Supporting Information for

A Macrocyclic Chalcogen Bonding Catalysis System

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1. General Information

All the chemicals were either purchased from commercial suppliers or purified by standard procedures as specified in *Purification of Laboratory Chemicals*, 7th Ed (Armarego, W. L. F.; Chai, C. L. L. Butterworth Heinemann: 2013). All reactions were carried out under nitrogen atmosphere. Analytical thin-layer chromatography (TLC) was performed on silica gel plates and analyzed by UV light or by potassium permanganate stains followed by heating. Flash chromatography was carried out utilizing silica gel (200-300 mesh). ^{1}H NMR, ^{13}C NMR spectra were recorded in $CDCl_3$ or CD_2Cl_2 at room temperature on a Bruker AM-400 spectrometer (400 MHz ^{1}H, 100 MHz ^{13}C). The chemical shifts are reported in ppm relative to either the residual solvent peak (^{13}C) (δ = 77.00 ppm for $CDCl_3$; δ = 53.84 ppm for CD_2Cl_2; δ = 29.84 ppm for $(CD_3)_2CO$), (^{1}H) (δ = 5.32 ppm for CD_2Cl_2, δ = 2.05 ppm for $(CD_3)_2CO$) or TMS (^{1}H) (δ = 0 ppm) as an internal standard. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet doublet), coupling constant (Hz), integration. Data for ^{13}C NMR are reported as chemical shift. HRMS were performed on a Bruker Apex II mass instrument (ESI).

2. Preparation of Catalysts and Glycoside Donors

Catalysts **MC1**–**MC8** as depicted below were evaluated in this work:

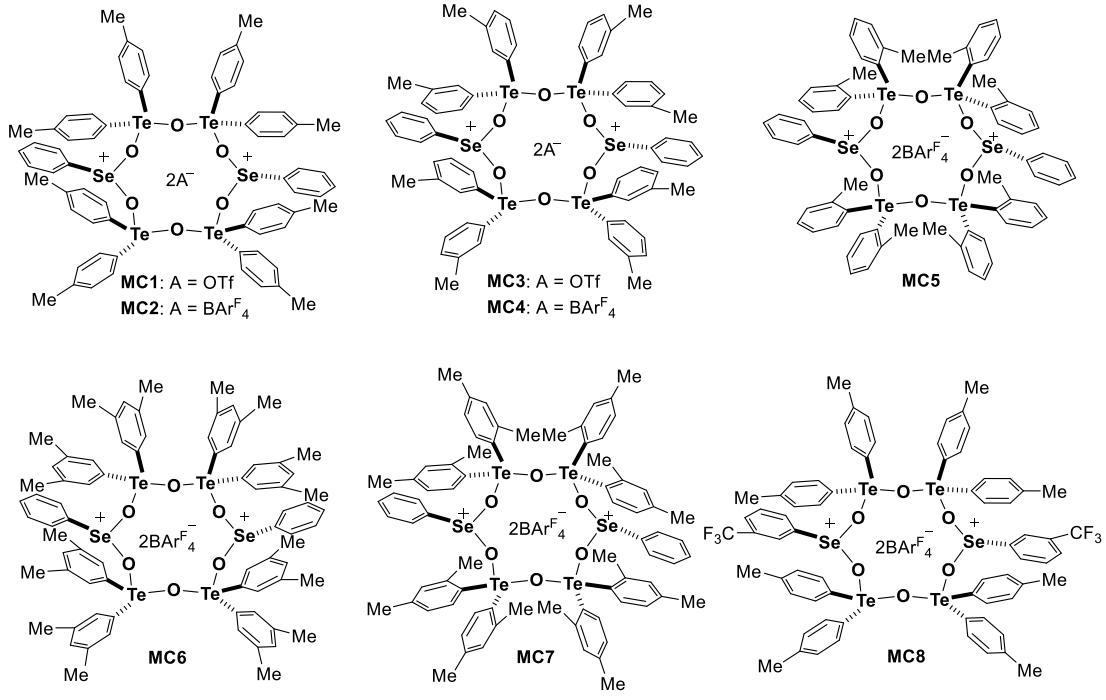
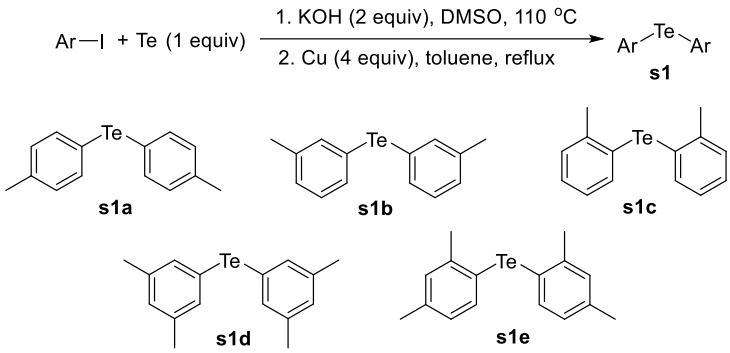


Fig. S1. Catalysts.

Catalysts MC1–MC8 were prepared using the following procedure:



To a reaction mixture of aryl iodide (120.0 mmol), Te (15.30 g, 120.0 mmol), and KOH (13.47 g, 240.0 mmol), in a 500 mL-Schlenk tube was added DMSO (240 mL) under argon atmosphere. The above reaction mixture was stirred at 110 °C for 10 h until the completion of the reaction as judged by TLC analysis. Then the reaction mixture was allowed to cool to room temperature and treated with ethyl acetate and H_2O. The organic layer was washed with sat. NH_4Cl solution, dried with Na_2SO_4, and concentrated under vacuum. The residue was purified by flash chromatography on silica gel with petroleum ether to afford a mixture of diaryl tellurides and diaryl ditellurides. The copper powder (30.50 g, 480.0 mmol) was added to a solution of diaryl tellurides and diaryl ditellurides in dry toluene (200 mL) and stirred at 110 °C for 24 h until the completion of the reaction as judged by TLC analysis. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel to give the desired products **s1**.

s1a: Pale yellow solid (62% yield); (1a) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65–7.57 (m, 4H), 7.08–7.01 (m, 4H), 2.35 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.04, 137.71, 130.33, 110.70, 21.17; HRMS (EI) exact mass calculated for $C_{14}H_{14}Te$ $[M]^+$: 312.0158, found: m/z 312.0153.

s1b: Pale yellow oil (67% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53–7.54 (m, 2H), 7.47–7.45 (m, 2H), 7.06–7.02 (m, 4H), 2.24 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.99, 138.51, 134.92, 129.14, 128.55, 114.51, 21.12; HRMS (EI) exact mass calculated for $C_{14}H_{14}Te$ $[M]^+$: 312.0158, found: m/z 312.0159.

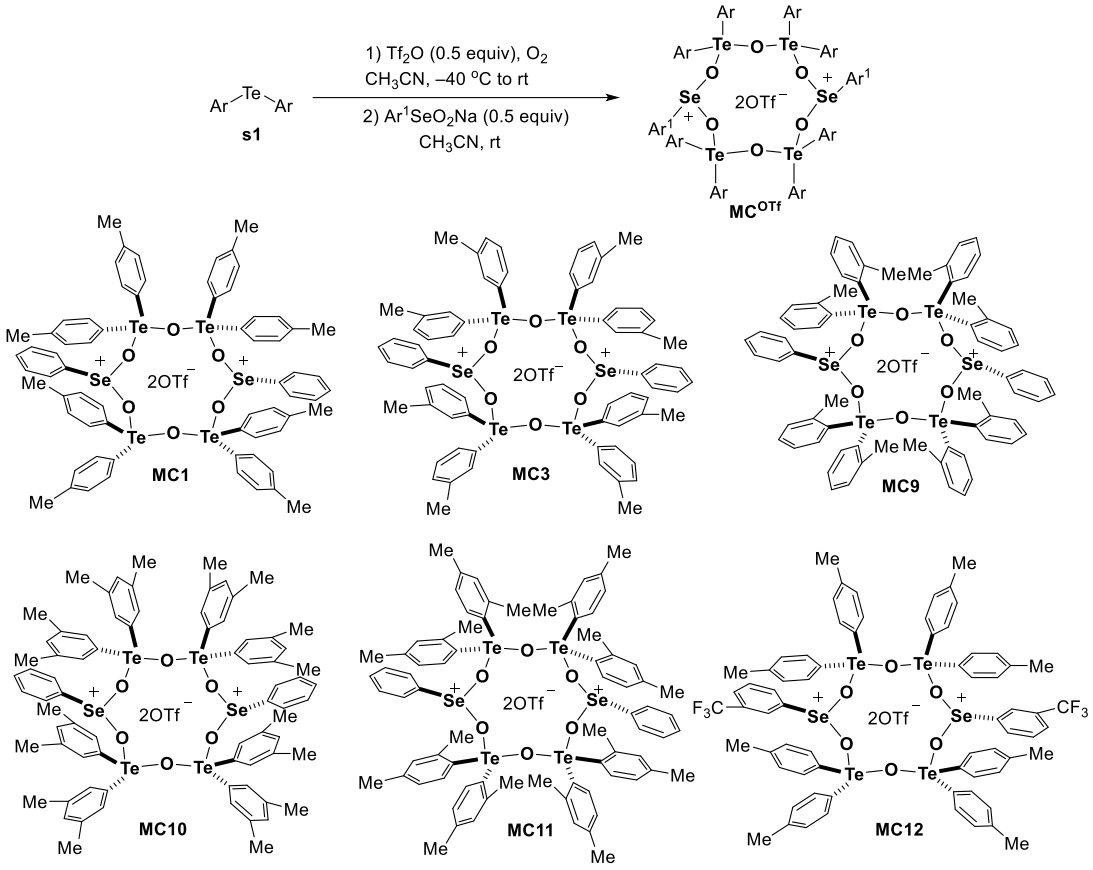
s1c: Colorless oil (71% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (dd, J = 7.7, 1.3 Hz, 2H), 7.25–7.17 (m, 4H), 6.94 (td, J = 7.4, 1.7 Hz, 2H), 2.42 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.53, 138.19, 129.36, 128.34, 126.82, 118.46, 26.21; HRMS (EI) exact mass calculated for $C_{14}H_{14}Te$ $[M]^+$: 312.0158, found: m/z 312.0155.

s1d: Colorless oil (66% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (s, 4H), 6.88 (s, 2H), 2.23 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.80, 135.63, 129.62, 114.35, 21.02; HRMS (EI) exact mass calculated for $C_{16}H_{18}Te$ $[M]^+$:

340.0471, found: m/z 340.0479.

s1e: Colorless oil (63% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, *J* = 7.7 Hz, 2H), 7.16 (d, *J* = 2.0 Hz, 2H), 6.88–6.86 (m, 2H), 2.48 (s, 6H), 2.38 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.56, 138.43, 138.30, 130.47, 127.85, 114.53, 26.27, 21.13; HRMS (EI) exact mass calculated for $C_{16}H_{18}Te$ $[M]^+$: 340.0471, found: m/z 340.0467.

The above data of product **s1a**–**s1e** is consistent with the reported references.[1-3]



General procedure for preparation of **MC1**, **MC3** and **MC9**–**12**: To a suspension of diaryl tellurides **s1** (15.00 mmol) in dry CH_3CN (120.0 mL) at -40 °C under an O_2 atmosphere was added triflic anhydride (1.26 mL, 7.50 mmol). The resulting homogeneous deep red solution was stirred at room temperature for 2.5 h, during which time it became pale orange. Volatile reagents were removed under reduced pressure and then 100.0 mL dry CH_3CN and sodium selenites (7.50 mmol) was added under argon atmosphere. The above reaction was run for 64 h to generate white solid. The precipitate was filtered off and washed by anhydrous diethyl ether to afford pure catalyst.

MC1: White solid (66% yield); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.58 (d, *J*=7.7 Hz, 26H), 7.11 (d, *J*=7.9 Hz, 16H), 2.36 (s, 24H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 141.92, 133.44,136.26, 131.99, 130.05, 129.56, 126.21,125.65,

122.46, 119.27, 116.08, 21.51; ^{19}F NMR (377 MHz, CD_2Cl_2): δ -78.34; HRMS (ESI+) exact mass calculated for $[M]^{2+}$ ($C_{68}H_{66}O_6Se_2Te_4$) requires m/z 825.9691, found m/z 825.9693.

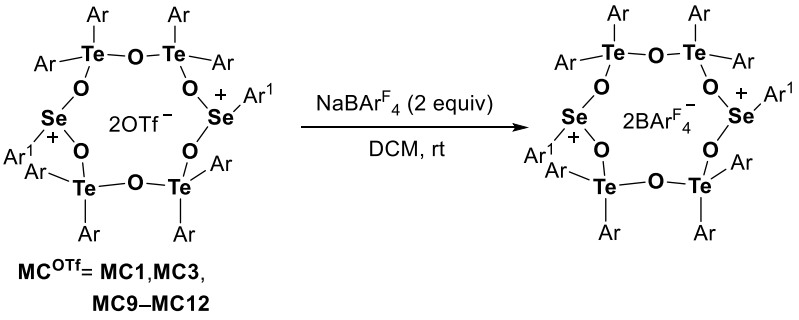
MC3: White solid (62% yield); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.83–6.98 (m, 42H), 2.16 (s, 24H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 139.33, 134.32, 131.98, 130.60, 129.53, 129.05, 126.17, 122.45, 119.26, 21.44; ^{19}F NMR (377 MHz, CD_2Cl_2): δ -78.66; HRMS (ESI+) exact mass calculated for $[M]^{2+}$ ($C_{68}H_{66}O_6Se_2Te_4$) requires m/z 825.9691, found m/z 825.9693.

MC9: White solid (53% yield); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.71–6.87 (m, 42H), 2.24 (s, 24H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 146.23, 141.98, 137.35, 132.90, 132.90, 132.68, 132.63, 131.73, 129.74, 127.94, 125.44, 122.43, 119.24, 116.05, 23.20; ^{19}F NMR (377 MHz, CD_2Cl_2): δ -78.79; ^{77}Se NMR (76 MHz, CD_2Cl_2): δ 1183.64; HRMS (ESI+) exact mass calculated for $[M]^{2+}$ ($C_{68}H_{66}O_6Se_2Te_4$) requires m/z 825.9691, found m/z 825.9690.

MC10: White solid (72% yield); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.78–6.78 (m, 34H), 2.16 (s, 48H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 139.26, 133.14, 132.04, 130.86, 129.44, 126.09, 122.55, 119.36, 21.34; ^{19}F NMR (377 MHz, CD_2Cl_2): δ -78.73; HRMS (ESI+) exact mass calculated for $[M]^{2+}$ ($C_{76}H_{82}O_6Se_2Te_4$) requires m/z 882.0317, found m/z 882.0322.

MC11: White solid (55% yield); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.57–6.85 (m, 34H), 2.46–2.12 (m, 48H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 143.59, 141.90, 132.93, 132.42, 132.34, 129.59, 128.73, 125.54, 122.53, 119.34, 23.06, 21.45; ^{19}F NMR (377 MHz, CD_2Cl_2): δ -78.83; HRMS (ESI+) exact mass calculated for $[M]^{2+}$ ($C_{76}H_{82}O_6Se_2Te_4$) requires m/z 882.0317, found m/z 882.0317.

MC12: White solid (57% yield); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.72–7.38 (m, 24H), 7.10 (d, *J* = 7.9 Hz, 16H), 2.34 (s, 24H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 141.53, 133.10, 129.63, 127.83, 122.84, 21.11; ^{19}F NMR (376 MHz, CD_2Cl_2): δ -63.09, -78.48; HRMS (ESI+) exact mass calculated for $[M]^{2+}$ ($C_{70}H_{64}F_6O_6Se_2Te_4$) requires m/z 893.9565, found m/z 893.9569.



To a reaction mixture of **MC^{OTf}** (1.0 mmol) and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (1.77 g, 2.0 mmol) was added DCM (6.0 mL) and run for 5 min to generate white suspended solid. Then the reaction mixture was filtered and the filtrate was concentrated to give a saturated solution under reduced pressure and then 10.0 mL *n*-hexane was slowly added. The two-phase solution was then placed at -20 ºC under argon and the desirable product precipitates out as a white solid. The precipitated white solid was collected by filtration and recrystallized from DCM and *n*-hexane to afford pure catalyst.

MC2: White solid (84% yield); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.79–7.77 (m, 16H), 7.59 (s, 8H), 7.43–7.16 (m, 42H), 2.35 (s, 24H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 162.38 (q, *J* = 49.6 Hz), 143.95, 135.41, 132.71, 131.27, 130.05, 129.51 (qq, *J* = 31.4, 3.0 Hz), 126.54, 126.05, 123.83, 121.12, 118.14–117.98 (m), 21.52; ^{19}F NMR (377 MHz, CD_2Cl_2): δ -62.64; ^{77}Se NMR (76 MHz, CD_2Cl_2): δ 1160.17; HRMS (ESI+) exact mass calculated for $[M]^{2+}$ ($C_{68}H_{66}O_6Se_2Te_4$) requires m/z 825.9691, found m/z 825.9691.

MC4: White solid (81% yield); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.54–7.73 (m, 16H), 7.56 (s, 8H), 7.47–7.32 (m, 42H), 2.17 (s, 24H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 162.36 (q, *J* = 49.7 Hz), 141.05, 137.45, 135.40, 133.59, 133.15, 130.06, 129.49 (qq, *J* = 31.4, 3.0 Hz), 126.52, 126.00, 123.81, 121.10, 118.14–117.97 (m), 21.55; ^{19}F NMR (377 MHz, CD_2Cl_2): δ -62.65; ^{77}Se NMR (76 MHz, CD_2Cl_2): δ 1157.55; HRMS (ESI+) exact mass calculated for $[M]^{2+}$ ($C_{68}H_{66}O_6Se_2Te_4$) requires m/z 825.9691, found m/z 825.9693.

MC5: White solid (85% yield); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.83–7.82 (m, 16H), 7.62 (s, 8H), 7.46–7.10 (m, 42H), 2.20 (s, 24H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 162.37 (q, *J* = 49.6 Hz), 145.78, 141.94, 136.78, 135.40, 133.23, 132.77, 132.16, 130.07, 129.51 (qq, *J* = 31.5, 2.9 Hz), 128.42, 126.52, 125.53, 123.81, 121.10, 118.11–118.03 (m), 23.33; ^{19}F NMR (377 MHz, CD_2Cl_2): δ -62.70; ^{77}Se NMR (76 MHz, CD_2Cl_2): δ 1172.06; HRMS (ESI+) exact mass calculated for $[M]^{2+}$ ($C_{68}H_{66}O_6Se_2Te_4$) requires m/z 825.9691, found m/z 825.9688.

MC6: White solid (81% yield); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.81–7.79 (m, 16H), 7.60–7.11 (m, 42H), 2.17 (s, 48H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 162.34 (q, *J* = 49.6 Hz), 140.96, 135.40, 134.74, 133.34, 133.34, 130.00, 129.49 (qq, *J* = 31.2, 3.0 Hz), 126.52, 126.00, 123.81, 121.11, 118.11–117.95 (m), 21.46; ^{19}F NMR (377 MHz, CD_2Cl_2): δ -62.71; ^{77}Se NMR (76 MHz, CD_2Cl_2): δ 1163.03; HRMS (ESI+) exact mass calculated for $[M]^{2+}$ ($C_{76}H_{82}O_6Se_2Te_4$) requires m/z 882.0317, found m/z 882.0321.

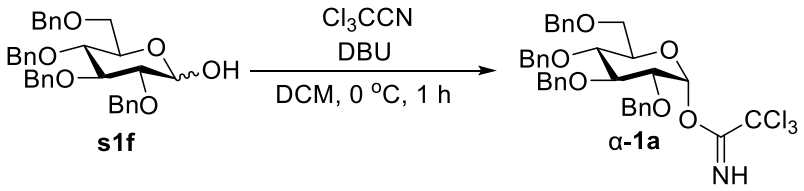
MC7: White solid (86% yield); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.83–7.82 (m, 16H), 7.62 (s, 8H), 7.47–7.42 (m, 2H), 7.29–7.07 (m, 32H), 2.35–2.20 (m, 48H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 162.37 (q, *J* = 49.5 Hz), 146.25,

144.36, 141.79, 135.42, 132.86, 132.79, 129.86, 129.52 (qq, *J* = 31.4, 3.0 Hz), 129.13, 126.54, 125.59, 123.83, 121.12, 118.13–117.97 (m), 23.17, 21.39; ^{19}F NMR (377 MHz, CD_2Cl_2): δ -62.72; ^{77}Se NMR (76 MHz, CD_2Cl_2): δ 1179.81; HRMS (ESI+) exact mass calculated for $[M]^{2+}$ ($C_{76}H_{82}O_6Se_2Te_4$) requires 882.0317, found m/z 882.0312.

MC8: White solid (82% yield); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.84–7.80 (m, 16H), 7.71–7.21(m, 48H), 2.36 (s, 24H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 162.40 (q, *J* = 49.6 Hz), 148.09, 144.15, 135.44, 132.78, 131.33, 130.63, 129.84, 129.54 (qq, *J* = 31.4, 3.0 Hz), 126.56, 125.13, 123.85, 123.02, 122.42, 121.15, 118.16–117.99 (m), 21.52; ^{19}F NMR (377 MHz, CD_2Cl_2): δ -62.69, 62.71; ^{77}Se NMR (76 MHz, CD_2Cl_2): δ 1160.79; HRMS (ESI+) exact mass calculated for $[M]^{2+}$ ($C_{70}H_{64}F_6O_6Se_2Te_4$) requires m/z 893.9565, found m/z 893.9562.

Glycoside donors were prepared using the following procedure:

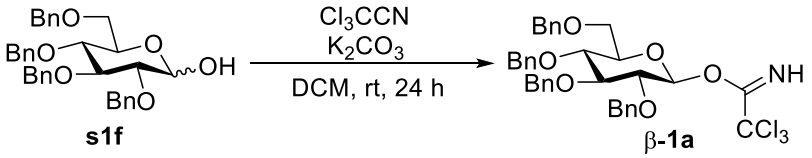
(2R,3R,4S,5R,6R)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl 2,2,2-trichloro-acetimidate (α-**1a**)



To a solution of **s1f** (5.57 g, 10.3 mmol) in CH_2Cl_2 (100.0 mL) was added CCl_3CN (10.0 mL, 99.7 mmol) and DBU (0.8 mL, 5.2 mmol) at 0 °C. The solution was stirred at room temperature for 1 h, and then the reaction mixture was concentrated. The residue was purified by silica gel column chromatography to give α-**1a** as a colorless solid in 78% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.57 (s, 1H), 7.33–7.24 (m, 18H), 7.15 (dd, *J* = 7.2, 2.4 Hz, 2H), 6.53 (d, *J* = 3.5 Hz, 1H), 4.96 (d, *J* = 11.0 Hz, 1H), 4.84 (t, *J* = 10.9 Hz, 2H), 4.76–4.66 (m, 2H), 4.60 (d, *J* = 12.0 Hz, 1H), 4.54–4.45 (m, 2H), 4.04–3.97 (m, 2H), 3.81–3.75 (m, 3H), 3.66 (dd, *J* = 10.9, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.27, 138.58, 138.02, 137.92, 137.82, 128.37, 128.34, 128.32, 128.30, 128.03, 127.96, 127.90, 127.77, 127.68, 127.67, 127.59, 127.56, 94.35, 91.25, 81.34, 79.33, 76.76, 75.60, 75.29, 73.44, 73.09, 72.83, 67.99. The above data of α-**1a** is consistent with the reported references.[4]

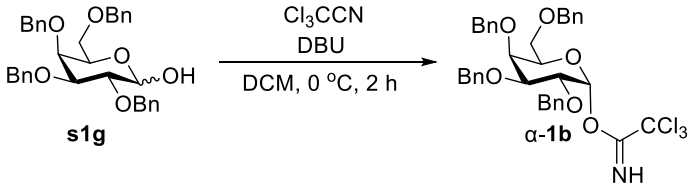
(2S,3R,4S,5R,6R)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl 2,2,2-trichloro-acetimidate (β-**1a**)



To a solution of **s1f** (6.43 g, 11.9 mmol) in CH_2Cl_2 (100.0 mL) was added CCl_3CN (10.0 mL, 99.7 mmol) and K_2CO_3 (7.12 g, 51.6 mmol) at room temperature. The solution was stirred at room temperature for 24 h, and then the reaction mixture was concentrated. The residue was purified by silica gel column chromatography to give **β-1a** as a colorless solid in 71% yield.

^{1}H NMR (400 MHz, $CDCl_3$): 8.70 (s, 1H), 7.32–7.24 (m, 18H), 7.17 (dd, *J* = 7.2, 2.4 Hz, 2H), 5.82–5.80 (m, 1H), 4.92 (dd, *J* = 14.1, 10.9 Hz, 2H), 4.83–4.74 (m, 3H), 4.63–4.52 (m, 3H), 3.77–3.71 (m, 5H), 3.66–3.63 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.19, 138.41, 138.09, 137.99, 137.93, 128.37, 128.35, 128.32, 127.95, 127.92, 127.84, 127.74, 127.61, 127.59, 98.33, 90.96, 84.55, 80.92, 77.25, 75.86, 75.57, 74.94, 74.86, 73.35, 68.21. The above data of **β-1a** is consistent with the reported references.[4]

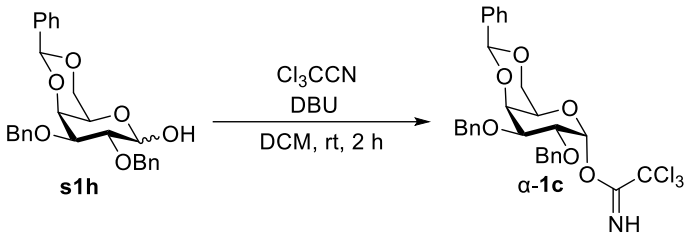
(2R,3R,4S,5S,6R)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl 2,2,2-trichloroacetimidate (**α-1b**)



To a solution of **s1g** (5.41 g, 10.0 mmol) in CH_2Cl_2 (100.0 mL) was added CCl_3CN (10.0 mL, 99.7 mmol) and DBU (0.8 mL, 5.2 mmol) at 0 °C. The solution was stirred at room temperature for 2 h, and then the reaction mixture was concentrated. The residue was purified by silica gel column chromatography to give **α-1b** as a colorless solid in 83% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (s, 1H), 7.35–7.23 (m, 22H), 6.52 (d, *J* = 3.4 Hz, 1H), 4.97 (d, *J* = 11.3 Hz, 1H), 4.83–4.80 (m, 1H), 4.76–4.73 (m, 3H), 4.59 (d, *J* = 11.3 Hz, 1H), 4.43 (q, *J* = 11.7 Hz, 2H), 4.24 (dd, *J* = 9.9, 3.5 Hz, 1H), 4.16 (t, *J* = 6.7 Hz, 1H), 4.06–4.00 (m, 2H), 4.64–4.59 (m, 1H), 3.55 (dd, *J* = 9.3, 5.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.22, 128.36, 128.27, 128.22, 128.18, 128.10, 127.81, 127.73, 127.58, 127.48, 127.39, 95.15, 91.40, 77.89, 75.85, 74.90, 74.61, 73.40, 72.95, 72.87, 72.14, 68.26. The above data of **α-1b** is consistent with the reported references.[4]

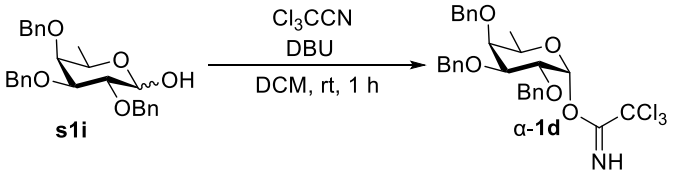
(2S,4aR,6R,7R,8S,8aS)-7,8-bis(benzyloxy)-2-phenylhexahydropyrano[3,2-d][1,3]dioxin-6-yl 2,2,2-trichloroacetimidate (**α-1c**)



To a solution of **s1h** (500 mg, 1.1 mmol) in CH_2Cl_2 (10.0 mL) was added CCl_3CN (1.1 mL, 11.2 mmol) and DBU (0.07 mL, 0.44 mmol) and stirred for 2 h at room temperature The reaction mixture was concentrated and purified by silica gel column chromatography to give **α-1c** as a colorless solid in 87% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56 (s, 1H), 7.53 (dd, *J* = 7.6, 2.1 Hz, 2H), 7.40–7.26 (m, 13H), 6.64 (d, *J* = 3.3 Hz, 1H), 5.51 (s, 1H), 4.84–4.74 (m, 4H), 4.30–4.26 (m, 3H), 4.10–4.07 (m, 1H), 4.01 (dd, *J* = 12.7, 1.8 Hz, 1H), 3.84 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.01, 138.37, 138.32, 137.64, 128.97, 128.27, 128.22, 128.15, 127.96, 127.63, 127.45, 127.38, 126.35, 101.08, 95.60, 91.36, 75.06, 74.69, 74.44, 73.11, 72.19, 69.05, 65.25. The above data of **α-1c** is consistent with the reported references.[5]

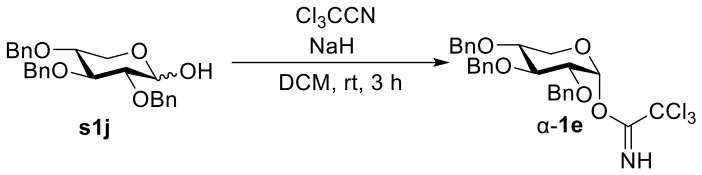
(2R,3R,4S,5S,6R)-3,4,5-tris(benzyloxy)-6-methyltetrahydro-2H-pyran-2-yl 2,2,2-trichloroacetimidate (α-**1d**)



To a solution of **s1i** (1.0 g, 2.3 mmol) in CH_2Cl_2 (25.0 mL) was added CCl_3CN (2.3 mL, 23.0 mmol) and DBU (0.52 mL, 3.5 mmol) and stirred for 1 h at room temperature The reaction mixture was concentrated and purified by silica gel column chromatography to give **α-1d** as a colorless solid in 65% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (s, 1H), 7.38–7.28 (m, 15H), 6.53 (d, *J* = 3.5 Hz, 1H), 5.02 (d, *J* = 11.5 Hz, 1H), 4.87 (d, *J* = 12.0 Hz, 1H), 4.79–4.75 (m, 3H), 4.69 (d, *J* = 11.6 Hz, 1H), 4.25 (dd, *J* = 10.1, 3.5 Hz, 1H), 4.12–4.07 (m, 1H), 4.03 (dd, *J* = 10.1, 2.8 Hz, 1H), 3.72 (dd, *J* = 2.8, 1.3 Hz, 1H), 1.17 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.22, 138.58, 138.41, 138.34, 128.39, 128.29, 128.21, 128.17, 127.65, 127.62, 127.50, 127.39, 95.29, 91.51, 78.21, 75.78, 74.91, 73.16, 72.78, 69.50, 16.65. The above data of α-**1d** is consistent with the reported references.[6]

(2R,3R,4S,5R)-3,4,5-tris(benzyloxy)tetrahydro-2H-pyran-2-yl 2,2,2-trichloroacetimidate (α-**1e**)

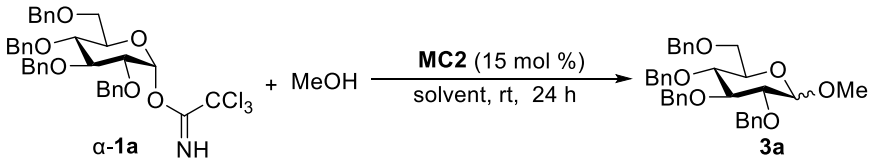


To a solution of **s1j** (2.0 g, 4.8 mmol) in CH_2Cl_2 (130.0 mL) was added CCl_3CN (2.4 mL, 23.8 mmol) and NaH (4.8 mmol) and stirred for 3 h at room temperature The reaction mixture was concentrated and purified by silica gel column chromatography to give α-**1e** as a colorless oil in 63% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.57 (s, 1H), 7.35–7.28 (m, 15H), 6.36 (d, *J* = 3.5 Hz, 1H), 4.94–4.86 (m, 2H), 4.78 (d, *J* = 11.6 Hz, 1H), 4.72 (d, *J* = 1.4 Hz, 2H), 4.65 (d, *J* = 11.6 Hz, 1H), 3.98 (t, *J* = 9.1 Hz, 1H), 3.82–3.71 (m, 2H), 3.69–3.62 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.45, 138.65, 138.04, 137.97, 128.47, 128.35, 128.31, 128.02, 127.91, 127.87, 127.70, 127.59, 127.56, 94.34, 91.24, 80.85, 79.07, 77.16, 75.70, 73.74, 73.01, 62.46. The above data of α-**1e** is consistent with the reported references.[7]

3. Optimization of Reaction Condition

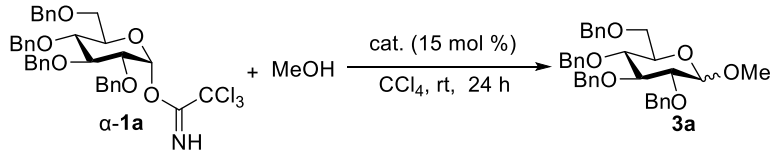
Table S1. *Evaluation of solvent*.



Entry	solvent	yield (%)	β-**3a**/α-**3a**
1	DCM	74	6:1
2	$CHCl_3$	57	6:1
3	DCE	69	5:1
4	CCl_4	76	8:1
5	DMF	<5	N.A.
6	DMSO	<5	N.A.

General procedure for optimization: To a reaction mixture of α-**1a** (0.15 mmol), **MC2** (0.015 mmol, 15 mol %) and MeOH (4.1 μL, 0.10 mmol) in a 10 mL-Schlenk tube was added corresponding solvent (0.5 mL) under argon atmosphere. The above reaction mixture was stirred at room temperature for 24 h. Then the reaction mixture was purified by flash chromatography on silica gel to give desired products **3a**.

Table S2. *Evaluation of **MC** catalysts.*[a]

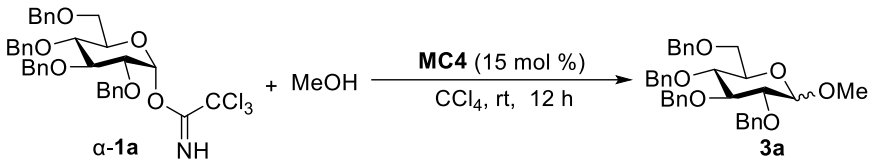


Entry	cat.	yield (%)	β-**3a**/α-**3a**
1	-	＜5%	-
2	**MC1**	42	6:1
3	**MC2**	76	8:1
4	**MC3**	54	8:1
5	**MC4**	78	12:1
6	**MC5**	69	6:1
7	**MC6**	81	11:1
8	**MC7**	70	5:1
9	**MC8**	65	9:1
10[b]	**MC4**	77	14:1
11[b]	TfOH	78	1:3
12[b]	TMSOTf	77	1:1
13[b]	$FeCl_3$	77	2:1
14[b]	$BF_3{\cdot}Et_2O$	83	3:1
15[b]	$Sc(OTf)_3$	68	3:1

[a]Unless otherwise indicated, reactions were carried out with α-**1a** (0.15 mmol), MeOH (0.10 mmol), cat. (15 mol %, 0.015 mmol) in CCl_4 (0.5 mL) at room temperature. [b]Reactions were carried out with α-**1a** (0.10 mmol), MeOH (0.10 mmol), cat. (15 mol %, 0.015 mmol) in CCl_4 (0.5 mL) at room temperature.

General procedure for optimization: To a reaction mixture of α-**1a** (0.15 mmol or 0.10 mmol), catalyst (0.015 mmol, 15 mol %) and MeOH (4.1 μL, 0.10 mmol) in a 10 mL-Schlenk tube was added CCl_4 (0.5 mL) under argon atmosphere. The above reaction mixture was stirred at room temperature for 24 h. Then the reaction mixture was purified by flash chromatography on silica gel to give desired products **3a**.

Table S3. *Evaluation of concentration of α-**1a** and MeOH*



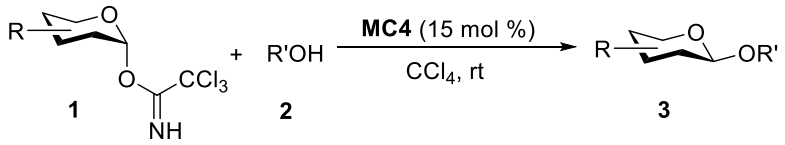
Entry	[α-**1a**]/[MeOH]	yield (%)	β-**3a**/α-**3a**
1	8:1	80	2:1
2	6:1	83	4:1
3	3:1	81	7:1
4	1.5:1	78	12:1
5	1:1	77	14:1
6	1:1.5	74	16:1
7	1:3	73	21:1
8	1:6	75	28:1

General procedure for optimization:

For entry 1–4: To a reaction mixture of α-**1a** (0.15–0.80 mmol, 1.5–8.0 equiv), catalyst **MC4** (50.6 mg, 0.015 mmol, 15 mol %) and MeOH (4.1 μL, 0.1 mmol) in a 10 mL-Schlenk tube was added CCl_4 (0.5 mL) under argon atmosphere. The above reaction mixture was stirred at room temperature for 12 h. Then the reaction mixture was purified by flash chromatography on silica gel to give desired products **3a**.

For entry 5-8: To a reaction mixture of α-**1a** (68.5 mg, 0.1 mmol), catalyst **MC4** (50.6 mg, 0.015 mmol, 15 mol %) and MeOH (0.1–0.6 mmol, 1.0–6.0 equiv) in a 10 mL-Schlenk tube was added CCl_4 (0.5 mL) under argon atmosphere. The above reaction mixture was stirred at room temperature for 12 h. Then the reaction mixture was purified by flash chromatography on silica gel to give desired products **3a**.

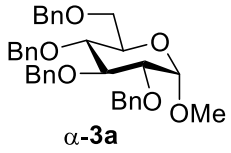
4. Optimized Procedure



To a reaction mixture of **1** (68.5 mg, 0.1 mmol), catalyst **MC4** (50.6 mg, 0.015 mmol, 15 mol %) and **2** (0.3–0.8 mmol, 3.0–8.0 equiv) in a 10 mL-Schlenk tube was added CCl_4 (0.5 mL) under argon atmosphere. The above reaction mixture was stirred at room temperature until the completion of the reaction as judged by TLC analysis. Then the reaction mixture was purified by flash chromatography on silica gel to give desired products **3**.

5. Analytical Data

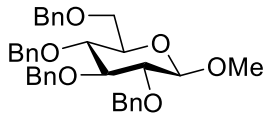
(2R,3R,4S,5R,6S)-3,4,5-tris(benzyloxy)-2-((benzyloxy)methyl)-6-methoxytetrahydro-2H-pyran (α-**3a**)



α-**3a**

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29–7.16 (m, 18H), 7.06–7.04 (m, 2H), 4.90 (d, *J* = 10.9 Hz, 1H), 4.76–4.70 (m, 3H), 4.60–4.51 (m, 3H), 4.41–4.38 (m, 2H), 3.91 (t, *J* = 9.3 Hz, 1H), 3.69–3.62 (m, 2H), 3.58–3.53 (m, 2H), 3.48 (dd, *J* = 9.7, 3.6 Hz, 1H), 3.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.76, 138.22, 138.13, 137.88, 128.41, 128.35, 128.32, 128.10, 127.94, 127.86, 127.81, 127.65, 127.62, 127.55, 98.17, 82.09, 79.79, 77.62, 75.72, 74.99, 73.44, 73.35, 70.01, 68.43, 55.13; HRMS (ESI+) exact mass calculated for $[M+H]^+$ ($C_{35}H_{38}O_6$) requires m/z 555.2742, found m/z 555.2714.

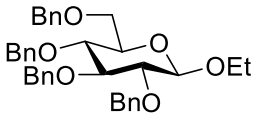
(2R,3R,4S,5R,6R)-3,4,5-tris(benzyloxy)-2-((benzyloxy)methyl)-6-methoxytetrahydro-2H-pyran (β-**3a**)



β-**3a**

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33–7.24 (m, 18H), 7.17–7.12 (m, 2H), 4.94–4.88 (m, 2H), 4.83–4.75 (m, 2H), 4.72–4.68 (m, 1H), 4.64–4.49 (m, 3H), 4.33–4.27 (m, 1H), 3.77–3.55 (m, 7H), 3.48–3.39 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.54, 138.47, 138.10, 138.04, 128.33, 128.29, 128.04, 127.91, 127.81, 127.72, 127.69, 127.57, 127.54, 104.64, 84.58, 82.26, 77.80, 75.62, 74.95, 74.78, 74.69, 73.43, 68.85, 57.05; HRMS (ESI+) exact mass calculated for $[M+Na]^+$ ($C_{35}H_{38}NaO_6$) requires m/z 577.2561, found m/z 577.2764.

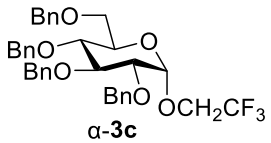
(2R,3R,4S,5R,6R)-3,4,5-tris(benzyloxy)-2-((benzyloxy)methyl)-6-ethoxytetrahydro-2H-pyran (β-**3b**)



β-**3b**

Colorless oil (44.4 mg, 78% yield, β/α = 15:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26–7.17 (m, 18H), 7.08–7.06 (m, 2H), 4.86 (t, *J* = 11.1 Hz, 2H), 4.75–4.63 (m, 3H), 4.54–4.42 (m, 3H), 4.32 (d, *J* = 7.8 Hz, 1H), 3.97–3.89 (m, 1H), 3.68–3.47 (m, 5H), 3.37 (t, *J* = 8.4 Hz, 2H), 1.21 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.60, 138.51, 138.16, 138.08, 128.34, 128.32, 128.30, 128.14, 127.93, 127.85, 127.73, 127.70, 127.61, 127.54, 103.44, 84.67, 82.26, 77.89, 75.64, 74.96, 74.80, 74.76, 73.43, 69.00, 65.54, 15.32; HRMS (ESI+) exact mass calculated for $[M+Na]^+$ ($C_{36}H_{40}NaO_6$) requires m/z 591.2714, found m/z 591.2706.

(2R,3R,4S,5R,6S)-3,4,5-tris(benzyloxy)-2-((benzyloxy)methyl)-6-(2,2,2-trifluoroethoxy)tetrahydro-2H-pyran (α-**3c**)

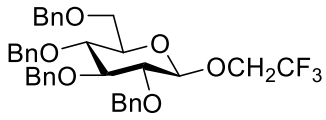


α-**3c**

Colorless oil (50.4 mg, 81% yield, β/α = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36–7.28 (m, 18H), 7.17–7.15 (m, 2H), 4.96 (d, *J* = 4.4 Hz, 1H), 4.93 (d, *J* = 4.1 Hz, 1H),

4.82 (t, *J* = 11.1 Hz, 2H), 4.70 (d, *J* = 10.7 Hz, 1H), 4.64–4.61 (m, 1H), 4.57–4.55 (m, 1H), 4.53–4.51 (m, 2H), 4.28–4.19 (m, 1H), 4.02–3.95 (m, 1H), 3.75–3.62 (m, 4H), 3.54–3.45 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.43, 137.95, 137.91, 128.45, 128.39, 127.96, 127.82, 127.82, 127.77, 127.71, 127.64, 103.61, 84.31, 81.69, 77.36, 75.72, 75.04, 74.98, 74.92, 73.48, 68.55, 66.51, 66.16, 65.82, 65.47; HRMS (ESI+) exact mass calculated for $[M+H]^+$ ($C_{36}H_{38}F_3O_6$) requires m/z 623.2615, found m/z 623.2616.

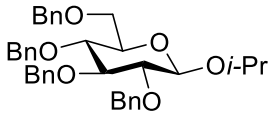
(2R,3R,4S,5R,6R)-3,4,5-tris(benzyloxy)-2-((benzyloxy)methyl)-6-(2,2,2-trifluoroethoxy)tetrahydro-2H-pyran (β-**3c**)



β-**3c**

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38–7.27 (m, 18H), 7.18–7.12 (m, 2H), 5.00 (d, *J* = 10.8 Hz, 1H), 4.86–4.79 (m, 4H), 4.63 (dd, *J* = 15.6, 12.0 Hz, 2H), 4.48 (dd, *J* = 11.4, 3.6 Hz, 2H), 4.00 (t, *J* = 9.3 Hz, 1H), 3.90 (q, *J* = 8.7 Hz, 2H), 3.80–3.59 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.68, 138.02, 137.71, 128.47, 128.38, 128.05, 127.96, 127.91, 127.89, 127.81, 127.75, 127.61, 97.78, 81.54, 79.63, 77.18, 75.76, 75.14, 73.48, 73.31, 70.88, 68.09, 65.14, 64.80, 64.45, 64.10; HRMS (ESI+) exact mass calculated for $[M+Na]^+$ ($C_{36}H_{37}F_3NaO_6$) requires m/z 645.2435, found m/z 645.2421.

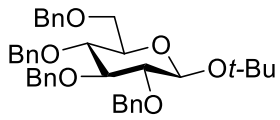
(2R,3R,4S,5R,6R)-3,4,5-tris(benzyloxy)-2-((benzyloxy)methyl)-6-isopropoxytetrahydro-2H-pyran (β-**3d**)



β-**3d**

Colorless oil (43.1 mg, 74% yield, β/α = 9:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27–7.16 (m, 18H), 7.09–7.07 (m, 2H), 4.89 (d, *J* = 10.8 Hz, 1H), 4.83 (d, *J* = 10.9 Hz, 1H), 4.71 (dd, *J* = 15.3, 10.9 Hz, 2H), 4.62 (d, *J* = 10.9 Hz, 1H), 4.54–4.43 (m, 3H), 4.38 (d, *J* = 7.8 Hz, 1H), 3.94 (p, *J* = 6.1 Hz, 1H), 3.65 (dd, *J* = 10.8, 2.0 Hz, 1H), 3.59–3.53 (m, 2H), 3.46 (t, *J* = 9.2 Hz, 1H), 3.39–3.32 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.64, 138.50, 138.26, 138.10, 128.36, 128.34, 128.31, 128.20, 127.98, 127.87, 127.72, 127.68, 127.63, 127.56, 127.52, 102.16, 84.82, 82.28, 77.96, 75.68, 74.97, 74.82, 74.79, 73.40, 72.35, 69.14, 23.72, 22.22; HRMS (ESI+) exact mass calculated for $[M+Na]^+$ ($C_{37}H_{42}NaO_6$) requires m/z 605.2874, found m/z 605.2879.

(2R,3R,4S,5R,6S)-3,4,5-tris(benzyloxy)-2-((benzyloxy)methyl)-6-(tert-butoxy)tetrahydro-2H-pyran (β-**3e**)

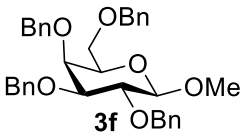


β-**3e**

Colorless oil (46.0 mg, 77% yield, β/α = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27–7.18 (m, 18H), 7.12–7.09 (m, 2H), 4.91 (d, *J* = 10.9 Hz, 1H), 4.84 (d, *J* = 10.9 Hz, 1H), 4.73 (dd, *J* = 16.0, 10.9 Hz, 2H), 4.64 (d, *J* = 11.0 Hz, 1H), 4.53–4.45 (m, 4H), 3.65–3.60 (m, 1H), 3.57–3.53 (m, 2H), 3.46 (t, *J* = 9.2 Hz, 1H), 3.40–3.33 (m, 2H), 1.25 (s, 9H); ^{13}C

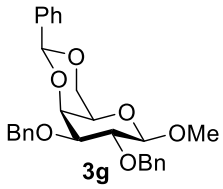
NMR (100 MHz, $CDCl_3$): δ 138.64, 138.48, 138.32, 138.15, 128.33, 128.26, 128.14, 127.92, 127.86, 127.68, 127.59, 127.54, 127.44, 97.82, 85.09, 82.35, 78.11, 76.03, 75.70, 74.90, 74.89, 74.60, 73.33, 69.33, 28.88; HRMS (ESI+) exact mass calculated for $[M+Na]^+$ ($C_{38}H_{44}NaO_6$) requires m/z 619.3030, found m/z 619.3037.

(2R,3S,4S,5R,6R)-3,4,5-tris(benzyloxy)-2-((benzyloxy)methyl)-6-methoxytetrahydro-2H-pyran (**3f**)



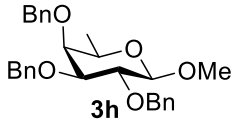
[**1**]/[**2**] = 1:5 used for reaction; Colourless oil (36.1 mg, 65% yield, β/α = 23:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40–7.26 (m, 20H), 4.96 (d, *J* = 11.7 Hz, 1H), 4.92 (d, *J* = 11.0 Hz, 1H), 4.79–4.74 (m, 3H), 4.64 (d, *J* = 11.6 Hz, 1H), 4.49–4.41 (m, 2H), 4.30 (d, *J* = 7.6 Hz, 1H), 3.92–3.91 (m, 1H), 3.83 (dd, *J* = 9.8, 7.7 Hz, 1H), 3.62 (dd, *J* = 6.3, 1.8 Hz, 2H), 3.59–3.52 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.80, 138.62, 138.48, 137.89, 128.39, 128.32, 128.24, 128.23, 128.12, 128.08, 127.85, 127.75, 127.52, 127.50, 127.47, 104.97, 82.12, 79.61, 75.11, 74.43, 73.52, 73.42, 73.35, 72.97, 68.83, 56.98; HRMS (ESI+) exact mass calculated for $[M+H]^+$ ($C_{35}H_{39}O_6$) requires m/z 555.2741, found m/z 555.2732.

(2S,4aR,6R,7R,8S,8aS)-7,8-bis(benzyloxy)-6-methoxy-2-phenylhexahydropyrano[3,2-d][1,3]dioxine (**3g**)



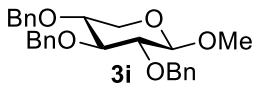
[**1**]/[**2**] = 1:5 used for reaction; Colorless oil (33.3 mg, 72% yield, β/α = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58–7.56 (m, 2H), 7.42–7.29 (m, 13H), 5.51 (s, 1H), 4.92 (d, *J* = 10.9 Hz, 1H), 4.81–4.77 (m, 3H), 4.34–4.31 (m, 2H), 4.13 (dd, *J* = 3.7, 1.1 Hz, 1H), 4.03 (dd, *J* = 12.4, 1.8 Hz, 1H), 3.85 (dd, *J* = 9.7, 7.7 Hz, 1H), 3.60–3.56 (m, 4H), 3.33 (d, *J* = 1.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.83, 138.34, 137.76, 128.90, 128.29, 128.22, 128.09, 127.98, 127.72, 127.63, 127.48, 126.46, 104.66, 101.29, 79.09, 78.41, 75.18, 73.88, 71.96, 69.16, 66.33, 57.03; HRMS (ESI+) exact mass calculated for $[M+H]^+$ ($C_{28}H_{31}O_6$) requires m/z 463.2115, found m/z 463.2113.

(2R,3R,4S,5S,6R)-3,4,5-tris(benzyloxy)-2-methoxy-6-methyltetrahydro-2H-pyran (**3h**)



[**1**]/[**2**] = 1:5 used for reaction; Colorless oil (34.5 mg, 77% yield, β/α = 19:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41–7.28 (m, 15H), 5.01 (d, *J* = 11.8 Hz, 1H), 4.94 (d, *J* = 11.0 Hz, 1H), 4.83–4.70 (m, 4H), 4.26 (d, *J* = 7.7 Hz, 1H), 3.82 (dd, *J* = 9.7, 7.6 Hz, 1H), 3.59–3.50 (m, 5H), 3.48 (qd, *J* = 6.4, 1.0 Hz, 1H), 1.22 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.90, 138.60, 138.57, 128.38, 128.31, 128.20, 128.06, 128.04, 127.50, 127.45, 127.41, 104.83, 82.45, 79.48, 76.23, 75.01, 74.47, 73.09, 70.23, 56.82, 16.80; HRMS (ESI+) exact mass calculated for $[M+H]^+$ ($C_{28}H_{33}O_5$) requires m/z 449.2323, found m/z 449.2329.

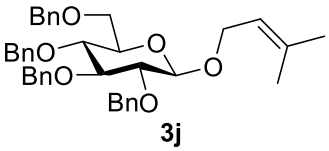
(2R,3R,4S,5R)-3,4,5-tris(benzyloxy)-2-methoxytetrahydro-2H-pyran(**3i**)



3i

[**1**]/[**2**] = 1:5 used for reaction; Colorless oil (32.6 mg, 75% yield, β/α = 21:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38–7.29 (m, 15H), 4.91–4.87 (m, 3H), 4.76–4.71 (m, 2H), 4.64 (d, *J* = 11.6 Hz, 1H), 4.27 (d, *J* = 7.5 Hz, 1H), 3.96 (dd, *J* = 11.5, 4.9 Hz, 1H), 3.66–3.59 (m, 2H), 3.55 (s, 3H), 3.37 (t, *J* = 1.3 Hz, 1H), 3.23 (dd, *J* = 11.6, 9.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.66, 138.55, 138.15, 128.44, 128.31, 127.99, 127.94, 127.82, 127.59, 127.57, 105.26, 83.66, 81.95, 77.88, 75.57, 74.82, 73.35, 63.86, 56.99; HRMS (ESI+) exact mass calculated for $[M+Na]^+$ ($C_{27}H_{30}NaO_5$) requires m/z 457.1985, found m/z 457.1986.

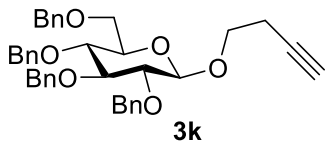
(2R,3R,4S,5R,6R)-3,4,5-tris(benzyloxy)-2-((benzyloxy)methyl)-6-((3-methylbut-2-en-1-yl)oxy)tetrahydro-2H-pyran (**3j**)



3j

[**1**]/[**2**] = 1:3 used for reaction; Colorless oil (40.8 mg, 67% yield, β/α = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41–7.29 (m, 18H), 7.22–7.19 (m, 2H), 5.44 (ddp, *J* = 8.0, 6.6, 1.4 Hz, 1H), 4.98 (dd, *J* = 13.4, 10.9 Hz, 2H), 4.84 (dd, *J* = 16.7, 10.8 Hz, 2H), 4.74 (d, *J* = 10.9 Hz, 1H), 4.68–4.65 (m, 1H), 4.61–4.56 (m, 2H), 4.49–4.40 (m, 2H), 4.26 (dd, *J* = 11.8, 7.6 Hz, 1H), 3.79 (dd, *J* = 10.8, 2.0 Hz, 1H), 3.75–3.71 (m, 1H), 3.69–3.60 (m, 2H), 3.53–3.47 (m, 2H), 1.80 (d, *J* = 1.3 Hz, 3H), 1.72 (d, *J* = 1.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.60, 138.53, 138.19, 138.10, 137.73, 128.34, 128.32, 128.30, 128.28, 128.18, 127.91, 127.86, 127.67, 127.59, 127.55, 127.51, 120.33, 102.16, 84.73, 82.26, 77.91, 75.66, 74.95, 74.83, 74.74, 73.40, 69.00, 65.66, 25.78, 17.97; HRMS (ESI+) exact mass calculated for $[M+Na]^+$ ($C_{39}H_{44}NaO_6$) requires m/z 631.3030, found m/z 631.3031.

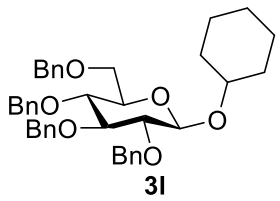
(2R,3R,4S,5R,6R)-3,4,5-tris(benzyloxy)-2-((benzyloxy)methyl)-6-(but-3-yn-1-yloxy)tetrahydro-2H-pyran (**3k**)



3k

[**1**]/[**2**] = 1:3 used for reaction; Colorless oil (49.2 mg, 83% yield, β/α = 8:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30–7.18 (m, 18H), 7.09–7.06 (m, 2H), 4.92 (d, *J* = 11.0 Hz, 1H), 4.86 (d, *J* = 10.9 Hz, 1H), 4.72 (dd, *J* = 12.5, 10.9 Hz, 2H), 4.64 (d, *J* = 11.0 Hz, 1H), 4.52–4.43 (m, 3H), 4.36 (d, *J* = 7.8 Hz, 1H), 4.00–3.94 (m, 1H), 3.67–3.52 (m, 5H), 3.41–3.36 (m, 2H), 2.50–2.46 (m, 2H), 1.88 (t, *J* = 2.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.55, 138.46, 138.07, 138.03, 128.36, 128.34, 128.30, 128.19, 127.95, 127.85, 127.77, 127.74, 127.62, 127.60, 127.58, 103.63, 84.56, 82.05, 81.15, 77.70, 75.68, 74.99, 74.80, 74.77, 73.46, 69.49, 68.80, 67.90, 20.00; HRMS (ESI+) exact mass calculated for $[M+Na]^+$ ($C_{38}H_{40}NaO_6$) requires m/z 615.2717, found m/z 615.2721.

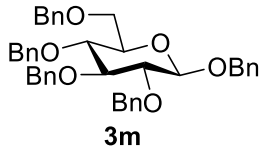
(2R,3R,4S,5R,6R)-3,4,5-tris(benzyloxy)-2-((benzyloxy)methyl)-6-(cyclohexyloxy)tetrahydro-2H-pyran (**3l**)



3l

[**1**]/[**2**] = 1:3 used for reaction; Colorless oil (43.6 mg, 70% yield, β/α = 12:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36–7.25 (m, 18H), 7.18–7.16 (m, 2H), 5.00 (d, *J* = 10.9 Hz, 1H), 4.92 (d, *J* = 10.9 Hz, 1H), 4.82 (d, *J* = 10.8 Hz, 1H), 4.78 (d, *J* = 10.9 Hz, 1H), 4.71 (d, *J* = 10.9 Hz, 1H), 4.62–4.59 (m, 1H), 4.57–4.50 (m, 3H), 3.76–3.69 (m, 2H), 3.67–3.61 (m, 2H), 3.55 (t, *J* = 9.2 Hz, 1H), 3.48–3.43 (m, 2H), 2.04–1.91 (m, 2H), 1.80–1.73 (m, 2H), 1.55–1.41 (m, 3H), 1.34–1.22 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.62, 138.48, 138.26, 138.07, 128.33, 128.30, 128.27, 128.15, 127.95, 127.82, 127.69, 127.62, 127.58, 127.50, 127.47, 101.90, 84.79, 82.23, 77.96, 77.71, 75.63, 74.94, 74.78, 74.75, 73.34, 69.11, 33.75, 31.97, 25.59, 24.05, 23.91; HRMS (ESI+) exact mass calculated for $[M+Na]^+$ ($C_{40}H_{46}NaO_6$) requires m/z 645.3187, found m/z 645.3186.

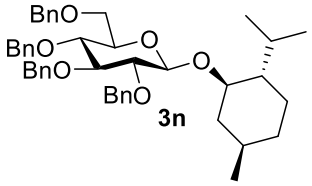
(2R,3R,4S,5R,6R)-2,3,4,5-tetrakis(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran (**3m**)



3m

[**1**]/[**2**] = 1:5 used for reaction; Colorless oil (41.0 mg, 65% yield, β/α=10:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39–7.25 (m, 23H), 7.17–7.12 (m, 2H), 5.00–4.91 (m, 3H), 4.80 (dd, *J* = 15.8, 10.9 Hz, 2H), 4.72 (d, *J* = 10.9 Hz, 1H), 4.69–4.62 (m, 2H), 4.58–4.51 (m, 3H), 3.78–3.75 (m, 1H), 3.72–3.69 (m, 1H), 3.67–3.59 (m, 2H), 3.55–3.51 (m, 1H), 3.49–3.46 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.56, 138.36, 138.16, 138.07, 137.45, 128.36, 128.34, 128.31, 128.16, 127.93, 127.91, 127.85, 127.73, 127.72, 127.62, 127.58, 102.58, 84.71, 82.27, 77.85, 75.69, 74.97, 74.87, 73.46, 71.12, 68.90; HRMS (ESI+) exact mass calculated for $[M+H]^+$ ($C_{41}H_{43}O_6$) requires m/z 631.3054, found m/z 631.3061.

(2R,3R,4S,5R,6R)-3,4,5-tris(benzyloxy)-2-((benzyloxy)methyl)-6-(((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl)oxy)tetrahydro-2H-pyran (**3n**)

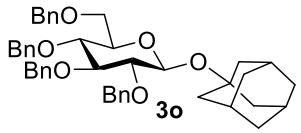


3n

[**1**]/[**2**] = 1:5 used for reaction; Colorless oil (44.8 mg, 66% yield, β/α = 9:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32–7.21 (m, 18H), 7.18–7.14 (m, 2H), 4.90 (t, *J* = 10.7 Hz, 2H), 4.77 (t, *J* = 10.8 Hz, 2H), 4.65 (d, *J* = 10.9 Hz, 1H), 4.59–4.49 (m, 3H), 4.44 (d, *J* = 7.8 Hz, 1H), 3.66 (d, *J* = 3.2 Hz, 2H), 3.58 (p, *J* = 9.0 Hz, 2H), 3.46 (td, *J* = 10.7, 4.2 Hz, 1H), 3.40–3.36 (m, 2H), 2.32 (pd, *J* = 7.0, 2.5 Hz, 1H), 2.10 (dt, *J* = 11.9, 4.2 Hz, 1H), 1.62 (dt, *J* = 12.8, 2.5 Hz, 2H), 1.27–1.20 (m, 2H), 1.02–0.78 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.77, 138.50, 138.32, 138.16, 128.35, 128.29, 128.26, 128.06, 127.75, 127.70, 127.61, 127.58, 127.47, 127.46, 100.76, 84.92, 82.16, 77.90, 77.74, 75.57, 74.96, 74.81, 74.74, 73.63, 69.26, 48.07, 40.94, 34.41, 31.42, 25.22,

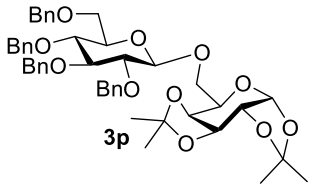
23.14, 22.22, 21.07, 15.91; HRMS (ESI+) exact mass calculated for $[M+H]^+$ ($C_{44}H_{55}O_6$) requires m/z 679.3993, found m/z 679.3995.

(2S,3R,4S,5R,6R)-2-(((3R,5R,7R)-adamantan-1-yl)oxy)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran (**3o**)



[**1**]/[**2**] = 1:5 used for reaction; Colorless oil (47.9 mg, 71% yield, β/α = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29–7.15 (m, 20H), 7.11 (dd, *J* = 7.4, 2.1 Hz, 2H), 4.93 (d, *J* = 11.0 Hz, 1H), 4.84 (d, *J* = 10.9 Hz, 1H), 4.74 (d, *J* = 10.9 Hz, 1H), 4.69 (d, *J* = 10.9 Hz, 1H), 4.64 (d, *J* = 7.7 Hz, 1H), 4.62 (d, *J* = 4.6 Hz, 1H), 4.53–4.45 (m, 3H), 3.66 (dd, *J* = 10.7, 1.8 Hz, 1H), 3.59–3.52 (m, 2H), 3.46–3.33 (m, 3H), 2.09–2.05 (m, 3H), 1.89–1.84 (m, 3H), 1.78–1.74 (m, 3H), 1.59–1.50 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.61, 138.49, 138.32, 138.11, 128.28, 128.26, 128.19, 128.15, 127.87, 127.81, 127.63, 127.51, 127.49, 127.47, 127.38, 96.16, 85.03, 82.24, 78.12, 75.63, 75.21, 74.83, 74.47, 73.26, 69.41, 42.70, 36.20, 30.61; HRMS (ESI+) exact mass calculated for $[M+H]^+$ ($C_{44}H_{51}O_6$) requires m/z 675.3680, found m/z 675.3676.

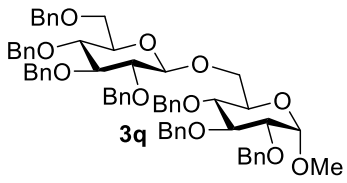
(3aR,5R,5aS,8aS,8bR)-2,2,7,7-tetramethyl-5-((((2R,3R,4S,5R,6R)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl)oxy)methyl)tetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran (**3p**)



[**1**]/[**2**] = 1:3 used for reaction; Colorless oil (45.4 mg, 58% yield, β/α = 6:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45–7.43 (m, 2H), 7.35–7.26 (m, 16H), 7.15 (dd, *J* = 7.2, 2.4 Hz, 2H), 5.59 (d, *J* = 5.0 Hz, 1H), 5.07 (d, *J* = 11.1 Hz, 1H), 4.98 (d, *J* = 10.9 Hz, 1H), 4.81 (dd, *J* = 13.5, 10.9 Hz, 2H), 4.74 (d, *J* = 11.2 Hz, 1H), 4.65–4.59 (m, 2H), 4.56–4.46 (m, 3H), 4.33 (dd, *J* = 5.0, 2.4 Hz, 1H), 4.26 (dd, *J* = 7.9, 1.9 Hz, 1H), 4.18 (dd, *J* = 10.7, 3.6 Hz, 1H), 4.13–4.09 (m, 1H), 3.77–3.71 (m, 3H), 3.66–3.62 (m, 2H), 3.50–3.44 (m, 2H), 1.52 (s, 3H), 1.47 (s, 3H), 1.34–1.33 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.65, 138.10, 138.09, 128.61, 128.33, 128.31, 128.17, 127.91, 127.85, 127.83, 127.67, 127.57, 127.50, 127.44, 109.33, 108.53, 104.35, 96.34, 84.50, 81.56, 77.66, 75.63, 74.95, 74.69, 74.30, 73.45, 71.40, 70.73, 70.43, 69.67, 68.70, 67.30, 26.00, 25.96, 24.99, 24.40; HRMS (ESI+) exact mass calculated for $[M+H]^+$ ($C_{46}H_{55}O_{11}$) requires m/z 783.3739, found m/z 783.3742.

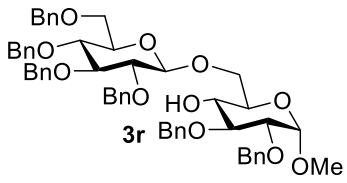
(2R,3R,4S,5R,6R)-3,4,5-tris(benzyloxy)-2-((benzyloxy)methyl)-6-(((2R,3R,4S,5R,6S)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2H-pyran-2-yl)methoxy)tetrahydro-2H-pyran (**3q**)

[**1**]/[**2**] = 1:3 used for reaction; Colorless oil (55.3 mg, 56% yield, β/α = 6:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26–



7.16 (m, 30H), 7.10 (dd, *J* = 6.9, 3.2 Hz, 6H), 4.90 (d, *J* = 4.7 Hz, 1H), 4.88 (d, *J* = 4.4 Hz, 1H), 4.83 (d, *J* = 10.9 Hz, 1H), 4.74–4.42 (m, 13H), 4.27 (d, *J* = 7.8 Hz, 1H), 4.10 (dd, *J* = 10.8, 2.0 Hz, 1H), 3.92 (t, *J* = 9.2 Hz, 1H), 3.77–3.73 (m, 1H), 3.63–3.41 (m, 10H), 3.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.77, 138.46, 138.31, 138.28, 138.17, 138.07, 138.04, 128.39, 128.33, 128.30, 128.28, 128.27, 128.08, 127.90, 127.88, 127.85, 127.81, 127.79, 127.69, 127.65, 127.59, 127.55, 127.52, 127.48, 127.45, 103.75, 97.99, 84.73, 82.01, 81.92, 81.61, 79.70, 77.93, 77.84, 77.20, 75.65, 75.62, 74.99, 74.93, 74.82, 73.36, 73.29, 72.29, 69.78, 68.94, 68.50, 55.14; HRMS (ESI+) exact mass calculated for $[M+H]^+$ ($C_{62}H_{67}O_{11}$) requires m/z 987.4678, found m/z 987.4678.

(2R,3R,4S,5R,6S)-4,5-bis(benzyloxy)-6-methoxy-2-((((2R,3R,4S,5R,6R)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl)oxy)methyl)tetrahydro-2H-pyran-3-ol (**3r**)

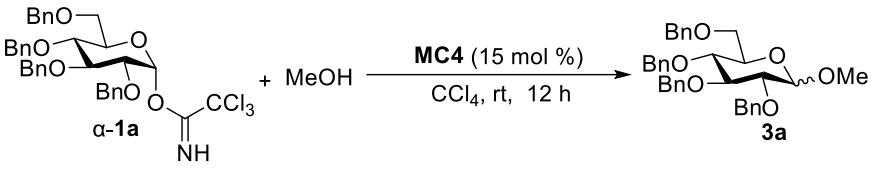


[**1**]/[**2**] = 1:3 used for reaction; Colorless oil (47.5 mg, 53% yield, β/α = 9:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28–7.17 (m, 30H), 7.07 (dd, *J* = 6.1, 2.5 Hz, 2H), 4.94–4.81 (m, 3H), 4.74–4.60 (m, 5H), 4.57–4.50 (m, 3H), 4.45–4.37 (m, 3H), 4.04 (dt, *J* = 10.6, 1.8 Hz, 1H), 3.74–3.47 (m, 9H), 3.43–3.36 (m, 3H), 3.26 (d, *J* = 1.2 Hz, 3H), 2.34 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.85, 138.52, 138.41, 138.08, 138.03, 128.52, 128.44, 128.35, 128.35, 128.33, 128.11, 127.99, 127.93, 127.90, 127.84, 127.77, 127.73, 127.61, 127.57, 103.72, 98.14, 84.64, 81.99, 81.39, 79.58, 77.72, 75.66, 75.34, 74.97, 74.84, 74.73, 73.38, 73.14, 70.36, 70.08, 68.81, 68.65, 55.22; HRMS (ESI+) exact mass calculated for $[M+H]^+$ ($C_{55}H_{61}NO_{11}$) requires m/z 897.4208, found m/z 897.4207.

6. Mechanistic Study

(1) *Evaluation of concentration of α-**1a** and MeOH*

Table S4. Evaluation of concentration of α-**1a** and MeOH by **MC4**



[MeOH]/[α-**1a**]	yield (%)	β-**3a**/α-**3a**
1:1	77	14:1
1:1.5	78	12:1
1:3	81	7:1
1:6	83	4:1

[α-**1a**]/[MeOH]	yield (%)	β-**3a**/α-**3a**
1:1	77	14:1
1:1.5	74	16:1
1:3	73	21:1
1:6	74	28:1

For **Table S4.** (left): to a reaction mixture of α-**1a** (0.1–0.6 mmol, 1.0–6.0 equiv), catalyst **MC4** (50.6 mg, 0.015 mmol, 15 mol %) and MeOH (4.1 μL, 0.1 mmol) in a 10 mL-Schlenk tube was added CCl_4 (0.5 mL) under argon atmosphere. The above reaction mixture was stirred at room temperature for 12 h. Then the reaction mixture was purified by flash chromatography on silica gel to give desired products **3a**.

For **Table S4.** (right): to a reaction mixture of α-**1a** (68.5 mg, 0.1 mmol), catalyst **MC4** (50.6 mg, 0.015 mmol, 15 mol %) and MeOH (0.1–0.6 mmol, 1.0–6.0 equiv) in a 10 mL-Schlenk tube was added CCl_4 (0.5 mL) under argon atmosphere. The above reaction mixture was stirred at room temperature for 12 h. Then the reaction mixture was purified by flash chromatography on silica gel to give desired products **3a**.

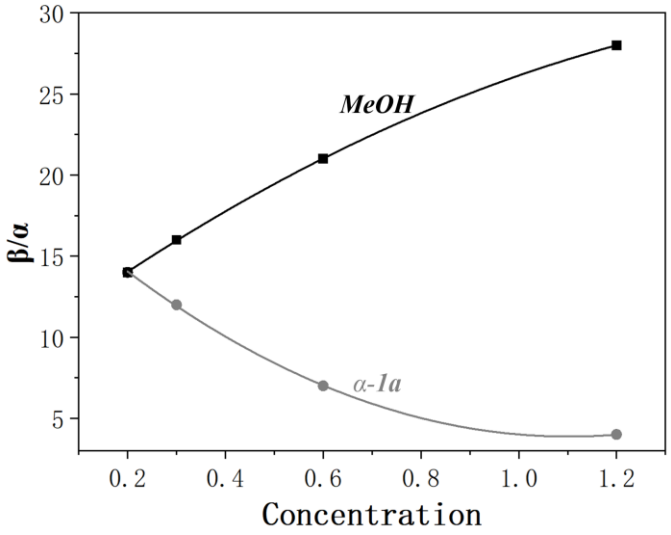


Fig. S2. Evaluation of concentration of α-**1a** and MeOH by **MC4**

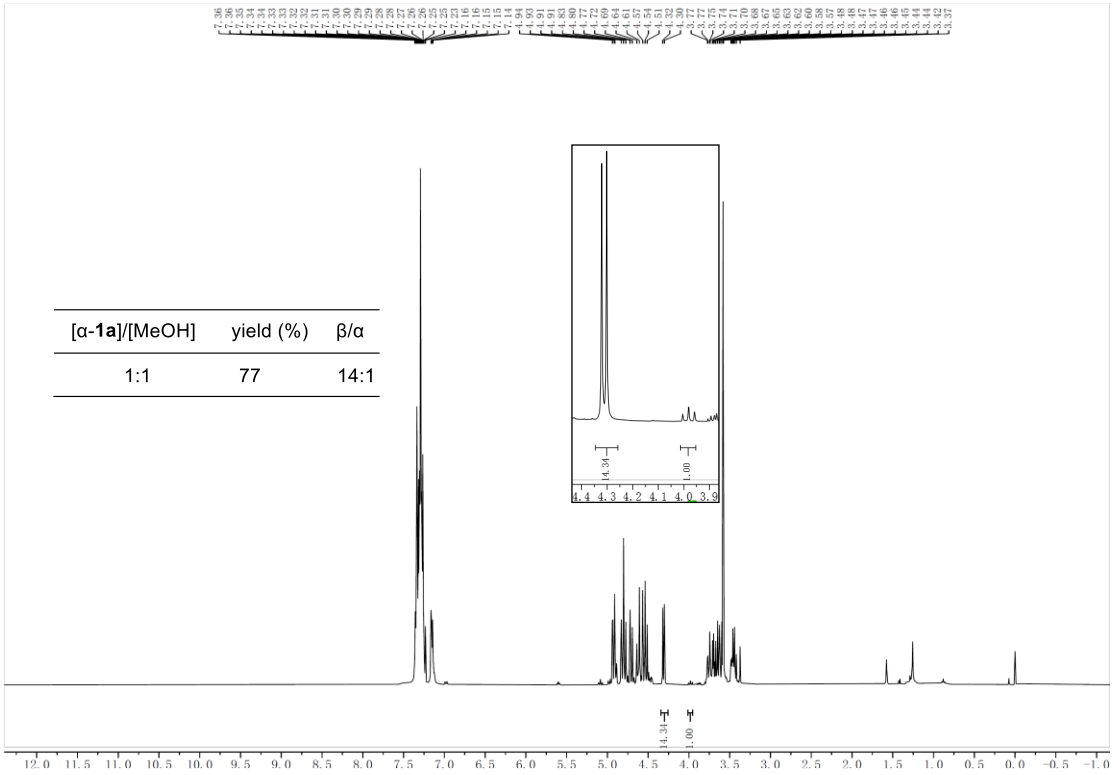


Fig. S3. β/α selectivity of reaction with [α-**1a**]/[MeOH] = 1:1 by **MC4**

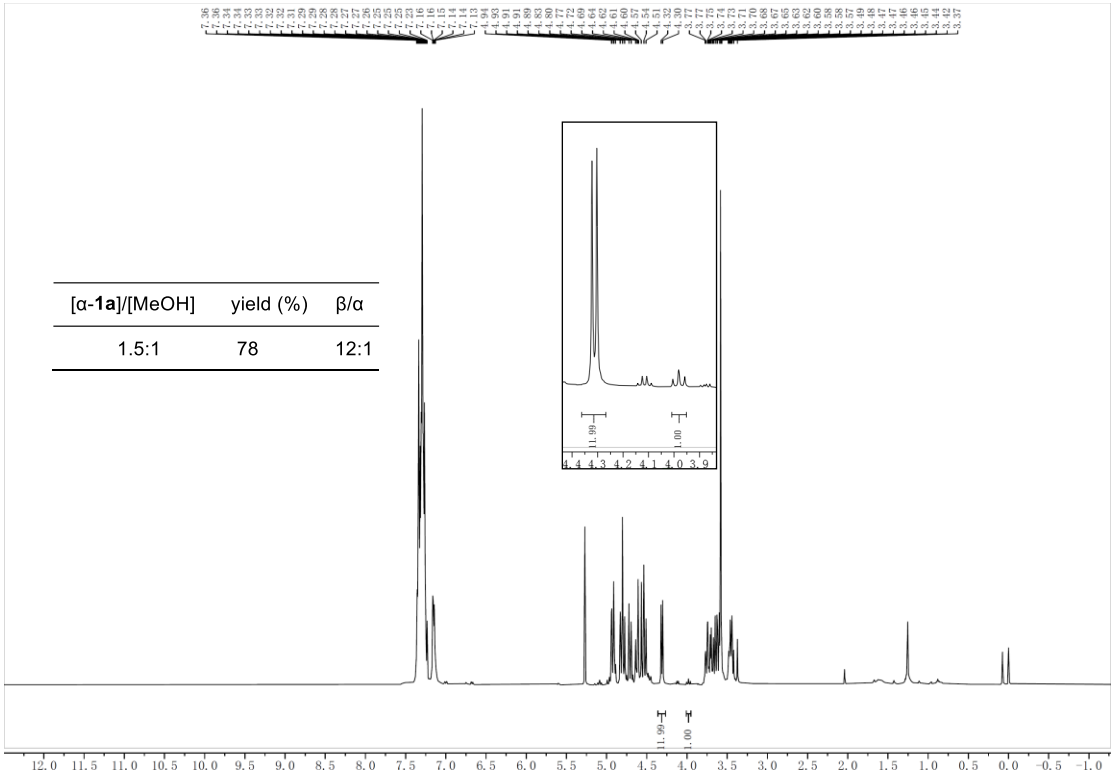


Fig. S4. β/α selectivity of reaction with [α-**1a**]/[MeOH] = 1.5:1 by **MC4**

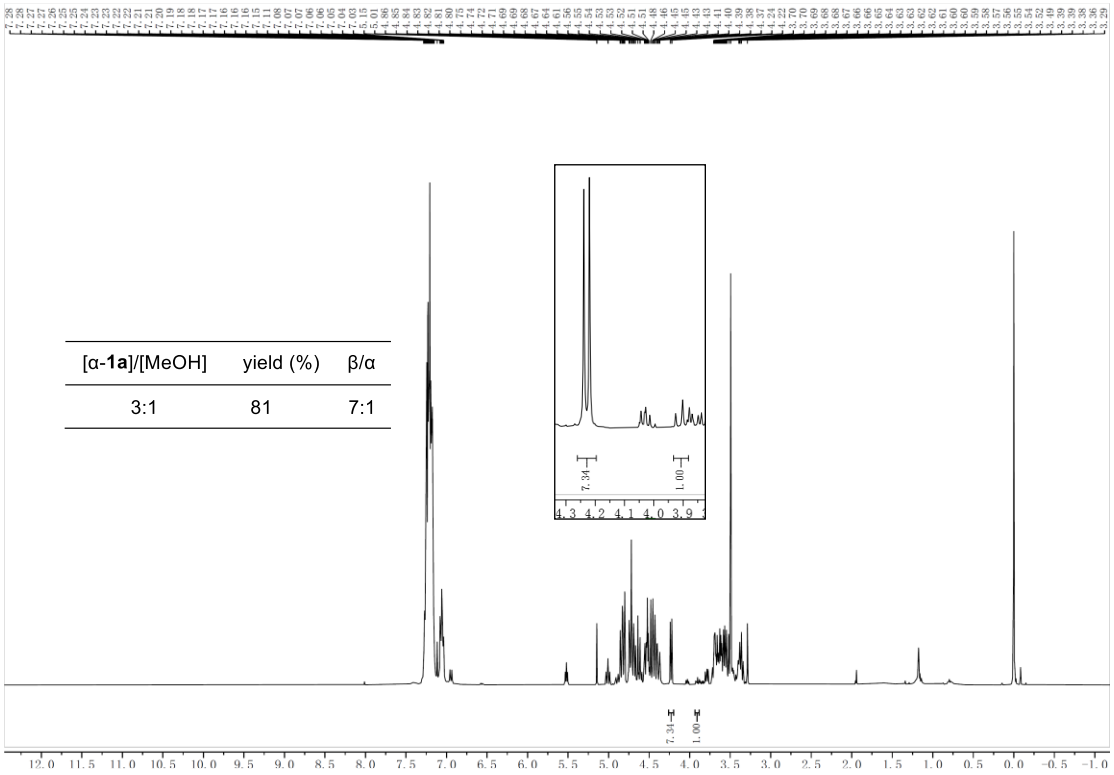


Fig. S5. β/α selectivity of reaction with [α-**1a**]/[MeOH] = 3:1 by **MC4**

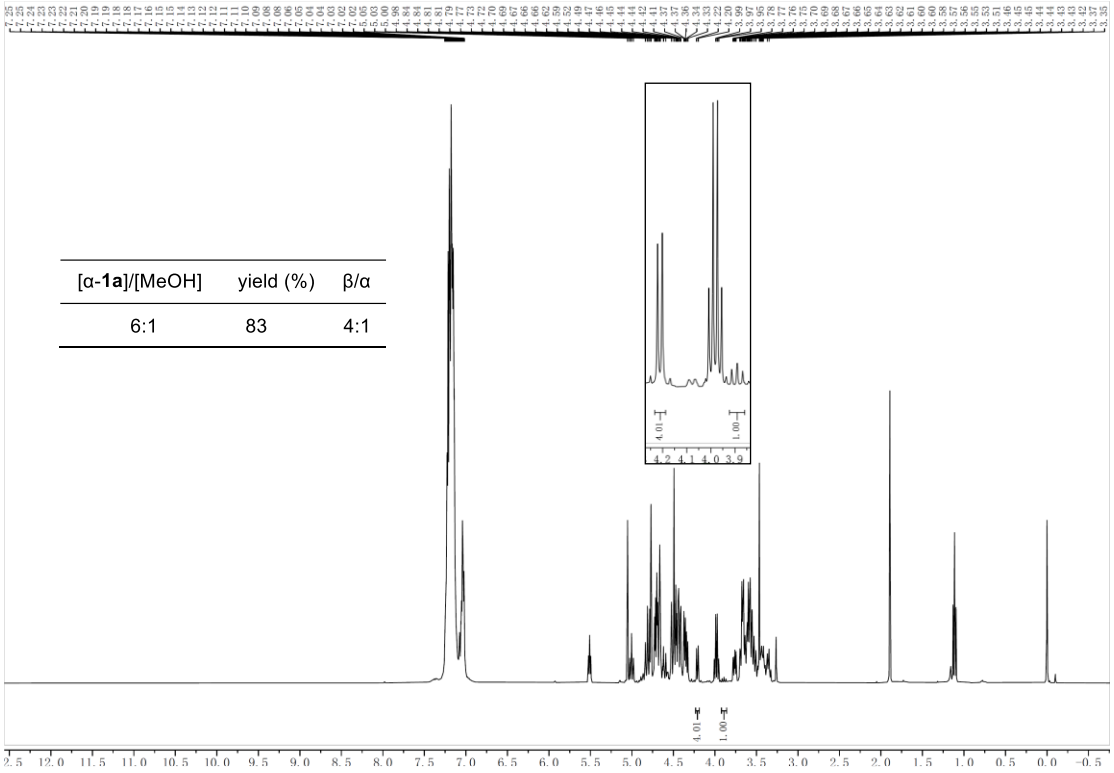


Fig. S6. β/α selectivity of reaction with [α-**1a**]/[MeOH] = 6:1 by **MC4**

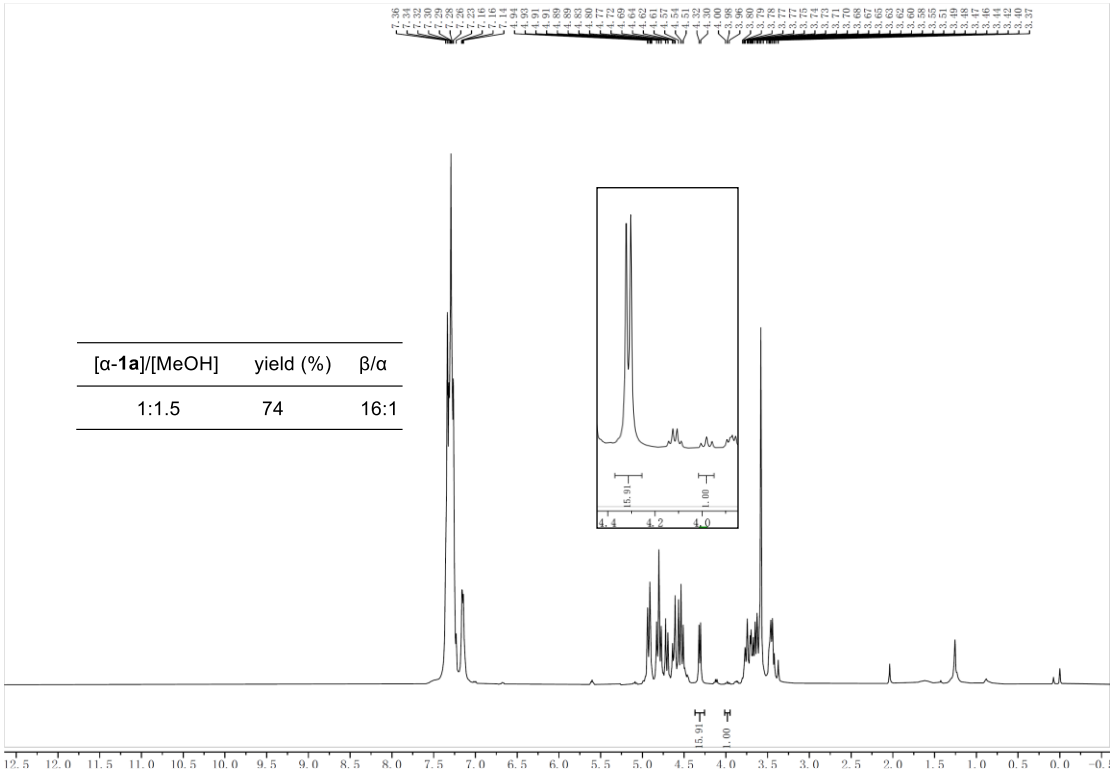


Fig. S7. β/α selectivity of reaction with [α-**1a**]/[MeOH] = 1:1.5 by **MC4**

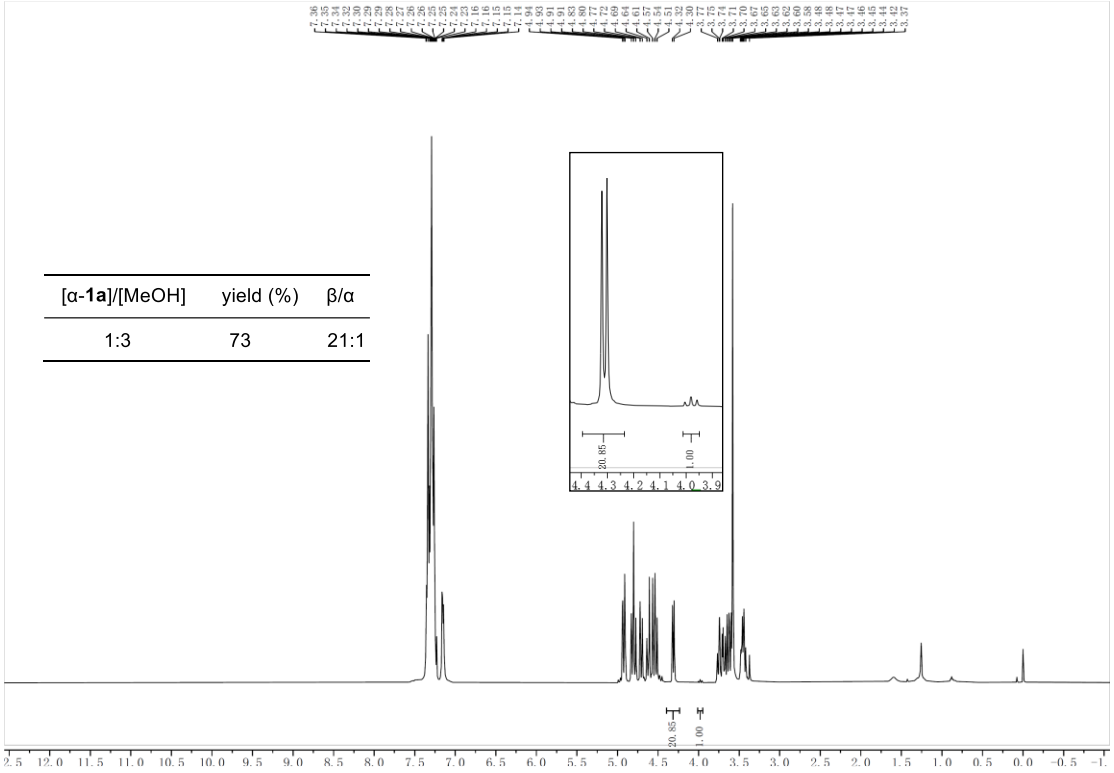


Fig. S8. β/α selectivity of reaction with [α-**1a**]/[MeOH] = 1:3 by **MC4**

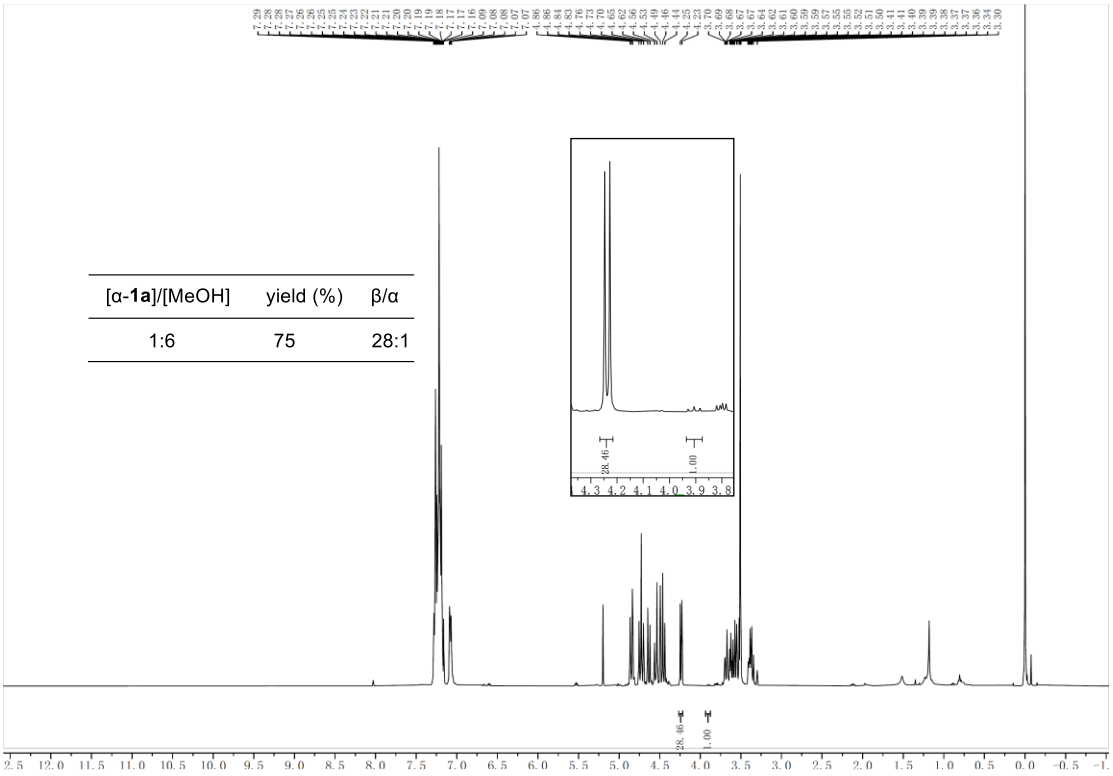
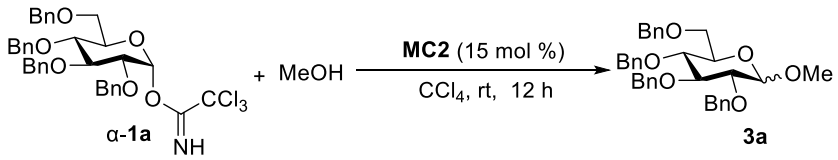


Fig. S9. β/α selectivity of reaction with [α-**1a**]/[MeOH] = 1:6 by **MC4**

Table S5. *Evaluation of concentration of α-**1a** and MeOH by **MC2***



Entry	[α-**1a**]/[MeOH]	yield (%)	β-**3a**/α-**3a**
1	6:1	77	3:1
2	3:1	74	7:1
3	1:3	74	14:1
4	1:6	75	23:1
5	1:8	76	31:1

For entries 1–2: To a reaction mixture of α-**1a** (0.3–0.6 mmol, 3.0–6.0 equiv), catalyst **MC2** (50.6 mg, 0.015 mmol, 15 mol %) and MeOH (4.1 μL, 0.1 mmol) in a 10 mL-Schlenk tube was added CCl_4 (0.5 mL) under argon atmosphere. The above reaction mixture was stirred at room temperature for 12 h. Then the reaction mixture was purified by flash chromatography on silica gel to give desired products **3a**.

For entries 3–5: To a reaction mixture of α-**1a** (68.5 mg, 0.1 mmol), catalyst **MC2** (50.6 mg, 0.015 mmol, 15 mol %) and MeOH (0.3–0.8 mmol, 3.0–8.0 equiv) in a 10 mL-Schlenk tube was added CCl_4 (0.5 mL) under argon

atmosphere. The above reaction mixture was stirred at room temperature for 12 h. Then the reaction mixture was purified by flash chromatography on silica gel to give desired products **3a**.

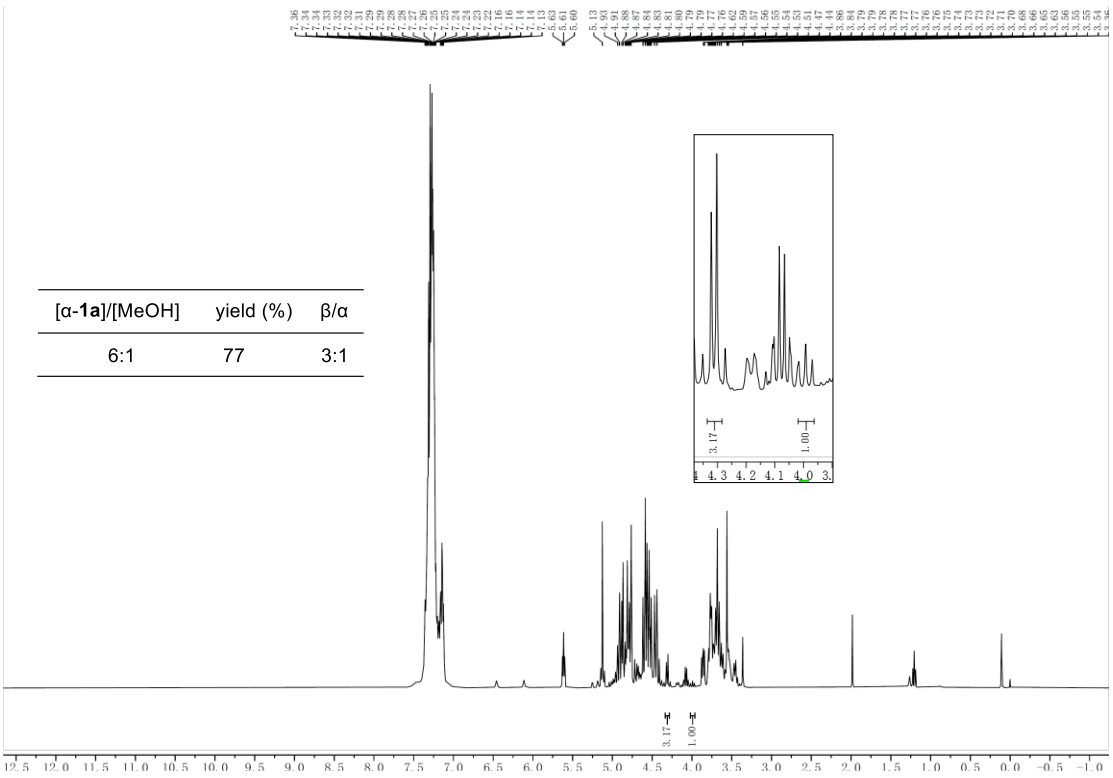


Fig. S10. β/α selectivity of reaction with [α-**1a**]/[MeOH] = 6:1 by **MC2**

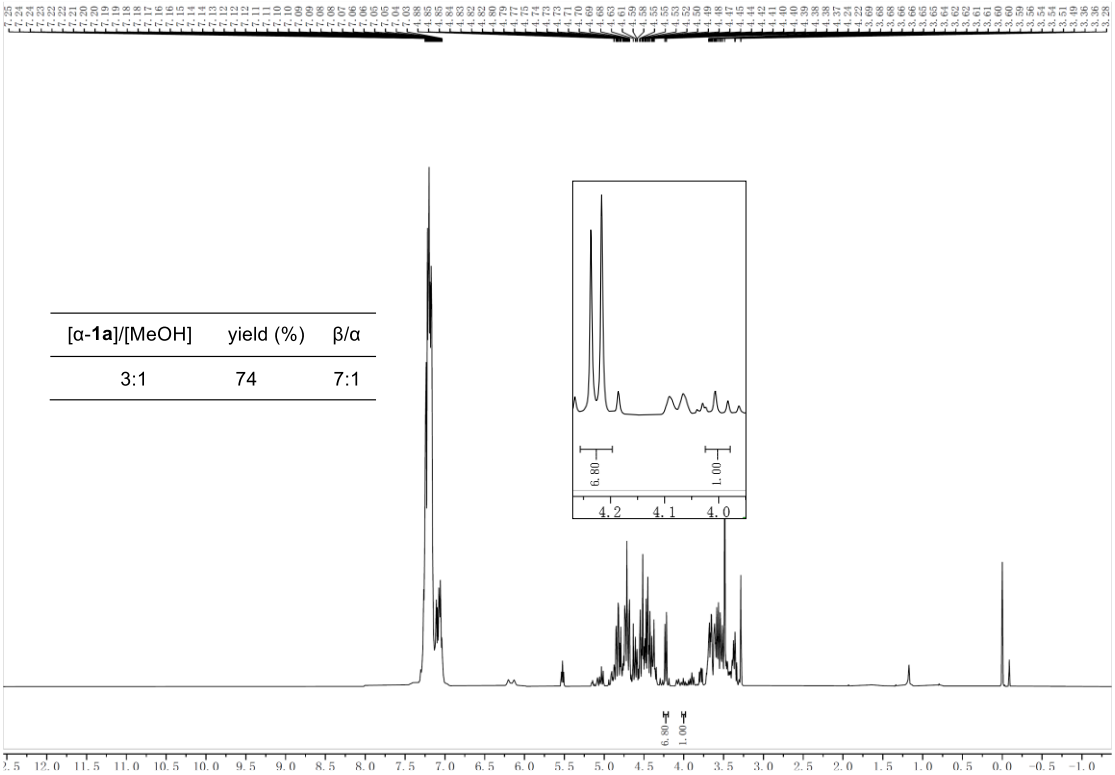


Fig. S11. β/α selectivity of reaction with [α-**1a**]/[MeOH] = 3:1 by **MC2**

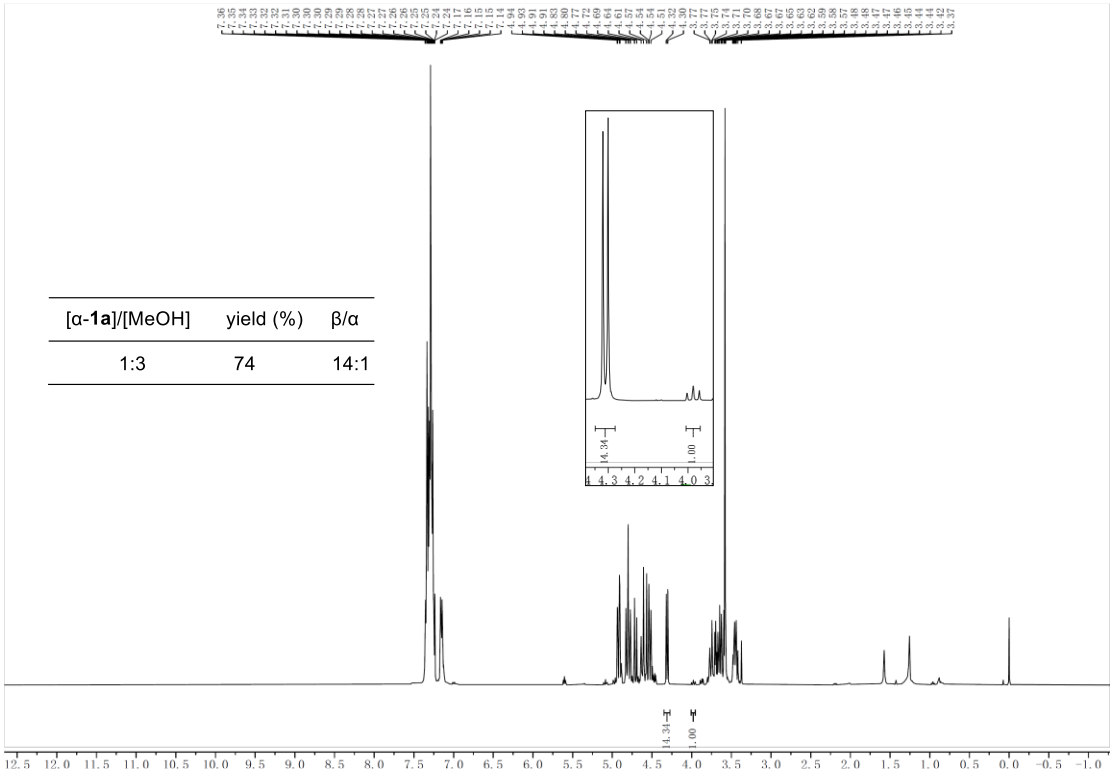


Fig. S12. β/α selectivity of reaction with [α-**1a**]/[MeOH] = 1:3 by **MC2**

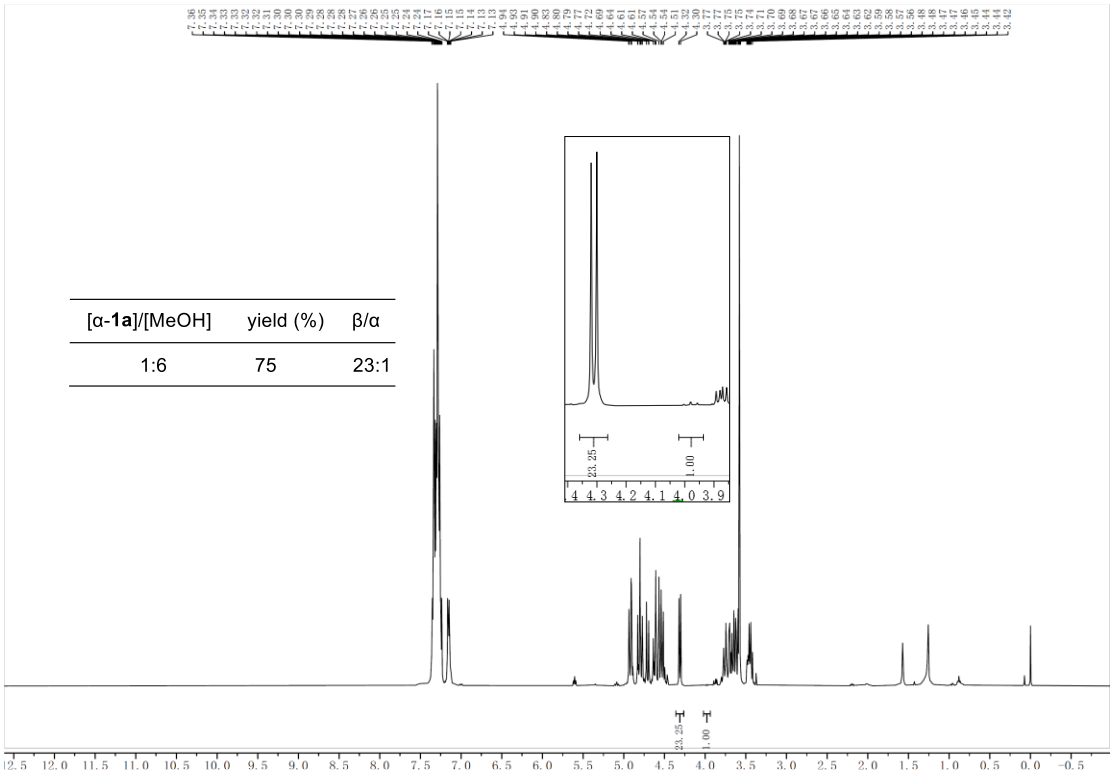


Fig. S13. β/α selectivity of reaction with [α-**1a**]/[MeOH] = 1:6 by **MC2**

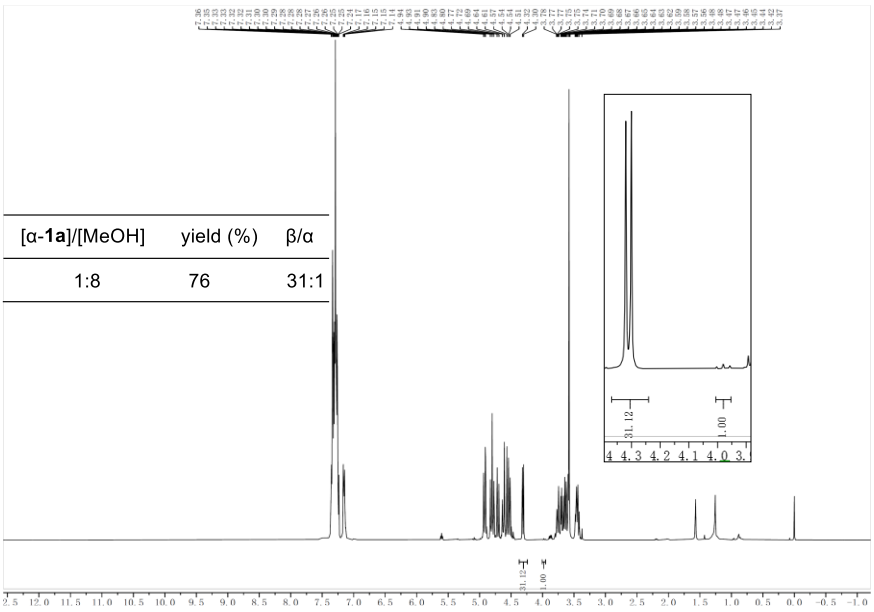
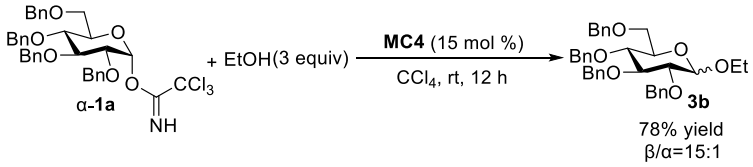


Fig. S14. β/α selectivity of reaction with [α-**1a**]/[MeOH] = 1:8 by **MC2**

(2) *Evaluation of electronic effect of alcohols*



To a reaction mixture of α-**1a** (68.5 mg, 0.1 mmol), catalyst **MC4** (50.6 mg, 0.015 mmol, 15 mol %) and EtOH (17.5 μL, 0.3 mmol, 3.0 equiv) in a 10 mL-Schlenk tube was added CCl_4 (0.5 mL) under argon atmosphere. The above reaction mixture was stirred at room temperature for 12 h. Then the reaction mixture was purified by flash chromatography on silica gel to give desired products **3b** (78% yield, β/α = 15:1).

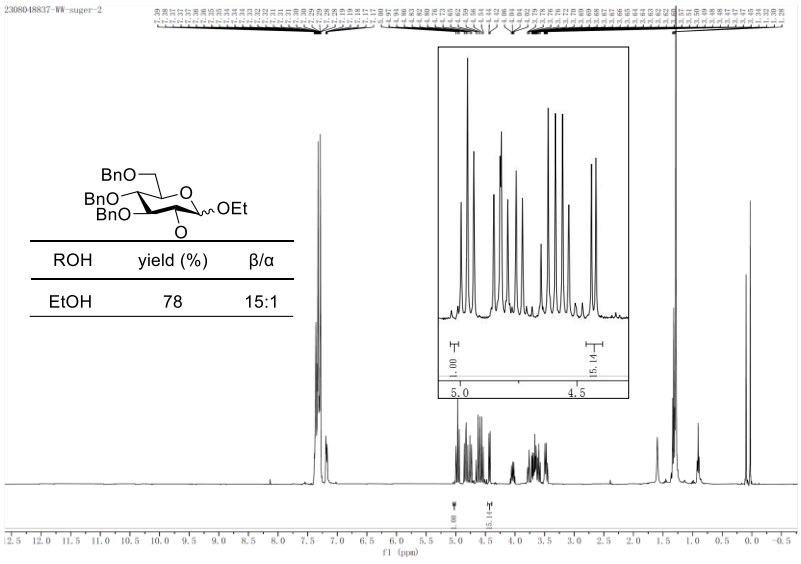
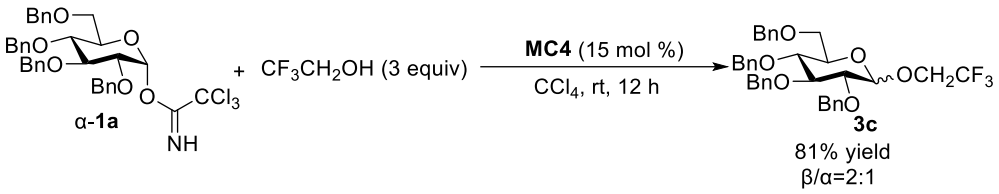


Fig. S15. β/α selectivity of reaction with [α-**1a**]/[EtOH] = 1:3



To a reaction mixture of α-**1a** (68.5 mg, 0.1 mmol), catalyst **MC4** (50.6 mg, 0.015 mmol, 15 mol %) and 2,2,2-trifluoroethan-1-ol (21.3 μL, 0.3 mmol, 3.0 equiv) in a 10 mL-Schlenk tube was added CCl_4 (0.5 mL) under argon atmosphere. The above reaction mixture was stirred at room temperature for 12 h. Then the reaction mixture was purified by flash chromatography on silica gel to give desired products **3c** (81% yield, β/α = 2:1).

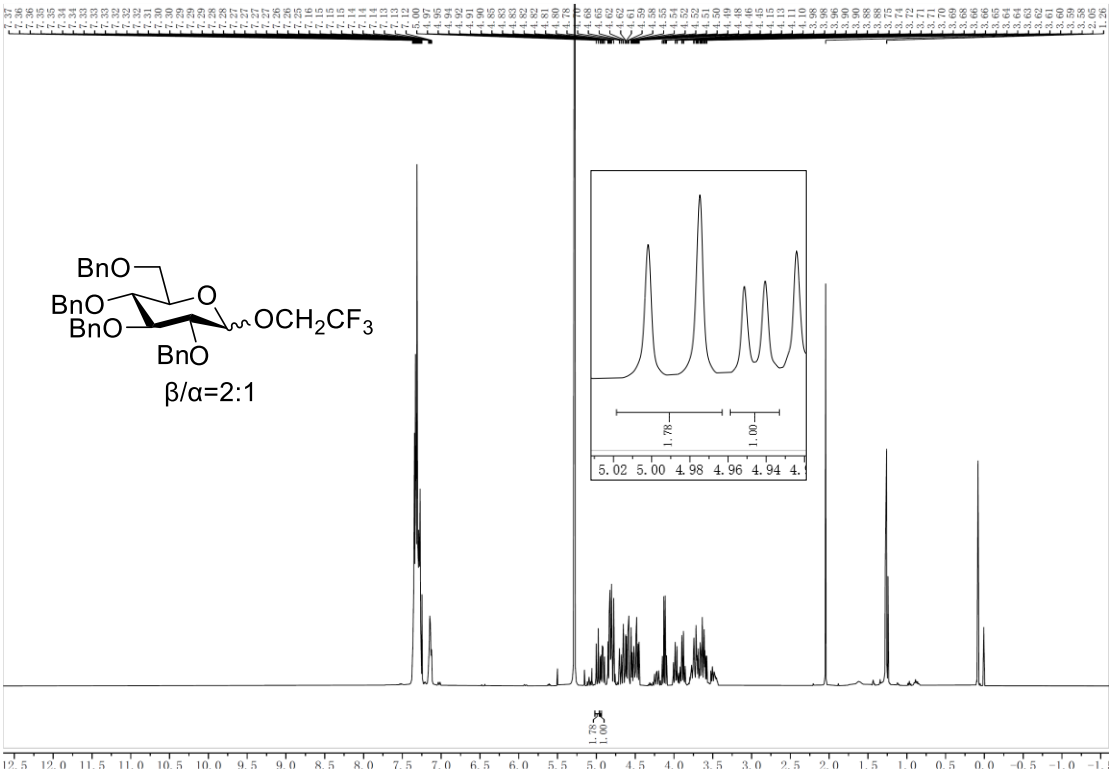
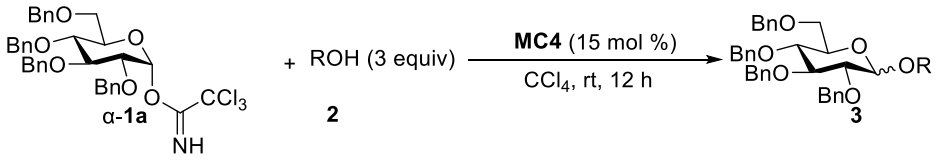


Fig. S16. β/α selectivity of reaction with [α-**1a**]/[CF_3CH_2OH] = 1:3

(3) *Evaluation of steric effect of alcohols*

Table S6. *Evaluation steric effect of alcohols by **MC4***



Entry	ROH	yield (%)	β/α
1	MeOH	73	21:1
2	EtOH	78	15:1
3	*i*-PrOH	74	9:1
4	*t*-BuOH	74	5:1

To a reaction mixture of α-**1a** (68.5 mg, 0.1 mmol), catalyst **MC4** (50.6 mg, 0.015 mmol, 15 mol %) and **2** (0.3 mmol, 3.0 equiv) in a 10 mL-Schlenk tube was added CCl_4 (0.5 mL) under argon atmosphere. The above reaction mixture was stirred at room temperature for 12 h. Then the reaction mixture was purified by flash chromatography on silica gel to give desired products **3**.

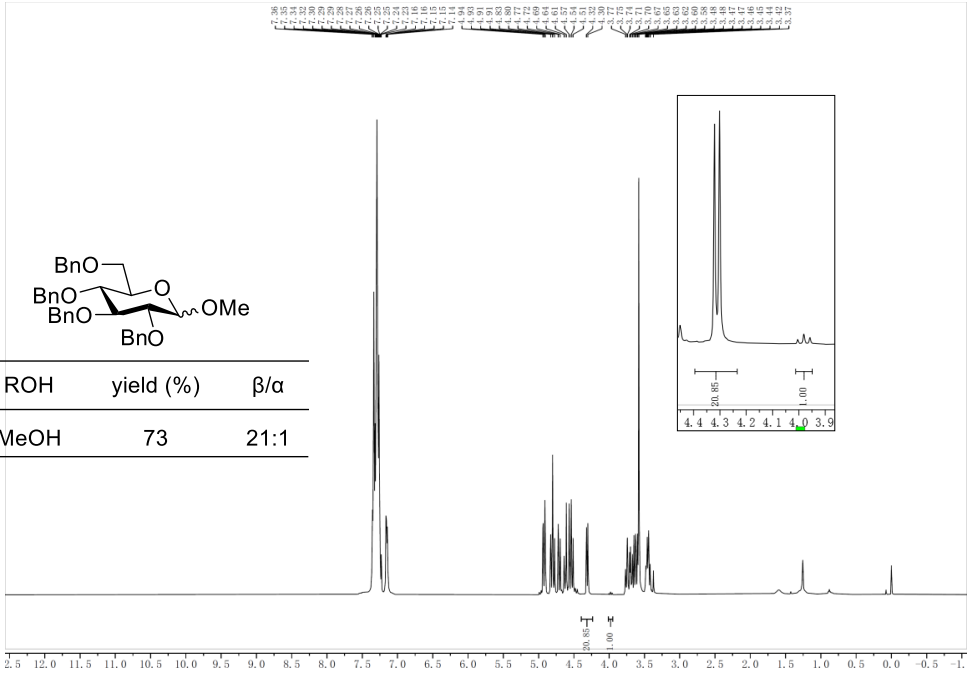


Fig. S17. β/α selectivity of reaction with [α-**1a**]/[MeOH] = 1:3

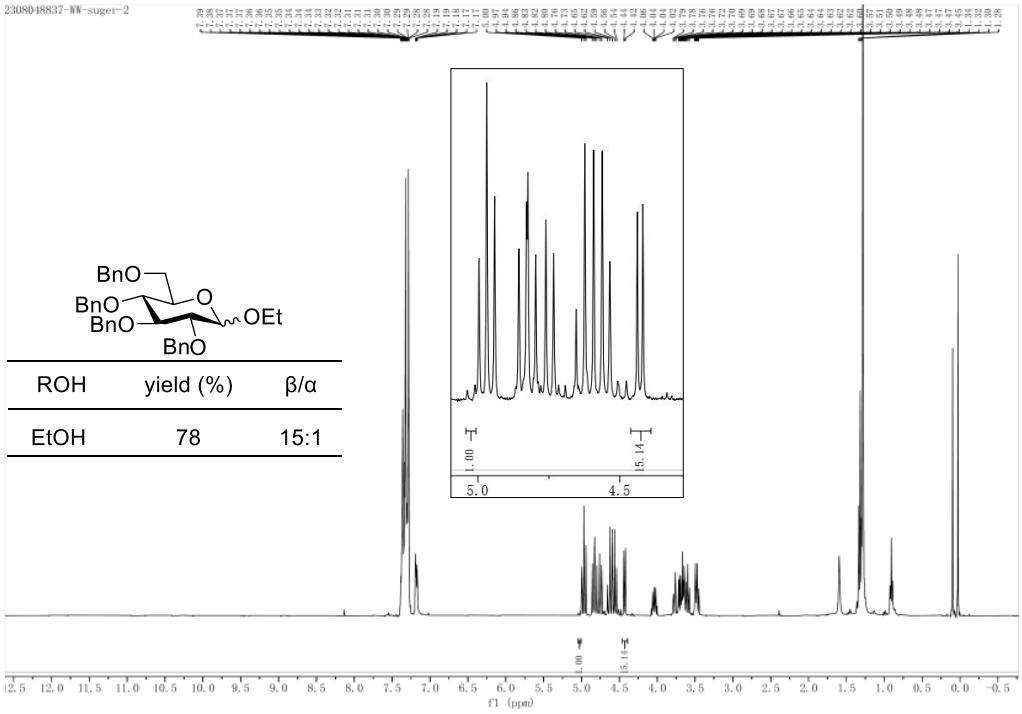
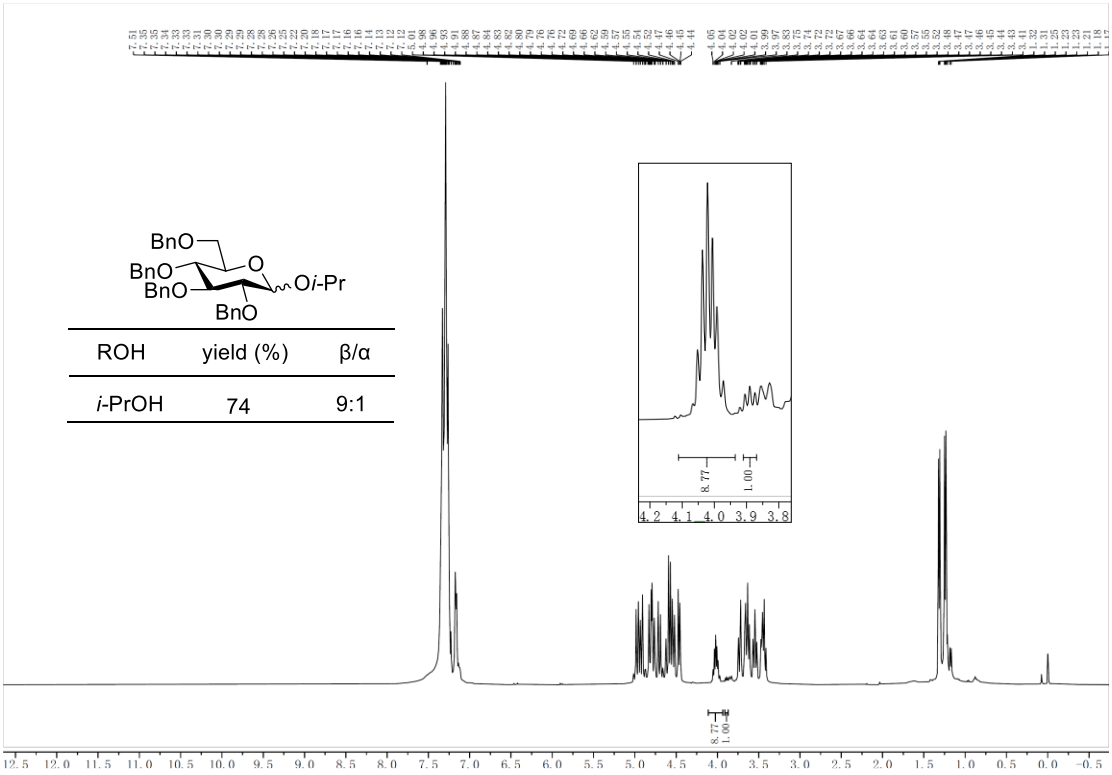
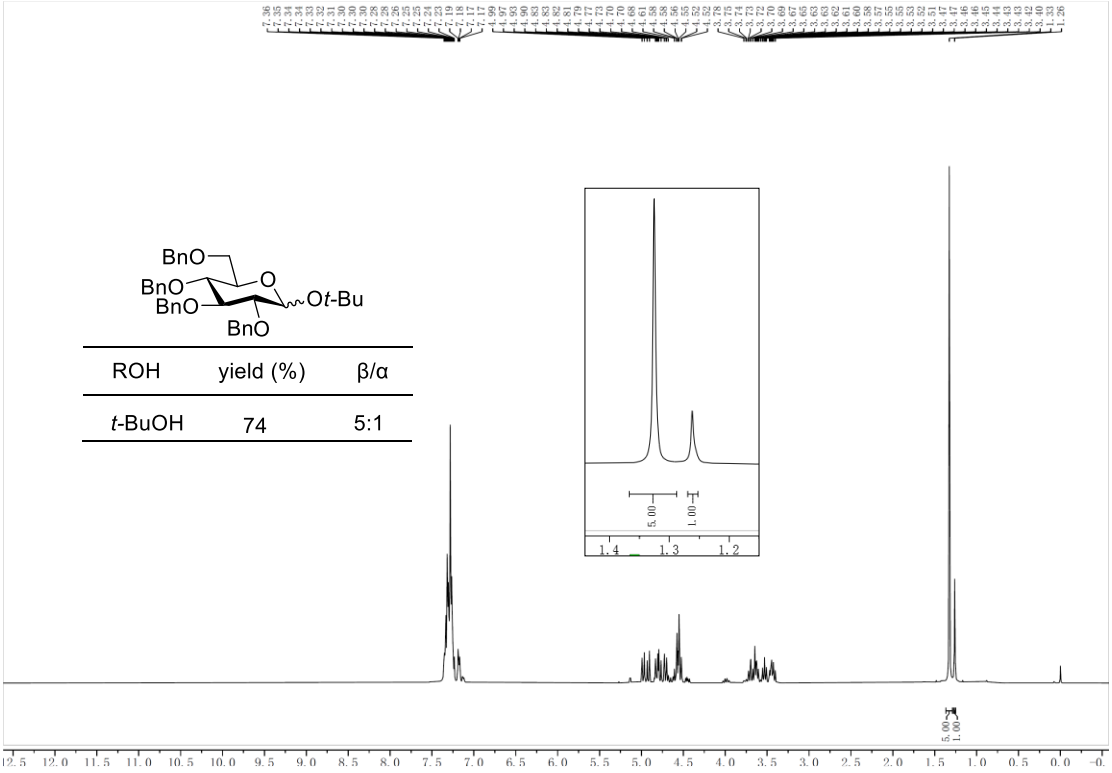


Fig. S18. β/α selectivity of reaction with [α-**1a**]/[EtOH] = 1:3



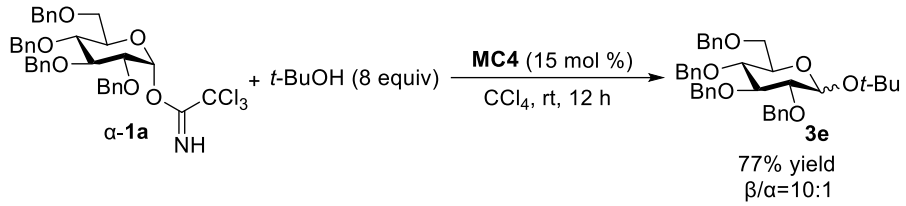
ROH	yield (%)	β/α
i-PrOH	74	9:1

Fig. S19. β/α selectivity of reaction with [α-**1a**]/[*i*-PrOH] = 1:3



ROH	yield (%)	β/α
t-BuOH	74	5:1

Fig. S20. β/α selectivity of reaction with [α-**1a**]/[*t*-BuOH] = 1:3



To a reaction mixture of α-**1a** (68.5 mg, 0.1 mmol), catalyst **MC4** (50.6 mg, 0.015 mmol, 15 mol %) and *t*-butyl alcohol (76.5 μL, 0.8 mmol, 8.0 equiv) in a 10 mL-Schlenk tube was added CCl_4 (0.5 mL) under argon atmosphere. The above reaction mixture was stirred at room temperature for 12 h. Then the reaction mixture was purified by flash chromatography on silica gel to give desired products **3e** (77% yield, β/α = 10:1).

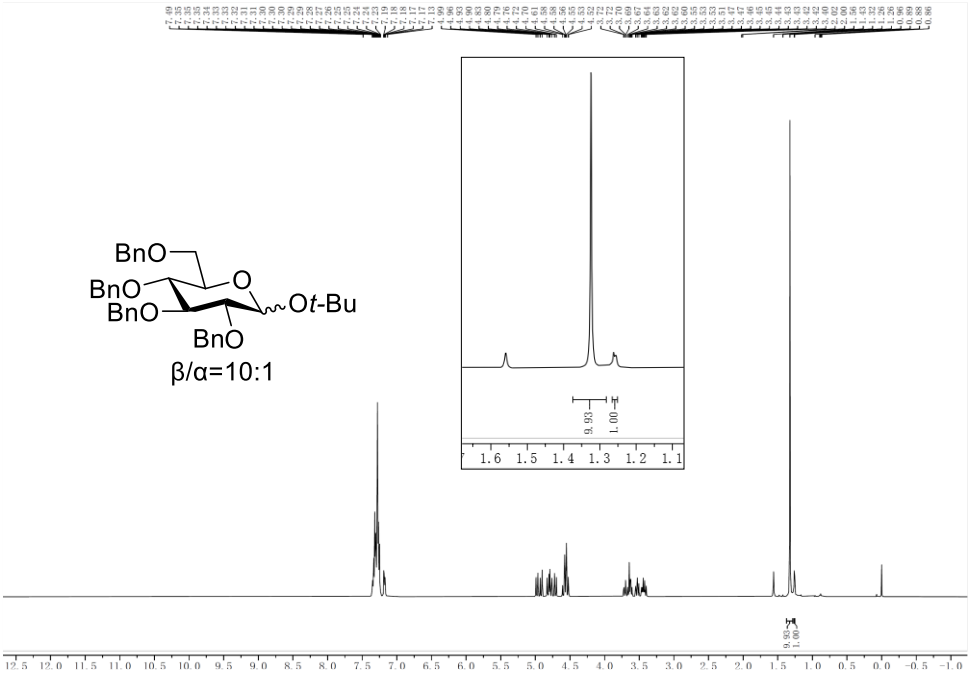
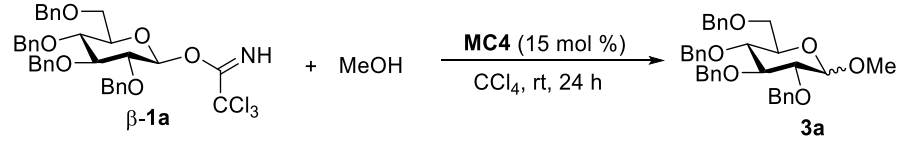


Fig. S21. β/α selectivity of reaction with [α-**1a**]/[*t*-BuOH] = 1:8

(4) *Evaluation of β-anomer β-**1a** as a reactant*

Table S7. *Evaluation of β-anomer β-**1a** as a reactant by **MC4***



Entry	[β-**1a**]/[MeOH]	yield (%)	β-**3a**/α-**3a**
1	4:1	75	2:1
2	1:3	70	1:3
3	1:20	76	1:10

For entry 1: To a reaction mixture of β-**1a** (0.4 mmol, 4.0 equiv), catalyst **MC4** (50.6 mg, 0.015 mmol, 15 mol %)

and MeOH (4.1 μL, 0.1 mmol) in a 10 mL-Schlenk tube was added CCl_4 (0.5 mL) under argon atmosphere. The above reaction mixture was stirred at room temperature for 24 h. Then the reaction mixture was purified by flash chromatography on silica gel to give desired products **3a**.

For entries 2–3: To a reaction mixture of β-**1a** (68.5 mg, 0.1 mmol), catalyst **MC4** (50.6 mg, 0.015 mmol, 15 mol %) and MeOH (0.3–2.0 mmol, 3.0–20.0 equiv) in a 10 mL-Schlenk tube was added CCl_4 (0.5 mL) under argon atmosphere. The above reaction mixture was stirred at room temperature for 24 h. Then the reaction mixture was purified by flash chromatography on silica gel to give desired products **3a**.

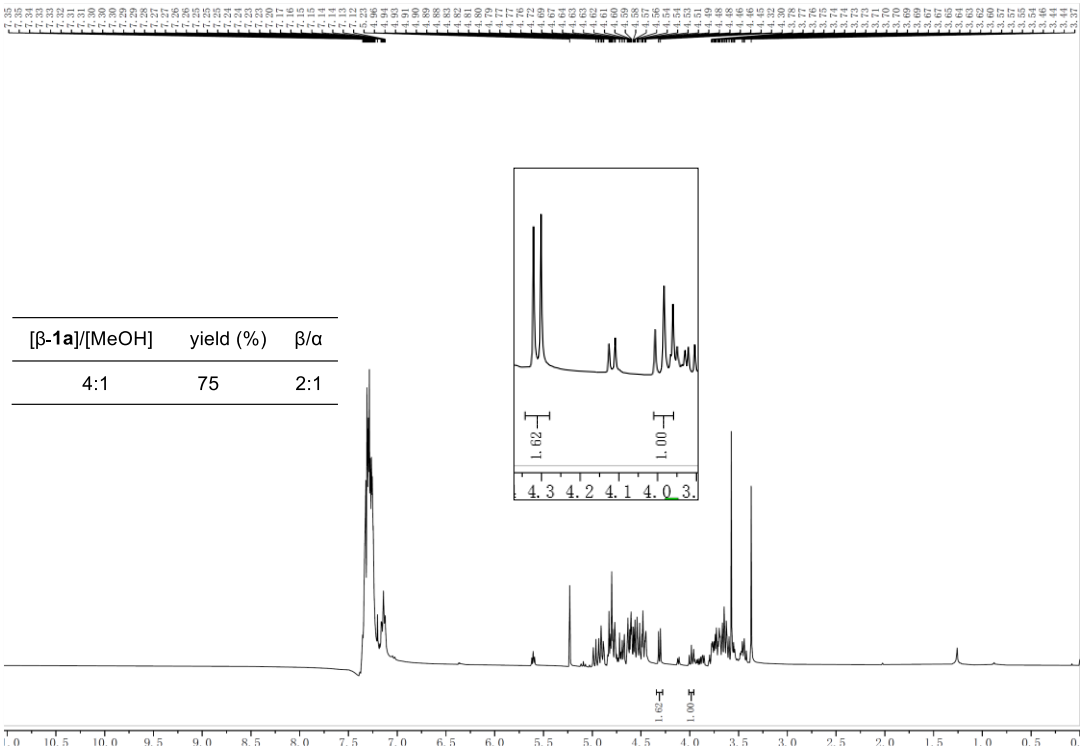


Fig. S22. β/α selectivity of reaction with [β-**1a**]/[MeOH] = 4:1

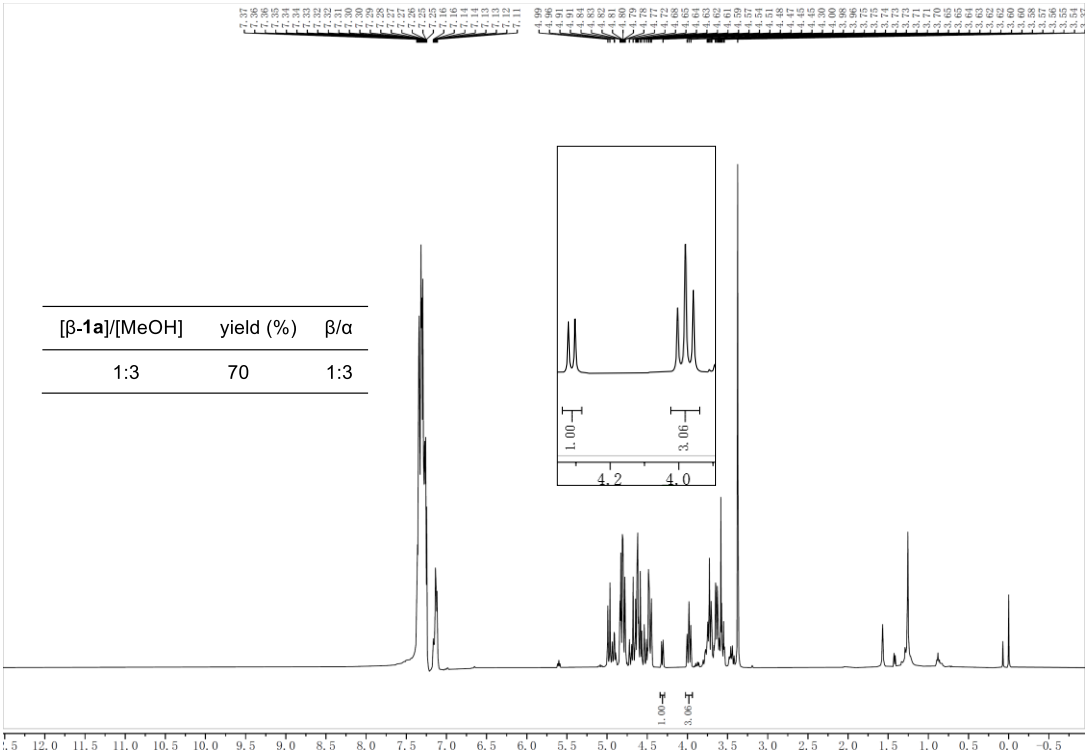


Fig. S23. β/α selectivity of reaction with [β-**1a**]/[MeOH] = 1:3

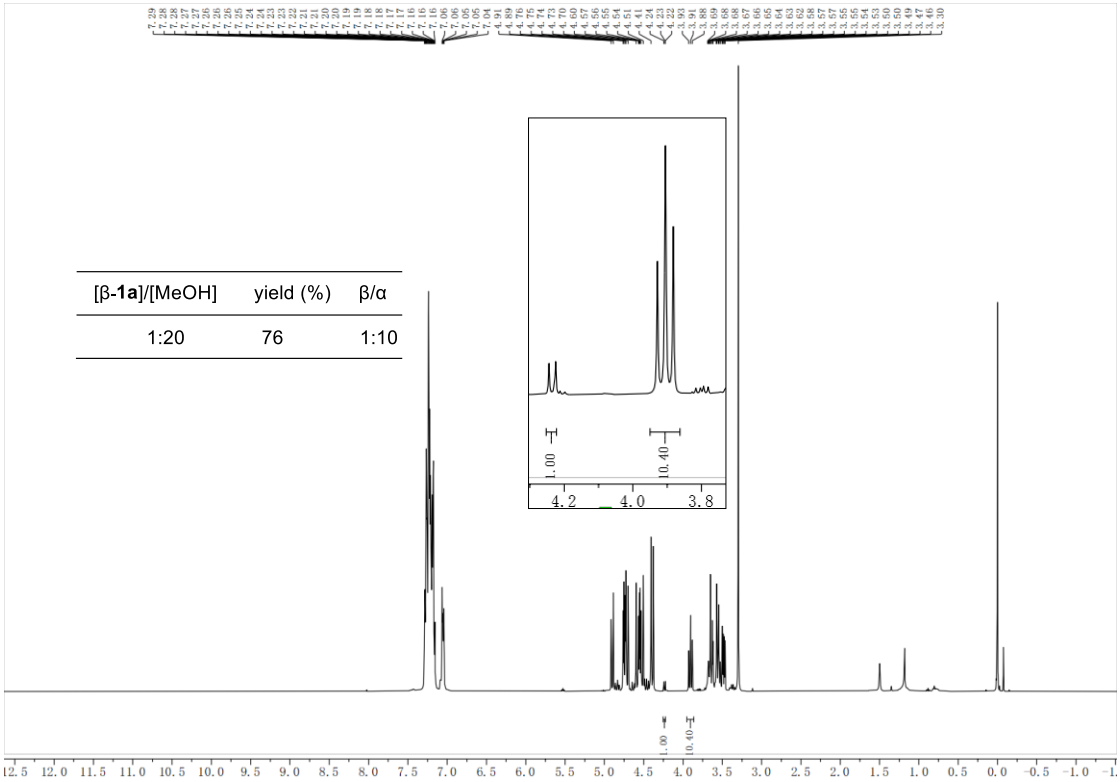
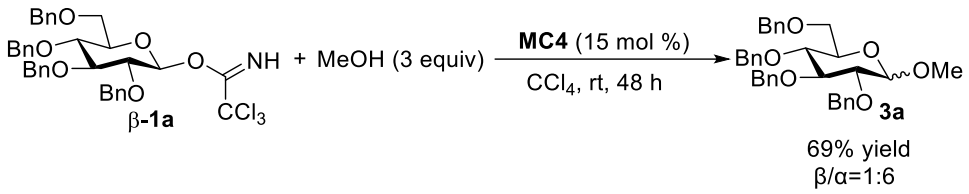


Fig. S24. β/α selectivity of reaction with [β-**1a**]/[MeOH] = 1:20



β-**1a** (6.85 mg/1 h×10, 0.1 mmol) was added in portions to a solution of catalyst **MC4** (50.6 mg, 0.015 mmol, 15 mol %) and MeOH (12.2 μL, 0.3 mmol, 3 equiv) in CCl_4 (0.5 mL) under argon atmosphere and the reaction mixture was stirred at room temperature for 48 h. Then the reaction mixture was purified by flash chromatography on silica gel to give desired products **3a** (69% yield, β/α = 1:6).

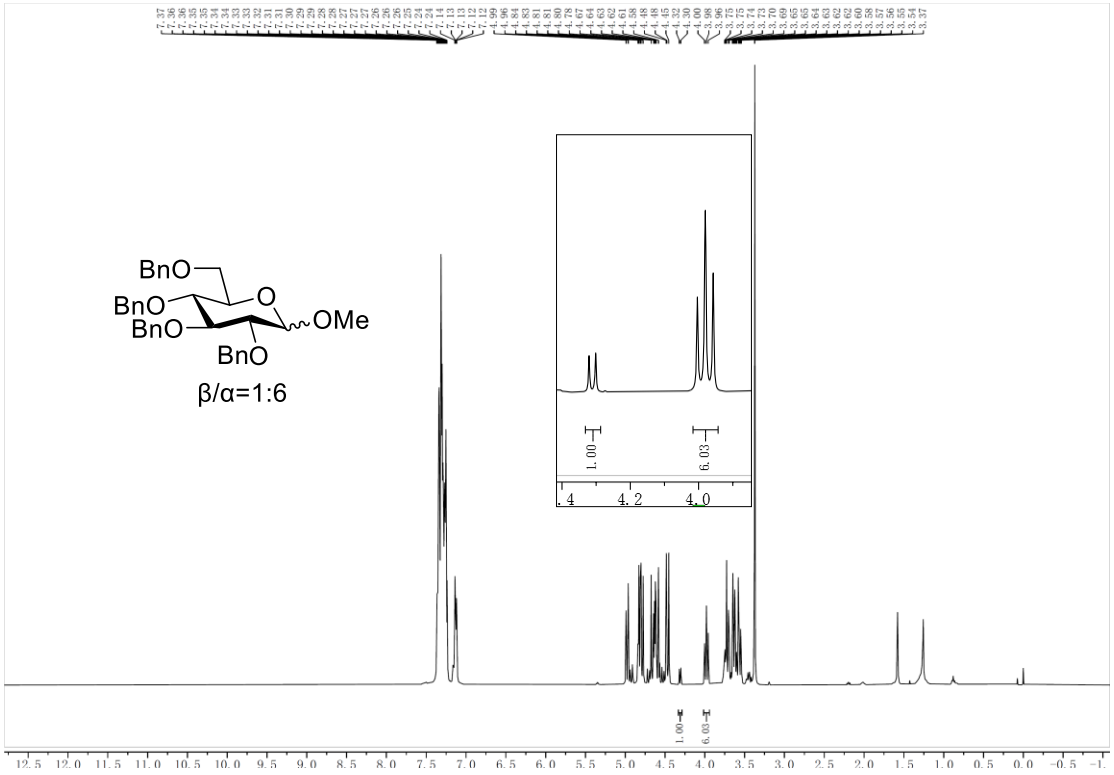
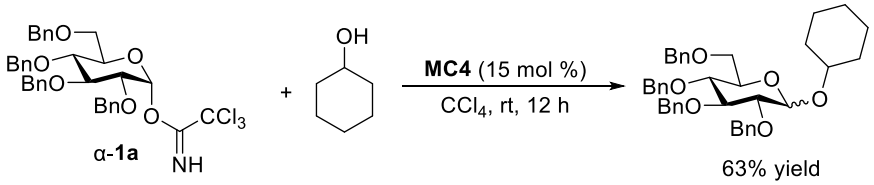


Fig. S25. β/α selectivity of reaction with β-**1a** added in ten portions every hour

(5) *Evaluation of inhibitors*

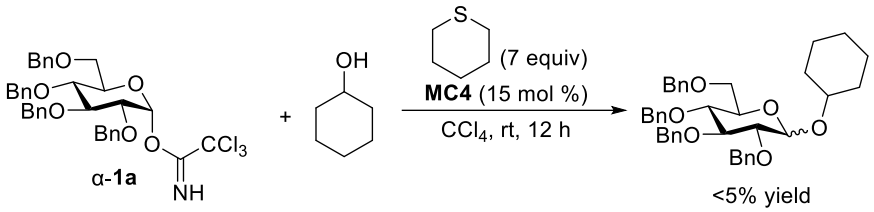
Standard condition



To a reaction mixture of α-**1a** (68.5 mg, 0.1 mmol), catalyst **MC4** (50.6 mg, 0.015 mmol, 15 mol %) and cyclohexanol (10.0 mg, 0.1 mmol, 1 equiv) in a 10 mL-Schlenk tube was added CCl_4 (0.5 mL) under argon atmosphere. The above reaction mixture was stirred at room temperature for 12 h. Then the reaction mixture was

purified by flash chromatography on silica gel to give desired products in 63% yield.

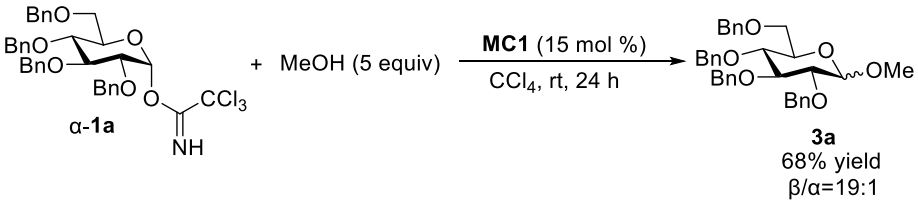
Addition of tetrahydro-2H-thiopyran to the standard condition



To a reaction mixture of α-**1a** (68.5 mg, 0.1 mmol), catalyst **MC4** (50.6 mg, 0.015 mmol, 15 mol %), tetrahydro-2H-thiopyran (71.5 mg, 0.7 mmol, 7 equiv) and cyclohexanol (10.0 mg, 0.1 mmol, 1 equiv) in a 10 mL-Schlenk tube was added CCl_4 (0.5 mL) under argon atmosphere. The above reaction mixture was stirred at room temperature for 12 h. Then the solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel to give desired products in less than 5% yield.

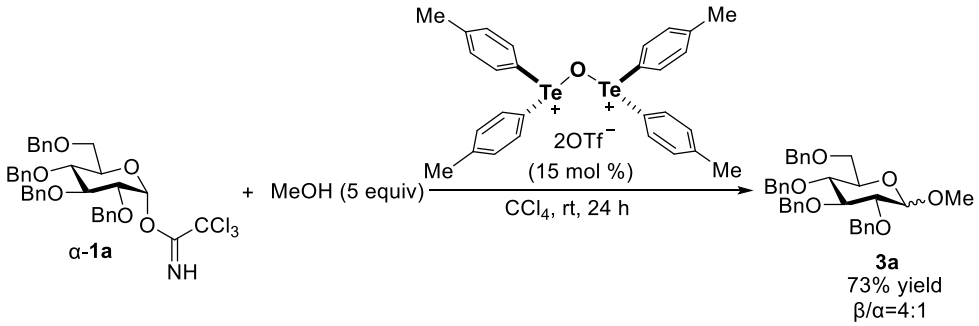
(6) *Evaluation of chain-type catalyst*

Standard condition



To a reaction mixture of α-**1a** (68.5 mg, 0.1 mmol), catalyst **MC1** (29.2 mg, 0.015 mmol, 15 mol %) and MeOH (20.5 μL, 0.5 mmol, 5.0 equiv) in a 10 mL-Schlenk tube was added CCl_4 (0.5 mL) under argon atmosphere. The above reaction mixture was stirred at room temperature for 24 h. Then the reaction mixture was purified by flash chromatography on silica gel to give desired products **3a** (68% yield, β/α = 19:1).

Catalysis with chain-type catalyst

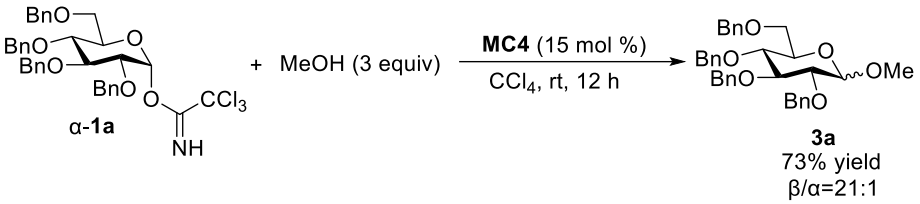


To a reaction mixture of α-**1a** (68.5 mg, 0.1 mmol), chain-type catalyst (14.0 mg, 0.015 mmol, 15 mol %) and MeOH (20.5 μL, 0.5 mmol, 5.0 equiv) in a 10 mL-Schlenk tube was added CCl_4 (0.5 mL) under argon atmosphere. The above reaction mixture was stirred at room temperature for 24 h. Then the reaction mixture was purified by

flash chromatography on silica gel to give desired products **3a** (73% yield, β/α = 4:1).

(6) *Evaluation of base*

Standard condition



Two parallel experiments were performed (one for isolated yields and the other one for determination of the anomeric ratio of the glycosylation products by ^{1}H NMR): To a reaction mixture of α-**1a** (68.5 mg, 0.1 mmol), catalyst **MC4** (50.6 mg, 0.015 mmol, 15 mol %) and MeOH (12.2 μL, 0.3 mmol, 3 equiv) in a 10 mL-Schlenk tube was added CCl_4 (0.5 mL) under argon atmosphere. The above reaction mixture was stirred at room temperature for 12 h. Then the reaction mixture was purified by flash chromatography on silica gel to give desired products **3a** (73% yield, β/α = 21:1).

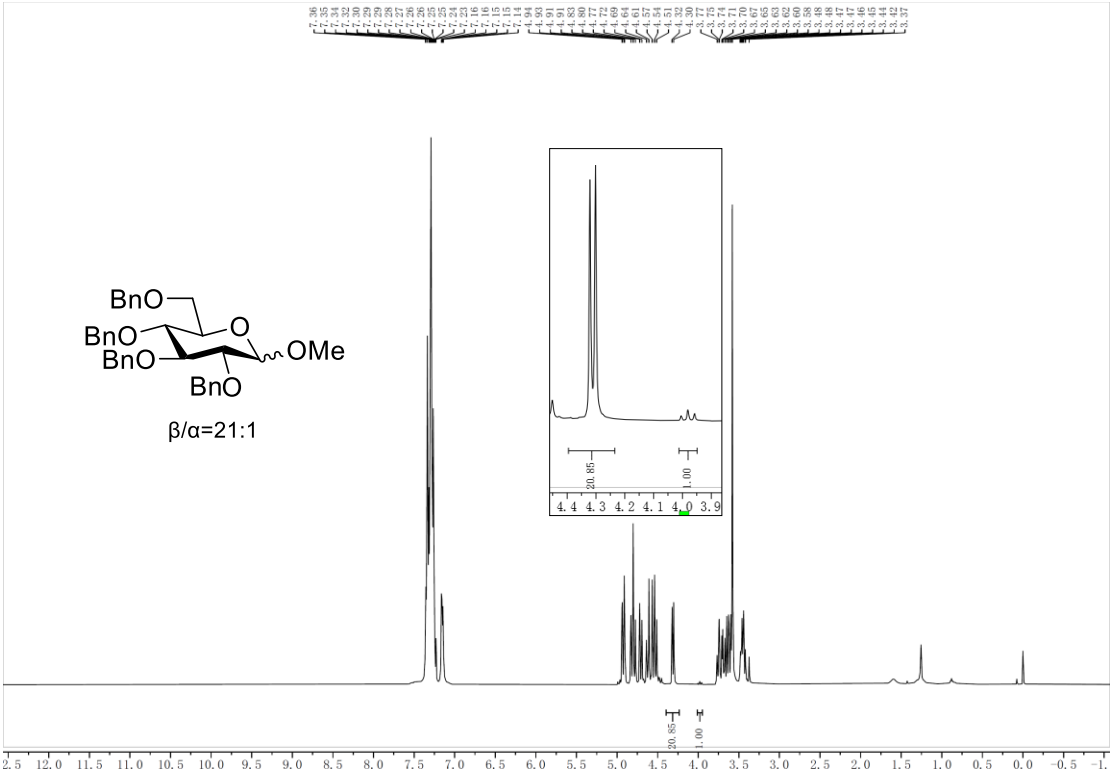
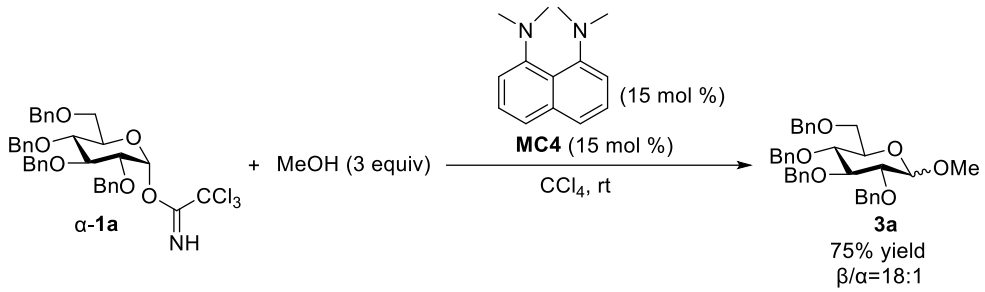


Fig. S26. β/α selectivity of reaction under standard condition

Addition of N^1,N^1,N^8,N^8-tetramethylnaphthalene-1,8-diamine to the standard condition



To a reaction mixture of α-**1a** (68.5 mg, 0.1 mmol), catalyst **MC4** (50.6 mg, 0.015 mmol, 15 mol %), N^1,N^1,N^8,N^8-tetramethylnaphthalene-1,8-diamine (3.2 mg, 0.015 mmol, 15 mol %) and MeOH (12.2 μL, 0.3 mmol, 3 equiv) in a 10 mL-Schlenk tube was added CCl_4 (0.5 mL) under argon atmosphere and the reaction mixture was stirred at room temperature until the completion of the reaction as judged by TLC analysis. Then the reaction mixture was purified by flash chromatography on silica gel to give desired products **3a** (75% yield, β/α = 18:1).

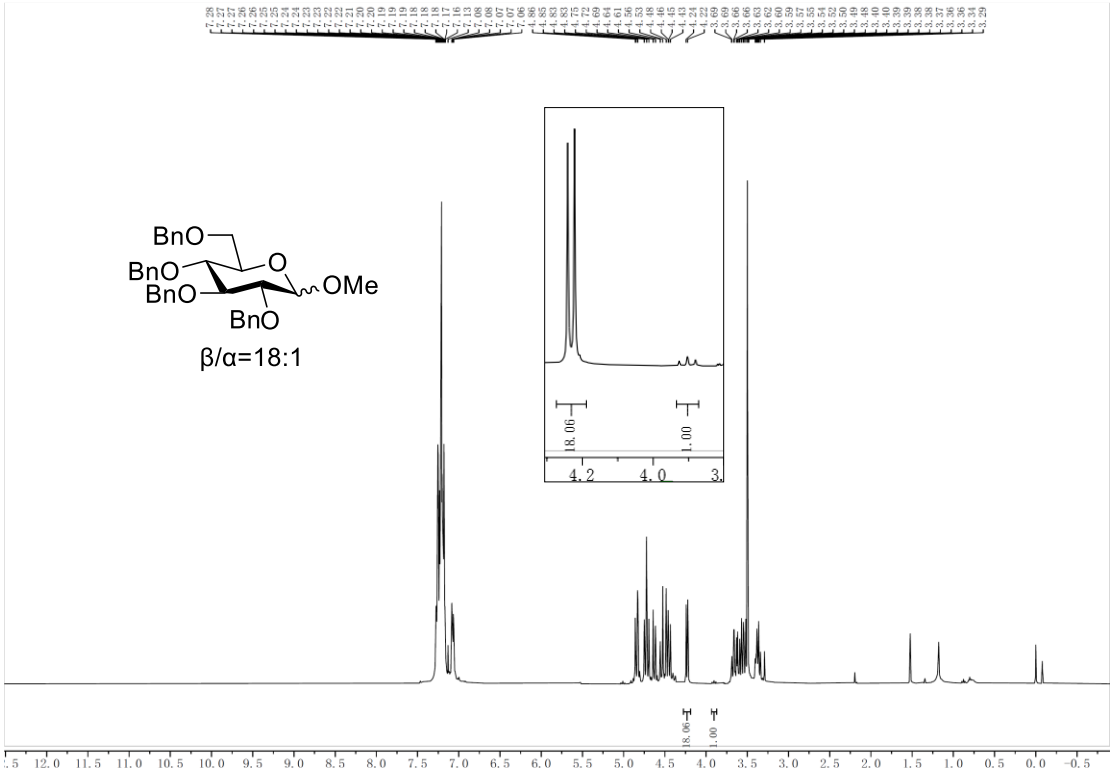
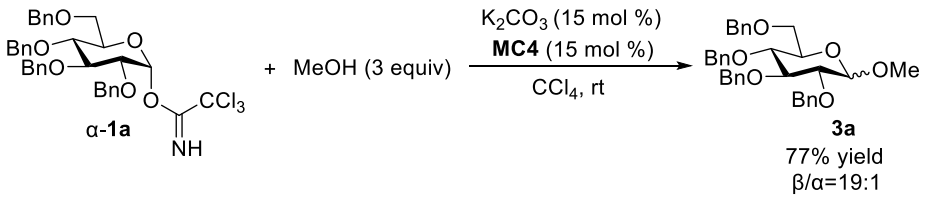


Fig. S27. β/α selectivity of reaction with N^1,N^1,N^8,N^8-tetramethylnaphthalene-1,8-diamine

Addition of K_2CO_3 to the standard condition



To a reaction mixture of α-**1a** (68.5 mg, 0.1 mmol), catalyst **MC4** (50.6 mg, 0.015 mmol, 15 mol %), K_2CO_3 (2.1 mg, 0.015 mmol, 15 mol %) and MeOH (12.2 μL, 0.3 mmol, 3 equiv) in a 10 mL-Schlenk tube was added CCl_4

(0.5 mL) under argon atmosphere and the reaction mixture was stirred at room temperature until the completion of the reaction as judged by TLC analysis. Then the reaction mixture was purified by flash chromatography on silica gel to give desired products **3a** (77% yield, β/α = 19:1).

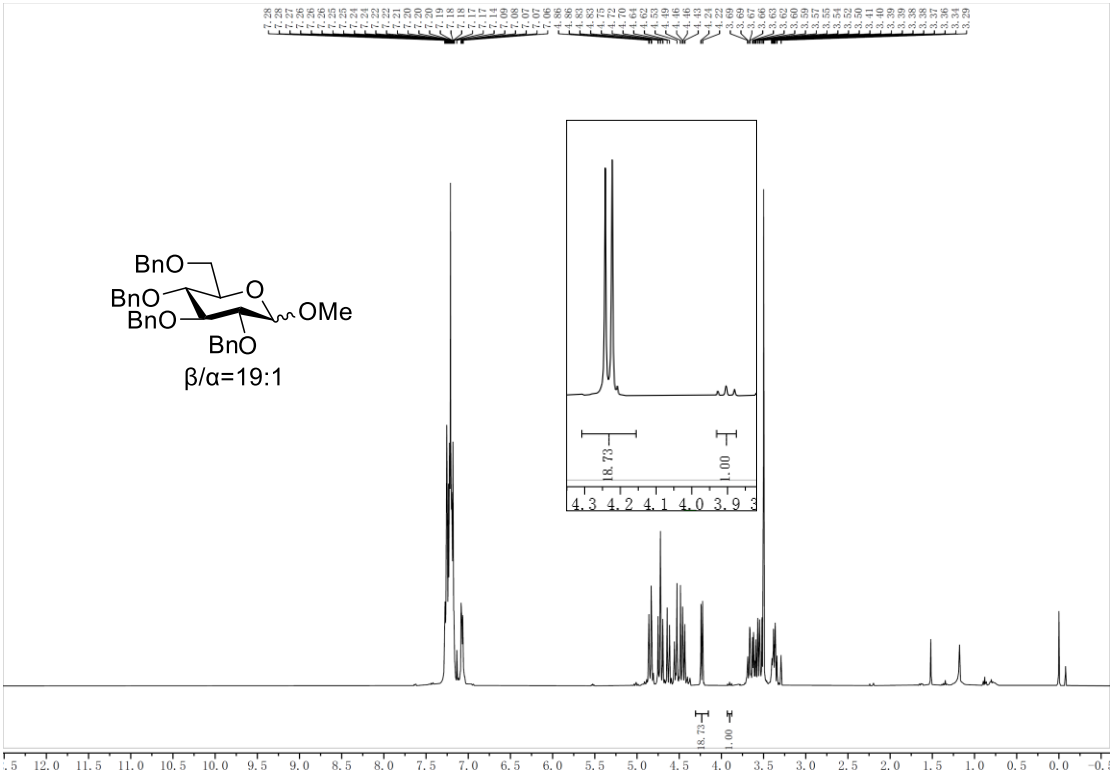


Fig. S28. β/α selectivity of reaction with K_2CO_3

(7) *The interaction between catalyst **MC4** and MeOH*

Catalyst **MC4** (337.4 mg, 0.1 mmol) in an NMR tube was added CD_2Cl_2 (0.6 mL) and then analysis of the solution by ^{77}Se NMR experiment.

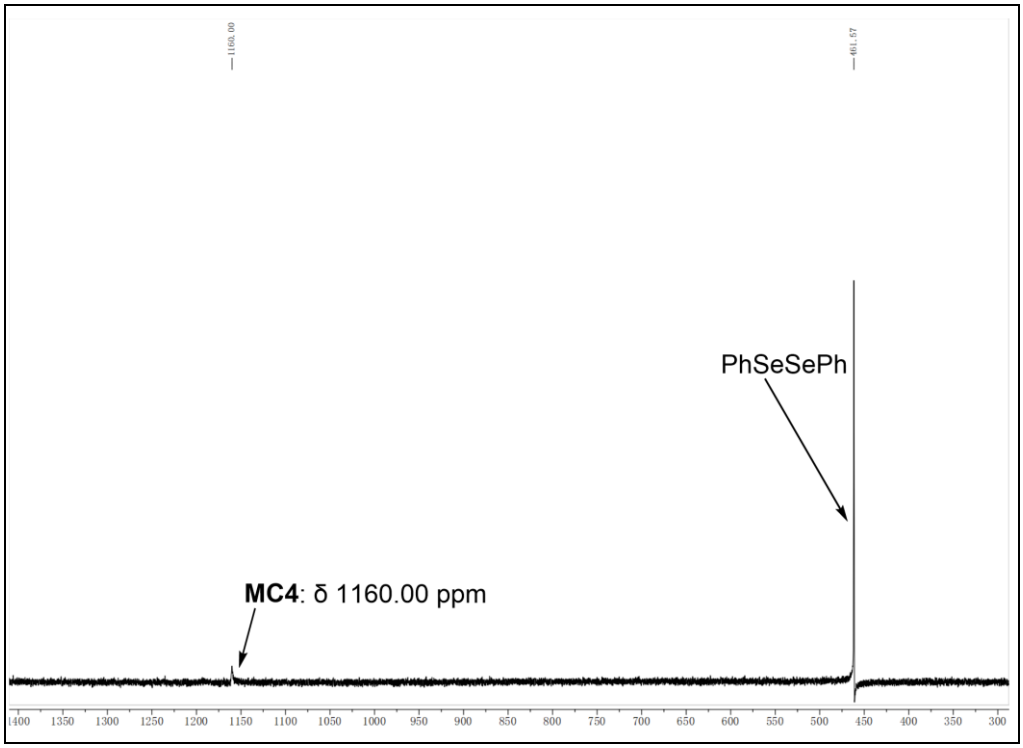


Fig. S29. The ^{77}Se NMR spectrum of catalyst **MC4**

A mixture of catalyst **MC4** (337.4 mg, 0.1 mmol) and MeOH (16.0 mg, 0.5 mmol) in an NMR tube was added CD_2Cl_2 (0.6 mL) and then analysis of the reaction mixture by ^{77}Se NMR experiment.

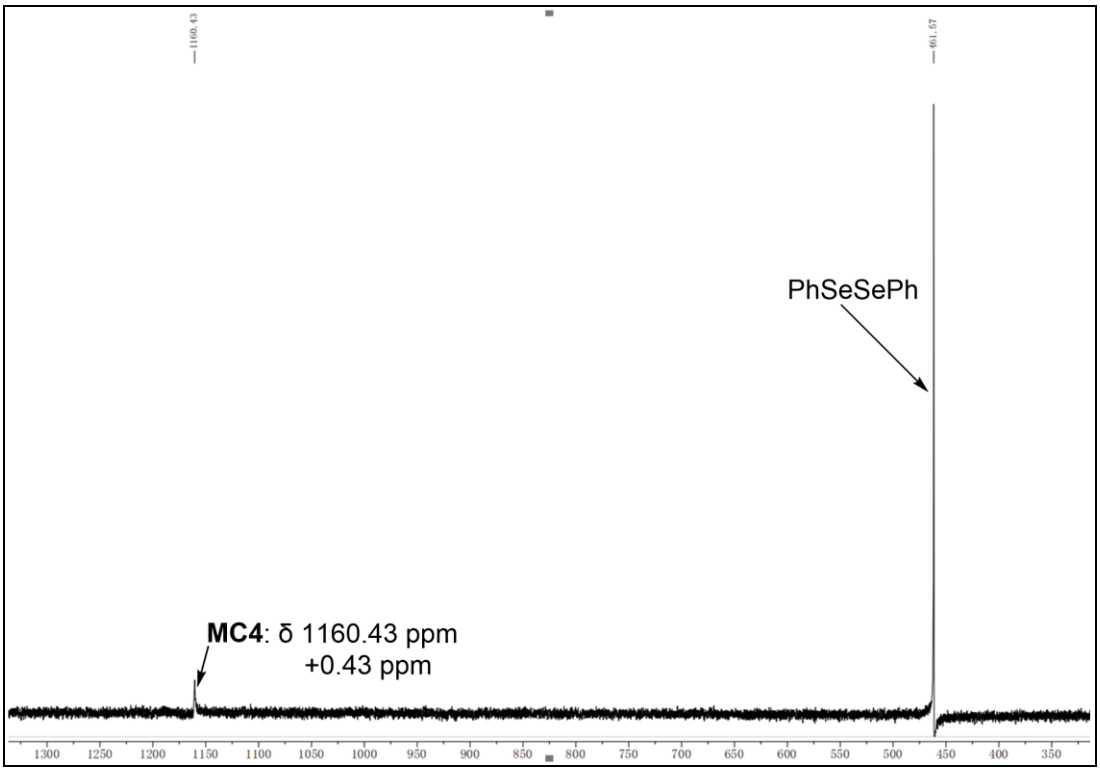


Fig. S30. The ^{77}Se NMR spectrum of catalyst **MC4** upon addition of MeOH

A mixture of catalyst **MC4** (283.3 mg, 0.084 mmol) and MeOH (9.0 mg, 0.28 mmol) in an NMR tube was added

$CDCl_3$ (0.6 mL) and then analysis of the reaction mixture by ^{13}C NMR experiment.

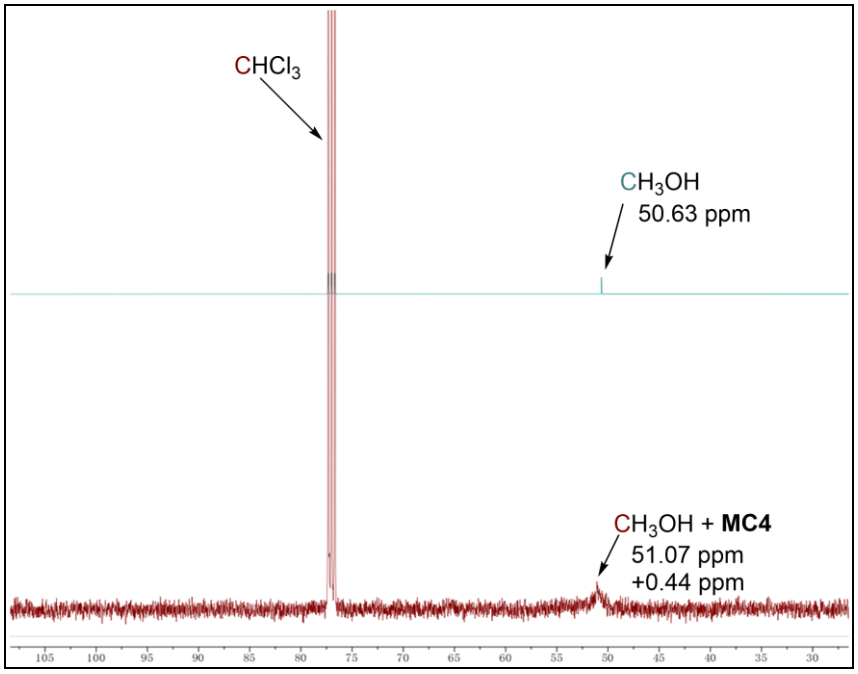


Fig. S31. The ^{13}C NMR spectrum of MeOH upon addition of catalyst **MC4**

(3) NMR Titration Experiments and determination of the binding constants

All experiments were conducted by mixing different ratios of the **MC4** and MeOH at ambient temperature (298.5 K) in NMR tubes. MeOH (1.0 equiv, 0.3 mmol) and the different equivalent of **MC4** (0 equiv, 0.033 equiv, 0.066 equiv, 0.132 equiv, 0.198 equiv, 0.264 equiv, 0.50 equiv) were dissolved in 0.5 mL $CDCl_3$. Then the mixtures were analyzed by ^{13}C NMR experiments.

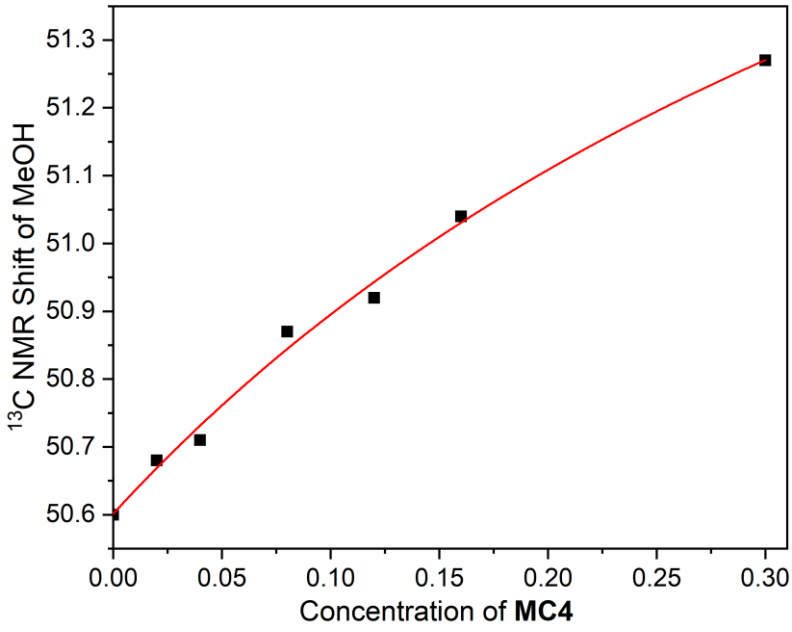
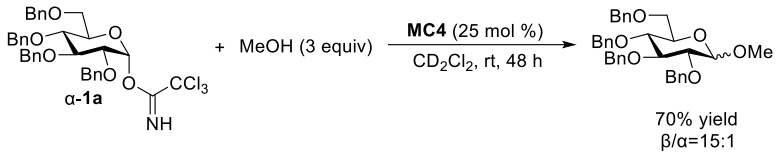


Fig. S32. NMR titration experiments between **MC4** with MeOH

For the determination of the binding constants (K) of **MC4** for MeOH, the shift of the methyl group was observed relative to the signal of the solvent. The measured shifts were plotted against the guest-concentrations and the resulting curve was fitted via http://supramolecular.org[8,9]. For the calculations of the binding constants (K) a 1:1 binding was assumed. K_{MeOH} = 2.66 M^{-1}.

(9) *Tracing the reaction process using ^{77}Se NMR*



To a reaction mixture of α-**1a** (68.5 mg, 0.1 mmol), catalyst **MC4** (84.4 mg, 0.025 mmol, 25 mol %) and MeOH (12.2 μL, 0.3 mmol, 3 equiv) in a 10 mL-Schlenk tube was added CD_2Cl_2 (0.5 mL) under argon atmosphere and stirred at room temperature. Then the reaction process was traced by ^{77}Se NMR when the reaction was run for 48 h (70% yield, β/α = 15:1). ^{77}Se NMR experiments only one ^{77}Se signal assigned to catalyst **MC4** was observed.

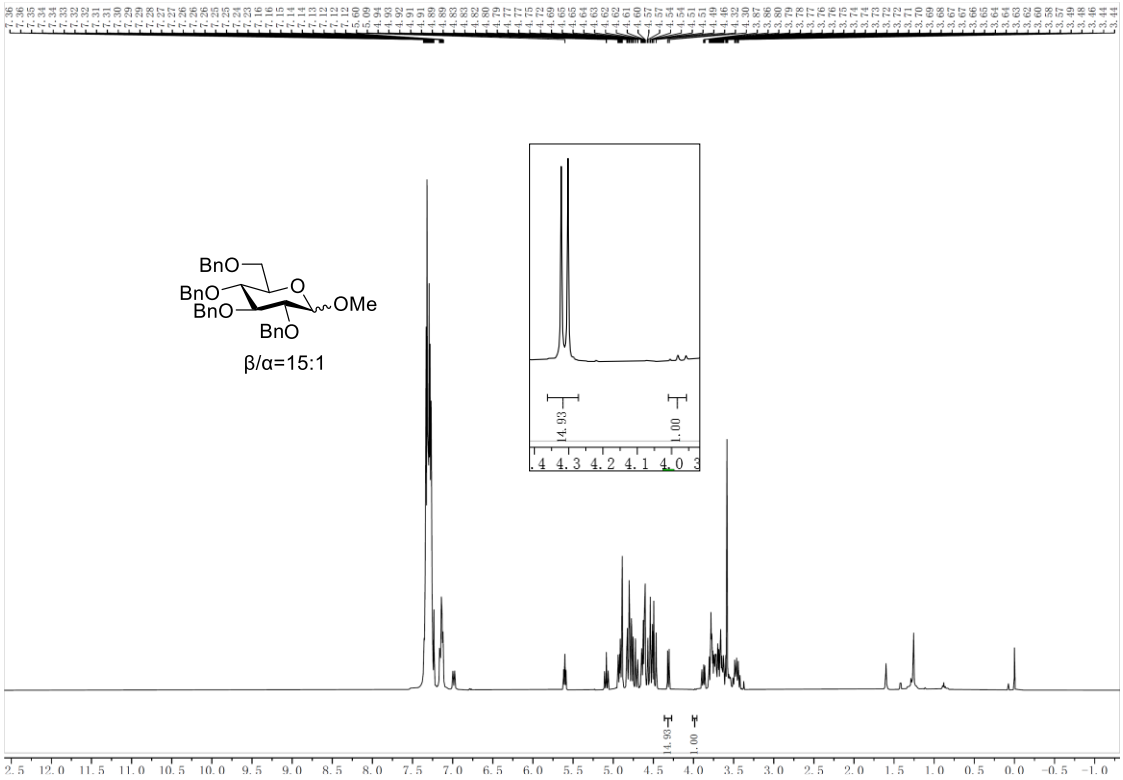


Fig. S33. β/α selectivity of reaction in CD_2Cl_2

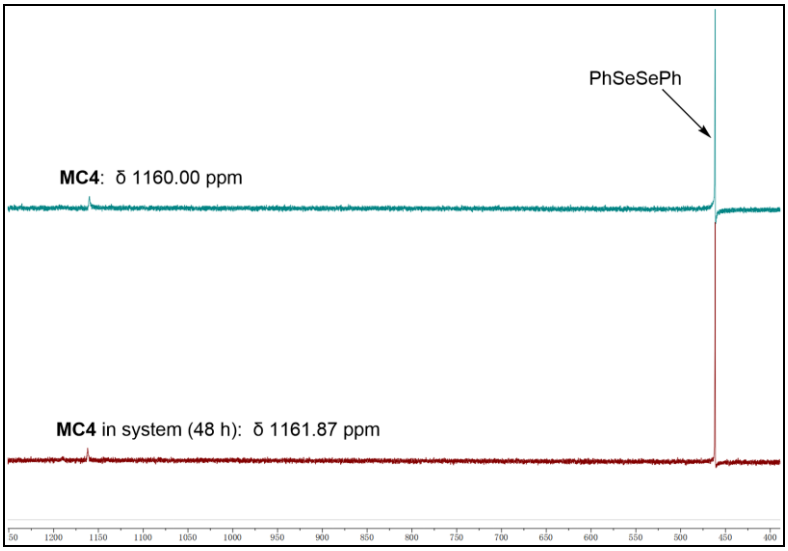
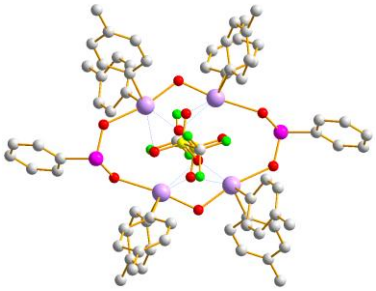


Fig. S34. Tracing the reaction process using ^{77}Se NMR

7. X-ray Crystallographic Data



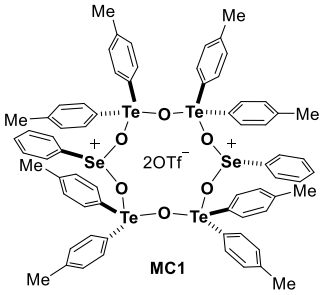


Fig. S35. X-ray crystallographic structure of **MC1** (CCDC: 2290511).

Table S8. *Crystal data and structure refinement for **MC1***

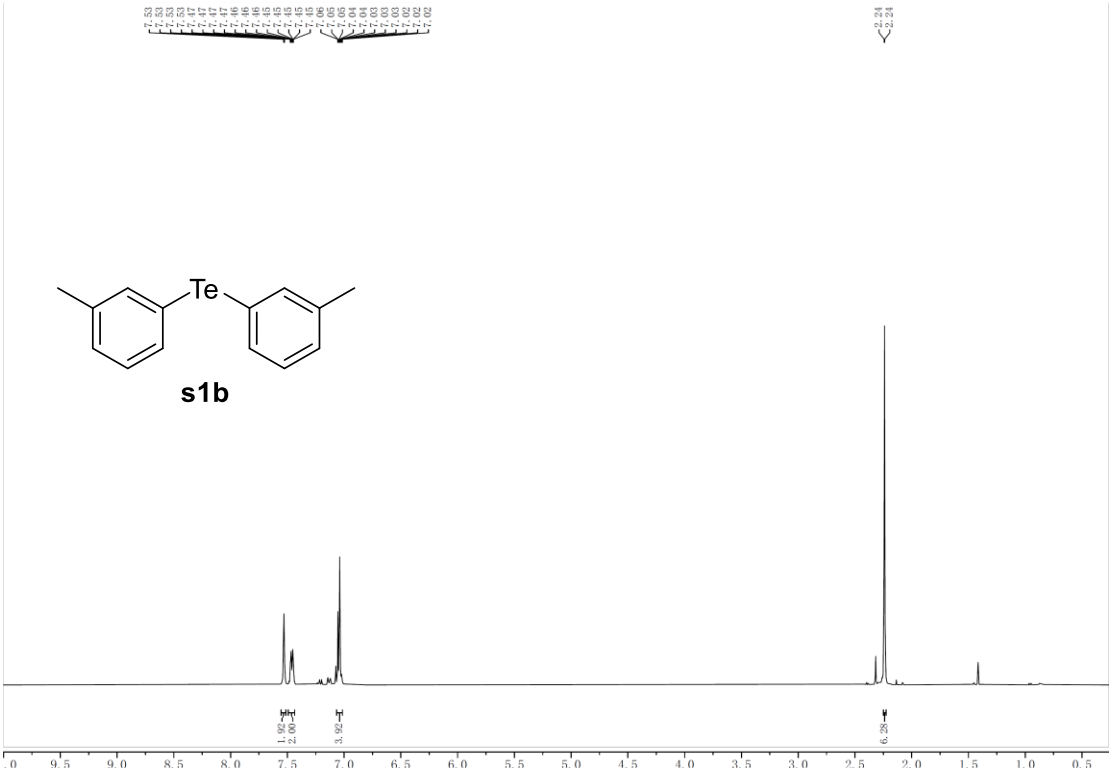
Identification code	cu_220730A_0m
Empirical formula	$C_{70}H_{66}F_6O_{12}S_2Se_2Te_4$
Formula weight	1945.74
Temperature/K	173.0
Crystal system	triclinic
Space group	P-1
a/Å	12.2642(11)
b/Å	13.1320(12)
c/Å	14.3067(13)
α/°	79.991(3)
β/°	66.928(3)
γ/°	88.801(3)
Volume/Å^3	2084.7(3)
Z	1
ρ_{calc}g/cm^3	1.668
μ/mm^{-1}	13.011
F(000)	1028.0
Crystal size/mm^3	0.12 × 0.11 × 0.1
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	8.756 to 133.214
Index ranges	-14 ≤ h ≤ 14, -15 ≤ k ≤ 14, -17 ≤ l ≤ 17
Reflections collected	25837
Independent reflections	7311 [R_{int} = 0.0416, R_{sigma} = 0.0351]
Data/restraints/parameters	7311/0/484
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0294, wR_2 = 0.0808
Final R indexes [all data]	R_1 = 0.0307, wR_2 = 0.0818
Largest diff. peak/hole / e Å^{-3}	1.16/-0.84

8. Copies of NMR Spectra

^{1}H NMR spectrum of compound **s1a** ($CDCl_3$, 400 MHz)

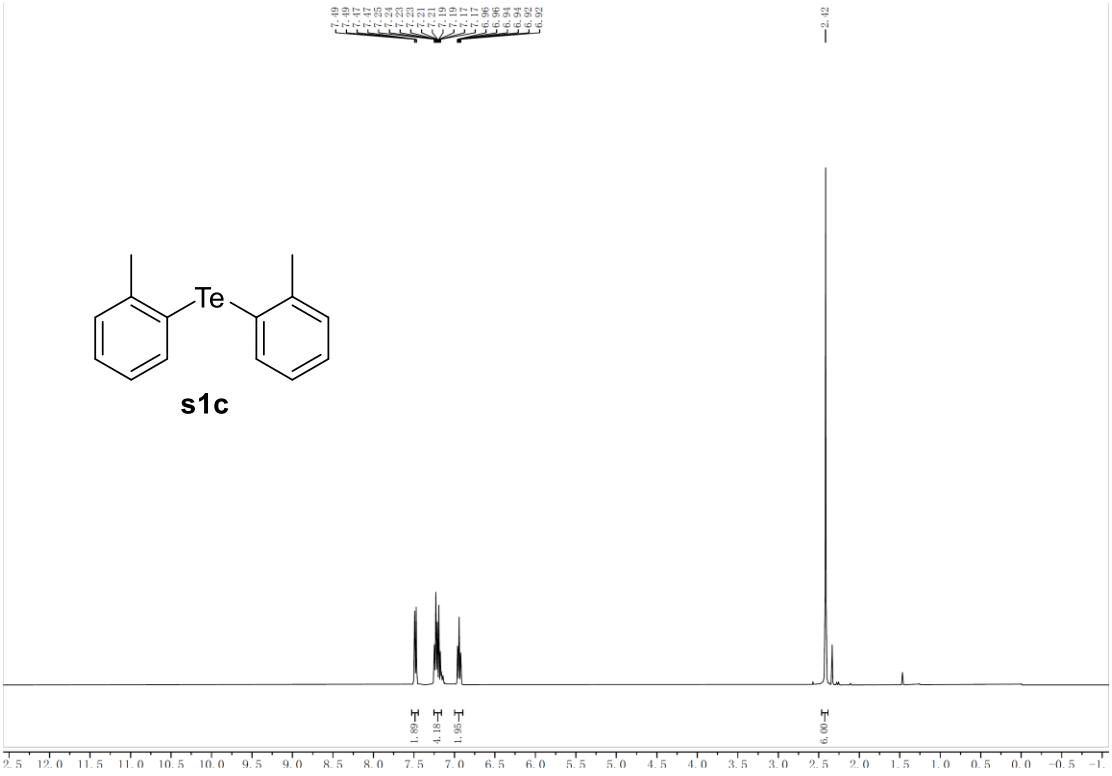
^{13}C NMR spectrum of compound **s1a** ($CDCl_3$, 100 MHz)

^{1}H NMR spectrum of compound **s1b** ($CDCl_3$, 400 MHz)

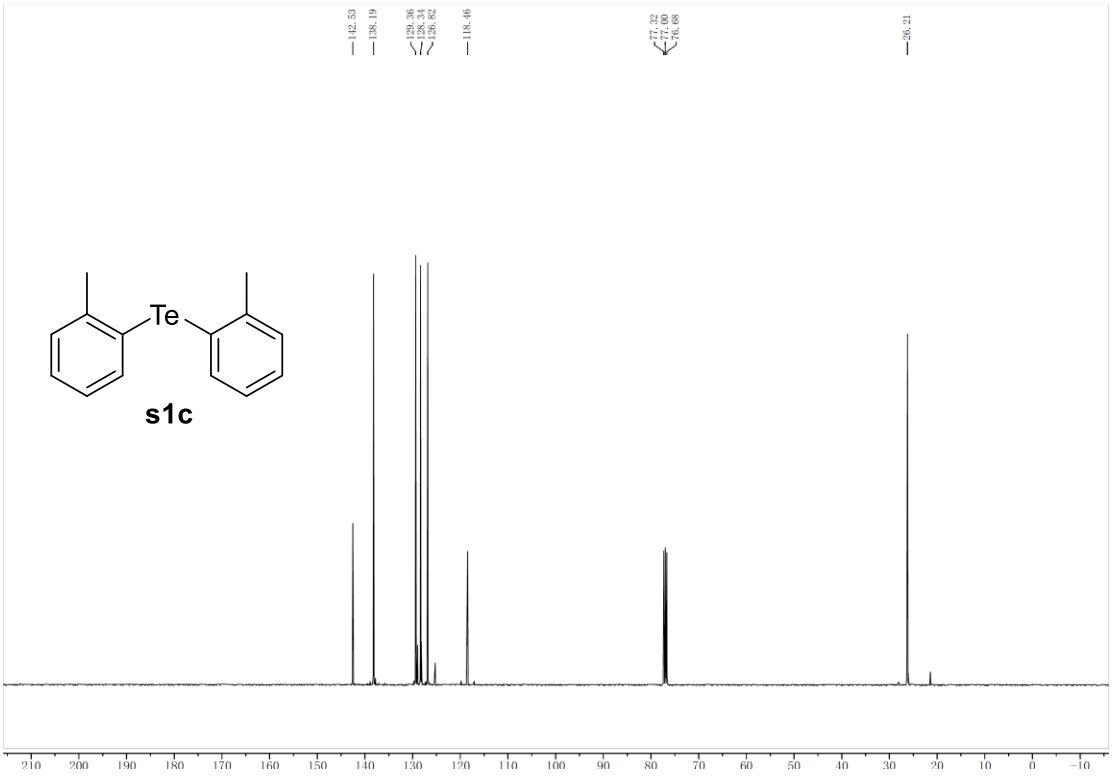


^{13}C NMR spectrum of compound **s1b** ($CDCl_3$, 100 MHz)

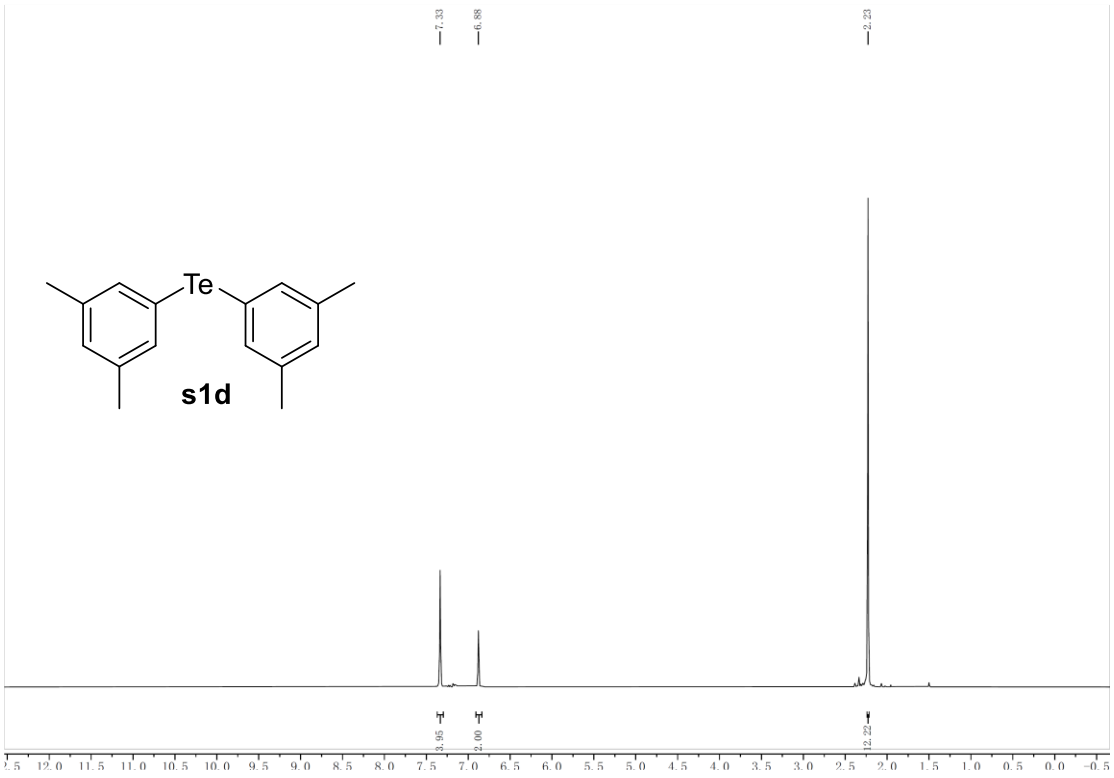
^{1}H NMR spectrum of compound **s1c** ($CDCl_3$, 400 MHz)



^{13}C NMR spectrum of compound **s1c** ($CDCl_3$, 100 MHz)



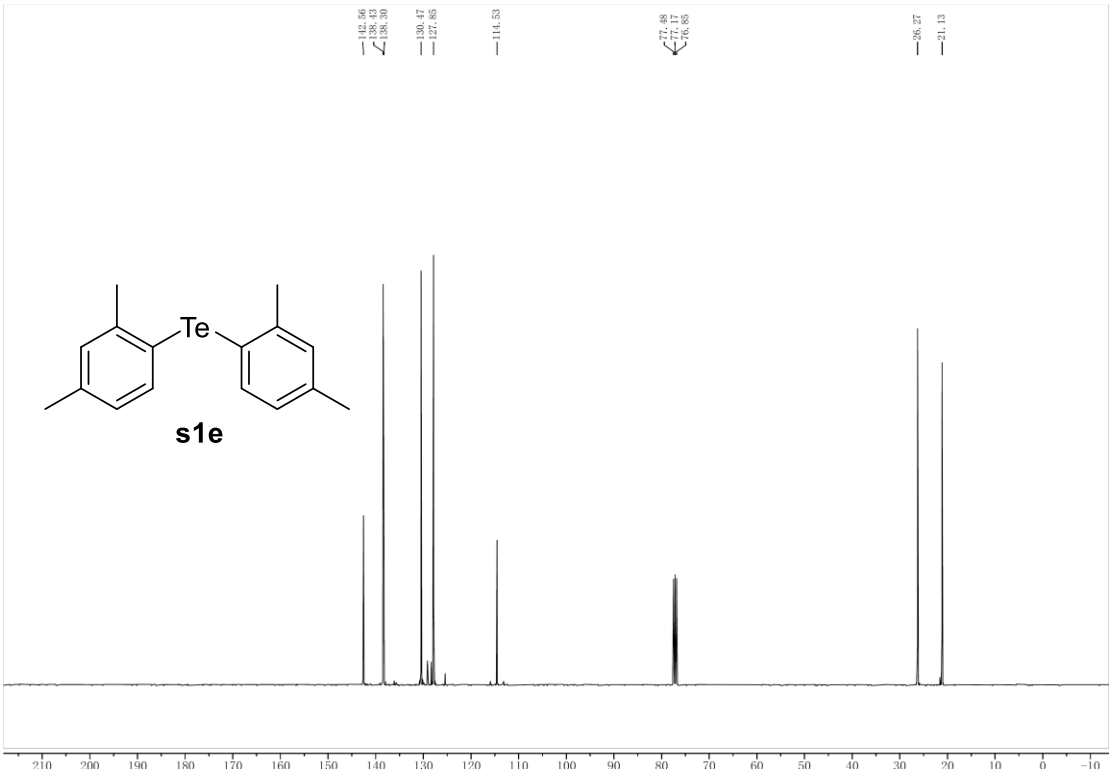
^{1}H NMR spectrum of compound **s1d** ($CDCl_3$, 400 MHz)



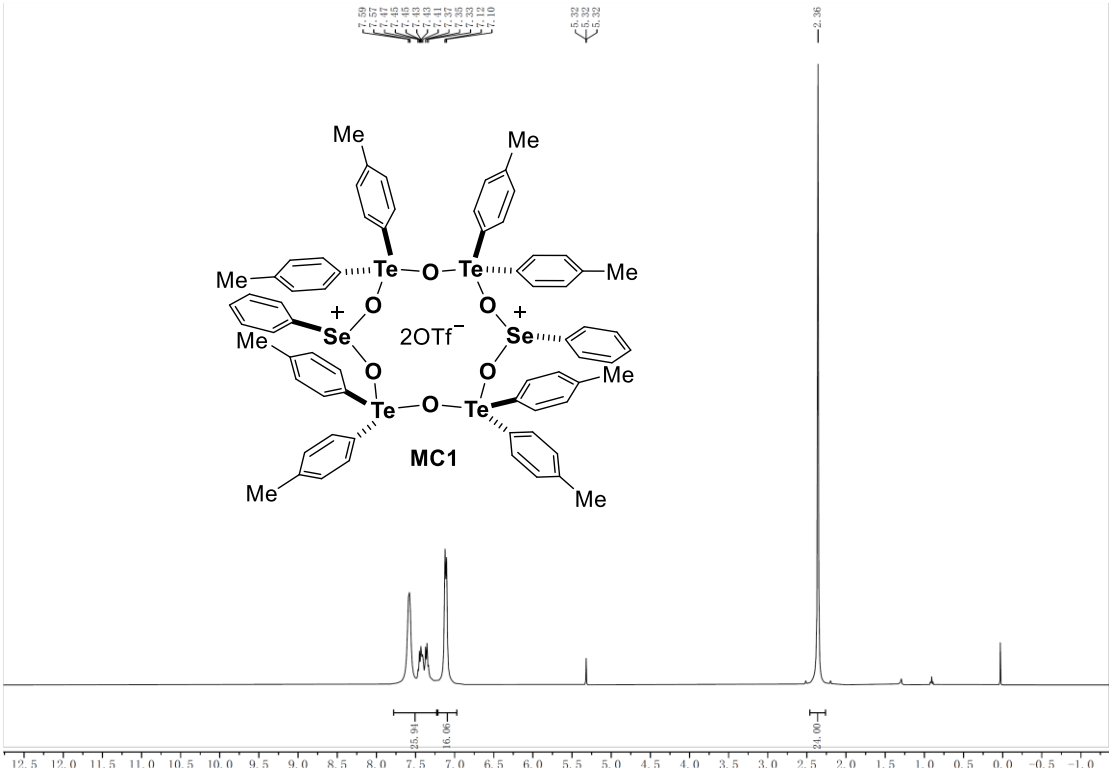
^{13}C NMR spectrum of compound **s1d** ($CDCl_3$, 100 MHz)

^{1}H NMR spectrum of compound **s1e** ($CDCl_3$, 400 MHz)

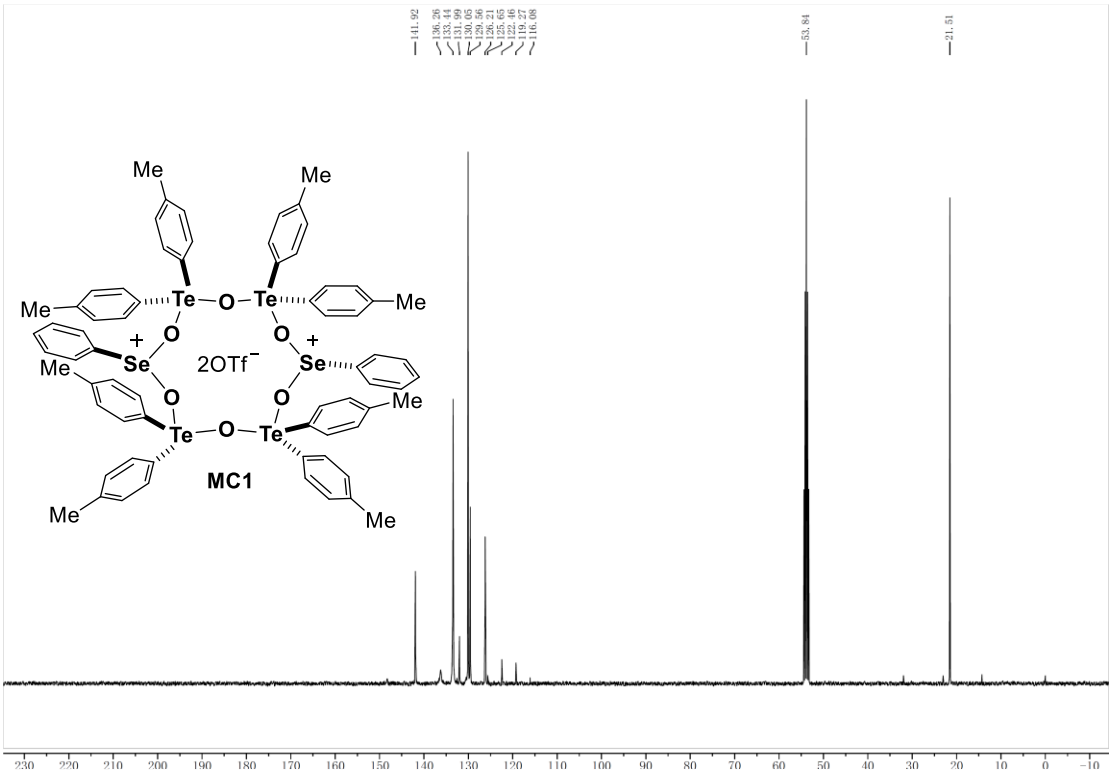
^{13}C NMR spectrum of compound **s1e** ($CDCl_3$, 100 MHz)



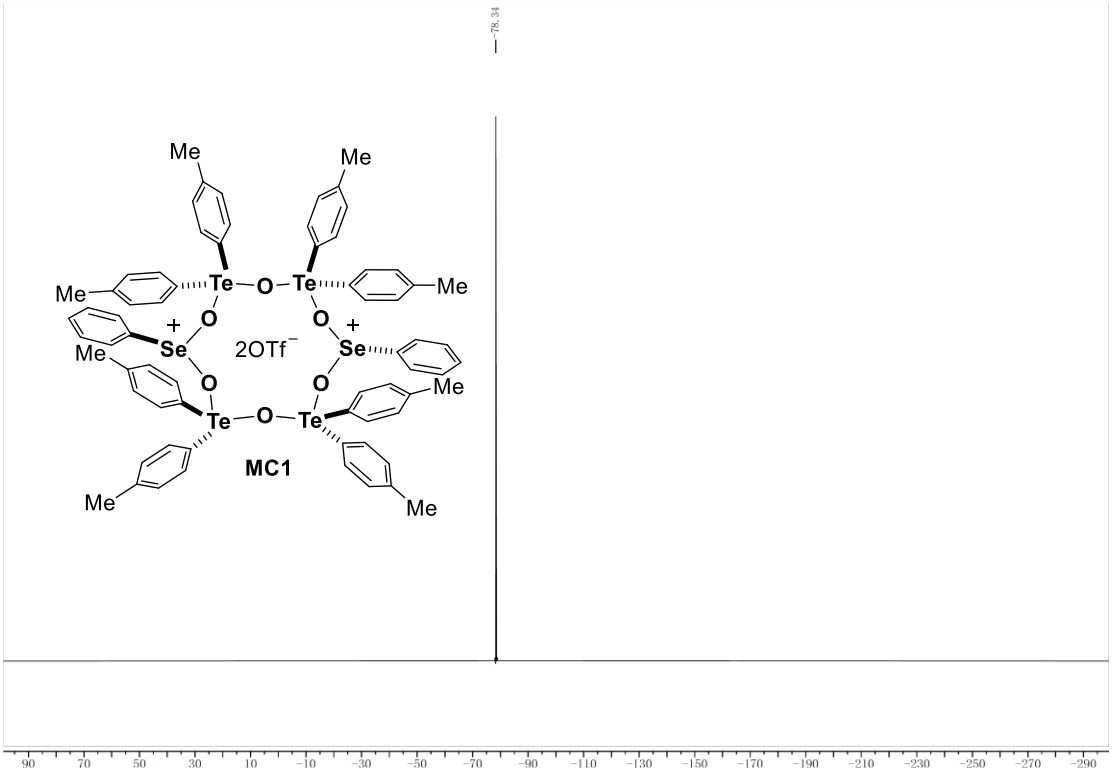
^{1}H NMR spectrum of compound **MC1** (CD_2Cl_2, 400 MHz)



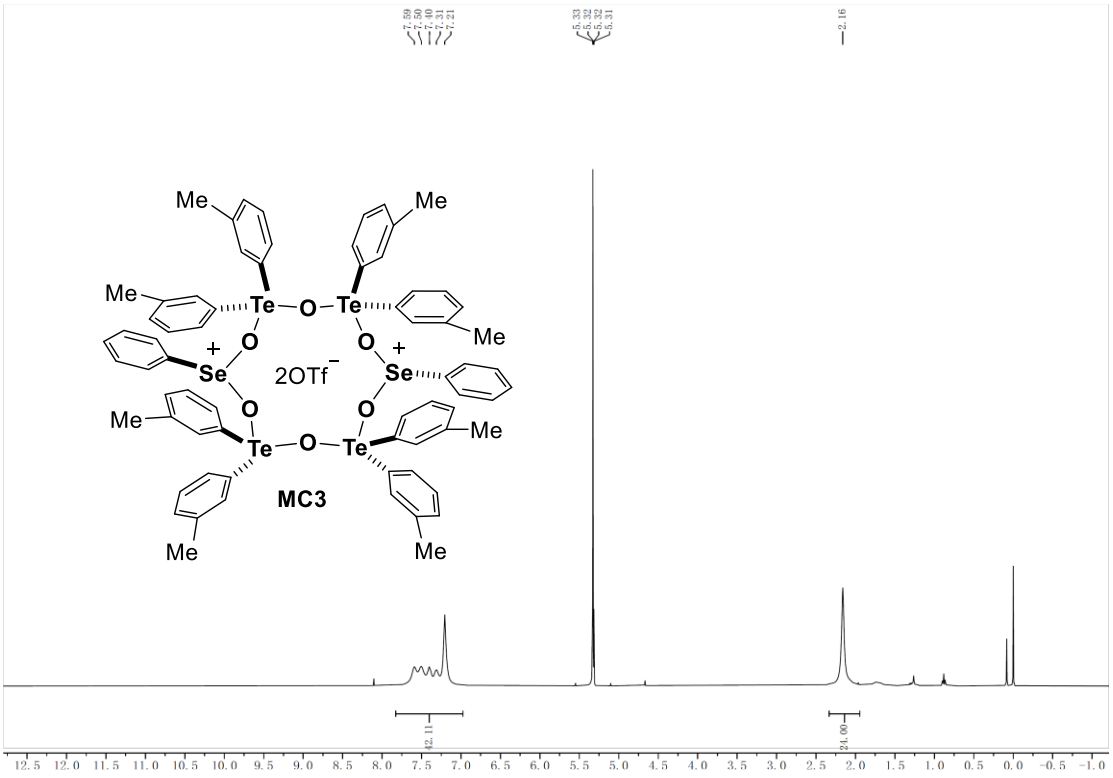
^{13}C NMR spectrum of compound **MC1** (CD_2Cl_2, 100 MHz)



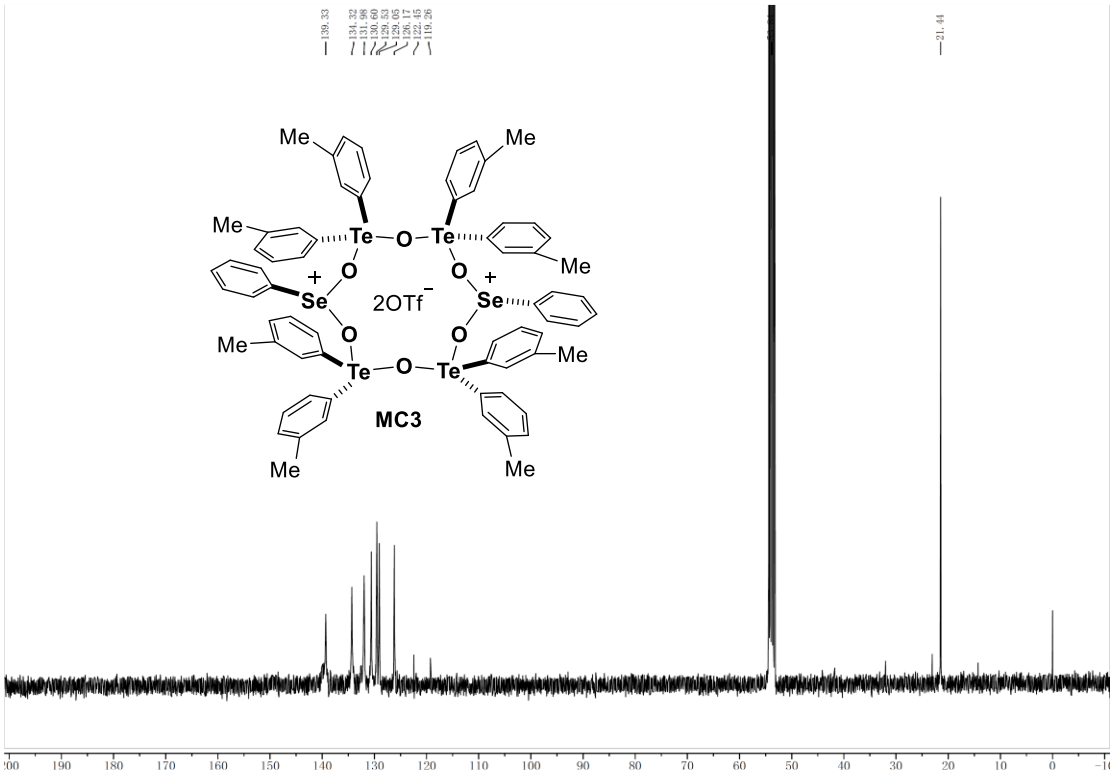
^{19}F NMR spectrum of compound **MC1** (CD_2Cl_2, 377 MHz)



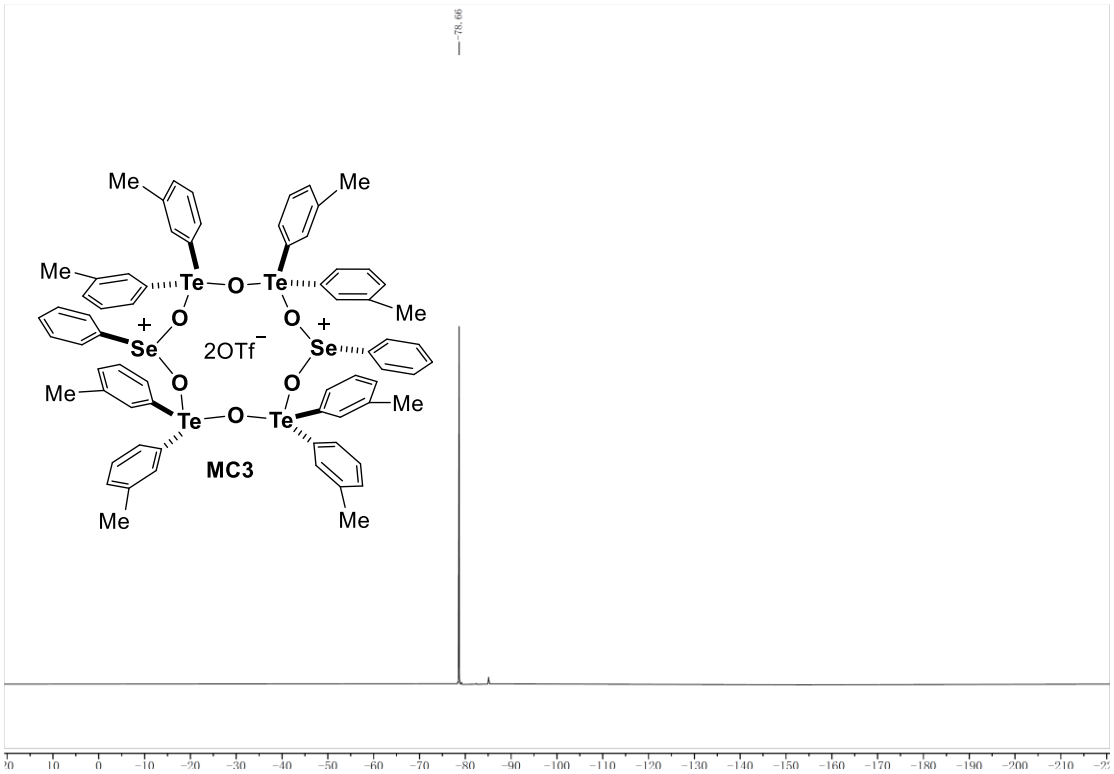
^{1}H NMR spectrum of compound **MC3** (CD_2Cl_2, 400 MHz)



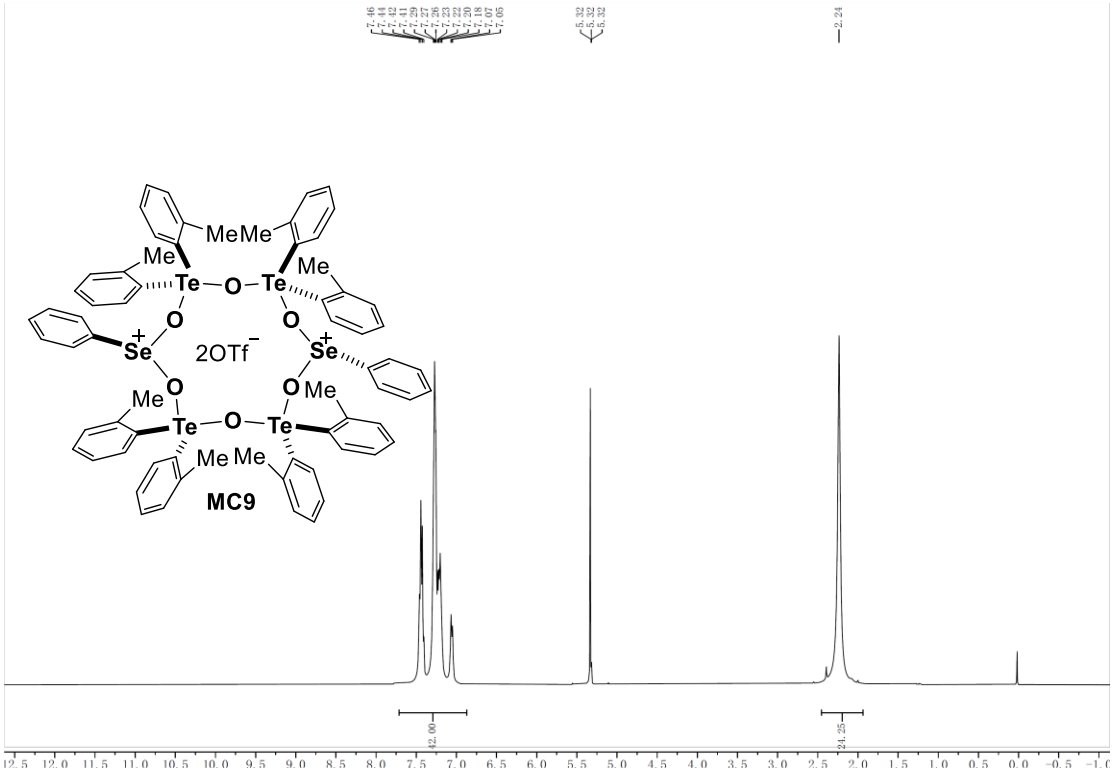
^{13}C NMR spectrum of compound **MC3** (CD_2Cl_2, 100 MHz)



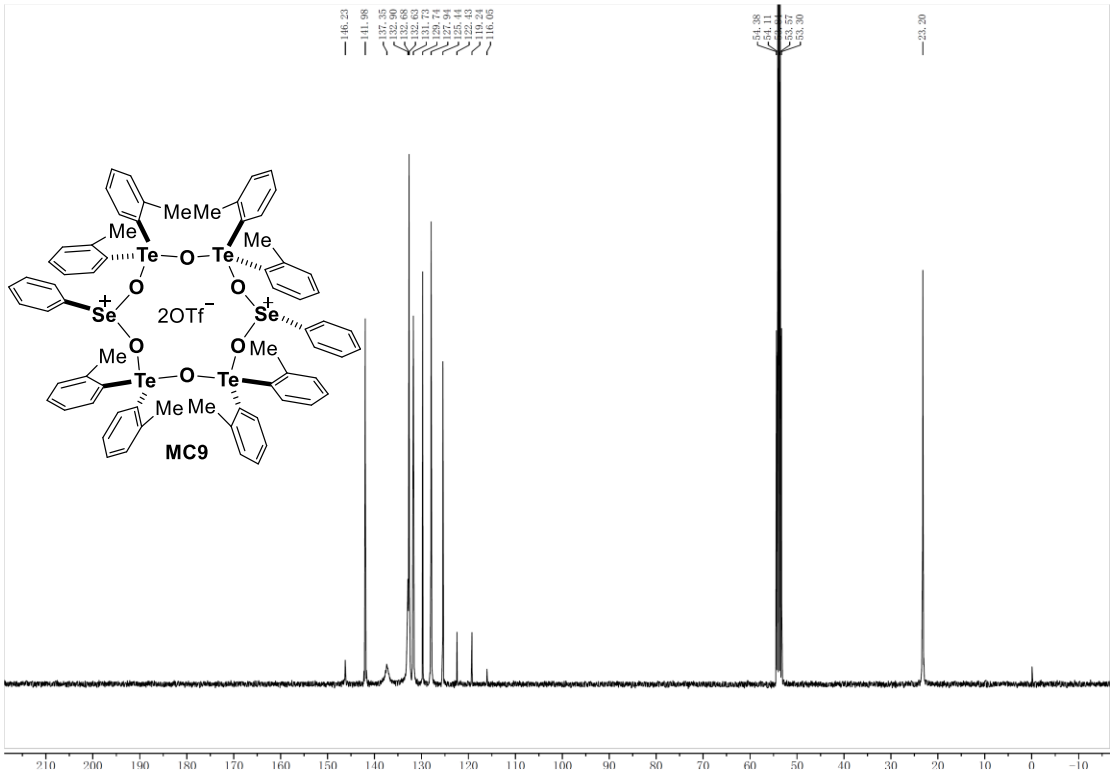
^{19}F NMR spectrum of compound **MC3** (CD_2Cl_2, 377 MHz)



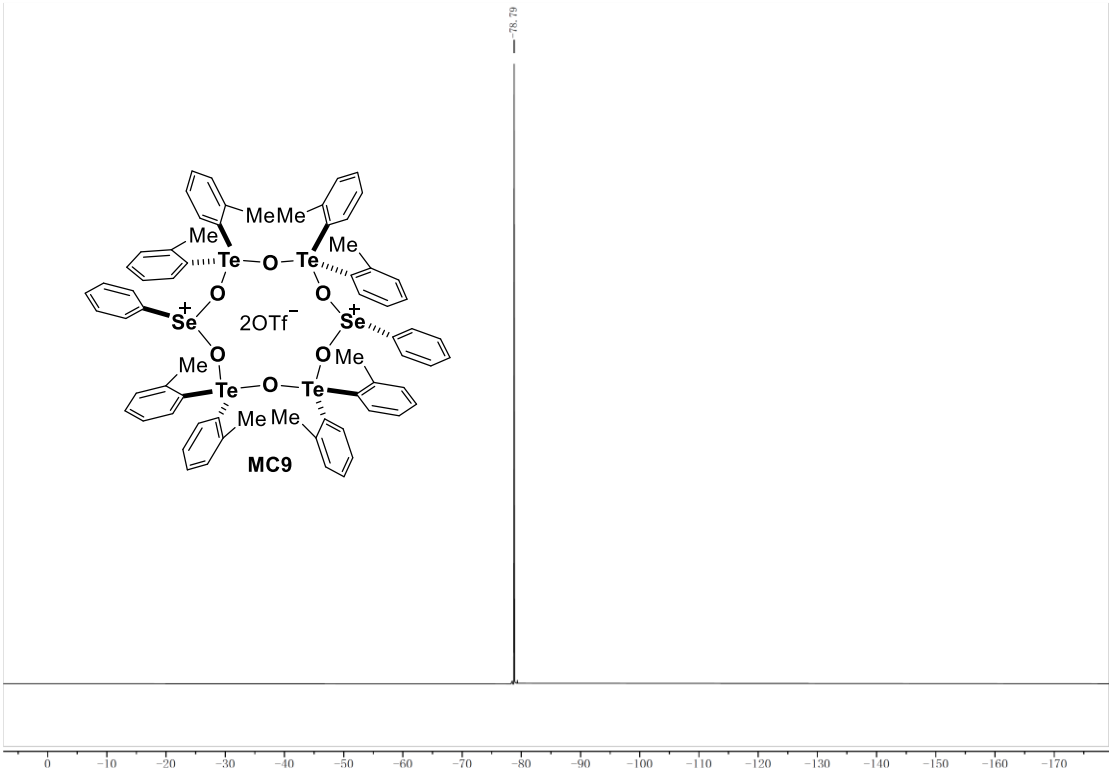
^{1}H NMR spectrum of compound **MC9** (CD_2Cl_2, 400 MHz)



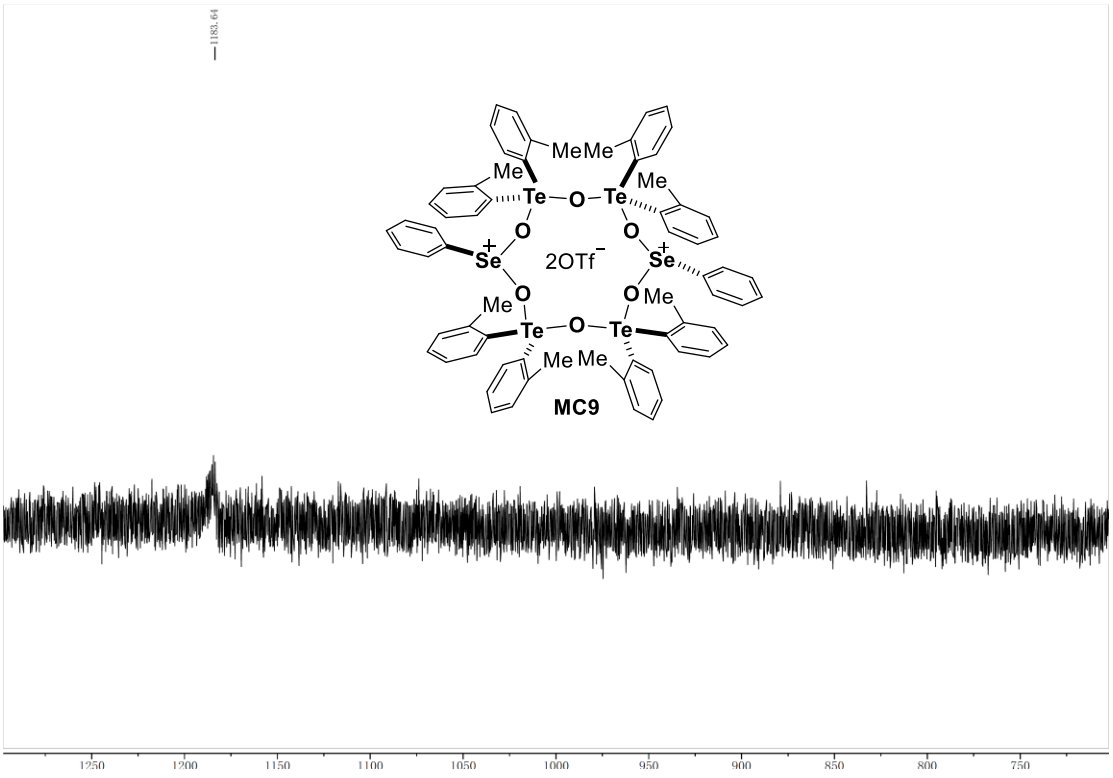
^{13}C NMR spectrum of compound **MC9** (CD_2Cl_2, 100 MHz)



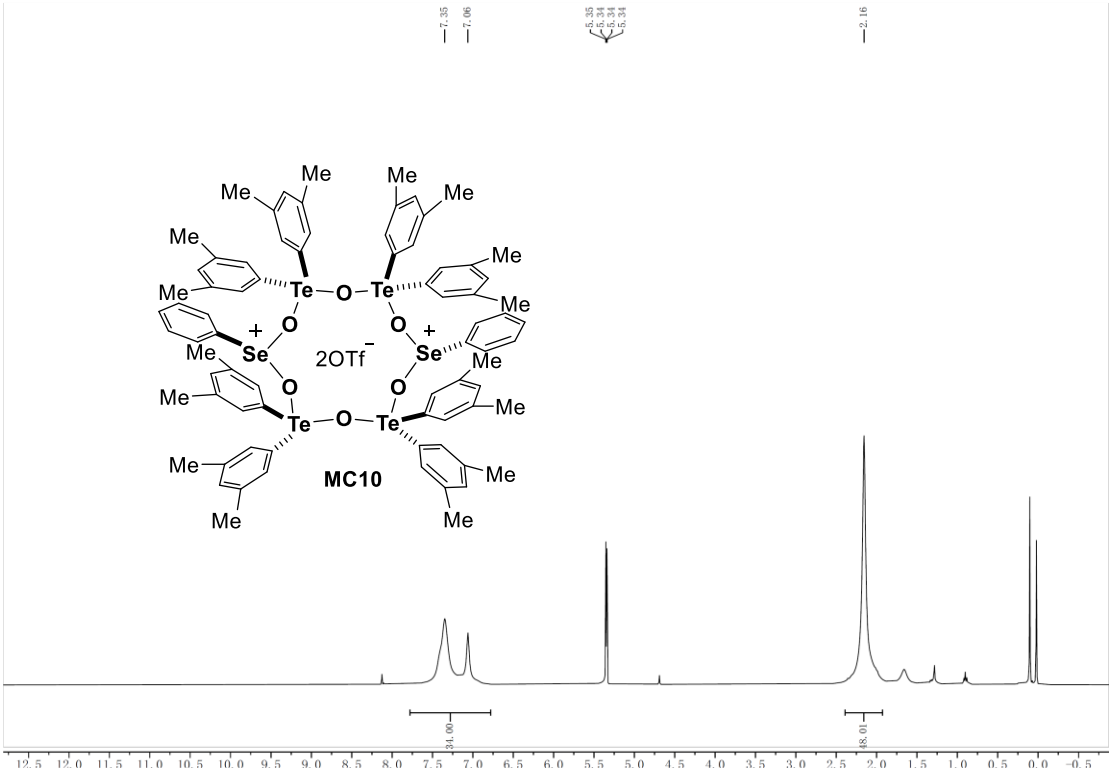
^{19}F NMR spectrum of compound **MC9** (CD_2Cl_2, 377 MHz)



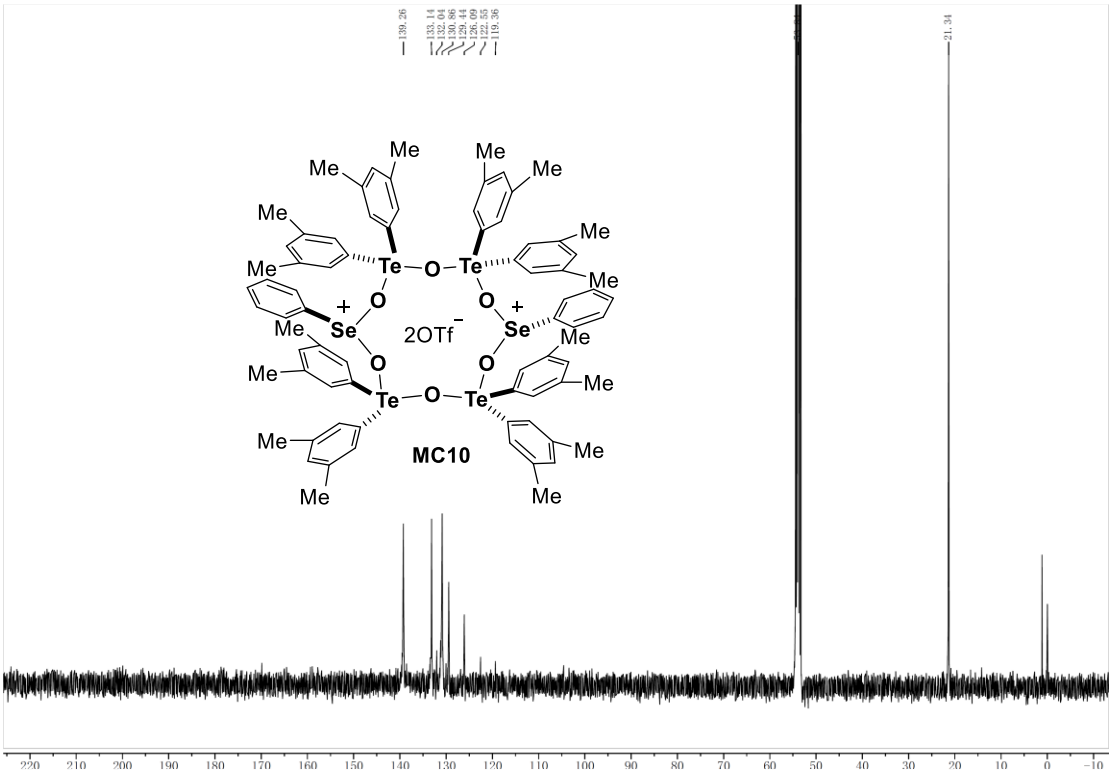
^{77}Se NMR spectrum of compound **MC9** (CD_2Cl_2, 76 MHz)



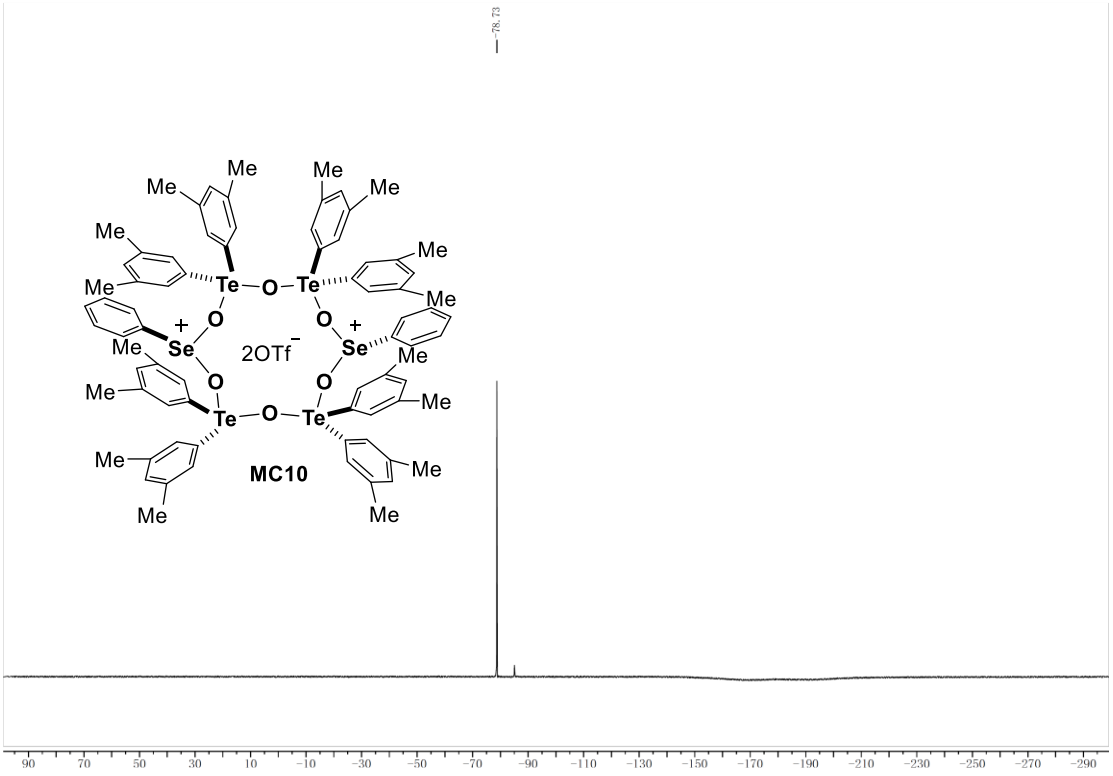
^{1}H NMR spectrum of compound **MC10** (CD_2Cl_2, 400 MHz)



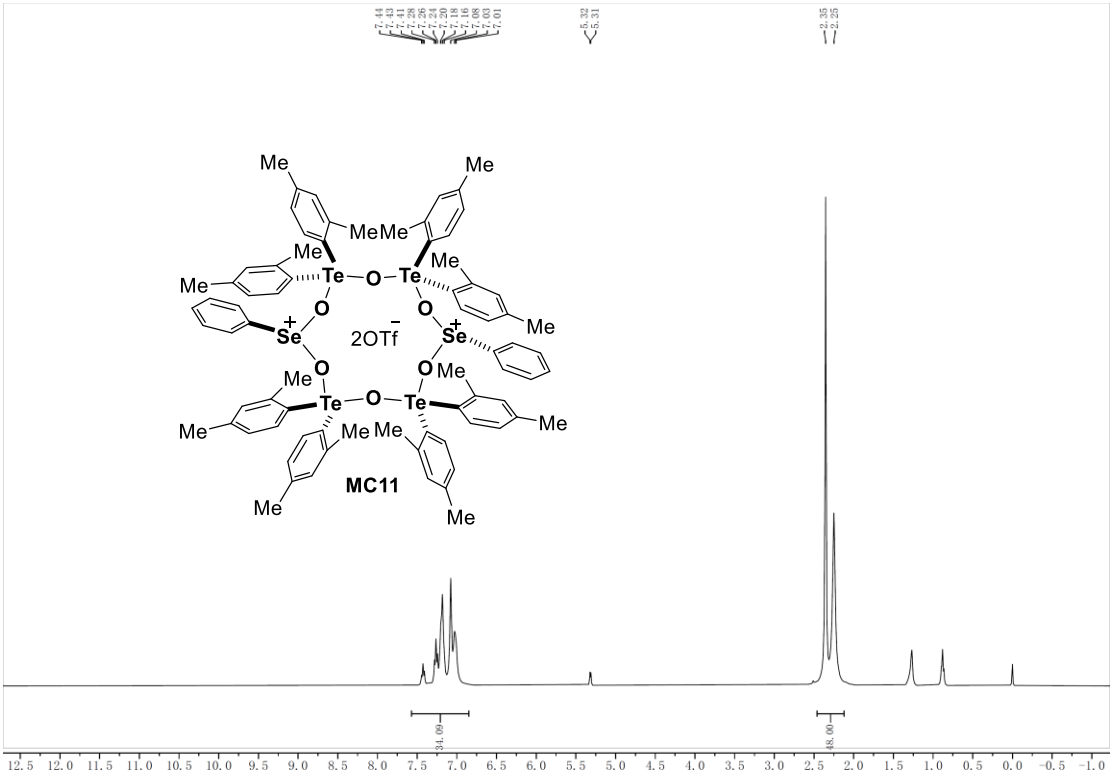
^{13}C NMR spectrum of compound **MC10** (CD_2Cl_2, 100 MHz)



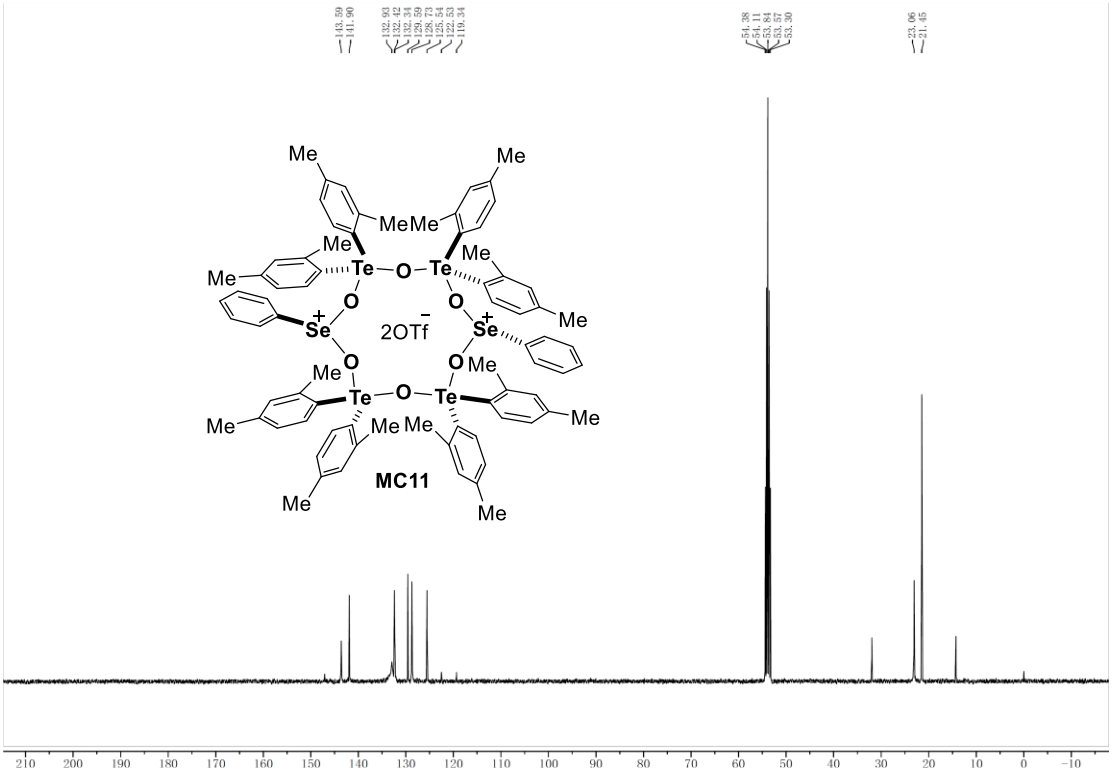
^{19}F NMR spectrum of compound **MC10** (CD_2Cl_2, 377 MHz)



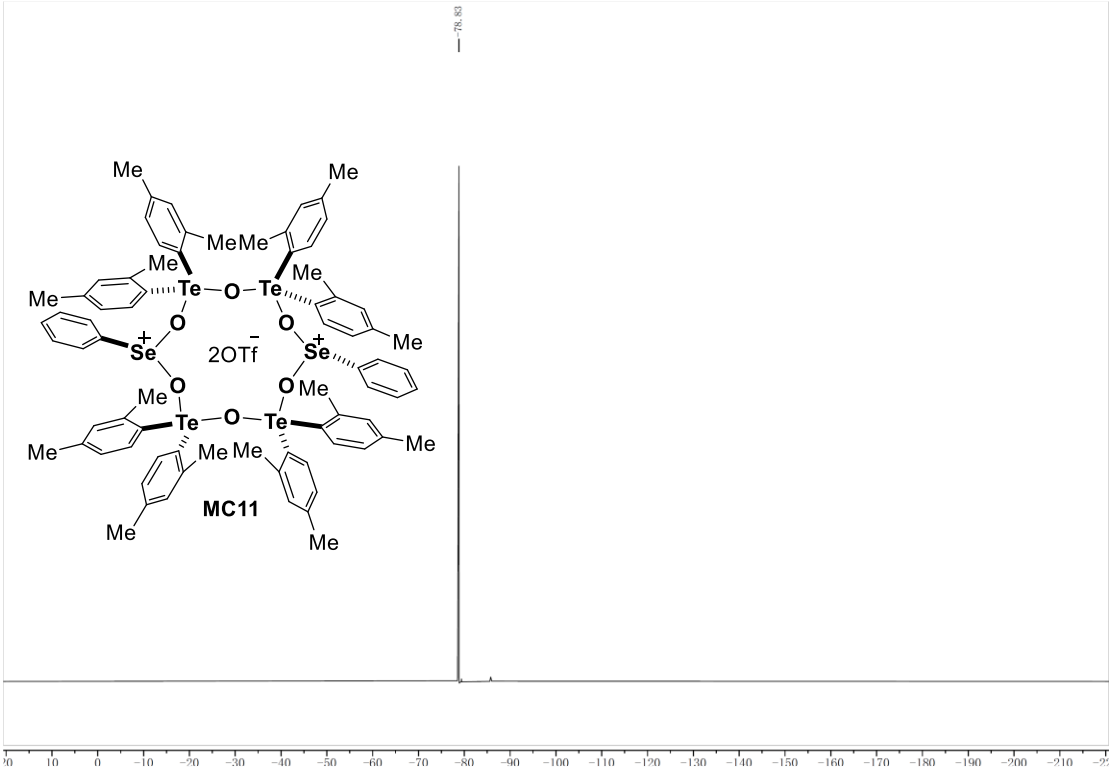
^{1}H NMR spectrum of compound **MC11** (CD_2Cl_2, 400 MHz)



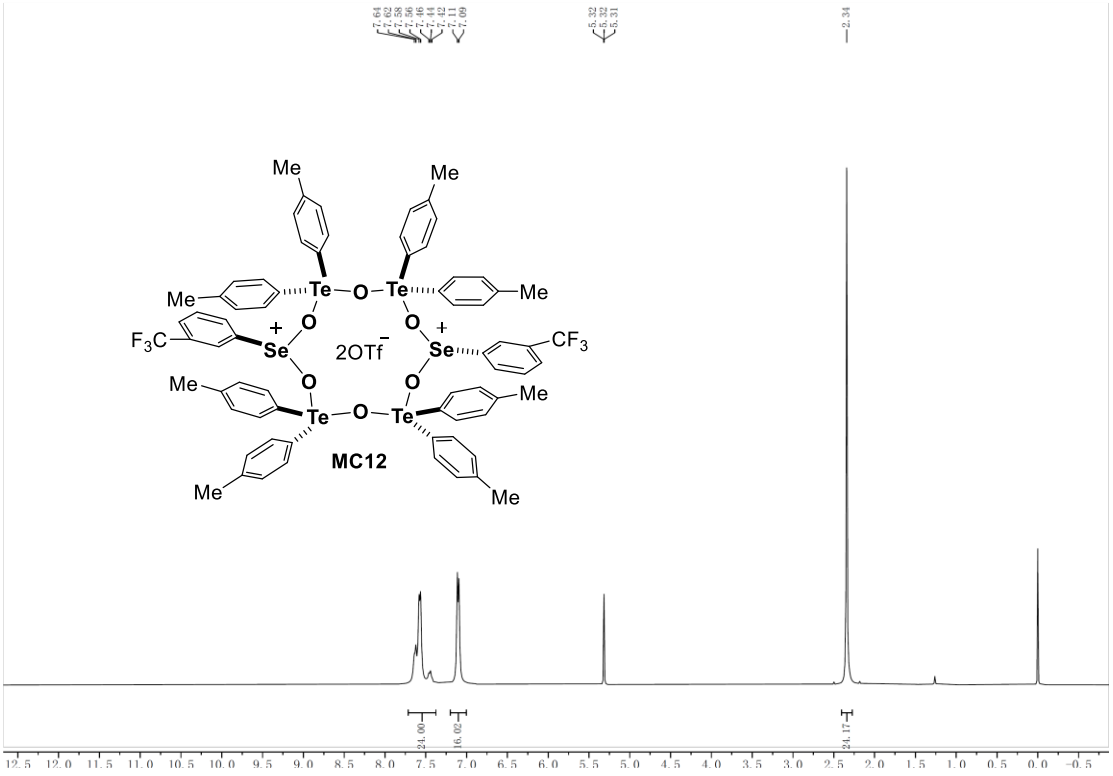
^{13}C NMR spectrum of compound **MC11** (CD_2Cl_2, 100 MHz)



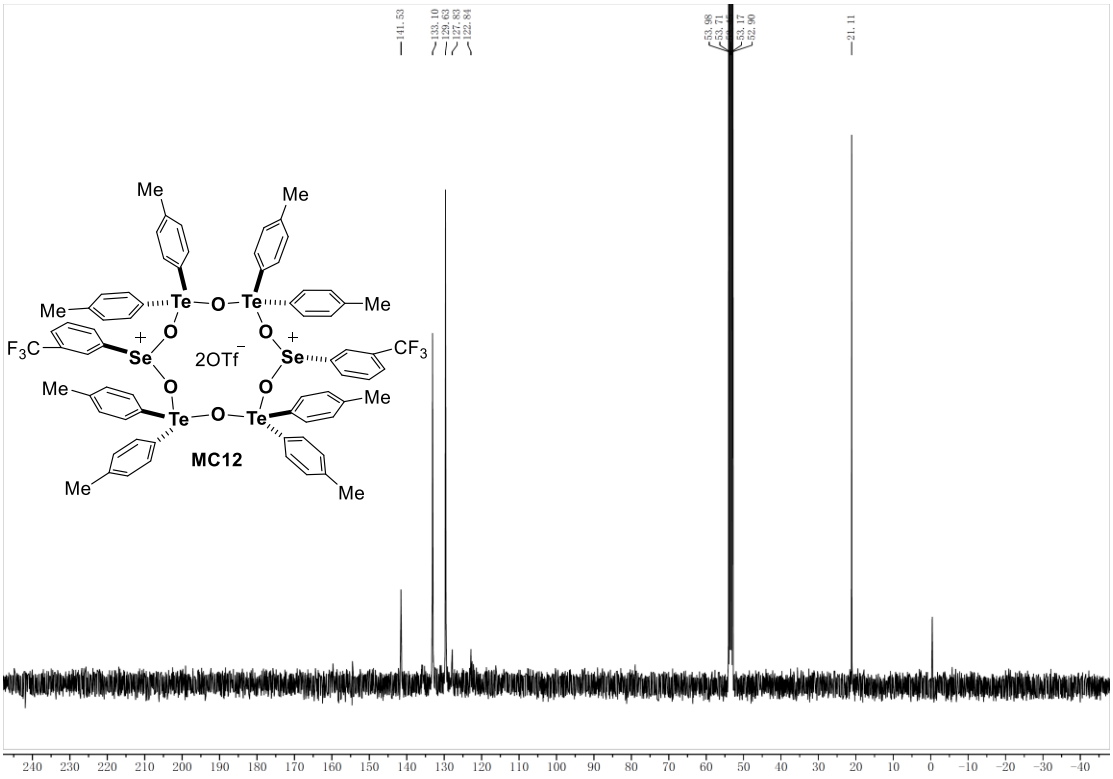
^{19}F NMR spectrum of compound **MC11** (CD_2Cl_2, 377 MHz)



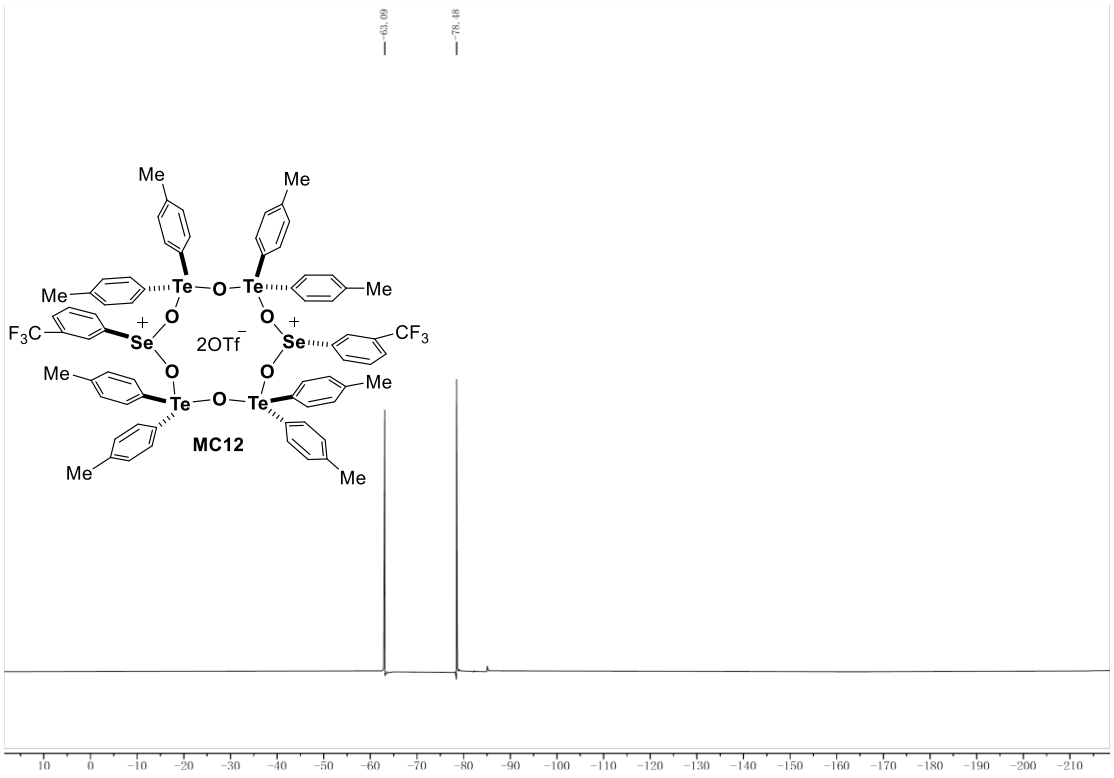
^{1}H NMR spectrum of compound **MC12** (CD_2Cl_2, 400 MHz)



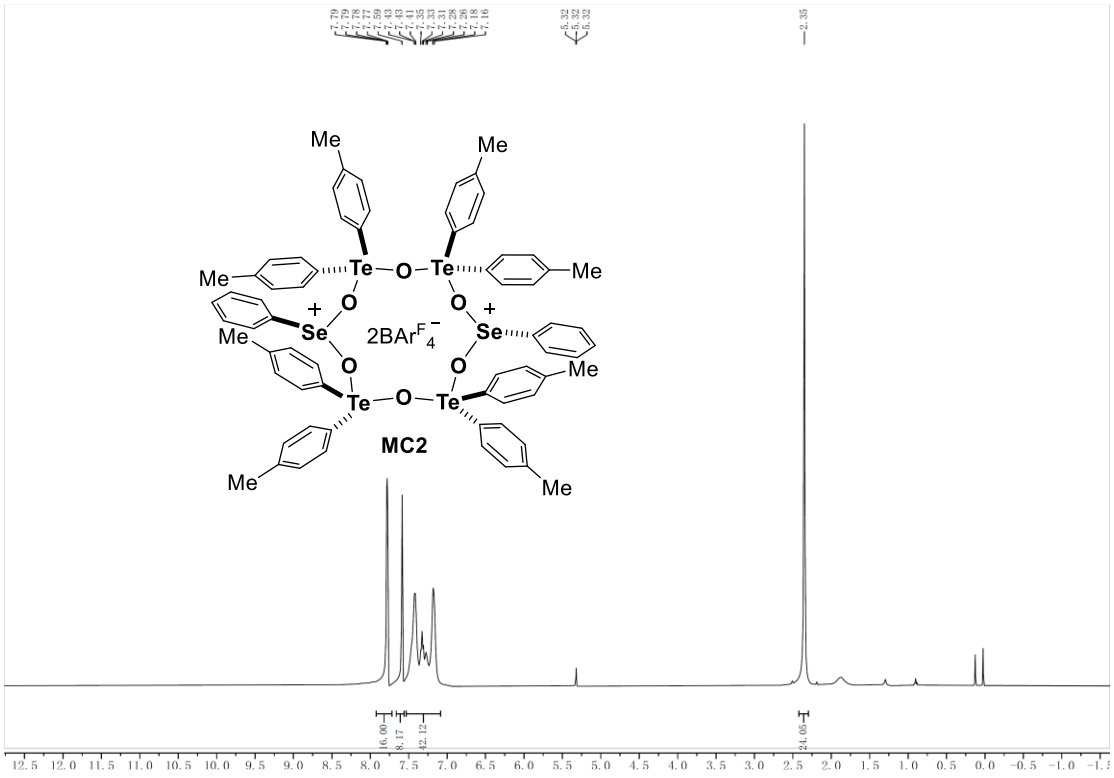
^{13}C NMR spectrum of compound **MC12** (CD_2Cl_2, 100 MHz)



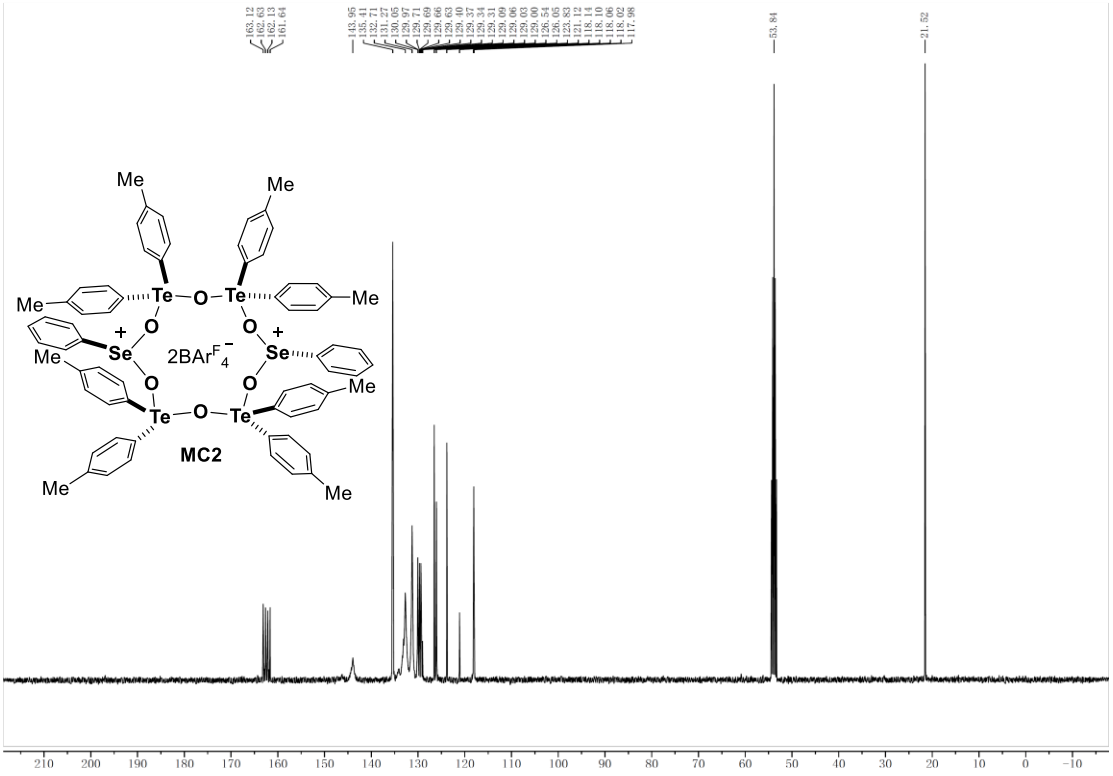
^{19}F NMR spectrum of compound **MC12** (CD_2Cl_2, 377 MHz)



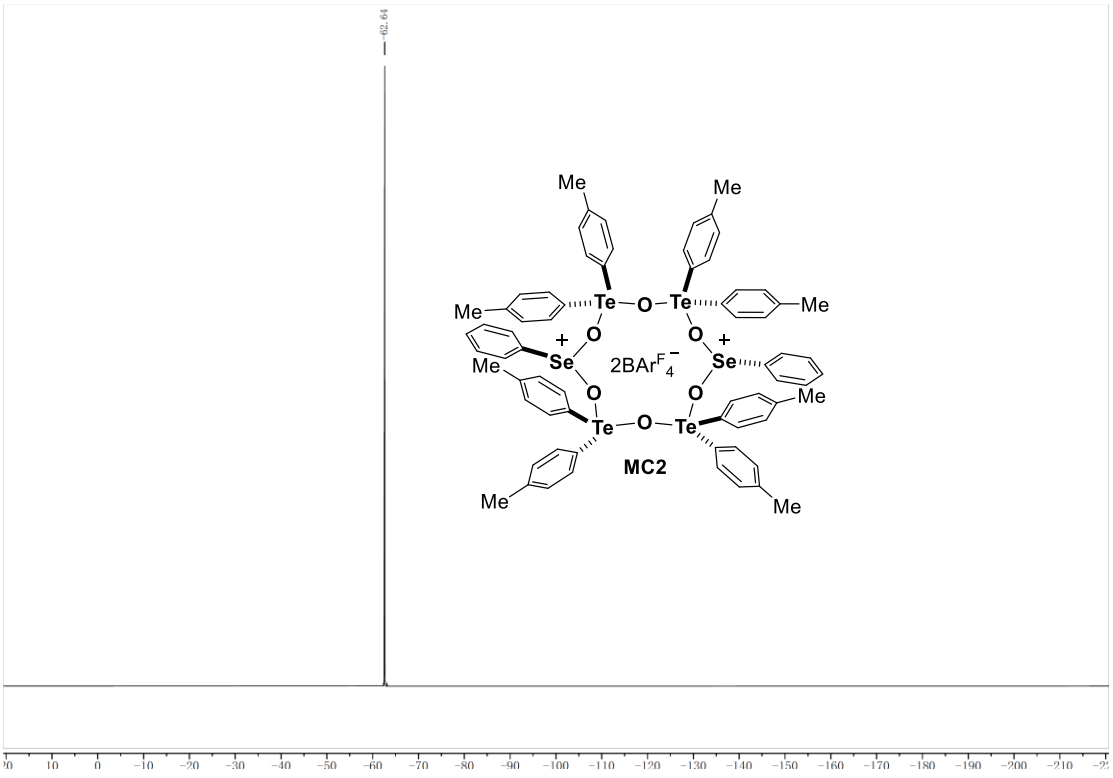
^{1}H NMR spectrum of compound **MC2** (CD_2Cl_2, 400 MHz)



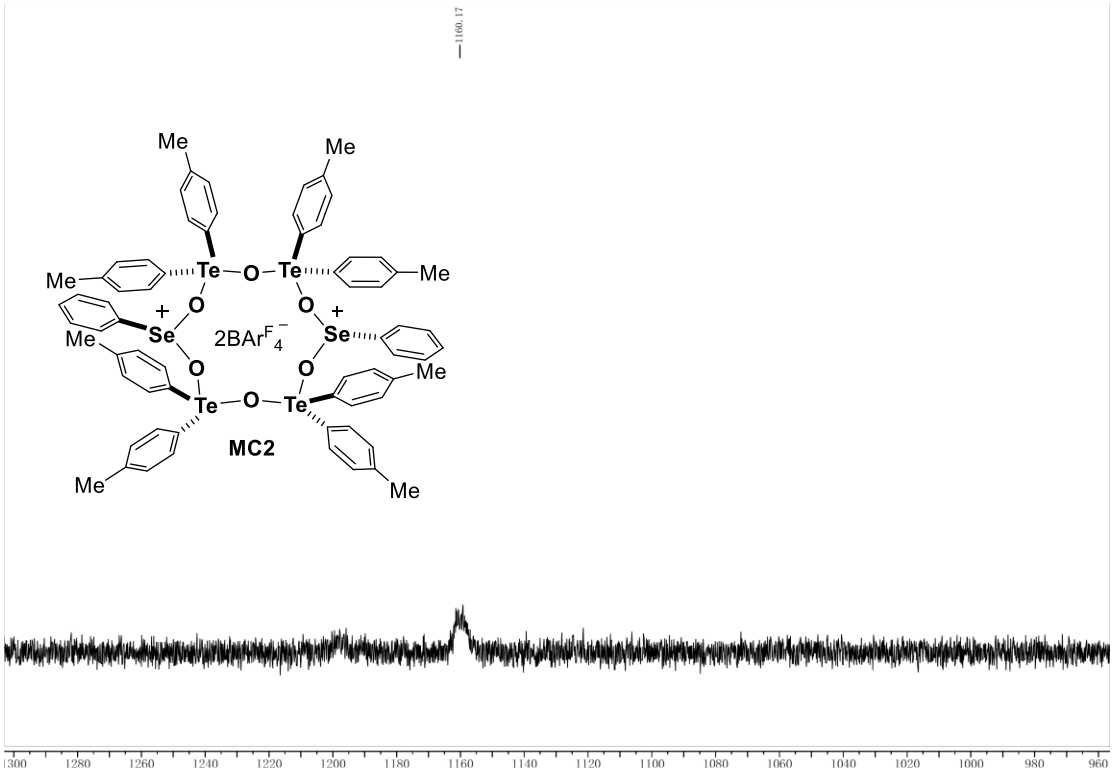
^{13}C NMR spectrum of compound **MC2** (CD_2Cl_2, 100 MHz)



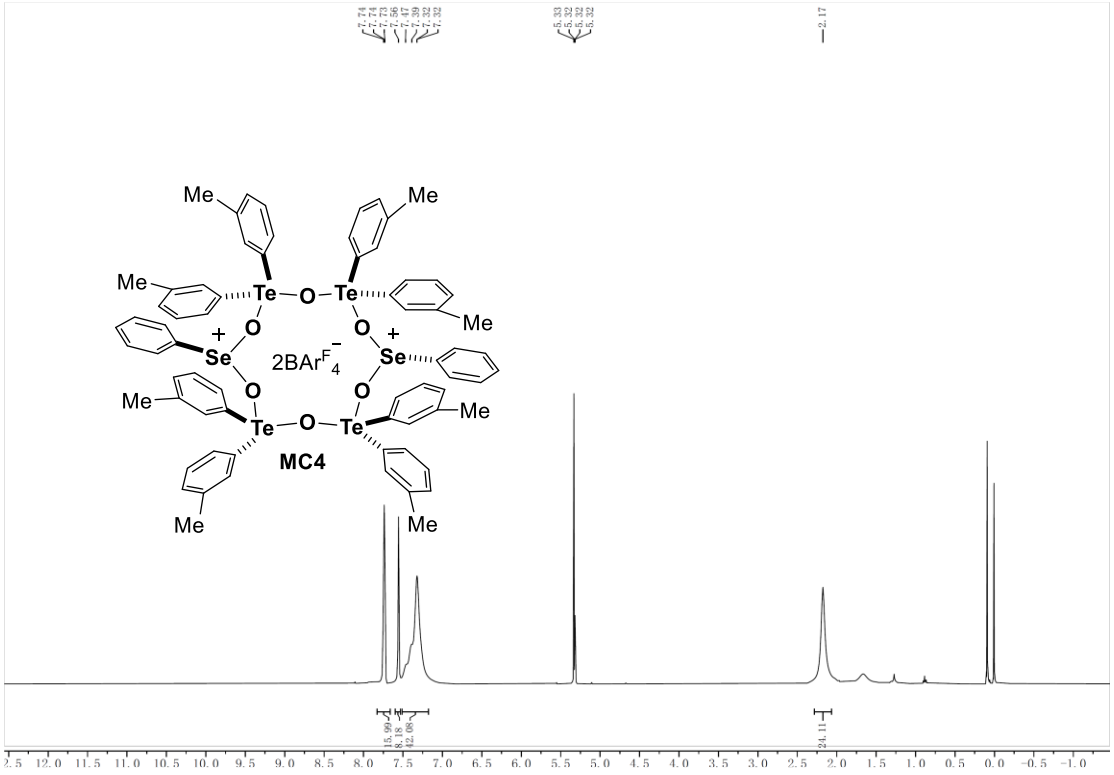
^{19}F NMR spectrum of compound **MC2** (CD_2Cl_2, 377 MHz)



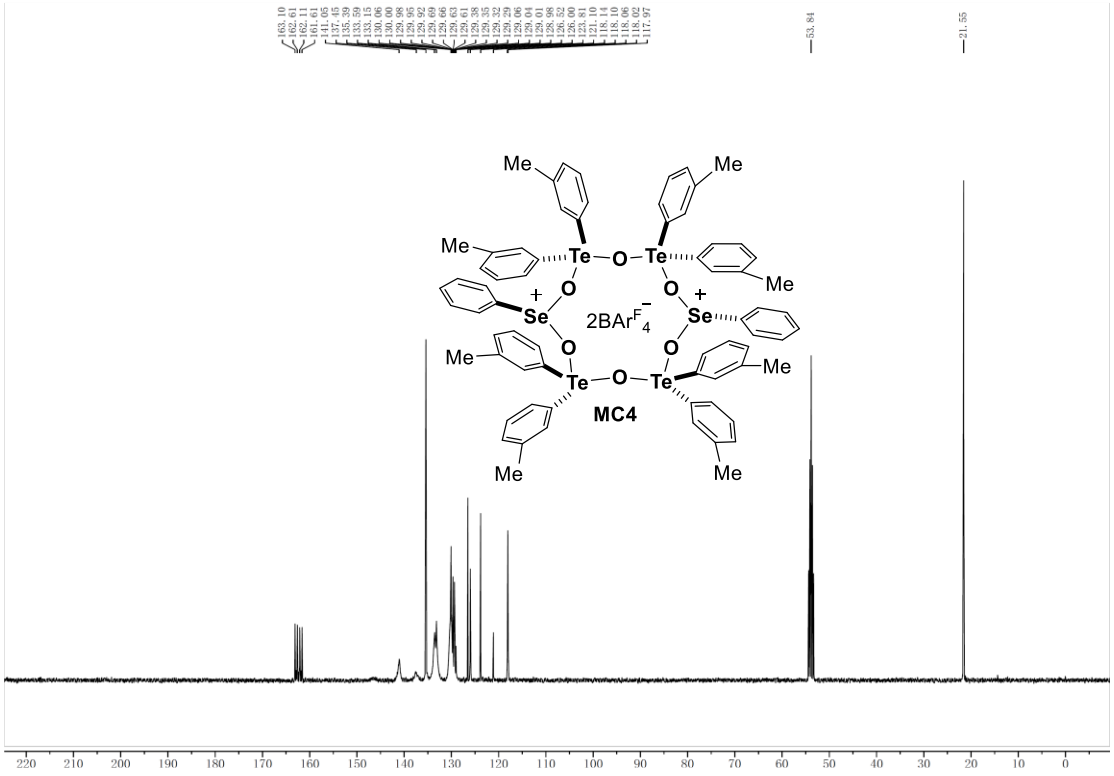
^{77}Se NMR spectrum of compound **MC2** (CD_2Cl_2, 76 MHz)



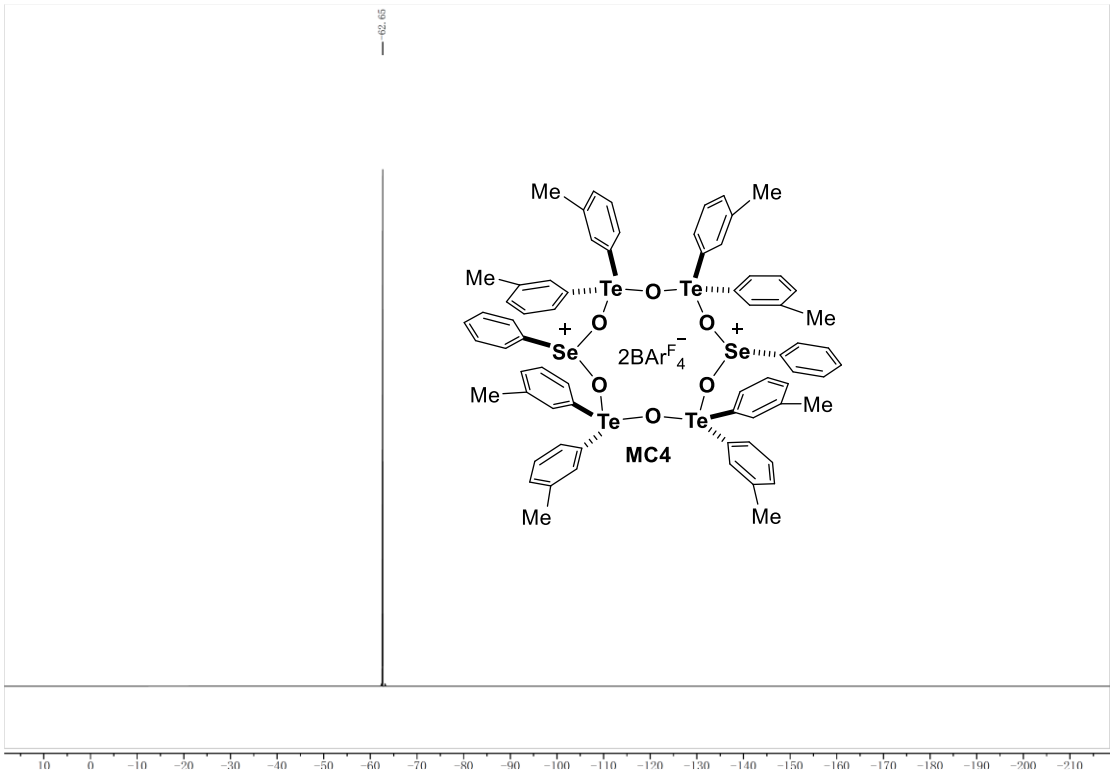
^{1}H NMR spectrum of compound **MC4** (CD_2Cl_2, 400 MHz)



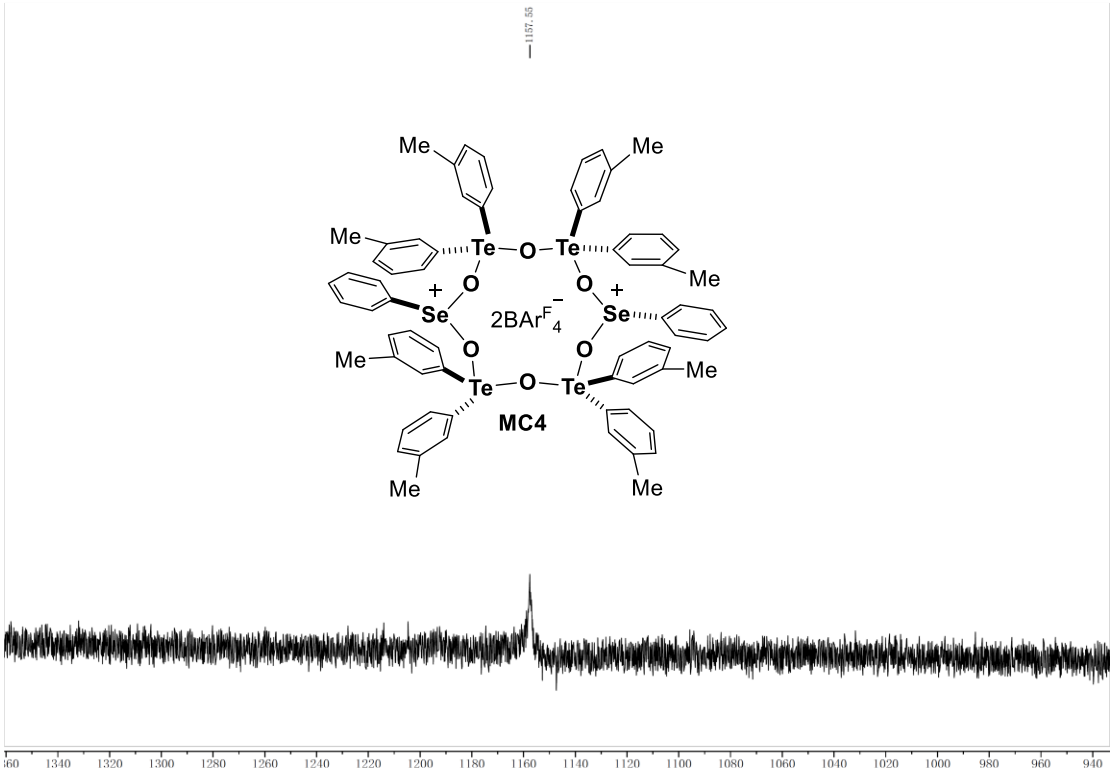
^{13}C NMR spectrum of compound **MC4** (CD_2Cl_2, 100 MHz)



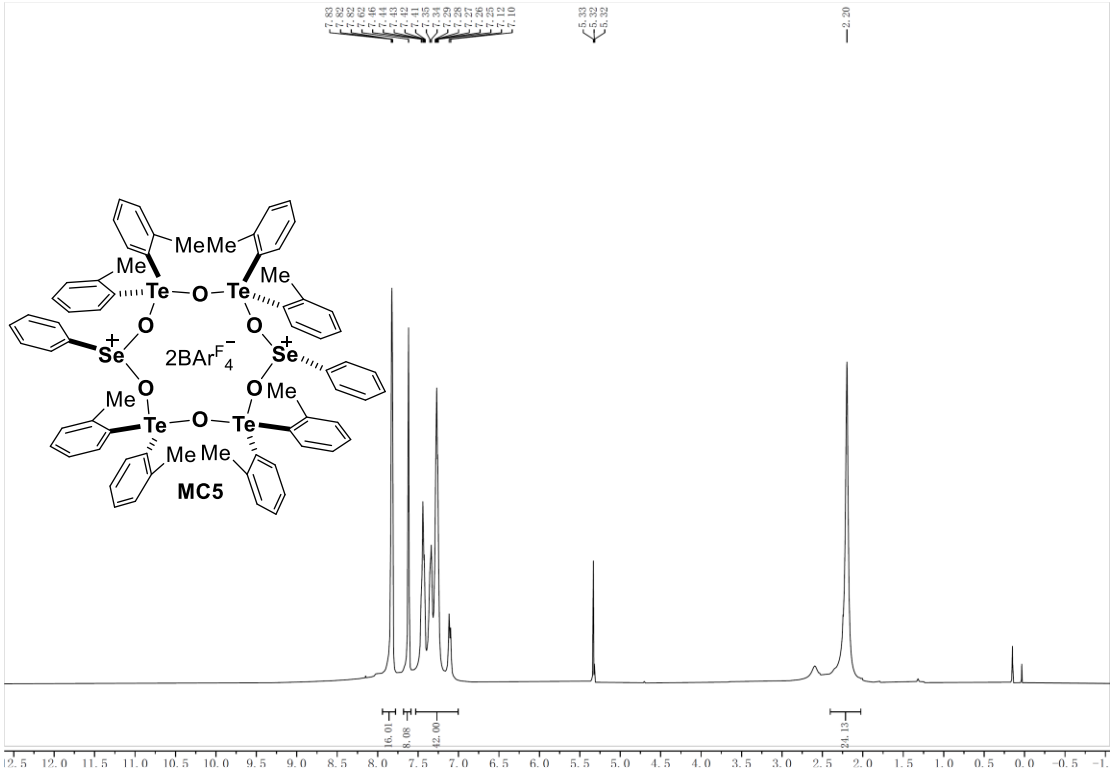
^{19}F NMR spectrum of compound **MC4** (CD_2Cl_2, 377 MHz)



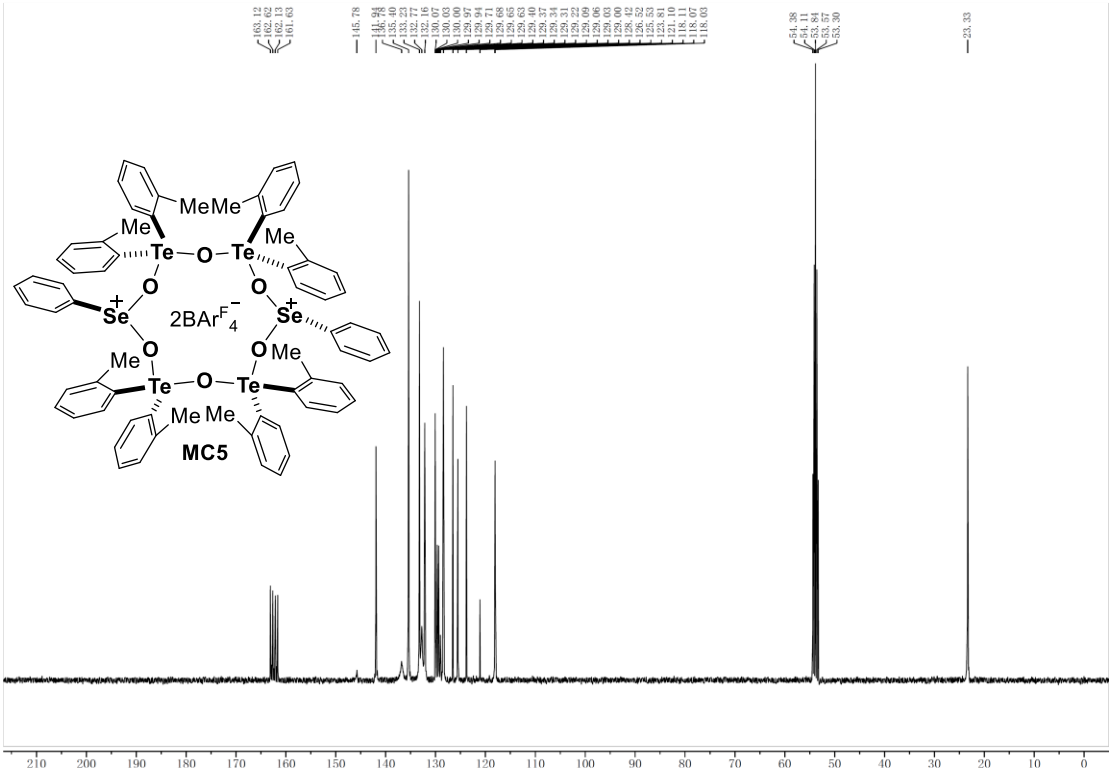
^{77}Se NMR spectrum of compound **MC4** (CD_2Cl_2, 76 MHz)



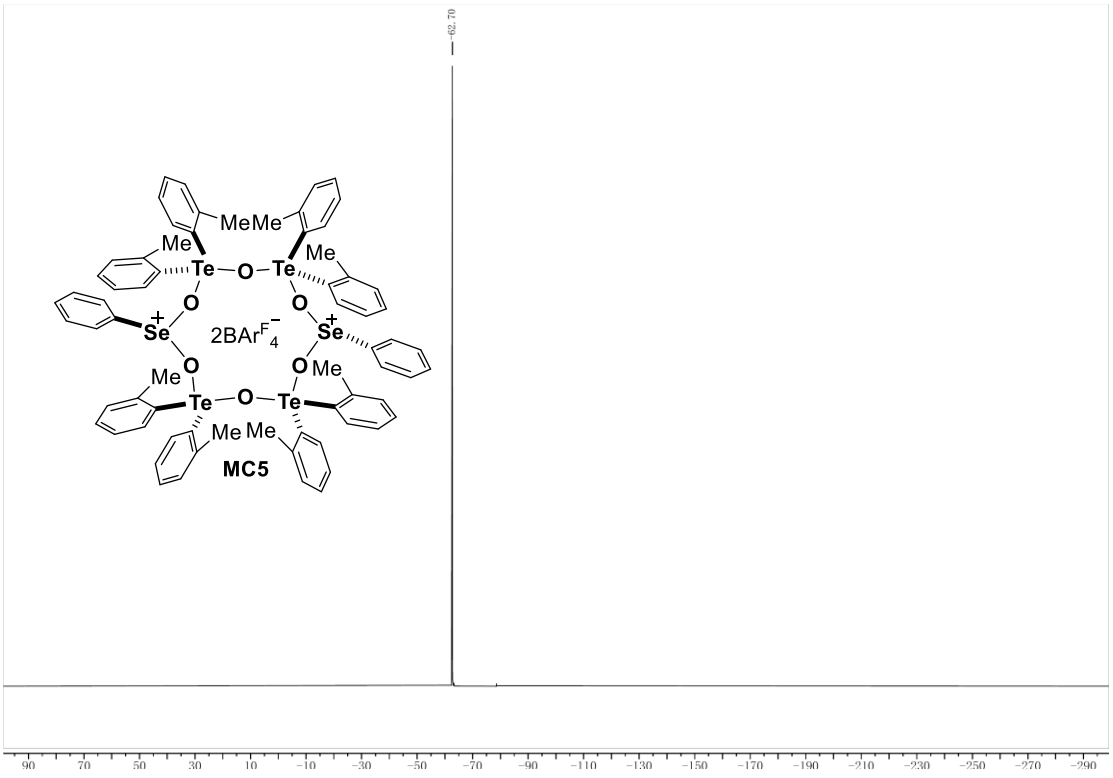
^{1}H NMR spectrum of compound **MC5** (CD_2Cl_2, 400 MHz)



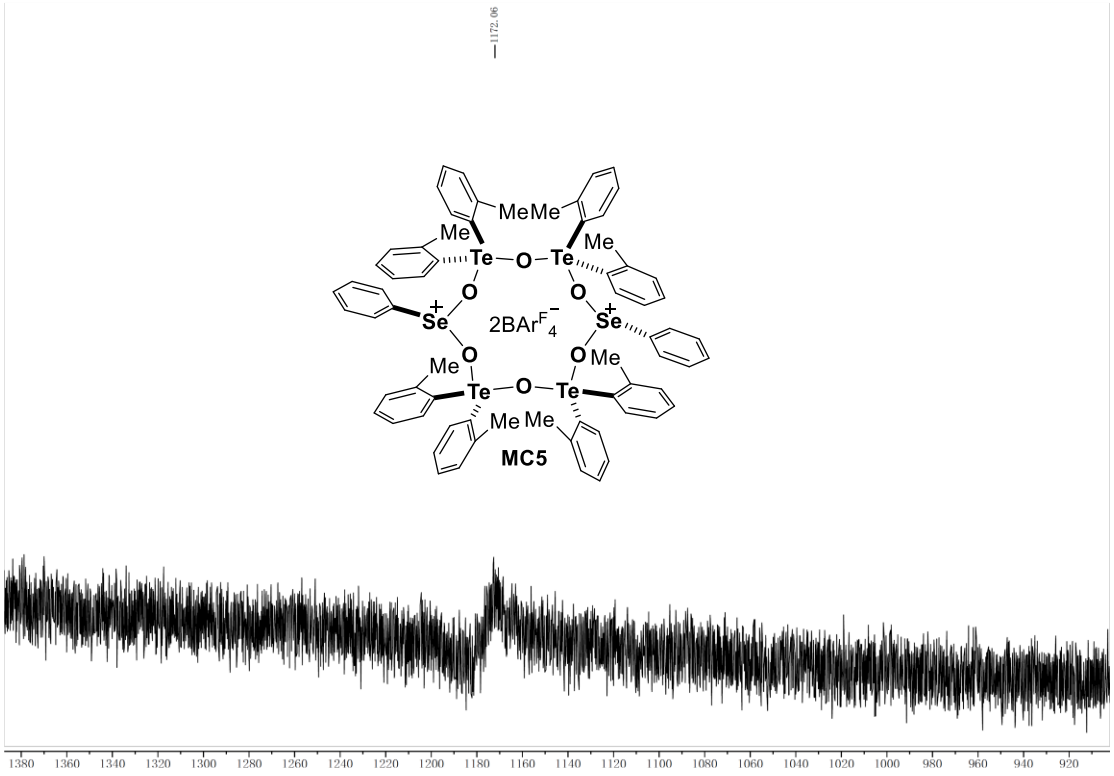
^{13}C NMR spectrum of compound **MC5** (CD_2Cl_2, 100 MHz)



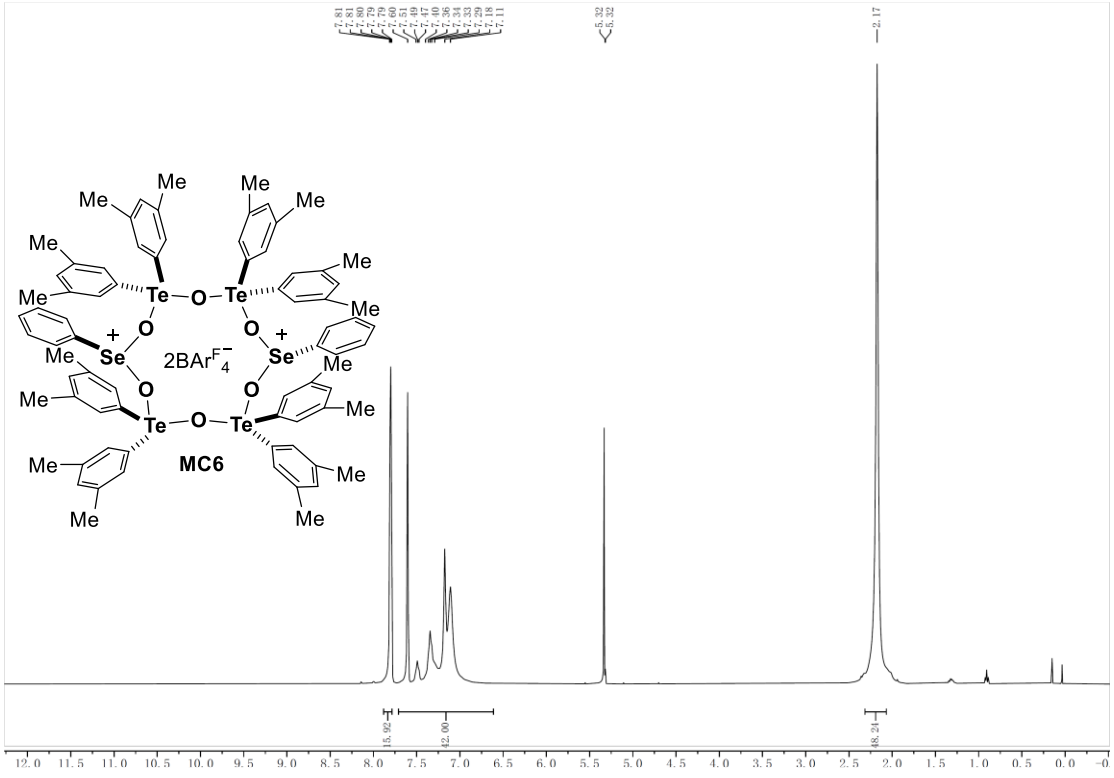
^{19}F NMR spectrum of compound **MC5** (CD_2Cl_2, 377 MHz)



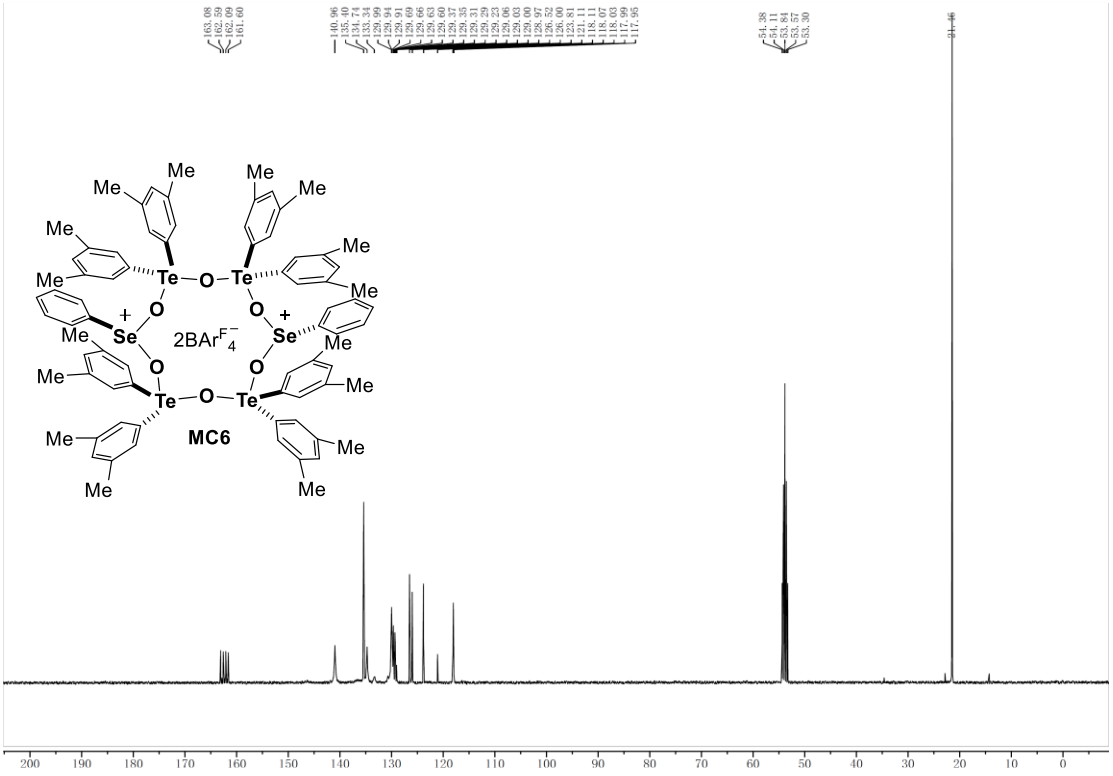
^{77}Se NMR spectrum of compound **MC5** (CD_2Cl_2, 76 MHz)



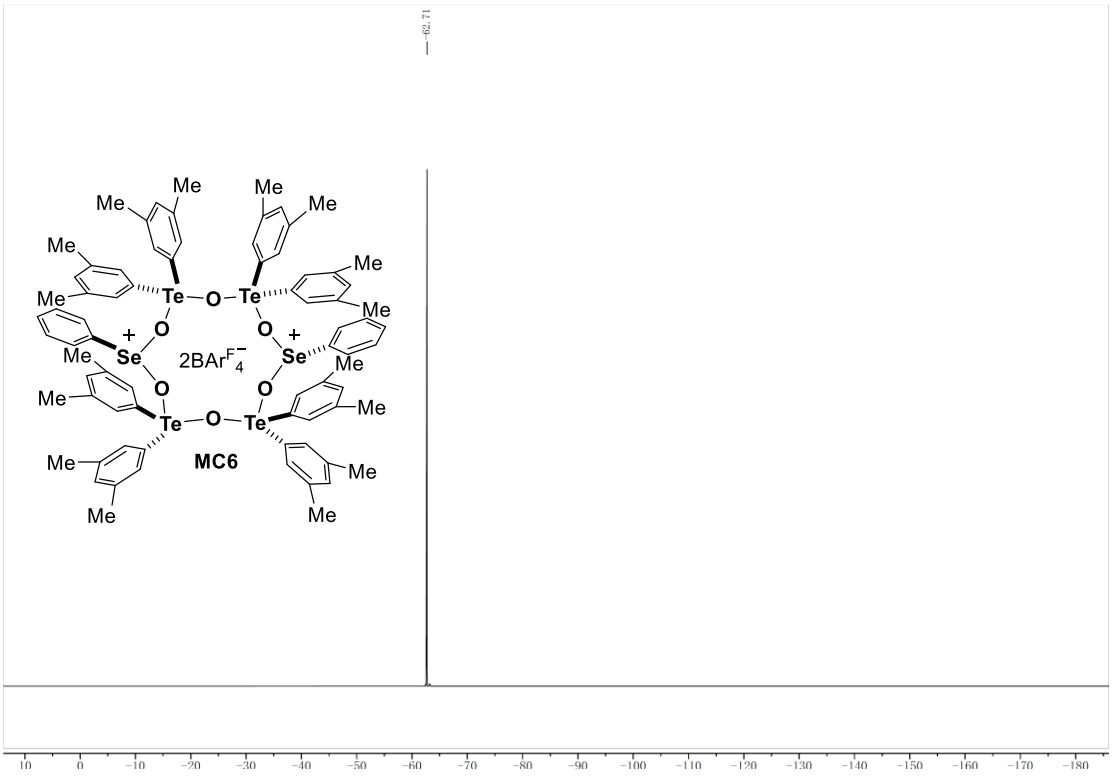
^{1}H NMR spectrum of compound **MC6** (CD_2Cl_2, 400 MHz)



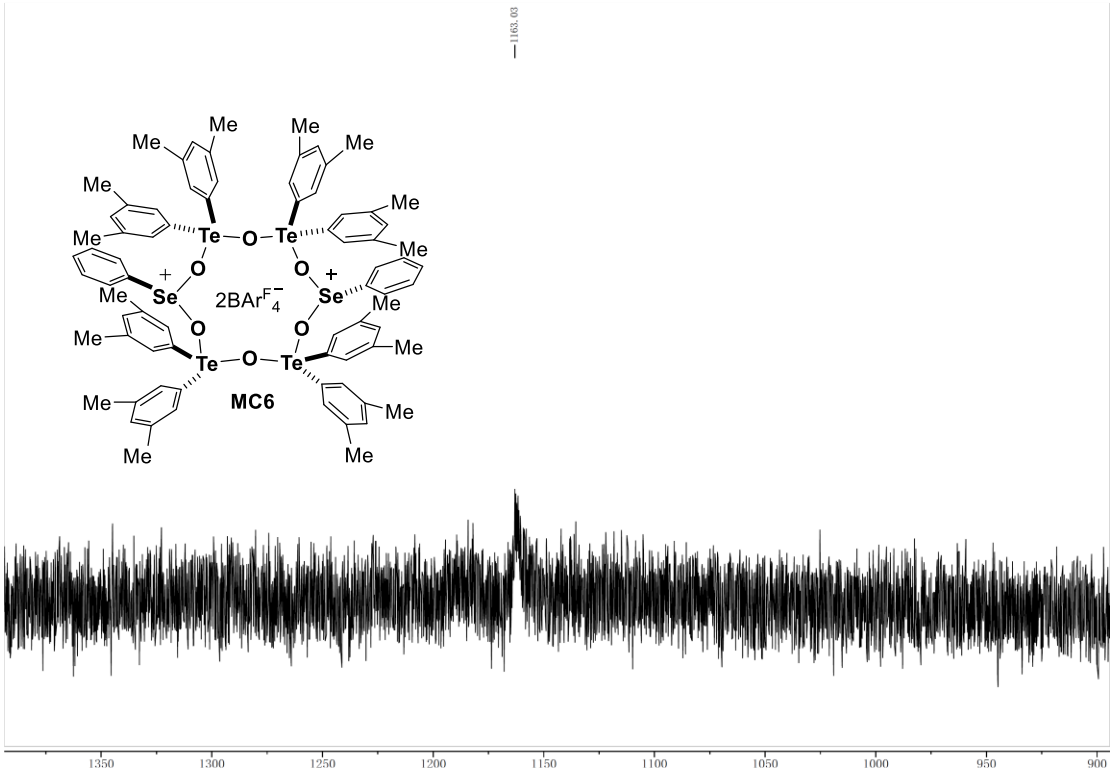
^{13}C NMR spectrum of compound **MC6** (CD_2Cl_2, 100 MHz)



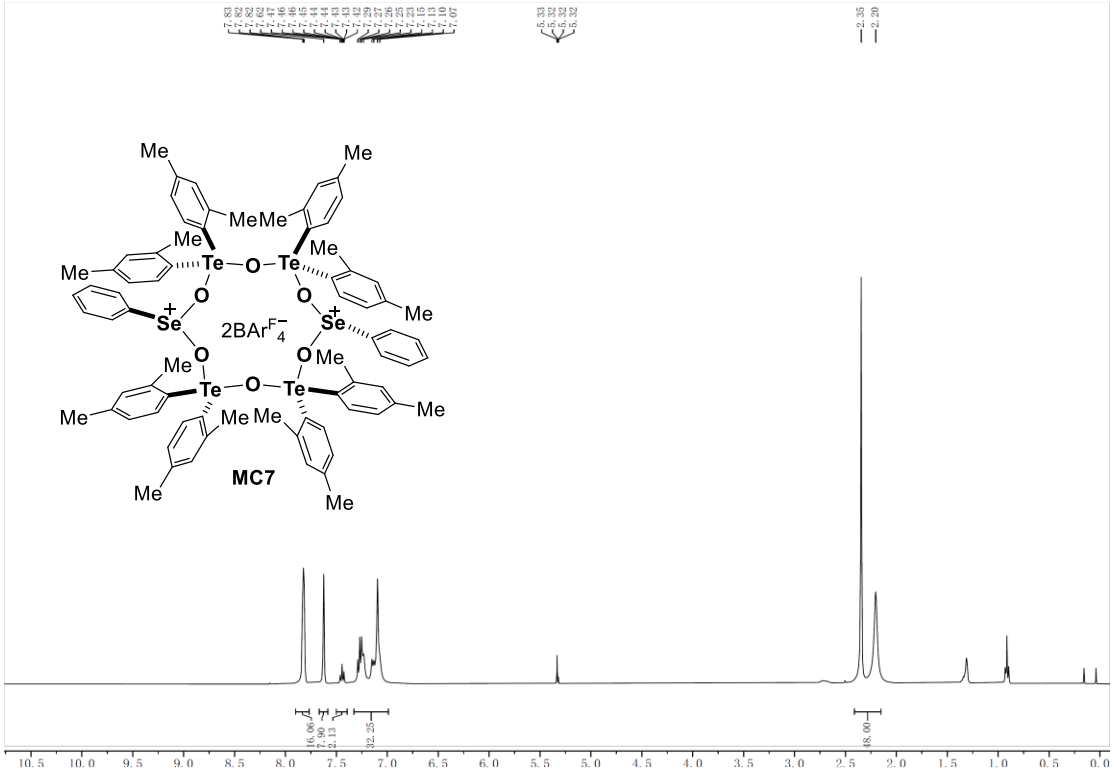
^{19}F NMR spectrum of compound **MC6** (CD_2Cl_2, 377 MHz)



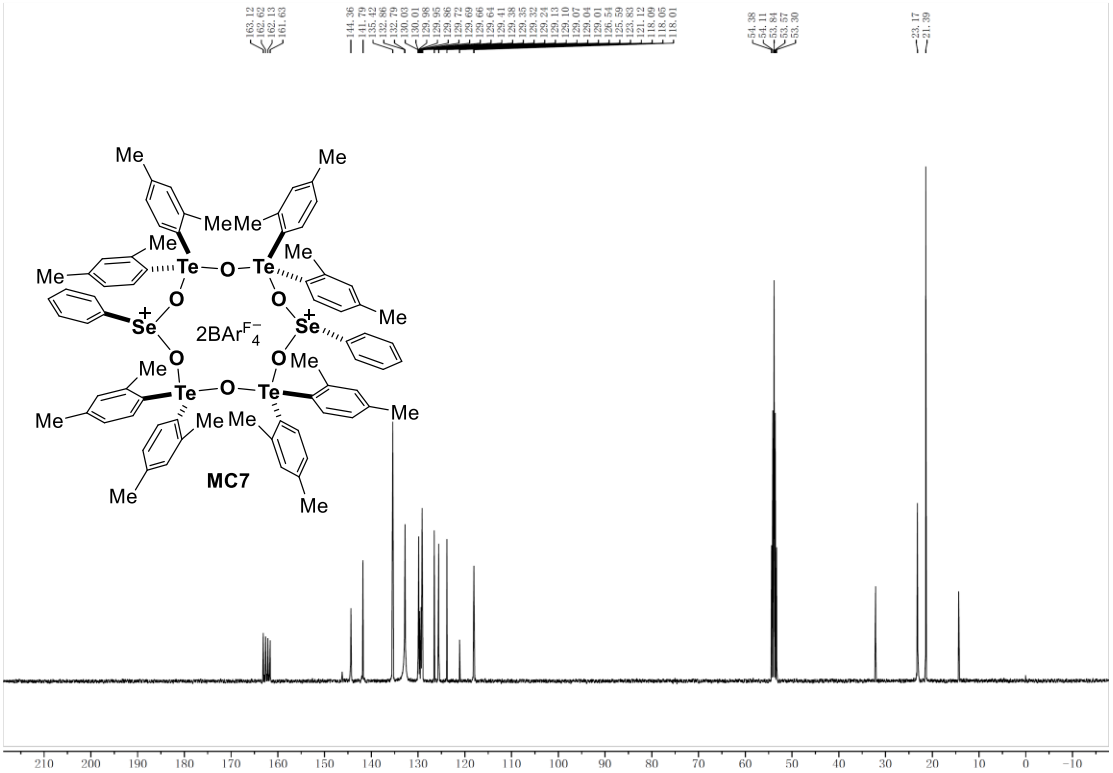
^{77}Se NMR spectrum of compound **MC6** (CD_2Cl_2, 76 MHz)



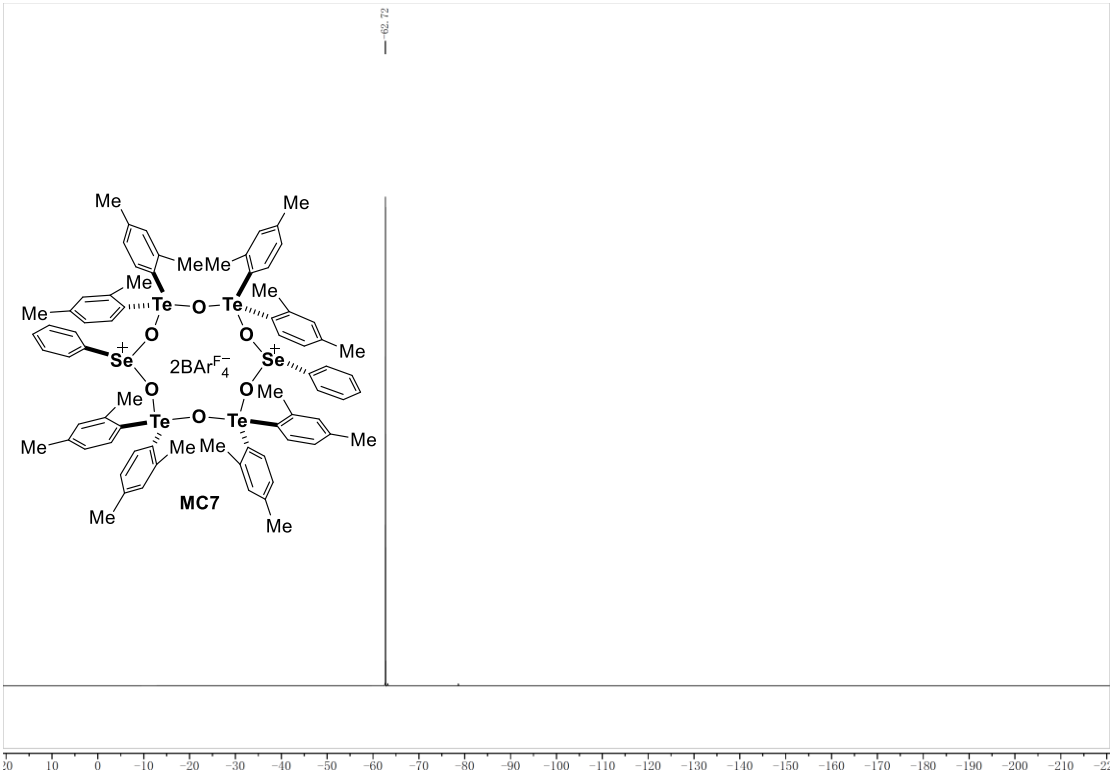
^{1}H NMR spectrum of compound **MC7** (CD_2Cl_2, 400 MHz)



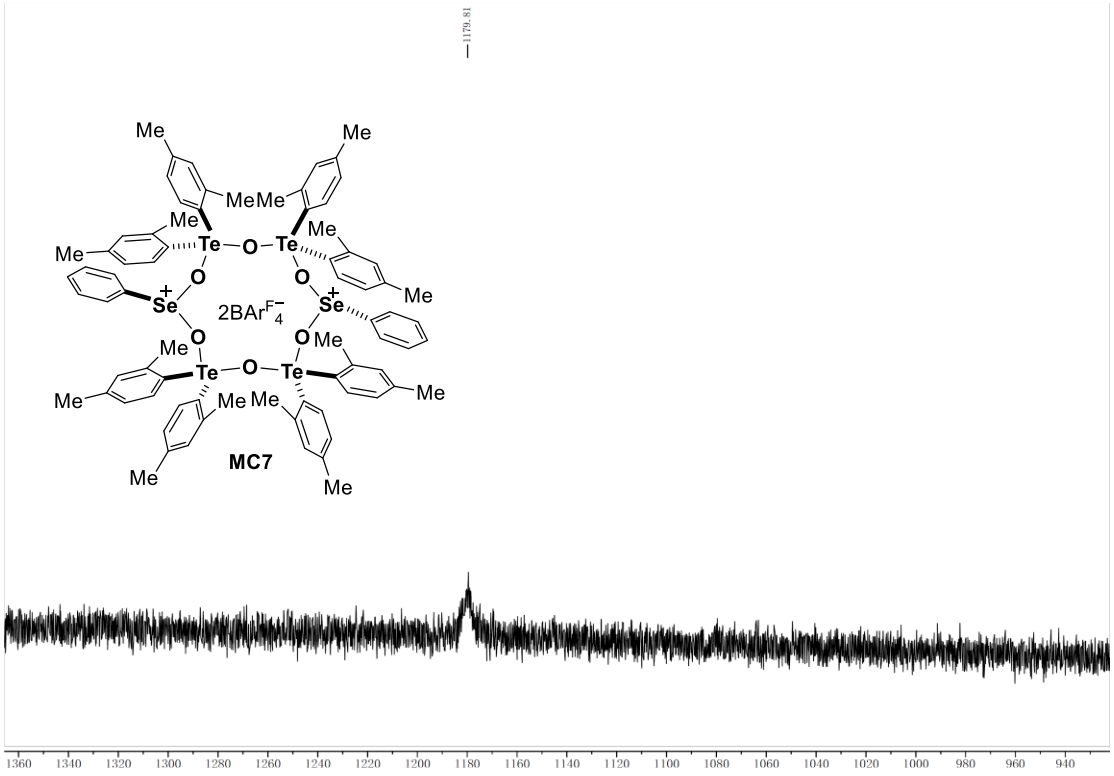
^{13}C NMR spectrum of compound **MC7** (CD_2Cl_2, 100 MHz)



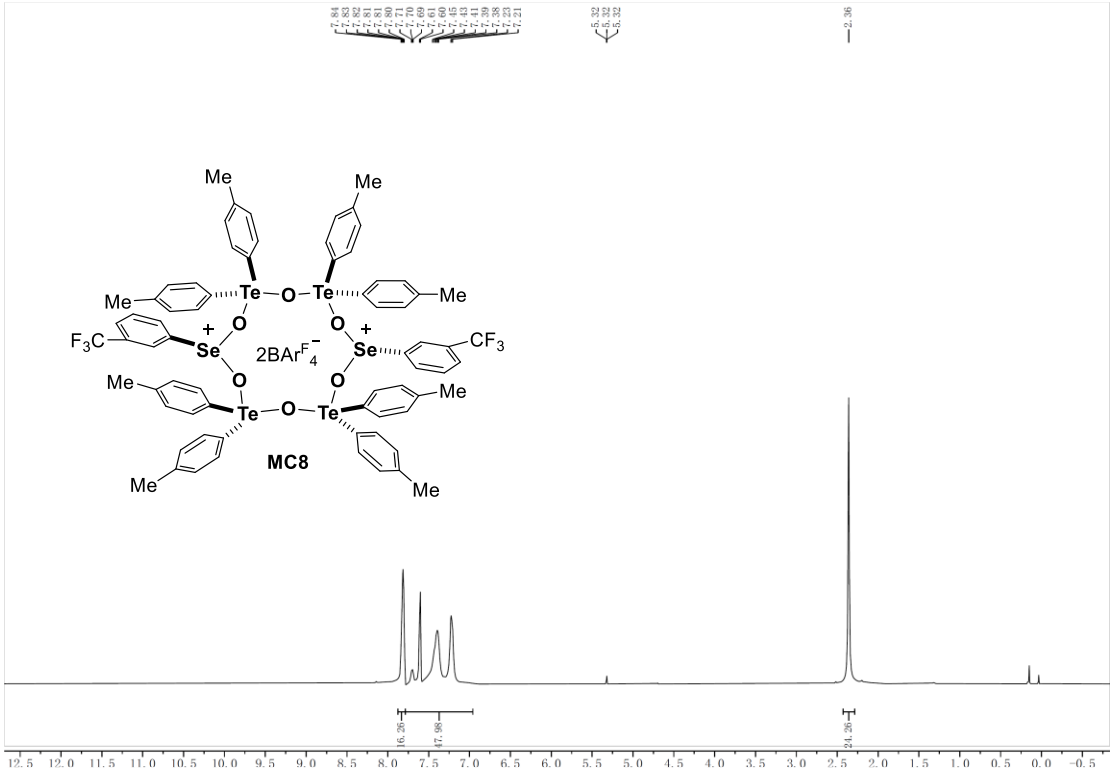
^{19}F NMR spectrum of compound **MC7** (CD_2Cl_2, 377 MHz)



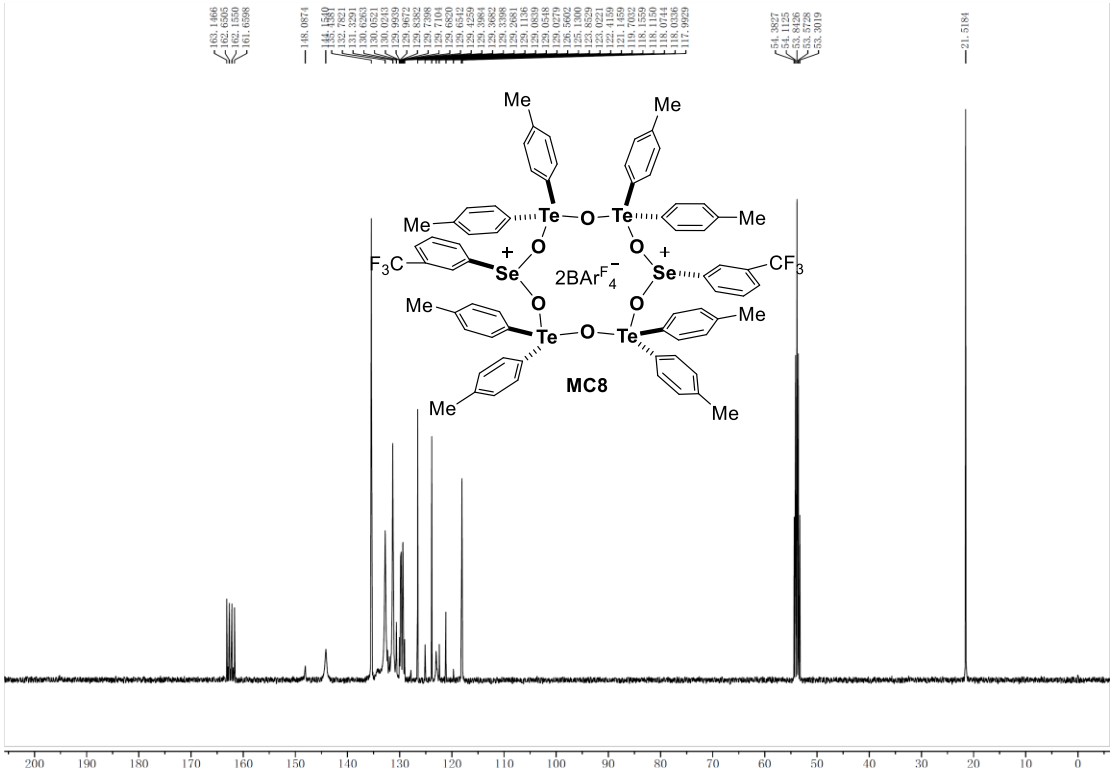
^{77}Se NMR spectrum of compound **MC7** (CD_2Cl_2, 76 MHz)



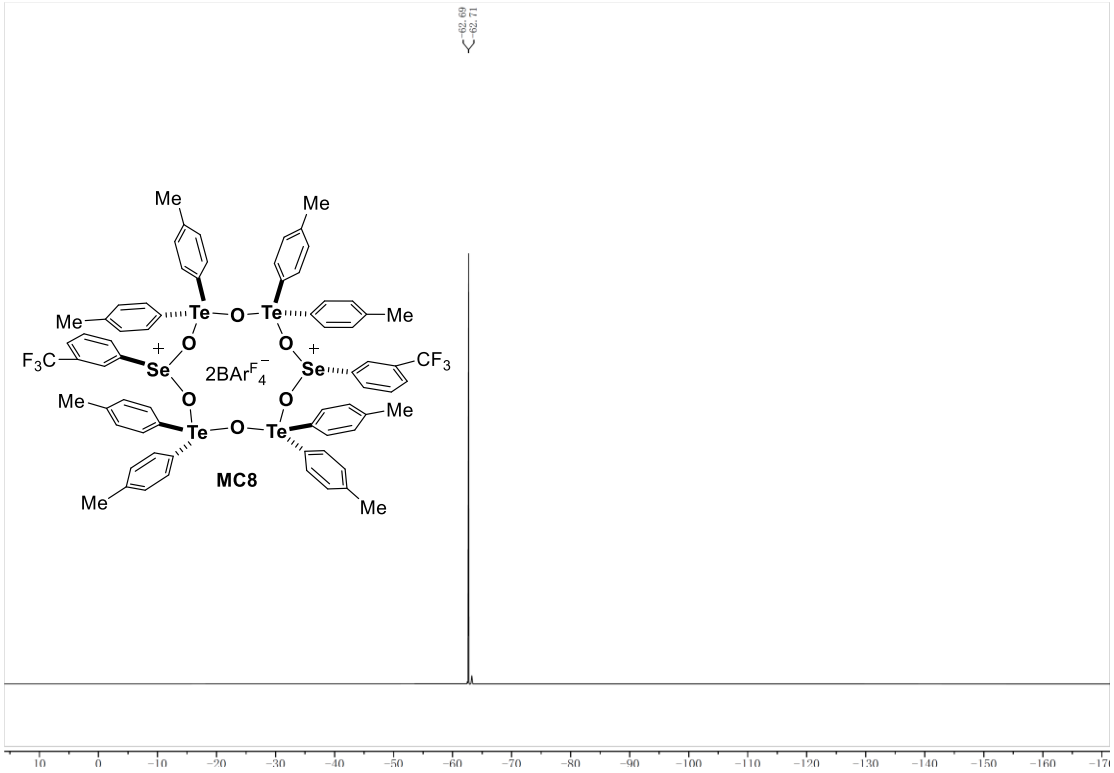
^{1}H NMR spectrum of compound **MC8** (CD_2Cl_2, 400 MHz)



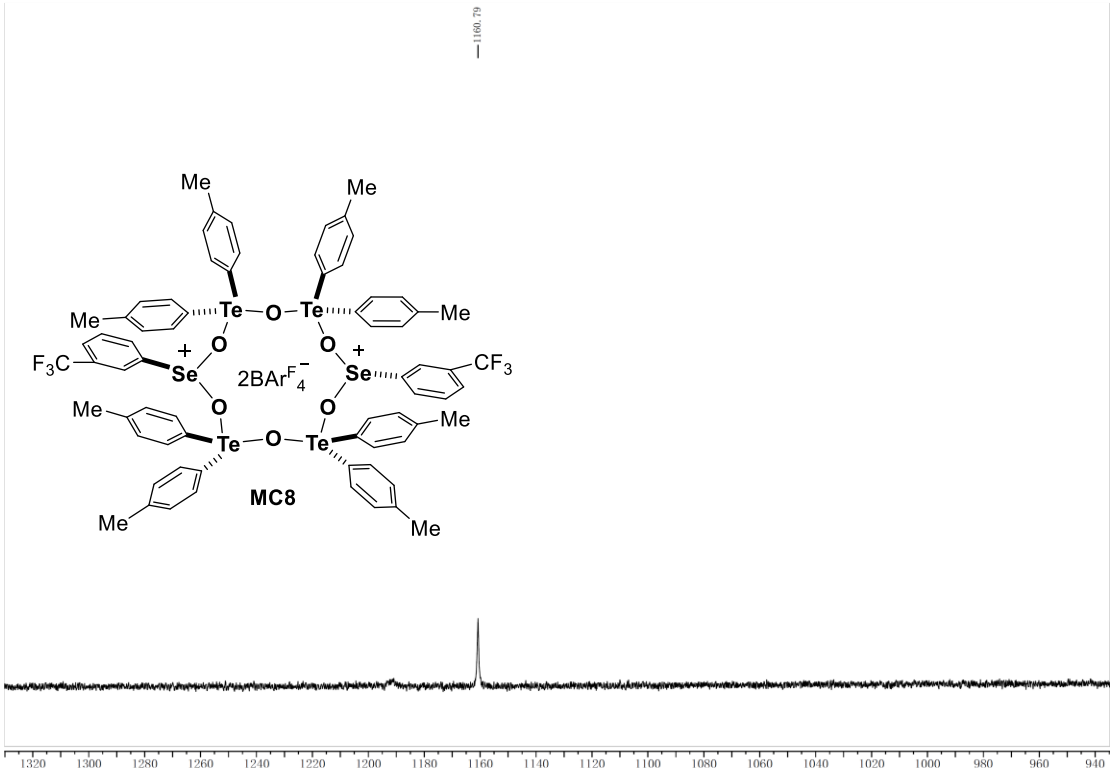
^{13}C NMR spectrum of compound **MC8** (CD_2Cl_2, 100 MHz)



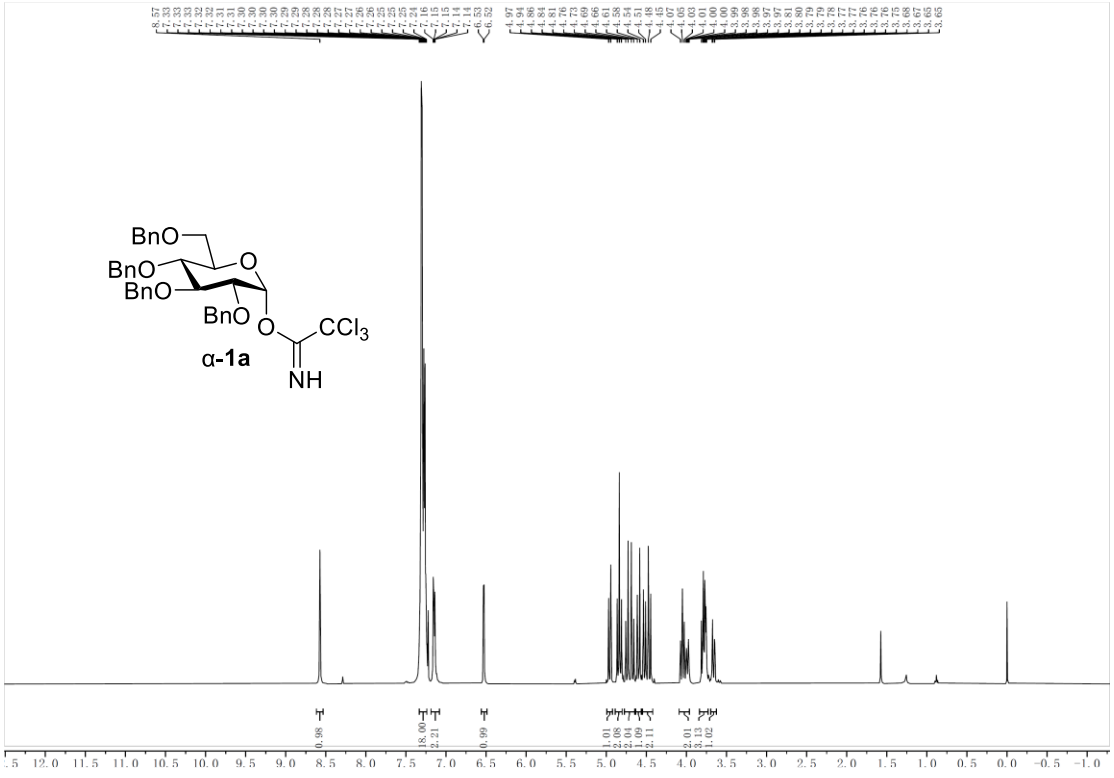
^{19}F NMR spectrum of compound **MC8** (CD_2Cl_2, 377 MHz)



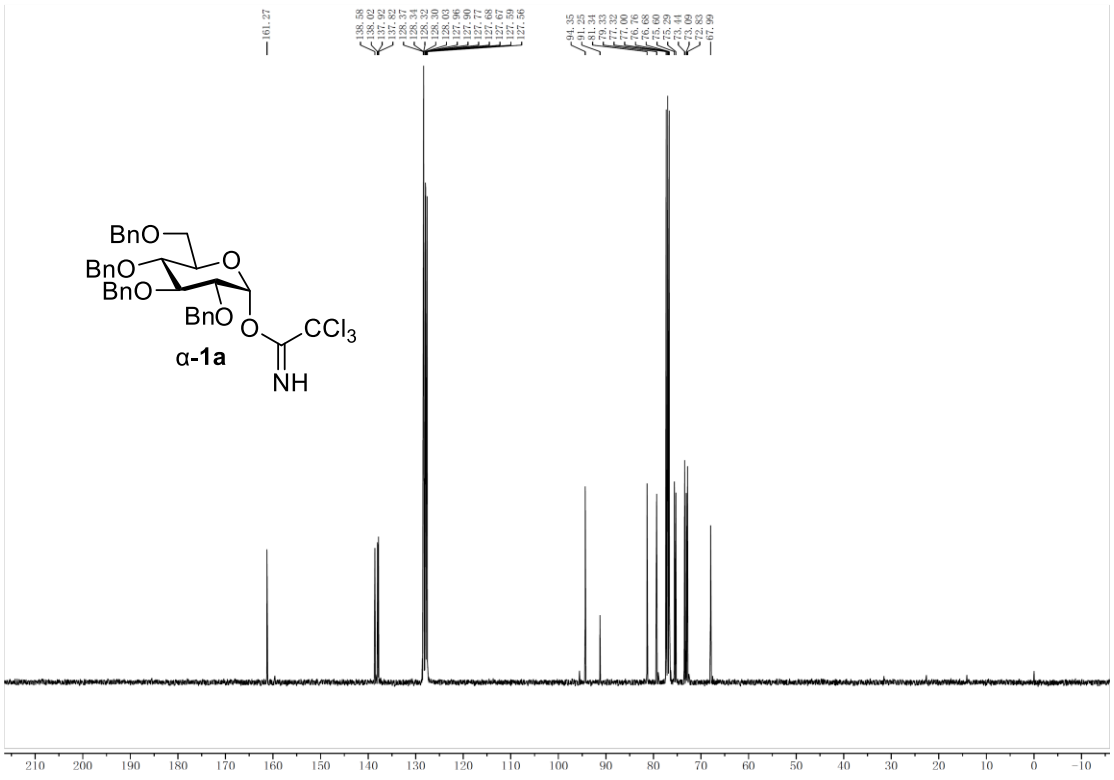
^{77}Se NMR spectrum of compound **MC8** (CD_2Cl_2, 76 MHz)



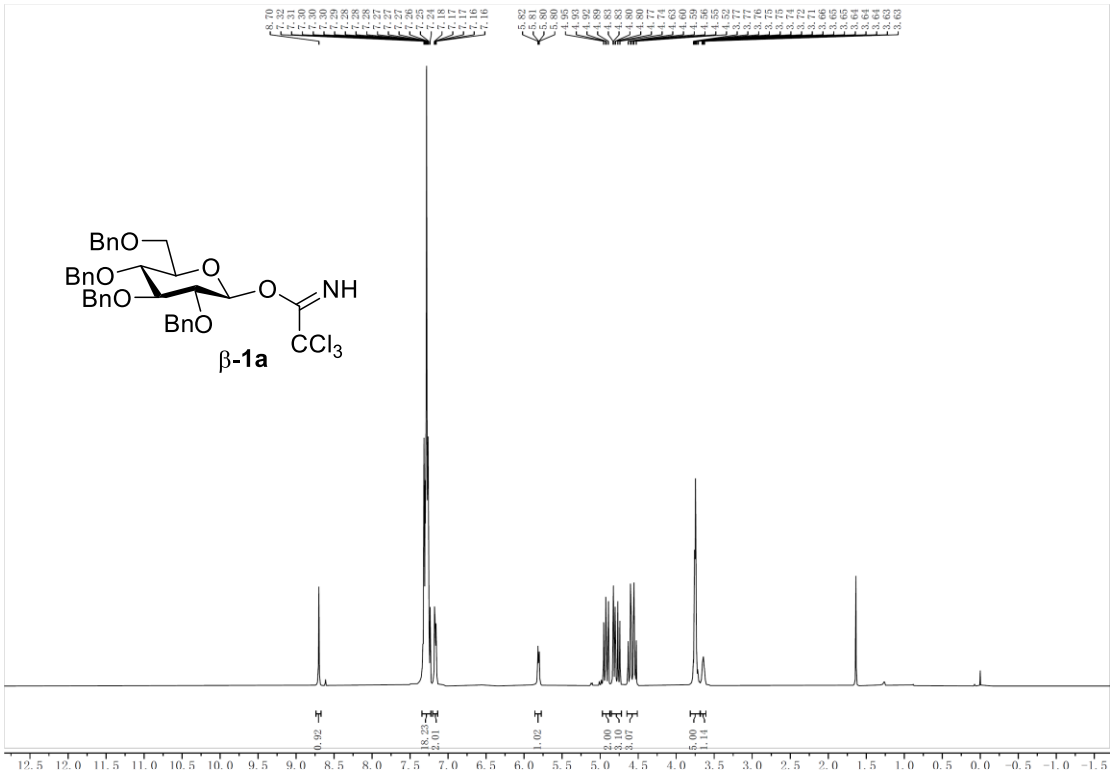
^{1}H NMR spectrum of compound α-**1a** ($CDCl_3$, 400 MHz)



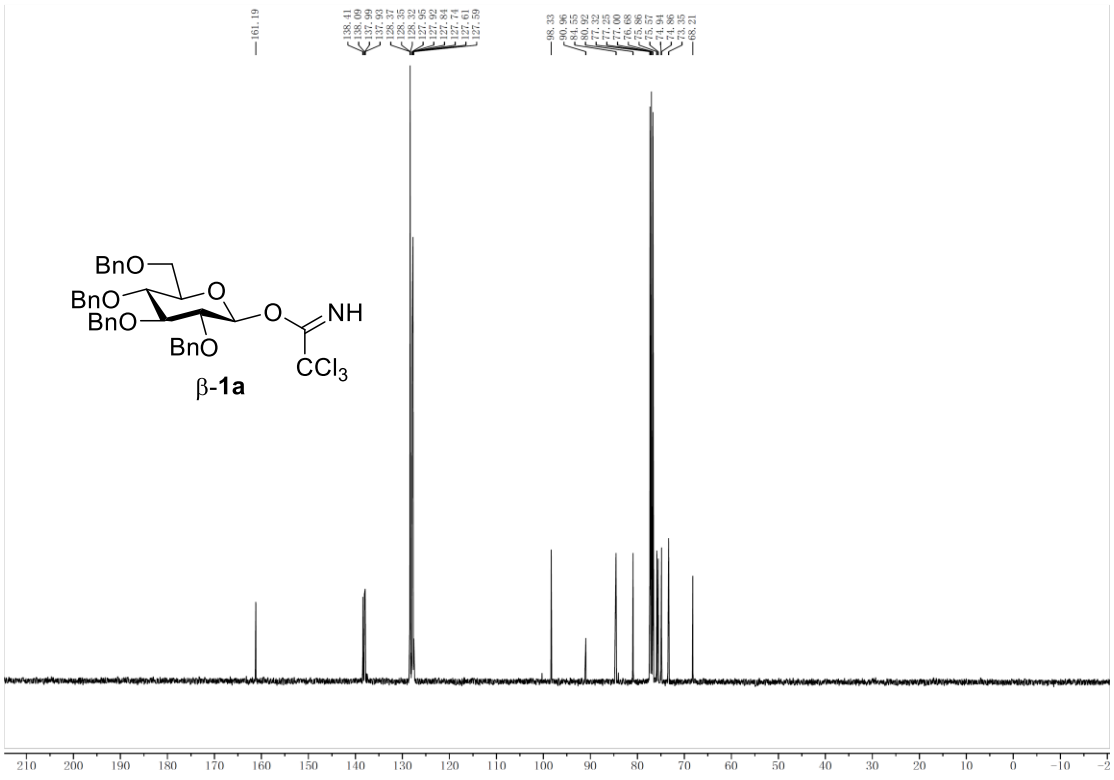
^{13}C NMR spectrum of compound α-**1a** ($CDCl_3$, 100 MHz)



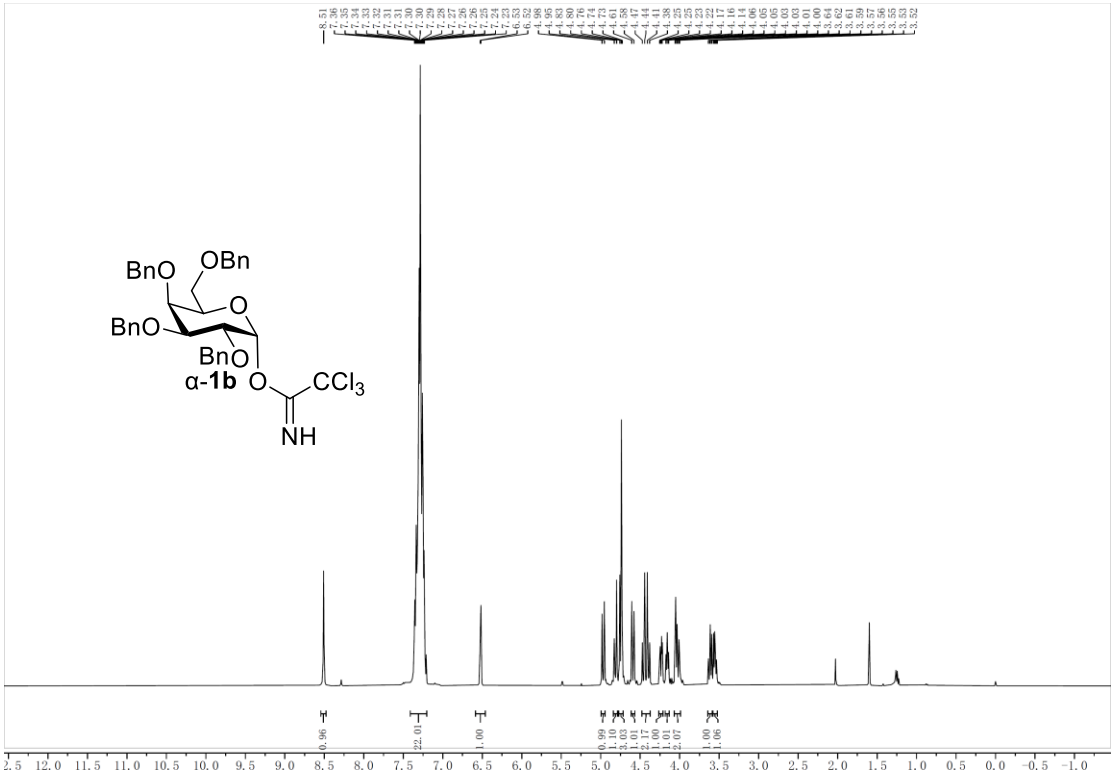
^{1}H NMR spectrum of compound β-**1a** ($CDCl_3$, 400 MHz)



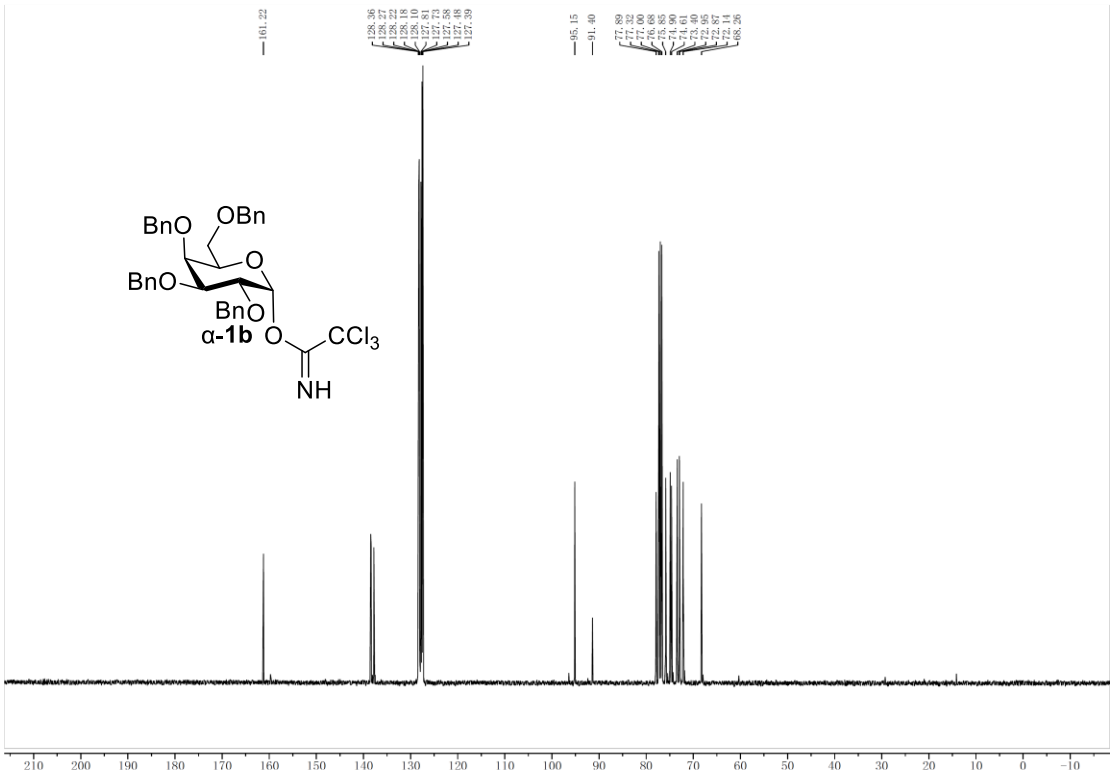
^{13}C NMR spectrum of compound β-**1a** ($CDCl_3$, 100 MHz)



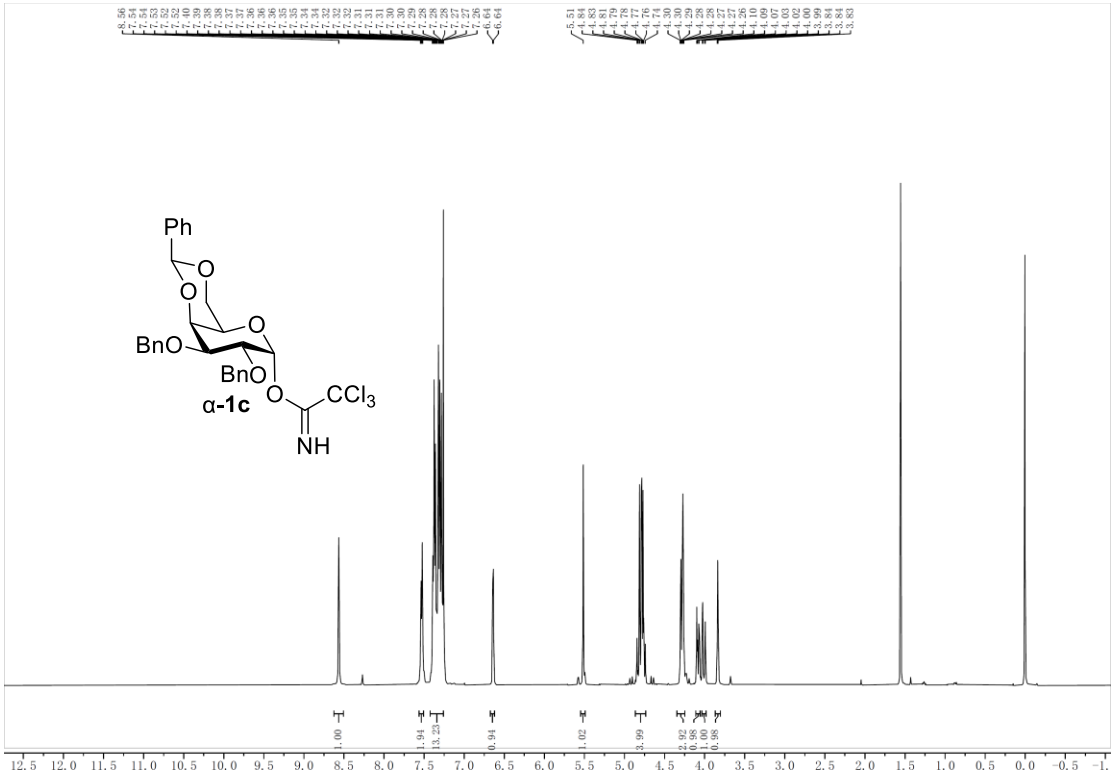
^{1}H NMR spectrum of compound α-**1b** ($CDCl_3$, 400 MHz)



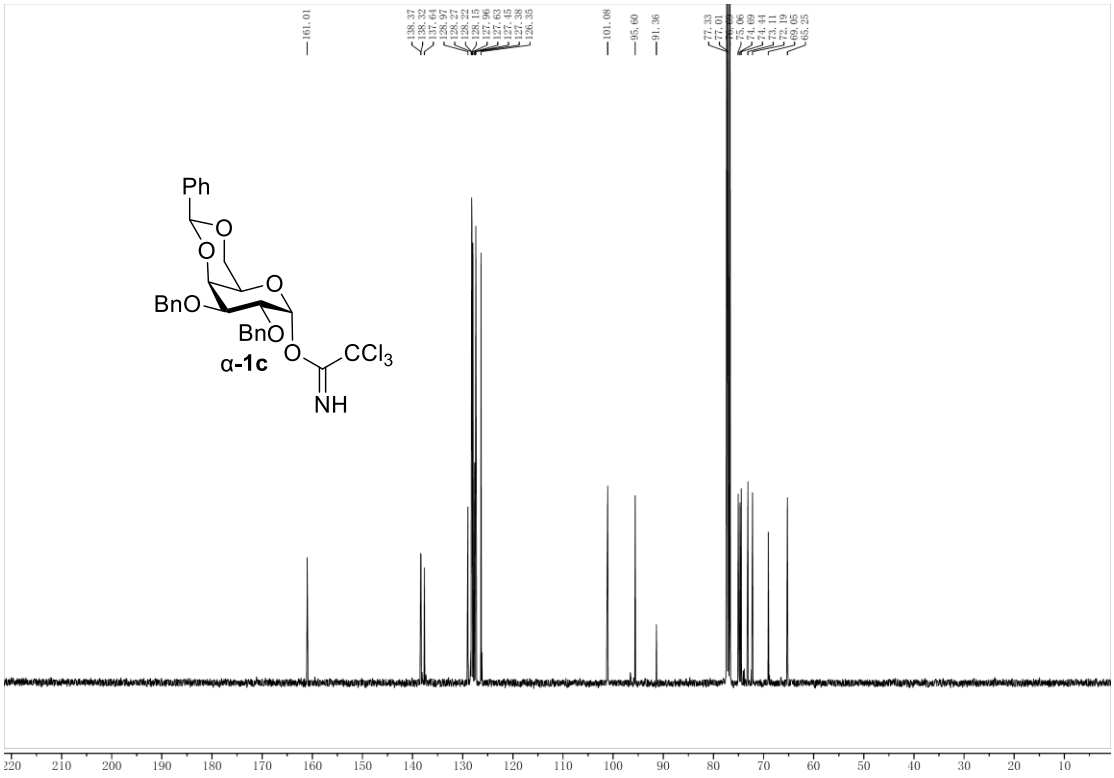
^{13}C NMR spectrum of compound α-**1b** ($CDCl_3$, 100 MHz)



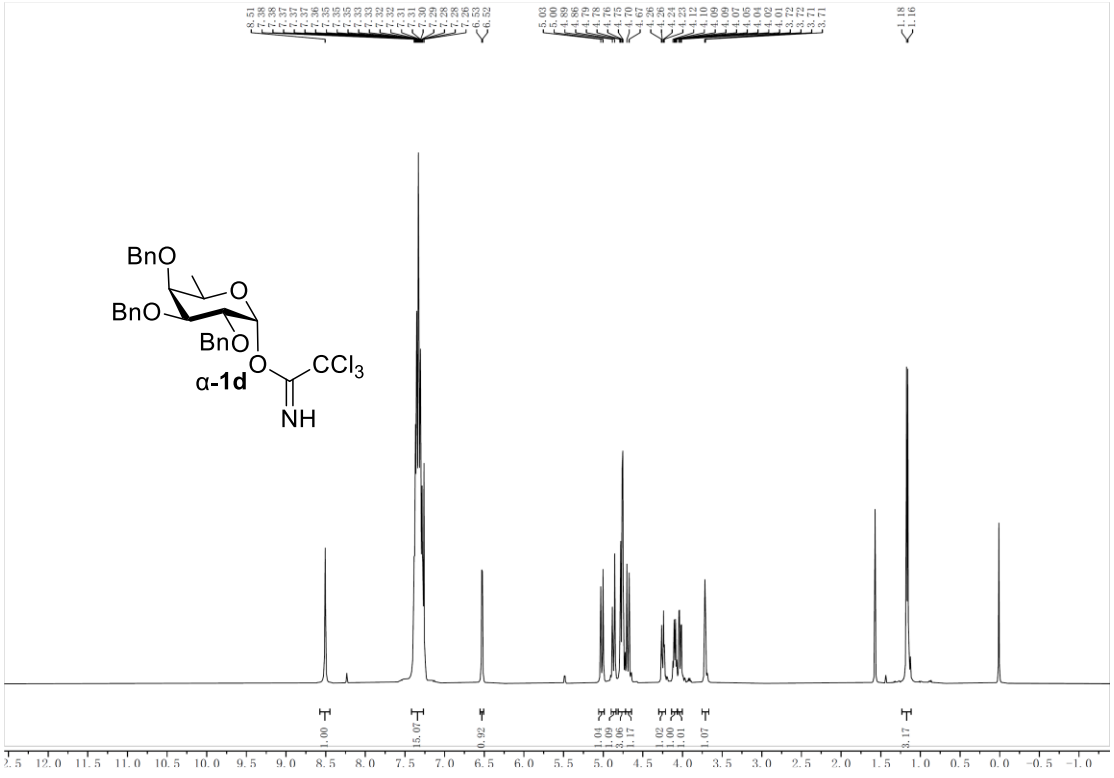
^{1}H NMR spectrum of compound α-**1c** ($CDCl_3$, 400 MHz)



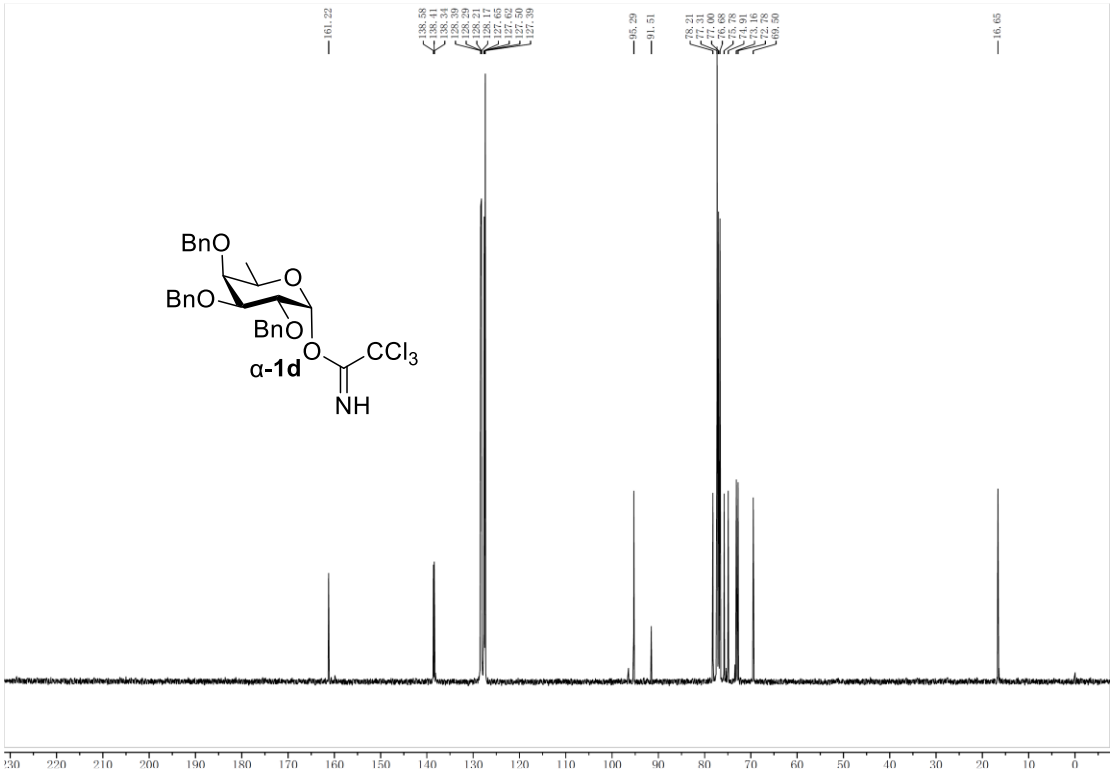
^{13}C NMR spectrum of compound α-**1c** ($CDCl_3$, 100 MHz)



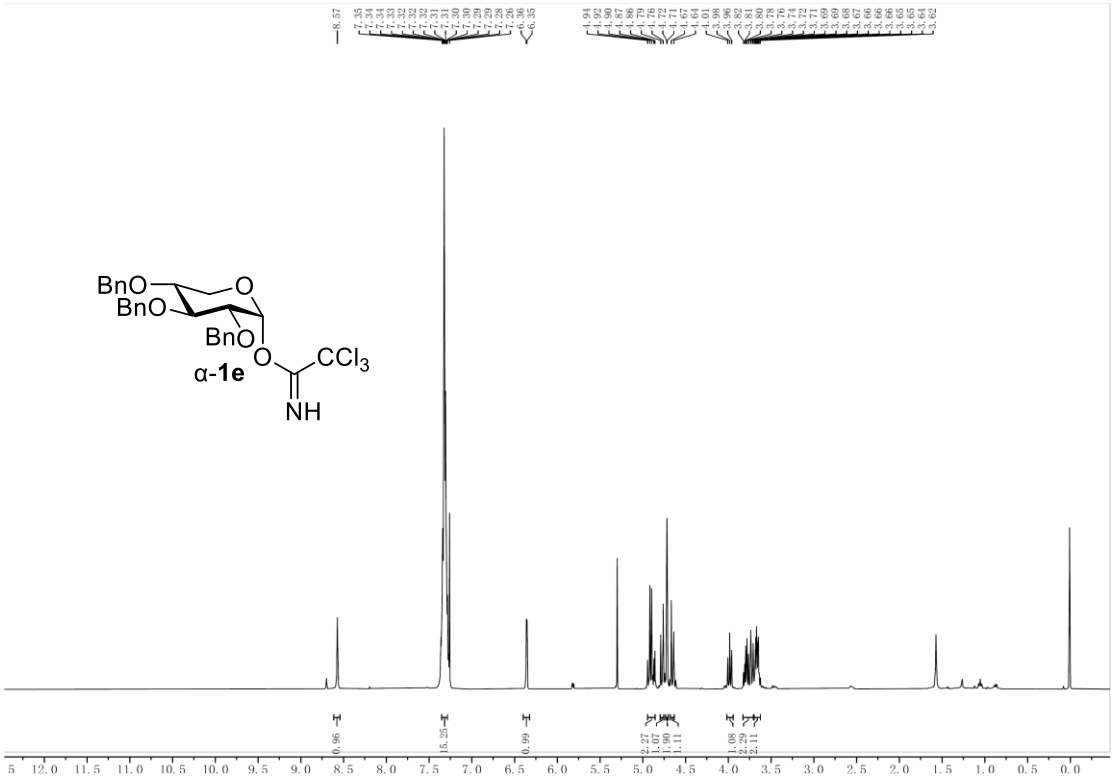
^{1}H NMR spectrum of compound α-**1d** ($CDCl_3$, 400 MHz)



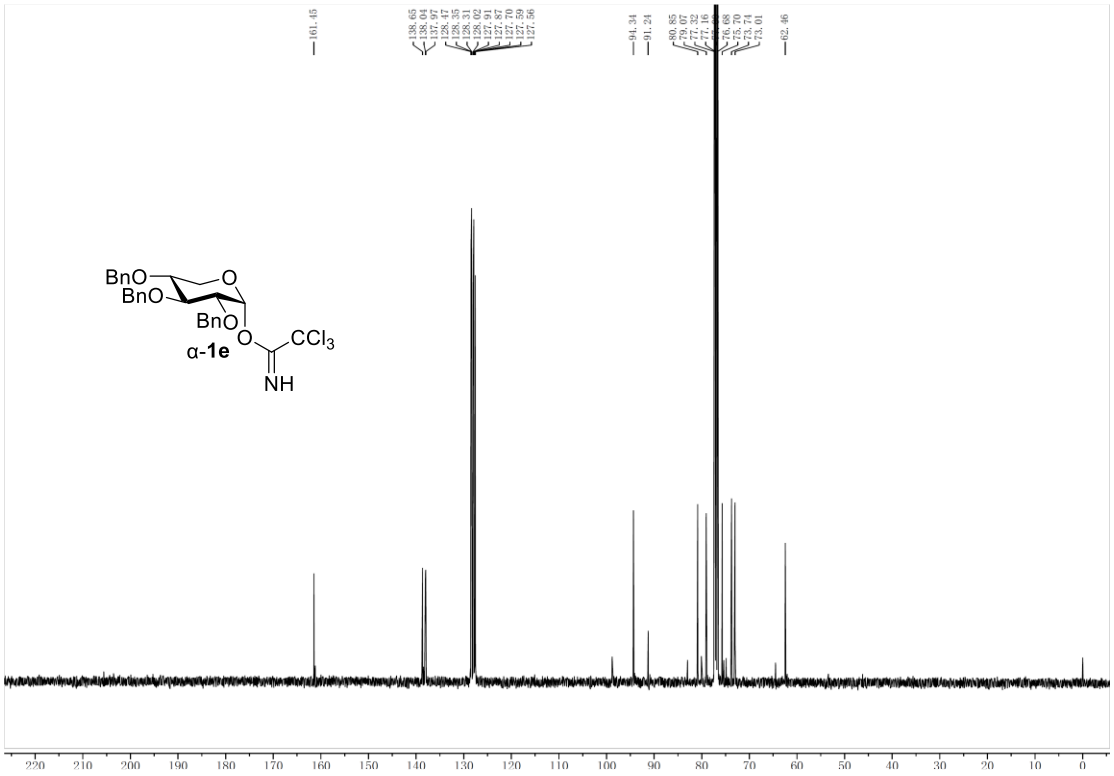
^{13}C NMR spectrum of compound α-**1d** ($CDCl_3$, 100 MHz)



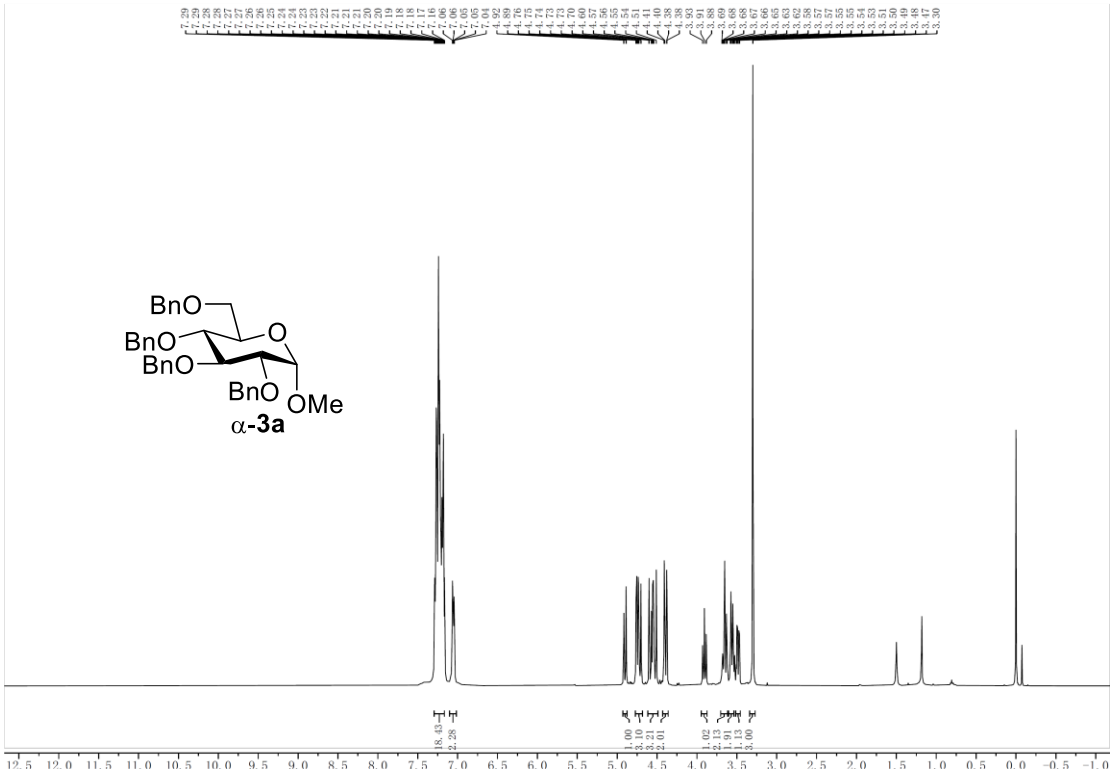
^{1}H NMR spectrum of compound α-**1e** ($CDCl_3$, 400 MHz)



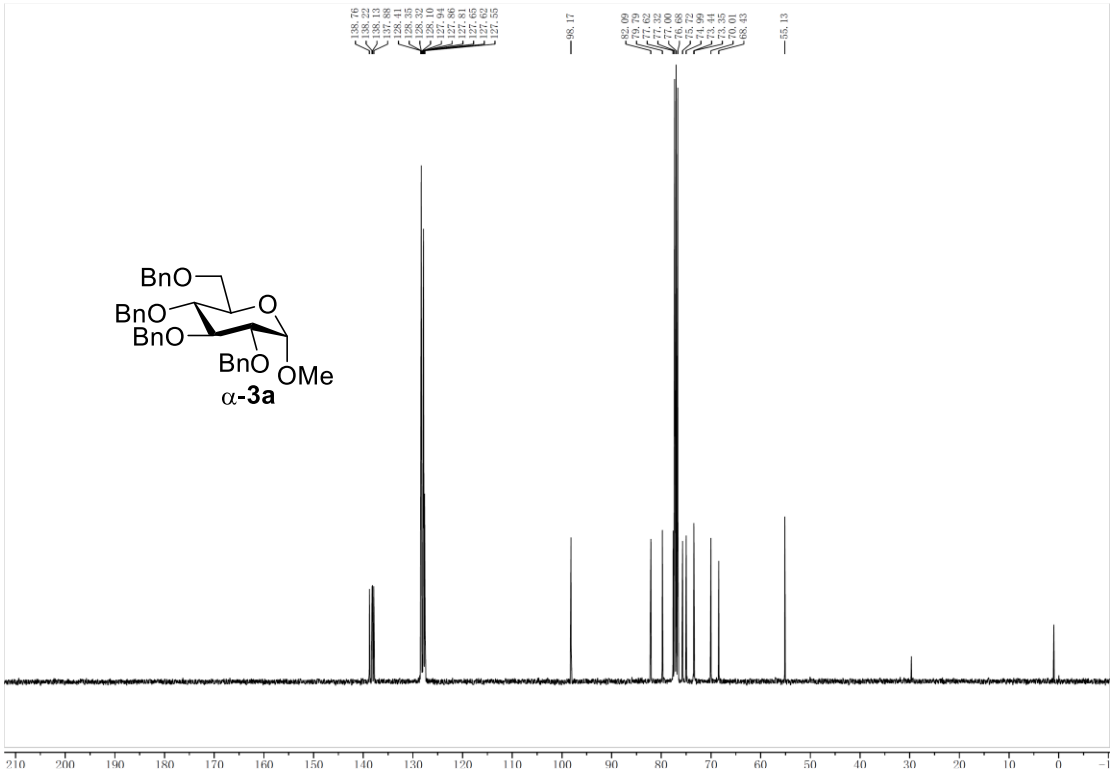
^{13}C NMR spectrum of compound α-**1e** ($CDCl_3$, 100 MHz)



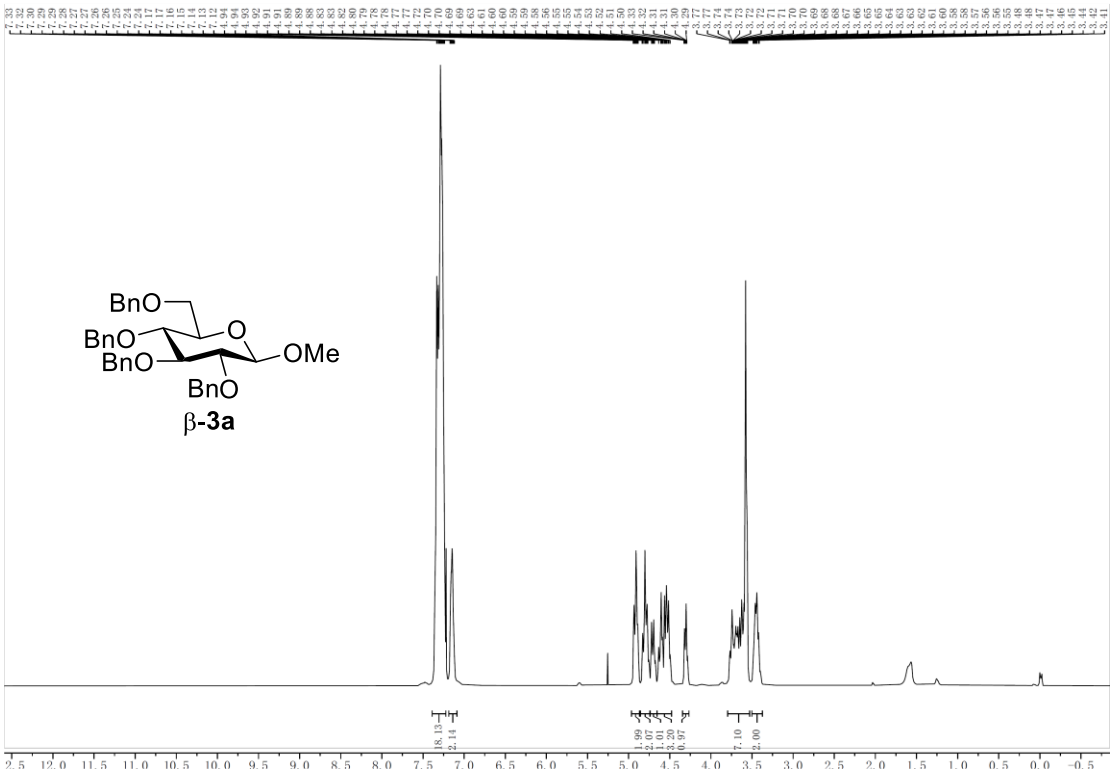
^{1}H NMR spectrum of compound α-**3a** ($CDCl_3$, 400 MHz)



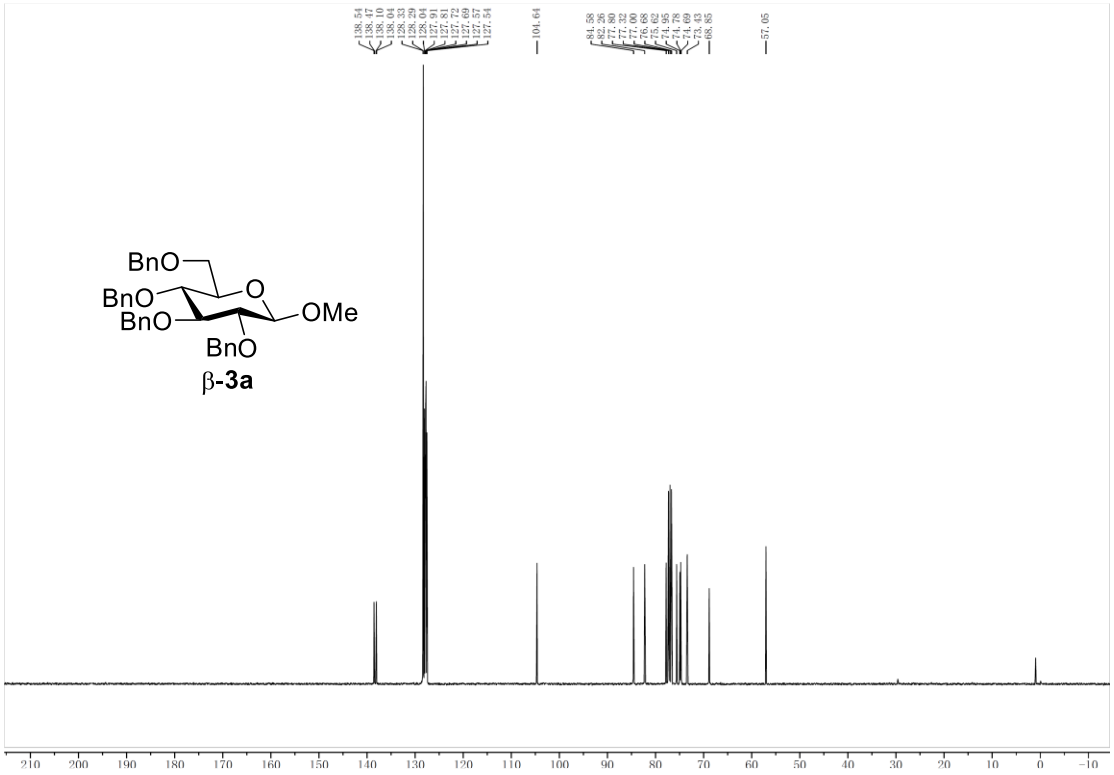
^{13}C NMR spectrum of compound α-**3a** ($CDCl_3$, 100 MHz)



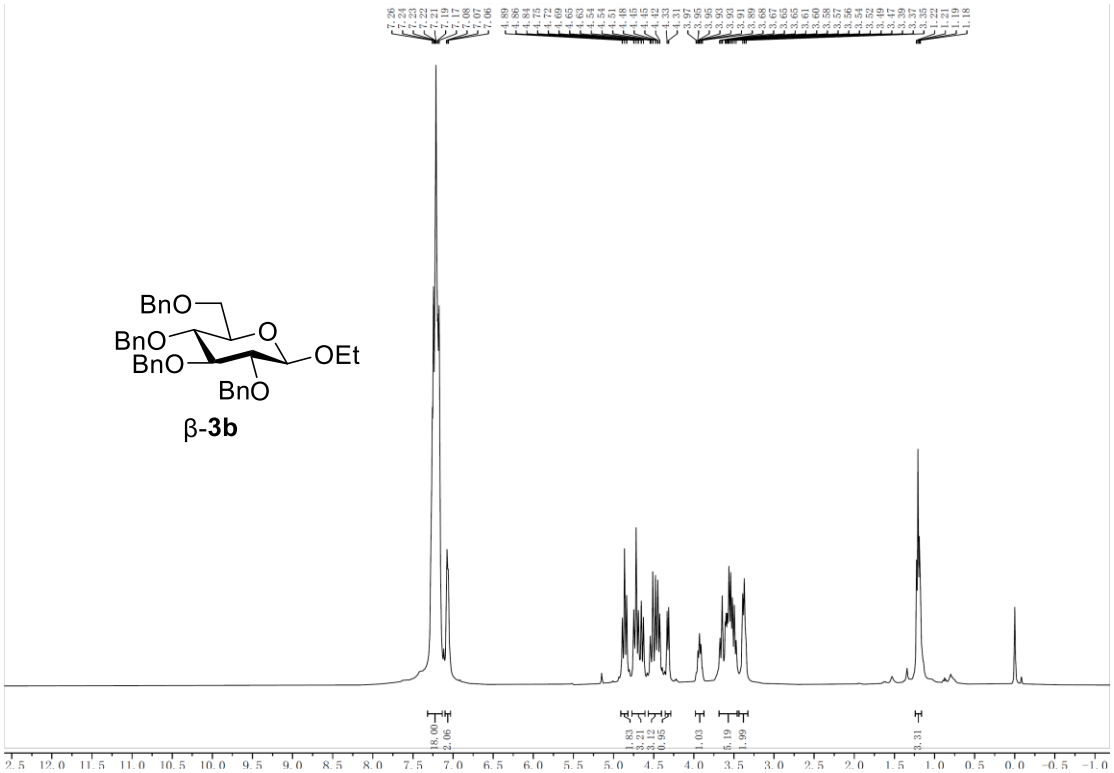
^{1}H NMR spectrum of compound β-**3a** ($CDCl_3$, 400 MHz)



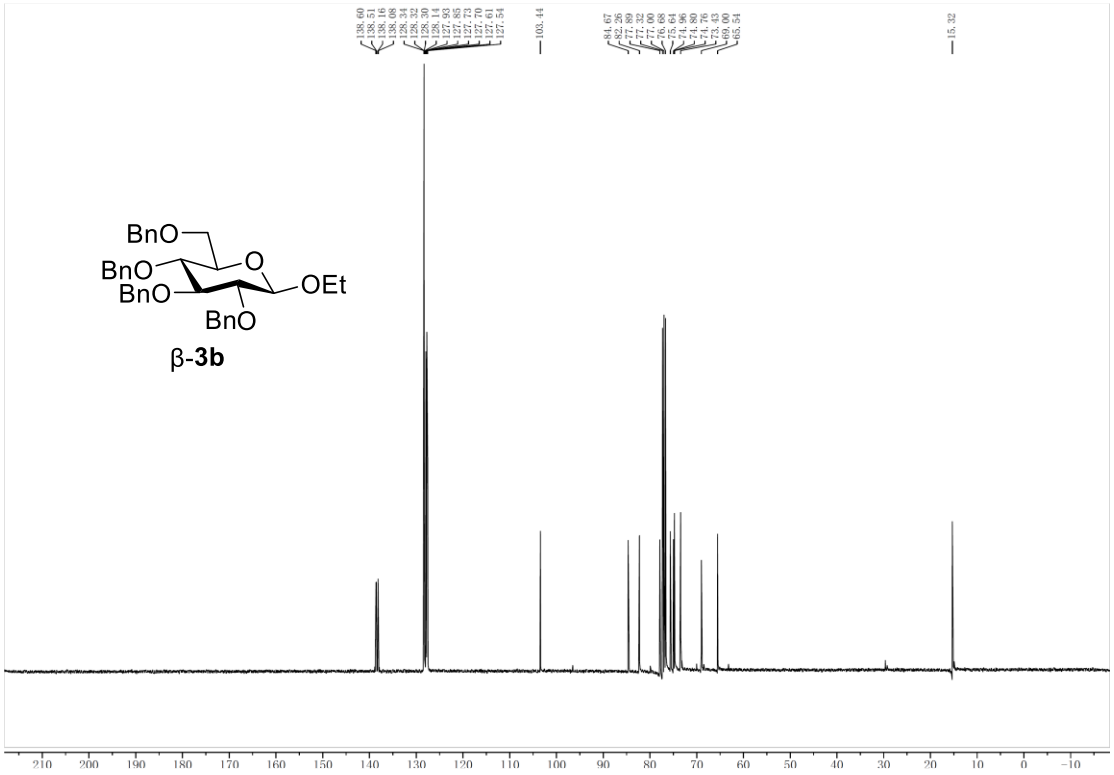
^{13}C NMR spectrum of compound β-**3a** ($CDCl_3$, 100 MHz)



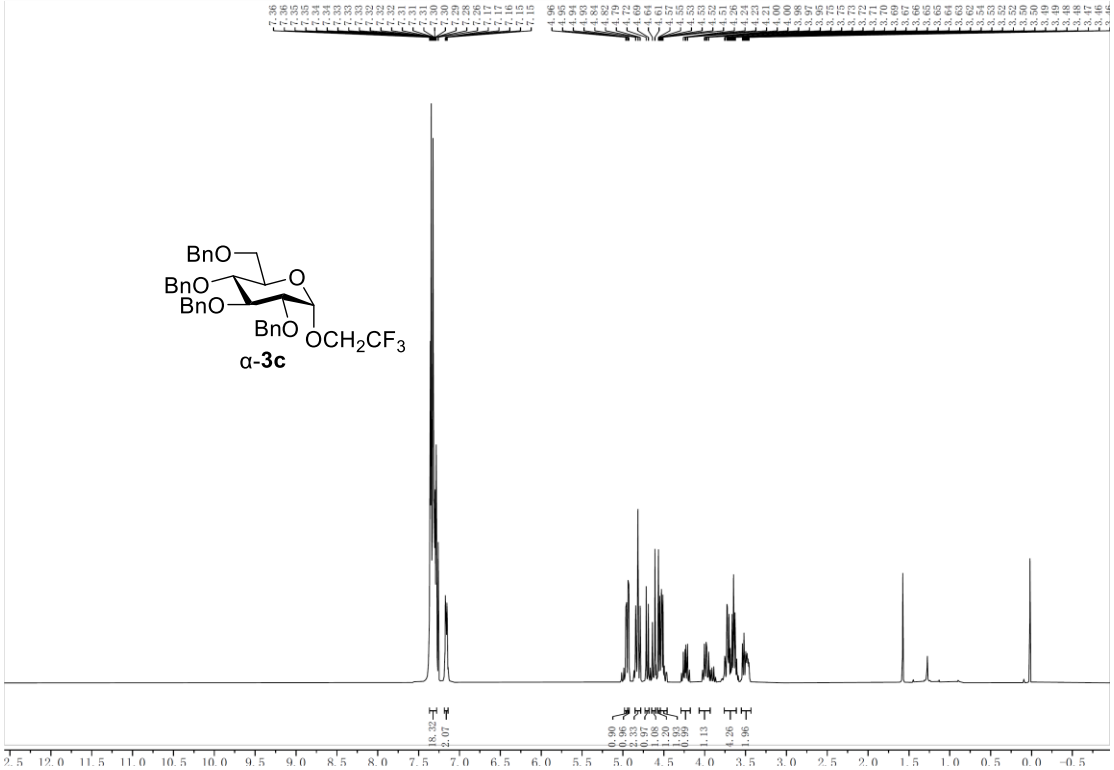
^{1}H NMR spectrum of compound β-**3b** ($CDCl_3$, 400 MHz)



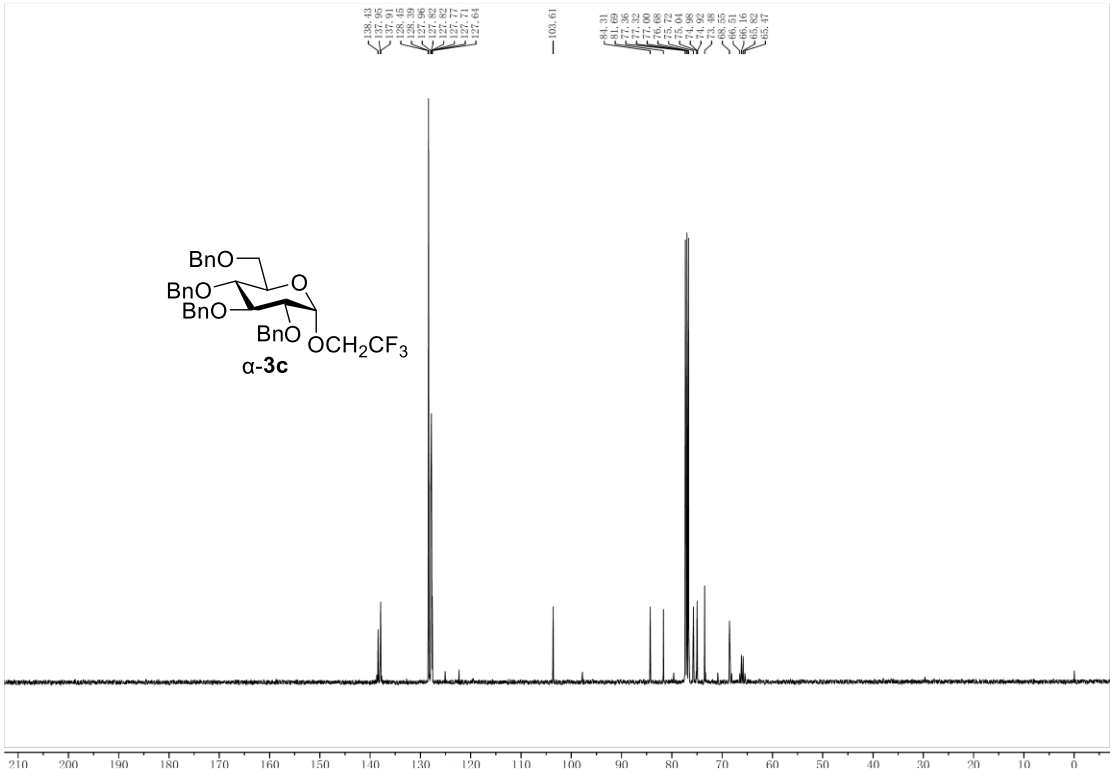
^{13}C NMR spectrum of compound β-**3b** ($CDCl_3$, 100 MHz)



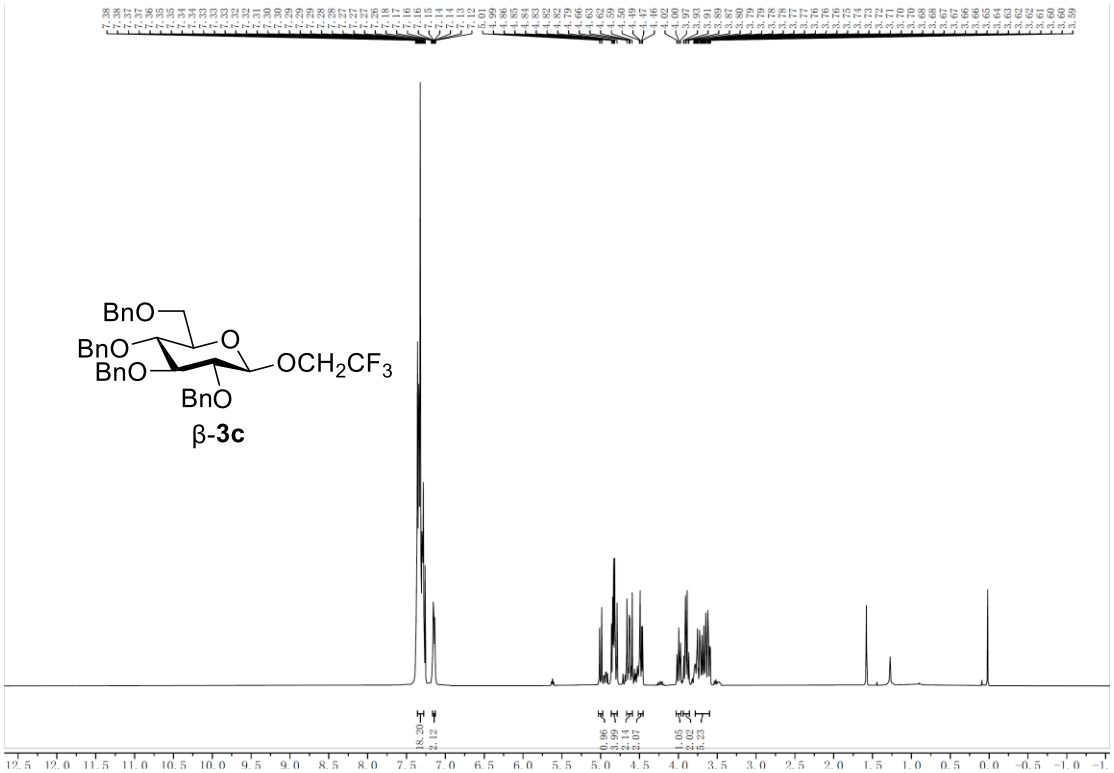
^{1}H NMR spectrum of compound α-**3c** ($CDCl_3$, 400 MHz)



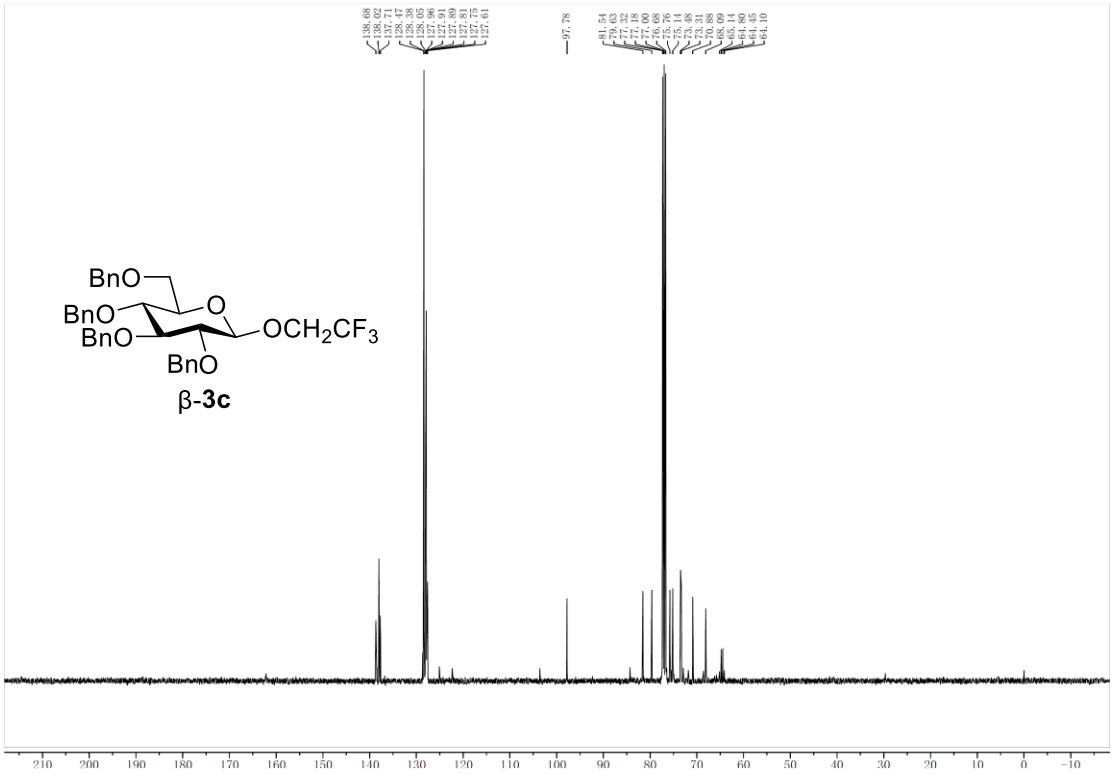
^{13}C NMR spectrum of compound α-**3c** ($CDCl_3$, 100 MHz)



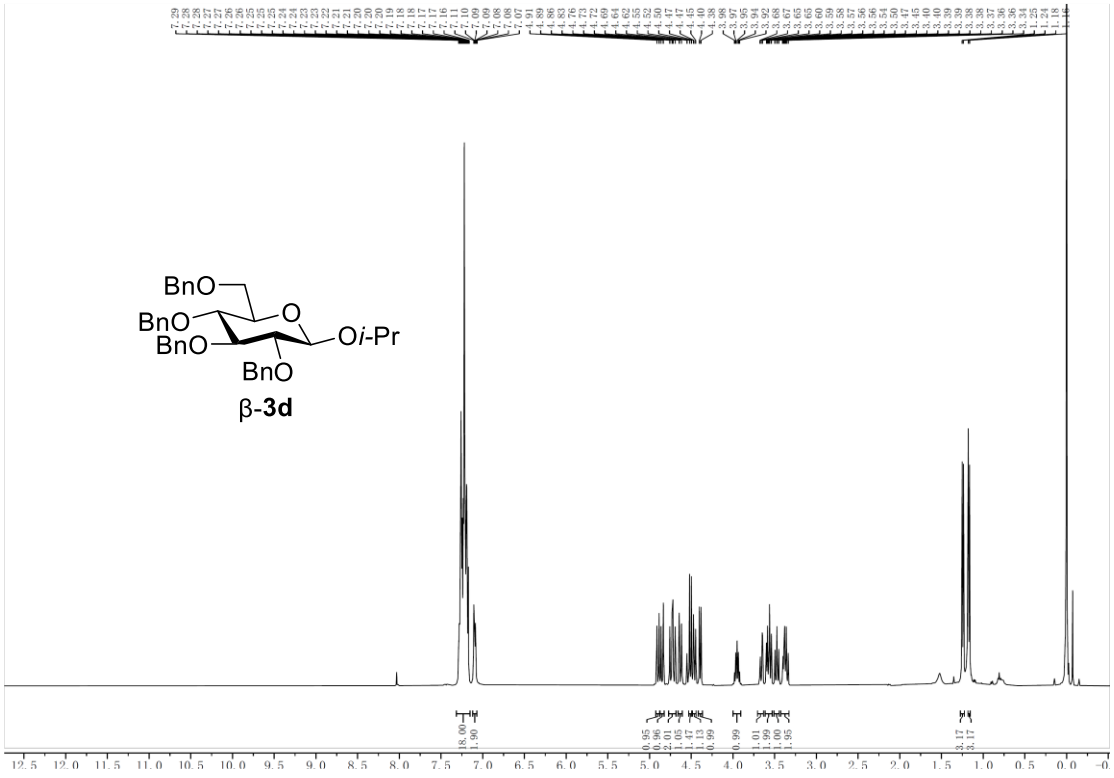
^{1}H NMR spectrum of compound β-**3c** ($CDCl_3$, 400 MHz)



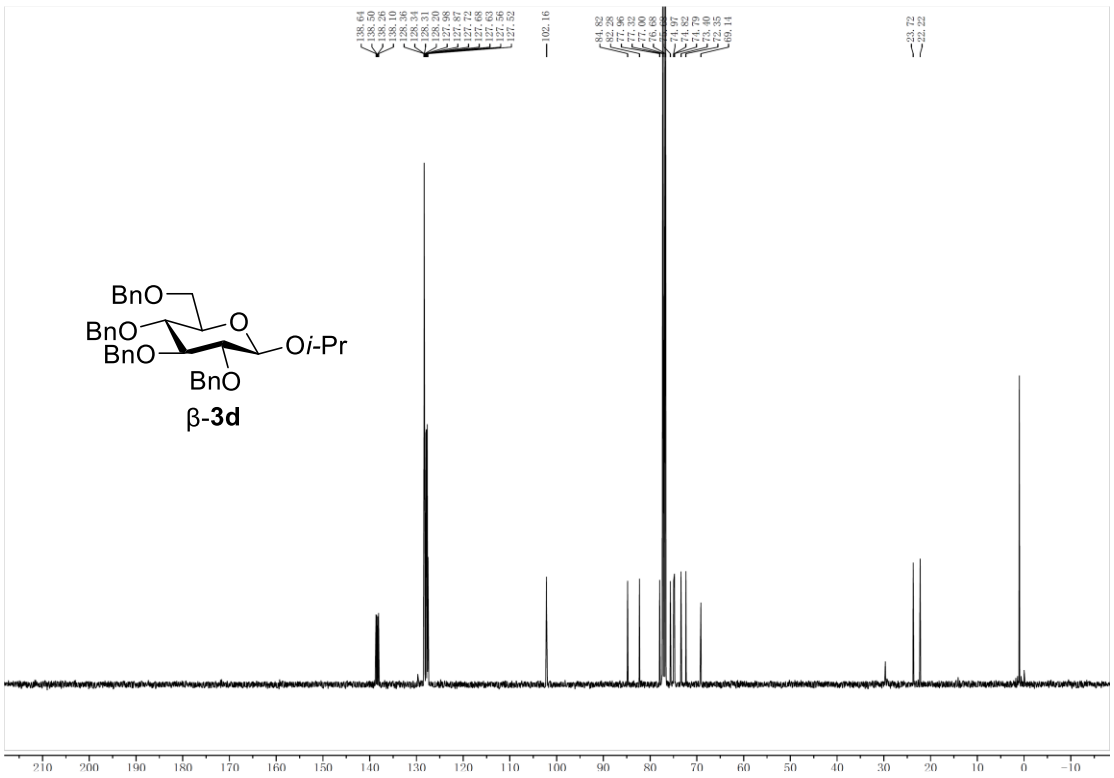
^{13}C NMR spectrum of compound β-**3c** ($CDCl_3$, 100 MHz)



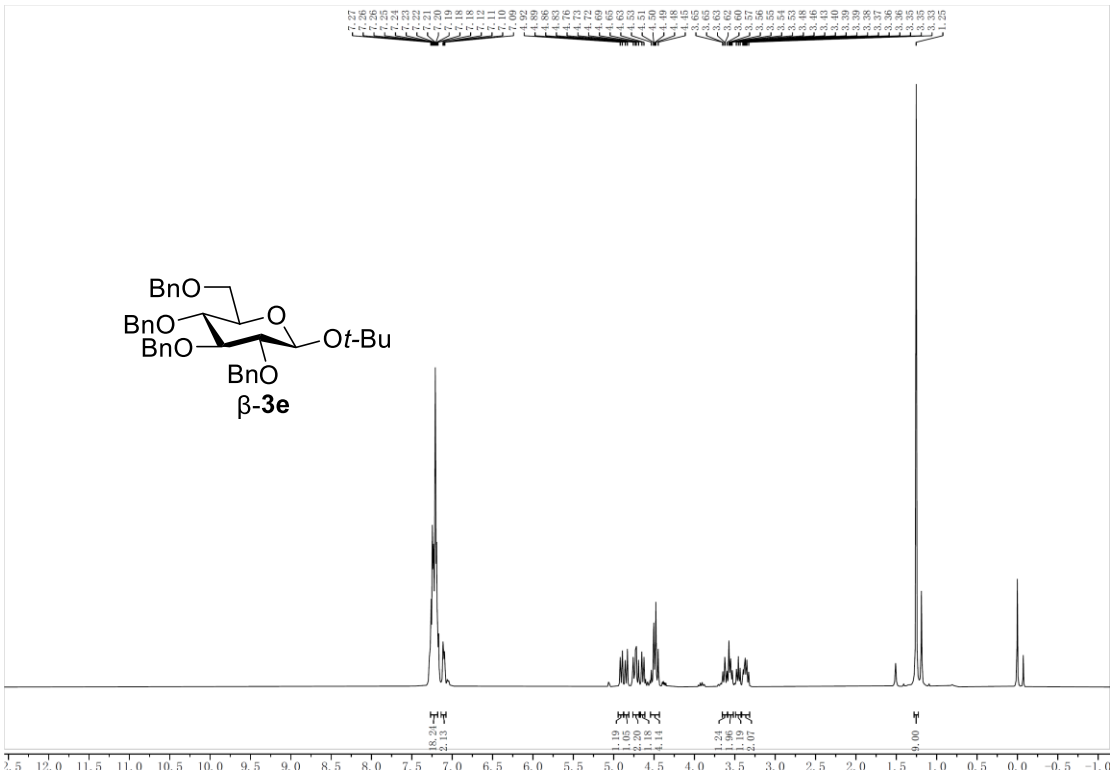
^{1}H NMR spectrum of compound β-**3d** ($CDCl_3$, 400 MHz)



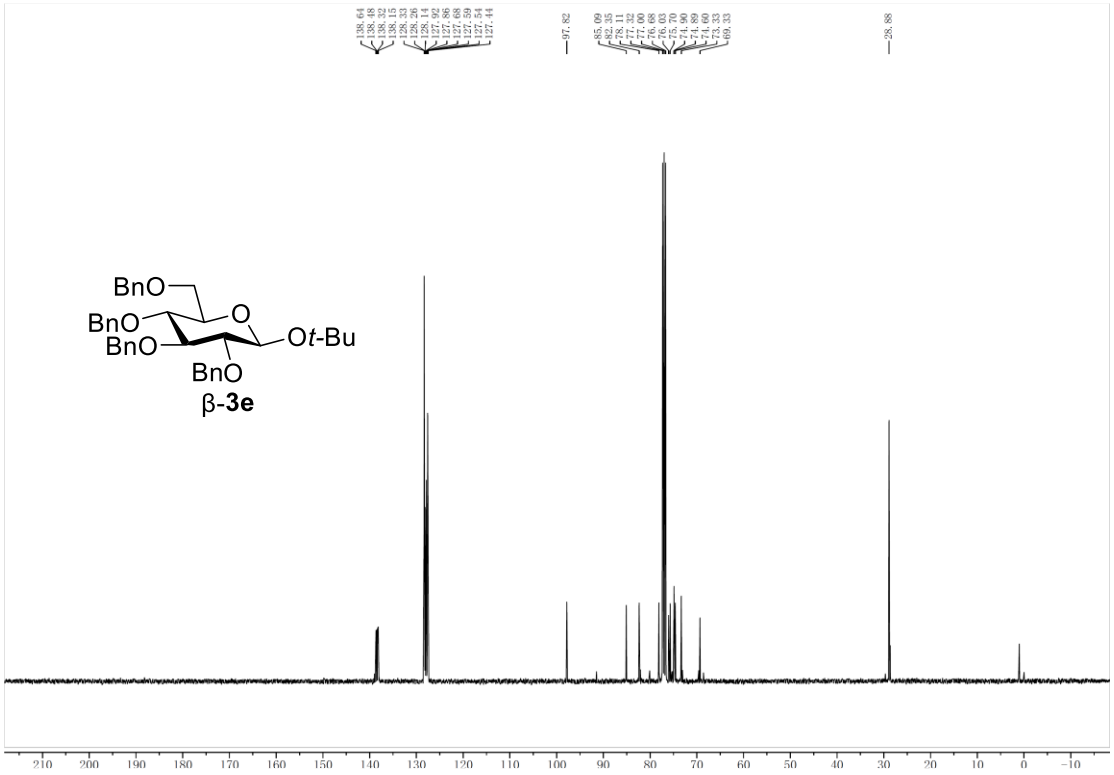
^{13}C NMR spectrum of compound β-**3d** ($CDCl_3$, 100 MHz)



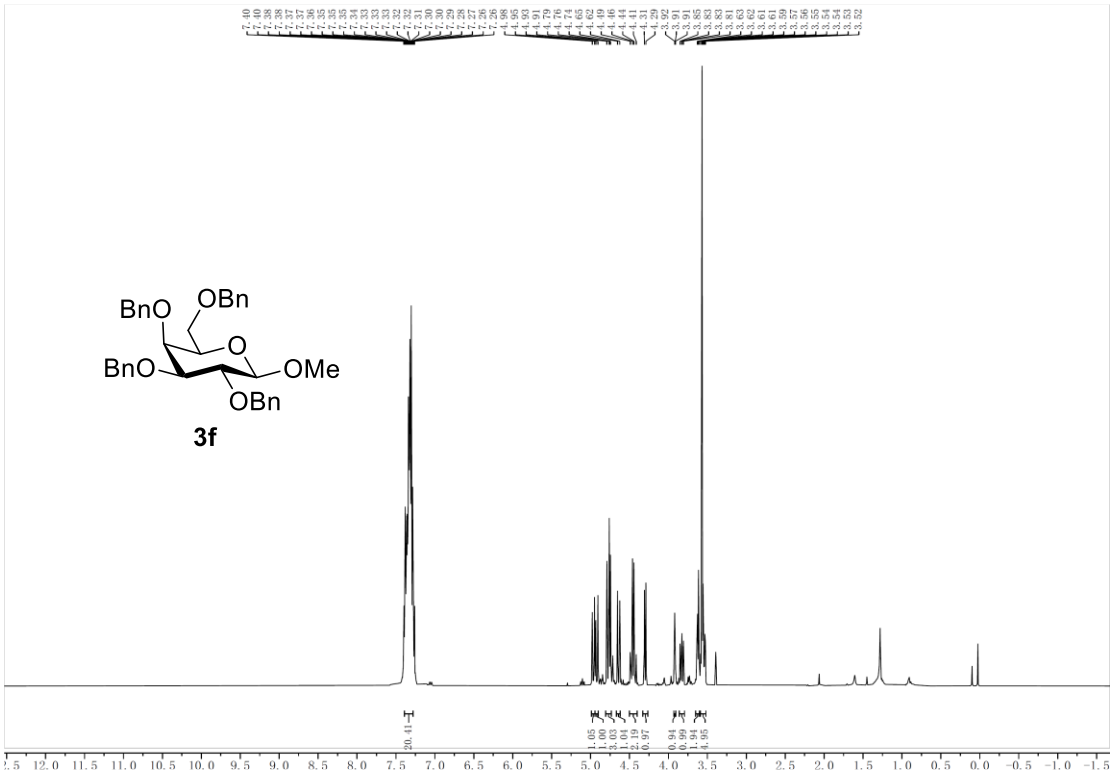
^{1}H NMR spectrum of compound β-**3e** ($CDCl_3$, 400 MHz)



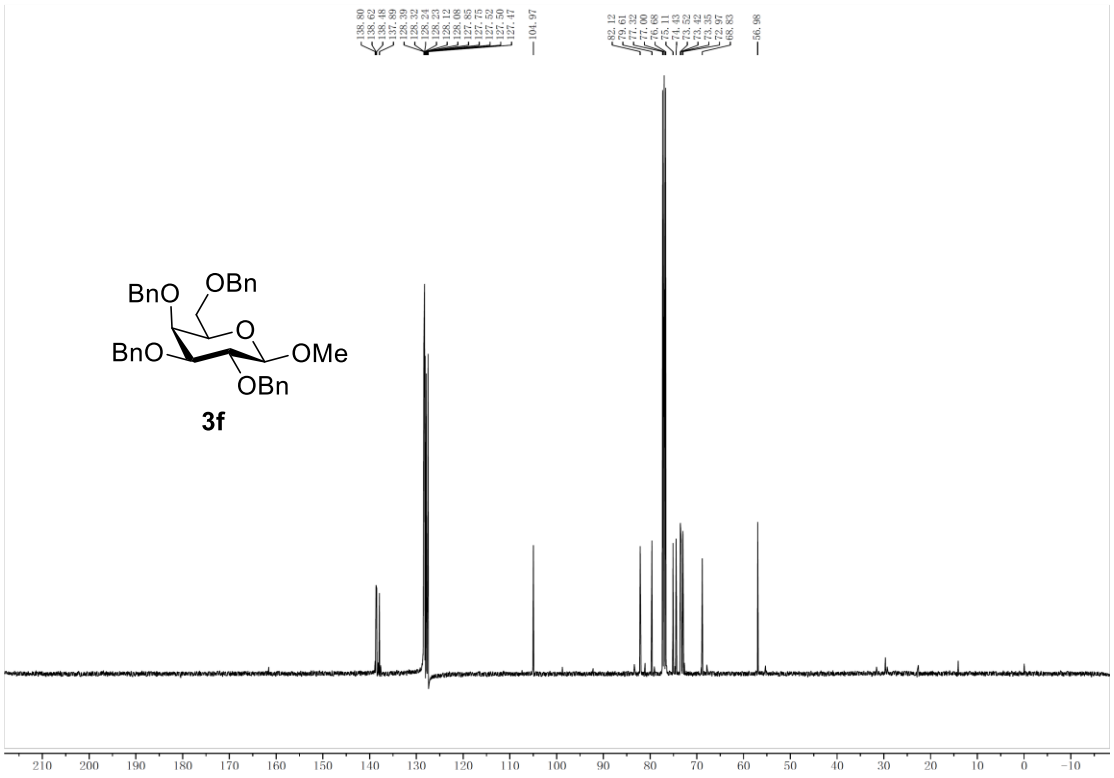
^{13}C NMR spectrum of compound β-**3e** ($CDCl_3$, 100 MHz)



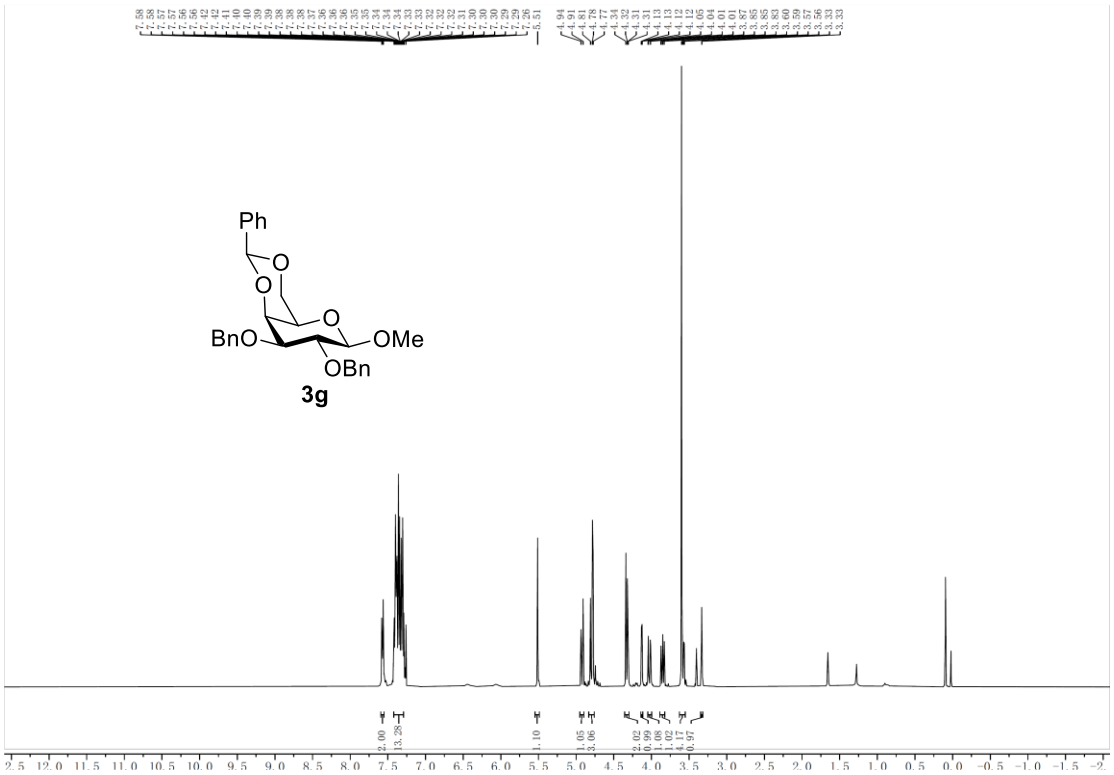
^{1}H NMR spectrum of compound **3f** ($CDCl_3$, 400 MHz)



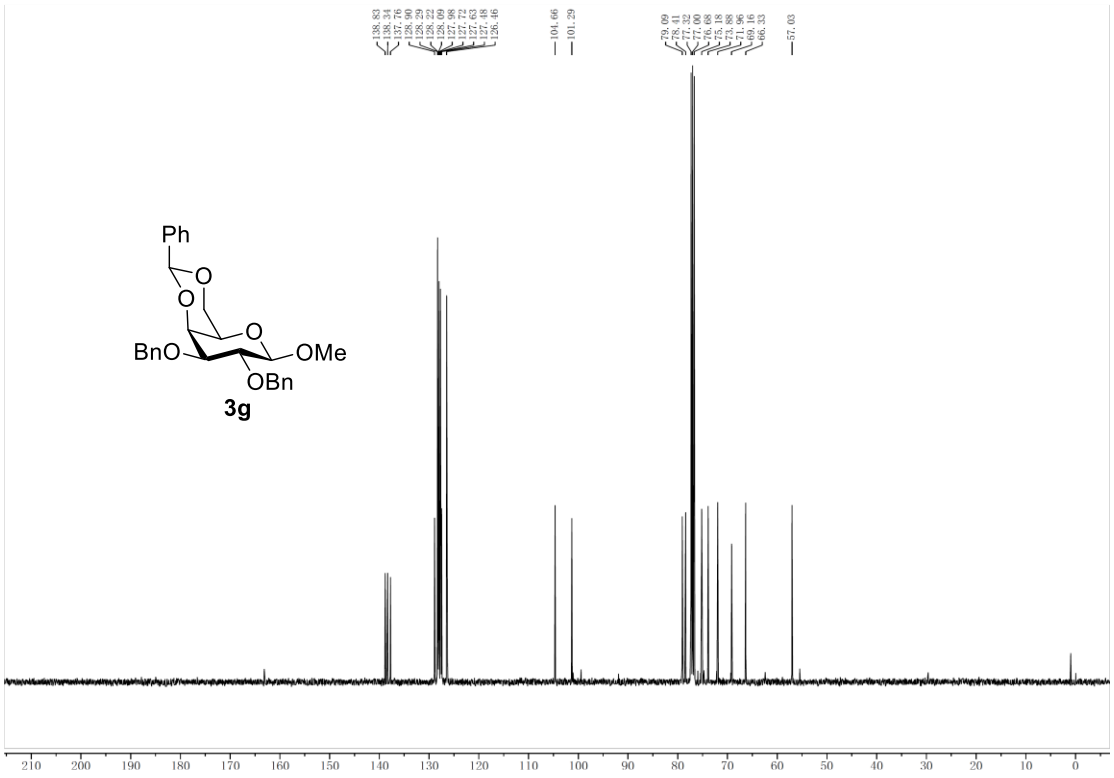
^{13}C NMR spectrum of compound **3f** ($CDCl_3$, 100 MHz)



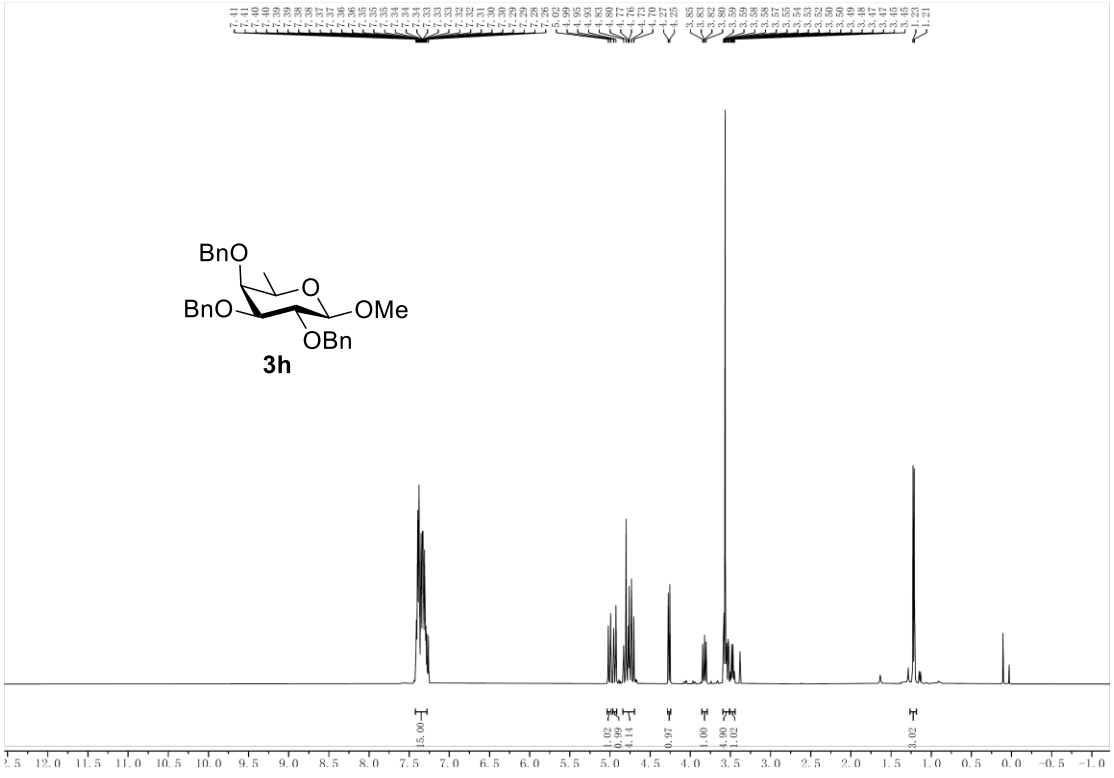
^{1}H NMR spectrum of compound **3g** ($CDCl_3$, 400 MHz)



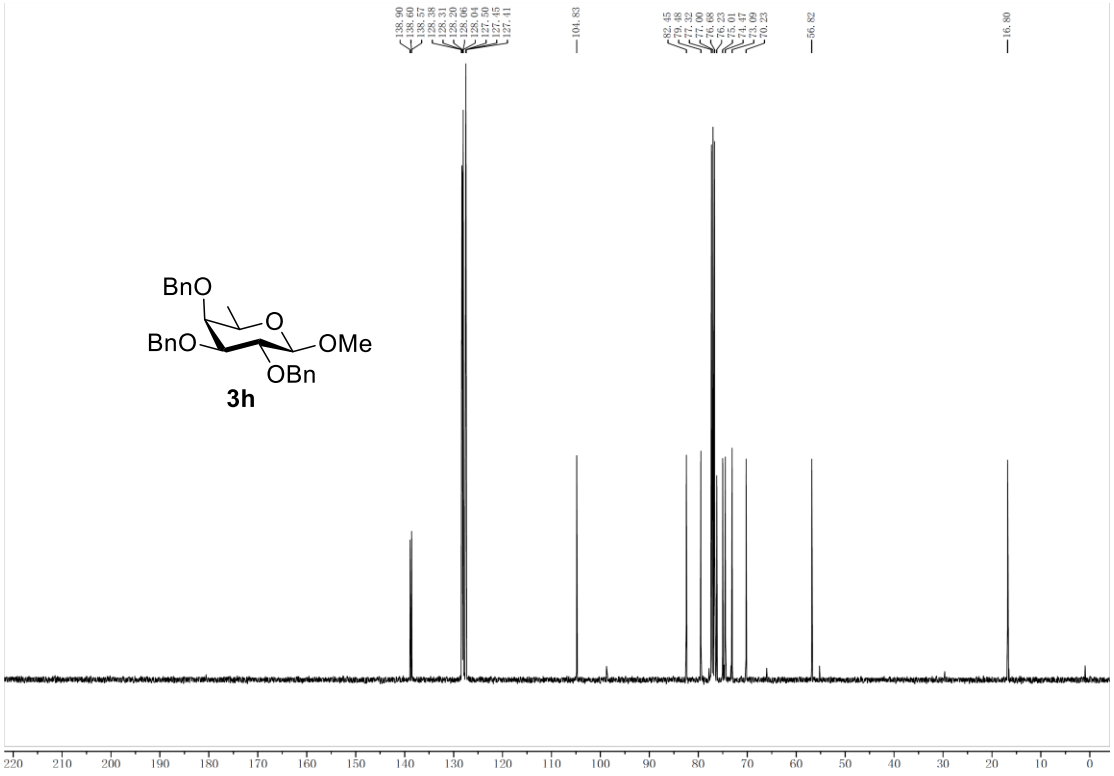
^{13}C NMR spectrum of compound **3g** ($CDCl_3$, 100 MHz)



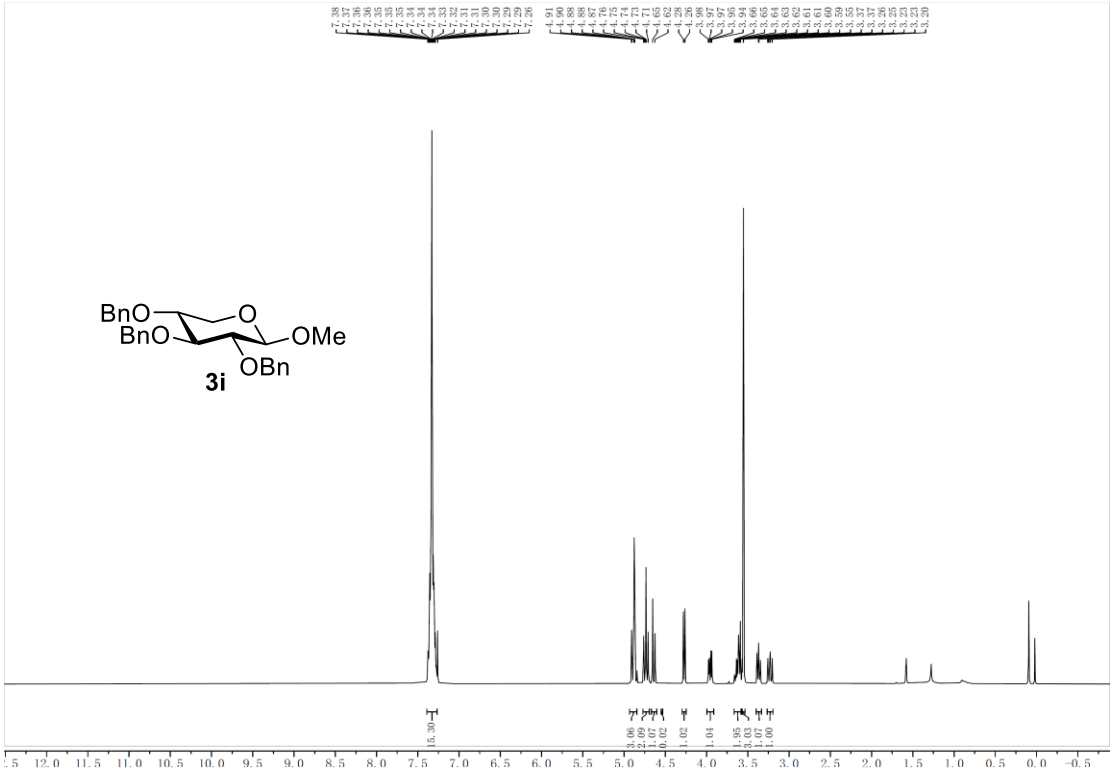
^{1}H NMR spectrum of compound **3h** ($CDCl_3$, 400 MHz)



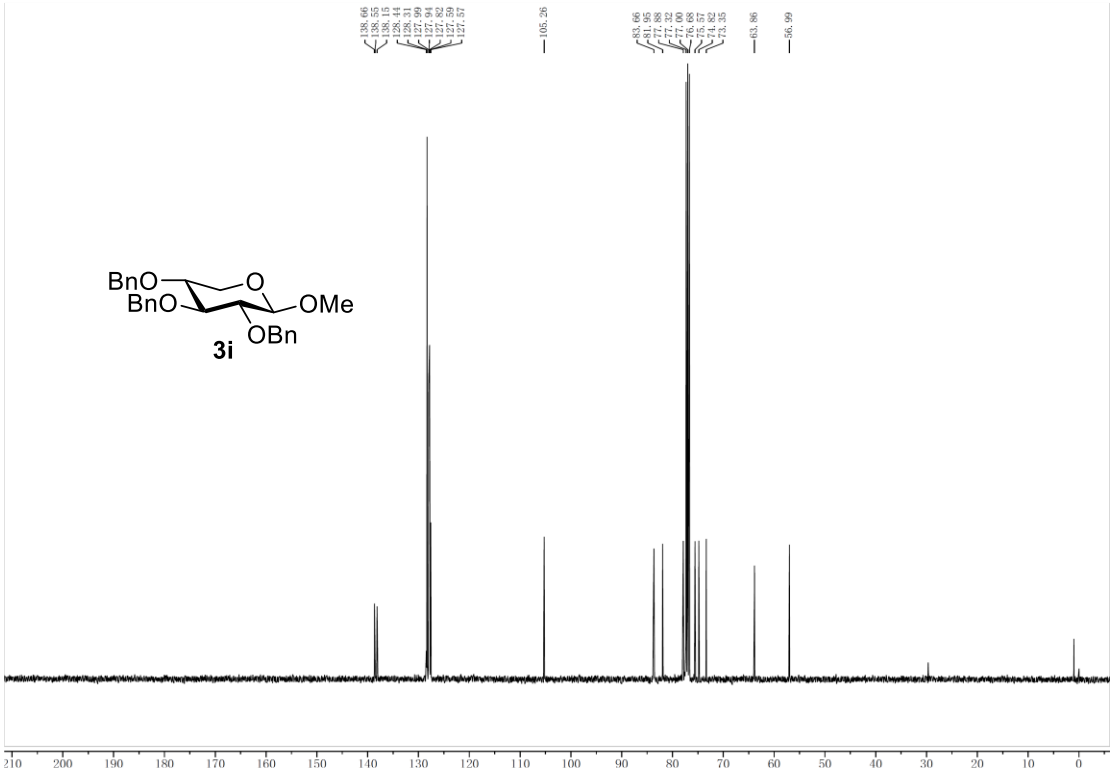
^{13}C NMR spectrum of compound **3h** ($CDCl_3$, 100 MHz)



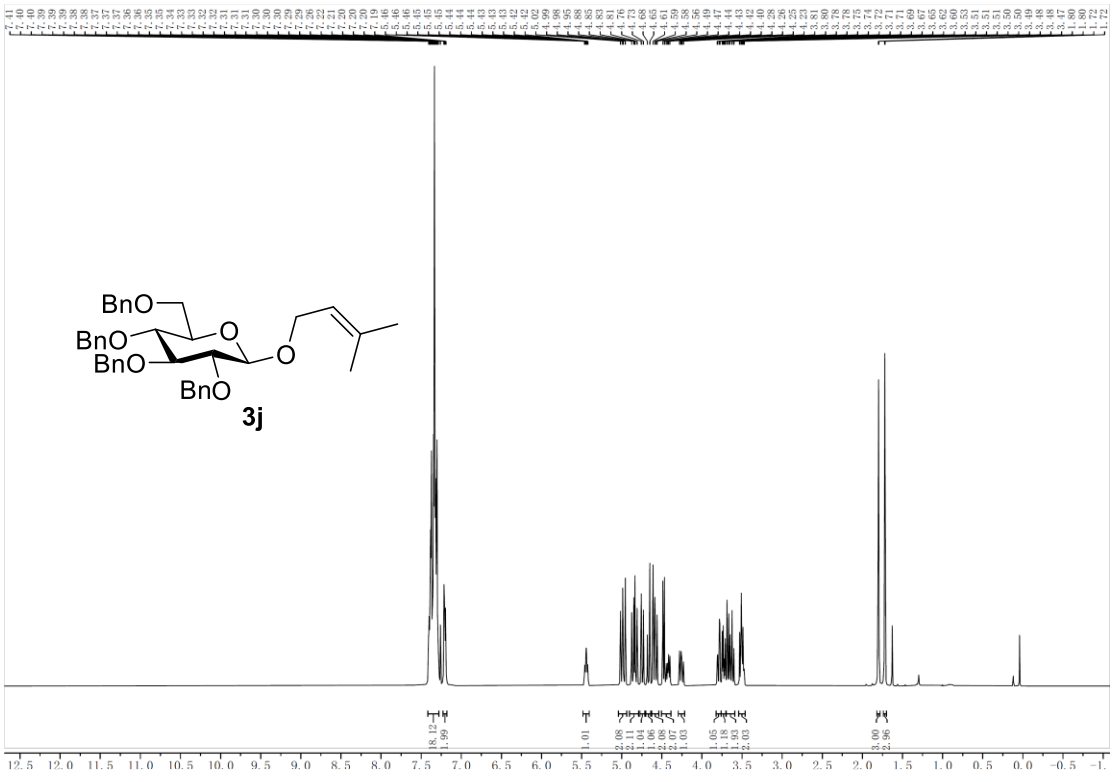
^{1}H NMR spectrum of compound **3i** ($CDCl_3$, 400 MHz)



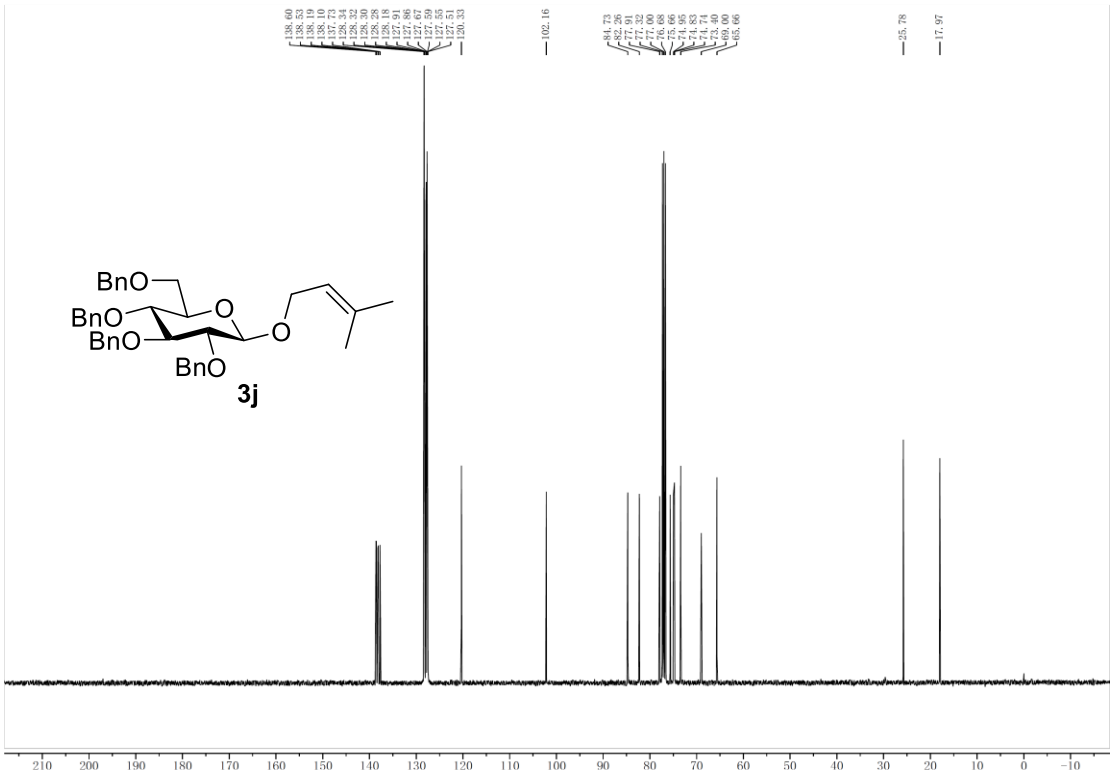
^{13}C NMR spectrum of compound **3i** ($CDCl_3$, 100 MHz)



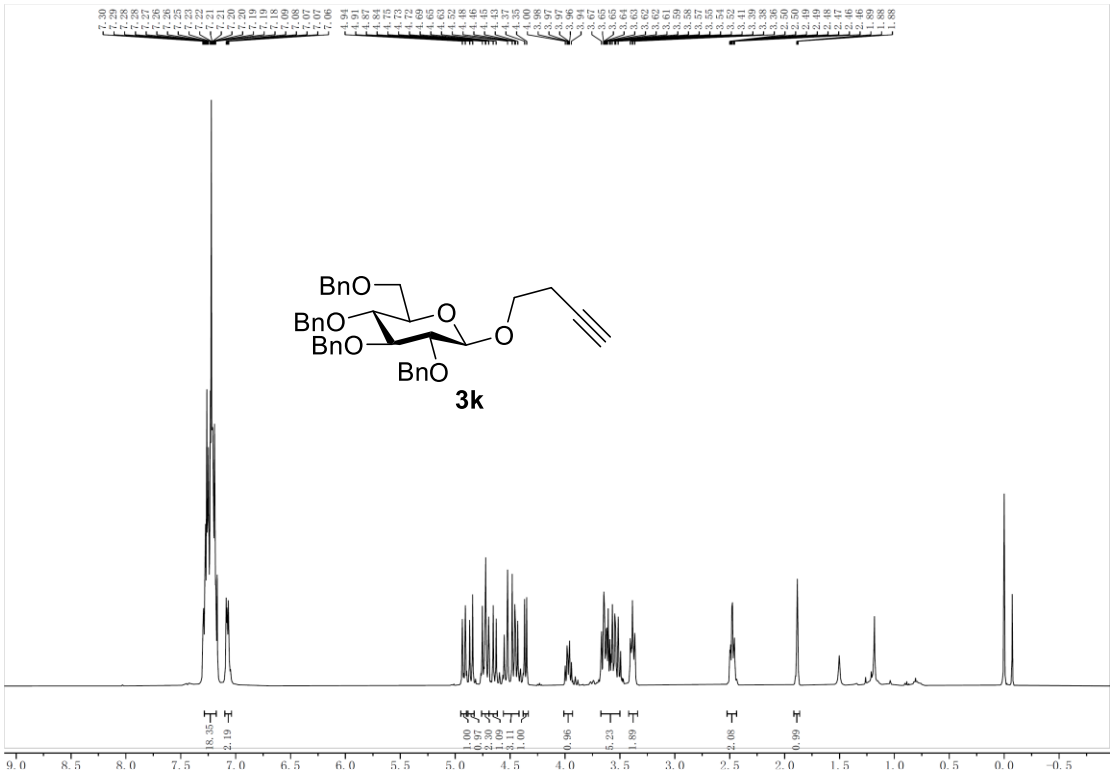
^{1}H NMR spectrum of compound **3j** ($CDCl_3$, 400 MHz)



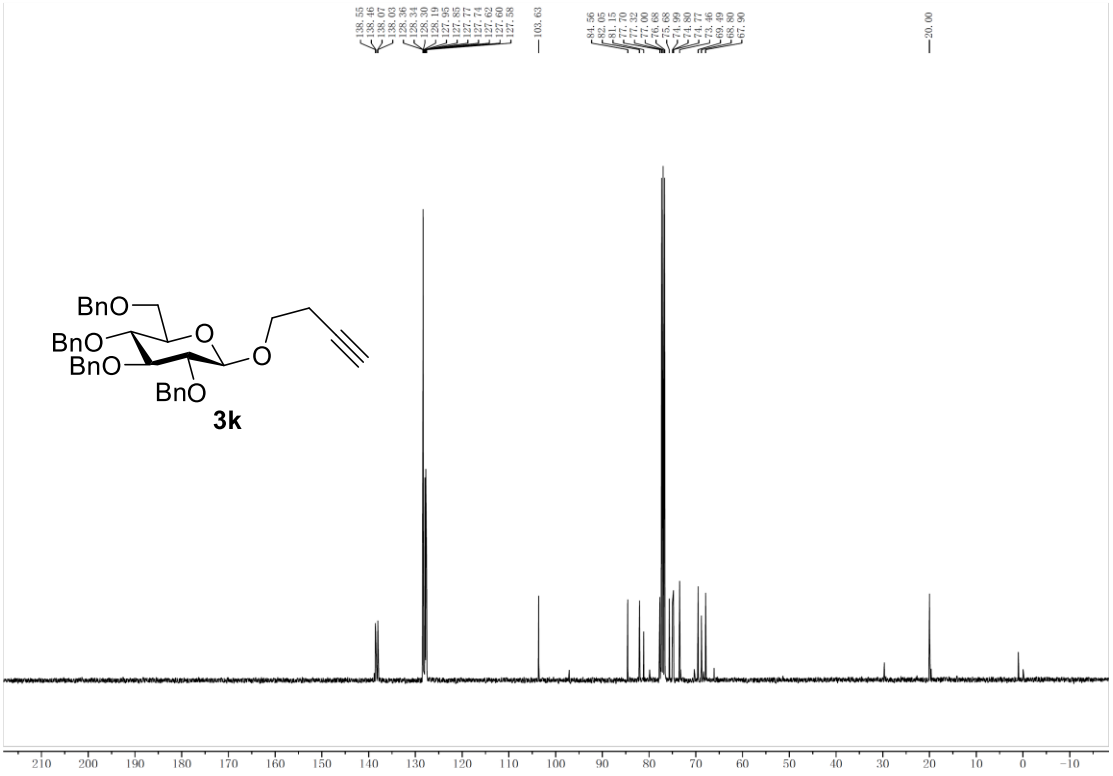
^{13}C NMR spectrum of compound **3j** ($CDCl_3$, 100 MHz)



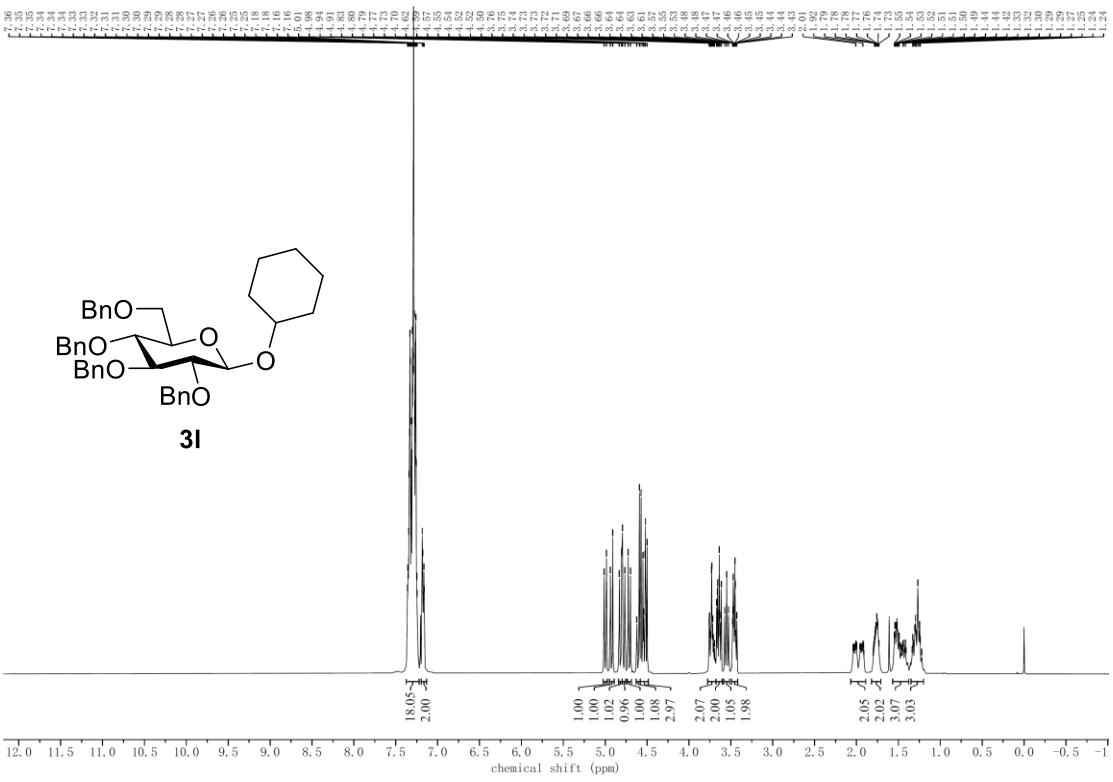
^{1}H NMR spectrum of compound **3k** ($CDCl_3$, 400 MHz)



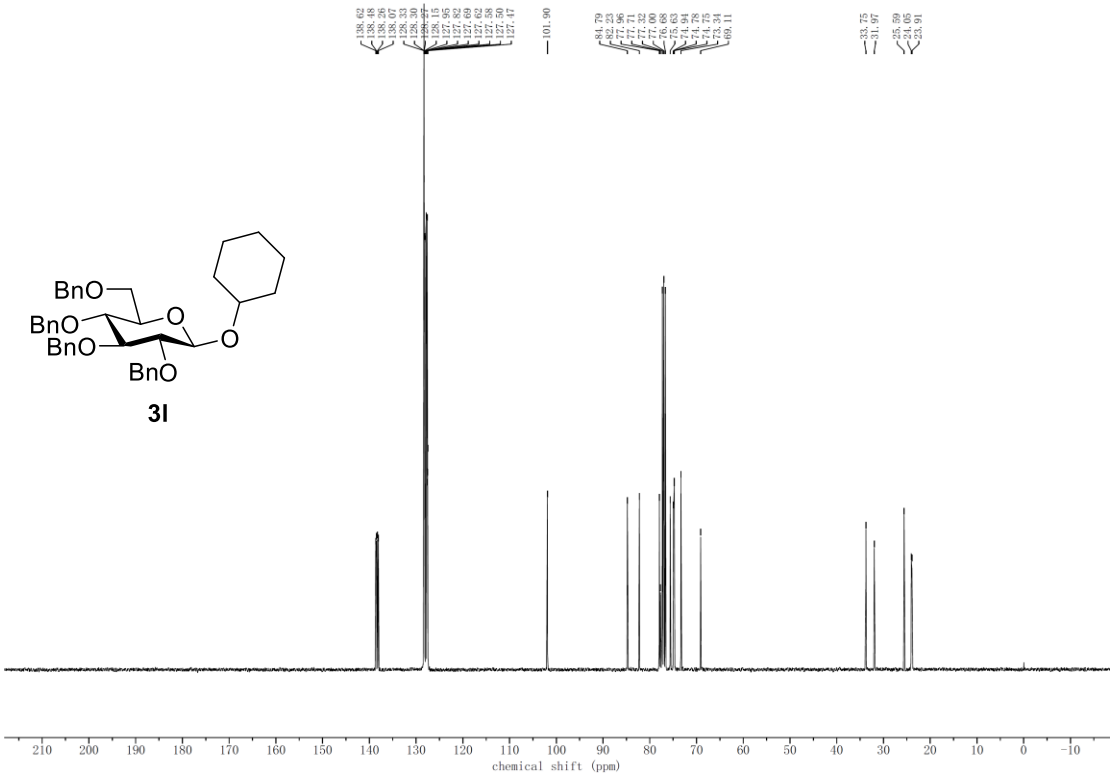
^{13}C NMR spectrum of compound **3k** ($CDCl_3$, 100 MHz)



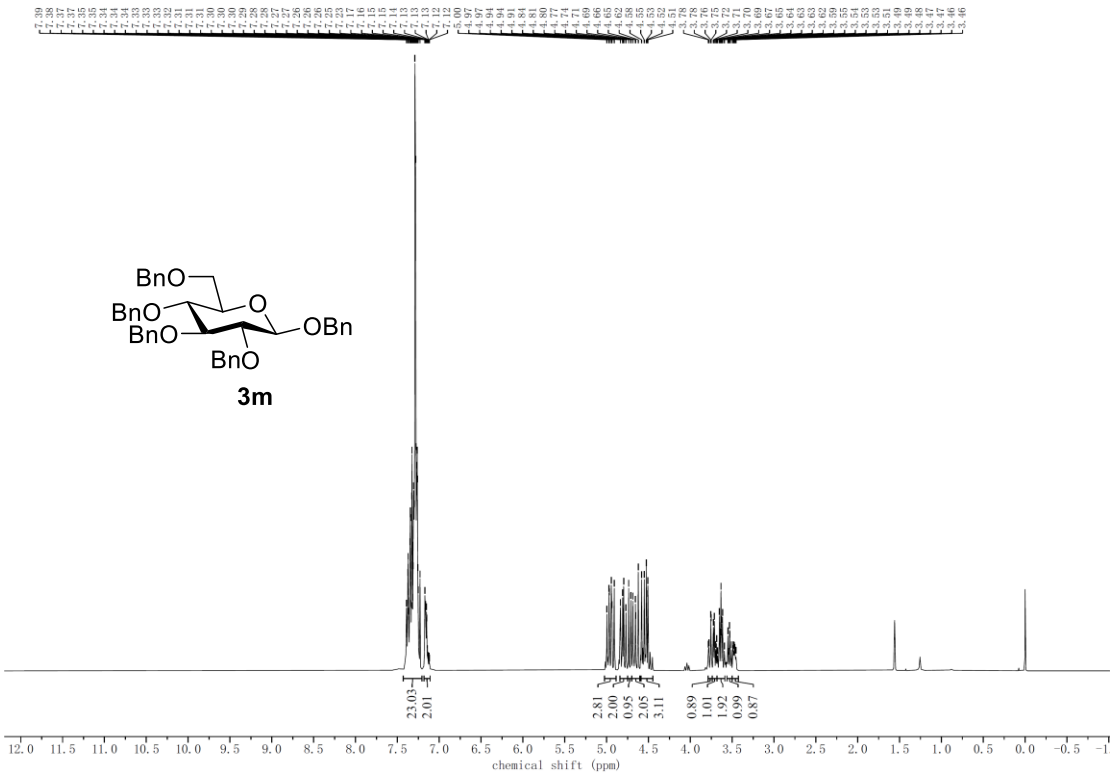
^{1}H NMR spectrum of compound **3l** ($CDCl_3$, 400 MHz)



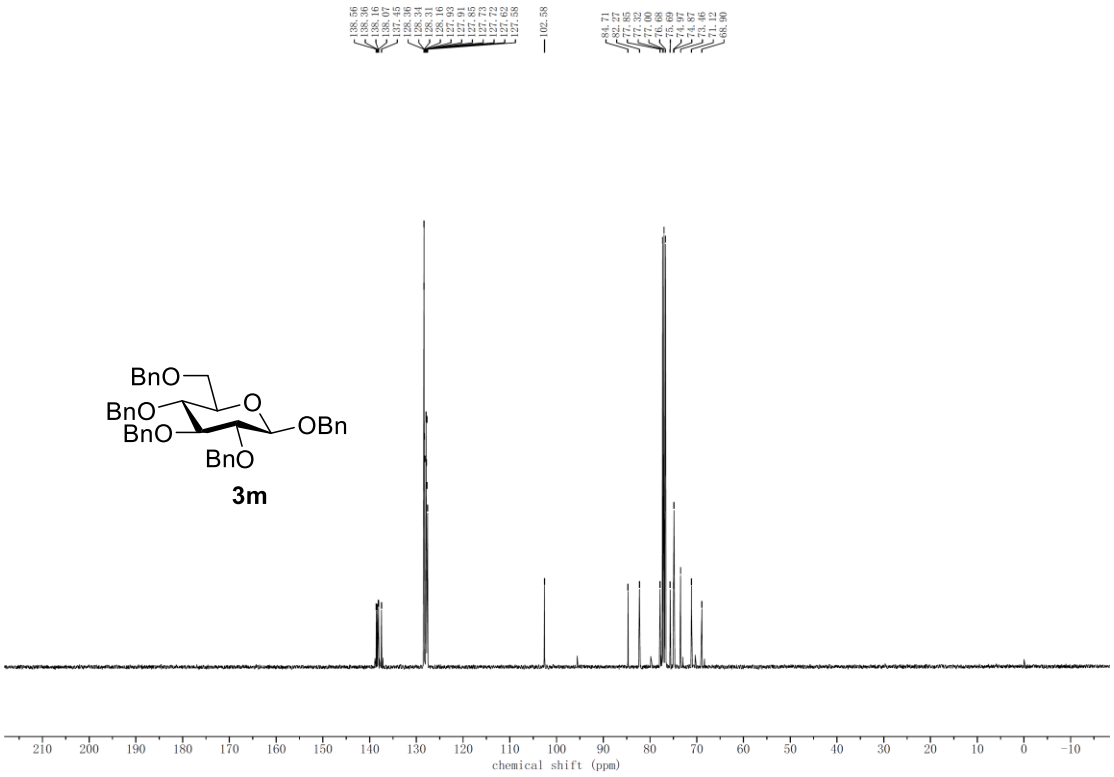
^{13}C NMR spectrum of compound **3l** ($CDCl_3$, 100 MHz)



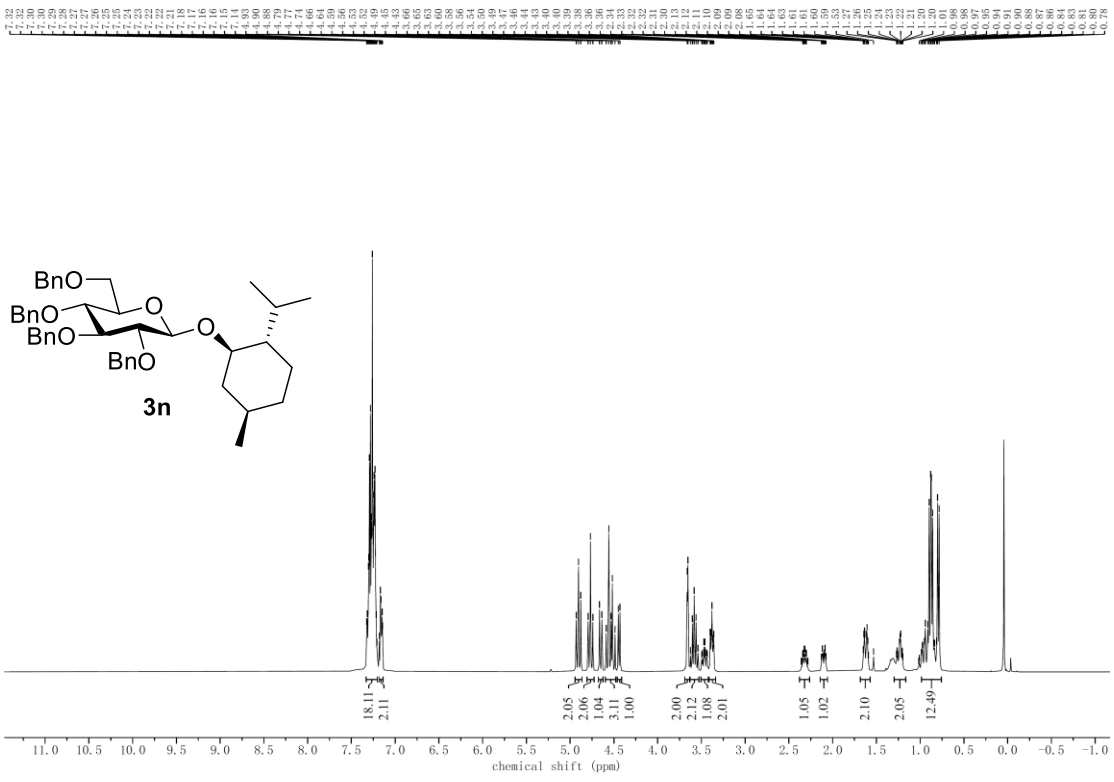
^{1}H NMR spectrum of compound **3m** ($CDCl_3$, 400 MHz)



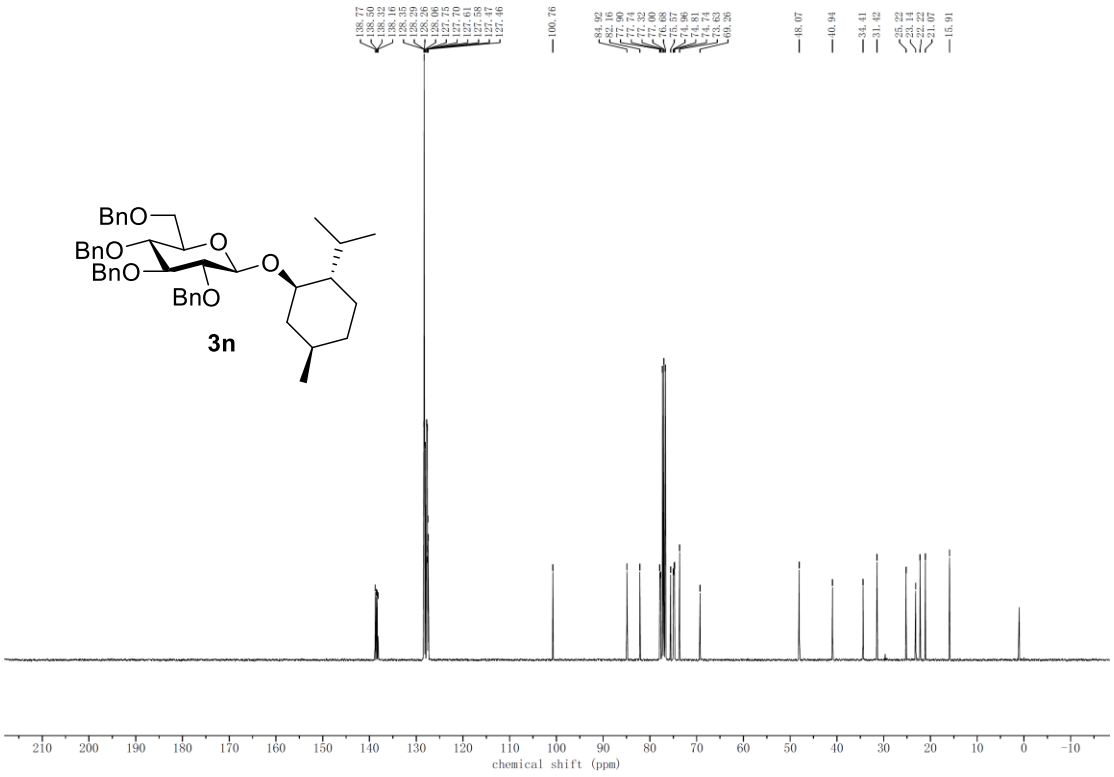
^{13}C NMR spectrum of compound **3m** ($CDCl_3$, 100 MHz)



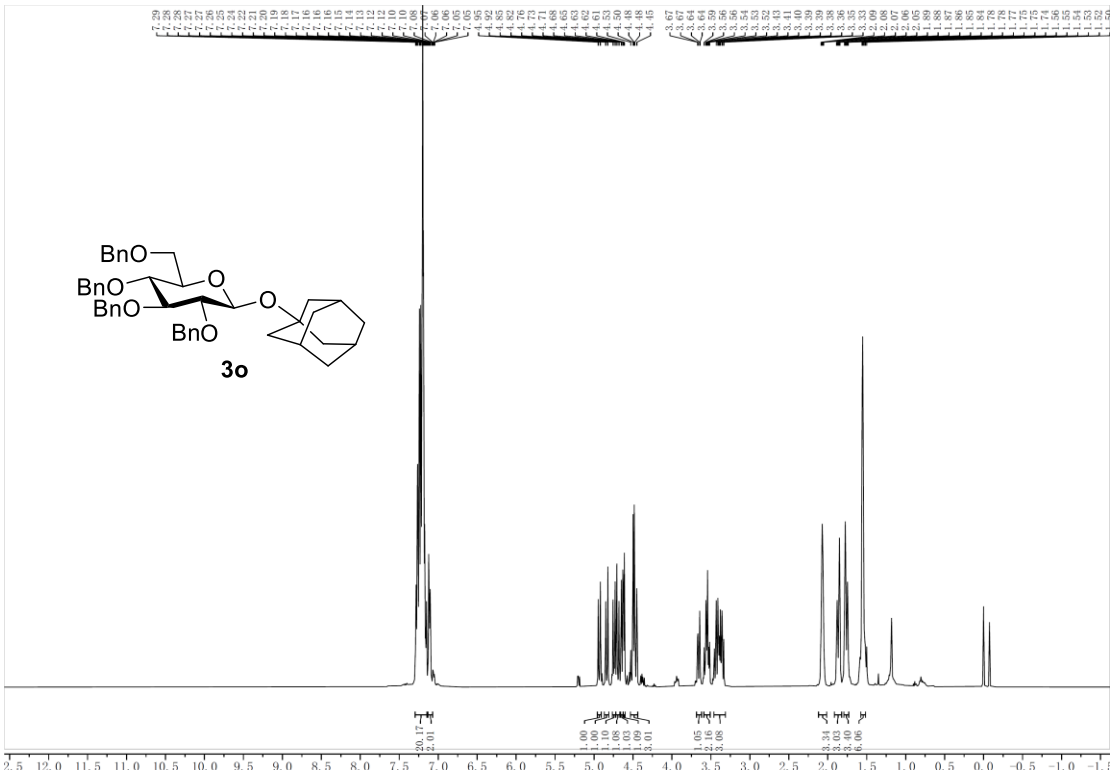
^{1}H NMR spectrum of compound **3n** ($CDCl_3$, 400 MHz)



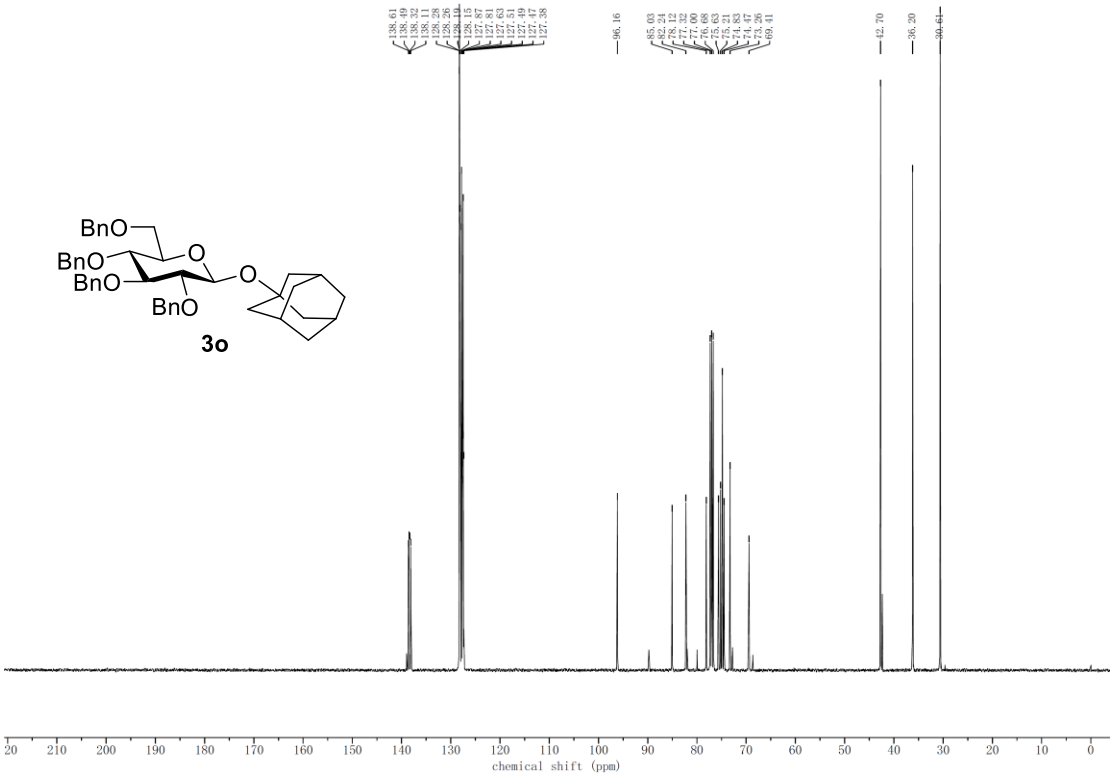
^{13}C NMR spectrum of compound **3n** ($CDCl_3$, 100 MHz)



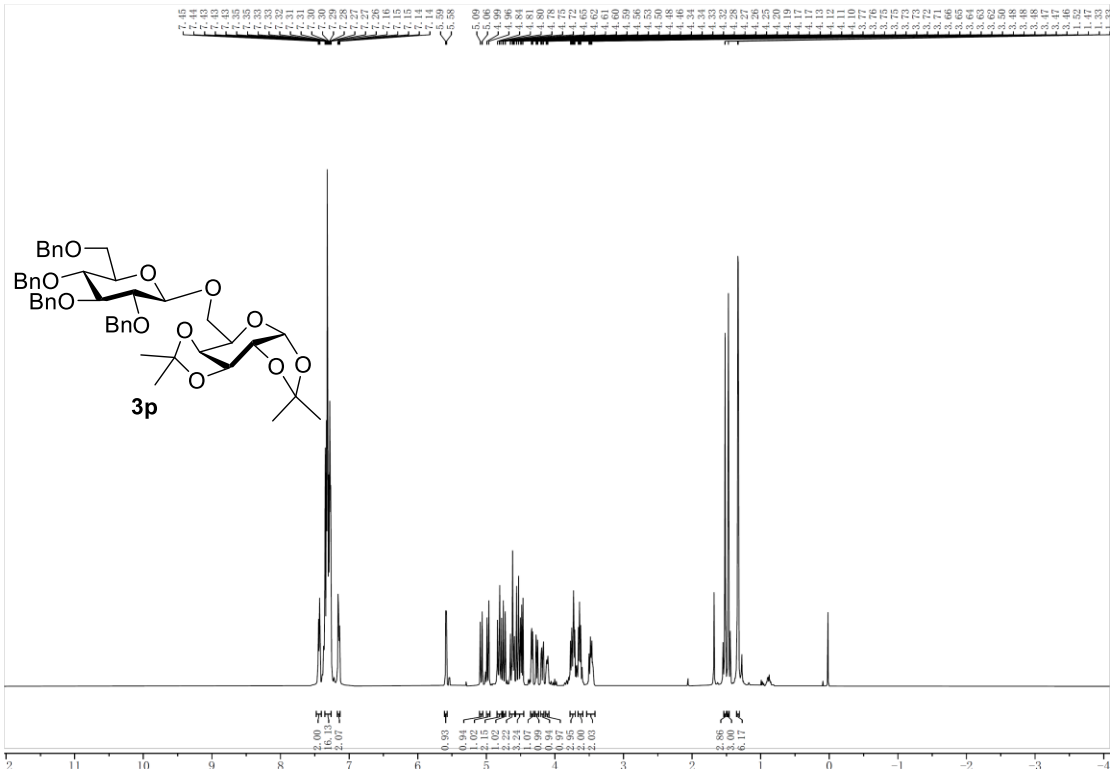
^{1}H NMR spectrum of compound **3o** ($CDCl_3$, 400 MHz)



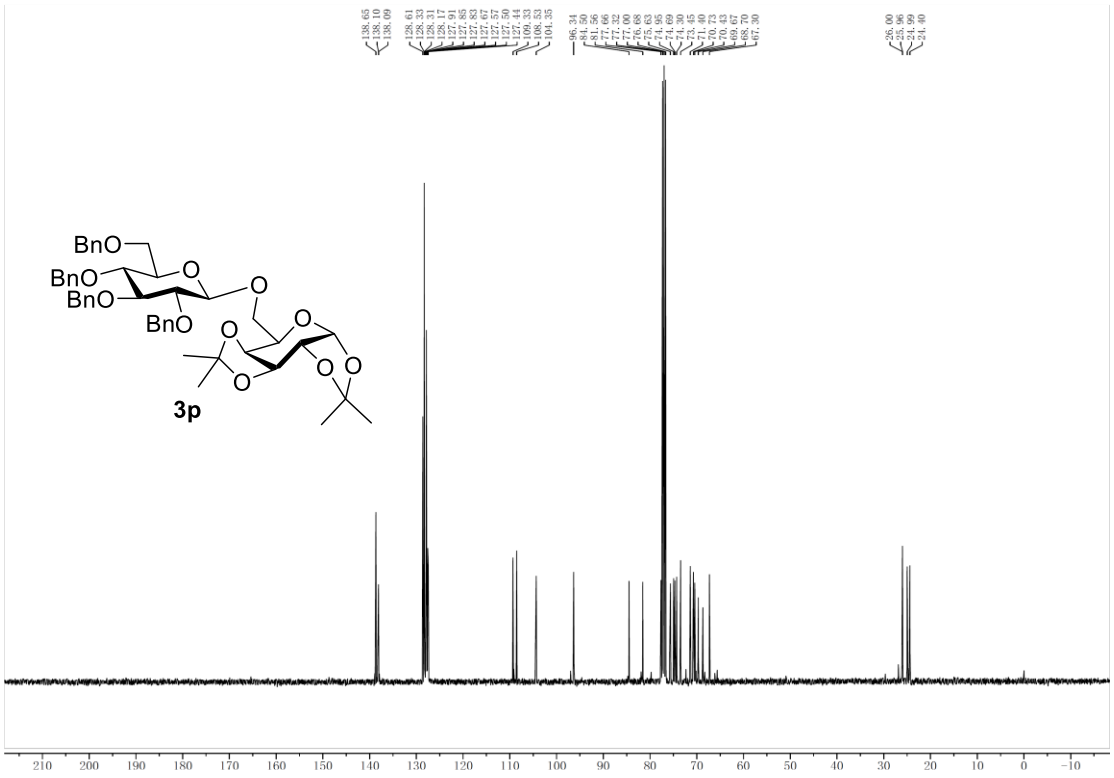
^{13}C NMR spectrum of compound **3o** ($CDCl_3$, 100 MHz)



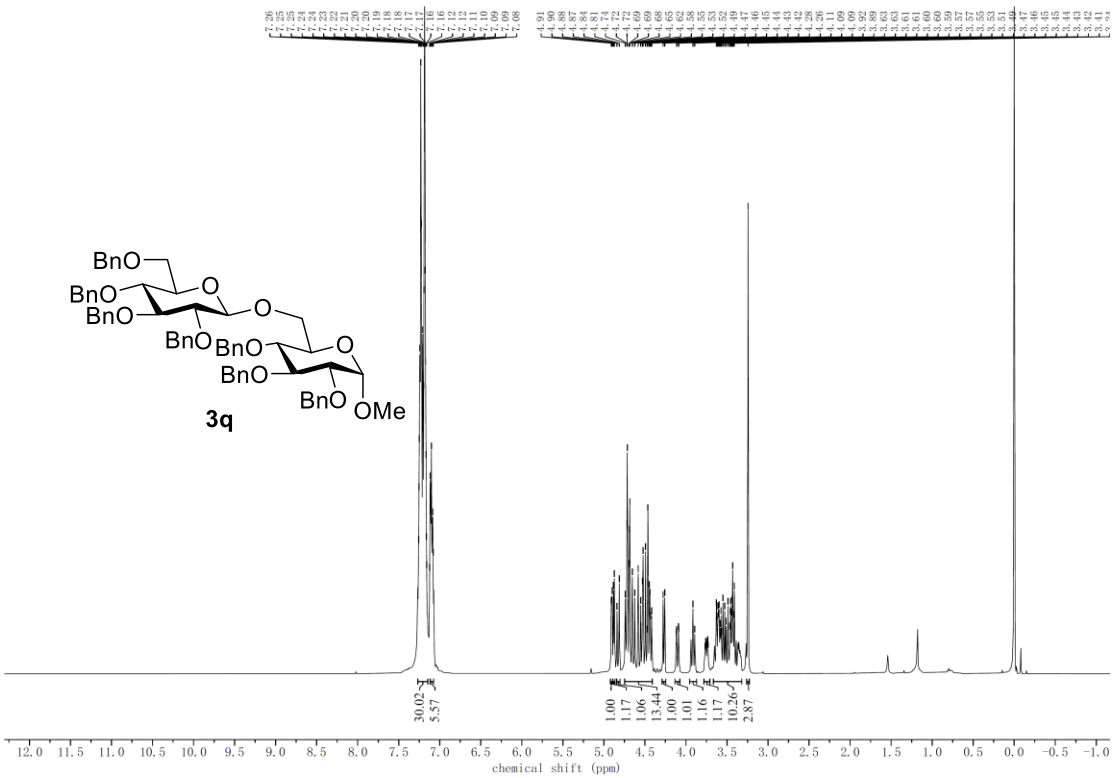
^{1}H NMR spectrum of compound **3p** ($CDCl_3$, 400 MHz)



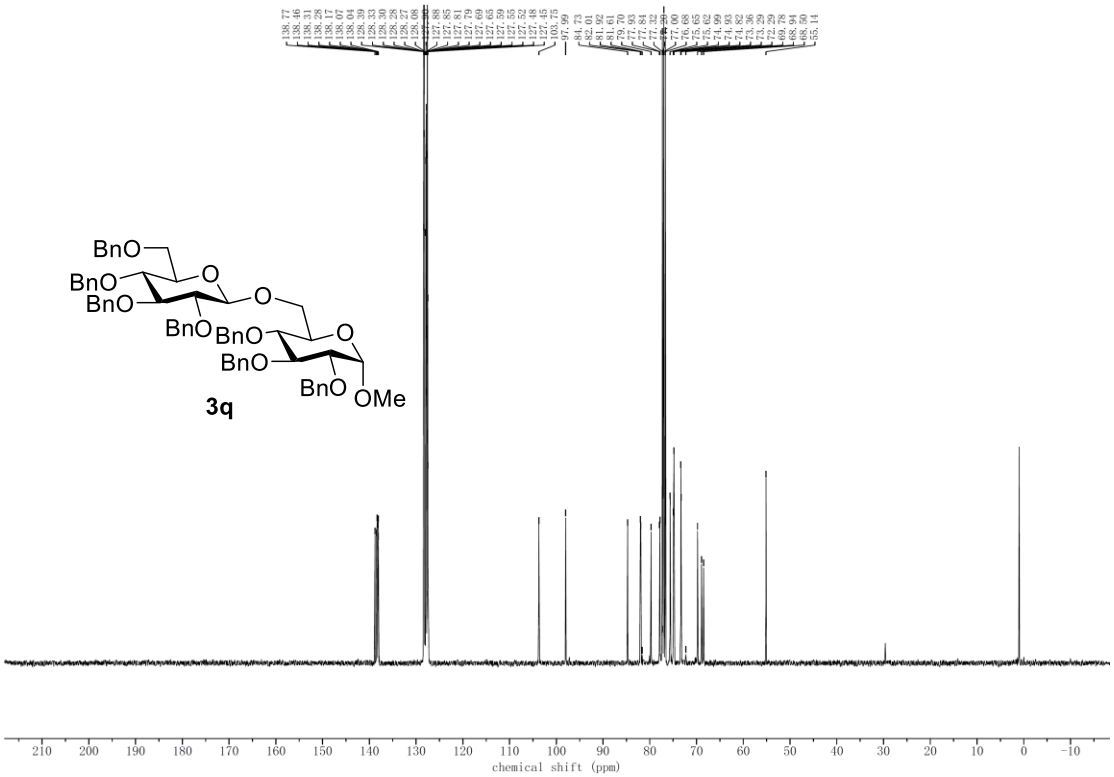
^{13}C NMR spectrum of compound **3p** ($CDCl_3$, 100 MHz)



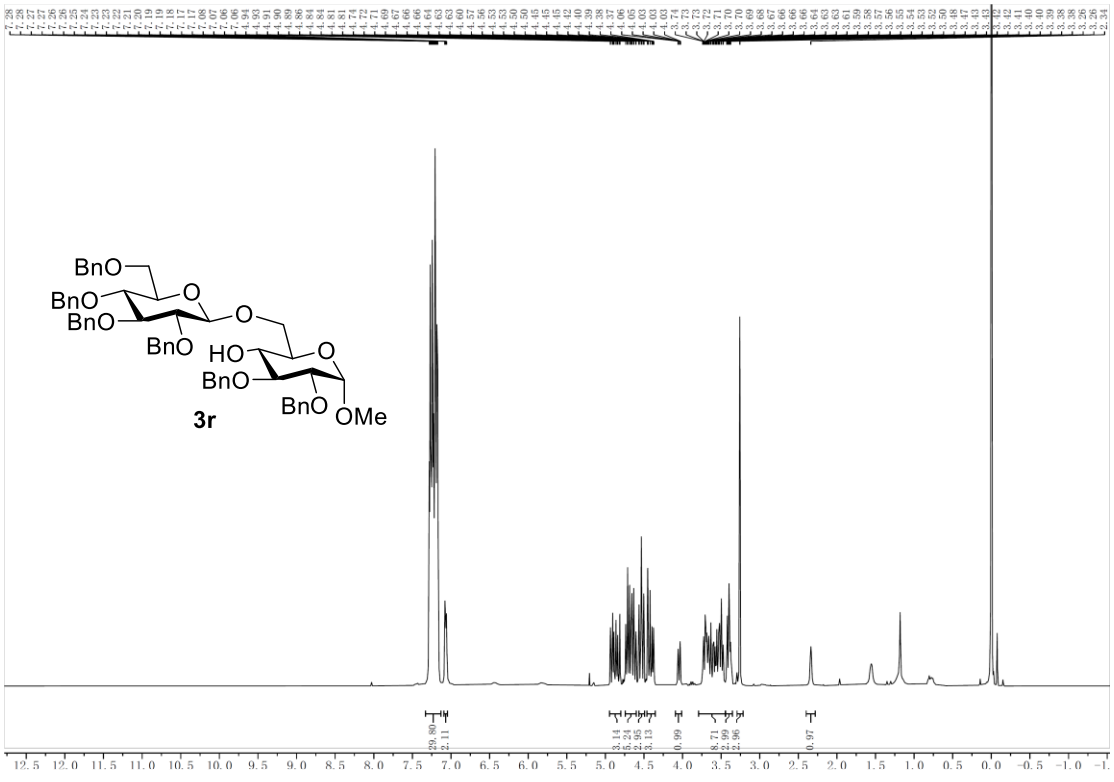
^{1}H NMR spectrum of compound **3q** ($CDCl_3$, 400 MHz)



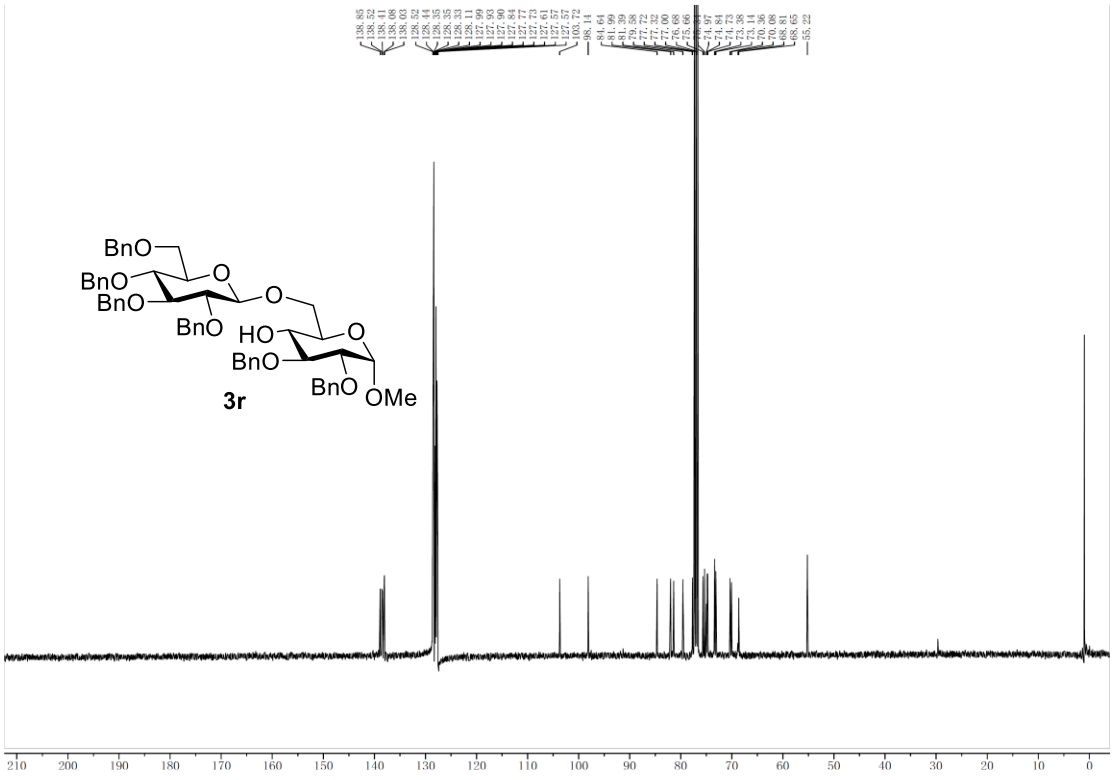
^{13}C NMR spectrum of compound **3q** ($CDCl_3$, 100 MHz)



^{1}H NMR spectrum of compound **3r** ($CDCl_3$, 400 MHz)



^{13}C NMR spectrum of compound **3r** ($CDCl_3$, 100 MHz)



9. References

1. S. Zhang, K. Karra, A. Koe, J. Jin, Catalyst free one-pot synthesis of symmetrical diaryl tellurides with Te^0/KOH. *Tetrahedron Lett.* **2013**, *54*, 2452–2454.

2. D. Tanini, L. Ricci, A. Capperucci, Rongalite-Promoted on Water Synthesis of Functionalised Tellurides and Ditellurides. *Adv. Synth. Catal.* **2020**, *362*, 1323–1332.

3. S. Zhang, L. Kolluru, S. K. Vedula, D. Whippie, J. Jin, Carbon-carbon bond forming reactions via Pd-catalyzed detellurative homocoupling of diorganyl tellurides. *Tetrahedron Lett.* **2017**, *58*, 3594–3597.

4. S. Chatterjee, S. Moon, F. Hentschel, K. Gilmore, P. H. Seeberger, An Empirical Understanding of the Glycosylation Reaction. *J. Am. Chem. Soc.* **2018**, *140*, 11942−11953.

5. N. Hartrampf, T. Seki, A. Baumann, P. Watson, N. A. Vepřek, B. E. Hetzler, A. Hoffmann-Röder, M. Tsuji, D. Trauner, Optical Control of Cytokine Production Using Photoswitchable Galactosylceramides. *Chem. Eur. J.* **2020**, *26*, 4476–4479.

6. J. M. H. Cheng, E. M. Dangerfield, M. S. M. Timmer, B. L. Stocker, A divergent approach to the synthesis of iGb3 sugar and lipid analogues via a lactosyl 2-azido-sphingosine intermediate. *Org. Biomol. Chem.*, **2014**, *12*, 2729–2736.

7. K. Deng, M. M. Adams, P. Damani, P. O. Livingston, G. Ragupathi, D.Y. Gin, Synthesis of the Xylose-Isomer of the Clinical Adjuvant QS-21. Establishing Immuno-Potentiating Activity of Synthetic QS-21 (sQS-21) with GD3-KLH Conjugate Melanoma Vaccine. *Angew. Chem. Int. Ed.* **2008**, *47*, 6395–6398.

8. P. Thordarson, Determining association constants from titration experiments in supramolecular chemistry. *Chem. Soc. Rev.* **2011**, *40*, 1305–1323.

9. D. Brynn Hibbert, P. Thordarson. The death of the Job plot, transparency, open science and online tools, uncertainty estimation methods and other developments in supramolecular chemistry data analysis. *Chem. Commun.* **2016**, *52*, 12792–12805.