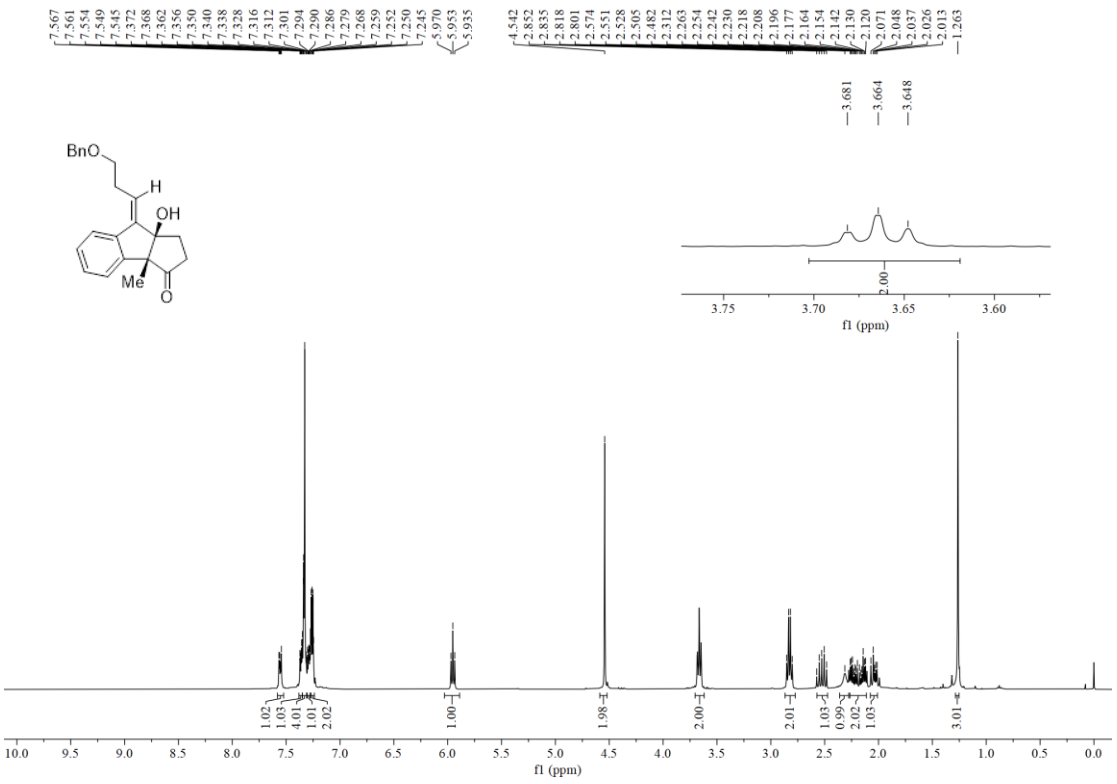
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

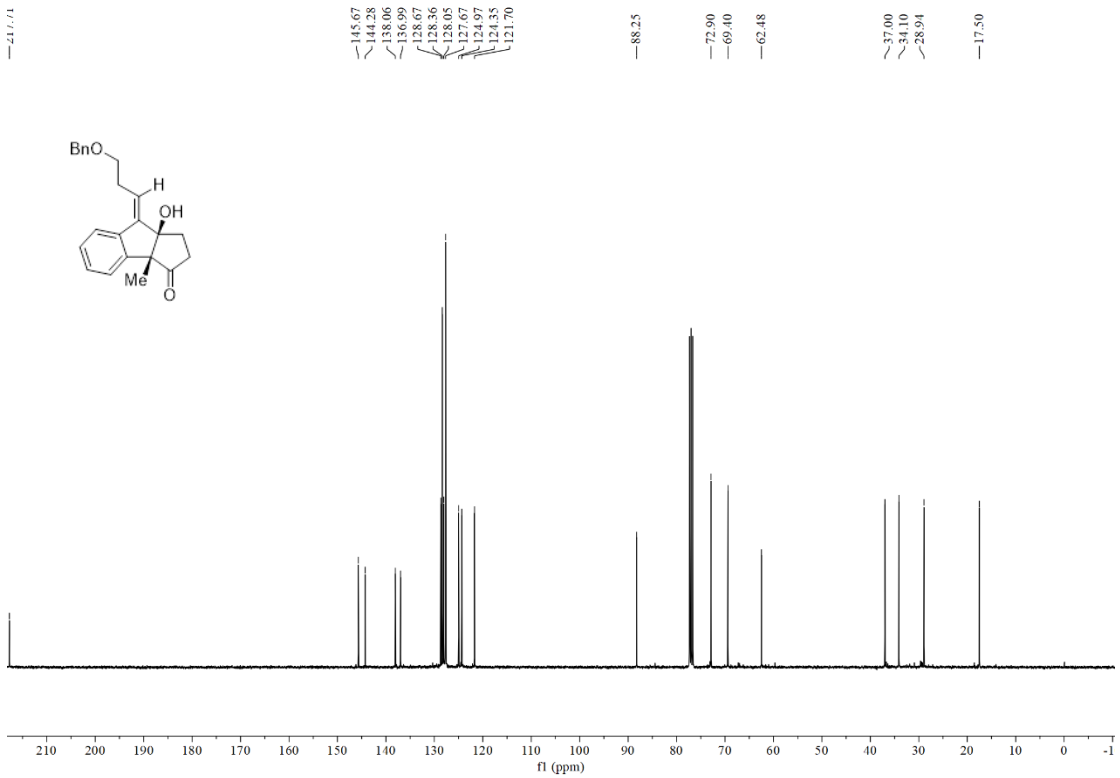
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.966	MF	0.1358	635.32983	77.97868	5.7367
2	7.673	MM	0.1738	1.04395e4	1000.98065	94.2633

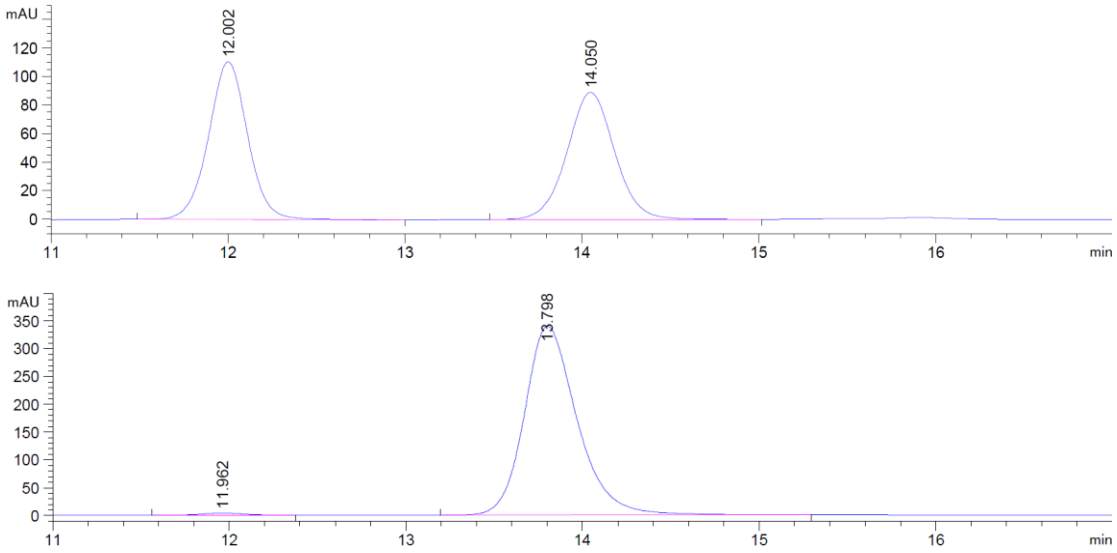
***(3aR,8aR,E)-8-(3-(Benzyloxy)propylidene)-8a-hydroxy-3a-methyl-1,3a,8,8a-tetra-hydrocyclopenta[a]inden-3(2H)-one* (*2s*)**



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow oil; 41 mg, 59% yield; $[\alpha]_D^{20}$ = -145.2 (*c* 0.5, CH_2Cl_2), 98% ee [Phenomenex Lux 5u Amylose-2 column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 90/10, 0.7 mL/min, 254 nm; t_{minor} = 12.0 min, t_{major} = 13.8 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58-7.54 (m, 1H), 7.37-7.35 (m, 1H), 7.34-7.31 (m, 4H), 7.30-7.28 (m, 1H), 7.27-7.25 (m, 2H), 5.95 (t, *J* = 6.8 Hz, 1H), 4.54 (s, 2H), 3.66 (t, *J* = 6.8 Hz, 2H), 2.83 (q, *J* = 6.8 Hz, 2H), 2.57-2.48 (m, 1H), 2.31 (s, 1H), 2.26-2.12 (m, 2H), 2.07-2.01 (m, 1H), 1.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 217.7, 145.7, 144.3, 138.1, 137.0, 128.7, 128.4, 128.0, 127.7, 125.0, 124.4, 121.7, 88.3, 72.9, 69.4, 62.5, 37.0, 34.1, 28.9, 17.5. HRMS *m*/*z* (ESI+): Calculated for $C_{23}H_{24}NaO_3^+$ ([M+Na]$^+$) 371.1618, found 371.1615.



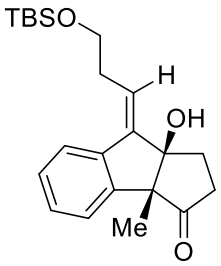




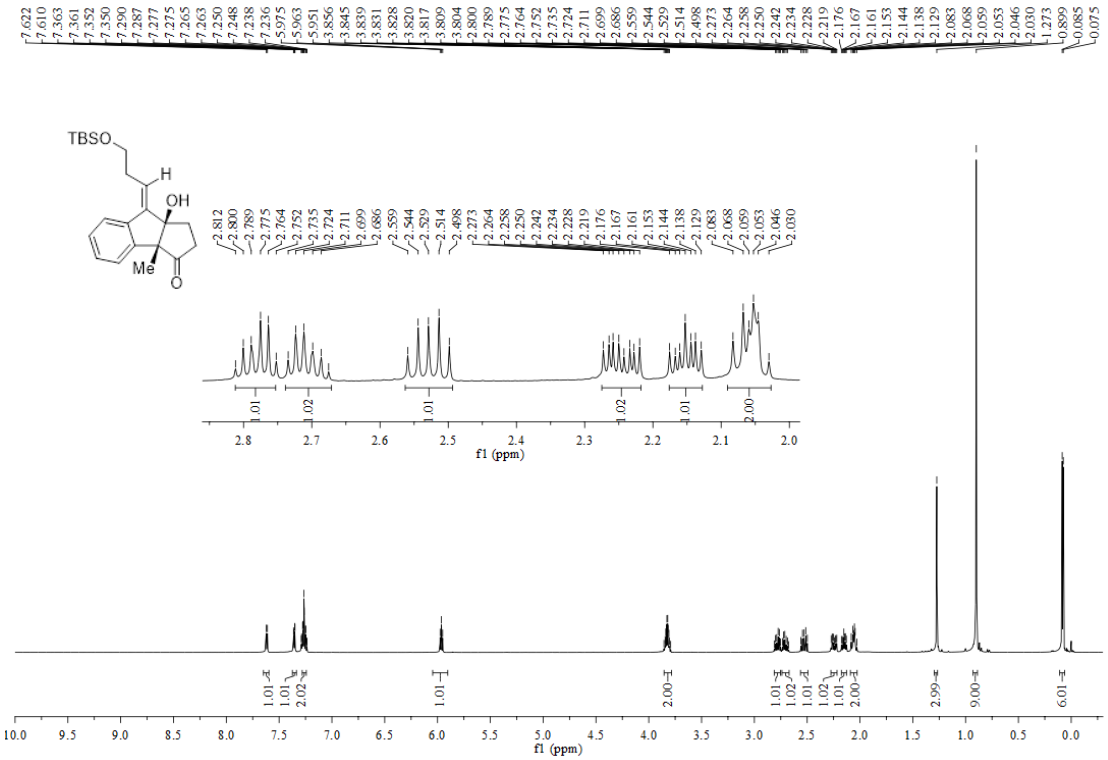
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

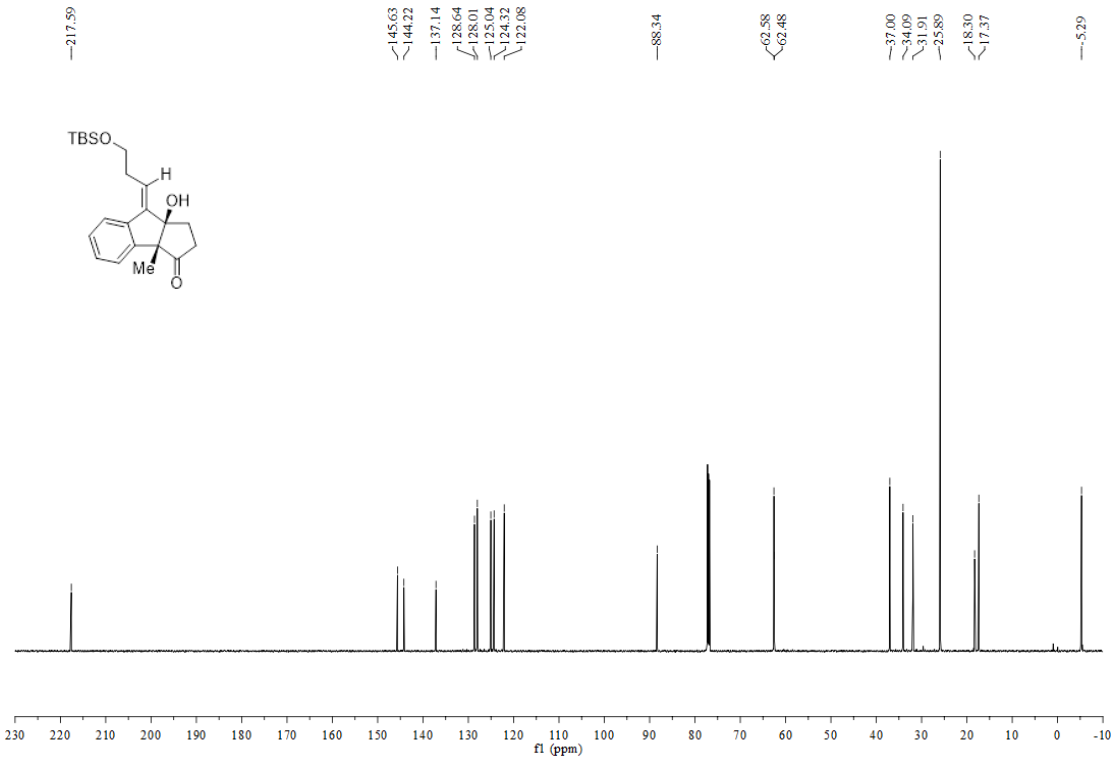
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.962	BB	0.2507	59.16324	3.65870	0.8335
2	13.798	BB	0.3137	7038.69678	339.68808	99.1665

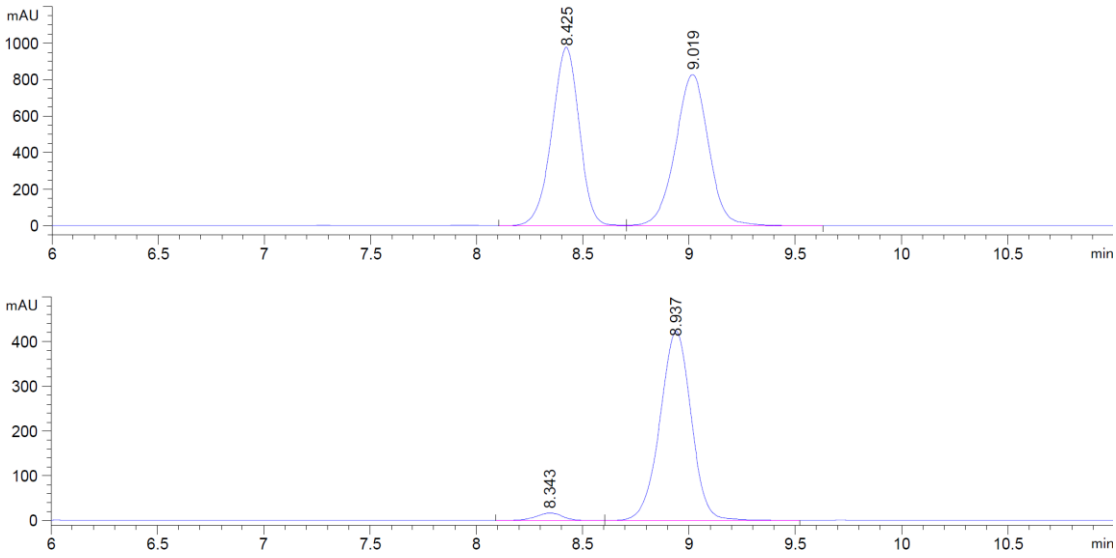
***(3aR,8aR,E)-8-(3-((tert-Butyldimethylsilyl)oxy)propylidene)-8a-hydroxy-3a-methyl-1,3a,8,8a-tetrahydrocyclopenta[a]inden-3(2H)-one* (*2t*)**



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); brown oil; 48 mg, 65% yield; $[\alpha]_D^{20}$ = -185.3 (*c* 0.5, CH_2Cl_2), 94% ee [Phenomenex Lux 5u Amylose-2 column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 90/10, 0.7 mL/min, 254 nm; t_{minor} = 8.3 min, t_{major} = 8.9 min]; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.2 Hz, 1H), 7.36 (dd, *J* = 6.6, 1.2 Hz, 1H), 7.29-7.24 (m, 2H), 5.96 (t, *J* = 7.2 Hz, 1H), 3.86-3.80 (m, 2H), 2.80-2.75 (m, 1H), 2.74-2.69 (m, 1H), 2.56-2.50 (m, 1H), 2.27-2.22 (m, 1H), 2.18-2.13 (m, 1H), 2.08-2.03 (m, 2H), 1.27 (s, 3H), 0.90 (s, 9H), 0.08 (d, *J* = 6.0 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 217.6, 145.6, 144.2, 137.1, 128.6, 128.0, 125.0, 124.3, 122.1, 88.3, 62.6, 62.5, 37.0, 34.1, 31.9, 25.9, 18.3, 17.4, -5.3. HRMS *m/z* (ESI+): Calculated for $C_{22}H_{32}NaO_3Si^+$ ($[M+Na]^+$) 395.2013, found 395.2010.



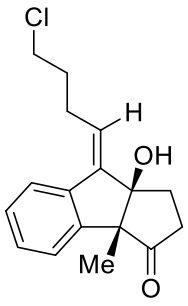




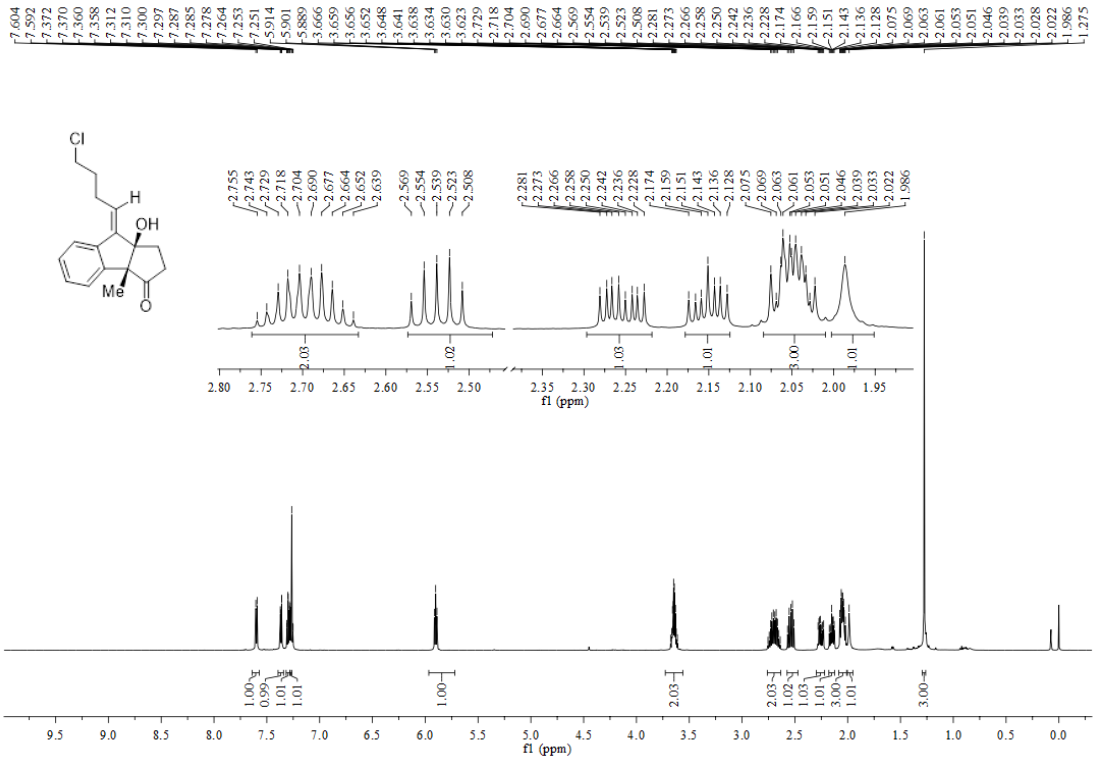
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

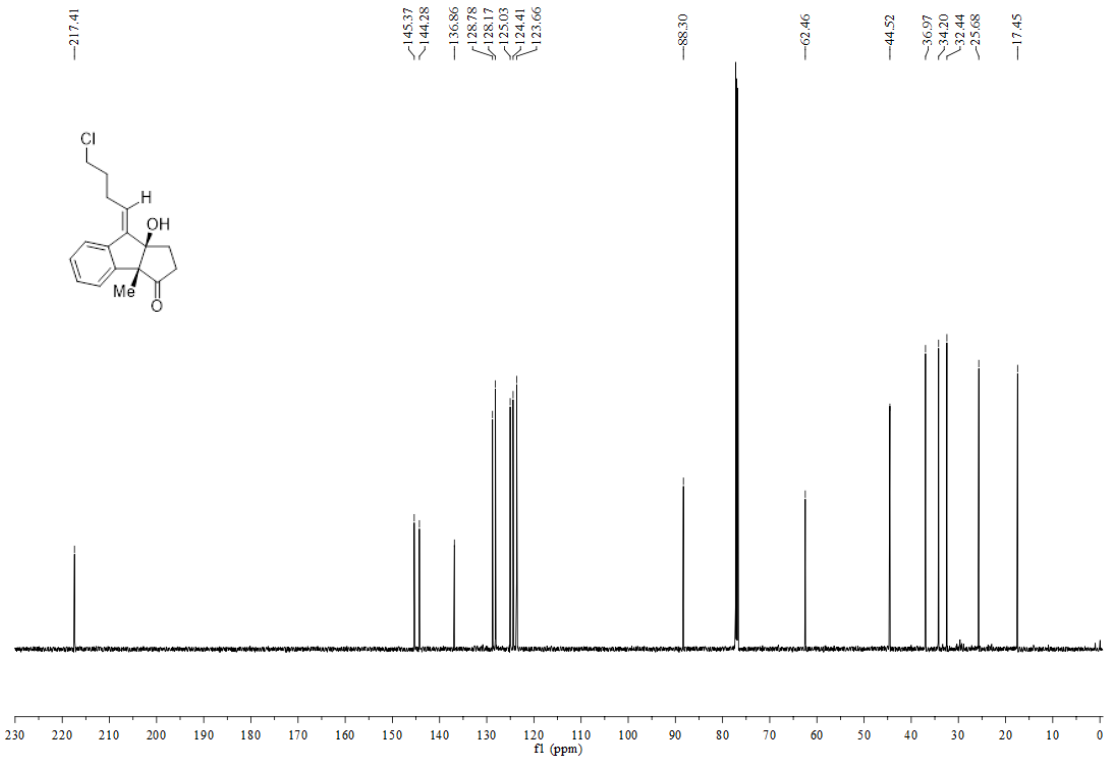
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.343	BB	0.1327	143.50595	16.62206	3.2222
2	8.937	BB	0.1567	4310.20654	423.55829	96.7778

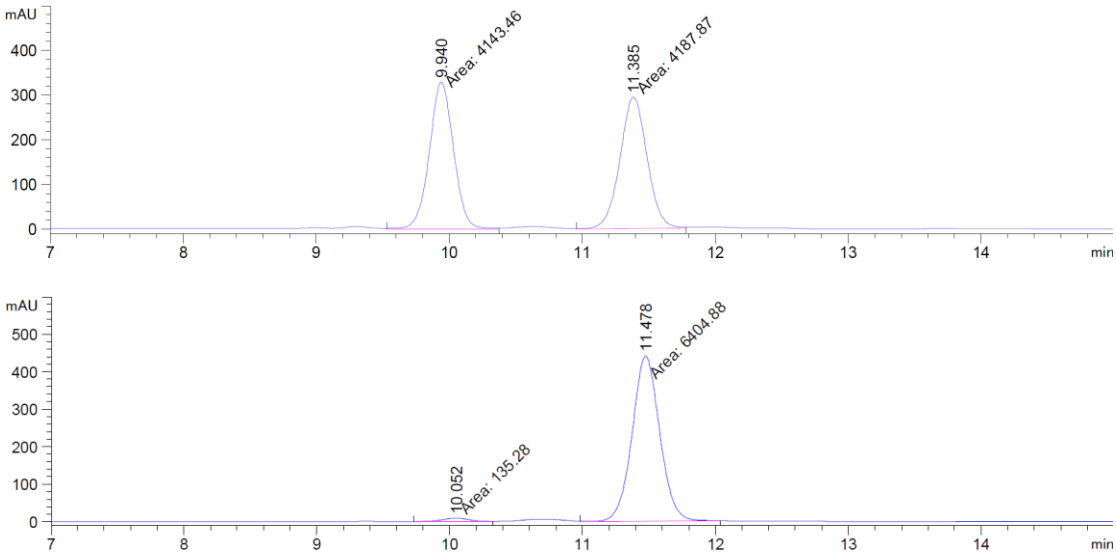
***(3aR,8aR,E)-8-(4-Chlorobutylidene)-8a-hydroxy-3a-methyl-1,3a,8,8a-tetrahydro-cyclopenta[a]inden-3(2H)-one* (*2u*)**



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); brown oil; 40 mg, 69% yield; $[\alpha]_D^{20}$ = -192.2 (*c* 0.5, CH_2Cl_2), 96% ee [Phenomenex Lux 5u Amylose-2 column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 90/10, 0.7 mL/min, 254 nm; t_{minor} = 10.1 min, t_{major} = 11.5 min]; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.2 Hz, 1H), 7.37 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.31-7.28 (m, 1H), 7.26-7.25 (m, 1H), 5.90 (t, *J* = 7.2 Hz, 1H), 3.67-3.62 (m, 2H), 2.76-2.64 (m, 2H), 2.57-2.51 (m, 1H), 2.28-2.23 (m, 1H), 2.17-2.13 (m, 1H), 2.08-2.02 (m, 3H), 1.99 (s, 1H), 1.28 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 217.4, 145.4, 144.3, 136.9, 128.8, 128.2, 125.0, 124.4, 123.7, 88.3, 62.5, 44.5, 37.0, 34.2, 32.4, 25.7, 17.5. HRMS *m*/*z* (ESI+): Calculated for $C_{17}H_{19}ClNaO_2^+$ ([M+Na]$^+$) 313.0966, found 313.0964.



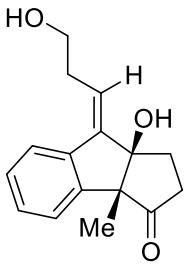




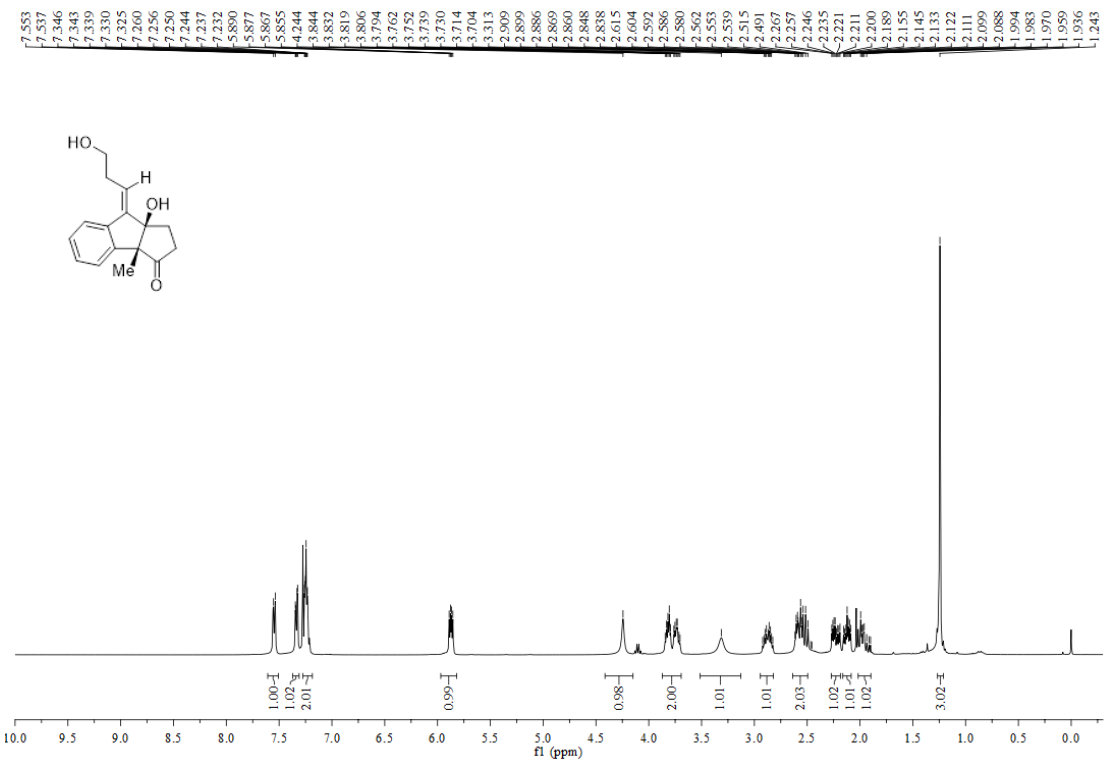
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

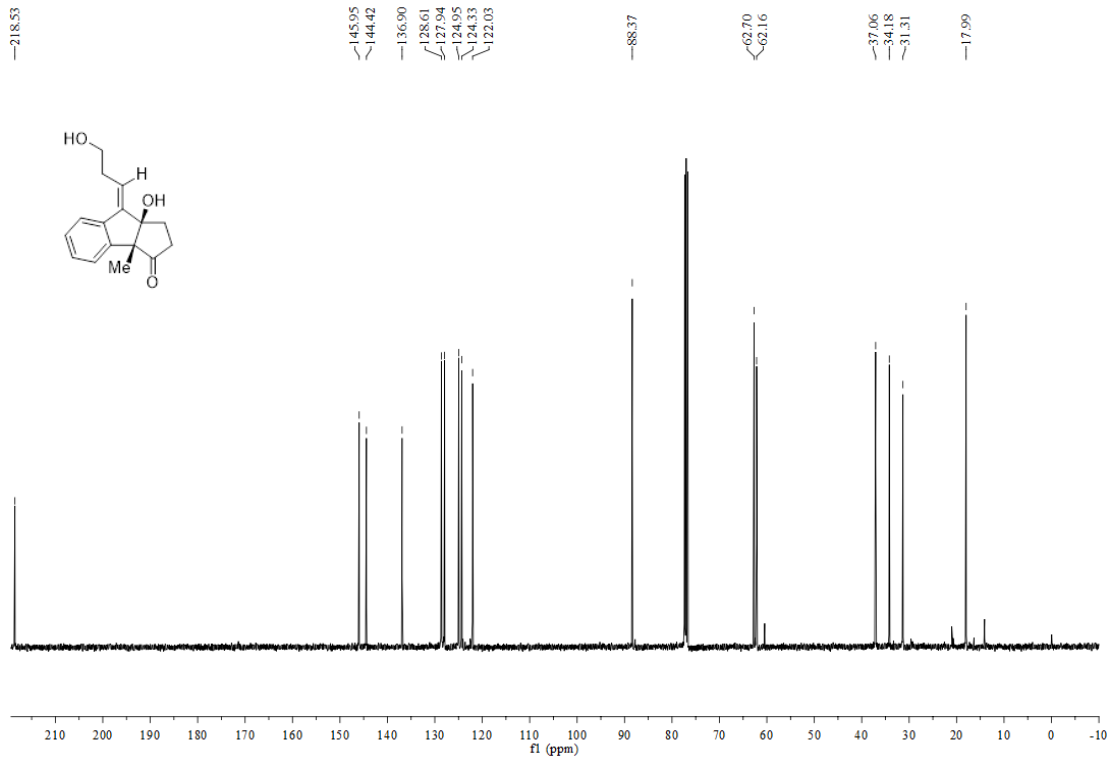
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.052	MM	0.2428	135.28043	9.28647	2.0685
2	11.478	MM	0.2418	6404.87549	441.40967	97.9315

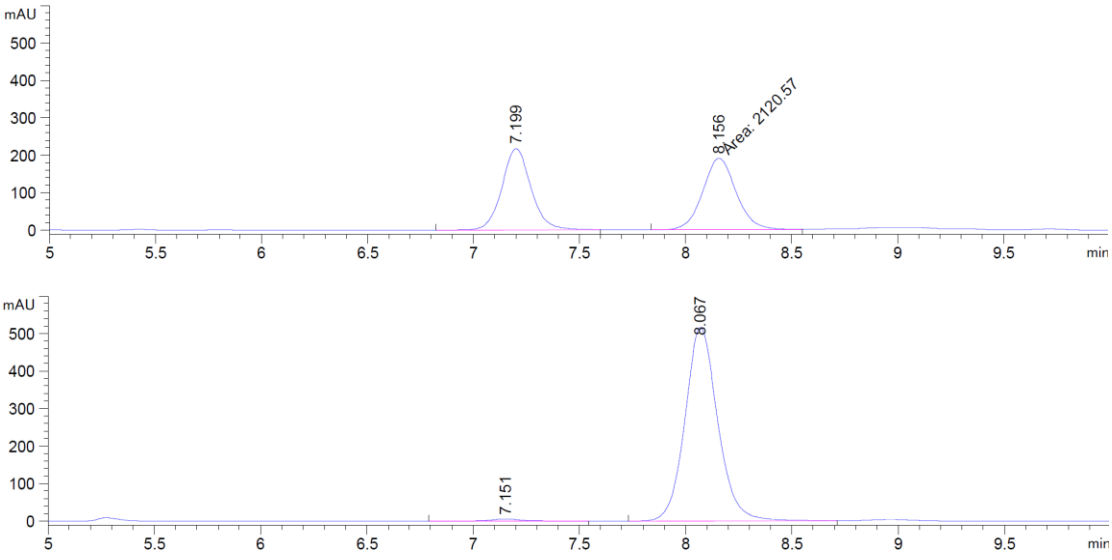
***(3aR,8aR,E)-8a-Hydroxy-8-(3-hydroxypropylidene)-3a-methyl-1,3a,8,8a-tetrahydro-cyclopenta[a]inden-3(2H)-one* (*2v*)**



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow oil; 36 mg, 69% yield; $[\alpha]_D^{20}$ = -182.5 (*c* 0.5, CH_2Cl_2), 98% ee [Phenomenex Lux 5u Amylose-2 column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 80/20, 0.7 mL/min, 254 nm; t_{minor} = 7.2 min, t_{major} = 8.1 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 6.4 Hz, 1H), 7.35-7.33 (m, 1H), 7.26-7.23 (m, 2H), 5.87 (dd, *J* = 8.8, 5.2 Hz, 1H), 4.24 (s, 1H), 3.84-3.70 (m, 2H), 3.31 (s, 1H), 2.91-2.84 (m, 1H), 2.62-2.49 (m, 2H), 2.27-2.19 (m, 1H), 2.16-2.09 (m, 1H), 1.99-1.94 (m, 1H), 1.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 218.5, 146.0, 144.4, 136.9, 128.6, 127.9, 125.0, 124.3, 122.0, 88.4, 62.7, 62.2, 37.1, 34.2, 31.3, 18.0. HRMS *m/z* (EI+): Calculated for $C_{16}H_{18}O_3^+$ ([M]$^+$) 258.1256, found 258.1264.



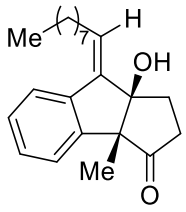




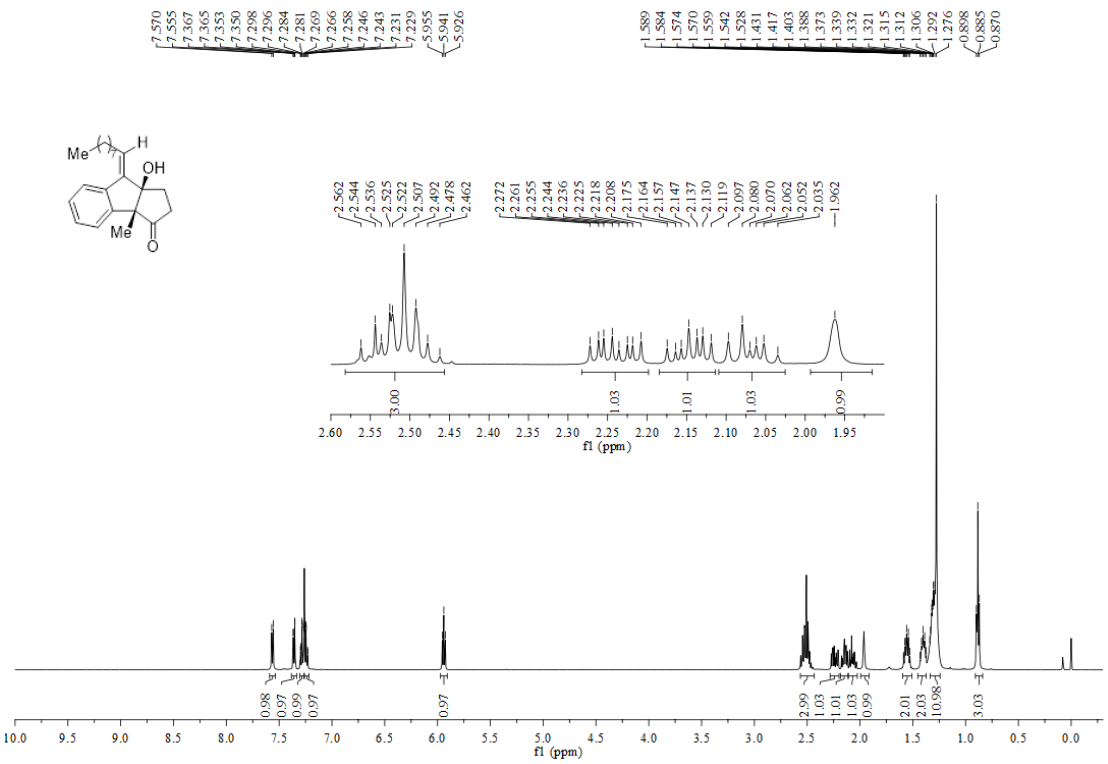
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

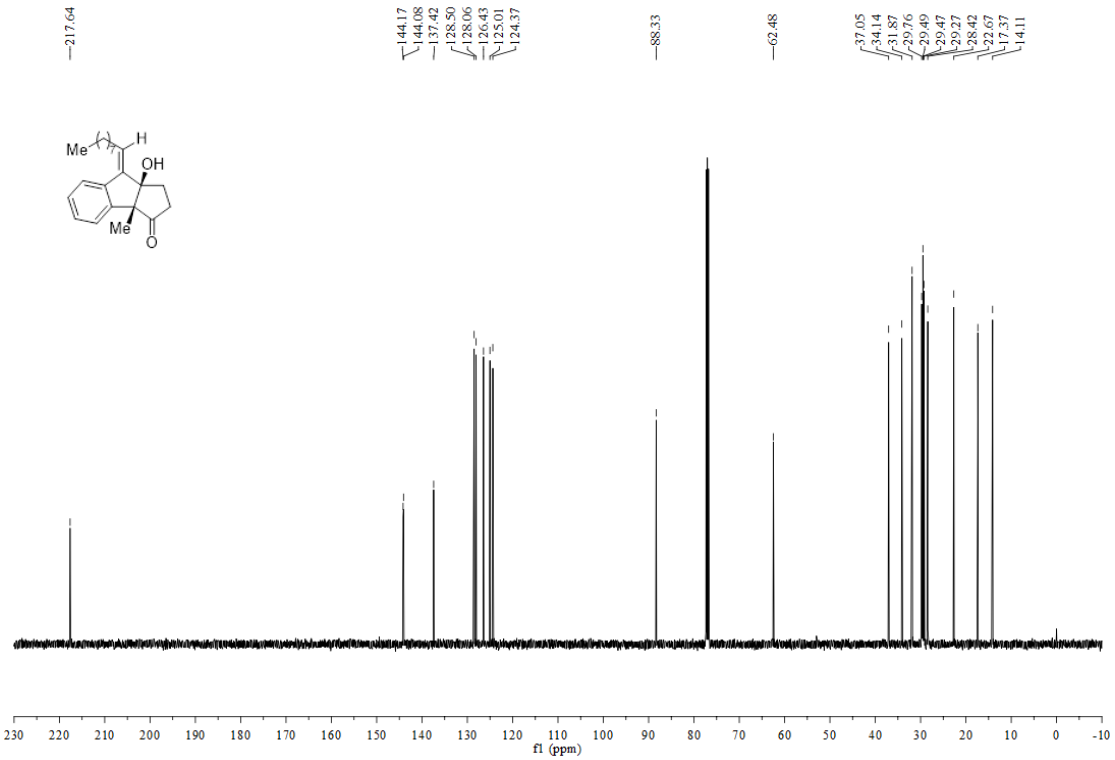
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.151	BB	0.1445	52.83349	5.47994	0.9490
2	8.067	BB	0.1626	5514.26465	516.26038	99.0510

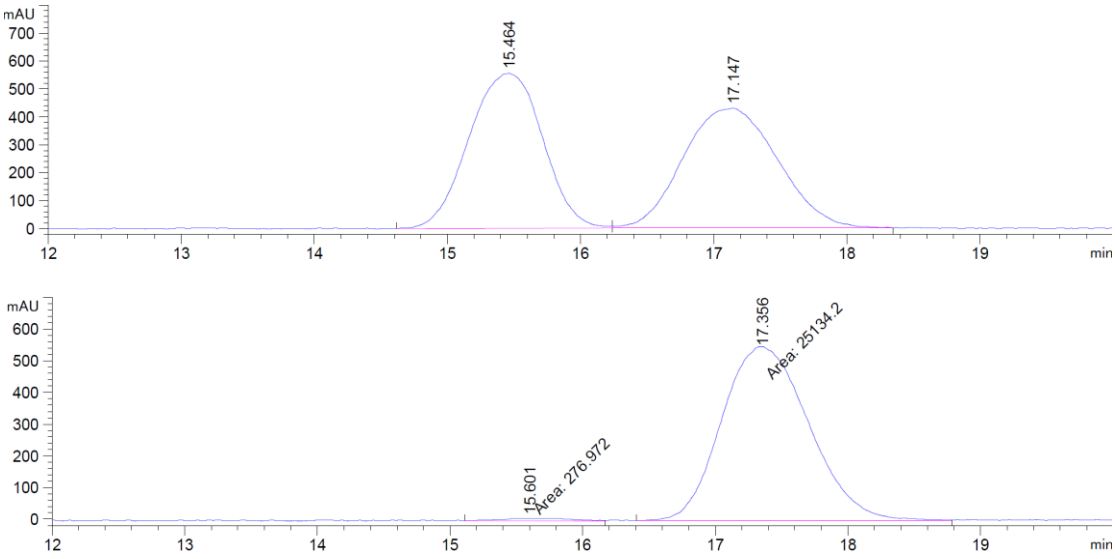
***(3aR,8aR,E)-8a-Hydroxy-3a-methyl-8-nonylidene-1,3a,8,8a-tetrahydrocyclopenta-[a]inden-3(2H)-one* (*2w*)**



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); colorless oil; 46 mg, 70% yield; $[\alpha]_D^{20}$ = -171.3 (*c* 0.5, CH_2Cl_2), 98% ee [Daicel Chiralcel OJ-H column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 99/01, 0.7 mL/min, 254 nm; t_{minor} = 15.6 min, t_{major} = 17.4 min]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.5 Hz, 1H), 7.36 (dd, *J* = 7.3, 1.0 Hz, 1H), 7.30-7.27 (m, 1H), 7.26-7.23 (m, 1H), 5.94 (t, *J* = 7.5 Hz, 1H), 2.56-2.46 (m, 3H), 2.27-2.21 (m, 1H), 2.18-2.12 (m, 1H), 2.10-2.04 (m, 1H), 1.96 (s, 1H), 1.59-1.53 (m, 2H), 1.43-1.37 (m, 2H), 1.34-1.28 (m, 11H), 0.88 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 217.6, 144.2, 144.1, 137.4, 128.5, 128.1, 126.4, 125.0, 124.4, 88.3, 62.5, 37.1, 34.1, 31.9, 29.8, 29.49, 29.47, 29.3, 28.4, 22.7, 17.4, 14.1. HRMS *m*/*z* (ESI+): Calculated for $C_{22}H_{31}O_2^+$ ($[M+H]^+$) 327.2319, found 327.2320.



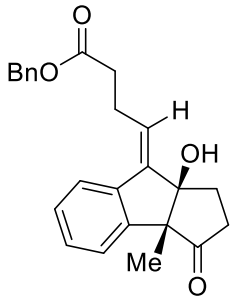




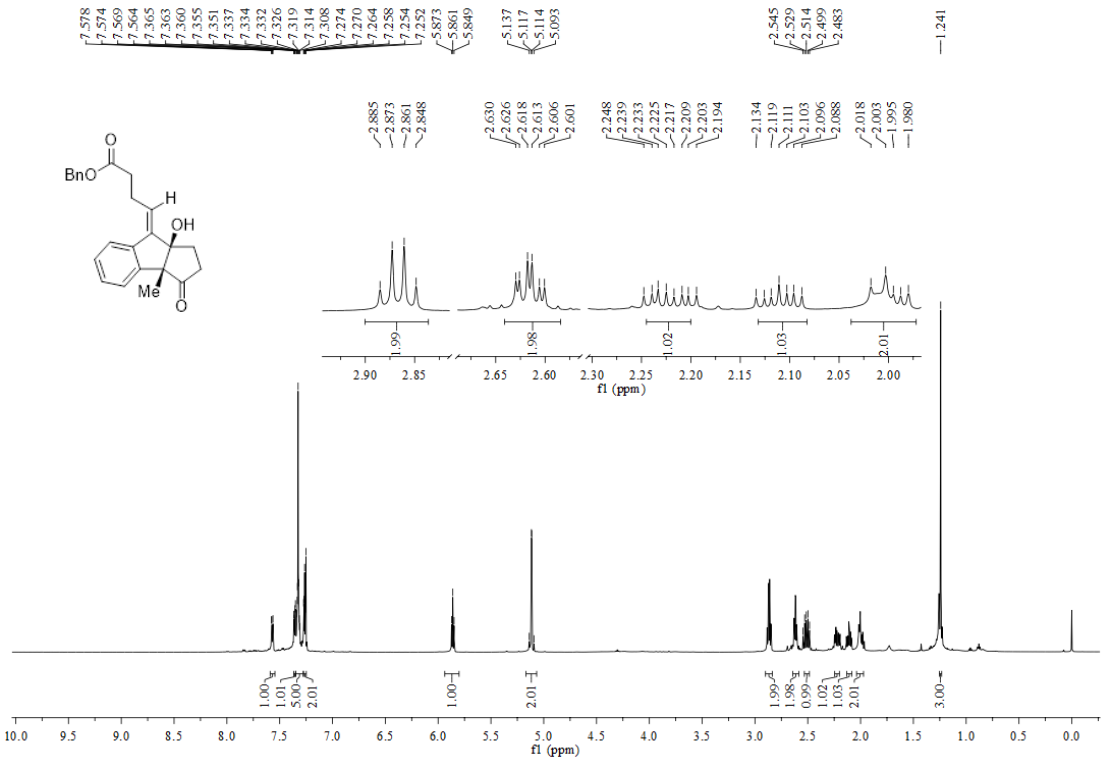
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

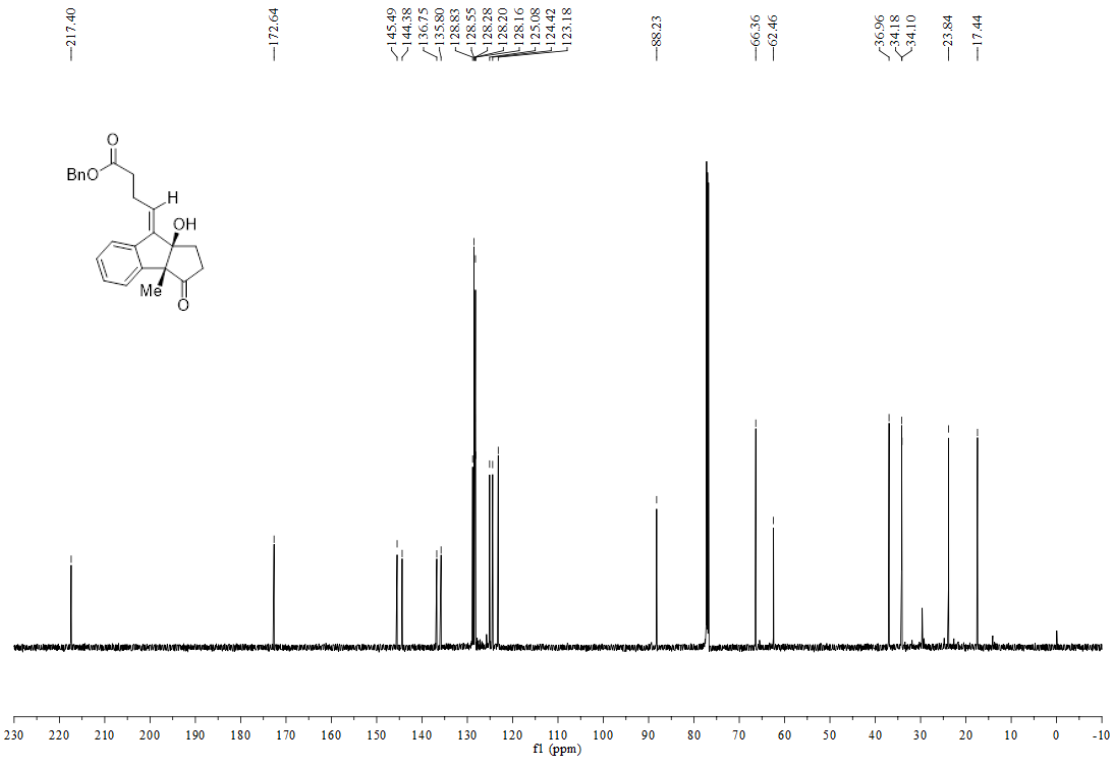
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.601	MM	0.6136	276.97174	7.52308	1.0900
2	17.356	MM	0.7618	2.51342e4	549.92072	98.9100

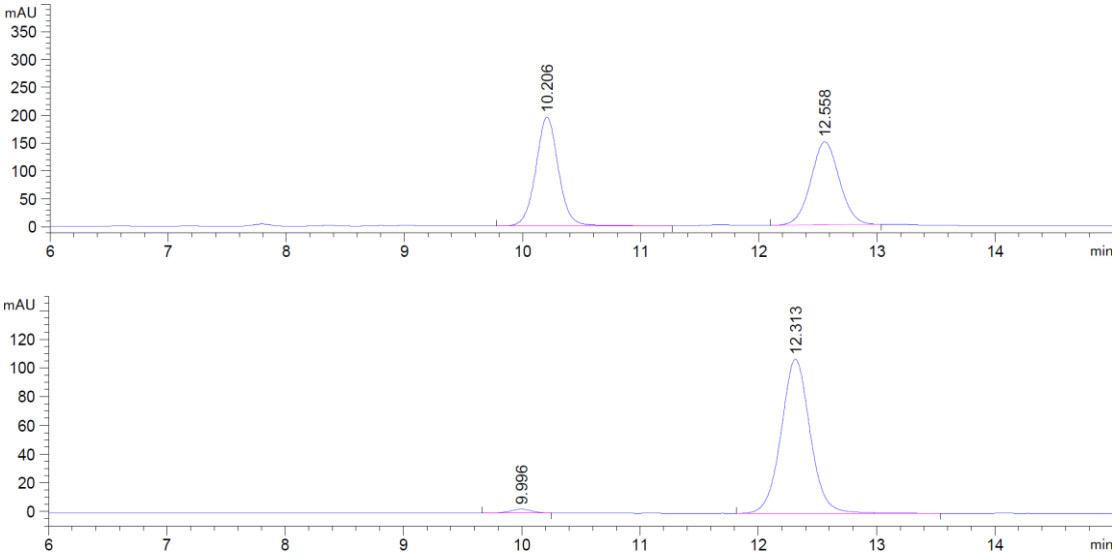
***Benzyl (E)-4-((3aR,8aR)-8a-hydroxy-3a-methyl-3-oxo-2,3,3a,8a-tetrahydrocyclopenta[a]inden-8(1H)-ylidene)butanoate* (*2x*)**



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow oil; 51 mg, 68% yield; $[\alpha]_D^{20}$ = -165.6 (*c* 0.5, CH_2Cl_2), 97% ee [Phenomenex Lux 5u Amylose-2 column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 80/20, 0.7 mL/min, 254 nm; t_{minor} = 10.0 min, t_{major} = 12.3 min]; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 6.0, 2.4 Hz, 1H), 7.37-7.35 (m, 1H), 7.34-7.31 (m, 5H), 7.27-7.25 (m, 2H), 5.86 (t, *J* = 7.2 Hz, 1H), 5.14-5.09 (m, 2H), 2.87 (q, *J* = 7.2 Hz, 2H), 2.63-2.60 (m, 2H), 2.55-2.48 (m, 1H), 2.25-2.19 (m, 1H), 2.13-2.09 (m, 1H), 2.02-1.98 (m, 2H), 1.24 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 217.4, 172.6, 145.5, 144.4, 136.8, 135.8, 128.8, 128.6, 128.3, 128.20, 128.16, 125.1, 124.4, 123.2, 88.2, 66.4, 62.5, 37.0, 34.2, 34.1, 23.8, 17.4. HRMS *m*/*z* (ESI+): Calculated for $C_{24}H_{24}NaO_4^+$ ([M+Na]$^+$) 399.1567, found 399.1565.



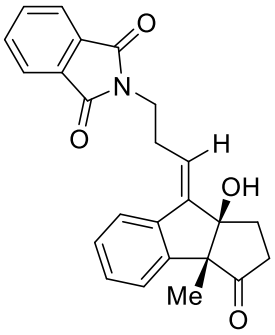




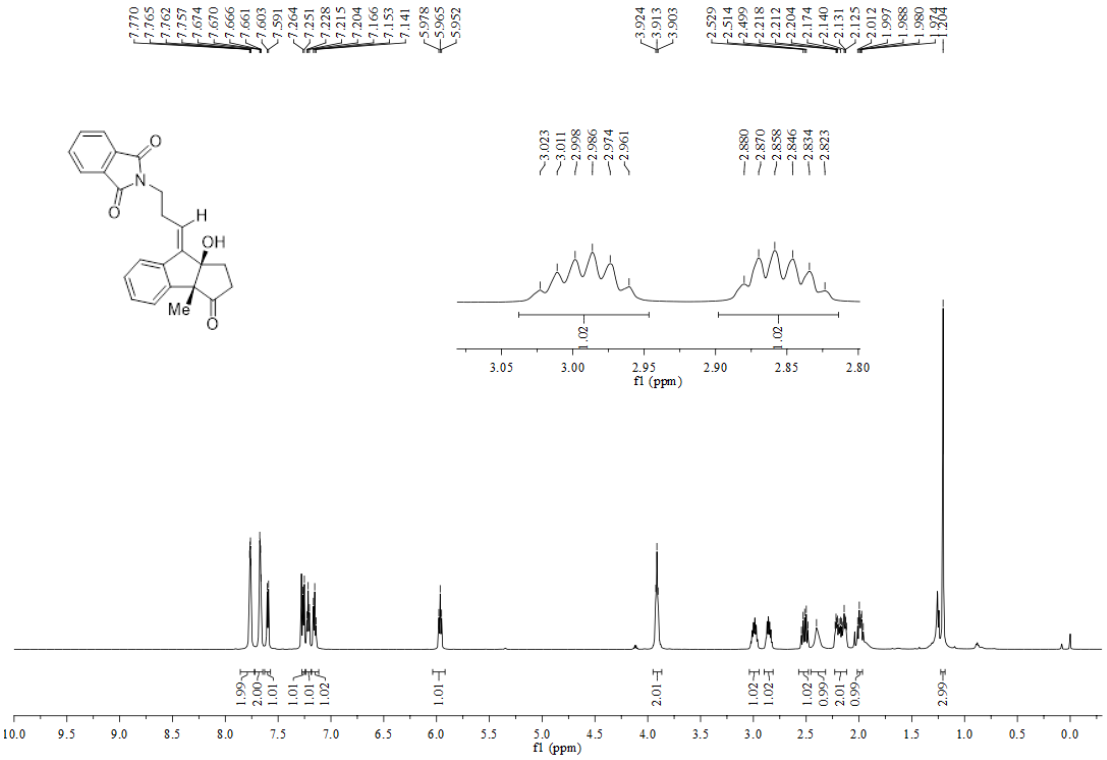
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

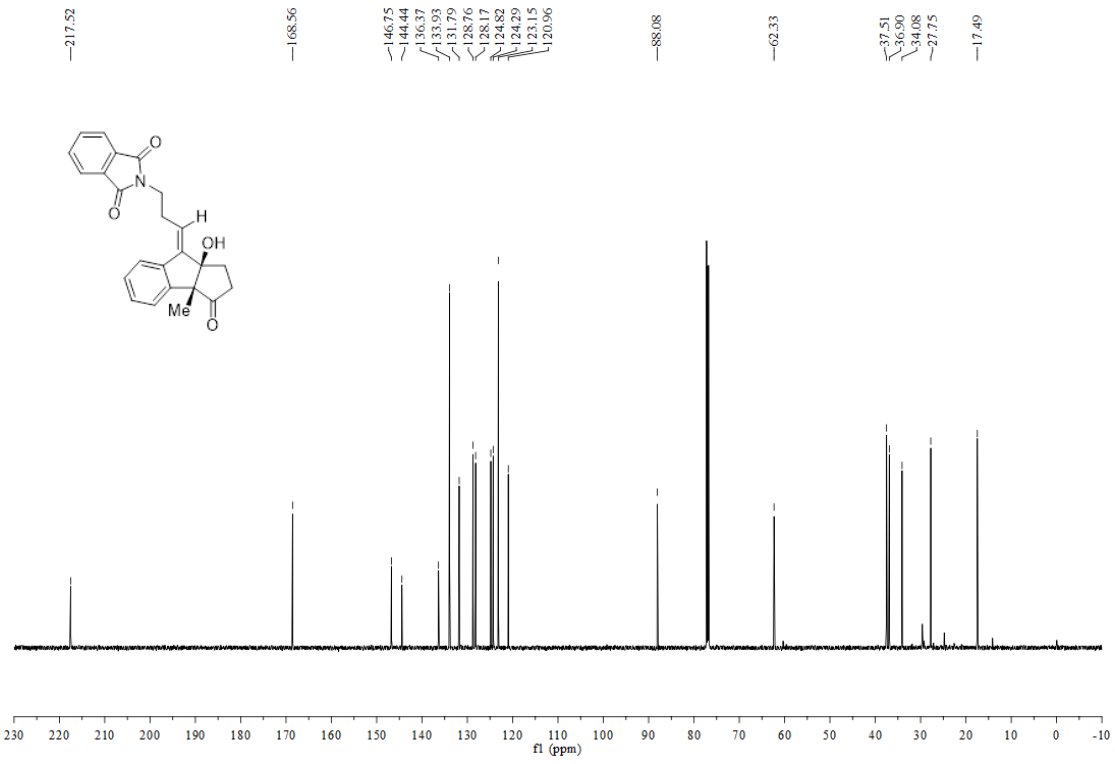
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.996	BB	0.1937	32.69878	2.65444	1.7543
2	12.313	BB	0.2611	1831.24036	107.32964	98.2457

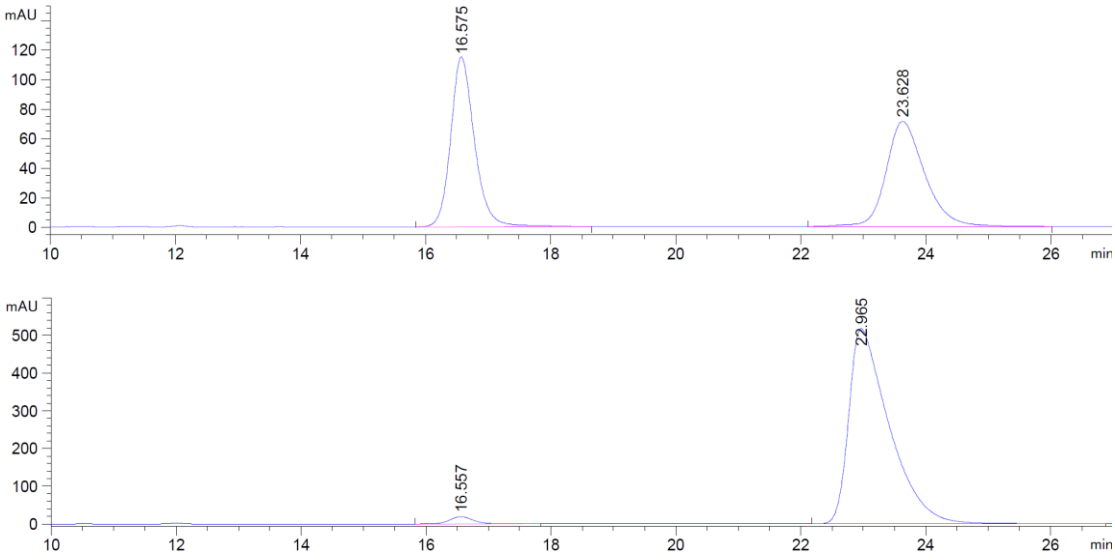
2-((E)-3-((3aR,8aR)-8a-Hydroxy-3a-methyl-3-oxo-2,3,3a,8a-tetrahydrocyclopenta-[a]inden-8(1H)-ylidene)propyl)isoindoline-1,3-dione (2y)



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow solid, Mp = 63-64 °C; 64 mg, 83% yield; $[\alpha]_D^{20}$ = -113.8 (*c* 0.5, CH_2Cl_2), 96% ee [Phenomenex Lux 5u Amylose-2 column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 80/20, 0.8 mL/min, 254 nm; t_{minor} = 16.6 min, t_{major} = 23.0 min]; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 4.8, 3.0 Hz, 2H), 7.67 (dd, *J* = 4.8, 3.0 Hz, 2H), 7.60 (d, *J* = 7.2 Hz, 1H), 7.26 (d, *J* = 7.8 Hz, 1H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.15 (t, *J* = 7.2 Hz, 1H), 5.97 (t, *J* = 7.8 Hz, 1H), 3.91 (t, *J* = 6.0 Hz, 2H), 3.02-2.96 (m, 1H), 2.88-2.82 (m, 1H), 2.53-2.50 (m, 1H), 2.40 (s, 1H), 2.22-2.13 (m, 2H), 2.01-1.97 (m, 1H), 1.20 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 217.5, 168.6, 146.8, 144.4, 136.4, 133.9, 131.8, 128.8, 128.2, 124.8, 124.3, 123.2, 121.0, 88.1, 62.3, 37.5, 36.9, 34.1, 27.8, 17.5. HRMS *m/z* (ESI+): Calculated for $C_{24}H_{21}NNaO_4^+$ ([M+Na]$^+$) 410.1363, found 410.1360.



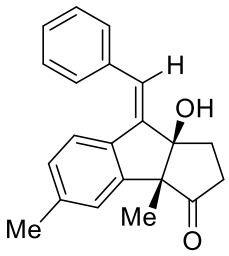




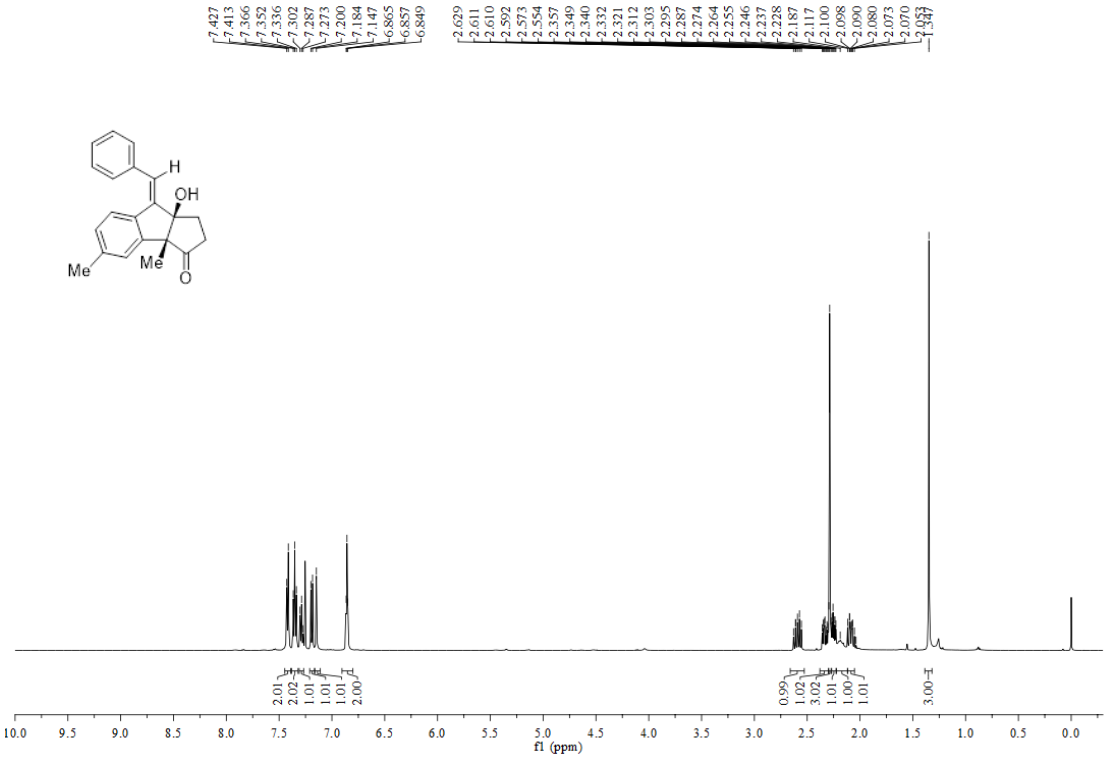
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

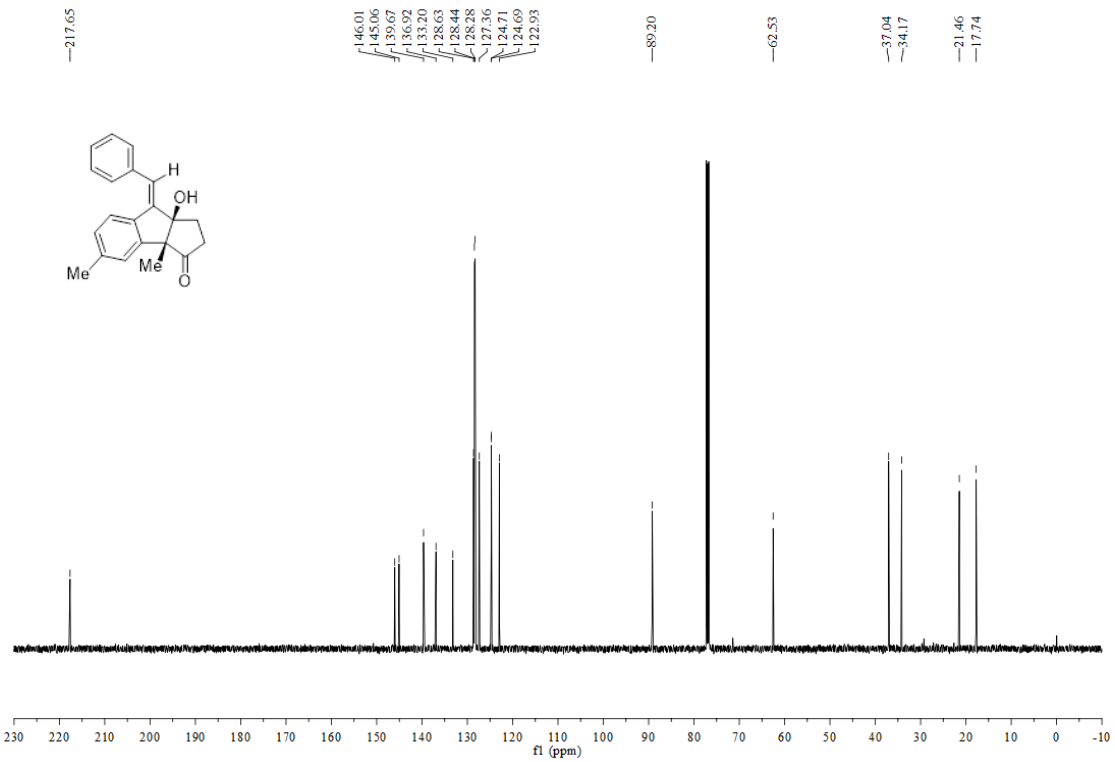
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.557	BB	0.4008	500.00568	19.13955	2.1049
2	22.965	BB	0.6561	2.32538e4	517.59906	97.8951

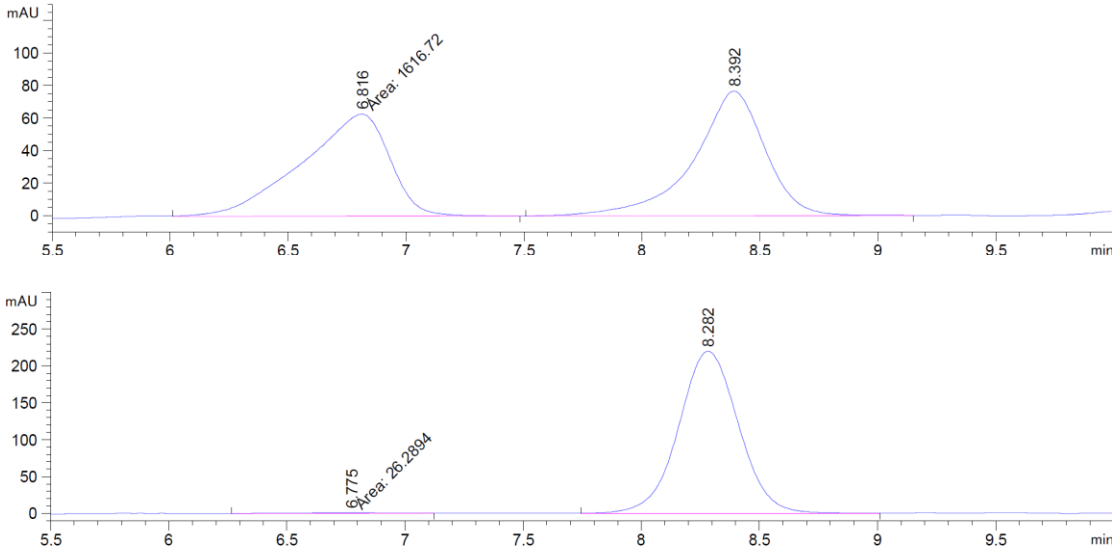
(3aR,8aR)-8-((E)-Benzylidene)-8a-hydroxy-3a,5-dimethyl-1,3a,8,8a-tetrahydro-cyclopenta[a]inden-3(2H)-one (2z)



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); brown solid, Mp = 168-169 °C; 49 mg, 81% yield; $[\alpha]_D^{20}$ = -160.2 (*c* 0.5, CH_2Cl_2), 99% ee [Phenomenex Lux 5u Amylose-2 column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 85/15, 0.7 mL/min, 254 nm; t_{minor} = 6.8 min, t_{major} = 8.3 min]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, J = 7.0 Hz, 2H), 7.35 (t, J = 7.5 Hz, 2H), 7.29 (t, J = 7.0 Hz, 1H), 7.19 (d, J = 8.0 Hz, 1H), 7.15 (s, 1H), 6.86 (t, J = 4.0 Hz, 2H), 2.63-2.55 (m, 1H), 2.36-2.30 (m, 1H), 2.29 (s, 3H), 2.27-2.23 (m, 1H), 2.19 (s, 1H), 2.12-2.05 (m, 1H), 1.35 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 217.7, 146.0, 145.1, 139.7, 136.9, 133.2, 128.6, 128.4, 128.3, 127.4, 124.71, 124.69, 122.9, 89.2, 62.5, 37.0, 34.2, 21.5, 17.7. HRMS m/z (ESI+): Calculated for $C_{21}H_{20}O_2^+$ ([M]$^+$) 304.1458, found 304.1460.



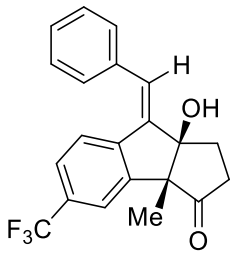




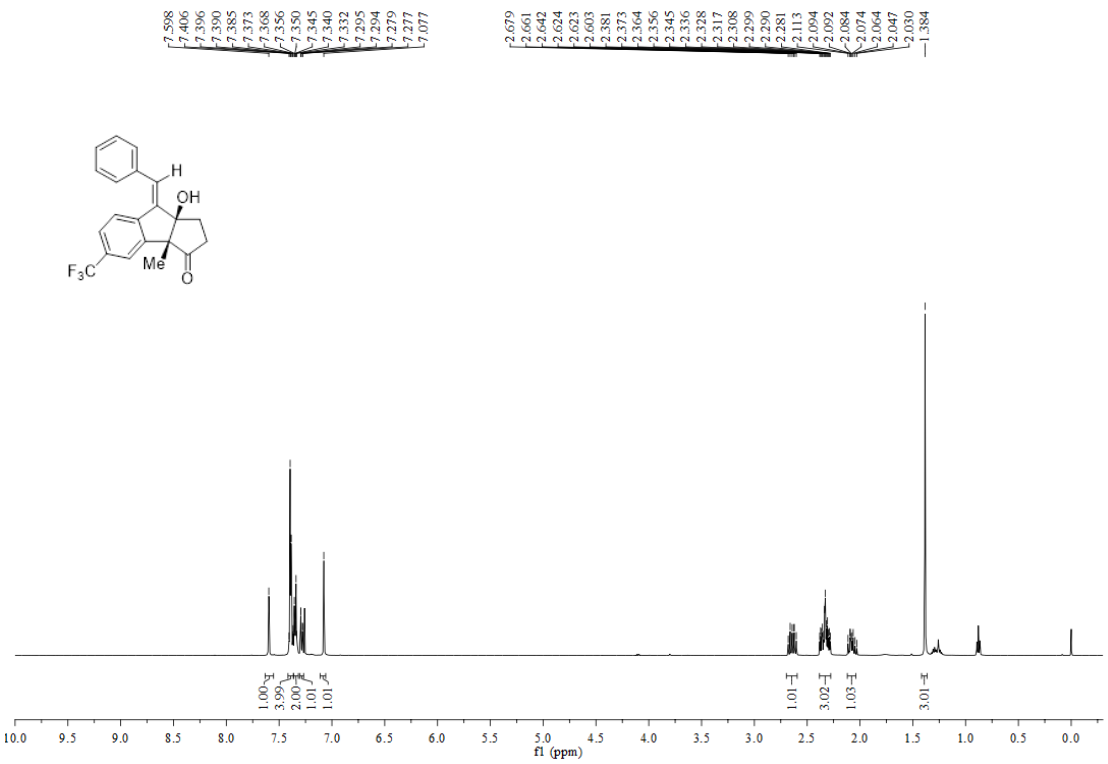
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

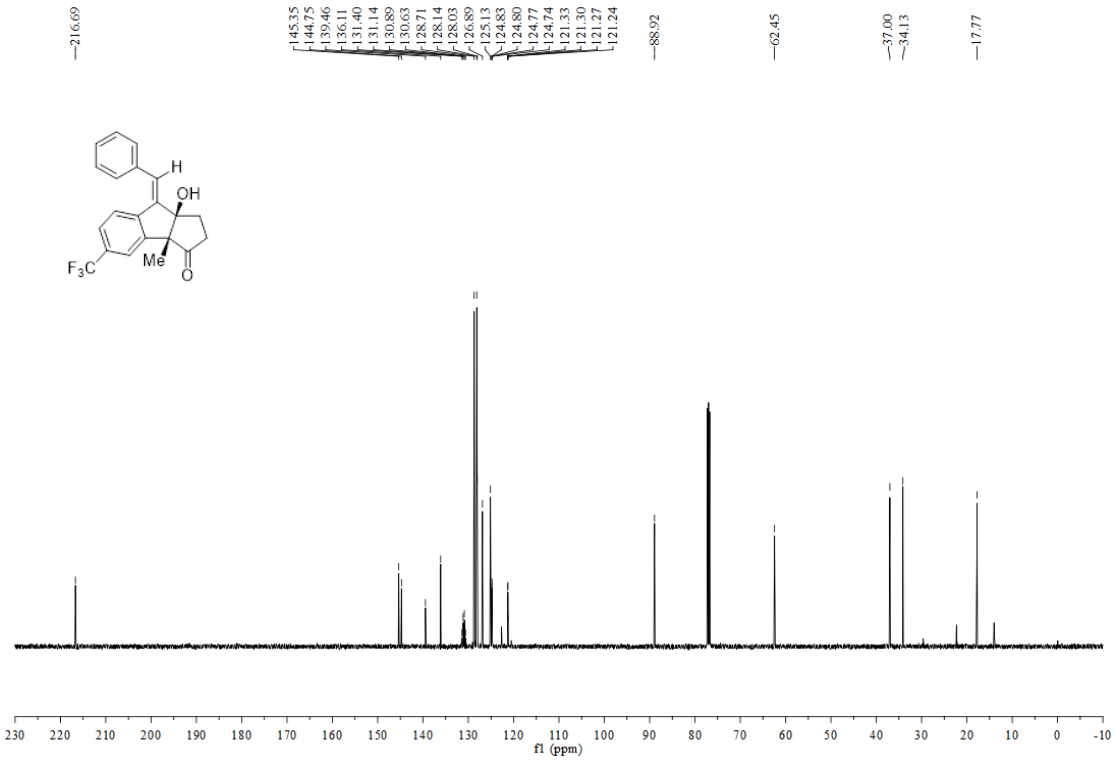
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.775	MM	0.3335	26.28944	1.31390	0.6737
2	8.282	BB	0.2737	3875.87720	219.81409	99.3263

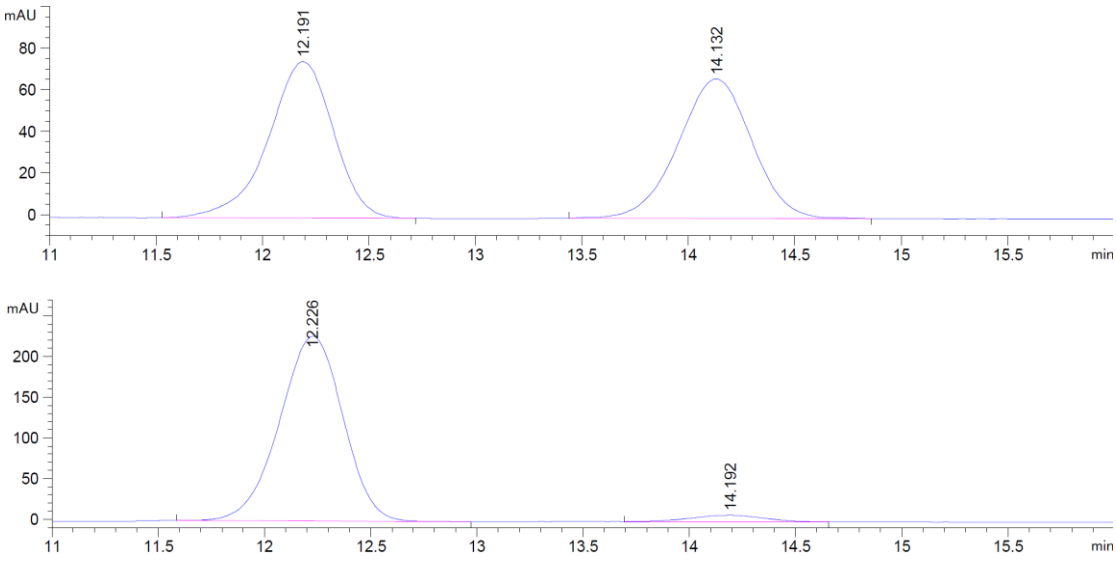
***(3aR,8aR)-8-((E)-Benzylidene)-8a-hydroxy-3a-methyl-5-(trifluoromethyl)-1,3a,8,8a-tetrahydrocyclopenta[a]inden-3(2H)-one* (*2aa*)**



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); brown oil; 57 mg, 80% yield; $[\alpha]_D^{20}$ = -172.4 (*c* 1.0, CH_2Cl_2), 93% ee [Phenomenex Lux 5u Cellulose-1 column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 90/10, 0.7 mL/min, 254 nm; t_{major} = 12.2 min, t_{minor} = 14.2 min]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.41-7.36 (m, 4H), 7.35-7.33 (m, 2H), 7.29 (dd, *J* = 8.0, 0.5 Hz, 1H), 7.08 (s, 1H), 2.68-2.60 (m, 1H), 2.38-2.28 (m, 3H), 2.11-2.03 (m, 1H), 1.38 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 216.7, 145.4, 144.8, 139.5, 136.1, 131.0 (q, *J* = 32.5 Hz), 128.7, 128.1, 128.0, 126.9, 125.1, 124.8 (q, *J* = 3.7 Hz), 121.3 (q, *J* = 3.8 Hz), 88.9, 62.5, 37.0, 34.1, 17.8. HRMS (ESI) *m*/*z* Calculated for $C_{21}H_{17}F_3O_2Na^+$ ([M+Na]+) 381.1073, found 381.1075.



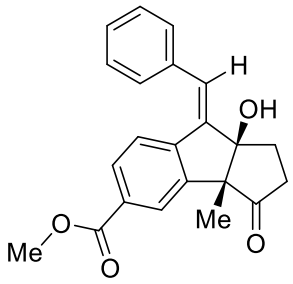




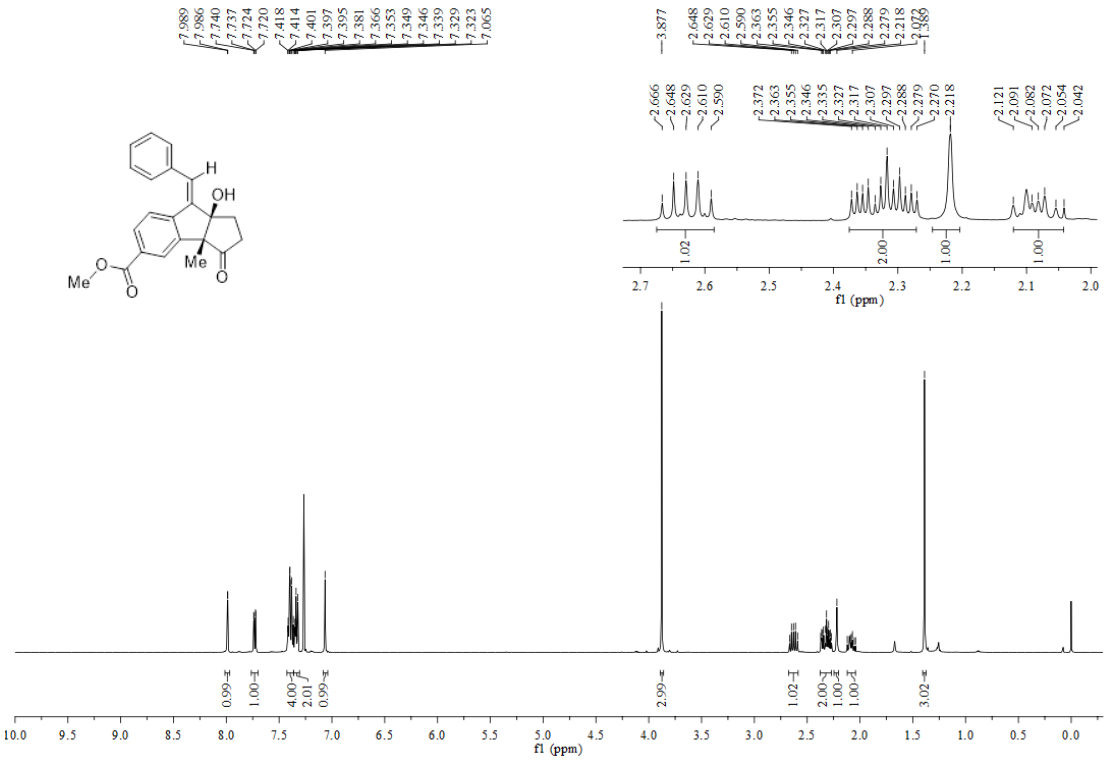
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

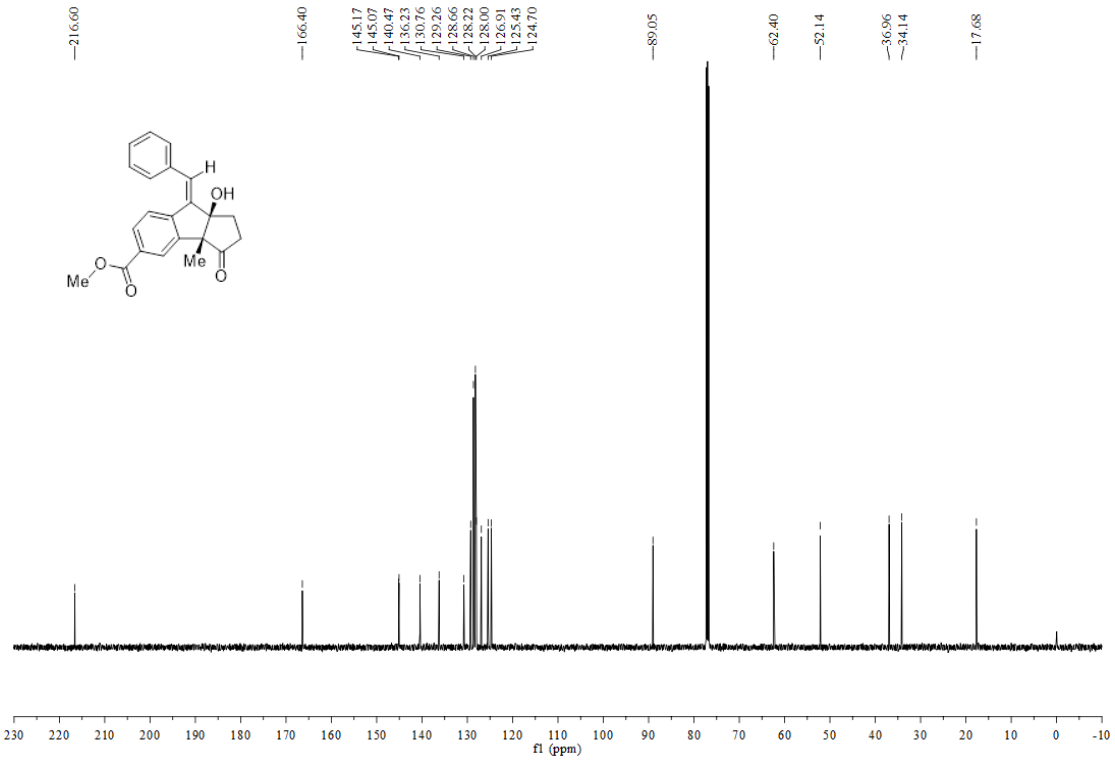
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.226	BB	0.3265	4722.60010	227.17953	96.2510
2	14.192	BB	0.2932	183.94580	7.97210	3.7490

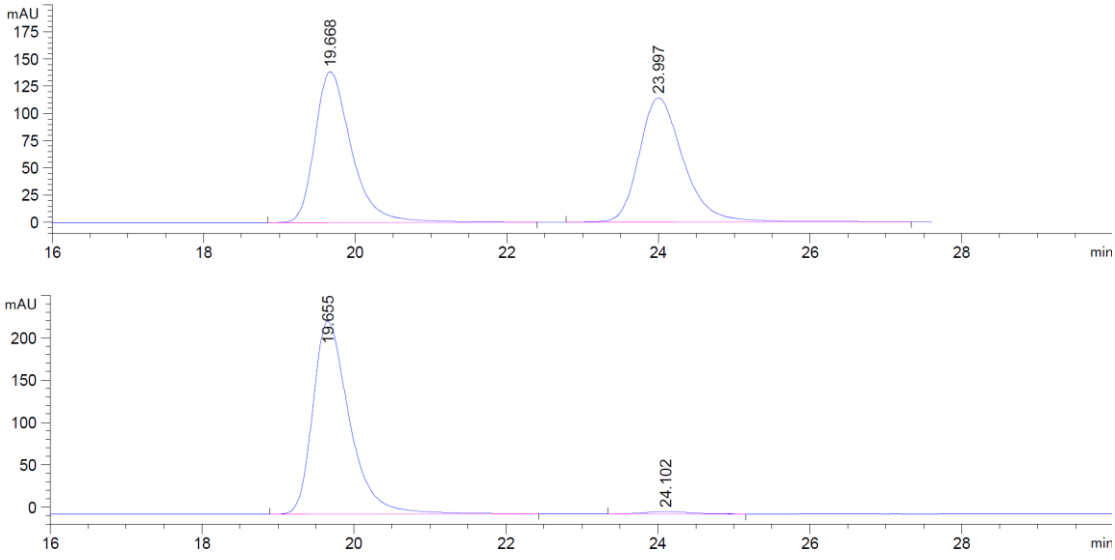
***Methyl (3aR,8aR)-8-((E)-benzylidene)-8a-hydroxy-3a-methyl-3-oxo-1,2,3,3a,8,8a-hexahydrocyclopenta[a]indene-5-carboxylate* (*2ab*)**



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:3 (v/v); yellow solid, Mp = 59-60 °C; 58 mg, 83% yield; $[\alpha]_D^{20}$ = -185.9 (*c* 0.5, CH_2Cl_2), 97% ee [Phenomenex Lux 5u Cellulose-2 column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 90/10, 0.7 mL/min, 280 nm; t_{major} = 19.7 min, t_{minor} = 24.1 min]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, J = 1.5 Hz, 1H), 7.73 (dd, J = 8.5, 1.5 Hz, 1H), 7.42-7.37 (m, 4H), 7.35-7.32 (m, 2H), 7.07 (s, 1H), 3.88 (s, 3H), 2.65-2.59 (m, 1H), 2.36-2.28 (m, 2H), 2.22 (s, 1H), 2.12-2.04 (m, 1H), 1.39 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 216.6, 166.4, 145.2, 145.1, 140.5, 136.2, 130.8, 129.3, 128.7, 128.2, 128.0, 126.9, 125.4, 124.7, 89.1, 62.4, 52.1, 37.0, 34.1, 17.7. HRMS *m*/*z* (ESI+): Calculated for $C_{22}H_{21}O_4^+$ ([M+H]$^+$) 349.1434, found 349.1437.



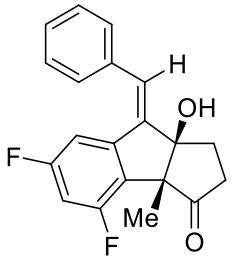




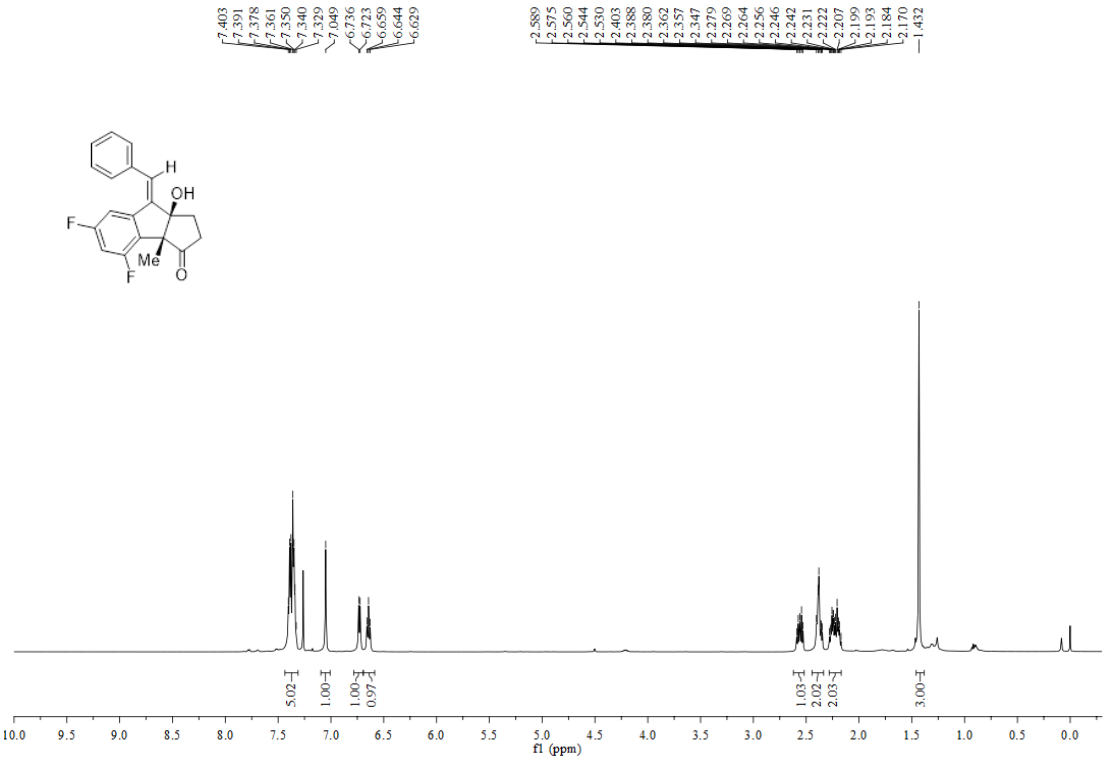
Signal 7: DAD1 G, Sig=280,4 Ref=360,100

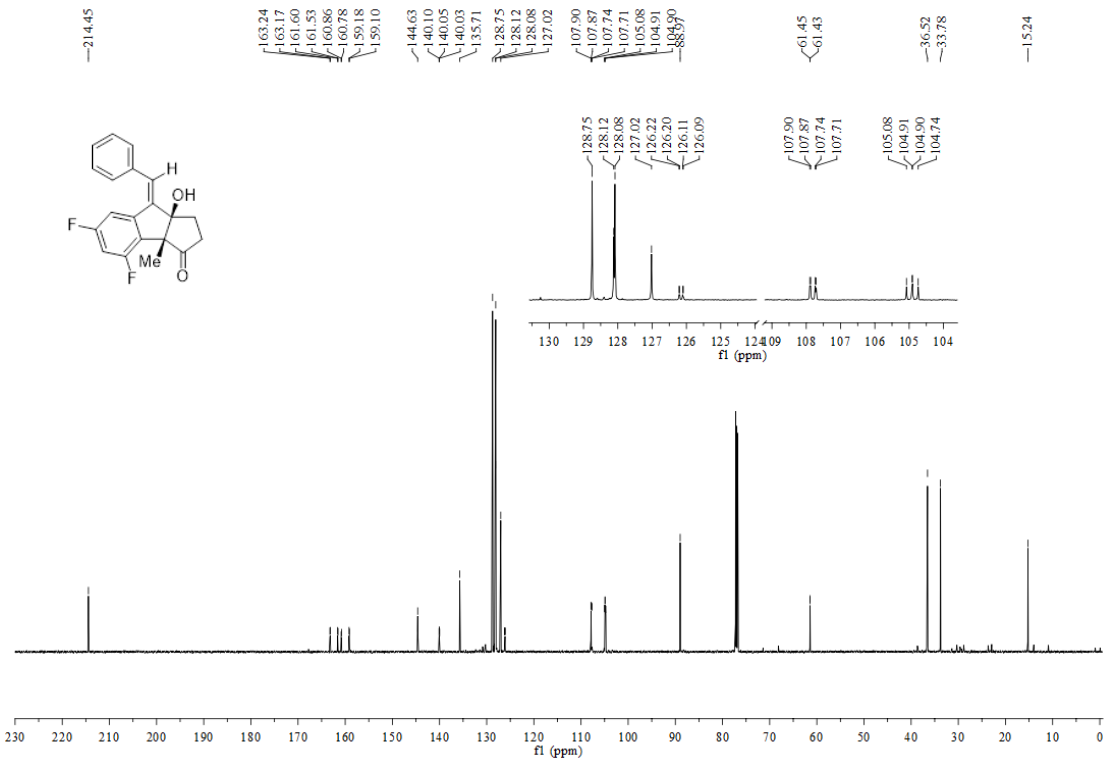
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.655	BB	0.5069	7622.26025	227.47009	98.5973
2	24.102	BB	0.4669	108.43837	2.78110	1.4027

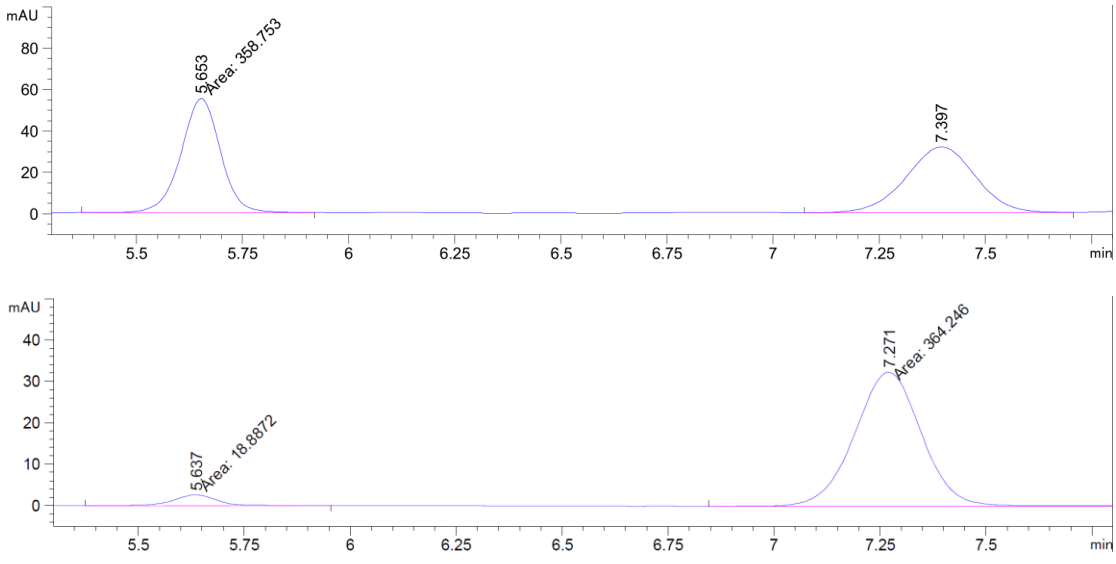
***(3aR,8aR)-8-((E)-Benzylidene)-4,6-difluoro-8a-hydroxy-3a-methyl-1,3a,8,8a-tetrahydrocyclopenta[a]inden-3(2H)-one* (*2ac*)**



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); brown solid, Mp = 124-125 °C; 49 mg, 65% yield; $[\alpha]_D^{20}$ = -181.4 (*c* 0.5, CH_2Cl_2), 90% ee [Phenomenex Lux 5u Amylose-2 column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 80/20, 0.8 mL/min, 254 nm; t_{minor} = 5.6 min, t_{major} = 7.3 min]; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40-7.33 (m, 5H), 7.05 (s, 1H), 6.73 (d, *J* = 7.8 Hz, 1H), 6.64 (t, *J* = 9.0 Hz, 1H), 2.59-2.53 (m, 1H), 2.40-2.35 (m, 2H), 2.28-2.17 (m, 2H), 1.43 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 214.5, 162.4 (dd, *J* = 246.0, 10.5 Hz), 160.0 (dd, *J* = 252.0, 12.0 Hz), 144.6, 140.0 (dd, *J* = 10.5, 7.5 Hz), 135.7, 128.8, 128.12, 128.08, 127.0, 126.2 (dd, *J* = 16.5, 3.0 Hz), 107.8 (dd, *J* = 23.9, 4.5 Hz), 104.9 (dd, *J* = 25.5, 24.0 Hz), 89.0, 61.4 (d, *J* = 3.7 Hz), 36.5, 33.8, 15.2. HRMS *m*/*z* (ESI+): Calculated for $C_{20}H_{16}F_2O_2Na^+$ ([M+Na]$^+$) 349.1011, found 349.1013.



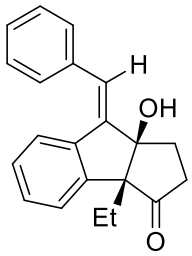




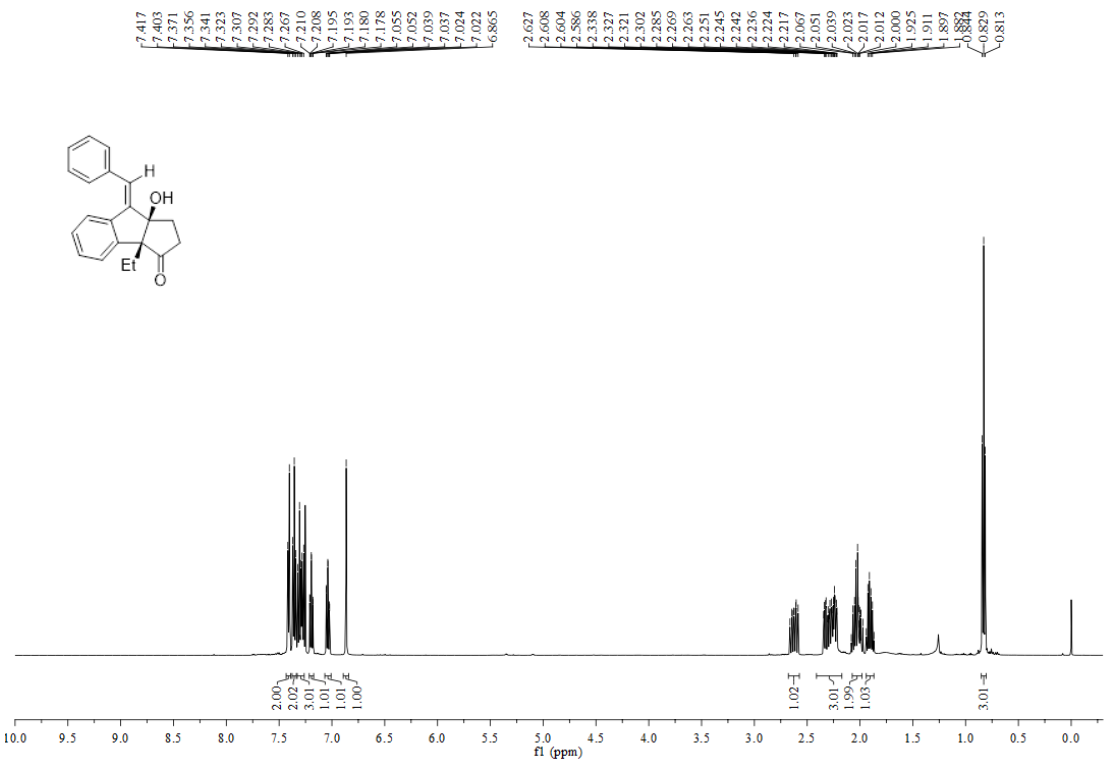
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

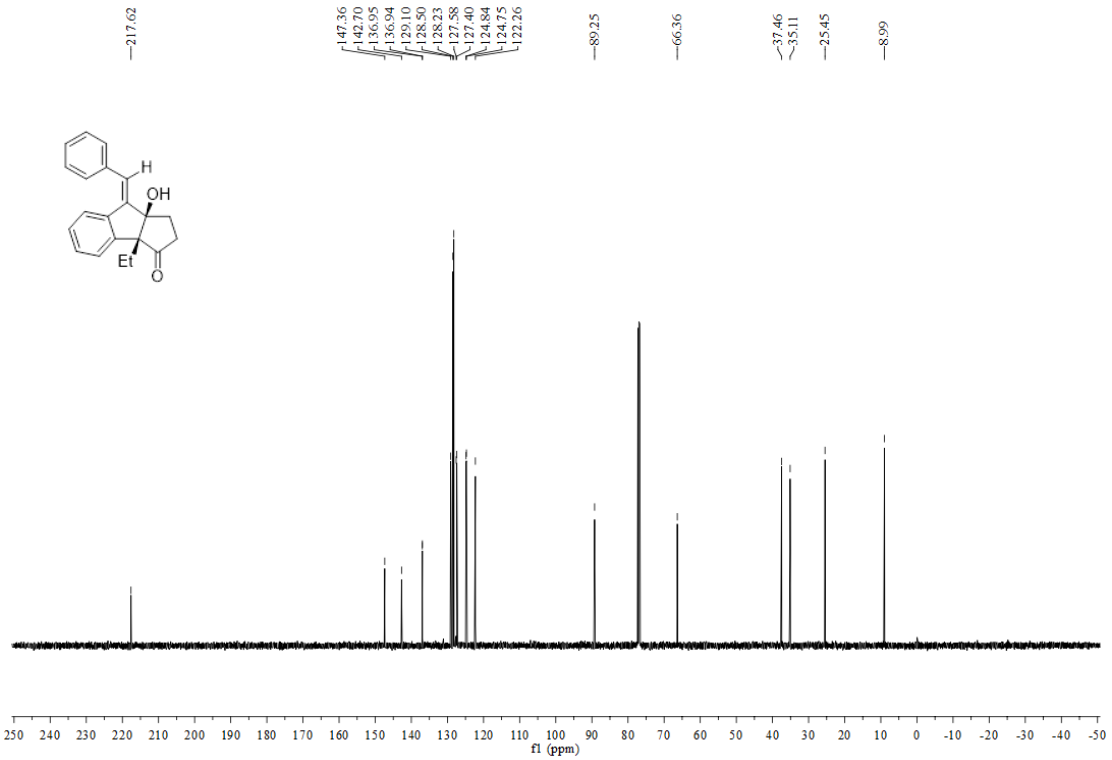
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.637	MM	0.1200	18.88716	2.62237	4.9297
2	7.271	MM	0.1865	364.24640	32.55622	95.0703

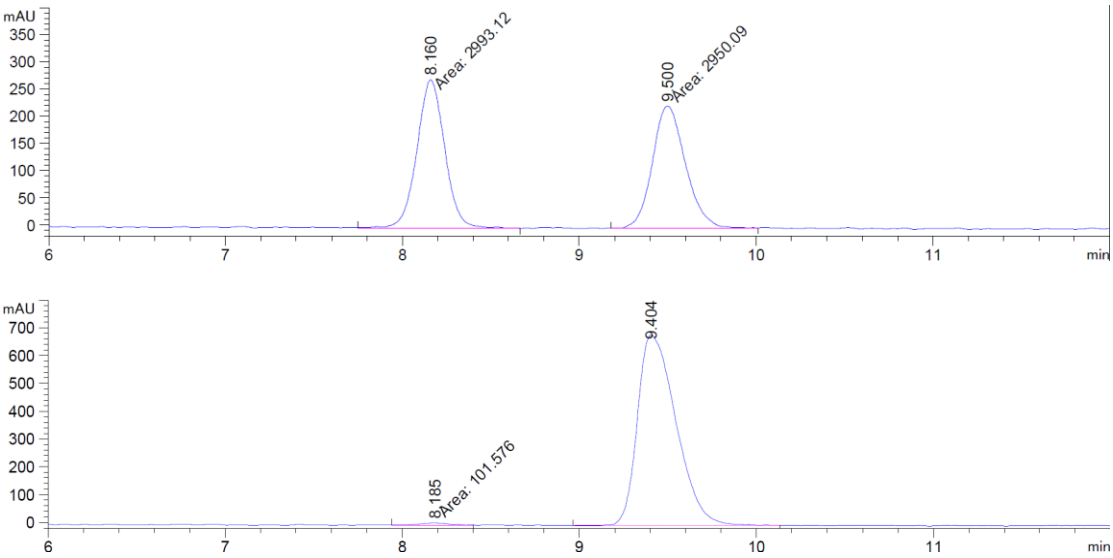
***(3aR,8aR)-8-((E)-Benzylidene)-3a-ethyl-8a-hydroxy-1,3a,8,8a-tetrahydrocyclo-penta[a]inden-3(2H)-one* (*2ad*)**



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); brown solid, Mp = 78-79 °C; 45 mg, 74% yield; $[\alpha]_D^{20}$ = -250.2 (*c* 0.5, CH_2Cl_2), 98% ee [Phenomenex Lux 5u Amylose-2 column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 90/10, 0.7 mL/min, 254 nm; t_{minor} = 8.2 min, t_{major} = 9.4 min]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, J = 7.0 Hz, 2H), 7.36 (t, J = 7.5 Hz, 2H), 7.32-7.27 (m, 3H), 7.21-7.18 (m, 1H), 7.06-7.02 (m, 1H), 6.87 (s, 1H), 2.63-2.59 (m, 1H), 2.34-2.22 (m, 3H), 2.07-2.00 (m, 2H), 1.93-1.88 (m, 1H), 0.83 (t, J = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 217.6, 147.4, 142.7, 136.95, 136.94, 129.1, 128.5, 128.2, 127.6, 127.4, 124.84, 124.75, 122.3, 89.3, 66.4, 37.5, 35.1, 25.5, 9.0. HRMS *m*/*z* (ESI+): Calculated for $C_{21}H_{20}O_2Na^+$ ([M+Na]$^+$) 327.1356, found 327.1356.



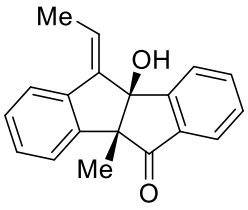




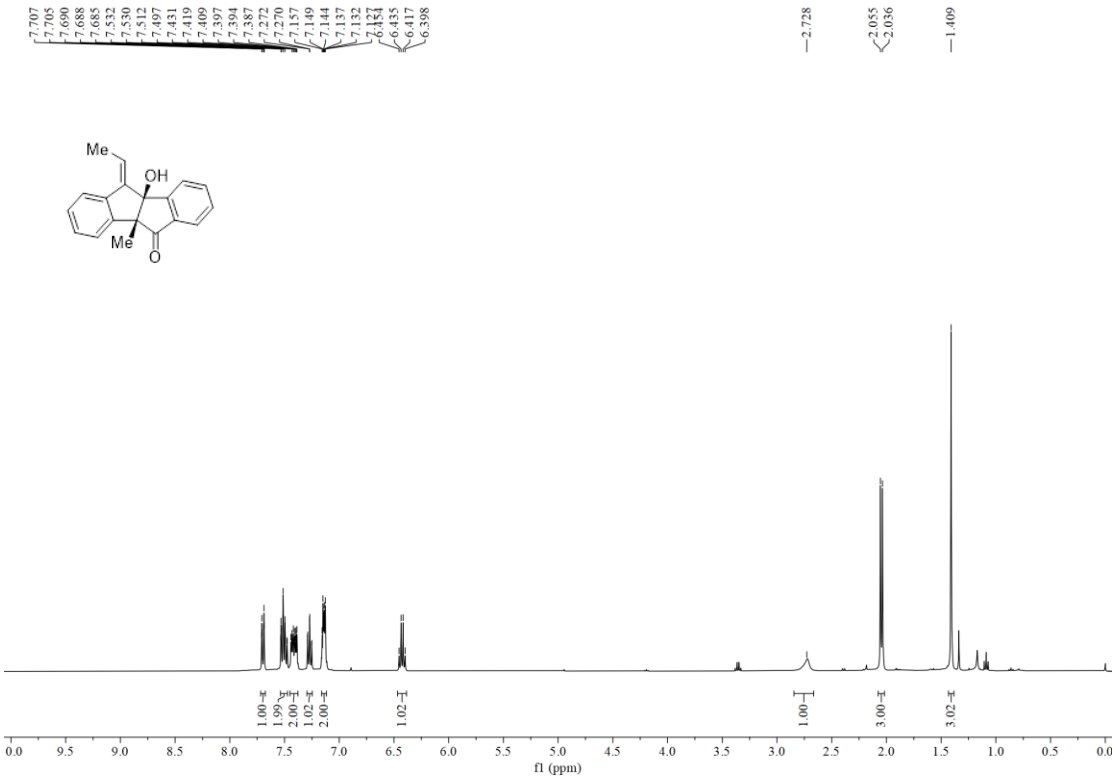
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

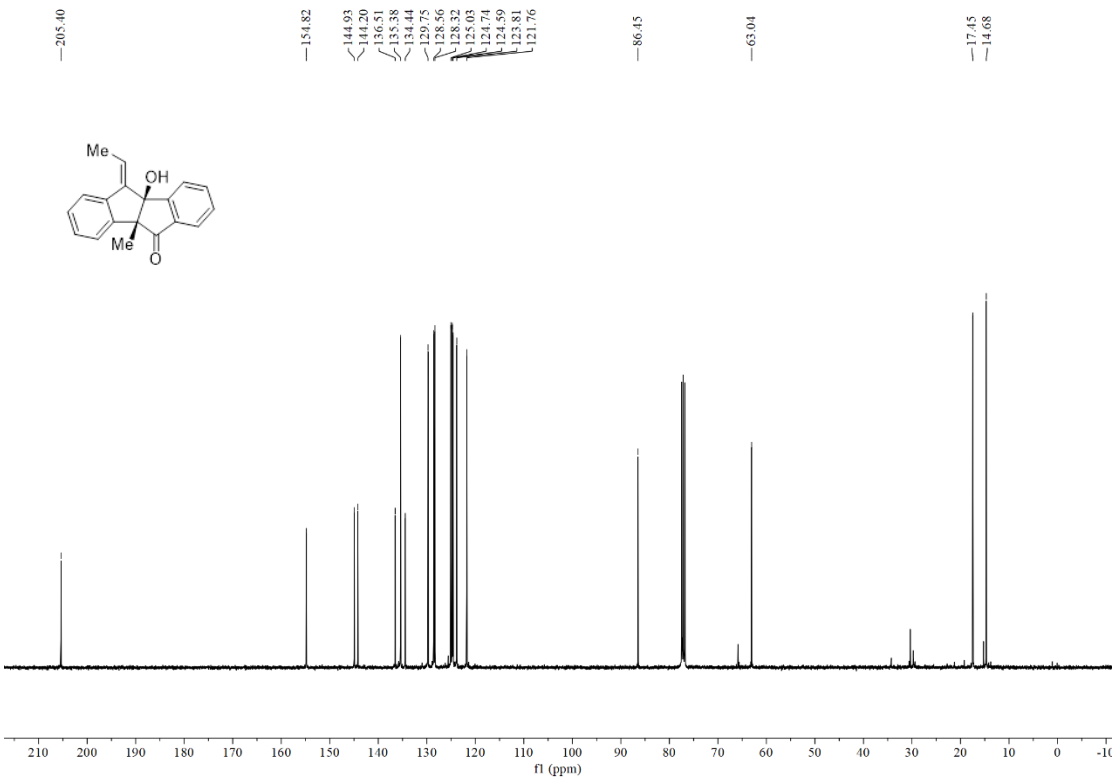
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.185	MM	0.1962	101.57608	8.62751	0.9688
2	9.404	VV R	0.2367	1.03829e4	685.52063	99.0312

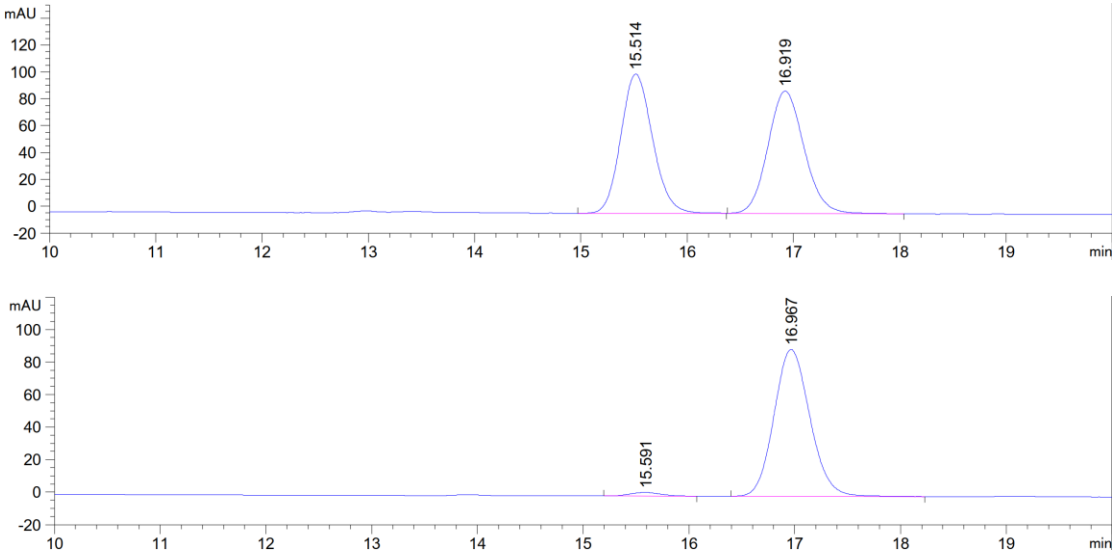
***(4bR,9bS,E)-10-Ethylidene-9b-hydroxy-4b-methyl-9b,10-dihydroindeno[2,1-a]inden-5(4bH)-one* (*2ae*)**



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow oil; 50 mg, 91% yield; $[\alpha]_D^{20}$ = -281.6 (*c* 0.5, CH_2Cl_2), 96% ee [Daicel Chiralcel OJ-H column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 90/10, 0.7 mL/min, 254 nm; t_{minor} = 15.6 min, t_{major} = 17.0 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71-7.69 (m, 1H), 7.53-7.50 (m, 2H), 7.43-7.39 (m, 2H), 7.29-7.25 (m, 1H), 7.15-7.13 (m, 2H), 6.43 (q, *J* = 8.0 Hz, 1H), 2.73 (s, 1H), 2.05 (d, *J* = 4.0 Hz, 3H), 1.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.4, 154.8, 144.9, 144.2, 136.5, 135.4, 134.4, 129.8, 128.6, 128.3, 125.0, 124.7, 124.6, 123.8, 121.8, 86.5, 63.0, 17.5, 14.7. HRMS *m*/*z* (ESI+): Calculated for $C_{19}H_{17}O_2^+$ ($[M+H]^+$) 277.1223, found 277.1220.



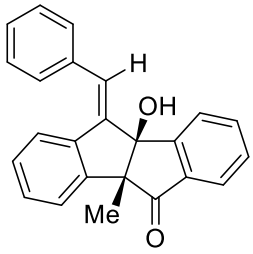




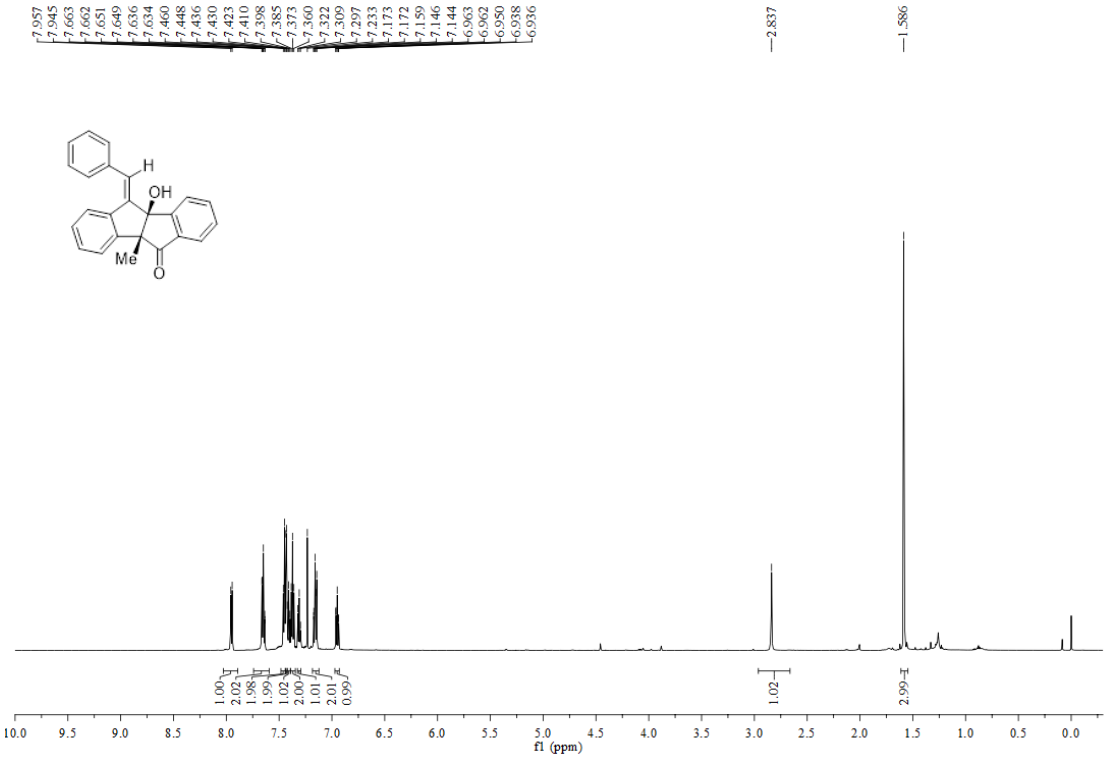
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

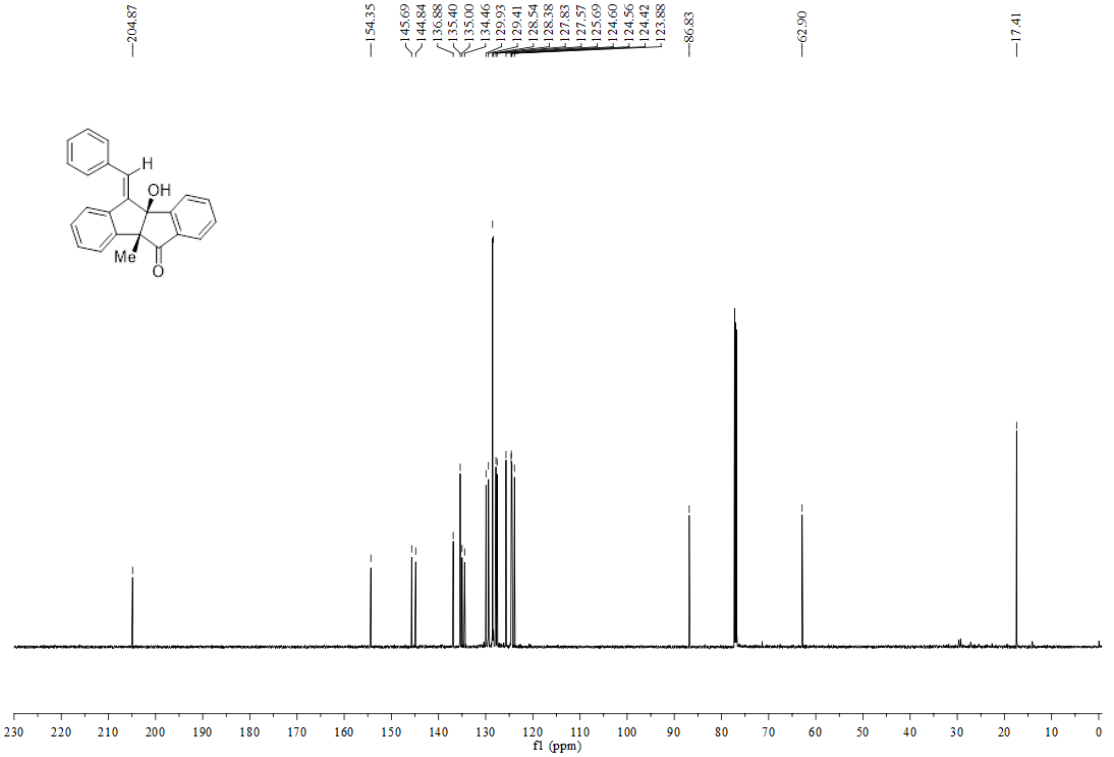
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.591	BB	0.2800	44.79495	2.19612	2.0581
2	16.967	BB	0.3654	2131.75073	90.31090	97.9419

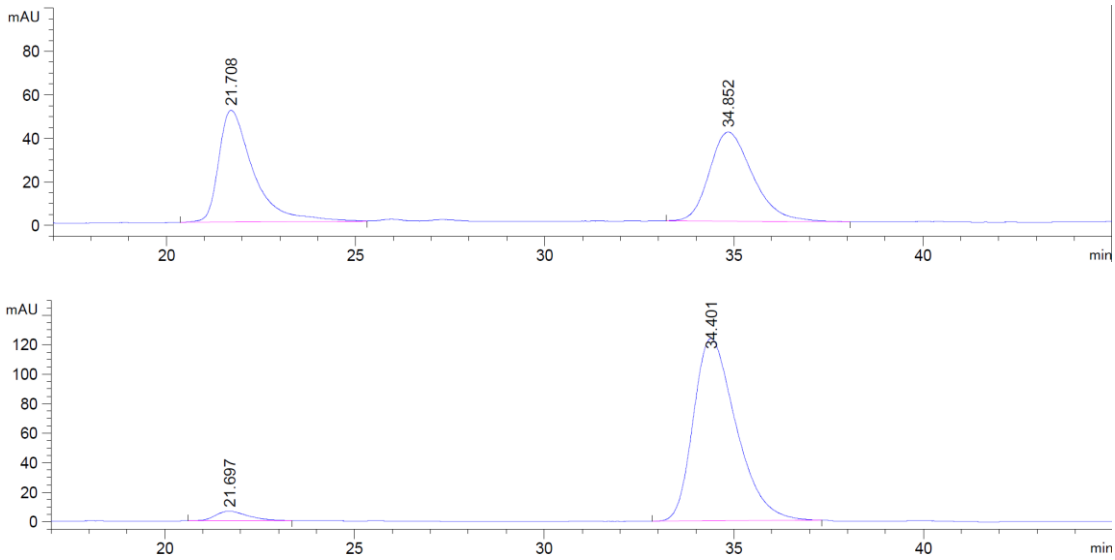
***(4bR,9bS)-10-((E)-Benzylidene)-9b-hydroxy-4b-methyl-9b,10-dihydroindeno[2,1-a]-inden-5(4bH)-one* (*2af*)**



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow solid, Mp = 214-215 °C; 61 mg, 87% yield; $[\alpha]_D^{20}$ = -224.1 (*c* 0.5, CH_2Cl_2), 93% ee [Daicel Chiralcel OJ-H column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 90/10, 0.8 mL/min, 254 nm; t_{minor} = 21.7 min, t_{major} = 34.4 min]; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.2 Hz, 1H), 7.66-7.63 (m, 2H), 7.45 (d, *J* = 7.2 Hz, 2H), 7.43 (d, *J* = 3.6 Hz, 2H), 7.41 (t, *J* = 7.2 Hz, 1H), 7.37 (t, *J* = 7.2 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.17-7.14 (m, 2H), 6.96-6.94 (m, 1H), 2.84 (s, 1H), 1.59 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 204.9, 154.4, 145.7, 144.8, 136.9, 135.4, 135.0, 134.5, 129.9, 129.4, 128.5, 128.4, 127.8, 127.6, 125.7, 124.60, 124.56, 124.4, 123.9, 86.8, 62.9, 17.4. HRMS *m*/*z* (ESI+): Calculated for $C_{24}H_{18}NaO_2^+$ ([M+Na]$^+$) 361.1199, found 361.1197.



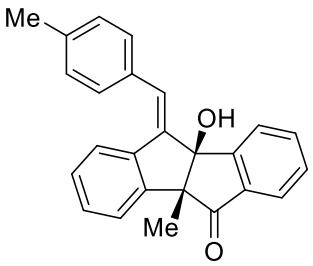




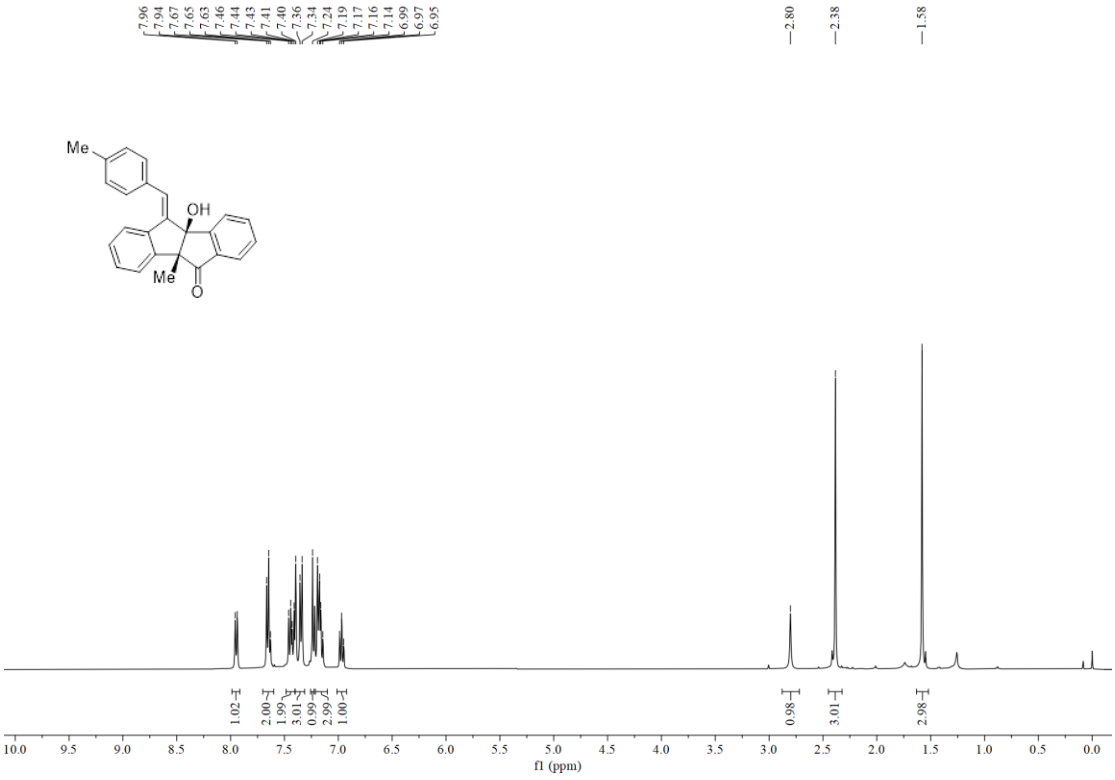
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

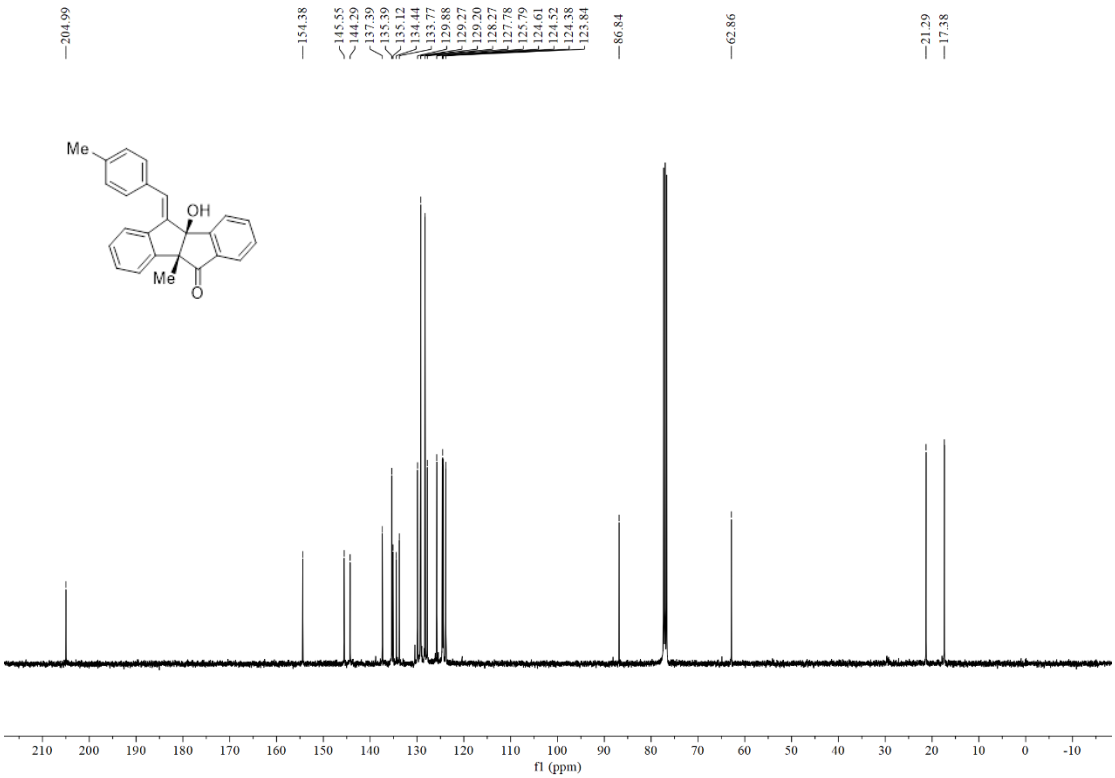
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.697	BB	0.6950	376.37433	6.42947	3.7362
2	34.401	BB	1.1584	9697.33594	123.73212	96.2638

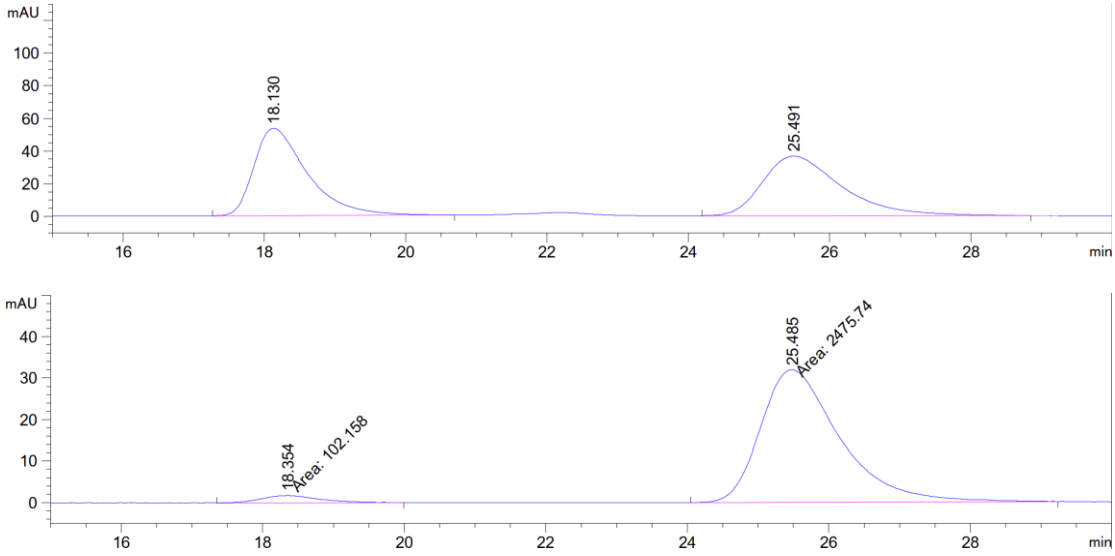
***(4bR,9bS)-9b-Hydroxy-4b-methyl-10-((E)-4-methylbenzylidene)-9b,10-dihydro-indeno[2,1-a]inden-5(4bH)-one* (*2ag*)**



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow oil; 40 mg, 57% yield; $[\alpha]_D^{20}$ = -350.1 (*c* 0.5, CH_2Cl_2), 92% ee [Daicel Chiralcel OJ-H column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 90/10, 0.7 mL/min, 280 nm; t_{minor} = 18.4 min, t_{major} = 25.5 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.0 Hz, 1H), 7.67-7.63 (m, 2H), 7.46-7.40 (m, 2H), 7.36-7.34 (m, 3H), 7.24 (s, 1H), 7.19-7.14 (m, 3H), 6.97 (t, *J* = 8.0 Hz, 1H), 2.80 (s, 1H), 2.38 (s, 3H), 1.58 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.0, 154.4, 145.6, 144.3, 137.4, 135.4, 135.1, 134.4, 133.8, 129.9, 129.3, 129.2, 128.3, 127.8, 125.8, 124.6, 124.5, 124.4, 123.8, 86.8, 62.9, 21.3, 17.4. HRMS *m*/*z* (ESI+): Calculated for $C_{25}H_{21}O_2^+$ ($[M+H]^+$) 353.1536, found 353.1530.



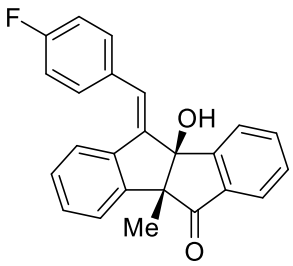




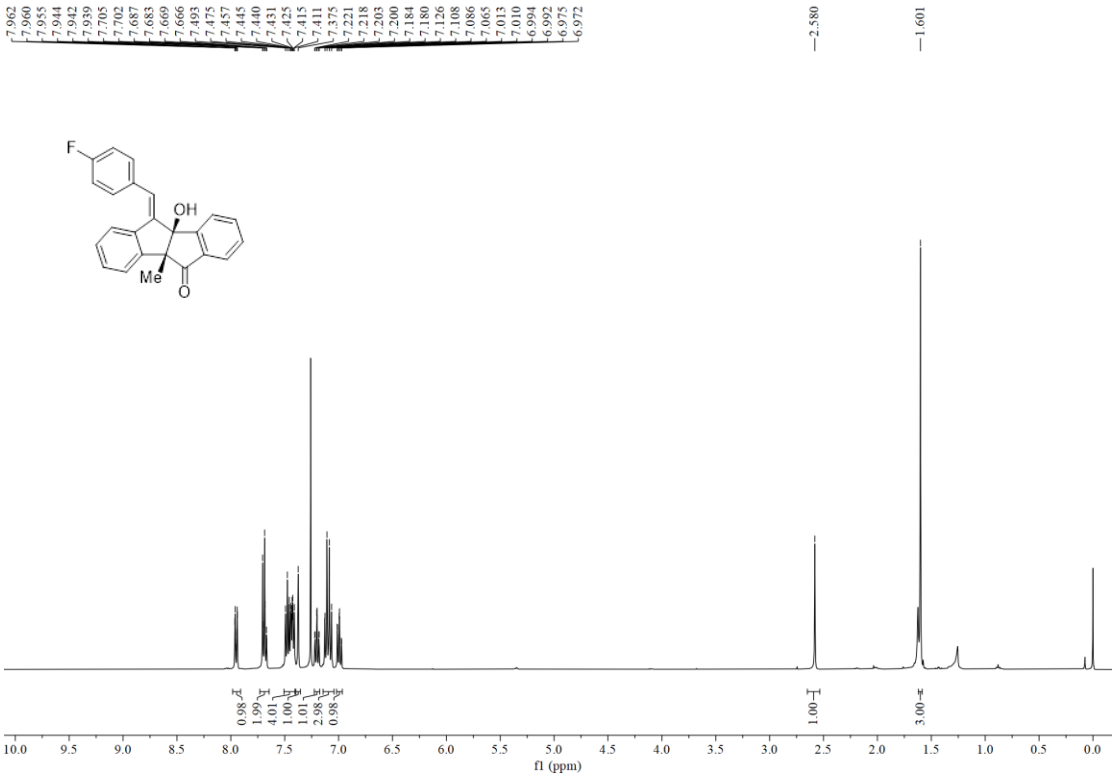
Signal 7: DAD1 G, Sig=280,4 Ref=360,100

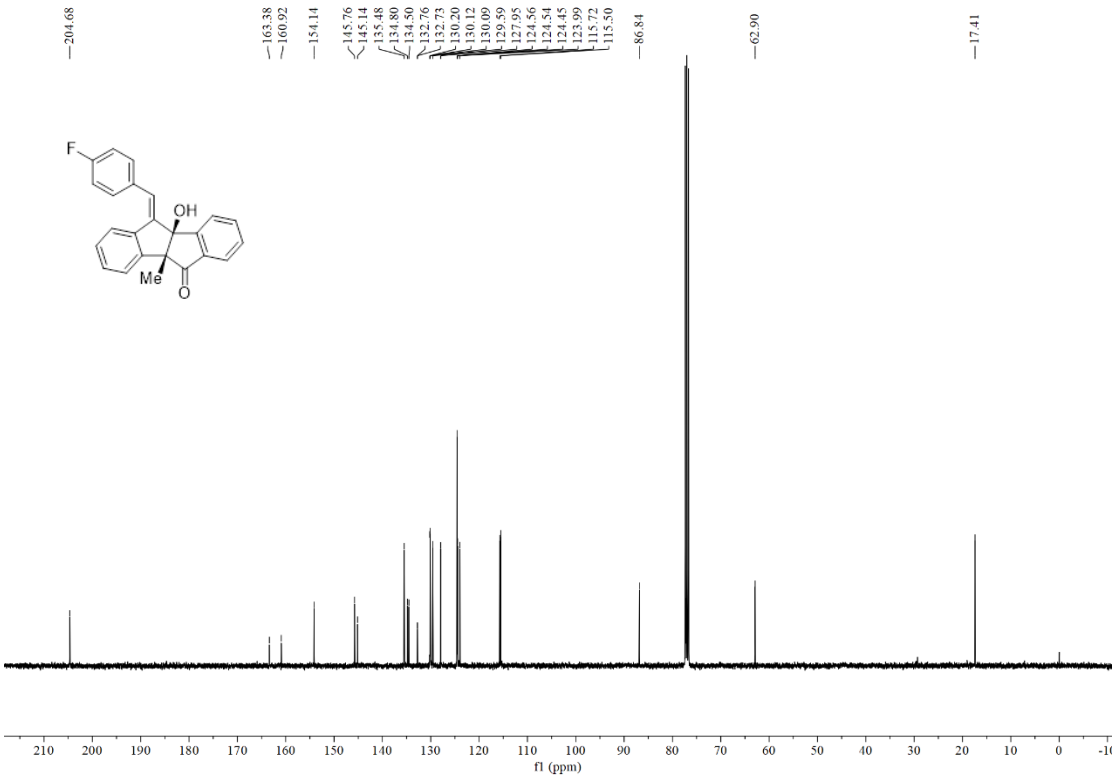
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.354	MM	0.9626	102.15778	1.76884	3.9628
2	25.485	MM	1.2907	2475.74390	31.96902	96.0372

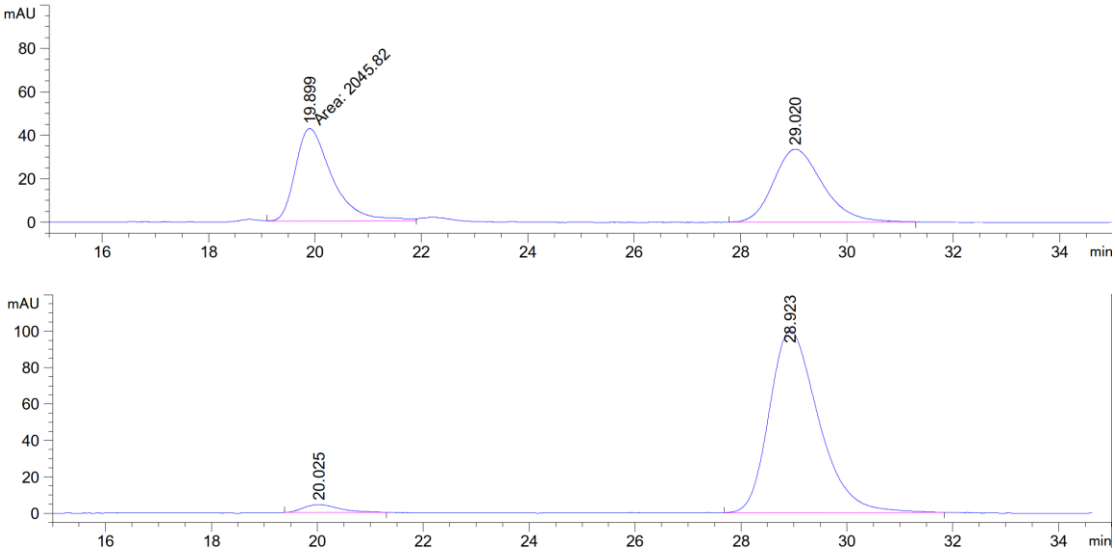
***(4bR,9bS)-10-((E)-4-Fluorobenzylidene)-9b-hydroxy-4b-methyl-9b,10-dihydro-indeno[2,1-a]inden-5(4bH)-one* (*2ah*)**



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow solid; 49 mg, 69% yield; $[\alpha]_D^{20}$ = -278.8 (*c* 0.5, CH_2Cl_2), 94% ee [Daicel Chiralcel OJ-H column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 90/10, 0.7 mL/min, 254 nm; t_{minor} = 20.0 min, t_{major} = 28.9 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96-7.94 (m, 1H), 7.71-7.67 (m, 2H), 7.49-7.41 (m, 4H), 7.38 (s, 1H), 7.22-7.18 (m, 1H), 7.13-7.07 (m, 3H), 7.01-6.97 (m, 1H), 2.58 (s, 1H), 1.60 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.7, 162.2 (d, J = 246.0 Hz), 154.1, 145.8, 145.1, 135.5, 134.8, 134.5, 132.8 (d, J = 3.0 Hz), 130.2 (d, J = 8.0 Hz), 130.1, 129.6, 128.0, 124.6, 124.54, 124.45, 124.0, 115.6 (d, J = 22.0 Hz), 86.8, 62.9, 17.4. HRMS *m*/*z* (ESI+): Calculated for $C_{20}H_{18}FO_2^+$ ([M+H]$^+$) 357.1285, found 357.1279.



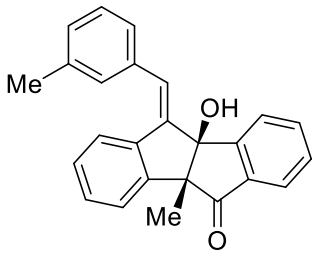




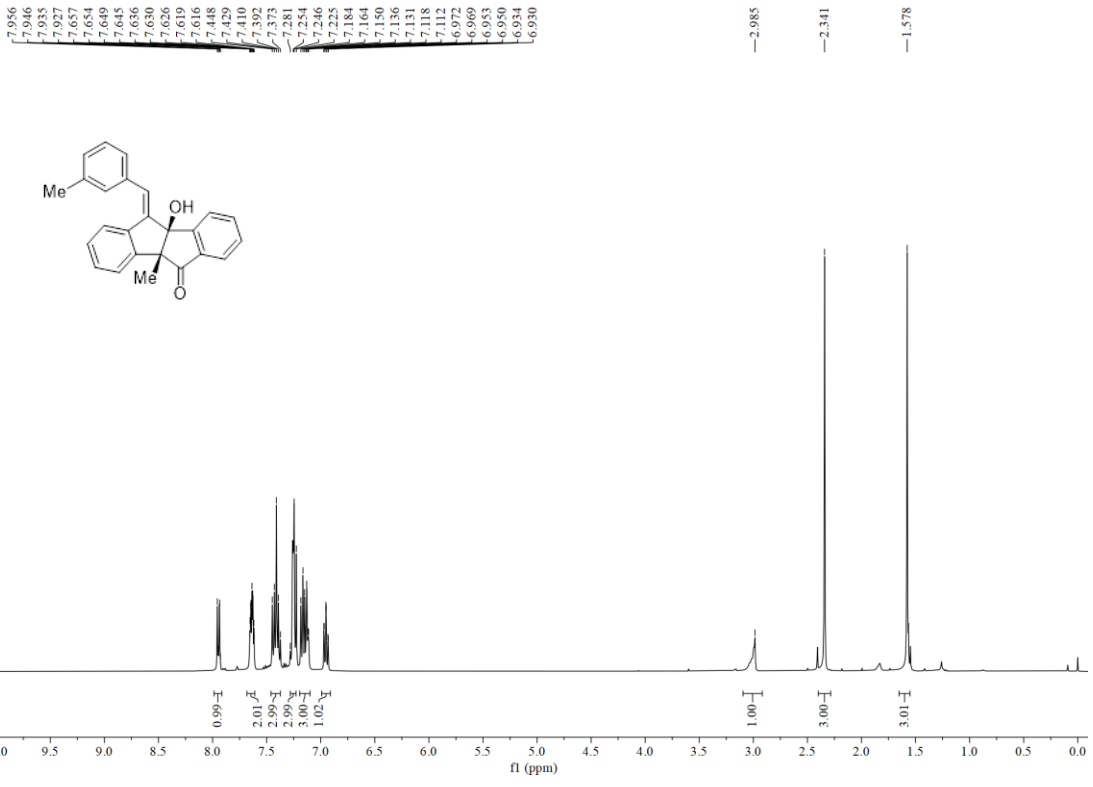
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

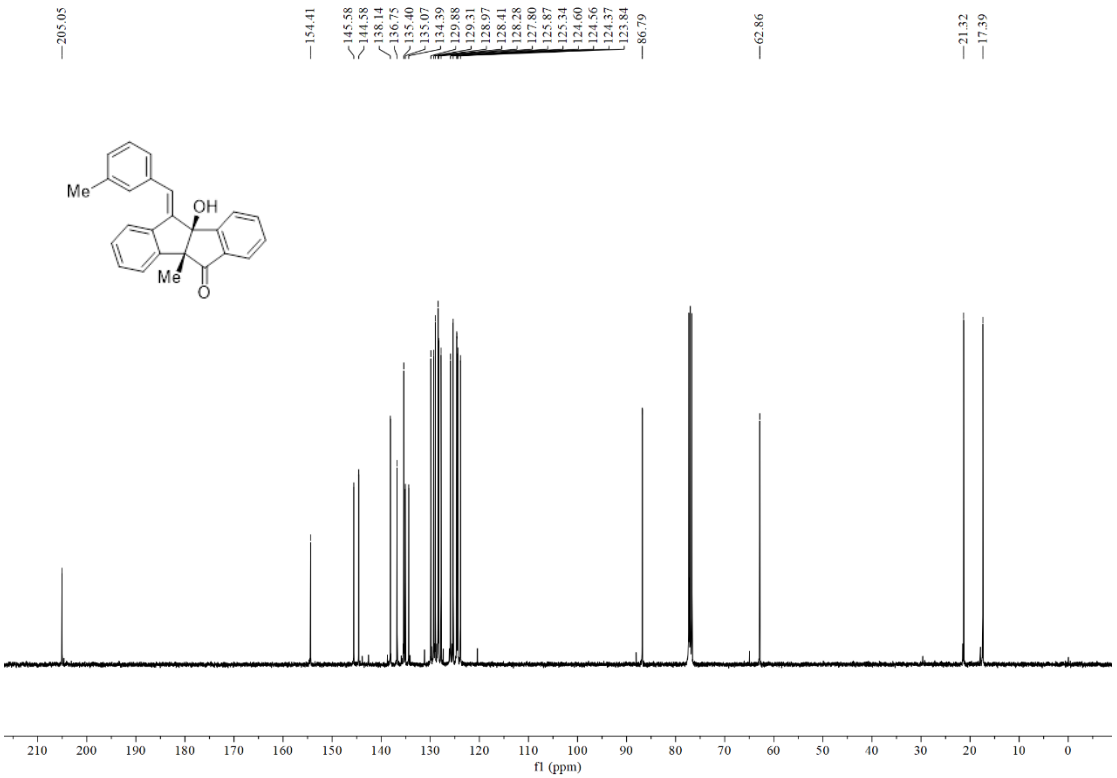
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.025	BB	0.5550	199.48627	4.25457	2.9998
2	28.923	BB	0.9079	6450.52539	100.08354	97.0002

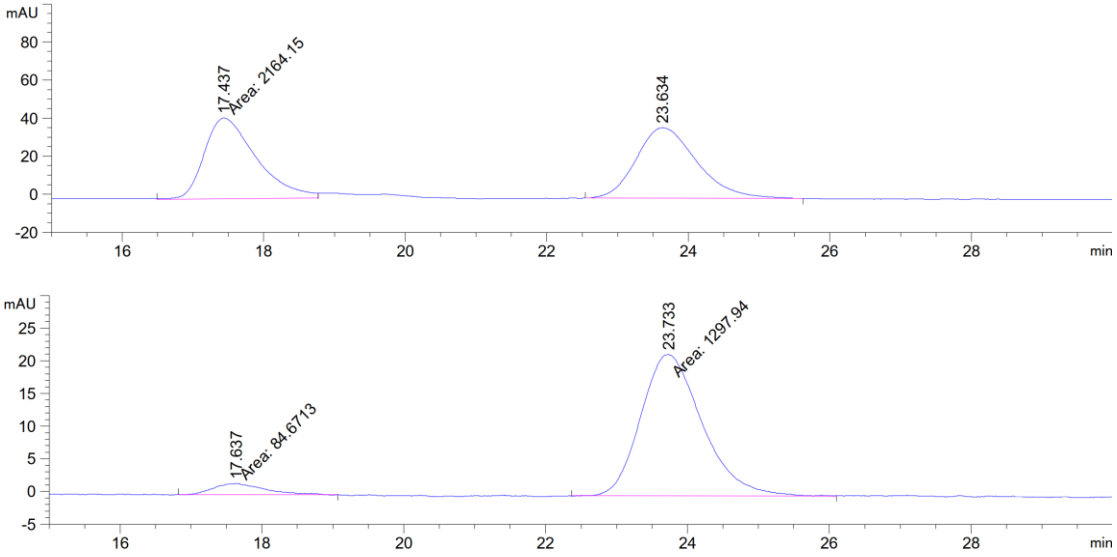
***(4bR,9bS)-9b-Hydroxy-4b-methyl-10-((E)-3-methylbenzylidene)-9b,10-dihydro-indeno[2,1-a]inden-5(4bH)-one* (*2ai*)**



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow oil; 56 mg, 80% yield; $[\alpha]_D^{20}$ = -278.8 (*c* 0.5, CH_2Cl_2), 88% ee [Daicel Chiralcel OJ-H column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 90/10, 0.7 mL/min, 254 nm; t_{minor} = 17.6 min, t_{major} = 23.7 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96-7.93 (m, 1H), 7.66-7.62 (m, 2H), 7.45-7.37 (m, 3H), 7.28-7.23 (m, 3H), 7.18-7.11 (m, 3H), 6.97-6.93 (m, 1H), 2.99 (s, 1H), 2.34 (s, 3H), 1.58 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.1, 154.4, 145.6, 144.6, 138.1, 136.8, 135.4, 135.1, 134.4, 129.9, 129.3, 129.0, 128.4, 128.3, 127.8, 125.9, 125.3, 124.60, 124.56, 124.4, 123.8, 86.8, 62.9, 21.3, 17.4. HRMS *m*/*z* (ESI+): Calculated for $C_{25}H_{21}O_2^+$ ($[M+H]^+$) 353.1536, found 353.1532.



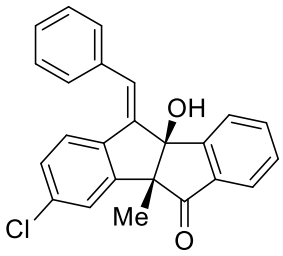




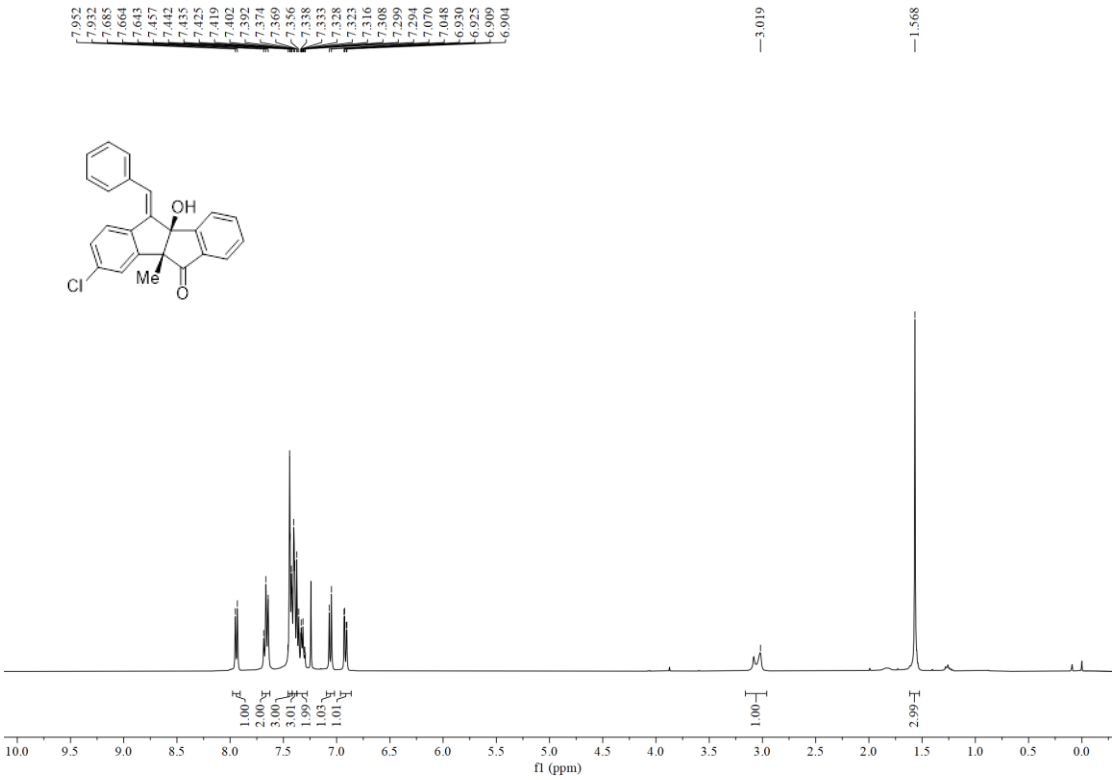
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

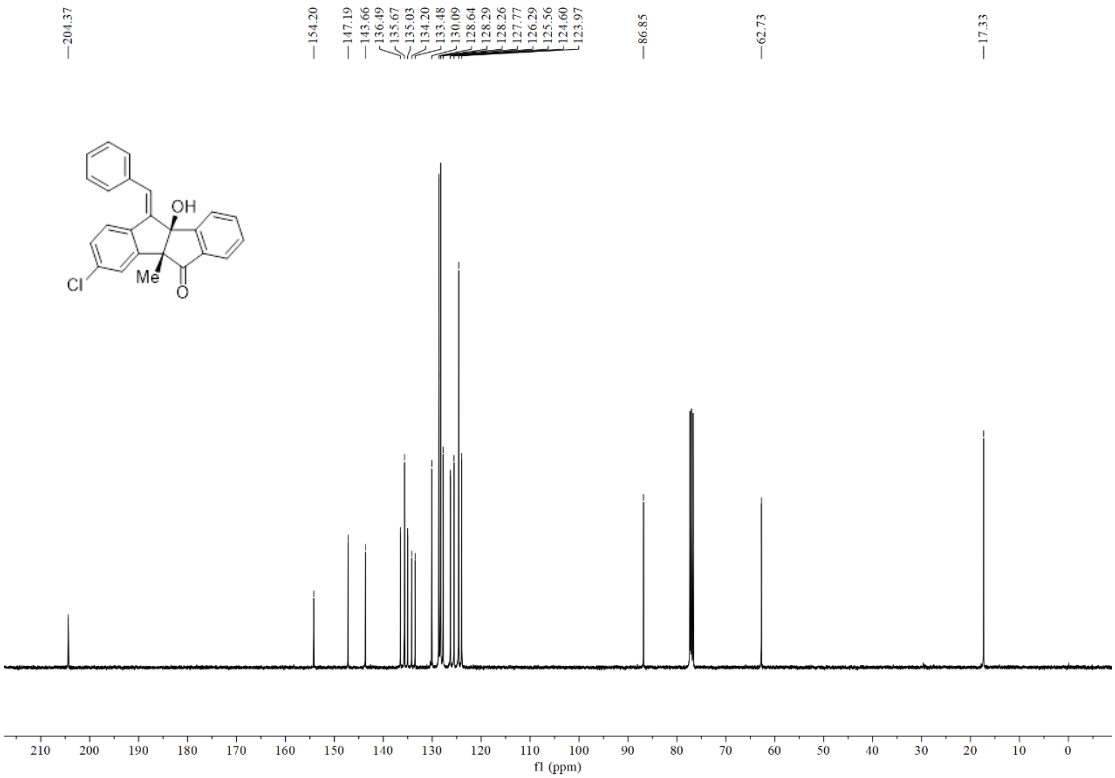
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.637	MM	0.8264	84.67126	1.70773	6.1240
2	23.733	MM	1.0010	1297.94067	21.61181	93.8760

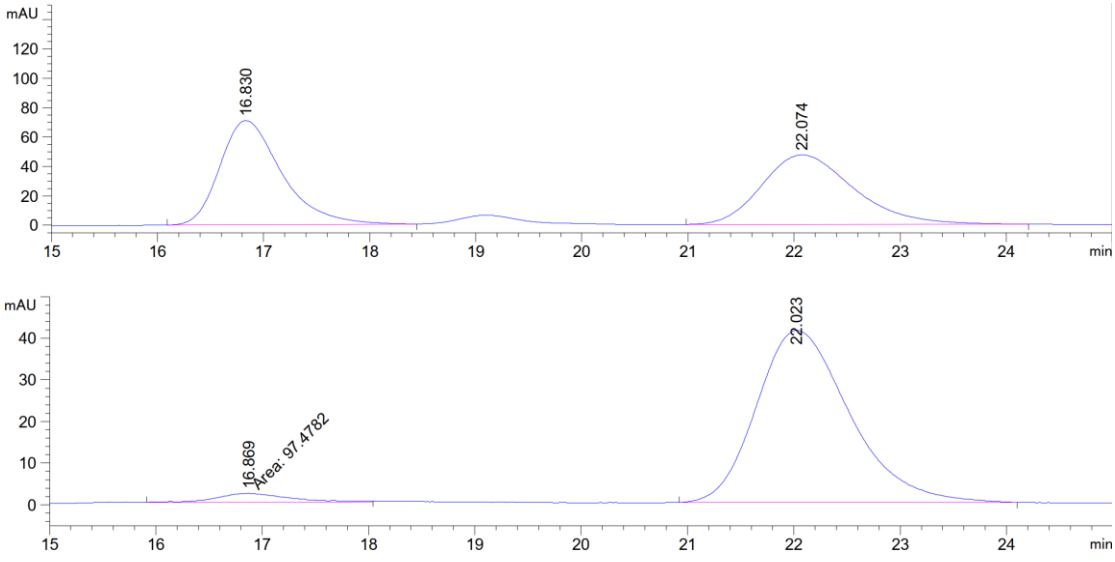
***(4bR,9bS)-10-((E)-Benzylidene)-3-chloro-9b-hydroxy-4b-methyl-9b,10-dihydro-indeno[2,1-a]inden-5(4bH)-one* (*2aj*)**



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow oil; 65 mg, 88% yield; $[\alpha]_D^{20}$ = -199.7 (*c* 0.5, CH_2Cl_2), 93% ee [Daicel Chiralcel OJ-H column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 90/10, 0.7 mL/min, 254 nm; t_{minor} = 16.9 min, t_{major} = 22.0 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.4 Hz, 1H), 7.66 (t, *J* = 8.0 Hz, 2H), 7.46-7.42 (m, 3H), 7.40-7.37 (m, 3H), 7.36-7.29 (m, 2H), 7.06 (d, *J* = 8.8 Hz, 1H), 6.93-6.90 (m, 1H), 3.02 (s, 1H), 1.57 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.4, 154.2, 147.2, 143.7, 136.5, 135.7, 135.0, 134.2, 133.5, 130.1, 128.6, 128.29, 128.26, 127.8, 126.3, 125.6, 124.6, 124.0, 86.8, 62.7, 17.3. HRMS *m*/*z* (ESI+): Calculated for $C_{24}H_{18}ClO_2^+$ ($[M+H]^+$) 373.0990, found 373.0984.



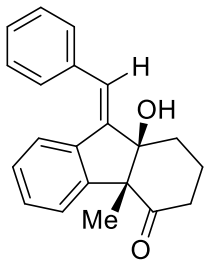




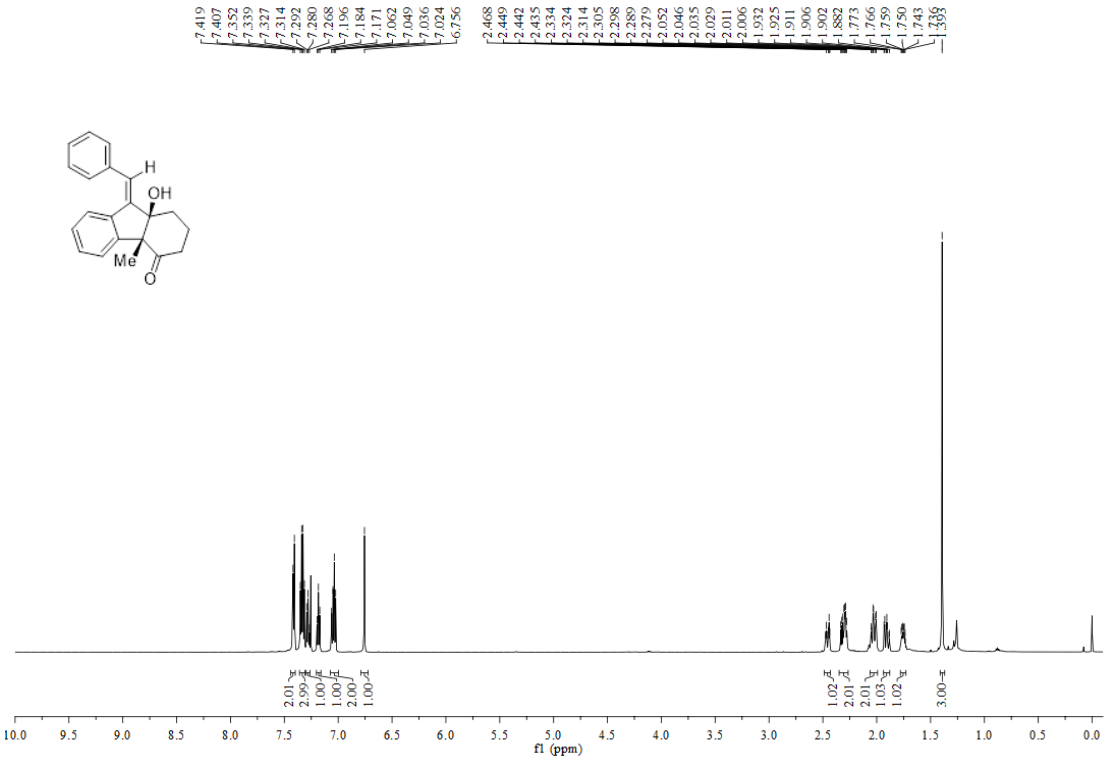
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

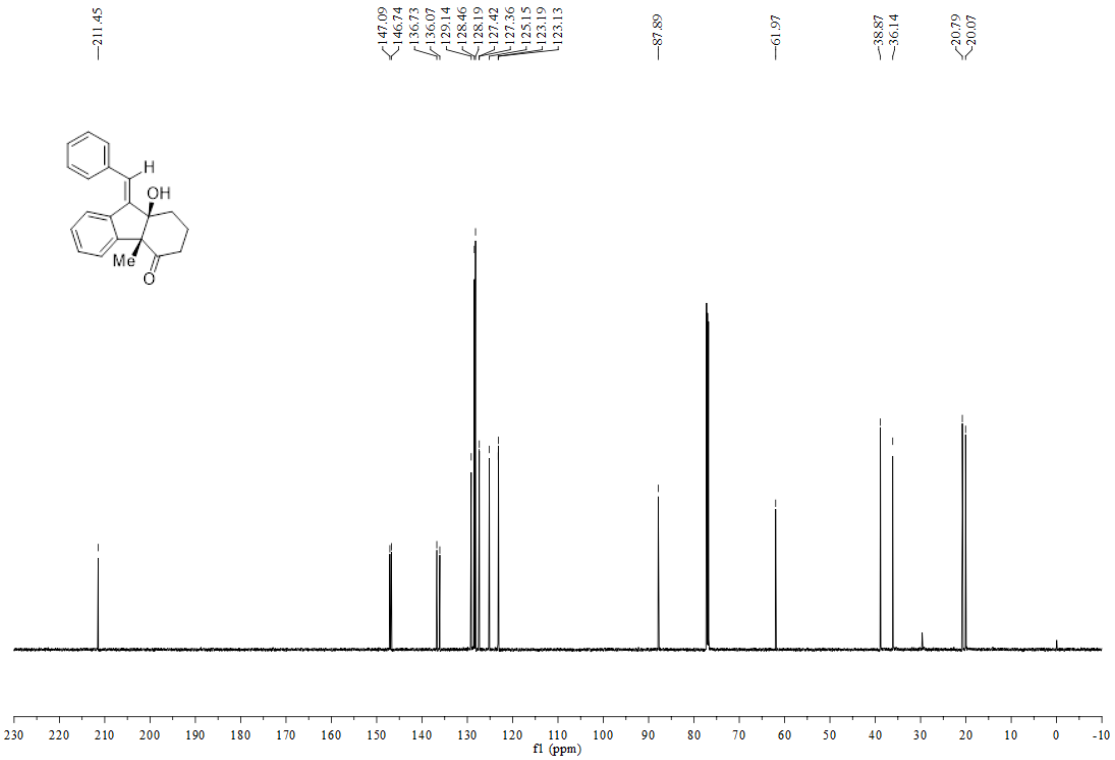
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.869	MM	0.7713	97.47817	2.10644	3.7326
2	22.023	BB	0.7518	2514.07251	41.31985	96.2674

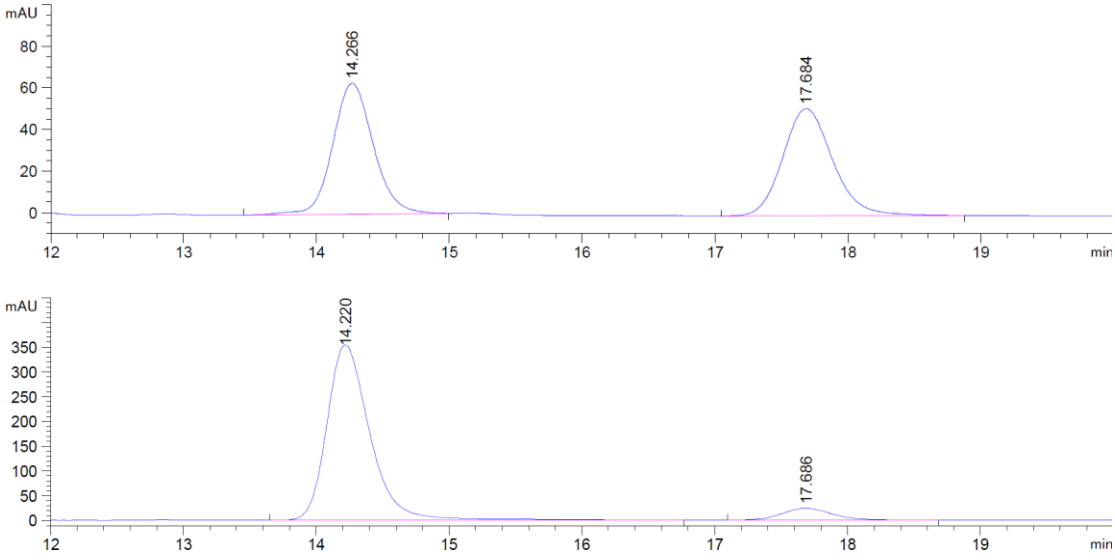
***(4aR,9aR)-9-((E)-Benzylidene)-9a-hydroxy-4a-methyl-1,2,3,4a,9,9a-hexahydro-4H-fluoren-4-one* (*2ak*)**



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); white solid, Mp = 148-149 °C; 43 mg, 71% yield; $[\alpha]_D^{20}$ = -149.8 (*c* 1.0, CH_2Cl_2), 86% ee [Phenomenex Lux 5u Cellulose-2 column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 90/10, 0.7 mL/min, 254 nm; t_{major} = 14.2 min, t_{minor} = 17.7 min]; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (d, J = 7.2 Hz, 2H), 7.33 (dd, J = 15.0, 7.5 Hz, 3H), 7.28 (t, J = 7.2 Hz, 1H), 7.18 (t, J = 7.8 Hz, 1H), 7.04 (dd, J = 15.6, 7.8 Hz, 2H), 6.76 (s, 1H), 2.47-2.44 (m, 1H), 2.33-2.28 (m, 2H), 2.05-2.01 (m, 2H), 1.93-1.88 (m, 1H), 1.77-1.74 (m, 1H), 1.39 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 211.5, 147.1, 146.7, 136.7, 136.1, 129.1, 128.5, 128.2, 127.42, 127.36, 125.2, 123.2, 123.1, 87.9, 62.0, 38.9, 36.1, 20.8, 20.1. HRMS m/z (ESI+): Calculated for $C_{21}H_{20}O_2Na^+$ ([M+Na]$^+$) 327.1356, found 327.1355.



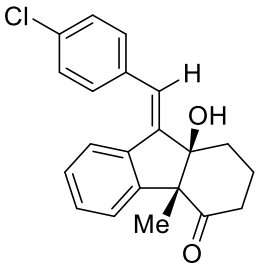




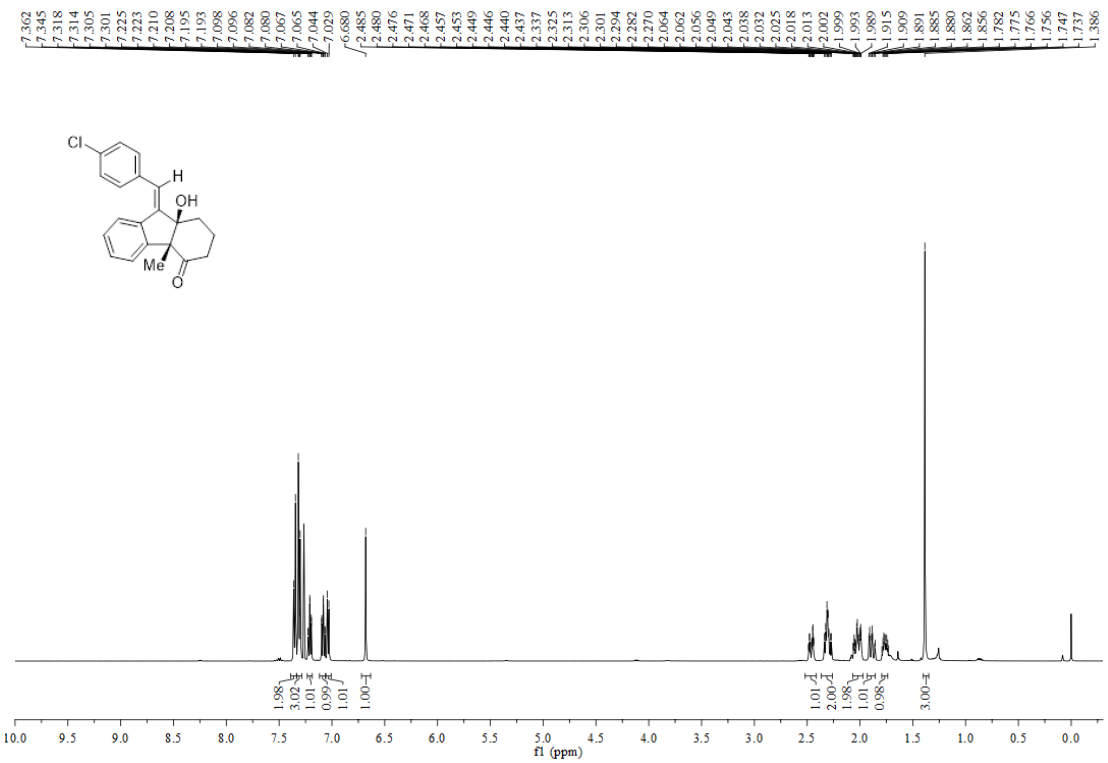
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

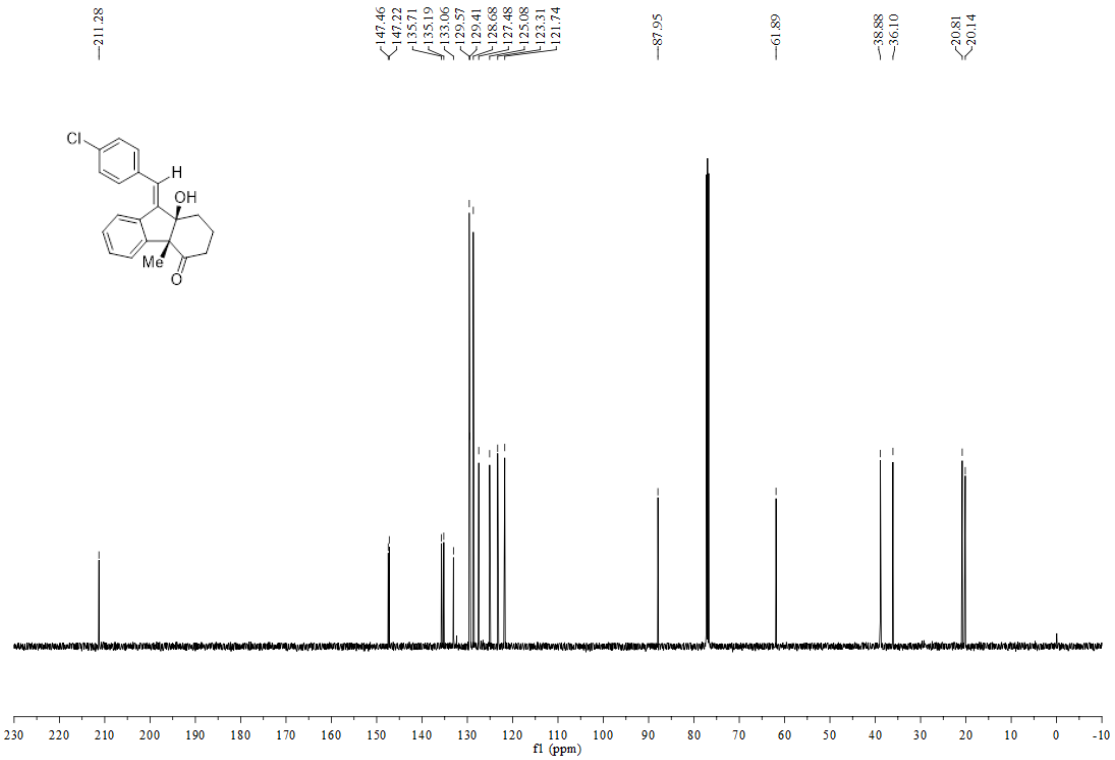
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.220	BB	0.3438	7940.74512	353.79892	92.8290
2	17.686	BB	0.3994	613.41754	23.59037	7.1710

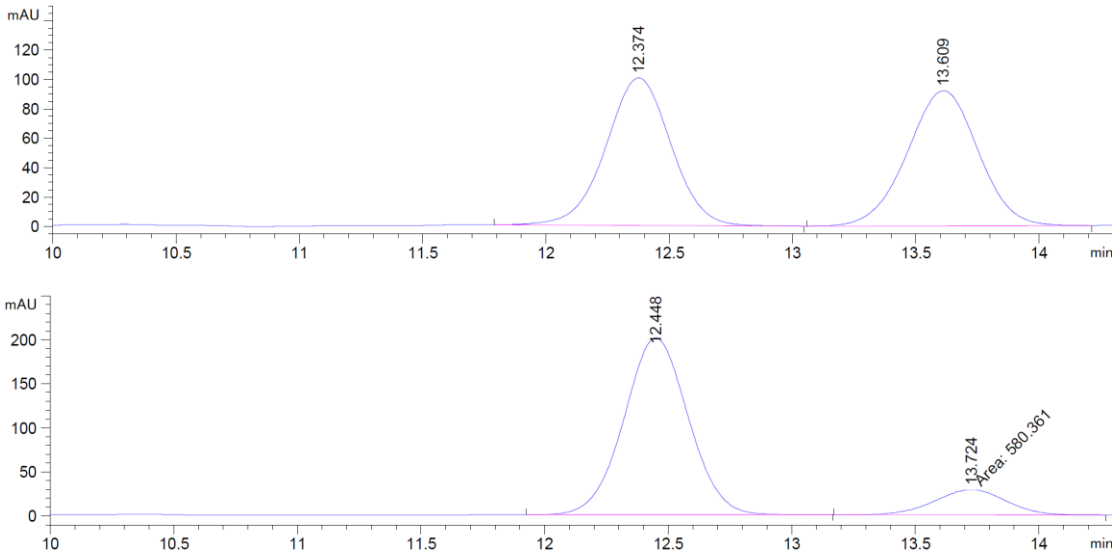
***(4aR,9aR)-9-((E)-4-Chlorobenzylidene)-9a-hydroxy-4a-methyl-1,2,3,4a,9,9a-hexahydro-4H-fluoren-4-one* (*2al*)**



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); white solid, Mp = 98-99 °C; 43 mg, 64% yield; $[\alpha]_D^{20}$ = -242.1 (*c* 0.5, CH_2Cl_2), 73% ee [Phenomenex Lux 5u Cellulose-1 column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 90/10, 0.7 mL/min, 254 nm; t_{major} = 12.4 min, t_{minor} = 13.7 min]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, J = 8.5 Hz, 2H), 7.32-7.30 (m, 3H), 7.23-7.19 (m, 1H), 7.10-7.07 (m, 1H), 7.04 (d, J = 7.5 Hz, 1H), 6.68 (s, 1H), 2.49-2.44 (m, 1H), 2.34-2.27 (m, 2H), 2.06-1.99 (m, 2H), 1.92-1.86 (m, 1H), 1.78-1.74 (m, 1H), 1.39 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.3, 147.5, 147.2, 135.7, 135.2, 133.1, 129.6, 129.4, 128.7, 127.5, 125.1, 123.3, 121.7, 88.0, 61.9, 38.9, 36.1, 20.8, 20.1. HRMS *m*/*z* (ESI+): Calculated for for $C_{21}H_{19}ClO_2Na^+$ ([M+Na]$^+$) 361.0966, found 361.0963.



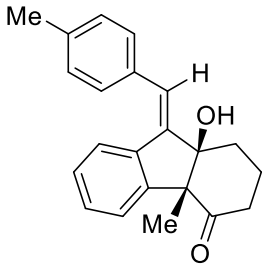




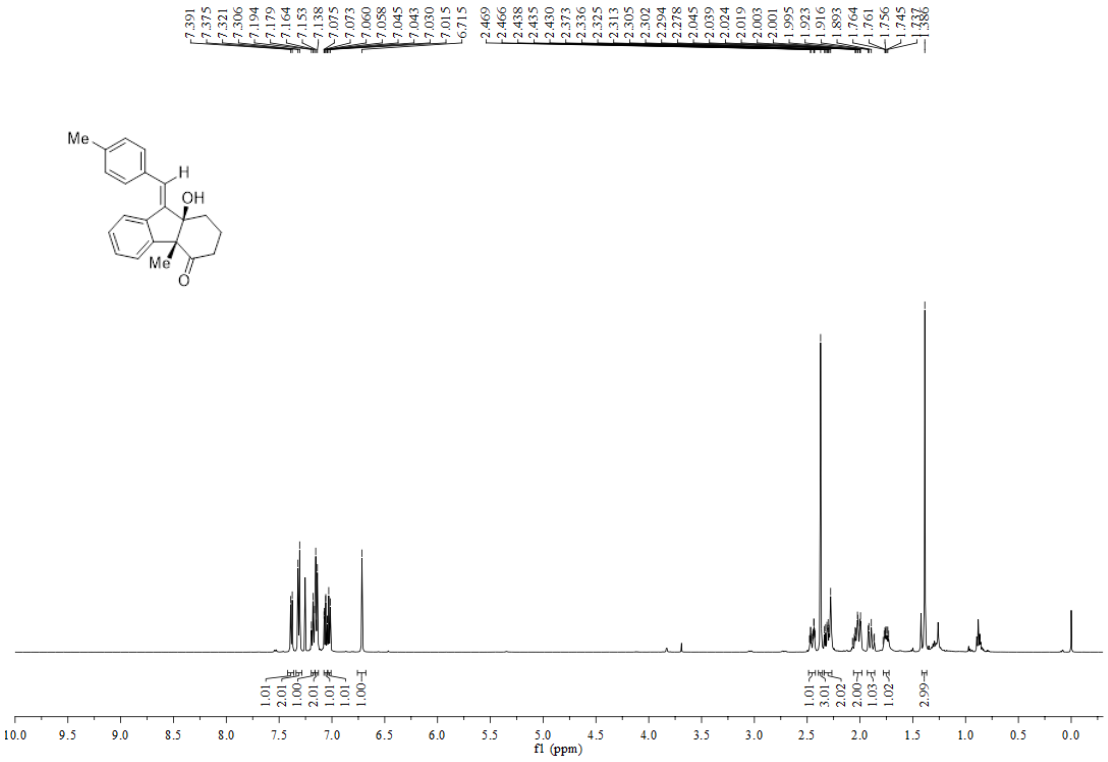
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

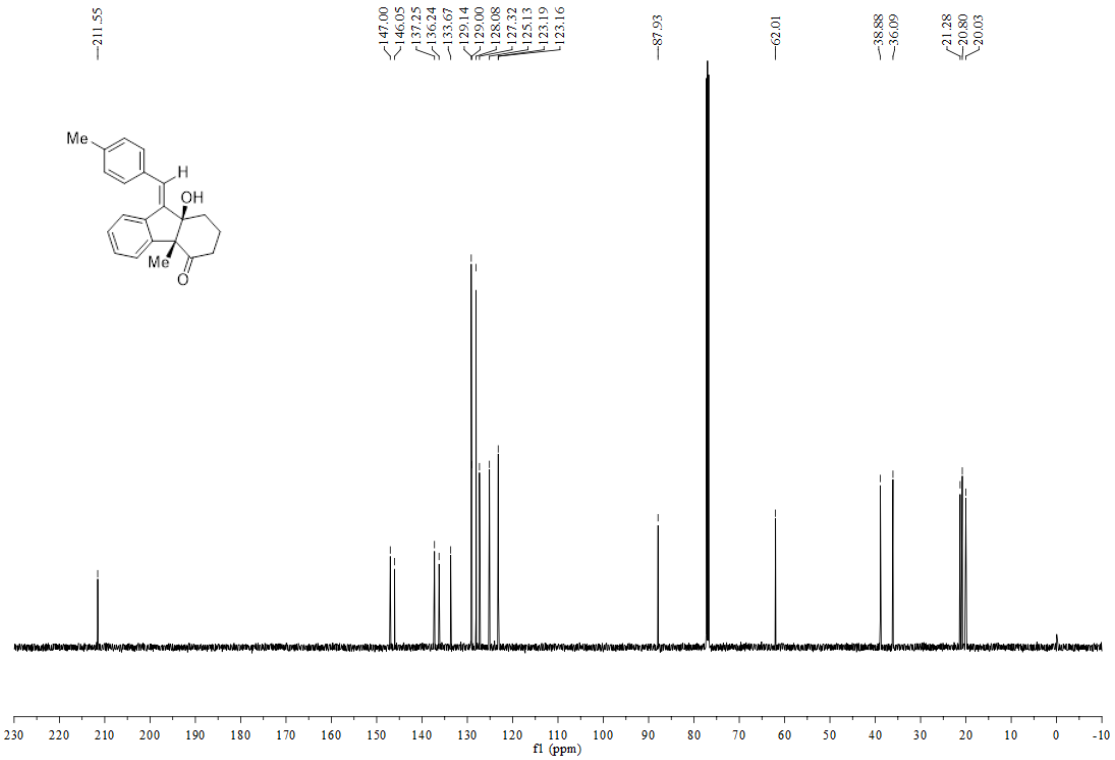
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.448	BB	0.2798	3648.80273	200.98268	86.2772
2	13.724	MM	0.3362	580.36121	28.77378	13.7228

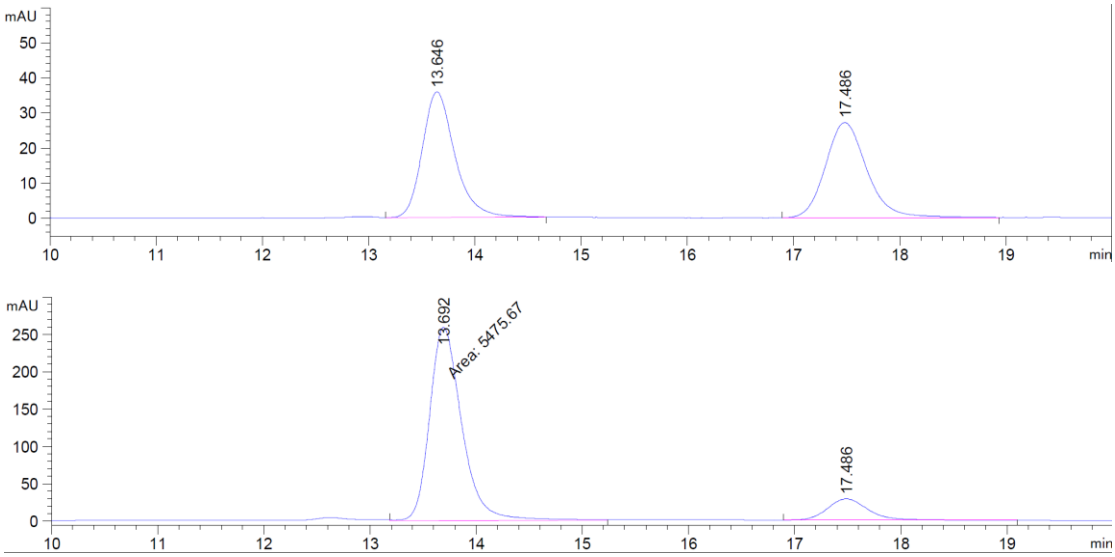
***(4aR,9aR)-9a-Hydroxy-4a-methyl-9-((E)-4-methylbenzylidene)-1,2,3,4a,9,9a-hexahydro-4H-fluoren-4-one* (*2am*)**



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); white solid, Mp = 81-82 °C; 43 mg, 68% yield; $[\alpha]_D^{20}$ = -91.0 (*c* 0.5, CH_2Cl_2), 76% ee [Phenomenex Lux 5u Cellulose-2 column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 90/10, 0.7 mL/min, 254 nm; t_{major} = 13.7 min, t_{minor} = 17.5 min]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 7.5 Hz, 2H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.15 (d, *J* = 7.5 Hz, 2H), 7.08-7.04 (m, 1H), 7.02 (d, *J* = 7.5 Hz, 1H), 6.72 (s, 1H), 2.47-2.43 (m, 1H), 2.37 (s, 3H), 2.34-2.28 (m, 2H), 2.05-2.00 (m, 2H), 1.92-1.89 (m, 1H), 1.76-1.74 (m, 1H), 1.39 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.6, 147.0, 146.1, 137.3, 136.2, 133.7, 129.1, 129.0, 128.1, 127.3, 125.1, 123.19, 123.16, 87.9, 62.0, 38.9, 36.1, 21.3, 20.8, 20.0. HRMS *m*/*z* (ESI+): Calculated for $C_{22}H_{22}O_2Na^+$ ([M+Na]+) 341.1512, found 341.1515.



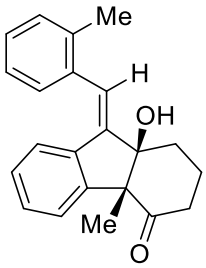




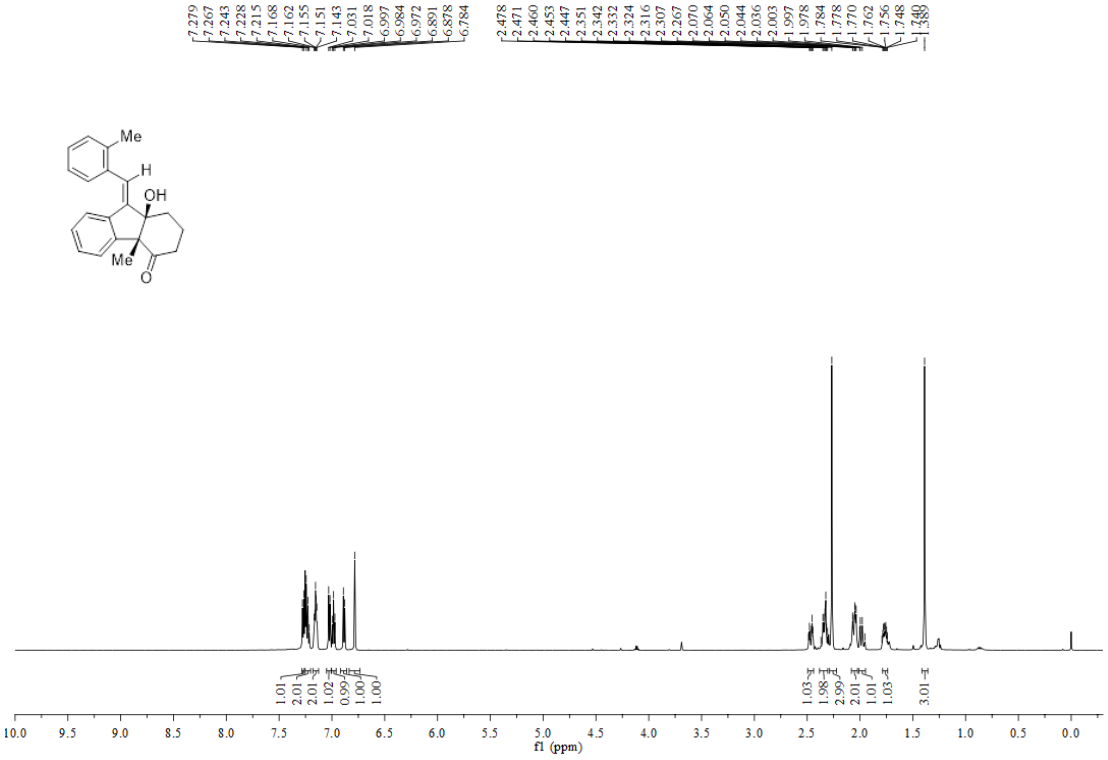
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

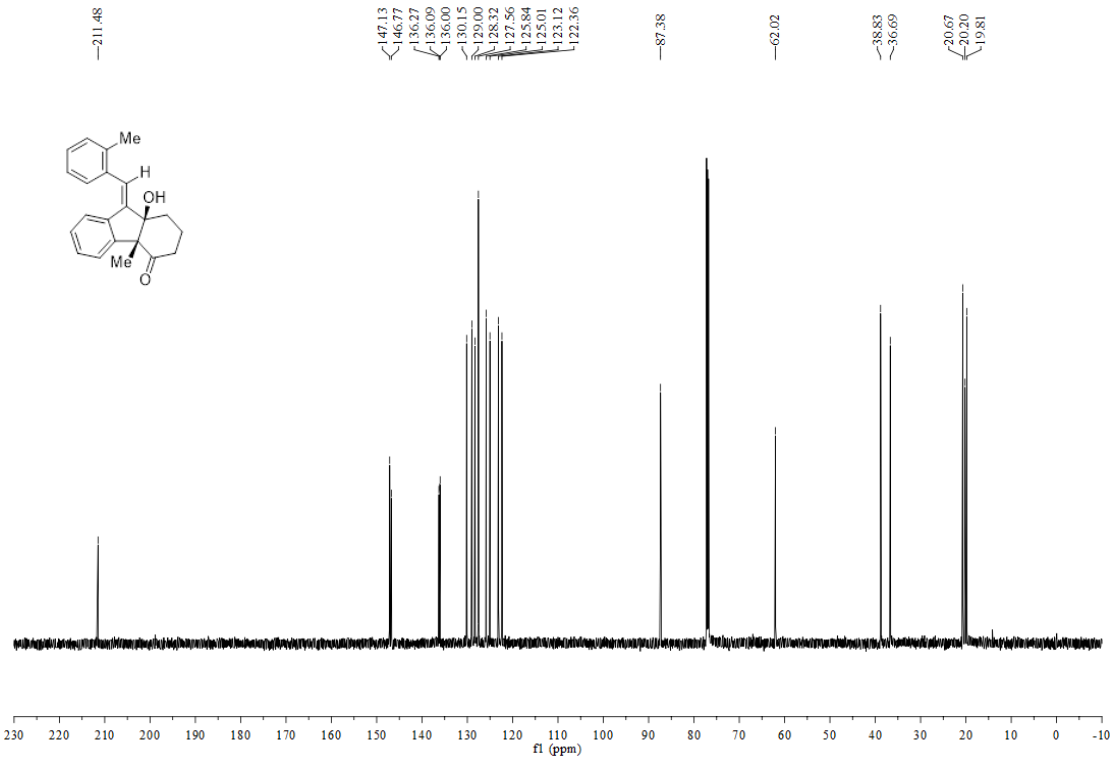
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.692	MM	0.3525	5475.66504	258.86172	87.7750
2	17.486	BB	0.4090	762.63354	28.42876	12.2250

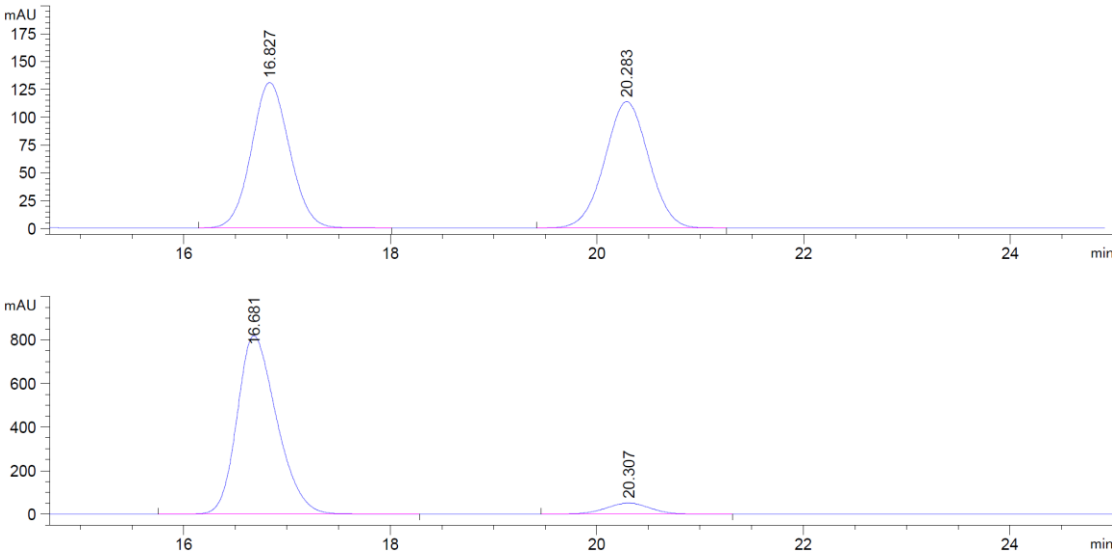
***(4aR,9aR)-9a-Hydroxy-4a-methyl-9-((E)-2-methylbenzylidene)-1,2,3,4a,9,9a-hexahydro-4H-fluoren-4-one* (*2an*)**



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow oil; 36 mg, 57% yield; $[\alpha]_D^{20}$ = -174.0 (*c* 0.5, CH_2Cl_2), 87% ee [Phenomenex Lux 5u Cellulose-1 column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 90/10, 0.7 mL/min, 254 nm; t_{major} = 16.7 min, t_{minor} = 20.3 min]; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 (d, *J* = 7.2 Hz, 1H), 7.24-7.22 (m, 2H), 7.17-7.14 (m, 2H), 7.02 (d, *J* = 7.8 Hz, 1H), 6.98 (t, *J* = 7.2 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 6.78 (s, 1H), 2.48-2.45 (m, 1H), 2.35-2.32 (m, 2H), 2.27 (s, 3H), 2.07-2.04 (m, 2H), 2.00-1.98 (m, 1H), 1.78-1.74 (m, 1H), 1.39 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 211.5, 147.1, 146.8, 136.3, 136.1, 136.0, 130.2, 129.0, 128.3, 127.6, 125.8, 125.0, 123.1, 122.4, 87.4, 62.0, 38.8, 36.7, 20.7, 20.2, 19.8. HRMS *m*/*z* (ESI+): Calculated for $C_{22}H_{22}O_2Na^+$ ([M+Na]$^+$) 341.1512, found 341.1514.



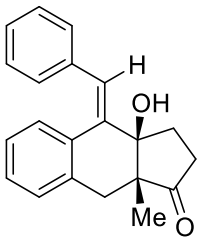




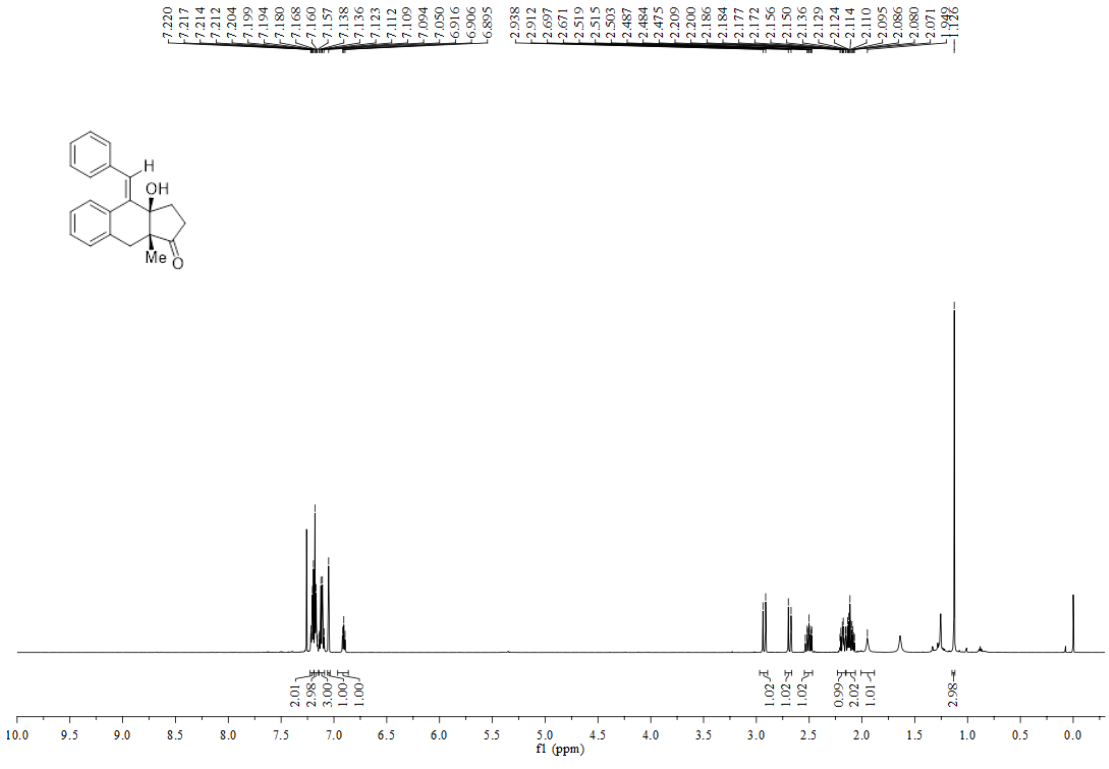
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

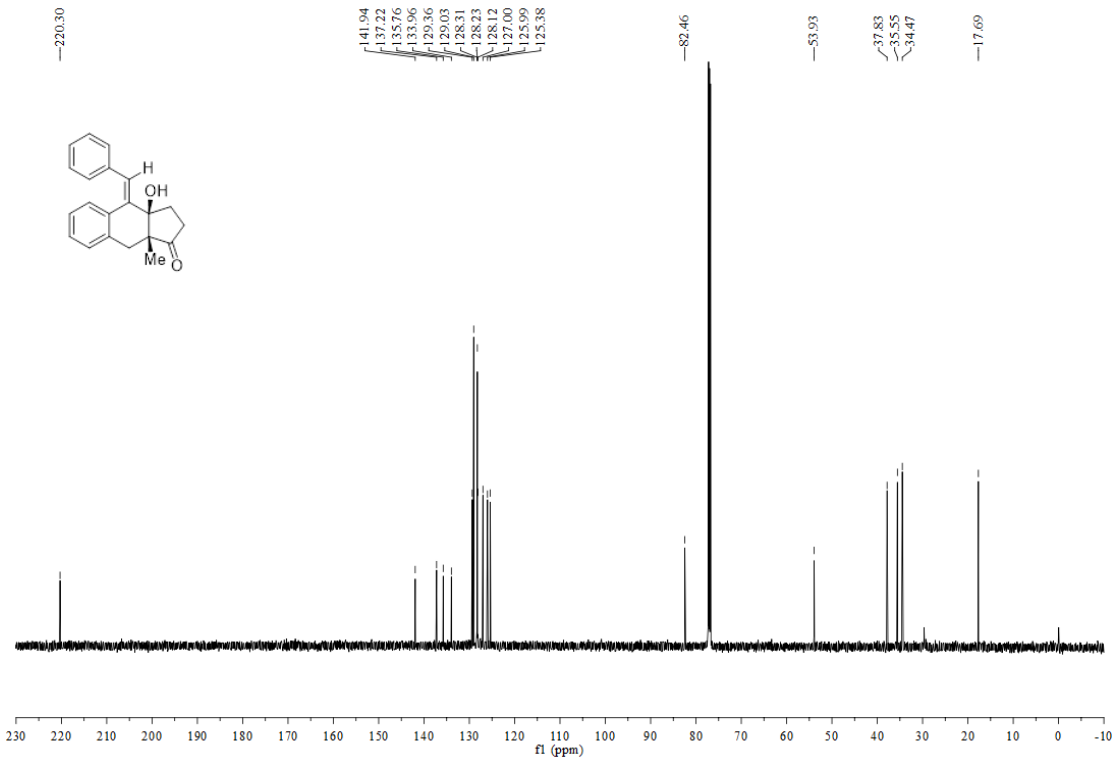
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.681	BB	0.4046	2.17954e4	818.73413	93.5451
2	20.307	BB	0.4604	1503.95581	50.65180	6.4549

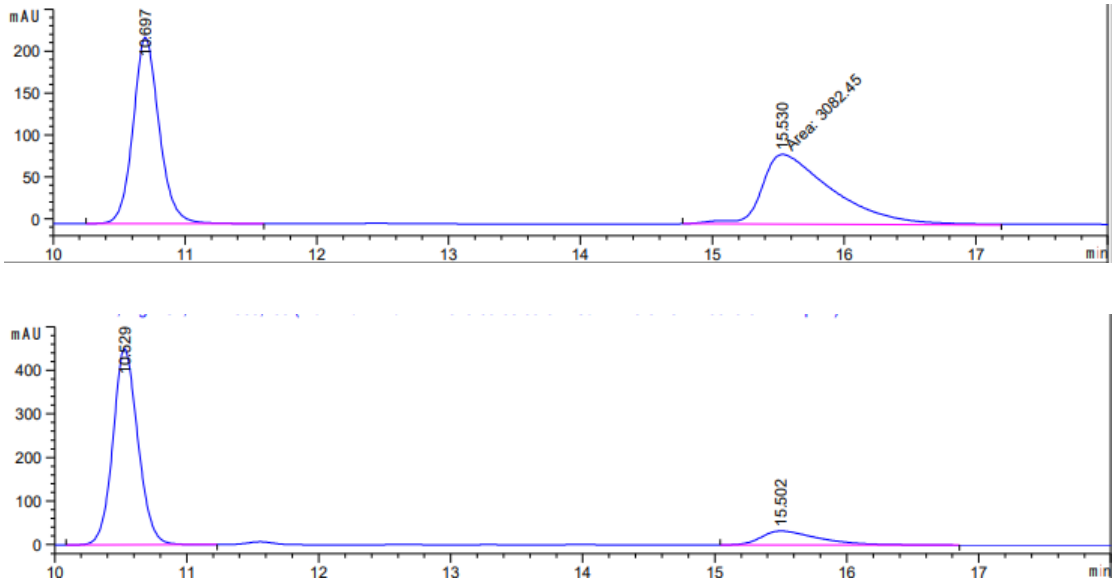
***(3aR,9aR)-4-((E)-Benzylidene)-3a-hydroxy-9a-methyl-2,3,3a,4,9,9a-hexahydro-1H-cyclopenta[b]naphthalen-1-one* (*2ao*)**



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow oil; 14 mg, 23% yield; $[\alpha]_D^{20}$ = -182.5 (*c* 0.5, CH_2Cl_2), 73% ee [Phenomenex Lux 5u Amylose-2 column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 90/10, 0.7 mL/min, 254 nm; t_{minor} = 10.5 min, t_{major} = 15.5 min]; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22-7.19 (m, 2H), 7.18-7.16 (m, 3H), 7.14-7.09 (m, 3H), 7.05 (s, 1H), 6.91 (t, *J* = 6.0 Hz, 1H), 2.92 (d, *J* = 15.6 Hz, 1H), 2.68 (d, *J* = 15.6 Hz, 1H), 2.52-2.48 (m, 1H), 2.21-2.16 (m, 1H), 2.15-2.07 (m, 2H), 1.95 (s, 1H), 1.13 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 220.3, 141.9, 137.2, 135.8, 134.0, 129.4, 129.0, 128.3, 128.2, 128.1, 127.0, 126.0, 125.4, 82.5, 53.9, 37.8, 35.6, 34.5, 17.7. HRMS *m*/*z* (ESI+): Calculated for $C_{21}H_{21}O_2^+$ ([M+H]$^+$) 305.1536, found 305.1533.



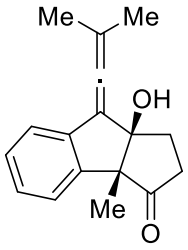




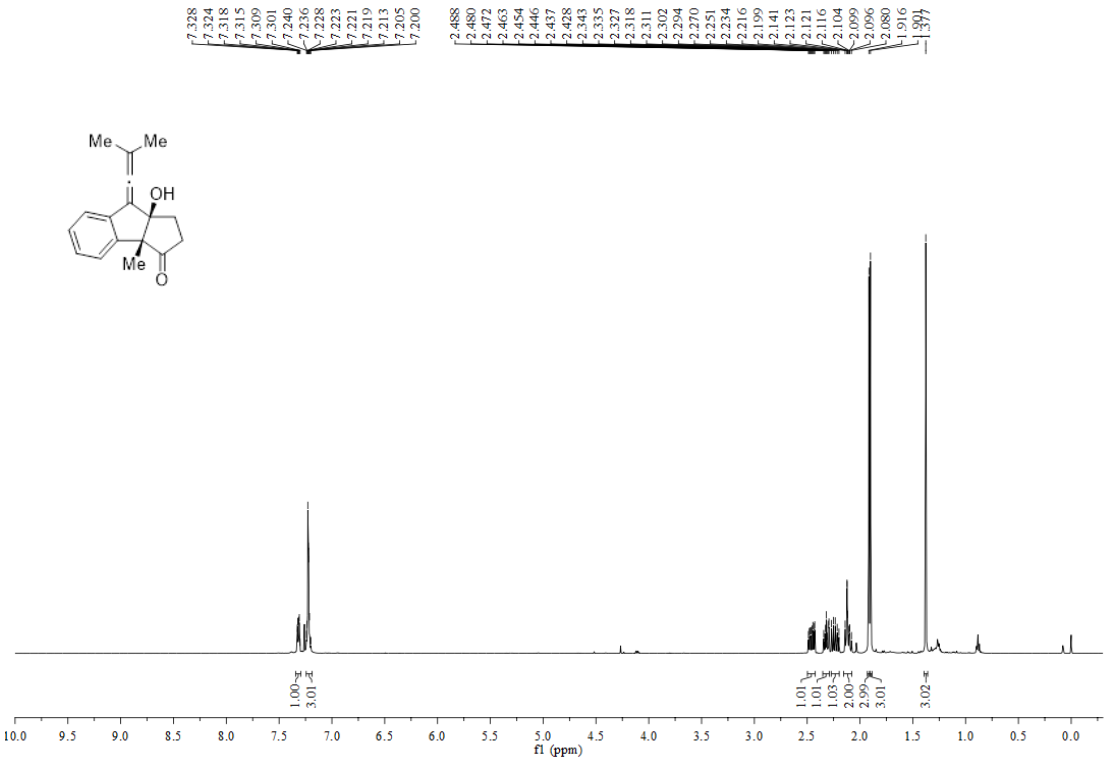
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

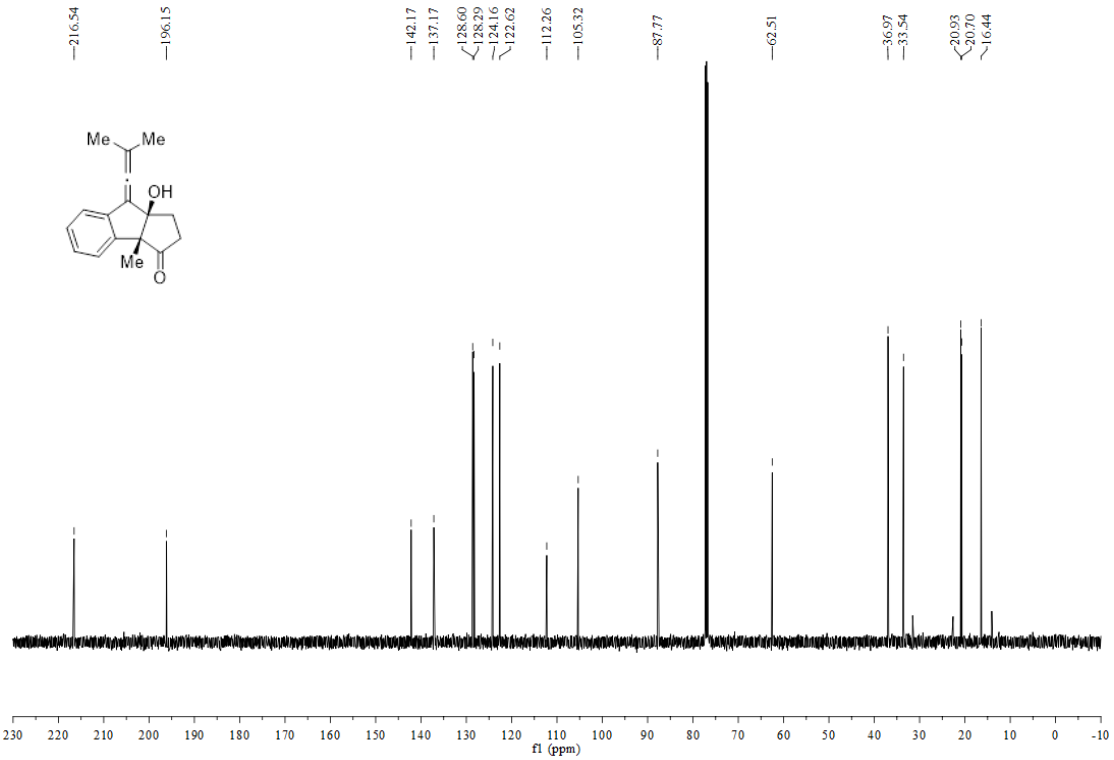
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.529	BB	0.1999	5930.41650	449.69058	86.2230
2	15.502	BB	0.4361	947.57837	31.76168	13.7770

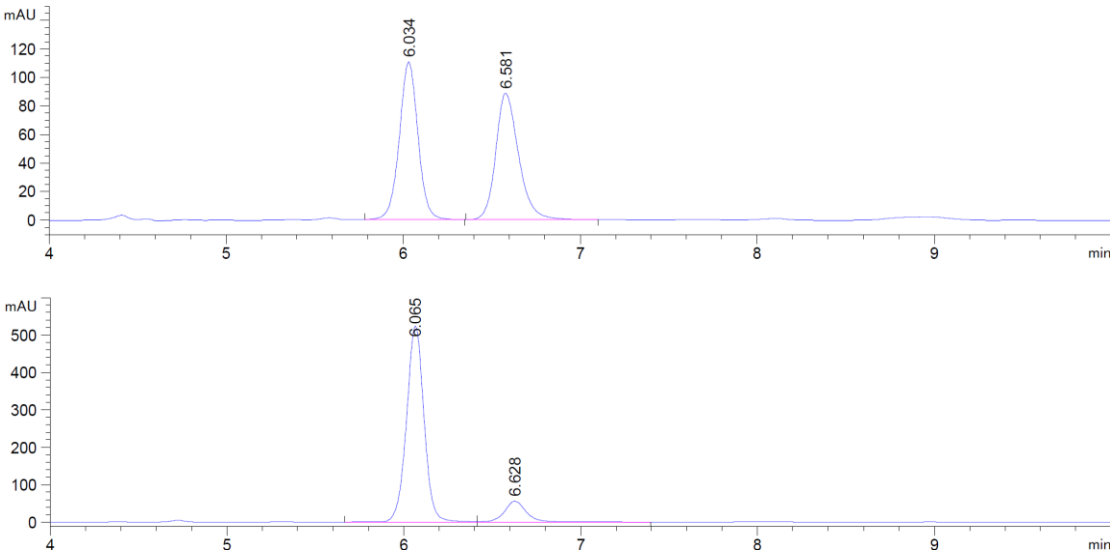
***(3aR,8aR)-8a-Hydroxy-3a-methyl-8-(2-methylprop-1-en-1-ylidene)-1,3a,8,8a-tetrahydrocyclopenta[a]inden-3(2H)-one* (*2ap*)**



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow solid, Mp = 74-75 °C; 46 mg, 90% yield; $[\alpha]_D^{20}$ = -102.0 (*c* 0.5, CH_2Cl_2), 76% ee [Phenomenex Lux 5u Amylose-2 column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 80/20, 0.7 mL/min, 254 nm; t_{major} = 6.1 min, t_{minor} = 6.6 min]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33-7.30 (m, 1H), 7.24-7.20 (m, 3H), 2.49-2.43 (m, 1H), 2.34-2.29 (m, 1H), 2.27-2.20 (m, 1H), 2.14-2.08 (m, 2H), 1.92 (s, 3H), 1.90 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 216.5, 196.2, 142.2, 137.2, 128.6, 128.3, 124.2, 122.6, 112.3, 105.3, 87.8, 62.5, 37.0, 33.5, 20.9, 20.7, 16.4. HRMS *m*/*z* (ESI+): Calculated $C_{17}H_{18}O_2Na^+$ ([M+Na]$^+$) 277.1199, found 277.1199.





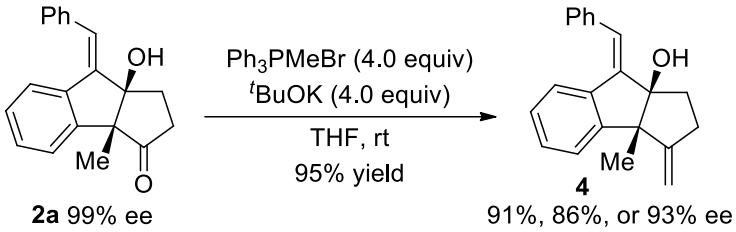


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.065	VV R	0.1063	3608.82349	524.48029	88.1408
2	6.628	VB	0.1292	485.56131	55.95907	11.8592

4. Synthetic transformations

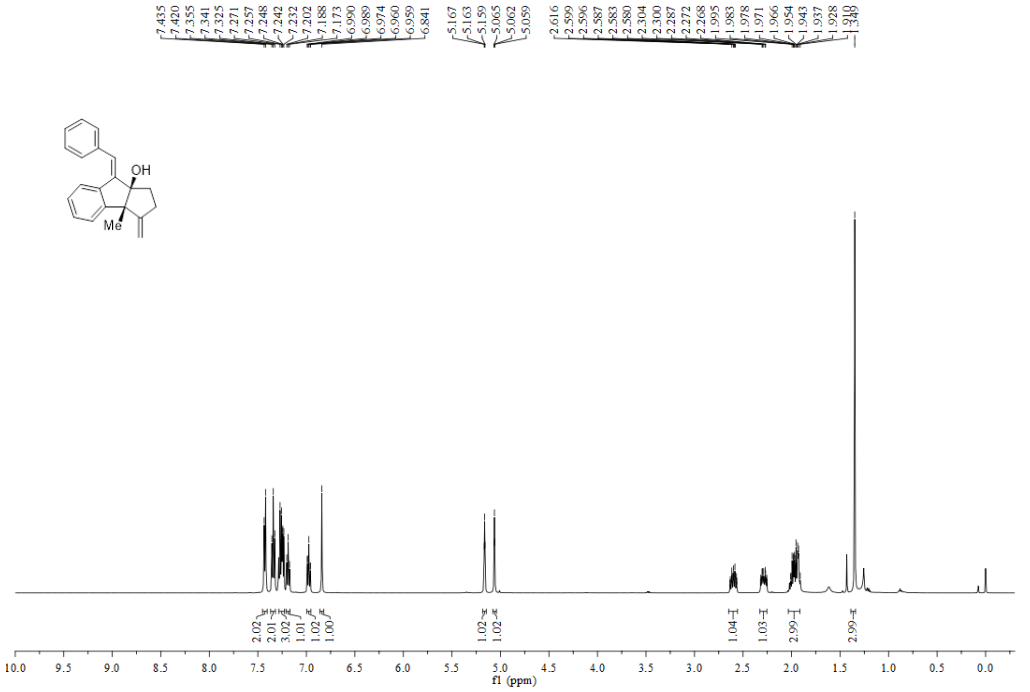
4.1 The Wittig reaction of 2a

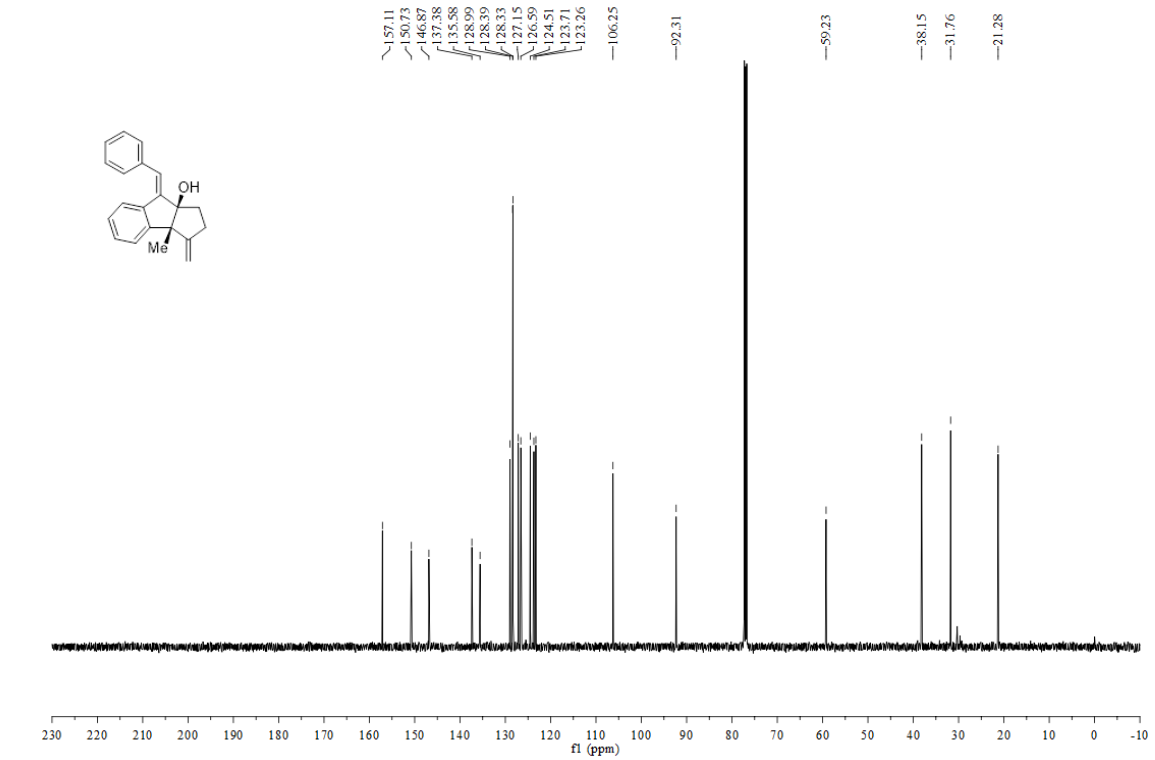


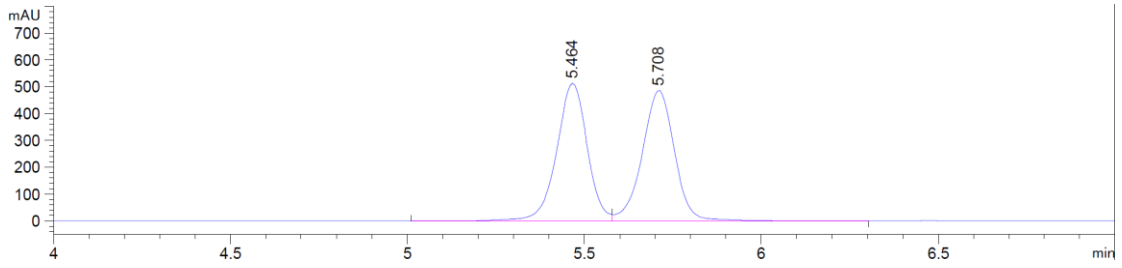
2a 99% ee

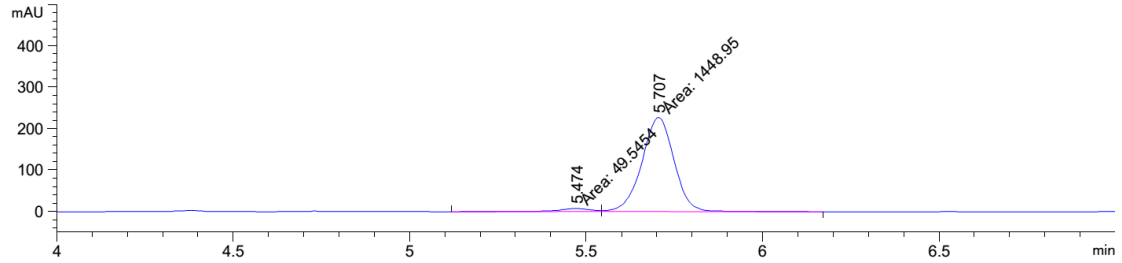
91%, 86%, or 93% ee

To a dried Schlenk flask was charged with Ph_3PMeBr (4.0 equiv, 0.8 mmol), ^tBuOK (4.0 equiv, 0.8 mmol), and THF (2 mL) under N_2 atmosphere. The resulting yellow mixture was stirred at 0 ºC for 30 min, to which a solution of **2a** (0.2 mmol) in anhydrous THF (2 mL) was then added via a syringe. After stirring at room temperature for 12 h, the reaction mixture was quenched by saturated aq. NH_4Cl (2 mL), extracted with ethyl acetate (2 mL×3), dried over Na_2SO_4, and concentrated under reduced pressure. The crude was purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v), to afford **4**. Colorless oil; For one of the results: 38 mg, 95% yield; $[\alpha]_D^{20}$ = -208.4 (*c* 0.5 , CH_2Cl_2), 93% ee [Phenomenex Lux 5u Amylose-2 column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 80/20, 0.7 mL/min, 254 nm; t_{minor} = 5.5 min, t_{major} = 5.7 min]; ^1H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, J = 7.5 Hz, 2H), 7.34 (t, J = 7.5 Hz, 2H), 7.27-7.23 (m, 3H), 7.19 (t, J = 7.5 Hz, 1H), 6.99-6.96 (m, 1H), 6.84 (s, 1H), 5.16 (t, J = 2.0 Hz, 1H), 5.06 (t, J = 1.5 Hz, 1H), 2.62-2.58 (m, 1H), 2.30-2.27 (m, 1H), 2.00-1.91 (m, 3H), 1.35 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.1, 150.7, 146.9, 137.4, 135.6, 129.0, 128.4, 128.3, 127.2, 126.6, 124.5, 123.7, 123.3, 106.3, 92.3, 59.2, 38.1, 31.8, 21.3. HRMS *m/z* (ESI+): Calculated for: $C_{21}H_{20}NaO^+$ ($[M+Na]^+$) 311.1406, found 311.1405.





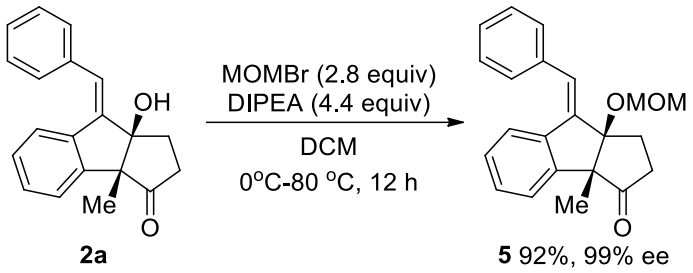




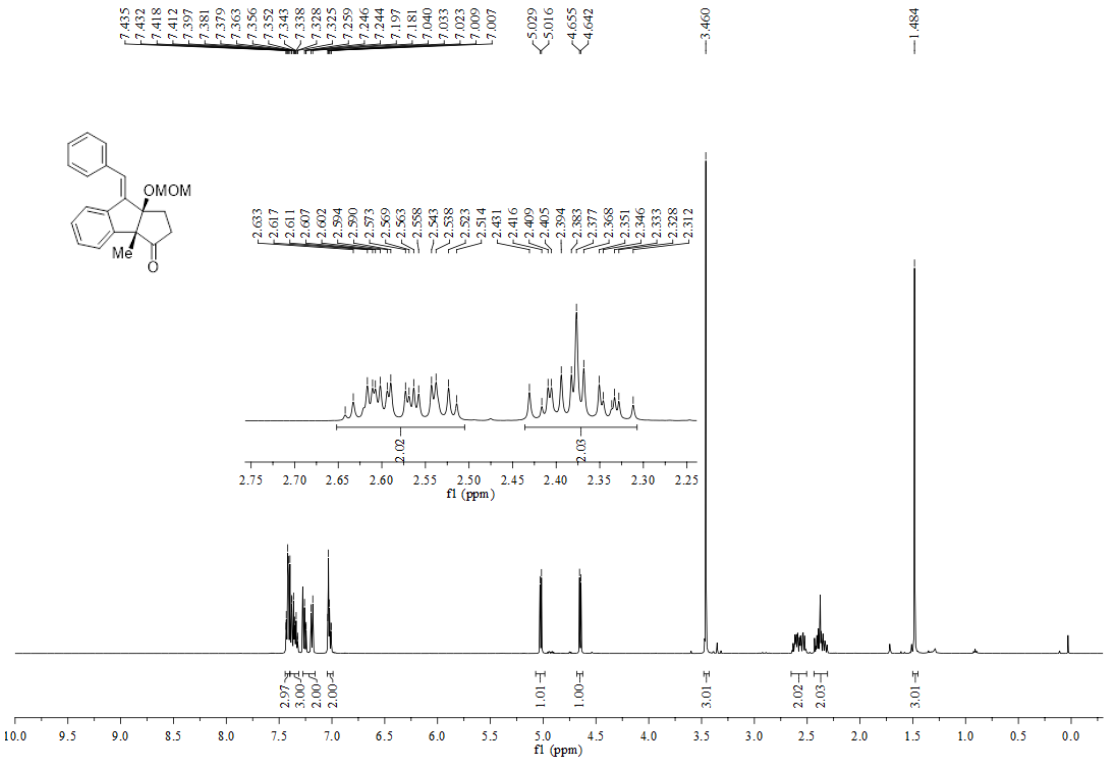
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

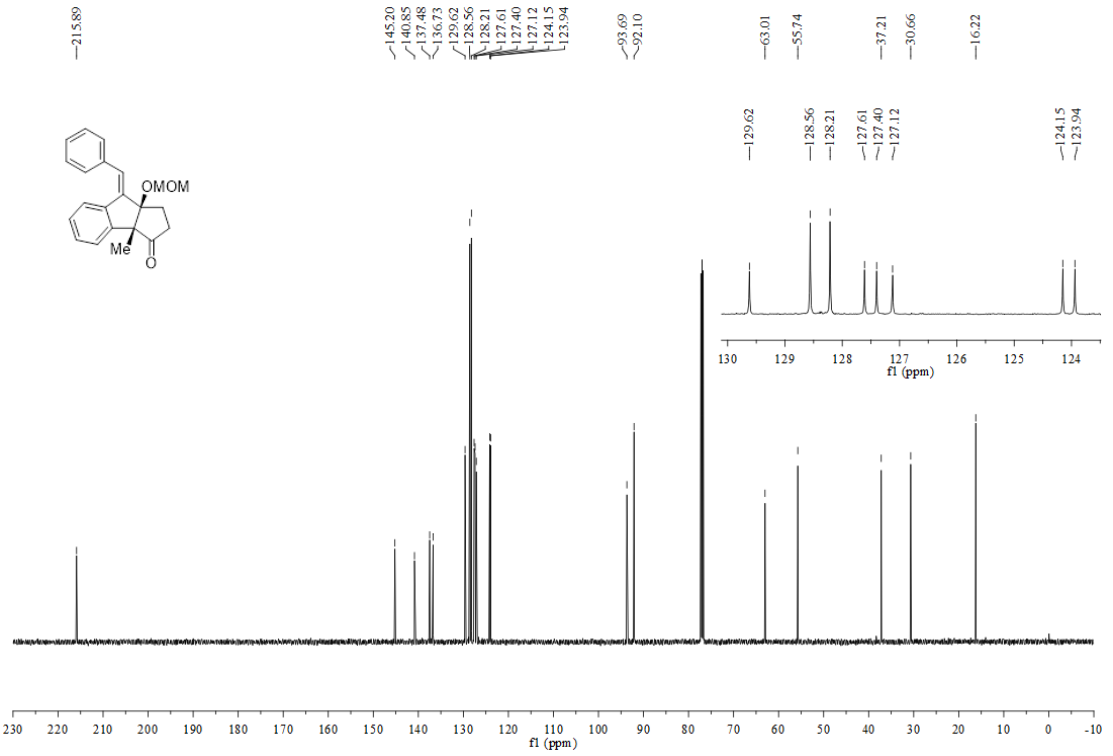
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.474	MM	0.1112	49.54544	7.42865	3.3063
2	5.707	MM	0.1059	1448.95251	228.02374	96.6937

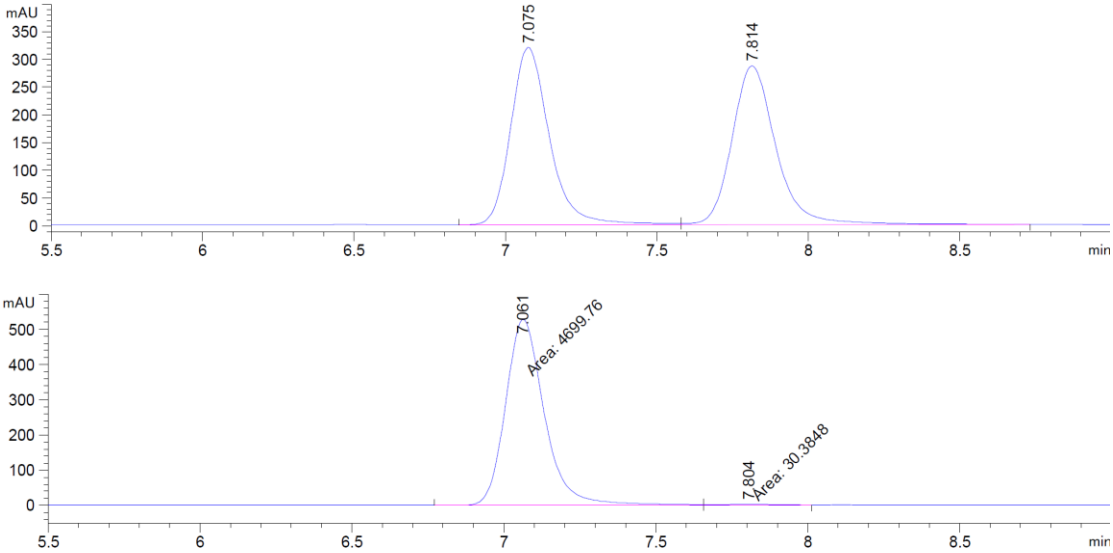
4.2 MOM-protection of compound 2a



To a solution of **2a** (1.0 equiv, 0.2 mmol) in DCM (4 mL) were added DIPEA (4.4 equiv) and MOMBr (2.8 equiv) at 0 °C, respectively. The reaction mixture was stirred at 60 °C until the reaction was completed. The solution was then quenched by saturated aq. NH_4Cl (2 mL), extracted with DCM (2 mL×3), dried over Na_2SO_4, and concentrated under reduced pressure. The crude was purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v), to afford **5**. Yellow oil; 62 mg, 92% yield; $[\alpha]_D^{20}$ = -63.4 (*c* 1.0, CH_2Cl_2), 99% ee [Phenomenex Lux 5u Cellulose-2 column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 90/10, 0.7 mL/min, 254 nm; t_{minor} = 7.1 min, t_{major} = 7.8 min]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44-7.40 (m, 2H), 7.38-7.33 (m, 3H), 7.26-7.18 (m, 2H), 7.04-7.01 (m, 2H), 5.02 (d, J = 6.5 Hz, 1H), 4.65 (d, J = 6.5 Hz, 1H), 3.46 (s, 3H), 2.63-2.51 (m, 2H), 2.43-2.31 (m, 2H), 1.48 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 215.9, 145.2, 140.9, 137.5, 136.7, 129.6, 128.6, 128.2, 127.6, 127.4, 127.1, 124.2, 123.9, 93.7, 92.1, 63.0, 55.7, 37.2, 30.7, 16.2. HRMS *m/z* (ESI+): Calculated for $C_{22}H_{22}O_3Na^+$ ([M+Na]$^+$) 357.1461, found 357.1462.



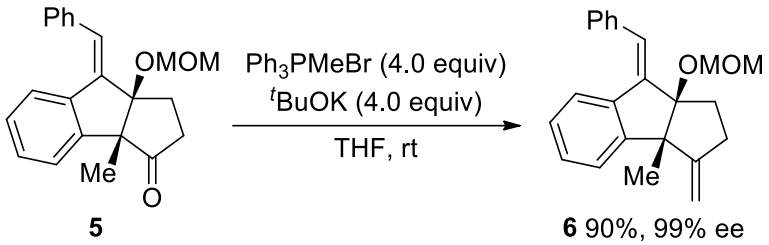




Signal 1: DAD1 A, Sig=254,4 Ref=360,100

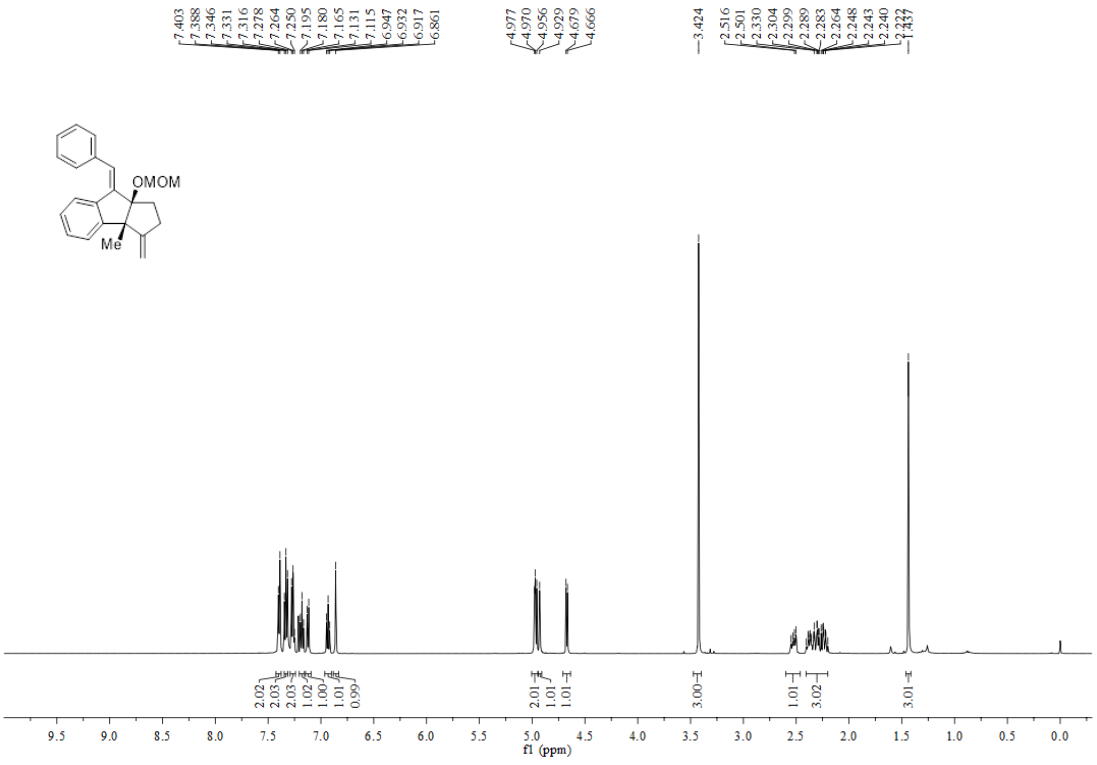
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.061	MF	0.1482	4699.75830	528.38263	99.3576
2	7.804	FM	0.2111	30.38482	2.39836	0.6424

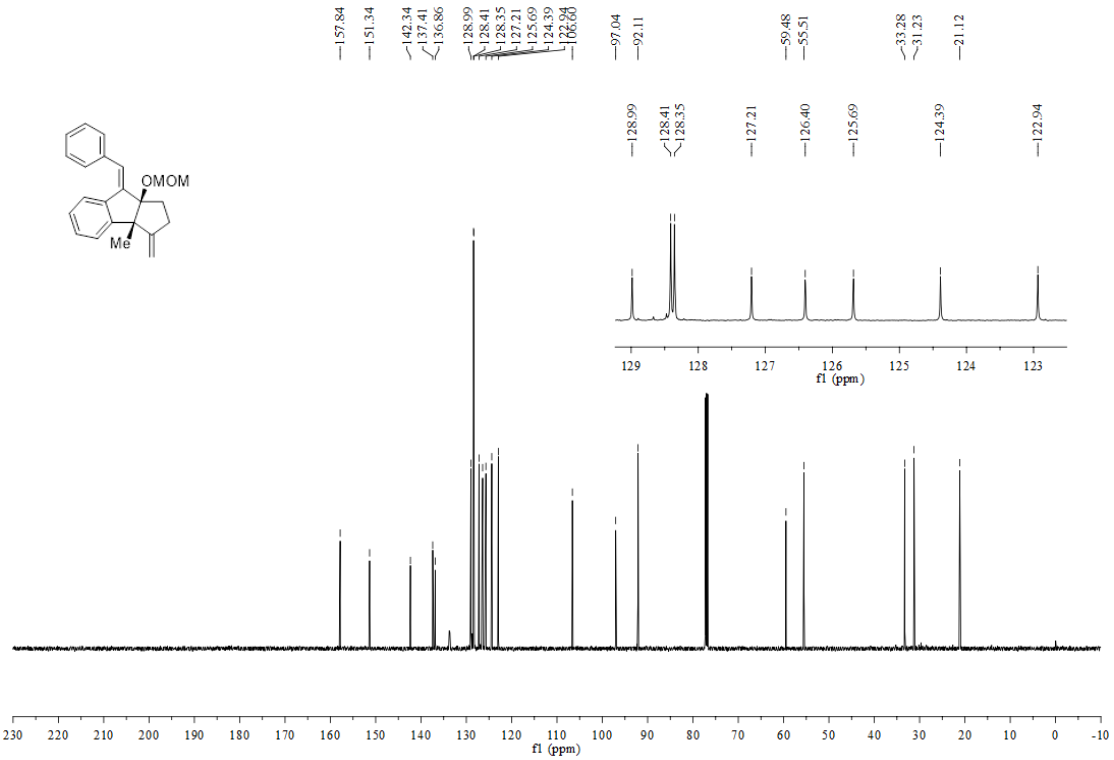
4.3 The Wittig reaction of 5

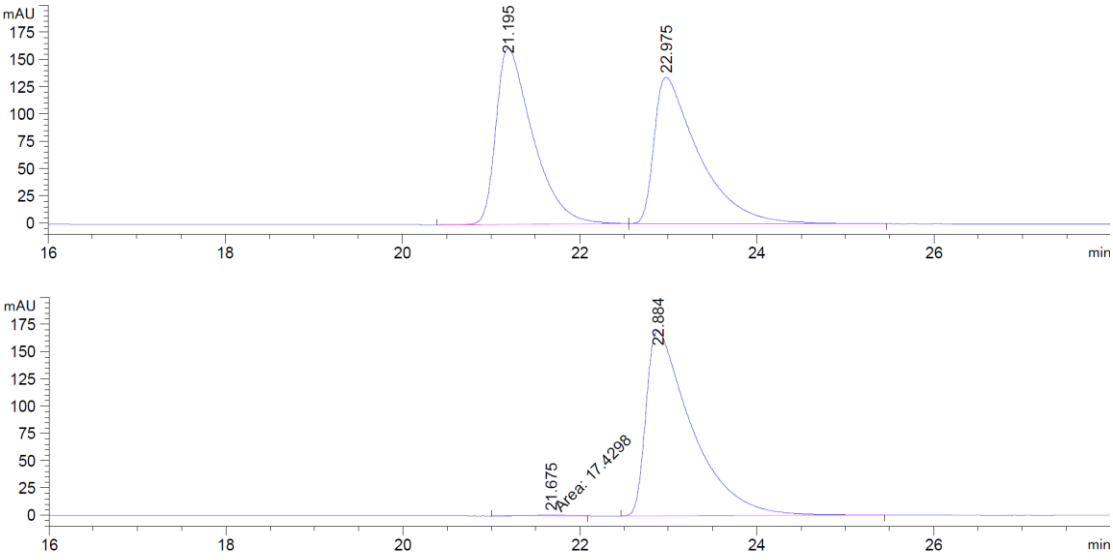


5 **6** 90%, 99% ee

The procedure for synthesis of **4** was followed. Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); yellow oil; 60 mg, 90% yield; $[\alpha]_D^{20}$ = -33.9 (*c* 0.5 , CH_2Cl_2), 99% ee [Phenomenex Lux 5u Cellulose-1 column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 99.9/0.1, 0.7 mL/min, 254 nm; t_{minor} = 21.7 min, t_{major} = 22.9 min]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, J = 7.5 Hz, 2H), 7.33 (t, J = 7.5 Hz, 2H), 7.18 (t, J = 7.0 Hz, 1H), 7.12 (d, J = 8.0 Hz, 1H), 6.93 (t, J = 7.5 Hz, 1H), 6.86 (s, 1H), 4.98-4.96 (m, 2H), 4.93 (s, 1H), 4.67 (d, J = 6.5 Hz, 1H), 3.42 (s, 3H), 2.52-2.46 (m, 1H), 2.33-2.22 (m, 3H), 1.44 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.8, 151.3, 142.3, 137.4, 136.9, 129.0, 128.41, 128.35, 127.2, 126.4, 125.7, 124.4, 122.9, 106.6, 97.0, 92.1, 59.5, 55.5, 33.3, 31.2, 21.1. HRMS *m/z* (EI+): Calculated for $C_{23}H_{24}O_2^+$ ([M]$^+$) 332.1776, found 332.1775.



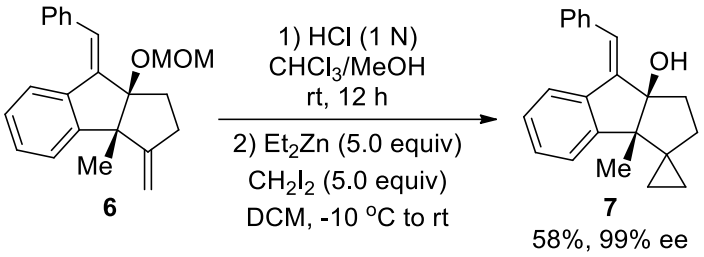




Signal 1: DAD1 A, Sig=254,4 Ref=360,100

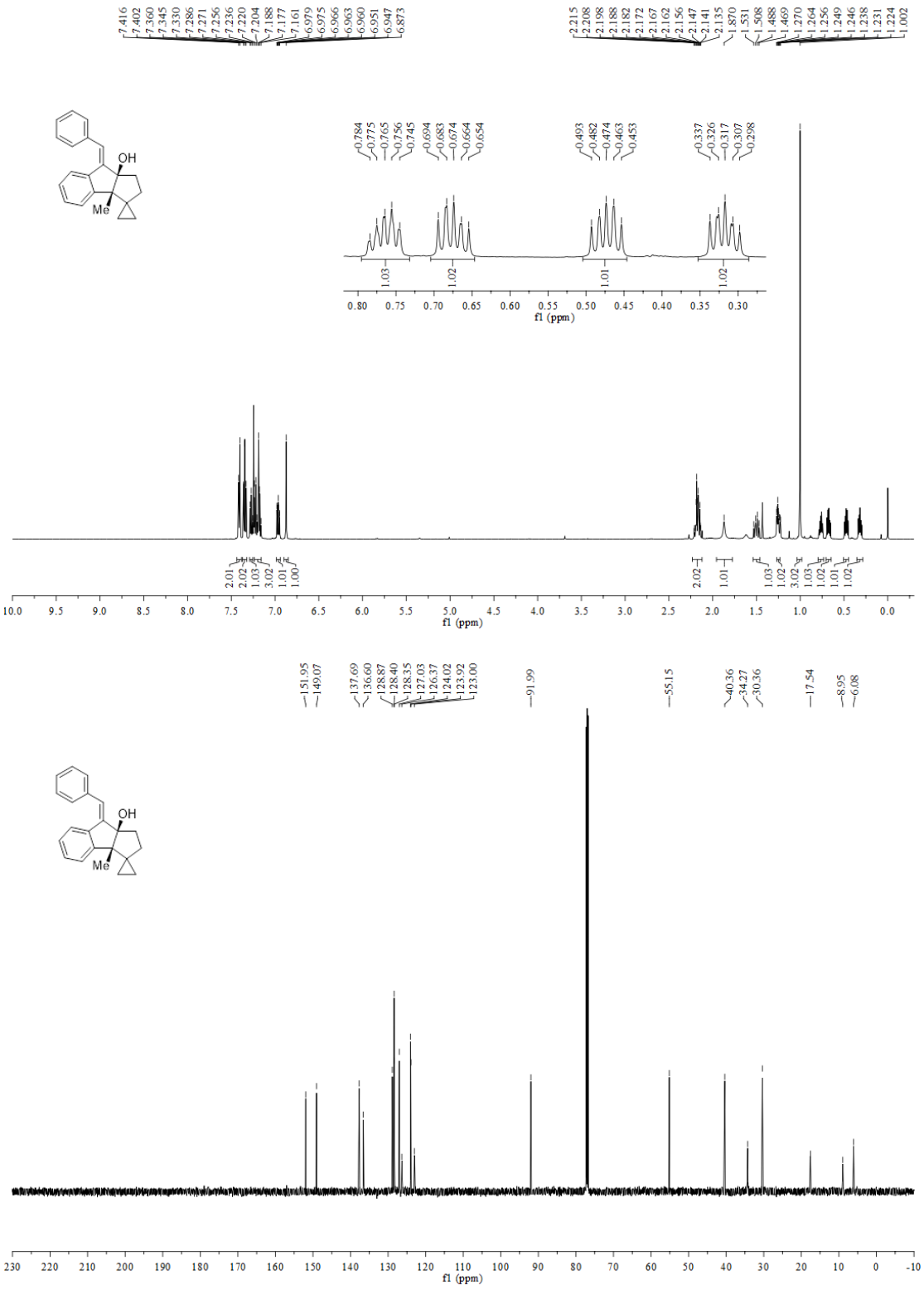
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.675	MM	0.4262	17.42982	6.81659e-1	0.2847
2	22.884	BB	0.5186	6104.57764	170.13115	99.7153

4.4 Cyclopropanation of 6

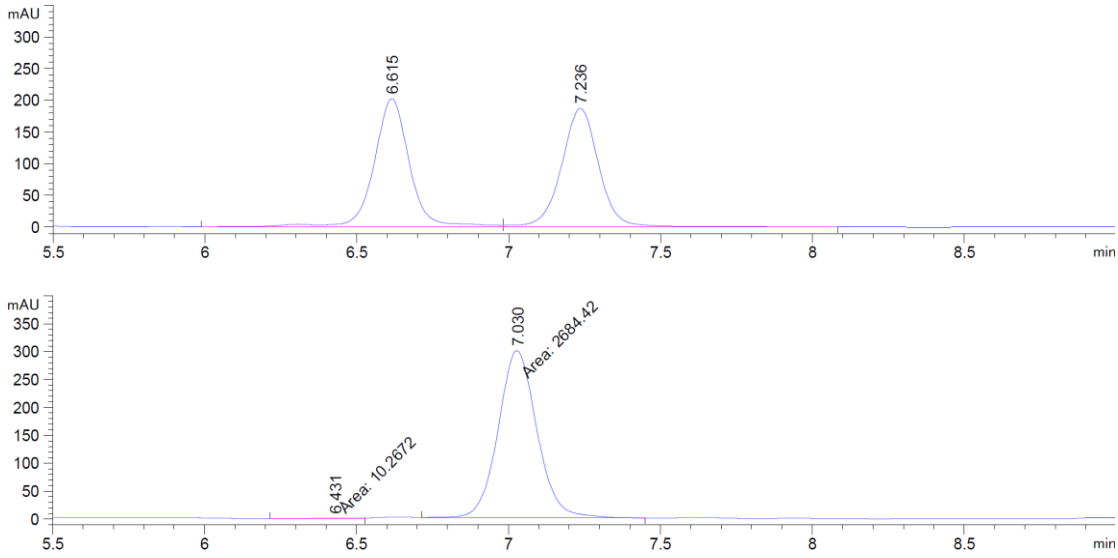


Step 1: To a 50 mL Schlenk flask was charged with **6** (0.2 mmol), HCl (1 N, 10 mL), $CHCl_3$ (4 mL), and MeOH (4 mL). After stirring at room temperature for 12 h, the resulting mixture was extracted with DCM, dried over Na_2SO_4, and concentrated under reduced pressure. The crude was then purified by flash chromatography on silica gal, eluting with ethyl acetate/petroleum ether 1:10 (v/v), to give compound **4**, which were used in the next step without further purification.

Step 2[5]: To a solution of the above crude product **4** (0.18 mmol) in anhydrous DCM at -10 °C was added Et_2Zn (5.0 equiv, 1.0 mmol/L in toluene) and CH_2I_2 (5.0 equiv) dropwise, respectively. The mixture was stirred at room temperature for 6 h. When the reaction was completed, DCM (10 mL) was then added. The diluted solution was quenched with saturated aq. NH_4Cl (5 mL) followed by treated with HCl (1 N, 5 mL). The organic phase was dried over Na_2SO_4, and concentrated under reduced pressure. The crude was purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v), to afford compound **7**. White solid, Mp = 88-89 °C; 35 mg, 58% yield; $[\alpha]_D^{20}$ = -33.9 (*c* 0.5 , CH_2Cl_2), 99% ee [Phenomenex Lux 5u Amylose-2 column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 90/10, 0.7 mL/min, 254 nm; t_{minor} = 6.4 min, t_{major} = 7.0 min]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, J = 7.0 Hz, 2H), 7.35 (t, J = 7.5 Hz, 2H), 7.27 (t, J = 7.5 Hz, 1H), 7.24-7.16 (m, 3H), 6.98-6.95 (m, 1H), 6.87 (s, 1H), 2.22-2.14 (m, 2H), 1.87 (s, 1H), 1.53-1.47 (m, 1H), 1.27-1.22 (m, 1H), 1.00 (s, 3H), 0.78-0.75 (m, 1H), 0.69-0.65 (m, 1H), 0.49-0.45 (m, 1H), 0.34-0.30 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.0, 149.1, 137.7, 136.6, 128.9, 128.40, 128.35, 127.0, 126.4, 124.0, 123.9, 123.0, 92.0, 55.2, 40.4, 34.3, 30.4, 17.5, 9.0, 6.1. HRMS *m*/*z* (ESI+): Calculated for $C_{22}H_{22}ONa^+$ ($[M+Na]^+$) 325.1563, found 325.1566.


OH
Me
f1 (ppm)

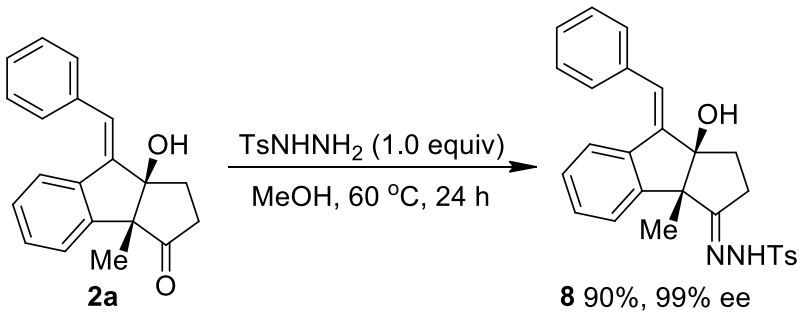
OH
Me
f1 (ppm)



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

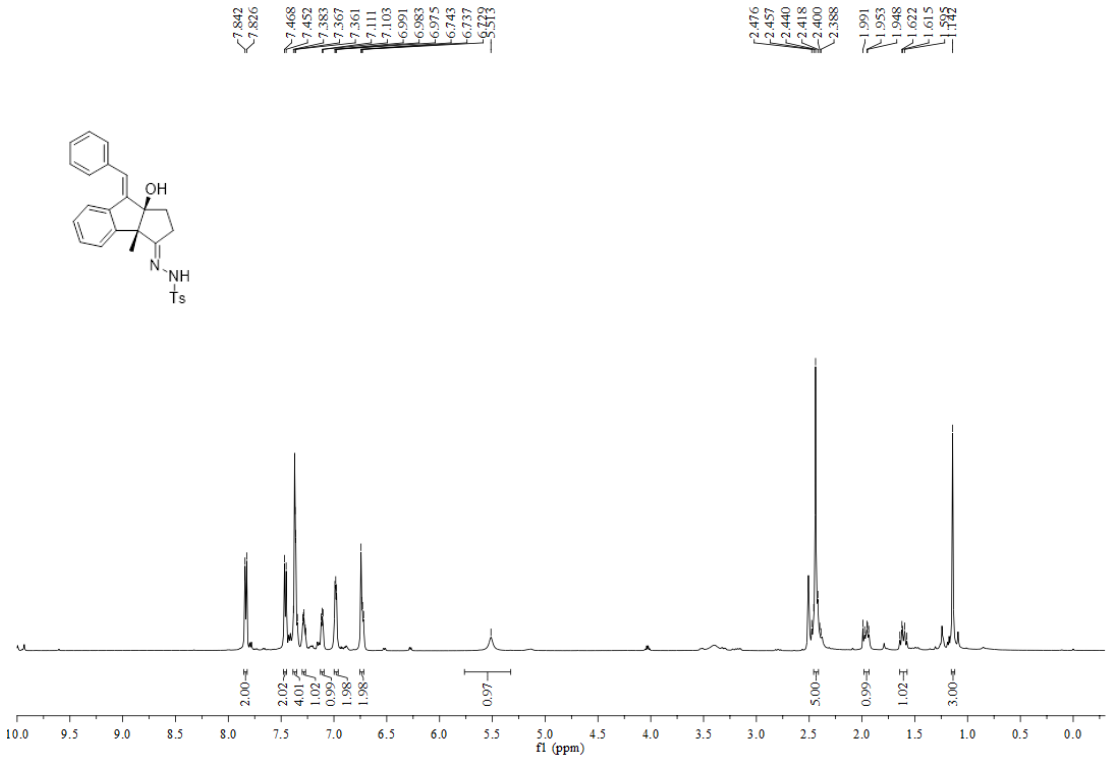
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.431	MM	0.1464	10.26723	1.16881	0.3810
2	7.030	MM	0.1489	2684.41919	300.44452	99.6190

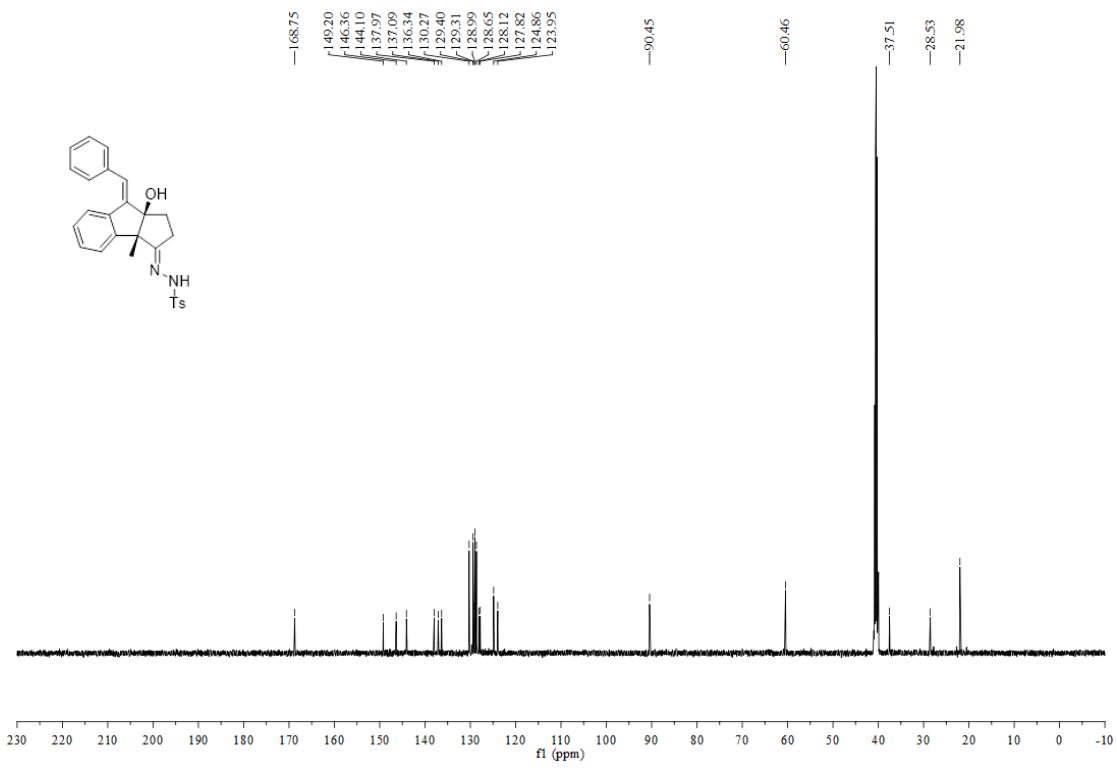
4.5 Condensation of 2a with $TsNHNH_2$

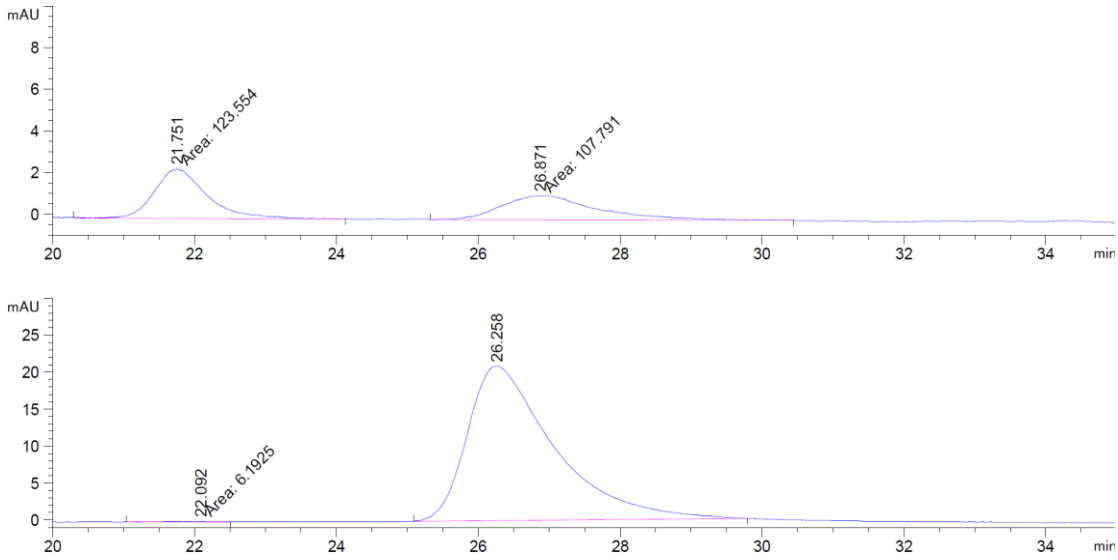


To a solution of **2a** (0.2 mmol) in MeOH was added *p*-toluenesulfonyl hydrazide (1.1 equiv). After stirring at 60 °C for 24 h, the resulting mixture was concentrated under reduced pressure. The crude was purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:2 (v/v), to give compound **8**. White solid, Mp = 218-219 °C; 82 mg, 90% yield; $[\alpha]_D^{20}$ = -221.0 (*c* 1.5, CH_2Cl_2), 99% ee [Phenomenex Lux 5u Amylose-2 column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 80/20, 0.7 mL/min, 254 nm; t_{minor} = 22.1 min, t_{major} = 26.3 min]; ^{1}H NMR (500 MHz, $(CD_3)_2SO$) δ 10.07 (s, 1H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.38-7.36 (m, 4H), 7.30-7.26 (m, 1H), 7.11-7.10 (m, 1H), 7.00-6.96 (m, 2H), 6.75-6.71 (m, 2H), 5.51 (s, 1H), 2.48-2.39 (m, 5H), 1.99-1.95 (m, 1H), 1.62-1.60 (m, 1H), 1.14 (s, 3H). ^{13}C NMR (125 MHz,

$(CD_3)_2SO$) δ 168.8, 149.2, 146.4, 144.1, 138.0, 137.1, 136.3, 130.3, 129.4, 129.3, 129.0, 128.7, 128.1, 127.8, 124.9, 124.0, 90.5, 60.5, 37.5, 28.5, 22.0. HRMS *m*/*z* (ESI+): Calculated for $C_{27}H_{26}N_2NaO_3S^+$ ([M+Na]$^+$) 481.1556, found 481.1556.





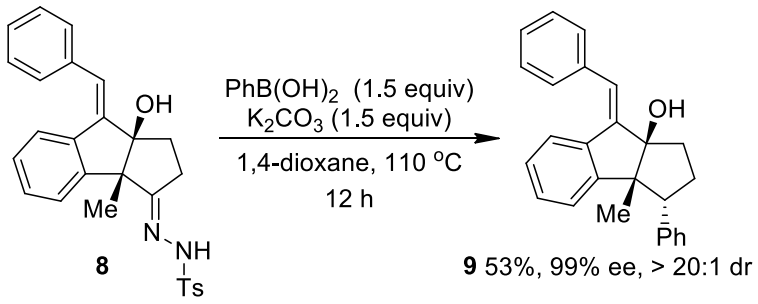


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.092	MM	0.8968	6.19250	1.15081e-1	0.3496
2	26.258	BB	1.0969	1765.03760	20.86504	99.6504

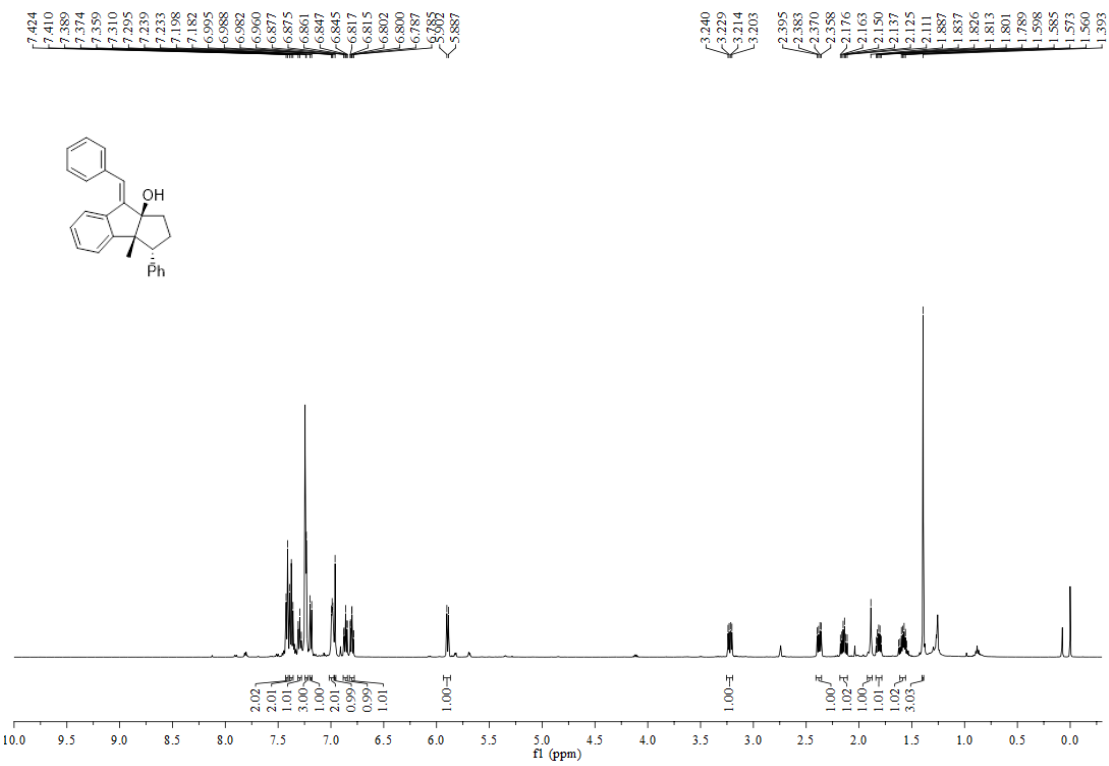
4.6 Coupling of 8 with $PhB(OH)_2$

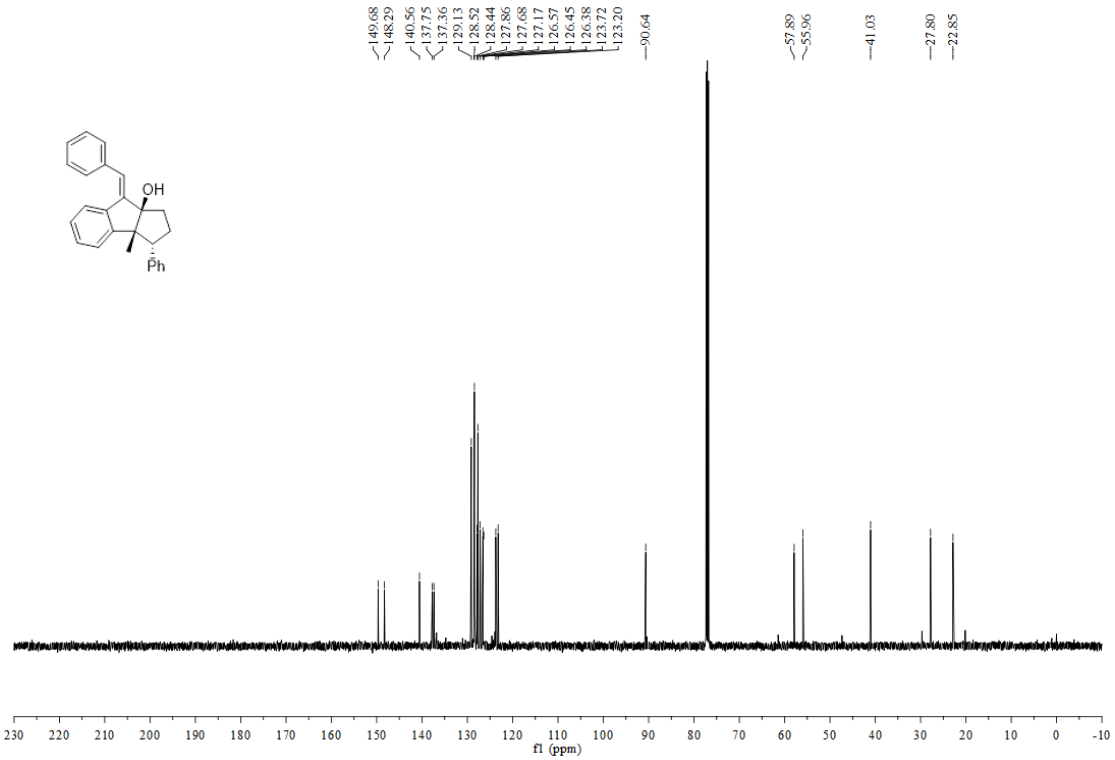
The modified procedure according to the literature was followed.[6]

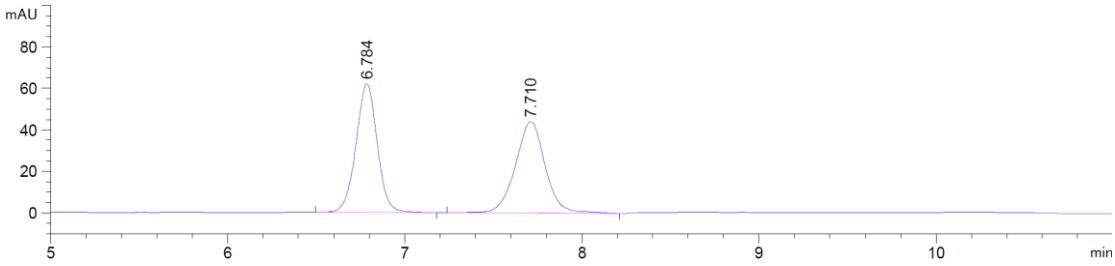


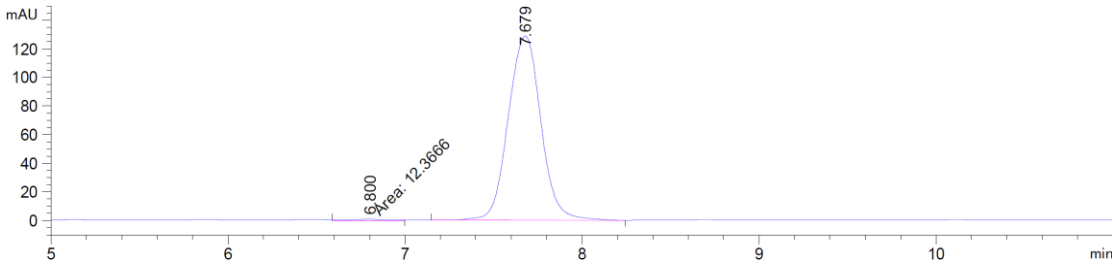
To a dried Schlenk flask was charged with **8** (0.2 mmol), K_2CO_3 (1.5 equiv, 0.3 mmol), phenylboronic acid (1.5 equiv, 0.3 mmol), and anhydrous 1,4-dioxane (2 mL) under N_2 atmosphere. The mixture was stirred at 110 °C for 12 h. When the reaction was completed, the solution was concentrated under reduced pressure. The crude was purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:3 (v/v), to give compound **9**; yellow oil; 37 mg, 53% yield; $[\alpha]_D^{20}$ = -153.3 (*c* 0.5, CH_2Cl_2), 99% ee [Phenomenex Lux 5u Amylose-2 column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 90/10, 0.7 mL/min, 254 nm; t_{minor} = 6.8 min, t_{major} = 7.7 min]; ^{1}H NMR (500

MHz, $CDCl_3$) δ 7.42 (d, J = 7.0 Hz, 2H), 7.37 (t, J = 7.5 Hz, 2H), 7.29 (t, J = 7.3 Hz, 1H), 7.24 (d, J = 3.0 Hz, 3H), 7.19 (d, J = 8.0 Hz, 1H), 7.00-6.98 (m, 2H), 6.96 (s, 1H), 6.88-6.85 (m, 1H), 6.82-6.79 (m, 1H), 5.89 (d, J = 7.5 Hz, 1H), 3.22 (dd, J = 13.0, 5.5 Hz, 1H), 2.38 (dd, J = 12.5, 6.0 Hz, 1H), 2.18-2.11 (m, 1H), 1.89 (s, 1H), 1.84-1.79 (m, 1H), 1.60-1.56 (m, 1H), 1.39 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.7, 148.3, 140.6, 137.8, 137.4, 129.1, 128.5, 128.4, 127.9, 127.7, 127.2, 126.6, 126.5, 126.4, 123.7, 123.2, 90.6, 57.9, 56.0, 41.0, 27.8, 22.9. HRMS *m*/*z* (ESI+): Calculated for $C_{26}H_{24}ONa^+$ ([M+Na]$^+$) 375.1719, found 375.1718.





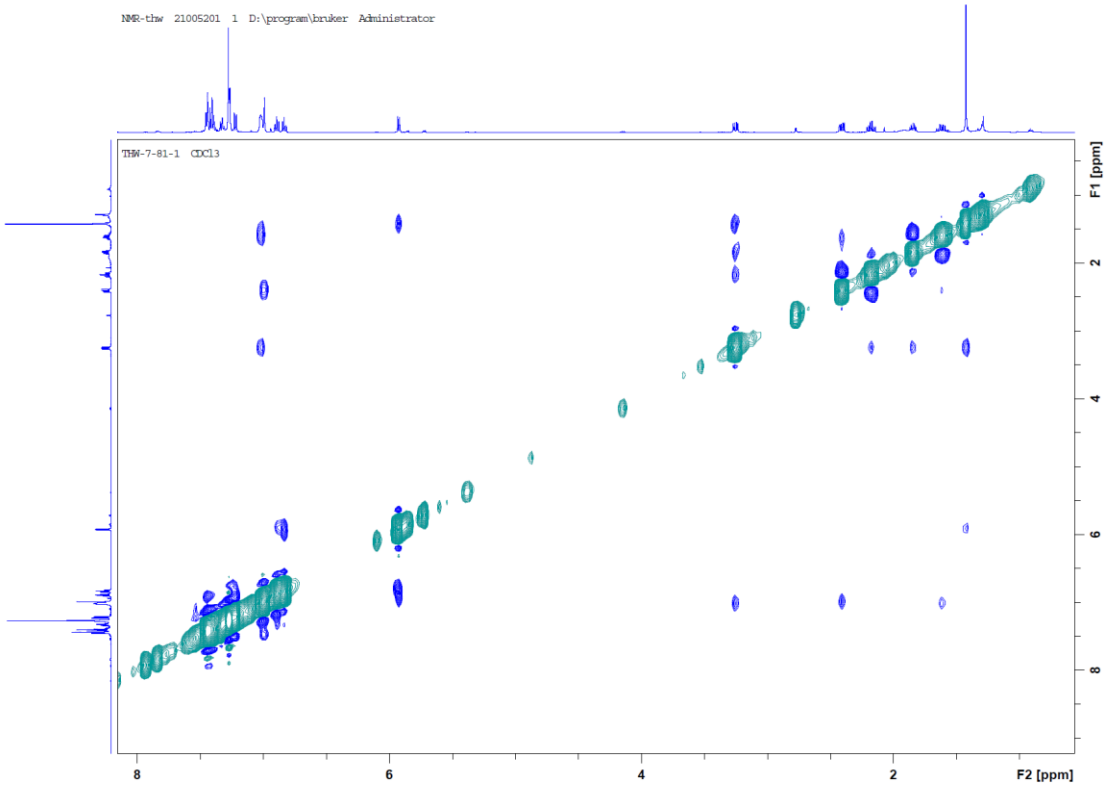




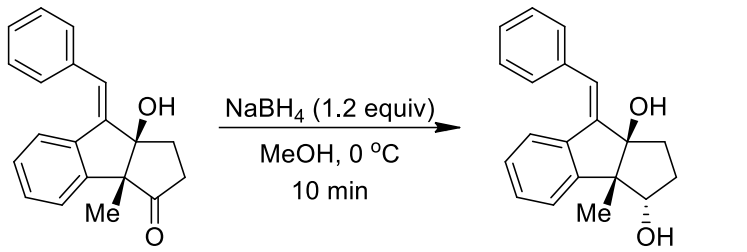
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.800	MM	0.2278	12.36664	9.04759e-1	0.7411
2	7.679	BB	0.2041	1656.31726	128.78018	99.2589

2d-NOESY spectrum of 9



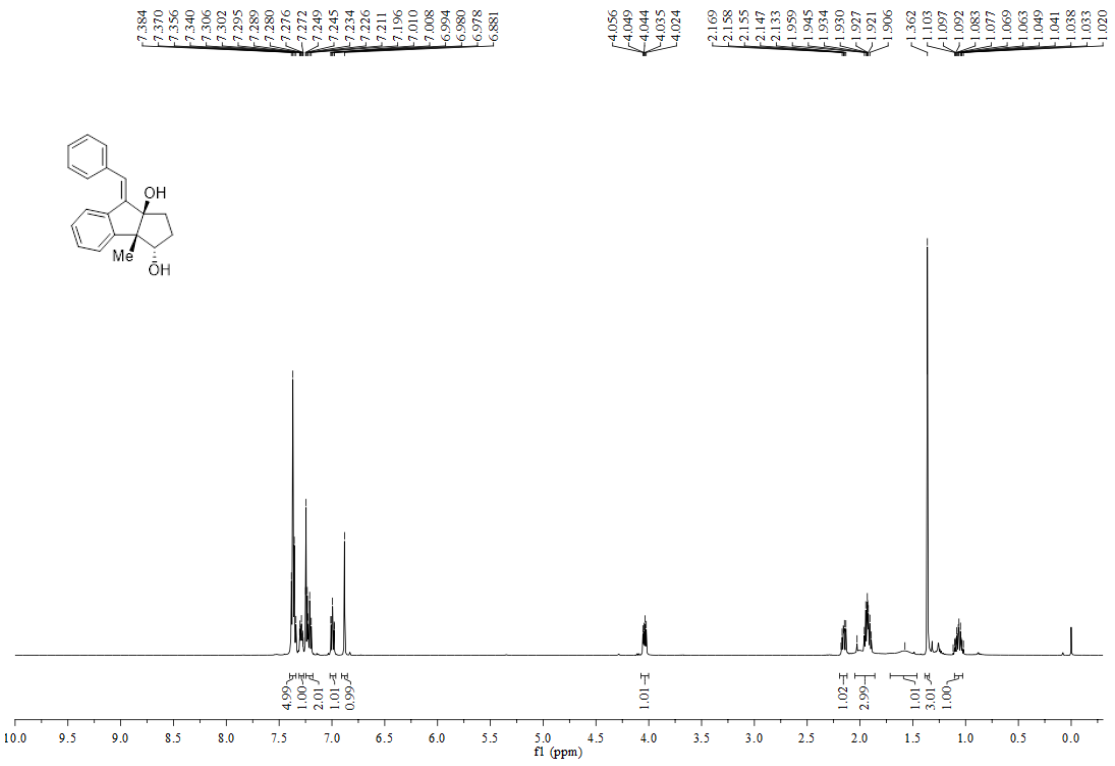
4.7 Reduction of 2a

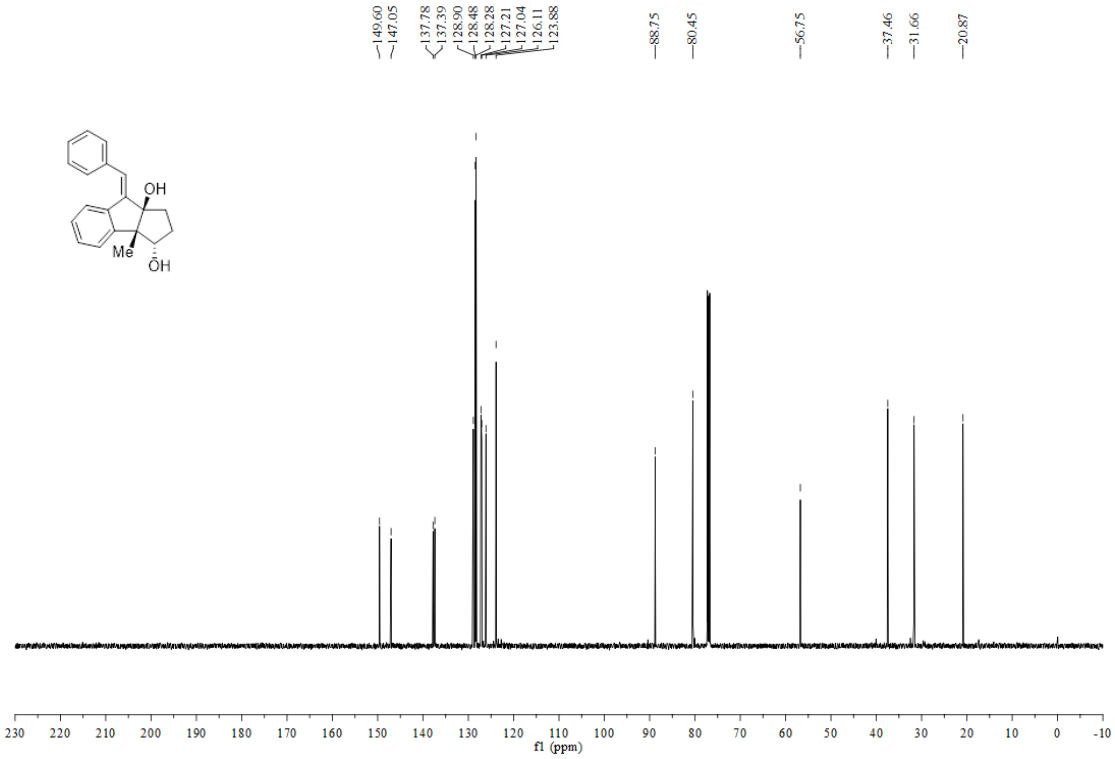


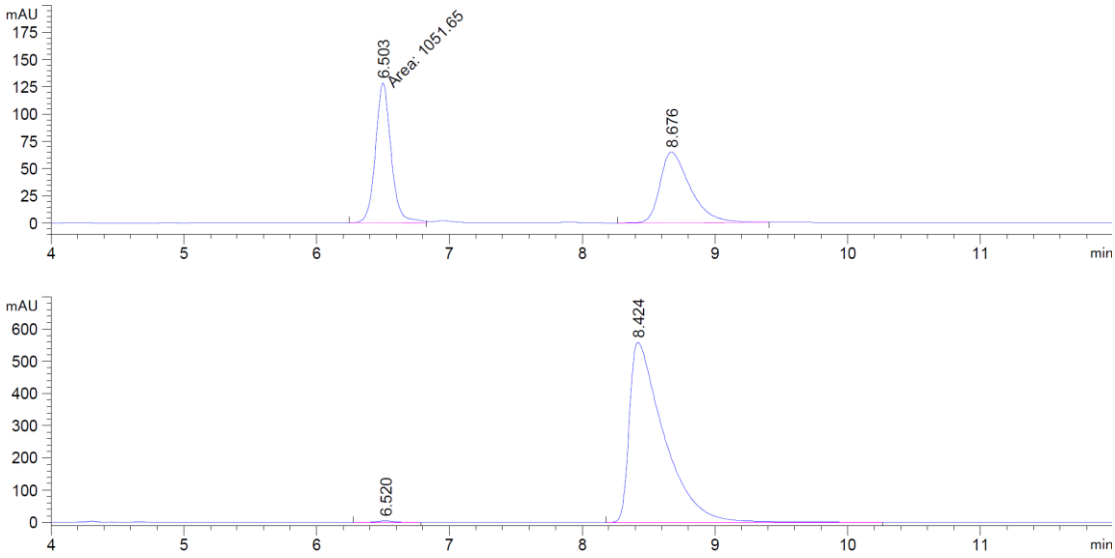
2a **10** 95%, 99% ee, > 20:1 dr

To a solution of **2a** (0.2 mmol) in MeOH (5 mL) was added $NaBH_4$ (1.2 equiv, 0.24 mmol) at 0 °C in portions. The resulting mixture was stirred for 10 min. The reaction was then quenched with a saturated aq. NH_4Cl (5 mL). The solution was extracted with ethyl acetate (2 mL×3), dried over Na_2SO_4, and concentrated under reduced pressure. The crude was purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:3 (v/v), to afford compound **10**. White solid, Mp = 73-74 °C; 56 mg, 95% yield; $[\alpha]_D^{20}$ = -26.0 (*c* 0.5, CH_2Cl_2), 99% ee [Phenomenex Lux 5u Amylose-2 column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 80/20, 0.7 mL/min, 254 nm; t_{minor} = 6.5 min, t_{major} = 8.4 min]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.34 (m, 5H), 7.31-7.27 (m, 1H), 7.25-7.20 (m, 2H), 7.01-6.98 (m, 1H), 6.88 (s, 1H), 4.06-4.02 (m, 1H), 2.17-2.13 (m, 1H), 1.96-1.91 (m, 3H), 1.57 (s, 1H), 1.36 (s, 3H), 1.10-1.02 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.6, 147.1, 137.8, 137.4, 128.9, 128.5, 128.3, 127.2, 127.0, 126.1, 123.9, 88.8, 80.5, 56.8, 37.5, 31.7, 20.9. HRMS *m/z* (ESI+):

Calculated $C_{20}H_{20}O_2Na^+$ ([M+Na]$^+$) 315.1356, found 315.1357.



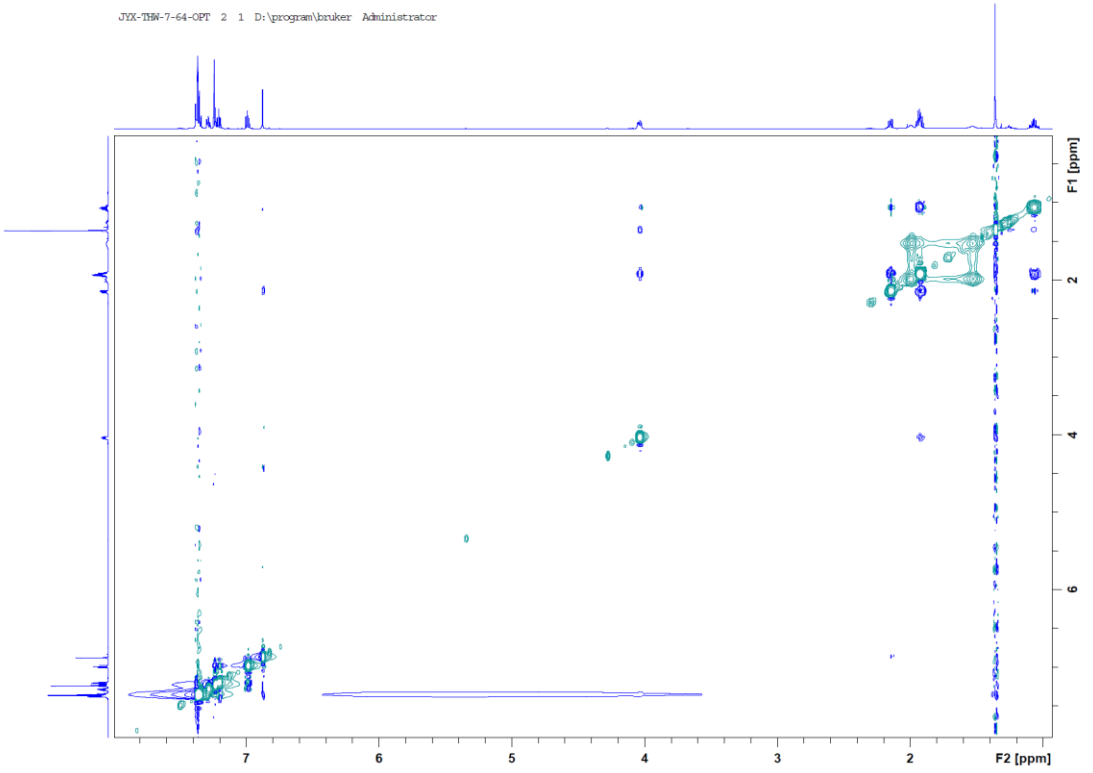




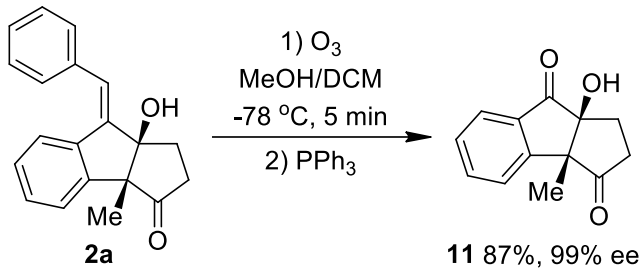
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.520	BB	0.1260	37.36382	4.44659	0.3710
2	8.424	BB	0.2574	1.00332e4	558.94476	99.6290

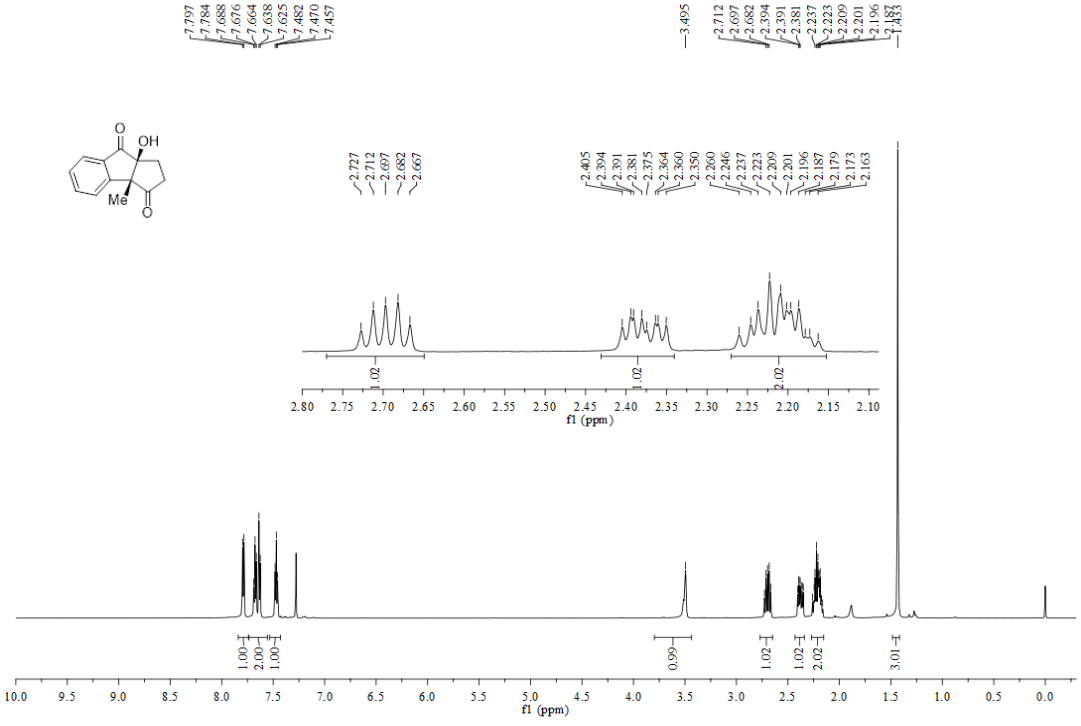
2d-NOESY spectrum of 10

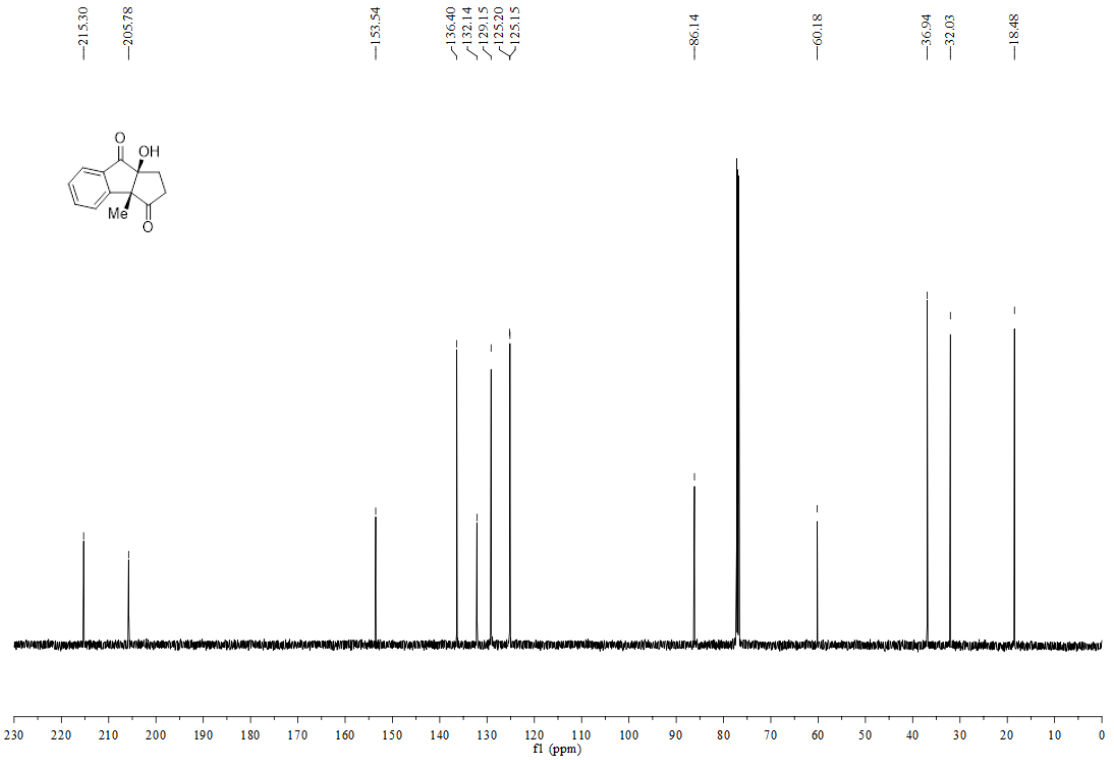


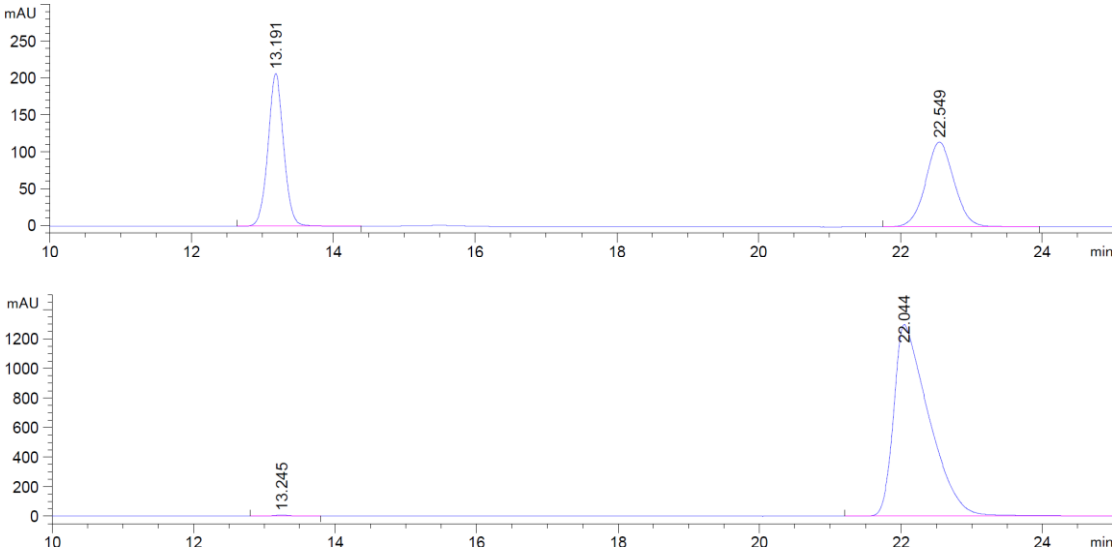
4.8 Oxidation of 2a



To a solution of **2a** (0.2 mmol) in the mixed solvent of DCM/MeOH (5 mL, V/V = 1/1) at -78 °C was purged with O_3 for 5 min until the starting material **2a** was all consumed (monitored by TLC). The solution was then sparged with a stream of N_2 to ensure removal of excess O_3. PPh_3 (0.8 mmol, 4.0 equiv) was then added to quench the reaction and the mixture was stirred at room temperature for 3 h. The solution was concentrated under reduced pressure. The residue was purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v), to afford compound **11**. Yellow solid, Mp = 77-78 °C; 38 mg, 87% yield; $[\alpha]_D^{20}$ = -281.6 (*c* 0.5 , CH_2Cl_2), 99% ee [Phenomenex Lux 5u Amylose-2 column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 90/10, 0.7 mL/min, 254 nm; t_{minor} = 13.2 min, t_{major} = 22.0 min]; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, J = 7.8 Hz, 1H), 7.69-7.63 (m, 2H), 7.47 (t, J = 7.2 Hz, 1H), 3.49 (s, 1H), 2.71-2.67 (m, 1H), 2.41-2.35 (m, 1H), 2.26-2.16 (m, 2H), 1.43 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 215.3, 205.8, 153.5, 136.4, 132.1, 129.2, 125.20, 125.15, 86.1, 60.2, 36.9, 32.0, 18.5. HRMS *m*/*z* (ESI+): Calculated for: $C_{13}H_{12}NaO_3^+$ ([M+Na]$^+$) 239.0679, found 239.0678.



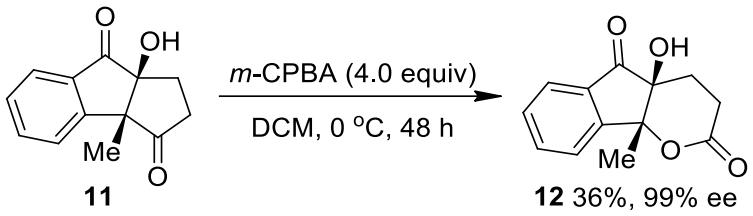




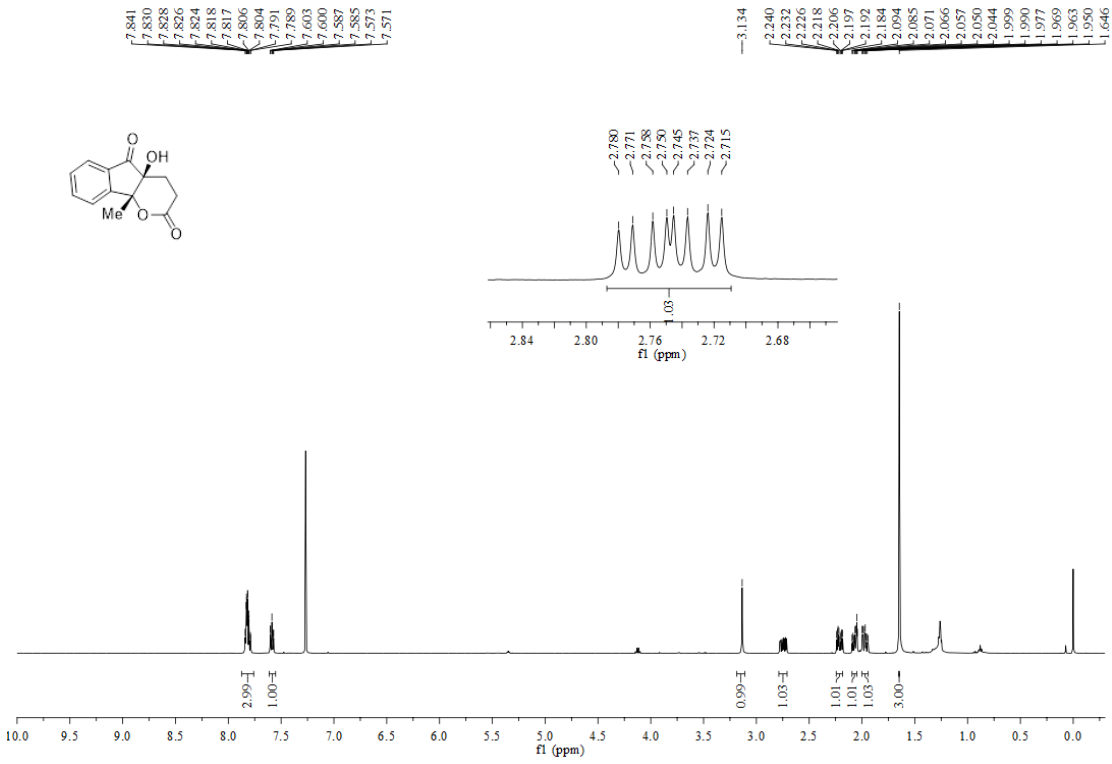
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

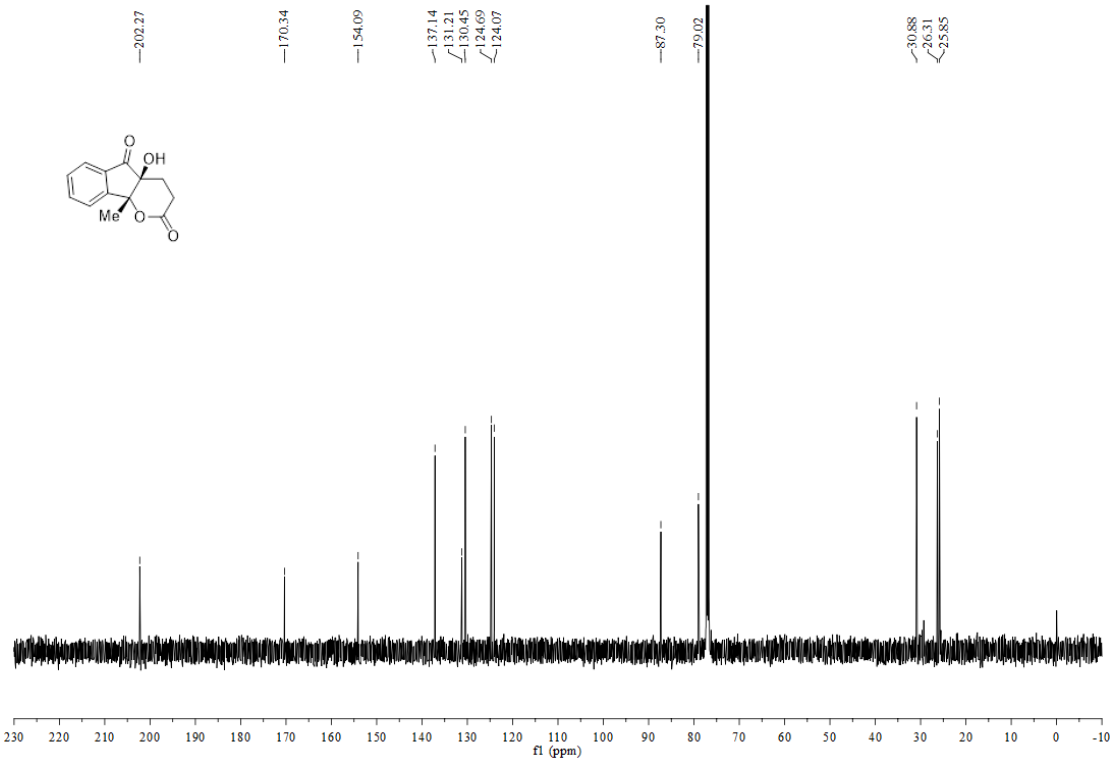
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.245	BB	0.2361	131.38722	8.51215	0.2938
2	22.044	BBA	0.4990	4.45945e4	1297.51660	99.7062

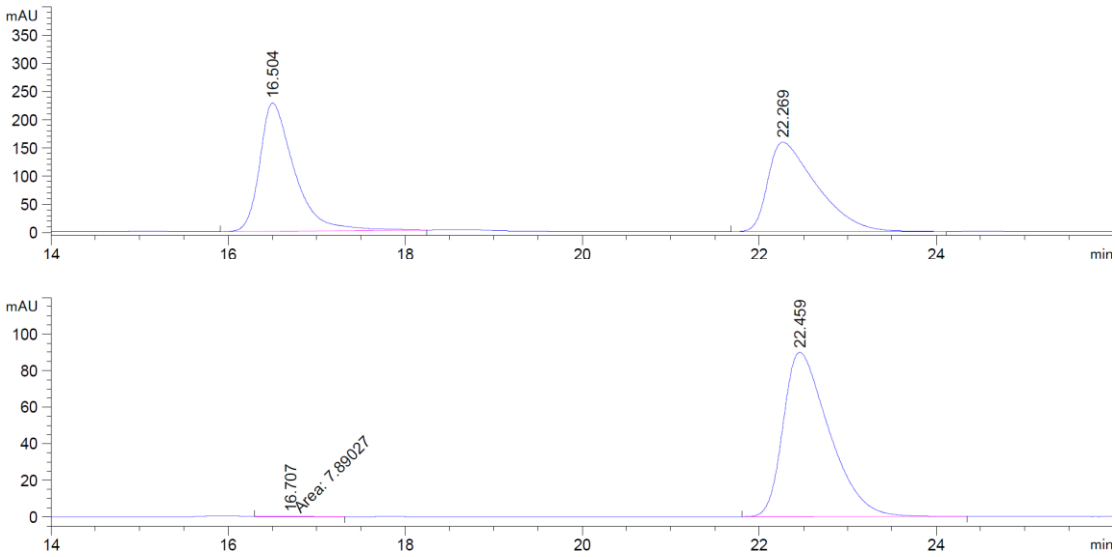
4.9 Baeyer-Villiger reaction of 11



To a solution of **11** (0.2 mmol) in anhydrous DCM was added *m*-CPBA (0.8 mmol, 4.0 equiv) at 0 °C in one portion. The resulting mixture was stirred at the same temperature for 48 h and then quenched with a solution of Na_2SO_3. After extracting with DCM, the combined organic phase was washed with saturated aqueous $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:3 (v/v), to give compound **12**. Colorless oil; 17 mg, 36% yield; $[\alpha]_D^{20}$ = -5.9 (*c* 0.28, CH_2Cl_2), 99% ee [Phenomenex Lux 5u Amylose-2 column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 80/20, 0.7 mL/min, 254 nm; t_{minor} = 16.7 min, t_{major} = 22.5 min]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84-7.79 (m, 3H), 7.60-7.57 (m, 1H), 3.13 (s, 1H), 2.78-2.72 (m, 1H), 2.24-2.18 (m, 1H), 2.09-2.04 (m, 1H), 2.00-1.95 (m, 1H), 1.65 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.3, 170.3, 154.1, 137.1, 131.2, 130.5, 124.7, 124.1, 87.3, 79.0, 30.9, 26.3, 25.9. HRMS *m*/*z* (ESI+): Calculated for $C_{13}H_{12}O_4Na^+$ ([M+Na]$^+$) 255.0628, found 255.0628.







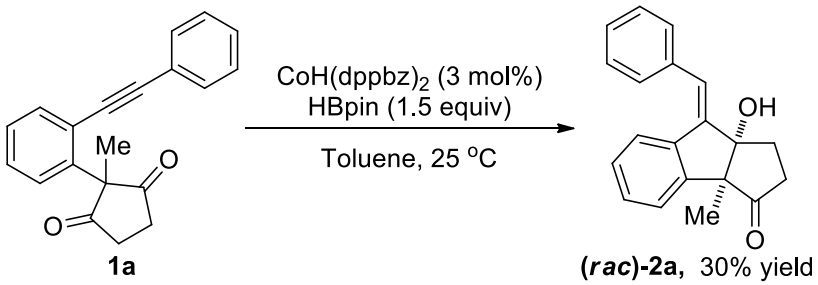
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.707	MM	0.7093	7.89027	1.85409e-1	0.2427
2	22.459	BB	0.5425	3243.33130	89.98299	99.7573

5. Control experiment and formation of by-product 3

5.1 Control experiments

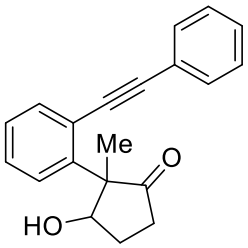
The complex of $CoH(dppbz)_2$ was prepared according to the known procedure.[1a]



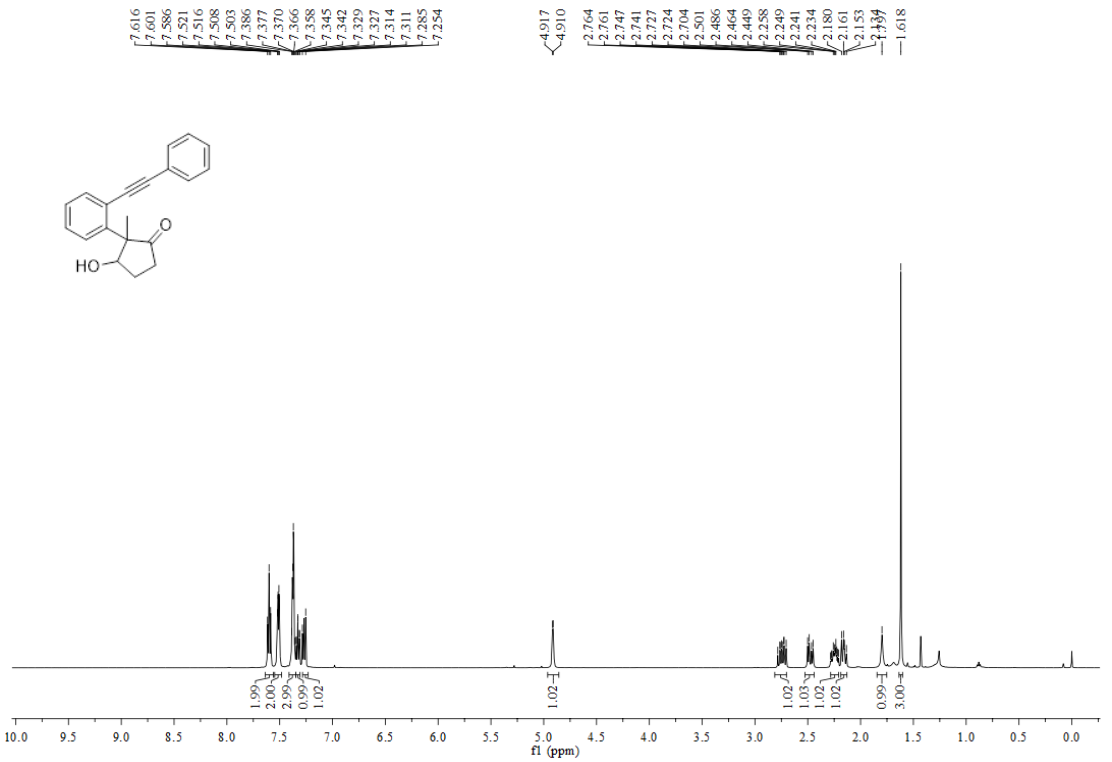
To a dried 25 mL Schlenk tube was charged with **1a** (0.2 mmol), $CoH(dppbz)_2$ (3 mol%, 0.006 mmol), and HBpin (1.5 equiv, 0.3 mmol) under N_2 atmosphere. Toluene (2 mL) was then introduced via a syringe. The resulting mixture was stirred at room temperature for 6 days. The reaction mixture was concentrated under reduced pressure, and the residue was purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v), to give **(*rac*)-2a** in 30% yield.

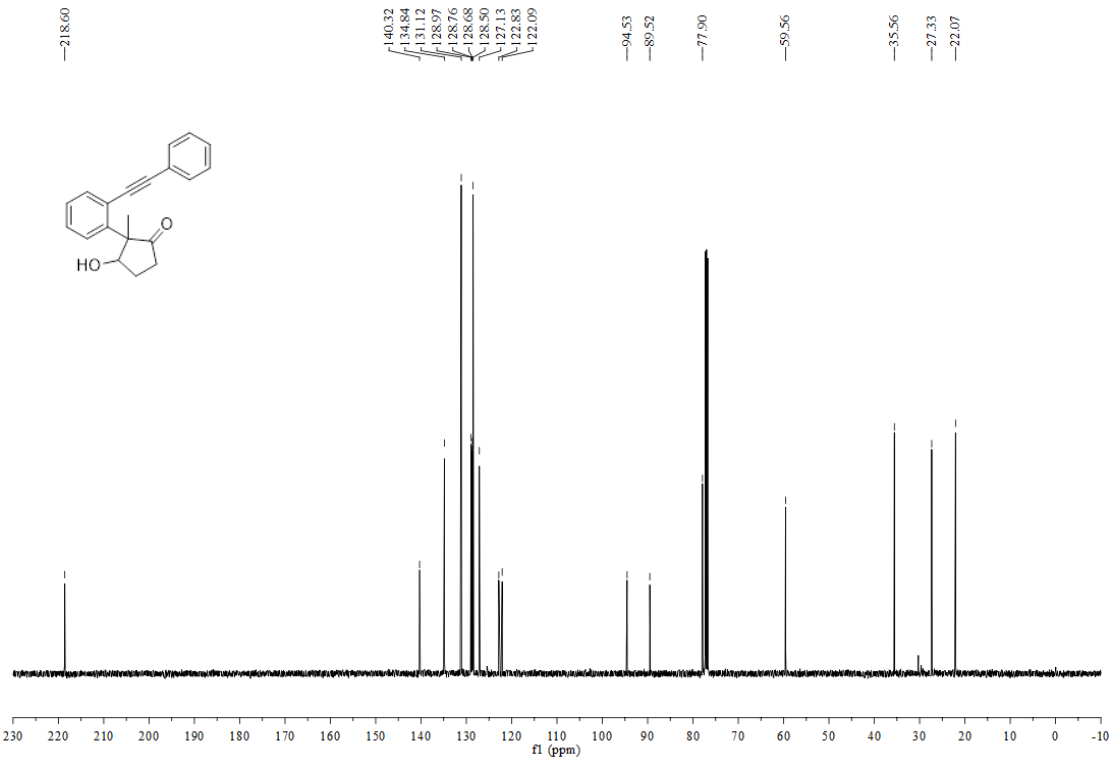
5.2 Formation of byproduct 3

3-Hydroxy-2-methyl-2-(2-(phenylethynyl)phenyl)cyclopentan-1-one (3)

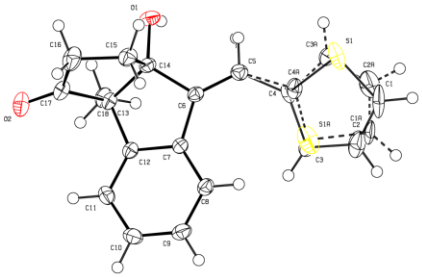


^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (t, J = 7.5 Hz, 2H), 7.51 (dd, J = 6.5, 2.5 Hz, 2H), 7.39-7.36 (m, 3H), 7.35-7.31 (m, 1H), 7.27 (d, J = 15.7 Hz, 1H), 4.91 (d, J = 3.5 Hz, 1H), 2.76-2.70 (m, 1H), 2.48 (dd, J = 18.5, 7.5 Hz, 1H), 2.26-2.23 (m, 1H), 2.18-2.13 (m, 1H), 1.80 (s, 1H), 1.62 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 218.6, 140.3, 134.8, 131.1, 129.0, 128.8, 128.7, 128.5, 127.1, 122.8, 122.1, 94.5, 89.5, 77.9, 59.6, 35.6, 27.3, 22.1. HRMS *m*/*z* (ESI+): Calculated for $C_{20}H_{18}NaO_2^+$ ($[M+Na]^+$) 313.1200, found 313.1199.


7.616
7.601
7.586
7.521
7.516
7.508
7.503
7.386
7.377
7.370
7.366
7.358
7.345
7.342
7.329
7.327
7.314
7.311
7.285
7.254
4.917
4.910
2.764
2.761
2.747
2.741
2.727
2.724
2.704
2.501
2.486
2.464
2.449
2.258
2.249
2.241
2.234
2.180
2.161
2.153
1.997
1.618
O
HO
1.99
2.00
2.99
0.99
1.02
1.02
1.02
1.03
1.02
1.02
0.99
3.00
f1 (ppm)


218.60
140.32
134.84
131.12
128.97
128.76
128.68
128.50
127.13
122.83
122.09
94.53
89.52
77.90
59.56
35.56
27.33
22.07
O
HO
f1 (ppm)

6. Crystal report of compound 2n



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 200730_thw_p22_0m

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: 200730_thw_p22_0m

Bond precision: C-C = 0.0021 A Wavelength=0.71073

Cell: a=7.349(2) b=11.275(3) c=17.533(4)
alpha=90 beta=90 gamma=90
Temperature: 170 K

	Calculated	Reported
Volume	1452.8(6)	1452.8(6)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C18 H16 O2 S	C18 H16 O2 S
Sum formula	C18 H16 O2 S	C18 H16 O2 S
Mr	296.37	296.37
Dx,g cm-3	1.355	1.355
Z	4	4
Mu (mm-1)	0.224	0.224
F000	624.0	624.0
F000'	624.75	
h,k,lmax	9,14,22	9,14,22
Nref	3192[1849]	3192
Tmin,Tmax	0.910,0.937	0.708,0.746
Tmin'	0.898	

Correction method= # Reported T Limits: Tmin=0.708 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 1.73/1.00 Theta(max)= 27.036

R(reflections)= 0.0280(3144) wR2(reflections)= 0.0748(3192)

S = 1.086 Npar= 232

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level G

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PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...         11 Report
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..............          1 Report
PLAT171_ALERT_4_G The CIF-Embedded .res File Contains EADP Records          1 Report
PLAT178_ALERT_4_G The CIF-Embedded .res File Contains SIMU Records          1 Report
PLAT230_ALERT_2_G Hirshfeld Test Diff for    S1       --C4       .        5.3 s.u.
PLAT301_ALERT_3_G Main Residue  Disorder ..............(Resd  1  )        24% Note
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..........          1 Note
PLAT791_ALERT_4_G Model has Chirality at C13         (Sohnke SpGr)         R Verify
PLAT791_ALERT_4_G Model has Chirality at C14         (Sohnke SpGr)         R Verify
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............        132 Note
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).          1 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          7 Info
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  0 ALERT level A = Most likely a serious problem - resolve or explain
  0 ALERT level B = A potentially serious problem, consider carefully
  0 ALERT level C = Check. Ensure it is not caused by an omission or oversight
 12 ALERT level G = General information/check it is not something unexpected

  0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
  3 ALERT type 2 Indicator that the structure model may be wrong or deficient
  3 ALERT type 3 Indicator that the structure quality may be low
  5 ALERT type 4 Improvement, methodology, query or suggestion
  1 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 16/07/2020; check.def file version of 12/07/2020

7. References

[1] (a) S. Yu, C. Wu and S. Ge, *J. Am. Chem. Soc.*, 2017, **139**, 6526–6529; (b) C. Wu, J. Liao and S. Ge, *Angew. Chem. Int. Ed.*, 2019, **58**, 8882–8886; (c) Z. Ding, Y. Wang, W. Liu, Y. Chen and W. Kong, *J. Am. Chem. Soc.*, 2021, **143**, 53−59.

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