Supporting Information for

Chiral phosphoric acid catalyzed enantioselective inverse-electron-demand oxa-Diels-Alder reactions to synthesize chiral tricyclic tetrahydropyran derivatives

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# equal contribution for those authors

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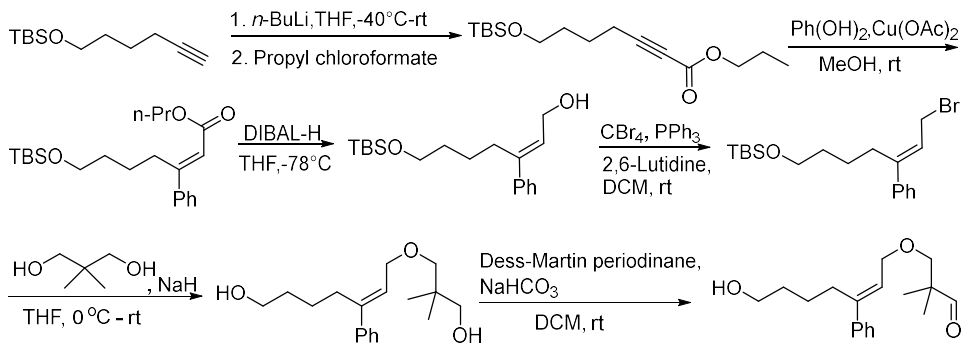
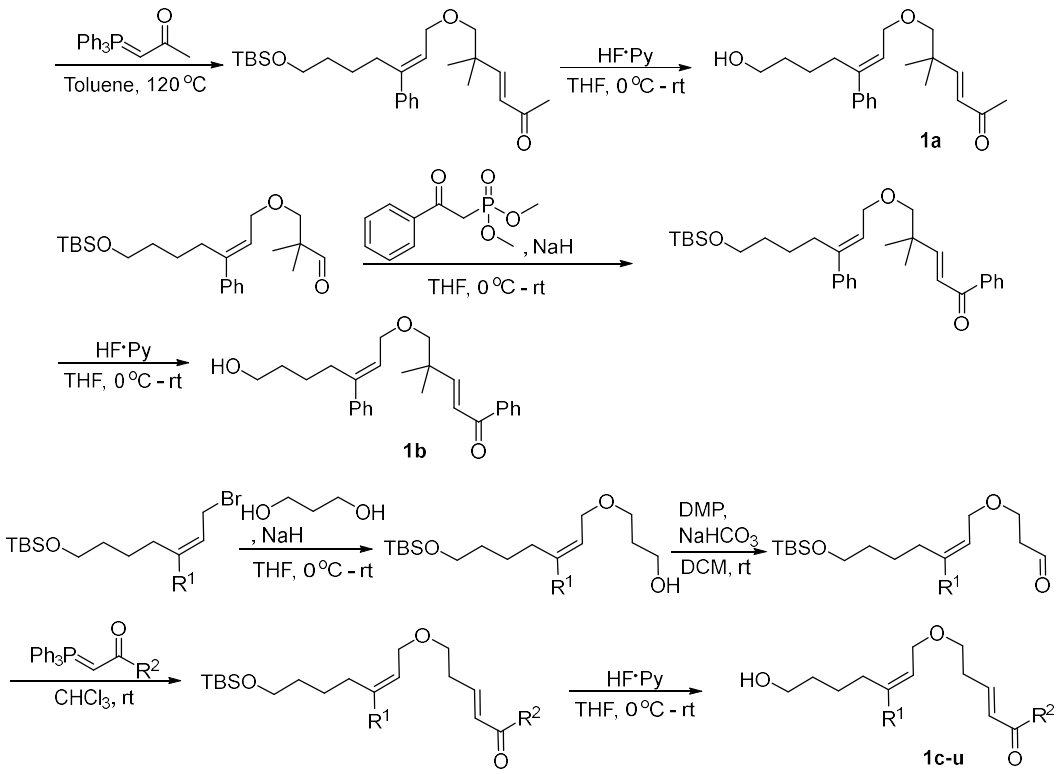
1. Materials and Methods

NMR spectra were recorded with tetramethylsilane as the internal standard. ^{1}H NMR spectra were recorded at 400 MHz、500 MHz、600 MHz or 800 MHz, respectively, ^{13}C NMR spectra were recorded at 100 MHz、125 MHz、150 MHz or 200 MHz (Bruker Avance), and ^{19}F NMR spectra were recorded at 471 MHz、376 MHz (Bruker Avance) respectively, by using $CDCl_3$ or acetone as internal references: the solvent ($CDCl_3$: δ_H = 7.26 ppm; δ_C = 77.16 ppm; acetone: δ_H = 2.05 ppm; δ_C = 29.84 ppm). Chemical shift values of NMR data are reported as values in ppm relative to (residual undeuterated) solvent signal as internal standard. Multiplicities for ^{1}H NMR signals are described using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. High resolution mass spectra were obtained with the Q-TOF-Premier mass spectrometer. Enantiomeric excess was determined by HPLC analysis on chiralpak AD-H, or OD-H columns. Optical rotations are reported as follows: $[\alpha]_D^{25}$ (589 nm, c = 1 corresponding to 10 mg ml^{-1}, DCM or Acetone).

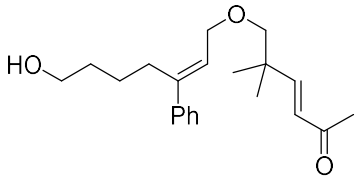
All reactions were performed under an argon atmosphere unless otherwise stated. Glassware was dried by heating under vacuum followed by flashing with argon gas prior to use. Solvents was dried and purified by standard procedures as specified in Purification of Laboratory Chemicals, 4th Ed (Armarego, W. L. F.; Perrin, D. D. Butterworth Heinemann: 1997) or purchased from commercial providers. 4Å molecular sieves were activated by high temperature of 210 degrees Celsius for 24 hours to use.

2. Synthesis and characterization of substrates 1a-u



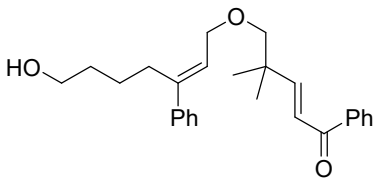


(*E*)-6-(((*E*)-7-hydroxy-3-phenylhept-2-en-1-yl)oxy)-5,5-dimethylhex-3-en-2-one (1a)



Yellow oil, 91% yield. **^{1}H NMR** (400 MHz, Acetone-d_6) δ 7.48 – 7.38 (m, 2H), 7.33 (t, J = 7.5 Hz, 2H), 7.28 – 7.21 (m, 1H), 6.91 (d, J = 16.4 Hz, 1H), 6.04 (d, J = 16.4 Hz, 1H), 5.81 (t, J = 6.5 Hz, 1H), 4.22 (d, J = 6.5 Hz, 2H), 3.50 (q, J = 5.8 Hz, 2H), 3.42 (t, J = 4.9 Hz, 1H), 3.36 (s, 2H), 2.59 (t, J = 7.6 Hz, 2H), 2.19 (s, 3H), 1.56 – 1.48 (m, 2H), 1.46 – 1.38 (m, 2H), 1.11 (s, 6H). **^{13}C NMR** (101 MHz, Acetone-d_6) δ 198.30, 155.03, 144.21, 143.16, 129.14, 128.88, 127.94, 127.15, 125.98, 79.08, 68.70, 62.22, 38.74, 33.43, 29.82, 27.06, 26.03, 24.26. **HRMS** (ESI): m/z Calcd. For $C_{21}H_{30}O_3Na$ ([M+Na]$^+$): 353.2093, found: 353.2090.

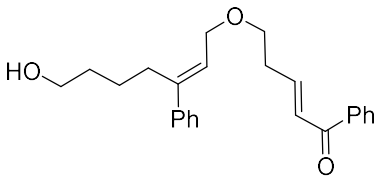
(*E*)-5-(((*E*)-7-hydroxy-3-phenylhept-2-en-1-yl)oxy)-4,4-dimethyl-1-phenylpent-2-en-1-one（1b）



Yellow oil, 93% yield. **^{1}H NMR** (500 MHz, Acetone-d_6) δ 8.02 – 7.97 (m, 2H), 7.65 – 7.57 (m, 1H), 7.54 – 7.47 (m, 2H), 7.44 – 7.37 (m, 2H), 7.35 – 7.29 (m, 2H), 7.28 – 7.21 (m, 1H), 7.15 – 6.92 (m, 2H), 5.83 (t, J =

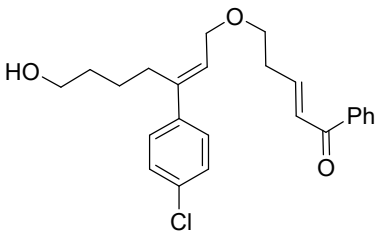
6.4 Hz, 1H), 4.24 (d, J = 6.5 Hz, 2H), 3.51 – 3.48 (m, 2H), 3.43 (s, 2H), 2.63 – 2.54 (m, 2H), 1.55 – 1.47 (m, 2H), 1.46 – 1.38 (m, 2H), 1.19 (s, 6H). **^{13}C NMR** (125 MHz, Acetone-d_6) δ 190.76, 156.60, 144.14, 143.10, 139.03, 133.43, 129.42, 129.23, 129.12, 127.90, 127.12, 125.97, 123.62, 79.15, 68.69, 62.19, 39.16, 33.39, 30.38, 26.01, 24.33. **HRMS** (ESI): m/z Calcd. For $C_{26}H_{32}O_3Na$ ([M+Na]$^+$): 415.2244, found: 415.2243.

(*E*)-5-(((*E*)-7-hydroxy-3-phenylhept-2-en-1-yl)oxy)-1-phenylpent-2-en-1-one (1c)



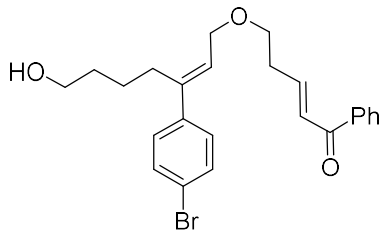
Colorless oil. 96% yield. **^{1}H NMR** (500 MHz, Acetone-d_6) δ 7.99 (dd, J = 8.4, 1.3 Hz, 2H), 7.63 – 7.59 (m, 1H), 7.53 – 7.50 (m, 2H), 7.41 (dd, J = 8.3, 1.3 Hz, 2H), 7.34 – 7.30 (m, 2H), 7.27 – 7.23 (m, 1H), 7.15 (dt, J = 15.4, 1.3 Hz, 1H), 7.06 (dt, J = 15.4, 6.6 Hz, 1H), 5.83 (t, J = 6.5 Hz, 1H), 4.25 (d, J = 6.4 Hz, 2H), 3.70 (t, J = 6.3 Hz, 2H), 3.49 (q, J = 6.2 Hz, 2H), 3.42 (t, J = 5.1 Hz, 1H), 2.66 – 2.62 (m, 2H), 2.61 – 2.56 (m, 2H), 1.54 – 1.48 (m, 2H), 1.45 – 1.38 (m, 2H). **^{13}C NMR** (125 MHz, Acetone-d_6) δ 190.25, 147.10, 144.10, 143.15, 138.85, 133.50, 129.47, 129.22, 129.14, 127.92, 127.80, 127.15, 126.05, 69.16, 68.11, 62.21, 33.82, 33.40, 30.39, 26.01. **HRMS** (ESI): m/z Calcd. For $C_{24}H_{28}O_3Na$ ([M+Na]$^+$): 387.1931, found: 387.1934.

(*E*)-5-(((*E*)-3-(4-chlorophenyl)-7-hydroxyhept-2-en-1-yl)oxy)-1-phenylpent-2-en-1-one (1d)



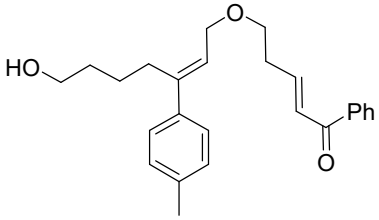
Colorless oil. 70% yield. **^{1}H NMR** (500 MHz, Acetone-d_6) δ 8.01 – 7.96 (m, 2H), 7.64 – 7.59 (m, 1H), 7.54 – 7.49 (m, 2H), 7.43 (d, J = 8.7 Hz, 2H), 7.36 – 7.32 (m, 2H), 7.14 (dt, J = 15.4, 1.3 Hz, 1H), 7.06 (dt, J = 15.4, 6.6 Hz, 1H), 5.85 (t, J = 6.4 Hz, 1H), 4.24 (d, J = 6.5 Hz, 2H), 3.70 (t, J = 6.3 Hz, 2H), 3.49 (td, J = 6.3, 5.1 Hz, 2H), 3.43 (t, J = 4.9 Hz, 1H), 2.65 – 2.61 (m, 2H), 2.60 – 2.54 (m, 2H), 1.54 – 1.47 (m, 2H), 1.45 – 1.37 (m, 2H). **^{13}C NMR** (125 MHz, Acetone-d_6) δ 190.20, 147.03, 142.80, 141.84, 138.82, 133.49, 133.17, 129.45, 129.19, 129.15, 128.82, 127.78, 126.84, 69.22, 68.04, 62.12, 33.78, 33.28, 30.21, 25.88. **HRMS** (ESI): m/z Calcd. For $C_{24}H_{27}ClO_3Na$ ([M+Na]$^+$): 421.1546, found:421.1546.

(*E*)-5-(((*E*)-3-(4-bromophenyl)-7-hydroxyhept-2-en-1-yl)oxy)-1-phenylpent-2-en-1-one (1e)



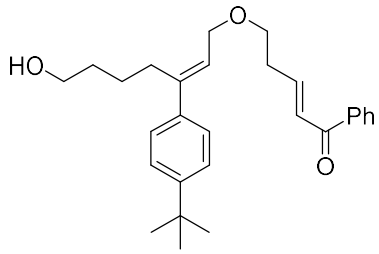
Colorless oil. 70% yield. **^{1}H NMR** (500 MHz, Acetone-d_6) δ 8.00 – 7.97 (m, 2H), 7.66 – 7.59 (m, 1H), 7.54 – 7.48 (m, 4H), 7.39 – 7.36 (m, 2H), 7.14 (dt, J = 15.4, 1.3 Hz, 1H), 7.06 (dt, J = 15.4, 6.7 Hz, 1H), 5.86 (t, J = 6.4 Hz, 1H), 4.24 (d, J = 6.4 Hz, 2H), 3.70 (t, J = 6.3 Hz, 2H), 3.49 (td, J = 6.3, 5.2 Hz, 2H), 3.39 (t, J = 5.2 Hz, 1H), 2.66 – 2.61 (m, 2H), 2.60 – 2.55 (m, 2H), 1.54 – 1.47 (m, 2H), 1.45 – 1.37 (m, 2H). **^{13}C NMR** (125 MHz, Acetone-d_6) δ 190.23, 147.05, 142.90, 142.33, 138.87, 133.52, 132.18, 129.49, 129.22, 129.21, 127.82, 126.94, 121.34, 69.26, 68.08, 62.15, 33.82, 33.33, 30.20, 25.92. **HRMS** (ESI): m/z Calcd. For $C_{24}H_{27}BrO_3Na$ ([M+Na]$^+$): 465.1036, found: 465.1034.

(*E*)-5-(((*E*)-7-hydroxy-3-(*p*-tolyl)hept-2-en-1-yl)oxy)-1-phenylpent-2-en-1-one (1f)



Colorless oil. 80% yield. **^{1}H NMR** (500 MHz, Acetone-d_6) δ 7.99 (dd, J = 8.3, 1.4 Hz, 2H), 7.63 – 7.59 (m, 1H), 7.51 (t, J = 7.8 Hz, 2H), 7.31 – 7.27 (m, 2H), 7.17 – 7.12 (m, 3H), 7.06 (dt, J = 15.4, 6.6 Hz, 1H), 5.80 (t, J = 6.5 Hz, 1H), 4.23 (d, J = 6.5 Hz, 2H), 3.69 (t, J = 6.3 Hz, 2H), 3.49 (td, J = 6.4, 5.2 Hz, 2H), 3.38 (t, J = 5.3 Hz, 1H), 2.66 – 2.61 (m, 2H), 2.59 – 2.54 (m, 2H), 2.30 (s, 3H), 1.50 (dt, J = 8.6, 5.9 Hz, 2H), 1.44 – 1.38 (m, 2H). **^{13}C NMR** (125 MHz, Acetone-d_6) δ 190.24, 147.11, 143.96, 140.21, 138.88, 137.46, 133.50, 129.79, 129.48, 129.23, 127.80, 127.05, 125.23, 69.14, 68.14, 62.24, 33.84, 33.44, 30.34, 26.05, 21.03. **HRMS** (ESI): m/z Calcd. For $C_{25}H_{30}O_3Na$ ([M+Na]$^+$): 401.2087, found: 401.2084.

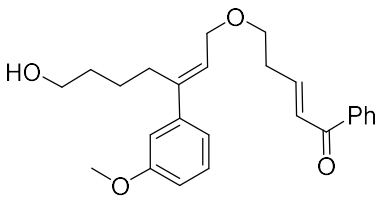
(*E*)-5-(((*E*)-3-(4-(tert-butyl)phenyl)-7-hydroxyhept-2-en-1-yl)oxy)-1-phenylpent-2-en-1-one (1g)



Colorless oil. 64% yield. **^{1}H NMR** (500 MHz, Acetone-d_6) δ 8.00 – 7.97 (m, 2H), 7.63 – 7.58 (m, 1H), 7.51 (t, J = 7.7 Hz, 2H), 7.48-7.34 (m, 4H), 7.15 (d, J = 15.5 Hz, 1H), 7.06 (dt, J = 15.4, 6.6 Hz, 1H), 5.83 (t, J = 6.5 Hz, 1H), 4.24 (d, J = 6.5 Hz, 2H), 3.70 (t, J =

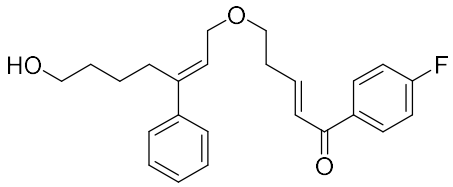
6.3 Hz, 2H), 3.51 (q, J = 6.1 Hz, 2H), 3.42 (t, J = 5.2 Hz, 1H), 2.63 (q, J = 6.3 Hz, 2H), 2.60 – 2.56 (m, 2H), 1.56 – 1.49 (m, 2H), 1.46 – 1.39 (m, 2H), 1.30 (s, 9H). **^{13}C NMR** (125 MHz, Acetone-d_6) δ 190.24, 150.69, 147.11, 143.80, 140.06, 138.85, 133.49, 129.47, 129.22, 127.79, 126.78, 125.98, 125.30, 69.10, 68.13, 62.22, 34.94, 33.83, 33.47, 31.61, 30.32, 26.15. **HRMS** (ESI): m/z Calcd. For $C_{28}H_{36}O_3Na$ ([M+Na]$^+$): 443.2562, found: 443.2562.

(*E*)-5-(((*E*)-7-hydroxy-3-(3-methoxyphenyl)hept-2-en-1-yl)oxy)-1-phenylpent-2-en-1-one (1h)



Colorless oil. 68% yield. **^{1}H NMR** (500 MHz, Acetone-d_6) δ 7.99 (dd, J = 8.4, 1.3 Hz, 2H), 7.63 – 7.58 (m, 1H), 7.53 – 7.48 (m, 2H), 7.23 (t, J = 7.9 Hz, 1H), 7.14 (dt, J = 15.4, 1.3 Hz, 1H), 7.06 (dt, J = 15.5, 6.6 Hz, 1H), 7.00 – 6.94 (m, 2H), 6.84 – 6.82 (m, 1H), 5.84 (t, J = 6.4 Hz, 1H), 4.24 (d, J = 6.5 Hz, 2H), 3.79 (s, 3H), 3.70 (t, J = 6.3 Hz, 2H), 3.50 (q, J = 6.2 Hz, 2H), 3.41 (t, J = 4.9 Hz, 1H), 2.65 – 2.61 (m, 2H), 2.60 – 2.54 (m, 2H), 1.55 – 1.48 (m, 2H), 1.46 – 1.38 (m, 2H). **^{13}C NMR** (125 MHz, Acetone-d_6) δ 190.23, 160.69, 147.08, 144.69, 144.02, 138.84, 133.49, 130.09, 129.46, 129.21, 127.79, 126.09, 119.53, 113.28, 112.90, 69.18, 68.10, 62.21, 55.42, 33.81, 33.40, 30.47, 26.02. **HRMS** (ESI): m/z Calcd. For $C_{25}H_{30}O_4Na$ ([M+Na]$^+$): 417.2036, found: 417.2035.

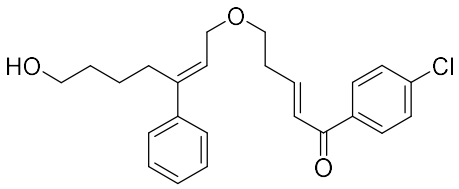
(*E*)-1-(4-fluorophenyl)-5-(((*E*)-7-hydroxy-3-phenylhept-2-en-1-yl)oxy)pent-2-en-1-one (1i)



Colorless oil. 70% yield. **^{1}H NMR** (500 MHz, Acetone-d_6) δ 8.11 – 8.05 (m, 2H), 7.43 – 7.40 (m, 2H), 7.32 (dd, J = 8.4, 6.8 Hz, 2H), 7.28-7.25 (m, 1H), 7.07 (dt, J = 15.4, 6.7 Hz, 1H), 5.82 (t, J = 6.5 Hz, 1H), 4.24 (d, J = 6.4 Hz, 2H), 3.70 (t, J = 6.3 Hz, 2H), 3.49 (q, J = 6.4, 5.9 Hz, 2H), 3.40 (t, J = 5.2 Hz, 1H), 2.66 – 2.61 (m, 2H), 2.61 – 2.57 (m, 2H), 1.51 (dd, J = 15.0, 6.7 Hz, 2H), 1.45 – 1.39 (m, 2H). **^{13}C NMR** (125 MHz, Acetone-d_6) δ 188.70, 166.29 (J = 251.8 Hz), 147.34, 144.13, 143.16, 135.41 (J = 3.0 Hz), 132.10 (J = 9.3 Hz), 129.16, 127.95, 127.49, 127.17, 126.06, 116.39 (J = 21.9 Hz), 69.14, 68.12, 62.22,

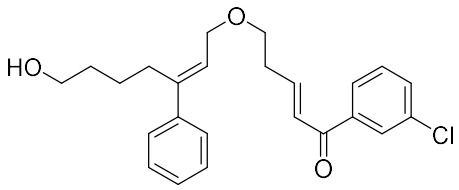
33.84, 33.42, 30.40, 26.03. **HRMS** (ESI): m/z Calcd. For $C_{24}H_{27}FO_3Na$ ([M+Na]$^+$): 405.1842, found: 405.1843.

(*E*)-1-(4-chlorophenyl)-5-(((*E*)-7-hydroxy-3-phenylhept-2-en-1-yl)oxy)pent-2-en-1-one (1j)



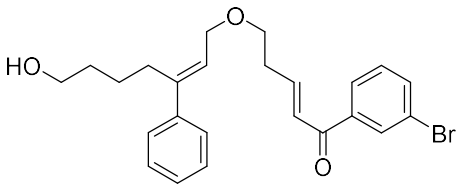
Colorless oil. 80% yield. **^{1}H NMR** (500 MHz, Acetone-d_6) δ 8.00 (d, J = 2.0 Hz, 1H), 7.99 (d, J = 2.0 Hz, 1H), 7.54 (d, J = 2.0 Hz, 1H), 7.53 (d, J = 2.0 Hz, 1H), 7.42 – 7.40 (m, 2H), 7.34 – 7.31 (m, 2H), 7.27 – 7.23 (m, 1H), 7.13 (d, J = 15.5 Hz, 1H), 7.08 (dt, J = 15.4, 6.2 Hz, 1H), 5.82 (t, J = 6.5 Hz, 1H), 4.24 (d, J = 6.5 Hz, 2H), 3.70 (t, J = 6.3 Hz, 2H), 3.49 (td, J = 6.4, 5.2 Hz, 2H), 3.41 (t, J = 5.2 Hz, 1H), 2.65 – 2.61 (m, 2H), 2.61 – 2.57 (m, 2H), 1.54 – 1.48 (m, 2H), 1.44 – 1.39 (m, 2H). **^{13}C NMR** (125 MHz, Acetone-d_6) δ 189.11, 147.78, 144.13, 143.14, 139.21, 137.40, 131.01, 129.66, 129.15, 127.94, 127.45, 127.15, 126.03, 69.09, 68.11, 62.21, 33.85, 33.40, 30.38, 26.02. **HRMS** (ESI): m/z Calcd. For $C_{24}H_{27}ClO_3Na$ ([M+Na]$^+$): 421.1546, found: 421.1545.

(*E*)-1-(3-chlorophenyl)-5-(((*E*)-7-hydroxy-3-phenylhept-2-en-1-yl)oxy)pent-2-en-1-one (1k)



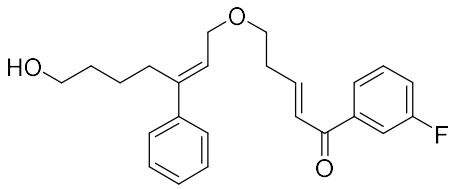
Colorless oil. 86% yield. **^{1}H NMR** (500 MHz, Acetone-d_6) δ 7.96 – 7.92 (m, 2H), 7.66 – 7.63 (m, 1H), 7.55 (t, J = 7.8 Hz, 1H), 7.41 (dd, J = 7.2, 1.3 Hz, 2H), 7.34 – 7.30 (m, 2H), 7.27 – 7.23 (m, 1H), 7.17 – 7.13 (m, 1H), 7.10 (dt, J = 15.4, 6.1 Hz, 1H), 5.82 (t, J = 6.4 Hz, 1H), 4.24 (d, J = 6.4 Hz, 2H), 3.71 (t, J = 6.3 Hz, 2H), 3.51 – 3.47 (m, 2H), 3.40 (t, J = 5.2 Hz, 1H), 2.65 (q, J = 6.3 Hz, 2H), 2.61 – 2.57 (m, 2H), 1.54 – 1.48 (m, 2H), 1.45 – 1.38 (m, 2H). **^{13}C NMR** (125 MHz, Acetone-d_6) δ 189.06, 148.26, 144.14, 143.15, 140.64, 135.21, 133.31, 131.33, 129.15, 129.00, 127.94, 127.72, 127.48, 127.16, 126.03, 69.09, 68.13, 62.21, 33.87, 33.41, 30.40, 26.02. **HRMS** (ESI): m/z Calcd. For $C_{24}H_{27}ClO_3Na$ ([M+Na]$^+$): 421.1546, found: 421.1547.

(*E*)-1-(3-bromophenyl)-5-(((*E*)-7-hydroxy-3-phenylhept-2-en-1-yl)oxy)pent-2-en-1-one (1l)



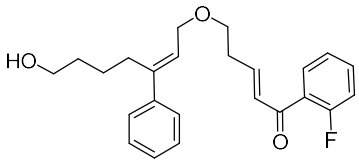
Colorless oil. 85% yield. **^{1}H NMR** (500 MHz, Acetone-d_6) δ 8.11 (t, J = 1.8 Hz, 1H), 7.97 (dt, J = 7.7, 1.3 Hz, 1H), 7.80 – 7.78 (m, 1H), 7.48 (t, J = 7.8 Hz, 1H), 7.41 (dd, J = 8.3, 1.3 Hz, 2H), 7.34 – 7.30 (m, 2H), 7.27 – 7.22 (m, 1H), 7.14 (d, J = 15.5 Hz, 1H), 7.09 (dt, J = 15.4, 5.9 Hz, 1H), 5.82 (t, J = 6.5 Hz, 1H), 4.24 (d, J = 6.5 Hz, 2H), 3.70 (t, J = 6.3 Hz, 2H), 3.49 (q, J = 6.3 Hz, 2H), 3.40 (t, J = 5.2 Hz, 1H), 2.68 – 2.62 (m, 2H), 2.61 – 2.57 (m, 2H), 1.51 (dd, J = 14.6, 6.2 Hz, 2H), 1.45 – 1.38 (m, 2H). **^{13}C NMR** (125 MHz, Acetone-d_6) δ 188.97, 148.27, 144.11, 143.13, 140.82, 136.26, 131.96, 131.56, 129.14, 128.10, 127.92, 127.44, 127.15, 126.03, 123.26, 69.08, 68.13, 62.20, 33.87, 33.40, 30.39, 26.01. **HRMS** (ESI): m/z Calcd. For $C_{24}H_{27}BrO_3Na$ ([M+Na]$^+$): 465.1041, found: 465.1040.

(*E*)-1-(3-fluorophenyl)-5-(((*E*)-7-hydroxy-3-phenylhept-2-en-1-yl)oxy)pent-2-en-1-one (1m)



Colorless oil. 70% yield. **^{1}H NMR** (500 MHz, Acetone-d_6) δ 7.85 – 7.82 (m, 1H), 7.71 – 7.68 (m, 1H), 7.57 (td, J = 8.0, 5.6 Hz, 1H), 7.42 – 7.37 (m, 3H), 7.34 – 7.30 (m, 2H), 7.27 – 7.22 (m, 1H), 7.15 (d, J = 15.5 Hz, 1H), 7.10 (dt, J = 15.4, 6.0 Hz, 1H), 5.82 (t, J = 6.5 Hz, 1H), 4.25 (d, J = 6.5 Hz, 2H), 3.71 (t, J = 6.3 Hz, 2H), 3.49 (td, J = 6.4, 5.2 Hz, 2H), 3.39 (t, J = 5.2 Hz, 1H), 2.67 – 2.62 (m, 2H), 2.61 – 2.57 (m, 2H), 1.54 – 1.48 (m, 2H), 1.45 – 1.38 (m, 2H). **^{13}C NMR** (125 MHz, Acetone-d_6) δ 189.02, 163.71 (J = 245.7 Hz), 148.09, 144.14, 143.15, 141.12 (J = 6.4 Hz), 131.60 (J = 7.8 Hz), 129.15, 127.94, 127.48, 127.16, 126.04, 125.28 (J = 2.9 Hz), 120.35 (J = 21.7 Hz), 115.62 (J = 22.4 Hz), 69.09, 68.13, 62.21, 33.86, 33.41, 30.40, 26.02. **HRMS** (ESI): m/z Calcd. For $C_{24}H_{27}FO_3Na$ ([M+Na]$^+$): 405.1842, found: 405.1841.

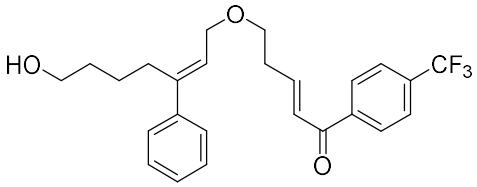
(E)-1-(2-fluorophenyl)-5-(((E)-7-hydroxy-3-phenylhept-2-en-1-yl)oxy)pent-2-en-1-one (1n)



Colorless oil. 66%yield. **^{1}H NMR** (400 MHz, Acetone-d6) δ 7.54 (t, J = 7.5 Hz, 1H), 7.45-7.43 (m, 1H), 7.26 (d, J = 7.3 Hz, 2H), 7.18 (t, J = 7.6 Hz, 3H), 7.15-7.07 (m,

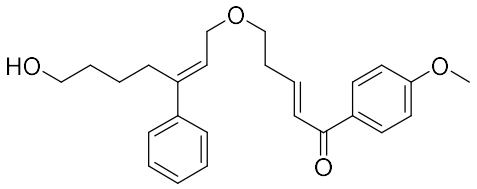
2H), 6.87-6.80 (m, 1H), 6.65 (d, J = 15.6 Hz, 1H), 5.66 (q, J = 3.7 Hz, 1H), 4.08 (d, J = 6.5 Hz, 2H), 3.53 (t, J = 6.3 Hz, 2H), 3.36 (br, 2H), 2.84 (br, 1H), 2.46-2.44 (m, 4H), 1.37-1.36 (m, 2H), 1.31-1.25 (m, 2H). **^{13}C NMR** (101 MHz, Acetone-d_6) δ 205.45 (d, $J_{C\text{-}F}$ = 13.8 Hz), 188.83 (d, $J_{C\text{-}F}$ = 1.71), 160.71 (d, $J_{C\text{-}F}$ = 251.3), 147.36, 143.24, 142.27, 133.78 ($J_{C\text{-}F}$ = 8.7 Hz), 130.63 ($J_{C\text{-}F}$ = 4.7 Hz), 130.53 ($J_{C\text{-}F}$ = 2.7 Hz), 128.30, 127.08, 126.29, 125.16, 124.6 ($J_{C\text{-}F}$ = 3.4 Hz), 116.38 ($J_{C\text{-}F}$ = 22.8 Hz), 68.13, 67.28, 61.38, 32.90, 32.53, 29.53, 25.15. **HRMS** (ESI):m/z Calcd. For $C_{24}H_{27}FO_3Na$ ([M+Na]$^+$): 405.1836, found: 405.1833.

(*E*)-5-(((*E*)-7-hydroxy-3-phenylhept-2-en-1-yl)oxy)-1-(4-(trifluoromethyl)phenyl) pent-2-en-1-one (1o)



Colorless oil. 83% yield. **^{1}H NMR** (500 MHz, Acetone-d_6) δ 8.16 (d, J = 8.0 Hz, 2H), 7.86 (d, J = 8.2 Hz, 2H), 7.42 – 7.40 (m, 2H), 7.34 – 7.30 (m, 2H), 7.28 – 7.23 (m, 1H), 7.15 (d, J = 15.6 Hz, 1H), 7.14 – 7.08 (m, 1H), 5.82 (t, J = 6.5 Hz, 1H), 4.25 (d, J = 6.5 Hz, 2H), 3.72 (t, J = 6.3 Hz, 2H), 3.51 – 3.47 (m, 2H), 3.41 (t, J = 5.2 Hz, 1H), 2.66 (q, J = 6.2 Hz, 2H), 2.61 – 2.57 (m, 2H), 1.54 – 1.48 (m, 2H), 1.45 – 1.39 (m, 2H). **^{13}C NMR** (125 MHz, Acetone-d_6) δ 189.77, 148.77, 144.18, 143.15, 142.05, 133.97 (J = 32.4 Hz), 129.92, 129.16, 127.95, 127.71, 127.16, 126.50, 126.46, 126.02, 69.01, 68.12, 62.21, 33.91, 33.40, 30.39, 26.03. **HRMS** (ESI): m/z Calcd. For $C_{25}H_{27}F_3O_3Na$ ([M+Na]$^+$): 455.1810, found: 455.1810.

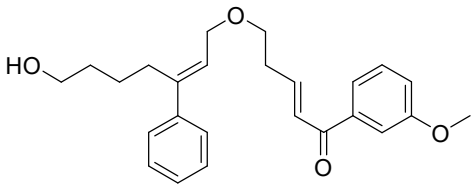
(*E*)-5-(((*E*)-7-hydroxy-3-phenylhept-2-en-1-yl)oxy)-1-(4-methoxyphenyl)pent-2-en-1-one (1p)



Colorless oil. 81% yield. **^{1}H NMR** (500 MHz, Acetone-d_6) δ 8.02 – 7.99 (m, 2H), 7.44 – 7.40 (m, 2H), 7.34 – 7.30 (m, 2H), 7.27 – 7.23 (m, 1H), 7.15 (dt, J = 15.4, 1.4 Hz, 1H), 7.06 – 7.00 (m, 3H), 5.83 (t, J = 6.4 Hz, 1H), 4.24 (d, J = 6.4 Hz, 2H), 3.88 (s, 3H), 3.69 (t, J = 6.3 Hz, 2H), 3.49 (q, J = 6.2 Hz, 2H), 3.42 (t, J = 5.1 Hz, 1H), 2.64 – 2.60 (m, 2H), 2.58 (d, J = 7.4 Hz, 2H), 1.55 – 1.48 (m, 2H), 1.45 – 1.39 (m, 2H). **^{13}C NMR** (125 MHz,

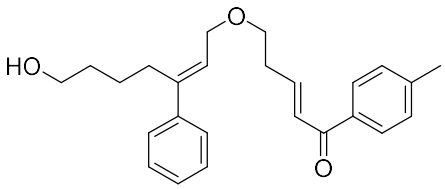
Acetone-d_6) δ 188.40, 164.33, 145.85, 144.07, 143.14, 131.61, 131.50, 129.14, 127.92, 127.53, 127.15, 126.06, 114.65, 69.26, 68.10, 62.21, 55.91, 33.77, 33.39, 30.38, 26.01. **HRMS** (ESI): m/z Calcd. For $C_{25}H_{30}O_4Na$ ([M+Na]$^+$): 417.2042, found: 417.2041.

(*E*)-5-(((*E*)-7-hydroxy-3-phenylhept-2-en-1-yl)oxy)-1-(3-methoxyphenyl)pent-2-en-1-one (1q)



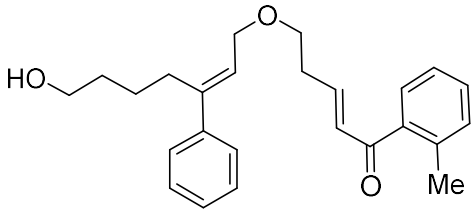
Colorless oil. 52% yield. **^{1}H NMR** (500 MHz, Acetone-d_6) δ 7.57 (dt, J = 7.6, 1.3 Hz, 1H), 7.49 (dd, J = 2.7, 1.5 Hz, 1H), 7.42 (dd, J = 8.7, 7.3 Hz, 3H), 7.34 – 7.31 (m, 2H), 7.27 – 7.23 (m, 1H), 7.18 – 7.14 (m, 1H), 7.13 – 7.09 (m, 1H), 7.09 – 7.02 (m, 1H), 5.82 (t, J = 6.4 Hz, 1H), 4.24 (d, J = 6.5 Hz, 2H), 3.85 (s, 3H), 3.70 (t, J = 6.3 Hz, 2H), 3.51 – 3.47 (m, 2H), 3.40 (t, J = 5.2 Hz, 1H), 2.66 – 2.62 (m, 2H), 2.61 – 2.57 (m, 2H), 1.54 – 1.48 (m, 2H), 1.45 – 1.39 (m, 2H). **^{13}C NMR** (125 MHz, Acetone-d_6) δ 190.01, 160.89, 147.13, 144.11, 143.16, 140.28, 130.56, 129.15, 127.93, 127.89, 127.16, 126.06, 121.66, 119.59, 113.78, 69.19, 68.13, 62.21, 55.74, 33.82, 33.41, 30.40, 26.02. **HRMS** (ESI): m/z Calcd. For $C_{25}H_{30}O_4Na$ ([M+Na]$^+$): 417.2042, found:417.2044.

(*E*)-5-(((*E*)-7-hydroxy-3-phenylhept-2-en-1-yl)oxy)-1-(*p*-tolyl)pent-2-en-1-one (1r)



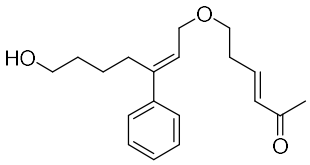
Colorless oil. 77% yield. **^{1}H NMR** (500 MHz, Acetone-d_6) δ 7.91 – 7.89 (m, 2H), 7.42 – 7.40 (m, 2H), 7.32 (t, J = 7.6 Hz, 4H), 7.28 – 7.23 (m, 1H), 7.14 (dt, J = 15.3, 1.3 Hz, 1H), 7.04 (dt, J = 15.3, 6.7 Hz, 1H), 5.82 (t, J = 6.4 Hz, 1H), 4.24 (d, J = 6.5 Hz, 2H), 3.69 (t, J = 6.3 Hz, 2H), 3.51 – 3.48 (m, 2H), 3.41 (t, J = 5.1 Hz, 1H), 2.64 – 2.61 (m, 2H), 2.58 (d, J = 7.6 Hz, 2H), 2.39 (s, 3H), 1.54 – 1.49 (m, 2H), 1.45 – 1.39 (m, 2H). **^{13}C NMR** (125 MHz, Acetone-d_6) δ 189.66, 146.52, 144.21, 144.09, 143.16, 136.32, 130.08, 129.37, 129.15, 127.92, 127.76, 127.16, 126.07, 69.22, 68.12, 62.21, 33.80, 33.41, 30.39, 26.02, 21.52. **HRMS** (ESI): m/z Calcd. For $C_{25}H_{30}O_3Na$ ([M+Na]$^+$): 401.2093, found: 401.2092.

(E)-5-(((E)-7-hydroxy-3-phenylhept-2-en-1-yl)oxy)-1-(o-tolyl)pent-2-en-1-one (1s)



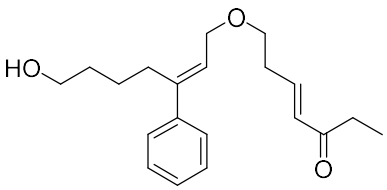
Colorless oil. 50% yield. **^{1}H NMR** (600 MHz, Acetone-d6) 7.43 (d, *J* = 7.7 Hz, 1H), 7.41-7.39 (m, 2H), 7.37 (dt, *J* = 1.2, 7.5 Hz, 1H), 7.33 (t, *J* = 7.7 Hz, 2H), 7.28 (d, *J* = 7.6 Hz, 1H), 7.25-7.24 (m, 2H), 6.74 (td, *J* = 6.8, 15.78 Hz, 1H), 6.60 (td, *J* = 1.4, 15.8 Hz, 1H), 5.79 (t, *J* = 6.5 Hz, 1H), 4.22 (d, *J* = 6.5 Hz, 2H), 3.66 (t, *J* = 6.2 Hz, 2H), 3.50-3.47 (m, 2H), 3.39 (t, *J* = 5.2 Hz, 1 H), 2.59-2.56 (m, 4H), 2.34 (s, 3H), 1.53-1.48 (m, 2H), 1.43-1.39 (m,2H). **^{13}C NMR** (151 MHz, Acetone-d_6) 196.50, 148.89, 144.22, 143.25, 140.14, 137.39, 132.57, 132.01, 131.15, 129.25, 128.97, 128.03, 127.25, 126.37, 126.12, 69.06, 68.15, 62.29, 33.82, 33.49, 30.47, 26.10, 20.31. **HRMS** (ESI): m/z Calcd. For $C_{25}H_{31}O_3$ ([M+H]$^+$): 379.2269, found: 379.2268.

(*E*)-6-(((*E*)-7-hydroxy-3-phenylhept-2-en-1-yl)oxy)hex-3-en-2-one (1t)



Colorless oil. 62% yield. **^{1}H NMR** (500 MHz, Acetone-*d*$_6$) δ 7.43 – 7.40 (m, 2H), 7.33 (t, *J* = 7.7 Hz, 2H), 7.27 – 7.24 (m, 1H), 6.89 (dt, *J* = 16.0, 6.8 Hz, 1H), 6.12 (dt, *J* = 16.1, 1.6 Hz, 1H), 5.81 (t, *J* = 6.5 Hz, 1H), 4.22 (d, *J* = 6.5 Hz, 2H), 3.64 (t, *J* = 6.3 Hz, 2H), 3.49 (d, *J* = 6.3 Hz, 2H), 3.44 (s, 1H), 2.60 – 2.57 (m, 2H), 2.54 – 2.49 (m, 2H), 2.18 (s, 3H), 1.54 – 1.49 (m, 2H), 1.45 – 1.39 (m, 2H). **^{13}C NMR** (125 MHz, Acetone-*d*$_6$) δ 197.95, 145.69, 144.08, 143.11, 133.15, 129.14, 127.92, 127.12, 126.01, 69.04, 68.08, 62.19, 33.57, 33.37, 30.36, 26.81, 25.99. **HRMS** (ESI): m/z Calcd. For $C_{19}H_{26}O_3Na$ ([M+Na]$^+$): 325.1774, found: 325.1774.

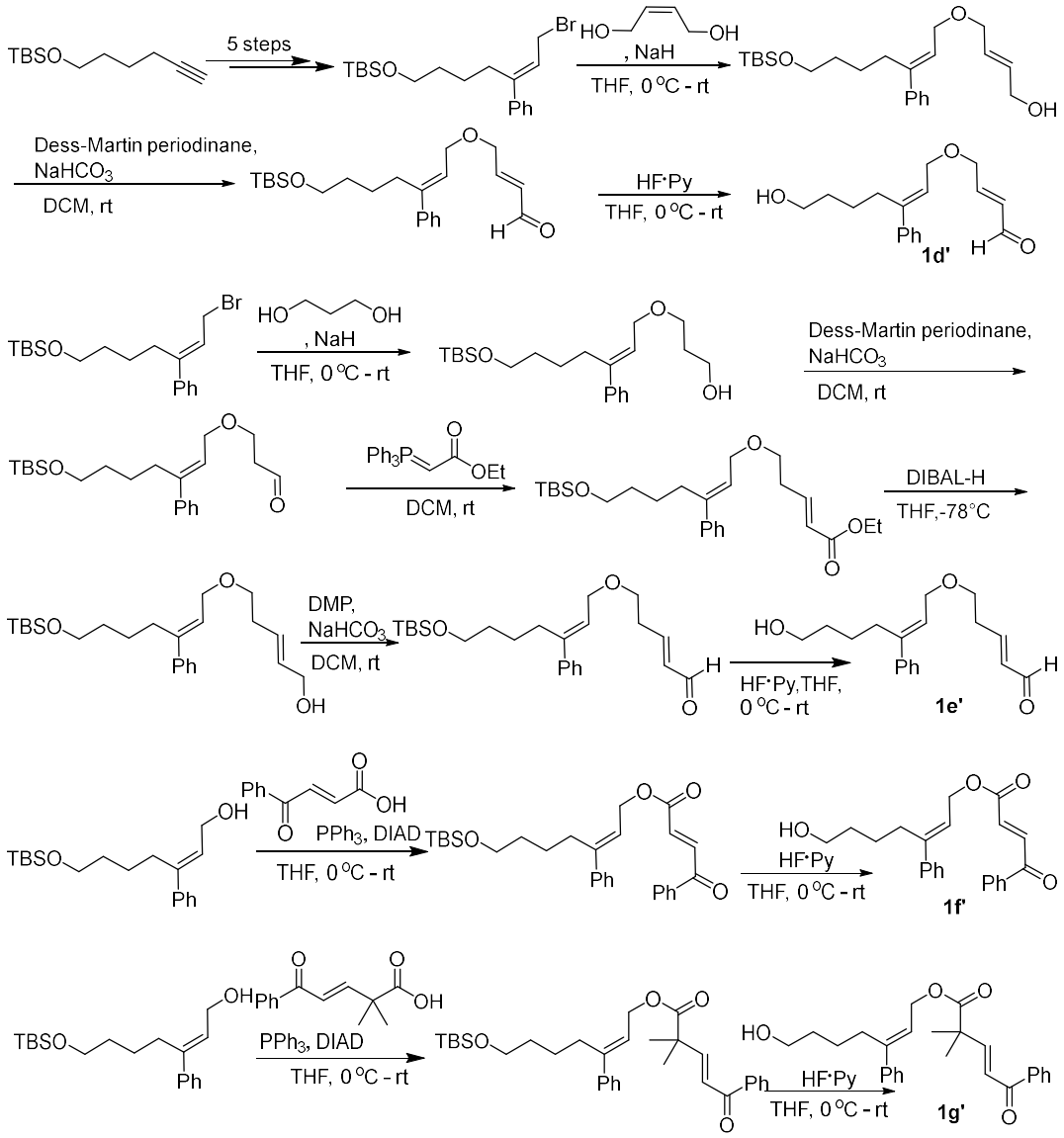
(*E*)-7-(((*E*)-7-hydroxy-3-phenylhept-2-en-1-yl)oxy)hept-4-en-3-one (1u)



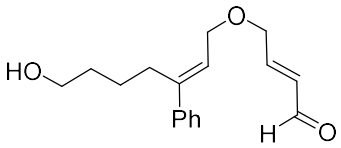
Colorless oil. 75% yield. **^{1}H NMR** (500 MHz, Acetone-*d*$_6$) δ 7.43 – 7.38 (m, 2H), 7.33 (t, *J* = 7.7 Hz, 2H), 7.29 – 7.23 (m, 1H), 6.88 (dt, *J* = 16.0, 6.9 Hz, 1H), 6.17 (dt, *J* = 16.0, 1.5 Hz, 1H), 5.80 (t, *J* = 6.4 Hz, 1H), 4.22 (d, *J* = 6.5 Hz, 2H), 3.63 (t, *J* = 6.4 Hz, 2H), 3.53 – 3.47 (m, 2H), 3.42 (t, *J* = 5.1 Hz, 1H), 2.61 – 2.54 (m, 4H), 2.52 – 2.48 (m, 2H), 1.51 (dt, *J* = 14.9, 6.4 Hz, 2H), 1.46 – 1.38 (m, 2H), 1.00 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (125 MHz, Acetone-*d*$_6$) δ 200.35, 144.25, 144.09, 143.15, 132.08, 129.15, 127.93, 127.14, 126.05, 69.13, 68.09, 62.20,

33.57, 33.40, 30.38, 26.01, 8.29. **HRMS** (ESI): m/z Calcd. For $C_{20}H_{28}O_3Na$ ([M+Na]$^+$): 339.1936, found: 339.1933.

3. Synthesis and characterization of substrates 1d'-g'



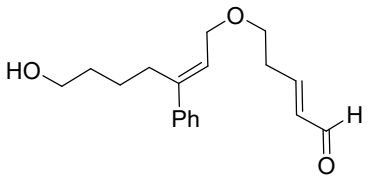
(*E*)-4-(((*E*)-7-hydroxy-3-phenylhept-2-en-1-yl)oxy)but-2-enal (1d')



Colorless oil. 72% yield. **^{1}H NMR** (400 MHz, Acetone-d_6) δ 9.60 (d, J = 8.0 Hz, 1H), 7.43 (d, J = 7.3 Hz, 2H), 7.34 (t, J = 7.5 Hz, 2H), 7.26 (t, J = 7.2 Hz, 1H), 7.09 – 7.00 (m, 1H), 6.31 (dd, J = 15.7, 8.0 Hz, 1H), 5.85 (t, J = 6.5 Hz, 1H), 4.36 (dd, J = 4.0, 2.0 Hz, 2H), 4.31 (d, J = 6.6 Hz, 2H), 3.50 (q, J = 5.7 Hz, 2H), 3.45 (t, J = 4.9 Hz, 1H), 2.60 (t, J = 7.6 Hz, 2H), 1.55 – 1.48 (m, 2H), 1.46 – 1.39 (m, 2H). **^{13}C NMR** (101 MHz, Acetone-d_6) δ 193.82, 154.98, 144.74, 142.99, 131.95, 129.15, 128.01, 127.15, 125.36,

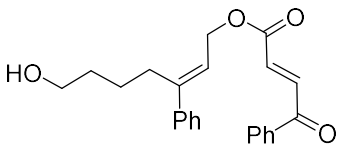
69.28, 68.16, 62.16, 33.35, 30.39, 26.01. **HRMS** (ESI): m/z Calcd. For $C_{17}H_{22}O_3Na$ ([M+Na]$^+$): 297.1461, found: 297.1463.

(*E*)-5-(((*E*)-7-hydroxy-3-phenylhept-2-en-1-yl)oxy)pent-2-enal (1e')



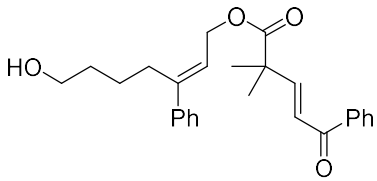
Colorless oil. 92% yield. **^{1}H NMR** (400 MHz, Acetone-d_6) δ 9.52 (d, J = 7.9 Hz, 1H), 7.41 (d, J = 7.1 Hz, 2H), 7.33 (t, J = 7.6 Hz, 2H), 7.26 (t, J = 7.2 Hz, 1H), 7.08 – 6.94 (m, 1H), 6.16 (dd, J = 15.7, 7.8 Hz, 1H), 5.81 (t, J = 6.5 Hz, 1H), 4.23 (d, J = 6.5 Hz, 2H), 3.68 (t, J = 6.2 Hz, 2H), 3.50 (q, J = 5.9 Hz, 2H), 3.43 (t, J = 5.0 Hz, 1H), 2.65 (t, J = 6.4 Hz, 2H), 2.59 (t, J = 7.6 Hz, 2H), 1.55 – 1.47 (m, 2H), 1.46 – 1.35 (m, 2H). **^{13}C NMR** (101 MHz, Acetone-d_6) δ 194.28, 156.52, 144.19, 143.12, 134.78, 129.15, 127.94, 127.14, 125.92, 68.70, 68.11, 62.19, 33.76, 33.38, 30.38, 26.00. **HRMS** (ESI): m/z Calcd. For $C_{18}H_{24}O_3Na$ ([M+Na]$^+$): 311.1618, found: 311.1619.

(*E*)-7-hydroxy-3-phenylhept-2-en-1-yl (*E*)-4-oxo-4-phenylbut-2-enoate (1f')



Yellow oil. 94% yield.**^{1}H NMR** (400 MHz, Acetone-d_6) δ 8.07 (d, J = 7.1 Hz, 2H), 7.99 (d, J = 15.6 Hz, 1H), 7.70 (t, J = 7.5 Hz, 1H), 7.59 (t, J = 7.6 Hz, 2H), 7.45 (d, J = 7.2 Hz, 2H), 7.36 (t, J = 7.4 Hz, 2H), 7.29 (t, J = 7.4 Hz, 1H), 6.83 (d, J = 15.6 Hz, 1H), 5.90 (t, J = 7.0 Hz, 1H), 4.99 (d, J = 7.0 Hz, 2H), 3.52 (q, J = 5.9 Hz, 2H), 3.43 (t, J = 5.2 Hz, 1H), 2.70 (t, J = 7.6 Hz, 2H), 1.59 – 1.53 (m, 2H), 1.50 – 1.44 (m, 2H). **^{13}C NMR** (101 MHz, Acetone-d_6) δ 189.07, 164.96, 146.05, 141.81, 136.70, 133.79, 131.79, 128.95, 128.76, 128.37, 127.49, 126.40, 121.51, 61.86, 61.33, 32.50, 29.58, 25.26. **HRMS** (ESI): m/z Calcd. For $C_{23}H_{24}O_4Na$ ([M+Na]$^+$): 387.1572, found: 387.1568.

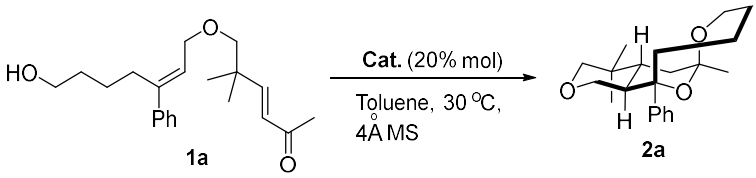
(*E*)-7-hydroxy-3-phenylhept-2-en-1-yl (*E*)-2,2-dimethyl-5-oxo-5-phenylpent-3-enoate (1g')



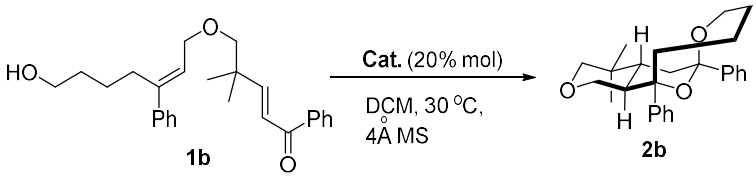
Yellow oil. 92% yield.**^{1}H NMR** (400 MHz, Acetone-d_6) δ 7.99 (d, J = 7.3 Hz, 2H), 7.60 (d, J = 6.8 Hz, 1H), 7.49 (t, J = 7.6 Hz, 2H), 7.41 (d, J = 6.9 Hz, 2H), 7.33 (t, J = 7.2 Hz, 2H), 7.27 (t, J = 7.3 Hz, 1H), 7.18 (d, J = 15.7

Hz, 1H), 7.07 (d, J = 15.7 Hz, 1H), 5.84 (t, J = 7.0 Hz, 1H), 4.87 (d, J = 7.1 Hz, 2H), 3.50 (q, J = 5.9 Hz, 2H), 3.42 (t, J = 5.1 Hz, 1H), 2.66 (t, J = 7.6 Hz, 2H), 1.55 – 1.49 (m, 2H), 1.46 (s, 6H), 1.45 – 1.39 (m, 2H). **^{13}C NMR** (101 MHz, Acetone-d_6) δ 190.54, 175.25, 152.23, 146.84, 142.74, 138.74, 133.70, 129.53, 129.34, 129.24, 128.33, 127.28, 124.42, 122.61, 62.55, 62.21, 45.76, 33.39, 30.44, 26.15, 24.99. **HRMS** (ESI): m/z Calcd. For $C_{26}H_{30}O_4Na$ ([M+Na]$^+$): 429.2042, found: 429.2046.

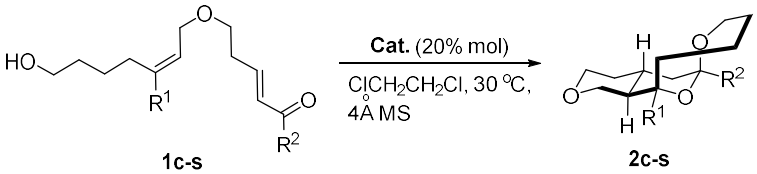
4. General procedure for oxa-IEDHDA-keto acetalization reactions with 1a-u



Substrate **1a** (15 mg, 1.0 eq.) was dissolved in Toluene (0.5 ml), then 4Å molecular sieves (30 mg) followed by catalyst **3n** (0.2 eq.) were added. The reaction mixture was stirred at 30 °C and monitored by TLC (generally for 120 h). When the reaction was completed, the mixture was purified by silica gel column to afford products **2a**.

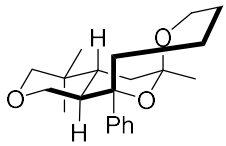


Substrate **1b** (15 mg, 1.0 eq.) was dissolved in DCM (0.5 ml), then 4Å molecular sieves (30 mg) followed by catalyst **3n** (0.2 eq.) were added. The reaction mixture was stirred at 30 °C and monitored by TLC (generally for 120h). When the reaction was completed, the mixture was purified by silica gel column to afford products **2b**.



Substrate **1c-u** (30 mg, 1.0 eq.) was dissolved in $ClCH_2CH_2Cl$ (1.0 ml), then 4Å molecular sieves (60 mg) followed by catalyst **3n** (0.2 eq.) were added. The reaction mixture was stirred at 30 °C and monitored by TLC (generally for 60-120h). When the reaction was completed, the mixture was purified by silica gel column to afford products **2c-u**.

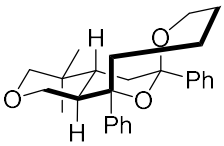
(4a*R*,12a*R*)-4,4,6-trimethyl-12-phenyldecahydro-1*H*,3*H*-6,12-epoxypyrano[4,3-*d*]oxecine (2a)



2a

White solid, m.p. 93-94 °C, 5.9 mg, 39% yield, 91% ee, dr > 20:1, determined by HPLC (Chiralcel column AD-H, hexane/i-PrOH = 96/4, flow rate 1.0 mL/min, UV detection at 254 nm), t_{major} = 7.7 min, t_{minor} = 4.4 min. **^{1}H NMR** (600 MHz, Acetone-d_6) δ 7.58 – 7.44 (m, 2H), 7.40 – 7.31 (m, 2H), 7.28 – 7.19 (m, 1H), 3.88 – 3.74 (m, 1H), 3.66 – 3.62 (m, 1H), 3.34 (dd, J = 10.9, 0.9 Hz, 1H), 3.29 (dd, J = 11.0, 4.4 Hz, 1H), 3.13 – 3.09 (m, 2H), 2.40 – 2.36 (m, 1H), 2.32 – 2.27 (m, 1H), 2.04 – 1.98 (m, 1H), 1.90 (dd, J = 13.2, 3.7 Hz, 1H), 1.78 – 1.68 (m, 2H), 1.58 – 1.52 (m, 2H), 1.48 (d, J = 13.0 Hz, 1H), 1.42 (s, 3H), 1.23 – 1.17 (m, 1H), 0.88 (s, 3H), 0.80 (s, 3H). **^{13}C NMR** (151 MHz, Acetone-d_6) δ 146.46, 128.63, 127.64, 127.56, 99.59, 80.72, 79.47, 69.28, 64.53, 46.76, 38.17, 36.43, 33.04, 32.51, 30.55, 26.81, 24.07, 22.83, 19.52. **HRMS** (ESI): m/z Calcd. For $C_{21}H_{30}O_3Na$ ([M+Na]$^+$): 353.2087, found: 353.2087. IR (KBr) ν 3433.0, 2959.5, 2930.5, 2855.6, 1627.7, 1460.6, 1261.8, 1150.6, 1057.3, 1019.3, 802.7, 702.8 cm^{-1}.

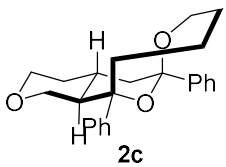
(4a*R*,12a*R*)-4,4-dimethyl-6,12-diphenyldecahydro-1*H*,3*H*-6,12-epoxypyrano[4,3-*d*]oxecine (2b)



2b

Colorless oil, $[\alpha]_D^{25}$ = -50.40 (c 0.20, DCM), 2.9 mg, 19% yield, 94% ee, dr > 20:1, determined by HPLC (Chiralcel column AD-H, hexane/i-PrOH = 97/3, flow rate 1.0 mL/min, UV detection at 254 nm), t_{major} = 6.5 min, t_{minor} = 4.5 min. **^{1}H NMR** (800 MHz, Chloroform-d) δ 7.59 (d, J = 7.8 Hz, 3H), 7.43 – 7.37 (m, 5H), 7.32 – 7.29 (m, 2H), 3.61 (d, J = 12.3 Hz, 1H), 3.45 – 3.41 (m, 2H), 3.32 (t, J = 12.4 Hz, 1H), 3.16 (t, J = 10.7 Hz, 2H), 2.53 (dd, J = 15.0, 7.8 Hz, 1H), 2.33 (dd, J = 15.0, 10.8 Hz, 2H), 2.18 – 2.11 (m, 2H), 2.05 – 1.98 (m, 2H), 1.77 (d, J = 12.8 Hz, 1H), 1.69 (dd, J = 10.3, 6.6 Hz, 1H), 1.47 (d, J = 8.1 Hz, 1H), 0.84 (d, J = 7.5 Hz, 6H). **^{13}C NMR** (201 MHz, Chloroform-d) δ 145.84, 145.31, 128.36, 128.33, 127.65, 127.29, 127.02, 101.60, 80.57, 79.62, 69.03, 66.95, 45.91, 38.27, 38.21, 32.81, 31.72, 30.20, 24.06, 22.12, 19.38. **HRMS** (ESI): m/z Calcd. For $C_{26}H_{32}O_3Na$ ([M+Na]$^+$): 415.2244, found: 415.2241.

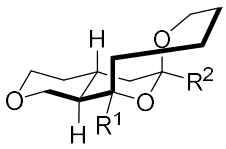
(4a*R*,12a*R*)-6,12-diphenyldecahydro-1*H*,3*H*-6,12-epoxypyrano[4,3-*d*]oxecine (2c)



2c

White solid, m.p. 169-170 °C, $[\alpha]_D^{25}$ = -41.24 (*c* 0.75, DCM), 19.2 mg, 64% yield, 98% ee, dr > 20:1, determined by HPLC (Chiralcel column AD-H, hexane/i-PrOH = 95/5, flow rate 1.0 mL/min, UV detection at 254 nm), t_{major} = 4.5 min, t_{minor} = 5.9 min. **^{1}H NMR** (500 MHz, Chloroform-d) δ 7.60 (d, *J* = 6.9 Hz, 4H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.37 (t, *J* = 7.9 Hz, 2H), 7.30 (q, *J* = 7.3 Hz, 2H), 3.91 (dd, *J* = 11.4, 3.2 Hz, 1H), 3.61 (dt, *J* = 12.1, 2.0 Hz, 1H), 3.48 – 3.40 (m, 2H), 3.35 (td, *J* = 12.4, 2.1 Hz, 1H), 3.16 (t, *J* = 11.0 Hz, 1H), 2.54 (dd, *J* = 14.3, 8.6 Hz, 1H), 2.45 – 2.36 (m, 1H), 2.32 (dd, *J* = 14.9, 11.2 Hz, 1H), 2.16 (dd, *J* = 13.7, 3.8 Hz, 1H), 1.82 (td, *J* = 11.2, 3.9 Hz, 2H), 1.75 – 1.65 (m, 3.7 Hz, 1H), 1.62 – 1.58 (m, 1H), 1.50 – 1.47 (m, 1H), 1.40 – 1.21 (m, 3H). **^{13}C NMR** (125 MHz, Chloroform-d) δ 145.45, 144.88, 128.33, 128.32, 127.64, 127.30, 127.05, 125.92, 101.20, 79.72, 68.53, 68.01, 66.75, 51.59, 45.10, 33.17, 31.82, 30.33, 30.01, 22.14. **HRMS** (ESI): m/z Calcd. For $C_{24}H_{28}O_3Na$ ($[M+Na]^+$): 387.1931, found: 387.1931. IR (KBr) *v* 3436.0, 2958.6, 2915.6, 1632.9, 1445.9, 1249.3, 1214.1, 1164.4, 1090.4, 1000.0, 767.2, 702.4 cm^{-1}.

(4a*R*,12a*R*)-12-(4-chlorophenyl)-6-phenyldecahydro-1*H*,3*H*-6,12-epoxypyrano[4, 3-*d*]oxecine (2d)

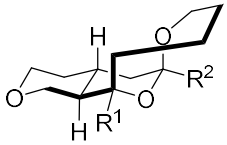


R^1=4-Cl-Ph, R^2=Ph

White solid, m.p. 184-185, $[\alpha]_D^{25}$ = -51.94 (*c* 0.90, DCM), 25.2 mg, 84% yield, 97% ee, dr > 20:1, determined by HPLC (Chiralcel column AD-H, hexane/i-PrOH = 97/3, flow rate 1.0 mL/min, UV detection at 254 nm), t_{major} = 5.6 min, t_{minor} = 6.3 min. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.43 (dd, *J* = 13.9, 8.1 Hz, 4H), 7.34 – 7.20 (m, 4H), 7.17 (dd, *J* = 14.4, 7.1 Hz, 1H), 3.80 (dd, *J* = 11.5, 4.4 Hz, 1H), 3.49 (dt, *J* = 11.9, 1.9 Hz, 1H), 3.37 – 3.27 (m, 2H), 3.21 (td, *J* = 12.4, 2.2 Hz, 1H), 3.03 (t, *J* = 11.0 Hz, 1H), 2.43 (dd, *J* = 15.0, 7.7 Hz, 1H), 2.33 – 2.22 (m, 1H), 2.13 (dd, *J* = 14.9, 10.5 Hz, 1H), 2.04 (dd, *J* = 13.8, 3.7 Hz, 1H), 1.65 (td, *J* = 10.5, 6.6 Hz, 2H), 1.60 – 1.52 (m, 1H), 1.40 – 1.33 (m, 2H), 1.23 – 1.14 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 145.20, 143.53, 133.15, 128.53, 128.45, 128.38, 127.73, 125.82, 101.22, 79.42, 68.51, 67.84, 66.75, 51.57, 45.01, 33.09, 31.70, 30.38, 29.98, 22.01. **HRMS** (EI): m/z Calcd. For $C_{24}H_{27}ClO_3$: 398.1643, found:398.1646. IR (KBr) *v* 3433.4, 2927.9, 2843.1, 1490.6,

1458.3, 1393.8, 1312.7, 1260.7, 1161.2, 1002.7, 823.8, 703.7 cm^{-1}.

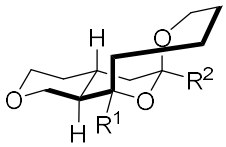
(4a*R*,12a*R*)-12-(4-bromophenyl)-6-phenyldecahydro-1*H*,3*H*-6,12-epoxypyrano[4,3-*d*]oxecine (2e)



R1=4-Br-Ph,R2=Ph

White solid, m.p. 162-163, $[\alpha]_D^{25}$ = -47.37 (*c* 0.95, DCM), 20.4 mg, 68% yield, 98% ee, dr > 20:1, determined by HPLC (Chiralcel column AD-H, hexane/i-PrOH = 95/5, flow rate 1.0 mL/min, UV detection at 254 nm), t_{major} = 5.2 min, t_{minor} = 5.8 min. **^{1}H NMR** (500 MHz, Chloroform-d) δ 7.54 (d, *J* = 8.6 Hz, 4H), 7.47 (d, *J* = 8.7 Hz, 2H), 7.37 (t, *J* = 7.9 Hz, 2H), 7.31 – 7.27 (m, 1H), 3.91 (dd, *J* = 11.4, 4.8 Hz, 1H), 3.61 (dt, *J* = 12.1, 2.0 Hz, 1H), 3.47 – 3.39 (m, 2H), 3.32 (td, *J* = 12.3, 2.1 Hz, 1H), 3.15 (t, *J* = 11.0 Hz, 1H), 2.57 – 2.51 (m, 1H), 2.43 – 2.35 (m, 1H), 2.24 (dd, *J* = 14.4, 10.6 Hz, 1H), 2.15 (dd, *J* = 13.8, 3.8 Hz, 1H), 1.75 (td, *J* = 11.0, 3.7 Hz, 2H), 1.71 – 1.64 (m, 1H), 1.51 – 1.45 (m, 2H), 1.39 – 1.18 (m, 3H). **^{13}C NMR** (125 MHz, Chloroform-d) δ 145.18, 144.08, 131.42, 128.92, 128.38, 127.74, 125.82, 121.34, 101.21, 79.47, 68.52, 67.83, 66.76, 51.52, 44.99, 33.09, 31.70, 30.33, 29.98, 22.00. **HRMS** (EI): m/z Calcd. For $C_{24}H_{27}BrO_3$: 442.1138, found: 442.1135. IR (KBr) ν 3432.4, 2927.1, 2843.3, 1586.2, 1487.3, 1389.1, 1312.7, 1260.4, 1161.1, 1000.8, 821.4, 704.3 cm^{-1}.

(4a*R*,12a*R*)-6-phenyl-12-(*p*-tolyl)decahydro-1*H*,3*H*-6,12-epoxypyrano[4,3-*d*]oxecine (2f)

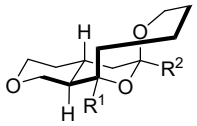


R1=4-Me-Ph,R2=Ph

White solid, m.p. 167-168 ºC, $[\alpha]_D^{25}$ = -53.68 (*c* 1.22, DCM), 28.2 mg, 94% yield, 97% ee, dr > 20:1, determined by HPLC (Chiralcel column AD-H, hexane/i-PrOH = 95/5, flow rate 1.0 mL/min, UV detection at 254 nm), t_{major} = 4.3 min, t_{minor} = 5.6 min. **^{1}H NMR** (500 MHz, Chloroform-d) δ 7.63 – 7.55 (m, 2H), 7.48 (d, *J* = 7.8 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.23 (d, *J* = 7.8 Hz, 2H), 3.91 (dd, *J* = 11.3, 4.5 Hz, 1H), 3.60 (dt, *J* = 12.1, 1.9 Hz, 1H), 3.43 (dd, *J* = 11.0, 4.1 Hz, 2H), 3.33 (t, *J* = 12.4 Hz, 1H), 3.15 (t, *J* = 11.0 Hz, 1H), 2.52 (dd, *J* = 14.9, 7.8 Hz, 1H), 2.43 – 2.39 (m, 1H), 2.38 (s, 3H), 2.29 (dd, *J* = 14.9, 10.5 Hz, 1H), 2.15 (dd, *J* = 13.7, 3.7 Hz, 1H), 1.81 (td, *J* = 11.3, 3.9 Hz, 2H), 1.72 – 1.65 (m, 1H), 1.49 (t, *J* = 13.0 Hz, 2H), 1.39 – 1.25 (m, 3H). **^{13}C NMR** (125 MHz, Chloroform-d) δ 145.49, 141.93, 136.86, 129.00, 128.29,

127.59, 126.97, 125.93, 101.14, 79.55, 68.52, 68.05, 66.71, 51.59, 45.08, 33.16, 31.85, 30.38, 29.99, 22.19, 21.11. **HRMS** (ESI): m/z Calcd. For $C_{25}H_{30}O_3K$ ($[M+K]^+$): 417.1827, found: 417.1824. IR (KBr) *v* 3433.4, 2922.6, 2845.8, 1512.5, 1446.7, 1360.8, 1252.0, 1166.8, 1087.4, 902.1, 807.6, 702.9 cm^{-1}.

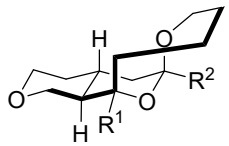
(4a*R*,12a*R*)-12-(4-(tert-butyl)phenyl)-6-phenyldecahydro-1*H*,3*H*-6,12-epoxypyrano[4,3-*d*]oxecine (2g)



R^1=4-C(Me)$_3$-Ph,R^2=Ph

White solid, m.p. 172-173 ºC, $[\alpha]_D^{25}$ = -36.38 (*c* 1.10, DCM), 15.9 mg, 53% yield, 84% ee, dr > 20:1, determined by HPLC (Chiralcel column AD-H, hexane/i-PrOH = 97/3, flow rate 1.0 mL/min, UV detection at 254 nm), t_{major} = 4.5 min, t_{minor} = 4.1 min. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.69 – 7.46 (m, 4H), 7.42 (d, *J* = 8.6 Hz, 2H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 1H), 3.91 (dd, *J* = 11.4, 4.4 Hz, 1H), 3.61 (dt, *J* = 12.3, 3.8 Hz, 1H), 3.50 – 3.40 (m, 2H), 3.38 – 3.30 (m, 1H), 3.15 (t, *J* = 11.0 Hz, 1H), 2.51 (dd, *J* = 14.8, 7.7 Hz, 1H), 2.45 – 2.35 (m, 1H), 2.31 (dd, *J* = 14.7, 10.3 Hz, 1H), 2.15 (dd, *J* = 13.7, 3.7 Hz, 1H), 1.84 – 1.76 (m, 2H), 1.73 – 1.64 (m, 1H), 1.53 – 1.44 (m, 2H), 1.34 (s, 9H), 1.31 – 1.23 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 149.99, 145.54, 141.76, 128.31, 127.60, 126.67, 125.94, 125.21, 101.19, 79.55, 68.54, 68.08, 66.73, 51.63, 45.13, 34.55, 33.19, 31.87, 31.52, 30.37, 29.99, 22.18. **HRMS** (EI): m/z Calcd. For $C_{28}H_{36}O_3$: 420.2659, found: 420.2660. IR (KBr) *v* 3435.4, 2956.7, 1632.2, 1461.0, 1362.2, 1250.6, 1166.1, 1087.6, 1004.7, 901.9, 825.9, 701.2 cm^{-1}.

(4a*R*,12a*R*)-12-(3-methoxyphenyl)-6-phenyldecahydro-1*H*,3*H*-6,12-epoxypyrano[4,3-*d*]oxecine (2h)

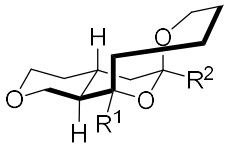


R^1=3-MeO-Ph,R^2=Ph

White solid, m.p. 169-170 ºC, $[\alpha]_D^{25}$ = -50.71 (*c* 1.50, DCM), 15.3 mg, 51% yield, 98% ee, dr > 20:1, determined by HPLC (Chiralcel column AD-H, hexane/i-PrOH = 95/5, flow rate 1.0 mL/min, UV detection at 254 nm), t_{major} = 7.6 min, t_{minor} = 7.3 min. **^{1}H NMR** (500 MHz, Chloroform-d) δ 7.74 – 7.50 (m, 2H), 7.38 – 7.34 (m, 2H), 7.34 – 7.26 (m, 2H), 7.19 (d, *J* = 2.2 Hz, 1H), 7.14 (d, *J* = 6.0 Hz, 1H), 6.85 (dd, *J* = 8.2, 2.5 Hz, 1H), 3.91 (dd, *J* = 11.3, 4.5 Hz, 1H), 3.87 (s, 3H), 3.61 (dt, *J* = 12.1, 2.0 Hz, 1H), 3.44 (td, *J* = 11.5, 2.7 Hz, 2H), 3.34 (td, *J* = 12.4, 2.0 Hz, 1H), 3.15 (t, *J* = 11.0 Hz, 1H), 2.53 (dd,

J = 15.0, 7.7 Hz, 1H), 2.43 – 2.35 (m, 1H), 2.28 (dd, *J* = 14.9, 10.6 Hz, 1H), 2.15 (dd, *J* = 13.8, 3.7 Hz, 1H), 1.84 – 1.77 (m, 2H), 1.74 – 1.64 (m, 1H), 1.60 (d, *J* = 11.2 Hz, 1H), 1.47 (d, *J* = 12.6 Hz, 1H), 1.39 – 1.24 (m, 3H). **^{13}C NMR** (125 MHz, Chloroform-d) δ 159.71, 146.69, 145.42, 129.16, 128.34, 127.64, 125.90, 119.41, 113.82, 112.03, 101.18, 79.72, 68.51, 68.03, 66.75, 55.39, 51.44, 45.06, 33.16, 31.78, 30.50, 29.99, 22.17. **HRMS** (ESI): m/z Calcd. For $C_{25}H_{30}O_4Na$ ($[M+Na]^+$): 417.2036, found: 417.2035. IR (KBr) *v* 3434.5, 2922.9, 1604.5, 1489.7, 1461.1, 1315.4, 1257.0, 1158.4, 1088.4, 1015.0, 903.4, 765.7 cm^{-1}.

(4a*R*,12a*R*)-6-(4-fluorophenyl)-12-phenyldecahydro-1*H*,3*H*-6,12-epoxypyrano[4, 3-*d*] oxecine (2i)

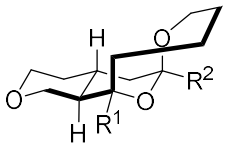


R^1=Ph, R^2=4-F-Ph

White solid, m.p. 163-164 ºC, $[\alpha]_D^{25}$ = -48.07 (*c* 0.86, DCM), 24.3 mg, 81% yield, 99% ee, dr > 20:1, determined by HPLC (Chiralcel column AD-H, hexane/i-PrOH = 97/3, flow rate 1.0 mL/min, UV detection at 254 nm), t_{major} = 4.8 min, t_{minor} = 6.3 min. **^{1}H NMR** (500 MHz, Chloroform-d) δ 7.57 (dd, *J* = 8.4, 1.3 Hz, 4H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.33 – 7.29 (m, 1H), 7.06 – 7.02 (m, 2H), 3.91 (dd, *J* = 11.4, 3.8 Hz, 1H), 3.58 (dt, *J* = 12.1, 2.0 Hz, 1H), 3.50 – 3.38 (m, 2H), 3.31 (td, *J* = 12.4, 2.1 Hz, 1H), 3.15 (t, *J* = 11.0 Hz, 1H), 2.52 (dd, *J* = 14.4, 7.2 Hz, 1H), 2.44 – 2.36 (m, 1H), 2.35 – 2.28 (m, 1H), 2.14 (dd, *J* = 13.8, 3.7 Hz, 1H), 1.84 – 1.77 (m, 2H), 1.75 – 1.65 (m, 1H), 1.62 – 1.60 (m, 1H), 1.49 – 1.42 (m, 2H), 1.37 – 1.26 (m, 2H). **^{13}C NMR** (125 MHz, Chloroform-d) δ 162.34 (*J* = 245.6 Hz), 144.71, 141.31 (*J* = 3.1 Hz), 128.36, 127.71 (*J* = 8.1 Hz), 127.37, 126.99, 115.07 (*J* = 21.3 Hz), 100.89, 79.86, 68.50, 67.96, 66.63, 51.54, 45.16, 33.13, 31.77, 30.26, 29.97, 22.13. **HRMS** (EI): m/z Calcd. For $C_{24}H_{27}FO_3$: 382.1939, found: 382.1937. IR (KBr) *v* 3433.81, 2964.5, 1505.1, 1456.3, 1261.4, 1261.4, 1218.4, 1163.9, 1009.1, 901.7, 803.5, 698.4 cm^{-1}.

(4a*R*,12a*R*)-6-(4-chlorophenyl)-12-phenyldecahydro-1*H*,3*H*-6,12-epoxypyrano[4, 3-*d*]oxecine (2j)

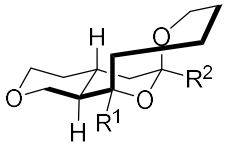
White solid, m.p. 186-187 ºC, $[\alpha]_D^{25}$ = -35.64 (*c* 1.04, DCM), 24.9 mg, 83% yield, 99%



R1=Ph,R2=4-Cl-Ph

ee, dr > 20:1, determined by HPLC (Chiralcel column AD-H, hexane/i-PrOH = 97/3, flow rate 1.0 mL/min, UV detection at 254 nm), t_{major} = 4.8 min, t_{minor} = 6.7 min. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.48 (t, J = 6.8 Hz, 4H), 7.34 (t, J = 7.6 Hz, 2H), 7.24 (dd, J = 13.9, 8.1 Hz, 3H), 3.84 (dd, J = 11.5, 4.5 Hz, 1H), 3.51 (dt, J = 11.9, 2.0 Hz, 1H), 3.41 – 3.29 (m, 2H), 3.22 (td, J = 12.3, 2.1 Hz, 1H), 3.07 (t, J = 11.0 Hz, 1H), 2.44 (dd, J = 14.9, 7.7 Hz, 1H), 2.37 – 2.27 (m, 1H), 2.24 (dd, J = 14.9, 10.5 Hz, 1H), 2.05 (dd, J = 13.7, 3.8 Hz, 1H), 1.73 (td, J = 11.1, 3.9 Hz, 2H), 1.64 – 1.57 (m, 1H), 1.52 (d, J = 11.4 Hz, 1H), 1.44 – 1.34 (m, 2H), 1.28 – 1.17 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 144.65, 144.01, 133.48, 128.49, 128.37, 127.46, 127.39, 126.98, 100.84, 79.89, 68.48, 67.93, 66.72, 51.53, 44.96, 33.12, 31.75, 30.25, 29.94, 22.12. **HRMS** (EI): m/z Calcd. For $C_{24}H_{27}ClO_3$: 398.1643, found: 398.1644. IR (KBr) ν 3433.3, 2921.1, 1488.3, 1461.4, 1395.7, 1251.9, 1163.1, 1008.9, 902.8, 835.3, 741.9, 699.5 cm^{-1}.

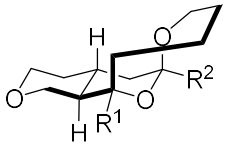
(4a*R*,12a*R*)-6-(3-chlorophenyl)-12-phenyldecahydro-1*H*,3*H*-6,12-epoxypyrano[4,3-*d*]oxecine (2k)



R1=Ph,R2=3-Cl-Ph

White solid, m.p. 186-187 °C, $[\alpha]_D^{25}$ = -55.59 (c 1.05, DCM), 24.0 mg, 80% yield, 98% ee, dr > 20:1, determined by HPLC (Chiralcel column AD-H, hexane/i-PrOH = 97/3, flow rate 1.0 mL/min, UV detection at 254 nm), t_{major} = 5.1 min, t_{minor} = 6.7 min. **^{1}H NMR** (500 MHz, Chloroform-d) δ 7.56 (d, J = 8.2 Hz, 2H), 7.42 (t, J = 7.8 Hz, 3H), 7.40 – 7.21 (m, 4H), 3.91 (dd, J = 11.7, 4.2 Hz, 1H), 3.61 (dt, J = 12.0, 2.0 Hz, 1H), 3.48 – 3.38 (m, 2H), 3.30 (td, J = 12.4, 2.1 Hz, 1H), 3.14 (t, J = 11.0 Hz, 1H), 2.51 (dd, J = 14.7, 8.0 Hz, 1H), 2.44 – 2.35 (m, 1H), 2.32 (dd, J = 14.9, 10.6 Hz, 1H), 2.13 (dd, J = 13.7, 3.7 Hz, 1H), 1.84 – 1.78 (m, 2H), 1.74 – 1.65 (m, 1H), 1.62 – 1.58 (m, 1H), 1.50 – 1.43 (m, 2H), 1.35 – 1.26 (m, 2H). **^{13}C NMR** (125 MHz, Chloroform-d) δ 147.60, 144.57, 134.33, 129.71, 128.40, 127.84, 127.42, 127.00, 126.32, 124.19, 100.76, 79.97, 68.49, 67.94, 66.86, 51.52, 44.88, 33.12, 31.73, 30.24, 29.95, 22.13. **HRMS** (EI): m/z Calcd. For $C_{24}H_{27}ClO_3$: 398.1643, found: 398.1641. IR (KBr) ν 3432.7, 2920.0, 1573.8, 1365.0, 1416.9, 1248.4, 1168.2, 1084.9, 1010.9, 894.9, 797.2, 701.9 cm^{-1}.

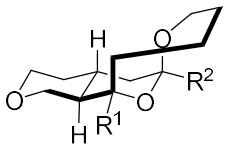
(4a*R*,12a*R*)-6-(3-bromophenyl)-12-phenyldecahydro-1*H*,3*H*-6,12-epoxypyrano[4,3-*d*]oxecine (2l)



R1=Ph,R2=3-Br-Ph

White solid, m.p. 161-162 ºC, $[\alpha]_D^{25}$ = -48.28 (*c* 1.03, DCM), 26.1 mg, 87% yield, 98% ee, dr > 20:1, determined by HPLC (Chiralcel column AD-H, hexane/i-PrOH = 97/3, flow rate 1.0 mL/min, UV detection at 254 nm), t_{major} = 5.3 min, t_{minor} = 7.2 min. **^{1}H NMR** (500 MHz, Chloroform-d) δ 7.56 (d, *J* = 7.0 Hz, 4H), 7.42 (t, *J* = 7.8 Hz, 3H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.23 (d, *J* = 7.9 Hz, 1H), 3.91 (dd, *J* = 11.4, 4.5 Hz, 1H), 3.61 (dt, *J* = 12.3, 2.4 Hz, 1H), 3.47 – 3.38 (m, 2H), 3.30 (t, *J* = 11.3 Hz, 1H), 3.14 (t, *J* = 11.0 Hz, 1H), 2.51 (dd, *J* = 15.0, 7.7 Hz, 1H), 2.43 – 2.36 (m, 1H), 2.31 (dd, *J* = 14.9, 10.5 Hz, 1H), 2.12 (dd, *J* = 13.7, 3.7 Hz, 1H), 1.94 – 1.77 (m, 2H), 1.74 – 1.70 (m, 1H), 1.61 (dt, *J* = 3.9, 1.8 Hz, 1H), 1.52 – 1.43 (m, 2H), 1.38 – 1.26 (m, 2H). **^{13}C NMR** (125 MHz, Chloroform-d) δ 147.83, 144.56, 130.77, 130.01, 129.25, 128.39, 127.41, 126.99, 124.70, 122.58, 100.67, 79.97, 68.48, 67.92, 66.85, 51.50, 44.89, 33.11, 31.72, 30.23, 29.94, 22.12. **HRMS** (EI): m/z Calcd. For $C_{24}H_{27}BrO_3$: 442.1138, found: 442.1137. IR (KBr) *v* 3433.0, 2919.0, 1467.8, 1247.3, 1208.5, 1167.1, 1087.1, 1009.9, 892.6, 795.7, 741.8, 700.5 cm^{-1}.

(4a*R*,12a*R*)-6-(3-fluorophenyl)-12-phenyldecahydro-1*H*,3*H*-6,12-epoxypyrano[4,3-*d*]oxecine (2m)

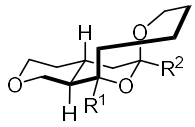


R1=Ph,R2=3-F-Ph

White solid, m.p. 181-182 ºC, $[\alpha]_D^{25}$ = -56.80 (*c* 0.82, DCM), 23.4 mg, 78% yield, 98% ee, dr > 20:1, determined by HPLC (Chiralcel column AD-H, hexane/i-PrOH = 97/3, flow rate 1.0 mL/min, UV detection at 254 nm), t_{major} = 5.0 min, t_{minor} = 6.5 min. **^{1}H NMR** (500 MHz, Chloroform-d) δ 7.59 – 7.55 (m, 2H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.39 – 7.26 (m, 4H), 6.98 (td, *J* = 8.8, 2.6 Hz, 1H), 3.91 (dd, *J* = 11.4, 3.3 Hz, 1H), 3.62 (dt, *J* = 11.8, 1.9 Hz, 1H), 3.50 – 3.37 (m, 2H), 3.32 (td, *J* = 12.4, 2.1 Hz, 1H), 3.15 (t, *J* = 11.0 Hz, 1H), 2.52 (dd, *J* = 15.0, 6.5 Hz, 1H), 2.40 (qt, *J* = 11.5, 3.8 Hz, 1H), 2.32 (dd, *J* = 14.3, 10.0 Hz, 1H), 2.13 (dd, *J* = 13.7, 3.8 Hz, 1H), 1.82 (td, *J* = 11.1, 3.8 Hz, 2H), 1.74 – 1.65 (m, 1H), 1.62 – 1.60 (m, 1H), 1.51 – 1.45 (m, 2H), 1.38 – 1.26 (m, 2H). **^{13}C NMR** (125 MHz, Chloroform-d) δ 164.01, 162.06, 148.23 (*J* = 6.5 Hz), 144.60, 129.87

(J = 8.0 Hz), 128.38, 127.39, 126.99, 121.63, 114.51 (J = 21.2 Hz), 100.76 (J = 2.1 Hz), 79.93, 68.49, 67.94, 66.84, 51.52, 44.84, 33.12, 31.74, 30.25, 29.94, 22.12. **HRMS** (EI): m/z Calcd. For $C_{24}H_{27}FO_3$: 382.1939, found: 382.1939. IR (KBr) ν 3434.7, 2924.8, 1590.0, 1438.0, 1362.4, 1260.7, 1169.8, 1087.1, 1012.6, 882.5, 796.0, 702.2 cm^{-1}.

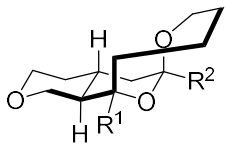
(4aR,12aR)-6-(2-fluorophenyl)-12-phenyldecahydro-1H,3H-6,12-epoxypyrano-[4,3-d]oxecine (2n)



R^1=Ph,R^2=2-F-Ph

Colorless oil, $[\alpha]_D^{25}$= -56.46 (c 1.64, DCM), 17.4 mg, 61% yield, 99% ee, determined by HPLC (CHIRAPAK AD-H, hexane/i-PrOH = 95/5, flowrate 1.0 mL/min, UV detection at 254 nm), t_{major} = 5.0 min, t_{minor} = 6.1 min.**^{1}H NMR** (500 MHz, $CDCl_3$) 7.80 (br, 1H), 7.57 (d, J = 5.9 Hz, 2H), 7.41 (t, J = 7.2 Hz, 2H), 7.31-7.27 (m, 2H), 7.13 (t, J = 7.4 Hz, 1H), 7.05 (t, J = 9.9 Hz, 1H), 3.92 (dd, J = 4.2, 11.3 Hz, 1H), 3.62 (br, 1H), 3.47-3.44 (m, 1H), 3.42-3.38 (m, 2H), 3.15 (t, J = 11.0 Hz, 1H), 2.60 (br, 1H), 2.54 (dd, J = 7.8, 14.9 Hz, 1H), 2.45-2.42 (m, 1H), 2.32 (dd, J = 10.6, 14.7 Hz, 1H), 1.84-1.78 (m, 2H), 1.75-1.70 (m, 1H), 1.64-1.61 (m, 1H), 1.57-1.54 (m, 1H), 1.51-1.49 (m, 1H), 1.38-1.36 (m, 1H), 1.32-1.30 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) 160.79, 144.57, 131.24, 129.56 (J_{C-F} = 8.5 Hz), 129.05, 128.21, 127.20, 126.94, 123.70, 116.32, 79.96, 68.42, 67.82, 66.00, 51.70, 41.96, 32.99, 31.34, 30.13, 29.45, 22.09. **HRMS** (ESI): m/z Calcd. For C24H28FO3 ($[M+H]^+$): 383.2023, found: 383.2023.

(4a*R*,12a*R*)-12-phenyl-6-(4-(trifluoromethyl)phenyl)decahydro-1*H*,3*H*-6,12-epoxypyrano[4,3-*d*]oxecine (2o)

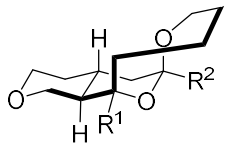


R^1=Ph,R^2=4-CF_3-Ph

White solid, m.p. 169-170 ºC, $[\alpha]_D^{25}$ = -41.06 (c 0.77, DCM), 24.9 mg, 83% yield, 99% ee, dr > 20:1, determined by HPLC (Chiralcel column AD-H, hexane/i-PrOH = 97/3, flow rate 1.0 mL/min, UV detection at 254 nm), t_{major} = 5.4 min, t_{minor} = 5.0 min. **^{1}H NMR** (500 MHz, Chloroform-d) δ 7.77 – 7.58 (m, 4H), 7.58 – 7.55 (m, 2H), 7.45 – 7.40 (m, 2H), 7.32 (t, J = 7.3 Hz, 1H), 3.92 (dd, J = 11.5, 3.5 Hz, 1H), 3.61 (dt, J = 12.1, 1.9 Hz, 1H), 3.48 – 3.39 (m, 2H), 3.27 (td, J = 12.3, 2.0 Hz, 1H), 3.16 (t, J = 11.0 Hz, 1H), 2.52 (dd, J = 14.9, 7.9 Hz, 1H), 2.46 – 2.37 (m, 1H), 2.33 (dd, J = 15.6, 10.5 Hz, 1H), 2.15 (dd, J = 13.7, 3.8 Hz, 1H), 1.83 (td, J = 11.1, 3.8 Hz, 2H), 1.74 – 1.66 (m, 1H), 1.63 –

1.59 (m, 1H), 1.50 – 1.43 (m, 2H), 1.34 – 1.26 (m, 2H). **^{13}C NMR** (125 MHz, Chloroform-d) δ 149.32, 144.53, 129.92 (J = 32.2 Hz), 128.41, 127.46, 126.98, 126.42, 125.43 (J = 3.6 Hz), 125.37 (J = 3.8 Hz), 100.85, 80.01, 68.48, 67.92, 66.96, 51.52, 44.81, 33.11, 31.74, 30.26, 29.93, 22.13. **HRMS** (EI): m/z Calcd. For $C_{25}H_{27}F_3O_3$: 432.1907, found: 432.1906. IR (KBr) v 3434.5, 2929.8, 1619.7, 1441.9, 1408.1, 1325.4, 1160.0, 1105.6, 1066.6, 1010.7, 841.5, 697.8 cm^{-1}.

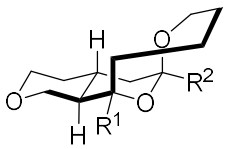
(4a*R*,12a*R*)-6-(4-methoxyphenyl)-12-phenyldecahydro-1*H*,3*H*-6,12-epoxypyrano [4,3-*d*]oxecine (2p)



R1=Ph,R2=4-MeO-Ph

White solid, m.p. 169-170 ºC, $[\alpha]_D^{25}$ = -36.16(c 1.10, DCM), 15.0 mg, 50% yield, 98% ee, dr > 20:1, determined by HPLC (Chiralcel column AD-H, hexane/i-PrOH = 98.5/1.5, flow rate 1.0 mL/min, UV detection at 254 nm), t_{major} = 5.6 min, t_{minor} = 10.3 min. **^{1}H NMR** (500 MHz, Chloroform-d) δ 7.61 – 7.47 (m, 4H), 7.41 (t, J = 7.7 Hz, 2H), 7.30 (t, J = 7.4 Hz, 1H), 6.90 (d, J = 9.0 Hz, 2H), 3.91 (dd, J = 11.2, 4.4 Hz, 1H), 3.81 (s, 3H), 3.62 – 3.55 (m, 1H), 3.48 – 3.39 (m, 2H), 3.36 (td, J = 12.4, 2.1 Hz, 1H), 3.15 (t, J = 11.0 Hz, 1H), 2.52 (dd, J = 14.7, 8.0 Hz, 1H), 2.43 – 2.36 (m, 1H), 2.31 (dd, J = 14.9, 10.5 Hz, 1H), 2.14 (dd, J = 13.8, 3.7 Hz, 1H), 1.82 – 1.76 (m, 2H), 1.74 – 1.64 (m, 1H), 1.63 – 1.59 (m, 1H), 1.48 (dd, J = 13.9, 12.2 Hz, 2H), 1.35 – 1.25 (m, 2H). **^{13}C NMR** (125 MHz, Chloroform-d) δ 159.07, 144.93, 137.81, 128.30, 127.27, 127.13, 127.04, 113.60, 101.07, 79.68, 68.53, 68.02, 66.50, 55.41, 51.59, 45.26, 33.17, 31.83, 30.32, 30.02, 22.13. **HRMS** (EI): m/z Calcd. For $C_{25}H_{30}O_4$: 394.2139, found: 394.2136. IR (KBr) v 3433.9, 2924.4, 1510.3, 1460.6, 1247.6, 1164.6, 1107.1, 1087.9, 1006.3, 900.2, 837.9, 700.1 cm^{-1}.

(4a*R*,12a*R*)-6-(3-methoxyphenyl)-12-phenyldecahydro-1*H*,3*H*-6,12-epoxypyrano [4,3-*d*]oxecine (2q)

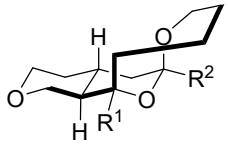


R1=Ph,R2=3-MeO-Ph

White solid, m.p. 141-142 ºC, $[\alpha]_D^{25}$ = -54.40 (c 1.39, DCM), 23.4 mg, 78% yield, 98% ee, dr > 20:1, determined by HPLC (Chiralcel column AD-H, hexane/i-PrOH = 97/3, flow rate 1.0 mL/min, UV detection at 254 nm), t_{major} = 5.9 min, t_{minor} = 8.4 min. **^{1}H NMR** (500 MHz, Chloroform-d) δ 7.59 (d, J = 8.3 Hz, 2H), 7.41 (t, J = 7.8 Hz, 2H), 7.29 (td,

J = 7.7, 2.2 Hz, 4H), 6.83 (dd, *J* = 8.6, 2.2 Hz, 1H), 3.91 (dd, *J* = 10.6, 4.4 Hz, 1H), 3.83 (s, 3H), 3.63 (dt, *J* = 12.0, 2.0 Hz, 1H), 3.49 – 3.40 (m, 2H), 3.36 (td, *J* = 12.4, 2.1 Hz, 1H), 3.16 (t, *J* = 11.0 Hz, 1H), 2.52 (dd, *J* = 15.0, 8.2 Hz, 1H), 2.43 – 2.35 (m, 1H), 2.31 (dd, *J* = 14.3, 10.5 Hz, 1H), 2.15 (dd, *J* = 13.8, 3.7 Hz, 1H), 1.81 (td, *J* = 11.2, 3.8 Hz, 2H), 1.74 – 1.65 (m, 1H), 1.63 – 1.59 (m, 1H), 1.54 – 1.44 (m, 2H), 1.38 – 1.26 (m, 2H). **^{13}C NMR** (125 MHz, Chloroform-d) δ 159.58, 147.09, 144.74, 129.26, 128.18, 127.15, 126.90, 118.28, 118.24, 112.79, 100.96, 79.62, 68.40, 67.86, 66.67, 55.19, 51.44, 44.84, 33.03, 31.69, 30.19, 29.87, 22.00. **HRMS** (EI): m/z Calcd. For $C_{25}H_{30}O_4$: 394.2139, found: 394.2138. IR (KBr) *v* 3448.6, 2921.8, 1587.1, 1481.0, 1314.9, 1260.9, 1170.6, 1089.9, 1021.7, 886.5, 804.8, 701.3 cm^{-1}.

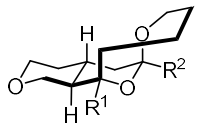
(4a*R*,12a*R*)-12-phenyl-6-(*p*-tolyl)decahydro-1*H*,3*H*-6,12-epoxypyrano[4,3-*d*]oxecine (2r)



R^1=Ph,R^2=4-Me-Ph

White solid, m.p. 136-137 ºC, $[\alpha]_D^{25}$ = -41.14 (*c* 0.86, DCM), 22.8 mg, 76% yield, 99% ee, dr > 20:1, determined by HPLC (Chiralcel column AD-H, hexane/i-PrOH = 99/1, flow rate 1.0 mL/min, UV detection at 254 nm), t_{major} = 7.8 min, t_{minor} = 7.1 min. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.53 (d, *J* = 7.4 Hz, 2H), 7.43 (d, *J* = 7.7 Hz, 2H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.24 (t, *J* = 7.4 Hz, 1H), 7.12 (d, *J* = 7.9 Hz, 2H), 3.85 (dd, *J* = 11.5, 4.5 Hz, 1H), 3.54 (dt, *J* = 11.7, 1.9 Hz, 1H), 3.42 – 3.34 (m, 2H), 3.30 (td, *J* = 12.4, 2.1 Hz, 1H), 3.10 (t, *J* = 11.0 Hz, 1H), 2.47 (dd, *J* = 14.9, 7.6 Hz, 1H), 2.39 – 2.31 (m, 1H), 2.30 (s, 3H), 2.28 – 2.21 (m, 1H), 2.09 (dd, *J* = 13.7, 3.7 Hz, 1H), 1.78 – 1.69 (m, 2H), 1.66 – 1.58 (m, 1H), 1.54 (d, *J* = 10.8 Hz, 1H), 1.43 (dd, *J* = 13.8, 12.2 Hz, 2H), 1.30 – 1.21 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 144.95, 142.58, 137.26, 129.01, 128.29, 127.25, 127.05, 125.84, 101.18, 79.66, 68.52, 68.01, 66.63, 51.61, 45.18, 33.18, 31.82, 30.34, 30.01, 22.14, 21.24. **HRMS** (ESI): m/z Calcd. For $C_{25}H_{30}O_3Na$ ([M+Na]$^+$): 401.2087, found: 401.2085. IR (KBr) *v* 3433.8, 2921.1, 2850.6, 1459.6, 1313.2, 1261.2, 1162.9, 1088.5, 1010.3, 901.1, 802.9, 699.1 cm^{-1}.

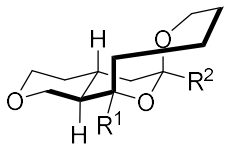
(4aR,12aR)-12-phenyl-6-(o-tolyl)decahydro-1H,3H-6,12-epoxypyrano[4,3-d]oxecine (2s)



R1=Ph,R2=2-Me-Ph

White solid, m.p. 132-133 ºC, $[\alpha]_D^{25}$= -43.11 (*c* 0.65, DCM), 13.3 mg, 51% yield, 99% ee, determined by HPLC (CHIRAPAK OD-H, hexane/i-PrOH = 97/3, flowrate 1.0 mL/min, UV detection at 254 nm), t_{major} = 4.1 min, t_{minor} = 5.9 min. **^{1}H NMR** (500 MHz, $CDCl_3$) 7.90-7.89 (m, 1H), 7.59 (d, *J* = 7.5 Hz, 2H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.21-7.18 (m, 2H), 7.14-7.13 (m,1H), 3.91 (dd, *J* = 4.3, 11.2 Hz, 1H), 3.58-3.56 (m, 1H), 3.49-3.45 (m, 1H), 3.42-3.38 (m, 1H), 3.37-3.32 (m, 1H), 3.15 (t, *J* = 11.0 Hz, 1H) , 2.55 (dd, *J* = 8.1, 14.1 Hz, 1H), 2.54 (s, 3H), 2.50-2.47 (m, 1H), 2.42-2.38 (m, 1H), 2.31 (dd, *J* = 10.6, 14.7 Hz, 1H), 1.85-1.81 (m, 2H), 1.70-1.67 (m, 1H), 1.62-1.61 (m, 2H), 1.49-1.47 (m, 1H), 1.41-1.38 (m, 1H), 1.31-1.30 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) 144.90, 142.42, 134.76, 132.12, 128.20, 127.68, 127.54, 127.13, 127.06, 125.77, 101.08, 79.78, 68.43, 67.90, 65.38, 51.82, 41.84, 33.09, 31.41, 30.14, 29.48, 22.18, 20.45. **HRMS** (ESI): m/z Calcd. For C25H30O3Na ($[M+Na]^+$):401.2087, found: 401.2087. IR (KBr) *ν* 3435.8, 2924.4, 1639.6, 1446.3, 1384.0, 1362.5, 1162.2, 1045.7, 700.2 cm^{-1}.

(4a*R*,12a*R*)-6-methyl-12-phenyldecahydro-1*H*,3*H*-6,12-epoxypyrano[4,3-*d*]oxecine (2t)

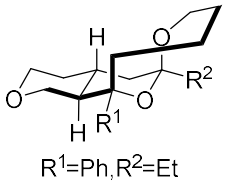


R1=Ph,R2=Me

White solid, m.p. 92-93 ºC, $[\alpha]_D^{25}$ = -5.69 (*c* 0.80, DCM), 22.8 mg, 76% yield, 97% ee, dr > 20:1, determined by HPLC (Chiralcel column AD-H, hexane/i-PrOH = 95/5, flow rate 1.0 mL/min, UV detection at 254 nm), t_{major} = 6.3 min, t_{minor} = 5.9 min. **^{1}H NMR** (400 MHz, Chloroform-d) *δ* 7.34 (d, *J* = 7.8 Hz, 2H), 7.25 (t, *J* = 7.7 Hz, 2H), 7.21 – 7.12 (m, 1H), 3.85 – 3.76 (m, 2H), 3.67 – 3.60 (m, 1H), 3.37 – 3.28 (m, 2H), 3.01 (t, *J* = 11.0 Hz, 1H), 2.30 (dd, *J* = 14.9, 6.6 Hz, 1H), 2.20 – 2.10 (m, 2H), 1.87 (dd, *J* = 13.6, 3.9 Hz, 1H), 1.72 – 1.64 (m, 1H), 1.58 – 1.49 (m, 4H), 1.41 (d, *J* = 12.5 Hz, 1H), 1.37 (s, 3H), 1.29 – 1.17 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-d) *δ* 144.74, 128.15, 127.10, 126.79, 98.78, 78.98, 68.50, 68.03, 64.19, 51.52, 43.08, 33.36, 31.96, 30.15, 29.27, 26.54, 22.20. **HRMS** (EI): m/z Calcd. For $C_{19}H_{26}O_3$: 302.1876, found: 302.1876. IR (KBr) *ν* 3433.5, 2922.0，2844.1, 1460.1, 1377.8, 1261.2, 1166.3, 1078.1, 972.0, 803.1, 738.9, 702.8 cm^{-1}.

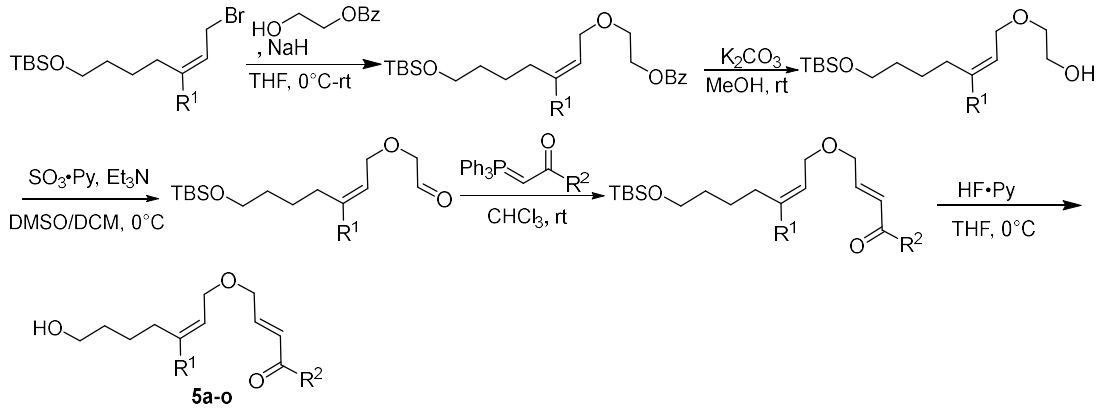
(4a*R*,12a*R*)-6-ethyl-12-phenyldecahydro-1*H*,3*H*-6,12-epoxypyrano[4,3-*d*]oxecine

(2u)

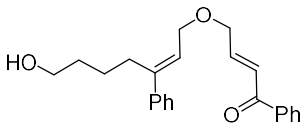


White solid, m.p. 90-91 ºC , $[\alpha]_D^{25}$ = -12.32 (*c* 0.90, DCM), 24.3 mg, 81% yield, 98% ee, dr > 20:1, determined by HPLC (Chiralcel column AD-H, hexane/i-PrOH = 97/3, flow rate 1.0 mL/min, UV detection at 254 nm), t_{major} = 4.7 min, t_{minor} = 5.3 min. **^{1}H NMR** (500 MHz, Chloroform-d) δ 7.42 (d, *J* = 7.2 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.23 (t, *J* = 7.3 Hz, 1H), 3.90 (dd, *J* = 11.3, 4.7 Hz, 1H), 3.81 (td, *J* = 11.9, 2.3 Hz, 1H), 3.68 (dt, *J* = 12.0, 2.6 Hz, 1H), 3.44 – 3.34 (m, 2H), 3.09 (t, *J* = 11.0 Hz, 1H), 2.38 (dd, *J* = 14.8, 8.1 Hz, 1H), 2.26 – 2.17 (m, 2H), 1.93 (dd, *J* = 13.5, 4.0 Hz, 1H), 1.87 (dt, *J* = 15.1, 7.5 Hz, 1H), 1.79 – 1.71 (m, 1H), 1.70 – 1.63 (m, 2H), 1.62 – 1.58 (m, 2H), 1.57 – 1.52 (m, 1H), 1.40 – 1.34 (m, 1H), 1.33 – 1.25 (m, 2H), 0.93 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (125 MHz, Chloroform-d) δ 144.88, 128.14, 127.10, 126.81, 100.77, 78.84, 68.53, 68.04, 63.49, 51.71, 39.71, 33.52, 32.00, 31.53, 30.24, 29.06, 22.21, 8.45. **HRMS** (EI): m/z Calcd. For $C_{20}H_{28}O_3$: 316.2033, found: 316.2031. IR (KBr) *v* 3433.3, 2964.0, 2911.8, 2832.4, 1460.8, 1297.6, 1261.8, 1157.2, 1029.4, 978.6, 803.4, 701.2 cm^{-1}.

5. Synthesis and characterization of substrates 5a-o



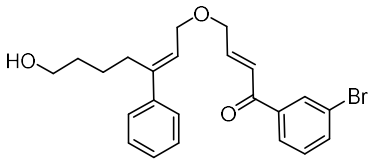
(*E*)-4-(((*E*)-7-hydroxy-3-phenylhept-2-en-1-yl)oxy)-1-phenylbut-2-en-1-one (5a)



Colorless oil. 56% yield. **^{1}H NMR** (400 MHz, Acetone-d6) δ 7.87-7.86 (m, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.5Hz, 2H), 7.31 (d, *J* = 7.4 Hz, 2H), 7.21 (t, *J* = 7.5 Hz, 2H), 7.18-7.17 (m, 1H), 7.15-7.11 (m, 1H), 6.93 (td, *J* = 4.2, 15.5 Hz, 1H), 5.75 (t, *J* = 6.5 Hz, 1H), 4.28-4.21 (m, 4H), 3.36 (q, *J* = 5.9 Hz, 2H), 3.24 (t, *J* = 5.2 Hz, 1H), 2.49 (t, *J* =

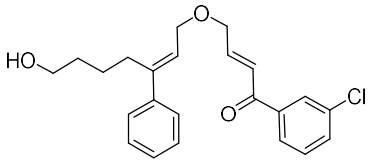
7.5 Hz, 2H), 1.41-1.36 (m, 2H), 1.32-1.28 (m, 2H). **^{13}C NMR** (126 MHz, Acetone-d6) δ 190.06, 145.83, 144.57, 143.06, 138.68, 133.63, 129.53, 129.22, 129.15, 127.99, 127.18, 125.64, 125.27, 69.81, 68.17, 62.18, 33.38, 30.42, 26.03. **HRMS** (ESI): m/z Calcd. For $C_{23}H_{26}O_3Na$ ([M+Na]$^+$): 373.1774, found: 373.1774.

(E)-1-(3-bromophenyl)-4-(((E)-7-hydroxy-3-phenylhept-2-en-1-yl)oxy)but-2-en-1-one (5b)



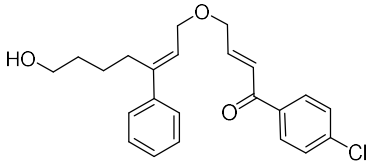
Colorless oil. 56% yield. **^{1}H NMR** (400 MHz, Acetone-d6) δ 7.97 (t, J = 1.6 Hz, 1H), 7.85 (d, J = 7.8 Hz, 1H), 7.66 (dd, J = 0.9, 8.0 Hz, 1H), 7.36 (t, J = 7.9 Hz, 1H), 7.31-7.29 (m, 2H), 7.22-7.20 (m, 2H), 7.15-7.11 (m, 2H), 6.96 (td, J = 4.1, 15.5 Hz, 1H), 5.74 (t, J = 6.5 Hz, 1H), 4.23 (dd, J = 2.0, 4.1 Hz, 2H), 4.20 (d, J = 6.6 Hz, 2H), 3.36 (q, J = 5.9 Hz, 2H), 3.26 (t, J = 5.2 Hz, 1H), 2.48 (t, J = 7.5 Hz, 2H), 1.39-1.35 (m, 2H), 1.31-1.27 (m, 2H). **^{13}C NMR** (101 MHz, Acetone-d6) δ 188.01, 146.08, 143.80, 142.21, 139.81, 135.52, 131.06, 130.76, 128.29, 127.29, 127.15, 126.33, 124.74, 124.05, 122.44, 68.90, 67.35, 61.32, 32.52, 29.58, 25.18. **HRMS**(EI):m/z Calcd. For $C_{23}H_{25}BrO_3Na$:451.0877, found: 451.0876.

(*E*)-1-(3-chlorophenyl)-4-(((*E*)-7-hydroxy-3-phenylhept-2-en-1-yl)oxy)but-2-en-1-one (5c)



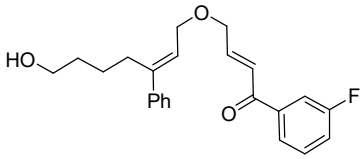
Colorless oil. 48% yield. **^{1}H NMR** (500 MHz, Acetone-d6) δ 7.94-7.92 (m, 2H), 7.65-7.64 (m, 1H), 7.58-7.54 (m, 1H), 7.43-7.42 (m, 2H), 7.32 (t, J = 7.5 Hz, 2H), 7.27-7.24 (m, 2H), 7.08 (td, J = 4.2, 15.5 Hz, 1H), 5.86 (t, J = 6.5 Hz, 1H), 4.36 (dd, J = 2.0, 4.2 Hz, 2H), 4.33 (d, J = 6.6 Hz, 2H), 3.62-3.59(m, 1H), 3.49-3.46(m, 2H), 2.60 (t, J = 7.7 Hz, 2H), 1.50-1.49 (m, 2H), 1.44-1.39 (m, 2H). **^{13}C NMR** (126 MHz, Acetone-d6) δ 189.05, 146.99, 144.64, 143.02, 140.41, 135.23, 133.46, 131.40, 129.15, 128.92, 128.00, 127.76, 127.16, 125.55, 124.90, 69.74, 68.18, 62.13, 33.30, 30.38, 25.99. **HRMS** (ESI): m/z Calcd. For $C_{23}H_{25}ClO_3Na$ ([M+Na]$^+$): 407.1384, found: 407.1382.

(*E*)-1-(4-chlorophenyl)-4-(((*E*)-7-hydroxy-3-phenylhept-2-en-1-yl)oxy)but-2-en-1-one (5d)



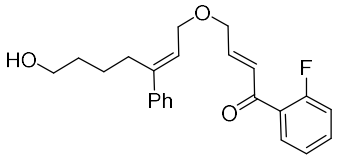
Colorless oil. 49% yield.[1]**H NMR** (500 MHz, Acetone-d6) δ 8.00 (d, J = 8.7 Hz, 2H), 7.56 (d, J = 8.7 Hz, 2H), 7.45-7.41 (m, 2H), 7.34-7.32 (m, 2H), 7.28-7.27 (m, 1H), 7.26-7.24 (m, 1H), 7.07 (td, J = 4.1, 15.4 Hz, 1H), 5.87 (t, J = 6.5 Hz, 1H), 4.35 (dd, J = 2.1, 4.1 Hz, 2H), 4.33 (d, J = 6.6 Hz, 2H), 3.50-3.47 (m, 2H), 3.42 (t, J = 5.2 Hz, 1H), 2.61 (t, J = 7.6 Hz, 2H) , 1.52-1.49 (m, 2H), 1.45-1.41 (m, 2H). **^{13}C NMR** (126 MHz, Acetone-d6) δ 188.94, 146.47, 144.62, 143.04, 139.34, 137.22, 131.02, 129.72, 129.14, 128.00, 127.17, 125.59, 124.83, 69.76, 68.18, 62.16, 33.36, 30.40, 26.02. **HRMS** (ESI): m/z Calcd. For $C_{23}H_{25}ClO_3Na$ ([M+Na]$^+$): 407.1384, found: 407.1383.

(E)-1-(3-fluorophenyl)-4-(((E)-7-hydroxy-3-phenylhept-2-en-1-yl)oxy)but-2-en-1-one (5e)



Colorless oil. 69% yield. [1]**H NMR** (500 MHz, Acetone-d6) δ 7.84-7.82 (m, 1H), 7.68 (ddd, J = 1.6, 2.5, 9.7 Hz, 1H), 7.59-7.55 (m, 1H), 7.43-7.41 (m, 2H), 7.40-7.38 (m, 1H), 7.34-7.31 (m, 2H), 7.28-7.26 (m, 1H), 7.25-7.24 (m, 1H), 7.09 (td, J = 4.2, 15.5 Hz, 1H), 5.87 (t, J = 6.5 Hz, 1H), 4.35 (dd, J = 2.0, 4.2 Hz, 2H), 4.33 (d, J = 6.6 Hz, 2H), 3.48 (q, J = 5.8 Hz, 2H), 3.41 (t, J = 5.1 Hz, 1H), 2.60 (t, J = 7.6 Hz, 2H), 1.52-1.48 (m, 2H), 1.45-1.40 (m, 2H). **^{13}C NMR** (126 MHz, Acetone-d6) δ 188.91 (J = 2.43 Hz), 163.69 (J = 245.6 Hz), 146.78, 144.60, 143.04, 140.92 (J = 6.3 Hz), 131.65 (J = 7.6 Hz), 129.14, 127.99, 127.17, 125.60, 125.31 (J = 2.7 Hz), 124.92, 120.47 (J = 21.4 Hz), 115.56 (J = 22.6 Hz), 69.75, 68.19, 62.16, 33.36, 30.41, 26.02. **HRMS** (ESI): m/z Calcd. For $C_{23}H_{25}FO_3Na$ ([M+Na]+): 391.1680, found: 391.1683.

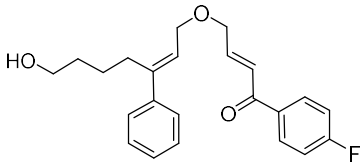
(E)-1-(2-fluorophenyl)-4-(((E)-7-hydroxy-3-phenylhept-2-en-1-yl)oxy)but-2-en-1-one (5f)



Colorless oil. 50% yield. [1]**H NMR** (500 MHz, Acetone-d6) δ 7.70 (dt, J = 1.8, 7.52 Hz, 1H), 7.64-759 (m, 1H), 7.43-7.41 (m, 2H), 7.34-7.30 (m, 3H), 7.27-7.24(m, 2H), 6.97-6.96 (m, 2H), 5.85 (t, J = 6.5 Hz, 1H), 4.33-4.31 (m, J = 2.9 Hz, 4H), 3.48 (q, J = 6.0 Hz, 2H), 3.39 (t, J = 5.2 Hz, 1H), 2.60 (t, J = 7.7 Hz, 2H), 1.52-1.47 (m, J = 2.7 Hz, 2H), 1.44-1.39 (m, J = 3.4 Hz, 2H). **^{13}C NMR** (126 MHz, Acetone-d6) δ 189.40 (J =

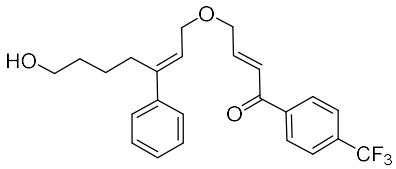
1.6 Hz), 161.62 (*J* = 251.5 Hz), 146.75, 144.65, 143.04, 134.79 (*J* = 9.0 Hz), 131.36 (*J* = 2.8 Hz), 129.13, 128.85 (*J* = 4.8 Hz), 127.98, 127.16, 125.51, 125.47, 117.25 (*J* = 22.7 Hz), 69.53, 68.13, 62.16, 33.37, 30.40, 26.02. **HRMS** (ESI): m/z Calcd. For $C_{23}H_{25}FO_3Na$ ([M+Na]+): 391.1680, found: 391.1683.

(*E*)-1-(4-fluorophenyl)-4-(((*E*)-7-hydroxy-3-phenylhept-2-en-1-yl)oxy)but-2-en-1-one (5g)



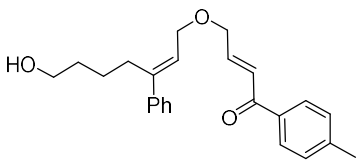
Colorless oil. 52% yield. **^{1}H NMR** (500 MHz, Acetone-d6) δ 8.09-8.06 (m, 2H), 7.43 (d, *J* = 7.4 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.34-7.24 (m, 4H), 7.07 (td, *J* = 4.2, 15.4 Hz, 1H), 5.87 (t, *J* = 6.5 Hz, 1H), 4.34 (dd, *J* = 2.1, 4.2 Hz, 2H), 4.33 (d, *J* = 6.6 Hz, 2H), 3.49-3.46 (m, 3 H), 2.60 (t, *J* = 7.6 Hz, 2H), 1.54-1.49 (m, 2H), 1.46-1.39 (m, 2H). **^{13}C NMR** (126 MHz, Acetone-d6) δ 188.53, 166.33 (*J* = 252.1 Hz), 146.05, 144.59, 143.05, 135.24, 132.13 (*J* = 9.6 Hz), 129.15, 128.00, 127.17, 125.62, 124.92, 116.44 (d, *J* = 21.9 Hz), 69.78, 68.17, 62.17, 33.36, 30.40, 26.02. **HRMS** (ESI): m/z Calcd. For $C_{23}H_{25}FO_3Na$ ([M+Na]+): 391.1680, found: 391.1681.

(*E*)-4-(((*E*)-7-hydroxy-3-phenylhept-2-en-1-yl)oxy)-1-(4-(trifluoromethyl)phenyl) but-2-en-1-one (5h)



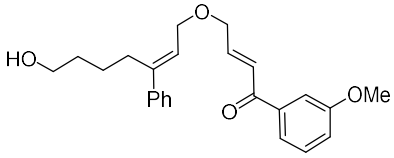
Colorless oil. 40% yield. **^{1}H NMR** (500 MHz, Acetone-d6) δ 8.16 (d, *J* = 8.1 Hz, 2H), 7.87 (d, *J* = 8.2 Hz, 2H), 7.44-7.42 (m, 2H), 7.34-7.29 (m, *J* = 3.0 Hz, 2H), 7.30-7.24 (m, 2H), 7.11 (td, *J* = 4.0, 15.4 Hz, 1H), 5.88 (t, *J* = 6.5 Hz, 1 H), 4.37 (dd, *J* = 2.1, 4.1 Hz, 2H), 4.34 (d, *J* = 6.6 Hz, 2H), 3.50-3.47 (m, 2H), 3.44-3.42 (m, 1H), 2.61 (t, *J* = 7.6 Hz, 2H), 1.53-1.50 (m, 2H), 1.46-1.41 (m, 2H). **^{13}C NMR** (126 MHz, Acetone-d6) δ 189.59, 147.40, 144.67, 143.03, 141.82, 134.05 (*J* = 32.2 Hz), 129.91, 129.15, 128.01, 127.16, 126.51 (*J* = 3.8 Hz), 125.55, 124.97, 69.72, 68.21, 62.16, 33.35, 30.39, 26.02. **HRMS** (ESI): m/z Calcd. For $C_{24}H_{25}F_3O_3Na$ ($[M+Na]^+$): 441.1648, found:441.1647

(E)-4-(((E)-7-hydroxy-3-phenylhept-2-en-1-yl)oxy)-1-(p-tolyl)but-2-en-1-one (5i)



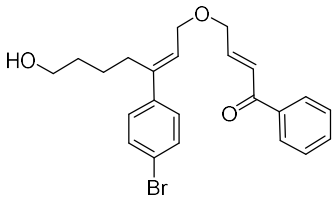
Colorless oil.64 % yield. **^{1}H NMR** (500 MHz, Acetone-d6) δ 7.90 (d, J = 8.2 Hz, 2H), 7.44-7.42 (m, 2H), 7.34-7.32 (m, 4H), 7.29-7.26 (m, J = 3.4 Hz, 2H), 7.03 (td, J = 4.3, 15.5 Hz, 1H), 5.87 (t, J = 6.5 Hz, 1H), 4.34-4.32 (m, 4H), 3.49 (q, J = 5.9 Hz, 2H), 3.40 (t, J = 5.2 Hz, 1 H), 2.61 (t, J = 7.6 Hz, 2H), 2.39 (s, 3H), 1.52-1.49 (m,2H), 1.44-1.41 (m, 2H). **^{13}C NMR** (126 MHz, Acetone-d6) δ 189.44, 145.27, 144.55, 144.39, 143.06, 136.15, 130.14, 129.37, 129.14, 127.98, 127.17, 125.66, 125.26, 69.83, 68.14, 62.17, 33.38, 30.41, 26.02, 21.52. **HRMS** (ESI): m/z Calcd. For $C_{24}H_{28}O_3Na$ ([M+Na]$^+$): 387.1931, found: 387.1931.

(E)-4-(((E)-7-hydroxy-3-phenylhept-2-en-1-yl)oxy)-1-(3-methoxyphenyl)but-2-en-1-one (5j)



Colorless oil.77% yield.**^{1}H NMR** (500 MHz, Acetone-d6) δ 7.58-7.57 (m, 1 H), 7.49 (dd, J = 1.6, 2.5 Hz, 1H), 7.44-7.41 (m, J = 2.0 Hz, 3H), 7.34-7.31 (m, 2 H), 7.27-7.26 (m, 1 H), 7.25-7.24 (m, 1 H), 7.17 (ddd, J = 0.9, 2.7, 8.2 Hz, 1H), 7.05 (td, J = 4.3, 15.4 Hz, 1H), 5.87 (t, J = 6.5 Hz, 1H), 4.34 (dd, J = 2.0, 4.3 Hz, 2H), 4.32 (d, J = 6.6 Hz, 2H), 3.84 (s, 3H), 3.48 (q, J = 5.9 Hz, 2H), 3.42 (t, J = 5.2 Hz, 1H), 2.60 (t, J = 7.6 Hz, 2H), 1.51-1.49 (m, 2H), 1.45-1.40 (m, 2H). **^{13}C NMR** (126 MHz, Acetone-d6) δ 189.82, 160.90, 145.86, 144.57, 143.05, 140.09, 130.62, 129.15, 127.99, 127.18, 125.64, 125.38, 121.70, 119.73, 113.72, 69.81, 68.17, 62.18, 55.73, 33.38, 30.42, 26.03. **HRMS** (ESI): m/z Calcd. For $C_{24}H_{28}O_4Na$ ([M+Na]$^+$): 403.1880, found:403.1883.

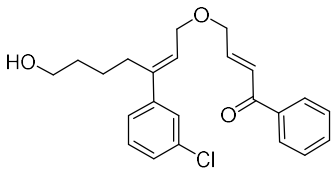
(*E*)-4-(((*E*)-3-(4-bromophenyl)-7-hydroxyhept-2-en-1-yl)oxy)-1-phenylbut-2-en-1-one (5k)



^{1}H NMR (800 MHz, Acetone-d6) 8.00 (d, J = 7.4 Hz, 2 H), 7.63 (t, J = 7.4 Hz, 1 H), 7.54-7.49 (m, 4H), 7.40 (d, J = 8.5 Hz, 2H), 7.29-7.27 (m, 1H), 7.06 (td, J = 4.2, 15.5 Hz, 1 H), 5.92 (t, J = 6.4 Hz, 1 H), 4.36 (dd, J = 2.0, 4.2 Hz, 2H), 4.34 (d, J = 6.5 Hz, 2H), 3.50 (q, J = 5.9 Hz, 2H), 3.43 (t, J = 5.2 Hz, 1 H), 2.60 (t, J = 7.8 Hz, 2H), 1.53-1.51 (m, 2 H), 1.45-1.41 (m, 2H). **^{13}C NMR** (201 MHz, Acetone-d6) 190.07, 145.76, 143.35, 142.22, 138.68, 133.67, 132.19, 129.55, 129.24, 126.53,

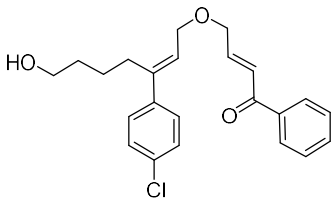
125.32, 121.43, 69.90, 68.13, 62.13, 33.30, 30.23, 25.94. **HRMS** (ESI): m/z Calcd. For $C_{23}H_{25}BrO_3Na$ ([M+Na]$^+$): 451.0879, found: 451.0877.

(*E*)-4-(((*E*)-3-(3-chlorophenyl)-7-hydroxyhept-2-en-1-yl)oxy)-1-phenylbut-2-en-1-one (5l)



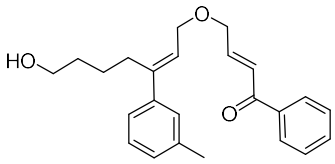
Colorless oil. 52% yield. **^{1}H NMR** (800 MHz, Acetone-d6) δ 8.00 (d, J = 7.8 Hz,2 H), 7.63 (t, J = 7.4 Hz, 1 H), 7.54 (t, J = 7.7 Hz, 2 H), 7.46 (s, 1H), 7.41 (d, J = 7.8 Hz, 1 H), 7.37 (t, J = 7.8 Hz, 1 H), 7.31-7.28 (m, 2 H), 7.06 (td, J = 4.2, 15.5 Hz, 1H), 5.94 (t, J = 6.4 Hz, 1H), 4.37 (dd, J = 1.2, 3.5 Hz, 2H), 4.35 (d, J = 6.4 Hz, 2H), 3.53-3.48 (m, 2 H), 3.42 (t, J = 5.2 Hz, 1 H), 2.62 (t, J = 7.8 Hz, 2 H), 1.53-1.50 (m, 2H), 1.45-1.39 (m, 2H). **^{13}C NMR** (201 MHz, Acetone-d6) δ 190.06, 145.73, 145.31, 143.23, 138.66, 134.65, 133.65, 130.82, 129.52, 129.22, 127.91, 127.14, 127.13, 125.77, 125.30, 69.88, 68.06, 62.10, 33.26, 30.29, 25.90. **HRMS** (ESI): m/z Calcd. For $C_{23}H_{25}ClO_3Na$ ([M+Na]+): 407.1384, found: 407.1385.

(*E*)-4-(((*E*)-3-(4-chlorophenyl)-7-hydroxyhept-2-en-1-yl)oxy)-1-phenylbut-2-en-1-one (5m)



Colorless oil. 64% yield. **^{1}H NMR** (500 MHz, Acetone-d6) δ 7.99-7.97 (m, 2H), 7.63-7.60 (m, 1H), 7.53-7.51 (m, 2H), 7.46-7.44 (m, 2H), 7.36-7.34 (m, 2H), 7.28 (td, J = 2.0, 15.5 Hz, 1H), 7.05 (td, J = 4.2, 15.4 Hz, 1H), 5.91 (t, J = 6.5 Hz, 1H), 4.35 (dd, J = 2.0, 4.3 Hz, 2H), 4.33 (d, J = 6.5 Hz, 2H), 3.50-3.44 (m, 3 H), 2.59 (t, J = 7.6 Hz, 2H), 1.52-1.49 (m, 2H), 1.43-1.40 (m, 2H). **^{13}C NMR** (126 MHz, Acetone-d6) δ 190.07, 145.75, 143.29, 141.77, 138.65, 133.65, 133.26, 129.53, 129.22, 129.18, 128.87, 126.45, 125.30, 69.87, 68.11, 62.11, 33.27, 30.26, 25.91. **HRMS** (ESI): m/z Calcd. For $C_{23}H_{25}ClO_3Na$ ([M+Na]$^+$): 407.1384, found: 407.1384.

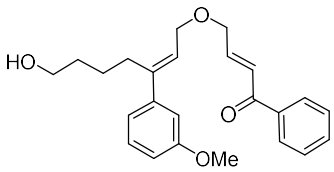
(E)-4-(((E)-7-hydroxy-3-(m-tolyl)hept-2-en-1-yl)oxy)-1-phenylbut-2-en-1-one (5n)



Colorless oil. 34% yield **^{1}H NMR** (800 MHz, Acetone-d6) δ 7.99 (d, J = 8.2 Hz, 2H), 7.62 (t, J = 7.4 Hz, 1H), 7.53 (t, J = 7.7 Hz, 2H), 7.28-7.26 (m, 1H), 7.25 (br, 1H), 7.21-7.20 (m, 2H), 7.08-7.07 (m, 1H), 7.05 (td, J = 4.2, 15.5 Hz, 1H), 5.85 (t, J = 6.5 Hz, 1H),

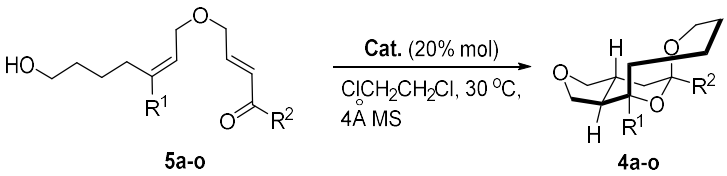
4.35 (dd, J = 1.9, 4.1 Hz, 2H), 4.32 (d, J = 6.5 Hz, 2H), 3.49-3.47 (m, 2H), 3.38 (br, 1H), 2.59 (t, J = 7.7 Hz, 2H), 2.32 (s, 3H), 1.51-1.48 (m, 2H), 1.44-1.41 (m, 2H). **^{13}C NMR** (201 MHz, Acetone-d6) δ 190.05, 145.87, 144.74, 143.12, 138.70, 138.51, 133.64, 129.54, 129.22, 129.03, 128.69, 127.90, 125.42, 125.27, 124.31, 69.79, 68.18, 62.19, 33.40, 30.45, 26.06, 21.45. **HRMS** (ESI): m/z Calcd. For $C_{24}H_{28}O_3Na$ ([M+Na]$^+$): 387.1931, found: 387.1931.

(E)-4-(((E)-7-hydroxy-3-(3-methoxyphenyl)hept-2-en-1-yl)oxy)-1-phenylbut-2-en-1-one (5o)



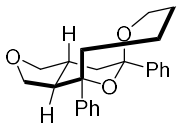
Colorless oil. 67% yield. **^{1}H NMR** (600 MHz, Acetone-d6) δ 8.01-7.99 (m, 2H), 7.64-7.62 (m, 1H), 7.54 (t, J = 7.7 Hz, 2H), 7.29 (td, J = 2.0, 15.4 Hz, 1H), 7.26 (t, J = 7.9 Hz, 1H), 7.06 (td, J = 4.2, 15.4 Hz, 1H), 7.02 (d, J = 7.9 Hz, 1H), 6.98-6.95 (m, 1H), 6.85 (dd, J = 2.4, 8.2 Hz, 1H), 5.90 (t, J = 6.5 Hz, 1H), 4.36 (dd, J = 2.0, 4.2 Hz, 2H), 4.34 (d, J = 6.5 Hz, 2H), 3.81 (s, 3H), 3.51-3.47 (m, 2H), 3.40 (t, J = 5.2 Hz, 1H), 2.60 (t, J = 7.7 Hz, 2H), 1.53-1.50 (m, 2H), 1.47-1.43 (m, 2H). **^{13}C NMR** (151 MHz, Acetone-d6) δ 190.07, 160.74, 145.87, 144.66, 144.54, 138.73, 133.68, 130.14, 129.58, 129.26, 125.75, 125.31, 119.58, 113.36, 113.00, 69.86, 68.19, 62.21, 55.45, 33.43, 30.53, 26.08. **HRMS** (ESI): m/z Calcd. For $C_{24}H_{28}O_4Na$ ([M+Na]$^+$): 403.1880, found: 403.1884.

6. General procedure for oxa-IEDHDA-keto acetalization reactions with 5a-o



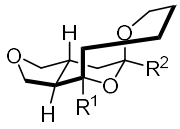
Substrate **5a-o** (1.0 eq) was dissolved in $ClCH_2CH_2Cl$ (1.0 ml), then 4Å molecular sieves (60 mg) followed by catalyst **3n** (0.2 eq.) were added. The reaction mixture was stirred at 30 °C and monitored by TLC (generally for 60-120h). When the reaction was completed, the mixture was purified by silica gel column to afford products **4a-o**.

(3a*R*,11a*R*)-5,11-diphenyldecahydro-1*H*-5,11-epoxyfuro[3,4-*d*]oxecin (4a)



White solid, m.p. 133-134 °C, $[\alpha]_D^{25}$= +45.52 (*c* 1.00, DCM), 11.6 mg, 74% yield, 97% ee, dr > 20:1, determined by HPLC (CHIRAPAK AD-H, hexane/i-PrOH = 95/5, flowrate1.0 mL/min, UV detection at 254 nm), t_{major} = 5.4 min, t_{minor} = 6.6 min. **^{1}H NMR** (600 MHz, Chloroform-d) δ 7.58 (br, 2H), 7.49 (d, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 4H), 7.26 (t, *J* = 7.3 Hz, 1H), 7.22 (t, *J* = 7.3 Hz, 1H), 4.02 (t, *J* = 7.3 Hz, 1H), 3.92 (t, *J* = 7.4 Hz, 1H), 3.70 (dd, *J* = 7.4, 11.3 Hz, 1H), 3.63 (d, *J* = 12.0 Hz, 1H), 3.43 (dt, *J* = 1.5, 12.3 Hz, 1H), 3.16 (dd, *J* = 7.4, 10.7 Hz, 1H), 2.77-2.70 (m, *J* = 3.8 Hz, 1H), 2.43 (dd, *J* = 8.3, 14.4 Hz, 1H), 2.26 (dd, *J* = 3.7, 13.3 Hz, 1H), 2.19 (dd, *J* = 10.5, 14.3 Hz, 1H), 1.99-1.93 (m, *J* = 6.2 Hz, 1 H), 1.63-1.56 (m, *J* = 6.2 Hz, 1H), 1.52-1.48 (m, 1H), 1.43-1.41 (m, 1H), 1.34 (t, *J* = 12.81 Hz, 1H), 1.25-1.22 (t, *J* = 10.50 Hz, 1H).**^{13}C NMR** (151 MHz, Chloroform-d) δ 146.05, 144.23, 127.28, 127.21, 126.61, 125.73, 124.87, 124.30, 100.14, 79.21, 71.19, 67.57, 65.83, 52.46, 40.21, 34.37, 31.73, 30.59, 19.80. **HRMS** (ESI): m/z Calcd. For $C_{23}H_{26}O_3Na$ ($[M+Na]^+$): 373.1774, found: 373.1772. IR (KBr) *v* 3467.2, 2925.7, 1648.2, 1493.0, 1446.0, 1222.2, 1136.9, 1093.0, 1027.8, 897.4, 766.1, 701.9 cm^{-1}.

(3aR,11aR)-5-(3-bromophenyl)-11-phenyldecahydro-1H-5,11-epoxyfuro[3,4-d]oxecine (4b)

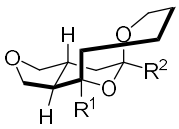


R^1=Ph, R^2=3-Br-Ph

White solid, m.p. 104-105 °C, $[\alpha]_D^{25}$= +42.65 (*c* 0.42, $CHCl_3$), 11.6 mg, 75% yield, 95% ee, dr > 20:1, determined by HPLC (CHIRAPAK DAD1, hexane/i-PrOH = 95/5, flowrate 1.0 mL/min, UV detection at 254 nm), t_{major} = 5.5 min, t_{minor} = 7.1 min. **^{1}H NMR** (500 MHz, Chloroform-d) δ 7.79 (br, 1H), 7.57 (br, 1H), 7.53-7.51 (m, 2H), 7.46-7.44 (m, 1H), 7.41 (t, *J* = 7.8 Hz, 2H), 7.31-7.28 (m, 2H), 4.09 (t, *J* = 7.3 Hz, 1H), 3.98 (t, *J* = 7.4 Hz, 1H), 3.75 (dd, *J* = 7.4, 11.3 Hz, 1H), 3.70 (d, *J* = 12.0 Hz, 1H), 3.46 (dt, *J* = 1.8, 12.2 Hz, 1H), 3.23 (dd, *J* = 7.5, 10.7 Hz, 1H), 2.83-2.74 (m, 1H), 2.47 (dd, *J* = 8.2, 14.4 Hz, 1H), 2.30 (dd, *J* = 3.8, 13.2 Hz, 1H), 2.25 (dd, *J* = 10.4, 14.3 Hz, 1H), 2.05-1.99 (m, 1H), 1.69-1.63 (m, 1H), 1.60-1.55 (m, 1H), 1.52-1.48 (m, 1H), 1.37 (t, *J* = 12.8 Hz, 1H), 1.29-1.28 (m, 1H). **^{13}C NMR** (126 MHz, Chloroform-d) δ 147.66, 146.75, 130.77, 130.01, 129.24, 128.32, 126.89, 125.27, 124.62, 122.54, 100.67, 80.56, 72.15, 68.56, 66.97, 53.41, 41.13, 35.30, 32.65, 31.54, 20.82. **HRMS** (EI): m/z Calcd. For $C_{23}H_{25}BrO_3$: 428.0982, found:

428.0981. IR (KBr) *v* 3433.7, 2927.3, 1630.3, 1493.6, 1445.1, 1228.7, 1136.5, 1093.4, 1026.2, 895.2, 788.4, 701.1 cm^{-1}.

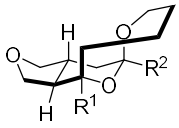
(3a*R*,11a*R*)-5-(3-chlorophenyl)-11-phenyldecahydro-1*H*-5,11-epoxyfuro[3,4-d] oxecine (4c)



R1=Ph,R2=3-Cl-Ph

White solid, m.p. 115-116 ºC, $[\alpha]_D^{25}$= +40.18 (*c* 0.89, DCM), 20.3 mg, 60% yield, 95% ee, dr > 20:1, determined by HPLC (CHIRAPAK AD-H, hexane/i-PrOH = 95/5, flowrate 1.0 mL/min, UV detection at 254 nm), t_{major} = 5.1 min, t_{minor} = 8.6 min. **^{1}H NMR** (500 MHz, Chloroform-d) δ 7.63 (br, 1H), 7.53-7.51(m, 3 H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.31-7.29 (m, 2 H), 4.09 (t, *J* = 7.3 Hz, 1H), 3.98 (t, *J* = 7.5 Hz, 1H), 3.76 (dd, *J* = 7.4, 11.3 Hz, 1H), 3.70 (d, *J* = 12.0 Hz, 1H), 3.46 (dt, *J* = 1.9, 12.3 Hz, 1H), 3.23 (dd, *J* = 7.4, 10.7 Hz, 1H), 2.81-2.77 (m, 1H), 2.48 (dd, *J* = 8.05, 14.5 Hz, 1H), 2.31 (dd, *J* = 3.8, 13.2 Hz, 1H), 2.26 (dd, *J* = 10.3, 14.3 Hz, 1H), 2.02 (dt, *J* = 7.6, 11.7 Hz, 1H), 1.70-1.64 (m, 1H), 1.63-1.60 (m, 1H), 1.51-1.48 (m,1H), 1.38 (t, *J* = 12.8 Hz, 1H), 1.32-1.29 (m, 1H). **^{13}C NMR** (126 MHz, Chloroform-d) δ 147.43, 146.76, 134.31, 129.70, 128.32, 127.84, 126.88, 126.32, 125.27, 124.15, 100.75, 80.55, 72.16, 68.56, 66.97, 53.43, 41.11, 35.30, 32.65, 31.54, 20.82. **HRMS** (EI): m/z Calcd. For $C_{23}H_{25}ClO_3$: 384.1487, found: 384.1488. IR (KBr) *v* 3432.9, 2926.3, 1647.5, 1493.2, 1445.2, 1261.6, 1136.2, 1095.4, 1026.9, 895.5, 801.9, 701.1 cm^{-1}.

(3aR,11aR)-5-(4-chlorophenyl)-11-phenyldecahydro-1H-5,11-epoxyfuro[3,4-d]oxecine (4d)

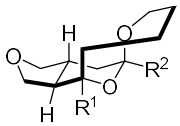


R1=Ph,R2=4-Cl-Ph

White solid, m.p. 139-140 ºC, $[\alpha]_D^{25}$= +25.72 (*c* 0.93, $CHCl_3$), 17.0 mg, 95% yield, 98% ee, dr > 20:1, determined by HPLC (CHIRAPAK DAD1, hexane/i-PrOH = 95/5, flowrate 1.0 mL/min, UV detection at 254 nm), t_{major} = 6.9 min, t_{minor} = 9.2 min. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.51 (d, *J* = 7.6 Hz, 2H), 7.44 (d, *J* = 7.7 Hz, 2H), 7.35-7.29 (m, 4H), 7.21 (t, *J* = 7.3 Hz, 1H), 4.01 (t, *J* = 7.3 Hz, 1H), 3.90 (t, *J* = 7.4 Hz, 1H), 3.68 (dd, *J* = 7.4, 11.3 Hz, 1H), 3.60 (d, *J* = 12.0 Hz, 1H), 3.38 (t, *J* = 11. 4 Hz, 1H), 3.16 (dd, *J* = 7.4, 10.6 Hz, 1H), 2.78-2.66 (m, 1H), 2.40 (dd, *J* = 8.2, 14.4 Hz, 1H), 2.25-2.12 (m, 2H), 1.98-1.90 (m, 1H), 1.53-1.40 (m, 3H), 1.29 (t, *J* = 11.8 Hz, 1H), 0.85-0.76 (m, 1H). **^{13}C NMR** (126

MHz, Acetone-d6) δ 147.98, 145.37, 133.71, 129.13, 129.00, 128.64, 127.49, 126.20, 101.70, 81.28, 72.34, 68.73, 67.26, 54.39, 41.74, 36.05, 33.07, 32.29, 21.67. **HRMS** (EI): m/z Calcd. For $C_{23}H_{25}ClO_3$: 384.1490, found: 384.1487. IR (KBr) ν 3438.0, 2932.1, 1715.6, 1625.6, 1464.3, 1255.1, 1166.9, 1101.9, 837.0, 774.7, 697.2 cm^{-1}.

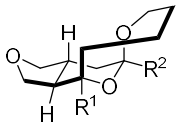
(3a*R*,11a*R*)-5-(3-fluorophenyl)-11-phenyldecahydro-1*H*-5,11-epoxyfuro[3,4-*d*] oxecine (4e)



R1=Ph,R2=3-F-Ph

White solid, m.p. 96-97 ºC, $[\alpha]_D^{25}$= +23.17 (*c* 0.98, DCM), 20.12 mg, 85% yield, 93% ee, dr > 20:1, determined by HPLC (CHIRAPAK AD-H, hexane/i-PrOH = 95/5, flowrate 1.0 mL/min, UV detection at 254 nm), t_{major} = 5.3 min, t_{minor} = 6.6 min. **^{1}H NMR** (500 MHz, Chloroform-d) δ 7.53 (d, *J* = 7.7 Hz, 2H), 7.42 (t, *J* = 7.7 Hz, 3H), 7.38-7.34 (m, 2H), 7.30 (t, *J* = 7.3 Hz, 1H), 7.02 (dt, *J* = 2.47, 8.5 Hz, 1H), 4.09 (t, *J* = 7.3 Hz, 1H), 3.98 (t, *J* = 7.4 Hz, 1H), 3.76 (dd, *J* = 7.4, 11.3 Hz, 1H), 3.70 (d, *J* = 12.1 Hz, 1H), 3.48 (dt, *J* = 1.7, 12.3 Hz, 1H), 3.24 (dd, *J* = 7.4, 10.7 Hz, 1H), 2.84-2.76 (m, 1 H), 2.48 (dd, *J* = 8.3, 14.5 Hz, 1H), 2.31 (dd, *J* = 3.7, 13.1 Hz, 1H), 2.26 (dd, *J* = 10.2, 14.1 Hz, 1H), 2.06-2.19 (m, 1H), 1.66-1.61 (m, 2H), 1.53-1.48 (m, 1 H), 1.39 (t, *J* = 12.8 Hz, 1H), 1.33-1.29 (m, 1H). **^{13}C NMR** (126 MHz, Chloroform-d) δ 162.96 (*J* = 245.2 Hz), 148.06 (*J* = 6.7 Hz), 146.80, 129.89 (*J* = 8.0 Hz), 128.32, 126.87, 125.27, 121.54, 114.54 (d, *J* = 21.1 Hz), 113.20 (*J* = 22.5 Hz), 100.76 (*J* = 1.6 Hz), 80.51, 72.17, 68.57, 66.95, 53.45, 41.06, 35.31, 32.66, 31.56, 20.83. **HRMS**(EI): m/z Calcd. For $C_{23}H_{25}FO_3$: 368.1783, found: 368.1782. IR (KBr) ν 3424.5, 2930.9, 1687.2, 1588.7, 1484.8, 1443.8, 1253.5, 1028.9, 789.3, 704.0 cm^{-1}.

(3a*R*,11a*R*)-5-(2-fluorophenyl)-11-phenyldecahydro-1*H*-5,11-epoxyfuro[3,4-*d*] oxecine (4f)

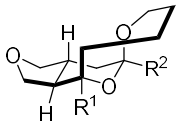


R1=Ph,R2=2-F-Ph

Colorless oil, $[\alpha]_D^{25}$= +32.38 (*c* 1.00, DCM), 20.3 mg, 76% yield, 87% ee, dr > 20:1, determined by HPLC (CHIRAPAK AD-H, hexane/i-PrOH = 95/5, flowrate 1.0 mL/min, UV detection at 254 nm), t_{major} = 5.1 min, t_{minor} = 8.6 min. **^{1}H NMR** (500 MHz, Chloroform-d) δ 7.93 (br, 1H), 7.55-7.54 (m, 2H), 7.41 (t, *J* = 7.3 Hz, 2H), 7.34-7.28 (m, 2 H), 7.21-7.19 (m, 1H), 7.09 (dd, *J* = 8.6, 11.3 Hz, 1H), 4.10 (t, *J* = 7.3 Hz, 1H), 3.92 (t, *J* = 7.5 Hz, 1H), 3.73 (dd, *J* = 7.4, 11.4 Hz, 2H), 3.57 (br, 1H), 3.26 (dd, *J* = 7.5, 10.6 Hz, 1H), 2.83 (br, 1H), 2.49-

2.48 (m, 1H), 2.29 (t, J = 12.4 Hz, 1H), 2.07-2.06 (m, 1H), 1.75-1.69 (m, 1H), 1.65-1.59 (m, 2H), 1.51-1.49 (m, 2H), 1.33-1.32 (m, 1H). **^{13}C NMR** (126 MHz, Chloroform-d) δ 159.82 (J = 255.1 Hz), 146.80 (J = 7.1 Hz), 131.24 (J = 10.4 Hz), 129.73 (J = 8.5 Hz), 128.93, 128.28, 126.85, 125.40, 123.77, 116.64, 80.83, 72.24, 68.52, 66.26, 53.76, 38.40, 34.94, 32.35, 31.27, 21.02. **HRMS** (ESI): m/z Calcd. For $C_{23}H_{25}FO_3Na$: ([M+Na]$^+$) 391.1680, found: 391.1680. IR (KBr) ν 3435.3, 2929.9, 1613.8, 1486.4, 1448.7, 1291.9, 1220.5, 1150.3, 1009.2, 895.9, 762.0, 701.7 cm^{-1}.

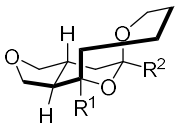
(3a*R*,11a*R*)-5-(4-fluorophenyl)-11-phenyldecahydro-1*H*-5,11-epoxyfuro[3,4-*d*] oxecine (4g)



R^1=Ph,R^2=4-F-Ph

White solid, m.p. 148-149 ºC, $[\alpha]_D^{25}$= +48.06 (c 1.00, DCM), 24.6 mg, 72% yield, 97% ee, dr > 20:1, determined by HPLC (CHIRAPAK AD-H, hexane/i-PrOH = 95/5, flowrate 1.0 mL/min, UV detection at 254 nm), t_{major} = 6.3 min, t_{minor} = 7.9 min. **^{1}H NMR** (500 MHz, Chloroform-d) δ 7.62 (br, 2H), 7.52 (d, J = 7.7 Hz, 2H), 7.41 (t, J = 7.7 Hz, 2H), 7.29 (t, J = 7.3 Hz, 1H), 7.09 (t, J = 8.8 Hz, 2H), 4.09 (t, J = 7.3 Hz, 1H), 3.98 (t, J = 7.4 Hz, 1H), 3.76 (dd, J = 7.4, 11.3 Hz, 1H), 3.67 (d, J = 12.1 Hz, 1H), 3.47 (dt, J = 1.9, 12.3 Hz, 1H), 3.23 (dd, J = 7.4, 10.7 Hz, 1H), 2.84-2.75 (m, 1H), 2.48 (dd, J = 8.2, 14.5 Hz, 1H), 2.31 (dd, J = 3.8, 13.2 Hz, 1H), 2.26 (dd, J = 10.4, 14.3 Hz, 1H), 2.05-1.98 (m, 1H), 1.71-1.65 (m, 1H), 1.61-1.58 (m, 1H), 1.52-1.48 (m, 1H), 1.38 (t, J = 12.8 Hz, 1H), 1.32-1.29 (m, 1H). **^{13}C NMR** (126 MHz, Chloroform-d) δ 162.29 (J = 245.8 Hz), 146.92, 141.13 (d, J = 3.0 Hz), 128.29, 127.69 (J = 7.9 Hz), 126.8, 125.3, 115.10 (d, J = 21.5 Hz), 100.9, 80.4, 72.2, 68.6, 66.7, 53.5, 41.3, 35.4, 32.7, 31.6, 20.8. **HRMS** (ESI): m/z Calcd. For $C_{23}H_{25}FO_3Na$ ([M+Na]$^+$): 391.1680, found: 391.1688. IR (KBr) ν 3435.7, 2928.3, 1606.5, 1507.0, 1223.1, 1136.1, 1010.0, 839.1, 702.2, 566.0 cm^{-1}.

(3a*R*,11a*R*)-11-phenyl-5-(4-(trifluoromethyl)phenyl)decahydro-1*H*-5,11epoxyfuro [3,4-*d*]oxecine (4h)

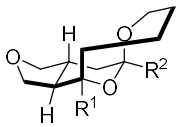


R^1=Ph,R^2=4-CF$_3$-Ph

White crystal, m.p. 130-131 ºC, $[\alpha]_D^{25}$= +25.01 (c 0.83, DCM), 23.9 mg, 76% yield, 95% ee, dr > 20:1, determined by HPLC (CHIRAPAK AD-H, hexane/i-PrOH = 95/5, flowrate 1.0 mL/min, UV detection at 254 nm), t_{major} = 5.1 min, t_{minor} = 6.5 min. **^{1}H NMR** (500 MHz, Acetone-d$_6$) δ 7.89 (d,

J = 7.4 Hz, 2H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.63-7.612 (m, 2H), 7.41 (t, *J* = 7.8 Hz, 2H), 7.30-7.16 (m, 1H), 4.01 (t, *J* = 7.3 Hz, 1 H), 3.83 (t, *J* = 7.5 Hz, 1 H), 3.73 (dd, *J* = 7.5, 11.3 Hz, 1 H), 3.71-3.68 (m, 1H), 3.37 (dt, *J* = 2.0, 12.2 Hz, 1H), 3.20 (dd, *J* = 7.4, 10.6 Hz, 1H), 2.79-2.71 (m, 1H), 2.50 (dd, *J* = 7.9, 14.3 Hz, 1H), 2.38-2.35 (m, 1H), 2.32 (dd, *J* = 3.7, 13.0 Hz, 1H), 2.03-1.98 (m, 1H), 1.66-1.63 (m, 1H), 1.61-1.54 (m, 1H), 1.50-1.46 (m, 1H), 1.40 (t, *J* = 12.7 Hz, 1H), 1.28-1.27 (m, 1H). **^{13}C NMR** (126 MHz, Acetone-d_6) δ 150.83, 147.87, 130.04 (*J* = 32.3 Hz), 129.02, 127.65, 127.53, 126.21, 126.08 (*J* = 3.7 Hz), 101.73, 81.45, 72.33, 68.74, 67.49, 54.34, 41.58, 36.00, 33.07, 32.27, 21.66. **HRMS** (ESI): m/z Calcd. For $C_{24}H_{25}F_3O_3$ ([M-H]$^-$): 417.1683, found: 417.1682. IR (KBr) *v* 3435.4, 2929.6, 1621.5, 1445.6, 1408.7, 1326.1, 1128.7, 1067.4, 1012.9, 845.5, 743.0, 702.4 cm^{-1}.

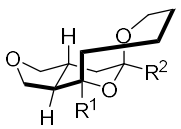
(3a*R*,11a*R*)-11-phenyl-5-(m-tolyl)decahydro-1*H*-5,11-epoxyfuro[3,4-*d*]oxecine (4i)



R^1=Ph,R^2=4-Me-Ph

White solid, m.p. 136-137 ºC, $[\alpha]_D^{25}$= +35.20 (*c* 1.00, DCM), 14.5 mg, 68% yield, 97% ee, dr > 20:1, determined by HPLC(CHIRAPAK AD-H, hexane/i-PrOH = 95/5, flowrate 1.0 mL/min, UV detection at 254 nm), t_{major} = 5.7 min, t_{minor} = 6.8 min. **^{1}H NMR** (500 MHz, Acetone-d_6) δ 7.62-7.61 (m, 2H), 7.53 (d, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.27 (t, *J* = 7.3 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 3.99 (t, *J* = 7.3 Hz, 1H), 3.82 (t, *J* = 7.5 Hz, 1H), 3.72 (dd, *J* = 7.5, 11.3 Hz, 1H), 3.62 (d, *J* = 12.0 Hz, 1H), 3.42 (dt, *J* = 2.0, 12.3 Hz, 1H), 3.17 (dd, *J* = 7.3, 10.7 Hz, 1H), 2.78-2.71 (m, 1H), 2.49 (dd, *J* = 7.8, 14.5 Hz, 1H), 2.35-2.31 (m, 4H), 2.27 (dd, *J* = 3.7, 13.0 Hz, 1H), 1.97-1.91 (m, *J* = 6.2 Hz, 1H), 1.63-1.59 (m, 1H), 1.54-1.53 (m, 1H), 1.48-1.44 (m, 1H), 1.35 (t, *J* = 12.7 Hz, 1H), 1.27-1.22 (m, *J* = 3.0 Hz, 1H). **^{13}C NMR** (126 MHz, Acetone-d6) 148.30, 143.57, 137.74, 129.63, 128.94, 127.39, 126.66, 126.23, 102.01, 80.93, 72.40, 68.76, 67.10, 54.52, 41.97, 36.15, 33.19, 32.38, 21.69, 21.03. **HRMS** (ESI): m/z Calcd. For $C_{24}H_{28}O_3Na$ ([M+Na]$^+$): 387.1931, found: 387.1932. IR (KBr) *v* 3434.2, 2976.3, 2924.1, 1639.7, 1382.2, 1046.1, 1004.7, 879.5, 664.9, 559.5 cm^{-1}.

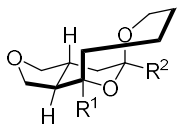
(3aR,11aR)-5-(3-methoxyphenyl)-11-phenyldecahydro-1H-5,11-epoxyfuro[3,4-d]oxecine (4j)



R1=Ph,R2=3-MeO-Ph

White solid, m.p. 132-133 ºC, $[\alpha]_D^{25}$= +46.41 (*c* 0.49, $CHCl_3$), 16.0 mg, 75% yield, 95% ee, dr > 20:1, determined by HPLC (CHIRAPAK DAD1 hexane/i-PrOH = 95/5, flowrate 1.0 mL/min, UV detection at 254 nm), t_{major} = 6.4 min, t_{minor} = 8.1 min. **^{1}H NMR** (500 MHz, Acetone-d6) δ 7.63-7.61 (m, 2H), 7.41 (t, *J* = 7.8 Hz, 2H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.27 (t, *J* = 7.3 Hz, 1H), 7.23-7.22 (m, 2H), 6.89 (ddd, J = 0.8, 2.6, 8.2 Hz, 1H), 3.99 (t, *J* = 7.3 Hz, 1H), 3.83 (s, 3H), 3.82 (t, *J* = 7.4 Hz, 1H), 3.72 (dd, *J* = 7.5, 11.30 Hz, 1H), 3.65 (d, *J* = 12.0 Hz, 1H), 3.43 (dt, *J* = 2.0, 12.27 Hz, 1H), 3.18 (dd, *J* = 7.3, 10.7 Hz, 1H), 2.78-7.68 (m, 1H), 2.49 (dd, *J* = 8.4, 14.3 Hz, 1H), 2.35-2.26 (m, *J* = 8.7 Hz, 2H), 1.97-1.90 (d, *J* = 7.6 Hz, 1H), 1.66-1.60 (m, 1H), 1.57-1.52 (m, 1H), 1.50-1.45 (m, 1H), 1.38 (t, J = 11.3 Hz, 1H), 1.26-1.20 (m, 1H). **^{13}C NMR** (126 MHz, Acetone-d6) δ 160.70, 148.24, 148.14, 130.11, 128.96, 127.43, 126.21, 118.88, 113.58, 112.53, 101.91, 81.04, 72.39, 68.75, 67.25, 55.40, 54.45, 41.75, 36.10, 33.16, 32.36, 21.69. **HRMS** (ESI): m/z Calcd. For $C_{24}H_{28}O_4Na$ ($[M+Na]^+$): 403.1880, found: 403.1881. IR (KBr) *v* 3435.9, 2931.9, 1607.1, 1487.9, 1261.4, 1133.9, 1030.6, 896.1, 743.1, 703.1 cm^{-1}.

(3a*R*,11a*R*)-11-(4-bromophenyl)-5-phenyldecahydro-1*H*-5,11-epoxyfuro[3,4-*d*] oxecine (4k)

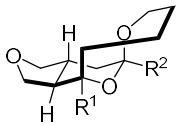


R1=4-Br-Ph, R2=Ph

White solid, m.p. 108-109 ºC, $[\alpha]D^{25}$ = +29.92 (*c* 1.00, DCM), 23.0 mg, 65% yield, 97% ee, dr > 20:1, determined by HPLC (CHIRAPAK AD-H, hexane/i-PrOH = 95/5, flow rate 1.0 mL/min, UV detection at 254 nm), t_{major} = 6.4 min, t_{minor} = 7.1 min. **^{1}H NMR** (500 MHz, Chloroform-d) δ 7.61 (d, *J* = 7.3 Hz, 2H), 7.53-7.51 (m, 2H), 7.43-7.39 (m, 4H), 7.34-7.31 (m, 1H), 4.09 (t, *J* = 7.3 Hz, 1H), 3.96 (t, *J* =7.4 Hz, 1H), 3.74 (dd, *J* = 7.3, 11.3 Hz, 1H), 3.70 (d, *J* = 12.1 Hz, 1H), 3.48 (dt, *J* = 1.9, 12.3 Hz, 1H), 3.23 (dd, *J* = 7.5, 10.7 Hz, 1H), 2.84-2.75 (m, 1 H), 2.50 (dd, *J* = 8.2, 14.5 Hz, 1H), 2.32 (dd, *J* = 3.7, 13.2 Hz, 1H), 2.18 (dd, *J* = 10.1, 14.6 Hz, 1H), 2.00-1.95 (m, 1H), 1.67-1.64 (m, 1H), 1.58-1.56 (m, 1H), 1.51-1.47 (m, 1H), 1.39 (t, *J* = 12.8 Hz, 1H), 1.23-1.20 (m, 1H). **^{13}C NMR** (126 MHz, Chloroform-d) δ 146.23, 145.01, 131.34, 128.38, 127.74, 127.24, 125.82, 120.72, 101.27, 80.07, 72.17, 68.42, 66.88, 53.36, 41.20, 35.38, 32.75, 31.53, 20.75. **HRMS** (ESI): m/z Calcd. For $C_{23}H_{25}BrO_3Na$ ($[M+Na]^+$): 451.0879, found: 451.0879. IR (KBr)

v 3467.8, 2924.4, 1646.4, 1489.4, 1445.6, 1261.4, 1135.8, 1091.0, 1026.8, 896.6, 805.0, 701.2 cm^{-1}.

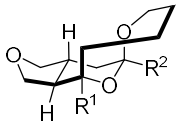
(3a*R*,11a*R*)-11-(3-chlorophenyl)-5-phenyldecahydro-1*H*-5,11-epoxyfuro[3,4-*d*] oxecine (4l)



R1=3-Cl-Ph, R2=Ph

White solid, m.p. 137-138 ºC, $[\alpha]D^{25}$ = +43.92 (*c* 1.00, DCM), 21.8 mg, 73% yield, 89% ee, dr >2 0:1, determined by HPLC (CHIRAPAK AD-H, hexane/i-PrOH = 95/5, flow rate 1.0 mL/min, UV detection at 254 nm), t_{major} = 4.9 min, t_{minor} = 6.3 min. **^{1}H NMR** (500 MHz, Chloroform-d) *δ* 7.62 (d, *J* = 6.7 Hz, 2H), 7.60 (t, *J* = 1.7 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.37-7.36 (m, 1H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.27 (m, *J* = 2.4 Hz, 1H), 4.09 (t, *J* = 7.3 Hz, 1H), 3.97 (t, *J* = 7.4 Hz, 1H), 3.75 (dd, *J* = 7.4, 11.3 Hz, 1H), 3.70 (d, *J* = 12.1 Hz, 1H), 3.50 (dt, *J* = 1.8, 12.3 Hz, 1H), 3.23 (dd, *J* = 7.5, 10.7 Hz, 1H), 2.82-2.77 (m, 1 H), 2.50 (dd, *J* = 8.3, 14.5 Hz, 1H), 2.32 (dd, *J* = 3.7, 13.2 Hz, 1H), 2.19 (dd, *J* = 10.7, 14.7 Hz, 1H), 2.02-1.96 (m, *J* = 6.2 Hz, 1H), 1.70-1.64 (m, 1H), 1.60-1.55 (m, 1H), 1.51-1.48 (m, 1H), 1.40 (t, *J* = 12.8 Hz, 1H), 1.29-1.27 (m, 1H). **^{13}C NMR** (126 MHz, Chloroform-d) *δ* 149.30, 144.96, 134.32, 129.54, 128.40, 127.75, 126.97, 125.91, 125.83, 123.49, 101.32, 80.07, 72.17, 68.41, 66.91, 53.30, 41.20, 35.40, 32.79, 31.51, 20.74. **HRMS** (ESI): m/z Calcd. For $C_{23}H_{25}ClO_3Na$ ([M+Na]+): 407.1384, found: 407.1382. IR (KBr) *v* 3435.1, 2925.5, 1645.8, 1446.0, 1261.5, 1222.7, 1136.1, 1092.0, 1026.6, 897.1, 804.2, 701.2 cm^{-1}.

(3a*R*,11a*R*)-11-(4-chlorophenyl)-5-phenyldecahydro-1*H*-5,11-epoxyfuro[3,4-*d*] oxecine (4m)

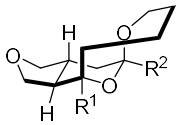


R1=4-Cl-Ph, R2=Ph

White solid, m.p. 139-140 ºC, $[\alpha]_D^{25}$ = +43.92 (*c* 1.00, DCM), 24.3 mg, 83% yield, 95% ee, dr > 20:1, determined by HPLC (CHIRAPAK AD-H, hexane/i-PrOH = 95/5, flow rate 1.0 mL/min, UV detection at 254 nm), t_{major} =6.1 min, t_{minor} = 7.0 min. **^{1}H NMR** (600 MHz, Chloroform-d) *δ* 7.61-7.60 (m, 2H), 7.49-7.47 (m, 2 H), 7.41 (t, *J* = 7.8 Hz, 2H), 7.39-7.37 (m, 2H), 7.33 (t, *J* = 7.3 Hz, 1H), 4.09 (t, *J* = 7.3 Hz, 1H), 3.96 (t, *J* = 7.4 Hz, 1H), 3.75 (dd, *J* = 7.4, 11.3 Hz, 1H), 3.70 (d, *J* = 12.1 Hz, 1H), 3.48 (dt, *J* = 1.8, 12.4 Hz, 1H), 3.23 (dd, *J* = 9.1, 9.1 Hz, 1H), 2.82-2.76 (m, 1H), 2.50 (dd, *J* = 8.2, 14.5 Hz, 1H), 2.32 (dd, *J* = 3.8, 13.2 Hz, 1H),

2.19 (dd, J = 10.4, 14.3 Hz, 1H), 2.00-1.96 (m,1 H), 1.69-1.62 (m, 1H), 1.58-1.56 (m, 1H), 1.51-1.48 (m, 1H), 1.40 (t, J = 12.8 Hz, 1H), 1.27-1.25 (m, 1H). **^{13}C NMR** (151 MHz, Chloroform-d) δ 145.88, 145.24, 132.78, 128.58, 127.95, 127.07, 126.04, 101.48, 80.23, 72.39, 68.65, 67.10, 53.63, 41.41, 35.59, 32.97, 31.74, 20.96. **HRMS** (ESI): m/z Calcd. For $C_{23}H_{25}ClO_3Na$ ([M+Na]+): 407.1384, found: 407.1391. IR (KBr) ν 3434.8, 2926.3, 1647.3, 1492.3, 1446.2, 1317.8, 1136.6, 1092.8, 1028.4, 897.9, 765.0, 701.6 cm^{-1}.

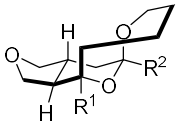
(3a*R*,11a*R*)-5-phenyl-11-(m-tolyl)decahydro-1*H*-5,11-epoxyfuro[3,4-*d*]oxecine (4n)



R^1=3-Me-Ph, R^2=Ph

White solid, m.p. 87-88 ºC, $[\alpha]_D^{25}$= +48.40 (c 1.00, DCM), 23.6 mg, 83% yield, 97% ee, dr > 20:1, determined by HPLC (CHIRAPAK AD-H, hexane/i-PrOH = 95/5, flowrate 1.0 mL/min, UV detection at 254 nm), t_{major} = 4.5 min, t_{minor} = 5.7 min. **^{1}H NMR** (600 MHz, Chloroform-d) δ 7.58 (br, 2H), 7.34 (t, J = 7.8 Hz, 2H), 7.29-7.25 (m, 3H), 7.22 (t, J = 7.6 Hz, 1 H), 7.03 (d, J = 7.4 Hz, 1 H), 4.01 (t, J = 7.3 Hz, 1H), 3.91 (t, J = 7. 4 Hz, 1H), 3.69 (dd, J = 7.4, 11.3 Hz, 1H), 3.62 (d, J = 12.0 Hz, 1H), 3.43 (dt, J = 1.8, 12.3 Hz, 1H), 3.15 (dd, J = 7.4, 10.7 Hz, 1H), 2.76-2.69 (m, 1H), 2.41 (dd, J = 8.2, 14.4 Hz, 1H), 2.34 (s, 3H), 2.25 (dd, J = 3.7, 13.2 Hz, 1H), 2.18 (dd, J = 10.5, 14.3 Hz, 1H), 1.97-1.92 (m, J = 6.2 Hz, 1H), 1.60-1.56 (m, 1H), 1.51-1.48 (m, 1H), 1.43-1.40 (m, 1H) 1.33 (t, J = 12.8 Hz, 1H), 1.26-1.22 (m, 1H). **^{13}C NMR** (151 MHz, Chloroform-d) δ 146.04, 144.30, 136.66, 127.27, 127.10, 126.58, 126.47, 125.06, 124.89, 121.41, 100.12, 79.20, 71.21, 67.62, 65.81, 52.47, 40.22, 34.35, 31.66, 30.63, 20.89, 19.86. **HRMS** (ESI): m/z Calcd. For $C_{24}H_{28}O_3Na$ ([M+Na]+): 387.1931, found: 387.1931. IR (KBr) ν 3433.3, 2925.1, 1646.2, 1446.0, 1261.7, 1222.8, 1135.5, 1092.9, 1025.6, 896.8, 766.2, 701.2 cm^{-1}.

(3a*R*,11a*R*)-11-(3-methoxyphenyl)-5-phenyldecahydro-1*H*-5,11-epoxyfuro[3,4-*d*] oxecine (4o)

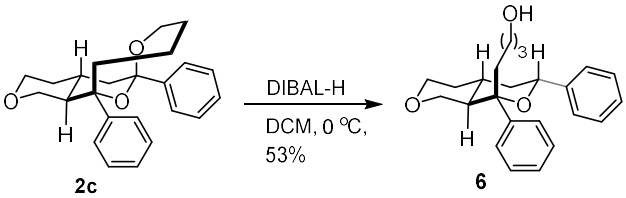


R^1=3-OMe-Ph, R^2=Ph

White solid, m.p. 135-136 ºC, $[\alpha]_D^{25}$= +39.47 (c 0.87, DCM), 11.3 mg, 75% yield, 98% ee, dr > 20:1, determined by HPLC (CHIRAPAK AD-H, hexane/i-PrOH = 95/5, flowrate 1.0 mL/min, UV detection at 254 nm), t_{major} = 5.8 min, t_{minor} = 8.0 min. **^{1}H NMR** (500 MHz, Chloroform-d) δ 7.65 (br, 2H), 7.42-7.40 (m, 2H), 7.33-7.30 (m, 2H), 7.20 (t, J = 2.1

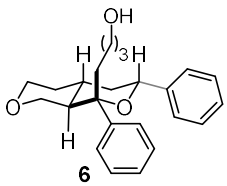
Hz, 1H), 7.07-7.05 (m, 1H), 6.84-6.82 (m, 1H), 4.08 (t, *J* = 7.3 Hz, 1H), 3.99 (t, *J* = 7.5 Hz, 1H), 3.86 (s, 3H), 3.76 (dd, *J* = 7.4, 11.3 Hz, 1H), 3.69 (d, *J* = 12.1 Hz, 1H), 3.50 (dt, *J* = 1.9, 12.3 Hz, 1H), 3.22 (m, *J* = 6.7 Hz, 1H), 2.82-2.77 (m, 1H), 2.48 (dd, *J* = 8.1, 14.3 Hz, 1H), 2.32 (dd, *J* = 3.7, 13.2 Hz, 1H), 2.23 (dd, *J* = 10.3, 14.1 Hz, 1H), 2.02-1.99 (q, *J* = 6.4 Hz, 1H), 1.67-1.64 (m, 1H), 1.55-1.53 (m, 1H), 1.49-1.47 (m, 1H), 1.38 (t, *J* = 12.7 Hz, 1H), 1.32-1.29 (m, 1H). **^{13}C NMR** (126 MHz, Chloroform-d) δ 159.57, 148.94, 145.26, 129.20, 128.32, 127.63, 125.89, 117.68, 112.06, 111.44, 101.19, 80.20, 72.23, 68.63, 66.87, 55.21, 53.43, 41.22, 35.40, 32.81, 31.63, 20.86. **HRMS** (ESI): m/z Calcd. For $C_{24}H_{28}O_4Na$ ([M+Na]+): 403.1884, found: 403.1181. IR (KBr) ν 3433.8, 2939.3, 1683.3, 1599.6, 1487.1, 1449.8, 1251.2, 1047.4, 754.5, 691.6 cm^{-1}.

7. Derivation of IEDHDA products



DIBAL-H (0.2 mL, 1.0 M in Toluene, 20.0 eq) was added to a solution of **2c** (1.0 eq, 5.2 mg, 0.014 mmol) in dry DCM at 0 °C. When the reaction completed by TLC analysis, then the mixture was quenched with saturated potassium and sodium tartrate solution, and washed with brine, extracted with ether. The organic layer was dried over Na_2SO_4, filtered, and concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel to afford alcohol **6** (2.8 mg, 53%).

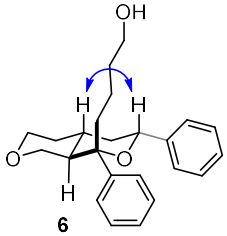
4-((1S,3R,4aR,8aR)-1,3-diphenylhexahydro-1H,3H-pyrano[3,4-c]pyran-1-yl)-butan-1-ol (6)

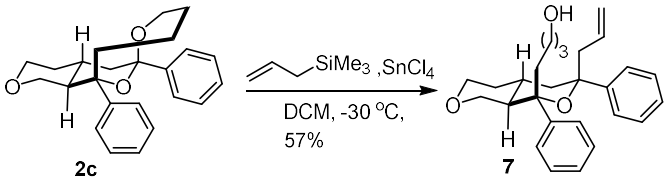


Colorless oil, $[\alpha]_D^{25}$= -47.07 (*c* 0.28, DCM), 2.8 mg, 53% yield, dr > 10:1, 97% ee , determined by HPLC (CHIRAPAK AD-H, hexane/i-PrOH = 80/20, flowrate 1.0 mL/min, UV detection at 254 nm), t_{major} = 4.4 min, t_{minor} = 5.2 min. **^{1}H NMR** (800 MHz, Acetone-d_6) δ 7.62 (d, *J* = 7.8 Hz, 2H), 7.53 (d, *J* = 7.4 Hz, 2H), 7.36-7.33 (m, 4H), 7.26-7.22 (m, *J* = 6.9 Hz, 2H), 4.91 (d, *J* = 11.5 Hz, 1H), 3.81 (dd, *J* = 3.8, 11.0 Hz, 1H), 3.51 (dd, J = 3.0, 10.9 Hz, 1H), 3.49-3.47 (m, 2H), 3.41 (t, *J* = 11.7 Hz, 1H), 3.36 (t, *J* = 5.1 Hz, 1H),

3.23 (t, J = 11.0 Hz, 1H), 2.51-2.46 (m, 1H), 2.21-2.19 (m, 1H), 2.07 (d, J = 13.5 Hz, 1H), 1.96-1.95 (m, 1 H), 1.94-1.91 (m, J = 5.6 Hz, 1H), 1.62 (d, J = 13.1 Hz, 1H), 1.56-1.53 (m, 2 H), 1.52 (dt, J = 3.8, 11.3 Hz, 1H), 1.45-1.40 (m, 1H), 1.33-1.32 (m, 1H), 1.32-1.31 (m, 1H), 1.09-1.06 (m, 1H). **^{13}C NMR** (201 MHz, Acetone-d_6) δ 145.14, 143.96, 128.11, 127.80, 127.01, 126.53, 126.27, 125.97, 79.25, 71.75, 67.74, 67.63, 61.56, 52.32, 40.78, 34.09, 33.65, 33.00, 26.86, 19.25. **HRMS** (ESI): m/z Calcd. For $C_{24}H_{30}O_3Na$ ([M+Na]$^+$): 389.2093, found: 389.2086.

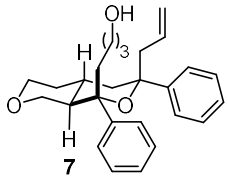
Key ^{1}H-^{1}H NOE:





A flame dried round bottom flask equipped with a stirring bar was charged with CH_2Cl_2 (0.5 mL), **2c** (5.0 mg, 0.014 mmol) and allyltrimethylsilane (0.1 mL). The reaction was then cooled to -30°C and $SnCl_4$ (1.0 M in methylene chloride, 0.14 mL, 0.14 mmol) was slowly added dropwise. The resulting mixture was stirred for 21 hours at this temperature and terminated by addition of a saturated aqueous $NaHCO_3$ solution which was extracted with Et_2O.The organic phases were combined, dried over Na_2SO_4, filtered and concentrated under reduced pressure and the residue was purified by silica gel chromatography to get product **7** (3.2 mg, 57% yield).

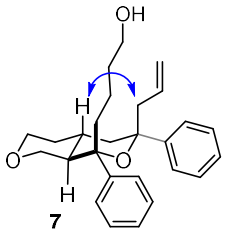
4-((1S,3R,4aR,8aR)-3-allyl-1,3-diphenylhexahydro-1H,3H-pyrano[3,4-c]pyran-1-yl)butan-1-ol (7)

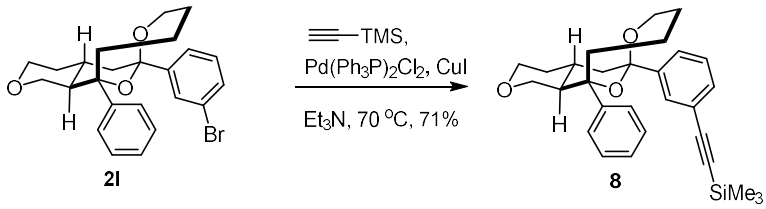


Colorless oil, $[\alpha]_D^{25}$= -34.14 (c 0.14, DCM), 3.2 mg, 57% yield, dr > 10:1, 96% ee, determined by HPLC (CHIRAPAK AD-H, hexane/i-PrOH = 95/5, flowrate 1.0 mL/min, UV detection at 254 nm), t_{major} = 15.6 min, t_{minor} = 17.9 min. **^{1}H NMR** (800 MHz, Acetone-d_6) δ 7.50 (d, J = 7.6 Hz, 2H), 7.44 (d, J = 7.7 Hz, 2H), 7.34 (t, J = 7.7 Hz, 2H), 7.28 (t, J = 7.7 Hz, 2H), 7.24 (t,

J = 7.4 Hz, 1H), 7.19 (t, *J* = 7.2 Hz, 1H), 5.37-5.32 (m, 1 H), 4.95 (d, *J* = 16.9 Hz, 1H), 4.85 (d, *J* = 10.3 Hz, 1H), 3.83 (dd, *J* = 4.0, 10.72 Hz, 1H), 3.63 (dd, *J* = 3.4, 10.8 Hz, 1H), 3.52-3.51 (m, 2H), 3.47 (t, *J* = 11.3 Hz, 1H), 3.39 (t, *J* = 5.2 Hz, 1H), 3.36 (t, *J* = 10.9 Hz, 1H), 3.10 (dd, *J* = 8.4, 13.65 Hz, 1H), 2.77-2.76 (m, 1H), 2.47-2.43 (m, 1H), 2.32-2.29 (m, 1H), 2.26-2.22 (m, *J* = 7.4 Hz, 1H), 2.11-2.09 (m, 1H), 1.78-1.76 (m, 1H), 1.72 (d, *J* = 13.1 Hz, 1H), 1.58-1.56 (m, 1H), 1.55 (t, *J* = 10.6 Hz, 1H), 1.38-1.37 (m, 1H), 1.26-1.23 (m, 1H). **^{13}C NMR** (201 MHz, Acetone-d_6) δ 149.20, 147.98, 136.00, 128.56, 128.44, 127.21, 127.18, 127.07, 126.12, 117.61, 81.10, 78.40, 68.47, 68.32, 62.53, 53.36, 46.20, 40.88, 34.59, 34.07, 33.65, 21.14. **HRMS** (ESI): m/z Calcd. For $C_{27}H_{34}O_3Na$ ([M+Na]$^+$): 429.2406, found: 429.2403.

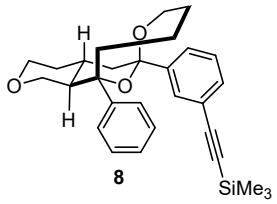
Key ^{1}H-^{1}H NOE:





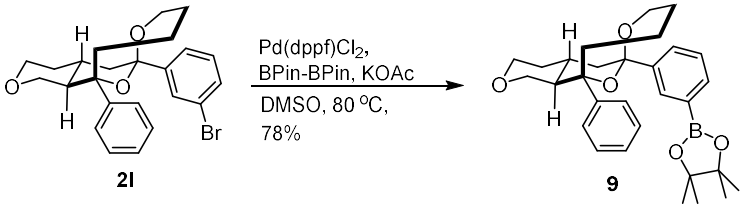
A flame dried vial equipped with a stirring bar was charged with $Pd(Ph_3P)_2Cl_2$ (0.82 mg, 1.2 μmol), **2l** (5.15 mg, 0.012 mmol), CuI (0.44 mg, 2.3 μmol) and Et_3N (0.5mL). The reaction mixture was then sealed and heated up to 70°C. After stirring overnight at this temperature, the mixture was concentrated under reduced pressure, and the residue was purified by silica gel chromatography to get product **8** (3.8 mg, 71% yield).

Trimethyl((3-((4aR,12aR)-12-phenyldecahydro-1H,6H-6,12-epoxypyrano[4,3-d]oxecin-6-yl)phenyl)ethynyl)silane (8)



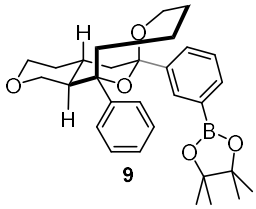
Colorless oil, $[\alpha]_D^{25}$= -40.16 (*c* 0.38, DCM), 3.8 mg, 71% yield, 98% ee, dr > 20:1, determined by HPLC (CHIRAPAK AD-H, hexane/i-PrOH = 97/3, flowrate1.0 mL/min, UV detection at 254 nm), t_{major} = 3.6 min, t_{minor} = 4.8 min. **^{1}H NMR** (800 MHz, Chloroform-d) δ 7.69 (dd, *J* = 7.8, 11.9 Hz, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.58 (d, *J* =

7.7 Hz, 1H), 7.50 (t, J = 4.5 Hz, 1H), 7.43 (t, J = 7.5 Hz, 2H), 7.41 (d, J = 7.5 Hz, 1H), 7.33-7.31 (m, 2H), 3.93 (dd, J = 3.7, 11.1 Hz, 1H), 3.63 (d, J = 12.1 Hz, 1H), 3.46 (t, J = 11.4 Hz, 1H), 3.42 (dd, J = 3.7, 10.9 Hz, 1H), 3.31 (t, J = 12.2 Hz, 1H), 3.17 (t, J = 11.0 Hz, 1H), 2.54-2.52 (m, 1H), 2.45-2.39 (m, J = 6.9 Hz, 1H), 2.33 (dd, J = 10.9, 14.7 Hz, 1H), 2.17-2.14 (dd, J = 3.9, 13.7 Hz, 1H), 1.84-1.79 (m, 2H), 1.73-1.68 (m, 1H), 1.62-1.61 (m, 1H), 1.49-1.44 (m, 2H), 1.39-1.35 (m, 1H), 1.31-1.29 (m, 1H). **^{13}C NMR** (201 MHz, Chloroform-d) δ 145.48, 144.56, 132.22, 131.02, 128.66, 128.60, 128.18, 127.23, 126.92, 122.93, 105.32, 100.73, 94.05, 79.70, 68.36, 67.81, 66.61, 51.39, 44.71, 32.99, 31.61, 30.11, 29.79, 21.98, -0.03. **HRMS** (ESI): m/z Calcd. For C29H36O3SiNa ([M+Na]$^+$): 483.2326, found: 483.2329.



A flame dried vial equipped with a stirring bar was charged with Pd(dppf)Cl_2 (2.2 mg, 3.0 μmol), **2l** (4.5 mg, 0.01 mmol), Bis(pinacolato)diboron (3.81 mg, 0.015 mmol) and KOAc (5.89 mg, 0.06 mol) in DMSO (0.5 mL) . The reaction mixture was then sealed and heated up to 80°C. After stirring overnight at this temperature, the reaction mixture was terminated by addition of water, which was extracted with Et_2O.The organic phases were combined, dried over Na_2SO_4, filtered and concentrated under reduced pressure and the residue was purified by silica gel chromatography to get product **9** (3.9 mg, 78% yield).

4,4,5,5-tetramethyl-2-(3-((4aR,12aR)-12-phenyldecahydro-1H,6H-6,12-epoxy-pyrano[4,3-d]oxecin-6-yl)phenyl)-1,3,2-dioxaborolane (9)



Colorless oil, $[\alpha]_D^{25}$= -15.10 (c 0.38, DCM), 3.9 mg, 78% yield, 94% ee, dr > 20:1, determined by HPLC (CHIRAPAK AD-H, hexane/i-PrOH = 98/2, flowrate1.0 mL/min, UV detection at 254 nm), t_{major} = 4.8 min, t_{minor} = 4.1 min. **^{1}H NMR** (800 MHz, Acetone-d_6) δ 8.05 (br, 1 H), 7.74-7.69 (m, 3H), 7.66 (d, J = 7.2 Hz, 1 H), 7.43 (t, J = 7.6 Hz, 2H), 7.39 (t, J = 7.4 Hz, 1H), 7.31 (t, J = 7.3 Hz, 1H), 3.81 (dd, J = 3.8, 11.0

Hz, 1H), 3.54 (d, J = 12.2 Hz, 1H), 3.43 (t, J = 11.7 Hz, 1H), 3.31 (d, J = 10.8 Hz, 1H), 3.23 (t, J = 12.3 Hz, 1H), 3.17 (t, J = 11.1 Hz, 1H), 2.55 (dd, J = 7.9, 15.1 Hz, 1H), 2.42-2.39 (m, 2H), 2.12-2.08 (m, J = 6.2 Hz, 1H), 1.77 (t, J = 13.6 Hz, 1H), 1.75-1.73 (m, 1H), 1.67-1.63 (m, 1H), 1.60 (d, J = 13.2 Hz, 1H), 1.43 (t, J = 12.9 Hz, 2H), 1.35 (s, 6H), 1.34 (s, 6H), 1.26-1.24 (m, 2H). **^{13}C NMR** (201 MHz, Acetone-d_6) δ 145.31, 145.03, 133.54, 132.15, 128.71, 127.98, 127.52, 127.04, 126.97, 100.98, 83.64, 79.54, 67.76, 67.33, 66.18, 61.92, 51.63, 44.93, 32.96, 31.58, 29.93, 29.78, 24.38, 21.98. **HRMS** (ESI): m/z Calcd. For $C_{30}H_{39}O_5BNa$ ([M+Na]$^+$): 513.2788, found: 513.2784.

8. Crystallography data for 2o and 4h

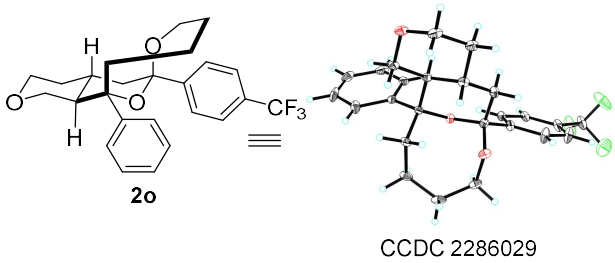


Figure 1. **The Crystal Structure of 2o**. The X-ray crystallographic coordinates for structures of **2o** has been deposited at the Cambridge Crystallographic Data Centre under deposition numbers CDCC-2286029.

Table 1. Crystal data and structure refinement for 2o.

Identification code	global	
Empirical formula	C25 H27 F3 O3	
Formula weight	432.46	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Hexagonal	
Space group	$P6_5$	
Unit cell dimensions	a = 17.6761(5) Å	α = 90°.
	b = 17.6761(5) Å	β = 90°.
	c = 12.4915(4) Å	γ = 120°.
Volume	3380.0(2) Å^3	
Z	6	
Density (calculated)	1.275 Mg/m^3	
Absorption coefficient	0.829 mm^{-1}	

F(000)	1368
Crystal size	0.280 x 0.200 x 0.180 mm^3
Theta range for data collection	2.887 to 69.982°.
Index ranges	-21<=h<=21, -21<=k<=21, -15<=l<=15
Reflections collected	37431
Independent reflections	4274 [R(int) = 0.0359]
Completeness to theta = 67.679°	99.9 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4274 / 1 / 280
Goodness-of-fit on F^2	1.096
Final R indices [I>2sigma(I)]	R1 = 0.0777, wR2 = 0.2275
R indices (all data)	R1 = 0.0780, wR2 = 0.2279
Absolute structure parameter	0.04(3)
Extinction coefficient	n/a
Largest diff. peak and hole	1.627 and -0.471 e.$Å^{-3}$

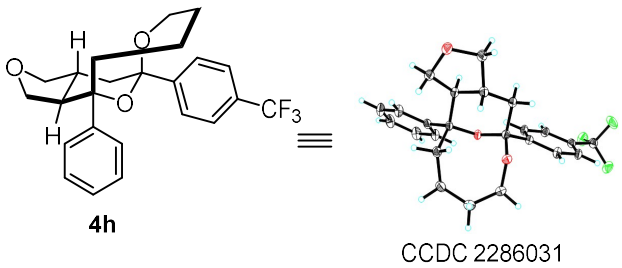


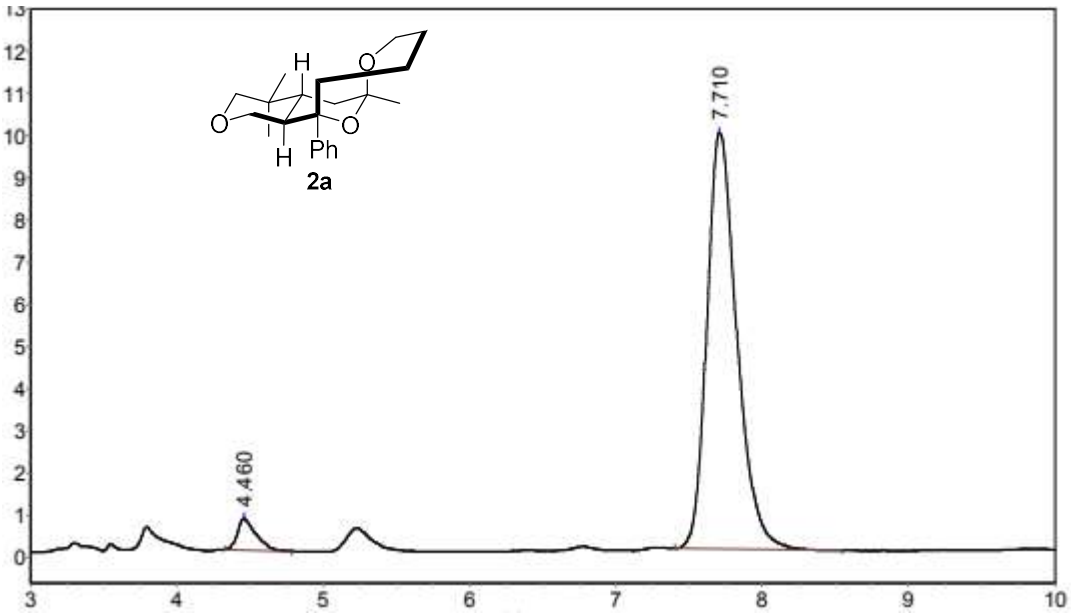
Figure 2. **The Crystal Structure of 4h**. The X-ray crystallographic coordinates for structures of **4h** has been deposited at the Cambridge Crystallographic Data Centre under deposition numbers CDCC-2286031.

Table 2. Crystal data and structure refinement for **4h**.

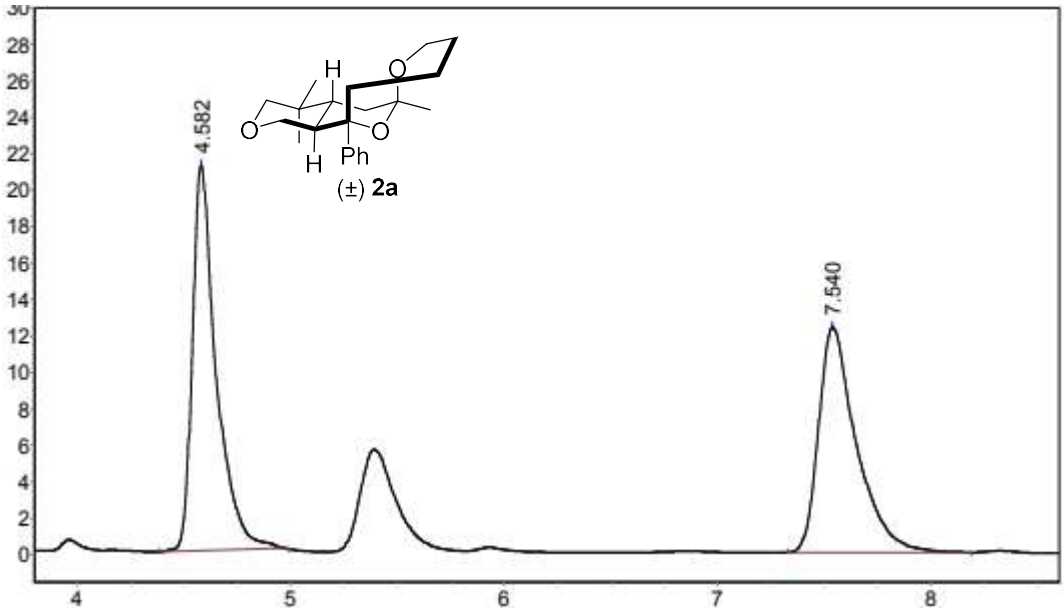
Identification code	global	
Empirical formula	C24 H25 F3 O3	
Formula weight	418.44	
Temperature	150(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 10.6597(2) Å	α = 90°.
	b = 15.6244(4) Å	β =

109.6180(10)°.	
	c = 13.1101(3) Å γ = 90°.
Volume	2056.76(8) $Å^3$
Z	4
Density (calculated)	1.351 Mg/m^3
Absorption coefficient	0.891 mm^{-1}
F(000)	880
Crystal size	0.400 x 0.200 x 0.100 mm^3
Theta range for data collection	3.58 to 70.12°.
Index ranges	-12<=h<=13, -16<=k<=18, -15<=l<=15
Reflections collected	51308
Independent reflections	7634 [R(int) = 0.0522]
Completeness to theta = 70.12°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.92 and 0.71
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7634 / 1 / 541
Goodness-of-fit on F^2	1.016
Final R indices [I>2sigma(I)]	R1 = 0.0301, wR2 = 0.0731
R indices (all data)	R1 = 0.0332, wR2 = 0.0753
Absolute structure parameter	0.11(5)
Largest diff. peak and hole	0.181 and -0.205 $e.Å^{-3}$

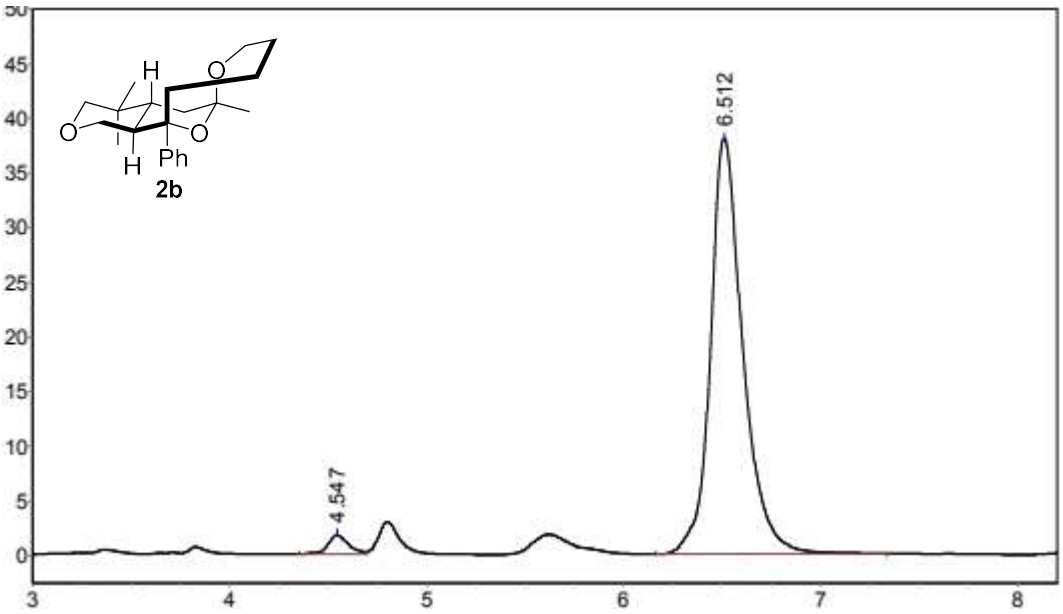
9. HPLC Chromatograms



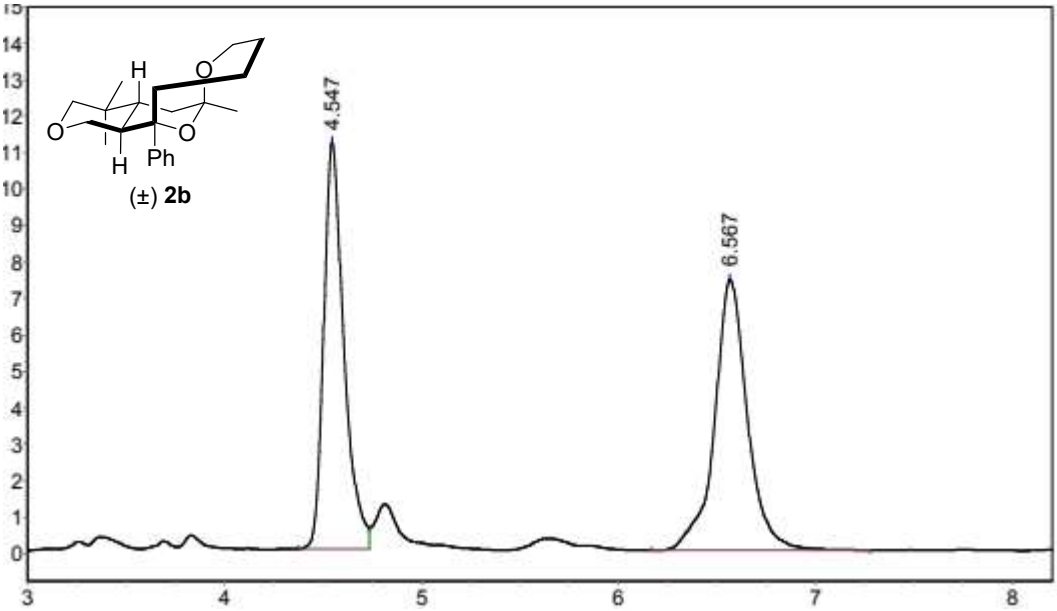
#	RT (time)	Heigh (mV*sec)	Area (mv)	Area (%)
1	4.460	1771.000	6788.655	4.5411
2	7.710	9881.150	142706.328	95.4589



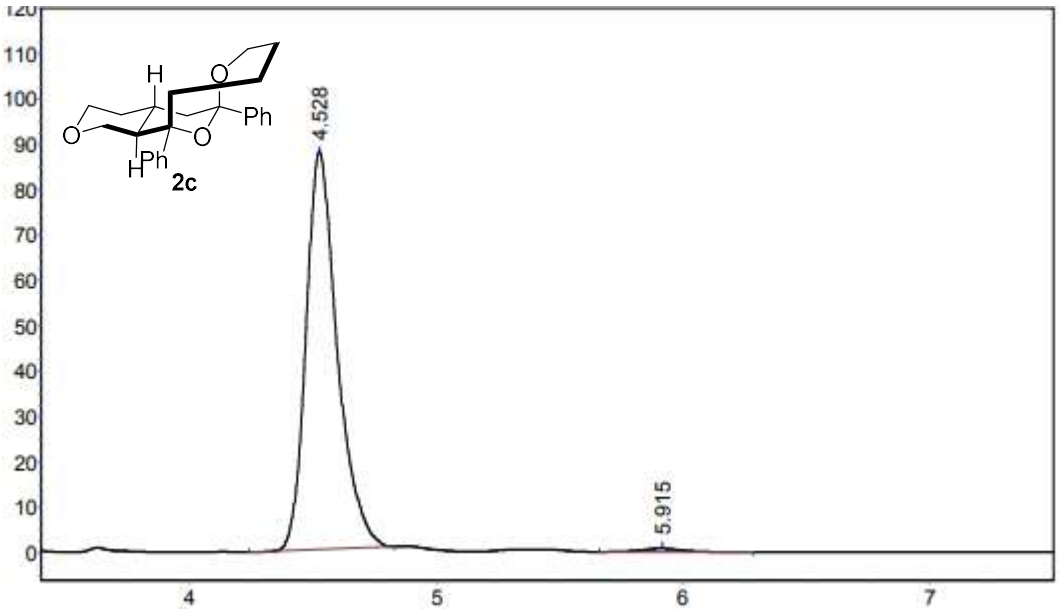
#	RT (time)	Heigh (mV*sec)	Area (mv)	Area (%)
1	4.582	21153.670	163763.203	51.8869
2	7.540	12341.280	151852.250	48.1131



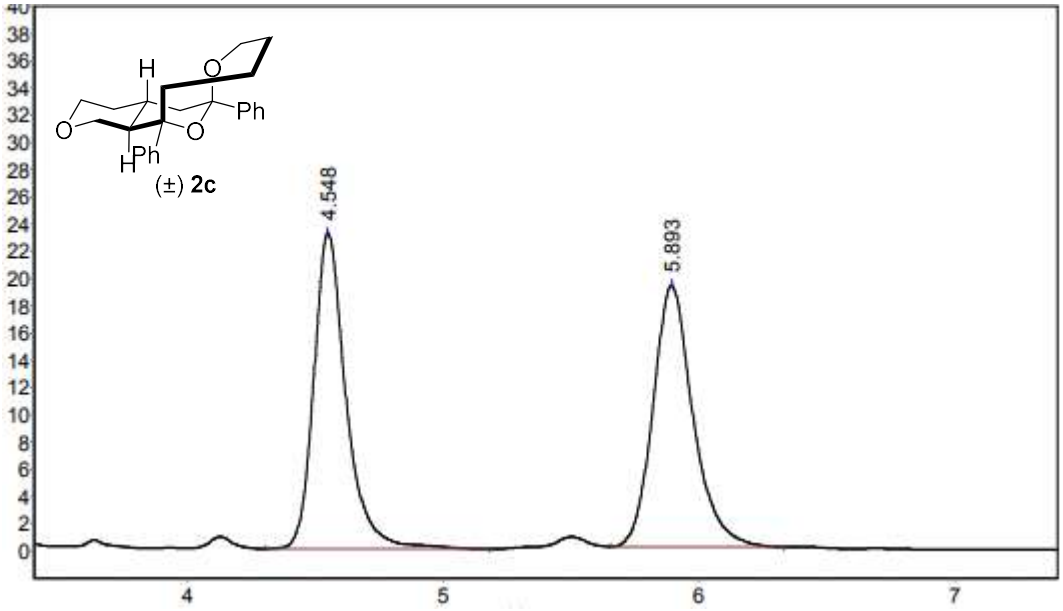
#	RT (time)	Heigh (mV*sec)	Area (mv)	Area (%)
1	4.547	1771.000	13278.399	2.9554
2	6.512	38006.566	436018.188	97.0446



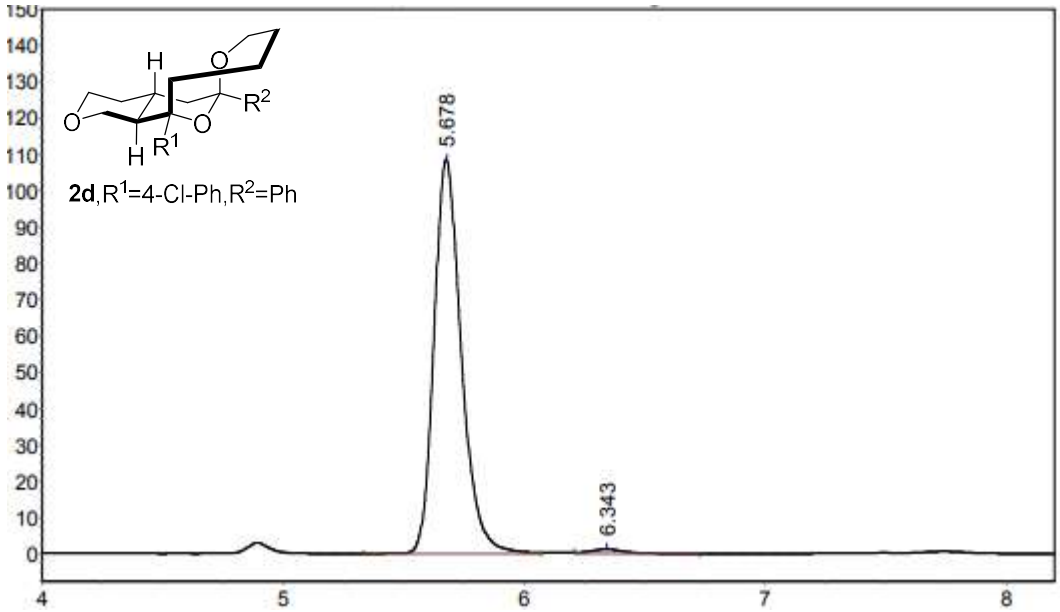
#	RT (time)	Heigh (mV*sec)	Area (mv)	Area (%)
1	4.547	11163.000	79754.797	48.0613
2	6.567	7424.342	86189.148	51.9387



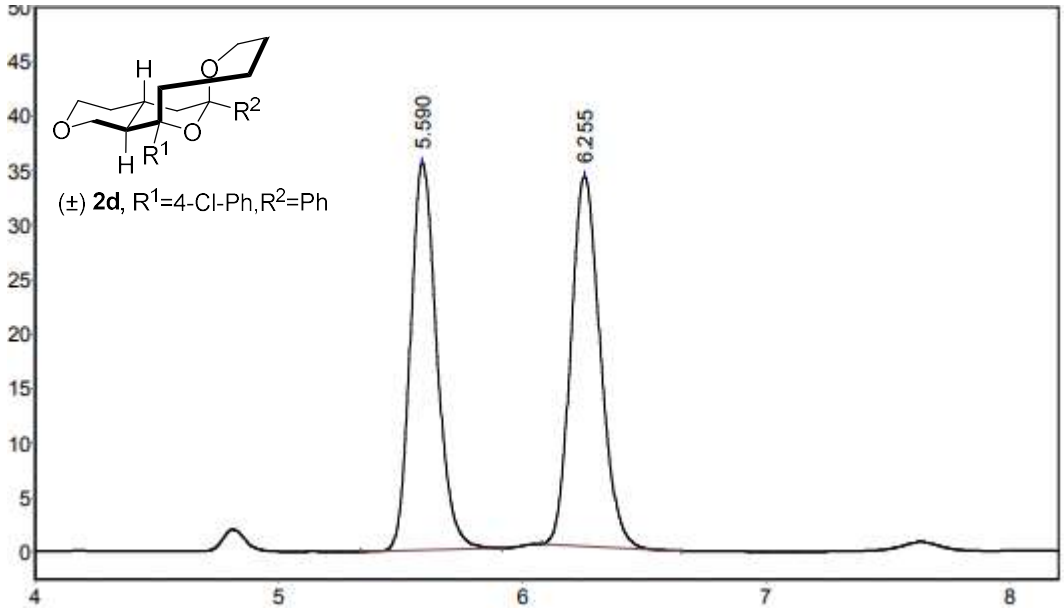
#	RT (time)	Heigh (mV*sec)	Area (mv)	Area (%)
1	4.528	87556.102	771446.125	98.8126
2	5.915	798.204	9270.100	1.1874



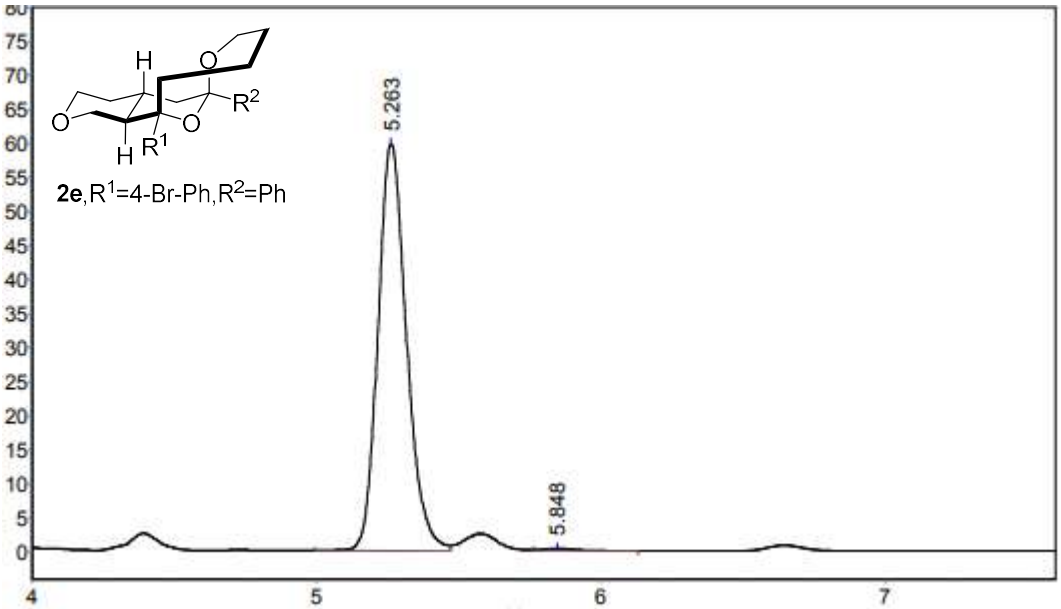
#	RT (time)	Heigh (mV*sec)	Area (mv)	Area (%)
1	4.548	23180.674	203984.000	49.2486
2	5.893	19233.775	210208.859	50.7514



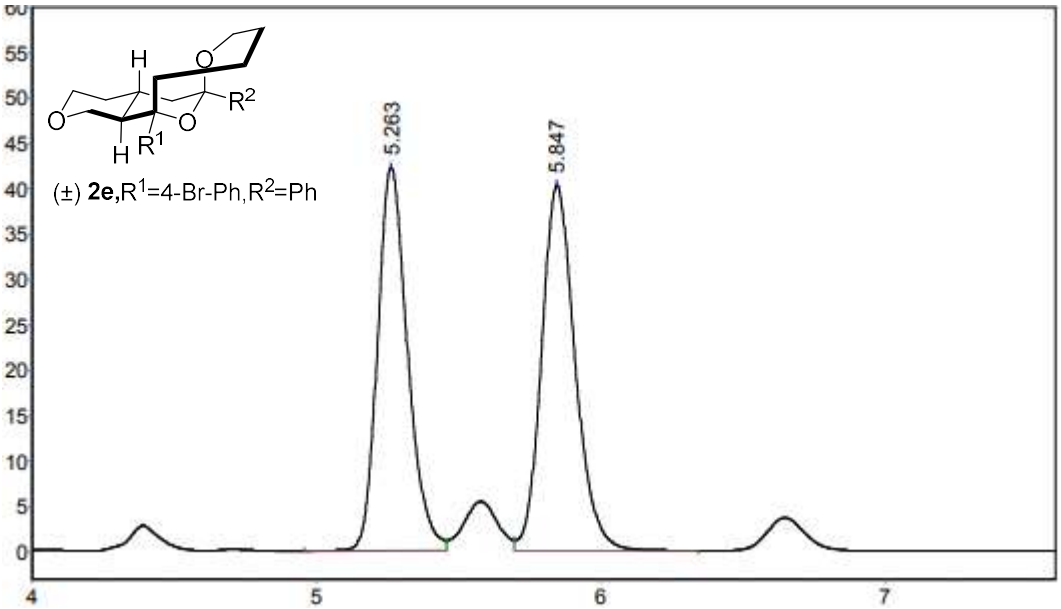
#	RT (time)	Heigh (mV*sec)	Area (mv)	Area (%)
1	5.678	108566.023	858816.813	98.5742
2	6.343	1250.208	12421.921	1.4258



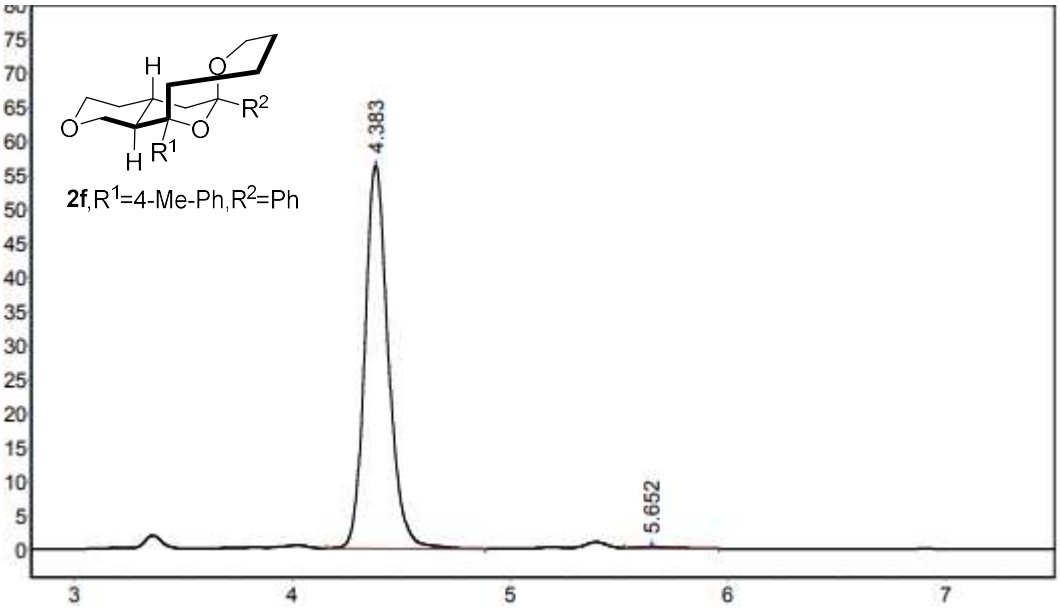
#	RT (time)	Heigh (mV*sec)	Area (mv)	Area (%)
1	5.590	35572.059	266646.656	48.4310
2	6.255	33899.156	283923.281	51.5690



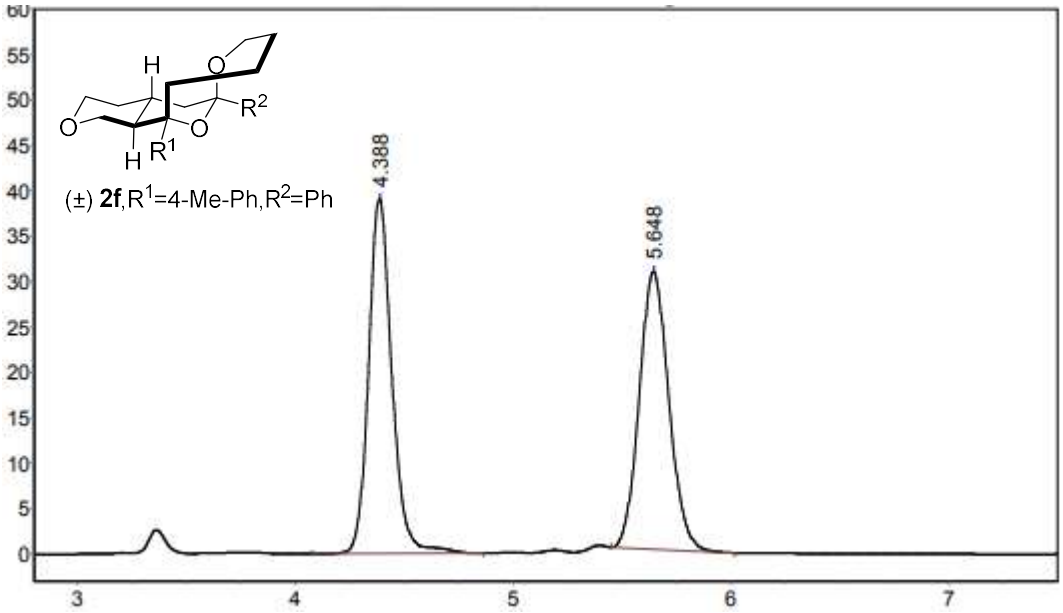
#	RT (time)	Heigh (mV*sec)	Area (mv)	Area (%)
1	5.263	59719.746	418283.656	99.2082
2	5.848	382.299	3338.541	0.7918



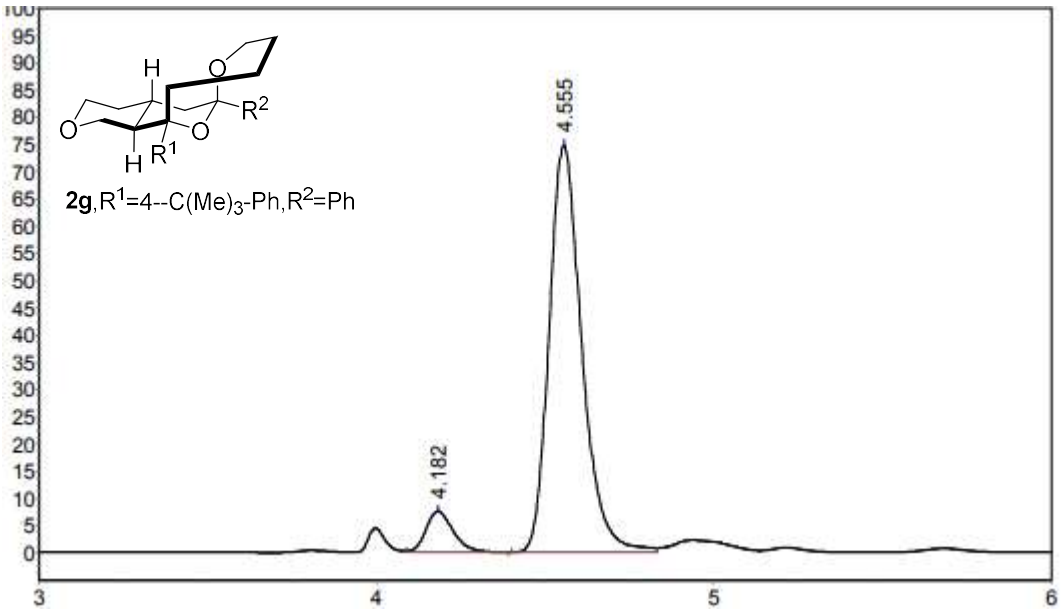
#	RT (time)	Heigh (mV*sec)	Area (mv)	Area (%)
1	5.263	42162.441	310212.625	48.4216
2	5.847	40239.996	330435.969	51.5783



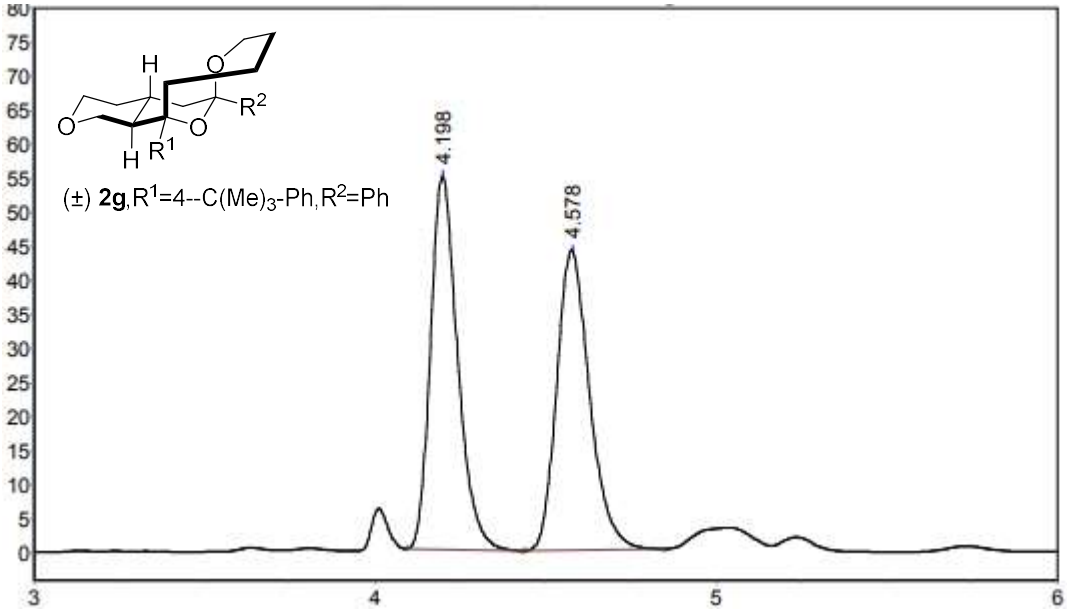
#	RT (time)	Heigh (mV*sec)	Area (mv)	Area (%)
1	4.383	56190.887	422468.313	97.5097
2	5.652	309.000	3671.900	0.8475



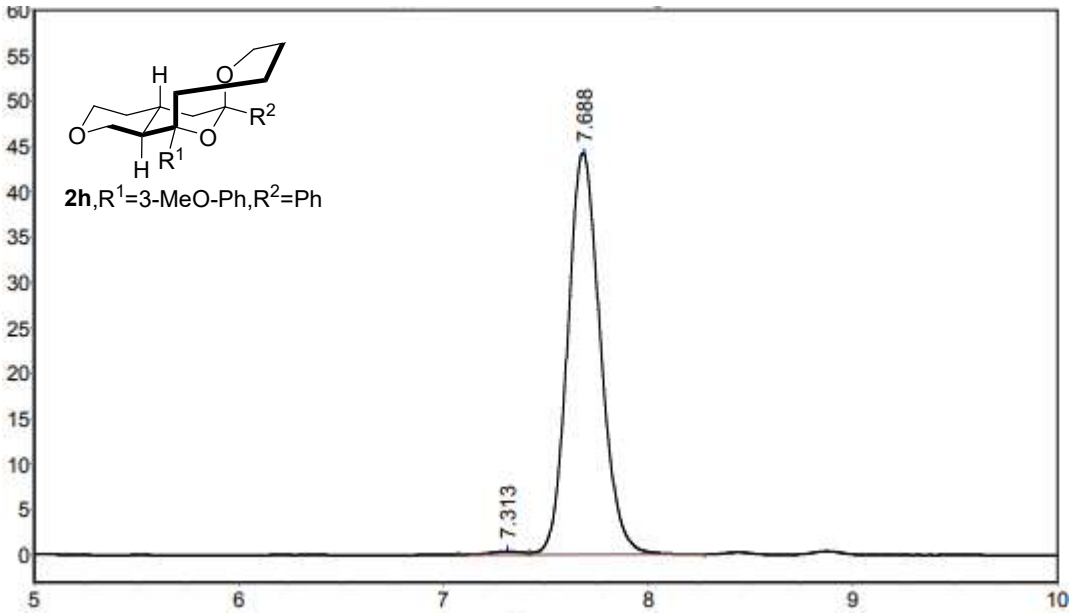
#	RT (time)	Heigh (mV*sec)	Area (mv)	Area (%)
1	4.388	39103.223	292129.750	50.2896
2	5.648	30571.168	288764.813	49.7104



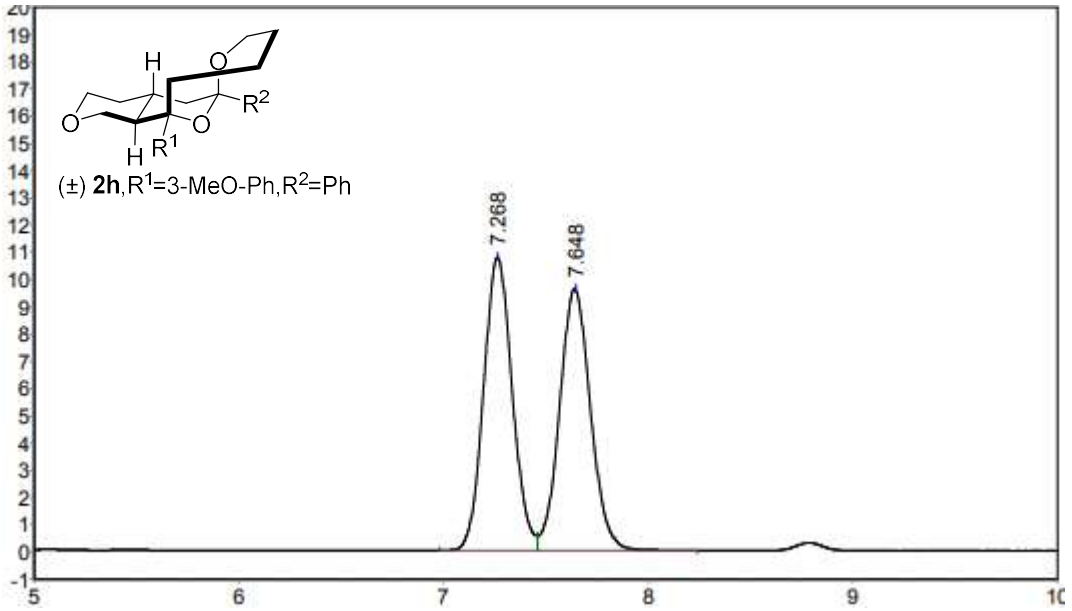
#	RT (time)	Heigh (mV*sec)	Area (mv)	Area (%)
1	4.182	7560.000	42328.098	7.7609
2	4.555	74722.000	503071.375	92.2391



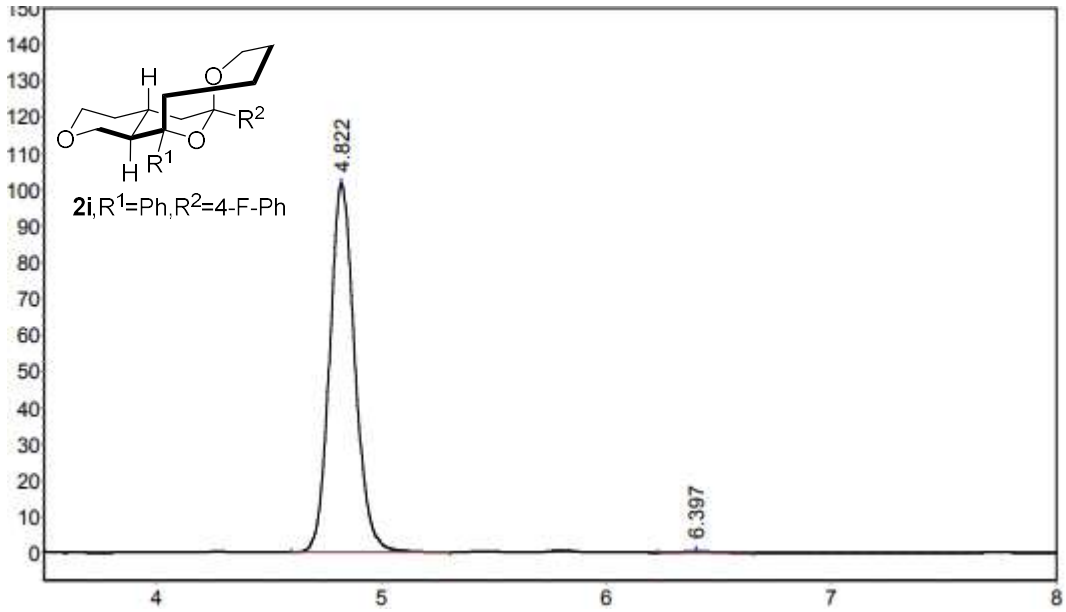
#	RT (time)	Heigh (mV*sec)	Area (mv)	Area (%)
1	4.198	54679.957	302947.188	50.6584
2	4.578	43978.391	295072.188	49.3416



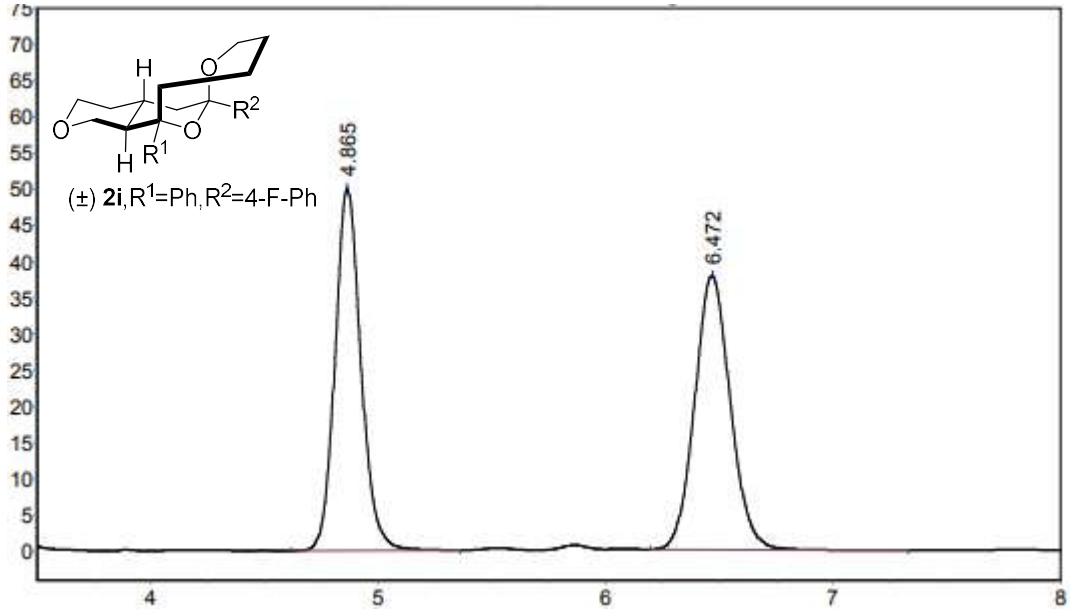
#	RT (time)	Heigh (mV*sec)	Area (mv)	Area (%)
1	7.313	381.676	4201.667	0.8453
2	7.688	44217.297	492853.781	99.1547



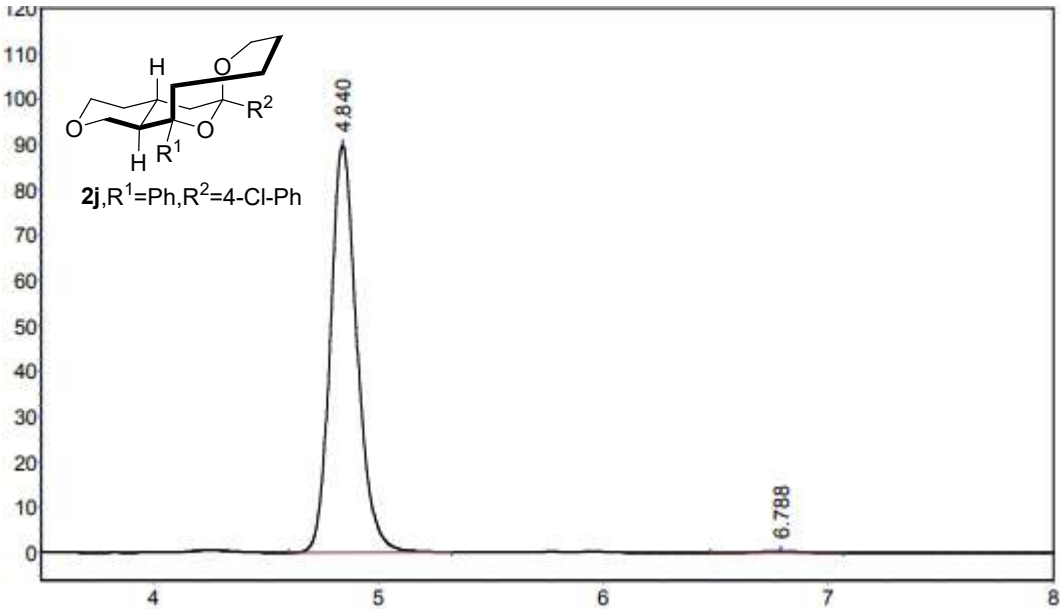
#	RT (time)	Heigh (mV*sec)	Area (mv)	Area (%)
1	7.268	10754.546	104730.813	50.8351
2	7.648	9597.940	101289.891	49.1649



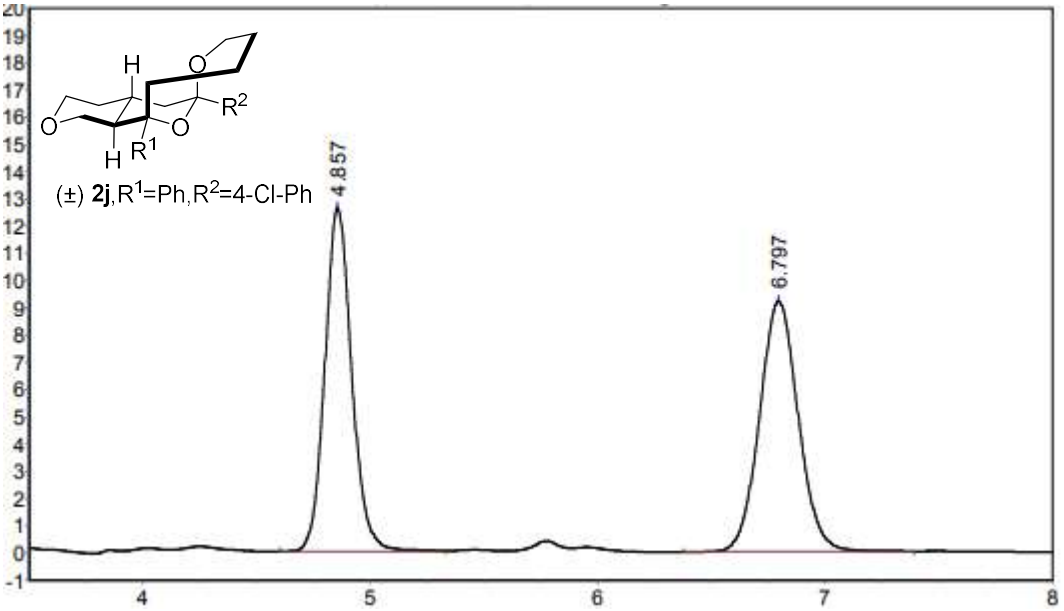
#	RT (time)	Heigh (mV*sec)	Area (mv)	Area (%)
1	4.822	101467.945	791441.063	99.5885
2	6.397	307.000	3269.900	0.4115



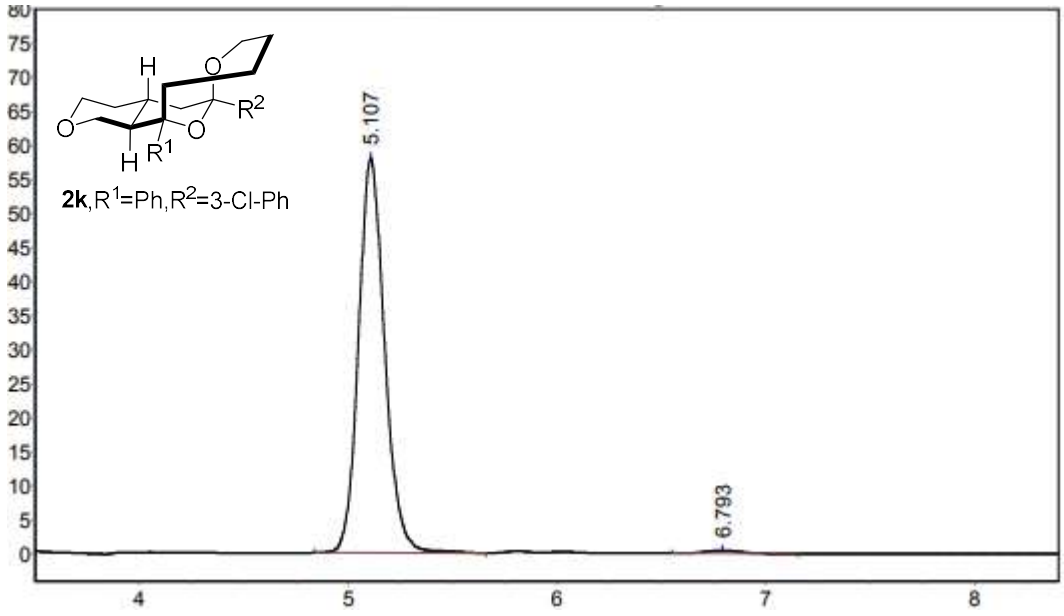
#	RT (time)	Heigh (mV*sec)	Area (mv)	Area (%)
1	4.865	49903.570	395161.625	48.8958
2	6.472	37791.602	413008.906	51.1042



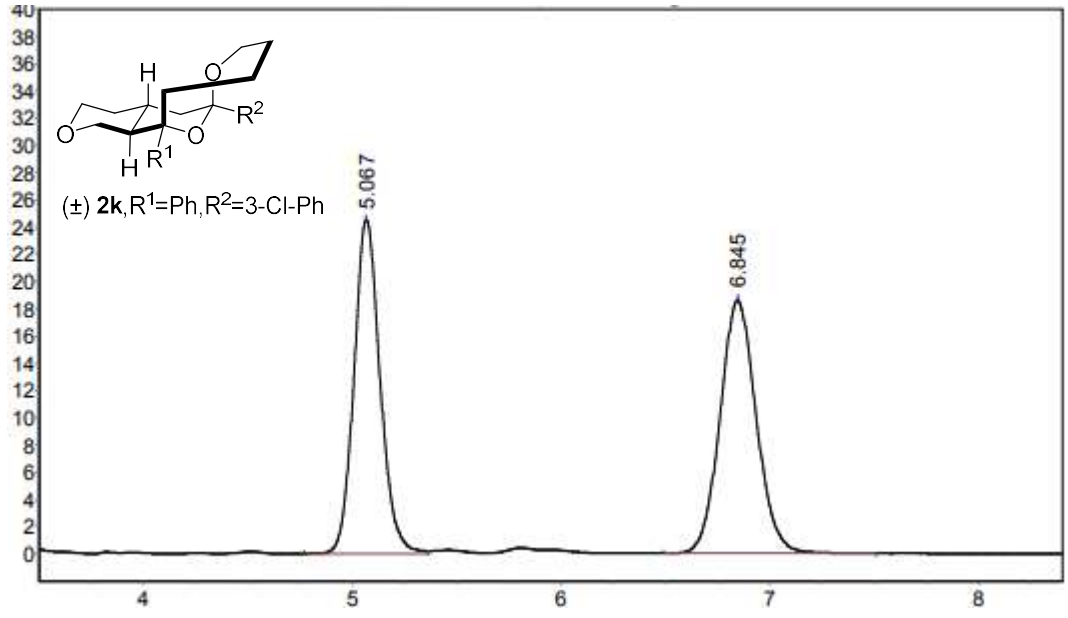
#	RT (time)	Heigh (mV*sec)	Area (mv)	Area (%)
1	4.840	89657.375	740885.813	99.4938
2	6.788	327.809	3769.400	0.5062



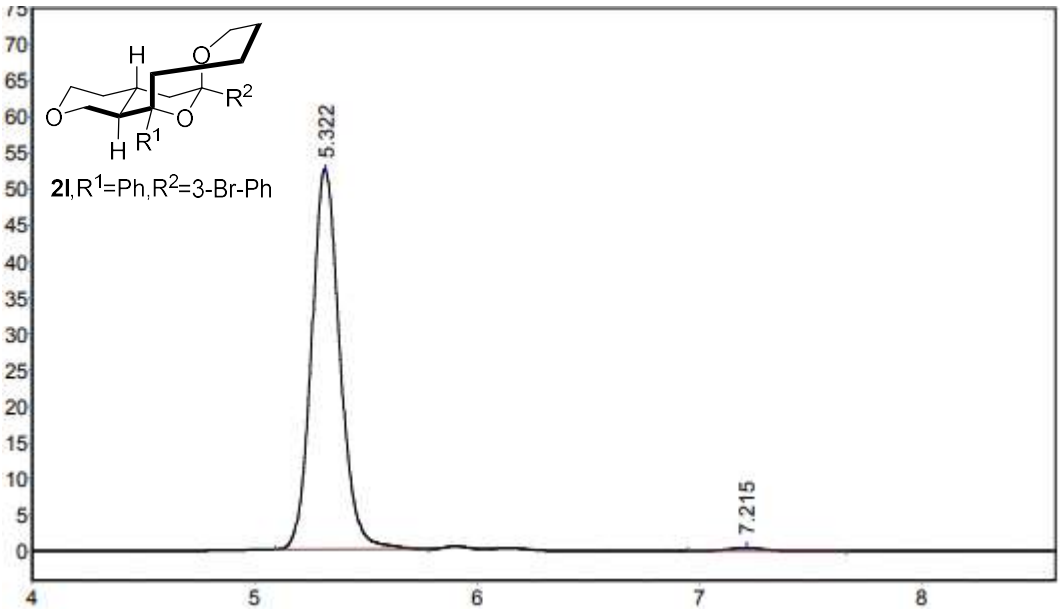
#	RT (time)	Heigh (mV*sec)	Area (mv)	Area (%)
1	4.857	12615.912	104203.453	48.9668
2	6.797	9191.795	108600.672	51.0332



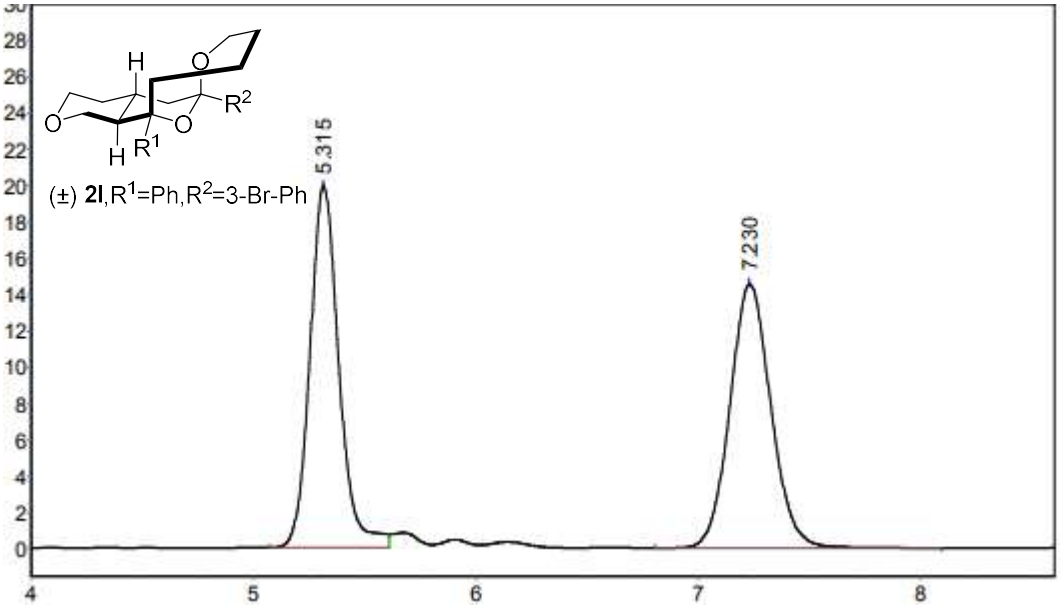
#	RT (time)	Heigh (mV*sec)	Area (mv)	Area (%)
1	5.107	57857.004	507987.625	98.8578
2	6.793	497.512	5869.462	1.1422



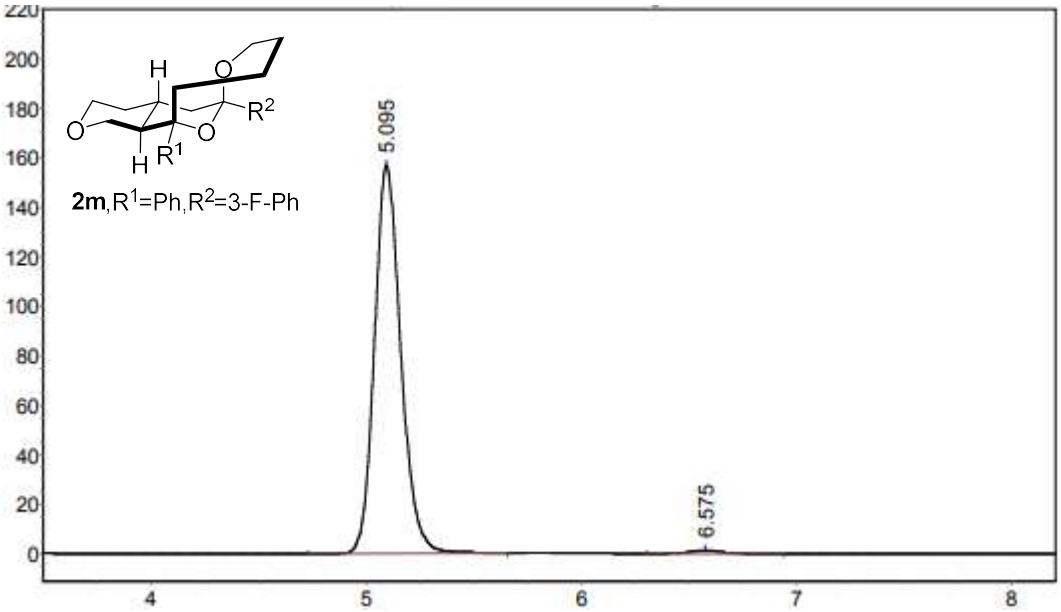
#	RT (time)	Heigh (mV*sec)	Area (mv)	Area (%)
1	5.067	24468.000	213636.391	48.7571
2	6.845	18569.850	224528.609	51.2429



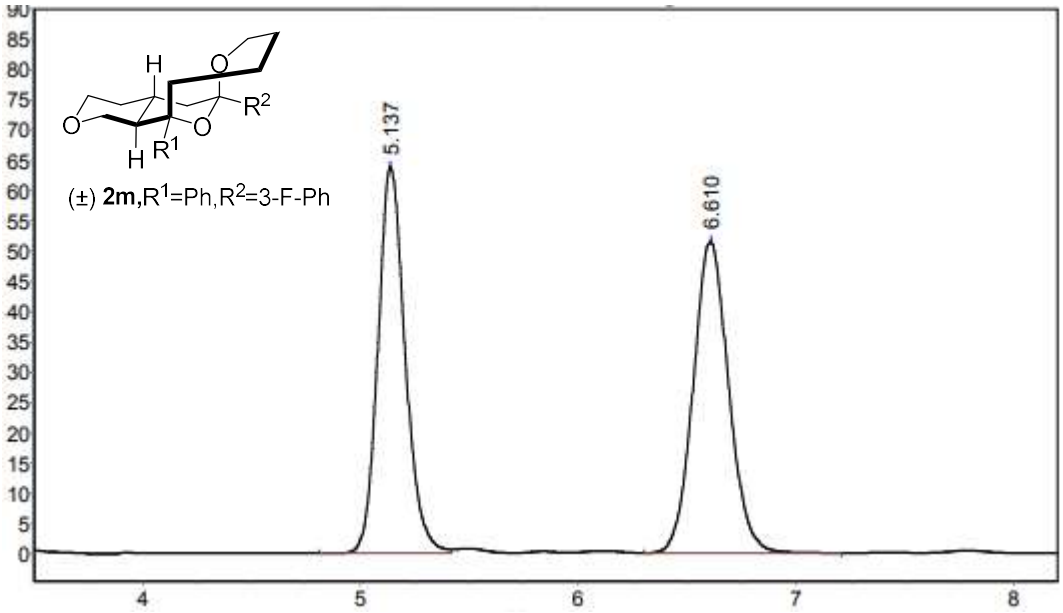
#	RT (time)	Heigh (mV*sec)	Area (mv)	Area (%)
1	5.322	52498.512	467171.094	98.8713
2	7.215	420.000	5333.000	1.1287



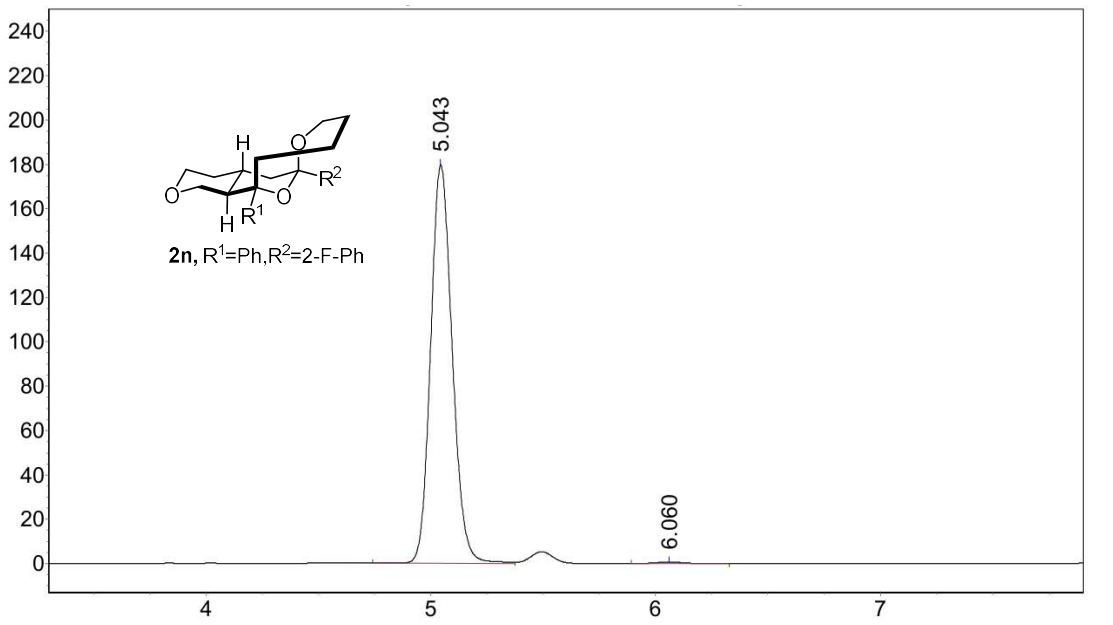
#	RT (time)	Heigh (mV*sec)	Area (mv)	Area (%)
1	5.315	19939.000	180427.813	49.1696
2	7.230	14541.649	186522.047	50.8304



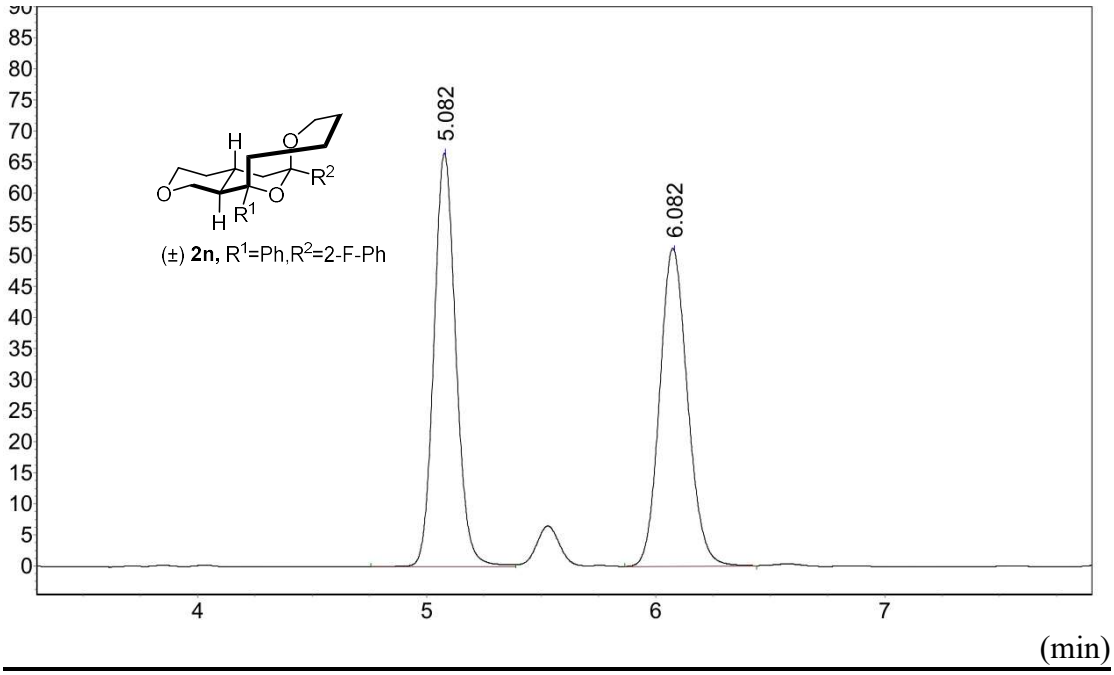
#	RT (time)	Heigh (mV*sec)	Area (mv)	Area (%)
1	5.095	156850.531	1339238.750	98.8818
2	6.575	1367.688	15145.200	1.1182



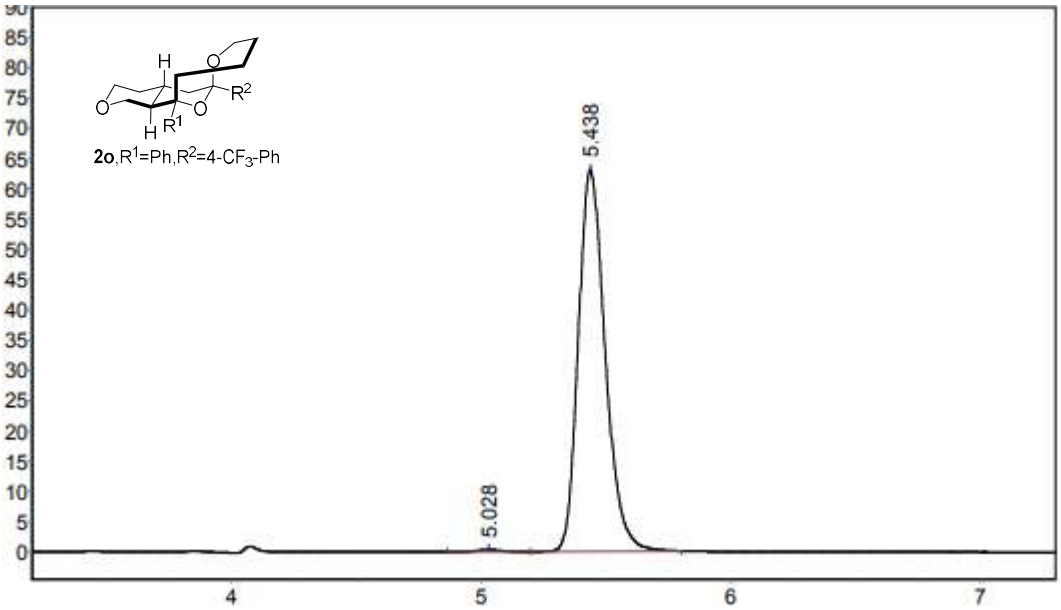
#	RT (time)	Heigh (mV*sec)	Area (mv)	Area (%)
1	5.137	63853.438	554532.063	48.7377
2	6.610	51466.301	583257.313	51.2623



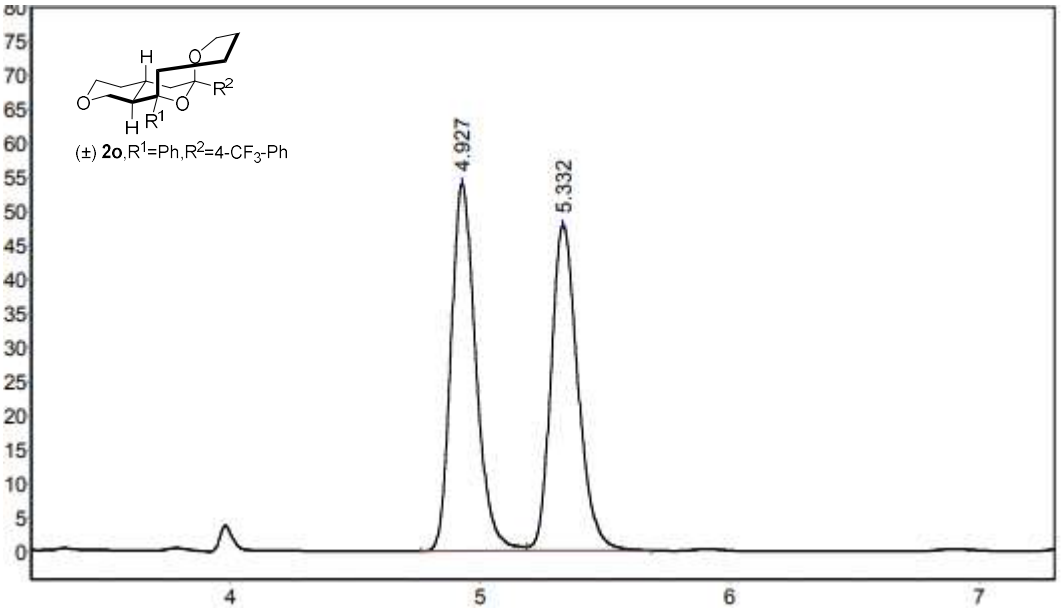
#	RT (time)	Heigh (mV*sec)	Area (mv)	Area (%)
1	5.043	179637.266	1198080.125	99.4258
2	6.060	768.000	6919.200	0.5742



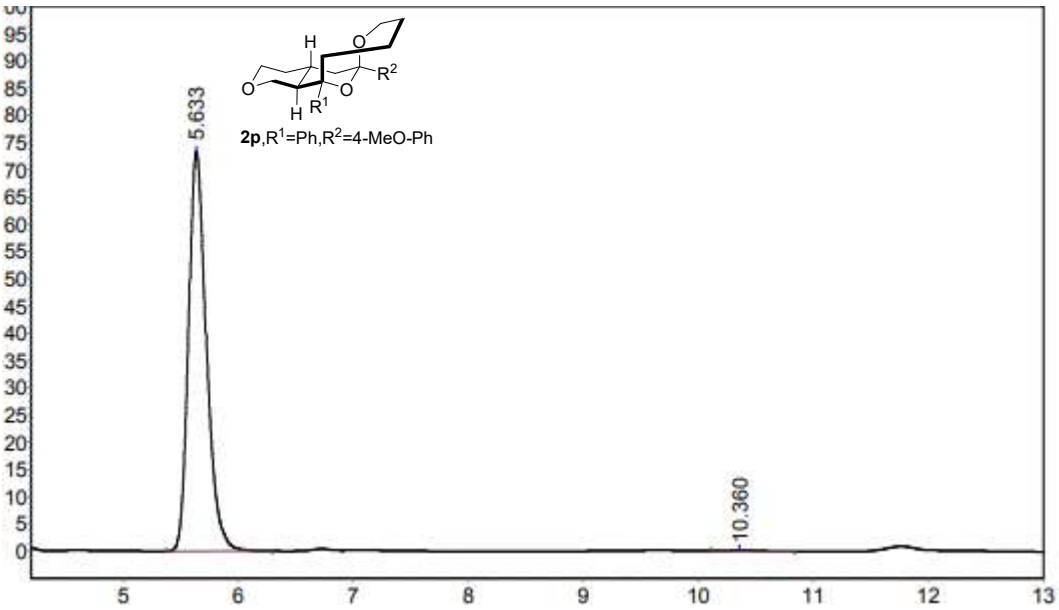
#	RT (time)	Heigh (mV*sec)	Area (mv)	Area (%)
1	5.082	66508.211	444217.063	50.4748
2	6.082	51084.645	435860.031	49.5252



#	RT (time)	Heigh (mV*sec)	Area (mv)	Area (%)
1	5.028	354.478	2404.550	0.5057
2	5.438	63036.688	473085.438	99.4943

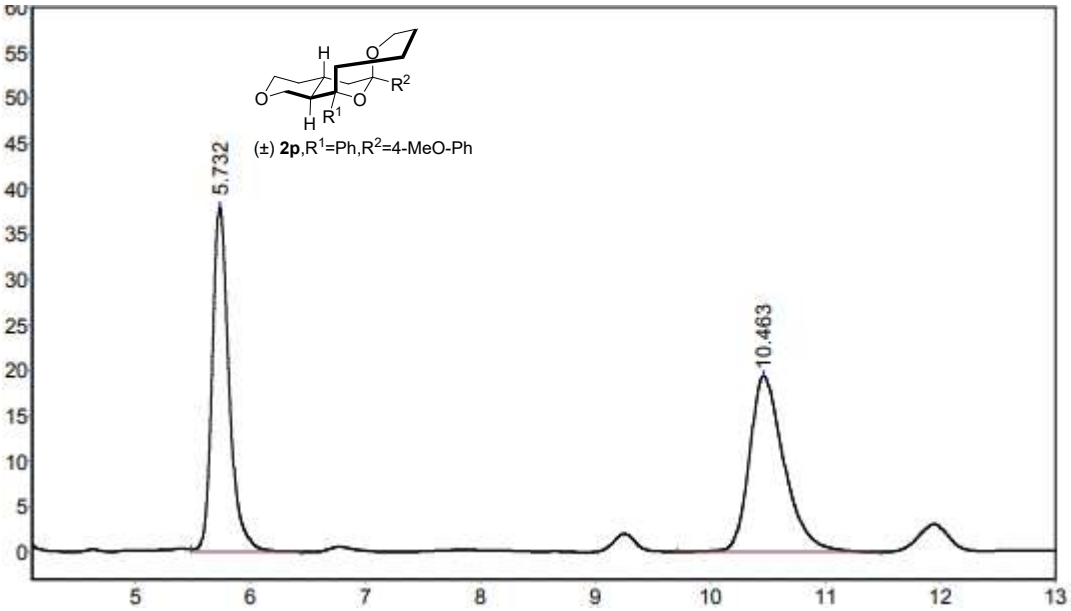


#	RT (time)	Heigh (mV*sec)	Area (mv)	Area (%)
1	4.927	53932.793	373252.344	51.0462
2	5.332	47790.918	357951.875	48.9537



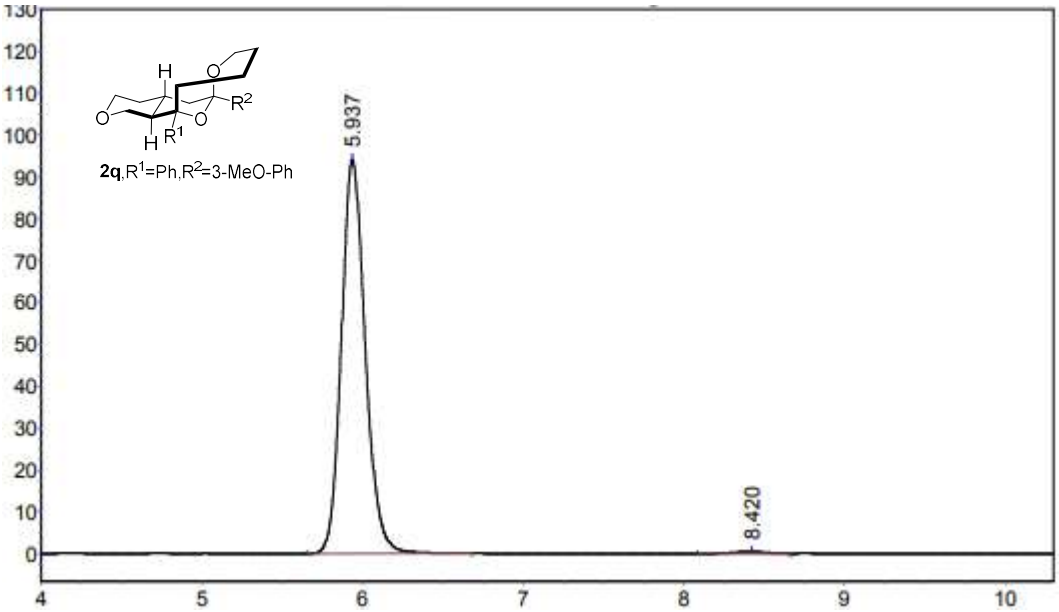
(min)

#	RT (time)	Heigh (mV*sec)	Area (mv)	Area (%)
1	5.633	73404.461	796308.625	99.2114
2	10.360	259.000	6329.200	0.7885

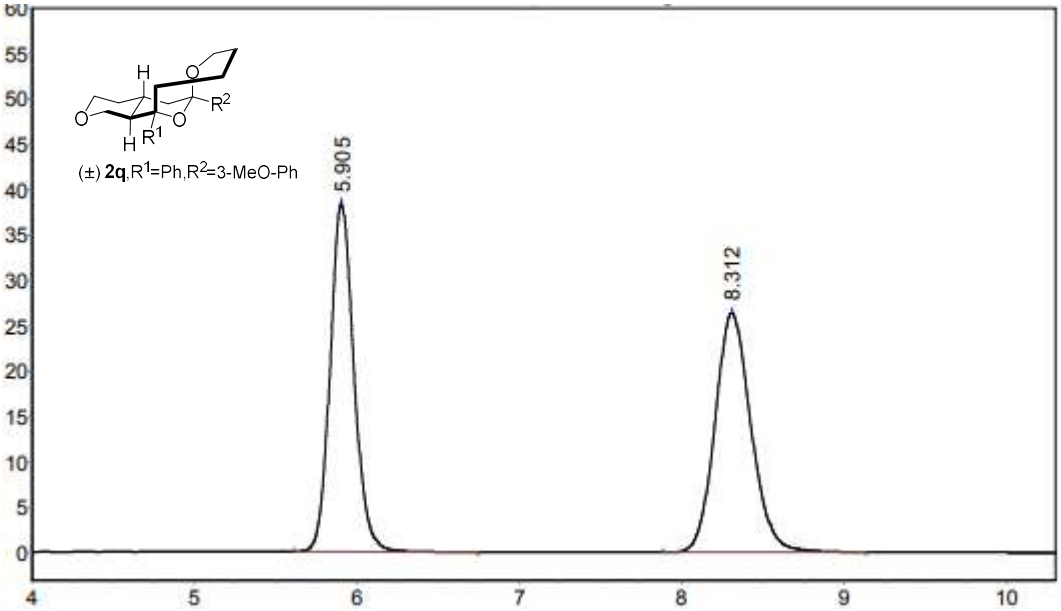


(min)

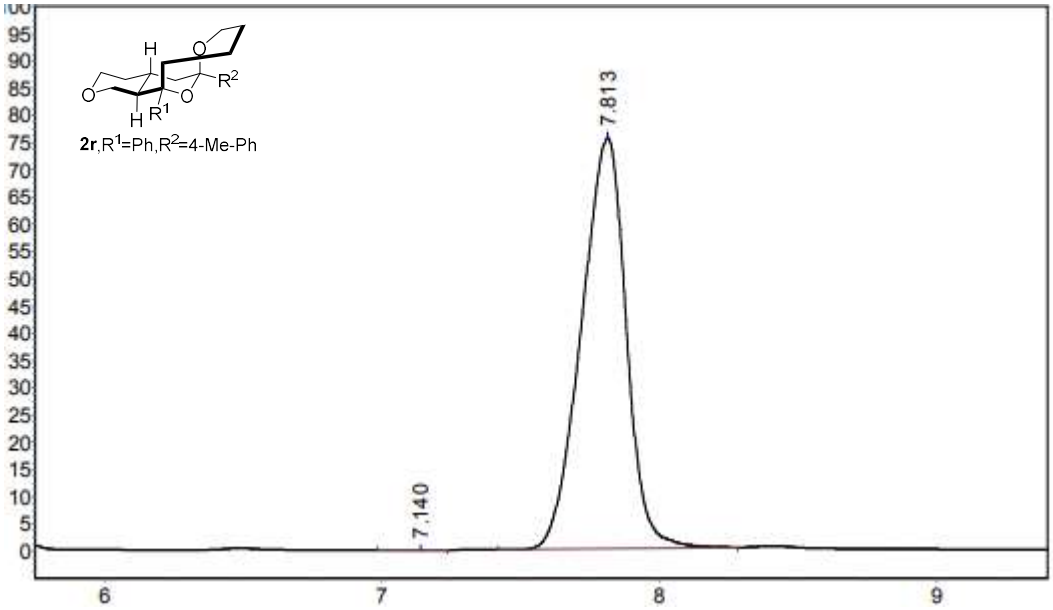
#	RT (time)	Heigh (mV*sec)	Area (mv)	Area (%)
1	5.732	37926.000	388589.500	48.8095
2	10.463	19359.207	407544.969	51.1905



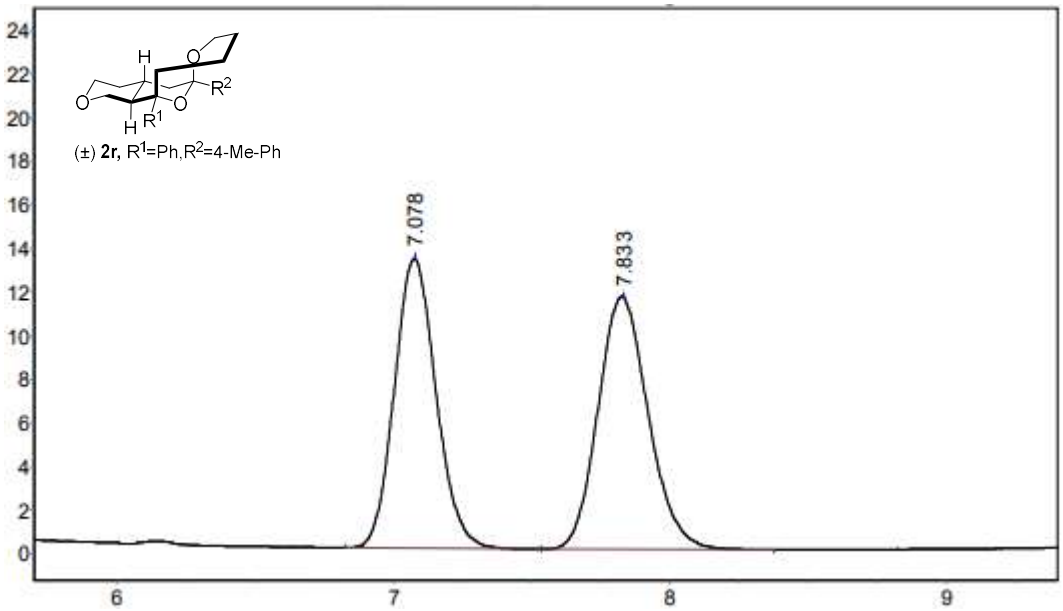
#	RT (time)	Heigh (mV*sec)	Area (mv)	Area (%)
1	5.937	94113.164	972937.625	99.2261
2	8.420	495.708	7588.222	0.7739



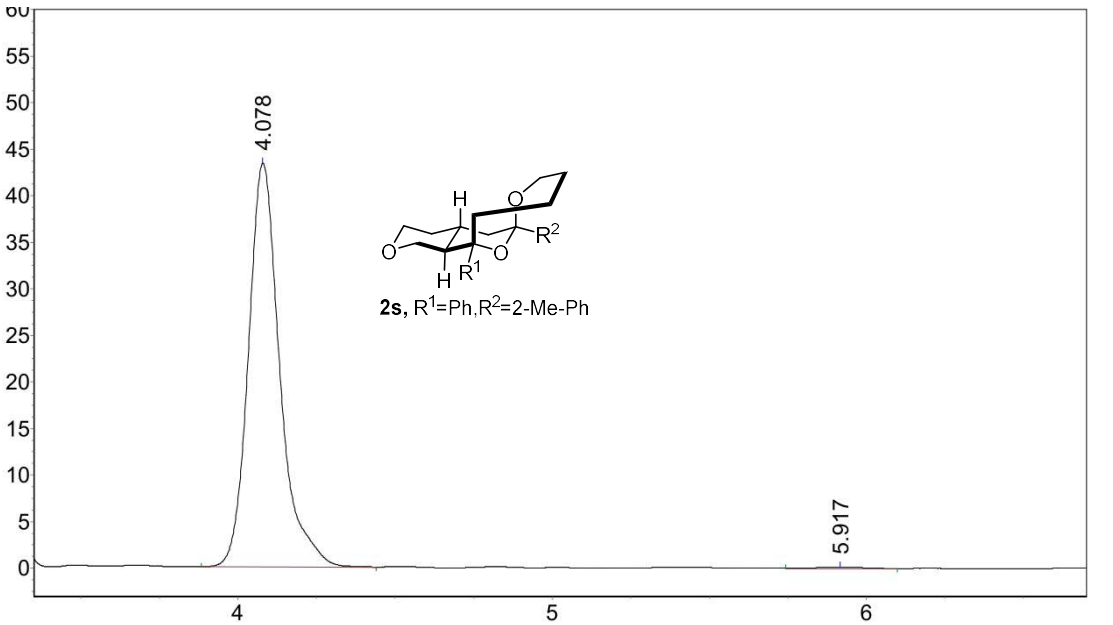
#	RT (time)	Heigh (mV*sec)	Area (mv)	Area (%)
1	5.905	38324.980	391357.563	48.9647
2	8.312	26352.021	407906.844	51.0353



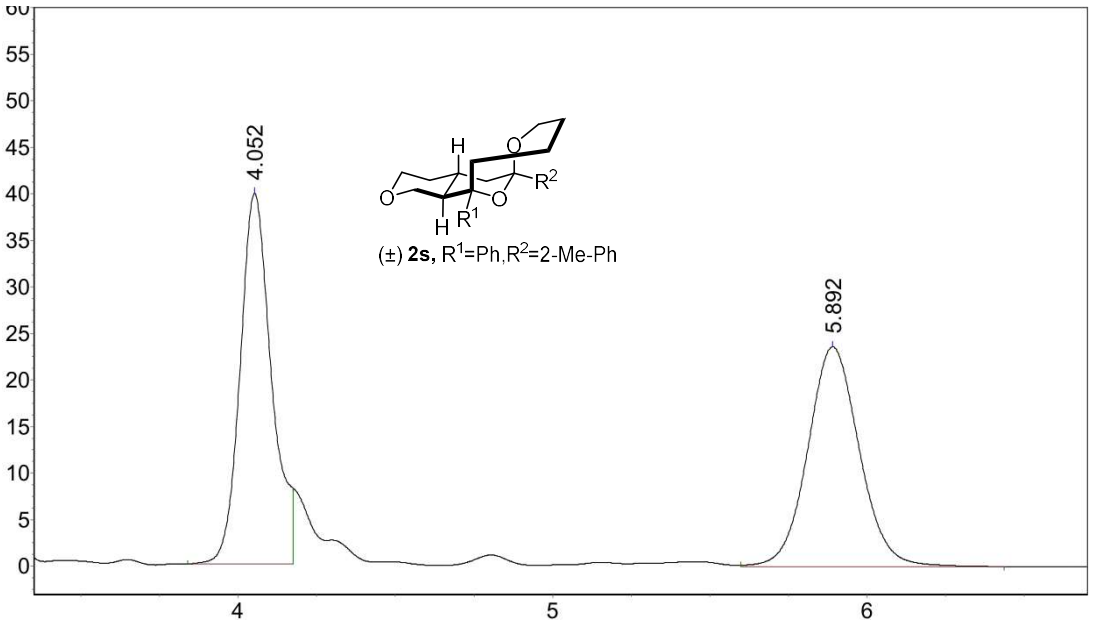
#	RT (time)	Heigh (mV*sec)	Area (mv)	Area (%)
1	7.140	8.609	55.100	0.0065
2	7.813	75389.180	847359.000	99.9935



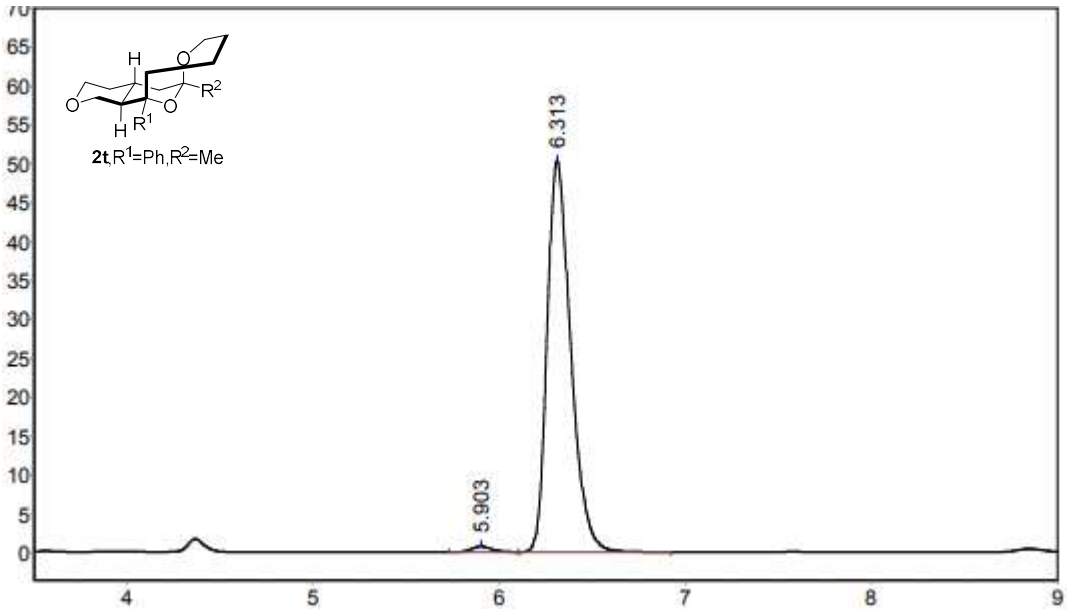
#	RT (time)	Heigh (mV*sec)	Area (mv)	Area (%)
1	7.078	13264.759	139122.453	48.7397
2	7.833	11555.357	146317.203	51.2603



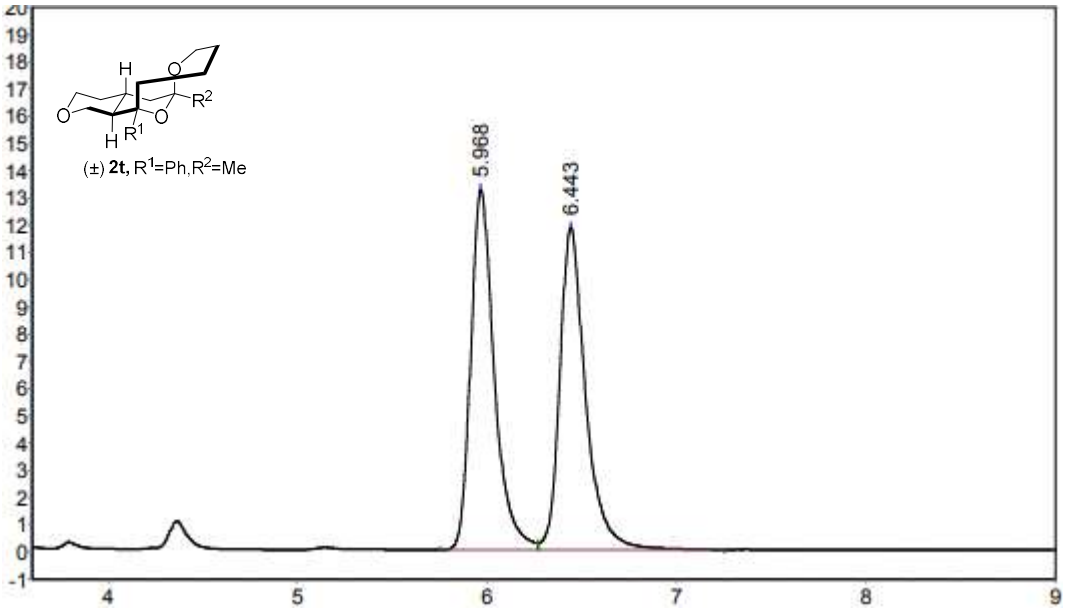
#	RT (time)	Heigh (mV*sec)	Area (mv)	Area (%)
1	4.078	43336.238	301287.406	99.4952
2	5.917	158.000	1528.600	0.5048



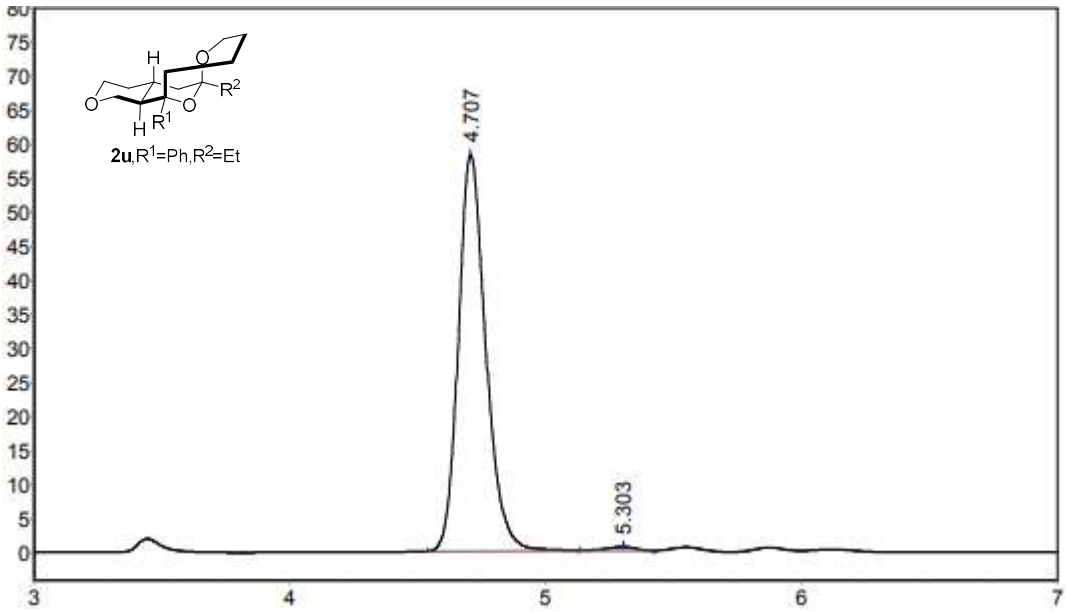
#	RT (time)	Heigh (mV*sec)	Area (mv)	Area (%)
1	4.052	39797.000	275902.906	50.6392
2	5.892	23589.000	268937.719	49.3608



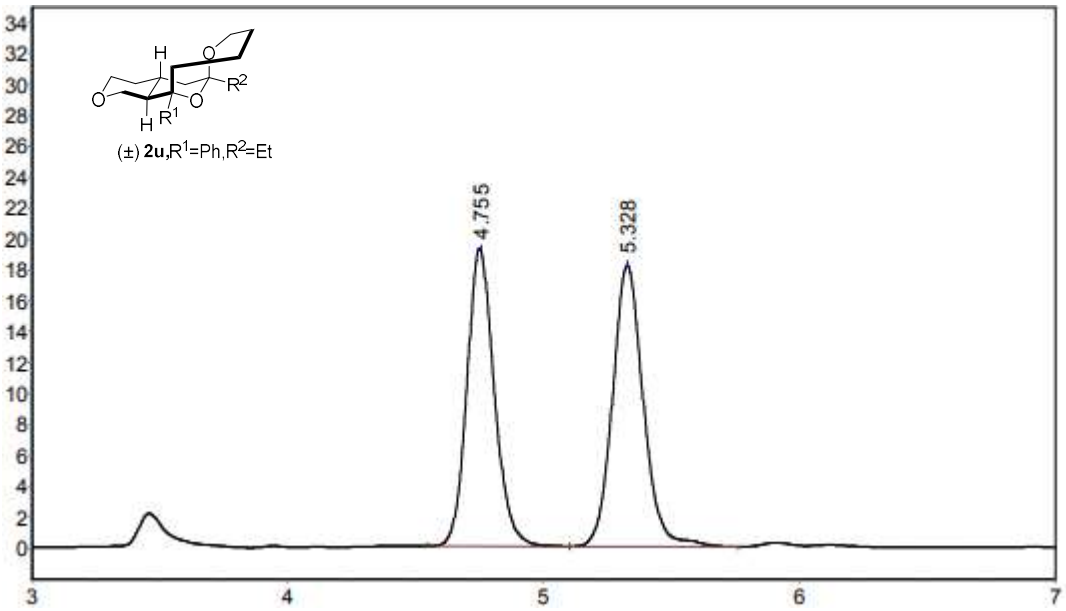
#	RT (time)	Heigh (mV*sec)	Area (mv)	Area (%)
1	5.903	761.571	5920.329	1.3156
2	6.313	50323.715	444096.375	98.6844



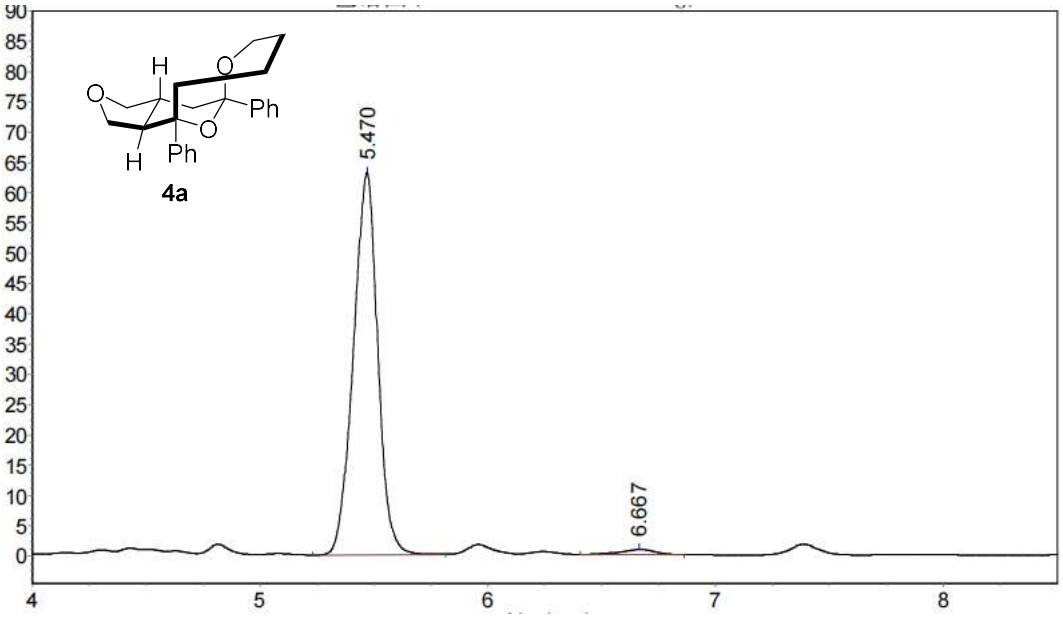
#	RT (time)	Heigh (mV*sec)	Area (mv)	Area (%)
1	5.968	13219.993	114784.039	50.4712
2	6.443	11829.560	112640.664	49.5288



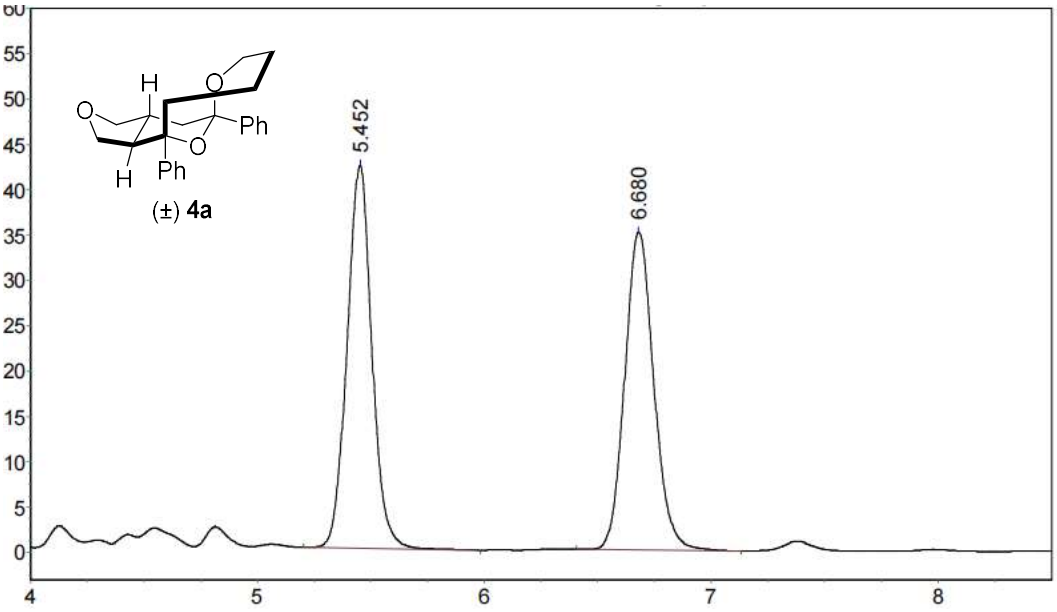
#	RT (time)	Heigh (mV*sec)	Area (mv)	Area (%)
1	4.707	58206.578	436852.844	98.7952
2	5.303	617.729	5327.229	1.2048



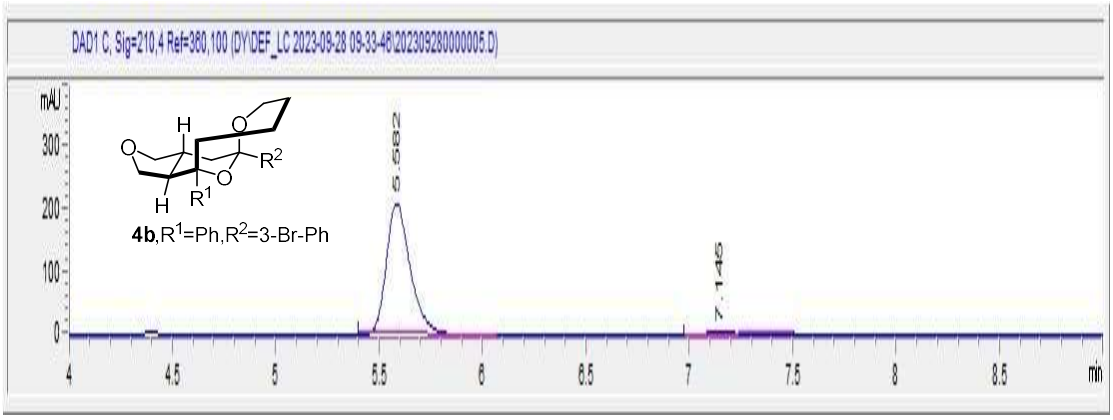
#	RT (time)	Heigh (mV*sec)	Area (mv)	Area (%)
1	4.755	19209.834	143915.281	48.4979
2	5.328	18153.018	152829.813	51.5021



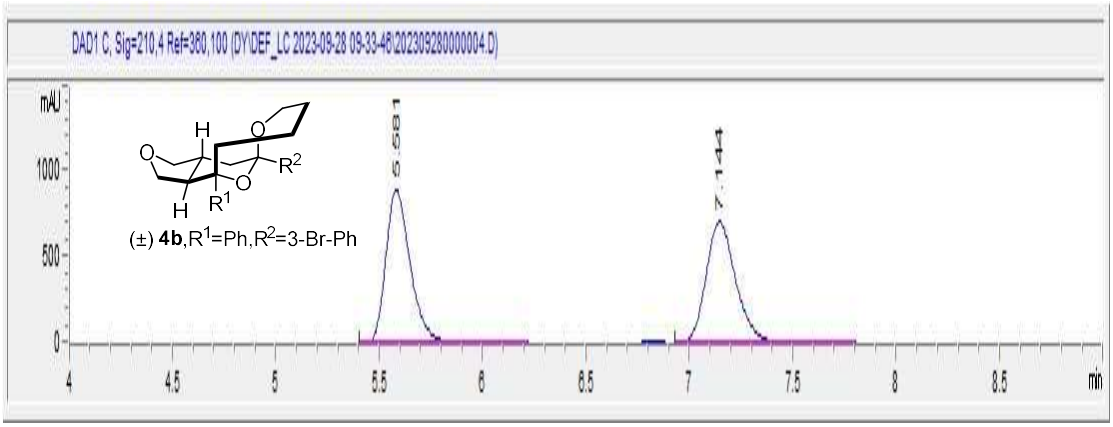
#	RT(time)	Heigh(mV*sec)	Area(mv)	Area(%)
1	5.470	63100.281	468674.750	98.0720
2	6.667	881.626	9213.799	1.9280



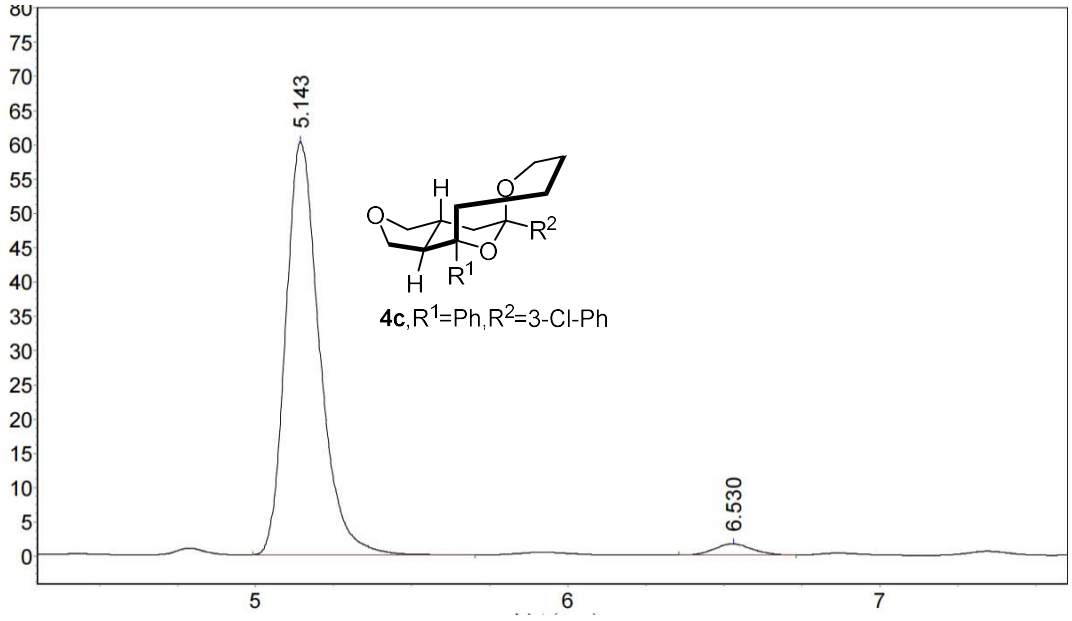
#	RT(time)	Heigh(mV*sec)	Area(mv)	Area(%)
1	5.452	42215.430	320951.344	50.6756
2	6.680	35032.762	312393.500	49.3244



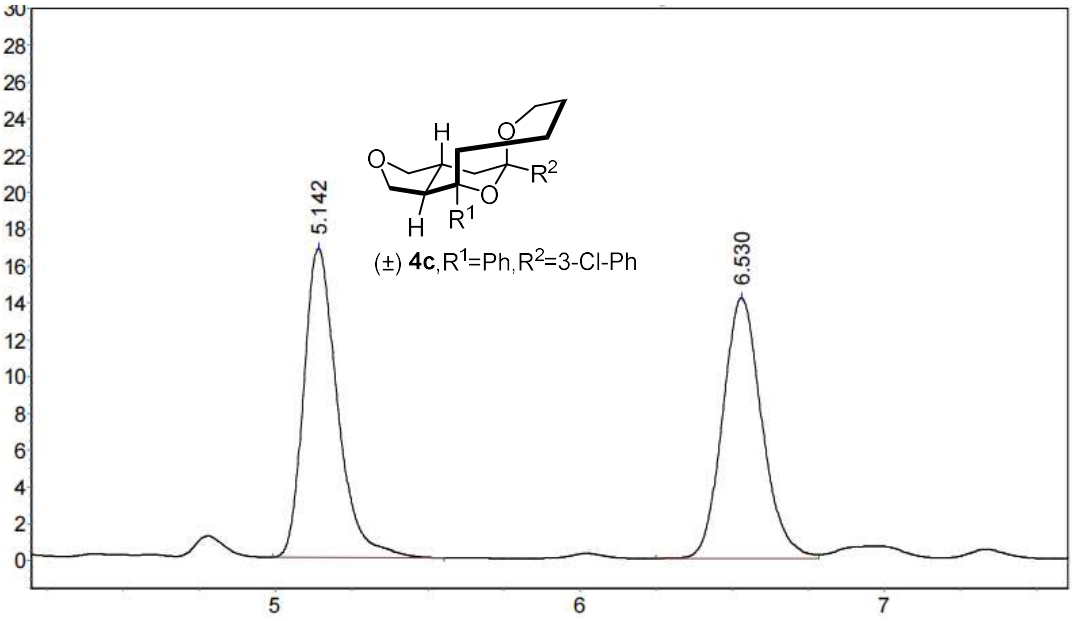
#	RT(time)	Heigh(mV*sec)	Area(mv)	Area(%)
1	5.582	209.6	1691	97.525
2	7.145	4.2	42.9	2.475



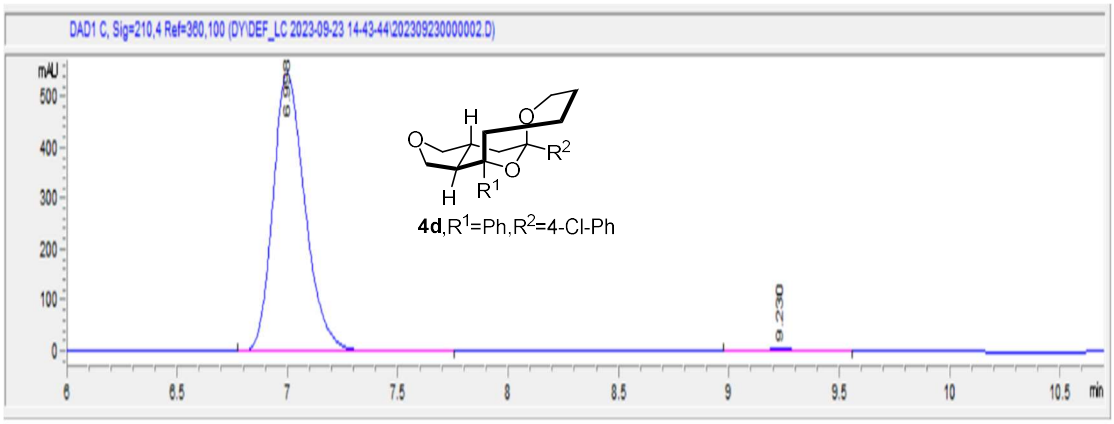
#	RT(time)	Heigh(mV*sec)	Area(mv)	Area(%)
1	5.581	894.6	7310.3	50.663
2	7.144	704.8	7119.1	49.337



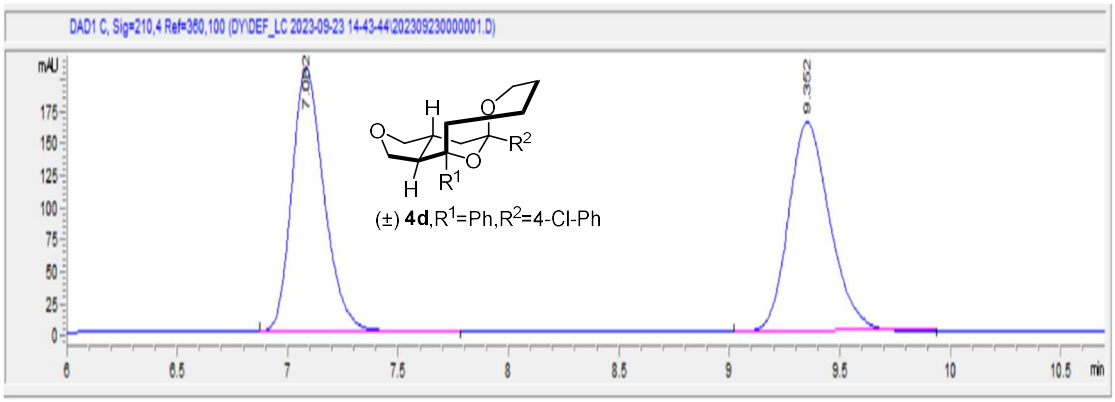
#	RT(time)	Heigh(mV*sec)	Area(mv)	Area(%)
1	5.143	60229.949	455228.313	97.0089
2	6.530	1593.429	14036.100	2.9911



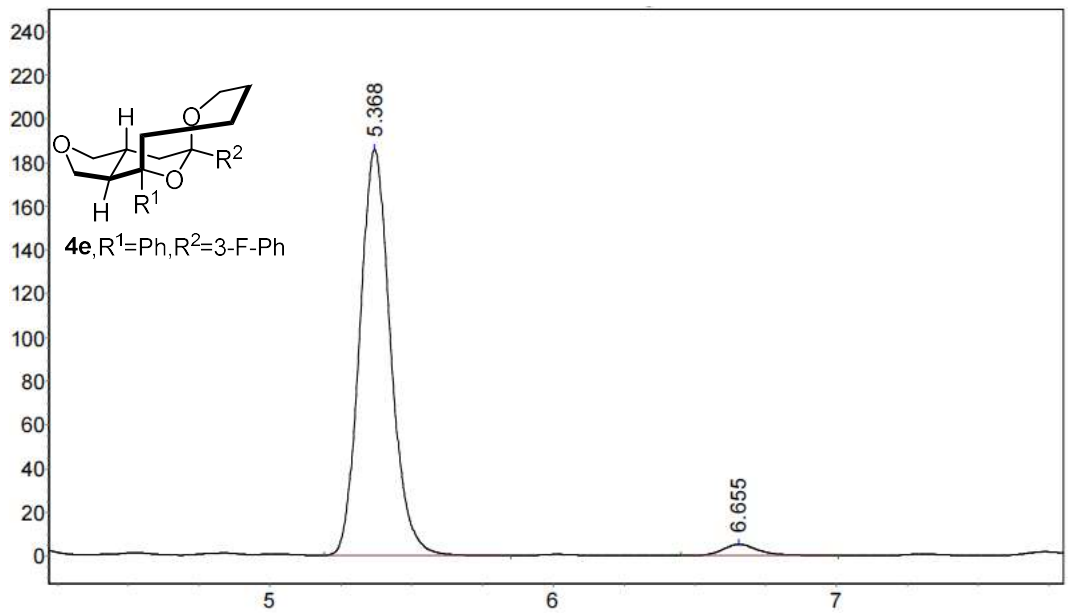
#	RT(time)	Heigh(mV*sec)	Area(mv)	Area(%)
1	5.142	16794.385	129154.398	50.4415
2	6.530	14154.000	126893.703	49.5585



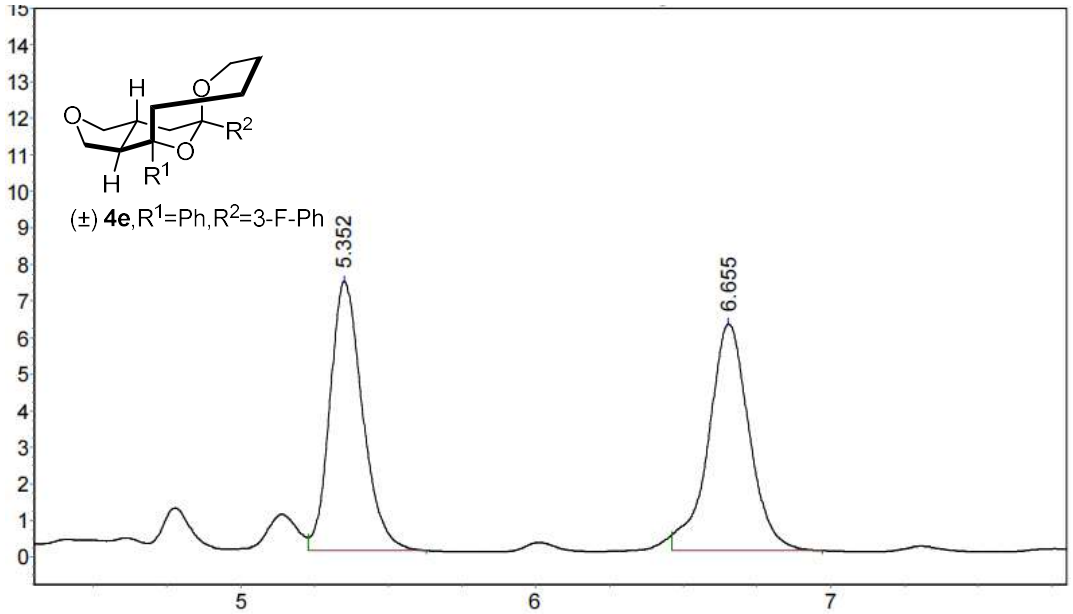
#	RT(time)	Heigh(mV*sec)	Area(mv)	Area(%)
1	6.998	548	5523.8	98.830
2	9.23	5	65.4	1.170



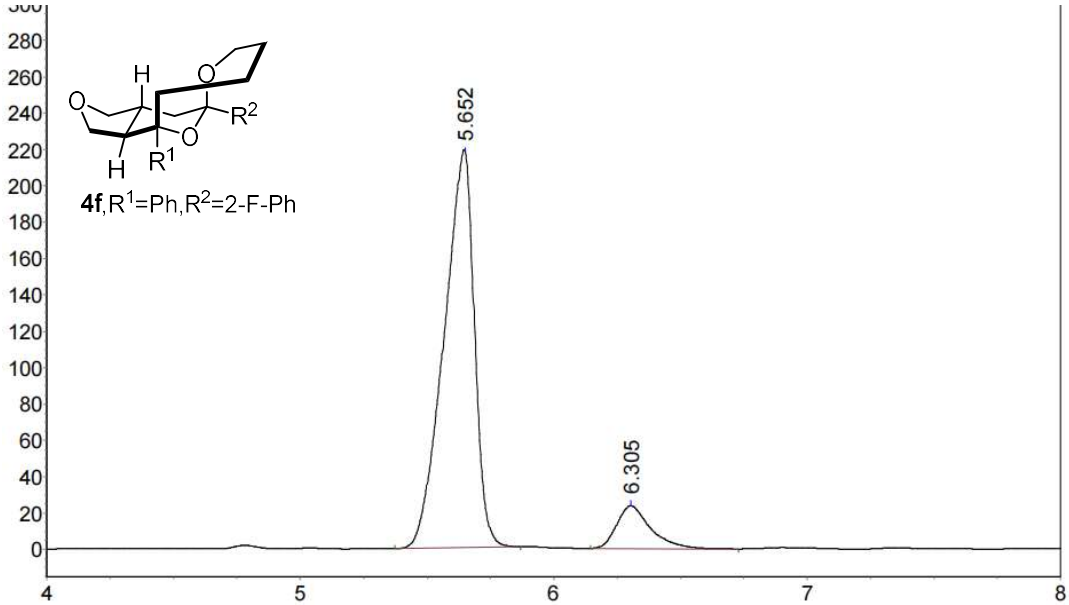
#	RT(time)	Heigh(mV*sec)	Area(mv)	Area(%)
1	7.082	205.9	2092.2	49.657
2	9.352	163	2121.1	50.343



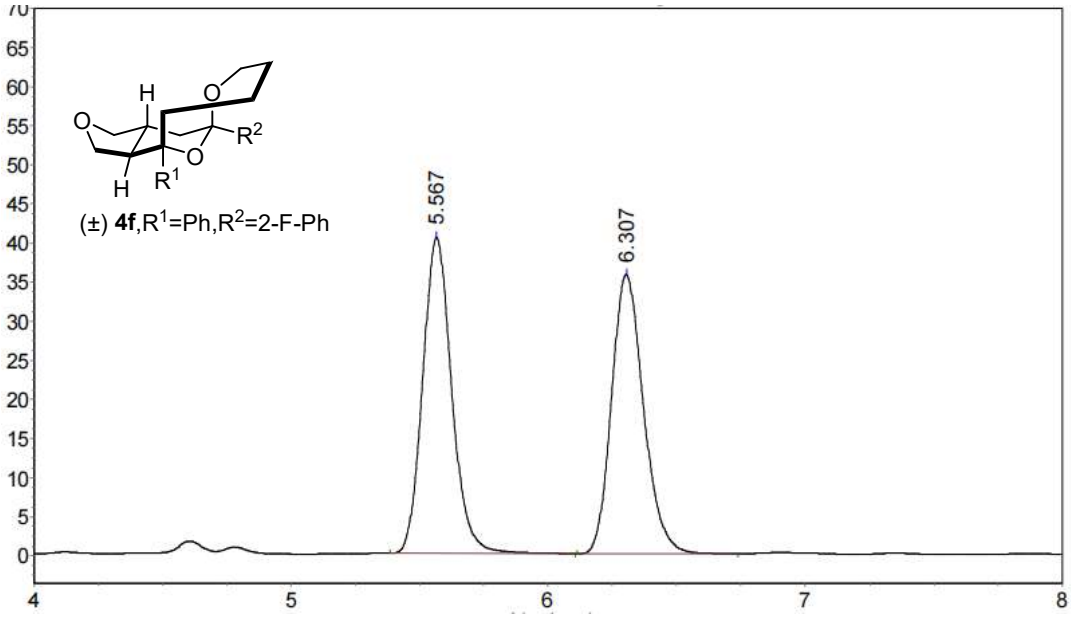
#	RT(time)	Heigh(mV*sec)	Area(mv)	Area(%)
1	5.368	185677.094	1403605.375	96.7897
2	6.655	5058.130	46554.145	3.2103



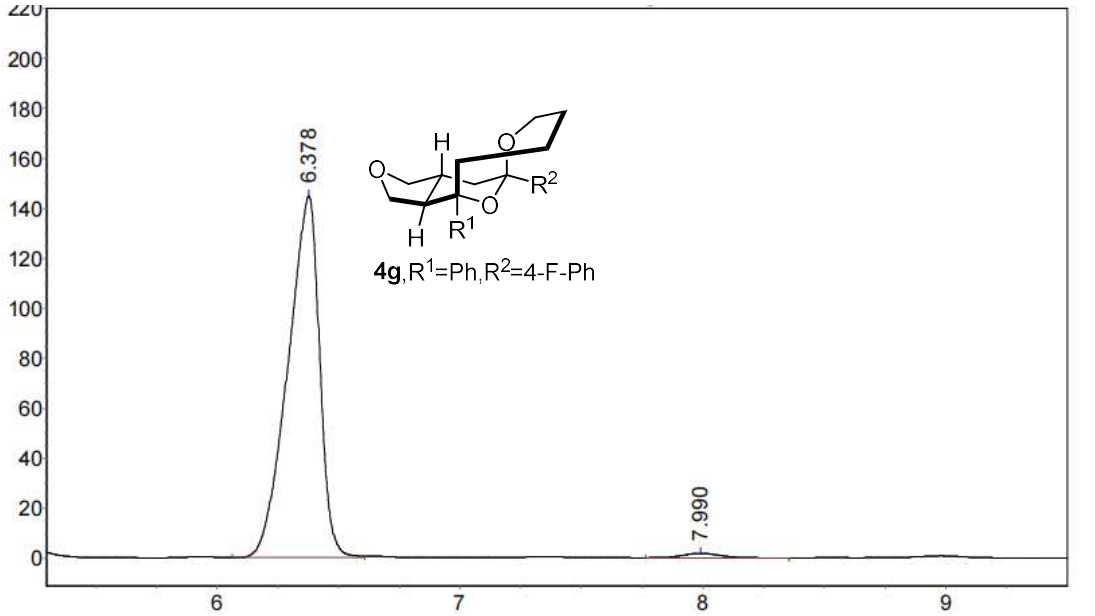
#	RT(time)	Heigh(mV*sec)	Area(mv)	Area(%)
1	5.352	7354.000	56424.000	48.7546
2	6.655	6191.000	59306.695	51.2454



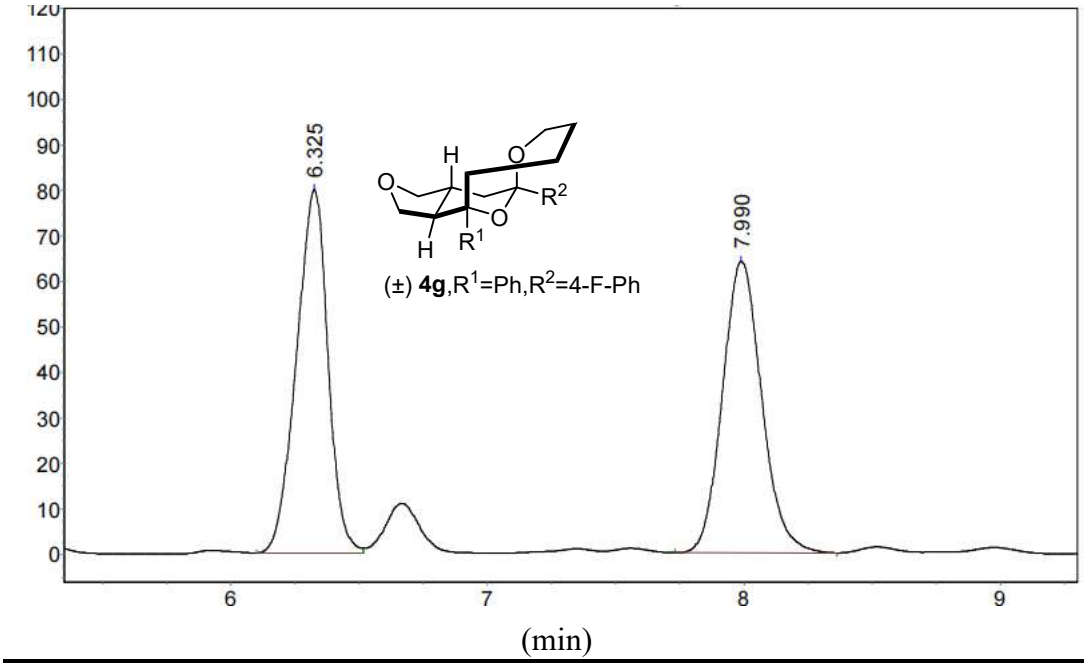
#	RT(time)	Heigh(mV*sec)	Area(mv)	Area(%)
1	5.652	218016.375	1820930.250	89.2189
2	6.305	23207.000	220039.906	2.7811



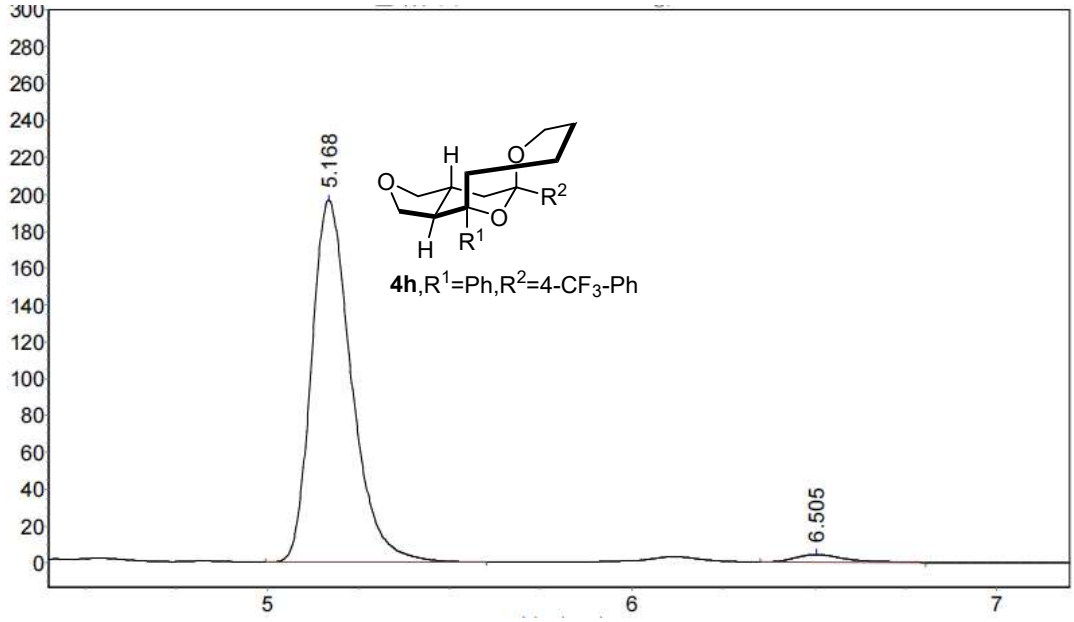
#	RT(time)	Heigh(mV*sec)	Area(mv)	Area(%)
1	5.567	40477.566	319962.375	50.8600
2	6.307	35732.500	309141.188	49.1400



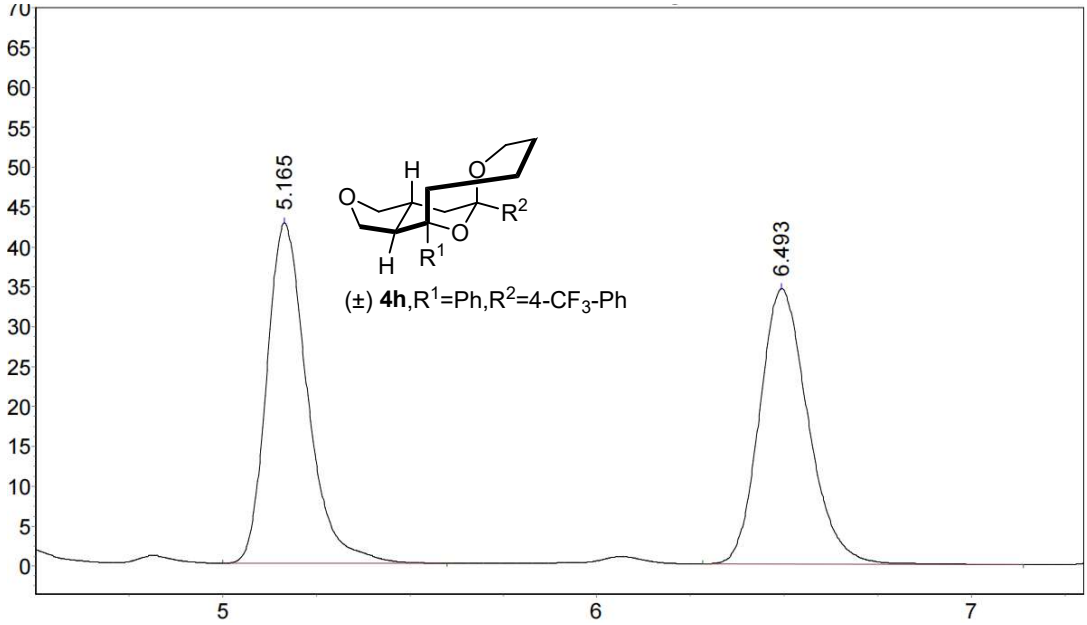
#	RT(time)	Heigh(mV*sec)	Area(mv)	Area(%)
1	6.378	144698.000	1314412.875	98.4861
2	7.990	1878.270	20204.449	1.5139



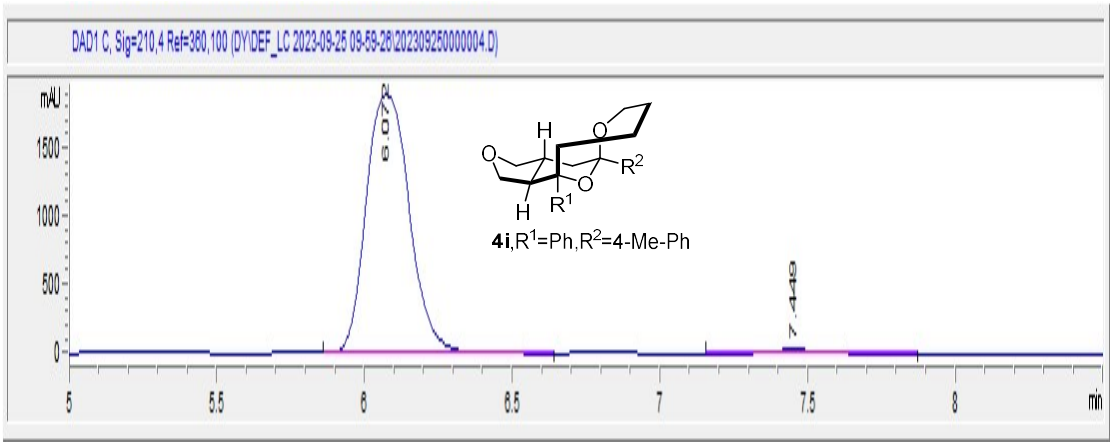
#	RT(time)	Heigh(mV*sec)	Area(mv)	Area(%)
1	6.325	79864.000	683069.375	50.0717
2	7.990	64046.051	681111.938	49.9283



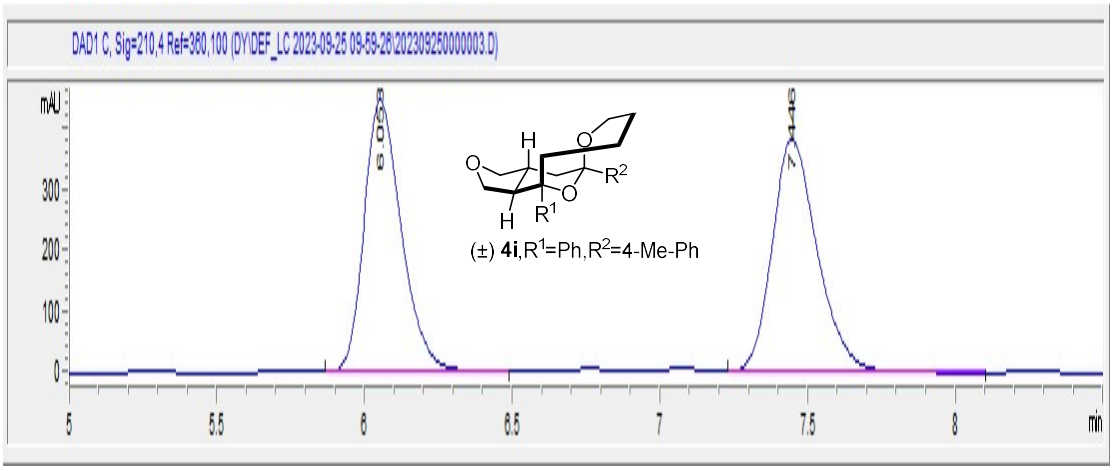
#	RT(time)	Heigh(mV*sec)	Area(mv)	Area(%)
1	5.168	196347.422	1495736.625	97.3978
2	6.505	4296.202	39961.797	2.6022



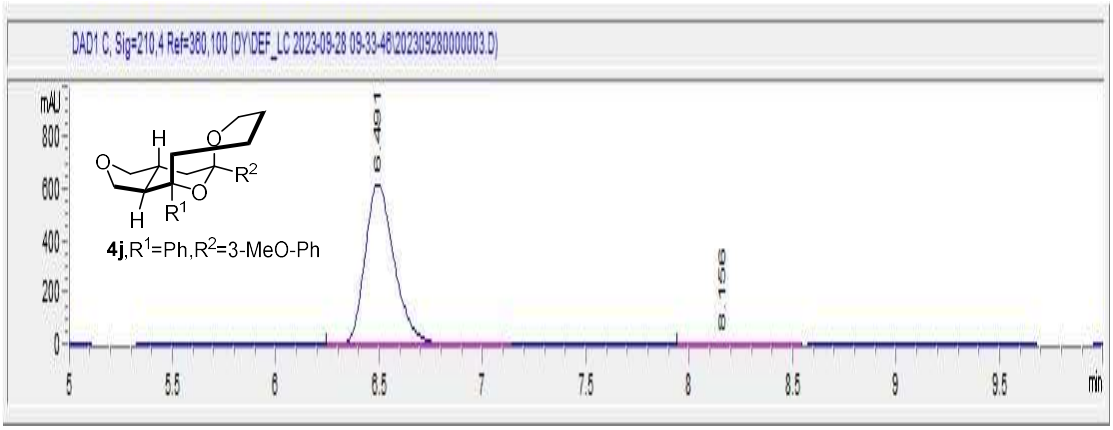
#	RT(time)	Heigh(mV*sec)	Area(mv)	Area(%)
1	5.165	42621.727	321429.094	50.8046
2	6.493	34503.273	311247.969	49.1954



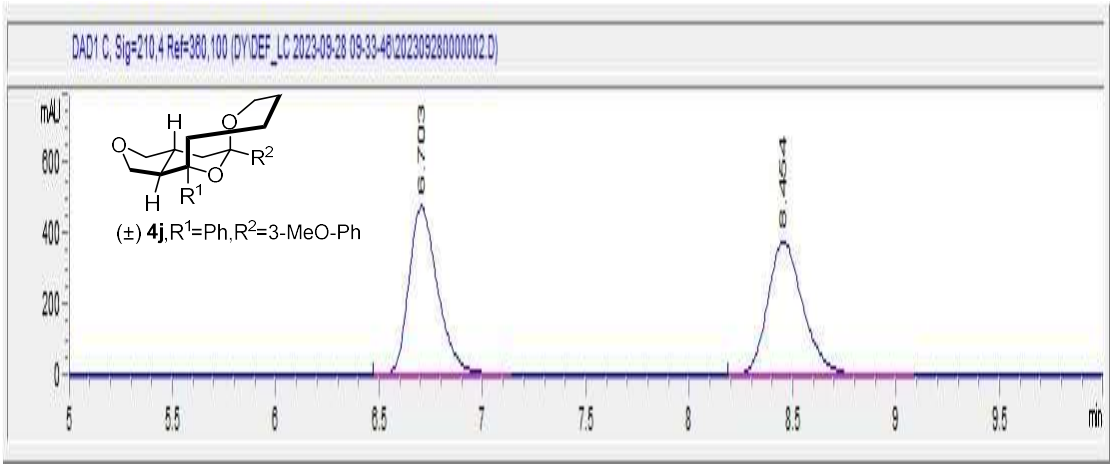
#	RT(time)	Heigh(mV*sec)	Area(mv)	Area(%)
1	6.072	1893.3	19335.9	98.495
2	7.449	27.8	295.5	1.505



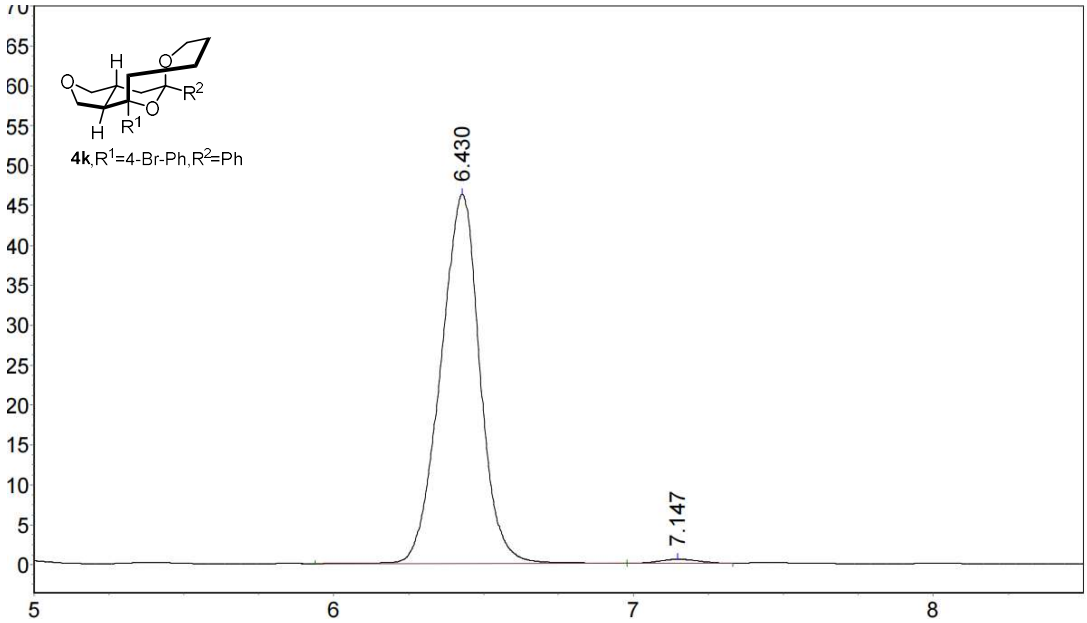
#	RT(time)	Heigh(mV*sec)	Area(mv)	Area(%)
1	6.053	447.4	3951.9	49.199
2	7.446	382.2	4080.5	50.801



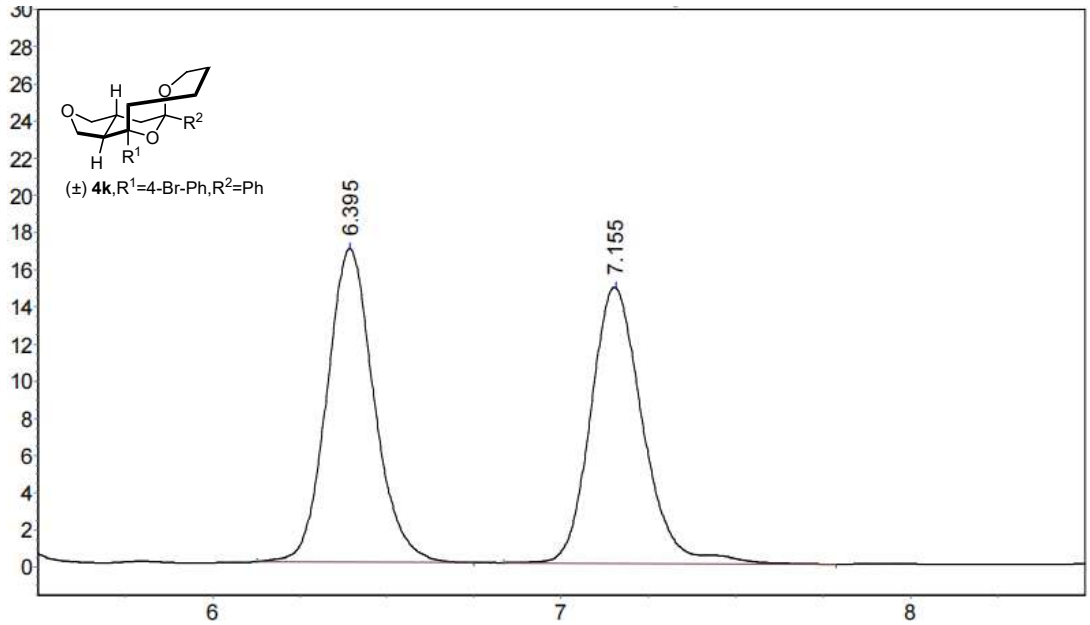
#	RT(time)	Heigh(mV*sec)	Area(mv)	Area(%)
1	6.491	621.7	6136.1	97.630
2	8.156	11.9	149	2.370



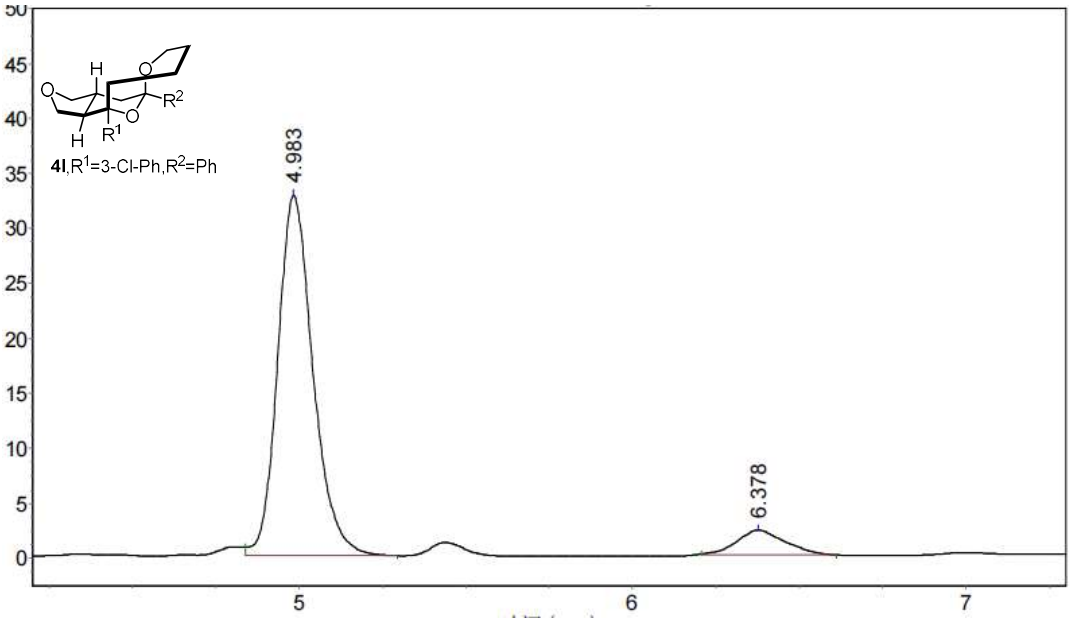
#	RT(time)	Heigh(mV*sec)	Area(mv)	Area(%)
1	6.703	480.1	4695.8	51.043
2	8.454	378.9	4503.9	48.957



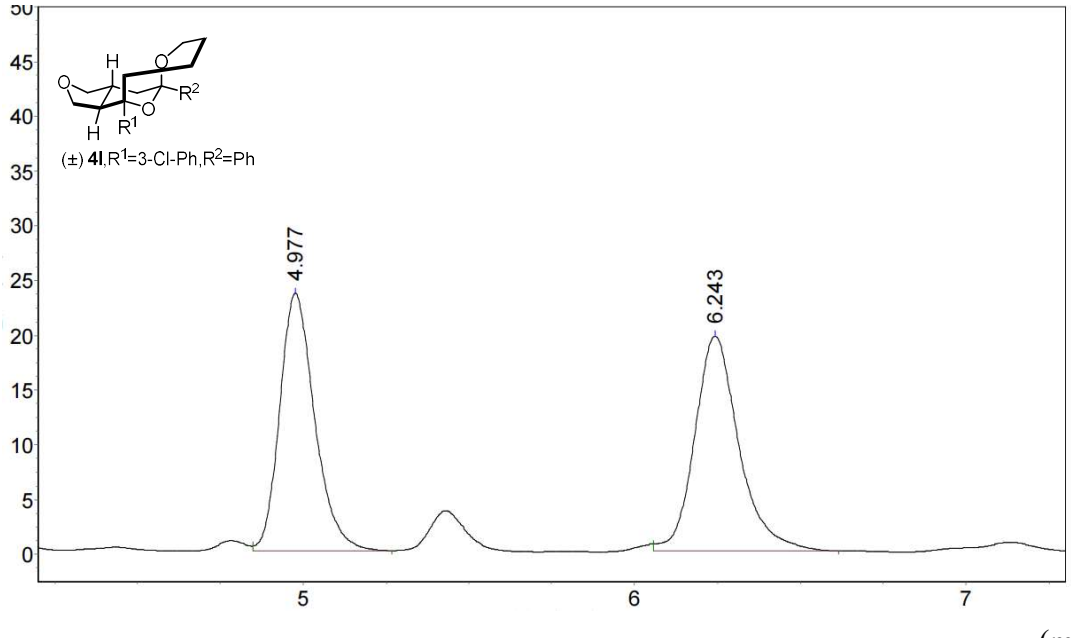
#	RT(time)	Heigh(mV*sec)	Area(mv)	Area(%)
1	6.430	46285.727	421427.281	98.8512
2	7.147	532.267	4897.624	1.1488



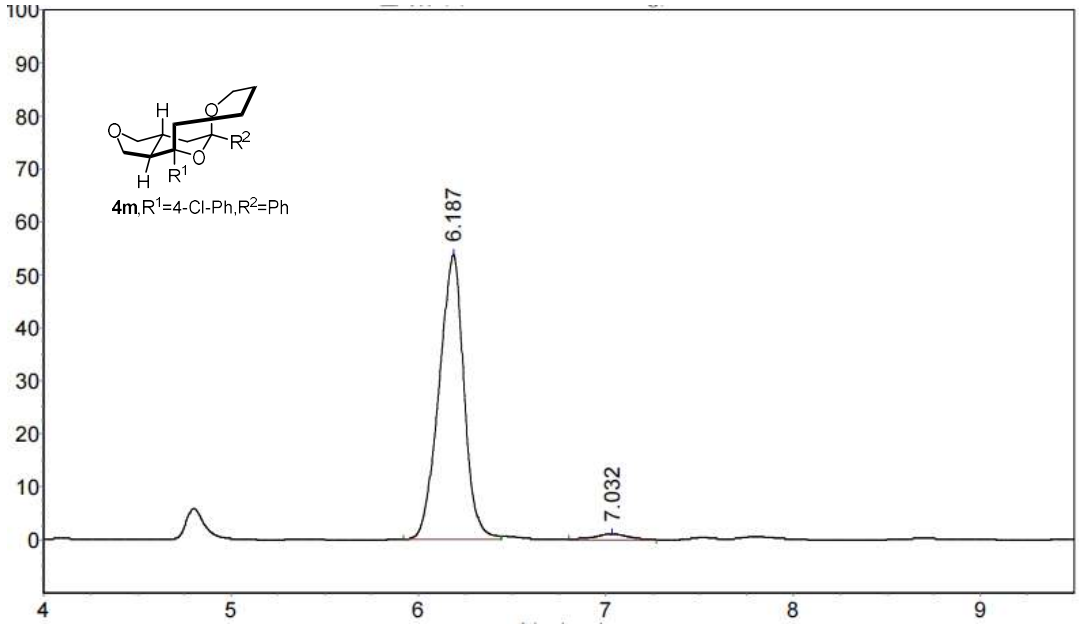
#	RT(time)	Heigh(mV*sec)	Area(mv)	Area(%)
1	6.395	16914.406	159465.828	50.9966
2	7.155	14825.854	153233.094	49.0034



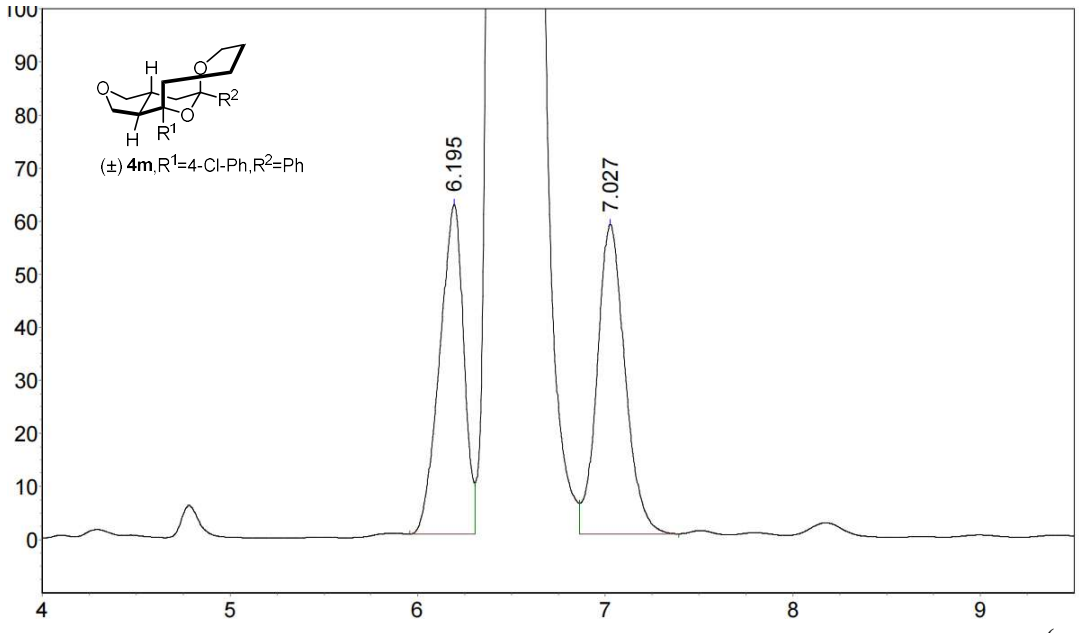
#	RT(time)	Heigh(mV*sec)	Area(mv)	Area(%)
1	4.983	32780.000	241843.000	91.3542
2	6.378	2217.000	22888.000	8.6458



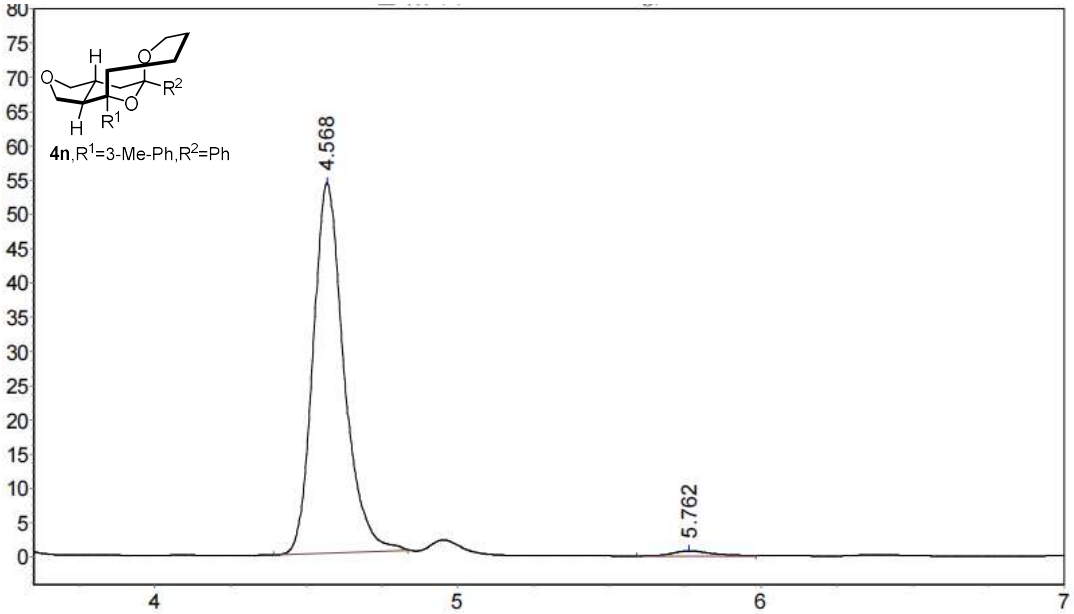
#	RT(time)	Heigh(mV*sec)	Area(mv)	Area(%)
1	4.977	23512.000	172283.703	48.6110
2	6.243	19612.000	182129.203	51.3890



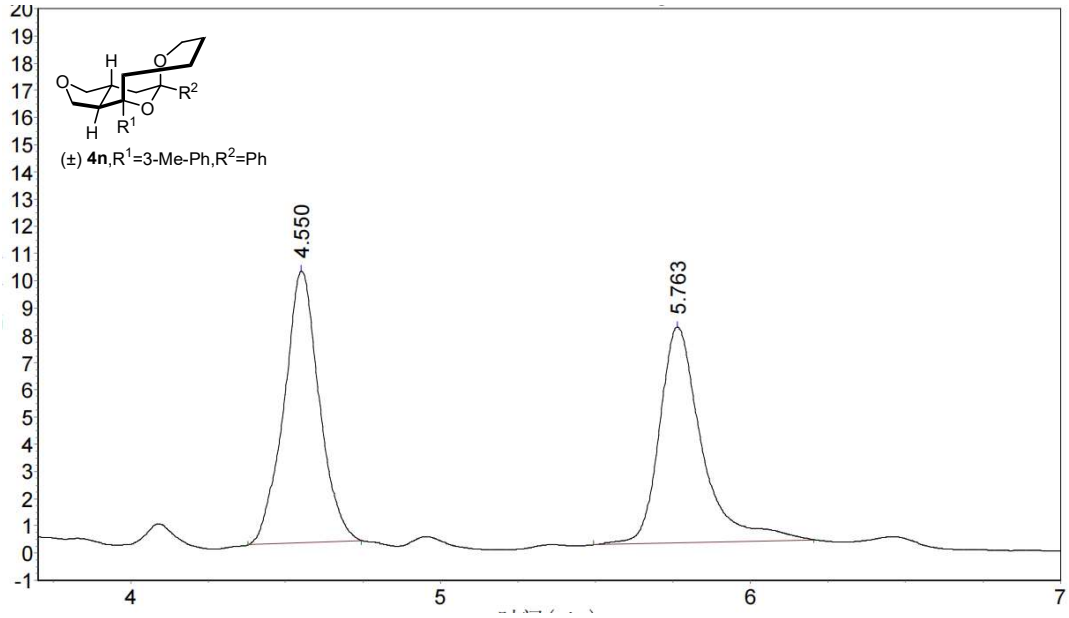
#	RT(time)	Heigh(mV*sec)	Area(mv)	Area(%)
1	6.187	53649.000	496649.500	97.7691
2	7.032	1019.000	11332.400	2.2309



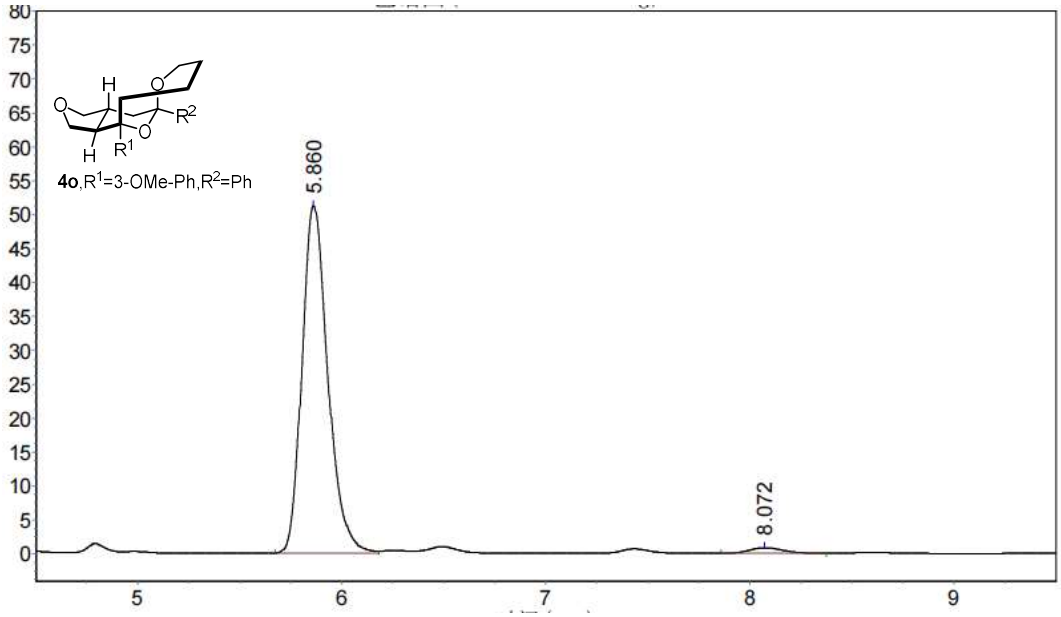
#	RT(time)	Heigh(mV*sec)	Area(mv)	Area(%)
1	6.195	62108.734	557147.000	47.9713
2	7.027	58295.797	604271.500	52.0287



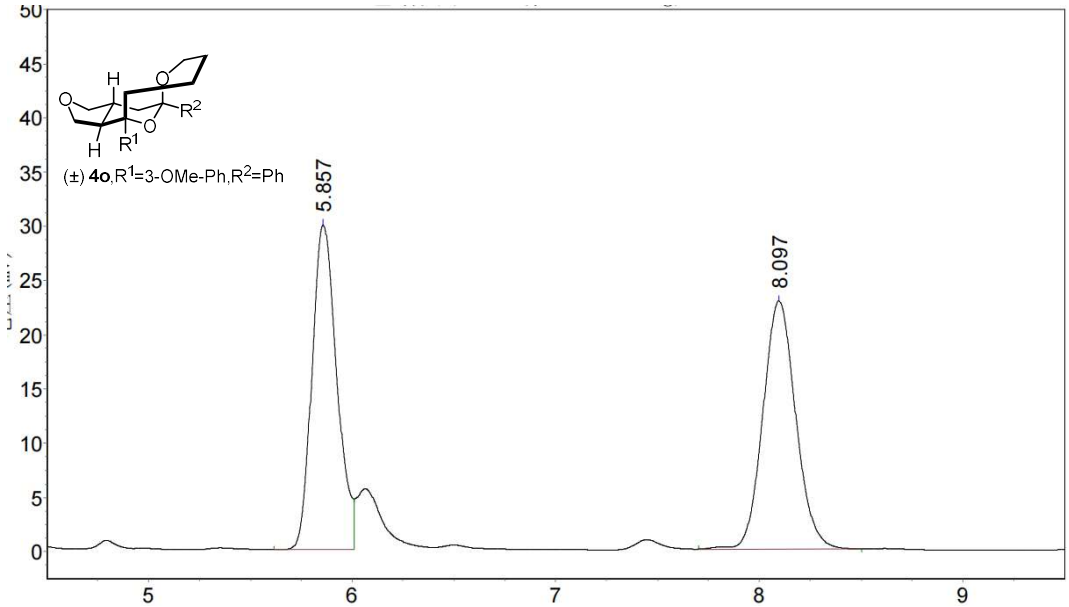
#	RT(time)	Heigh(mV*sec)	Area(mv)	Area(%)
1	4.568	54012.223	382630.906	98.2307
2	5.762	762.000	6892.000	1.7693



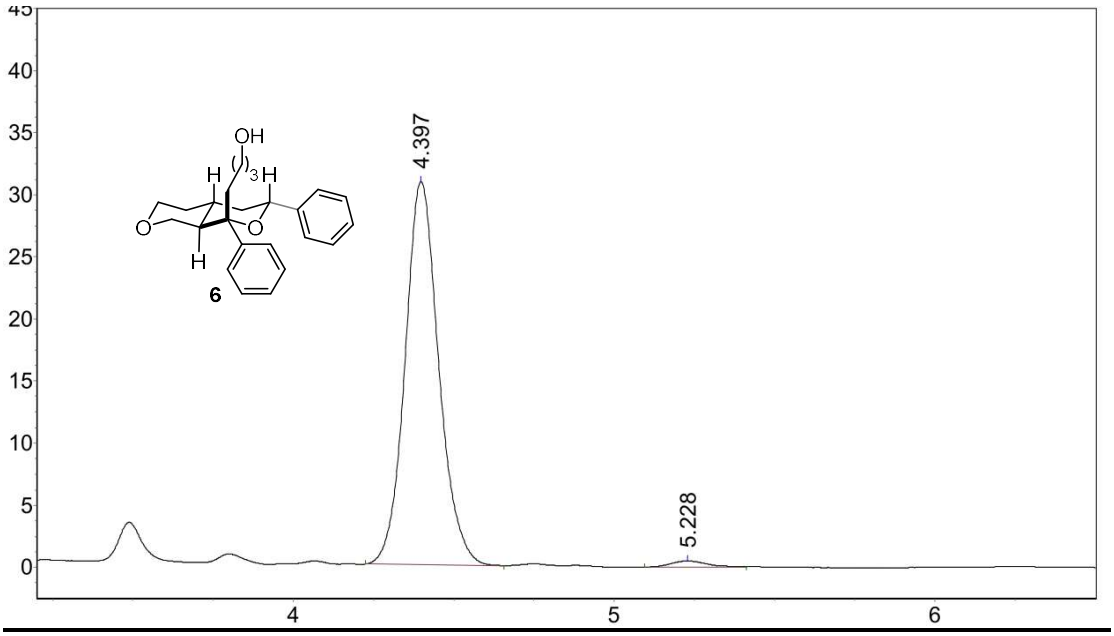
#	RT(time)	Heigh(mV*sec)	Area(mv)	Area(%)
1	4.550	9981.546	78853.805	51.0186
2	5.763	7931.999	75705.148	48.9814



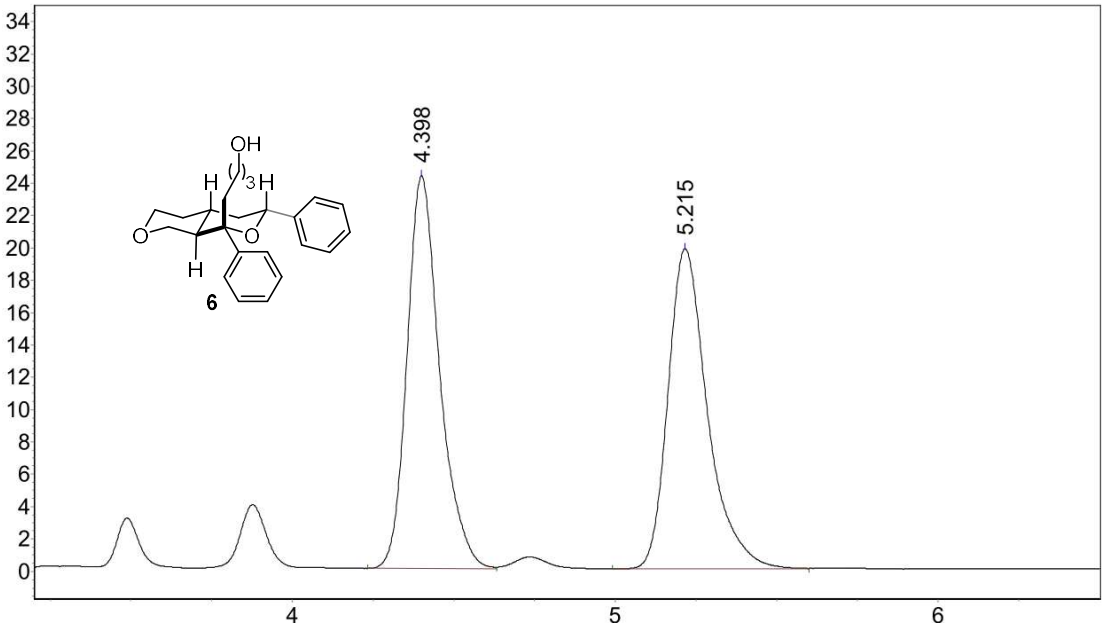
#	RT(time)	Heigh(mV*sec)	Area(mv)	Area(%)
1	5.860	51135.000	450510.500	97.8464
2	8.072	865.000	9915.800	2.1536



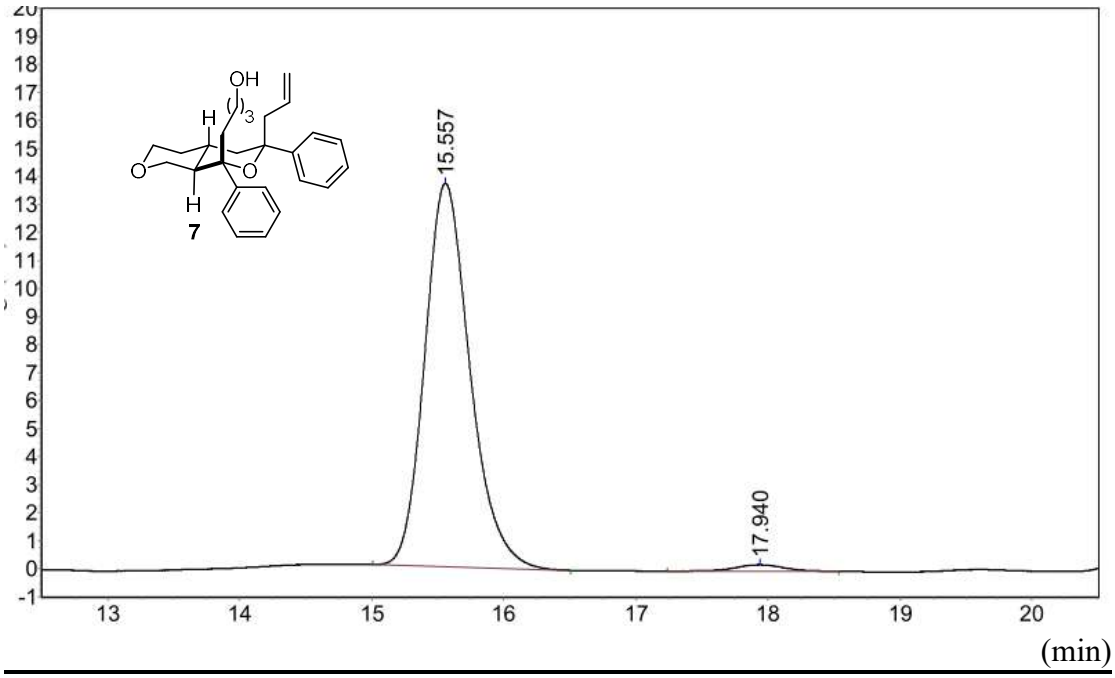
#	RT(time)	Heigh(mV*sec)	Area(mv)	Area(%)
1	5.857	29937.748	255155.438	49.7591
2	8.097	22875.250	257626.453	50.2409



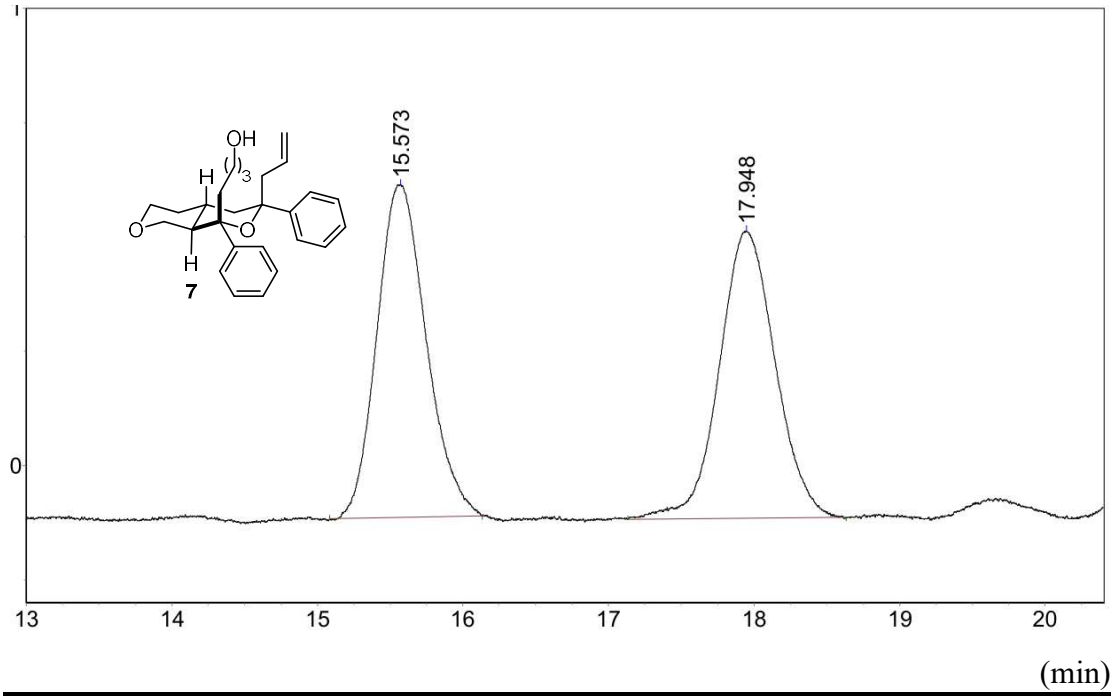
#	RT(time)	Heigh(mV*sec)	Area(mv)	Area(%)
1	4.397	30839.613	225033.000	98.3177
2	5.228	488.000	3850.500	1.6823



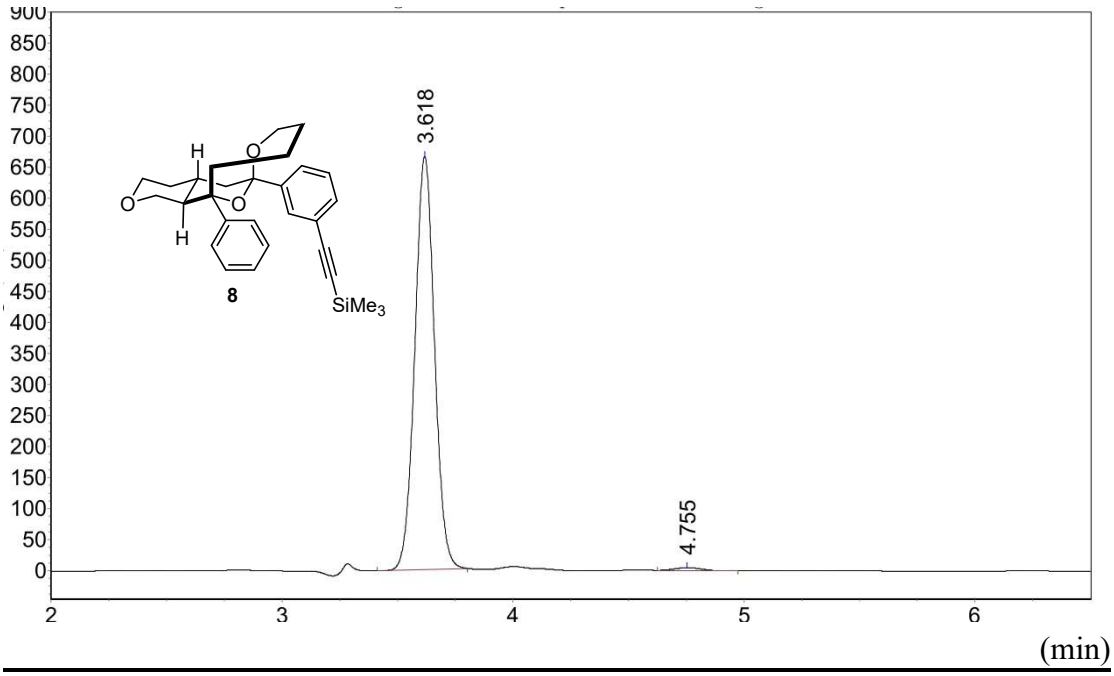
#	RT(time)	Heigh(mV*sec)	Area(mv)	Area(%)
1	4.398	24148.572	171162.359	50.4175
2	5.215	19738.945	168327.797	49.5825



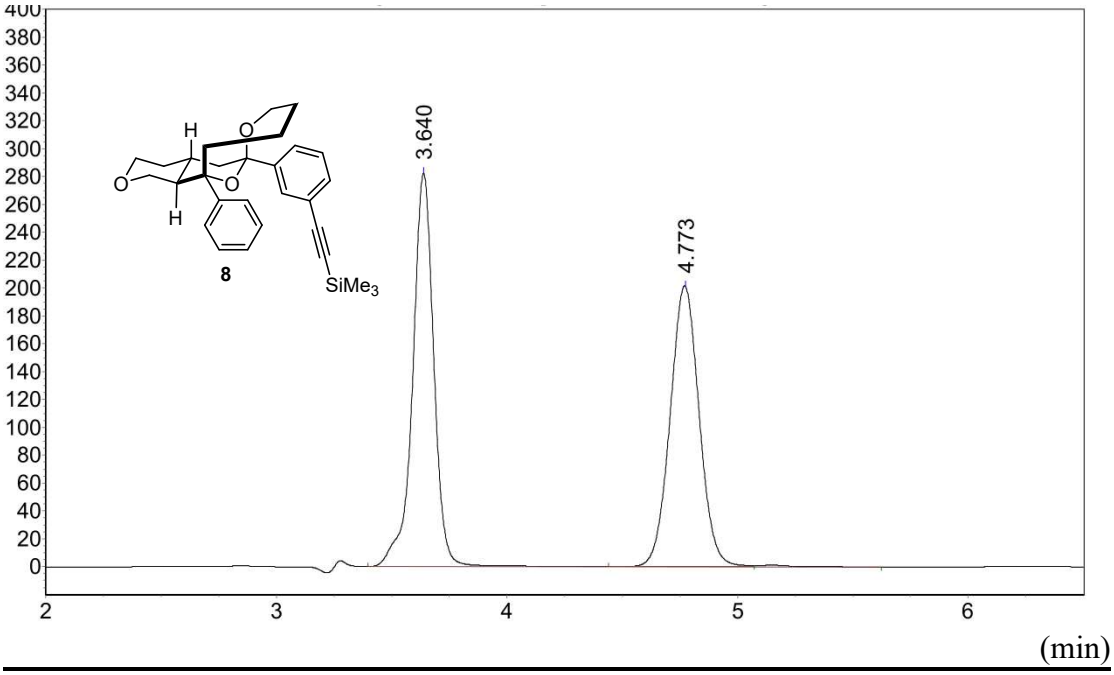
#	RT (time)	Heigh (mV*sec)	Area (mv)	Area (%)
1	15.557	13674.479	325633.844	98.1386
2	17.940	236.617	6176.450	1.8614



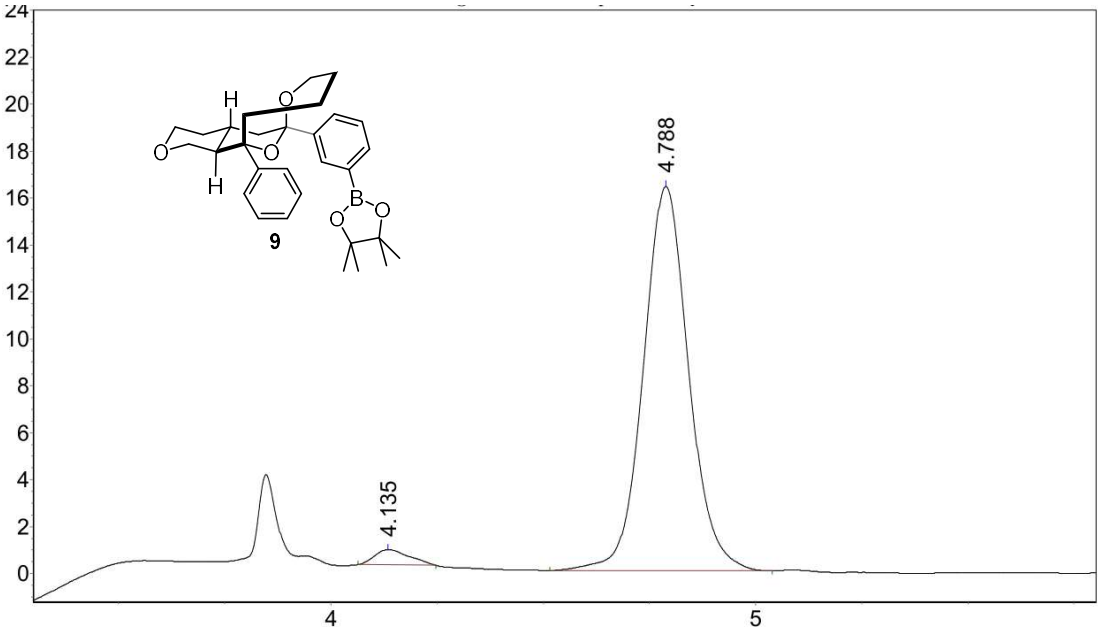
#	RT (time)	Heigh (mV*sec)	Area (mv)	Area (%)
1	15.573	728.849	17226.301	50.6007
2	17.948	626.911	16817.301	49.3993



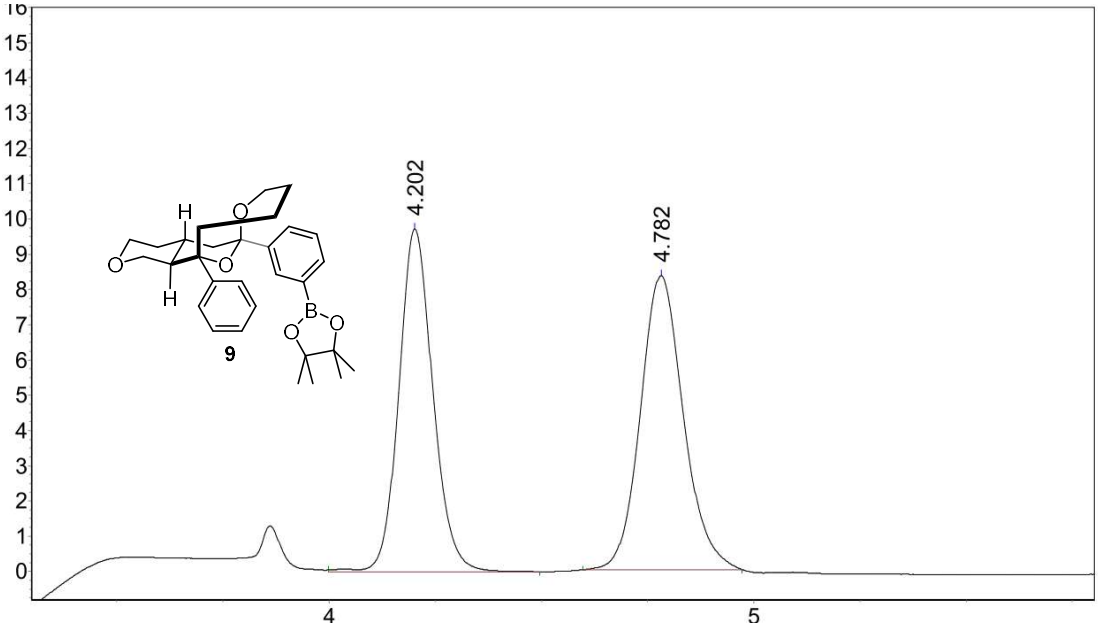
#	RT (time)	Heigh (mV*sec)	Area (mv)	Area (%)
1	3.618	665062.188	3938077.500	98.8379
2	4.755	5227.000	46304.301	1.1621



#	RT (time)	Heigh (mV*sec)	Area (mv)	Area (%)
1	3.640	281587.281	1809739.000	50.6482
2	4.773	201250.141	1763415.000	49.3518

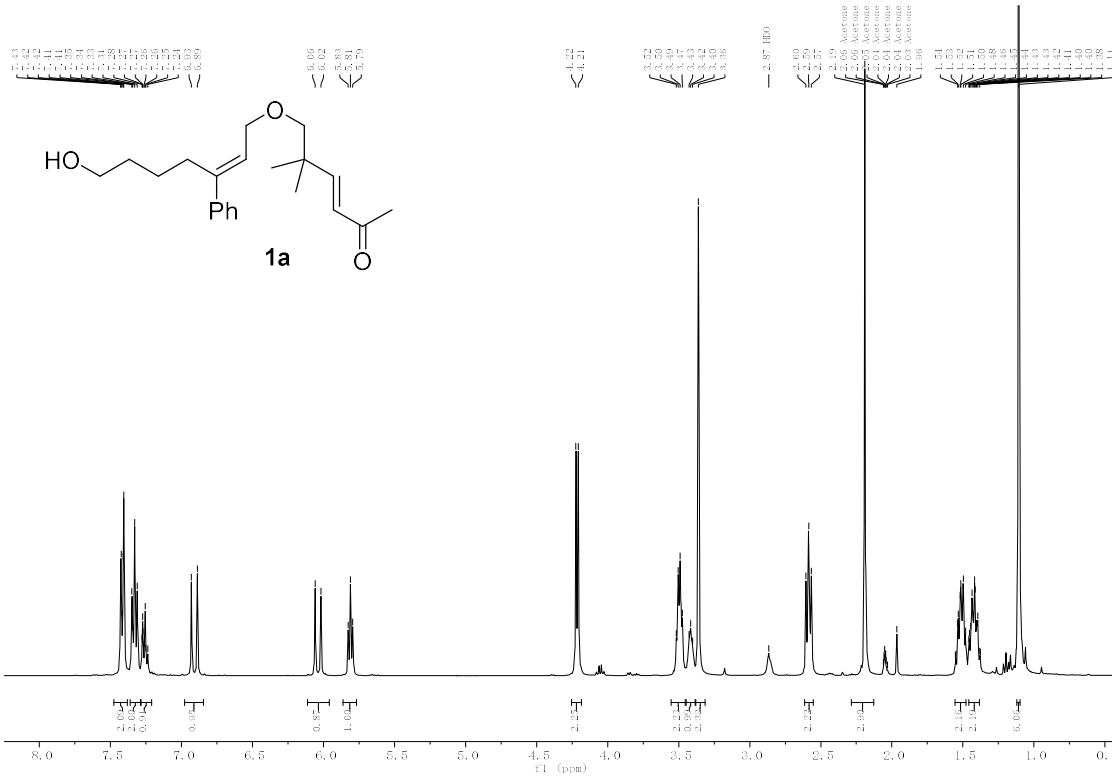


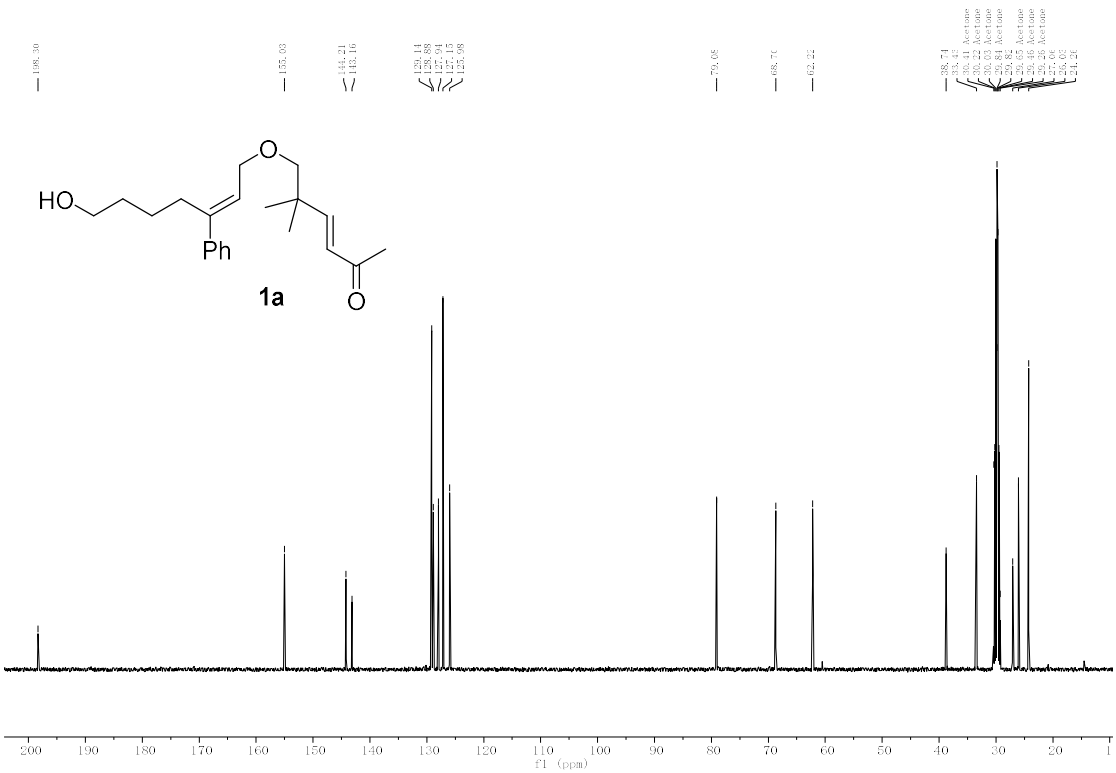
#	RT (time)	Heigh (mV*sec)	Area (mv)	Area (%)
1	4.135	652.332	3660.687	2.9253
2	4.788	16366.671	121479.000	97.0747

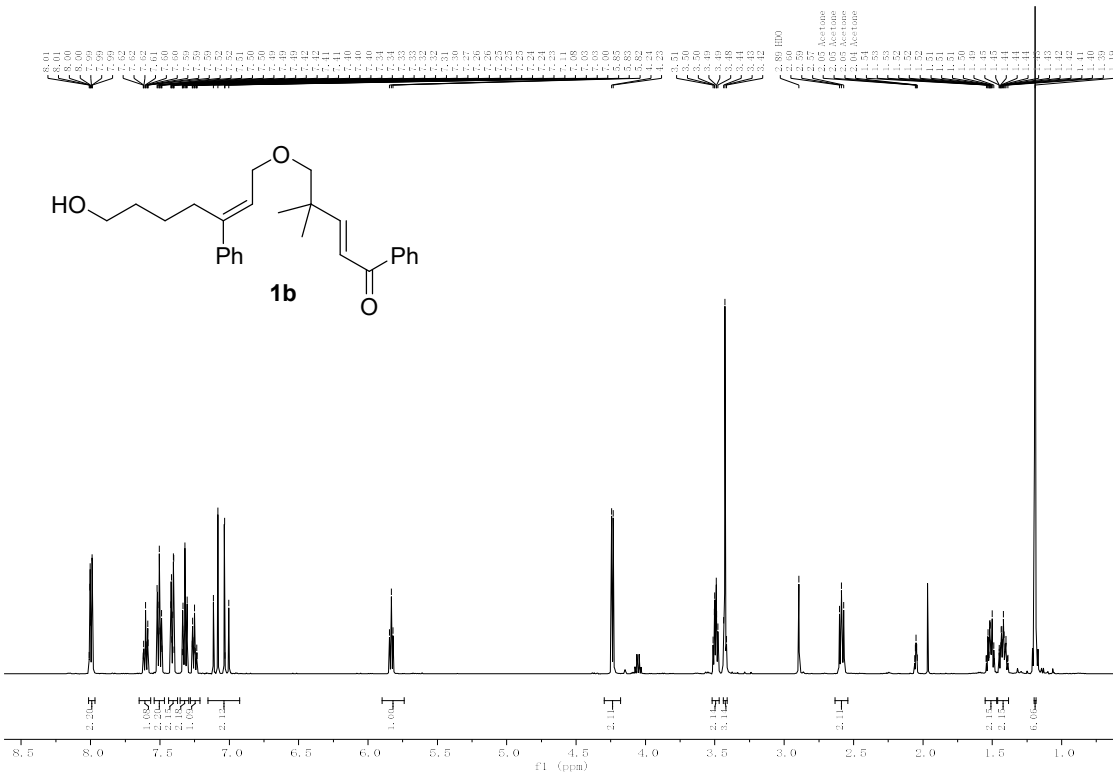


#	RT (time)	Heigh (mV*sec)	Area (mv)	Area (%)
1	4.202	9720.000	54288.301	48.0352
2	4.782	8341.183	58729.453	51.9648

10. ^{1}H NMR、^{13}C NMR and ^{19}F NMR spectra



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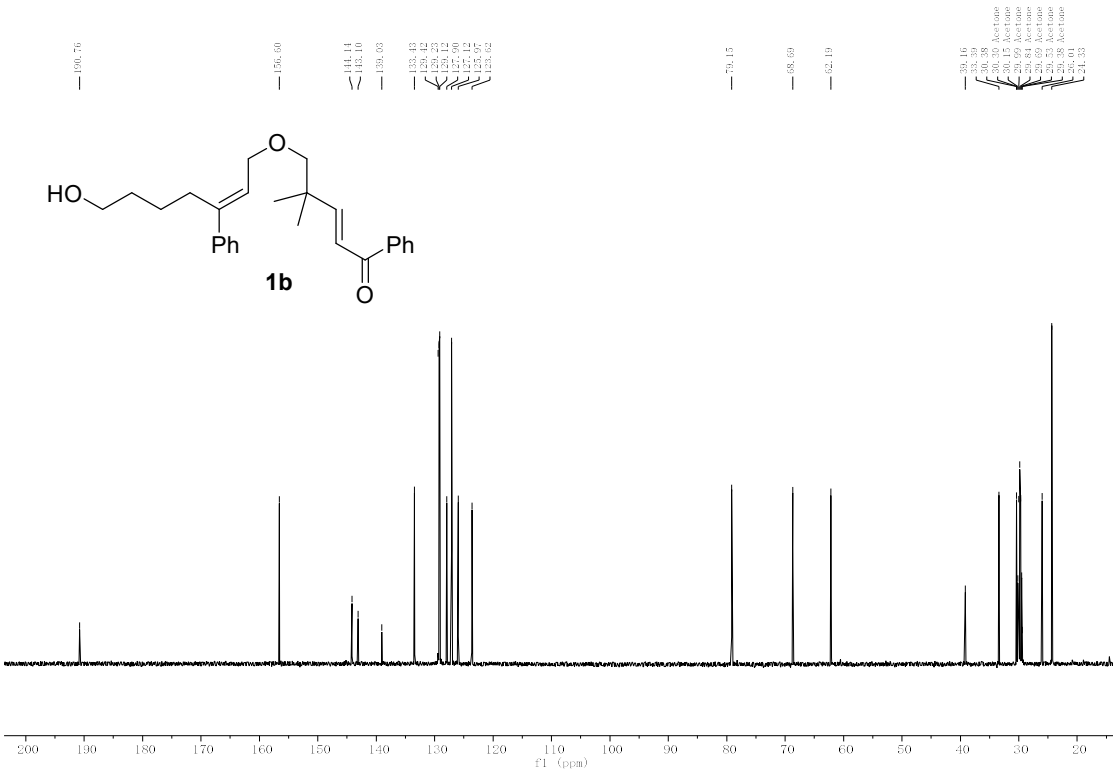
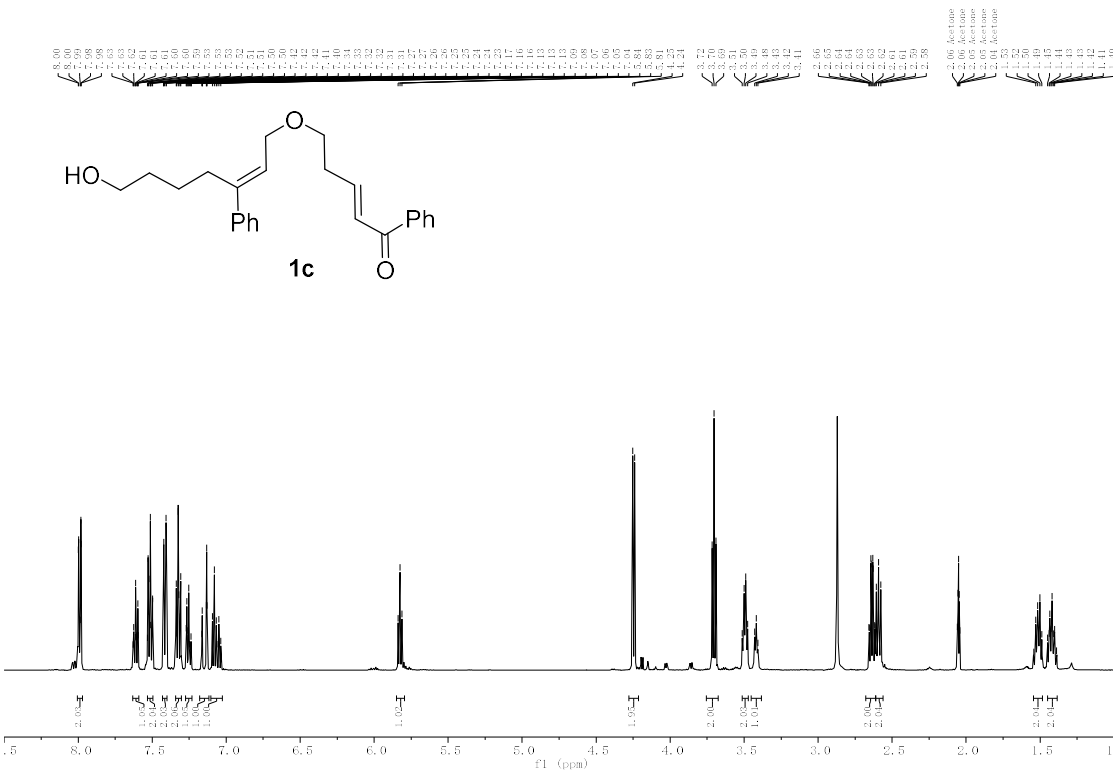
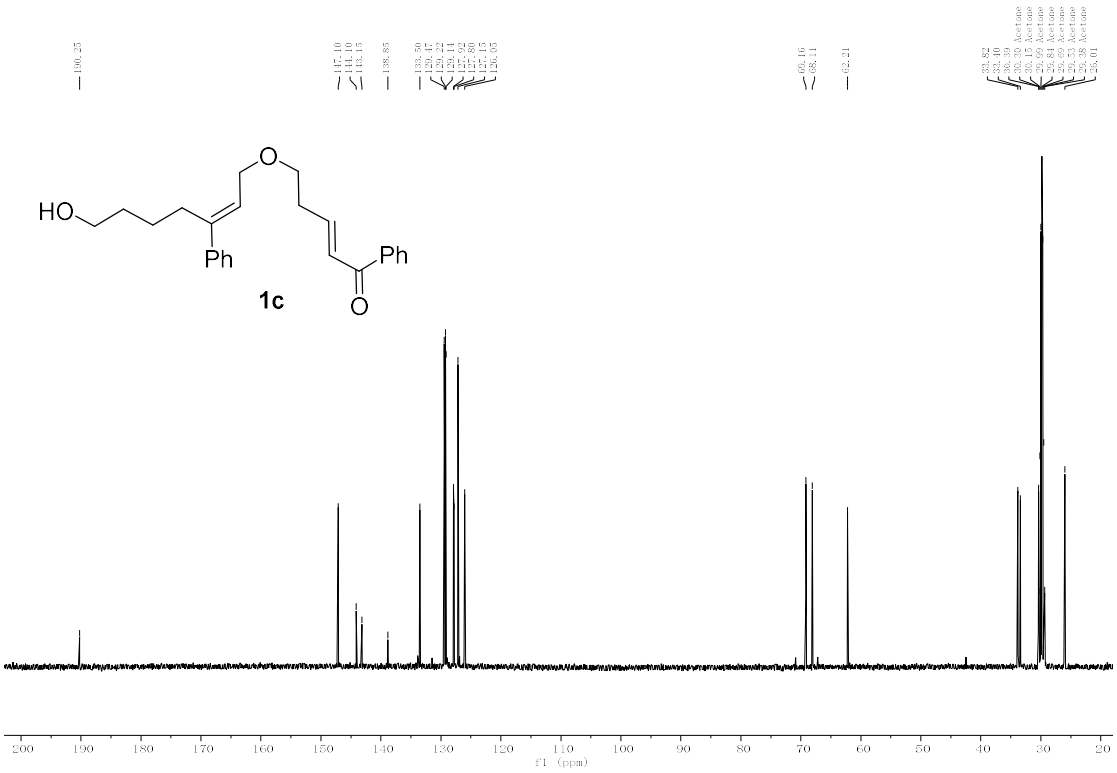
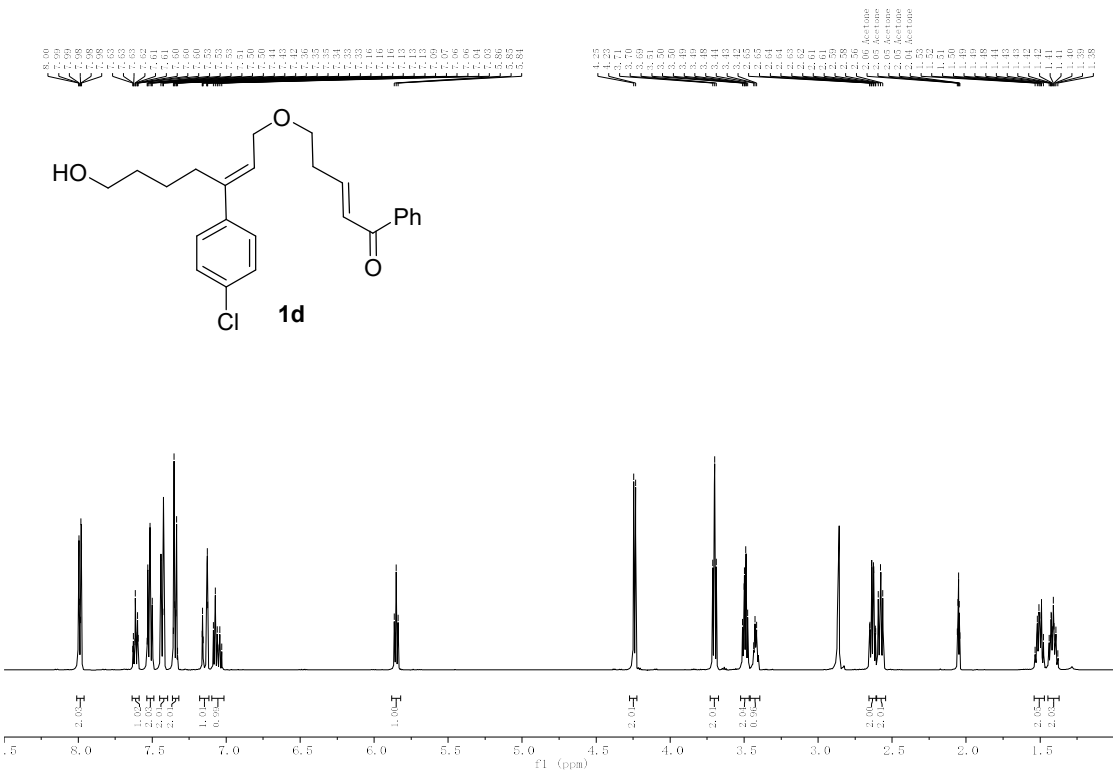
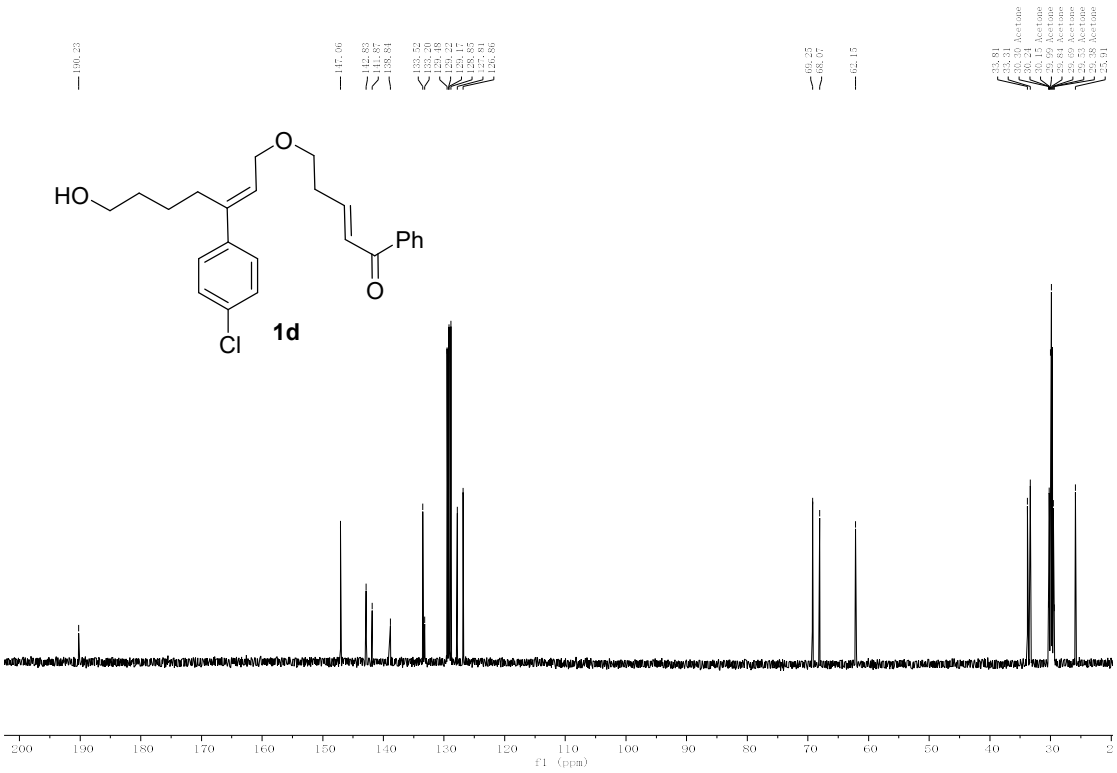
O
Ph
Ph
O
1b
f1 (ppm)


HO
O
Ph
Ph
O
1b
f1 (ppm)


HO
O
Ph
Ph
O
1c
f1 (ppm)


HO
O
Ph
Ph
O
1c
f1 (ppm)


HO
O
Ph
O
Cl
1d
f1 (ppm)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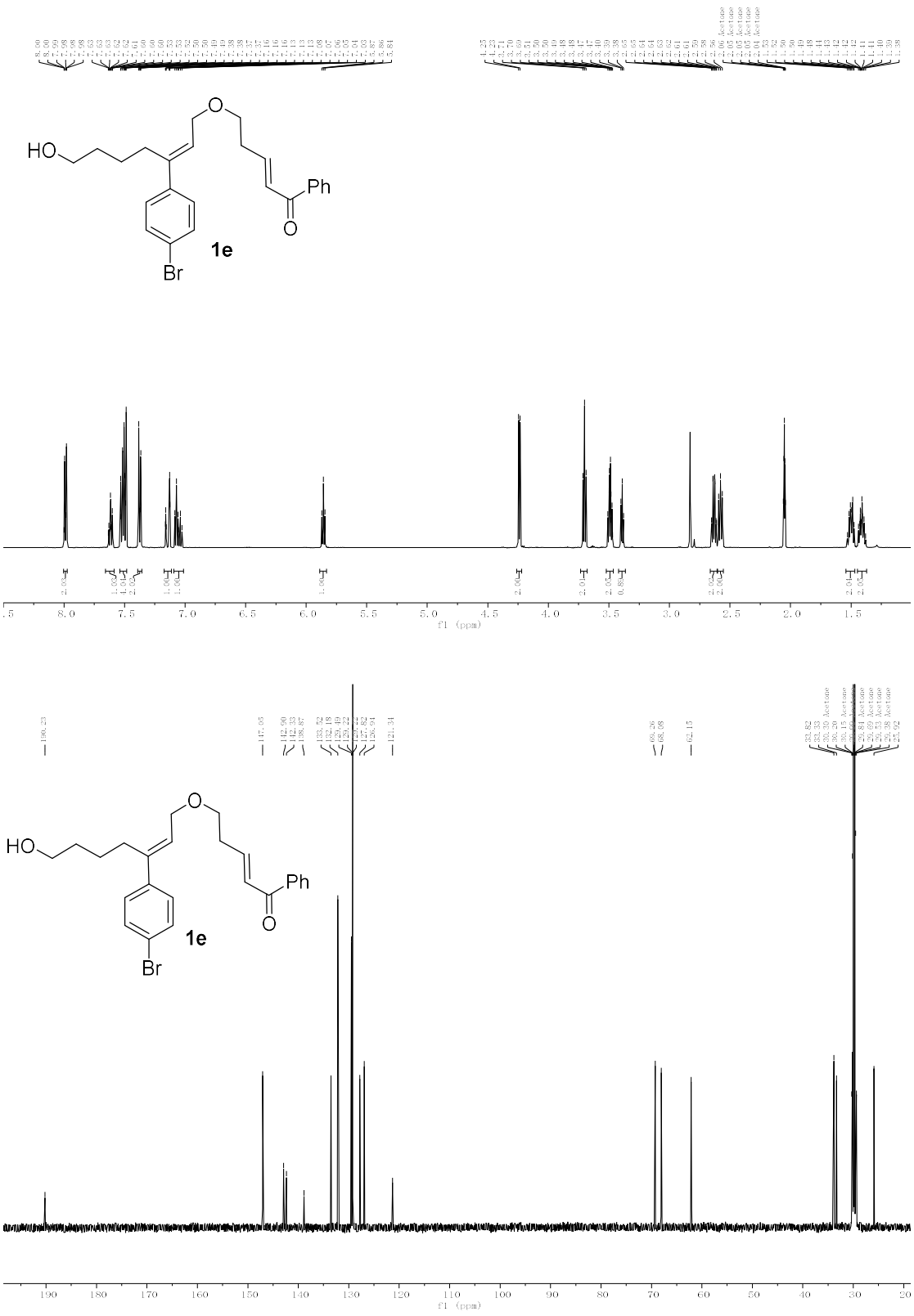
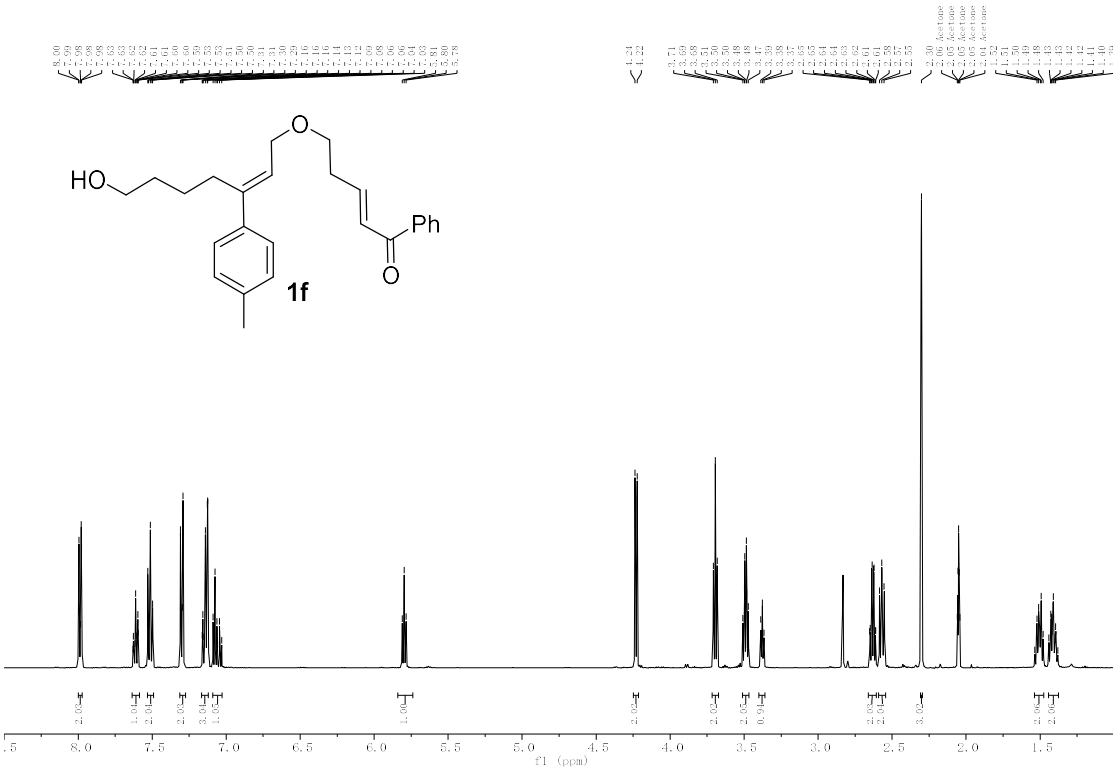
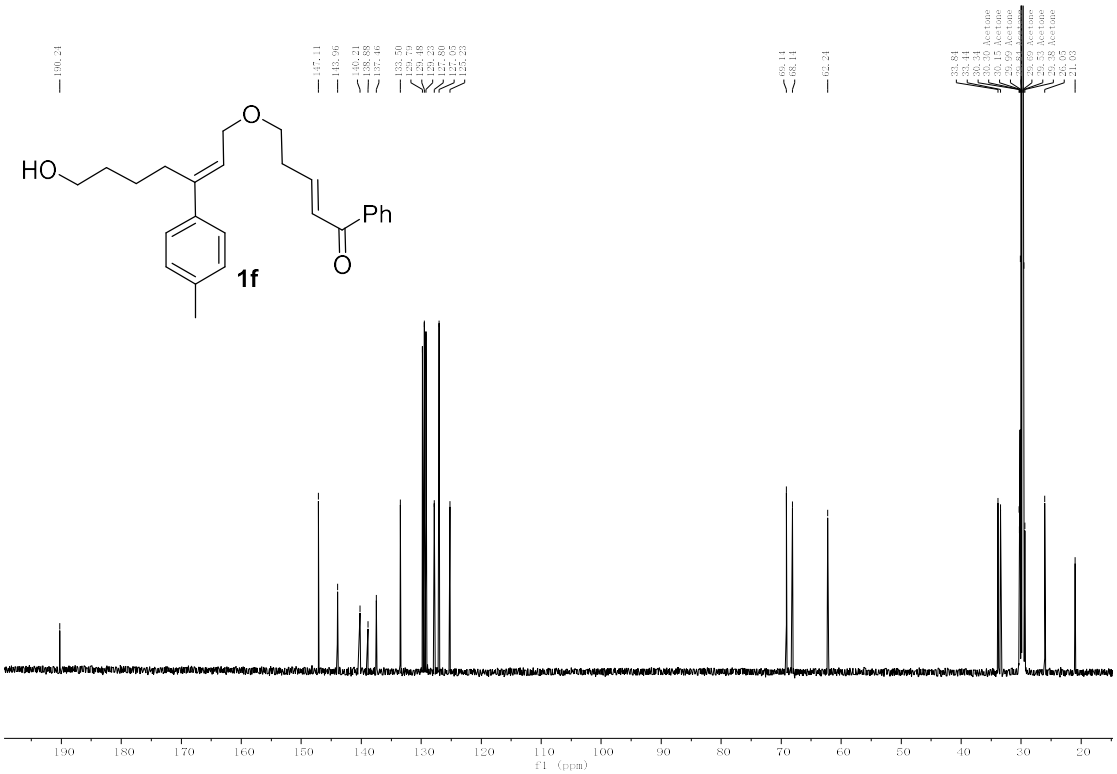
O
Ph
O
Cl
1d
f1 (ppm)


HO
O
Ph
O
Br
1e
f1 (ppm)


HO
O
Ph
O
1f
f1 (ppm)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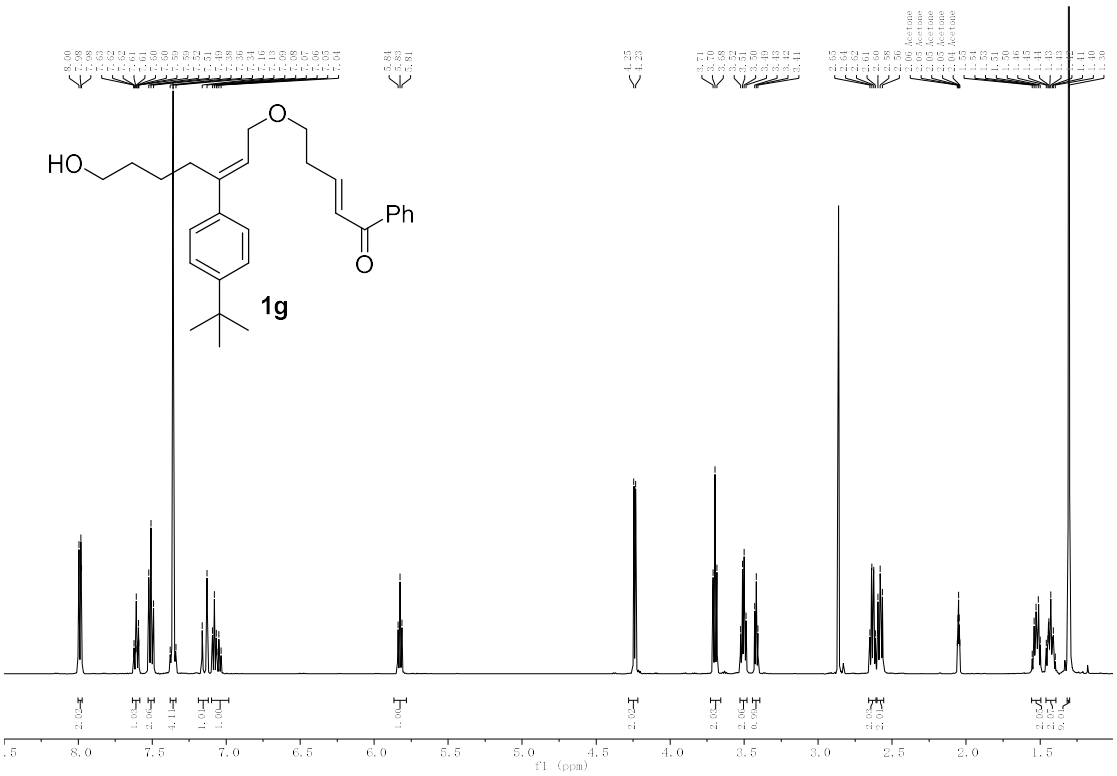
Ph
O
1f
f1 (ppm)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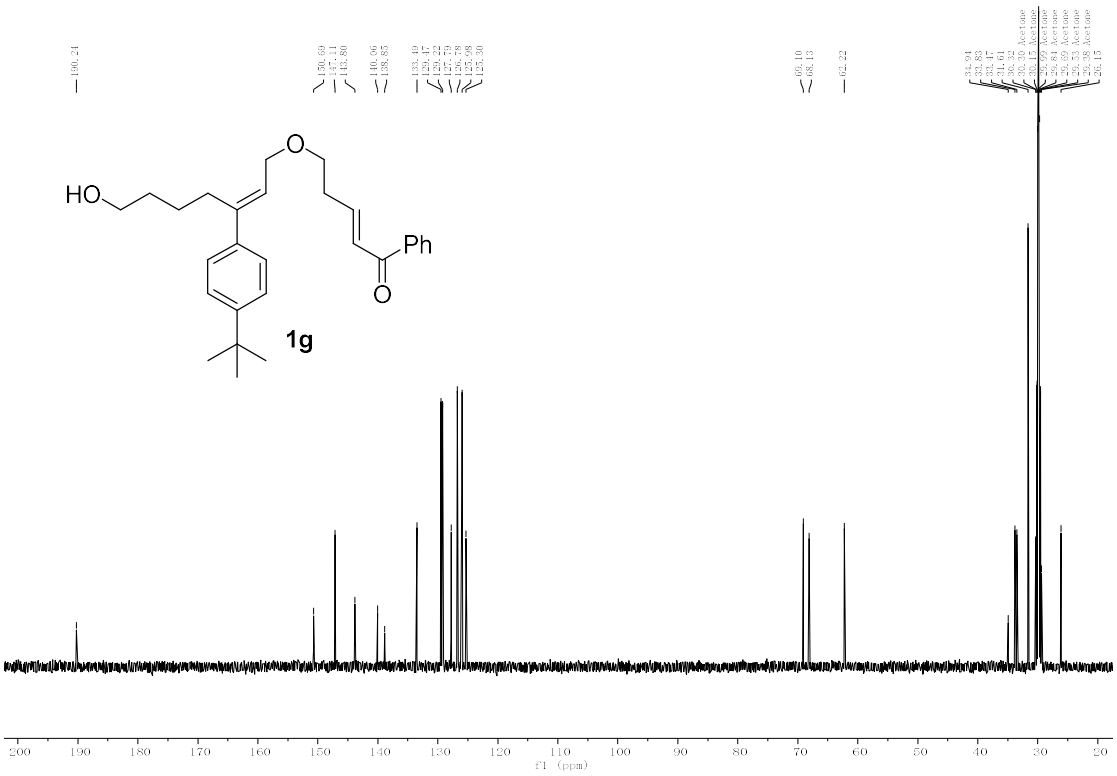
Ph
O
1g
f1 (ppm)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Ph
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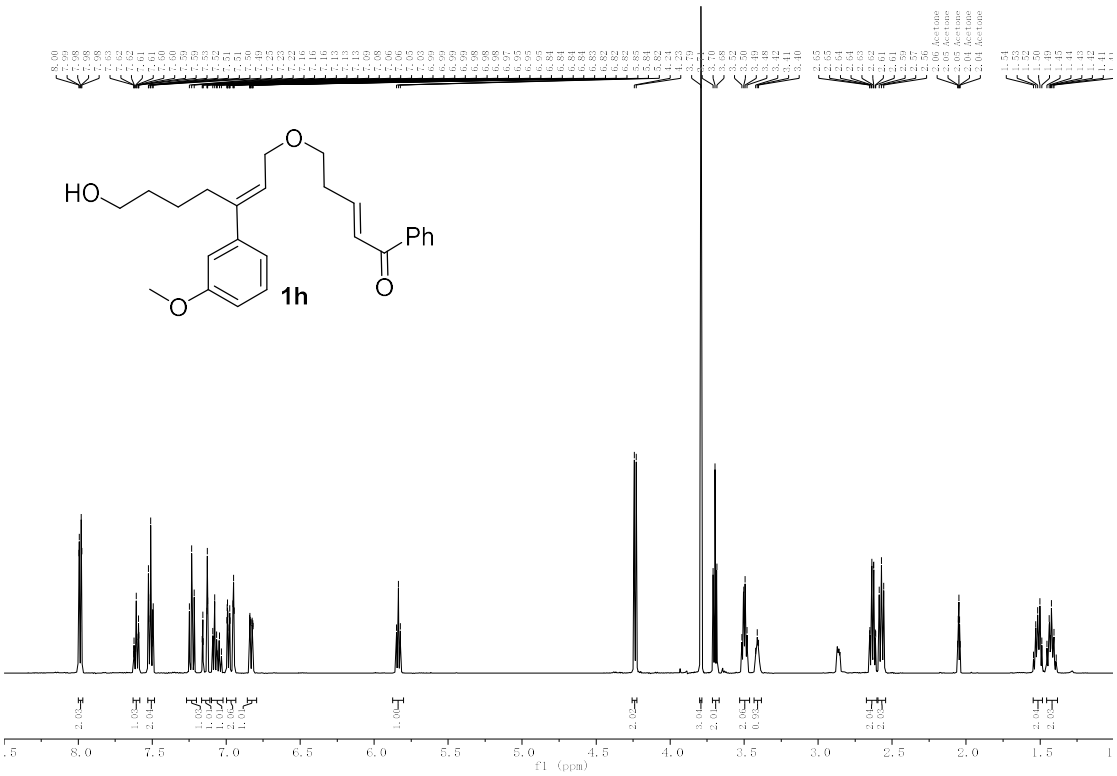
f1 (ppm)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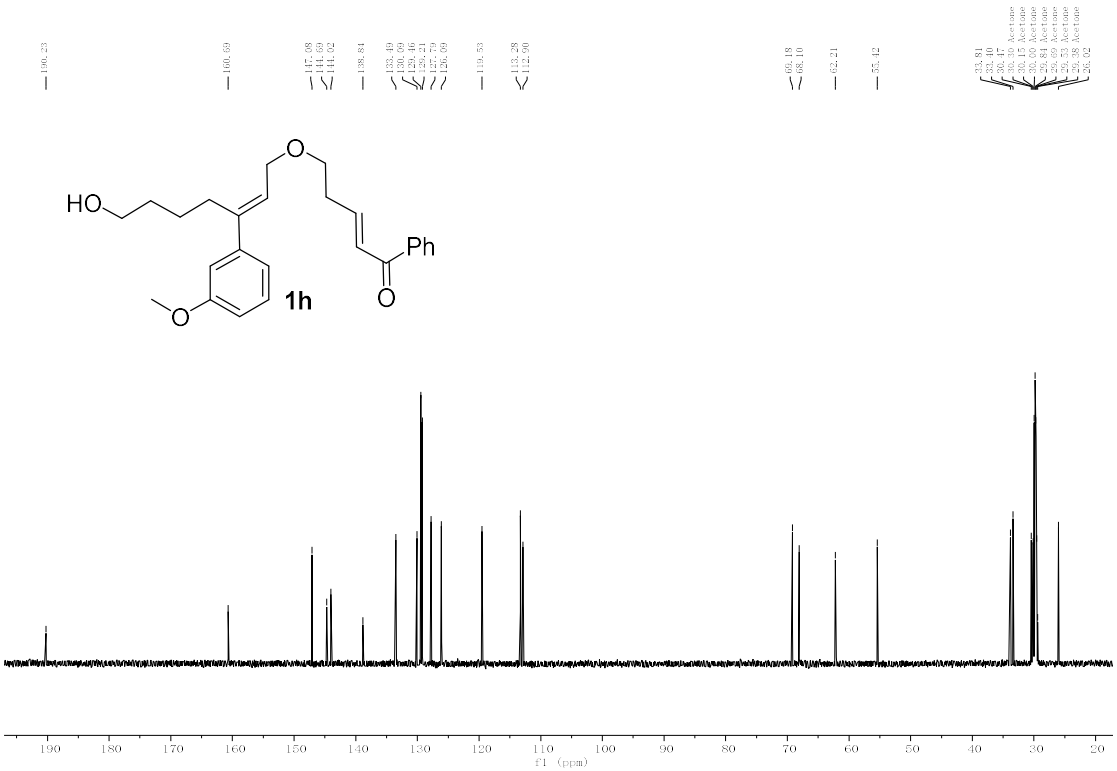
Ph
O
O
1h
f1 (ppm)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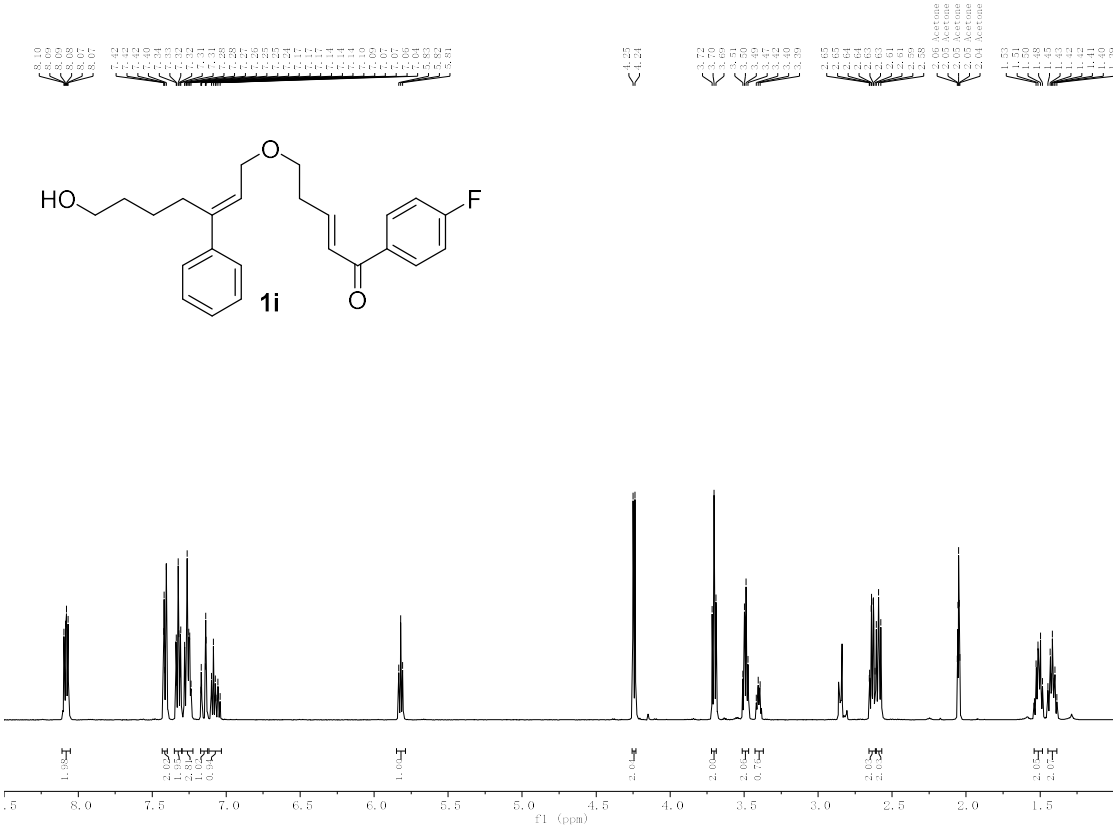
O
Ph
O
O
1h
f1 (ppm)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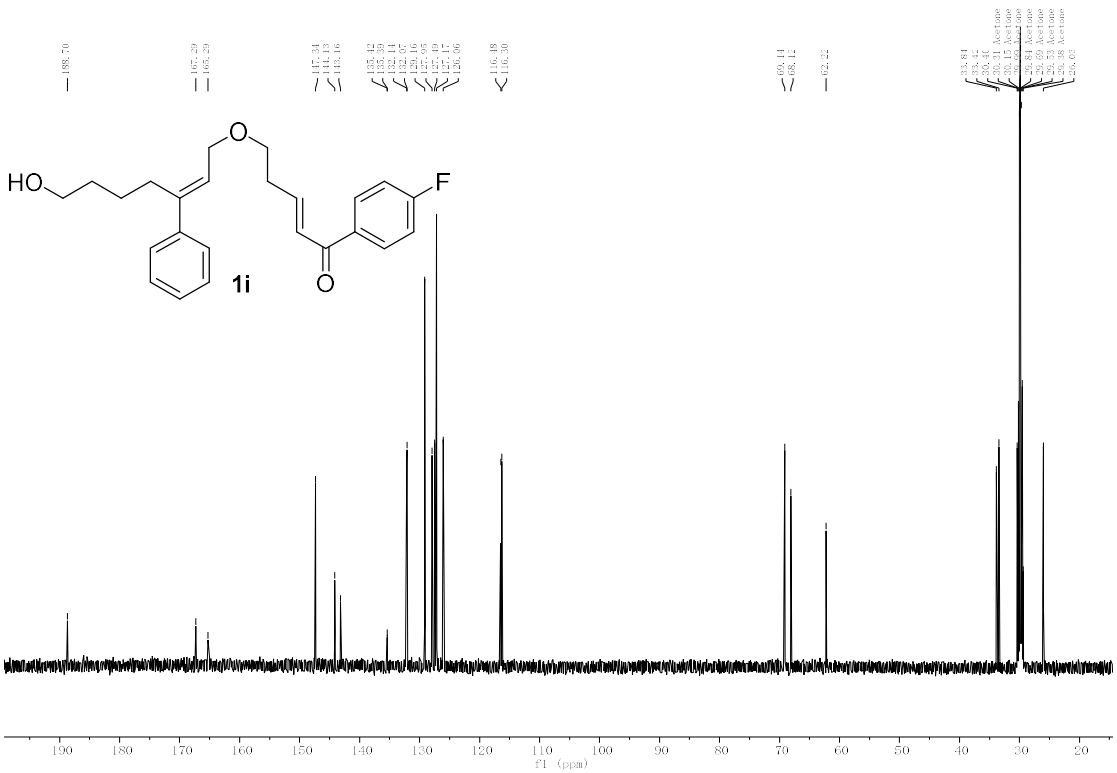
O
F
O
1i
f1 (ppm)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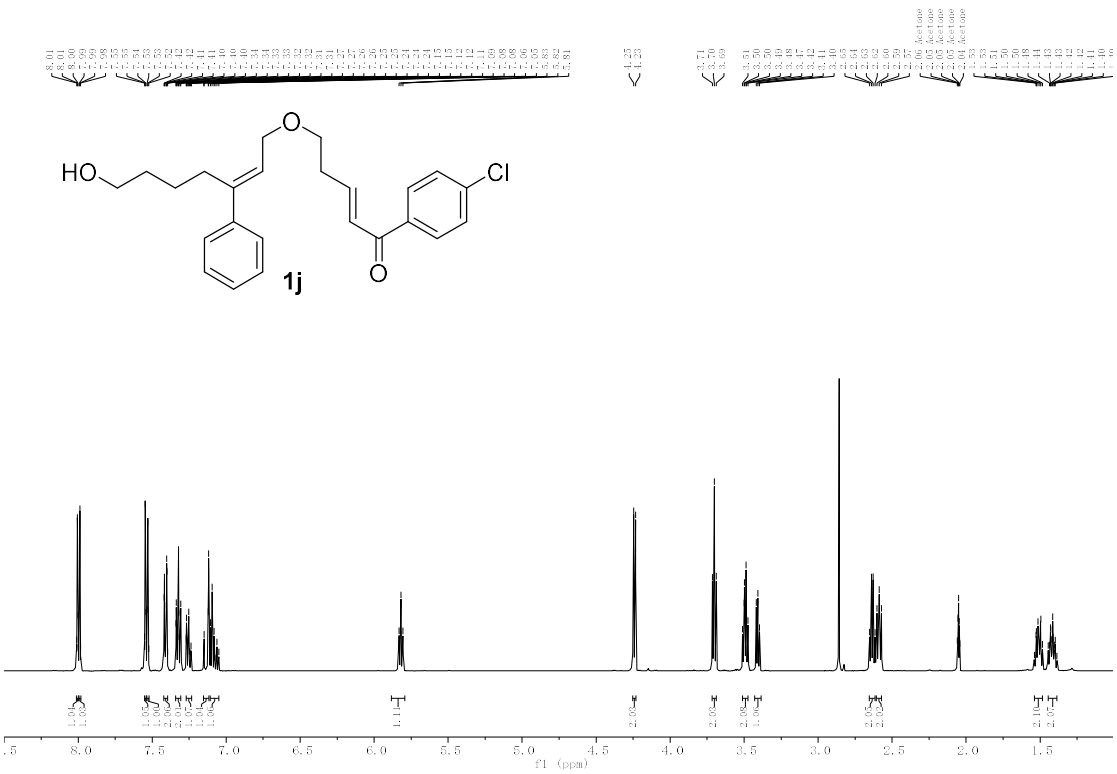
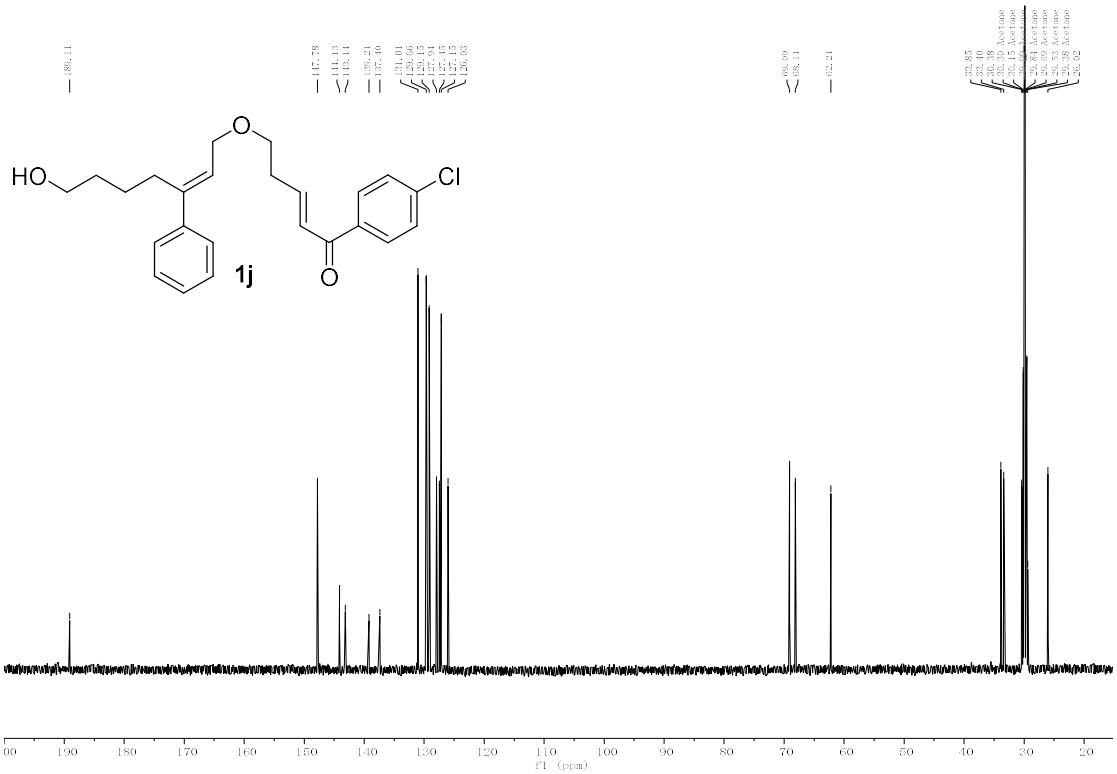
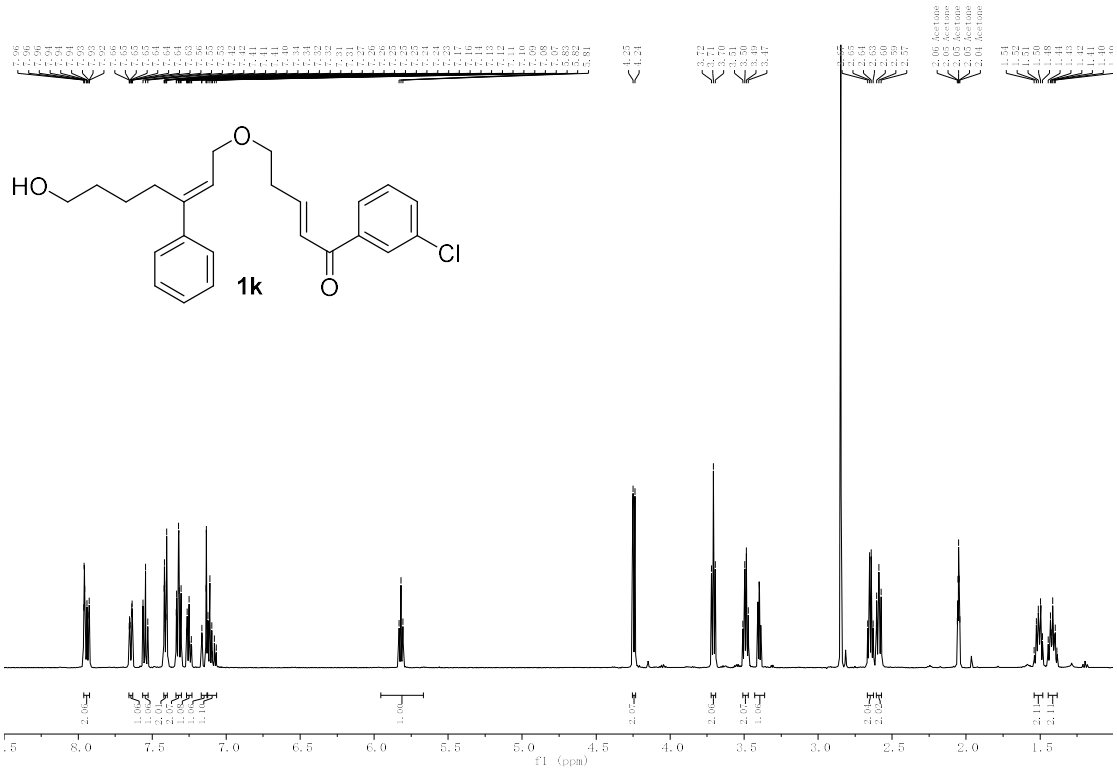
O
F
O
1i
f1 (ppm)


HO
O
Cl
O
1j
f1 (ppm)


HO
O
Cl
O
1j
f1 (ppm)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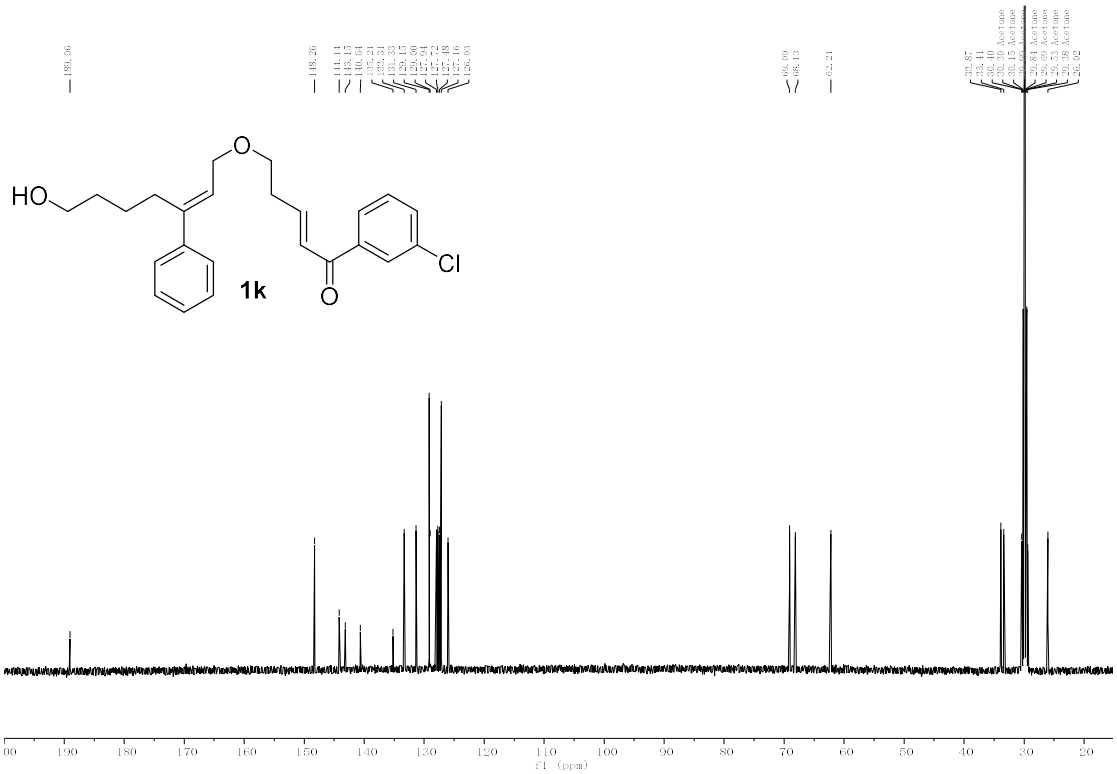
Cl
O
1k
f1 (ppm)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Cl
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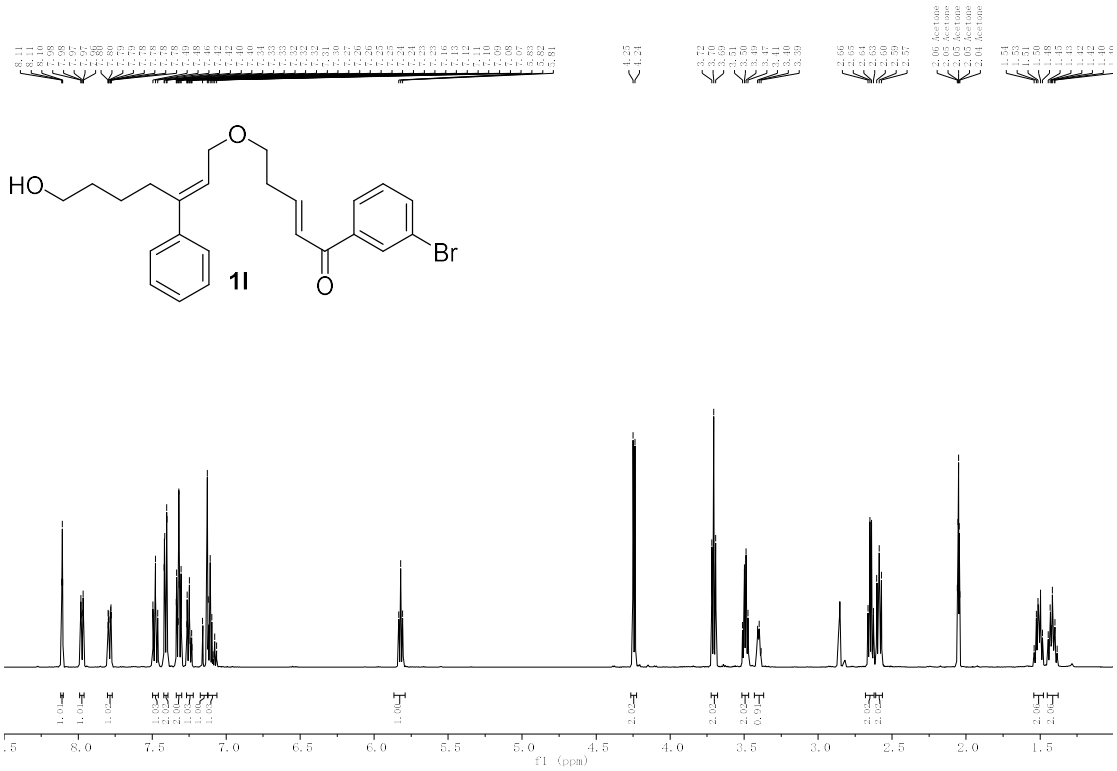
1k
f1 (ppm)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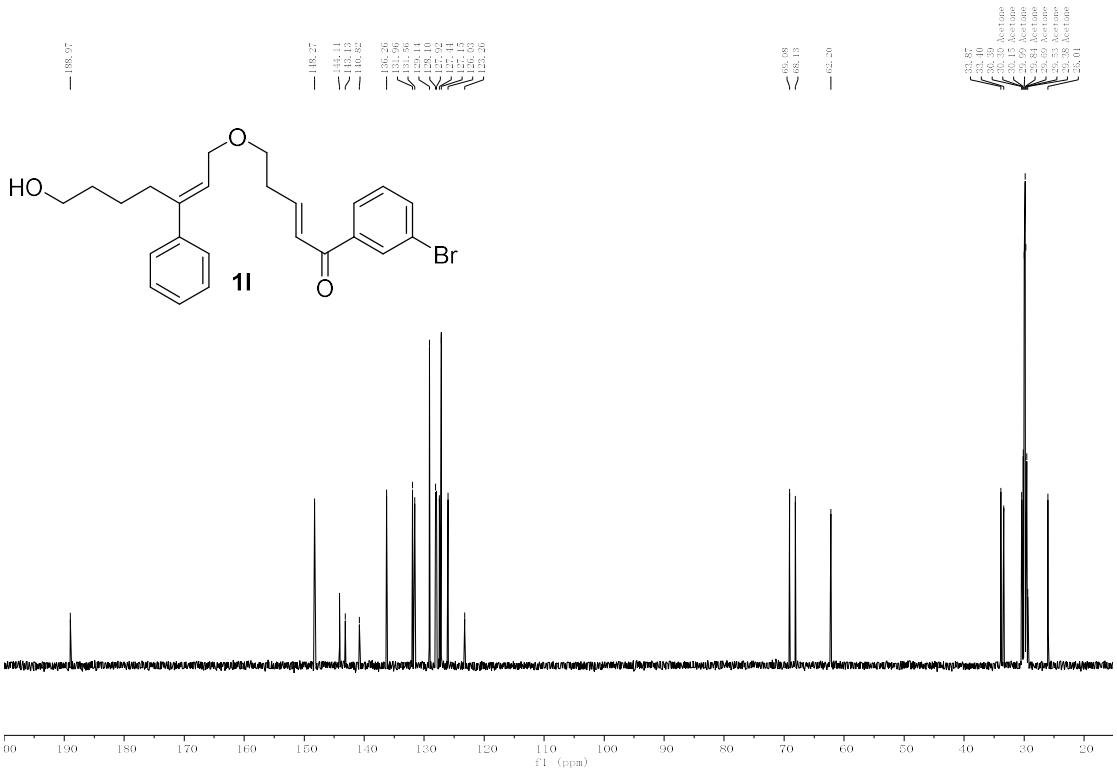
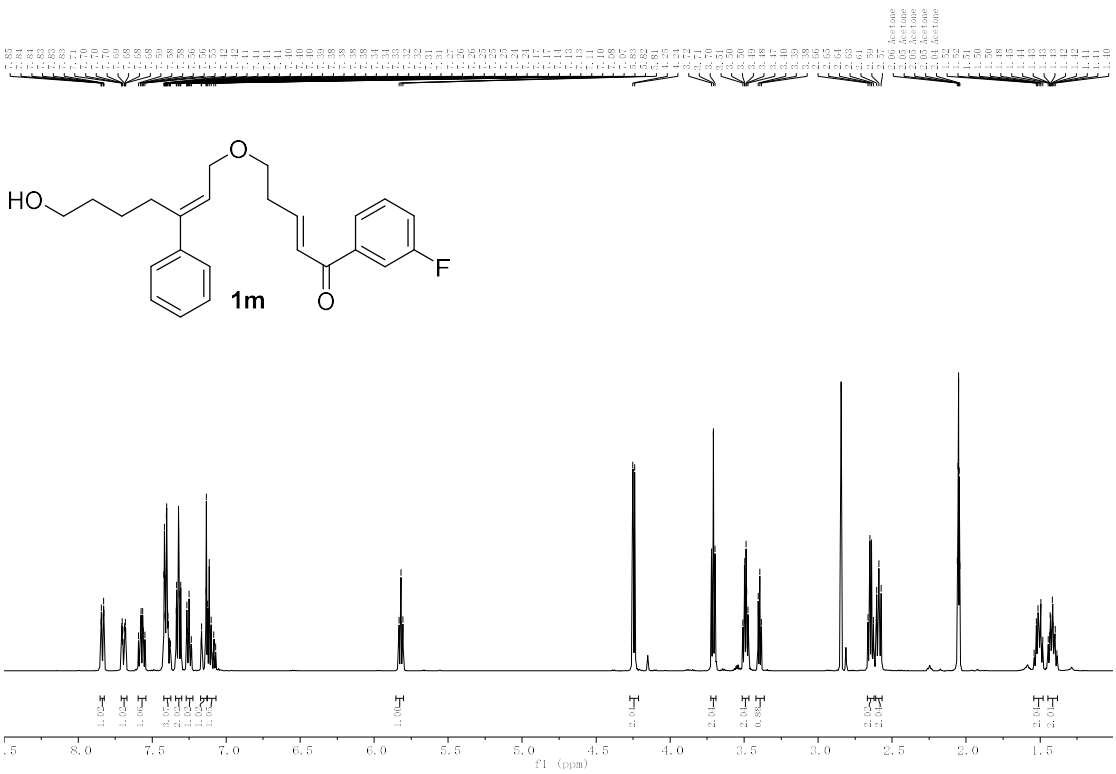
Br
1l
f1 (ppm)


HO
O
Br
1l
f1 (ppm)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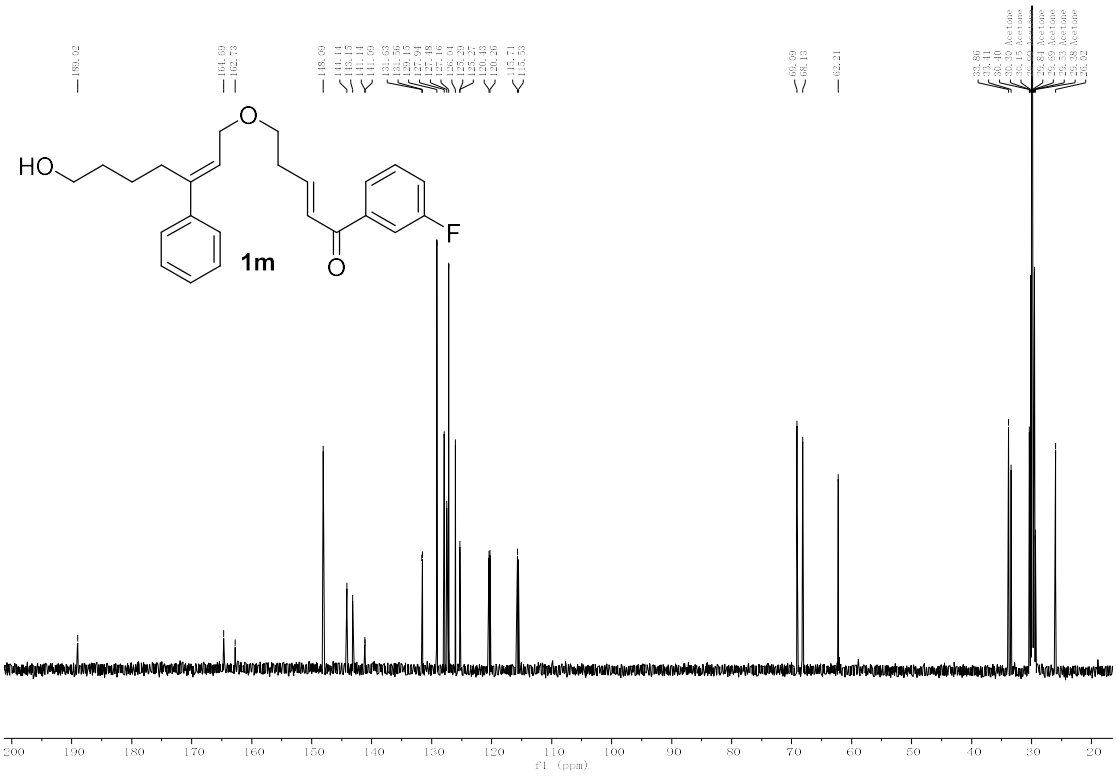
F
1m
O
f1 (ppm)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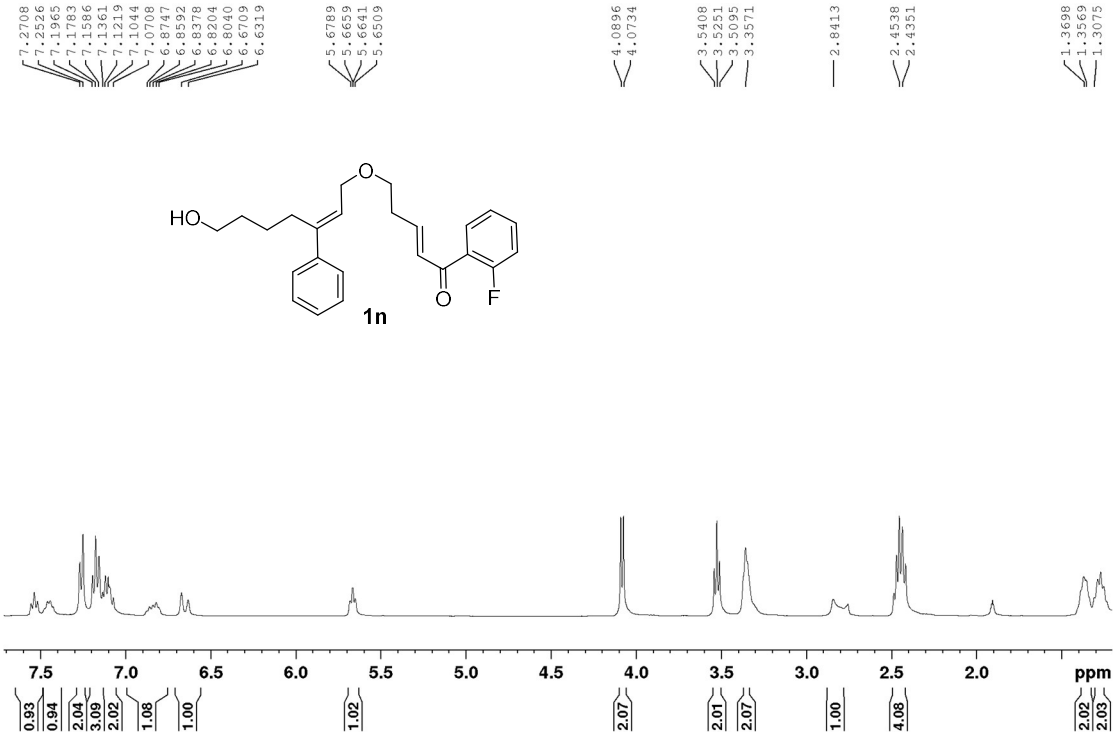
F
1m
O
f1 (ppm)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O
O
F
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6.0
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4.0
3.5
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ppm
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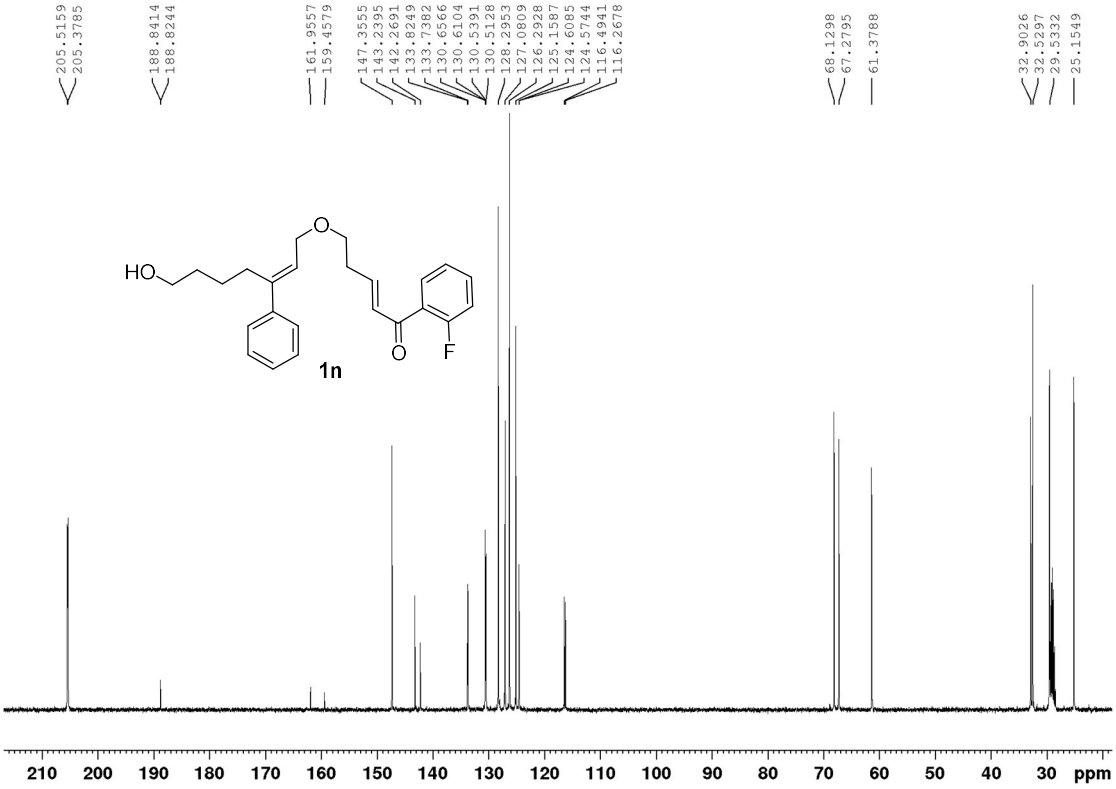
2.02
2.03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61.3788
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O
O
F
1n
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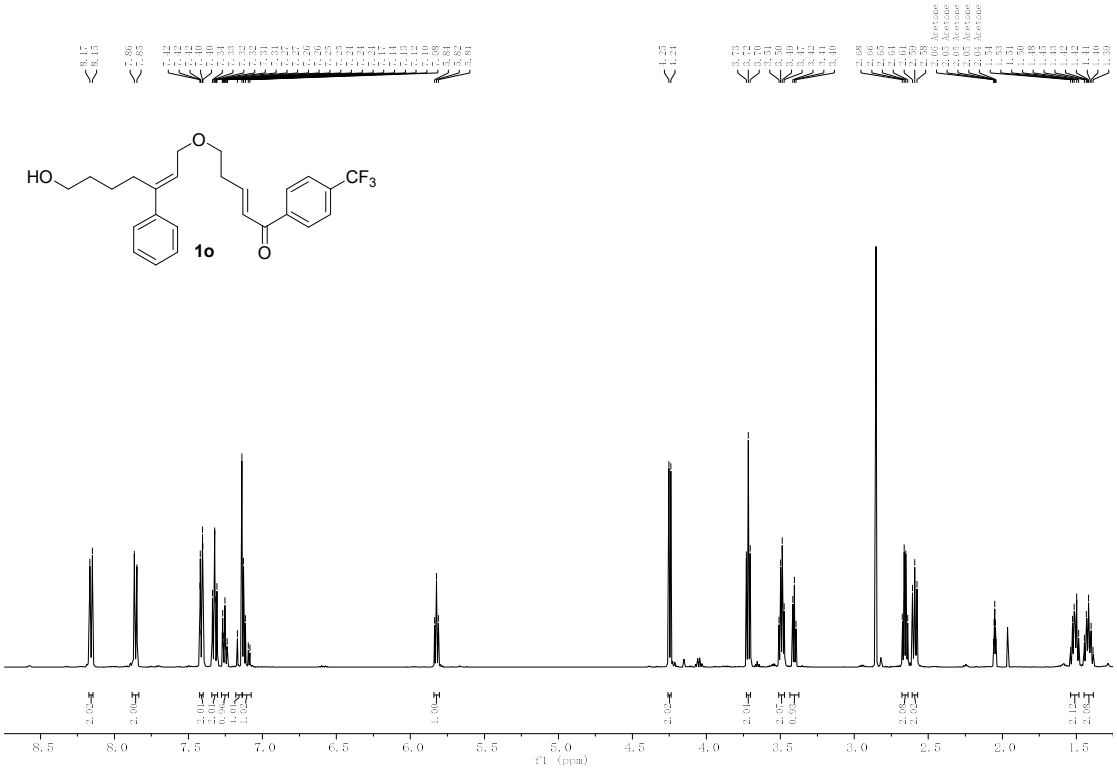
ppm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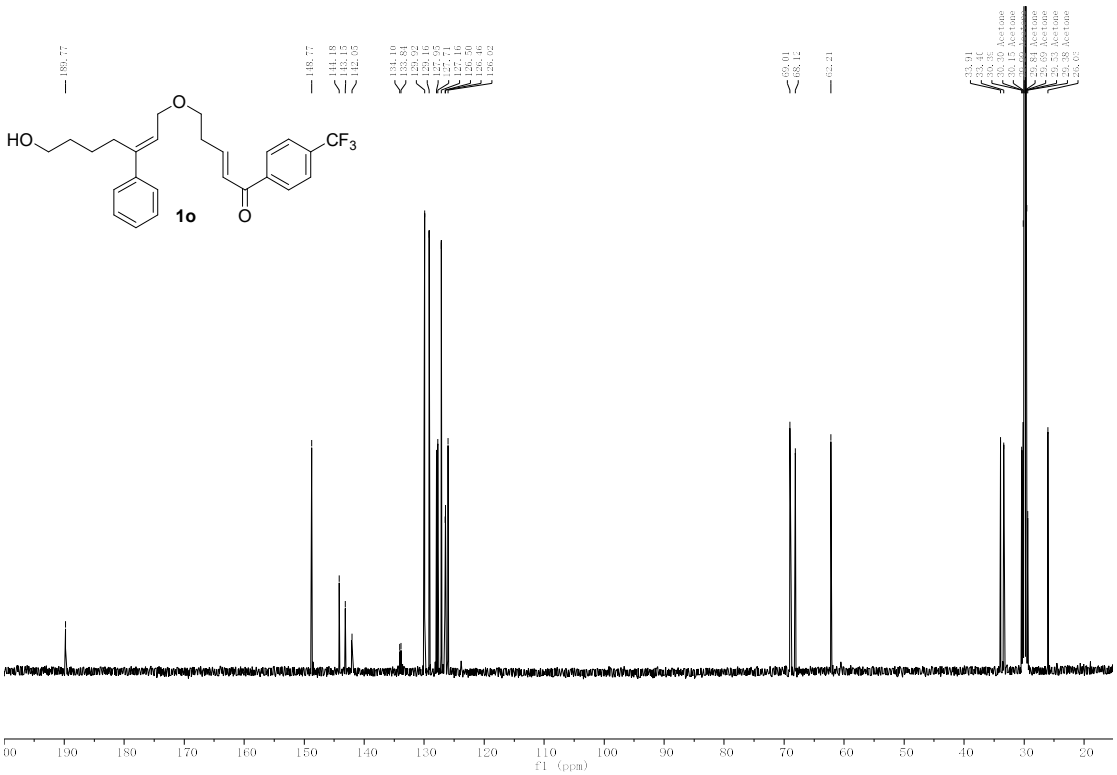
1o
O
f1 (ppm)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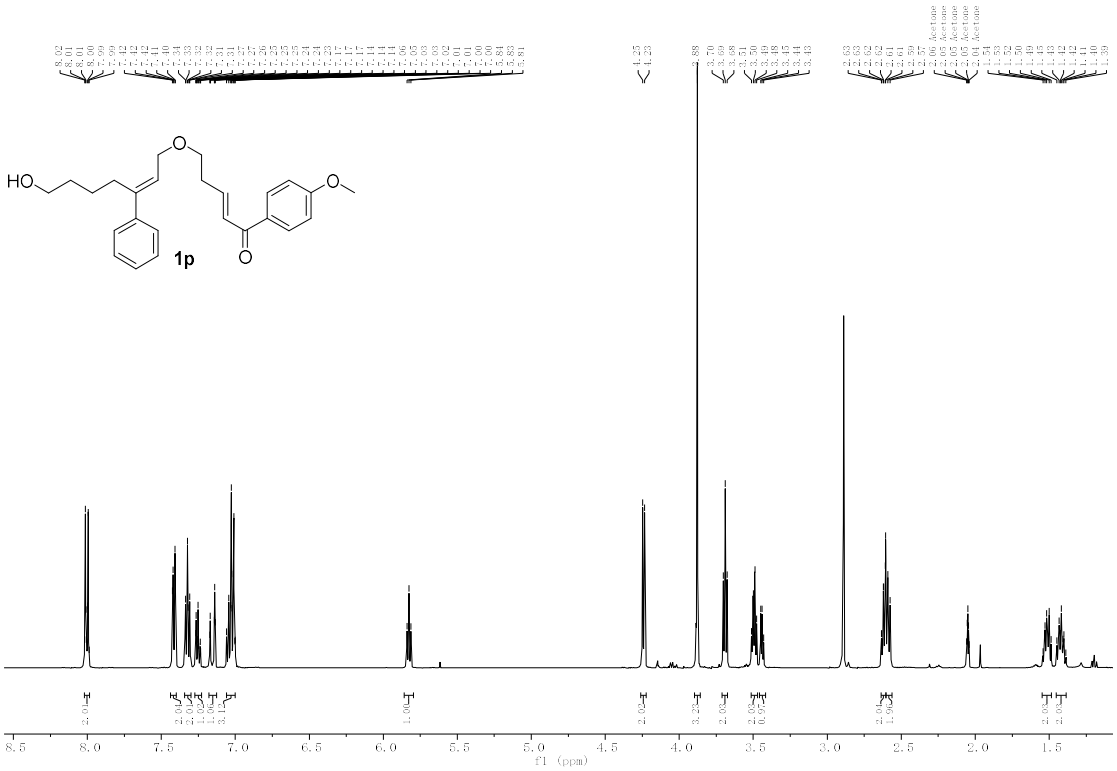
CF3
1o
O
f1 (ppm)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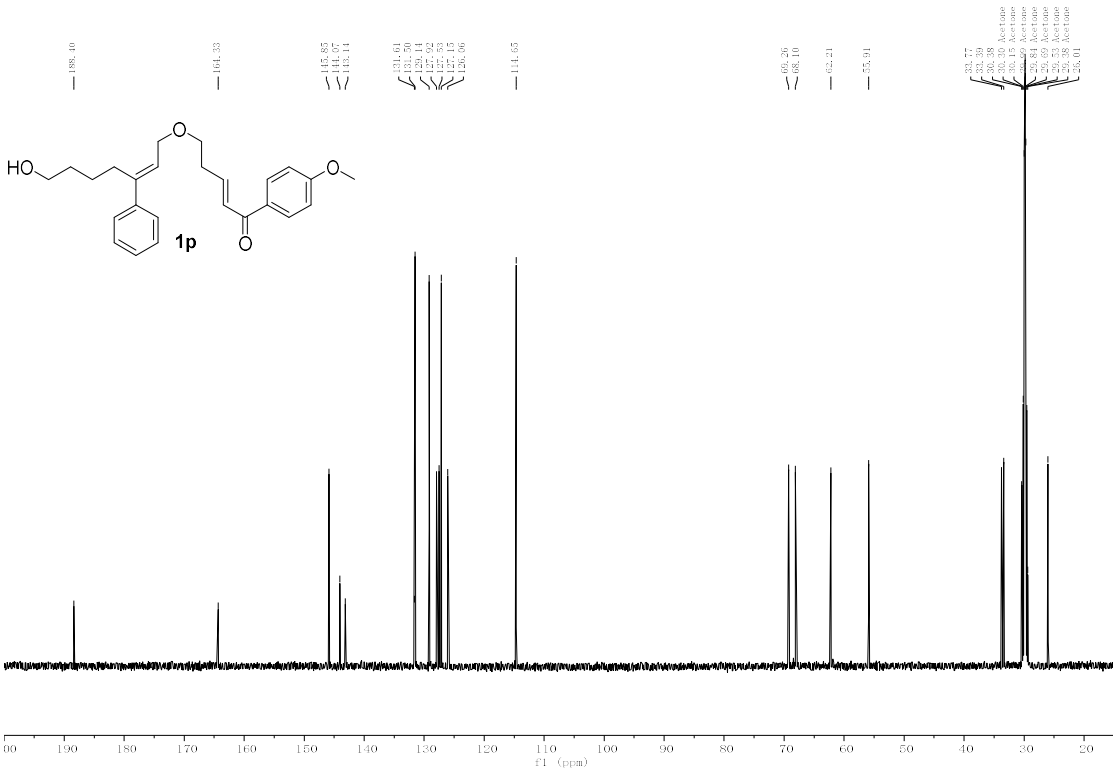
1p
f1 (ppm)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O
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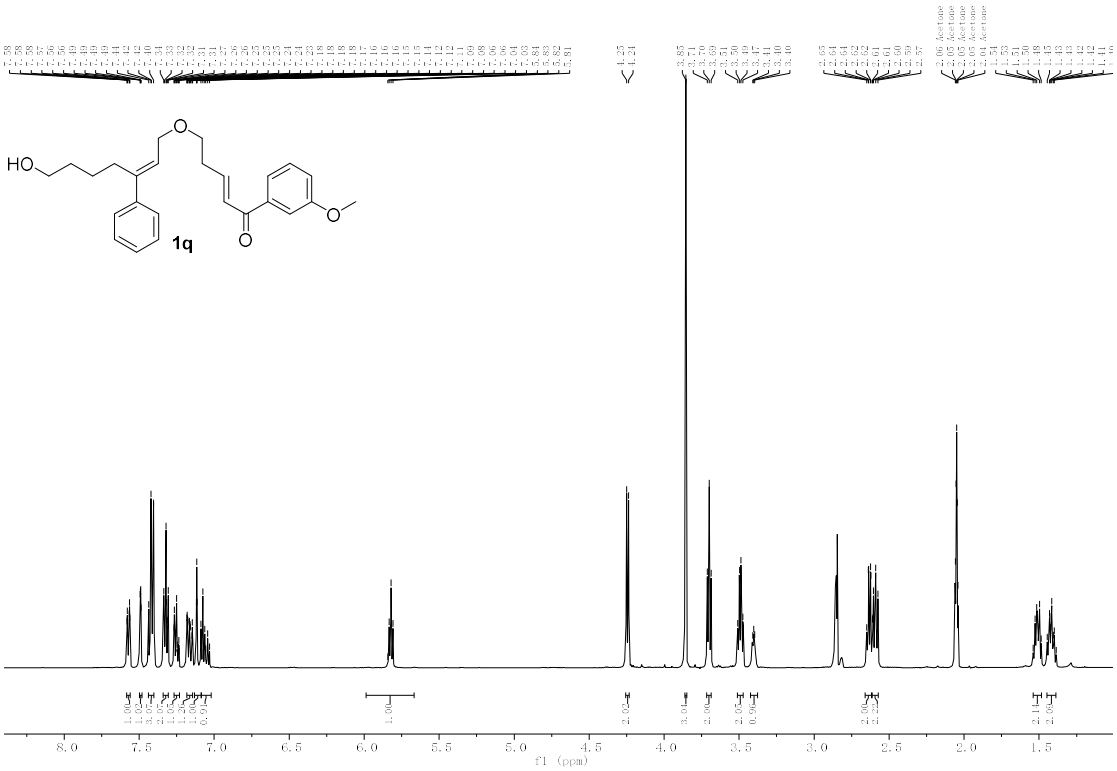
1p
f1 (ppm)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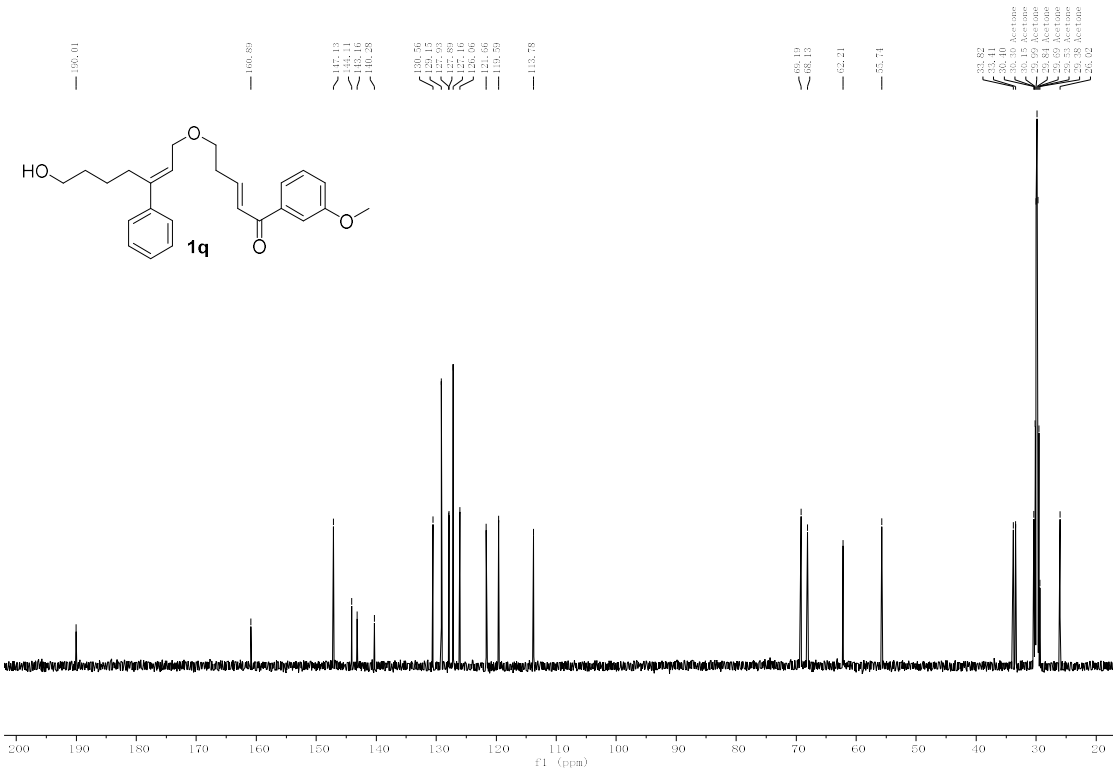
1q
f1 (ppm)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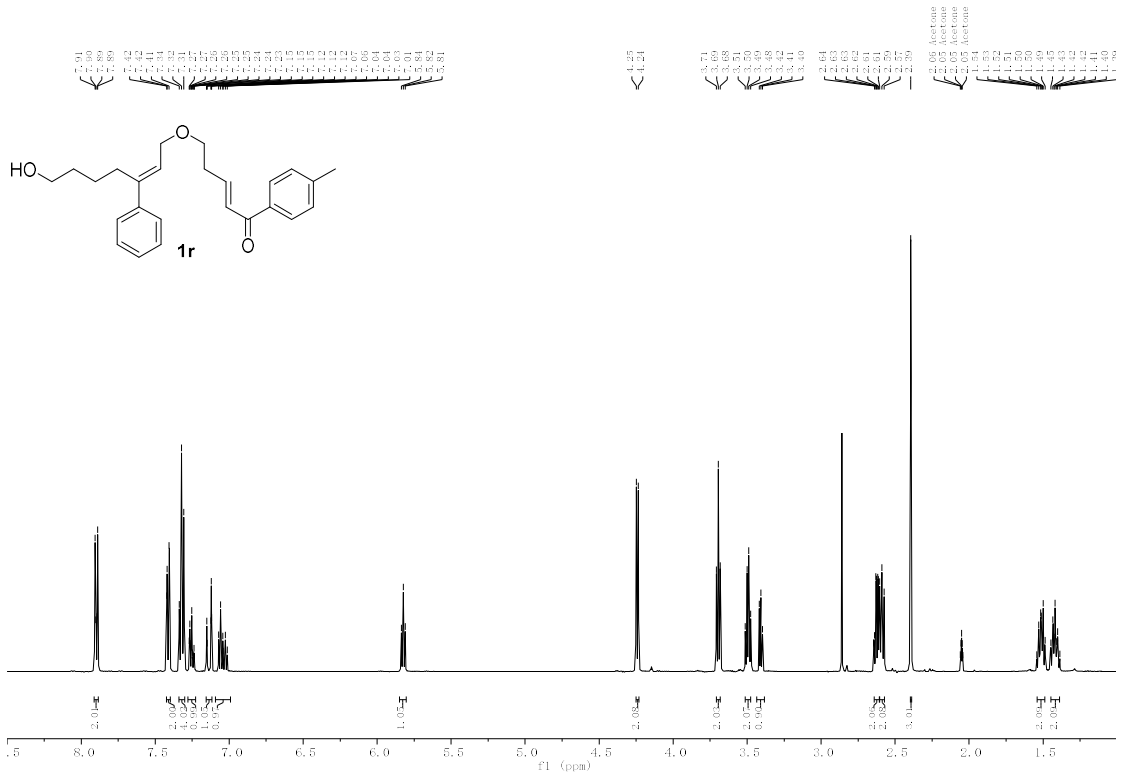
O
O
1q
f1 (ppm)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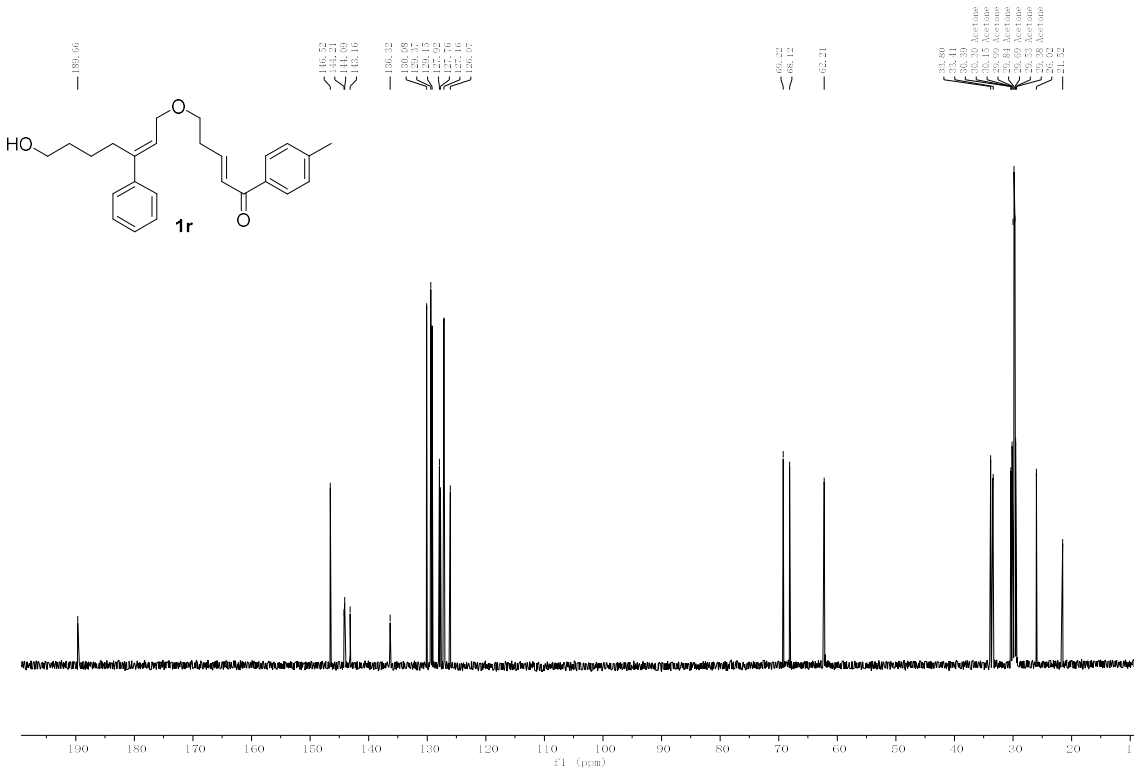
O
1r
f1 (ppm)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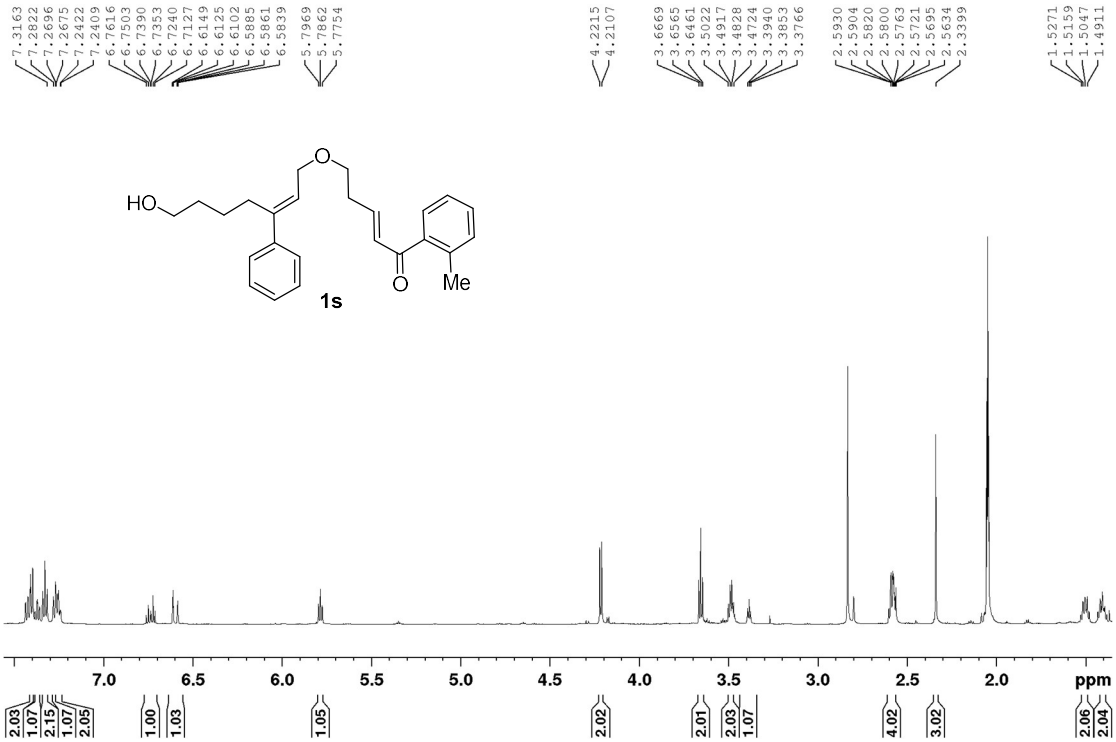
1r
f1 (ppm)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3.3766
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1.4911
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2.5
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ppm
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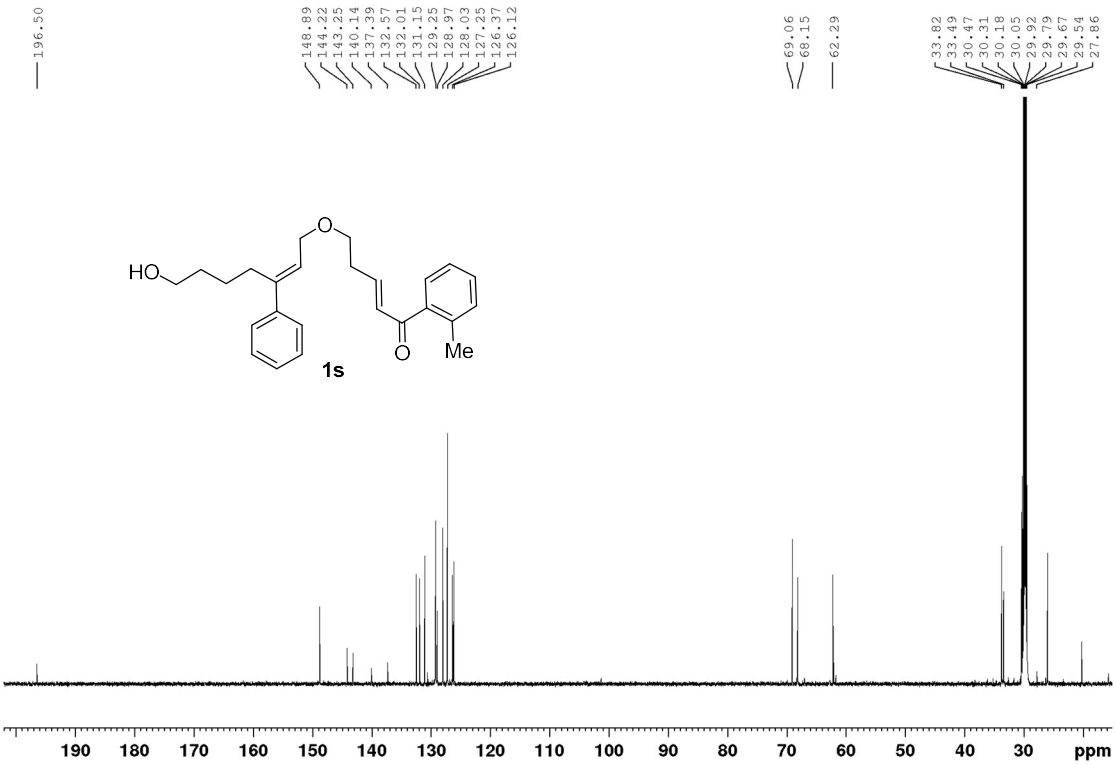
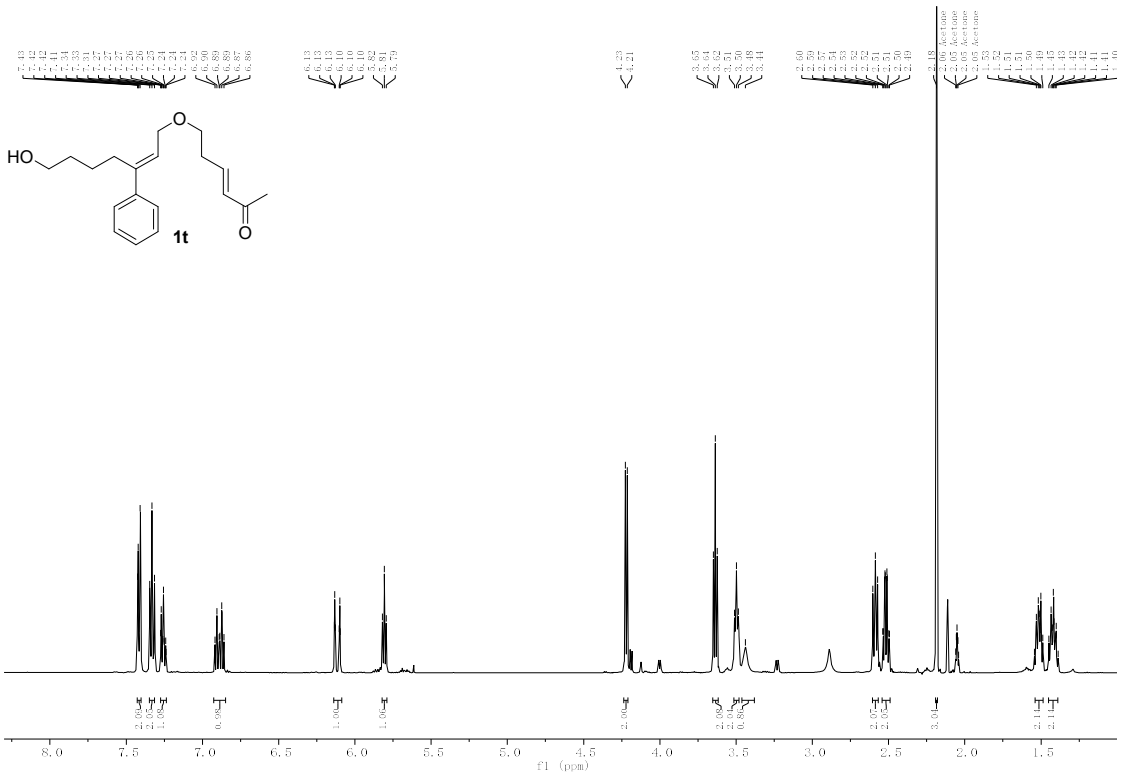
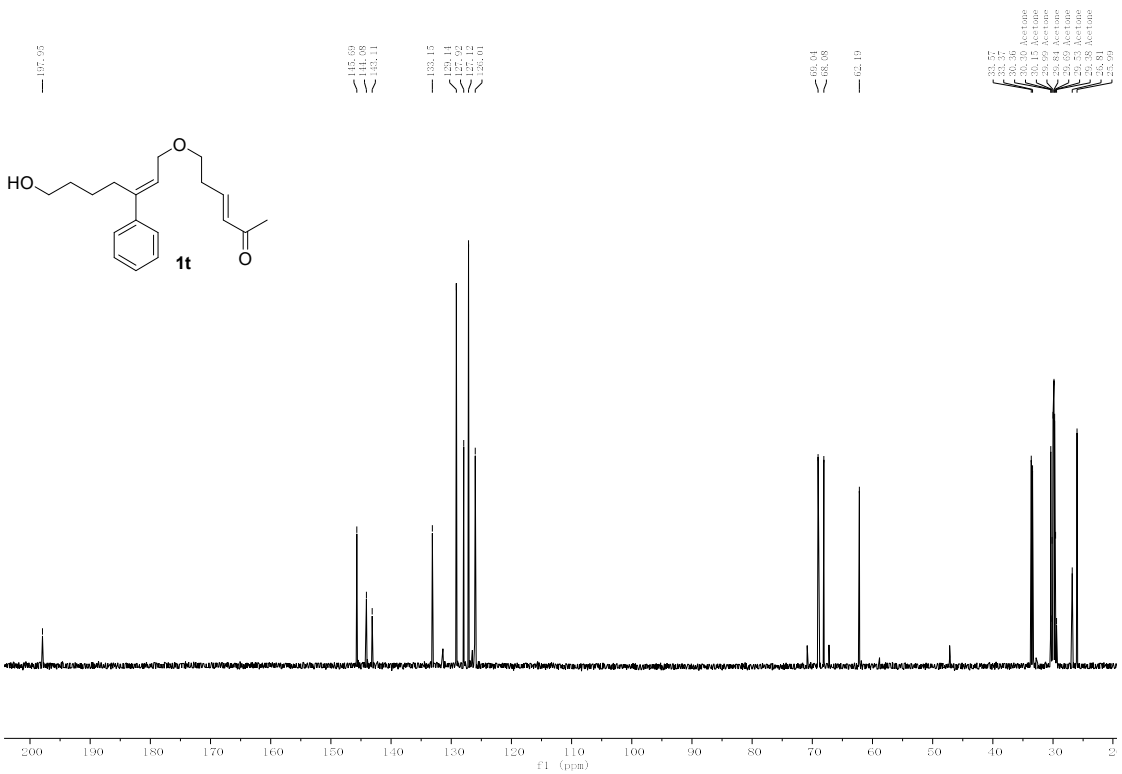
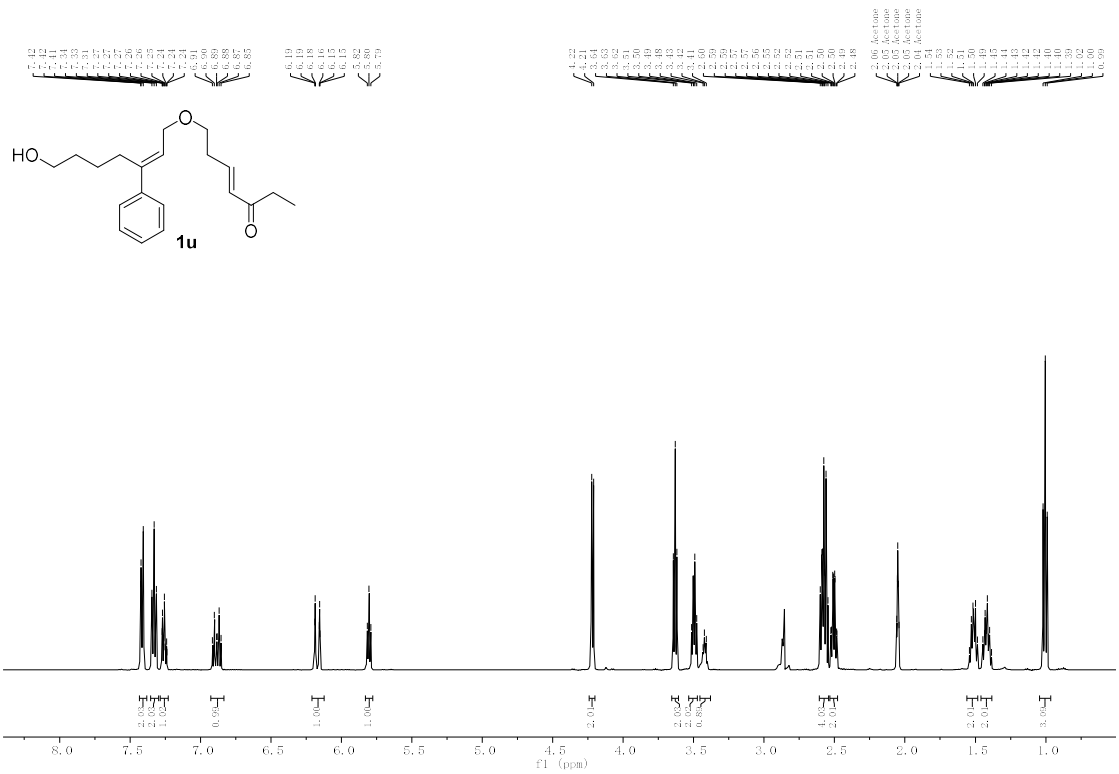
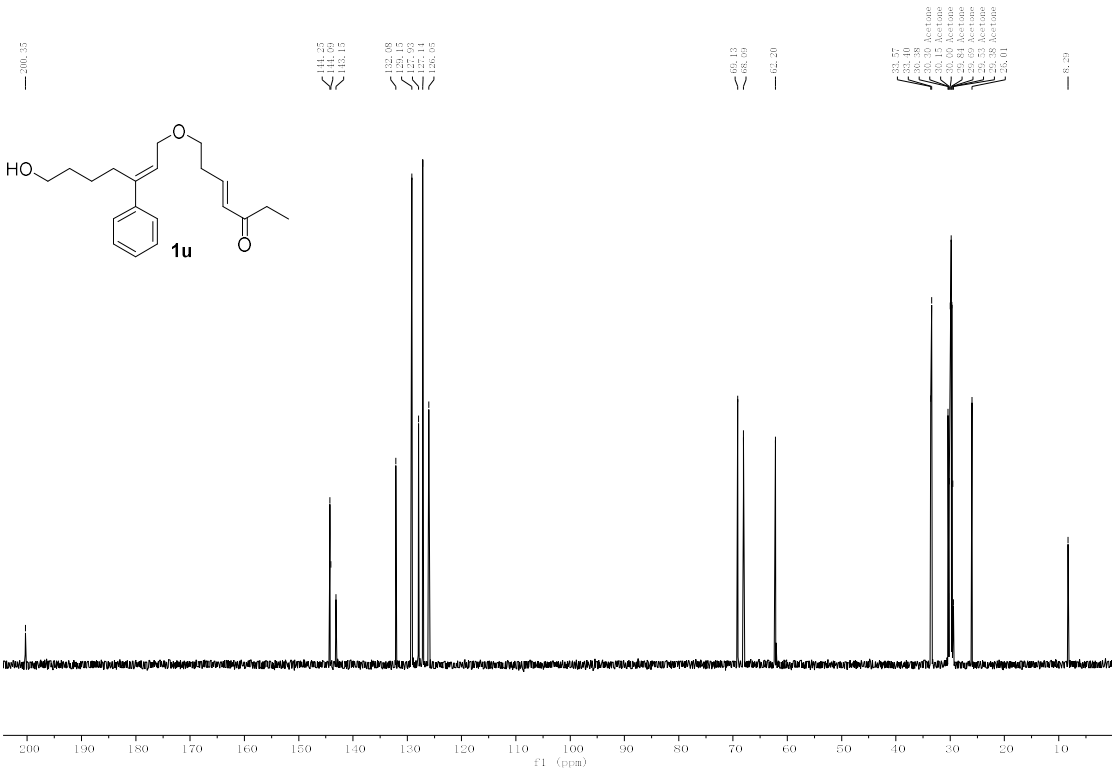
1.07
2.15
1.07
2.05
1.00
1.03
1.05
2.02
2.01
2.03
1.07
4.02
3.02
2.06
2.04

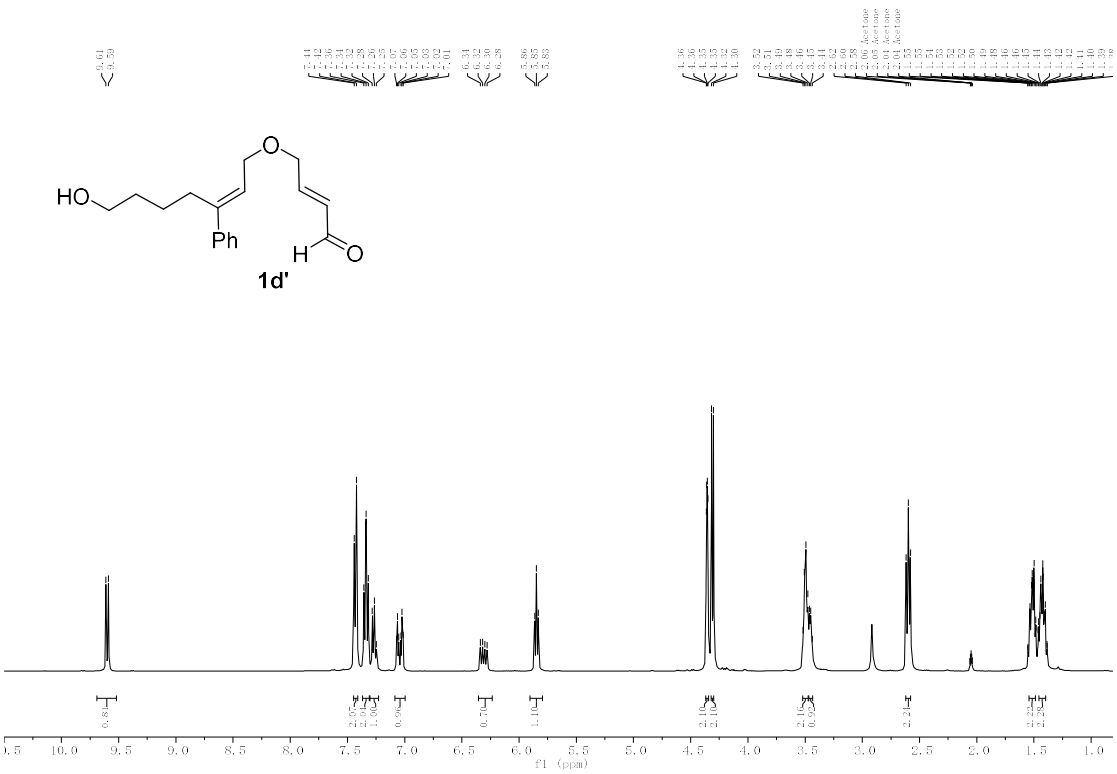

196.50
148.89
144.22
143.25
140.14
137.39
132.57
132.01
131.15
129.25
128.97
128.03
127.25
126.37
126.12
69.06
68.15
62.29
33.82
33.49
30.47
30.31
30.18
30.05
29.92
29.79
29.67
29.54
27.86
HO
O
O
Me
1s
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

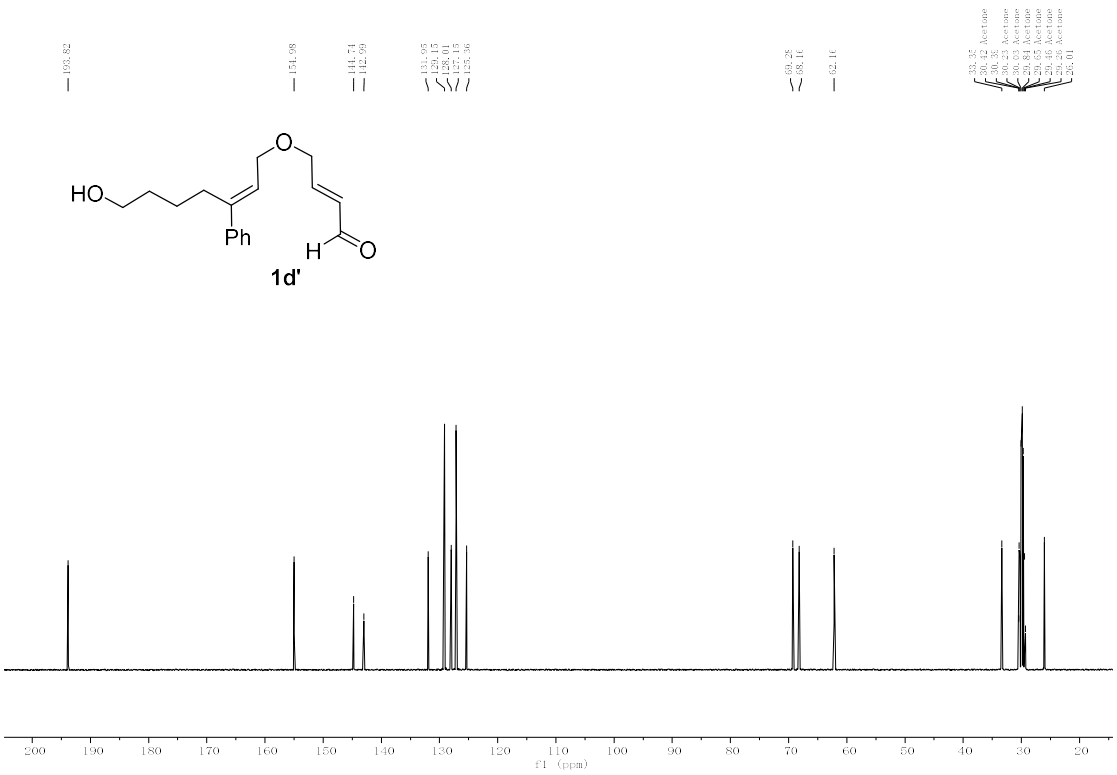

HO
O
O
1t
f1 (ppm)

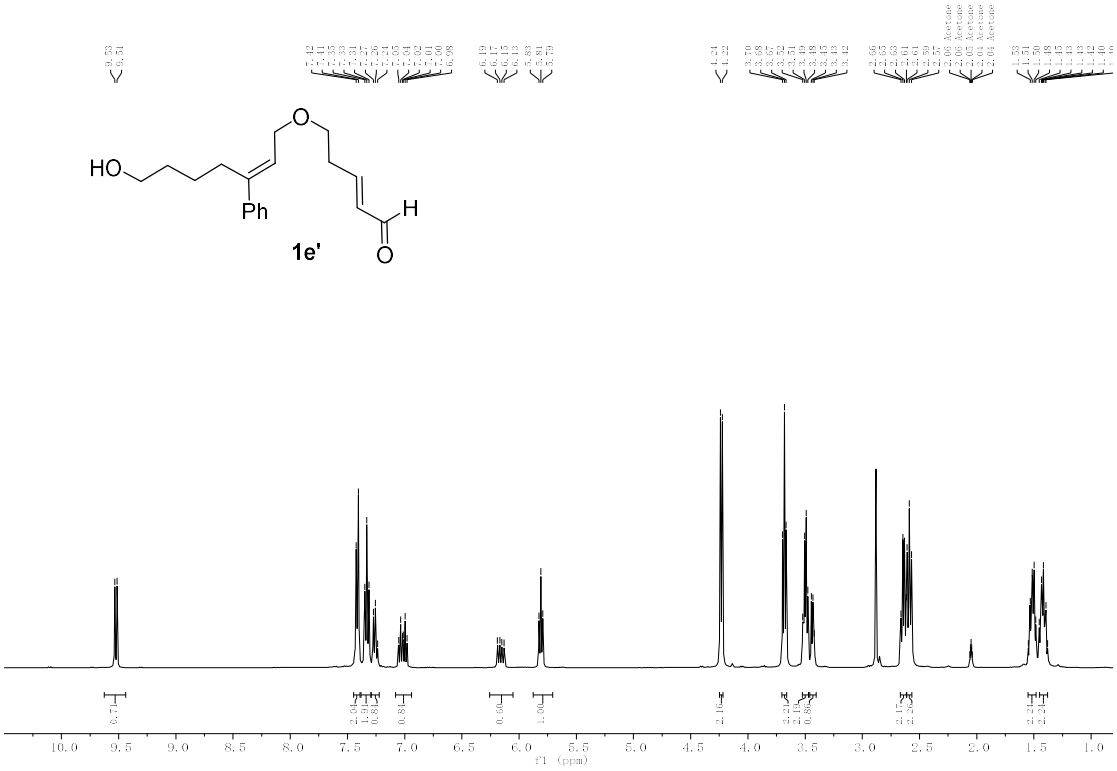

HO
O
O
1t
f1 (ppm)

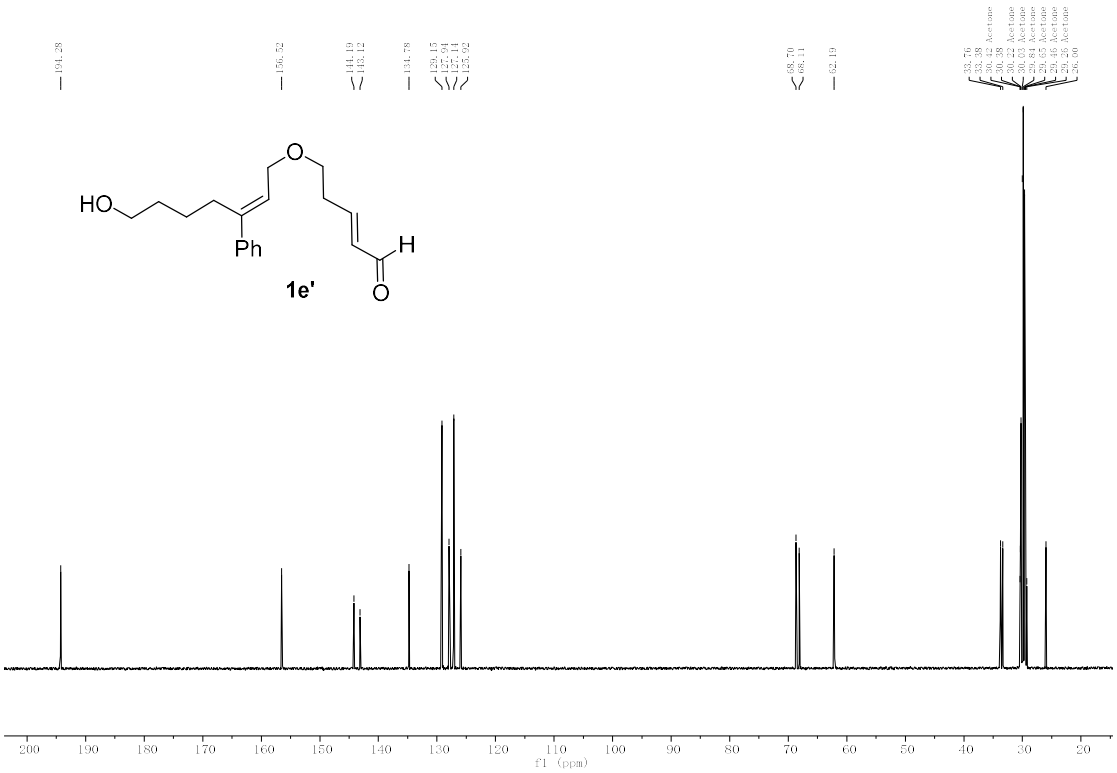

HO
O
O
1u
f1 (ppm)

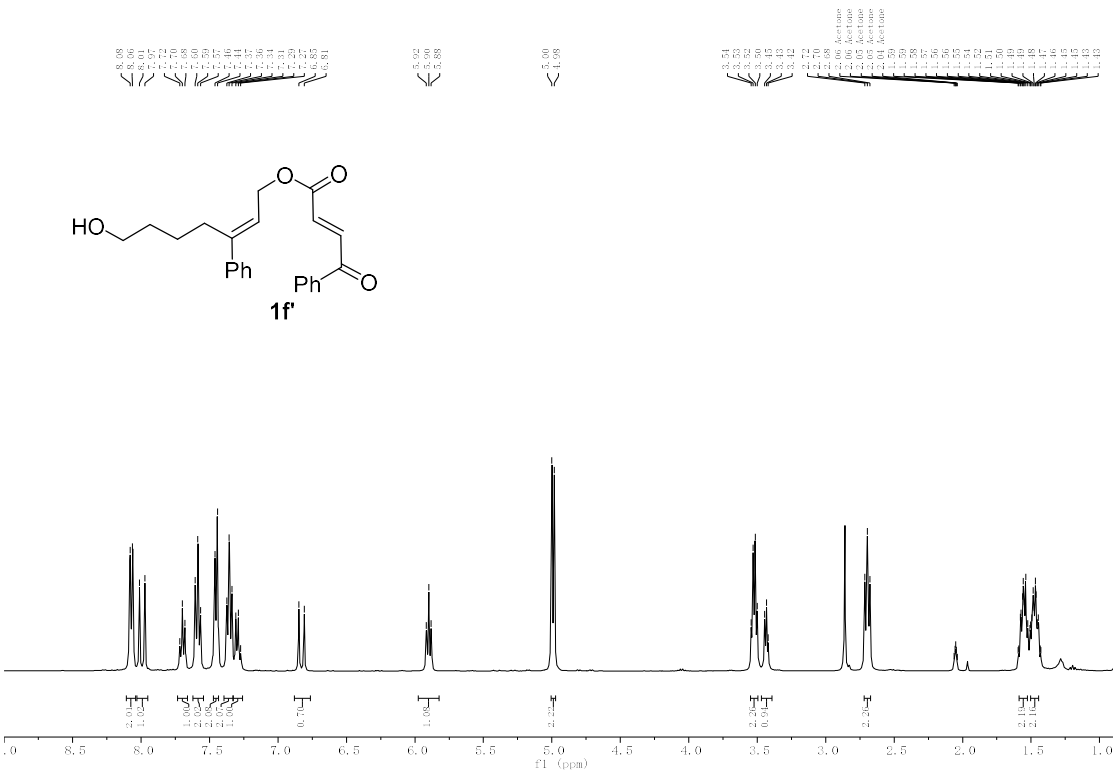

HO
O
O
1u
f1 (ppm)

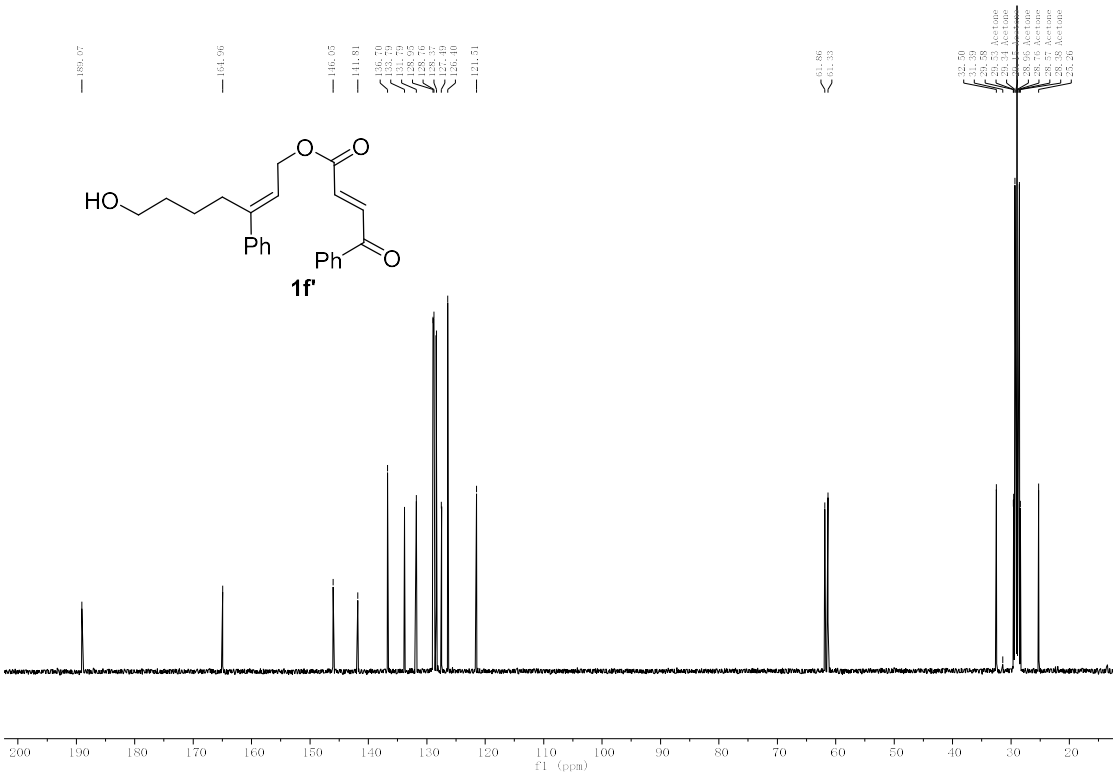

HO
Ph
O
H
O
1d'
f1 (ppm)

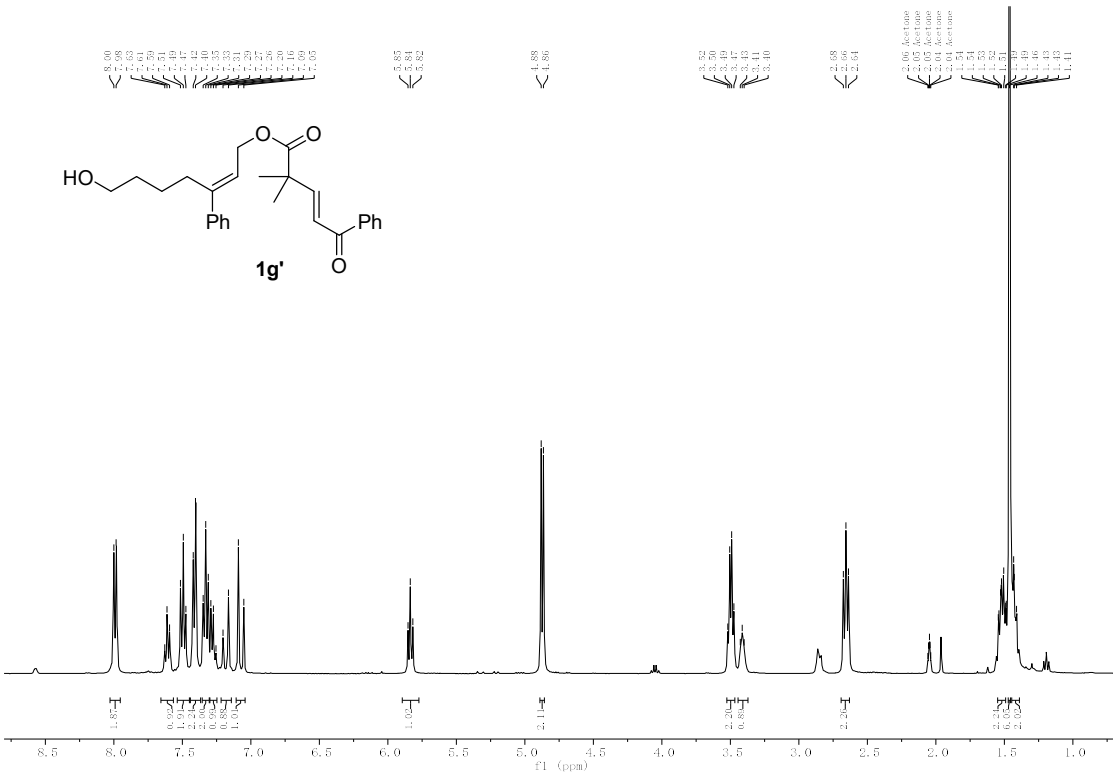

HO
Ph
O
H
O
1d'
f1 (ppm)

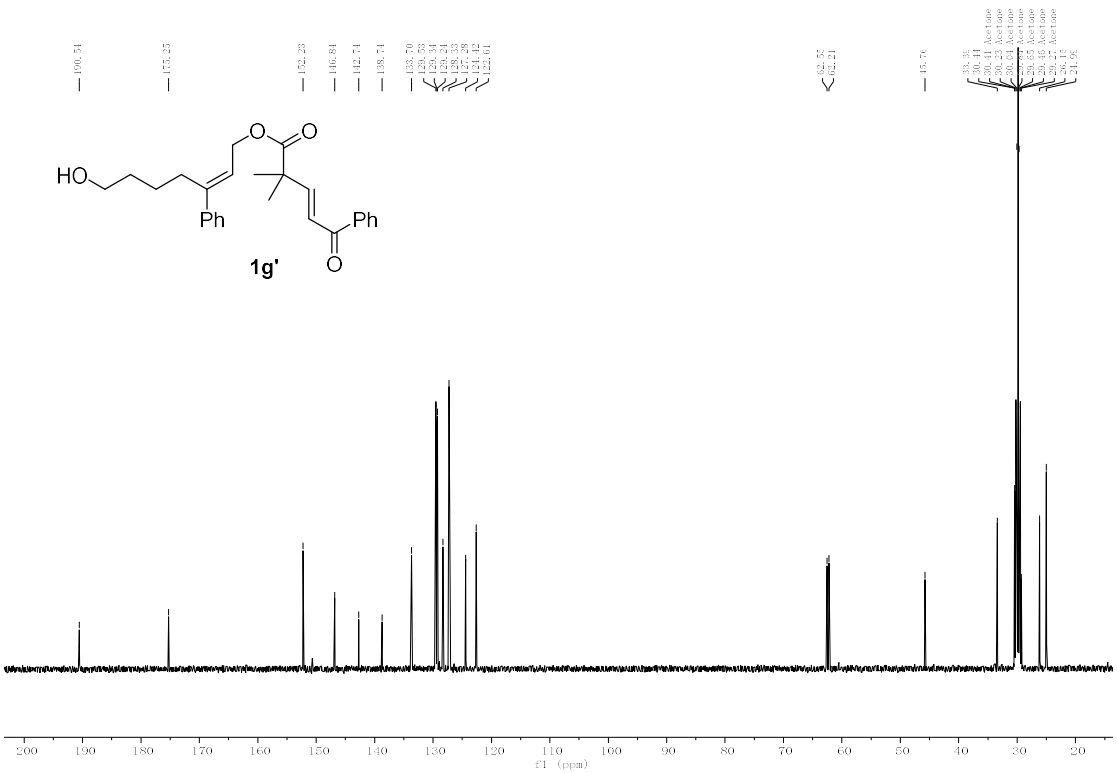

HO
O
Ph
H
O
1e'
f1 (ppm)

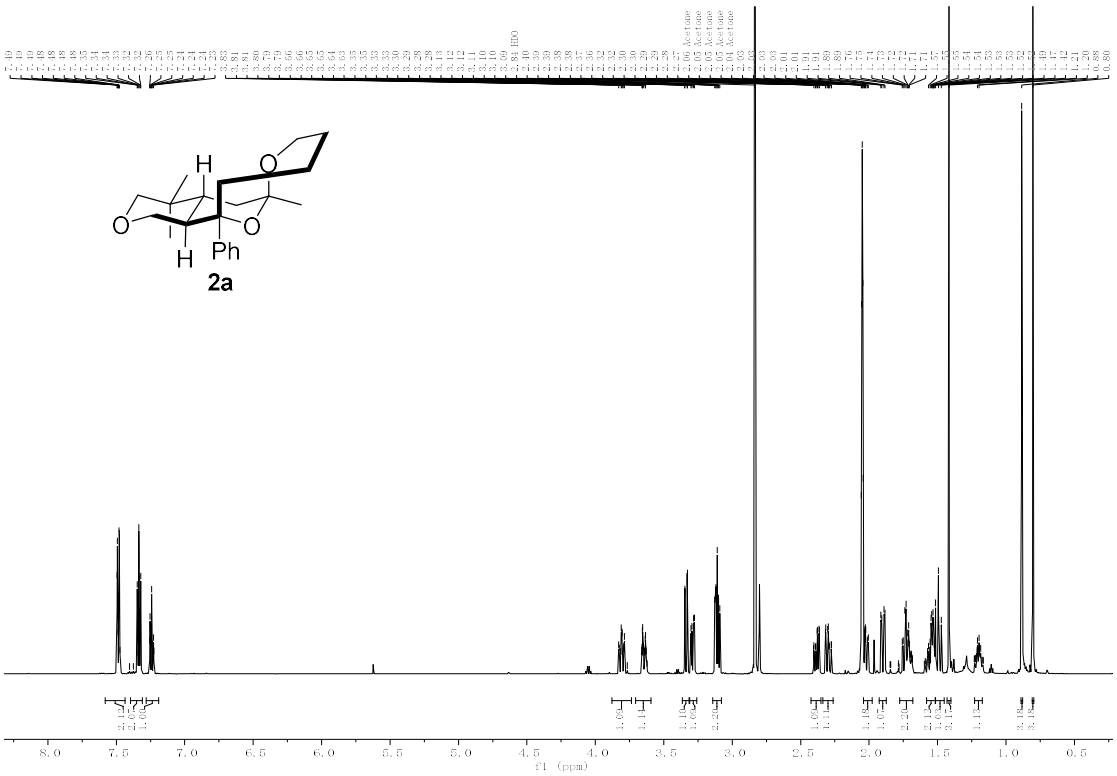

HO
O
Ph
H
O
1e'
f1 (ppm)

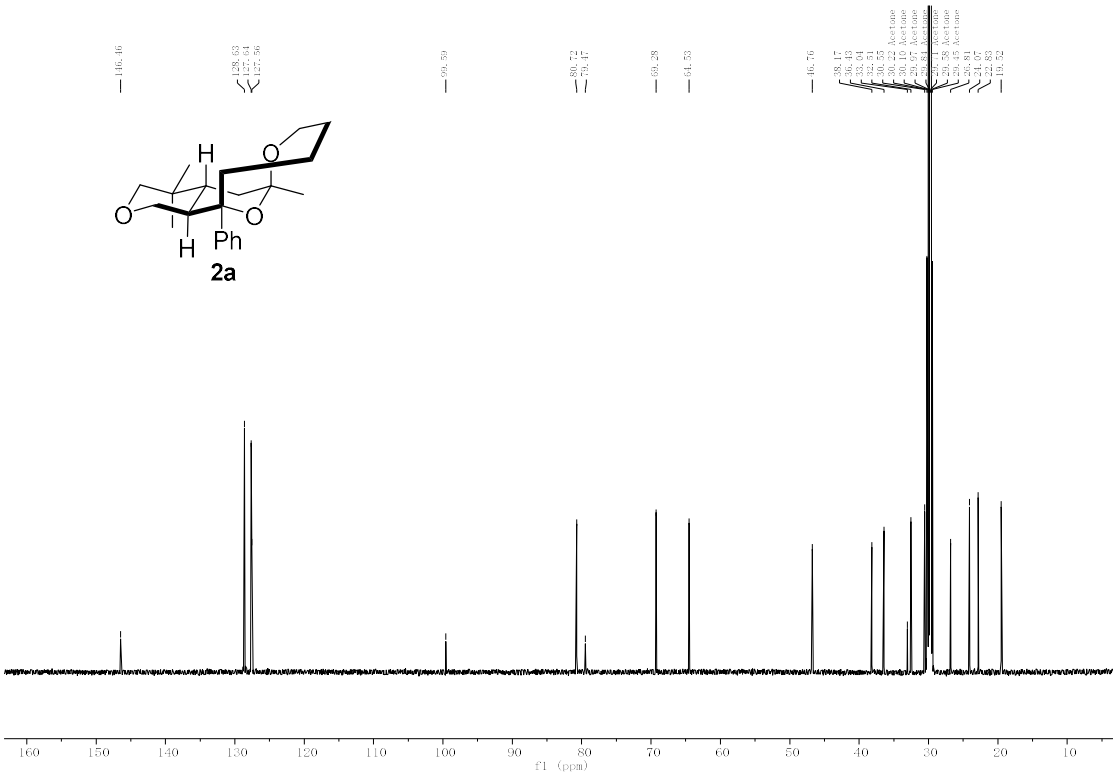

HO
Ph
Ph
O
O
O
O
1f'
f1 (ppm)

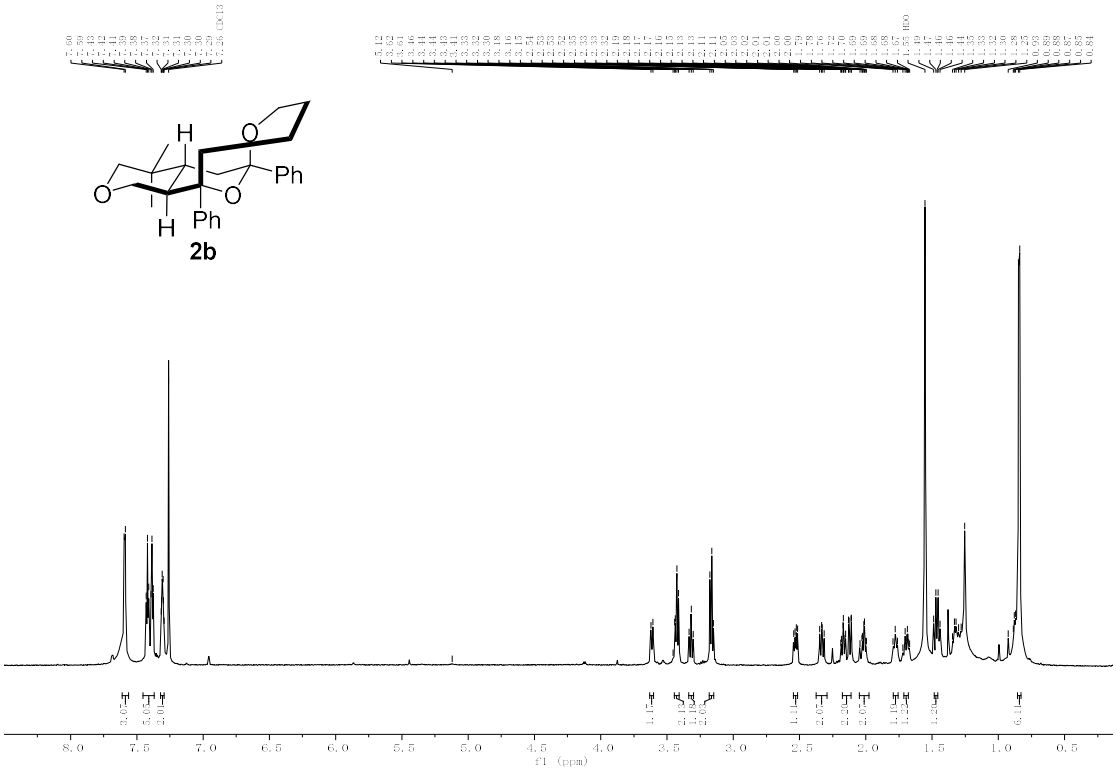

HO
Ph
Ph
O
O
O
O
1f'
f1 (ppm)

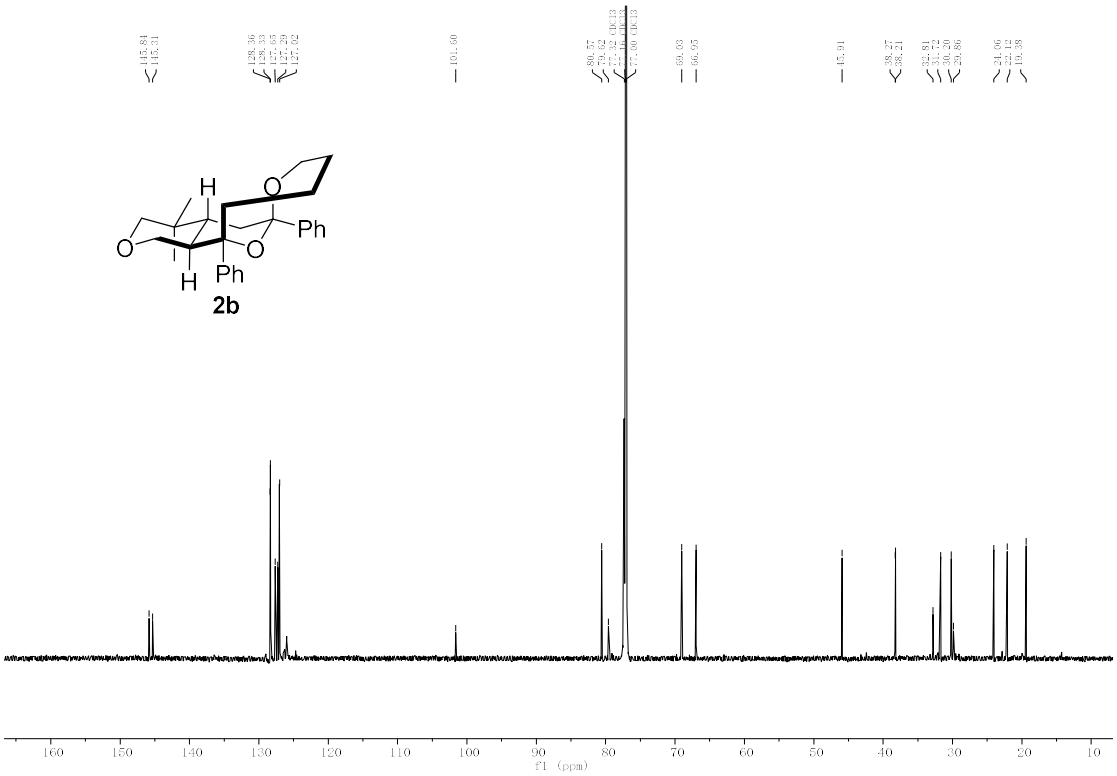

HO
O
O
Ph
Ph
O
1g'
f1 (ppm)

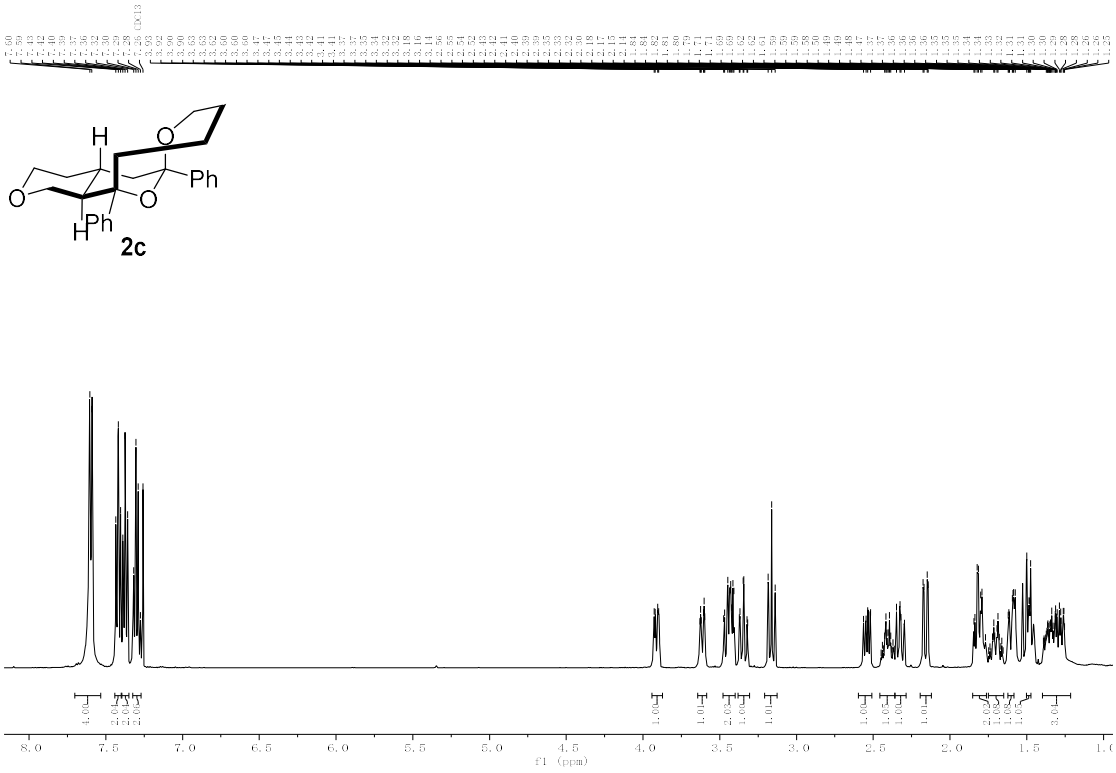

HO
O
O
Ph
Ph
O
1g'
f1 (ppm)

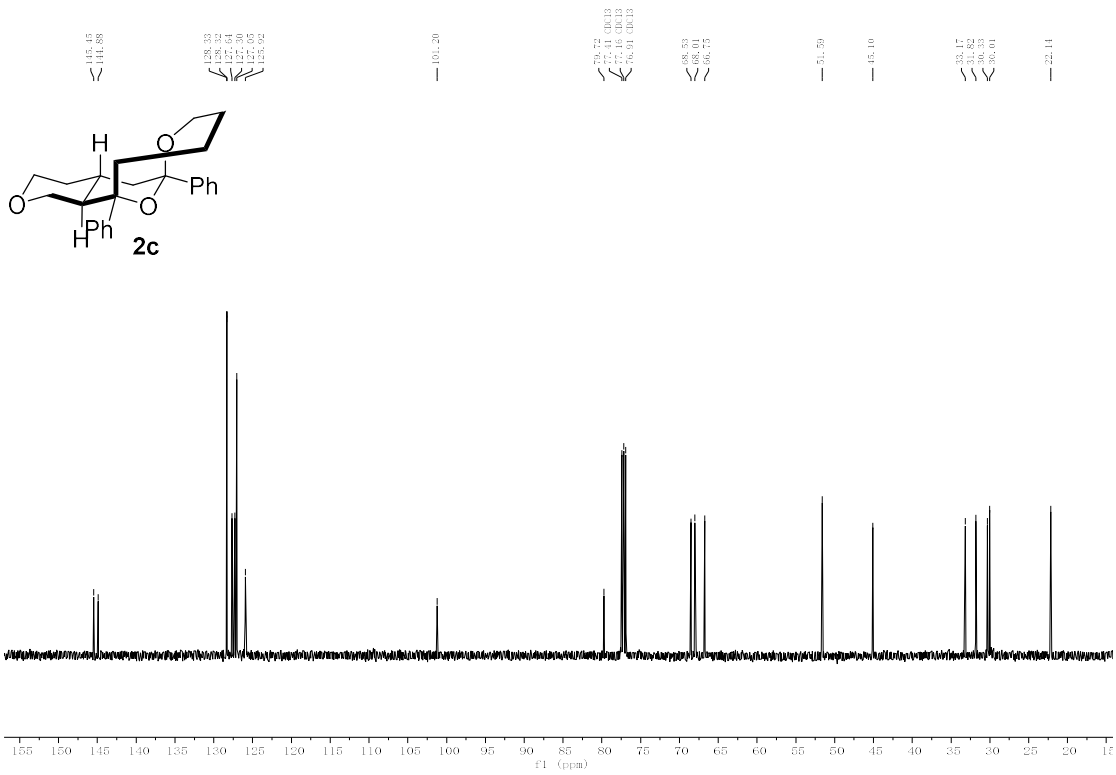

H
O
O
O
H
Ph
2a
f1 (ppm)

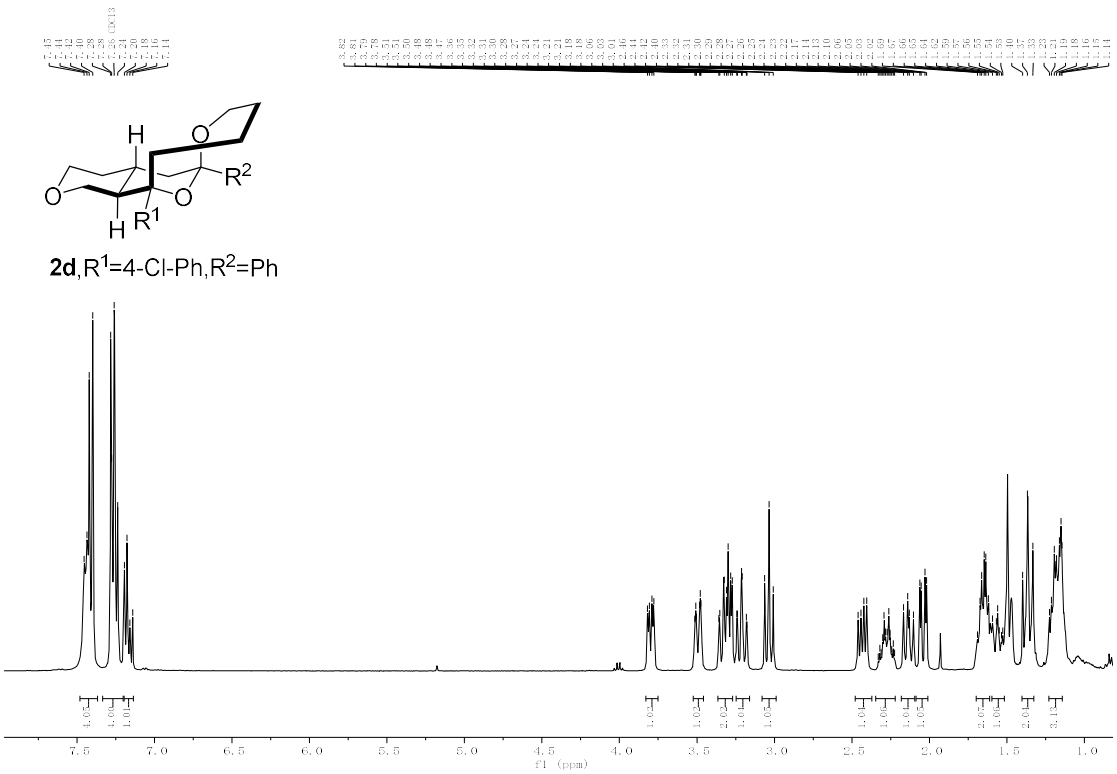

H
O
O
O
H
Ph
2a
f1 (ppm)

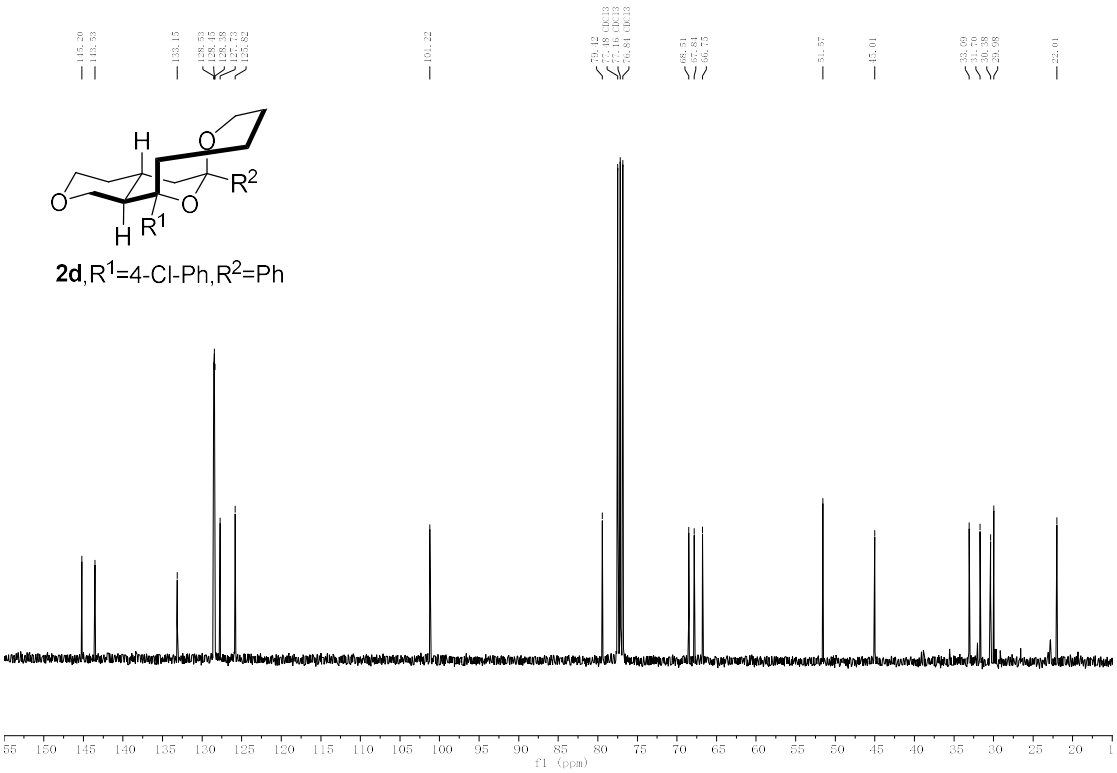

H
O
Ph
O
O
H
Ph
2b
f1 (ppm)

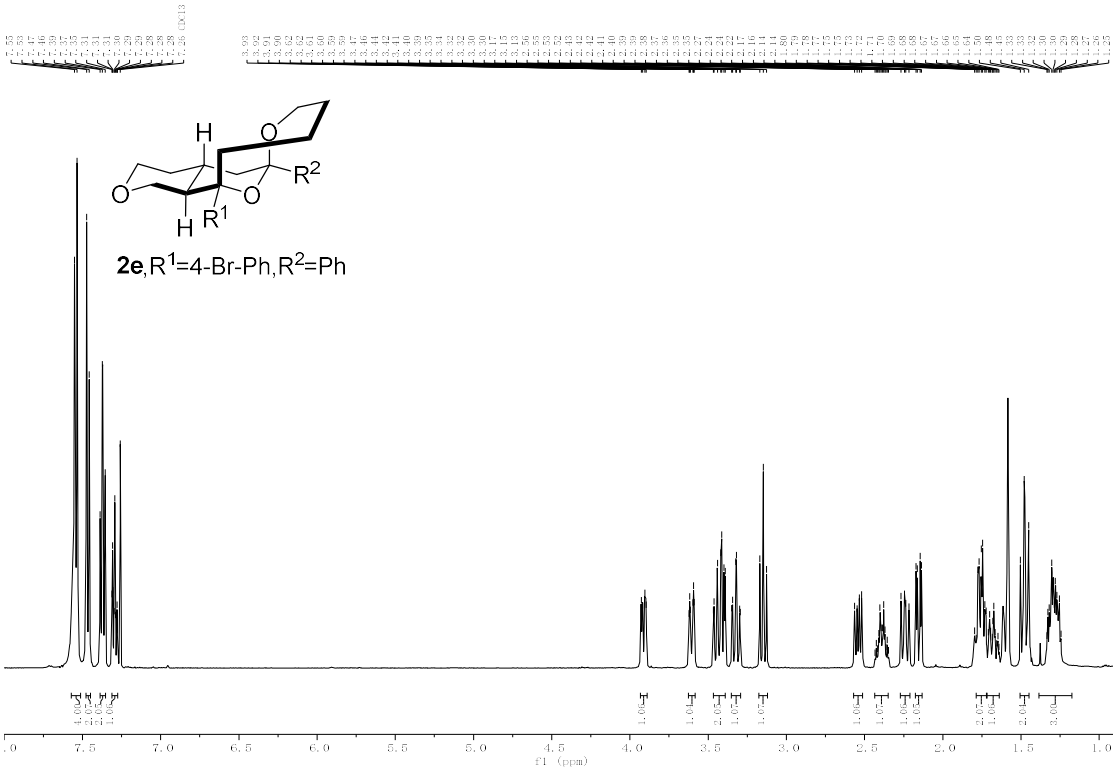

H
O
Ph
O
O
H
Ph
2b
f1 (ppm)

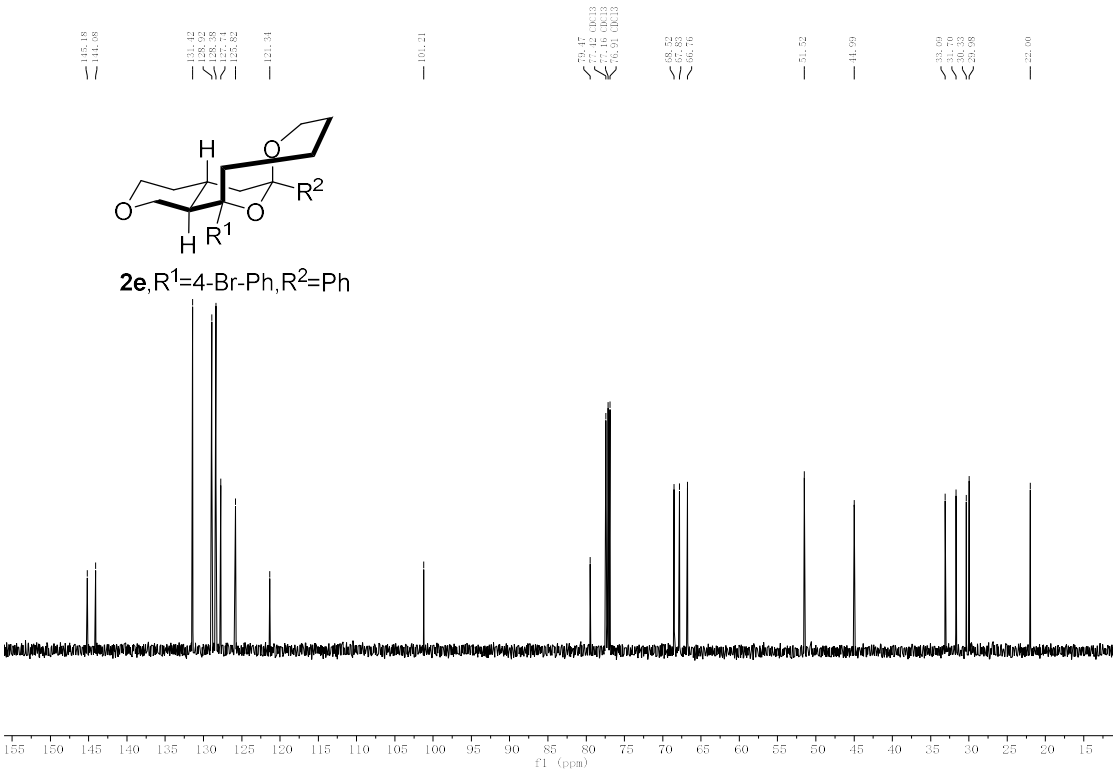

2c
f1 (ppm)

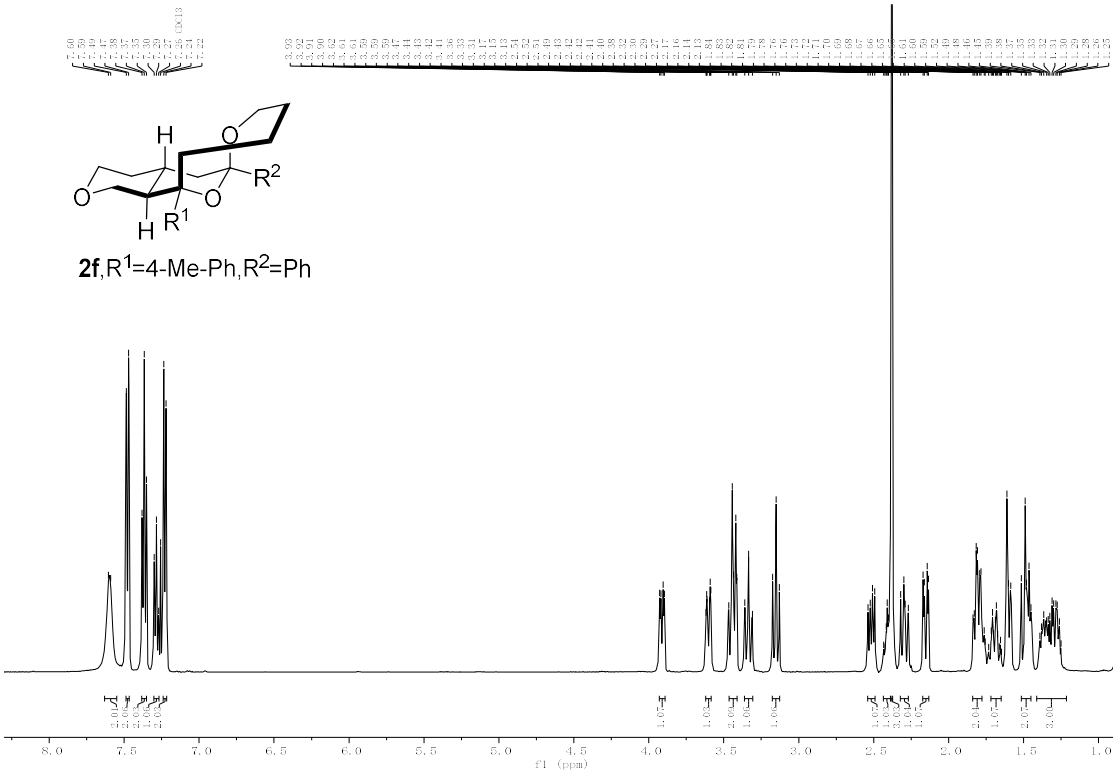

2c
f1 (ppm)

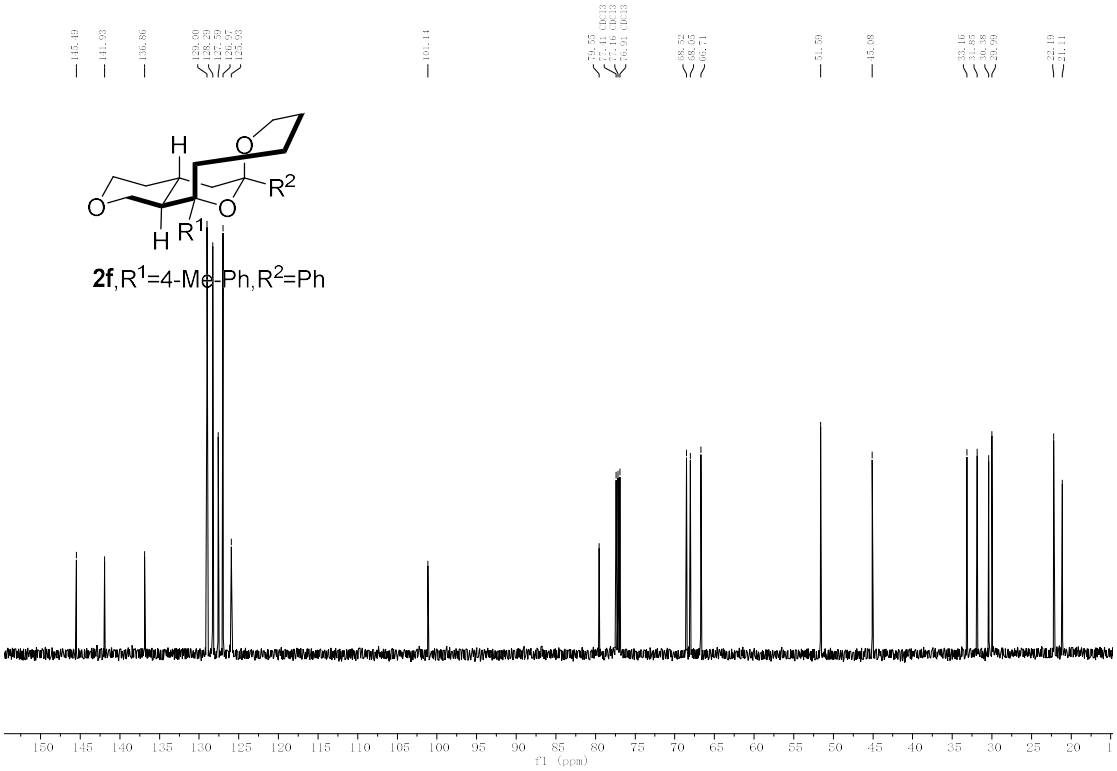

H
O
R2
O
O
H
R1
2d,R1=4-Cl-Ph,R2=Ph
f1 (ppm)

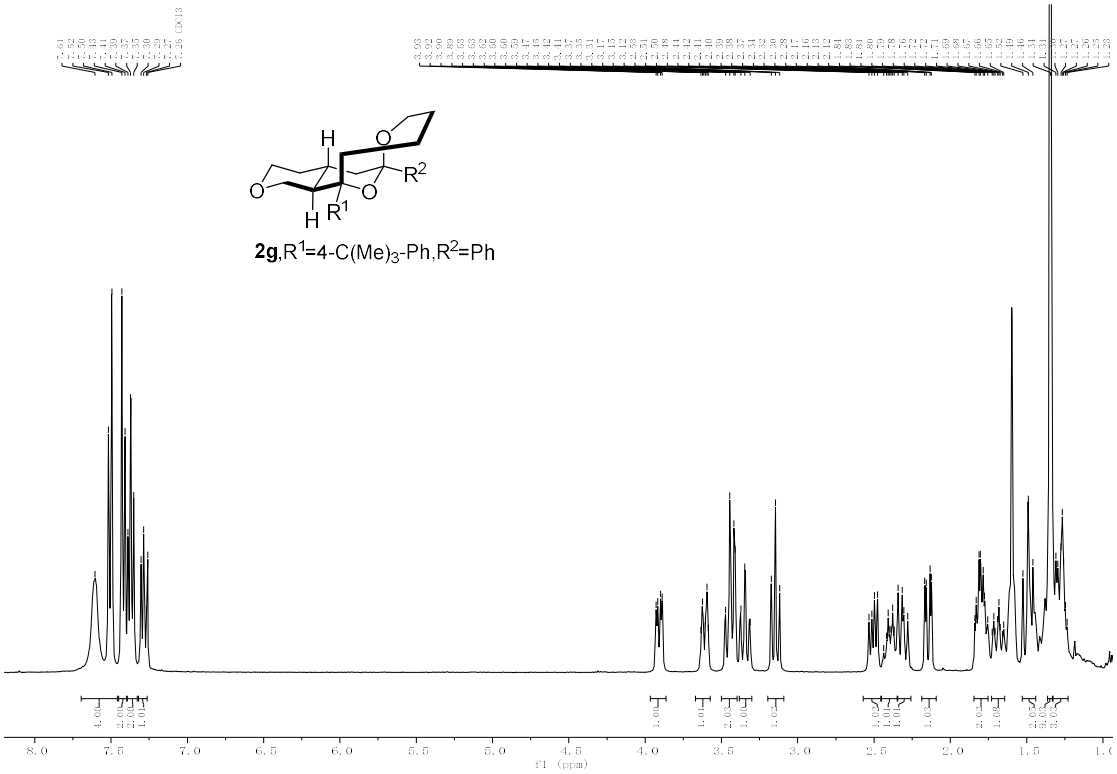

H
O
R2
O
O
H
R1
2d,R1=4-Cl-Ph,R2=Ph
f1 (ppm)

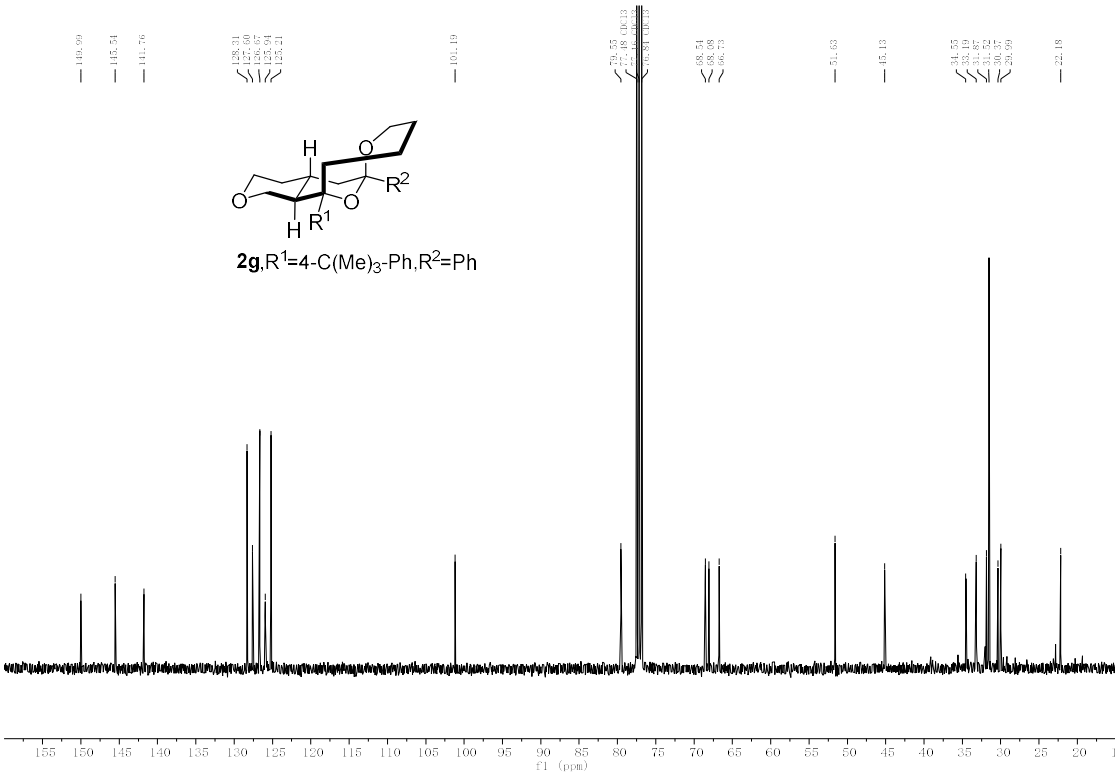

H
O
R2
O
O
H
R1
2e,R1=4-Br-Ph,R2=Ph
f1 (ppm)

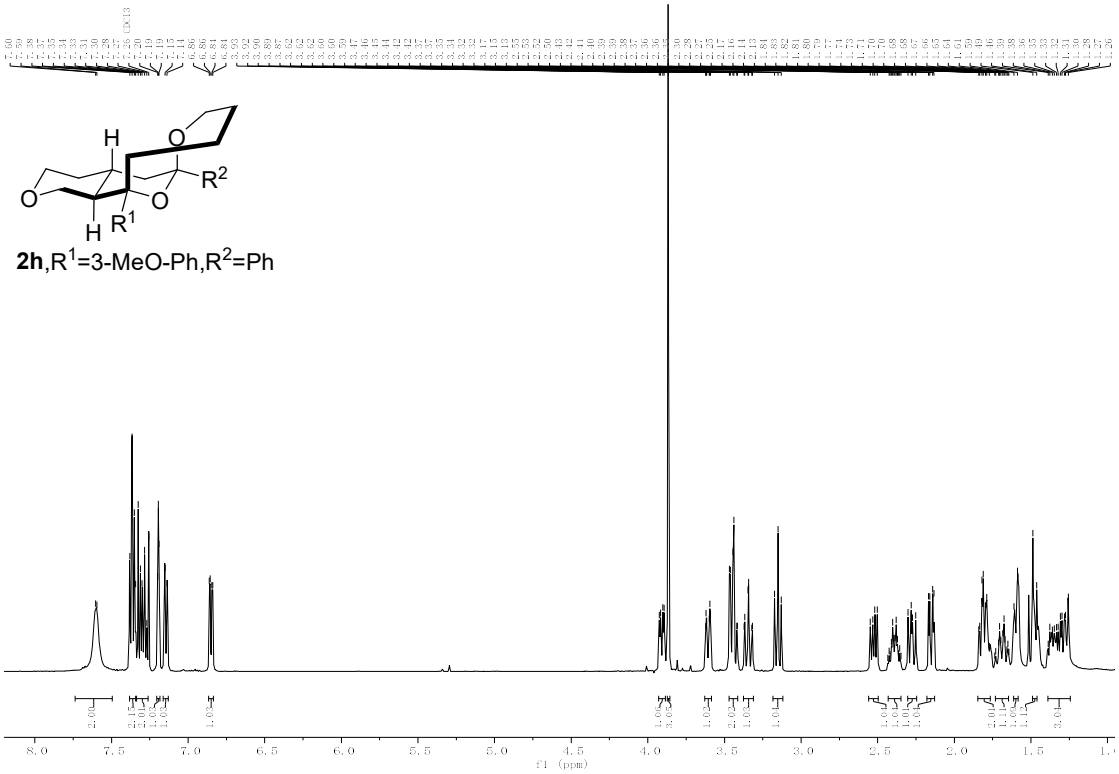

H
O
R2
O
O
H
R1
2e,R1=4-Br-Ph,R2=Ph
f1 (ppm)


H
O
R2
O
O
H
R1
2f,R1=4-Me-Ph,R2=Ph
f1 (ppm)

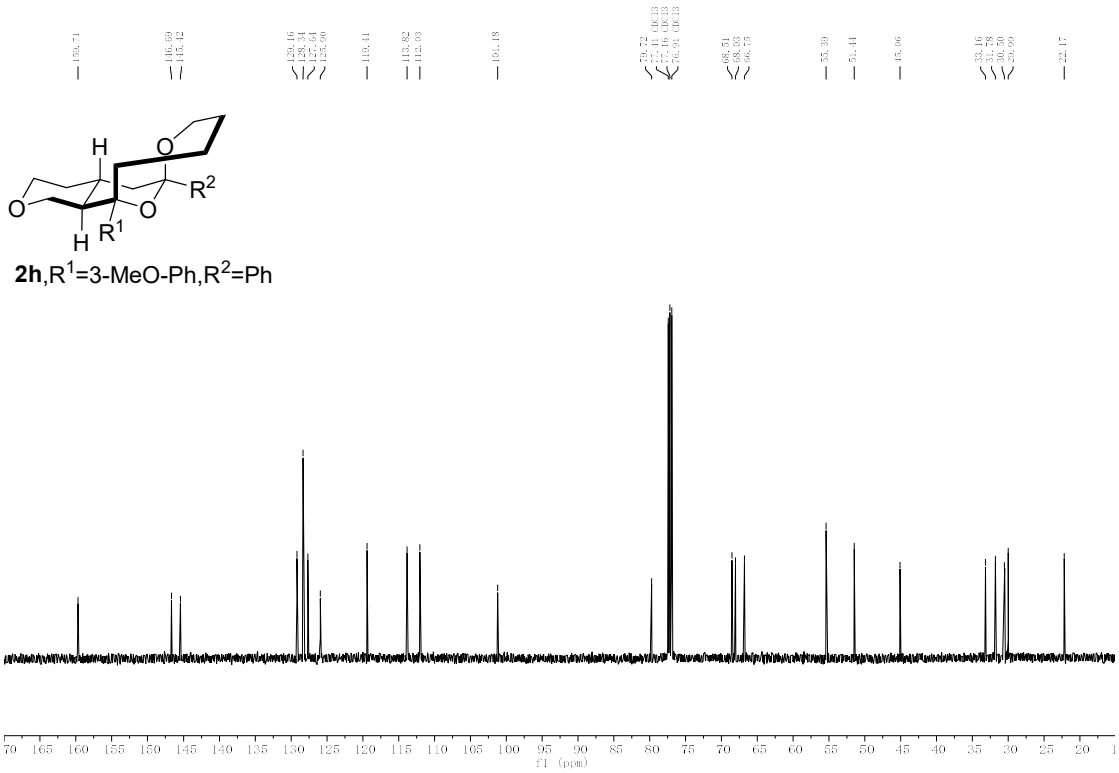

H
O
R2
O
O
H
R1
2f,R1=4-Me-Ph,R2=Ph
f1 (ppm)


H
O
R2
O
O
H
R1
2g,R1=4-C(Me)3-Ph,R2=Ph
f1 (ppm)

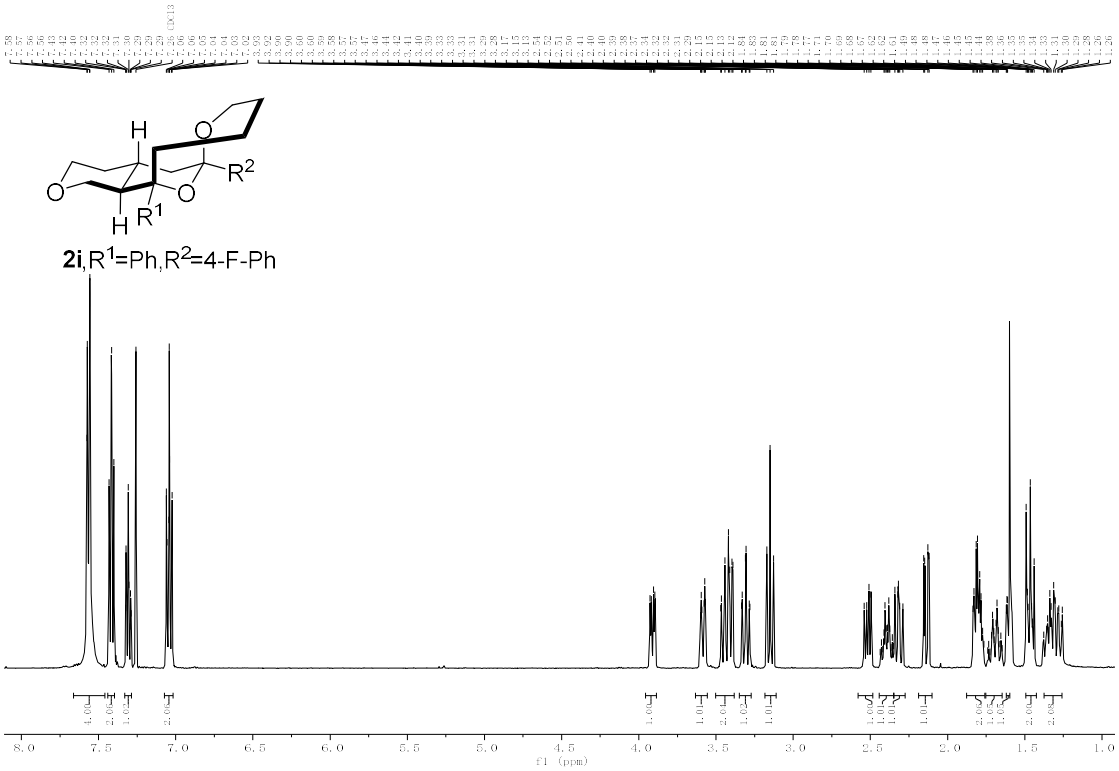

H
O
R2
O
O
H
R1
2g,R1=4-C(Me)3-Ph,R2=Ph
f1 (ppm)

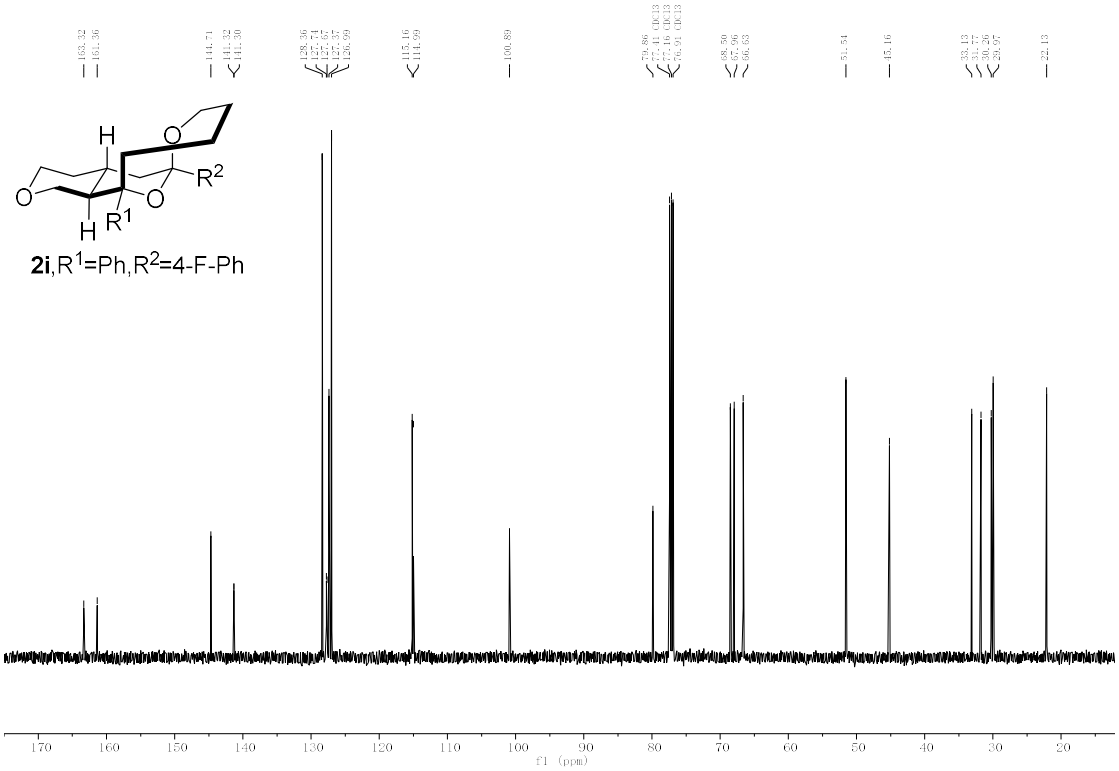


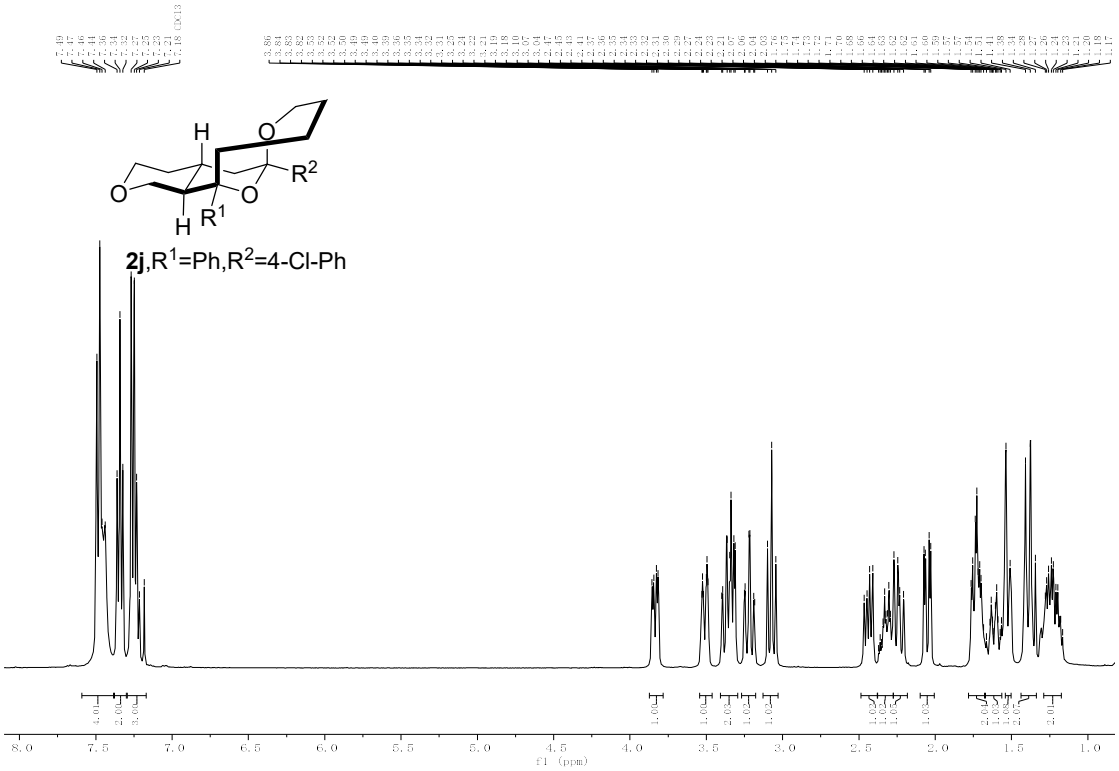
2h,R^1=3-MeO-Ph,R^2=Ph

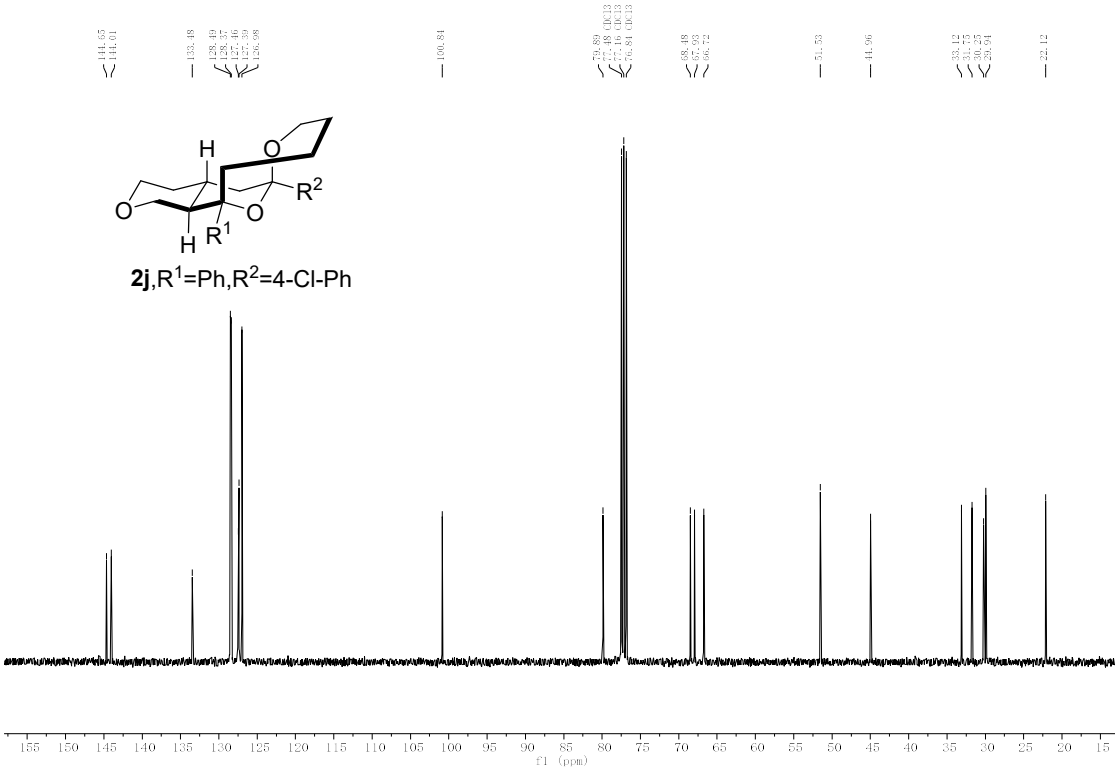


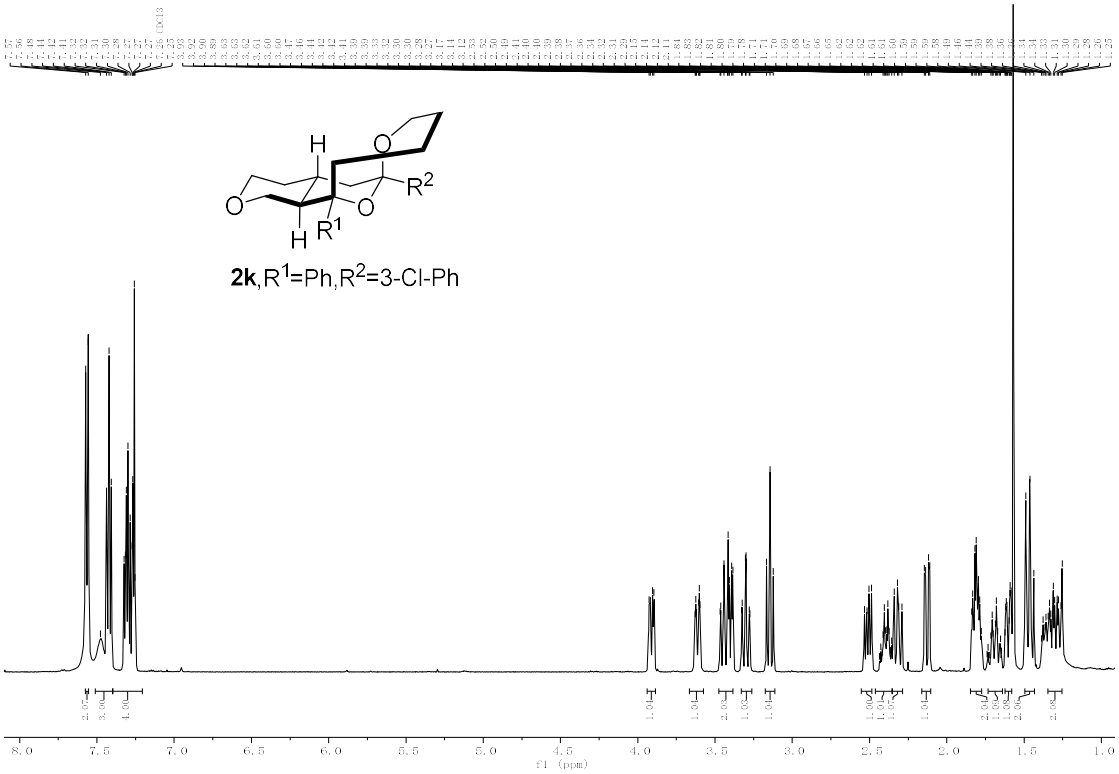
2h,R^1=3-MeO-Ph,R^2=Ph

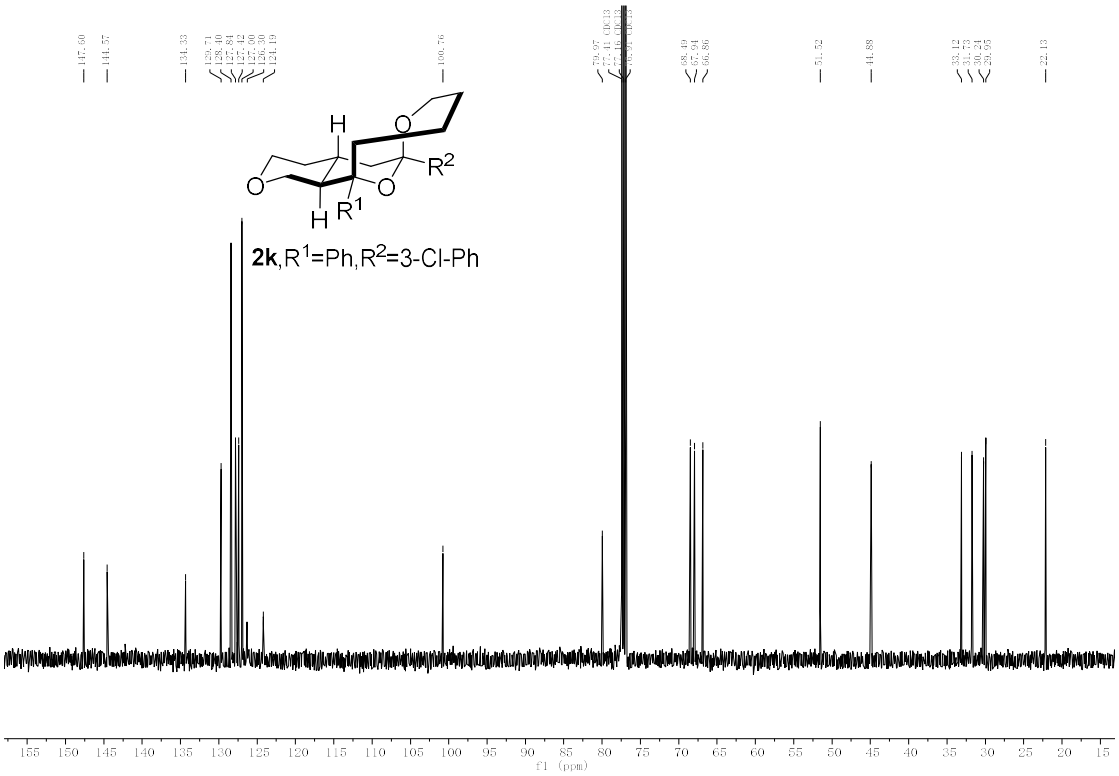

2i,R1=Ph,R2=4-F-Ph
f1 (ppm)

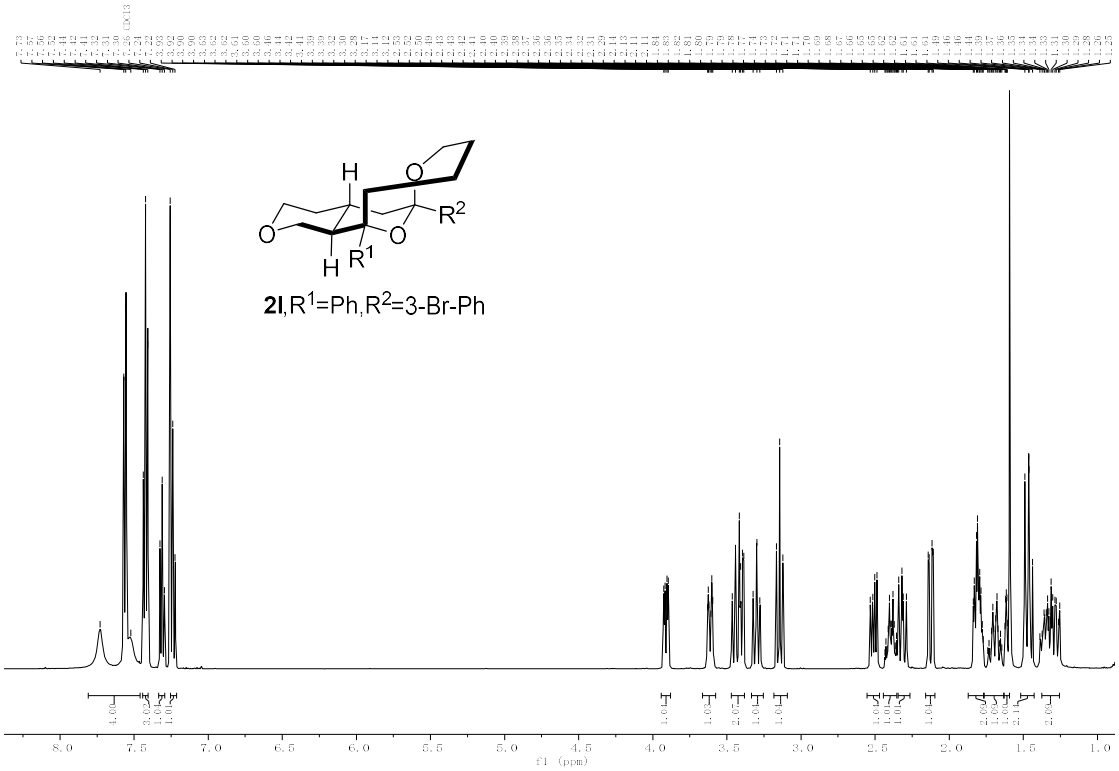

2i,R1=Ph,R2=4-F-Ph
f1 (ppm)

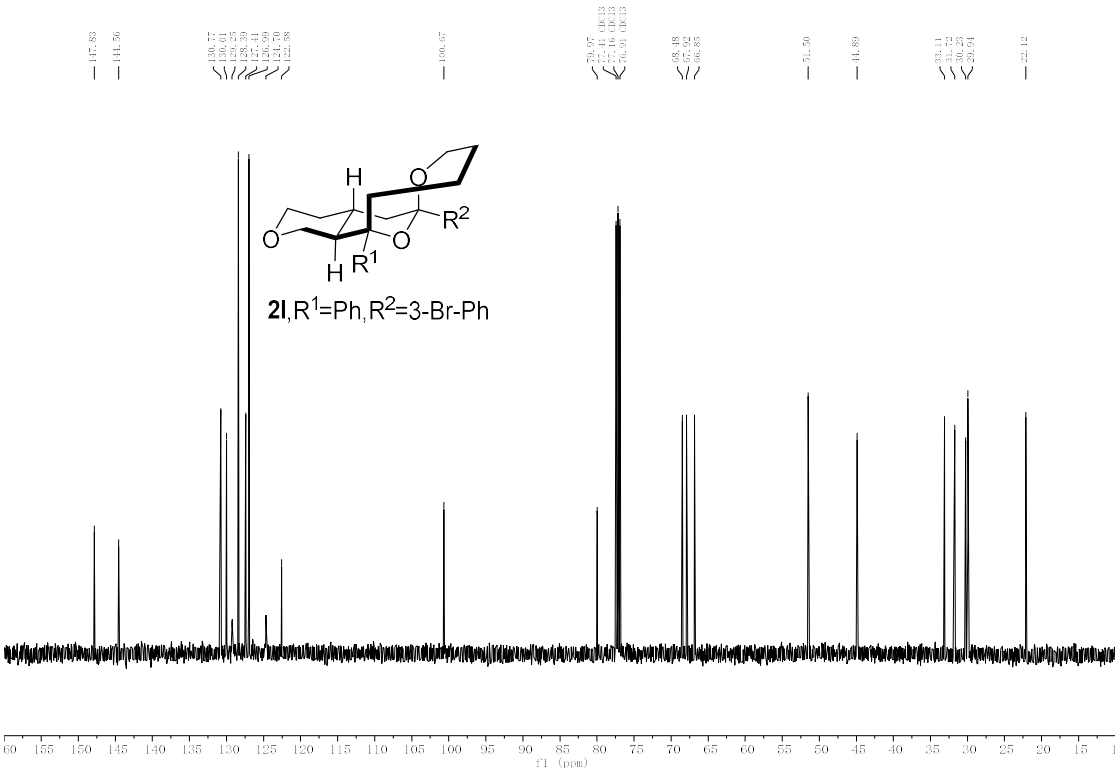

H
O
R2
O
O
H
R1
2j,R1=Ph,R2=4-Cl-Ph
f1 (ppm)

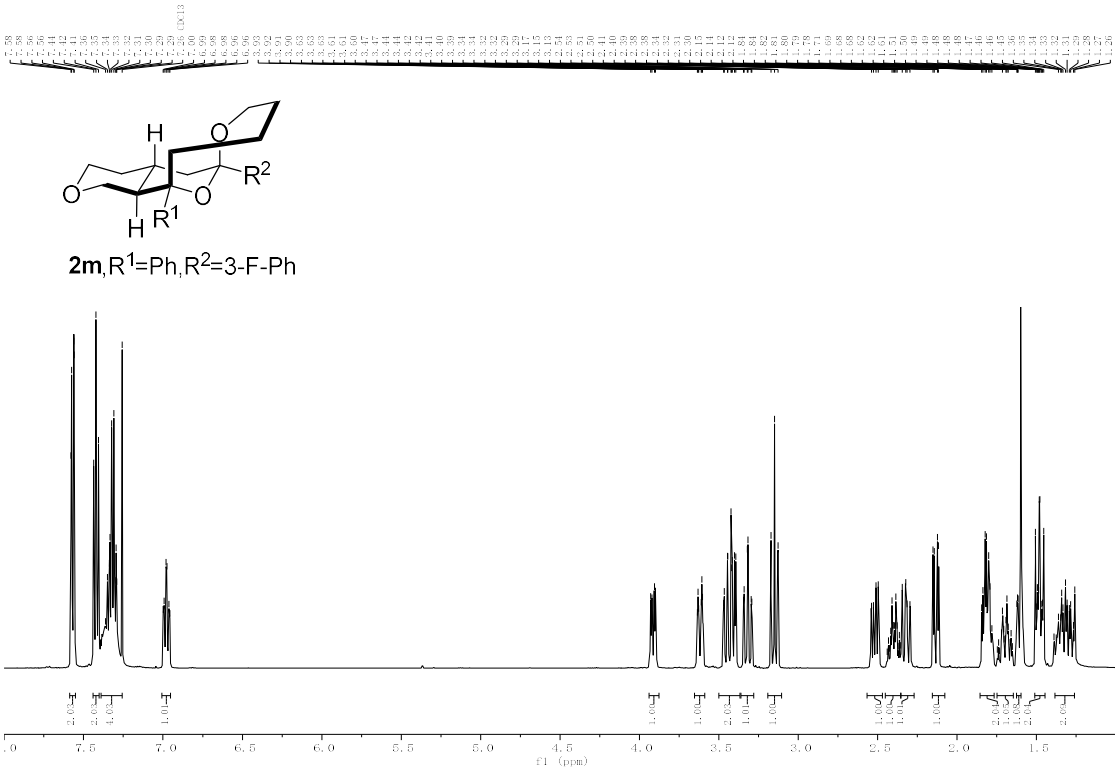

H
O
R2
O
O
H
R1
2j,R1=Ph,R2=4-Cl-Ph
f1 (ppm)

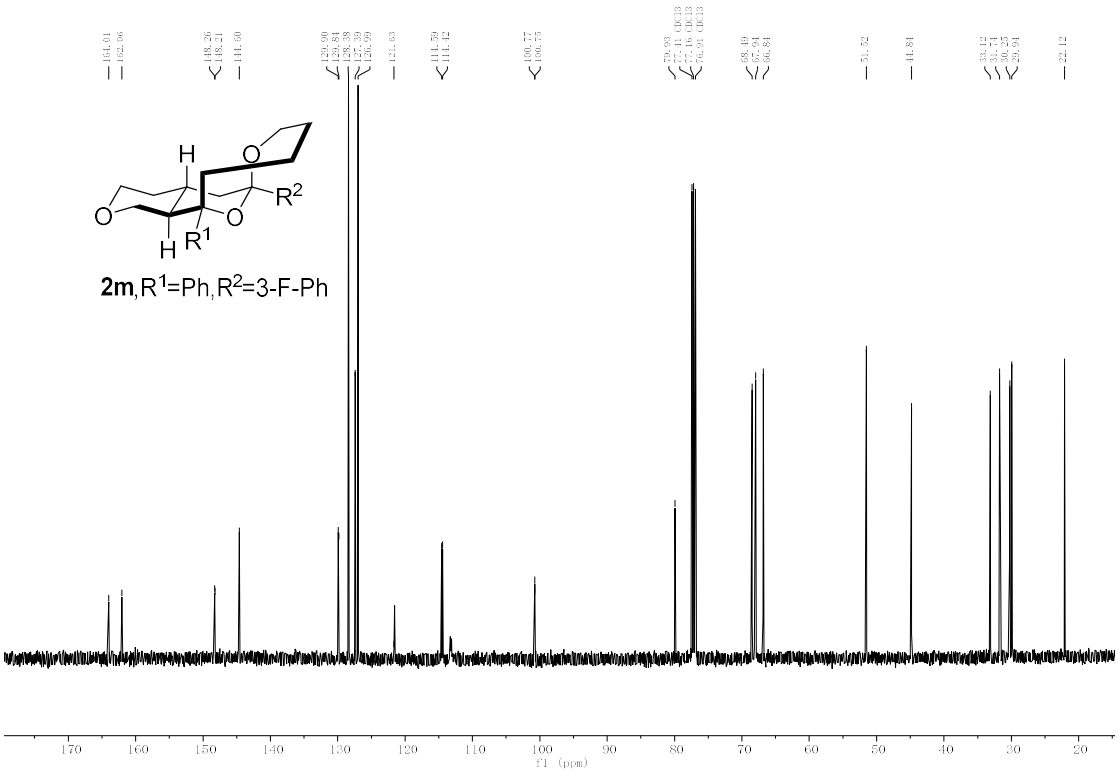

H
O
R2
O
O
H
R1
2k,R1=Ph,R2=3-Cl-Ph
f1 (ppm)

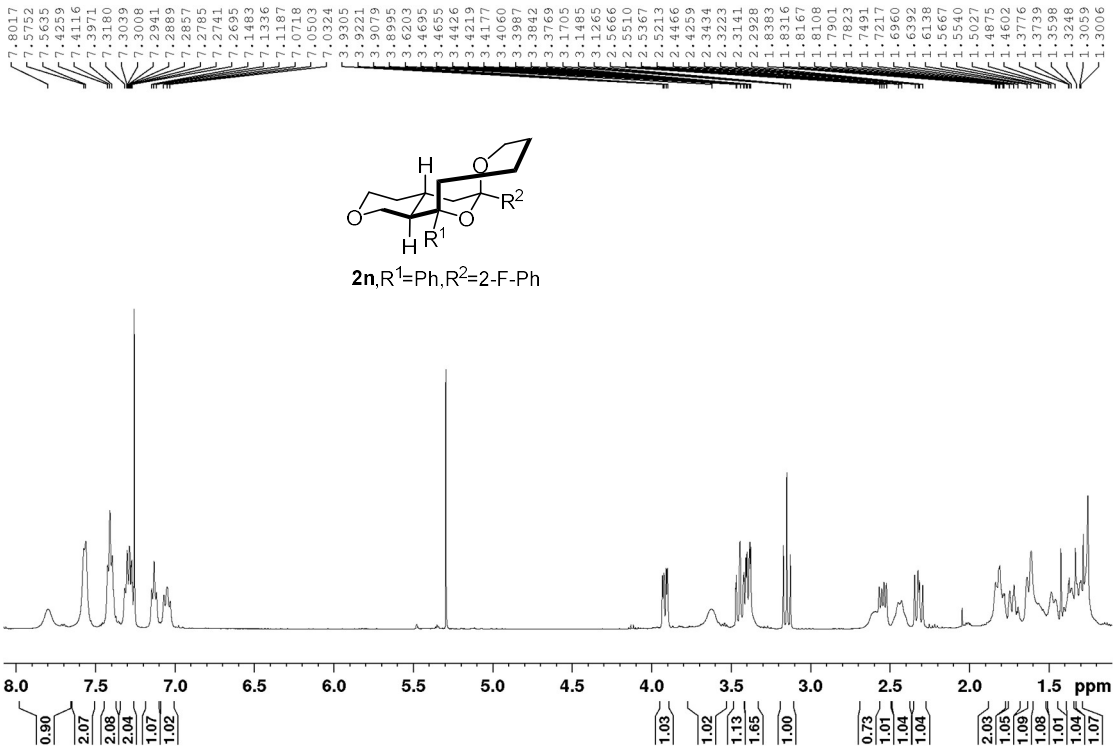

H
O
R2
O
O
H
R1
2k,R1=Ph,R2=3-Cl-Ph
f1 (ppm)

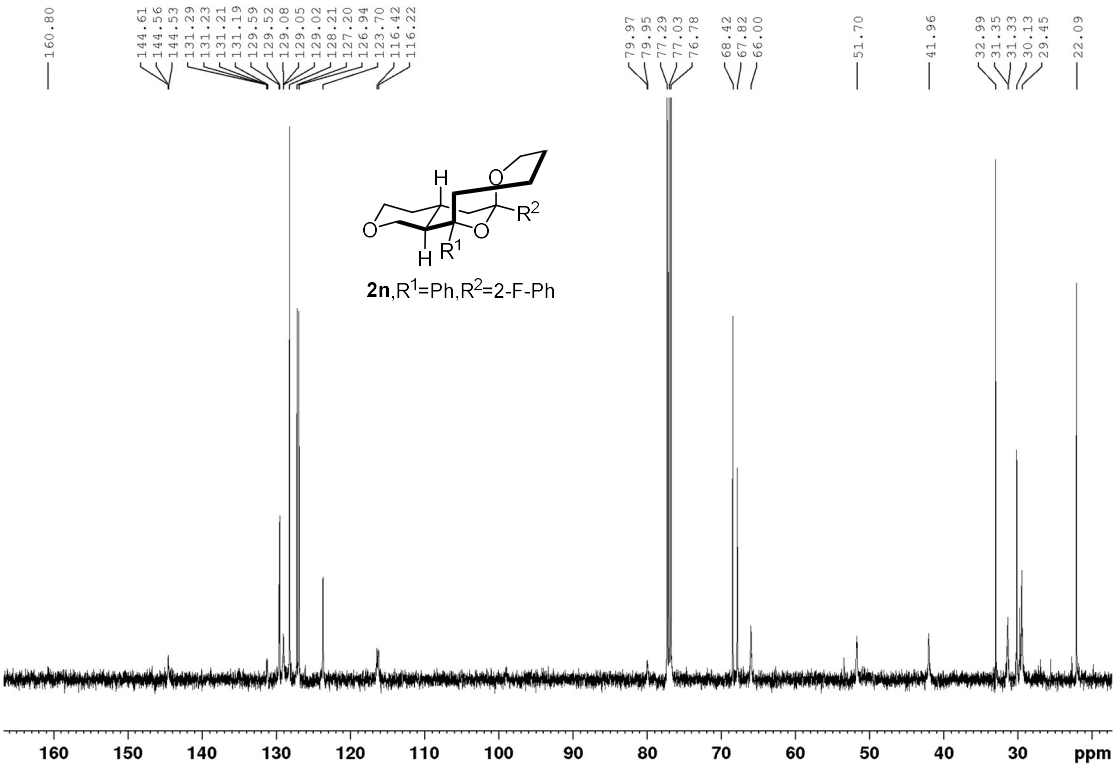

2l,R1=Ph,R2=3-Br-Ph
f1 (ppm)

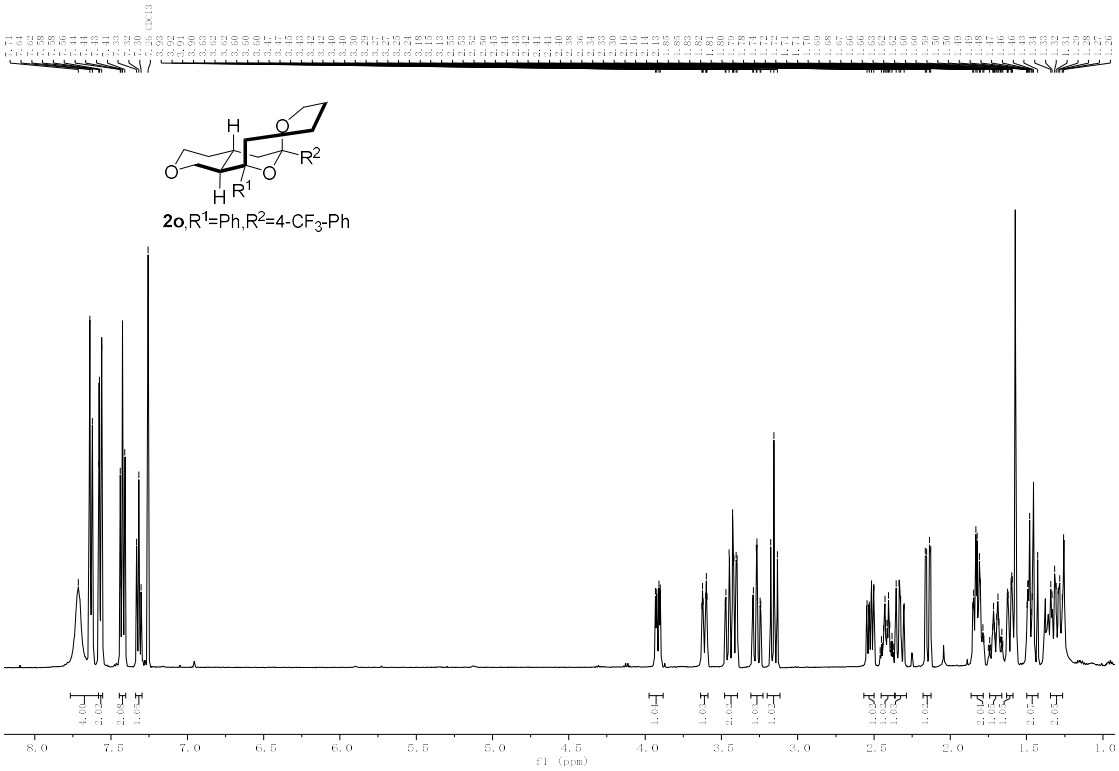

2l,R1=Ph,R2=3-Br-Ph
f1 (ppm)

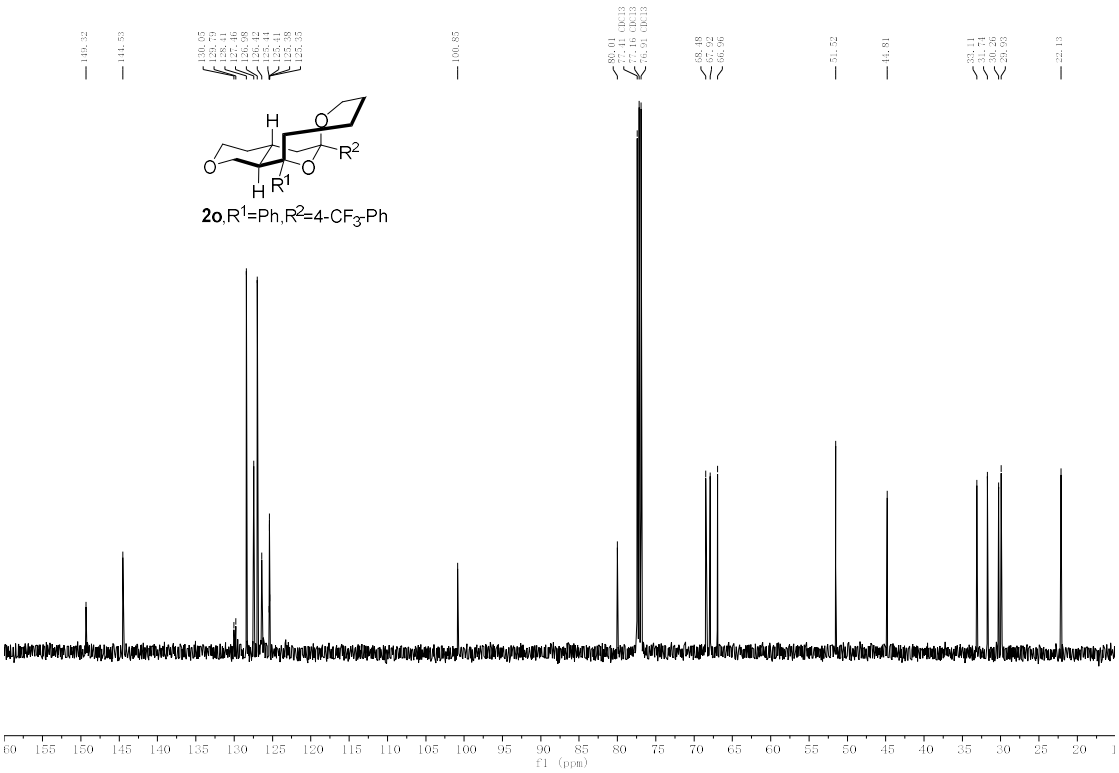

H
O
R2
O
O
H
R1
2m,R1=Ph,R2=3-F-Ph
f1 (ppm)

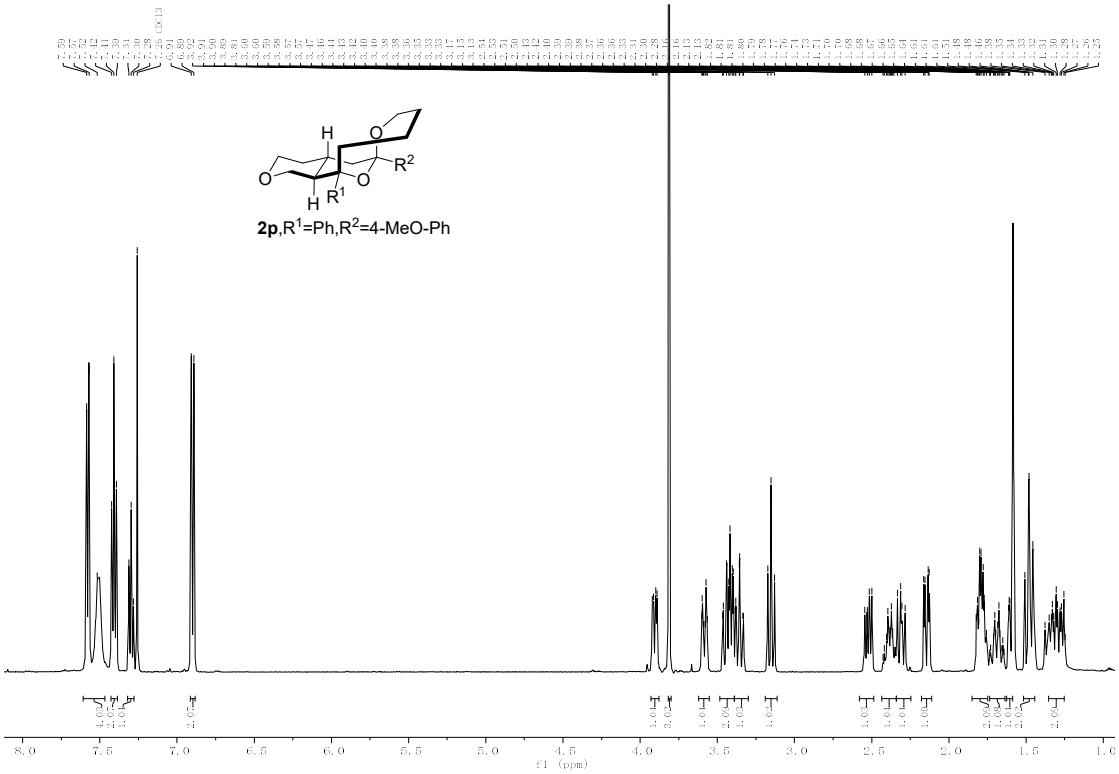

H
O
R2
O
O
H
R1
2m,R1=Ph,R2=3-F-Ph
f1 (ppm)

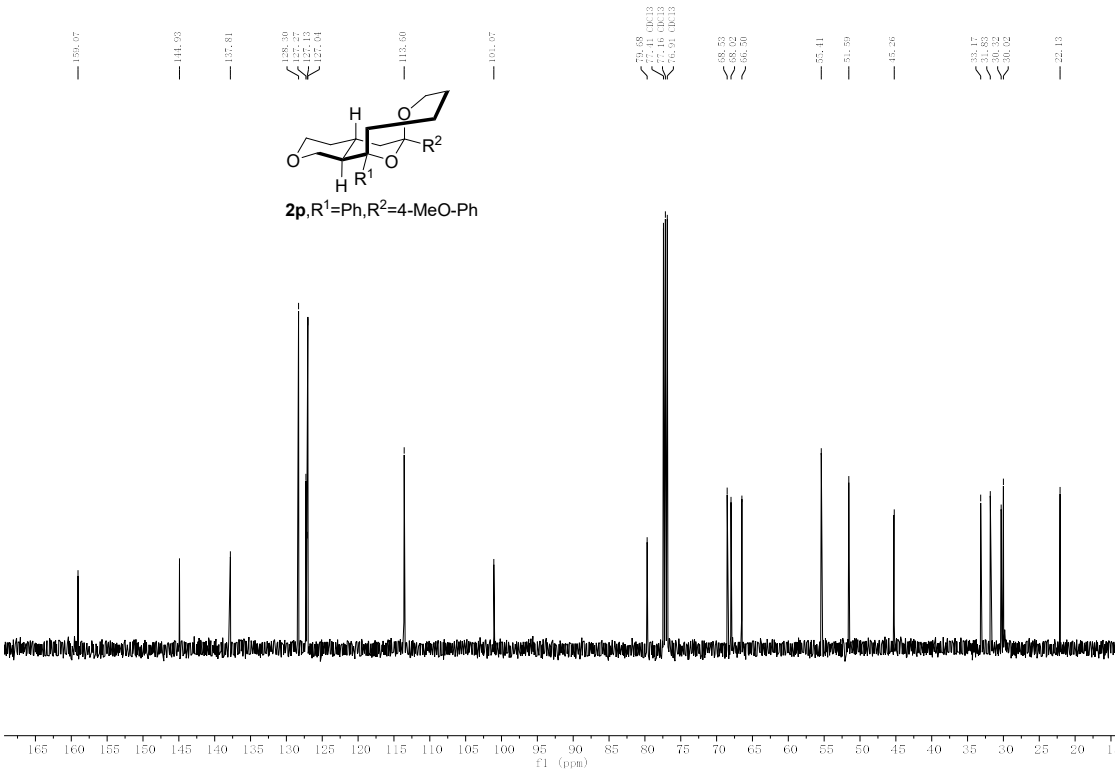

7.8017 7.5752 7.5635 7.4259 7.4116 7.3971 7.3180 7.3039 7.3008 7.2941 7.2889 7.2857 7.2785 7.2741 7.2695 7.1483 7.1336 7.1187 7.0718 7.0503 7.0324 3.9305 3.9221 3.9079 3.8995 3.6203 3.4695 3.4655 3.4426 3.4219 3.4177 3.4060 3.3987 3.3842 3.3769 3.1705 3.1485 3.1265 2.5666 2.5510 2.5367 2.5213 2.4466 2.4259 2.3434 2.3223 2.3141 2.2928 1.8383 1.8316 1.8167 1.8108 1.7901 1.7823 1.7491 1.7217 1.6960 1.6392 1.6138 1.5667 1.5540 1.5027 1.4875 1.4602 1.3776 1.3739 1.3598 1.3248 1.3059 1.3006
H
O
R2
O
O
H R1
2n,R1=Ph,R2=2-F-Ph
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 ppm
0.90 2.07 2.08 2.04 1.07 1.02 1.03 1.02 1.13 1.65 1.00 0.73 1.01 1.04 1.04 2.03 1.05 1.09 1.08 1.01 1.04 1.07

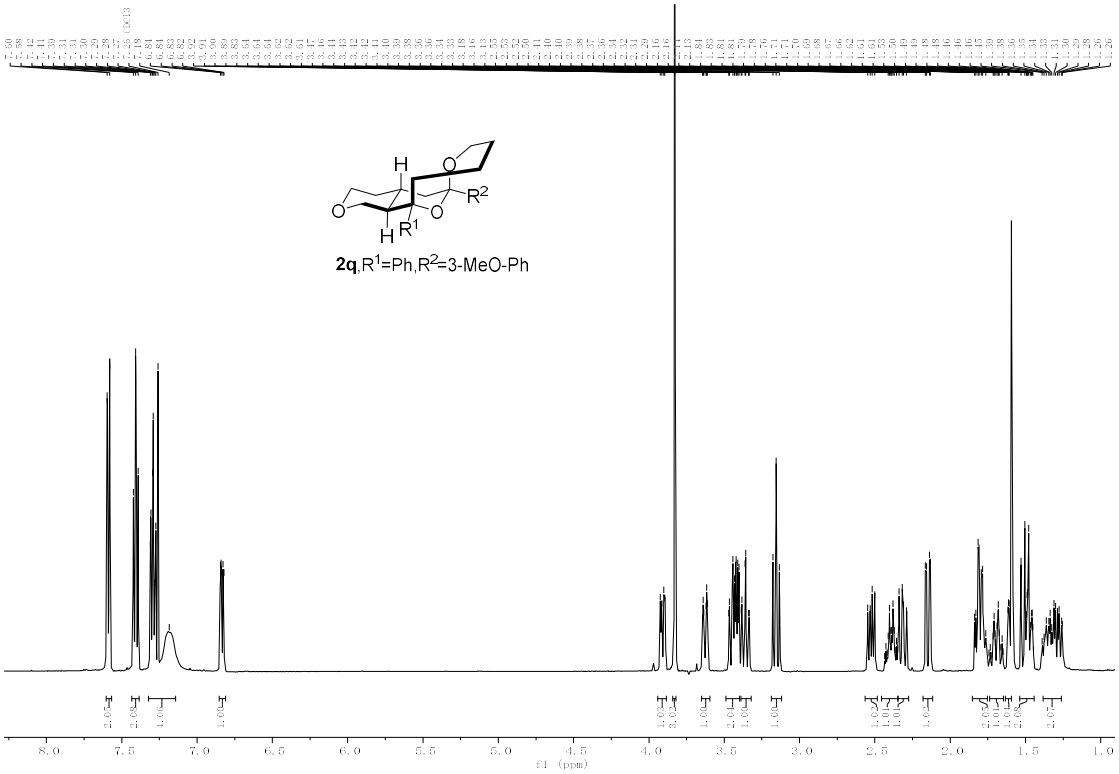

160.80 144.61 144.56 144.53 131.29 131.23 131.21 131.19 129.59 129.52 129.08 129.05 129.02 128.21 127.20 126.94 123.70 116.42 116.22 79.97 79.95 77.29 77.03 76.78 68.42 67.82 66.00 51.70 41.96 32.99 31.35 31.33 30.13 29.45 22.09
H
O
R2
O
O
H R1
2n,R1=Ph,R2=2-F-Ph
160 150 140 130 120 110 100 90 80 70 60 50 40 30 ppm

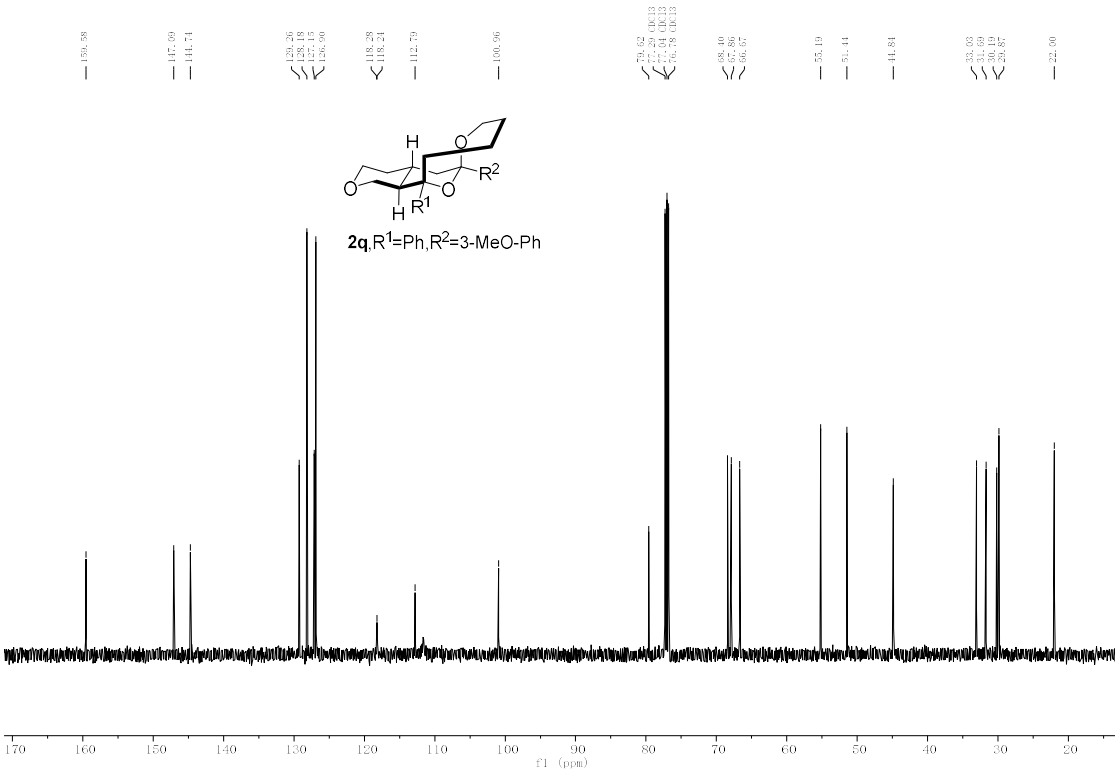

2o,R1=Ph,R2=4-CF3-Ph
f1 (ppm)

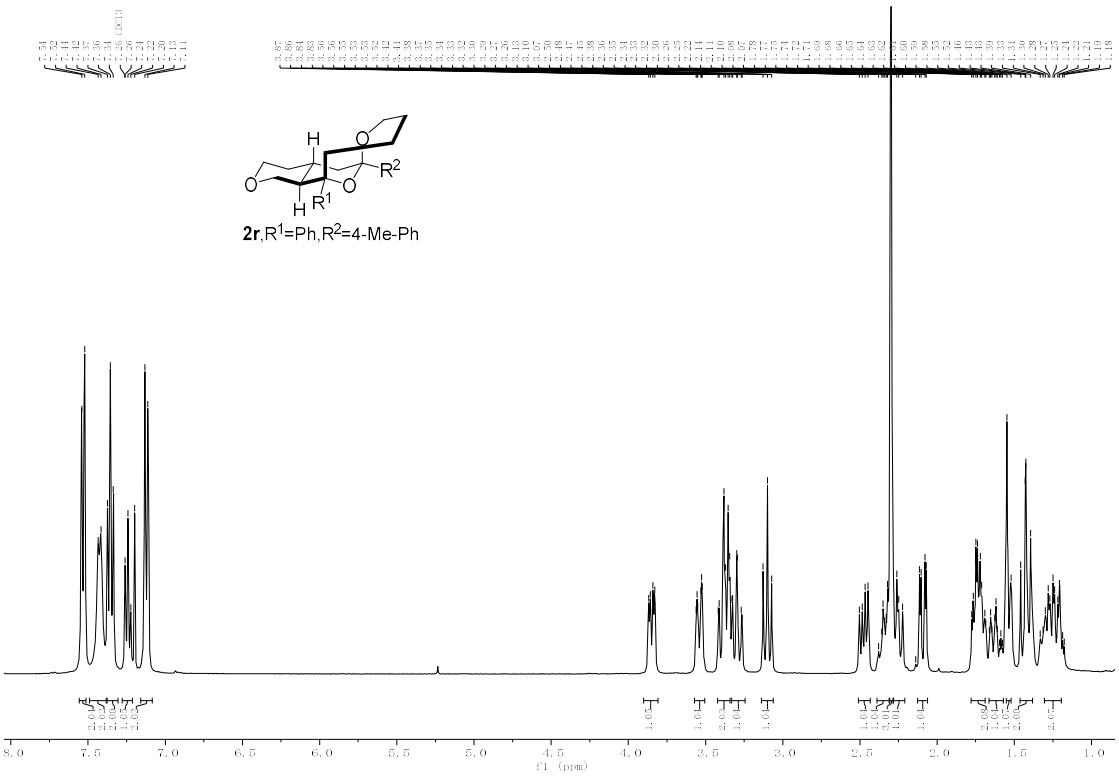

2o,R1=Ph,R2=4-CF3-Ph
f1 (ppm)

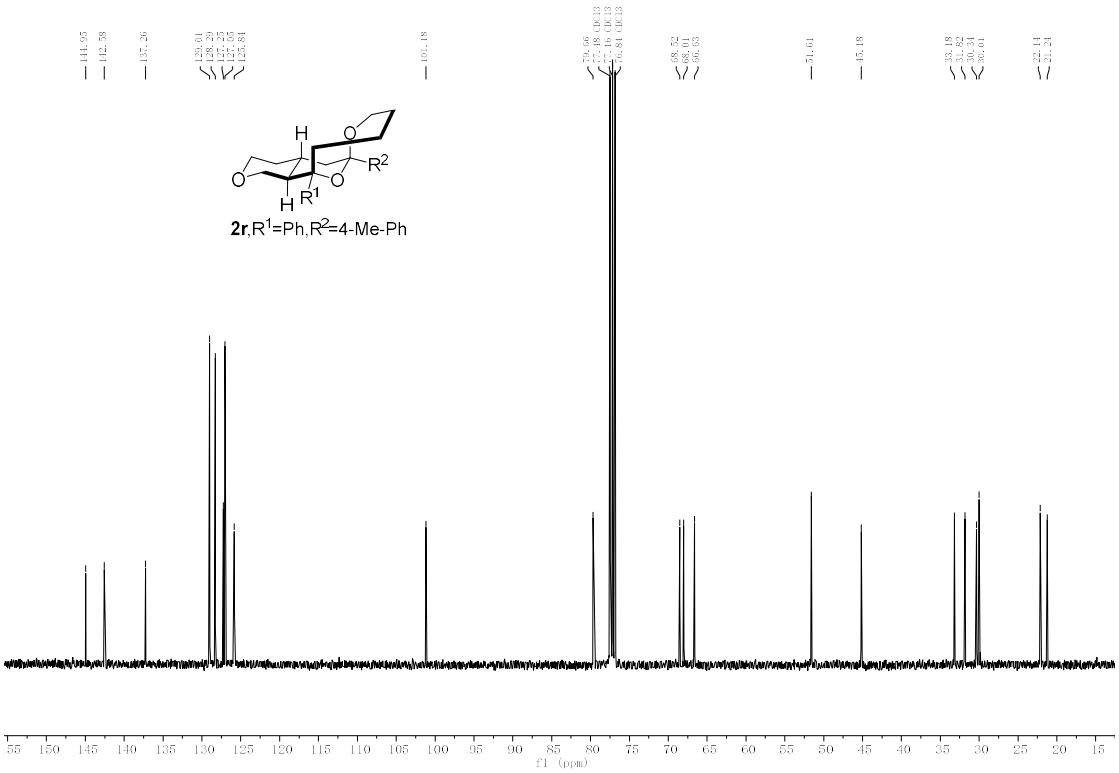

2p,R1=Ph,R2=4-MeO-Ph
f1 (ppm)

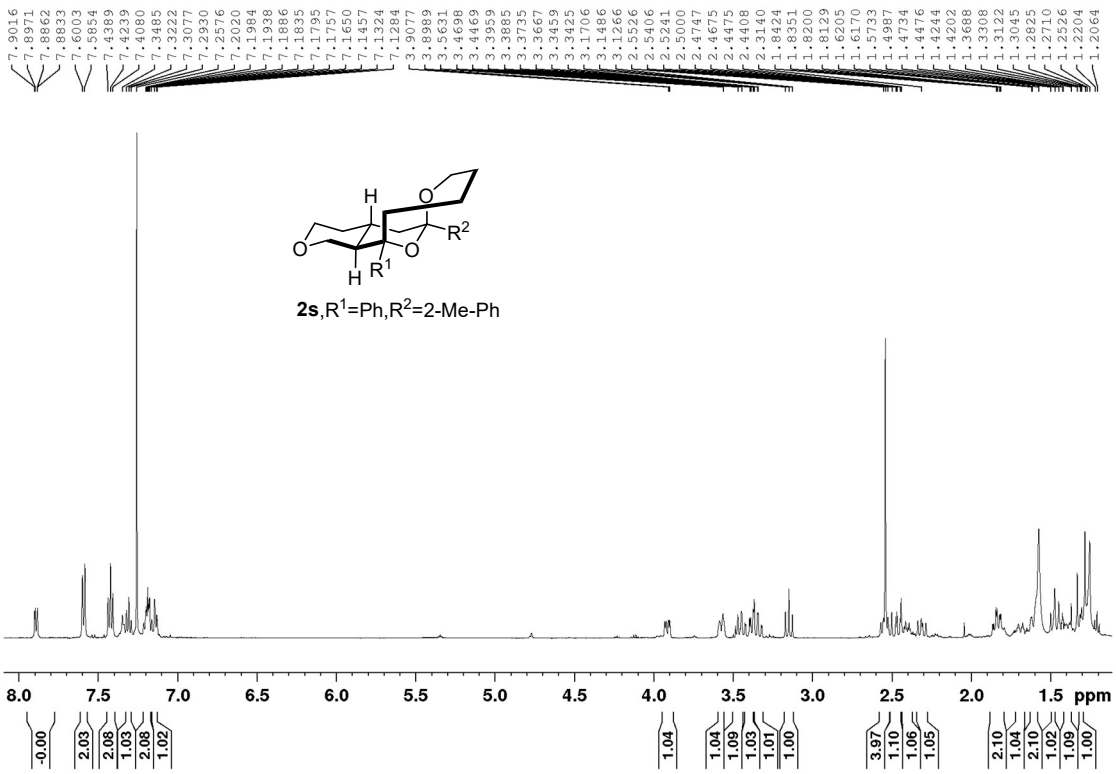

2p,R1=Ph,R2=4-MeO-Ph
f1 (ppm)

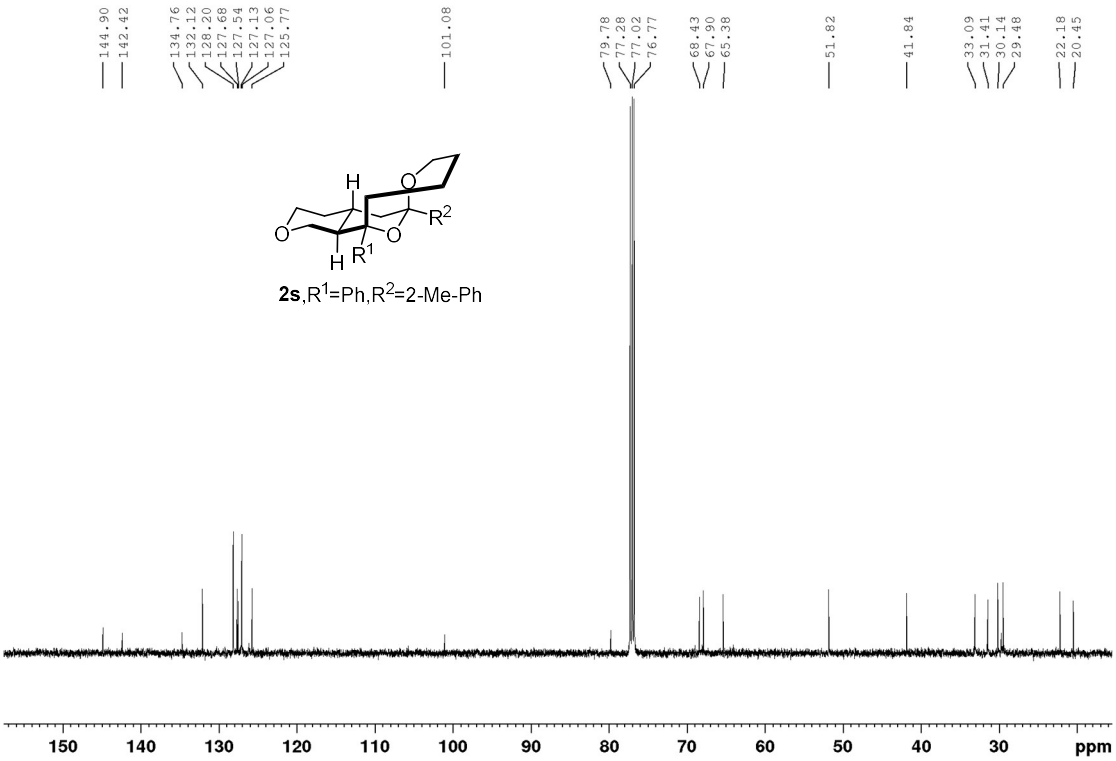

2q,R1=Ph,R2=3-MeO-Ph
f1 (ppm)

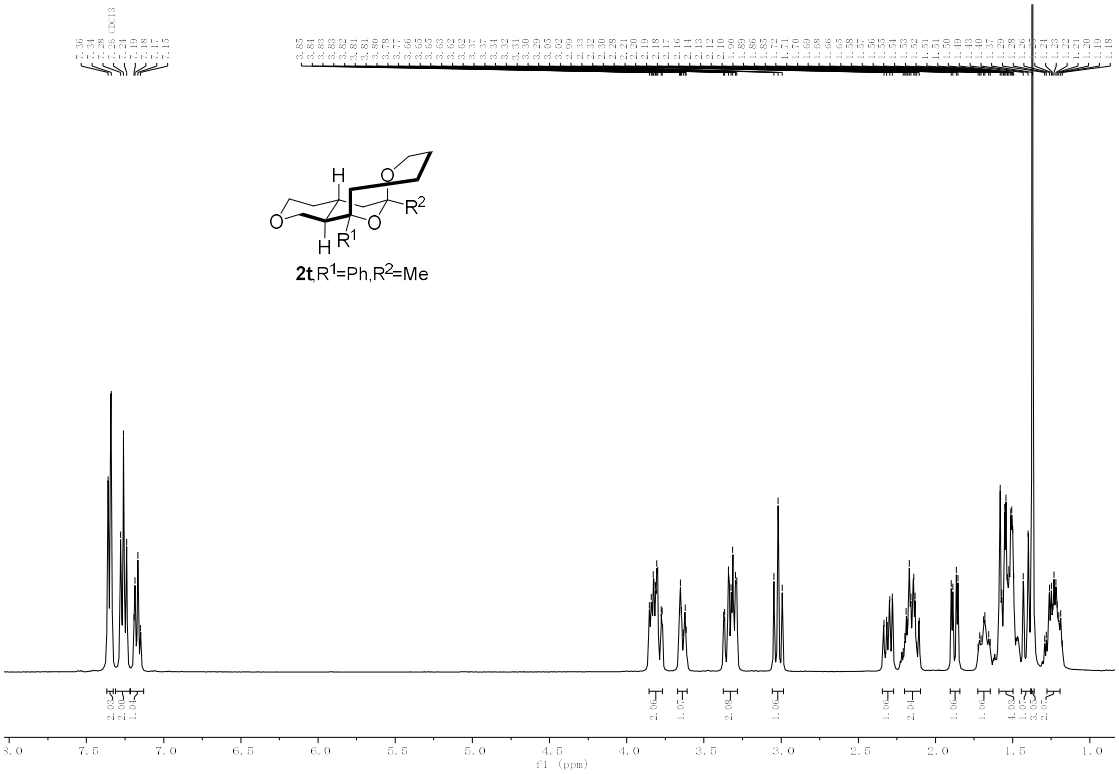

2q,R1=Ph,R2=3-MeO-Ph
f1 (ppm)

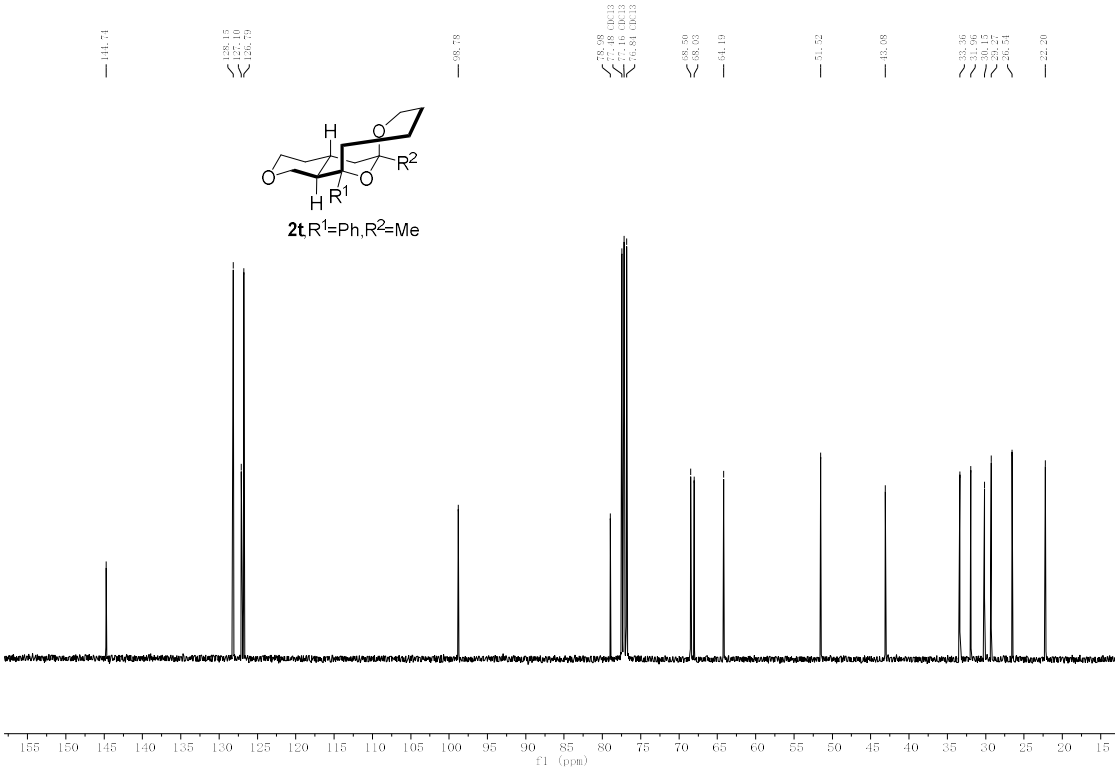

2r,R1=Ph,R2=4-Me-Ph
f1 (ppm)

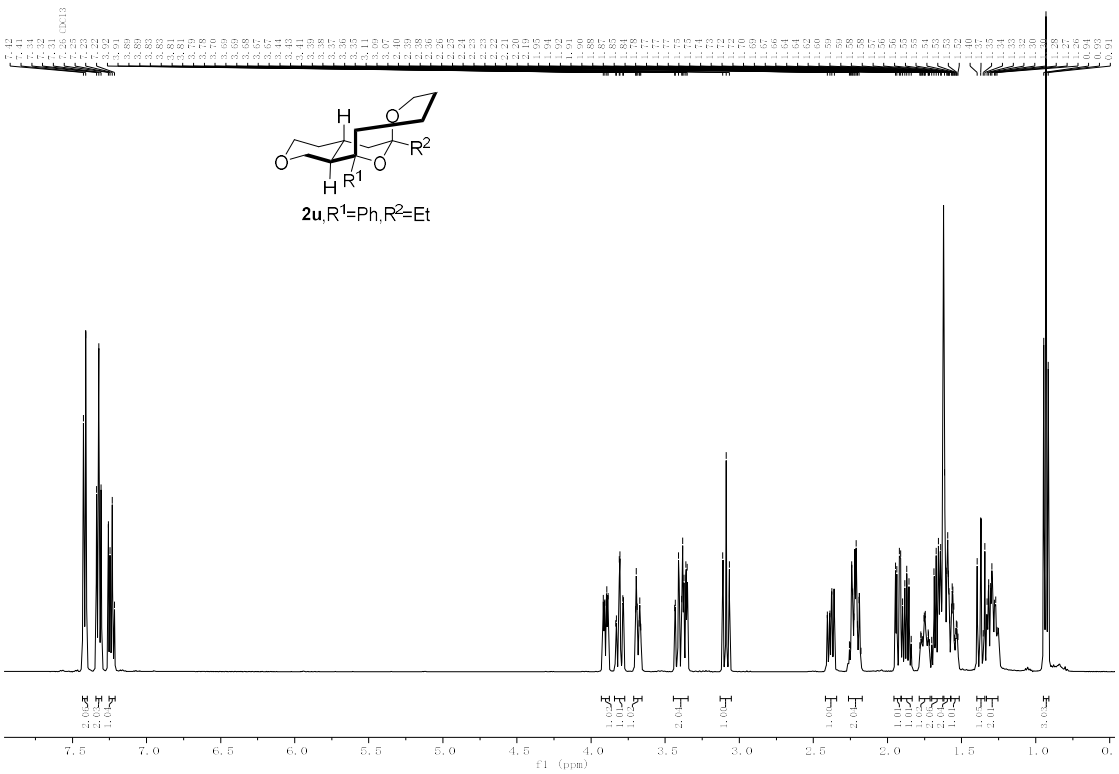

2r,R1=Ph,R2=4-Me-Ph
f1 (ppm)

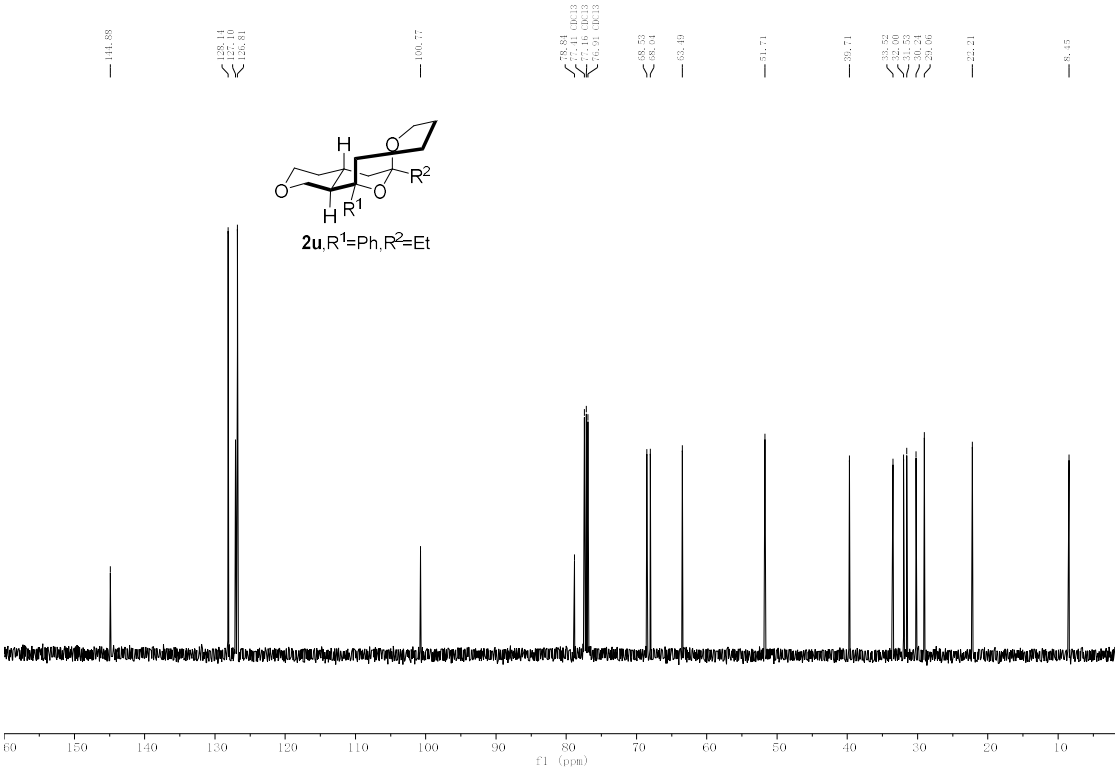

7.9016 7.8971 7.8862 7.8833 7.6003 7.5854 7.4389 7.4239 7.4080 7.3485 7.3222 7.3077 7.2930 7.2576 7.2020 7.1984 7.1938 7.1886 7.1835 7.1795 7.1757 7.1650 7.1457 7.1324 7.1284 3.9077 3.8989 3.5631 3.4698 3.4469 3.3959 3.3885 3.3735 3.3667 3.3459 3.3425 3.1706 3.1486 3.1266 2.5526 2.5406 2.5241 2.5000 2.4747 2.4675 2.4475 2.4408 2.3140 1.8424 1.8351 1.8200 1.8129 1.6205 1.6170 1.5733 1.4987 1.4734 1.4476 1.4244 1.4202 1.3688 1.3308 1.3122 1.3045 1.2825 1.2710 1.2526 1.2204 1.2064
H
O
R2
O
O
H
R1
2s,R1=Ph,R2=2-Me-Ph
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 ppm
-0.00 2.03 2.08 1.03 2.08 1.02 1.04 1.04 1.09 1.03 1.01 1.00 3.97 1.10 1.06 1.05 2.10 1.04 2.10 1.02 1.09 1.00

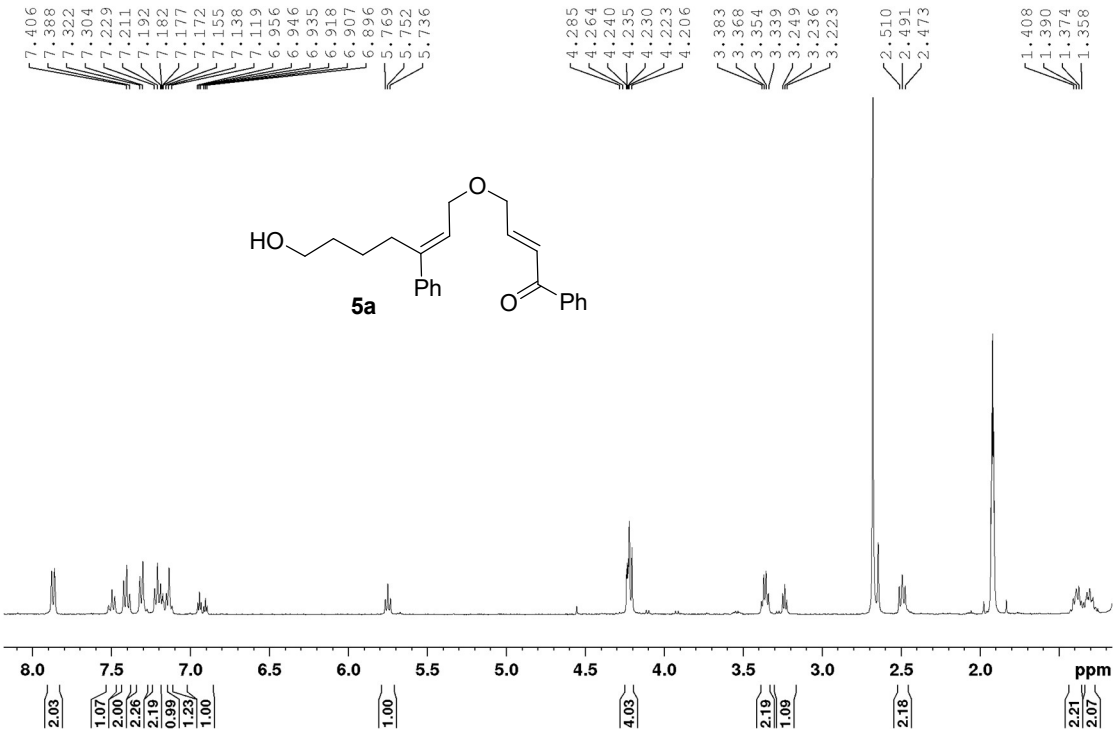

144.90 142.42 134.76 132.12 128.20 127.68 127.54 127.13 127.06 125.77 101.08 79.78 77.28 77.02 76.77 68.43 67.90 65.38 51.82 41.84 33.09 31.41 30.14 29.48 22.18 20.45
H
O
R2
O
O
H
R1
2s,R1=Ph,R2=2-Me-Ph
150 140 130 120 110 100 90 80 70 60 50 40 30 ppm


2t,R1=Ph,R2=Me
f1 (ppm)


2t,R1=Ph,R2=Me
f1 (ppm)


2u,R1=Ph,R2=Et
f1 (ppm)


2u,R1=Ph,R2=Et
f1 (ppm)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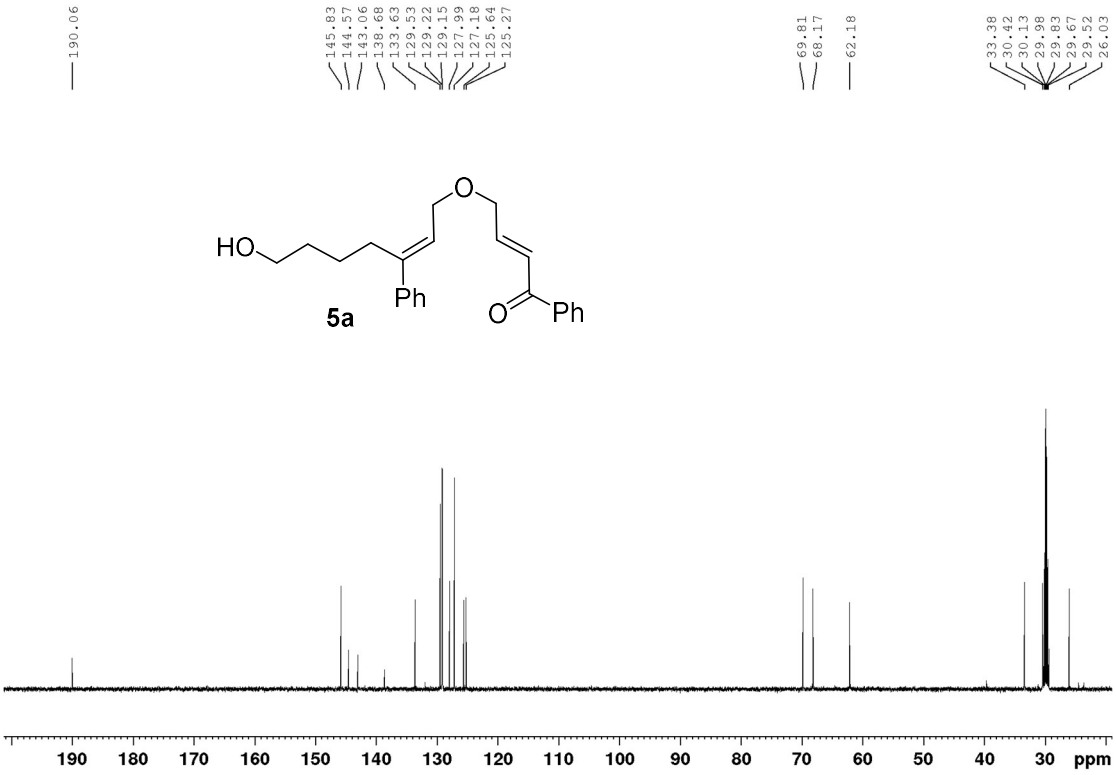
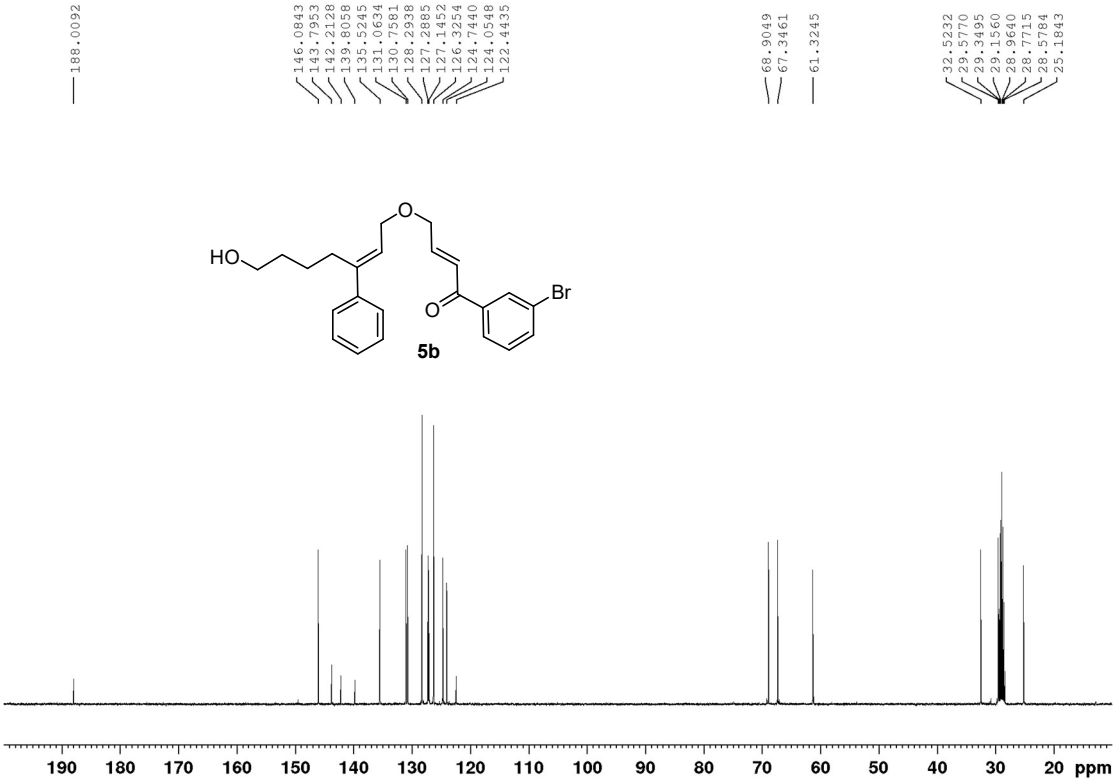
7.388
7.322
7.304
7.229
7.211
7.192
7.182
7.177
7.172
7.155
7.138
7.119
6.956
6.946
6.935
6.918
6.907
6.896
5.769
5.752
5.736
4.285
4.264
4.240
4.235
4.230
4.223
4.206
3.383
3.368
3.354
3.339
3.249
3.236
3.223
2.510
2.491
2.473
1.408
1.390
1.374
1.358
HO
O
Ph
O
Ph
5a
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
2.03
1.07
2.00
2.26
2.19
0.99
1.23
1.00
1.00
4.03
2.19
1.09
2.18
2.21
2.07


190.06
145.83
144.57
143.06
138.68
133.63
129.53
129.22
129.15
127.99
127.18
125.64
125.27
69.81
68.17
62.18
33.38
30.42
30.13
29.98
29.83
29.67
29.52
26.03
HO
O
Ph
O
Ph
5a
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm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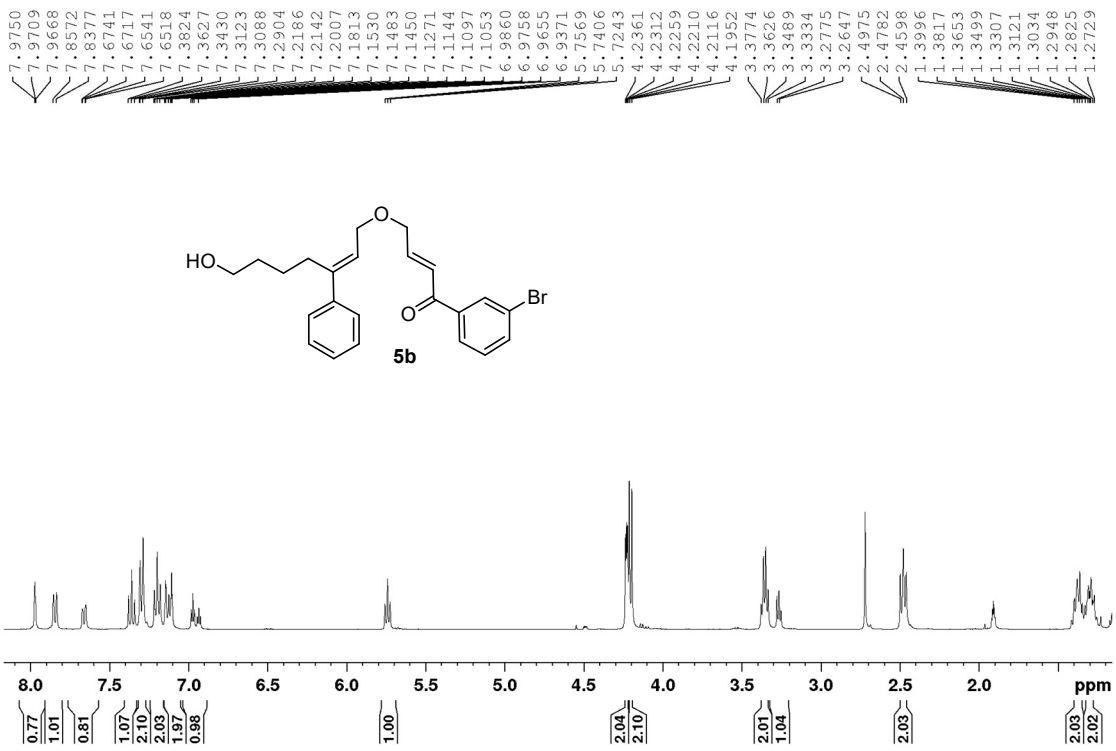
143.7953
142.2128
139.8058
135.5245
131.0634
130.7581
128.2938
127.2885
127.1452
126.3254
124.7440
124.0548
122.4435
68.9049
67.3461
61.3245
32.5232
29.5770
29.3495
29.1560
28.9640
28.7715
28.5784
25.1843
HO
O
O
Br
5b
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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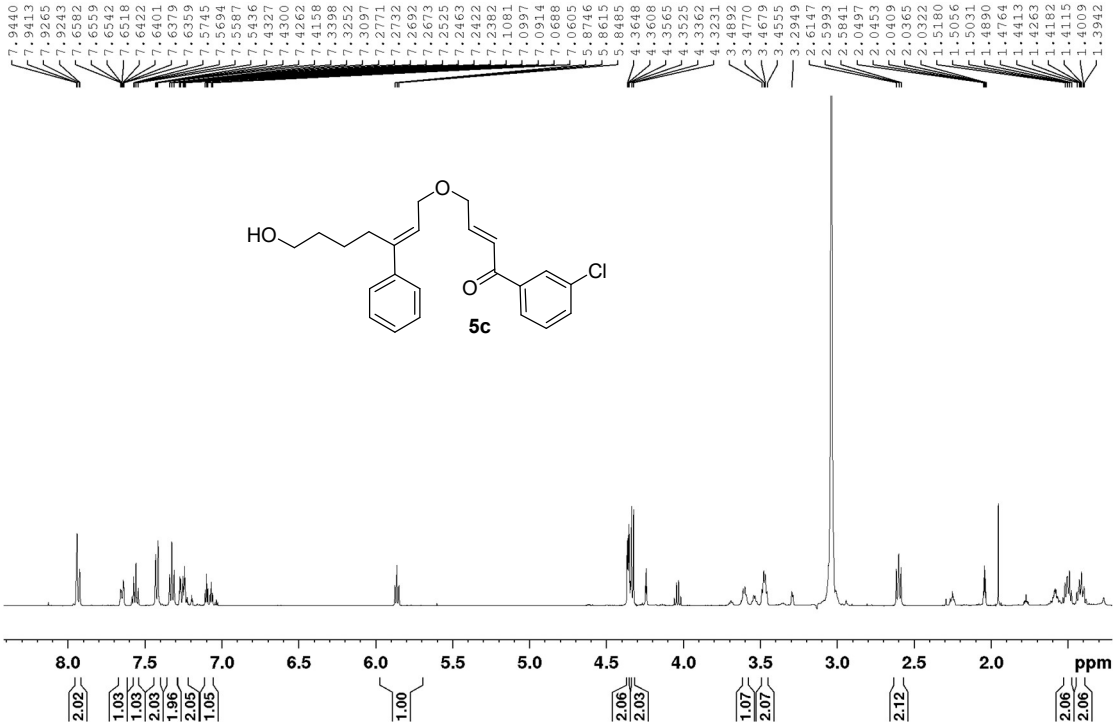
7.9709
7.9668
7.8572
7.8377
7.6741
7.6717
7.6541
7.6518
7.3824
7.3627
7.3430
7.3123
7.3088
7.2904
7.2186
7.2142
7.2007
7.1813
7.1530
7.1483
7.1450
7.1271
7.1144
7.1097
7.1053
6.9860
6.9758
6.9655
6.9371
5.7569
5.7406
5.7243
4.2361
4.2312
4.2259
4.2210
4.2116
4.1952
3.3774
3.3626
3.3489
3.3334
3.2775
3.2647
2.4975
2.4782
2.4598
1.3996
1.3817
1.3653
1.3499
1.3307
1.3121
1.3034
1.2948
1.2825
1.2729
HO
O
O
Br
5b
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 ppm
0.77
1.01
0.81
1.07
2.10
2.03
1.97
0.98
1.00
2.04
2.10
2.01
1.04
2.03
2.03
2.02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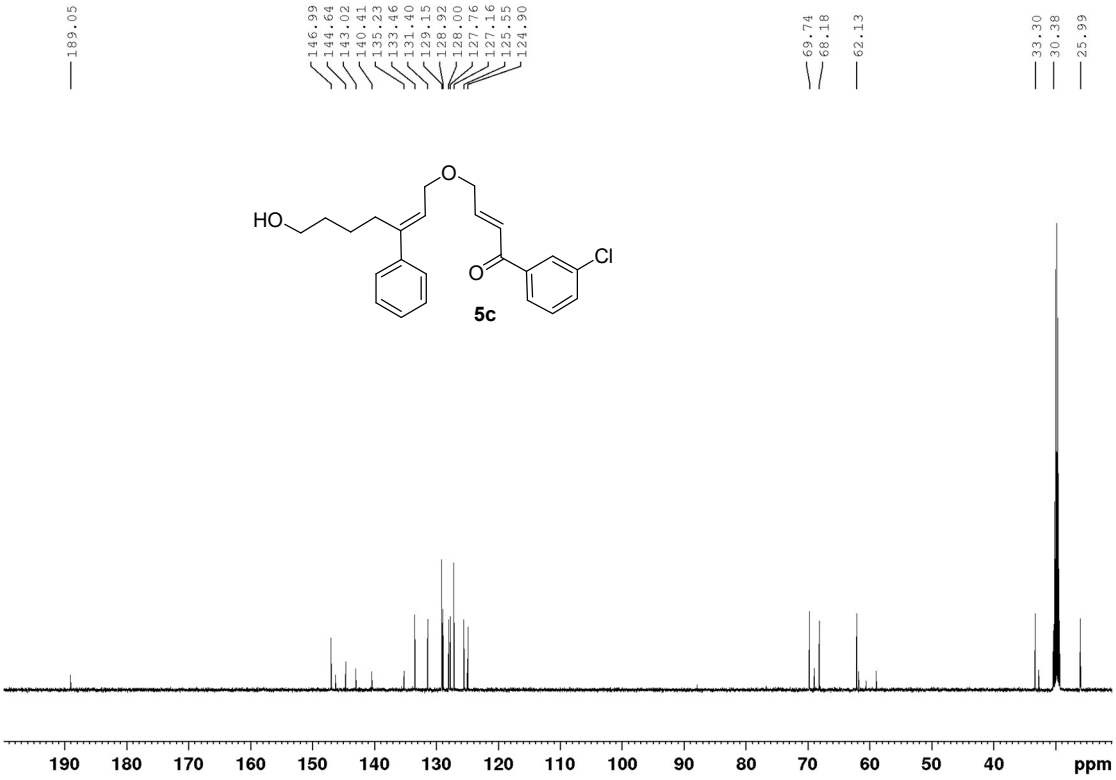
7.9243
7.6582
7.6559
7.6542
7.6518
7.6422
7.6401
7.6379
7.6359
7.5745
7.5694
7.5587
7.5436
7.4327
7.4300
7.4262
7.4158
7.3398
7.3252
7.3097
7.2771
7.2732
7.2692
7.2673
7.2525
7.2463
7.2422
7.2382
7.1081
7.0997
7.0914
7.0688
7.0605
5.8746
5.8615
5.8485
4.3648
4.3608
4.3565
4.3525
4.3362
4.3231
3.4892
3.4770
3.4679
3.4555
3.2949
2.6147
2.5993
2.5841
2.0497
2.0453
2.0409
2.0365
2.0322
1.5180
1.5056
1.5031
1.4890
1.4764
1.4413
1.4263
1.4182
1.4115
1.4009
1.3942
HO
O
O
Cl
5c
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
2.02
1.03
1.03
2.03
1.96
2.05
1.05
1.00
2.06
2.03
1.07
2.07
2.12
2.06
2.06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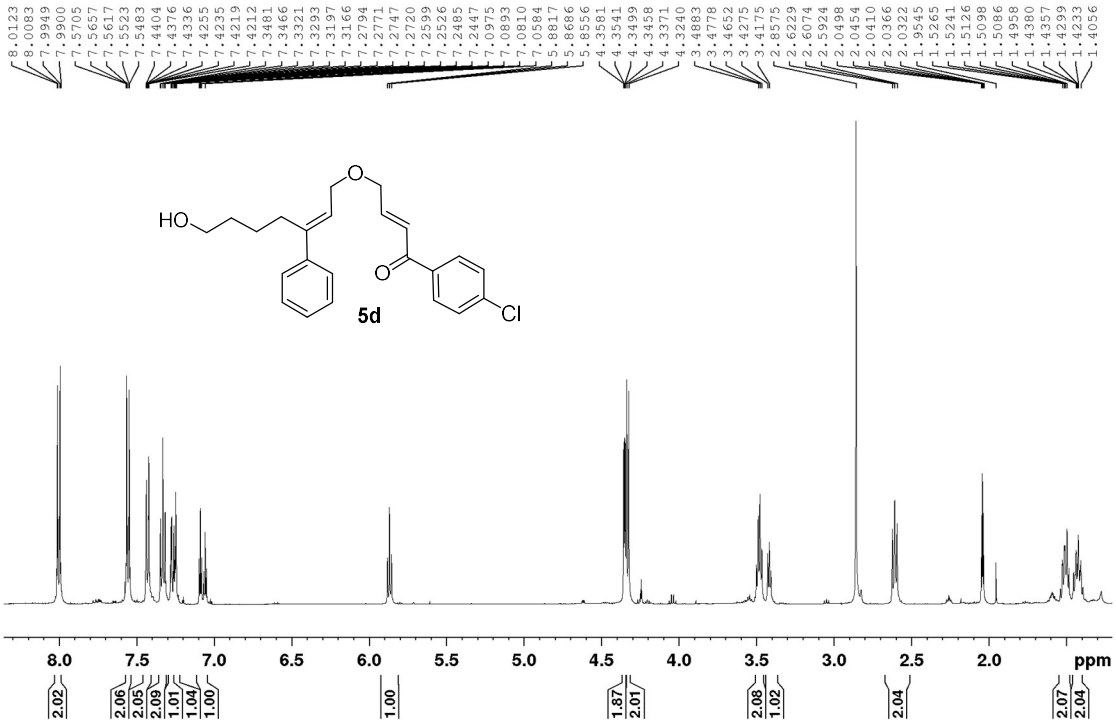
144.64
143.02
140.41
135.23
133.46
131.40
129.15
128.92
128.00
127.76
127.16
125.55
124.90
69.74
68.18
62.13
33.30
30.38
25.99
HO
O
O
Cl
5c
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm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7.9949
7.9900
7.5705
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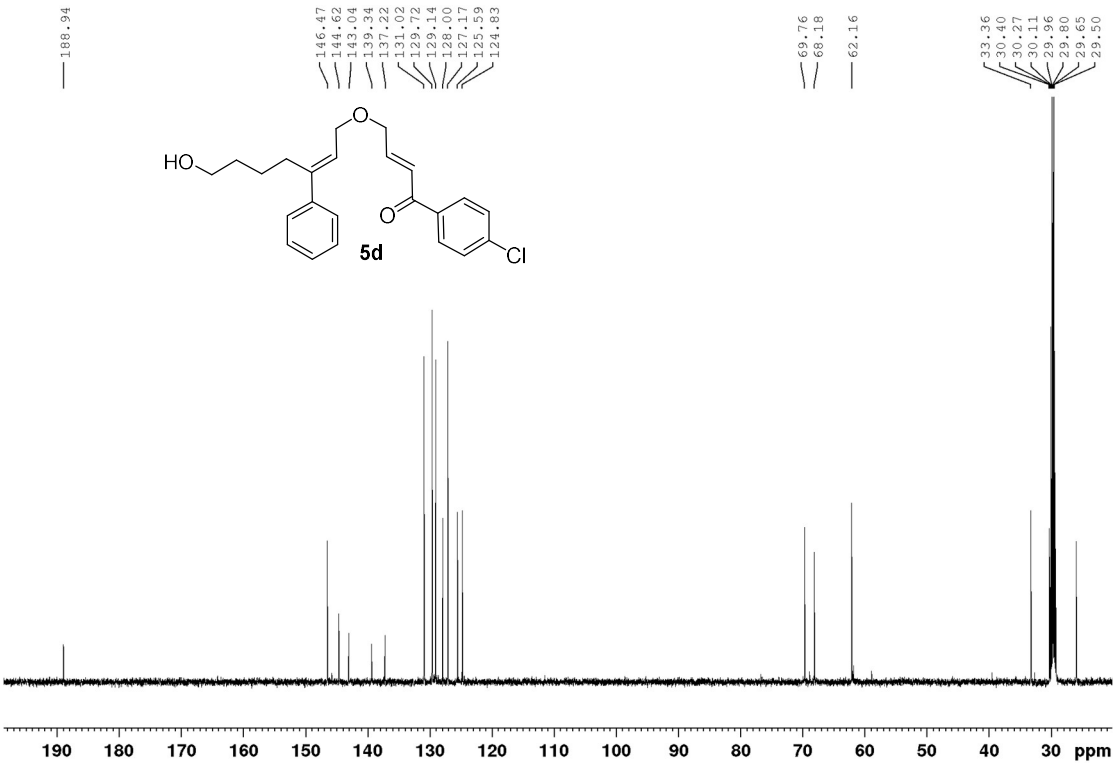
7.5523
7.5483
7.4404
7.4376
7.4336
7.4255
7.4235
7.4219
7.4212
7.3481
7.3466
7.3321
7.3293
7.3197
7.3166
7.2794
7.2771
7.2747
7.2720
7.2599
7.2526
7.2485
7.2447
7.0975
7.0893
7.0810
7.0584
5.8817
5.8686
5.8556
4.3581
4.3541
4.3499
4.3458
4.3371
4.3240
3.4883
3.4778
3.4652
3.4275
3.4175
2.8575
2.6229
2.6074
2.5924
2.0498
2.0454
2.0410
2.0366
2.0322
1.9545
1.5265
1.5241
1.5126
1.5098
1.5086
1.4958
1.4380
1.4357
1.4299
1.4233
1.4056
HO
O
O
Cl
5d
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
2.02
2.06
2.05
2.09
1.01
1.04
1.00
1.00
1.87
2.01
2.08
1.02
2.04
2.07
2.04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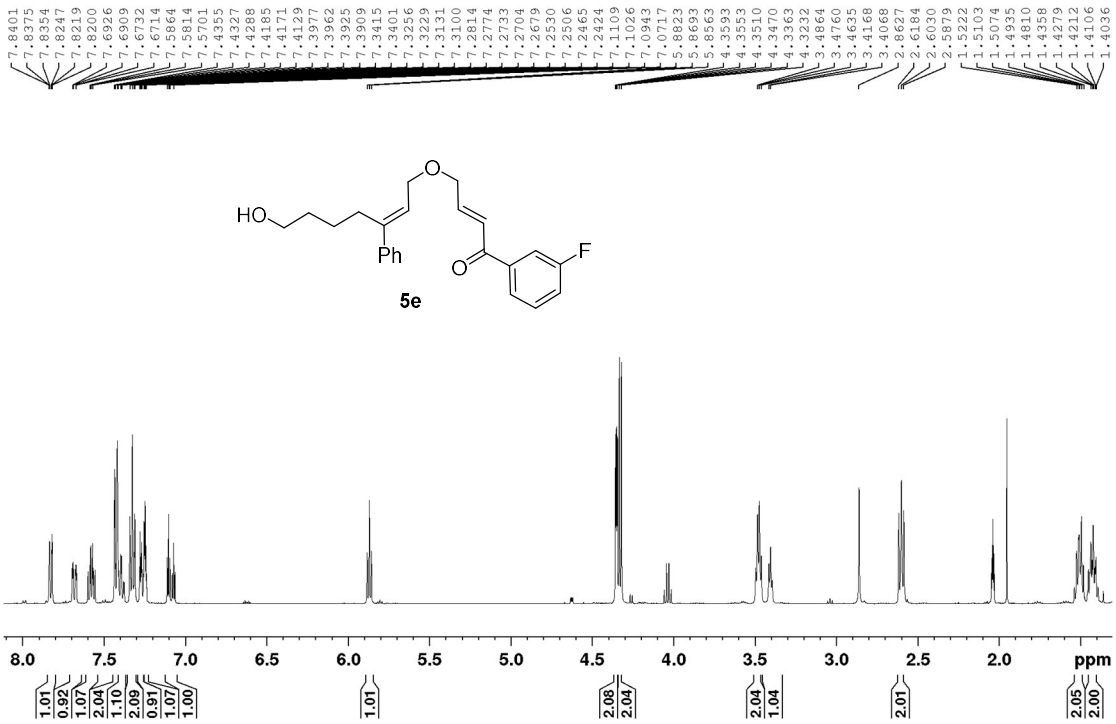
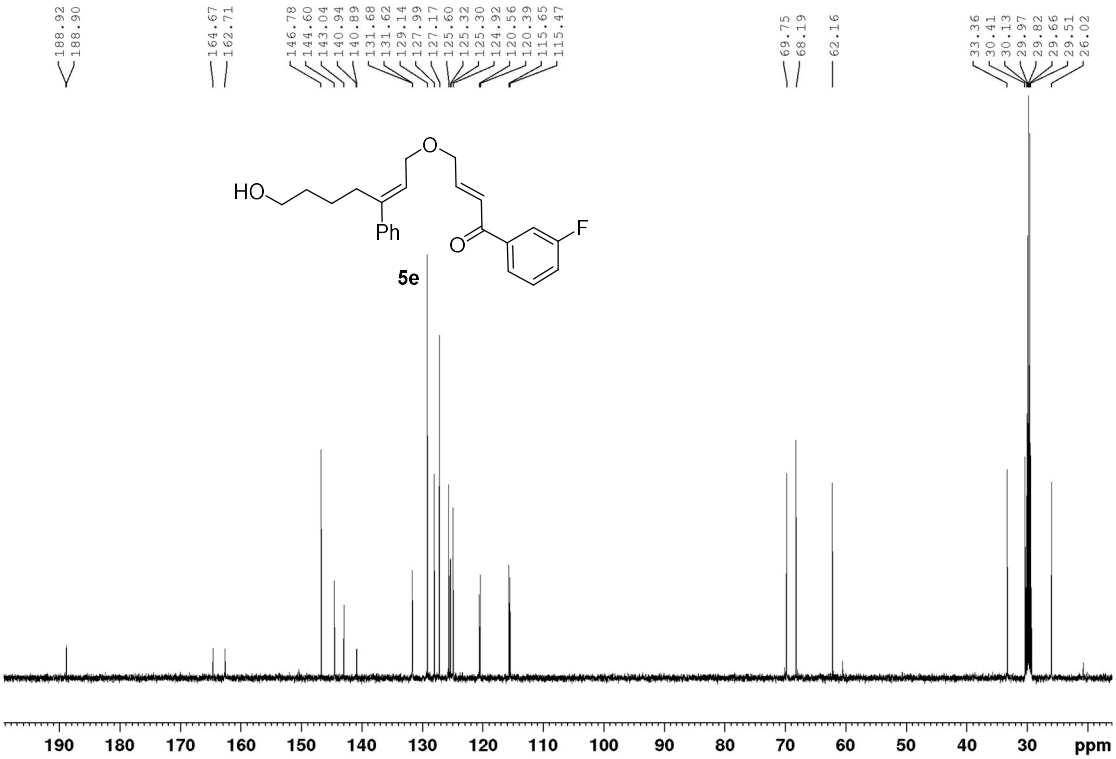
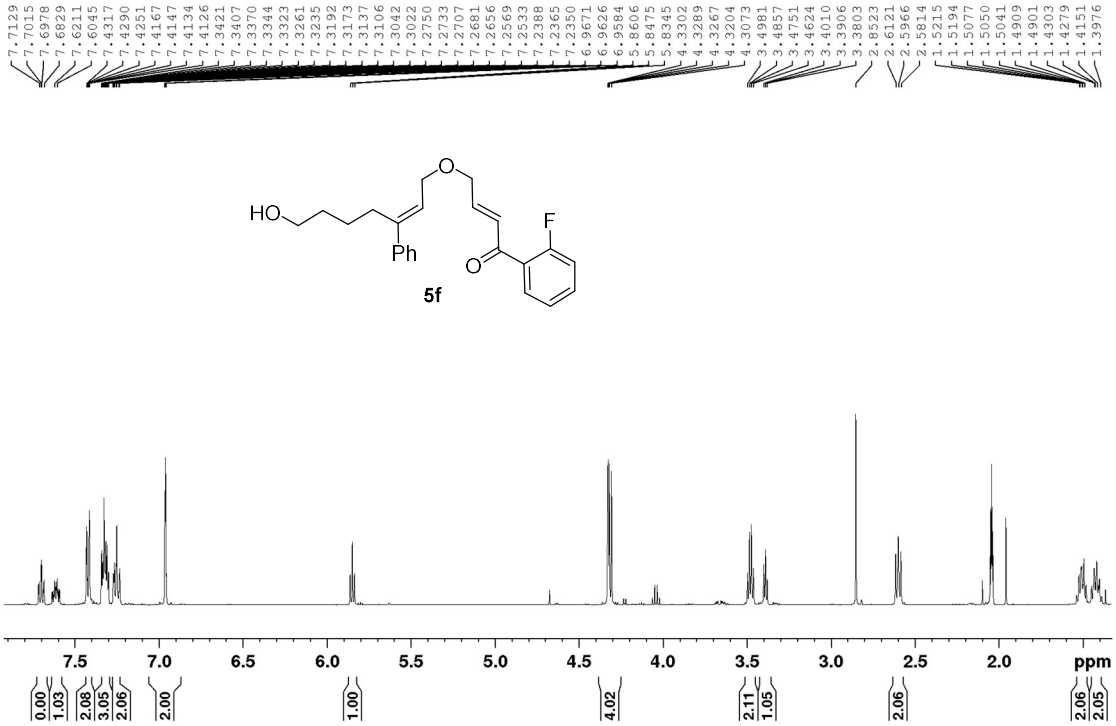
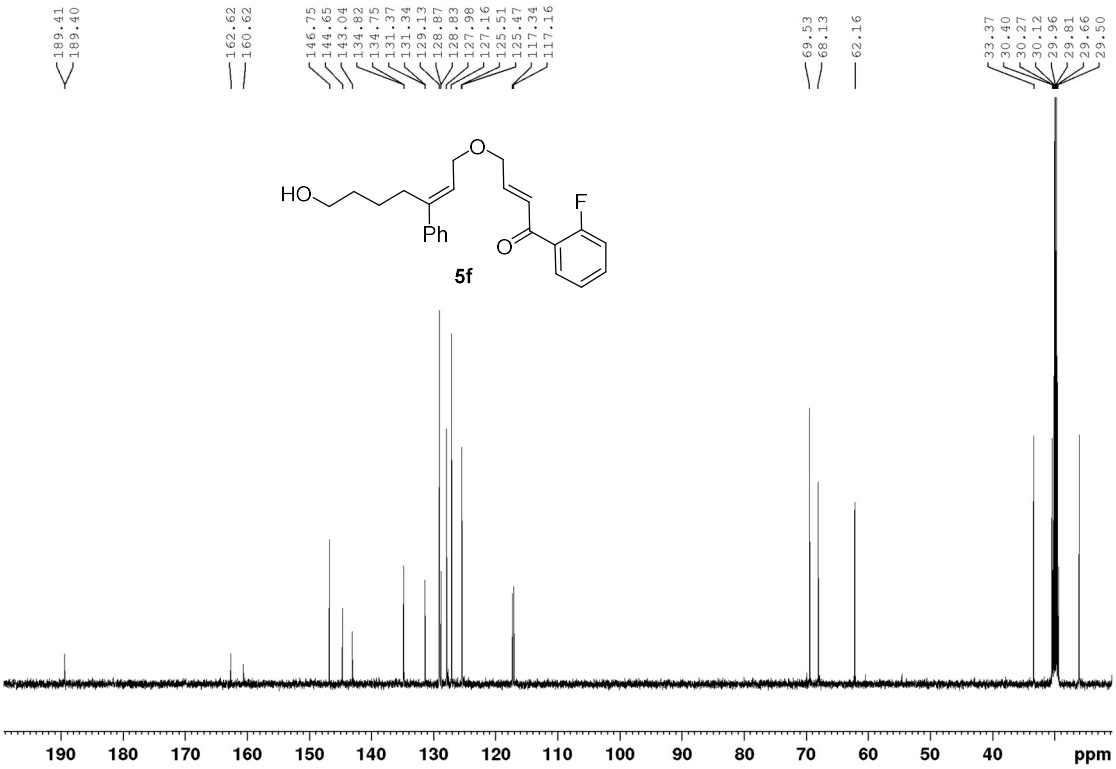
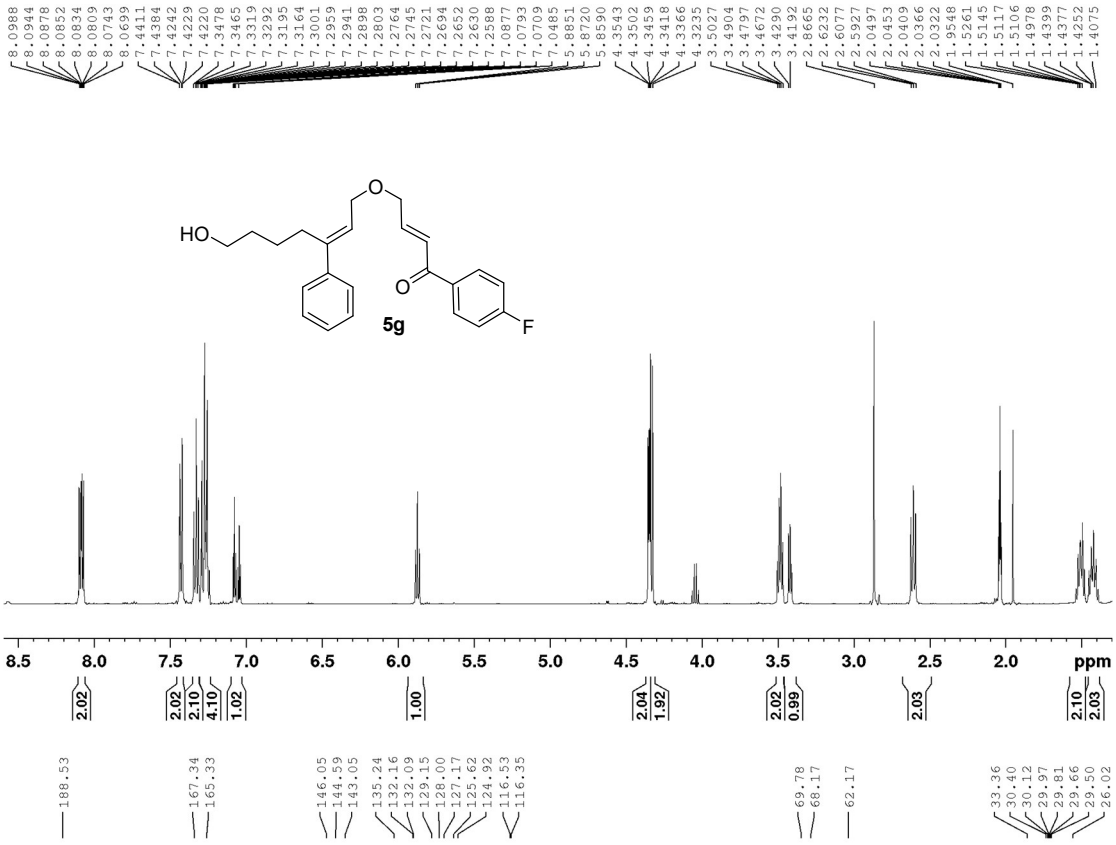
144.62
143.04
139.34
137.22
131.02
129.72
129.14
128.00
127.17
125.59
124.83
69.76
68.18
62.16
33.36
30.40
30.27
30.11
29.96
29.80
29.65
29.50
HO
O
O
Cl
5d
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm


7.8401 7.8375 7.8354 7.8247 7.8219 7.8200 7.6926 7.6909 7.6732 7.6714 7.5864 7.5814 7.5701 7.4355 7.4327 7.4288 7.4185 7.4171 7.4129 7.3977 7.3962 7.3925 7.3909 7.3415 7.3401 7.3256 7.3229 7.3131 7.3100 7.2814 7.2774 7.2733 7.2704 7.2679 7.2530 7.2506 7.2465 7.2424 7.1109 7.1026 7.0943 7.0717 5.8823 5.8693 5.8563 4.3593 4.3553 4.3510 4.3470 4.3363 4.3232 3.4864 3.4760 3.4635 3.4168 3.4068 2.8627 2.6184 2.6030 2.5879 1.5222 1.5103 1.5074 1.4935 1.4810 1.4358 1.4279 1.4212 1.4106 1.4036
HO
O
Ph
O
F
5e
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 ppm
1.01 0.92 1.07 2.04 1.10 2.09 0.91 1.07 1.00
1.01
2.08 2.04
2.04 1.04
2.01
2.05 2.00


188.92 188.90
164.67 162.71
146.78 144.60 143.04 140.94 140.89 131.68 131.62 129.14 127.99 127.17 125.60 125.32 125.30 124.92 120.56 120.39 115.65 115.47
69.75 68.19
62.16
33.36 30.41 30.13 29.97 29.82 29.66 29.51 26.02
HO
O
Ph
O
F
5e
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 ppm


7.7129 7.7015 7.6978 7.6829 7.6211 7.6045 7.4317 7.4290 7.4251 7.4167 7.4147 7.4134 7.4126 7.3421 7.3407 7.3370 7.3344 7.3323 7.3261 7.3235 7.3192 7.3173 7.3137 7.3106 7.3042 7.3022 7.2750 7.2733 7.2707 7.2681 7.2656 7.2569 7.2533 7.2388 7.2365 7.2350 6.9671 6.9626 6.9584 5.8606 5.8475 5.8345 4.3302 4.3289 4.3267 4.3204 4.3073 3.4981 3.4857 3.4751 3.4624 3.4010 3.3906 3.3803 2.8523 2.6121 2.5966 2.5814 1.5215 1.5194 1.5077 1.5050 1.5041 1.4909 1.4901 1.4303 1.4279 1.4151 1.3976
HO
Ph
O
O
F
5f
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 ppm
0.00 1.03 2.08 3.05 2.06 2.00 1.00 4.02 2.11 1.05 2.06 2.06 2.05


189.41 189.40 162.62 160.62 146.75 144.65 143.04 134.82 134.75 131.37 131.34 129.13 128.87 128.83 127.98 127.16 125.51 125.47 117.34 117.16 69.53 68.13 62.16 33.37 30.40 30.27 30.12 29.96 29.81 29.66 29.50
HO
Ph
O
O
F
5f
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 ppm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7.4411 7.4384 7.4242 7.4229 7.4220 7.3478 7.3465 7.3319 7.3292 7.3195 7.3164 7.3001 7.2959 7.2941 7.2898 7.2803 7.2764 7.2745 7.2721 7.2694 7.2652 7.2630 7.2588 7.0877 7.0793 7.0709 7.0485 5.8851 5.8720 5.8590
4.3543 4.3502 4.3459 4.3418 4.3366 4.3235
3.5027 3.4904 3.4797 3.4672 3.4290 3.4192
2.8665 2.6232 2.6077 2.5927 2.0497 2.0453 2.0409 2.0366 2.0322
1.9548 1.5261 1.5145 1.5117 1.5106 1.4978 1.4399 1.4377 1.4252 1.4075
HO
O
O
F
5g
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 ppm
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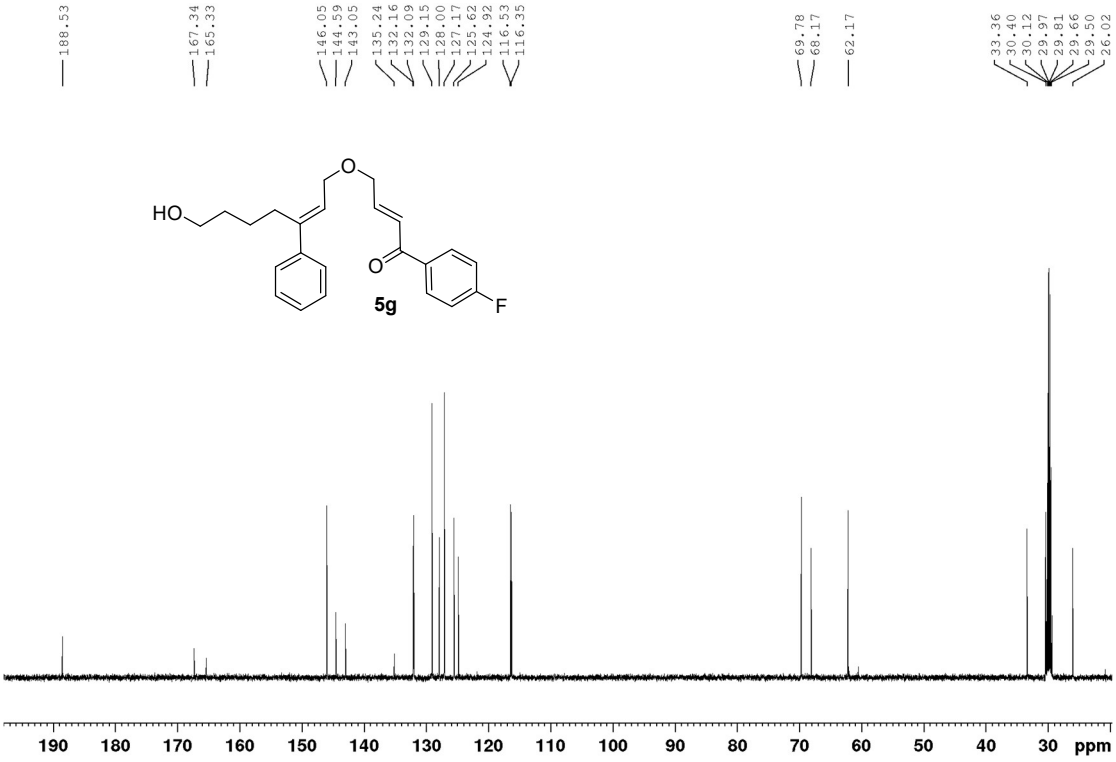
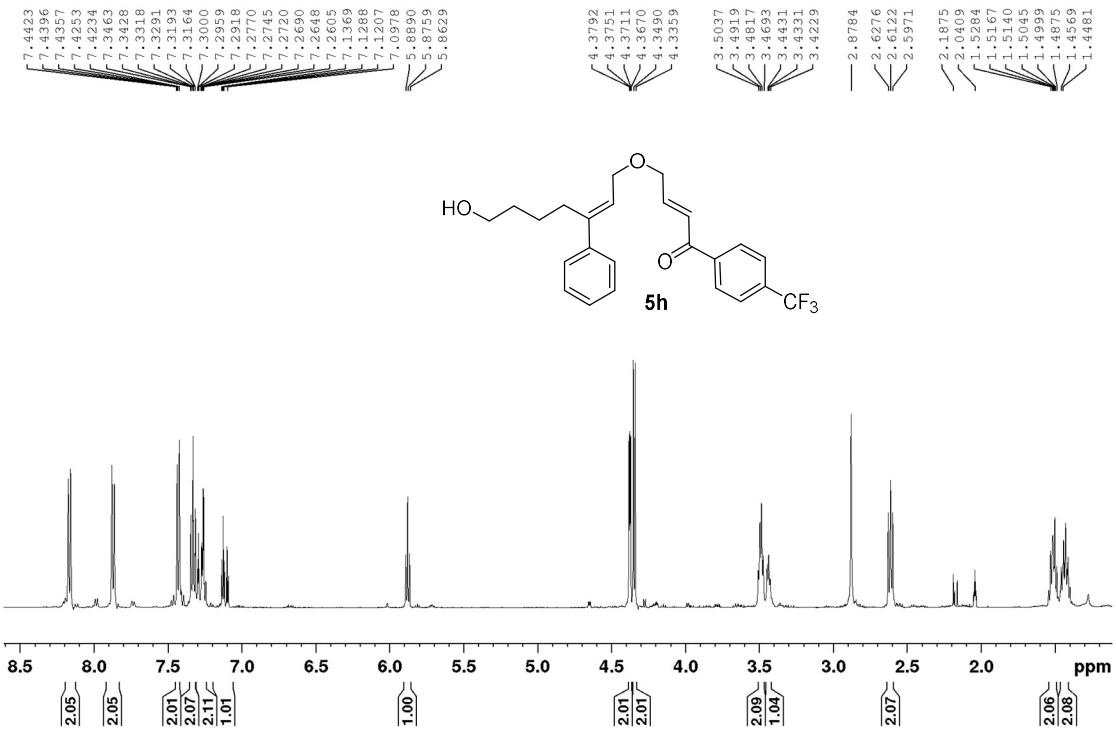

188.53
167.34 165.33
146.05 144.59 143.05 135.24 132.16 132.09 129.15 128.00 127.17 125.62 124.92 116.53 116.35
69.78 68.17 62.17
33.36 30.40 30.12 29.97 29.81 29.66 29.50 26.02
HO
O
O
F
5g
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 ppm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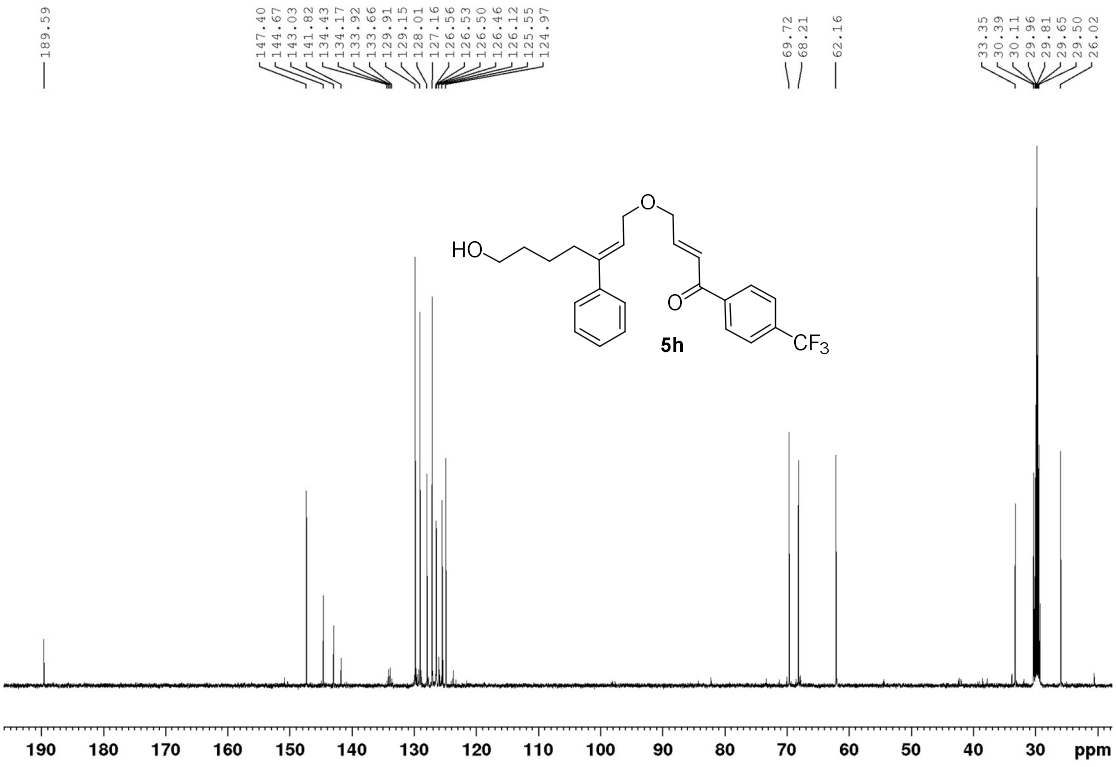
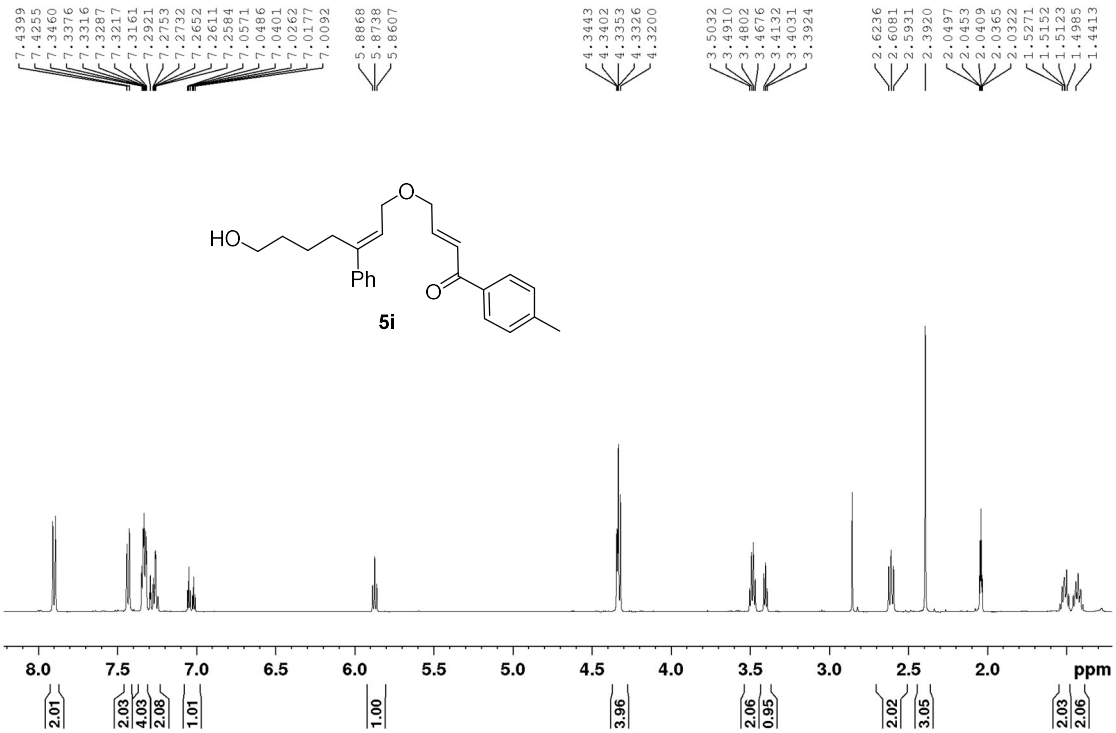
4.3792 4.3751 4.3711 4.3670 4.3490 4.3359
3.5037 3.4919 3.4817 3.4693 3.4431 3.4331 3.4229
2.8784
2.6276 2.6122 2.5971
2.1875 2.0409 1.5284 1.5167 1.5140 1.5045 1.4999 1.4875 1.4569 1.4481
HO
O
O
CF3
5h
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 ppm
2.05 2.05 2.01 2.07 2.11 1.01 1.00 2.01 2.01 2.09 1.04 2.07 2.06 2.08


189.59
147.40 144.67 143.03 141.82 134.43 134.17 133.92 133.66 129.91 129.15 128.01 127.16 126.56 126.53 126.50 126.46 126.12 125.55 124.97
69.72 68.21
62.16
33.35 30.39 30.11 29.96 29.81 29.65 29.50 26.02
HO
O
O
CF3
5h
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 ppm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7.2732
7.2652
7.2611
7.2584
7.0571
7.0486
7.0401
7.0262
7.0177
7.0092
5.8868
5.8738
5.8607
4.3443
4.3402
4.3353
4.3326
4.3200
3.5032
3.4910
3.4802
3.4676
3.4132
3.4031
3.3924
2.6236
2.6081
2.5931
2.3920
2.0497
2.0453
2.0409
2.0365
2.0322
1.5271
1.5152
1.5123
1.4985
1.4413
HO
O
Ph
O
5i
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
2.01
2.03
4.03
2.08
1.01
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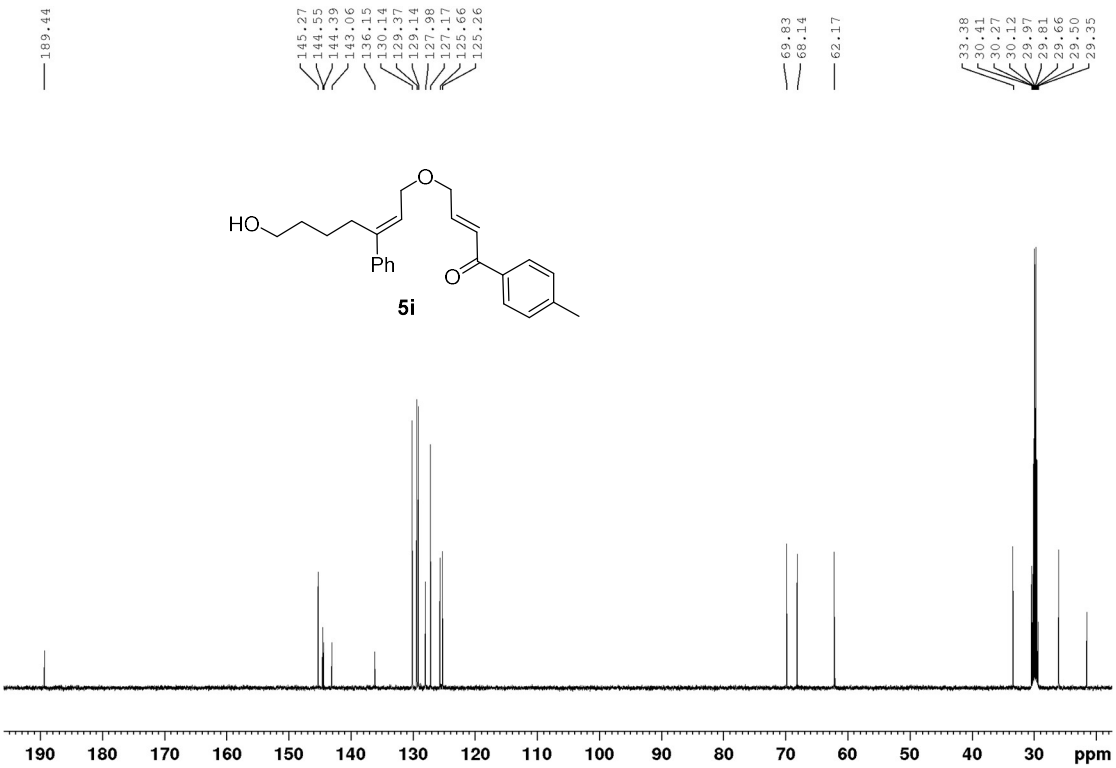
3.96
2.06
0.95
2.02
3.05
2.03
2.06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144.55
144.39
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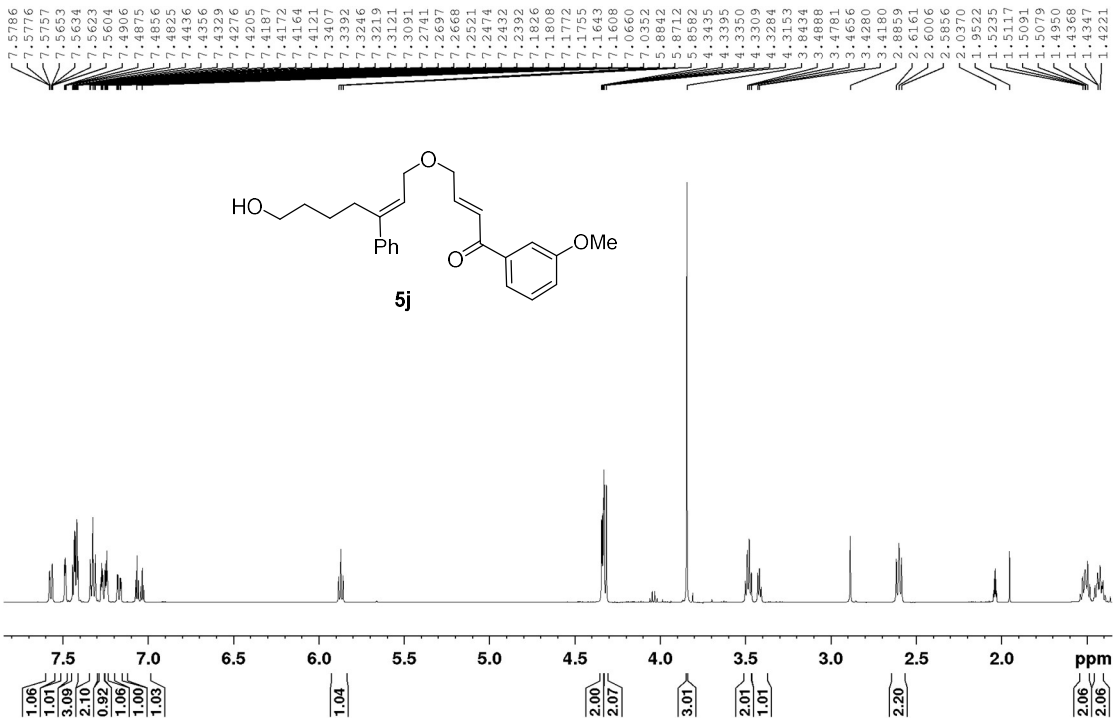
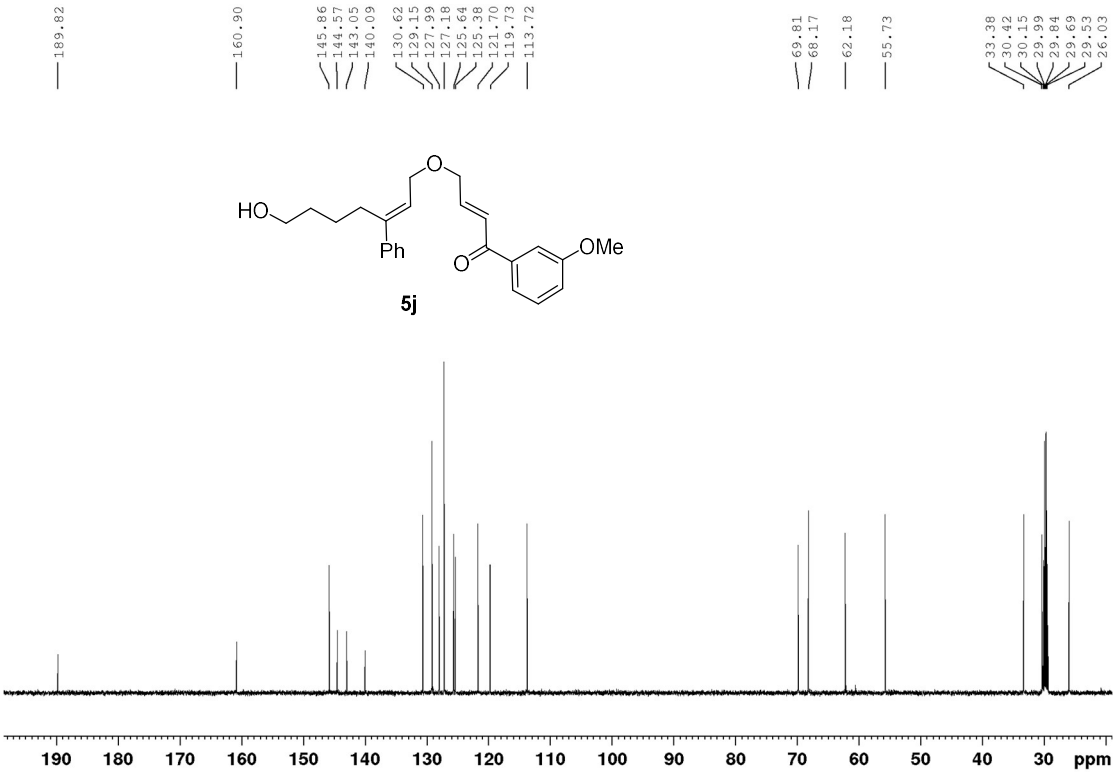
136.15
130.14
129.37
129.14
127.98
127.17
125.66
125.26
69.83
68.14
62.17
33.38
30.41
30.27
30.12
29.97
29.81
29.66
29.50
29.35
HO
O
Ph
O
5i
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm


HO
Ph
O
O
OMe
5j
ppm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Ph
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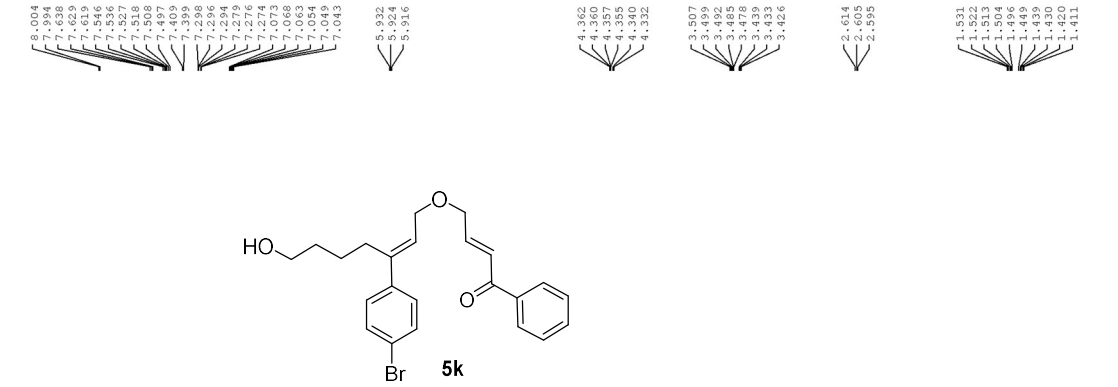
OMe
5j
ppm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7.527
7.518
7.508
7.497
7.499
7.299
7.298
7.296
7.294
7.279
7.276
7.274
7.073
7.068
7.063
7.054
7.049
7.043
5.932
5.924
5.916
4.362
4.360
4.357
4.355
4.340
4.332
3.507
3.499
3.492
3.485
3.478
3.439
3.433
3.426
2.614
2.605
2.595
1.531
1.522
1.513
1.504
1.496
1.449
1.439
1.430
1.420
1.411
HO
O
O
Br
5k
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
2.03
1.02
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2.08
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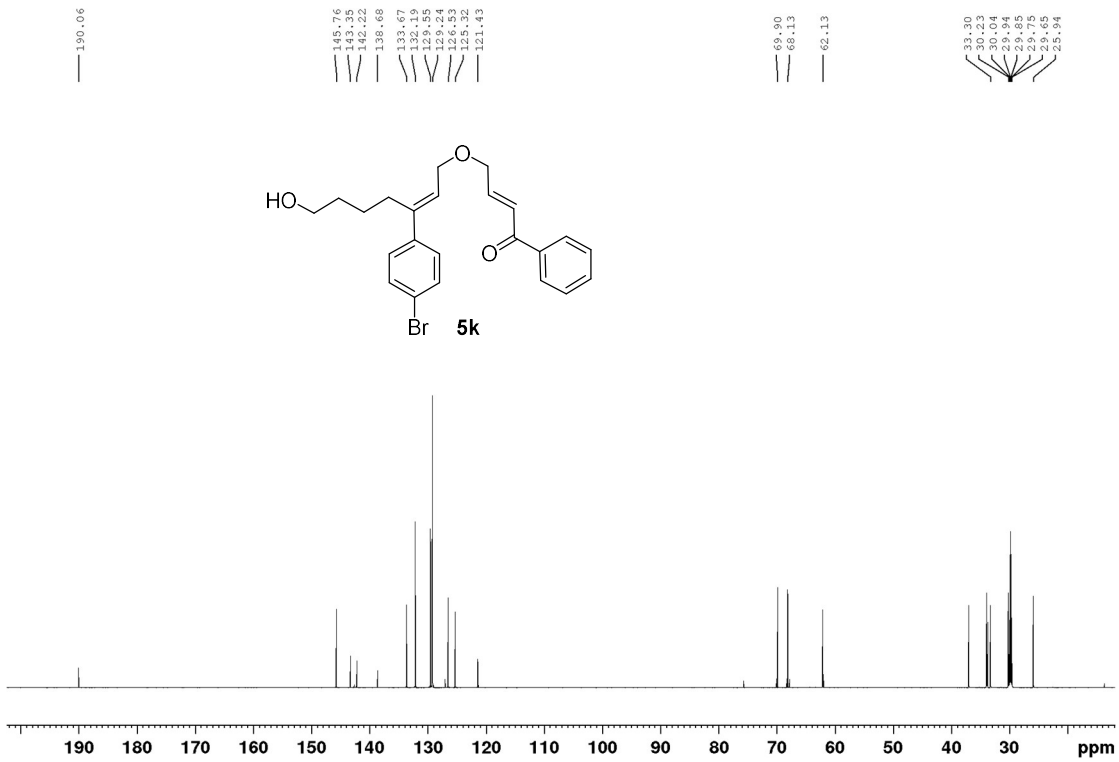
2.10
2.03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132.19
129.55
129.24
126.53
125.32
121.43
69.90
68.13
62.13
33.30
30.23
30.04
29.94
29.85
29.75
29.65
25.94
HO
O
O
Br
5k
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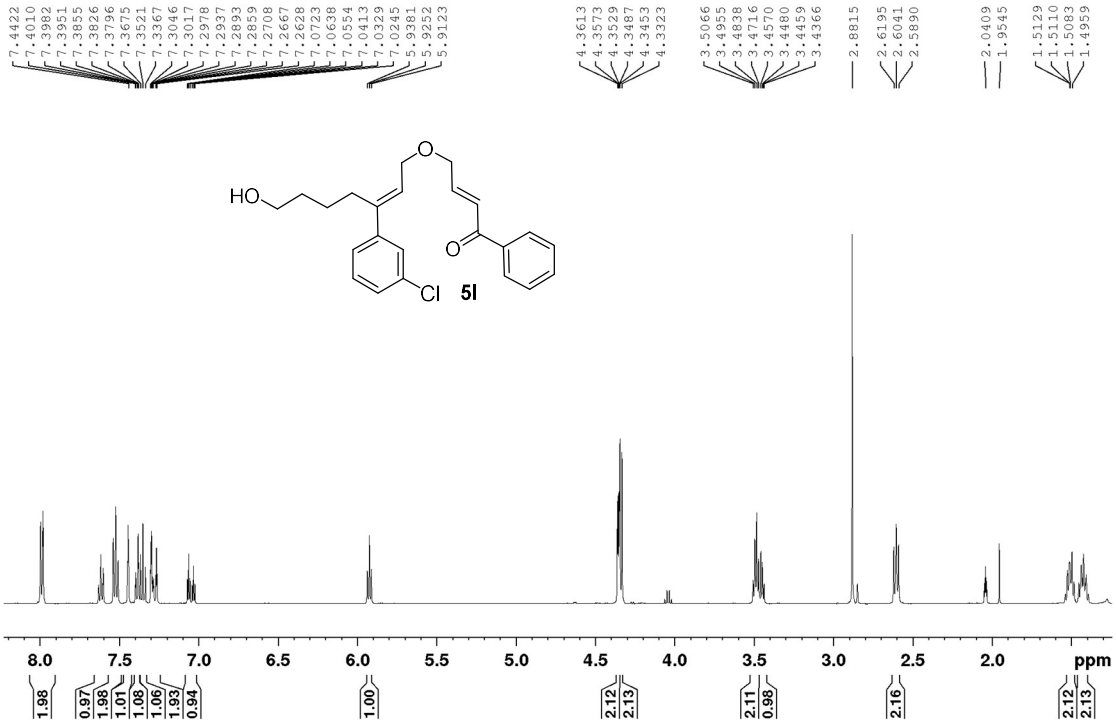
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm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7.3046
7.3017
7.2978
7.2937
7.2893
7.2859
7.2708
7.2667
7.2628
7.0723
7.0638
7.0554
7.0413
7.0329
7.0245
5.9381
5.9252
5.9123
4.3613
4.3573
4.3529
4.3487
4.3453
4.3323
3.5066
3.4955
3.4838
3.4716
3.4570
3.4480
3.4459
3.4366
2.8815
2.6195
2.6041
2.5890
2.0409
1.9545
1.5129
1.5110
1.5083
1.4959
HO
O
O
Cl
5l
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
1.98
0.97
1.98
1.01
1.08
1.06
1.93
0.94
1.00
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2.11
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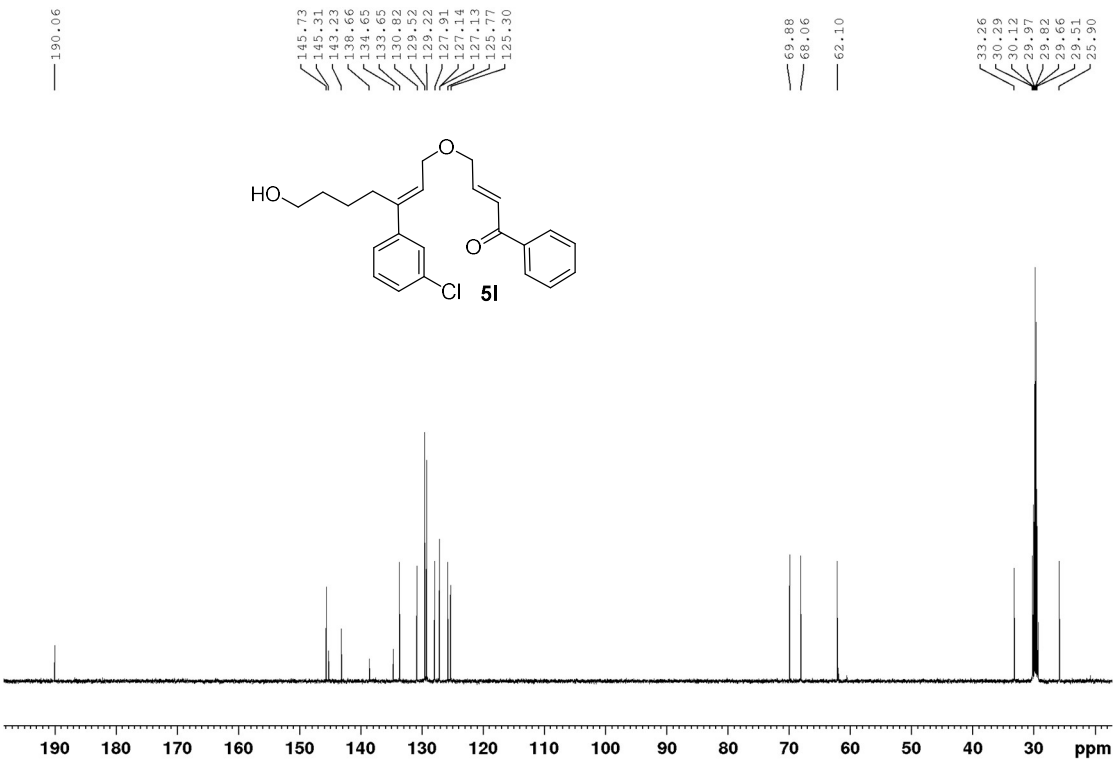
2.12
2.13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133.65
130.82
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129.22
127.91
127.14
127.13
125.77
125.30
69.88
68.06
62.10
33.26
30.29
30.12
29.97
29.82
29.66
29.51
25.90
HO
O
O
Cl
5l
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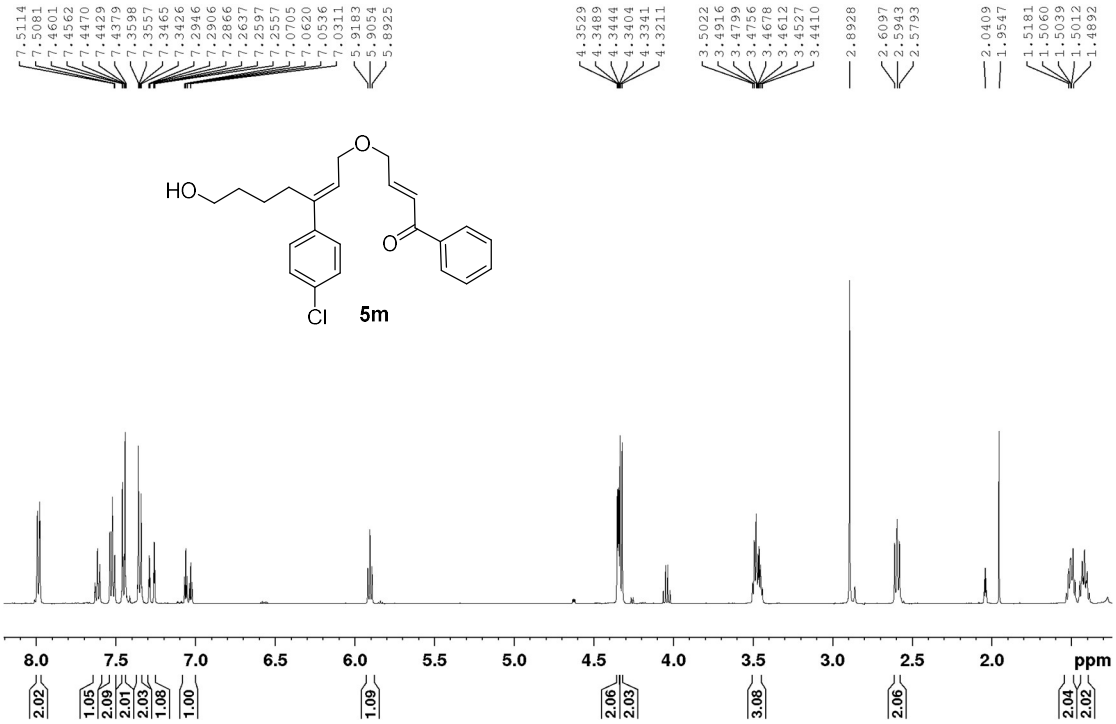
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm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7.2637
7.2597
7.2557
7.0705
7.0620
7.0536
7.0311
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5.9054
5.8925
4.3529
4.3489
4.3444
4.3404
4.3341
4.3211
3.5022
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3.4799
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1.9547
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1.5060
1.5039
1.5012
1.4892
HO
O
O
Cl
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7.0
6.5
6.0
5.5
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3.5
3.0
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2.0
ppm
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1.08
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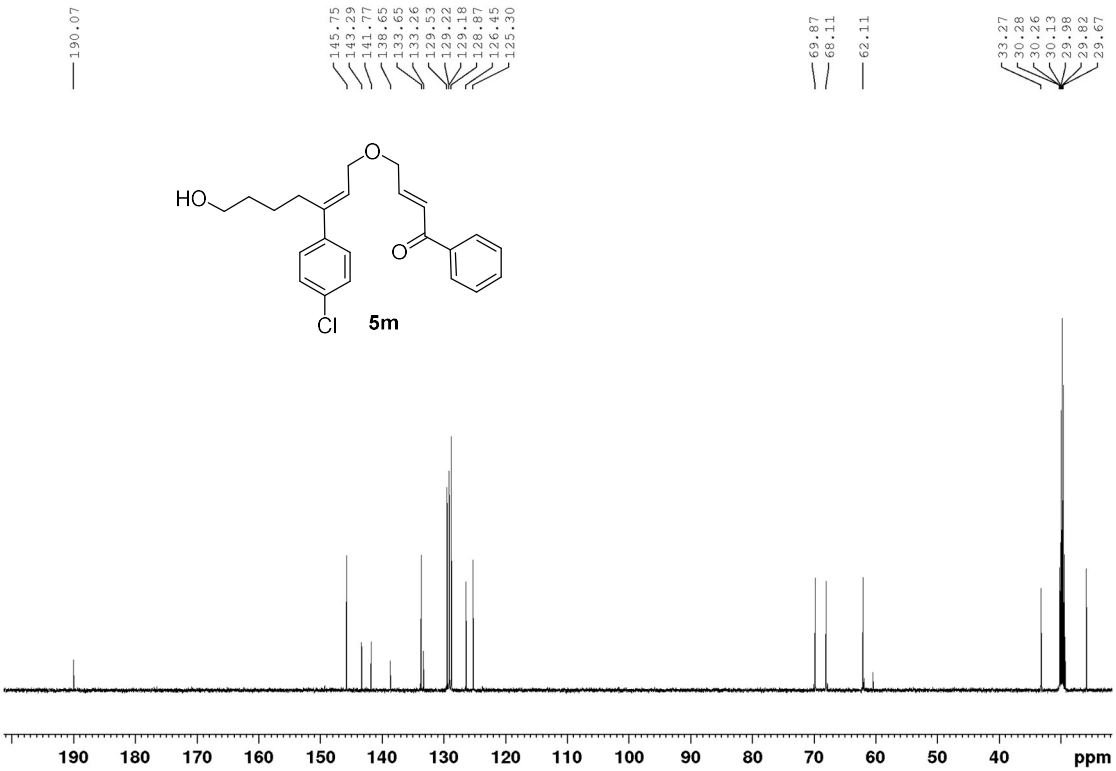
1.09
2.06
2.03
3.08
2.06
2.04
2.02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129.53
129.22
129.18
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126.45
125.30
69.87
68.11
62.11
33.27
30.28
30.26
30.13
29.98
29.82
29.67
HO
O
O
Cl
5m
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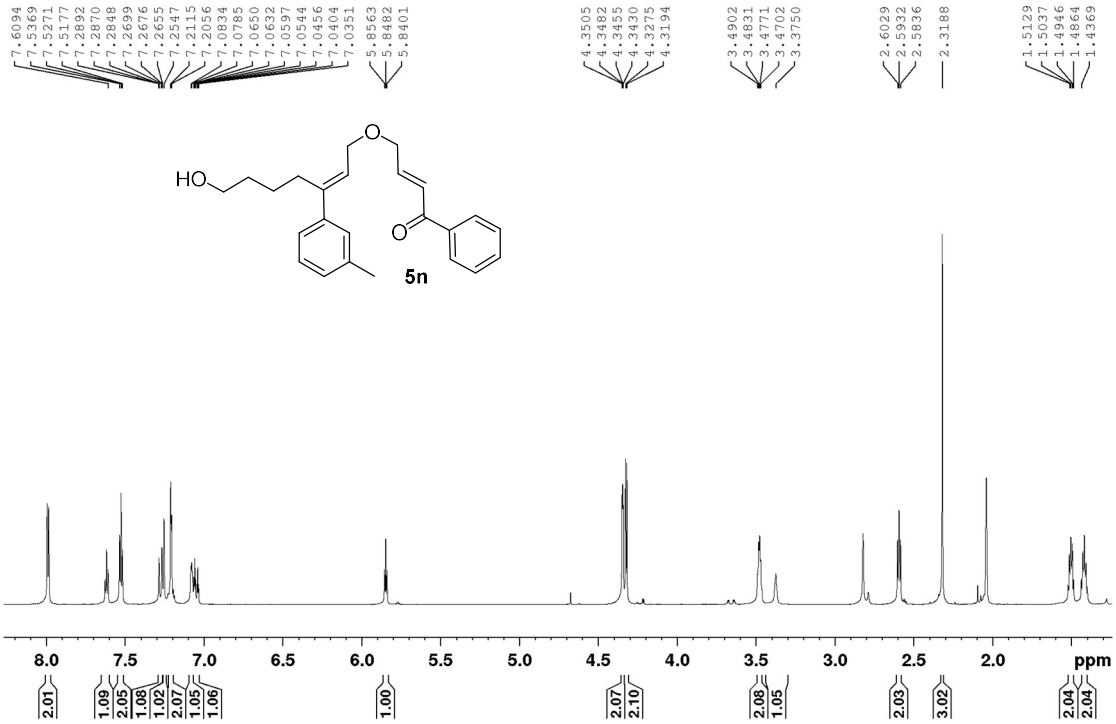
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm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7.0834
7.0785
7.0650
7.0632
7.0597
7.0544
7.0456
7.0404
7.0351
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5.8482
5.8401
4.3505
4.3482
4.3455
4.3430
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3.4771
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2.3188
1.5129
1.5037
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HO
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O
5n
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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
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1.09
2.05
1.08
1.02
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1.06
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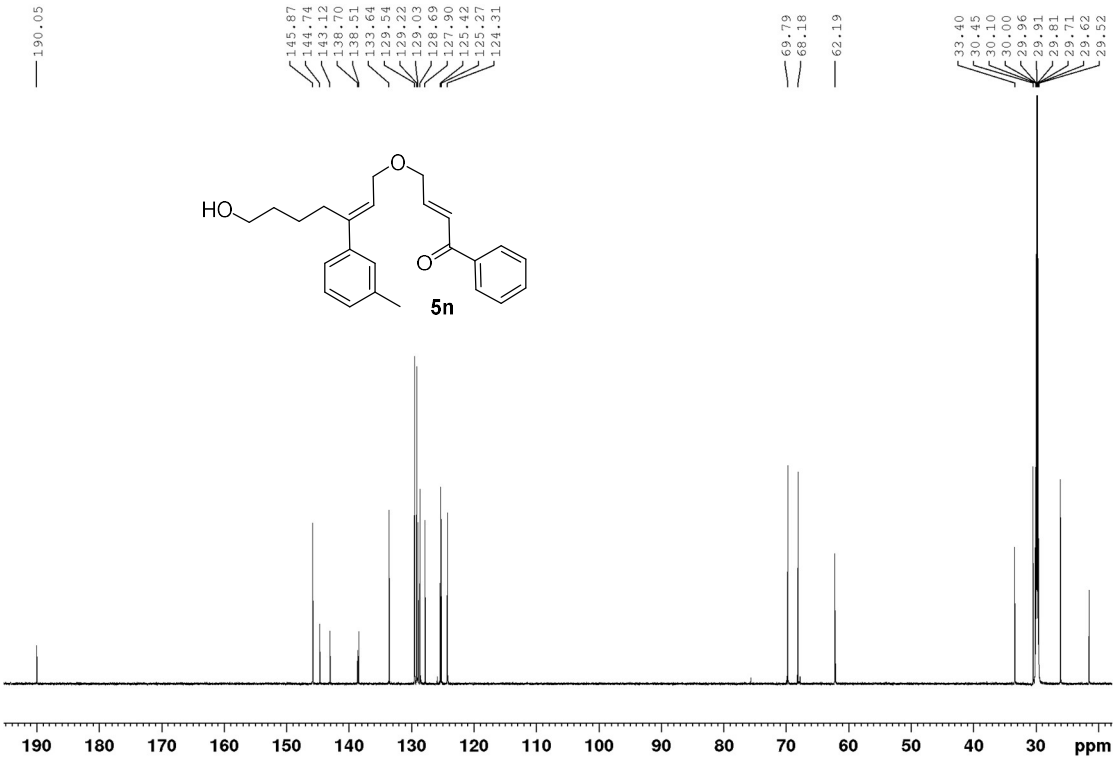
2.08
1.05
2.03
3.02
2.04
2.04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129.22
129.03
128.69
127.90
125.42
125.27
124.31
69.79
68.18
62.19
33.40
30.45
30.10
30.00
29.96
29.91
29.81
29.71
29.62
29.52
HO
O
O
5n
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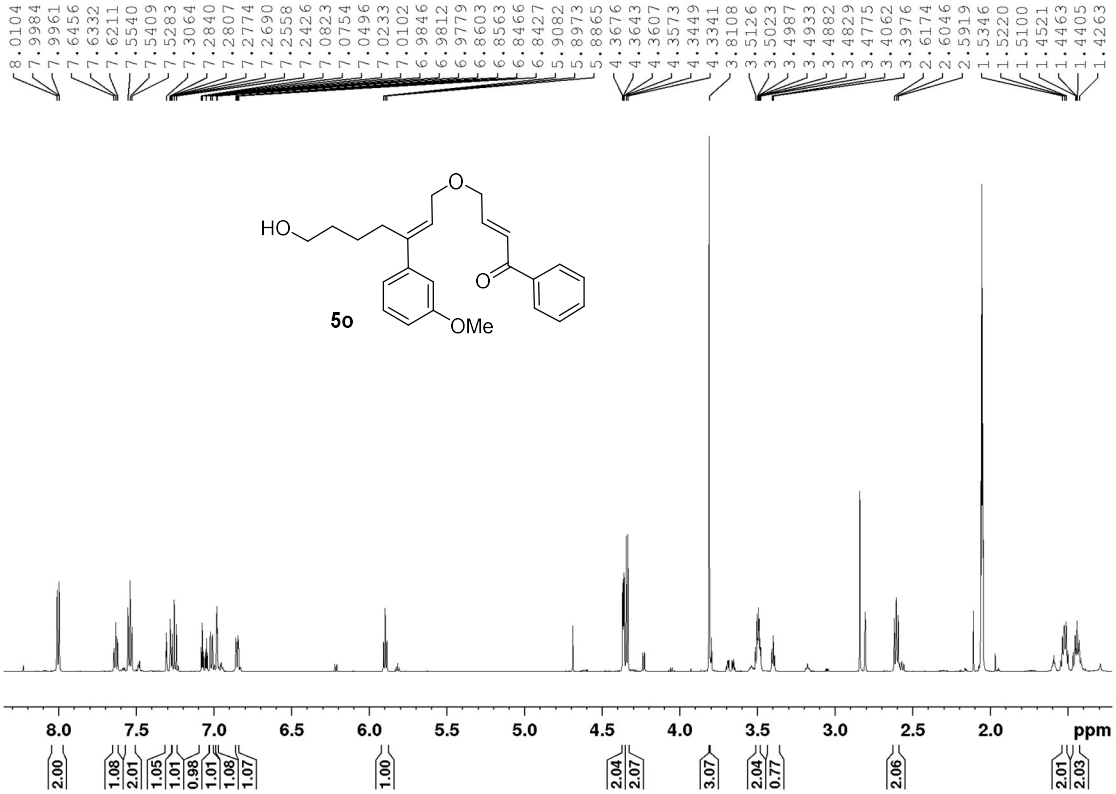
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm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7.2807
7.2774
7.2690
7.2558
7.2426
7.0823
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7.0496
7.0233
7.0102
6.9846
6.9812
6.9779
6.8603
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6.8466
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5.8865
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4.3643
4.3607
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3.5023
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3.4933
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3.4775
3.4062
3.3976
2.6174
2.6046
2.5919
1.5346
1.5220
1.5100
1.4521
1.4463
1.4405
1.4263
HO
O
O
OMe
5o
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
2.00
1.08
2.01
1.05
1.01
0.98
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1.00
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2.07
3.07
2.04
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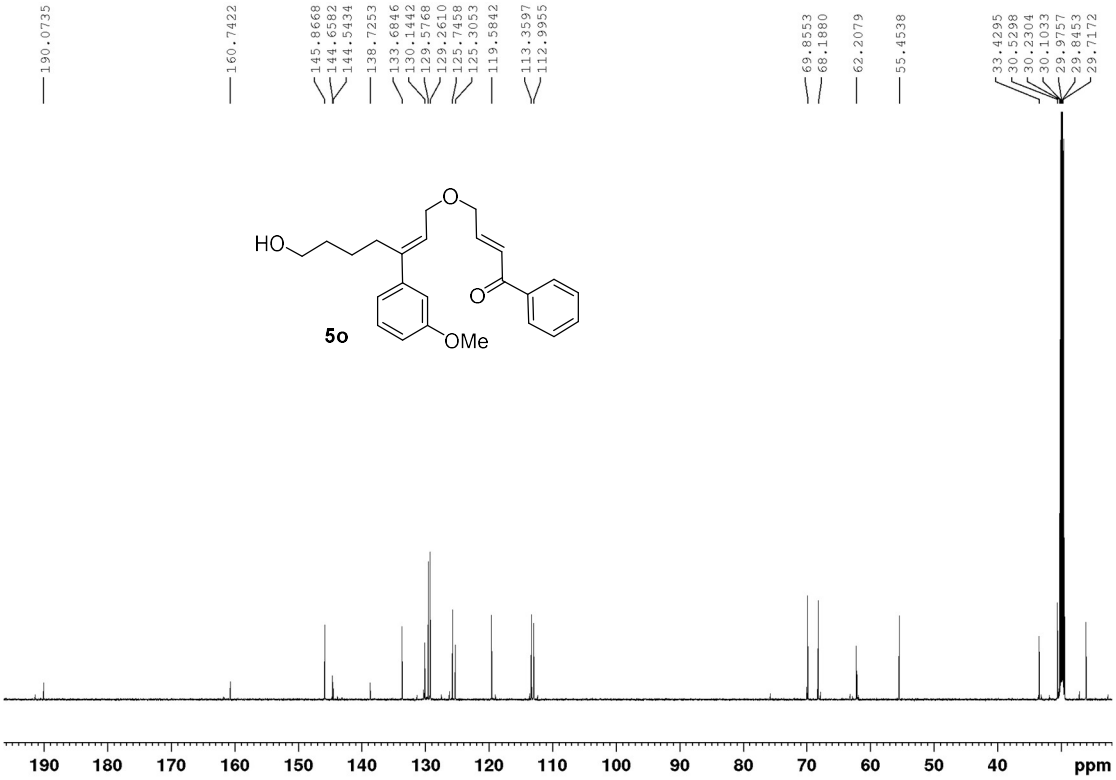
2.03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113.3597
112.9955
69.8553
68.1880
62.2079
55.4538
33.4295
30.5298
30.2304
30.1033
29.9757
29.8453
29.7172
HO
O
O
OMe
5o
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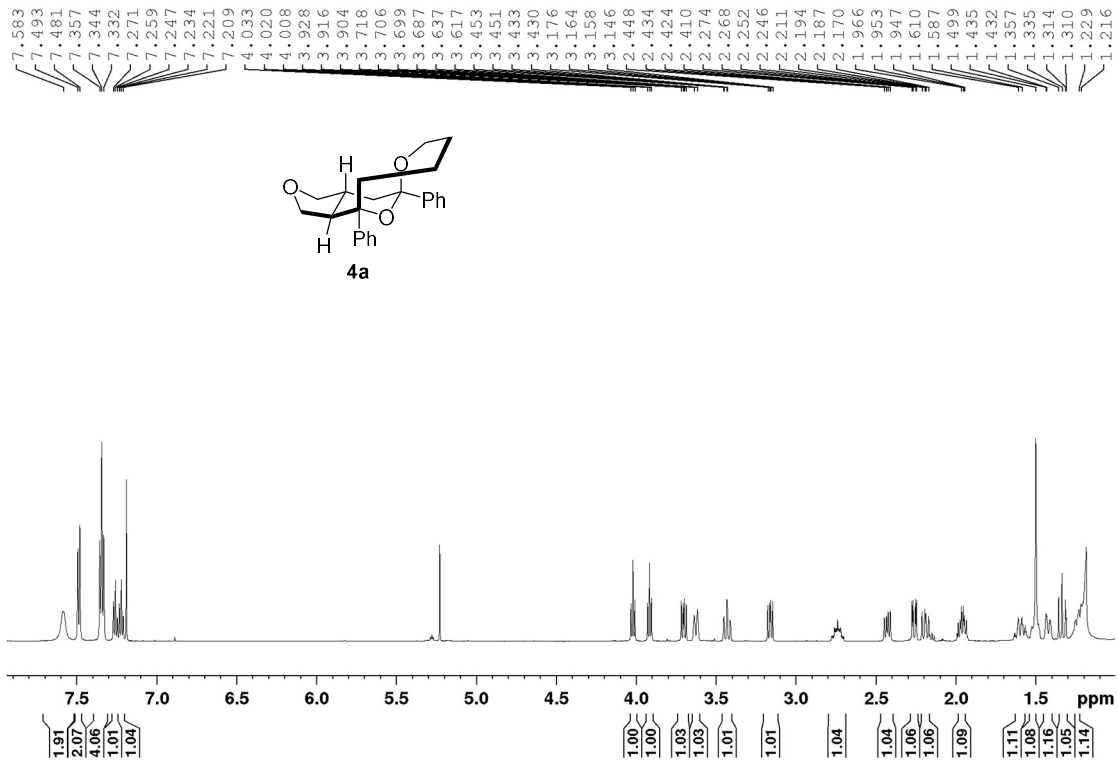
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm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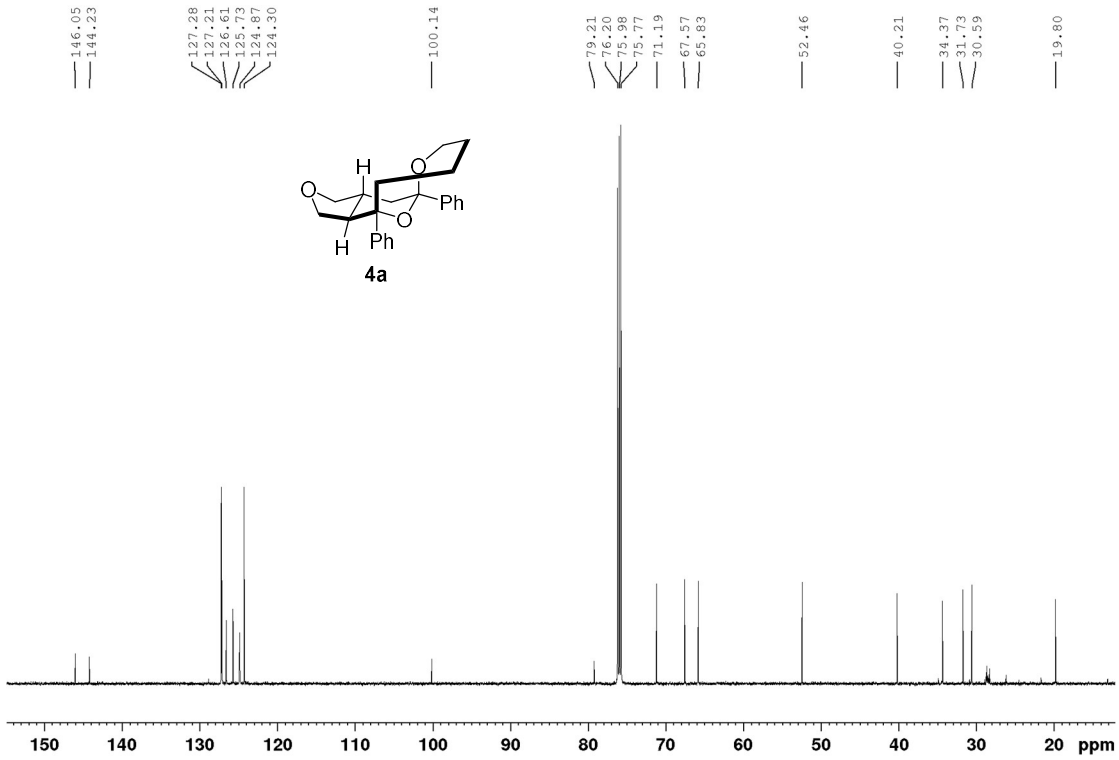
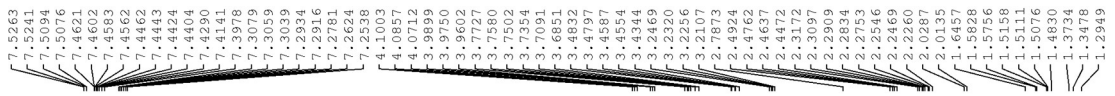
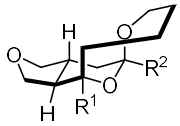
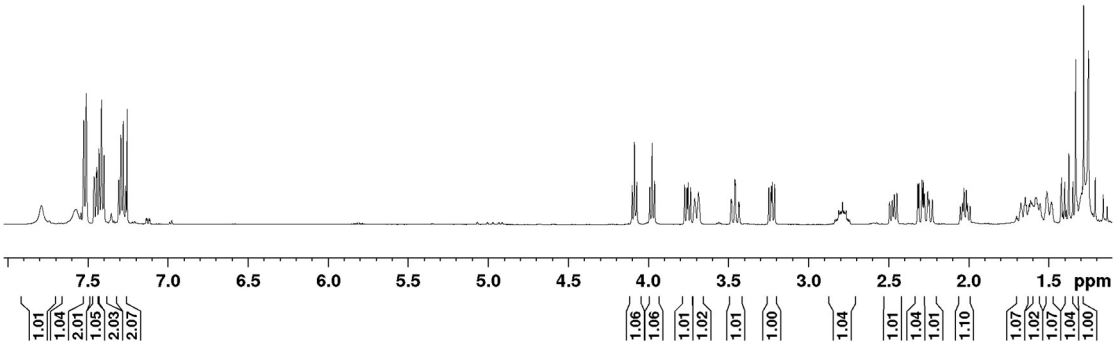
H
O
O
Ph
O
H
Ph
4a
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 ppm
1.91 2.07 4.06 1.01 1.04 1.00 1.00 1.03 1.03 1.01 1.01 1.04 1.04 1.06 1.06 1.09 1.11 1.08 1.16 1.05 1.14

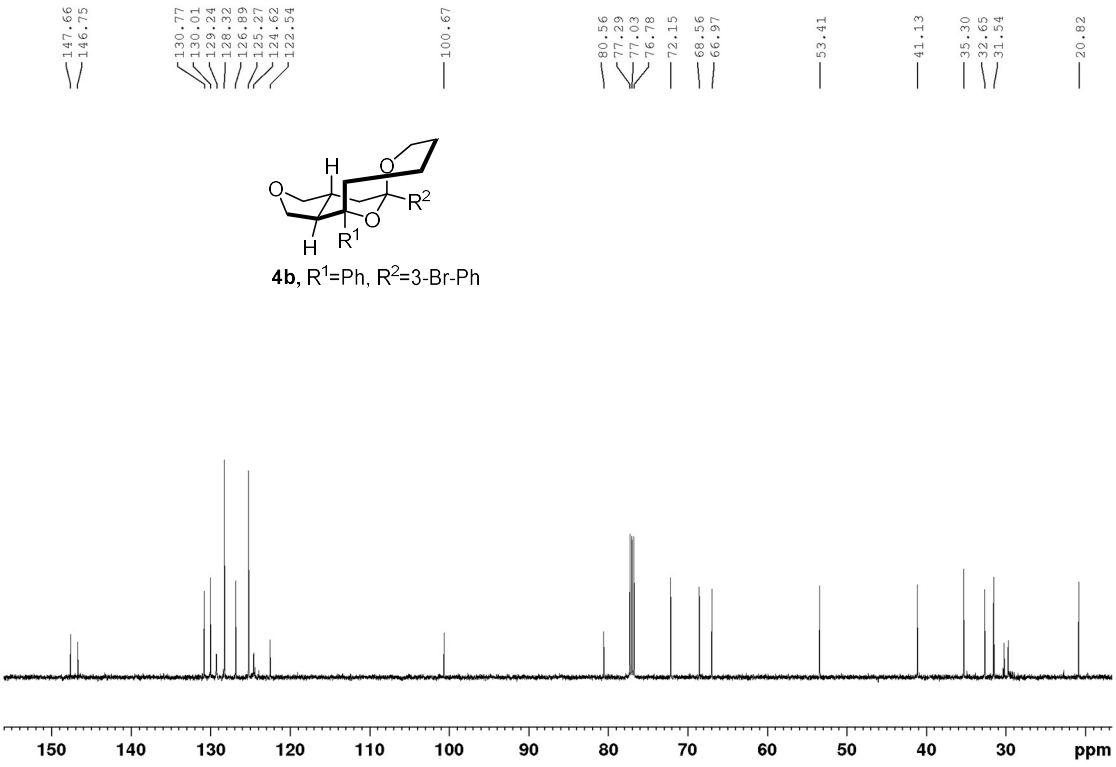

146.05 144.23 127.28 127.21 126.61 125.73 124.87 124.30 100.14 79.21 76.20 75.98 75.77 71.19 67.57 65.83 52.46 40.21 34.37 31.73 30.59 19.80
H
O
O
Ph
O
H
Ph
4a
150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm



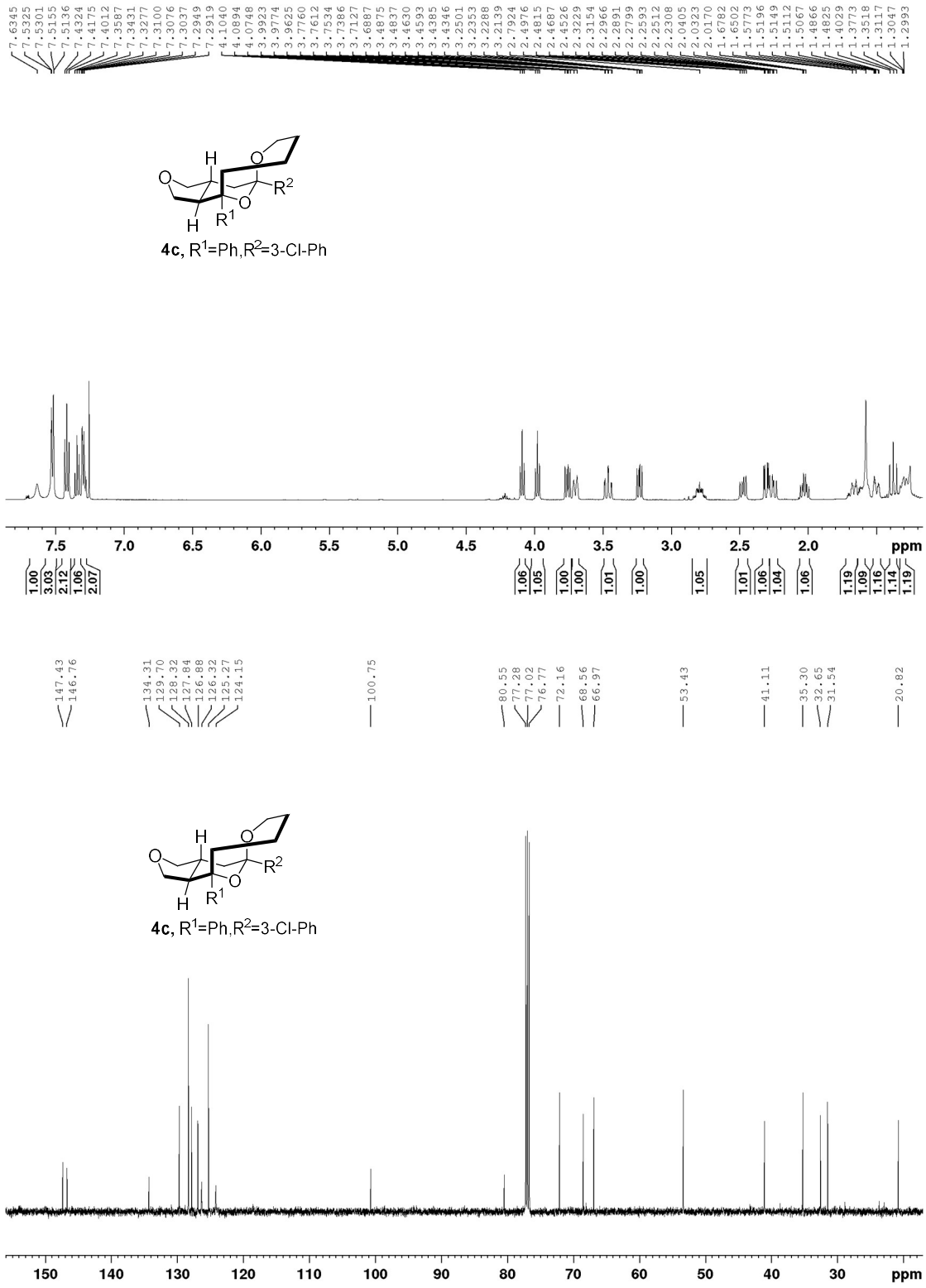


4b, R^1=Ph, R^2=3-Br-Ph





4b, R^1=Ph, R^2=3-Br-Ph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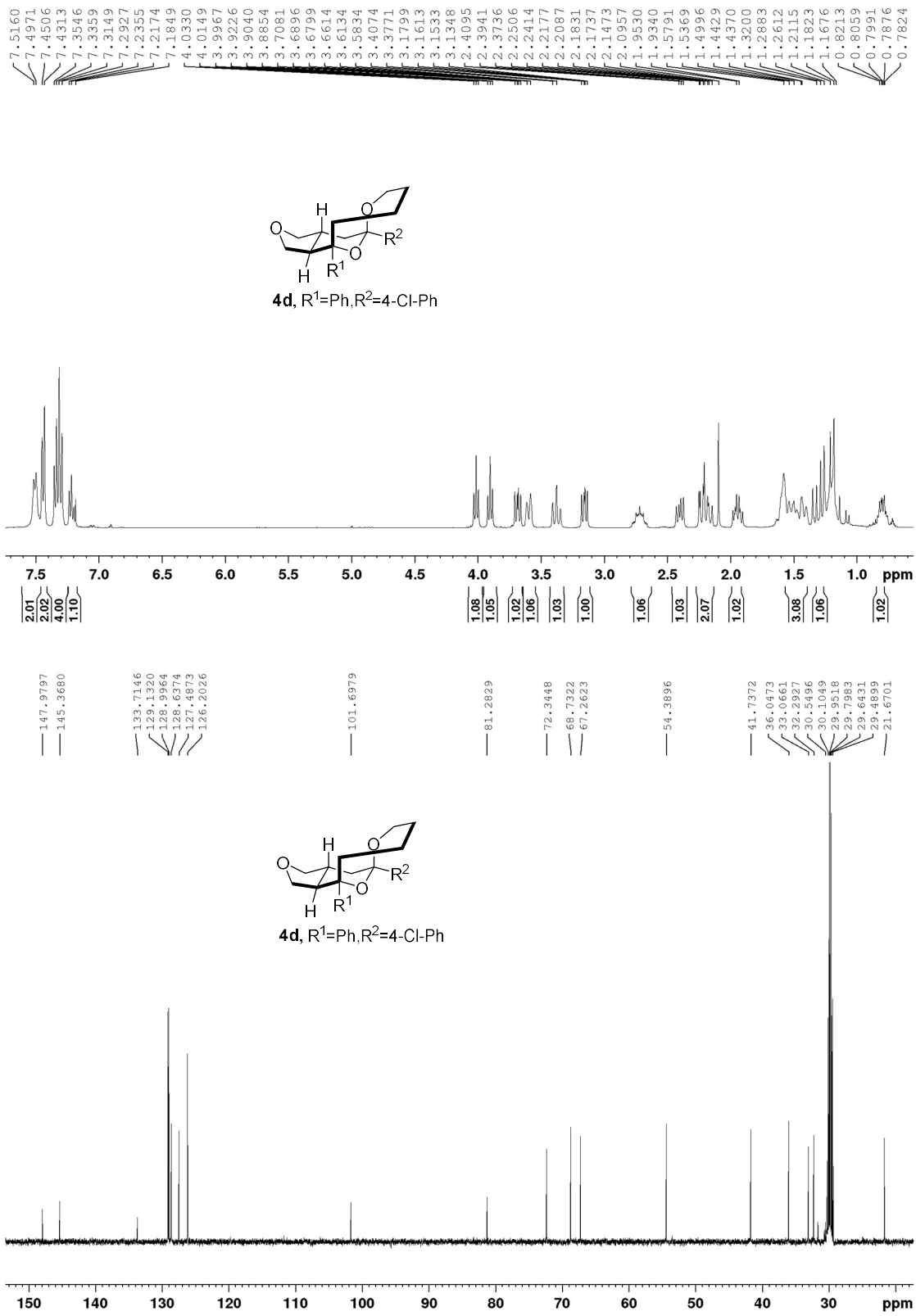
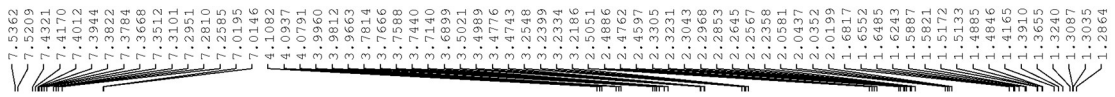
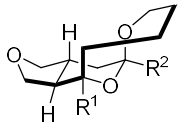
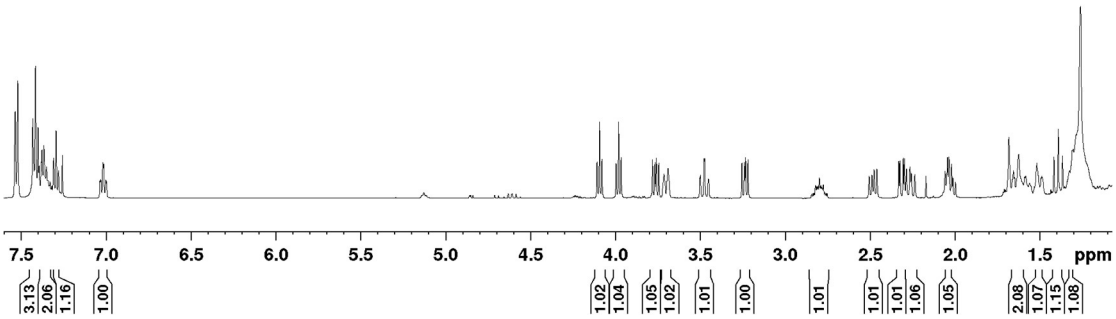
H
O
O
R2
O
H
R1
4c, R1=Ph,R2=3-Cl-Ph
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 ppm
1.00 3.03 2.12 1.06 2.07 1.06 1.05 1.00 1.00 1.01 1.00 1.05 1.01 1.06 1.04 1.06 1.19 1.09 1.16 1.14 1.19
147.43 146.76 134.31 129.70 128.32 127.84 126.88 126.32 125.27 124.15 100.75 80.55 77.28 77.02 76.77 72.16 68.56 66.97 53.43 41.11 35.30 32.65 31.54 20.82
H
O
O
R2
O
H
R1
4c, R1=Ph,R2=3-Cl-Ph
150 140 130 120 110 100 90 80 70 60 50 40 30 ppm

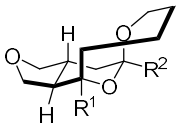

7.5160 7.4971 7.4506 7.4313 7.3546 7.3359 7.3149 7.2927 7.2355 7.2174 7.1849
4.0330 4.0149 3.9967 3.9226 3.9040 3.8854 3.7081 3.6896 3.6799 3.6614 3.6134 3.5834 3.4074 3.3771 3.1799 3.1613 3.1533 3.1348 2.4095 2.3941 2.3736 2.2506 2.2414 2.2177 2.2087 2.1831 2.1737 2.1473 2.0957 1.9530 1.9340 1.5791 1.5369 1.4996 1.4429 1.4370 1.3200 1.2883 1.2612 1.2115 1.1823 1.1676 0.8213 0.8059 0.7991 0.7876 0.7824
H
O
O
R2
O
H
R1
4d, R1=Ph,R2=4-Cl-Ph
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.01 2.02 4.00 1.10 1.08 1.05 1.02 1.06 1.03 1.00 1.06 1.03 2.07 1.02 3.08 1.06 1.02
147.9797 145.3680 133.7146 129.1320 128.9964 128.6374 127.4873 126.2026 101.6979 81.2829 72.3448 68.7322 67.2623 54.3896 41.7372 36.0473 33.0661 32.2927 30.5496 30.1049 29.9518 29.7983 29.6431 29.4899 21.6701
H
O
O
R2
O
H
R1
4d, R1=Ph,R2=4-Cl-Ph
150 140 130 120 110 100 90 80 70 60 50 40 30 ppm



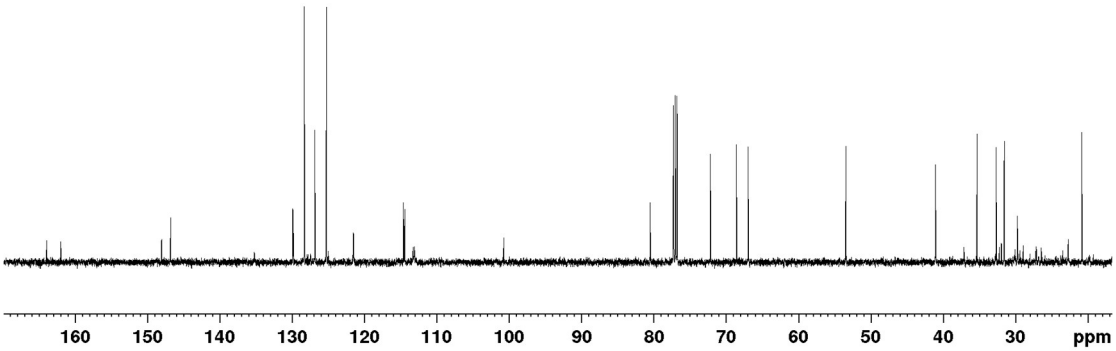


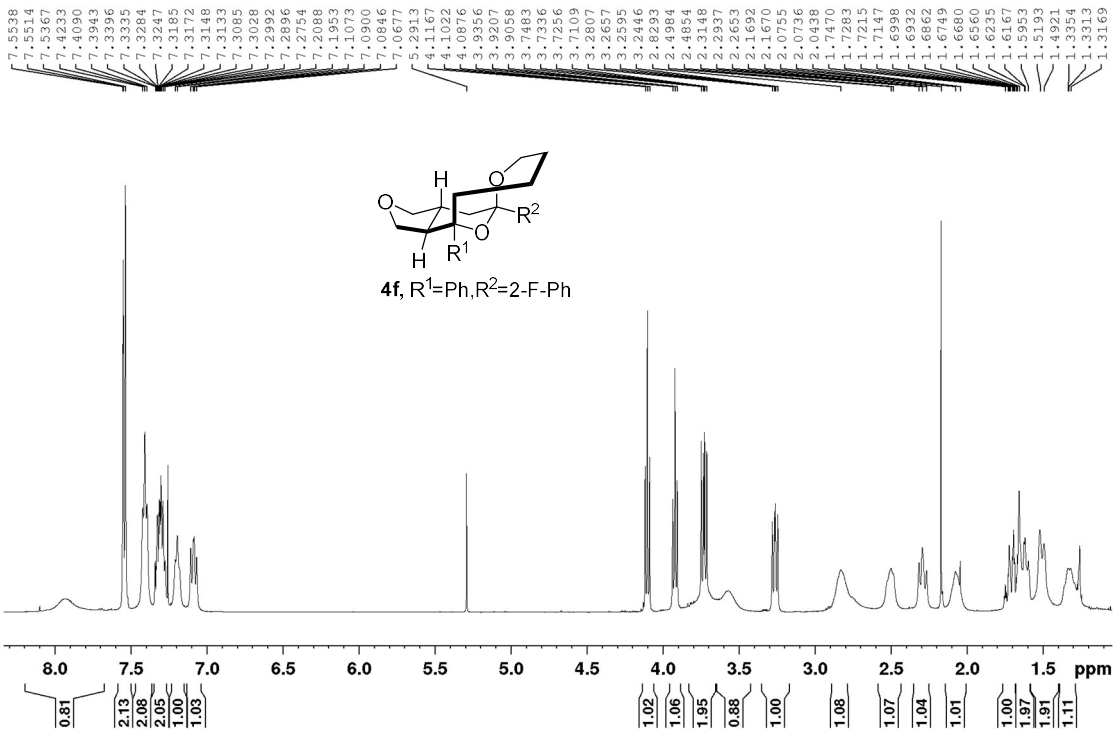
4e, R^1=Ph,R^2=3-F-Ph

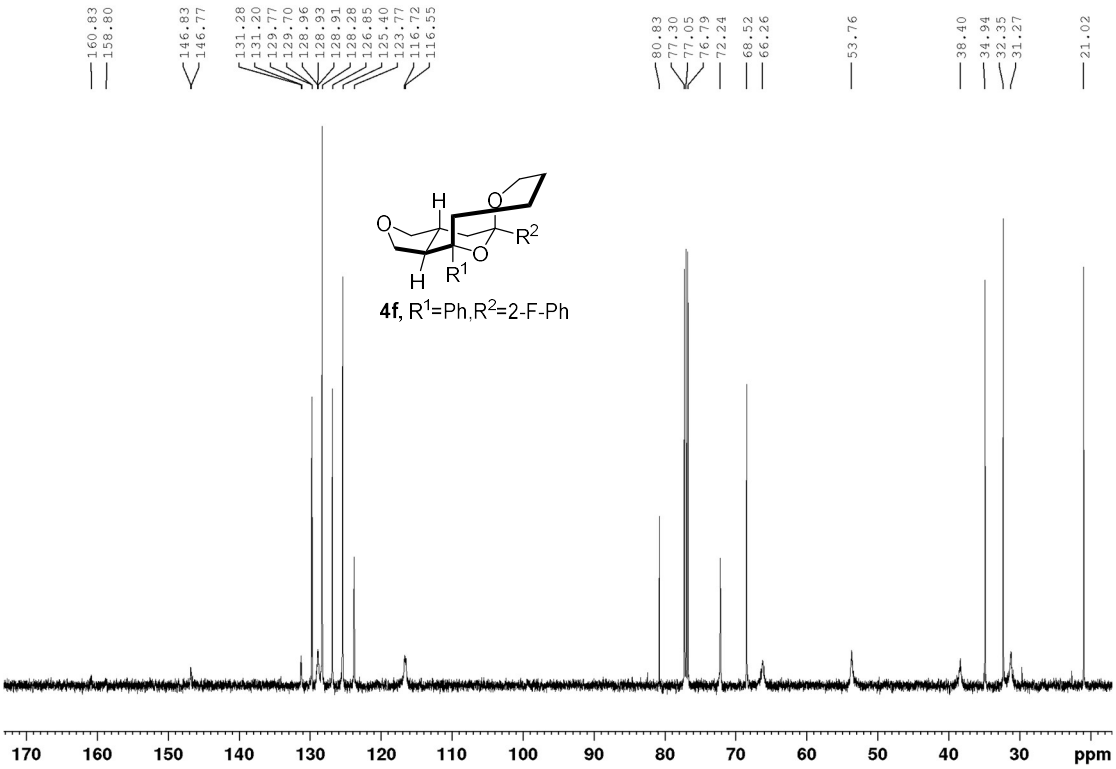


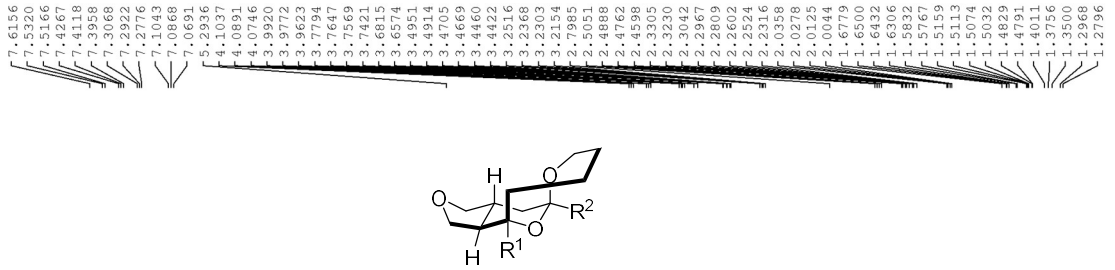


4e, R^1=Ph,R^2=3-F-Ph

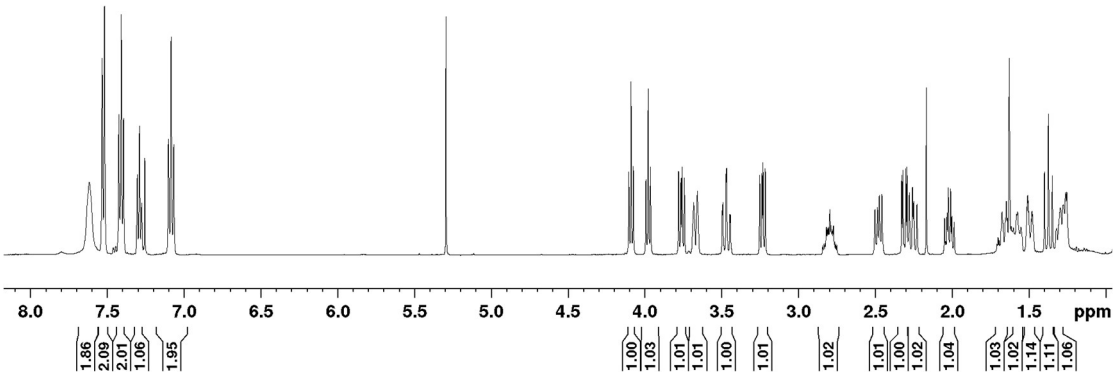


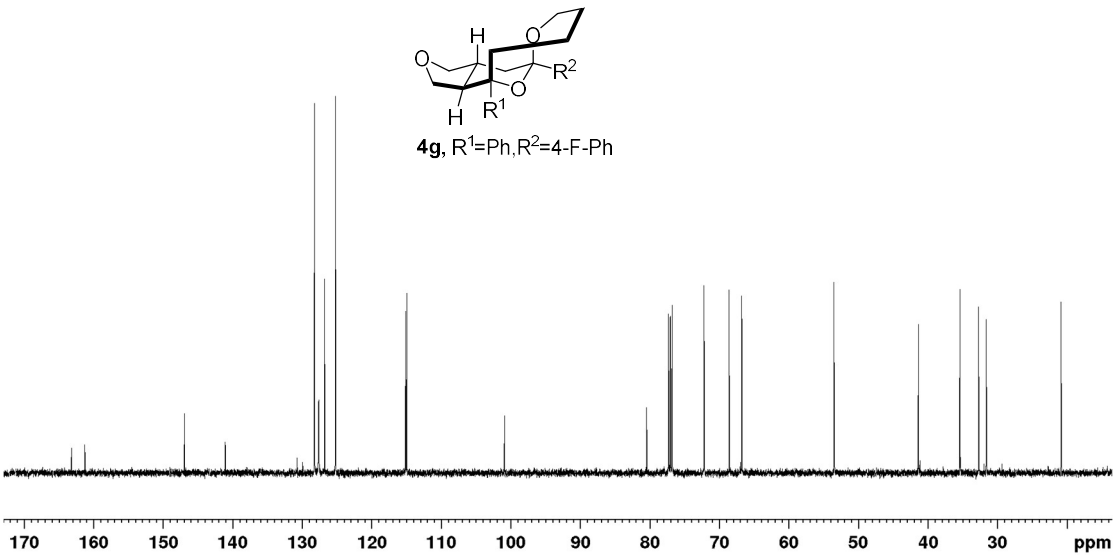

4f, R1=Ph,R2=2-F-Ph
ppm


4f, R1=Ph,R2=2-F-Ph
ppm

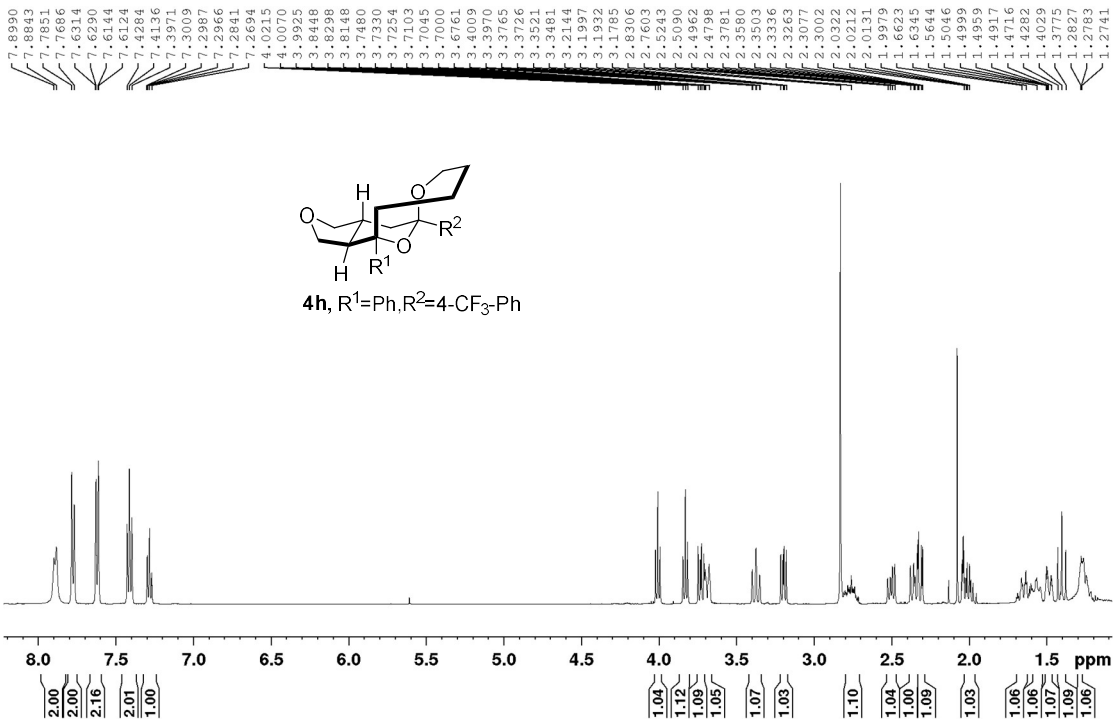


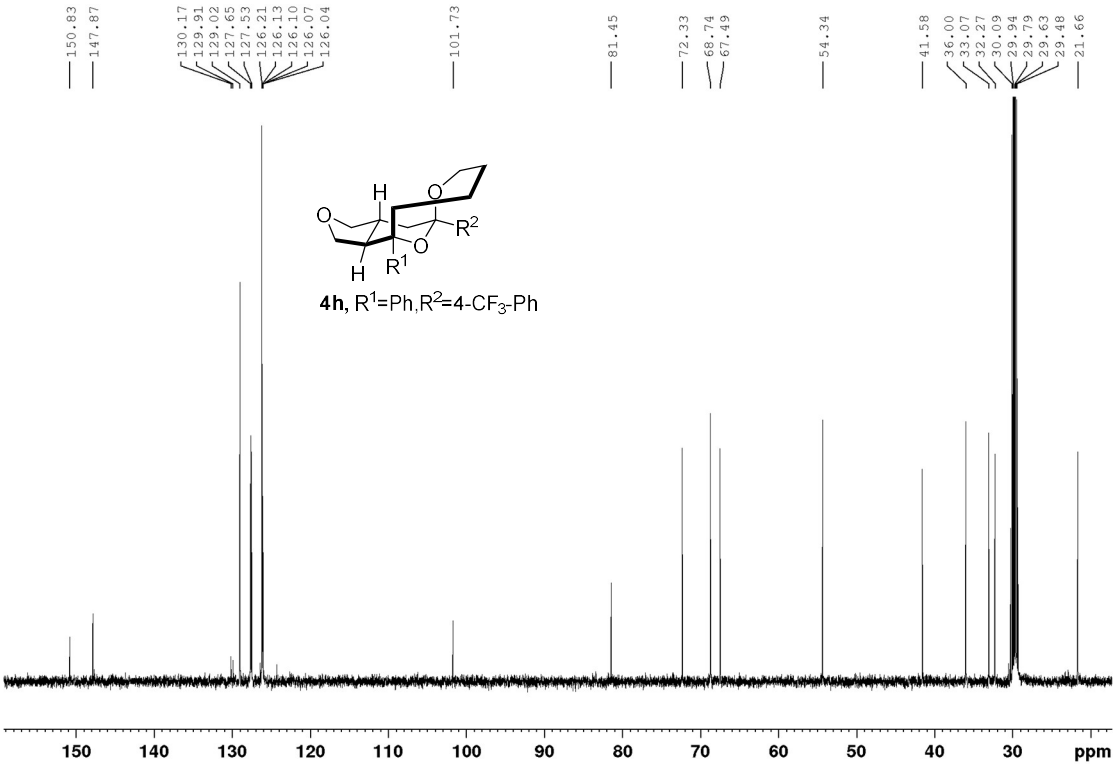
4g, R^1=Ph,R^2=4-F-Ph

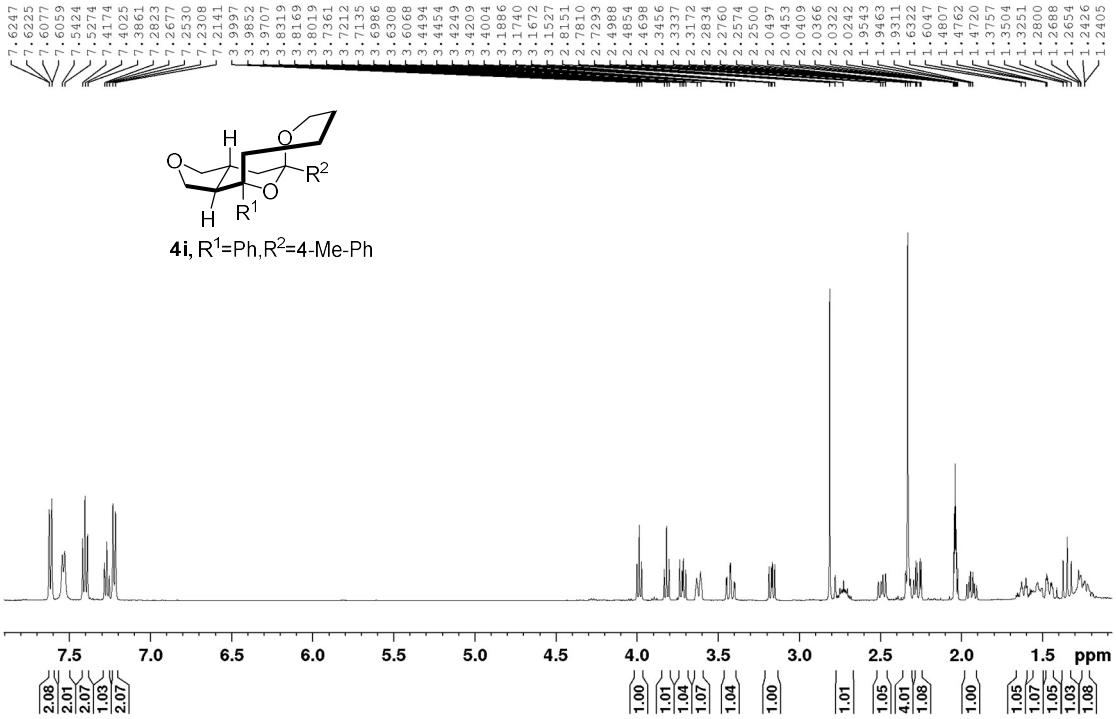




4g, R^1=Ph,R^2=4-F-Ph


4h, R1=Ph,R2=4-CF3-Ph
ppm


4h, R1=Ph,R2=4-CF3-Ph
ppm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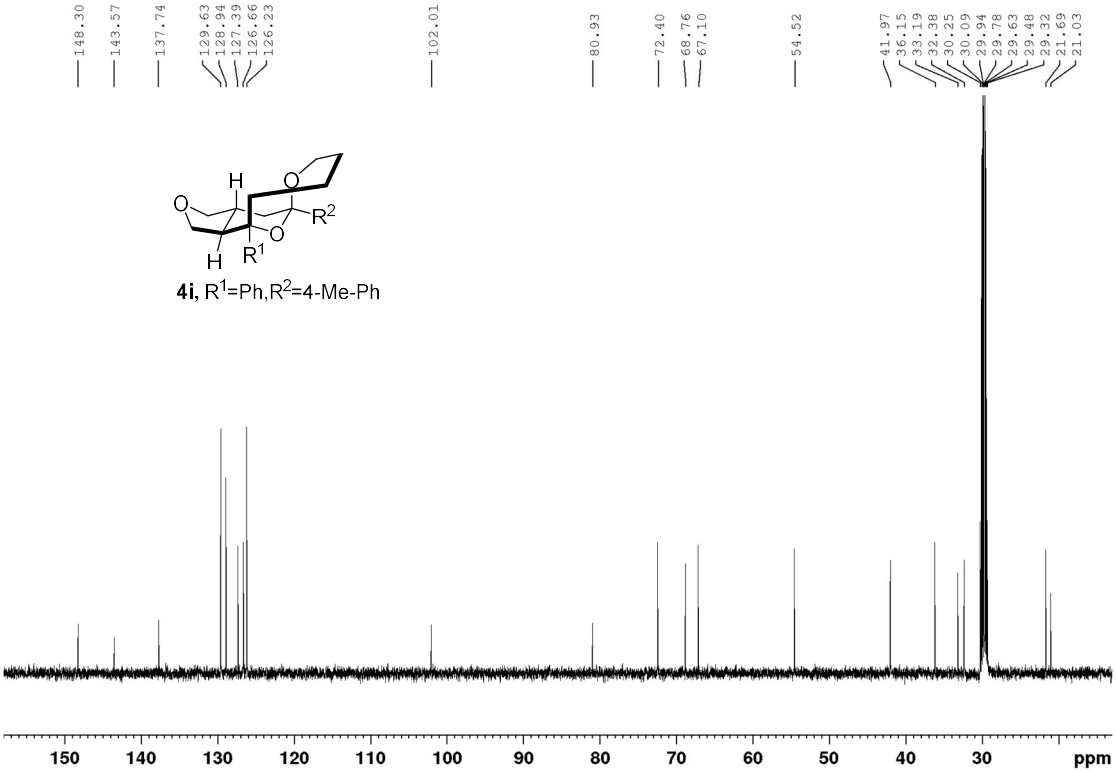
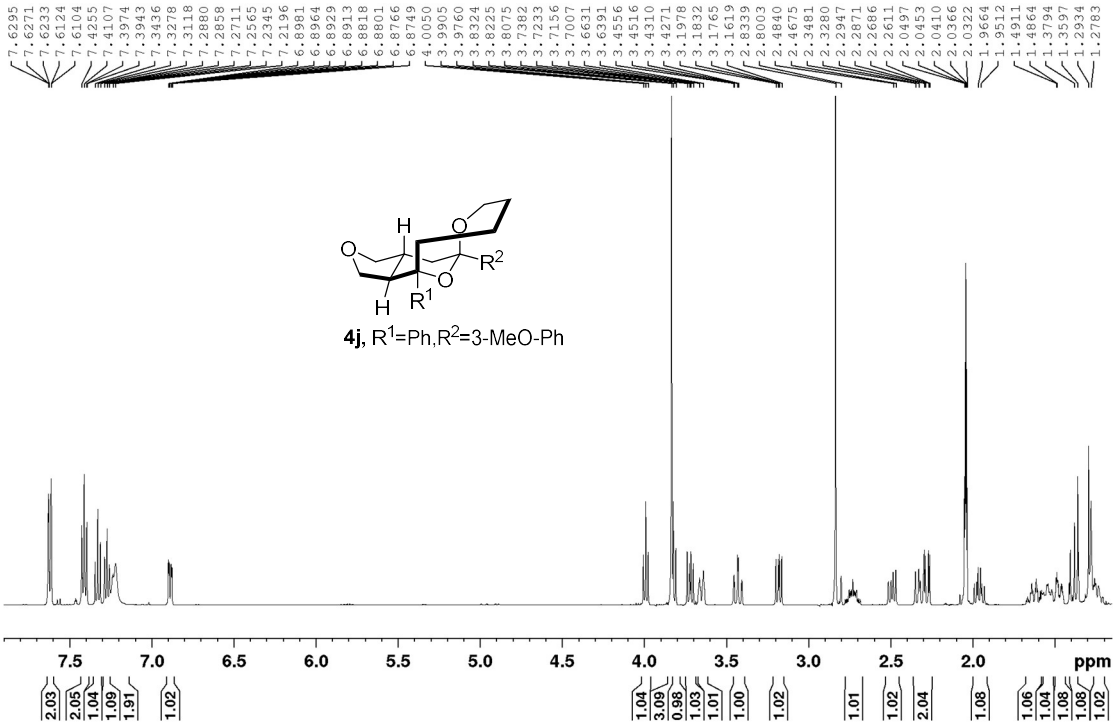
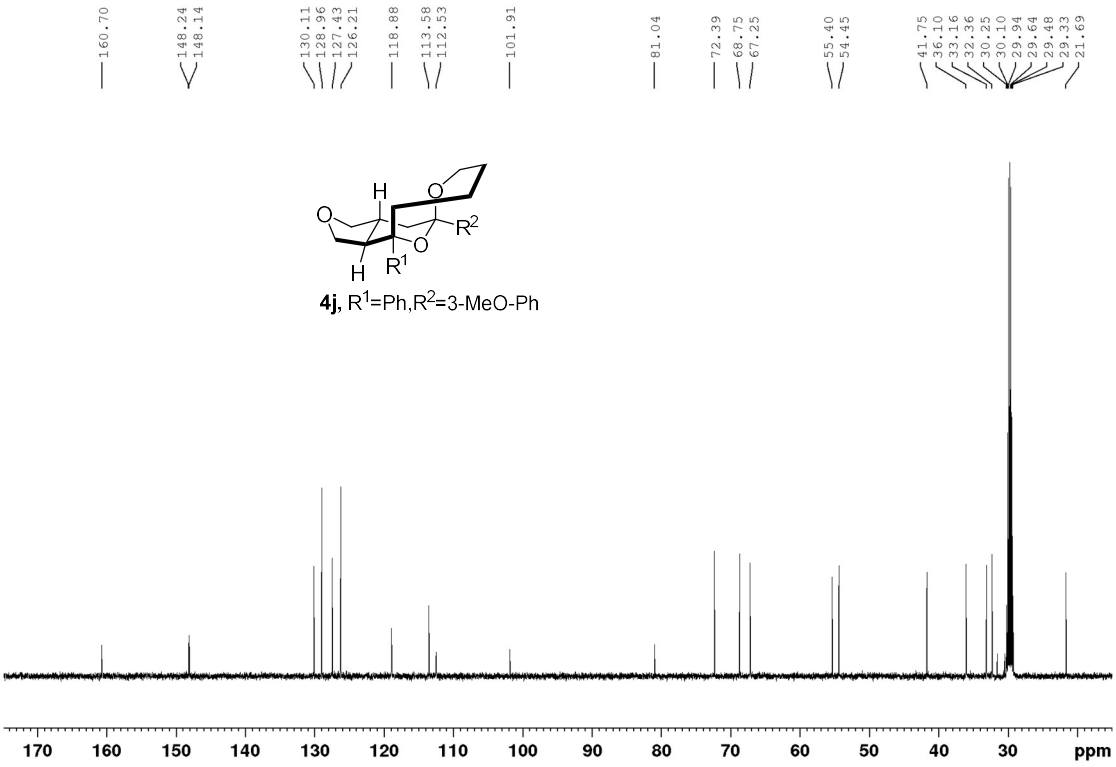
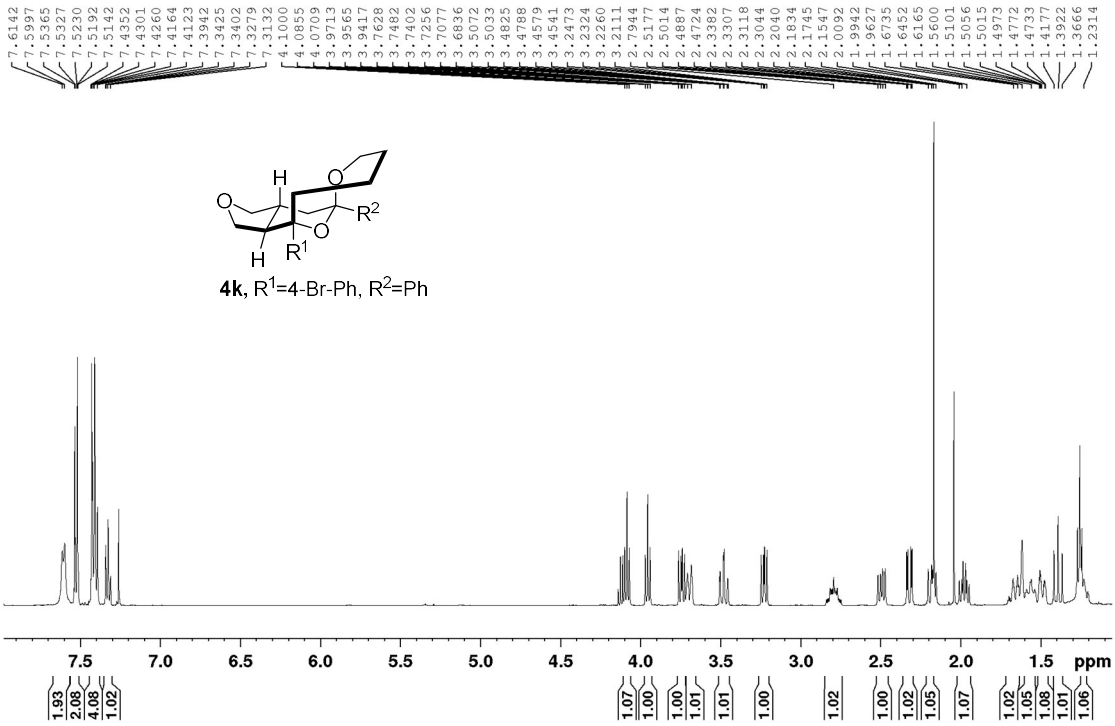
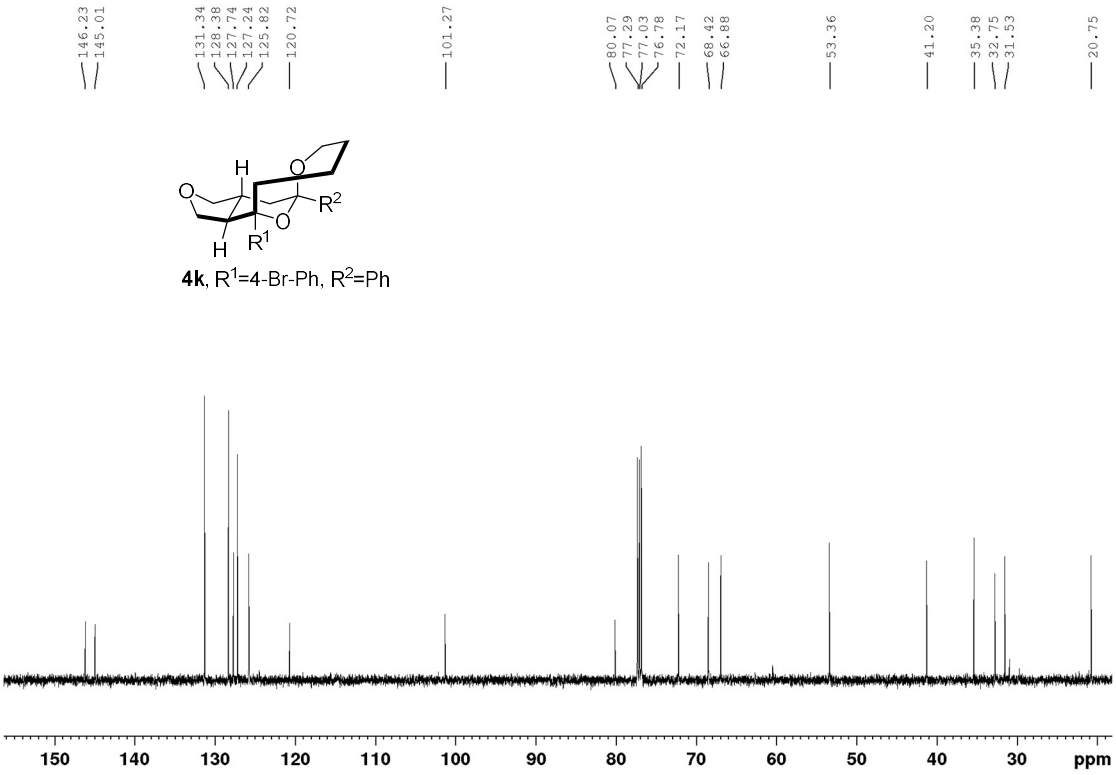
3.9997 3.9852 3.9707 3.8319 3.8169 3.8019 3.7361 3.7212 3.7135 3.6986 3.6308 3.6068 3.4494 3.4454 3.4249 3.4209 3.4004 3.1886 3.1740 3.1672 3.1527 2.8151 2.7810 2.7293 2.4988 2.4854 2.4698 2.3456 2.3337 2.3172 2.2834 2.2760 2.2574 2.2500 2.0497 2.0453 2.0409 2.0366 2.0322 2.0242 1.9543 1.9463 1.9311 1.6322 1.6047 1.4807 1.4762 1.4720 1.3757 1.3504 1.3251 1.2800 1.2688 1.2654 1.2426 1.2405
H
O
O
R2
O
H
R1
4i, R1=Ph,R2=4-Me-Ph
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 ppm
2.08 2.01 2.07 1.03 2.07
1.00 1.01 1.04 1.07 1.04 1.00 1.01 1.05 4.01 1.08 1.00 1.05 1.07 1.05 1.03 1.08

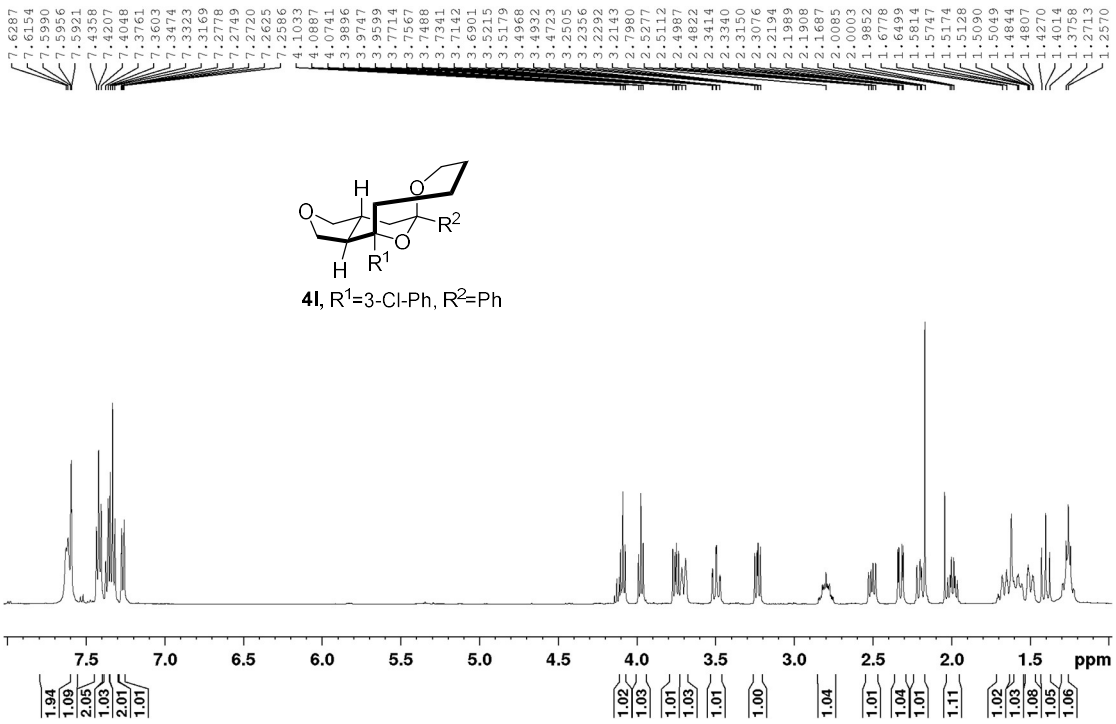

148.30 143.57 137.74 129.63 128.94 127.39 126.66 126.23 102.01 80.93 72.40 68.76 67.10 54.52 41.97 36.15 33.19 32.38 30.25 30.09 29.94 29.78 29.63 29.48 29.32 21.69 21.03
H
O
O
R2
O
H
R1
4i, R1=Ph,R2=4-Me-Ph
150 140 130 120 110 100 90 80 70 60 50 40 30 ppm

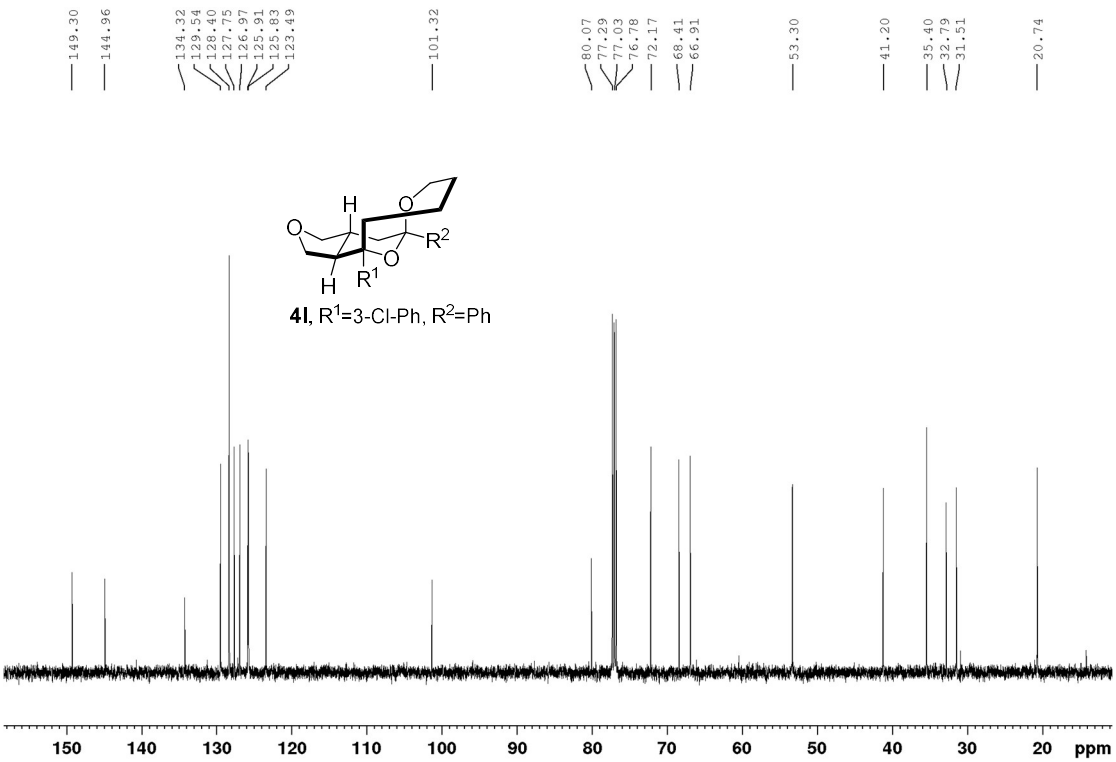

4j, R1=Ph,R2=3-MeO-Ph
ppm

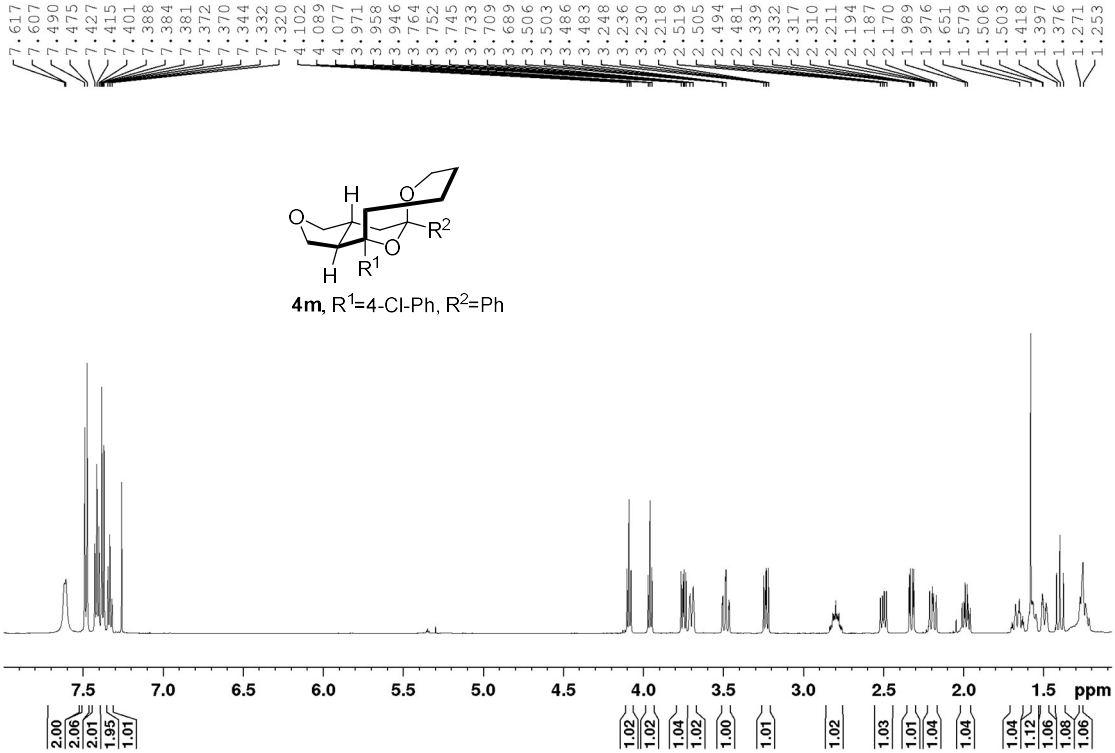

4j, R1=Ph,R2=3-MeO-Ph
ppm

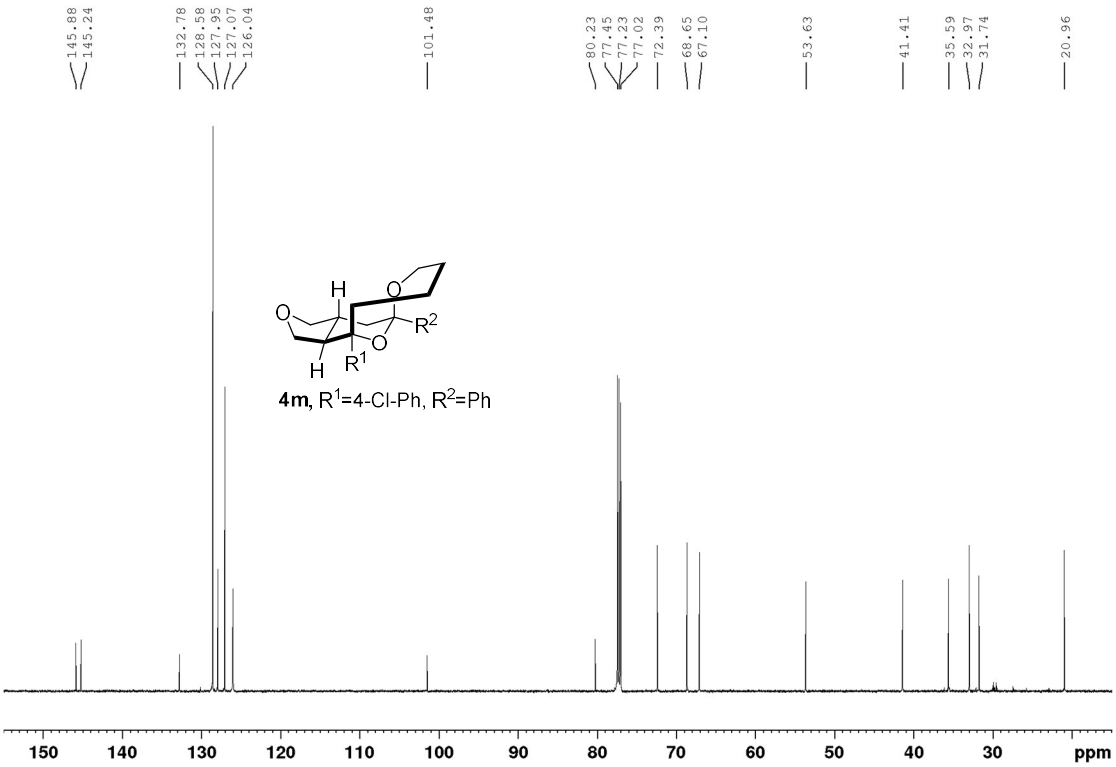

7.6142 7.5997 7.5365 7.5327 7.5230 7.5192 7.5142 7.4352 7.4301 7.4260 7.4164 7.4123 7.3942 7.3425 7.3402 7.3279 7.3132 4.1000 4.0855 4.0709 3.9713 3.9565 3.9417 3.7628 3.7482 3.7402 3.7256 3.7077 3.6836 3.5072 3.5033 3.4825 3.4788 3.4579 3.4541 3.2473 3.2324 3.2260 3.2111 2.7944 2.5177 2.5014 2.4887 2.4724 2.3382 2.3307 2.3118 2.3044 2.2040 2.1834 2.1745 2.1547 2.0092 1.9942 1.9627 1.6735 1.6452 1.6165 1.5600 1.5101 1.5056 1.5015 1.4973 1.4772 1.4733 1.4177 1.3922 1.3666 1.2314
H
O
O
R2
O
H
R1
4k, R1=4-Br-Ph, R2=Ph
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 ppm
1.93 2.08 4.08 1.02 1.07 1.00 1.00 1.01 1.01 1.00 1.02 1.00 1.02 1.05 1.07 1.02 1.05 1.08 1.01 1.06

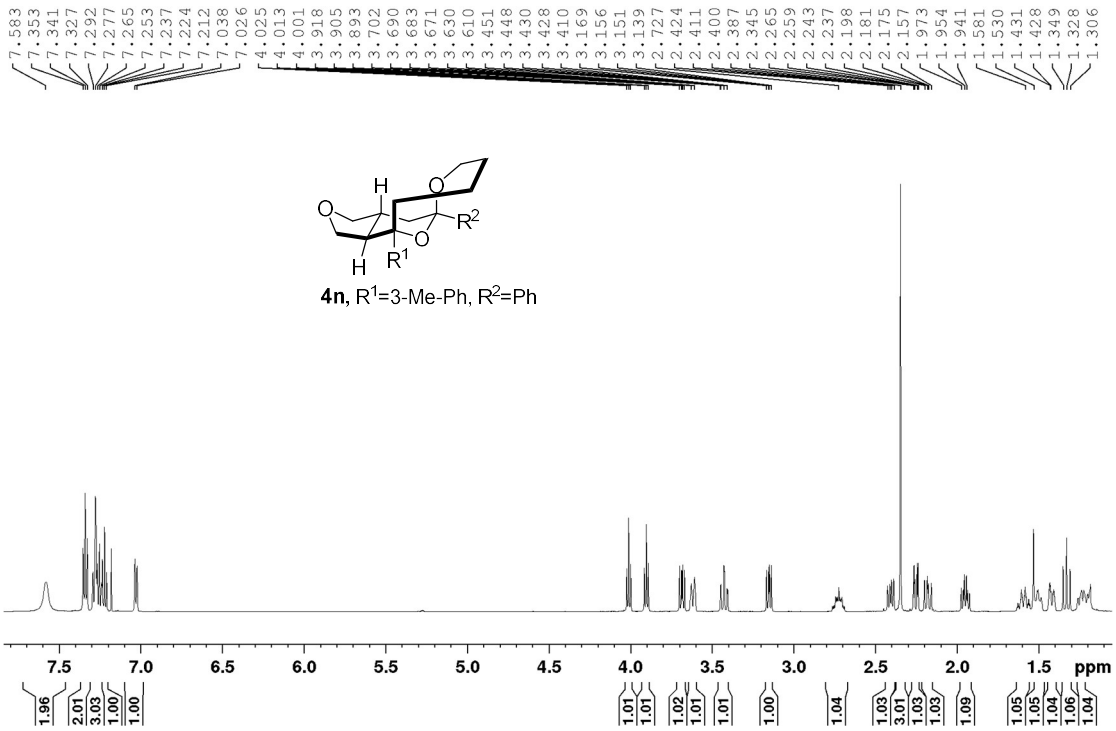

146.23 145.01 131.34 128.38 127.74 127.24 125.82 120.72 101.27 80.07 77.29 77.03 76.78 72.17 68.42 66.88 53.36 41.20 35.38 32.75 31.53 20.75
H
O
O
R2
O
H
R1
4k, R1=4-Br-Ph, R2=Ph
150 140 130 120 110 100 90 80 70 60 50 40 30 ppm

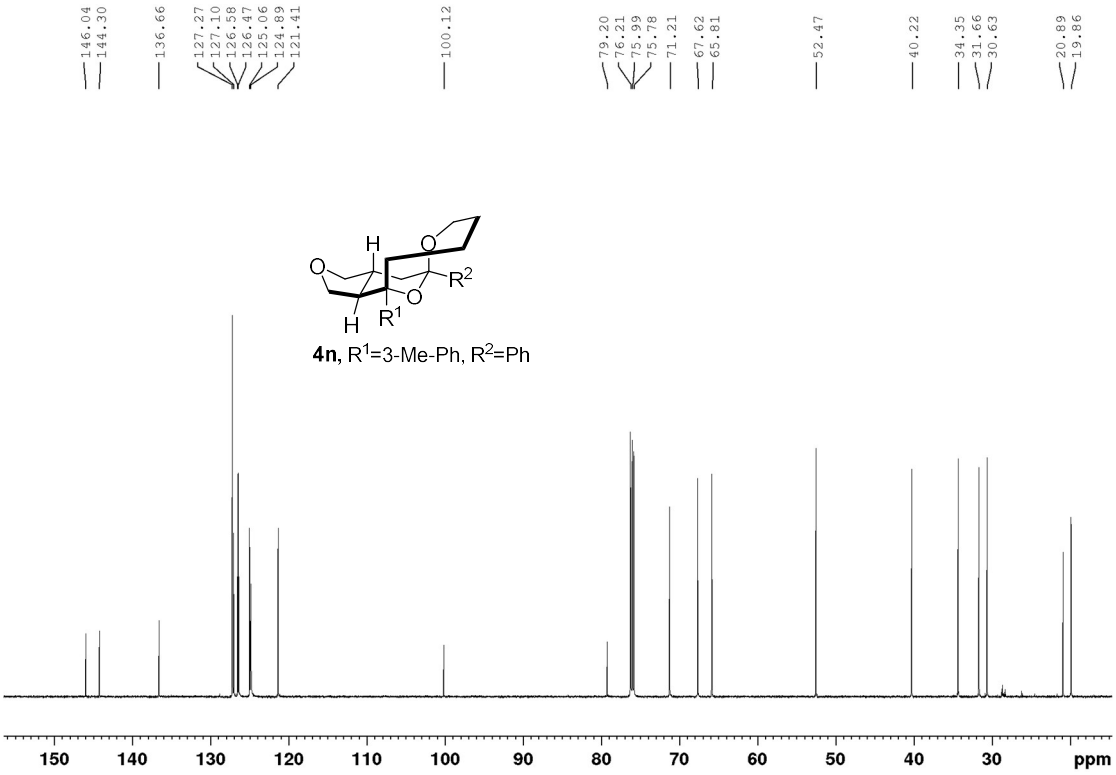

7.6287 7.6154 7.5990 7.5956 7.5921 7.4358 7.4207 7.4048 7.3761 7.3603 7.3474 7.3323 7.3169 7.2778 7.2749 7.2720 7.2625 7.2586
4.1033 4.0087 4.0741 3.9996 3.9747 3.9599 3.7714 3.7567 3.7488 3.7341 3.7142 3.6901 3.5215 3.5179 3.4968 3.4932 3.4723 3.2505 3.2356 3.2292 3.2143 2.7980 2.5277 2.5112 2.4987 2.4822 2.3414 2.3340 2.3150 2.3076 2.2194 2.1989 2.1908 2.1687 2.0085 2.0003 1.9852 1.6778 1.6499 1.5814 1.5747 1.5174 1.5128 1.5090 1.5049 1.4844 1.4807 1.4270 1.4014 1.3758 1.2713 1.2570
H
O
O
R2
O
H
R1
4l, R1=3-Cl-Ph, R2=Ph
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 ppm
1.94 1.09 2.05 1.03 2.01 1.01
1.02 1.03 1.01 1.03 1.01 1.00 1.04 1.01 1.04 1.01 1.11 1.02 1.03 1.08 1.05 1.06

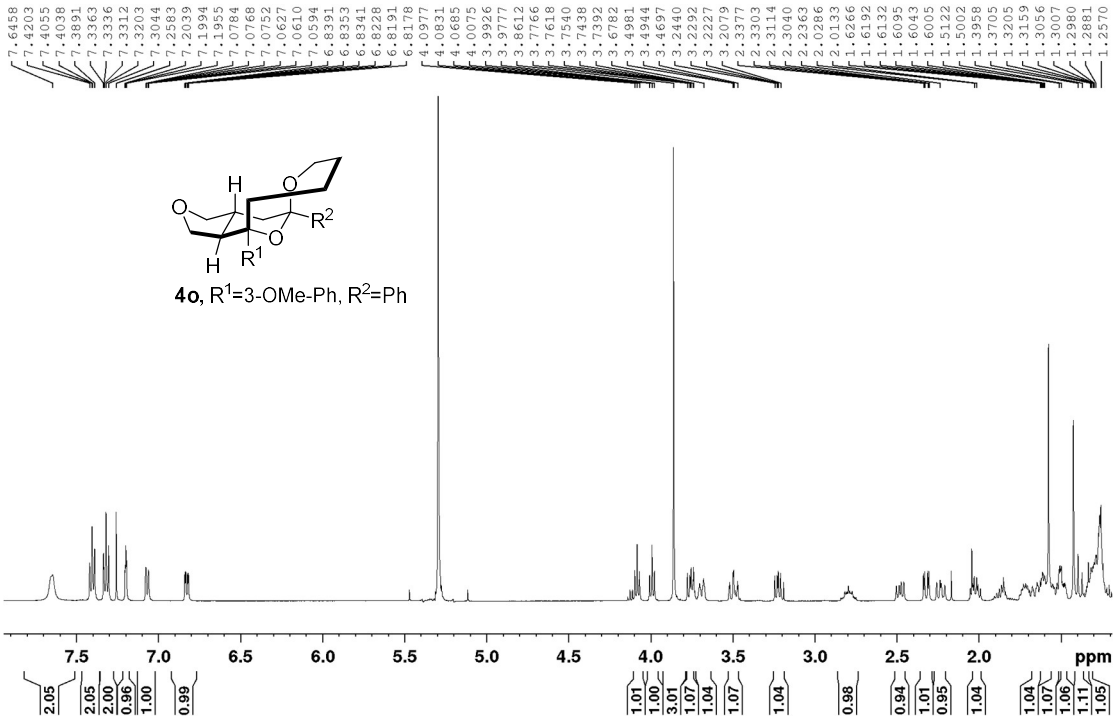

149.30 144.96 134.32 129.54 128.40 127.75 126.97 125.91 125.83 123.49 101.32 80.07 77.29 77.03 76.78 72.17 68.41 66.91 53.30 41.20 35.40 32.79 31.51 20.74
H
O
O
R2
O
H
R1
4l, R1=3-Cl-Ph, R2=Ph
150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

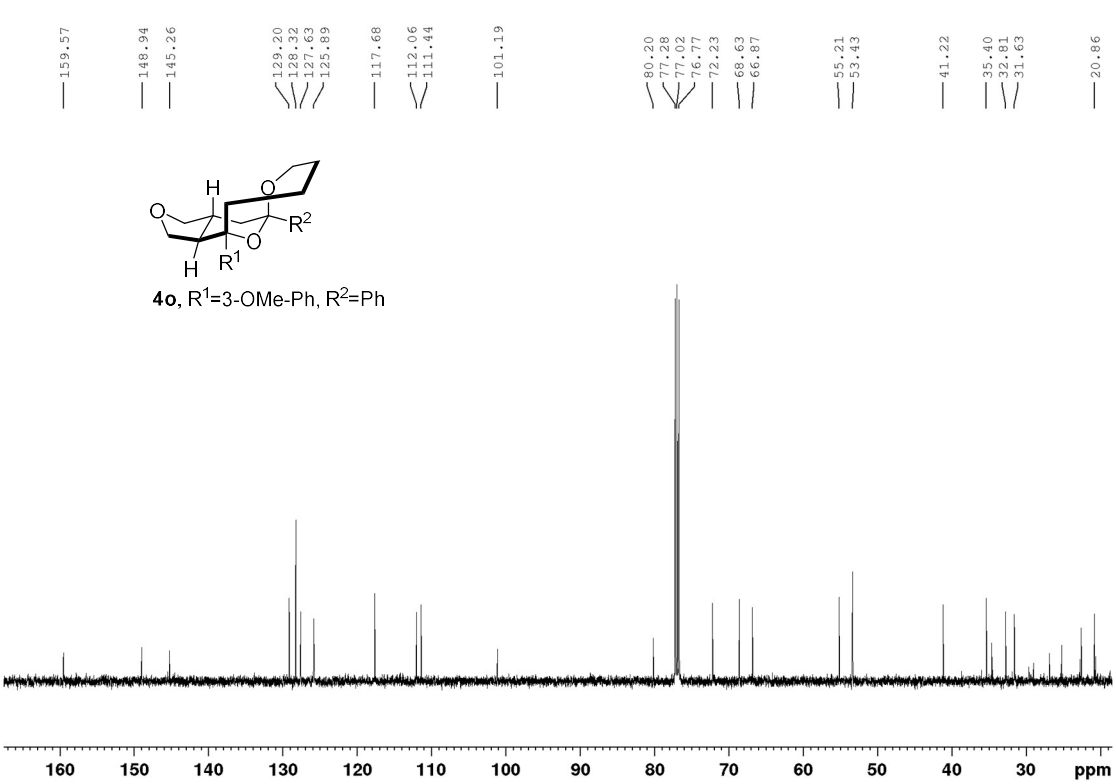

7.617 7.607 7.490 7.475 7.427 7.415 7.401 7.388 7.384 7.381 7.372 7.370 7.344 7.332 7.320 4.102 4.089 4.077 3.971 3.958 3.946 3.764 3.752 3.745 3.733 3.709 3.689 3.506 3.503 3.486 3.483 3.248 3.236 3.230 3.218 2.519 2.505 2.494 2.481 2.339 2.332 2.317 2.310 2.211 2.194 2.187 2.170 1.989 1.976 1.651 1.579 1.506 1.503 1.418 1.397 1.376 1.271 1.253
H
O
O
R2
O
H
R1
4m, R1=4-Cl-Ph, R2=Ph
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 ppm
2.00 2.06 2.01 1.95 1.01 1.02 1.02 1.04 1.02 1.00 1.01 1.02 1.03 1.01 1.04 1.04 1.04 1.12 1.06 1.08 1.06

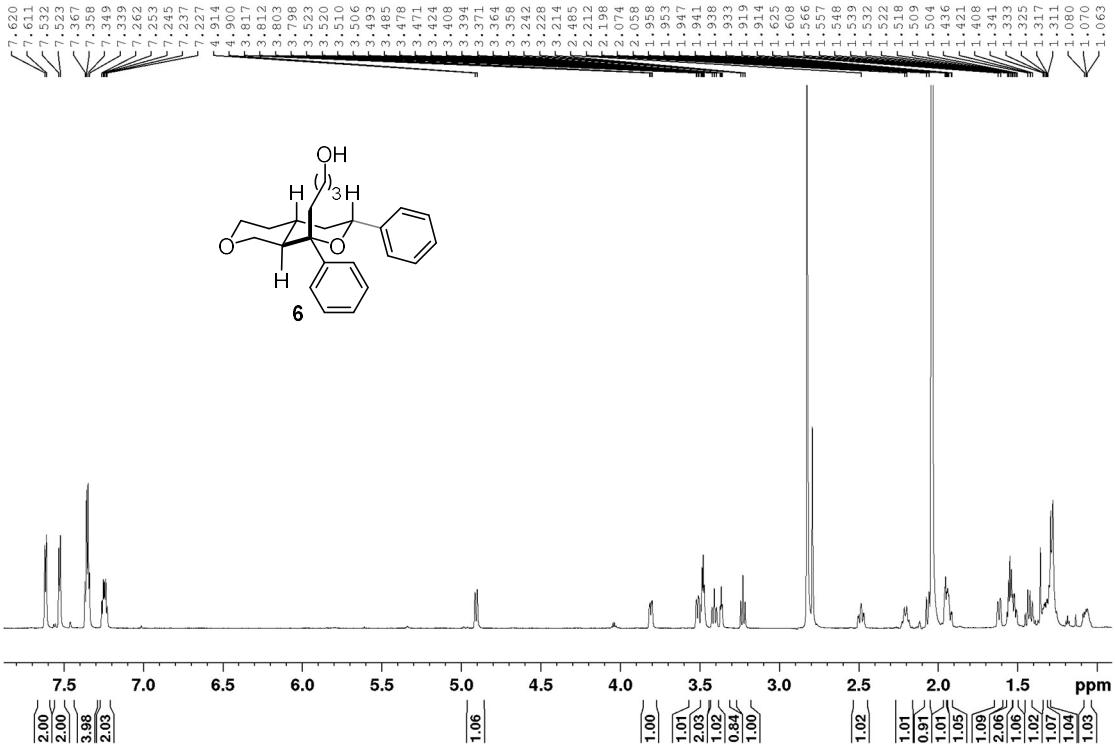

145.88 145.24 132.78 128.58 127.95 127.07 126.04 101.48 80.23 77.45 77.23 77.02 72.39 68.65 67.10 53.63 41.41 35.59 32.97 31.74 20.96
H
O
O
R2
O
H
R1
4m, R1=4-Cl-Ph, R2=Ph
150 140 130 120 110 100 90 80 70 60 50 40 30 ppm

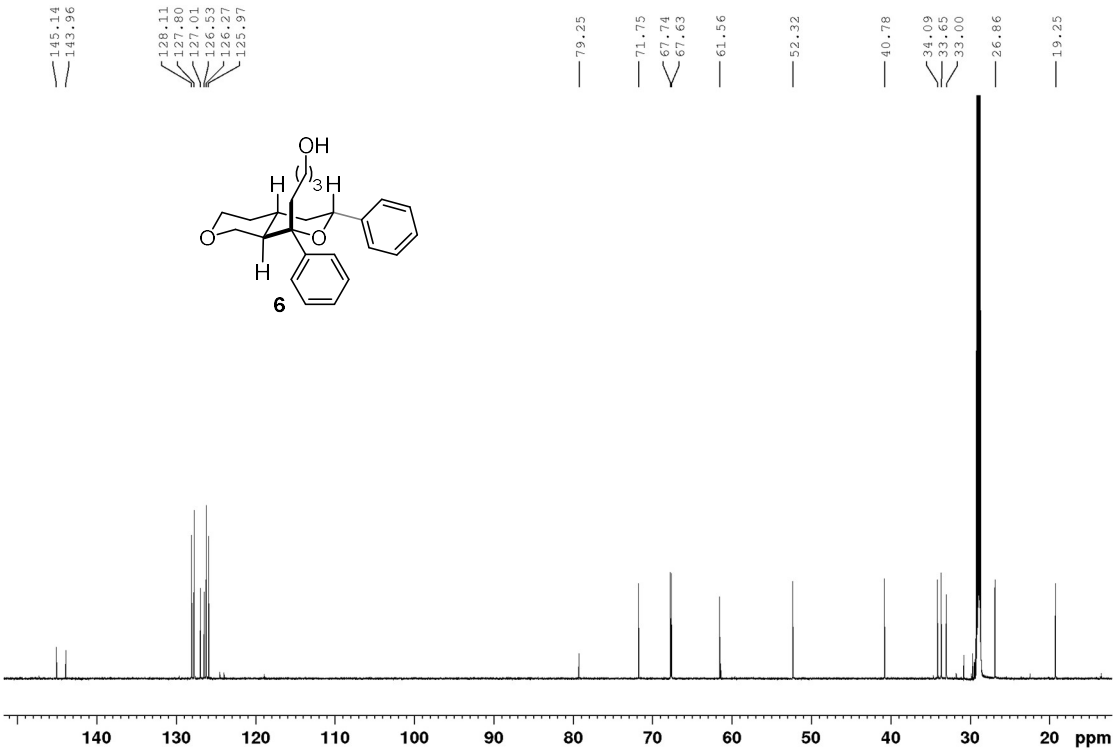

7.583 7.353 7.341 7.327 7.292 7.277 7.265 7.253 7.237 7.224 7.212 7.038 7.026
4.025 4.013 4.001 3.918 3.905 3.893 3.702 3.690 3.683 3.671 3.630 3.610 3.451 3.448 3.430 3.428 3.410 3.169 3.156 3.151 3.139 2.727 2.424 2.411 2.400 2.387 2.345 2.265 2.259 2.243 2.237 2.198 2.181 2.175 2.157 1.973 1.954 1.941 1.581 1.530 1.431 1.428 1.349 1.328 1.306
H
O
O
R2
O
H
R1
4n, R1=3-Me-Ph, R2=Ph
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 ppm
1.96 2.01 3.03 1.00 1.00 1.01 1.01 1.02 1.01 1.01 1.00 1.04 1.03 3.01 1.03 1.03 1.09 1.05 1.05 1.04 1.06 1.04

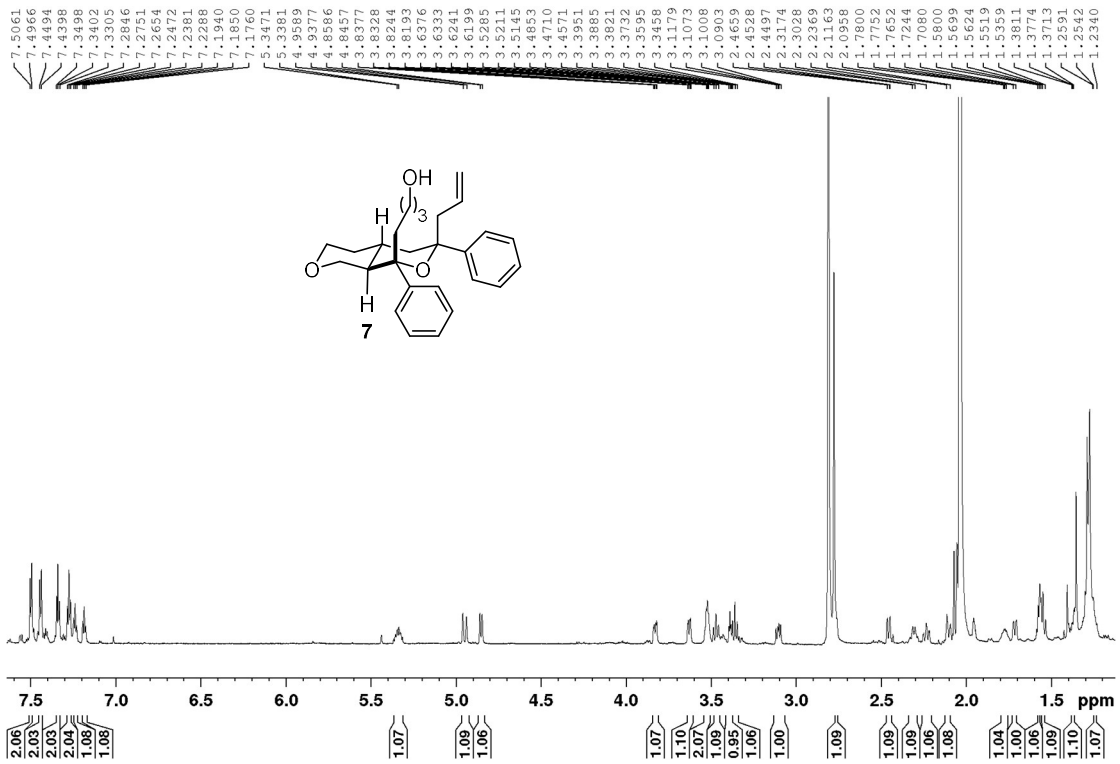

146.04 144.30 136.66 127.27 127.10 126.58 126.47 125.06 124.89 121.41 100.12 79.20 76.21 75.99 75.78 71.21 67.62 65.81 52.47 40.22 34.35 31.66 30.63 20.89 19.86
H
O
O
R2
O
H
R1
4n, R1=3-Me-Ph, R2=Ph
150 140 130 120 110 100 90 80 70 60 50 40 30 ppm


7.6458 7.4203 7.4055 7.4038 7.3891 7.3363 7.3336 7.3312 7.3203 7.3044 7.2583 7.2039 7.1994 7.1955 7.0784 7.0768 7.0752 7.0627 7.0610 7.0594 6.8391 6.8353 6.8341 6.8228 6.8191 6.8178 4.0977 4.0831 4.0685 4.0075 3.9926 3.9777 3.8612 3.7766 3.7618 3.7540 3.7438 3.7392 3.6782 3.4981 3.4944 3.4697 3.2440 3.2292 3.2227 3.2079 2.3377 2.3303 2.3114 2.3040 2.2363 2.0286 2.0133 1.6266 1.6192 1.6132 1.6095 1.6043 1.6005 1.5122 1.5002 1.3958 1.3705 1.3205 1.3159 1.3056 1.3007 1.2980 1.2881 1.2570
H
O
O
R2
O
H
R1
4o, R1=3-OMe-Ph, R2=Ph
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 ppm
2.05 2.05 2.00 0.96 1.00 0.99 1.01 1.00 3.01 1.07 1.04 1.07 1.04 0.98 0.94 1.01 0.95 1.04 1.04 1.07 1.06 1.11 1.05


159.57 148.94 145.26 129.20 128.32 127.63 125.89 117.68 112.06 111.44 101.19 80.20 77.28 77.02 76.77 72.23 68.63 66.87 55.21 53.43 41.22 35.40 32.81 31.63 20.86
H
O
O
R2
O
H
R1
4o, R1=3-OMe-Ph, R2=Ph
160 150 140 130 120 110 100 90 80 70 60 50 40 30 ppm


OH
H
3
H
O
O
H
6
7.620 7.611 7.532 7.523 7.367 7.358 7.349 7.339 7.262 7.253 7.245 7.237 7.227 4.914 4.900 3.817 3.812 3.803 3.798 3.523 3.520 3.510 3.506 3.493 3.485 3.478 3.471 3.424 3.408 3.394 3.371 3.364 3.358 3.242 3.228 3.214 2.485 2.212 2.198 2.074 2.058 1.958 1.953 1.947 1.941 1.938 1.933 1.919 1.914 1.625 1.608 1.566 1.557 1.548 1.539 1.532 1.522 1.518 1.509 1.504 1.436 1.421 1.408 1.341 1.333 1.325 1.317 1.311 1.080 1.070 1.063
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 ppm
2.00 2.00 3.98 2.03 1.06 1.00 1.01 2.03 1.02 0.84 1.00 1.02 1.01 0.91 1.01 1.05 1.09 2.06 1.06 1.02 1.07 1.04 1.03


145.14 143.96 128.11 127.80 127.01 126.53 126.27 125.97 79.25 71.75 67.74 67.63 61.56 52.32 40.78 34.09 33.65 33.00 26.86 19.25
OH
H
3
H
O
O
H
6
140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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7.2751
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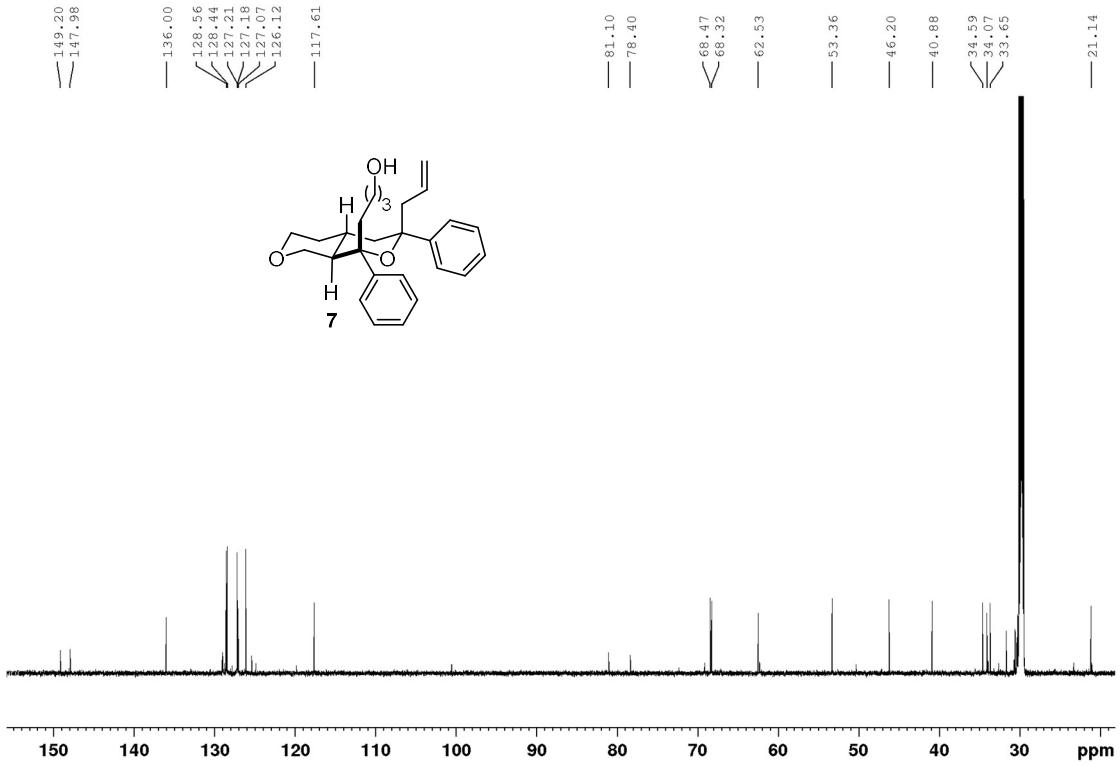
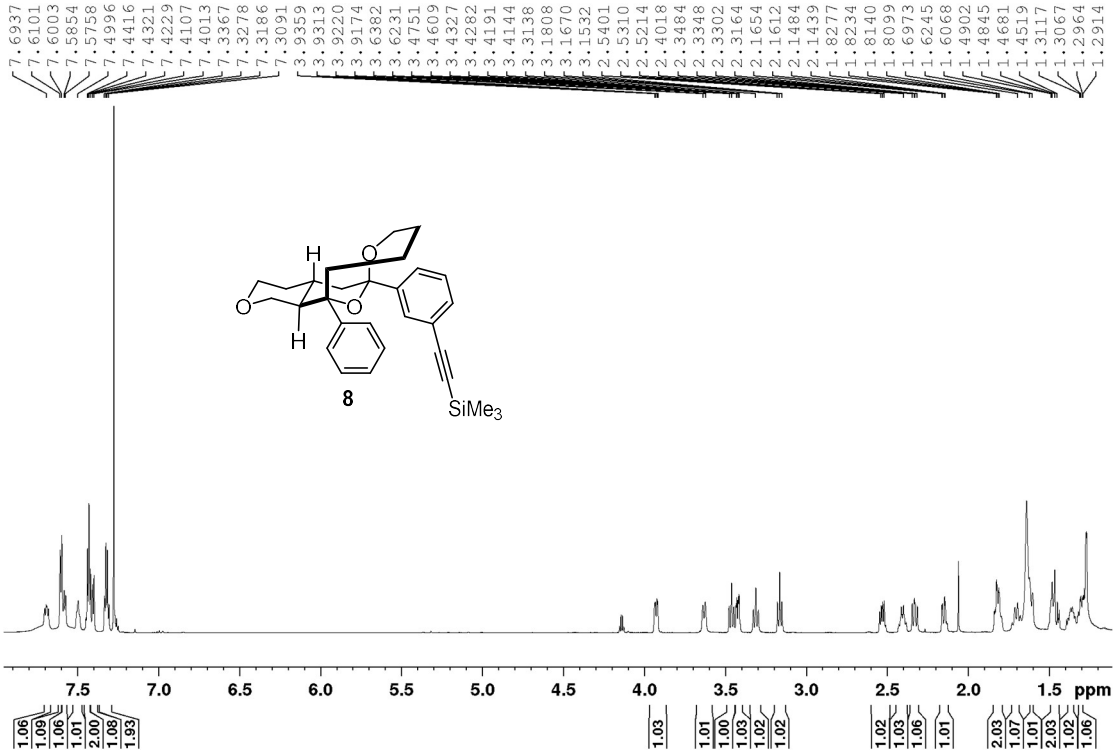
7.2472
7.2381
7.2288
7.1940
7.1850
7.1760
5.3471
5.3381
4.9589
4.9377
4.8586
4.8457
3.8377
3.8328
3.8244
3.8193
3.6376
3.6333
3.6241
3.6199
3.5285
3.5211
3.5145
3.4853
3.4710
3.4571
3.3951
3.3885
3.3821
3.3732
3.3595
3.3458
3.1179
3.1073
3.1008
3.0903
2.4659
2.4528
2.4497
2.3174
2.3028
2.2369
2.1163
2.0958
1.7800
1.7752
1.7652
1.7244
1.7080
1.5800
1.5699
1.5624
1.5519
1.5359
1.3811
1.3774
1.3713
1.2591
1.2542
1.2340
OH
3
H
O
O
H
7
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
2.06
2.03
2.03
2.04
1.08
1.08
1.07
1.09
1.06
1.07
1.10
2.07
1.09
0.95
1.06
1.00
1.09
1.09
1.09
1.06
1.08
1.04
1.00
1.06
1.09
1.10
1.07


149.20
147.98
136.00
128.56
128.44
127.21
127.18
127.07
126.12
117.61
81.10
78.40
68.47
68.32
62.53
53.36
46.20
40.88
34.59
34.07
33.65
21.14
OH
3
H
O
O
H
7
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm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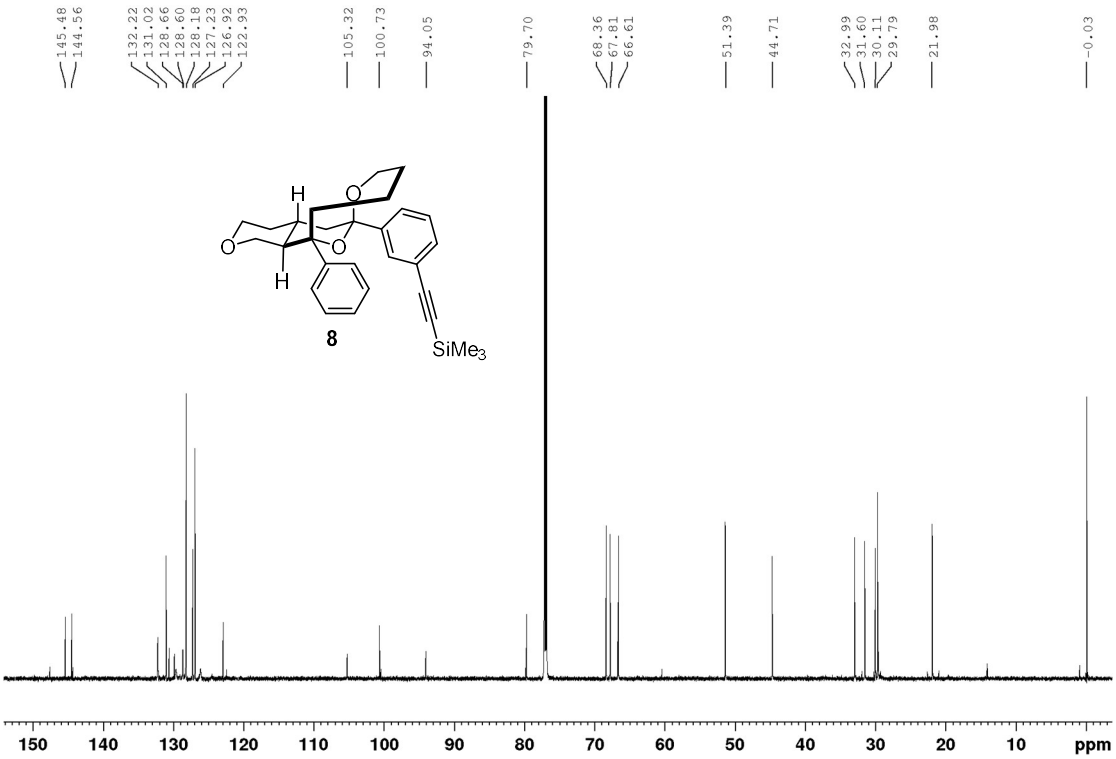
7.5758
7.4996
7.4416
7.4321
7.4229
7.4107
7.4013
7.3367
7.3278
7.3186
7.3091
3.9359
3.9313
3.9220
3.9174
3.6382
3.6231
3.4751
3.4609
3.4327
3.4282
3.4191
3.4144
3.3138
3.1808
3.1670
3.1532
2.5401
2.5310
2.5214
2.4018
2.3484
2.3348
2.3302
2.3164
2.1654
2.1612
2.1484
2.1439
1.8277
1.8234
1.8140
1.8099
1.6973
1.6245
1.6068
1.4902
1.4845
1.4681
1.4519
1.3117
1.3067
1.2964
1.2914
H
O
O
O
H
8
SiMe3
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5 ppm
1.06
1.09
1.06
1.01
2.00
1.08
1.93
1.03
1.01
1.00
1.03
1.02
1.02
1.02
1.03
1.06
1.01
2.03
1.07
1.01
2.03
1.02
1.06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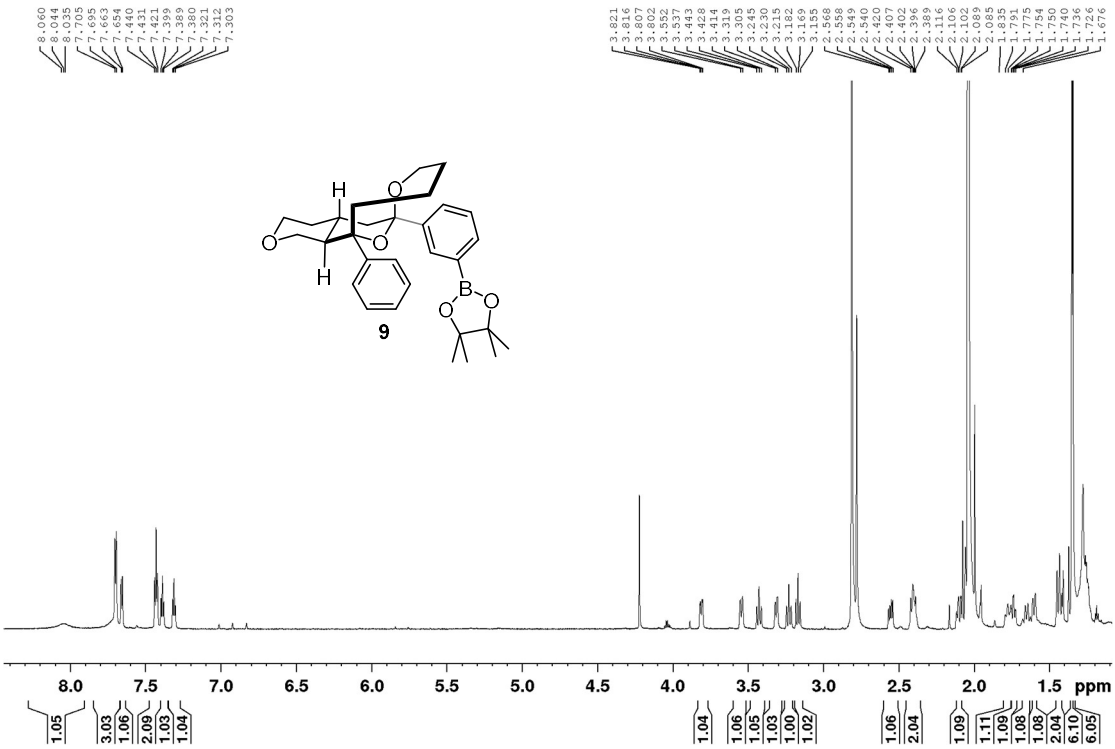
144.56
132.22
131.02
128.66
128.60
128.18
127.23
126.92
122.93
105.32
100.73
94.05
79.70
68.36
67.81
66.61
51.39
44.71
32.99
31.60
30.11
29.79
21.98
-0.03
H
O
O
O
H
8
SiMe3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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8.035
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7.663
7.654
7.440
7.431
7.421
7.399
7.389
7.380
7.321
7.312
7.303
3.821
3.816
3.807
3.802
3.552
3.537
3.433
3.428
3.414
3.319
3.305
3.245
3.230
3.215
3.182
3.169
3.155
3.158
2.558
2.549
2.540
2.420
2.407
2.402
2.396
2.389
2.156
2.106
2.102
2.089
2.085
1.835
1.791
1.775
1.754
1.740
1.736
1.726
1.676
H
O
O
O
H
B
O
O
9
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
1.05
3.03
1.06
2.09
1.03
1.04
1.04
1.06
1.05
1.03
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1.06
2.04
1.09
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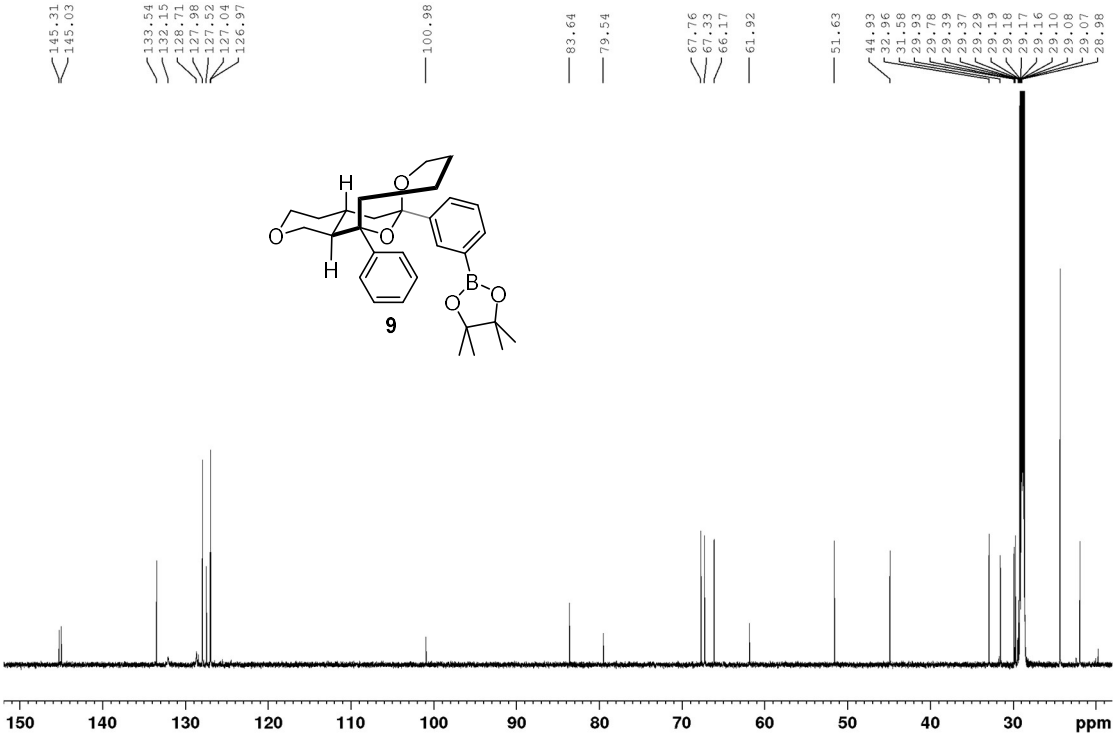
1.09
1.08
1.08
2.04
6.10
6.05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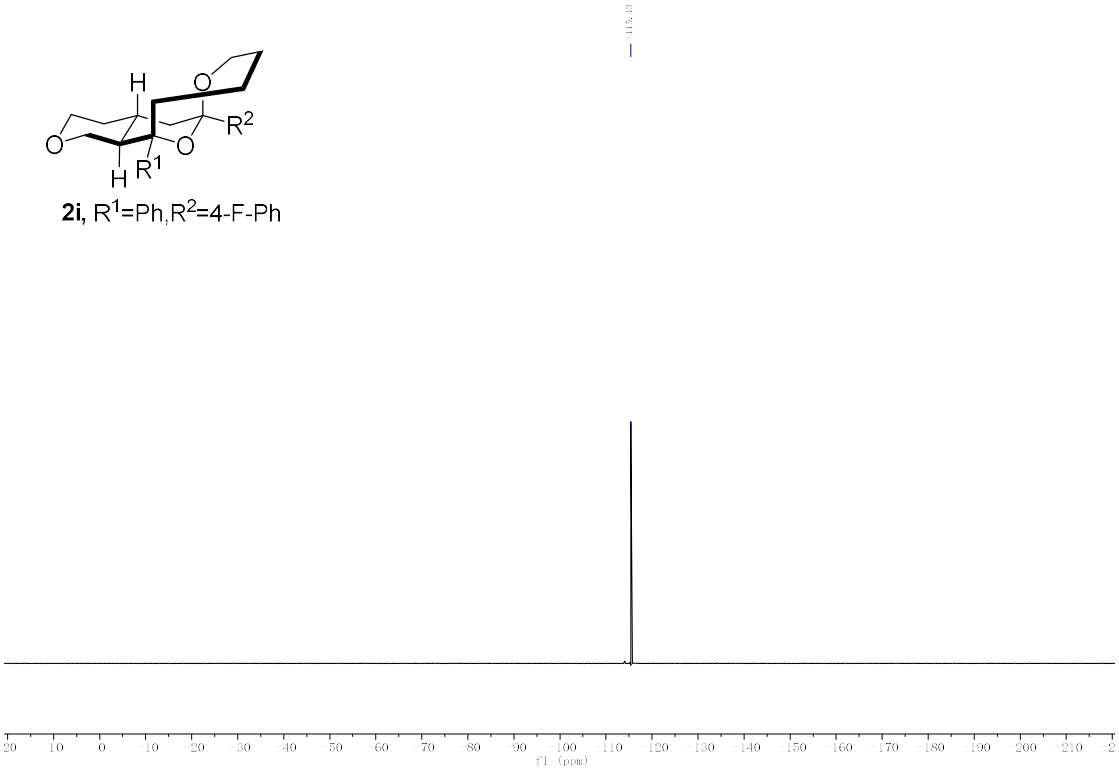
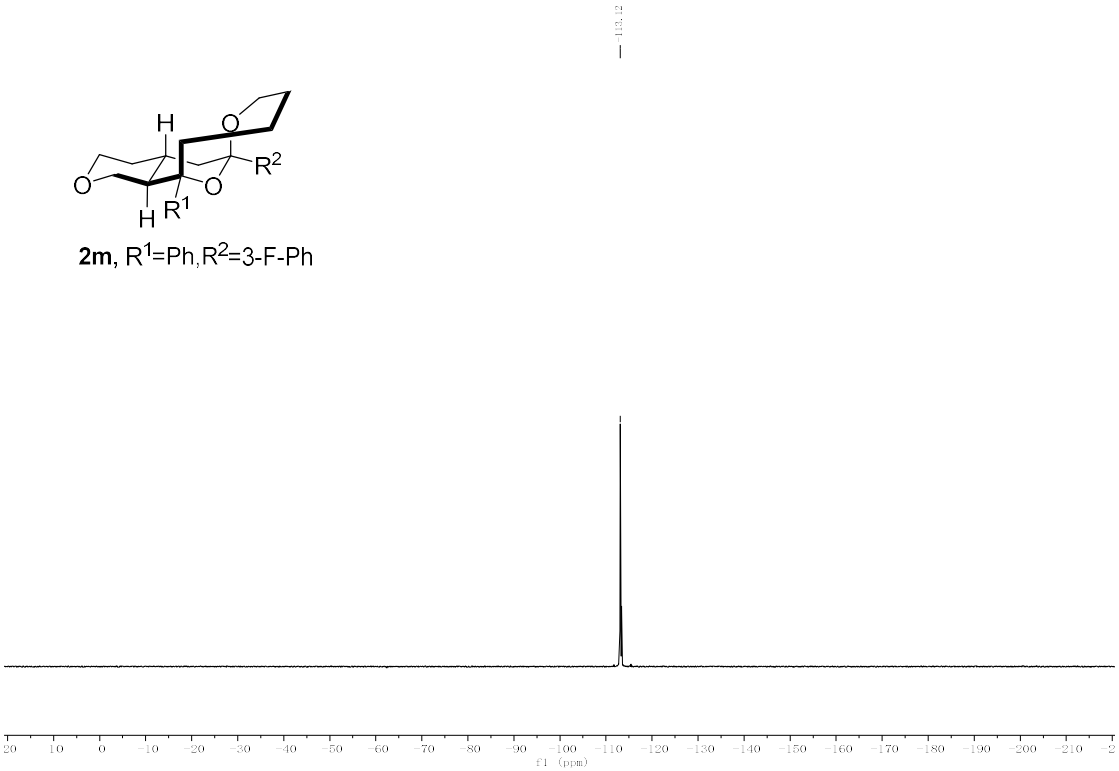
145.03
133.54
132.15
128.71
127.98
127.52
127.04
126.97
100.98
83.64
79.54
67.76
67.33
66.17
61.92
51.63
44.93
32.96
31.58
29.93
29.78
29.39
29.37
29.29
29.19
29.18
29.17
29.16
29.10
29.08
29.07
28.98
H
O
O
O
H
B
O
O
9
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

^{19}F NMR spectrum

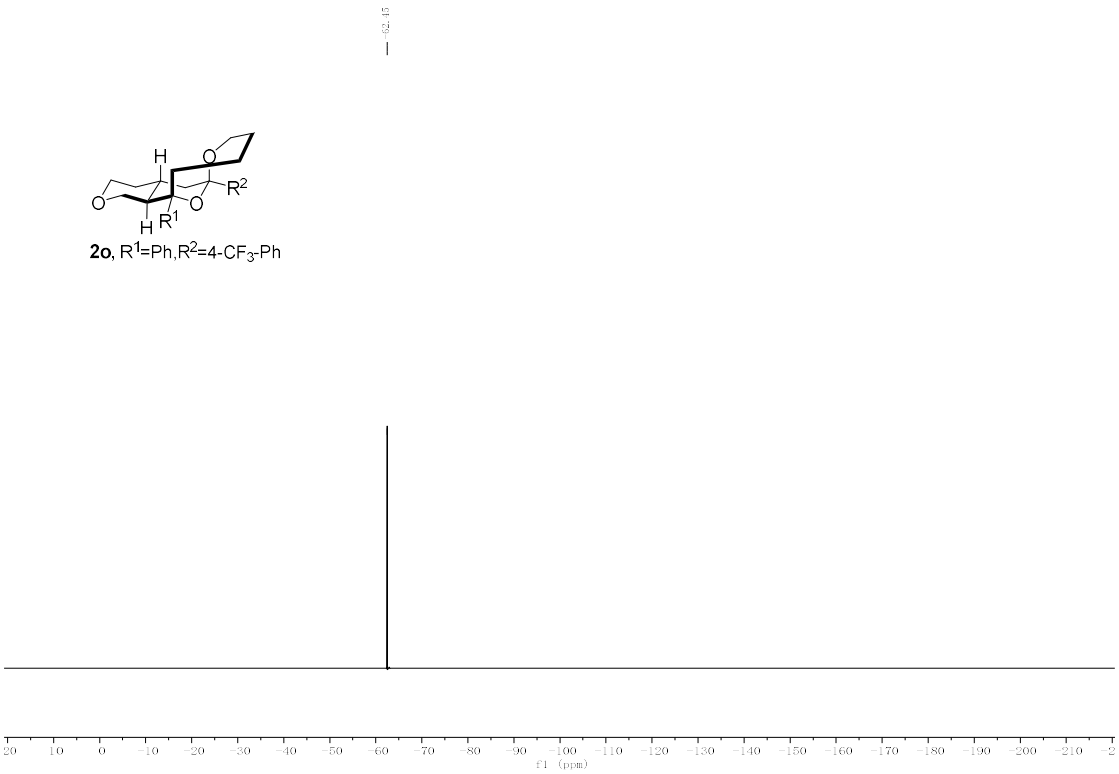
2i, R^1=Ph,R^2=4-F-Ph



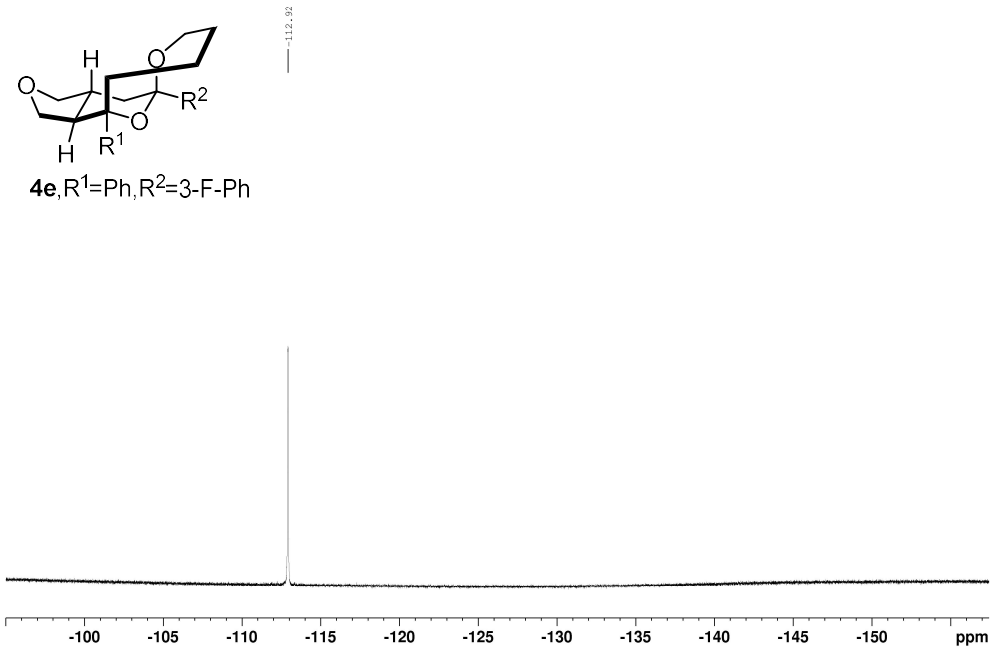
2m, R^1=Ph,R^2=3-F-Ph



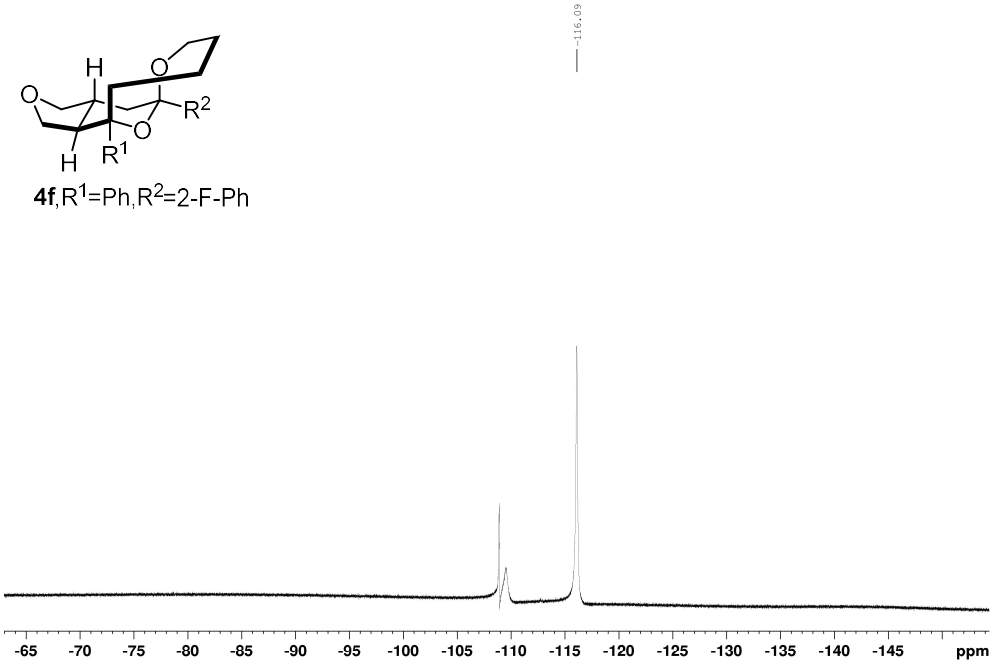
2o, R^1=Ph,R^2=4-CF_3-Ph



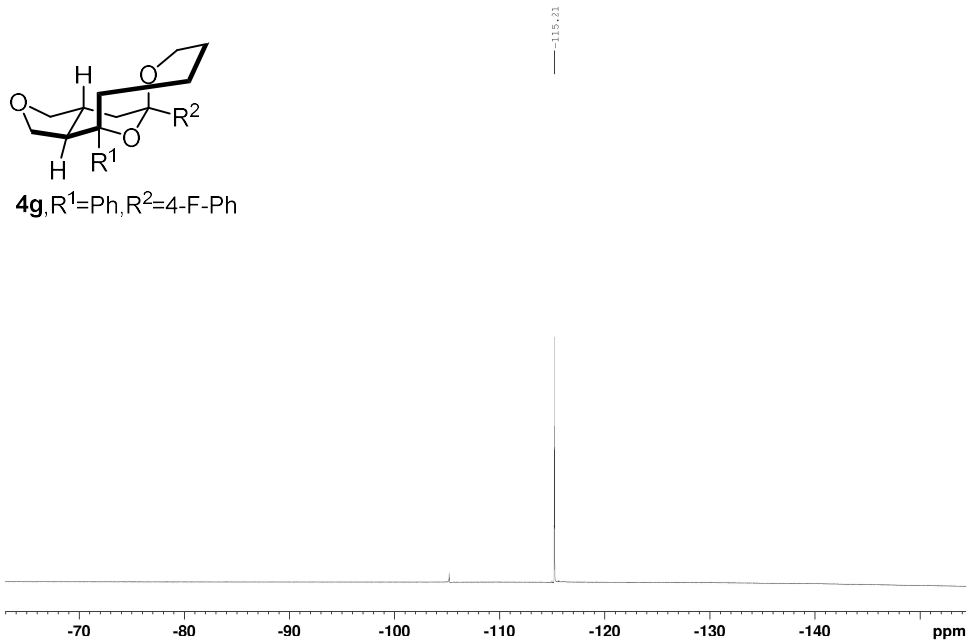
4e,R^1=Ph,R^2=3-F-Ph



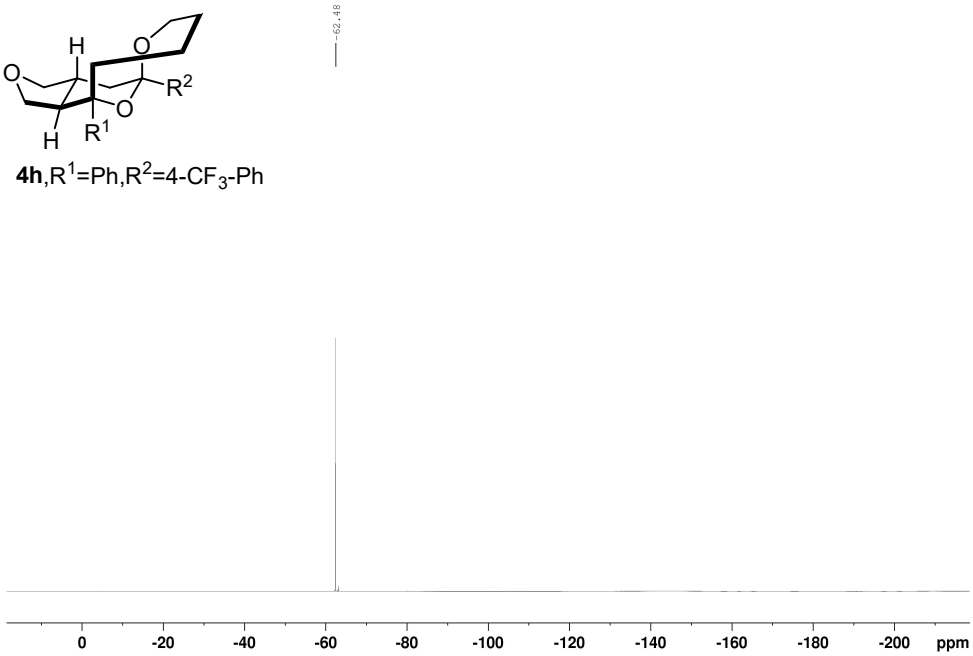
4f,R^1=Ph,R^2=2-F-Ph



4g,R^1=Ph,R^2=4-F-Ph



4h,R^1=Ph,R^2=4-CF_3-Ph



2n, R^1=Ph,R^2=2-F-Ph