Supplementary Materials for

A General, Modular Method for the Catalytic Asymmetric Synthesis of Alkylboranes

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This PDF file includes:

Table of Contents

I. General Information

Unless otherwise noted, reagents were used as received from commercial suppliers. (*S,S*)–**L*** and **(***R,R*)–**L*** were synthesized according to published procedures.[26,27] All reactions were performed under an atmosphere of dry nitrogen. Dry *N,N*-dimethylacetamide (DMA) was purchased from Sigma-Aldrich and stored under nitrogen. Other solvents were purified with activated aluminum oxide using a solvent-purification system. NMR spectra were recorded on a Bruker spectrometer with a Prodigy broadband cryoprobe (400 MHz for ^{1}H and 100 MHz for ^{13}C); chemical shifts (δ) are reported in ppm downfield from tetramethylsilane, using the solvent resonance as the internal standard. Optical rotation data were obtained with a Jasco P-2000 polarimeter at 589 nm and at 25 °C, using a 100 mm path-length cell in the solvent and at the concentration indicated. Mass spectra were obtained on a JEOL JMS-600H or an Agilent 7890A GC-MS system with an Agilent 5975C detector. HPLC analyses were carried out on an Agilent 1100 series system with Daicel CHIRALPAK® or Daicel CHIRALCEL® columns (4.6 × 250 mm, particle size 5 μm). IR spectra were recorded on a Thermo Scientific Nicolet iS5 (iD5 ATR) spectrometer by attenuated total reflection (ATR).

II. Catalytic Asymmetric Cross-Couplings

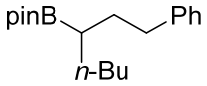
Preparation of the organozinc reagent.[28,29] A 20 mL vial charged with zinc dust (1.47 g, 22.5 mmol, 1.50 equiv) and a cross-shaped stir bar was capped with a PTFE-lined pierceable cap, wrapped with electrical tape (to help seal the vial), and heated at 70 °C under high vacuum for 1 h. After the vial had been placed under nitrogen and allowed to cool to room temperature, iodine (190 mg, 0.75 mmol, 0.050 equiv) in DMA (3 mL) was added under N_2, and the suspension was stirred until the solution was colorless. In turn, DMA (7 mL) and the primary alkyl bromide (15.0 mmol, 1.00 equiv) were added under N_2 via syringe. The vial was disconnected from the nitrogen-filled manifold, the puncture hole in the septum was covered with grease, and the suspension was heated at 70 °C for 12 h (stir-rate: 1500 rpm). Next, the mixture was cooled to room temperature and filtered with a syringe filter (pore-size: 0.45 μM, PTFE). A sample of the solution was titrated by dropping it into a solution of iodine in THF with stirring at room temperature.

General Procedure 1 (GP-1): Catalytic asymmetric cross-couplings (without the use of a glovebox). *As indicated below, all of the coupling reactions in Figure 2 were run without the use of a glovebox. Nevertheless, we strongly recommend the use of a glovebox, if one is available.* In the air, an oven-dried 8 mL vial equipped with a magnetic stir bar was charged with $NiBr_2$•diglyme (24.7 mg, 0.0700 mmol, 0.100 equiv) and **L*** (24.4 mg, 0.0910 mmol, 0.130 equiv), and then it was capped with a PTFE-lined pierceable cap. The vial was evacuated and backfilled with nitrogen (three cycles). THF (3.00 mL) and DMA (1.46 mL = the total volume of DMA, including the solution of the nucleophile) were added via syringe, and the mixture was stirred at room temperature for 1 h (until the blue suspension turned yellow-green). Meanwhile, in the air, a separate oven-dried 20 mL vial equipped with a magnetic stir bar was charged with the electrophile (0.700 mmol, 1.00 equiv), capped with a PTFE-lined pierceable cap, and wrapped with electrical tape (to help seal the vial). The vial was evacuated and backfilled with nitrogen (three cycles). The suspension of the catalyst was transferred via syringe to the 20 mL vial. The 8 mL vial was rinsed with THF (2 x 2.14 mL), and the washes were transferred to the 20 mL vial. The reaction mixture was equipped with an argon-filled balloon and then cooled to 0 °C. After 30 min, the precooled (0 °C) solution of the nucleophile (1.26 mmol, 1.80 equiv) was added dropwise via syringe. The balloon was removed, and the puncture hole in the septum was covered with grease. The reaction mixture was stirred at 0 °C for 18 h, during which time the reaction mixture became dark. Next, the cap was removed, and MeOH (20% in Et_2O; 1.00 mL) was added. The mixture was stirred for 5 min, and then it was filtered through a small plug of silica gel, which was flushed with Et_2O (3 x 50 mL). All volatiles were removed with a rotary evaporator, and the residue was purified by flash chromatography on silica gel.

General Procedure 2 (GP-2): Catalytic asymmetric cross-couplings (with the use of a glovebox). In a nitrogen-filled glovebox, an oven-dried 4 mL vial (vial A) equipped with a magnetic stir bar was charged with $NiBr_2$•diglyme (3.5 mg, 0.010 mmol, 0.10 equiv) and **L*** (3.5 mg, 0.013 mmol, 0.13 equiv). THF (500 μL) and DMA (208 μL = the total volume of DMA, including the solution of the nucleophile) were added via syringe, and then vial A was capped with a PTFE-lined pierceable cap, and the mixture was stirred at room temperature for 1 h (until the blue suspension turned yellow-green). Meanwhile, in the glovebox, a separate oven-dried 4 mL vial (vial B) was charged with the electrophile (0.100 mmol, 1.00 equiv). The catalyst suspension was transferred via syringe to vial B. Vial A was rinsed with THF (540 μL), and the

wash and the stir bar were transferred to vial B. Vial B was capped with a PTFE-lined pierceable cap, wrapped with electrical tape (to help seal the vial), removed from the glovebox, and cooled to 0 °C with a cryostat. After 30 min, the precooled (0 °C) solution of the nucleophile (in DMA; 0.180 mmol, 1.80 equiv) was added dropwise, and then the puncture hole in the septum was covered with grease. The reaction was stirred at 0 °C for 18 h. during which time the reaction mixture became dark. Next, the cap was removed, and MeOH (20% in Et_2O, 0.50 mL) was added. The mixture was stirred for 5 min, and then it was filtered through a small plug of silica gel,which was rinsed with Et_2O (10 mL).

General Procedure 3 (GP-3): Determination of stereoselectivity. The purified product (~10 mg) was oxidized with $NaBO_3 \cdot 4\ H_2O$ (~150 mg) in THF/H_2O (1:1; 2 mL) at room temperature for 4 h. The mixture was extracted with Et_2O (2 x 2 mL), the combined organic phases were dried over $MgSO_4$, and the volatiles were removed. The ee of the alcohol was determined via HPLC.



4,4,5,5-Tetramethyl-2-(1-phenylheptan-3-yl)-1,3,2-dioxaborolane (Figure 2A, entry 1). The title compound was prepared according to **GP-1** from 2-(1-chloro-3-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (196 mg, 0.700 mmol) and purified by column chromatography on silica gel (4→7% Et_2O in hexanes). Colorless oil.

(*R,R*)–**L***: 150 mg (0.496 mmol, 71%), + 92% ee; (*S,S*)–**L***: 153 mg (0.506 mmol, 72%), – 92% ee.

HPLC analysis: The ee was determined after oxidation (**GP-3)** via HPLC on a CHIRALPAK IB column (5% 2-PrOH in hexane, 1.0 mL/min) with t_r = 7.8 min (major (*S,S*)–**L***), 10.0 min (major *(R,R)*–**L***);

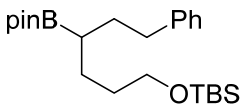
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.23 (m, 2H), 7.20 – 7.13 (m, 3H), 2.66 – 2.52 (m, 2H), 1.80 – 1.59 (m, 2H), 1.51 – 1.35 (m, 2H), 1.33 – 1.22 (m, 4H), 1.26 (s, 12H), 1.09 – 0.99 (m, 1H), 0.94 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 128.5, 128.4, 125.7, 83.1, 35.8, 33.7, 31.6, 31.1, 25.02, 24.96, 23.1, 14.3;

FT-IR (ATR) 2977, 2956, 2924, 2857, 1457, 1387, 1371, 1315, 1233, 1115, 967, 851, 748, 699 cm^{-1};

HR-MS (FAB) *m/z* $[M+H]^+$ calcd for $C_{19}H_{32}BO_2$: 303.2490, found: 303.2509;

$[\alpha]^{25}_D$ = – 4.18 (c = 1.47, $CHCl_3$); 92% ee from (*S,S*)–**L***.



***Tert*-butyldimethyl((6-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)oxy)silane (Figure 2A, entry 2)**. The title compound was prepared according to **GP-1** from 2-(1-chloro-3-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (196 mg, 0.700 mmol) and purified by column chromatography on silica gel (0→8% Et_2O in hexanes). Colorless oil.

(*R,R*)–**L***: 235 mg (0.562 mmol, 80%), + 90% ee; (*S,S*)–**L***: 244 mg (0.583 mmol, 83%), – 90% ee.

HPLC analysis: The ee was determined after oxidation (**GP-3)** via HPLC on a CHIRALCEL OD-H column (5% 2-PrOH in hexane, 1.0 mL/min) with t_r = 8.1 min (major (*S,S*)–**L***), 10.7 min (major *(R,R)*–**L***);

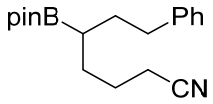
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.23 (m, 2H), 7.20 – 7.13 (m, 3H), 3.59 (t, *J* = 6.4 Hz, 2H), 2.68 – 2.52 (m, 2H), 1.82 – 1.39 (m, 6H), 1.26 (s, 12H), 1.12 – 1.00 (m, 1H), 0.89 (s, 9H), 0.04 (s, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 128.4, 128.2, 125.5, 83.0, 63.5, 35.6, 33.5, 32.4, 27.3, 26.0, 24.89, 24.85, 18.4, -5.2;

FT-IR (ATR) 3062, 3026, 2977, 2928, 2856, 1604, 1496, 1471, 1463, 1387, 1371, 1317, 1256, 1145, 1101, 1031, 1006, 967, 939, 835, 813, 775, 747 cm^{-1};

MS (FAB) *m/z* $[M+H]^+$ calcd for $C_{24}H_{44}BO_3Si$: 419.3147, found: 419.3135;

$[\alpha]^{25}_D$ = – 1.5 (c = 1.02, $CHCl_3$); 90% ee from (*S,S*)–**L***.



7-Phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptanenitrile (Figure 2A, entry 3). The title compound was prepared according to **GP-1** from 2-(1-iodo-3-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (260 mg, 0.700 mmol) and purified by column chromatography on silica gel (15→35% Et_2O in hexanes). Colorless oil.

(*R,R*)–**L***: 206 mg (0.658 mmol, 94%), + 82% ee; (*S,S*)–**L***: 211 mg (0.674 mmol, 96%), – 82% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD-H column (0.5% 2-PrOH in hexane, 1.0 mL/min) with t_r = 17.3 min (major (*S,S*)–**L***), 19.3 min (major *(R,R)*–**L***);

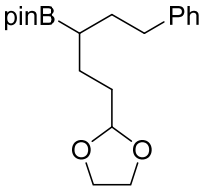
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 2H), 7.20 – 7.13 (m, 3H), 2.70 – 2.53 (m, 2H), 2.32 (t, *J* = 7.0 Hz, 2H), 1.83 – 1.46 (m, 6H), 1.27 (s, 12H), 1.11 – 1.00 (m, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 128.5, 128.4, 125.8, 120.0, 83.4, 35.5, 33.3, 30.4, 25.1, 25.0, 17.5;

FT-IR (ATR) 3062, 3026, 2977, 2929, 2857, 2245, 1603, 1495, 1455, 1386, 1372, 1322, 1270, 1229, 1214, 1167, 1143, 1109, 1031, 1030, 967, 854, 802, 749 cm^{-1};

MS (FAB) *m/z* $[M+H]^+$ calcd for $C_{19}H_{29}BNO_2$: 314.2286, found: 314.2279;

$[\alpha]^{25}_D$ = – 3.3 (c = 0.97, $CHCl_3$); 82% ee from (*S,S*)–**L***.



2-(1-(1,3-Dioxolan-2-yl)-5-phenylpentan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Figure 2A, entry 4). The title compound was prepared according to **GP-1**, except that the reaction temperature was 10 °C, from 2-(1-chloro-3-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (196 mg, 0.700 mmol) and purified by column chromatography on silica gel (10→30% Et_2O in hexanes). Colorless oil.

(*R,R*)–**L***: 142 mg (0.410 mmol, 59%), +95% ee; (*S,S*)–**L***: 145 mg (0.419 mmol, 60%), – 95% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD-H column (0.3% 2-PrOH in hexane, 1.0 mL/min) with t_r = 18.7 min (major *(R,R)*–**L***), 20.2 min (major (*S,S*)–**L***);

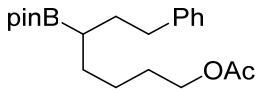
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.22 (m, 2H), 7.19 – 7.12 (m, 3H), 4.84 (t, *J* = 4.7 Hz, 1H), 4.00 – 3.80 (m, 4H), 2.68 – 2.54 (m, 2H), 1.82 – 1.48 (m, 6H), 1.26 (s, 12H), 1.11 – 1.03 (m, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0, 128.4, 128.2, 125.6, 104.8, 83.0, 64.81, 64.78, 35.5, 33.4, 33.4, 25.4, 24.9;

FT-IR (ATR) 3060, 3024, 2976, 2928, 2860, 1603, 1496, 1457, 1405, 1388, 1371, 1319, 1262, 1235, 1214, 1031, 966, 849, 748 cm^{-1};

MS (FAB) *m/z* $[M-H]^+$ calcd for $C_{20}H_{30}BO_4$: 345.2232, found: 345.2245;

$[\alpha]^{25}_D$ = – 3.6 (c = 0.99, $CHCl_3$); 95% ee from (*S,S*)–**L***.



7-Phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptyl acetate (Figure 2A, entry 5). The title compound was prepared according to **GP-1**, except that 12% Ni and 15.6% **L*** were used, from 2-(1-chloro-3-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (196 mg, 0.700 mmol) and purified by column chromatography on silica gel (0→25% Et_2O in hexanes). Colorless oil.

(*R,R*)–**L***: 192 mg (0.533 mmol, 76%), + 92% ee; (*S,S*)–**L***: 185 mg (0.513 mmol, 73%), – 92% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD-H column (0.2% 2-PrOH in hexane, 1.0 mL/min) with t_r = 10.6 min (major *(R,R)*–**L***), 12.4 min (major (*S,S*)–**L***);

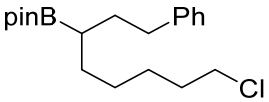
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.23 (m, 2H), 7.20 – 7.13 (m, 3H), 4.04 (t, *J* = 6.7 Hz, 2H), 2.67 – 2.52 (m, 2H), 2.03 (s, 3H), 1.81 – 1.29 (m, 8H), 1.26 (s, 12H), 1.10 – 1.00 (m, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 143.1, 128.5, 128.4, 125.7, 83.1, 64.7, 35.7, 33.6, 31.0, 29.0, 25.6, 25.00, 24.96, 21.1;

FT-IR (ATR) 3085, 3062, 3025, 2977, 2929, 2857, 1741, 1603, 1496, 1454, 1410, 1388, 1371, 1317, 1240, 1166, 1144, 1111, 1041, 967, 867, 852, 749 cm^{-1};

MS (FAB) *m/z* $[M+H]^+$ calcd for $C_{21}H_{34}BO_4$: 361.2545, found: 361.2536;

$[\alpha]^{25}_D$ = –1.6 (c = 1.04, $CHCl_3$); 92% ee from (*S,S*)–**L***.



2-(8-Chloro-1-phenyloctan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Figure 2A, entry 6). The title compound was prepared according to **GP-1** from 2-(1-chloro-3-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (196 mg, 0.700 mmol) and purified by column chromatography on silica gel (4→8% Et_2O in hexanes). Colorless oil.

(*R,R*)–**L***: 182 mg (0.519 mmol, 74%), + 90% ee; (*S,S*)–**L***: 192 mg (0.547 mmol, 78%), – 90% ee.

HPLC analysis: The ee was determined after oxidation (**GP-3)** via HPLC on a CHIRALPAK IB-3 column (10% 2-PrOH in hexane, 1.0 mL/min) with t_r = 8.7 min (major (*S,S*)–**L***), 10.7 min (major *(R,R)*–**L***);

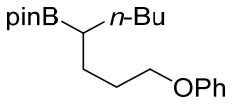
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 2H), 7.20 – 7.13 (m, 3H), 3.52 (t, *J* = 6.8 Hz, 2H), 2.68 – 2.51 (m, 2H), 1.82 – 1.29 (m, 10H), 1.27 (s, 12H), 1.09 – 0.98 (m, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 128.5, 128.4, 125.7, 83.1, 45.3, 35.8, 33.6, 32.7, 31.2, 28.5, 27.3, 25.01, 24.97;

FT-IR (ATR) 2977, 2928, 2856, 1456, 1379, 1371, 1317, 1157, 967, 748, 699 cm^{-1};

MS (FAB) *m*/*z* [M+H$^+$] calcd for $C_{20}H_{33}BClO_2$: 351.2257, found: 351.2270;

$[\alpha]^{25}_D$ = – 2.12 (c = 1.30, $CHCl_3$); 93% ee from (*S*,*S*)–**L***.



4,4,5,5-Tetramethyl-2-(1-phenoxyoctan-4-yl)-1,3,2-dioxaborolane (Figure 2B, entry 1). The title compound was prepared according to **GP-1** from 2-(1-chloropentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (163 mg, 0.700 mmol) and purified by column chromatography on silica gel (5→8% Et_2O in hexanes). Colorless oil.

(*R*,*R*)–**L***: 183 mg (0.551 mmol, 79%), + 91% ee; (*S*,*S*)–**L***: 188 mg (0.566 mmol, 81%), – 91% ee;

HPLC analysis: The ee was determined after oxidation (**GP-3)** via HPLC on a CHIRALPAK IB-3 column (3% 2-PrOH in hexane, 1.0 mL/min) with t_r = 18.7 min (major (*S*,*S*)–**L***), 25.6 min (major *(R,R)*–**L***);

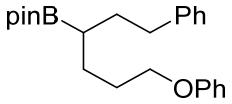
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.23 (m, 2H), 6.94 – 6.86 (m, 3H), 3.95 (t, *J* = 6.7 Hz, 2H), 1.84 – 1.74 (m, 2H), 1.62 – 1.26 (m, 8H), 1.25 (s, 12H), 1.07 – 0.97 (m, 1H), 0.89 (t, *J* = 6.9 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 129.5, 120.5, 114.7, 83.1, 68.2, 31.6, 31.1, 29.0, 27.8, 25.0, 24.9, 23.1, 14.2;

FT-IR (ATR) 2977, 2955, 2928, 2858, 1601, 1587, 1498, 1469, 1388, 1371, 1316, 1245, 1170, 1145, 1113, 1079, 1039, 968, 861, 753 cm^{-1};

MS (FAB) *m*/*z* [M$^+$] calcd for $C_{20}H_{33}BO_3$: 332.2517, found: 332.2523;

$[\alpha]^{25}_D$ = + 4.1 (c = 1.05, $CHCl_3$); 91% ee from (*S*,*S*)–**L***.



4,4,5,5-Tetramethyl-2-(6-phenoxy-1-phenylhexan-3-yl)-1,3,2-dioxaborolane (Figure 2B, entry 2). The title compound was prepared according to **GP-1** from 2-(1-chloro-3-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (196 mg, 0.700 mmol) and purified by column chromatography on silica gel (4→7% Et_2O in hexanes). Colorless solid.

(*R*,*R*)–**L***: 213 mg (0.560 mmol, 80%), + 90% ee; (*S*,*S*)–**L***: 210 mg (0.552 mmol, 79%), – 89% ee.

HPLC analysis: The ee was determined after oxidation (**GP-3)** via HPLC on a CHIRALPAK AS-H column (3% 2-PrOH in hexane, 1.0 mL/min) with t_r = 15.5 min (major *(R,R)*–**L***), 20.7 min (major (*S*,*S*)–**L***);

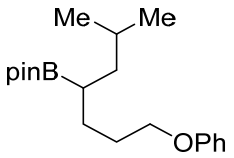
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.23 (m, 4H), 7.21 – 7.13 (m, 3H), 6.95 – 6.85 (m, 3H), 3.94 (t, *J* = 6.6 Hz, 2H), 2.70 – 2.54 (m, 2H), 1.86 – 1.55 (m, 6H), 1.26 (s, 12H), 1.15 – 1.06 (m, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 143.1, 129.5, 128.6, 128.4, 125.7, 120.5, 114.7, 83.2, 68.1, 35.7, 33.5, 28.9, 27.6, 25.0;

FT-IR (ATR) 3061, 3026, 2976, 2929, 2859, 1601, 1586, 1497, 1470, 1455, 1388, 1371, 1317, 1245, 1170, 1143, 1110, 1079, 1032, 967, 880, 861, 814 cm^{-1};

MS (FAB) *m*/*z* $[M]^+$ calcd for $C_{24}H_{33}BO_3$: 380.2517, found: 380.2507;

$[\alpha]^{25}_D$ = – 0.2 (c = 0.97, $CHCl_3$); 89% ee from (*S,S*)–**L***.



4,4,5,5-Tetramethyl-2-(6-methyl-1-phenoxyheptan-4-yl)-1,3,2-dioxaborolane (Figure 2B, entry 3). The title compound was prepared according to **GP-1** from 2-(1-chloro-3-methylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (163 mg, 0.700 mmol) and purified by column chromatography on silica gel (0→15% Et_2O in hexanes). Colorless oil.

(*R,R*)–**L***: 192 mg (0.578 mmol, 83%), + 90% ee; (*S,S*)–**L***: 197 mg (0.593 mmol, 85%), – 91% ee.

HPLC analysis: The ee was determined after oxidation (**GP-3)** via HPLC on a CHIRALPAK AS-H column (3% 2-PrOH in hexane, 1.0 mL/min) with t_r = 7.9 min (major (*S,S*)–**L***), 10.5 min (major *(R,R)*–**L***);

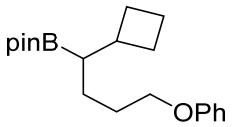
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.20 (m, 2H), 6.95 – 6.84 (m, 3H), 3.94 (t, *J* = 6.6 Hz, 2H), 1.85 – 1.72 (m, 2H), 1.63 – 1.29 (m, 4H), 1.24 (s, 12H), 1.22 – 1.02 (m, 2H), 0.87 (dd, *J* = 6.6 Hz, *J* = 1.4 Hz, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 129.5, 120.5, 114.7, 83.0, 68.2, 40.8, 29.0, 28.0, 27.4, 25.0, 24.9, 23.2, 22.7;

FT-IR (ATR) 2976, 2952, 2868, 1601, 1587, 1497, 1469, 1388, 1318, 1245, 1170, 1144, 1079, 1038, 966, 861, 753 cm^{-1};

MS (FAB) *m*/*z* $[M]^+$ calcd for $C_{20}H_{33}BO_3$: 332.2517, found: 332.2511;

$[\alpha]^{25}_D$ = + 5.2 (c = 0.94, $CHCl_3$); 91% ee from (*S,S*)–**L***.



2-(1-Cyclobutyl-4-phenoxybutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Figure 2B, entry 4). The title compound was prepared according to **GP-1** from 2-(cyclobutyliodomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (225 mg, 0.700 mmol) and purified by column chromatography on silica gel (4→7% Et_2O in hexanes). Colorless solid.

(*R,R*)–**L***: 202 mg (0.612 mmol, 87%), + 91% ee; (*S,S*)–**L***: 195 mg (0.590 mmol, 84%), – 90% ee.

HPLC analysis: The ee was determined after oxidation (**GP-3)** via HPLC on a CHIRALPAK IB-3 column (10% 2-PrOH in hexane, 1.0 mL/min) with t_r = 9.2 min (major *(R,R)*–**L***), 13.0 min (major (*S,S*)–**L***);

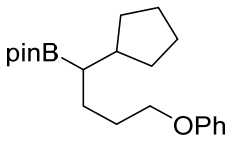
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.22 (m, 2H), 6.94 – 6.86 (m, 3H), 3.93 (t, *J* = 6.7 Hz, 2H), 2.37 – 2.26 (m, 1H), 2.12 – 2.03 (m, 1H), 2.02 – 1.93 (m, 1H), 1.87 – 1.35 (m, 8H), 1.23 (s, 12H), 1.06 – 1.00 (m, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 129.5, 120.5, 114.7, 83.1, 68.2, 38.1, 29.8, 29.3, 28.5, 25.7, 25.0, 24.9, 18.6;

FT-IR (ATR) 2975, 2934, 2864, 1601, 1497, 1472, 1379, 1317, 1245, 1144, 1035, 969, 753 cm^{-1};

MS (FAB) *m*/*z* $[M]^+$ calcd for $C_{20}H_{31}BO_3$: 330.2361, found: 330.2357;

$[\alpha]^{25}_D$ = + 11.2 (c = 1.07, $CHCl_3$); 90% ee from (*S,S*)–**L***.



2-(1-Cyclopentyl-4-phenoxybutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Figure 2B, entry 5). The title compound was prepared according to **GP-1** from 2-(cyclopentyliodomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (235 mg, 0.700 mmol) and purified by column chromatography on silica gel (5→7% Et_2O in hexanes). Colorless solid.

(*R,R*)–**L***: 202 mg (0.587 mmol, 84%), + 93% ee; (*S,S*)–**L***: 199 mg (0.578 mmol, 83%), – 93% ee.

HPLC analysis: The ee was determined after oxidation (**GP-3)** via HPLC on a CHIRALPAK IB-3 column (10% 2-PrOH in hexane, 1.0 mL/min) with t_r = 9.0 min (major *(R,R)*–**L***), 13.3 min (major (*S,S*)–**L***);

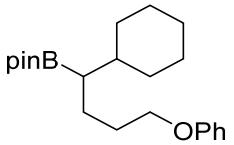
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.23 (m, 2H), 6.94 – 6.86 (m, 3H), 3.97 – 3.91 (m, 2H), 1.89 – 1.41 (m, 11H), 1.25 (s, 12H), 1.18 – 1.04 (m, 2H), 0.97 – 0.87 (m, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 129.5, 120.5, 114.7, 83.1, 68.2, 42.1, 32.7, 32.3, 29.3, 27.2, 25.4, 25.3, 25.1, 25.0;

FT-IR (ATR) 2976, 2945, 2866, 1601, 1507, 1497, 1473, 1457, 1379, 1318, 1248, 1144, 1040, 966, 753, 691 cm^{-1};

MS (FAB) *m*/*z* $[M]^+$ calcd for $C_{21}H_{33}BO_3$: 344.2517, found: 344.2532;

$[\alpha]^{25}_D$ = + 14.9 (c = 1.16, $CHCl_3$); 93% ee from (*S,S*)–**L***.



2-(1-Cyclohexyl-4-phenoxybutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Figure 2B, entry 6). The title compound was prepared according to **GP-1** from 2-(cyclohexyliodomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (245 mg, 0.700 mmol) and purified by column chromatography on silica gel (5→8% Et_2O in hexanes). Colorless solid.

(*R,R*)–**L***: 213 mg (0.594 mmol, 85%), + 94% ee; (*S,S*)–**L***: 209 mg (0.583 mmol, 83%), – 95% ee.

HPLC analysis: The ee was determined after oxidation (**GP-3)** via HPLC on a CHIRALPAK IB-3 column (10% 2-PrOH in hexane, 1.0 mL/min) with t_r = 9.4 min (major *(R,R)*–**L***), 15.5 min (major (*S,S*)–**L***);

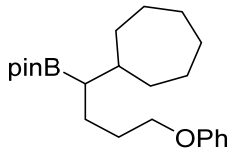
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.23 (m, 2H), 6.94 – 6.86 (m, 3H), 3.94 (t, *J* = 6.6 Hz, 2H), 1.85 – 1.51 (m, 9H), 1.44 – 1.34 (m, 1H), 1.252 (s, 6H), 1.247 (s, 6H), 1.22 – 0.84 (m, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 129.5, 120.5, 114.7, 83.1, 68.2, 39.8, 33.0, 32.5, 29.4, 27.0, 26.92, 26.89, 25.20, 25.18, 25.0;

FT-IR (ATR) 2977, 2923, 2851, 1600, 1497, 1471, 1371, 1314, 1248, 1162, 1144, 972, 752, 691 cm^{-1};

MS (FAB) *m*/*z* [M^+] calcd for $C_{22}H_{35}BO_3$: 358.2674, found: 358.2682;

$[\alpha]^{25}_D$ = + 2.91 (c = 1.05, $CHCl_3$); 95% ee from (*S*,*S*)–**L***.



2-(1-Cycloheptyl-4-phenoxybutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Figure 2B, entry 7). The title compound was prepared according to **GP-1** from 2-(cycloheptyliodomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (255 mg, 0.700 mmol) and purified by column chromatography on silica gel (4→7% Et_2O in hexanes). Colorless oil.

(*R*,*R*)–**L***: 215 mg (0.577 mmol, 83%), + 94% ee; (*S*,*S*)–**L***: 212 mg (0.569 mmol, 82%), – 95% ee.

HPLC analysis: The ee was determined after oxidation (**GP-3)** via HPLC on a CHIRALPAK IB-3 column (10% 2-PrOH in hexane, 1.0 mL/min) with t_r = 9.3 min (major *(R,R)*–**L***), 15.8 min (major (*S*,*S*)–**L***);

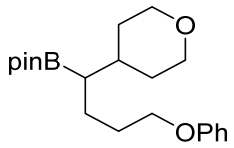
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.23 (m, 2H), 6.94 – 6.87 (m, 3H), 3.94 (t, *J* = 6.7 Hz, 2H), 1.85 – 1.19 (m, 17H), 1.25 (s, 6H), 1.24 (s, 6H), 1.00 – 0.95 (m, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 129.5, 120.5, 114.7, 83.0, 68.3, 41.6, 34.3, 33.6, 29.4, 28.3, 28.2, 27.42, 27.38, 25.5, 25.1, 24.9;

FT-IR (ATR) 2977, 2922, 2855, 1600, 1586, 1497, 1469, 1379, 1370, 1313, 1248, 1144, 752, 691 cm^{-1};

MS (FAB) *m*/*z* [$M]^+$ calcd for $C_{23}H_{37}BO_3$: 372.2830, found: 372.2835;

$[\alpha]^{25}_D$ = + 3.02 (c = 1.16, $CHCl_3$); 95% ee from (*S*,*S*)–**L***.



4,4,5,5-Tetramethyl-2-(4-phenoxy-1-(tetrahydro-2*H*-pyran-4-yl)butyl)-1,3,2-dioxaborolane (Figure 2B, entry 8). The title compound was prepared according to **GP-1** from 2-(iodo(tetrahydro-2H-pyran-4-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (246 mg, 0.700 mmol) and purified by column chromatography on silica gel (25→35% Et_2O in hexanes). Colorless solid.

(*R*,*R*)–**L***: 213 mg (0.59 mmol, 84%), + 93% ee; (*S*,*S*)–**L***: 218 mg (0.61 mmol, 86%), – 93% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD-H column (3% 2-PrOH in hexane, 1.0 mL/min) with t_r = 5.5 min (major *(R,R)*–**L***), 6.9 min (major (*S*,*S*)–**L***);

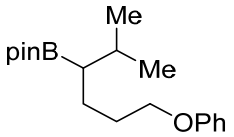
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 2H), 6.94 – 6.86 (m, 3H), 3.99 – 3.90 (m, 4H), 3.41 – 3.31 (m, 2H), 1.86 – 1.67 (m, 2H), 1.67 – 1.53 (m, 5H), 1.48 – 1.30 (m, 2H), 1.25 (s, 12H), 0.99 – 0.91 (m, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 129.5, 120.6, 114.6, 83.3, 68.7, 68.5, 68.1, 37.0, 32.9, 32.4, 29.1, 25.2, 25.0, 24.9;

FT-IR (ATR) 2976, 2932, 2843, 1600, 1497, 1471, 1379, 1317, 1247, 1143, 1109, 856, 754, 692 cm^{-1};

MS (FAB) *m*/*z* $[M+H]^+$ calcd for $C_{21}H_{34}BO_4$: 361.2545, found: 361.2541;

$[\alpha]^{25}_D$ = + 1.89 (c = 1.64, $CHCl_3$); 93% ee from (*S,S*)–**L***.



4,4,5,5-Tetramethyl-2-(2-methyl-6-phenoxyhexan-3-yl)-1,3,2-dioxaborolane (Figure 2B, entry 9). The title compound was prepared according to **GP-1** from 2-(1-iodo-2-methylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (217 mg, 0.700 mmol) and purified by column chromatography on silica gel (4→7% Et_2O in hexanes). Colorless solid.

(*R,R*)–**L***: 187 mg (0.588 mmol, 84%), + 93% ee; (*S,S*)–**L***: 186 mg (0.584 mmol, 83%), – 93% ee.

HPLC analysis: The ee was determined after oxidation (**GP-3)** via HPLC on a CHIRALPAK IB-3 column (10% 2-PrOH in hexane, 1.0 mL/min) with t_r = 8.0 min (major *(R,R)*–**L***), 13.1 min (major (*S,S*)–**L***);

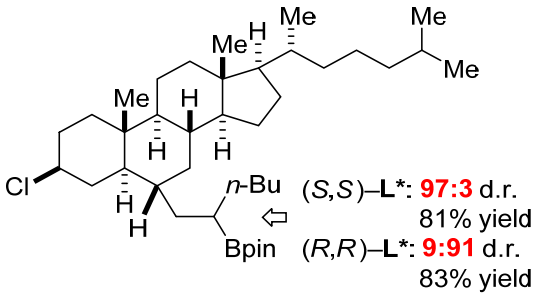
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 2H), 6.95 – 6.87 (m, 3H), 3.95 (t, *J* = 6.6 Hz, 2H), 1.86 – 1.67 (m, 3H), 1.60 – 1.48 (m, 2H), 1.251 (s, 6H), 1.248 (s, 6H), 0.94 (dd, *J* = 6.8 Hz, *J* = 5.4 Hz, 6H), 0.91 – 0.85 (m, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 129.5, 120.5, 114.7, 83.1, 68.2, 31.8, 29.8, 29.3, 25.6, 25.1, 25.0, 22.4, 21.8;

FT-IR (ATR) 2954, 2868, 1601, 1497, 1472, 1380, 1371, 1315, 1253, 1215, 1170, 1143, 1039, 971, 849, 753, 691 cm^{-1};

MS (FAB) *m*/*z* $[M]^+$ calcd for $C_{19}H_{31}BO_3$: 318.2361, found: 318.2353;

$[\alpha]^{25}_D$ = + 8.20 (c = 1.00, $CHCl_3$); 93% ee from (*S,S*)–**L***.



2-(1-((3*S*,5*R*,6*S*,8*S*,9*S*,10*S*,13*R*,14*S*,17*R*)-3-Chloro-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-6-yl)hexan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Figure 3A). The title compound was prepared according to **GP-2** from 2-(1-chloro-2-((3*S*,5*R*,6*R*,8*S*,9*S*,10*S*,13*R*,14*S*,17*R*)-3-chloro-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-6-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (105 mg, 0.200 mmol) and *n*-butylzinc bromide (0.360 mmol). The product was purified by column chromatography on silica gel (0→20% Et_2O in hexanes). Colorless oil.

(*S*,*S*)–**L***: 100 mg (0.162 mmol, 81%), 97:3 d.r.; (*R*,*R*)–**L***: 103 mg (0.167 mmol, 83%), 9:91 d.r.;

HPLC analysis: The d.r. was determined via HPLC on a CHIRALCEL AD-H column (1% 2-PrOH in hexane, 1.0 mL/min) with t_r = 4.1 min (major (*S*,*S*)–**L***), 4.6 min (major *(R,R)*–**L***);

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.87 – 3.73 (m, 1H), 2.25 – 2.16 (m, 1H), 2.05 – 1.91 (m, 2H), 1.86 – 1.68 (m, 4H), 1.66 – 0.75 (m, 34H), 1.24 (s, 12H), 0.91 – 0.81 (m, 12H), 0.67 – 0.54 (m, 1H), 0.64 (s, 3H);[a]

^{13}C NMR (100 MHz, $CDCl_3$) δ 83.0, 61.5, 56.6, 56.4, 54.2, 52.4, 42.7, 40.1, 39.7, 39.0, 38.2, 36.3, 36.0, 35.8, 35.4, 35.1, 34.8, 34.5, 33.0, 31.5, 30.4, 28.4, 28.2, 25.0, 24.9, 24.4, 24.0, 23.1, 23.0, 22.7, 21.3, 18.8, 14.3, 13.5, 12.2 (from *S*,*S*–**L***);

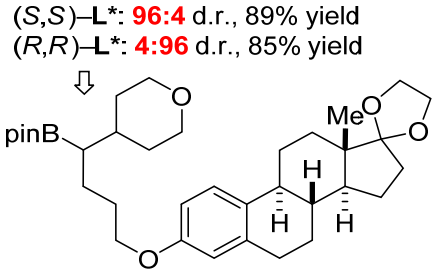
^{13}C NMR (100 MHz, $CDCl_3$) δ 82.9, 61.5, 56.6, 56.4, 54.2, 51.9, 42.7, 40.1, 39.7, 39.0, 38.2, 36.3, 36.02, 35.99, 35.8, 35.7, 35.3, 35.0, 33.0, 32.7, 31.7, 28.4, 28.2, 25.1, 25.0, 24.4, 24.0, 23.1, 23.0, 22.7, 21.3, 18.8, 14.2, 13.5, 12.2 (from *R*,*R*–**L***);

FT-IR (ATR) 2929, 2868, 1467, 1379, 1314, 1144, 966, 860, 755 cm^{-1};

MS (FAB) *m*/*z* [M-H_2+H^+] calcd for $C_{39}H_{69}BClO_2$: 615.5074, found: 615.5054;

$[\alpha]^{25}_D$ = + 45.8 (c = 0.55, $CHCl_3$); 97:3 d.r. from (*S*,*S*)–**L***;

$[\alpha]^{25}_D$ = + 57.9 (c = 2.40, $CHCl_3$); 9:91 d.r. from (*R*,*R*)–**L***.



4,4,5,5-Tetramethyl-2-(4-(((8*R*,9*S*,13*S*,14*S*)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[a]phenanthrene-17,2'-[1,3]dioxolan]-3-yl)oxy)-1-(tetrahydro-2H-

[a] The ^{1}H NMR spectra are identical for the two diastereomers.

pyran-4-yl)butyl)-1,3,2-dioxaborolane (Figure 3A). The title compound was prepared according to **GP-2** from 2-(iodo(tetrahydro-2*H*-pyran-4-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (70.0 mg, 0.200 mmol) and (3-(((8*R*,9*S*,13*S*,14*S*)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[a]phenanthrene-17,2'-[1,3]dioxolan]-3-yl)oxy)propyl)zinc bromide (0.36 mmol). The product was purified by column chromatography on silica gel (20→40% Et_2O in hexanes). Colorless foam.

(*S*,*S*)–**L***: 103 mg (0.177 mmol, 89%), 96:4 d.r.; (*R*,*R*)–**L***: 98.5 mg (0.170 mmol, 85%), 4:96 d.r.;

HPLC analysis: The d.r. was determined via HPLC on a CHIRALCEL OD-H column (1% 2-PrOH in hexane, 1.0 mL/min) with t_r = 8.9 min (major *(R,R)*–**L***), 10.1 min (major (*S*,*S*)–**L***);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (dd, *J* = 8.8 Hz, *J* = 1.0 Hz, 1H), 6.68 (dd, *J* = 8.6 Hz, *J* = 2.7 Hz, 1H), 6.61 (d, *J* = 2.7 Hz, 1H), 4.01 – 3.84 (m, 8H), 3.41 – 3.29 (m, 2H), 2.87 – 2.78 (m, 2H), 2.36 – 2.17 (m, 2H), 2.08 – 1.97 (m, 1H), 1.93 – 1.20 (m, 19H), 1.25 (s, 12H), 0.99 – 0.90 (m, 1H), 0.88 (s, 3H);[b]

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 138.0, 132.6, 126.4, 119.6, 114.6, 112.2, 83.2, 68.6, 68.5, 68.1, 65.4, 64.7, 49.5, 46.3, 43.8, 39.2, 37.0, 34.4, 32.9, 32.4, 30.9, 29.9, 29.2, 27.1, 26.3, 25.1, 25.0, 24.9, 22.5, 14.5;[b]

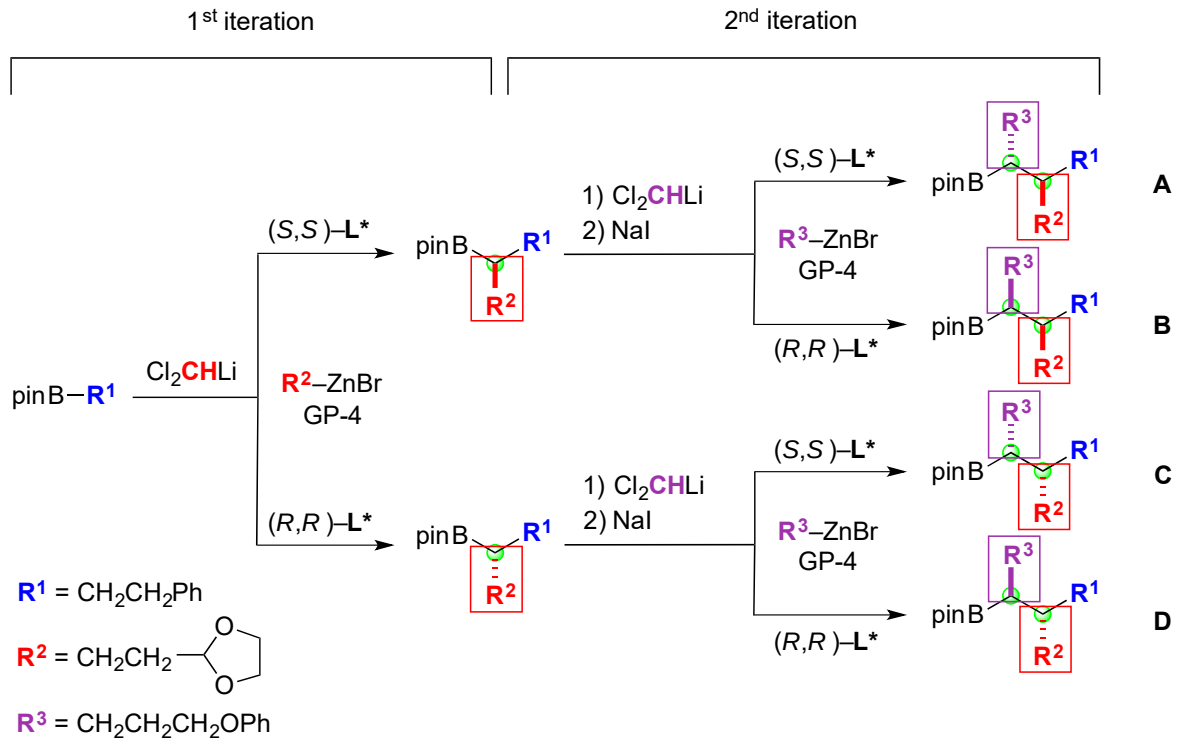
FT-IR (ATR) 2934, 2867, 1608, 1498, 1379, 1240, 1142, 1105, 1043, 908, 743, 647 cm^{-1};

MS (FAB) *m*/*z* $[M]^+$ calcd for $C_{35}H_{53}BO_6$: 580.3930, found: 580.3920;

$[\alpha]^{25}_D$ = + 15.0 (c = 5.30, $CHCl_3$); 96:4 d.r. from (*S*,*S*)–**L***;

$[\alpha]^{25}_D$ = + 12.5 (c = 6.18, $CHCl_3$); 4:96 d.r. from (*R*,*R*)–**L***.

[b] The ^{1}H NMR and the ^{13}C NMR spectra are identical for the two diastereomers.



	ligand 1st iteration	ligand 2nd iteration	A : B : C : D
A	(*S*,*S*)-**L***	(*S*,*S*)-**L***	95 : 3 : 2 : 0
B		(*R*,*R*)-**L***	3 : 95 : 0 : 2
C	(*R*,*R*)-**L***	(*S*,*S*)-**L***	2 : 0 : 95 : 3
D		(*R*,*R*)-**L***	0 : 2 : 3 : 95
D	(*R*,*R*)-**L***	(*R*,*R*)-**L***	0 : 2 : 3 : 95

2-(3-(2-(1,3-Dioxolan-2-yl)ethyl)-7-phenoxy-1-phenylheptan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Figure 3B).

1st iteration: *n*-Butyllithium (2.50 M in hexane; 1.26 mL, 3.15 mmol, 4.50 equiv) was added dropwise to a solution of CH_2Cl_2 (0.224 mL, 3.50 mmol, 5.00 equiv) in THF (20 mL) at –78 °C. The resulting mixture was stirred for 45 min, and then a solution of 4,4,5,5-tetramethyl-2-phenethyl-1,3,2-dioxaborolane (162 mg, 0.700 mmol, 1.00 equiv) in THF (5.0 mL) was added to the solution of Cl_2CHLi at –78 °C. The mixture was stirred at –78 °C for 45 min. Then, $ZnCl_2$ (477 mg, 3.50 mmol, 5.00 equiv) was added, and then the solution was stirred at room temperature for 1 h. Next, NH_4Cl (saturated aqueous solution; 10 mL), Et_2O (20 mL), and hexanes (20 mL) were added. The organic phase was washed with H_2O (1 x 15 mL) and NH_4Cl (saturated aqueous solution; 1 x 15 mL), and then it was filtered through a small plug of silica gel/$MgSO_4$ (1:1). The plug was flushed with Et_2O/hexane (1/1), and then all volatiles were removed. The resulting residue was then reacted with (2-(1,3-dioxolan-2-yl)ethyl)zinc bromide according to **GP-2**. For isolation and analytical data, see below.

(*R*,*R*)–**L***: 128 mg (0.370 mmol, 53%), +95% ee; (*S*,*S*)–**L***: 130 mg (0.375 mmol, 54%), – 95% ee.

2*nd* iteration: *n*-Butyllithium (2.50 M in hexane; 0.900 mL, 2.25 mmol, 4.50 equiv) was added dropwise to a solution of CH_2Cl_2 (160 μL, 2.50 mmol, 5.00 equiv) in THF (10 mL) at –78 °C. The resulting mixture was stirred for 45 min, and then a solution of 2-(1-(1,3-dioxolan-2-yl)-5-phenylpentan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (173 mg, 0.500 mmol, 1.00 equiv) in THF (5.0 mL) was added to the solution of Cl_2CHLi at –78 °C. The mixture was stirred at –30 °C for 45 min. Then, $ZnCl_2$ (341 mg, 2.50 mmol, 5.00 equiv) was added, and then the solution was stirred at room temperature for 1 h. Next, NH_4Cl (saturated aqueous solution; 10 mL) was added. The mixture was extracted with Et_2O (3 x 15 mL), and the combined organic phases were dried over $MgSO_4$ and then concentrated. The crude product was dissolved in acetone (10 mL), sodium iodide (225 mg, 1.50 mmol, 3.00 equiv) was added, and the suspension was heated at 60 °C for 2 h. After cooling to room temperature, the mixture was diluted with Et_2O (50 mL) and washed with NH_4Cl (saturated aqueous solution; 2 x 20 mL) and H_2O (1 x 20 mL). The organic phase was filtered through a small plug of silica gel/$MgSO_4$, and all volatiles were then removed. The product was purified by column chromatography on silica gel (10→50% Et_2O in hexanes). Yellow oil.

(*R,R*)–**L***: 133 mg (0.274 mmol, 55%); (*S,S*)–**L***: 126 mg (0.259 mmol, 52%).

Next, 2-(2-(2-(1,3-dioxolan-2-yl)ethyl)-1-iodo-4-phenylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (48.6 mg, 0.100 mmol) was reacted with (3-phenoxypropyl)zinc bromide according to **GP-2**. The title compound was isolated by column chromatography on silica gel (5→30% Et_2O in hexanes). Colorless oil.

A: 40.7 mg (0.0823 mmol, 82%); **B**: 39.1 mg (0.0791 mmol, 79%); **C**: 40.2 mg (0.0813 mmol, 81%); **D**: 37.0 mg (0.0748 mmol, 75%).

In the case of the fifth entry in the above illustration, 2-(1-(1,3-dioxolan-2-yl)-5-phenylpentan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (104 mg, 0.300 mmol, 1.00 equiv) was reacted according to the procedure in the 2*nd* iteration described above, but the α-iodoborane was used without isolation. 76.0 mg (0.154 mmol, 51%).

HPLC analysis: The stereoselectivity was determined via HPLC on a CHIRALCEL IA column (2% 2-PrOH in hexane, 1.0 mL/min) with t_r = 48.5, 50.6, 54.3, 61.3 min;

A, **D**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.22 (m, 4H), 7.19 – 7.12 (m, 3H), 6.94 – 6.86 (m, 3H), 4.83 (t, *J* = 4.7 Hz, 1H), 3.98 – 3.89 (m, 4H), 3.88 – 3.79 (m, 2H), 2.69 – 2.51 (m, 2H), 1.89 – 1.35 (m, 12H), 1.24 (s, 6H), 1.23 (s, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 143.3, 129.5, 128.5, 128.4, 125.7, 120.5, 114.7, 105.0, 83.1, 68.2, 65.0, 39.3, 35.1, 33.7, 32.1, 29.5, 26.9, 25.2, 25.0, 24.9, 24.5;

B and **C**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.22 (m, 4H), 7.19 – 7.12 (m, 3H), 6.94 – 6.85 (m, 3H), 4.83 (t, *J* = 4.8 Hz, 1H), 3.99 – 3.89 (m, 4H), 3.87 – 3.81 (m, 2H), 2.73 – 2.49 (m, 2H), 1.88 – 1.45 (m, 12H), 1.23 (s, 6H), 1.22 (s, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 143.2, 129.5, 128.5, 128.4, 125.7, 120.5, 114.7, 105.1, 83.1, 68.2, 64.97, 64.95, 39.1, 35.0, 33.9, 31.5, 29.4, 26.8, 25.2, 25.01, 24.96, 24.5;

A: FT-IR (ATR) 2976, 2929, 2865, 1600, 1496, 1471, 1454, 1379, 1371, 1314, 1243, 1141, 1032, 967, 860, 752, 692 cm^{-1};

C: FT-IR (ATR) 2976, 2929, 2866, 1600, 1586, 1496, 1471, 1454, 1379, 1371, 1314, 1243, 1141, 1032, 967, 943, 881, 850, 752, 692, 669 cm^{-1};

MS (FAB) *m/z* $[M-H]^+$ calcd for $C_{30}H_{42}BO_5$: 493.3120, found: 493.3114;

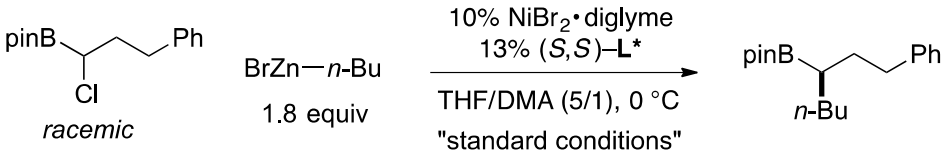
A: $[\alpha]^{25}_D$ – 5.4 (c = 0.24, $CHCl_3$);

B: $[\alpha]^{25}_D$ – 2.7 (c = 1.05, $CHCl_3$).

III. Effect of Reaction Parameters

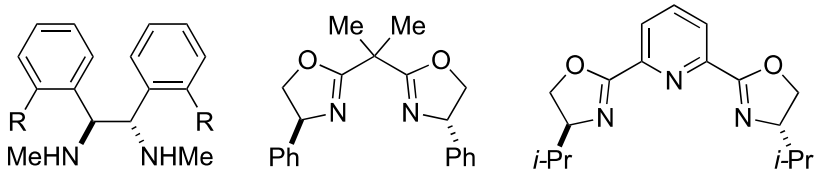
2-(1-Chloro-3-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.10 mmol) was reacted with *n*-butylzinc bromide according to **GP-2** at 0 °C for 18 h. The yield was determined via GC analysis with tetradecane as an internal standard. The ee was determined via HPLC analysis after stereospecific oxidation (**GP-3**) of the crude reaction mixture and purification by preparative thin-layer chromatography.

Table S–1.



entry	change from the "standard conditions"	yield (%)[a]	ee (%)[b]
1	none	76	91
2	no $NiBr_2$•diglyme	<1	–
3	no **L***	<1	–
4	rt, instead of 0 °C	40	87
5	**L1**, instead of **L***	72	87
6	**L2**, instead of **L***	13	28
7	**L3**, instead of **L***	33	10
8	5% $NiBr_2$•diglyme, 6.5% **L***	46	88
9	1.1 equiv BrZn–*n*-Bu	74	84
10	DMA only	79	66
11	under air, instead of under N_2	24	84
12	0.1 equiv water added	30	85

All data are the average of two experiments. [a] Determined through GC analysis versus a calibrated standard. [b] Determined through HPLC analysis after stereospecific oxidation.



R = Me **L***
R = H **L1**

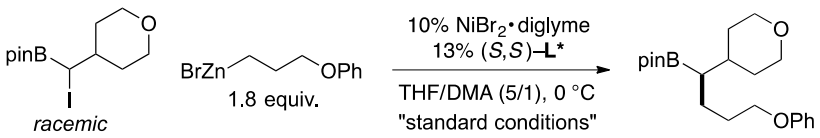
L2

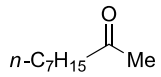
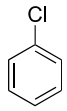
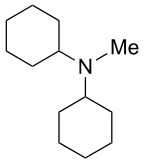
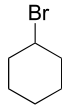
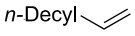
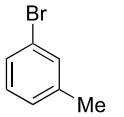
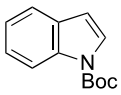
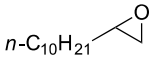
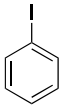
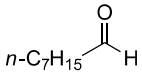
L3

IV. Functional-Group Compatibility

2-(Iodo(tetrahydro-2H-pyran-4-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.10 mmol) was reacted with (3-phenoxypropyl)zinc bromide according to **GP-2** at 0 °C for 18 h. The yield was determined via GC analysis with tetradecane as an internal standard. The ee was determined via HPLC analysis (without oxidation) after purification by preparative thin-layer chromatography.

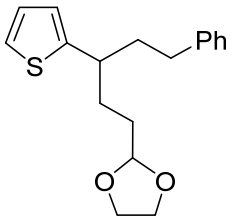
Table S–2.



additive	recovery of additive (%)[a]	yield,[a] ee[b] (%)	additive	recovery of additive (%)[a]	yield,[a] ee[b] (%)
no additive	–	92, 93		>95	89, 93
	>95	90, 93		90	81, 93
	>95	92, 92		84	85, 94
	>95	95, 93		82	91, 94
	>95	92, 93		68	63, 92
	>95	89, 94		62	92, 93
	90	89, 93		–	<10; –

All data are the average of two experiments. [a] Determined through GC analysis versus a calibrated standard. [b] Determined through HPLC analysis.

V. Derivatization of Cross-Coupling Products



2-(5-Phenyl-3-(thiophen-2-yl)pentyl)-1,3-dioxolane.[30] *n*-Butyllithium (2.50 M in hexane; 72.0 μL, 0.180 mmol, 1.20 equiv) was added dropwise to a solution of thiophene (14.0 μL, 0.180 mmol, 1.20 equiv) in THF (10 mL) at –78 °C, and then the mixture was stirred at room temperature for 30 min. A solution of 2-(1-(1,3-dioxolan-2-yl)-5-phenylpentan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (51.9 mg, 0.150 mmol, 1.00 equiv) in THF (2.5 mL) was added dropwise to the solution of 2-lithiothiophene at –78 °C, and the reaction mixture was stirred for 1 h. Next, a solution of NBS (32.0 mg, 0.180 mmol, 1.20 equiv) in THF (2.5 mL) was added at –78 °C, and the resulting reaction mixture was stirred at –78 °C for 1 h. Na_2SO_3 (saturated aqueous solution; 5 mL) was added at –78 °C, and then the mixture was allowed to warm to room temperature and was extracted with Et_2O (3 x 15 mL). The combined organic phases were dried over $MgSO_4$ and concentrated under reduced pressure. The title compound was isolated by column chromatography on silica gel (15→30% Et_2O in hexanes). Colorless oil.

(*S,S*)–**L***: 43.3 mg (0.143 mmol, 95%), + 95% ee; (*R,R*)–**L***: 44.0 mg (0.145 mmol, 97%), – 95% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD-H column (5% 2-PrOH in hexane, 1.0 mL/min) with t_r = 10.9 min (major *(R,R)*–**L***), 15.1 min (major (*S,S*)–**L***);

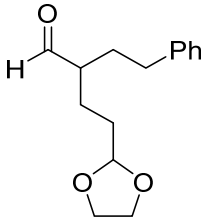
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.24 (m, 2H), 7.20 – 7.11 (m, 4H), 6.94 (dd, *J* = 5.1 Hz, *J* = 3.4 Hz, 1H), 6.81 (dd, *J* = 3.4 Hz, *J* = 1.2 Hz, 1H), 4.80 (t, *J* = 4.7 Hz, 1H), 3.95 – 3.89 (m, 2H), 3.86 – 3.78 (m, 2H), 2.97 – 2.86 (m, 1H), 2.63 – 2.46 (m, 2H), 2.07 – 1.97 (m, 1H), 1.96 – 1.79 (m, 2H), 1.75 – 1.52 (m, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2, 142.3, 128.6, 128.4, 126.6, 125.9, 124.4, 123.1, 104.5, 65.00, 64.97, 40.8, 39.8, 33.7, 32.3, 31.9;

FT-IR (ATR) 3025, 2948, 2856, 1602, 1495, 1453, 1408, 1137, 1029, 942, 896, 848, 825, 748, 700 cm^{-1};

GC-MS (EI) m/z $[M]^+$ calcd for $C_{18}H_{22}O_2S$: 302.1, found: 302.2;

$[\alpha]^{25}_D$ = – 9.8 (c = 1.45, $CHCl_3$); 95% ee from (*S,S*)–**L***.



2-(2-(1,3-Dioxolan-2-yl)ethyl)-4-phenylbutanal.[31,32] *n*-Butyllithium (2.50 M in hexane; 0.270 mL, 0.680 mmol, 4.50 equiv) was added dropwise to a solution of CH_2Cl_2 (48.0 µL, 0.750 mmol, 5.00 equiv) in THF (7.5 mL) at –78 °C, and the resulting mixture was stirred for 45 min. A solution of 2-(1-(1,3-dioxolan-2-yl)-5-phenylpentan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (51.9 mg, 0.150 mmol, 1.00 equiv) in THF (2.5 mL) was added to the solution of Cl_2CHLi at –78 °C, and the resulting mixture was stirred at –30 °C for 45 min. Next, $ZnCl_2$ (102 mg, 0.750 mmol, 5.00 equiv) was added, and then the mixture was stirred at room temperature for 2 h. Water (pH=7, phosphate buffer; 5 mL) and $NaBO_3 \cdot 4\ H_2O$ (115 mg, 0.750 mmol, 5.00 equiv) were added, and the suspension was stirred at room temperature for 4 h. Next, the reaction mixture was diluted with water and extracted with Et_2O (3 x 50 mL). The combined organic phases were dried over $MgSO_4$ and concentrated under reduced pressure. The title compound was isolated by column chromatography on silica gel (15→50% Et_2O in hexanes). Colorless oil.

(*S,S*)–**L***: 37.1 mg (0.149 mmol, 100%), + 95% ee; (*R,R*)–**L***: 36.4 mg (0.146 mmol, 98%), – 95% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL AD-H column (15% 2-PrOH in hexane, 1.0 mL/min) with t_r = 6.9 min (major *(R,R)*–**L***), 8.4 min (major (*S,S*)–**L***);

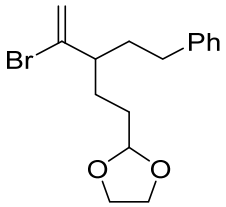
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.62 (t, *J* = 2.6 Hz, 1H), 7.33 – 7.25 (m, 2H), 7.23 – 7.13 (m, 3H), 4.85 (t, *J* = 4.4 Hz, 1H), 4.01 – 3.91 (m, 2H), 3.90 – 3.80 (m, 2H), 2.71 – 2.55 (m, 2H), 2.41 – 2.30 (m, 1H), 2.05 – 1.93 (m, 1H), 1.85 – 1.59 (m, 5H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 204.7, 128.6, 128.5, 126.2, 104.1, 65.08, 65.07, 50.9, 33.2, 31.2, 30.6, 22.9;

FT-IR (ATR) 2928, 2864, 1721, 1496, 1454, 1408, 1139, 1030, 944, 865, 748, 699 cm^{-1};

GC-MS (EI) m/z $[M]^+$ calcd for $C_{15}H_{20}O_3$: 248.1, found: 248.2;

$[\alpha]^{25}_D$ – 1.8 (c = 1.06, $CHCl_3$); 95% ee from (*S,S*)–**L***.



2-(4-Bromo-3-phenethylpent-4-en-1-yl)-1,3-dioxolane.[33] 2-(1-(1,3-Dioxolan-2-yl)-5-phenylpentan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (51.9 mg, 0.150 mmol) and vinyl bromide (1.00 M in THF; 0.300 mL, 0.300 mmol, 2.00 equiv) were dissolved in Et_2O (1 mL), and the resulting solution was cooled to –95 °C. Freshly prepared LDA (0.86 M; 0.35 mL, 0.300 mmol, 2.00 equiv) was added dropwise over 10 min, and then the reaction mixture was stirred at –95 °C for 1 h. A solution of iodine (83.7 mg, 0.330 mmol, 2.20 equiv) in MeOH (1 mL) was added dropwise, and the resulting mixture was stirred at –95 °C for 5 min and then at room

temperature for 1 h. Na_2SO_3 (saturated aqueous solution; 10 mL) was added, and the reaction mixture was extracted with Et_2O (3 x 15 mL). The combined organic phases were dried over $MgSO_4$ and concentrated. The title compound was purified by column chromatography on silica gel (10→25% Et_2O in hexanes). Colorless oil.

(*S,S*)–**L***: 36.5 mg (0.112 mmol, 75%), + 95% ee; (*R,R*)–**L***: 40.5 mg (0.125 mmol, 83%), – 95% ee;

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD-H column (5% 2-PrOH in hexane, 1.0 mL/min) with t_r = 6.8 min (major *(R,R)*–**L***), 11.2 min (major (*S,S*)–**L***);

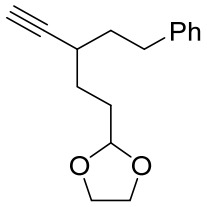
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 2H), 7.21 – 7.14 (m, 3H), 5.64 (d, *J* = 1.4 Hz, 1H), 5.54 (d, *J* = 1.4 Hz, 1H), 4.84 (t, *J* = 4.4 Hz, 1H), 4.00 – 3.90 (m, 2H), 3.89 – 3.79 (m, 2H), 2.69 – 2.62 (m, 1H), 2.51 – 2.43 (m, 1H), 2.24 – 2.14 (m, 1H), 1.85 – 1.45 (m, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 139.1, 128.6, 128.5, 126.0, 118.6, 104.4, 65.0, 65.0, 49.1, 35.4, 33.3, 31.5, 27.9;

FT-IR (ATR) 2949, 2858, 1624, 1602, 1496, 1453, 1409, 1127, 1029, 942, 889, 748, 698 cm^{-1};

GC-MS (EI) m/z $[M\text{-}Br]^+$ calcd for $C_{16}H_{21}O_2$: 245.1, found: 245.2;

$[\alpha]^{25}_D$ = –2.90 (c = 0.23, $CHCl_3$); 95% ee from *(R,R)*–**L***.



2-(3-Phenethylpent-4-yn-1-yl)-1,3-dioxolane.[33] 2-(1-(1,3-Dioxolan-2-yl)-5-phenylpentan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (51.9 mg, 0.150 mmol) and vinyl bromide (1.00 M in THF; 0.300 mL, 0.300 mmol, 2.00 equiv) were dissolved in Et_2O (1 mL), and the resulting solution was cooled to –95 °C. Freshly prepared LDA (0.860 M; 0.350 mL, 0.300 mmol, 2.00 equiv) was added dropwise over 10 min, and then the reaction mixture was stirred at –95 °C for 1 h. A solution of iodine (83.7 mg, 0.330 mmol, 2.20 equiv) in MeOH (1 mL) was added dropwise, and the resulting mixture was stirred at –95 °C for 5 min and then at room temperature for 1 h. Na_2SO_3 (saturated aqueous solution; 10 mL) was added, and then the reaction mixture was extracted with Et_2O (3 x 15 mL). The combined organic phases were dried over $MgSO_4$ and concentrated. The crude mixture was dissolved in DMF (2 mL), and then tetrabutylammonium fluoride trihydrate (237 mg, 0.750 mmol, 5.00 equiv) was added and the mixture was heated at 60 °C for 2 h. After the reaction was complete, the mixture was diluted with H_2O (30 mL) and extracted with Et_2O (3 x 30 mL). The combined organic phases were dried over $MgSO_4$ and concentrated. The title compound was purified by column chromatography on silica gel (10→20% Et_2O in hexanes). Colorless oil.

(*S,S*)–**L***: 26.1 mg (0.107 mmol, 71%), + 95% ee; (*R,R*)–**L***: 27.2 mg (0.111 mmol, 74%), – 95% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD-H column (5% 2-PrOH in hexane, 1.0 mL/min) with t_r = 8.3 min (major (*S,S*)–**L***), 10.1 min (major *(R,R)*–**L***);

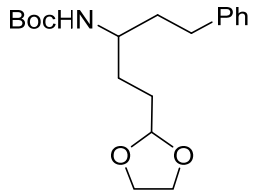
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.25 (m, 2H), 7.22 – 7.16 (m, 3H), 4.87 (t, *J* = 4.6 Hz, 1H), 4.00 – 3.90 (m, 2H), 3.90 – 3.78 (m, 2H), 2.91 – 2.81 (m, 1H), 2.77 – 2.66 (m, 1H), 2.44 – 2.32 (m, 1H), 2.14 (d, *J* = 2.4 Hz, 1H), 1.98 – 1.88 (m, 1H), 1.82 – 1.70 (m, 3H), 1.68 – 1.56 (m, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 128.6, 128.5, 126.0, 104.4, 87.0, 70.4, 65.1, 65.0, 36.9, 33.6, 31.6, 31.0, 29.2;

FT-IR (ATR) 3290, 2951, 2860, 1496, 1454, 1409, 1137, 1029, 943, 746, 702, 632 cm^{-1};

GC-MS (EI) m/z (M^+) calcd for $C_{16}H_{20}O_2$: 244.1, found: 244.2;

$[\alpha]^{25}_D$ – 28.4 (c = 0.76, $CHCl_3$); 95% ee from (*S,S*)–**L***.



***Tert*-butyl (1-(1,3-dioxolan-2-yl)-5-phenylpentan-3-yl)carbamate.**[34] A solution of *O*-methylhydroxylamine (2.82 M in THF; 0.160 mL, 0.450 mmol, 3.00 equiv) was diluted with THF (1 mL). *n*-Butyllithium (2.50 M in hexanes; 0.180 mL, 0.450 mmol, 3.00 equiv) was added at –78 °C, and the resulting mixture was stirred for 45 min. Next, a solution of 2-(1-(1,3-dioxolan-2-yl)-5-phenylpentan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (51.9 mg, 0.150 mmol, 1.00 equiv) in THF (1 mL) was added dropwise at –78 °C. The reaction mixture was stirred at 60 °C overnight. Next, the mixture was allowed to cool to room temperature, and then di-*tert*-butyl dicarbonate (0.140 mL, 0.600 mmol, 4.00 equiv) was added. The resulting mixture was stirred at room temperature for 1 h. Next, all volatiles were removed, and the title compound was isolated by column chromatography on silica gel (10→70% Et_2O in hexanes). Colorless solid.

(*S,S*)–**L***: 40.0 mg (0.119 mmol, 79%), + 95% ee; (*R,R*)–**L***: 43.0 mg (0.128 mmol, 85%), – 95% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD-H column (20% 2-PrOH in hexane, 1.0 mL/min) with t_r = 9.1 min (major (*S,S*)–**L***), 15.7 min (major *(R,R)*–**L***);

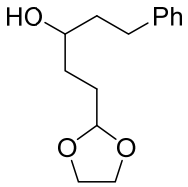
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.23 (m, 2H), 7.21 – 7.13 (m, 3H), 4.87 (t, *J* = 4.4 Hz, 1H), 4.41 – 4.30 (m, 1H), 4.00 – 3.90 (m, 2H), 3.89 – 3.80 (m, 2H), 3.72 – 3.57 (m, 1H), 2.76 – 2.56 (m, 2H), 1.86 – 1.58 (m, 5H), 1.54 – 1.39 (m, 1H), 1.45 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 142.0, 128.39, 128.37, 125.8, 104.2, 79.1, 64.94, 64.91, 50.3, 37.8, 32.4, 30.2, 29.6, 28.4;

FT-IR (ATR) 3369, 2977, 2947, 2860, 1695, 1513, 1454, 1389, 1361, 1245, 1170, 1145, 1126, 1030, 987, 941, 870, 777, 743, 700, 602 cm^{-1};

HR-MS (FAB) m/z $[M+H]^+$ calcd for $C_{19}H_{30}NO_4$: 336.2169, found: 336.2161;

$[\alpha]^{25}_D$ – 6.2 (c = 1.90, $CHCl_3$); 95% ee from (*R,R*)–**L***.



1-(1,3-Dioxolan-2-yl)-5-phenylpentan-3-ol.[35] 2-(1-(1,3-Dioxolan-2-yl)-5-phenylpentan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (51.9 mg, 0.150 mmol, 1.00 equiv) was dissolved in a mixture of THF and H_2O (1:1; 10 mL), and then $NaBO_3 \cdot 4\ H_2O$ (115 mg, 0.750 mmol, 5.00 equiv) was added at room temperature. The suspension was stirred overnight. After the reaction was complete, water (20 mL) was added. The aqueous phase was extracted with Et_2O (3 x 20 mL), and the combined organic phases were dried over $MgSO_4$ and concentrated. The residue was purified by column chromatography on silica gel (50→100% Et_2O in hexanes). Colorless oil.

(*S,S*)–**L***: 35.1 mg (0.149 mmol, 99%), + 95% ee; (*R,R*)–**L***: 33.2 mg (0.140 mmol, 94%), – 95% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD-H column (20% 2-PrOH in hexane, 1.0 mL/min) with t_r = 10.1 min (major (*S,S*)–**L***), 11.6 min (major *(R,R)*–**L***);

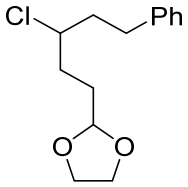
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.25 (m, 2H), 7.23 – 7.15 (m, 3H), 4.90 (t, *J* = 4.5 Hz, 1H), 4.02 – 3.95 (m, 2H), 3.89 – 3.83 (m, 2H), 3.71 – 3.60 (m, 1H), 2.85 – 2.76 (m, 1H), 2.72 – 2.62 (m, 1H), 1.86 – 1.52 (m, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 128.6, 128.5, 125.9, 104.6, 71.0, 65.1, 65.0, 39.3, 32.3, 31.6, 30.1;

FT-IR (ATR) 3439, 2927, 2880, 1602, 1495, 1453, 1408, 1138, 1028, 941, 747, 701 cm^{-1};

GC-MS (EI) m/z $[M-H]^+$ calcd for $C_{14}H_{19}O_3$: 235.1, found: 235.2;

$[\alpha]^{25}_D$ = – 9.1 (c = 1.39, $CHCl_3$); 95% ee from (*S,S*)–**L***.



2-(3-Chloro-5-phenylpentyl)-1,3-dioxolane.[36] *n*-Butyllithium (2.50 M in hexanes; 90.0 μL, 0.230 mmol, 1.50 equiv) was added dropwise to a solution of (3,5-bis(trifluoromethyl)phenyl)tributylstannane (133 mg, 0.230 mmol, 1.50 equiv) in THF (2 mL) at –78 °C. The mixture was stirred at –78 °C for 1 h, and then a solution of 2-(1-(1,3-dioxolan-2-yl)-5-phenylpentan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (51.9 mg, 0.150 mmol 1.00 equiv) in THF (1 mL) was added. The mixture was stirred at –78 °C for 30 min, and then it was warmed to –40 °C, and a solution of trichloroisocyanuric acid (52.3 mg, 0.230 mmol, 1.50 equiv) in MeCN (1 mL) was added. After 15 min at –40 °C, Na_2SO_3 (saturated aqueous solution; 10 mL) was added, and the reaction mixture was extracted with Et_2O (3 x 15 mL). The combined organic phases were dried over $MgSO_4$ and concentrated. The title compound was purified by column chromatography on silica gel (10→20% Et_2O in hexanes). Colorless oil.

(*S,S*)–**L***: 35.7 mg (0.140 mmol, 93%), + 95% ee; (*R,R*)–**L***: 35.1 mg (0.138 mmol, 92%), – 95% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD-H column (5% 2-PrOH in hexane, 1.0 mL/min) with t_r = 9.2 min (major (*S,S*)–**L***), 14.8 min (major *(R,R)*–**L***);

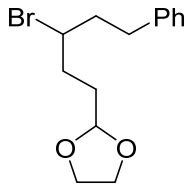
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.25 (m, 2H), 7.23 – 7.16 (m, 3H), 4.88 (t, *J* = 4.2 Hz, 1H), 4.00 – 3.80 (m, 5H), 2.93 – 2.83 (m, 1H), 2.80 – 2.70 (m, 1H), 2.07 – 1.99 (m, 2H), 1.99 – 1.73 (m, 4H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 128.7, 128.6, 126.2, 104.0, 65.10, 65.06, 62.9, 40.3, 32.79, 32.77, 30.9;

FT-IR (ATR) 3026, 2952, 2881, 1603, 1496, 1454, 1309, 1279, 1180, 1135, 1029, 943, 878, 752, 699 cm^{-1};

GC-MS (EI) m/z $[M-H]^+$ calcd for $C_{14}H_{18}ClO_2$: 253.1, found: 253.1;

$[\alpha]^{25}_D$ + 22.5 (c = 1.53, $CHCl_3$); 95% ee from (*S,S*)–**L***.



2-(3-Bromo-5-phenylpentyl)-1,3-dioxolane.[36] *n*-Butyllithium (2.50 M in hexanes; 90.0 μL, 0.230 mmol, 1.50 equiv) was added dropwise to a solution of 1-bromo-3,5-bis(trifluoromethyl)benzene (65.9 mg, 0.230 mmol, 1.50 equiv) in THF (2 mL) at –78 °C. The mixture was stirred at –78 °C for 1 h, and then a solution of 2-(1-(1,3-dioxolan-2-yl)-5-phenylpentan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (51.9 mg, 0.150 mmol 1.00 equiv) in THF (1 mL) was added. The mixture was stirred at –78 °C for 30 min. Next, *N*-bromosuccinimide (40.0 mg, 0.230 mmol, 1.50 equiv) was added as a solid[c] at –78 °C. The reaction mixture was stirred at –78 °C for 5 min, and then it was warmed to room temperature and stirred for 1 h. Na_2SO_3 (saturated aqueous solution; 10 mL) was added, and the reaction mixture was extracted with Et_2O (3 x 15 mL). The combined organic phases were dried over $MgSO_4$ and concentrated. The title compound was purified by column chromatography on silica gel (10→20% Et_2O in hexanes). Colorless oil.

(*S,S*)–**L***: 41.6 mg (0.139 mmol, 93%), + 95% ee; (*R,R*)–**L***: 42.0 mg (0.140 mmol, 94%), – 95% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD-H column (5% 2-PrOH in hexane, 1.0 mL/min) with t_r = 10.2 min (major (*S,S*)–**L***), 18.3 min (major *(R,R)*–**L***);

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 – 7.25 (m, 2H), 7.23 – 7.15 (m, 3H), 4.88 (t, *J* = 4.1 Hz, 1H), 4.07 – 3.90 (m, 3H), 3.89 – 3.79 (m, 2H), 2.96 – 2.85 (m, 1H), 2.82 – 2.70 (m, 1H), 2.21 – 2.05 (m, 2H), 2.03 – 1.89 (m, 3H), 1.87 – 1.70 (m, 1H);

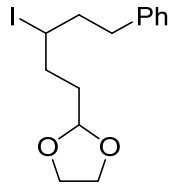
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1, 128.7, 128.6, 126.2, 103.9, 65.10, 65.07, 57.2, 40.9, 33.8, 33.4, 31.9;

FT-IR (ATR) 2954, 2881, 1603, 1496, 1454, 1309, 1279, 1180, 1134, 1028, 942, 878, 747, 698 cm^{-1};

GC-MS (EI) m/z $[M-H]^+$ calcd for $C_{14}H_{18}BrO_2$: 297.0, found: 297.1;

[c] In a preliminary experiment, inferior results were obtained when NBS was added as a solution in THF.

$[\alpha]^{25}_{D}$ + 22.4 (c = 1.70, $CHCl_3$); 95% ee from (*S,S*)–**L***.



2-(3-Iodo-5-phenylpentyl)-1,3-dioxolane.[36] *n*-Butyllithium (2.50 M in hexanes; 90.0 μL, 0.230 mmol, 1.50 equiv) was added dropwise to a solution of 1-bromo-3,5-bis(trifluoromethyl)benzene (65.9 mg, 0.230 mmol, 1.50 equiv) in THF (2 mL) at –78 °C. The mixture was stirred at –78 °C for 1 h, and then a solution of 2-(1-(1,3-dioxolan-2-yl)-5-phenylpentan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (51.9 mg, 0.150 mmol 1.00 equiv) in THF (1 mL) was added. The mixture was stirred at –78 °C for 30 min. Next, a solution of *N*-iodosuccinimide (50.6 mg, 0.230 mmol, 1.50 equiv) in THF (1 mL) was added dropwise at –78 °C. The reaction mixture was stirred at –78 °C for 5 min, and then it was warmed to room temperature and stirred for 1 h. Na_2SO_3 (saturated aqueous solution; 10 mL) was added, and the reaction mixture was extracted with Et_2O (3 x 15 mL). The combined organic phases were dried over $MgSO_4$ and concentrated. The title compound was purified by column chromatography on silica gel (10→20% Et_2O in hexanes). Yellow oil.

(*S,S*)–**L***: 44.8 mg (0.129 mmol, 86%), + 93% ee; (*R,R*)–**L***: 41.9 mg (0.121 mmol, 81%), – 94% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD-H column (5% 2-PrOH in hexane, 1.0 mL/min) with t_r = 10.5 min (major (*S,S*)–**L***), 21.1 min (major *(R,R)*–**L***);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.25 (m, 2H), 7.23 – 7.17 (m, 3H), 4.88 (t, *J* = 4.2 Hz, 1H), 4.12 – 4.03 (m, 1H), 4.00 – 3.90 (m, 2H), 3.89 – 3.78 (m, 2H), 2.94 – 2.84 (m, 1H), 2.78 – 2.67 (m, 1H), 2.24 – 2.13 (m, 1H), 2.05 – 1.83 (m, 4H), 1.82 – 1.72 (m, 1H);

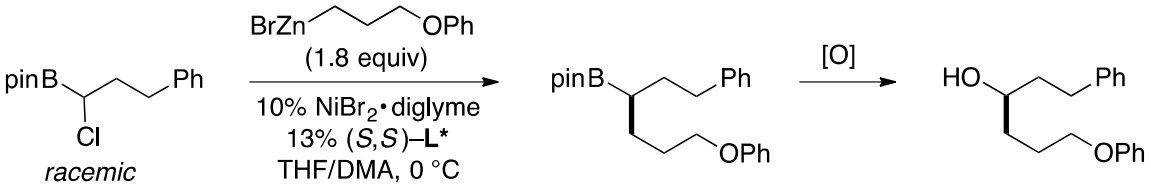
^{13}C NMR (100 MHz, $CDCl_3$) δ 140.9, 128.7, 128.6, 126.3, 103.8, 65.11, 65.07, 42.4, 38.4, 35.7, 34.9, 33.8;

FT-IR (ATR) 2950, 2880, 1495, 1453, 1408, 1309, 1279, 1135, 1028, 942, 878, 747, 698 cm^{-1};

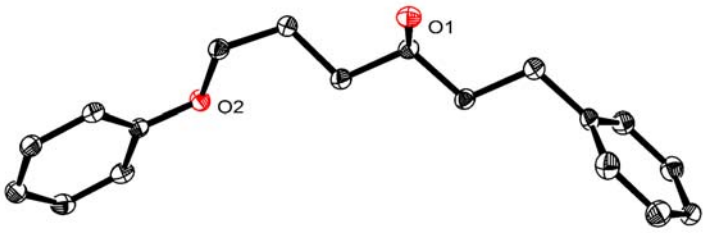
GC-MS (EI) m/z $[M-H]^+$ calcd for $C_{14}H_{18}IO_2$: 345.0, found: 345.1;

$[\alpha]^{25}_{D}$ = + 30.1 (c = 1.73, $CHCl_3$); 93% ee from (*S,S*)–**L***.

VI. Assignment of Absolute Configuration



(*S*)-6-Phenoxy-1-phenylhexan-3-ol. 4,4,5,5-Tetramethyl-2-(6-phenoxy-1-phenylhexan-3-yl)-1,3,2-dioxaborolane was prepared according to **GP-1**, using (*S*,*S*)–**L***. The boronate ester was stereospecifically oxidized as described in **GP-3**, and the alcohol was crystallized from hexane at 5 °C.



A suitable crystal of $C_{18}H_{22}O_2$ was selected and mounted in a nylon loop in immersion oil. All measurements were made on a Bruker Photon diffractometer with filtered Cu-Kα radiation at a temperature of 100 K. Using Olex2,[37] the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL refinement package[38] using Least Squares minimization. The absolute stereochemistry was determined on the basis of the absolute structure parameter.

Table S–3. Crystal data and structure refinement for crystal_01.

Identification code	crystal_01	
Empirical formula	$C_{18}H_{22}O_2$	
Formula weight	270.35	
Temperature	100 K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 11.2951(3) Å	α = 90°.
	b = 4.99060(10) Å	β = 101.4324(10) °.
	c = 13.4518(4) Å	γ = 90 °.
Volume	743.22(3) $Å^3$	
Z	2	
Density (calculated)	1.208 Mg/m^3	
Absorption coefficient	0.603 mm^{-1}	
F(000)	292	
Crystal size	0.19 x 0.11 x 0.05 mm^3	
Theta range for data collection	3.352 to 70.021°.	
Index ranges	-13<=h<=13, -6<=k<=5, -16<=l<=16	
Reflections collected	25775	
Independent reflections	2779 [R(int) = 0.0292]	
Completeness to theta = 67.679°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7533 and 0.6201	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2779 / 1 / 182	
Goodness-of-fit on F^2	1.107	
Final R indices [I>2sigma(I)]	R1 = 0.0279, wR2 = 0.0704	
R indices (all data)	R1 = 0.0284, wR2 = 0.0711	
Absolute structure parameter	0.03(5)	
Largest diff. peak and hole	0.191 and -0.226 $e/Å^{-3}$	

Table S–4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for crystal_01. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	5249(1)	7907(2)	9646(1)	19(1)
O(2)	3997(1)	3898(2)	6172(1)	18(1)
C(1)	8910(1)	6266(3)	11218(1)	19(1)
C(2)	10078(2)	6971(4)	11137(1)	22(1)
C(3)	11070(2)	5666(4)	11711(1)	24(1)
C(4)	10912(2)	3631(4)	12372(1)	24(1)
C(5)	9751(2)	2909(4)	12456(1)	27(1)
C(6)	8763(2)	4221(4)	11888(1)	24(1)
C(7)	7826(1)	7652(3)	10589(1)	22(1)
C(8)	7245(1)	6028(3)	9652(1)	18(1)
C(9)	6130(1)	7389(3)	9030(1)	16(1)
C(10)	5551(1)	5776(3)	8098(1)	19(1)
C(11)	4553(1)	7362(3)	7404(1)	20(1)
C(12)	3530(1)	5652(3)	6846(1)	18(1)
C(13)	3189(1)	2192(3)	5596(1)	16(1)
C(14)	3651(2)	596(3)	4909(1)	19(1)
C(15)	2912(2)	-1245(4)	4316(1)	22(1)
C(16)	1705(1)	-1512(4)	4390(1)	22(1)
C(17)	1251(2)	91(3)	5066(1)	21(1)
C(18)	1980(1)	1949(3)	5673(1)	18(1)

Table S–5. Bond lengths [Å] and angles [°] for crystal_01.

O(1)-C(9)	1.4385(18)
O(2)-C(12)	1.4344(19)
O(2)-C(13)	1.3710(18)
C(1)-C(2)	1.391(2)
C(1)-C(6)	1.393(2)
C(1)-C(7)	1.511(2)
C(2)-C(3)	1.390(2)
C(3)-C(4)	1.384(3)
C(4)-C(5)	1.387(2)
C(5)-C(6)	1.385(2)
C(7)-C(8)	1.532(2)
C(8)-C(9)	1.527(2)
C(9)-C(10)	1.524(2)
C(10)-C(11)	1.533(2)
C(11)-C(12)	1.511(2)
C(13)-C(14)	1.396(2)
C(13)-C(18)	1.394(2)
C(14)-C(15)	1.383(2)
C(15)-C(16)	1.393(2)
C(16)-C(17)	1.384(2)
C(17)-C(18)	1.392(2)
C(13)-O(2)-C(12)	116.70(11)
C(2)-C(1)-C(6)	118.21(15)
C(2)-C(1)-C(7)	121.07(15)
C(6)-C(1)-C(7)	120.71(14)
C(3)-C(2)-C(1)	120.69(16)
C(4)-C(3)-C(2)	120.60(15)
C(3)-C(4)-C(5)	119.14(15)
C(6)-C(5)-C(4)	120.26(17)
C(5)-C(6)-C(1)	121.10(16)
C(1)-C(7)-C(8)	112.69(14)
C(9)-C(8)-C(7)	112.79(13)
O(1)-C(9)-C(8)	110.77(12)
O(1)-C(9)-C(10)	109.64(12)
C(10)-C(9)-C(8)	112.85(13)

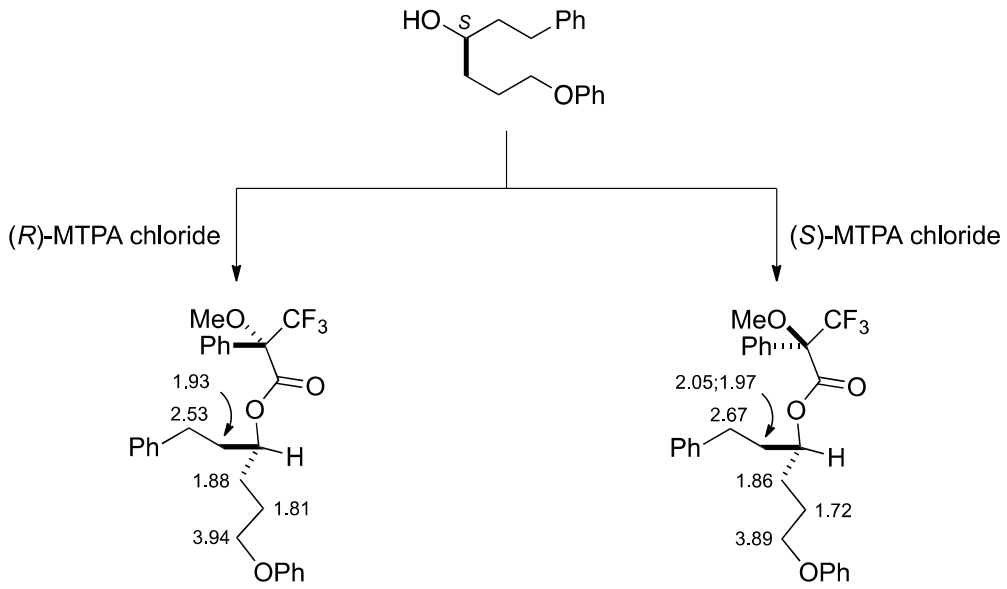
C(9)-C(10)-C(11) 111.83(13)
C(12)-C(11)-C(10)114.11(13)
O(2)-C(12)-C(11) 108.54(12)
O(2)-C(13)-C(14) 115.70(13)
O(2)-C(13)-C(18) 124.33(13)
C(18)-C(13)-C(14)119.96(14)
C(15)-C(14)-C(13)119.90(14)
C(14)-C(15)-C(16)120.63(15)
C(17)-C(16)-C(15)119.15(15)
C(16)-C(17)-C(18)121.11(15)
C(17)-C(18)-C(13)119.25(14)

Table S–6. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for crystal_01. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

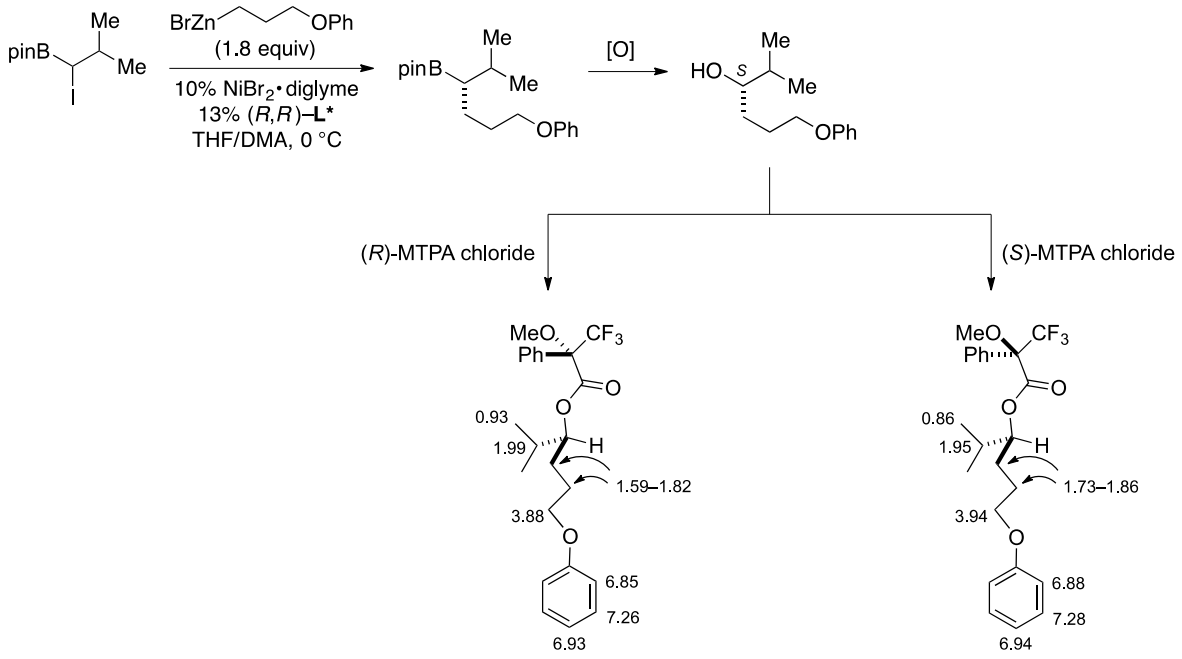
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	18(1)	18(1)	22(1)	0(1)	8(1)	1(1)
O(2)	15(1)	20(1)	20(1)	-3(1)	5(1)	-1(1)
C(1)	20(1)	19(1)	15(1)	-4(1)	1(1)	1(1)
C(2)	23(1)	21(1)	21(1)	1(1)	4(1)	-1(1)
C(3)	19(1)	28(1)	25(1)	-2(1)	4(1)	1(1)
C(4)	26(1)	22(1)	20(1)	-2(1)	-2(1)	6(1)
C(5)	34(1)	25(1)	22(1)	5(1)	3(1)	-2(1)
C(6)	23(1)	27(1)	23(1)	1(1)	5(1)	-5(1)
C(7)	20(1)	21(1)	22(1)	-2(1)	1(1)	2(1)
C(8)	16(1)	19(1)	18(1)	0(1)	3(1)	2(1)
C(9)	15(1)	17(1)	17(1)	0(1)	4(1)	1(1)
C(10)	19(1)	19(1)	19(1)	-1(1)	2(1)	3(1)
C(11)	21(1)	18(1)	19(1)	-1(1)	0(1)	2(1)
C(12)	18(1)	19(1)	18(1)	-1(1)	3(1)	2(1)
C(13)	18(1)	15(1)	15(1)	3(1)	1(1)	0(1)
C(14)	21(1)	20(1)	18(1)	4(1)	7(1)	3(1)
C(15)	30(1)	19(1)	16(1)	0(1)	6(1)	4(1)
C(16)	27(1)	18(1)	18(1)	2(1)	-2(1)	-1(1)
C(17)	17(1)	18(1)	24(1)	3(1)	1(1)	0(1)
C(18)	18(1)	17(1)	20(1)	2(1)	3(1)	3(1)

Table S–7. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for crystal_01.

	x	y	z	U(eq)
H(1)	4999	6447	9838	28
H(2)	10200	8358	10684	26
H(3)	11862	6176	11650	29
H(4)	11592	2740	12763	28
H(5)	9632	1509	12905	33
H(6)	7972	3718	11957	29
H(7A)	8079	9419	10368	26
H(7B)	7219	7967	11014	26
H(8A)	7847	5756	9217	21
H(8B)	7014	4242	9872	21
H(9)	6388	9153	8792	19
H(10A)	5205	4106	8317	23
H(10B)	6179	5271	7713	23
H(11A)	4220	8698	7818	24
H(11B)	4915	8353	6900	24
H(12A)	3176	4590	7336	22
H(12B)	2890	6806	6456	22
H(14)	4471	774	4850	23
H(15)	3231	-2338	3854	26
H(16)	1200	-2778	3981	26
H(17)	427	-80	5117	25
H(18)	1659	3040	6134	22



(*S*)-6-Phenoxy-1-phenylhexan-3-ol was reacted with Mosher's acid chloride (*R* and *S*) in two separate experiments.[39] Comparison of both ^{1}H- and HSQC-NMR spectra confirmed the (*S*) configuration of the alcohol.

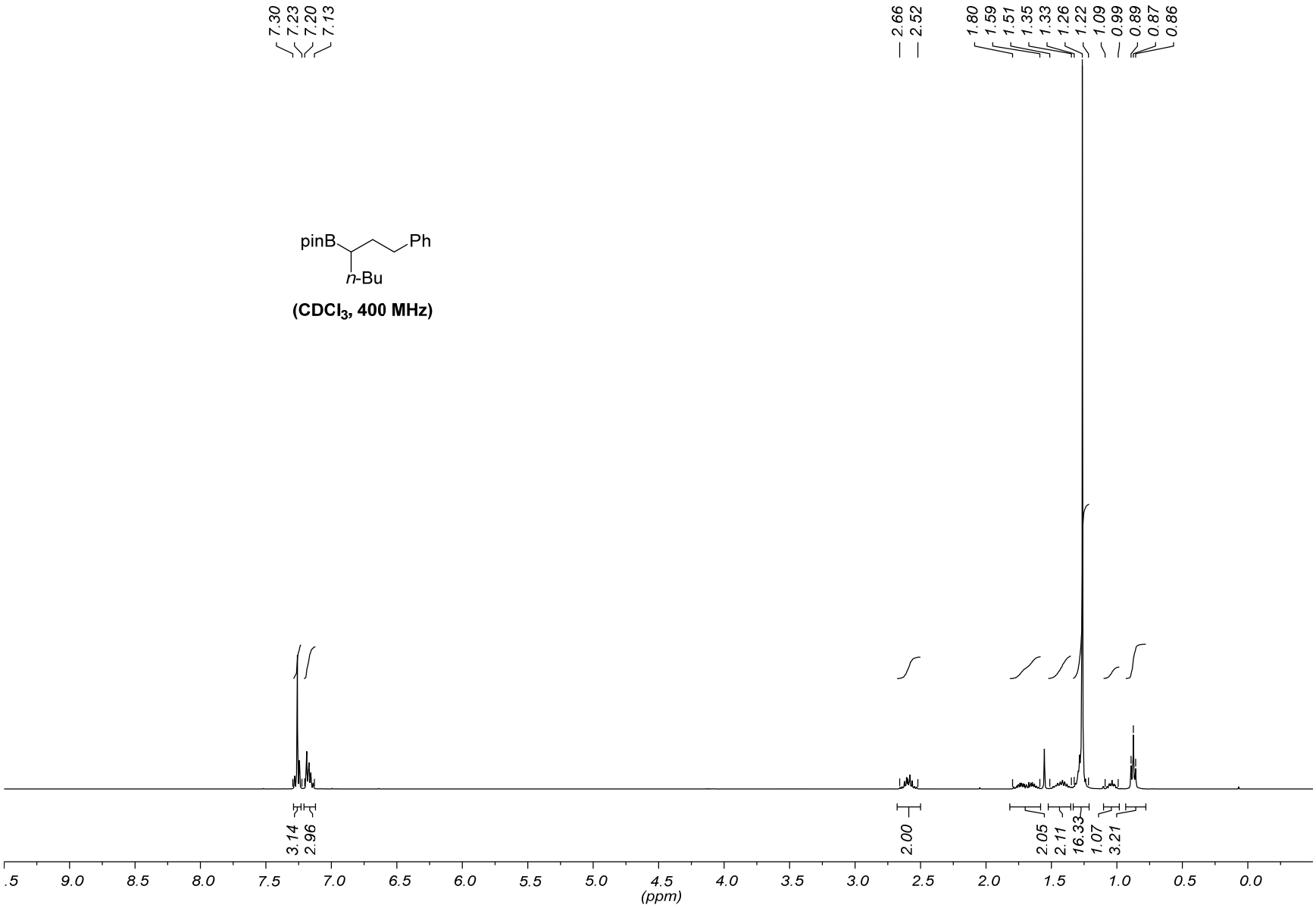


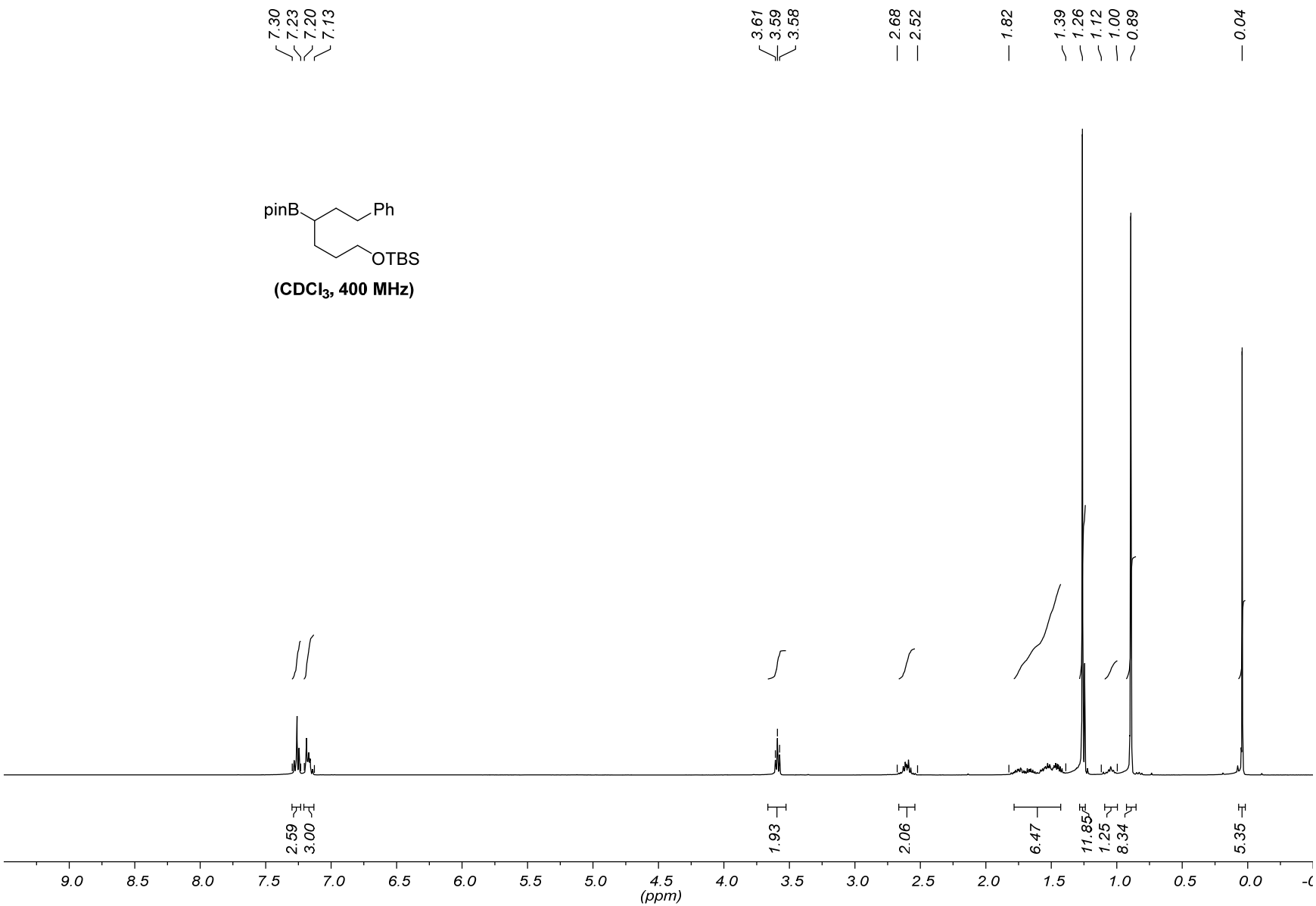
(*S*)-2-Methyl-6-phenoxyhexan-3-ol. 4,4,5,5-Tetramethyl-2-(2-methyl-6-phenoxyhexan-3-yl)-1,3,2-dioxaborolane was prepared according to **GP-1**, using (*R,R*)–**L***. The boronate ester was stereospecifically oxidized as described in **GP-3**, and the alcohol was reacted with Mosher's acid chloride (*R* and *S*) in two separate experiments. Comparison of the ^{1}H NMR spectra confirmed the (*S*) configuration of the alcohol.

VII. References

26. S. E. Denmark, X. Su, Y. Nishigaichi, D. M. Coe, K.-T. Wong, S. B. D. Winter, J. Y. Choi, *J. Org. Chem.* **64**, 1958–1967 (1999).
27. C. J. Cordier, R. J. Lundgren, G. C. Fu, *J. Am. Chem. Soc.* **135**, 10946–10949 (2013).
28. S. Lou, G. C. Fu, *Org. Synth.* **87**, 330–338 (2010).
29. J. T. Binder, C. J. Cordier, G. C. Fu, *J. Am. Chem. Soc.* **134**, 17003–17006 (2012).
30. A. Bonet, M. Odachowski, D. Leonori, S. Essafi, V. K. Aggarwal, *Nat. Chem.* **6**, 584–589 (2014).
31. Y. Xi, J. F. Hartwig, *J. Am. Chem. Soc*. **138**, 6703–6706 (2016).
32. D. S. Matteson, D. Majumdar, *J. Am. Chem. Soc.* **102**, 7588–7590 (1980).
33. Y. Wang, A. Noble, E. L. Myers, V. K. Aggarwal, *Angew. Chem. Int. Ed.* **55**, 4270–4274 (2016).
34. S. N. Mlynarski, A. S. Karns, J. P. Morken, *J. Am. Chem. Soc.* **134**, 16449–16451 (2012).
35. G. W. Kabalka, T. M. Shoup, N. M. Goudgaon, *J. Org. Chem.* **54**, 5930-5933 (1989).
36. R. Larouche-Gauthier, T. G. Elford, V. K. Aggarwal, *J. Am. Chem. Soc*. **133**, 16794–16797 (2011).
37. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* **42**, 339–341 (2009).
38. G. M. Sheldrick, *Acta Cryst. A* **64**, 112–122 (2008).
39. T. R. Hoye, C. S. Jeffrey, F. Shao, *Nat. Protoc.* **2**, 2451–2458 (2007).

VIII. ^{1}H-NMR Spectra

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7.23
7.20
7.13
3.61
3.59
3.58
2.68
2.52
1.82
1.39
1.26
1.12
1.00
0.89
0.04
pinB
Ph
OTBS
(CDCl3, 400 MHz)
2.59
3.00
1.93
2.06
6.47
11.85
1.25
8.34
5.35
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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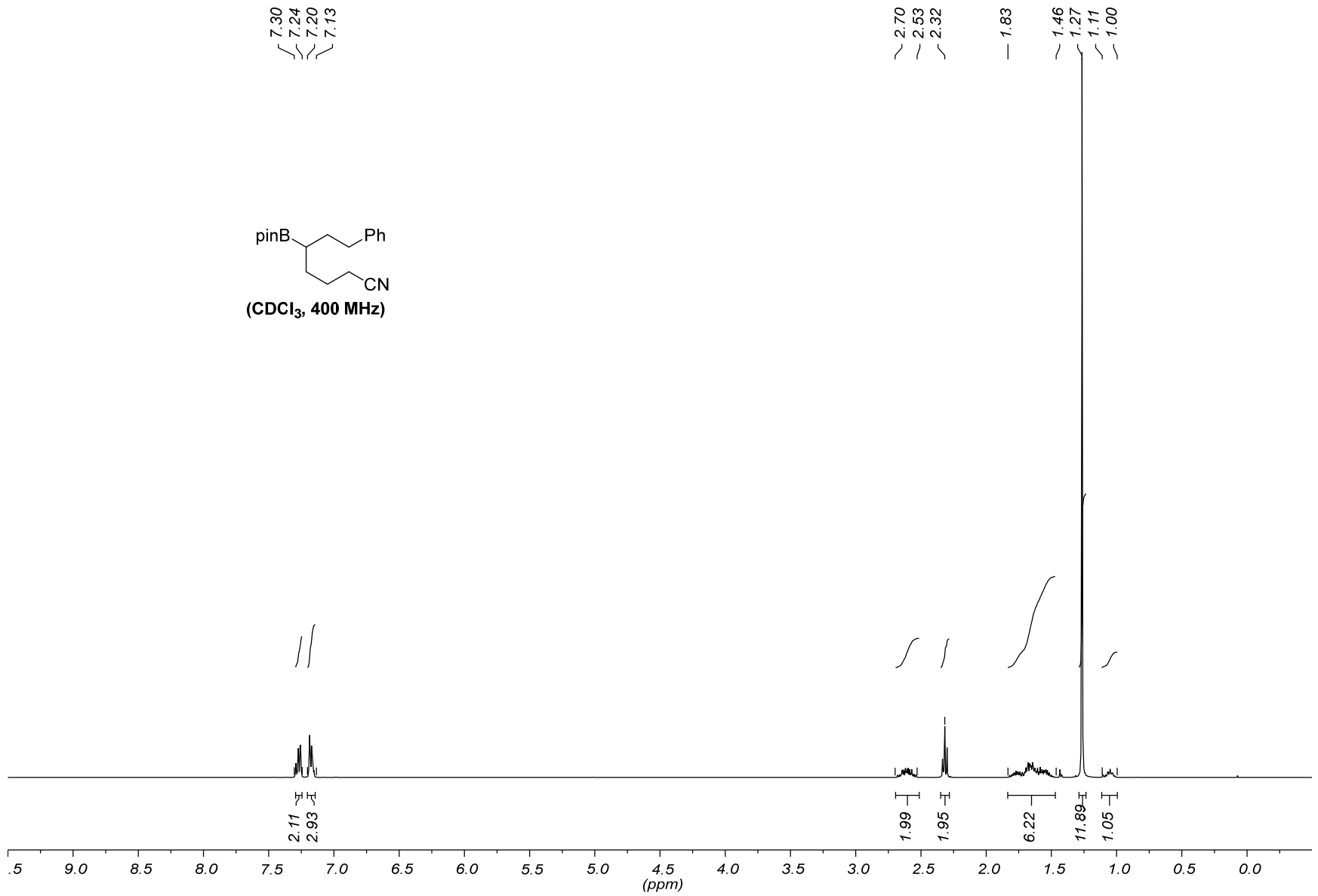
(ppm)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Ph
CN
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1.99
1.95
6.22
11.89
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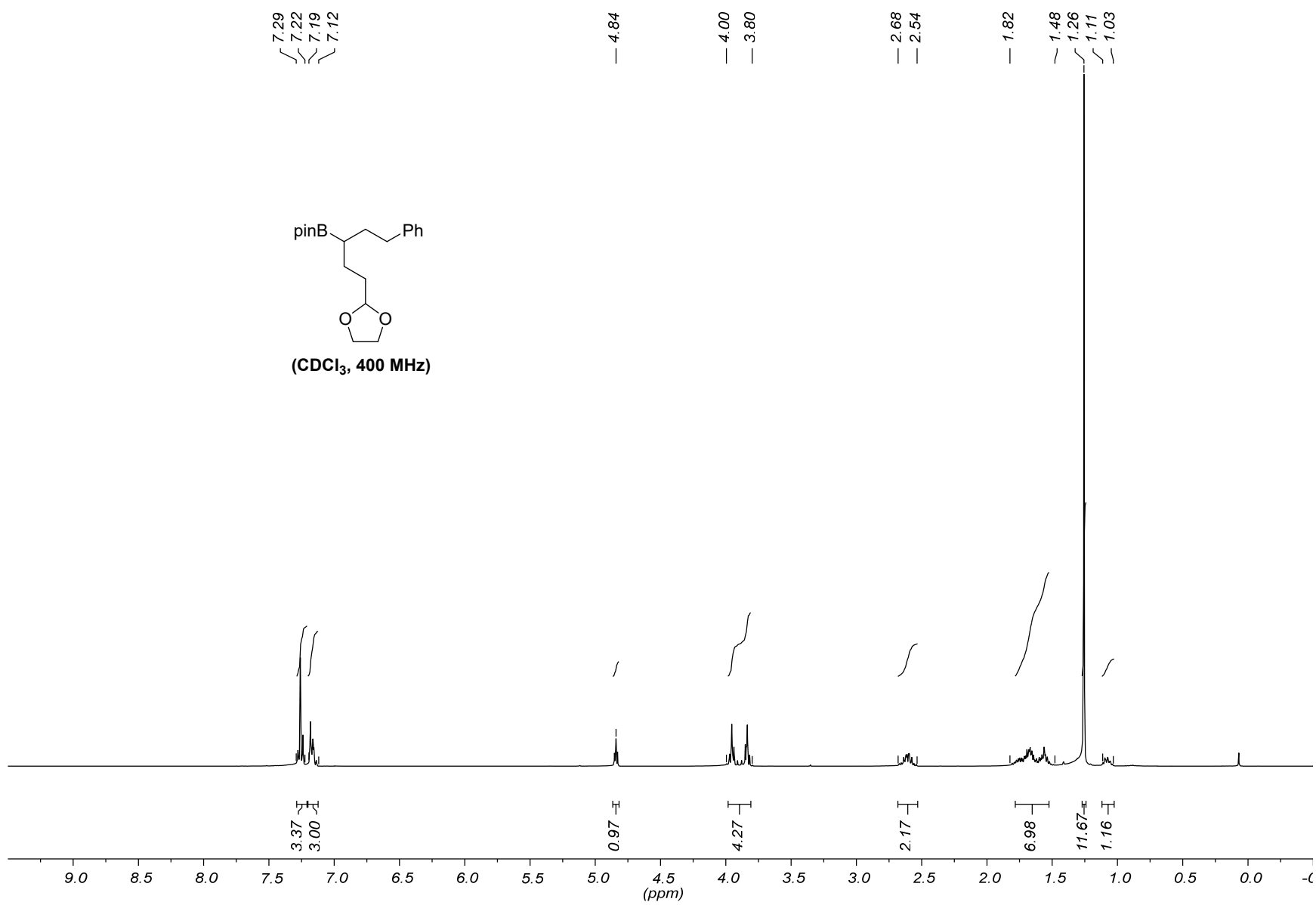
(ppm)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1.26
1.11
1.03
pinB
Ph
O
O
(CDCl3, 400 MHz)
3.37
3.00
0.97
4.27
2.17
6.98
11.67
1.16
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
3.5
3.0
2.5
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1.5
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0.5
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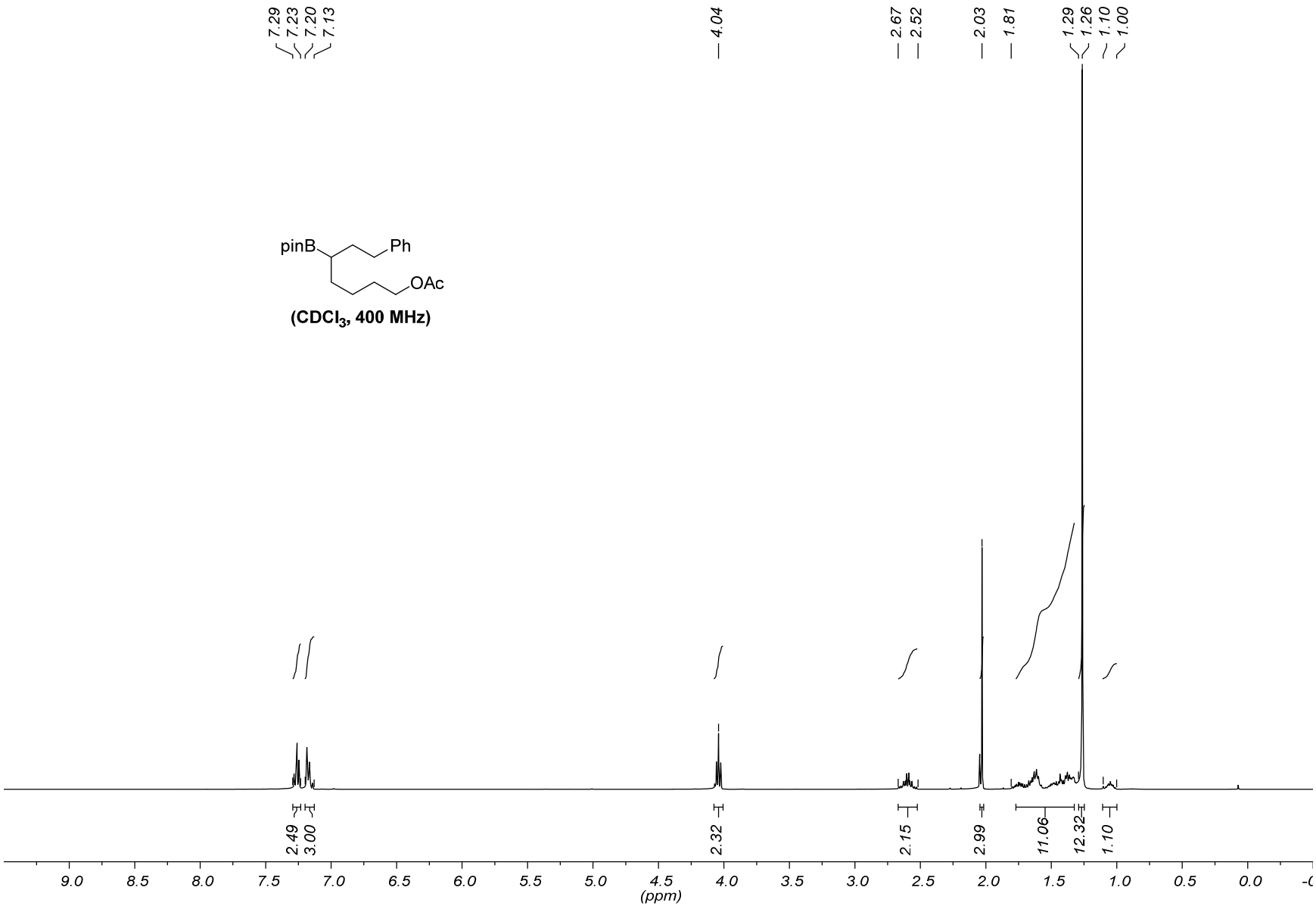
(ppm)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Ph
OAc
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3.00
2.32
2.15
2.99
11.06
12.32
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8.0
7.5
7.0
6.5
6.0
5.5
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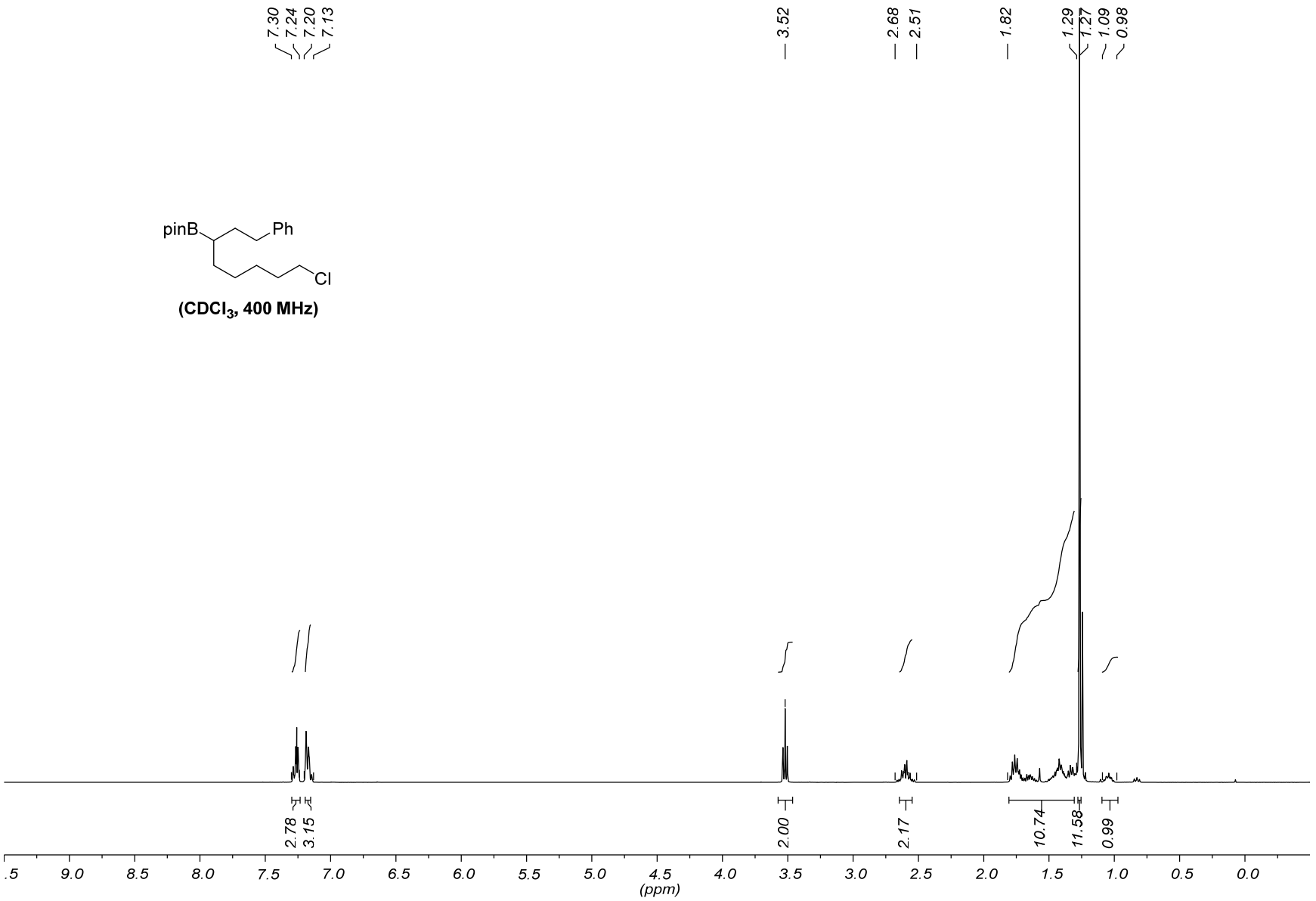
(ppm)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Ph
Cl
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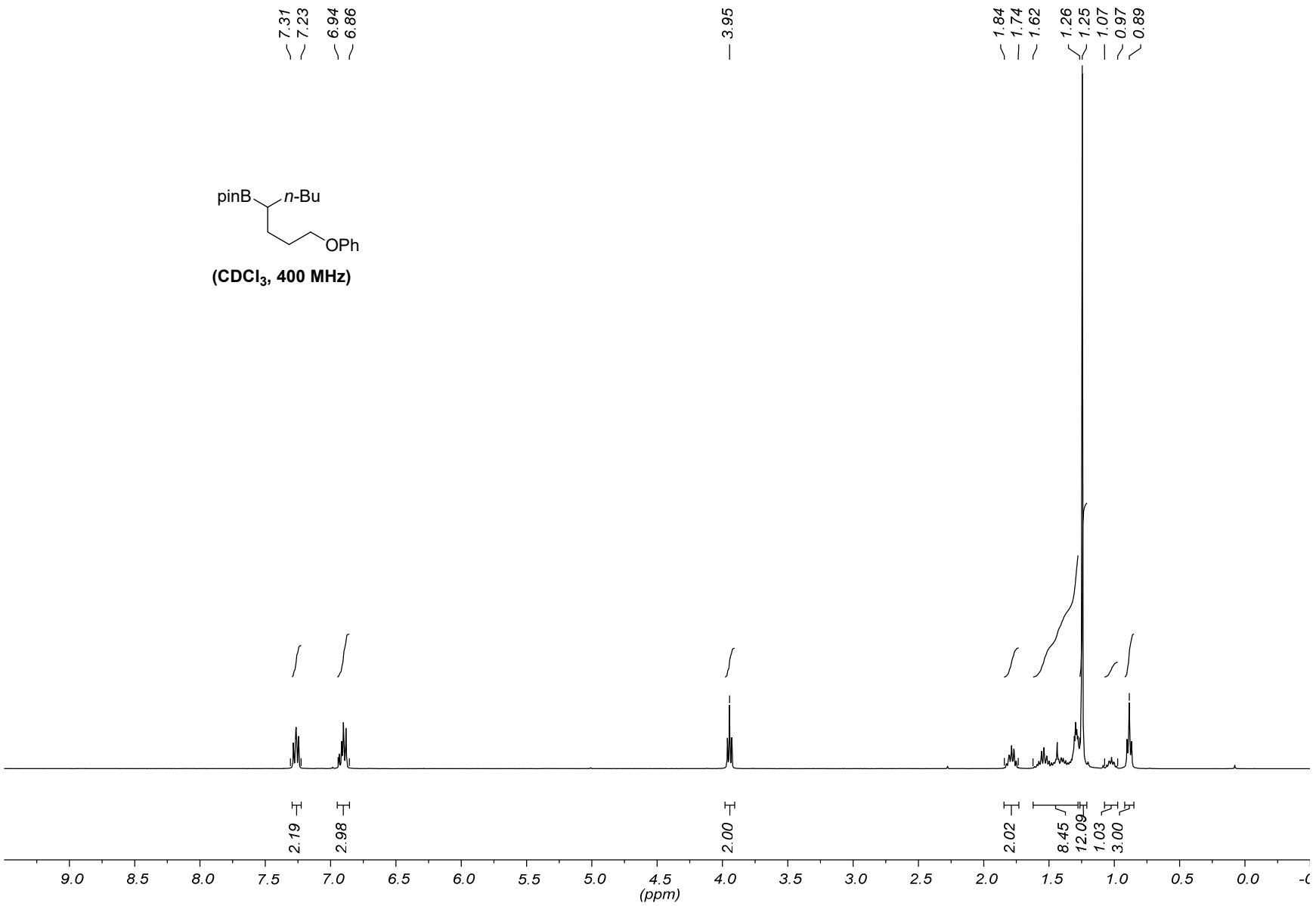
0.99
(ppm)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1.25
1.07
0.97
0.89
pinB
n-Bu
OPh
(CDCl3, 400 MHz)
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2.98
2.00
2.02
8.45
12.09
1.03
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
4.0
3.5
3.0
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1.5
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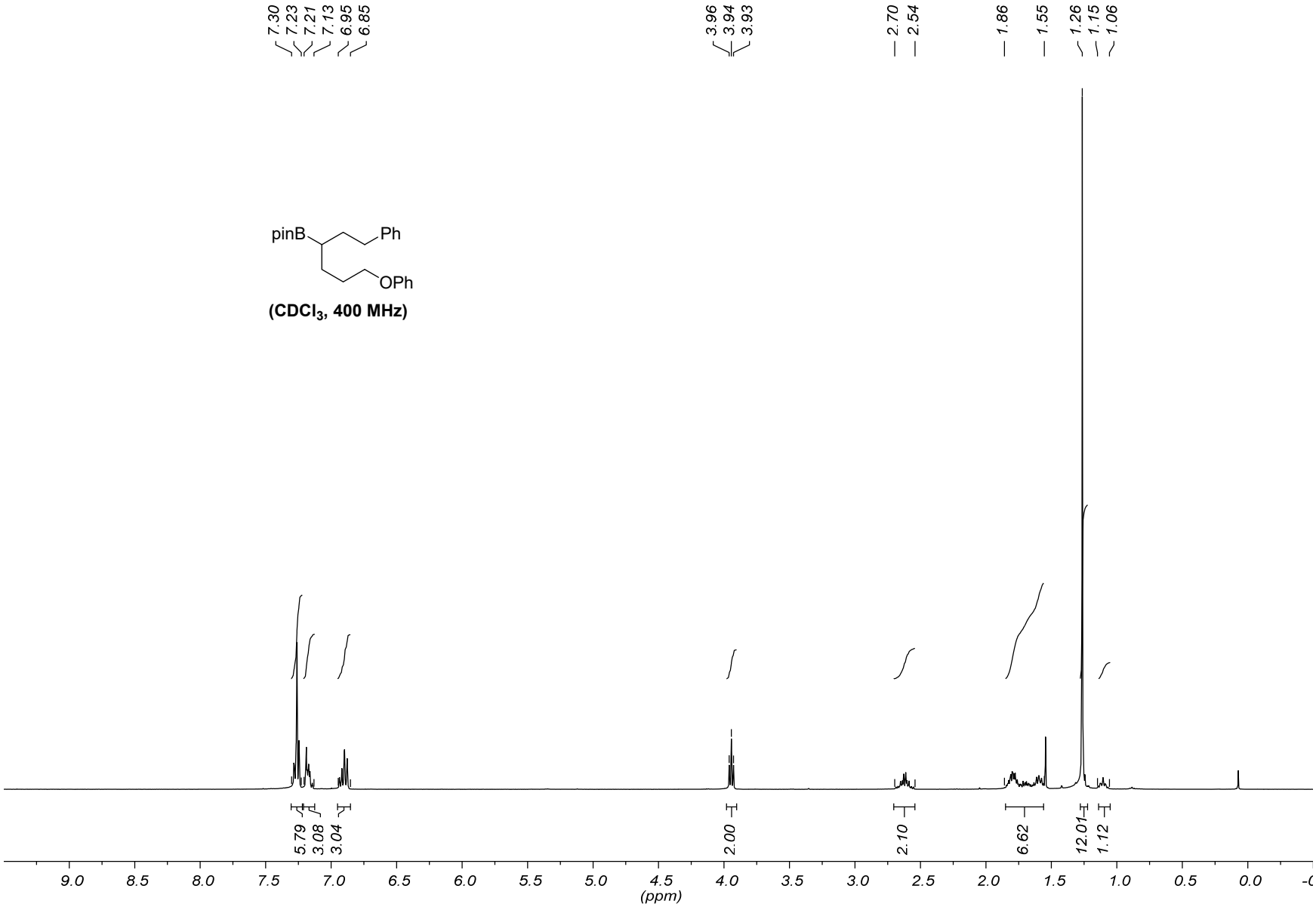
(ppm)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2.54
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1.55
1.26
1.15
1.06
pinB
Ph
OPh
(CDCl3, 400 MHz)
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3.04
2.00
2.10
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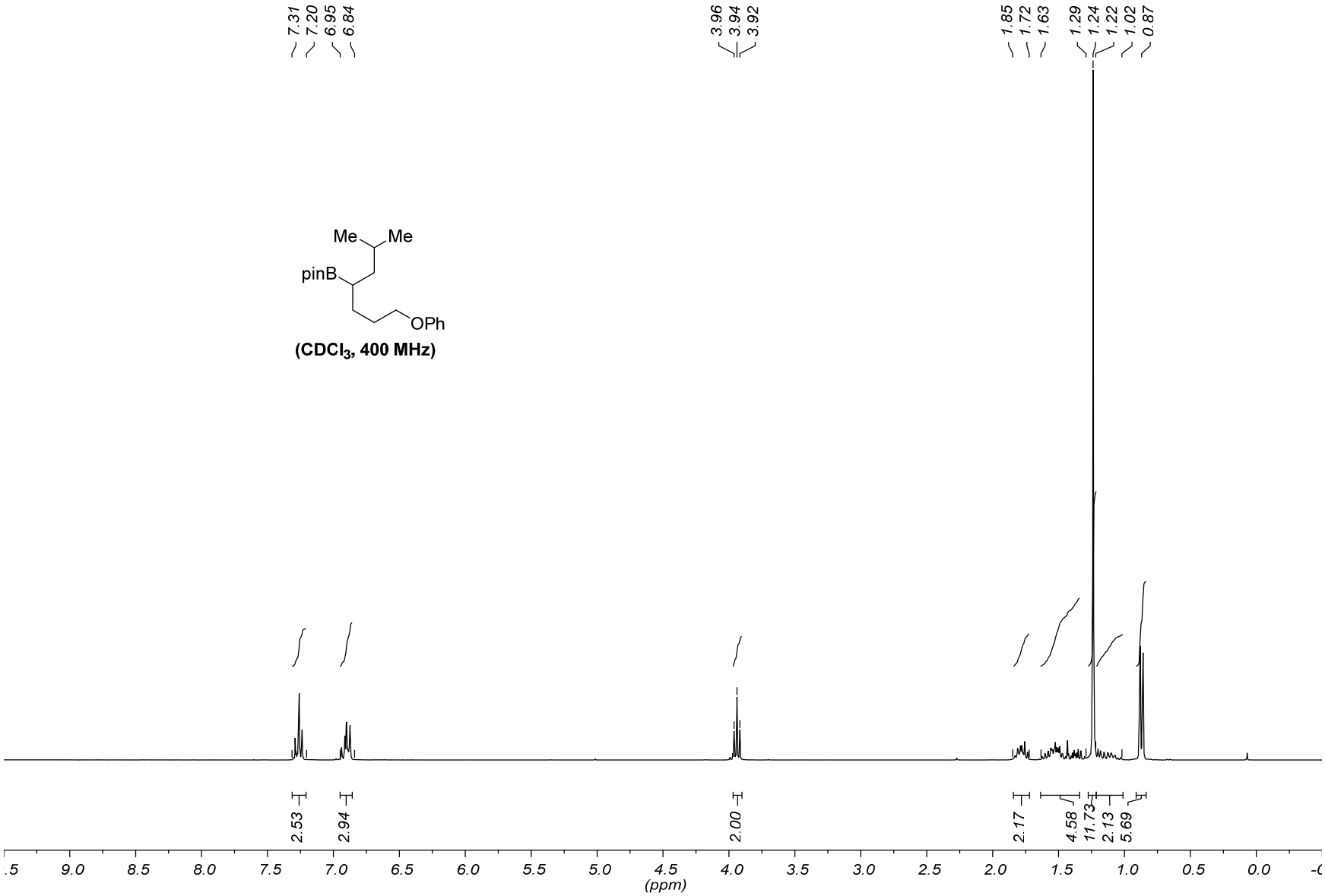
(ppm)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1.02
0.87
Me
Me
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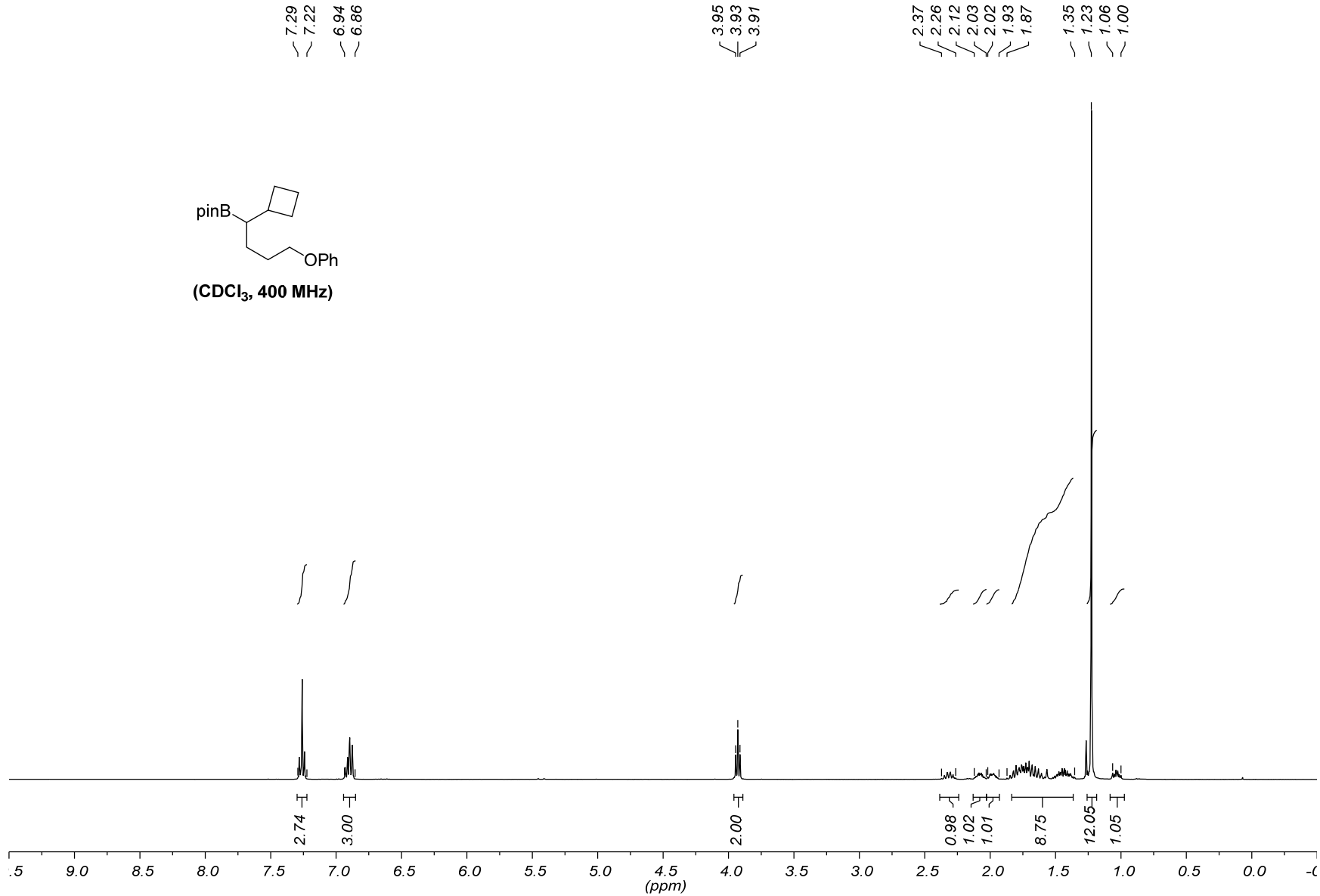
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1.06
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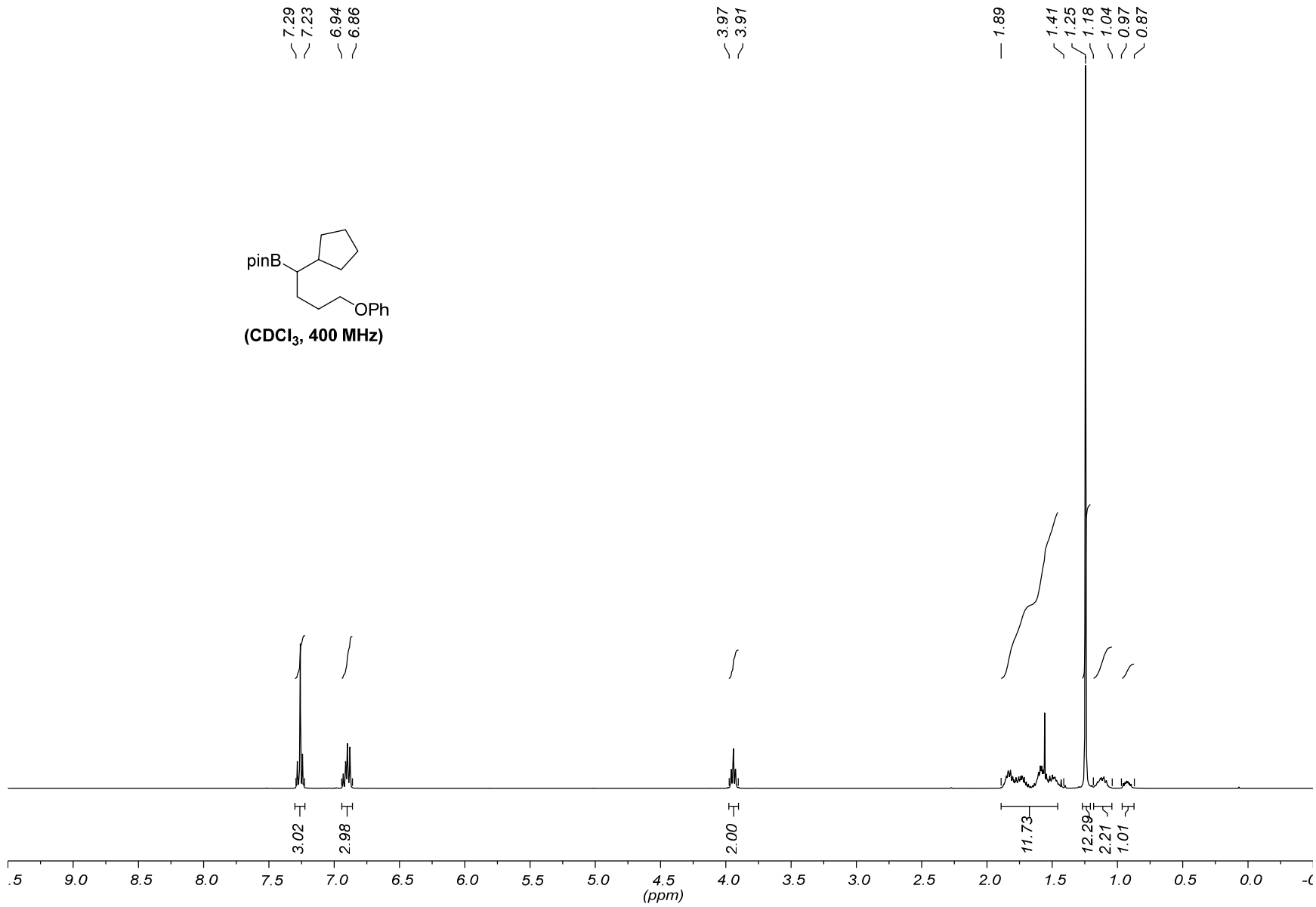
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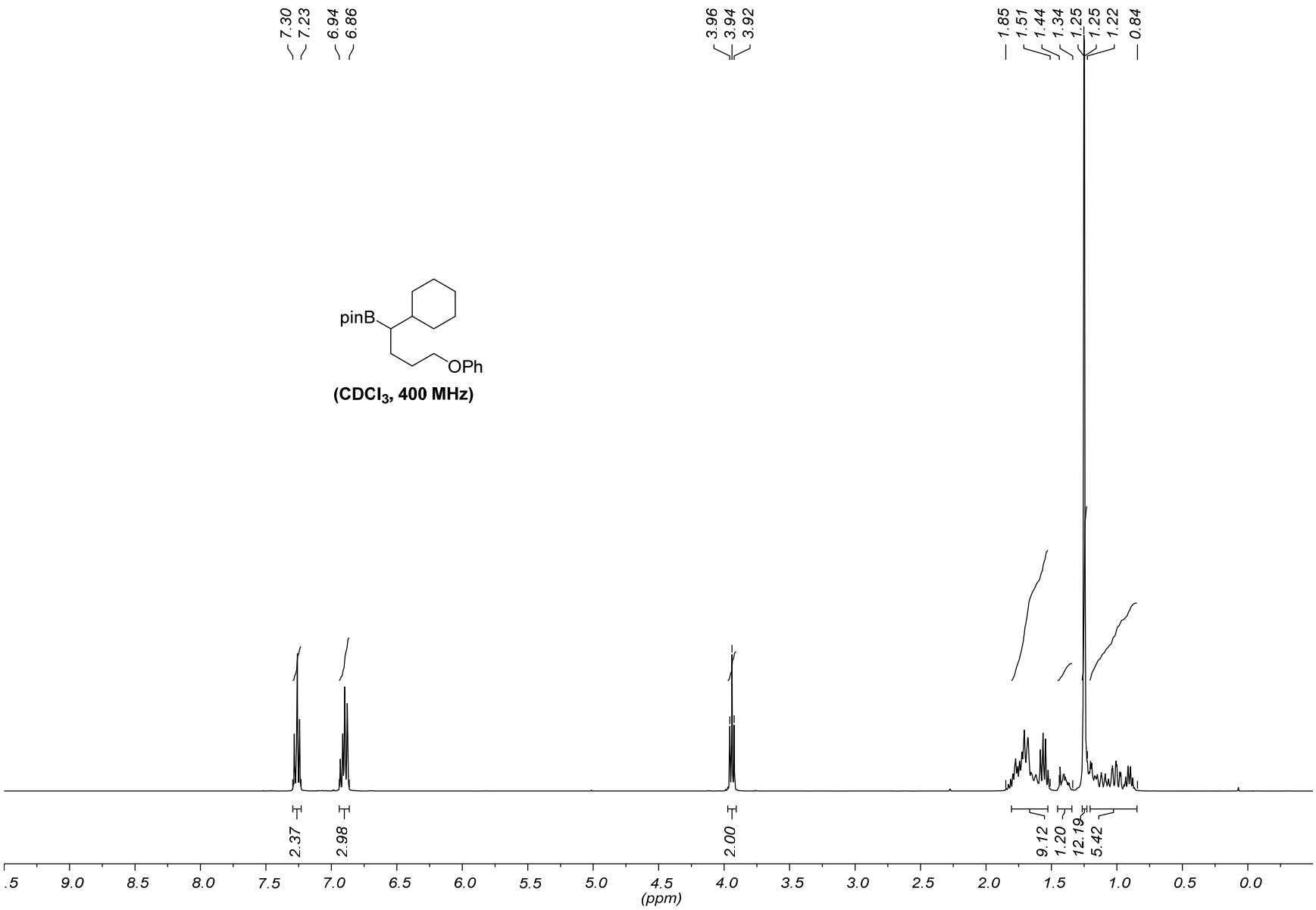
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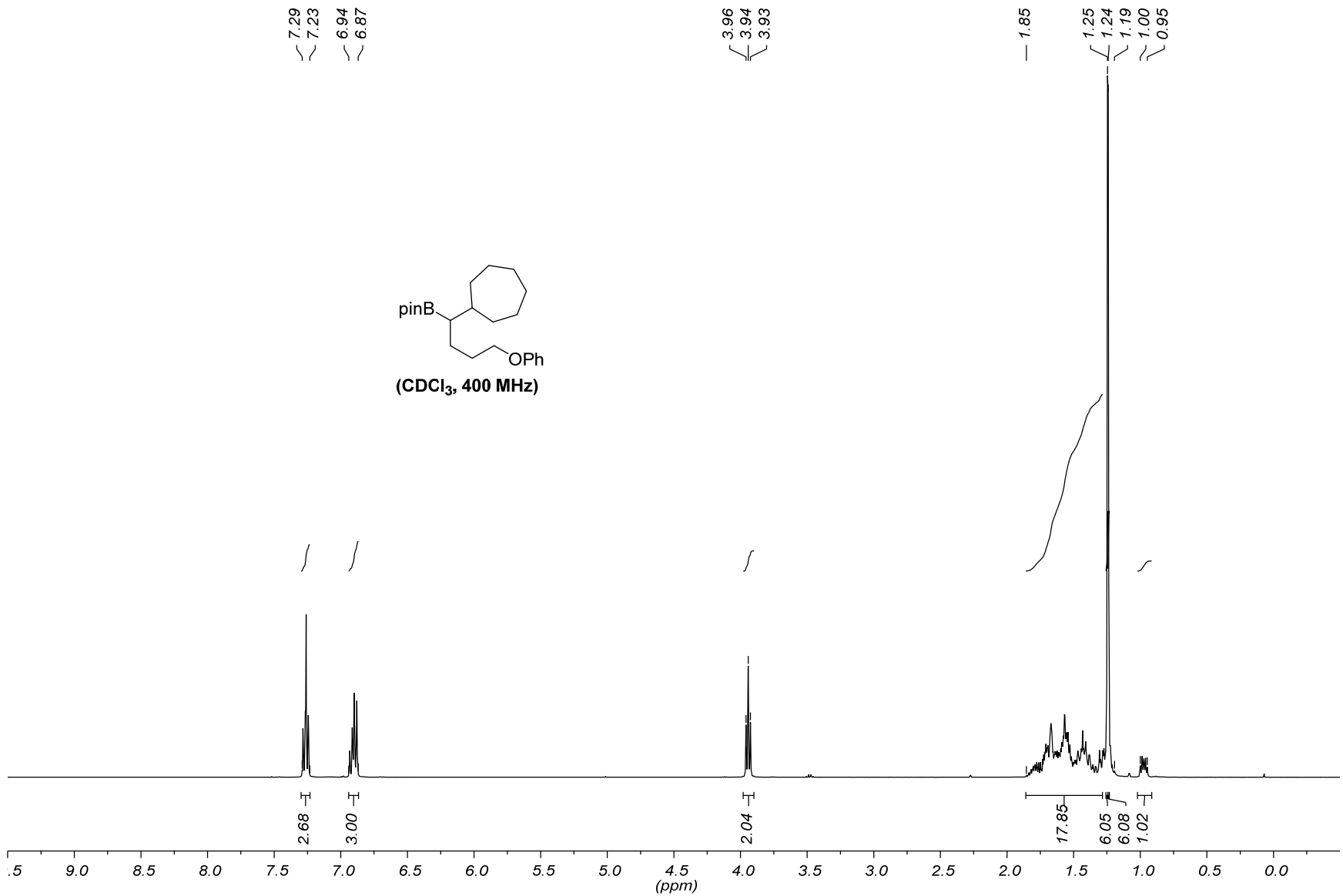
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(CDCl3, 400 MHz)
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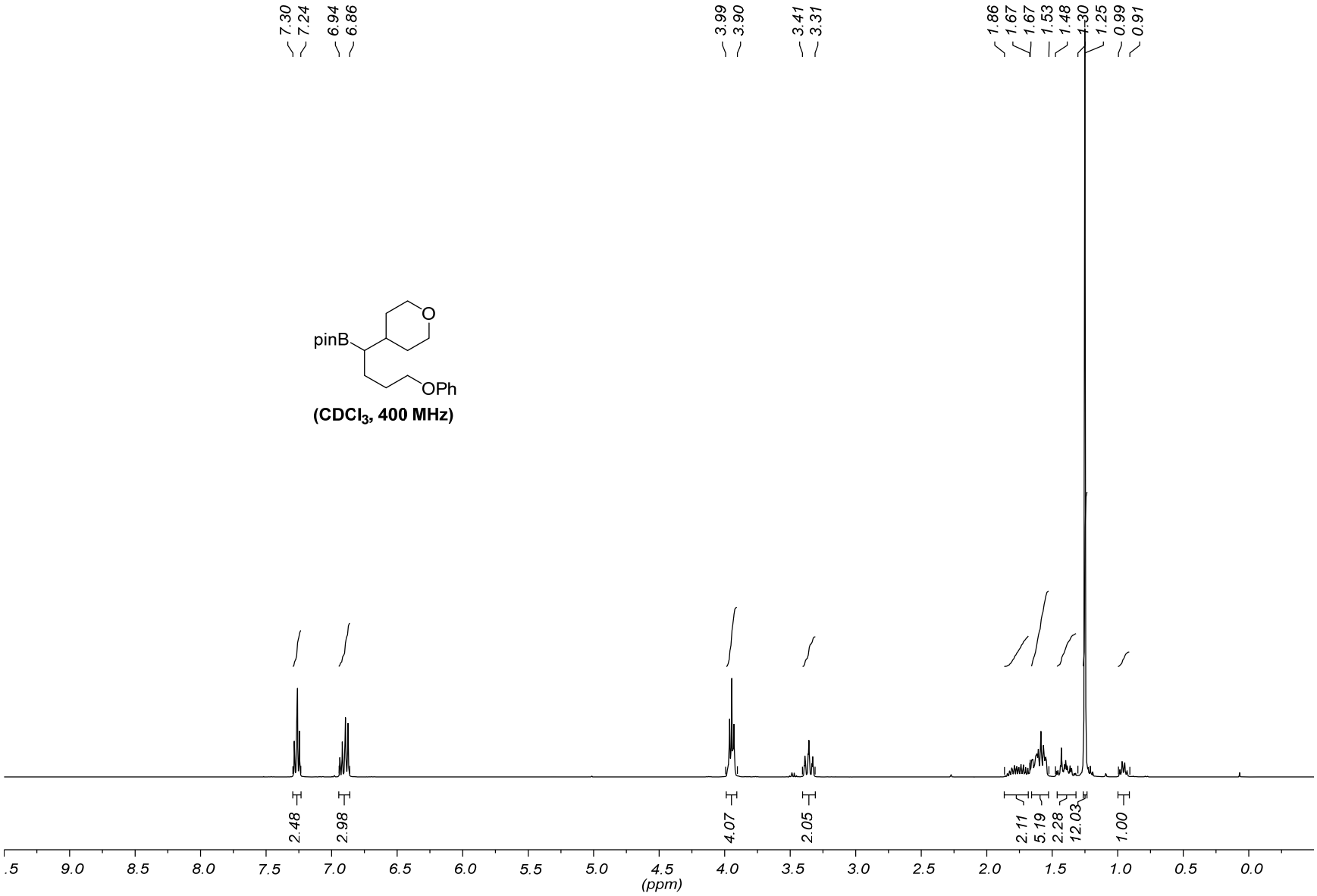
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1.30
1.25
0.99
0.91
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O
OPh
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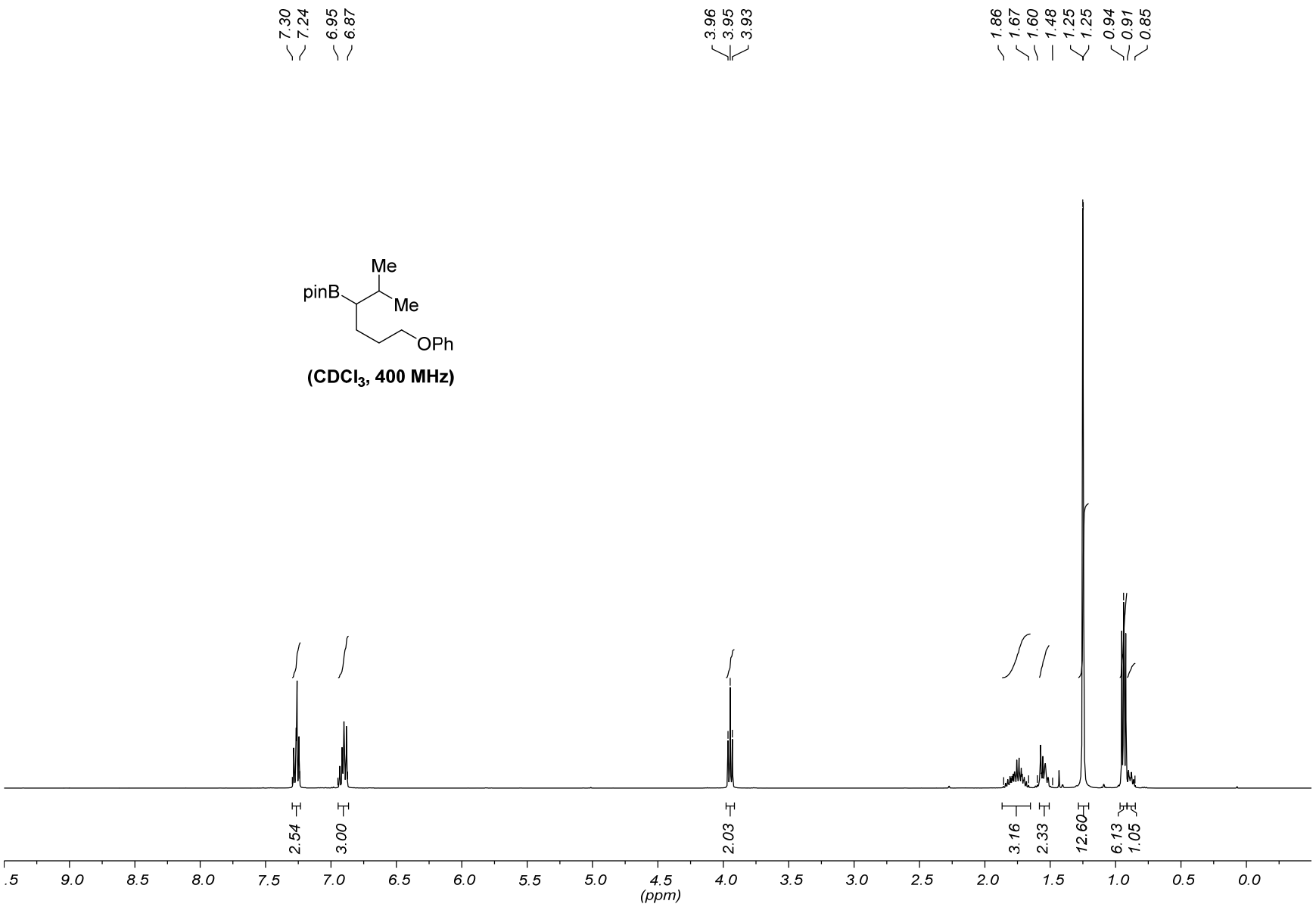
(ppm)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6.87
3.96
3.95
3.93
1.86
1.67
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1.48
1.25
1.25
0.94
0.91
0.85
Me
pinB
Me
OPh
(CDCl3, 400 MHz)
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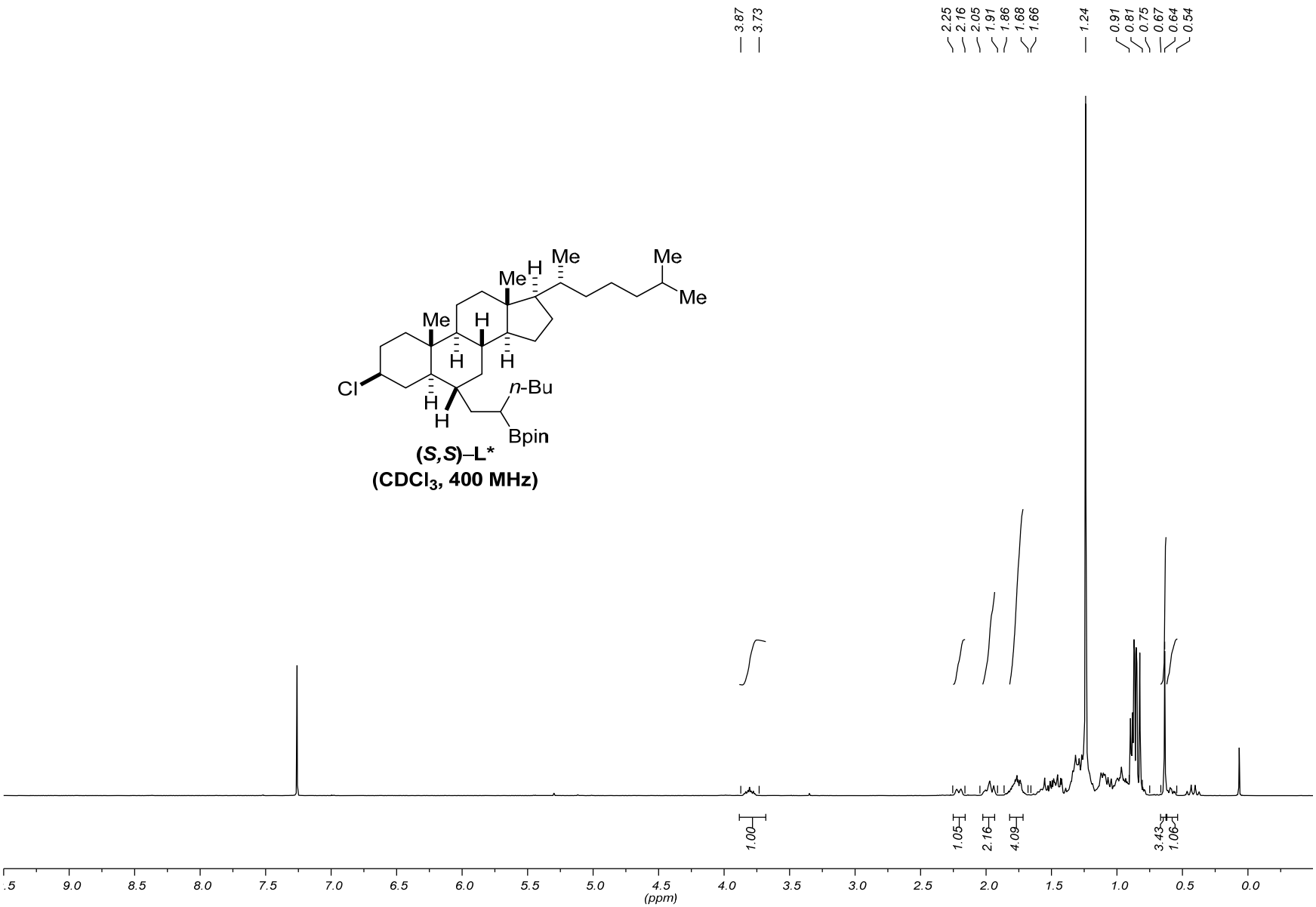
2.33
12.60
6.13
1.05
(ppm)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0.75
0.67
0.64
0.54
Me
H
Me
Me
Me
Me
H
H
H
Cl
H
H
n-Bu
Bpin
(S,S)–L*
(CDCl3, 400 MHz)
1.00
1.05
2.16
4.09
3.43
1.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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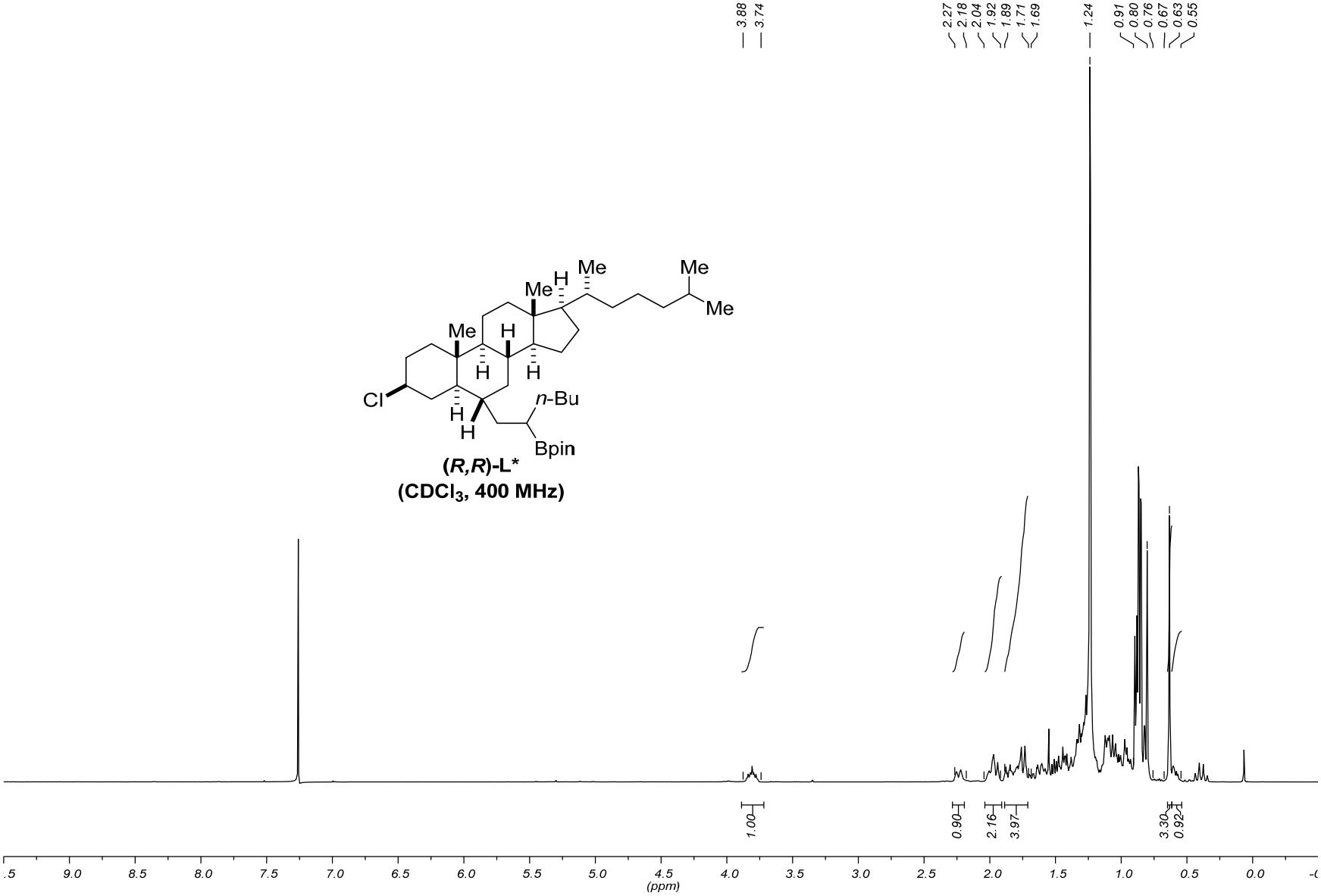
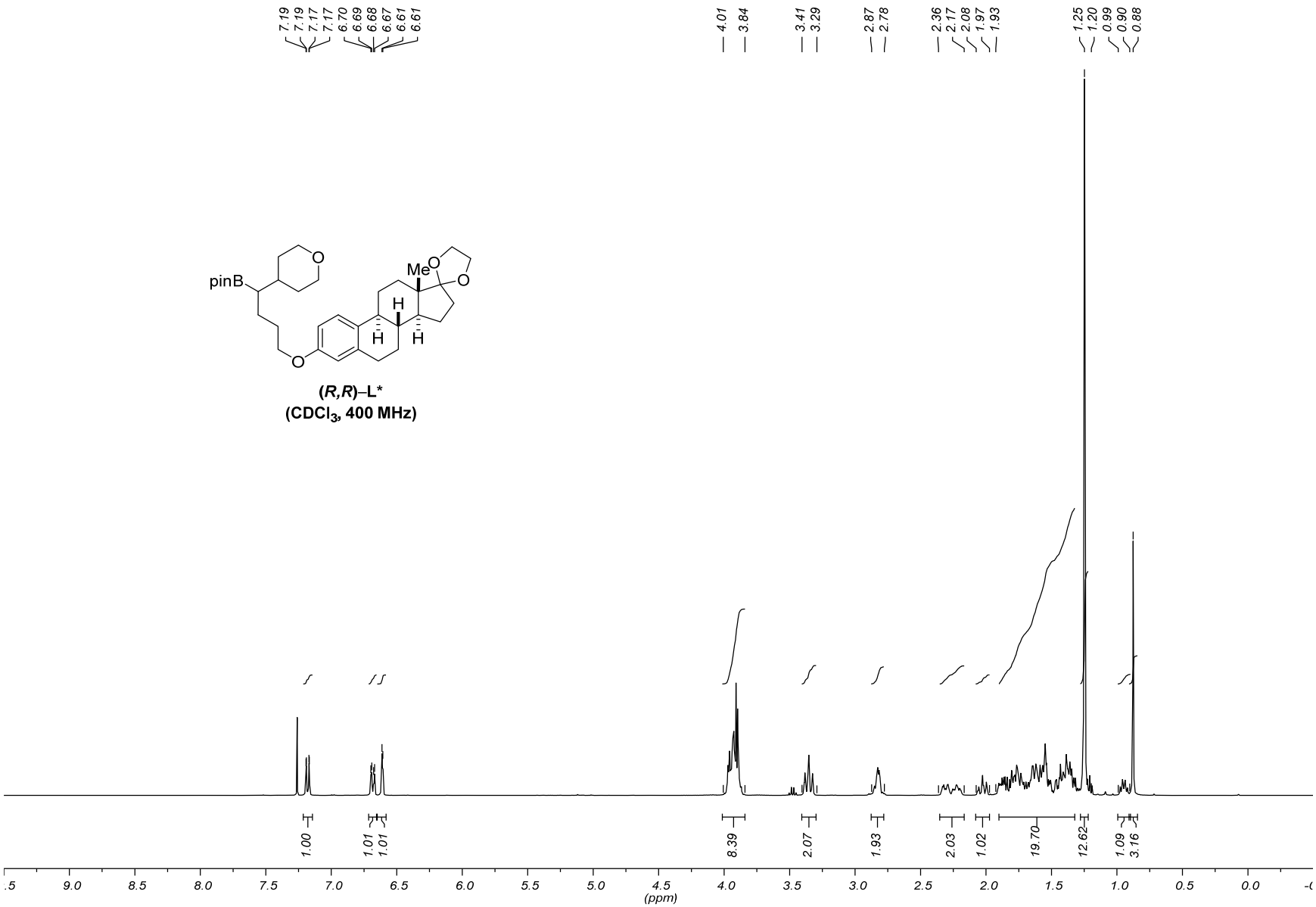
(ppm)

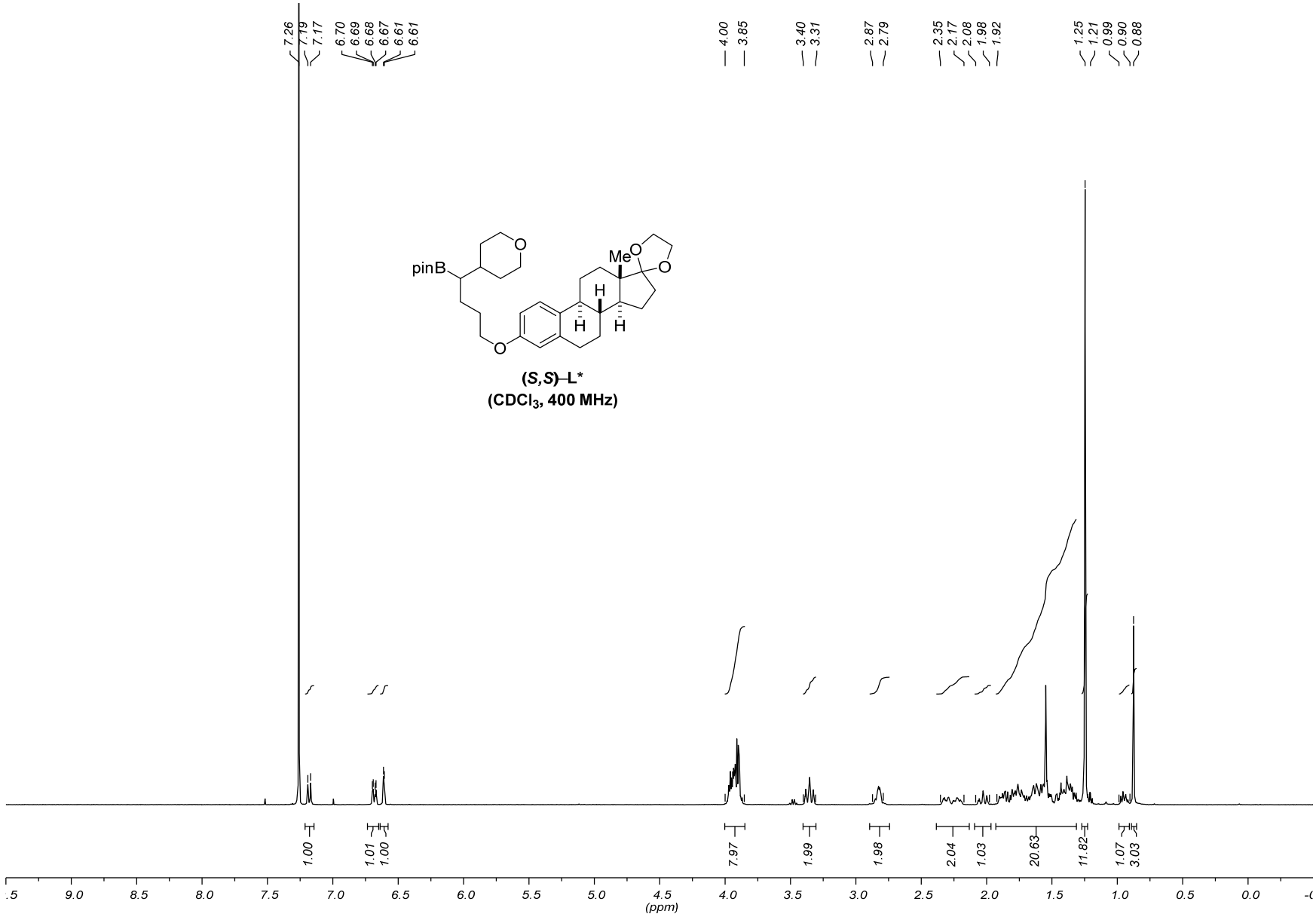


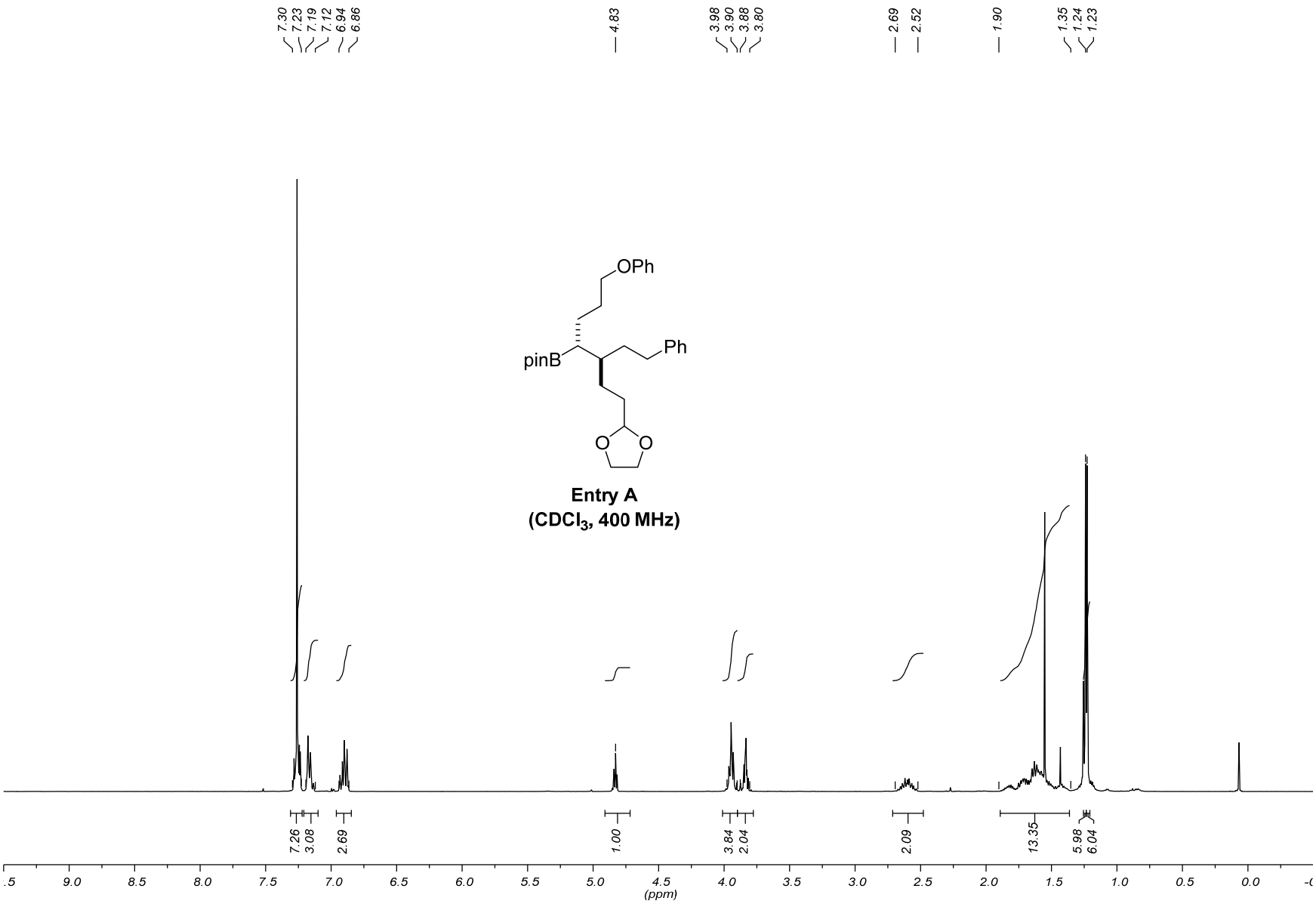
(*R,R*)-L*

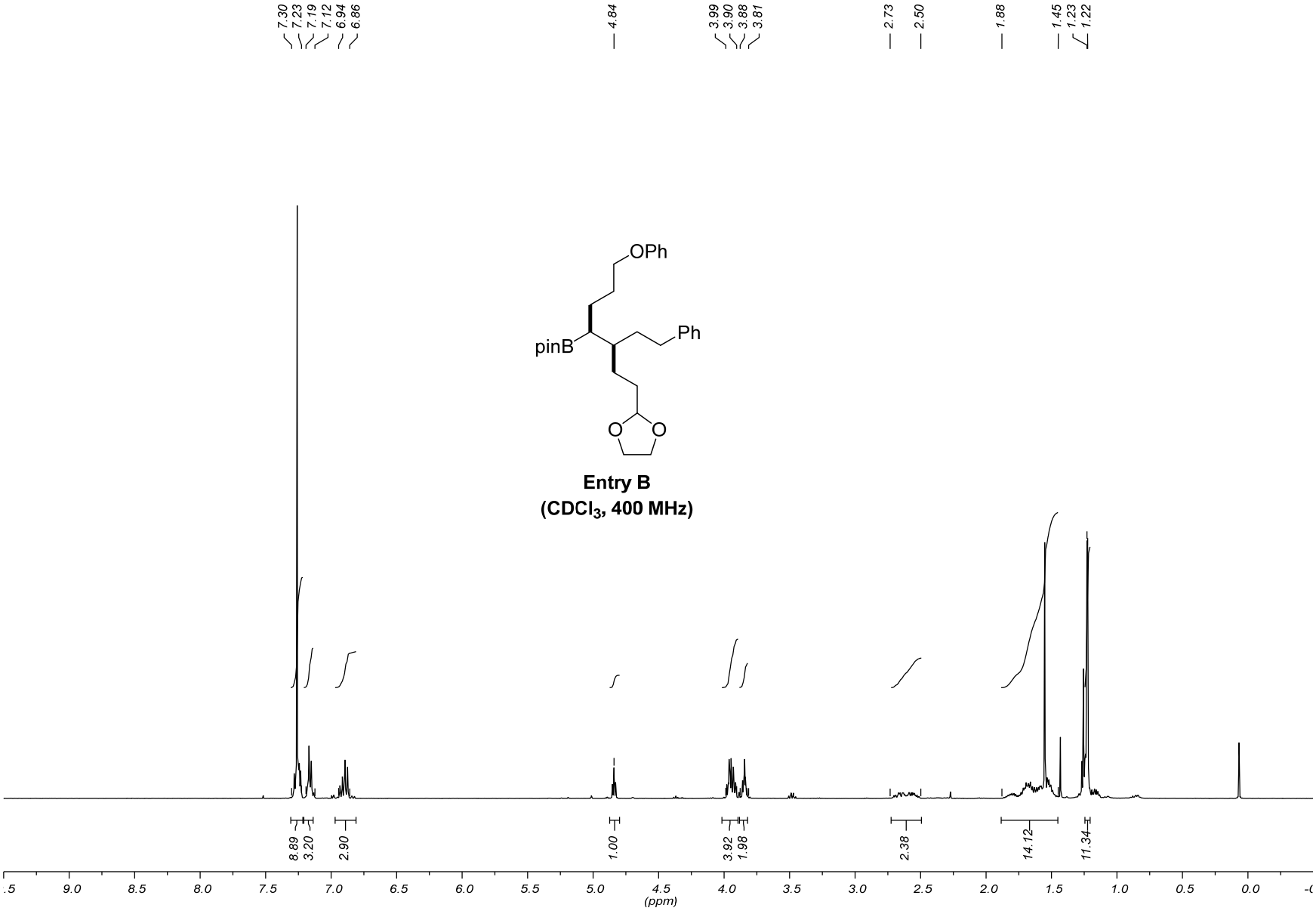
($CDCl_3$, 400 MHz)

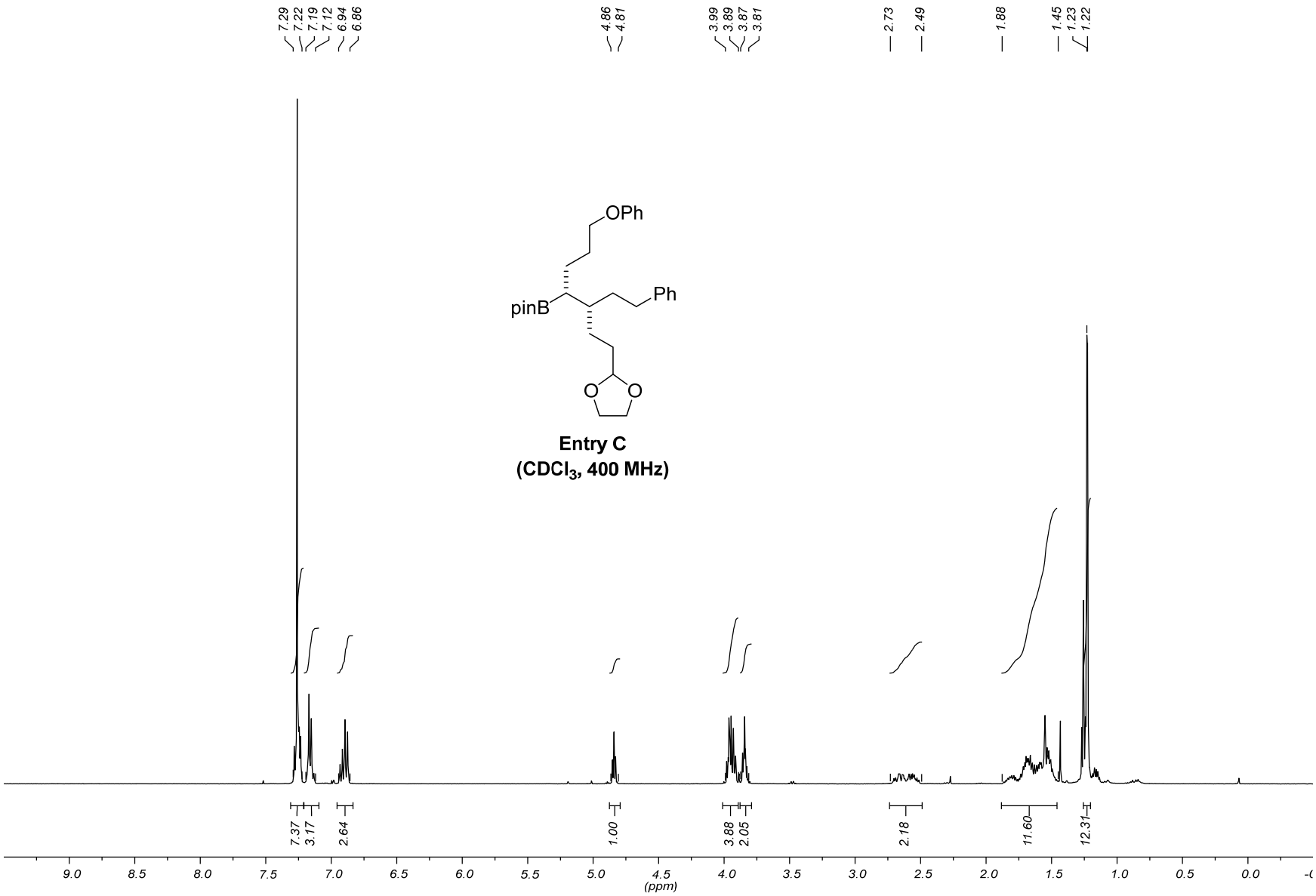


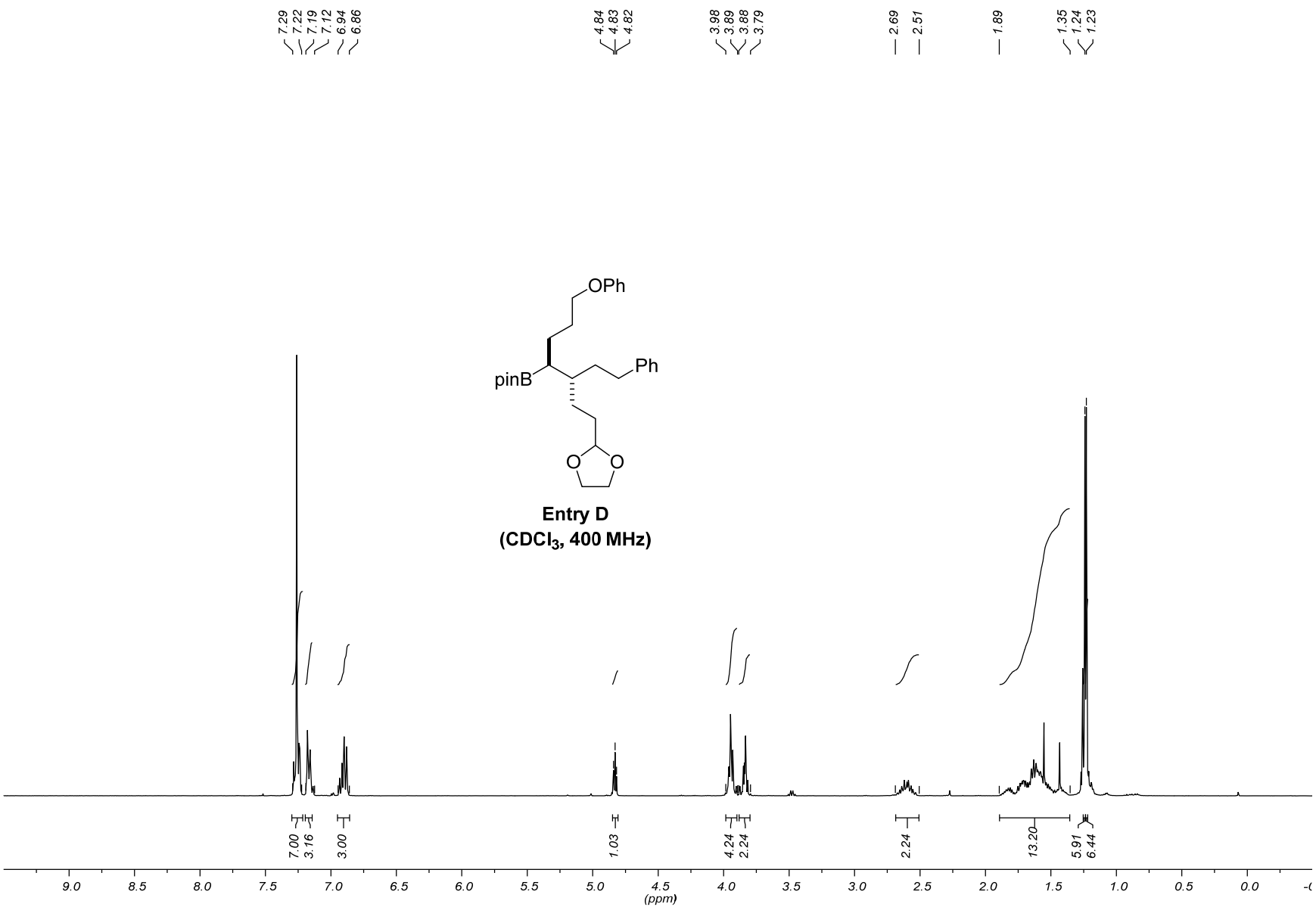
(*R*,*R*)–L*
($CDCl_3$, 400 MHz)

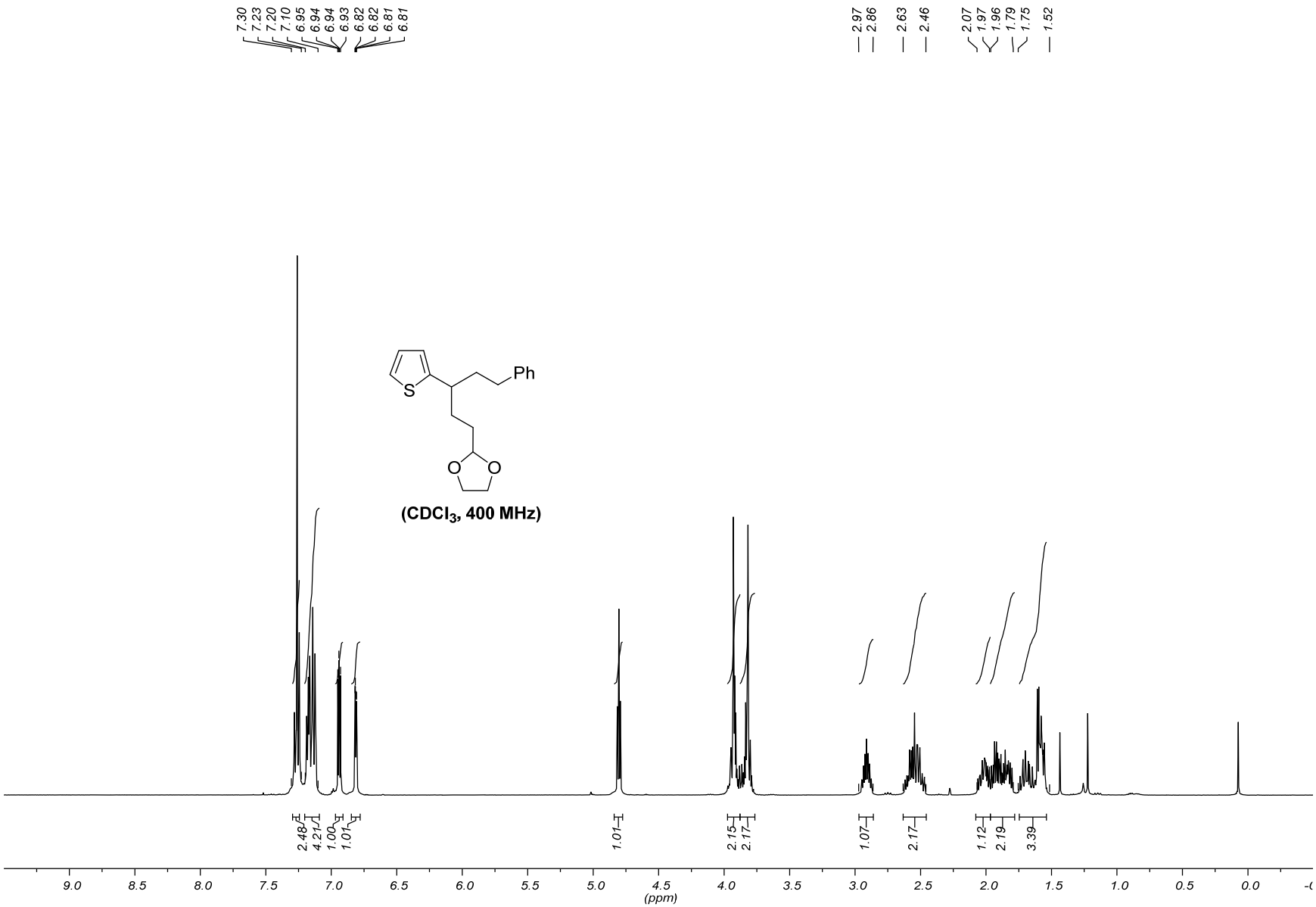

7.26
7.19
7.17
6.70
6.69
6.68
6.67
6.61
6.61
4.00
3.85
3.40
3.31
2.87
2.79
2.35
2.17
2.08
1.98
1.92
1.25
1.21
0.99
0.90
0.88
pinB
O
Me
O
O
H
H
H
O
(S,S)–L*
(CDCl3, 400 MHz)
1.00
1.01
1.00
7.97
1.99
1.98
2.04
1.03
20.63
11.82
1.07
3.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

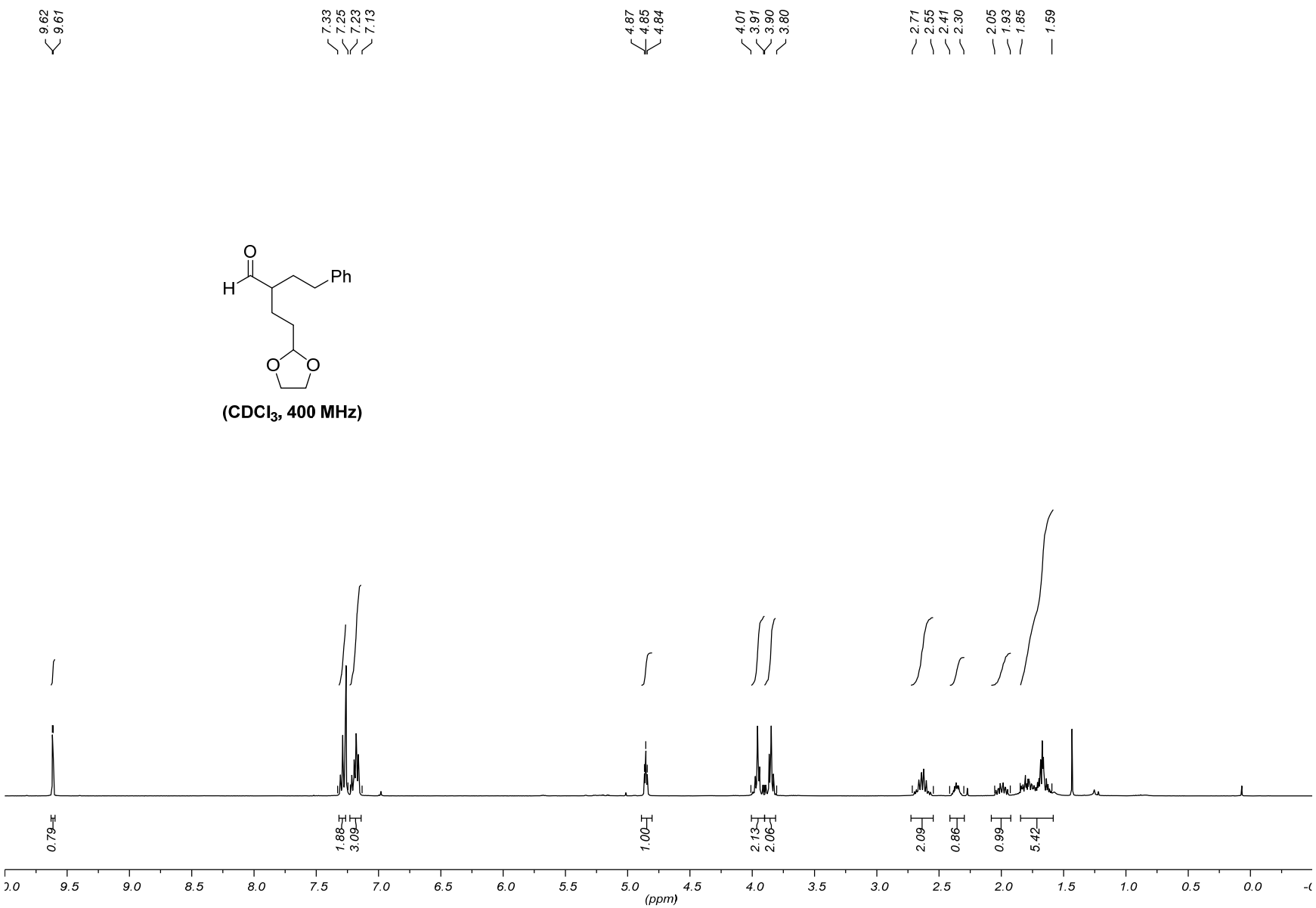

7.30
7.23
7.19
7.12
6.94
6.86
4.83
3.98
3.90
3.88
3.80
2.69
2.52
1.90
1.35
1.24
1.23
OPh
Ph
pinB
O
O
Entry A
(CDCl3, 400 MHz)
7.26
3.08
2.69
1.00
3.84
2.04
2.09
13.35
5.98
6.04
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

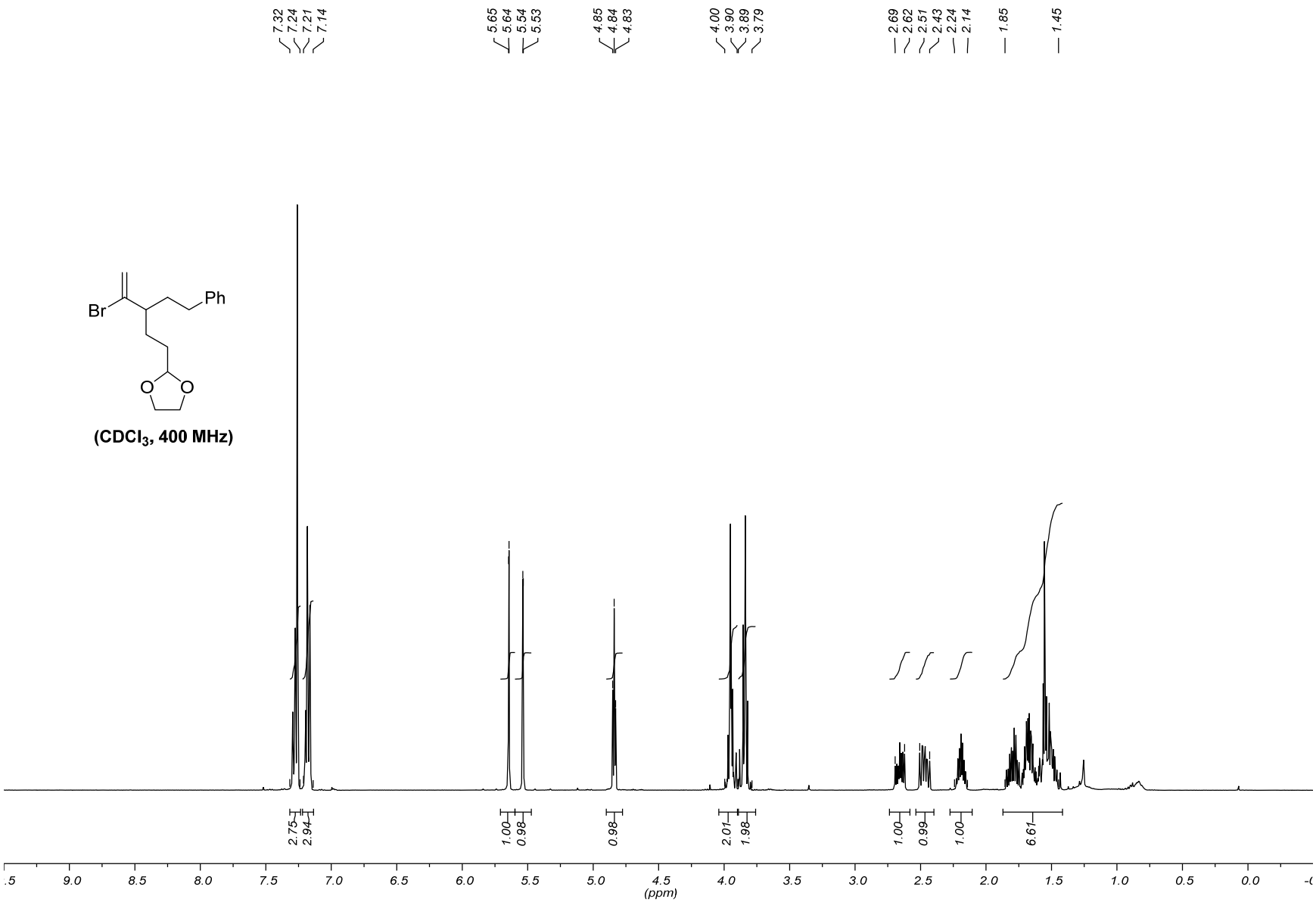

7.30
7.23
7.19
7.12
6.94
6.86
4.84
3.99
3.90
3.88
3.81
2.73
2.50
1.88
1.45
1.23
1.22
OPh
Ph
pinB
O
O
Entry B
(CDCl3, 400 MHz)
8.89
3.20
2.90
1.00
3.92
1.98
2.38
14.12
11.34
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

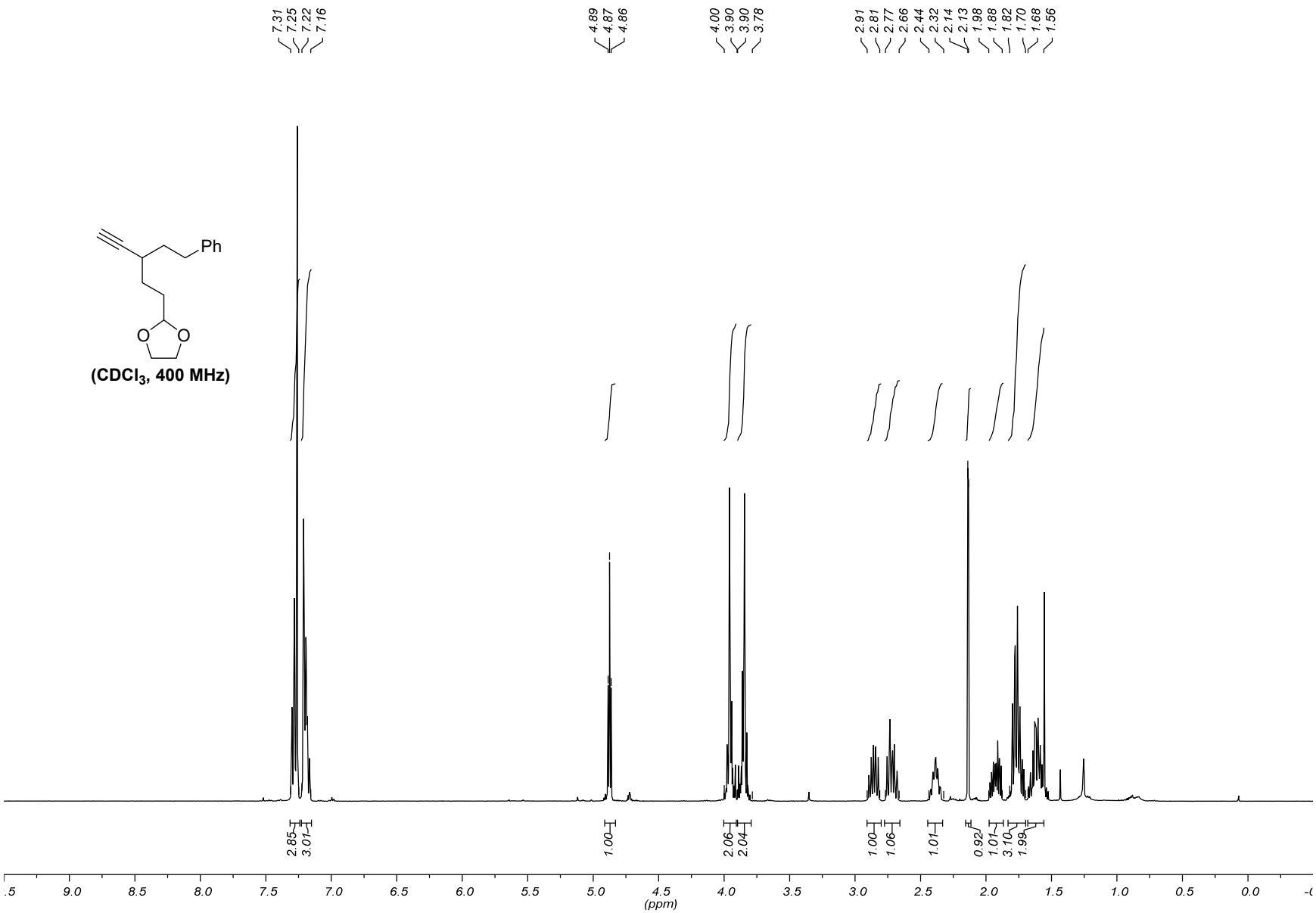

7.29
7.22
7.19
7.12
6.94
6.86
4.86
4.81
3.99
3.89
3.87
3.81
2.73
2.49
1.88
1.45
1.23
1.22
OPh
Ph
pinB
O
O
Entry C
(CDCl3, 400 MHz)
7.37
3.17
2.64
1.00
3.88
2.05
2.18
11.60
12.31
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

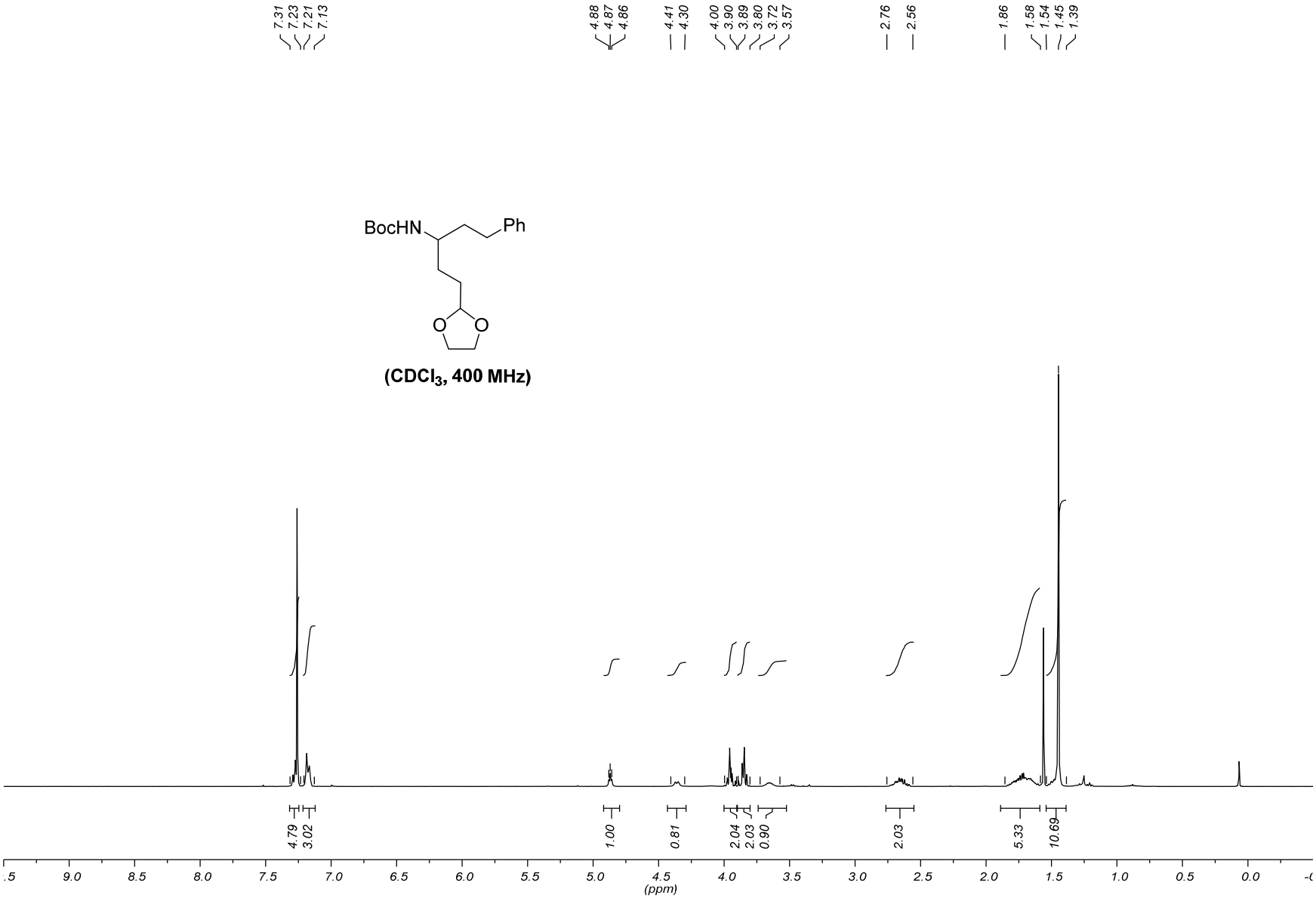

7.29
7.22
7.19
7.12
6.94
6.86
4.84
4.83
4.82
3.98
3.89
3.88
3.79
2.69
2.51
1.89
1.35
1.24
1.23
OPh
Ph
pinB
O
O
Entry D
(CDCl3, 400 MHz)
7.00
3.16
3.00
1.03
4.24
2.24
2.24
13.20
5.91
6.44
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

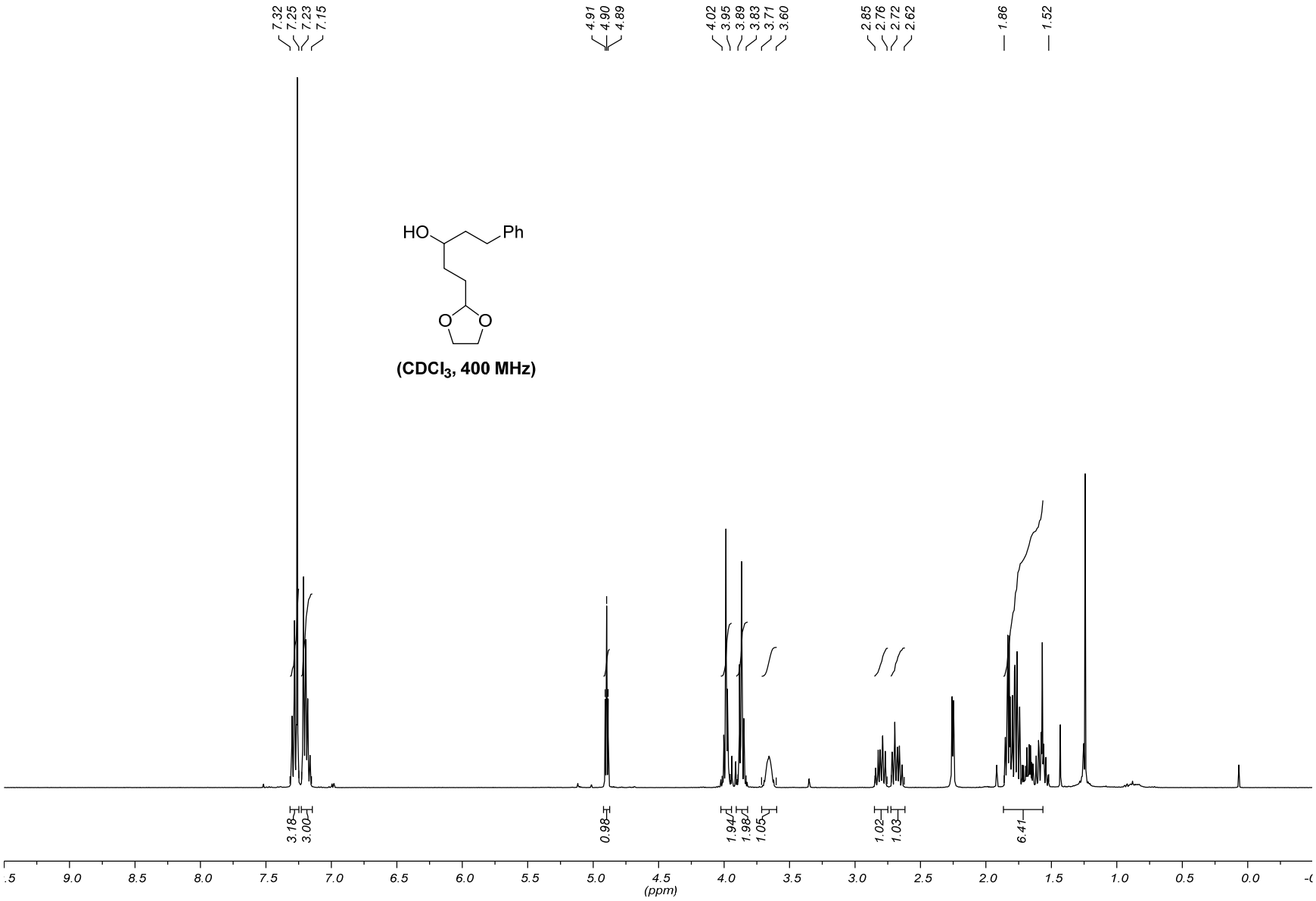

7.30
7.23
7.20
7.10
6.95
6.94
6.94
6.93
6.82
6.82
6.81
6.81
2.97
2.86
2.63
2.46
2.07
1.97
1.96
1.79
1.75
1.52
S
Ph
O
O
(CDCl3, 400 MHz)
2.48
4.21
1.00
1.01
1.01
2.15
2.17
1.07
2.17
1.12
2.19
3.39
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

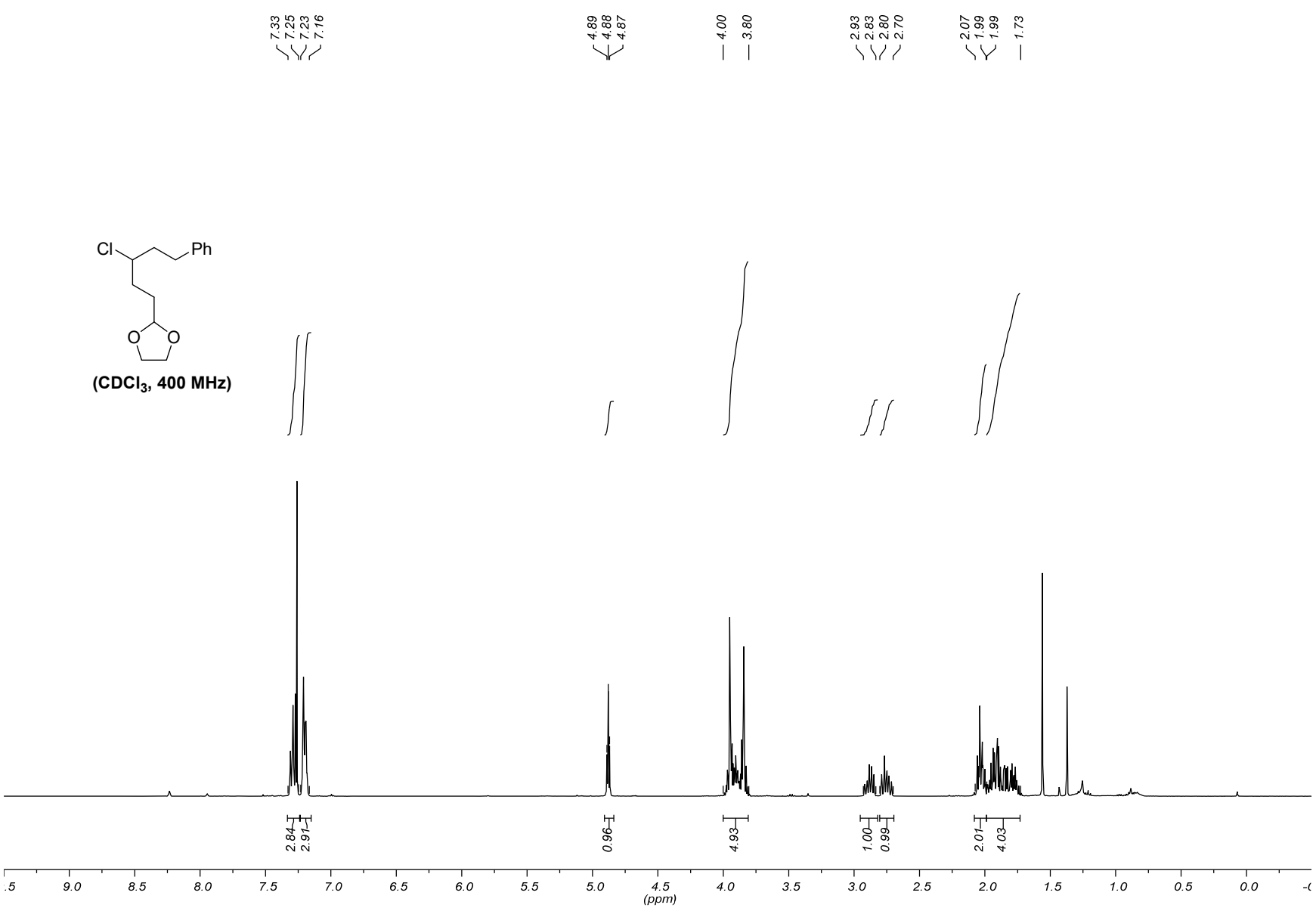

9.62
9.61
7.33
7.25
7.23
7.13
4.87
4.85
4.84
4.01
3.91
3.90
3.80
2.71
2.55
2.41
2.30
2.05
1.93
1.85
1.59
O
H
Ph
O
O
(CDCl3, 400 MHz)
0.79
1.88
3.09
1.00
2.13
2.06
2.09
0.86
0.99
5.42
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

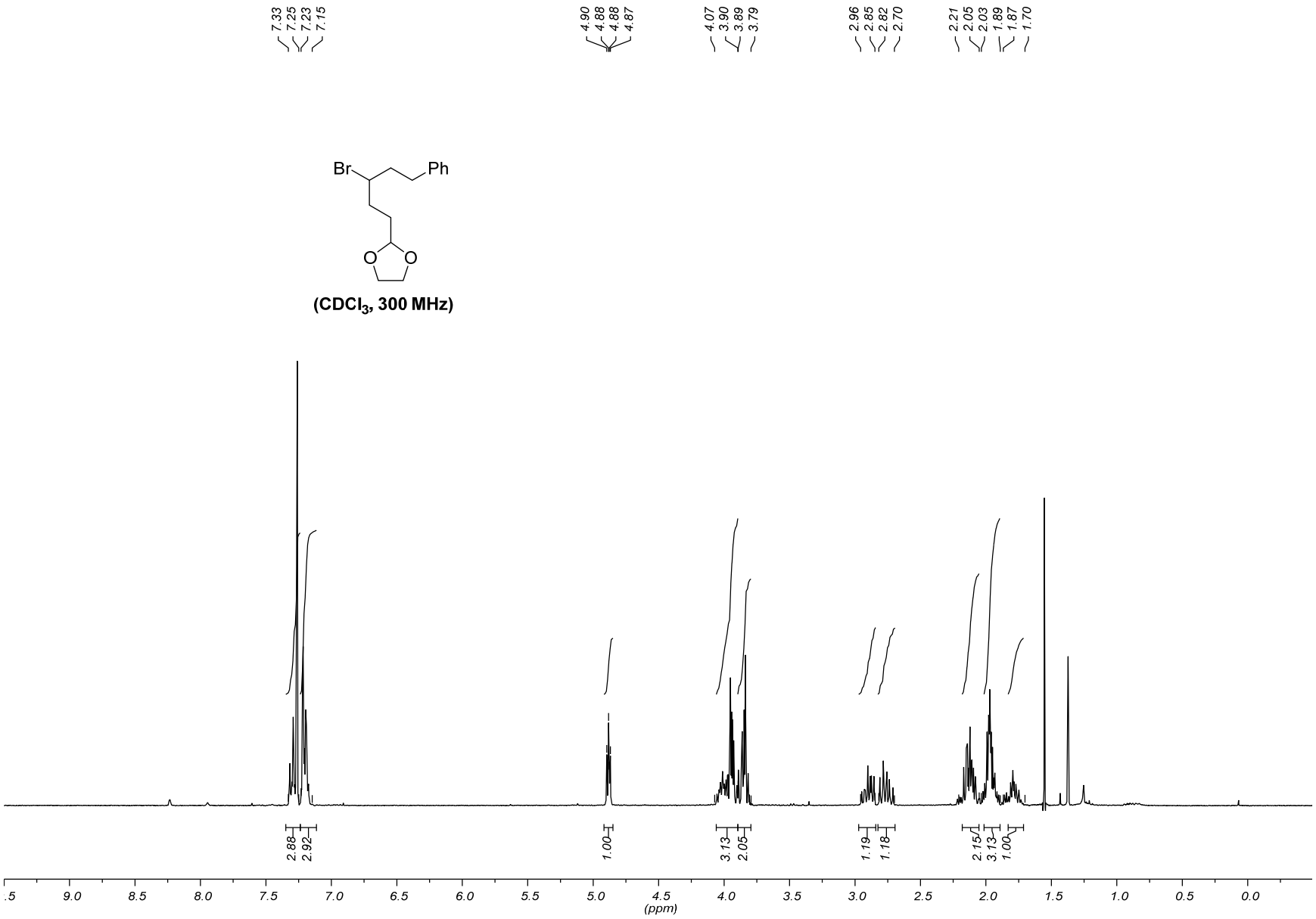

7.32
7.24
7.21
7.14
5.65
5.64
5.54
5.53
4.85
4.84
4.83
4.00
3.90
3.89
3.79
2.69
2.62
2.51
2.43
2.24
2.14
1.85
1.45
Br
Ph
O
O
(CDCl3, 400 MHz)
2.75
2.94
1.00
0.98
0.98
2.01
1.98
1.00
0.99
1.00
6.61
(ppm)

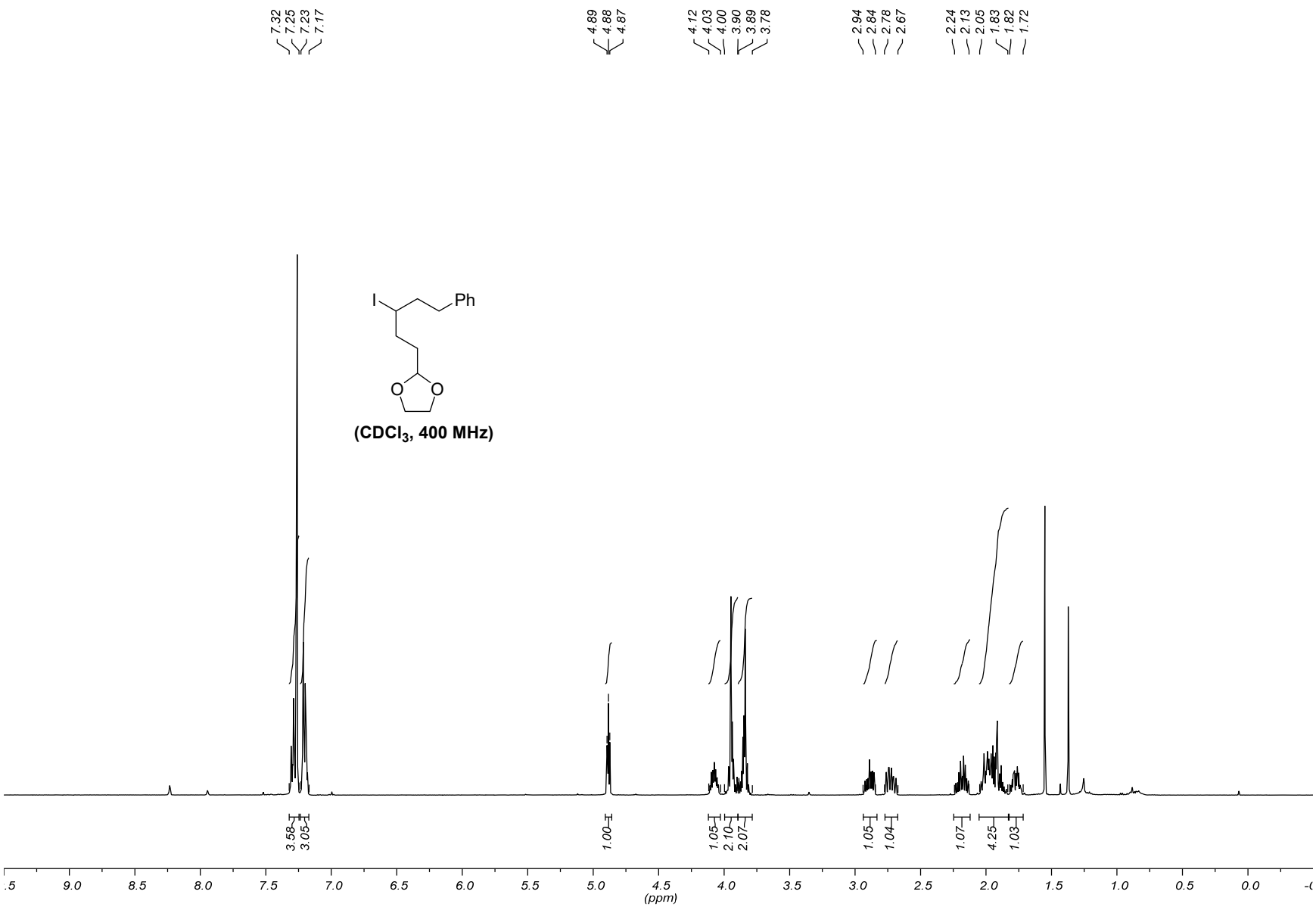

7.31
7.25
7.22
7.16
4.89
4.87
4.86
4.00
3.90
3.90
3.78
2.91
2.81
2.77
2.66
2.44
2.32
2.14
2.13
1.98
1.88
1.82
1.70
1.68
1.56
Ph
O
O
(CDCl3, 400 MHz)
2.85
3.01
1.00
2.06
2.04
1.00
1.06
1.01
0.92
1.01
3.10
1.99
(ppm)

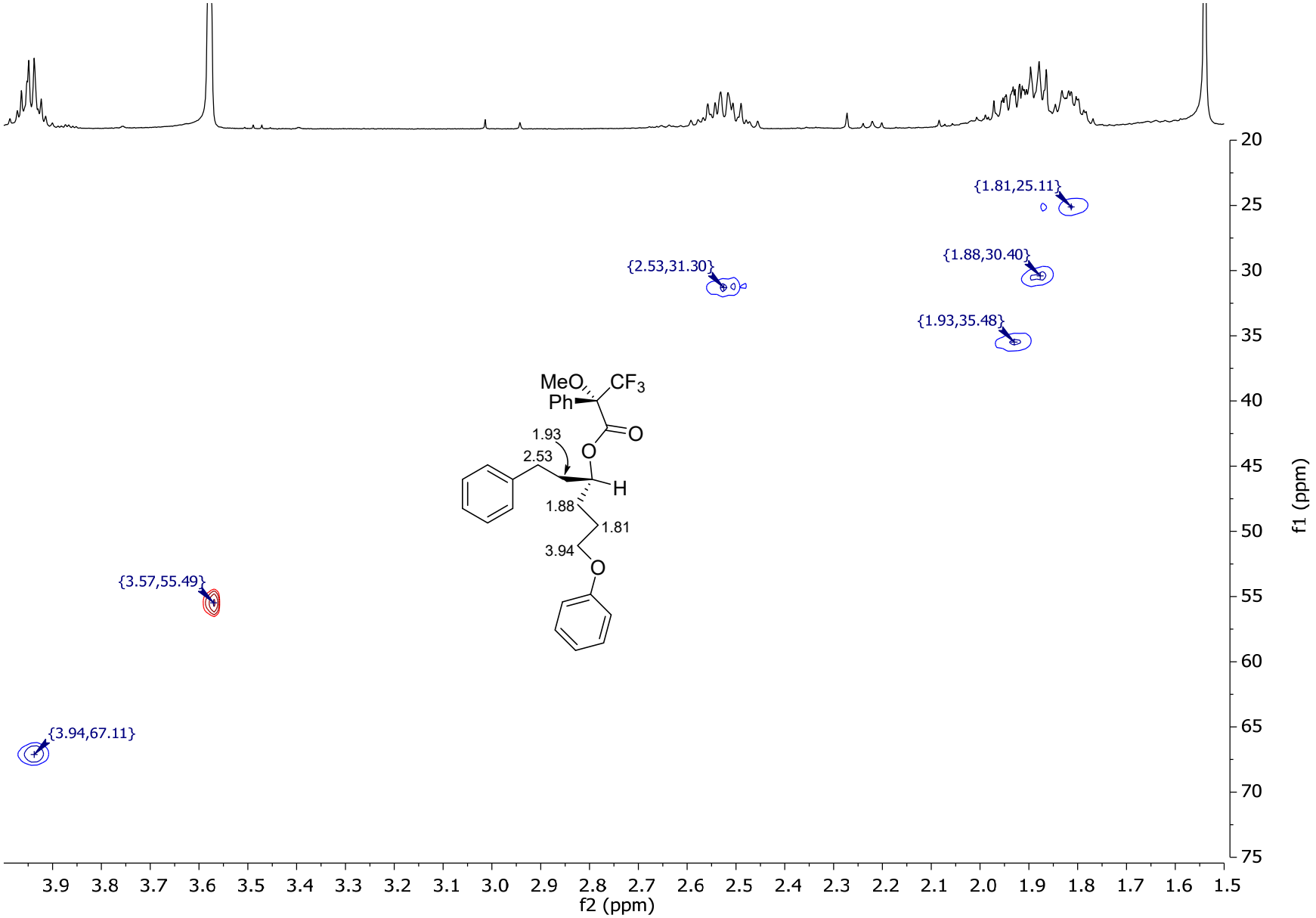

7.31
7.23
7.21
7.13
4.88
4.87
4.86
4.41
4.30
4.00
3.90
3.89
3.80
3.72
3.57
2.76
2.56
1.86
1.58
1.54
1.45
1.39
BocHN
Ph
O
O
(CDCl3, 400 MHz)
4.79
3.02
1.00
0.81
2.04
2.03
0.90
2.03
5.33
10.69
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

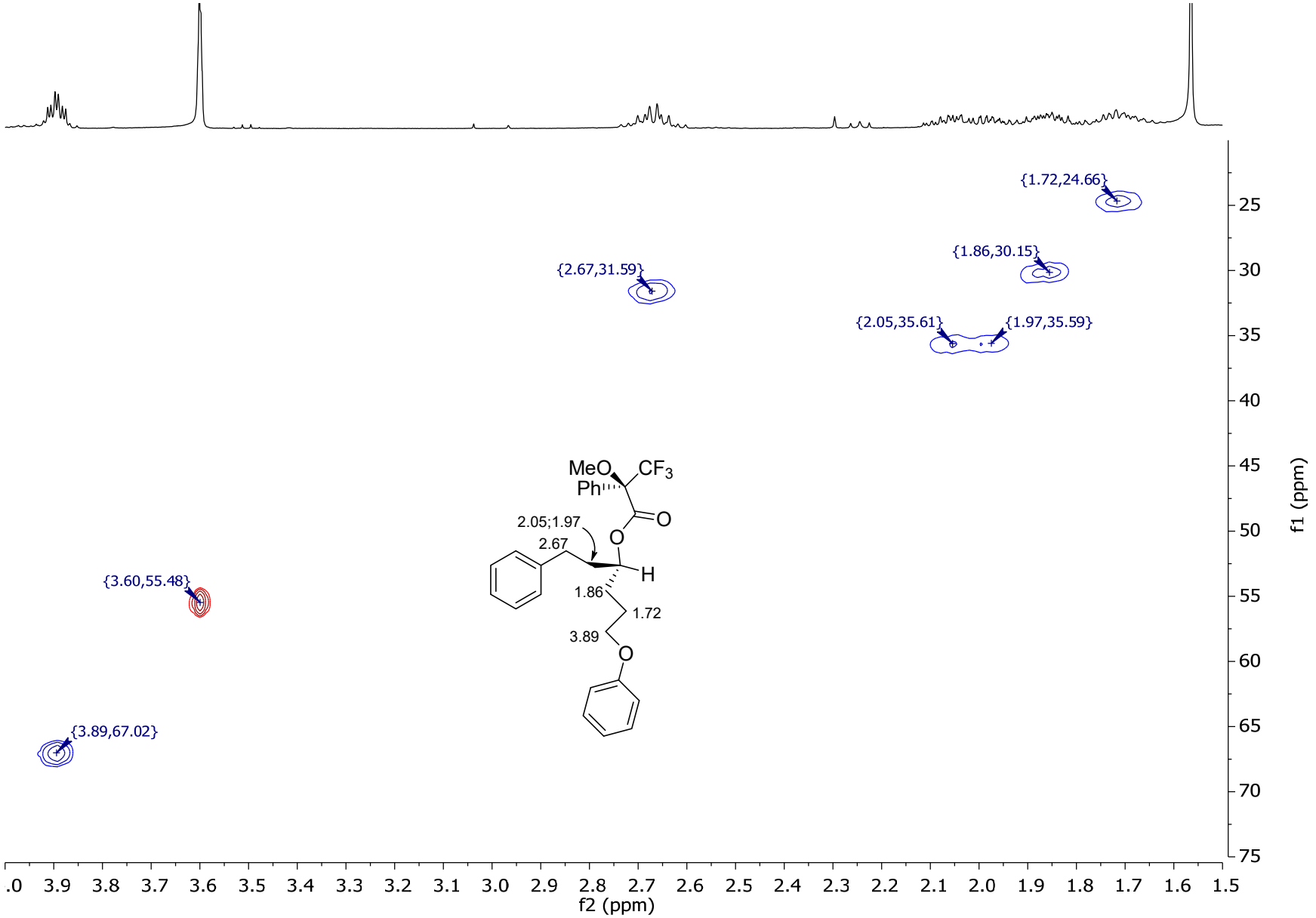

7.32
7.25
7.23
7.15
4.91
4.90
4.89
4.02
3.95
3.89
3.83
3.71
3.60
2.85
2.76
2.72
2.62
1.86
1.52
HO
Ph
O
O
(CDCl3, 400 MHz)
3.18
3.00
0.98
1.94
1.98
1.05
1.02
1.03
6.41
(ppm)

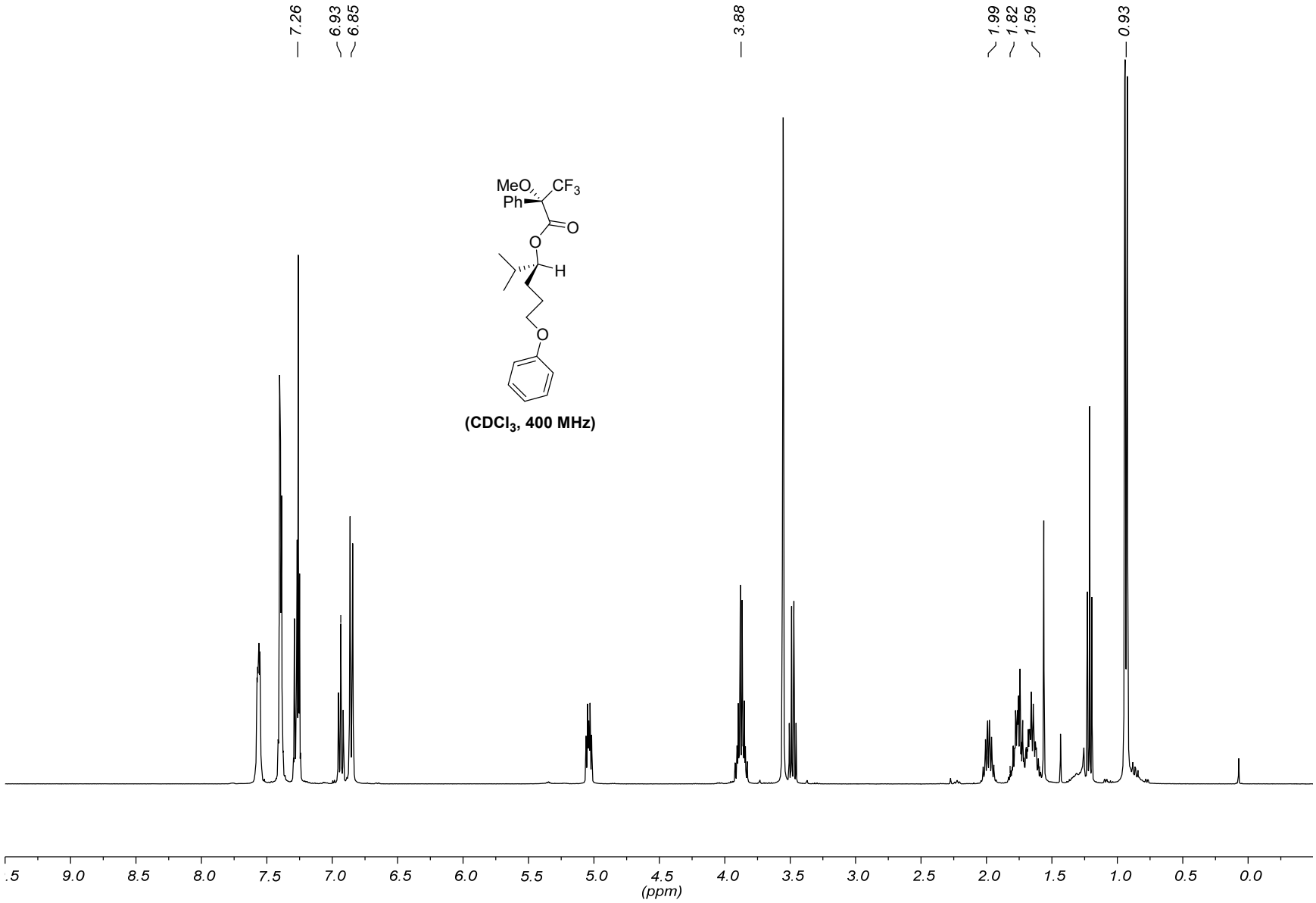

7.33
7.25
7.23
7.16
4.89
4.88
4.87
4.00
3.80
2.93
2.83
2.80
2.70
2.07
1.99
1.99
1.73
Cl
Ph
O
O
(CDCl3, 400 MHz)
2.84
2.91
0.96
4.93
1.00
0.99
2.01
4.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

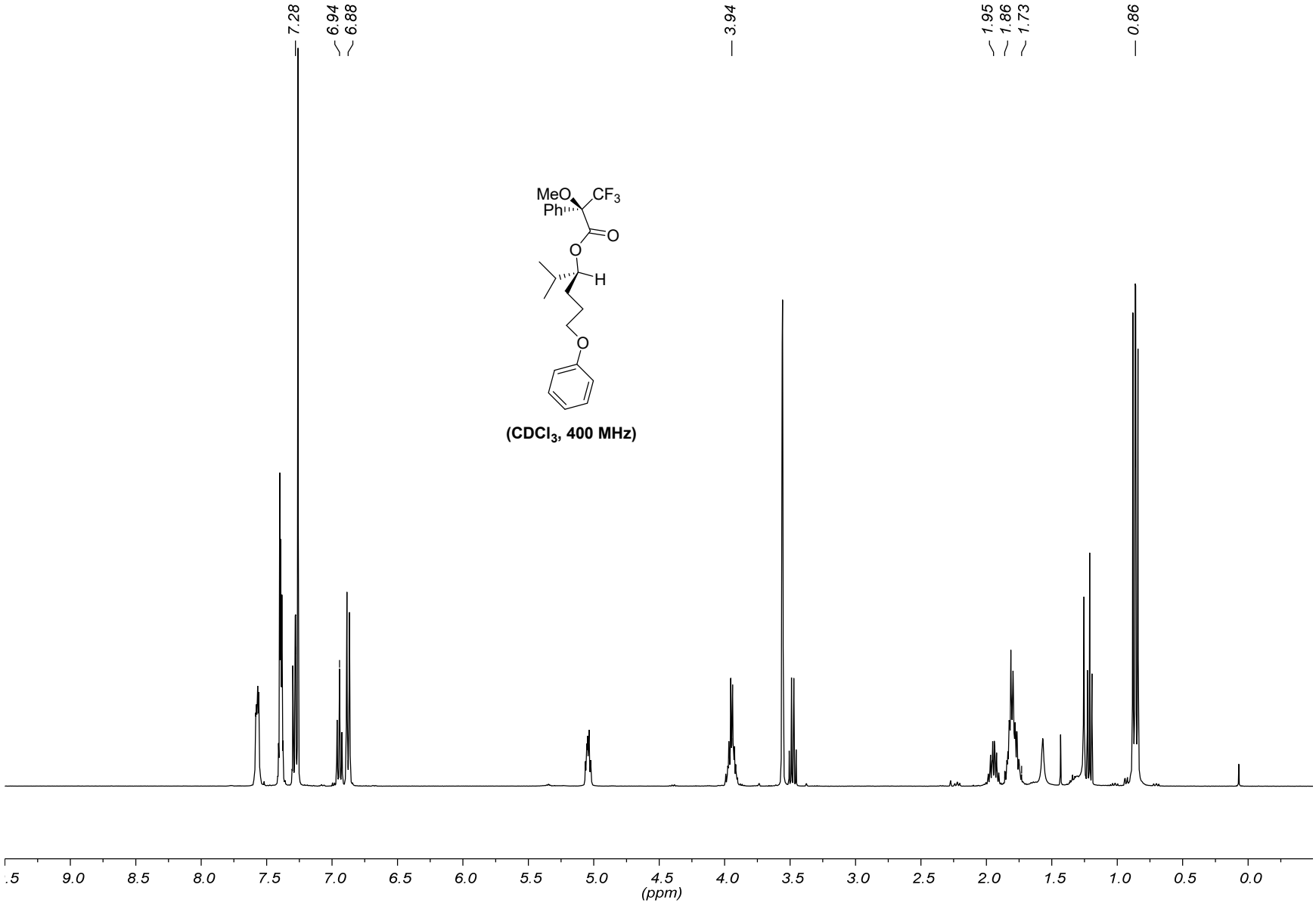

7.33
7.25
7.23
7.15
4.90
4.88
4.88
4.87
4.07
3.90
3.89
3.79
2.96
2.85
2.82
2.70
2.21
2.05
2.03
1.89
1.87
1.70
Br
Ph
O
O
(CDCl3, 300 MHz)
2.88
2.92
1.00
3.13
2.05
1.19
1.18
2.15
3.13
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)


7.32
7.25
7.23
7.17
4.89
4.88
4.87
4.12
4.03
4.00
3.90
3.89
3.78
2.94
2.84
2.78
2.67
2.24
2.13
2.05
1.83
1.82
1.72
I
Ph
O
O
(CDCl3, 400 MHz)
3.58
3.05
1.00
1.05
2.10
2.07
1.05
1.04
1.07
4.25
1.03
(ppm)


{1.81,25.11}
{2.53,31.30}
{1.88,30.40}
{1.93,35.48}
{3.57,55.49}
{3.94,67.11}
MeO
CF3
Ph
O
O
H
1.93
2.53
1.88
1.81
3.94
O
f2 (ppm)
f1 (ppm)


{1.72,24.66}
{1.86,30.15}
{2.67,31.59}
{2.05,35.61}
{1.97,35.59}
{3.60,55.48}
{3.89,67.02}
MeO
CF3
Ph
O
O
H
2.05;1.97
2.67
1.86
1.72
3.89
O
f1 (ppm)
f2 (ppm)


7.26
6.93
6.85
3.88
1.99
1.82
1.59
0.93
MeO
CF3
Ph
O
O
H
O
(CDCl3, 400 MHz)
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)


7.28
6.94
6.88
3.94
1.95
1.86
1.73
0.86
MeO
Ph
CF3
O
O
H
O
(CDCl3, 400 MHz)
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)