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Supporting Information

Table of Contents

I.	General Information	S-1
II.	Preparation of Electrophiles	S-3
III.	Cross-Couplings	S-19
IV.	Mechanistic Experiments	S-33
V.	Determination of Absolute Stereochemistry	S-34
VI.	¹ H and ¹³ C NMR Data; ee Analysis	S-42

I. General Information

All manipulations of air-sensitive materials were carried out in oven-dried glassware under an atmosphere of argon or nitrogen using standard Schlenk or glovebox techniques. Glovebox manipulations were carried out under an atmosphere of nitrogen. THF and CH₂Cl₂ were purified and dried using a solvent purification system that contained activated alumina under argon. Unless otherwise noted, all commercially available reagents were used as received, including NiBr₂·diglyme (Sigma-Aldrich) and DMA (anhydrous, 99.8%, Sigma-Aldrich). Ligand L* (one step)¹ and 3-phenyl-1-(trimethylsilyl)propan-1-one² were prepared according to literature procedures. Aldehydes that are not commercially available were prepared according to a literature procedure.³

¹H and ¹³C NMR data were collected on a Bruker 400 MHz, a Varian 300 MHz, or a Varian 500 MHz spectrometer at ambient temperature and are reported in ppm relative to residual CHCl₃ (δ 7.26, ¹H NMR; δ 77.36, ¹³C NMR); s = singlet, d = doublet, t = triplet, q = quartet, p =

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- (1) Espelt, L. R.; McPherson, I. S.; Wiensch, E. M.; Yoon, T. P. *J. Am. Chem. Soc.* **2015**, *137*, 2452–2455.
 - (2) Decostanzi, M.; Van Der Lee, A.; Campagne, J.-M.; Leclerc, E. *Adv. Synth. Catal.* **2015**, *357*, 3091–3097.
 - (3) Hoover, J. M.; Stahl, S. S. *Org. Synth.* **2013**, *90*, 240–250.

pentet, sept = septuplet, m = multiplet, br = broad. IR spectra were obtained on a PerkinElmer Paragon 1000 spectrometer using thin films deposited on NaCl plates and are reported in frequency of absorption (cm^{-1}). HR-MS were acquired by the Caltech Mass Spectrometry Facility using a JEOL JMS-600H MS in fast atom bombardment (FAB+) or electron ionization (EI+) mode, or using a Waters LCT Premier XE TOF MS in electrospray ionization (ESI+) mode. LC-MS were obtained on an Agilent 5975C GC/MSD System in electron ionization (EI+) mode. Optical rotations were measured on a Jasco P-2000 polarimeter operating on the sodium D-line (589 nm) using a 100 mm pathlength cell. Analytical SFC was performed on a Mettler SFC supercritical CO_2 analytical chromatography system utilizing CHIRALPAK (AD-H, IC-3) or CHIRALCEL (OD-H, OJ) columns (4.6 mm \times 25 cm) obtained from Daicel Chemical Industries, Ltd. Preparative SFC was performed on a JASCO SFC supercritical CO_2 preparative chromatography system utilizing a CHIRALPAK AD-H column (10 mm \times 250 cm) obtained from Daicel Chemical Industries, Ltd. GC analyses were obtained on an Agilent 6890N GC. Flash column chromatography was performed using silica gel (SiliaFlash[®] P60, particle size 40-63 μm , Silicycle). Thin-layer chromatography (TLC) and preparatory TLC were performed using Merck silica gel 60 F₂₅₄ pre-coated plates (0.25 mm) and visualized by UV fluorescence quenching and KMnO_4 staining. X-ray crystallographic analysis was carried out by the Caltech X-Ray Crystallography Facility using a Bruker APEX-II CCD diffractometer. ESI-MS experiments were conducted by direct injection using a Thermo Scientific LTQ linear ion trap mass spectrometer. X-band EPR measurements were collected on a Bruker EMX spectrometer; EPR simulation was conducted using EasySpin.⁴

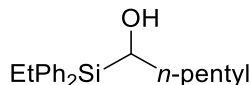
(4) Stoll, S.; Schweiger, A. *J. Magn. Reson.* **2006**, *178*, 42-55.

II. Preparation of Electrophiles

The yields have not been optimized.

General Procedure A: Preparation of α -hydroxysilanes (for substrates that contain at least one aryl substituent on silicon). A flame-dried round-bottom flask was charged with a glass-covered magnetic stir bar, pellets of Li metal (2.3 equiv), and R_3SiCl (if a solid), and then it was sealed with a rubber septum cap. Next, the flask was evacuated and backfilled with an argon-filled balloon (three cycles). THF (to generate a solution with $[R_3SiCl] = 1.0$ M) was then added, followed by R_3SiCl (if a liquid) as a steady stream. The resulting mixture was stirred at room temperature for 16 h (note: after ~20 min of stirring, the reaction mixture had turned dark green or brown).

Next, a solution of the aldehyde (0.75 equiv) in THF ($[aldehyde] = 0.38$ M) was prepared in a flame-dried round-bottom flask under an atmosphere of nitrogen. The resulting solution was cooled to -78 °C, and the solution of the lithiated silane was then added dropwise over 5 min. Next, the reaction mixture was warmed to room temperature and stirred for 16 h. The mixture was quenched through the addition of a saturated solution of NH_4Cl (1.0 mL/mmol of R_3SiCl), and the resulting mixture was extracted three times with EtOAc. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated. The resulting α -hydroxysilane was purified via flash chromatography (the α -hydroxysilane can be visualized using $KMnO_4$).



1-(Ethyldiphenylsilyl)hexan-1-ol. The title compound was synthesized according to **General Procedure A** from *n*-hexanal (0.83 mL, 6.8 mmol) and chloro(ethyl)diphenylsilane⁵ (2.22 g, 9.0 mmol). The product was purified by flash chromatography (2 → 5% EtOAc in hexanes), which provided 1.60 g (76% yield) of a colorless oil.

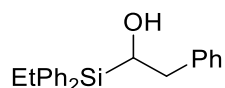
¹H NMR (400 MHz, $CDCl_3$) δ 7.66–7.53 (m, 4H), 7.47–7.31 (m, 6H), 3.98 (dd, $J = 9.4, 3.2$ Hz, 1H), 1.66–1.52 (m, 3H), 1.38–1.11 (m, 8H), 1.06 (t, $J = 7.8$ Hz, 3H), 0.87 (t, $J = 6.9$ Hz, 3H);

¹³C NMR (101 MHz, $CDCl_3$) δ 135.8, 135.7, 134.1, 133.9, 129.8, 129.7, 128.17, 128.16, 64.2, 33.8, 31.8, 26.9, 22.9, 14.3, 7.8, 3.1;

FT-IR (thin film) 3368, 3070, 2962, 1428, 1261, 1094, 1030, 863 cm^{-1} ;

HR-MS (FAB+) m/z $[M+H]^+ - H_2$ calcd for $C_{20}H_{27}OSi$: 311.1831, found: 311.1835.

(5) Kwak, Y.-W.; Lee, K.-K. *J. Organomet. Chem.* **1997**, *542*, 219–225.



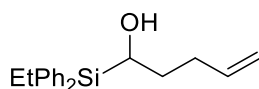
1-(Ethyldiphenylsilyl)-2-phenylethan-1-ol. The title compound was synthesized according to **General Procedure A** from 2-phenylacetaldehyde (0.80 mL, 6.8 mmol) and chloro(ethyl)diphenylsilane (2.22 g, 9.0 mmol). The product was purified by flash chromatography (0 → 6% EtOAc in hexanes), which provided 0.41 g (18% yield) of a colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.69 – 7.63 (m, 4H), 7.44 – 7.37 (m, 6H), 7.33 – 7.27 (m, 2H), 7.25 – 7.18 (m, 3H), 4.16 (dd, $J = 12.0, 2.7$ Hz, 1H), 2.93 (dd, $J = 14.0, 2.7$ Hz, 1H), 2.76 (dd, $J = 14.0, 11.9$ Hz, 1H), 1.53 (s, 1H), 1.27 – 1.17 (m, 2H), 1.08 (t, $J = 7.6$ Hz, 3H);

^{13}C NMR (101 MHz, CDCl_3) δ 139.9, 135.94, 135.88, 134.6, 134.01, 133.97, 129.93, 129.91, 129.4, 128.9, 128.31, 128.28, 128.25, 126.8, 65.4, 40.3, 7.9, 3.2;

FT-IR (thin film) 3546, 3068, 2913, 1454, 1428, 1260, 1111, 1012, 856 cm^{-1} ;

HR-MS (FAB+) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{25}\text{OSi}$: 333.1675, found: 333.1646.



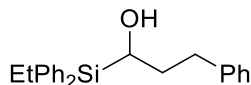
1-(Ethyldiphenylsilyl)pent-4-en-1-ol. The title compound was synthesized according to **General Procedure A** from pent-4-enal (0.50 mL, 5.06 mmol) and chloro(ethyl)diphenylsilane (1.68 g, 6.8 mmol). The product was purified by flash chromatography (2 → 4% EtOAc in hexanes), which provided 0.42 g (27% yield) of a colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.65 – 7.54 (m, 4H), 7.47 – 7.33 (m, 6H), 5.95 – 5.73 (m, 1H), 5.04 (dq, $J = 17.1, 1.7$ Hz, 1H), 4.98 (ddt, $J = 10.1, 2.1, 1.2$ Hz, 1H), 4.07 – 3.94 (m, 1H), 2.44 – 2.25 (m, 1H), 2.15 (dtdd, $J = 14.5, 7.4, 2.6, 1.3$ Hz, 1H), 1.77 – 1.66 (m, 2H), 1.30 – 1.10 (m, 3H), 1.05 (t, $J = 7.6$ Hz, 3H);

^{13}C NMR (101 MHz, CDCl_3) δ 138.9, 135.9, 135.8, 135.0, 134.0, 133.9, 129.92, 129.89, 128.3, 115.5, 63.7, 33.1, 31.7, 7.9, 3.1;

FT-IR (thin film) 3436, 3069, 2958, 1428, 1261, 1111, 1011, 912 cm^{-1} ;

HR-MS (FAB+) m/z $[\text{M}+\text{H}]^+ - \text{H}_2$ calcd for $\text{C}_{19}\text{H}_{23}\text{OSi}$: 295.1518, found: 295.1515.

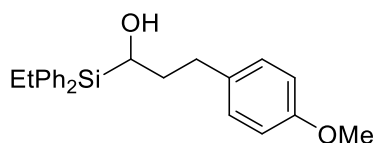


1-(Ethyldiphenylsilyl)-3-phenylpropan-1-ol. The title compound was synthesized according to **General Procedure A** from 3-phenylpropanal (0.99 mL, 7.5 mmol) and chloro(ethyl)diphenylsilane (2.47 g, 10.0 mmol). The product was purified by flash chromatography (5 → 10% EtOAc in hexanes), which provided 1.21 g (46% yield) of a colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.62 – 7.52 (m, 4H), 7.46 – 7.33 (m, 6H), 7.31 – 7.25 (m, 2H), 7.22 – 7.13 (m, 3H), 3.99 (ddd, J = 9.8, 5.3, 3.9 Hz, 1H), 2.94 (ddd, J = 14.1, 8.6, 5.8 Hz, 1H), 2.66 (ddd, J = 13.6, 8.7, 7.3 Hz, 1H), 2.00 – 1.84 (m, 2H), 1.19 – 1.10 (m, 3H), 1.03 (t, J = 7.6 Hz, 3H);
 ^{13}C NMR (101 MHz, CDCl_3) δ 142.3, 135.85, 135.79, 133.84, 133.76, 130.0, 129.9, 128.9, 128.7, 128.32, 128.31, 126.1, 63.6, 35.8, 33.6, 7.8, 3.1;

FT-IR (thin film) 3568, 3447, 3067, 2954, 1602, 1496, 1454, 1428, 1379, 1232, 1190, 1111, 1027, 955, 914 cm^{-1} ;

HR-MS (FAB+) m/z $[\text{M}+\text{H}]^+-\text{H}_2$ calcd for $\text{C}_{23}\text{H}_{25}\text{OSi}$: 345.1669, found: 345.1668.



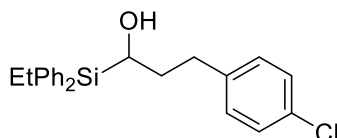
1-(Ethyldiphenylsilyl)-3-(4-methoxyphenyl)propan-1-ol. The title compound was synthesized according to **General Procedure A** from 3-(4-methoxyphenyl)propanal (1.11 g, 6.8 mmol) and chloro(ethyl)diphenylsilane (2.22 g, 9.0 mmol). The product was purified by flash chromatography (5 \rightarrow 15% EtOAc in hexanes), which provided 2.20 g (87% yield) of a colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.61–7.51 (m, 4H), 7.45–7.33 (m, 6H), 7.11–7.04 (m, 2H), 6.85–6.79 (m, 2H), 3.97 (dt, J = 9.8, 4.9 Hz, 1H), 3.79 (s, 3H), 2.87 (ddd, J = 13.9, 8.2, 6.1 Hz, 1H), 2.61 (dt, J = 13.8, 8.2 Hz, 1H), 1.94–1.83 (m, 2H), 1.20–1.11 (m, 2H), 1.02 (t, J = 7.7 Hz, 3H);

^{13}C NMR (101 MHz, CDCl_3) δ 158.0, 135.8, 135.7, 134.2, 133.8, 133.7, 129.83, 129.81, 129.7, 128.22, 128.21, 114.0, 63.4, 55.5, 35.8, 32.5, 7.8, 3.0;

FT-IR (thin film) 3448, 3068, 2954, 1611, 1517, 1458, 1427, 1300, 1246, 1177, 1110, 1035, 808 cm^{-1} ;

HR-MS (FAB+) m/z $[\text{M}+\text{H}]^+-\text{H}_2$ calcd for $\text{C}_{24}\text{H}_{27}\text{O}_2\text{Si}$: 375.1780, found: 375.17890.



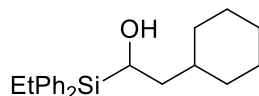
3-(4-Chlorophenyl)-1-(ethyldiphenylsilyl)propan-1-ol. The title compound was synthesized according to **General Procedure A** from 3-(4-chlorophenyl)propanal (1.14 g, 6.8 mmol) and chloro(ethyl)diphenylsilane (2.22 g, 9.0 mmol). The product was purified by flash chromatography (5 \rightarrow 7% EtOAc in hexanes), which provided 1.13 g (44% yield) of a colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.60–7.51 (m, 4H), 7.43–7.33 (m, 6H), 7.23 (d, J = 8.4 Hz, 2H), 7.08 (d, J = 8.4 Hz, 2H), 3.94 (q, J = 6.3 Hz, 1H), 2.90 (dt, J = 14.0, 7.1 Hz, 1H), 2.64 (dt, J = 14.0, 8.4 Hz, 1H), 1.93–1.82 (m, 2H), 1.19–1.12 (m, 3H), 1.02 (t, J = 7.6 Hz, 3H);

^{13}C NMR (101 MHz, CDCl_3) δ 140.6, 135.71, 135.66, 133.6, 133.5, 131.7, 130.2, 129.93, 129.91, 128.7, 128.28, 128.27, 63.2, 35.5, 32.7, 7.7, 3.0;

FT-IR (thin film) 3434, 3068, 2956, 1492, 1428, 1260, 1111, 1092, 1015, 808 cm^{-1} ;

HR-MS (FAB+) m/z $[\text{M}+\text{H}]^+-\text{H}_2$ calcd for $\text{C}_{23}\text{H}_{24}\text{ClOSi}$: 379.1285, found: 379.1288.



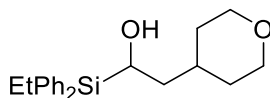
2-Cyclohexyl-1-(ethyldiphenylsilyl)ethan-1-ol. The title compound was synthesized according to **General Procedure A** from 2-cyclohexylacetaldehyde (0.82 g, 6.5 mmol) and chloro(ethyl)diphenylsilane (2.14 g, 8.66 mmol). The product was purified by flash chromatography (0 \rightarrow 5% EtOAc in hexanes), which provided 2.24 g (>99% yield, nominally pure) of a pale-yellow oil.

^1H NMR (300 MHz, CDCl_3) δ 7.67–7.51 (m, 4H), 7.46–7.31 (m, 6H), 4.15 (ddd, J = 11.4, 5.6, 2.2 Hz, 1H), 1.90 (d, J = 12.5 Hz, 1H), 1.78–1.45 (m, 7H), 1.42–1.34 (m, 1H), 1.23–1.11 (m, 4H), 1.08–0.99 (m, 5H), 0.83–0.68 (m, 1H);

^{13}C NMR (101 MHz, CDCl_3) δ 135.8, 135.7, 134.0, 133.9, 129.74, 129.71, 128.2, 128.1, 60.8, 41.4, 34.9, 34.1, 32.1, 26.9, 26.7, 26.4, 7.7, 3.0;

FT-IR (thin film) 3445, 3069, 2913, 1427, 1236, 1189, 1110, 1013, 872 cm^{-1} ;

HR-MS (FAB+) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{31}\text{OSi}$: 339.2144, found: 339.2153.



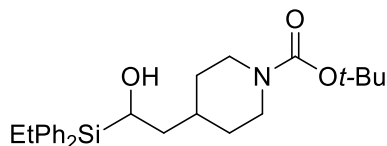
1-(Ethyldiphenylsilyl)-2-(tetrahydro-2H-pyran-4-yl)ethan-1-ol. The title compound was synthesized according to **General Procedure A** from 2-(tetrahydro-2H-pyran-4-yl)acetaldehyde (0.87 g, 6.75 mmol) and chloro(ethyl)diphenylsilane (2.22 g, 9.0 mmol). The product was purified by flash chromatography (20 \rightarrow 40% EtOAc in hexanes), which provided 1.55 g (67% yield) of a colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.64–7.54 (m, 4H), 7.44–7.34 (m, 6H), 4.14 (ddd, J = 12.0, 5.8, 2.4 Hz, 1H), 3.96 (ddd, J = 11.3, 4.3, 1.6 Hz, 1H), 3.91 (ddd, J = 11.3, 4.5, 1.6 Hz, 2H), 3.36 (tdd, J = 11.7, 7.8, 2.2 Hz, 2H), 1.89–1.73 (m, 2H), 1.63–1.56 (m, 1H), 1.54–1.46 (m, 1H), 1.41 (ddd, J = 14.4, 9.7, 2.3 Hz, 1H), 1.36–1.28 (m, 1H), 1.20–1.13 (m, 2H), 1.05 (t, J = 7.7 Hz, 3H), 1.00 (d, J = 6.0 Hz, 1H);

^{13}C NMR (101 MHz, CDCl_3) δ 135.63, 135.57, 133.6, 133.4, 129.83, 129.80, 128.184, 128.176, 68.24, 68.18, 60.2, 40.7, 34.3, 32.0, 31.5, 7.6, 2.8;

FT-IR (thin film) 3436, 3068, 2913, 1724, 1428, 1386, 1300, 1261, 1190, 1110, 1013, 872 cm^{-1} ;

HR-MS (FAB+) m/z $[\text{M}+\text{H}]^+-\text{H}_2$ calcd for $\text{C}_{21}\text{H}_{27}\text{O}_2\text{Si}$: 339.1780, found: 339.1774.



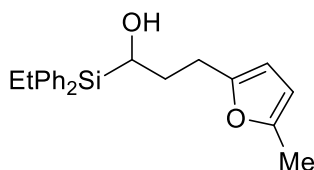
Tert-butyl 4-(2-(ethyldiphenylsilyl)-2-hydroxyethyl)piperidine-1-carboxylate. The title compound was synthesized according to **General Procedure A** from *tert*-butyl 4-(2-oxoethyl)piperidine-1-carboxylate (1.53 g, 6.75 mmol) and chloro(ethyl)diphenylsilane (2.22 g, 9.0 mmol). The product was purified by flash chromatography (20 → 30% EtOAc in hexanes), which provided 2.40 g (81% yield) of a colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.62–7.53 (m, 4H), 7.46–7.32 (m, 6H), 4.12 (ddd, $J = 12.0, 5.8, 2.2$ Hz, 1H), 4.08 (br s, 2H), 2.66 (t, $J = 10.6$ Hz, 2H), 1.84 (d, $J = 12.5$ Hz, 1H), 1.79–1.67 (m, 1H), 1.64–1.50 (m, 2H), 1.44 (s, 9H), 1.39 (ddd, $J = 14.4, 9.8, 2.2$ Hz, 1H), 1.21–1.08 (m, 3H), 1.04 (t, $J = 7.6$ Hz, 3H), 1.07–1.01 (m, 1H), 1.01–0.95 (m, 1H);

^{13}C NMR (101 MHz, CDCl_3) δ 155.1, 135.7, 135.6, 133.6, 133.5, 129.92, 129.89, 128.3, 79.4, 60.6, 44.2 (br), 40.4, 33.5, 32.6, 31.1, 28.7, 7.7, 2.9;

FT-IR (thin film) 3447, 3069, 2916, 1694, 1668, 1428, 1366, 1279, 1246, 1167, 1111, 1011, 974, 869 cm^{-1} ;

HR-MS (FAB+) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{38}\text{NO}_3\text{Si}$: 440.2621, found: 440.2632.



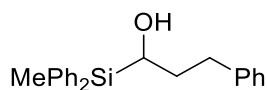
1-(Ethyldiphenylsilyl)-3-(5-methylfuran-2-yl)propan-1-ol. The title compound was synthesized according to **General Procedure A** from 3-(5-methylfuran-2-yl)propanal (0.95 mL, 7.1 mmol) and chloro(ethyl)diphenylsilane (2.35 g, 9.5 mmol). The product was purified by flash chromatography (5 → 10% EtOAc in hexanes), which provided 1.94 g (77% yield) of a colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.66–7.51 (m, 4H), 7.48–7.30 (m, 6H), 5.88–5.80 (m, 2H), 3.98 (dd, $J = 11.5, 2.6$ Hz, 1H), 2.85 (ddd, $J = 13.6, 8.2, 5.2$ Hz, 1H), 2.69 (dt, $J = 15.5, 7.8$ Hz, 1H), 2.27 (s, 3H), 2.03–1.92 (m, 1H), 1.91–1.78 (m, 1H), 1.44 (br s, 1H), 1.23–1.13 (m, 2H), 1.04 (t, $J = 7.8$ Hz, 3H);

^{13}C NMR (101 MHz, CDCl_3) δ 154.0, 150.6, 135.73, 135.67, 133.73, 133.67, 129.82, 129.79, 128.19, 128.18, 106.1, 106.0, 63.3, 32.4, 25.7, 13.8, 7.7, 3.0;

FT-IR (thin film) 3293, 3070, 2959, 1590, 1458, 1428, 1261, 1118, 1012, 829 cm^{-1} ;

HR-MS (FAB+) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{27}\text{O}_2\text{Si}$: 351.1780, found: 351.1782.



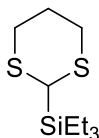
1-(Methyldiphenylsilyl)-3-phenylpropan-1-ol. The title compound was synthesized according to **General Procedure A** from 3-phenylpropanal (0.94 mL, 7.1 mmol) and chloro(methyl)diphenylsilane (2.00 mL, 9.5 mmol). The product was purified by flash chromatography (5 → 10% EtOAc in hexanes), which provided 2.09 g (88% yield) of a colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.57 – 7.49 (m, 4H), 7.46 – 7.32 (m, 6H), 7.31 – 7.25 (m, 2H), 7.22 – 7.14 (m, 3H), 3.93 (dd, $J = 8.9, 5.3$ Hz, 1H), 2.95 (ddd, $J = 14.1, 8.5, 6.4$ Hz, 1H), 2.66 (dt, $J = 13.6, 8.1$ Hz, 1H), 2.02 – 1.85 (m, 2H), 1.19 (s, 1H), 0.61 (s, 3H);

^{13}C NMR (101 MHz, CDCl_3) δ 142.3, 135.4, 135.3, 135.1, 134.8, 130.00, 129.96, 128.9, 128.7, 128.37, 128.36, 126.1, 64.2, 35.5, 33.6, –6.4;

FT-IR (thin film) 3566, 3443, 3068, 2924, 1602, 1496, 1454, 1428, 1253, 1112, 1028, 914 cm^{-1} ;
HR-MS (FAB+) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{25}\text{OSi}$: 333.1675, found: 333.1680.

General Procedure B: Preparation of α -(dithiane)silanes (for substrates that lack an aryl substituent on silicon). The method of Christmann was used.⁶



(1,3-Dithian-2-yl)triethylsilane. The title compound was synthesized according to **General Procedure B** from chlorotriethylsilane (16.8 mL, 100 mmol). The product was purified by high-vacuum distillation, which provided 16.9 g (87% yield) of a colorless oil.

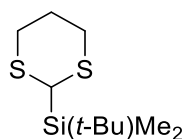
^1H NMR (400 MHz, CDCl_3) δ 3.82 (s, 1H), 2.94 – 2.83 (m, 2H), 2.78 – 2.66 (m, 2H), 2.18 – 1.95 (m, 2H), 1.01 (t, $J = 7.9$ Hz, 9H), 0.70 (q, $J = 7.9$, 6H);

^{13}C NMR (101 MHz, CDCl_3) δ 32.5, 31.8, 26.8, 7.8, 2.5;

FT-IR (thin film) 2951, 2875, 1458, 1420, 1260, 1240, 1163, 1084, 1019, 778 cm^{-1} ;

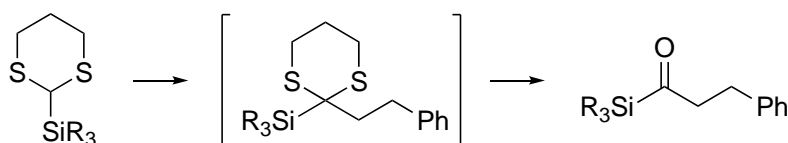
HR-MS (FAB+) m/z $[\text{M}+\text{H}]^+ - \text{H}_2$ calcd for $\text{C}_{10}\text{H}_{21}\text{S}_2\text{Si}$: 233.0854, found: 233.0846.

(6) Winter, P.; Hiller, W.; Christmann, M. *Angew. Chem. Int. Ed.* **2012**, *51*, 3396–3400.



Tert-butyl(1,3-dithian-2-yl)dimethylsilane.⁷ The title compound was synthesized according to **General Procedure B** from *tert*-butyl(chloro)dimethylsilane (15.1 g, 100 mmol). The product was purified by high-vacuum distillation, which provided 16.2 g (83 yield) of a pale-purple oil.

¹H NMR (300 MHz, CDCl₃) δ 3.80 (s, 1H), 2.98 – 2.76 (m, 2H), 2.69 (ddd, J = 14.0, 4.1, 3.1 Hz, 2H), 2.17 – 1.90 (m, 2H), 0.96 (d, J = 0.6 Hz, 9H), 0.10 (d, J = 0.5 Hz, 6H).

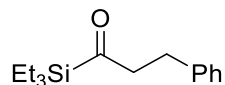


General Procedure C: Preparation of acylsilanes (for substrates that lack an aryl substituent on silicon). The alkylation of α -dithiane silanes was performed according to a literature procedure.⁸ In a flame-dried round-bottom flask, *n*-BuLi (1.05 equiv) was added dropwise to a stirring solution of the α -dithiane silane (1.00 equiv) in THF (0.4 M with respect to the α -dithiane silane) at room temperature under an atmosphere of nitrogen. The solution was stirred for 10 min at room temperature, and then it was cooled to -40 °C. Next, (2-bromoethyl)benzene (1.10 equiv) was added dropwise over 1–2 min. The reaction mixture was then warmed to room temperature and stirred for 2 h. Next, the reaction was quenched through the addition of a saturated aqueous solution of NH₄Cl. The resulting mixture was extracted with Et₂O three times, and the organic phases were collected, dried over MgSO₄, filtered, and concentrated. This material was used in the next step without further purification.

The deprotection of the α -alkyl- α -dithiane silanes was performed according to a literature procedure.² In a round-bottom flask, the α -alkyl- α -dithiane silane was dissolved in a 4:1 mixture of THF/H₂O (0.9 M with respect to the α -dithiane silane). The solution was cooled to 0 °C, and then CaCO₃ (15.6 equiv) was added, followed by I₂ (12.0 equiv; added in portions). The reaction was warmed to room temperature and stirred for 16 h. The reaction mixture was diluted with Et₂O (15 mL/mmol of α -dithiane silane), and the reaction was quenched by the addition of a saturated solution of Na₂S₂O₃. The biphasic mixture was filtered through Celite and transferred to a separatory funnel (note: if the color of iodine remains, the organic layer was washed with an additional quantity of the saturated solution of Na₂S₂O₃). The organic layer was separated, dried over MgSO₄, filtered, and concentrated. The acyl silane can be used in **General Procedure D** without further purification.

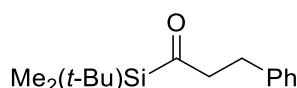
(7) Scheller, M. E.; Frei, B. *Helv. Chim. Acta.* **1984**, *67*, 1734–1747.

(8) Smith, A. B., III; Xian, M.; Kim, W.-S.; Kim, D.-S. *J. Am. Chem. Soc.* **2006**, *128*, 12368–12369.



3-Phenyl-1-(triethylsilyl)propan-1-one.⁹ The title compound was synthesized according to **General Procedure C** from (1,3-dithian-2-yl)triethylsilane (2.13 g, 9.10 mmol). The product was purified by flash chromatography (0 → 3% EtOAc in hexanes), which provided 1.08 g (48% yield over two steps) of a colorless oil.

¹H NMR (300 MHz, CDCl₃) δ 7.31 – 7.24 (m, 2H), 7.22 – 7.13 (m, 3H), 2.95 – 2.76 (m, 4H), 0.96 (t, *J* = 7.8 Hz, 9H), 0.73 (q, *J* = 7.9 Hz, 6H).



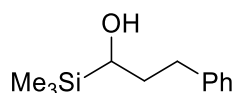
1-(Tert-butyl dimethylsilyl)-3-phenylpropan-1-one.¹⁰ The title compound was synthesized according to **General Procedure C** from *tert*-butyl(1,3-dithian-2-yl)dimethylsilane (4.00 g, 17.1 mmol). The product was purified by flash chromatography (0 → 2% EtOAc in hexanes), which provided 4.25 g (>99% yield of nominally pure material over two steps) of a white solid.

¹H NMR (300 MHz, CDCl₃) δ 7.40 – 7.30 (m, 2H), 7.30 – 7.20 (m, 3H), 3.07 – 2.78 (m, 4H), 0.99 (s, 9H), 0.25 (s, 6H).

General Procedure D: Reduction of acylsilanes (for substrates that lack an aryl substituent on silicon). In a round-bottom flask charged with a stir bar, LiAlH₄ (4.9 equiv) was slowly dissolved in THF (~40 mL/mmol of acyl silane) at 0 °C. The resulting solution was stirred for 10 min. A solution of the acyl silane in THF (~1.5 mL/mmol of acyl silane) was added in a slow, steady stream to the solution of LiAlH₄ at 0 °C. Next, the reaction mixture was warmed to room temperature and stirred for 3 h. The reaction was then quenched and worked up using the Fieser method.

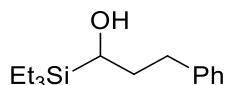
(9) Reddy, G. P.; Reddy, J. S.; Das, S.; Roisnel, T.; Yadav, J. S.; Chandrasekhar, S.; Gree, R. *Org. Lett.* **2013**, *15*, 1524–1527.

(10) Reich, H. J.; Holtan, R. C.; Bolm, C. *J. Am. Chem. Soc.* **1990**, *112*, 5609–5617.



3-Phenyl-1-(trimethylsilyl)propan-1-ol.¹¹ The title compound was synthesized according to **General Procedure D** from 3-phenyl-1-(trimethylsilyl)propan-1-one (1.84 g, 9.8 mmol). The product was purified by flash chromatography (5 → 10% EtOAc in hexanes), which provided 1.65 g (89% yield) of a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.34 – 7.27 (m, 2H), 7.25 – 7.17 (m, 3H), 3.39 – 3.29 (m, 1H), 2.99 – 2.87 (m, 1H), 2.71 – 2.61 (m, 1H), 1.91 – 1.74 (m, 2H), 1.11 (s, 1H), 0.05 (s, 9H).



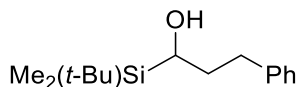
3-Phenyl-1-(triethylsilyl)propan-1-ol. The title compound was synthesized according to **General Procedure D** from 3-phenyl-1-(triethylsilyl)propan-1-one (1.08 g, 4.35 mmol). The product was purified by flash chromatography (5% EtOAc in hexanes), which provided 0.82 g (75% yield) of a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.33 – 7.26 (m, 2H), 7.24 – 7.12 (m, 3H), 3.51 (dd, J = 11.2, 2.9 Hz, 1H), 2.96 (ddd, J = 13.7, 9.8, 5.0 Hz, 1H), 2.66 (tdd, J = 13.6, 8.7, 6.9 Hz, 1H), 1.96 – 1.75 (m, 2H), 1.50 (s, 1H), 1.03 – 0.93 (m, 9H), 0.68 – 0.49 (m, 6H);

¹³C NMR (101 MHz, CDCl₃) δ 140.6, 126.83, 126.77, 124.1, 62.5, 34.3, 31.9, 5.9, 0.0;

FT-IR (thin film) 3448, 3026, 2953, 1708, 1604, 1496, 1455, 1415, 1260, 1239, 1018, 912 cm⁻¹;

HR-MS (FAB+) m/z [M+H]⁺-H₂ calcd for C₁₅H₂₅OSi: 249.1675, found: 249.1679.



1-(Tert-butyldimethylsilyl)-3-phenylpropan-1-ol. The title compound was synthesized according to **General Procedure D** from 1-(tert-butyldimethylsilyl)-3-phenylpropan-1-one (2.49 g, 10.0 mmol). The product was purified by flash chromatography (0 → 15% EtOAc in hexanes), which provided 1.75 g (70% yield) of a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.34 – 7.27 (m, 2H), 7.25 – 7.15 (m, 3H), 3.53 (dd, J = 9.8, 4.2 Hz, 1H), 2.96 (ddd, J = 13.6, 9.0, 6.0 Hz, 1H), 2.65 (ddd, J = 13.5, 8.9, 7.2 Hz, 1H), 1.96 – 1.77 (m, 2H), 1.08 (s, 1H), 0.94 (s, 9H), 0.02 (s, 3H), -0.04 (s, 3H);

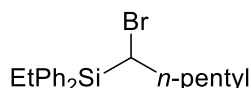
¹³C NMR (101 MHz, CDCl₃) δ 142.6, 128.82, 128.77, 126.2, 64.4, 36.7, 33.8, 27.4, 17.1, -7.2, -8.2;

FT-IR (thin film) 3467, 3027, 2954, 1604, 1496, 1471, 1362, 1255, 1024, 914, 832 cm⁻¹;

HR-MS (FAB+) m/z [M+H]⁺-H₂ calcd for C₁₅H₂₅OSi: 249.1675, found: 249.1673.

(11) Goddard, J.-P.; Le Gall, T.; Mioskowski, C. *Org. Lett.* **2000**, *2*, 1455–1456.

General Procedure E: Preparation of α -bromosilanes. PPh₃ (1.50 equiv) and imidazole (1.50 equiv) were dissolved in CH₂Cl₂ (6.0 mL/mmol of α -hydroxysilane), and the resulting solution was cooled to 0 °C. At this temperature, I₂ (1.50 equiv) was added in portions, and the resulting mixture was stirred for 10 min. Next, a solution of the α -hydroxysilane (1.00 equiv) in CH₂Cl₂ (4.0 mL/mmol) was added in a steady stream, and the resulting mixture was allowed to warm to room temperature and stirred overnight. Then, the reaction mixture was quenched with H₂O and then extracted with EtOAc. The organic layer was dried over Na₂SO₄, filtered, and concentrated. The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography on silica gel to afford the pure product.



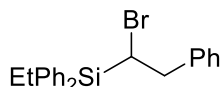
(1-Bromohexyl)(ethyl)diphenylsilane. The title compound was synthesized according to **General Procedure E** from 1-(ethyldiphenylsilyl)hexan-1-ol (1.60 g, 5.1 mmol). The product was purified by flash chromatography (2 → 5% EtOAc in hexanes), which provided 1.46 g (76% yield) of a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.66–7.54 (m, 4H), 7.49–7.34 (m, 6H), 3.81 (dd, J = 11.9, 2.7 Hz, 1H), 1.94–1.81 (m, 1H), 1.79–1.62 (m, 2H), 1.47–1.35 (m, 1H), 1.35–1.22 (m, 5H), 1.22–1.12 (m, 1H), 1.04 (t, J = 7.8 Hz, 3H), 0.87 (t, J = 7.0 Hz, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 136.0, 135.8, 133.5, 133.0, 130.0, 129.9, 128.1, 128.0, 41.2, 33.6, 31.1, 29.1, 22.8, 14.3, 7.6, 4.4;

FT-IR (thin film) 3070, 2959, 1458, 1428, 1261, 1106, 1029, 802 cm⁻¹;

HR-MS (FAB+) m/z [M]⁺ calcd for C₂₀H₂₇⁷⁹BrSi: 374.1065, found: 374.1060.



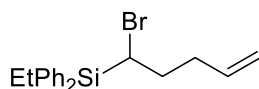
(1-Bromo-2-phenylethyl)(ethyl)diphenylsilane. The title compound was synthesized according to **General Procedure E** from 1-(ethyldiphenylsilyl)-2-phenylethan-1-ol (0.70 g, 2.11 mmol). The product was purified by flash chromatography (20% CHCl₃ in hexanes), which provided 0.64 g (76% yield) of a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.74 – 7.60 (m, 4H), 7.52 – 7.38 (m, 6H), 7.32 – 7.21 (m, 3H), 7.20 – 7.15 (m, 2H), 3.98 (dd, J = 12.3, 2.7 Hz, 1H), 3.36 (dd, J = 15.2, 2.6 Hz, 1H), 2.86 (dd, J = 15.1, 12.3 Hz, 1H), 1.41 – 1.19 (m, 2H), 1.13 – 0.99 (m, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 140.4, 136.1, 135.9, 133.2, 132.7, 130.3, 130.2, 129.1, 128.6, 128.4, 128.3, 126.9, 40.9, 40.0, 7.7, 4.6;

FT-IR (thin film) 3068, 2962, 1588, 1496, 1454, 1427, 1261, 1105, 1030, 801 cm⁻¹;

HR-MS (FAB+) m/z [M]⁺ calcd for C₂₂H₂₃⁷⁹BrSi: 394.0752, found: 394.0762.



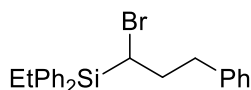
(1-Bromopent-4-en-1-yl)(ethyl)diphenylsilane. The title compound was synthesized according to **General Procedure E** from 1-(ethyldiphenylsilyl)pent-4-en-1-ol (1.06 g, 3.58 mmol). The product was purified by flash chromatography (5 → 20% CHCl₃ in hexanes), which provided 0.87 g (68% yield) of a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.65 – 7.55 (m, 4H), 7.48 – 7.35 (m, 6H), 5.72 (dddd, J = 17.1, 10.1, 7.7, 5.9 Hz, 1H), 5.11 – 4.98 (m, 2H), 3.83 (dd, J = 12.3, 2.5 Hz, 1H), 2.49 – 2.33 (m, 1H), 2.27 – 2.15 (m, 1H), 2.01 – 1.89 (m, 1H), 1.80 (dddd, J = 14.9, 12.3, 7.8, 4.5 Hz, 1H), 1.36 – 1.19 (m, 2H), 1.07 – 0.98 (m, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 137.3, 136.1, 135.9, 133.4, 132.9, 130.13, 130.08, 128.24, 128.18, 116.5, 40.0, 33.2, 32.8, 7.6, 4.5;

FT-IR (thin film) 3070, 2961, 1640, 1589, 1488, 1428, 1261, 1110, 1028, 916, 803 cm⁻¹;

HR-MS (FAB+) m/z [M]⁺ calcd for C₁₉H₂₃⁷⁹BrSi: 358.0752, found: 358.0746.



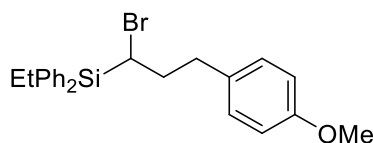
(1-Bromo-3-phenylpropyl)(ethyl)diphenylsilane. The title compound was synthesized according to **General Procedure E** from 1-(ethyldiphenylsilyl)-3-phenylpropan-1-ol (1.21 g, 3.49 mmol). The product was purified by flash chromatography (0 → 5% EtOAc in hexanes), which provided 1.07 g (75% yield) of a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.59 – 7.53 (m, 2H), 7.49 – 7.26 (m, 10H), 7.25 – 7.19 (m, 1H), 7.18 – 7.11 (m, 2H), 3.72 (dd, J = 12.2, 2.2 Hz, 1H), 3.00 (ddd, J = 13.8, 7.9, 4.3 Hz, 1H), 2.73 (dt, J = 13.6, 8.1 Hz, 1H), 2.24 – 2.11 (m, 1H), 2.01 (dddd, J = 15.0, 12.1, 7.8, 4.3 Hz, 1H), 1.31 – 1.16 (m, 2H), 1.03 – 0.88 (m, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 140.8, 135.7, 135.5, 133.0, 132.4, 129.8, 129.7, 128.8, 128.4, 127.87, 127.86, 126.1, 39.3, 35.1, 34.7, 7.2, 4.2;

FT-IR (thin film) 3069, 2961, 1589, 1496, 1454, 1428, 1261, 1110, 802 cm⁻¹;

HR-MS (FAB+) m/z [M-C₂H₅]⁺ calcd for C₂₁H₂₀⁷⁹BrSi: 379.0518, found: 379.0504.



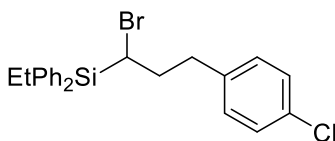
(1-Bromo-3-(4-methoxyphenyl)propyl)(ethyl)diphenylsilane. The title compound was synthesized according to **General Procedure E** from 1-(ethyldiphenylsilyl)-3-(4-methoxyphenyl)propan-1-ol (2.20 g, 5.8 mmol). The product was purified by flash chromatography (0 → 5% EtOAc in hexanes), which provided 1.68 g (65% yield) of a colorless oil.

^1H NMR (300 MHz, CDCl_3) δ 7.65–7.58 (m, 2H), 7.55–7.49 (m, 2H), 7.49–7.34 (m, 6H), 7.17–7.08 (m, 2H), 6.93–6.85 (m, 2H), 3.84 (s, 3H), 3.77 (dd, $J = 12.1, 2.3$ Hz, 1H), 2.97 (ddd, $J = 13.6, 7.4, 4.3$ Hz, 1H), 2.74 (dt, $J = 13.8, 8.2$ Hz, 1H), 2.19 (dtd, $J = 15.1, 7.8, 2.2$ Hz, 1H), 2.03 (dddd, $J = 15.0, 12.0, 7.6, 4.3$ Hz, 1H), 1.39–1.24 (m, 2H), 1.03 (t, $J = 7.7$ Hz, 3H);

^{13}C NMR (101 MHz, CDCl_3) δ 158.2, 135.9, 135.7, 133.2, 133.0, 132.6, 130.00, 129.95, 129.9, 128.1, 128.0, 114.0, 55.4, 39.5, 35.5, 33.9, 7.5, 4.4;

FT-IR (thin film) 3070, 2955, 1611, 1512, 1428, 1301, 1247, 1177, 1111, 1037, 807 cm^{-1} ;

HR-MS (FAB+) m/z $[\text{M}]^+$ calcd for $\text{C}_{24}\text{H}_{27}^{81}\text{BrOSi}$: 440.0991, found: 440.0997.



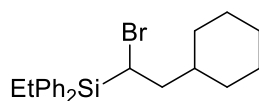
(1-Bromo-3-(4-chlorophenyl)propyl)(ethyl)diphenylsilane. The title compound was synthesized according to **General Procedure E** from 3-(4-chlorophenyl)-1-(ethyldiphenylsilyl)propan-1-ol (1.13 g, 2.97 mmol). The product was purified by flash chromatography (5 → 10% EtOAc in hexanes), which provided 0.63 g (48% yield) of a colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.60–7.54 (m, 2H), 7.49–7.32 (m, 8H), 7.26 (d, $J = 8.4$ Hz, 2H), 7.08 (d, $J = 8.4$ Hz, 2H), 3.67 (dd, $J = 12.2, 2.3$ Hz, 1H), 2.95 (ddd, $J = 13.7, 7.6, 4.2$ Hz, 1H), 2.72 (dt, $J = 13.8, 8.0$ Hz, 1H), 2.13 (dddd, $J = 15.1, 8.6, 7.7, 2.2$ Hz, 1H), 1.99 (dddd, $J = 15.1, 12.1, 7.6, 4.3$ Hz, 1H), 1.31–1.21 (m, 2H), 0.99 (t, $J = 7.8$ Hz, 3H);

^{13}C NMR (101 MHz, CDCl_3) δ 139.4, 135.9, 135.7, 133.1, 132.5, 132.1, 130.4, 130.1, 130.0, 128.8, 128.14, 128.12, 39.2, 35.1, 34.2, 7.5, 4.3;

FT-IR (thin film) 3069, 2955, 1589, 1492, 1428, 1262, 1218, 1152, 1112, 1015, 998, 956, 843, 812 cm^{-1} ;

HR-MS (FAB+) m/z $[\text{M}-\text{Br}]^+$ calcd for $\text{C}_{23}\text{H}_{24}\text{ClSi}$: 363.1336, found: 363.1333.



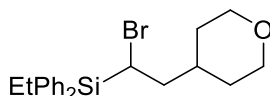
(1-Bromo-2-cyclohexylethyl)(ethyl)diphenylsilane. The title compound was synthesized according to **General Procedure E** from 2-cyclohexyl-1-(ethyldiphenylsilyl)ethan-1-ol (2.24 g, 6.6 mmol). The product was purified by flash chromatography (0 → 5% EtOAc in hexanes), which provided 1.58 g (59% yield) of a colorless oil.

^1H NMR (300 MHz, CDCl_3) δ 7.65–7.48 (m, 4H), 7.45–7.33 (m, 6H), 3.96 (dd, J = 12.4, 2.1 Hz, 1H), 1.92 (d, J = 12.5 Hz, 1H), 1.78–1.59 (m, 5H), 1.59–1.47 (m, 1H), 1.33–1.07 (m, 6H), 1.02 (t, J = 7.8 Hz, 3H), 0.93–0.80 (m, 1H), 0.71 (qd, J = 12.4, 3.4 Hz, 1H);

^{13}C NMR (101 MHz, CDCl_3) δ 136.0, 135.8, 133.5, 132.9, 130.0, 129.9, 128.1, 128.0, 40.9, 37.8, 35.7, 34.3, 31.2, 26.8, 26.5, 26.2, 7.5, 4.4;

FT-IR (thin film) 3069, 2923, 1589, 1488, 1448, 1428, 1261, 1110, 1029, 803 cm^{-1} ;

HR-MS (EI+) m/z $[\text{M}]^+$ calcd for $\text{C}_{22}\text{H}_{29}^{79}\text{BrSi}$: 400.1222, found: 400.1251.



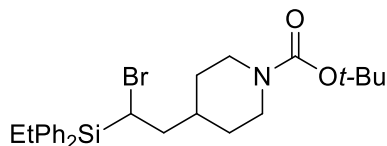
(1-Bromo-2-(tetrahydro-2H-pyran-4-yl)ethyl)(ethyl)diphenylsilane. The title compound was synthesized according to **General Procedure E** from 1-(ethyldiphenylsilyl)-2-(tetrahydro-2H-pyran-4-yl)ethan-1-ol (1.55 g, 4.6 mmol). The product was purified by flash chromatography (3 → 5% EtOAc in hexanes), which provided 1.25 g (68% yield) of a colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.63–7.53 (m, 4H), 7.48–7.34 (m, 6H), 3.98 (dd, J = 11.4, 4.2 Hz, 1H), 3.92 (dd, J = 12.9, 2.3 Hz, 1H), 3.89 (dd, J = 11.4, 4.4 Hz, 1H), 3.38 (dtd, J = 16.8, 11.9, 2.3 Hz, 2H), 1.99–1.85 (m, 1H), 1.84–1.70 (m, 2H), 1.62 (ddd, J = 15.0, 10.0, 2.4 Hz, 1H), 1.49–1.40 (m, 1H), 1.34–1.18 (m, 3H), 1.11 (td, J = 12.1, 4.5 Hz, 1H), 1.02 (t, J = 7.8 Hz, 3H);

^{13}C NMR (101 MHz, CDCl_3) δ 136.0, 135.8, 133.2, 132.6, 130.1, 130.0, 128.2, 128.1, 68.2, 68.1, 40.3, 36.7, 33.7, 33.2, 31.2, 7.5, 4.4;

FT-IR (thin film) 3070, 2929, 1428, 1190, 1111, 1012, 849 cm^{-1} ;

HR-MS (FAB+) m/z $[\text{M}+\text{H}]^+ - \text{H}_2$ calcd for $\text{C}_{21}\text{H}_{26}^{79}\text{BrOSi}$: 401.0936, found: 401.0918.



Tert-butyl 4-(2-bromo-2-(ethyldiphenylsilyl)ethyl)piperidine-1-carboxylate. The title compound was synthesized according to **General Procedure E** from *tert*-butyl 4-(2-(ethyldiphenylsilyl)-2-hydroxyethyl)piperidine-1-carboxylate (2.40 g, 5.5 mmol). The product

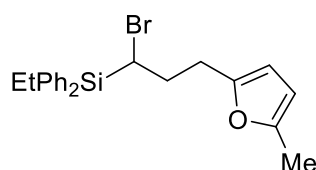
was purified by flash chromatography (3 → 7% EtOAc in hexanes), which provided 2.02 g (74% yield) of a colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.64–7.53 (m, 4H), 7.48–7.36 (m, 6H), 4.13 (br s, 1H), 4.04 (br s, 1H), 3.92 (dd, J = 12.8, 2.1 Hz, 1H), 2.69 (q, J = 11.5 Hz, 2H), 1.95–1.73 (m, 3H), 1.60 (ddd, J = 14.8, 9.7, 2.2 Hz, 1H), 1.55–1.47 (m, 1H), 1.45 (s, 9H), 1.32–1.24 (m, 2H), 1.16–1.06 (m, 1H), 1.03 (t, J = 7.9 Hz, 3H), 0.96–0.89 (m, 1H);

^{13}C NMR (101 MHz, CDCl_3) δ 155.0, 135.9, 135.7, 133.1, 132.5, 130.1, 130.0, 128.2, 128.1, 79.5, 43.9 (br; two carbons), 40.0, 37.0, 34.3, 32.9, 30.2, 28.7, 7.5, 4.3;

FT-IR (thin film) 3070, 2931, 1694, 1428, 1365, 1261, 1162, 1111, 1026, 865 cm^{-1} ;

HR-MS (FAB+) m/z $[\text{M}+\text{H}]^+ - \text{H}_2$ calcd for $\text{C}_{26}\text{H}_{35}^{79}\text{BrNO}_2\text{Si}$: 500.1620, found: 500.1618.



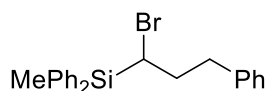
(1-Bromo-3-(5-methylfuran-2-yl)propyl)(ethyl)diphenylsilane. The title compound was synthesized according to **General Procedure E** from 1-(ethyldiphenylsilyl)-3-(5-methylfuran-2-yl)propan-1-ol (1.94 g, 5.5 mmol). The product was purified by flash chromatography (0 → 5% EtOAc in hexanes), which provided 1.14 g (50% yield) of a colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.63–7.55 (m, 2H), 7.55–7.48 (m, 2H), 7.48–7.30 (m, 6H), 5.94–5.80 (m, 2H), 3.76 (dd, J = 12.4, 2.0 Hz, 1H), 2.90 (ddd, J = 15.1, 7.0, 4.5 Hz, 1H), 2.77 (ddd, J = 15.7, 8.6, 7.4 Hz, 1H), 2.26 (s, 3H), 1.92 (dddd, J = 15.1, 12.4, 7.1, 4.2 Hz, 1H), 1.31–1.24 (m, 2H), 0.99 (t, J = 7.8 Hz, 3H);

^{13}C NMR (101 MHz, CDCl_3) δ 152.7, 150.9, 136.0, 135.8, 133.2, 132.6, 130.05, 129.96, 128.10, 128.08, 107.0, 106.1, 39.4, 32.3, 27.4, 13.8, 7.4, 4.4;

FT-IR (thin film) 3070, 2960, 1568, 1428, 1261, 1109, 1020, 800 cm^{-1} ;

HR-MS (FAB+) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{25}^{79}\text{BrOSi}$: 412.0858, found: 412.0840.



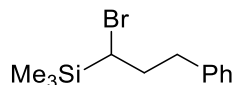
(1-Bromo-3-phenylpropyl)(methyl)diphenylsilane. The title compound was synthesized according to **General Procedure E** from 1-(methyldiphenylsilyl)-3-phenylpropan-1-ol (1.00 g, 3.01 mmol). The product was purified by flash chromatography (0 → 5% EtOAc in hexanes), which provided 2.03 g (86% yield) of a colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.55 – 7.48 (m, 4H), 7.46 – 7.27 (m, 8H), 7.24 – 7.17 (m, 1H), 7.17 – 7.10 (m, 2H), 3.68 (dd, J = 11.8, 2.7 Hz, 1H), 3.01 (ddd, J = 12.9, 8.0, 4.4 Hz, 1H), 2.77 – 2.69 (m, 1H), 2.23 – 1.97 (m, 2H), 0.71 (s, 3H);

^{13}C NMR (101 MHz, CDCl_3) δ 141.1, 135.4, 135.3, 134.6, 134.3, 130.13, 130.07, 129.1, 128.8, 128.3, 128.2, 126.4, 40.7, 35.4, 35.1, -5.2;

FT-IR (thin film) 3069, 2962, 1603, 1589, 1496, 1454, 1428, 1260, 1113, 1029, 998 cm^{-1} ;

HR-MS (FAB+) m/z $[\text{M}-\text{C}_6\text{H}_6]^+$ calcd for $\text{C}_{16}\text{H}_{17}^{79}\text{BrSi}$: 316.0283, found: 316.0296.



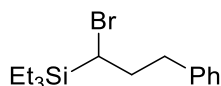
(1-Bromo-3-phenylpropyl)trimethylsilane. The title compound was synthesized according to **General Procedure E** from 3-phenyl-1-(trimethylsilyl)propan-1-ol (1.65 g, 7.9 mmol). The product was purified by flash chromatography (0 \rightarrow 1% EtOAc in hexanes), which provided 1.80 g (84% yield) of a colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.36 – 7.28 (m, 2H), 7.27 – 7.20 (m, 3H), 3.23 (dd, J = 11.5, 3.3 Hz, 1H), 3.08 (ddd, J = 13.3, 8.4, 4.7 Hz, 1H), 2.76 (ddd, J = 13.6, 8.7, 7.6 Hz, 1H), 2.17 – 1.94 (m, 2H), 0.15 (s, 9H);

^{13}C NMR (101 MHz, CDCl_3) δ 141.5, 129.0, 128.8, 126.3, 44.6, 35.54, 35.46, -2.7;

FT-IR (thin film) 3027, 2955, 1604, 1496, 1454, 1250, 1110, 1075, 1030, 867, 840 cm^{-1} ;

HR-MS (EI+) m/z $[\text{M}]^+$ calcd for $\text{C}_{12}\text{H}_{19}^{79}\text{BrSi}$: 270.0439, found: 270.0419.



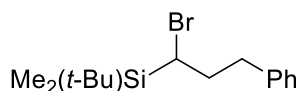
(1-Bromo-3-phenylpropyl)triethylsilane. The title compound was synthesized according to **General Procedure E** from 3-phenyl-1-(triethylsilyl)propan-1-ol (4.8 g, 19.3 mmol). The product was purified by flash chromatography (0 \rightarrow 2% EtOAc in hexanes), which provided 3.38 g (56% yield) of a colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.33 – 7.27 (m, 2H), 7.25 – 7.18 (m, 3H), 3.37 – 3.27 (m, 1H), 3.07 (ddd, J = 13.3, 7.3, 5.5 Hz, 1H), 2.71 (dt, J = 13.6, 8.1 Hz, 1H), 2.14 – 1.98 (m, 2H), 0.96 (t, J = 7.9 Hz, 9H), 0.68 (q, J = 7.4, 6H);

^{13}C NMR (101 MHz, CDCl_3) δ 141.5, 129.0, 128.8, 126.3, 42.1, 35.9, 35.7, 7.8, 2.9;

FT-IR (thin film) 3027, 2955, 1604, 1496, 1454, 1415, 1260, 1096, 1019, 804 cm^{-1} ;

HR-MS (FAB+) m/z $[\text{M}]^+$ calcd for $\text{C}_{15}\text{H}_{25}^{79}\text{BrSi}$: 312.0909, found: 312.0918.



(1-Bromo-3-phenylpropyl)(tert-butyl)dimethylsilane. The title compound was synthesized according to **General Procedure E** from 1-(tert-butyl)dimethylsilyl-3-

phenylpropan-1-ol (2.00 g, 8.00 mmol). The product was purified by flash chromatography (0 → 1% EtOAc in hexanes), which provided 1.94 g (77% yield) of a colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.33 – 7.28 (m, 2H), 7.25 – 7.18 (m, 3H), 3.34 (dd, J = 11.8, 2.8 Hz, 1H), 3.07 (ddd, J = 13.3, 8.5, 4.5 Hz, 1H), 2.74 (ddd, J = 13.5, 8.7, 7.6 Hz, 1H), 2.22 – 1.96 (m, 2H), 0.93 (s, 9H), 0.13 (s, 3H), 0.07 (s, 3H);

^{13}C NMR (101 MHz, CDCl_3) δ 141.5, 129.0, 128.8, 126.4, 42.6, 36.7, 35.6, 27.7, 17.9, –5.6, –6.9;

FT-IR (thin film) 3027, 2958, 2930, 1604, 1496, 1470, 1364, 1259, 1096, 1030, 823 cm^{-1} ;

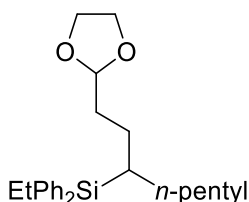
HR-MS (FAB+) m/z $[\text{M}-\text{C}(\text{CH}_3)_3]^+$ calcd for $\text{C}_{11}\text{H}_{16}^{79}\text{BrSi}$: 255.0205, found: 255.0208.

III. Cross-Couplings

Preparation of alkylzinc reagent. An oven-dried 40 mL vial was charged with Zn⁰ powder (3.0 equiv) and a cross-shaped stir bar. The vial was then sealed with a pierceable septum cap and placed under vacuum on a Schlenk line. Next, the vial was heated with a heat gun for ~4 min, and then it was allowed to cool to room temperature under vacuum. With the aid of an argon-filled balloon, the vial was placed under an argon atmosphere, and then anhydrous DMA was added (1.0 mL/mmol of alkyl bromide, including the 1.0 mL used for the solution of I₂). To this stirring suspension of Zn⁰ powder was added a solution of I₂ (0.050 equiv in 1.0 mL of DMA); the mixture was allowed to stir until the yellow color dissipated. Then, the alkyl bromide (1.0 equiv) was added, vacuum grease was applied to the septum punctures to minimize leakage, and the reaction mixture was warmed to 50 °C and stirred for 16 h. After cooling to room temperature, the argon-filled balloon was removed, and the reaction mixture was brought into a glovebox. The suspension was passed through syringe filters (1-micron and then 0.45-micron) to remove residual zinc powder. The alkylzinc bromide solution (can range from nearly colorless to dark red or dark green) was then titrated with a known amount of I₂ in THF (1.0 mL).¹²

General Procedure. An oven-dried 4-mL vial was charged with the α -bromosilane (0.50 mmol), followed by NiBr₂-diglyme (15.4 mg, 0.050 mmol) and then L* (21.4 mg, 0.065 mmol). Next, an oven-dried stir bar was added, and the reaction vial was capped with a pierceable septum cap and wrapped with electrical tape. The reaction vial was placed under high vacuum on a Schlenk line for 10 min. Next, with the aid of an argon-filled balloon, the vial was placed under an argon atmosphere (running the reaction under an atmosphere of nitrogen can lead to lower reproducibility). Then, anhydrous DMA (2.1 mL) was added, and the reaction mixture was allowed to stir for 15 min, after which it appeared cloudy and orange (the reaction mixture should be orange; if there is contamination by oxygen, the reaction mixture may appear nearly colorless). Next, the solution of the alkylzinc bromide (0.60 mmol; the use of solutions between 0.70 M and 1.00 M is recommended) was added as a stream over 10–20 seconds, leading to a dark red-black/brown reaction mixture (if there is contamination by oxygen, the reaction mixture may appear bright red). Vacuum grease was then liberally applied to cover the punctures in the septum cap, the argon balloon was removed, and vacuum grease was applied to cover the puncture. The reaction mixture was then stirred at room temperature at ~800 rpm for 20 h. Next, the reaction mixture was directly transferred to a column of silica gel for purification without any additional workup.

(12) Son, S.; Fu, G. C. *J. Am. Chem. Soc.* **2008**, *130*, 2756–2757.



(1-(1,3-Dioxolan-2-yl)octan-3-yl)(ethyl)diphenylsilane (Table 2, entry 1). The title compound was synthesized according to the General Procedure from (1-bromohexyl)(ethyl)diphenylsilane (188 mg, 0.500 mmol) and (2-(1,3-dioxolan-2-yl)ethyl)zinc bromide (0.600 mmol). The product was purified by flash chromatography (0 → 3% EtOAc in hexanes). Colorless oil.

(*S,S*)-L*: 122 mg (62% yield), +90% ee; (*R,R*)-L*: 133 mg (67% yield), -91% ee.

SFC analysis: The ee was determined via SFC on a CHIRALCEL OJ column (5% *i*-PrOH in supercritical CO₂, 3.5 mL/min) with *t_r* = 3.2 min (major (*S,S*)-L*), 3.7 min (major (*R,R*)-L*).

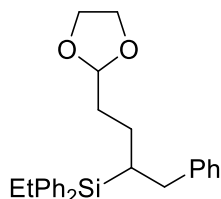
¹H NMR (400 MHz, CDCl₃) δ 7.58–7.47 (m, 4H), 7.42–7.29 (m, 6H), 4.73 (t, *J* = 4.5 Hz, 1H), 3.97–3.85 (m, 2H), 3.85–3.75 (m, 2H), 1.79–1.65 (m, 2H), 1.65–1.50 (m, 2H), 1.49–1.38 (m, 1H), 1.38–1.25 (m, 3H), 1.25–1.13 (m, 5H), 1.13–1.06 (m, 2H), 0.96 (t, *J* = 7.7 Hz, 3H), 0.82 (t, *J* = 6.9 Hz, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 135.8, 135.70, 135.68, 135.6, 129.22, 129.21, 127.89, 127.88, 105.0, 65.01, 64.99, 34.1, 32.4, 30.0, 29.5, 24.5, 23.0, 22.8, 14.3, 7.9, 4.5;

FT-IR (thin film) 3068, 2953, 2929, 2873, 1456, 1428, 1140, 1109, 1036, 944 cm⁻¹;

HR-MS (FAB+) *m/z* [M+H]⁺-H₂ calcd for C₂₅H₃₅O₂Si: 395.2406, found: 395.2392;

[α]²³_D = -0.8 (*c* = 0.72, CHCl₃); +90% ee from (*S,S*)-L*.



(4-(1,3-Dioxolan-2-yl)-1-phenylbutan-2-yl)(ethyl)diphenylsilane (Table 2, entry 2). The title compound was synthesized according to the General Procedure from (1-bromo-2-phenylethyl)(ethyl)diphenylsilane (198 mg, 0.500 mmol) and (2-(1,3-dioxolan-2-yl)ethyl)zinc bromide (0.600 mmol). The product was purified by flash chromatography (10 → 15% EtOAc in hexanes). Colorless waxy solid.

(*S,S*)-L*: 136 mg (65% yield), +93% ee; (*R,R*)-L*: 135 mg (65% yield), -94% ee.

SFC analysis: The ee was determined via SFC on a CHIRALPAK IC-3 column (2% *i*-PrOH in supercritical CO₂, 3.5 mL/min) with *t_r* = 13.6 min (major (*S,S*)-L*), 16.2 min (major (*R,R*)-L*).

¹H NMR (400 MHz, CDCl₃) δ 7.61 – 7.54 (m, 4H), 7.43 – 7.34 (m, 6H), 7.25 – 7.20 (m, 2H), 7.17 – 7.12 (m, 3H), 4.59 (t, *J* = 4.6 Hz, 1H), 3.87 – 3.77 (m, 2H), 3.77 – 3.68 (m, 2H), 2.93 (dd, *J* =

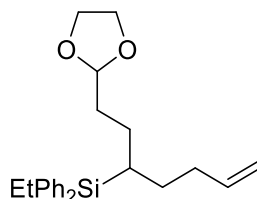
14.1, 3.9 Hz, 1H), 2.46 (dd, $J = 14.1, 10.1$ Hz, 1H), 1.76 – 1.62 (m, 2H), 1.50 – 1.39 (m, 3H), 1.06 (q, $J = 7.3$ Hz, 2H), 0.93 (t, $J = 7.6$ Hz, 3H);

^{13}C NMR (101 MHz, CDCl_3) δ 142.7, 135.50, 135.46, 135.0, 134.9, 129.2, 128.78, 128.77, 128.2, 127.80, 127.79, 125.7, 104.7, 64.7, 64.6, 36.4, 33.6, 25.1, 24.0, 7.6, 4.3;

FT-IR (thin film) 3023, 2952, 2874, 1601, 1495, 1493, 1427, 1134, 1108, 1030, 944 cm^{-1} ;

HR-MS (FAB+) m/z $[\text{M}+\text{H}]^+ - \text{H}_2$ calcd for $\text{C}_{27}\text{H}_{31}\text{O}_2\text{Si}$: 415.2093, found: 415.2073;

$[\alpha]^{23}_{\text{D}} = -1.4$ ($c = 0.50$, CHCl_3); +93% ee from (*S,S*)-**L***.



(1-(1,3-Dioxolan-2-yl)hept-6-en-3-yl)(ethyl)diphenylsilane (Table 2, entry 3). The title compound was synthesized according to the General Procedure from (1-bromopent-4-en-1-yl)(ethyl)diphenylsilane (180 mg, 0.500 mmol) and (2-(1,3-dioxolan-2-yl)ethyl)zinc bromide (0.600 mmol). The product was purified by flash chromatography (5% EtOAc in hexanes). Colorless oil.

(*S,S*)-**L***: 100 mg (53% yield), –90% ee; (*R,R*)-**L***: 104 mg (55% yield), +92% ee.

SFC analysis: The ee was determined via SFC on a CHIRALCEL OJ column (7% *i*-PrOH in supercritical CO_2 , 3.5 mL/min) with $t_{\text{r}} = 7.0$ min (major (*S,S*)-**L***), 3.5 min (major (*R,R*)-**L***).

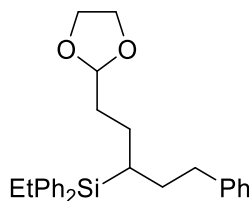
^1H NMR (400 MHz, CDCl_3) δ 7.58 – 7.48 (m, 4H), 7.42 – 7.31 (m, 6H), 5.71 (ddt, $J = 17.0, 10.2, 6.7$ Hz, 1H), 4.98 – 4.86 (m, 2H), 4.74 (t, $J = 4.5$ Hz, 1H), 3.96 – 3.84 (m, 2H), 3.87 – 3.74 (m, 2H), 2.16 – 2.04 (m, 1H), 2.03 – 1.92 (m, 1H), 1.79 – 1.63 (m, 3H), 1.62 – 1.53 (m, 1H), 1.51 – 1.37 (m, 2H), 1.37 – 1.29 (m, 1H), 1.12 (q, $J = 7.8$ Hz, 2H), 0.96 (t, $J = 7.7$ Hz, 3H);

^{13}C NMR (101 MHz, CDCl_3) δ 139.0, 135.59, 135.55, 135.4, 135.3, 129.22, 129.20, 127.85, 127.84, 114.7, 104.9, 64.93, 64.90, 33.9, 33.6, 29.4, 24.1, 22.2, 7.8, 4.3;

FT-IR (thin film) 3069, 2952, 2925, 2875, 1427, 1415, 1139, 1108, 1038, 998, 911 cm^{-1} ;

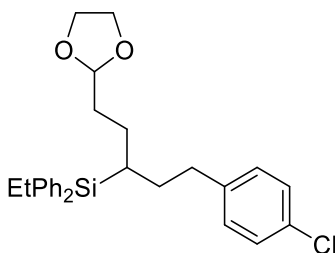
HR-MS (ESI+) m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{24}\text{H}_{32}\text{NaO}_2\text{Si}$: 403.2069, found: 403.2066;

$[\alpha]^{23}_{\text{D}} = +4.0$ ($c = 0.72$, CHCl_3); –90% ee from (*S,S*)-**L***.



(1-(1,3-Dioxolan-2-yl)-5-phenylpentan-3-yl)(ethyl)diphenylsilane (Table 2, entry 4). The title compound was synthesized according to the General Procedure from (1-bromo-3-

HR-MS (FAB+) m/z $[M+H]^+-H_2$ calcd for $C_{29}H_{35}O_3Si$: 459.2356, found: 459.2345;
 $[\alpha]^{23}_D = +11.9$ ($c = 0.52$, $CHCl_3$); -90% ee from (*S,S*)-**L***.



(1-(4-Chlorophenyl)-5-(1,3-dioxolan-2-yl)pentan-3-yl)(ethyl)diphenylsilane (Table 2, entry 6). The title compound was synthesized according to the General Procedure from (1-bromo-3-(4-chlorophenyl)propyl)(ethyl)diphenylsilane (222 mg, 0.500 mmol) and (2-(1,3-dioxolan-2-yl)ethyl)zinc bromide (0.600 mmol). The product was purified by flash chromatography (0 → 5% EtOAc in hexanes). Colorless oil.

(*S,S*)-**L***: 116 mg (50% yield), -90% ee; (*R,R*)-**L***: 140 mg (60% yield), +92% ee.

SFC analysis: The ee was determined via SFC on a CHIRALCEL OJ column (35% *i*-PrOH in supercritical CO_2 , 3.5 mL/min) with $t_r = 10.7$ min (major (*S,S*)-**L***), 4.8 min (major (*R,R*)-**L***).

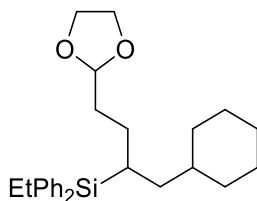
1H NMR (400 MHz, $CDCl_3$) δ 7.56–7.44 (m, 4H), 7.43–7.29 (m, 6H), 7.20 (d, $J = 8.3$ Hz, 2H), 6.95 (d, $J = 8.3$ Hz, 2H), 4.76 (t, $J = 4.6$ Hz, 1H), 3.98–3.87 (m, 2H), 3.87–3.77 (m, 2H), 2.60 (ddd, $J = 13.7, 10.3, 5.1$ Hz, 1H), 2.45 (ddd, $J = 13.7, 10.3, 6.6$ Hz, 1H), 1.92–1.67 (m, 3H), 1.66–1.46 (m, 3H), 1.34 (ddt, $J = 8.7, 7.6, 4.5$ Hz, 1H), 1.16–1.08 (m, 2H), 0.96 (t, $J = 7.8$ Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.2, 135.7, 135.6, 135.4, 135.2, 131.5, 130.0, 129.42, 129.38, 128.5, 128.02, 128.00, 104.8, 65.1, 65.0, 35.1, 33.9, 32.2, 24.2, 22.4, 7.9, 4.4;

FT-IR (thin film) 3068, 2950, 2874, 1491, 1427, 1134, 1108, 1037, 1014, 808 cm^{-1} ;

HR-MS (FAB+) m/z $[M+H]^+-H_2$ calcd for $C_{28}H_{32}ClO_2Si$: 463.1860, found: 463.1869;

$[\alpha]^{23}_D = +14.8$ ($c = 0.47$, $CHCl_3$); -90% ee from (*S,S*)-**L***.



(1-Cyclohexyl-4-(1,3-dioxolan-2-yl)butan-2-yl)(ethyl)diphenylsilane (Table 2, entry 7). The title compound was synthesized according to the General Procedure from (1-bromo-2-cyclohexylethyl)(ethyl)diphenylsilane (201 mg, 0.500 mmol) and (2-(1,3-dioxolan-2-yl)ethyl)zinc bromide (0.600 mmol). The product was purified by flash chromatography (0 → 3% EtOAc in hexanes). Colorless oil.

(*S,S*)-**L***: 132 mg (62% yield), +90% ee; (*R,R*)-**L***: 119 mg (56% yield), -91% ee.

SFC analysis: The ee was determined via SFC on a CHIRALCEL OJ column (5% *i*-PrOH in supercritical CO₂, 3.5 mL/min) with *t_r* = 4.7 min (major (*S,S*)-L*), 5.6 min (major (*R,R*)-L*).

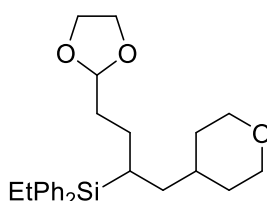
¹H NMR (400 MHz, CDCl₃) δ 7.58–7.49 (m, 4H), 7.42–7.31 (m, 6H), 4.71 (t, *J* = 4.6 Hz, 1H), 3.95–3.85 (m, 2H), 3.85–3.75 (m, 2H), 1.78 (d, *J* = 13.0 Hz, 1H), 1.74–1.53 (m, 7H), 1.48–1.32 (m, 3H), 1.30–1.07 (m, 7H), 0.96 (t, *J* = 7.7 Hz, 3H), 0.88–0.64 (m, 2H);

¹³C NMR (101 MHz, CDCl₃) δ 135.74, 135.67, 135.66, 135.6, 129.22, 129.19, 127.88, 127.86, 105.0, 65.0 (two carbons), 38.2, 36.4, 34.6, 34.0, 32.9, 26.9, 26.65, 26.57, 24.9, 19.3, 7.9, 4.4;

FT-IR (thin film) 3068, 2922, 2851, 1448, 1428, 1260, 1229, 1131, 1108, 1033, 945 cm⁻¹;

HR-MS (FAB+) *m/z* [M+H]⁺–H₂ calcd for C₂₇H₃₇O₂Si: 421.2563, found: 421.2576;

[α]²³_D = –4.1 (*c* = 0.48, CHCl₃); +90% ee from (*S,S*)-L*.



(4-(1,3-Dioxolan-2-yl)-1-(tetrahydro-2H-pyran-4-yl)butan-2-yl)(ethyl)diphenylsilane (Table 2, entry 8). The title compound was synthesized according to the General Procedure from (1-bromo-2-(tetrahydro-2H-pyran-4-yl)ethyl)(ethyl)diphenylsilane (202 mg, 0.500 mmol) and (2-(1,3-dioxolan-2-yl)ethyl)zinc bromide (0.600 mmol). The product was purified by flash chromatography (5 → 15% EtOAc in hexanes). Colorless oil.

(*S,S*)-L*: 136 mg (64% yield), –91% ee; (*R,R*)-L*: 150 mg (71% yield), +92% ee.

SFC analysis: The ee was determined via SFC on a CHIRALCEL OJ column (10% *i*-PrOH in supercritical CO₂, 3.5 mL/min) with *t_r* = 23.6 min (major (*S,S*)-L*), 3.4 min (major (*R,R*)-L*).

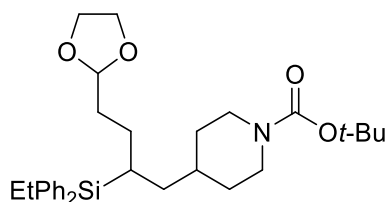
¹H NMR (400 MHz, CDCl₃) δ 7.57–7.47 (m, 4H), 7.42–7.30 (m, 6H), 4.71 (t, *J* = 4.6 Hz, 1H), 3.96–3.74 (m, 6H), 3.25 (tdd, *J* = 11.4, 9.3, 2.2 Hz, 2H), 1.78–1.52 (m, 4H), 1.51–1.36 (m, 5H), 1.30–1.15 (m, 2H), 1.14–1.03 (m, 3H), 0.95 (t, *J* = 7.7 Hz, 3H);

¹³C NMR (101 MHz CDCl₃) δ 135.7, 135.6, 135.4, 135.2, 129.39, 129.36, 127.98, 127.97, 104.9, 68.33, 68.30, 65.024, 65.016, 37.7, 34.2, 34.0, 33.8, 32.8, 24.8, 19.0, 7.9, 4.3;

FT-IR (thin film) 3069, 2928, 2876, 1427, 1236, 1131, 1108, 1091, 1015, 982 cm⁻¹;

HR-MS (FAB+) *m/z* [M+H]⁺ calcd for C₂₆H₃₇O₃Si: 425.2512, found: 425.2527;

[α]²³_D = –4.8 (*c* = 0.52, CHCl₃); –91% ee from (*S,S*)-L*.



Tert-butyl 4-(4-(1,3-dioxolan-2-yl)-2-(ethyldiphenylsilyl)butyl)piperidine-1-carboxylate (Table 2, entry 9). The title compound was synthesized according to the General Procedure from *tert*-butyl 4-(2-bromo-2-(ethyldiphenylsilyl)ethyl)piperidine-1-carboxylate (251 mg, 0.500 mmol) and (2-(1,3-dioxolan-2-yl)ethyl)zinc bromide (0.600 mmol). The product was purified by flash chromatography (5 → 15% EtOAc in hexanes). Colorless oil.

(*S,S*)-L*: 178 mg (68% yield), –90% ee; (*R,R*)-L*: 180 mg (69% yield), +90% ee.

SFC analysis: The ee was determined via SFC on a CHIRALPAK AD-H column (10% *i*-PrOH in supercritical CO₂, 3.5 mL/min) with *t*_r = 4.6 min (major (*S,S*)-L*), 3.9 min (major (*R,R*)-L*).

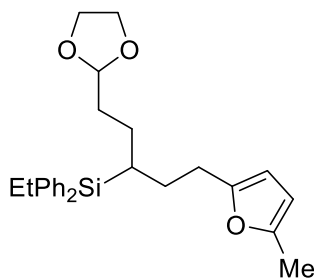
¹H NMR (500 MHz, *d*₆-DMSO, 75 °C) δ 6.98 – 6.88 (m, 4H), 6.85 – 6.75 (m, 6H), 4.16 – 3.96 (m, 1H), 3.23 – 3.07 (m, 4H), 2.02 – 1.88 (m, 4H), 1.10 – 1.01 (m, 2H), 1.00 – 0.74 (m, 16H), 0.69 – 0.59 (m, 1H), 0.53 (q, *J* = 8.0, 2.5 Hz, 2H), 0.37 (t, *J* = 7.6 Hz, 3H), 0.32 – 0.13 (m, 2H);

¹³C NMR (126 MHz, *d*₆-DMSO, 75 °C) δ 154.5, 135.7, 135.63, 135.56, 135.5, 129.68, 129.66, 128.34, 128.33, 104.4, 79.0, 64.75, 64.72, 44.2 (br; two carbons), 37.5, 34.9, 33.9, 33.1, 32.0, 28.8, 25.2, 19.8, 8.1, 4.0;

FT-IR (thin film) 3069, 2929, 2875, 1693, 1427, 1365, 1281, 1241, 1169, 1109, 1033, 947 cm⁻¹;

HR-MS (FAB+) *m/z* [M+H]⁺–H₂ calcd for C₃₁H₄₄NO₄Si: 522.3040, found: 522.3051;

[α]_D²³ = +8.2 (*c* = 0.56, CHCl₃); –90% ee from (*S,S*)-L*.



(1-(1,3-Dioxolan-2-yl)-5-(5-methylfuran-2-yl)pentan-3-yl)(ethyl)diphenylsilane (Table 2, entry 10). The title compound was synthesized according to the General Procedure from (1-bromo-3-(5-methylfuran-2-yl)propyl)(ethyl)diphenylsilane (207 mg, 0.500 mmol) and (2-(1,3-dioxolan-2-yl)ethyl)zinc bromide (0.600 mmol). The product was purified by flash chromatography (0 → 5% EtOAc in hexanes). Pale-yellow oil.

(*S,S*)-L*: 152 mg (70% yield), –89% ee; (*R,R*)-L*: 158 mg (73% yield), +91% ee.

SFC analysis: The ee was determined via SFC on a CHIRALCEL OJ column (15% *i*-PrOH in supercritical CO₂, 3.5 mL/min) with *t*_r = 11.6 min (major (*S,S*)-L*), 8.1 min (major (*R,R*)-L*).

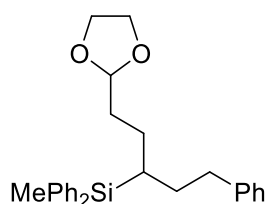
^1H NMR (400 MHz, CDCl_3) δ 7.54–7.45 (m, 4H), 7.41–7.30 (m, 6H), 5.82 (dd, $J = 3.0, 1.0$ Hz, 1H), 5.76 (d, $J = 3.0$ Hz, 1H), 4.73 (t, $J = 4.6$ Hz, 1H), 3.95–3.85 (m, 2H), 3.85–3.75 (m, 2H), 2.60 (ddd, $J = 14.7, 9.3, 5.4$ Hz, 1H), 2.50 (ddd, $J = 15.8, 8.7, 7.2$ Hz, 1H), 2.24 (d, $J = 0.6$ Hz, 3H), 1.93 (dddd, $J = 13.8, 9.3, 7.0, 4.3$ Hz, 1H), 1.80–1.56 (m, 4H), 1.52–1.40 (m, 1H), 1.34 (ddt, $J = 8.4, 7.2, 4.3$ Hz, 1H), 1.11 (q, $J = 7.8$ Hz, 2H), 0.94 (t, $J = 7.8$ Hz, 3H);

^{13}C NMR (101 MHz, CDCl_3) δ 154.4, 150.4, 135.7, 135.6, 135.4, 135.3, 129.4, 129.3, 127.97, 125.95, 105.9, 105.8, 104.9, 65.03, 65.00, 33.9, 28.6, 27.8, 24.1, 21.9, 13.8, 7.9, 4.4;

FT-IR (thin film) 3068, 2951, 2875, 1568, 1427, 1218, 1134, 1108, 1021, 943 cm^{-1} ;

HR-MS (FAB+) m/z $[\text{M}+\text{H}]^+ - \text{H}_2$ calcd for $\text{C}_{27}\text{H}_{33}\text{O}_3\text{Si}$: 433.2199, found: 433.2181;

$[\alpha]^{23}_{\text{D}} = -3.8$ ($c = 0.58$, CHCl_3); -89% ee from (*S,S*)-**L***.



(1-(1,3-Dioxolan-2-yl)-5-phenylpentan-3-yl)(methyl)diphenylsilane (Table 2, entry 11).

The title compound was synthesized according to the General Procedure from (1-bromo-3-phenylpropyl)(methyl)diphenylsilane (198 mg, 0.500 mmol) and (2-(1,3-dioxolan-2-yl)ethyl)zinc bromide (0.600 mmol). The product was purified by flash chromatography (0 \rightarrow 7% EtOAc in hexanes). Colorless oil.

(*S,S*)-**L***: 163 mg (78% yield), -86% ee; (*R,R*)-**L***: 170 mg (82% yield), $+84\%$ ee.

HPLC analysis: The ee was determined via SFC on a CHIRALCEL OJ column (15% *i*-PrOH in hexane, 3.5 mL/min) with $t_{\text{r}} = 8.7$ min (major (*S,S*)-**L***), 4.4 min (major (*R,R*)-**L***).

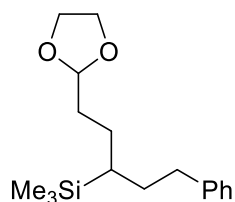
^1H NMR (400 MHz, CDCl_3) δ 7.58 – 7.47 (m, 4H), 7.43 – 7.30 (m, 6H), 7.26 – 7.21 (m, 2H), 7.20 – 7.13 (m, 1H), 7.07 – 6.98 (m, 2H), 4.76 (t, $J = 4.3$ Hz, 1H), 4.00 – 3.87 (m, 2H), 3.86 – 3.75 (m, 2H), 2.64 (ddd, $J = 13.4, 10.5, 5.2$ Hz, 1H), 2.47 (ddd, $J = 13.4, 10.5, 6.3$ Hz, 1H), 1.95 – 1.57 (m, 6H), 1.35 (tt, $J = 7.2, 4.7$ Hz, 1H), 0.61 (s, 3H);

^{13}C NMR (101 MHz, CDCl_3) δ 142.8, 137.0, 136.8, 135.02, 134.95, 129.35, 129.32, 128.7, 128.4, 128.03, 128.02, 125.9, 104.9, 65.01, 64.99, 35.7, 33.7, 32.2, 24.2, 23.4, -5.1 ;

FT-IR (thin film) 3067, 3023, 2924, 2858, 1602, 1495, 1454, 1427, 1252, 1133, 1110, 1038, 944, 873 cm^{-1} ;

HR-MS (ESI+) m/z $[\text{M}+\text{H}]^+ - \text{H}_2$ calcd for $\text{C}_{27}\text{H}_{31}\text{O}_2\text{Si}$: 415.2093, found: 415.2083;

$[\alpha]^{23}_{\text{D}} = -5.3$ ($c = 0.53$, CHCl_3); -86% ee from (*S,S*)-**L***.



(1-(1,3-Dioxolan-2-yl)-5-phenylpentan-3-yl)trimethylsilane (Table 2, entry 12). The title compound was synthesized according to the General Procedure from (1-bromo-3-phenylpropyl)trimethylsilane (137 mg, 0.500 mmol) and (2-(1,3-dioxolan-2-yl)ethyl)zinc bromide (0.600 mmol). The product was purified by flash chromatography (0 → 2% EtOAc in hexanes). Colorless oil.

(*S,S*)-L*: 114 mg (78% yield), +86% ee; (*R,R*)-L*: 121 mg (83% yield), -84% ee.

SFC analysis: The ee was determined via SFC on a CHIRALPAK AD-H column (2% *i*-PrOH in supercritical CO₂, 3.5 mL/min) with *t_r* = 2.5 min (major (*S,S*)-L*), 2.8 min (major (*R,R*)-L*).

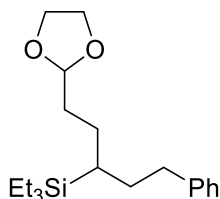
¹H NMR (400 MHz, CDCl₃) δ 7.33 – 7.25 (m, 2H), 7.21 – 7.15 (m, 3H), 4.84 (t, *J* = 4.7 Hz, 1H), 4.03 – 3.94 (m, 2H), 3.92 – 3.81 (m, 2H), 2.70 (ddd, *J* = 13.5, 10.9, 5.3 Hz, 1H), 2.56 (ddd, *J* = 13.5, 10.9, 6.0 Hz, 1H), 1.82 – 1.45 (m, 6H), 0.67 (tt, *J* = 7.4, 5.1 Hz, 1H), 0.03 (s, 9H);

¹³C NMR (101 MHz, CDCl₃) δ 143.2, 128.6, 128.5, 125.9, 105.1, 65.08, 65.06, 35.7, 33.5, 32.0, 25.5, 24.0, -1.9;

FT-IR (thin film) 3026, 2950, 2859, 1603, 1496, 1454, 1407, 1248, 1135, 1092, 1040, 944, 855, 834 cm⁻¹;

HR-MS (ESI+) *m/z* [M+H]⁺-H₂ calcd for C₁₇H₂₇O₂Si: 291.1780, found: 291.1782;

[α]²³_D = -6.7 (*c* = 0.68, CHCl₃); +86% ee from (*S,S*)-L*.



(1-(1,3-Dioxolan-2-yl)-5-phenylpentan-3-yl)triethylsilane (Table 2, entry 13). The title compound was synthesized according to the General Procedure from (1-bromo-3-phenylpropyl)triethylsilane (157 mg, 0.500 mmol) and (2-(1,3-dioxolan-2-yl)ethyl)zinc bromide (0.600 mmol). The product was purified by flash chromatography (0 → 5% EtOAc in hexanes). Colorless oil.

(*S,S*)-L*: 77 mg (46% yield), +92% ee; (*R,R*)-L*: 92 mg (55% yield), -89% ee.

SFC analysis: The ee was determined via SFC on a CHIRALCEL OJ column (1% *i*-PrOH in supercritical CO₂, 3.5 mL/min) with *t_r* = 6.1 min (major (*S,S*)-L*), 7.3 min (major (*R,R*)-L*).

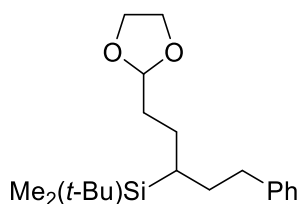
¹H NMR (400 MHz, CDCl₃) δ 7.31 – 7.23 (m, 2H), 7.21 – 7.12 (m, 3H), 4.83 (t, *J* = 4.7 Hz, 1H), 4.07 – 3.92 (m, 2H), 3.91 – 3.79 (m, 2H), 2.71 (ddd, *J* = 13.4, 11.0, 5.1 Hz, 1H), 2.54 (ddd, *J* = 13.4,

10.9, 5.9 Hz, 1H), 1.84 – 1.44 (m, 6H), 0.94 (t, J = 7.9 Hz, 9H), 0.80 – 0.76 (m, 1H), 0.58 (q, J = 8.1 Hz, 6H);

^{13}C NMR (101 MHz, CDCl_3) δ 143.2, 128.6, 128.5, 125.9, 105.1, 65.11, 65.08, 36.1, 34.0, 32.3, 24.2, 22.7, 8.0, 3.1;

FT-IR (thin film) 3026, 2951, 2910, 2874, 1496, 1454, 1413, 1238, 1137, 1092, 1040, 1016, 944, 872 cm^{-1} ;

HR-MS (ESI+) m/z $[\text{M}+\text{H}]^+-\text{H}_2$ calcd for $\text{C}_{20}\text{H}_{33}\text{O}_2\text{Si}$: 333.2250, found: 333.2250;
 $[\alpha]^{23}_{\text{D}} = -7.0$ ($c = 0.49$, CHCl_3); +92% ee from (*S,S*)-**L***.



(1-(1,3-Dioxolan-2-yl)-5-phenylpentan-3-yl)(*tert*-butyl)dimethylsilane (Table 2, entry 14).

The title compound was synthesized according to the General Procedure from (1-bromo-3-phenylpropyl)(*tert*-butyl)dimethylsilane (157 mg, 0.500 mmol) and (2-(1,3-dioxolan-2-yl)ethyl)zinc bromide (0.600 mmol). The product was purified by flash chromatography (0 → 2% EtOAc in hexanes). Colorless oil.

(*S,S*)-**L***: 46 mg (27% yield), +84% ee; (*R,R*)-**L***: 39 mg (23% yield), –85% ee.

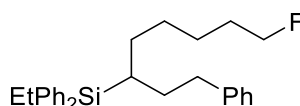
SFC analysis: The ee was determined via SFC on a CHIRALCEL OJ column (1% *i*-PrOH in supercritical CO_2 , 3.5 mL/min) with $t_r = 3.4$ min (major (*S,S*)-**L***), 3.8 min (major (*R,R*)-**L***).

^1H NMR (400 MHz, CDCl_3) δ 7.31 – 7.24 (m, 2H), 7.22 – 7.15 (m, 3H), 4.84 (t, J = 4.4 Hz, 1H), 4.04 – 3.94 (m, 2H), 3.92 – 3.80 (m, 2H), 2.71 (ddd, J = 13.4, 11.1, 5.0 Hz, 1H), 2.54 (ddd, J = 13.5, 11.0, 5.9 Hz, 1H), 1.89 – 1.47 (m, 6H), 0.89 (s, 9H), 0.87 – 0.81 (m, 1H), –0.01 (s, 6H);

^{13}C NMR (101 MHz, CDCl_3) δ 143.1, 128.6, 128.5, 125.9, 105.1, 65.11, 65.08, 35.6, 33.4, 32.4, 27.5, 24.2, 22.4, 17.7, –6.0;

FT-IR (thin film) 3026, 2953, 2928, 2856, 1496, 1471, 1409, 1362, 1250, 1138, 1040, 941, 837, 806 cm^{-1} ;

HR-MS (ESI+) m/z $[\text{M}+\text{H}]^+-\text{H}_2$ calcd for $\text{C}_{20}\text{H}_{33}\text{O}_2\text{Si}$: 333.2250, found: 333.2235;
 $[\alpha]^{23}_{\text{D}} = -5.5$ ($c = 0.74$, CHCl_3); +84% ee from (*S,S*)-**L***.



Ethyl(8-fluoro-1-phenyloctan-3-yl)diphenylsilane (Table 3, entry 1). The title compound was synthesized according to the General Procedure from (1-bromo-3-phenylpropyl)(ethyl)diphenylsilane (205 mg, 0.500 mmol) and (5-fluoropentyl)zinc bromide

(0.600 mmol). The product was purified by flash chromatography (0 → 25% CH₂Cl₂ in hexanes). Colorless oil.

(*S,S*)-L*: 125 mg (58% yield), -87% ee; (*R,R*)-L*: 118 mg (55% yield), +87% ee.

SFC analysis: The ee was determined via SFC on a CHIRALCEL OJ column (20% *i*-PrOH in supercritical CO₂, 3.5 mL/min) with *t_r* = 6.8 min (major (*S,S*)-L*), 5.5 min (major (*R,R*)-L*).

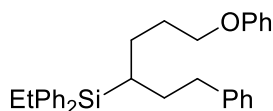
¹H NMR (400 MHz, CDCl₃) δ 7.55 – 7.46 (m, 4H), 7.43 – 7.31 (m, 6H), 7.28 – 7.22 (m, 2H), 7.20 – 7.14 (m, 1H), 7.09 – 7.02 (m, 2H), 4.38 (dt, *J* = 47.3, 6.2 Hz, 2H), 2.64 (ddd, *J* = 13.4, 10.6, 5.2 Hz, 1H), 2.50 (ddd, *J* = 13.4, 10.4, 6.3 Hz, 1H), 1.90 (dddd, *J* = 13.8, 10.6, 6.3, 4.3 Hz, 1H), 1.71 – 1.56 (m, 4H), 1.47 – 1.22 (m, 6H), 1.12 (q, *J* = 7.8 Hz, 2H), 0.97 (t, *J* = 7.7 Hz, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 142.7, 135.45, 135.42, 135.40, 134.9, 129.09, 129.07, 128.5, 128.3, 127.74, 127.72, 125.7, 84.2 (d, *J* = 164.1 Hz), 35.9, 32.2, 30.3 (d, *J* = 19.4 Hz), 29.8, 29.1, 25.5 (d, *J* = 5.5 Hz), 22.4, 7.7, 4.3;

FT-IR (thin film) 3024, 2932, 2857, 1455, 1428, 1108, 1010 cm⁻¹;

HR-MS (ESI+) *m/z* [M+Na]⁺ calcd for C₂₈H₃₅FNaSi: 441.2390, found: 441.2390;

[α]_D²³ = +8.1 (*c* = 0.70, CHCl₃); -87% ee from (*S,S*)-L*.



Ethyl(6-phenoxy-1-phenylhexan-3-yl)diphenylsilane (Table 3, entry 2). The title compound was synthesized according to the General Procedure from (1-bromo-3-phenylpropyl)(ethyl)diphenylsilane (205 mg, 0.500 mmol) and (3-phenoxypropyl)zinc bromide (0.600 mmol). The product was purified by flash chromatography with silica gel: column #1 (0 → 2% EtOAc in hexanes); column #2 (20 → 40% CH₂Cl₂ in hexanes). Colorless oil.

(*S,S*)-L*: 193 mg (83% yield), +87% ee; (*R,R*)-L*: 182 mg (78% yield), -89% ee.

SFC analysis: The ee was determined via SFC on a CHIRALCEL OD-H column (30% *i*-PrOH in supercritical CO₂, 3.5 mL/min) with *t_r* = 3.0 min (major (*S,S*)-L*), 3.8 min (major (*R,R*)-L*).

¹H NMR (400 MHz, CDCl₃) δ 7.59–7.47 (m, 4H), 7.44–7.32 (m, 6H), 7.31–7.22 (m, 4H), 7.17 (tt, *J* = 7.3, 1.3 Hz, 1H), 7.10–7.03 (m, 2H), 6.94 (tt, *J* = 7.3, 1.0 Hz, 1H), 6.90–6.83 (m, 2H), 3.94–3.81 (m, 2H), 2.66 (ddd, *J* = 13.6, 10.6, 5.2 Hz, 1H), 2.52 (ddd, *J* = 13.6, 10.4, 6.4 Hz, 1H), 2.00–1.49 (m, 6H), 1.41 (tt, *J* = 7.7, 4.4 Hz, 1H), 1.20–1.10 (m, 2H), 0.97 (t, *J* = 7.8 Hz, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 159.2, 142.8, 135.7, 135.6, 135.5, 135.4, 129.6, 129.4, 129.3, 128.7, 128.5, 128.00, 127.98, 125.9, 120.7, 114.7, 67.9, 35.9, 32.3, 29.2, 26.3, 22.3, 7.9, 4.4;

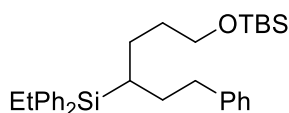
FT-IR (thin film) 3067, 3024, 2930, 2873, 1600, 1586, 1496, 1469, 1427, 1301, 1244, 1172, 1108, 1080, 1030 cm⁻¹;

HR-MS (FAB+) *m/z* [M+H]⁺-H₂ calcd for C₃₂H₃₅OSi: 463.2457, found: 463.2457;

[α]_D²³ = -0.6 (*c* = 0.60, CHCl₃); +87% ee from (*S,S*)-L*.

Gram-Scale Reaction. An oven-dried 1020-mL vial was charged with (1-bromo-3-phenylpropyl)(ethyl)diphenylsilane (1.64 g, 4.00 mmol), followed by NiBr₂·diglyme (123 mg,

0.400 mmol) and then (*S,S*)-L* (171 mg, 0.520 mmol). Next, an oven-dried stir bar was added, and the reaction vial was capped with a pierceable septum cap and wrapped with electrical tape. The reaction vial was placed under high vacuum on a Schlenk line for 10 min. Next, with the aid of an argon-filled balloon, the vial was placed under an argon atmosphere. Then, anhydrous DMA (8.8 mL; on a gram-scale, the reaction was conducted at a higher concentration) was added, and the reaction mixture was allowed to stir for 15 min, after which it appeared cloudy and orange. Next, (3-phenoxypropyl)zinc bromide (4.80 mmol) was added as a stream over 10–20 seconds, leading to a dark red-black/brown reaction mixture. Vacuum grease was then liberally applied to cover the punctures in the septum cap, the argon balloon was removed, and vacuum grease was applied to cover the puncture. The reaction mixture was then stirred at room temperature at ~800 rpm for 20 h. Next, the reaction mixture was directly transferred to a column of silica gel for purification without any additional workup. The reaction mixture was then purified by flash chromatography with silica gel: column #1 (0 → 2% EtOAc in hexanes); column #2 (20 → 40% CH₂Cl₂ in hexanes), which provided 1.66 g (89% yield) of a colorless oil (+88% ee).



Tert-butyl((4-(ethyl-diphenylsilyl)-6-phenylhexyl)oxy)dimethylsilane (Table 3, entry 3).

The title compound was synthesized according to the General Procedure from (1-bromo-3-phenylpropyl)(ethyl)diphenylsilane (205 mg, 0.500 mmol) and (3-((*tert*-butyldimethylsilyl)oxy)propyl)zinc bromide (0.600 mmol). The product was purified by flash chromatography (0 → 20% CH₂Cl₂ in hexanes). Colorless oil.

(*S,S*)-L*: 164 mg (65% yield), –87% ee; (*R,R*)-L*: 182 mg (73% yield), +88% ee.

SFC analysis: The ee was determined via SFC on a CHIRALCEL OJ column (10% *i*-PrOH in supercritical CO₂, 3.5 mL/min) with *t_r* = 3.4 min (major (*S,S*)-L*), 2.3 min (major (*R,R*)-L*).

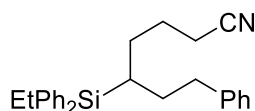
¹H NMR (400 MHz, CDCl₃) δ 7.57–7.45 (m, 4H), 7.41–7.30 (m, 6H), 7.27–7.21 (m, 2H), 7.20–7.13 (m, 1H), 7.08–7.02 (m, 2H), 3.54 (t, *J* = 6.0 Hz, 2H), 2.64 (ddd, *J* = 13.3, 10.8, 5.1 Hz, 1H), 2.49 (13.3, 10.5, 6.4 Hz, 1H), 1.89 (dddd, *J* = 14.0, 10.7, 6.4, 4.3 Hz, 1H), 1.76–1.56 (m, 3H), 1.53–1.39 (m, 2H), 1.39–1.31 (m, 1H), 1.12 (q, *J* = 7.8 Hz, 2H), 0.96 (t, *J* = 7.8 Hz, 3H), 0.88 (s, 9H), 0.02 (s, 6H);

¹³C NMR (101 MHz, CDCl₃) δ 143.0, 135.70, 135.68, 135.64, 135.60, 129.3, 129.2, 128.7, 128.5, 127.94, 127.93, 125.8, 63.6, 36.0, 33.0, 32.4, 26.23, 26.22, 22.5, 18.6, 7.9, 4.5, –5.00, –5.02;

FT-IR (thin film) 3068, 3025, 2953, 2929, 2856, 1462, 1427, 1386, 1255, 1107, 1008, 953, 836 cm⁻¹;

HR-MS (ESI+) *m/z* [M+Na]⁺ calcd for C₃₂H₄₆NaOSi₂: 525.2985, found: 525.2969;

[α]²³_D = +7.2 (*c* = 0.76, CHCl₃); –87% ee from (*S,S*)-L*.



5-(Ethyldiphenylsilyl)-7-phenylheptanenitrile (Table 3, entry 4). The title compound was synthesized according to the General Procedure from (1-bromo-3-phenylpropyl)(ethyl)diphenylsilane (205 mg, 0.500 mmol) and (3-cyanopropyl)zinc bromide (0.600 mmol). The product was purified by flash chromatography (3 → 5% EtOAc in hexanes). Colorless oil.

(*S,S*)-L*: 108 mg (54% yield), +88% ee; (*R,R*)-L*: 93 mg (47% yield), -86% ee.

SFC analysis: The ee was determined via SFC on a CHIRALCEL OJ column (45% MeOH in supercritical CO₂, 3.5 mL/min) with *t_r* = 7.2 min (major (*S,S*)-L*), 19.7 min (major (*R,R*)-L*).

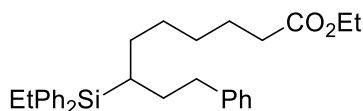
¹H NMR (400 MHz, CDCl₃) δ 7.58–7.45 (m, 4H), 7.45–7.31 (m, 6H), 7.29–7.23 (m, 2H), 7.22–7.14 (m, 1H), 7.11–7.02 (m, 2H), 2.63 (ddd, *J* = 13.7, 10.1, 5.4 Hz, 1H), 2.51 (ddd, *J* = 13.7, 10.1, 6.6 Hz, 1H), 2.28–2.12 (m, 2H), 1.93 (dddd, *J* = 14.2, 10.6, 6.6, 4.4 Hz, 1H), 1.80–1.71 (m, 1H), 1.70–1.58 (m, 2H), 1.58–1.47 (m, 2H), 1.38–1.28 (m, 1H), 1.13 (q, *J* = 7.8 Hz, 2H), 0.97 (t, *J* = 7.7 Hz, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 142.4, 135.56, 135.53, 134.95, 134.93, 129.57, 129.55, 128.7, 128.6, 128.14, 128.11, 126.1, 119.9, 35.8, 32.0, 29.5, 25.4, 22.3, 17.6, 7.9, 4.3;

FT-IR (thin film) 3067, 3024, 2931, 2873, 2244, 1454, 1427, 1108, 1010 cm⁻¹;

HR-MS (FAB+) *m/z* [M+H]⁺-H₂ calcd for C₂₇H₃₀NSi: 396.2148, found: 396.2142;

[α]_D²³ = +10.6 (*c* = 0.48, CHCl₃); +88% ee from (*S,S*)-L*.



Ethyl 7-(ethyldiphenylsilyl)-9-phenylnonanoate (Table 3, entry 5). The title compound was synthesized according to the General Procedure from (1-bromo-3-phenylpropyl)(ethyl)diphenylsilane (205 mg, 0.500 mmol) and (6-ethoxy-6-oxohexyl)zinc bromide (0.600 mmol). The product was purified by flash chromatography with silica gel: column #1 (0 → 5% EtOAc in hexanes); column #2 (30 → 60% CH₂Cl₂ in hexanes). Colorless oil.

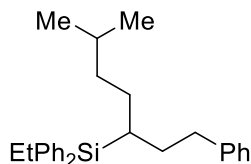
(*S,S*)-L*: 142 mg (60% yield), -88% ee; (*R,R*)-L*: 136 mg (58% yield), +86% ee.

SFC analysis: The ee was determined via SFC on a CHIRALCEL OJ column (20% *i*-PrOH in supercritical CO₂, 3.5 mL/min) with *t_r* = 13.9 min (major (*S,S*)-L*), 9.5 min (major (*R,R*)-L*).

¹H NMR (400 MHz, CDCl₃) δ 7.54 – 7.46 (m, 4H), 7.41 – 7.30 (m, 6H), 7.27 – 7.22 (m, 2H), 7.20 – 7.13 (m, 1H), 7.08 – 7.03 (m, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.62 (ddd, *J* = 13.4, 10.6, 5.1 Hz, 1H), 2.48 (ddd, *J* = 13.5, 10.4, 6.3 Hz, 1H), 2.23 (t, *J* = 7.6 Hz, 2H), 1.88 (dddd, *J* = 13.7, 10.5, 6.3, 4.2 Hz, 1H), 1.67 – 1.51 (m, 4H), 1.44 – 1.19 (m, 9H), 1.11 (q, *J* = 7.4 Hz, 2H), 0.95 (t, *J* = 7.7 Hz, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 174.0, 142.8, 135.6, 135.54, 135.52, 129.19, 129.16, 128.6, 128.4, 127.84, 127.82, 125.8, 60.3, 36.0, 34.5, 32.3, 29.9, 29.6, 29.3, 25.0, 22.6, 14.4, 7.8, 4.4;

FT-IR (thin film) 3068, 3024, 2930, 2856, 1735, 1454, 1427, 1373, 1180, 1108, 1030 cm^{-1} ;
HR-MS (FAB+) m/z $[M+H]^+-H_2$ calcd for $C_{31}H_{39}O_2Si$: 471.2719, found: 471.2732;
 $[\alpha]^{23}_D = +4.5$ ($c = 0.52$, $CHCl_3$); -88% ee from (*S,S*)-**L***.



Ethyl(6-methyl-1-phenylheptan-3-yl)diphenylsilane (Table 3, entry 6). The title compound was synthesized according to the General Procedure from (1-bromo-3-phenylpropyl)(ethyl)diphenylsilane (205 mg, 0.500 mmol) and isopentylzinc bromide (0.600 mmol). The product was purified by flash chromatography (0 \rightarrow 5% CH_2Cl_2 in hexanes). Colorless oil.

(*S,S*)-**L***: 129 mg (65% yield), +91% ee; (*R,R*)-**L***: 132 mg (66% yield), -91% ee.

SFC analysis: The ee was determined via SFC on a CHIRALCEL OJ column (15% *i*-PrOH in supercritical CO_2 , 3.5 mL/min) with $t_r = 3.5$ min (major (*S,S*)-**L***), 5.1 min (major (*R,R*)-**L***).

1H NMR (400 MHz, $CDCl_3$) δ 7.56–7.45 (m, 4H), 7.41–7.30 (m, 6H), 7.27–7.21 (m, 2H), 7.16 (tt, $J = 7.3, 1.3$ Hz, 1H), 7.09–7.03 (m, 2H), 2.63 (ddd, $J = 13.5, 10.7, 5.0$ Hz, 1H), 2.48 (ddd, $J = 13.5, 10.5, 6.3$ Hz, 1H), 1.88 (dddd, $J = 14.0, 10.6, 6.4, 4.3$ Hz, 1H), 1.71–1.56 (m, 2H), 1.50–1.33 (m, 2H), 1.33–1.20 (m, 2H), 1.19–1.06 (m, 3H), 0.96 (t, $J = 7.8$ Hz, 3H), 0.81 (t, $J = 6.6$ Hz, 6H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.0, 135.85, 135.76, 135.7, 135.6, 129.24, 129.22, 128.7, 128.4, 127.90, 127.89, 125.8, 39.1, 36.1, 32.5, 28.6, 27.7, 23.0, 22.9, 22.7, 8.0, 4.5;

FT-IR (thin film) 3068, 3025, 2953, 2925, 2872, 1496, 1458, 1427, 1108, 1010 cm^{-1} ;

HR-MS (ESI+) m/z $[M+H]^+-H_2$ calcd for $C_{28}H_{35}Si$: 399.2508, found: 399.2499;

$[\alpha]^{23}_D = +10.6$ ($c = 0.60$, $CHCl_3$); +91% ee from (*S,S*)-**L***.

IV. Mechanistic Experiments

(1-Bromo-3-phenylpropyl)(ethyl)diphenylsilane was separated via preparative-scale SFC on a CHIRALPAK AD-H column (2% *i*-PrOH, 4.0 mL/min) with t_r = 3.9 min, 5.0 min.

Procedure. In a glovebox, an oven-dried 4-mL vial was charged with *rac*-, (+)-, or (-)-(1-bromo-3-phenylpropyl)(ethyl)diphenylsilane (29 mg, 0.070 mmol), followed by NiBr₂·diglyme (2.5 mg, 0.0070 mmol) and then L* (3.0 mg, 0.0091 mmol). Next, an oven-dried stir bar was added, followed by anhydrous DMA (0.3 mL). The reaction mixture was stirred for 10 min, and then (2-(1,3-dioxolan-2-yl)ethyl)zinc bromide (0.084 mmol) was added, and the vial was capped and removed from the glovebox. The vial cap was wrapped with electrical tape, and the mixture was allowed to stir at room temperature for 30 min. After 30 min, EtOH (0.20 mL) was added, and the mixture was allowed to stir for 10 min. Next, tetradecane (internal standard for GC analysis; 20 μ L), hexanes (0.50 mL), and Et₂O (2.0 mL) were added. The mixture was then passed through a short plug of silica gel into a test tube, flushing with Et₂O. An aliquot of the filtrate was removed for GC analysis. The remaining filtrate was concentrated, and H₂O (~2 mL) and 1:1 hexanes/Et₂O (~1 mL) were added. The test tube was capped and thoroughly shaken. The organic layer was extracted and placed on a preparative TLC plate to separate the remaining electrophile from the product (eluent 50:1 hexanes/Et₂O; electrophile: R_f ~ 0.6; product: R_f ~ 0.2).

SFC analysis of remaining electrophile: The ee was determined via SFC on a CHIRALCEL OJ column (3% *i*-PrOH in supercritical CO₂, 3.5 mL/min) with t_r = 4.6 min, 5.6 min.

SFC analysis of product: The ee was determined via SFC on a CHIRALCEL OJ column (35% *i*-PrOH in supercritical CO₂, 3.5 mL/min) with t_r = 6.8 min (major (*S,S*)-L*), 4.4 min (minor (*S,S*)-L*).

V. Determination of Absolute Stereochemistry

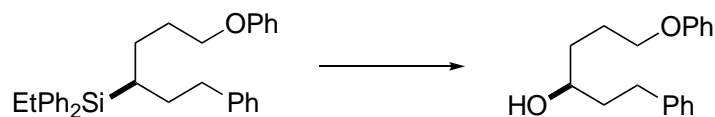
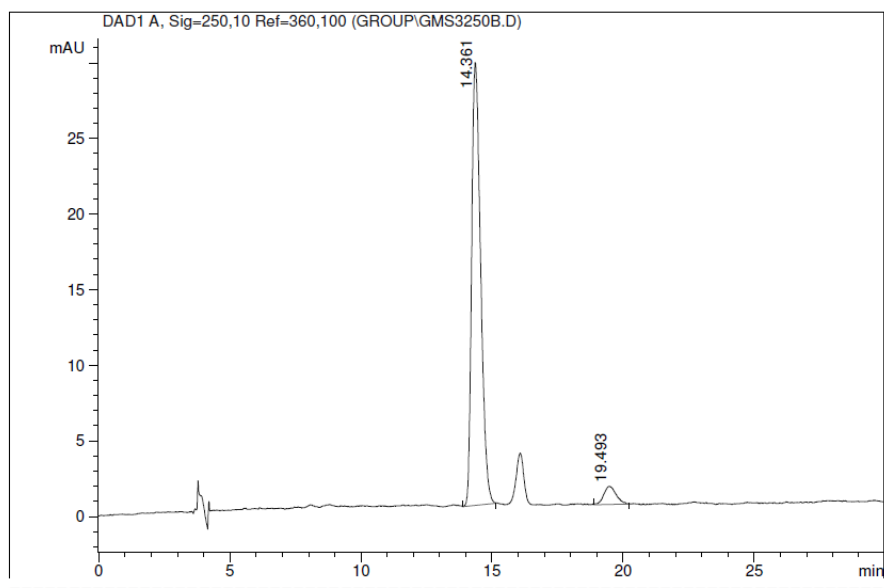


Table 3, entry 2: The absolute configuration of (*R*)-ethyl(6-phenoxy-1-phenylhexan-3-yl)diphenylsilane ((*R,R*)-**L***) was determined after an enantiospecific Fleming-Tamao oxidation¹³ to yield (*R*)-6-phenoxy-1-phenylhexan-3-ol. The absolute configuration of this molecule has previously been determined by single crystal x-ray diffraction.¹⁴ Comparison of HPLC data established the absolute configuration illustrated above.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AS-H column (3% *i*-PrOH in hexanes, 1.0 mL/min) with t_r = 19.5 min (major (*S,S*)-**L***), 14.4 min (major (*R,R*)-**L***).



Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RT [min]	Width [min]	Area	Area %
1	14.361	0.396	696.396	94.715
2	19.493	0.543	38.859	5.285

Table 2, entry 2: Single crystals of (*S*)-(4-(1,3-dioxolan-2-yl)-1-phenylbutan-2-yl)(ethyl)diphenylsilane ((*S,S*)-**L***) were obtained after slow evaporation from Et₂O. The crystal

(13) Suginome, M.; Iwanami, T.; Ohmori, Y.; Matsumoto, A.; Ito, Y. *Chem. Eur. J.* **2005**, *11*, 2954–2965.

(14) Schmidt, J.; Choi, J.; Liu, A. T.; Slusarczyk, M.; Fu, G. C. *Science* **2016**, *354*, 1265–1269.

was kept at 99.95 K during data collection. Using Olex2,¹⁵ the structure was solved with the XT¹⁶ structure solution program using intrinsic phasing and refined with the ShelXL¹⁷ refinement package using least squares minimization.

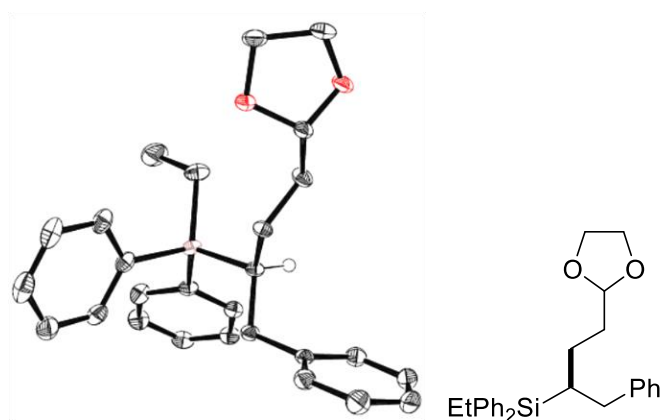


Table S1. Crystal data and structure refinement for (S)-4-(1,3-dioxolan-2-yl)-1-phenylbutan-2-yl(ethyl)diphenylsilane.

Identification code	(S)-4-(1,3-dioxolan-2-yl)-1-phenylbutan-2-yl(ethyl)diphenylsilane
Empirical formula	C ₂₇ H ₃₂ O ₂ Si
Formula weight	416.61
Temperature/K	99.95
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a/Å	10.5454(9)
b/Å	12.0533(11)
c/Å	18.5574(17)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	2358.8(4)
Z	4
ρ _{calc} /cm ³	1.173

(15) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Crystallogr.* **2009**, *42*, 339–341.

(16) Sheldrick, G. M. *Acta Cryst.* **2015**, *A71*, 3–8.

(17) Sheldrick, G. M. *Acta Cryst.* **2015**, *C71*, 3–8.

μ/mm^{-1}	0.120
F(000)	896.0
Crystal size/ mm^3	$0.27 \times 0.23 \times 0.18$
Radiation	MoK α ($\lambda = 0.71073$)
2Θ range for data collection/	4.442 to 55.002
Index ranges	$-13 \leq h \leq 13, -15 \leq k \leq 15, -24 \leq l \leq 24$
Reflections collected	111480
Independent reflections	5412 [$R_{\text{int}} = 0.0467, R_{\text{sigma}} = 0.0137$]
Data/restraints/parameters	5412/0/272
Goodness-of-fit on F^2	1.038
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0316, wR_2 = 0.0845$
Final R indexes [all data]	$R_1 = 0.0330, wR_2 = 0.0852$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.46/-0.28
Flack parameter	0.018(12)

Table S2. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (S)-(4-(1,3-dioxolan-2-yl)-1-phenylbutan-2-yl)(ethyl)diphenylsilane. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
Si01	6941.8(4)	874.1(4)	6709.4(3)	17.18(12)
O002	2430.2(12)	2989.1(13)	5609.7(8)	23.9(3)
O003	2811.4(12)	2372.1(14)	6747.5(8)	28.2(3)
C004	8442.3(18)	175.9(15)	6410.0(11)	18.3(4)
C005	10176.5(19)	-53.2(18)	5557.1(11)	22.9(4)
C006	9083.7(18)	495.2(16)	5785.6(11)	20.1(4)
C007	6863.4(16)	2354.5(14)	6376.8(9)	16.0(3)
C008	3278.3(16)	3093.8(17)	6196.7(10)	19.1(4)
C009	8028.1(16)	4213.3(15)	6387(1)	18.7(3)
C00A	8238.1(18)	4379.8(17)	5651.3(11)	23.0(4)
C00B	7956.2(17)	3052.1(14)	6694.5(10)	18.2(3)
C00C	5568.1(16)	2884.7(16)	6565.2(10)	17.1(4)
C00D	4590.6(17)	2750.8(18)	5967.3(11)	21.4(4)
C00E	1220.8(18)	2897(2)	5947.1(12)	26.1(4)
C00F	8931.4(19)	-729.8(17)	6793.5(12)	25.0(4)
C00G	8064(2)	985.1(16)	8121.2(11)	25.2(4)
C00H	8295.2(19)	5445.9(19)	5367.0(12)	28.1(4)

C00I	10635.8(18)	-945.3(18)	5946.2(11)	24.6(4)
C00J	6937.4(18)	920.2(15)	7722.4(10)	20.9(4)
C00K	5793(2)	970.4(18)	8106.0(11)	26.2(4)
C00L	10010(2)	-1293.9(18)	6561.9(12)	27.3(5)
C00M	7903(2)	6208.7(17)	6538.7(12)	30.5(5)
C00N	1496.9(19)	2189(2)	6607.0(12)	28.6(5)
C00O	7863.2(19)	5140.6(16)	6824.8(11)	23.9(4)
C00P	8129(2)	6360.0(18)	5809.3(13)	31.2(5)
C00Q	8053(3)	1094.3(18)	8867.7(12)	32.3(5)
C00R	5546(2)	62.5(18)	6356.3(13)	27.8(5)
C00S	6905(3)	1139.6(18)	9231.5(12)	35.3(5)
C00T	5775(2)	1080.0(19)	8852.8(13)	32.9(5)
C00U	5590(3)	-1169(2)	6518.8(16)	41.1(6)

Table S3. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (*S*)-(4-(1,3-dioxolan-2-yl)-1-phenylbutan-2-yl)(ethyl)diphenylsilane.. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Si01	13.3(2)	14.1(2)	24.1(2)	-1.95(19)	2.36(19)	-0.82(19)
O002	13.1(6)	36.1(8)	22.6(7)	2.7(6)	-3.7(5)	0.9(6)
O003	14.4(6)	43.8(9)	26.4(7)	10.4(7)	-2.6(5)	-5.2(6)
C004	16.3(8)	14.3(8)	24.2(9)	-4.3(7)	0.0(7)	-1.1(6)
C005	20.1(9)	25.8(10)	22.7(10)	-4.9(8)	3.2(7)	0.4(8)
C006	18.9(8)	17.5(9)	23.9(10)	-2.1(7)	-1.7(7)	0.9(7)
C007	11.7(7)	16.9(8)	19.6(8)	-1.6(7)	-0.1(7)	0.9(6)
C008	13.8(8)	23.4(9)	20.2(9)	0.8(7)	-1.3(7)	1.0(7)
C009	12.2(7)	18.4(8)	25.6(9)	2.2(7)	-4.0(7)	-1.2(7)
C00A	18.5(8)	24.8(10)	25.6(9)	-0.8(8)	0.0(7)	0.9(7)
C00B	13.7(7)	16.7(8)	24.2(9)	1.6(7)	-3.1(8)	0.3(6)
C00C	12.7(7)	19.1(9)	19.4(9)	-1.6(7)	-0.8(6)	2.5(7)
C00D	15.0(8)	30.1(11)	19.1(9)	-1.3(8)	-0.9(7)	4.8(7)
C00E	12.6(8)	31.7(11)	34.0(11)	-3.2(9)	-2.7(8)	-0.6(8)
C00F	24.8(9)	21.3(10)	28.9(10)	1.4(9)	5.2(8)	3.3(8)
C00G	28.7(9)	18.1(9)	28.9(10)	1.5(8)	3.2(8)	-5.3(8)
C00H	21.9(10)	33.1(11)	29.4(10)	9.1(9)	-1.6(8)	-2.2(8)
C00I	18.8(8)	24.4(10)	30.7(10)	-7.9(9)	0.3(7)	3.3(8)

C00J	24.7(8)	12.6(7)	25.5(9)	1.1(7)	4.3(8)	-0.5(8)
C00K	28.4(10)	20.1(10)	30.1(11)	6.0(8)	8.0(8)	4.3(8)
C00L	24.8(10)	21.2(10)	35.8(12)	0.5(9)	-1.2(8)	7.4(8)
C00M	35.4(11)	18.6(9)	37.6(12)	-1.6(8)	-5.6(10)	-0.1(8)
C00N	18.4(9)	41.5(12)	25.9(11)	-1.8(9)	-2.3(8)	-10.1(8)
C00O	24.8(9)	20.8(9)	26.2(10)	-0.5(8)	-3.5(8)	-1.5(8)
C00P	29.7(10)	22.0(9)	41.8(12)	10.6(9)	-6.4(10)	-3.8(9)
C00Q	43.7(12)	23.9(11)	29.1(10)	1.3(8)	-4(1)	-10.1(10)
C00R	22.7(10)	24.3(11)	36.5(12)	-6.1(9)	-0.2(9)	-6.2(8)
C00S	58.5(15)	22.5(10)	24.9(10)	-0.1(8)	9.1(11)	-3.5(10)
C00T	44.7(13)	23.6(12)	30.4(11)	5.5(9)	15.4(10)	5.6(9)
C00U	42.9(14)	25.3(12)	55.1(16)	1.7(11)	-5.9(12)	-10.6(10)

Table S4. Bond lengths for (S)-(4-(1,3-dioxolan-2-yl)-1-phenylbutan-2-yl)(ethyl)diphenylsilane.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Si01	C004	1.8763(19)	C009	C00O	1.393(3)
Si01	C007	1.8899(18)	C00A	C00H	1.390(3)
Si01	C00J	1.8806(19)	C00C	C00D	1.523(3)
Si01	C00R	1.885(2)	C00E	C00N	1.521(3)
O002	C008	1.415(2)	C00F	C00L	1.393(3)
O002	C00E	1.425(2)	C00G	C00J	1.402(3)
O003	C008	1.430(2)	C00G	C00Q	1.392(3)
O003	C00N	1.428(2)	C00H	C00P	1.385(3)
C004	C006	1.396(3)	C00I	C00L	1.385(3)
C004	C00F	1.402(3)	C00J	C00K	1.403(3)
C005	C006	1.395(3)	C00K	C00T	1.392(3)
C005	C00I	1.383(3)	C00M	C00O	1.393(3)
C007	C00B	1.544(2)	C00M	C00P	1.386(3)
C007	C00C	1.548(2)	C00Q	C00S	1.388(4)
C008	C00D	1.506(2)	C00R	C00U	1.515(3)
C009	C00A	1.397(3)	C00S	C00T	1.385(4)
C009	C00B	1.513(2)			

Table S5. Bond angles for (S)-(4-(1,3-dioxolan-2-yl)-1-phenylbutan-2-yl)(ethyl)diphenylsilane.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C004	Si01	C007	111.32(8)	C00H	C00A	C009	120.68(19)
C004	Si01	C00J	108.14(9)	C009	C00B	C007	113.40(14)
C004	Si01	C00R	108.83(9)	C00D	C00C	C007	112.89(15)
C00J	Si01	C007	107.36(8)	C008	C00D	C00C	112.76(16)
C00J	Si01	C00R	111.16(10)	O002	C00E	C00N	103.08(15)
C00R	Si01	C007	110.02(9)	C00L	C00F	C004	121.60(19)
C008	O002	C00E	103.55(14)	C00Q	C00G	C00J	121.6(2)
C00N	O003	C008	107.34(15)	C00P	C00H	C00A	120.3(2)
C006	C004	Si01	122.06(15)	C005	C00I	C00L	120.00(18)
C006	C004	C00F	117.25(18)	C00G	C00J	Si01	121.81(15)
C00F	C004	Si01	120.62(15)	C00G	C00J	C00K	117.33(17)
C00I	C005	C006	119.95(19)	C00K	C00J	Si01	120.71(15)
C005	C006	C004	121.48(19)	C00T	C00K	C00J	121.4(2)
C00B	C007	Si01	110.91(12)	C00I	C00L	C00F	119.7(2)
C00B	C007	C00C	110.34(14)	C00P	C00M	C00O	119.9(2)
C00C	C007	Si01	110.77(12)	O003	C00N	C00E	104.25(16)
O002	C008	O003	106.16(15)	C009	C00O	C00M	121.02(19)
O002	C008	C00D	109.80(15)	C00H	C00P	C00M	119.72(19)
O003	C008	C00D	110.59(16)	C00S	C00Q	C00G	119.7(2)
C00A	C009	C00B	120.60(17)	C00U	C00R	Si01	114.53(17)
C00O	C009	C00A	118.33(18)	C00T	C00S	C00Q	120.1(2)
C00O	C009	C00B	121.06(17)	C00S	C00T	C00K	119.9(2)

Table S6. Torsion angles for (S)-(4-(1,3-dioxolan-2-yl)-1-phenylbutan-2-yl)(ethyl)diphenylsilane.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Si01	C004	C006	C005	-177.98(15)	C00B	C009	C00O	C00M	-178.64(19)
Si01	C004	C00F	C00L	176.90(17)	C00C	C007	C00B	C009	-63.0(2)
Si01	C007	C00B	C009	173.86(12)	C00E	O002	C008	O003	38.07(19)
Si01	C007	C00C	C00D	-91.97(17)	C00E	O002	C008	C00D	157.63(17)
Si01	C00J	C00K	C00T	-175.63(17)	C00F	C004	C006	C005	-0.9(3)
O002	C008	C00D	C00C	177.77(16)	C00G	C00J	C00K	C00T	0.0(3)
O002	C00E	C00N	O003	24.9(2)	C00G	C00Q	C00S	C00T	-0.2(3)

O003	C008	C00D	C00C	-65.4(2)	C00I	C005	C006	C004	1.0(3)
C004	Si01	C007	C00B	-62.49(14)	C00J	Si01	C004	C006	-144.74(16)
C004	Si01	C007	C00C	174.63(12)	C00J	Si01	C004	C00F	38.25(18)
C004	Si01	C00J	C00G	30.26(18)	C00J	Si01	C007	C00B	55.69(14)
C004	Si01	C00J	C00K	-154.32(16)	C00J	Si01	C007	C00C	-67.19(14)
C004	Si01	C00R	C00U	51.1(2)	C00J	Si01	C00R	C00U	-67.9(2)
C004	C00F	C00L	C00I	1.3(3)	C00J	C00G	C00Q	C00S	0.1(3)
C005	C00I	C00L	C00F	-1.2(3)	C00J	C00K	C00T	C00S	-0.1(3)
C006	C004	C00F	C00L	-0.2(3)	C00N	O003	C008	O002	-21.9(2)
C006	C005	C00I	C00L	0.1(3)	C00N	O003	C008	C00D	-140.90(17)
C007	Si01	C004	C006	-27.02(18)	C00O	C009	C00A	C00H	0.7(3)
C007	Si01	C004	C00F	155.97(16)	C00O	C009	C00B	C007	117.41(19)
C007	Si01	C00J	C00G	-89.97(17)	C00O	C00M	C00P	C00H	1.0(3)
C007	Si01	C00J	C00K	85.45(17)	C00P	C00M	C00O	C009	-1.0(3)
C007	Si01	C00R	C00U	173.35(18)	C00Q	C00G	C00J	Si01	175.60(16)
C007	C00C	C00D	C008	170.42(16)	C00Q	C00G	C00J	C00K	0.0(3)
C008	O002	C00E	C00N	-38.2(2)	C00Q	C00S	C00T	C00K	0.2(3)
C008	O003	C00N	C00E	-2.1(2)	C00R	Si01	C004	C006	94.40(18)
C009	C00A	C00H	C00P	-0.8(3)	C00R	Si01	C004	C00F	-82.61(18)
C00A	C009	C00B	C007	-61.3(2)	C00R	Si01	C007	C00B	176.78(13)
C00A	C009	C00O	C00M	0.1(3)	C00R	Si01	C007	C00C	53.90(15)
C00A	C00H	C00P	C00M	-0.1(3)	C00R	Si01	C00J	C00G	149.66(16)
C00B	C007	C00C	C00D	144.82(16)	C00R	Si01	C00J	C00K	-34.92(19)
C00B	C009	C00A	C00H	179.53(17)					

Table S7. Hydrogen atom coordinates ($\text{\AA}\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2\times 10^3$) for (S)-4-(1,3-dioxolan-2-yl)-1-phenylbutan-2-yl(ethyl)diphenylsilane.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
H005	10605	186	5134	27
H006	8769	1100	5510	24
H007	6955	2348	5840	19
H008	3288	3877	6374	23
H00A	8343	3758	5342	28
H00B	7846	3102	7223	22
H00C	8769	2667	6601	22
H00D	5237	2539	7011	20

H00E	5693	3685	6662	20
H00F	4851	3204	5548	26
H00G	4572	1965	5813	26
H00H	601	2529	5625	31
H00I	889	3635	6087	31
H00J	8517	-965	7222	30
H00K	8854	954	7876	30
H00L	8449	5548	4867	34
H00M	11381	-1319	5791	30
H00N	5013	929	7851	31
H00O	10315	-1915	6825	33
H00P	7775	6833	6843	37
H00Q	972	2426	7022	34
H00R	1329	1396	6507	34
H00S	7721	5043	7326	29
H00T	8171	7087	5614	37
H00U	8828	1138	9127	39
H00V	4761	375	6566	33
H00W	5500	164	5828	33
H00X	6893	1212	9741	42
H00Y	4989	1114	9102	39
H00Z	6305	-1506	6262	62
H	4797	-1517	6361	62
HA	5698	-1280	7038	62

VI. ^1H and ^{13}C NMR Data; ee Analysis

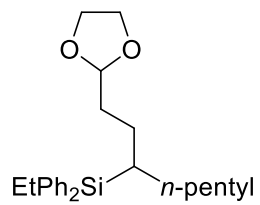
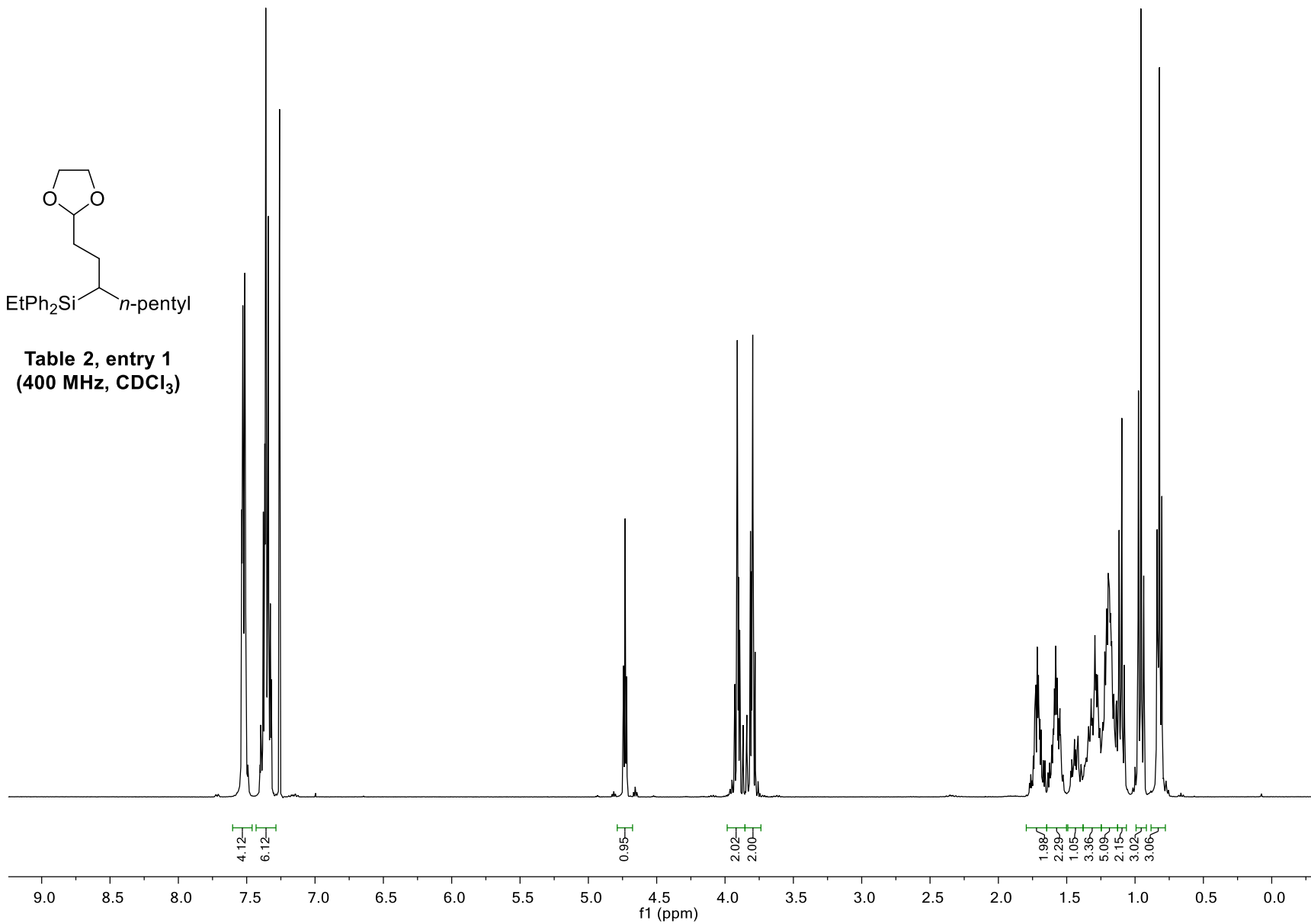
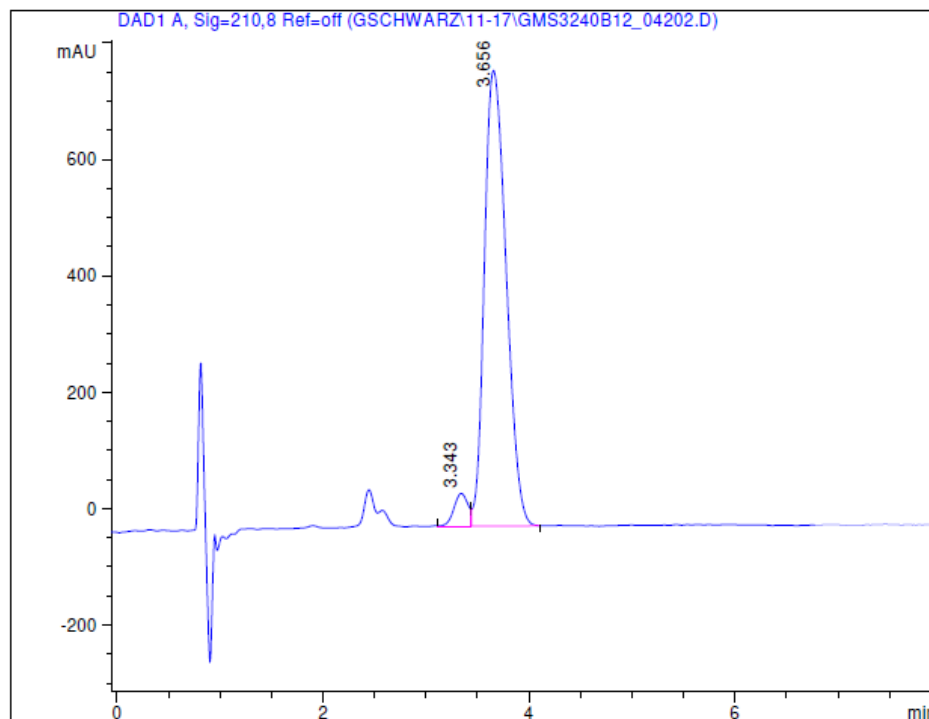
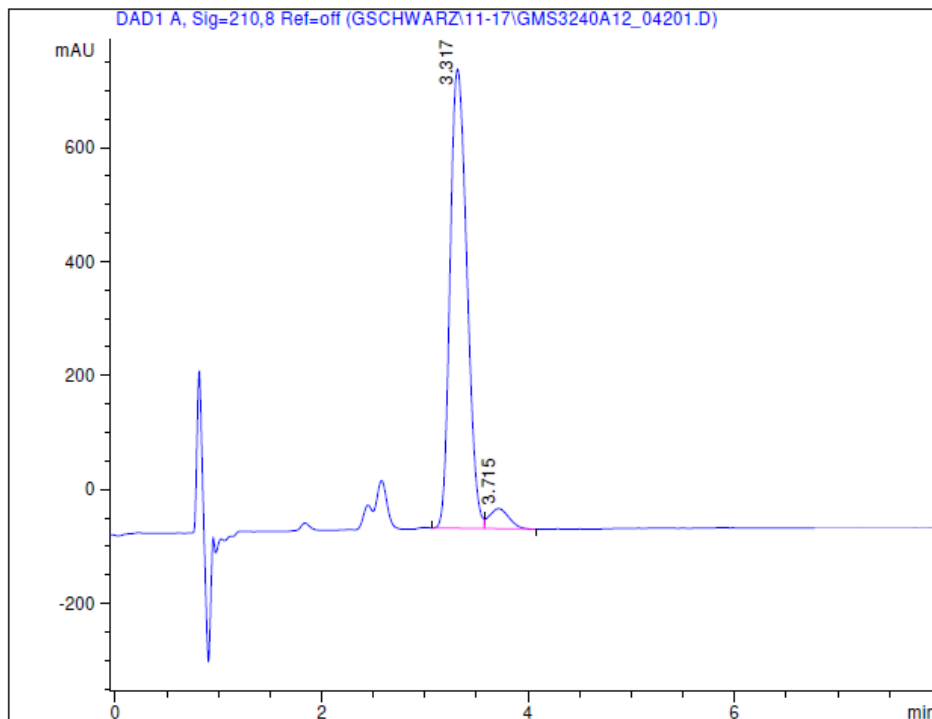


Table 2, entry 1
(400 MHz, CDCl₃)





Signal 1:DAD1 A, Sig=210,8 Ref=off

Peak #	RT [min]	Width [min]	Area	Area %
1	3.32	0.19	9114	95.19
2	3.72	0.22	461	4.81

Signal 1:DAD1 A, Sig=210,8 Ref=off

Peak #	RT [min]	Width [min]	Area	Area %
1	3.34	0.16	535	4.45
2	3.66	0.24	11498	95.55

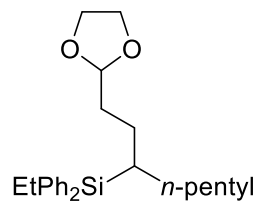


Table 2, entry 1
SFC: CHIRALCEL OJ column (5% 2-PrOH in supercritical CO₂, 3.5 mL/min)

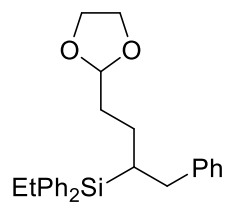
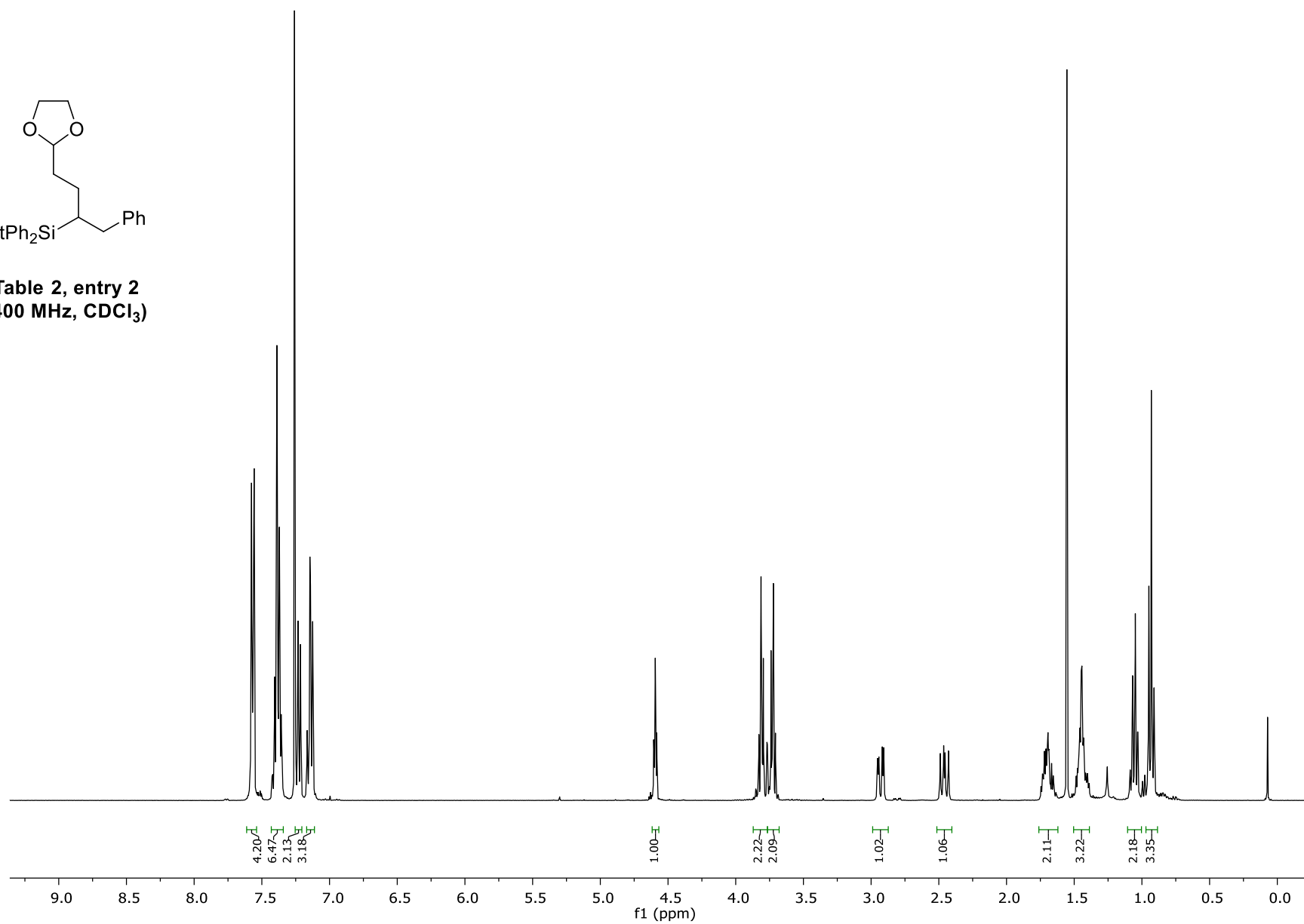


Table 2, entry 2
(400 MHz, CDCl₃)



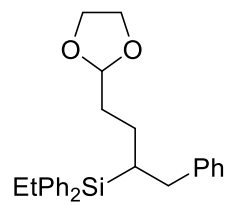
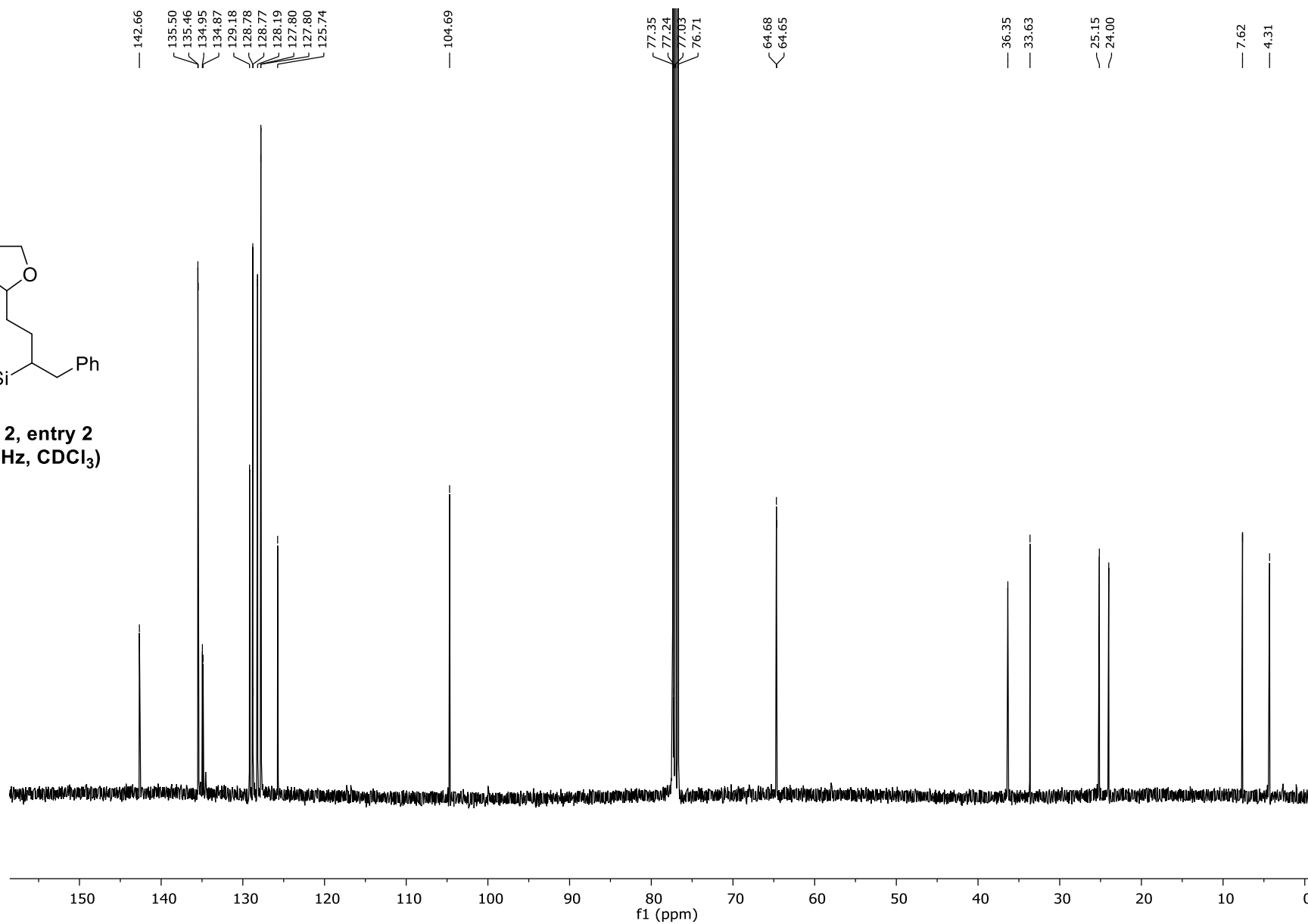
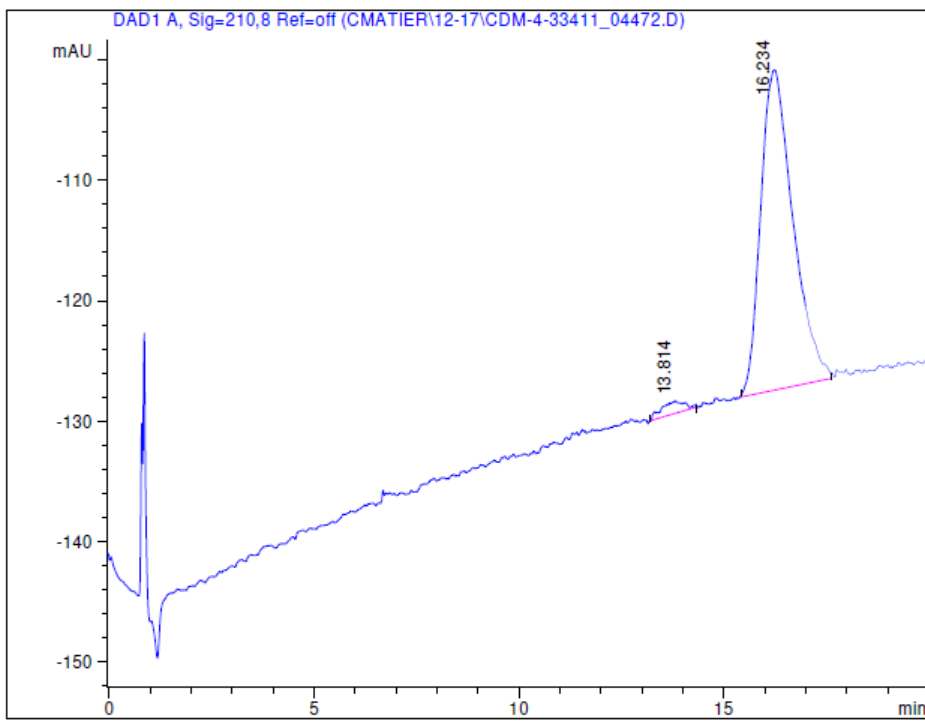
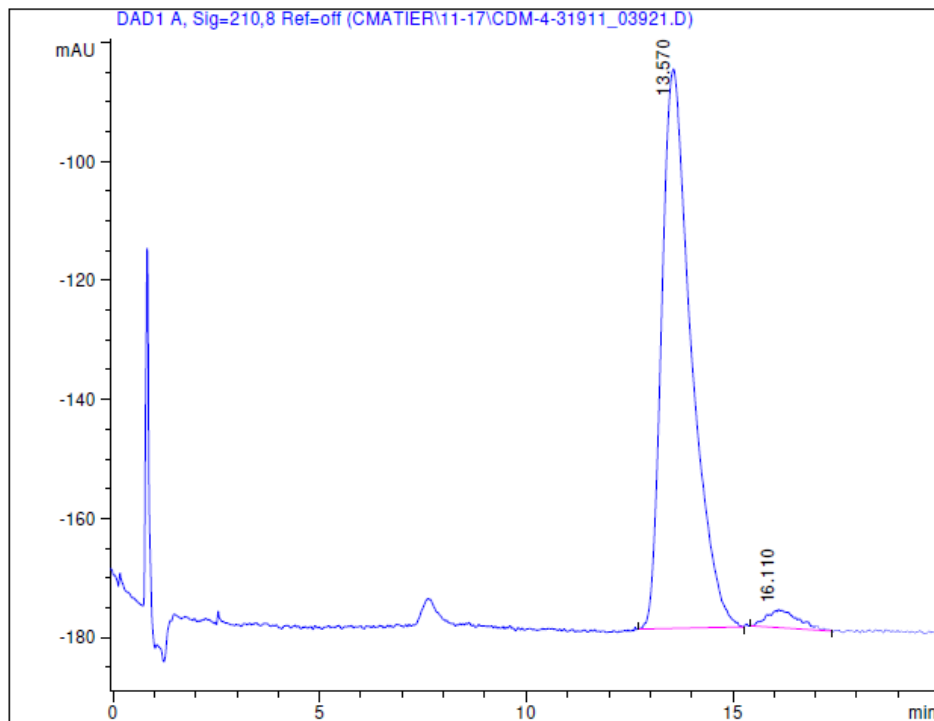


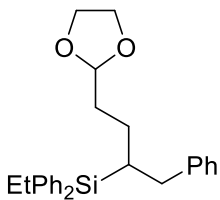
Table 2, entry 2
(101 MHz, CDCl₃)





Signal 1:DAD1 A, Sig=210,8 Ref=off

Peak #	RT [min]	Width [min]	Area	Area %
1	13.57	0.83	4667	96.64
2	16.11	0.89	162	3.36



Signal 1:DAD1 A, Sig=210,8 Ref=off

Peak #	RT [min]	Width [min]	Area	Area %
1	13.81	0.66	42	2.80
2	16.23	0.69	1453	97.20

Table 2, entry 2

SFC: CHIRALPAK IC-3 column (2% 2-PrOH in supercritical CO₂, 3.5 mL/min)

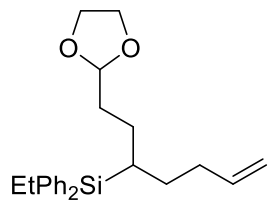
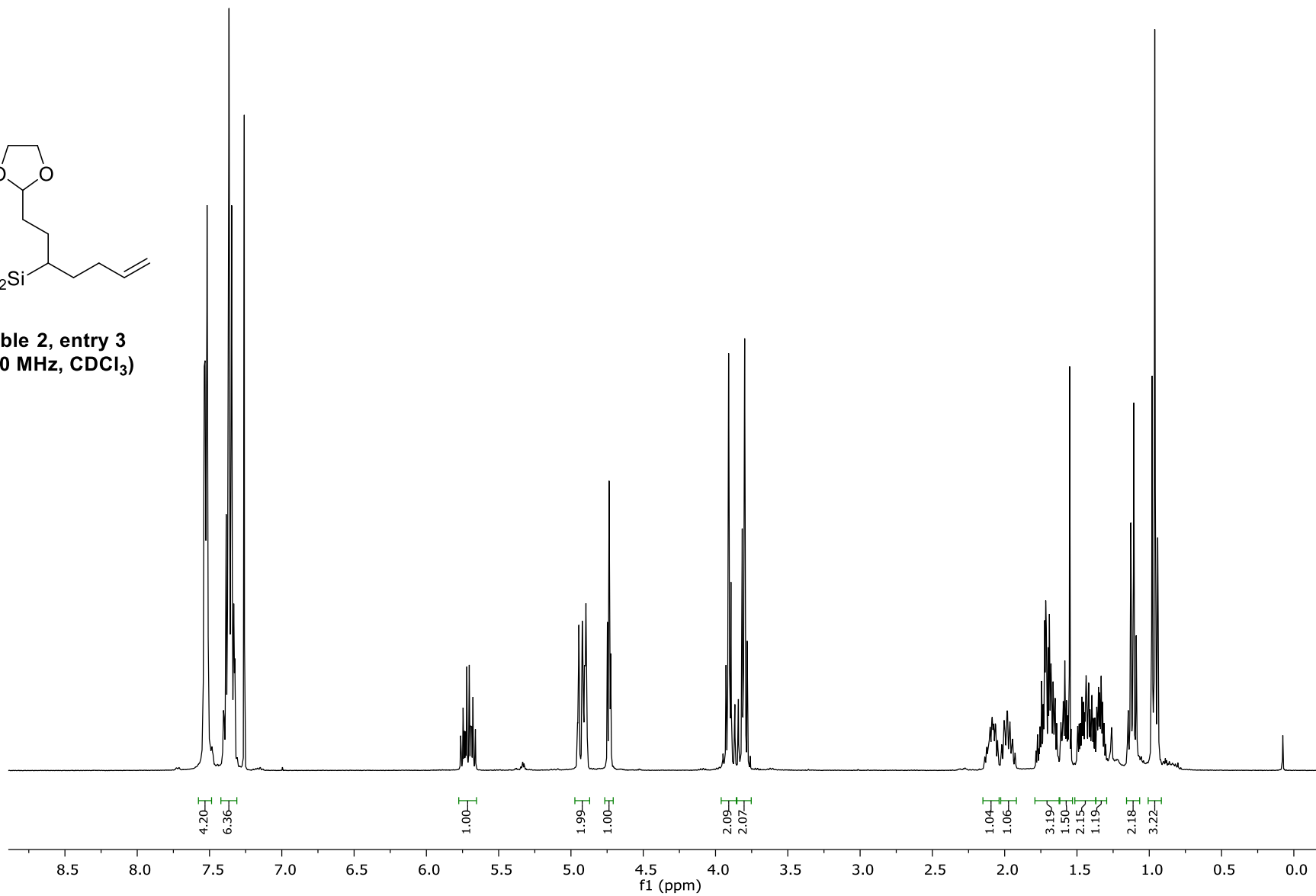


Table 2, entry 3
(400 MHz, CDCl₃)



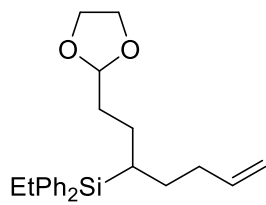
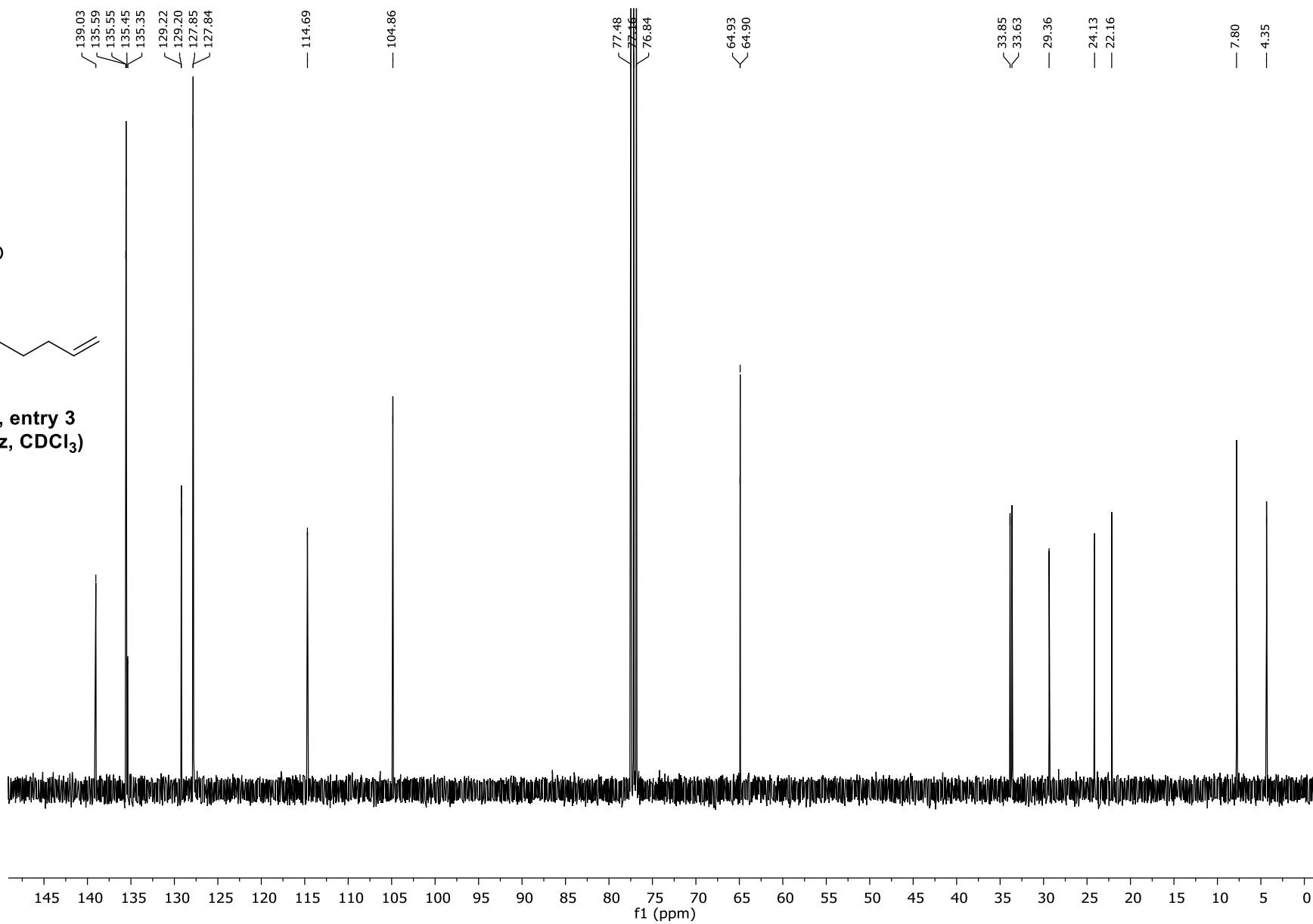
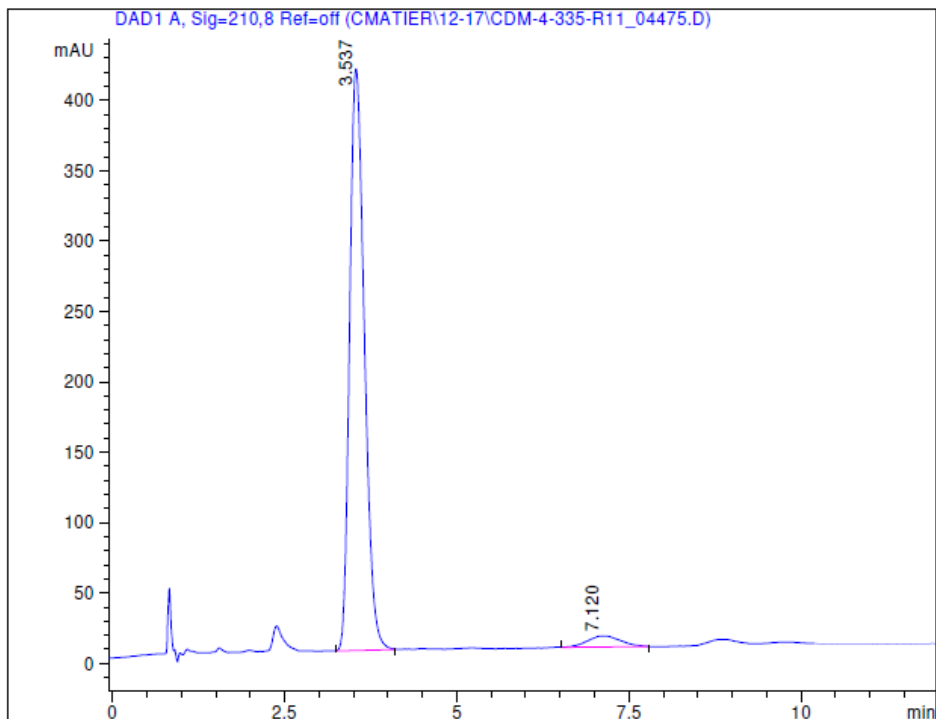
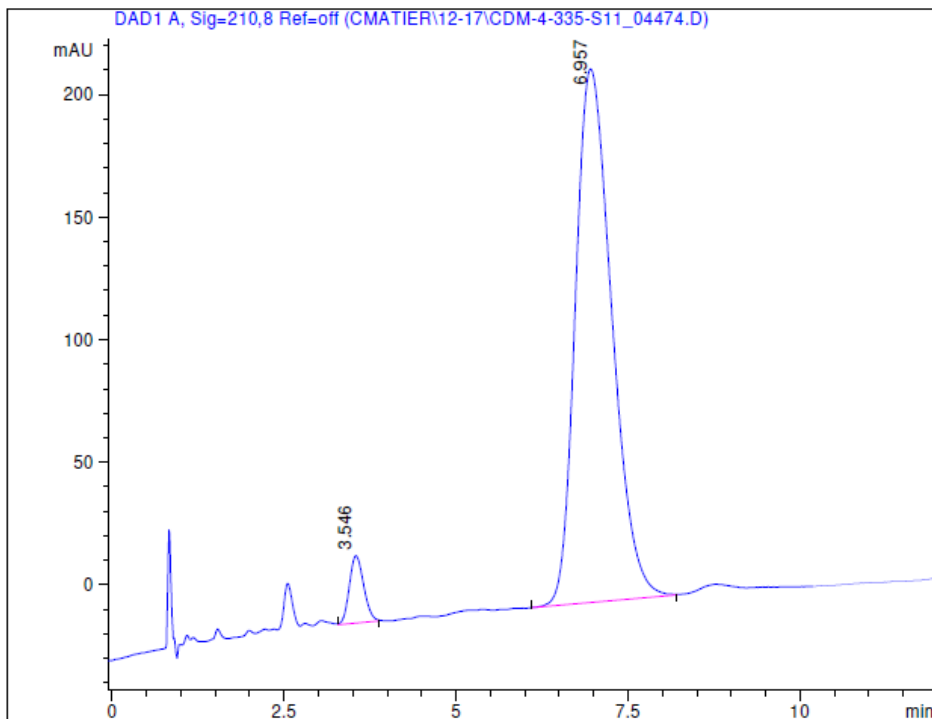


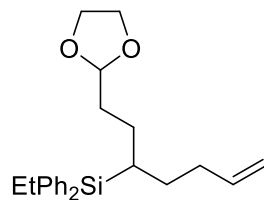
Table 2, entry 3
(101 MHz, CDCl₃)





Signal 1:DAD1 A, Sig=210,8 Ref=off

Peak #	RT [min]	Width [min]	Area	Area %
1	3.55	0.24	399	4.76
2	6.96	0.61	7984	95.24



Signal 1:DAD1 A, Sig=210,8 Ref=off

Peak #	RT [min]	Width [min]	Area	Area %
1	3.54	0.25	6140	95.94
2	7.12	0.56	260	4.06

Table 2, entry 3
SFC: CHIRALCEL OJ column (7% 2-PrOH in supercritical CO₂, 3.5 mL/min)

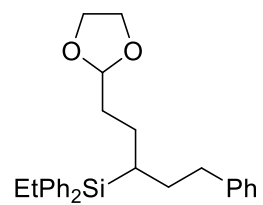
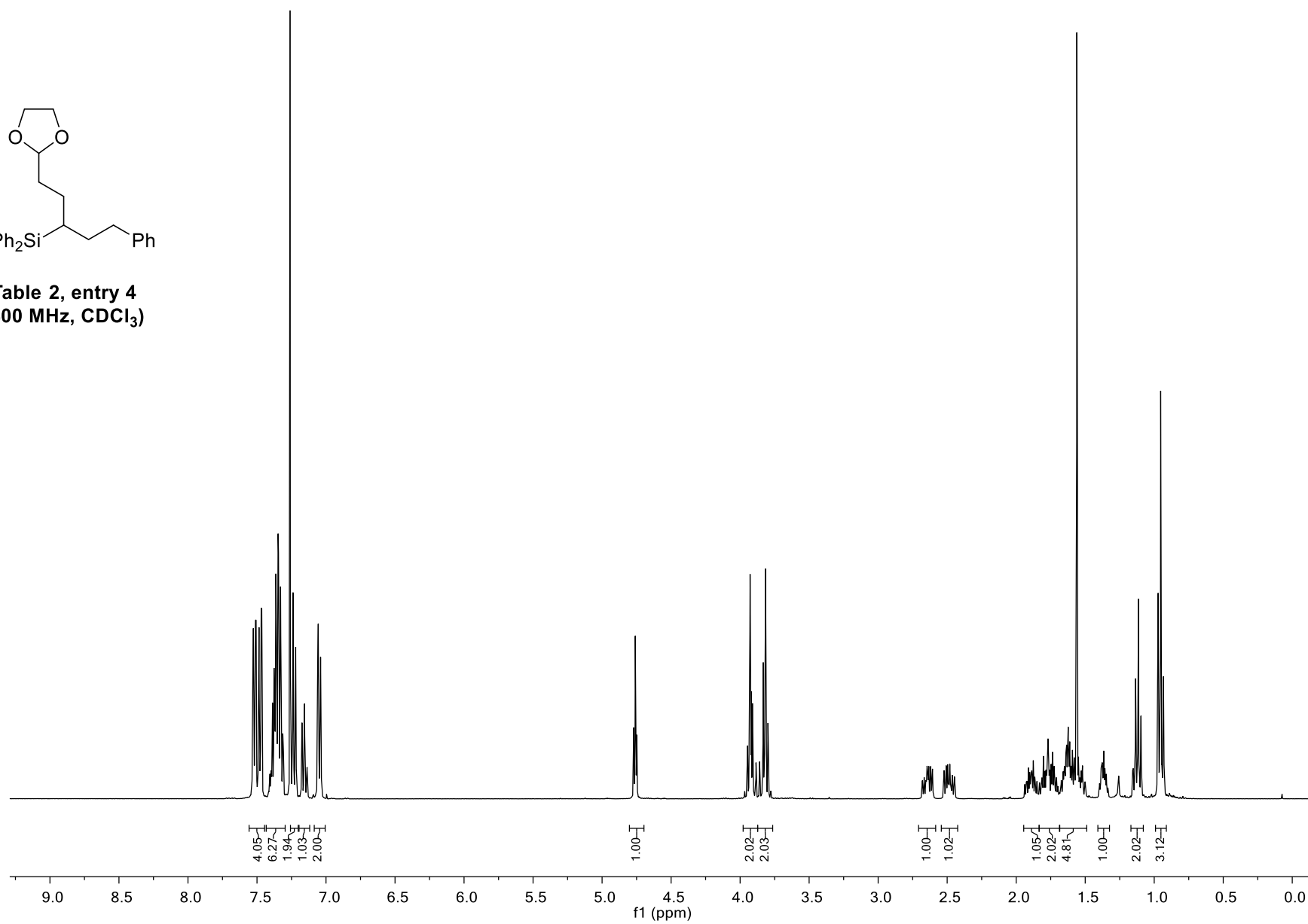


Table 2, entry 4
(400 MHz, CDCl₃)



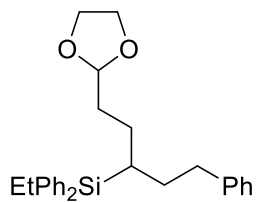
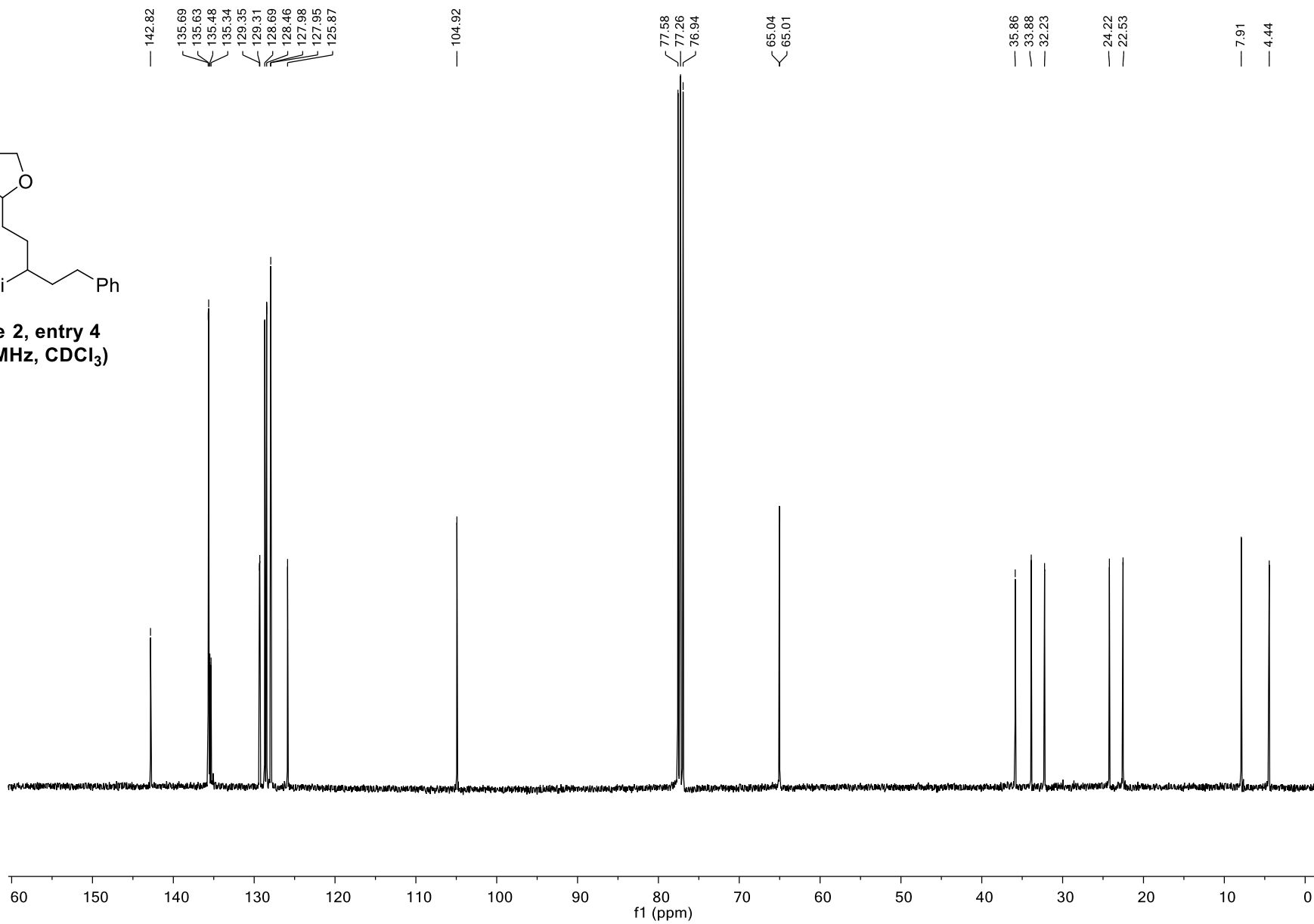
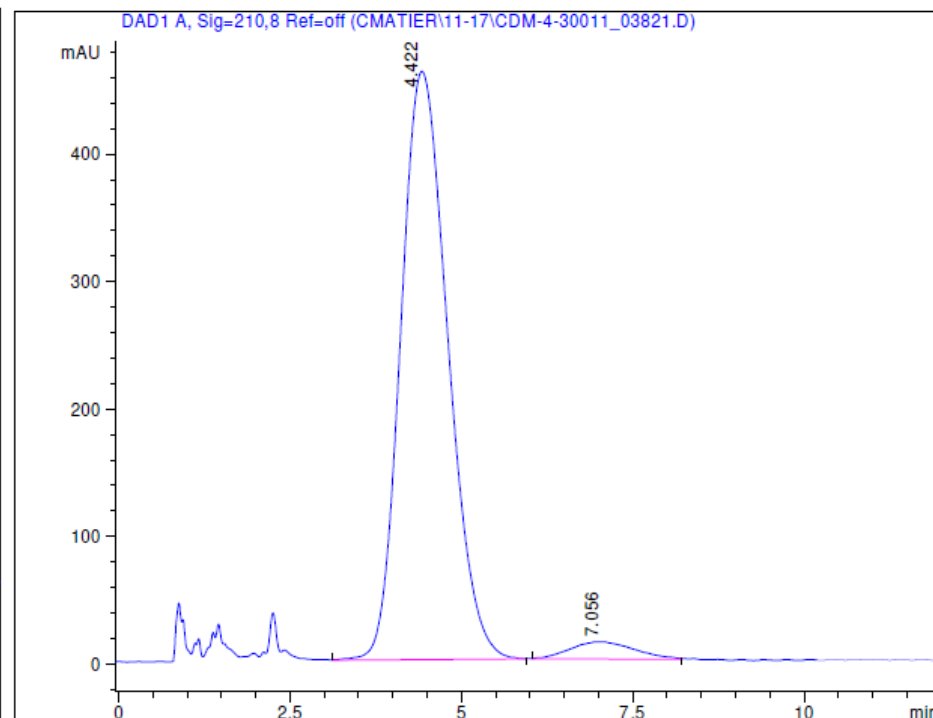
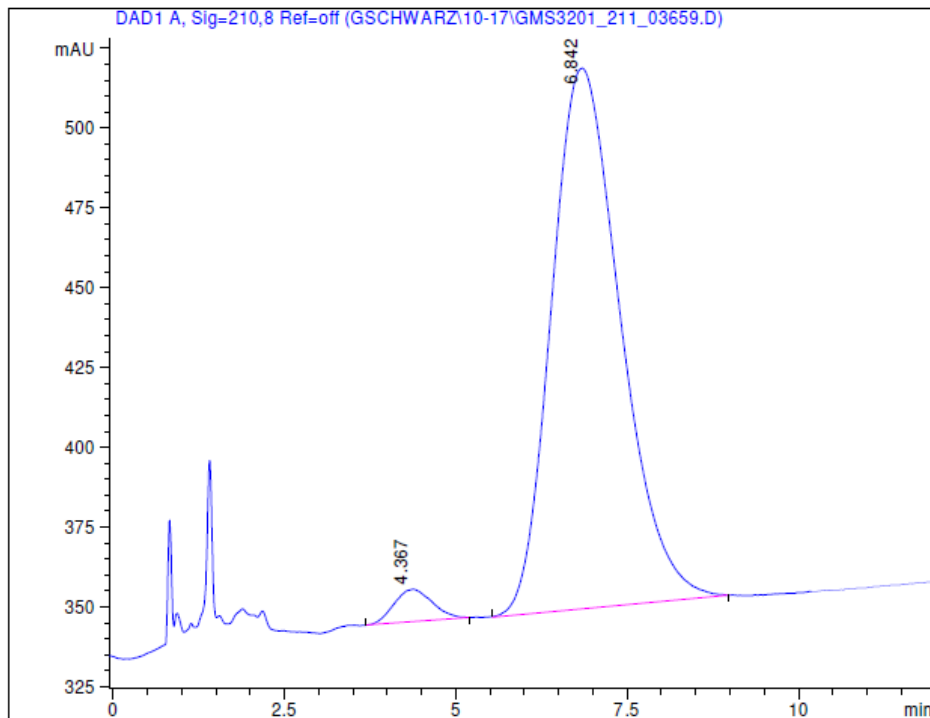


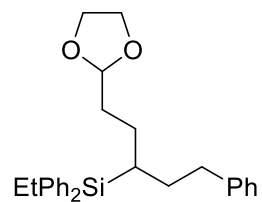
Table 2, entry 4
(101 MHz, CDCl₃)





Signal 1:DAD1 A, Sig=210,8 Ref=off

Peak #	RT [min]	Width [min]	Area	Area %
1	4.37	0.64	388	3.18
2	6.84	1.16	11821	96.82



Signal 1:DAD1 A, Sig=210,8 Ref=off

Peak #	RT [min]	Width [min]	Area	Area %
1	4.42	0.79	22006	96.18
2	7.06	1.08	875	3.82

Table 2, entry 4

SFC: CHIRALCEL OJ column (35% 2-PrOH in supercritical CO₂, 3.5 mL/min)

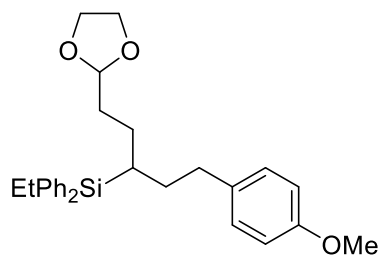
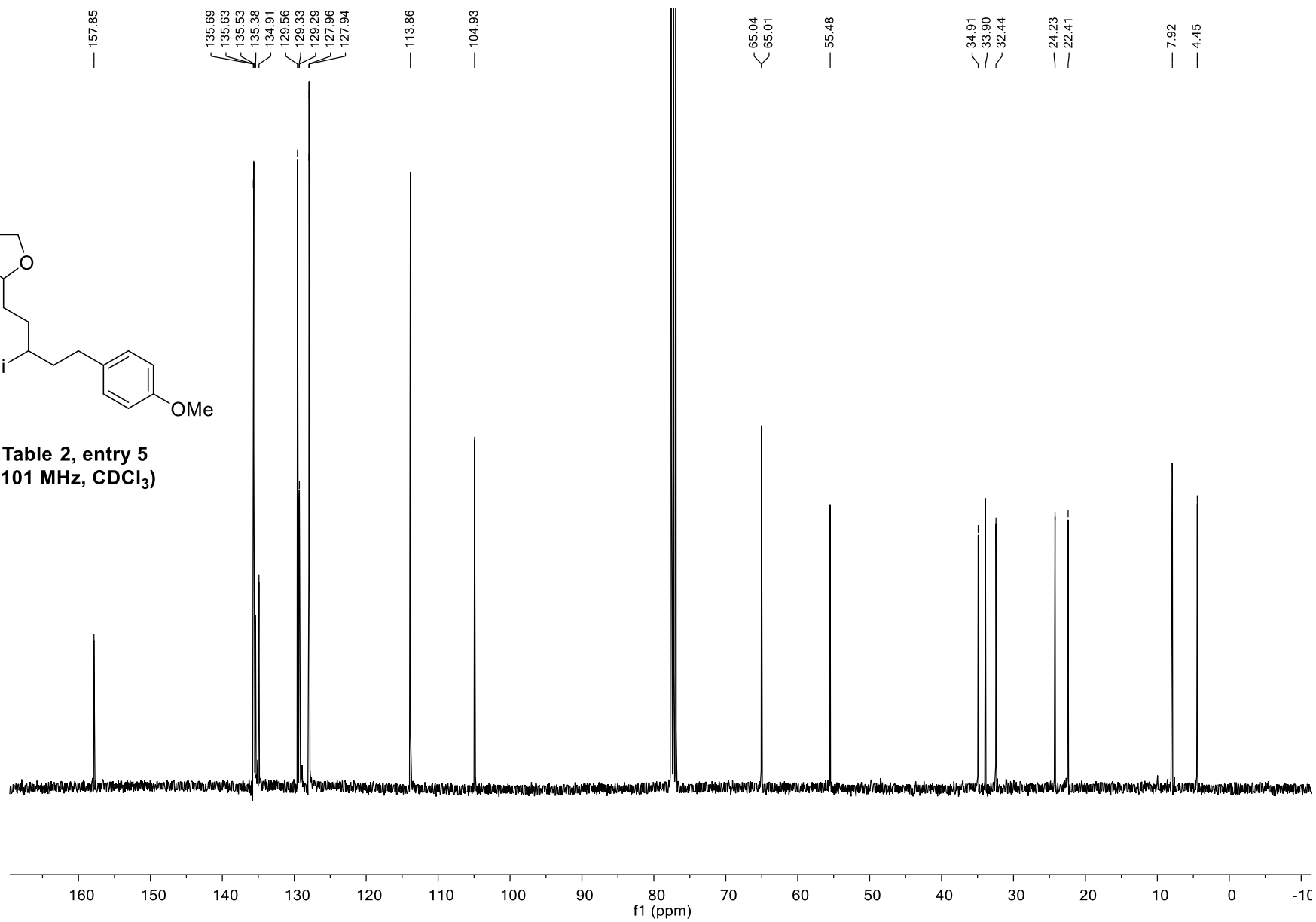
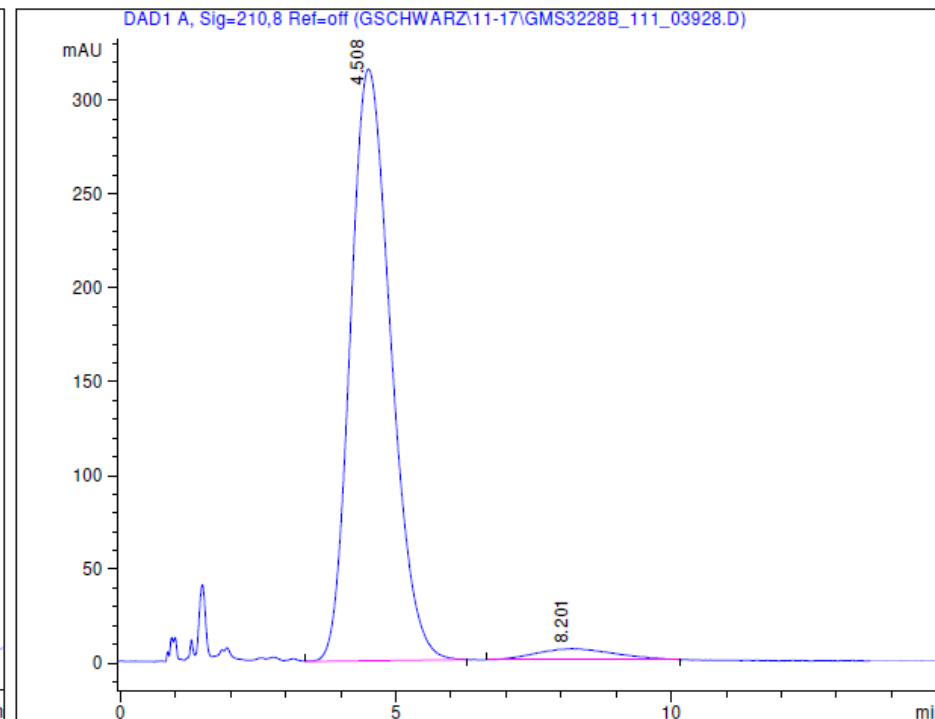
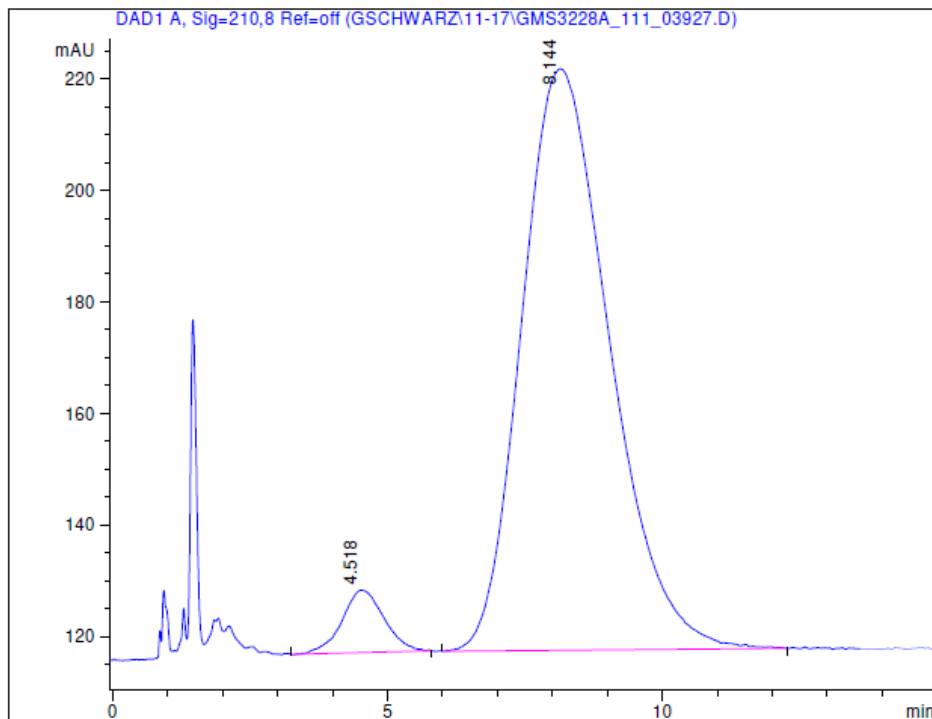


Table 2, entry 5
(101 MHz, CDCl₃)





Signal 1:DAD1 A, Sig=210,8 Ref=off

Peak #	RT [min]	Width [min]	Area	Area %
1	4.52	1.00	593	4.87
2	8.14	1.85	11576	95.13

Signal 1:DAD1 A, Sig=210,8 Ref=off

Peak #	RT [min]	Width [min]	Area	Area %
1	4.51	0.85	16037	96.39
2	8.20	1.70	600	3.61

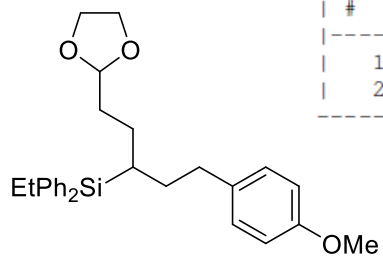


Table 2, entry 5
SFC: CHIRALCEL OJ column (40% 2-PrOH in supercritical CO₂, 3.5 mL/min)

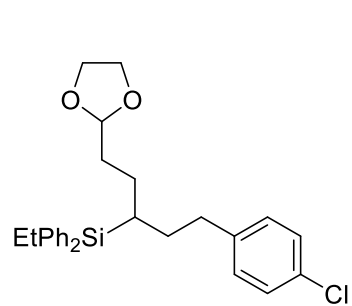
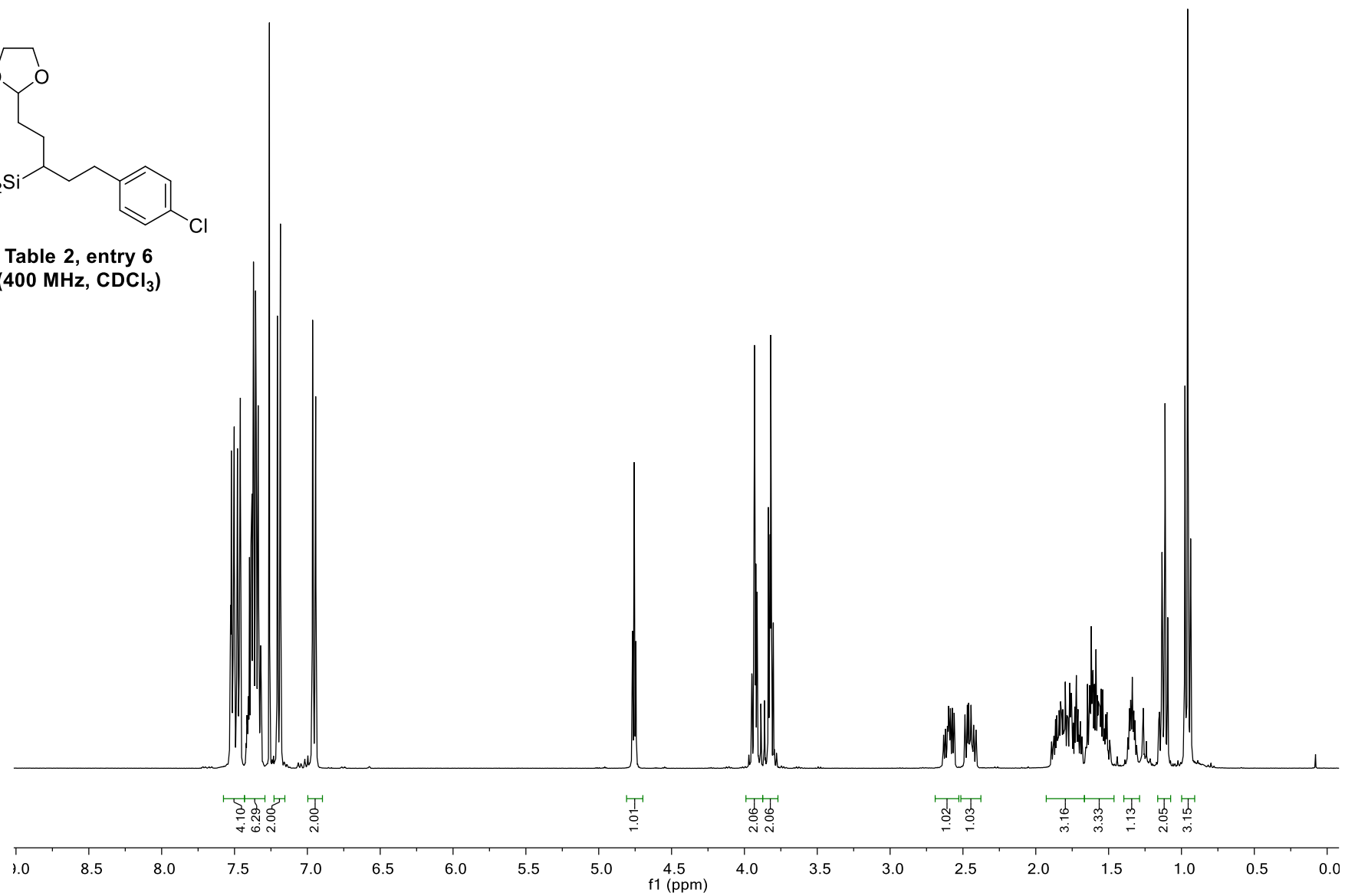


Table 2, entry 6
(400 MHz, CDCl₃)



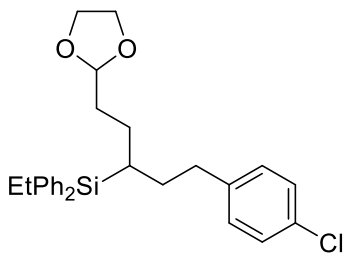
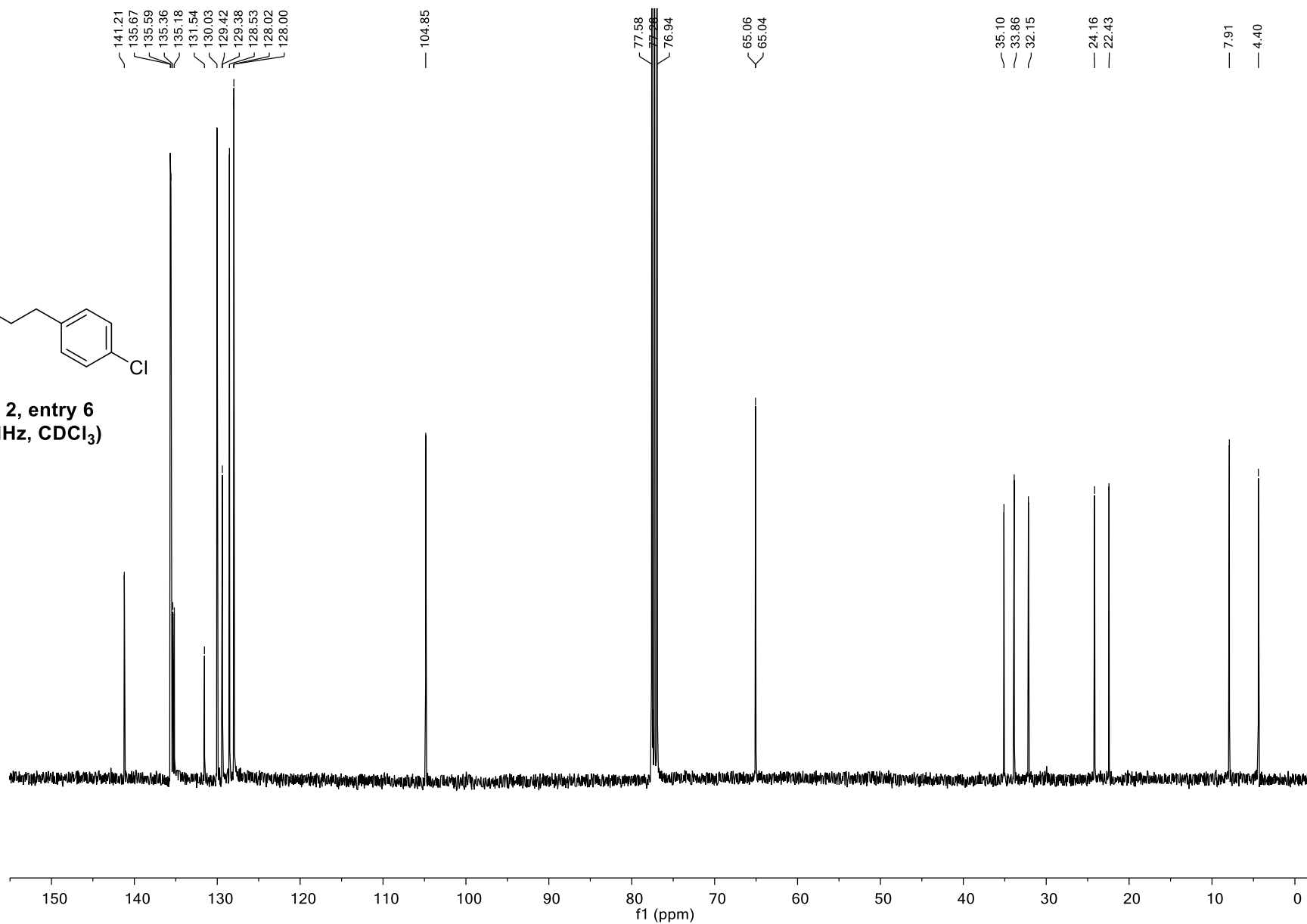
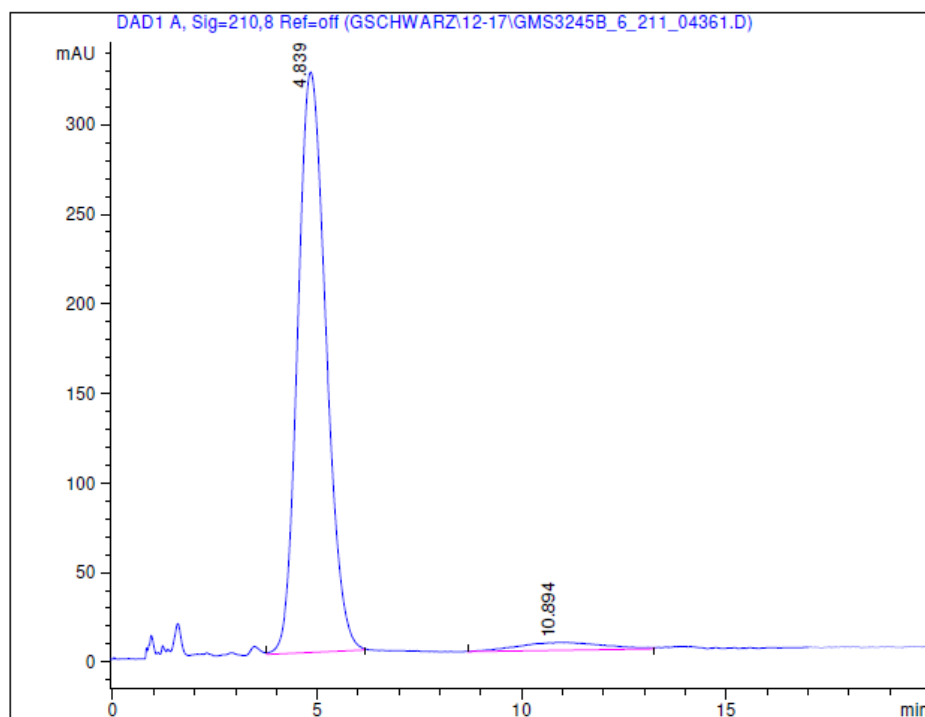
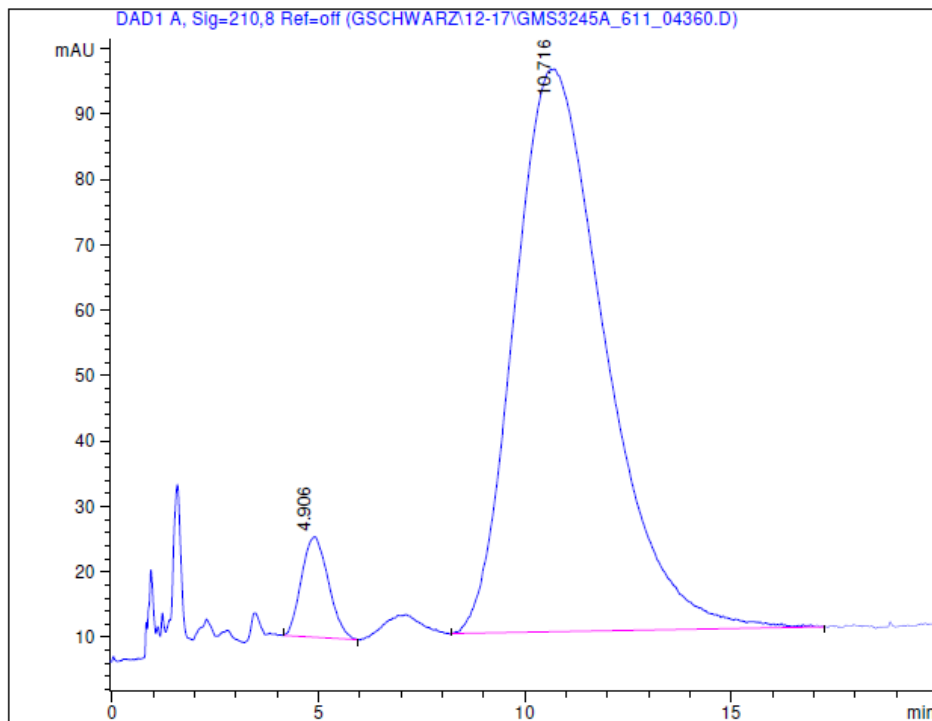


Table 2, entry 6
(101 MHz, CDCl₃)





Signal 1:DAD1 A, Sig=210,8 Ref=off

Peak #	RT [min]	Width [min]	Area	Area %
1	4.91	0.75	696	5.04
2	10.72	2.54	13120	94.96

Signal 1:DAD1 A, Sig=210,8 Ref=off

Peak #	RT [min]	Width [min]	Area	Area %
1	4.84	0.74	15527	95.96
2	10.89	2.45	654	4.04

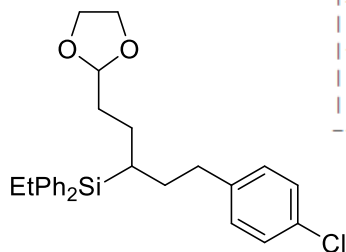


Table 2, entry 6

SFC: CHIRALCEL OJ column (35% 2-PrOH in supercritical CO₂, 3.5 mL/min)

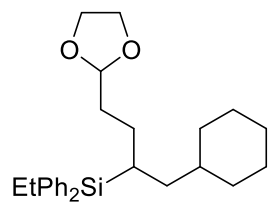
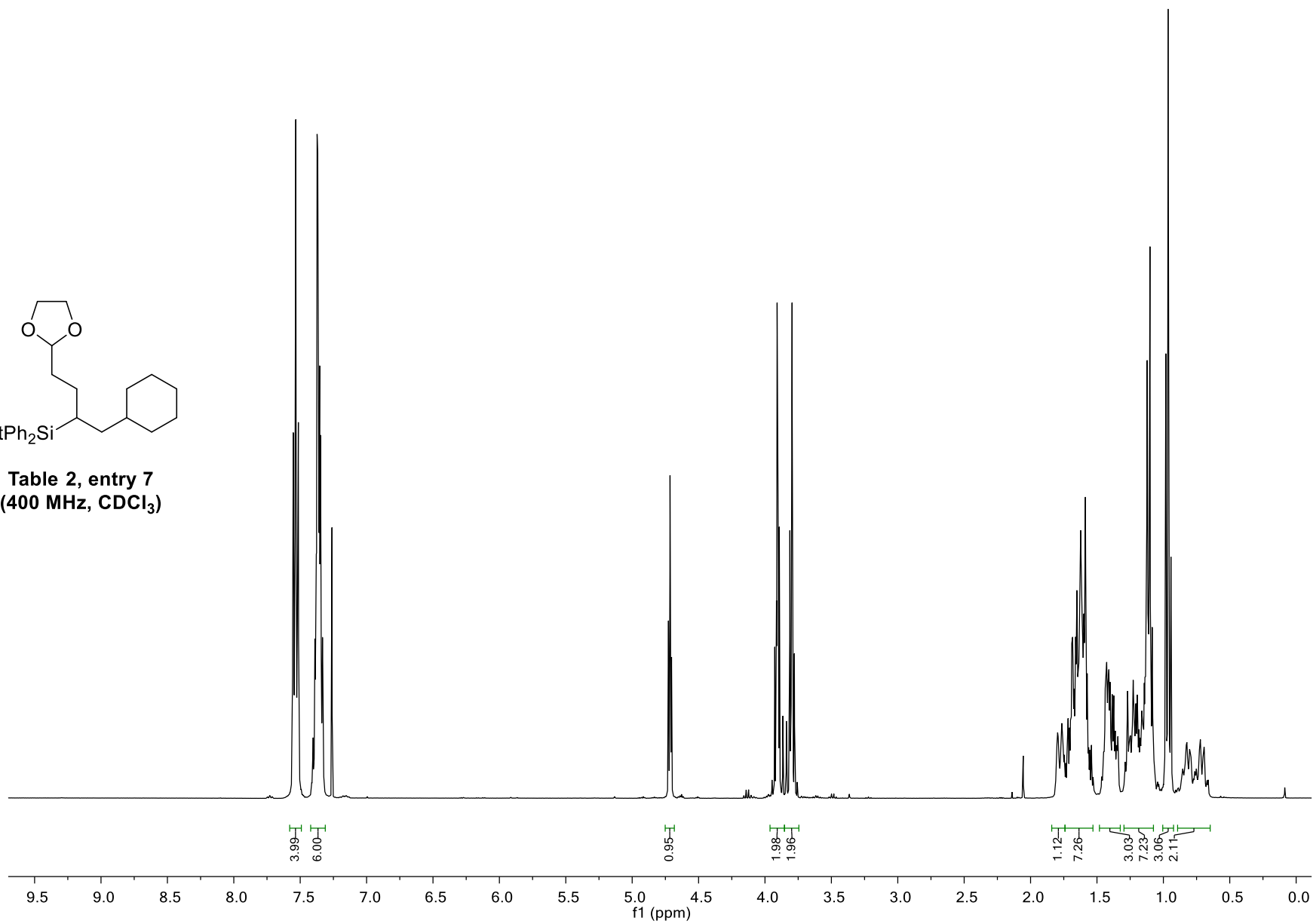


Table 2, entry 7
(400 MHz, CDCl₃)



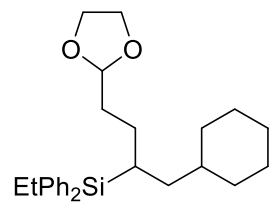
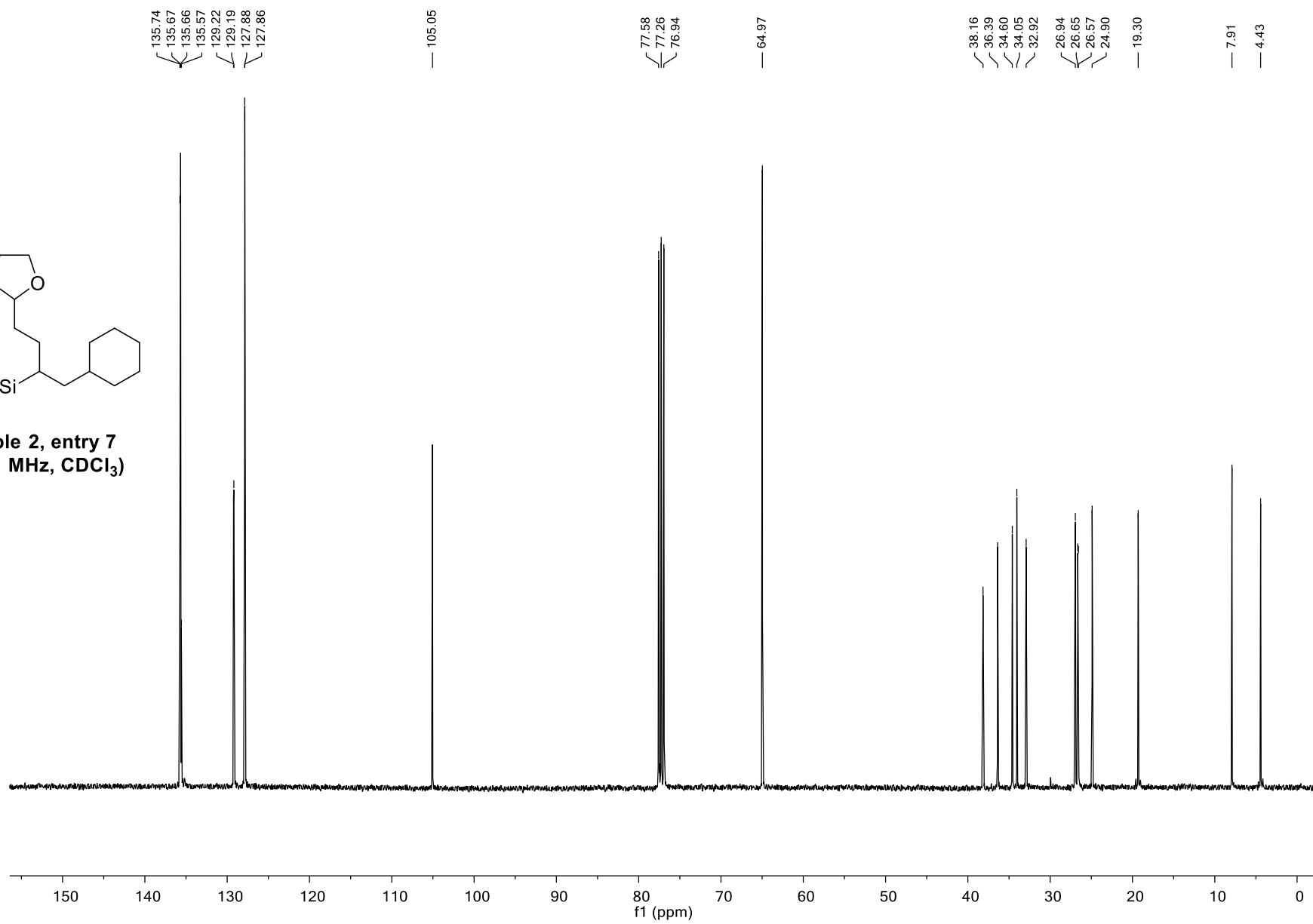
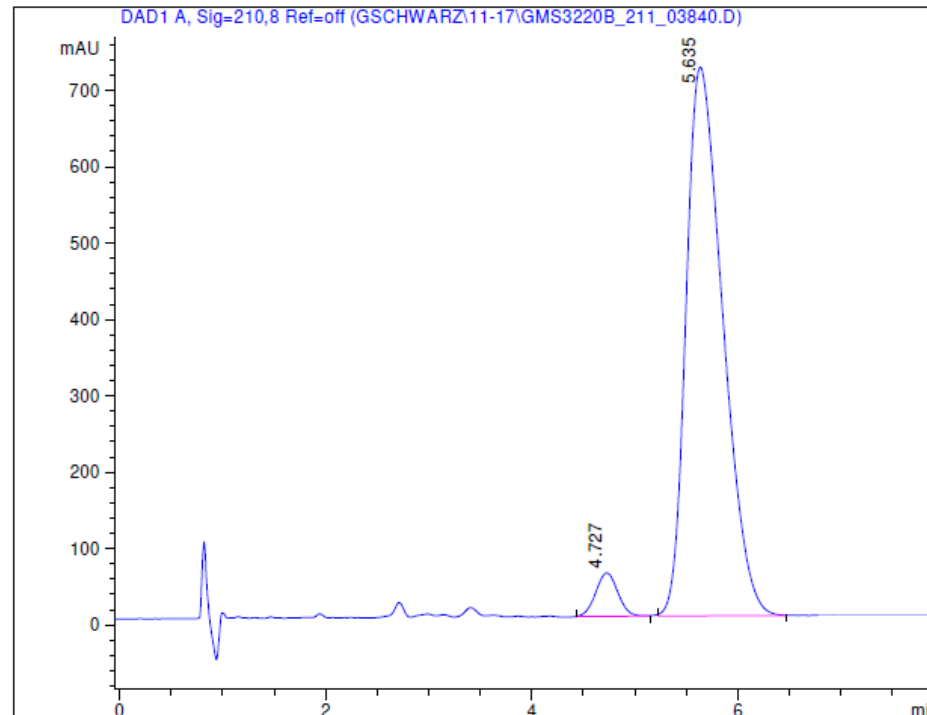
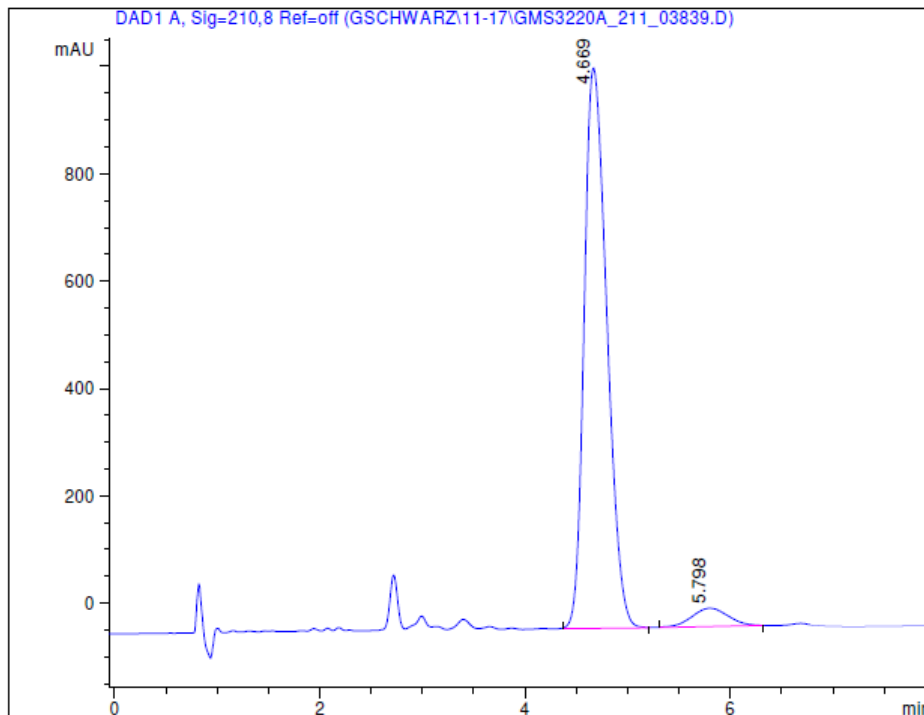


Table 2, entry 7
(101 MHz, CDCl₃)





Signal 1:DAD1 A, Sig=210,8 Ref=off

Peak #	RT [min]	Width [min]	Area	Area %
1	4.67	0.24	16035	95.02
2	5.80	0.41	840	4.98

Signal 1:DAD1 A, Sig=210,8 Ref=off

Peak #	RT [min]	Width [min]	Area	Area %
1	4.73	0.23	849	4.57
2	5.63	0.38	17728	95.43

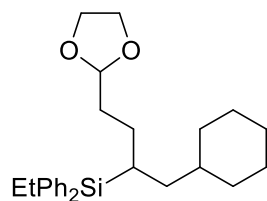
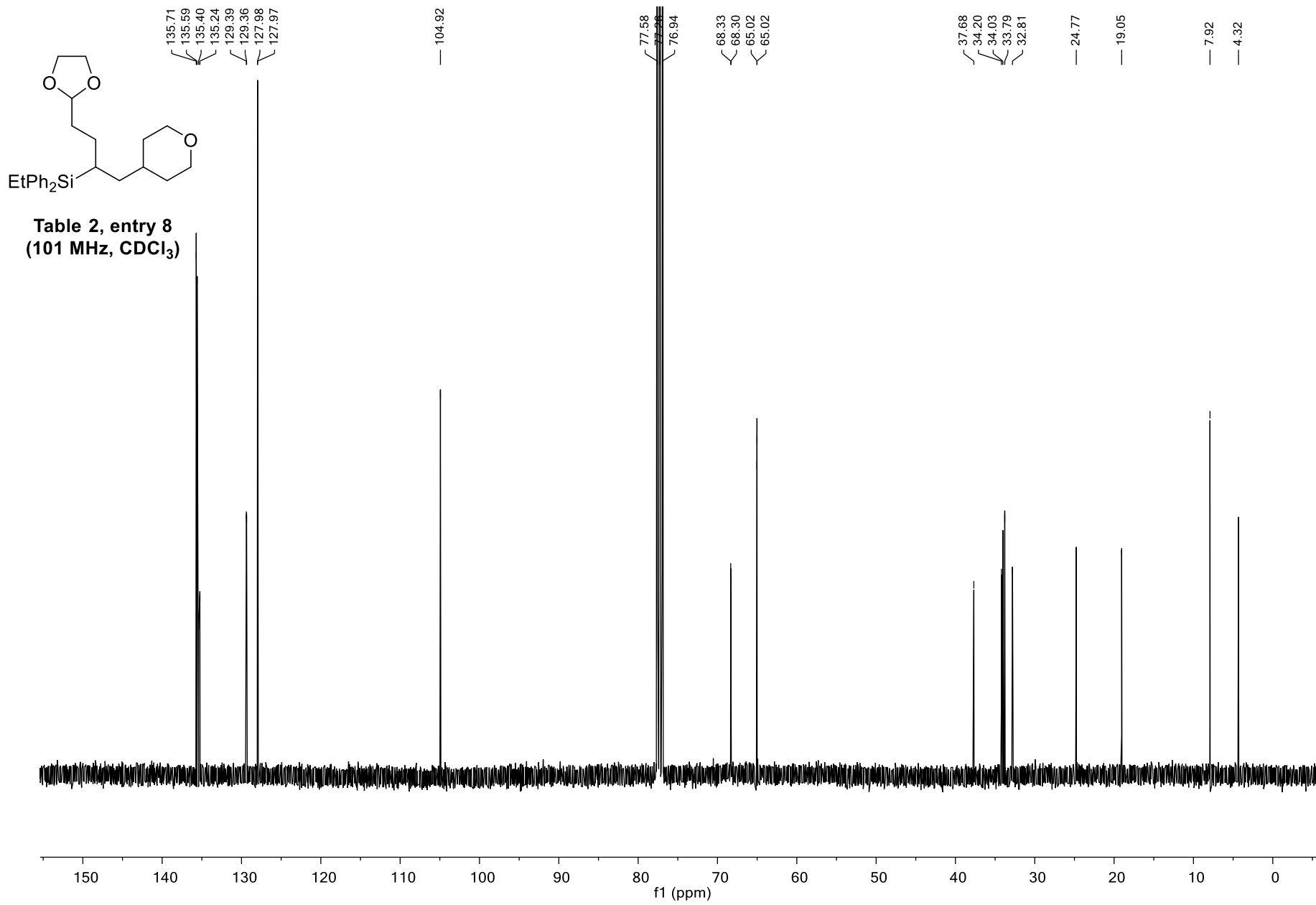
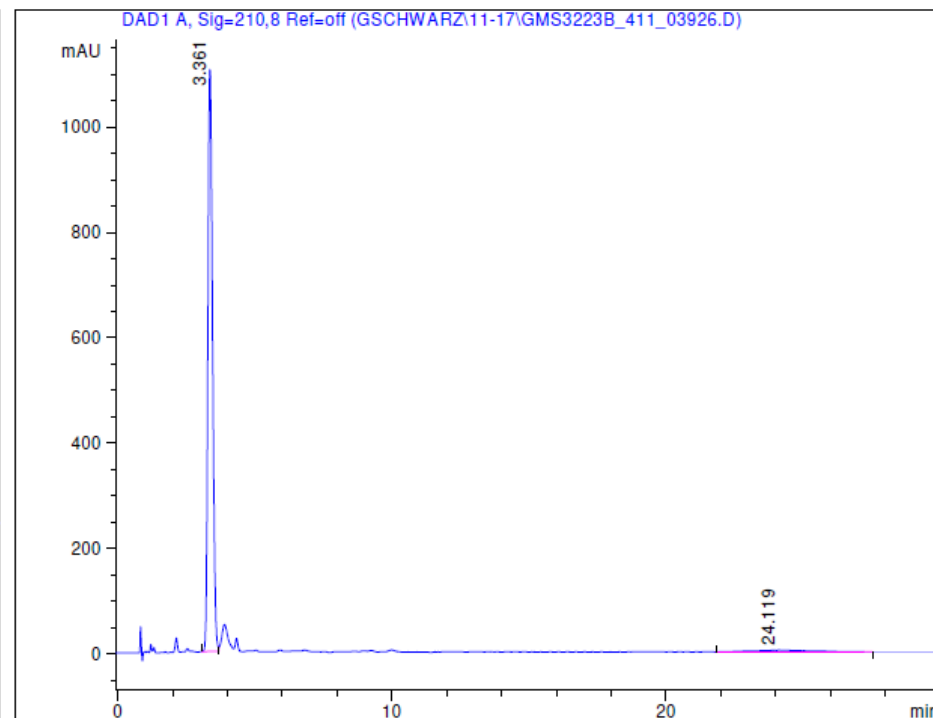
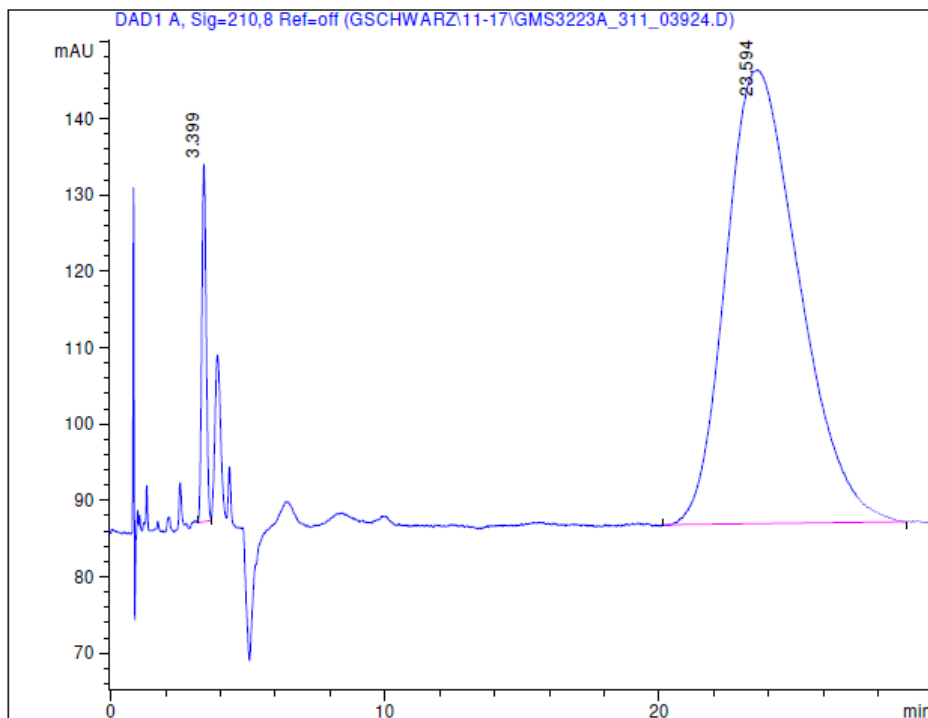


Table 2, entry 7

SFC: CHIRALCEL OJ column (5% 2-PrOH in supercritical CO₂, 3.5 mL/min)





Signal 1:DAD1 A, Sig=210,8 Ref=off

Peak #	RT [min]	Width [min]	Area	Area %
1	3.40	0.18	517	4.49
2	23.59	3.08	10992	95.51

Signal 1:DAD1 A, Sig=210,8 Ref=off

Peak #	RT [min]	Width [min]	Area	Area %
1	3.36	0.19	12880	95.93
2	24.12	2.50	547	4.07

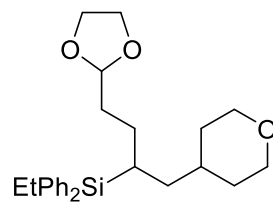


Table 2, entry 8

SFC: CHIRALCEL OJ column (10% 2-PrOH in supercritical CO₂, 3.5 mL/min)

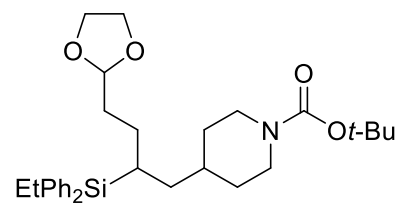
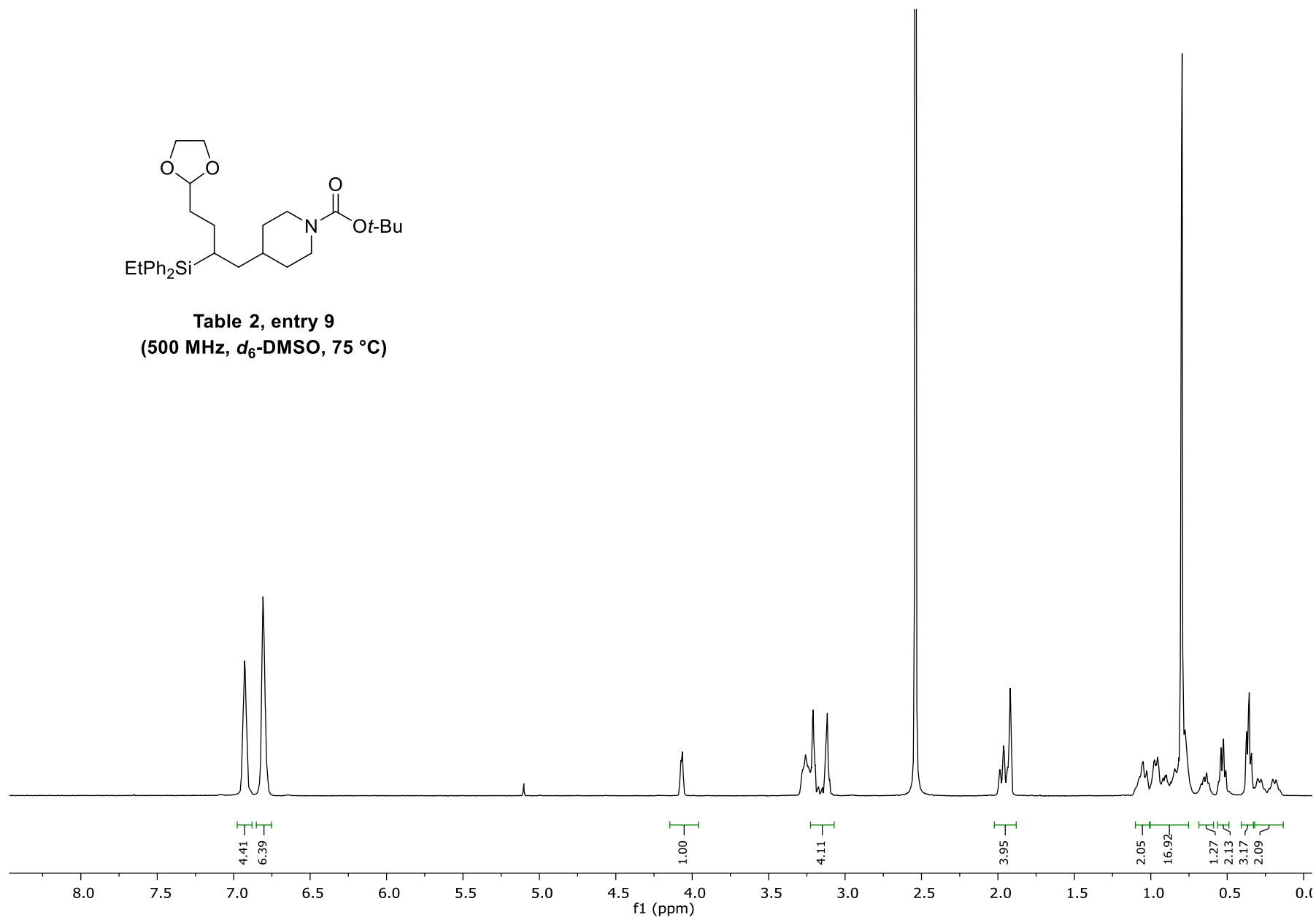


Table 2, entry 9
(500 MHz, d_6 -DMSO, 75 °C)



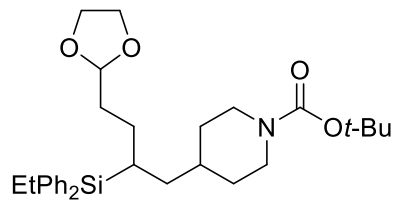
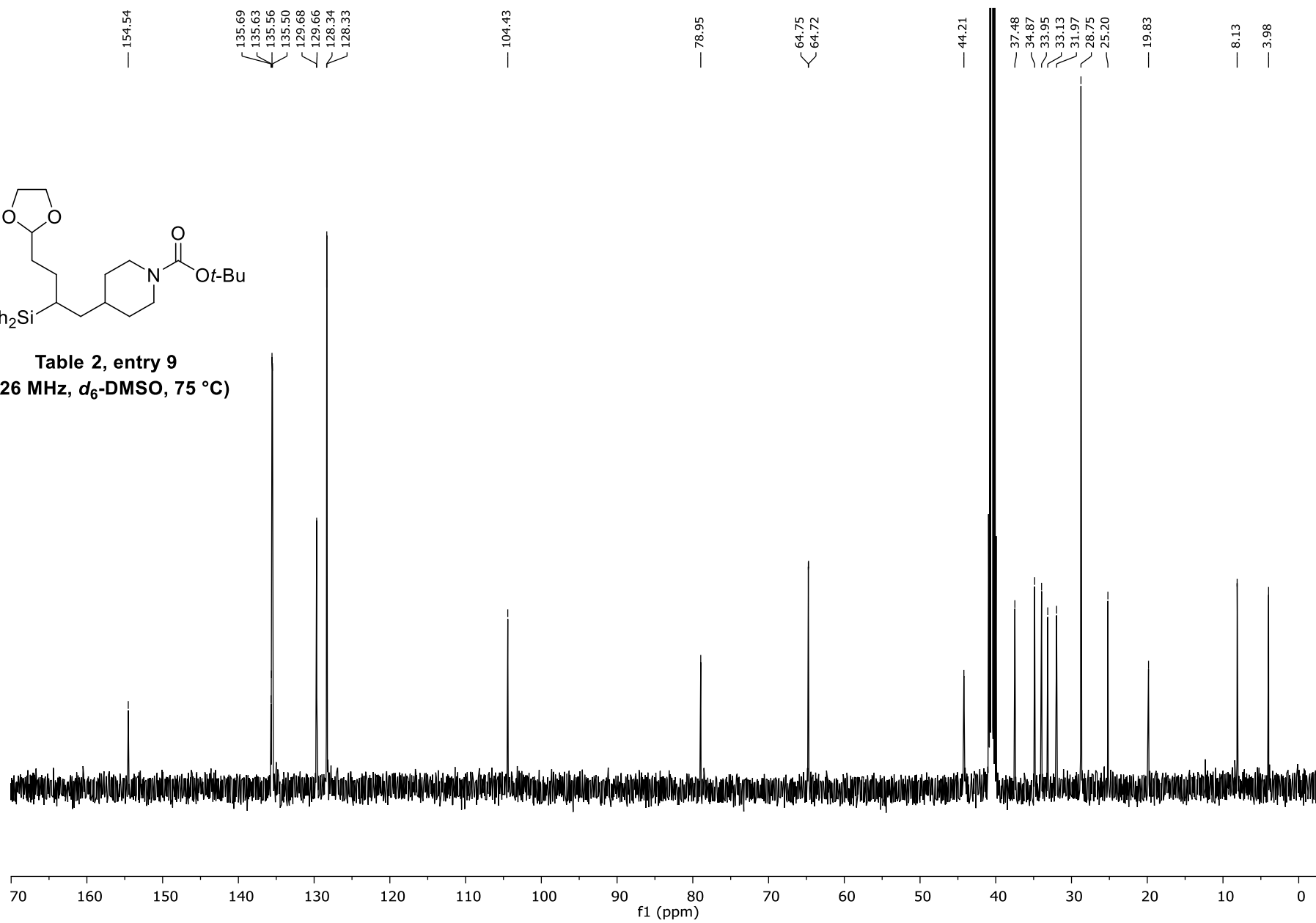
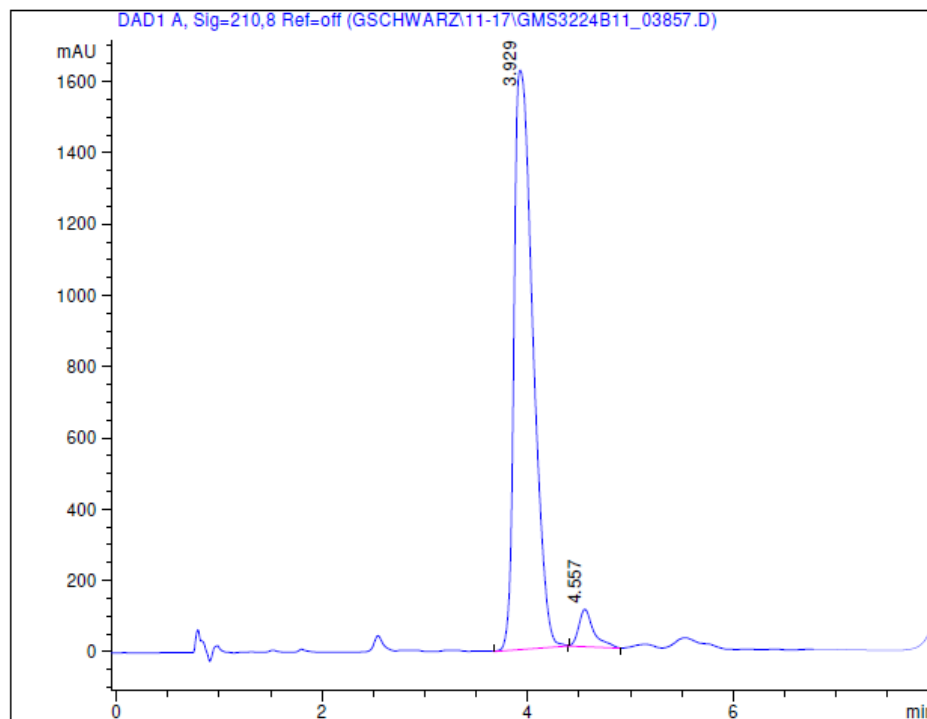
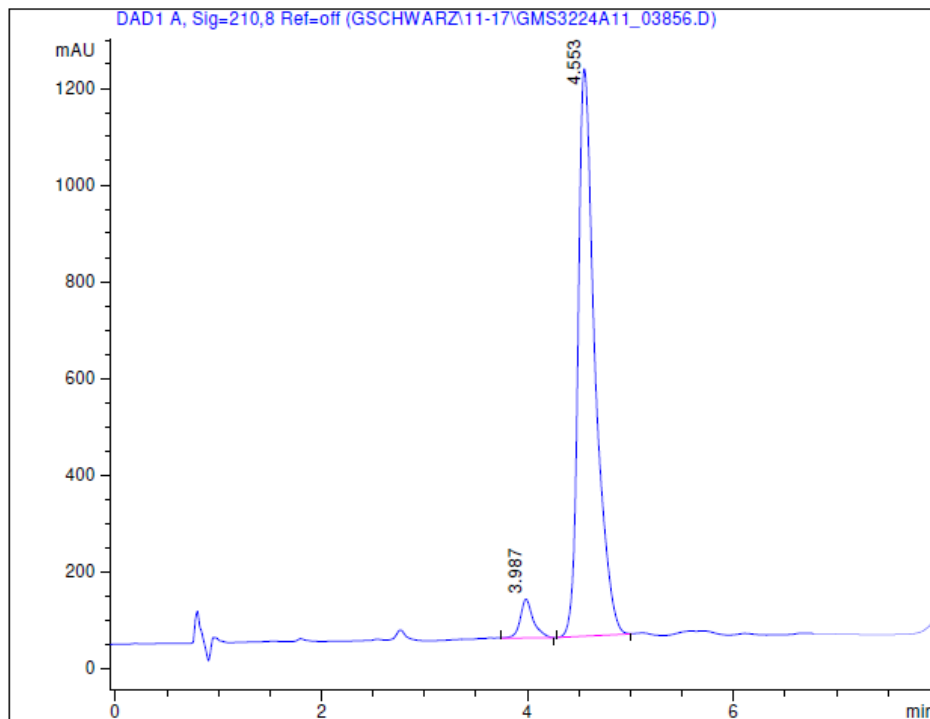


Table 2, entry 9
(126 MHz, d_6 -DMSO, 75 °C)





Signal 1:DAD1 A, Sig=210,8 Ref=off

Peak #	RT [min]	Width [min]	Area	Area %
1	3.99	0.15	702	4.98
2	4.55	0.19	13392	95.02

Signal 1:DAD1 A, Sig=210,8 Ref=off

Peak #	RT [min]	Width [min]	Area	Area %
1	3.93	0.21	20680	95.14
2	4.56	0.17	1057	4.86

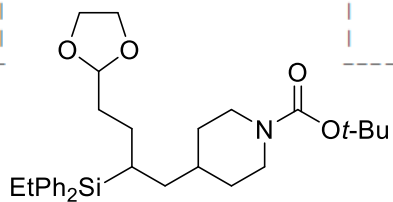


Table 2, entry 9

SFC: CHIRALPAK AD-H column (10% 2-PrOH in supercritical CO₂, 3.5 mL/min)

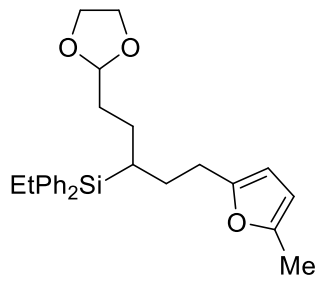
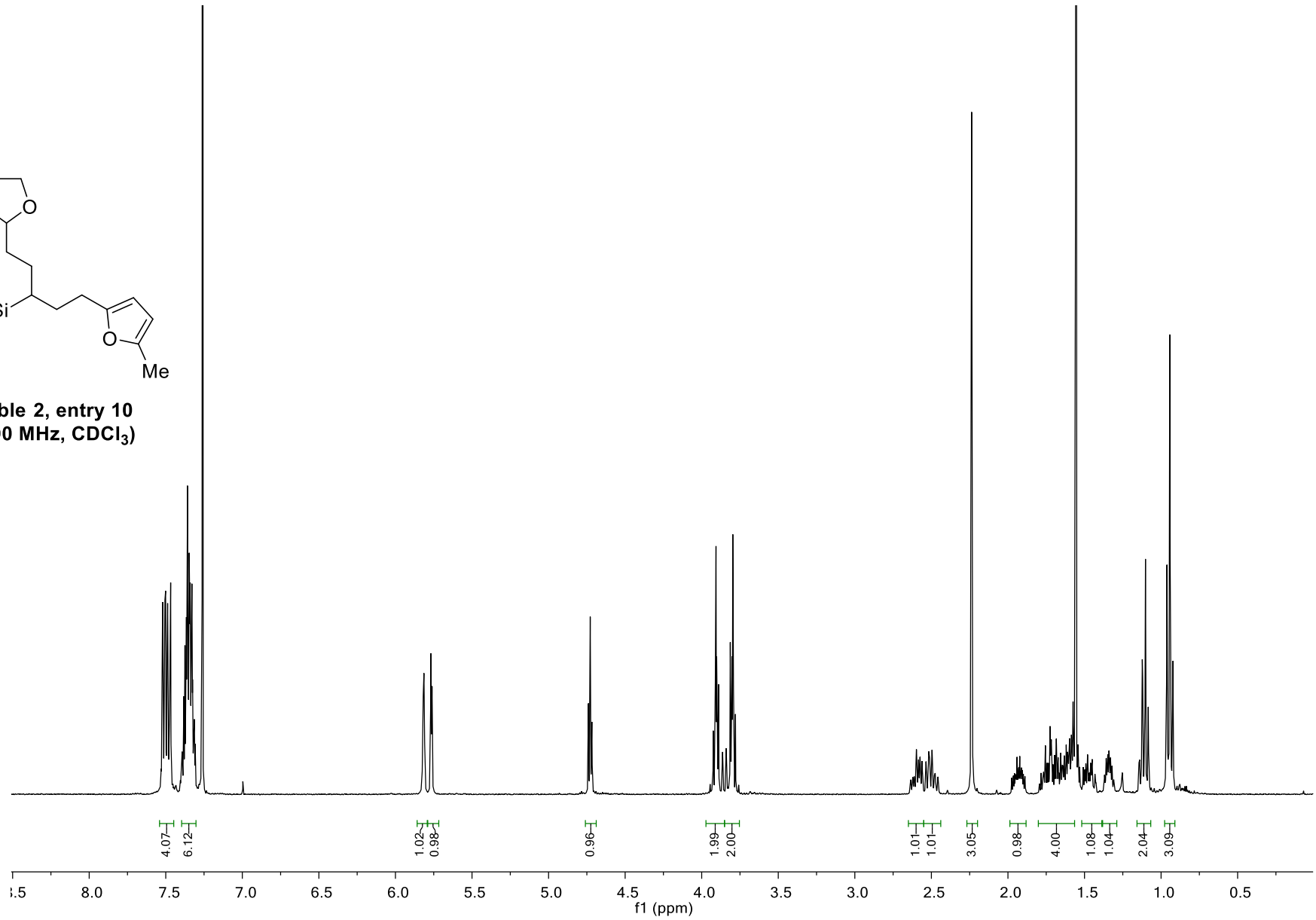
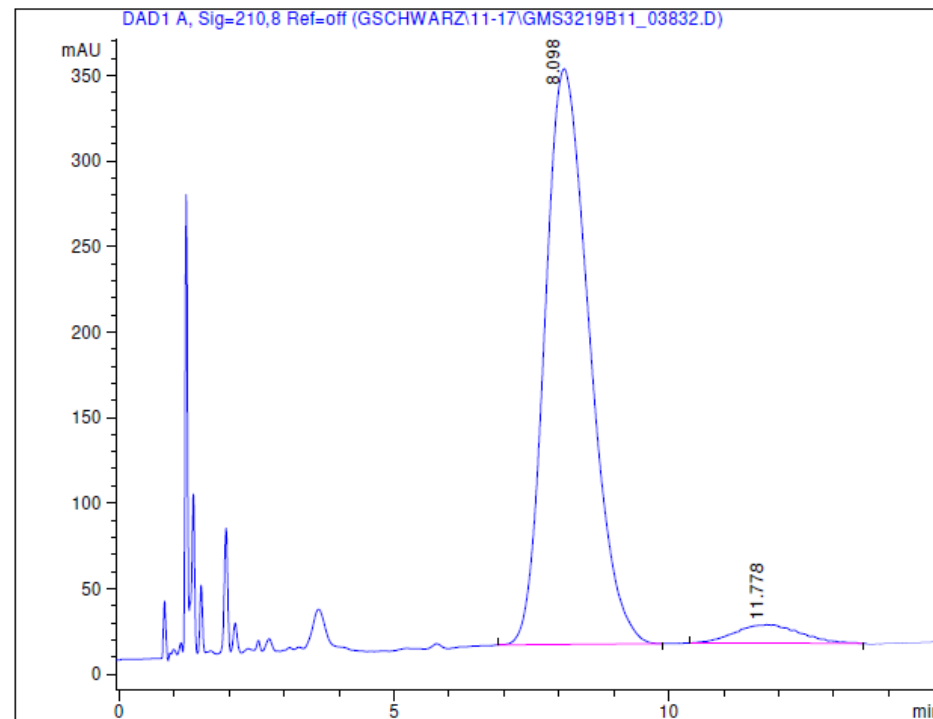
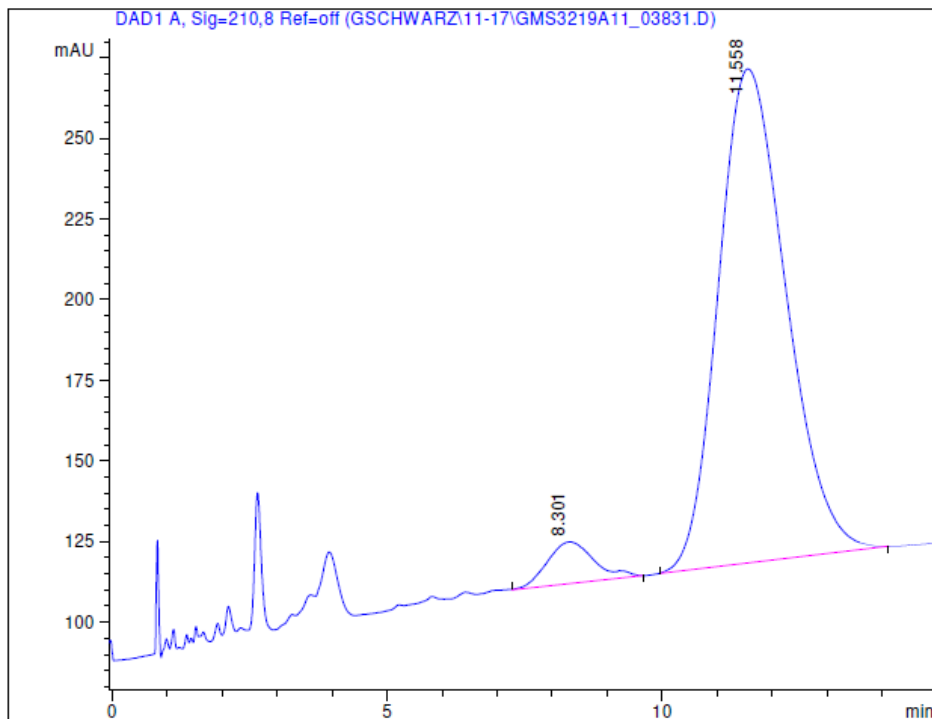


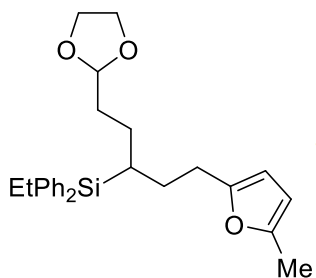
Table 2, entry 10
(400 MHz, CDCl₃)





Signal 1:DAD1 A, Sig=210,8 Ref=off

Peak #	RT [min]	Width [min]	Area	Area %
1	8.30	0.98	762	5.50
2	11.56	1.43	13106	94.50



Signal 1:DAD1 A, Sig=210,8 Ref=off

Peak #	RT [min]	Width [min]	Area	Area %
1	8.10	0.93	18863	95.49
2	11.78	1.37	892	4.51

Table 2, entry 10
SFC: CHIRALCEL OJ column (15% 2-PrOH in supercritical CO₂, 3.5 mL/min)

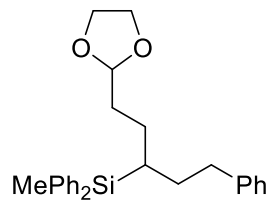
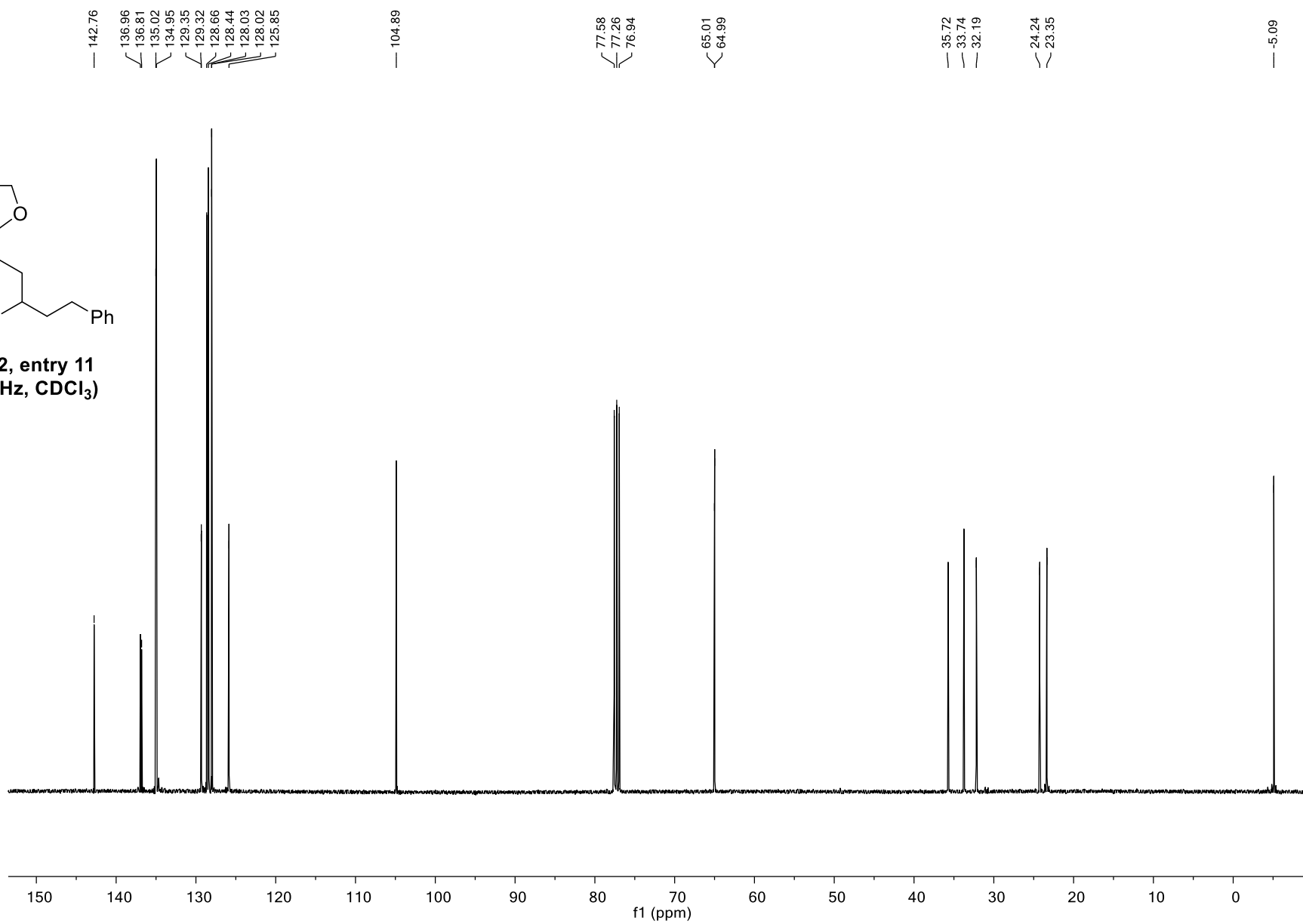
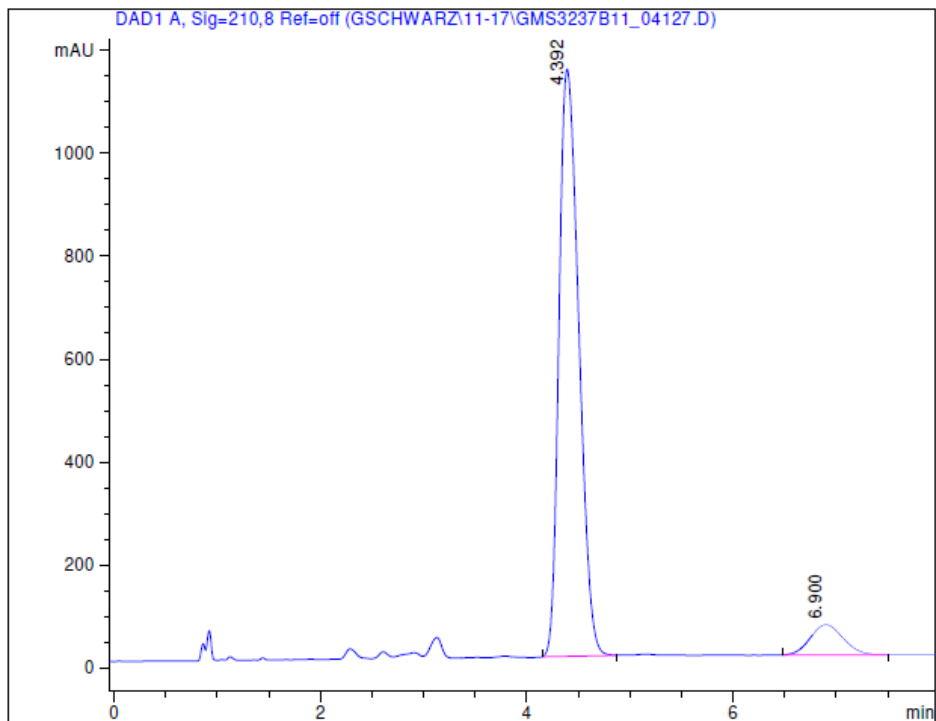
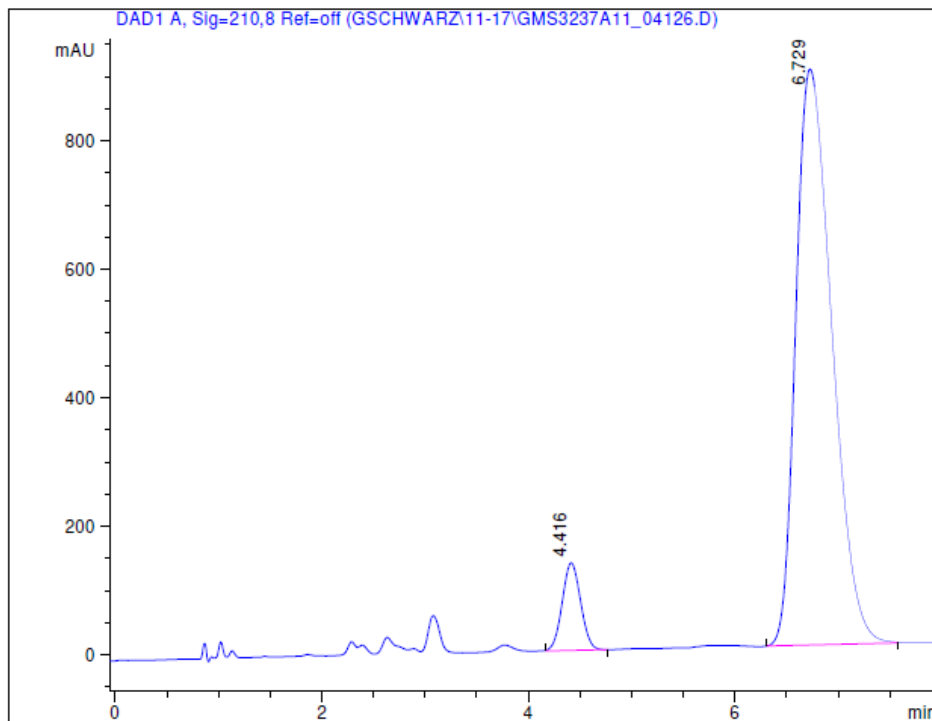


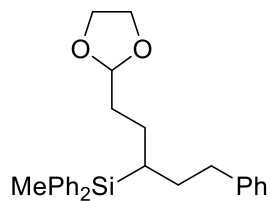
Table 2, entry 11
(101 MHz, CDCl₃)





Signal 1:DAD1 A, Sig=210,8 Ref=off

Peak #	RT [min]	Width [min]	Area	Area %
1	4.42	0.20	1690	7.22
2	6.73	0.38	21711	92.78



Signal 1:DAD1 A, Sig=210,8 Ref=off

Peak #	RT [min]	Width [min]	Area	Area %
1	4.39	0.21	15193	92.03
2	6.90	0.35	1315	7.97

Table 2, entry 11

SFC: CHIRALCEL OJ column (15% 2-PrOH in supercritical CO₂, 3.5 mL/min)

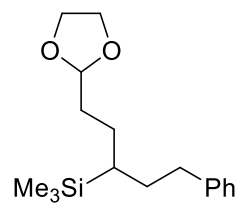
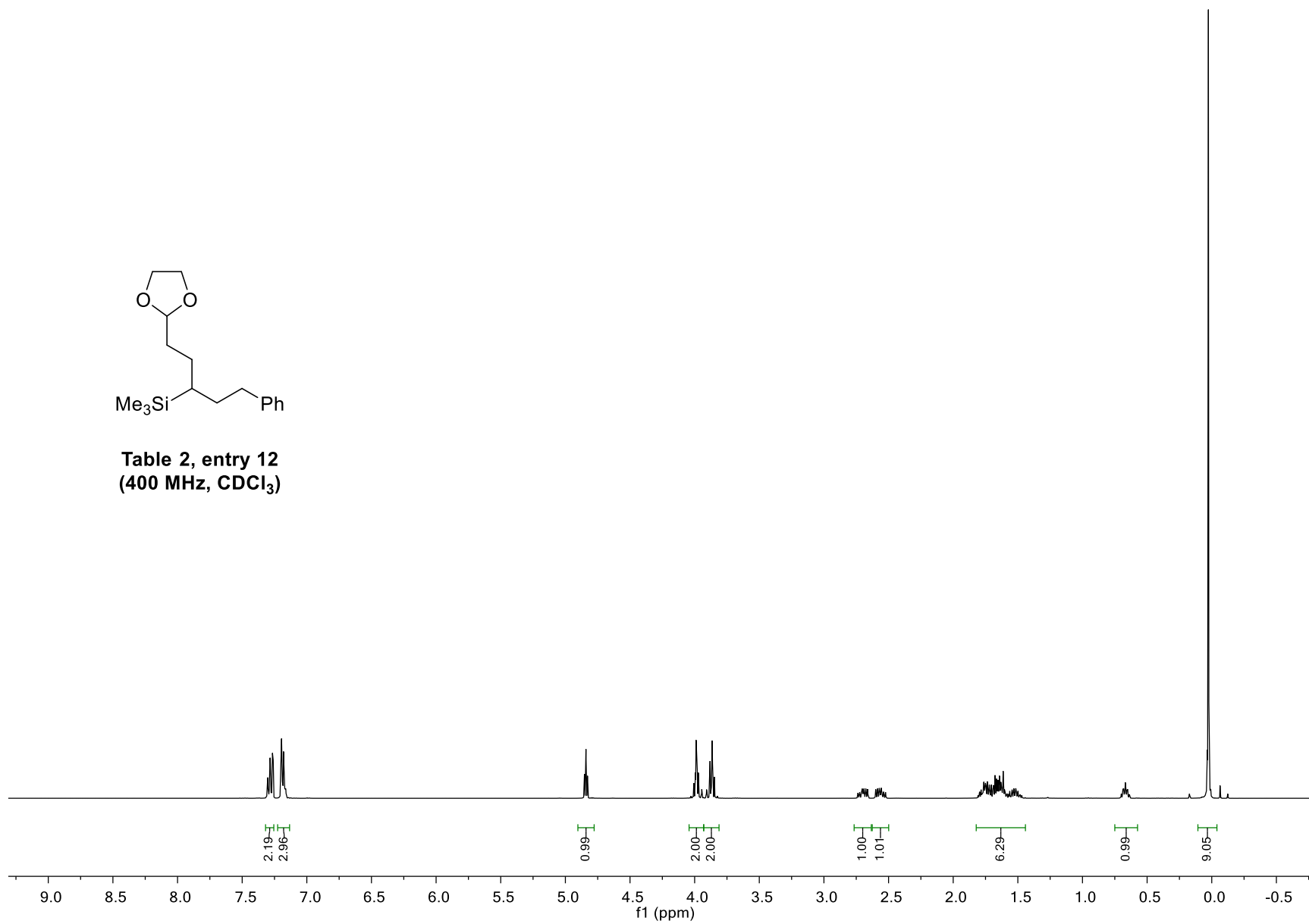


Table 2, entry 12
(400 MHz, CDCl₃)



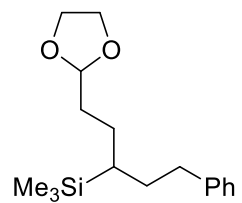
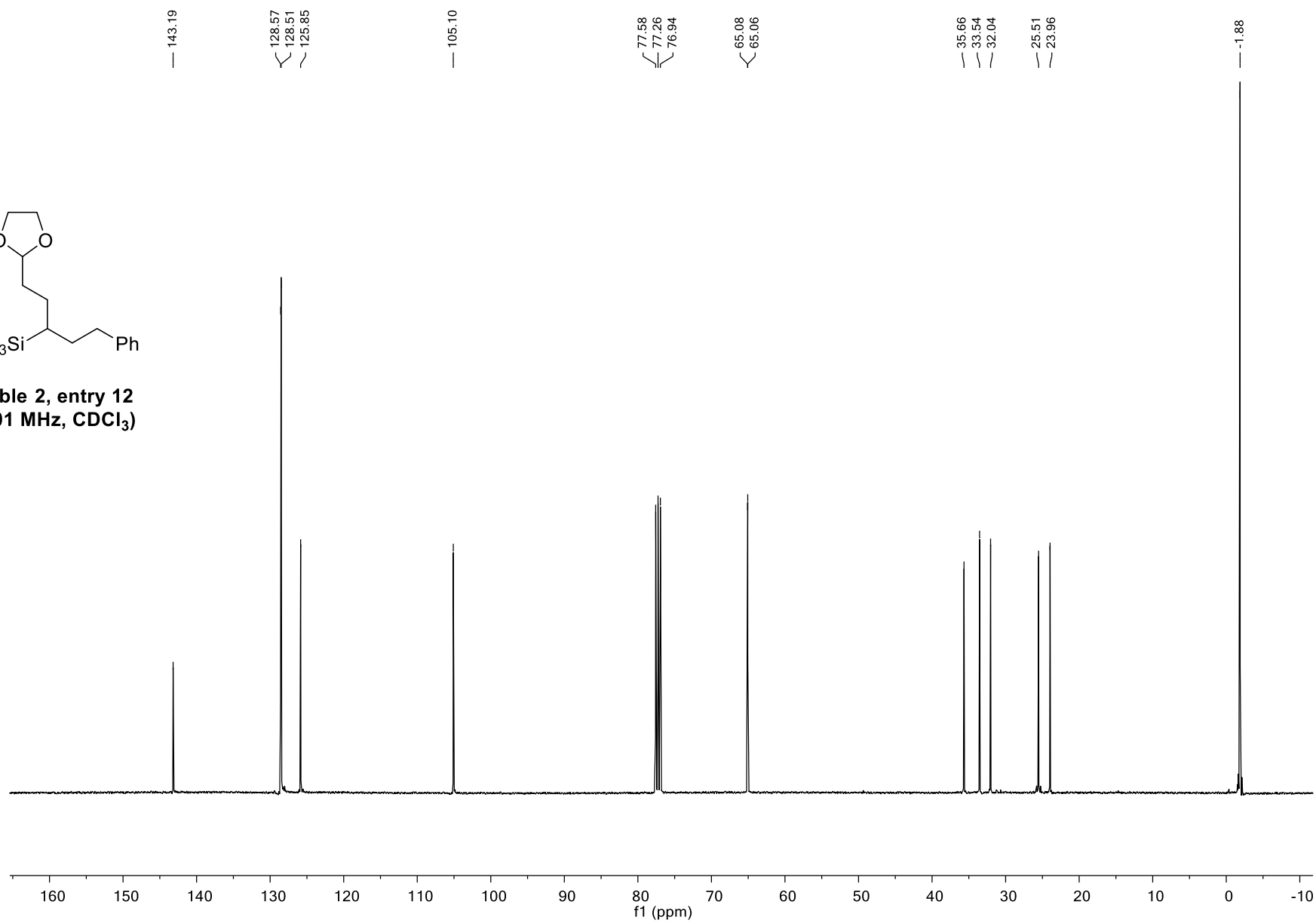
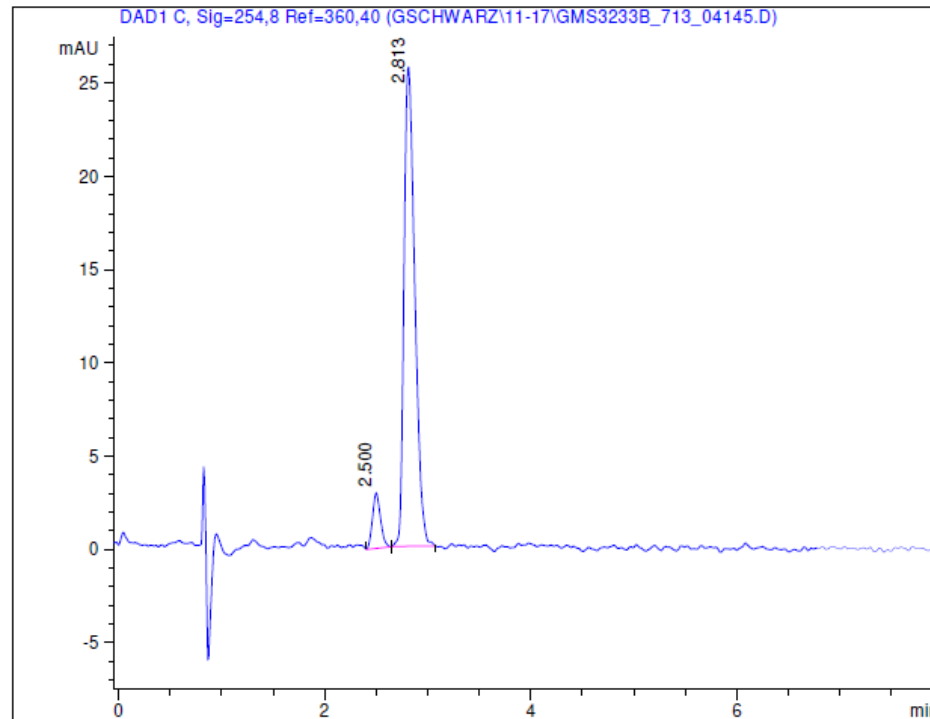
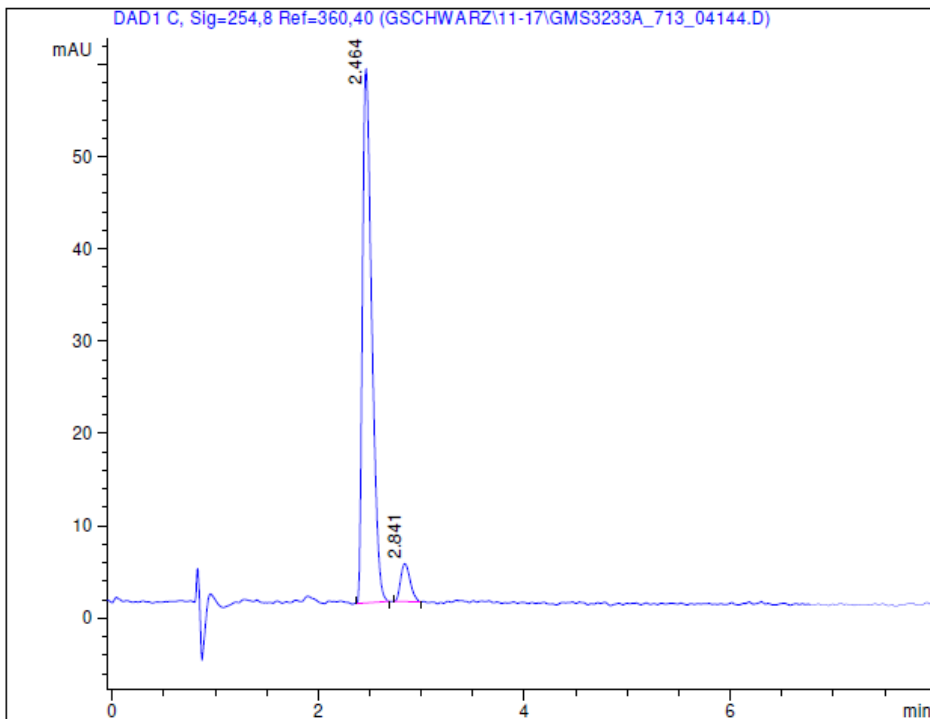


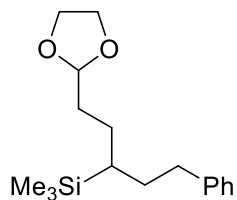
Table 2, entry 12
(101 MHz, CDCl₃)





Signal 1:DAD1 C, Sig=254,8 Ref=360,40

Peak #	RT [min]	Width [min]	Area	Area %
1	2.46	0.10	364	93.24
2	2.84	0.11	26	6.76



Signal 1:DAD1 C, Sig=254,8 Ref=360,40

Peak #	RT [min]	Width [min]	Area	Area %
1	2.50	0.09	16	8.02
2	2.81	0.12	186	91.98

Table 2, entry 12
SFC: CHIRALPAK AD-H column (2% 2-PrOH in supercritical CO₂, 3.5 mL/min)

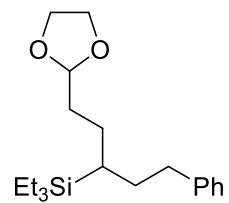
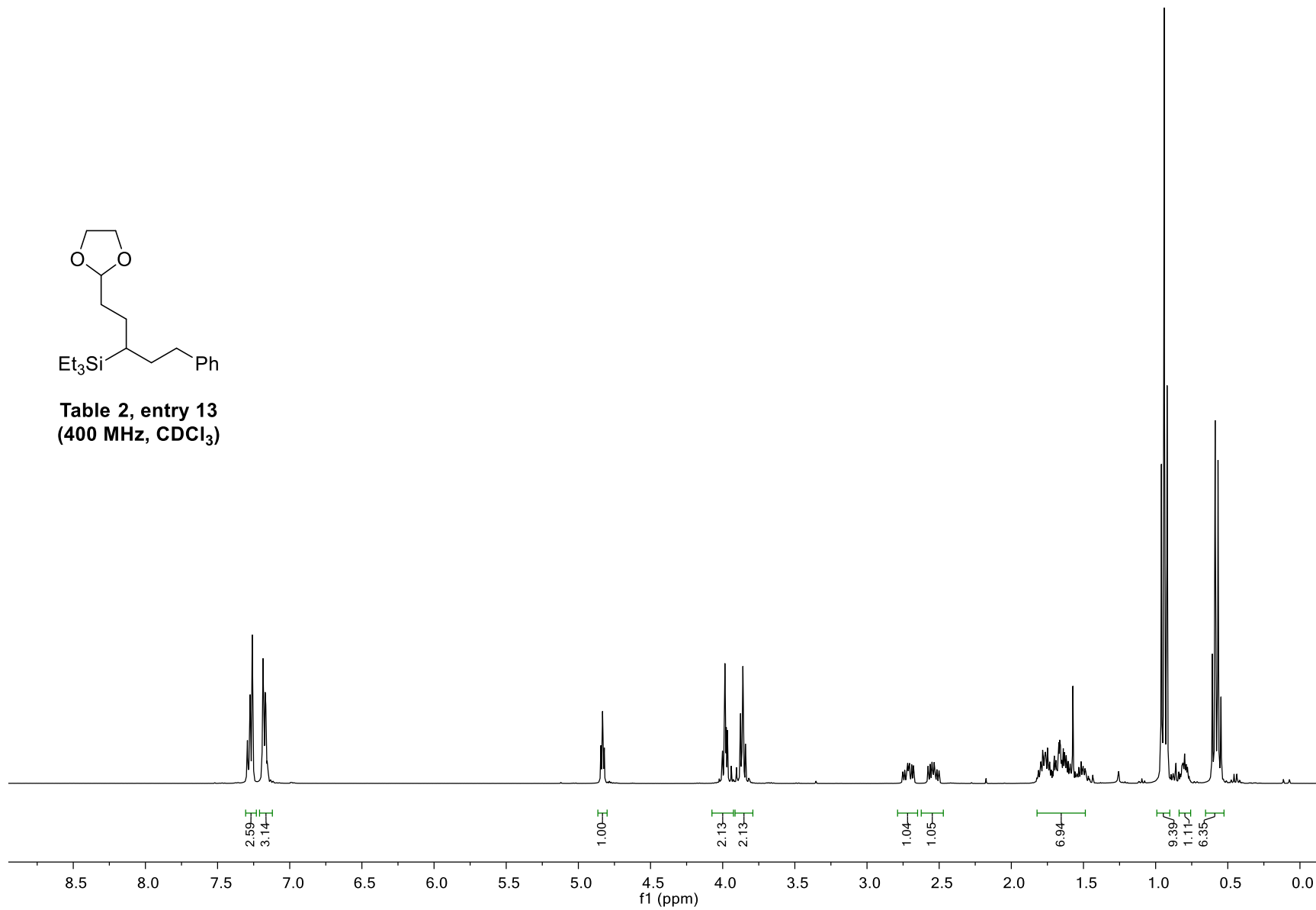


Table 2, entry 13
(400 MHz, CDCl₃)



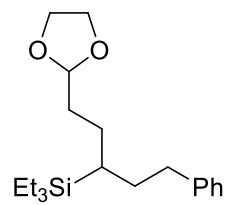
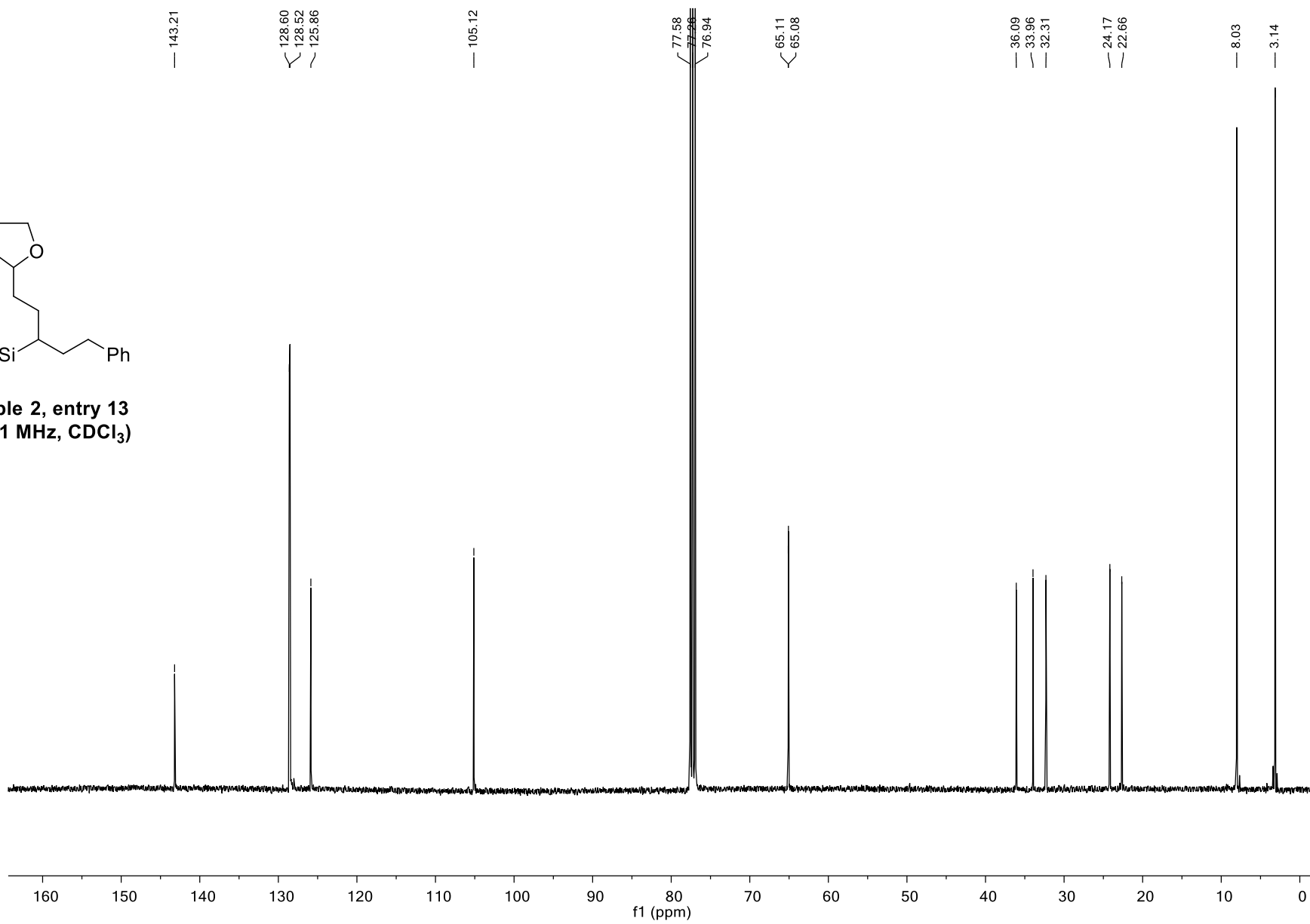
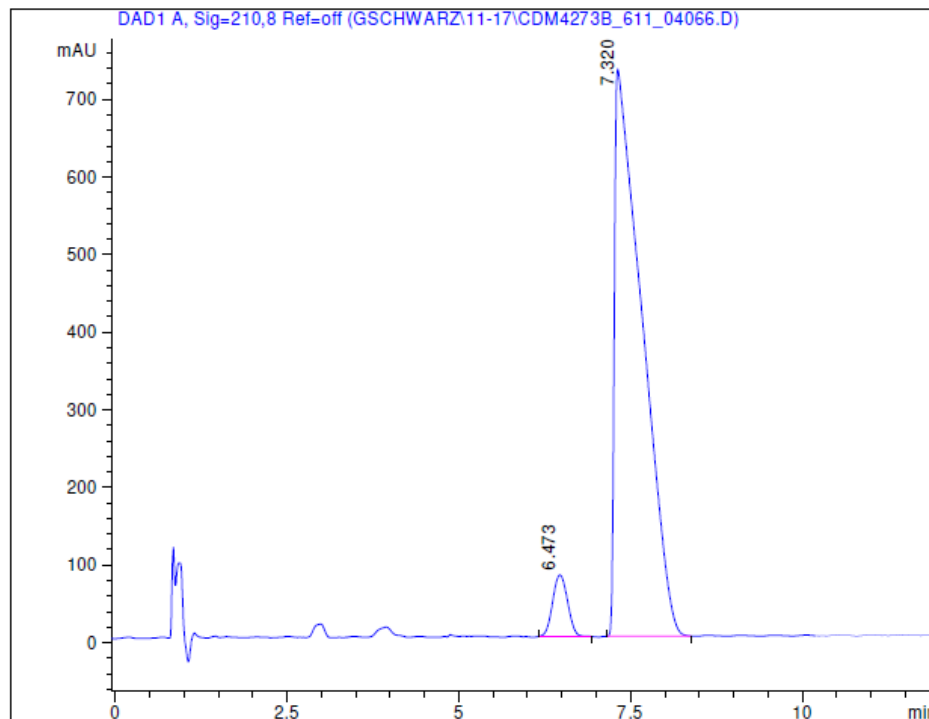
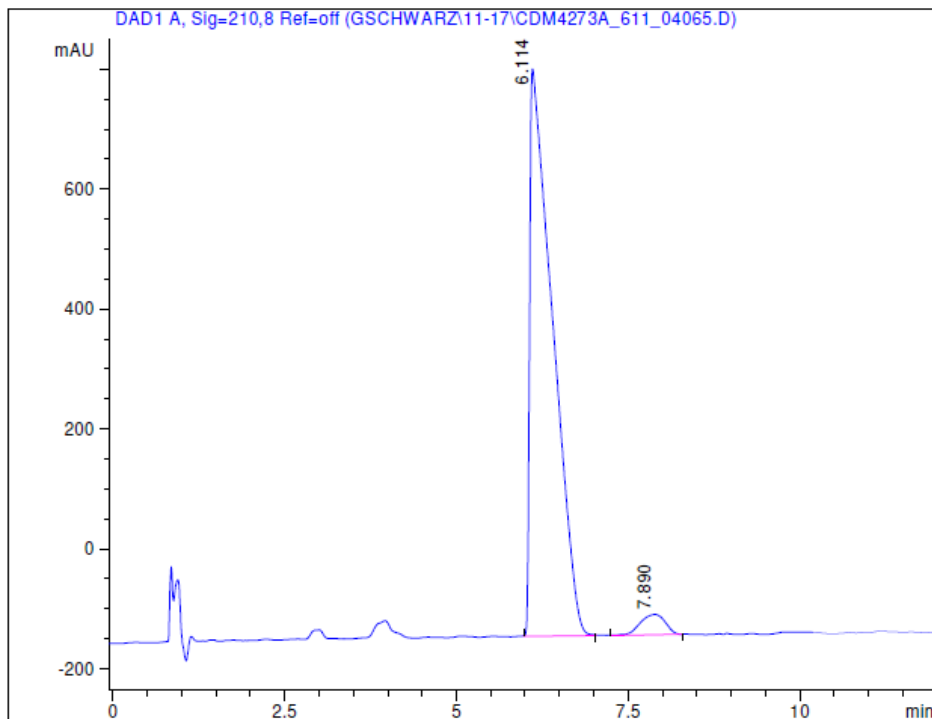


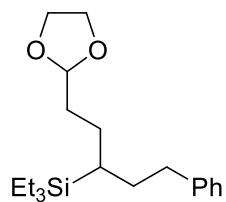
Table 2, entry 13
(101 MHz, CDCl₃)





Signal 1:DAD1 A, Sig=210,8 Ref=off

Peak #	RT [min]	Width [min]	Area	Area %
1	6.11	0.32	21721	96.20
2	7.89	0.42	857	3.80



Signal 1:DAD1 A, Sig=210,8 Ref=off

Peak #	RT [min]	Width [min]	Area	Area %
1	6.47	0.24	1202	5.60
2	7.32	0.39	20242	94.40

Table 2, entry 13
SFC: CHIRALCEL OJ column (1% 2-PrOH in supercritical CO₂, 3.5 mL/min)

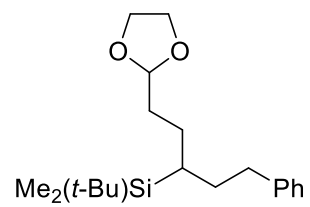
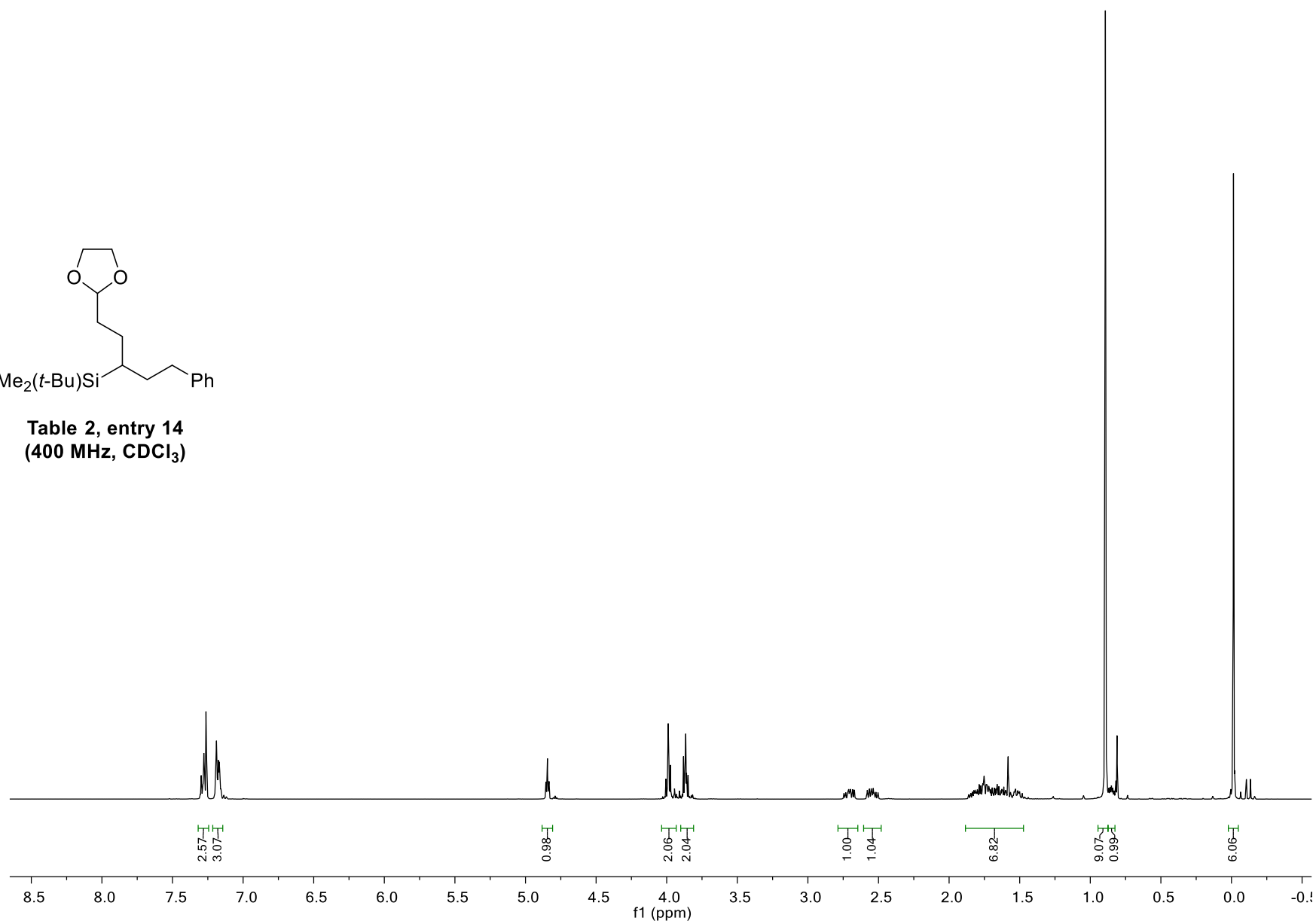


Table 2, entry 14
(400 MHz, CDCl₃)



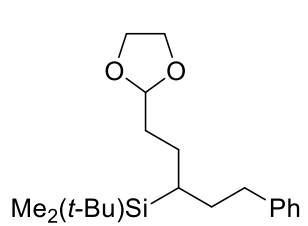
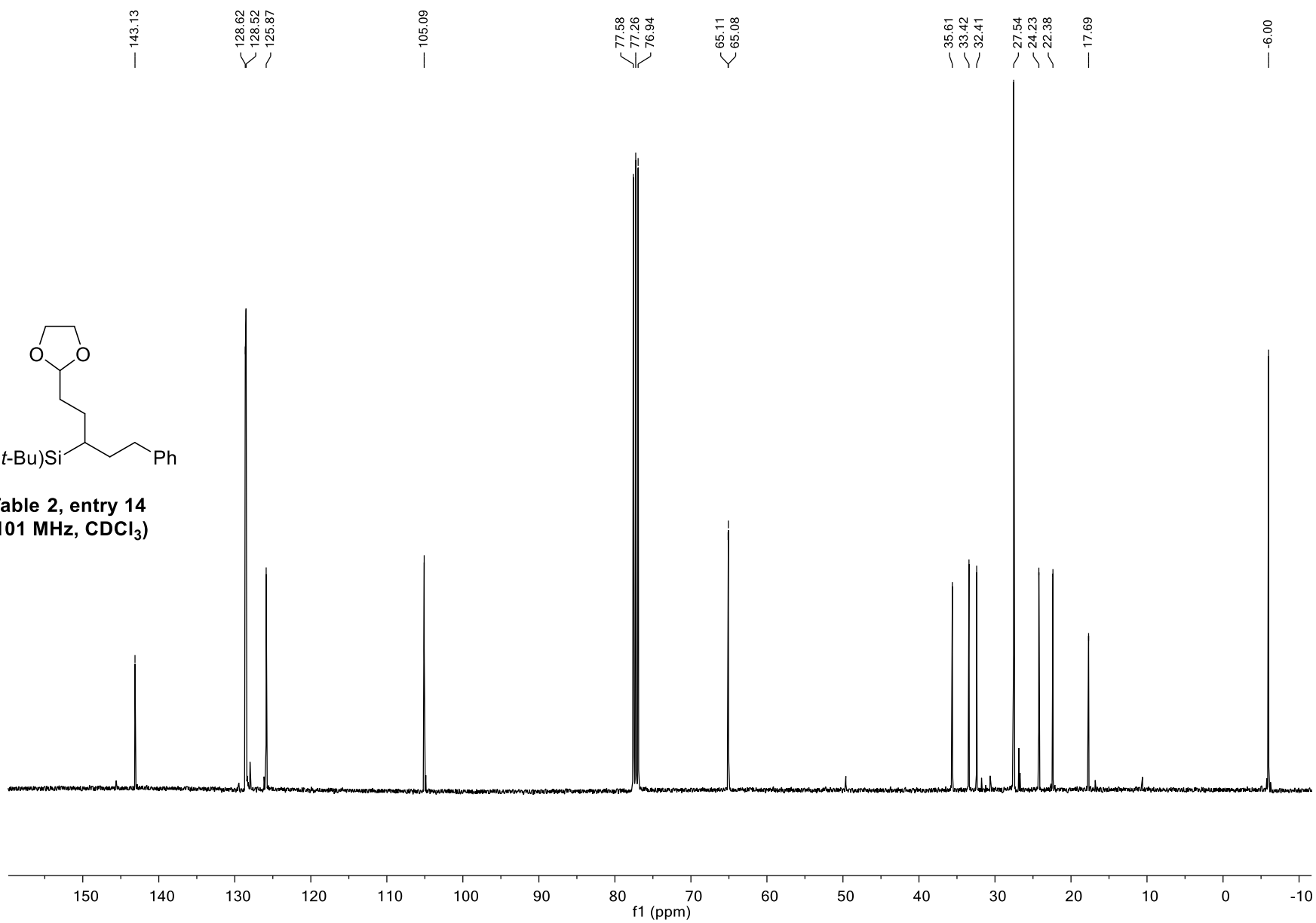
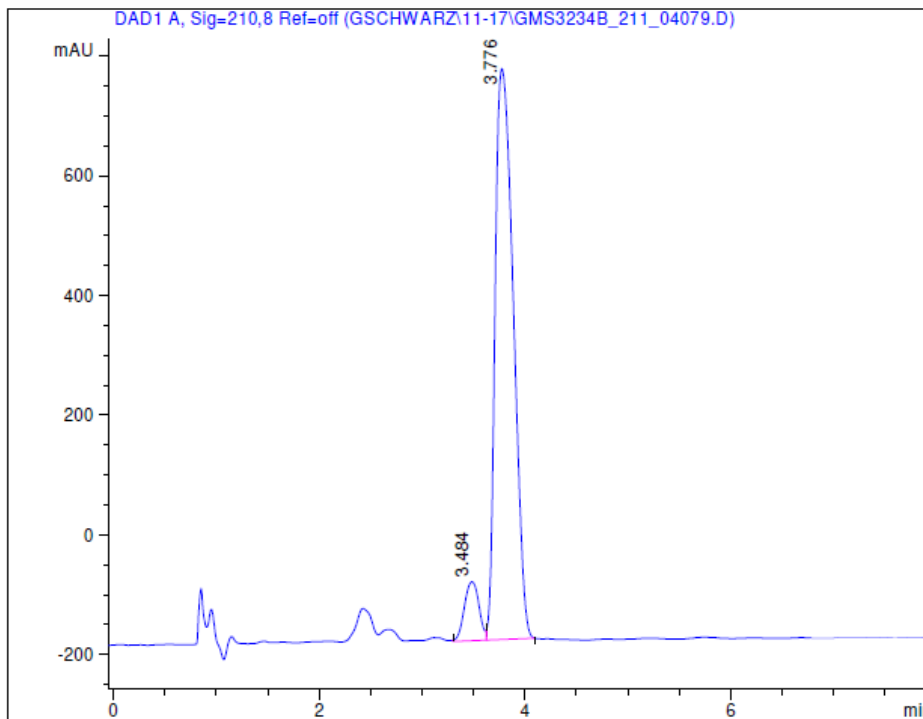
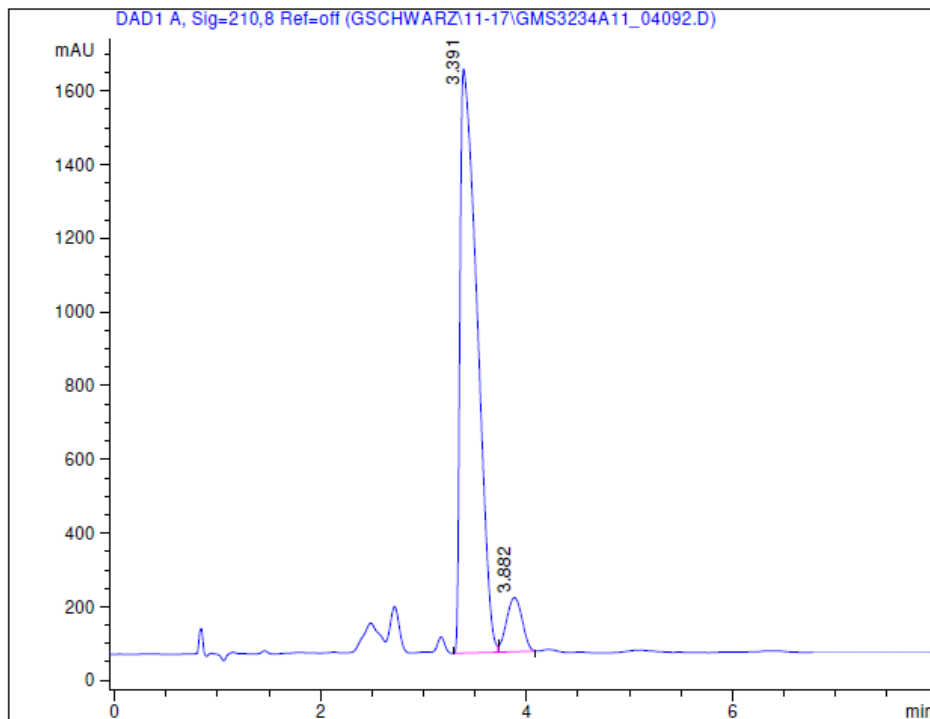


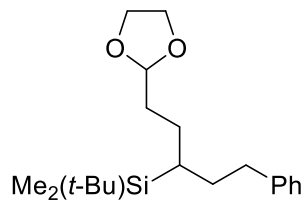
Table 2, entry 14
(101 MHz, CDCl₃)





Signal 1:DAD1 A, Sig=210,8 Ref=off

Peak #	RT [min]	Width [min]	Area	Area %
1	3.39	0.19	18101	92.11
2	3.88	0.18	1552	7.89



Signal 1:DAD1 A, Sig=210,8 Ref=off

Peak #	RT [min]	Width [min]	Area	Area %
1	3.48	0.17	980	7.74
2	3.78	0.20	11678	92.26

Table 2, entry 14
SFC: CHIRALCEL OJ column (1% 2-PrOH in supercritical CO₂, 3.5 mL/min)

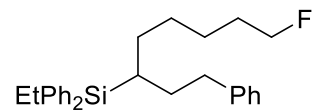
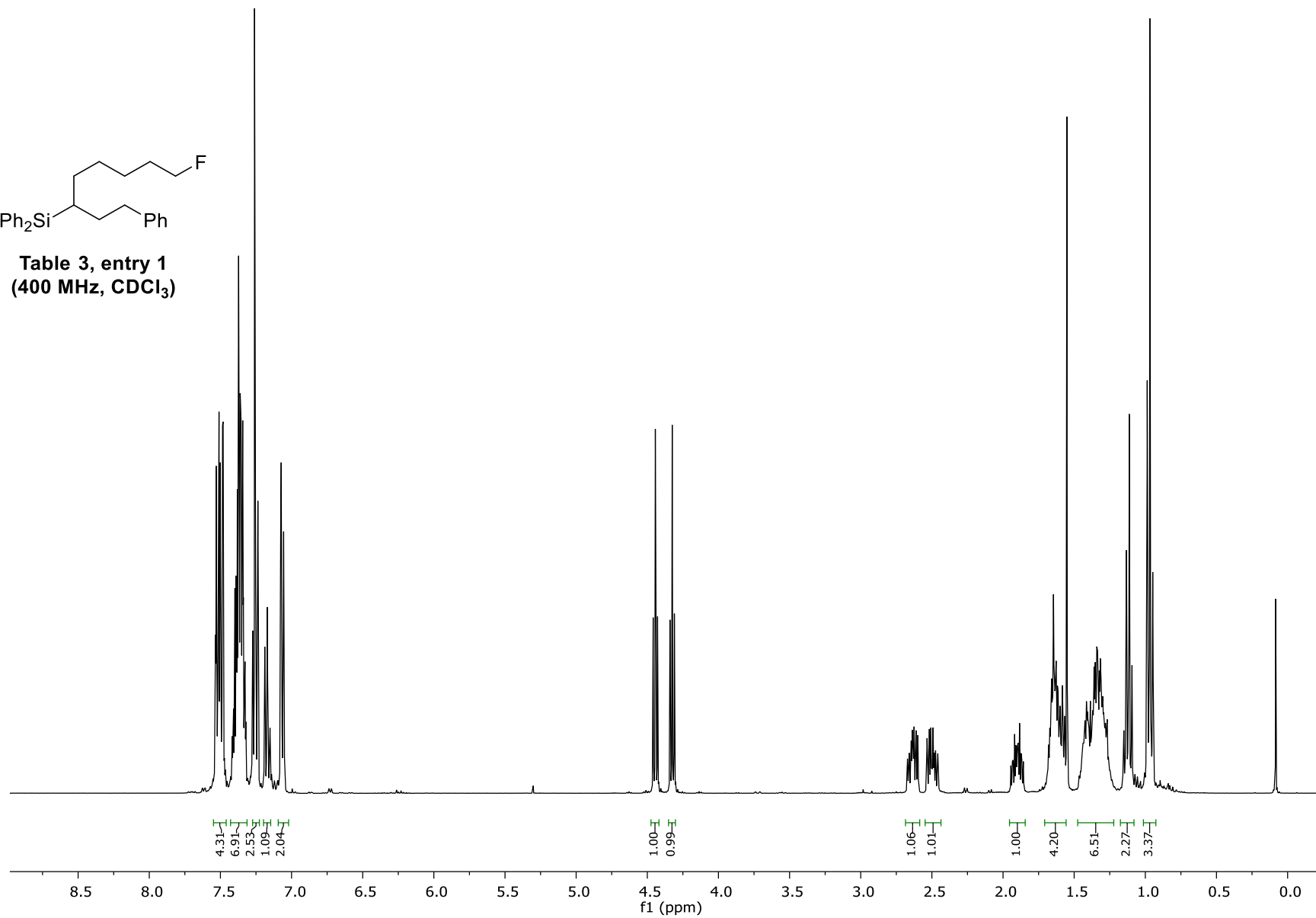


Table 3, entry 1
(400 MHz, CDCl₃)



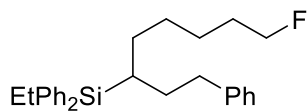
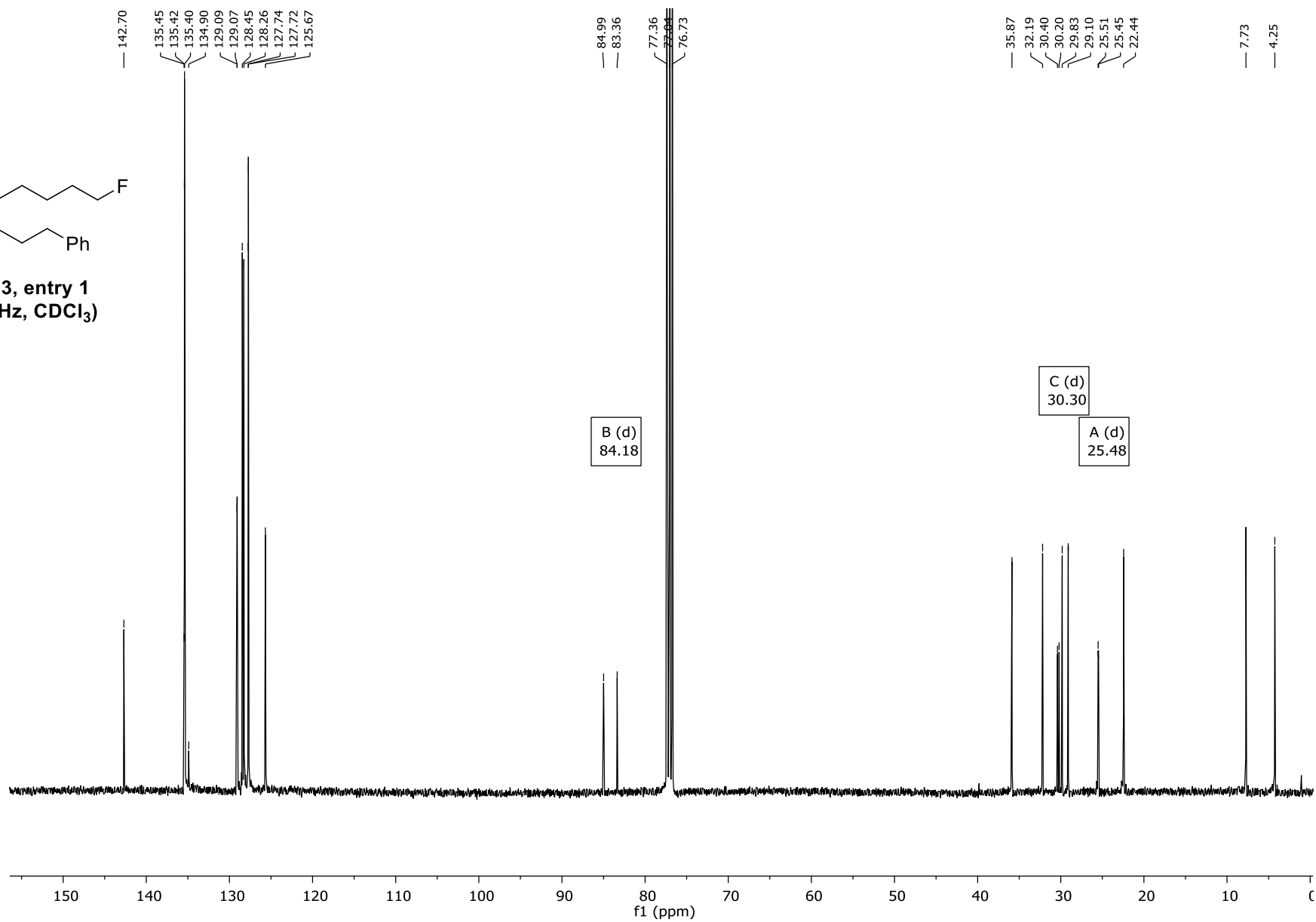
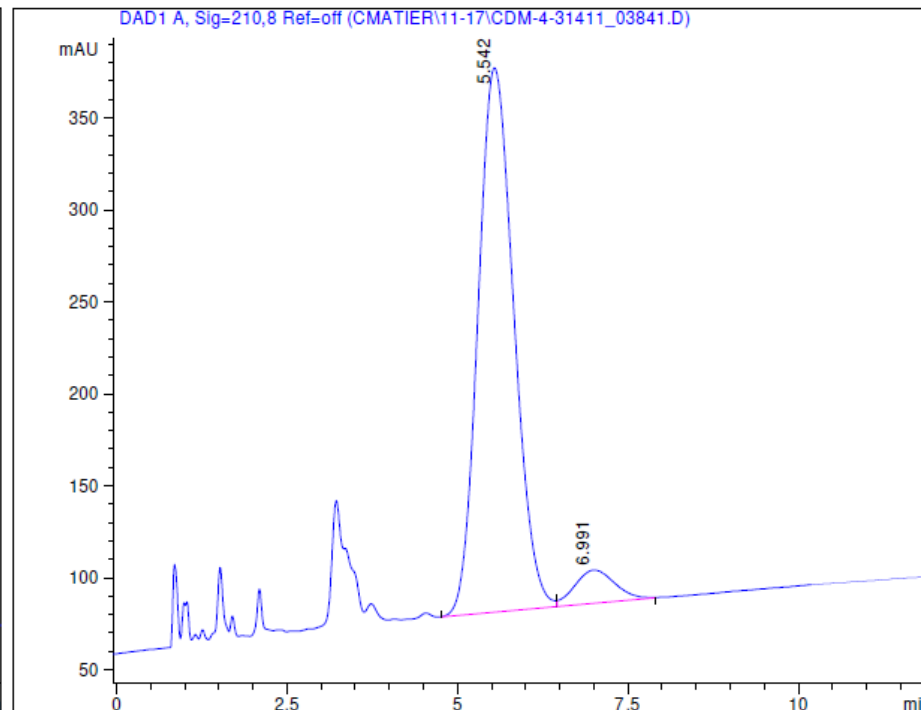
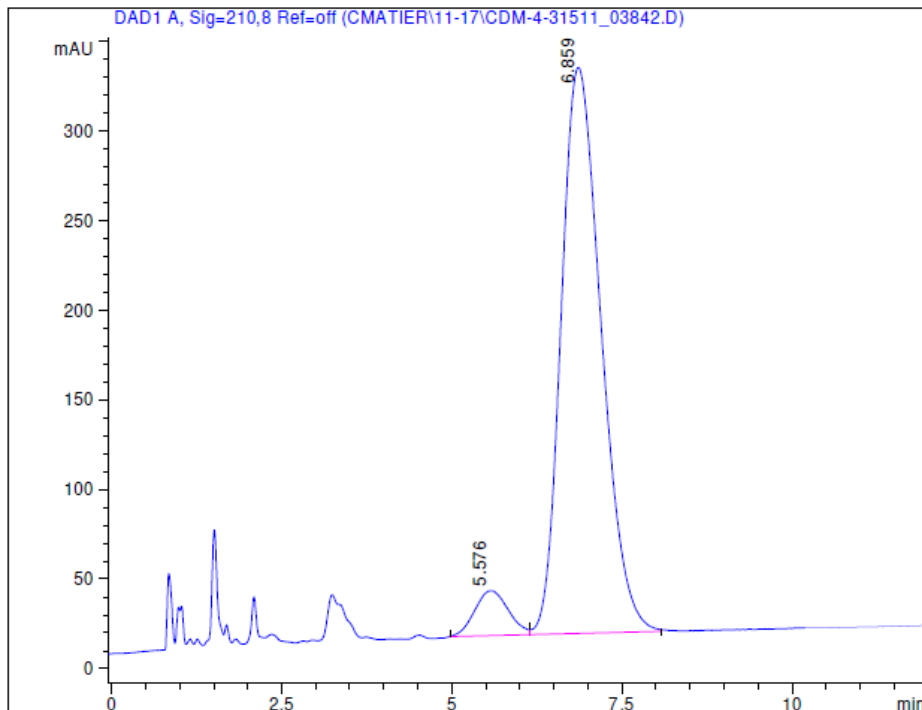


Table 3, entry 1
(101 MHz, CDCl₃)





Signal 1:DAD1 A, Sig=210,8 Ref=off

Peak #	RT [min]	Width [min]	Area	Area %
1	5.58	0.51	861	6.27
2	6.86	0.64	12878	93.73

Signal 1:DAD1 A, Sig=210,8 Ref=off

Peak #	RT [min]	Width [min]	Area	Area %
1	5.54	0.61	10748	93.57
2	6.99	0.68	739	6.43

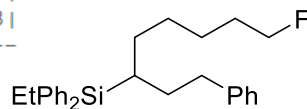


Table 3, entry 1

SFC: CHIRALCEL OJ column (20% 2-PrOH in supercritical CO₂, 3.5 mL/min)

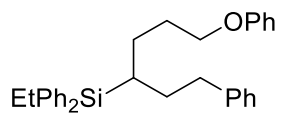
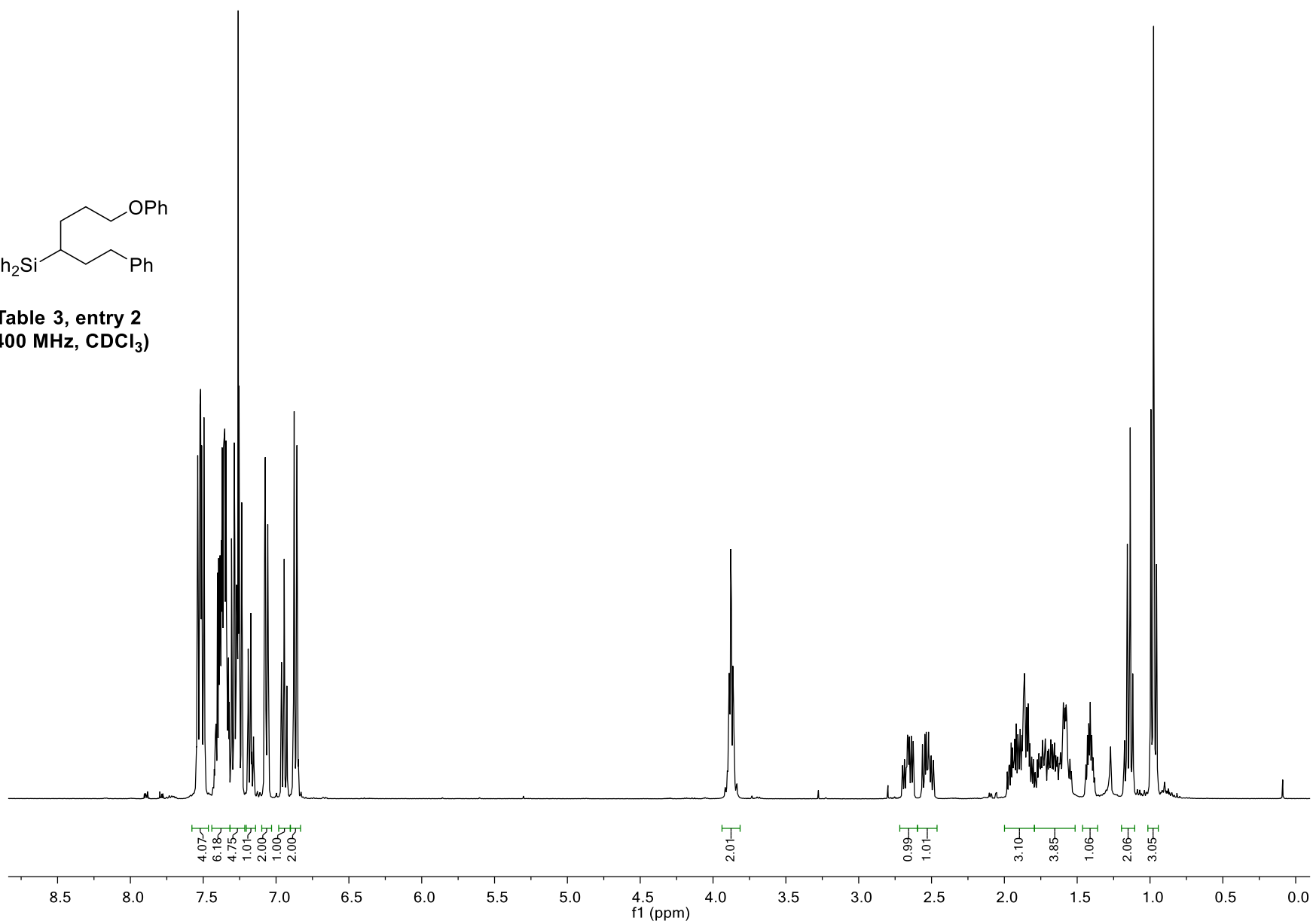


Table 3, entry 2
(400 MHz, CDCl₃)



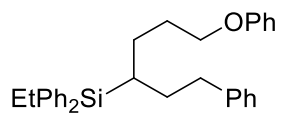
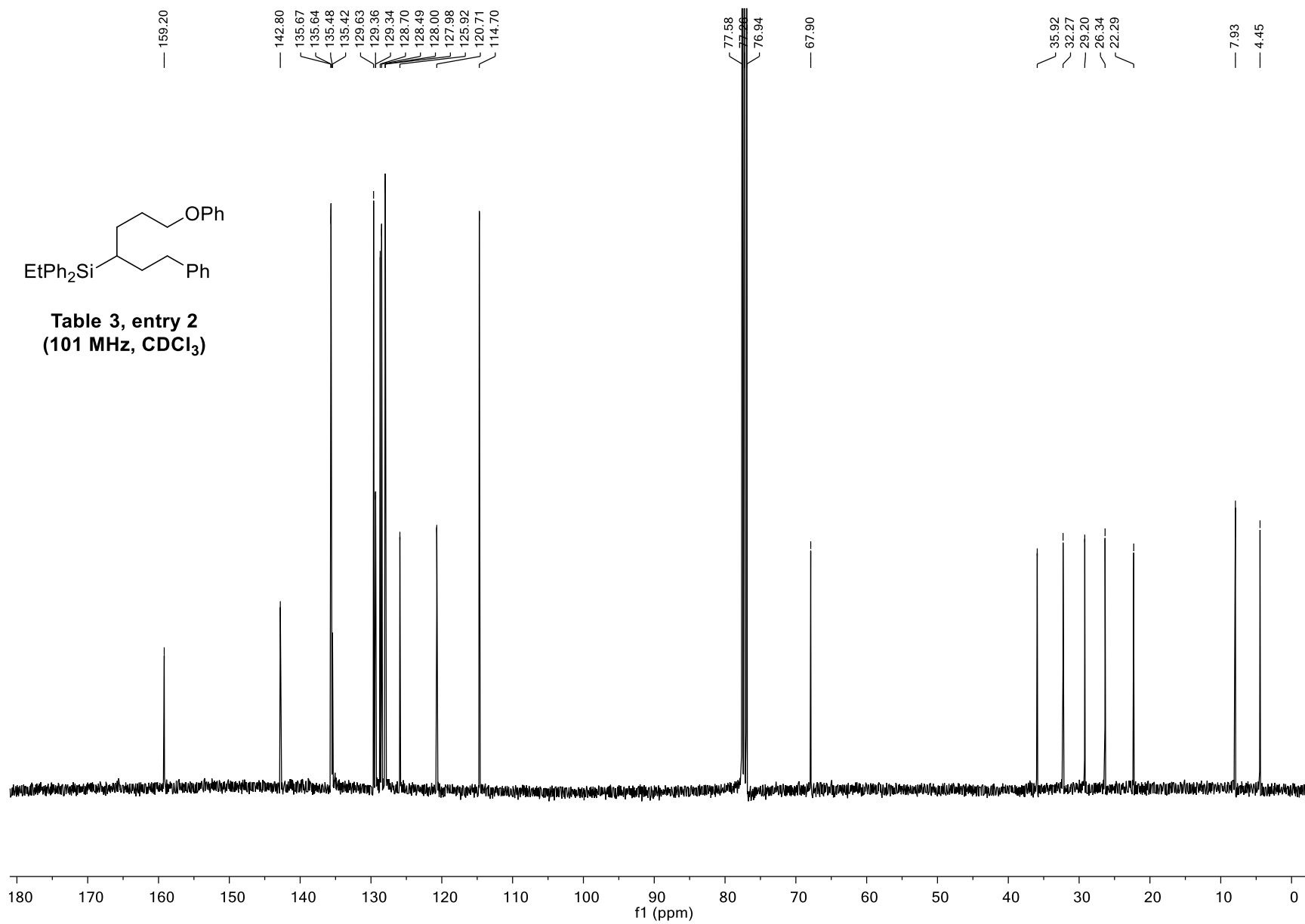
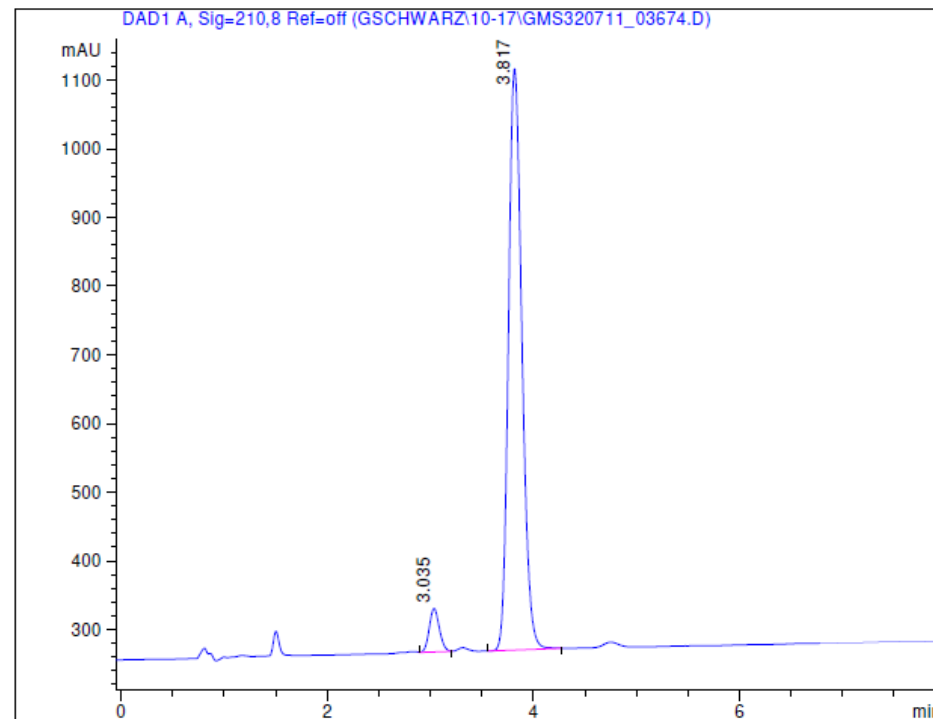
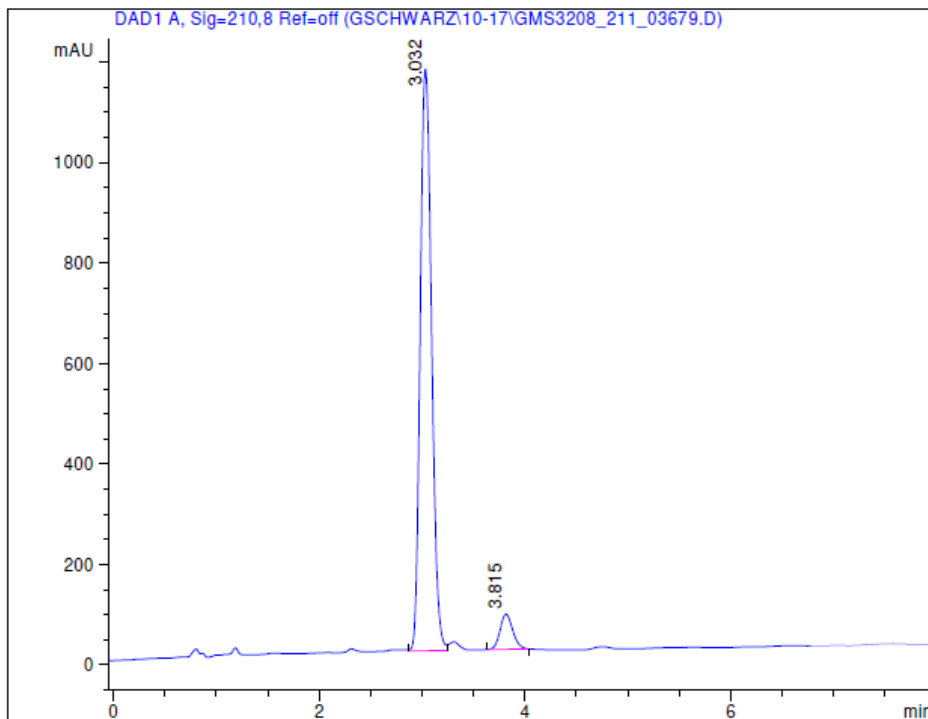


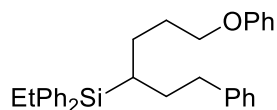
Table 3, entry 2
(101 MHz, CDCl₃)





Signal 1:DAD1 A, Sig=210,8 Ref=off

Peak #	RT [min]	Width [min]	Area	Area %
1	3.03	0.13	8826	93.68
2	3.81	0.14	596	6.32



Signal 1:DAD1 A, Sig=210,8 Ref=off

Peak #	RT [min]	Width [min]	Area	Area %
1	3.04	0.11	428	5.29
2	3.82	0.15	7669	94.71

Table 3, entry 2

SFC: CHIRALCEL OD-H column (30% 2-PrOH in supercritical CO₂, 3.5 mL/min)

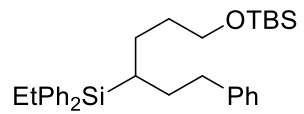
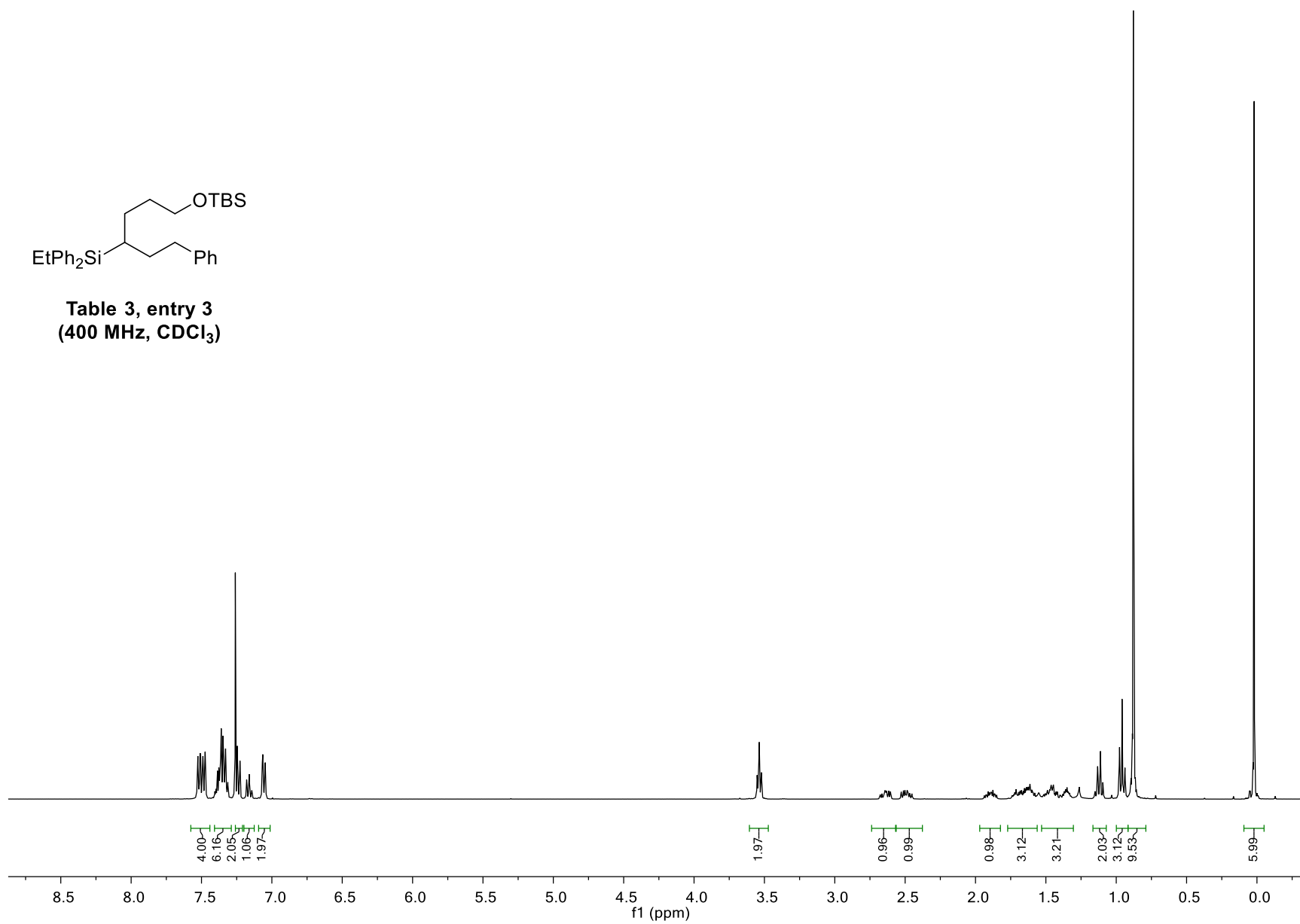
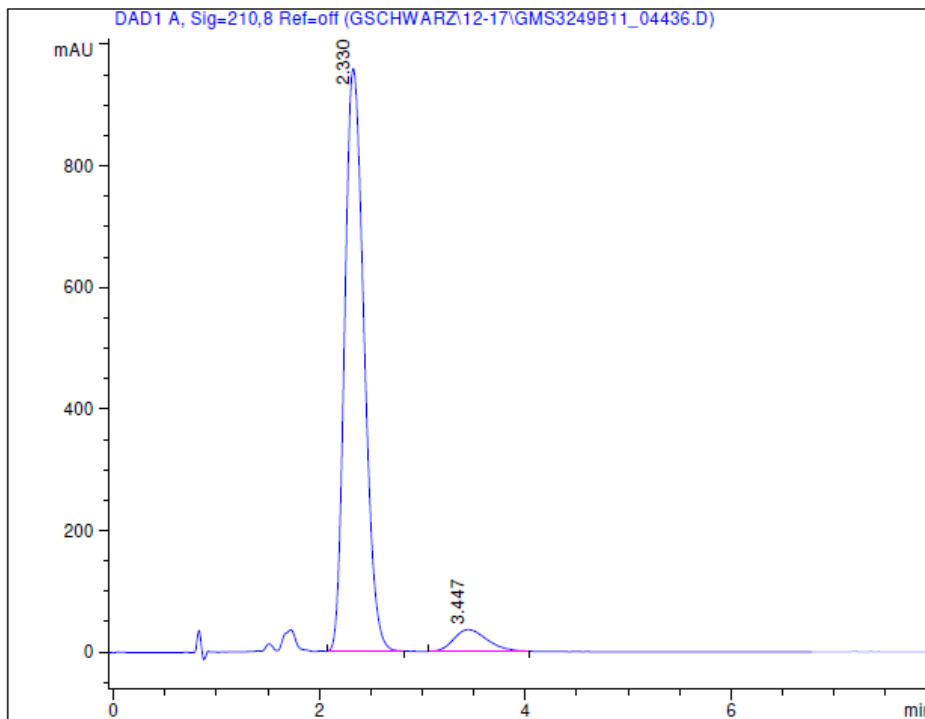
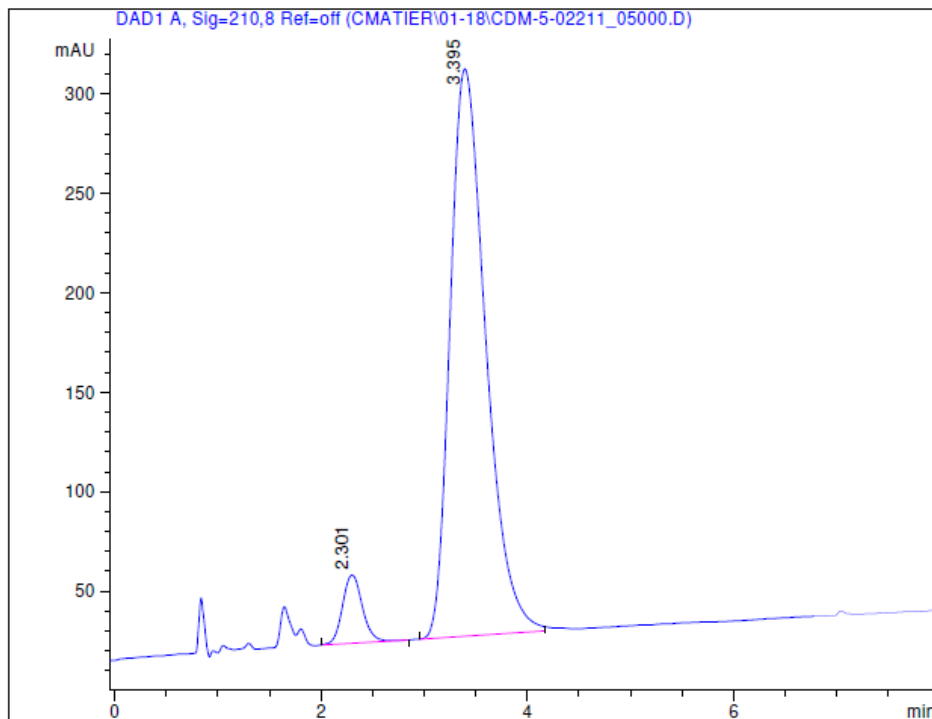


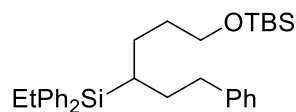
Table 3, entry 3
(400 MHz, CDCl₃)





Signal 1:DAD1 A, Sig=210,8 Ref=off

Peak #	RT [min]	Width [min]	Area	Area %
1	2.30	0.21	461	6.31
2	3.39	0.37	6845	93.69



Signal 1:DAD1 A, Sig=210,8 Ref=off

Peak #	RT [min]	Width [min]	Area	Area %
1	2.33	0.21	12526	94.00
2	3.45	0.37	800	6.00

Table 3, entry 3
SFC: CHIRALCEL OJ column (10% 2-PrOH in supercritical CO₂, 3.5 mL/min)

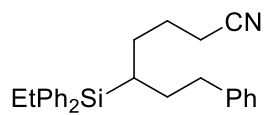
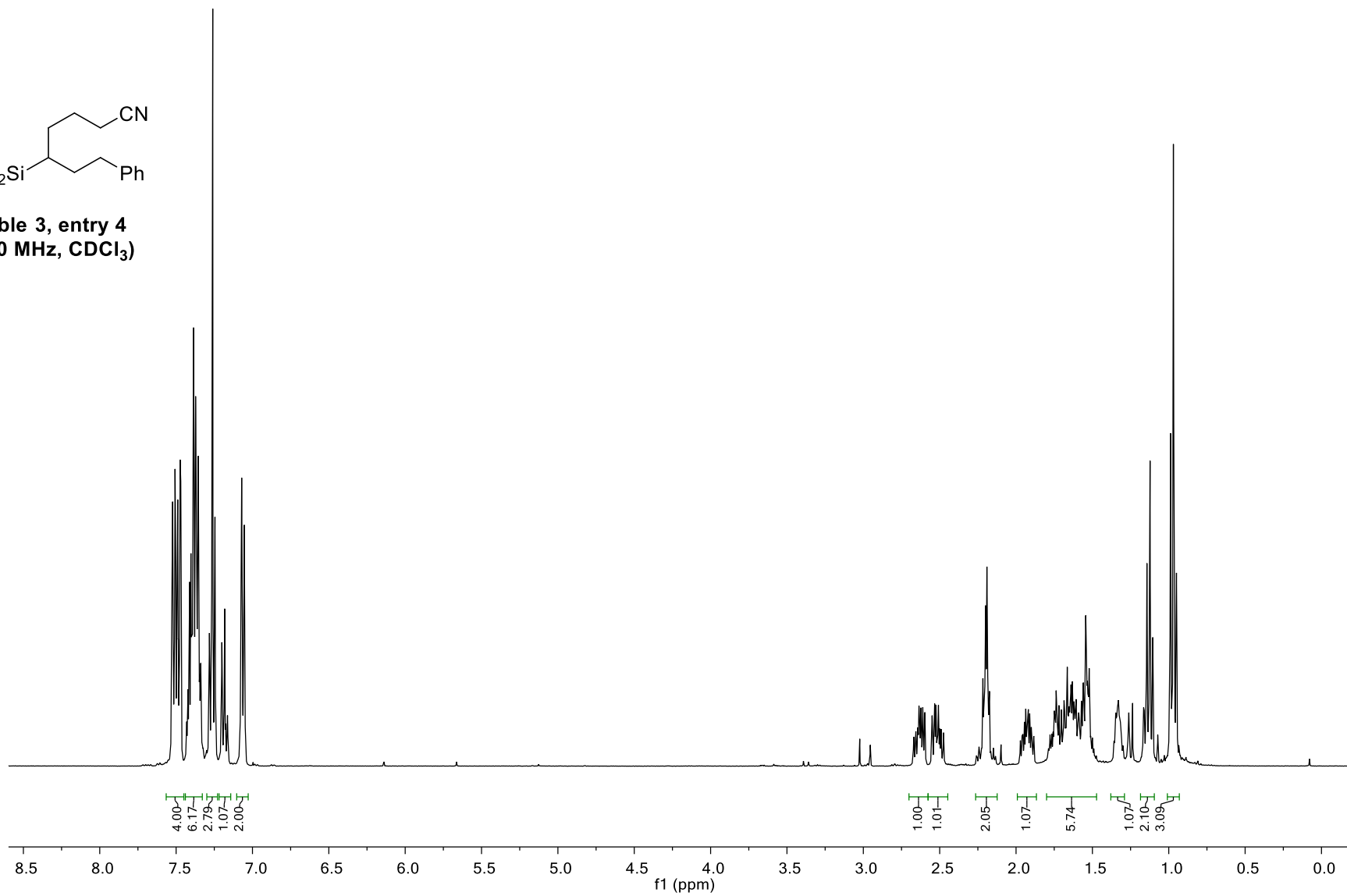


Table 3, entry 4
(400 MHz, CDCl₃)



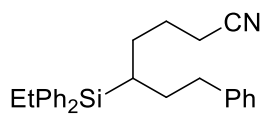
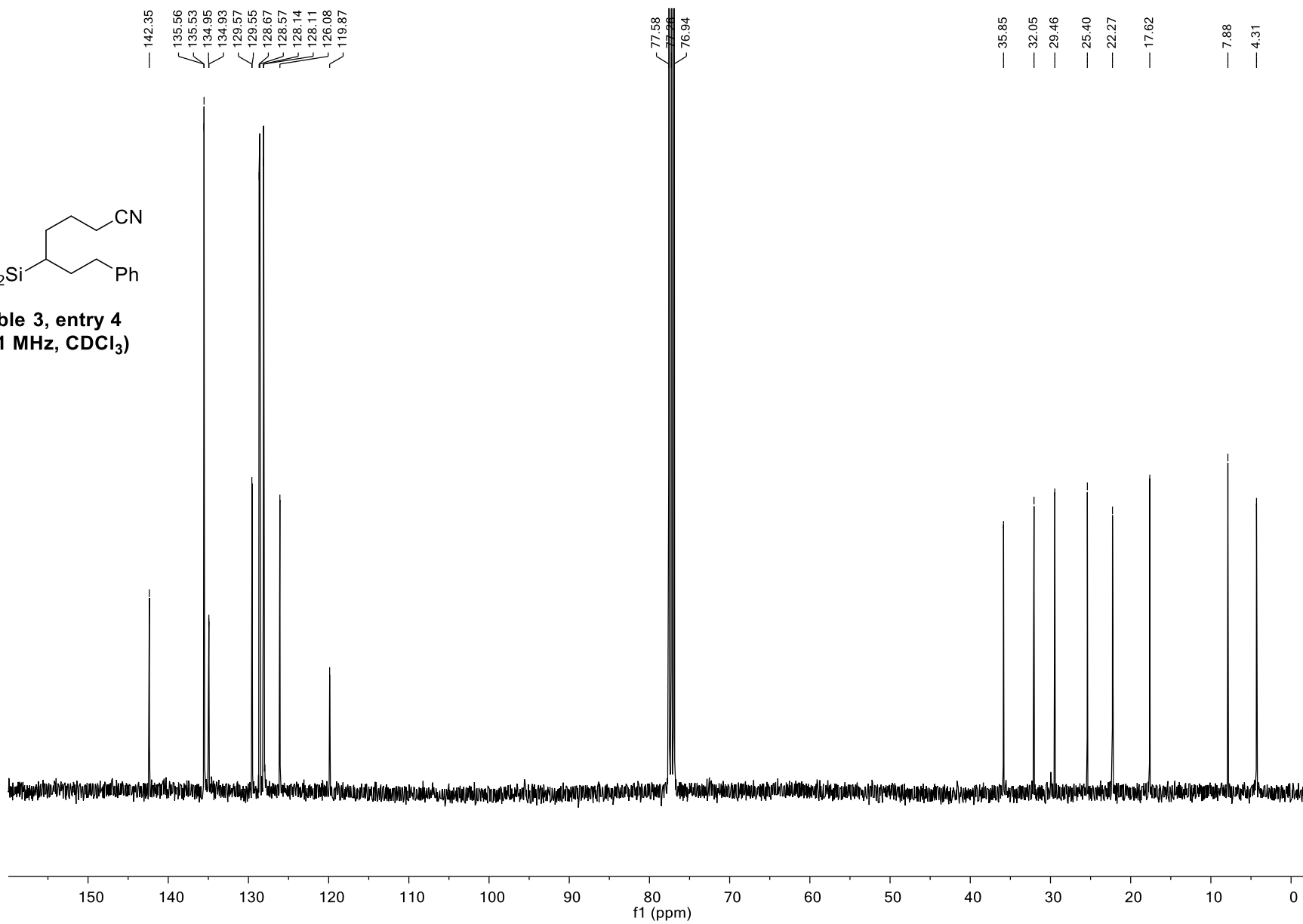
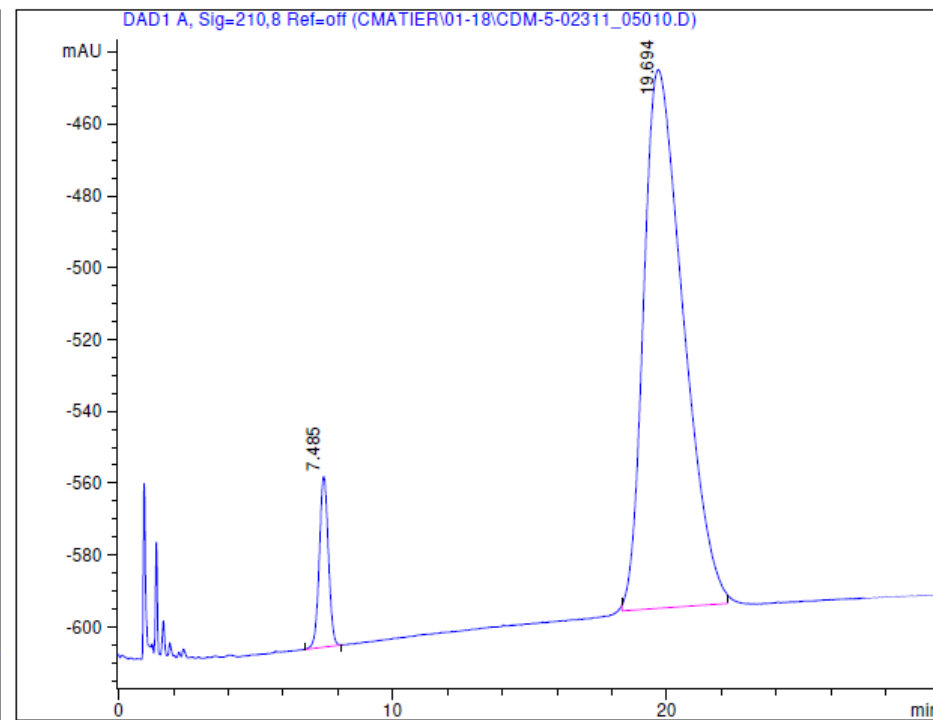
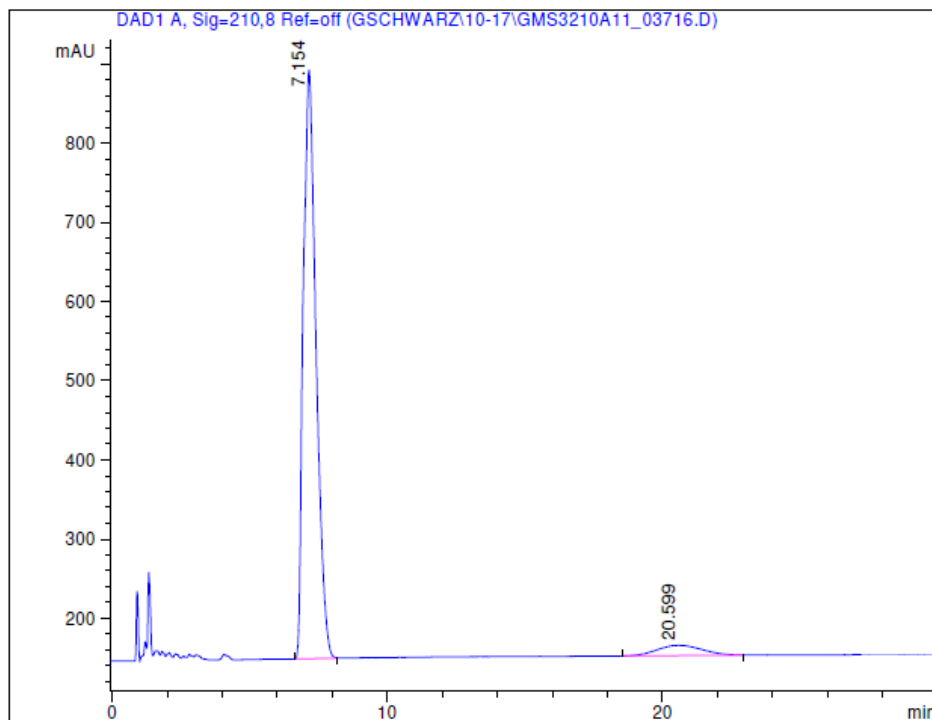


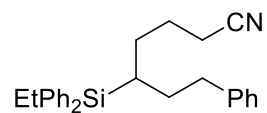
Table 3, entry 4
(101 MHz, CDCl₃)





Signal 1:DAD1 A, Sig=210,8 Ref=off

Peak #	RT [min]	Width [min]	Area	Area %
1	7.15	0.45	23814	94.12
2	20.60	1.89	1487	5.88



Signal 1:DAD1 A, Sig=210,8 Ref=off

Peak #	RT [min]	Width [min]	Area	Area %
1	7.49	0.38	1095	6.79
2	19.69	1.49	15032	93.21

Table 3, entry 4

SFC: CHIRALCEL OJ column (45% MeOH in supercritical CO₂, 3.5 mL/min)

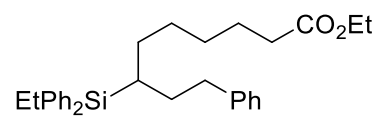
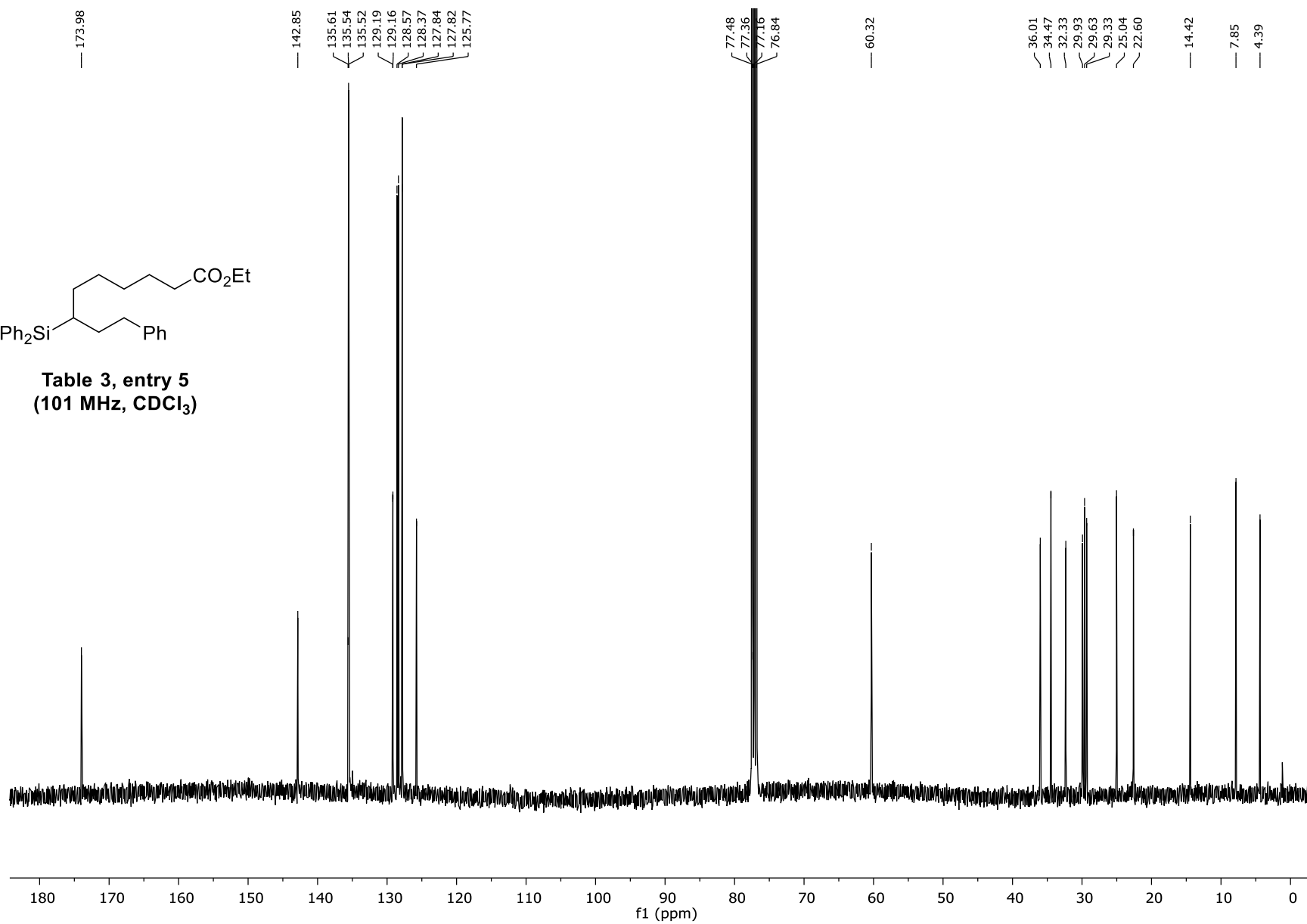


Table 3, entry 5
(101 MHz, CDCl₃)



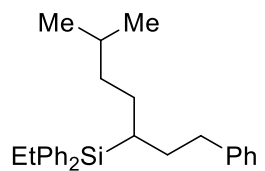
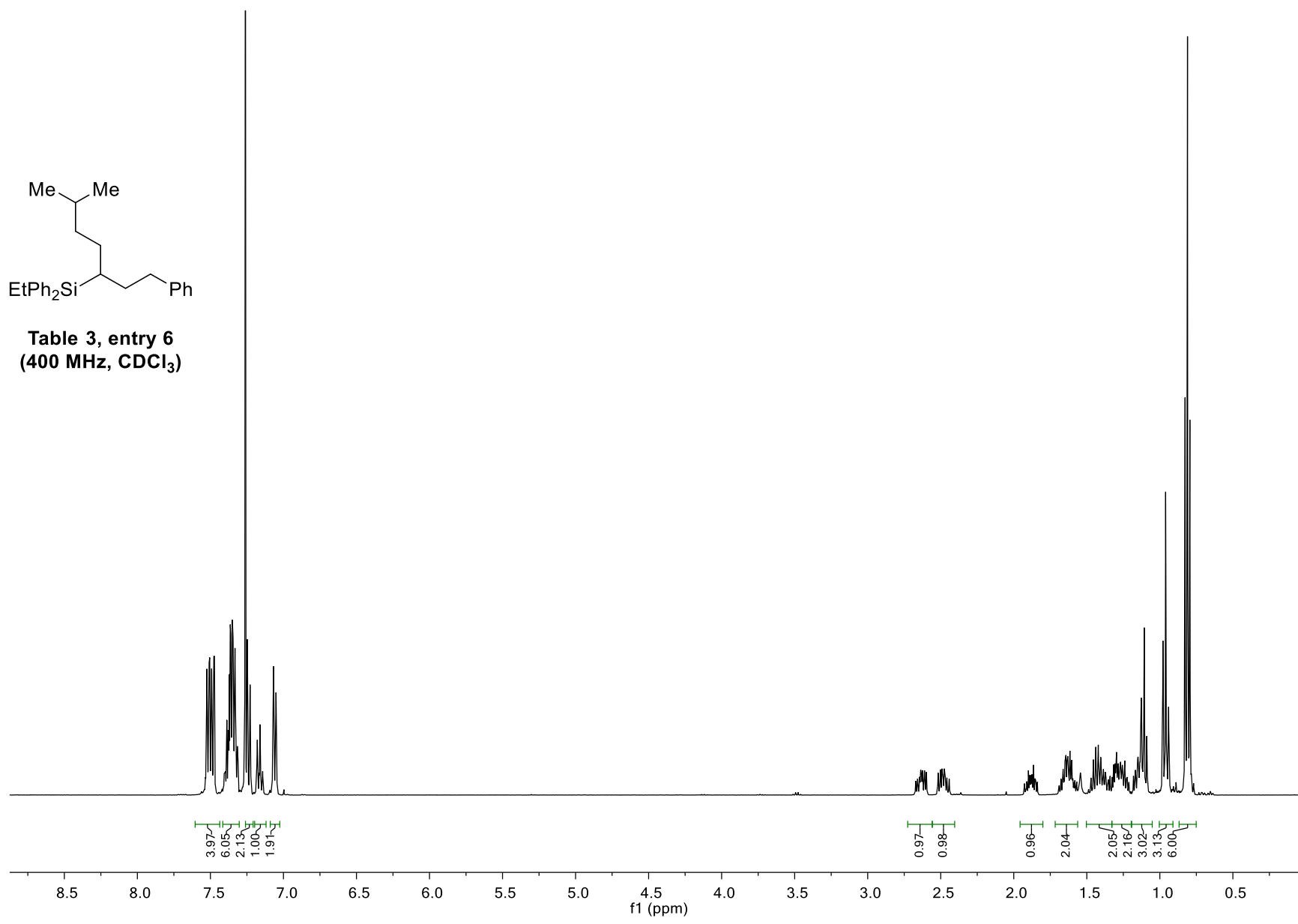


Table 3, entry 6
(400 MHz, CDCl₃)



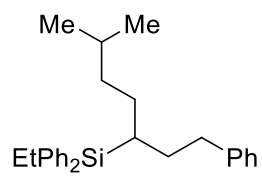
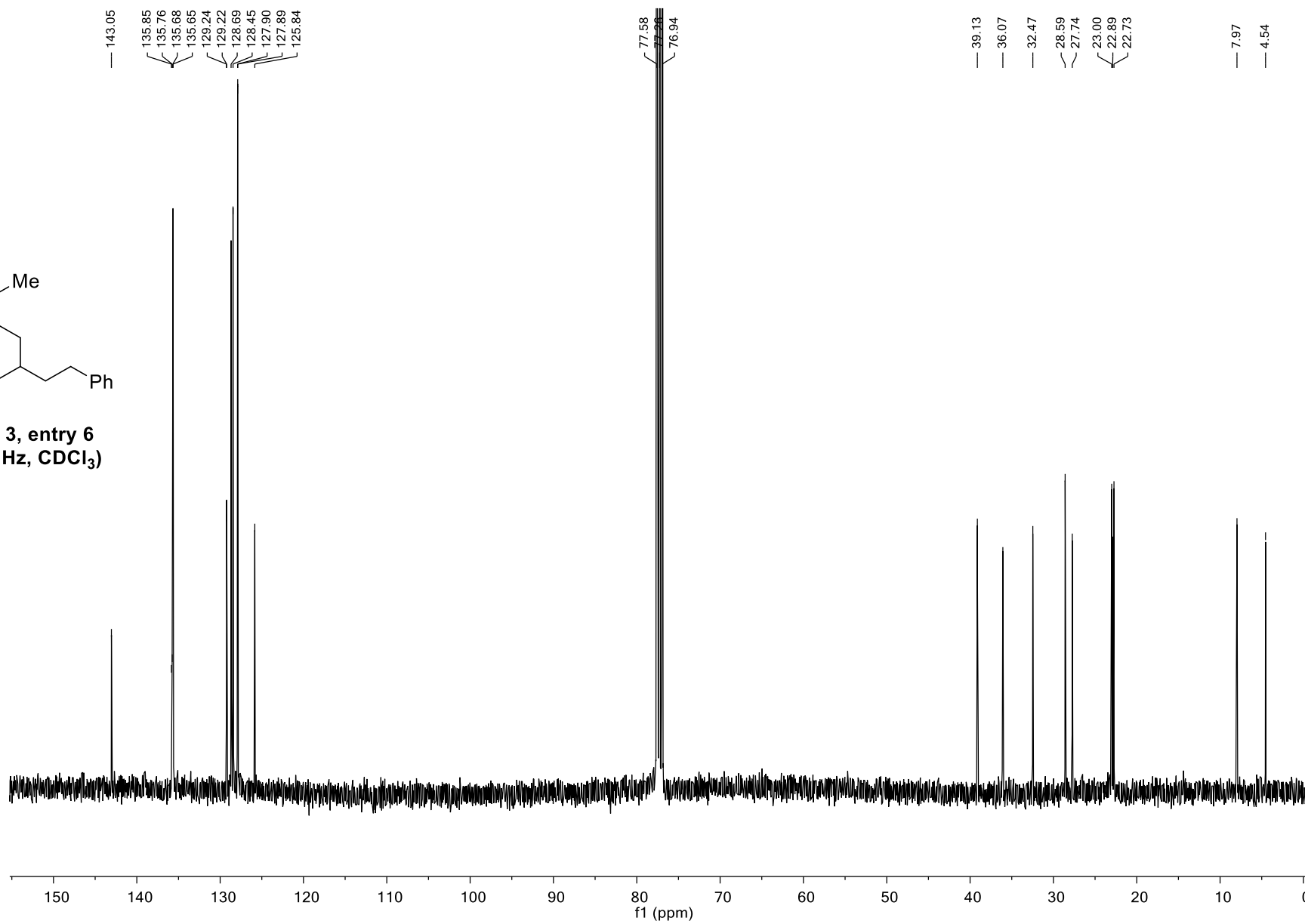
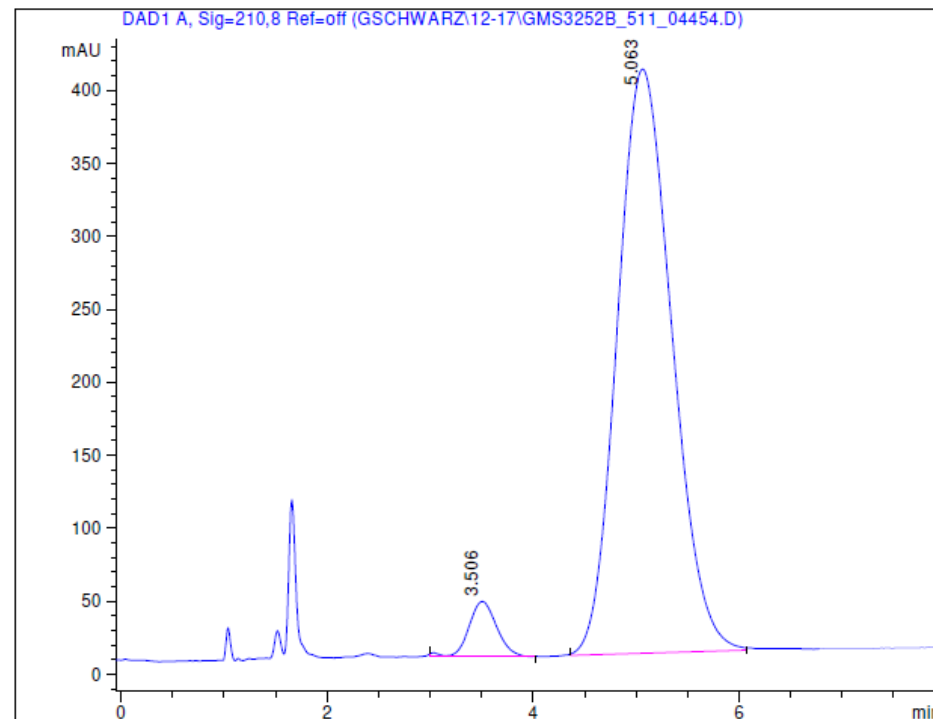
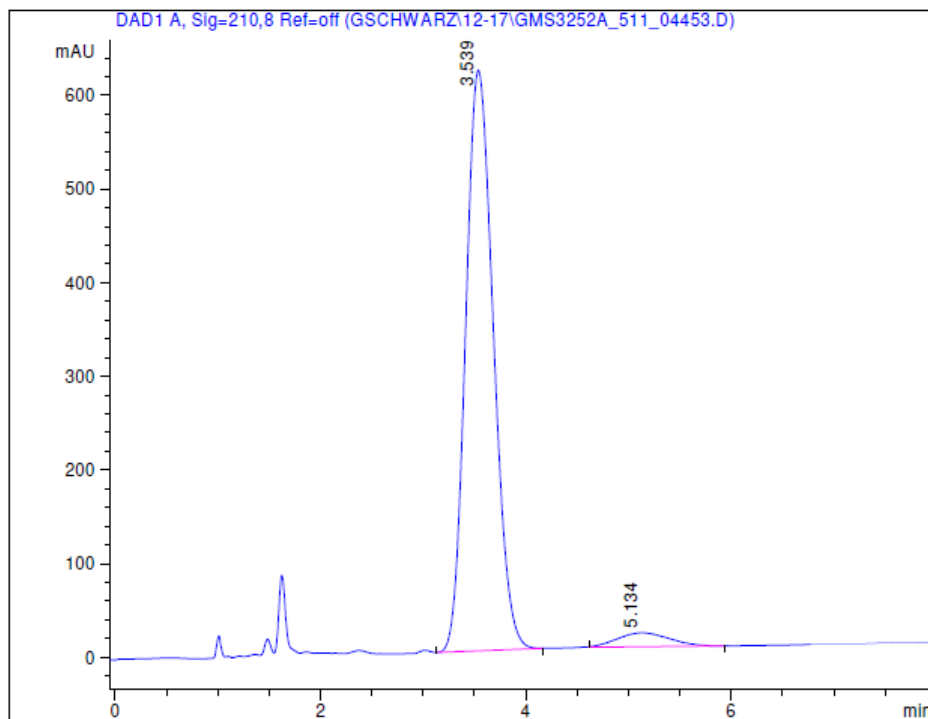


Table 3, entry 6
(101 MHz, CDCl₃)





Signal 1:DAD1 A, Sig=210,8 Ref=off

Peak #	RT [min]	Width [min]	Area	Area %
1	3.54	0.29	11596	95.72
2	5.13	0.51	519	4.28

Signal 1:DAD1 A, Sig=210,8 Ref=off

Peak #	RT [min]	Width [min]	Area	Area %
1	3.51	0.29	699	4.54
2	5.06	0.58	14721	95.46

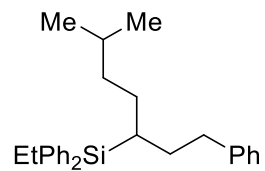


Table 3, entry 6

SFC: CHIRALCEL OJ column (15% 2-PrOH in supercritical CO₂, 3.5 mL/min)