Supporting Information

Lewis Acid-catalyzed Cycloaddition of Methylenecyclopropanes with Salicylaldehydes

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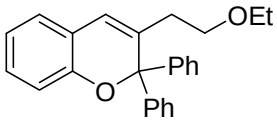
Contents

General Remarks. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-400 spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard; *J*-values are in Hz. Mass spectra were recorded by EI methods, and HRMS was measured on a Finnigan MA^+ mass spectrometer. The employed solvents were dry up by the standard procedures. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF_{254} silica gel coated plates. Flash column chromatography was carried out using 300-400 mesh silica gel at increased pressure.

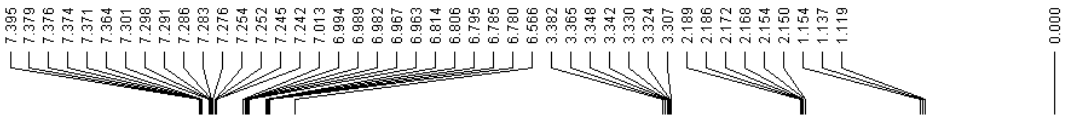
General Procedure for this Reaction.

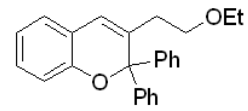
Preparation of the products 3a: Under an argon atmosphere, to a solution of salicylaldehyde **1a** (30 mg, 0.25 mmol) and $CH(OEt)_3$ (44 mg, 0.3 mmol) in 1,2-dichloroethane (DCE) $Sc(OTf)_3$ (15 mg, 0.03 mmol) was added, the reaction mixture was stirred at room temperature (20 ^{o}C) for 0.5 h. The diphenylmethylenecyclopropane **2a** (42 mg, 0.2 mmol) was added for 24 h at room temperature (monitored by TLC plates). Then the solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (SiO_2) to give the corresponding products **3a** (53 mg, 78%) as a white solid.

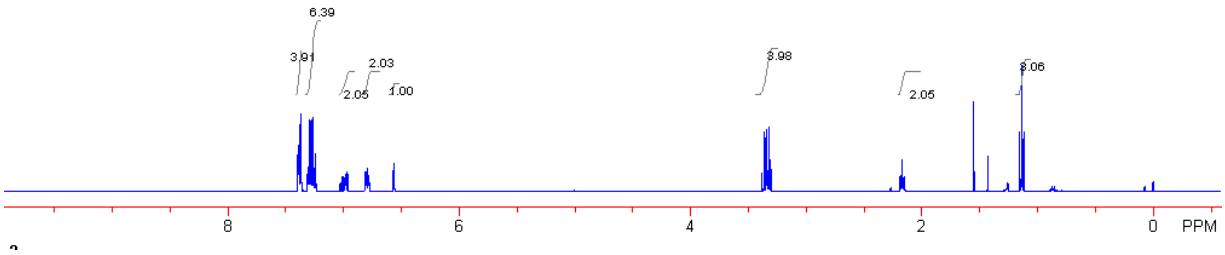
Preparation of the products 5a: Under an argon atmosphere, to a solution of salicylaldehyde **1a** (30 mg, 0.25 mmol) and $CH(OEt)_3$ (44 mg, 0.3 mmol) in 1,2-dichloroethane (DCE) $Sc(OTf)_3$ (15 mg, 0.03 mmol) was added, the reaction mixture was stirred at room temperature (20 ^{o}C) for 0.5 h. The diphenylmethylenecyclopropane **2a** (42 mg, 0.2 mmol) was added for 10 h at 60 ^{o}C (monitored by TLC plates). Then the solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (SiO_2) to give the corresponding products **5a** (63 mg, 84%) as a white solid.

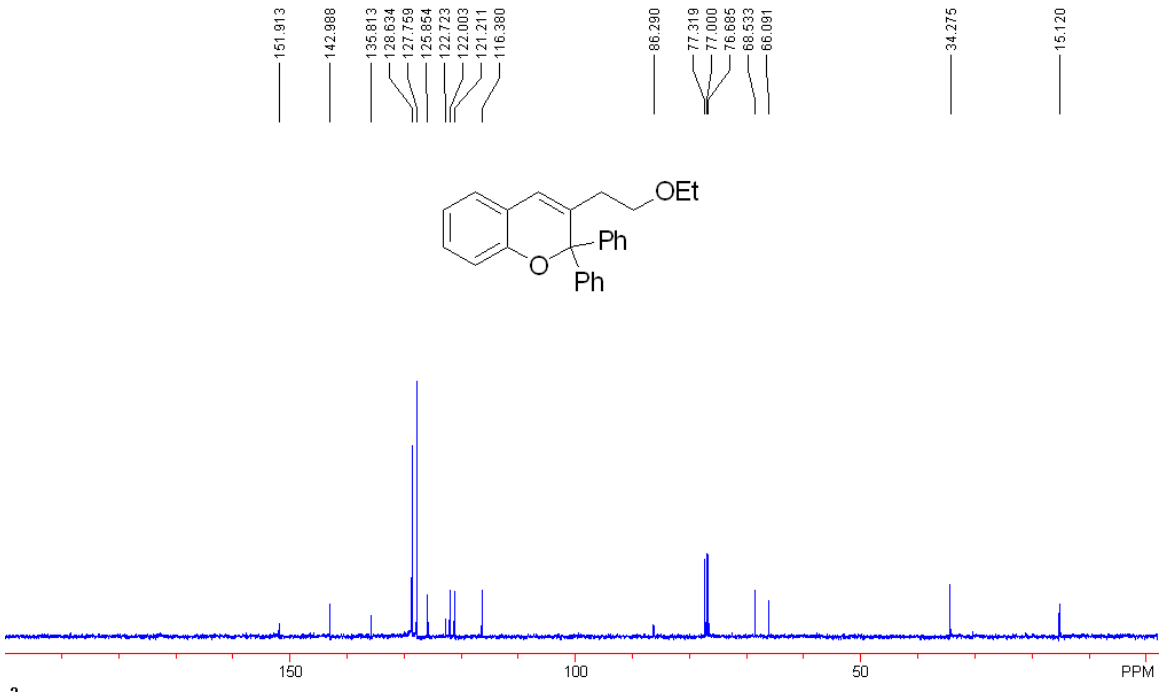


Compound 3a: A white solid, m.p. 112-114 ^{o}C; IR (CH_2Cl_2): ν 3060, 2975, 2865, 1664, 1607, 1486, 1447, 1377, 1240, 1109, 936, 847, 760 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.14 (3H, t, *J* = 6.8 Hz, CH_3), 2.17 (2H, td, *J* = 6.8, 1.2 Hz, CH_2), 3.31-3.38 (4H, m, CH_2), 6.57 (1H, s, =CH), 6.78-6.81 (2H, m, ArH), 6.96-7.03 (2H, m, ArH), 7.24-7.30 (6H, m, ArH), 7.37-7.40 (4H, m, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 15.1, 34.3, 66.1, 68.5, 86.3, 116.4, 121.2, 122.0, 122.7, 125.9, 127.8, 128.5, 128.6, 135.8, 143.0, 151.9; MS (EI) *m/z* (%): 356 (96.54) [M^+], 310 (94.81), 279 (40.45), 233 (100.00), 219 (35.99), 165 (14.66), 107 (8.70), 91 (16.63); HRMS (EI) Calcd. for $C_{25}H_{24}O_2$ (M^+) requires 356.1776, Found: 356.1777.





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135.813
128.634
127.759
125.854
122.723
122.003
121.211
116.380
86.290
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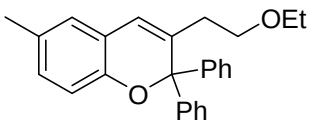
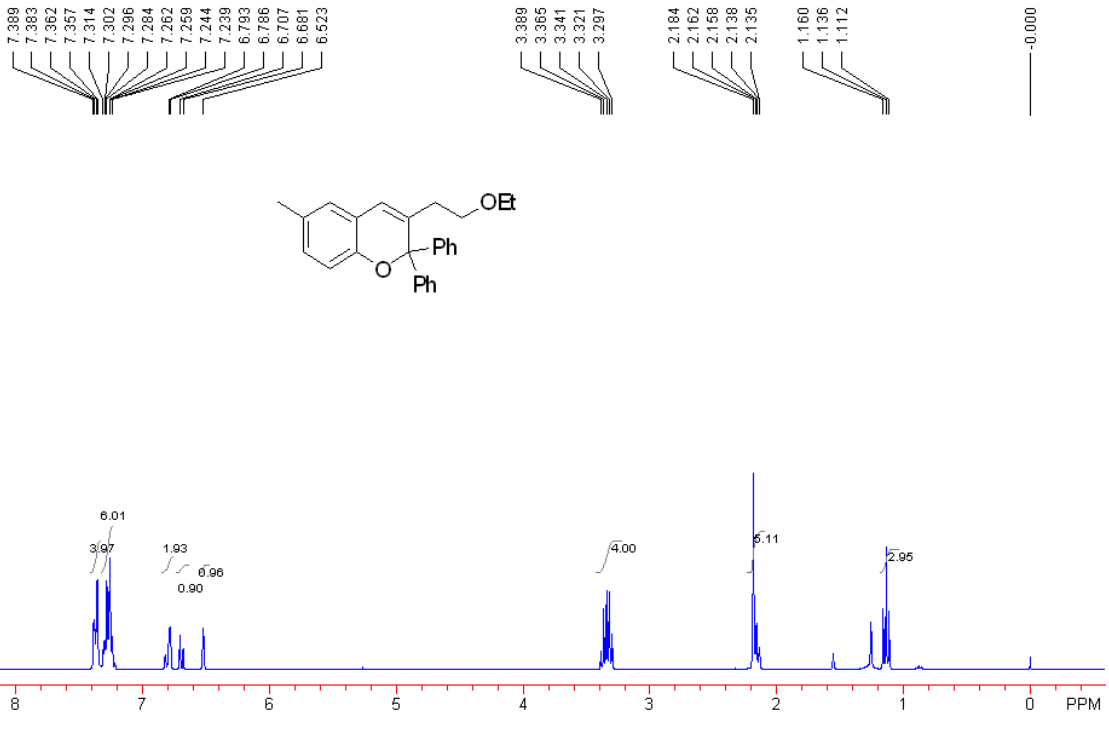
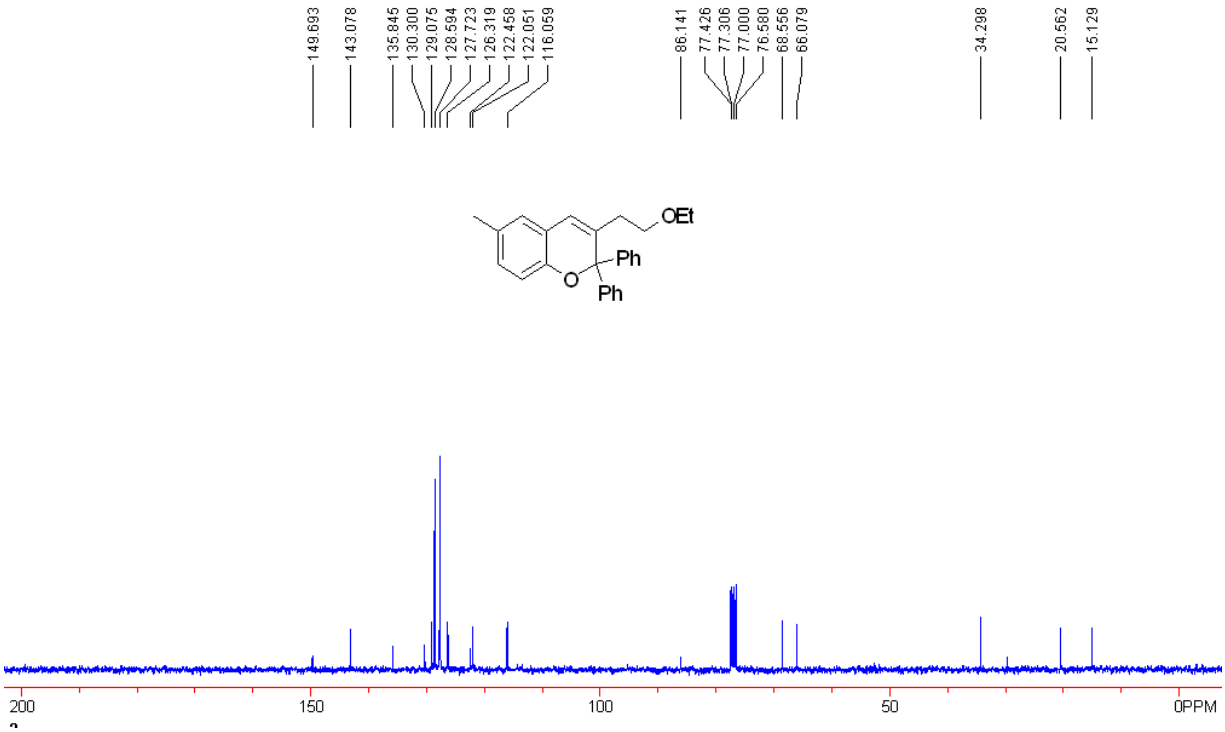
Ph
O
Ph
150
100
50
PPM



Compound 3b: A colorless oil; IR (CH_2Cl_2): ν 3060, 2974, 2865, 2800, 1601, 1583, 1480, 1414, 1263, 1227, 1082, 814, 756, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.14 (3H, t, *J* = 7.2 Hz, CH_3), 2.14-2.18 (5H, m, CH_2, CH_3), 3.30-3.39 (4H, m, CH_2), 6.52 (1H, s, =CH), 6.69 (1H, d, *J* = 7.8 Hz, ArH), 6.79-6.82 (2H, m, ArH), 7.24-7.31 (6H, m, ArH), 7.36-7.39 (4H, m, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 15.1, 20.6, 34.3, 66.1, 68.6, 86.1, 116.1, 122.1, 122.5, 126.3 127.7, 128.6, 129.1, 130.3, 135.8, 143.1, 149.7; MS (EI) *m/z* (%): 370 (100.00) [M^+], 324 (71.58), 309 (40.21), 297 (39.35), 247 (76.97), 233 (37.70), 165 (17.74), 71 (29.28); HRMS (EI) Calcd. for $C_{26}H_{26}O_2$ (M^+) requires 370.1933, Found: 370.1934.

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129.075
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127.723
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122.051
116.059
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77.306
77.000
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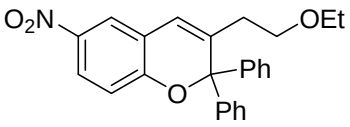
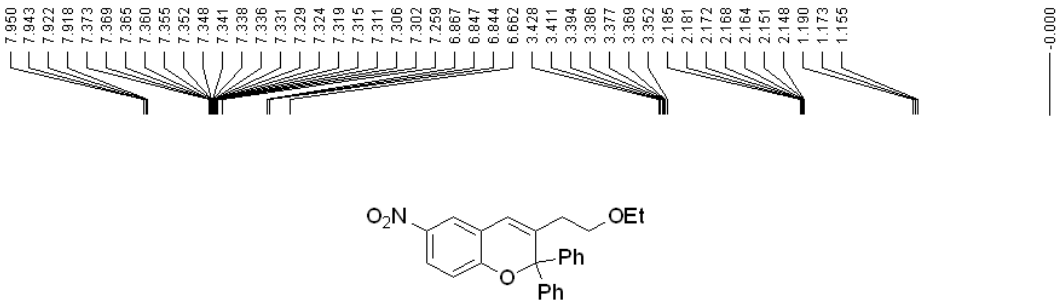
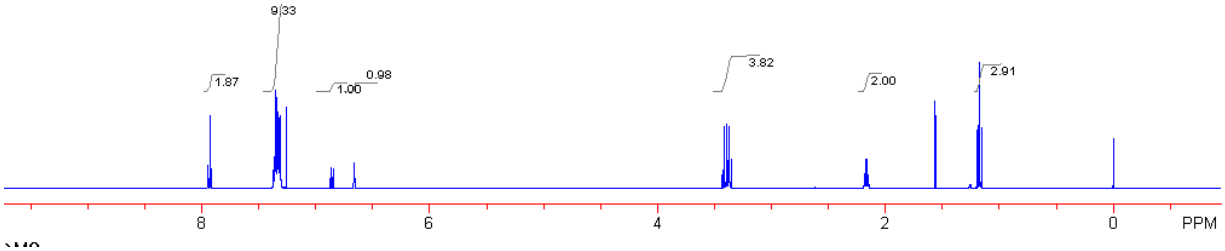
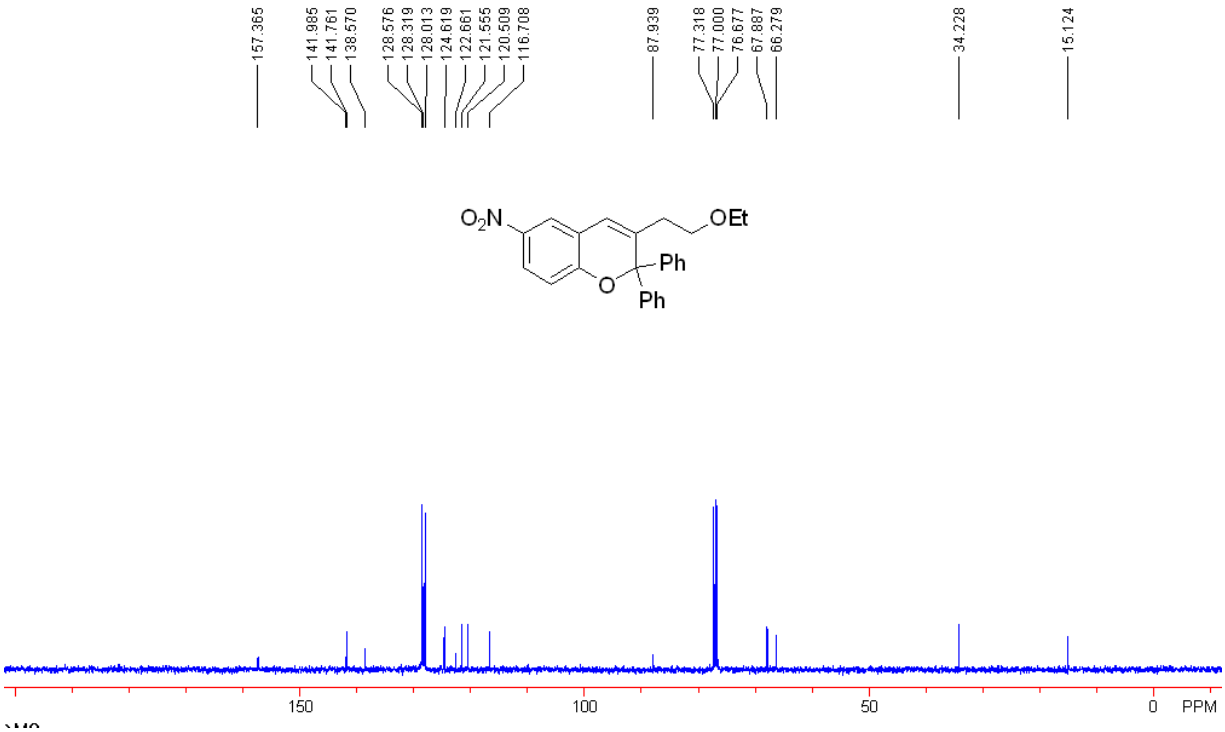
OEt
Ph
O
Ph
200
150
100
50
0PPM



Compound 3c: A colorless oil; IR (CH_2Cl_2): ν 3062, 2973, 2866, 1613, 1578, 1519, 1481, 1343, 1266, 1248, 1107, 1090, 980, 908, 832, 751, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.17 (3H, t, *J* = 7.2 Hz, CH_3), 2.17 (2H, td, *J* = 5.2, 1.2 Hz, CH_2), 3.32-3.43 (4H, m, CH_2), 6.66 (1H, s, =CH), 6.86 (1H, d, *J* = 8.0 Hz, ArH), 7.31-7.37 (10H, m, ArH), 7.92-7.95 (2H, m, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 15.1, 34.2, 66.3, 67.9, 87.9, 116.7, 120.5, 121.6, 122.7, 124.6, 128.0, 128.3, 128.6, 138.6, 141.8, 157.4; MS (EI) *m/z* (%): 401 (31.93) [M^+], 355 (100.00), 338 (31.04), 328 (26.77), 278 (68.15), 218 (15.32), 165 (15.48), 59 (27.53); HRMS (EI) Calcd. for $C_{25}H_{23}O_4N$ (M^+) requires 401.1627, Found: 401.1620.



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141.761
138.570
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128.319
128.013
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122.661
121.555
120.509
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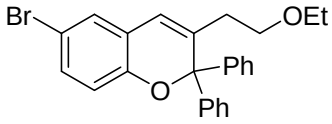
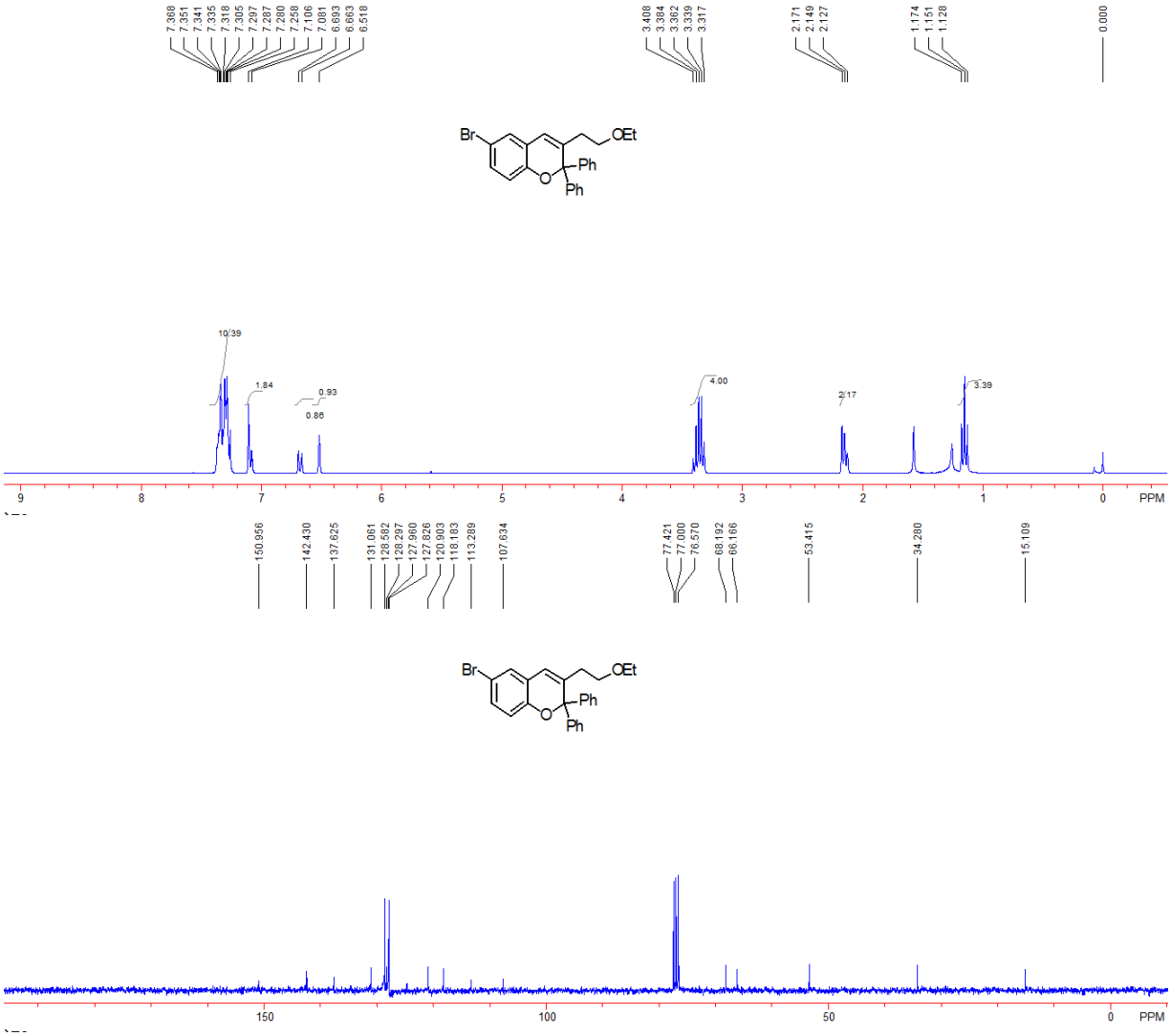
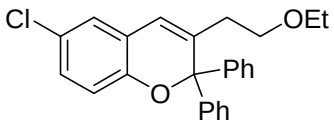
77.318
77.000
76.677
67.887
66.279
34.228
15.124
O2N
OEt
Ph
O
Ph
150
100
50
0
PPM

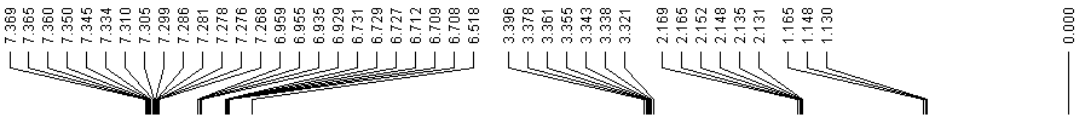


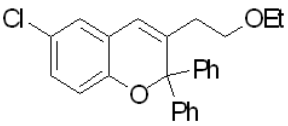
Compound 3d: A colorless oil, m.p. 116-118 ^{o}C; IR (CH_2Cl_2): ν 3059, 2973, 2864, 1477, 1446, 1224, 1107, 986, 899, 812, 755, 728, 700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.15 (3H, t, *J* = 6.9 Hz, CH_3), 2.15 (2H, t, *J* = 6.6 Hz, CH_2), 3.32-3.41 (4H, m, CH_2), 6.52 (1H, s, =CH), 6.88 (1H, d, *J* = 9.6 Hz, ArH), 7.07-7.11 (2H, m, ArH), 7.26-7.37 (10H, m, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 15.1, 34.3, 53.4, 66.2, 68.2, 107.6, 113.3, 118.2, 120.9, 127.8, 128.0, 128.3, 128.6, 131.1, 137.6, 142.4, 151.0; MS (EI) *m/z* (%): 434 (60.52) [M^+], 388 (94.07), 309 (100.00), 296 (94.45), 252 (37.43), 218 (55.84), 165 (38.69), 91 (33.41); HRMS (EI) Calcd. for $C_{25}H_{23}O_2Br$ (M^+) requires 434.0881, Found: 434.0874.

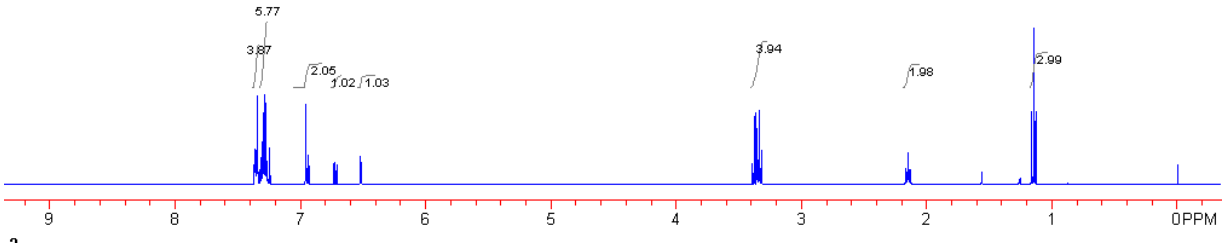


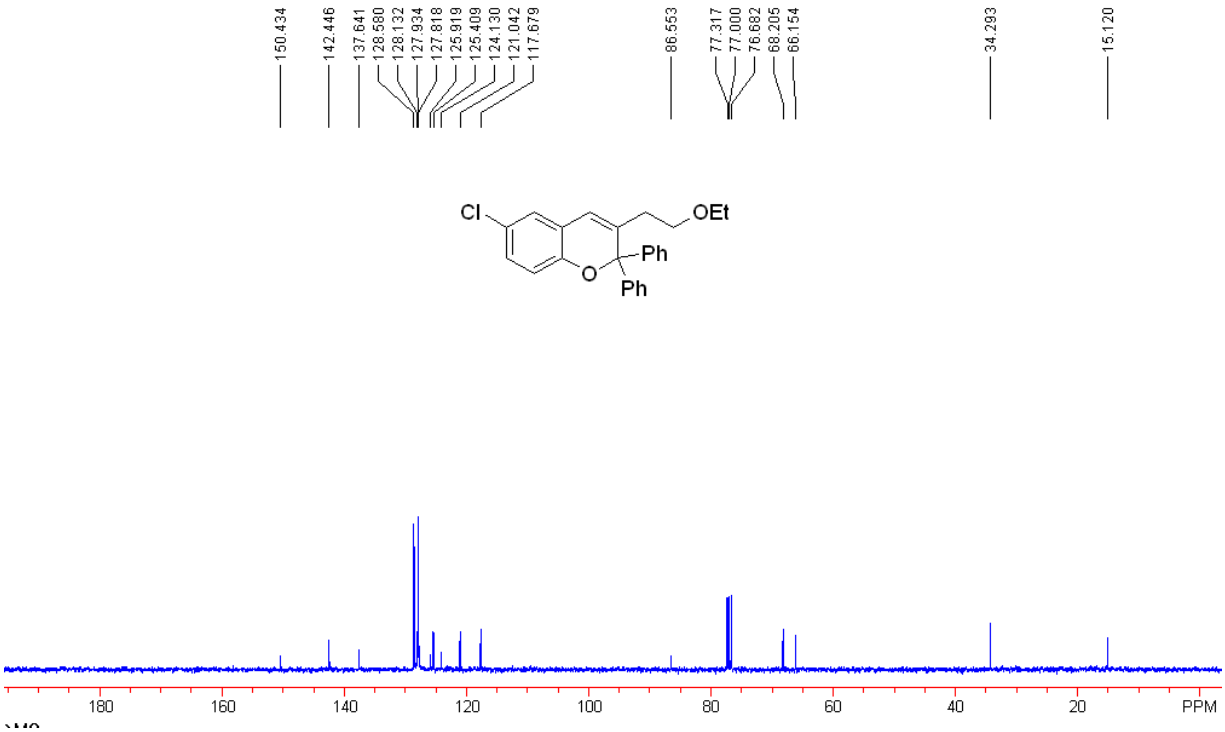


Compound 3e: A colorless oil; IR (CH_2Cl_2): ν 3060, 2974, 2865, 2800, 1956, 1601, 1583, 1480, 1446, 1263, 1227, 1108, 987, 903, 885, 757 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.15 (3H, t, *J* = 7.2 Hz, CH_3), 2.15 (2H, td, *J* = 7.2, 1.6 Hz, CH_2), 3.32-3.40 (4H, m, CH_2), 6.52 (1H, s, =CH), 6.71-6.73 (1H, m, ArH), 6.93-6.96 (2H, m, ArH), 7.24-7.37 (10H, m, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 15.1, 34.3, 66.2, 68.2, 86.6, 117.7, 121.0, 124.1, 125.4, 125.9, 127.8, 127.9, 128.1, 128.6, 137.6, 142.4, 150.4; MS (EI) *m/z* (%): 390 (5.11) [M^+], 370 (4.79), 309 (8.95), 267 (9.13), 203 (8.70), 155 (10.31), 85 (56.27), 57 (100.00); HRMS (EI) Calcd. for $C_{25}H_{23}O_2Cl$ (M^+) requires 390.1387, Found: 390.1395.





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77.317
77.000
76.682
68.205
66.154
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OEt
Ph
O
Ph
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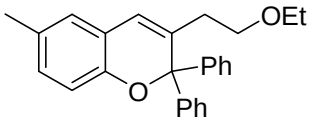
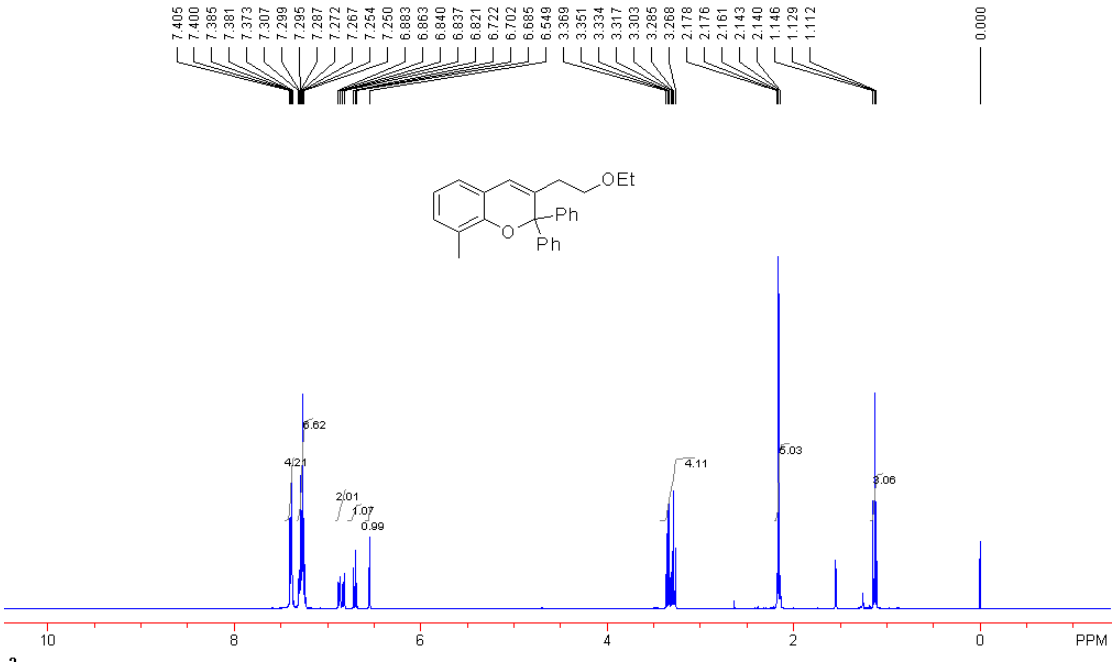
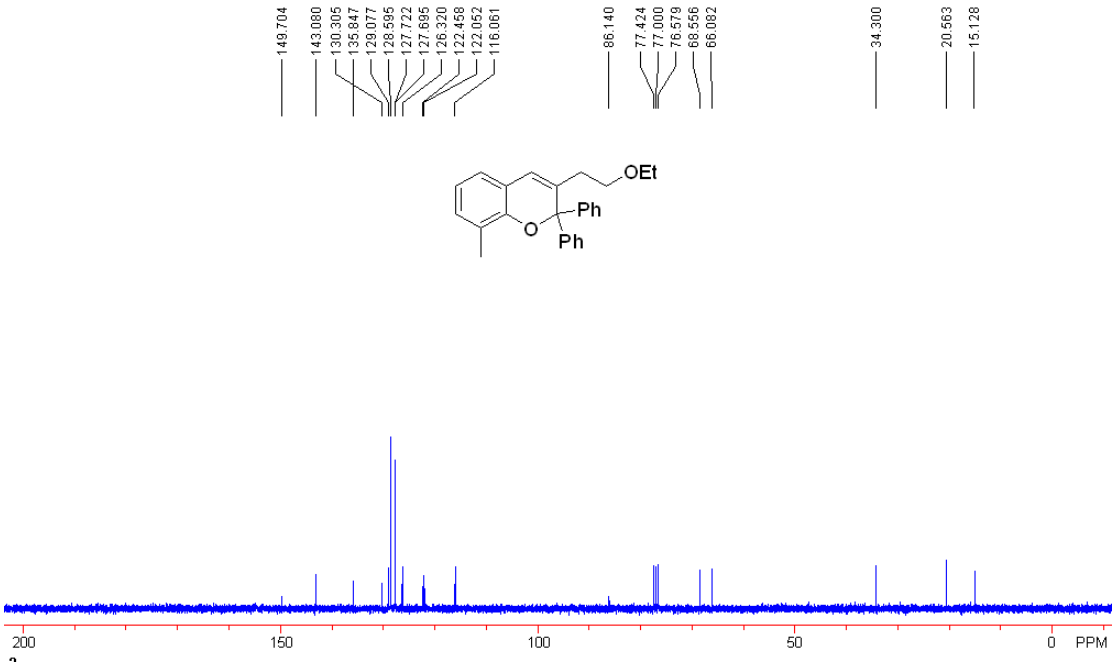
160
140
120
100
80
60
40
20
PPM



Compound 3f: A colorless oil; IR (CH_2Cl_2): ν 3060, 2974, 2865, 2800, 1601, 1583, 1480, 1414, 1263, 1227, 1082, 814, 756, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.13 (3H, t, *J* = 6.8 Hz, CH_3), 2.14-2.18 (2H, m, CH_2), 2.16 (3H, s, CH_3), 3.27-3.37 (4H, m, CH_2), 6.55 (1H, s, =CH), 6.70 (1H, t, *J* = 8.0 Hz, ArH), 6.82-6.88 (2H, m, ArH), 7.25-7.31 (6H, m, ArH), 7.37-7.41 (4H, m, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 15.1, 20.6, 34.3, 66.1, 68.6, 86.1, 116.1, 122.1, 122.5, 126.3 127.7, 128.6, 129.1, 130.3, 135.8, 143.1, 149.7; MS (EI) *m/z* (%): 370 (100.00) [M^+], 324 (71.58), 309 (40.21), 297 (39.35), 247 (76.97), 233 (37.70), 165 (17.74), 71 (29.28); HRMS (EI) Calcd. for $C_{26}H_{26}O_2$ (M^+) requires 370.1933, Found: 370.1934.

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77.424
77.000
76.579
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20.563
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OEt
Ph
O
Ph
200
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100
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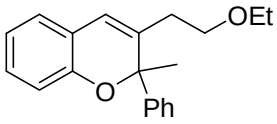
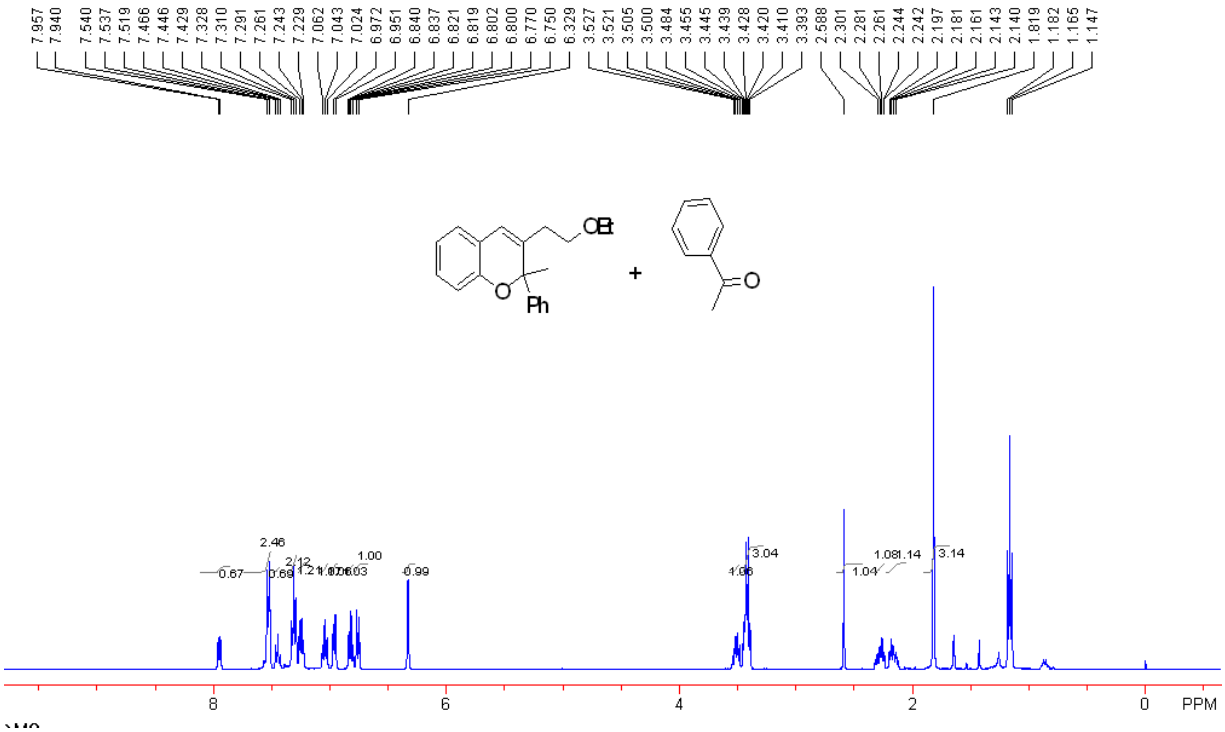
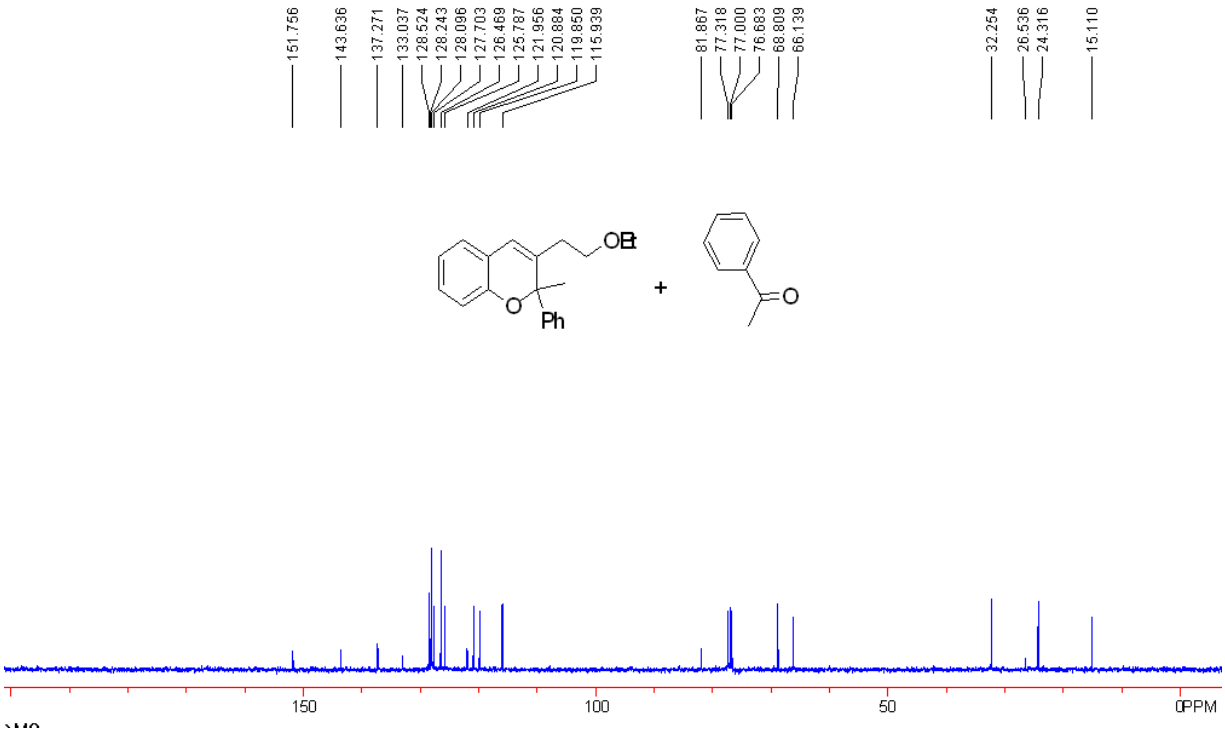
0
PPM



Compound 3g having some acetophenone: A colorless oil; IR (CH_2Cl_2): ν 3059, 2975, 2866, 2801, 1686, 1578, 1486, 1374,1245, 1109, 1027, 930, 753, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.17 (3H, t, *J* = 6.8 Hz, CH_3), 1.82 (3H, s, CH_3), 2.14-2.20 (1H, m, CH_2), 2.24-2.30 (3H, m, CH_2), 3.39-3.46 (3H, m, CH_2), 3.45-3.54 (1H, m, CH_2), 6.33 (1H, s, =CH), 6.76 (1H, d, *J* = 8.0 Hz, ArH), 6.80-6.84 (1H, m, ArH), 6.96 (1H, d, *J* = 8.4 Hz, ArH), 7.02-7.07 (1H, m, ArH), 7.31 (3H, t, *J* = 7.2 Hz, ArH), 7.53 (2H, d, *J* = 7.2 Hz, ArH); having some acetophenone ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 2.59 (3H, s, CH_3), 7.24 (2H, t, *J* = 7.2 Hz, ArH), 7.45 (1H, t, *J* = 7.2 Hz, ArH), 7.94 (2H, d, *J* = 8.4 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 15.1, 24.3, 26.5, 32.2, 66.1, 68.8, 81.9, 115.9, 119.8, 120.9, 121.9, 125.8, 126.5, 127.7, 128.1, 128.2, 128.5, 133.0, 137.3, 143.6, 151.7; MS (EI) *m/z* (%): 294 (38.13) [M^+], 279 (100.00), 235 (24.21), 217 (28.84), 173 (6.43), 141 (8.21), 91 (15.67), 43 (16.63); HRMS (EI) Calcd. for $C_{20}H_{22}O_2$ (M^+) requires 294.1620, Found: 294.1621.

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137.271
133.037
128.524
128.243
128.096
127.703
126.469
125.787
121.956
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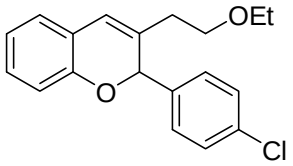
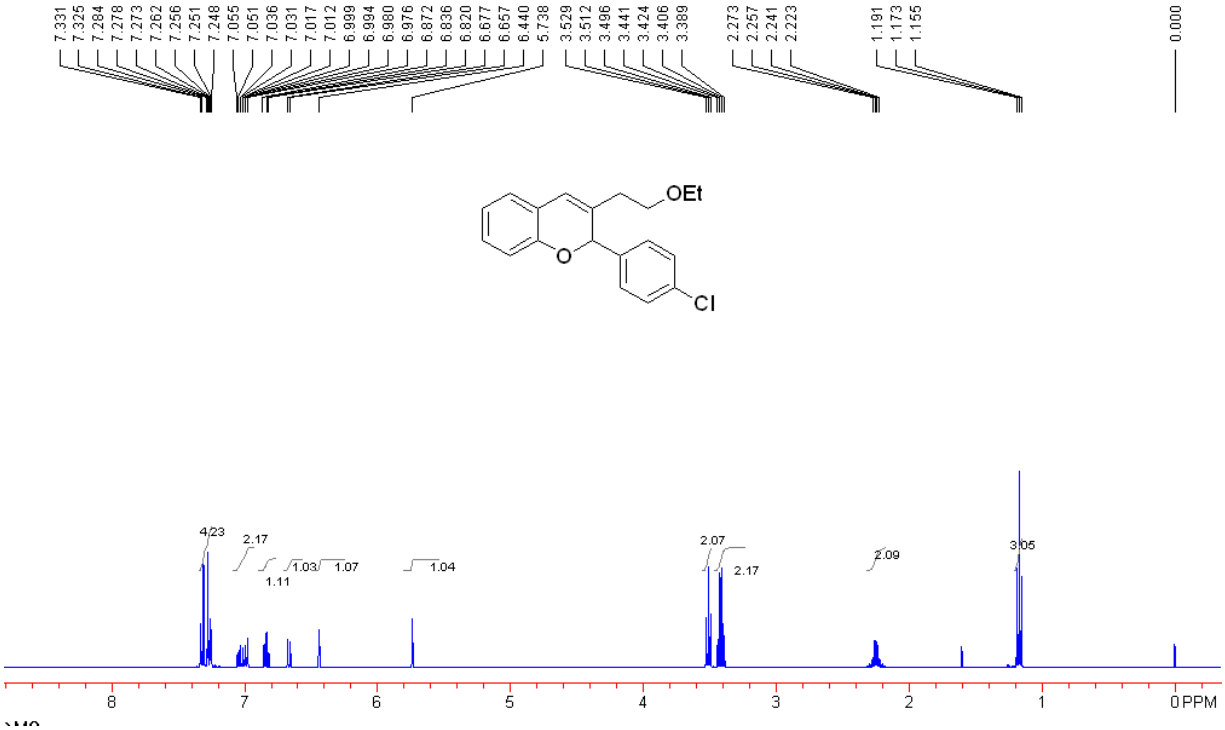
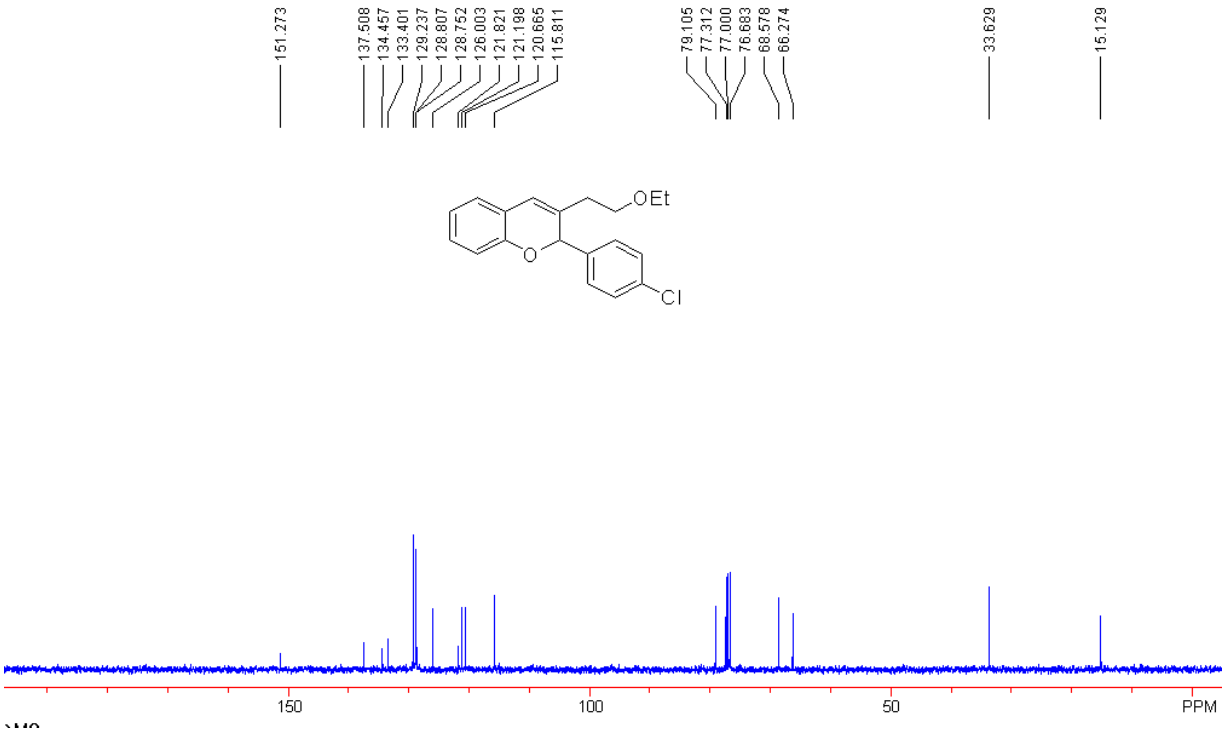
119.850
115.939
81.867
77.318
77.000
76.683
68.809
66.139
32.254
26.536
24.316
15.110
OEt
O
Ph
+
O
150
100
50
0PPM



Compound 3h: A colorless oil; IR (CH_2Cl_2): ν 3422, 2974, 2866, 2801, 1906, 1774, 1741, 1593, 1492, 1378, 997, 835, 737, 703 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.17 (3H, t, *J* = 7.2 Hz, CH_3), 2.22-2.27 (2H, m, CH_2), 3.41 (2H, q, *J* = 7.2 Hz, CH_2), 3.51 (2H, t, *J* = 7.2 Hz, CH_2), 5.74 (1H, s, CH), 6.44 (1H, s, =CH), 6.67 (1H, d, *J* = 8.0 Hz, ArH), 6.82-6.86 (1H, m, ArH), 6.98-7.06 (2H, m, ArH), 7.25-7.33 (4H, m, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 15.1, 33.6, 66.3, 68.6, 79.1, 115.8, 120.7, 121.2, 121.8, 126.0, 128.7, 128.8, 129.2, 133.4, 134.5, 137.5, 151.3; MS (EI) *m/z* (%): 314 (9.44) [M^+], 139 (100.00), 113 (12.26), 111 (20.14), 85 (17.00), 71 (19.69), 57 (31.44), 43 (15.16); HRMS (EI) Calcd. for $C_{19}H_{19}O_2Cl$ (M^+) requires 314.1074, Found: 314.1070.




151.273
137.508
134.457
133.401
129.237
128.807
128.752
126.003
121.821
121.198
120.665
115.811
79.105
77.312
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76.683
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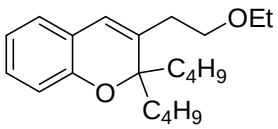
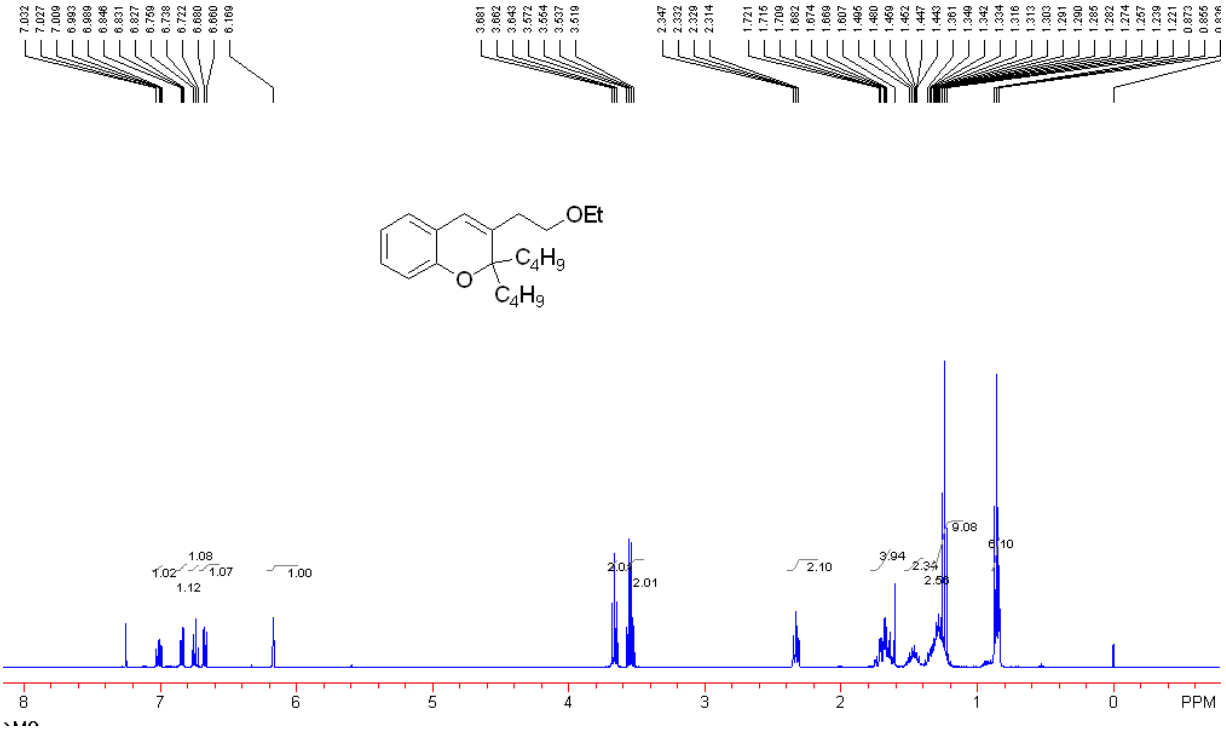
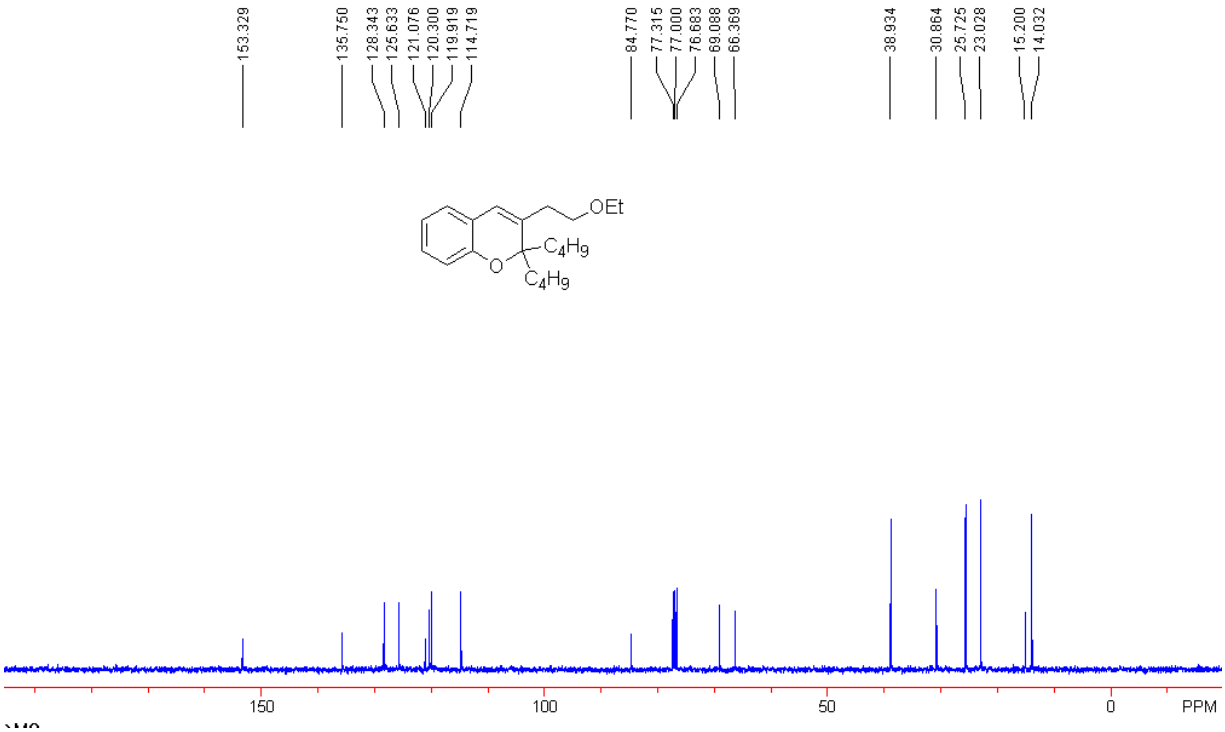
33.629
15.129
OEt
O
Cl
150
100
50
PPM



Compound 3i: A colorless oil; IR (CH_2Cl_2): ν 3024, 2956, 2870, 1606, 1580, 1488, 1378, 1246, 1224, 1112, 1030, 925, 871, 749 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 0.86 (6H, t, *J* = 7.2 Hz, CH_3), 1.22-1.36 (9H, m, CH_2), 1.43-1.50 (2H, m, CH_2), 1.64-1.74 (4H, m, CH_2), 2.31-2.35 (2H, m, CH_2), 3.54 (2H, q, *J* = 7.2 Hz, CH_2), 3.66 (2H, t, *J* = 6.0 Hz, CH_2), 6.17 (1H, s, =CH), 6.67 (1H, d, *J* = 8.0 Hz, ArH), 6.72-6.76 (1H, m, ArH), 6.83-6.85 (1H, m, ArH), 6.99-7.03 (1H, m, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 14.0, 15.2, 23.0, 25.7, 30.9, 38.9, 66.4, 69.1, 84.8, 114.7, 119.9, 120.3, 121.1, 125.6, 128.3, 135.8, 153.3; MS (EI) *m/z* (%): 316 (3.60) [M^+], 259 (100.00), 213 (5.20), 171 (6.63), 145 (5.50), 131 (6.57), 71 (5.08), 41 (7.37); HRMS (EI) Calcd. for $C_{21}H_{32}O_2$ (M^+) requires 316.2402, Found: 316.2405.




153.329
135.750
128.343
125.633
121.076
120.300
119.919
114.719
84.770
77.315
77.000
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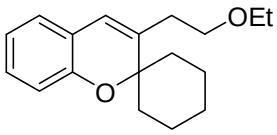
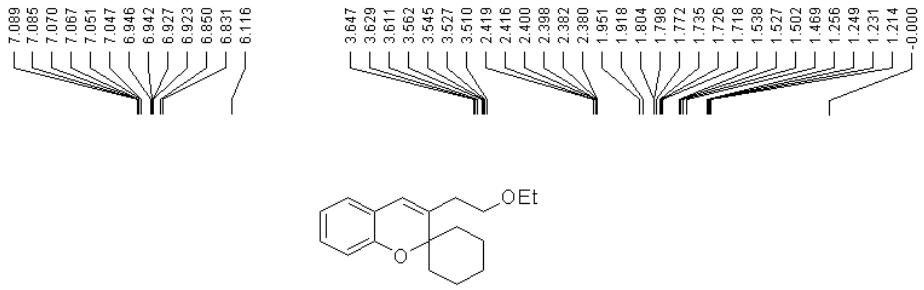
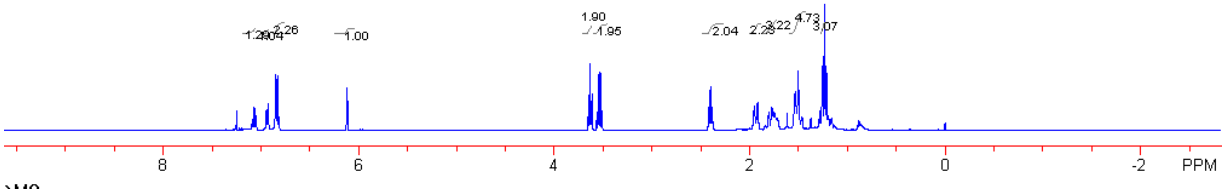
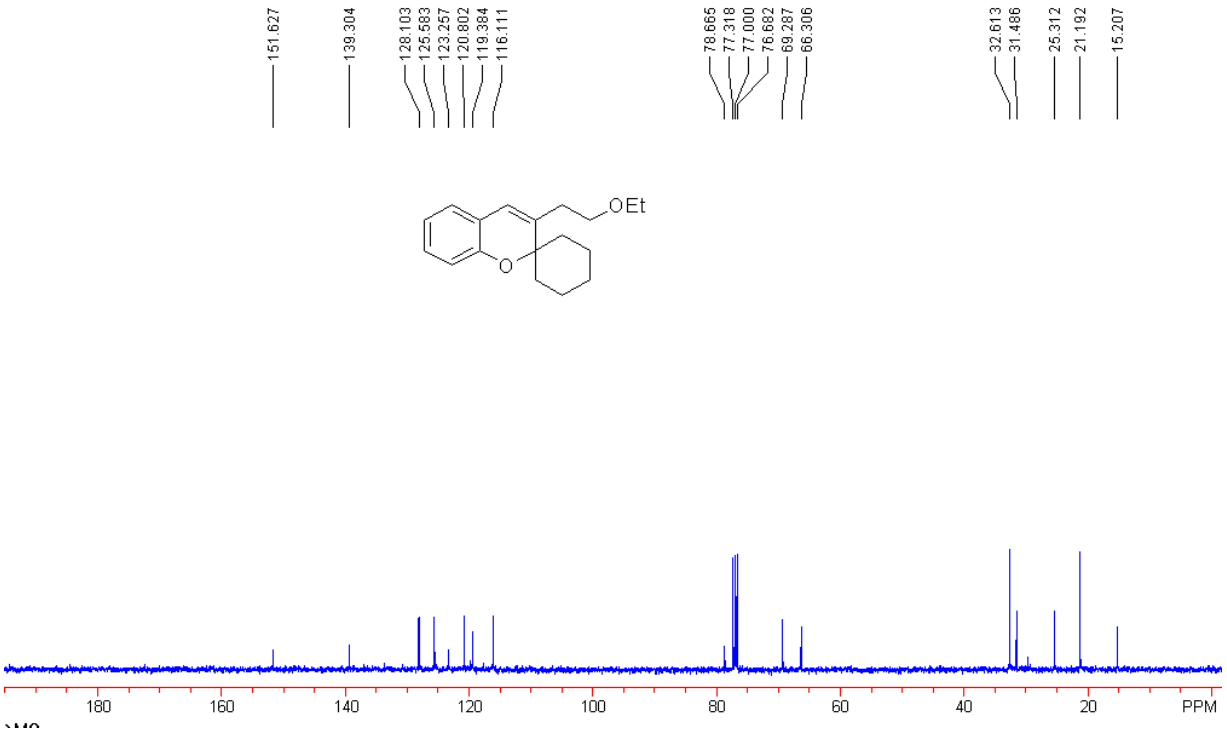
69.088
66.369
38.934
30.864
25.725
23.028
15.200
14.032
OEt
C4H9
C4H9
O
150
100
50
0
PPM



Compound 3j: A colorless oil; IR (CH_2Cl_2): ν 3024, 2930, 2861, 1665, 1577, 1486, 1455, 1273, 1111, 956, 931, 852, 752, 736 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.23 (3H, t, *J* = 7.2 Hz, CH_3), 1.46-1.54 (5H, m, CH_2), 1.72-1.80 (3H, m, CH_2), 1.91-1.95 (2H, m, CH_2), 2.38-2.42 (2H, m, CH_2), 3.53 (2H, q, *J* = 7.2 Hz, CH_2), 3.63 (2H, t, *J* = 7.2 Hz, CH_2), 6.12 (1H, s, =CH), 6.82-6.85 (2H, m, ArH), 6.93 (1H, d, *J* = 7.6 Hz, ArH), 7.05-7.09 (1H, m, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 15.2, 21.2, 25.3, 31.5, 32.6, 66.3, 69.3, 78.7, 116.1, 119.4, 120.8, 123.3, 125.6, 128.1, 139.3, 151.6; MS (EI) *m/z* (%): 272 (88.15) [M^+], 243 (100.00), 229 (87.92), 201 (81.09), 185 (83.82), 131 (31.24), 84 (38.45), 49 (50.19); HRMS (EI) Calcd. for $C_{18}H_{24}O_2$ (M^+) requires 272.1776, Found: 272.1772.






151.627
139.304
128.103
125.583
123.257
120.802
119.384
116.111
78.665
77.318
77.000
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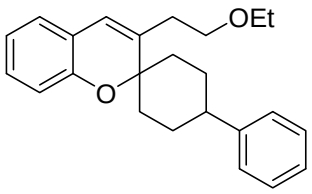
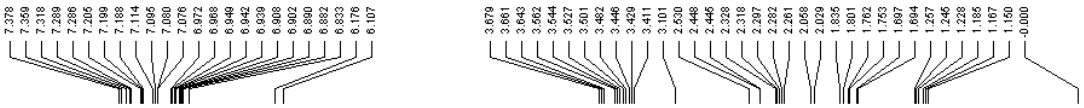
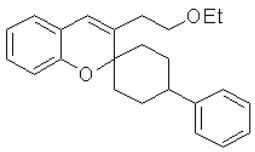
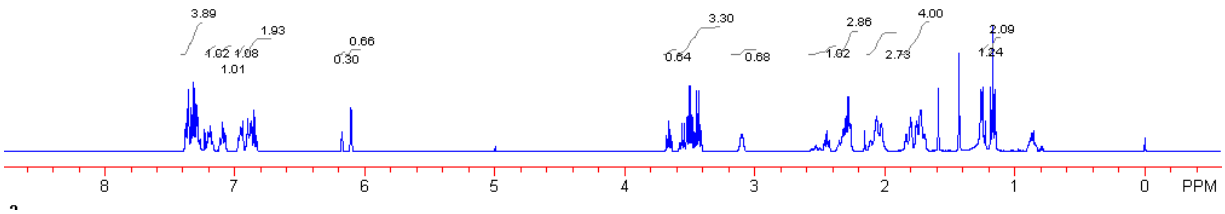
69.287
66.306
32.613
31.486
25.312
21.192
15.207
OEt
O
180
160
140
120
100
80
60
40
20
PPM

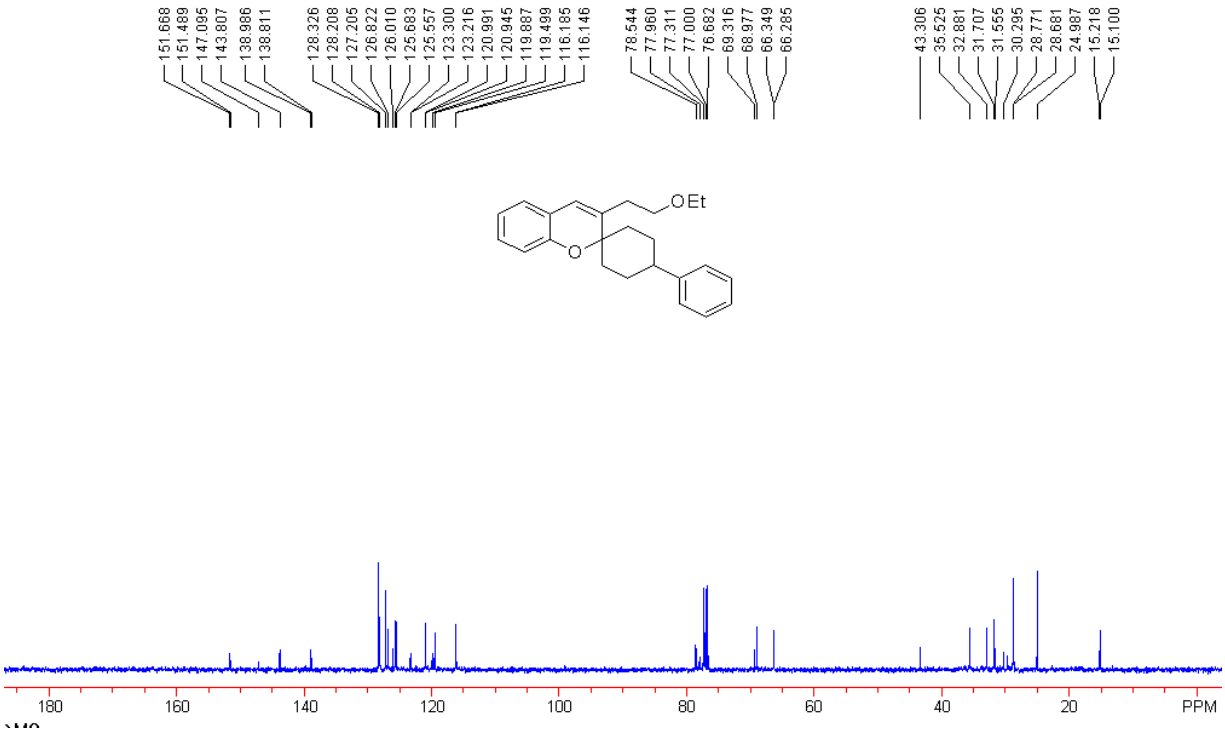


Compound 3k (a diastereoisomeric mixture, ratio = 2:1): A colorless oil; IR (CH_2Cl_2): ν 3058, 2930, 2866, 1603, 1577, 1455, 1375, 1224, 1111, 948, 754, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.17 (2H, t, *J* = 7.2 Hz, CH_3), 1.25 (1H, t, *J* = 7.2 Hz, CH_3), 1.69-1.84 (4H, m, CH_2), 2.03-2.07 (3H, m, CH_2), 2.26-2.33 (3H, m, CH), 2.43-2.47 (0.66H, m, CH), 2.50-2.54 (0.33H, m, CH), 3.43 (1.32H, q, *J* = 7.2 Hz, CH_2), 3.50 (1.32H, t, *J* = 7.2 Hz, CH_2), 3.55 (0.66H, q, *J* = 7.2 Hz, CH_2), 3.66 (0.66H, t, *J* = 7.2 Hz, CH_2), 6.11 (0.66H, s, =CH), 6.18 (0.33H, s, =CH), 6.83-6.97 (3H, m, ArH), 7.08-7.10 (1H, m, ArH), 7.19-7.21 (1H, m, ArH), 7.23-7.38 (4H, m, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 15.1, 15.2, 25.0, 28.7, 28.8, 30.3, 31.6, 31.7, 32.9, 35.5, 43.3, 66.2, 66.3, 69.0, 69.3, 78.0, 78.5, 116.1, 116.2, 119.5, 119.9, 120.9, 121.0, 123.3, 125.6, 125.7, 126.0, 126.8, 127.2, 128.20, 128.24, 128.3, 138.3, 138.8, 139.0, 143.8, 147.1, 151.5, 151.7; MS (EI) *m/z* (%): 348 (11.59) [M^+], 229 (100.00), 183 (13.41), 172 (12.68), 128 (6.84), 115 (6.35), 107 (3.18), 91 (8.05); HRMS (EI) Calcd. for $C_{24}H_{28}O_2$ (M^+) requires 348.2089, Found: 348.2085.








151.668
151.489
147.095
143.807
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138.811
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128.208
127.205
126.822
126.010
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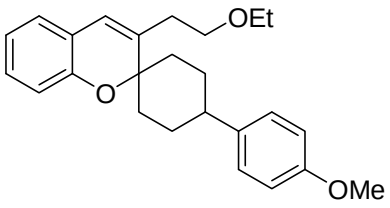
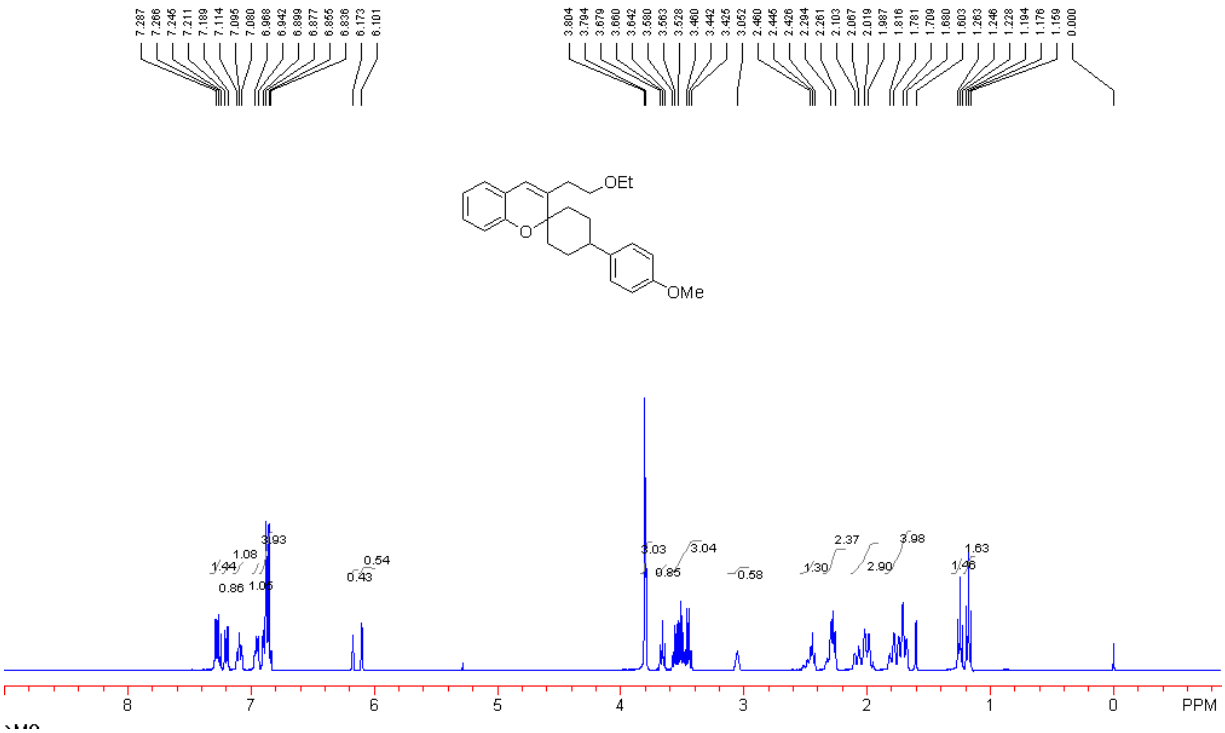
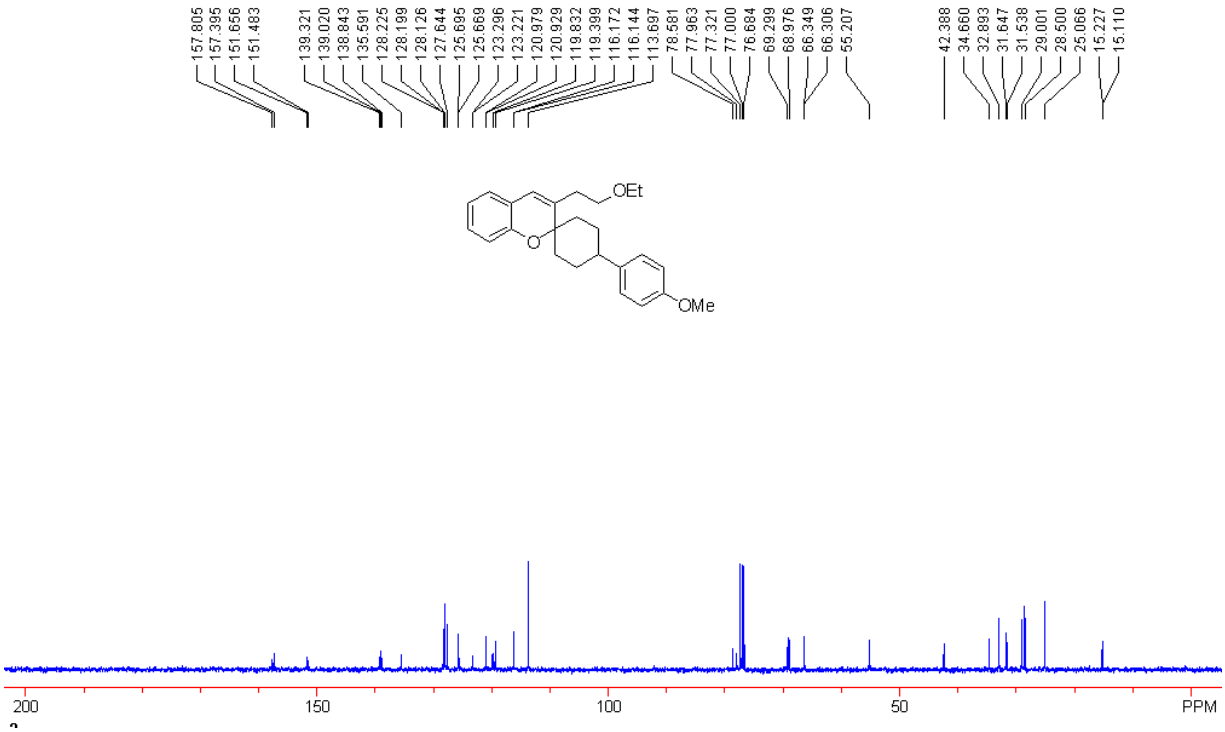
125.557
123.300
123.216
120.991
120.945
119.887
119.499
116.185
116.146
78.544
77.960
77.311
77.000
76.682
69.316
68.977
66.349
66.285
43.306
35.525
32.881
31.707
31.555
30.295
28.771
28.681
24.987
15.218
15.100
OEt
O
180
160
140
120
100
80
60
40
20
PPM



Compound 3l (a diastereoisomeric mixture, ratio = 1.6:1.4): A colorless oil; IR (CH_2Cl_2): ν 3037, 2933, 2865, 1609, 1512, 1486, 1455, 1253, 1181, 1110, 948, 836, 753, 737 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.18 (1.6H, t, *J* = 7.2 Hz, CH_3), 1.25 (1.4H, t, *J* = 7.2 Hz, CH_3), 1.68-1.82 (4H, m, CH_2), 1.99-2.10 (3H, m, CH_2), 2.26-2.33 (2H, m, CH_2), 2.43-2.48 (1.47H, m, CH_2), 3.05 (0.53H, s, CH_2), 3.43-3.58 (3H, m, CH_2), 3.66 (1H, t, *J* = 7.2 Hz, CH_2), 3.79 (1.4H, s, OCH_3), 3.80 (1.6H, s, OCH_3), 6.10 (0.53H, s, =CH), 6.17 (0.47H, s, =CH), 6.84-6.90 (4H, m, ArH), 6.94-6.97 (1H, m, ArH), 7.10 (1H, t, *J* = 8.8 Hz, ArH), 7.20 (1H, d, *J* = 8.8 Hz, ArH), 7.27 (1H, d, *J* = 7.6 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 15.1, 15.2, 25.1, 28.5, 29.0, 31.5, 31.6, 32.9, 34.7, 42.4, 55.2, 66.3, 66.4, 69.0, 69.3, 78.0, 78.6, 113.7, 116.1, 116.2, 119.4, 119.8, 120.9, 121.0, 123.2, 123.3, 125.6, 125.7, 127.6, 128.12, 128.19, 128.2, 135.6, 138.8, 139.0, 139.3, 151.5, 151.7, 157.4, 157.8; MS (EI) *m/z* (%): 378 (14.00) [M^+], 229 (100.00), 183 (10.38), 172 (12.20), 134 (7.10), 121 (5.66), 107 (2.47), 91 (5.01); HRMS (EI) Calcd. for $C_{25}H_{30}O_3$ (M^+) requires 378.2195, Found: 378.2192.




157.805
157.395
151.656
151.483
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139.020
138.843
135.591
128.225
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125.695
125.669
123.296
123.221
120.979
120.929
119.832
119.399
116.172
116.144
113.697
78.581
77.963
77.321
77.000
76.684
69.299
68.976
66.349
66.306
55.207
42.388
34.660
32.893
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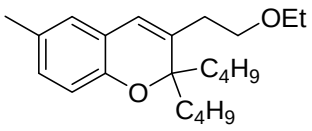
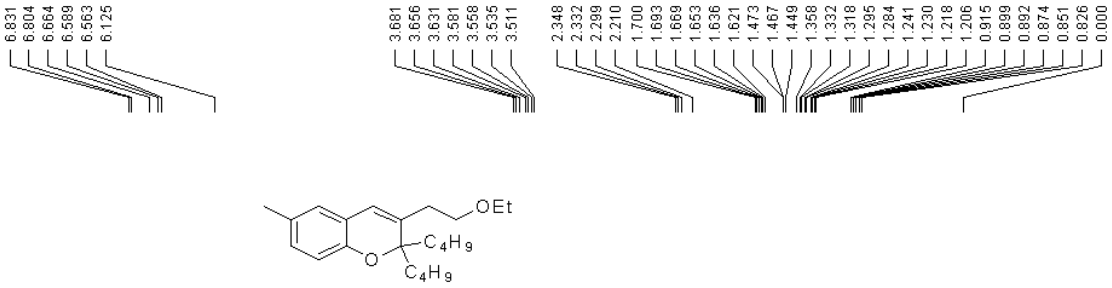
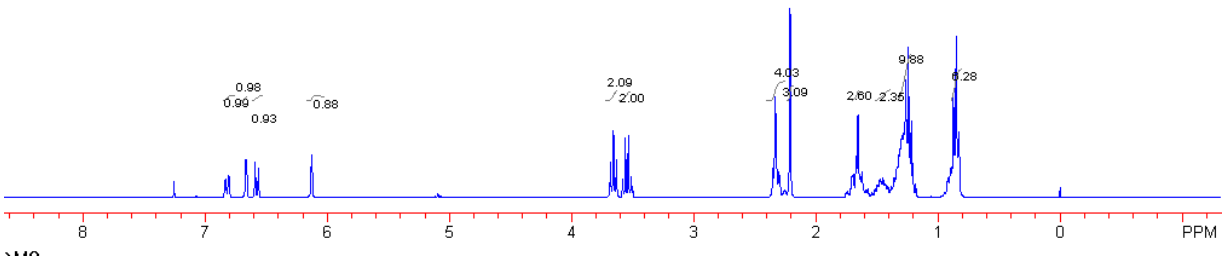
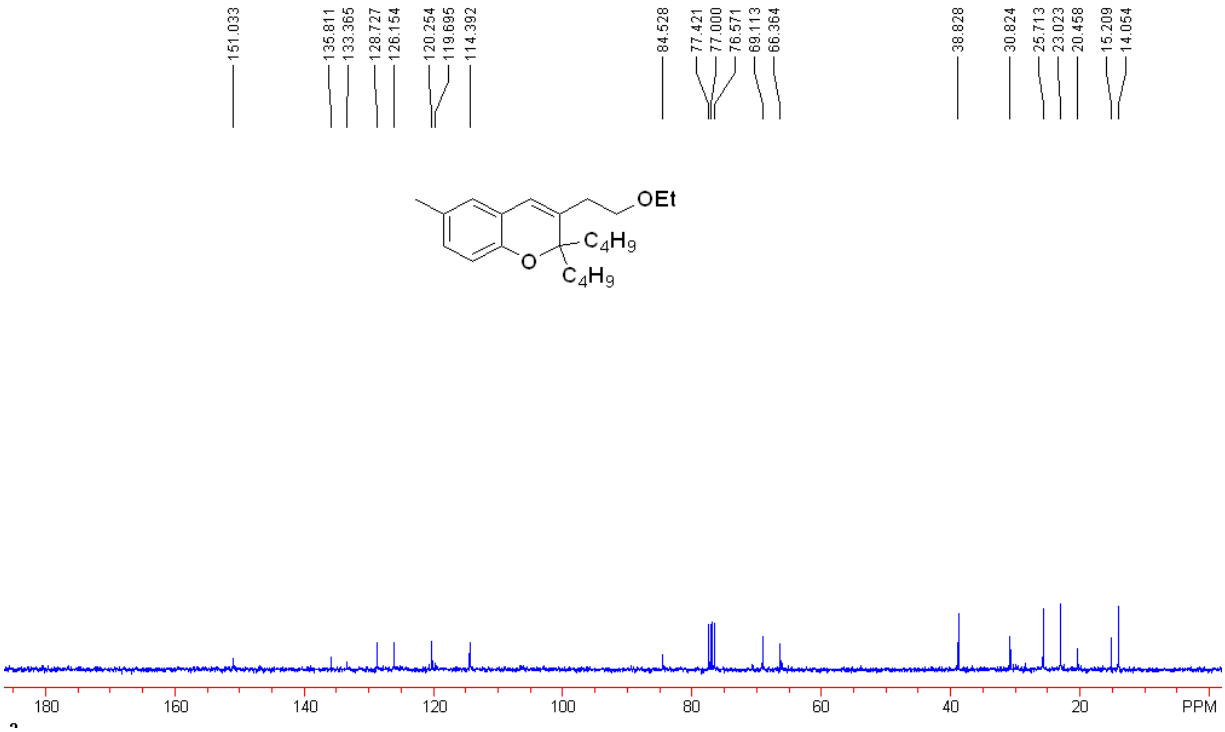
OEt
O
OMe
200
150
100
50
PPM



Compound 3m: A colorless oil; IR (CH_2Cl_2): ν 2957, 2864, 1659, 1589, 1495, 1467, 1271, 1227, 1114, 996, 887, 813, 732 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 0.85 (3H, t, *J* = 7.2 Hz, CH_3), 1.21-1.28 (9H, m, CH_2, CH_3), 1.43-1.50 (2H, m, CH_2), 1.65-1.70 (2H, m, CH_2), 2.21 (3H, s, CH_3), 2.33 (2H, t, *J* = 7.5 Hz, CH_2), 3.54 (2H, q, *J* = 7.2 Hz, CH_2), 3.66 (2H, t, *J* = 7.5 Hz, CH_2), 6.13 (1H, s, =CH), 6.57 (1H, d, *J* = 7.8 Hz, ArH), 6.66 (1H, s, ArH), 6.81 (1H, d, *J* = 8.1 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 14.1, 15.2, 20.5, 23.0, 25.7, 30.8, 38.8, 66.4, 69.1, 84.5, 114.4, 119.7, 120.3, 126.2, 128.7, 133.4, 135.8, 151.0; MS (EI) *m/z* (%): 330 (4.92) [M^+], 273 (100.00), 227 (4.14), 185 (5.62), 159 (3.79), 145 (5.62), 121 (4.34), 71 (6.62); HRMS (EI) Calcd. for $C_{22}H_{34}O_2$ (M^+) requires 330.2559, Found: 330.2557.






151.033
135.811
133.365
128.727
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120.254
119.695
114.392
84.528
77.421
77.000
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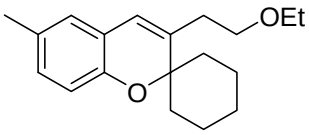
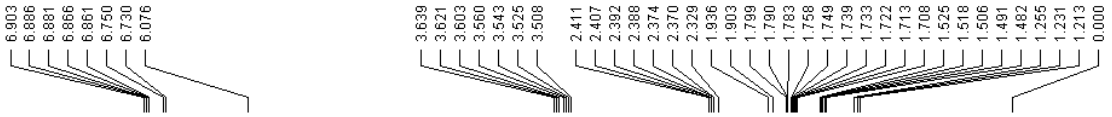
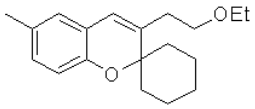
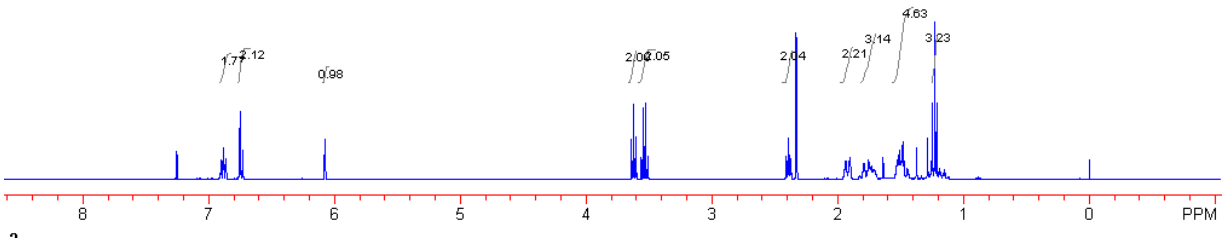
69.113
66.364
38.828
30.824
25.713
23.023
20.458
15.209
14.054
OEt
C4H9
O
C4H9
180
160
140
120
100
80
60
40
20
PPM

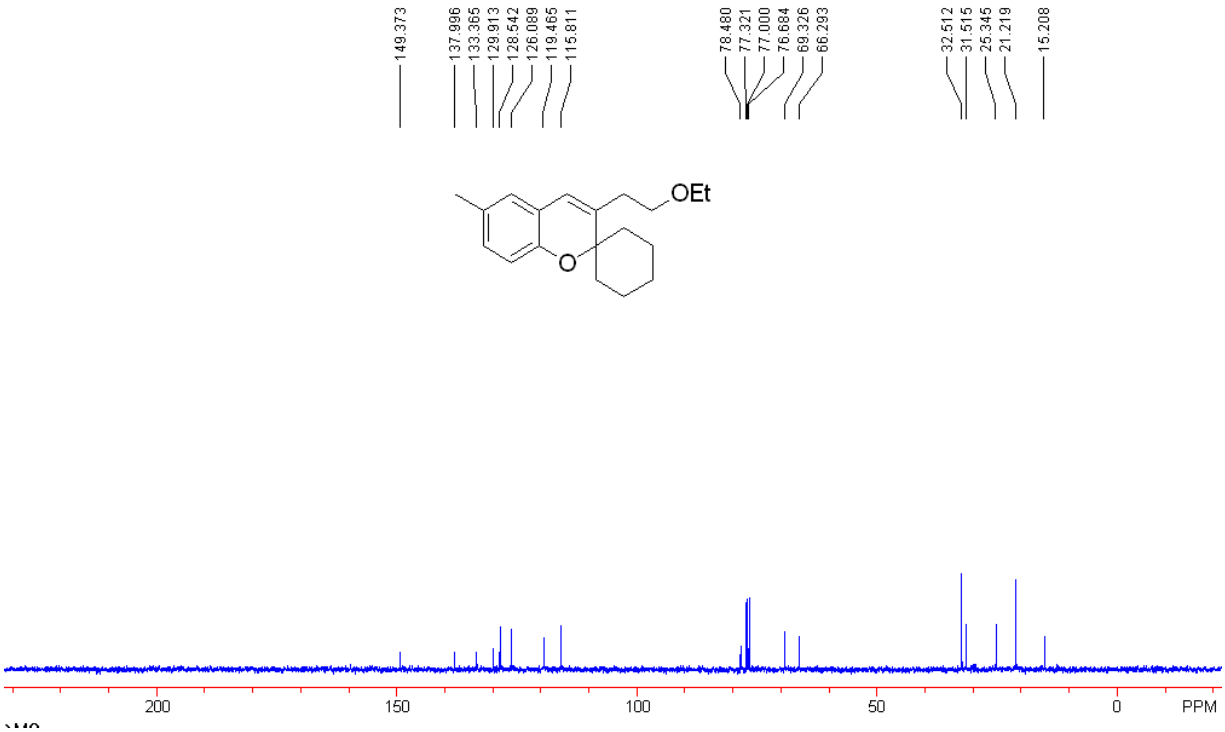


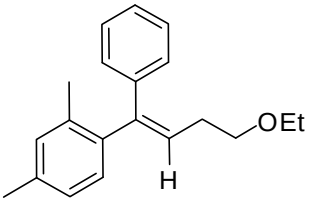
Compound 3n: A colorless oil; IR (CH_2Cl_2): ν 3011, 2929, 2861, 1657, 1590, 1493, 1447, 1282, 1236, 1109, 959, 931, 815 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.23 (3H, t, *J* = 7.2 Hz, CH_3), 1.47-1.53 (5H, m, CH_2), 1.73-1.79 (3H, m, CH_2), 1.90-1.94 (2H, m, CH_2), 2.24 (3H, s, CH_3), 2.37-2.41 (2H, m, CH_2), 3.53 (2H, q, *J* = 7.2 Hz, CH_2), 3.62 (2H, t, *J* = 7.2 Hz, CH_2), 6.08 (1H, s, =CH), 6.75 (1H, s, ArH), 6.86-6.90 (2H, m, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 15.2, 21.2, 25.3, 31.5, 32.5, 66.3, 69.3, 78.5, 115.8, 119.5, 126.1, 128.5, 129.9, 138.0, 149.4; MS (EI) *m/z* (%): 286 (94.83) [M^+], 257 (100.00), 243 (95.93), 215 (80.44), 199 (67.79), 185 (19.32), 84 (41.21), 49 (52.30); HRMS (EI) Calcd. for $C_{19}H_{26}O_2$ (M^+) requires 286.1933, Found: 286.1935.





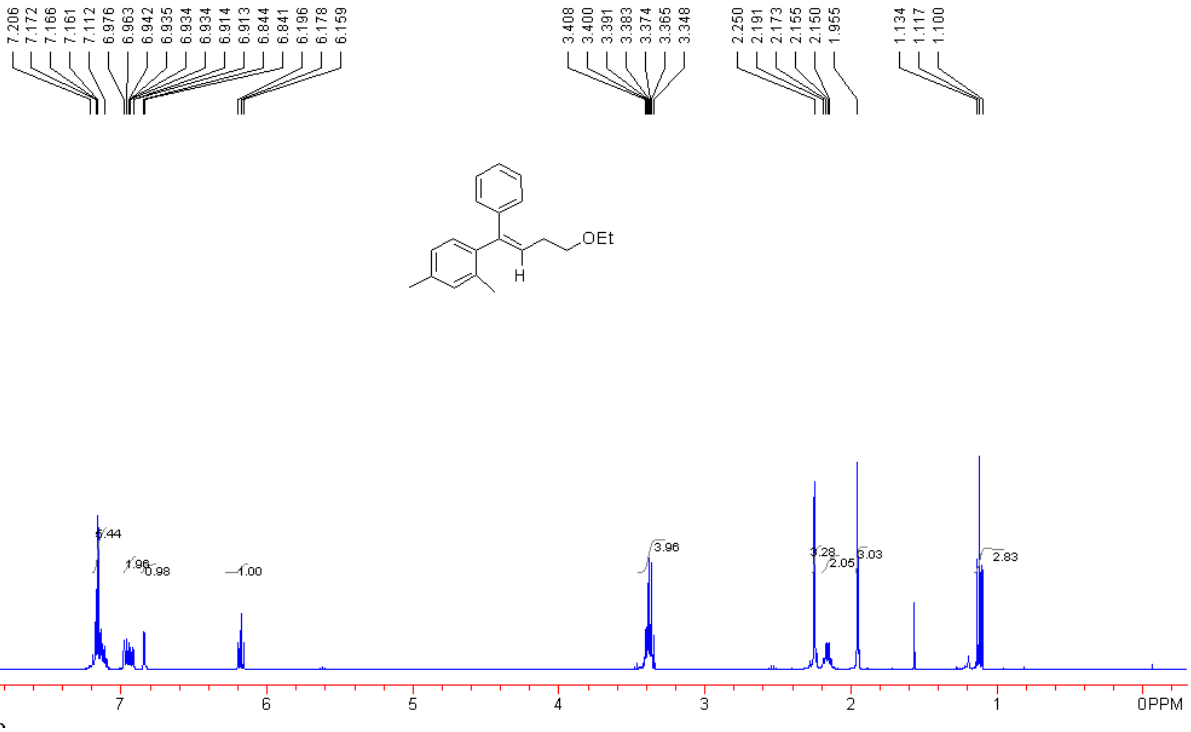


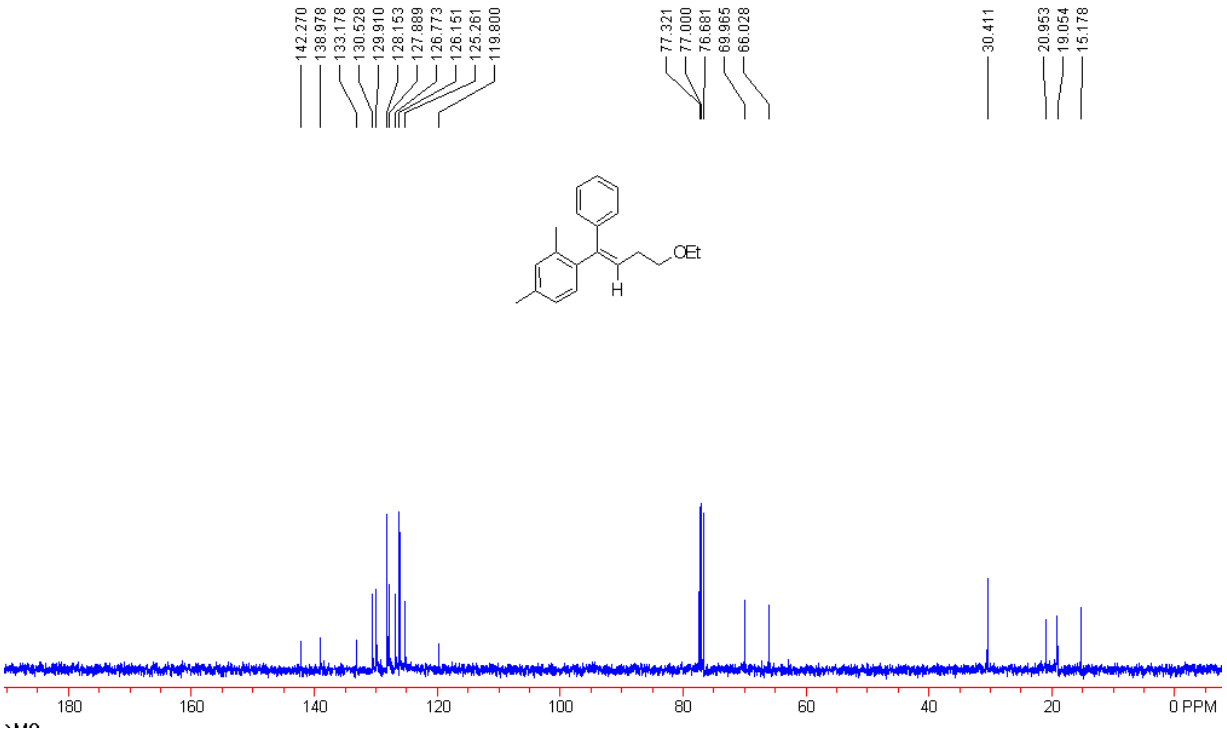

149.373
137.996
133.365
129.913
128.542
126.089
119.465
115.811
78.480
77.321
77.000
76.684
69.326
66.293
32.512
31.515
25.345
21.219
15.208
OEt
O
200
150
100
50
0
PPM

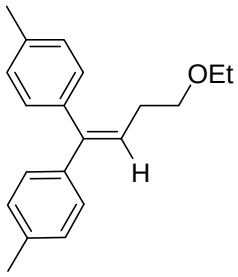


E-isomer

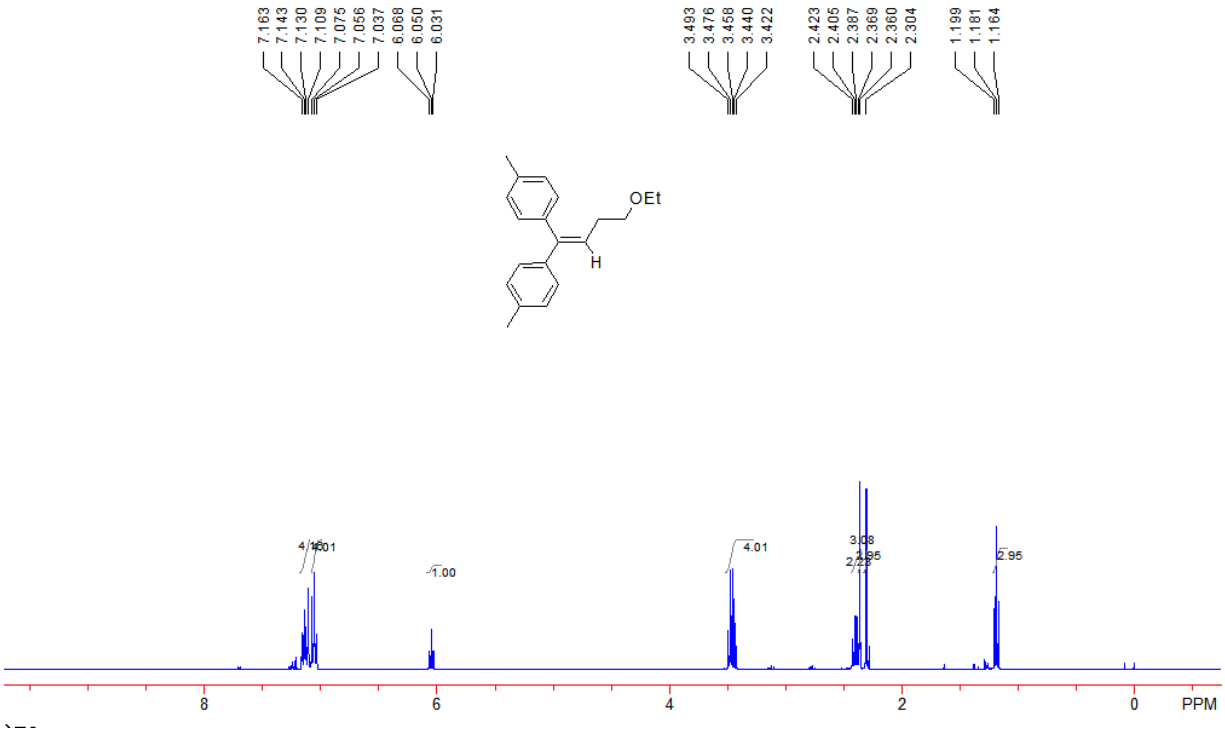
Compound 4a: A colorless oil; IR (CH_2Cl_2): ν 3014, 2974, 2862, 1730, 1671, 1597, 1494, 1376, 1112, 1031, 863, 810, 768, 695 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.18 (3H, t, *J* = 7.2 Hz, CH_3), 2.01 (3H, s, CH_3), 2.21-2.24 (2H, m, CH_2), 2.31 (3H, s, CH_3), 3.41-3.47 (4H, m, CH_2), 6.24 (1H, t, *J* = 7.2 Hz, =CH), 6.90 (1H, s, ArH), 6.98-7.04 (2H, m, ArH), 7.18-7.26 (5H, m, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 15.2, 19.1, 21.0, 30.4, 66.0, 70.0, 119.8, 125.3, 126.2, 126.8, 127.9, 128.2, 129.9, 130.5, 133.2, 139.0, 142.3; MS (EI) *m/z* (%): 280 (27.92) [M^+], 236 (20.10), 221 (100.00), 206 (18.42), 193 (27.50), 143 (29.20), 115 (52.04), 59 (10.17); HRMS (EI) Calcd. for $C_{20}H_{24}O$ (M^+) requires 280.1827, Found: 280.1838.

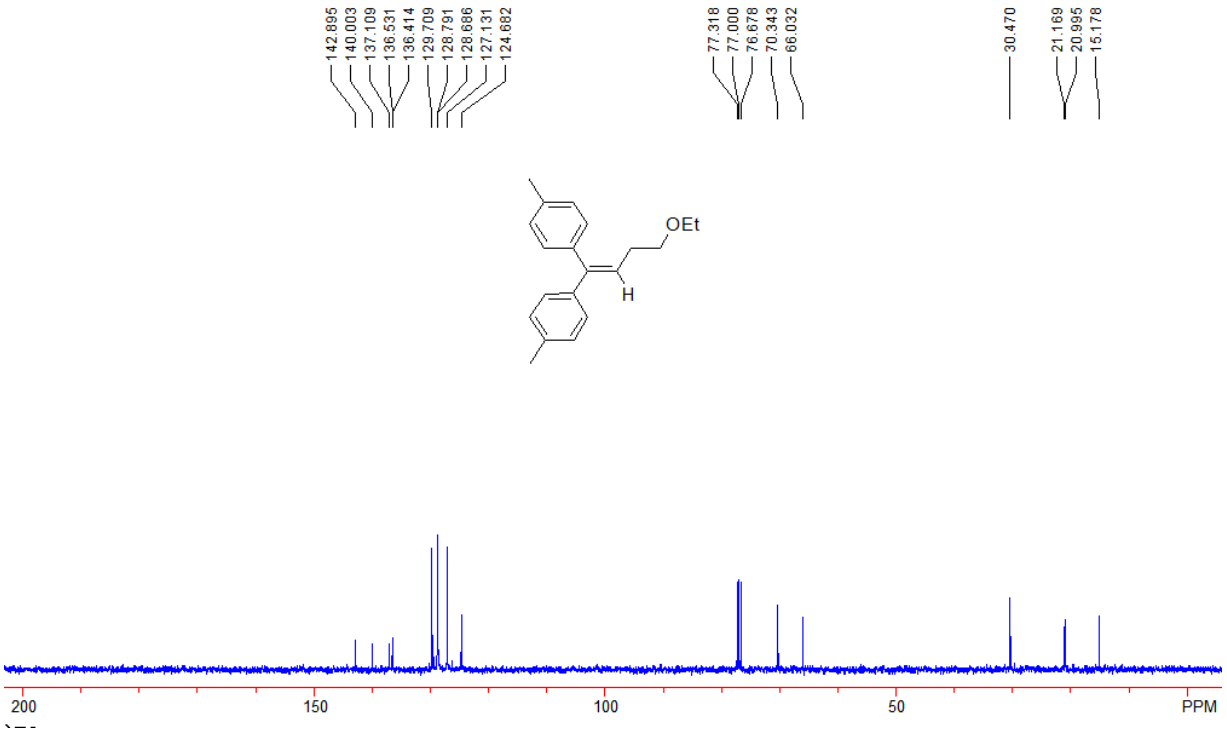



142.270
138.978
133.178
130.528
129.910
128.153
127.889
126.773
126.151
125.261
119.800
77.321
77.000
76.681
69.965
66.028
30.411
20.953
19.054
15.178
OEt
H
180
160
140
120
100
80
60
40
20
0 PPM



Compound 4b: This is a known compound; A colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.18 (3H, t, *J* = 7.2 Hz, CH_3), 2.28 (3H, s, CH_3), 2.30 (3H, s, CH_3), 2.39 (2H, q, *J* = 6.8 Hz, CH_2), 3.42-3.49 (4H, m, CH_2), 6.05 (1H, t, *J* = 7.2 Hz, =CH), 7.04-7.08 (4H, m, ArH), 7.11-7.16 (4H, m, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 15.2, 30.5, 55.2, 55.3, 66.1, 70.4, 113.4, 113.5, 123.8, 128.4, 131.0, 132.5, 135.7, 142.2, 158.5, 158.7. Their spectroscopic data are consistent with those reported in the literature.[1]




142.895
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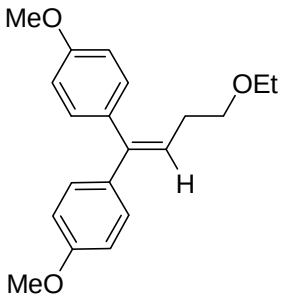
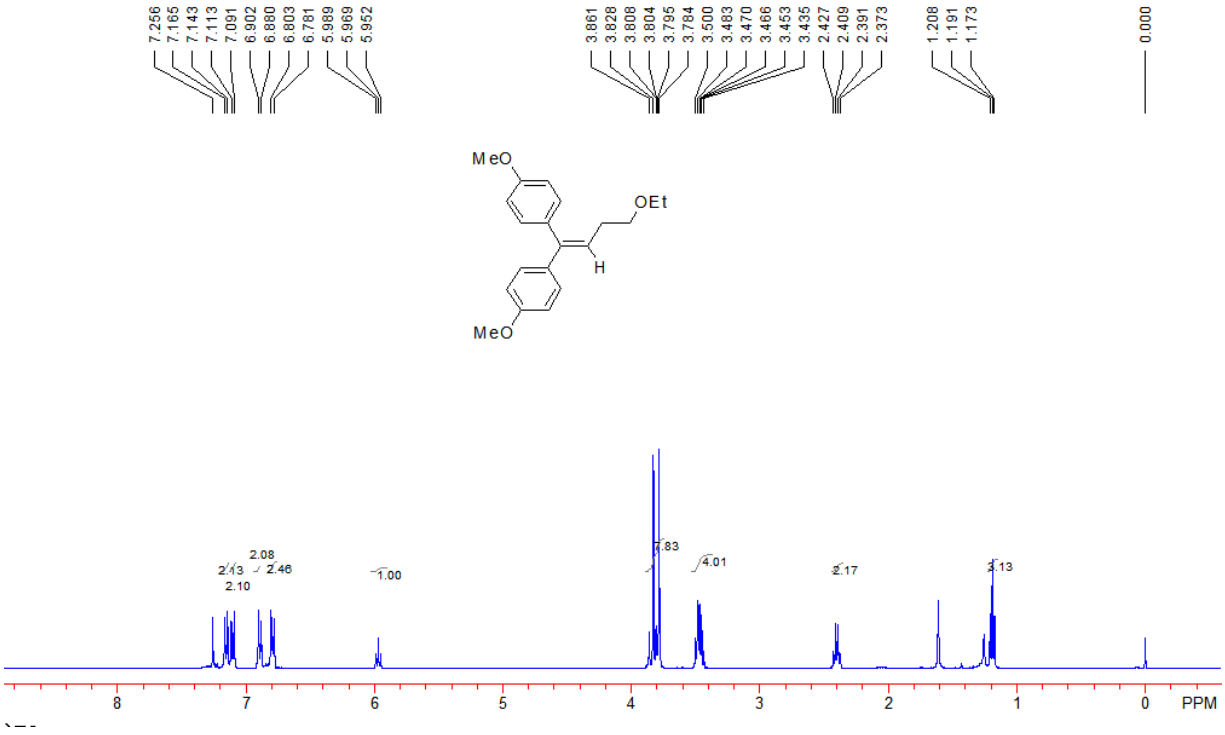
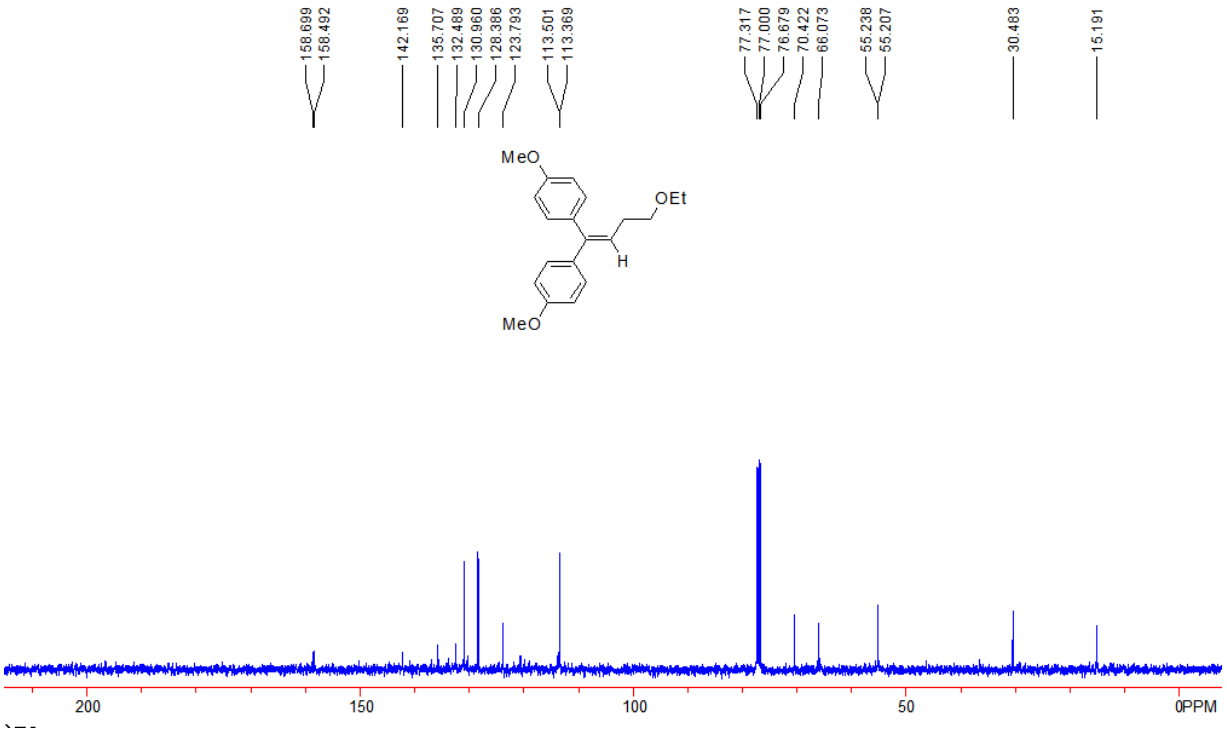
137.109
136.531
136.414
129.709
128.791
128.686
127.131
124.682
77.318
77.000
76.678
70.343
66.032
30.470
21.169
20.995
15.178
OEt
H
200
150
100
50
PPM



Compound 4c: This is a known compound; A colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.19 (3H, t, *J* = 7.2 Hz, CH_3), 2.39 (2H, q, *J* = 7.2 Hz, CH_2), 3.44-3.50 (4H, m, CH_2), 3.78 (3H, s, OCH_3), 3.83 (3H, s, OCH_3), 5.97 (1H, t, *J* = 7.2 Hz, =CH), 6.79 (2H, d, *J* = 8.8 Hz, ArH), 6.89 (2H, d, *J* = 8.8 Hz, ArH), 7.10 (2H, d, *J* = 8.8 Hz, ArH), 7.15 (2H, d, *J* = 8.8 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 15.2, 30.5, 55.2, 55.3, 66.1, 70.4, 113.4, 113.5, 123.8, 128.4, 131.0, 132.5, 135.7, 142.2, 158.5, 158.7. Their spectroscopic data are consistent with those reported in the literature.[1]




158.699
158.492
142.169
135.707
132.489
130.960
128.386
123.793
113.501
113.369
77.317
77.000
76.679
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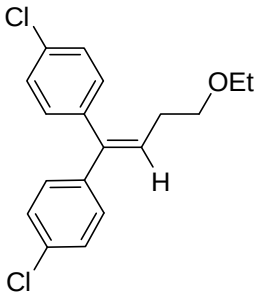
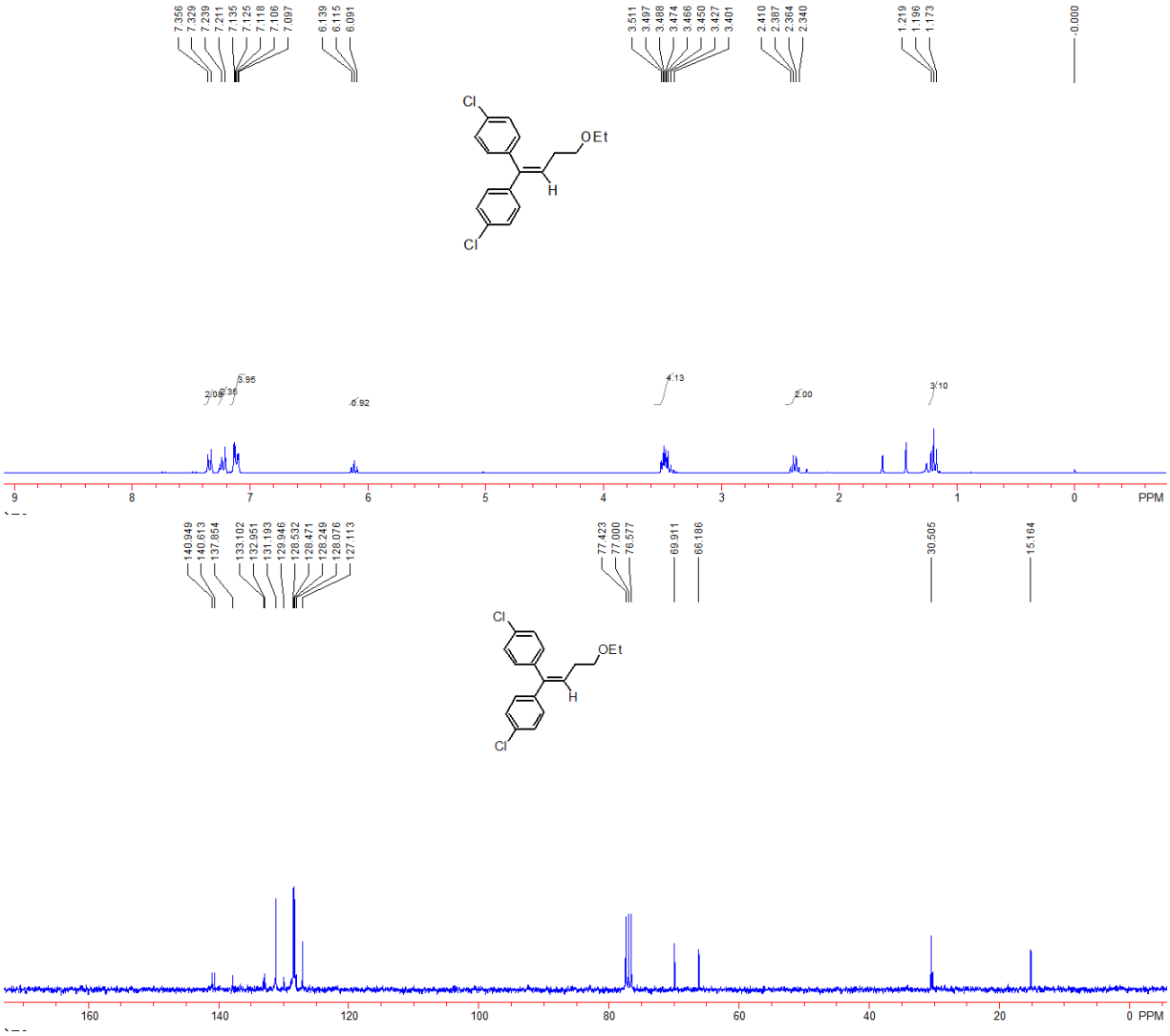
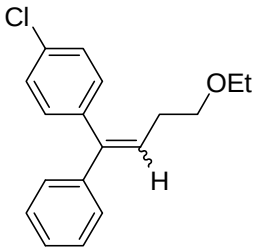
MeO
OEt
H
MeO
200
150
100
50
0PPM



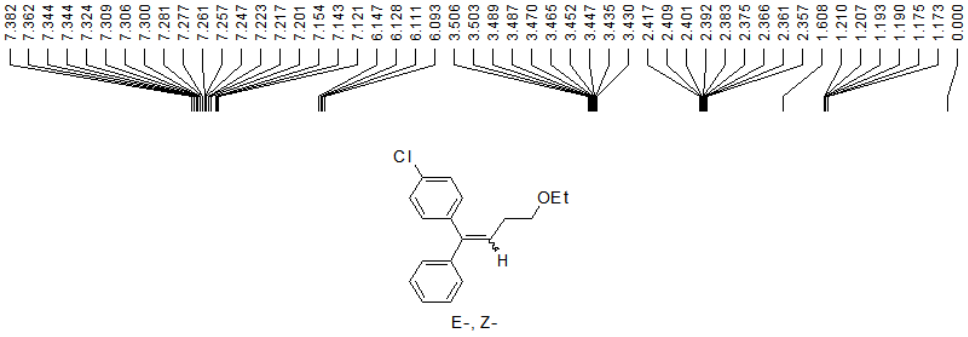
Compound 4d: This is a known compound; A colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.20 (3H, t, *J* = 6.9 Hz, CH_3), 2.37 (2H, q, *J* = 7.2 Hz, CH_2), 3.43-3.51 (4H, m, CH_2), 6.12 (1H, t, *J* = 7.2 Hz, =CH), 7.10-7.14 (4H, m, ArH), 7.22 (2H, d, *J* = 8.4 Hz, ArH), 7.35 (2H, d, *J* = 8.4 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 15.2, 30.5, 66.2, 69.9, 127.1, 128.1, 128.2, 128.4, 128.5, 128.7, 129.9, 131.2, 133.0, 133.1, 137.9, 140.6, 140.9. Their spectroscopic data are consistent with those reported in the literature.[1]



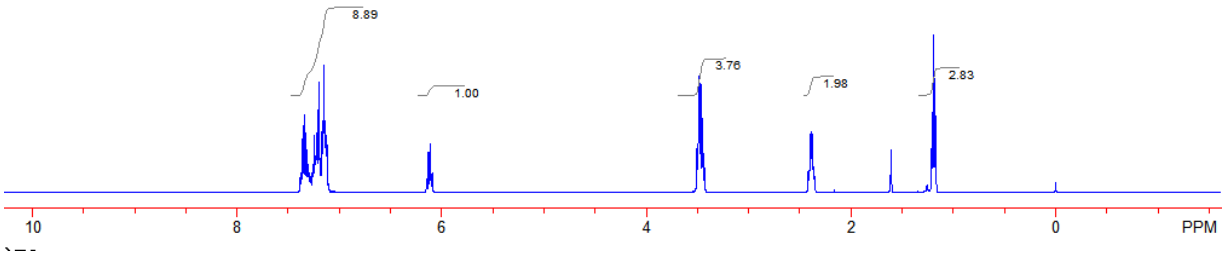


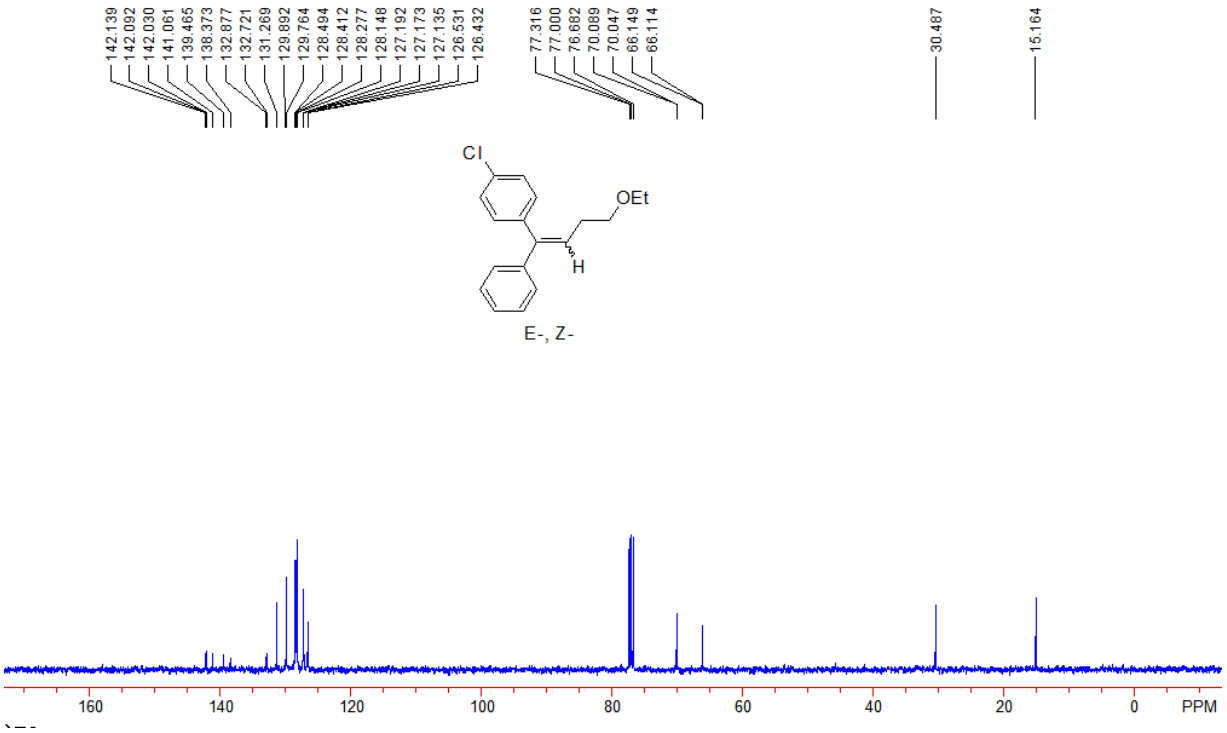
E-, Z-

Compound 4e: This is a known compound; A colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.17-1.21 (3H, m, CH_3), 2.36-2.42 (2H, m, CH_2), 3.43-3.51 (4H, m, CH_2), 6.09-6.15 (1H, m, =CH), 7.12-7.26 (5H, m, ArH), 7.29-7.38 (4H, m, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 15.2, 30.4, 30.5, 66.1, 66.2, 70.0, 70.1, 126.4, 126.5, 127.1, 127.2, 127.3, 128.1, 128.2, 128.3, 128.4, 128.5, 129.8, 131.3, 132.7, 132.9, 138.4, 139.5, 141.1, 142.0, 142.1. Their spectroscopic data are consistent with those reported in the literature.[1]



E-, Z-

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142.030
141.061
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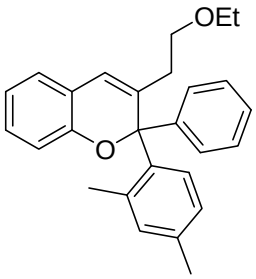
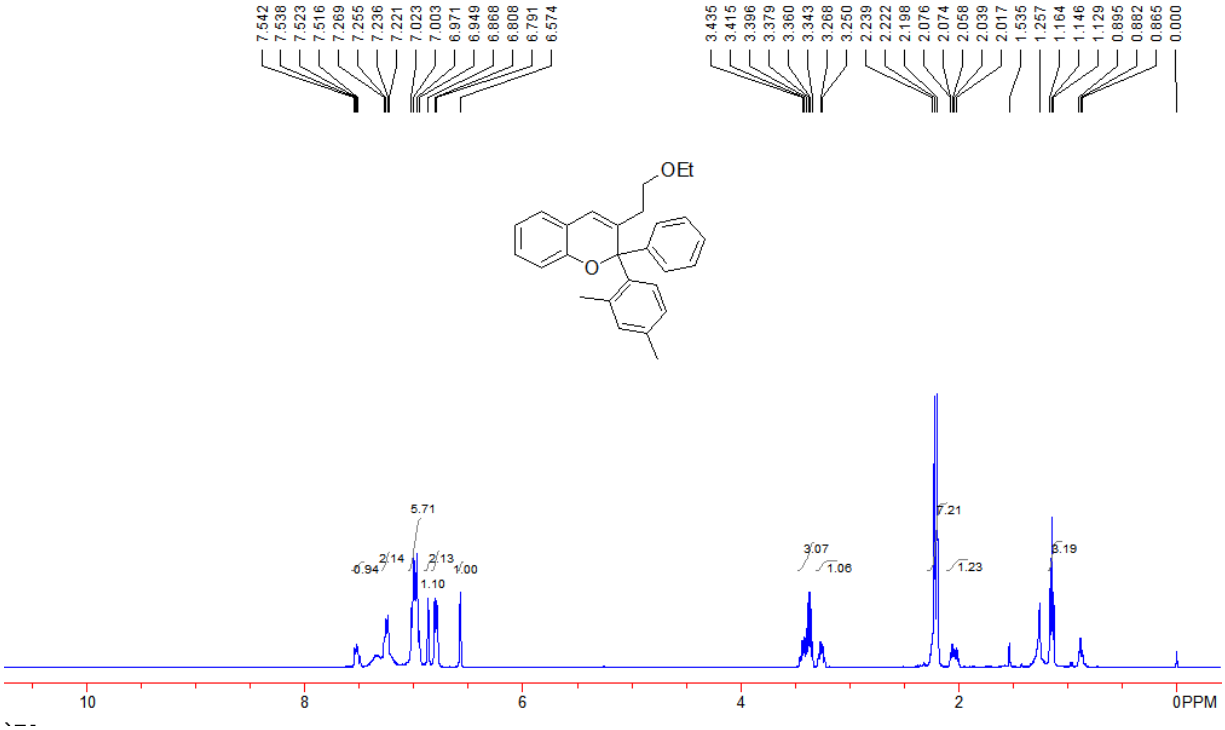
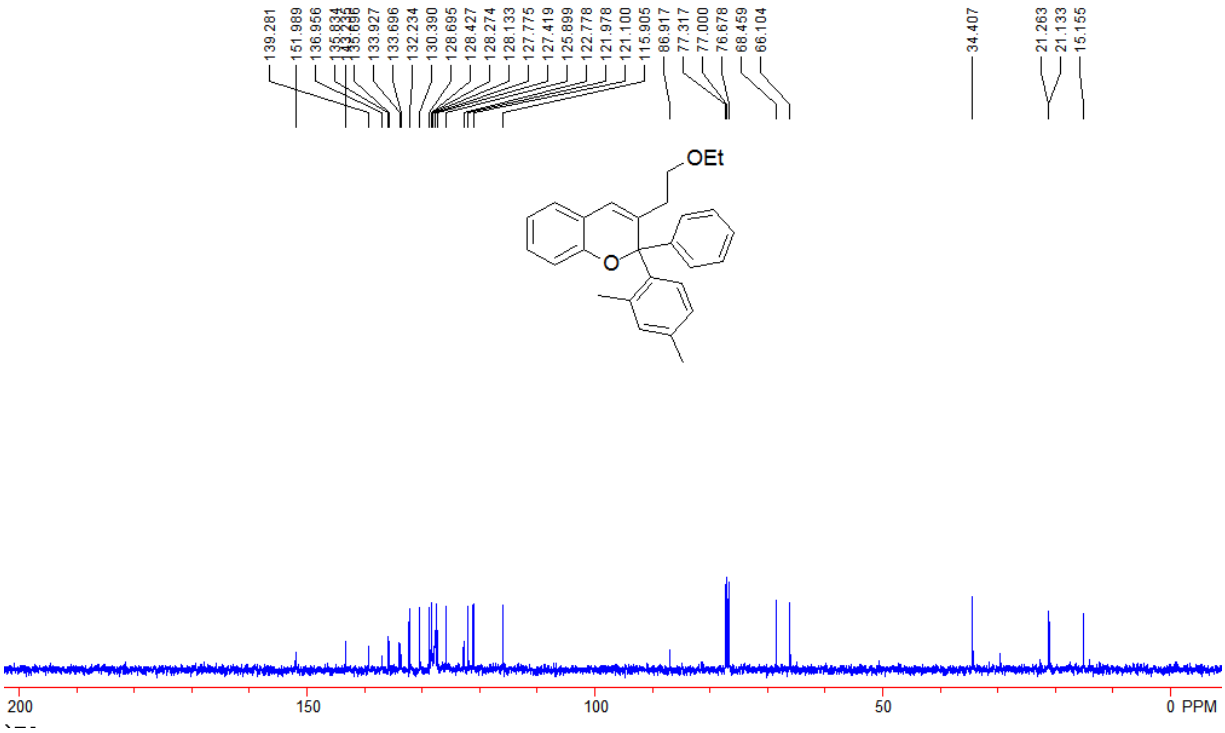
138.373
132.877
132.721
131.269
129.892
129.764
128.494
128.412
128.277
128.148
127.192
127.173
127.135
126.531
126.432
77.316
77.000
76.682
70.089
70.047
66.149
66.114
30.487
15.164
Cl
OEt
H
E-, Z-
160
140
120
100
80
60
40
20
0
PPM



Compound 3o: A colorless oil; IR (CH_2Cl_2): ν 3024, 2972, 2926, 2867, 1644, 1607, 1575, 1485, 1455, 1243, 1108, 1030, 986, 934, 886, 849, 761, 703 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.15 (3H, t, *J* = 7.2 Hz, CH_3), 2.02-2.08 (1H, m, CH_2), 2.20-2.26 (1H, m, CH_2), 2.20 (3H, s, CH_3), 2.22 (3H, s, CH_3), 3.25-3.29 (1H, m, CH_2), 3.34-3.46 (3H, m, CH_2), 6.57 (1H, s, =CH), 6.80 (2H, d, *J* = 6.8 Hz, ArH), 6.87 (1H, s, ArH), 6.95-7.02 (6H, m, ArH), 7.22-7.27 (2H, m, ArH), 7.49-7.54 (1H, m, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 15.2, 21.1, 21.3, 34.4, 66.1, 68.5, 86.9, 115.9, 121.1, 122.0, 122.8, 125.9, 127.4, 127.6, 127.8, 128.1, 128.4, 128.7, 130.4, 132.2, 133.9, 135.7, 135.8, 139.3, 143.2, 152.0; MS (EI) *m/z* (%): 384 (80.40) [M^+], 338 (69.43), 323 (100.00), 279 (21.48), 233 (55.77), 219 (31.92), 107 (21.10), 91 (22.76); HRMS (EI) Calcd. for $C_{27}H_{28}O_2$ (M^+) requires 384.2089, Found: 384.2092.

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132.234
130.390
128.695
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128.274
128.133
127.775
127.419
125.899
122.778
121.978
121.100
115.905
86.917
77.317
77.000
76.678
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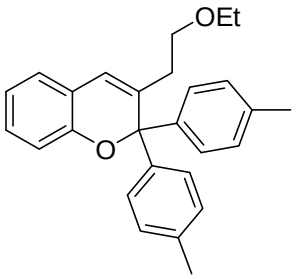
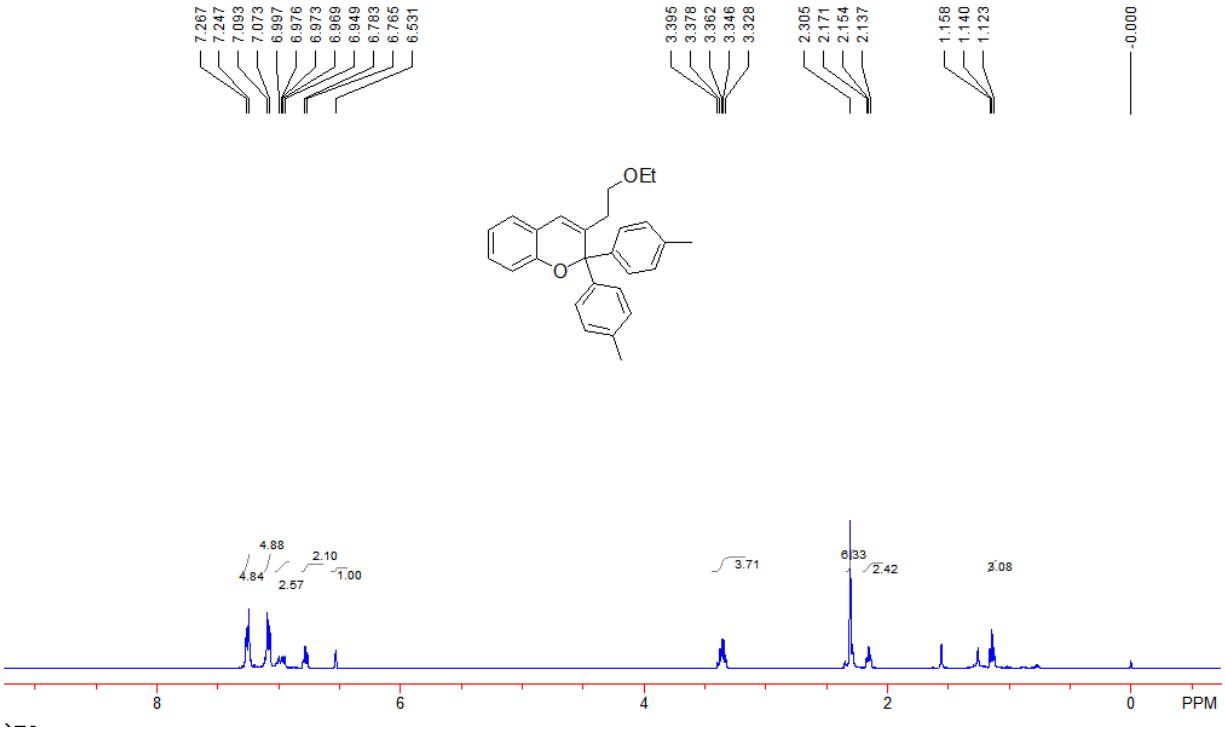
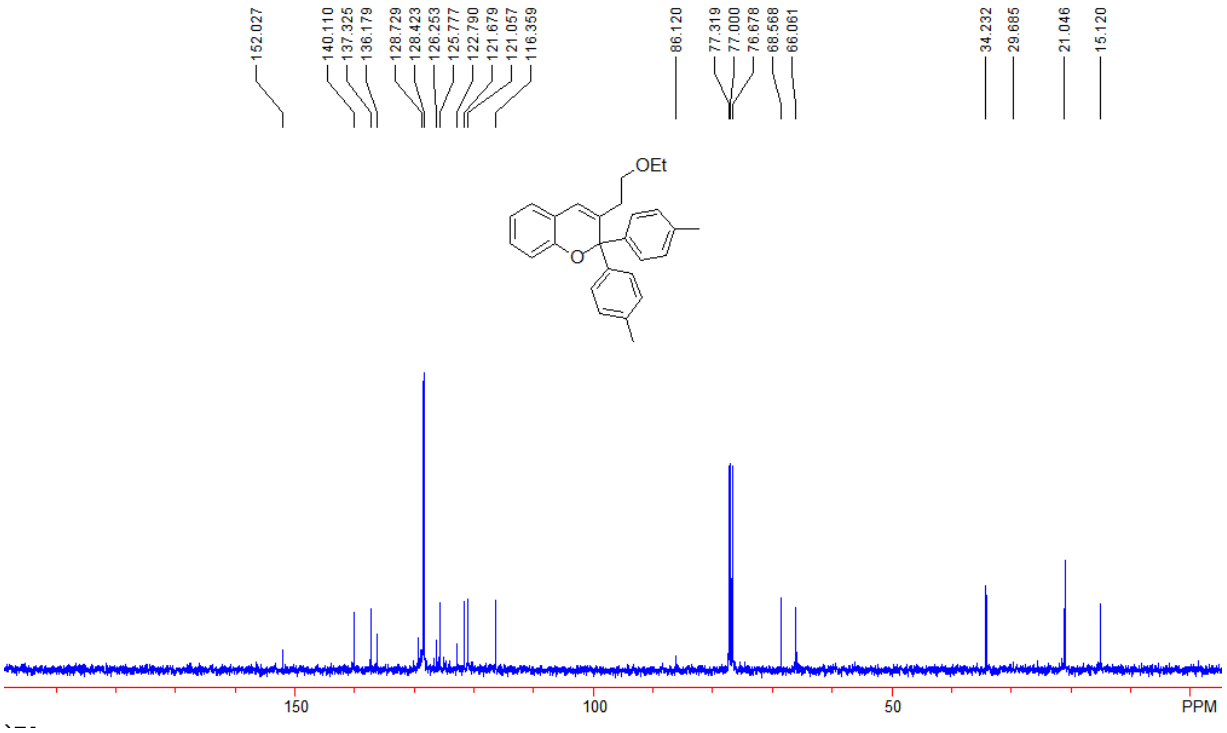
66.104
34.407
21.263
21.133
15.155
OEt
O
200
150
100
50
0 PPM



Compound 3p: A colorless oil; IR (CH_2Cl_2): ν 2922, 2851, 1686, 1604, 1512, 1459, 1375, 1265, 1017, 834 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.14 (3H, t, *J* = 7.2 Hz, CH_3), 2.15 (2H, t, *J* = 7.2 Hz, CH_2), 2.31 (6H, s, CH_3), 3.33-3.38 (4H, m, CH_2), 6.53 (1H, s, =CH), 6.76-6.80 (2H, m, ArH), 6.95-7.00 (2H, m, ArH), 7.08 (4H, d, *J* = 8.0 Hz, ArH), 7.26 (4H, d, *J* = 8.0 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 15.1, 21.0, 34.2, 66.1, 68.6, 86.1, 116.4, 121.1, 121.7, 122.8, 125.8, 126.3, 128.3, 128.4, 128.5, 128.6, 128.7, 128.8, 129.3, 136.2, 137.3, 140.1, 152.0; MS (EI) *m/z* (%): 384 (100.00) [M^+], 323 (81.82), 311 (68.21), 293 (34.83), 247 (61.92), 178 (13.18), 119 (16.49), 71 (12.48); HRMS (EI) Calcd. for $C_{27}H_{28}O_2$ (M^+) requires 384.2089, Found: 384.2090.




152.027
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136.179
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128.423
126.253
125.777
122.790
121.679
121.057
116.359
86.120
77.319
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15.120
OEt
O
150
100
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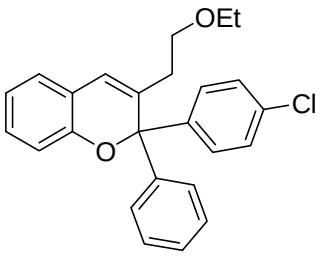
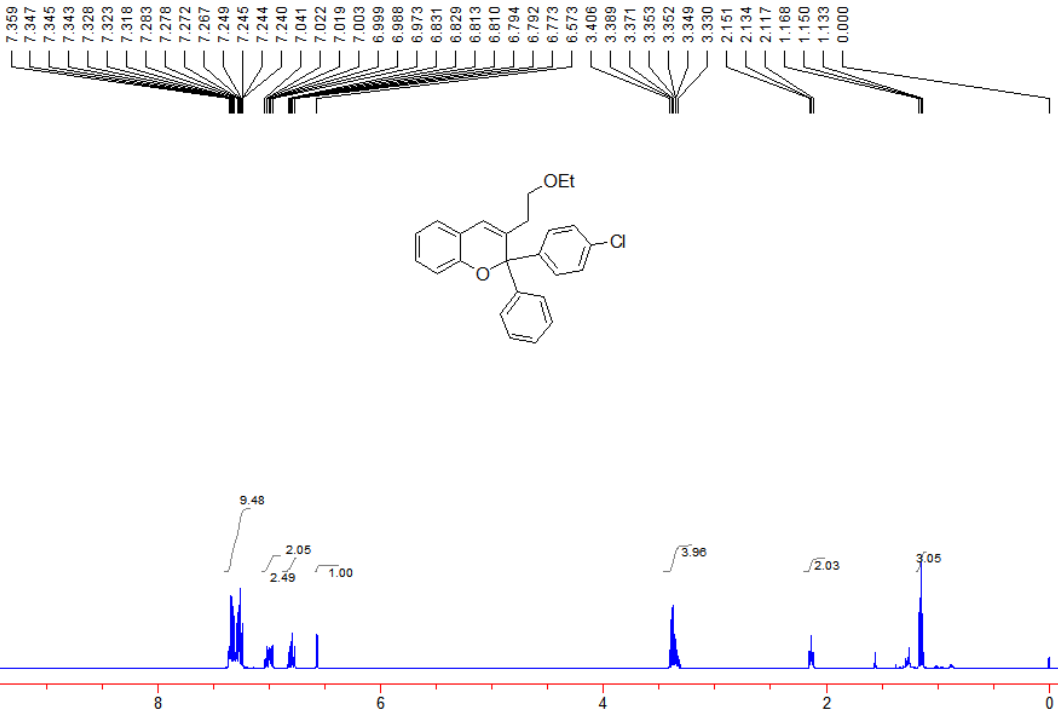
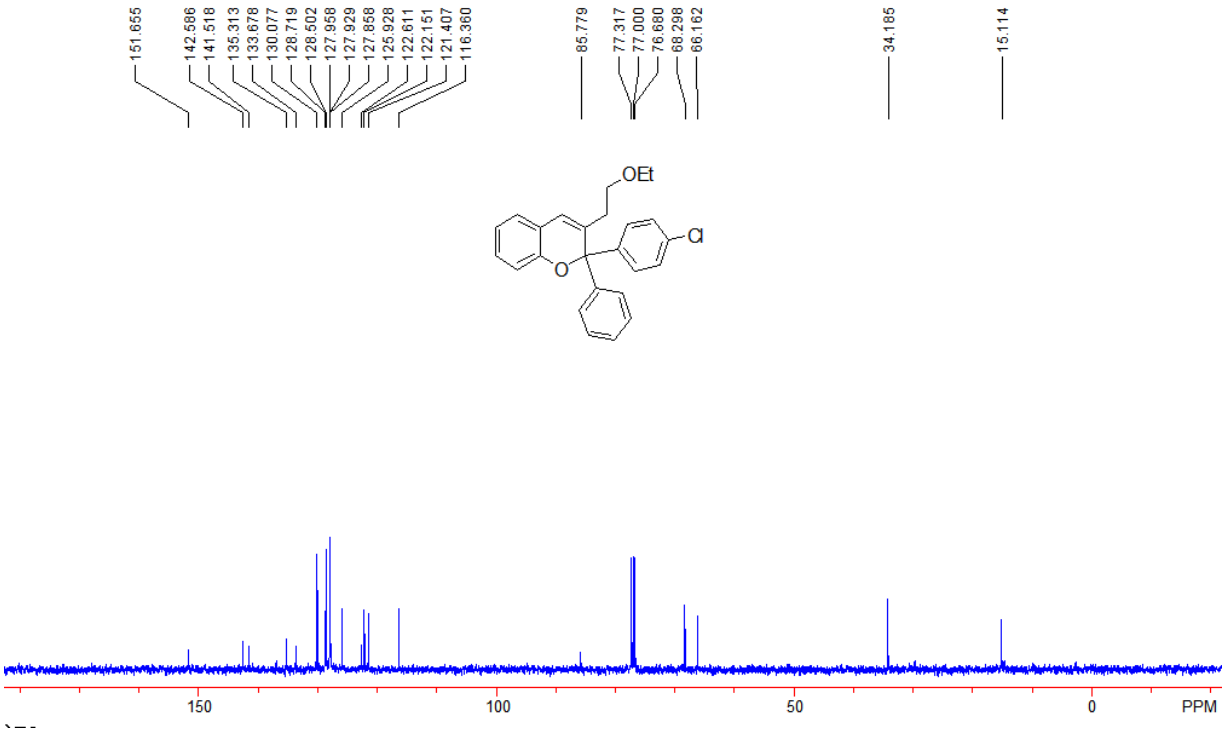
PPM



Compound 3q: A colorless oil; IR (CH_2Cl_2): ν 3061, 3036, 2973, 2865, 1903, 1813, 1606, 1578, 1488, 1455, 1233, 1093, 991, 933, 829, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.15 (3H, t, *J* = 7.2 Hz, CH_3), 2.13 (2H, t, *J* = 6.8 Hz, CH_2), 3.33-3.41 (4H, m, CH_2), 6.57 (1H, s, =CH), 6.77-6.83 (2H, m, ArH), 6.97-7.02 (2H, m, ArH), 7.24-7.36 (9H, m, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 15.1, 34.2, 66.2, 68.3, 85.8, 116.4, 121.4, 122.2, 122.6, 125.9, 127.8, 127.9, 128.0, 128.5, 128.7, 130.1, 133.7, 135.3, 141.5, 142.6, 151.7; MS (EI) *m/z* (%): 390 (10.05) [M^+], 344 (9.45), 309 (11.98), 267 (11.03), 233 (14.69), 99 (24.49), 71 (70.31), 57 (100.00); HRMS (EI) Calcd. for $C_{25}H_{23}O_2Cl$ (M^+) requires 390.1387, Found: 390.1381.




151.655
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135.313
133.678
130.077
128.719
128.502
127.958
127.929
127.858
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122.611
122.151
121.407
116.360
85.779
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77.000
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68.298
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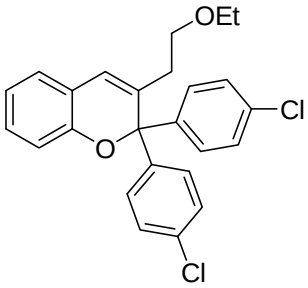
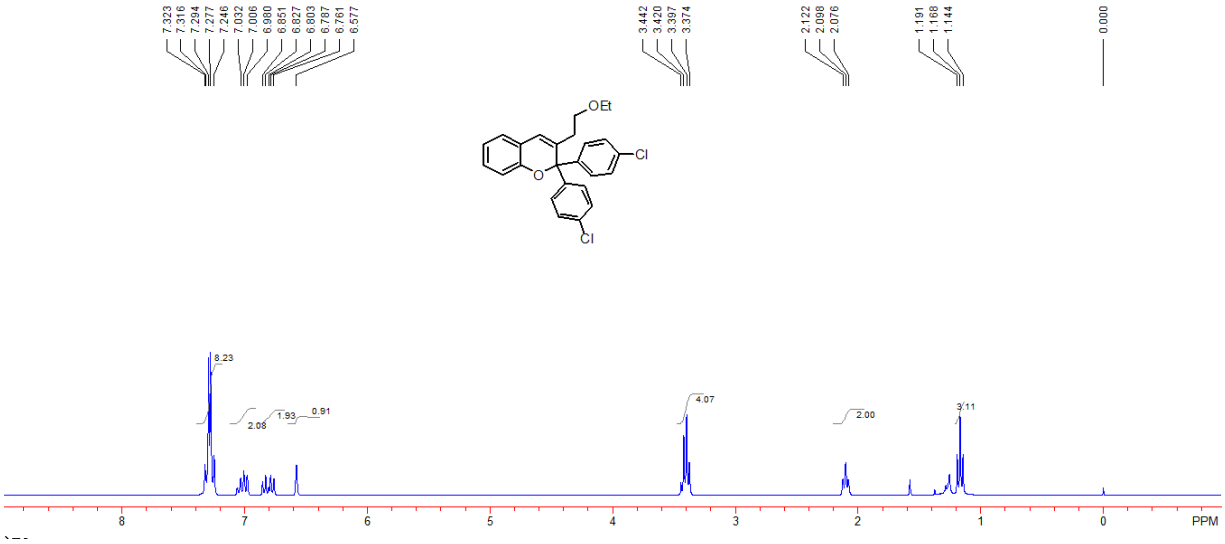
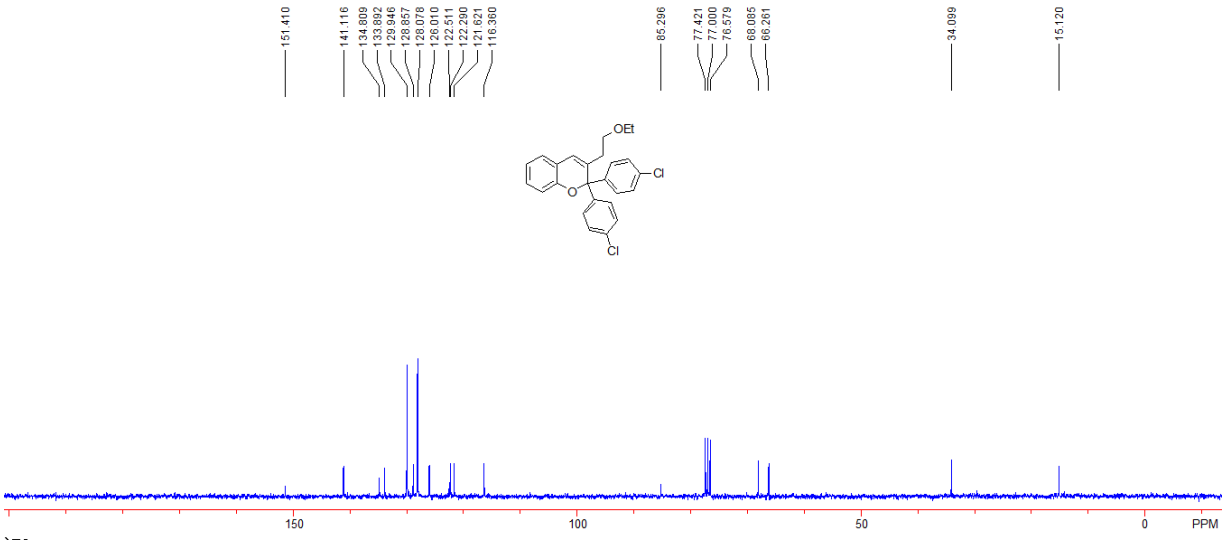
34.185
15.114
OEt
Cl
O
150
100
50
0
PPM



Compound 3r: A colorless oil; IR (CH_2Cl_2): ν 3024, 2972, 2926, 2867, 1644, 1607, 1575, 1485, 1455, 1243, 1108, 1030, 986, 934, 886, 849, 761, 703 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.17 (3H, t, *J* = 7.2 Hz, CH_3), 2.10 (2H, t, *J* = 7.2 Hz, CH_2), 3.37-3.44 (4H, m, CH_2), 6.58 (1H, s, =CH), 6.76-6.85 (2H, m, ArH), 6.98-7.06 (2H, m, ArH), 7.25-7.32 (8H, m, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 15.1, 34.1, 66.3, 68.1, 85.3, 116.4, 121.6, 122.3, 122.5, 126.0, 128.1, 128.9, 129.9, 133.9, 134.8, 141.1, 151.4; MS (EI) *m/z* (%): 424 (74.51) [M^+], 378 (58.33), 343 (100.00), 267 (93.53), 218 (19.39), 131 (12.08), 107 (8.66), 59 (18.65); HRMS (EI) Calcd. for $C_{25}H_{22}O_2Cl_2$ (M^+) requires 424.0997, Found: 424.0993.

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128.078
126.010
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122.290
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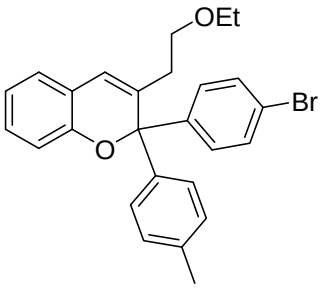
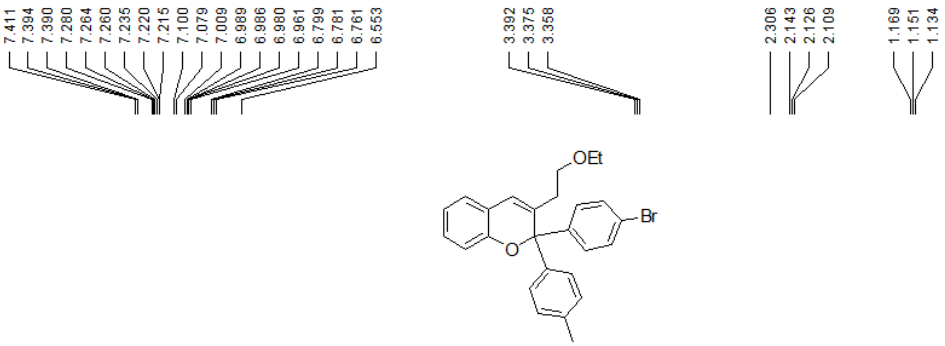
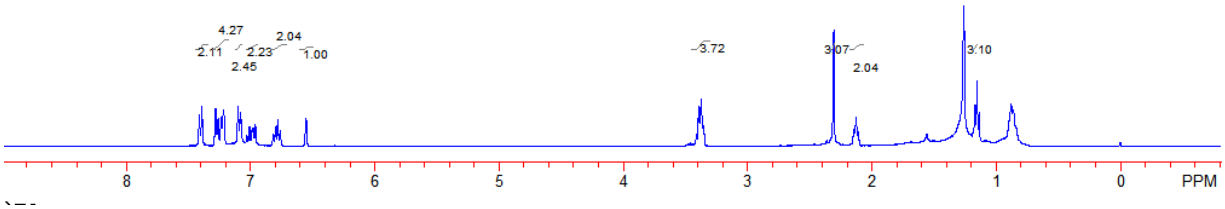
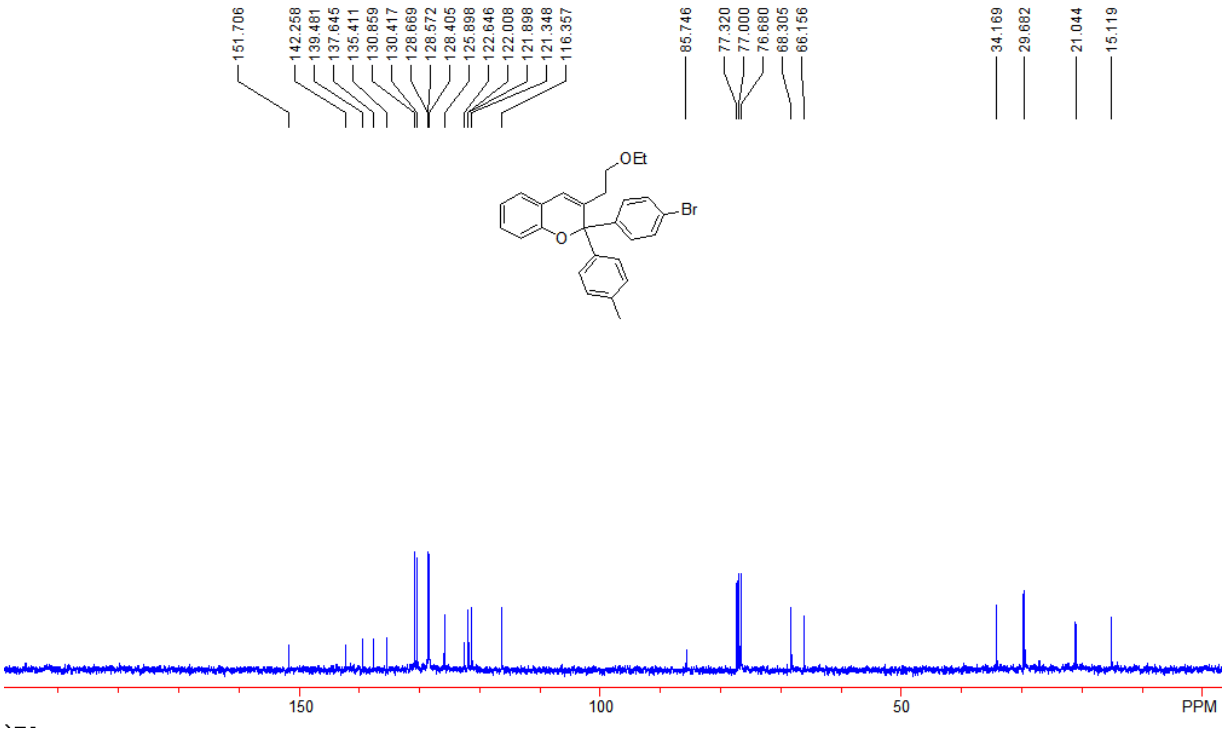
77.421
77.000
76.579
68.085
66.261
34.099
15.120
OEt
Cl
Cl
O
150
100
50
0
PPM



Compound 3s: A colorless oil; IR (CH_2Cl_2): ν 3026, 2925, 2856, 1607, 1511, 1485, 1456, 1377, 1231, 1108, 1012, 991, 822, 753 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.15 (3H, t, *J* = 7.2 Hz, CH_3), 2.13 (2H, t, *J* = 7.2 Hz, CH_2), 2.31 (3H, s, CH_3), 3.35-3.39 (4H, m, CH_2), 6.55 (1H, s, =CH), 6.78 (2H, t, *J* = 8.0 Hz, ArH), 6.96-7.01 (2H, m, ArH), 7.09 (2H, d, *J* = 8.4 Hz, ArH), 7.22-7.28 (4H, m, ArH), 7.40 (2H, d, *J* = 8.4 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 15.1, 21.0, 29.3, 34.2, 66.2, 68.3, 85.7, 116.4, 121.3, 121.9, 122.0, 122.6, 125.9, 128.4, 128.6, 128.7, 130.4, 130.9, 135.4, 137.6, 139.5, 142.3, 151.7; MS (EI) *m/z* (%): 448 (98.32) [M^+], 404 (61.66), 323 (80.36), 247 (88.64), 233 (26.22), 189 (11.93), 131 (13.10), 59 (15.05); HRMS (EI) Calcd. for $C_{26}H_{25}O_2Br$ (M^+) requires 448.1038, Found: 448.1033.



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77.320
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29.682
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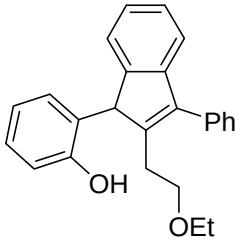
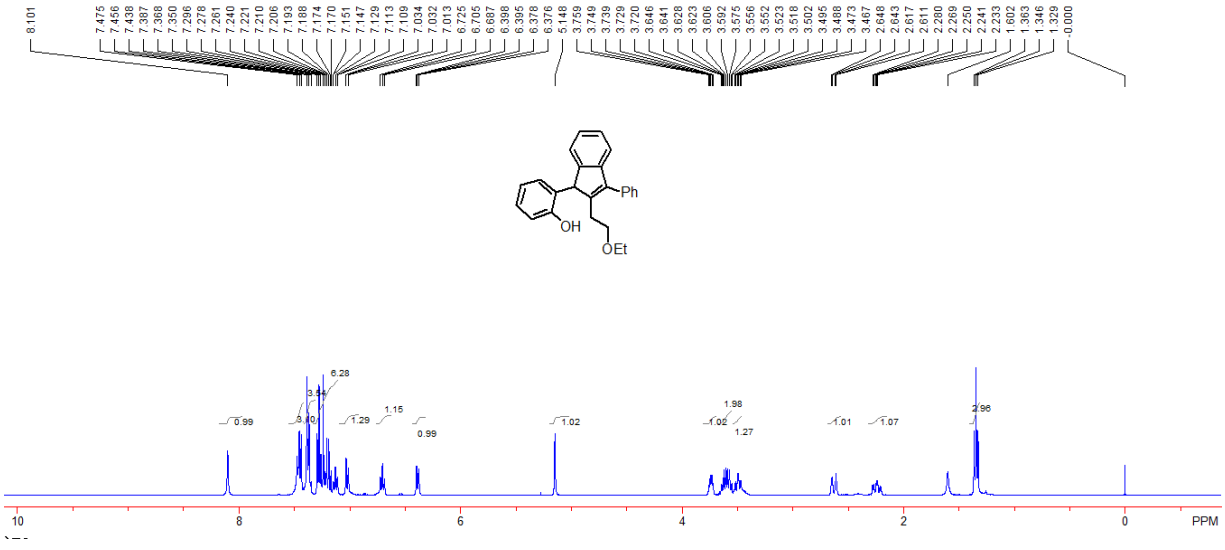
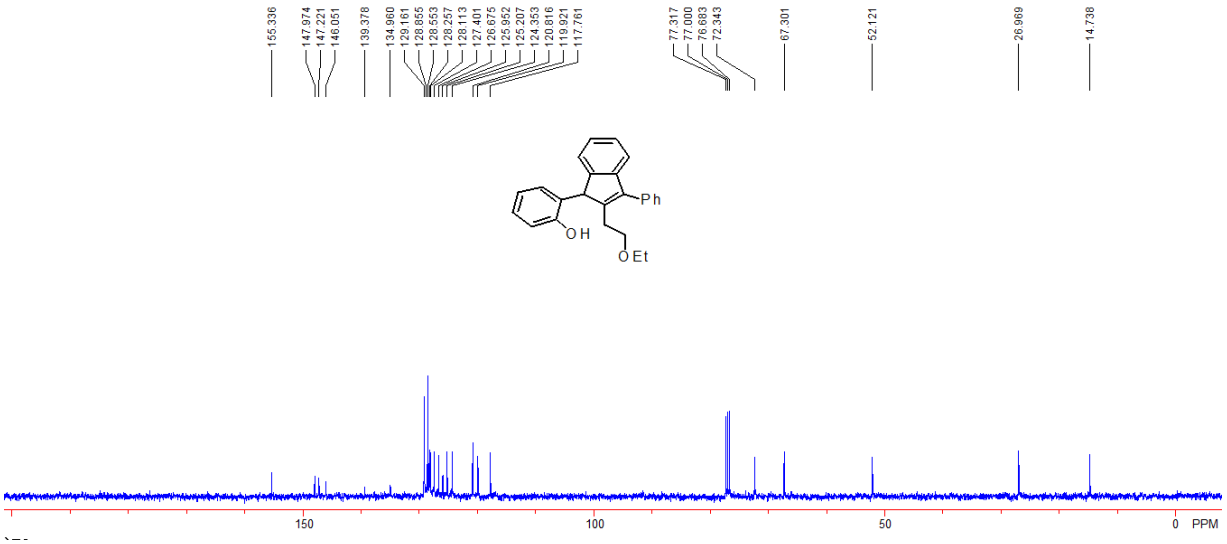
OEt
Br
O
150
100
50
PPM



Compound 5a: A white solid, m.p. 104-106 ^{o}C; IR (CH_2Cl_2): ν 3297, 3065, 2970, 2925, 2864, 1738, 1596, 1487, 1454, 1364, 1217, 1097, 774, 754, 702 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.35 (3H, t, *J* = 6.8 Hz, CH_3), 2.20-2.28 (1H, m, CH_2), 2.61-2.65 (1H, m, CH_2), 3.47-3.52 (1H, m, CH_2), 3.55-3.65 (2H, m, CH_2), 3.72-3.75 (1H, m, CH_2), 5.15 (1H, s, CH), 6.38-6.40 (1H, m, ArH), 6.71 (1H, t, *J* = 8.0 Hz, ArH), 7.02 (1H, d, *J* = 7.6 Hz, ArH), 7.10-7.26 (4H, m, ArH), 7.39 (4H, d, *J* = 7.6 Hz, ArH), 7.46 (2H, t, *J* = 7.6 Hz, ArH), 8.10 (1H, s, OH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 14.7, 27.0, 52.1, 67.3, 72.3, 117.8, 119.9, 120.8, 124.4, 125.2, 126.0, 126.7, 127.4, 128.1, 128.3, 128.5, 129.2, 146.0, 147.2, 148.0, 155.3; MS (EI) *m/z* (%): 356 (18.76) [M^+], 310 (100.00), 297 (19.64), 277 (7.85), 203 (27.16), 191 (4.69), 84 (23.55), 71 (14.54); HRMS (EI) Calcd. for $C_{25}H_{24}O_2$ (M^+) requires 356.1776, Found: 356.1772.

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125.952
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124.353
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77.317
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67.301
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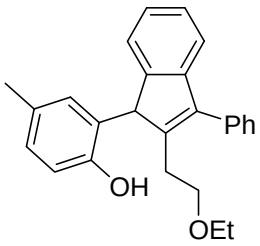
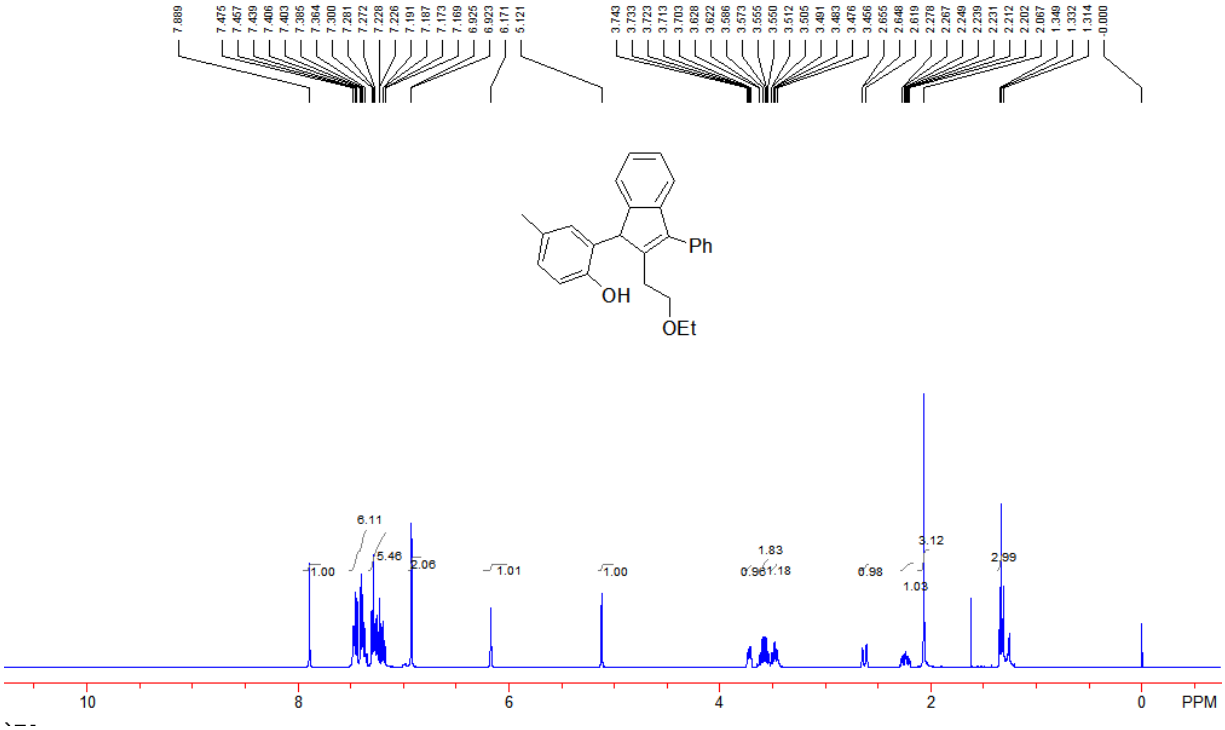
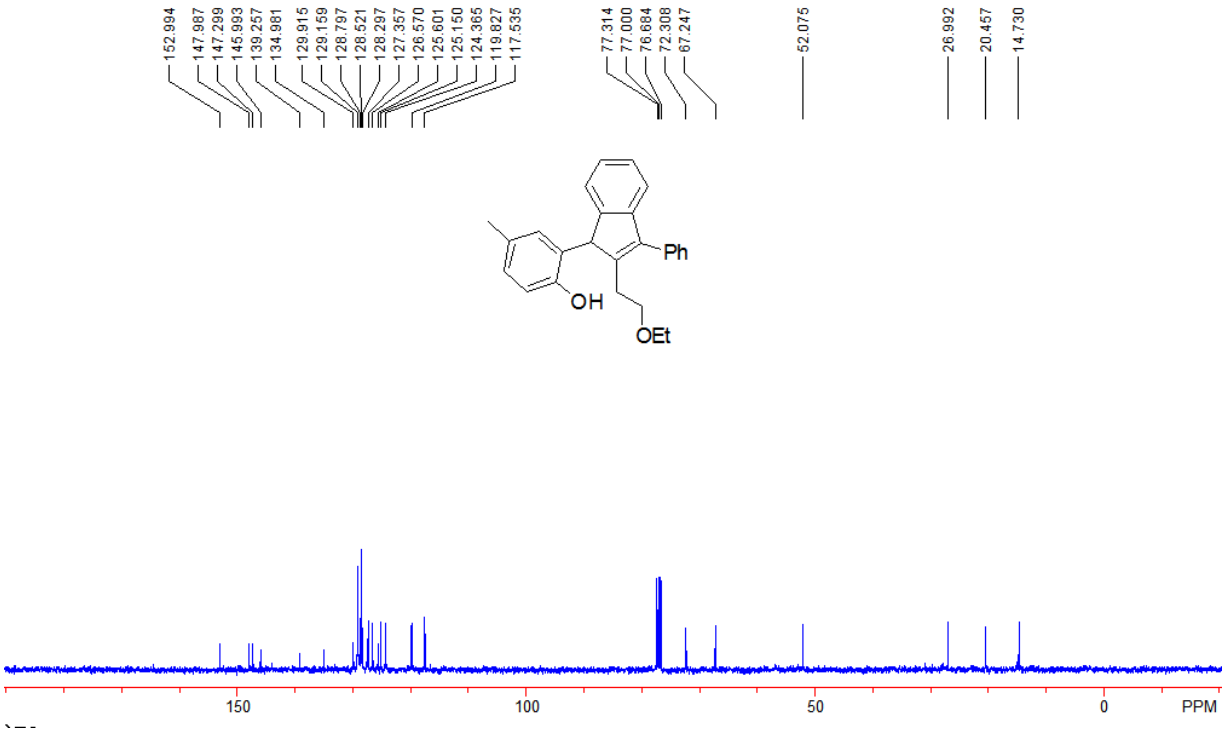
Ph
OH
OEt
150
100
50
0
PPM



Compound 5b: A colorless oil; IR (CH_2Cl_2): ν 3390, 3059, 3026, 2925, 2867, 1715, 1661, 1596, 1498, 1448, 1269, 1105, 928, 811, 765, 702 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.33 (3H, t, *J* = 6.8 Hz, CH_3), 2.07 (3H, s, CH_3), 2.20-2.29 (1H, m, CH_2), 2.61-2.65 (1H, m, CH_2), 3.46-3.51 (1H, m, CH_2), 3.55-3.61 (2H, m, CH_2), 3.71-3.73 (1H, m, CH_2), 5.12 (1H, s, CH), 6.17 (1H, s, ArH), 6.92 (2H, s, ArH), 7.17-7.30 (4H, m, ArH), 7.36-7.48 (5H, m, ArH), 7.89 (1H, s, OH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 14.7, 20.5, 27.0, 52.1, 67.2, 72.3, 117.5, 119.8, 124.4, 125.1, 125.6, 126.6, 127.4, 128.3, 128.5, 128.8, 129.2, 129.9, 135.0, 139.3, 146.0, 147.3, 148.0, 153.0; MS (EI) *m/z* (%): 370 (3.46) [M^+], 338 (63.73), 324 (13.36), 233 (35.36), 218 (8.80), 189 (7.05), 105 (100.00), 77 (77.55); HRMS (EI) Calcd. for $C_{26}H_{26}O_2$ (M^+) requires 370.1933, Found: 370.1931.

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77.000
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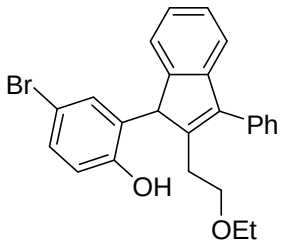
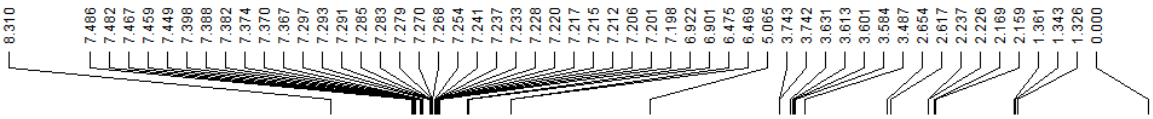
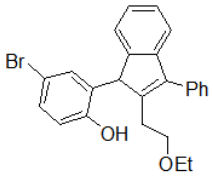
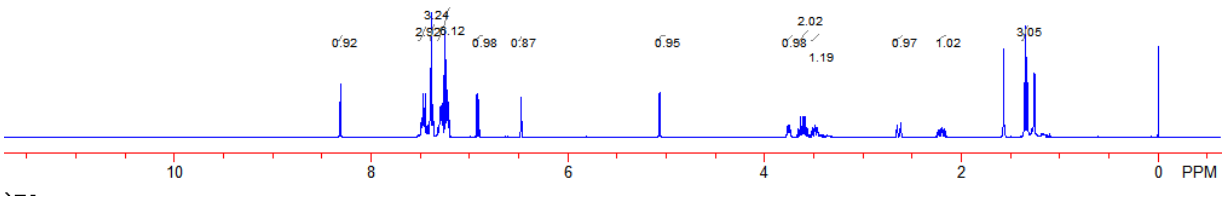
PPM

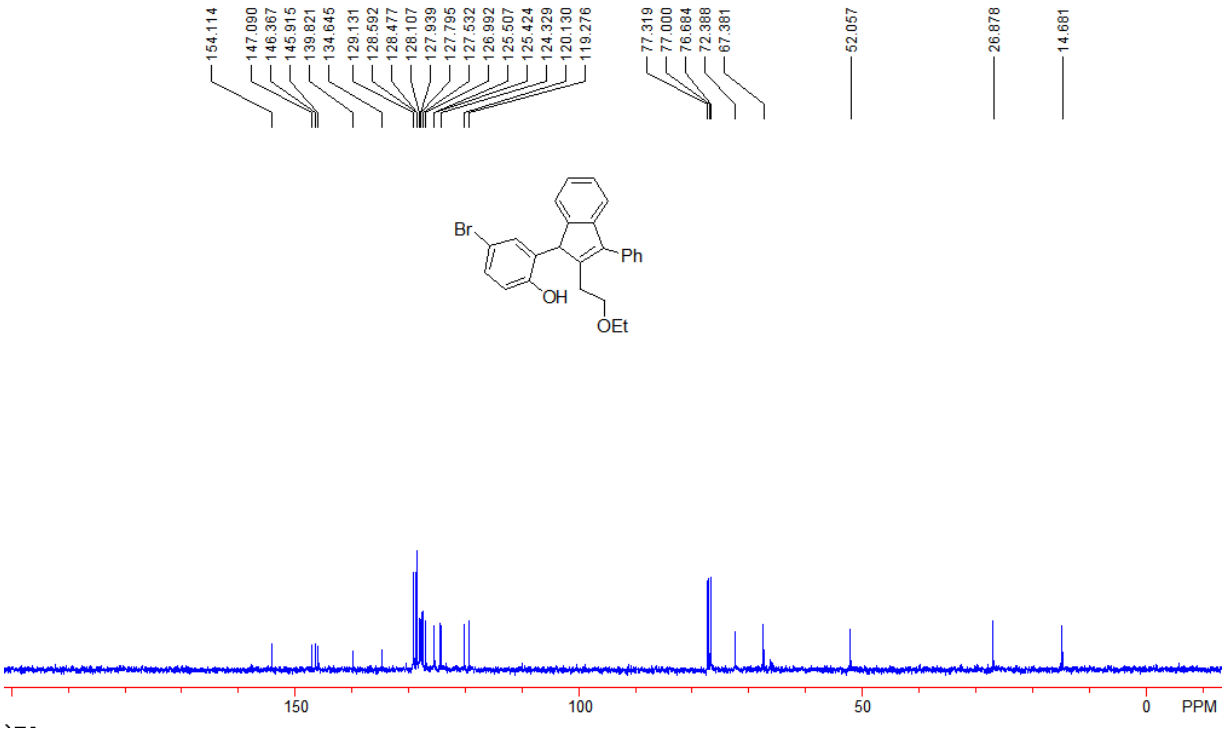


Compound 5c: A colorless oil; IR (CH_2Cl_2): ν 3379, 3063, 2926, 2870, 1714, 1661, 1470, 1449, 1272, 1108, 932, 810, 764, 702 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.34 (3H, t, *J* = 7.2 Hz, CH_3), 2.16-2.24 (1H, m, CH_2), 2.61-2.66 (1H, m, CH_2), 3.46-3.52 (1H, m, CH_2), 3.56-3.65 (2H, m, CH_2), 3.73-3.79 (1H, m, CH_2), 5.07 (1H, s, CH), 6.47 (1H, d, *J* = 2.4 Hz, ArH), 6.91 (1H, d, *J* = 8.4 Hz, ArH), 7.20-7.32 (5H, m, ArH), 7.36-7.38 (2H, m, ArH), 7.43-7.46 (3H, m, ArH), 8.31 (1H, s, OH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 14.7, 26.9, 52.1, 67.4, 72.4, 119.3, 120.1, 124.3, 125.4, 125.5, 127.0, 127.5, 127.8, 127.9, 128.1, 128.5, 128.6, 129.1, 134.6, 139.8, 145.9, 146.4, 147.1, 154.1. MS (EI) *m/z* (%): 448 (15.34) [M^+], 401 (100.00), 372 (39.56), 298 (20.09), 294 (30.08), 218 (71.37), 105 (91.75), 77 (40.73); HRMS (EI) Calcd. for $C_{26}H_{25}O_2Br$ (M^+) requires 448.1038, Found: 448.1034.





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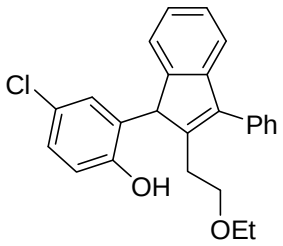
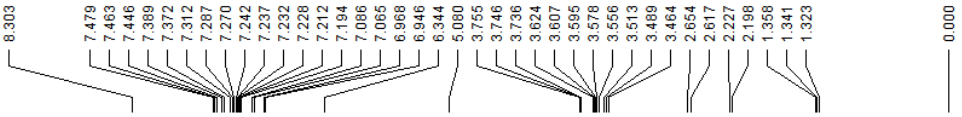
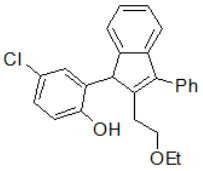
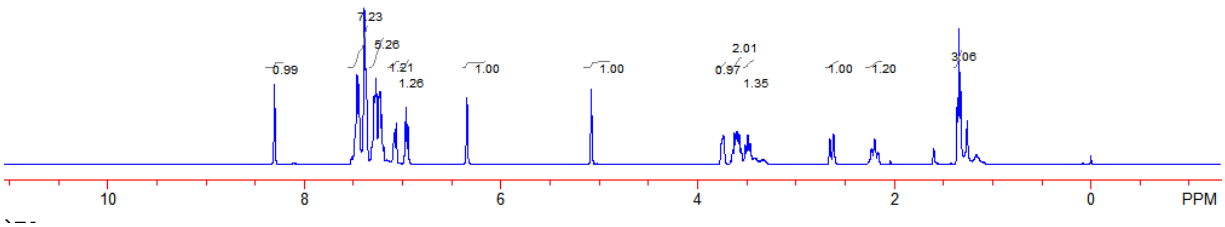
PPM

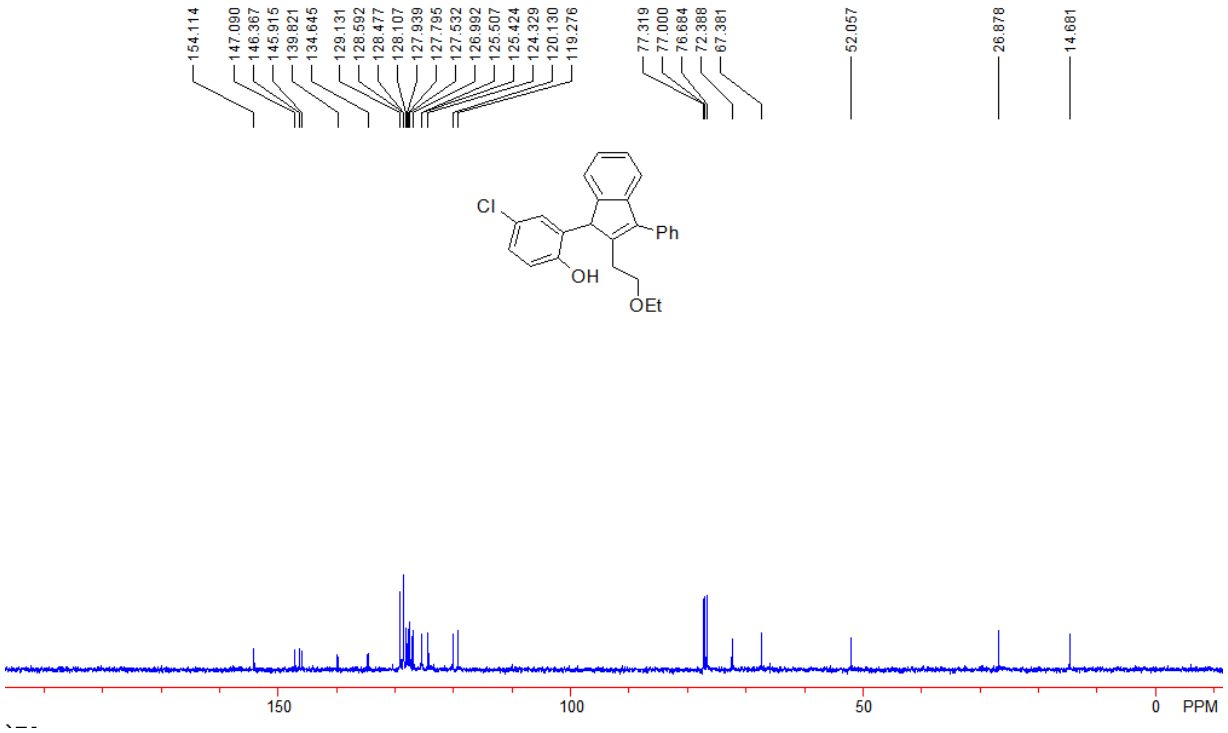


Compound 5d: A colorless oil; IR (CH_2Cl_2): ν 3375, 2974, 2870, 1715, 1663, 1596, 1474, 1449, 1287, 1110, 927, 807, 765, 704, 639 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.34 (3H, t, *J* = 7.2 Hz, CH_3), 2.17-2.20 (1H, m, CH_2), 2.61-2.65 (1H, m, CH_2), 3.46-3.51 (1H, m, CH_2), 3.55-3.62 (2H, m, CH_2), 3.73-3.75 (1H, m, CH_2), 5.08 (1H, s, CH), 6.34 (1H, s, ArH), 6.95 (1H, d, *J* = 8.4 Hz, ArH), 7.07 (1H, d, *J* = 8.4 Hz, ArH), 7.19-7.31 (4H, m, ArH), 7.37-7.48 (5H, m, ArH), 8.30 (1H, s, OH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 14.7, 26.9, 52.1, 67.4, 72.4, 119.3, 120.1, 124.3, 125.4, 125.5, 127.0, 127.5, 127.8, 127.9, 128.1, 128.6, 129.1, 134.6, 139.8, 145.9, 146.4, 147.1, 154.1; MS (EI) *m/z* (%): 390 (3.69) [M^+], 358 (75.52), 344 (18.09), 309 (12.50), 253 (36.14), 218 (27.00), 189 (9.53), 105 (100.00); HRMS (EI) Calcd. for $C_{25}H_{23}O_2Cl$ (M^+) requires 390.1387, Found: 390.1384.





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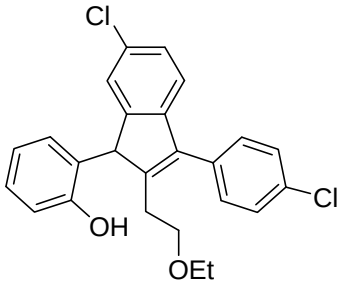
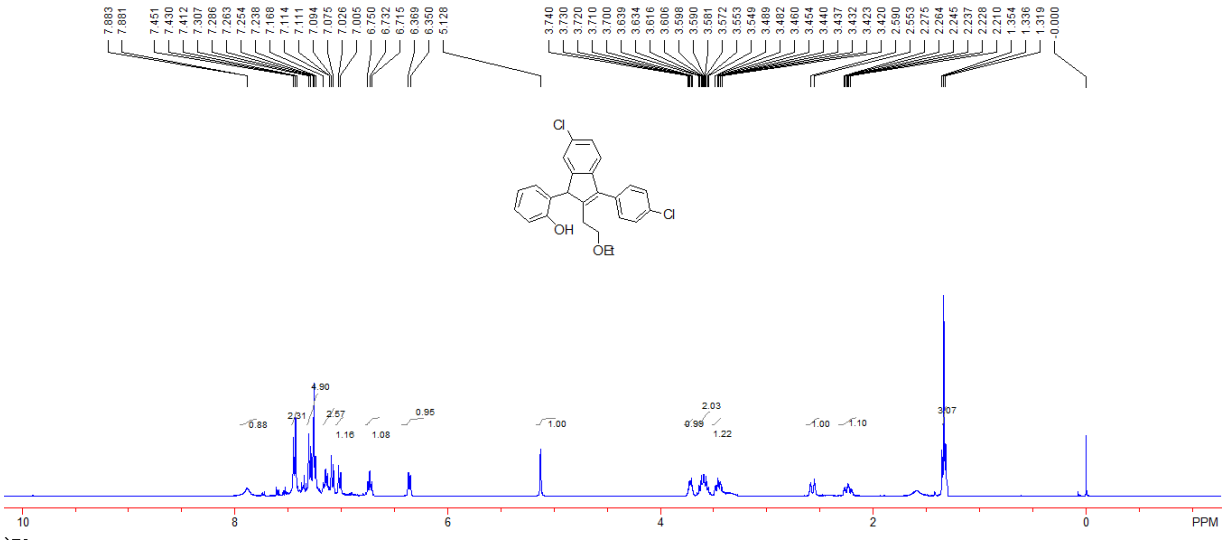
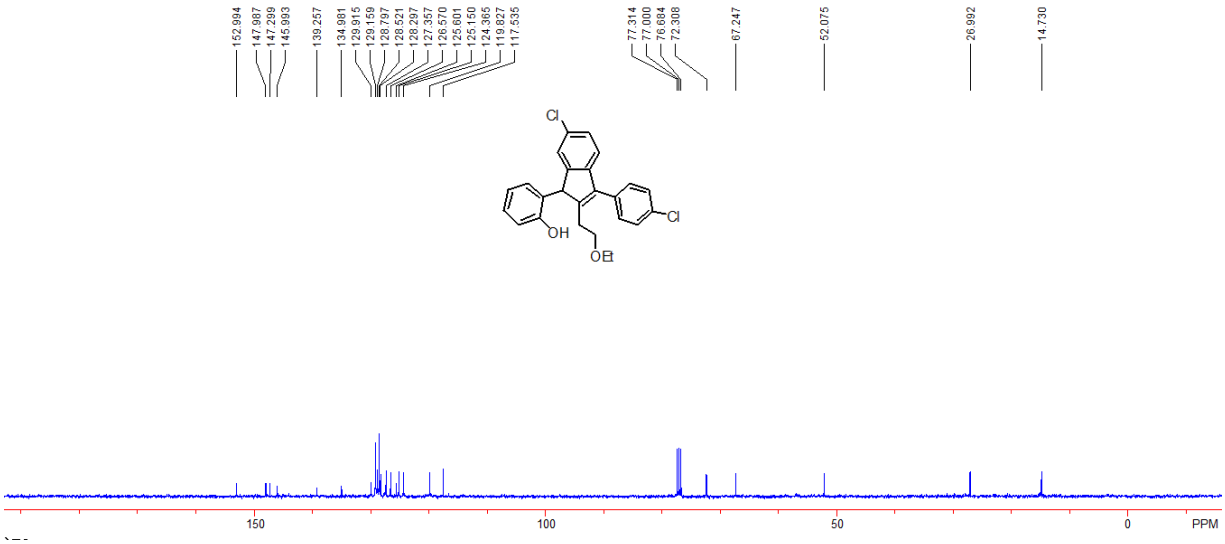


Compound 5e: A colorless oil; IR (CH_2Cl_2): ν 3354, 3065, 2973, 2928, 2870, 1714, 1669, 1587, 1487, 1455, 1399, 1286, 1246, 1091, 1014, 929, 751 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.34 (3H, t, *J* = 7.2 Hz, CH_3), 2.21-2.28 (1H, m, CH_2), 2.55-2.59 (1H, m, CH_2), 3.42-3.49 (1H, m, CH_2), 3.55-3.64 (2H, m, CH_2), 3.70-3.74 (1H, m, CH_2), 5.13 (1H, s, CH), 6.36 (1H, d, *J* = 7.6 Hz, ArH), 6.73 (1H, t, *J* = 7.2 Hz, ArH), 7.02 (1H, d, *J* = 8.4 Hz, ArH), 7.08-7.17 (2H, m, ArH), 7.24-7.31 (5H, m, ArH), 7.41-7.45 (2H, m, ArH), 7.88 (1H, s, OH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 14.7, 27.0, 52.1, 67.2, 72.3, 117.5, 119.8, 124.4, 125.1, 125.6, 126.6, 127.4, 128.3, 128.5, 128.8, 129.2, 129.9, 135.0, 139.3, 146.0, 147.3, 148.0, 153.0. MS (EI) *m/z* (%): 424 (11.27) [M^+], 392 (91.16), 378 (31.61), 338 (64.77), 253 (74.71), 218 (54.53), 139 (98.35), 59 (100.00); HRMS (EI) Calcd. for $C_{25}H_{22}O_2Cl_2$ (M^+) requires 424.0997, Found: 424.1001.

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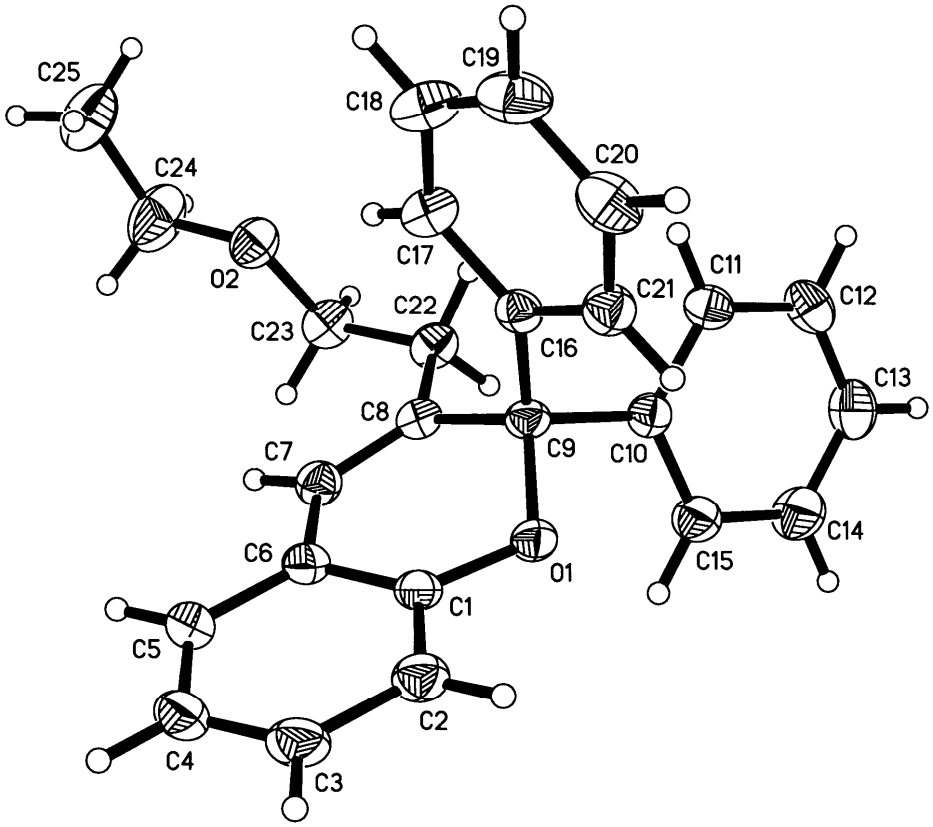
125.150
124.365
119.827
117.535
77.314
77.000
76.684
72.308
67.247
52.075
26.992
14.730
Cl
OH
OEt
Cl
150
100
50
0
PPM

Reference:

1. Shi, M.; Xu, B. *Org. Lett.* **2002**, *4*, 2145-2148.



The crystal data of **3a** have been deposited in CCDC with number 760083. Empirical Formula: $C_{25}H_{24}O_2$; Formula Weight: 356.44; Crystal Color, Habit: colorless, prismatic; Crystal Dimensions: 0.402 x 0.307 x 0.231 mm; Crystal System: Monoclinic; Lattice Type: Primitive; Lattice Parameters: a = 9.4459(9)Å, b = 11.0752(10)Å, c = 18.8988(18)Å, $\alpha = 90^o$, $\beta = 100.572(2)^o$, $\gamma = 90^o$, V = 1943.5(3)Å^3; Space group: P2(1)/n; Z = 4; D_{calc}= 1.218 g/cm^3; F_{000} = 760; Diffractometer: Rigaku AFC7R; Residuals: R; Rw: 0.0479, 0.1174.

Table 1. Crystal data and structure refinement for cd29665.

Identification code	cd29665
Empirical formula	C25 H24 O2
Formula weight	356.44
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 9.4459(9) A alpha = 90 deg. b = 11.0752(10) A beta = 100.572(2) deg. c = 18.8988(18) A gamma = 90 deg.
Volume	1943.5(3) A^3
Z, Calculated density	4, 1.218 Mg/m^3
Absorption coefficient	0.076 mm^-1
F(000)	760
Crystal size	0.402 x 0.307 x 0.231 mm
Theta range for data collection	2.14 to 25.50 deg.
Limiting indices	-11<=h<=9, -12<=k<=13, -22<=l<=22
Reflections collected / unique	10083 / 3619 [R(int) = 0.0439]
Completeness to theta = 25.50	99.8 %
Absorption correction	Empirical
Max. and min. transmission	1.00000 and 0.68648
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3619 / 0 / 245
Goodness-of-fit on F^2	0.993
Final R indices [I>2sigma(I)]	R1 = 0.0479, wR2 = 0.1174
R indices (all data)	R1 = 0.0645, wR2 = 0.1271
Largest diff. peak and hole	0.180 and -0.189 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for cd29665.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	5017(1)	6945(1)	208(1)	42(1)
O(2)	9003(1)	10276(1)	1351(1)	53(1)
C(1)	4158(2)	7479(1)	632(1)	39(1)
C(2)	2932(2)	6880(2)	724(1)	50(1)
C(3)	1993(2)	7449(2)	1099(1)	58(1)
C(4)	2273(2)	8589(2)	1371(1)	59(1)
C(5)	3517(2)	9170(2)	1279(1)	51(1)
C(6)	4486(2)	8623(1)	908(1)	42(1)
C(7)	5788(2)	9193(1)	763(1)	44(1)
C(8)	6770(2)	8576(1)	493(1)	39(1)
C(9)	6547(2)	7225(1)	370(1)	37(1)
C(10)	7096(2)	6813(1)	-304(1)	39(1)
C(11)	8464(2)	6335(1)	-261(1)	45(1)
C(12)	8963(2)	6004(2)	-876(1)	55(1)
C(13)	8102(2)	6130(2)	-1537(1)	60(1)
C(14)	6757(2)	6602(2)	-1586(1)	65(1)
C(15)	6252(2)	6952(2)	-975(1)	52(1)
C(16)	7210(2)	6480(1)	1030(1)	39(1)
C(17)	8123(2)	6963(2)	1618(1)	52(1)
C(18)	8703(2)	6228(2)	2188(1)	67(1)
C(19)	8374(2)	5027(2)	2188(1)	67(1)
C(20)	7461(2)	4543(2)	1613(1)	60(1)
C(21)	6882(2)	5261(2)	1035(1)	49(1)
C(22)	8124(2)	9118(1)	310(1)	46(1)
C(23)	8520(2)	10352(2)	600(1)	53(1)
C(24)	9421(3)	11391(2)	1659(1)	90(1)
C(25)	10154(3)	11285(2)	2405(1)	87(1)

Table 3. Bond lengths [A] and angles [deg] for cd29665.

O(1)-C(1)	1.3740(18)
O(1)-C(9)	1.4549(17)
O(2)-C(24)	1.391(2)
O(2)-C(23)	1.4128(19)
C(1)-C(2)	1.373(2)
C(1)-C(6)	1.384(2)
C(2)-C(3)	1.383(2)
C(2)-H(2)	0.9300
C(3)-C(4)	1.370(3)
C(3)-H(3)	0.9300
C(4)-C(5)	1.379(2)
C(4)-H(4)	0.9300
C(5)-C(6)	1.390(2)
C(5)-H(5)	0.9300
C(6)-C(7)	1.453(2)
C(7)-C(8)	1.327(2)
C(7)-H(7)	0.9300
C(8)-C(22)	1.509(2)
C(8)-C(9)	1.523(2)
C(9)-C(16)	1.530(2)
C(9)-C(10)	1.531(2)
C(10)-C(15)	1.376(2)
C(10)-C(11)	1.385(2)
C(11)-C(12)	1.381(2)
C(11)-H(11)	0.9300
C(12)-C(13)	1.366(3)
C(12)-H(12)	0.9300
C(13)-C(14)	1.362(3)
C(13)-H(13)	0.9300
C(14)-C(15)	1.384(2)
C(14)-H(14)	0.9300
C(15)-H(15)	0.9300
C(16)-C(17)	1.383(2)
C(16)-C(21)	1.386(2)
C(17)-C(18)	1.381(2)
C(17)-H(17)	0.9300
C(18)-C(19)	1.366(3)
C(18)-H(18)	0.9300
C(19)-C(20)	1.366(3)
C(19)-H(19)	0.9300
C(20)-C(21)	1.381(2)
C(20)-H(20)	0.9300
C(21)-H(21)	0.9300
C(22)-C(23)	1.494(2)
C(22)-H(22A)	0.9700
C(22)-H(22B)	0.9700
C(23)-H(23A)	0.9700
C(23)-H(23B)	0.9700
C(24)-C(25)	1.457(3)
C(24)-H(24A)	0.9700
C(24)-H(24B)	0.9700
C(25)-H(25A)	0.9600
C(25)-H(25B)	0.9600
C(25)-H(25C)	0.9600

C(1)-O(1)-C(9)	117.13(11)
C(24)-O(2)-C(23)	112.43(14)
C(2)-C(1)-O(1)	117.96(14)
C(2)-C(1)-C(6)	121.97(15)
O(1)-C(1)-C(6)	119.91(14)
C(1)-C(2)-C(3)	118.69(17)
C(1)-C(2)-H(2)	120.7
C(3)-C(2)-H(2)	120.7
C(4)-C(3)-C(2)	120.94(17)
C(4)-C(3)-H(3)	119.5
C(2)-C(3)-H(3)	119.5
C(3)-C(4)-C(5)	119.52(16)
C(3)-C(4)-H(4)	120.2

C(5)-C(4)-H(4)	120.2
C(4)-C(5)-C(6)	121.03(18)
C(4)-C(5)-H(5)	119.5
C(6)-C(5)-H(5)	119.5
C(1)-C(6)-C(5)	117.83(15)
C(1)-C(6)-C(7)	117.74(14)
C(5)-C(6)-C(7)	124.37(16)
C(8)-C(7)-C(6)	121.61(15)
C(8)-C(7)-H(7)	119.2
C(6)-C(7)-H(7)	119.2
C(7)-C(8)-C(22)	124.39(15)
C(7)-C(8)-C(9)	118.57(14)
C(22)-C(8)-C(9)	117.03(13)
O(1)-C(9)-C(8)	110.22(12)
O(1)-C(9)-C(16)	107.39(11)
C(8)-C(9)-C(16)	112.36(12)
O(1)-C(9)-C(10)	103.67(11)
C(8)-C(9)-C(10)	111.23(12)
C(16)-C(9)-C(10)	111.55(12)
C(15)-C(10)-C(11)	118.27(15)
C(15)-C(10)-C(9)	120.37(14)
C(11)-C(10)-C(9)	121.32(14)
C(12)-C(11)-C(10)	120.72(17)
C(12)-C(11)-H(11)	119.6
C(10)-C(11)-H(11)	119.6
C(13)-C(12)-C(11)	120.22(17)
C(13)-C(12)-H(12)	119.9
C(11)-C(12)-H(12)	119.9
C(14)-C(13)-C(12)	119.62(17)
C(14)-C(13)-H(13)	120.2
C(12)-C(13)-H(13)	120.2
C(13)-C(14)-C(15)	120.65(19)
C(13)-C(14)-H(14)	119.7
C(15)-C(14)-H(14)	119.7
C(10)-C(15)-C(14)	120.50(17)
C(10)-C(15)-H(15)	119.8
C(14)-C(15)-H(15)	119.8
C(17)-C(16)-C(21)	118.55(15)
C(17)-C(16)-C(9)	123.25(15)
C(21)-C(16)-C(9)	118.20(14)
C(18)-C(17)-C(16)	119.90(18)
C(18)-C(17)-H(17)	120.0
C(16)-C(17)-H(17)	120.0
C(19)-C(18)-C(17)	121.07(19)
C(19)-C(18)-H(18)	119.5
C(17)-C(18)-H(18)	119.5
C(18)-C(19)-C(20)	119.56(18)
C(18)-C(19)-H(19)	120.2
C(20)-C(19)-H(19)	120.2
C(19)-C(20)-C(21)	120.22(19)
C(19)-C(20)-H(20)	119.9
C(21)-C(20)-H(20)	119.9
C(20)-C(21)-C(16)	120.70(17)
C(20)-C(21)-H(21)	119.7
C(16)-C(21)-H(21)	119.7
C(23)-C(22)-C(8)	116.44(14)
C(23)-C(22)-H(22A)	108.2
C(8)-C(22)-H(22A)	108.2
C(23)-C(22)-H(22B)	108.2
C(8)-C(22)-H(22B)	108.2
H(22A)-C(22)-H(22B)	107.3
O(2)-C(23)-C(22)	109.02(13)
O(2)-C(23)-H(23A)	109.9
C(22)-C(23)-H(23A)	109.9
O(2)-C(23)-H(23B)	109.9
C(22)-C(23)-H(23B)	109.9
H(23A)-C(23)-H(23B)	108.3
O(2)-C(24)-C(25)	112.42(19)
O(2)-C(24)-H(24A)	109.1
C(25)-C(24)-H(24A)	109.1
O(2)-C(24)-H(24B)	109.1
C(25)-C(24)-H(24B)	109.1

H(24A)-C(24)-H(24B)	107.9
C(24)-C(25)-H(25A)	109.5
C(24)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
C(24)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for cd29665.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
O(1)	29(1)	51(1)	46(1)	-9(1)	6(1)	-5(1)
O(2)	57(1)	46(1)	56(1)	-4(1)	7(1)	-11(1)
C(1)	30(1)	50(1)	35(1)	0(1)	3(1)	3(1)
C(2)	37(1)	60(1)	53(1)	-3(1)	7(1)	-6(1)
C(3)	33(1)	86(2)	57(1)	-1(1)	11(1)	-4(1)
C(4)	42(1)	84(2)	50(1)	-5(1)	10(1)	14(1)
C(5)	43(1)	60(1)	48(1)	-7(1)	4(1)	9(1)
C(6)	36(1)	49(1)	39(1)	0(1)	2(1)	5(1)
C(7)	43(1)	40(1)	47(1)	-2(1)	4(1)	-2(1)
C(8)	36(1)	43(1)	36(1)	2(1)	2(1)	-3(1)
C(9)	27(1)	45(1)	39(1)	-2(1)	5(1)	-3(1)
C(10)	37(1)	40(1)	41(1)	-1(1)	9(1)	-4(1)
C(11)	39(1)	50(1)	49(1)	3(1)	12(1)	-1(1)
C(12)	52(1)	53(1)	68(1)	4(1)	29(1)	3(1)
C(13)	73(1)	64(1)	51(1)	-4(1)	30(1)	-2(1)
C(14)	70(1)	85(2)	40(1)	-2(1)	9(1)	4(1)
C(15)	48(1)	66(1)	42(1)	-2(1)	7(1)	7(1)
C(16)	33(1)	45(1)	39(1)	1(1)	11(1)	0(1)
C(17)	47(1)	60(1)	45(1)	3(1)	3(1)	-6(1)
C(18)	58(1)	87(2)	50(1)	11(1)	-7(1)	-5(1)
C(19)	57(1)	83(2)	60(1)	25(1)	5(1)	11(1)
C(20)	61(1)	52(1)	70(1)	16(1)	18(1)	8(1)
C(21)	48(1)	50(1)	49(1)	0(1)	9(1)	-1(1)
C(22)	44(1)	49(1)	46(1)	1(1)	9(1)	-10(1)
C(23)	53(1)	52(1)	54(1)	4(1)	13(1)	-12(1)
C(24)	125(2)	55(1)	80(2)	-12(1)	-2(2)	-19(1)
C(25)	103(2)	87(2)	69(2)	-18(1)	9(1)	-28(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for cd29665.

	x	y	z	U(eq)
H(2)	2736	6108	539	60
H(3)	1161	7053	1166	70
H(4)	1628	8967	1617	70
H(5)	3711	9940	1468	61
H(7)	5937	10011	861	52
H(11)	9053	6236	186	54
H(12)	9889	5695	-841	66
H(13)	8432	5894	-1950	72
H(14)	6171	6691	-2036	78
H(15)	5336	7283	-1017	63
H(17)	8345	7782	1630	62
H(18)	9327	6556	2579	81
H(19)	8768	4542	2576	81
H(20)	7230	3727	1611	72
H(21)	6264	4923	646	59
H(22A)	8920	8578	487	56
H(22B)	8020	9147	-210	56
H(23A)	9274	10685	372	63
H(23B)	7689	10881	496	63
H(24A)	8577	11897	1638	107
H(24B)	10059	11782	1381	107
H(25A)	9620	10752	2659	131
H(25B)	10220	12067	2628	131
H(25C)	11104	10967	2420	131

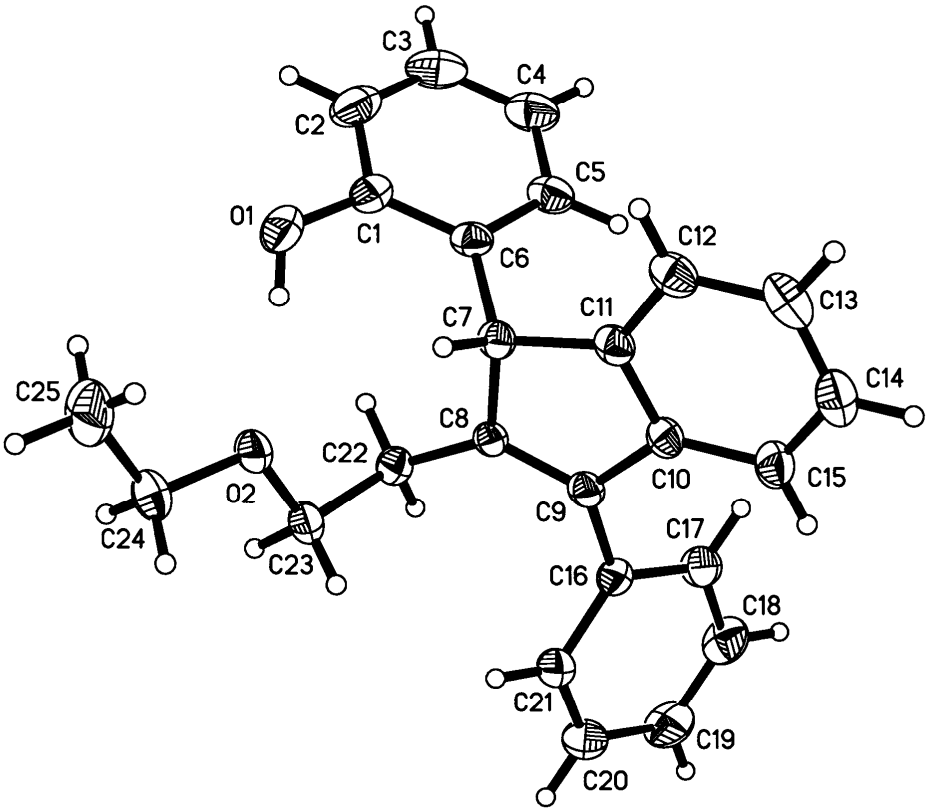
Table 6. Torsion angles [deg] for cd29665.

C(9)-O(1)-C(1)-C(2)	-151.48(14)
C(9)-O(1)-C(1)-C(6)	33.00(19)
O(1)-C(1)-C(2)-C(3)	-174.65(14)
C(6)-C(1)-C(2)-C(3)	0.8(3)
C(1)-C(2)-C(3)-C(4)	0.2(3)
C(2)-C(3)-C(4)-C(5)	-0.9(3)
C(3)-C(4)-C(5)-C(6)	0.6(3)
C(2)-C(1)-C(6)-C(5)	-1.0(2)
O(1)-C(1)-C(6)-C(5)	174.34(13)
C(2)-C(1)-C(6)-C(7)	-178.30(15)
O(1)-C(1)-C(6)-C(7)	-3.0(2)
C(4)-C(5)-C(6)-C(1)	0.3(2)
C(4)-C(5)-C(6)-C(7)	177.39(15)
C(1)-C(6)-C(7)-C(8)	-12.2(2)
C(5)-C(6)-C(7)-C(8)	170.74(15)
C(6)-C(7)-C(8)-C(22)	178.22(14)
C(6)-C(7)-C(8)-C(9)	-3.0(2)
C(1)-O(1)-C(9)-C(8)	-45.08(16)
C(1)-O(1)-C(9)-C(16)	77.62(15)
C(1)-O(1)-C(9)-C(10)	-164.20(12)
C(7)-C(8)-C(9)-O(1)	30.23(19)
C(22)-C(8)-C(9)-O(1)	-150.93(13)
C(7)-C(8)-C(9)-C(16)	-89.51(17)
C(22)-C(8)-C(9)-C(16)	89.33(15)
C(7)-C(8)-C(9)-C(10)	144.63(14)
C(22)-C(8)-C(9)-C(10)	-36.53(18)
O(1)-C(9)-C(10)-C(15)	36.41(19)
C(8)-C(9)-C(10)-C(15)	-82.01(18)
C(16)-C(9)-C(10)-C(15)	151.67(15)
O(1)-C(9)-C(10)-C(11)	-146.03(14)
C(8)-C(9)-C(10)-C(11)	95.55(17)
C(16)-C(9)-C(10)-C(11)	-30.76(19)
C(15)-C(10)-C(11)-C(12)	-0.2(2)
C(9)-C(10)-C(11)-C(12)	-177.79(15)
C(10)-C(11)-C(12)-C(13)	-0.9(3)
C(11)-C(12)-C(13)-C(14)	1.1(3)
C(12)-C(13)-C(14)-C(15)	-0.3(3)
C(11)-C(10)-C(15)-C(14)	1.0(3)
C(9)-C(10)-C(15)-C(14)	178.68(16)
C(13)-C(14)-C(15)-C(10)	-0.8(3)
O(1)-C(9)-C(16)-C(17)	-132.20(15)
C(8)-C(9)-C(16)-C(17)	-10.84(19)
C(10)-C(9)-C(16)-C(17)	114.85(16)
O(1)-C(9)-C(16)-C(21)	48.03(17)
C(8)-C(9)-C(16)-C(21)	169.39(13)
C(10)-C(9)-C(16)-C(21)	-64.92(17)
C(21)-C(16)-C(17)-C(18)	1.1(2)
C(9)-C(16)-C(17)-C(18)	-178.69(15)
C(16)-C(17)-C(18)-C(19)	-1.0(3)
C(17)-C(18)-C(19)-C(20)	0.3(3)
C(18)-C(19)-C(20)-C(21)	0.4(3)
C(19)-C(20)-C(21)-C(16)	-0.3(3)
C(17)-C(16)-C(21)-C(20)	-0.5(2)
C(9)-C(16)-C(21)-C(20)	179.31(14)
C(7)-C(8)-C(22)-C(23)	13.6(2)
C(9)-C(8)-C(22)-C(23)	-165.12(14)
C(24)-O(2)-C(23)-C(22)	178.75(16)
C(8)-C(22)-C(23)-O(2)	71.55(19)
C(23)-O(2)-C(24)-C(25)	-169.82(18)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for cd29665 [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)



The crystal data of **5a** have been deposited in CCDC with number 739822. Empirical Formula: $C_{25}H_{24}O_2$; Formula Weight: 356.44; Crystal Color, Habit: colorless, prismatic; Crystal Dimensions: 0.401 x 0.311 x 0.269 mm; Crystal System: Monoclinic; Lattice Type: Primitive; Lattice Parameters: a = 15.829(2)Å, b = 7.5020(12)Å, c = 16.492(3)Å, $\alpha = 90^o$, $\beta = 95.853(3)^o$, $\gamma = 90^o$, V = 1948.2(5)Å^3; Space group: P2(1)/n; Z = 4; D_{calc}= 1.215 g/cm^3; F_{000} = 760; Diffractometer: Rigaku AFC7R; Residuals: R; Rw: 0.0593, 0.1714.

Table 1. Crystal data and structure refinement for cd29352.

Identification code	cd29352
Empirical formula	C25 H24 O2
Formula weight	356.44
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 15.829(2) A alpha = 90 deg. b = 7.5020(12) A beta = 95.853(3) deg. c = 16.492(3) A gamma = 90 deg.
Volume	1948.2(5) A^3
Z, Calculated density	4, 1.215 Mg/m^3
Absorption coefficient	0.075 mm^-1
F(000)	760
Crystal size	0.401 x 0.311 x 0.269 mm
Theta range for data collection	1.70 to 27.00 deg.
Limiting indices	-19<=h<=20, -6<=k<=9, -20<=l<=21
Reflections collected / unique	10768 / 4242 [R(int) = 0.0418]
Completeness to theta = 27.00	99.7 %
Absorption correction	Empirical
Max. and min. transmission	1.00000 and 0.78729
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4242 / 1 / 249
Goodness-of-fit on F^2	1.045
Final R indices [I>2sigma(I)]	R1 = 0.0593, wR2 = 0.1714
R indices (all data)	R1 = 0.0866, wR2 = 0.1821
Largest diff. peak and hole	0.220 and -0.182 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for cd29352.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	8781(1)	2750(3)	-937(1)	72(1)
O(2)	9222(1)	2934(2)	721(1)	52(1)
C(1)	7939(2)	2819(3)	-1224(1)	51(1)
C(2)	7726(2)	3759(4)	-1948(2)	69(1)
C(3)	6893(2)	3864(4)	-2279(2)	75(1)
C(4)	6267(2)	3030(4)	-1908(2)	66(1)
C(5)	6475(2)	2099(3)	-1208(1)	51(1)
C(6)	7313(1)	1951(3)	-846(1)	42(1)
C(7)	7501(1)	933(3)	-48(1)	38(1)
C(8)	7336(1)	2081(3)	687(1)	36(1)
C(9)	6744(1)	1292(3)	1101(1)	38(1)
C(10)	6495(1)	-431(3)	723(1)	40(1)
C(11)	6933(1)	-660(3)	34(1)	40(1)
C(12)	6815(1)	-2177(3)	-440(1)	50(1)
C(13)	6266(2)	-3484(4)	-209(2)	60(1)
C(14)	5853(2)	-3283(4)	482(2)	61(1)
C(15)	5956(1)	-1772(3)	950(2)	53(1)
C(16)	6341(1)	2037(3)	1803(1)	41(1)
C(17)	5455(1)	2101(4)	1767(1)	52(1)
C(18)	5057(2)	2811(4)	2395(2)	64(1)
C(19)	5530(2)	3468(4)	3078(2)	69(1)
C(20)	6403(2)	3415(4)	3129(1)	66(1)
C(21)	6811(2)	2699(3)	2499(1)	52(1)
C(22)	7777(1)	3810(3)	870(1)	43(1)
C(23)	8681(1)	3627(4)	1285(1)	52(1)
C(24)	10095(1)	3072(4)	1022(2)	66(1)
C(25)	10640(2)	2443(5)	408(2)	88(1)

Table 3. Bond lengths [A] and angles [deg] for cd29352.

O(1)-C(1)	1.370(3)
O(1)-H(1)	0.849(17)
O(2)-C(24)	1.424(3)
O(2)-C(23)	1.426(3)
C(1)-C(6)	1.385(3)
C(1)-C(2)	1.398(4)
C(2)-C(3)	1.377(4)
C(2)-H(2)	0.9300
C(3)-C(4)	1.367(4)
C(3)-H(3)	0.9300
C(4)-C(5)	1.360(3)
C(4)-H(4)	0.9300
C(5)-C(6)	1.403(3)
C(5)-H(5)	0.9300
C(6)-C(7)	1.525(3)
C(7)-C(11)	1.509(3)
C(7)-C(8)	1.530(3)
C(7)-H(7)	0.9800
C(8)-C(9)	1.351(3)
C(8)-C(22)	1.490(3)
C(9)-C(10)	1.472(3)
C(9)-C(16)	1.486(3)
C(10)-C(15)	1.395(3)
C(10)-C(11)	1.400(3)
C(11)-C(12)	1.382(3)
C(12)-C(13)	1.388(4)
C(12)-H(12)	0.9300
C(13)-C(14)	1.379(4)
C(13)-H(13)	0.9300
C(14)-C(15)	1.372(4)
C(14)-H(14)	0.9300
C(15)-H(15)	0.9300
C(16)-C(21)	1.393(3)
C(16)-C(17)	1.398(3)
C(17)-C(18)	1.374(3)
C(17)-H(17)	0.9300
C(18)-C(19)	1.378(4)
C(18)-H(18)	0.9300
C(19)-C(20)	1.376(4)
C(19)-H(19)	0.9300
C(20)-C(21)	1.386(3)
C(20)-H(20)	0.9300
C(21)-H(21)	0.9300
C(22)-C(23)	1.527(3)
C(22)-H(22A)	0.9700
C(22)-H(22B)	0.9700
C(23)-H(23A)	0.9700
C(23)-H(23B)	0.9700
C(24)-C(25)	1.474(4)
C(24)-H(24A)	0.9700
C(24)-H(24B)	0.9700
C(25)-H(25A)	0.9600
C(25)-H(25B)	0.9600
C(25)-H(25C)	0.9600

C(1)-O(1)-H(1)	118(2)
C(24)-O(2)-C(23)	111.91(17)
O(1)-C(1)-C(6)	122.9(2)
O(1)-C(1)-C(2)	117.1(2)
C(6)-C(1)-C(2)	120.0(2)
C(3)-C(2)-C(1)	120.3(2)
C(3)-C(2)-H(2)	119.8
C(1)-C(2)-H(2)	119.8
C(4)-C(3)-C(2)	120.3(2)
C(4)-C(3)-H(3)	119.9
C(2)-C(3)-H(3)	119.9
C(5)-C(4)-C(3)	119.4(3)
C(5)-C(4)-H(4)	120.3

C(3)-C(4)-H(4)	120.3
C(4)-C(5)-C(6)	122.5(2)
C(4)-C(5)-H(5)	118.7
C(6)-C(5)-H(5)	118.7
C(1)-C(6)-C(5)	117.4(2)
C(1)-C(6)-C(7)	122.59(19)
C(5)-C(6)-C(7)	119.97(19)
C(11)-C(7)-C(6)	114.09(16)
C(11)-C(7)-C(8)	102.94(15)
C(6)-C(7)-C(8)	111.56(17)
C(11)-C(7)-H(7)	109.3
C(6)-C(7)-H(7)	109.3
C(8)-C(7)-H(7)	109.3
C(9)-C(8)-C(22)	127.86(18)
C(9)-C(8)-C(7)	109.69(18)
C(22)-C(8)-C(7)	122.44(16)
C(8)-C(9)-C(10)	109.85(17)
C(8)-C(9)-C(16)	127.1(2)
C(10)-C(9)-C(16)	122.90(18)
C(15)-C(10)-C(11)	119.8(2)
C(15)-C(10)-C(9)	131.58(19)
C(11)-C(10)-C(9)	108.57(18)
C(12)-C(11)-C(10)	120.6(2)
C(12)-C(11)-C(7)	130.47(19)
C(10)-C(11)-C(7)	108.89(18)
C(11)-C(12)-C(13)	118.6(2)
C(11)-C(12)-H(12)	120.7
C(13)-C(12)-H(12)	120.7
C(14)-C(13)-C(12)	120.8(2)
C(14)-C(13)-H(13)	119.6
C(12)-C(13)-H(13)	119.6
C(15)-C(14)-C(13)	121.1(2)
C(15)-C(14)-H(14)	119.5
C(13)-C(14)-H(14)	119.5
C(14)-C(15)-C(10)	119.0(2)
C(14)-C(15)-H(15)	120.5
C(10)-C(15)-H(15)	120.5
C(21)-C(16)-C(17)	118.11(19)
C(21)-C(16)-C(9)	122.67(18)
C(17)-C(16)-C(9)	119.21(18)
C(18)-C(17)-C(16)	121.1(2)
C(18)-C(17)-H(17)	119.4
C(16)-C(17)-H(17)	119.4
C(17)-C(18)-C(19)	120.1(2)
C(17)-C(18)-H(18)	119.9
C(19)-C(18)-H(18)	119.9
C(20)-C(19)-C(18)	119.9(2)
C(20)-C(19)-H(19)	120.1
C(18)-C(19)-H(19)	120.1
C(19)-C(20)-C(21)	120.5(2)
C(19)-C(20)-H(20)	119.8
C(21)-C(20)-H(20)	119.8
C(20)-C(21)-C(16)	120.3(2)
C(20)-C(21)-H(21)	119.8
C(16)-C(21)-H(21)	119.8
C(8)-C(22)-C(23)	114.29(19)
C(8)-C(22)-H(22A)	108.7
C(23)-C(22)-H(22A)	108.7
C(8)-C(22)-H(22B)	108.7
C(23)-C(22)-H(22B)	108.7
H(22A)-C(22)-H(22B)	107.6
O(2)-C(23)-C(22)	109.76(17)
O(2)-C(23)-H(23A)	109.7
C(22)-C(23)-H(23A)	109.7
O(2)-C(23)-H(23B)	109.7
C(22)-C(23)-H(23B)	109.7
H(23A)-C(23)-H(23B)	108.2
O(2)-C(24)-C(25)	110.7(2)
O(2)-C(24)-H(24A)	109.5
C(25)-C(24)-H(24A)	109.5
O(2)-C(24)-H(24B)	109.5
C(25)-C(24)-H(24B)	109.5

H(24A)-C(24)-H(24B)	108.1
C(24)-C(25)-H(25A)	109.5
C(24)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
C(24)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for cd29352.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
O(1)	48(1)	112(2)	59(1)	9(1)	16(1)	-11(1)
O(2)	29(1)	77(1)	49(1)	-6(1)	1(1)	-4(1)
C(1)	50(1)	64(2)	41(1)	-3(1)	12(1)	-2(1)
C(2)	90(2)	71(2)	48(1)	6(1)	24(1)	-7(2)
C(3)	103(2)	77(2)	41(1)	6(1)	-6(1)	18(2)
C(4)	69(2)	80(2)	44(1)	1(1)	-8(1)	13(2)
C(5)	48(1)	62(2)	41(1)	-5(1)	-4(1)	8(1)
C(6)	43(1)	48(1)	34(1)	-6(1)	5(1)	6(1)
C(7)	28(1)	47(1)	39(1)	-3(1)	3(1)	4(1)
C(8)	26(1)	49(1)	33(1)	1(1)	0(1)	1(1)
C(9)	28(1)	49(1)	36(1)	-2(1)	0(1)	1(1)
C(10)	28(1)	48(1)	44(1)	2(1)	-2(1)	1(1)
C(11)	30(1)	47(1)	42(1)	-1(1)	-3(1)	4(1)
C(12)	42(1)	56(2)	50(1)	-8(1)	-5(1)	8(1)
C(13)	52(1)	48(2)	76(2)	-13(1)	-14(1)	1(1)
C(14)	48(1)	54(2)	79(2)	5(1)	-6(1)	-9(1)
C(15)	38(1)	61(2)	59(1)	3(1)	2(1)	-8(1)
C(16)	36(1)	50(1)	38(1)	1(1)	7(1)	-2(1)
C(17)	37(1)	71(2)	49(1)	1(1)	5(1)	4(1)
C(18)	45(1)	81(2)	70(2)	7(2)	21(1)	14(1)
C(19)	76(2)	74(2)	62(2)	-11(1)	33(1)	9(2)
C(20)	75(2)	80(2)	45(1)	-17(1)	13(1)	-16(2)
C(21)	43(1)	68(2)	43(1)	-3(1)	6(1)	-9(1)
C(22)	38(1)	49(1)	43(1)	-3(1)	8(1)	-2(1)
C(23)	37(1)	69(2)	50(1)	-11(1)	5(1)	-14(1)
C(24)	32(1)	94(2)	69(2)	2(2)	-5(1)	-6(1)
C(25)	38(1)	118(3)	108(2)	-7(2)	12(1)	6(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for cd29352.

	x	y	z	U(eq)
H(2)	8149	4317	-2207	82
H(3)	6755	4504	-2757	89
H(4)	5705	3099	-2132	79
H(5)	6045	1537	-961	61
H(7)	8095	546	9	46
H(12)	7097	-2319	-903	60
H(13)	6177	-4507	-525	72
H(14)	5498	-4187	633	73
H(15)	5670	-1643	1412	63
H(17)	5130	1655	1310	63
H(18)	4467	2848	2360	77
H(19)	5260	3947	3503	83
H(20)	6721	3862	3589	79
H(21)	7401	2661	2540	62
H(22A)	7446	4509	1219	52
H(22B)	7797	4463	365	52
H(23A)	8887	4782	1481	62
H(23B)	8683	2833	1750	62
H(24A)	10203	2365	1514	79
H(24B)	10230	4304	1159	79
H(25A)	10527	1206	294	131
H(25B)	11226	2588	614	131
H(25C)	10524	3125	-83	131
H(1)	8912(18)	2630(40)	-428(11)	71(9)

Table 6. Torsion angles [deg] for cd29352.

O(1)-C(1)-C(2)-C(3)	179.1(3)
C(6)-C(1)-C(2)-C(3)	1.5(4)
C(1)-C(2)-C(3)-C(4)	-0.8(4)
C(2)-C(3)-C(4)-C(5)	0.1(4)
C(3)-C(4)-C(5)-C(6)	-0.1(4)
O(1)-C(1)-C(6)-C(5)	-178.9(2)
C(2)-C(1)-C(6)-C(5)	-1.5(3)
O(1)-C(1)-C(6)-C(7)	3.8(4)
C(2)-C(1)-C(6)-C(7)	-178.8(2)
C(4)-C(5)-C(6)-C(1)	0.8(3)
C(4)-C(5)-C(6)-C(7)	178.2(2)
C(1)-C(6)-C(7)-C(11)	-147.9(2)
C(5)-C(6)-C(7)-C(11)	34.8(3)
C(1)-C(6)-C(7)-C(8)	95.9(2)
C(5)-C(6)-C(7)-C(8)	-81.3(2)
C(11)-C(7)-C(8)-C(9)	-1.9(2)
C(6)-C(7)-C(8)-C(9)	120.83(18)
C(11)-C(7)-C(8)-C(22)	178.88(17)
C(6)-C(7)-C(8)-C(22)	-58.4(2)
C(22)-C(8)-C(9)-C(10)	-178.33(18)
C(7)-C(8)-C(9)-C(10)	2.5(2)
C(22)-C(8)-C(9)-C(16)	5.5(3)
C(7)-C(8)-C(9)-C(16)	-173.68(17)
C(8)-C(9)-C(10)-C(15)	175.5(2)
C(16)-C(9)-C(10)-C(15)	-8.1(3)
C(8)-C(9)-C(10)-C(11)	-2.2(2)
C(16)-C(9)-C(10)-C(11)	174.24(17)
C(15)-C(10)-C(11)-C(12)	2.2(3)
C(9)-C(10)-C(11)-C(12)	-179.87(18)
C(15)-C(10)-C(11)-C(7)	-177.10(18)
C(9)-C(10)-C(11)-C(7)	0.9(2)
C(6)-C(7)-C(11)-C(12)	60.3(3)
C(8)-C(7)-C(11)-C(12)	-178.6(2)
C(6)-C(7)-C(11)-C(10)	-120.48(18)
C(8)-C(7)-C(11)-C(10)	0.6(2)
C(10)-C(11)-C(12)-C(13)	-1.3(3)
C(7)-C(11)-C(12)-C(13)	177.8(2)
C(11)-C(12)-C(13)-C(14)	-0.6(3)
C(12)-C(13)-C(14)-C(15)	1.5(4)
C(13)-C(14)-C(15)-C(10)	-0.6(4)
C(11)-C(10)-C(15)-C(14)	-1.2(3)
C(9)-C(10)-C(15)-C(14)	-178.6(2)
C(8)-C(9)-C(16)-C(21)	-52.9(3)
C(10)-C(9)-C(16)-C(21)	131.3(2)
C(8)-C(9)-C(16)-C(17)	126.4(2)
C(10)-C(9)-C(16)-C(17)	-49.4(3)
C(21)-C(16)-C(17)-C(18)	0.6(4)
C(9)-C(16)-C(17)-C(18)	-178.7(2)
C(16)-C(17)-C(18)-C(19)	-0.3(4)
C(17)-C(18)-C(19)-C(20)	0.1(4)
C(18)-C(19)-C(20)-C(21)	-0.2(4)
C(19)-C(20)-C(21)-C(16)	0.5(4)
C(17)-C(16)-C(21)-C(20)	-0.7(4)
C(9)-C(16)-C(21)-C(20)	178.6(2)
C(9)-C(8)-C(22)-C(23)	101.7(2)
C(7)-C(8)-C(22)-C(23)	-79.2(2)
C(24)-O(2)-C(23)-C(22)	168.2(2)
C(8)-C(22)-C(23)-O(2)	70.4(2)
C(23)-O(2)-C(24)-C(25)	-176.7(2)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for cd29352 [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1)...O(2)	0.849(17)	1.923(18)	2.757(2)	167(3)

Symmetry transformations used to generate equivalent atoms: