Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

A Facile Method for the Synthesis of Trifluoromethylthio/Chloro-Homoallylic alcohol from Methylenecyclopropanes

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Contents

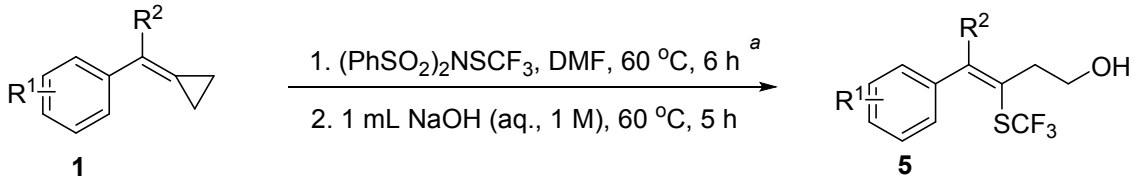
General Remarks

^{1}H NMR spectra were recorded on a Varian Mercury-300 and 400 spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard; coupling constants *J* are given in Hz. ^{13}C NMR spectra were recorded on a Varian Mercury-300 and 400 spectrophotometers (75 or 100 MHz) with complete proton decoupling spectrophotometers ($CDCl_3$: 77.0 ppm). Mass and HRMS spectra were recorded by EI method. Organic solvents used were dried by standard methods when necessary. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1}. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. Commercially obtained reagents were used without further purification. All these reactions were monitored by TLC with silica gel coated plates or ^{19}F NMR. Flash column chromatography was carried out using silica gel at increased pressure. All the MCPs involved are known compounds prepared according to a general procedure in literature.[1]

General Procedure for the Preparation of 3[2]

$(PhSO_2)_2NCl$ (3.3 g, 10 mmol) and $AgSCF_3$ (2.5 g, 12 mmol) were placed in a flask and DCM (30 mL) was added. The mixture was stirred at ambient temperature for about 2 h. Then the mixture was transferred into a 250 mL flask and the solvent was removed under vacuum. The residue was dissolve with minimum DCM and 100 mL PE was added. Shake the flask carefully and white precipitate occur. Stop shaking and wait for the solvent to become clear. Filter and the residue was re-extracted in the same procedure for another twice. Combine the solvent and concentrate under vacuum to obtain milky oil, which would become white crystal when dealt with on the oil pump. The yield is about 70%. ($(PhSO_2)_2NCl$ is instantly available by stirring $(PhSO_2)_2NH$ (60.0 mmol, 17.8 g) with t-BuOCl (84.0 mmol, 10 mL) in MeOH for 5 min in a yield of about 50%).[2]

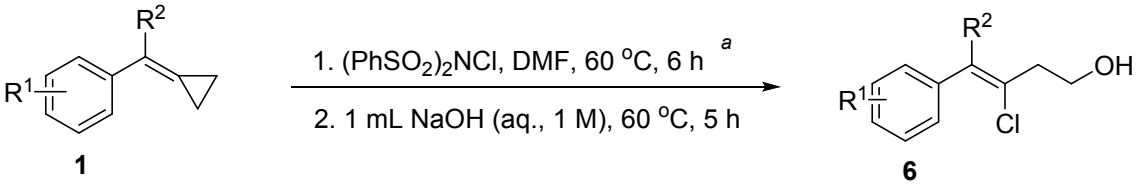
General Procedure for the Synthesis of trifluoromethylthio-homoallylic alcohol from MCPs



1 **5**

Compound **1** (0.2mmol) and $(PhSO_2)_2NSCF_3$ (158.8 mg, 0.4 mmol) were placed in a Schlenk tube. The tube was evacuated and backfilled with Ar for three times and then DMF (2 mL) was injected. Afterwards, the reaction mixture was stirred at 60 °C in an oil bath for 6 h. Then 1 mL NaOH (aq. 1 M) was injected and continued to stir for another 5 h. When the reaction completed, the product was extracted with EtOAc and washed with water. The organic layer was dried over Na_2SO_4 and concentrated on a rotary evaporator. The residue was purified by the silica gel flash chromatography (PE: EA=10:1) to give pure product **5**.

General Procedure for the Synthesis of chloro-homoallylic alcohol from MCPs

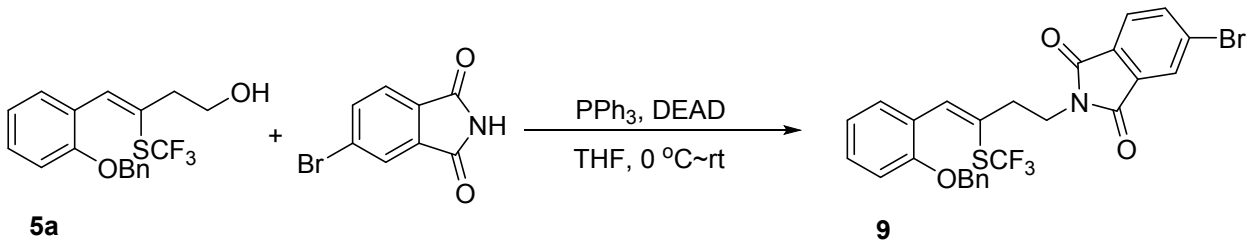


1 **6**

Compound **1** (0.2mmol) and $(PhSO_2)_2Cl$ (132.4 mg, 0.4 mmol) were placed in a Schlenk tube. The tube was evacuated and backfilled with Ar for three times and then DMF (2 mL) was injected. Afterwards, the reaction mixture was stirred at 60 °C in an oil bath for 6 h. Then 1 mL NaOH (aq. 1 M) was injected and continued to stir for another 5 h. When the reaction completed, the product was extracted with EtOAc and washed with water. The organic layer was dried over Na_2SO_4 and concentrated on a rotary evaporator. The residue was purified by the silica gel flash

chromatography (PE: EA=10:1) to give pure product **5**.

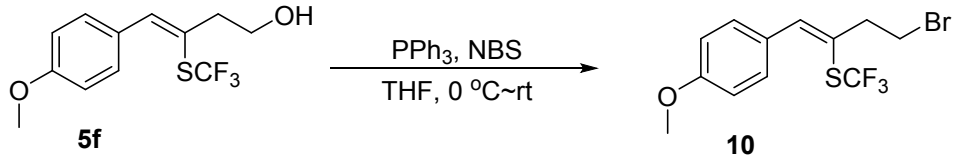
Procedure for the transformation of product 5a to 9



5a **9**

5a (70.9 mg, 0.2 mmol), 4-Bromophthalimide (45.2 mg, 0.2 mmol), PPh_3 (62.9mg, 0.24 mmol) were weighed into a 50 mL flask and Ar was flushed. 20 mL THF was injected and the mixture was placed in an ice-water bath. Then DEAD (56.4 μL, 0.36 mmol) was injected dropwise until the solution turned to light yellow and the mixture was continued to stir at room temperature overnight. When finished, the solvent was removed on a rotary evaporator and purified by the silica gel choromatography (PE:EA = 10 :1) to afford product **9** (white solid) in a yield of 50%, 56.2 mg.

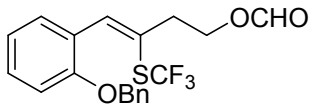
Procedure for the transformation of product 5f to 10



5f **10**

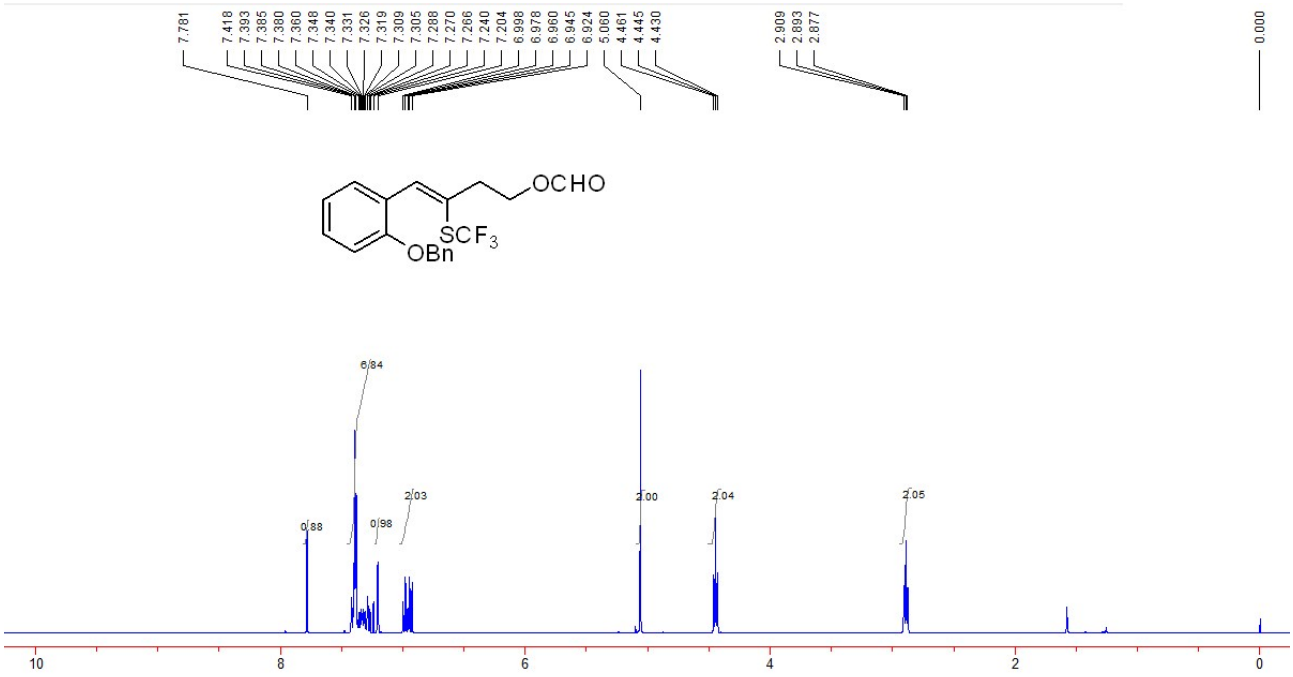
5f (55.6 mg, 0.2 mmol) and PPh_3 (104.8 mg, 0.4 mmol) were weighed into a 50 mL flask and 10 mL THF was injected. The flask was placed in an ice-water bath and NBS (71.2 mg, 0.4 mmol) dissolved in 10 mL THF was added dropwise. The mixture was continued to stir at room temperature overnight. When finished, the solvent was removed on a rotary evaporator and purified by the silica gel choromatography (PE:EA = 50 :1) to afford product **10** in a yield of 70%, 47.6 mg.

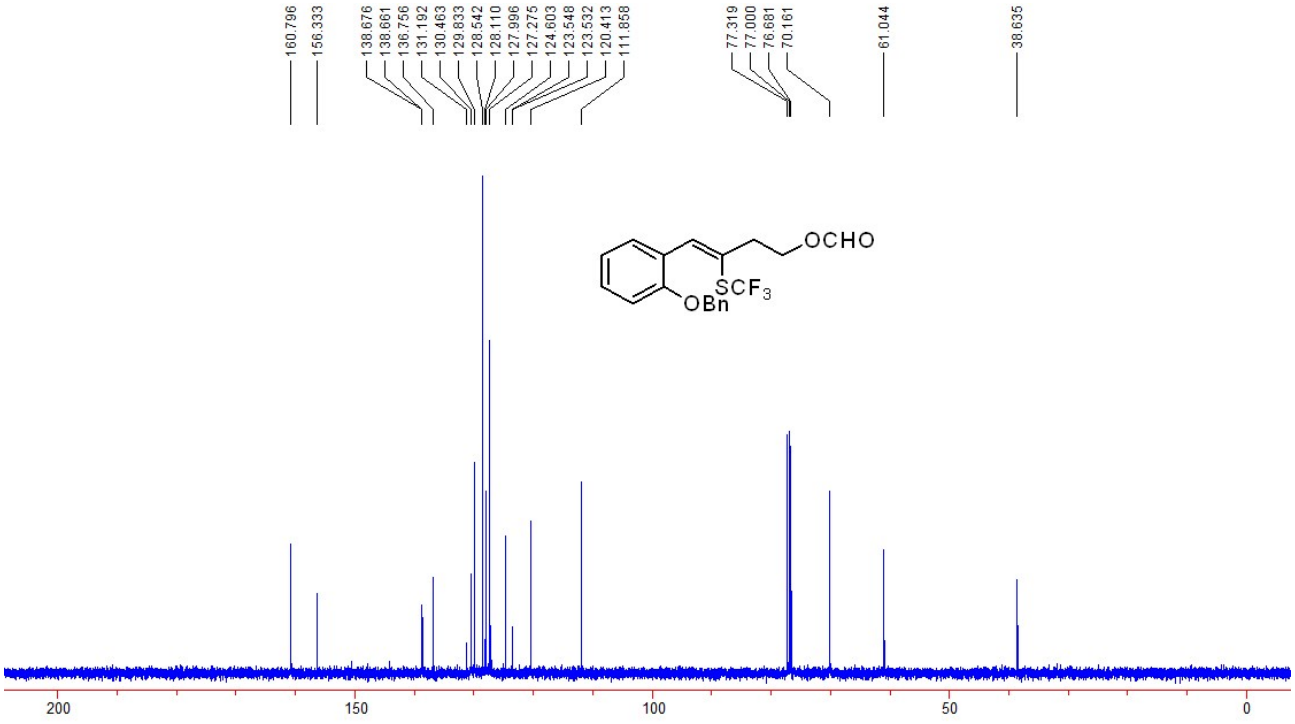
Spectroscopic Data of products 4a, 5, 6, 6', 9 and 10



(Z)-4-(2-(benzyloxy)phenyl)-3-((trifluoromethyl)thio)but-3-en-1-yl formate (4a).

A colorless oil, 39.0 mg, 51% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ. 2.89 (t, J = 6.4 Hz, 2H, CH_2), 4.45 (t, J = 6.4 Hz, 2H, CH_2), 5.06 (s, 2H, CH_2), 6.92-7.00 (m, 2H, ArH), 7.20 (s, 1H, CH), 7.24-7.42 (m, 7H, ArH), 7.78 (s, 1H, CH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 38.6, 61.0, 70.2, 111.8, 120.4, 123.5 (q, J = 1.6 Hz), 124.6, 127.3, 128.0, 128.5, 129.6 (q, J = 308.2 Hz), 129.8, 130.5, 136.8, 138.7 (q, J = 1.5 Hz), 156.3, 160.8. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -39.03. IR (CH_2Cl_2) ν 3034, 2928, 1723, 1484, 1451, 1246, 1152, 1106, 1088, 1019, 751, 696 cm^{-1}. MS (%) m/e 246 (4.63), 245 (6.83), 145 (17.62), 144 (9.39), 131 (4.96), 92 (10.14), 91 (M^+, 100.00), 65 (5.24). HRMS (EI) calcd. for $C_{19}H_{17}O_3F_3S$: 382.0851, Found: 382.0849.

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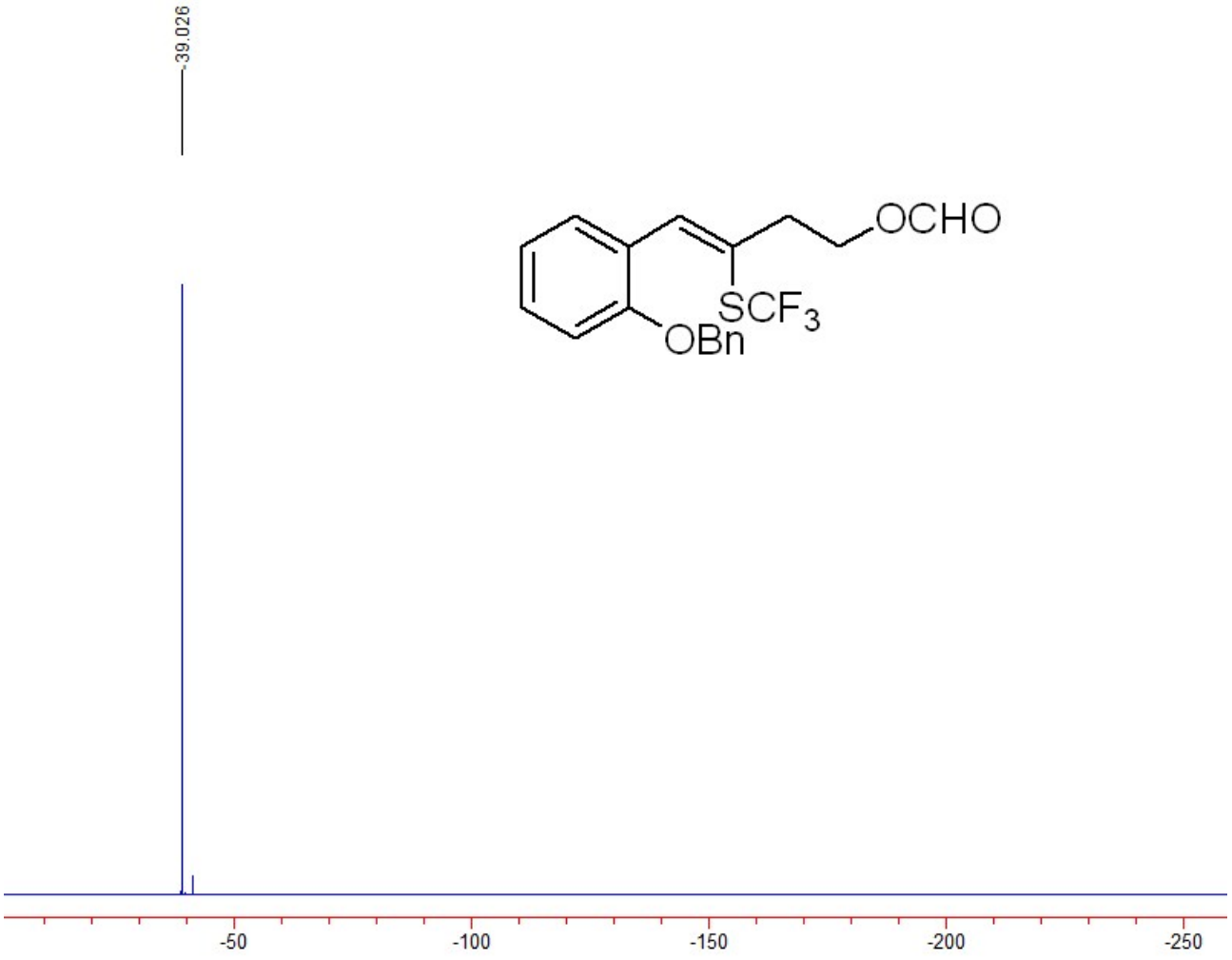
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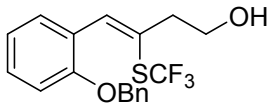
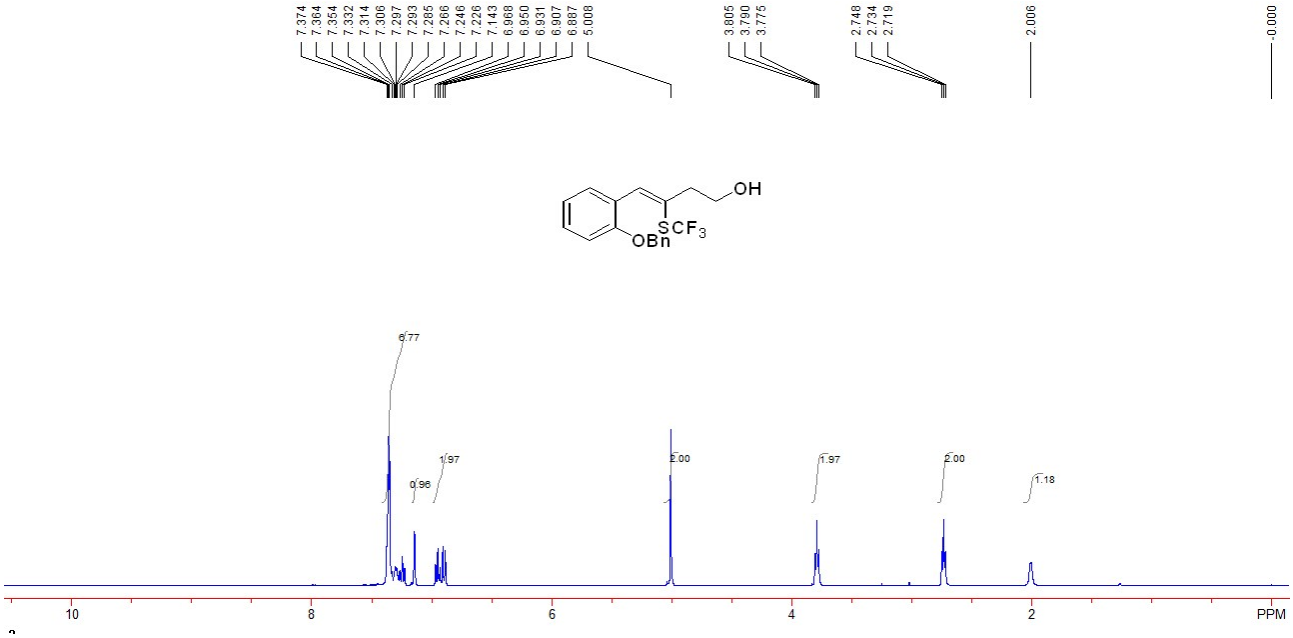
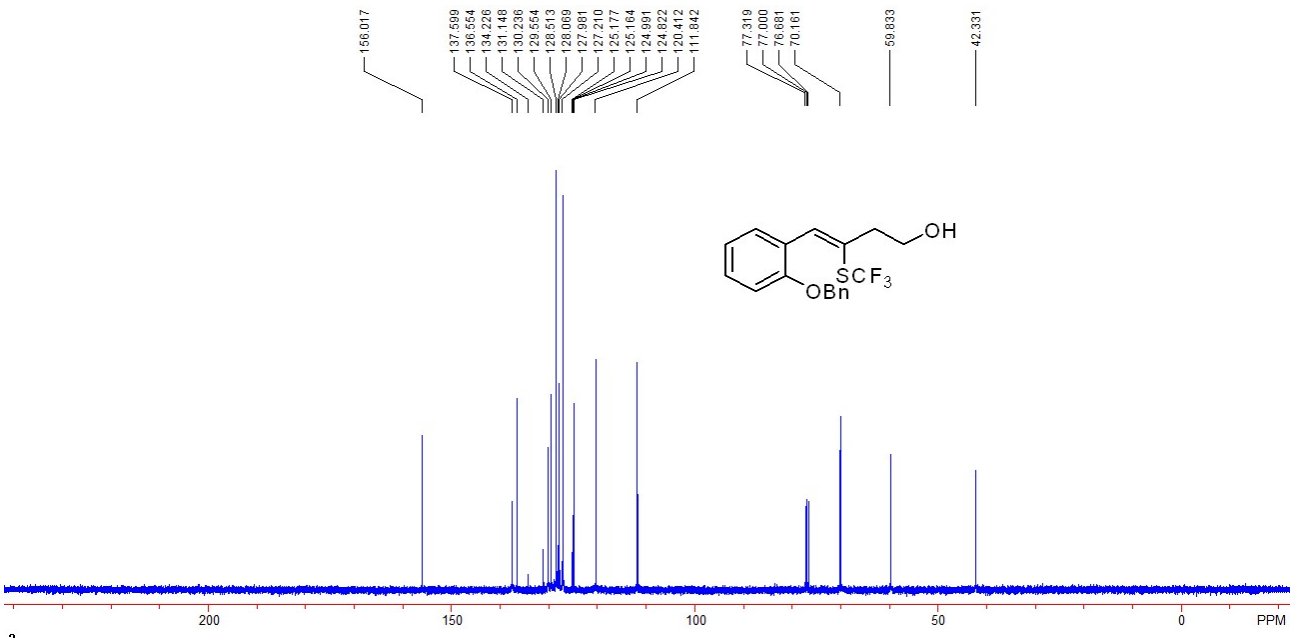
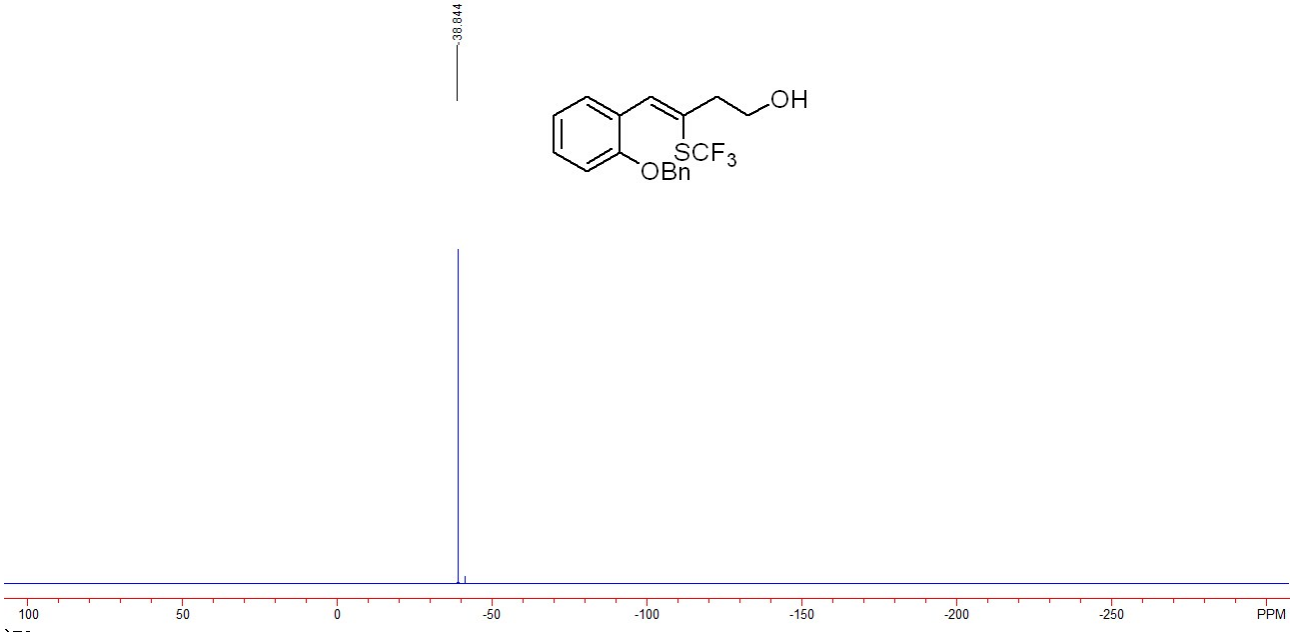


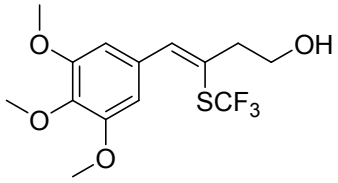
(Z)-4-(2-(benzyloxy)phenyl)-3-((trifluoromethyl)thio)but-3-en-1-ol (5a).

A colorless oil, 35.4 mg, 50% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.01 (s, 1H, OH), 2.73 (t, *J* = 6.0 Hz, 2H, CH_2), 3.79 (t, *J* = 6.0 Hz, 2H, CH_2), 5.01 (s, 2H, CH_2), 6.89-6.97 (m, 2H, ArH), 7.14 (s, 1H, ArH), 7.23-7.37 (m, 7H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 42.3, 59.8, 70.2, 111.8, 120.4, 124.8, 125.2 (q, *J* = 1.3 Hz), 127.2, 128.0, 128.5, 129.5, 129.6 (q, *J* = 307.9 Hz), 130.2, 136.5, 137.6, 156.0. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -38.84. IR (CH_2Cl_2) ν 3354, 3029, 2926, 2879, 1445, 1244, 1150, 1106, 1086, 1045, 752 cm^{-1}. MS (%) m/e 235 (5.74), 163 (5.79), 147 (8.71), 145 (5.88), 91 (M^+, 100.00), 131 (14.48), 92 (9.25), 65 (7.93). HRMS (EI) calcd. for $C_{18}H_{17}O_2F_3S$: 354.0901, Found: 354.0908.





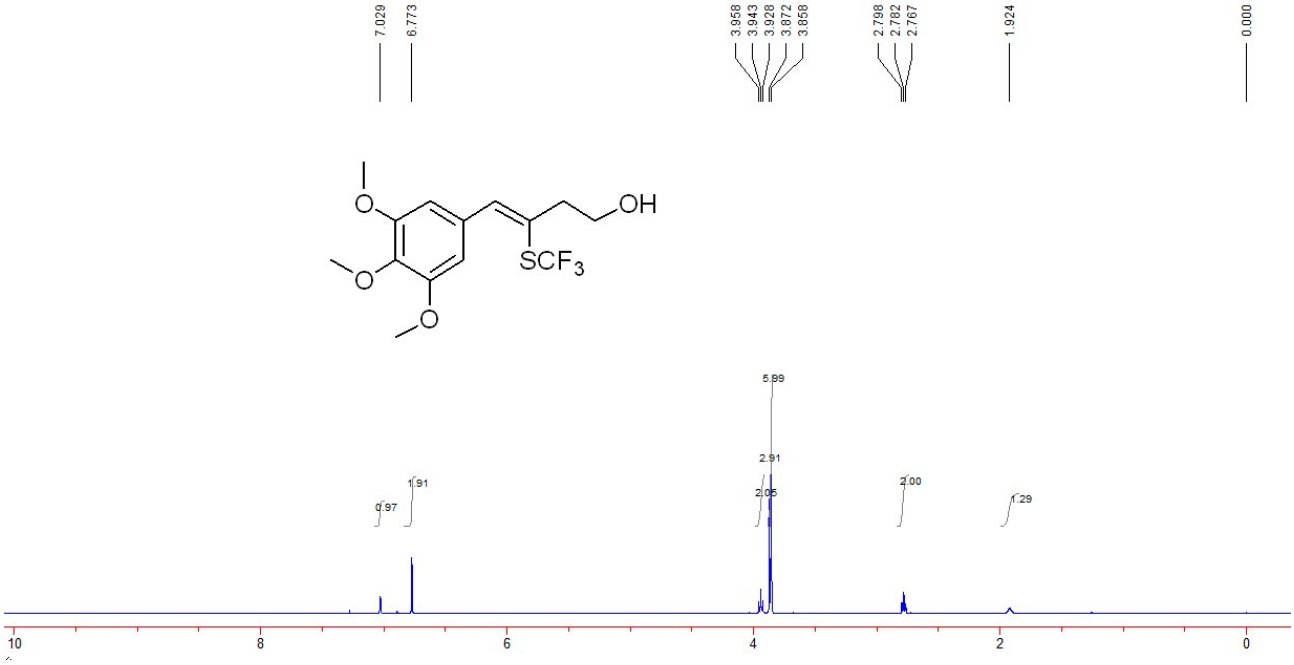


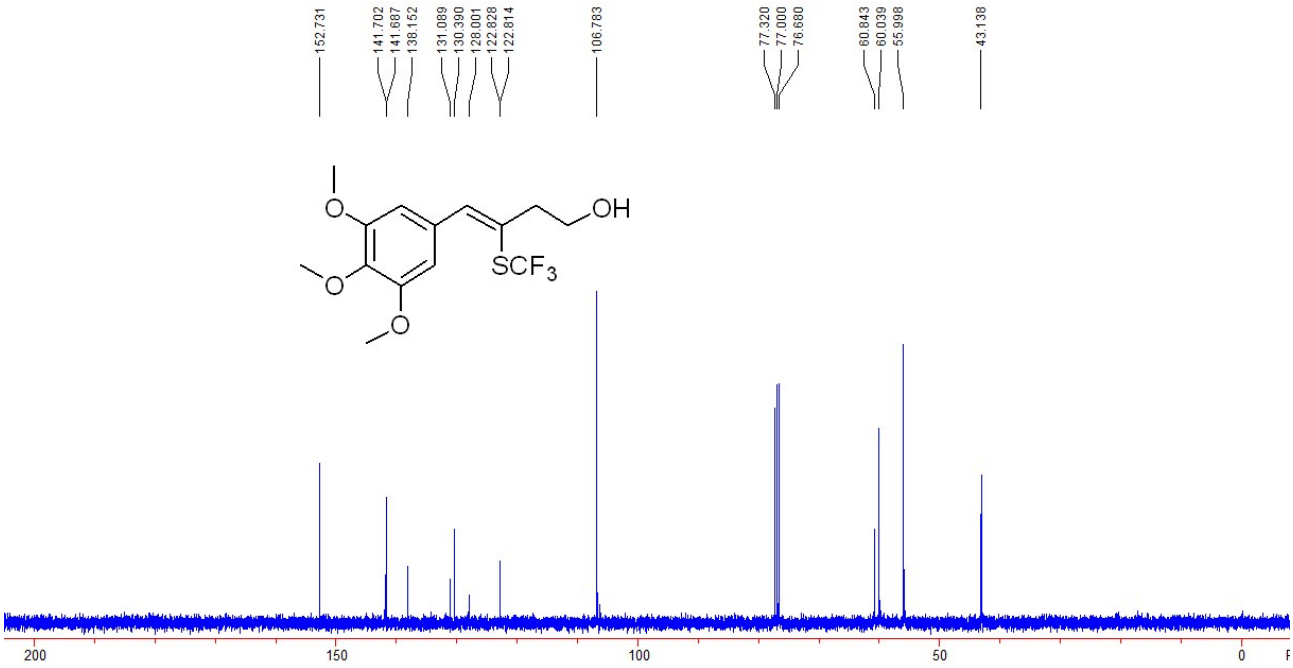


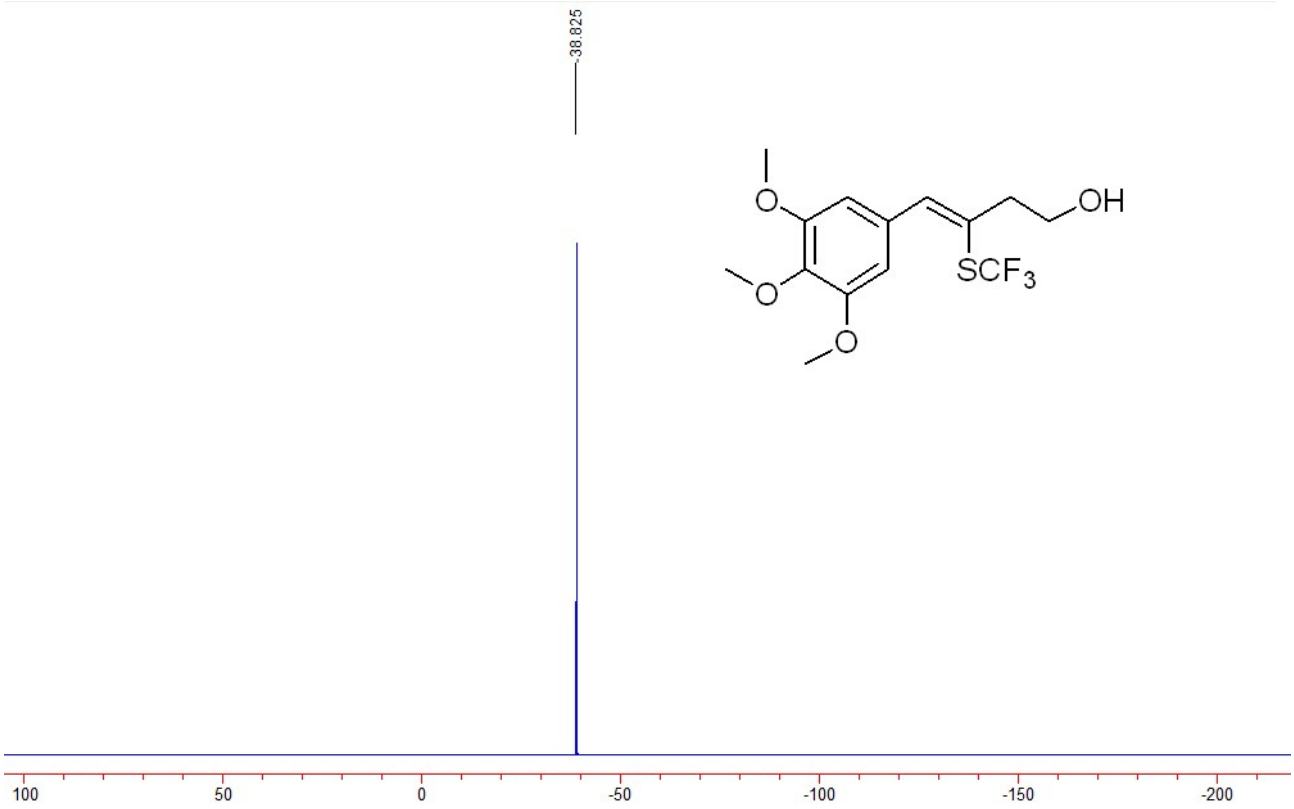
(Z)-3-((trifluoromethyl)thio)-4-(3,4,5-trimethoxyphenyl)but-3-en-1-ol (5b).

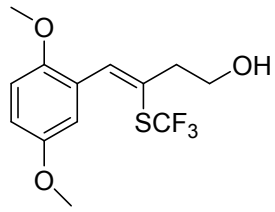
A colorless oil, 40.6 mg, 60% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.92 (s, 1H, OH), 2.78 (t, J = 6.0 Hz, 2H, CH_2), 3.86 (s, 6H, CH_3), 3.87 (s, 3H, CH_3), 3.94 (t, J = 6.0 Hz, 2H, CH_2), 6.77 (s, 2H, ArH), 7.02 (s, 1H, CH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 43.1, 56.0, 60.0, 60.8, 106.8, 112.8 (q, J = 1.4 Hz), 129.5 (q, J = 308.8 Hz), 130.4, 138.2, 141.7 (q, J = 1.5 Hz), 152.7. ^{19}F NMR

(376 MHz, $CDCl_3$, $CFCl_3$) δ -38.83. IR (CH_2Cl_2) ν 3385, 2938, 2838, 1580, 1505, 1412, 1329, 1239, 1108, 1084, 1044, 999 cm^{-1}. MS (%) m/e 220 (20.03), 205 (8.72), 190 (14.34), 189 (M^+, 100.00), 162 (9.87), 145 (11.54), 119 (7.13), 91 (8.68). MS (%) m/e 338 (93.69), 251 (37.02), 207 (71.79), 206 (34.65), 191 (57.94), 175 (86.16), 77 (M^+, 100.00), 51 (32.22). HRMS (EI) calcd. for $C_{14}H_{17}O_4F_3S$: 338.0809, Found: 338.0800.



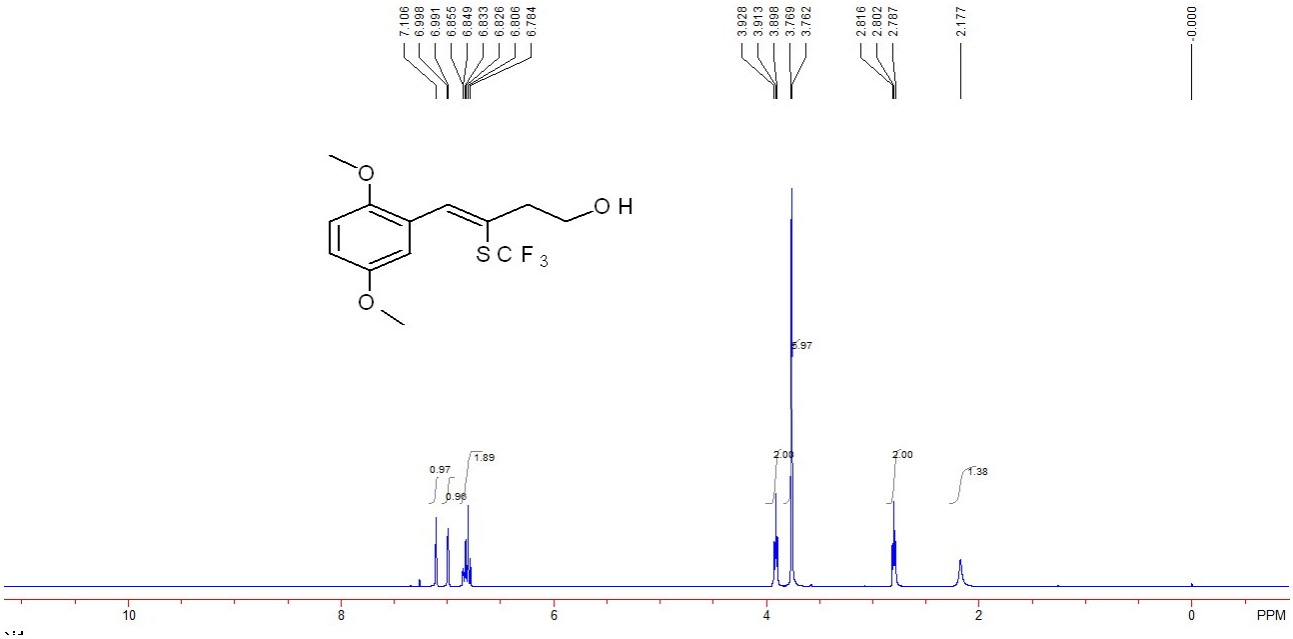






(Z)-4-(2,5-dimethoxyphenyl)-3-((trifluoromethyl)thio)but-3-en-1-ol (5c).

A colorless oil, 40.6 mg, 66% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.18 (s, 1H, OH), 2.80 (t, J = 6.0 Hz, 2H, CH_2), 3.76 (s, 3H, CH_3), 3.77 (s, 3H, CH_3), 3.91 (t, J = 6.0 Hz, 2H, CH_2), 6.78-6.86 (m, 2H, ArH), 7.00 (d, J = 2.8 Hz, 1H, ArH), 7.12 (s, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 42.5, 55.6 (q, J = 2.4 Hz), 55.9 (q, J = 2.5 Hz), 59.8, 111.4, 114.7, 115.6, 124.9, 125.2 (q, J = 1.2 Hz), 129.6 (q, J = 307.9 Hz), 137.2, 151.2, 152.9. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -38.88. IR (CH_2Cl_2) ν 3334, 2944, 2835, 1492, 1280, 1222, 1148, 1107, 1085, 1044, 800, 717 cm^{-1}. MS (%) m/e 308 (32.36), 262 (35.73), 130 (64.38), 129 (M^+, 100.00), 175 (39.34), 161 (47.02), 128 (36.89), 115 (53.69). HRMS (EI) calcd. for $C_{13}H_{15}O_3F_3S$: 308.0694, Found: 308.0693.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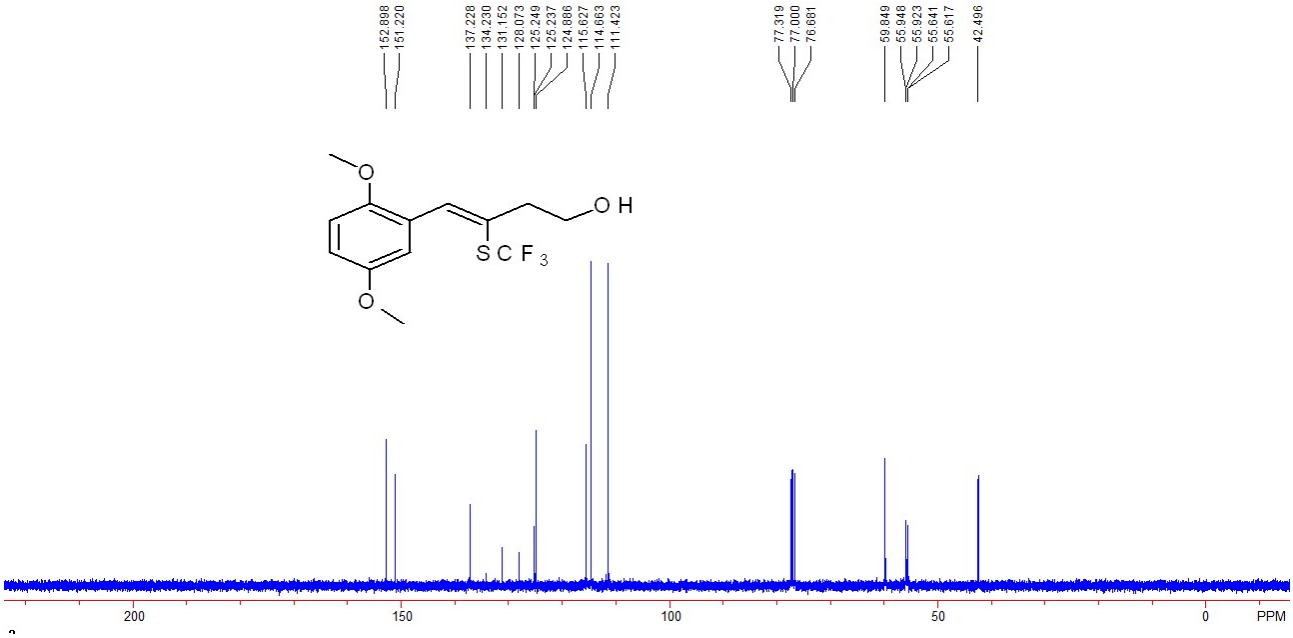
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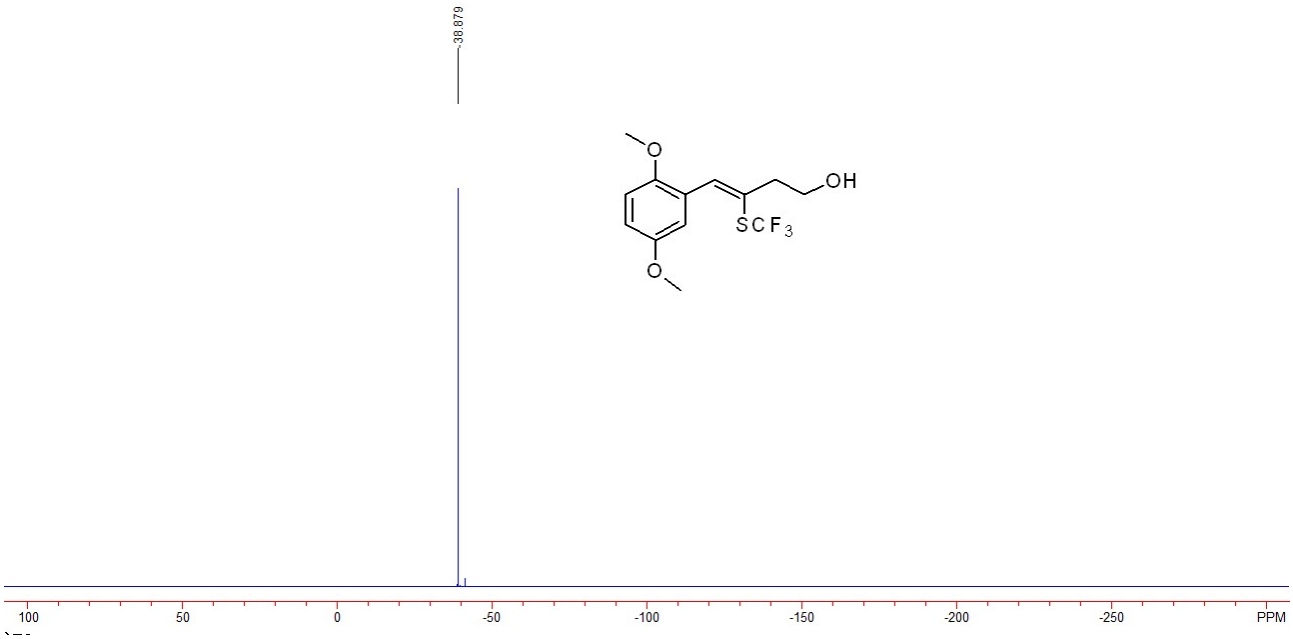
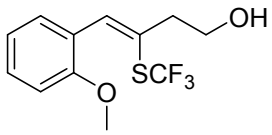
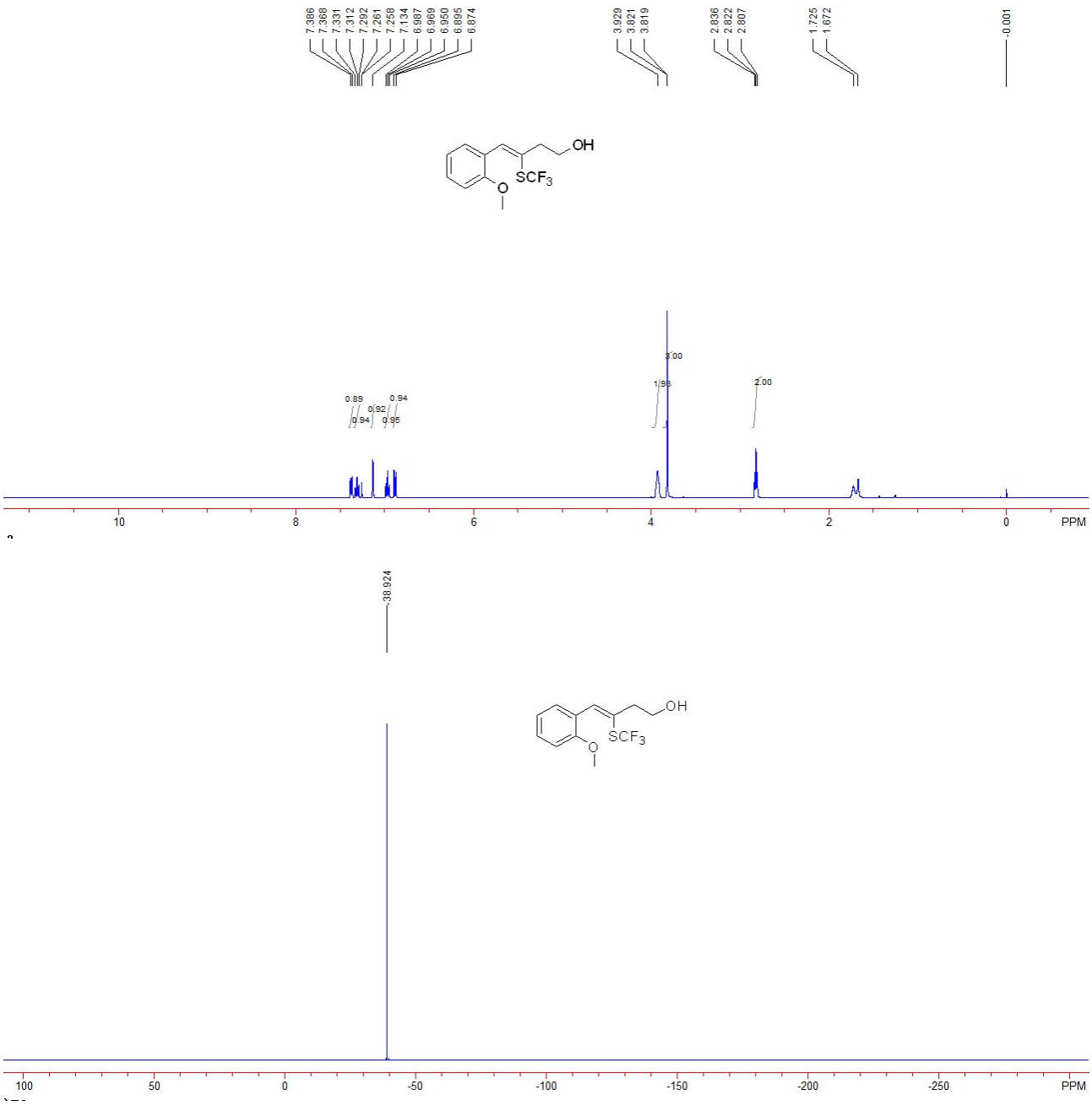




((Z)-4-(2-methoxyphenyl)-3-((trifluoromethyl)thio)but-3-en-1-ol (5d).

A white solid, 30.6 mg, 55% yield. M.p.: 70-73 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.72 (s, 1H, OH), 2.82 (t, J = 6.0 Hz, 2H, CH_2), 3.82 (s, 3H, CH_3), 3.93 (t, J = 6.0 Hz, 2H, CH_2), 6.88 (d, J = 8.4 Hz, 1H, ArH), 6.97 (t, J = 7.2 Hz, 1H, ArH), 7.13 (s, 1H, ArH), 7.31 (t, J = 7.6 Hz, 1H, ArH), 7.38 (d, J = 7.2 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 42.4, 55.4 (q, J = 2.0 Hz), 59.9, 110.3, 120.1, 124.2, 124.9 (q, J = 1.2 Hz), 129.6 (q, J = 307.9 Hz), 129.7, 130.2, 137.5, 156.9. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -38.92. IR (CH_2Cl_2) ν 3313, 2933, 2840, 1487, 1464, 1248, 1149, 1104, 1084, 1050, 1026, 751 cm^{-1}. MS (%) m/e 278 (M^+, 100.00), 191 (34.02), 159 (74.66), 147 (34.15), 146 (96.75), 145 (55.39), 131 (70.53), 115 (38.94). HRMS (EI) calcd. for $C_{12}H_{13}O_2F_3S$: 278.0588, Found: 278.0586.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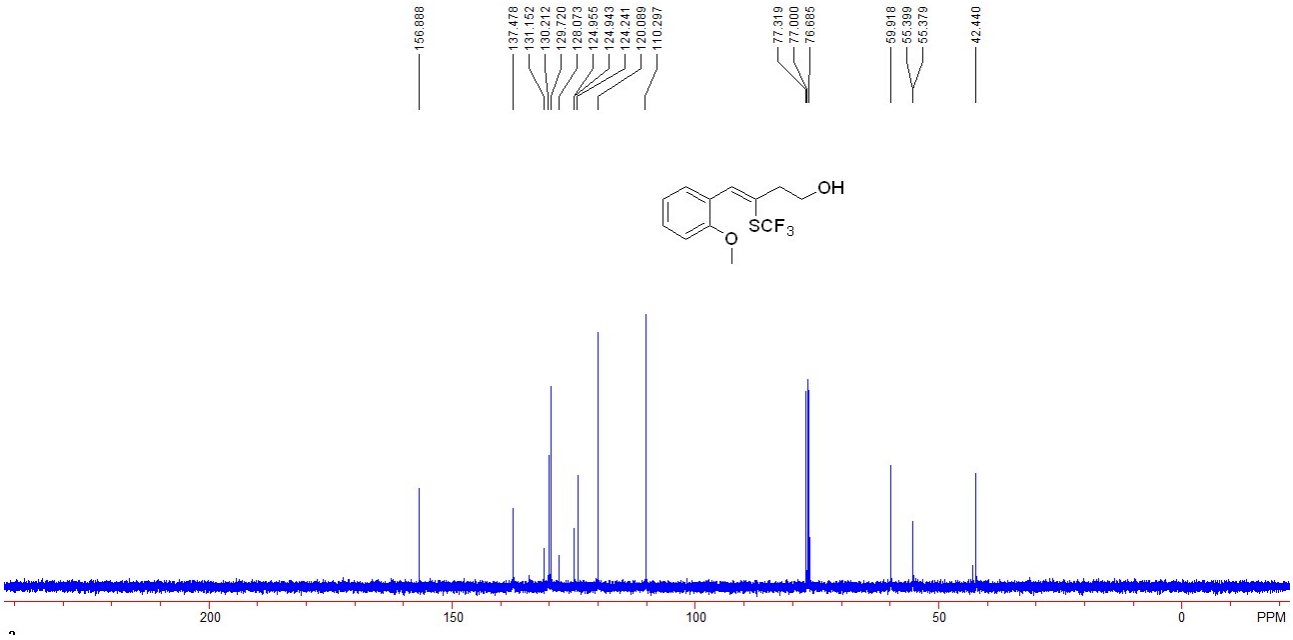
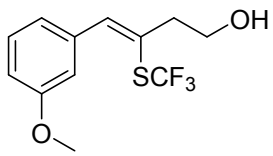
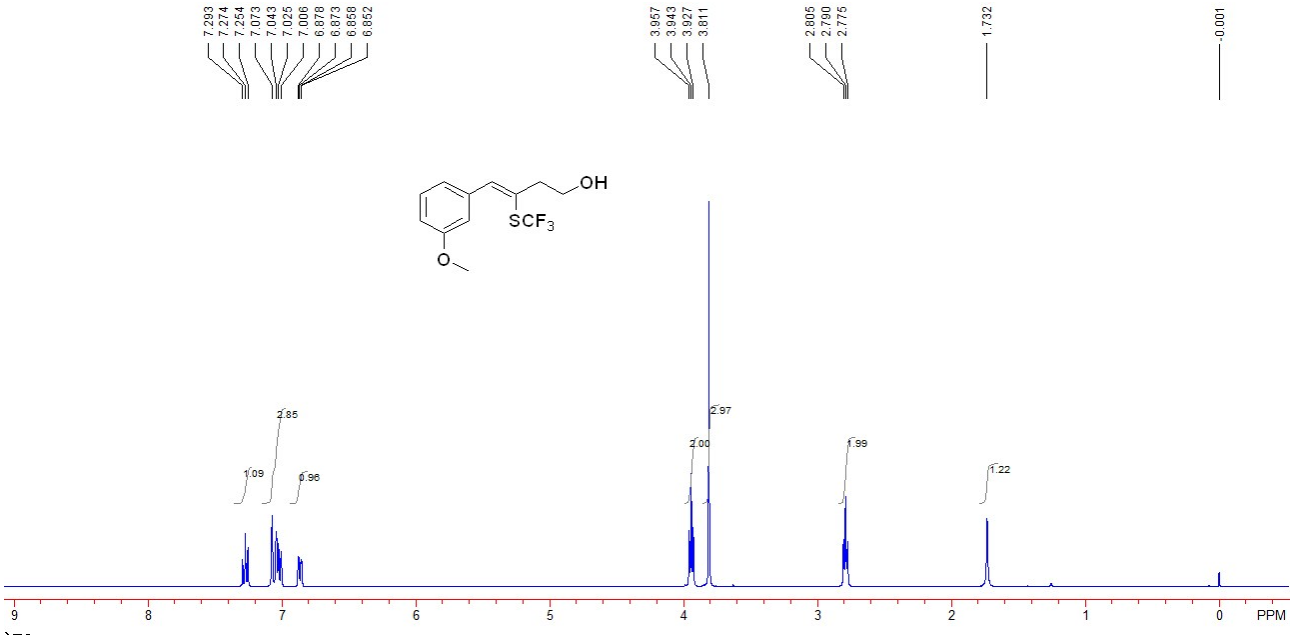




(Z)-4-(3-methoxyphenyl)-3-((trifluoromethyl)thio)but-3-en-1-ol (5e).

A colorless oil, 34.5 mg, 62% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.73 (s, 1H, OH), 2.79 (t, J = 6.0 Hz, 2H, CH_2), 3.81 (s, 3H, CH_3), 3.94 (t, J = 6.0 Hz, 2H, CH_2), 6.86 (dd, J = 0.5, 2.0 Hz, 1H, ArH), 7.01-7.07 (m, 3H, ArH), 7.27 (t, J = 8.0 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 42.9, 55.2, 60.1, 114.1, 114.6, 122.0, 124.1, 129.2, 129.5 (q, J = 308.2 Hz), 136.3, 141.5 (q, J = 1.5 Hz), 159.2. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -38.76. IR (CH_2Cl_2) ν 3326, 2972, 2882, 2832, 1575, 1262, 1152, 1111, 1086, 1044, 753, 692 cm^{-1}. MS (%) m/e 191 (73.53), 146 (49.07), 145 (29.59), 132 (M^+, 100.00), 115 (39.87), 103 (35.49), 88 (71.96), 74 (39.74). HRMS (EI) calcd. for $C_{12}H_{13}O_2F_3S$: 278.0588, Found: 278.0596.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7.025
7.006
6.878
6.873
6.858
6.852
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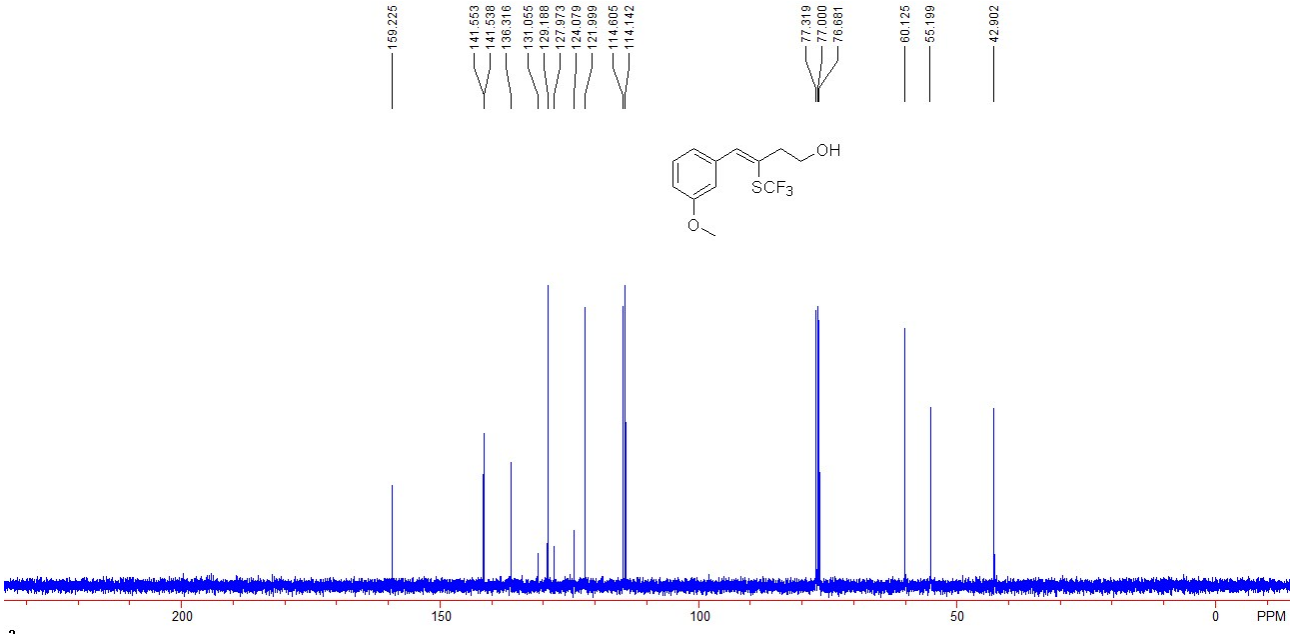
3.943
3.927
3.811
2.805
2.790
2.775
1.732
0.001
OH
SCF3
O
2.85
2.97
2.00
1.99
1.22
1.09
0.96
9
8
7
6
5
4
3
2
1
0
PPM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124.079
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114.605
114.142
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60.125
55.199
42.902
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SCF3
O
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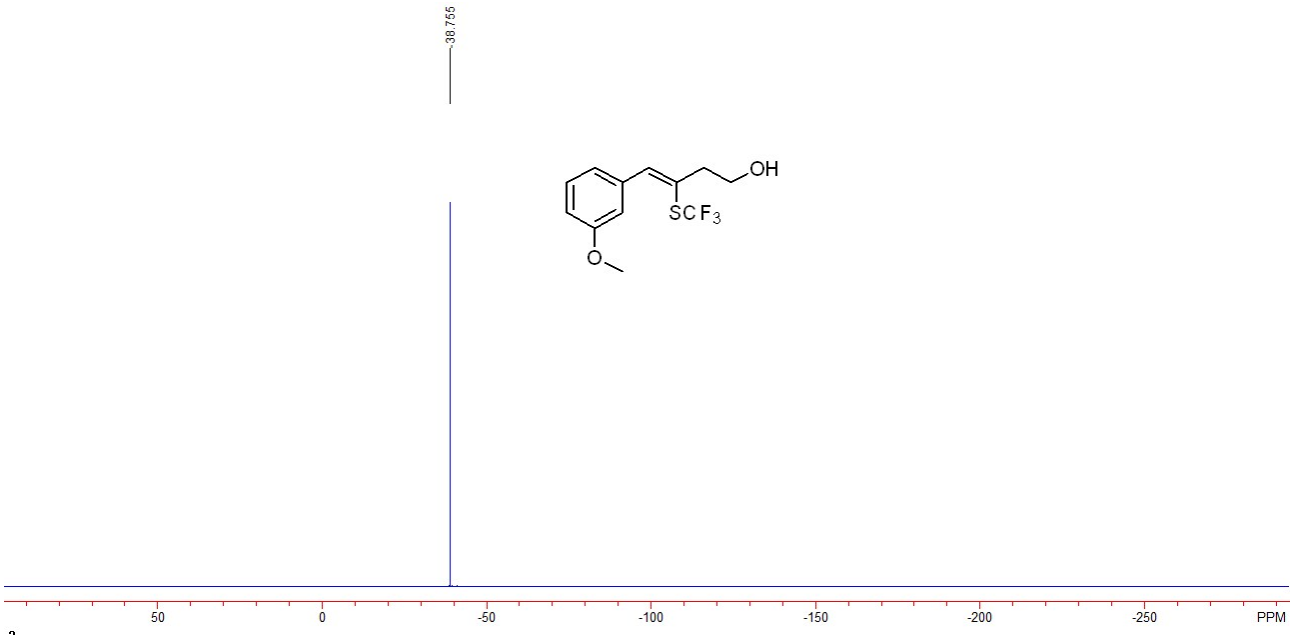
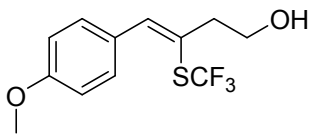
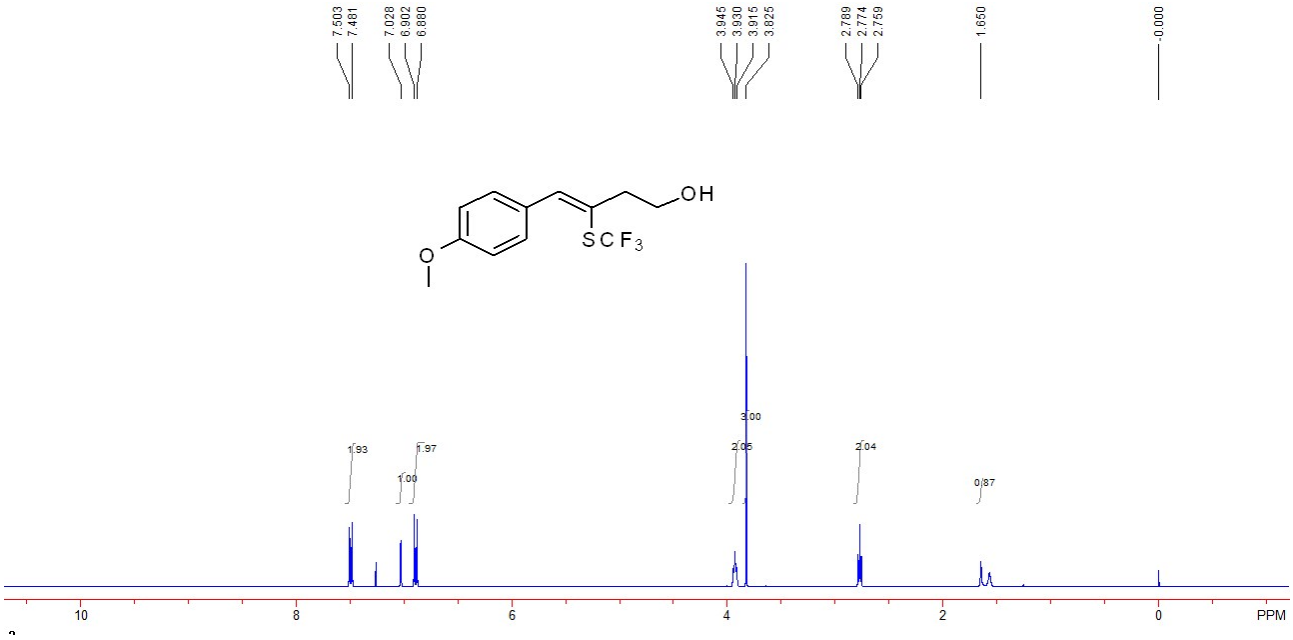
150
100
50
0
PPM





(Z)-4-(4-methoxyphenyl)-3-((trifluoromethyl)thio)but-3-en-1-ol (5f).

A colorless oil, 37.8 mg, 68% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.65 (s, 1H, OH), 2.77 (t, *J* = 6.0 Hz, 2H, CH_2), 3.82 (s, 3H, CH_3), 3.93 (t, *J* = 6.0 Hz, 2H, CH_2), 6.89 (d, *J* = 8.8 Hz, 2H, ArH), 7.03 (s, 1H, ArH), 7.49 (d, *J* = 8.8 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 43.2, 55.1, 60.1, 113.5, 120.9, 127.5, 129.6 (q, *J* = 308.9 Hz), 131.0, 141.6 (q, *J* = 1.5 Hz), 159.5. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -39.05. IR (CH_2Cl_2) ν 3331, 2962, 2843, 1603, 1509, 1252, 1105, 1081, 1034, 823 cm^{-1}. MS (%) m/e 278 (36.96), 247 (22.40), 147 (22.61), 146 (M^+, 100.00), 145 (31.37), 131 (26.45), 115 (23.14), 103 (24.98). HRMS (EI) calcd. for $C_{12}H_{13}O_2F_3S$: 278.0588, Found: 278.0598.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3.945
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2.789
2.774
2.759
1.650
0.000
OH
SCF3
O
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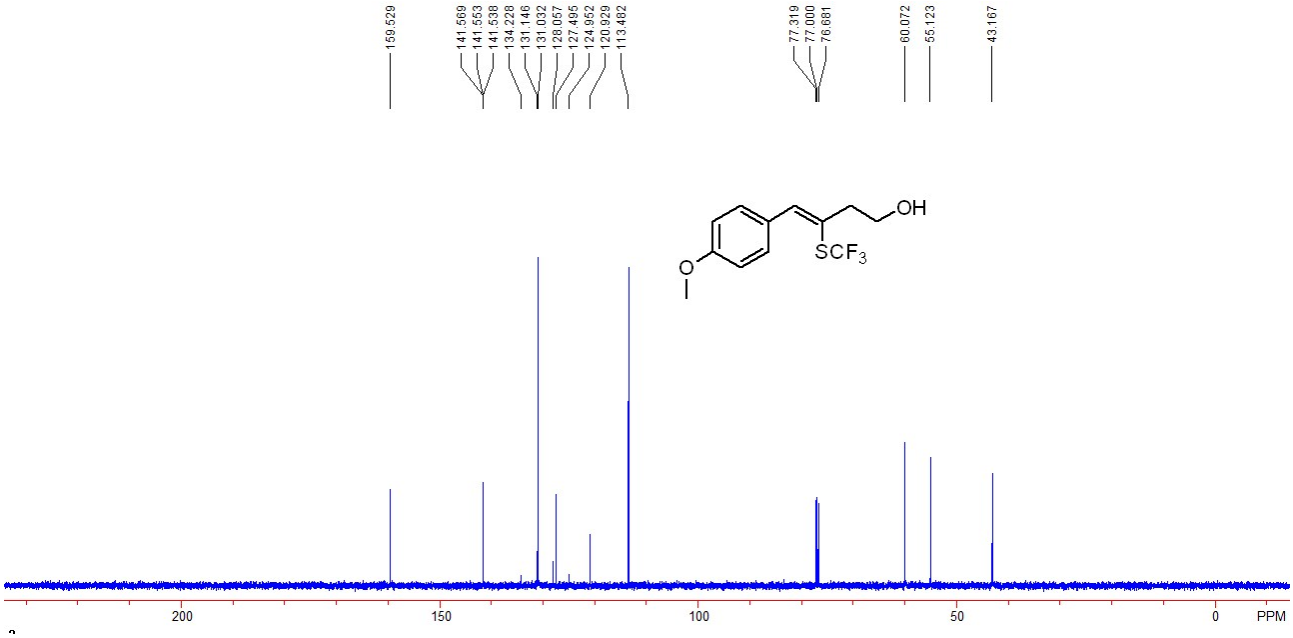
1.97
1.00
2.05
2.04
0.87
10
8
6
4
2
0
PPM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131.146
131.032
128.057
127.495
124.952
120.929
113.482
77.319
77.000
76.681
60.072
55.123
43.167
OH
SCF3
O
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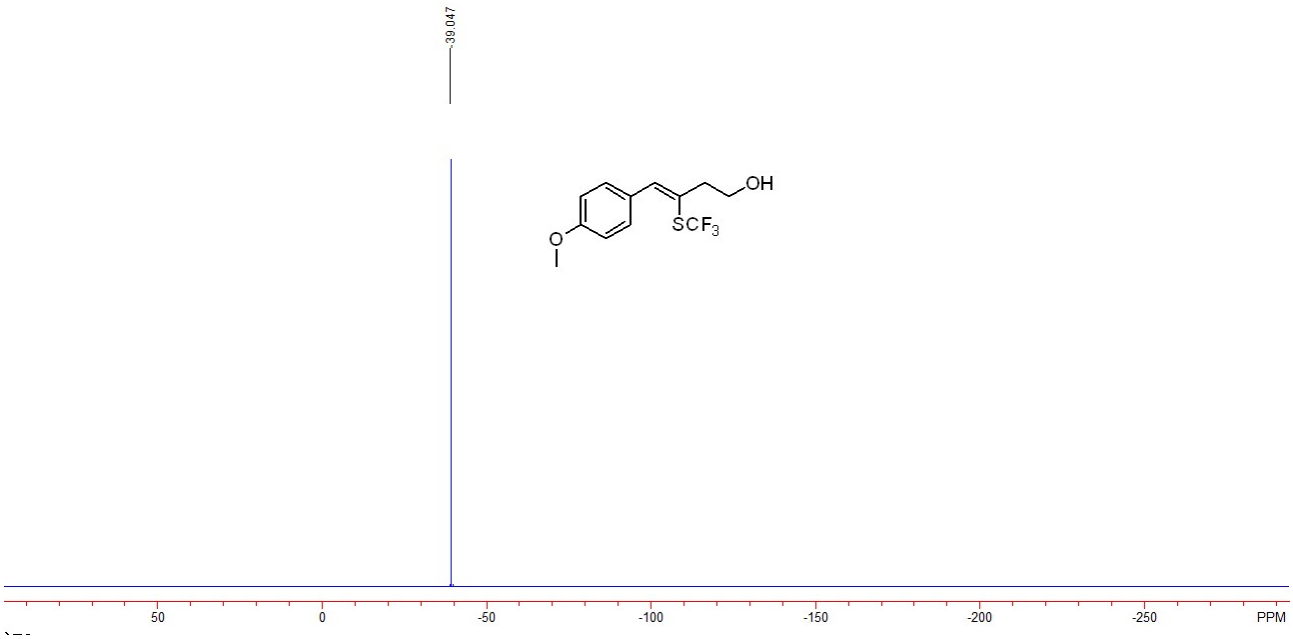
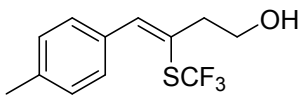
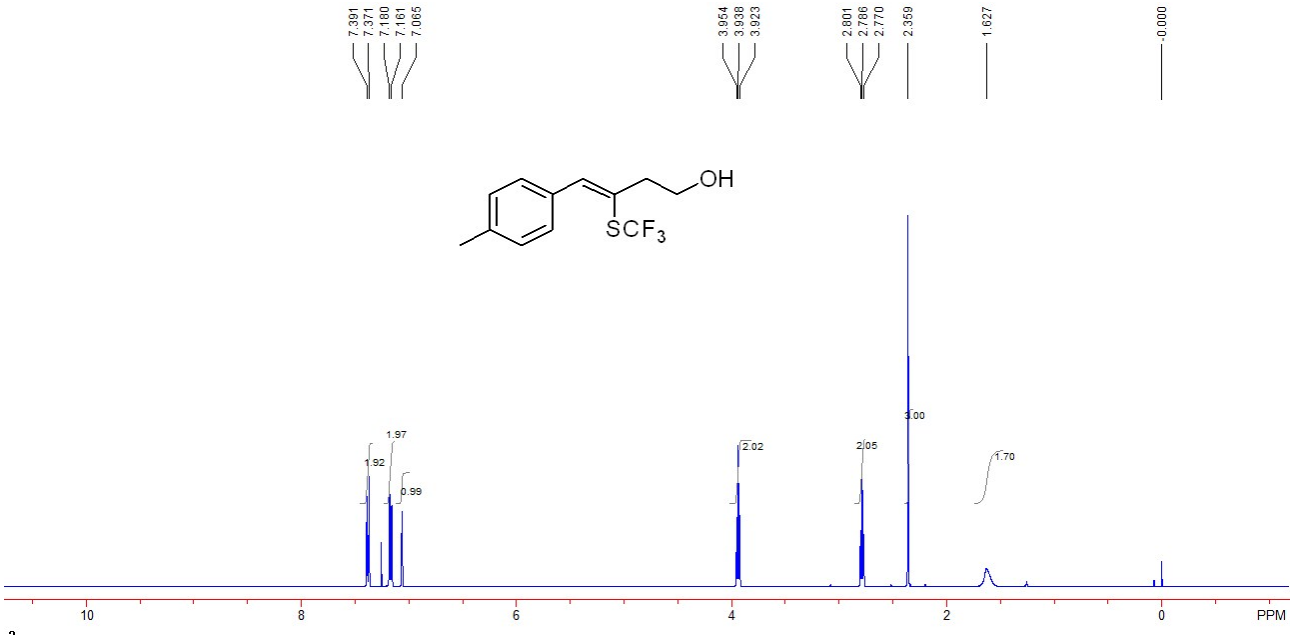
150
100
50
0
PPM





(Z)-4-(p-tolyl)-3-((trifluoromethyl)thio)but-3-en-1-ol (5g).

A colorless oil, 27.8 mg, 53% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.63 (s, 1H, OH), 2.36 (s, 3H, CH_3), 2.79 (t, *J* = 6.0 Hz, 2H, CH_2), 3.94 (t, *J* = 6.0 Hz, 2H, CH_2), 7.06 (s, 1H, ArH), 7.17 (d, *J* = 8.0 Hz, 2H, ArH), 7.38 (d, *J* = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.1, 42.9, 60.0, 122.6, 128.8, 129.4, 129.6 (q, *J* = 309.0 Hz), 132.1, 138.3, 141.7 (q, *J* = 1.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -38.93. IR (CH_2Cl_2) ν 3318, 2923, 2874, 1151, 1106, 1082, 1040, 810, 753 cm^{-1}. MS (%) m/e 262 (M^+, 100.00), 231 (31.63), 175 (55.38), 147 (18.65), 130 (76.99), 129 (86.55), 128 (26.57), 115 (37.35). HRMS (EI) calcd. for $C_{12}H_{13}OF_3S$: 262.0639, Found: 262.0645.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3.954
3.938
3.923
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2.770
2.359
1.627
0.000
OH
SCF3
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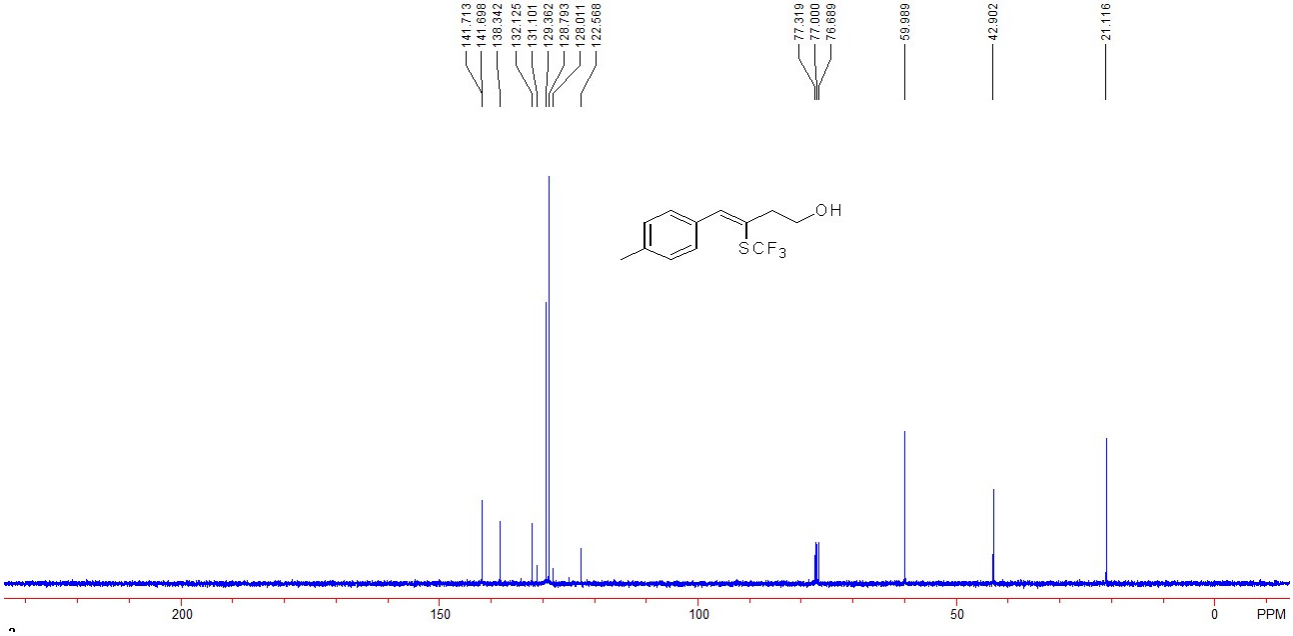
2.02
2.05
3.00
1.70
10
8
6
4
2
0
PPM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129.362
128.793
128.011
122.568
77.319
77.000
76.689
59.989
42.902
21.116
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SCF3
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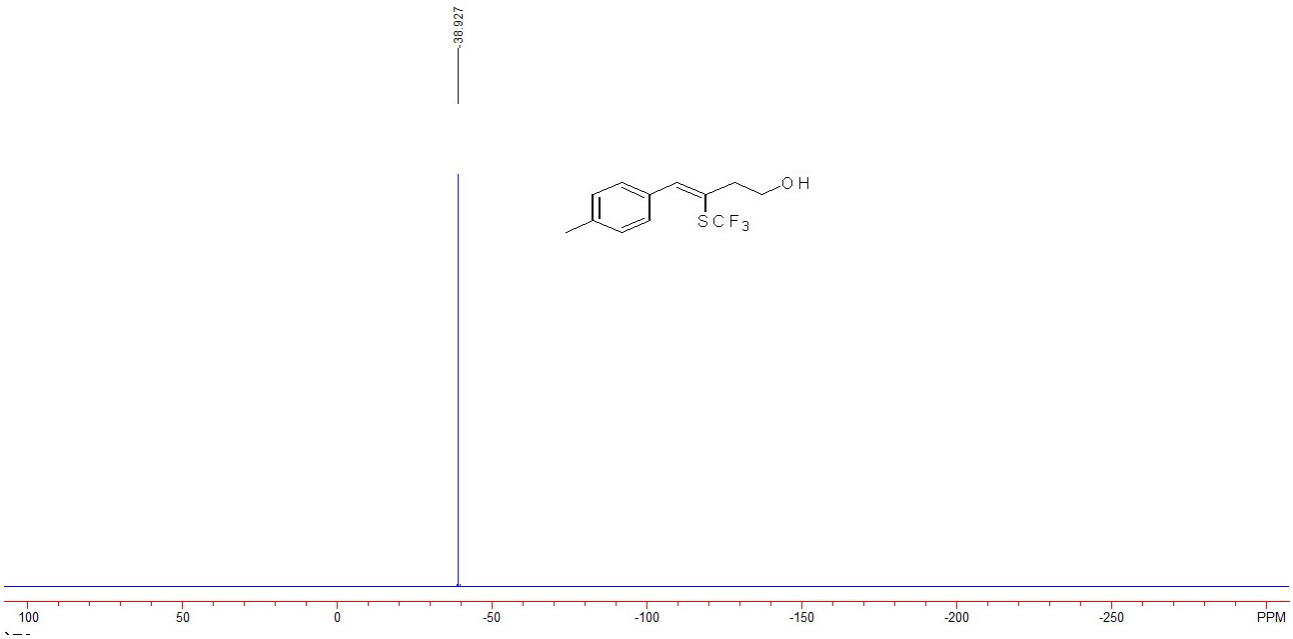
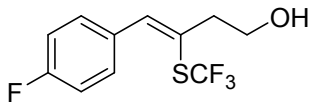
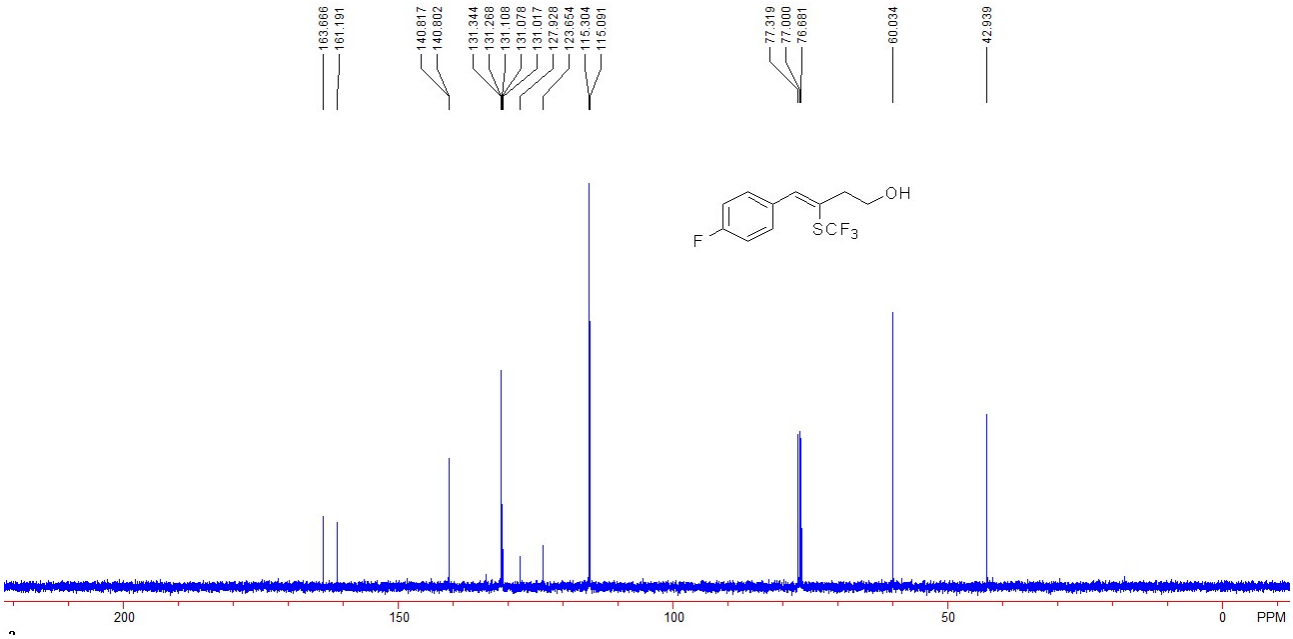
150
100
50
0
PPM





(Z)-4-(4-fluorophenyl)-3-((trifluoromethyl)thio)but-3-en-1-ol (5h).

A colorless oil, 16.0 mg, 30% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.00 (s, 1H, OH), 2.78 (t, *J* = 6.0 Hz, 2H, CH_2), 3.93 (t, *J* = 6.0 Hz, 2H, CH_2), 7.02-7.06 (m, 3H, ArH), 7.46-7.48 (m, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 42.9, 60.0, 115.2 (d, *J* = 21.3 Hz), 123.6, 129.5 (q, *J* = 308.9 Hz), 131.1 (d, *J* = 3.0 Hz), 131.3 (d, *J* = 7.6 Hz), 140.8 (d, *J* = 1.5 Hz), 162.4 (d, *J* = 247.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -38.91, -112.42. IR (CH_2Cl_2) ν 3334, 2931, 2882, 1507, 1232, 1158, 1111, 1098, 1081, 1048, 826 cm^{-1}. MS (%) m/e 266 (35.89), 179 (16.81), 165 (17.01), 146 (17.82), 135 (15.71), 134 (78.58), 133 (M^+, 100.00), 109 (14.76). HRMS (EI) calcd. for $C_{11}H_{10}OF_4S$: 266.0388, Found: 266.0391.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77.319
77.000
76.681
60.034
42.939
OH
SCF3
F
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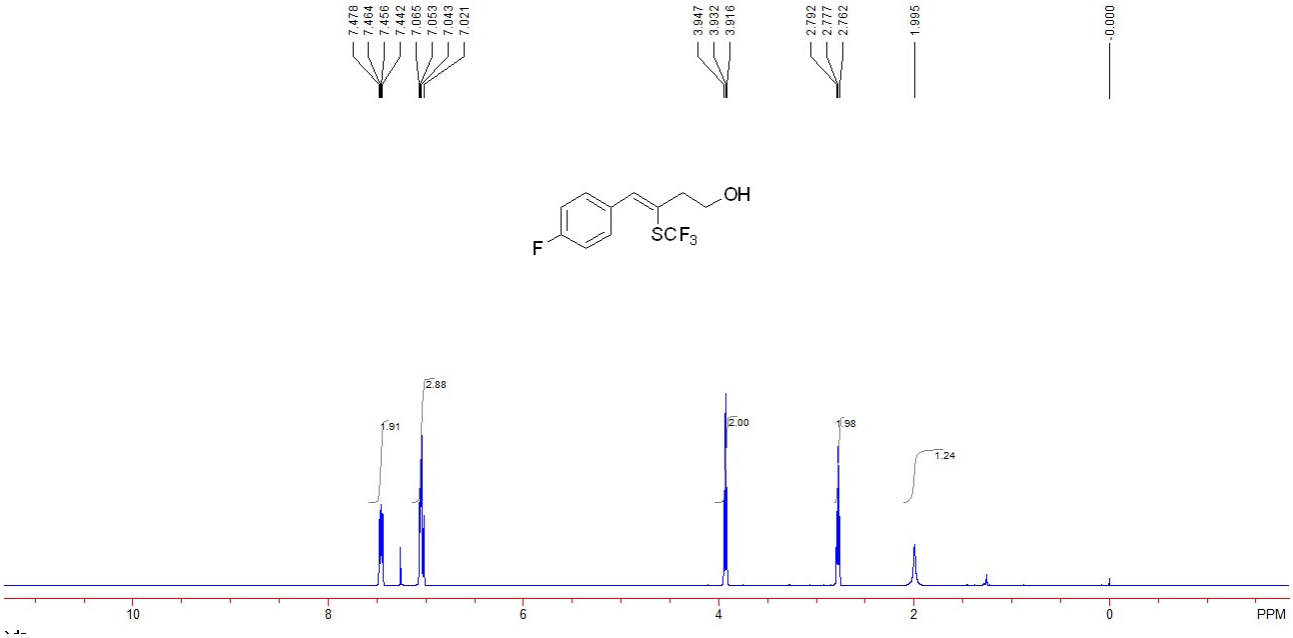
150
100
50
0
PPM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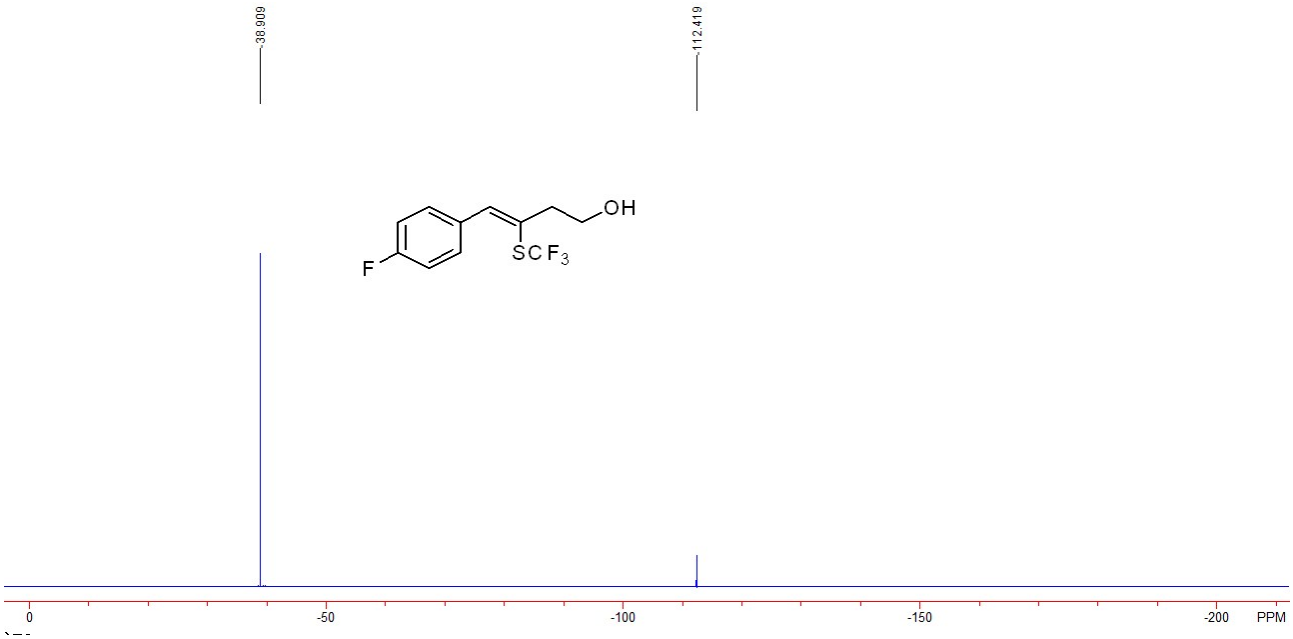
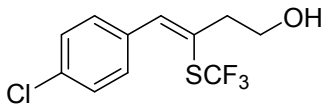
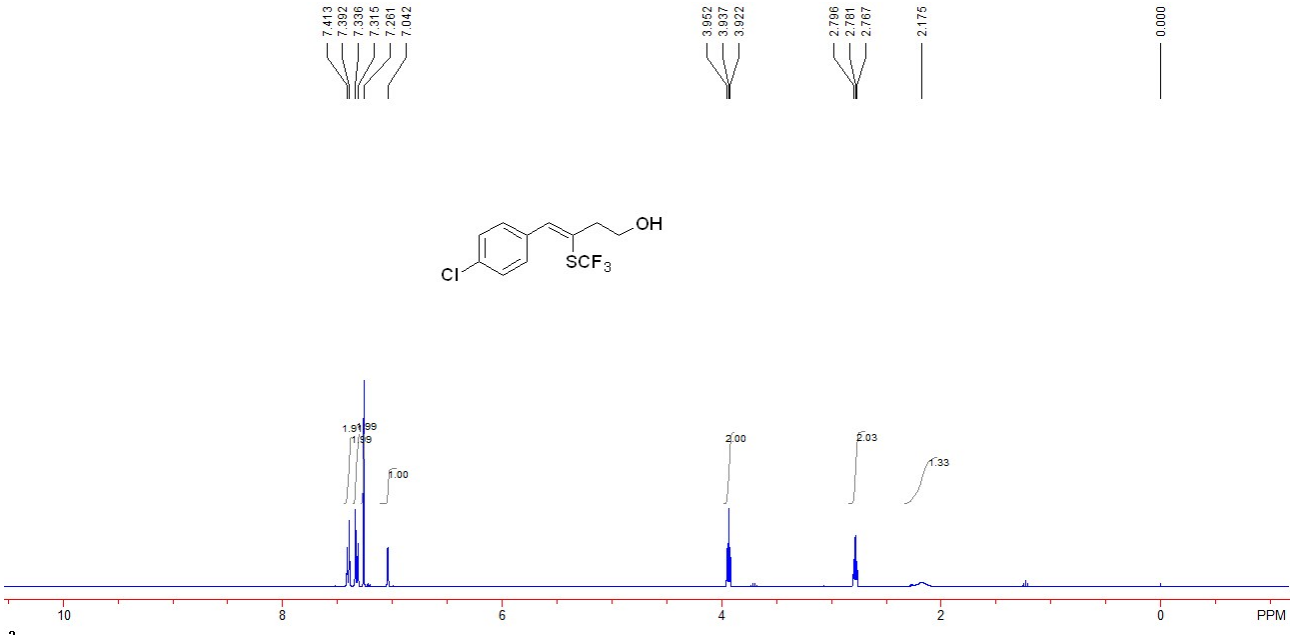
7.065
7.053
7.043
7.021
3.947
3.932
3.916
2.792
2.777
2.762
1.995
-0.000
OH
SCF3
F
2.88
1.91
2.00
1.98
1.24
10
8
6
4
2
0
PPM





(Z)-4-(4-chlorophenyl)-3-((trifluoromethyl)thio)but-3-en-1-ol (5i).

A colorless oil, 19.7 mg, 35% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.18 (s, 1H, OH), 2.78 (t, *J* = 6.0 Hz, 2H, CH_2), 3.94 (t, *J* = 6.0 Hz, 2H, CH_2), 7.04 (s, 1H, ArH), 7.26 (s, 1H, ArH), 7.32 (d, *J* = 8.4 Hz, 2H, ArH), 7.40 (d, *J* = 8.4 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 42.9, 60.0, 124.6, 128.4, 129.4 (q, *J* =308.2 Hz), 130.7, 133.4. 134.2, 140.6 (q, *J* = 1.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -38.81. IR (CH_2Cl_2) ν 3316, 2936, 2882, 1484, 1154, 1104, 1081, 1014, 813 cm^{-1}. MS (%) m/e 282 (39.65), 195 (24.21), 152 (21.48), 151 (32.24), 150 (61.16), 149 (63.04), 147 (24.67), 115 (M^+, 100.00). HRMS (EI) calcd. for $C_{11}H_{10}OF_3SCl$: 282.0093, Found: 282.0102.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3.937
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2.767
2.175
0.000
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Cl
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1.00
2.00
2.03
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10
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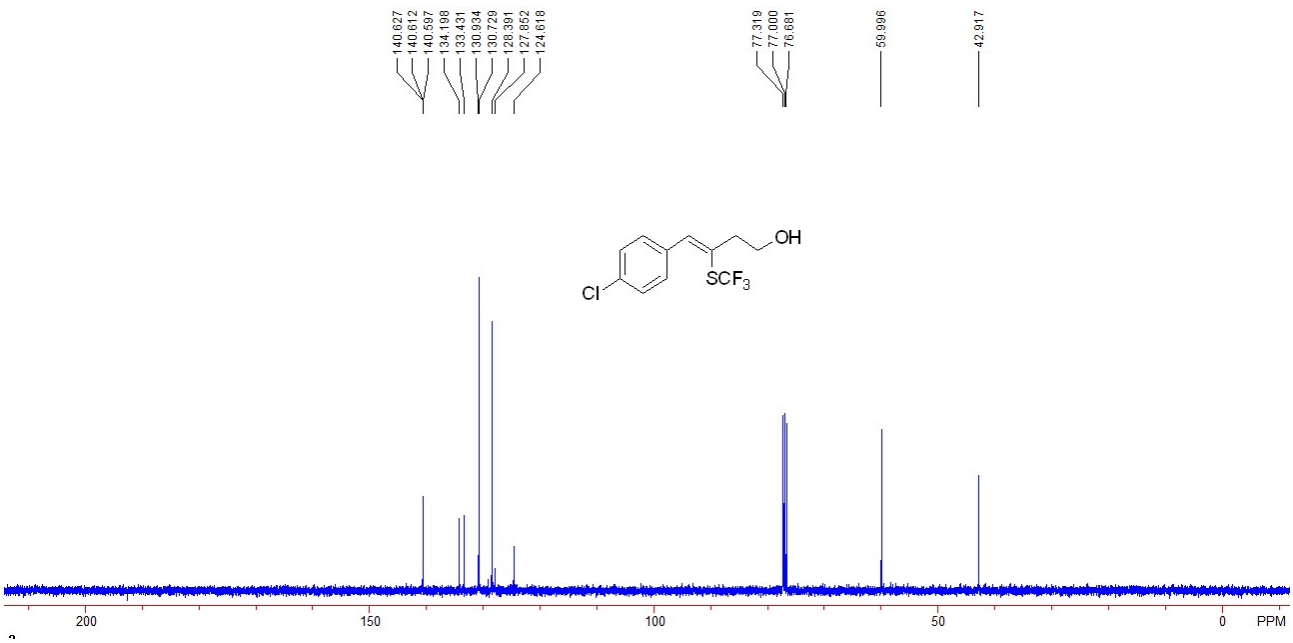
4
2
0
PPM


140.627
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133.431
130.934
130.729
128.391
127.852
124.618
77.319
77.000
76.681
59.996
42.917
OH
Cl
SCF3
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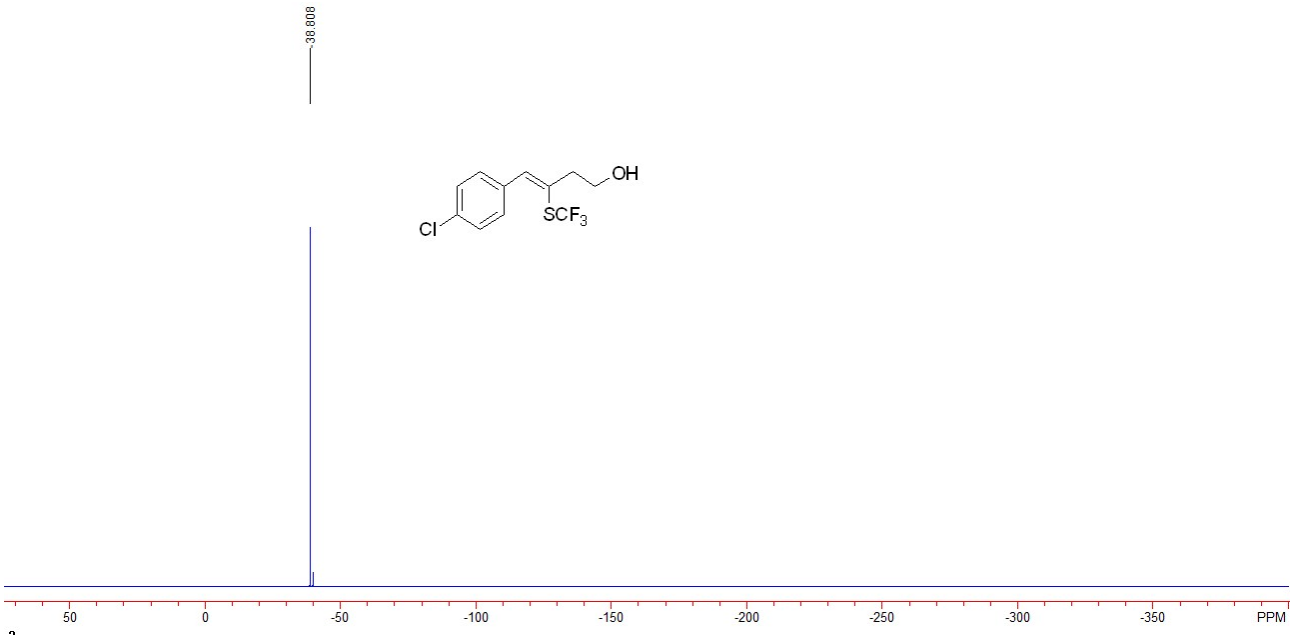
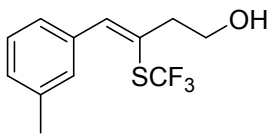
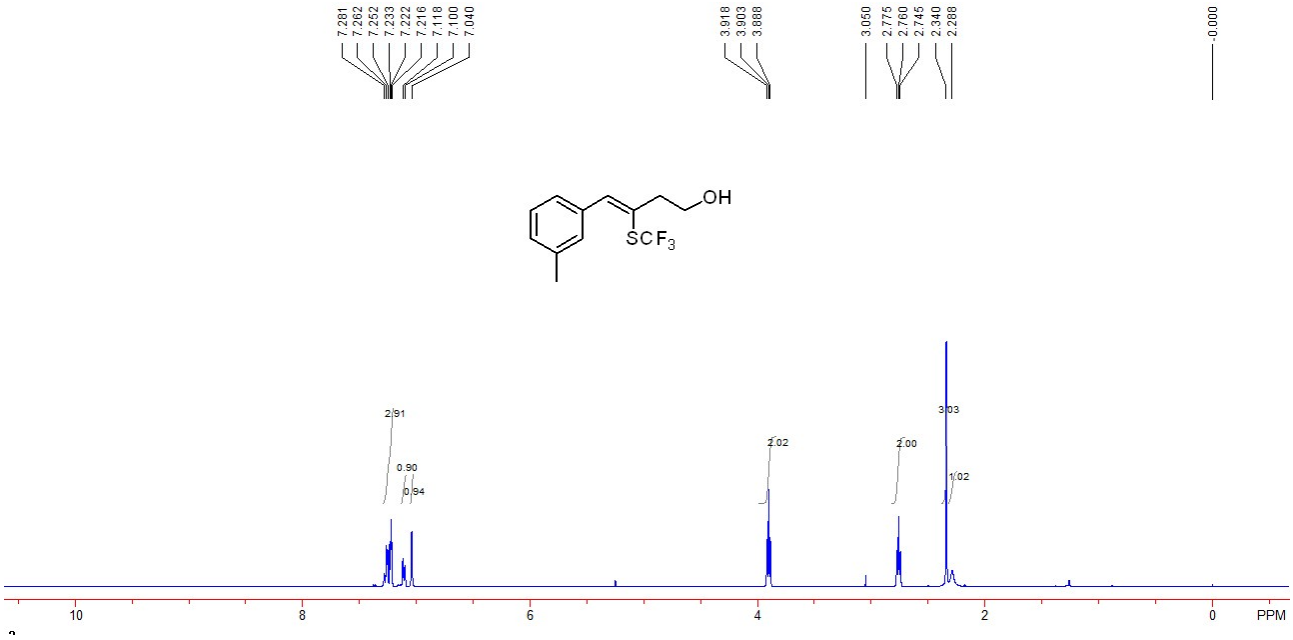
150
100
50
0
PPM





(Z)-4-(m-tolyl)-3-((trifluoromethyl)thio)but-3-en-1-ol (5j).

A colorless oil, 28.8 mg, 55% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.29 (s, 1H, OH), 2.34 (s, 3H, CH_3), 2.76 (t, *J* = 6.0 Hz, 2H, CH_2), 3.90 (t, *J* = 6.0 Hz, 2H, CH_2), 7.04 (s, 2H, ArH), 7.11 (d, *J* = 7.2 Hz, 1H, ArH), 7.22-7.28 (m, 3H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.3, 42.8, 60.1, 123.5 (q, *J* = 1.5 Hz), 126.4, 128.0 129.0, 129.5 (q, *J* = 308.9 Hz), 130.1, 135.0, 137.7, 141.7 (q, *J* = 1.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -38..81. IR (CH_2Cl_2) ν 3318, 2925, 2879, 1152, 1110, 1083, 1042, 691 cm^{-1}. MS (%) m/e 262 (35.56), 175 (79.64), 147 (21.89), 142 (19.42), 130 (80.24), 129 (M^+, 100.00), 128 (42.11), 115 (65.14). HRMS (EI) calcd. for $C_{12}H_{13}OF_3S$: 262.0639, Found: 262.0640.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3.050
2.775
2.760
2.745
2.340
2.288
0.000
OH
SCF3
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0.94
2.02
2.00
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1.02
10
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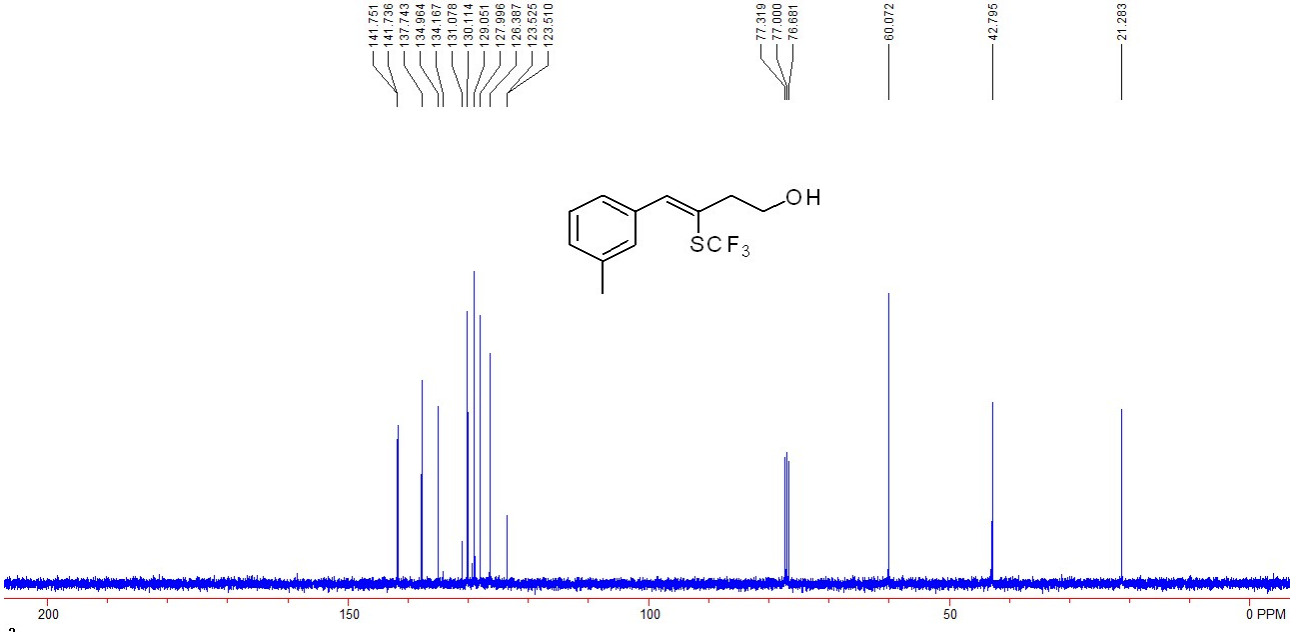
4
2
0
PPM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130.114
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127.996
126.387
123.525
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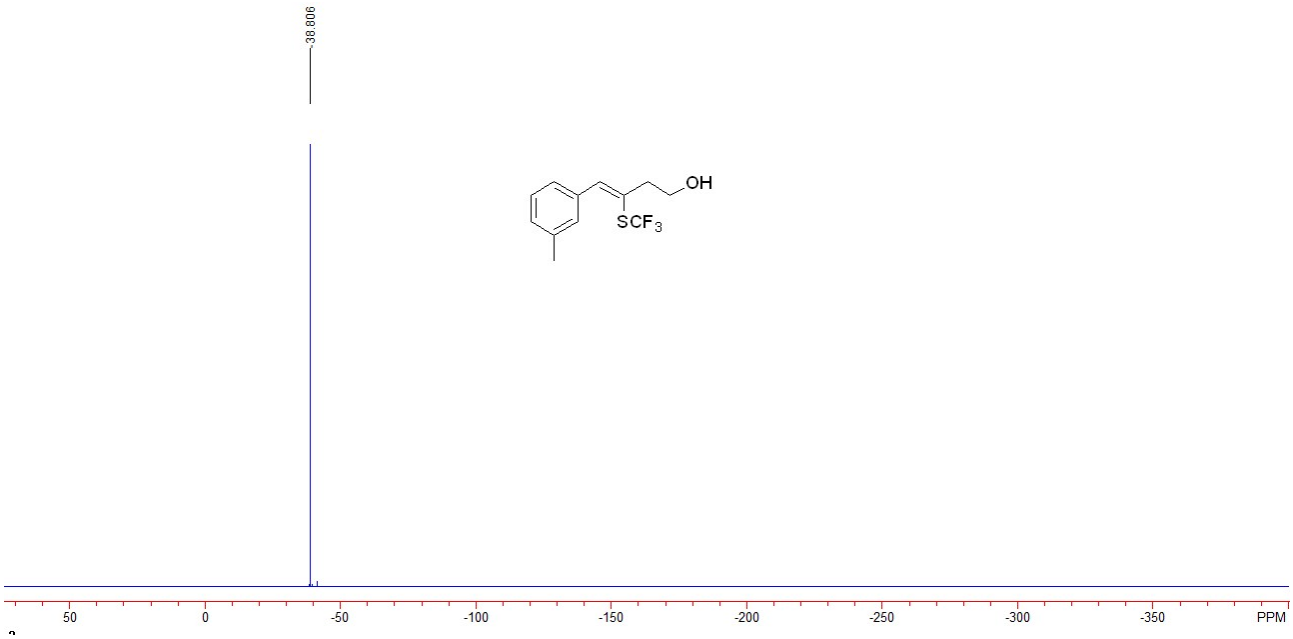
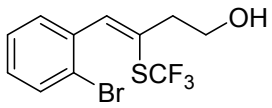
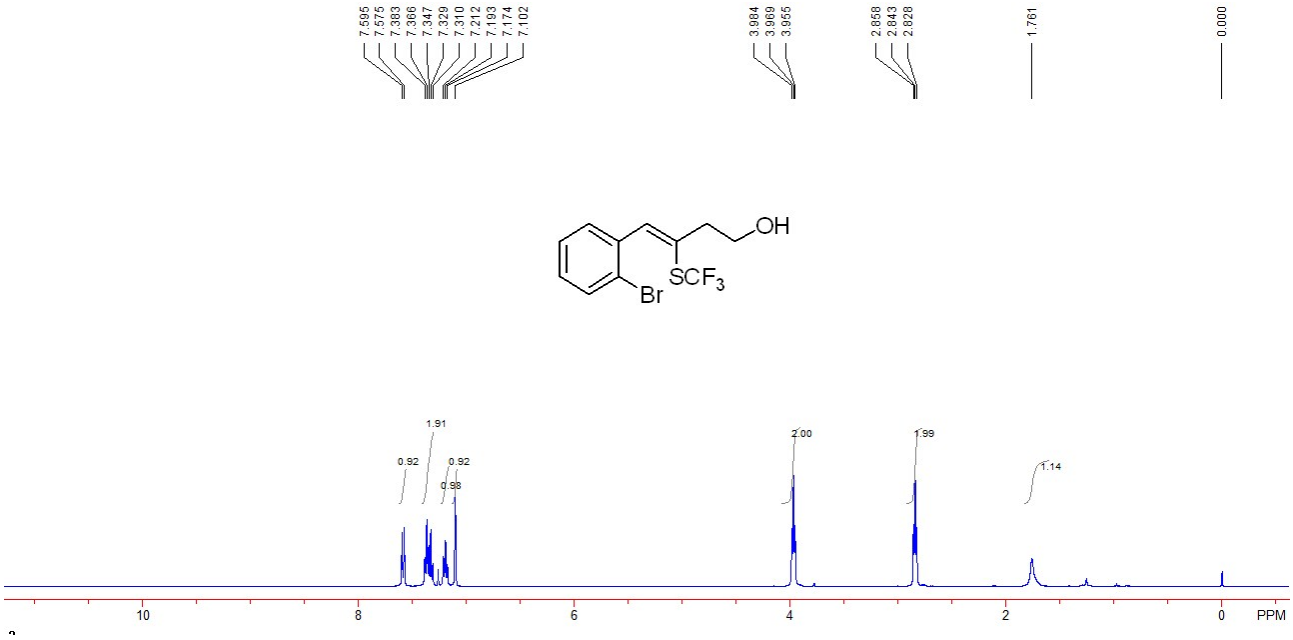
21.283
OH
SCF3
200
150
100
50
0 PPM





(Z)-4-(2-bromophenyl)-3-((trifluoromethyl)thio)but-3-en-1-ol (5k).

A colorless oil, 19.6 g, 30% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.76 (s, 1H, OH), 2.84 (t, *J* = 6.0 Hz, 2H, CH_2), 3.97 (t, *J* = 6.0 Hz, 2H, CH_2), 7.10 (s, 1H, ArH), 7.19 (t, *J* = 7.6 Hz, 1H, ArH), 7.31-7.38 (m, 2H, ArH), 7.58 (d, *J* = 8.0 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 42.0, 60.0, 123.7, 127.1, 127.2 (q, *J* = 1.2 Hz), 129.4 (q, *J* = 307.9 Hz), 129.6, 130.9, 132.3, 135.9, 141.2. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -38.65. IR (CH_2Cl_2) ν 3341, 2944, 2879, 1466, 1435, 1154, 1110, 1085, 1050, 1022, 750 cm^{-1}. MS (%) m/e 247 (47.74), 148 (22.94), 147 (61.62), 178 (61.54), 116 (18.98), 115 (M^+, 100.00), 89 (16.97), 63 (13.98). HRMS (EI) calcd. for $C_{11}H_{10}OF_3SBr$: 325.9588, Found: 325.9586.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3.955
2.858
2.843
2.828
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OH
SCF3
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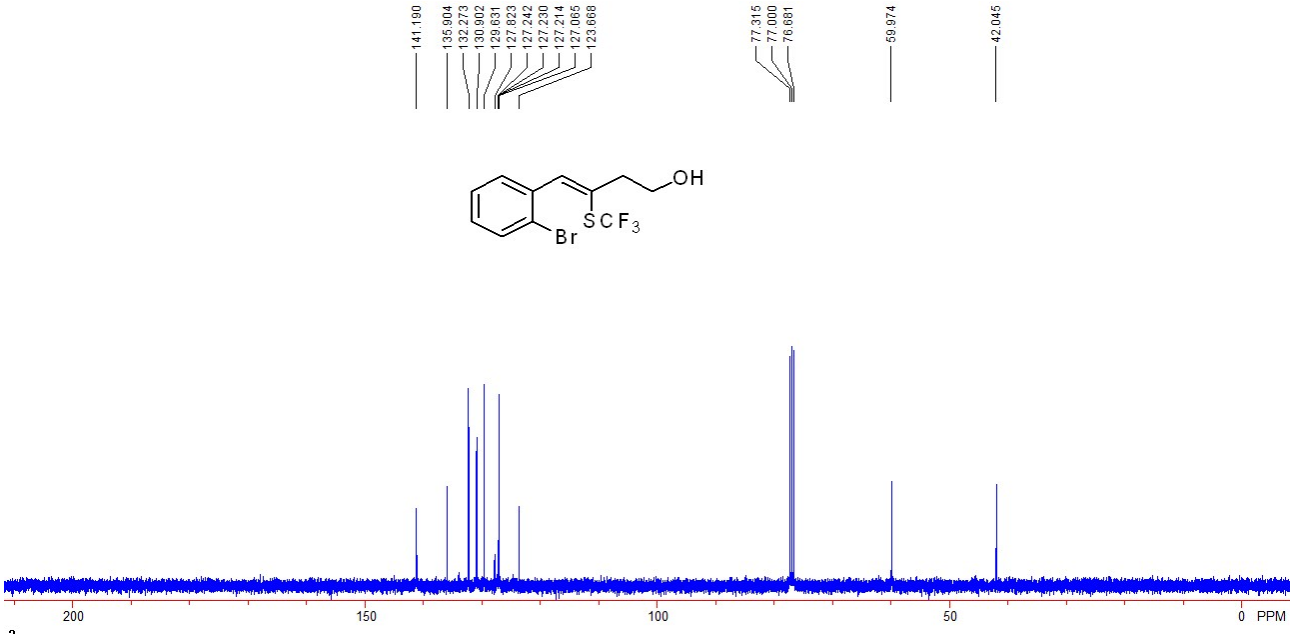
1.14
10
8
6
4
2
0
PPM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135.904
132.273
130.902
129.631
127.823
127.242
127.230
127.214
127.065
123.668
77.315
77.000
76.681
59.974
42.045
OH
SCF3
Br
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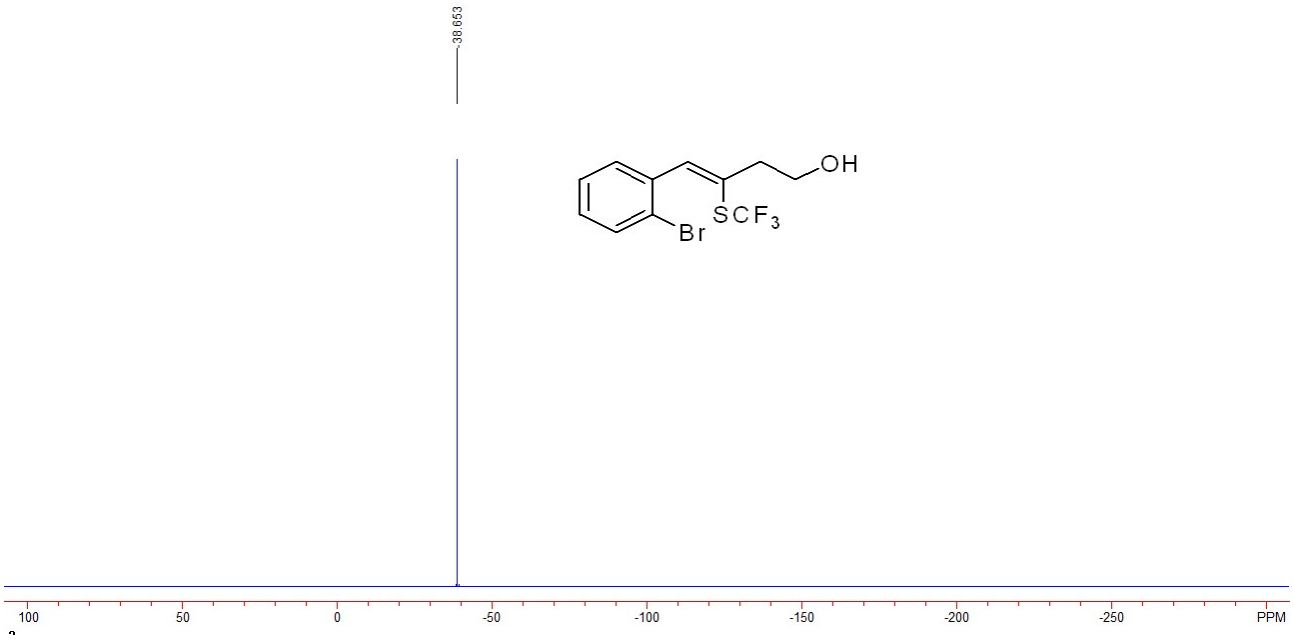
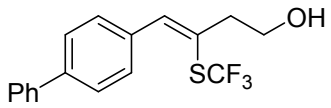
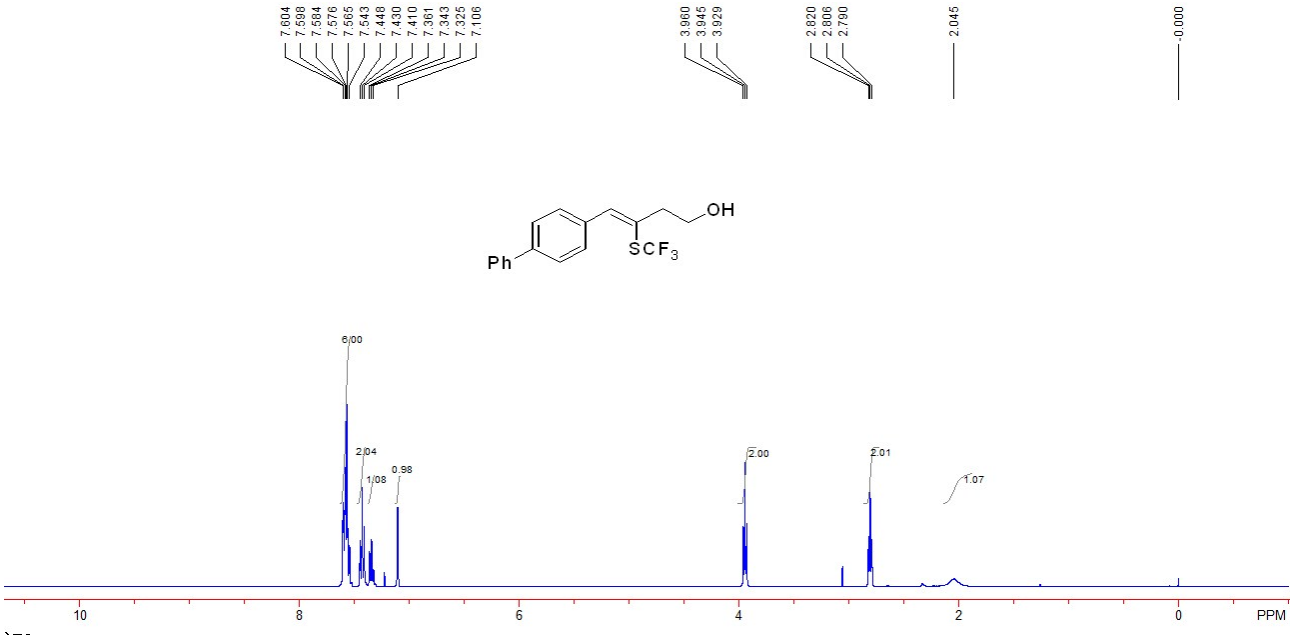
150
100
50
0
PPM





(Z)-4-([1,1'-biphenyl]-4-yl)-3-((trifluoromethyl)thio)but-3-en-1-ol (5l).

A white solid, 46.6 mg, 72% yield. M.p.: 71-73 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.04 (s, 1H, OH), 2.81 (t, J = 6.4 Hz, 2H, CH_2), 3.94 (t, J = 6.4 Hz, 2H, CH_2), 7.11 (s, 1H, ArH), 7.34 (t, J = 7.2 Hz, 1H, ArH), 7.43 (t, J = 8.0 Hz, 2H, ArH), 7.54-7.60 (m, 6H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 43.0, 60.0, 123.5 (q, J = 1.2 Hz), 126.7, 126.9, 127.5, 128.7, 129.5 (q, J = 308.2 Hz), 130.0, 133.9, 140.2, 141.0, 141.3. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -38.70. IR (CH_2Cl_2) ν 3321, 2931, 2882, 1132, 1109, 1083, 1056, 1037, 761, 690 cm^{-1}. MS (%) m/e 325 (14.47), 324 (67.32), 293 (15.68), 237 (25.26), 192 (76.85), 191 (M^+, 100.00), 189 (22.59), 165 (23.92). HRMS (EI) calcd. for $C_{17}H_5OF_3S$: 324.0796, Found: 324.0798.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7.430
7.410
7.361
7.343
7.325
7.106
3.960
3.945
3.929
2.820
2.806
2.790
2.045
0.000
OH
SCF3
Ph
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1.08
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2.00
2.01
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10
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4
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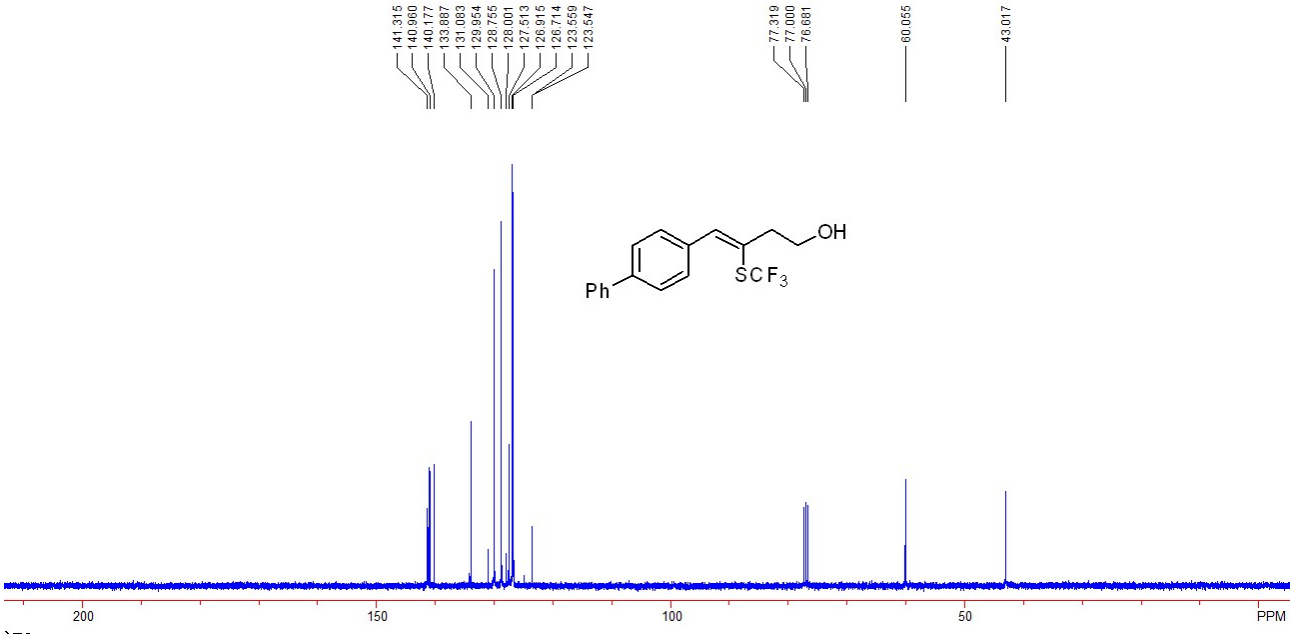
PPM


141.315
140.960
140.177
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131.083
129.954
128.755
128.001
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126.915
126.714
123.559
123.547
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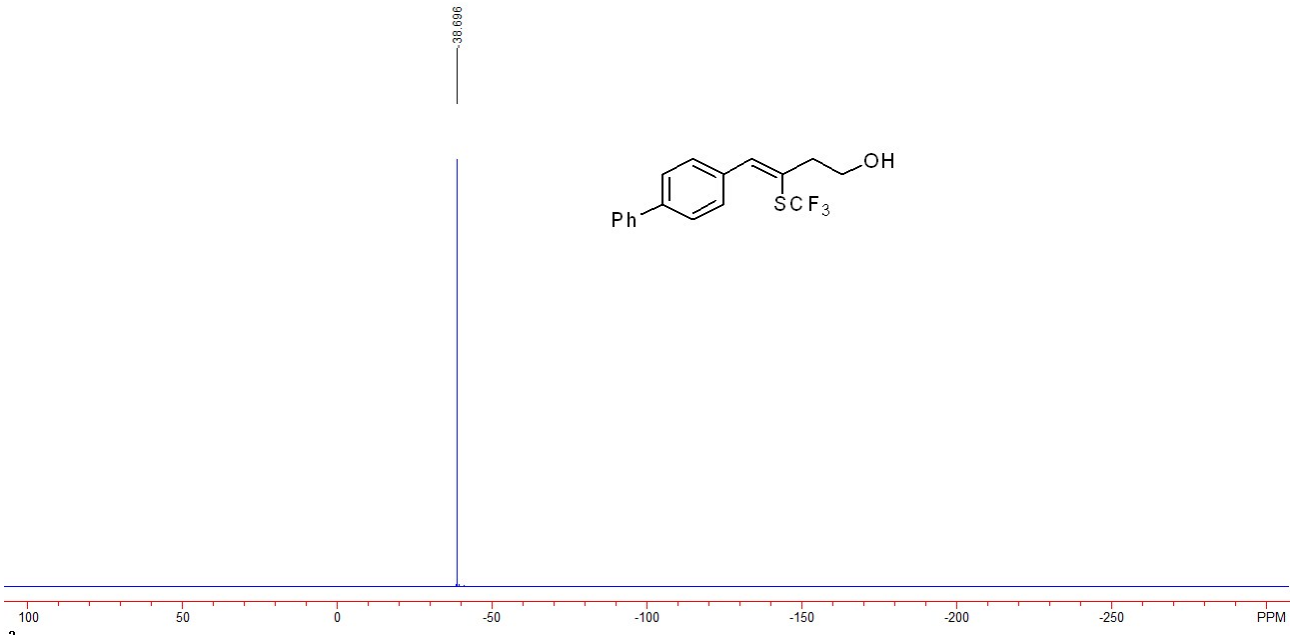
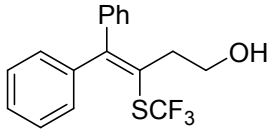
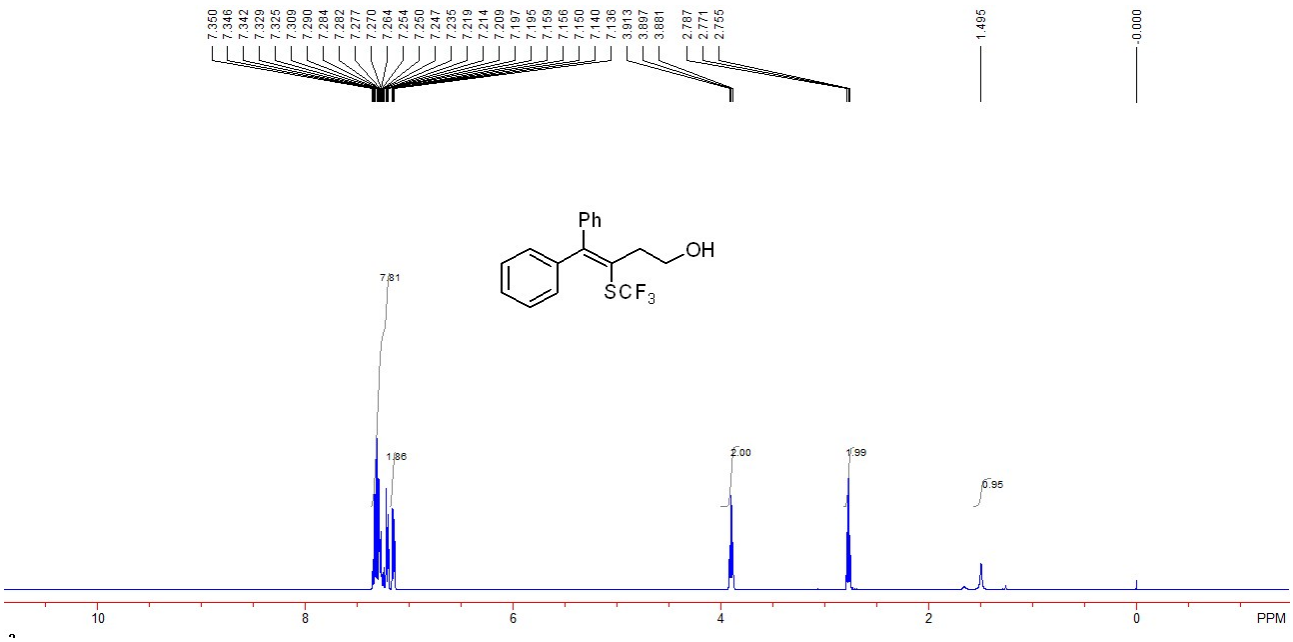
77.000
76.681
60.055
43.017
OH
SCF3
Ph
200
150
100
50
PPM





4,4-diphenyl-3-((trifluoromethyl)thio)but-3-en-1-ol (5m).

A colorless oil, 48.0 g, 74% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.50 (s, 1H, OH), 2.77 (t, *J* = 6.4 Hz, 2H, CH_2), 3.90 (t, *J* = 6.4 Hz, 2H, CH_2), 7.14-7.16 (m, 2H, ArH), 7.20-7.35 (m, 8H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 37.8, 60.7, 123.0, 127.7, 127.8, 128.0, 128.5, 128.6, 129.0, 129.7 (q, *J* = 308.2 Hz), 140.8, 141.7, 156.3 (q, *J* = 1.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -39.56. IR (CH_2Cl_2) ν 3310, 3055, 2882, 1440, 1147, 1113, 1087, 1042, 751, 698 cm^{-1}. MS (%) m/e 324 (35.14), 237 (37.43), 222 (33.45), 221 (34.14), 192 (M^+, 100.00), 191 (73.20), 189 (25.85), 165 (28.46). HRMS (EI) calcd. for $C_{17}H_{15}OF_3S$: 324.0796, Found: 324.0800.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7.309
7.290
7.284
7.282
7.277
7.270
7.264
7.254
7.250
7.247
7.235
7.219
7.214
7.209
7.197
7.195
7.159
7.156
7.150
7.140
7.136
3.913
3.897
3.881
2.787
2.771
2.755
1.495
0.000
Ph
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SCF3
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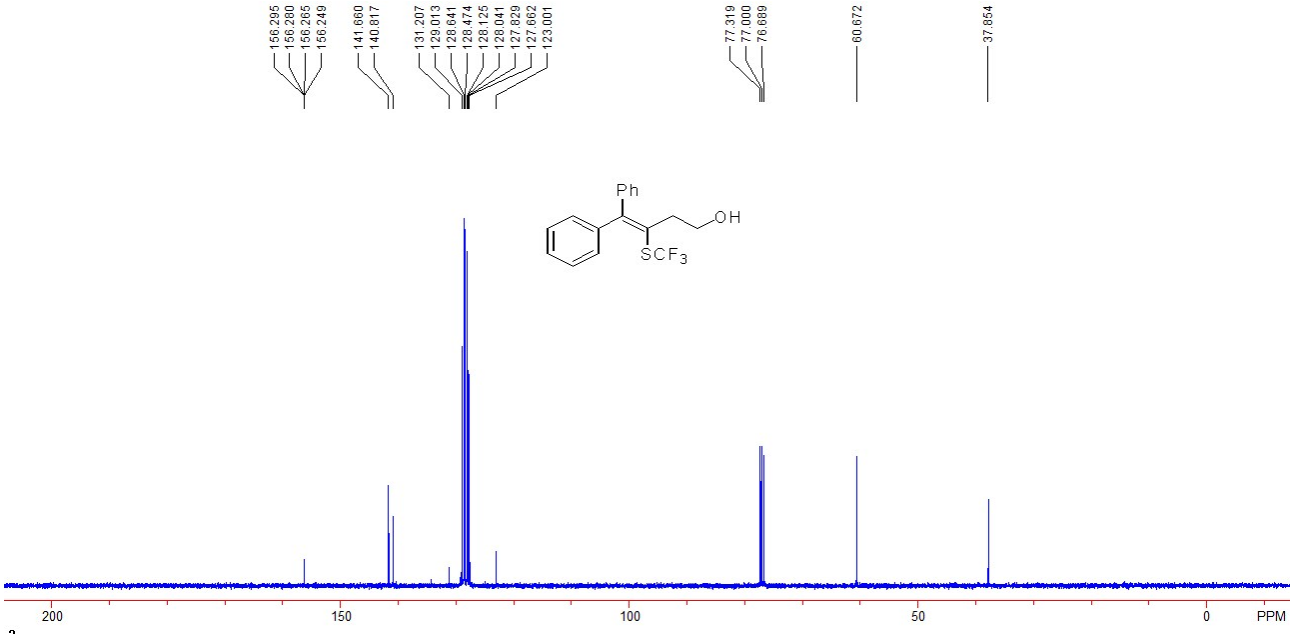
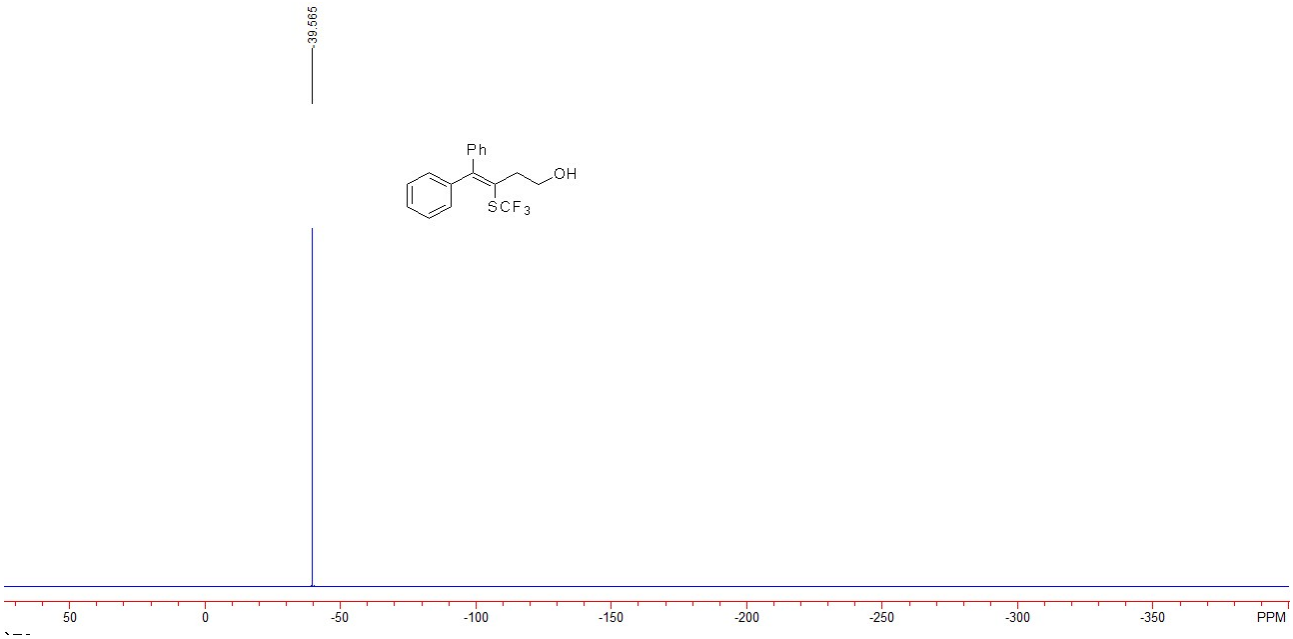
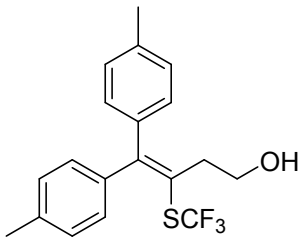
2.00
1.99
0.95
10
8
6
4
2
0
PPM

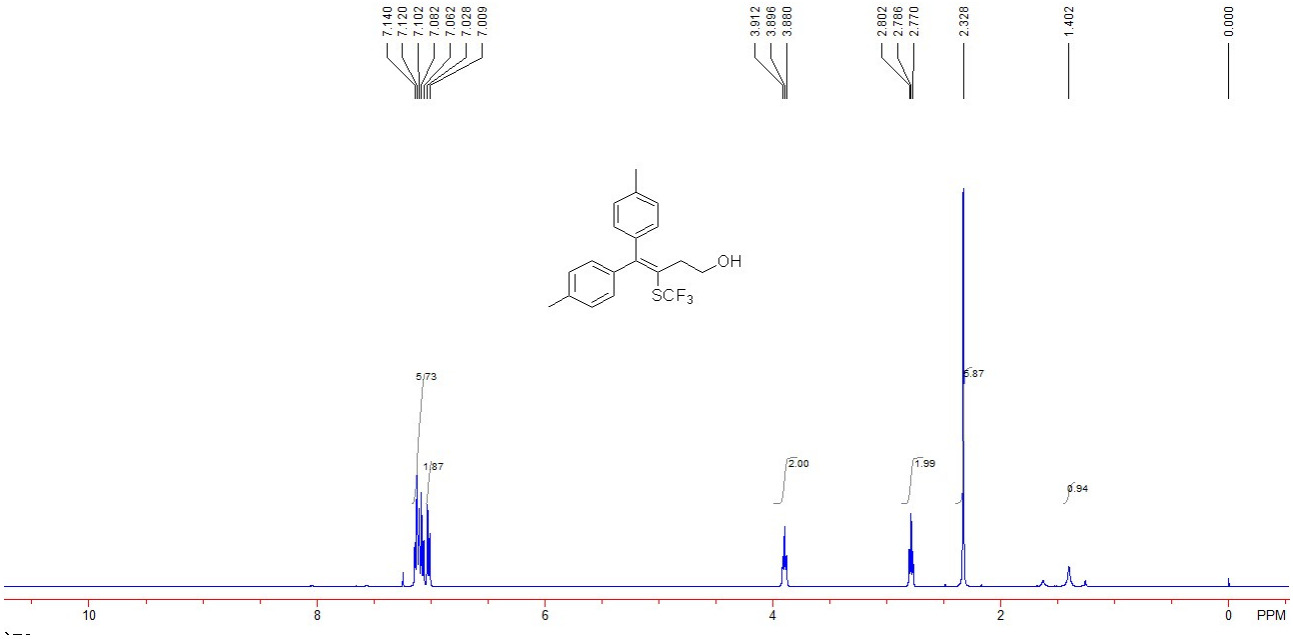

156.295
156.280
156.265
156.249
141.660
140.817
131.207
129.013
128.641
128.474
128.125
128.041
127.829
127.662
123.001
77.319
77.000
76.689
60.672
37.854
Ph
OH
SCF3
200
150
100
50
0
PPM





4,4-di-p-tolyl-3-((trifluoromethyl)thio)but-3-en-1-ol (5n).

A colorless oil, 43.6 mg, 62% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.40 (s, 1H, OH), 2.33 (s, 6H, CH_3), 2.79 (t, *J* = 6.4 Hz, 2H, CH_2), 3.90 (t, *J* = 6.4 Hz, 2H, CH_2), 7.02 (d, *J* = 7.6 Hz, 2H, ArH), 7.06-7.14 (m, 6H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.16, 21.23, 38.0, 60.8, 122.0, 128.6, 128.7, 129.0, 129.1, 129.7 (q, *J* = 308.2 Hz), 137.5, 137.6, 138.2, 139.0, 156.3. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -39.66. IR (CH_2Cl_2) ν 3316, 3021, 2923, 2871, 1149, 1116, 1089, 1042, 815 cm^{-1}. HRMS (TOF EI) calcd. for $C_{19}H_{19}OF_3S$: 352.1109, Found: 352.1107.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7.028
7.009
3.912
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3.880
2.802
2.786
2.770
2.328
1.402
0.000
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SCF3
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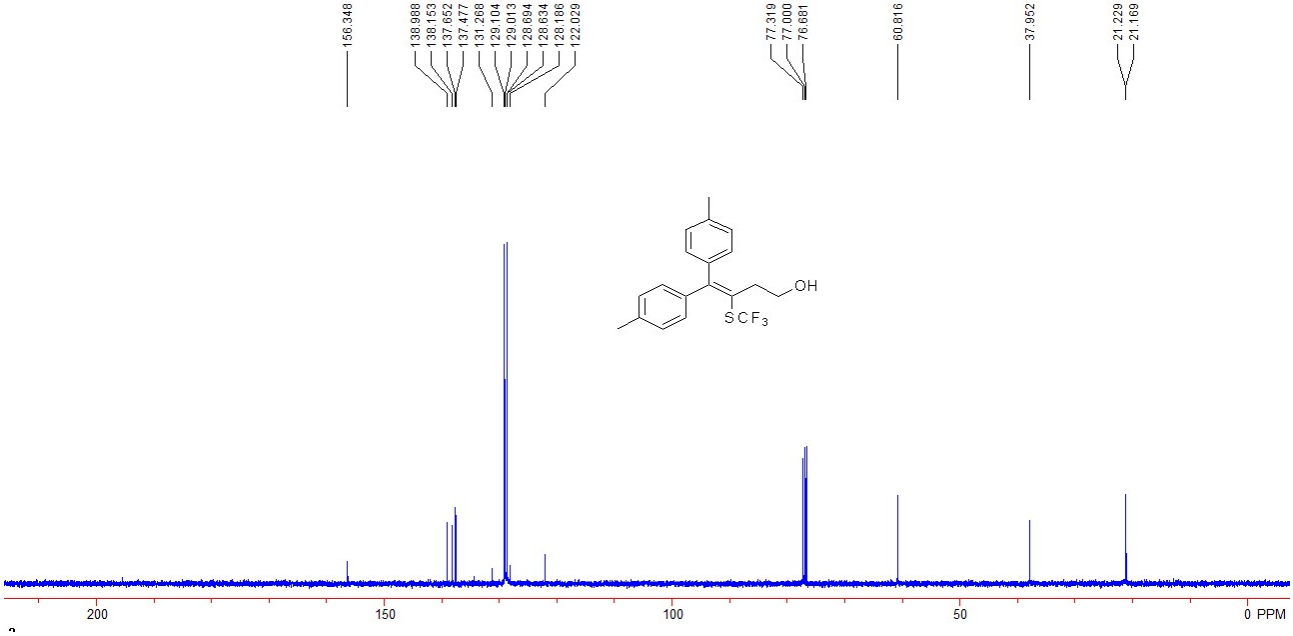
2.00
1.99
5.87
0.94
10
8
6
4
2
0
PPM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137.477
131.266
129.104
129.013
128.694
128.634
128.186
122.029
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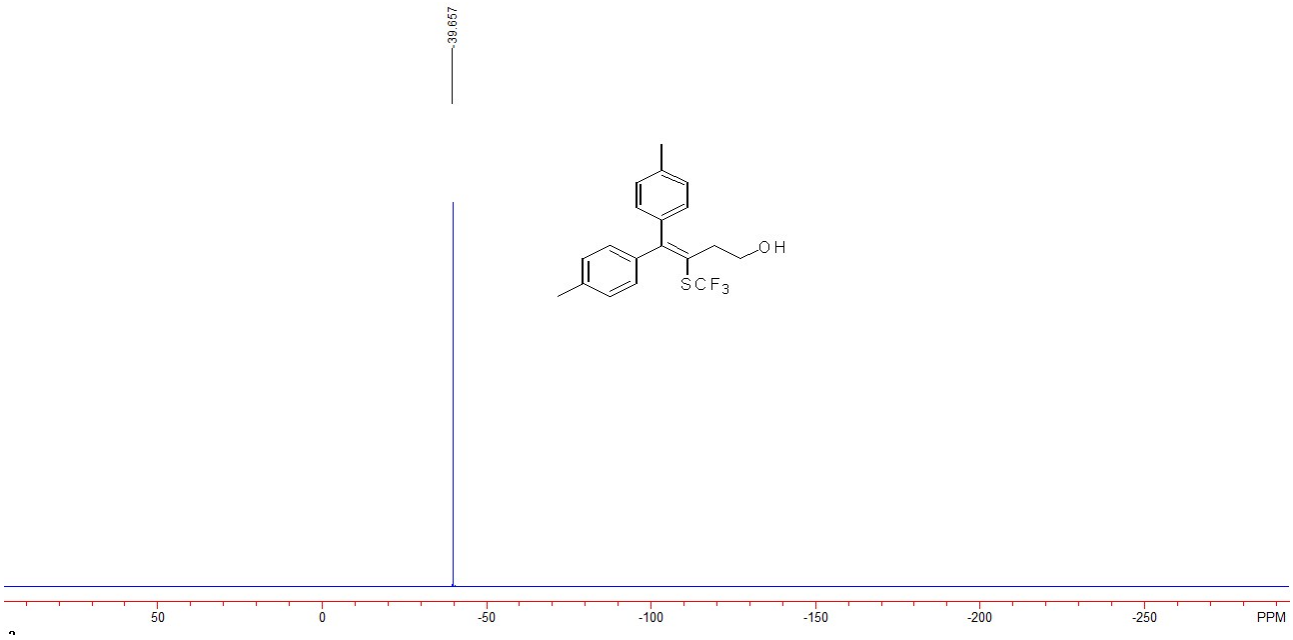
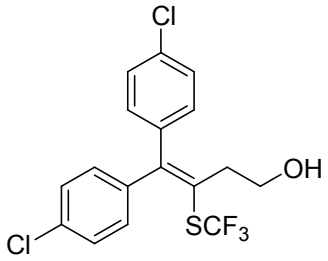
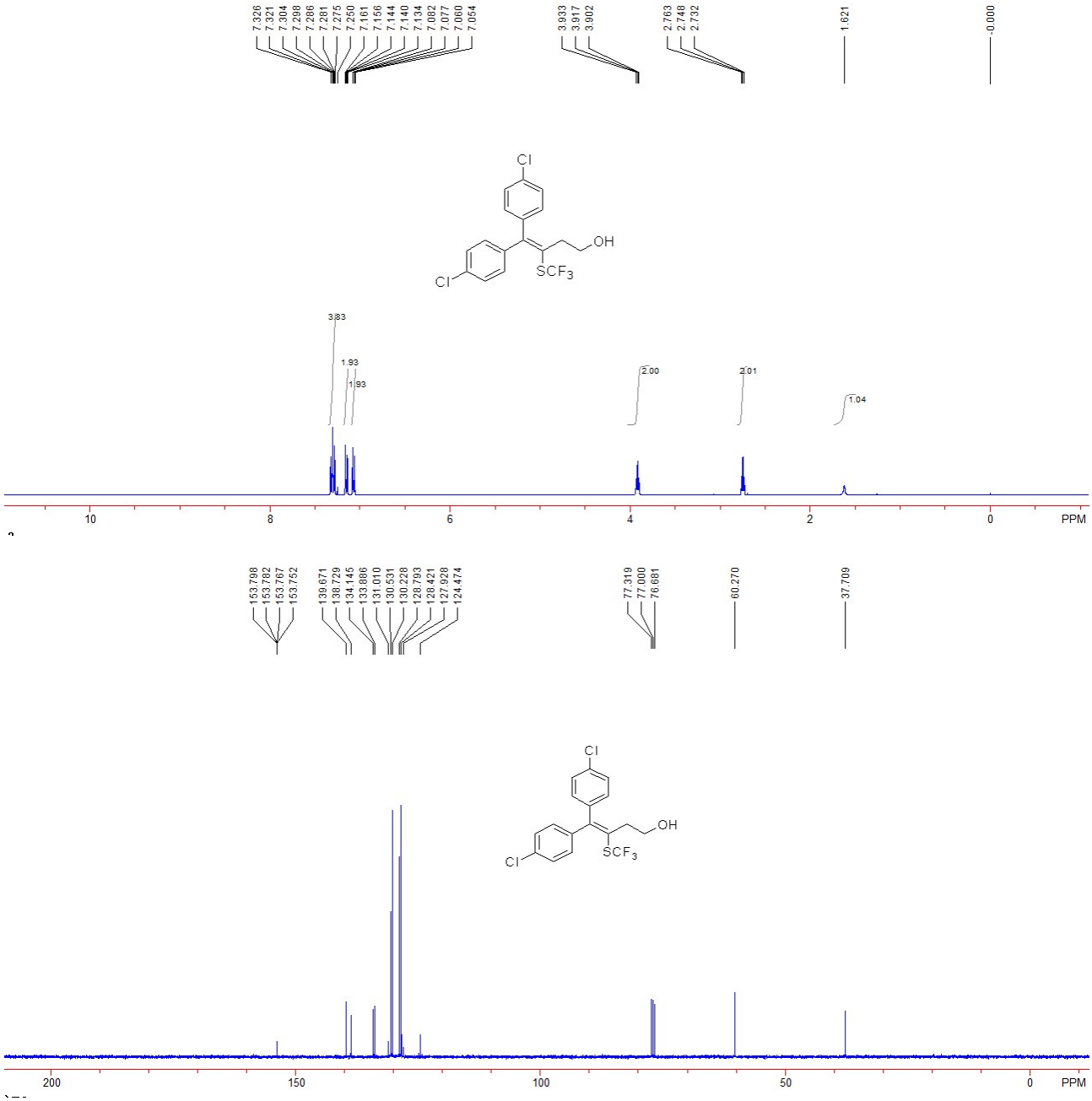
21.169
OH
SCF3
200
150
100
50
0 PPM





4,4-bis(4-chlorophenyl)-3-((trifluoromethyl)thio)but-3-en-1-ol (5o).

A colorless oil, 56.4 mg, 72% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.62 (s, 1H, OH), 2.75 (t, J = 6.0 Hz, 2H, CH_2), 3.92 (t, J = 6.0 Hz, 2H, CH_2), 7.05-7.08 (m, 2H, ArH), 7.13-7.16 (m, 2H, ArH), 7.27-7.33 (m, 4H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 37.7, 60.3, 124.5, 128.4, 128.8, 129.5 (q, J = 308.2 Hz), 130.2, 130.5, 133.9, 134.1, 138.7, 139.7, 153.8 (q, J = 1.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -39.45. IR (CH_2Cl_2) ν 3316, 2967, 2879, 1489, 1153, 1116, 1088, 1015, 823 cm^{-1}. MS (%) m/e 392 (43.66), 270 (47.98), 260 (52.20), 227 (33.89), 225 (M^+, 100.00), 221 (50.79), 189 (67.41), 125 (34.27). HRMS (EI) calcd. for $C_{17}H_{13}OF_3SCl_2$: 392.0016, Found: 392.0012.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7.156
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7.140
7.134
7.082
7.077
7.060
7.054
3.933
3.917
3.902
2.763
2.748
2.732
1.621
0.000
Cl
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SCF3
Cl
3.83
1.93
1.93
2.00
2.01
1.04
10
8
6
4
2
0
PPM

153.798
153.782
153.767
153.752
139.671
138.729
134.145
133.886
131.010
130.531
130.228
128.793
128.421
127.928
124.474
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77.000
76.681
60.270
37.709
Cl
OH
SCF3
Cl
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100
50
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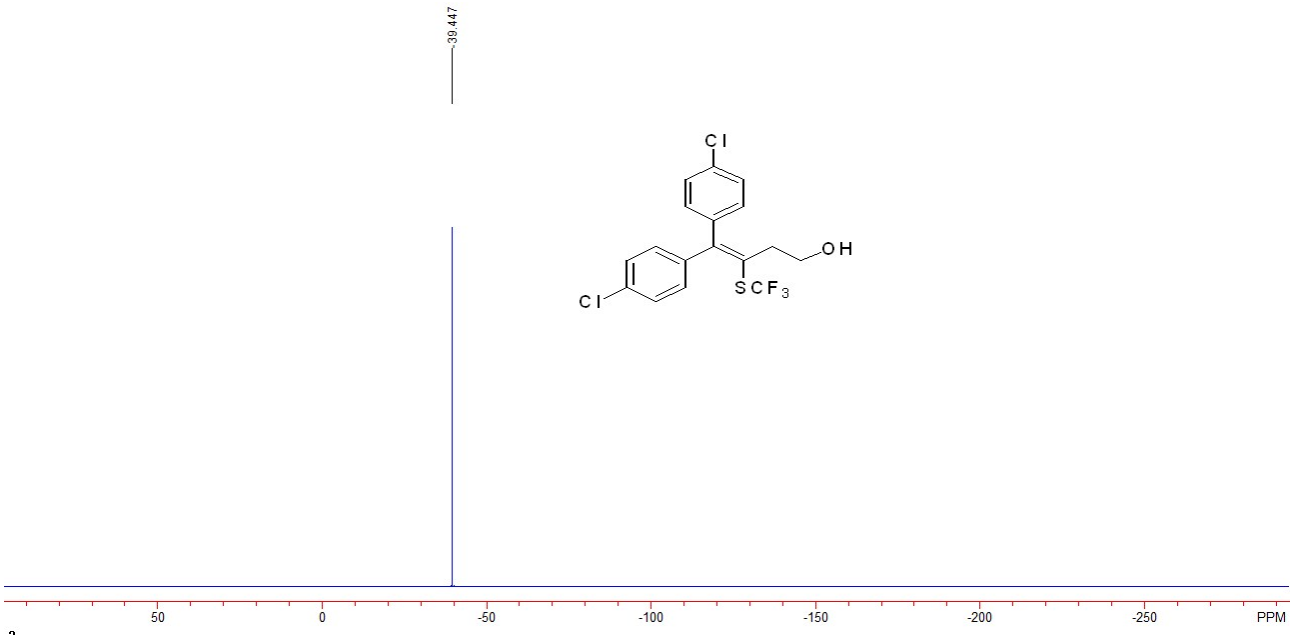
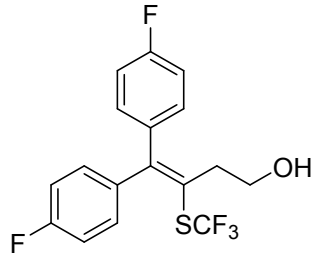
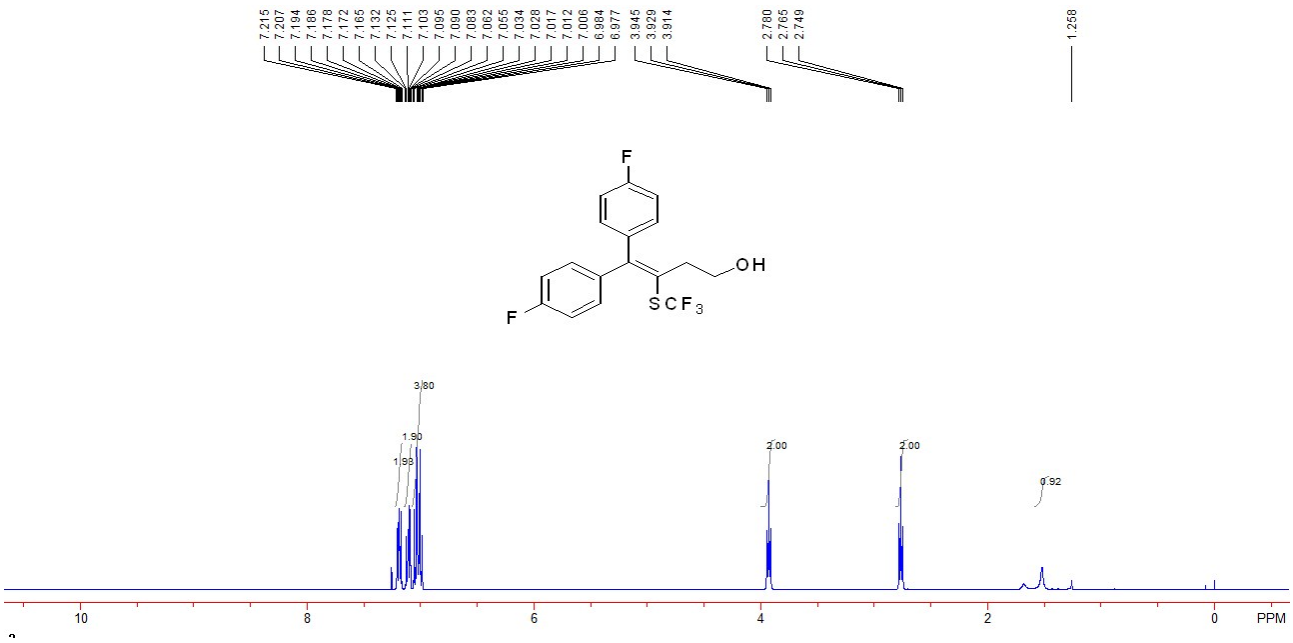
PPM





4,4-bis(4-fluorophenyl)-3-((trifluoromethyl)thio)but-3-en-1-ol (5p).

A colorless oil, 56.2 mg, 78% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.26 (s, 1H, OH), 2.76 (t, *J* = 6.0 Hz, 2H, CH_2), 3.93 (t, *J* = 6.0 Hz, 2H, CH_2), 6.98-7.06 (m, 4H, ArH), 7.08-7.13 (m, 2H, ArH), 7.16-7.22 (m, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 37.8, 60.3, 115.2 (d, *J* = 40.2 Hz), 115.4 (d, *J* = 40.3 Hz), 123.8, 129.5 (q, *J* =308.9 Hz), 130.6 (d, *J* = 8.3 Hz), 131.0 (d, *J* = 8.4 Hz), 136.5 (d, *J* = 3.1 Hz), 137.5 (d, *J* = 3.8 Hz), 154.2 (d, *J* = 1.6 Hz), 162.1 (d, *J* = 246.7), 162.2 (d, *J* = 246.7 Hz), ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -113.59, -39.62. IR (CH_2Cl_2) ν 3321, 2972, 2887, 1598, 1505, 1225, 1157, 1115, 1085, 1046, 835 cm^{-1}. MS (%) m/e 360 (37.65), 360 (35.65), 329 (14.54), 258 (18.62), 257 (14.46), 229 (19.78), 228 (M^+, 100.00), 227 (35.31). HRMS (EI) calcd. for $C_{17}H_{13}OF_5S$: 360.0607, Found: 360.0599.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2.780
2.765
2.749
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F
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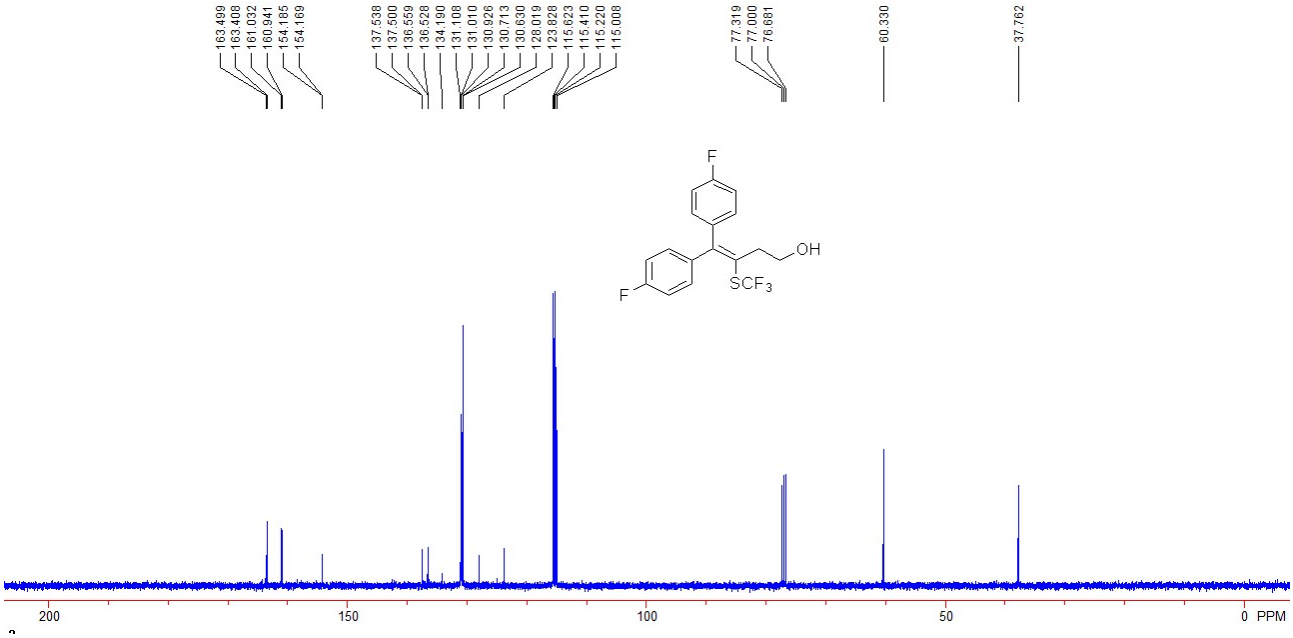
PPM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136.528
134.190
131.108
131.010
130.926
130.713
130.630
128.019
123.828
115.623
115.410
115.220
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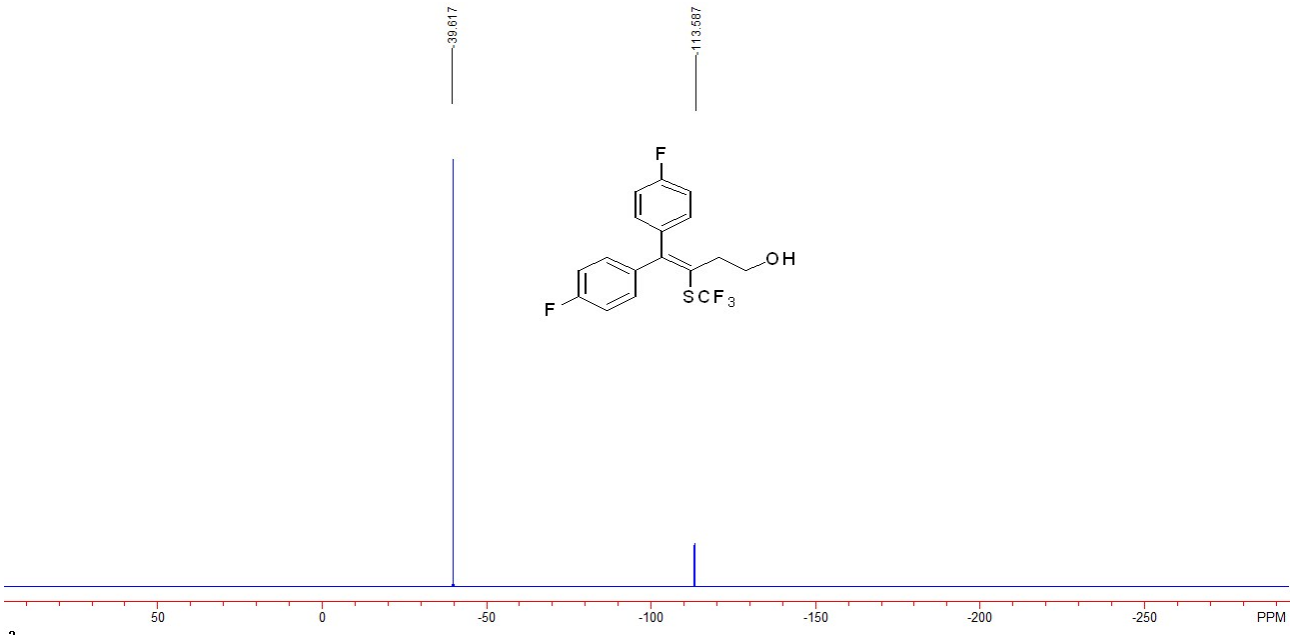
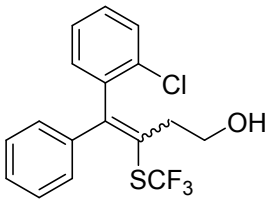
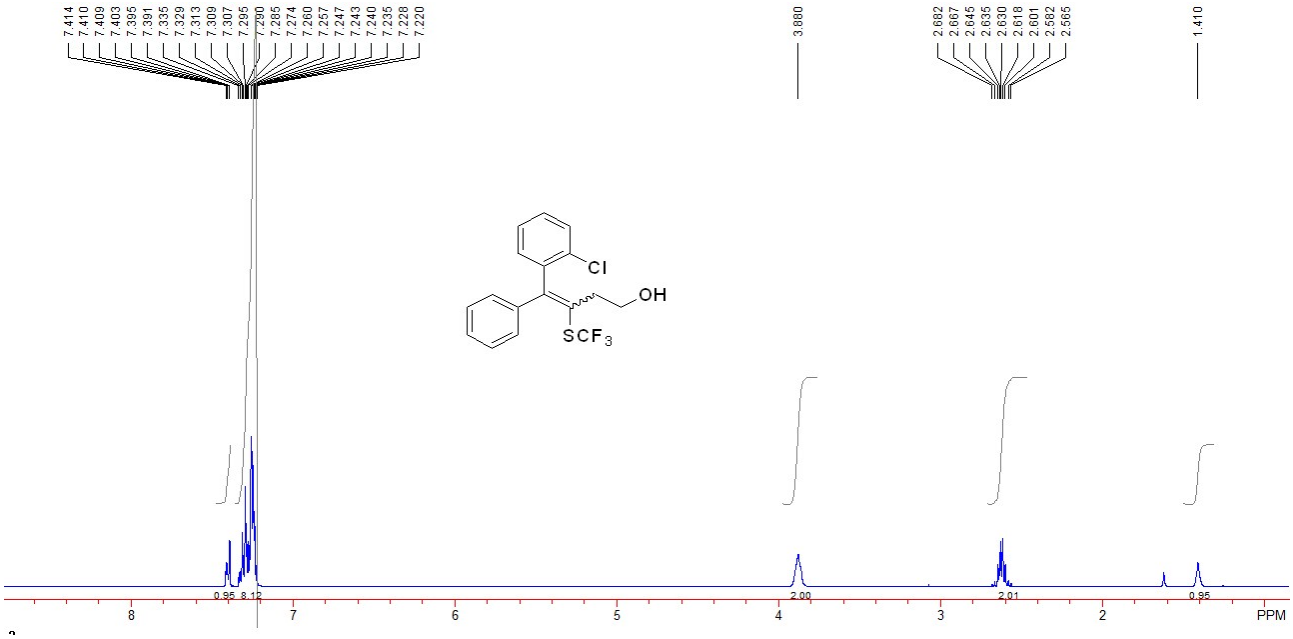
76.681
60.330
37.762
F
OH
SCF3
F
200
150
100
50
0
PPM





4-(2-chlorophenyl)-4-phenyl-3-((trifluoromethyl)thio)but-3-en-1-ol (5q).

A colorless oil, 46.7 mg, 65% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.41 (s, 1H, OH), 2.55-2.68 (m, 2H, CH_2), 3.88 (s, 2H, CH_2), 7.22-7.34 (m, 8H, ArH), 7.39-7.41 (m, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 38.5 (q, J = 1.2 Hz), 60.5, 125.4 (q, J = 1.1 Hz), 127.0, 127.90, 127.94, 129.1, 129.3, 129.6 (q, J = 308.7 Hz), 130.1, 130.2, 132.3, 139.5, 139.7, 152.5 (q, J = 1.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -39.13. IR (CH_2Cl_2) ν 3330, 2962, 2880, 1472, 1438, 1150, 1115, 1086, 1054, 751, 697 cm^{-1}. HRMS (DART) ($M+NH_4$) calcd. for $C_{17}H_{18}ONClF_3S$: 376.0744, Found: 376.0743.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7.240
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2.682
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2.645
2.635
2.630
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2.601
2.582
2.565
1.410
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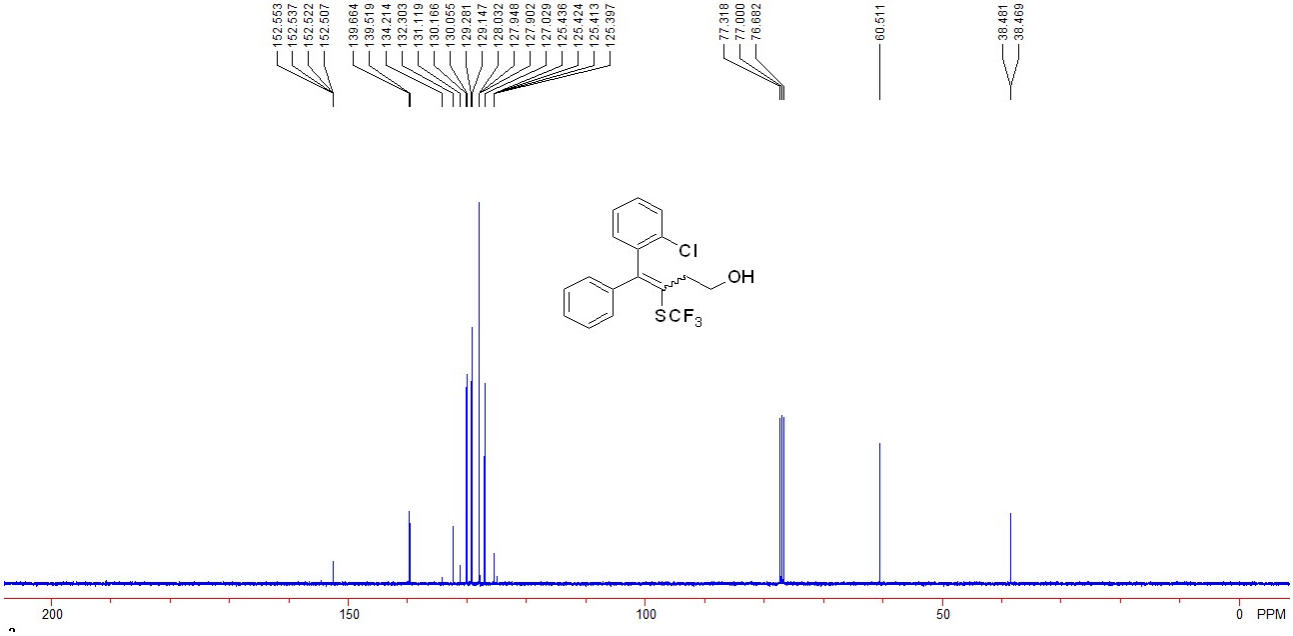
3
2
PPM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125.397
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76.682
60.511
38.481
38.469
Cl
OH
SCF3
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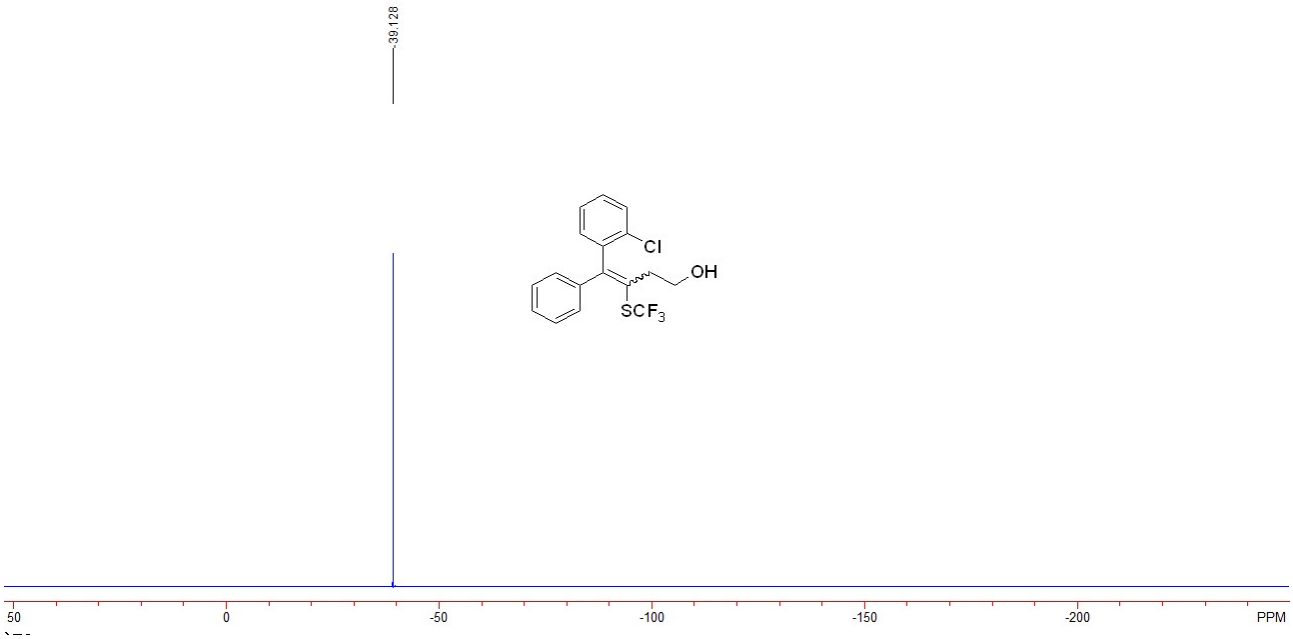
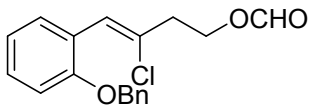
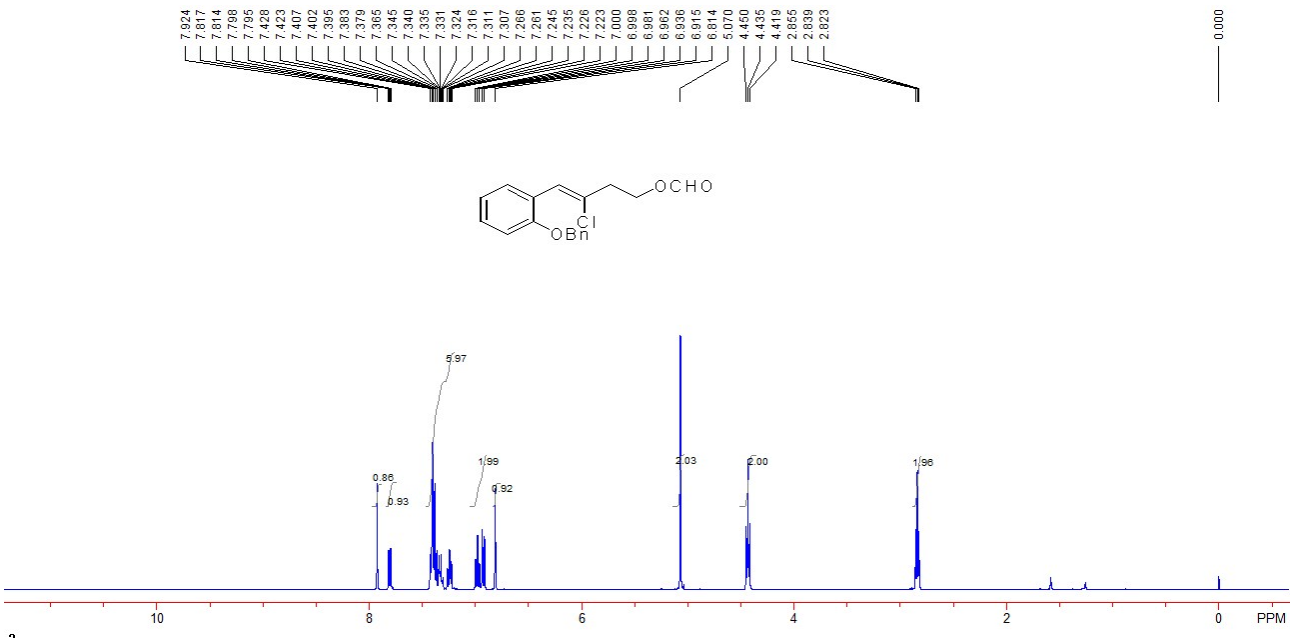
100
50
0
PPM

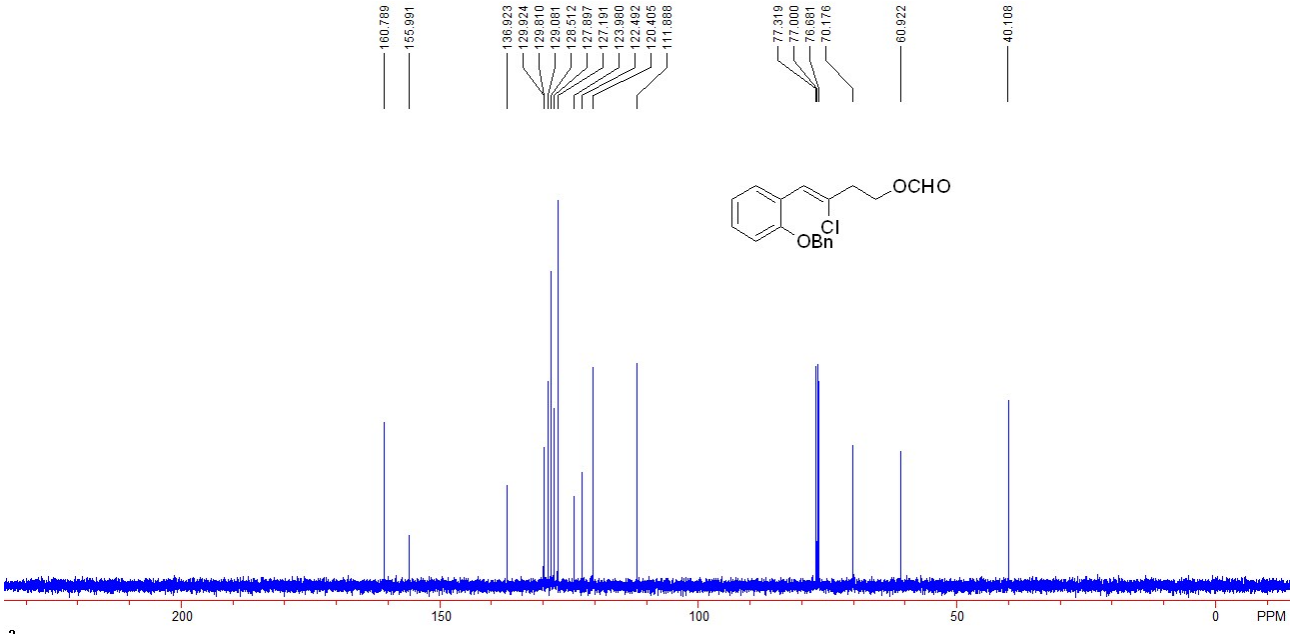


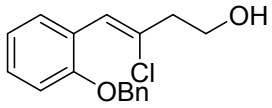


(Z)-4-(2-(benzyloxy)phenyl)-3-chlorobut-3-en-1-yl formate (6').

A colorless oil, 33.5 mg, 53% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.84 (t, *J* = 6.4 Hz, 2H, CH_2), 4.44 (t, *J* = 6.4 Hz), 2H, CH_2), 5.07 (s, 2H, CH_2), 6.81 (s, 1H, ArH), 6.92-7.00 (m, 2H, ArH), 7.22-7.43 (m, 6H, ArH), 7.81 (dd, *J* = 1.2 Hz, 7.6 Hz, 1H, ArH), 7.92 (s, 1H, CH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 40.1, 60.9, 70.2, 111.9, 120.4, 122.5, 124.0, 127.2, 127.9, 128.5, 129.1, 129.8, 129.9, 136.9, 156.0, 160.8. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -40.10. IR (CH_2Cl_2) ν 3037, 2933, 1720, 1598, 1487, 1449, 1243, 1162, 1118, 1014, 749, 696 cm^{-1}. MS (%) m/e 179 (3.65), 145 (6.36), 144 (7.14), 115 (3.53), 92 (8.66), 91 (M^+, 100.00), 77 (4.13), 65 (6.38). HRMS (EI) calcd. for $C_{18}H_{17}O_3Cl$: 316.0866, Found: 316.0869.



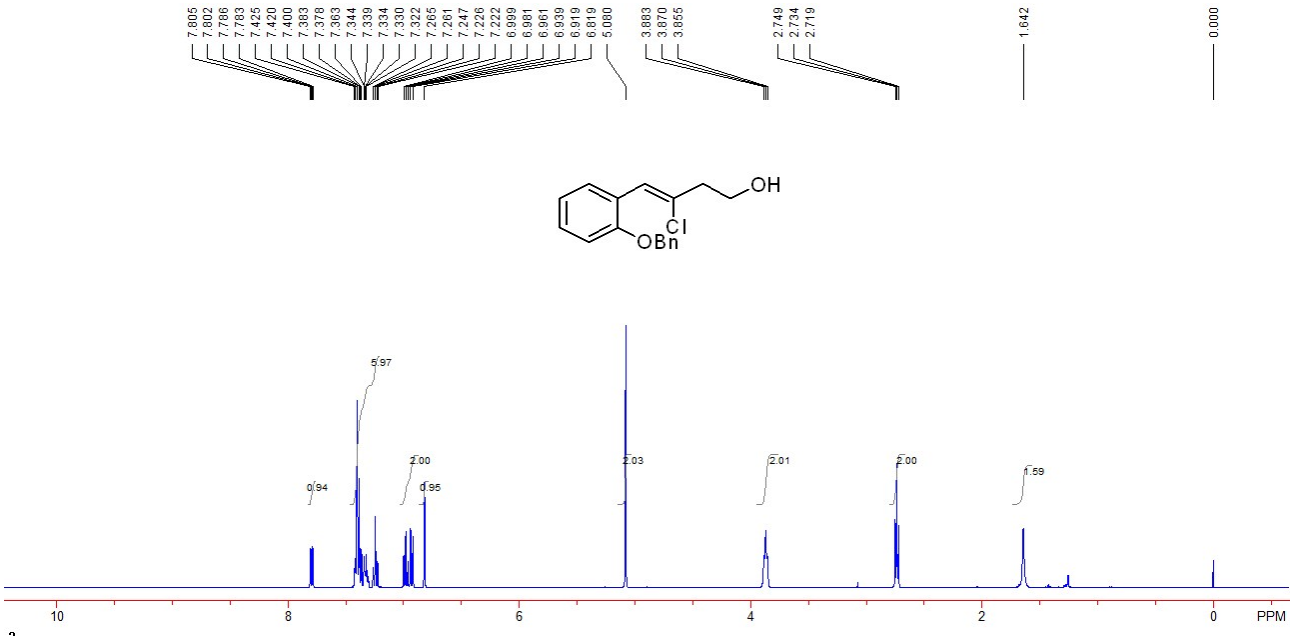


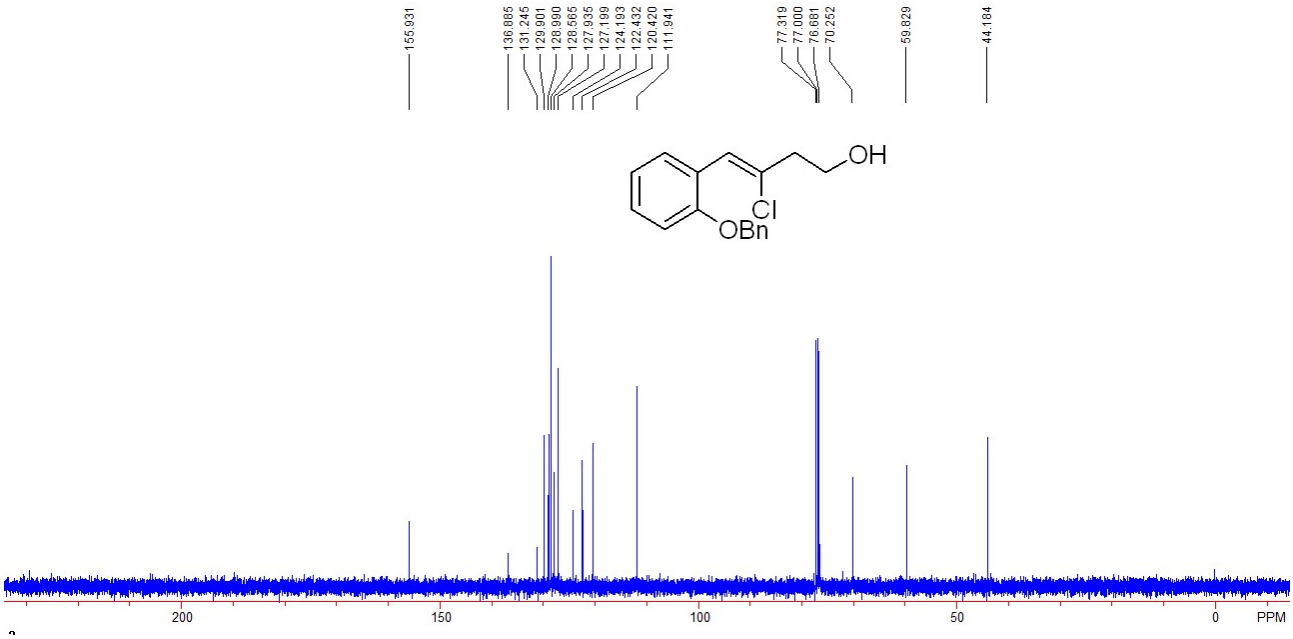


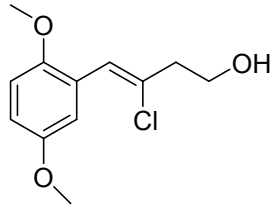
(Z)-4-(2-(benzyloxy)phenyl)-3-chlorobut-3-en-1-ol (6a).

A colorless oil, 30.0 mg, 52% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.64 (s, 1H, OH), 2.73 (t, J = 6.0 Hz, 2H, CH_2), 3.87 (t, J = 6.0 Hz, 2H, CH_2), 5.08 (s, 2H, CH_2), 6.82 (s, 1H, ArH), 6.92-7.00 (m, 2H, ArH), 7.22-7.42 (m, 6H, ArH), 7.79 (dd, J = 1.2 Hz, 7.6 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 44.2, 59.8, 70.2, 111.9, 120.4, 122.4, 124.2, 127.2, 127.9, 128.6, 129.0, 129.9, 131.2, 136.9, 155.9. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -40.10. IR (CH_2Cl_2) ν 3313, 2967, 2874,

1485, 1449, 1380, 1242, 1118, 1086, 1046, 879, 750, 696 cm^{-1}. MS (%) m/e 167 (6.26), 146 (9.87), 145 (5.06), 131 (12.21), 92 (8.95), 91 (M^+, 100.00), 77 (4.64) 65 (6.95). HRMS (EI) calcd. for $C_{17}H_{17}O_2Cl$: 288.0917, Found: 288.0922.

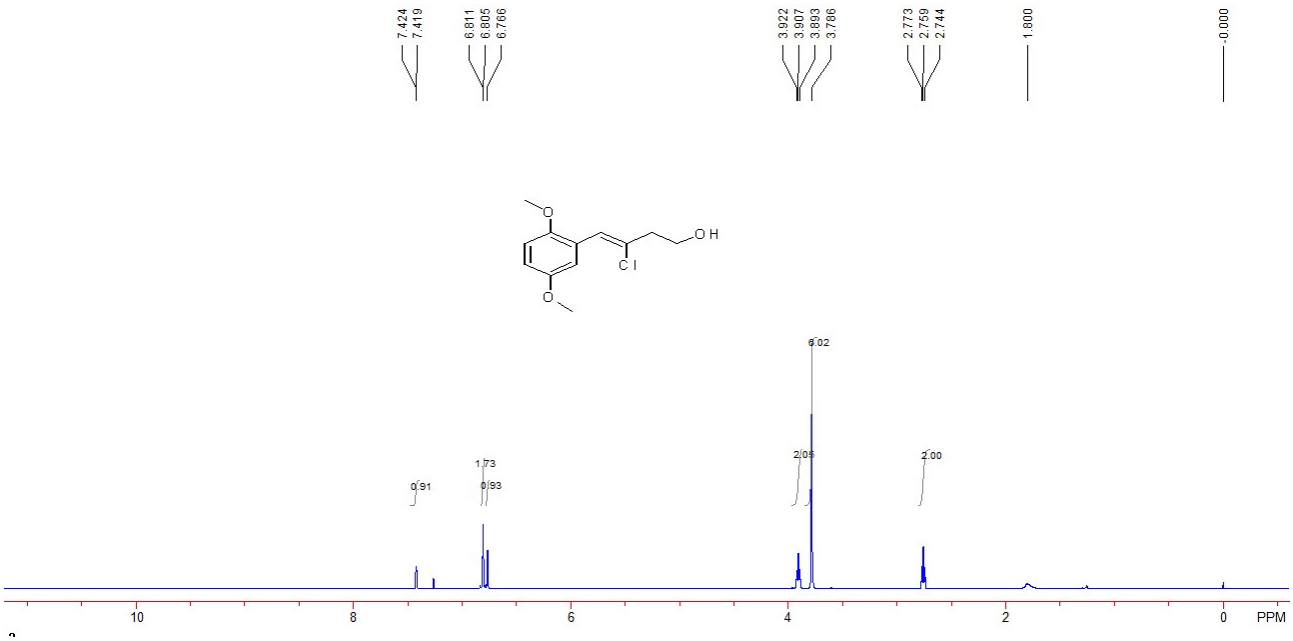


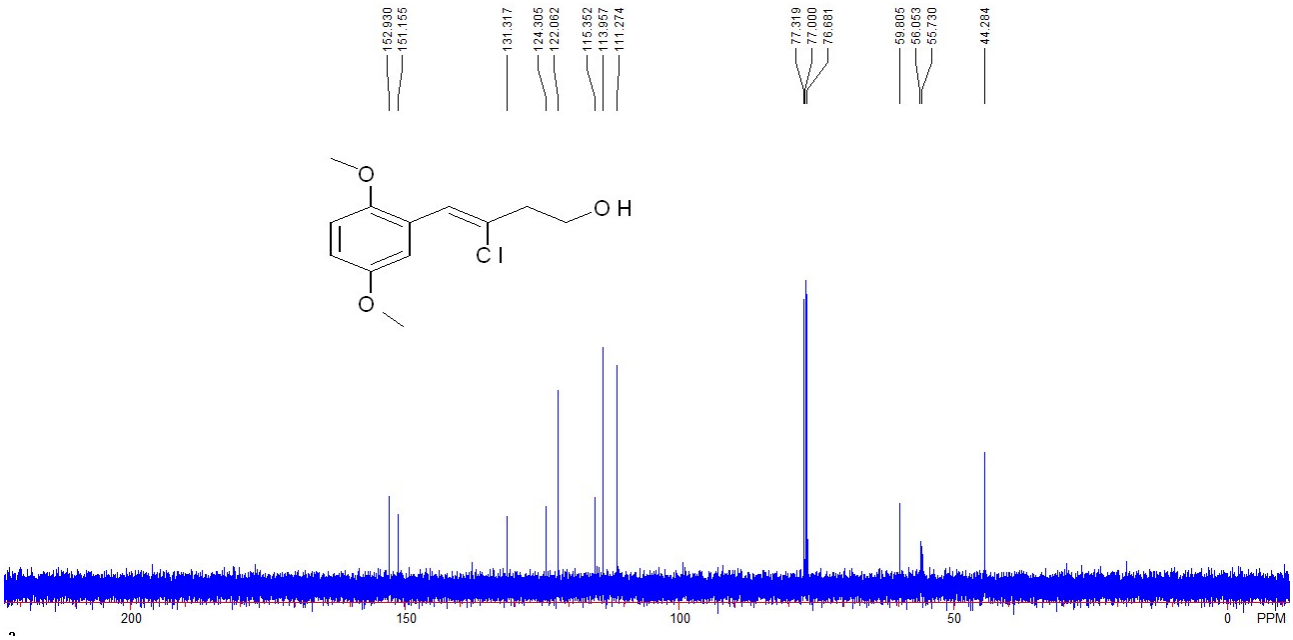


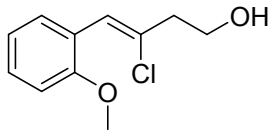


(Z)-3-chloro-4-(2,5-dimethoxyphenyl)but-3-en-1-ol (6c).

A colorless oil, 28.1 mg, 58% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.80 (s, 1H, OH), 2.76 (t, J = 6.0 Hz, 2H, CH_2), 3.79 (s, 6H, CH_3), 3.91 (t, J = 6.0 Hz, 2H, CH_2), 6.77 (s, 1H, ArH), 6.81 (d, J = 2.4 Hz, 2H, ArH), 7.42 (d, J = 2.0 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 44.3, 55.7, 56.0, 59.8, 111.3, 114.0, 115.4, 122.1, 124.3, 131.3, 151.2, 152.9. IR (CH_2Cl_2) ν 3390, 2946, 2838, 1492, 1283, 1221, 1046, 802 cm^{-1}. MS (%) m/e 244 (35.00), 242 (M^+, 100.00), 211 (36.55), 176 (62.44), 175 (60.07), 161 (91.39), 145 (48.95), 115 (32.58). HRMS (EI) calcd. for $C_{12}H_{15}O_3Cl$: 242.0710, Found: 242.0721.

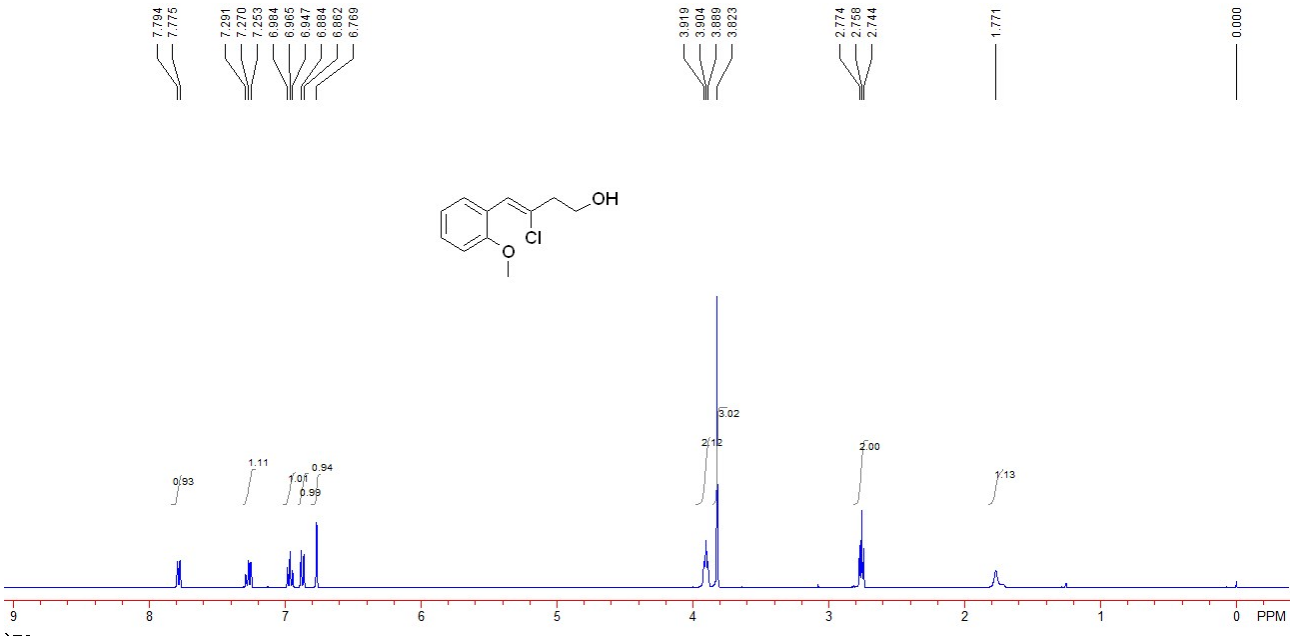


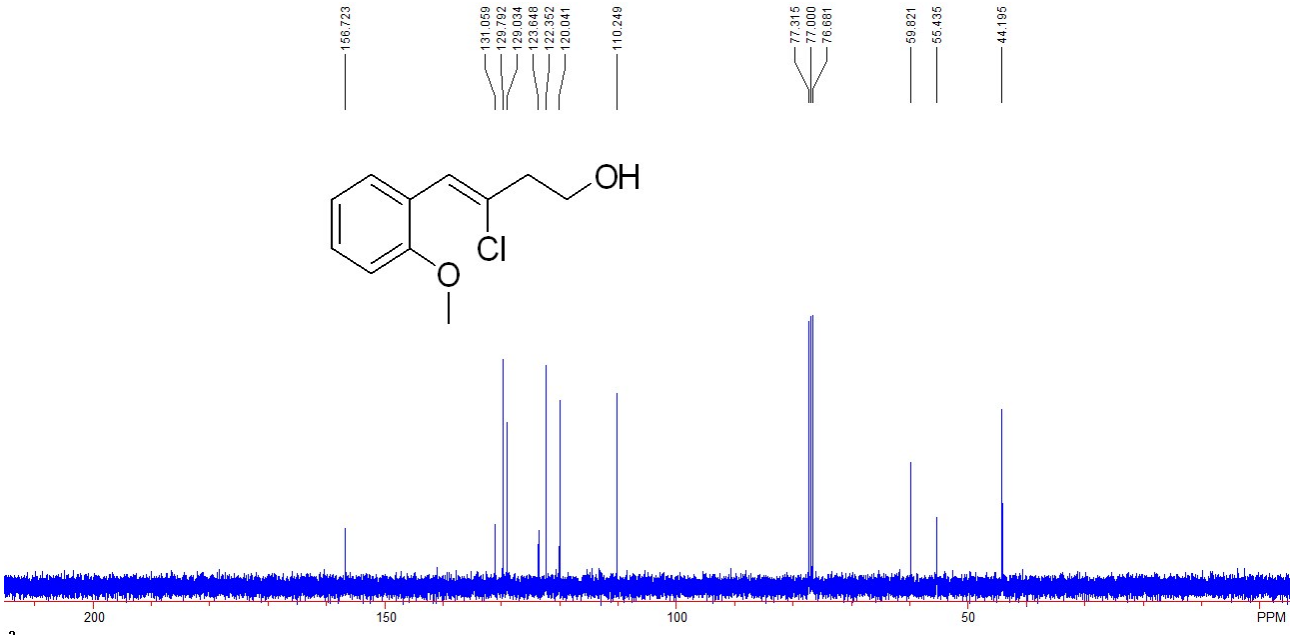


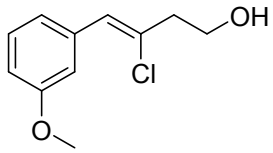


(Z)-3-chloro-4-(2-methoxyphenyl)but-3-en-1-ol (6d).

A colorless oil, 21.2 mg, 50% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.77 (s, 1H, OH), 2.76 (t, *J* = 6.0 Hz, 2H, CH_2), 3.82 (s, 3H, CH_3), 3.90 (t, *J* = 6.0 Hz, 2H, CH_2), 6.77 (s, 1H, ArH), 6.87 (d, *J* = 8.8 Hz, 1H, ArH), 6.96 (t, *J* = 7.6 Hz, 1H, ArH), 7.27 (t, *J* = 8.4 Hz, 1H, ArH), 7.78 (d, *J* = 7.6 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 44.2, 55.4[, 59.8, 110.2, 120.0, 122.4, 123.6, 129.0, 129.8, 131.0, 156.7. IR (CH_2Cl_2) ν 3352, 2949, 2887, 2835, 1598, 1487, 1463, 1432, 1245, 1119, 1050, 1027, 752 cm^{-1}. MS (%) m/e 212 (87.73), 181 (68.02), 159 (72.85), 146 (58.63), 145 (M^+, 100.00), 131 (91.32), 115 (99.83), 77 (34.17). HRMS (EI) calcd. for $C_{11}H_{13}O_2Cl$: 212.0604, Found: 212.0609.

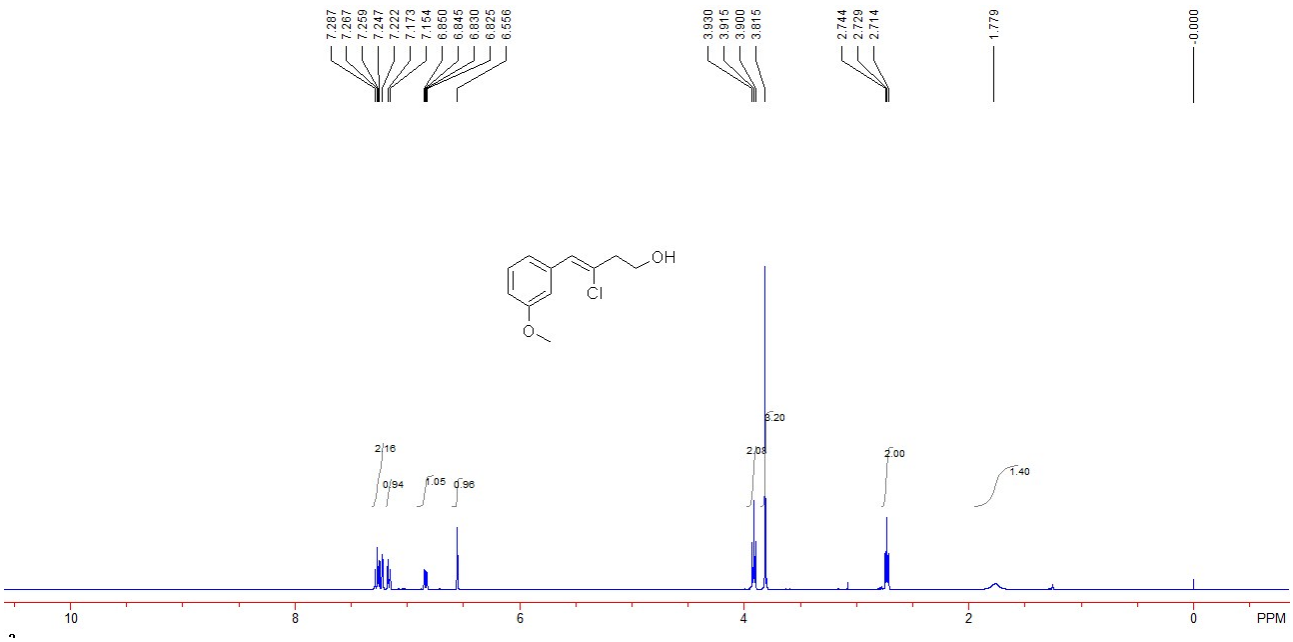


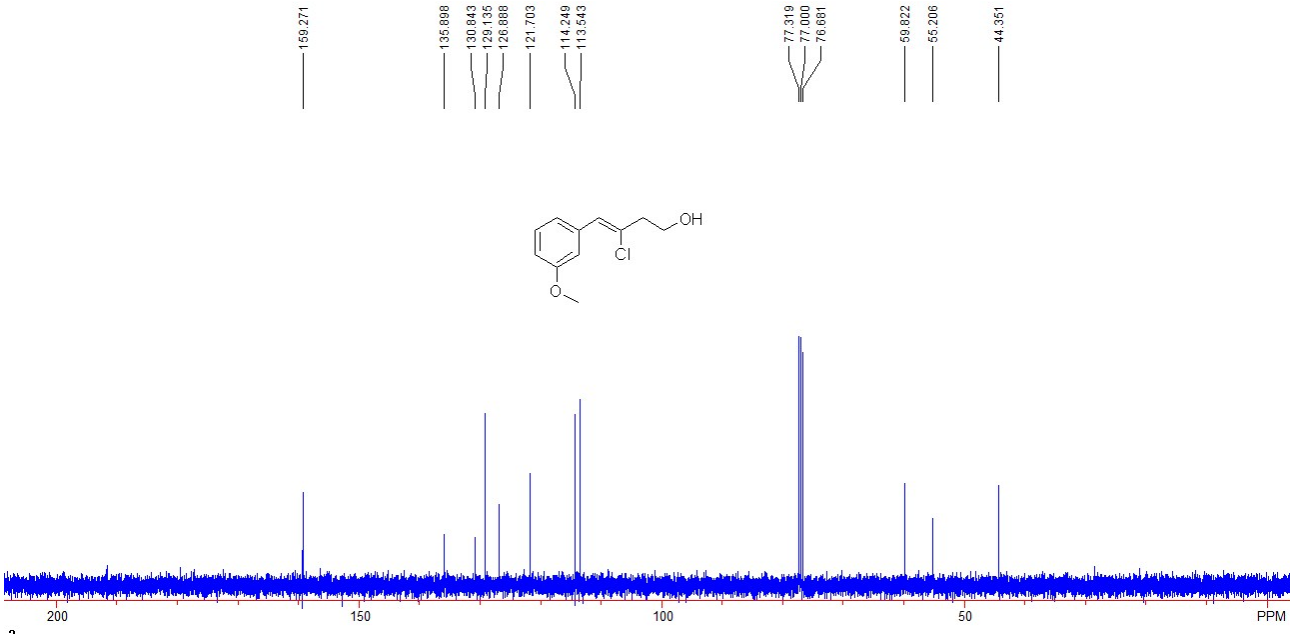


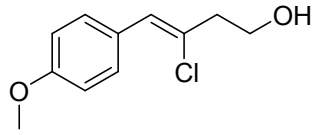


(Z)-3-chloro-4-(3-methoxyphenyl)but-3-en-1-ol (6e).

A colorless oil, 19.1 mg, 45% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.78 (s, 1H, OH), 2.73 (t, J = 6.0 Hz, 2H, CH_2), 3.82 (s, 3H,, CH_3), 3.92 (t, J = 6.0 Hz, 2H, CH_2), 6.56 (s, 1H, ArH), 6.84 (dd, J = 2.0 Hz, 8.0 Hz, 1H, ArH), 7.16 (d, J = 7.6 Hz, 1H, ArH), 7.22-7.29 (m, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 44.4, 55.2, 59.8, 113.5, 114.2, 121.7, 126.9, 129.1, 130.8, 135.9, 159.3. IR (CH_2Cl_2) ν 3336, 2944, 2832, 1599, 1578, 1489, 1464, 1272, 1261, 1157, 1046, 692 cm^{-1}. MS (%) m/e 214 (36.05), 212 (M^+, 100.00), 181 (39.85), 159 (55.32), 146 (66.11), 145 (78.95), 115 (68.97), 103 (36.68). HRMS (EI) calcd. for $C_{11}H_{13}O_2Cl$: 212.0604, Found: 212.0608.



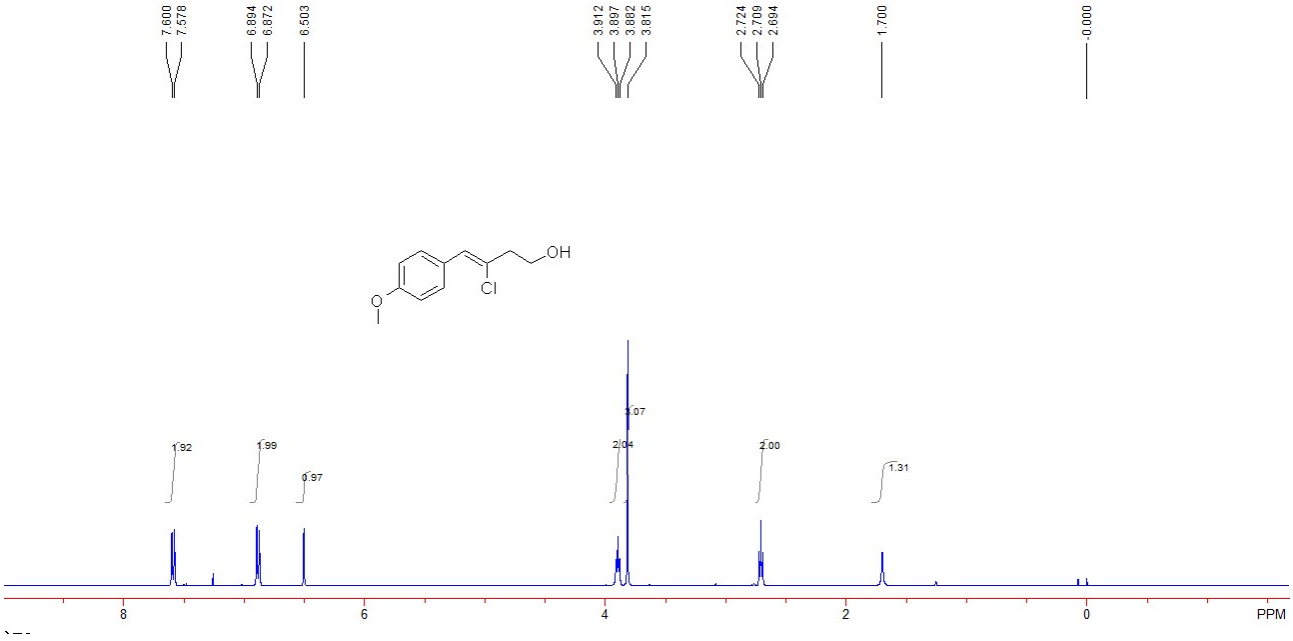


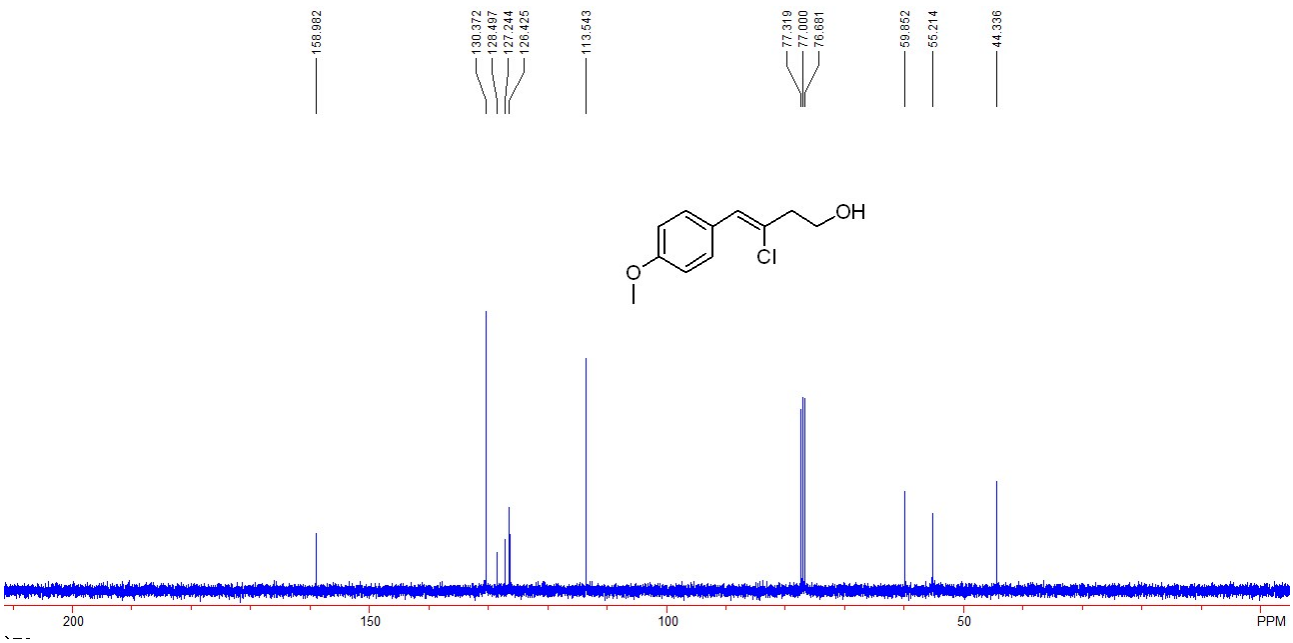


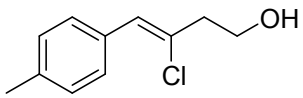
(Z)-3-chloro-4-(4-methoxyphenyl)but-3-en-1-ol (6f).

A colorless oil, 25.4 mg, 60% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.70 (s, 1H, OH), 2.71 (t, J = 6.0 Hz, 2H, CH_2), 3.82 (s, 3H, CH_3), 3.90 (t, J = 6.0 Hz, 2H, CH_2), 6.50 (s, 1H, ArH), 6.88 (d, J = 8.8 Hz, 2H, ArH), 7.59 (d, J = 8.8 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 44.3, 55.2, 59.8, 113.5, 126.4, 127.2, 128.5, 130.4, 159.0df. IR (CH_2Cl_2) ν 3344, 2946, 2835, 1607, 1510, 1461,

1251, 1179, 1035, 851 cm^{-1}. MS (%) m/e 212 (56.82), 183 (34.54), 181 (M^+, 100.00), 146 (59.27), 145 (54.49), 131 (22.17), 115 (30.83), 103 (21.86). HRMS (EI) calcd. for $C_{11}H_{13}O_2Cl$: 212.0604, Found: 212.0610.



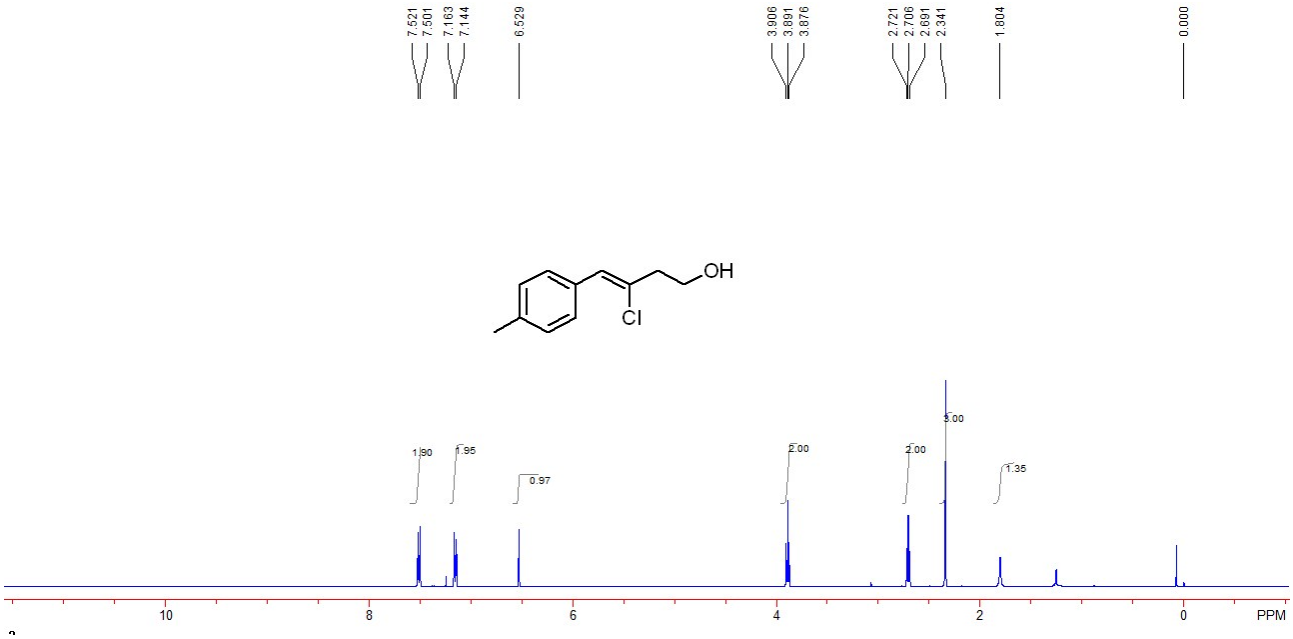


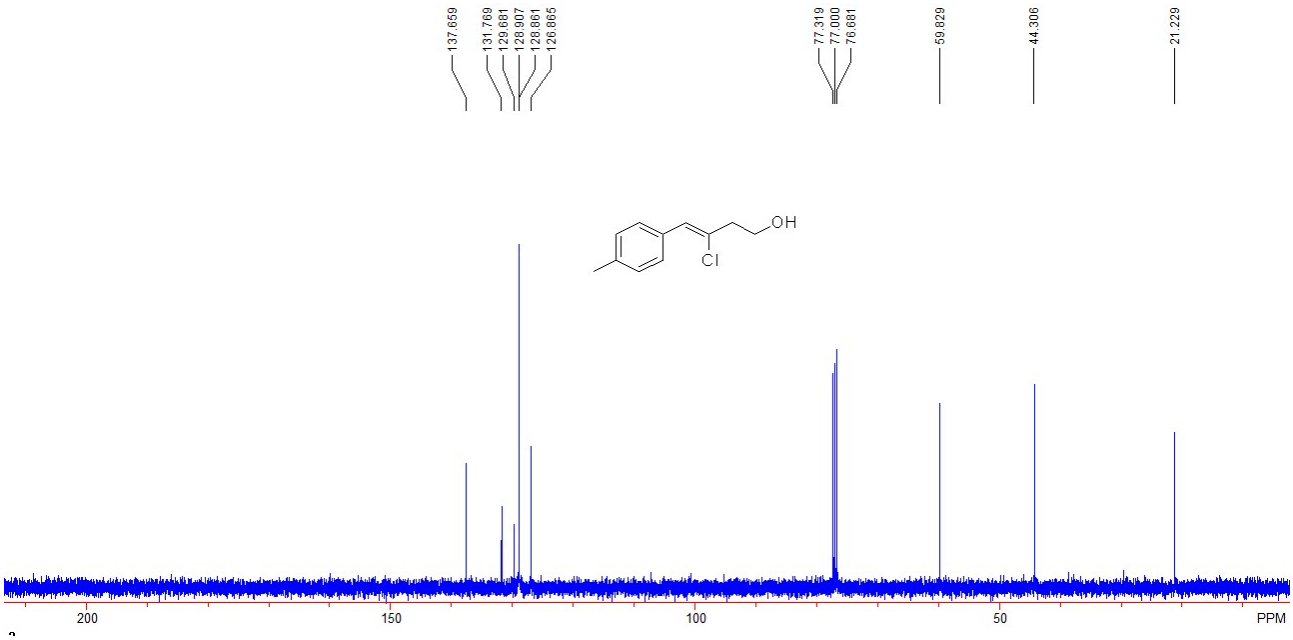


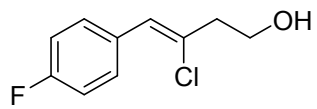
(Z)-3-chloro-4-(p-tolyl)but-3-en-1-ol (6g).

A colorless oil, 33.5 mg, 64% yield. ^1H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.80 (s, 1H, OH), 2.34 (s, 3H, CH_3), 2.71 (t, J = 6.0 Hz, 2H, CH_2), 3.89 (t, J = 6.0 Hz, 2H, CH_2), 6.53 (s, 1H, ArH), 7.15 (d, J

= 7.6 Hz, 1H, ArH), 7.51 (d, *J* = 7.6 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.2, 44.3, 59.8, 126.9, 128.8, 128.9, 129.7, 131.8, 137.6. IR (CH_2Cl_2) ν 3334, 3029, 2962, 2926, 1644, 1511, 1090, 1046, 854, 806 cm^{-1}. MS (%) m/e 198 (29.03), 196 (79.80), 167 (27.58), 165 (71.19), 130 (37.86), 129 (M^+, 100.00), 128 (36.67), 115 (36.61). HRMS (EI) calcd. for $C_{11}H_{13}OCl$: 196.0655, Found: 196.0658.

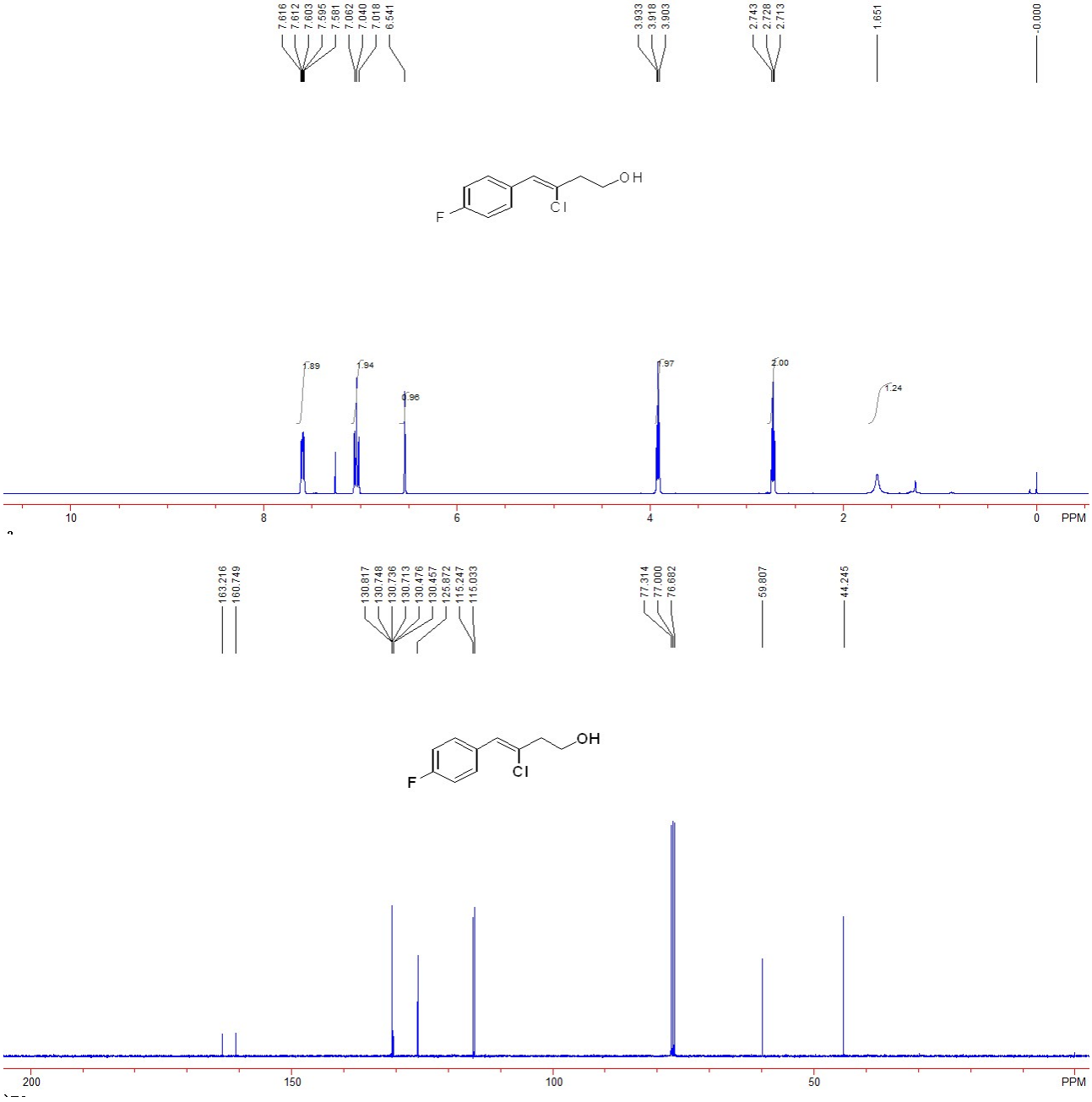


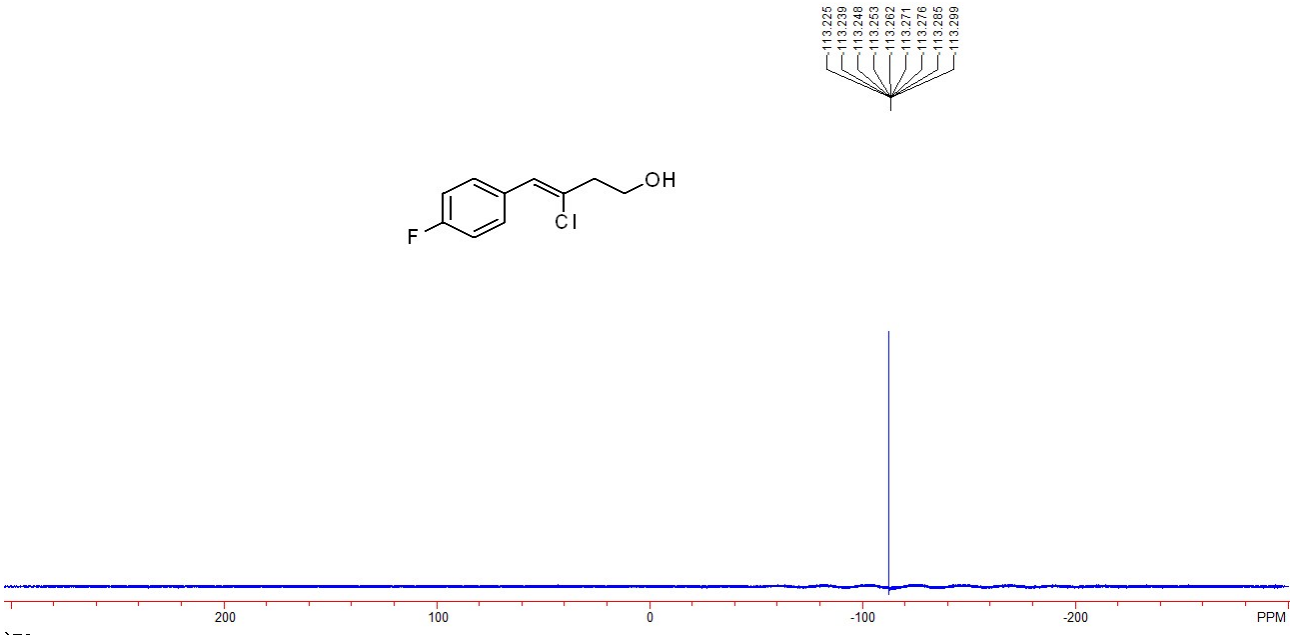


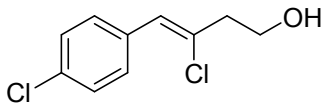


(Z)-3-chloro-4-(4-fluorophenyl)but-3-en-1-ol (6h).

A colorless oil, 12.0 mg, 30% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.65 (s, 1H, OH), 2.73 (t, J = 6.0 Hz, 2H, CH_2), 3.92 (t, J = 6.0 Hz, 2H, CH_2), 6.54 (s, 1H, ArH), 7.04 (t, J = 8.8 Hz, 2H, ArH), 7.58-7.62 (m, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 44.2, 59.8, 115.1 (d, J = 21.4 Hz), 125.9, 130.5 (d, J = 1.9 Hz), 130.7 (d, J = 3.5 Hz), 130.8 (d, J = 8.1 Hz), 162.0 (d, J = 246.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -113.26. IR (CH_2Cl_2) ν 3341, 2956, 2884, 1603, 1508, 1231, 1159, 1045, 841 cm^{-1}. MS (%) m/e 202 (12.46), 200 (35.54), 171 (11.33), 170 (15.62), 169 (29.95), 135 (19.95), 134 (41.26), 133 (M^+, 100.00). HRMS (EI) calcd. for $C_{10}H_{10}OFCl$: 200.0404, Found: 200.0406.

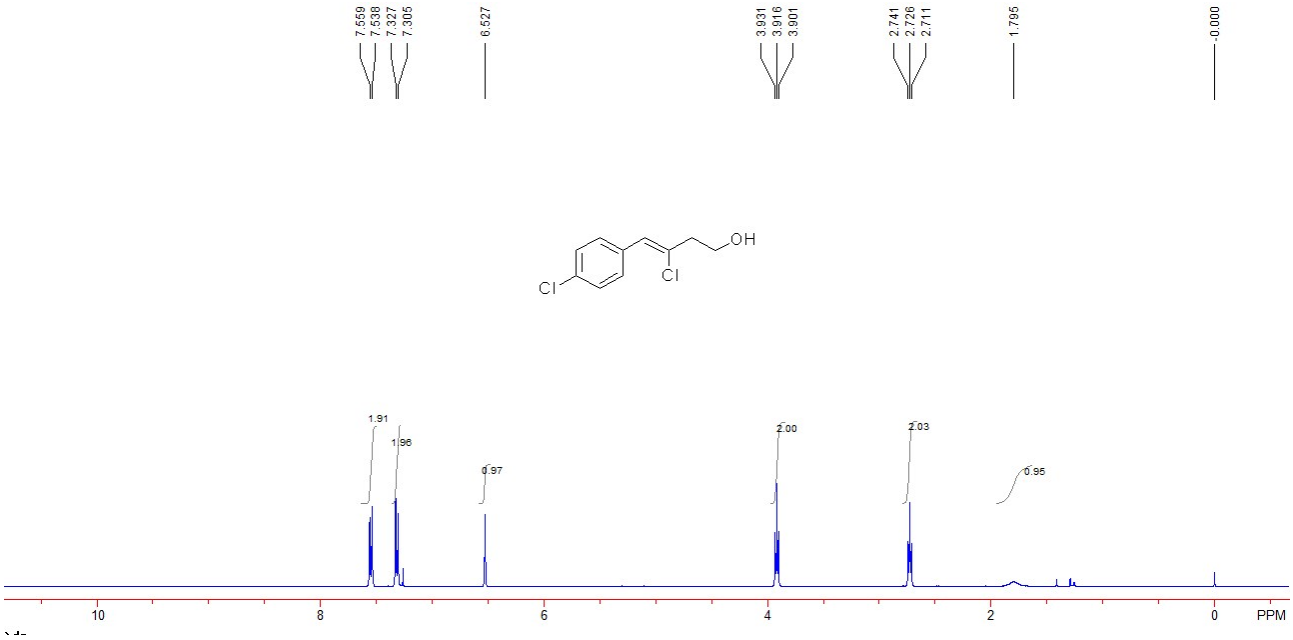


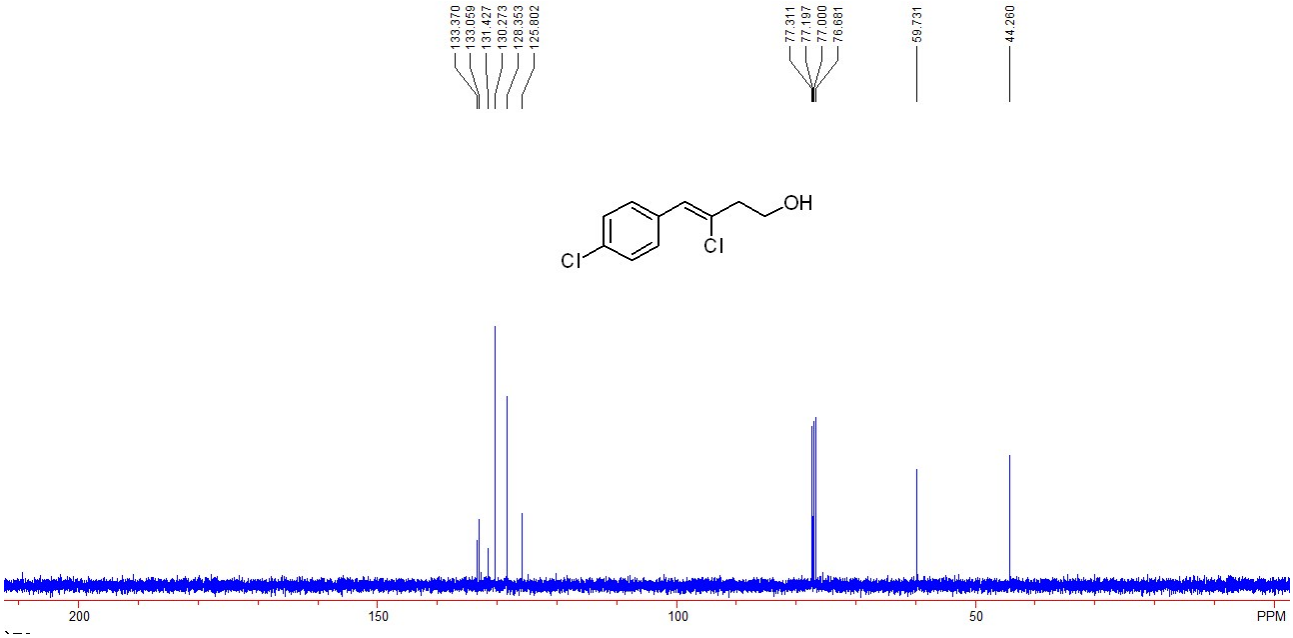


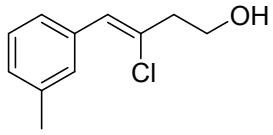


(Z)-3-chloro-4-(4-chlorophenyl)but-3-en-1-ol (6i).

A colorless oil, 14.7 mg, 34% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.80 (s, 1H, OH), 2.73 (t, *J* = 6.0 Hz, 2H, CH_2), 3.92 (t, *J* = 6.0 Hz, 2H, CH_2), 6.53 (s, 1H, ArH), 7.32 (d, *J* = 8.4 Hz, 2H, ArH), 7.55 (d, *J* = 8.4 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 44.3, 59.7, 125.8, 128.4, 130.3, 131.4, 133.0, 133.4. IR (CH_2Cl_2) ν 3323, 2967, 2879, 1490, 1402, 1091, 1046, 1013, 846 cm^{-1}. MS (%) m/e 218 (32.48), 216 (51.49), 187 (28.94), 185 (39.87), 151 (67.13), 150 (51.14), 149 (94.23), 115 (M^+, 100.00). HRMS (EI) calcd. for $C_{10}H_{10}OCl_2$: 216.0109, Found: 216.0112.



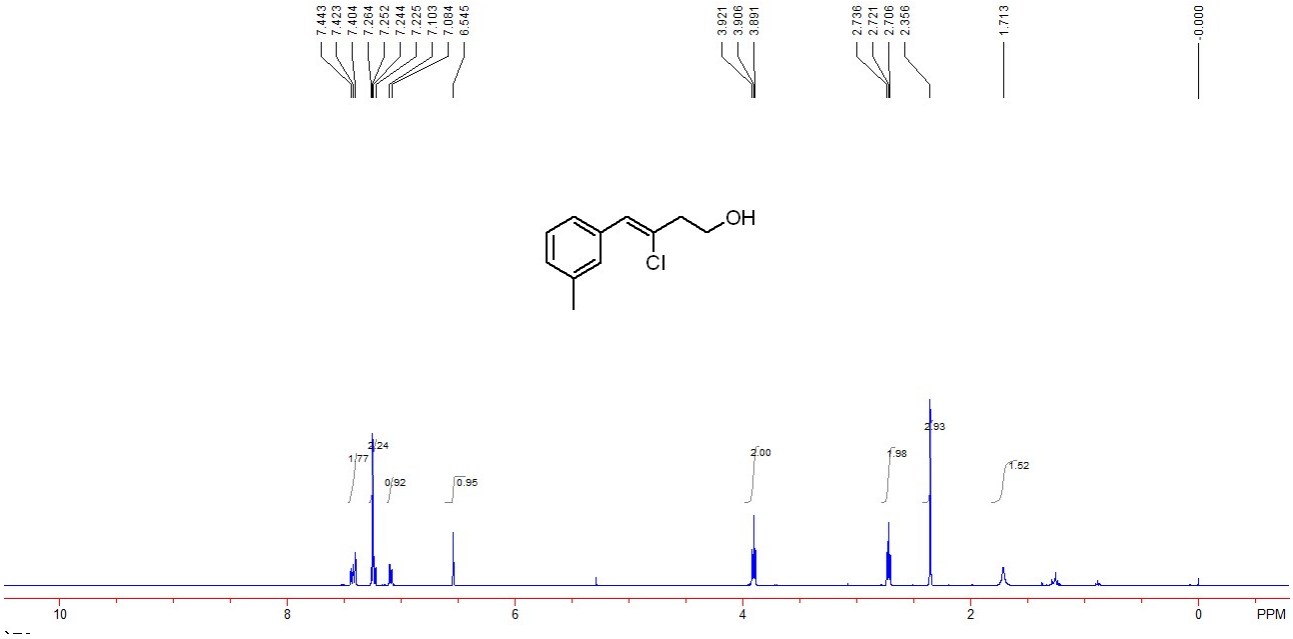


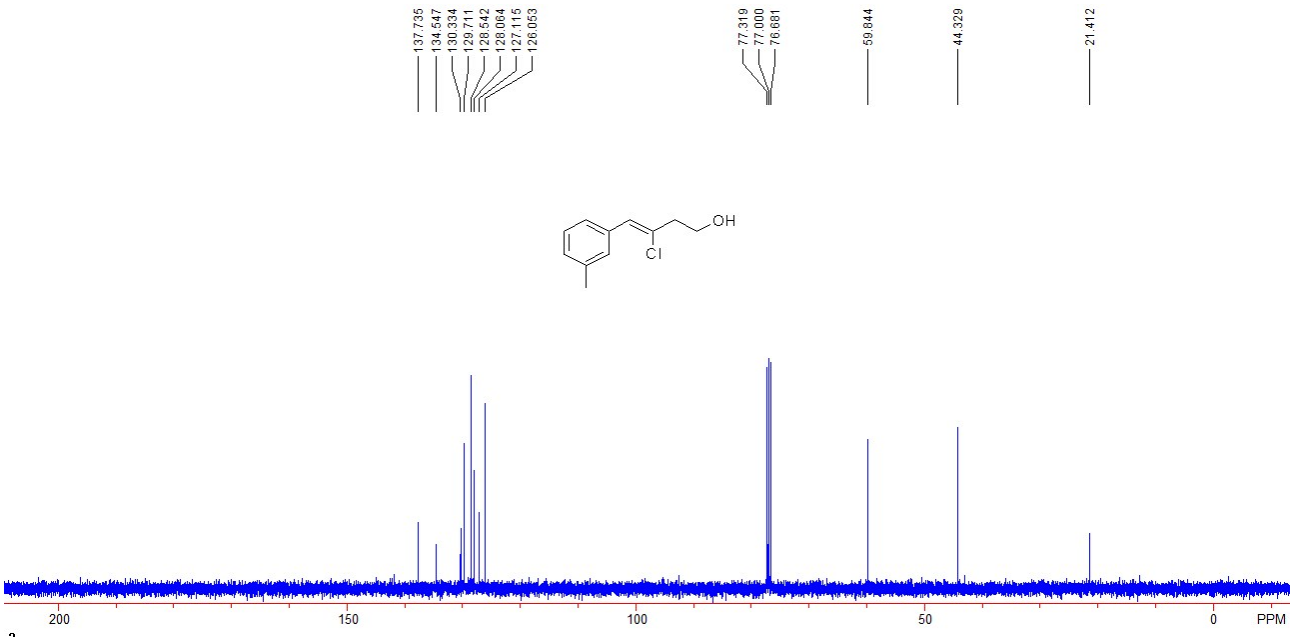


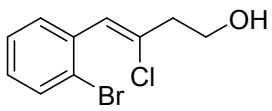
(Z)-3-chloro-4-(m-tolyl)but-3-en-1-ol (6j).

A colorless oil, 18.8 mg, 48% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.71 (s, 1H, OH), 2.36 (s, 3H, CH_3), 2.72 (t, J = 6.0 Hz, 2H, CH_2), 3.91 (t, J = 6.0 Hz, 2H, CH_2), 6.54 (s, 1H, ArH), 7.09 (d, J = 7.6 Hz, 1H, ArH), 7.22-7.26 (m, 2H, ArH), 7.40-7.44 (m, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.4, 44.3, 59.8, 126.0, 127.1, 128.1, 128.5, 129.7, 130.3, 134.5, 137.7. IR (CH_2Cl_2) ν 3323,

2956, 2918, 2843, 1102, 1042, 831, 780, 694 cm^{-1}. MS (%) m/e 196 (63.27), 131 (33.33), 130 (45.92), 129 (M^+, 100.00), 128 (46.18), 166 (22.46), 165 (38.50), 115 (49.81). HRMS (EI) calcd. for $C_{11}H_{13}OCl$: 196.0655, Found: 196.0659.



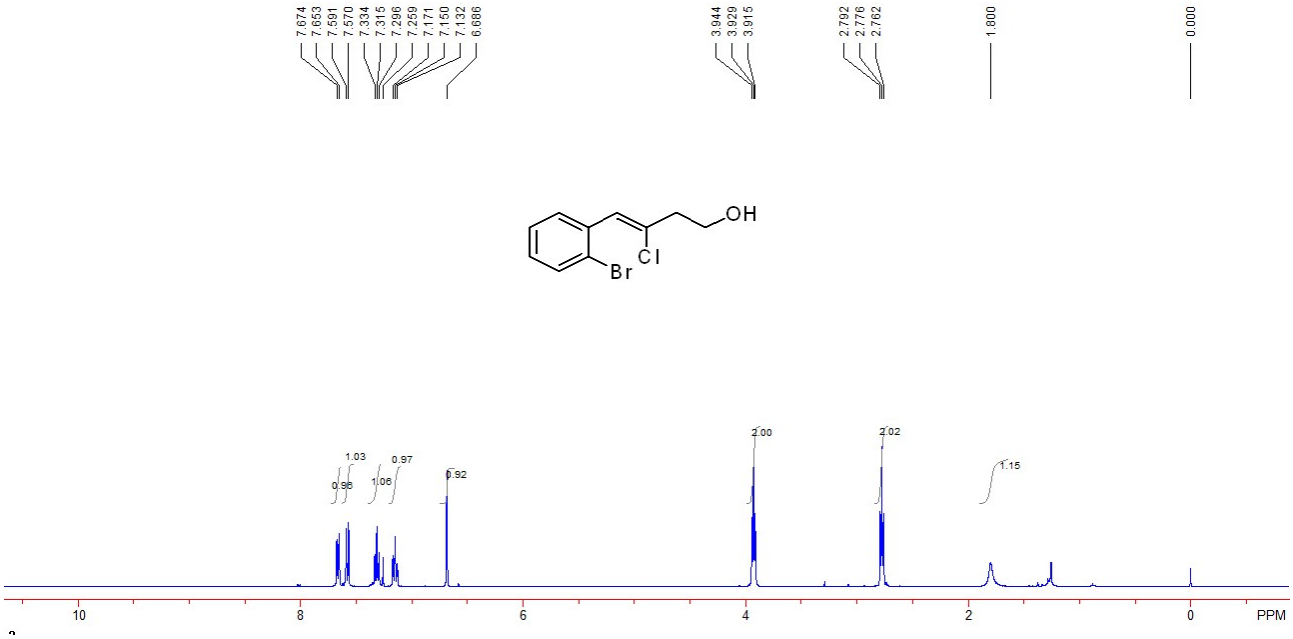


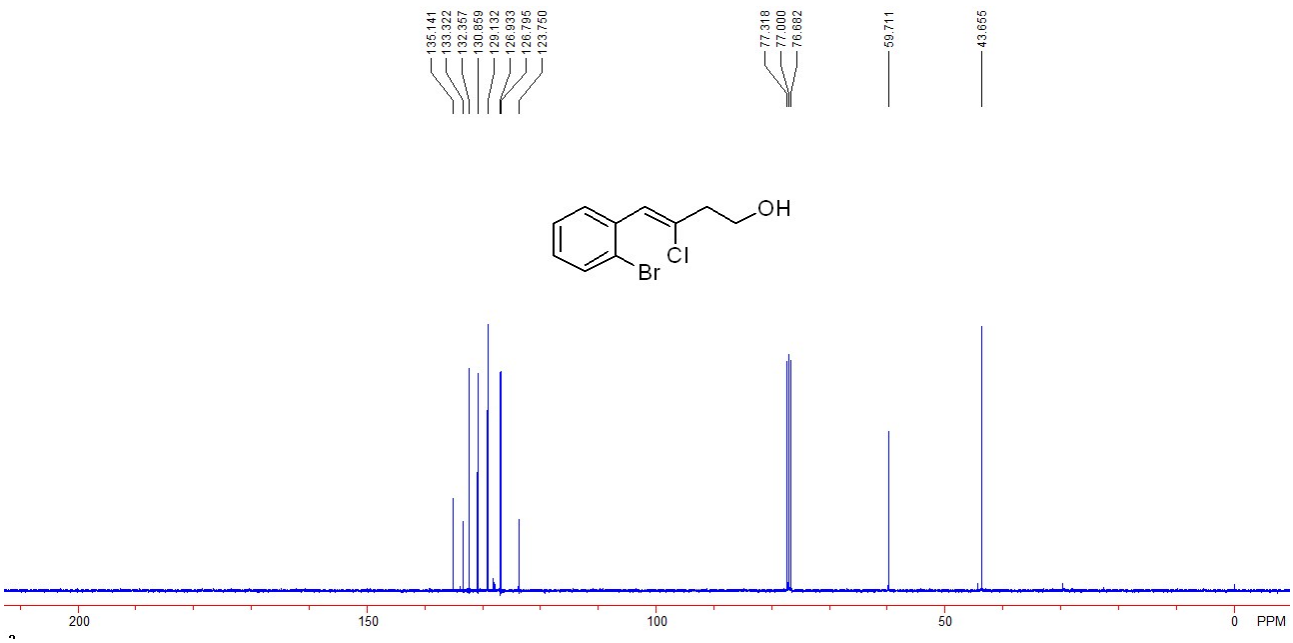


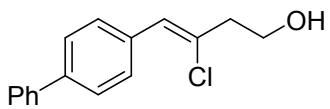
(Z)-4-(2-bromophenyl)-3-chlorobut-3-en-1-ol (6k).

A colorless oil, 16.1 mg, 31% yield. ^1H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.80 (s, 1H, OH), 2.78 (t, J = 6.0 Hz, 2H, CH_2), 3.93 (t, J = 6.0 Hz, 2H, CH_2), 6.69 (s, 1H, ArH), 7.15 (t, J =8.4 Hz, 1H, ArH),

7.32 (t, J = 7.6 Hz, 1H, ArH), 7.58 (d, J = 8.4 Hz, 1H, ArH), 7.66 (d, J = 8.4 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 43.6, 59.7, 123.8, 126.8, 126.9, 129.1, 130.8, 132.4, 133.3, 135.1. IR (CH_2Cl_2) ν 3353, 2954, 2925, 2879, 2845, 1466, 1434, 1091, 1046, 1025, 751, 720 cm^{-1}. MS (%) m/e 262 (25.58), 260 (20.69), 232 (18.66), 152 (16.01), 151 (27.70), 150 (41.61), 116 (24.94), 115 (M^+, 100.00). HRMS (EI) calcd. for $C_{10}H_{10}OClBr$: 259.9604, Found: 259.9610.

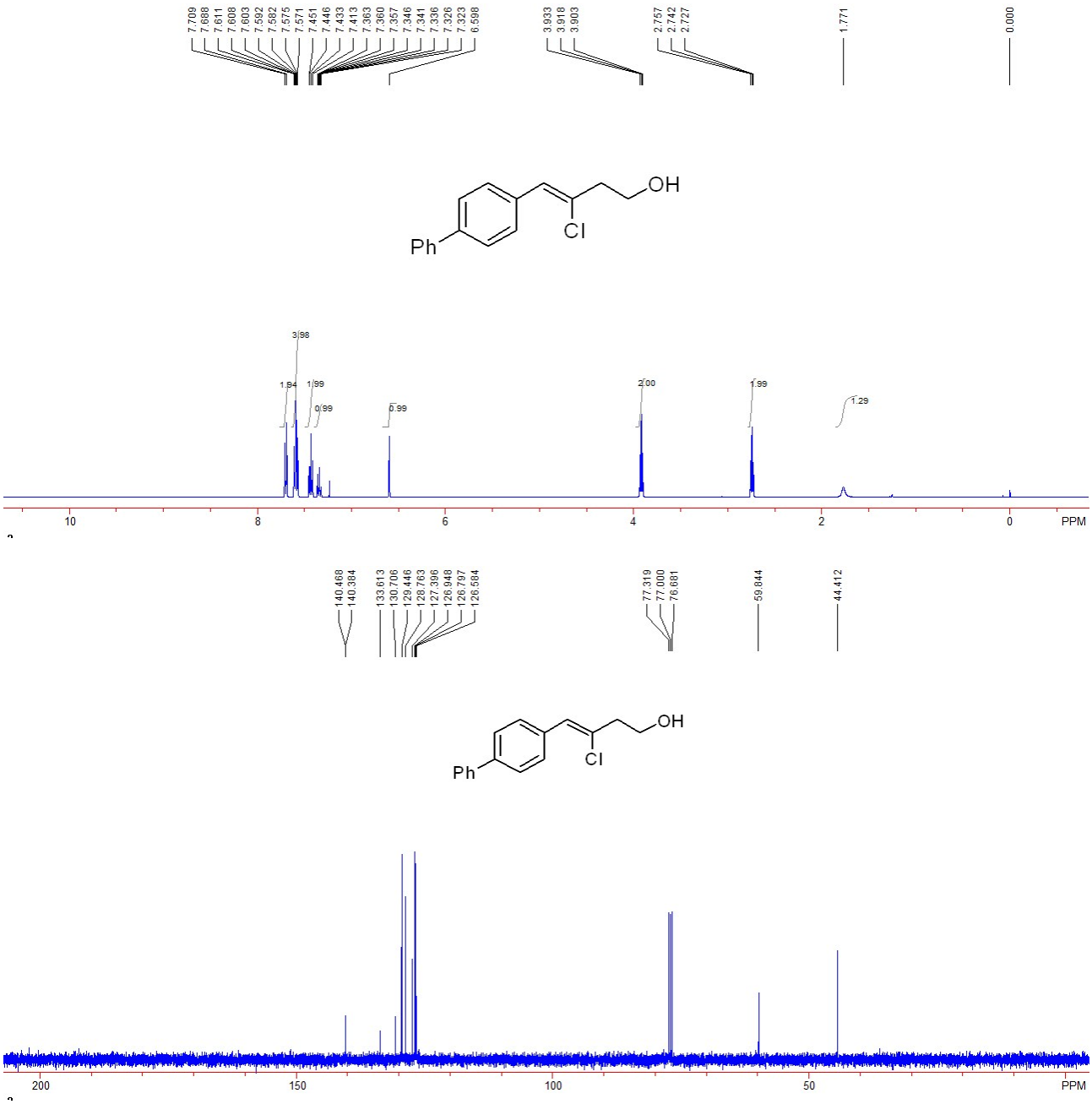


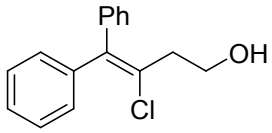




(Z)-4-([1,1'-biphenyl]-4-yl)-3-chlorobut-3-en-1-ol (6l).

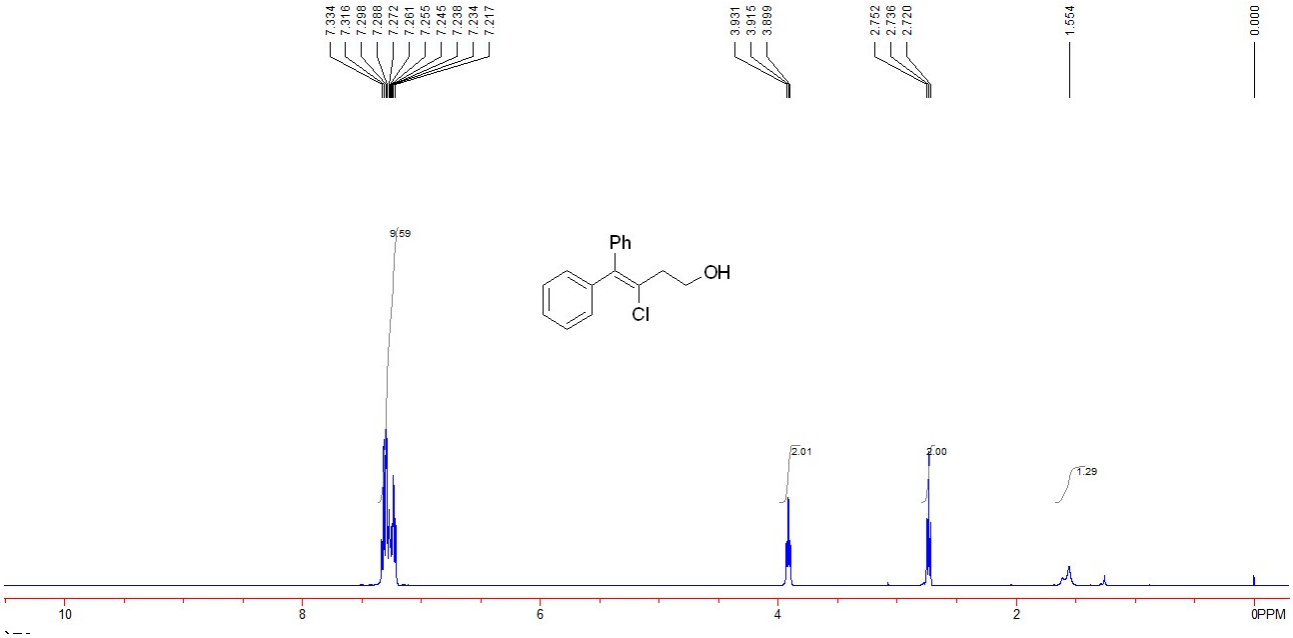
A white solid, 39.7 mg, 77% yield. M.p.: 114-115 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.77 (s, 1H, OH), 2.74 (t, *J* = 6.0 Hz, 2H, CH_2), 3.92 (t, *J* = 6.0 Hz, 2H, CH_2), 6.60 (s, 1H, ArH), 7.32-7.36 (m, 1H, ArH), 7.41-7.45 (m, 2H, ArH), 7.57-7.61 (m, 4H, ArH), 7.69 (d, *J* = 8.4 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 44.4, 59.8, 126.6, 126.8, 126.9, 127.4, 128.8, 129.4, 130.7, 133.6, 140.4, 140.5. IR (CH_2Cl_2) ν 3279, 2969, 2874, 1404, 1091, 1048, 875, 758 cm^{-1}. MS (%) m/e 258 (36.70), 227 (17.89), 192 (40.79), 191 (M^+, 100.00), 190 (19.67), 189 (29.62), 165 (25.16), 115 (13.14). HRMS (EI) calcd. for $C_{16}H_{15}OCl$: 258.0811, Found: 258.0817.

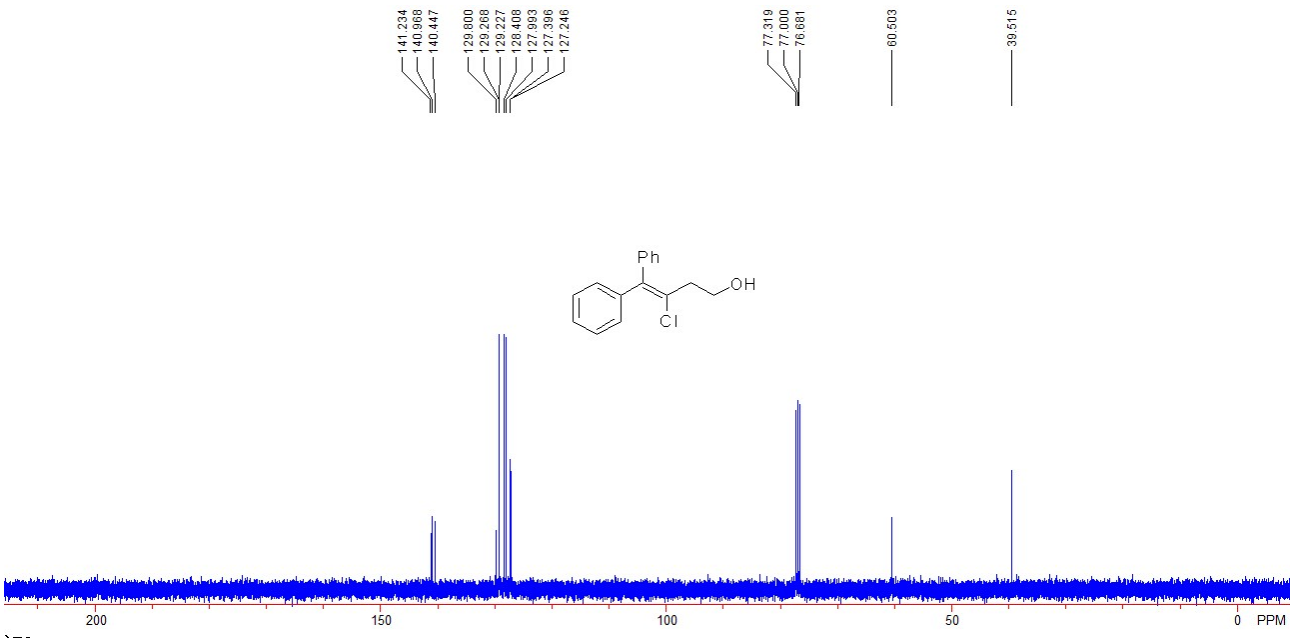


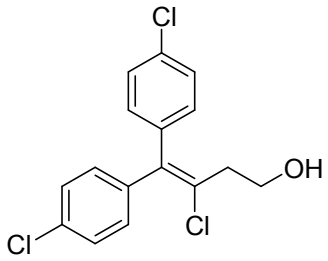


3-chloro-4,4-diphenylbut-3-en-1-ol (6m).

A colorless oil, 38.7 mg, 75% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.55 (s, 1H, OH), 2.74 (t, *J* = 6.4 Hz, 2H, CH_2), 3.92 (t, *J* = 6.4 Hz, 2H, CH_2), 7.22-7.33 (m, 10H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 39.5, 60.5, 127.2, 127.4, 128.0, 128.4, 129.2, 129.3, 129.8, 140.4, 141.0, 141.2. IR (CH_2Cl_2) ν 3313, 2972, 2887, 1443, 1089, 1046, 882, 745, 697 cm^{-1}. MS (%) m/e 258 (42.38), 227 (40.05), 192 (50.66), 191 (M^+, 100.00), 189 (32.05), 165 (21.95), 149 (20.09), 115 (22.08). HRMS (EI) calcd. for $C_{16}H_{15}OCl$: 258.0811, Found: 258.0813.

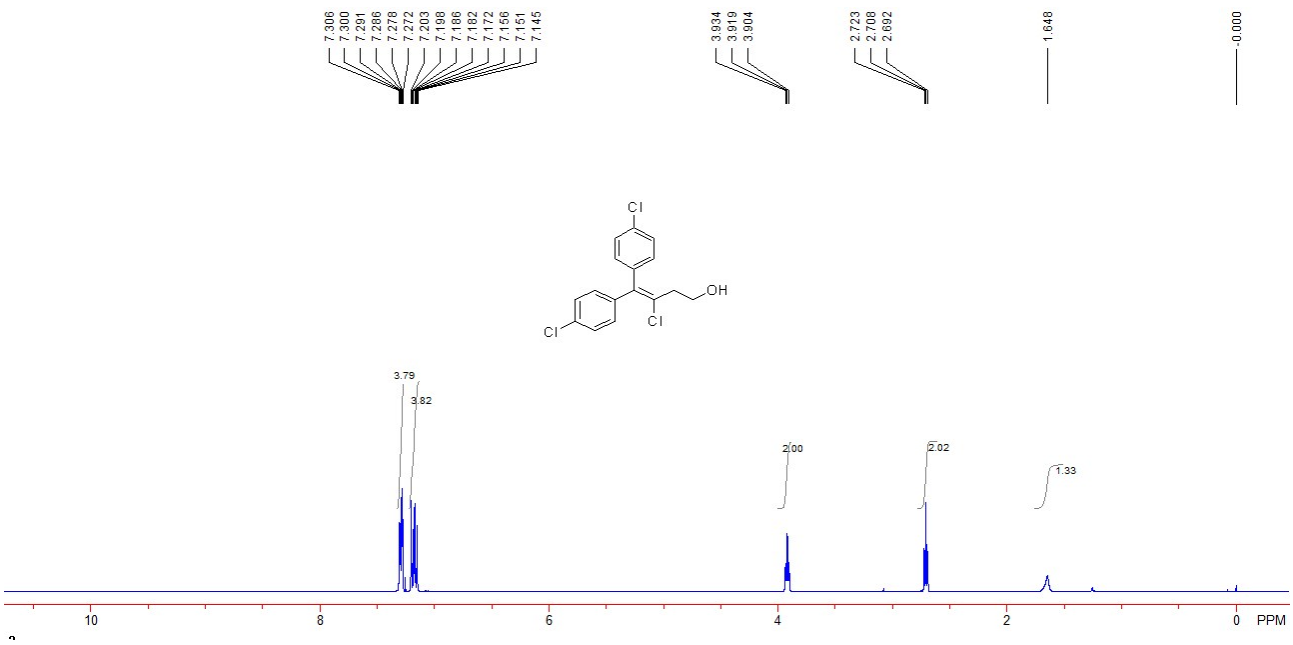


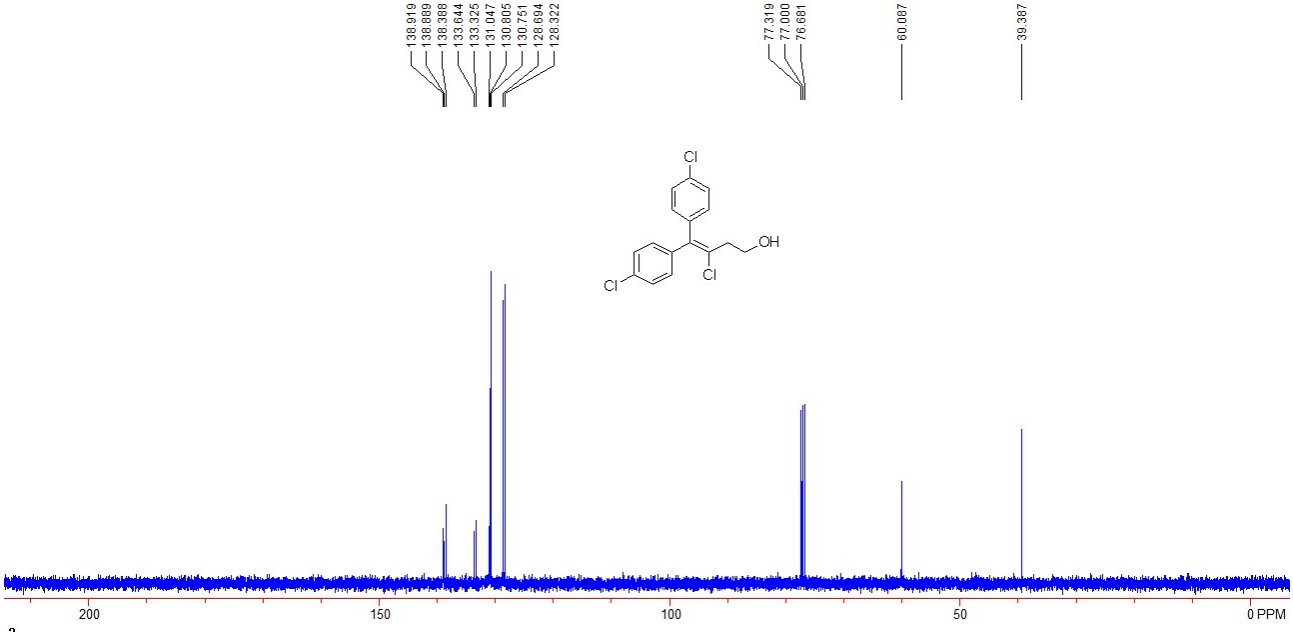


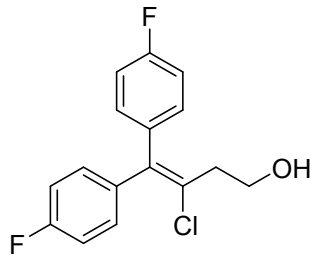


3-chloro-4,4-bis(4-chlorophenyl)but-3-en-1-ol (6o).

A colorless oil, 48.9 mg, 75% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.65 (s, 1H, OH), 2.71 (t, J = 6.0 Hz, 2H, CH_2), 3.92 (t, J = 6.0 Hz, 2H, CH_2), 7.14-7.20 (m, 4H, ArH), 7.27-7.31 (m, 4H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 39.4, 60.1, 128.3, 128.7, 130.7, 130.8, 131.0, 133.3, 133.6, 138.4, 138.8, 139.9. IR (CH_2Cl_2) ν 3318, 2969, 2879, 1489, 1396, 1088, 1046, 1015, 826, 784 cm^{-1}. MS (%) m/e 328 (51.93), 326 (53.29), 297 (74.53), 295 (77.86), 261 (61.66), 259 (79.62), 225 (M^+, 100.00), 189 (87.08). HRMS (EI) calcd. for $C_{16}H_{13}OCl_3$: 326.0032, Found: 326.0037.



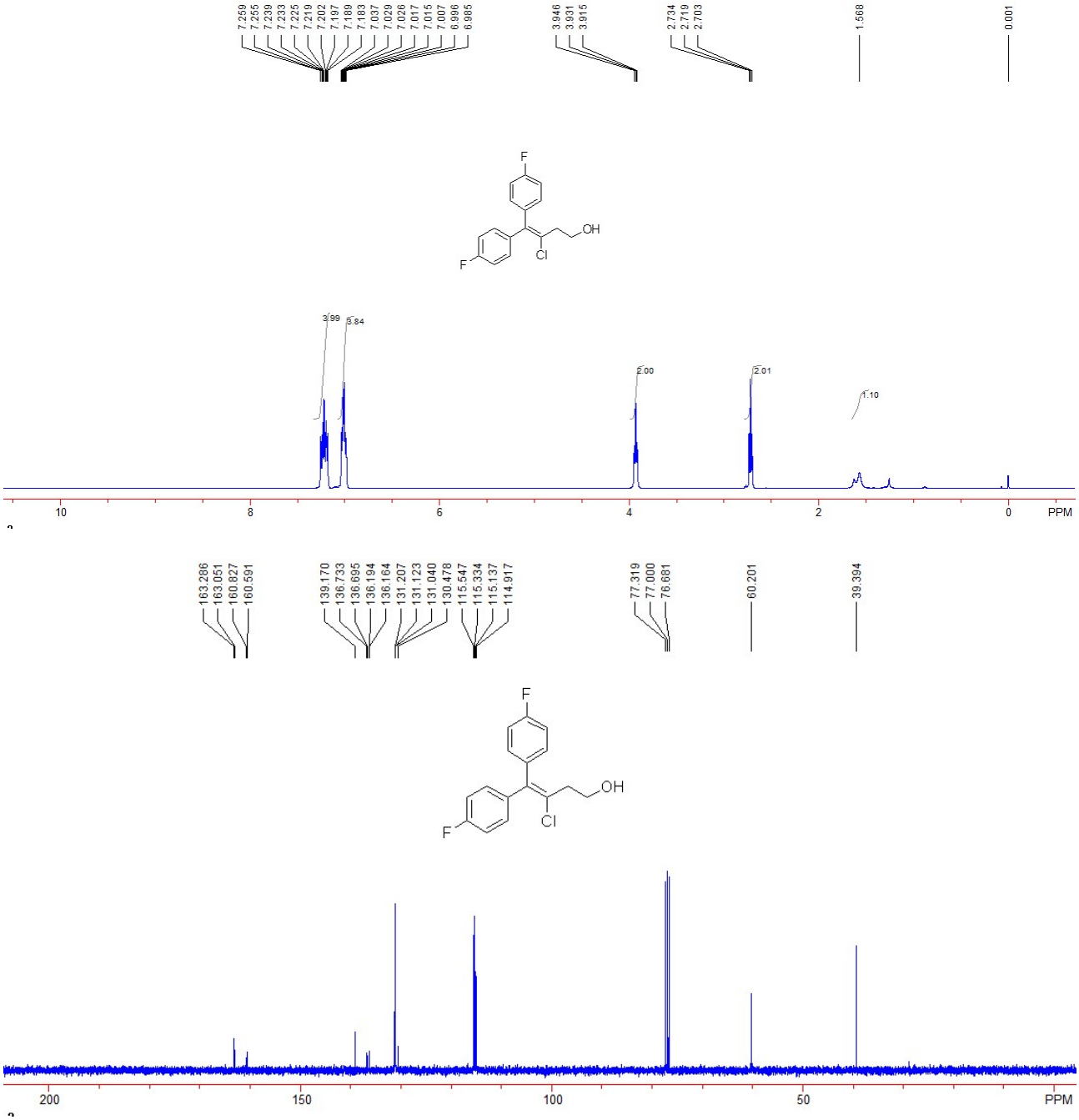


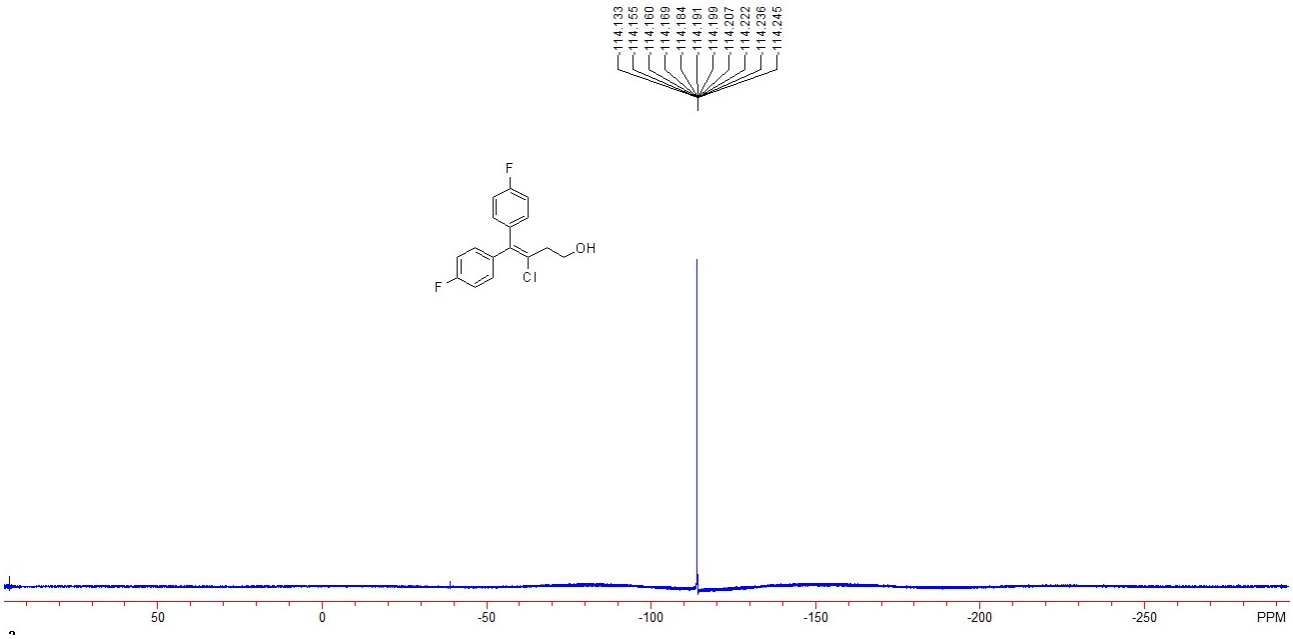


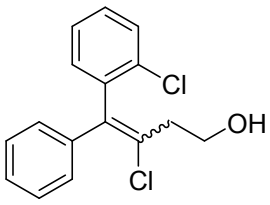
3-chloro-4,4-bis(4-fluorophenyl)but-3-en-1-ol (6p).

A colorless oil, 42.3 mg, 72% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.57 (s, 1H, OH), 2.72 (t, *J* = 6.4 Hz, 2H, CH_2), 3.93 (t, *J* = 6.4 Hz, 2H, CH_2), 6.98-7.04 (m, 4H, ArH), 7.18-7.26 (m, 4H,

ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 39.4, 60.2, 115.0 (d, J = 22.0 Hz), 115.4 (d, J = 21.3 Hz), 130.5, 131.1 (d, J = 8.3 Hz), 131.2 (d, J = 8.4 Hz), 136.2 (d, J = 3.0 Hz), 136.7 (d, J = 3.8 Hz), 139.2, 161.8 (d, J = 246.0 Hz), 162.0 (d, J = 245.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -114.19. IR (CH_2Cl_2) ν 3316, 2972, 2882, 1598, 1504, 1221, 1156, 1094, 1046, 834 cm^{-1}. MS (%) m/e 294 (40.52), 265 (19.29), 263 (56.75), 228 (75.22), 227 (M^+, 100.00), 225 (16.92), 207 (17.88), 201 (21.16). HRMS (EI) calcd. for $C_{16}H_{13}OF_2Cl$: 294.0623, Found: 294.0632.

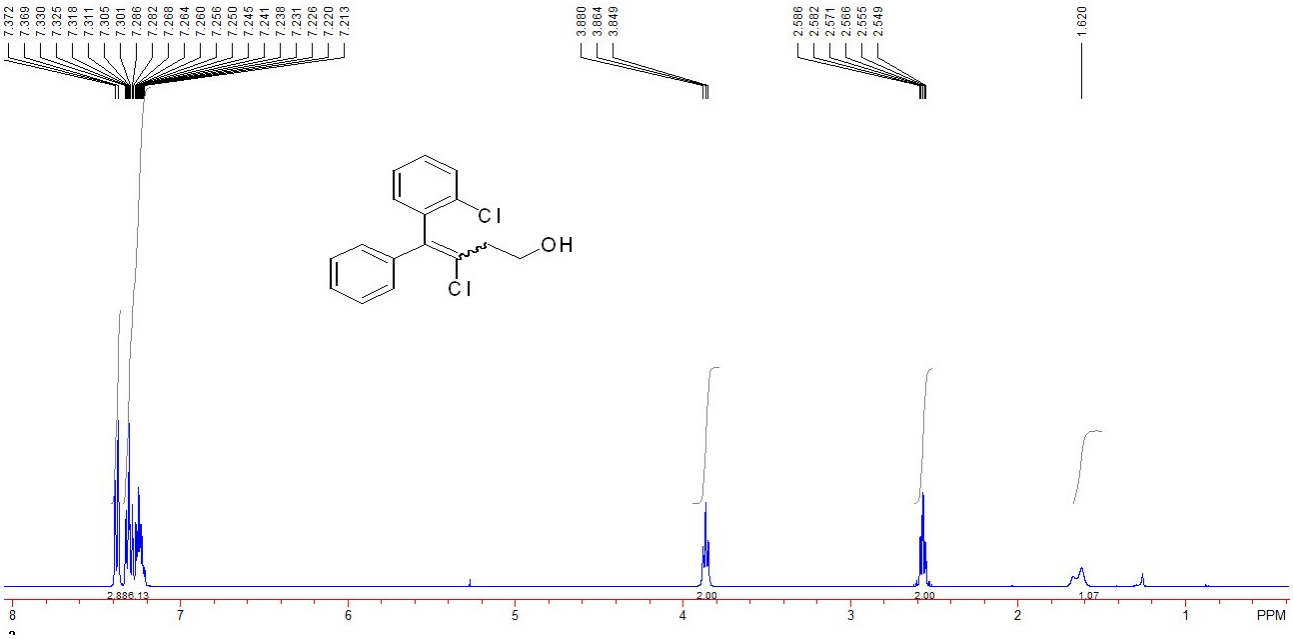


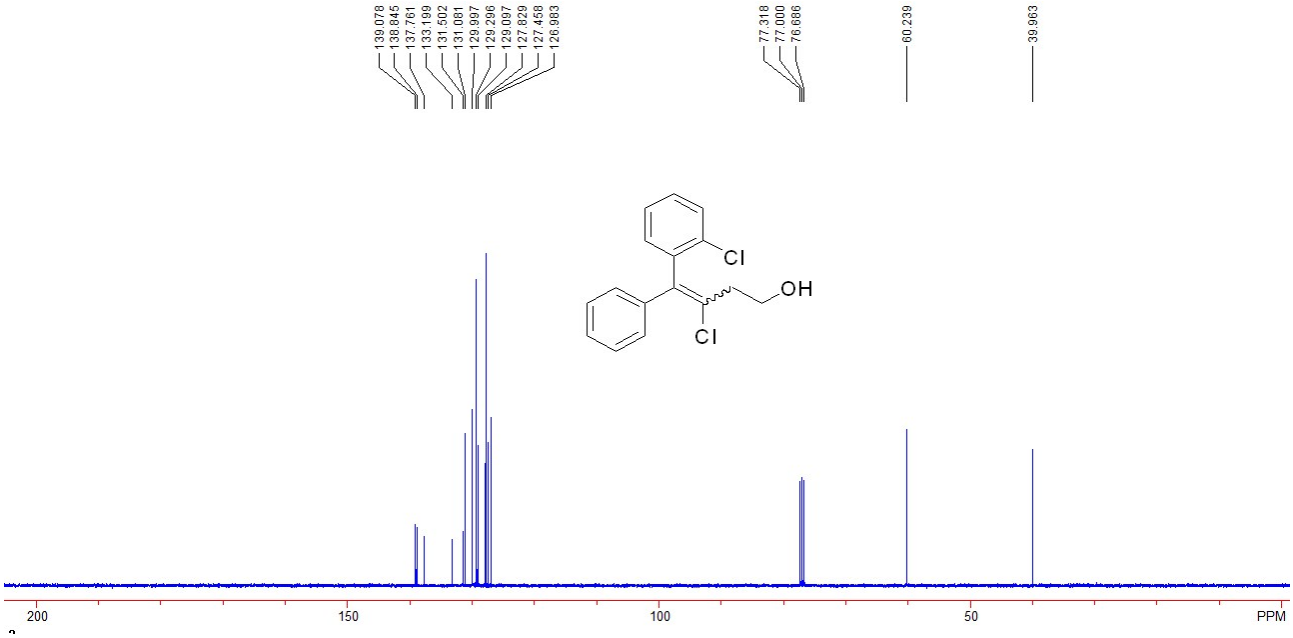


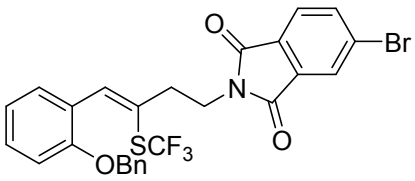


3-chloro-4-(2-chlorophenyl)-4-phenylbut-3-en-1-ol (6q).

A colorless oil, 35.2 mg, 60% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.62 (s, 1H, OH), 2.55-2.59 (m, 2H, CH_2), 3.86 (t, J = 6.0 Hz, 2H, CH_2), 7.21-7.33 (m, 6H, ArH), 7.37-7.39 (m, 3H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 40.0, 60.2, 127.0, 127.4, 127.8, 129.1, 129.3, 130.0, 131.1, 131.5, 133.2, 137.8, 138.8, 139.1. IR (CH_2Cl_2) ν 3324, 3047, 2928, 1472, 1438, 1101, 1034, 750, 696 cm^{-1}. HRMS (DART) ($M+NH_4$) calcd. for $C_{16}H_{18}ONCl_2$: 310.0760, Found: 310.0759.



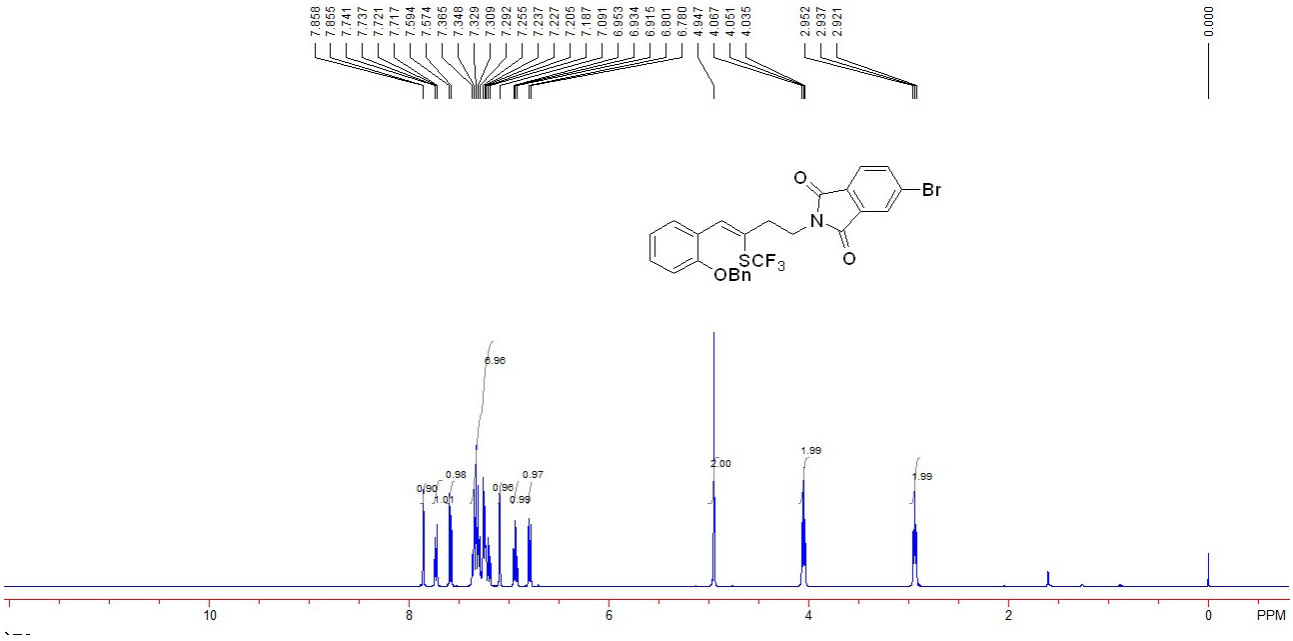


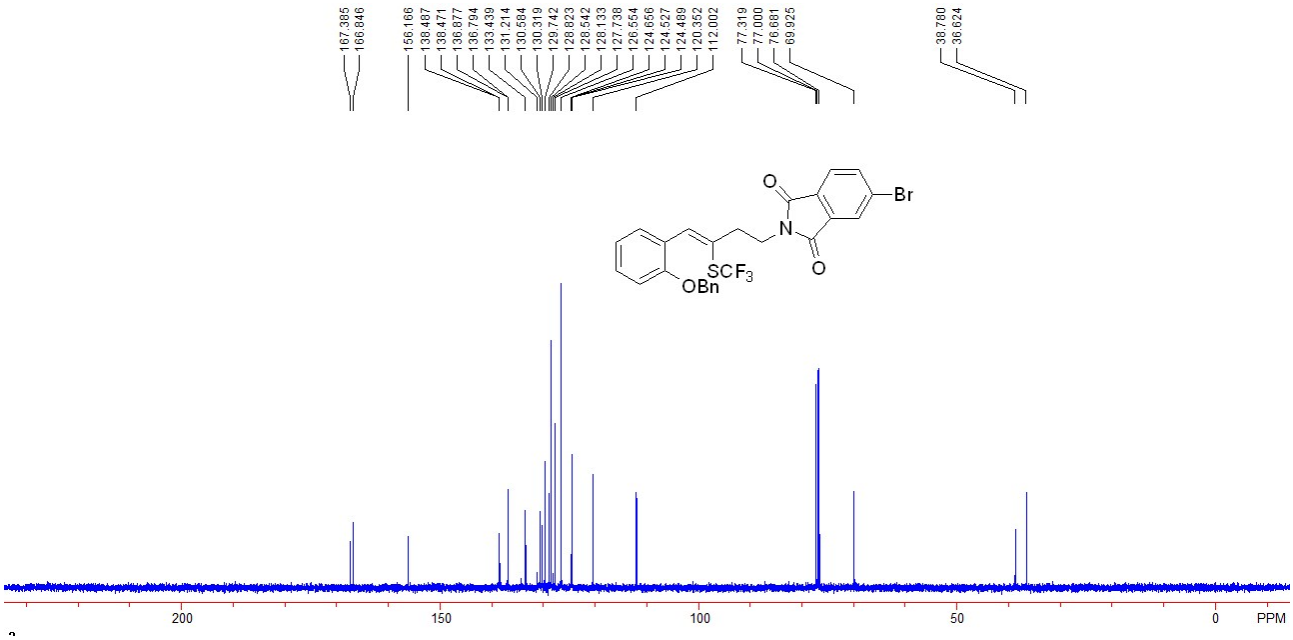


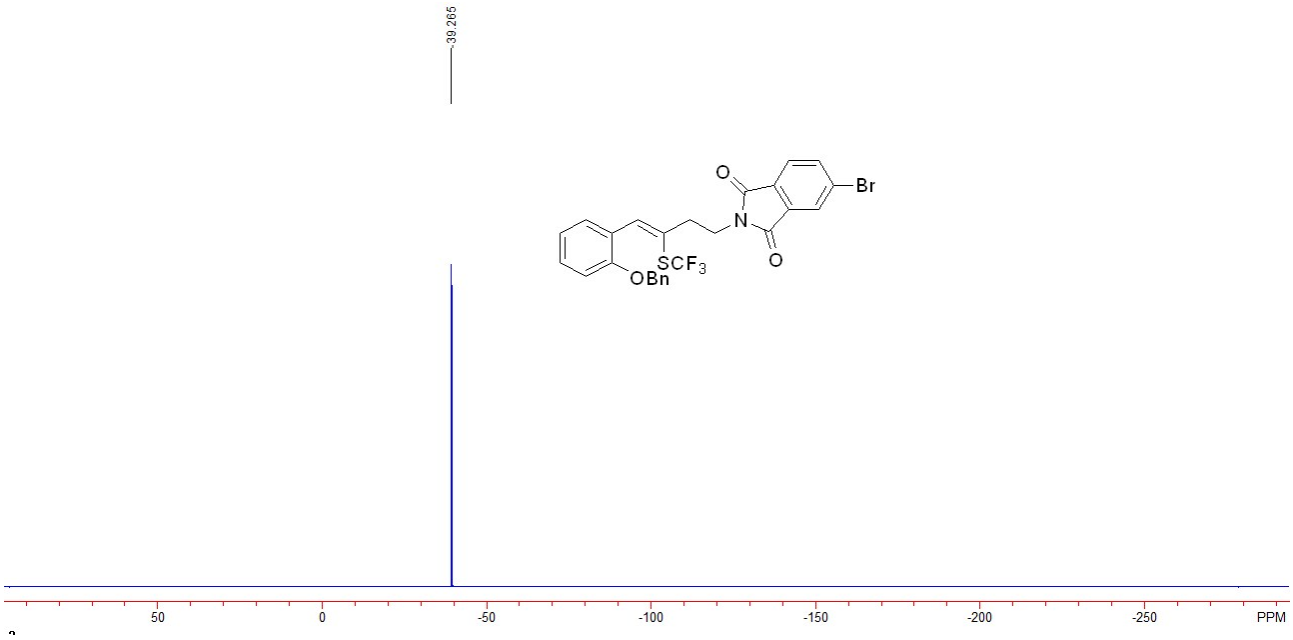
(Z)-2-(4-(2-(benzyloxy)phenyl)-3-((trifluoromethyl)thio)but-3-en-1-yl)-5-bromo-1H-indene-1,3(2H)-dione (9).

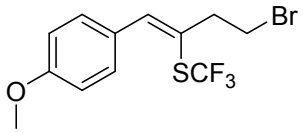
A sticky liquid, 56.2 mg, 50% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.94 (t, *J* = 6.4 Hz, 2H, CH_2), 4.05 (t, *J* = 6.4 Hz, 2H, CH_2), 4.95 (s, 2H, CH_2), 6.79 (d, *J* = 8.4 Hz, 1H, ArH), 6.93 (t, *J* = 7.6 Hz, 1H, ArH), 7.09 (s, 1H, ArH), 7.18-7.36 (m, 7H, ArH), 7.58 (d, *J* = 8.0 Hz, 1H, ArH), 7.73

(dd, J = 1.6 Hz, 8.0 Hz, 1H, ArH), 7.86 (d, J = 1.2 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 36.6, 38.8, 69.9, 112.0, 120.4, 124.48, 124.5, 124.6, 126.6, 127.7, 128.5, 128.8, 129.6 (q, J = 308.1 Hz), 129.7, 130.3, 130.6, 133.4, 136.8, 136.9, 138.5 (q, J = 1.6 Hz), 156.2, 166.8, 167.4. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -39.26. IR (CH_2Cl_2) ν 2923, 2851, 1774, 1716, 1451, 1389, 1154, 1104, 742 cm^{-1}. HRMS (DART) calcd. for $C_{26}H_{20}O_3NBrF_3S$: 562.0294, Found: 562.0294.



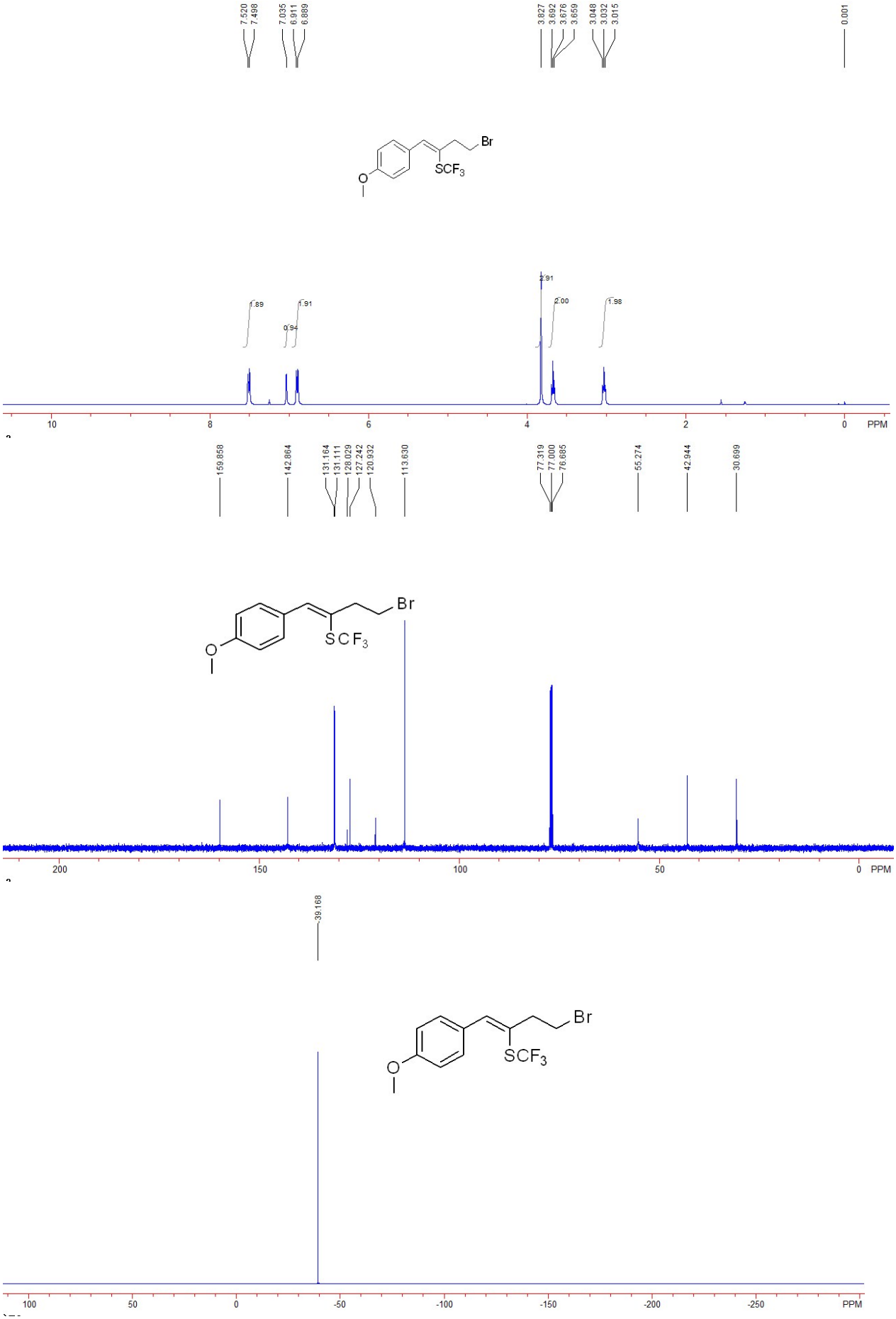






(Z)-(4-bromo-1-(4-methoxyphenyl)but-1-en-2-yl)(trifluoromethyl)sulfane (10).

A colorless oil, 47.6 mg, 70% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 3.03 (t, *J* = 6.4 Hz, 2H, CH_2), 3.68 (t, *J* = 6.4 Hz, 2H, CH_2), 3.83 (s, 3H, CH_3), 6.90 (d, *J* = 8.8 Hz, 2H, ArH), 7.04 (s, 1H, ArH), 7.51 (d, *J* = 8.8 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 30.7, 42.9, 55.3, 113.6, 120.9, 127.2, 129.6 (q, *J* = 308.2 Hz), 131.2, 142.9, 159.8. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -39.17. IR (CH_2Cl_2) ν 2967, 2931, 2835, 1603, 1509, 1253, 1179, 1154, 1103, 1032, 820 cm^{-1}. MS (%) m/e 342 (62.31), 340 (61.07), 191 (46.79), 164 (M^+, 100.00), 149 (54.54), 146 (69.31), 115 (48.19), 91 (39.63). HRMS (EI) calcd. for $C_{12}H_{12}OF_3SBr$: 339.9744, Found: 339.9742.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3.827
3.692
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3.659
3.048
3.032
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0.001
Br
SCF3
O
1.89
1.91
0.94
2.91
2.00
1.98
10
8
6
4
2
0
PPM
159.858
142.864
131.164
131.111
128.029
127.242
120.932
113.630
77.319
77.000
76.685
55.274
42.944
30.699
Br
SCF3
O
200
150
100
50
0
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O
100
50
0
-50
-100
-150
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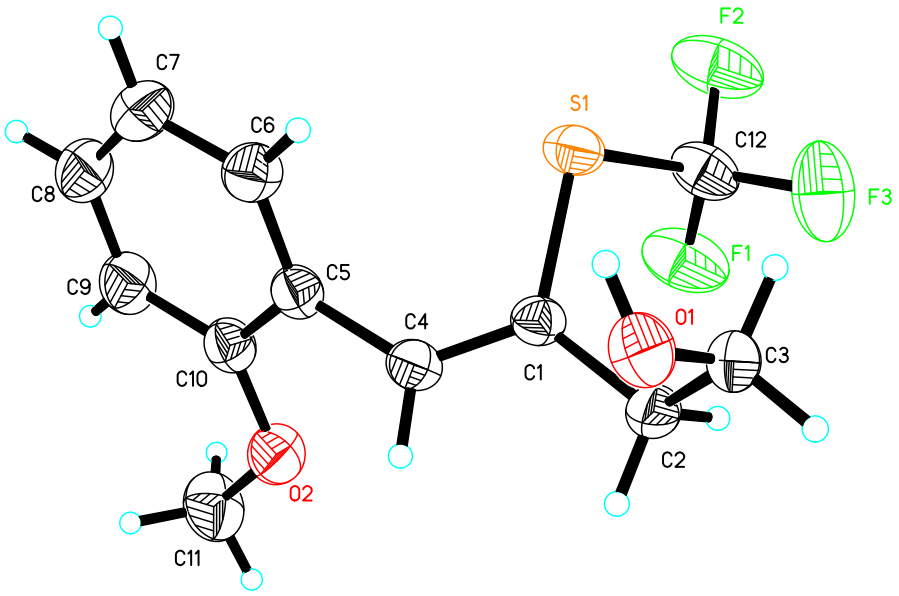
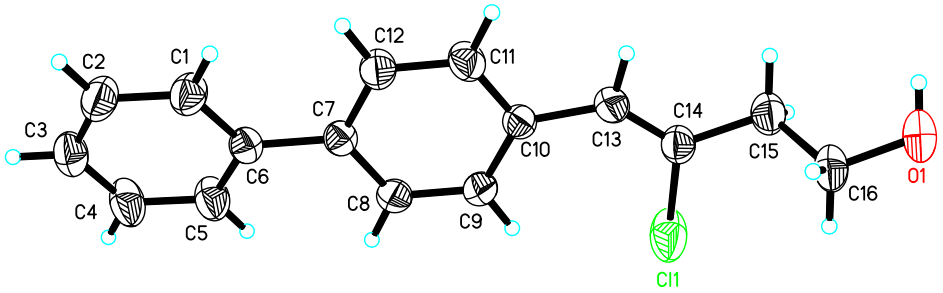
-250
PPM

The Crystal Data of 5d



The crystal data of **X** have been deposited in CCDC with number 1588850. Empirical formula: $C_{12}H_{13}F_3O_2S$, Formula weight: 278.28, Crystal system: Triclinic, Space group: P -1, Unit cell dimensions: a = 10.0641(3) Å, α = 90.0330(10)°; b = 10.4692(2) Å, β = 93.7370(10)°; c = 12.4244(3) Å, γ = 96.6490(10)°. Volume: 1297.46(6) $Å^3$, Z = 4, Density (calculated): 1.425 Mg/m^3, F(000) = 576, Crystal size: 0.180 x 0.150 x 0.120 mm^3, Final R indices [I>2sigma(I)]: R1 = 0.0413, wR2 = 0.1119.

The Crystal Data of 6l



The crystal data of **X** have been deposited in CCDC with number 1576900. Empirical formula: C16H15ClO, Formula weight: 258.73, Crystal system: Orthorhombic, Space group: P b c n, Unit cell dimensions: a = 57.5837(19) Å, α = 90°; b = 5.8021(2) Å, β = 90°; c = 8.0527(3) Å, γ = 90°. Volume: 2690.46(16) $Å^3$, Z = 8, Density (calculated): 1.277 Mg/m^3, F(000) = 1088, Crystal size: 0.220 x 0.200 x 0.100 mm^3, Final R indices [I>2sigma(I)]: R1 = 0.0509, wR2 = 0.1230.

References

1. M.-T. Chen, X.-Y. Tang and M. Shi, *Org. Chem. Front.*, 2017, **4**, 86.

2. P. Zhang, M. Li, X.-S. Xue, C. Xu, Q. Zhao, Y. Liu, H. Wang,Y. Guo, L. Lu and Q. Shen, *J. Org. Chem.*, 2016, **81**, 7486.