Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

SUPPLEMENTARY INFORMATION

Catalytic Asymmetric Deuterosilylation of Exocyclic Olefins with Mannose-Derived Thiols and Deuterium Oxide

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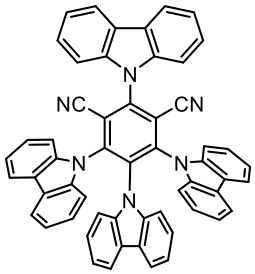
1. General Information

Unless otherwise stated all reactions were set up under nitrogen atmosphere utilizing oven-dried glassware. Solvents were either purchased from Adamas or *J&K* (Sure/Seal bottles) or dried with activated 4 Å molecular sieves and stored in a glovebox under nitrogen atmosphere. Column chromatography was performed using silica gel (200-300 mesh). All other reagents were purchased from various commercial sources and used as received. A blue LED (λ_{max} = 441 nm, 30 W) was used as the light source for all the photo-reactions. Reactions were monitored by thin-layer chromatography on Leyan silica gel plates (60 GF254) which were rendered visible by ultraviolet light and/or spraying with basic $KMnO_4$ solution, followed by heating.

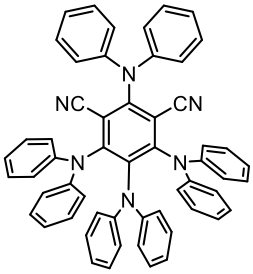
^{1}H NMR spectra were recorded on a Bruker AVIII 400 (400 MHz), AVIII 500 (500 MHz) spectrometer and are reported in ppm, relative to tetramethylsilane (TMS, δ 0 ppm) or residual solvent signals ($CDCl_3$ referenced at δ 7.26 ppm). Data are reported as follows: (brs = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet; coupling constant(s) in Hz; integration). ^{13}C NMR spectra were recorded on a Bruker AVIII 400 (100 MHz) spectrometer and are reported in ppm, relative to residual solvent signals ($CDCl_3$ referenced at δ 77.0 ppm). High resolution mass spectra (HRMS) were performed at Instrumental Analysis Center of Shanghai Jiao Tong University with electrospray spectrometer Waters Micromass Q-TOF Premier Mass Spectrometer. Enantiomeric ratios (e.r.) and diastereomeric ratios (d.r.) were determined by chiral High Performance Liquid Chromatography (HPLC) analysis. UV detection was monitored at 214 nm or 190 nm at the same time. HPLC samples were dissolved in HPLC grade isopropanol (IPA) and hexane unless otherwise stated. HPLC analysis on chiral stationary phase was performed on a Shimadzu LC-2030 Plus-series instrument. Chiralpak AD-H, OD-H, OJ-H, IC-H, or AS-H columns were used with hexane and IPA being the eluents. Gas chromatography-mass spectrometry (GC-MS) analysis were performed on a Shimadzu GCMS-QP2020NX system. Liquid chromatography-mass spectrometry (LC-MS) analysis were performed on a Shimadzu LCMS 2020 system. Melting points were measured with microscope WRX-4 (Shanghai Yice). Optical rotations were measured on Anton Paar MCP100 automatic polarimeter using a 100 mm path-length cell at 589 nm and reported as follows; $[\alpha]_{\lambda}^{T\,℃}$ (*c* = g/100 mL, solvent).

2. Synthesis of Catalysts and Substrates

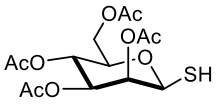
The photocatalyst 4CzIPN[1] and 4DPAIPN,[2] **S1**,[3] **S2**,[4] **S3-S6**,[3] olefins,[5] and silanes[6] were either commercially available or synthesized according to the reported procedures.



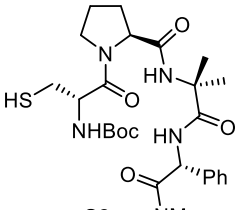
4CzIPN



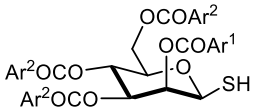
4DPAIPN



S1

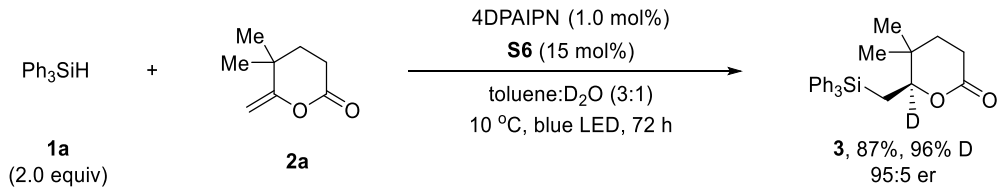


S2 NMe_2



Ar^1 **=** Ar^2 = C_6H_5 (**S3**)
Ar^1 **=** Ar^2 = 4-F-C_6H_4 (**S4**)
Ar^1 **=** Ar^2 = 4-^{t}Bu-C_6H_4 (**S5**)
Ar^1 = 4-^{t}Bu-C_6H_4, Ar^2 = 4-F-C_6H_4 (**S6**)

3. Synthesis and Characterization of Products



1a (2.0 equiv)

2a

3, 87%, 96% D
95:5 er

Typical procedure: To an oven-dried 16 x 60 mm vial containing a dry Teflon stir bar were charged with photocatalyst 4DPAIPN (1.7 mg, 0.002 mmol), thiol catalyst **S6** (21.5 mg, 0.03 mmol) and triphenylsilane **1a** (104.4 mg, 0.4 mmol). After sequential addition of dry toluene (1.5 mL), D_2O (0.5 mL), and olefin **2a** (28.2 mg, 0.2 mmol), the reaction mixture was flushed with nitrogen gas for two minutes and then the vial was sealed with a cap and parafilm. The vial was placed in a cooling station and a 30 W blue LED (λ_{max} = 441 nm) was then placed at the top of the cooling station (**Figure S1**), which is connected to a chiller to maintain the temperature of the cooling water at 10 ℃. The reaction mixture was stirred at 10 ℃ under irradiation for 72 h. When the reaction is complete as monitored by TLC and GC, CH_2Cl_2 (10 mL) and H_2O (5 mL) were added, the organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (10 mL × 3). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. After filtration and evaporation, the residue was purified by chromatography on silica gel (eluent: petroleum ether/dichloromethane/ether = 14/10/1) to afford **3** (70.0 mg, 87%, 96% D) as a colorless solid: 95:5 er (HPLC conditions: Chiralcel AD-H column, hexane/*i*-PrOH = 98.5/1.5, 1.0 mL/min, λ = 214 nm, t_R (minor) = 13.0 min, t_R (major) = 16.4 min); $[\alpha]_D^{25}$ = -68.8 (*c* = 0.50, $CHCl_3$); **m.p.** 85-87 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.68-7.54 (m, 6 H), 7.46-7.31 (m, 9 H), 4.11 (dd, J_1 = 11.6 Hz, J_2 = 2.4 Hz, 0.04 H), 2.51-2.31 (m, 2 H), 1.78 (d, *J* = 15.2 Hz, 1 H), 1.65-1.52 (m, 3 H), 1.00 (s, 3 H), 0.92 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 170.9, 135.9, 134.5, 129.5, 127.8, 84.2 (t, J_{C-D} = 21.9 Hz), 34.0, 33.0, 27.4, 26.5, 19.3, 14.9; **HRMS** (ESI) calcd for $C_{26}H_{27}DNaO_2Si$ [M+Na^+]: 424.1814, found: 424.1811.

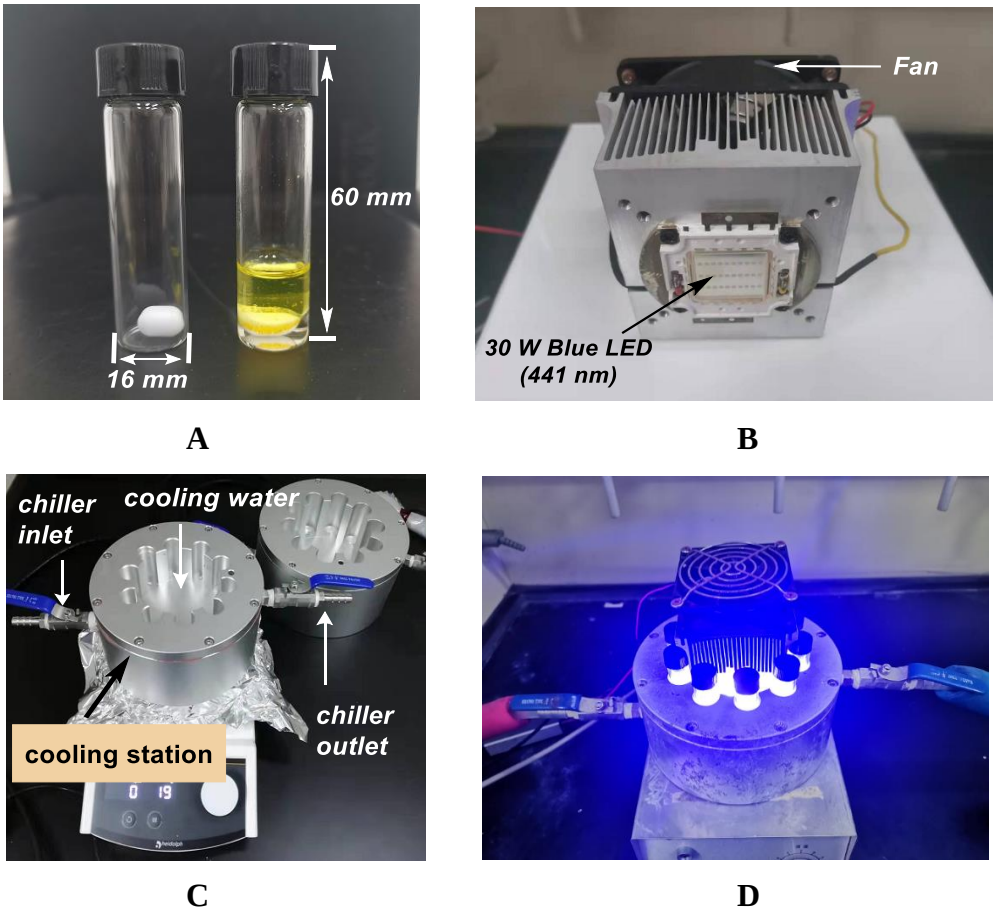
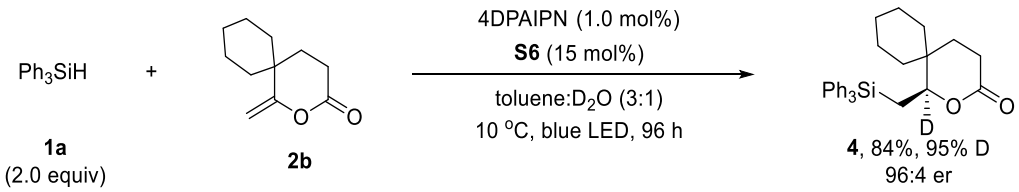


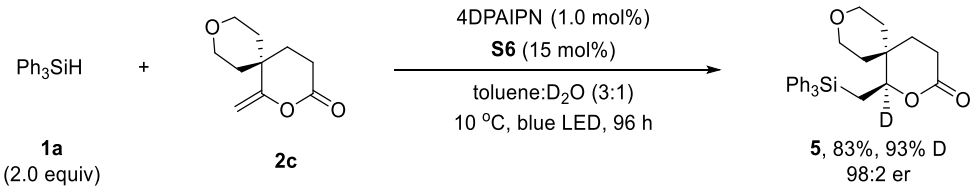
Figure S1. **Reaction setup.** (**A**) 8-mL vial used for the reaction. (**B**) 30 W blue LED (λ = 441 nm) used for the reaction. (**C**) A custom-made cooling station, connected to a chiller to maintain the reaction temperature at 10 °C. (**D**) Reaction setup (covered by a cardboard box when the light is on).

The following compounds **4**-**35** were prepared according to the above **Typical Procedure** unless otherwise stated. All the racemic samples for HPLC measurement were also prepared according to this procedure but using Ph_3SiSH or CySH instead of a chiral thiol catalyst.

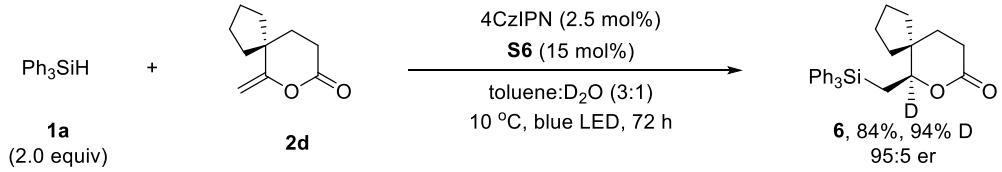


The reaction of 4DPAIPN (2.0 mg, 0.002 mmol), **1a** (104.4 mg, 0.4 mmol), **2b** (36.3 mg, 0.2 mmol), **S6** (21.9 mg, 0.03 mmol), toluene (1.5 mL) and D_2O (0.5 mL) afforded **4** (74.8 mg,

84%, 95% D) (eluent: petroleum ether/ethtyl acetate = 5/1) as a colorless foamy solid: 96:4 er (HPLC conditions: Chiralcel OD-H column, hexane/*i*-PrOH = 98.5/1.5, 1.0 mL/min, λ = 214 nm, t_R (major) = 11.8 min, t_R (minor) = 13.3 min); $[\alpha]_D^{25}$ = -65.3 (*c* = 0.21, $CHCl_3$); **m.p.** 99-101 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.64-7.51 (m, 6 H), 7.47-7.28 (m, 9 H), 4.16 (dd, J_1 = 11.4 Hz, J_2 = 2.2 Hz, 0.05 H), 2.46-2.14 (m, 2 H), 1.95-1.75 (m, 2 H), 1.70-1.05 (m, 12 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 171.3, 135.9, 134.4, 129.5, 127.9, 35.9, 33.3, 29.2, 26.7, 26.4, 26.0, 21.3, 20.9, 14.4; **HRMS** (ESI) calcd for $C_{29}H_{31}DNaO_2Si$ [M+Na$^+$]: 464.2127, found: 464.2126.

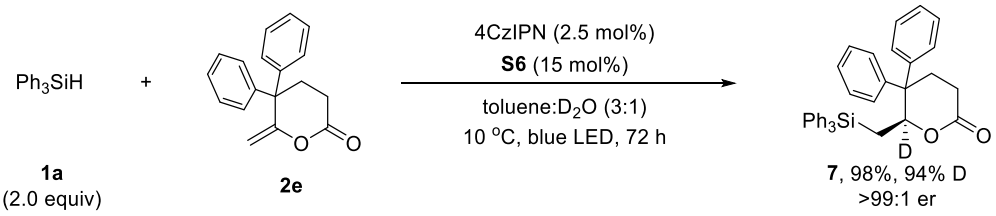


The reaction of 4DPAIPN (2.0 mg, 0.002 mmol), **1a** (104.7 mg, 0.4 mmol), **2c** (37.1 mg, 0.2 mmol), **S6** (22.2 mg, 0.03 mmol), toluene (1.5 mL) and D_2O (0.5 mL) afforded **5** (74.7 mg, 83%, 93% D) (eluent: petroleum ether/ethyl acetate = 3/2) as a colorless foamy solid: 98:2 er (HPLC conditions: Chiralcel AD-H column, hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 214 nm, t_R (minor) = 14.1 min, t_R (major) = 15.3 min); $[\alpha]_D^{25}$ = -62.4 (*c* = 0.21, $CHCl_3$); **m.p.** 139-141 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.67-7.53 (m, 6 H), 7.47-7.32 (m, 9 H), 4.17 (dd, J_1 = 11.6 Hz, J_2 = 2.4 Hz, 0.07 H), 3.87-3.72 (m, 2 H), 3.61-3.43 (m, 2 H), 2.46-2.26 (m, 2 H), 2.02-1.90 (m, 1 H), 1.87-1.72 (m, 3 H), 1.71-1.56 (m, 2 H), 1.37-1.28 (m, 1 H), 1.20-1.10 (m, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 170.7, 135.7, 134.1, 129.6, 127.9, 83.4 (t, J_{C-D} = 22.2 Hz), 63.1, 63.0, 34.2, 33.2, 30.2, 26.3, 25.7, 14.3; **HRMS** (ESI) calcd for $C_{28}H_{29}DNaO_3Si$ [M+Na$^+$]: 466.1919, found: 466.1917.



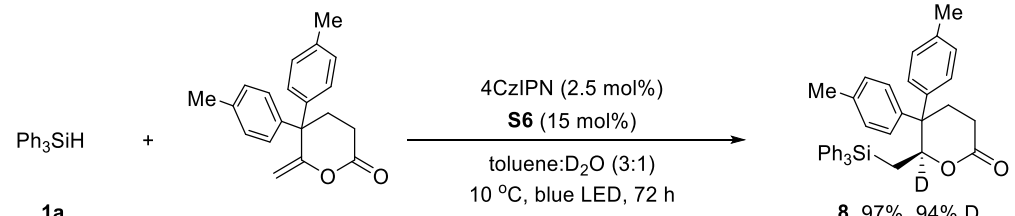
The reaction of 4CzIPN (4.1 mg, 0.005 mmol), **1a** (104.2 mg, 0.4 mmol), **2d** (33.4 mg, 0.2 mmol), **S6** (22.1 mg, 0.03 mmol), toluene (1.5 mL) and D_2O (0.5 mL) afforded **6** (72.0 mg, 84%, 94% D) (eluent: petroleum ether/DCM/ether = 14/10/1) as a colorless solid: 95:5 er (HPLC conditions: Chiralcel AD-H column, hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 214 nm, t_R (major)

= 8.3 min, t_R (minor) = 9.0 min); $[\alpha]_D^{25}$ = -61.0 (*c* = 0.50, $CHCl_3$); **m.p.** 115-118 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.71-7.52 (m, 6 H), 7.49-7.32 (m, 9 H), 4.32 (dd, J_1 = 11.5 Hz, J_2 = 2.5 Hz, 0.06 H), 2.54-2.38 (m, 2 H), 1.90-1.78 (m, 2 H), 1.72-1.48 (m, 8 H), 1.42-1.32 (m, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 170.7, 135.9, 134.4, 129.6, 127.9, 45.1, 36.1, 32.4, 30.8, 27.5, 25.4, 25.0, 16.5; **HRMS** (ESI) calcd for $C_{28}H_{29}DNaO_2Si$ [M+Na^+]: 450.1970, found: 450.1971.



1a (2.0 equiv) **2e** **7**, 98%, 94% D, >99:1 er

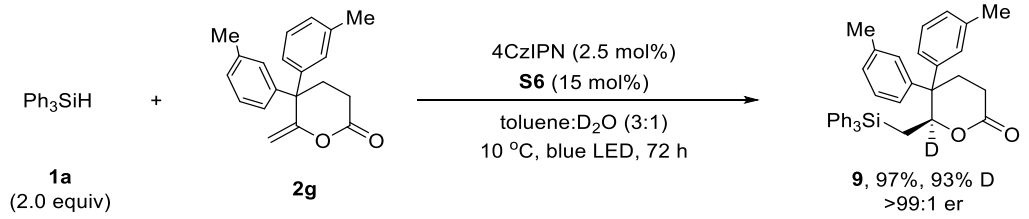
The reaction of 4CzIPN (4.2 mg, 0.005 mmol), **1a** (104.9 mg, 0.4 mmol), **2e** (53.9 mg, 0.2 mmol), **S6** (22.2 mg, 0.03 mmol), toluene (1.5 mL) and D_2O (0.5 mL) afforded **7** (105.2 mg, 98%, 94% D) (eluent: petroleum ether/DCM/ether = 14/10/1) as a colorless foamy solid: >99:1 er (HPLC conditions: Chiralcel OD-H column, hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 214 nm, t_R (major) = 6.7 min, t_R (minor) = 8.7 min); $[\alpha]_D^{25}$ = -192.0 (*c* = 0.50, $CHCl_3$); **m.p.** 72-74 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.51-7.10 (m, 23 H), 7.00 (d, *J* = 7.6 Hz, 2 H), 5.38 (d, *J* = 10.8 Hz, 0.06 H), 2.97-2.84 (m, 1 H), 2.56-2.40 (m, 2 H), 2.15-2.00 (m, 1 H), 1.75 (d, *J* = 15.2 Hz, 1 H), 1.25 (d, *J* = 15.2 Hz, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 169.0, 144.4, 143.8, 135.8, 134.0, 129.6, 128.7, 127.9, 127.6, 127.3, 126.8, 126.6, 49.1, 27.5, 26.5, 17.7; **HRMS** (ESI) calcd for $C_{36}H_{31}DNaO_2Si$ [M+Na^+]: 548.2127, found: 548.2125.



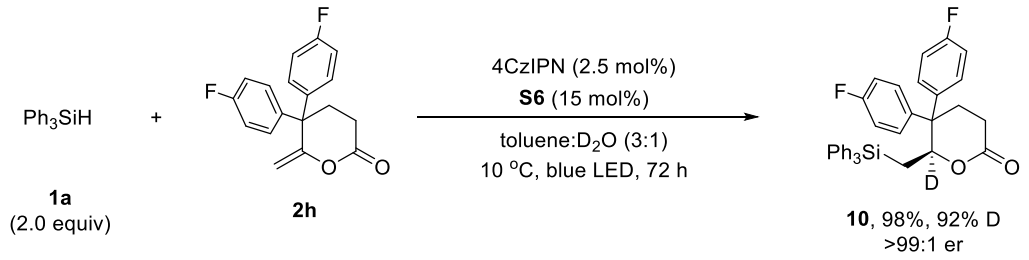
1a (2.0 equiv) **2f** **8**, 97%, 94% D, >99:1 er

The reaction of 4CzIPN (4.1 mg, 0.005 mmol), **1a** (105.3 mg, 0.4 mmol), **2f** (58.7 mg, 0.2 mmol), **S6** (22.2 mg, 0.03 mmol), toluene (1.5 mL) and D_2O (0.5 mL) afforded **8** (108.2 mg, 97%, 94% D) (eluent: petroleum ether/DCM/ether = 14/10/1) as a colorless foamy solid: >99:1 er (HPLC conditions: Chiralcel OD-H column, hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 214 nm, t_R (major) = 5.4 min, t_R (minor) = 7.3 min); $[\alpha]_D^{25}$ = -181.0 (*c* = 0.50, $CHCl_3$); **m.p.** 82-84 °C; **^{1}H**

NMR (400 MHz, $CDCl_3$) δ = 7.51-7.28 (m, 15 H), 7.08-6.97 (m, 6 H), 6.88 (d, *J* = 8.0 Hz, 2 H), 5.33 (d, *J* = 11.2 Hz, 0.06 H), 2.92-2.76 (m, 1 H), 2.52-2.36 (m, 2 H), 2.35-2.18 (m, 6 H), 2.16-2.00 (m, 1 H), 1.74 (d, *J* = 15.2 Hz, 1 H), 1.29 (d, *J* = 15.2 Hz, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 169.3, 141.5, 140.9, 136.2, 136.1, 135.8, 134.1, 129.5, 129.32, 129.30, 127.8, 127.4, 127.2, 81.6 (t, $J_{C\text{-}D}$ = 18.4 Hz), 48.4, 27.5, 26.6, 20.9, 20.8, 17.6; **HRMS** (ESI) calcd for $C_{38}H_{35}DNaO_2Si$ [M+Na^+]: 576.2440, found: 576.2434.

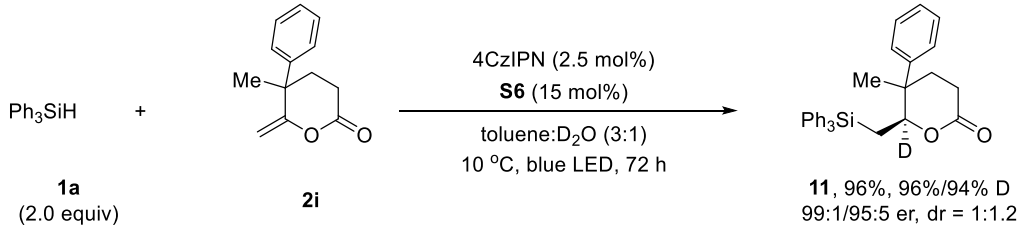


The reaction of 4CzIPN (4.5 mg, 0.005 mmol), **1a** (104.6 mg, 0.4 mmol), **2g** (59.2 mg, 0.2 mmol), **S6** (22.0 mg, 0.03 mmol), toluene (1.5 mL) and D_2O (0.5 mL) afforded **9** (109.3 mg, 97%, 93% D) (eluent: petroleum ether/DCM/ether = 14/10/1) as a colorless foamy solid: >99:1 er (HPLC conditions: Chiralcel OD-H column, hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 214 nm, t_R (major) = 6.6 min, t_R (minor) = 8.2 min); $[\alpha]_D^{25}$ = -169.6 (*c* = 0.50, $CHCl_3$); **m.p.** 78-82 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.50-7.28 (m, 15 H), 7.17-7.06 (m, 2 H), 7.04-6.91 (m, 4 H), 6.82 (d, *J* = 8.0 Hz, 1 H), 6.77 (s, 1 H), 5.35 (d, *J* = 11.6 Hz, 0.07 H), 2.92-2.76 (m, 1 H), 2.53-2.41 (m, 2 H), 2.30-2.17 (m, 6 H), 2.14-2.00 (m, 1 H), 1.72 (d, *J* = 15.2 Hz, 1 H), 1.25 (d, *J* = 15.2 Hz, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 169.3, 144.4, 143.7, 138.2, 138.1, 135.8, 134.1, 129.6, 128.51, 128.46, 128.1, 127.92, 127.86, 127.5, 127.4, 124.7, 124.3, 48.8, 27.6, 26.5, 21.64, 21.62, 17.6; **HRMS** (ESI) calcd for $C_{38}H_{35}DNaO_2Si$ [M+Na^+]: 576.2440, found: 576.2437.



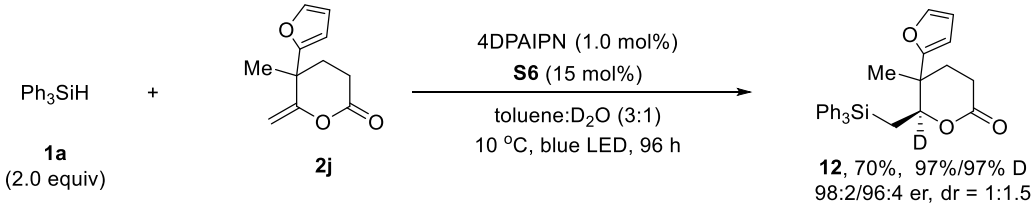
The reaction of 4CzIPN (4.2 mg, 0.005 mmol), **1a** (104.3 mg, 0.4 mmol), **2h** (60.5 mg, 0.2 mmol), **S6** (22.3 mg, 0.03 mmol), toluene (1.5 mL) and D_2O (0.5 mL) afforded **10** (111.2 mg, 98%, 92% D) (eluent: petroleum ether/DCM/ ether = 14/10/1) as a colorless foamy solid: >99:1

er (HPLC conditions: Chiralcel OD-H column, hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 214 nm, t_R (major) = 10.0 min, t_R (minor) = 11.2 min); $[\alpha]_D^{25}$ = -149.8 (*c* = 0.51, $CHCl_3$); **m.p.** 97-102 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.50-7.28 (m, 15 H), 7.17-7.06 (m, 2 H), 6.99-6.85 (m, 6 H), 5.28 (d, *J* = 11.2 Hz, 0.08 H), 2.97-2.77 (m, 1 H), 2.56-2.34 (m, 2 H), 2.20-1.96 (m, 1 H), 1.74 (d, *J* = 15.2 Hz, 1 H), 1.22 (d, *J* = 15.2 Hz, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 168.5, 162.6 (d, J_{C-F} = 6.6 Hz), 160.1 (d, J_{C-F} = 6.4 Hz), 140.0 (d, J_{C-F} = 3.3 Hz), 139.3 (d, J_{C-F} = 3.2 Hz), 135.7, 133.7, 129.7, 129.3 (d, J_{C-F} = 7.8 Hz), 128.9 (d, J_{C-F} = 7.8 Hz), 127.9, 115.8 (d, J_{C-F} = 1.6 Hz), 115.5 (d, J_{C-F} = 1.5 Hz), 48.3, 27.3, 26.9, 17.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -115.0, -115.3; **HRMS** (ESI) calcd for $C_{36}H_{29}DF_2NaO_2Si$ [M+Na^+]: 584.1938, found: 584.1935.

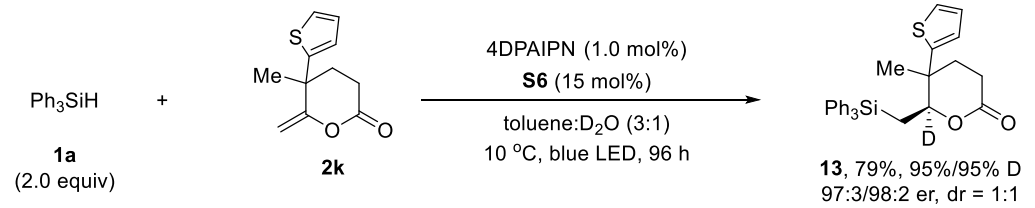


1a (2.0 equiv) **2i** **11**, 96%, 96%/94% D 99:1/95:5 er, dr = 1:1.2

The reaction of 4CzIPN (4.0 mg, 0.005 mmol), **1a** (104.4 mg, 0.4 mmol), **2i** (40.7 mg, 0.2 mmol), **S6** (21.9 mg, 0.03 mmol), toluene (1.5 mL) and D_2O (0.5 mL) afforded **11** (90.9 mg, 96%, 96%/94% D) (eluent: petroleum ether/DCM/ether = 14/10/1) as a colorless foamy solid: 99:1/95:5 er, dr = 1:1.2 (HPLC conditions: Chiralcel OD-H column, hexane/*i*-PrOH = 99.8/0.2, 1.0 mL/min, λ = 214 nm, t_1 = 39.0 min, t_2 = 41.5 min, t_3 = 45.5 min, t_4 = 50.3 min); $[\alpha]_D^{25}$ = -38.1 (*c* = 0.22, $CHCl_3$); **m.p.** 56-58 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.75-7.00 (m, 35.0 H), 4.68 (dd, J_1 = 11.4 Hz, J_2 = 1.0 Hz, 0.04 H), 4.47 (dd, J_1 = 11.4 Hz, J_2 = 2.2 Hz, 0.06 H), 2.66-2.38 (m, 3.5 H), 2.37-2.12 (m, 1.8 H), 2.02-1.87 (m, 1 H), 1.83-1.72 (m, 0.8 H), 1.69 (d, *J* = 15.2 Hz, 1 H), 1.58 (d, *J* = 15.2 Hz, 1 H), 1.44 (s, 2 H), 1.39-1.29 (m, 4 H), 1.23-1.15 (m, 0.8 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 171.3, 171.0, 145.1, 144.0, 135.78, 135.75, 134.19, 134.17, 129.51, 129.46, 128.7, 128.5, 127.80, 127.75, 126.8, 126.7, 126.6, 125.9, 84.3-82.6 (m), 40.9, 40.8, 35.0, 31.8, 28.0, 27.5, 25.3, 17.3, 16.2, 14.5; **HRMS** (ESI) calcd for $C_{31}H_{29}DNaO_2Si$ [M+Na^+]: 486.1970, found: 486.1962.

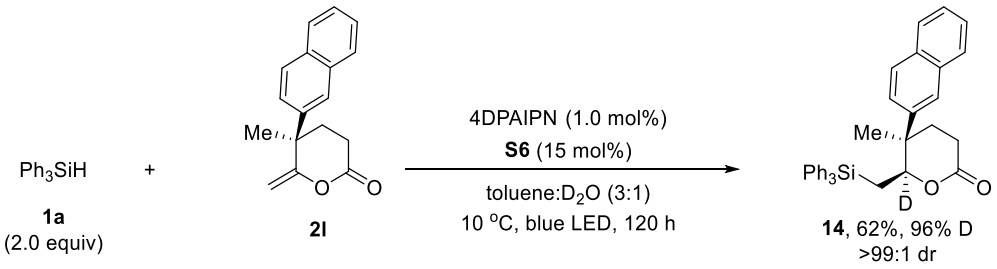


The reaction of 4DPAIPN (2.0 mg, 0.002 mmol), **1a** (104.7 mg, 0.4 mmol), **2j** (38.5 mg, 0.2 mmol), **S6** (21.1 mg, 0.03 mmol), toluene (1.5 mL) and D_2O (0.5 mL) for 96 hours afforded **12** (63.8 mg, 70%, 97%/97% D) (eluent: petroleum ether/DCM/ether = 14/10/1) as a colorless oil: 98:2/96:4 er, dr = 1:1.5 (HPLC conditions: Chiralcel AD-H column, hexane/*i*-PrOH = 99.2/0.8, 1 mL/min, λ = 214 nm, t_1 = 24.3 min, t_2 = 27.3 min, t_3 = 34.4 min, t_4 = 43.0 min); $[\alpha]_D^{25}$ = -50.0 (*c* = 0.24, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.17-6.97 (m, 35.0 H), 6.40-6.24 (m, 1.8 H), 6.16 (d, *J* = 3.2 Hz, 1 H), 6.12 (d, *J* = 3.2 Hz, 0.8 H), 4.69 (dd, J_1 = 11.4 Hz, J_2 = 1.4 Hz, 0.03 H), 4.31 (dd, J_1 = 11.4 Hz, J_2 = 2.6 Hz, 0.03 H), 2.70-2.24 (m, 5 H), 2.21-2.11 (m, 1 H), 1.85-1.64 (m, 4 H), 1.53 (d, *J* = 15.2 Hz, 1 H), 1.43-1.20 (m, 7 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 170.9, 170.7, 158.0, 156.4, 142.0, 141.8, 135.80, 135.78, 134.4, 134.2, 129.47, 129.46, 127.78, 127.77, 110.2, 109.9, 107.1, 106.1, 39.0, 38.9, 31.7, 31.6, 27.6, 27.2, 23.3, 16.5, 15.8, 14.8; **HRMS** (ESI) calcd for $C_{29}H_{27}DNaO_3Si$ [M+Na^+]: 476.1763, found: 476.1765.

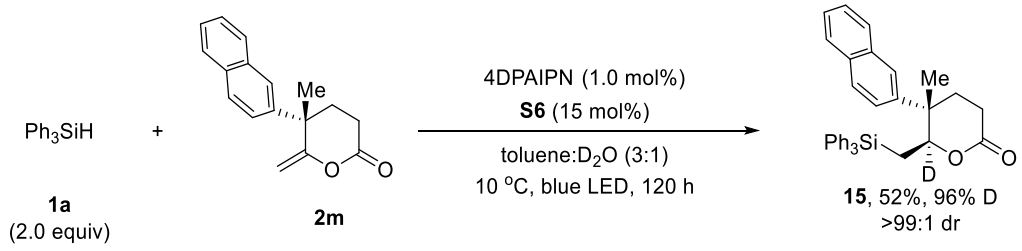


The reaction of 4DPAIPN (1.6 mg, 0.002 mmol), **1a** (104.5 mg, 0.4 mmol), **2k** (41.6 mg, 0.2 mmol), **S6** (21.8 mg, 0.03 mmol), toluene (1.5 mL) and D_2O (0.5 mL) for 96 hours afforded **13** (74.4 mg, 79%, 95%/95% D) (eluent: petroleum ether/DCM/ether = 14/10/1) as a colorless oil: 97:3/98:2 er, dr = 1:1 (HPLC conditions: Chiralcel AD-H column, hexane/*i*-PrOH = 99.5/0.5, 0.5 mL/min, λ = 190 nm, t_1 = 41.7 min, t_2 = 43.9 min, t_3 = 56.2 min, t_4 = 61.7 min); $[\alpha]_D^{25}$ = -47.0 (*c* = 0.22, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.60-7.26 (m, 30 H), 7.24-7.17 (m, 2 H), 7.00-6.92 (m, 2 H), 6.92-6.87 (m, 1 H), 6.84-6.79 (m, 1 H), 4.55 (dd, J_1 = 11.6 Hz, J_2 = 1.2 Hz, 0.05 H), 4.34 (dd, J_1 = 11.4 Hz, J_2 = 2.4 Hz, 0.05 H), 2.57-2.35 (m, 4 H), 2.26-2.10 (m, 2 H), 2.01-1.85 (m, 2 H), 1.80 (d, *J* = 15.2 Hz, 1 H), 1.73 (d, *J* = 15.2 Hz, 1 H), 1.60-1.34 (m, 8 H); **^{13}C**

NMR (101 MHz, $CDCl_3$) δ = 170.7, 170.4, 150.3, 147.2, 135.83, 135.81, 134.3, 134.2, 129.52, 129.49, 127.83, 127.78, 126.9, 126.8, 124.8, 124.0, 123.9, 123.7, 40.4, 40.2, 36.2, 34.4, 27.6, 26.8, 18.3, 15.7, 14.7; **HRMS** (ESI) calcd for $C_{29}H_{27}DNaO_2SSi$ [M+Na^+]: 492.1534, found: 492.1532.

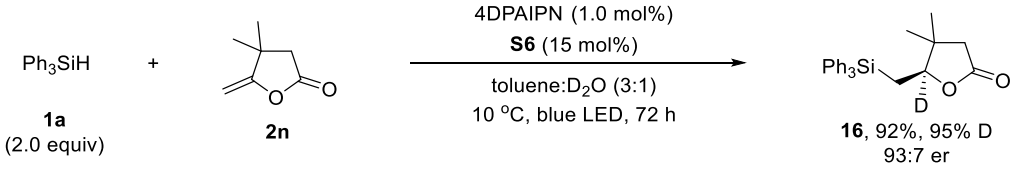


The reaction of 4DPAIPN (1.8 mg, 0.002 mmol), **1a** (104.6 mg, 0.4 mmol), (*R*)-**2l** (obtained via preparative HPLC, >99:1 er, 50.7 mg, 0.2 mmol), **S6** (21.6 mg, 0.03 mmol), toluene (1.5 mL) and D_2O (0.5 mL) for 120 hours afforded **14** (63.6 mg, 62%, 96% D) (eluent: petroleum ether/ethyl acetate = 5/1) as a colorless foamy solid: >99:1 dr (HPLC conditions: Chiralcel AD-H column, hexane/*i*-PrOH = 99.3/0.7, 0.5 mL/min, λ = 214 nm, t_1 (major) = 19.5 min, t_2 (minor) = 27.8 min); $[\alpha]_D^{25}$ = -62.5 (*c* = 0.11, $CHCl_3$); **m.p.** 71-73 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.99-7.64 (m, 4 H), 7.61-7.06 (m, 18 H), 4.57 (dd, J_1 = 11.4 Hz, J_2 = 2.2 Hz, 0.04 H), 2.66-2.27 (m, 3 H), 2.12-1.99 (m, 1 H), 1.65 (d, *J* = 15.2 Hz, 1 H), 1.51-1.30 (m, 4 H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 171.4, 141.6, 135.8, 134.2, 133.1, 132.1, 129.6, 128.4, 128.1, 127.9, 127.4, 126.2, 126.0, 125.3, 125.0, 41.1, 32.0, 27.6, 25.3, 16.4; **HRMS** (ESI) calcd for $C_{35}H_{31}DNaO_2Si$ [M+Na^+]: 536.2127, found: 536.2120.

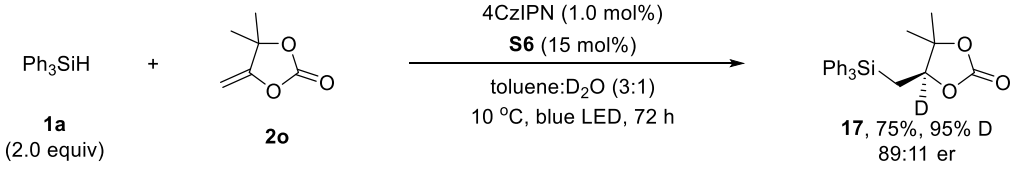


The reaction of 4DPAIPN (1.6 mg, 0.002 mmol), **1a** (104.7 mg, 0.4 mmol), (*S*)-**2m** (obtained via preparative HPLC, >99:1 er, 50.6 mg, 0.2 mmol), **S6** (21.8 mg, 0.03 mmol), toluene (1.5 mL) and D_2O (0.5 mL) for 120 hours afforded **15** (53.3 mg, 52%, 96% D) (eluent: petroleum ether/ethyl acetate = 5/1) as a colorless foamy solid: >99:1 dr (HPLC conditions:

Chiralcel AD-H column, hexane/*i*-PrOH = 99.3/0.7, 0.5 mL/min, λ = 214 nm, t_1 (minor) = 21.5 min, t_2 (major) = 32.1 min); $[\alpha]_D^{25}$ = +16.8 (*c* = 0.20, $CHCl_3$); **m.p.** 149-150 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.86-7.74 (m, 3 H), 7.69 (brs, 1 H), 7.54-7.46 (m, 2 H), 7.44-7.32 (m, 9 H), 7.31-7.22 (m, 7 H), 4.84 (d, *J* = 10.8 Hz, 0.04 H), 2.61-2.53 (m, 2 H), 2.40-2.28 (m, 1 H), 1.88-1.78 (m, 1 H), 1.74 (d, *J* = 15.2 Hz, 1 H), 1.57 (s, 3 H), 1.22 (d, *J* = 15.2 Hz, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 171.1, 142.5, 135.8, 134.2, 133.3, 132.1, 129.5, 128.6, 128.1, 127.8, 127.4, 126.4, 126.1, 125.1, 123.9, 41.2, 35.1, 28.1, 17.5, 14.7; **HRMS** (ESI) calcd for $C_{35}H_{31}DNaO_2Si$ [M+Na^+]: 536.2127, found: 536.2128.

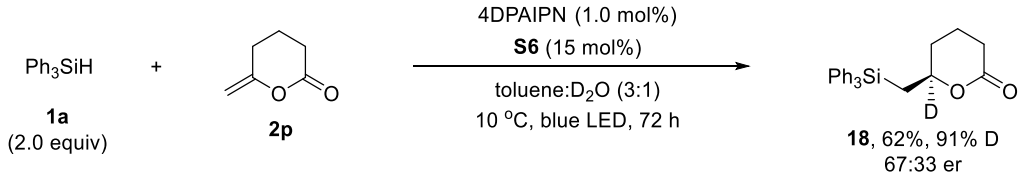


The reaction of 4DPAIPN (2.1 mg, 0.002 mmol), **1a** (105.2 mg, 0.4 mmol), **2n** (25.6 mg, 0.2 mmol), **S6** (21.6 mg, 0.03 mmol), toluene (1.5 mL) and D_2O (0.5 mL) afforded **16** (72.1 mg, 92%, 95% D) (eluent: petroleum ether/DCM/ether = 14/10/1) as a colorless solid: 93:7 er (HPLC conditions: Chiralcel AD-H column, hexane/*i*-PrOH = 98.5/1.5, 1.0 mL/min, λ = 214 nm, t_R (minor) = 10.2 min, t_R (major) = 19.5 min); $[\alpha]_D^{25}$ = -59.1 (*c* = 0.22, $CHCl_3$); **m.p.** 132-135 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.60-7.50 (m, 6 H), 7.47-7.32 (m, 9 H), 4.23 (dd, J_1 = 11.6 Hz, J_2 = 2.0 Hz, 0.05 H), 2.29 (s, 2 H), 1.76 (d, *J* = 15.2 Hz, 1 H), 1.51 (d, *J* = 15.2 Hz, 1 H), 1.08 (s, 3 H), 1.03 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 175.8, 135.8, 134.0, 129.7, 127.9, 85.5 (t, $J_{C\text{-}D}$ = 22.5 Hz), 44.3, 40.3, 24.5, 21.4, 13.4; **HRMS** (ESI) calcd for $C_{25}H_{25}DNaO_2Si$ [M+Na^+]: 410.1657, found: 410.1659.

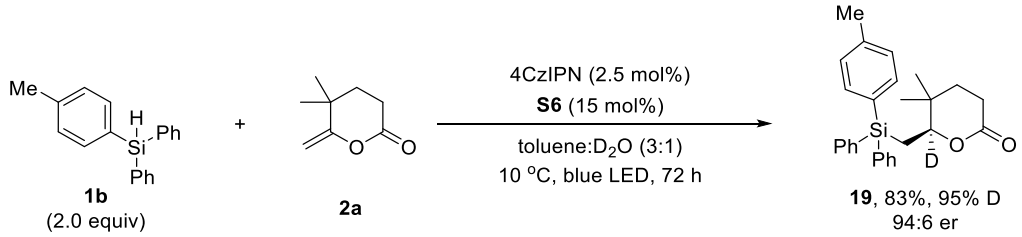


The reaction of 4CzIPN (1.9 mg, 0.002 mmol), **1a** (104.3 mg, 0.4 mmol), **2o** (27.0 mg, 0.2 mmol), **S6** (22.0 mg, 0.03 mmol), toluene (1.5 mL) and D_2O (0.5 mL) afforded **17** (61.9 mg, 75%, 95% D) (eluent: petroleum ether/DCM/ether = 14/10/1) as a white solid: 89:11 er (HPLC conditions: Chiralcel AD-H column, hexane/*i*-PrOH = 96/4, 1.0 mL/min, λ = 214 nm, t_R (minor)

= 7.9 min, t_R (major) = 13.2 min); $[\alpha]_D^{25}$ = -30.0 (*c* = 0.22, $CHCl_3$); **m.p.** 142-144 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.61-7.50 (m, 6 H), 7.48-7.35 (m, 9 H), 4.40 (dd, J_1 = 11.4 Hz, J_2 = 3.0 Hz, 0.05 H), 1.90 (d, *J* = 15.2 Hz, 1 H), 1.49 (d, *J* = 14.8 Hz, 1 H), 1.40 (s, 3 H), 1.33 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 153.7, 135.7, 133.2, 130.0, 128.1, 84.9, 82.8 (t, $J_{C\text{-}D}$ = 22.6 Hz), 25.1, 21.4, 14.1; **HRMS** (ESI) calcd for $C_{24}H_{23}DNaO_3Si$ [M+Na$^+$]: 412.1450, found: 412.1444.

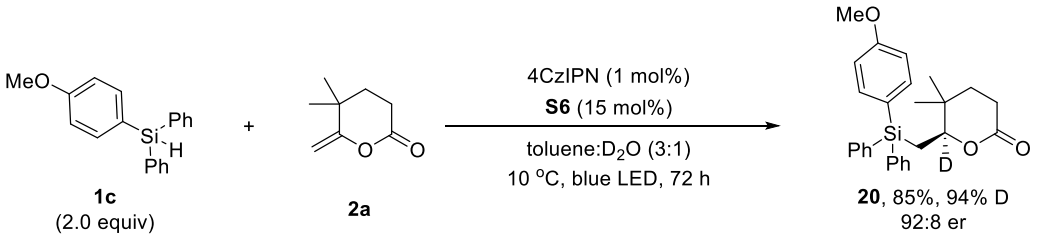


The reaction of 4DPAIPN (1.8 mg, 0.002 mmol), **1a** (106.5 mg, 0.4 mmol), **2p** (22.3 mg, 0.2 mmol), **S6** (22.7 mg, 0.03 mmol), toluene (1.5 mL) and D_2O (0.5 mL) afforded **18** (46.3 mg, 62%, 91% D) (eluent: petroleum ether/ethyl acetate = 5/1) as a white solid: 67:33 er (HPLC conditions: Chiralcel AD-H column, hexane/*i*-PrOH = 96/4, 1.0 mL/min, λ = 214 nm, t_R (minor) = 10.2 min, t_R (major) = 12.9 min); $[\alpha]_D^{25}$ = -6.88 (*c* = 0.16, $CHCl_3$); **m.p.** 81-83 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.60-7.50 (m, 6 H), 7.45-7.31 (m, 9 H), 4.53-4.40 (m, 0.10 H), 2.53-2.22 (m, 2 H), 2.11 (d, *J* = 14.8 Hz, 1 H), 1.87-1.52 (m, 4 H), 1.48-1.35 (m, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 171.6, 135.5, 134.0, 129.8, 128.0, 30.3, 29.1, 21.7, 18.5; **HRMS** (ESI) calcd for $C_{24}H_{23}DNaO_2Si$ [M+Na$^+$]: 396.1501, found: 396.1498.

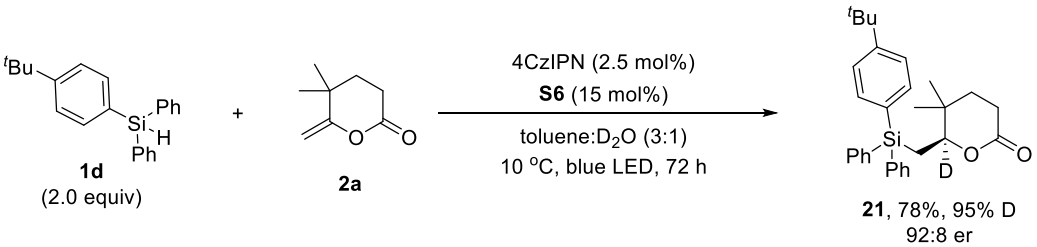


The reaction of 4CzIPN (4.0 mg, 0.005 mmol), **1b** (110.9 mg, 0.4 mmol), **2a** (28.3 mg, 0.2 mmol), **S6** (21.1 mg, 0.03 mmol), toluene (1.5 mL) and D_2O (0.5 mL) afforded **19** (69.0 mg, 83%, 95% D) (eluent: petroleum ether/DCM/ether = 14/10/1) as a colorless solid: 94:6 er (HPLC conditions: Chiralcel AD-H column, hexane/*i*-PrOH = 98/2, 1.0 mL/min, λ = 214 nm, t_R (minor) = 11.4 min, t_R (major) = 14.6 min); $[\alpha]_D^{25}$ = -66.3 (*c* = 0.51, $CHCl_3$); **m.p.** 83-84 °C; **^{1}H NMR**

(400 MHz, $CDCl_3$) δ = 7.63-7.54 (m, 4 H), 7.48 (d, J = 7.6 Hz, 2 H), 7.43-7.30 (m, 6 H), 7.19 (d, J = 7.6 Hz, 2 H), 4.10 (dd, J_1 = 11.6 Hz, J_2 = 2.4 Hz, 0.05 H), 2.53-2.27 (m, 5 H), 1.76 (d, J = 14.8 Hz, 1 H), 1.64-1.50 (m, 3 H), 0.99 (s, 3 H), 0.91 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 170.9, 139.4, 135.9, 135.8, 134.77, 134.76, 130.7, 129.4, 128.7, 127.8, 84.2 (t, $J_{C\text{-}D}$ = 22.6 Hz), 34.0, 32.9, 27.4, 26.5, 21.5, 19.3, 15.0; **HRMS** (ESI) calcd for $C_{27}H_{29}DNaO_2Si$ [M+Na^+]: 438.1970, found: 438.1974.

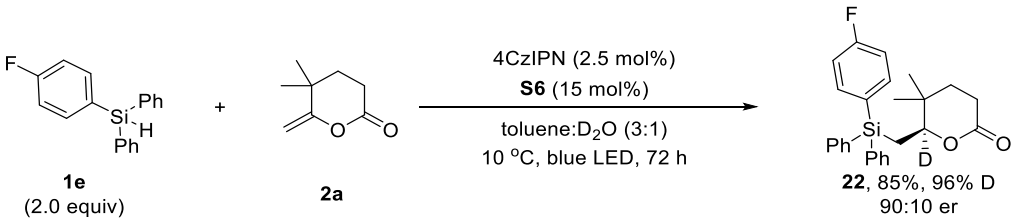


The reaction of 4CzIPN (1.8 mg, 0.002 mmol), **1c** (116.9 mg, 0.4 mmol), **2a** (28.6 mg, 0.2 mmol), **S6** (22.0 mg, 0.03 mmol), toluene (1.5 mL) and D_2O (0.5 mL) afforded **20** (74.5 mg, 85%, 94% D) (eluent: petroleum ether/DCM/ether = 14/10/1) as a colorless solid: 92:8 er (HPLC conditions: Chiralcel AD-H column, hexane/*i*-PrOH = 98/2, 1.0 mL/min, λ = 214 nm, t_R (minor) = 19.8 min, t_R (major) = 23.9 min); $[\alpha]_D^{25}$ = -57.0 (*c* = 0.50, $CHCl_3$); **m.p.** 80-82 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.64-7.46 (m, 6 H), 7.44-7.29 (m, 6 H), 6.92 (d, J = 8.4 Hz, 2 H), 4.10 (dd, J_1 = 11.6 Hz, J_2 = 2.0 Hz, 0.06 H), 3.80 (s, 3 H), 2.52-2.28 (m, 2 H), 1.75 (d, J = 14.8 Hz, 1 H), 1.66-1.48 (m, 3 H),1.00 (s, 3 H), 0.91 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 171.0, 160.7, 137.5, 135.8, 135.02, 134.95, 129.4, 127.8, 125.0, 113.6, 84.3 (t, $J_{C\text{-}D}$ = 22.6 Hz), 55.0, 34.0, 32.9, 27.4, 26.5, 19.3, 15.1; **HRMS** (ESI) calcd for $C_{27}H_{29}DNaO_3Si$ [M+Na^+]: 454.1919, found: 454.1920.

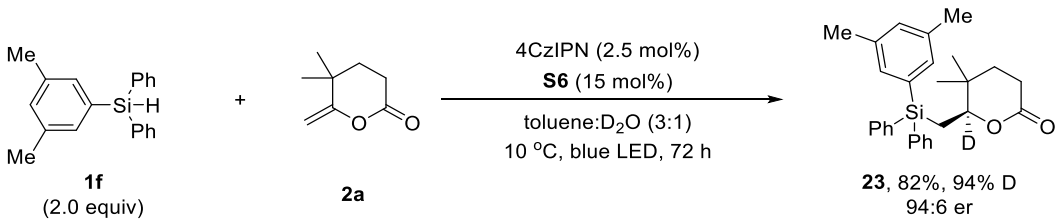


The reaction of 4CzIPN (4.2 mg, 0.005 mmol), **1d** (128.0 mg, 0.4 mmol), **2a** (28.6 mg, 0.2 mmol), **S6** (22.7 mg, 0.03 mmol), toluene (1.5 mL) and D_2O (0.5 mL) afforded **21** (73.0 mg,

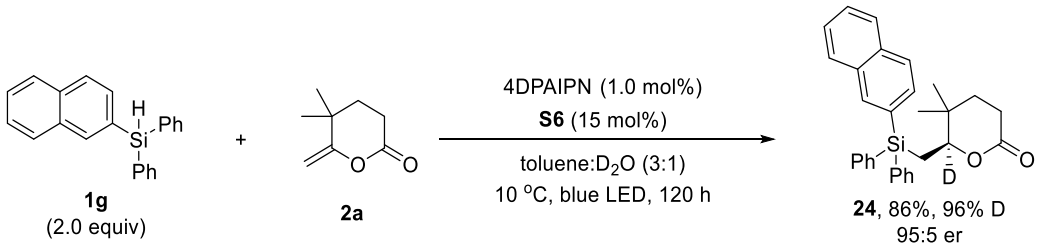
78%, 95% D) (eluent: petroleum ether/DCM/ether = 14/10/1) as a colorless solid: 92:8 er (HPLC conditions: Chiralcel AD-H column, hexane/*i*-PrOH = 98.5/1.5, 1.0 mL/min, λ = 214 nm, t_R (minor) = 7.5 min, t_R (major) = 9.8 min); $[\alpha]_D^{25}$ = -59.7 (*c* = 0.51, $CHCl_3$); **m.p.** 116-118 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.62-7.55 (m, 4 H), 7.54-7.49 (m, 2 H), 7.44-7.31 (m, 8 H), 4.11 (dd, J_1 = 11.4 Hz, J_2 = 2.2 Hz, 0.05 H), 2.50-2.30 (m, 2 H), 1.76 (d, *J* = 15.2 Hz, 1 H), 1.62-1.53 (m, 3 H), 1.32 (s, 9 H), 1.00 (s, 3 H), 0.91 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 171.0, 152.4, 135.9, 135.8, 135.7, 134.8, 134.7, 130.8, 129.4, 127.7, 124.8, 84.2 (t, J_{C-D} = 22.2 Hz), 34.6, 33.9, 32.9, 31.2, 27.4, 26.5, 19.3, 15.0; **HRMS** (ESI) calcd for $C_{30}H_{35}DNaO_2Si$ [M+Na$^+$]: 480.2440, found: 480.2440.



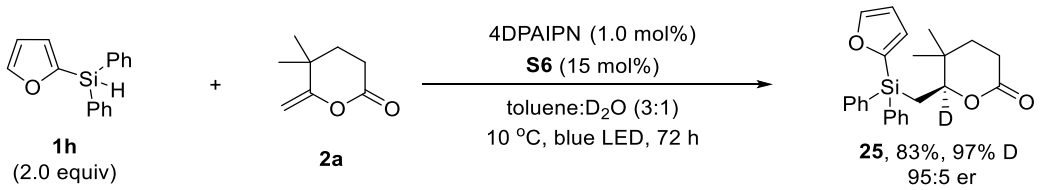
The reaction of 4CzIPN (4.2 mg, 0.005 mmol), **1e** (113.1 mg, 0.4 mmol), **2a** (28.7 mg, 0.2 mmol), **S6** (21.3 mg, 0.03 mmol), toluene (1.5 mL) and D_2O (0.5 mL) afforded **22** (71.0 mg, 85%, 96% D) (eluent: petroleum ether/DCM/ether = 14/10/1) as a colorless solid: 90:10 er (HPLC conditions: Chiralcel AD-H column, hexane/*i*-PrOH = 98/2, 1.0 mL/min, λ = 214 nm, t_R (minor) = 10.7 min, t_R (major) = 12.9 min); $[\alpha]_D^{25}$ = -61.2 (*c* = 0.50, $CHCl_3$); **m.p.** 97-99 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.80-7.30 (m, 12 H), 7.07 (t, *J* = 8.8 Hz, 2 H), 4.08 (dd, J_1 = 11.4 Hz, J_2 =2.2 Hz, 0.04 H), 2.60-2.20 (m, 2 H), 1.85-1.41 (m, 4 H), 1.10-0.79 (m, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 170.9, 164.0 (d, J_{C-F} = 247.7 Hz), 138.1, 138.0, 135.8, 135.7, 134.4 (d, J_{C-F} = 29.9 Hz), 129.9 (d, J_{C-F} = 3.7 Hz), 129.64, 129.62, 127.9, 115.1 (d, J_{C-F} = 19.6 Hz), 34.0, 32.9, 27.4, 26.5, 19.2, 15.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -111.1; **HRMS** (ESI) calcd for $C_{26}H_{26}DFNaO_2Si$ [M+Na$^+$]: 442.1719, found: 442.1714.



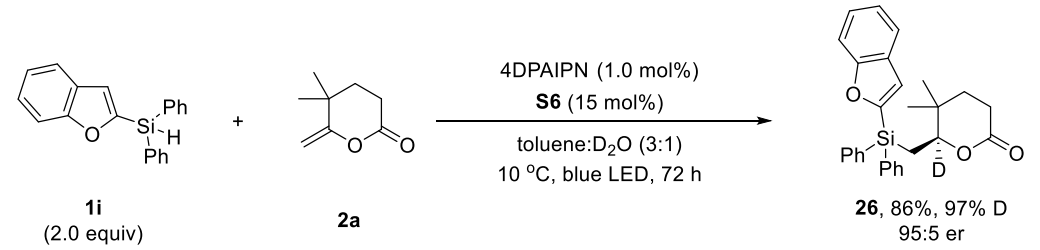
The reaction of 4CzIPN (4.1 mg, 0.005 mmol), **1f** (116.1 mg, 0.4 mmol), **2a** (28.1 mg, 0.2 mmol), **S6** (21.8 mg, 0.03 mmol), toluene (1.5 mL) and D_2O (0.5 mL) afforded **23** (71.0 mg, 82%, 94% D) (eluent: petroleum ether/DCM/ether = 14/10/1) as a colorless solid: 94:6 er (HPLC conditions: Chiralcel AD-H column, hexane/*i*-PrOH = 98/2, 1.0 mL/min, λ = 214 nm, t_R (minor) = 6.0 min, t_R (major) = 7.1 min); $[\alpha]_D^{25}$ = -53.2 (*c* = 0.22, $CHCl_3$); **m.p.** 78-79 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.63-7.53 (m, 4 H), 7.44-7.32 (m, 6 H), 7.18 (s, 2 H), 7.04 (s, 1 H), 4.10 (dd, J_1 = 11.4 Hz, J_2 = 2.2 Hz, 0.06 H), 2.50-2.22 (m, 8 H), 1.75 (d, *J* = 14.8 Hz, 1 H), 1.62-1.51 (m, 3 H), 1.00 (s, 3 H), 0.91 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 171.0, 137.1, 135.94, 135.91, 134.8, 134.6, 134.2, 133.5, 131.3, 129.41, 129.39, 127.8, 84.2 (t, $J_{C\text{-}D}$ = 22.6 Hz), 34.0, 33.0, 27.4, 26.5, 21.4, 19.4, 15.0; **HRMS** (ESI) calcd for $C_{28}H_{31}DNaO_2Si$ [M+Na^+]:452.2127, found: 452.2122.



The reaction of 4DPAIPN (2.1 mg, 0.002 mmol), **1g** (126.1 mg, 0.4 mmol), **2a** (29.0 mg, 0.2 mmol), **S6** (21.3 mg, 0.03 mmol), toluene (1.5 mL) and D_2O (0.5 mL) for 120 hours afforded **24** (80.1 mg, 86 %, 96% D) (eluent: petroleum ether/DCM/ether = 14/10/1) as a colorless solid: 95:5 er (HPLC conditions: Chiralcel AD-H column, hexane/*i*-PrOH = 95.5/4.5, 1.0 mL/min, λ = 214 nm, t_R(minor) = 10.7 min, t_R(major) = 12.8 min); $[\alpha]_D^{25}$ = -56.7 (*c* = 0.21, $CHCl_3$); **m.p.** 63-67 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.11 (s, 1 H), 7.88-7.73 (m, 3 H), 7.71-7.54 (m, 5 H), 7.53-7.29 (m, 8 H), 4.14 (dd, J_1 = 11.8 Hz, J_2 = 2.2 Hz, 0.04 H), 2.53-2.25 (m, 2 H), 1.86 (d, *J* = 15.2 Hz, 1 H), 1.72-1.46 (m, 3 H), 1.02 (s, 3 H), 0.92 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 170.9, 137.2, 135.93, 135.90, 134.53, 134.45, 133.8, 132.8, 131.9, 131.6, 129.6, 129.5, 128.4, 127.9, 127.6, 127.0, 126.7, 125.9, 34.0, 32.9, 27.4, 26.5, 19.2, 15.0; **HRMS** (ESI) calcd for $C_{30}H_{29}DNaO_2Si$ [M+Na^+]: 474.1970, found: 474.1963.

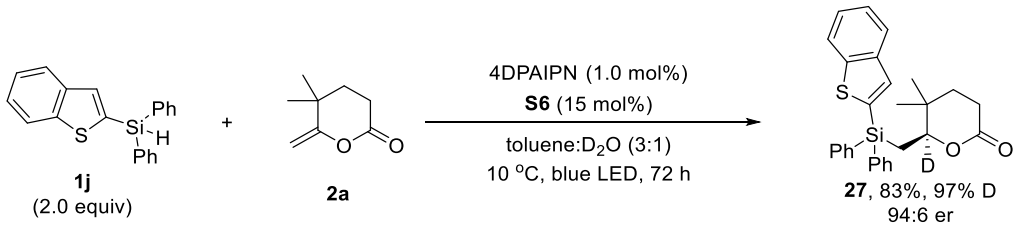


The reaction of 4DPAIPN (2.0 mg, 0.002 mmol), **1h** (100.9 mg, 0.4 mmol), **2a** (28.0 mg, 0.2 mmol), **S6** (21.1 mg, 0.03 mmol), toluene (1.5 mL) and D_2O (0.5 mL) afforded **25** (64.6 mg, 83%, 97% D) (eluent: petroleum ether/DCM/ether = 14/10/1) as a colorless solid: 95:5 er (HPLC conditions: Chiralcel AD-H column, hexane/*i*-PrOH = 98.7/1.3, 1.0 mL/min, λ = 214 nm, t_R (minor) = 17.0 min, t_R (major) = 18.5 min); $[\alpha]_D^{25}$ = -68.0 (*c* = 0.50, $CHCl_3$); **m.p.** 85-87 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.75 (d, *J* = 1.6 Hz, 1 H), 7.67-7.58 (m, 4 H), 7.46-7.32 (m, 6 H), 6.83 (d, *J* = 3.6 Hz, 1 H), 6.45 (dd, J_1 = 3.2 Hz, J_2 = 1.6 Hz, 1 H), 4.15 (dd, J_1 = 11.2 Hz, J_2 = 2.4 Hz, 0.03 H), 2.56-2.30 (m, 2 H), 1.71 (d, *J* = 15.2 Hz, 1 H), 1.65-1.54 (m, 3 H), 0.99 (s, 3 H), 0.93 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 171.0, 155.1, 147.8, 135.6, 135.5, 133.4, 133.3, 129.8, 127.90, 127.86, 124.1, 109.8, 84.0 (t, $J_{C\text{-}D}$ = 22.2 Hz), 33.9, 32.9, 27.4, 26.4, 19.3, 14.8; **HRMS** (ESI) calcd for $C_{24}H_{25}DNaO_3Si$ [M+Na^+]: 414.1606, found: 414.1607.

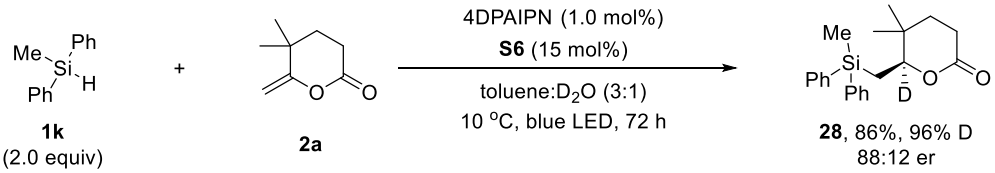


The reaction of 4DPAIPN (1.8 mg, 0.002 mmol), **1i** (120.7 mg, 0.4 mmol), **2a** (28.5 mg, 0.2 mmol), **S6** (21.7 mg, 0.03 mmol), toluene (1.5 mL) and D_2O (0.5 mL) afforded **26** (77.6 mg, 86%, 97% D) (eluent: petroleum ether/DCM/ether = 14/10/1) as a colorless solid: 95:5 er (HPLC conditions: Chiralcel AD-H column, hexane/*i*-PrOH = 98/2, 1.0 mL/min, λ = 214 nm, t_R (minor) = 34.0 min, t_R (major) = 37.3 min); $[\alpha]_D^{25}$ = -66.4 (*c* = 0.50, $CHCl_3$); **m.p.** 98-100 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.77-7.61 (m, 4 H), 7.58 (d, *J* = 7.6 Hz, 1 H), 7.52 (d, *J* = 8.0 Hz, 1 H), 7.48-7.35 (m, 6 H), 7.32-7.26 (m, 1 H), 7.24-7.17 (m, 1 H), 7.12 (s, 1 H), 4.20 (dd, J_1 = 11.2 Hz, J_2 = 2.8 Hz, 0.03 H), 2.52-2.32 (m, 2 H), 1.80 (d, *J* = 14.8 Hz, 1 H), 1.69 (d, *J* = 15.2 Hz, 1 H), 1.64-1.56 (m, 2 H), 1.01 (s, 3 H), 0.95 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 170.8, 158.7, 158.5, 135.8, 135.6, 132.8, 132.5, 130.00, 129.98, 128.0, 127.9, 127.8, 124.7, 122.5, 121.4, 120.6,

111.4, 84.0 (t, $J_{C\text{-}D}$ = 22.3 Hz), 33.9, 32.9, 27.4, 26.4, 19.2, 14.7; **HRMS** (ESI) calcd for $C_{28}H_{27}DNaO_3Si$ [M+Na$^+$]: 464.1763, found: 464.1763.

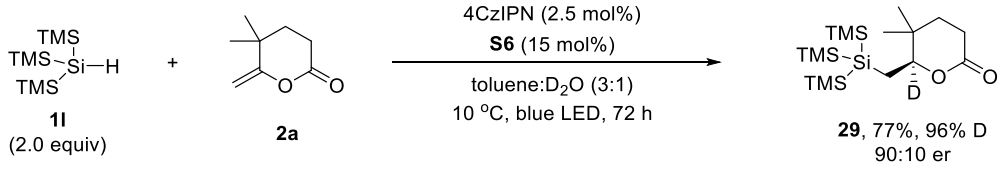


The reaction of 4DPAIPN (1.9 mg, 0.002 mmol), **1j** (126.0 mg, 0.4 mmol), **2a** (28.1 mg, 0.2 mmol), **S6** (22.0 mg, 0.03 mmol), toluene (1.5 mL) and D_2O (0.5 mL) afforded **27** (76.5 mg, 83%, 97% D) (eluent: petroleum ether/DCM/ether = 14/10/1) as a colorless solid: 94:6 er (HPLC conditions: Chiralcel AD-H column, hexane/*i*-PrOH = 97/3, 1.0 mL/min, λ = 214 nm, t_R (minor) = 29.7 min, t_R (major) = 31.7 min); $[\alpha]_D^{25}$ = -46.6 (*c* = 0.50, $CHCl_3$); **m.p.** 99-100 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.92-7.75 (m, 2 H), 7.73-7.64 (m, 4 H), 7.62 (s, 1 H), 7.52-7.28 (m, 8 H), 4.21 (dd, J_1 = 11.8 Hz, J_2 = 2.6 Hz, 0.03 H), 2.53-2.35 (m, 2 H), 1.84 (d, *J* = 15.2 Hz, 1 H), 1.72-1.49 (m, 3 H), 1.02 (s, 3 H), 0.95 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 170.7, 144.3, 140.9, 136.2, 135.7, 135.6, 135.3, 133.73, 133.72, 129.91, 129.88, 127.92, 127.89, 124.5, 124.0, 123.9, 122.1, 84.1 (t, $J_{C\text{-}D}$ = 22.0 Hz), 34.0, 32.9, 27.4, 26.4, 19.1, 15.8; **HRMS** (ESI) calcd for $C_{28}H_{27}DNaO_2SSi$ [M+Na$^+$]: 480.1534, found: 480.1537.

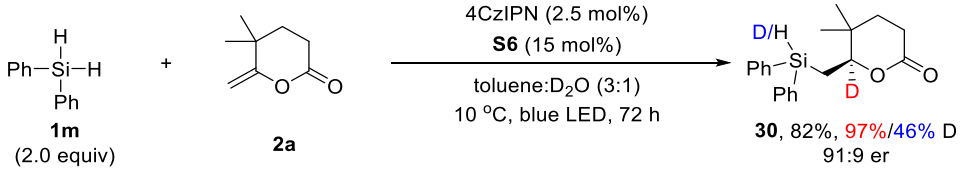


The reaction of 4DPAIPN (1.9 mg, 0.002 mmol), **1k** (80.3 mg, 0.4 mmol), **2a** (28.3 mg, 0.2 mmol), **S6** (22.1 mg, 0.03 mmol), toluene (1.5 mL) and D_2O (0.5 mL) afforded **28** (58.7 mg, 86%, 96% D) (eluent: petroleum ether/DCM/ether = 14/10/1) as a colorless oil: 88:12 er (HPLC conditions: Chiralcel AD-H column, hexane/*i*-PrOH = 99.5/0.5, 1.0 mL/min, λ = 214 nm, t_R (minor) = 25.7 min, t_R (major) = 31.3 min); $[\alpha]_D^{25}$ = -79.3 (*c* = 0.22, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.64-7.47 (m, 4 H), 7.46-7.27 (m, 6 H), 4.09-4.03 (m, 0.04 H), 2.54-2.38 (m, 2 H), 1.67-1.53 (m, 2 H), 1.35 (s, 2 H), 0.97 (s, 3 H), 0.92 (s, 3 H), 0.75 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 171.3, 137.2, 135.8, 134.7, 134.4, 129.3, 129.2, 127.9, 127.8, 84.9 (t, $J_{C\text{-}D}$ = 21.9 Hz),

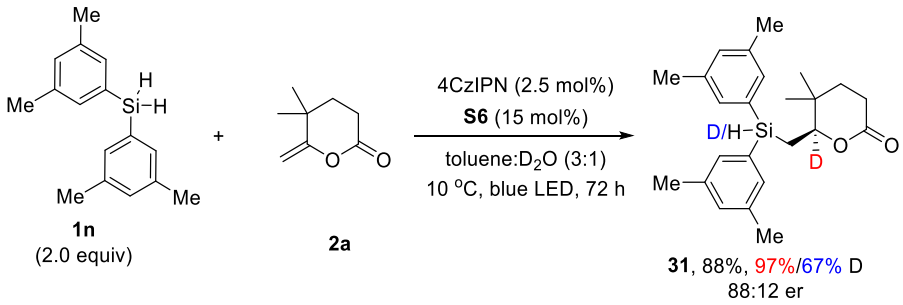
33.9, 32.8, 27.4, 26.4, 19.2, 15.5, -3.1; **HRMS** (ESI) calcd for $C_{21}H_{25}DNaO_2Si$ [M+Na$^+$]: 362.1657, found: 362.1655.



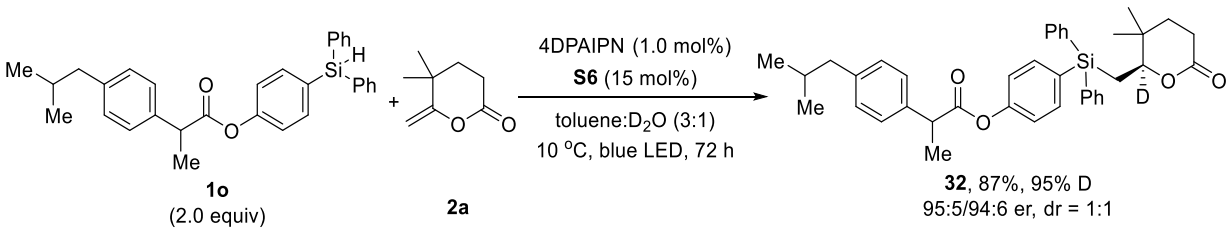
The reaction of 4CzIPN (4.3 mg, 0.005 mmol), **1l** (62.7 mg, 0.26 mmol), **2a** (28.2 mg, 0.2 mmol), **S6** (23.0 mg, 0.03 mmol), toluene (1.5 mL) and D_2O (0.5 mL) afforded **29** (59.8 mg, 77%, 96% D) (eluent: petroleum ether/ethyl acetate = 20/1) as a colorless solid: 90:10 er (HPLC conditions: Chiralcel OD-H column, hexane/*i*-PrOH = 99.3/0.7, 0.5 mL/min, λ = 214 nm, t_R (minor) = 8.7 min, t_R (major) = 9.1 min); $[\alpha]_D^{25}$ = -57.8 (*c* = 0.50, $CHCl_3$); **m.p.** 61-62 ℃, **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 4.02 (dd, J_1 = 11.6 Hz, J_2 = 2.4 Hz, 0.04 H), 2.60-2.42 (m, 2 H), 1.76-1.50 (m, 2 H), 1.10-0.96 (m, 5 H), 0.92 (s, 3 H), 0.20 (s, 27 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 171.3, 86.9 (t, J_{C-D} = 22.4 Hz), 34.5, 33.5, 27.7, 26.9, 18.7, 8.7, 1.1; **HRMS** (ESI) calcd for $C_{17}H_{39}DNaO_2Si_4$ [M+Na$^+$]:412.2060, found: 412.2054.



The reaction of 4CzIPN (4.1 mg, 0.005 mmol), **1m** (75.1 mg, 0.4 mmol), **2a** (28.2 mg, 0.2 mmol), **S6** (22.2 mg, 0.03 mmol), toluene (1.5 mL) and D_2O (0.5 mL) afforded **30** (53.8 mg, 82%, 97/46% D) (eluent: petroleum ether/DCM/ether = 14/10/1) as a colorless solid: 91:9 er (HPLC conditions: Chiralcel OJ-H column, hexane/*i*-PrOH = 98.5/1.5, 1.0 mL/min, λ = 214 nm, t_R (major) = 19.8 min, t_R (minor) = 25.0 min); $[\alpha]_D^{25}$ = -91.8 (*c* = 0.27, $CHCl_3$); **m.p.** 43-44 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.70-7.52 (m, 4 H), 7.47-7.29 (m, 6 H), 5.08 (dd, J_1 = 5.0 Hz, J_2 = 2.2 Hz, 0.54 H), 4.11 (dd, J_1 = 11.2 Hz, J_2 = 3.2 Hz, 0.03 H), 2.57-2.40 (m, 2 H), 1.61 (t, *J* = 7.4 Hz, 2 H), 1.53-1.35 (m, 2 H), 1.04-0.87 (m, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 171.2, 135.3, 135.1, 133.7, 133.3, 129.74, 129.67, 128.1, 128.0, 84.7 (t, J_{C-D} = 22.3 Hz), 33.9, 32.8, 27.4, 26.4, 19.0, 14.3, 14.2; **HRMS** (ESI) calcd for $C_{20}H_{23}DNaO_2Si$ [M+Na$^+$]: 348.1501, found: 348.1497.

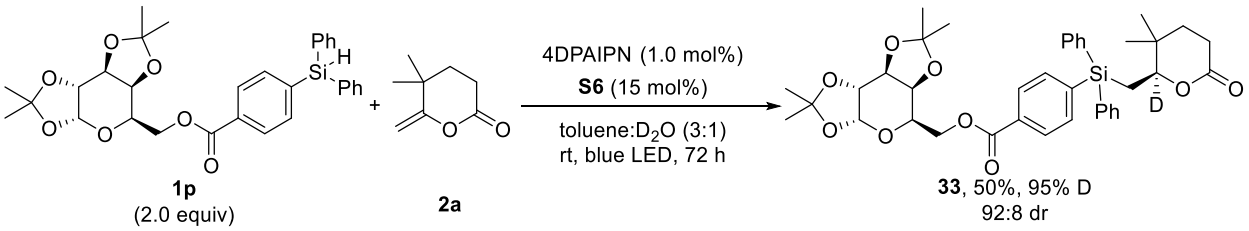


The reaction of 4CzIPN (4.1 mg, 0.005 mmol), **1n** (95.7 mg, 0.4 mmol), **2a** (28.7 mg, 0.2 mmol), **S6** (22.1 mg, 0.03 mmol), toluene (1.5 mL) and D_2O (0.5 mL) afforded **31** (68.8 mg, 88%, 97%/67% D) (eluent: petroleum ether/DCM/ether = 14/10/1) as a colorless solid: 88:12 er (HPLC conditions: Chiralcel AD-H column, hexane/*i*-PrOH = 99/1, 1.0 mL/min, λ = 214 nm, t_R (major) = 7.4 min, t_R (minor) = 8.5 min); $[\alpha]_D^{25}$ = -69.2 (*c* = 0.51, $CHCl_3$); **m.p.** 74-75 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.24 (s, 2 H), 7.18 (s, 2 H), 7.03 (d, *J* = 9.6 Hz, 2 H), 4.99 (dd, J_1 = 4.8 Hz, J_2 = 2.4 Hz, 0.33 H), 4.11 (dd, J_1 = 10.0 Hz, J_2 = 4.0 Hz, 0.03 H), 2.53-2.44 (m, 2 H), 2.39-2.22 (m, 12 H), 1.62 (t, *J* = 7.2 Hz, 2 H), 1.50-1.30 (m, 2 H), 1.03-0.89 (m, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 171.4, 137.42, 137.36, 133.81, 133.78, 133.2, 133.1, 132.8, 131.6, 131.5, 84.8 (t, J_{C-D} = 22.2 Hz), 34.0, 33.0, 27.5, 26.5, 21.39, 21.36, 19.3, 14.5, 14.4; **HRMS** (ESI) calcd for $C_{24}H_{30}D_2NaO_2Si$ [M+Na$^+$]: 405.2189, found: 405.2182.

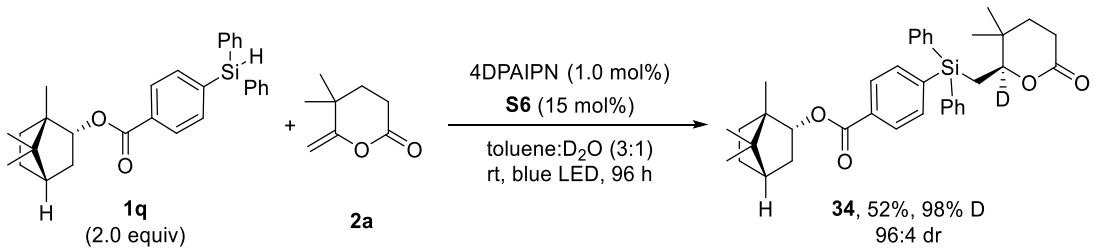


The reaction of 4DPAIPN (2.1 mg, 0.002 mmol), **1o** (186.3 mg, 0.4 mmol), **2a** (28.1 mg, 0.2 mmol), **S6** (22.1 mg, 0.03 mmol), toluene (1.5 mL) and D_2O (0.5 mL) afforded **32** (105.6 mg, 87%, 95% D) (eluent: petroleum ether/DCM/ether = 14/10/1) as a colorless oil: 95:5/94:6 er, dr = 1:1 (HPLC conditions: Chiralcel IC-H column, hexane/*i*-PrOH = 90/10, 0.5 mL/min, λ = 214 nm, t_1 = 25.7 min, t_2 = 28.9 min, t_3 = 30.3 min, t_4 = 34.3 min); $[\alpha]_D^{25}$ = -39.2 (*c* = 0.26, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.62-7.47 (m, 6 H), 7.45-7.32 (m, 6 H), 7.29 (d, *J* = 8.0 Hz, 2 H), 7.13 (d, *J* = 8.0 Hz, 2 H), 7.01 (d, *J* = 8.4 Hz, 2 H), 4.07 (dd, J_1 = 11.6 Hz, J_2 = 2.0 Hz, 0.05 H), 3.93 (q, *J* = 7.2 Hz, 1 H), 2.56-2.24 (m, 4 H), 1.93-1.80 (m, 1 H), 1.75 (d, *J* = 14.8 Hz, 1 H),

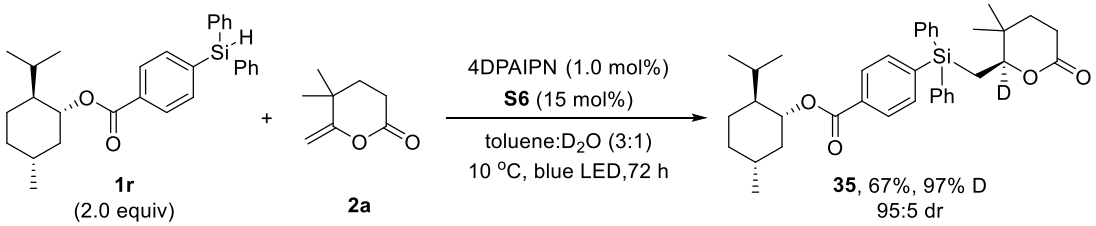
1.65-1.44 (m, 6 H), 0.99 (s, 3 H), 0.94-0.81 (m, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 173.1, 170.9, 152.1, 140.8, 137.2, 137.1, 135.8, 134.29, 134.27, 131.8, 129.6, 129.5, 127.9, 127.1, 120.9, 84.2 (t, $J_{C\text{-}D}$ = 22.3 Hz), 45.2, 45.0, 33.9, 32.9, 30.1, 27.4, 26.5, 22.4, 19.2, 18.4, 14.9; **HRMS** (ESI) calcd for $C_{39}H_{43}DNaO_4Si$ [M+Na$^+$]: 628.2964, found: 628.2957.



The reaction of 4DPAIPN (1.9 mg, 0.002 mmol), **1p** (206.1 mg, 0.4 mmol), **2a** (28.0 mg, 0.2 mmol), **S6** (21.2 mg, 0.03 mmol), toluene (1.5 mL) and D_2O (0.5 mL) under room temperature afforded **33** (68.6 mg, 50%, 95% D) (eluent: petroleum ether/ethyl acetate = 7/3) as a colorless oil: 92:8 dr (HPLC conditions: Chiralcel AD-H column, hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 214 nm, t_1 (minor) = 9.6 min, t_2 (major) = 14.2 min); $[\alpha]_D^{25}$ = -62.5 (*c* = 0.12, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.02 (d, *J* = 8.4 Hz, 2 H), 7.67 (d, *J* = 8.4 Hz, 2 H), 7.60-7.50 (m, 4 H), 7.47-7.33 (m, 6 H), 5.56 (d, *J* = 4.8 Hz, 1 H), 4.65 (dd, J_1 = 7.8 Hz, J_2 = 2.6 Hz, 1 H), 4.54-4.40 (m, 2 H), 4.38-4.30 (m, 2 H), 4.22-4.14 (m, 1 H), 4.09 (dd, J_1 = 14.2 Hz, J_2 = 2.6 Hz, 0.05 H), 2.52-2.30 (m, 2 H), 1.81 (d, *J* = 15.2 Hz, 1 H), 1.64-1.55 (m, 3 H), 1.52 (s, 3 H), 1.48 (s, 3 H), 1.39-1.30 (m, 6 H), 1.02 (s, 3 H), 0.93 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 170.7, 166.5, 141.1, 135.85, 135.82, 135.81, 133.8, 133.7, 130.8, 129.7, 128.6, 128.0, 109.6, 108.8, 96.3, 84.4 (t, $J_{C\text{-}D}$ = 21.6 Hz), 71.0, 70.7, 70.5, 66.0, 63.8, 34.0, 32.9, 27.4, 26.5, 26.0, 25.9, 24.9, 24.5, 19.1, 14.8; **HRMS** (ESI) calcd for $C_{39}H_{45}DNaO_9Si$ [M+Na$^+$]: 710.2866, found: 710.2866.



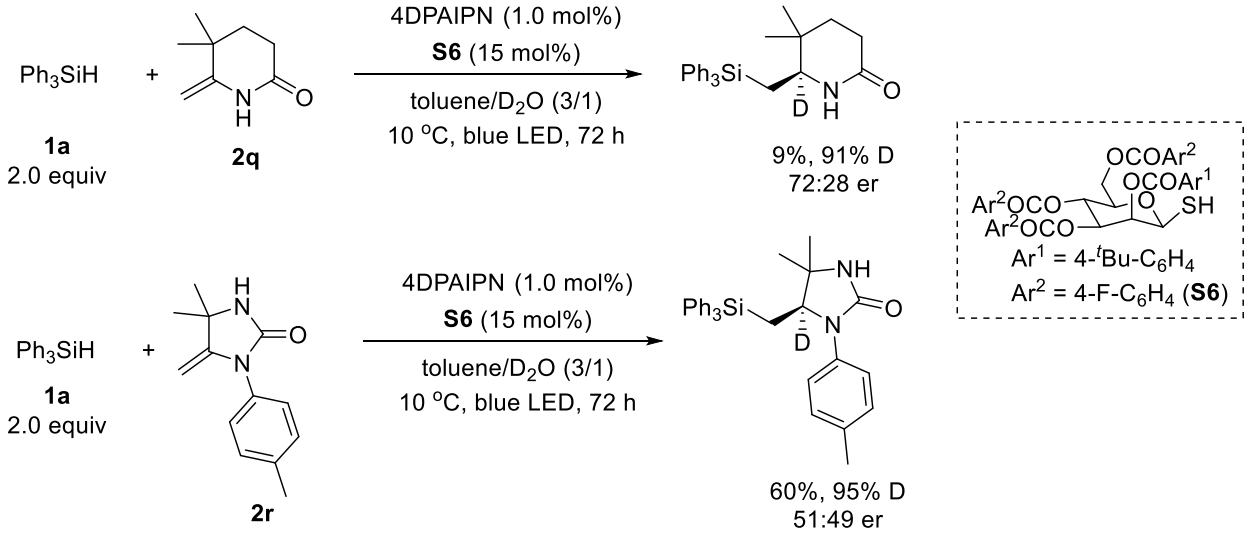
The reaction of 4DPAIPN (2.0 mg, 0.002 mmol), **1q** (167.6 mg, 0.4 mmol), **2a** (28.6 mg, 0.2 mmol), **S6** (22.0 mg, 0.03 mmol), toluene (1.5 mL) and D_2O (0.5 mL) for 96 hours under room temperature afforded **34** (55.5 mg, 52%, 98% D) (eluent: petroleum ether/ethyl acetate = 5/1) as a colorless oil: 96:4 dr (HPLC conditions: Chiralcel AD-H column, hexane/*i*-PrOH = 98/2, 1.0 mL/min, λ = 214 nm, t_1 (minor) = 15.4 min, t_2 (major) = 17.2 min); $[\alpha]_D^{25}$ = -46.6 (*c* = 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.04 (d, *J* = 8.0 Hz, 2 H), 7.69 (d, *J* = 8.0 Hz, 2 H), 7.61-7.51 (m, 4 H), 7.47-7.32 (m, 6 H), 5.15-5.07 (m, 1 H), 4.10 (dd, J_1 = 11.4 Hz, J_2 = 2.6 Hz, 0.02 H), 2.53-2.33 (m, 3 H), 2.17-2.06 (m, 1 H), 1.82 (d, *J* = 15.2 Hz, 1 H), 1.73 (t, *J* = 8.8 Hz, 1 H), 1.67-1.53 (m, 3 H), 1.46-1.20 (m, 3 H), 1.11 (dd, J_1 = 13.8 Hz, J_2 = 3.4 Hz, 1 H), 1.02 (s, 3 H), 0.98-0.86 (m, 12 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 170.8, 166.9, 140.8, 135.9, 135.85, 135.79, 134.0, 133.7, 131.6, 129.7, 128.5, 128.0, 84.2 (t, $J_{C\text{-}D}$ = 22.1 Hz), 80.6, 49.1, 47.9, 45.0, 36.9, 34.0, 32.9, 28.0, 27.4, 27.3, 26.5, 19.7, 19.1, 18.9, 14.8, 13.6; **HRMS** (ESI) calcd for $C_{37}H_{43}DNaO_4Si$ [M+Na^+]: 604.2964, found: 604.2951.



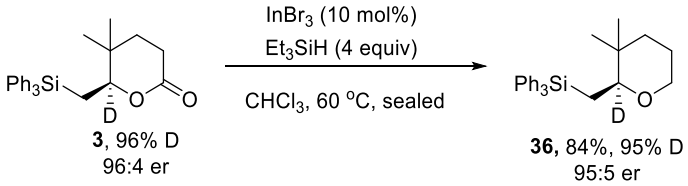
The reaction of 4DPAIPN (1.8 mg, 0.002 mmol), **1r** (179.1 mg, 0.4 mmol), **2a** (29.0 mg, 0.2 mmol), **S6** (22.1 mg, 0.03 mmol), toluene (1.5 mL) and D_2O (0.5 mL) afforded **35** (78.5 mg, 67%, 97% D) (eluent: petroleum ether/DCM/ether = 14/10/1) as a colorless oil: 95:5 dr (HPLC conditions: Chiralcel AD-H column, hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 214 nm, t_1 (minor) = 10.3 min, t_2 (major) = 14.3 min); $[\alpha]_D^{25}$ = -68.3 (*c* = 0.22, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.02 (d, *J* = 8.0 Hz, 2 H), 7.68 (d, *J* = 8.4 Hz, 2 H), 7.60-7.52 (m, 4 H), 7.47-7.33 (m, 6 H), 4.93 (td, J_1 = 10.8 Hz, J_2 = 4.4 Hz, 1 H), 4.10 (dd, J_1 = 11.6 Hz, J_2 = 2.4 Hz, 0.03 H), 2.55-2.28 (m, 2 H), 2.18-2.05 (m, 1 H), 2.03-1.91 (m, 1 H), 1.81 (d, *J* = 14.8 Hz, 1 H), 1.76-1.67 (m, 2 H), 1.65-1.48 (m, 6 H), 1.20-1.04 (m, 2 H), 1.02 (s, 3 H), 0.95-0.89 (m, 9 H), 0.79 (d, *J* = 6.8 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 170.8, 166.1, 140.7, 135.83, 135.81, 135.77, 134.9, 133.9, 133.7, 131.6, 129.7, 128.5, 127.9, 74.8, 47.2, 40.9, 34.2, 34.0, 32.9, 31.4, 27.4, 26.5, 26.3, 23.4,

22.0, 20.8, 19.1, 16.4, 14.7; **HRMS** (ESI) calcd for $C_{37}H_{45}DNaO_4Si$ [M+Na$^+$]: 606.3120, found: 606.3111.

4. Unsuccessful Substrates

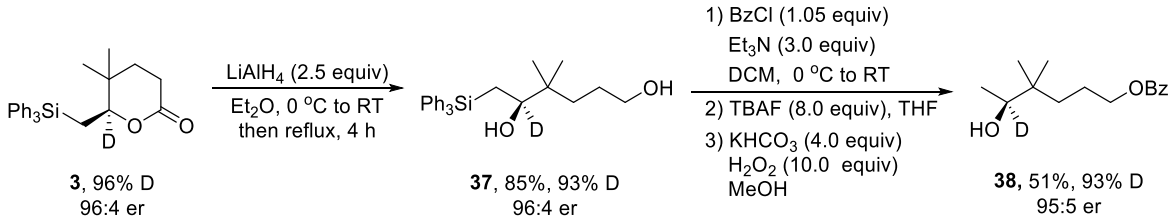


5. Synthetic applications



Following a reported procedure,[7] **3** (46.5 mg, 0.1 mmol), $InBr_3$ (4.2 mg, 0.01 mmol), Et_3SiH (0.1 mL, 0.4 mmol), and freshly distilled $CHCl_3$ (1.0 mL) were sequentially added to a screw-capped vial under N_2 atmosphere. The vial was sealed with a cap containing a PTFE septum. During the stirring of the reaction mixture at 60 ˚C (oil bath temperature), the solution turned from colorless to yellow, then to orange. After the reaction is complete as monitored by TLC, H_2O (3 mL) was added and the resulting orange suspension was stirred continuously until the disappearance of the color. The aqueous layer was extracted with CH_2Cl_2 (5 mL), the combined organic phase was dried over anhydrous Na_2SO_4 filtered, and then evaporated under reduced pressure. The residue was purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 50/1) to give the product **36** (32.5 mg, 84%, 95% D) as a white solid: 95:5 er (HPLC conditions: Chiralcel AD-H column, CO_2/*i*-PrOH = 95/5, 1 mL/min, λ = 230 nm, t_R

(minor) = 3.2 min, t_R (major) = 3.6 min); $[\alpha]_D^{25}$ = -15.0 (*c* = 0.13, $CHCl_3$); **m.p.** 44-45 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.64-7.47 (m, 6 H), 7.43-7.26 (m, 9 H), 3.70-3.56 (m, 1 H), 3.02 (dd, J_1 = 11.4 Hz, J_2 = 2.6 Hz, 0.05 H), 2.87-2.68 (m, 1 H), 1.84-1.36 (m, 4 H), 1.23-1.09 (m, 2 H), 0.99 (s, 3 H), 0.77 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 136.0, 135.9, 129.0, 127.5, 81.9 (t, $J_{C\text{-}D}$ = 20.9 Hz), 68.3, 38.8, 33.7, 27.8, 23.0, 18.6, 14.5; **HRMS** (ESI) calcd for $C_{26}H_{29}DNaOSi$ [M+Na$^+$]: 410.2021, found: 410.2017.



3, 96% D
96:4 er

37, 85%, 93% D
96:4 er

38, 51%, 93% D
95:5 er

To a stirred suspension of lithium aluminum hydride (10.3 mg, 0.25 mmol) in dry Et_2O (4 mL) was added dropwise a solution of **3** (40.1 mg, 0.1 mmol) in Et_2O (1 mL) at 0 ℃ under nitrogen atmosphere. After addition, the reaction was stirred and heated to reflux for 4 h. After the reaction reached completion, the reaction was quenched by adding H_2O (0.1 mL) slowly at 0 ℃. After stirring for 10 minutes, a 15% NaOH solution (0.1 mL) was added slowly, followed by H_2O (0.3 mL). The reaction mixture was passed through a Celite pad. The filtrate was dried over $MgSO_4$, concentrated under vacuum, and purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5/1) to afford **37** (34.4 mg, 85%, 93% D) as a white solid: 96:4 er (HPLC conditions: Chiralcel OD-H column, hexane/*i*-PrOH = 95/5, 1 mL/min, λ = 214 nm, t_R (major) = 6.8 min, t_R (minor) = 8.3 min); $[\alpha]_D^{25}$ = -17.5 (*c* = 0.13, $CHCl_3$); **m.p.** 100-102 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.71-7.48 (m, 6 H), 7.46-7.22 (m, 9 H), 3.66 (dd, J_1 = 9.2 Hz, J_2 = 4.4 Hz, 0.06 H), 3.49 (t, *J* = 6.4 Hz, 2 H), 1.94-1.16 (m, 8 H), 1.01-0.74 (m, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 135.7, 135.1, 129.4, 127.8, 74.6 (t, $J_{C\text{-}D}$ = 20.8 Hz), 63.3, 38.0, 34.2, 26.8, 22.7, 22.2, 16.1; **HRMS** (ESI) calcd for $C_{26}H_{31}DNaO_2Si$ [M+Na$^+$]: 428.2127, found: 428.2122.

To a solution of **37** (40.7 mg, 0.1 mmol) in CH_2Cl_2 (1 mL) was added Et_3N (45.0 μL, 0.3 mmol) followed by benzoyl chloride (BzCl) (15.0 μL, 0.11 mmol) at 0 °C, and the mixture was stirred at room temperature for 8 h. When the reaction is complete as monitored by TLC, CH_2Cl_2 (10 mL) and H_2O (5 mL) were added, the organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (10 mL × 3). The combined organic layer was washed with brine and

dried over anhydrous Na_2SO_4. After filtration and evaporation, the residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5/1) to afford the intermediate as a white solid. Then, to a solution of the intermediate (119.5 mg, 0.2 mmol) in dry tetrahydrofuran (1 mL) was added a 1 M solution of tetrabutylammonium fluoride in tetrahydrofuran (1.6 mL, 1.6 mmol). The mixture was stirred at room temperature for 12 h. After the reaction reached completion, potassium bicarbonate (80.3 mg, 0.8 mmol), dry methanol (1 mL), and 30% H_2O_2 (0.8 mL, 2.0 mmol) were added sequentially, the mixture was further stirred at room temperature for 10 h. When the reaction is complete as monitored by TLC, the mixture was poured into an aqueous solution of sodium bicarbonate and the aqueous layer was extracted with ether (10 mL × 3). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. After filtration and evaporation, the residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5/1) to afford **38** (31.1 mg, 51%, 93% D over 3 steps) as a colorless oil: 95:5 er (HPLC conditions: Chiralcel OJ-H column, hexane/*i*-PrOH = 99.8/0.2, 1 mL/min, λ = 214 nm, t_R (major) = 46.6 min, t_R (minor) = 52.8 min); $[\alpha]_D^{25}$ = -16.3 (*c* = 0.14, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.09-7.96 (m, 2 H), 7.59-7.51 (m, 1 H), 7.49-7.38 (m, 2 H), 4.30 (t, *J* = 6.8 Hz, 2 H), 3.58 (q, *J* = 6.4 Hz, 0.07 H), 1.87-1.66 (m, 2 H), 1.60-1.32 (m, 3 H), 1.14 (s, 3 H), 0.96-0.80 (m, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 166.7, 132.8, 130.4, 129.5, 128.3, 73.7 (t, J_{C-D} = 21.4 Hz), 65.8, 37.0, 34.7, 23.4, 22.6, 22.3, 17.6; **HRMS** (ESI) calcd for $C_{15}H_{21}DNaO_3$ [M+Na^+]: 274.1524, found: 274.1524.

6. Mechanistic Studies

6.1. Cyclic Voltammetry Measurements

Cyclic voltammetry (CV) experiments of **S1**, **S3**, **S6** were recorded on a CHI 600E electrochemical workstation. Electrolyte solution was prepared by dissolving the substrates (0.05 mmol, 5 mM) and tetraethylammonium hexafluorophosphate (387.4 mg, 1 mmol, 100 mM) in MeCN (10 mL) and bubbling with nitrogen for two minutes. Measurements were performed in a 3-compartment electrochemical cell, in which glassy carbon electrode (GCE) was used as a working electrode, silver-silver chloride (Ag/AgCl) in saturated KCl as the reference electrode, and Pt wire as the counter electrode. The scan rate was set at 100 mV/s.

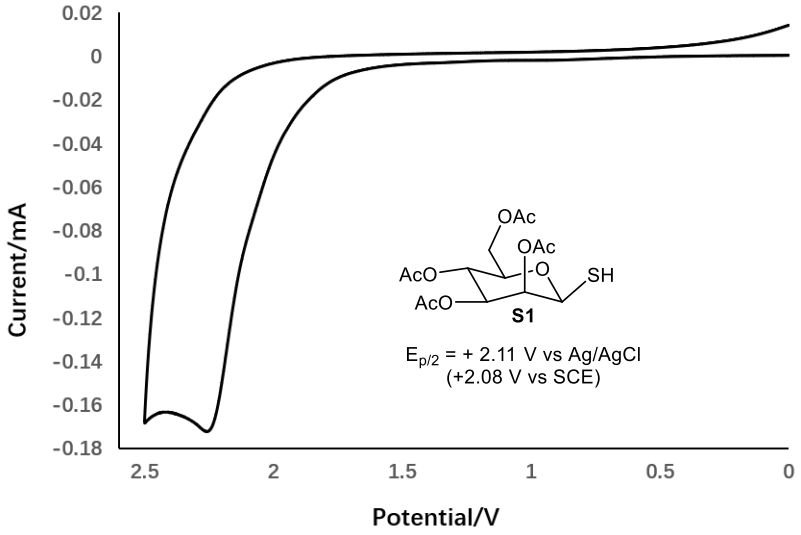


Figure S2. CV curve of **S1.**

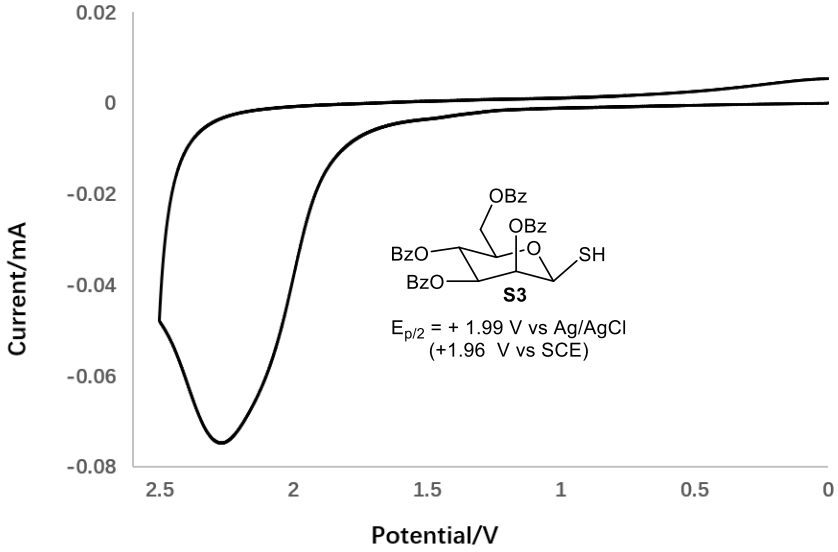


Figure S3. CV curve of **S3.**

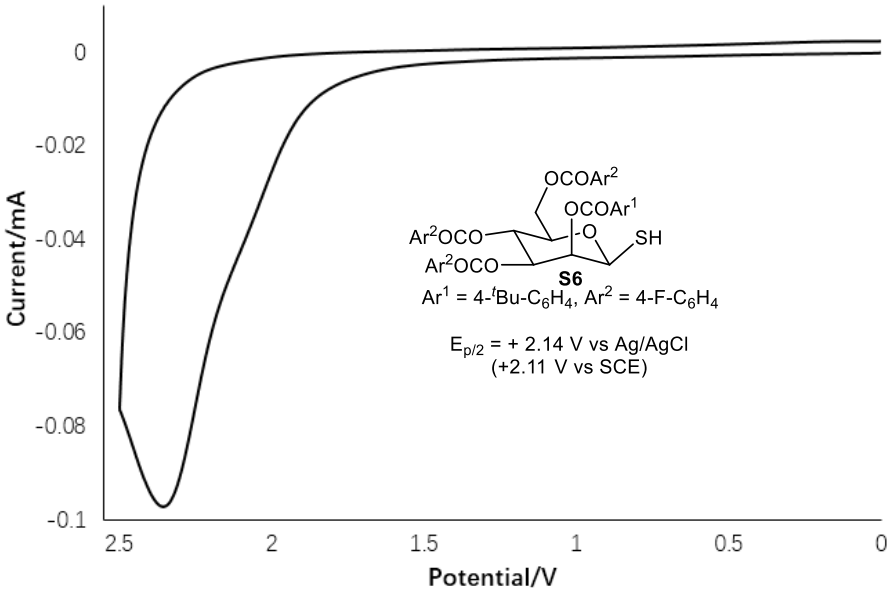


Figure S4. CV curve of **S6.**

6.2. Stern-Volmer Experiments

Stern-Volmer luminescence quenching experiments were carried out with freshly prepared solutions of 4DPAIPN (10^{-5} M) at room temperature. For **1a** and **2a**, the solutions were prepared in toluene and was irradiated at 350 nm and the luminescence were measured at 523 nm. For **S6**, the solution was prepared in DMF due to its poor solubility in toluene and was irradiated at 350 nm and the luminescence were measured at 530 nm. For each sample, the luminescence was acquired three times and averaged (**Tables S1-S4**), the averages of the results were used for the graphical representation (**Figures S5-S9**).

Table S1. Fluorescence quenching data with solutions of 4DPAIPN and **1a**.

Species	Concentration (mM)
4DPAIPN	0.01
1a	varied

[Sub] (mM)	**Scan 1**	**Scan 2**	**Scan 3**	**Average**	**I_0/I**
0	1294	1295	1293	1294	1.000
5	1302	1302	1301	1302	0.994
10	1290	1289	1290	1290	1.003
15	1290	1290	1289	1290	1.003
20	1338	1338	1337	1338	0.967
25	1291	1290	1289	1290	1.003

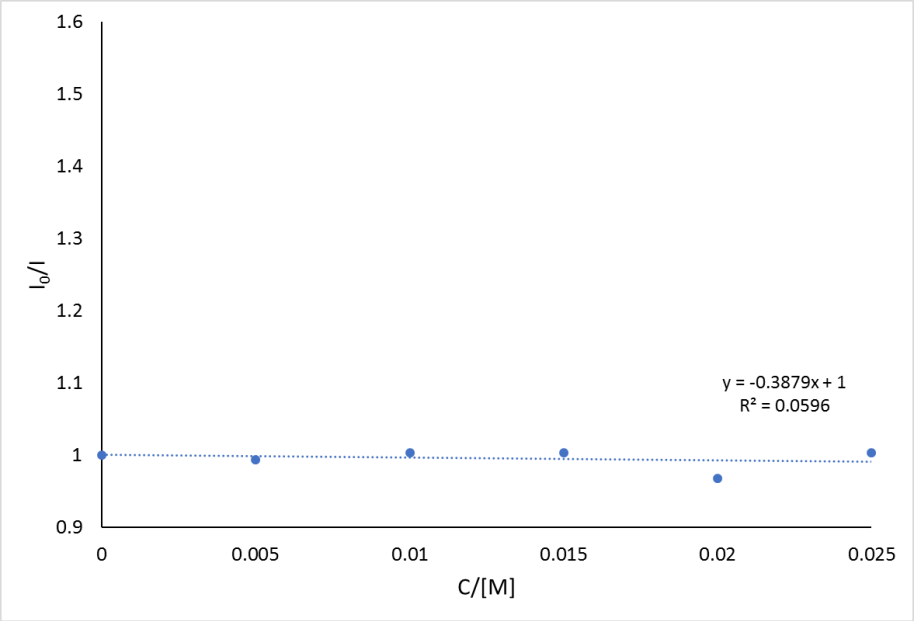


Figure S5. Stern-Volmer plot of 4DPAIPN quenching with varying concentration of **1a**.

Table S2. Fluorescence quenching data with solutions of 4DPAIPN and **2a**.

Species	Concentration (mM)
4DPAIPN	0.01
2a	varied

[Sub] (mM)	**Scan 1**	**Scan 2**	**Scan 3**	**Average**	**I_0/I**
0	1270	1269	1268	1269	1.000
5	1271	1270	1270	1270	0.999
10	1286	1286	1285	1286	0.987
15	1269	1267	1264	1267	1.002
20	1308	1304	1298	1303	0.974
25	1268	1267	1267	1267	1.002

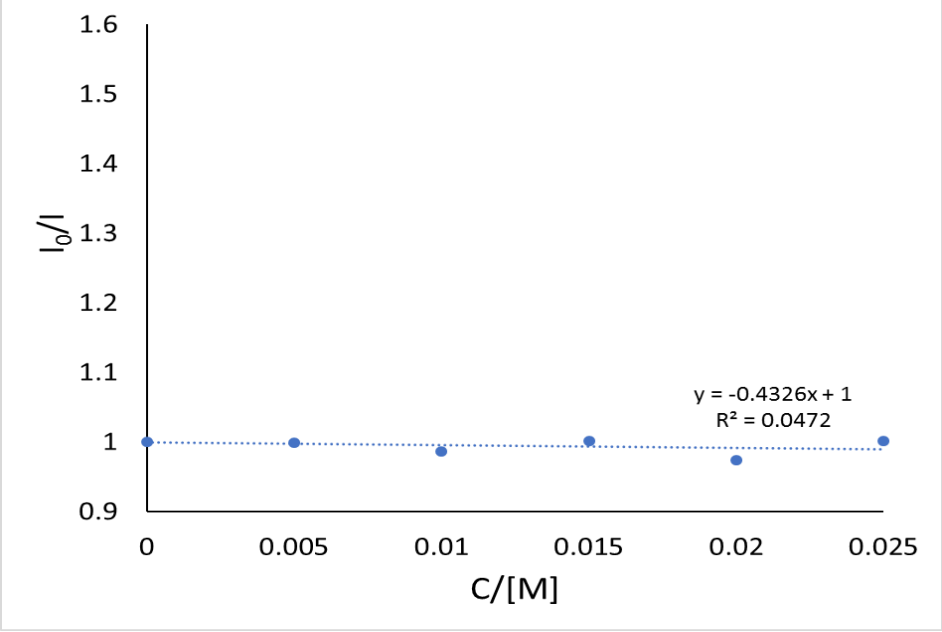


Figure S6. Stern-Volmer plot of 4DPAIPN quenching with varying concentration of **2a**.

Table S3. Fluorescence quenching data with solutions of 4DPAIPN and **S6**.

Species	Concentration (mM)
4DPAIPN	0.01
S6	varied

[Sub] (mM)	**Scan 1**	**Scan 2**	**Scan 3**	**Average**	**I_0/I**
0	1034	1034	1035	1034	1.000
1	1004	1004	1004	1004	1.030
2	990	990	990	990	1.044
3	957	957	957	957	1.080
4	929	929	929	929	1.113
5	901	900	900	900	1.149

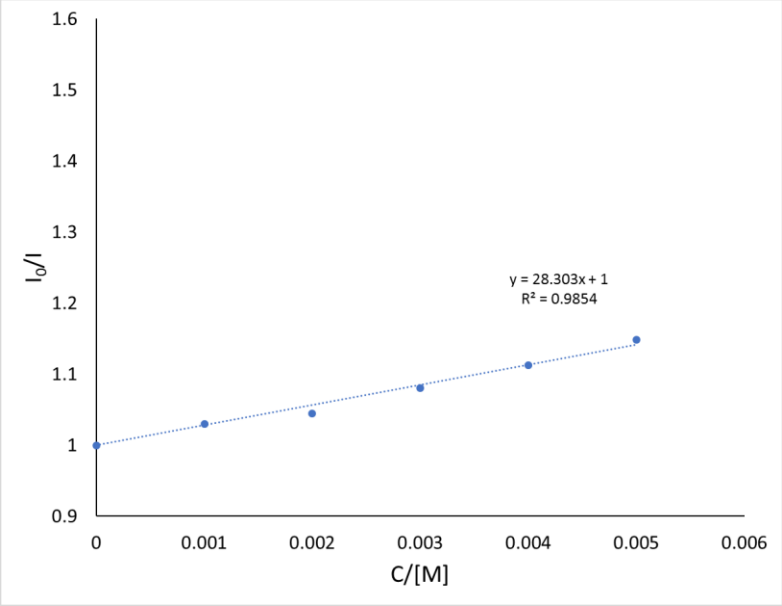


Figure S7. Stern-Volmer plot of 4DPAIPN quenching with varying concentration of **S6**.

Table S4. Fluorescence quenching data with solutions of 4DPAIPN, and **S6** in the presence of D_2O (5.0 M).

Species	Concentration (mM)
4DPAIPN	0.01
D_2O	5000
S6	varied

[Sub] (mM)	**Scan 1**	**Scan 2**	**Scan 3**	**Average**	**I_0/I**
0	1043	1044	1044	1044	1.000
1	1011	1011	1011	1011	1.033
2	964	964	964	964	1.083
3	939	938	938	938	1.113
4	936	936	936	936	1.115
5	928	927	927	927	1.126

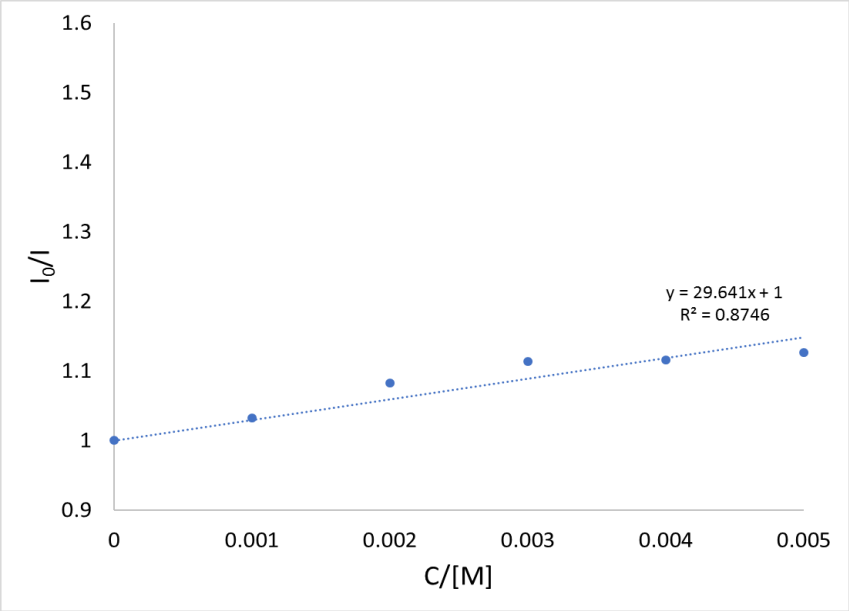


Figure S8. Stern-Volmer plot of 4DPAIPN quenching with varying concentration of **S6** in the presence of D_2O (5.0 M).

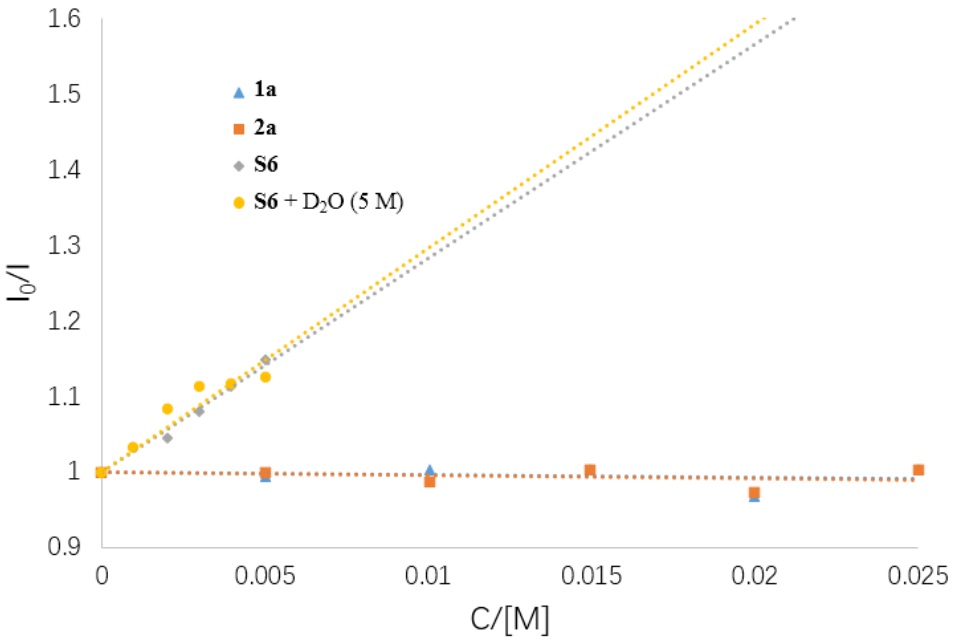


Figure S9. Summary of Stern-Volmer plots.

6.3. Quantum Yield Measurements

Emission spectra of the blue LED (30 W) was recorded on a Steady-State & Time-Resolved Fluorescence Spectrofluorometer (**Figure S10**). According to the spectra, emission range of light source was 400 – 500 nm, and the maximum emission wavelength was 441 nm.

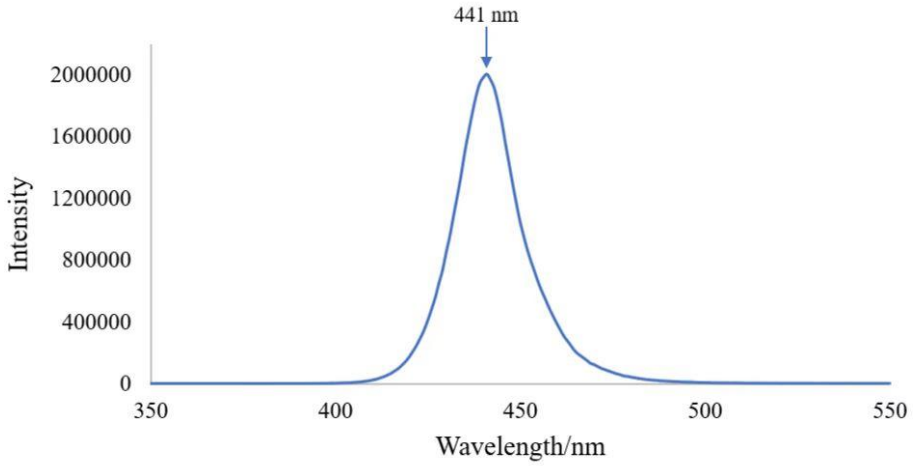
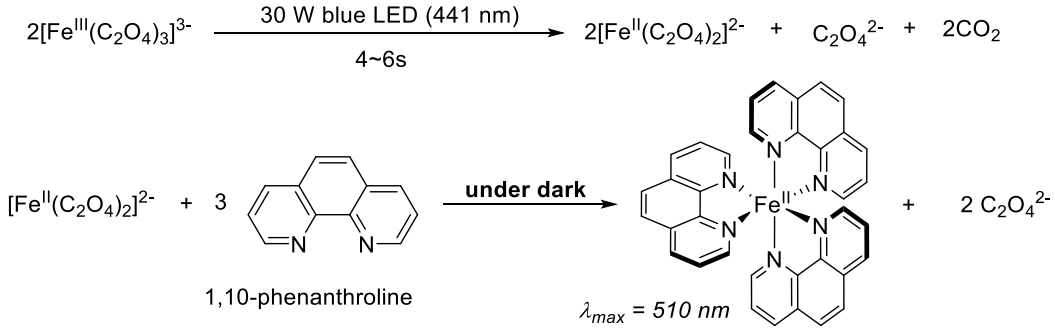


Figure S10. Emission spectra of the blue LED

Quantum yield measurements were determined using standard ferrioxalate chemical actinometry as described by Yoon,[8] Ritter,[9] Aleman,[10] and Glorious.[11] In this part, we use a 30 W blue LED (λ = 441 nm) as light source to determine the quantum yield.

6.3.1. Determination of the photon flux at 441 nm:

The photon flux of the 30 W blue LED (441 nm) was determined by monitoring the photoreduction of Fe(III) in potassium ferrioxalate to Fe(II), upon complexation with 1,10-phenanthroline:



The following solutions were prepared:

a. Actinometer solution: 589.5 mg (1.2 mmol) of potassium ferrioxalate trihydrate and 278 μL of H_2SO_4 96% were added to a 100 mL volumetric flask and filled to the mark with Nanopure water.

b. Phenanthroline-buffer solution: 100 mg (0.55 mmol) of 1, 1,10-phenanthroline, 9.88 g (120.4 mmol) of sodium acetate and 2.0 mL of H_2SO_4 96% were added to a 100 mL volumetric flask and filled to the mark with Nanopure water.

1 mL of the actinometer solution was added to a vial (16 x 60 mm) and was irradiated by the 30 W blue LED for 4 seconds. After the irradiation, the mixture was quantitatively transferred to a 5 mL volumetric flask containing 1.0 mL of the phenanthroline-buffer solution. Then, the flask was filled to the mark with Nanopure water, wrapped up with aluminum foil, and was left in the dark for 1 h to ensure the quantitative formation of $Fe^{II}(phen)_3^{2+}$ complex. This procedure was repeated one more time by changing the irradiation time to 6 seconds.

Additionally, the experiment of a control sample was carried out under dark, following the same sample treatment.

The absorbance of each solution at 510 nm was measured using a Perkin-Elmer Lambda 35 UV-Vis spectrophotometer, establishing the blank with Nanopure water. For each sample, the absorbance was acquired three times and averaged. According to Lambert-Beer law, the moles of Fe(II) in each sample are related to the absorbance:

$$n\,[Fe^{2+}] = \frac{V \cdot \Delta A}{l \cdot \varepsilon}$$

Where:

- ΔA is the absorbance difference between irradiated sample and non-irradiated sample.
- V is the volume (in L) of the measurement sample (5 mL).
- ε is the extinction coefficient of the complex $Fe^{II}(phen)_3^{2+}$ at 510 nm (11100 L mol^{-1} cm^{-1})
- l is the optical path of the sample in the spectrophotometer (1 cm).

The photon flux can be calculated using the following equation:

$$photon\ flux = \frac{n\,[Fe^{2+}]}{\Phi \cdot t \cdot f}$$

Where:

- Φ is the quantum yield for the photoreduction of ferrioxalate at 441 nm, which is 1.11.[12]
- t is the reaction time (4 s or 6 s).
- f is the fraction of light absorbed, and is calculated as $f = 1 - 10^{-A_{441\,nm}}$
- where $A_{441\,nm}$ is the absorbance of the actinometer solution at 441 nm (which is 0.3877 according to the UV-Vis spectra of actinometer solution (**Figure S11**).

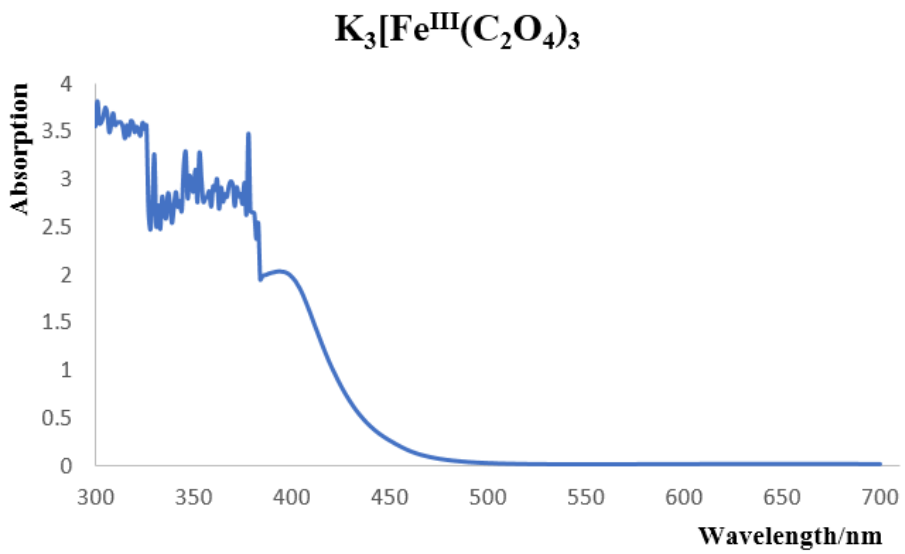


Figure S11. UV-Vis spectra of actinometer solution (12 mM in aqueous solution).

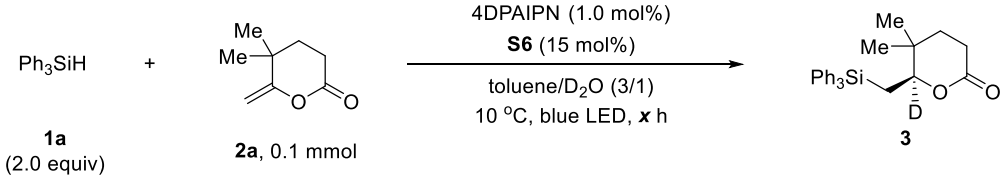
The photon flux of the 30 W blue LED (441 nm) was thus determined to be $2.65*10^{-7}$ einsten s^{-1} (**Table S5**).

Table S5. UV-Vis absorption data and calculated results of photo flux

scan time	**UV-Vis absorption at 510 nm**		
	$\mathbf{A_{4s}}$	$\mathbf{A_{6s}}$	$\mathbf{A_{dark}}$
1	1.480	2.195	0.016
2	1.644	2.452	0.019
Average	1.562	2.324	0.018
ΔA (=A-A_{dark})	1.545	2.306	-
n [Fe^{2+}] (mol)	$6.96*10^{-7}$	$1.04*10^{-7}$	
Photon flux (einstein/s)	$2.654*10^{-7}$	$2.642*10^{-7}$	
	(average) $2.648*10^{-7}$		

6.3.2. Determination of quantum yield at 441 nm:

Once we have determined the photon flux of the 30 W blue LED (λ_{max} = 441 nm), the same equation must be employed for the determination of the quantum yield of our photoreaction system. For that, the moles of product for a given time must be determined.



Following the **Typical Procedure**, the reaction of **1a** and **2a** in the presence of 4DPAIPN, **S6**, toluene (0.75 mL) and D_2O (0.25 mL) was carried out and stopped after 1 h of irradiation. The solvent of reaction mixture was evaporated *in vacuo*. The amount of product **3** was determined to be $0.17*10^{-4}$ mol by ^1H NMR analysis of the crude reaction mixture using CH_2Br_2 as the internal standard. Another run with an irradiation time of 2 h was also carried out, and the amount of **3** was determined to be $0.32*10^{-4}$ mol.

$$\Phi' = \frac{\text{n}\,[prod.]}{\text{photon flux} \cdot t' \cdot f'}$$

Where:

- n [prod.] is the amount of **3** (in mol) that has been formed during the irradiation time.
- *t'* (s) is the irradiation time (in seconds).
- *f'* is the fraction of light absorbed, and is calculated as $f' = 1 - 10^{-A_{441\,nm}}$ where $A_{441\,nm}$ is the absorbance of the actinometer solution at 441 nm, and was determined to be 2.5939 according to the UV-Vis spectra of 1 mM solution of **PC** in toluene (**Figure S12**).

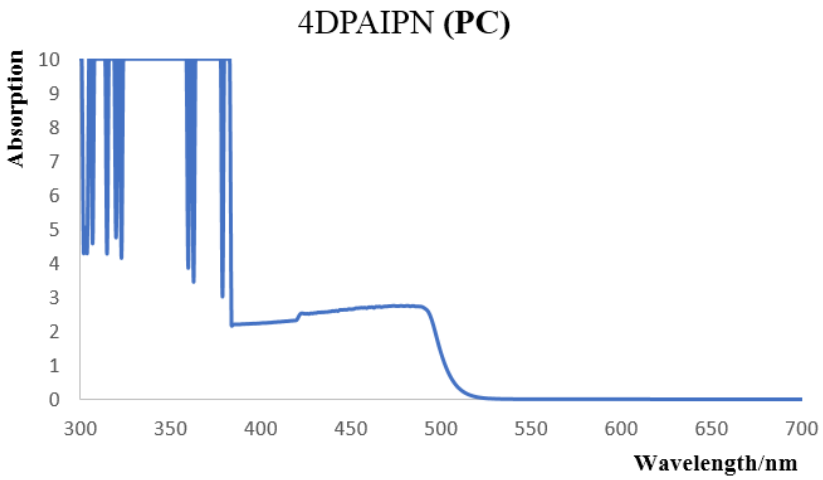


Figure S12. UV-Vis spectra of **PC** solution (1 mM in toluene)

The quantum yield of the reaction was thus determined to be 0.018 (average of two runs, **Table S6**).

Table S6. Calculations of quantum yield

entry	**reaction time/s**	**NMR yield/%**	**n[prod.]/mol**	**quantum yield** (Φ')	**temp./℃**
1	7200	32	$0.32*10^{-4}$	0.017	10
2	3600	17	$0.17*10^{-4}$	0.018	10

Φ' = (0.017+0.018)/2 = 0.018

7. X-Ray Crystallographic Data of Compound 6 and 15

7.1 X-Ray Crystallographic Data of Compound 6

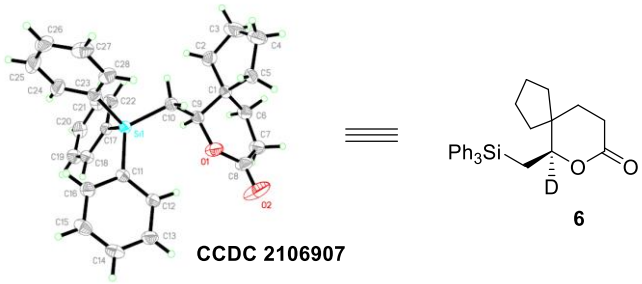


Figure S13. X-Ray Structure of Compound **6** (CCDC 2106907). Crystals suitable for X-ray structure analysis were obtained *via* recrystallization from dichloromethane and pentane.

Table S7. Crystal data and structure refinement for **6**.

Identification code	**6**
Empirical formula	$C_{28}H_{30}O_2Si$
Formula weight	426.61
Temperature	297(2) K
Wavelength	1.54178 A
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)
Unit cell dimensions	a = 9.6379(4) A alpha = 90 deg.
	b = 11.7392(5) A beta = 90 deg.
	c = 21.0292(8) A gamma = 90 deg.
Volume	2379.27(17) A^3
Z, Calculated density	4, 1.191 Mg/m^3
Absorption coefficient	1.028 mm^-1
F(000)	912
Crystal size	0.200 x 0.180 x 0.160 mm
Theta range for data collection	4.204 to 68.396 deg.
Limiting indices	-11<=h<=11, -14<=k<=12, -25<=l<=24
Reflections collected / unique	18832 / 4346 [R(int) = 0.0388]
Completeness to theta = 67.679	99.8 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4346 / 1 / 280
Goodness-of-fit on F^2	1.023

Final R indices [I>2sigma(I)]	R1 = 0.0473, wR2 = 0.1221
R indices (all data)	R1 = 0.0540, wR2 = 0.1302
Absolute structure parameter	0.033(14)
Extinction coefficient	n/a
Largest diff. peak and hole	0.200 and -0.230 e. A^-3

7.2 X-Ray Crystallographic Data of Compound 15

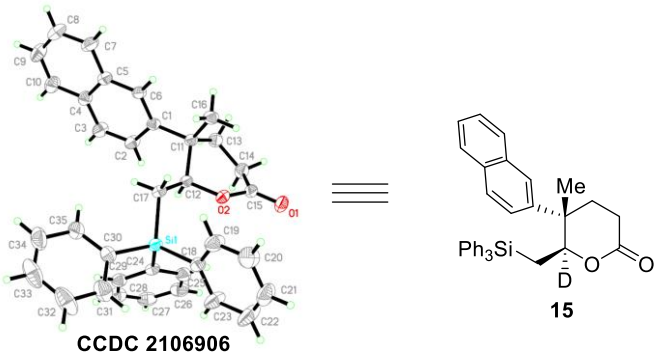


Figure S14. X-Ray Structure of Compound **15** (CCDC 2106906). Crystals suitable for X-ray structure analysis were obtained via recrystallization from tetrahydrofuran and pentane.

Table S8. Crystal data and structure refinement for **15**

Identification code	**15**
Empirical formula	$C_{35}H_{32}O_2Si$
Formula weight	512.69
Temperature	296(2) K
Wavelength	1.54178 A
Crystal system, space group	Monoclinic, P2(1)
Unit cell dimensions	a = 10.0090(12) A alpha = 90 deg. b = 9.9699(10) A beta = 98.738(6) deg. c = 16.3765(18) A gamma = 90 deg.
Volume	1615.2(3) A^3
Z, Calculated density	2, 1.054 Mg/m^3
Absorption coefficient	0.835 mm^-1
F(000)	544
Crystal size	0.220 x 0.200 x 0.180 mm
Theta range for data collection	6.519 to 66.581 deg.

Limiting indices	-11<=h<=11, -11<=k<=11, -19<=l<=19
Reflections collected / unique	26927 / 5639 [R(int) = 0.0431]
Completeness to theta = 66.581	99.0 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5639 / 1 / 344
Goodness-of-fit on F^2	0.977
Final R indices [I>2sigma(I)]	R1 = 0.0392, wR2 = 0.1174
R indices (all data)	R1 = 0.0442, wR2 = 0.1233
Absolute structure parameter	-0.006(10)
Extinction coefficient	n/a
Largest diff. peak and hole	0.181 and -0.132 e. A^-3

8. Computational Details

8.1 General Information

All the DFT calculations were carried out in Gaussian 16 (C.01).[13] Optimizations were performed using the ωB97xD functional[14] in combination with the 6-31+G(d,p) basis set. To characterize the nature of the stationary points as transition states (one imaginary frequency) of minima (zero imaginary frequencies), frequency calculations were calculated at the same level of theory. Furthermore, thermochemistry data was generated using the Goodvibes program at 283.15K and 1M concentration, including quasi-harmonic corrections with the method developed by Grimme,[15] and a cut-off value of 100 wavenumbers. In order to refine the potential energies, single point energy calculations were recalculated using the larger basis set (6-311++G(3d,2p)) and PBE0[16] as the functional including Grimme's empirical dispersion (GD3BJ). The ωB97xD functional was selected for optimizations due to its general good performance in geometry optimization[17] and to directly compared the result with our previous study on the topic. Finally, implicit solvation was introduced in all the calculations, using the CPCM implicit solvent model[18] and toluene as the solvent.

Finally, CREST(xtb)[19] method was used to explore the conformational space of the key enantioselectivity determining transition states (constraining the reactive internal coordinates). The TSs showed in the manuscript correspond to the most stable transition states found.

NCI analyses were performed using the NCIplot[20] program and all the 3D representations were prepared in PyMOL.

8.2 Full Free Energy Profile of the Deuterosilylation of Methylenelactone 2a using Thiol S3

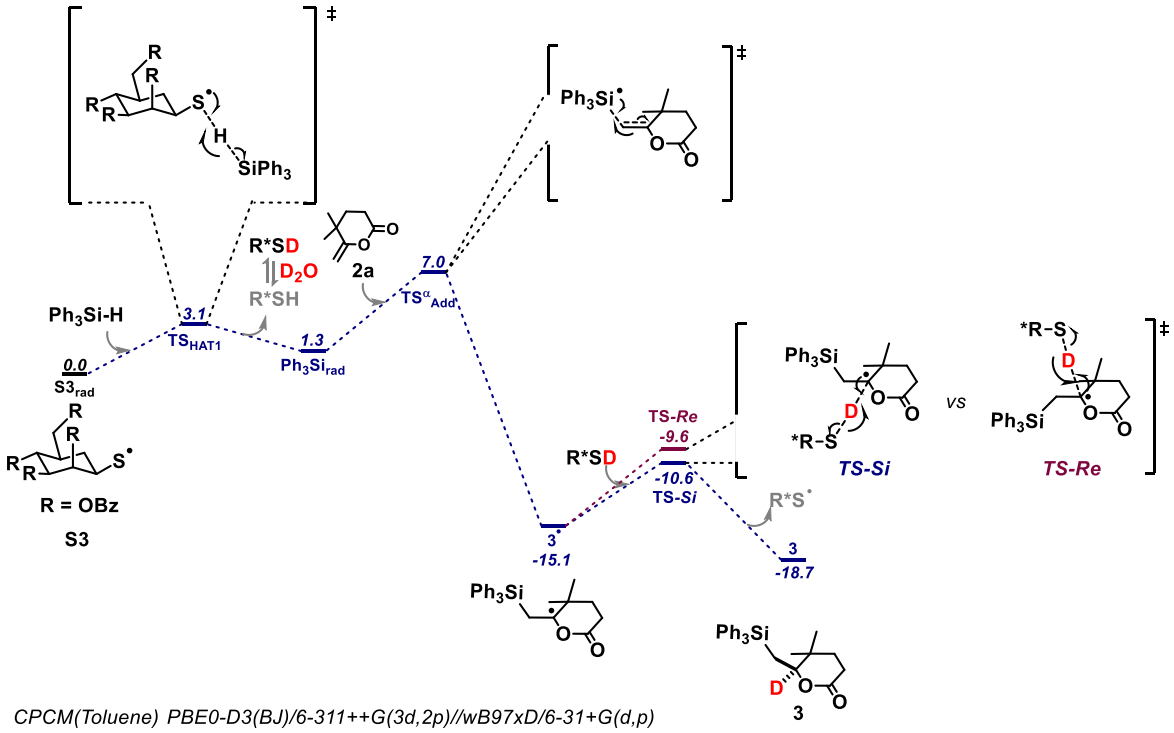


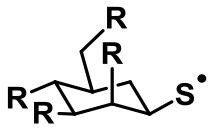
Figure S15. Free energy profile of the deuterosilylation of methylenelactone **2a** using thiol catalyst **S3**. All energies in kcal/mol.

The calculation starts with a polarity matched HAT between the silane and the thiyl radical. The barrier is very low and the resulting silane radical, Ph_3Si ; reacts with the methylenelactone at the external position. This addition is also kinetically accessible (7.0 kcal/mol) and thermodynamically very favored (-16.4 kcal/mol). Once the tertiary prochiral radical is formed, the enantioselectivity is determined by the subsequent deuterium atom transfer from the in-situ generated deuterated thiol catalyst *d*-**S3**. This step is determined by the non-covalent interactions of the different benzoyl in the backbone of the thiol catalyst with the substrate, providing a rigid conformation. This approach is able to differentiate both *Si* and *Re* faces, favoring the formation of the product **3** in an enantioselective way.

8.3 XYZ Coordinated and Energies of the Calculated Species

Final free energies are calculated as the sum of E (large basis set) + G_{Corr}. G^{D}_{Corr} refers to the free energy correction of deuterated species. Energies for distortion/interaction analysis are included in the TS-*Re* and TS-*Si* .

$S3_{rad}$



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E = -2385.420035
G_{Corr}= 0.490207

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O	-1.09007600	-2.28382300	-0.30190800
O	-3.08227500	-2.60336600	-1.31125200
O	-1.92493300	0.21051700	-0.88202200
O	-2.60312200	0.53012700	-3.00580900
O	0.36058500	1.74051300	-0.28077000
O	-0.44162700	1.87811900	1.82435300
O	4.02536200	-0.19021100	0.12033000
O	4.87849600	0.67188600	2.00925900
C	0.90184900	-2.13305300	-1.62757500
C	-0.55649100	-1.68536700	-1.48173800
C	-0.62242700	-0.16193200	-1.31156500
C	0.34079400	0.31596100	-0.23749000
C	1.74911900	-0.21647700	-0.52382300
C	2.71848600	0.16749900	0.57075100
C	-2.41132700	-2.57672700	-0.30276300
C	-2.85797100	0.47433200	-1.82243200
C	-0.10332000	2.41784800	0.79383600
C	5.03916700	0.10796900	0.94584400
H	1.26896100	-1.75920500	-2.60025000
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H	-0.39423800	0.31930200	-2.26799100
H	0.00519000	-0.01973500	0.74694800
H	2.10761000	0.18804600	-1.48371100
H	2.48436000	-0.36742700	1.49566800
H	2.67709900	1.24281000	0.76083800
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C	-2.11310000	-2.72539000	2.19473100
C	-4.28605500	-3.14011700	1.20281300
C	-2.65648600	-2.93077500	3.45898300
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C	-4.82429300	-3.34296500	2.46825800
H	-4.90572400	-3.20639100	0.31506700
C	-4.00963800	-3.23870200	3.59616600
H	-2.02506000	-2.84635400	4.33716900
H	-5.87780200	-3.57892200	2.57635000
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C	-5.25834300	1.01940200	-2.06616300
C	-4.42523800	0.49282800	0.14799000
C	-6.53632000	1.18631800	-1.54434600
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H	-3.60504000	0.21898500	0.80168500
C	-6.76074900	1.00352900	-0.17960900
H	-7.35759800	1.45479400	-2.20056300
H	-5.88103600	0.50972600	1.72506700
H	-7.75958300	1.13002600	0.22623800
C	-0.13300300	3.88489900	0.55810800
C	-0.52051700	4.70992700	1.61802200
C	0.20479100	4.44354200	-0.67866400
C	-0.56830800	6.08824200	1.44253000
H	-0.78062500	4.25987200	2.57000900
C	0.15381500	5.82336000	-0.84977600
H	0.50102500	3.80079200	-1.49937300
C	-0.23127000	6.64521200	0.20884900
H	-0.86800400	6.72794600	2.26596400
H	0.41361700	6.25738900	-1.80960900
H	-0.26958700	7.72131300	0.07201000
C	6.35876000	-0.32576300	0.40966400
C	7.50308800	-0.01863300	1.15083100
C	6.47191500	-1.02481200	-0.79614200
C	8.75567200	-0.40621800	0.68717500
H	7.39739600	0.52226100	2.08513300
C	7.72707300	-1.41227600	-1.25535900
H	5.58136700	-1.26572400	-1.36510900
C	8.86819900	-1.10302800	-0.51587600
H	9.64336800	-0.16619200	1.26310000
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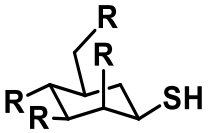
H	9.84592100	-1.40650100	-0.87685200

S3



R=OBz

E = -2386.064066
G_{Corr}= 0.499986
G^{D}_{Corr}= 0.497274

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O	-3.08474400	-2.59784100	-1.30220100
O	-1.93245100	0.22539800	-0.87881000
O	-2.61214300	0.53803200	-3.00312900
O	0.35081700	1.75821100	-0.27961100
O	-0.43291500	1.89967200	1.83216800
O	4.01873800	-0.16683200	0.12697400
O	4.86689500	0.66465400	2.03188600
C	0.89483800	-2.10483100	-1.63117400
C	-0.56097300	-1.67062400	-1.47566900
C	-0.62945300	-0.14702100	-1.30799800
C	0.33319700	0.33332000	-0.23399000
C	1.74294900	-0.19732500	-0.51861900
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C	-2.86617600	0.48357300	-1.81938300
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H	2.10210500	0.21069900	-1.47684800
H	2.47715400	-0.35523200	1.50076500
H	2.66609100	1.25907200	0.77378900
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C	-4.28312600	-3.13223400	1.21450500
C	-2.64219000	-2.95278900	3.46485100
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C	-3.99671700	-3.25297000	3.60569000
H	-2.00611000	-2.88063400	4.34078700
H	-5.87161700	-3.57237500	2.59149600
H	-4.41448800	-3.41535300	4.59434700
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C	-5.26702900	1.02782900	-2.06308100
C	-4.43539600	0.49320300	0.14957300
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H	-7.36649600	1.46235700	-2.19750700
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H	-0.86188700	6.74983500	2.26602500
H	0.36957000	6.27036100	-1.82394400
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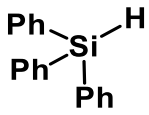
C	6.35178800	-0.30349200	0.41871200
C	7.49290500	-0.01836900	1.17339600
C	6.47005300	-0.97011100	-0.80483500
C	8.74716500	-0.39607400	0.70601200
H	7.38338700	0.49786700	2.12110700
C	7.72682000	-1.34736400	-1.26811300
H	5.58194700	-1.19255000	-1.38505600
C	8.86470300	-1.06057800	-0.51467000
H	9.63229300	-0.17326300	1.29269500
H	7.81864200	-1.86601300	-2.21679800
H	9.84373600	-1.35600200	-0.87874500

Ph_3Si-H



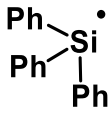
E = -984.3475484

G_{Corr}= 0.243652

G^{D}_{Corr}= 0.241107

Si	0.00017300	0.00107100	-0.98087200
H	-0.00259600	0.00089500	-2.46984600
C	-1.72588800	0.42057400	-0.36640500
C	-1.93127100	1.30740100	0.70005600
C	-2.85077500	-0.18769500	-0.94528700
C	-3.21468300	1.57532000	1.17624600
H	-1.08036200	1.79877600	1.16563200
C	-4.13499600	0.07615600	-0.47463900
H	-2.72600300	-0.87980300	-1.77529400
C	-4.31815500	0.95951300	0.58931000
H	-3.35235700	2.26517500	2.00345200
H	-4.99167000	-0.40452000	-0.93723600
H	-5.31821900	1.16776200	0.95753700
C	1.22752400	1.28601400	-0.36849000
C	2.12809600	1.00695000	0.66914700
C	1.23525900	2.57696600	-0.92029600
C	3.00482300	1.98284800	1.14330800
H	2.14891300	0.01522100	1.11414200
C	2.10861600	3.55579200	-0.45134200
H	0.54843500	2.82635900	-1.72636300
C	2.99555400	3.25864900	0.58358900
H	3.69418400	1.74652500	1.94820300
H	2.09869300	4.54806100	-0.89192100
H	3.67768800	4.01942400	0.95086100
C	0.49901100	-1.70440500	-0.36856000
C	1.60228000	-2.36551900	-0.93115700
C	-0.18274000	-2.33576800	0.68129300
C	2.01220900	-3.61121300	-0.46146000
H	2.15317300	-1.90307600	-1.74735300
C	0.22349400	-3.58232900	1.15695600
H	-1.04421500	-1.85118600	1.13473100
C	1.32222400	-4.22128800	0.58632900
H	2.86749000	-4.10623900	-0.91150100
H	-0.31845800	-4.05379000	1.97130300
H	1.63940300	-5.19237900	0.95427100

Ph_3Si_{rad}



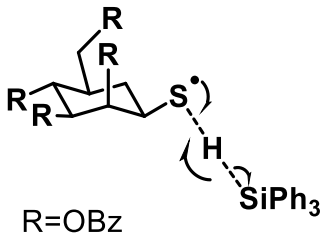
E = -983.7035102

G_{Corr}= 0.236084

C	0.42437700	-0.62796700	1.25113200
Si	0.00116200	-0.00037900	-0.98190000
H	-0.00126700	0.00071400	-2.47063800
C	-1.40056700	1.09089000	-0.36783100
C	-1.22537300	1.97652000	0.70478500
C	-2.67431800	1.00412400	-0.95119600
C	-2.28555800	2.74665900	1.18272800
H	-0.24873600	2.07031900	1.17365700
C	-3.73712100	1.77079200	-0.47848400
H	-2.84357000	0.32773300	-1.78614500
C	-3.54312300	2.64407800	0.59171500
H	-2.12870200	3.42693000	2.01434700
H	-4.71456400	1.68917000	-0.94429100

H	-4.36917900	3.24398100	0.96140300
C	1.64690100	0.66936800	-0.36905300
C	2.34876600	0.05283300	0.67630400
C	2.18635800	1.83903400	-0.92715800
C	3.54654400	0.58675900	1.15187100
H	1.95836900	-0.85694100	1.12591200
C	3.38216600	2.37685600	-0.45692700
H	1.66662900	2.34158100	-1.73998200
C	4.06441500	1.74979700	0.58579100
H	4.07459100	0.09410400	1.96270700
H	3.78278000	3.28211900	-0.90301700
H	4.99708900	2.16640500	0.95388200
C	-0.24221000	-1.76021600	-0.36770200
C	0.50119700	-2.81347000	-0.92305000
C	-1.13224600	-2.05859600	0.67343000
C	0.36380500	-4.11800200	-0.45454500
H	1.20012800	-2.61534300	-1.73274500
C	-1.27419700	-3.36292600	1.14706000
H	-1.72542500	-1.26498900	1.12105000
C	-0.52641700	-4.39423000	0.58328400
H	0.94761500	-4.91832100	-0.89899000
H	-1.96944300	-3.57326700	1.95408300
H	-0.63672000	-5.41049200	0.94922900

TS_{HAT1}



R=OBz

E = -3369.786817

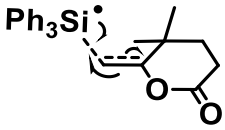
G_{Corr}= 0.758024

G^{D}_{Corr}= 0.756619

Si	3.92402900	-1.65073600	-0.51905100
C	5.05171600	-3.11337700	-0.78223400
C	6.17816400	-3.33499800	0.02639900
C	4.74817500	-4.06572800	-1.77139800
C	6.98667100	-4.45400700	-0.16345100
H	6.42828200	-2.62940300	0.81406400
C	5.55452600	-5.18416700	-1.96282400
H	3.86517000	-3.94145500	-2.39402300
C	6.67856200	-5.37800000	-1.16026400
H	7.85566300	-4.60542700	0.46943600
H	5.30276400	-5.90724200	-2.73237600
H	7.30752900	-6.25063500	-1.30675700
C	4.39993500	-0.55454700	0.92054000
C	5.65331700	0.07895200	0.95007800
C	3.52144400	-0.34275000	1.99360800
C	6.02415400	0.88348900	2.02382000
H	6.34904300	-0.04871700	0.12360400
C	3.89000400	0.46503100	3.06794900
H	2.53562800	-0.79912100	1.98662000
C	5.14265700	1.07365600	3.08610500
H	6.99257300	1.37374200	2.02458000
H	3.19455200	0.62604500	3.88588300
H	5.42570800	1.70963400	3.91904500
C	3.55666700	-0.67490800	-2.06884200
C	2.73802900	0.45894300	-1.93702000
C	4.01227400	-1.01682900	-3.35067800
C	2.38219400	1.22531800	-3.04234000
H	2.38657500	0.74683600	-0.94920200
C	3.65887800	-0.25074600	-4.46079600
H	4.65781100	-1.87967400	-3.48826800
C	2.84121300	0.86825000	-4.31044300
H	1.75305300	2.10199500	-2.91514700
H	4.02485600	-0.52704900	-5.44486800
H	2.56612400	1.46174800	-5.17671600
S	0.87069800	-2.87201300	0.29266100
O	0.37871000	-0.28998900	0.53045000
O	-1.95568800	-2.00148600	0.76215800
O	-3.34799700	-3.45144000	-0.26155900
O	-3.51084700	-0.41022200	-0.74720600
O	-3.70674200	-0.99801400	-2.91264600
O	-2.22526300	2.06553600	-0.44511000
O	-3.51021500	2.37037200	1.38526300
O	1.63520000	2.37109600	0.77081000
O	1.77892200	3.46135300	2.72739100
C	0.08884000	-1.36917200	-0.34383000
C	-1.41662700	-1.58565600	-0.49152000
C	-2.10119700	-0.26782900	-0.87023000
C	-1.69392400	0.84883600	0.07605600
C	-0.16604600	0.95452700	0.11878600
C	0.29517600	1.99970200	1.11111400
C	-3.00333300	-2.85146800	0.73400500
C	-4.20533100	-0.84794800	-1.81812600
C	-3.17087900	2.71019200	0.27280300
C	2.27840600	3.13462300	1.66937200
H	2.25253200	-2.39794100	-0.05671200
H	0.49538700	-1.14795100	-1.34185900
H	-1.61340200	-2.34522200	-1.25079600
H	-1.84234400	-0.00425300	-1.90041600
H	-2.09389200	0.66738600	1.07651400
H	0.19427000	1.21778000	-0.88793500
H	0.26367000	1.59259900	2.12452300
H	-0.33851500	2.88900100	1.06469100
C	-3.68767300	-2.93953800	2.04950900
C	-3.26294000	-2.19335300	3.15301700
C	-4.81346300	-3.76203000	2.14796800
C	-3.96319800	-2.27708600	4.35242300
H	-2.39304700	-1.55234800	3.06806000
C	-5.51088800	-3.84080900	3.34797400
H	-5.13390500	-4.32397400	1.27727600
C	-5.08558000	-3.09890200	4.45035400
H	-3.63516700	-1.69838600	5.20955100
H	-6.38618900	-4.47755300	3.42394500
H	-5.63124000	-3.15956700	5.38682700
C	-5.62592200	-1.11723900	-1.47728800
C	-6.49086600	-1.49952100	-2.50578900
C	-6.09352500	-1.02829800	-0.16208400
C	-7.82088700	-1.78832000	-2.22116800
H	-6.10909100	-1.57069700	-3.51862800
C	-7.42356000	-1.32327200	0.11837300
H	-5.41899900	-0.73856900	0.63557000
C	-8.28700700	-1.70169300	-0.90910300
H	-8.49283100	-2.08468100	-3.01987600
H	-7.78395700	-1.26089900	1.13991200
H	-9.32440800	-1.93177600	-0.68708100
C	-3.72459000	3.88009500	-0.45873700
C	-4.65067000	4.68918200	0.20582500
C	-3.35234600	4.17476200	-1.77412900
C	-5.20061200	5.78997200	-0.44133000
H	-4.92995400	4.44484100	1.22499500

C	-3.90708300	5.27622800	-2.41828600
H	-2.63792100	3.54208400	-2.28780000
C	-4.82925200	6.08365400	-1.75340500
H	-5.91858200	6.41801100	0.07560600
H	-3.62112400	5.50364100	-3.43991000
H	-5.26015700	6.94217300	-2.25886900
C	3.64124900	3.53718100	1.22801000
C	4.42195000	4.28192600	2.11658800
C	4.15117200	3.19089000	-0.02428200
C	5.70729600	4.66895600	1.75714200
H	4.01262800	4.54242700	3.08673100
C	5.43825300	3.57993800	-0.38220300
H	3.54997400	2.61509600	-0.71530000
C	6.21773300	4.31615100	0.50724000
H	6.31261000	5.24390900	2.45050300
H	5.83169400	3.30236200	-1.35480200
H	7.22286500	4.61651900	0.22758900

TS^{α}_{Add}

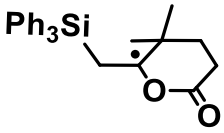


E = -1445.871488

G_{Corr}= 0.416484

C	-3.37911100	-1.28373700	-0.09760700
C	-4.07458400	0.00226800	0.32944500
C	-2.82367700	-1.19328900	-1.53009400
H	-5.06169900	0.09464700	-0.13941700
H	-4.23956800	0.03403000	1.40834100
H	-2.55528900	-1.49913100	0.58756400
H	-4.08189700	-2.12089800	-0.03114000
O	-2.40733600	1.20329300	-1.02609900
C	-3.33168900	1.26044900	-0.03749100
O	-3.54240300	2.33853500	0.46793100
C	-1.93648200	0.02565400	-1.60831900
C	-2.03428200	-2.47014300	-1.83673500
H	-2.68674700	-3.33874700	-1.70294000
H	-1.67101900	-2.48534700	-2.86853700
H	-1.17914300	-2.57816900	-1.16273300
C	-3.96919400	-1.04445200	-2.55485300
H	-3.56900600	-1.05208700	-3.57273700
H	-4.67218300	-1.87835200	-2.45213200
H	-4.52717900	-0.11241000	-2.42626200
C	-0.71338200	0.13333900	-2.17289700
H	-0.30384200	-0.69005000	-2.74290500
H	-0.27506800	1.11462600	-2.31641800
Si	1.09842900	-0.01760100	-0.13317400
C	1.50305100	1.80937700	0.00529400
C	2.67953300	-1.02277000	-0.29246700
C	0.02548200	-0.62983100	1.27580500
C	2.83204300	2.24197700	0.15393100
C	0.49760900	2.79068400	-0.06474300
C	3.22752300	-1.76064100	0.76979800
C	3.37181600	-1.02308100	-1.51537000
C	-0.09211400	-2.00736700	1.53540600
C	-0.75508200	0.24676700	2.04846400
C	3.14320000	3.59729100	0.24542400
H	3.63551900	1.51161200	0.20338700
C	0.80562800	4.14570100	0.03385300
H	-0.54069600	2.50164100	-0.20701600
C	4.41819300	-2.46911800	0.61647400
H	2.72640400	-1.77657300	1.73398900
C	4.56474100	-1.72516200	-1.67233800
H	2.97554300	-0.46193200	-2.35905500
C	-0.93780600	-2.48730500	2.53233500
H	0.48569200	-2.71966800	0.95106700
C	-1.61169500	-0.22980900	3.03916500
H	-0.69219000	1.31899600	1.88470200
C	2.12990900	4.55298600	0.18922600
H	4.17755200	3.90646700	0.36331200
H	0.00971700	4.88253100	-0.01686800
C	5.08929900	-2.45345600	-0.60527800
H	4.82451500	-3.02937000	1.45331500
H	5.08268600	-1.70699400	-2.62652800
C	-1.70430600	-1.59844700	3.28640100
H	-1.00430200	-3.55545600	2.71602800
H	-2.20440600	0.47127000	3.61919200
H	2.37108500	5.60913400	0.26188400
H	6.01689000	-3.00483000	-0.72505700
H	-2.36919500	-1.97044900	4.05976200

3_{rad}



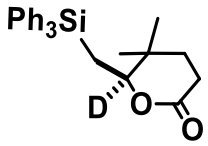
E = -1445.906253

G_{Corr}= 0.416017

C	3.82067300	1.06410100	-0.18153200
C	4.49393600	-0.27420100	-0.46430800
C	2.66670000	1.35140700	-1.15948300
H	5.13986300	-0.20758400	-1.34787600
H	5.13699100	-0.59043700	0.35973700
H	3.42296400	1.06645900	0.83993100
H	4.56217400	1.86827600	-0.23612000
O	2.28113400	-1.10989500	-1.12589400
C	3.53987400	-1.40984000	-0.74331000
O	3.85862400	-2.57691000	-0.69210600
C	1.73547300	0.17160500	-1.11622900
C	1.94720800	2.62866500	-0.70615600
H	2.65834100	3.46119800	-0.68996700
H	1.13242000	2.90136600	-1.38260800
H	1.52409300	2.51683400	0.29694900
C	3.19994500	1.55530800	-2.59727100
H	2.37688000	1.80377000	-3.27451200
H	3.92323000	2.37832100	-2.62196900
H	3.68979200	0.65803700	-2.98711000
C	0.31876800	0.14123500	-1.55935900
H	0.05800100	1.05403000	-2.10729600
H	0.16954800	-0.69922200	-2.24928300
Si	-0.92292300	-0.04860800	-0.11748200
C	-2.54102100	-0.71519800	-0.81012100
C	-1.21764600	1.64736600	0.64534500
C	-0.22541800	-1.22782600	1.17037200
C	-3.77745800	-0.13795400	-0.48614300
C	-2.54222300	-1.83573400	-1.65692900
C	-1.05216900	1.90332600	2.01294000
C	-1.61295300	2.71478900	-0.17707300
C	0.95524200	-0.90565900	1.86021500
C	-0.83492500	-2.45621100	1.45855200

C	-4.97030100	-0.65676000	-0.98880900
H	-3.81294500	0.73061300	0.16649600
C	-3.73022000	-2.35981600	-2.16175000
H	-1.60419600	-2.31741700	-1.92495900
C	-1.25672800	3.17939900	2.53904500
H	-0.75643600	1.09928700	2.68142400
C	-1.82161700	3.99014400	0.33997800
H	-1.76146400	2.55292200	-1.24303700
C	1.51314300	-1.77735800	2.79040000
H	1.45100700	0.04314000	1.66594600
C	-0.28273500	-3.33491000	2.39113500
H	-1.75274300	-2.73746200	0.94888900
C	-4.94832500	-1.76861300	-1.82823200
H	-5.91578200	-0.19251800	-0.72496300
H	-3.70577000	-3.22784600	-2.81353500
C	-1.63811900	4.22576600	1.70282300
H	-1.11834500	3.35442600	3.60170500
H	-2.12532000	4.79957300	-0.31702500
C	0.89361800	-2.99858000	3.05598600
H	2.42986700	-1.50710300	3.30583200
H	-0.77106700	-4.28298600	2.59500300
H	-5.87592200	-2.17360100	-2.22121900
H	-1.79591500	5.21988100	2.10988000
H	1.32725000	-3.68373100	3.77793000

3



E = -1446.559952
G_{Corr}= 0.430550
G^{D}_{Corr}= 0.426925

C	4.24999700	1.30782800	-0.68100700
C	4.57714100	-0.11914900	-0.25053600
C	2.96845200	1.37773100	-1.52884100
H	5.05345400	-0.67204800	-1.06873700
H	5.28360000	-0.14414700	0.58219400
H	4.11703800	1.93951300	0.20603500
H	5.09379500	1.72407400	-1.24169100
O	2.15798000	-0.54840000	-0.19162700
C	3.38635800	-0.96222000	0.14604600
O	3.50174400	-2.04002200	0.69043900
C	1.84979300	0.79869000	-0.64317800
C	2.66345600	2.84929800	-1.83532300
H	3.51781100	3.30634600	-2.34524800
H	1.79250200	2.95628000	-2.48828900
H	2.47611700	3.41798000	-0.91752500
C	3.12954800	0.59883000	-2.84188900
H	2.27394600	0.76283400	-3.50316200
H	4.02736600	0.93738200	-3.36955300
H	3.21927100	-0.47975800	-2.68061900
C	0.46275800	0.70101400	-1.26055300
H	0.15440400	1.70577800	-1.57032600
H	0.49707100	0.08213200	-2.16468200
Si	-0.88961500	0.03728000	-0.09341400
C	-2.47619100	0.99140000	-0.45441300
C	-0.37064000	0.36745800	1.68672200
C	-1.23290800	-1.79471700	-0.36983300
C	-3.40288800	1.28585400	0.55668300
C	-2.79502500	1.37851900	-1.76525000
C	0.07815900	-0.65627400	2.53168900
C	-0.35412900	1.68192500	2.18040500
C	-0.19868200	-2.74308000	-0.44164900
C	-2.55364400	-2.25564000	-0.48802200
C	-4.59919700	1.94341200	0.27281600
H	-3.18891900	1.00097200	1.58391600
C	-3.98877100	2.03572400	-2.05751500
H	-2.10606300	1.16225700	-2.57909700
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C	-0.47506700	-4.09703500	-0.62178800
H	0.83416700	-2.42171700	-0.34927400
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H	-3.37943400	-1.55025500	-0.44200500
C	-4.89398500	2.32037300	-1.03611100
H	-5.29982300	2.16171000	1.07320600
H	-4.21263400	2.32496200	-3.07995400
C	0.53800400	0.93129000	4.29268100
H	0.87385900	-1.18975700	4.45814200
H	0.09651500	2.98962200	3.82981000
C	-1.79409100	-4.53373700	-0.73636300
H	0.34187000	-4.81083200	-0.67074200
H	-3.86477400	-3.94049000	-0.75906000
H	-5.82436400	2.83356200	-1.25965700
H	0.88822900	1.14748000	5.29752200
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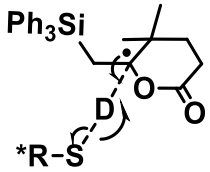
H	1.79504000	1.41496800	0.26420400

TS-*Si*



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G^{D}_{Corr}= 0.945209

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C	3.85983200	-1.39476300	-1.90728100
H	2.02458600	-2.43054500	-4.37199500
H	3.19168900	-3.74009800	-4.27629500
H	4.86574900	-2.25075800	-3.60844000
H	3.75258900	-0.96709500	-4.03166700
O	1.74640000	-2.56293800	-1.54698100
C	2.03105600	-3.42959200	-2.55621300
O	1.61182000	-4.55819800	-2.46680200
C	2.40256400	-1.33084200	-1.44487600
C	4.63394000	-2.42990900	-1.06207100
H	5.68499800	-2.42052900	-1.36747600
H	4.59564600	-2.19330000	0.00226100
H	4.25923100	-3.44923600	-1.20021900
C	4.53122200	-0.02387800	-1.78590000
H	4.67356700	0.25835400	-0.74192500

H	5.51658700	-0.06086400	-2.26176500
H	3.94142600	0.75452500	-2.27918000
C	1.94375300	-0.59704600	-0.22184700
H	2.25395900	0.45012600	-0.30819900
H	0.84821500	-0.57280900	-0.26498100
Si	2.29799900	-1.03361700	1.60609500
C	1.26760900	0.23285100	2.56243000
C	4.11073300	-0.81532100	2.07572200
C	1.74829900	-2.75475000	2.13483600
C	1.83885700	1.33712700	3.21039400
C	-0.12883300	0.10067600	2.62055900
C	4.81394700	-1.83316600	2.73646100
C	4.79847100	0.37424100	1.78304800
C	1.22680500	-2.94743000	3.42422400
C	1.93424700	-3.88910500	1.33167000
C	1.05120800	2.27952900	3.87003600
H	2.91491700	1.47591100	3.19974600
C	-0.92344500	1.02954700	3.28961300
H	-0.60945900	-0.75392300	2.15196000
C	6.15631400	-1.67791000	3.08090300
H	4.31180000	-2.76632500	2.97862800
C	6.13886100	0.53506000	2.12638700
H	4.28270300	1.18822900	1.27864500
C	0.90281200	-4.21944700	3.89207100
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H	2.31722900	-3.78380100	0.32358800
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H	1.52157400	3.12930900	4.35577600
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C	6.82264600	-0.49356900	2.77371400
H	6.68082100	-2.48250000	3.58751300
H	6.64977600	1.46333600	1.88763100
C	1.09726500	-5.33182500	3.07592000
H	0.49920200	-4.34054700	4.89307900
H	1.75306700	-6.02102200	1.14239400
H	-0.94899800	2.85838400	4.42761800
H	7.86841100	-0.37116600	3.03913300
H	0.84211600	-6.32430100	3.43570500
S	1.33080400	0.37265100	-3.67688800
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O	-3.41020800	0.03453800	-1.62001400
O	-5.02221700	1.46848000	-2.27810400
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O	-3.40513500	0.57565800	1.32738400
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C	-2.37812000	0.96827200	-1.90965600
C	-1.81737300	1.54901000	-0.61217200
C	-0.63634600	2.46397800	-0.95376800
C	0.03970300	3.02471800	0.28403200
C	-1.27033900	-2.12776400	-2.18824600
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C	2.31005100	3.60815800	-0.13870200
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H	-0.41367800	1.93906100	-3.55524000
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H	-1.49064100	0.74724500	0.05371800
H	-0.99004600	3.29627700	-1.58381200
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H	-0.67864600	3.56484400	0.90115400
C	-1.40724600	-3.03744400	-1.02489300
C	-1.62388500	-2.53034800	0.25891600
C	-1.38222100	-4.41719100	-1.23839600
C	-1.80395500	-3.39944400	1.32866100
H	-1.69165600	-1.45911700	0.40847300
C	-1.55494300	-5.28326200	-0.16527000
H	-1.21047300	-4.79700900	-2.23890800
C	-1.76393500	-4.77566900	1.11706600
H	-1.97080800	-3.00351800	2.32512200
H	-1.51862200	-6.35564600	-0.32666500
H	-1.88948300	-5.45436900	1.95448500
C	3.19996800	4.63589000	-0.74514200
C	2.71030600	5.85253700	-1.22850100
C	4.56483400	4.34642100	-0.83200300
C	3.58651700	6.77542600	-1.79206100
H	1.65084300	6.07138300	-1.16217300
C	5.43655800	5.26981000	-1.39802600
H	4.92652900	3.39478800	-0.45659700
C	4.94773000	6.48519800	-1.87754900
H	3.20703000	7.72053500	-2.16637300
H	6.49534800	5.04277100	-1.46700700
H	5.62827500	7.20618400	-2.31947900
C	-5.63664900	-0.64543700	-1.33005500
C	-5.18411200	-1.80535100	-0.69355300
C	-7.00523000	-0.43785400	-1.52309400
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H	-5.74841000	-3.65422300	0.23709800
H	-8.98095000	-1.23152400	-1.23765100
H	-8.18060200	-3.29321000	-0.11252900
C	-4.55655800	2.65312900	1.59274400
C	-5.37316000	2.15648200	2.61287300
C	-4.70130200	3.97386400	1.15722100
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H	-5.25157600	1.12712400	2.93275200
C	-5.65876900	4.79321900	1.74661700
H	-4.07214300	4.35180300	0.35999000
C	-6.47061700	4.29789000	2.76657400
H	-6.96219800	2.59356600	3.99043200
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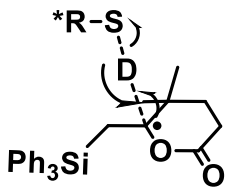
TS-*Re*



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C	2.30251800	3.14697500	-0.10841600
H	-0.70976700	3.44866400	1.61113900
H	0.84654100	3.36795400	2.41631800
H	1.17483800	4.87429500	0.54248500
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O	1.24079600	1.02123000	0.60857500
C	0.32414600	1.62694700	1.39950700
O	-0.40153200	0.92186100	2.06298900
C	1.98280000	1.67594000	-0.37669100
C	3.34166600	3.27136900	1.02315700
H	3.05337100	2.72476200	1.92373800
H	3.46465200	4.32772300	1.28489000
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C	2.85561000	3.83686900	-1.36102900
H	3.81656200	3.41663200	-1.66604700
H	3.01980100	4.89600300	-1.13919700
H	2.16115700	3.77721600	-2.20303100
C	2.97128900	0.70715800	-0.95868700
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H	2.39008200	-0.16288500	-1.28628000
Si	4.39694400	-0.05111300	0.07655000
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C	4.06475900	-0.05238500	1.92645500
C	4.55412400	-1.83684500	-0.50919200
C	7.16267100	0.47229700	0.48816000
C	6.21744300	1.73185200	-1.32112900
C	3.06291700	-0.89302500	2.43299600
C	4.75207500	0.76785100	2.83189800
C	5.00070600	-2.84511200	0.35667600
C	4.28847000	-2.18817300	-1.84131300
C	8.41048900	1.03634600	0.23668400
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C	7.46330400	2.30232700	-1.58081300
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H	5.53205900	1.43557800	2.47584300
C	5.17305900	-4.15449200	-0.08746700
H	5.20284100	-2.61263600	1.39930100
C	4.45661100	-3.49556900	-2.29228100
H	3.93744000	-1.43969600	-2.54783500
C	8.56262100	1.95865500	-0.79826600
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H	7.57343600	3.01177300	-2.39528600
C	3.43843800	-0.07781700	4.67186800
H	1.95860700	-1.55753200	4.15033000
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H	-2.04833400	1.46897000	-2.92184500
H	-1.09829900	-0.77529000	-2.99263800
H	-3.45103100	-0.60204000	-2.28741600
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H	-2.55616800	1.95655000	1.56681900
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C	0.61577500	-2.61429900	-0.01176600
C	0.00078300	-2.27656900	1.19742700
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H	-0.65663900	-1.41917200	1.25325000
C	1.75238600	-4.44670600	1.06758400
H	1.96659800	-3.94804700	-1.01877100
C	1.11845600	-4.12685900	2.26850400
H	-0.25075000	-2.78934200	3.26413100
H	2.44687400	-5.27869800	1.01949600
H	1.31308900	-4.71903200	3.15762900
C	-2.57372600	-4.43156900	-1.59537700
C	-2.60330700	-5.49650600	-2.49940100
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C	-2.00970100	-5.95261800	0.18967500
H	-2.25724200	-3.83123400	0.45126200
C	-2.03446500	-7.01461600	-0.71351600
H	-2.35217400	-7.61412600	-2.75914400
H	-1.77438300	-6.12778600	1.23433600
H	-1.81885300	-8.02191700	-0.37077000
C	-6.03993100	-1.40931000	1.37766800
C	-6.38933000	-2.24868600	2.43938700
C	-7.03204300	-0.88023300	0.54623500
C	-7.72515200	-2.55859200	2.66866700
H	-5.60661800	-2.65044600	3.07383000
C	-8.36769600	-1.19193100	0.78067900
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C	-8.71470600	-2.03013900	1.83956500
H	-7.99526300	-3.21126800	3.49225100
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C	-3.34223600	5.82860200	-0.26643400
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C	-3.80510700	8.05530200	-1.07582300
H	-5.20232900	6.41155500	-1.16340300
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H	-4.48285200	8.76426900	-1.53973800
H	-2.20759200	9.48206200	-0.85789100

9. Supplementary References

1. Luo, J., Zhang, J. *ACS Catal.* **2016**, *6*, 873-877.
2. Garreau, M., Vaillant, F. L., Waser, J. *Angew. Chem. Int. Ed.* **2019**, *58*, 8182-8186.
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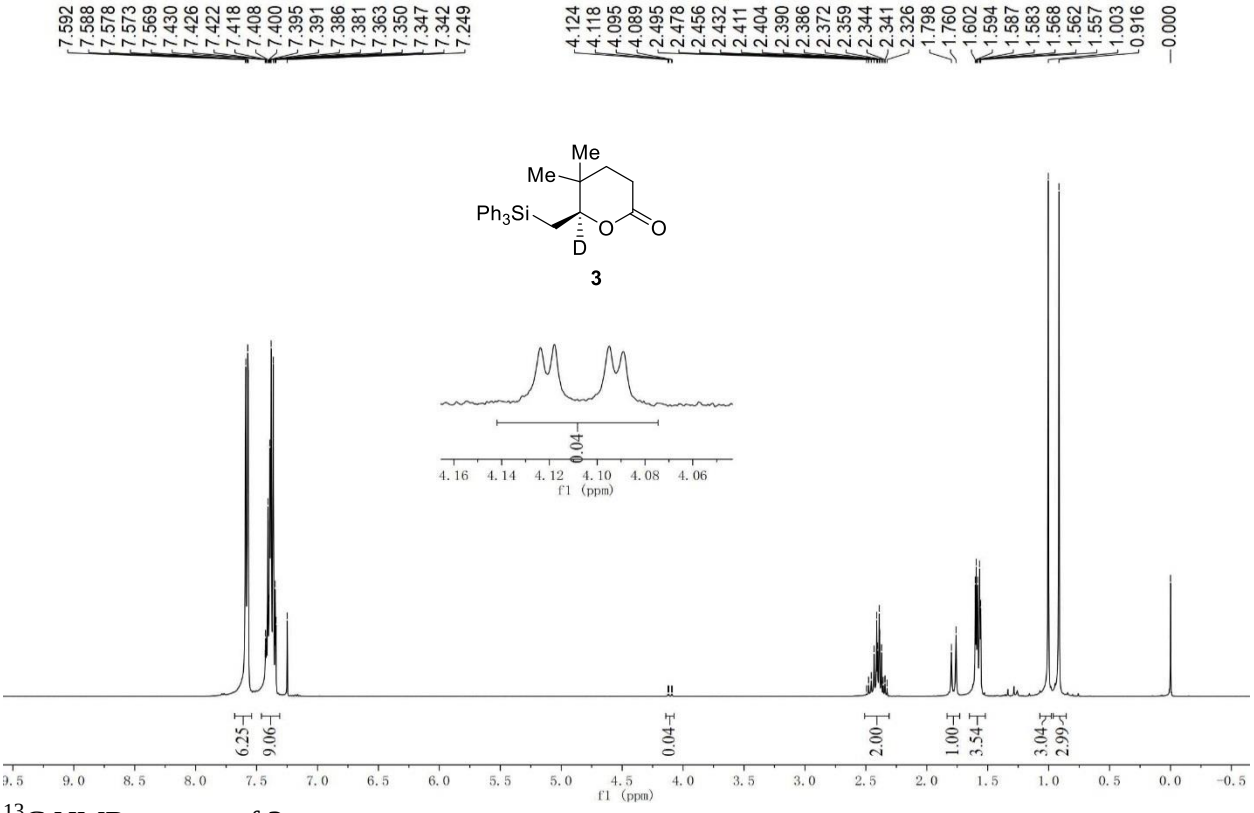
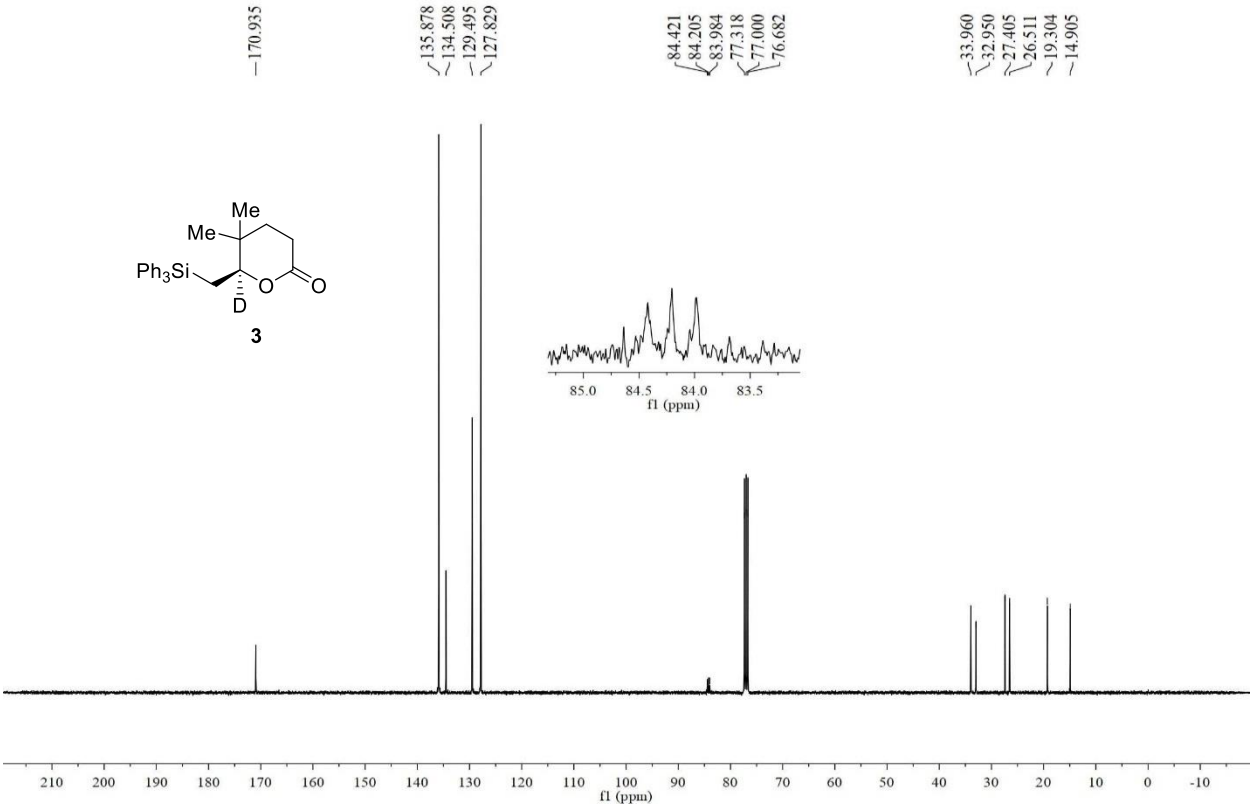
10. NMR Spectra and HPLC Spectra

^{1}H NMR spectra of **3**



^{13}C NMR spectra of **3**



HPLC spectra of racemic **3**

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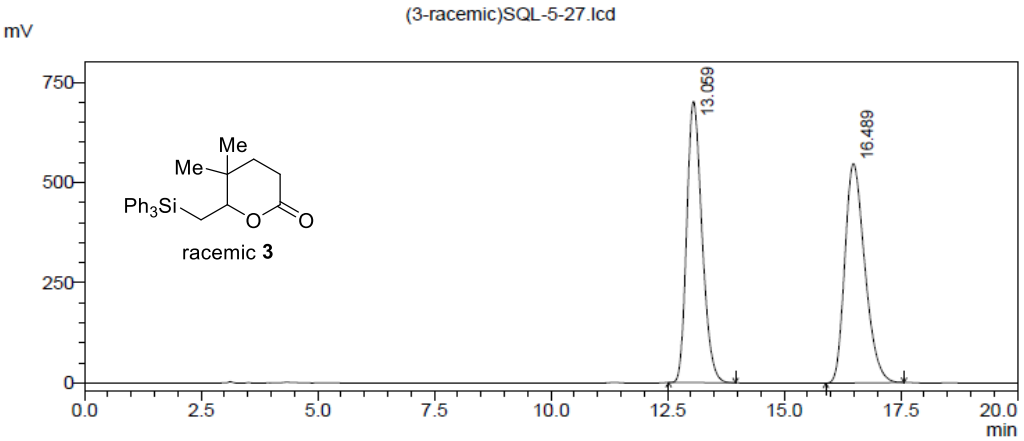

<Data Analysis>

DetA 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	13.059	701032	15969014	49.394
2	16.489	546518	16360904	50.606
Total		1247550	32329918	100.000

HPLC spectra of **3**

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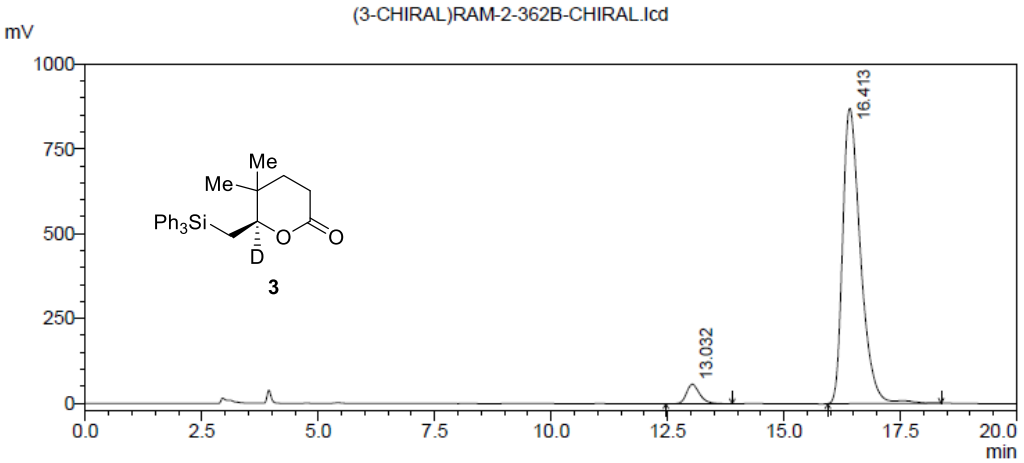
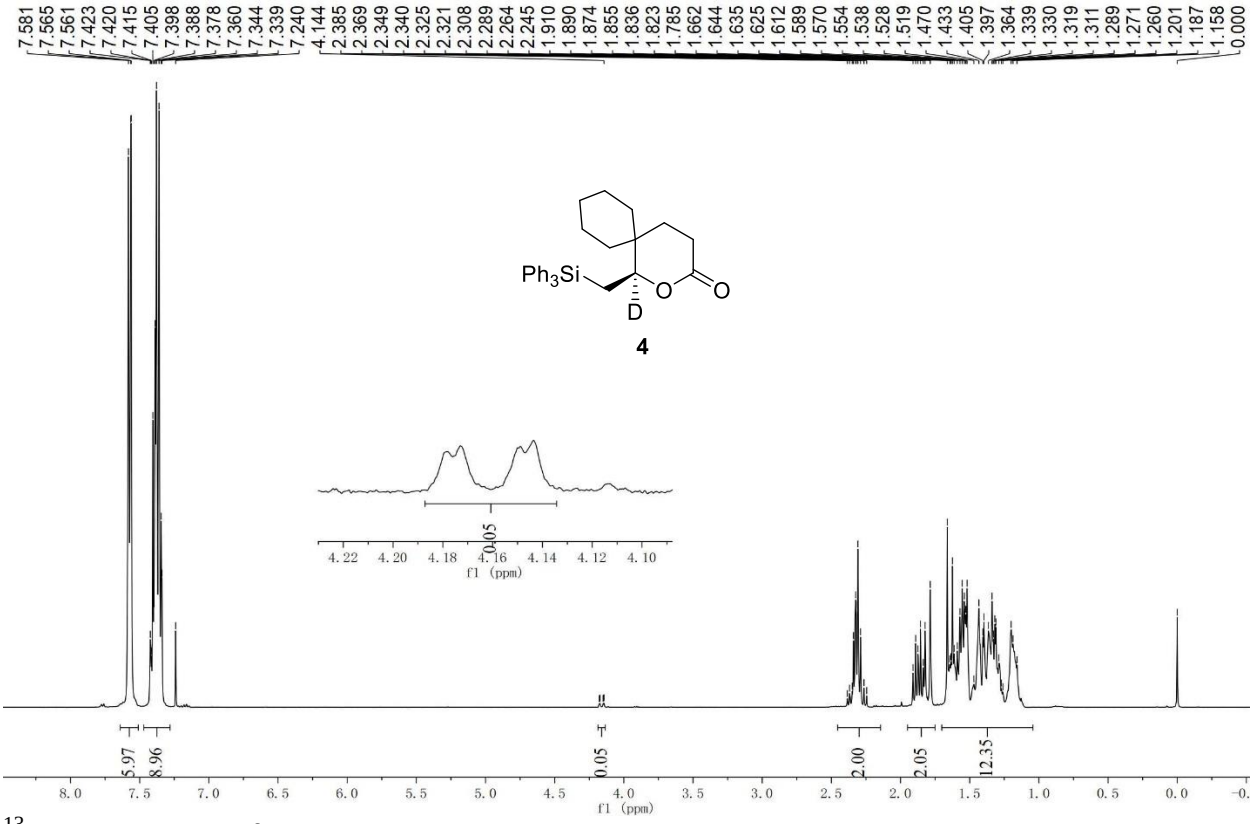


<Data Analysis>

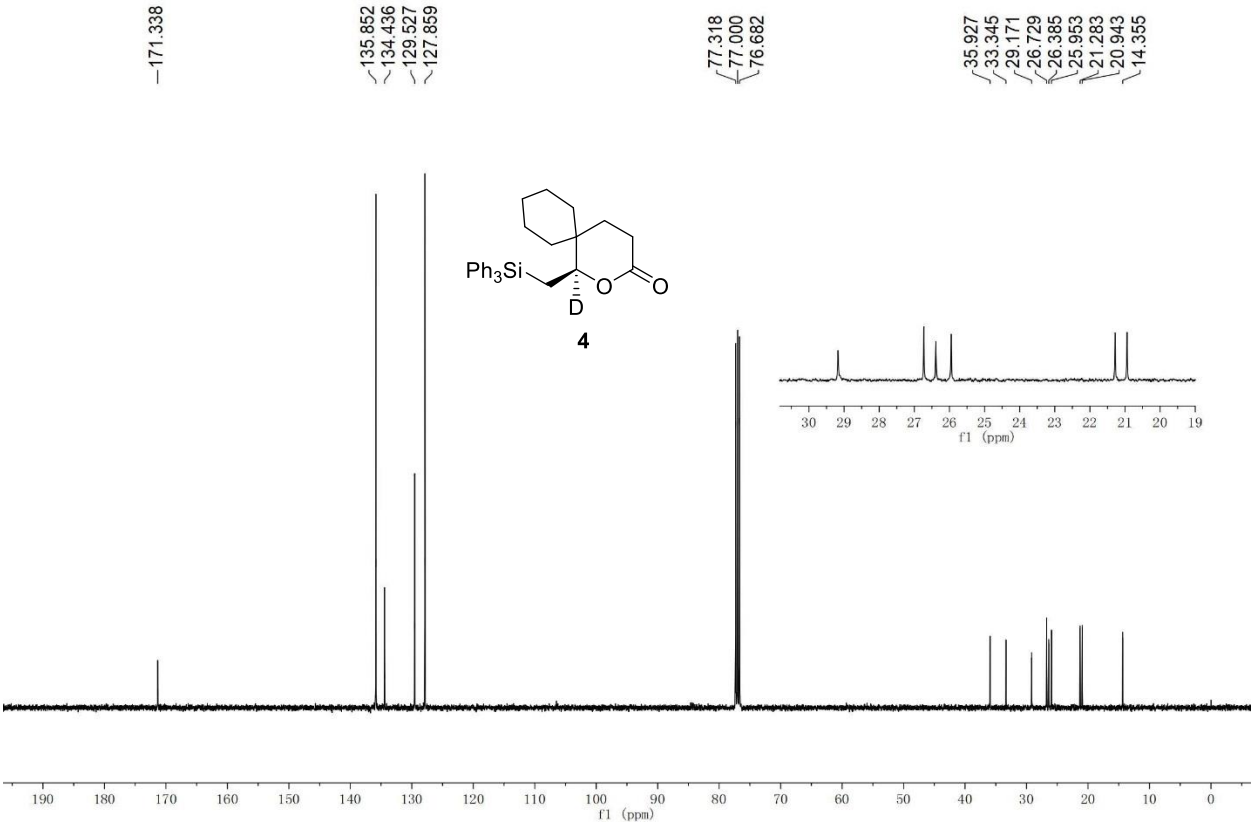
DetA 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	13.032	57269	1112174	4.577
2	16.413	869816	23188127	95.423
Total		927085	24300300	100.000

^{1}H NMR spectra of **4**



^{13}C NMR spectra of **4**



HPLC spectra of racemic **4**

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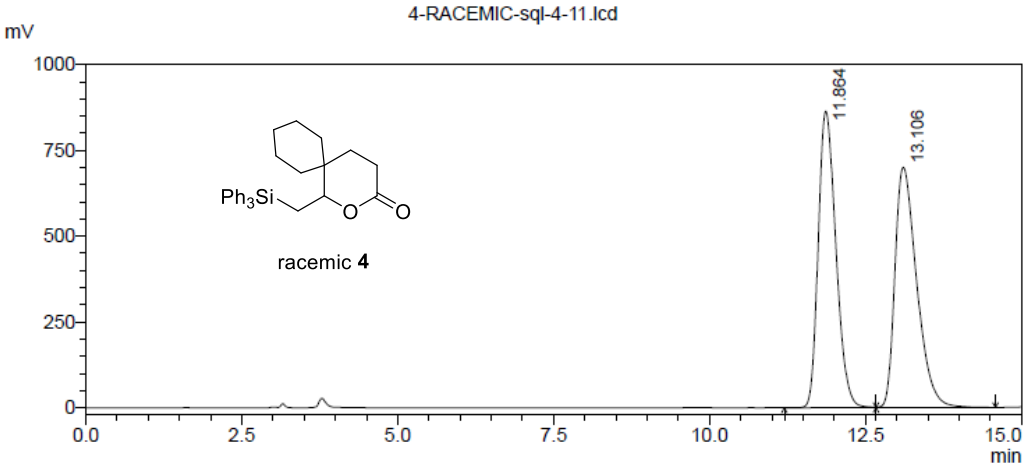

<Data Analysis>

DetA 214nm

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1	11.864	864007	17014581	49.940
2	13.106	699883	17055156	50.060
Total		1563891	34069737	100.000

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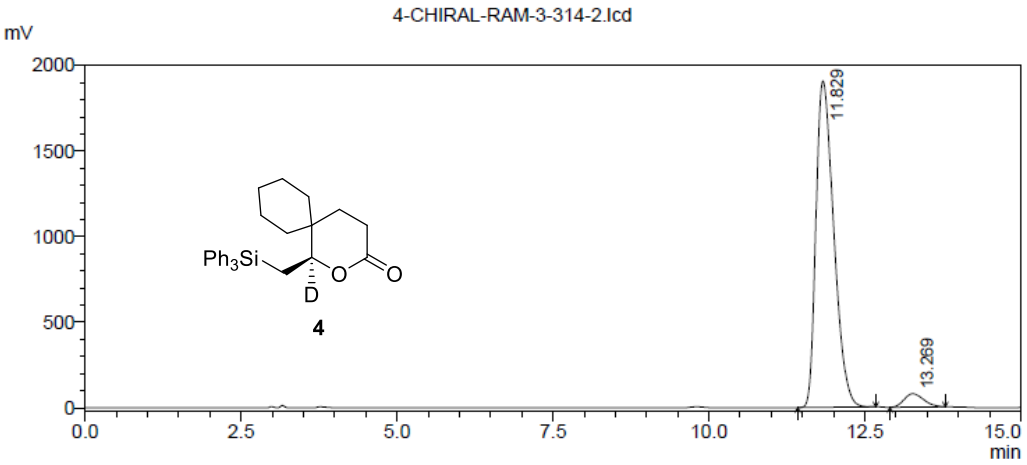

<Data Analysis>

DetA 214nm

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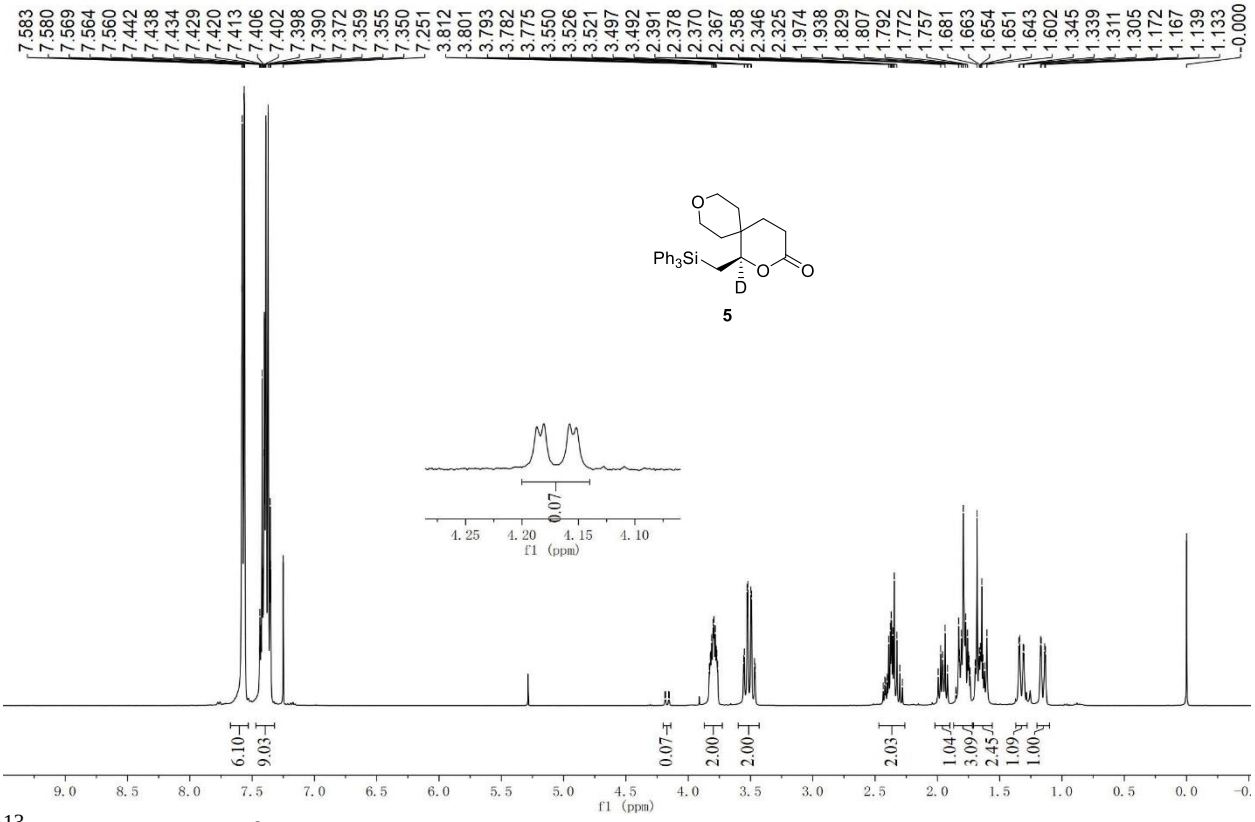
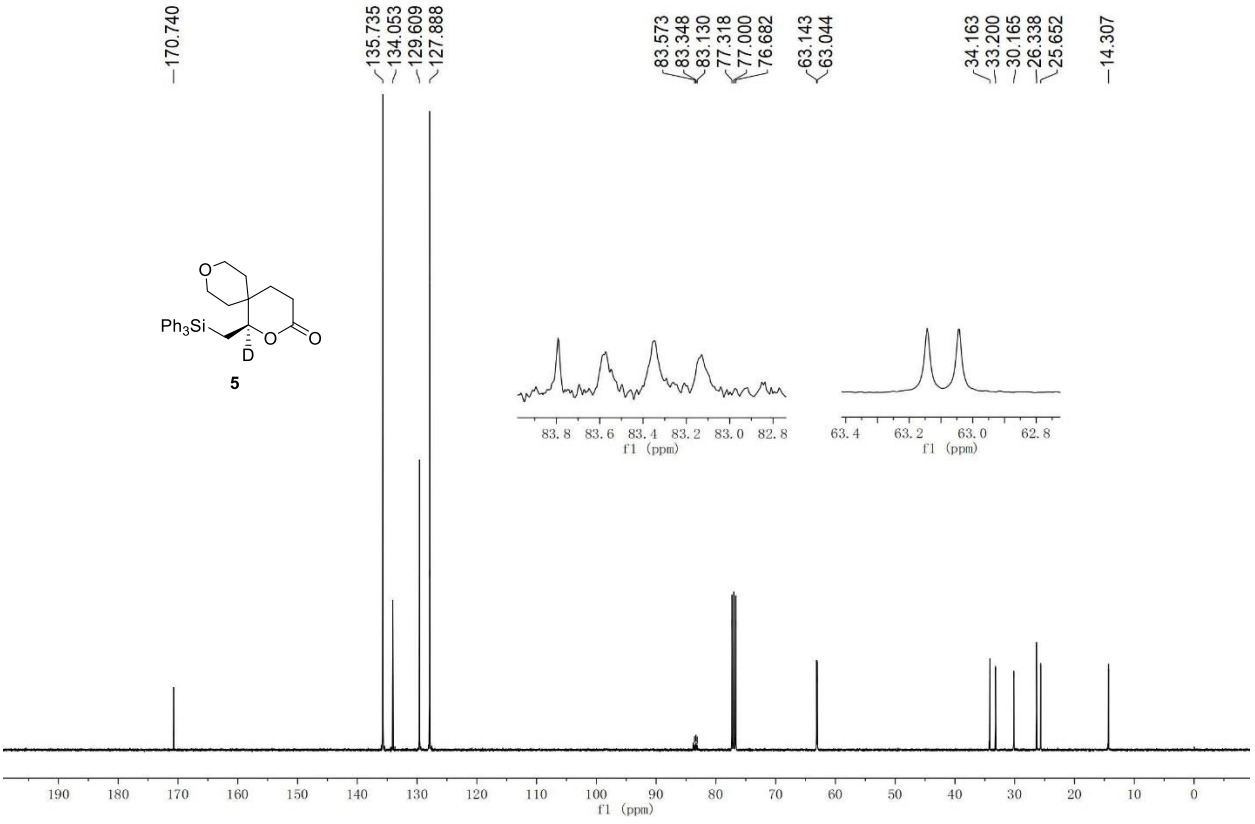
1	11.829	1905801	37839866	95.697
2	13.269	78230	1701439	4.303
Total		1984031	39541305	100.000

^{1}H NMR spectra of **5**



^{13}C NMR spectra of **5**



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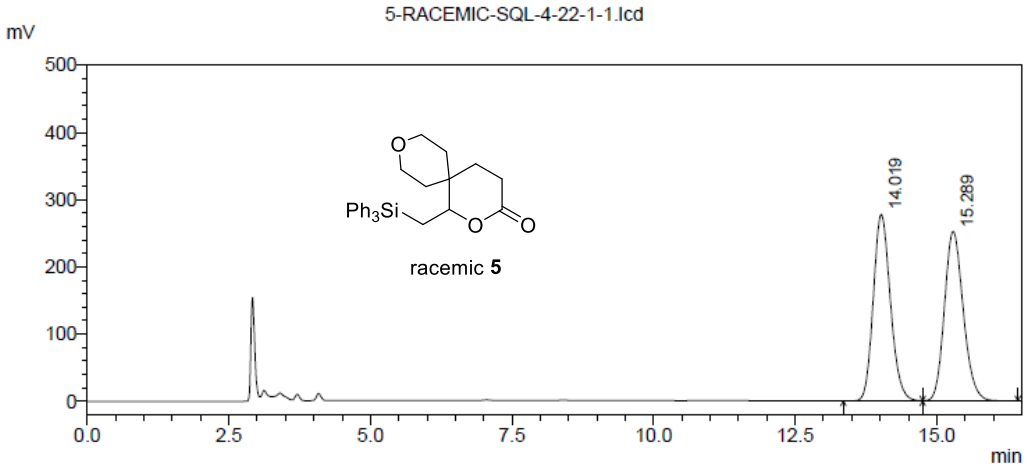

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???A 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	14.019	277553	5842874	49.982
2	15.289	252266	5846979	50.018
Total		529820	11689854	100.000

HPLC spectra of **5**

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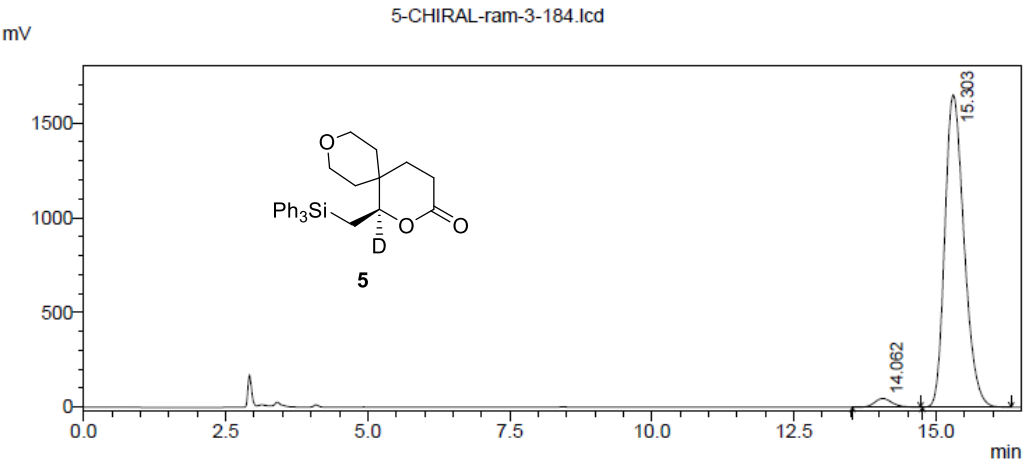

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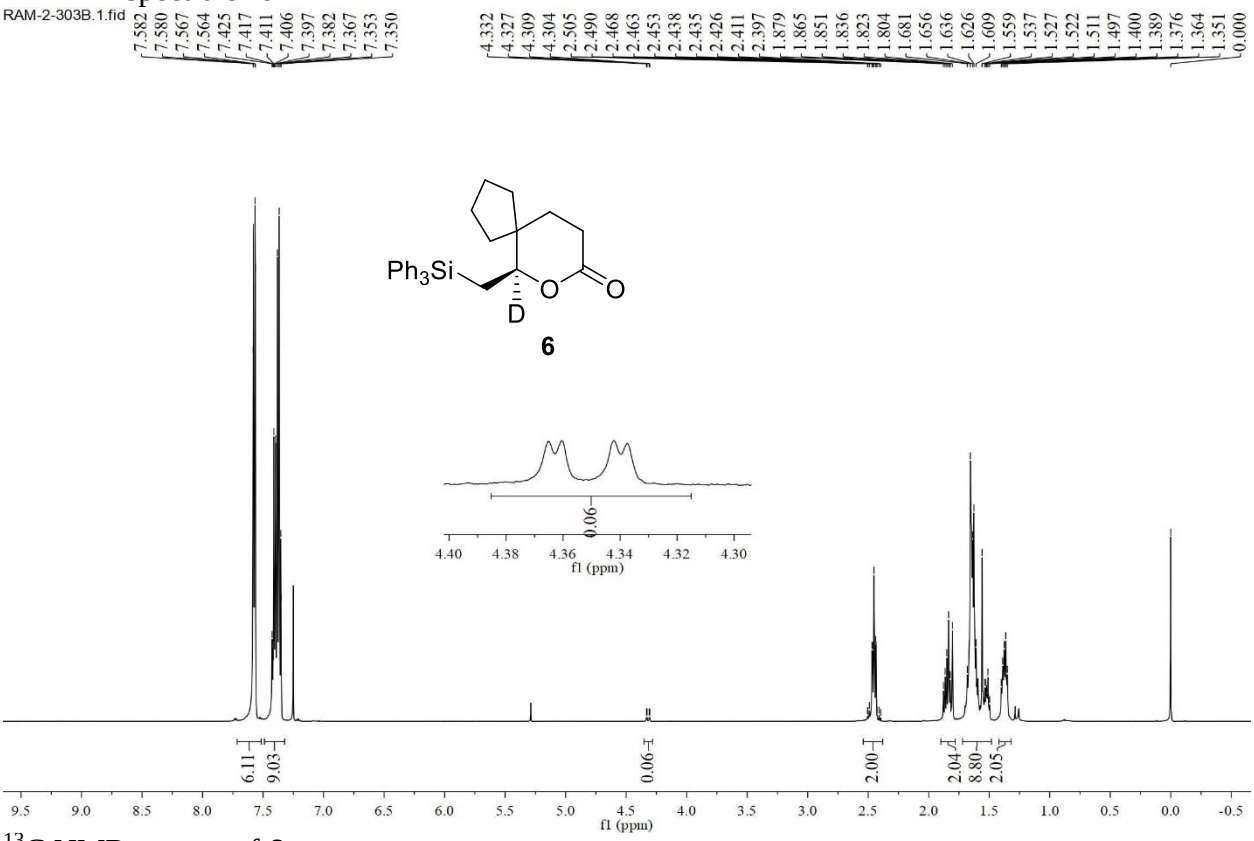
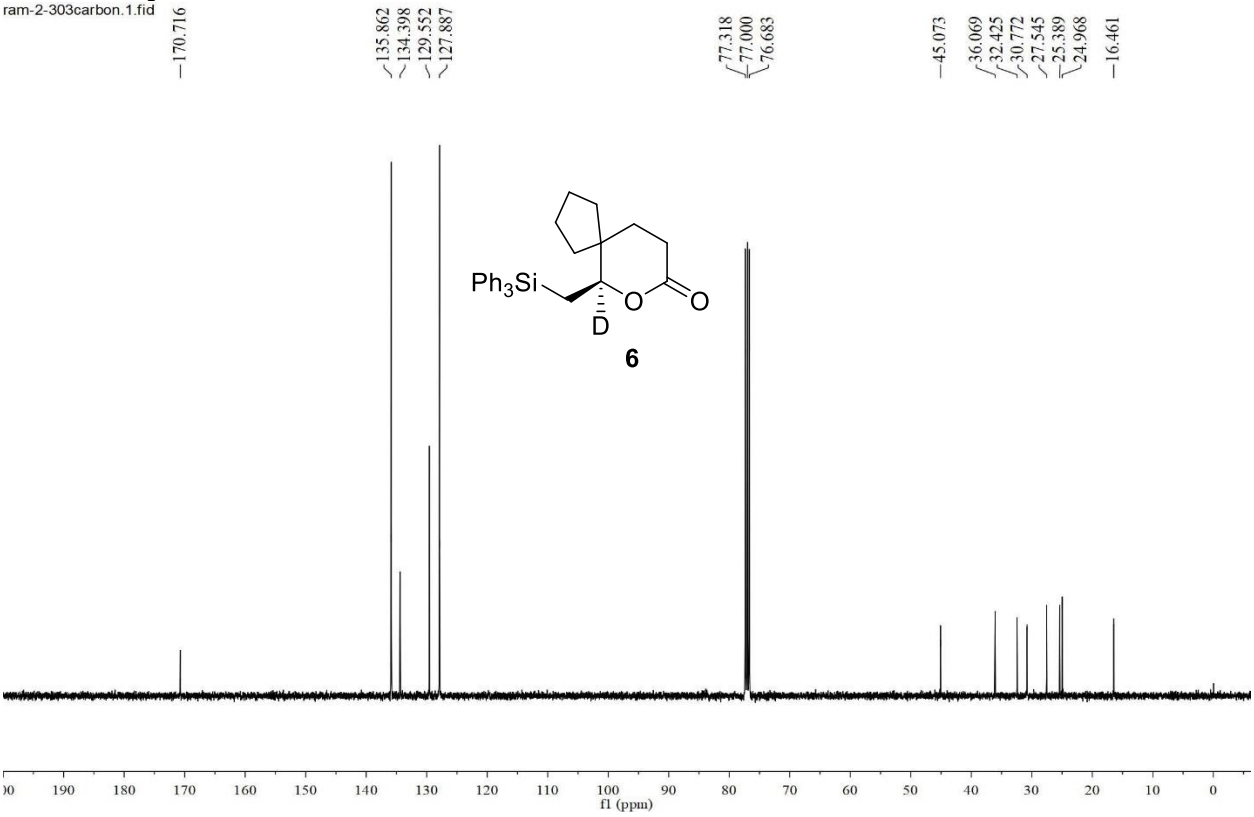
???A 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	14.062	45903	973578	2.445
2	15.303	1647211	38840778	97.555
Total		1693114	39814356	100.000

^{1}H NMR spectra of **6**



^{13}C NMR spectra of **6**



HPLC spectra of racemic **6**

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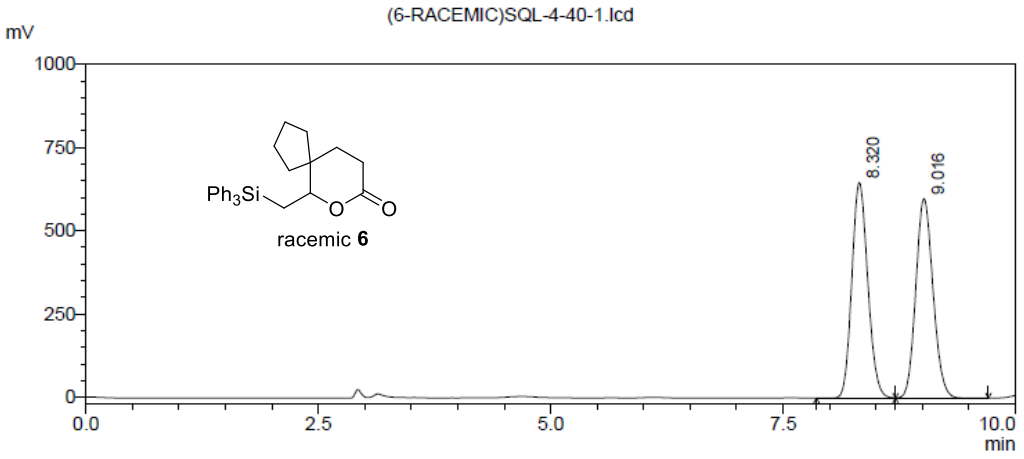

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???A 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	8.320	647764	7744973	50.056
2	9.016	599142	7727609	49.944
Total		1246906	15472582	100.000

HPLC spectra of **6**

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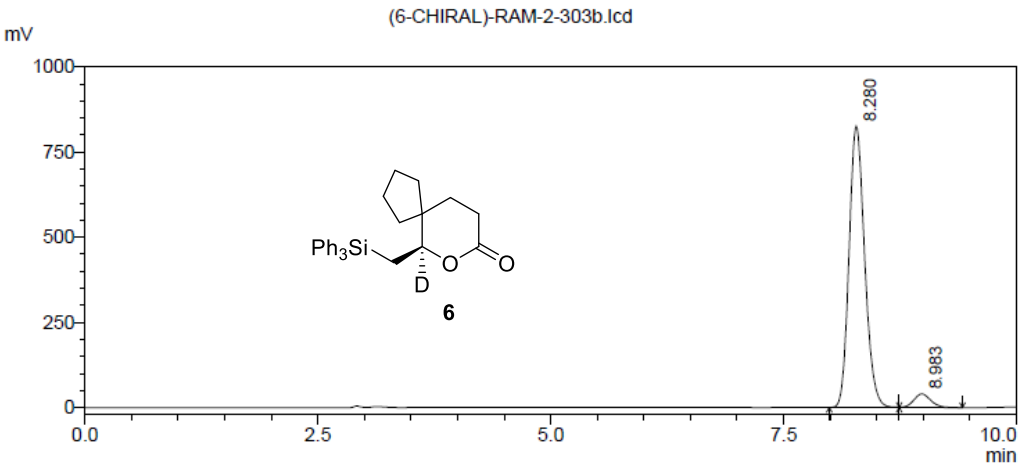
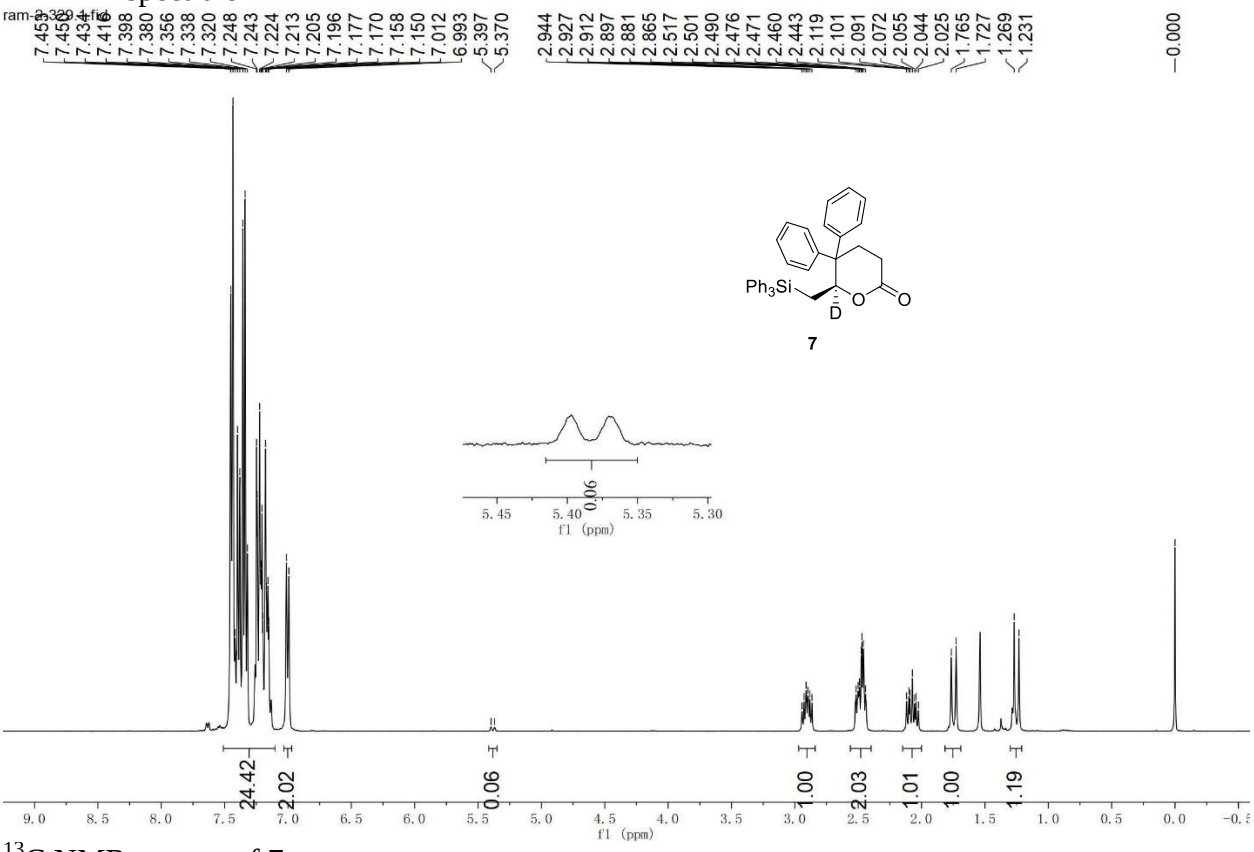


<Data Analysis>

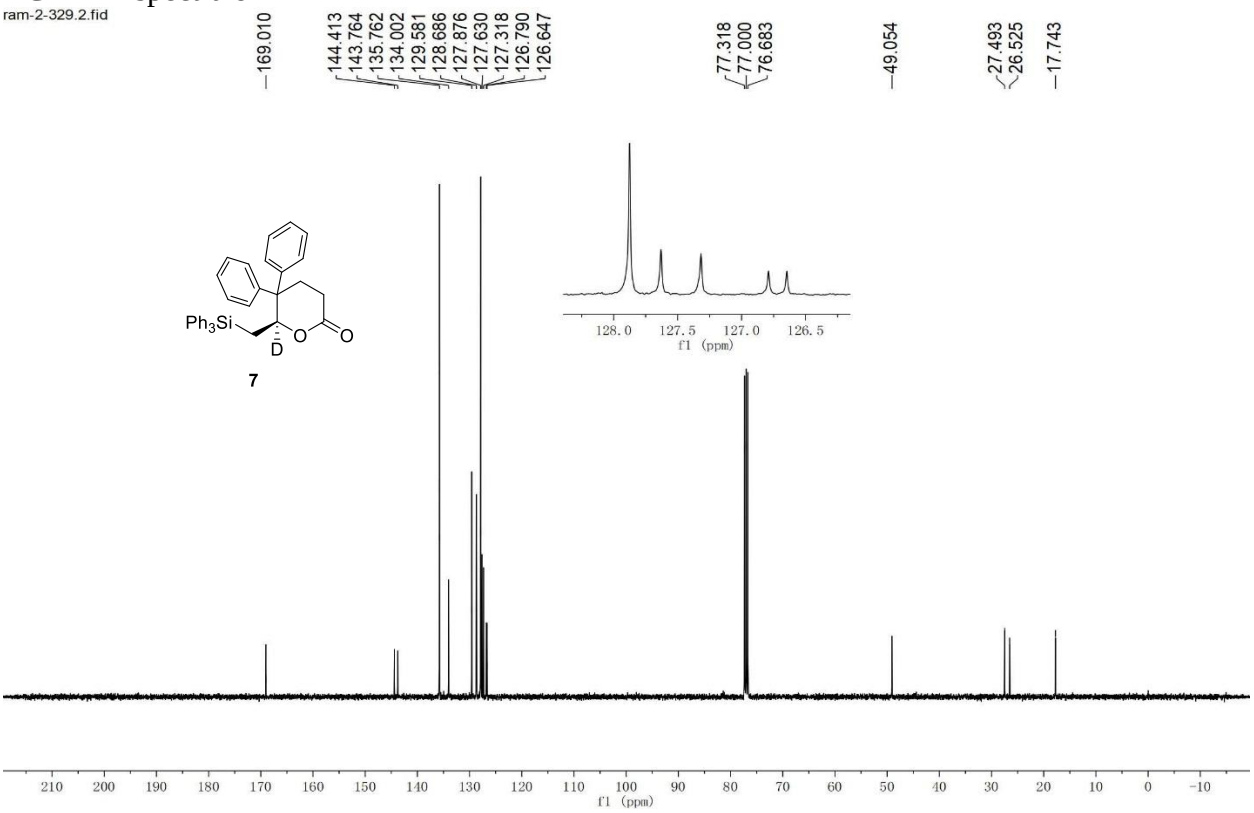
???A 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	8.280	825721	9612403	95.051
2	8.983	39690	500435	4.949
Total		865411	10112838	100.000

^{1}H NMR spectra of **7**



^{13}C NMR spectra of **7**



HPLC spectra of racemic **7**

Data File : 7-RACEMIC-sql-5-151-1.lcd
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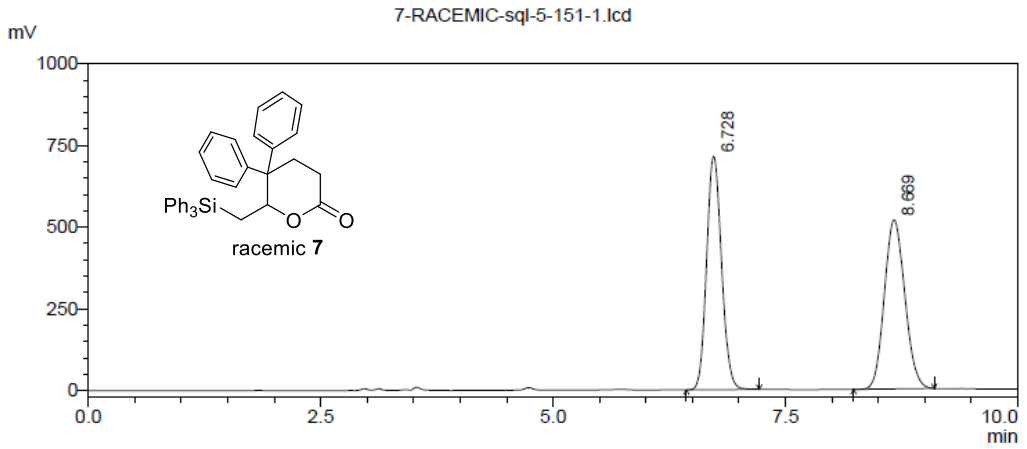

<Data Analysis>

DetA 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	6.728	713735	7967917	50.091
2	8.669	517537	7938880	49.909
Total		1231272	15906798	100.000

HPLC spectra of **7**

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Method File : 4OD-H-90-1-214-25min.lcm
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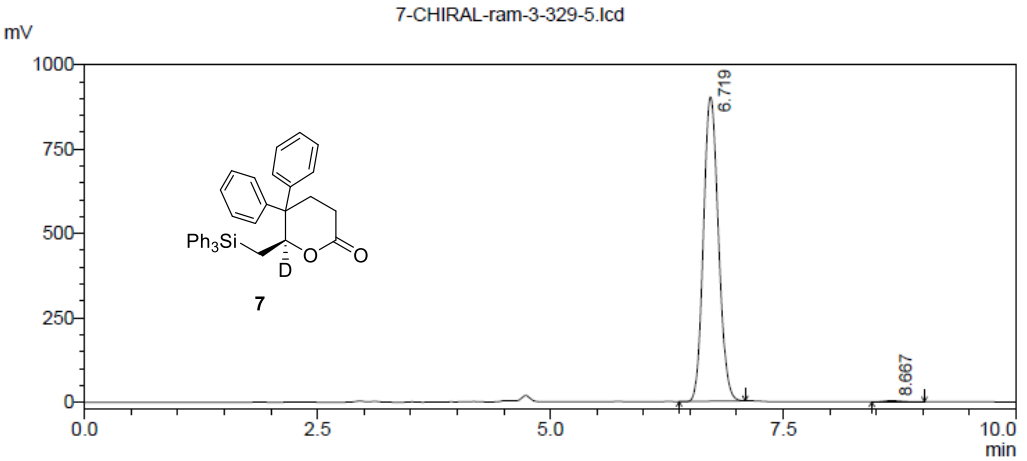
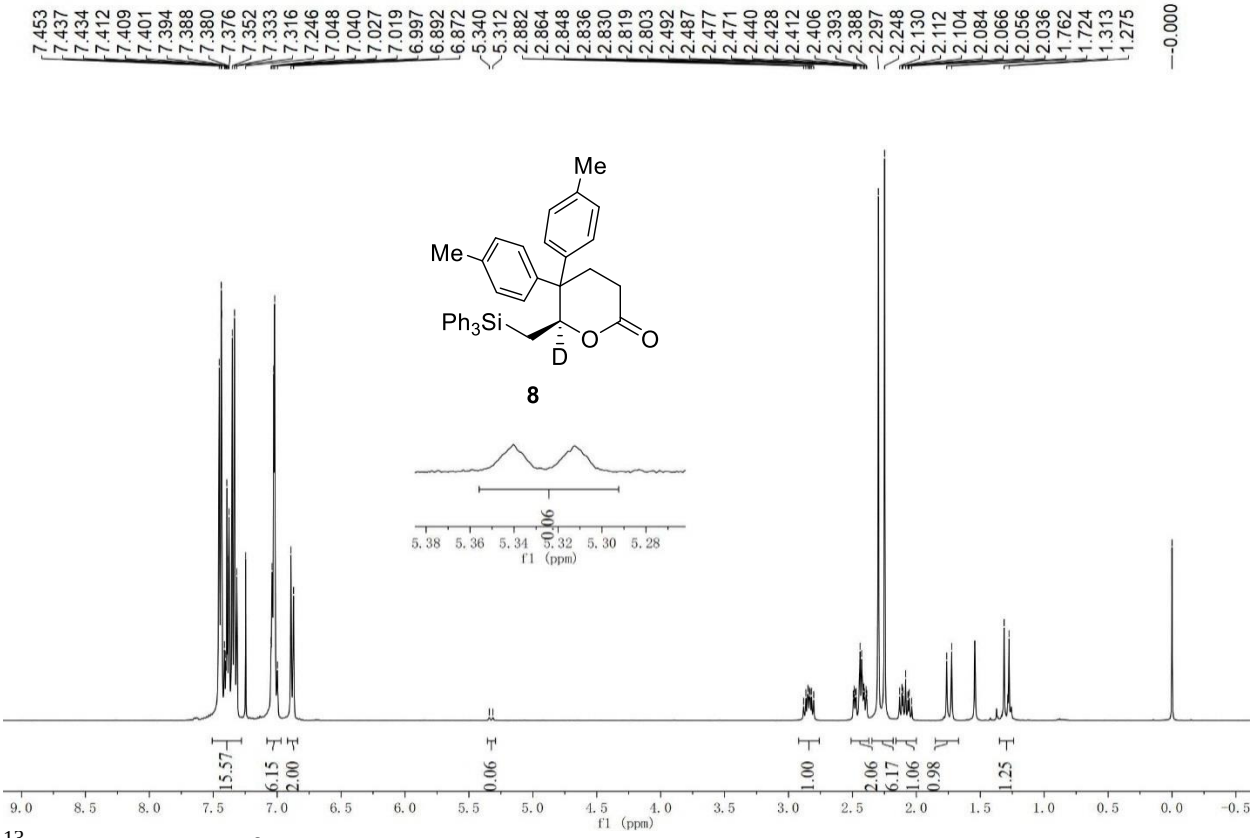


<Data Analysis>

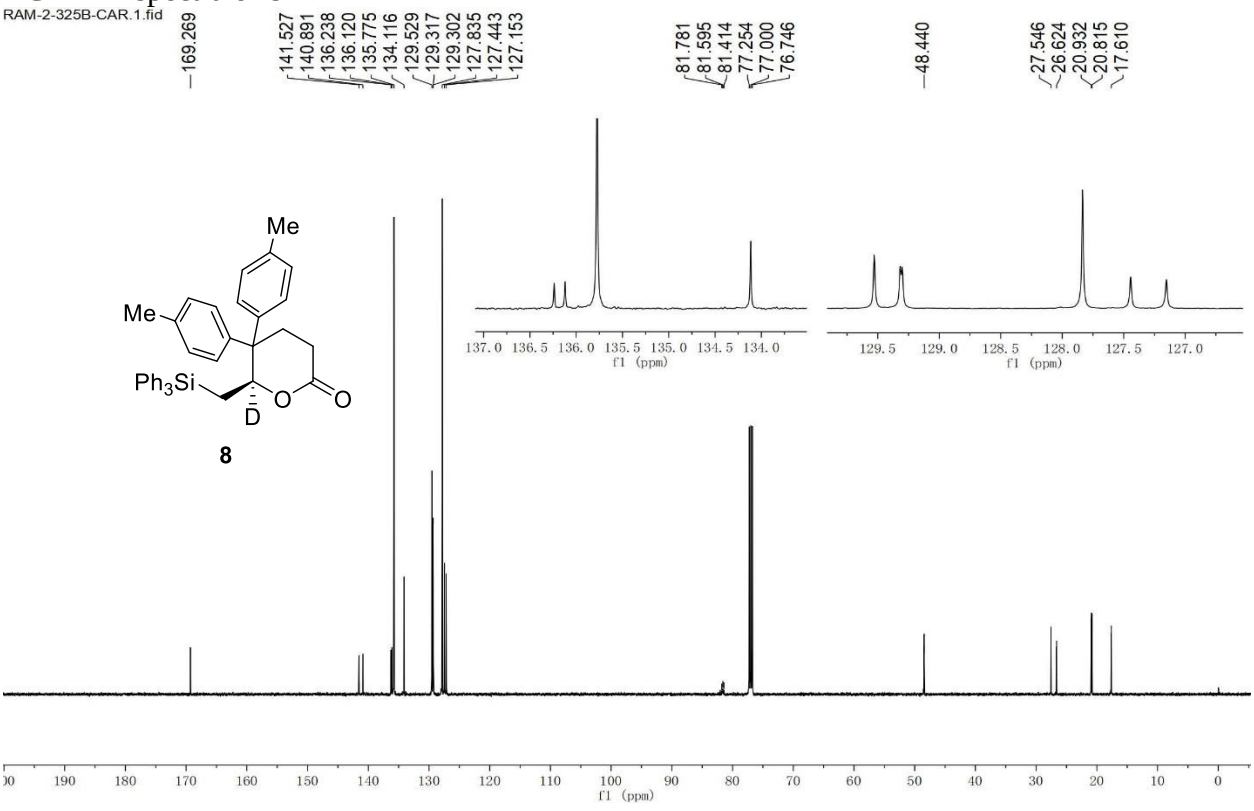
DetA 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	6.719	901360	10060934	99.530
2	8.667	3086	47482	0.470
Total		904446	10108417	100.000

^{1}H NMR spectra of **8**



^{13}C NMR spectra of **8**



HPLC spectra of racemic **8**

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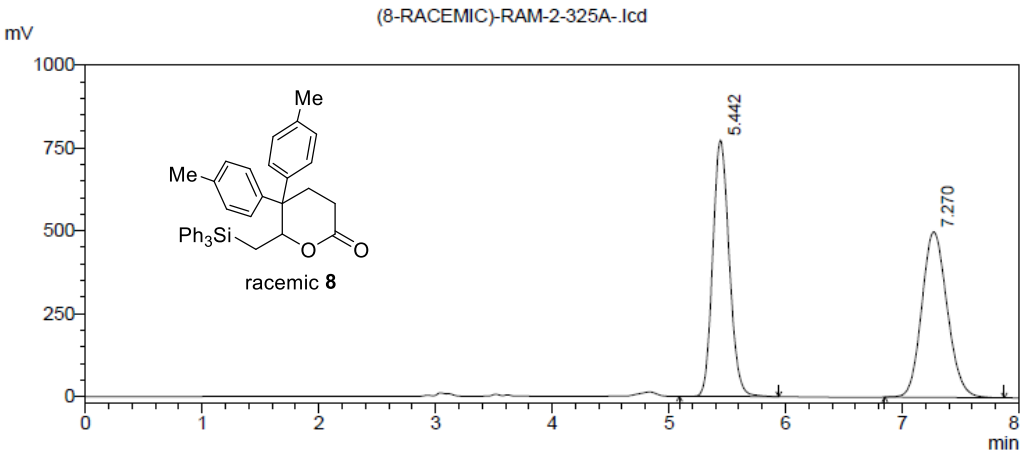

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???A 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	5.442	772563	7594788	50.044
2	7.270	499575	7581491	49.956
Total		1272138	15176278	100.000

HPLC spectra of **8**

Data File : (8-CHIRAL)RAM-2-325B-.lcd
Method File : OD-H-90+10-1-214.lcm
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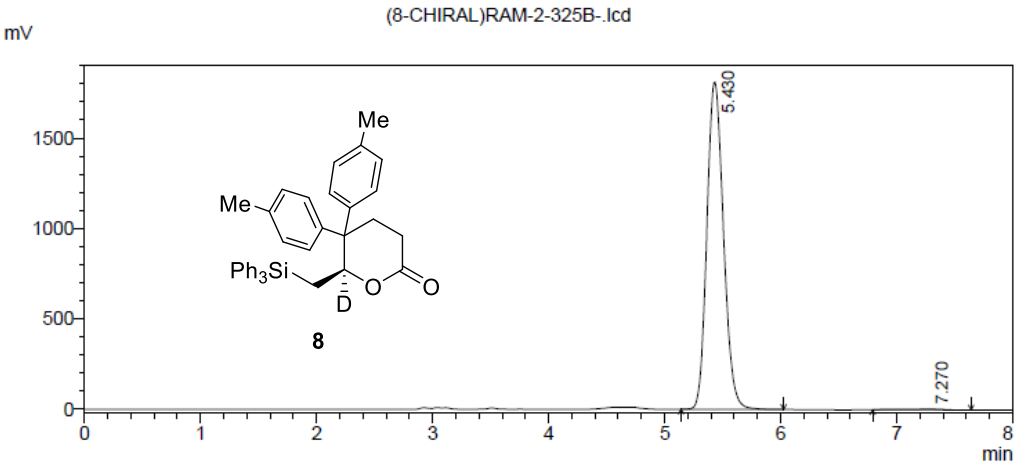
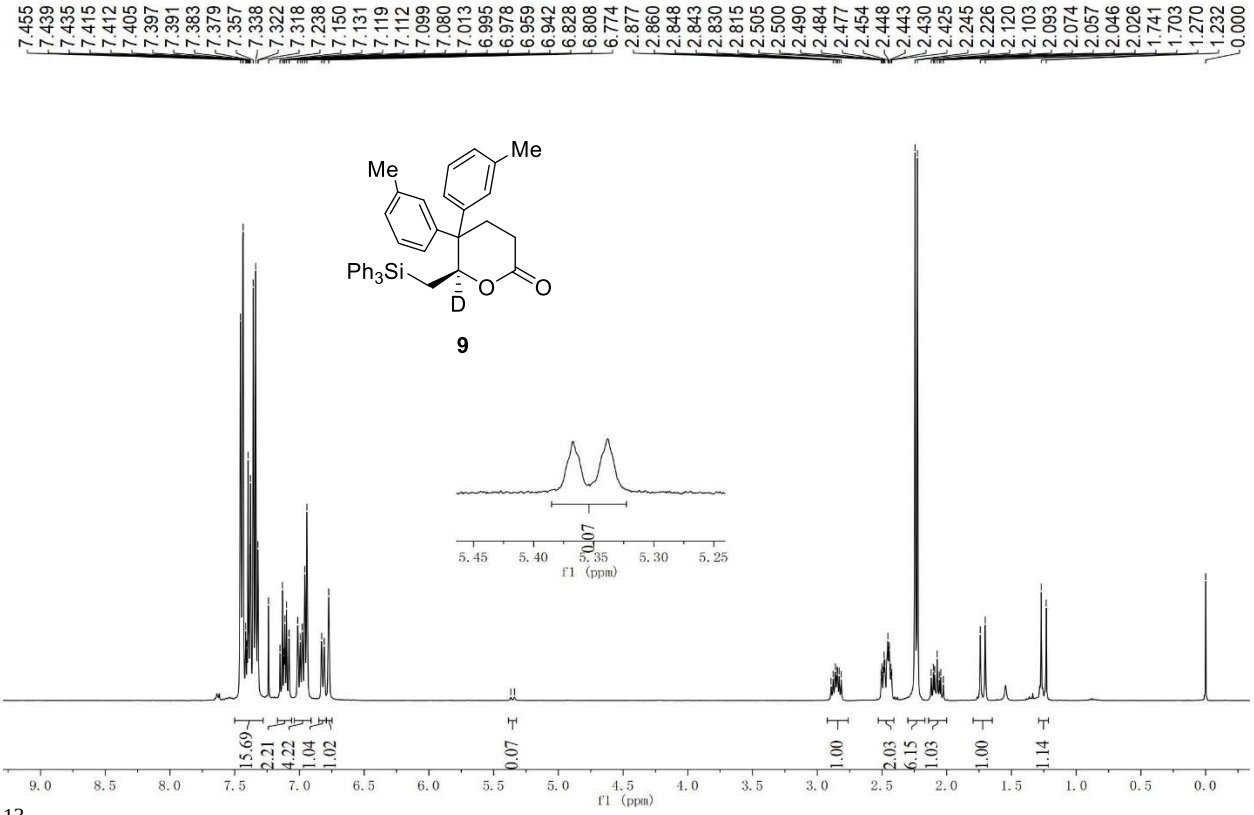


<Data Analysis>

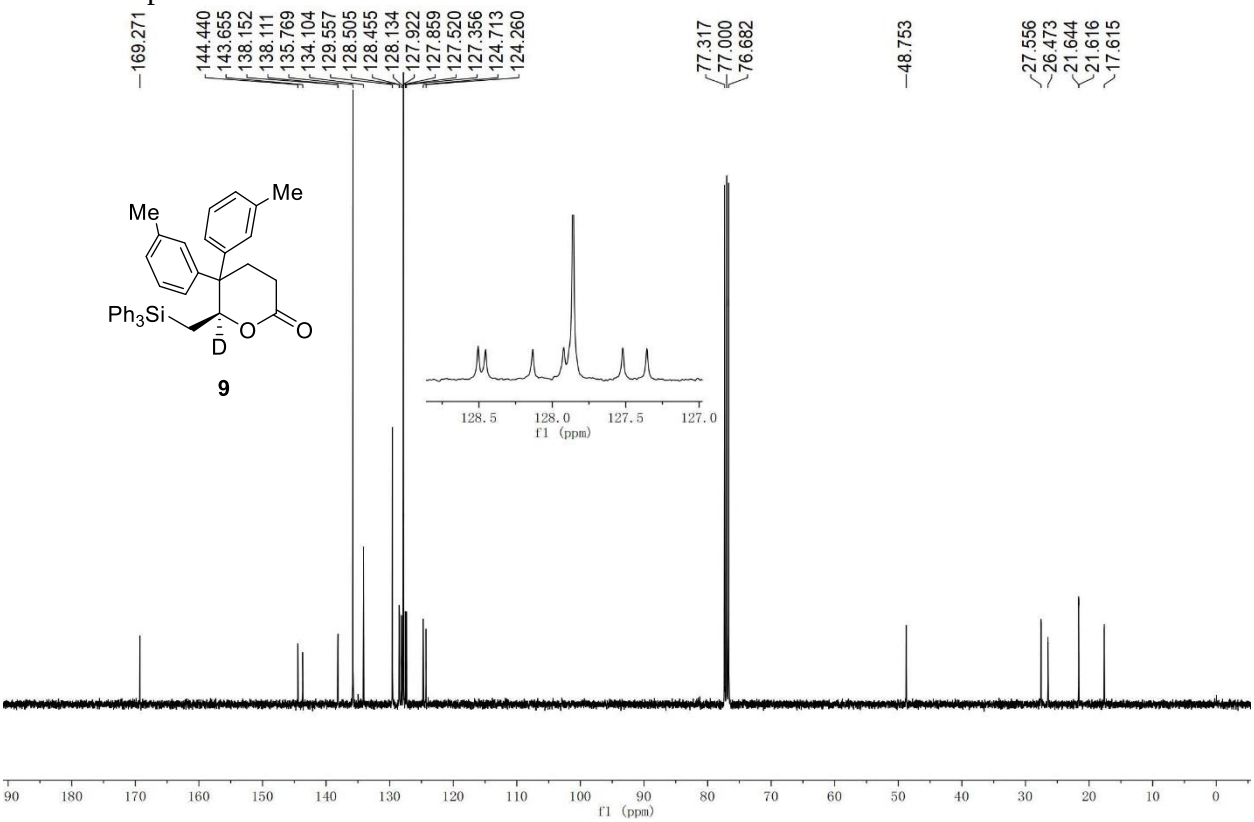
???A 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	5.430	1808669	17984377	99.341
2	7.270	5719	119299	0.659
Total		1814388	18103676	100.000

^{1}H NMR spectra of **9**



^{13}C NMR spectra of **9**



HPLC spectra of racemic **9**

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Method File : OD-H-95+5-1-214.lcm
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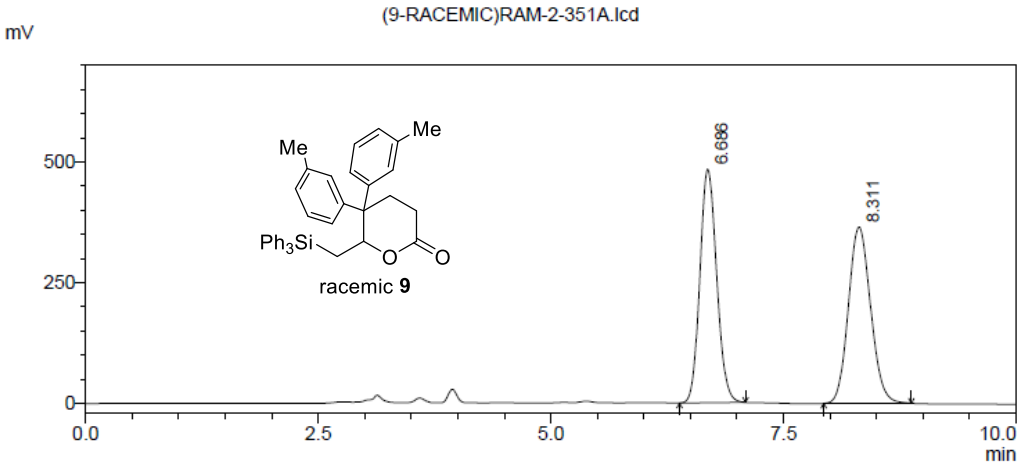

<Data Analysis>

???A 214nm

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1	6.686	482957	6070714	50.005
2	8.311	365025	6069473	49.995
Total		847982	12140187	100.000

HPLC spectra of **9**

Data File : (9-CHIRAL)RAM-2-351B.lcd
Method File : OD-H-95+5-1-214.lcm
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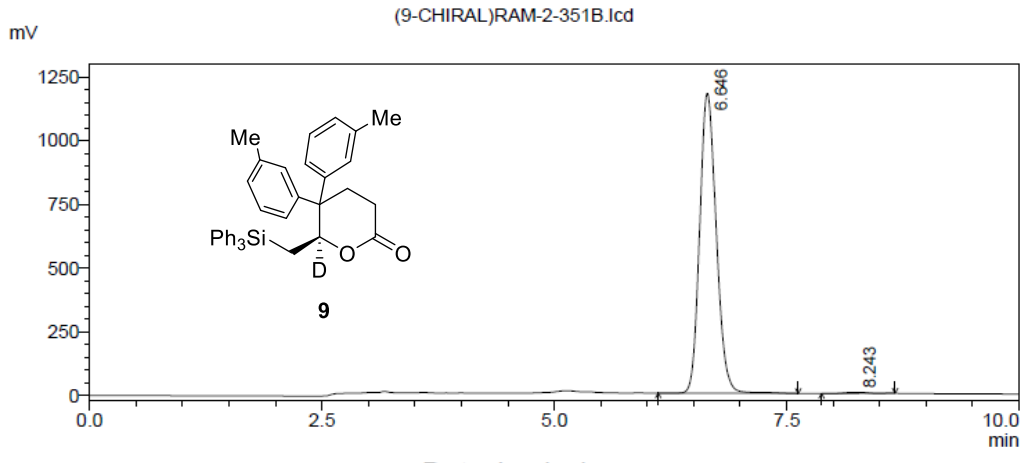
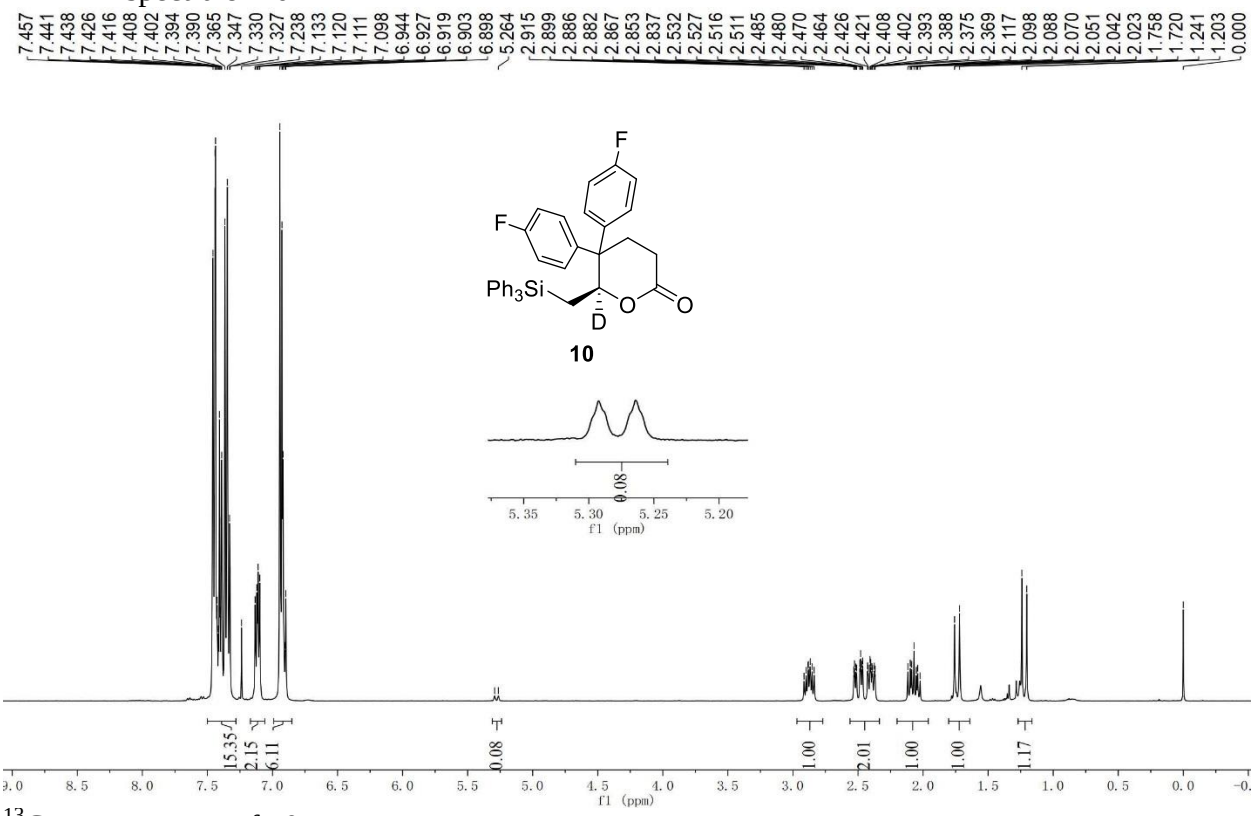


<Data Analysis>

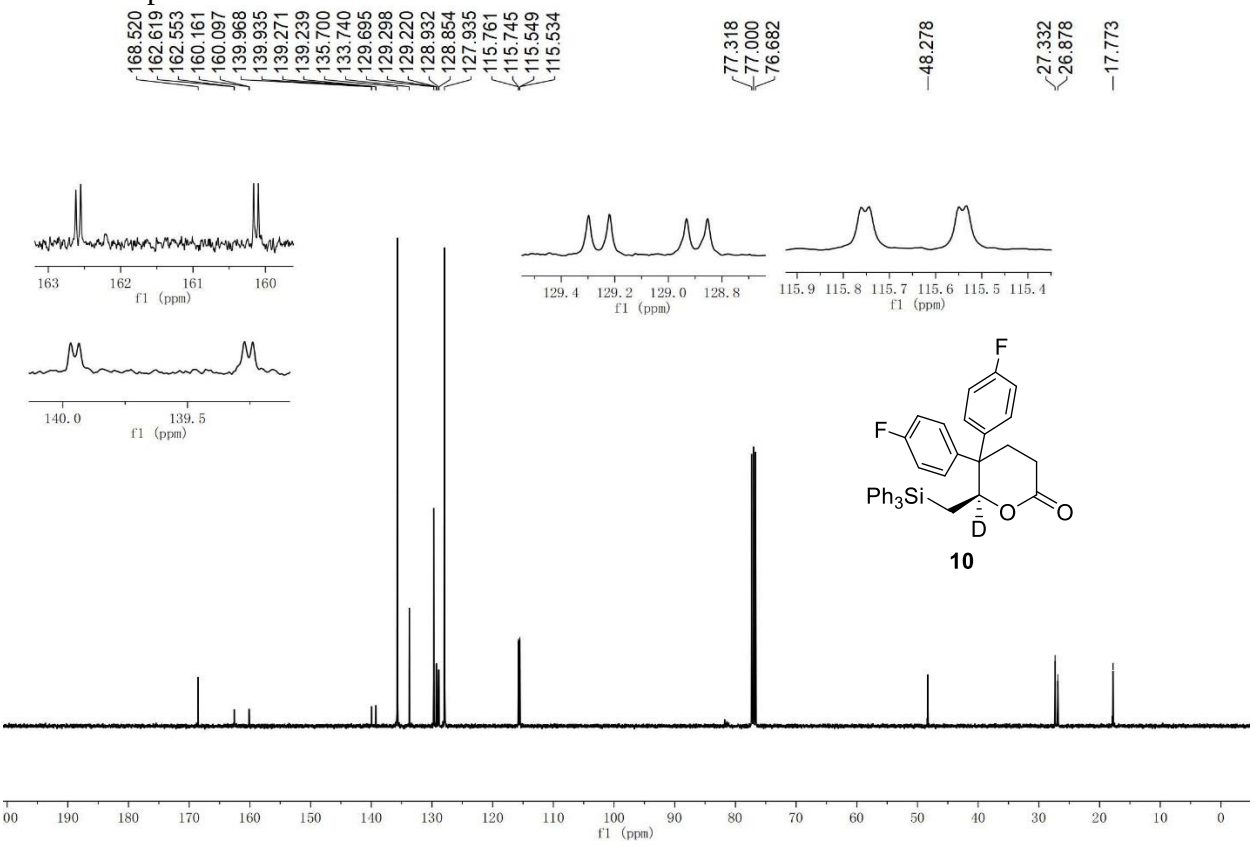
???A 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	6.646	1176807	14651262	99.615
2	8.243	4199	56565	0.385
Total		1181006	14707826	100.000

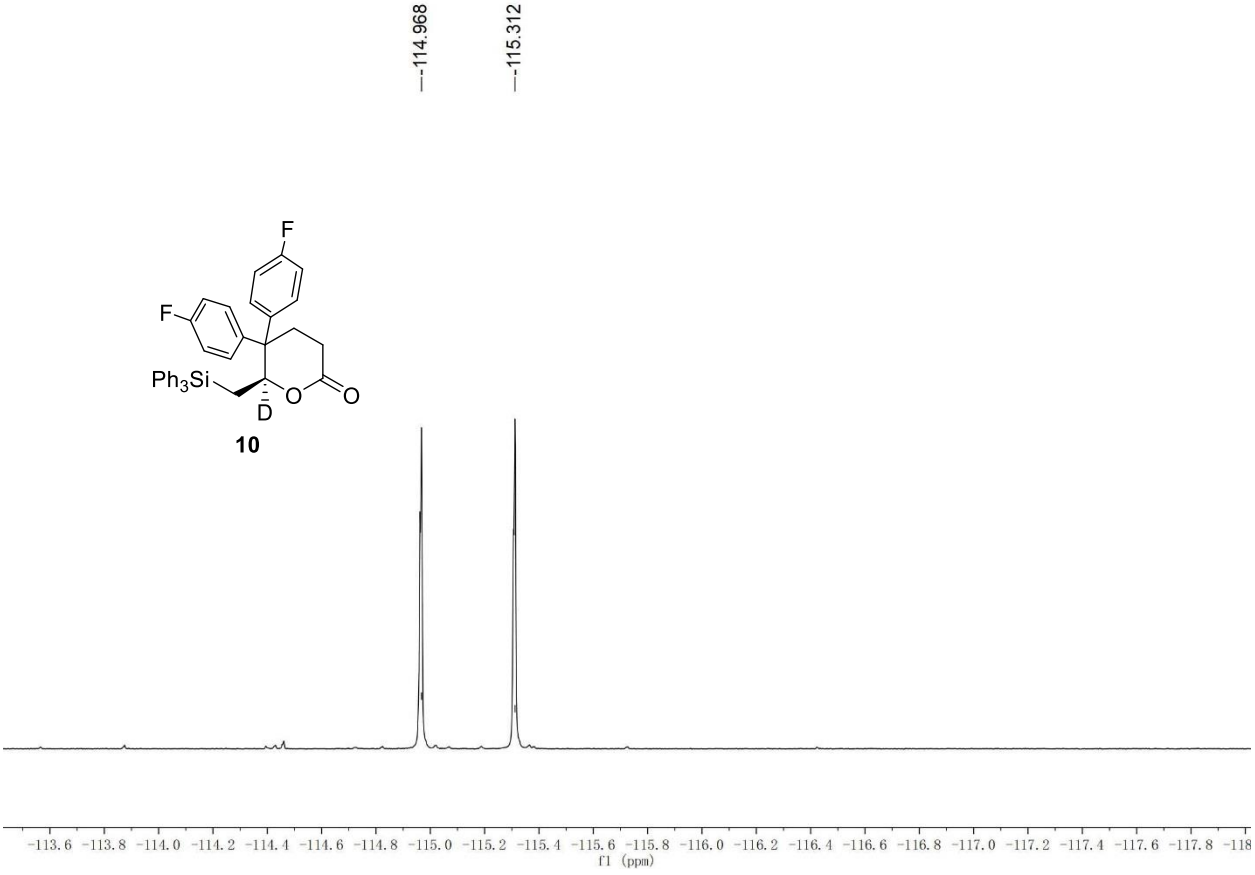
[1]H NMR spectra of **10**



[13]C NMR spectra of **10**



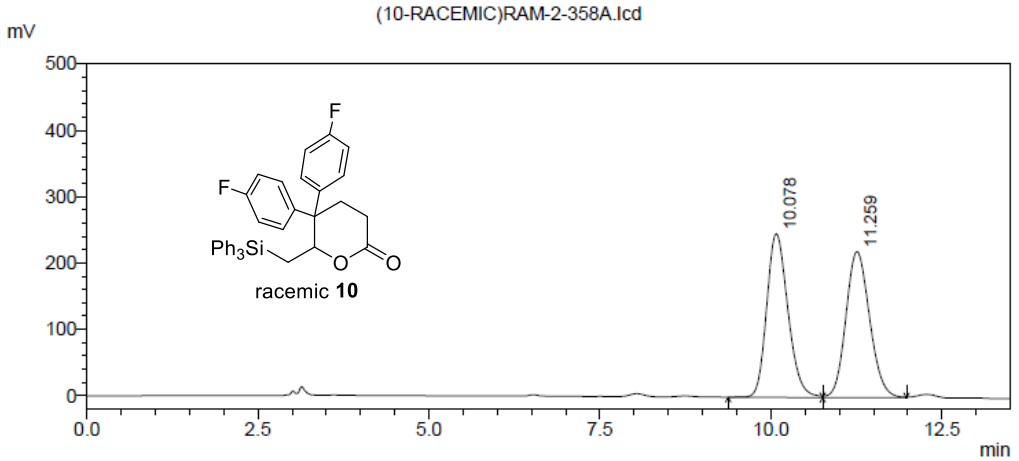
^{19}F NMR spectra of **10**



HPLC spectra of **10**

Data File : (10-RACEMIC)RAM-2-358A.lcd
Method File : OD-H-95+5-1-214.lcm
Date Processed : 7/17/2021 10:21:35 AM

<Chromatogram View>



<Data Analysis>

???A 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	10.078	246512	5344265	50.043
2	11.259	220201	5335136	49.957
Total		466712	10679401	100.000

HPLC spectra of **10**

Data File : (10CHIRAL)RAM-2-358B.lcd
Method File : OD-H-95+5-1-214.lcm
Date Processed : 7/17/2021 10:21:47 AM

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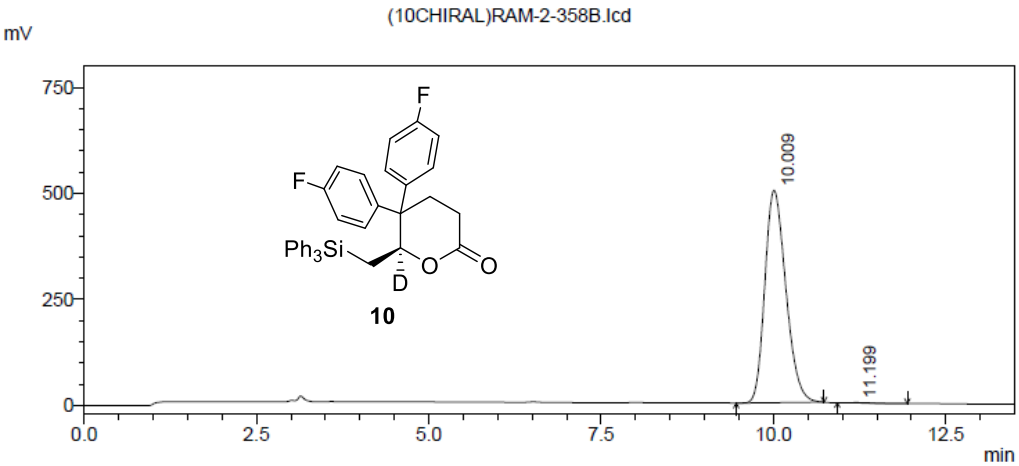
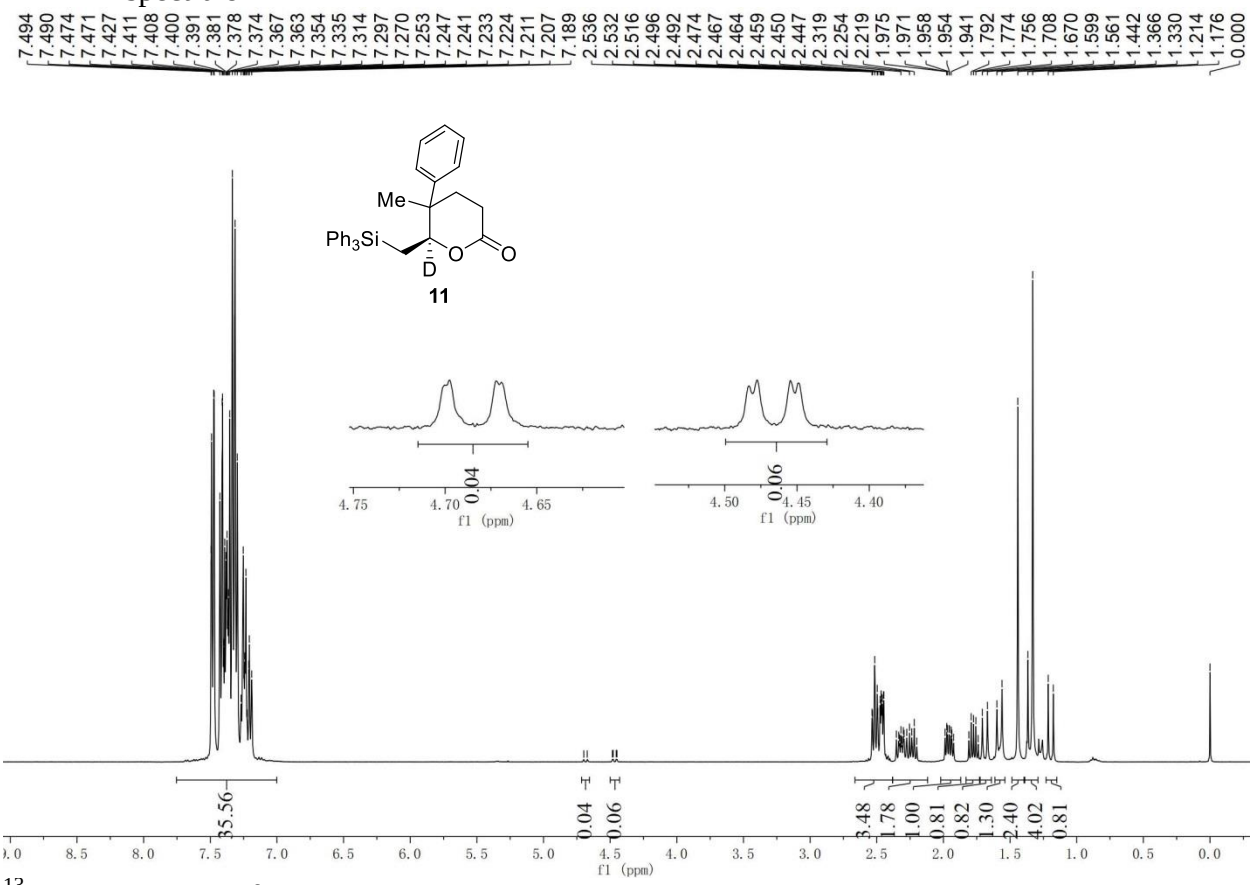


<Data Analysis>

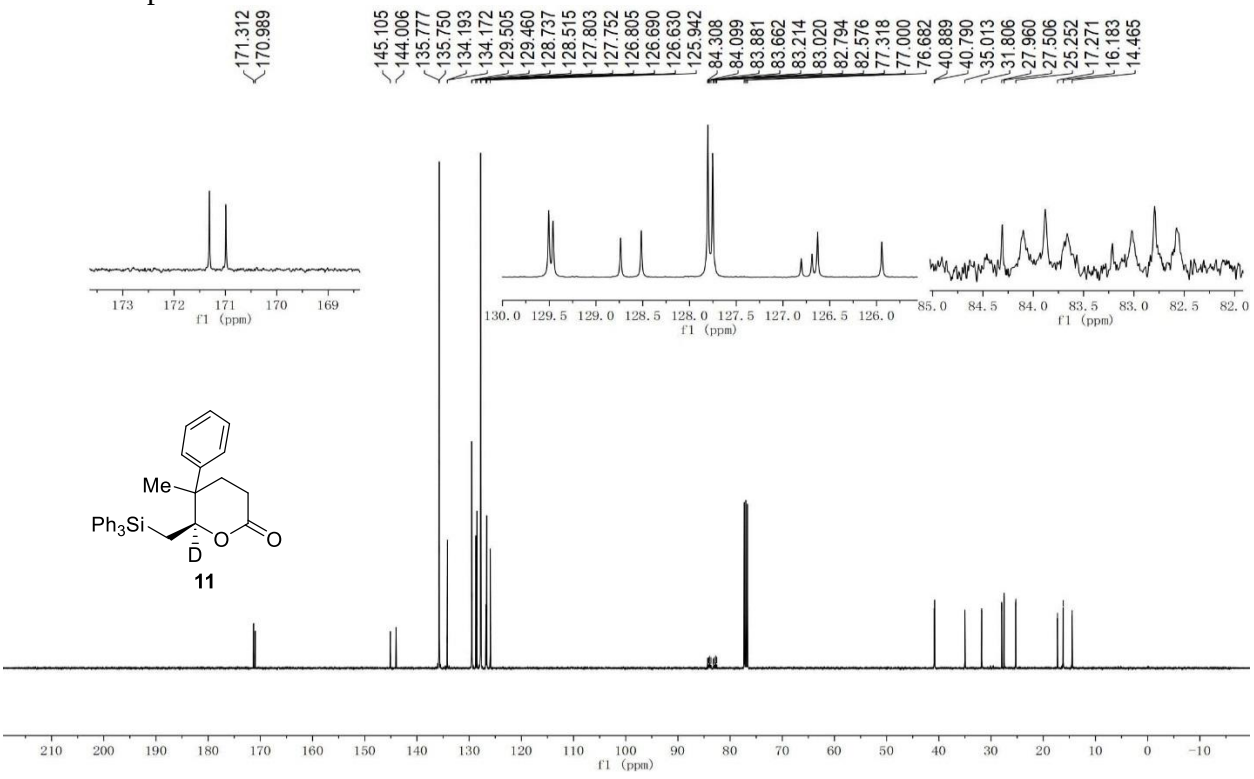
???A 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	10.009	500339	10624159	99.854
2	11.199	1242	15501	0.146
Total		501581	10639660	100.000

^{1}H NMR spectra of **11**



^{13}C NMR spectra of **11**



HPLC spectra of racemic **11**

Data File : (11-RACEMIC)RAM-2-333-14.lcd
Method File : OD-H-99.8+0.2-1-214.lcm
Date Processed : 7/17/2021 10:40:16 AM

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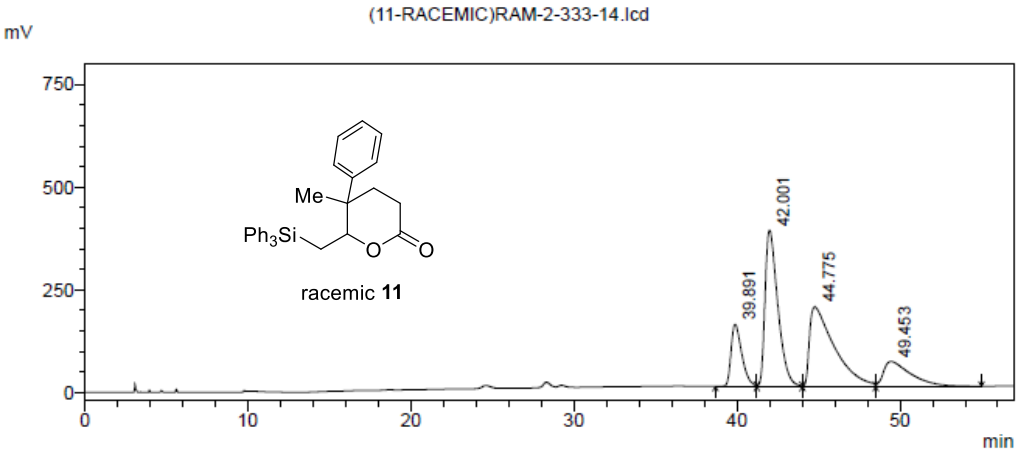

<Data Analysis>

???A 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	39.891	151132	6928347	12.538
2	42.001	380291	20723219	37.502
3	44.775	193375	20463404	37.032
4	49.453	60734	7143272	12.927
Total		785532	55258241	100.000

HPLC spectra of **11**

Data File : (11-CHIRAL)RAM-2-334.lcd
Method File : OD-H-99.8+0.2-1-214.lcm
Date Processed : 7/17/2021 10:39:48 AM

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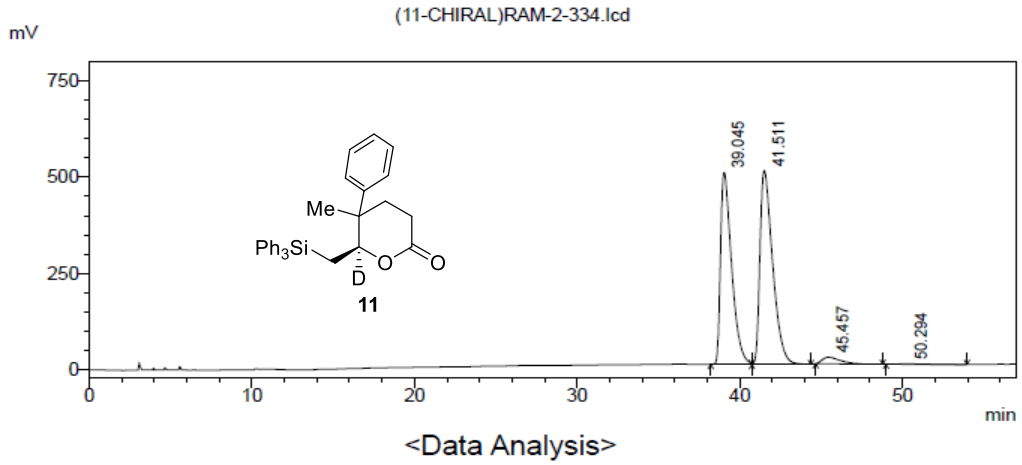
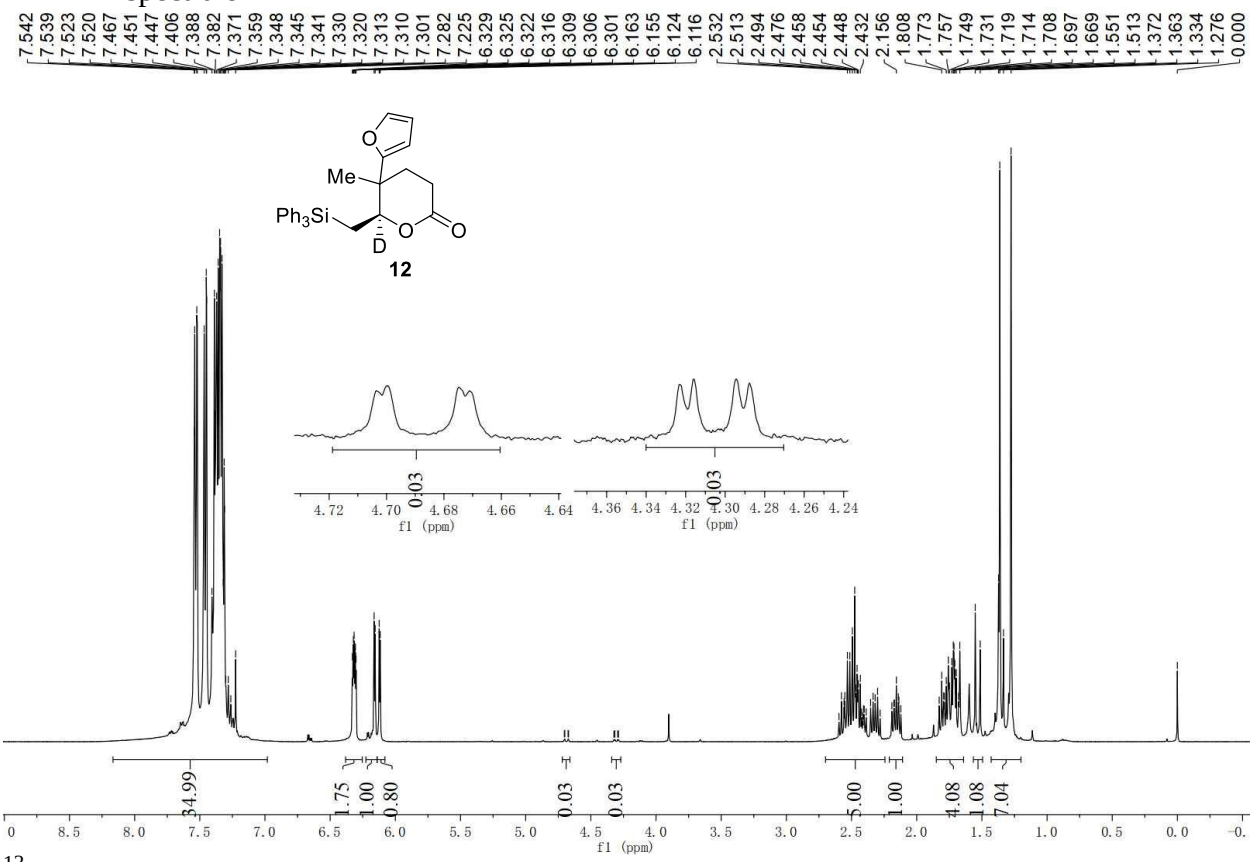


<Data Analysis>

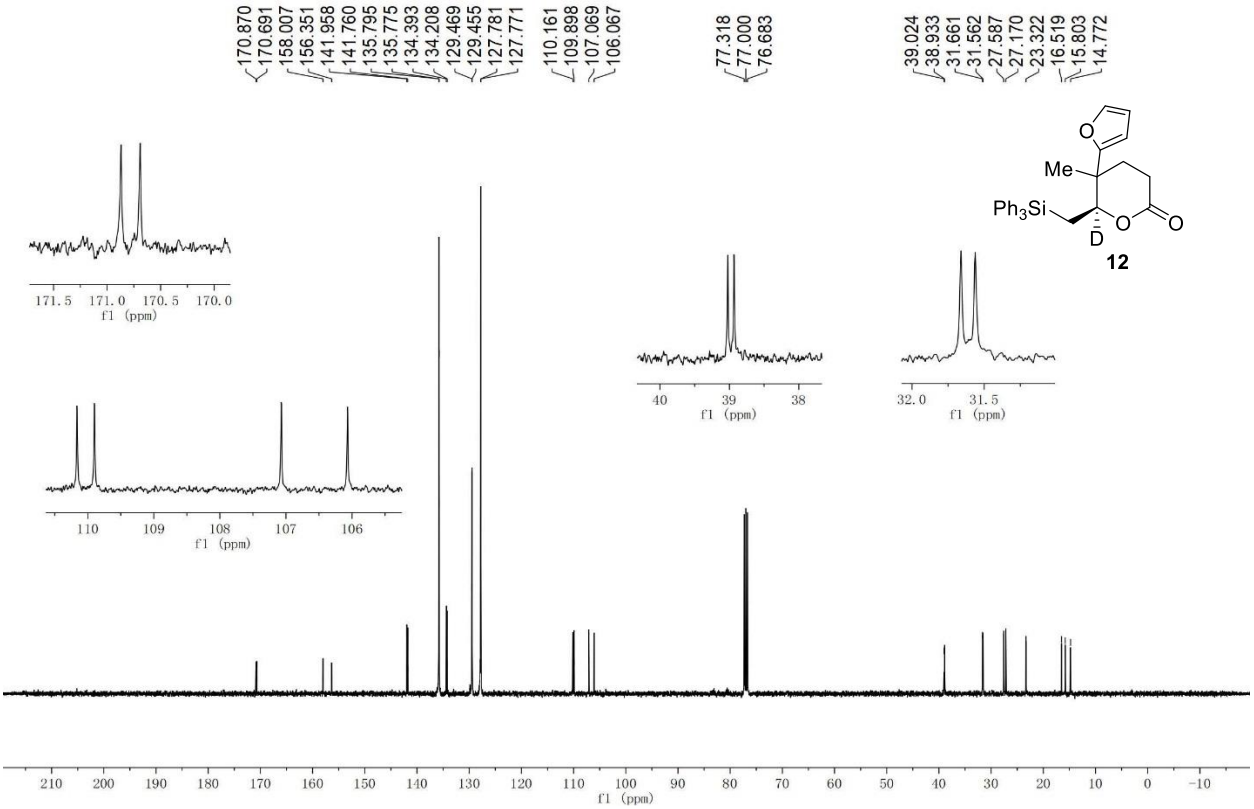
???A 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	39.045	498683	23579308	44.991
2	41.511	503531	27352841	52.191
3	45.457	17154	1330742	2.539
4	50.294	1659	145863	0.278
Total		1021026	52408754	100.000

^{1}H NMR spectra of **12**



^{13}C NMR spectra of **12**



HPLC spectra of racemic **12**

Data File : 12-RACEMIC-RAM-3-29-18.lcd
Method File : 3AD-H-99.2-1-214-70min.lcm
Date Processed : 7/17/2021 10:45:55 AM

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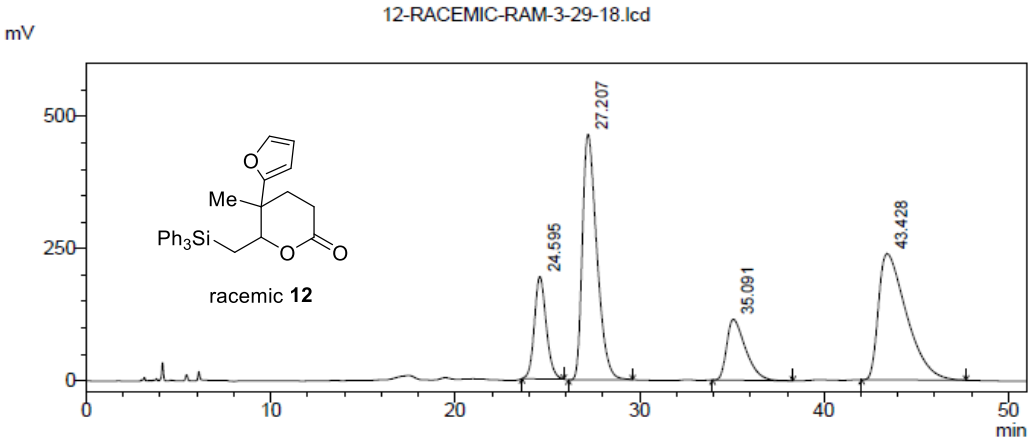

<Data Analysis>

DetA 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	24.595	193515	8631303	12.842
2	27.207	464004	25184564	37.470
3	35.091	114962	8197243	12.196
4	43.428	237962	25199969	37.493
Total		1010442	67213080	100.000

HPLC spectra of **12**

Data File : 12-CHIRAL-RAM-3-187-2--12.lcd
Method File : 3AD-H-99.2-1-214-70min.lcm
Date Processed : 7/17/2021 10:46:20 AM

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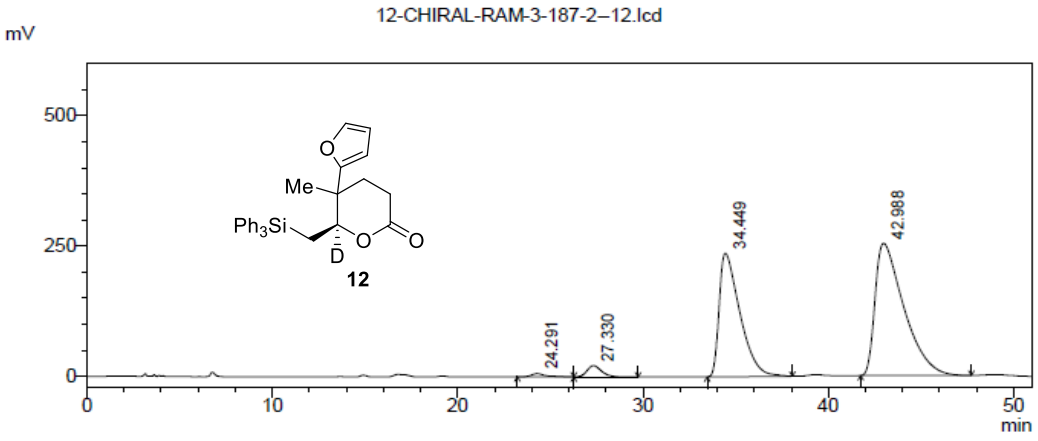
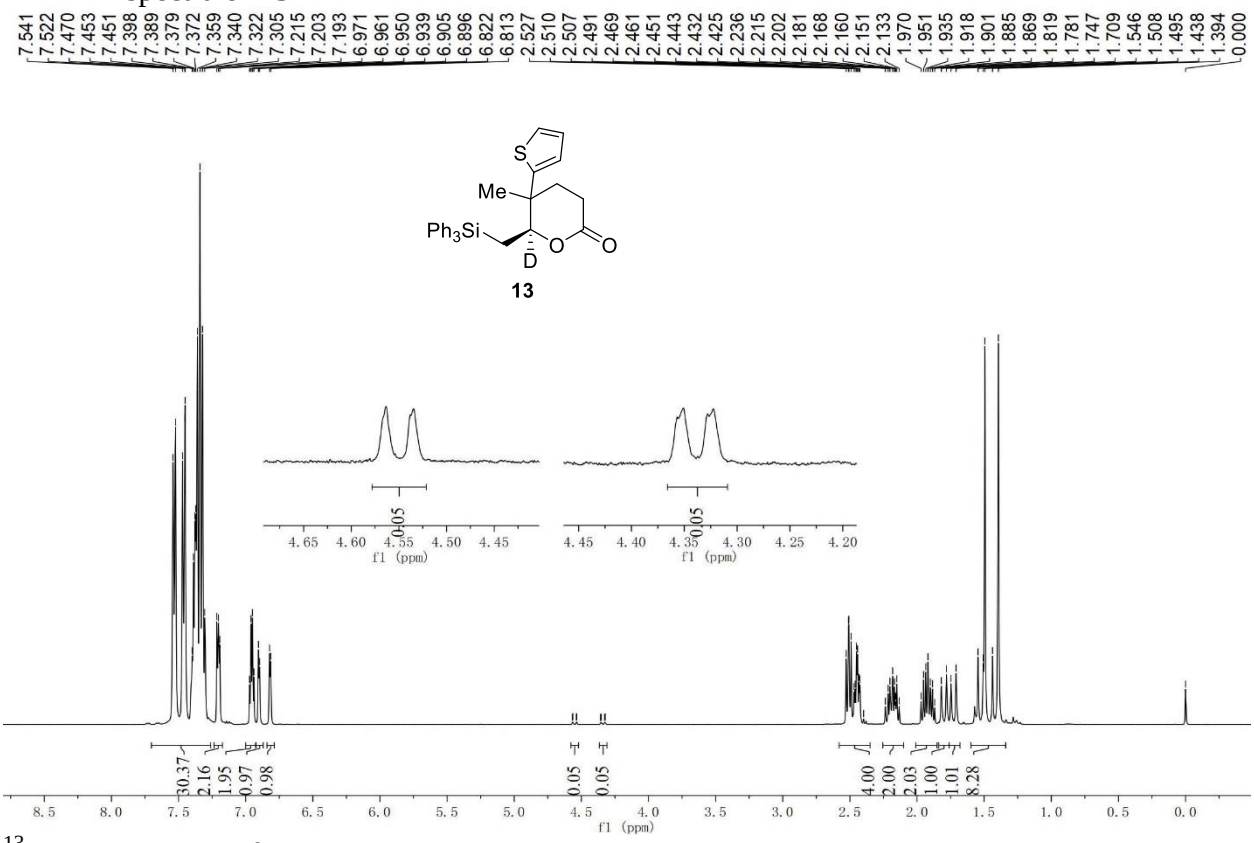


<Data Analysis>

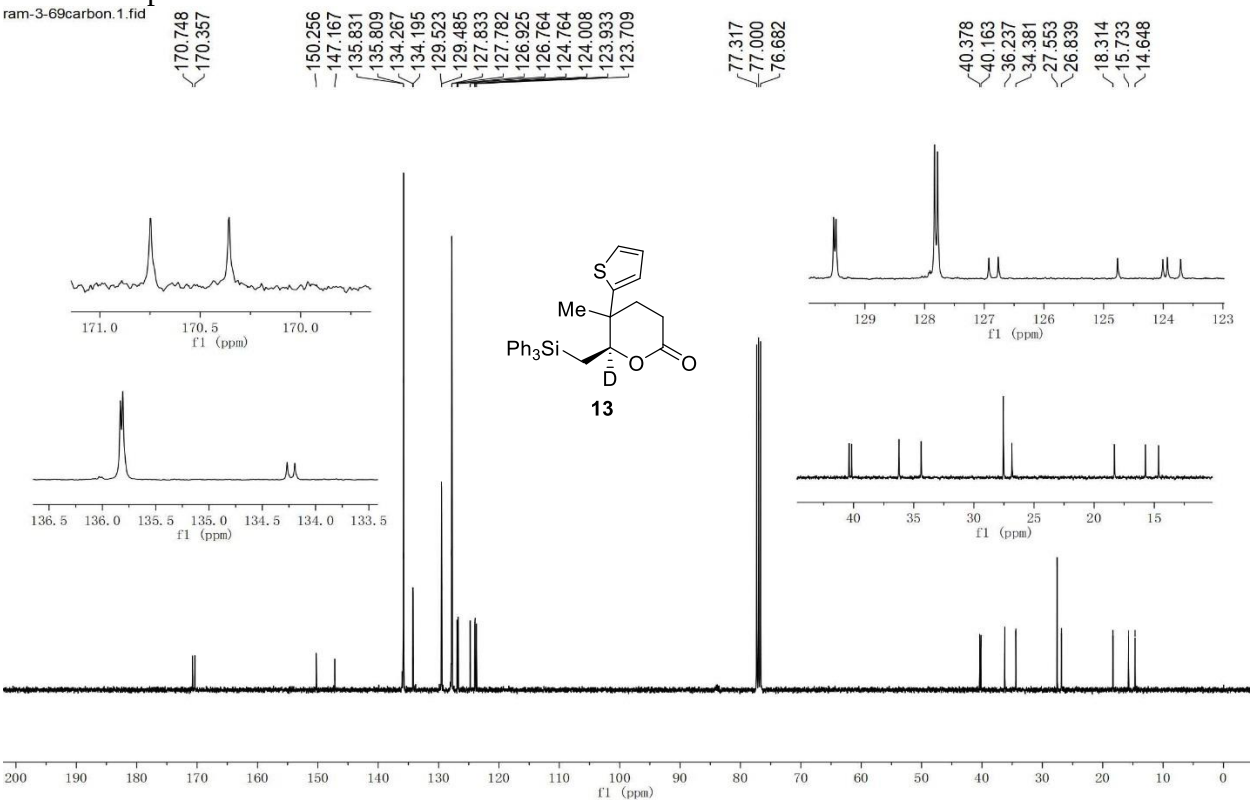
DetA 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	24.291	6344	331920	0.701
2	27.330	21661	1167809	2.467
3	34.449	236801	18442371	38.966
4	42.988	253076	27386737	57.865
Total		517882	47328837	100.000

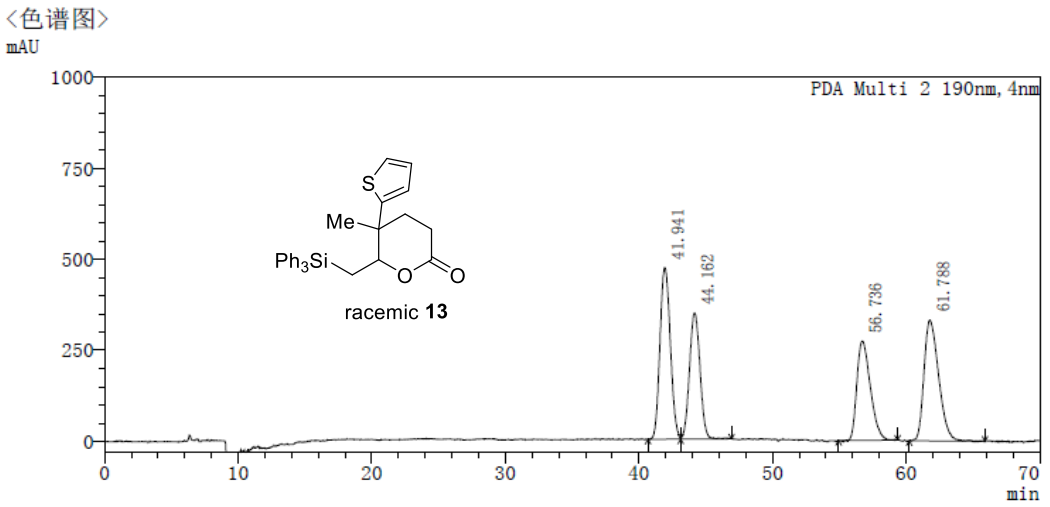
[1]H NMR spectra of **13**



[13]C NMR spectra of **13**



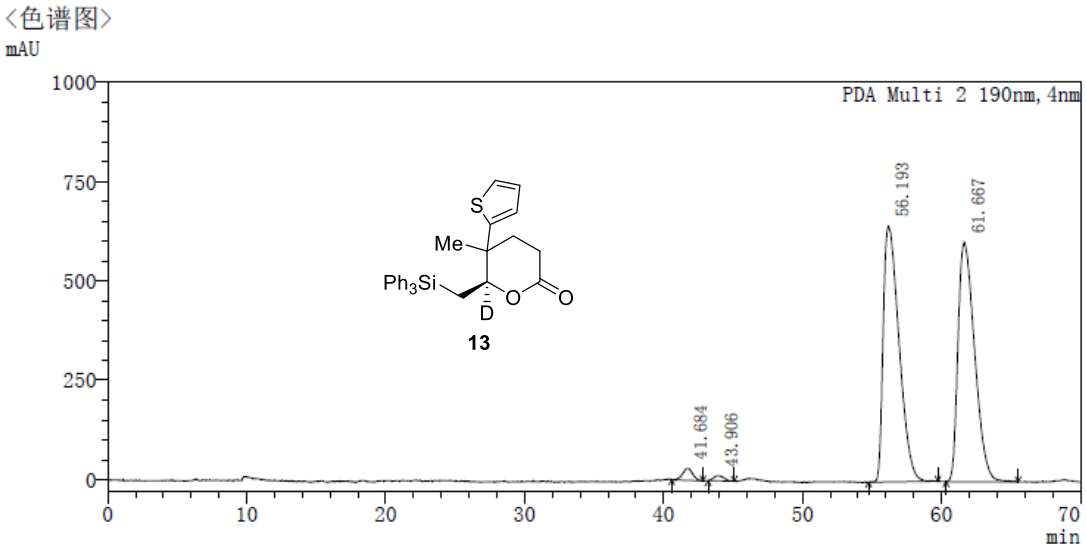
HPLC spectra of racemic **13**



PDA Ch2 190nm

Peak	Time	Area	Area%
1	41.941	25423282	28.696
2	44.162	18971098	21.414
3	56.736	19054884	21.508
4	61.788	25144819	28.382
总计		88594083	100.000

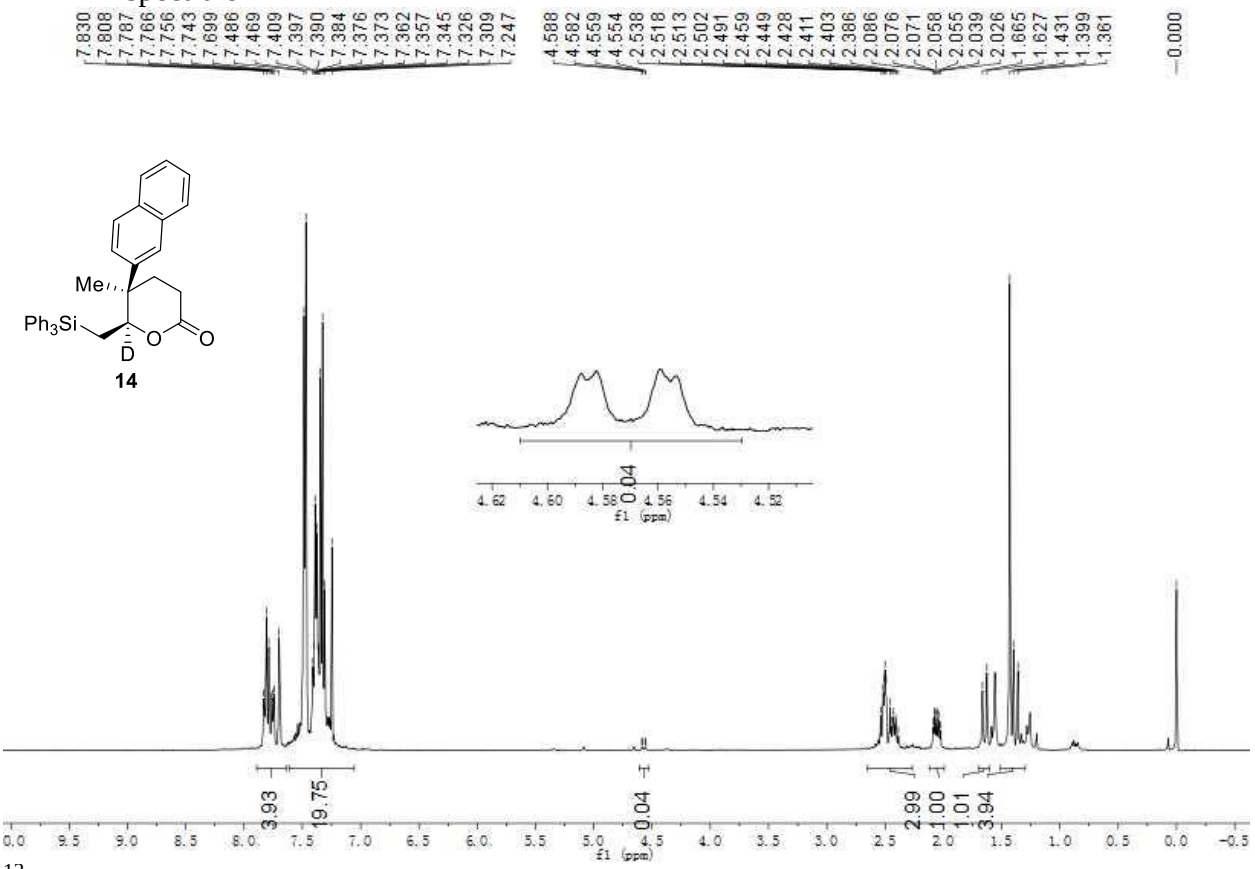
HPLC spectra of **13**



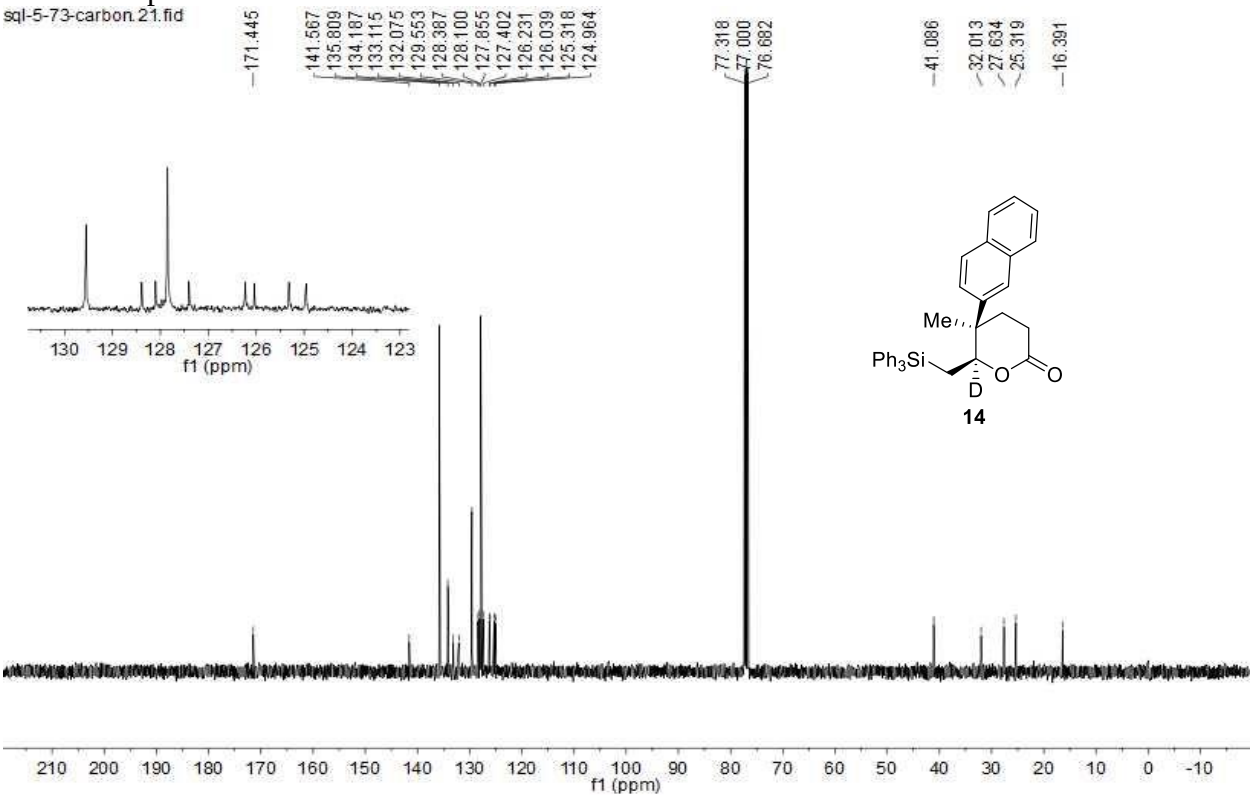
PDA Ch2 190nm

Peak	Time	Area	Area%
1	41.684	1509831	1.464
2	43.906	651099	0.631
3	56.193	50874603	49.331
4	61.667	50094479	48.574
总计		103130012	100.000

^{1}H NMR spectra of **14**

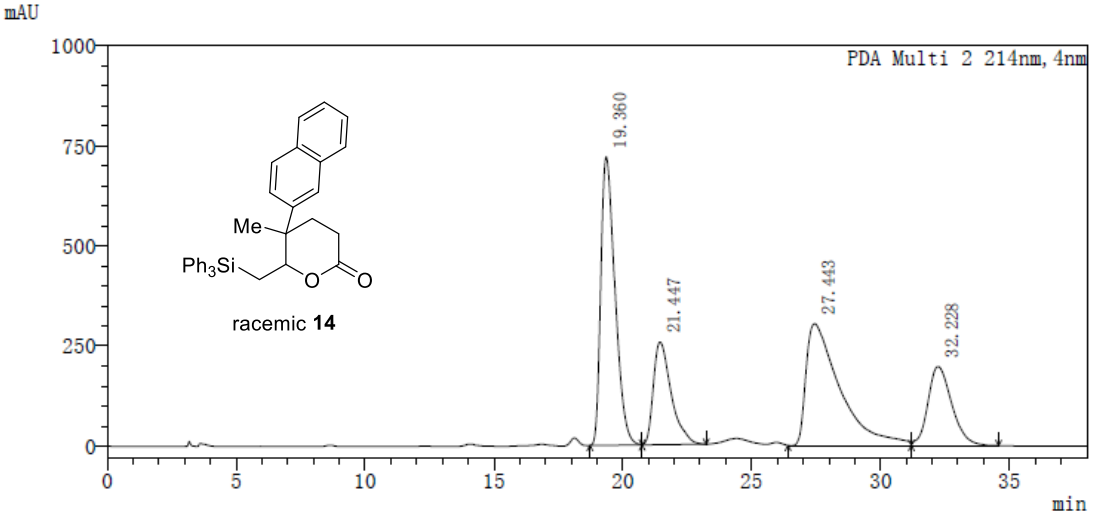


^{13}C NMR spectra of **14**



HPLC spectra of racemic **14**

<色谱图>

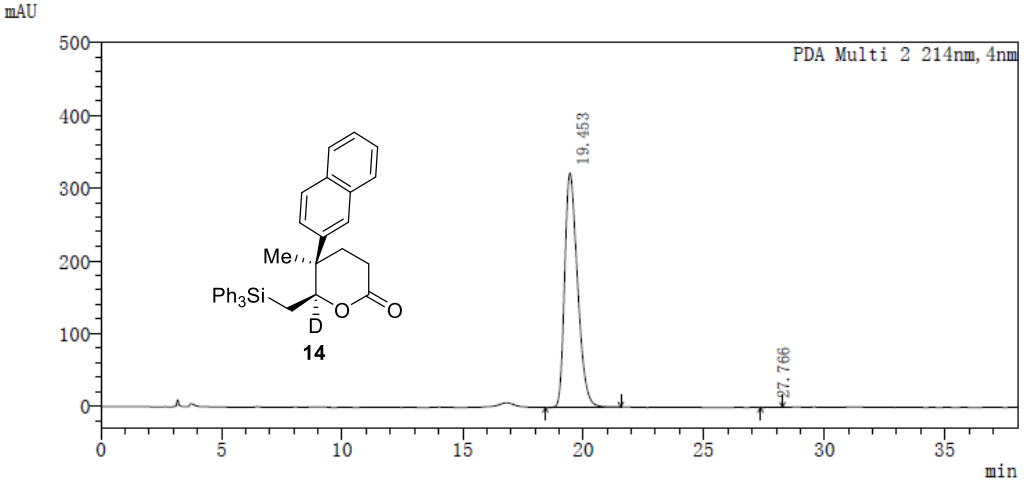


PDA Ch2 214nm

Peak	Time	Area	Area%
1	19.360	27626820	34.357
2	21.447	12308026	15.306
3	27.443	27798281	34.570
4	32.228	12677954	15.766
总计		80411080	100.000

HPLC spectra of **14**

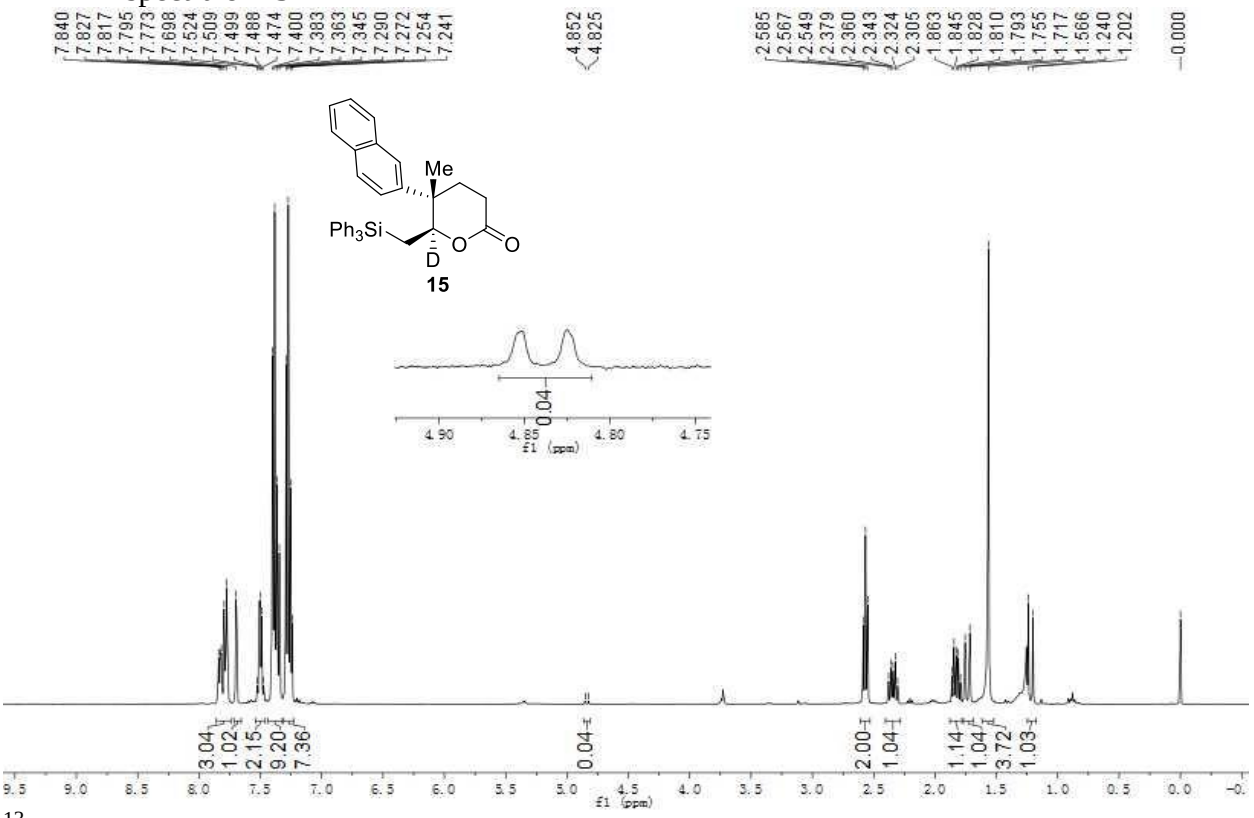
<色谱图>



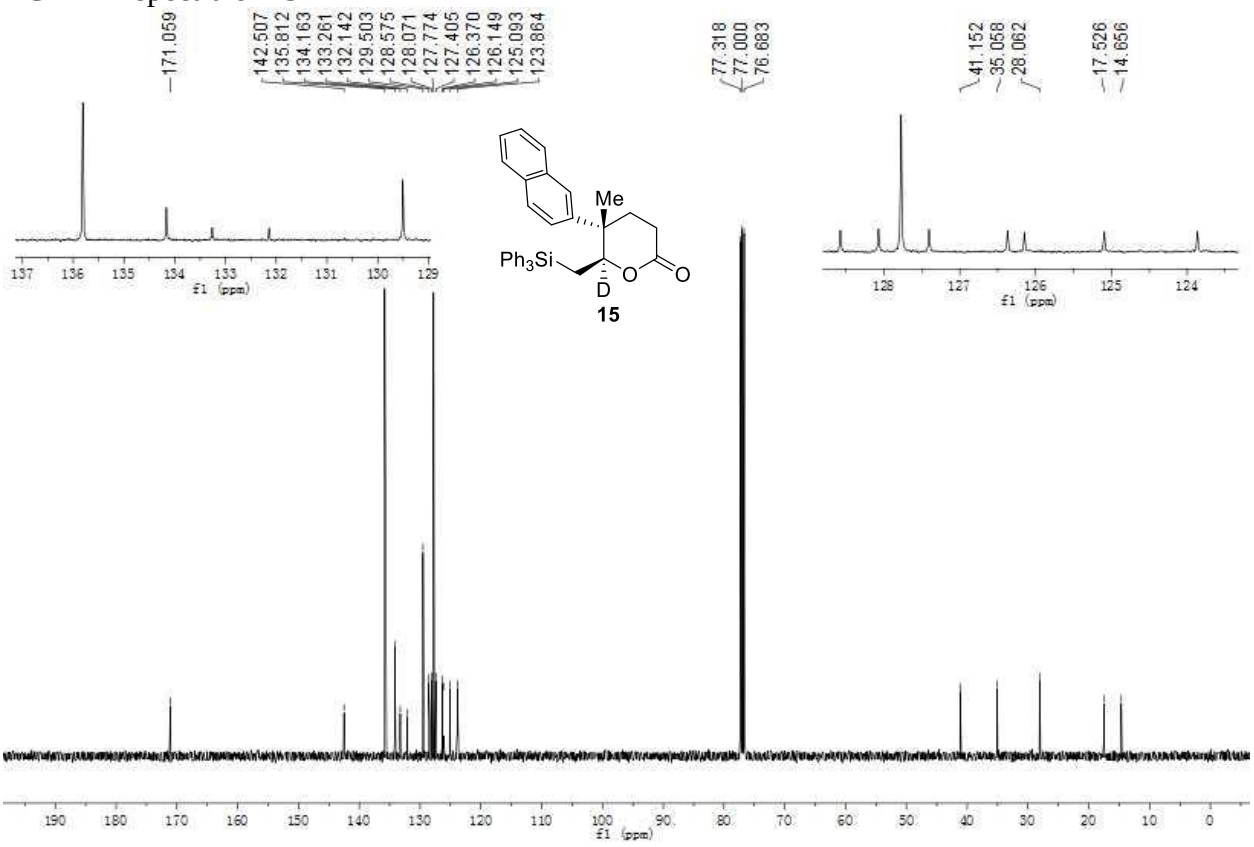
PDA Ch2 214nm

Peak	Time	Area	Area%
1	19.453	11932801	99.941
2	27.766	7053	0.059
总计		11939854	100.000

^{1}H NMR spectra of 15

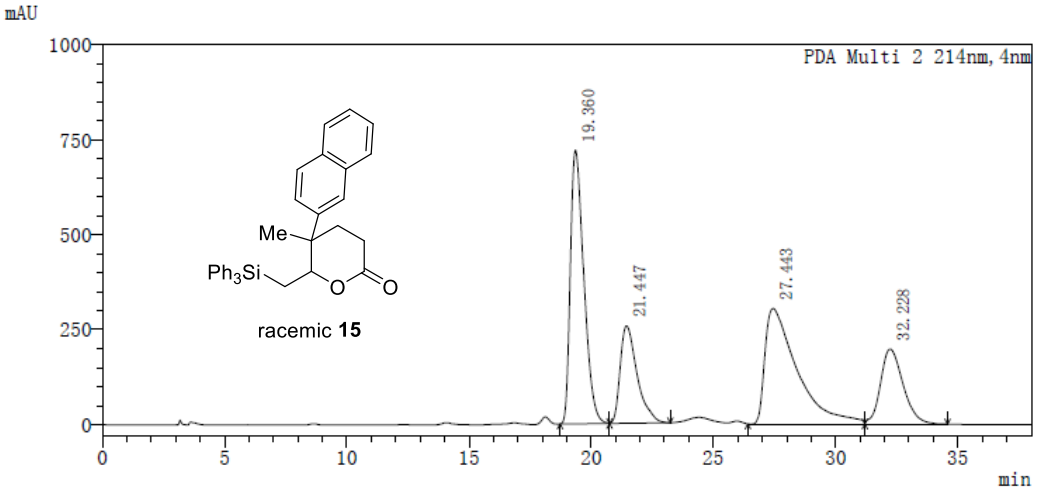


^{13}C NMR spectra of **15**



HPLC spectra of racemic **15**

<色谱图>

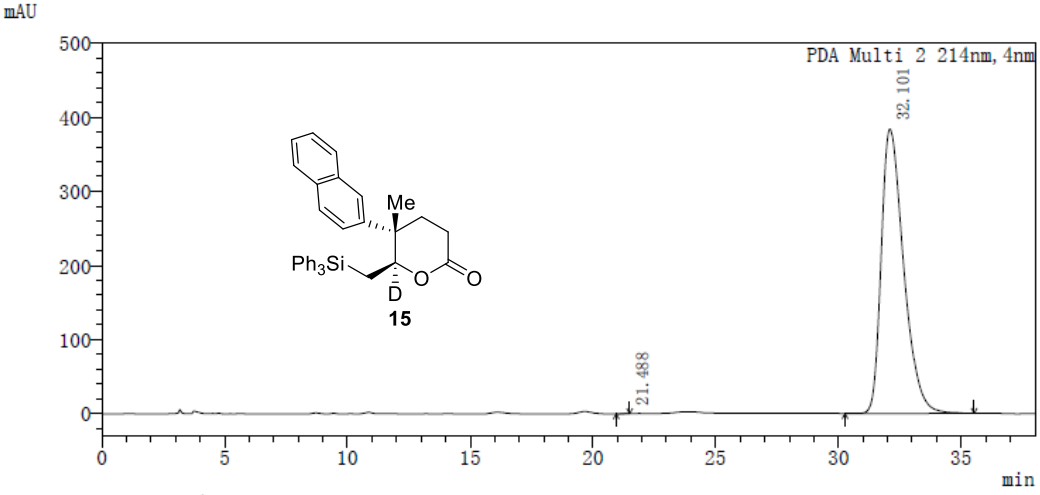


PDA Ch2 214nm

Peak	Time	Area	Area%
1	19.360	27626820	34.357
2	21.447	12308026	15.306
3	27.443	27798281	34.570
4	32.228	12677954	15.766
总计		80411080	100.000

HPLC spectra of **15**

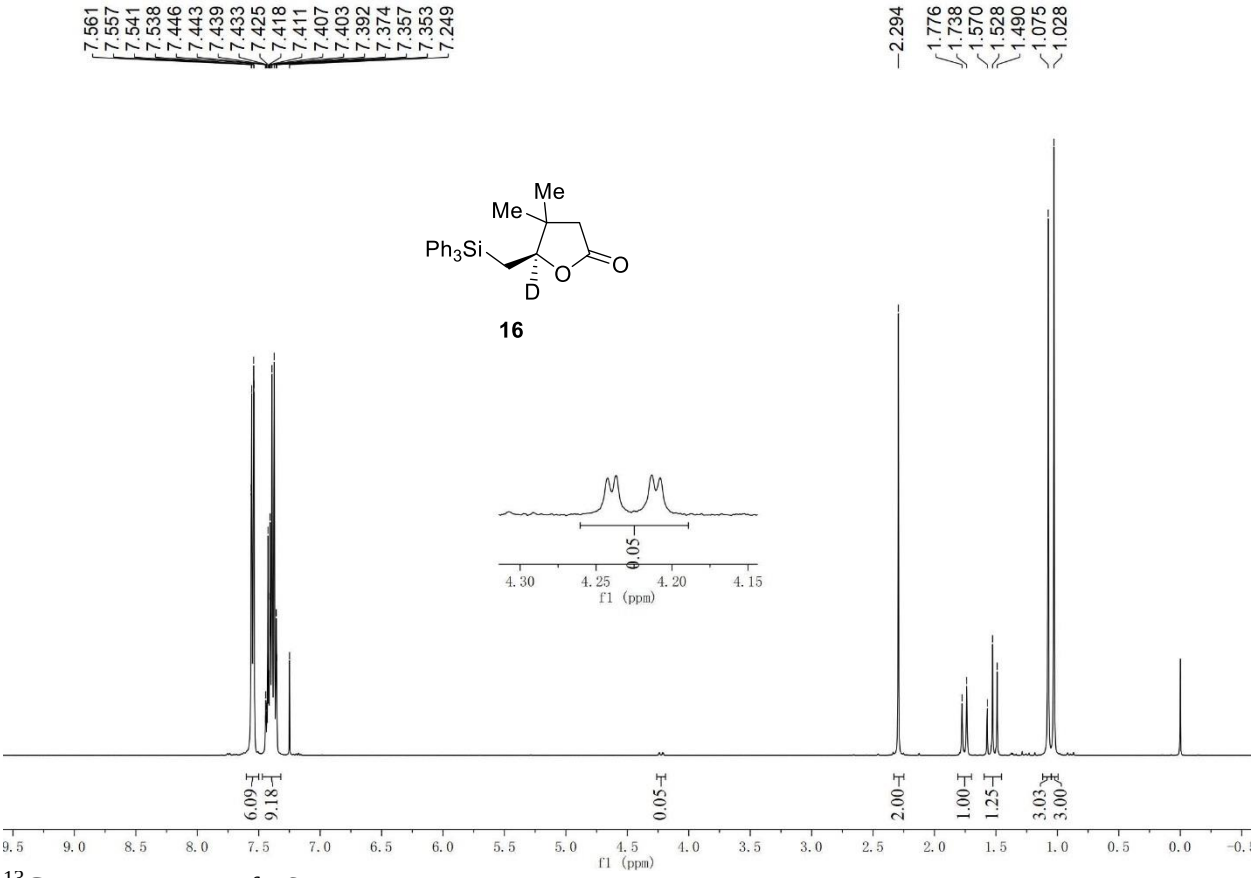
<色谱图>



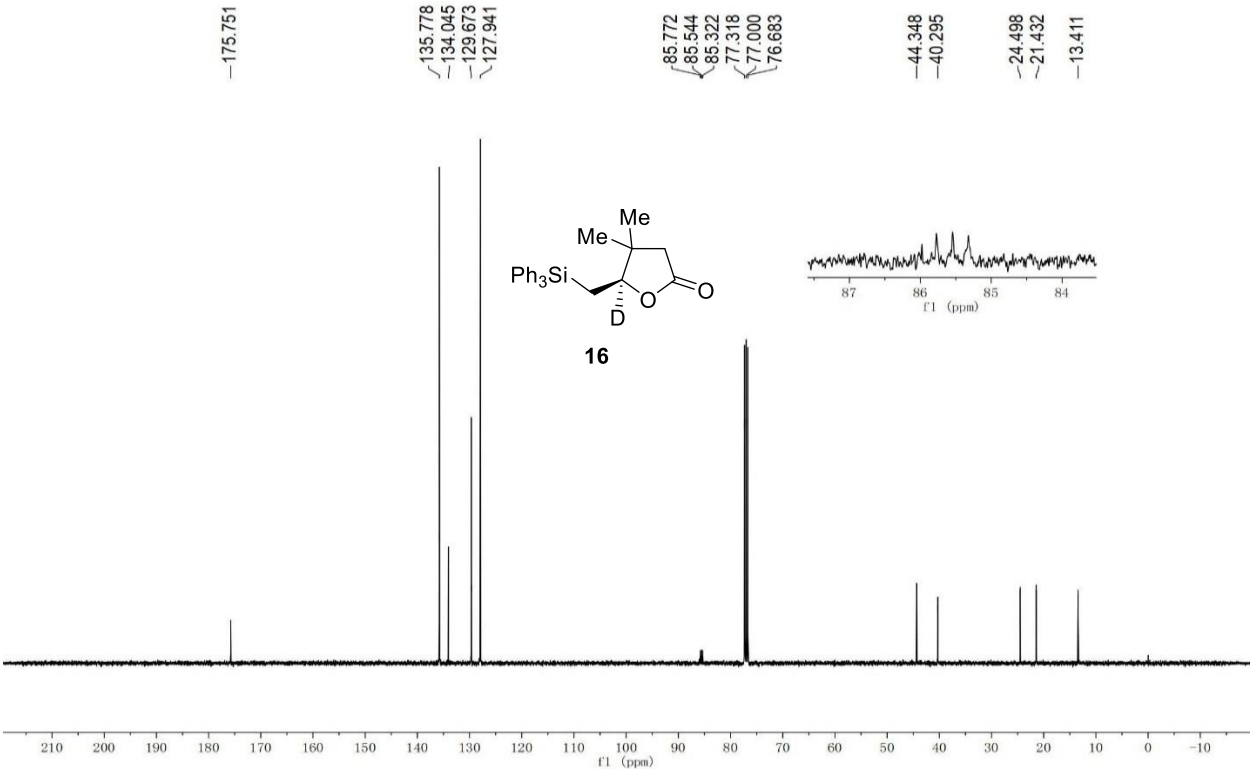
PDA Ch2 214nm

Peak	Time	Area	Area%
1	21.488	919	0.004
2	32.101	24346503	99.996
总计		24347422	100.000

^{1}H NMR spectra of **16**



^{13}C NMR spectra of **16**



HPLC spectra of racemic **16**

Data File : (16-RACEMIC)SQL-3-87-2.lcd
Method File : AD-H-98.5+1.5-1-214.lcm
Date Processed : 7/17/2021 10:51:00 AM

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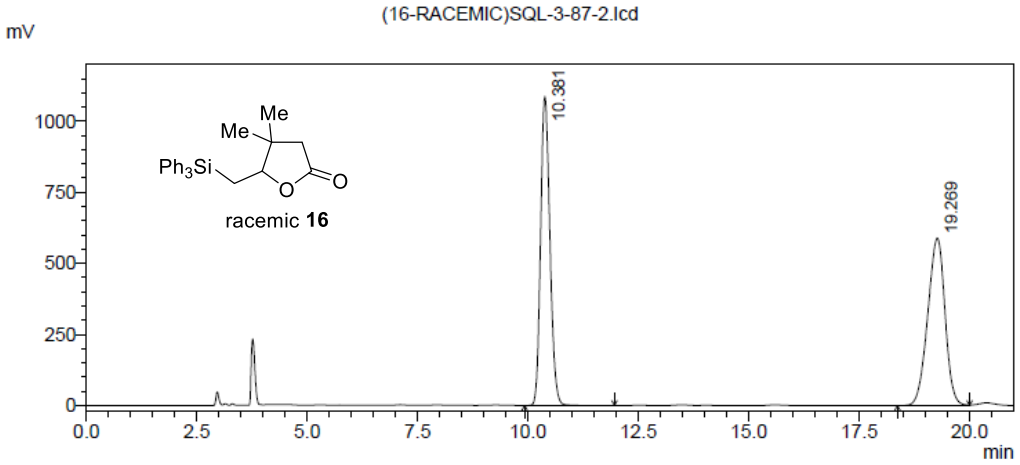

<Data Analysis>

???A 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	10.381	1084901	15936371	49.882
2	19.269	588448	16011929	50.118
Total		1673349	31948300	100.000

HPLC spectra of **16**

Data File : (16-CHIRAL)RAM-3-128.lcd
Method File : AD-H-98.5-1-214.lcm
Date Processed : 7/17/2021 10:51:29 AM

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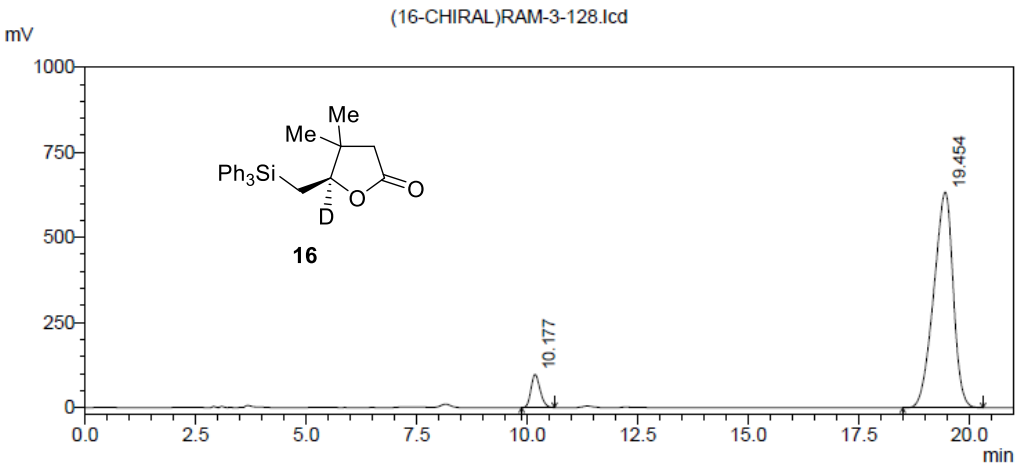
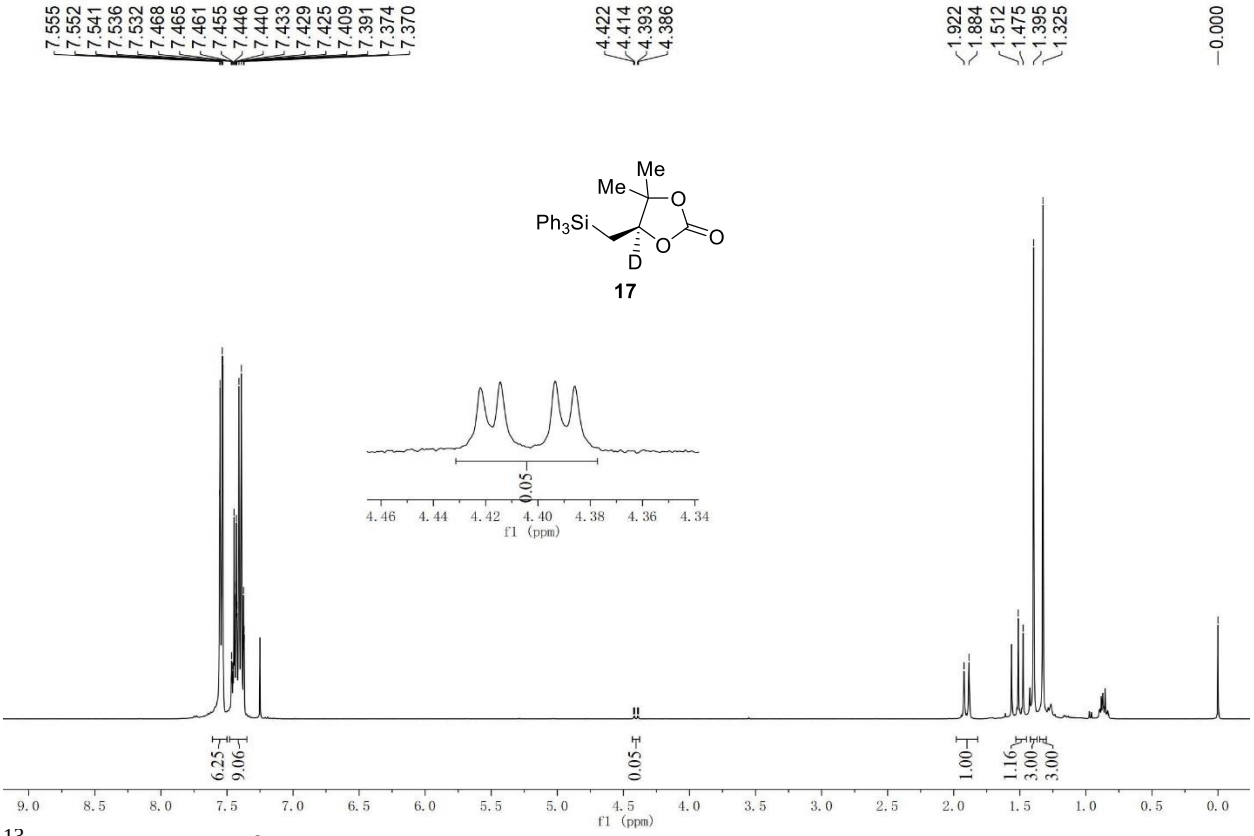


<Data Analysis>

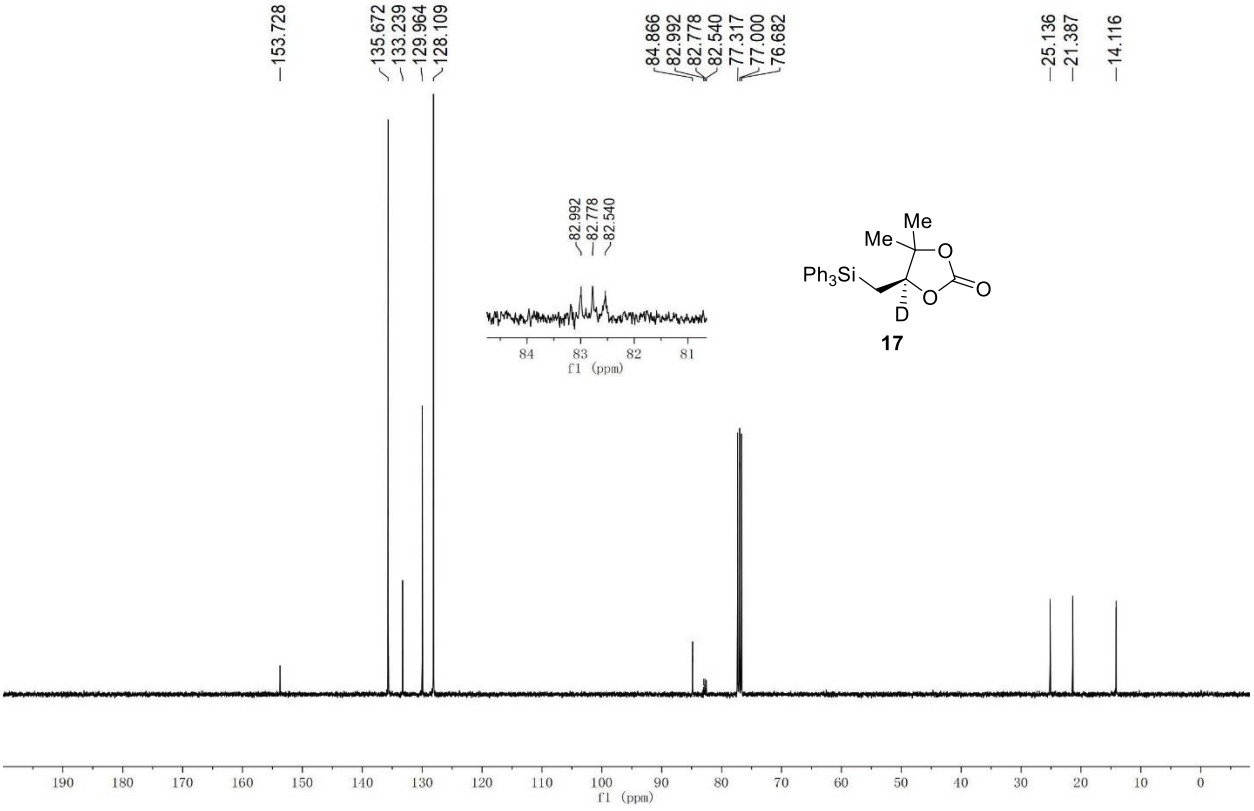
DetA 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	10.177	97154	1401033	6.730
2	19.454	633708	19418162	93.270
Total		730862	20819195	100.000

^{1}H NMR spectra of **17**



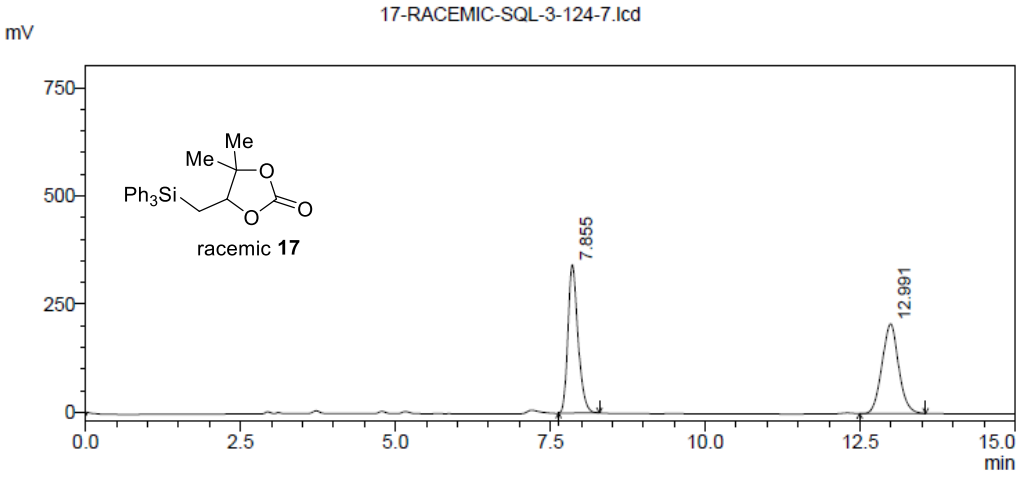
^{13}C NMR spectra of **17**



HPLC spectra of racemic **17**

Data File : 17-RACEMIC-SQL-3-124-7.lcd
Method File : 3AD-H-96-1-214.lcm
Date Processed : 7/17/2021 10:59:56 AM

<Chromatogram View>



<Data Analysis>

DetA 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	7.855	341854	3894683	50.095
2	12.991	206828	3879886	49.905
Total		548681	7774568	100.000

HPLC spectra of **17**

Data File : 17-CHIRAL-RAM-3-71-3.lcd
Method File : 3AD-H-96-1-214.lcm
Date Processed : 7/17/2021 10:55:38 AM

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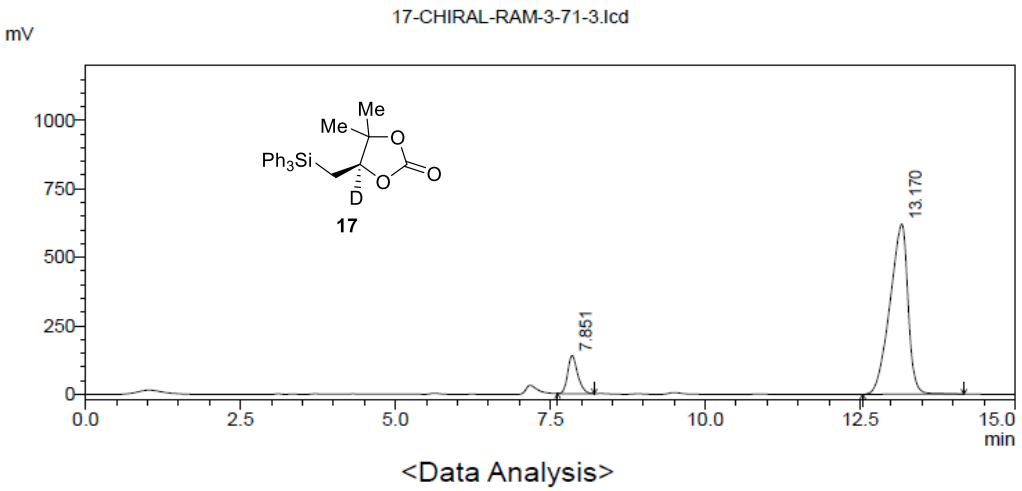
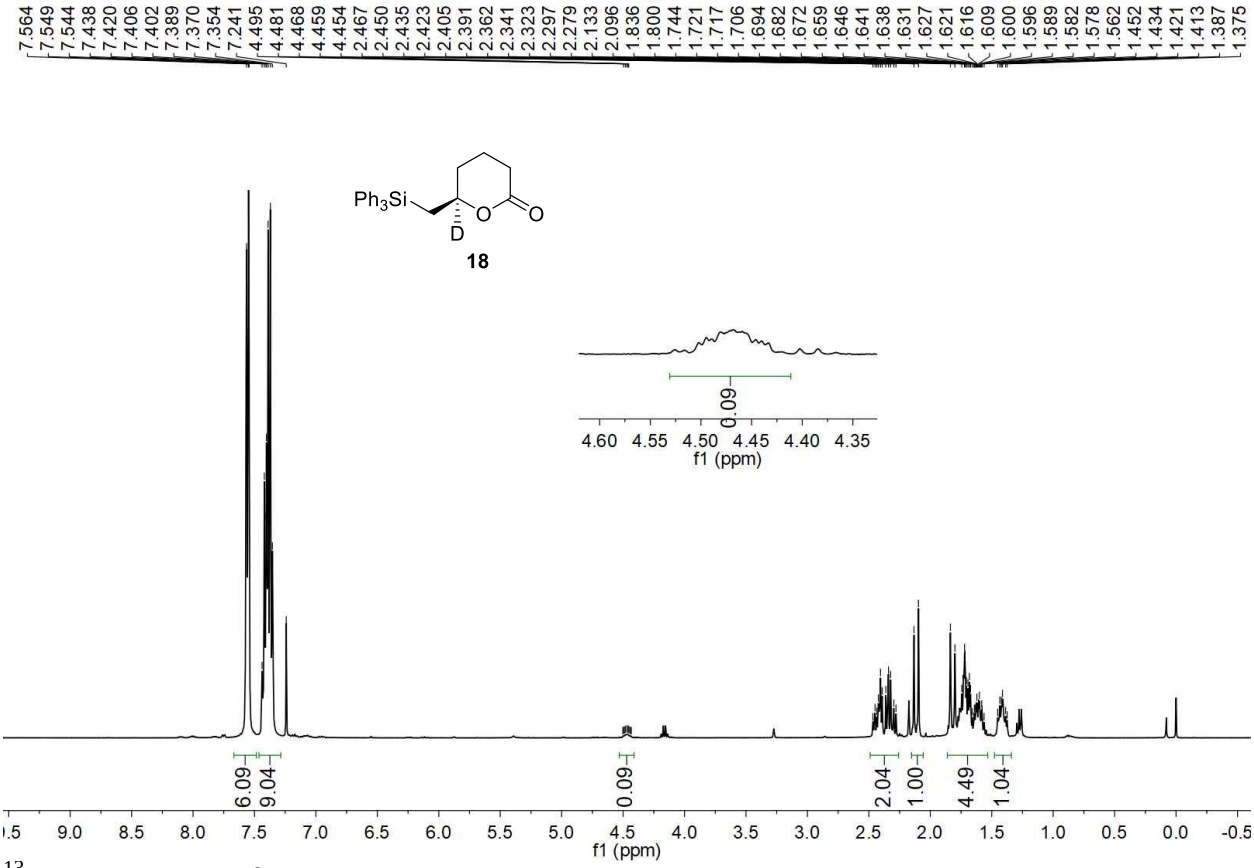


<Data Analysis>

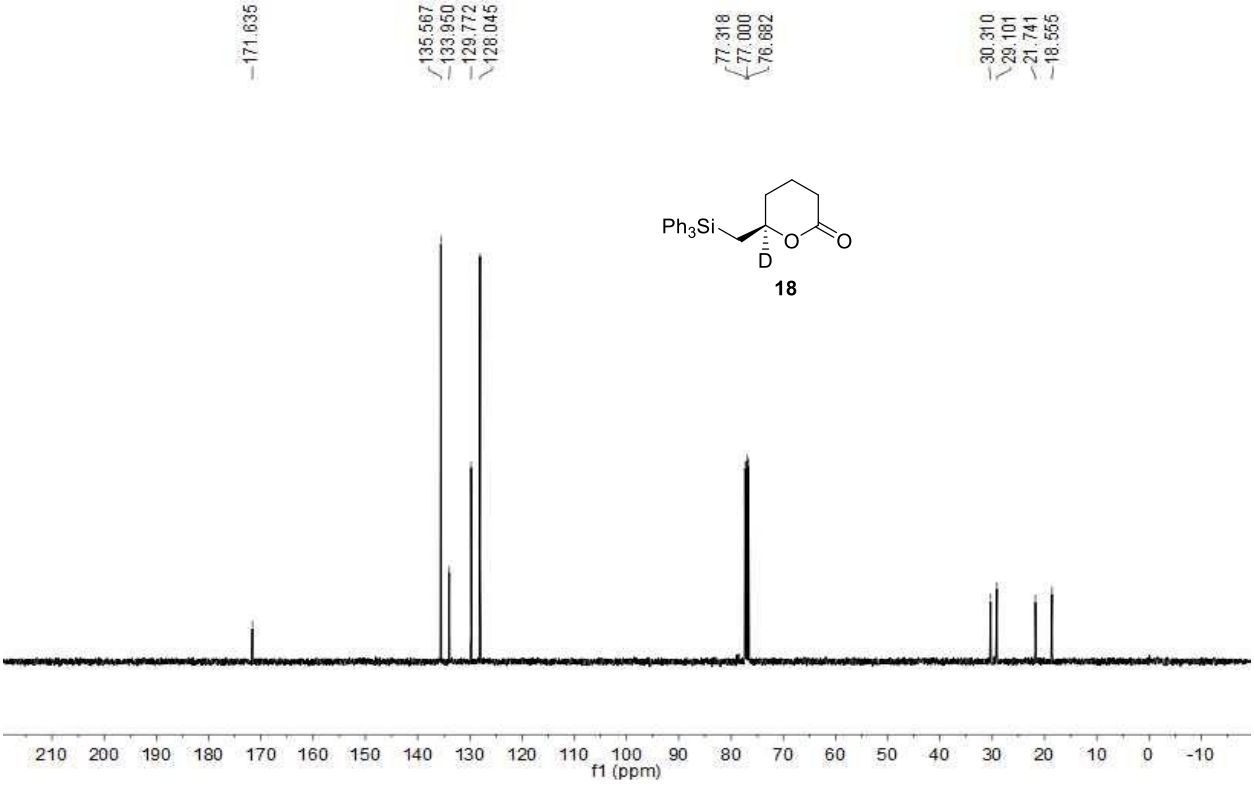
DetA 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	7.851	138850	1564533	11.023
2	13.170	620976	12628511	88.977
Total		759826	14193045	100.000

^{1}H NMR spectra of **18**



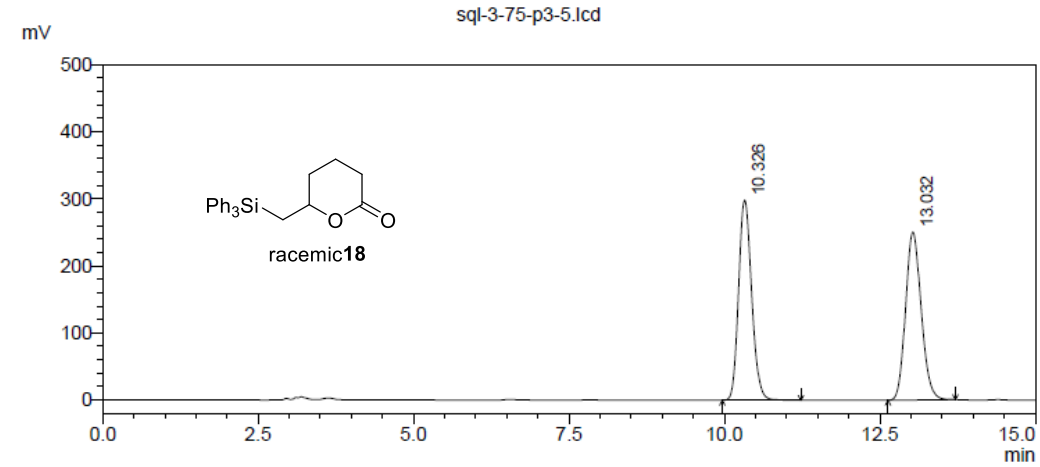
^{13}C NMR spectra of **18**



HPLC spectra of racemic **18**

Data File : sql-3-75-p3-5.lcd
Method File : 3AD-H-96-1-214-20min.lcm
Date Processed : 9/2/2021 1:07:06 AM

<Chromatogram View>



<Data Analysis>

Detector A 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	10.326	298674	4364115	49.833
2	13.032	250703	4393391	50.167
Total		549376	8757506	100.000

HPLC spectra of **18**

Data File : SQL-6-23-1.lcd
Method File : 3AD-H-96-1-214-20min.lcm
Date Processed : 8/7/2021 10:54:55 AM

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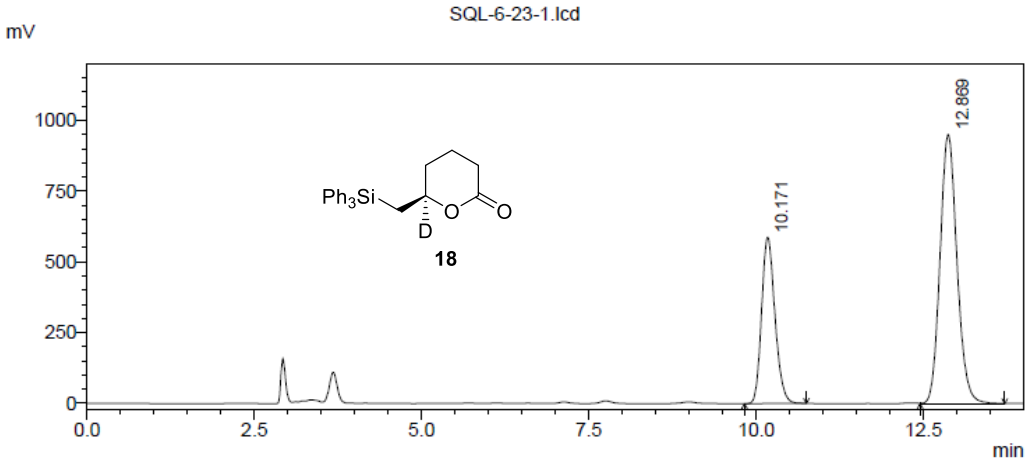
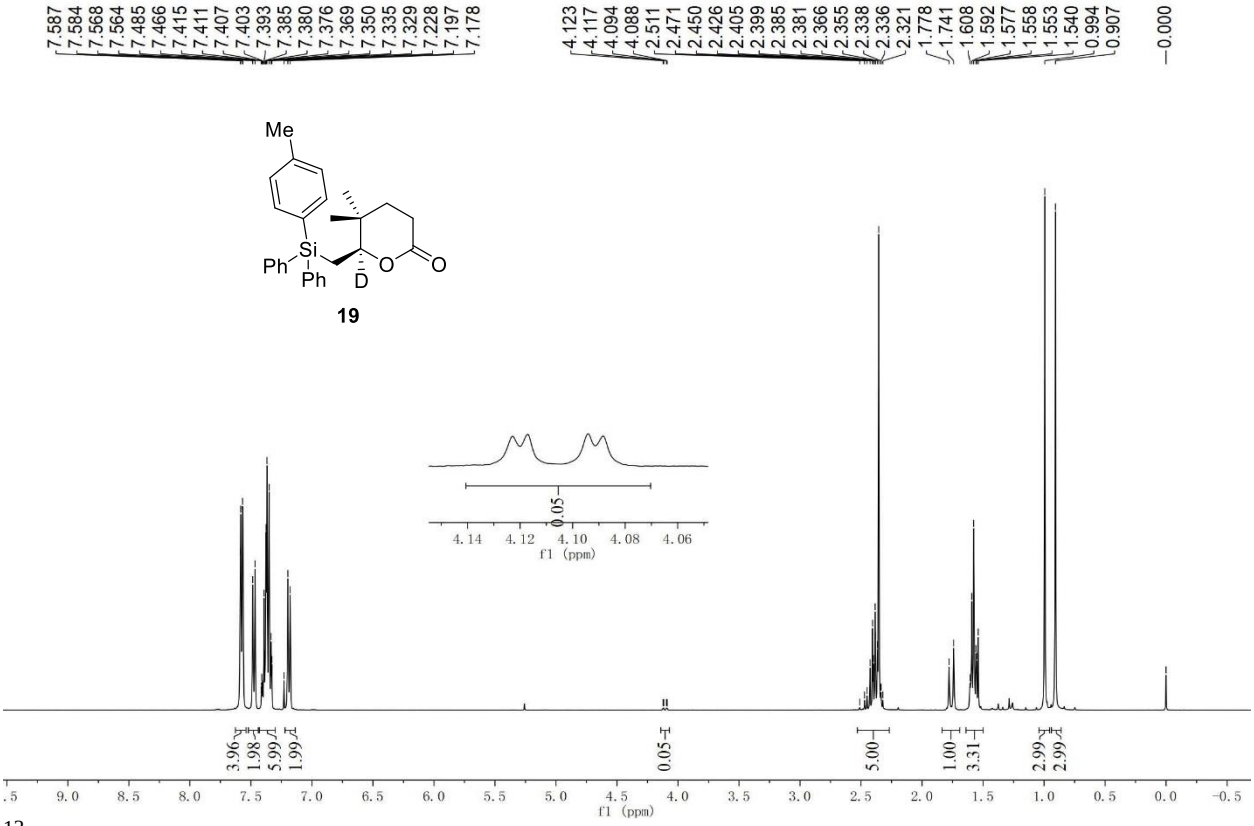


<Data Analysis>

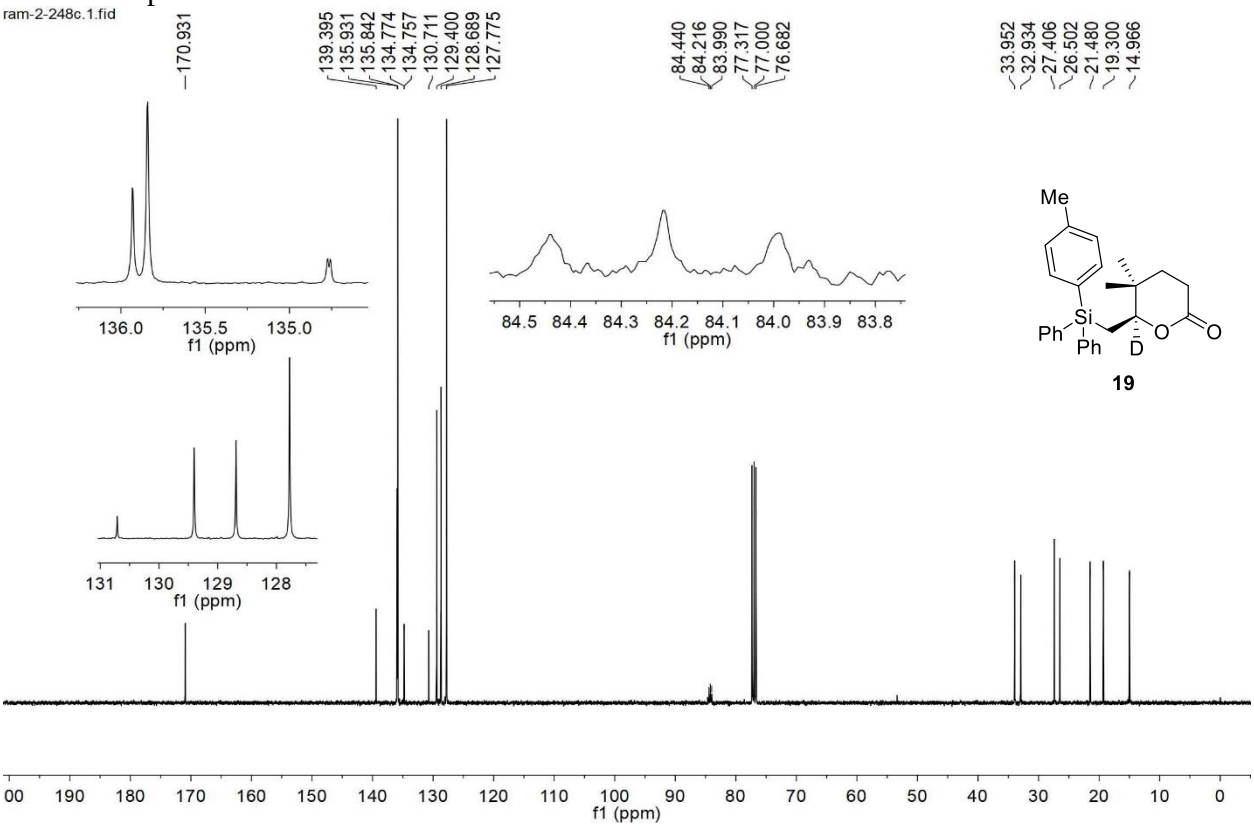
Detector A 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	10.171	586923	8166660	32.776
2	12.869	950476	16749671	67.224
Total		1537400	24916331	100.000

^{1}H NMR spectra of **19**



^{13}C NMR spectra of **19**



HPLC spectra of racemic **19**

Data File : (22-RACEMIC)SQL-3-106-2.lcd
Method File : 3AD-H-98-1-214.lcm
Date Processed : 8/8/2021 12:45:27 PM

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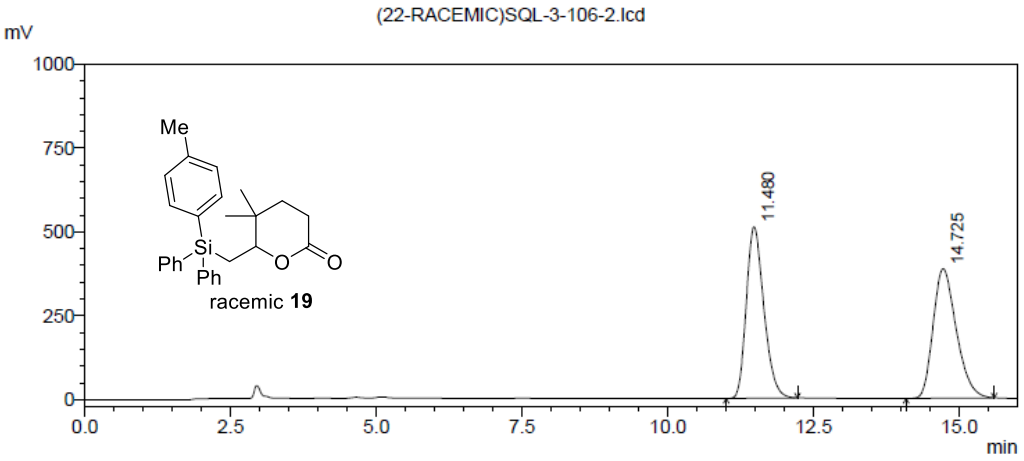


<Data Analysis>

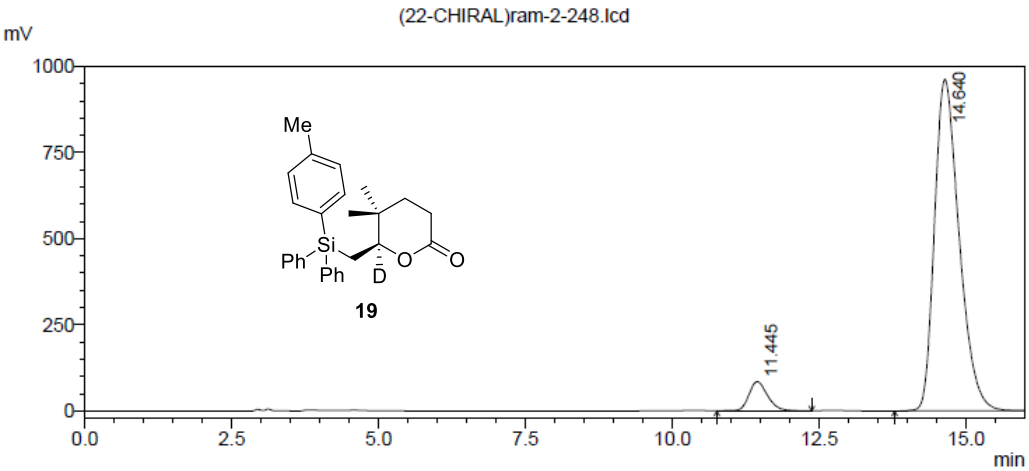
DetA 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	11.480	510940	10709039	50.059
2	14.725	386319	10683683	49.941
Total		897259	21392722	100.000

HPLC spectra of **19**

Data File : (22-CHIRAL)ram-2-248.lcd
Method File : 3AD-H-98-1-214.lcm
Date Processed : 8/8/2021 12:45:39 PM

<Chromatogram View>

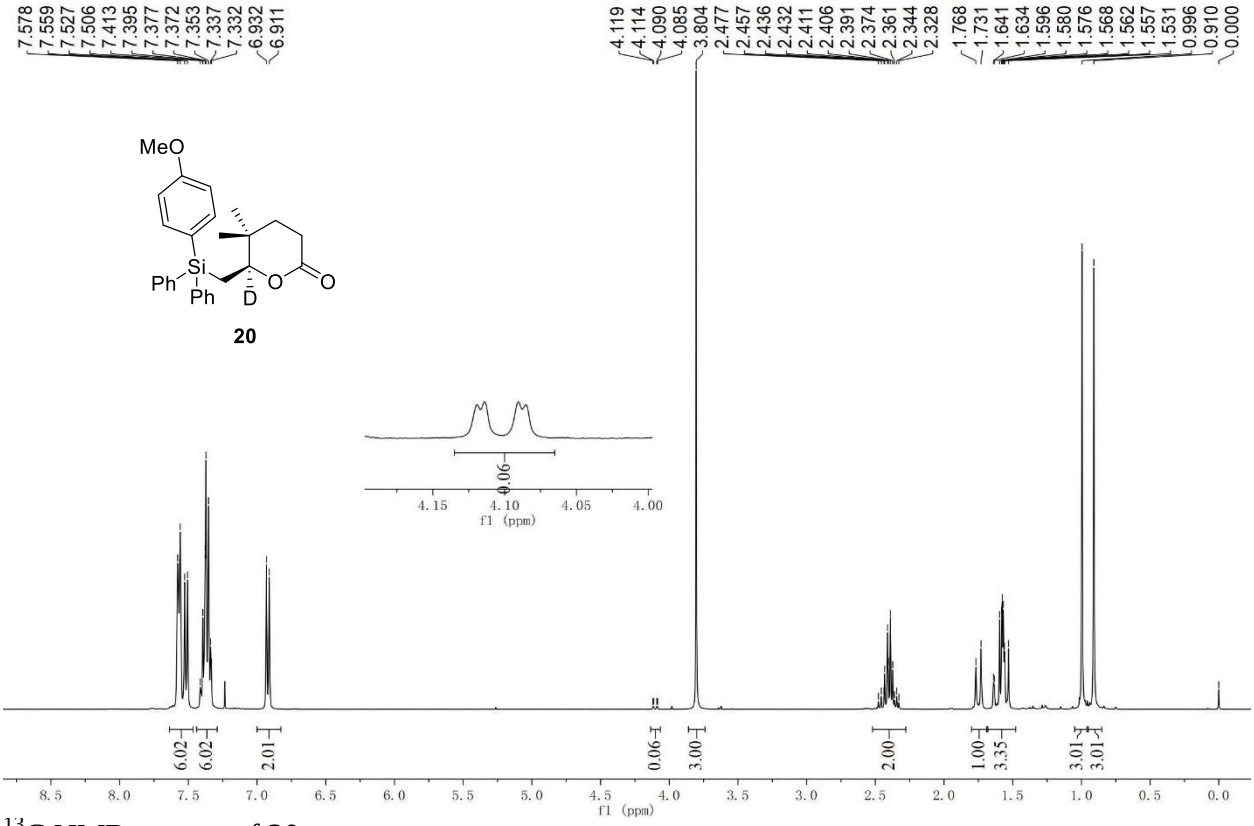


<Data Analysis>

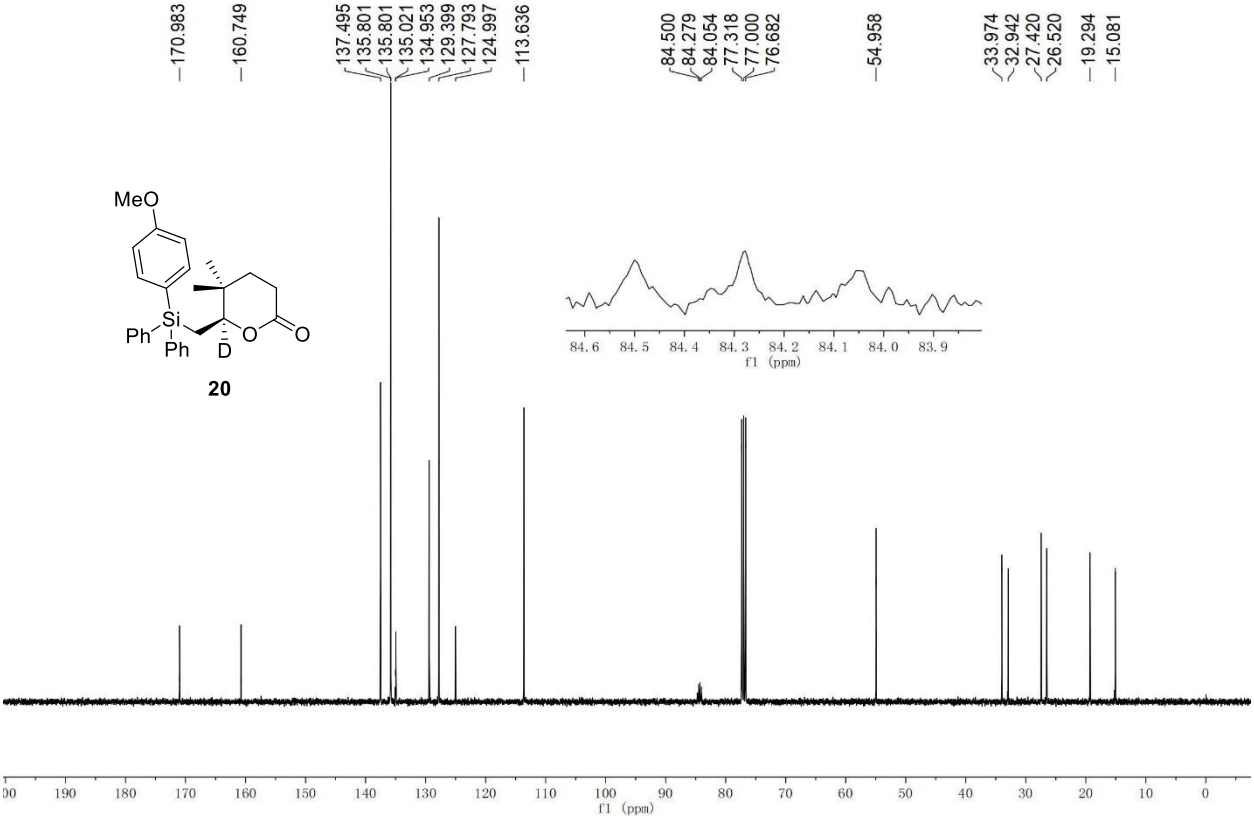
DetA 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	11.445	85181	1911021	6.363
2	14.640	962668	28120980	93.637
Total		1047850	30032001	100.000

^{1}H NMR spectra of **20**



^{13}C NMR spectra of **20**



HPLC spectra of racemic **20**

Data File : (23-racemic)SQL-3-94-2RACEMIC001.lcd
Method File : 3AD-H-98-1-214-30min.lcm
Date Processed : 8/8/2021 12:44:38 PM

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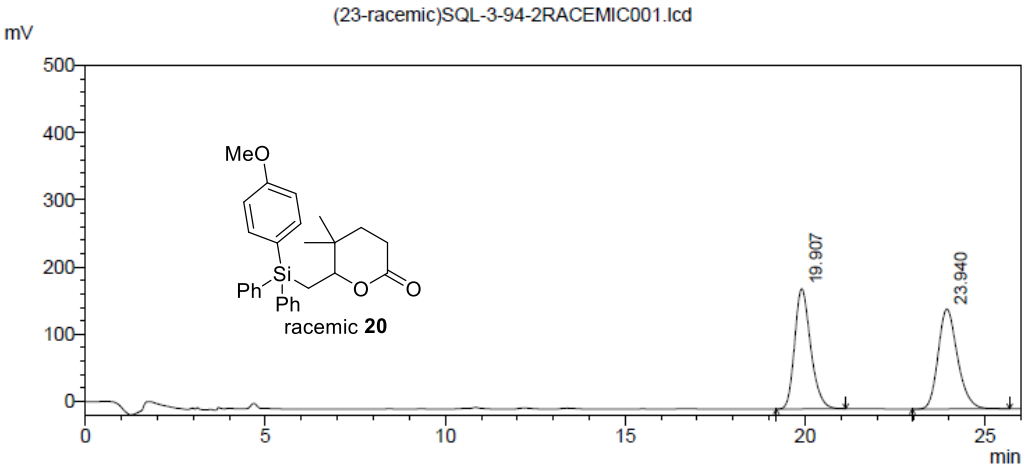


<Data Analysis>

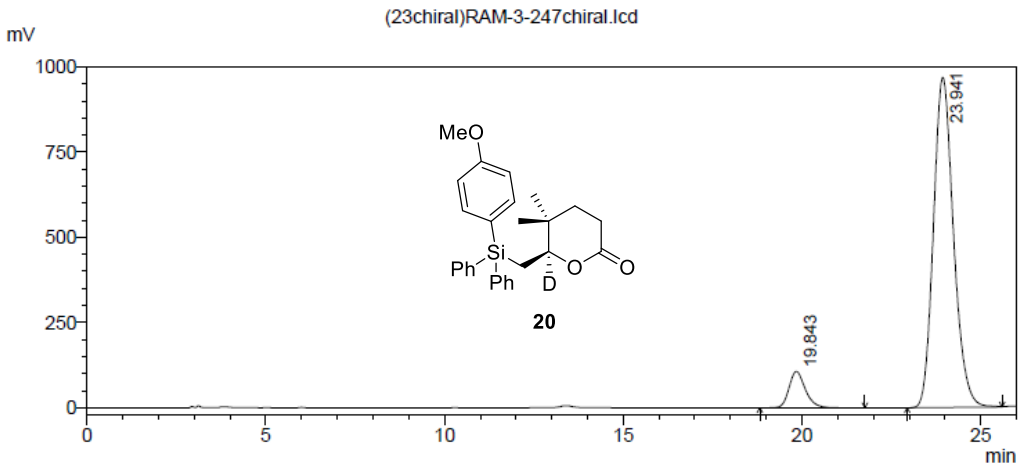
DetA 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	19.907	178450	5531869	49.767
2	23.940	148659	5583556	50.233
Total		327109	11115426	100.000

HPLC spectra of **20**

Data File : (23chiral)RAM-3-247chiral.lcd
Method File : 3AD-H-98-1-214-30min.lcm
Date Processed : 8/8/2021 12:44:22 PM

<Chromatogram View>

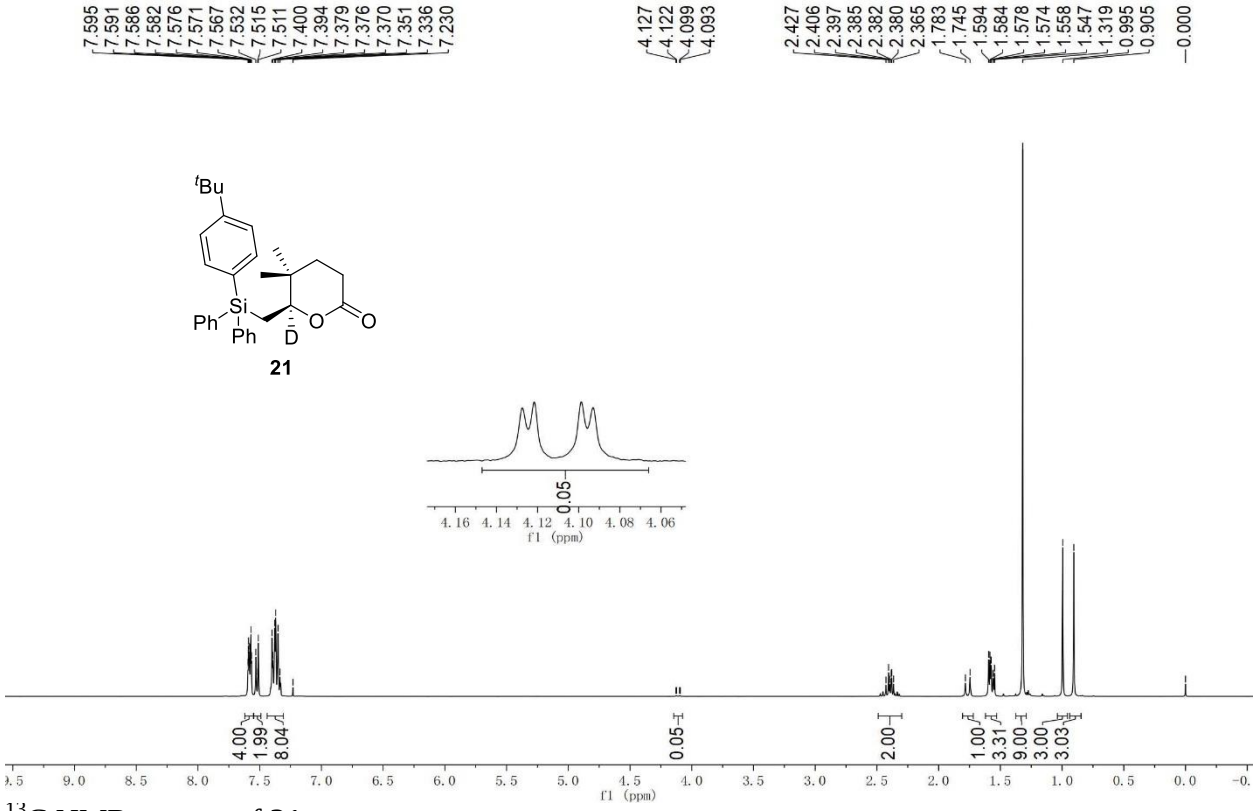


<Data Analysis>

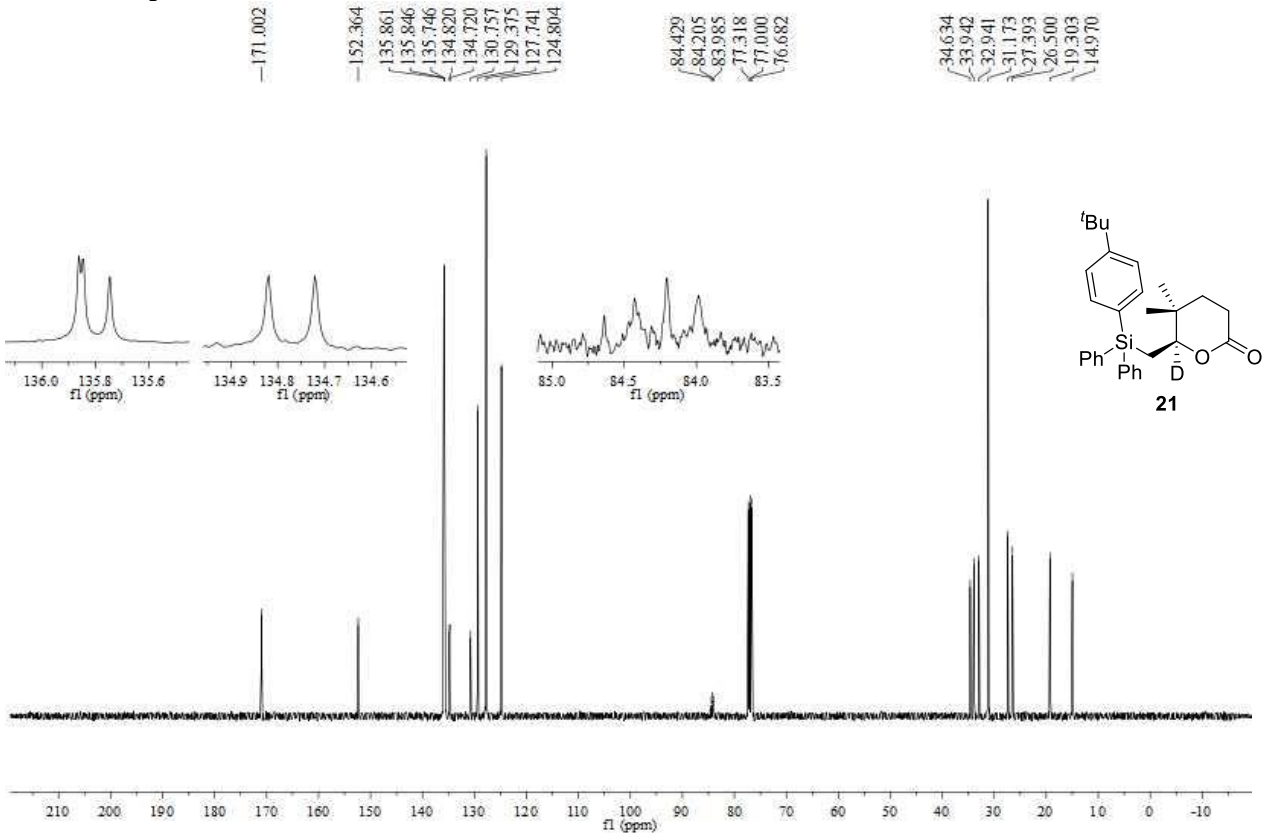
DetA 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	19.843	106719	3394332	8.223
2	23.941	969018	37884357	91.777
Total		1075737	41278689	100.000

^{1}H NMR spectra of **21**



^{13}C NMR spectra of **21**



HPLC spectra of racemic **21**

Data File : (24-RACEMIC)SQL-3-119-2.lcd
Method File : AD-H-98.5+1.5-1-214.lcm
Date Processed : 8/8/2021 12:43:54 PM

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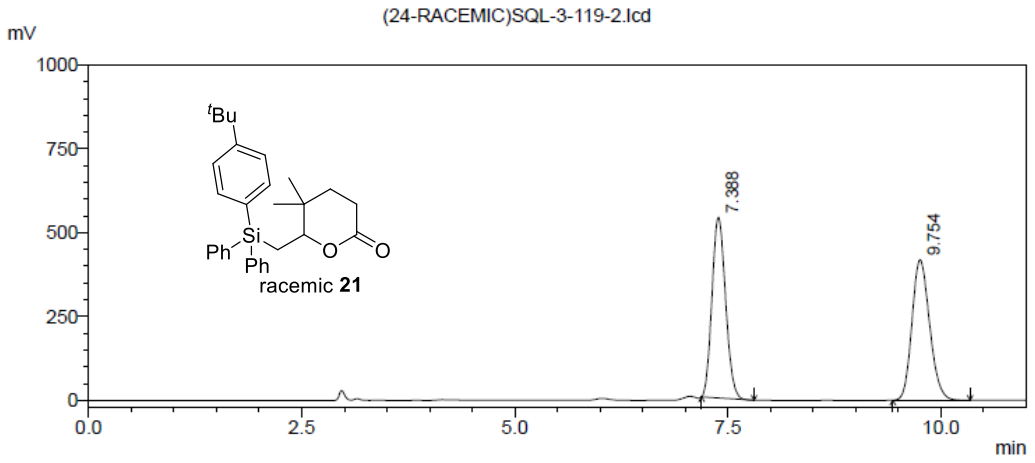


<Data Analysis>

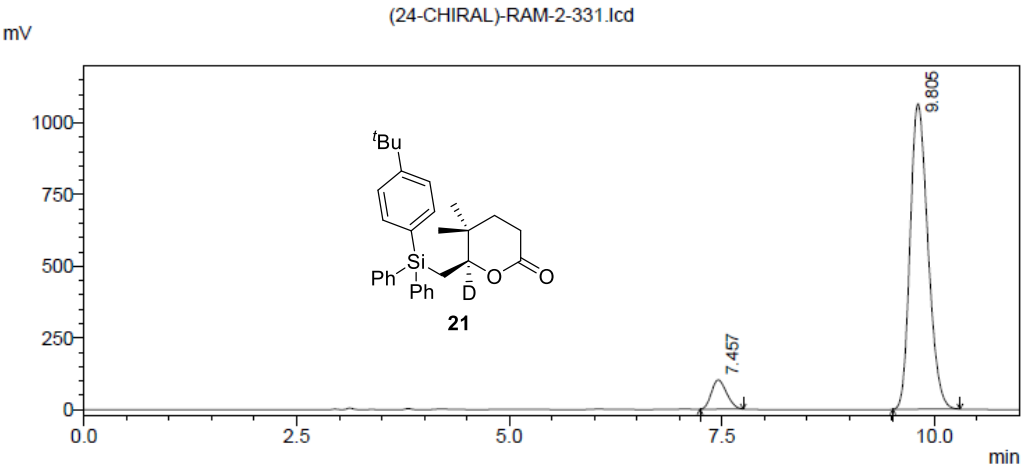
???A 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	7.388	538245	5976197	49.702
2	9.754	418608	6047791	50.298
Total		956853	12023987	100.000

HPLC spectra of **21**

Data File : (24-CHIRAL)-RAM-2-331.lcd
Method File : AD-H-98.5+1.5-1-214.lcm
Date Processed : 8/8/2021 12:44:05 PM

<Chromatogram View>

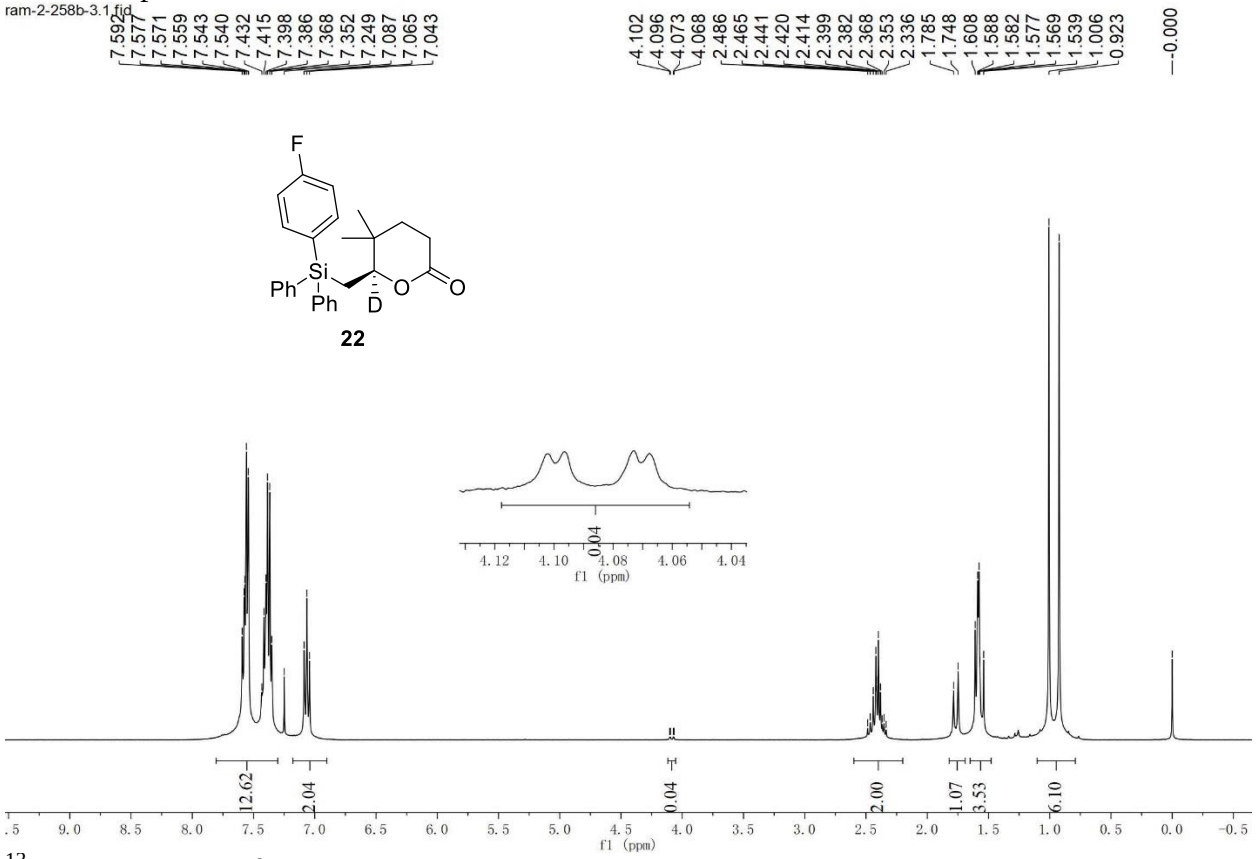


<Data Analysis>

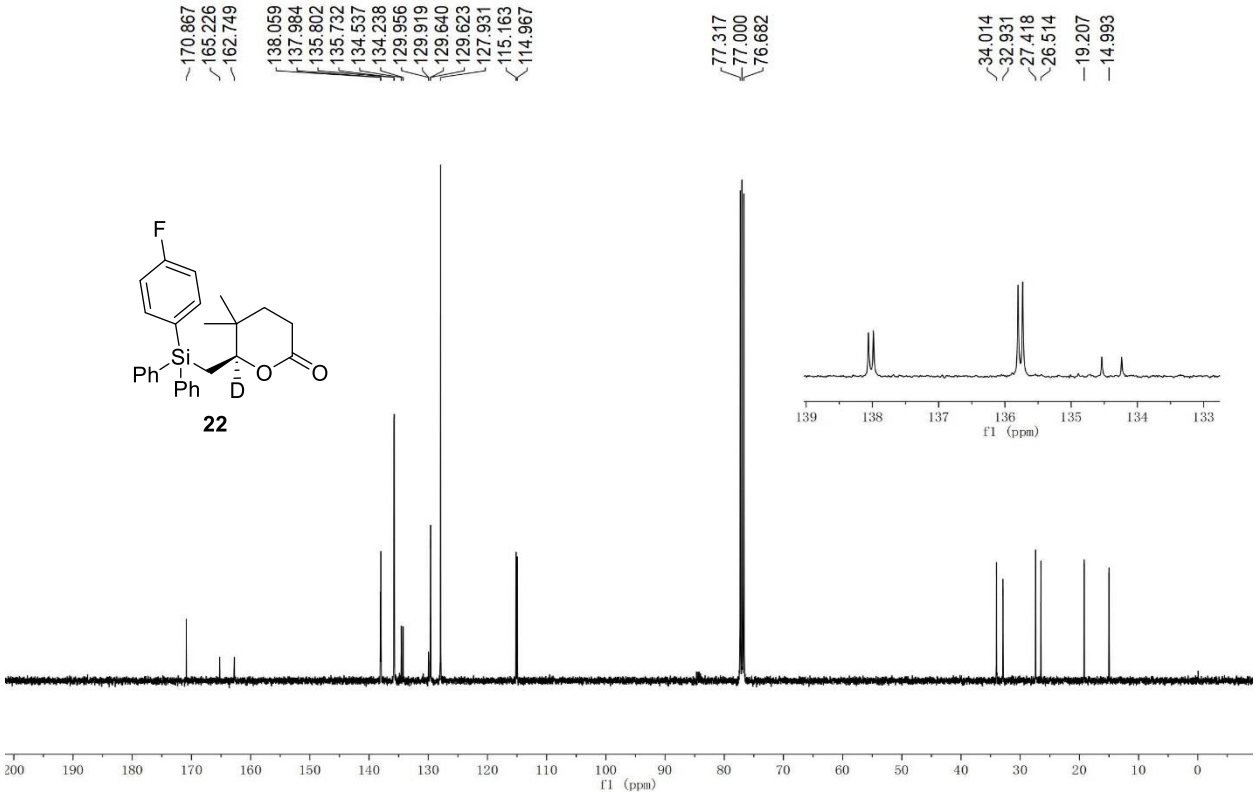
???A 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	7.457	101892	1264009	7.536
2	9.805	1065230	15508625	92.464
Total		1167122	16772634	100.000

^{1}H NMR spectra of **22**

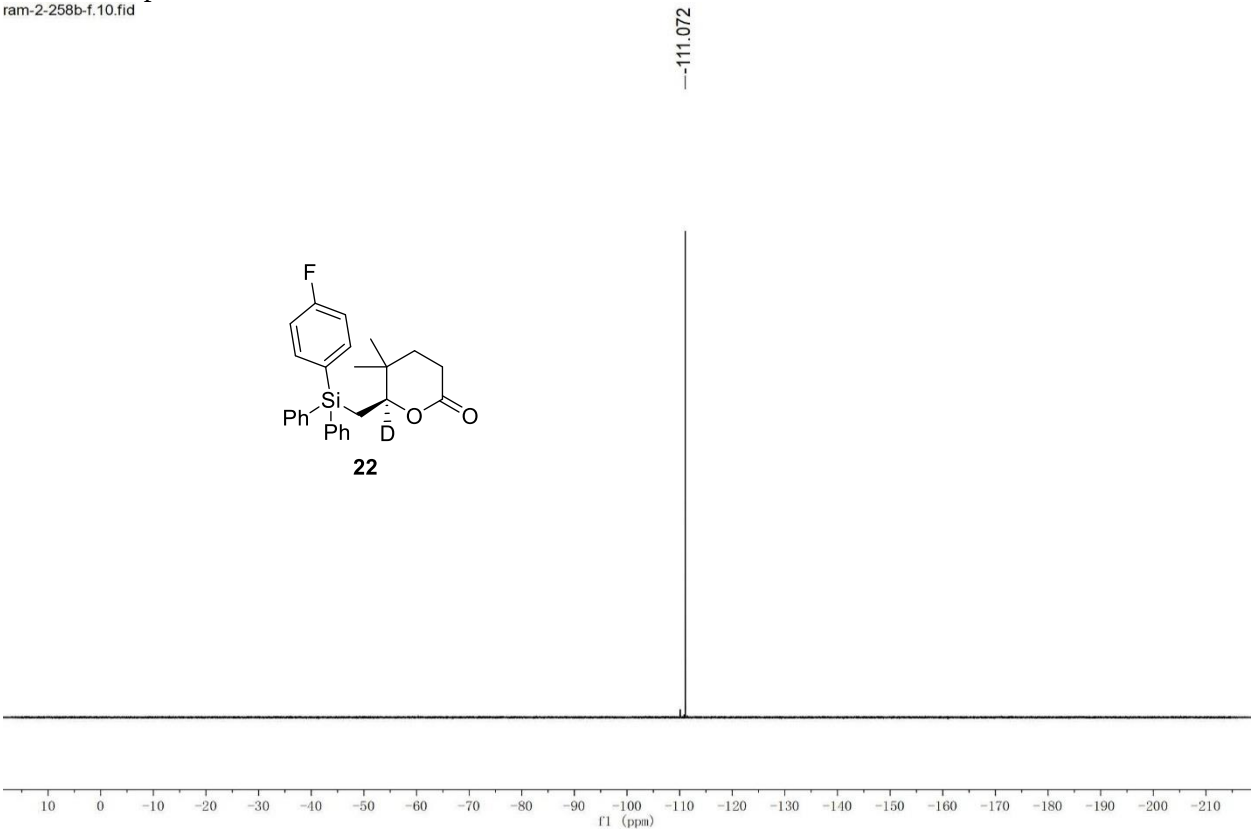


^{13}C NMR spectra of **22**



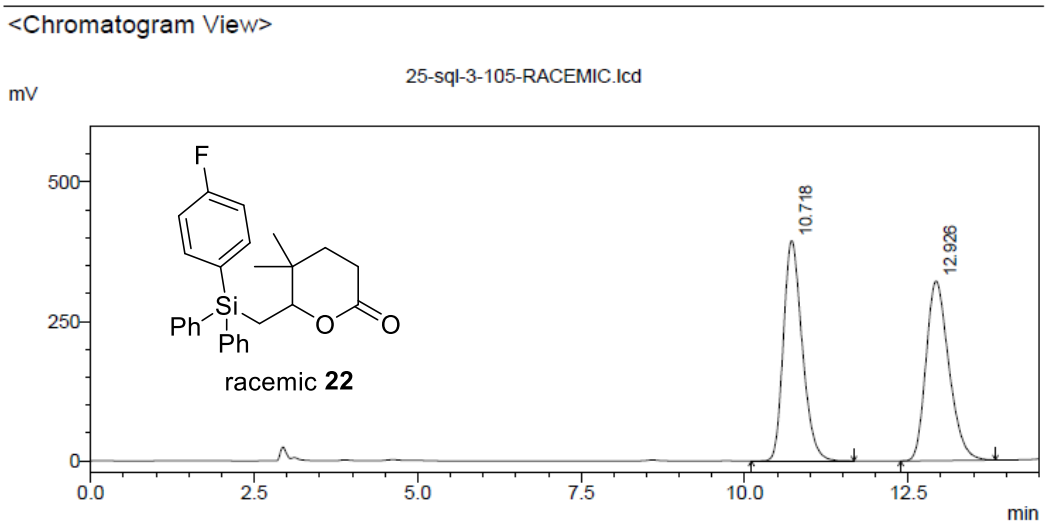
^{19}F NMR spectra of **22**

ram-2-258b-f.10.fid



HPLC spectra of racemic **22**

Data File	: 25-sql-3-105-RACEMIC.lcd
Method File	: 3AD-H-98-1-214.lcm
Date Processed	: 6/25/2021 2:38:41 PM



<Data Analysis>

DetA 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	10.718	394814	7903651	50.158
2	12.926	321829	7853985	49.842
Total		716643	15757636	100.000

HPLC spectra of **22**

Data File : 25-RAM-2-258B.lcd
Method File : 3AD-H-98-1-214.lcm
Date Processed : 6/25/2021 2:58:31 PM

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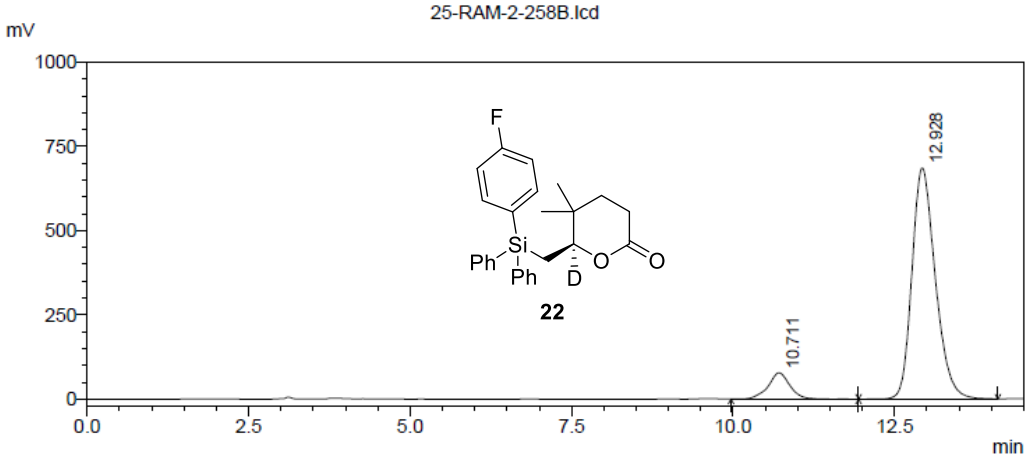
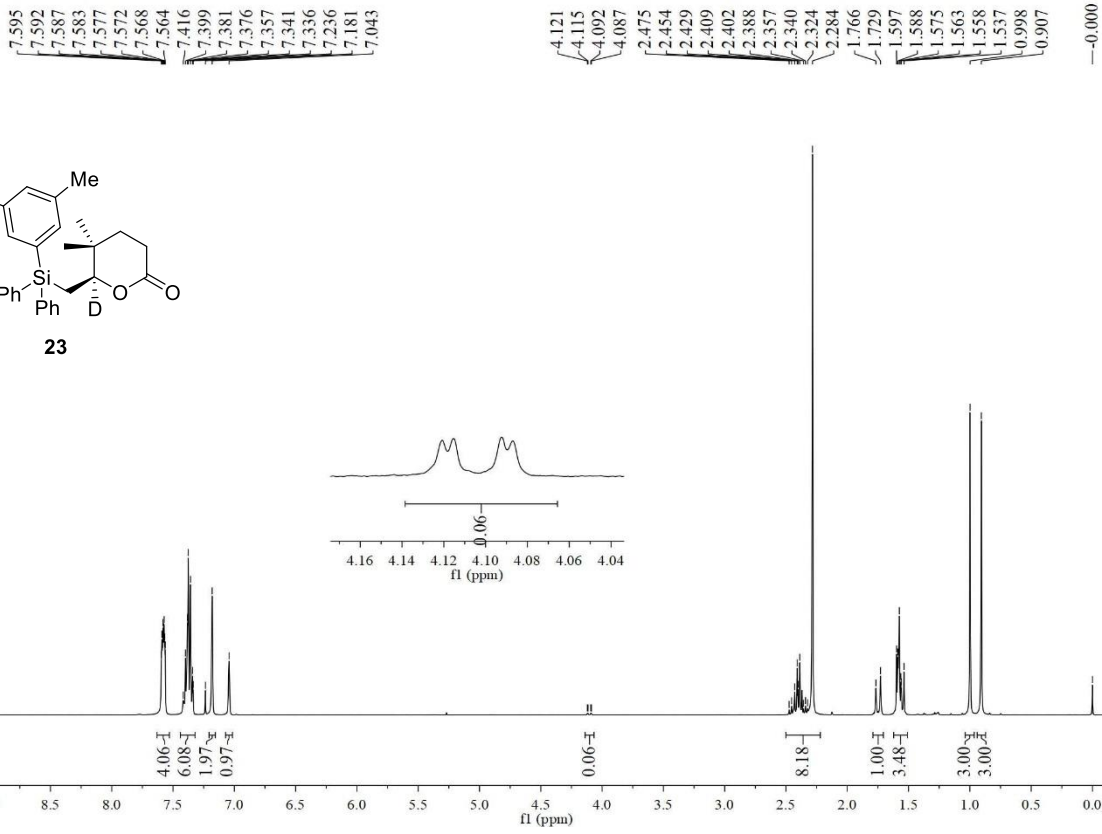


<Data Analysis>

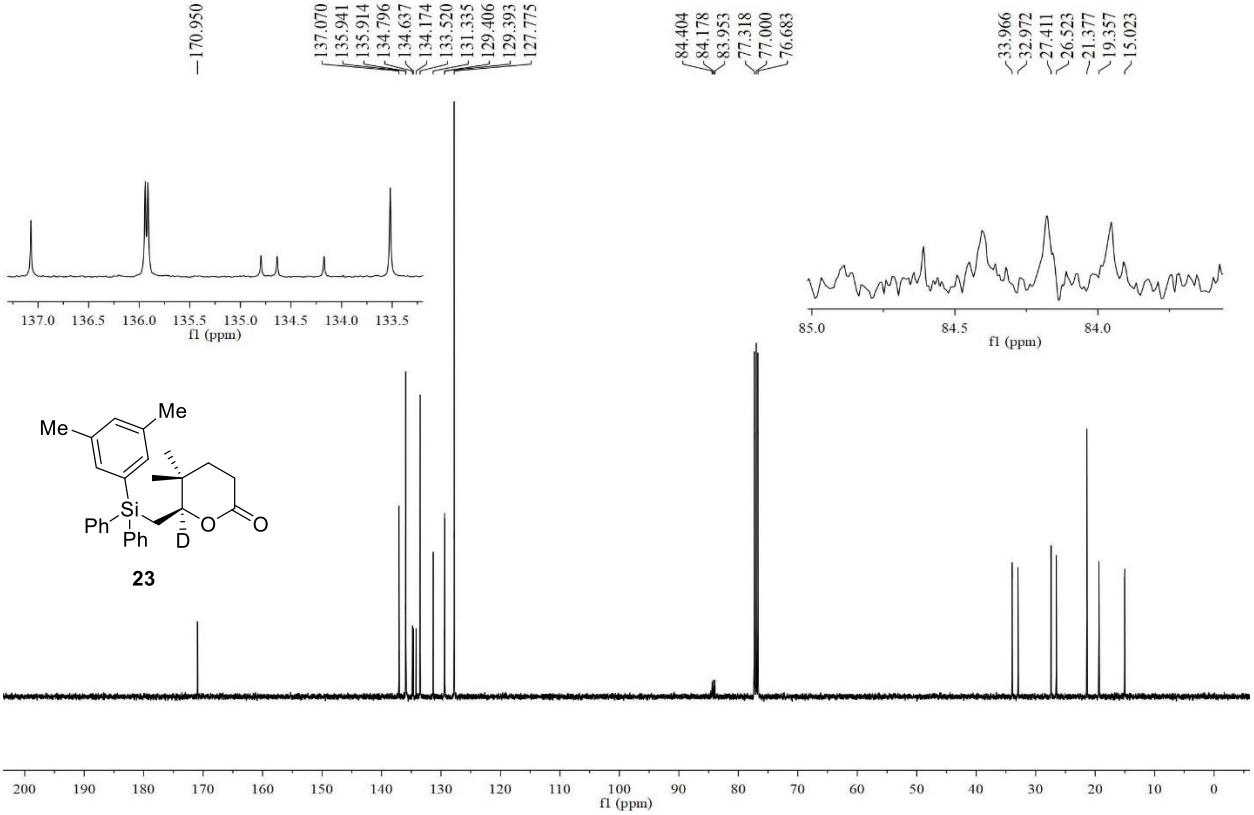
DetA 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	10.711	77917	1832328	9.567
2	12.928	685622	17320759	90.433
Total		763539	19153087	100.000

^{1}H NMR spectra of **23**

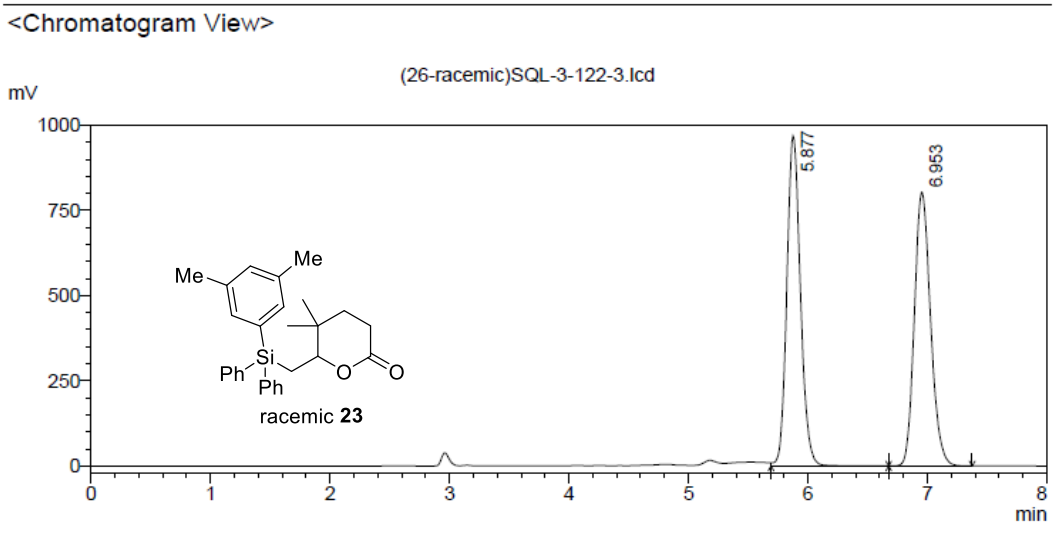


^{13}C NMR spectra of **23**



HPLC spectra of racemic **23**

Data File : (26-racemic)SQL-3-122-3.lcd
Method File : AD-H-98.5+1.5-1-214.lcm
Date Processed : 8/8/2021 12:44:54 PM



<Data Analysis>

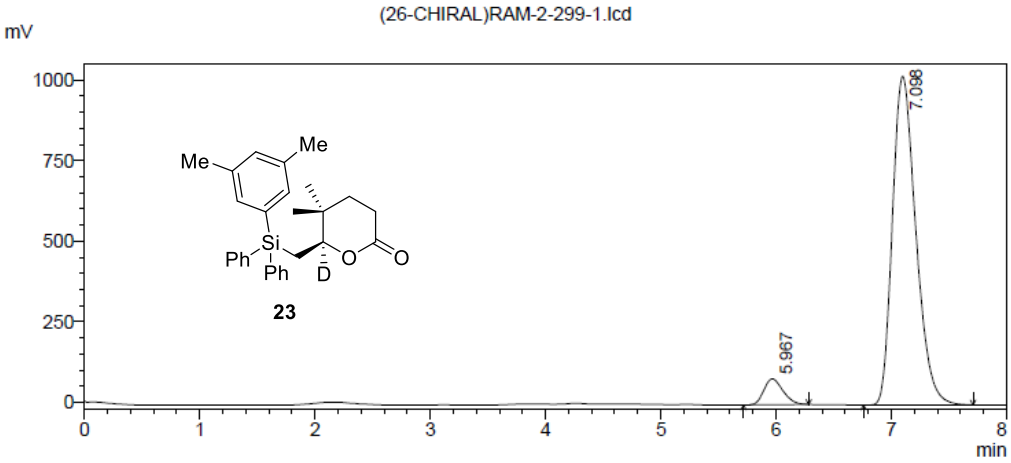
???A 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	5.877	969046	7673680	50.288
2	6.953	803512	7585727	49.712
Total		1772558	15259407	100.000

HPLC spectra of **23**

Data File : (26-CHIRAL)RAM-2-299-1.lcd
Method File : 3AD-H-98-1-214-10MIN.lcm
Date Processed : 8/8/2021 12:45:05 PM

<Chromatogram View>

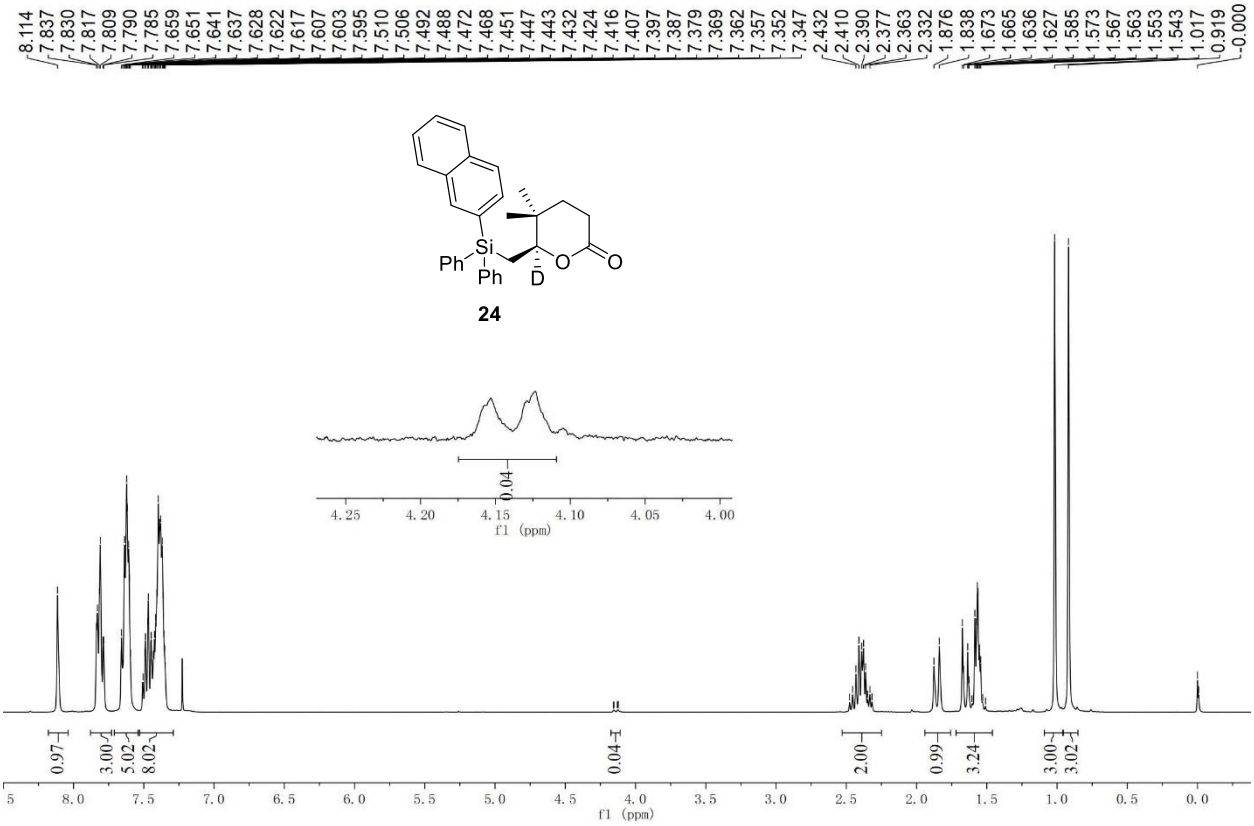


<Data Analysis>

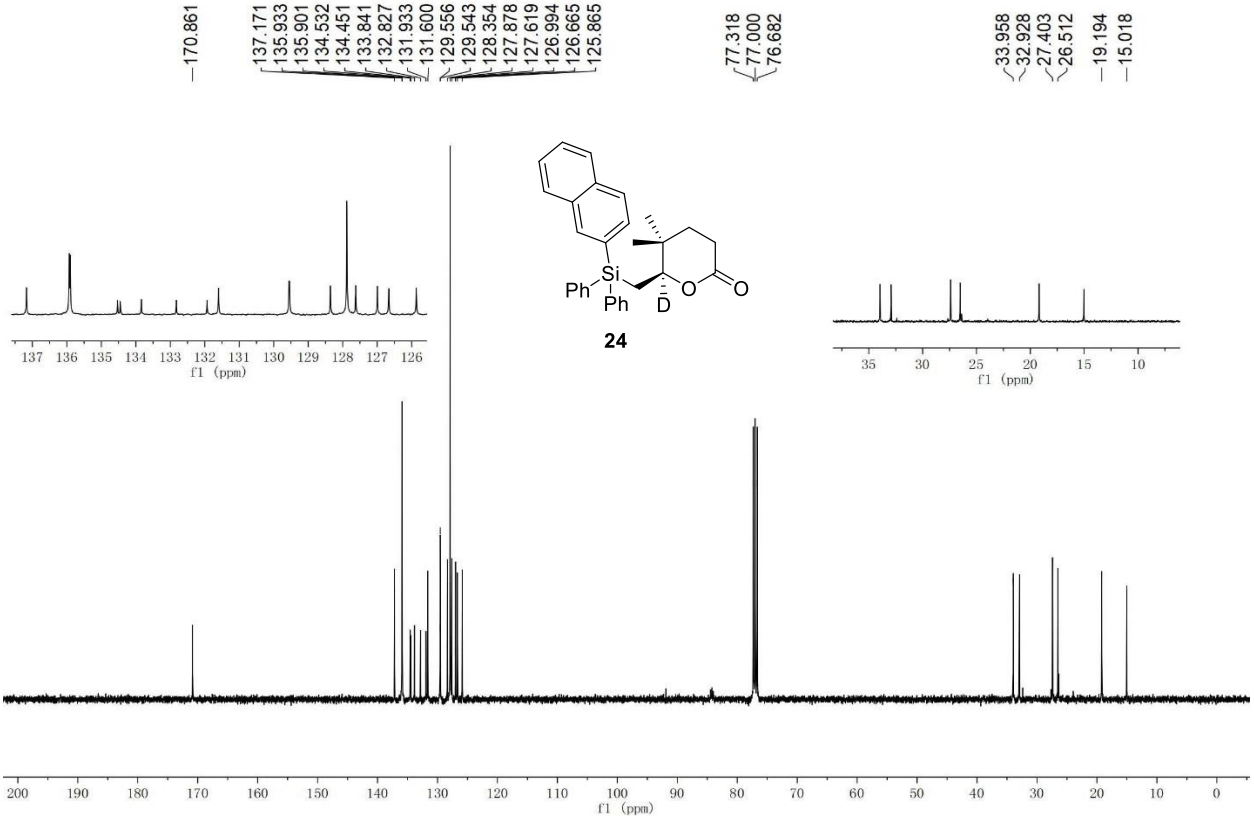
DetA 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	5.967	80247	925329	6.039
2	7.098	1018794	14398387	93.961
Total		1099041	15323717	100.000

^{1}H NMR spectra of **24**



^{13}C NMR spectra of **24**



HPLC spectra of racemic **24**

Data File	: (27-RACEMIC)RAM-3-18A.lcd
Method File	: AD-H-95.5+4.5-1-214.lcm
Date Processed	: 8/8/2021 12:45:58 PM

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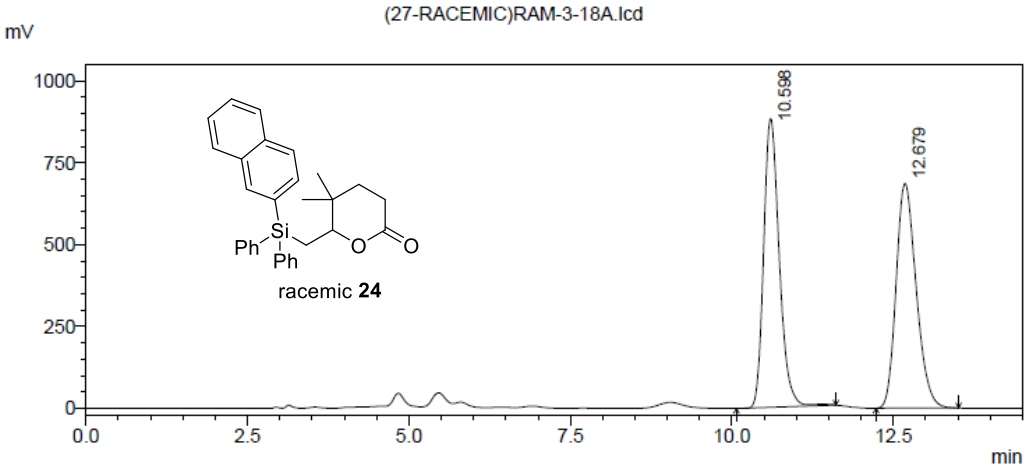


<Data Analysis>

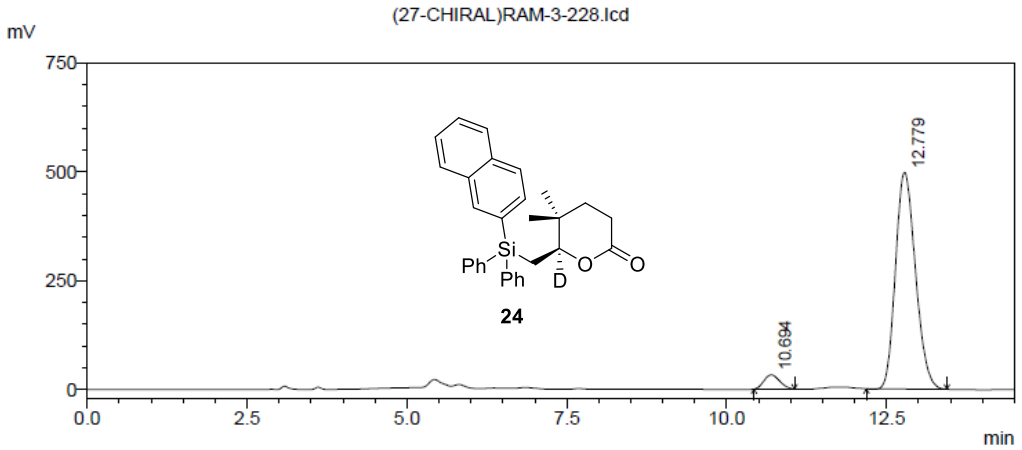
???A 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	10.598	881467	14786990	49.925
2	12.679	685909	14831129	50.075
Total		1567376	29618120	100.000

HPLC spectra of **24**

Data File : (27-CHIRAL)RAM-3-228.lcd
Method File : 3AD-H-95.5-1-214.lcm
Date Processed : 8/8/2021 12:46:13 PM

<Chromatogram View>



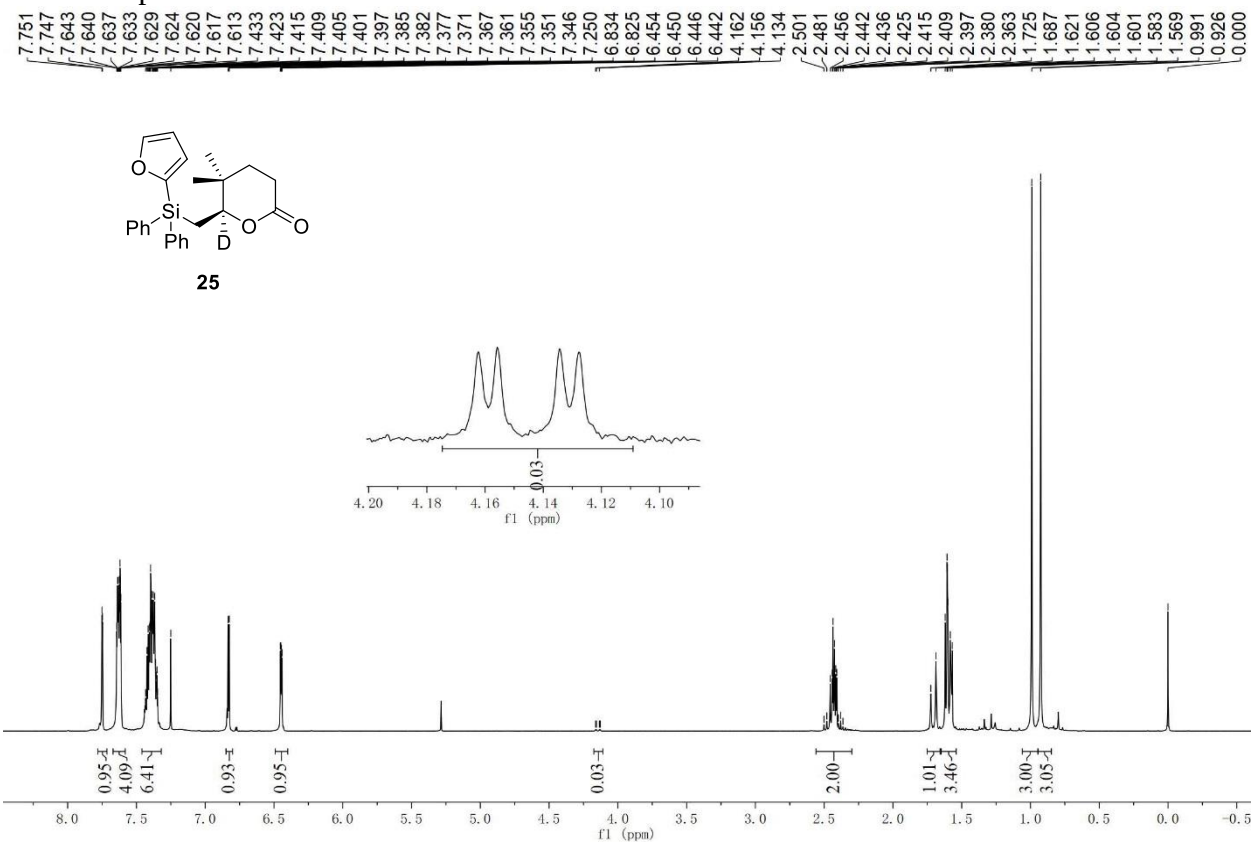
24

<Data Analysis>

DetA 214nm

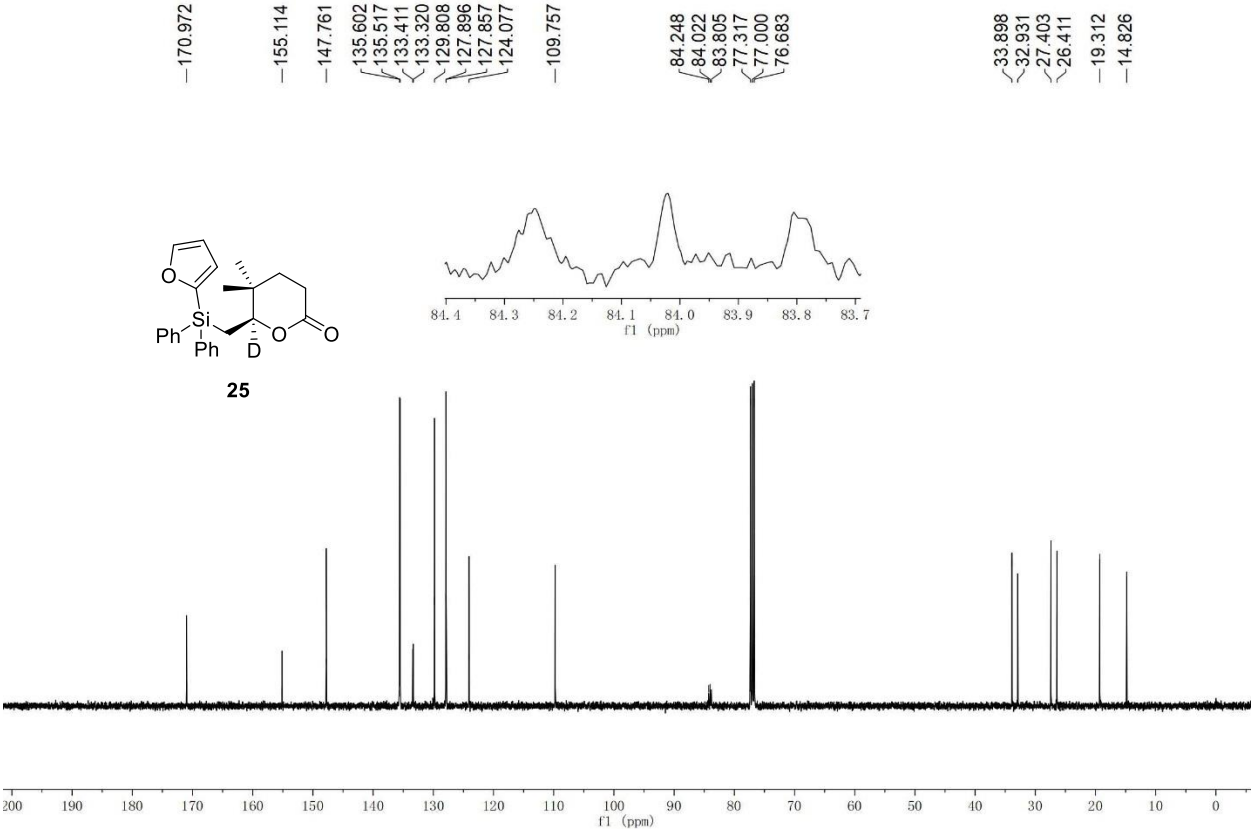
Pesk #	Ret. Time	Height	Area	Area%
1	10.694	32648	556854	4.895
2	12.779	497783	10820189	95.105
Total		530431	11377043	100.000

^{1}H NMR spectra of **25**



25

^{13}C NMR spectra of **25**



HPLC spectra of racemic **28**

Data File : 28-RAM-2-353-8-racemic.lcd
Method File : AD-H-98.7+1.3-1-214 30 min.lcm
Date Processed : 8/8/2021 1:29:04 PM

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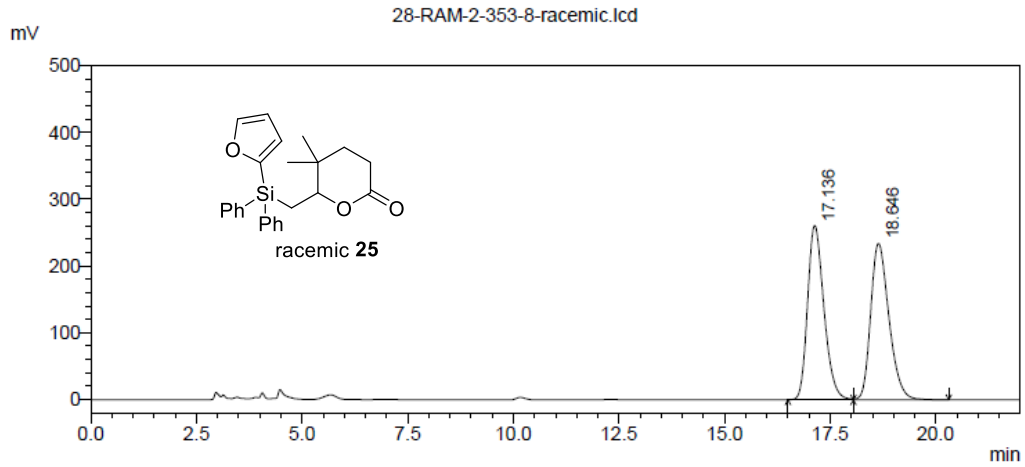


<Data Analysis>

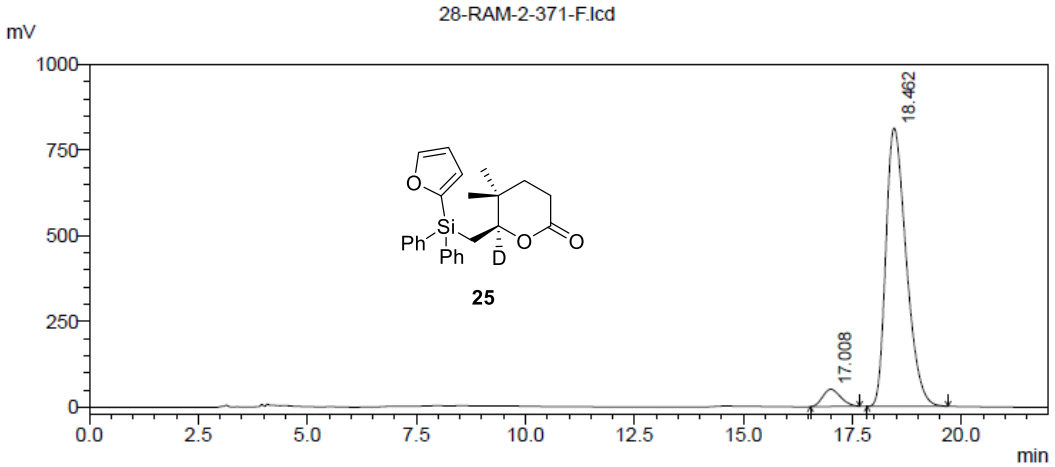
???A 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	17.136	260784	7027681	49.929
2	18.646	233952	7047546	50.071
Total		494737	14075227	100.000

HPLC spectra of **25**

Data File : 28-RAM-2-371-F.lcd
Method File : AD-H-98.7+1.3-1-214 30 min.lcm
Date Processed : 8/8/2021 1:30:15 PM

<Chromatogram View>



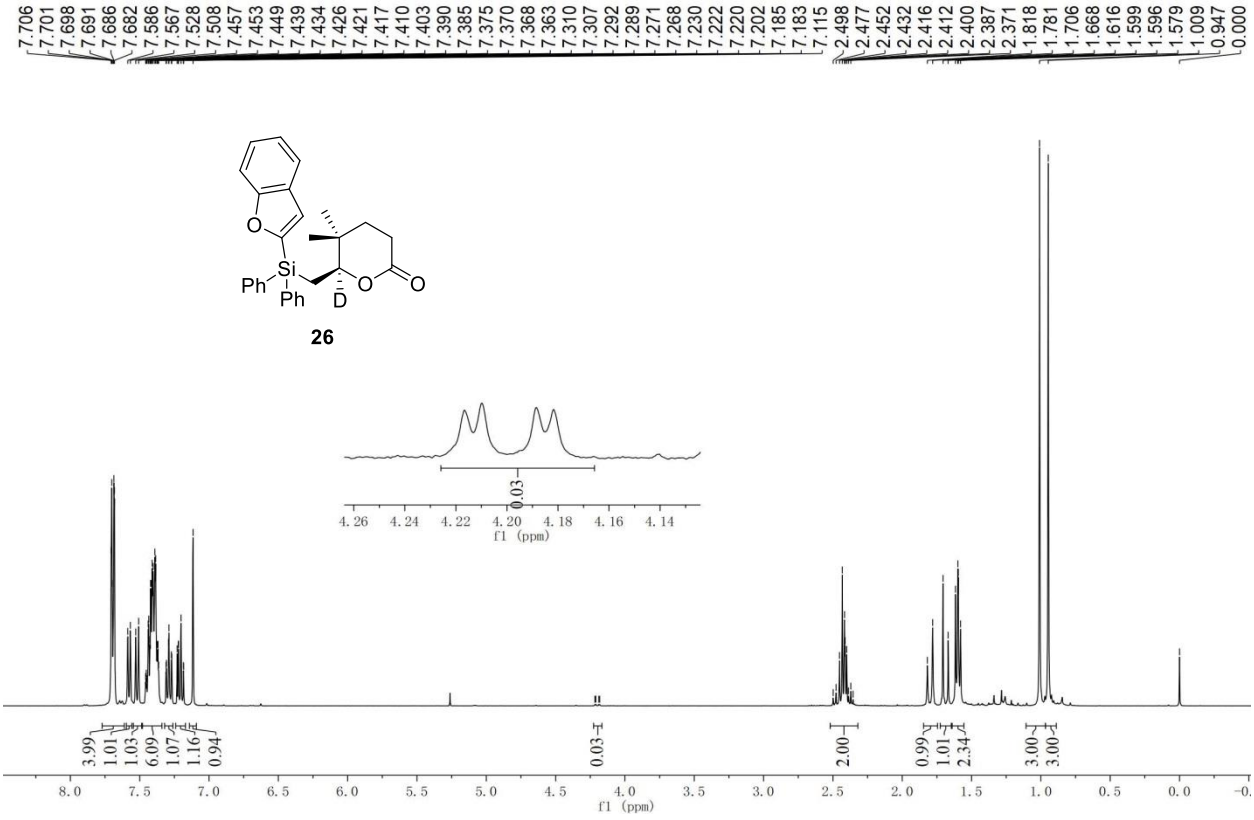
25

<Data Analysis>

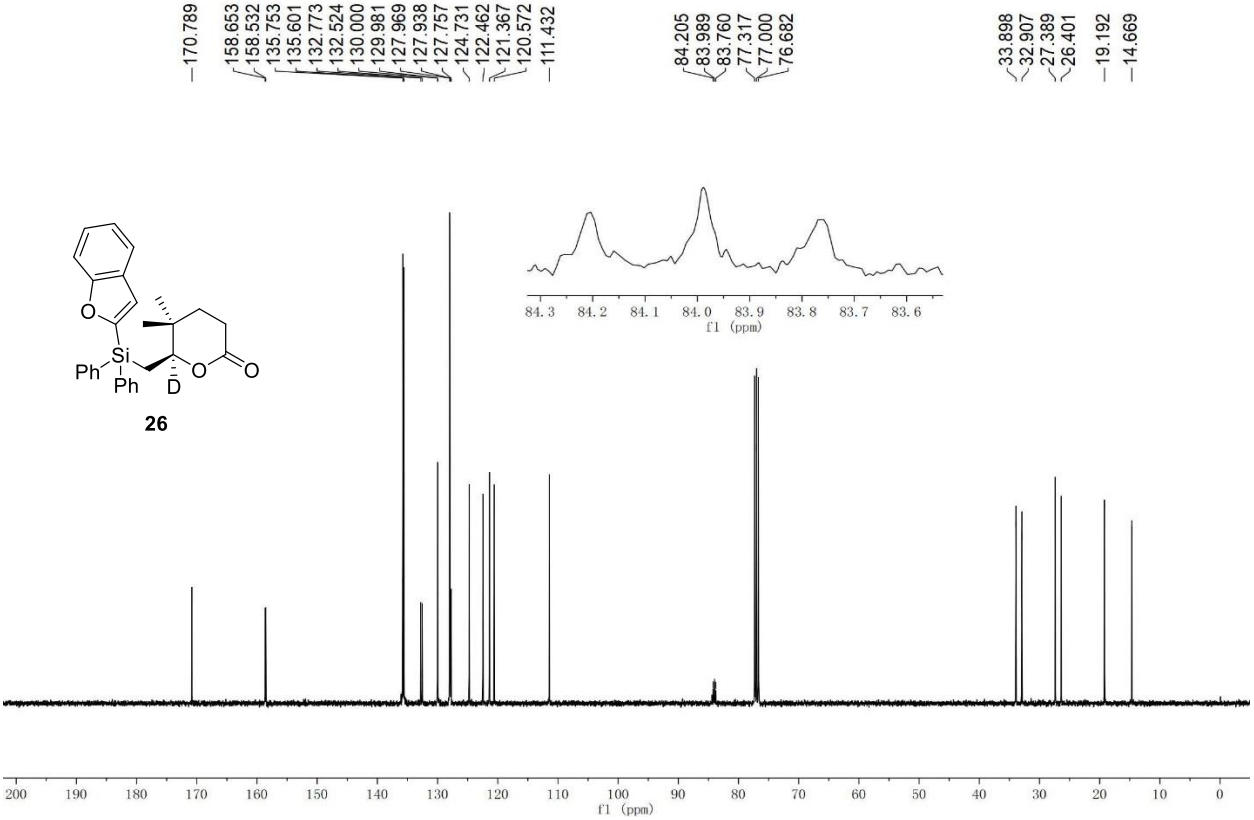
???A 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	17.008	50431	1439747	5.171
2	18.462	812594	26401258	94.829
Total		863025	27841004	100.000

^{1}H NMR spectra of **26**



^{13}C NMR spectra of **26**



HPLC spectra of racemic **26**

Data File : 29-RACEMIC-RAM-2-326.lcd
Method File : 3AD-H-98-1-214-40MIN.lcm
Date Processed : 7/17/2021 12:11:53 PM

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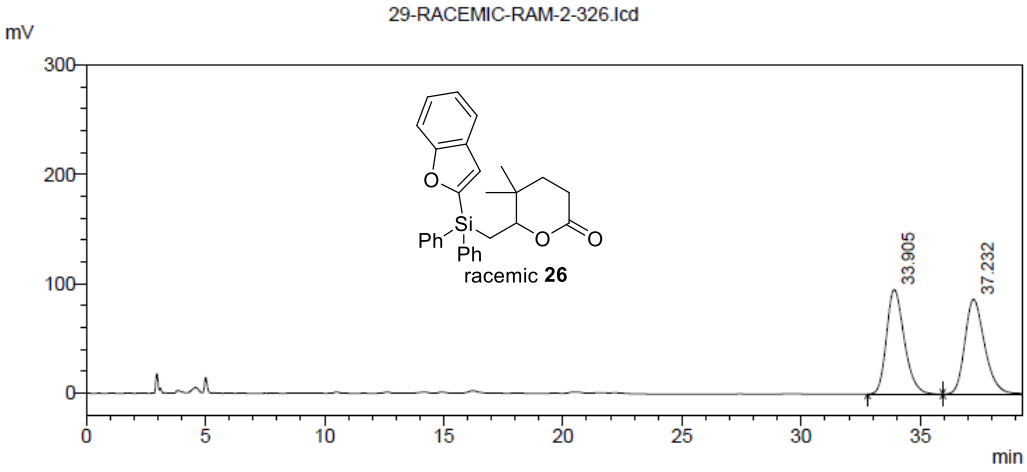

<Data Analysis>

DetA 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	33.905	95545	4957109	49.822
2	37.232	86534	4992482	50.178
Total		182079	9949591	100.000

HPLC spectra of **26**

Data File : 29-CHIRAL-RAM-2-372.lcd
Method File : 3AD-H-98-1-214-40MIN.lcm
Date Processed : 7/17/2021 12:14:27 PM

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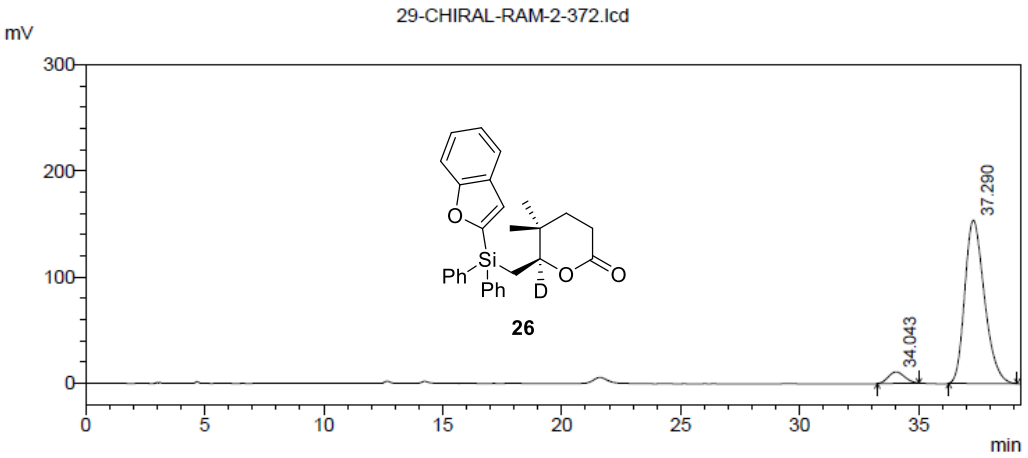


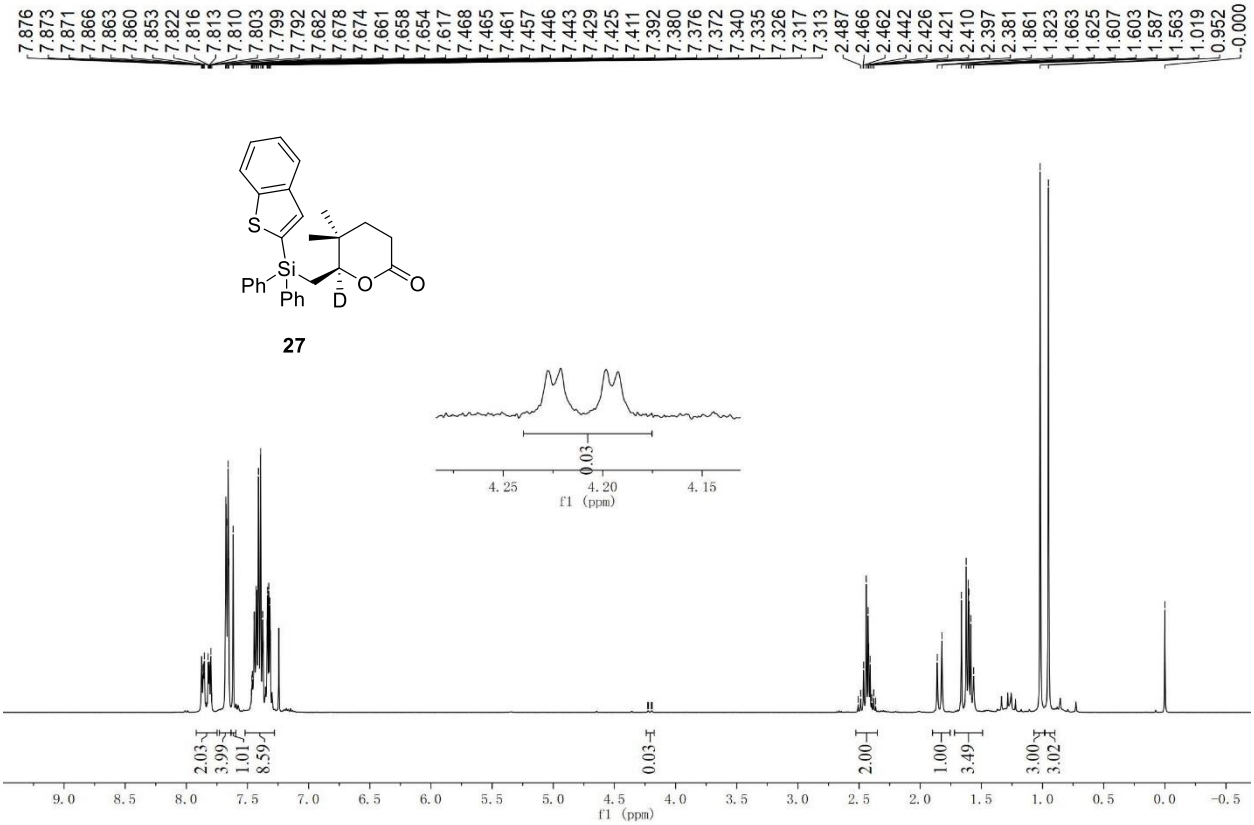
26

<Data Analysis>

DetA 214nm

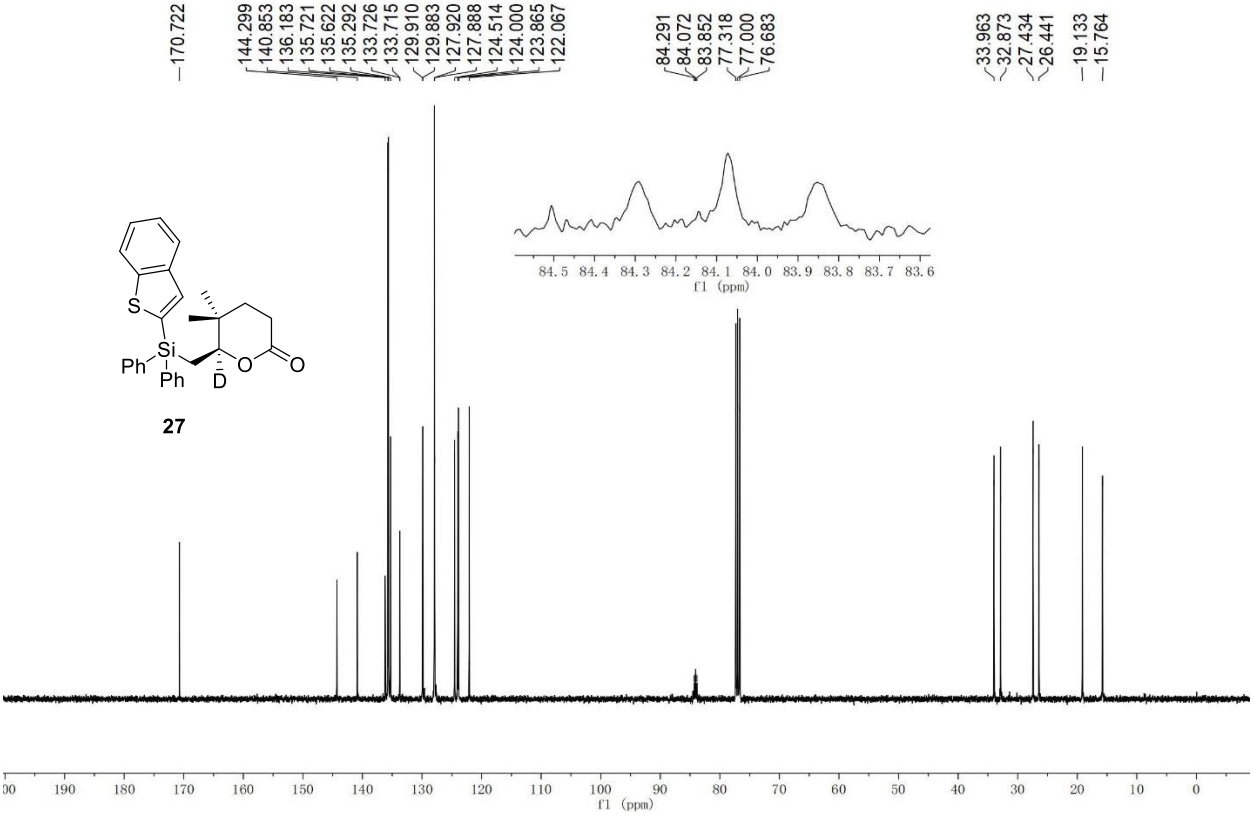
Pesk #	Ret. Time	Height	Area	Area%
1	34.043	10826	512013	5.477
2	37.290	153639	8836492	94.523
Total		164466	9348506	100.000

^{1}H NMR spectra of **27**



27

^{13}C NMR spectra of **27**



HPLC spectra of racemic **27**

Data File : (30-racemic)-RAM-2-335-.lcd
Method File : AD-H-97+3-1-214 50 min.lcm
Date Processed : 7/17/2021 12:15:11 PM

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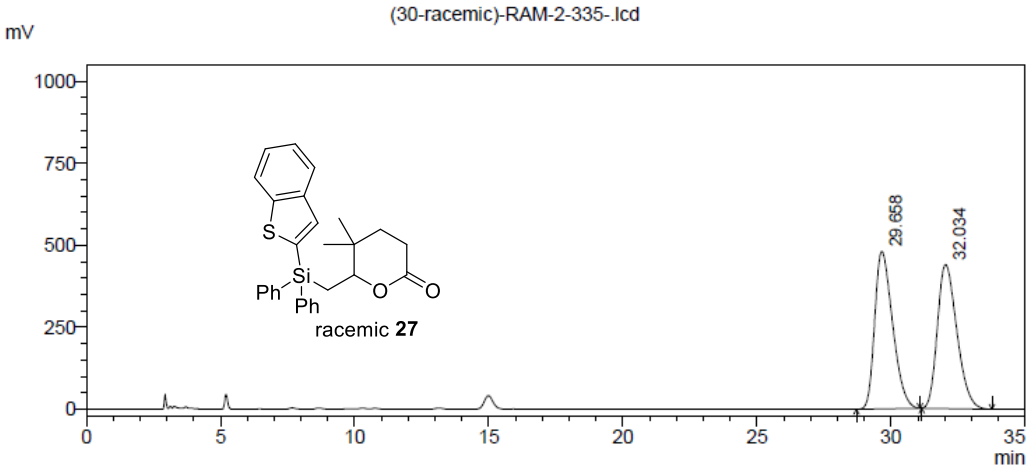

<Data Analysis>

???A 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	29.658	479990	22308822	50.050
2	32.034	439339	22264366	49.950
Total		919329	44573187	100.000

HPLC spectra of **27**

Data File : (30-chiral)RAM-2-373-.lcd
Method File : AD-H-97+3-1-214 40 min.lcm
Date Processed : 7/17/2021 12:15:22 PM

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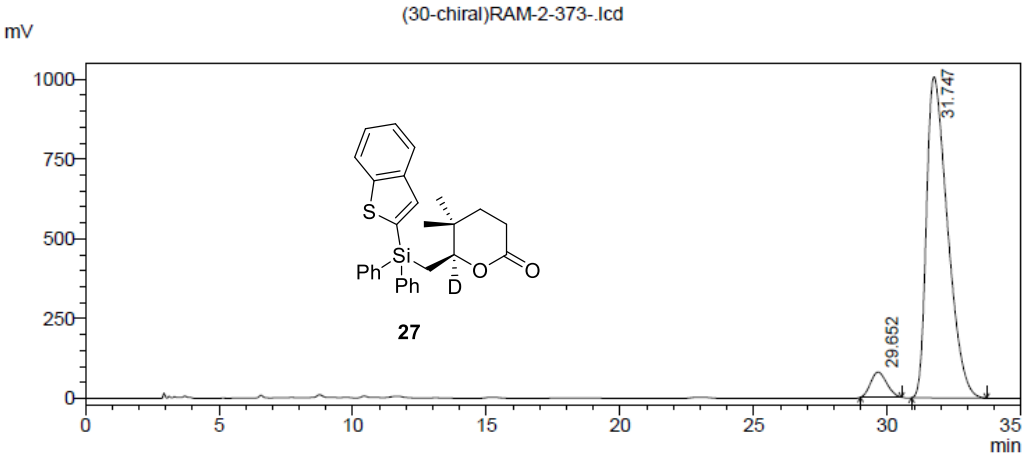


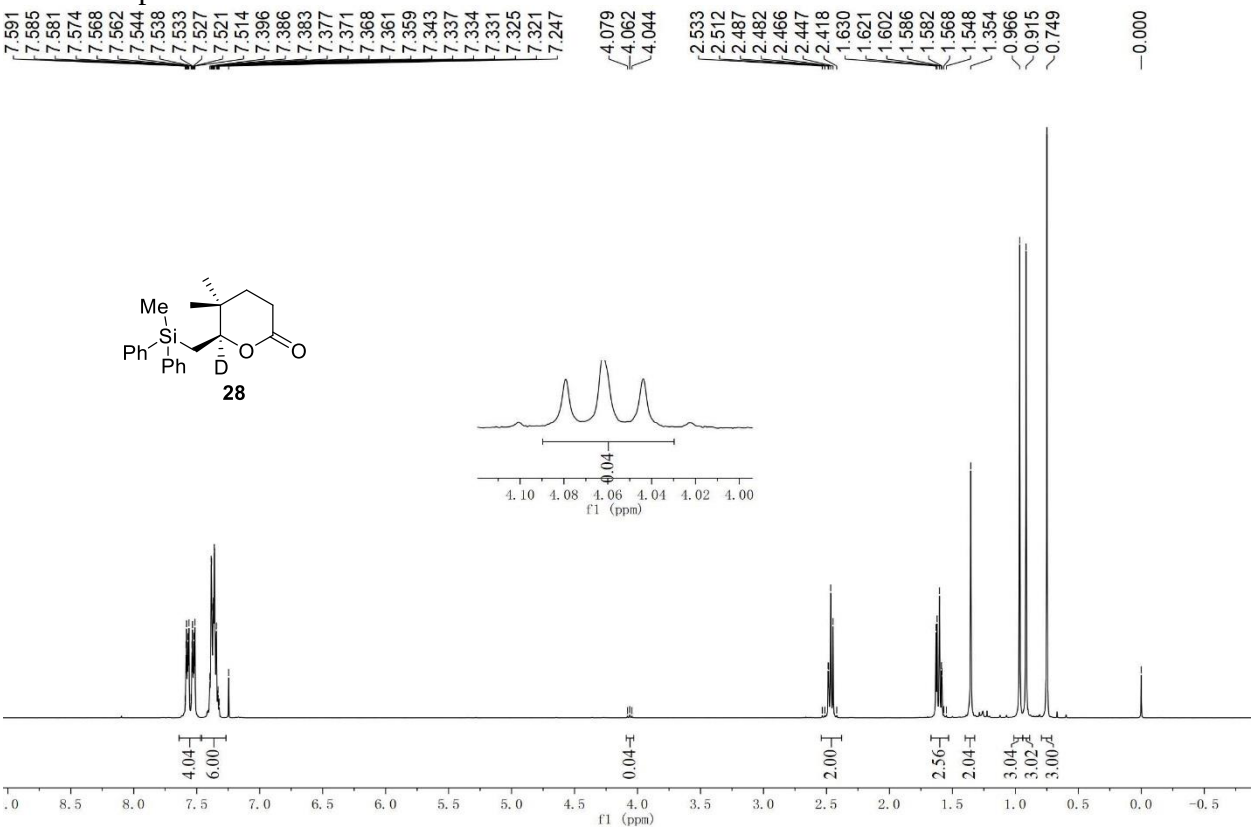
27

<Data Analysis>

???A 214nm

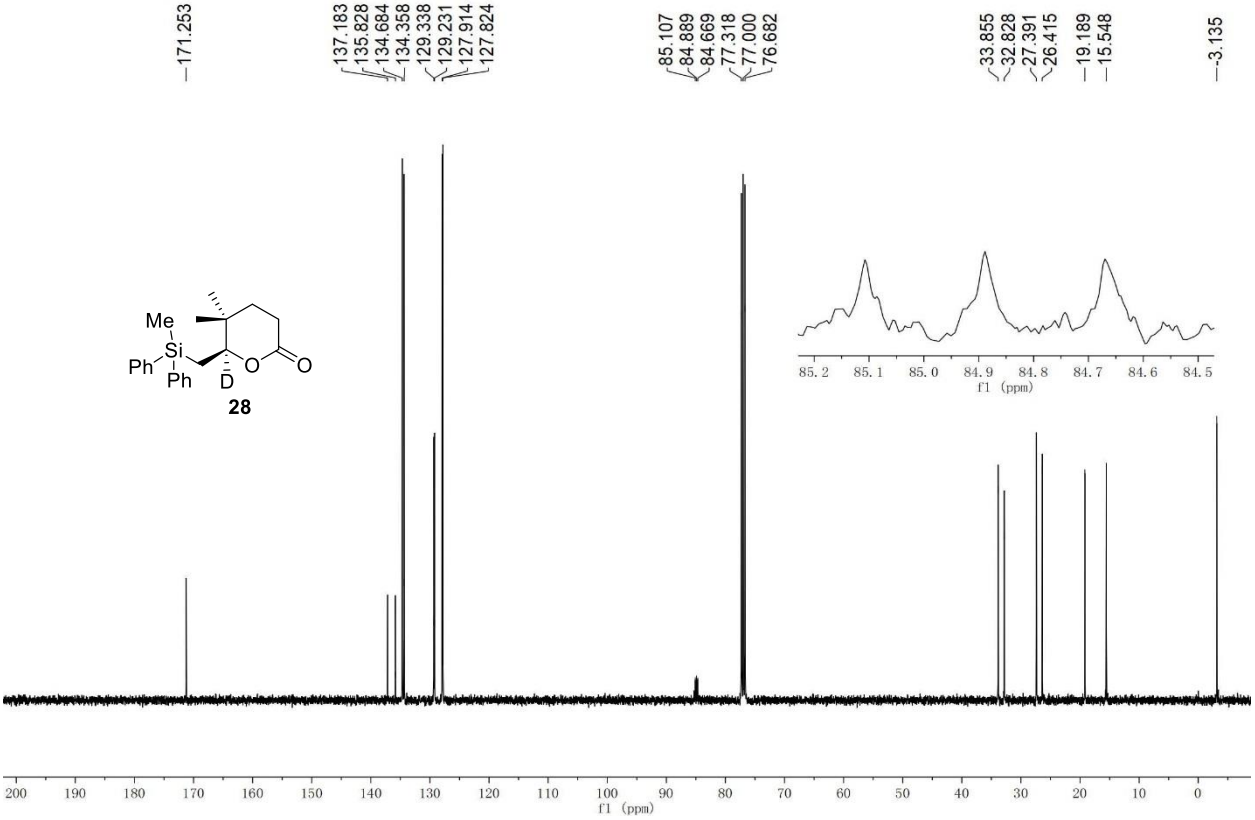
Pesk #	Ret. Time	Height	Area	Area%
1	29.652	78719	3295191	5.635
2	31.747	1005560	55183772	94.365
Total		1084280	58478963	100.000

^{1}H NMR spectra of **28**



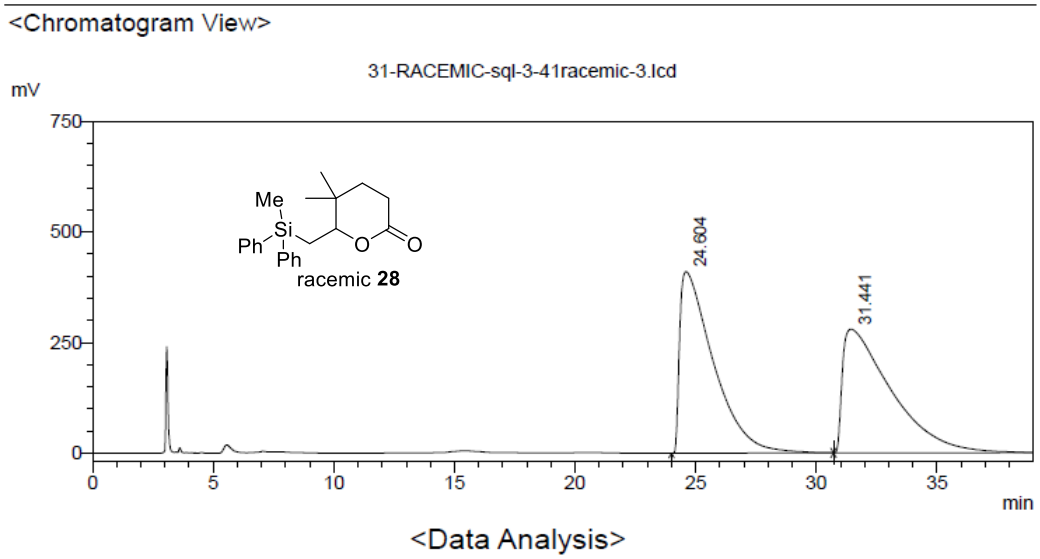
28

^{13}C NMR spectra of **28**



HPLC spectra of racemic **28**

Data File	: 31-RACEMIC-sql-3-41racemic-3.lcd
Method File	: 3AD-H-99.5-1-214-60min.lcm
Date Processed	: 7/17/2021 12:19:09 PM



<Data Analysis>

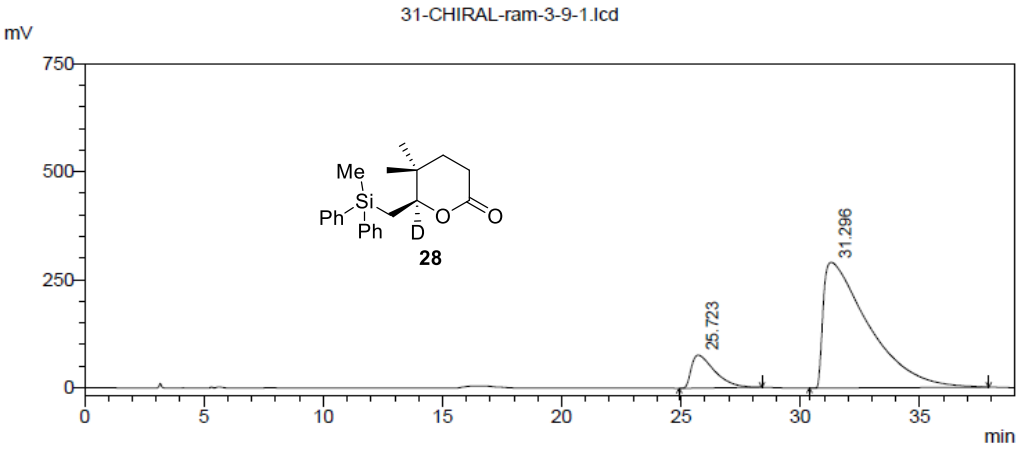
DetA 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	24.604	410169	39855154	50.255
2	31.441	279599	39450904	49.745
Total		689768	79306058	100.000

HPLC spectra of **28**

Data File : 31-CHIRAL-ram-3-9-1.lcd
Method File : 3AD-H-99.5-1-214-60min.lcm
Date Processed : 7/17/2021 12:18:15 PM

<Chromatogram View>

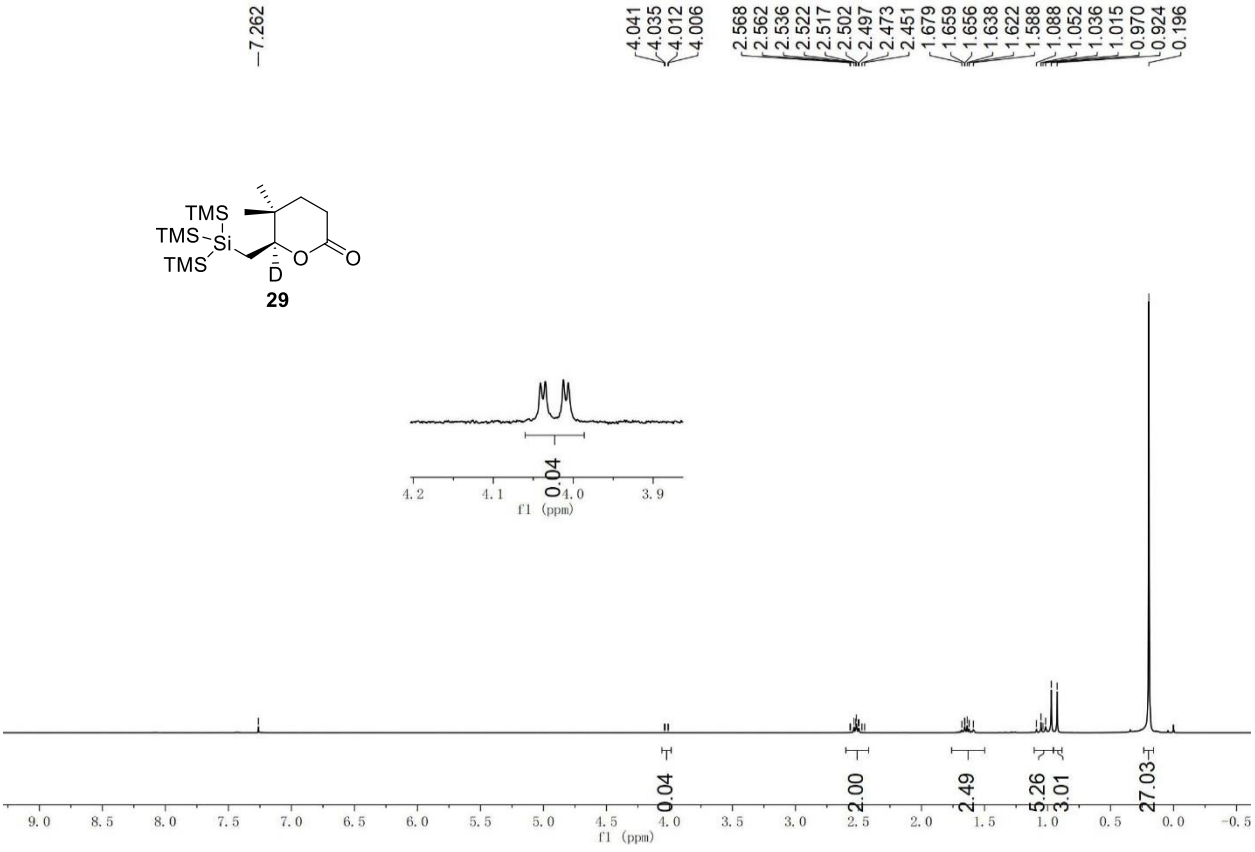


<Data Analysis>

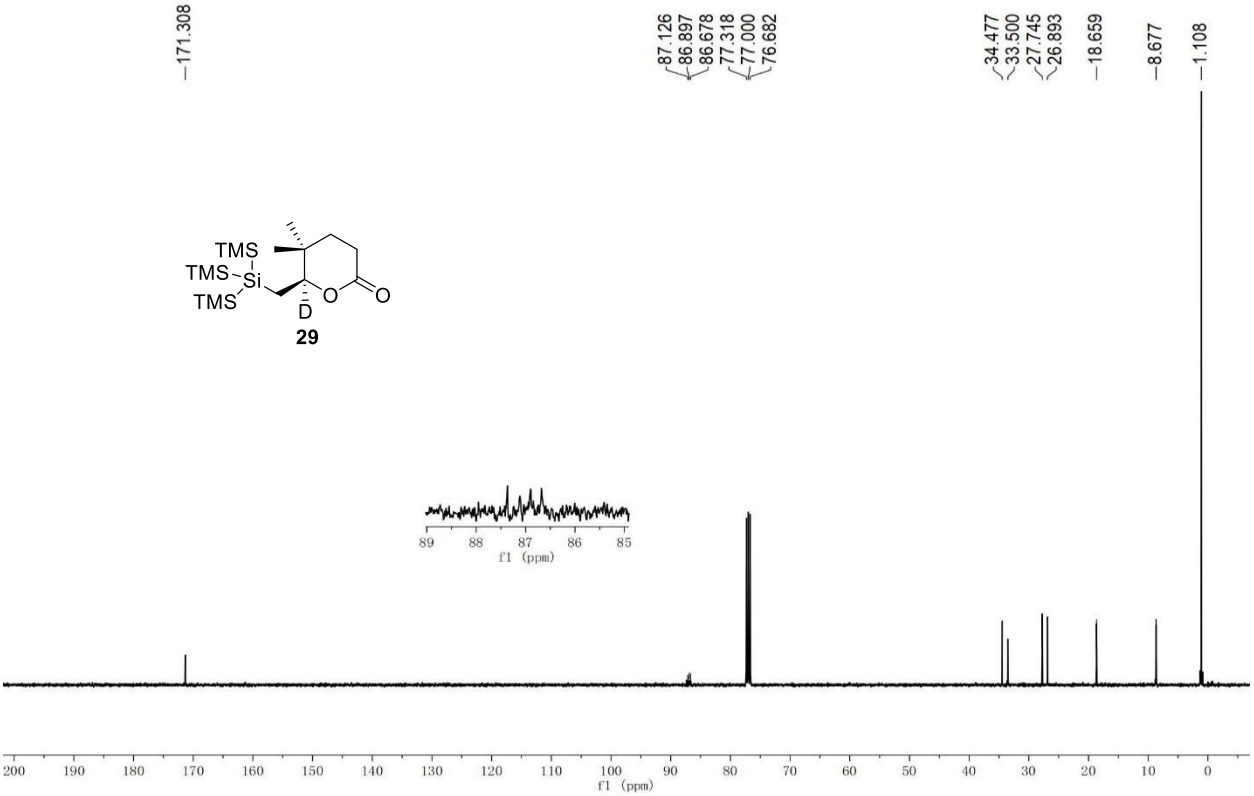
DetA 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	25.723	76056	5183828	11.897
2	31.296	290709	38390047	88.103
Total		366764	43573875	100.000

^{1}H NMR spectra of **29**



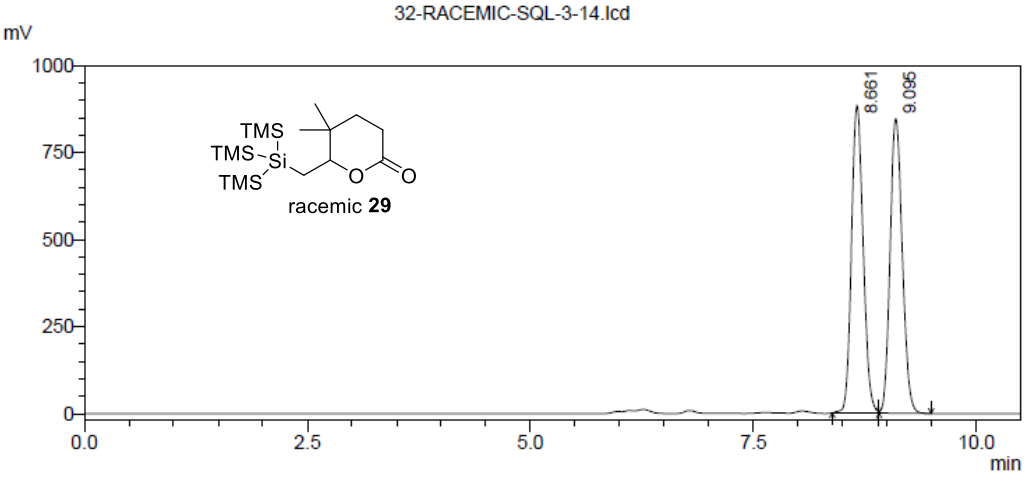
^{13}C NMR spectra of **29**



HPLC spectra of racemic **29**

Data File : 32-RACEMIC-SQL-3-14.lcd
Method File : 4OD-H-99.3-0.5-214-20min.lcm
Date Processed : 7/17/2021 12:25:19 PM

<Chromatogram View>



<Data Analysis>

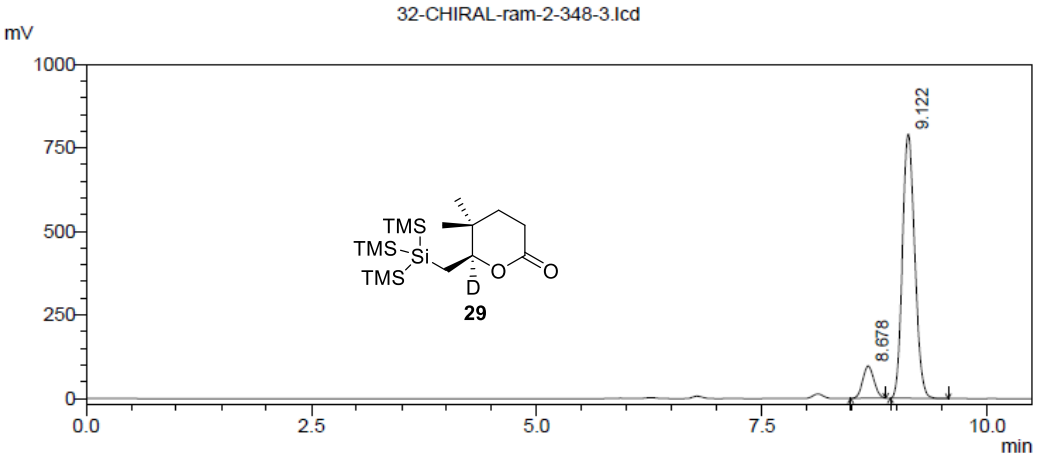
DetA 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	8.661	882522	8050036	50.009
2	9.095	845124	8047288	49.991
Total		1727646	16097324	100.000

HPLC spectra of **29**

Data File	: 32-CHIRAL-ram-2-348-3.lcd
Method File	: 4OD-H-99.3-0.5-214-20min.lcm
Date Processed	: 7/17/2021 12:24:43 PM

<Chromatogram View>



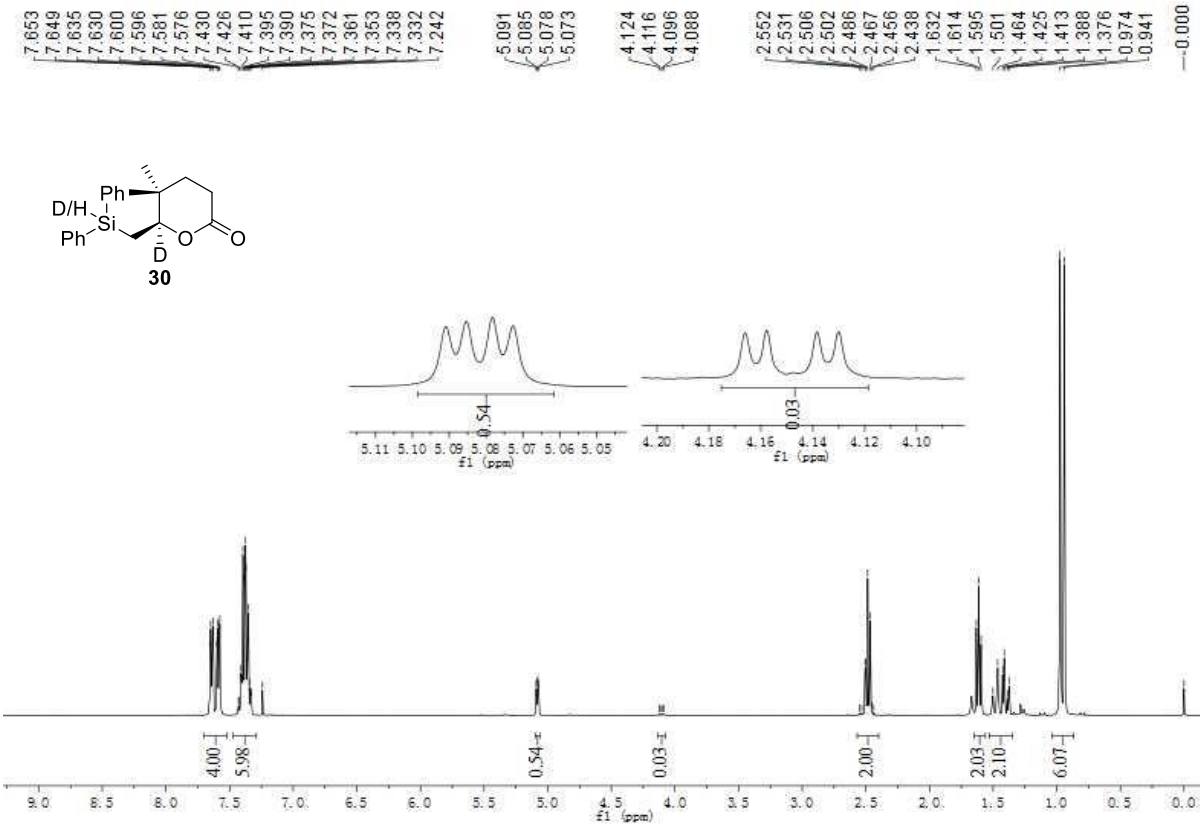
29

<Data Analysis>

DetA 214nm

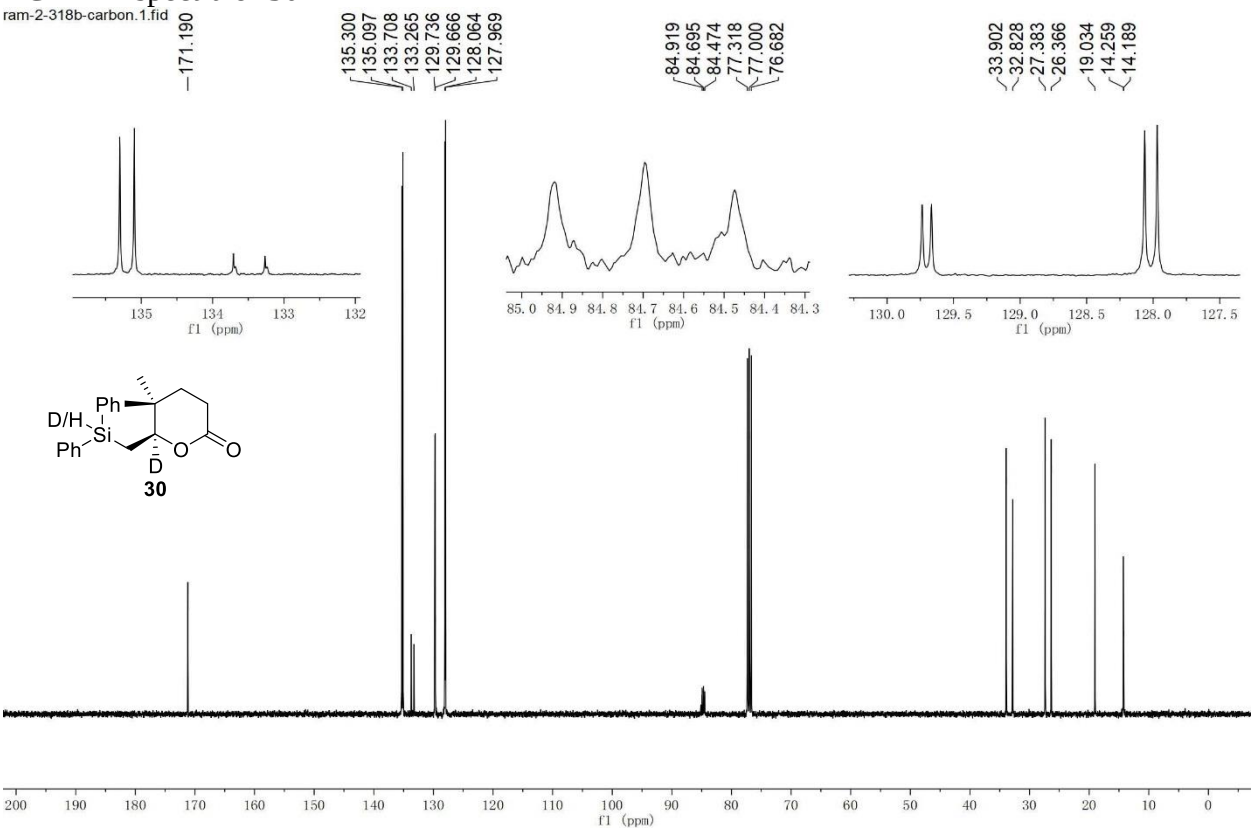
Pesk #	Ret. Time	Height	Area	Area%
1	8.678	96365	839248	10.034
2	9.122	790474	7525139	89.966
Total		886839	8364388	100.000

^{1}H NMR spectra of **30**



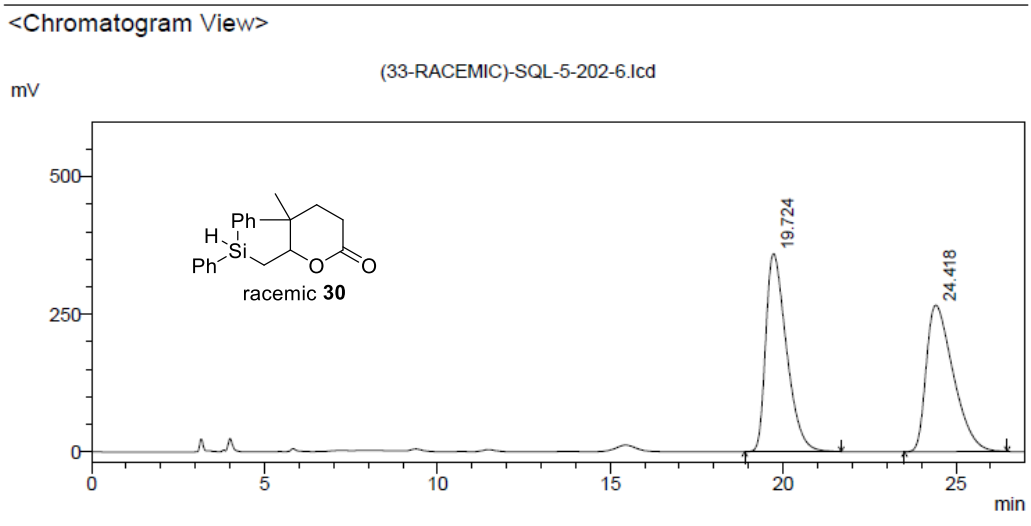
30

^{13}C NMR spectra of **30**



HPLC spectra of racemic **30**

Data File : (33-RACEMIC)-SQL-5-202-6.lcd
Method File : 1OJ-H-98.5-1-214.lcm
Date Processed : 7/17/2021 12:25:57 PM



<Data Analysis>

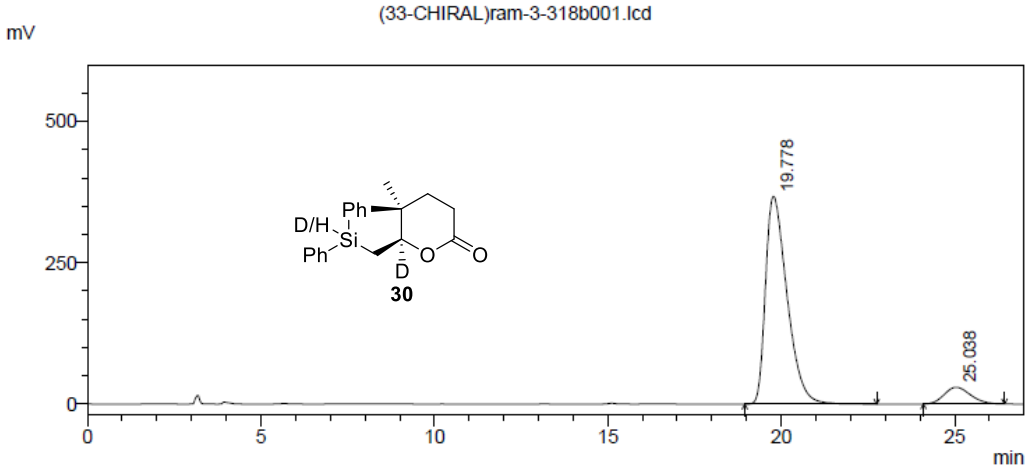
DetA 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	19.724	359585	14986446	50.820
2	24.418	266194	14502857	49.180
Total		625779	29489303	100.000

HPLC spectra of **30**

Data File : (33-CHIRAL)ram-3-318b001.lcd
Method File : 1OJ-H-98.5-1-214.lcm
Date Processed : 7/17/2021 12:26:23 PM

<Chromatogram View>

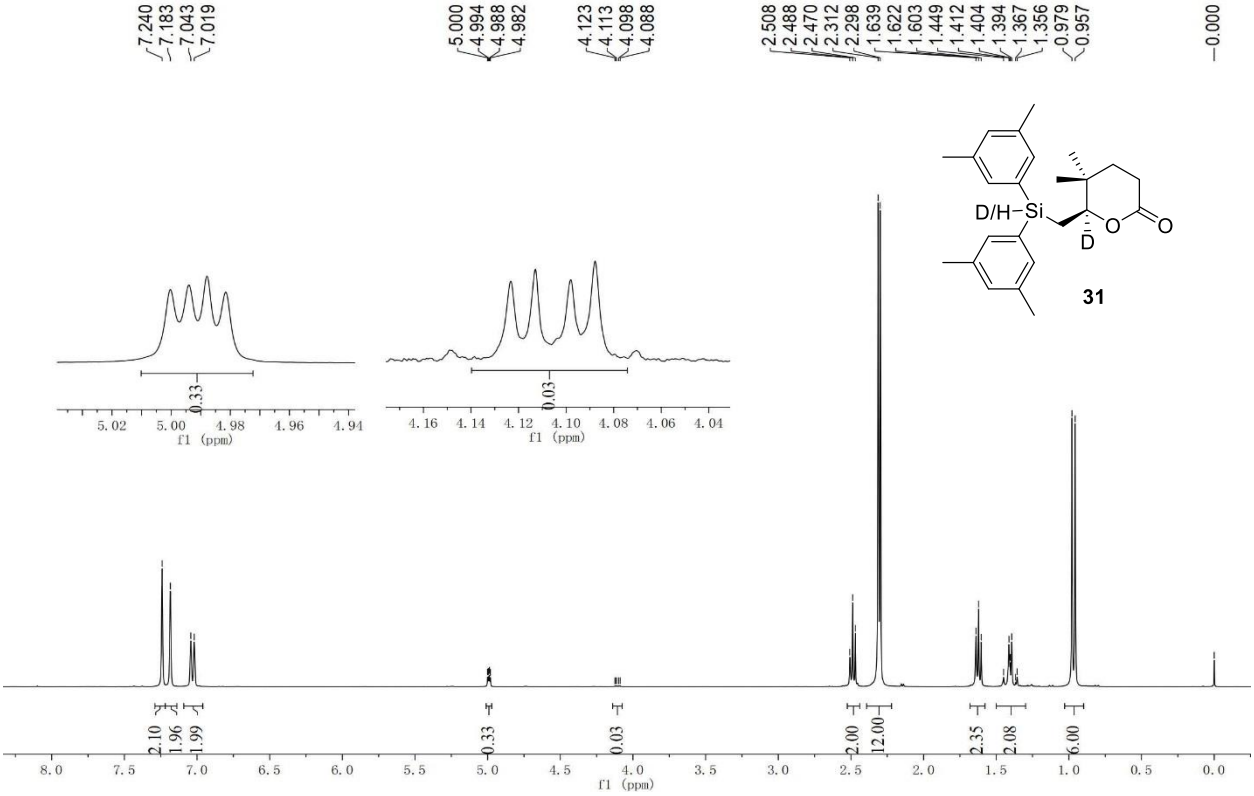


<Data Analysis>

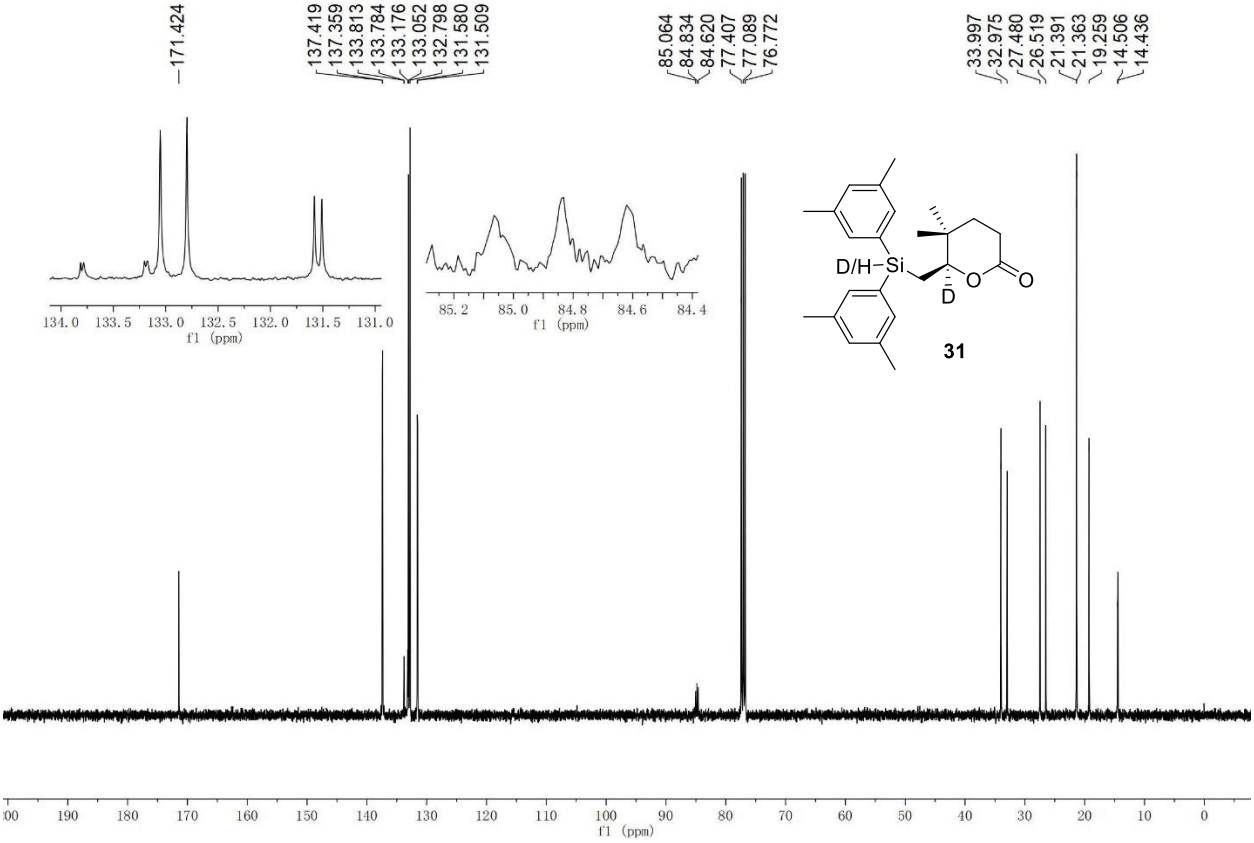
DetA 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	19.778	367860	15960054	90.998
2	25.038	29684	1578929	9.002
Total		397543	17538983	100.000

^{1}H NMR spectra of **31**



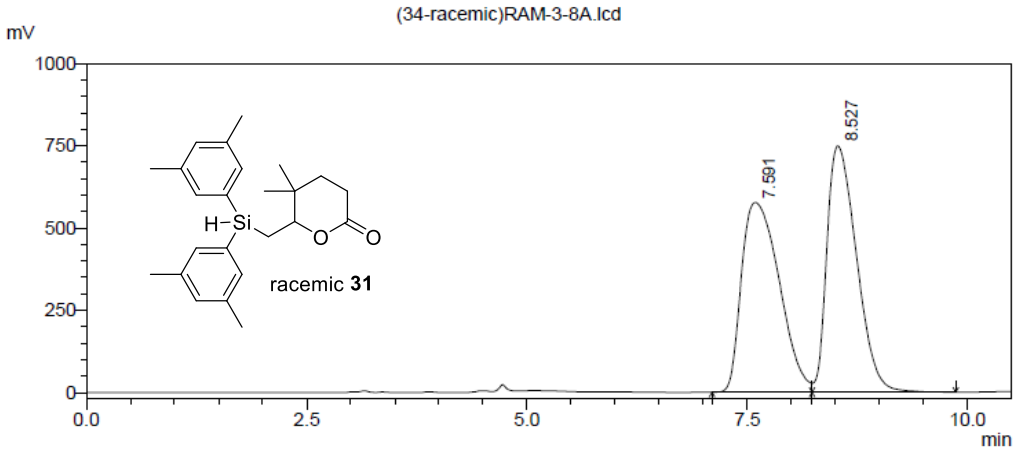
^{13}C NMR spectra of **31**



HPLC spectra of racemic **31**

Data File : (34-racemic)RAM-3-8A.lcd
Method File : AD-H-99+1-1.0-214.lcm
Date Processed : 7/17/2021 12:26:48 PM

<Chromatogram View>



<Data Analysis>

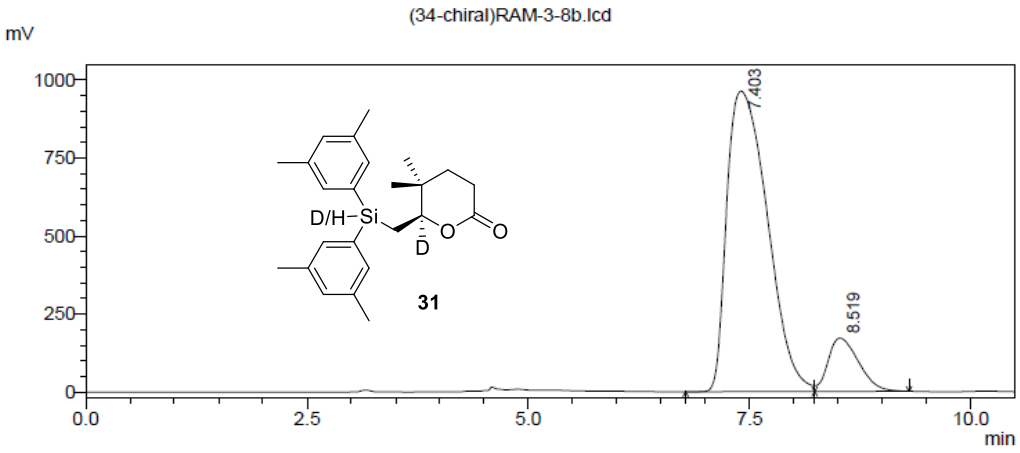
???A 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	7.591	576544	17197938	49.504
2	8.527	748455	17542280	50.496
Total		1324999	34740218	100.000

HPLC spectra of **31**

Data File : (34-chiral)RAM-3-8b.lcd
Method File : AD-H-99+1-1.0-214.lcm
Date Processed : 7/17/2021 12:27:05 PM

<Chromatogram View>

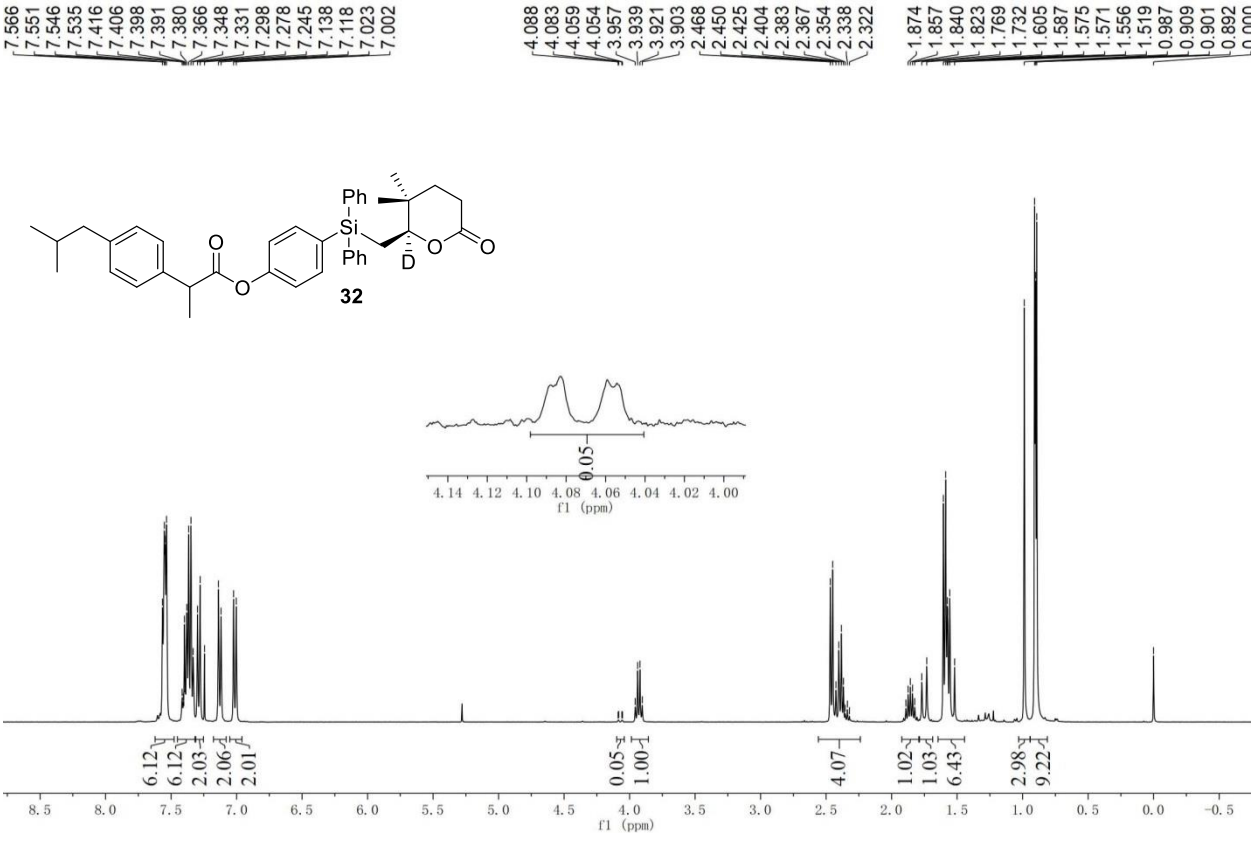


<Data Analysis>

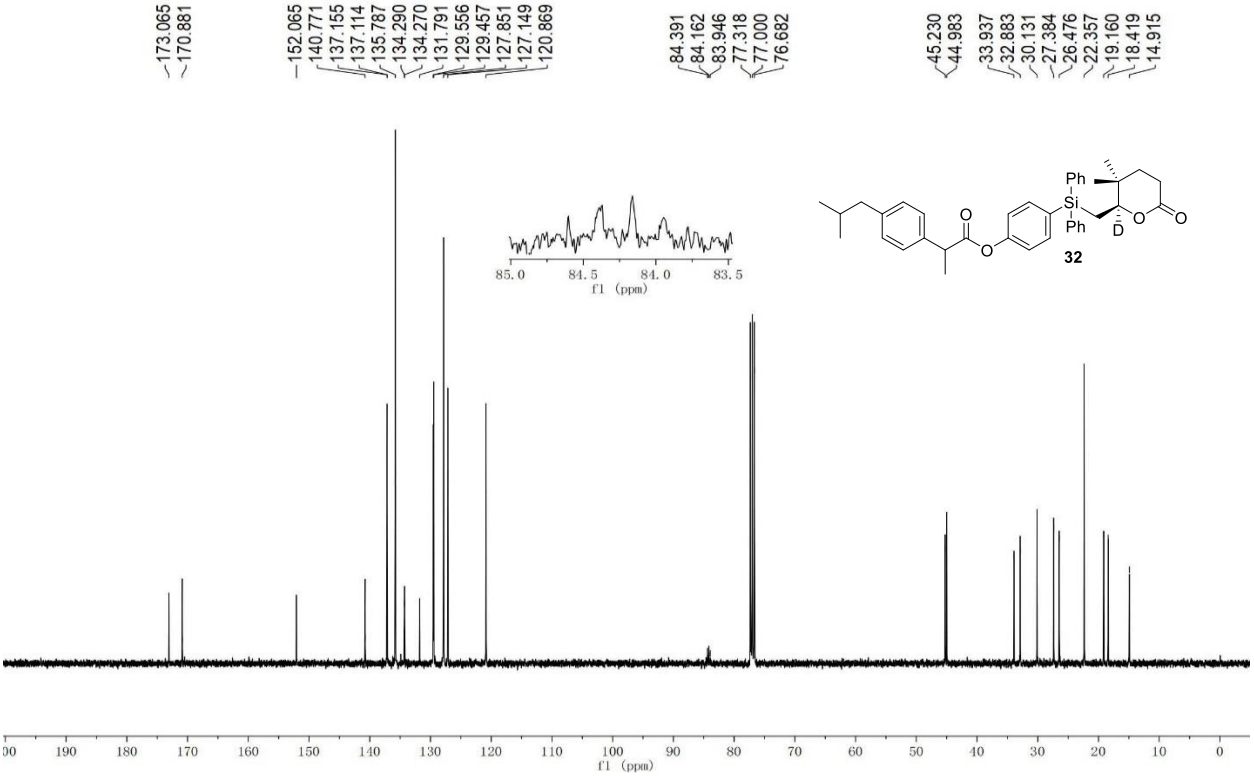
???A 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	7.403	962081	30697991	88.227
2	8.519	170584	4096189	11.773
Total		1132665	34794180	100.000

^{1}H NMR spectra of **32**



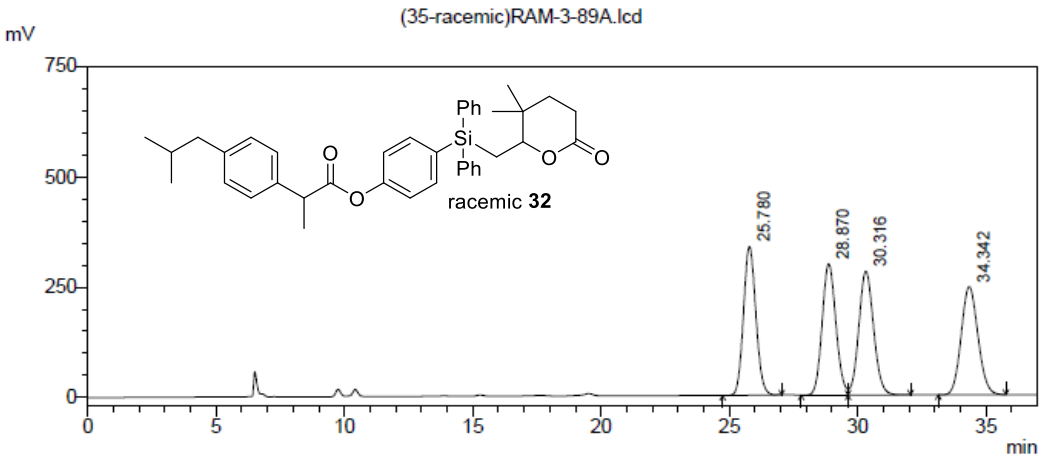
^{13}C NMR spectra of **32**



HPLC spectra of racemic **35**

Data File : (35-racemic)RAM-3-89A.lcd
Method File : IC-H-90-0.5-214.lcm
Date Processed : 7/17/2021 12:27:53 PM

<Chromatogram View>



<Data Analysis>

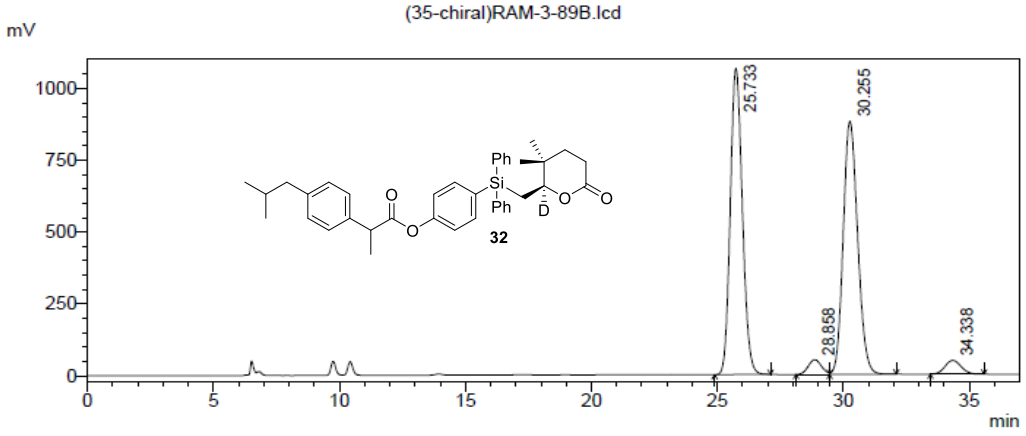
DetA 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	25.780	337052	11311214	25.264
2	28.870	296808	11076879	24.741
3	30.316	279784	11230702	25.085
4	34.342	244735	11152547	24.910
Total		1158379	44771340	100.000

HPLC spectra of **32**

Data File : (35-chiral)RAM-3-89B.lcd
Method File : IC-H-90-0.5-214.lcm
Date Processed : 7/17/2021 12:27:35 PM

<Chromatogram View>

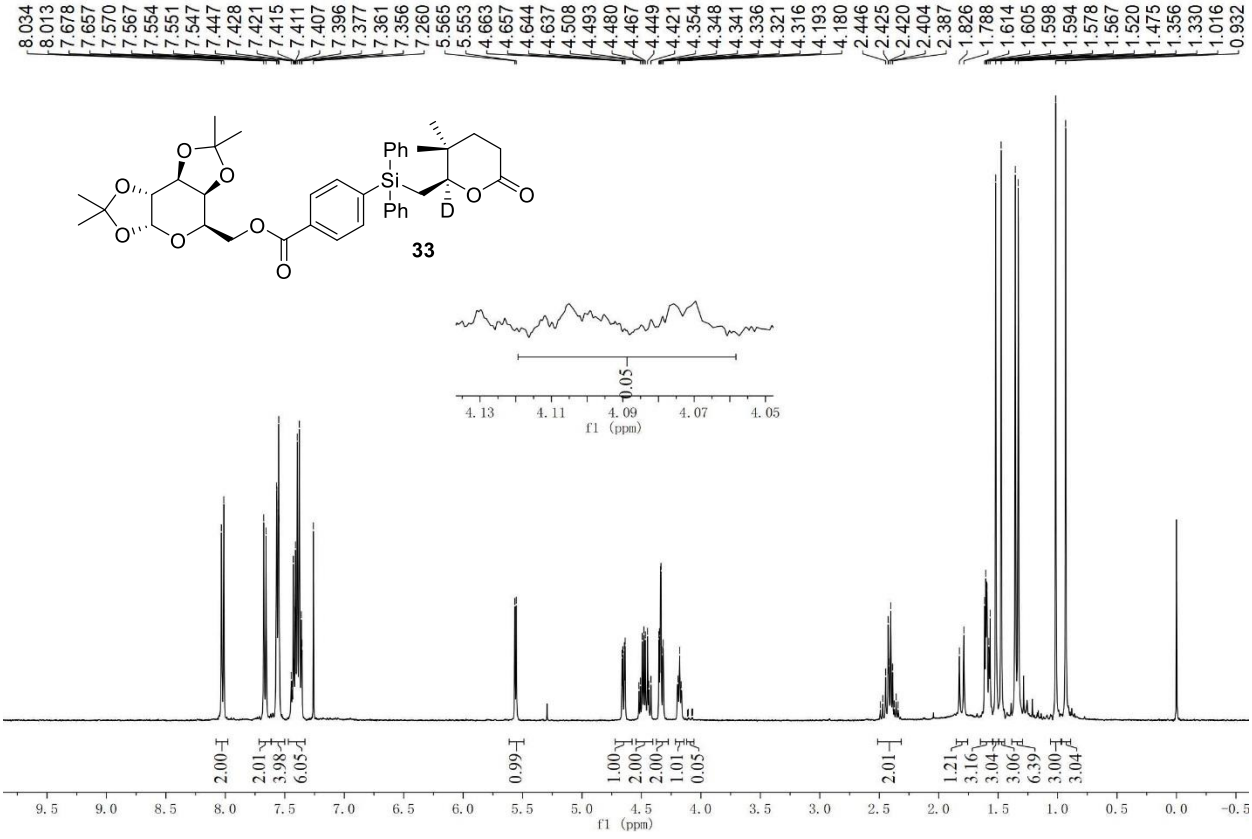


<Data Analysis>

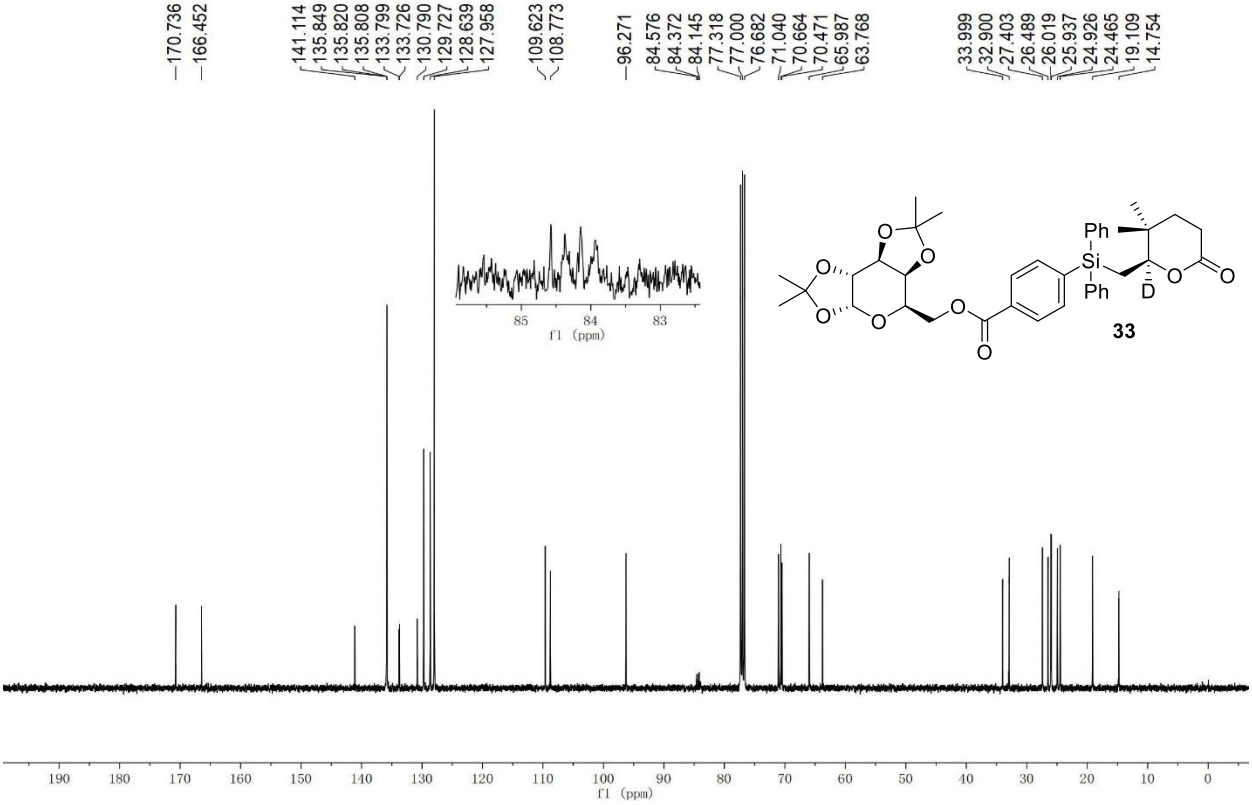
DetA 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	25.733	1064950	35480169	47.582
2	28.858	51185	1860322	2.495
3	30.255	880327	35070991	47.033
4	34.338	48224	2155190	2.890
Total		2044687	74566673	100.000

^{1}H NMR spectra of **33**



^{13}C NMR spectra of **33**



HPLC spectra of racemic **33**

Data File : (36-racemic)RAM-3-88A-.lcd
Method File : AD-H-90-10-1-214.lcm
Date Processed : 7/17/2021 12:28:33 PM

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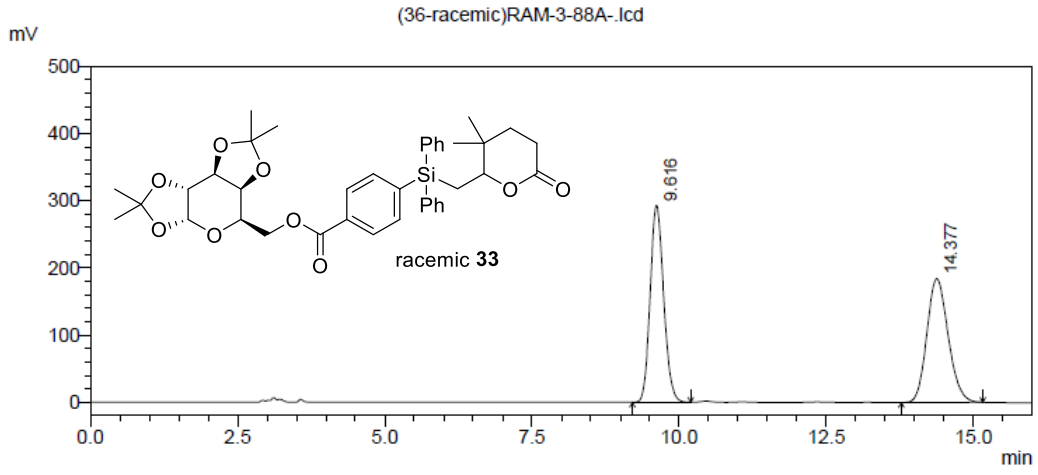


<Data Analysis>

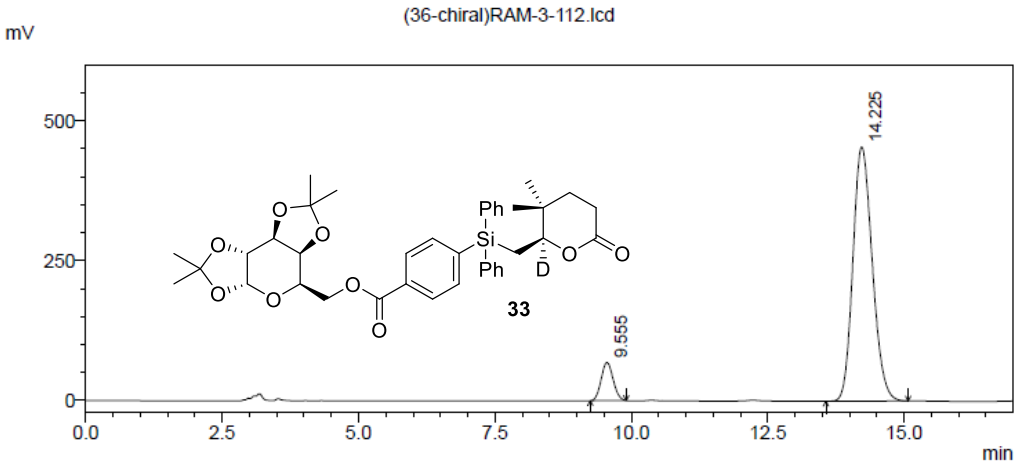
DetA 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	9.616	292937	4675074	50.153
2	14.377	184230	4646485	49.847
Total		477167	9321559	100.000

HPLC spectra of **33**

Data File : (36-chiral)RAM-3-112.lcd
Method File : AD-H-90-10-1-214.lcm
Date Processed : 10/23/2021 4:22:43 PM

<Chromatogram View>

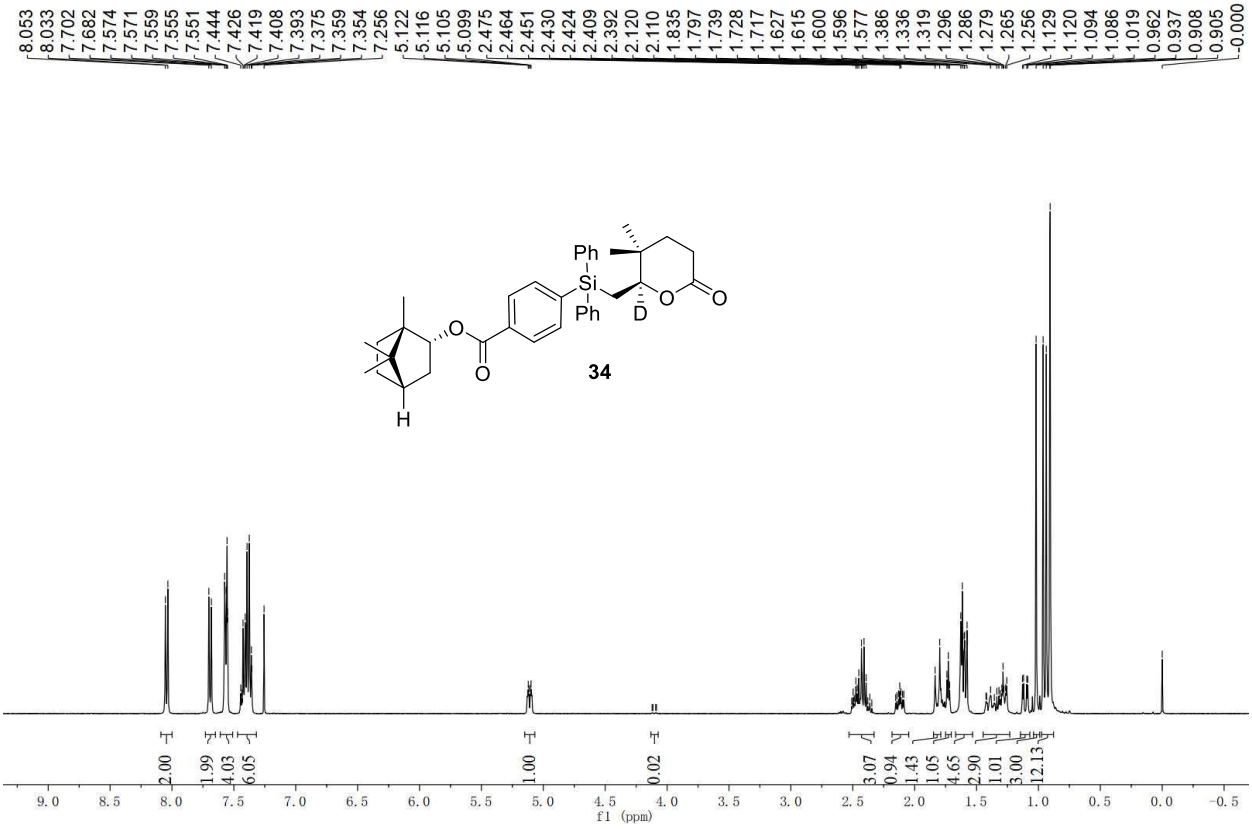


<Data Analysis>

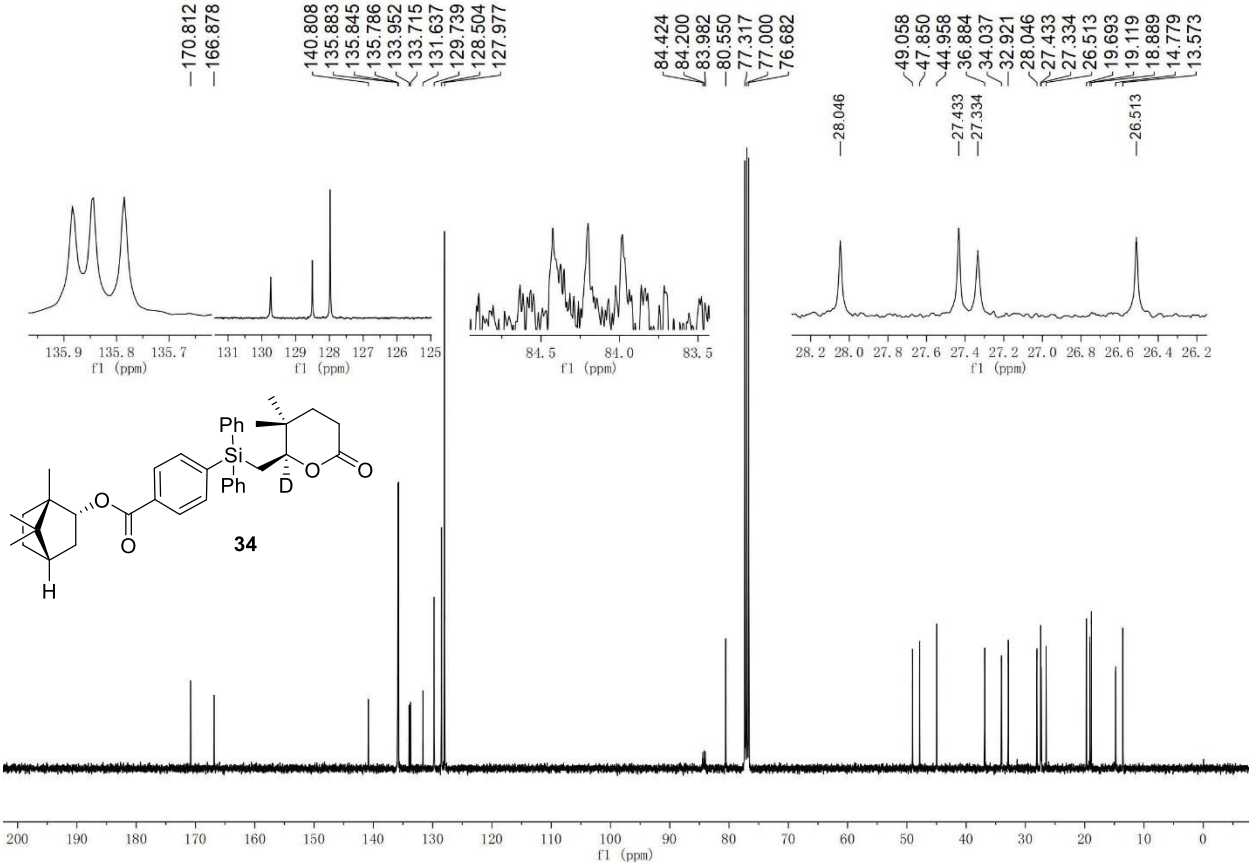
DetA 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	9.555	68219	1041022	8.478
2	14.225	454573	11237639	91.522
Total		522792	12278662	100.000

^{1}H NMR spectra of **34**



^{13}C NMR spectra of **34**



HPLC spectra of racemic **34**

Data File	: 37-RACEMIC-ram-3-137a-7.lcd
Method File	: 3AD-H-98-1-214.lcm
Date Processed	: 7/17/2021 12:31:42 PM

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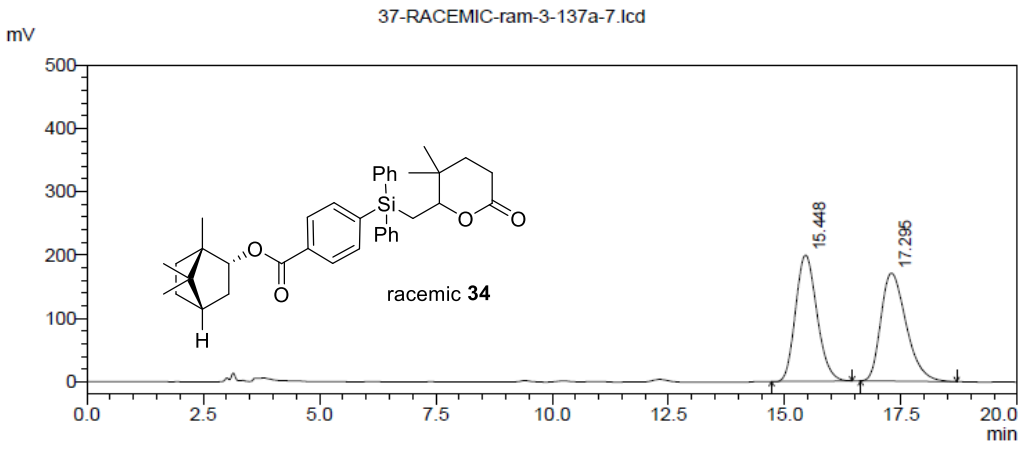

<Data Analysis>

DetA 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	15.448	199395	6381038	49.670
2	17.295	170567	6465753	50.330
Total		369962	12846791	100.000

HPLC spectra of **34**

Data File : 37CHIRAL-ram-3-242-6.lcd
Method File : 3AD-H-98-1-214.lcm
Date Processed : 7/17/2021 12:30:00 PM

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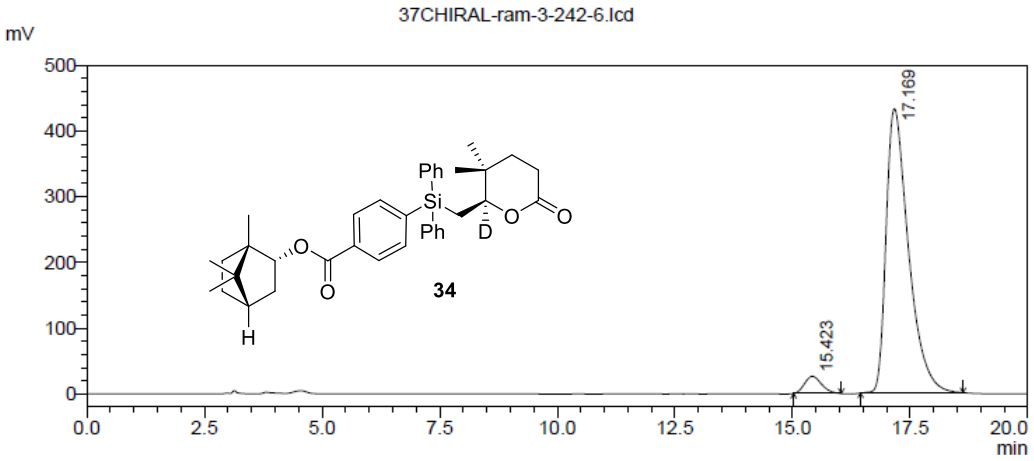
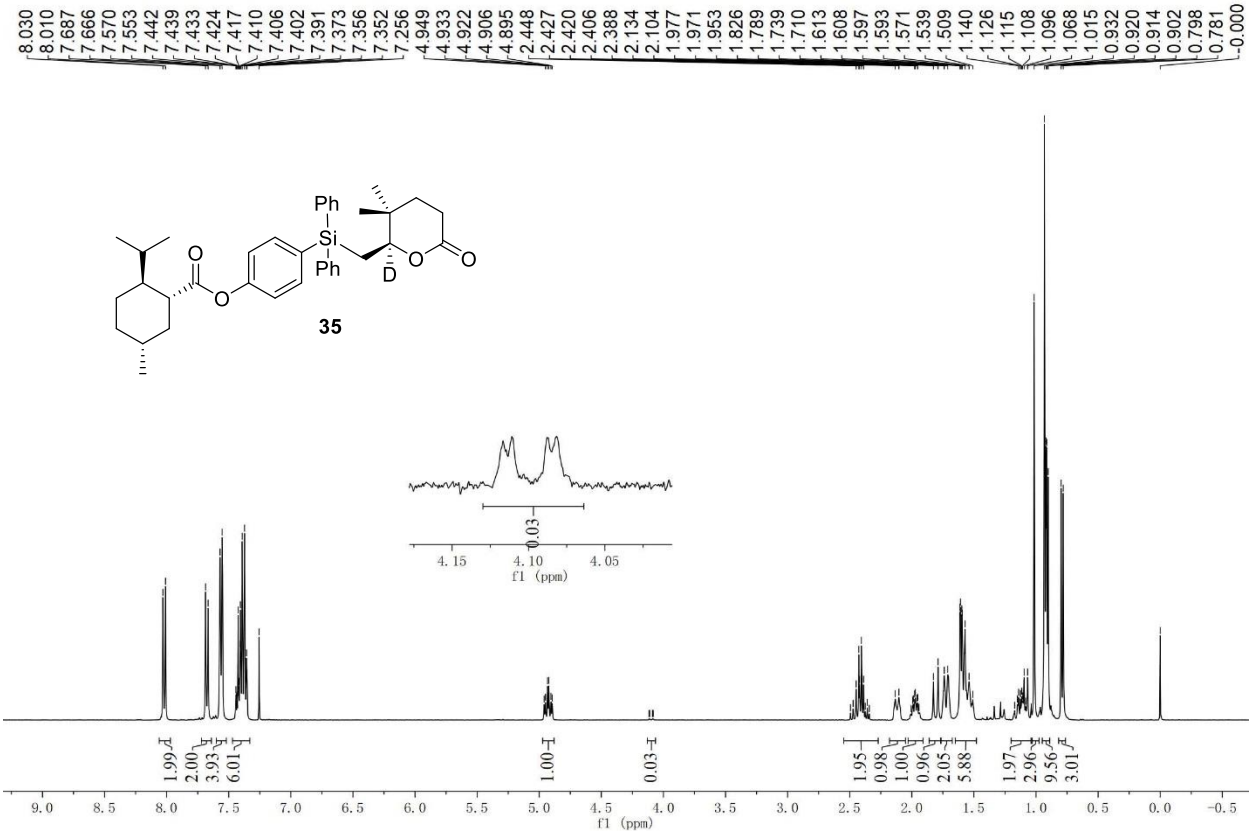


<Data Analysis>

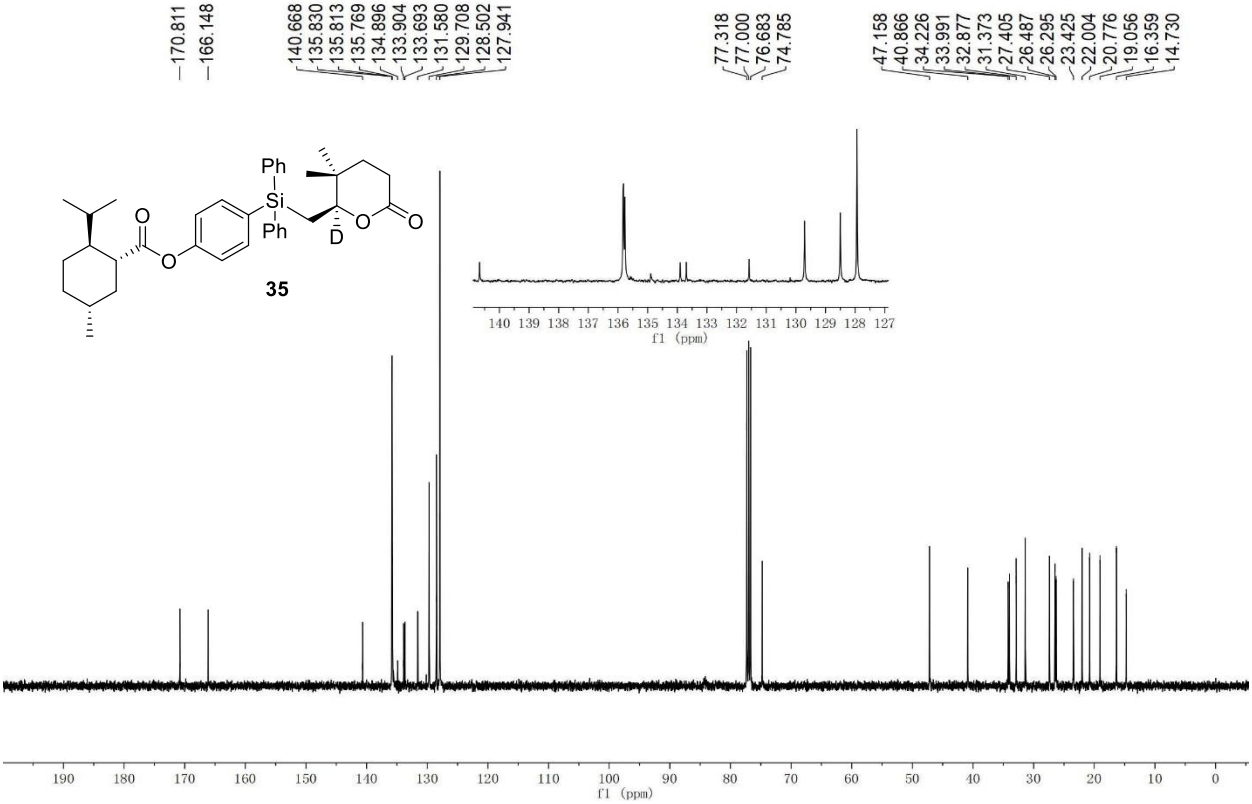
DetA 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	15.423	26259	664673	4.433
2	17.169	432590	14328938	95.567
Total		458849	14993610	100.000

^{1}H NMR spectra of **35**



^{13}C NMR spectra of **35**



HPLC spectra of racemic **35**

Data File : (38-racemic)RAM-3-67A.lcd
Method File : AD-H-95+5-1-214.lcm
Date Processed : 7/17/2021 12:32:07 PM

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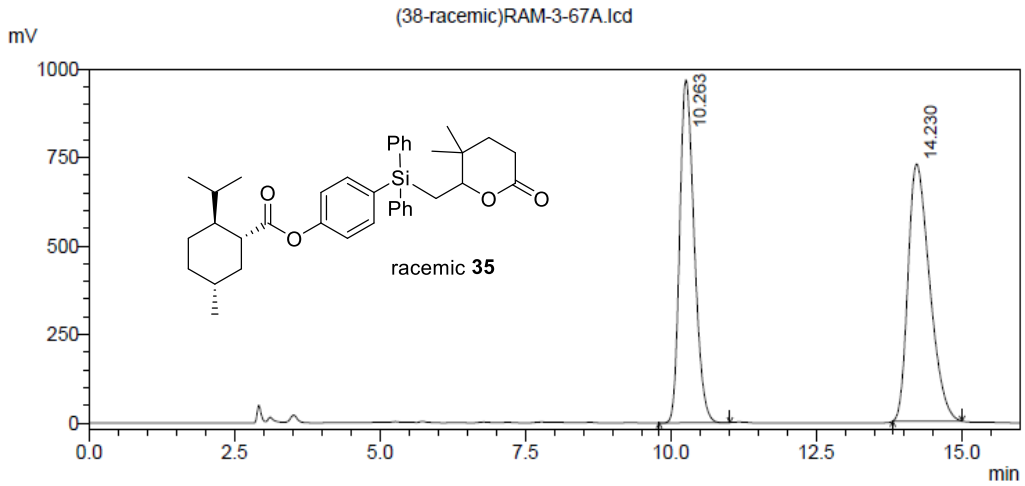

<Data Analysis>

???A 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	10.263	968436	16812862	47.192
2	14.230	726969	18813294	52.808
Total		1695405	35626156	100.000

HPLC spectra of **35**

Data File : (38-chiral)RAM-3-67B.lcd
Method File : AD-H-95+5-1-214.lcm
Date Processed : 7/17/2021 12:32:22 PM

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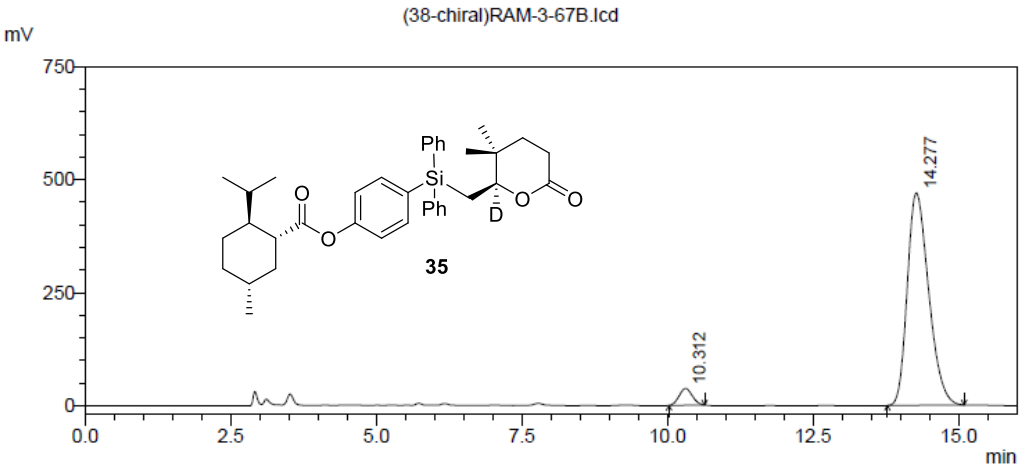
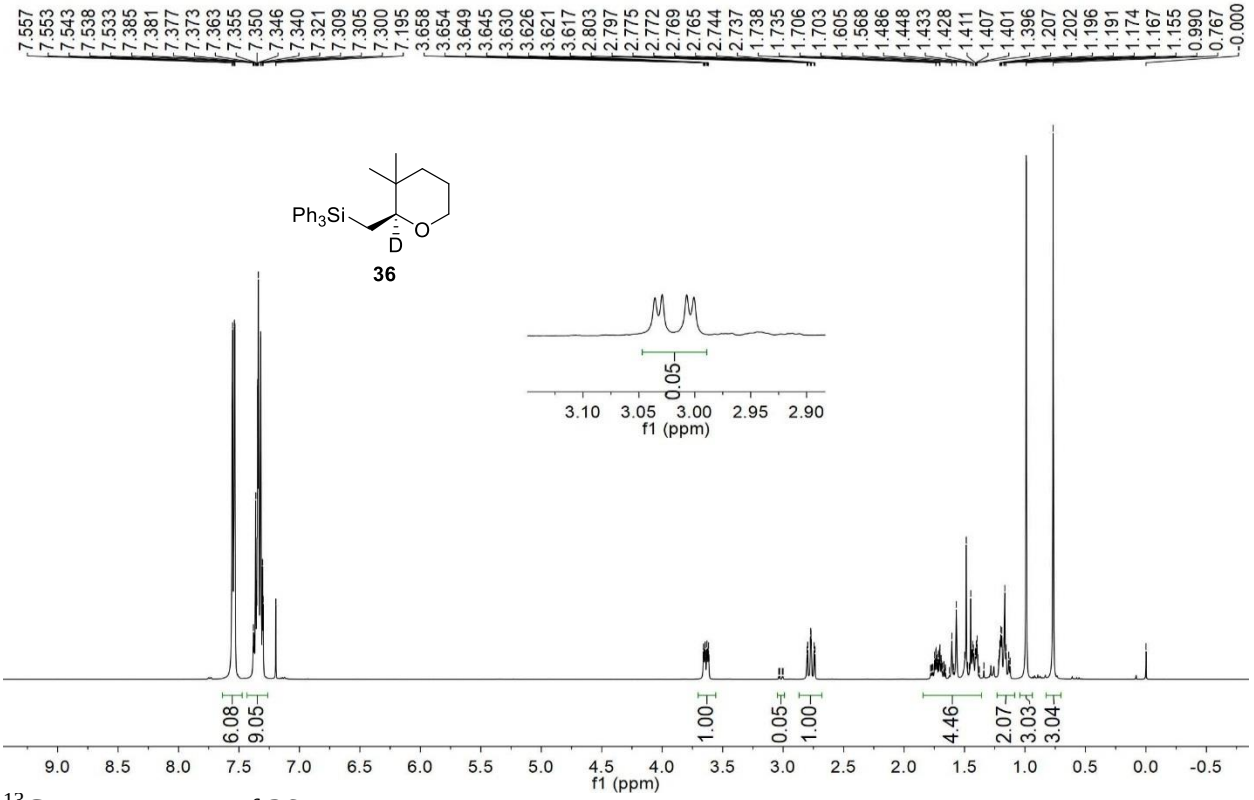


<Data Analysis>

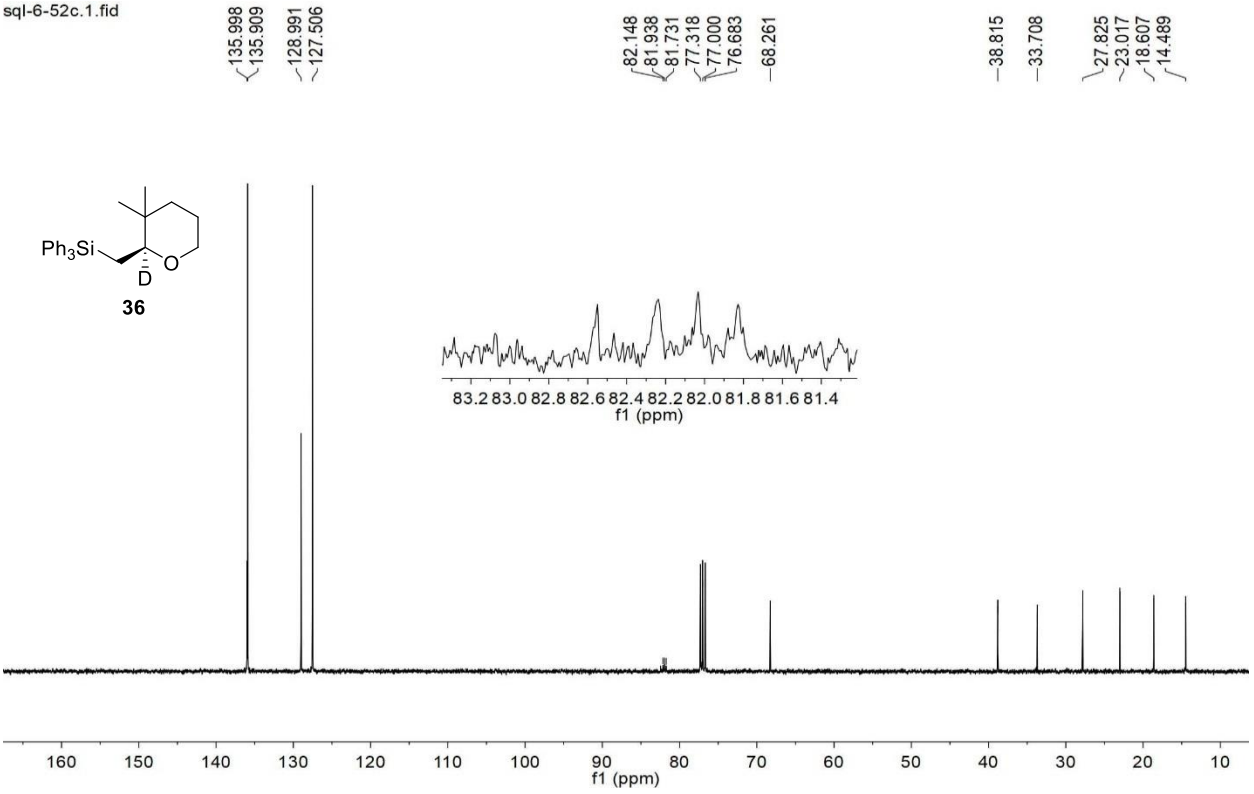
???A 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	10.312	36934	580715	4.610
2	14.277	469504	12015950	95.390
Total		506438	12596665	100.000

^{1}H NMR spectra of **36**



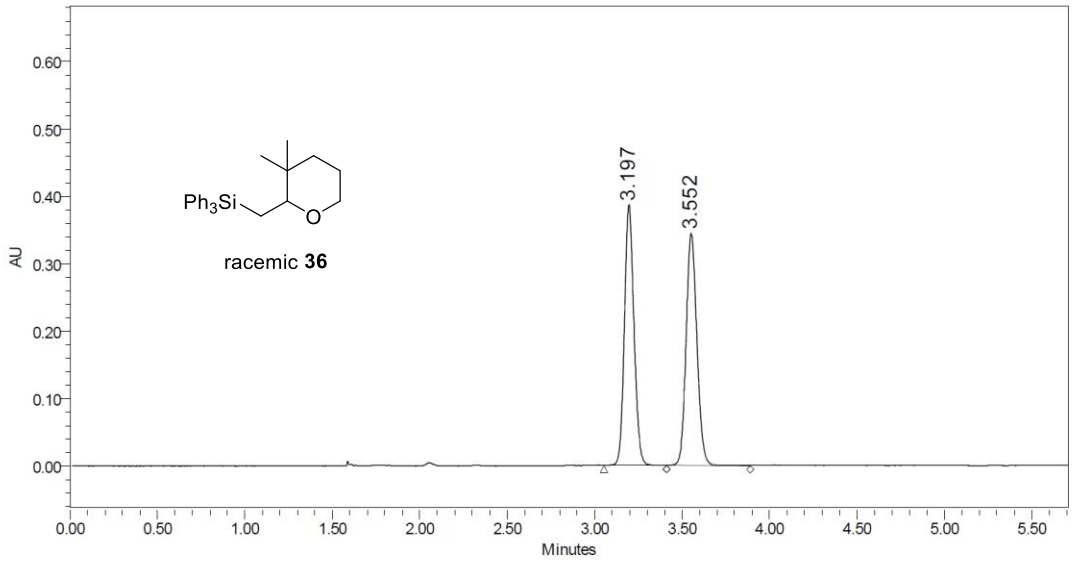
^{13}C NMR spectra of **36**



HPLC spectra of racemic **36**

SAMPLE INFORMATION

Sample Name:	sql-5-134-ad-h-8-2	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	
Vial:	1:A,2	Acq. Method Set:	test_1
Injection #:	1	Processing Method	Default
Injection Volume:	2.00 ul	Channel Name:	PDA Ch1 230nm@4.8nm
Run Time:	30.0 Minutes	Proc. Chnl. Descr.:	PDA Ch1 230nm@4.8nm
Date Acquired:	8/27/2021 1:59:02 PM CST		
Date Processed:	9/3/2021 3:52:04 PM CST		

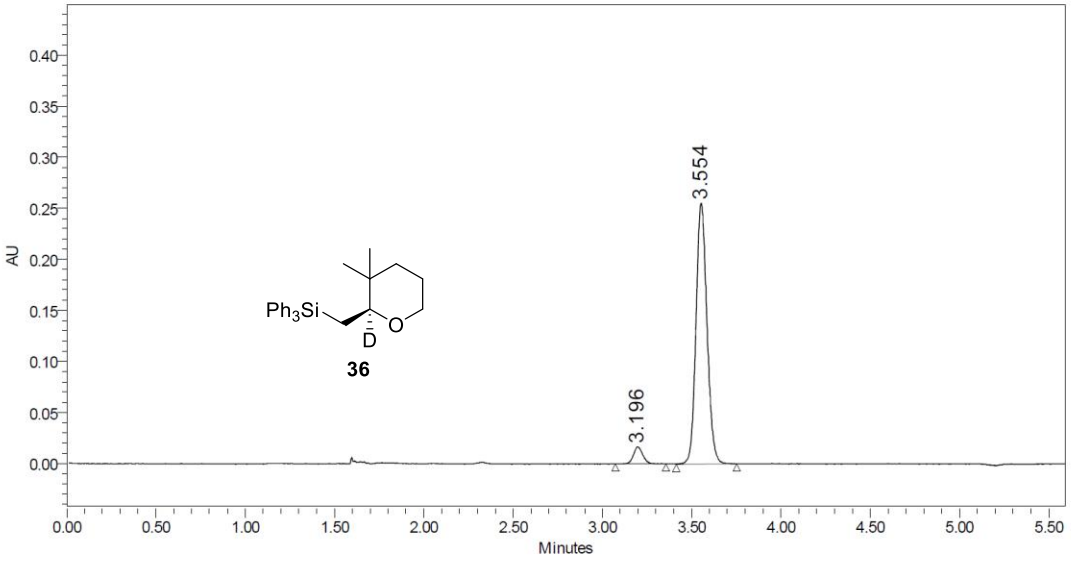


	RT	Height	Width (sec)	Area	% Area
1	3.197	386475	21.500	1464289	49.68
2	3.552	344729	28.650	1482979	50.32

HPLC spectra of **36**

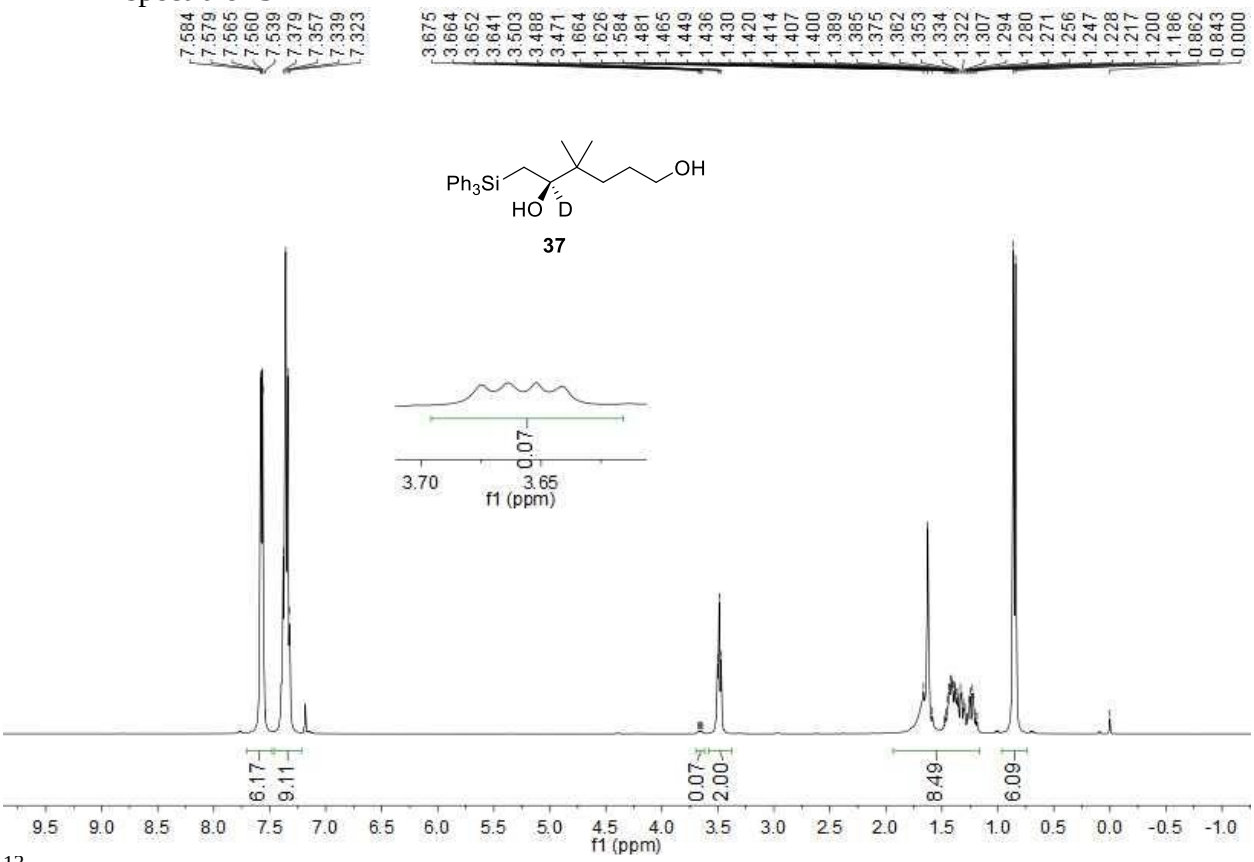
SAMPLE INFORMATION

Sample Name:	sql-6-52	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	
Vial:	1:A,3	Acq. Method Set:	test_1
Injection #:	1	Processing Method	Default
Injection Volume:	2.00 ul	Channel Name:	PDA Ch1 230nm@4.8nm
Run Time:	30.0 Minutes	Proc. Chnl. Descr.:	PDA Ch1 230nm@4.8nm
Date Acquired:	8/27/2021 2:06:02 PM CST		
Date Processed:	9/3/2021 3:52:23 PM CST		

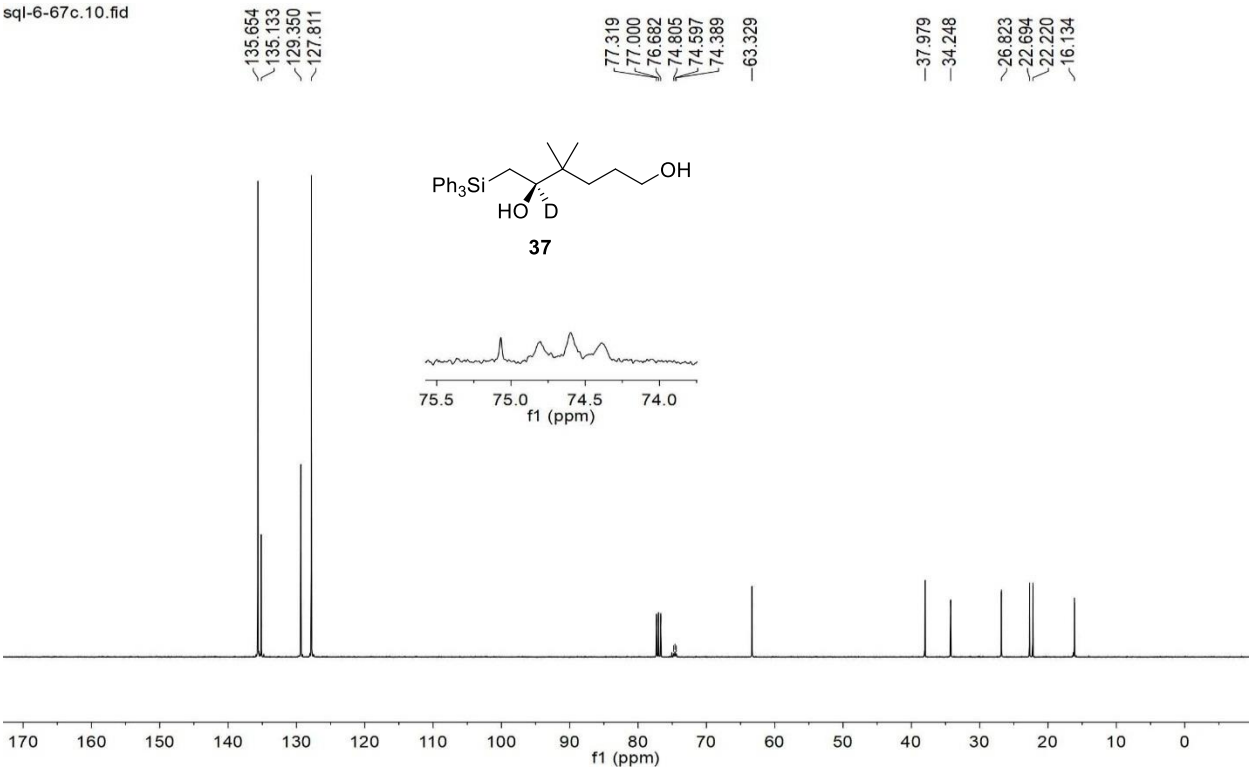


	RT	Height	Width (sec)	Area	% Area
1	3.196	16609	17.000	61242	5.28
2	3.554	255563	20.350	1099417	94.72

^{1}H NMR spectra of **37**



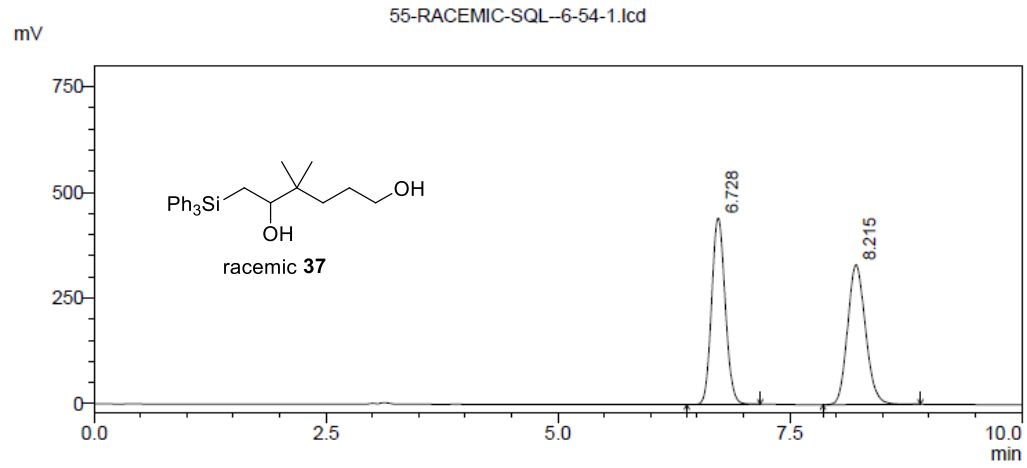
^{13}C NMR spectra of **37**



HPLC spectra of racemic **37**

Data File : 55-RACEMIC-SQL--6-54-1.lcd
Method File : 4OD-H-95-1-214-20min.lcm
Date Processed : 9/2/2021 12:15:20 AM

<Chromatogram View>



racemic **37**

<Data Analysis>

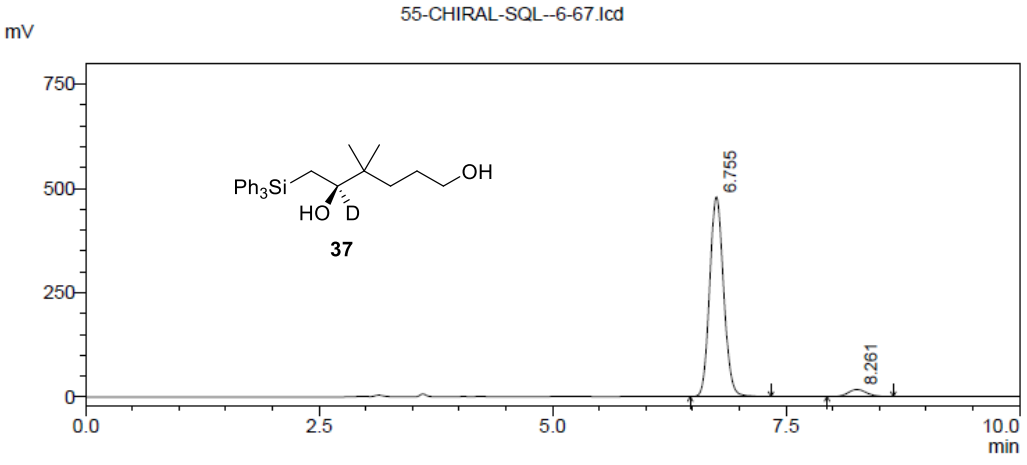
Detector A 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	6.728	440851	4492834	50.142
2	8.215	330837	4467467	49.858
Total		771688	8960301	100.000

HPLC spectra of **37**

Data File : 55-CHIRAL-SQL--6-67.lcd
Method File : 4OD-H-95-1-214-20min.lcm
Date Processed : 9/2/2021 12:15:50 AM

<Chromatogram View>



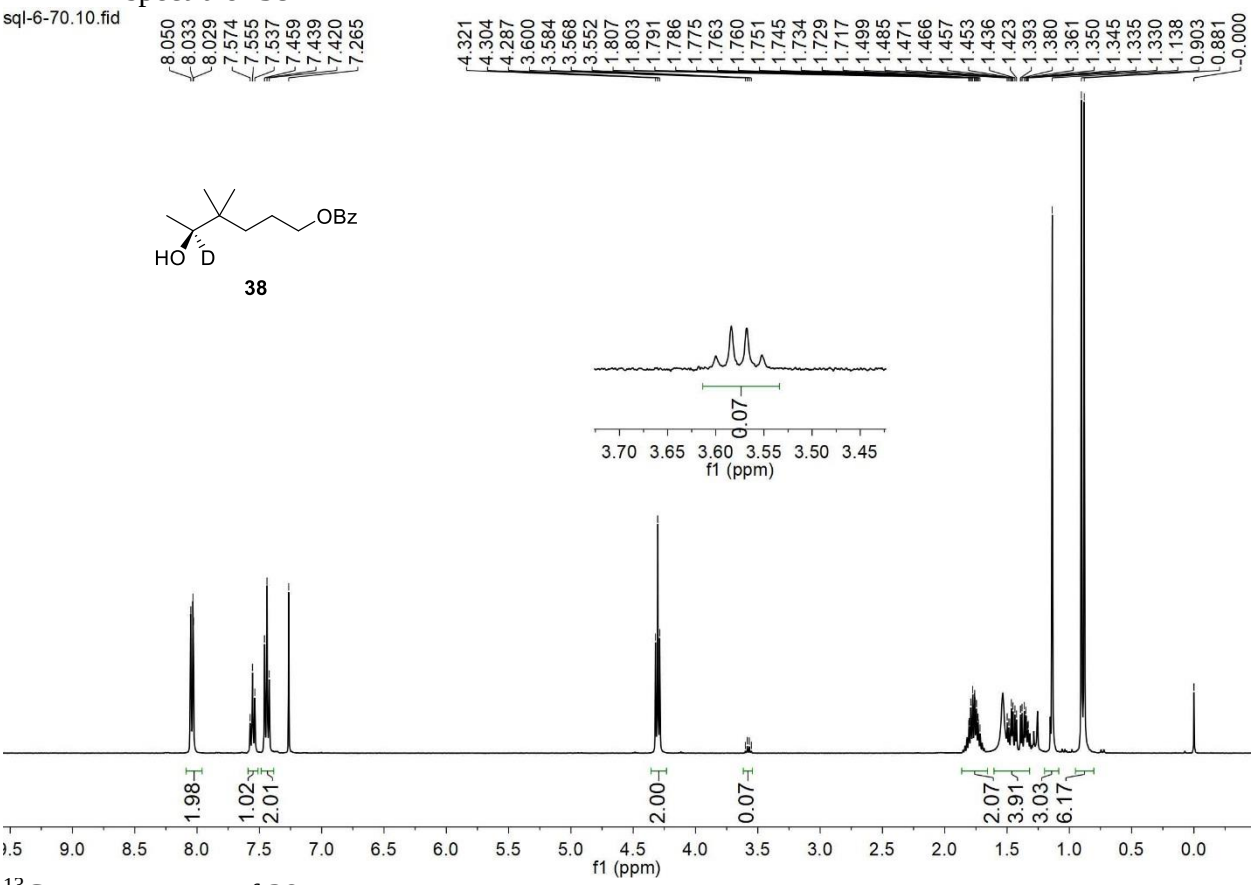
37

<Data Analysis>

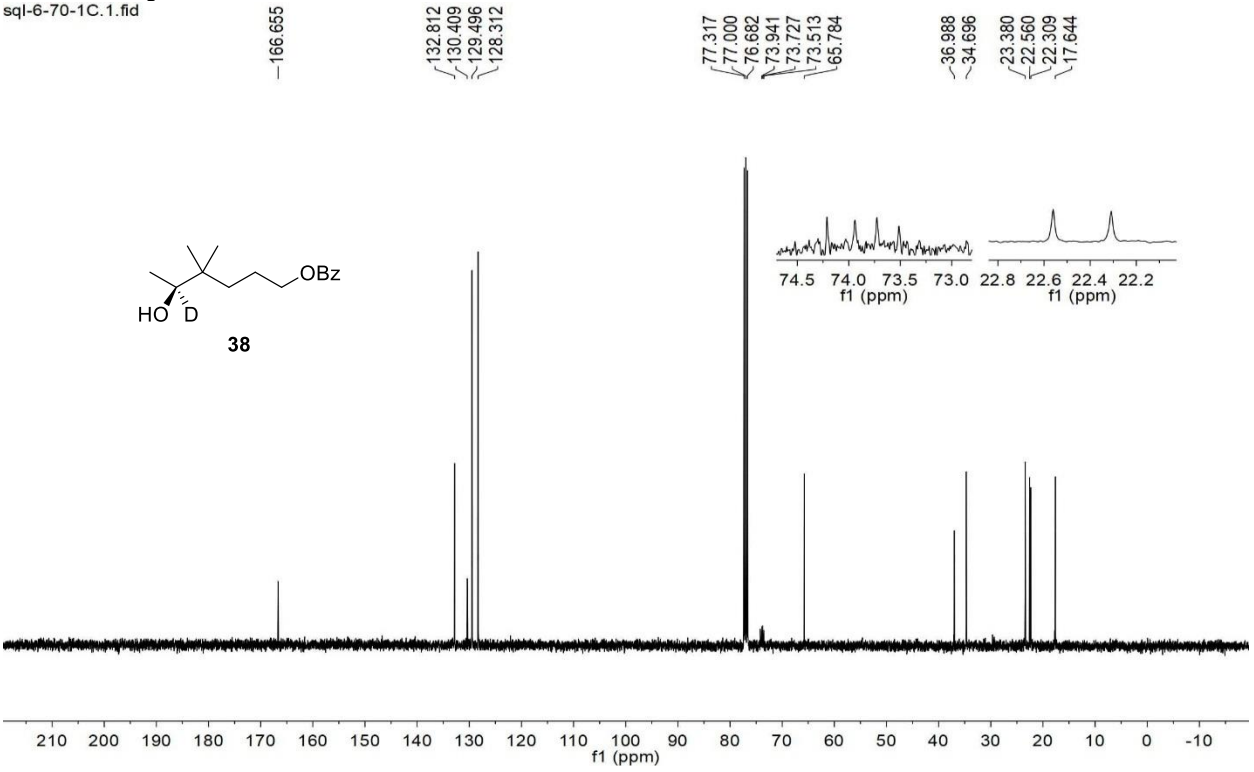
Detector A 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	6.755	478180	4986603	95.552
2	8.261	16978	232107	4.448
Total		495159	5218710	100.000

^{1}H NMR spectra of **38**



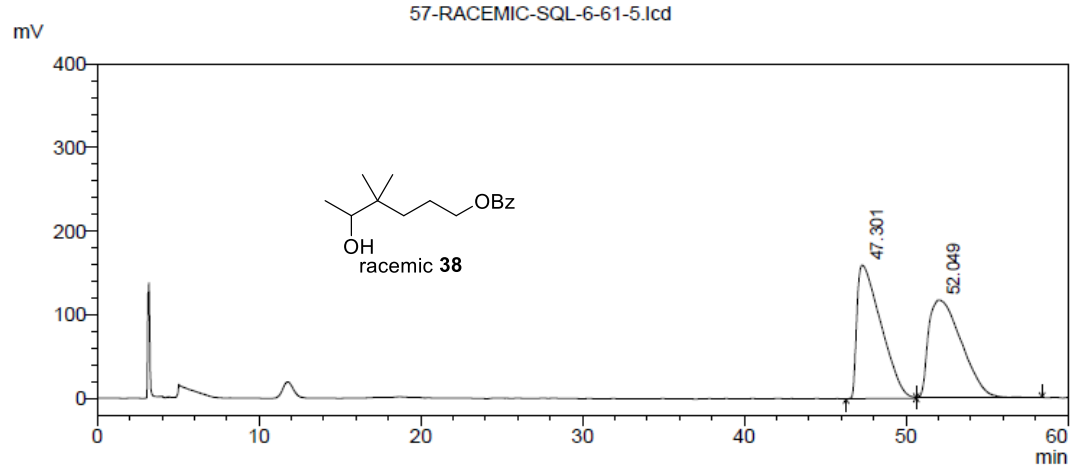
^{13}C NMR spectra of **38**



HPLC spectra of racemic **38**

Data File : 57-RACEMIC-SQL-6-61-5.lcd
Method File : 1OJ-H-99.8-1-214-55min.lcm
Date Processed : 9/2/2021 12:18:21 AM

<Chromatogram View>



<Data Analysis>

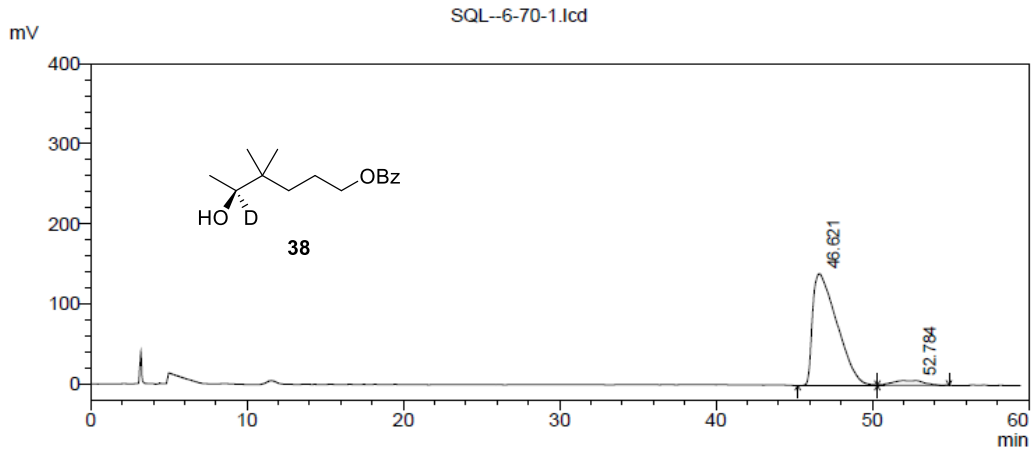
Detector A 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	47.301	159752	16514396	50.168
2	52.049	116421	16403545	49.832
Total		276172	32917941	100.000

HPLC spectra of **38**

Data File : SQL--6-70-1.lcd
Method File : 1OJ-H-99.8-1-214-55min.lcm
Date Processed : 9/2/2021 12:17:14 AM

<Chromatogram View>



<Data Analysis>

Detector A 214nm

Pesk #	Ret. Time	Height	Area	Area%
1	46.621	139739	15112400	95.023
2	52.784	5893	791596	4.977
Total		145632	15903996	100.000