Enantioselective Organocatalytic Reductive Amination-Coupling

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Supporting Information

General Information. Aniline, *p*-trifluoromethyl aniline and commercially available ketones were distilled prior to use. Commercially available *p*-anisidine was purified by vacuum sublimation followed by recrystallization from water. All solvents were purified according to the method of Grubbs.[1] Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. Sieves (5Å powdered) were activated by flame under vacuum and stored at 180 ˚C. Chromatographic purification of products was accomplished using flash chromatography on Silicycle 230-400 mesh silica gel. Thin-layer chromatography (TLC) was carried out on Silicycle 0.25mm silica gel plates. Visualization of the developed chromatogram was performed by fluorescence quenching, iodine or $KMnO_4$ staining.

^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 Spectrometer (300 MHz and 75 MHz respectively), and are internally referenced to residual protic solvent signals ($CHCl_3$ = 7.24 ppm, DMSO = 2.50 ppm, benzene = 7.16 ppm). Data for ^{1}H are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration, coupling constant (Hz) and assignment. Data for ^{13}C NMR are reported in terms of chemical shift and in cases where fluorine coupling is seen all observed peaks are reported. IR spectra were recorded on a Perkin Elmer Paragon 1000 spectrometer and are reported in terms of frequency of absorption (cm^{-1}). Mass spectra were obtained from the California Institute of Technology Mass Spectroscopy Facility. X-ray structure analysis was carried out at the California Institute of Technology X-ray Crystallography facility. Gas liquid chromatography (GLC) was carried out on a Hewlett-Packard 6850 Series gas chromatograph equipped with a splitmode capillary injection system and flame ionization detectors using Varian CP-

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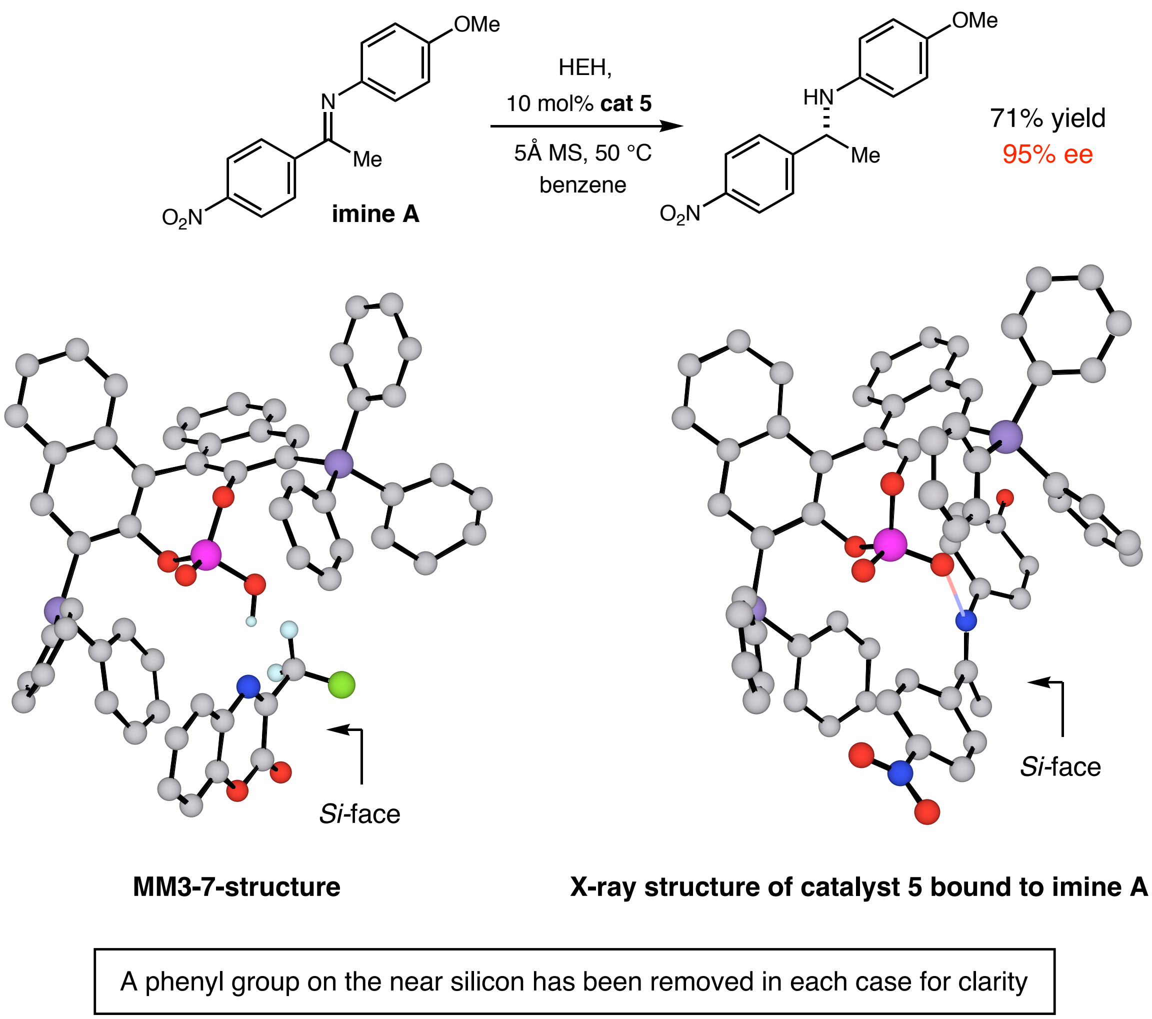
[1] Pangborn, A.B; Giardello, M.A.; Grubbs, R. H.; Rosen, R.K.; Timmers, F.J. *Organometallics* **1996**, *15*, 1518.

Chirasil-Dex-CB and Bodman Chiraldex Γ-TA (30 m x 0.25 mm) columns. High performance liquid chromatography (HPLC) was performed on Hewlett-Packard 1100 Series chromatographs using a Daicel Chiracel OD-H column (25 cm) and equivalent guard column (5 cm). Analytical supercritical fluid chromatography (SFC) was performed on a Berger Instruments SFC with built-in photometric detector (λ = 214 nm) using Daicel Chiracel OJ-H, OD-H, AS-H, and AD-H columns (25 cm) as noted. Optical rotations were measured on a Jasco P-1010 polarimeter, and $[\alpha]_D$ values are reported in 10^{-1} dg cm^2 g^{-1}; concentration (c) is in g/100 mL.

Figure 1. **X-ray Crystal Structure.**



Synthesis of catalysts:

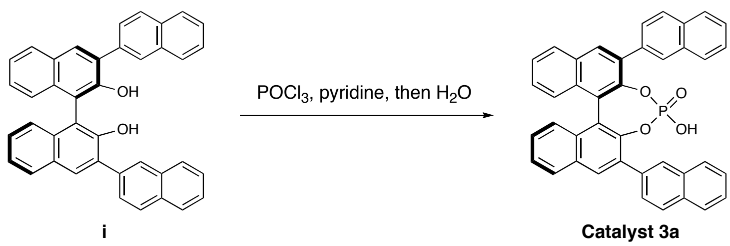
Catalyst **1** was prepared using the Takemoto procedures.[2]

Catalyst **2** (TADDOL) was purchased from Aldrich and used as supplied.

Catalyst **3b** was purchased from Aldrich and used as supplied.

Catalyst **3d** was prepared as described by Akiyama.[3]

Catalyst **3a**:



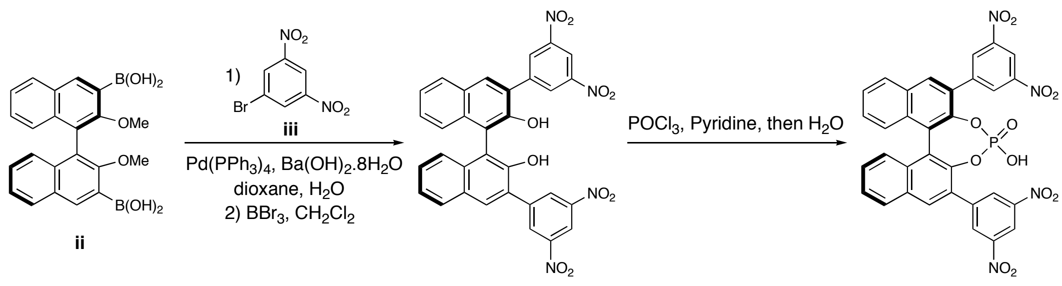
(*R*)-2,6-Bis-(naphthalen-2-yl)-4-oxo-3,5-dioxa-4λ^5-phospha-cyclohepta[2,1-a;3,4-a'] dinaphthalen-4-ol (catalyst 3a)

Diol **i** was prepared as described by Jørgensen.[4] Diol **i** (300 mg, 0.43 mmol) was dissolved in pyridine (1.1 mL). Phosphorous oxychloride (133 mg, 0.081 mL, 0.86 mmol) was added dropwise at room temperature with rapid stirring and the resulting solution was stirred for 6 hours. Water (1.0 mL) was added and the resulting biphasic suspension was stirred at room temperature for a further 30 mins. The reaction mixture was diluted with CH_2Cl_2 and the pyridine extracted by washing with 1*N* HCl. The combined organic phase was dried over Na_2SO_4 concentrated and the crude solid was purified by flash column chromatography (1.5% MeOH in CH_2Cl_2) to yield catalyst **3a** as a white solid (280 mg, 86% yield). IR (film) 1253, 1108, 740 cm^{-1}; ^{1}H NMR (300 MHz, $(CD_3)_2SO$) δ 7.13 (s, 2H, ArH), 7.36-7.26 (m, 2H, ArH), 7.42-7.62 (m, 6H, ArH), 7.92-8.06 (m, 6H, ArH), 8.12 (d, 2H, *J* = 8.4 Hz, ArH), 8.23 (s, 2H, ArH), 8.27-8.36 (m, 2H, ArH), 8.51 (s, 2H, ArH); ^{13}C NMR (75 MHz, $(CD_3)_2SO$) δ 122.76, 124.90, 126.00, 126.01, 126.27, 127.02, 127.47, 128.28, 128.51, 128.92, 129.05, 130.23, 130.63, 131.93, 132.15, 132.99, 134.37, 135.79, 147.55, 147.68; HRMS (FAB+) exact mass calculated

[2] Okino, T.; Hoashi, Y.; Takemoto, Y. *J. Am. Chem. Soc.* **2003**, *125*, 12672.
[3] Akiyama, T.; Morita, H.; Itoh, J.; Fuchibe, K. *Org. Lett.* **2005**, *7*, 2583.
[4] Simonsen, K. B.; Gothelf, K. V.; Jørgensen, K. A. *J. Org. Chem.* **1998**, *63*, 7536.

for [M+H] ($C_{40}H_{26}O_4P$) requires *m/z* 601.1569, found *m/z* 601.1565. $[\alpha]_D^{23}$ = –322.8° (c = 1.02, $CHCl_3$).

Catalyst **3c**:



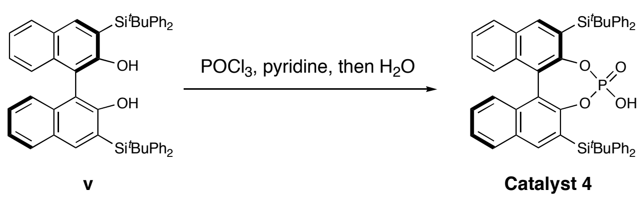
(*R*)-2,6-Bis-(3,5-dinitrophenyl)-4-oxo-3,5-dioxa-4λ^5-phospha-cyclohepta[2,1-a;3,4-a'] dinaphthalen-4-ol (catalyst 3c)

Boronic acid **ii** was prepared as described by Jørgensen.[4] Degassed dioxane (6.0 mL) and degassed water (2.0 mL) were added to a mixture of boronic acid **ii** (188 mg, 0.47 mmol), bromide[5] **iii** (371 mg, 1.50 mmol), barium hydroxide octahydrate (435 mg, 1.38 mmol) and $Pd(PPh_3)_4$ (58 mg, 0.05 mmol) under argon. The reaction mixture was heated to 70 ˚C for 48 h, then cooled to room temperature. The dioxane was removed, and the resulting residue was redissolved in CH_2Cl_2, washed with 1 N HCl solution and brine, dried over Na_2SO_4 and concentrated to give crude product as a red oil. The crude oil was dissolved in CH_2Cl_2 (18.0 mL) and cooled to 0 ˚C. A solution of BBr_3 in CH_2Cl_2 (5.0 mL, 1.0 M) was then added dropwise over 10 mins. The reaction mixture was allowed to warm to room temperature and stirred overnight. The mixture was cooled to 0 ˚C, then quenched by slow addition of water. The reaction mixture was diluted with CH_2Cl_2, washed with water then brine. The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The crude product was purified by silica flash column chromatography (2:1 CH_2Cl_2:hexanes) to yield diol **iv** as an orange solid (187 mg, 65% yield over 2 steps).

[5] Duan, J.; Zhang, L. H.; Dolbier Jr., W. R. *Synlett* **1999**, 1245.

Diol **iv** (140 mg, 0.23 mmol) was dissolved in pyridine (0.8 mL). Phosphorous oxychloride (69.3 mg, 0.05 mL, 0.45 mmol) was added dropwise at room temperature with rapid stirring and the resulting solution was stirred for 6 hours. Water (1.0 mL) was added and the resulting biphasic suspension was stirred at room temperature for a further 30 mins. The reaction mixture was diluted with CH_2Cl_2 and the pyridine was removed via washing with 1*N* HCl. The combined organic phase was dried over Na_2SO_4 and purified by flash column chromatography (1:20 MeOH:CH_2Cl_2) to yield catalyst **3c** as a pale yellow solid (142 mg, 92% yield). IR (film) 1540, 1345, 1107, 732 cm^{-1}; ^{1}H NMR (300 MHz, $(CD_3)_2SO$) δ 7.16 (d, 2H, *J* = 8.7 Hz, ArH), 7.37 (dd, 2H, *J* = 8.7, 6.9 Hz ArH), 7.51 (dd, 2H, *J* = 8.1, 6.9 Hz ArH), 8.14 (d, 2H, *J* = 8.1 Hz, ArH), 8.40 (s, 2H, ArH), 8.89 (t, 2H, *J* = 2.0 Hz, ArH), 8.89 (d, 4H, *J* = 2.0 Hz, ArH); ^{13}C NMR (75 MHz, $(CD_3)_2SO$) δ 117.40, 122.82, 125.43, 126.00, 127.31, 128.99, 130.06, 130.23, 130.71, 131.56, 132.50, 141.16, 146.89, 148.00; HRMS (FAB+) exact mass calculated for [M+H] ($C_{32}H_{18}N_4O_{12}P$) requires *m/z* 681.0659, found *m/z* 681.0666. $[\alpha]_D^{23}$ = –290.4° (c = 0.34, $CHCl_3$).

Catalyst **4**:



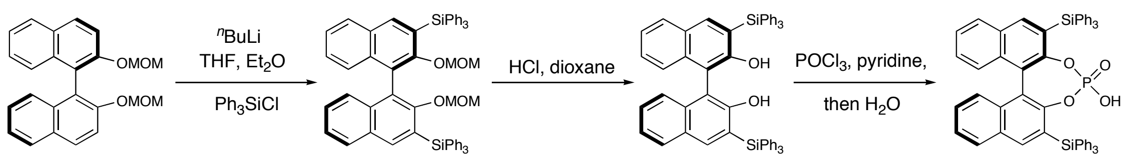
(*R*)-2,6-Bis-(*tert*-butyldimethylsilyl)-4-oxo-3,5-dioxa-4λ^5-phospha-cyclohepta [2,1a;3,4-a'] dinaphthalen-4-ol (catalyst 4)

Diol **v** was prepared as described by Yamamoto.[6] Diol **v** (95 mg, 0.18 mmol) was dissolved in pyridine (1.0 mL). Phosphorous oxychloride (56 mg, 0.04 mL, 0.36 mmol) was added dropwise at room temperature and the resulting solution was heated to 90 ˚C with stirring for 36 hours. The mixture was cooled to room temperature and water (1.0 mL) was added slowly. The resulting biphasic suspension was stirred for a further 30 mins, then diluted with CH_2Cl_2 and the pyridine was extracted by washing with 1*N* HCl.

[6] Maruoka, K.; Itoh, T.; Araki, Y.; Shirasaka, T.; Yamamoto, H. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 2975.

The combined organic phase was dried over Na_2SO_4 concentrated and purified by flash column chromatography (1:20 MeOH:CH_2Cl_2) to yield catalyst **4** as a white solid (61 mg, 58% yield). IR (film) 3070, 2934, 2859, 1427, 1254, 1104, 1091, 984, 702 cm^{-1}; ^{1}H NMR (300 MHz, $(CD_3)_2SO$) δ 1.23 (s, 18H, ^{t}Bu), 6.86-6.96 (m, 2H, ArH), 7.20-7.48 (m, 20H, ArH), 7.55-7.64 (m, 2H, ArH), 7.64-7.76 (m, 6H, ArH); ^{13}C NMR (75 MHz, $(CD_3)_2SO$) δ 18.75, 29.45, 121.40, 124.10, 125.23, 126.96, 127.38, 127.57, 128.17, 133.91, 135.23, 135.94, 136.61, 140.81, 154.26, 154.37; HRMS (FAB+) exact mass calculated for [M+Na] ($C_{52}H_{49}O_4Si_2PNa$) requires *m/z* 847.2805, found *m/z* 847.2795. $[\alpha]_D^{23} = -171.5°$ (c = 0.42, $CHCl_3$).

Catalyst **5**:



(*R*)-2-(methoxymethoxy)-1-(2-(methoxymethoxy)-3-(triphenylsilyl)naphthalen-1-yl)-3-(triphenylsilyl)naphthalene vii

Silylated BINOL derivative **vii** was prepared using a modification of a Snieckus procedure.[7] MOM protected (*R*)-BINOL **vi** can be purchased directly or synthesized in quantitative yield following the procedure described by Kobayashi.[8] Binol diether **vi** (20.0 g, 53.4 mmol) was dissolved in Et_2O (920 mL) followed by dropwise addition of ^{n}BuLi (53.0 mL, 2.3 M, 123 mmol) over 10 mins at room temperature. The resulting suspension was stirred at room temperature for 1 hour 30 mins (note: a color change was observed over the initial 30 mins from a yellow solution to a brown suspension). The mixture was cooled to 0 ˚C and THF (440 mL) was added. After a further 15 mins at 0 ˚C a solution of Ph_3SiCl (39.4 g, 133.5 mmol) in THF (100 mL) was added. The reaction mixture was warmed to room temperature and stirred for 30 hours (note: after addition of the THF and Ph_3SiCl the color darkened from light brown to very dark brown over the first hour. The colour faded through green to orange and finally pale yellow over the 30

[7] Cox, P. J.; Wang, W.; Snieckus, V. *Tetrahedron Lett.* **1992**, *33*, 2253.
[8] Kobayashi, S.; Kusakabe, K.; Komiyama, S.; Ishitani, H. *J. Org. Chem.* **1999**, *64*, 4220.

hour period). The reaction was quenched by addition of sat. NH_4Cl, then extracted into CH_2Cl_2. The organics were washed with brine and dried over Na_2SO_4, filtered and concentrated to yield the crude product as a viscous yellow oil. The product was purified by silica flash column chromatography (1:1:20 CH_2Cl_2:Et_2O:pentane) to yield the title product **vii** as a white solid (32.2 g, 68% yield). IR (film) 3068, 1428, 1108, 700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.36 (s, 6H, OCH_3), 3.86 (d, 2H, *J* = 5.0 Hz, OC**H**HO), 3.93 (d, 2H, *J* = 5.0 Hz, OCH**H**O), 7.28-7.60 (m, 24H, ArH), 7.65-7.92 (m, 14H, ArH), 7.99 (s, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 56.41, 98.06, 123.34, 124.81, 126.26, 127.66, 128.06, 128.88, 129.44, 129.67, 130.44, 135.32, 136.41, 136.90, 141.56, 158.50; HRMS (FAB+) exact mass calculated for [M+] ($C_{60}H_{50}O_4Si$) requires *m/z* 890.3248, found *m/z* 890.3291. $[\alpha]_D^{23}$ = +53.4° (c = 1.01, $CHCl_3$).

(*R*)-1-(2-hydroxy-3-(triphenylsilyl)naphthalen-1-yl)-3-(triphenylsilyl)naphthalen-2-ol viii[6]

Concentrated HCl (3.0 mL) was added to a solution of MOM protected binol **vii** (25.7 g, 28.8 mmol) in dioxane (200 mL). The resulting solution was heated to 70 ˚C for 24 h (note: fitted with reflux condensor but not quite refluxing). The reaction mixture was cooled to room temperature and quenched by addition of sat. $NaHCO_3$ solution. The product was extracted into EtOAc and washed with water, then brine. The combined organics were dried over Na_2SO_4, filtered and concentrated to yield the crude product as a pink solid. Trituration/washing with hot CH_2Cl_2 : Et_2O (1:10) provided pure diol **viii** as a white solid. The washings were concentrated and the procedure repeated on the residue twice to provide a combined yield of pure diol **viii** as a white solid (20.5 g, 89% yield). IR (film) 3521, 3068, 1581, 1428, 1108, 699 cm^{-1}; ^1H NMR (300 MHz, C_6D_6) δ 4.68 (s, 2H, O**H**), 6.90-7.38 (m, 26H, ArH), 7.80-7.84 (m, 12H, ArH), 8.14 (s, 2H, ArH); ^{13}C NMR (75 MHz, C_6D_6) δ 110.84, 124.09, 124.23, 124.39, 127.92, 128.20, 129.45, 129.78, 129.93, 135.09, 135.50, 136.91, 142.42, 156.98; HRMS (FAB+) exact mass calculated for [M+] ($C_{56}H_{42}O_2Si_2$) requires *m/z* 802.2723, found *m/z* 802.2700. $[\alpha]_D^{23}$ = +102.7° (c = 1.20, $CHCl_3$).

(*R*)-2,6-Bis-(triphenylsilyl)-4-oxo-3,5-dioxa-4λ^5-phospha-cyclohepta [2,1a;3,4-a'] dinaphthalen-4-ol (catalyst 5)

Diol **v** (9.7 g, 12.1 mmol) was suspended in pyridine (34.0 mL). Phosphorous oxychloride (3.7 g, 2.3 mL, 24.2 mmol) was added dropwise at room temperature with rapid stirring and the resulting suspension was heated to 95 ˚C. Upon reaching 95 ˚C all material had dissolved to provide a pale yellow clear solution (note: reaction carried out in a 1-neck flask equipped with a condensor – $POCl_3$ added via long needle down condensor. Mixture not refluxed). The reaction mixture was stirred for 24 hours at 95 ˚C until all starting material was deemed consumed by tlc (note: by the end of the reaction a precipitate of pyridine-HCl salt forms). The reaction mixture was cooled to 0 ˚C and water (10 mL) was added very slowly. The resulting biphasic suspension was heated to 95 ˚C for an additional 6 h. The reaction mixture was diluted with CH_2Cl_2 and the pyridine was removed via washing with 1*N* HCl. The combined organic phase was dried over Na_2SO_4, filtered and concentrated to give crude product as a pale yellow solid. Purification by flash column chromatography (gradient from 1% to 4% MeOH in CH_2Cl_2) yielded catalyst **5** as a white solid (9.02 g, 86% yield). IR (film) 1428, 1106, 701 cm^{-1}; ^1H NMR (300 MHz, $(CD_3)_2SO$) δ 7.08 (d, 2H, J = 8.1 Hz, ArH), 7.28-7.47 (m, 22H, ArH), 7.52-7.63 (m, 12H, ArH), 7.87 (d, 2H, J = 7.8 Hz, ArH), 8.05 (s, 2H, ArH); ^{13}C NMR (75 MHz, $(CD_3)_2SO$) δ 121.19, 125.41, 125.78, 126.17, 127.74, 128.76, 129.51, 129.76, 133.50, 134.01, 136.32, 141.10, 152.10, 152.12; HRMS (FAB+) exact mass calculated for [M+] ($C_{56}H_{41}O_4Si_2P$) requires m/z 864.2281, found m/z 864.2296. $[\alpha]_D^{23}$ = –156.0º (c = 1.02, $CHCl_3$).

Reductive Amination General Procedure: A 20 mL vial equipped with a magnetic stir bar was charged with amine (123 mg, 1.0 equiv), Hantzsch ester (304 mg, 1.2 equiv), catalyst (86 mg, 10 mol%) and 5Å molecular sieves (1 g). Benzene (10 mL) was added followed by ketone (3.0 equiv). The reaction mixture was heated with stirring to 40-50 ºC as noted and monitored by TLC. Upon completion or 96 hours, the reaction mixture was filtered through a plug of silica, eluting with Et_2O to remove the molecular sieves and unreacted Hantzsch, then concentrated *in vacuo*.

Workup procedure A: The crude product was dissolved in Et_2O (100 mL) and extracted with 1N HCl (2 × 60 mL). The combined aqueous phases were basified to pH 10 with aqueous KOH and extracted with CH_2Cl_2 (2 × 80 mL). The combined organic phase was dried ($MgSO_4$) and concentrated *in vacuo*. The product was purified by silica gel chromatography (solvents noted) to yield the title compounds.

Workup procedure B: The crude product was directly purified by silica gel column chromatography (solvents noted) to yield the title compounds.

Absolute configurations of known compounds were assigned by comparison of HPLC retention times and optical rotations to literature values.

(*R*)-*N*-(4-methoxyphenyl)-[1-(phenyl)-ethyl]amine (Table 2, entry 1):

Prepared according to the general procedure from *p*-anisidine (83 mg, 0.67 mmol) and acetophenone (235 μL, 2.01 mmol) at 50 ºC for 24 h, using workup procedure B to provide the title compound as a yellow oil (162 mg, 87% yield, 94% ee) following silica gel chromatography (10% Et_2O/pentane). IR (film) 3395, 2977, 1514, 1450, 1235, 1034, 822, 758, 703 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.51 (d, 3H, *J* = 6.6 Hz, -C**H**$_3$), 3.69 (s, 3H, -OC**H**$_3$), 4.41 (q, 1H, *J* = 6.9 Hz, -C**H**CH_3), 6.47-6.50 (m, 2H, ArH), 6.67-6.70 (m, 2H, ArH), 7.22-7.26 (m, 1H, ArH), 7.26-7.38 (m, 4H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.18, 54.27, 55.75, 114.58, 114.78, 125.93, 126.86, 128.65, 141.59, 145.52, 151.91; HRMS (EI) exact mass calculated for ($C_{15}H_{17}NO$) requires *m/z* 227.1310, found *m/z* 227.1335. $[\alpha]_D^{25}$ = +3.9º (c = 0.18, $CHCl_3$).[9] The enantiomeric ratio was determined by

[9] Zhang, X.; Chi, Y.; Zhou, Y.G. *J. Org. Chem.* **2003**, *68*, 4120. (reported a rotation of + 7.0º (c = 2, $CHCl_3$) for a product that was 94% ee)

GLC using a Chirasil-Dex-CB column (150 ºC isotherm for 150 minutes, 1 mL/min); major enantiomer t_r = 81.43 min and minor enantiomer t_r = 79.91 min.

(+)-*N*-(4-methoxyphenyl)-[1-(4-tolyl)-ethyl]amine (Table 2, entry 2):
Prepared according to the general procedure from *p*-anisidine (105 mg, 0.853 mmol) and 4'-methylacetophenone (342 μL, 2.56 mmol) at 50 ºC for 72 h, using workup procedure B to provide the title compound as a yellow oil (161 mg, 79% yield, 91% ee) following silica gel chromatography (5% Et_2O/pentane). IR (film) 3401, 2962, 2831, 1618, 1511, 1443, 1370, 1295, 1235, 1178, 1140, 1111, 1038, 816, 758 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.48 (d, 3H, *J* = 6.9 Hz, C**H**$_3$), 2.32 (s, 3H, -C_6H_4C**H**$_3$), 3.68 (s, 3H, -OC**H**$_3$), 4.38 (q, 1H, *J* = 6.6 Hz, -C**H**CH_3), 6.45-6.51 (m, 2H, ArH), 6.67-6.72 (m, 2H, ArH), 7.11-7.14 (m, 2H, ArH), 7.24-7.27 (m, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.07, 25.14, 53.96, 55.73, 114.55, 114.73, 125.79, 129.29, 136.34, 141.58, 142.42, 151.84; HRMS (EI) exact mass calculated for ($C_{16}H_{19}NO$) requires *m/z* 241.1467 found *m/z* 241.1476. $[\alpha]_D^{28}$ = +6.9º (c = 0.20, $CHCl_3$). The enantiomeric ratio was determined by SFC using a Chiralcel AD-H column (5-50% methanol/CO_2, 35 ºC, 100 bar, 4 mL/min, ramp rate = 5% /min); major enantiomer t_r = 3.88 min and minor enantiomer t_r = 3.57 min.

(+)-*N*-(4-methoxyphenyl)-[1-(4-methoxyphenyl)-ethyl]amine (Table 2, entry 3):
Prepared according to the general procedure from *p*-anisidine (110 mg, 0.890 mmol) and 4'-methoxyacetophenone (401 mg, 2.67 mmol) at 50 ºC for 72 h, using workup procedure A to provide the title compound as a tan solid (177 mg, 77% yield, 90% ee) following silica gel chromatography (3% Et_2O/toluene). IR (film) 3401, 2938, 2834, 1611, 1511, 1463, 1372, 1283, 1236, 1177, 1141, 1111, 1037, 819 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.47 (d, 3H, *J* = 6.6 Hz, -C**H**$_3$), 3.69 (s, 3H, -OC**H**$_3$), 3.78 (s, 3H, -OC**H**$_3$), 4.37 (q, 1H, *J* = 6.6 Hz, -C**H**CH_3), 6.46-6.49 (m, 2H, ArH), 6.68-6.70 (m, 2H, ArH), 6.84-6.86 (m, 2H, ArH), 7.26-7.29 (m, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.09, 53.71, 55.24, 55.73, 113.95, 114.66, 114.71, 126.94, 137.39, 141.48, 151.90, 158.42; HRMS (EI) exact mass calculated for ($C_{16}H_{19}NO_2$) requires *m/z* 257.1416, found *m/z* 257.1425. $[\alpha]_D^{22}$ = +16.1º (c = 1.95, $CHCl_3$). The enantiomeric ratio was determined

by HPLC using a Chiralcel OD-H column (5% isopropanol/hexanes); major enantiomer t_r = 20.62 min and minor enantiomer t_r = 22.64 min.

(+)-*N*-(4-methoxyphenyl)-[1-(4-nitrophenyl)-ethyl]amine (Table 2, entry 4):
Prepared according to the general procedure from *p*-anisidine (114 mg, 0.927 mmol) and 4'-nitroacetophenone (459 mg, 2.78 mmol) at 50 ºC for 72 h, using workup procedure A to provide the title compound as an orange solid (118 mg, 71% yield, 95% ee) following silica gel chromatography (30% Et_2O/pentane). IR (film) 3402, 2968, 1598, 1511, 1451, 1344, 1235, 1178, 1143, 1109, 1036, 855, 819, 751, 700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.52 (d, 3H, *J* = 6.6 Hz, -C**H**$_3$), 3.68 (s, 3H, -OC**H**$_3$), 4.49 (q, 1H, *J* = 6.9 Hz, -C**H**CH_3), 6.38-6.41 (m, 2H, ArH), 6.67-6.70 (m, 2H, ArH), 7.52-7.55 (m, 2H, ArH), 8.16-8.19 (m, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.99, 54.03, 55.68, 114.53, 114.82, 124.04, 126.78, 140.69, 146.99, 152.29, 153.50; HRMS (EI) exact mass calculated for ($C_{15}H_{16}N_2O_3$) requires *m/z* 272.1161, found *m/z* 272.1164. $[\alpha]_D^{25}$ = +29.8º (c = 0.20, $CHCl_3$). The enantiomeric ratio was determined by SFC using a Chiralcel OD-H column (10% methanol/CO_2, 35 ºC, 100 bar, 4 mL/min); major enantiomer t_r = 8.41 min and minor enantiomer t_r = 7.88 min.

(+)-*N*-(4-methoxyphenyl)-[1-(4-chlorophenyl)-ethyl]amine (Table 2, entry 5):
Prepared according to the general procedure from *p*-anisidine (101 mg, 0.818 mmol) and 4'-chloroacetophenone (379 mg, 2.45 mmol) at 50 ºC for 72 h, using workup procedure A to provide the title compound as a yellow oil (161 mg, 75% yield, 95% ee) following silica gel chromatography (15% Et_2O/pentane). IR (film) 3401, 2964, 2831, 1618, 1512, 1490, 1464, 1451, 1407, 1372, 1289, 1235, 1204, 1179, 1141, 1092, 1038, 1013, 942, 819, 778, 759 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.47 (d, 3H, *J* = 6.9 Hz, -C**H**$_3$), 3.69 (s, 3H, -OC**H**$_3$), 4.38 (q, 1H, *J* = 6.6 Hz, -C**H**CH_3), 6.42-6.45 (m, 2H, ArH), 6.67-6.70 (m, 2H, ArH), 7.26-7.29 (m, 4H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.21, 53.75, 55.73, 114.60, 114.80, 127.36, 128.80, 132.34, 141.28, 144.16, 152.05; HRMS (EI) exact mass calculated for ($C_{15}H_{16}NOCl$) requires *m/z* 261.0920, found *m/z* 261.0912. $[\alpha]_D^{24}$ = +14.8º (c = 1.88, $CHCl_3$). The enantiomeric ratio was determined by GLC using a Chirasil-Dex-

CB column (160 ºC isotherm for 150 minutes, 1mL/min); major enantiomer t_r = 134.59 min and minor enantiomer t_r = 132.02 min.

(–)-*N*-(4-methoxyphenyl)-[1-(4-fluorophenyl)-ethyl]amine (Table 2, entry 6): Prepared according to the general procedure from *p*-anisidine (126 mg, 1.02 mmol) and 4'-fluoroacetophenone (371 μL, 3.07 mmol) at 50 ºC for 72 h, using workup procedure A to provide the title compound as a yellow oil (188 mg, 75% yield, 94% ee) following silica gel chromatography (2% Et_2O/toluene). IR (film) 3402, 2965, 2833, 1603, 1511, 1464, 1414, 1373, 1293, 1235, 1180, 1155, 1140, 1093, 1038, 835, 819, 758 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.48 (d, 3H, *J* = 6.6 Hz, -C**H**$_3$), 3.70 (s, 3H, -OC**H**$_3$), 4.39 (q, 1H, *J* = 6.9Hz, -C**H**CH_3), 6.44-6.47 (m, 2H, ArH), 6.68-6.71 (m, 2H, ArH), 6.96-7.02 (m, 2H, ArH), 7.30-7.35 (m, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.27, 53.69, 55.72, 114.63, 114.78, 115.27, 115.55, 127.34, 127.45, 141.16, 141.20, 141.36, 152.02, 160.12, 163.35; HRMS (EI) exact mass calculated for ($C_{15}H_{16}NFO$) requires *m/z* 245.1216, found *m/z* 245.1206. $[\alpha]_D^{26}$ = –19.4º (c = 0.29, $CHCl_3$). The enantiomeric ratio was determined by SFC using a Chiralcel AD-H column (5-50% methanol/CO_2, 35 ºC, 100 bar, 4 mL/min, ramp rate = 5% /min); major enantiomer t_r = 3.30 min and minor enantiomer t_r = 2.99 min.

(–)-*N*-(4-methoxyphenyl)-[1-(3-fluorophenyl)-ethyl]amine (Table 2, entry 7): Prepared according to the general procedure from *p*-anisidine (122 mg, 0.993 mmol) and 3'-fluoroacetophenone (366 μL, 2.98 mmol) at 50 ºC for 72 h, using workup procedure B to provide the title compound as a yellow oil (198 mg, 81% yield, 95% ee) following silica gel chromatography (1% Et_2O/toluene). IR (film) 3401, 2966, 2833, 1613, 1590, 1512, 1482, 1449, 1407, 1373, 1341, 1294, 1235, 1173, 1154, 1123, 1038, 895, 819, 786, 697 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.49 (d, 3H, *J* = 6.6 Hz, -C**H**$_3$), 3.70 (s, 3H, -OC**H**$_3$), 4.39 (q, 1H, *J* = 6.9, -C**H**CH_3), 6.46 (m, 2H, ArH), 6.68-6.71 (m, 2H, ArH), 6.90-6.94 (m, 1H, ArH), 7.05-7.15 (m, 2H, ArH), 7.26-7.31 (m, 1H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.11, 53.97, 55.72, 112.60, 112.88, 113.57, 113.85, 114.53, 114.77, 121.51, 121.55, 130.07, 130.18, 141.23, 148.53, 148.61, 152.05, 161.63, 164.88; HRMS (EI) exact mass calculated for ($C_{15}H_{16}NFO$) requires *m/z* 245.1216, found *m/z* 245.1209. $[\alpha]_D^{27}$

= –5.2° (c = 0.19, $CHCl_3$). The enantiomeric ratio was determined by SFC using a Chiralcel AD-H column (5-50% isopropanol/CO_2, 35 °C, 100 bar, 4 mL/min, ramp rate = 5% /min); major enantiomer t_r = 3.45 min and minor enantiomer t_r = 3.70 min.

(+)-*N*-(4-methoxyphenyl)-[1-(2-fluorophenyl)-ethyl]amine (Table 2, entry 8): Prepared according to the general procedure from *p*-anisidine (135 mg, 1.10 mmol) and 2'-fluoroacetophenone (400 μL, 3.29 mmol) at 50 °C for 72 h, using workup procedure B to provide the title compound as a yellow oil (160 mg, 60% yield, 83% ee) following silica gel chromatography (10% Et_2O/pentane). IR (film) 3401, 2969, 1615, 1586, 1513, 1486, 1451, 1408, 1374, 1354, 1293, 1267, 1236, 1221, 1181, 1156, 1143, 1110, 1084, 1038, 943, 820, 758 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.50 (d, 3H, *J* = 6.6 Hz, -C**H**$_3$), 3.67 (s, 3H, -OC**H**$_3$), 4.72 (q, 1H, *J* = 6.6Hz, -C**H**CH_3), 6.45-6.48 (m, 2H, ArH), 6.66-6.69 (m, 2H, ArH), 6.97-7.06 (m, 2H, ArH), 7.14-7.18 (m, 1H, ArH), 7.32-7.37 (m, 1H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.39, 48.23, 48.26, 55.67, 114.51, 114.79, 115.31, 124.36, 124.41, 127.25, 127.32, 128.19, 128.30, 131.86, 132.03, 141.13, 152.07, 158.92, 162.16; HRMS (EI) exact mass calculated for ($C_{15}H_{16}FNO$) requires *m/z* 245.1216, found *m/z* 245.1211. $[\alpha]_D^{27}$ = +18.8° (c = 0.19, $CHCl_3$). The enantiomeric ratio was determined by SFC using a Chiralcel OJ-H column (5-50% methanol/CO_2, 35 °C, 100 bar, 4 mL/min, ramp rate = 5% /min); major enantiomer t_r = 3.46 min and minor enantiomer t_r = 3.81 min.

(*R*)-*N*-(4-methoxyphenyl)-[1-(naphthalen-2-yl)-ethyl]amine (Table 2, entry 9): Prepared according to the general procedure from *p*-anisidine (126 mg, 1.02 mmol) and 2'-acetonapthone (521 mg, 3.06 mmol) at 50 °C for 72 h. Upon completion the reaction was filtered through silica eluting with Et_2O and concentrated *in vacuo*. The crude residue was dissolved in 50 mL Et_2O and stirred for 1 hour with 1N HCl (100 mL). The white HCl salt was collected *via* gravity filtration, dissolved in CH_2Cl_2 and stirred with saturated aqueous $NaHCO_3$ for 30 minutes. The layers were separated, the organic phase dried over $MgSO_4$ and concentrated *in vacuo* to provide the title compound as a light pink solid (207 mg 73% yield, 96% ee). IR (film) 3401, 2963, 2832, 2361, 1601, 1512, 1441, 1373, 1294, 1234, 1179, 1134, 1037,895, 858, 818, 749 cm^{-1}; ^1H NMR (300 MHz,

$CDCl_3$) δ 1.60 (d, 3H, *J* = 6.6 Hz, -C**H**$_3$), 3.67 (s, 3H, -OC**H**$_3$), 4.57 (q, 1H, *J* = 6.9 Hz, -C**H**CH_3), 6.54-6.57 (m, 2H, ArH), 6.65-6.68 (m, 2H, ArH), 7.42-7.53 (m, 3H, ArH), 7.77-7.82 (m, 4H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.19, 54.55, 55.74, 114.67, 114.79, 124.36, 124.50, 125.51, 126.02, 127.71, 127.86, 128.48, 132.77, 133.62, 141.60, 143.07, 151.97; HRMS (EI) exact mass calculated for ($C_{19}H_{19}NO$) requires *m/z* 277.1467, found *m/z* 277.1423. $[\alpha]_D^{25}$ = +30.9° (c = 0.20, $CHCl_3$).[10] The enantiomeric ratio was determined by HPLC using a Chiralcel OD-H column (3% isopropanol/hexanes); major enantiomer t_r = 21.96 min and minor enantiomer t_r = 26.97 min.

(+)-*N*-(4-methoxyphenyl)-aminoindane (Table 2, entry 10):

Prepared according to the general procedure from *p*-anisidine (101 mg, 0.823 mmol) and 1-indanone (326 mg, 2.47 mmol) at 50 ° C for 72 h, using workup procedure B to provide the title compound as a brown solid (149 mg, 75% yield, 85% ee) following silica gel chromatography (5% Et_2O/pentane). IR (film) 3370, 3028, 2934, 2826, 2361, 1628, 1511, 1460, 1232, 1178, 1079, 1037, 818, 755 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.85-1.97 (m, 1H, -CH(C**H**$_2$)$_2$$C_6H_4$), 2.51-2.62 (m, 1H, -CH(C**H**$_2$)$_2$$C_6H_4$), 2.83-2.93 (m, 1H, -CH(C**H**$_2$)$_2$$C_6H_4$), 2.97-3.07 (m, 1H, -CH(C**H**$_2$)$_2$$C_6H_4$), 3.71 (s, 3H, -OC**H**$_3$), 4.96 (q, 1H, *J* = 6.6 Hz, -C**H**CH_3), 6.69-6.72 (m, 2H, ArH), 6.80-6.83 (m, 2H, ArH), 7.20-7.27 (m, 3H, ArH), 7.37 (d, 1H, *J* = 6.9 ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 30.23, 33.85, 55.85, 59.55, 114.66, 114.99, 124.29, 124.86, 126.59, 127.85, 141.92, 143.60, 144.76, 152.16; HRMS (EI) exact mass calculated for ($C_{16}H_{17}NO$) requires *m/z* 239.1310, found *m/z* 239.1284. $[\alpha]_D^{24}$ = +45.4° (c = 0.22, $CHCl_3$). The enantiomeric ratio was determined by SFC using a Chiralcel AD-H column (5-50% methanol/CO_2, 35 °C, 100 bar, 4 mL/min, ramp rate = 5% /min); major enantiomer t_r = 5.06 min and minor enantiomer t_r = 5.73 min.

(+)-*N*-(4-methoxyphenyl)-[2-fluoro-(1-phenyl)-ethyl]amine (Table 2, entry 11):

Prepared according to the general procedure from *p*-anisidine (53 mg, 0.43 mmol) and 2-fluoroacetophenone (177 μL, 1.28 mmol) at 5 °C for 96 h, using workup procedure B to

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[10] Nakamura, S.; Yasuda, H.; Toru, T. *Tetrahedron: Asymmetry* **2002**, *13*, 1509 (reported HPLC retention times *R*t_r = 18.1 min and *S*t_r = 21.3 min using a Chiralcel OD-H column, 10% hexane/^{i}PrOH)

provide the title compound as a yellow oil (71 mg, 70% yield, 88% ee) following silica gel chromatography (7% Et_2O/pentane). IR (film) 3400, 3029, 2951, 2902, 2833, 1618, 1513, 1453, 1293, 1243, 1179, 1094, 1036, 1005, 939, 920, 820, 755, 701 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.68 (s, 3H, -OC**H**$_3$), 4.37-4.71 (m, 3H, -C**H**C**H**$_2$$CH_2$F), 6.49-6.52 (m, 2H, ArH), 6.66-6.69 (m, 2H, ArH), 7.24-7.42 (m, 5H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.68, 59.34, 59.59, 84.99, 87.35, 114.74, 115.26, 127.05, 128.00, 128.90, 138.50, 138.58, 141.09, 152.54. HRMS (EI) exact mass calculated for ($C_{15}H_{16}NOF$) requires *m/z* 245.1216 found *m/z* 245.1204. $[\alpha]_D^{28}$ = +9.8° (c = 0.26, $CHCl_3$). The enantiomeric ratio was determined by SFC using a Chiralcel AD-H column (5-50% methanol/CO_2, 35 °C, 100 bar, 4 mL/min, ramp rate = 5% /min); major enantiomer t_r = 3.80 min and minor enantiomer t_r = 4.46 min.

(–)-3-methyl-3,4-dihydro-benzo-[1,4]-oxazin-2-one (6) (Table 2, entry 12):

An oven dried 20 mL vial equipped with a magnetic stir bar was charged with imine (200 mg, 0.621 mmol), Hantzsch ester (378 mg, 0.745 mmol) and catalyst (54 mg, 0.031 mmol). Benzene (6.2 mL) was added and the reaction mixture was heated at 40 °C for 7 h. Upon completion the product was isolated using workup procedure B to provide the title compound as a white solid (163 mg, 82% yield, 97% ee) following silica gel chromatography (25% Et_2O/pentane). IR (film) 3317, 1752, 1619, 1595, 1503, 1457, 1339, 1306, 1292, 1208, 1197, 1182, 1097, 1040, 748, 690 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.54 (d, 3H, *J* = 6.6 Hz, -C**H**$_3$), 3.98 (q, 1H, *J* = 6.6Hz, -C**H**CH_3), 6.75-6.78 (m, 1H, ArH), 6.84-6.89 (m, 1H, ArH), 6.97-7.26 (m, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.21, 50.57, 115.02, 116.88, 120.49, 124.91, 132.96, 141.43, 167.25; HRMS (EI) exact mass calculated for ($C_9H_9NO_2$) requires *m/z* 163.0633, found *m/z* 163.0633. $[\alpha]_D^{27}$ = –38.4° (c = 0.24, $CHCl_3$). The enantiomeric ratio was determined by GLC using a Chiraldex Γ-TA column (150 °C isotherm for 30 minutes); major enantiomer t_r = 20.08 min and minor enantiomer t_r = 18.95 min.

(–)-*N-sec*-butyl-(4-methoxyphenyl)amine (Table 3, entry 1):

Prepared according to the general procedure from *p*-anisidine (105 mg, 0.853 mmol) and 2-butanone (185 μL, 2.56 mmol) at 40 °C for 72 h, using workup procedure B to provide the title compound as a yellow oil (107 mg, 71% yield, 83% ee) following silica gel chromatography (9% Et_2O/pentane). IR (film) 3392, 2963, 2931, 2875, 2832, 1512, 1464, 1407, 1375, 1294, 1232, 1164, 1041, 819, 755 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.94 (dd, 3H, *J* = 7.5, 7.5 Hz, -CH_2**C**$\mathbf{H}_3$), 1.14 (d, 3H, *J* = 6.0 Hz, -**C**$\mathbf{H}_3$), 1.35-1.68 (m, 2H, -**C**$\mathbf{H}_2$$CH_3$), 3.31 (sextet, 1H, *J* = 6.3 Hz, -**CH**CH_3), 3.71 (s, 3H, -O**C**$\mathbf{H}_3$), 6.55-6.58 (m, 2H, ArH), 6.76-6.79 (m, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 10.40, 20.27, 29.64, 50.80, 55.80, 114.70, 114.94, 141.99, 151.78; HRMS (EI) exact mass calculated for ($C_{11}H_{17}NO$) requires *m/z* 179.1310, found *m/z* 179.1302. $[\alpha]_D^{28}$ = –25.2º (c = 0.24, $CHCl_3$). The enantiomeric ratio was determined by GLC using a CP-Chirasil-Dex-CB column (100 ºC isotherm for 140 minutes); major enantiomer t_r = 130.90 min and minor enantiomer t_r = 128.72 min.

(–)-*N*-(4-methoxyphenyl)-[1-(methyl)-heptyl]amine (Table 3, entry 2):

Prepared according to the general procedure from *p*-anisidine (105 mg, 0.853 mmol) and 2-octanone (400 μL, 2.56 mmol) at 40 ºC for 96 h, using workup procedure B to provide the title compound as a clear oil (144 mg, 72% yield, 91% ee) following silica gel chromatography (4% Et_2O/pentane). IR (film) 3393, 2957, 2929, 2856, 2832, 1840, 1618, 1512, 1465, 1407, 1376, 1294, 1234, 1180, 1157, 1108, 1042, 818, 757, 724 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.86 (t, 3H, *J* = 6.6 Hz, -$(CH_2)_5$**C**$\mathbf{H}_3$), 1.12 (d, 3H, *J* = 6.3 Hz, -**C**$\mathbf{H}_3$), 1.26-1.41 (m, 10H, -CH(**C**$\mathbf{H}_2$)$_5$$CH_3$), 3.33 (m, 1H, *J* = 6.3, -**CH**CH_3), 3.73 (s, 3H, -O**C**$\mathbf{H}_3$), 6.52-6.55 (m, 2H, ArH), 6.74-6.77 (m, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.14, 20.82, 22.67, 26.19, 29.44, 31.90, 37.28, 49.50, 55.78, 114.66, 114.94, 142.02, 151.76; HRMS (EI) exact mass calculated for ($C_{15}H_{25}NO$) requires *m/z* 235.1936, found *m/z* 235.1932. $[\alpha]_D^{27}$ = –8.0º (c = 1.14, CH_2Cl_2). The enantiomeric ratio was determined by SFC using a Chiralcel OJ-H column (5-10% methanol/CO_2, 35 ºC, 100 bar, 4 mL/min, ramp rate = 0.5% /min); major enantiomer t_r = 2.70 min and minor enantiomer t_r = 2.94 min.

***(R)*-*N*-(4-methoxyphenyl)-[1-(methyl)-3-phenylpropyl]amine (Table 3, entry 3):**

Prepared according to the general procedure from *p*-anisidine (124 mg, 1.01 mmol) and benzylacetone (450 μL, 3.03 mmol) at 40 ºC for 72 h, using workup procedure A to provide the title compound as a yellow oil (193 mg, 75% yield, 94% ee) following silica gel chromatography (10% Et_2O/pentane). IR (film) 3392, 3025, 2930, 2830, 1714, 1602, 1511, 1453, 1407, 1373, 1293, 1234, 1179, 1153, 1039, 819, 748, 699 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.18 (d, 3H, *J* = 6.3 Hz, -C**H**$_3$), 1.66-1.76 (m, 1H, -CHC**H**$_2$CH$_2$C$_6$H$_5$), 1.78-1.92 (m, 1H, -CHC**H**$_2$CH$_2$C$_6$H$_5$), 2.68-2.73 (dd, 2H, *J* = 7.8, -CHCH$_2$C**H**$_2$C$_6$H$_5$), 3.33-3.41 (m, 1H, *J* = 7.8, 7.8 Hz, -C**H**CH$_3$), 3.72 (s, 3H, -OC**H**$_3$), 6.46-6.53 (m, 2H, ArH), 6.71-6.77 (m, 2H, ArH), 7.14-7.19 (m, 3H, ArH), 7.25-7.30 (m, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.90, 32.55, 38.87, 48.99, 55.83, 114.83, 114.99, 125.88, 128.44, 128.50, 141.78, 142.15, 151.93; HRMS (EI) exact mass calculated for ($C_{17}H_{21}NO$) requires *m/z* 255.1623, found *m/z* 255.1623. $[\alpha]_D^{27}$ = –2.8° (c = 1.20, CH_2Cl_2).[11] The enantiomeric ratio was determined by SFC using a Chiralcel AD-H column (5-50% methanol/CO_2, 35 °C, 100 bar, 4 mL/min, ramp rate = 5% /min); major enantiomer t_r = 3.88 min and minor enantiomer t_r = 4.57 min.

(–)-*N*-(4-methoxyphenyl)-[1-(cyclohexyl)-ethyl]amine (Table 3, entry 4): Prepared according to the general procedure from *p*-anisidine (123 mg, 1.00 mmol) and cyclohexylmethyl ketone (413 μL, 3.00 mmol) at 50 °C for 96 h, using workup procedure B to provide the title compound as a yellow oil (115 mg, 49% yield, 86% ee) following silica gel chromatography (10% Et_2O/pentane). IR (film) 3400, 2924, 2851, 1618, 1511, 1464, 1449, 1407, 1372, 1294, 1236, 1180, 1159, 1102, 1041, 890, 817, 754 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.99-1.21 (m, 5H, -C$_6$**H**$_{11}$) 1.06 (d, 3H, *J* = 6.6 Hz, C**H**$_3$), 1.39-1.43 (m, 1H, -C$_6$**H**$_{11}$), 1.66-1.75 (m, 5H, -C$_6$**H**$_{11}$), 3.18-3.22 (m, 1H, -C**H**CH$_3$), 3.72 (s, 3H, -OC**H**$_3$), 6.52-6.55 (m, 2H, ArH), 6.73-6.76 (m, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.35, 26.38, 26.53, 26.69, 28.27, 29.88, 42.86, 54.14, 55.83, 114.53, 114.95, 142.22, 151.60; HRMS (EI) exact mass calculated for ($C_{15}H_{23}NO$) requires *m/z* 233.1780, found *m/z* 233.1786. $[\alpha]_D^{28}$ = –4.3° (c = 1.09, $CHCl_3$). The enantiomeric ratio was determined by SFC using a Chiralcel AS-H column (5-25% methanol/CO_2, 35 °C, 100

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[11] Arrasate, S.; Lete, E.; Sotomayor, N. *Tetrahedron: Asymmetry*, **2001**, *12*, 2077. (reported a rotation of –9.1° (c = 1.2, CH_2Cl_2) for a product that was 23% ee and HPLC retention times *R*t_r = 23.6 min and *S*t_r = 26.6 min using a Chiralcel OD column, 2% hexanes/2-propanol)

bar, 4 mL/min, ramp rate = 2% /min); major enantiomer t_r = 2.49 min and minor enantiomer t_r = 1.90 min.

(+)-*N*-(4-methoxyphenyl)-[1-(methyl)-2-benzoate-ethyl]amine (Table 3, entry 5): Prepared according to the general procedure from *p*-anisidine (53 mg, 0.43 mmol) and 2-oxopropyl benzoate (230 µL , 1.29 mmol) at 40 ºC for 96 h, using workup procedure B to provide the title compound as a yellow oil (73 mg, 72% yield, 81% ee) following silica gel chromatography (1% Et_2O/ toluene). IR (film) 3392, 2968, 2359, 1719, 1601, 1513, 1451, 1387, 1371, 1315, 1274, 1234, 1177, 1111, 1071, 1027, 821, 712 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.30 (d, 3H, *J* = 6.6 Hz, -C**H**$_3$), 3.73 (s, 3H, -OC**H**$_3$), 3.79-3.84 (m, 1H, -C**H**CH_3), 4.17-4.22 (m, 1H, -C**H**$_2OCOC_6H_5$), 4.41-4.46 (m, 1H, -C**H**$_2OCOC_6H_5$), 6.64-6.67 (m, 2H, ArH), 6.74-6.78 (m, 2H, ArH), 7.39-7.45 (m, 2H, ArH), 7.52-7.57 (m, 1H, ArH), 7.98-8.02 (m, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.30, 48.86, 55.78, 67.98, 114.99, 115.08, 128.41, 129.62, 130.02, 133.08, 141.04, 152.39, 166.57. HRMS (EI) exact mass calculated for ($C_{17}H_{19}NO_3$) requires *m/z* 285.1365, found *m/z* 285.1367. $[\alpha]_D^{26}$ = +12.8º (c = 0.21, CH_2Cl_2). The enantiomeric ratio was determined by SFC using a Chiralcel AD-H column (5-50% methanol/CO_2, 35 ºC, 100 bar, 4 mL/min, ramp rate = 5% /min); major enantiomer t_r = 6.80 min and minor enantiomer t_r = 4.97 min.

(–)-*N*-(4-methoxyphenyl)-[1-(methyl)-pent-4-enyl]amine (Table 3, entry 6): Prepared according to the general procedure from *p*-anisidine (70 mg, 0.57 mmol) and 5-hexen-2-one (200 µL, 1.70 mmol) at 40 ºC for 96 h, using workup procedure B to provide the title compound as a yellow oil (70 mg, 60% yield, 90% ee) following silica gel chromatography (10% Et_2O/ pentane). IR (film) 3391, 3075, 2960, 2932, 2832, 2852, 2360, 2069, 1840, 1712, 1640, 1618, 1513, 1464, 1442, 1408, 1375, 1293, 1235, 1180, 1157, 1040, 996, 911, 819, 755 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.14 (d, 3H, *J* = 6.3 Hz, -C**H**$_3$), 1.41-1.54 (m, 1H, -C**H**$_2CH_2CHCH_2$), 1.61-1.66 (m, 1H, -C**H**$_2CH_2CHCH_2$), 2.10-2.17 (m, 2H, -CH_2C**H**$_2CHCH_2$), 3.38 (q, 1H, *J* = 6.3 Hz, -C**H**CH_3), 3.72 (s, 3H, -OC**H**$_3$), 4.93-5.05 (m, 2H, -CH_2CH_2CHC**H**$_2$), 5.76-5.85 (m, 1H, -CH_2CH_2C**H**CH_2), 6.53-6.56 (m, 2H, ArH), 6.74-6.77 (m, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.77, 30.46, 36.26, 49.03, 55.79, 114.73, 114.74, 114.95, 138.45, 141.84, 151.84. HRMS (EI) exact mass calculated for ($C_{13}H_{19}NO$) requires *m/z* 205.1467, found *m/z* 205.1470. $[\alpha]_D^{28}$ = –3.8º (c = 0.40, $CHCl_3$). The enantiomeric ratio was determined by SFC using a Chiralcel OJ-H column (5-50% isopropanol/CO_2, 35 ºC, 100 bar, 4 mL/min, ramp rate = 5% /min); major enantiomer t_r = 2.74 min and minor enantiomer t_r = 2.98 min.

***(R)*-*N*-[1-(phenyl)-ethyl]aniline (Table 4, entry 1):**

Prepared according to the general procedure from aniline (93 mg, 1.0 mmol) and acetophenone (351 uL, 3.00 mmol) at 50 ºC for 24 h, using workup procedure B to provide the title compound as a yellow oil (145 mg, 73% yield, 93% ee) following silica gel chromatography (8% Et_2O/pentane). IR (film) 3410, 3052, 3023, 2966, 2924, 2867, 1947, 1817, 1720, 1601, 1505, 1449, 1428, 1372, 1352, 1319, 1280, 1258, 1206, 1180, 1140, 1077, 1029, 749, 700, 692 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.50 (d, 3H, *J* = 6.6 Hz, C**H**$_3$), 4.47 (q, 1H, *J* = 6.6 Hz, -C**H**CH_3), 6.48-6.51 (m, 2H, ArH), 6.60-6.66 (m, 1H, ArH), 7.04-7.10 (m, 2H, ArH), 7.18-7.24 (m, 2H, ArH), 7.27-7.37 (m, 3H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.43, 53.80, 113.69, 117.62, 126.24, 127.26, 129.04, 129.51, 145.63, 147.67; HRMS (EI) exact mass calculated for ($C_{14}H_{15}N$) requires *m/z* 197.1205 found *m/z* 197.1196. $[\alpha]_D^{28}$ = –16.9º (c = 1.35, CH_3OH).[12] The enantiomeric ratio was determined by HPLC using an OD-H column (2% isopropanol/hexanes); major enantiomer t_r = 20.68 min and minor enantiomer t_r = 17.46 min.

(–)-*N*-1-(phenylethyl)-[4-(trifluoromethyl)-phenyl]amine (Table 4, entry 2):

Prepared according to the general procedure from *p*-(trifluoromethyl)aniline (124 μL, 1.00 mmol) and acetophenone (351 μL, 3.00 mmol) at 40 ºC for 24 h, using workup procedure B to provide the title compound as a clear oil (145.3 mg, 55% yield, 95% ee) following silica gel chromatography (2% Et_2O/pentane). IR (film) 3421, 3064, 3031, 2970, 2928, 2872, 2599, 1892, 1721, 1617, 1531, 1490, 1451, 1328, 1109, 1066, 824, 764, 701 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.54 (d, 3H, *J* = 6.6 Hz, C**H**$_3$), 4.52 (q, 1H, *J* = 6.9 Hz, -C**H**CH_3), 6.51 (d, 2H, *J* = 8.7 Hz, Ar-H), 7.23-7.34 (m, 7H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.86, 53.22, 112.45, 125.71, 126.39, 126.44, 126.49, 126.54,

[12] Kanth, J.V.B.; Periasamy, M. *J. Org. Chem.* **1993**, *58*, 3156. (reported a rotation of –16º (c = 1.0, CH_3OH) for a product that was 98% ee)

127.20, 128.82, 144.23, 149.60; HRMS (EI) exact mass calculated for ($C_{15}H_{14}NF_3$) requires *m/z* 265.1078 found *m/z* 265.1076. $[\alpha]_D^{28}$ = –1.4º (c = 0.25, $CHCl_3$). The enantiomeric ratio was determined by SFC using a Chiralcel AD-H column (5-50% isopropanol/CO_2, 35 ºC, 100 bar, 4 mL/min, ramp rate = 5% /min); major enantiomer t_r = 2.52 min and minor enantiomer t_r = 2.91 min.

(+)-*N*-(6,7,8,9-tetrahydrodibenzo[*β,δ*]furan-2)-[1-(phenyl)ethyl]amine (Table 4, entry 3):

Prepared according to the general procedure from 6,7,8,9-tetrahydrodibenzo[*β,δ*]furan-2-amine (106 mg, 0.568 mmol) and acetophenone (170 μL , 1.70 mmol) at 40 ºC for 72 h; using workup procedure B to provide the title compound as a yellow oil (142.4 mg, 92% yield, 91% ee) following silica gel chromatography (100% toluene). IR (film) 3411, 3025, 2927, 2834, 1618, 1595, 1471, 1353, 1276, 1237, 1218, 1188, 1123, 834, 795, 762, 701 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.51 (d, 3H, *J* = 6.6 Hz, -C**H**$_3$), 1.73-1.88 (m, 4H, -C(C**H**$_2$)$_4$C-), 2.42-2.47 (m, 2H, -C(C**H**$_2$)$_4$C-), 2.61-2.65 (m, 2H, -C(C**H**$_2$)$_4$C-), 4.49 (q, 1H, *J* = 6.6 Hz, -C**H**CH$_3$), 6.42-6.47 (m, 2H, ArH), 7.08-7.11 (m, 1H, ArH), 7.17-7.32 (m, 3H, Ar-H), 7.35-7.39 (m, 2H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.52, 22.76, 23.03, 23.60, 25.13, 54.39, 101.85, 110.74, 110.91, 112.60, 126.01, 126.85, 128.67, 129.51, 143.25, 145.66, 148.11, 154.31; HRMS (EI) exact mass calculated for ($C_{20}H_{21}NO$) requires *m/z* 291.1623, found *m/z* 291.1620. $[\alpha]_D^{24}$ = +32.6º (c = 0.20, $CHCl_3$). The enantiomeric ratio was determined by SFC using a Chiralcel AD-H column (5-50% methanol/CO_2, 35 ºC, 100 bar, 4 mL/min, ramp rate = 5% /min); major enantiomer t_r = 6.70 min and minor enantiomer t_r = 5.75 min.

(+)-*N*-(5-benzo[*δ*]thiazol)-[1-(phenyl)-ethyl]amine (Table 4, entry 4):

Prepared according to the general procedure from benzothiazol-5-ylamine (85.3 mg, 0.568 mmol) and acetophenone (170 μL, 1.70 mmol) at 50 ºC for 72 h; using workup procedure B to provide the title compound as a yellow oil (93.0 mg, 70% yield, 91% ee) following silica gel chromatography (30% Et_2O/pentane). IR (film) 3412, 3305, 3061, 2967, 1605, 1560, 1482, 1449, 1402, 1373, 1327, 1261, 820, 701 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.55 (d, 3H, *J* = 6.9 Hz, -C**H**$_3$), 4.51 (q, 1H, *J* = 6.6 Hz, -C**H**CH$_3$), 6.76-

6.85 (m, 2H, Ar-H), 7.22-7.25 (m, 2H, Ar-H), 7.29-7.39 (m, 3H, Ar-H), 7.80-7.83 (m, 1H, Ar-H), 8.59 (s, 1H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.07, 53.85, 102.91, 115.06, 123.66, 125.80, 127.14, 128.81, 135.68, 144.53, 145.54, 145.85, 149.12; HRMS (EI) exact mass calculated for ($C_{15}H_{14}N_2S$) requires *m/z* 254.0878, found *m/z* 254.0883. $[\alpha]_D^{25}$ = +85.4° (c = 0.28, $CHCl_3$). The enantiomeric ratio was determined by SFC using a Chiralcel OJ-H column (5-50% methanol/CO_2, 35 °C, 100 bar, 4 mL/min, ramp rate = 5% /min); major enantiomer t_r = 6.70 min and minor enantiomer t_r = 5.82 min.

(+)-*N*-[1-(phenyl)-ethyl]-1-tosyl-1*H*-indol-5-amine (Table 4, entry 5):

Prepared according to the general procedure from 5-amino-*N*-tosylindole (123 mg, 0.427 mmol) and acetophenone (150 μL, 1.28 mmol) at 40 °C for 48 h, using workup procedure B to provide the title compound as a white solid (150 mg, 90% yield, 93% ee) following silica gel chromatography (17% Et_2O/pentane). IR (film) 3412, 2967, 1619, 1596, 1534, 1492, 1467, 1452, 1365, 1305, 1234, 1188, 1176, 1162, 1127, 1092, 1018, 994, 811, 759, 717, 702, 677, 665 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.49 (d, 3H, *J* = 6.9 Hz, -C**H**$_3$), 2.30 (s, 3H, -$SO_2C_6H_4C$**H**$_3$), 4.42 (q, 1H, *J* = 6.6 Hz, -C**H**CH_3), 6.36-6.38 (m, 1H, ArH), 6.47-6.48 (m, 1H, ArH), 6.57-6.61 (m, 1H, ArH), 7.05-7.36 (m, 8H, ArH), 7.65-7.71 (m, 3H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.53, 25.19, 54.05, 103.28, 109.28, 113.22, 114.25, 125.86, 126.54, 126.72, 126.92, 128.00, 128.70, 129.75, 132.00, 135.35, 144.09, 144.59, 145.30. HRMS (EI) exact mass calculated for ($C_{23}H_{22}N_2O_2S$) requires *m/z* 390.1402 found *m/z* 390.1410. $[\alpha]_D^{28}$ = +7.1° (c = 0.20, $CHCl_3$). The enantiomeric ratio was determined by SFC using a Chiralcel OJ-H column (5-55% isopropanol/CO_2, 35 °C, 100 bar, 4 mL/min, ramp rate 5.5% /min); major enantiomer t_r = 10.09 min and minor enantiomer t_r = 8.42 min.

(–)-*N*-[1-(methyl)-heptyl]-1-tosyl-1*H*-indol-5-amine (Table 4, entry 6):

Prepared according to the general procedure from 5-amino-*N*-tosylindole (123 mg, 0.427 mmol) and 2-octanone (200 μL, 1.28 mmol) at 40 °C for 72 h, using workup procedure B to provide the title compound as a yellow oil (127 mg, 75% yield, 90% ee) following silica gel chromatography (10% Et_2O/pentane). IR (film) 3410, 3140, 2956, 2927, 2855, 1618, 1596, 1582, 1534, 1494, 1467, 1398, 1367, 1305, 1233, 1188, 1176, 1164, 1129, 1092, 994, 811, 757, 716, 703, 677 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.83-0.87 (m, 3H, -$(CH_2)_5C\mathbf{H}_3$), 1.13 (d, 3H, *J* = 6.3 Hz, -$C\mathbf{H}_3$), 1.17-1.55 (m, 10H, -$(C\mathbf{H}_2)_5CH_3$), 2.31 (s, 3H, -$SO_2C_6H_4C\mathbf{H}_3$), 3.36-3.43 (m, 1H, -$C\mathbf{H}CH_3$), 6.45-6.47 (m, 1H, ArH), 6.56-6.60 (m, 2H, ArH), 7.15-7.18 (m, 2H, ArH), 7.39 (d, 1H, *J* = 3.6 Hz, ArH), 7.67-7.75 (m, 3H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.12, 20.72, 21.51, 22.64, 26.16, 29.38, 31.85, 37.19, 49.09, 102.89, 109.25, 113.34, 114.45, 126.63, 126.71, 127.83, 129.71, 132.22, 135.34, 144.46, 144.54. HRMS (EI) exact mass calculated for ($C_{23}H_{30}N_2O_2S$) requires *m/z* 398.2028 found *m/z* 398.2011. $[\alpha]_D^{28}$ = –1.3° (c = 0.49, $CHCl_3$). The enantiomeric ratio was determined by SFC using a Chiralcel AD-H column (5-50% methanol/CO_2, 35 ºC, 100 bar, 4 mL/min, ramp rate = 5% /min); major enantiomer t_r = 7.05 min and minor enantiomer t_r = 6.18 min.

(+)-1-(4-(1-(4-methoxyphenylamino)ethyl)phenyl)propan-1-one (9):

Prepared according to the general procedure from *p*-anisidine (35 mg, 0.28 mmol) and 1-(4-acetyl-phenyl)-propan-1-one (150 mg, 0.852 mmol) at 40 ºC for 72 h; using workup procedure B to provide the title compound as a yellow oil (68.0 mg, 85% yield, 96% ee) following silica gel chromatography (10% Et_2O/pentane). IR (film) 3391, 2975, 2831, 1682, 1606, 1513, 1460, 1412, 1235, 1037, 952, 820, 800, 759 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.19 (t, 3H, *J* = 7.2 Hz, -$COCH_2C\mathbf{H}_3$), 1.49 (d, 3H, *J* = 6.6 Hz, -$CHC\mathbf{H}_3$), 2.95 (q, 2H, *J* = 7.5 Hz, -$COC\mathbf{H}_2CH_3$), 3.67 (s, 3H, -$OC\mathbf{H}_3$), 4.43 (q, 1H, *J* = 6.6 Hz, -$C\mathbf{H}CH_3$), 6.40-6.43 (m, 2H, Ar-H), 6.65-6.68 (m, 2H, Ar-H), 7.42-7.45 (m, 2H, Ar-H), 7.88-7.92 (m, 2H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 8.29, 24.99, 31.74, 54.19, 55.69, 114.56, 114.75, 126.09, 128.53, 135.76, 141.08, 150.99, 152.07, 200.49; HRMS (EI) exact mass calculated for ($C_{19}H_{21}NO_2$) requires *m/z* 283.1572, found *m/z* 283.1575. $[\alpha]_D^{24}$ = +33.1° (c = 0.27, $CHCl_3$). The enantiomeric ratio was determined by SFC using a Chiralcel AD-H column (5-50% methanol/CO_2, 35 ºC, 100 bar, 4 mL/min, ramp rate = 5% /min); *Major* diastereomer: major enantiomer t_r = 8.04 min and minor enantiomer t_r = 7.06 min; *minor* diastereomer: major enantiomer t_r = 7.52 min and minor enantiomer t_r = 6.66 min.

(–)-3-ethyl-3,4-dihydro-benzo-[1,4]-oxazin-2-one (7):

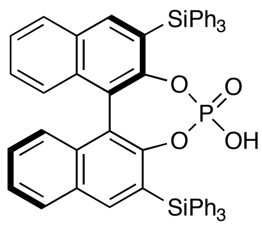
A vial equipped with a magnetic stir bar was charged with imine (100 mg, 0.568 mmol), Hantzsch ester (174 mg, 0.682 mmol) and catalyst (50 mg, 0.057 mmol). Benzene (5.8 mL) was added and the reaction mixture was heated at 40 ºC for 50 h. Upon completion the product was isolated using workup procedure B to provide the title compound as a colorless oil (27 mg, 27% yield, 79% ee) following silica gel chromatography (20% Et_2O/pentane). IR (film) 3365, 2970, 2934, 2878, 1765, 1617, 1501, 1340, 1301, 1191, 746 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.07 (t, 3H, *J* = 7.4 Hz, -$CH_2C\mathbf{H_3}$), 1.79-2.01 (m, 2H, -$C\mathbf{H_2}CH_3$), 3.87 (dd, 1H, *J* = 7.4, 5.3 Hz, -C**H**NHAr), 6.74-6.87 (m, 2H, ArH), 6.96-7.03 (m, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 9.59, 24.47, 55.93, 114.99, 116.74, 120.18, 124.91, 132.35, 141.00, 166.47; HRMS (EI) exact mass calculated for ($C_{10}H_{11}NO_2$) requires *m/z* 177.0790, found *m/z* 177.0790. $[\alpha]_D^{25}$ = –23.4º (c = 0.22, $CHCl_3$). The enantiomeric ratio was determined by GLC using a Chirasil-Dex-CB column (170 ºC isotherm for 30 minutes); major enantiomer t_r = 11.93 min and minor enantiomer t_r = 11.54 min.

(*R*)-2-(2-methoxy-phenylamino)-propionic acid methyl ester (proof of absolute stereochemistry for cyclic amine 6:

Cyclic amine (30 mg, 0.18 mmol) was dissolved in methanol (10 mL), followed by addition of PPTS (3 mg). The reaction mixture was stirred for 10 minutes at room temperature then quenched by the addition of saturated Na_2CO_3 (10 mL). Product was extracted into CH_2Cl_2 (4 × 10 mL) and the combined organics dried over Na_2SO_4, filtered and concentrated to yield a yellow oil that was used directly in the next reaction. The crude alcohol was dissolved in acetone (2.0 mL). Iodomethane (0.4 mL, 6.4 mmol) was added at RT followed by potassium carbonate (103 mg, 0.75 mmol). The mixture was stirred at room temperature for 4 hours then quenched by addition of saturated NH_4Cl (10 mL). The product was extracted using CH_2Cl_2 (4 × 10 mL) and the combined organics dried over Na_2SO_4, filtered and concentrated. The crude oil was purified by flash chromatography (10% Et_2O/pentane) to yield the product as a colorless oil (29 mg, 74% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.51 (d, 3H, *J* = 6.9 Hz, -$CHC\mathbf{H}_3$), 3.71 (s, 3H, -

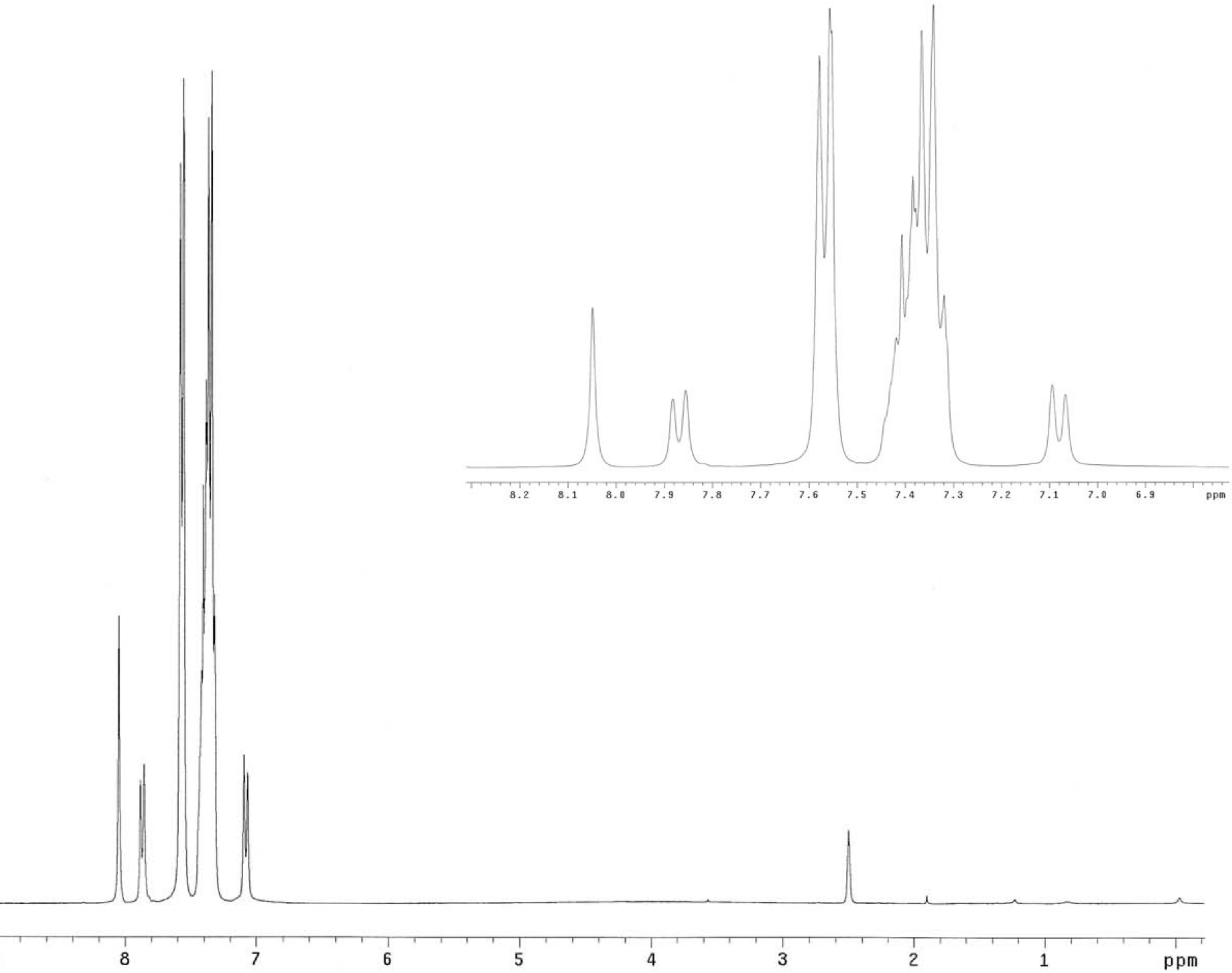
O$C\mathbf{H}_3$), 3.86 (s, 3H, -$CO_2C\mathbf{H}_3$) 4.14 (q, 1H, *J* = 6.9 Hz, -C**H**CH_3), 6.51 (d, 1H, *J* = 8.1 Hz, ArH), 6.70-6.86 (m, 3H, ArH); $[\alpha]_D^{27}$ = +28.0 (c = 0.17, THF).[13]

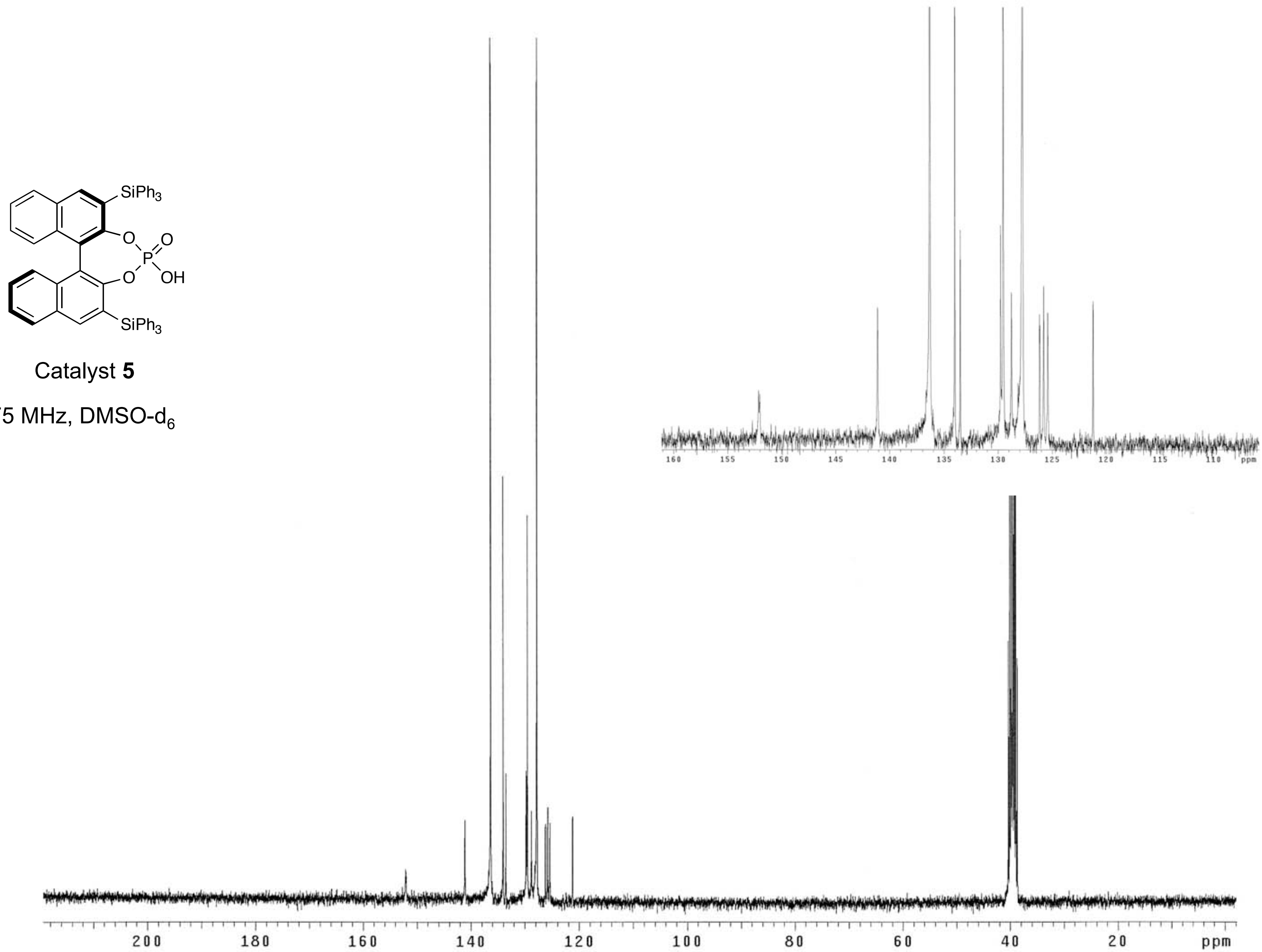
[13] Norton, J.R; Gately, D.A. *J. Am. Chem. Soc* **1996**, *118*, 3479. (reported a rotation of –42.8° (c = 0.15, THF) for *S* product that was 97% ee)



Catalyst **5**

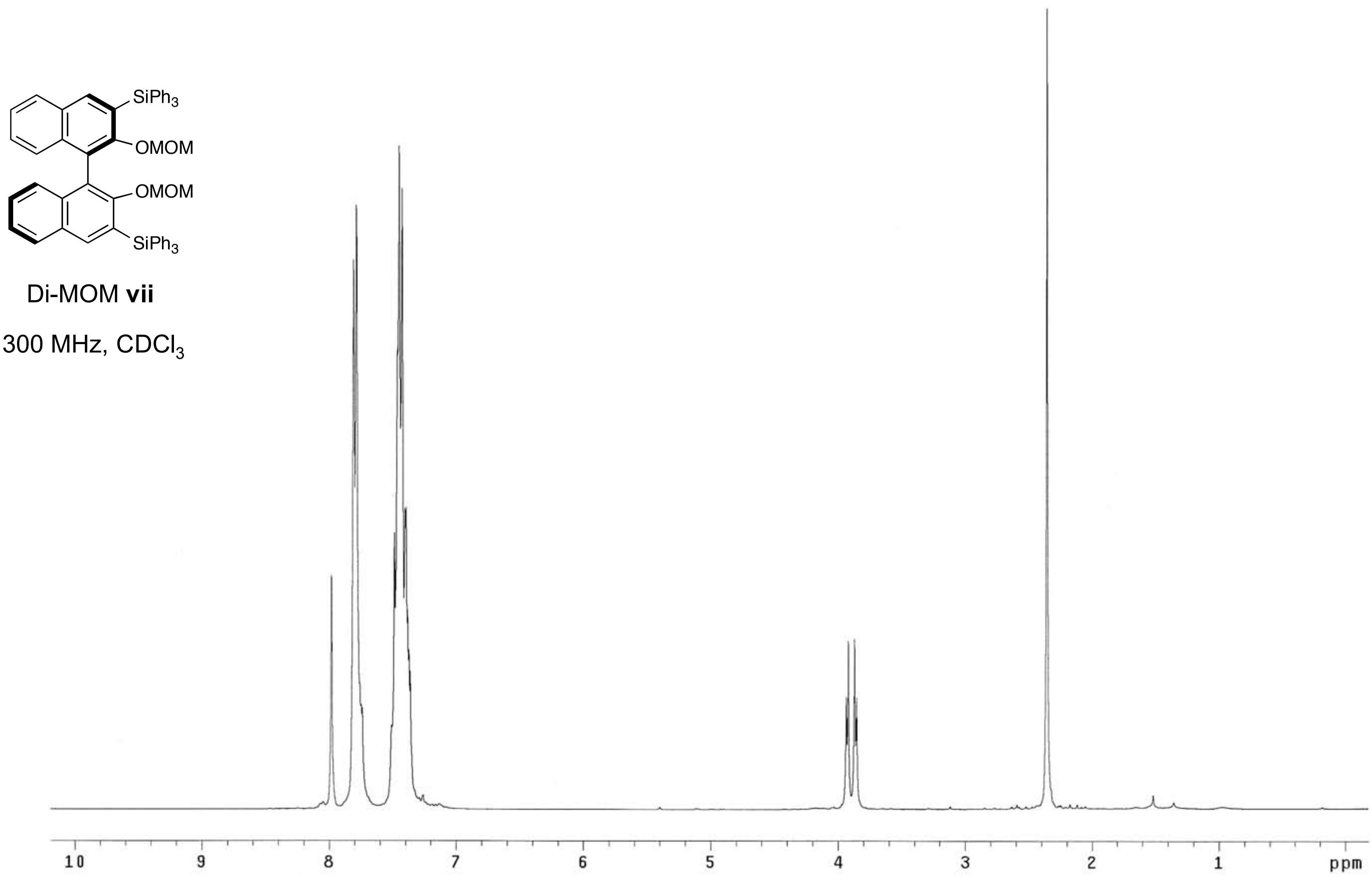
300 MHz, DMSO-d_6





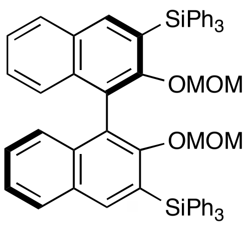
Catalyst **5**

75 MHz, DMSO-d_6



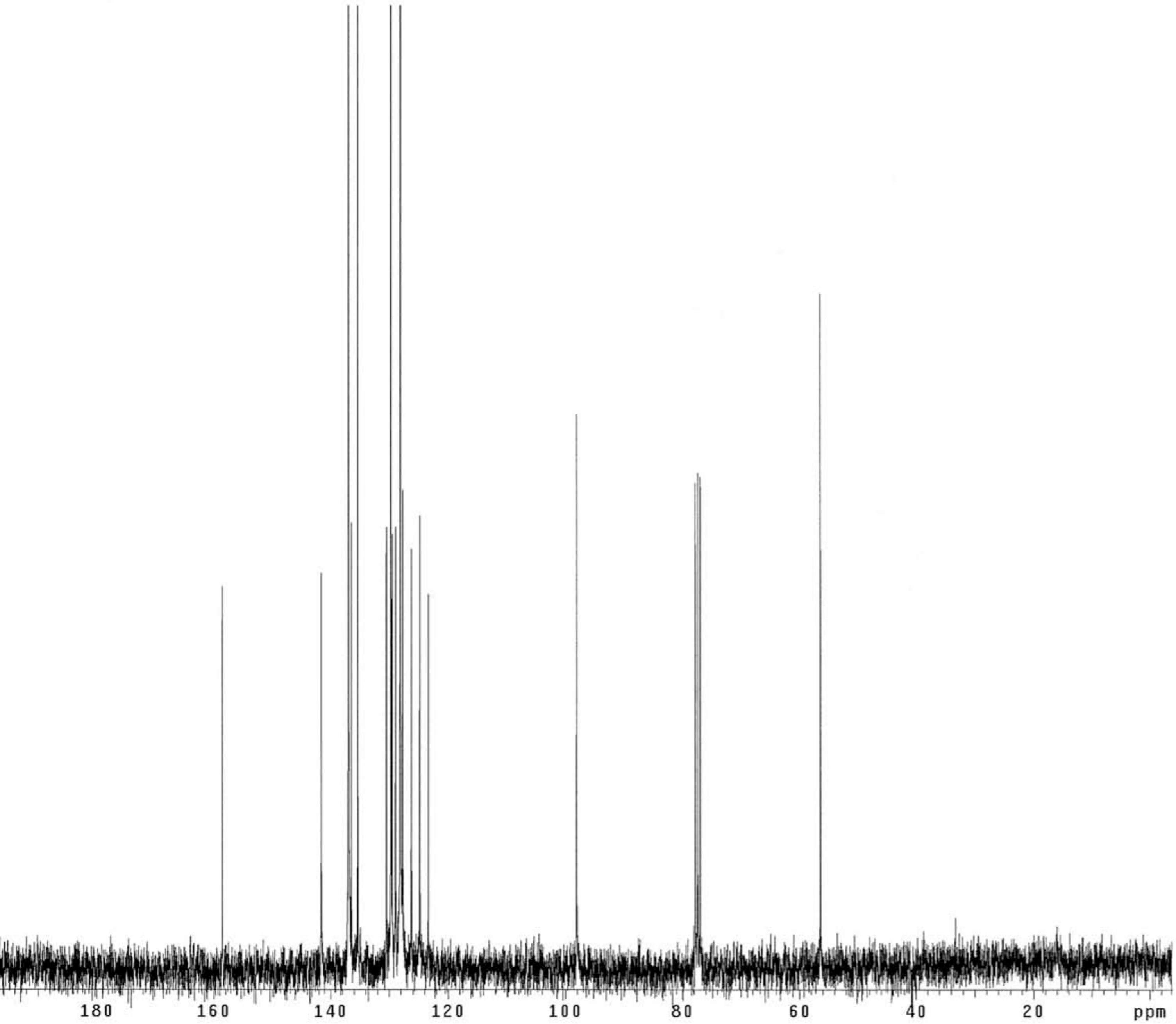
Di-MOM **vii**

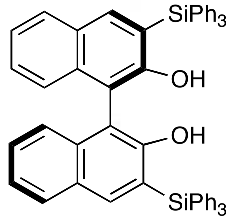
300 MHz, $CDCl_3$



Di-MOM **vii**

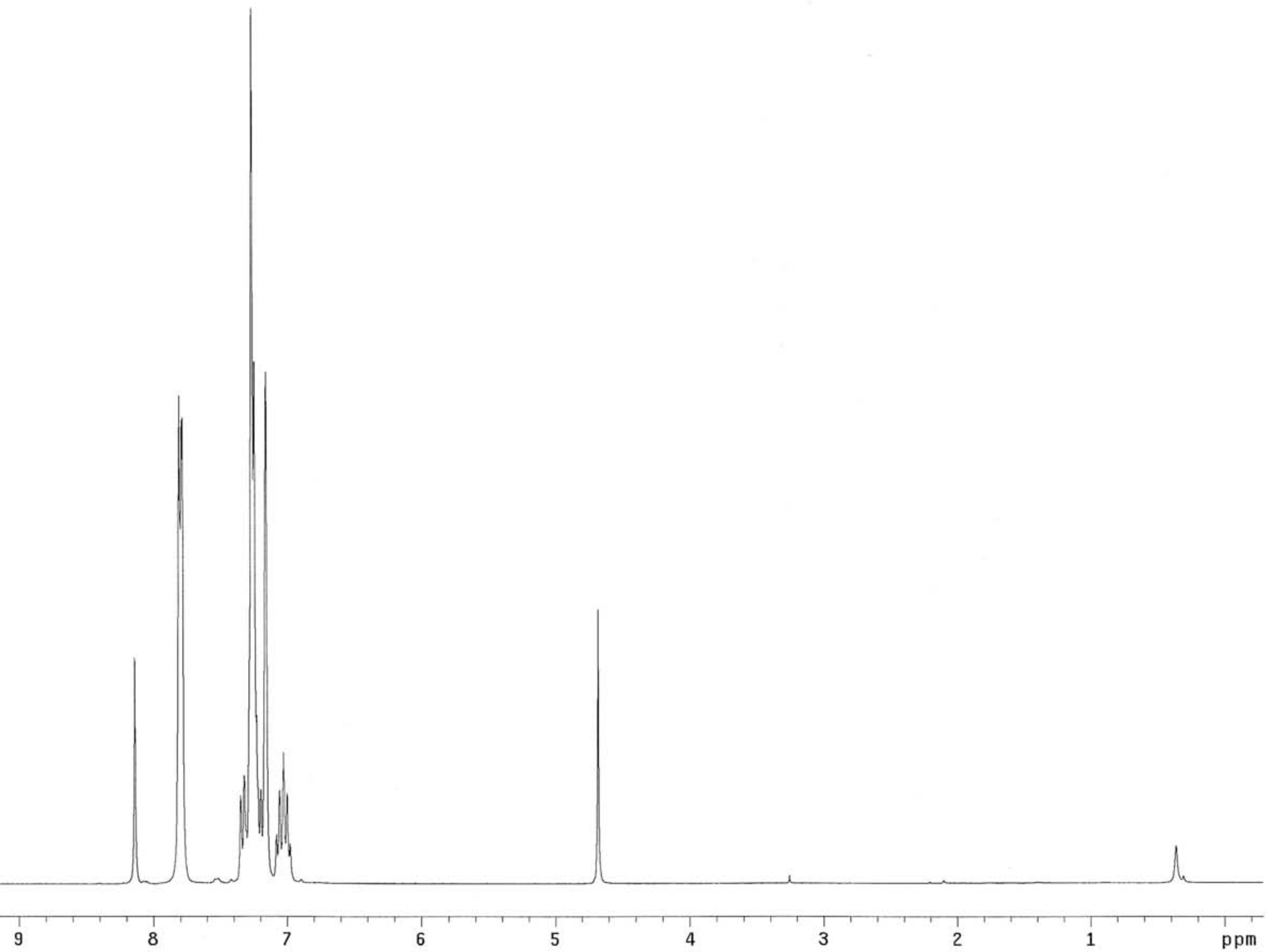
75 MHz, $CDCl_3$

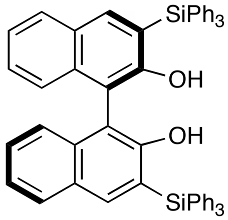




diol **viii**

300 MHz, C_6D_6





diol **viii**

75 MHz, C_6D_6

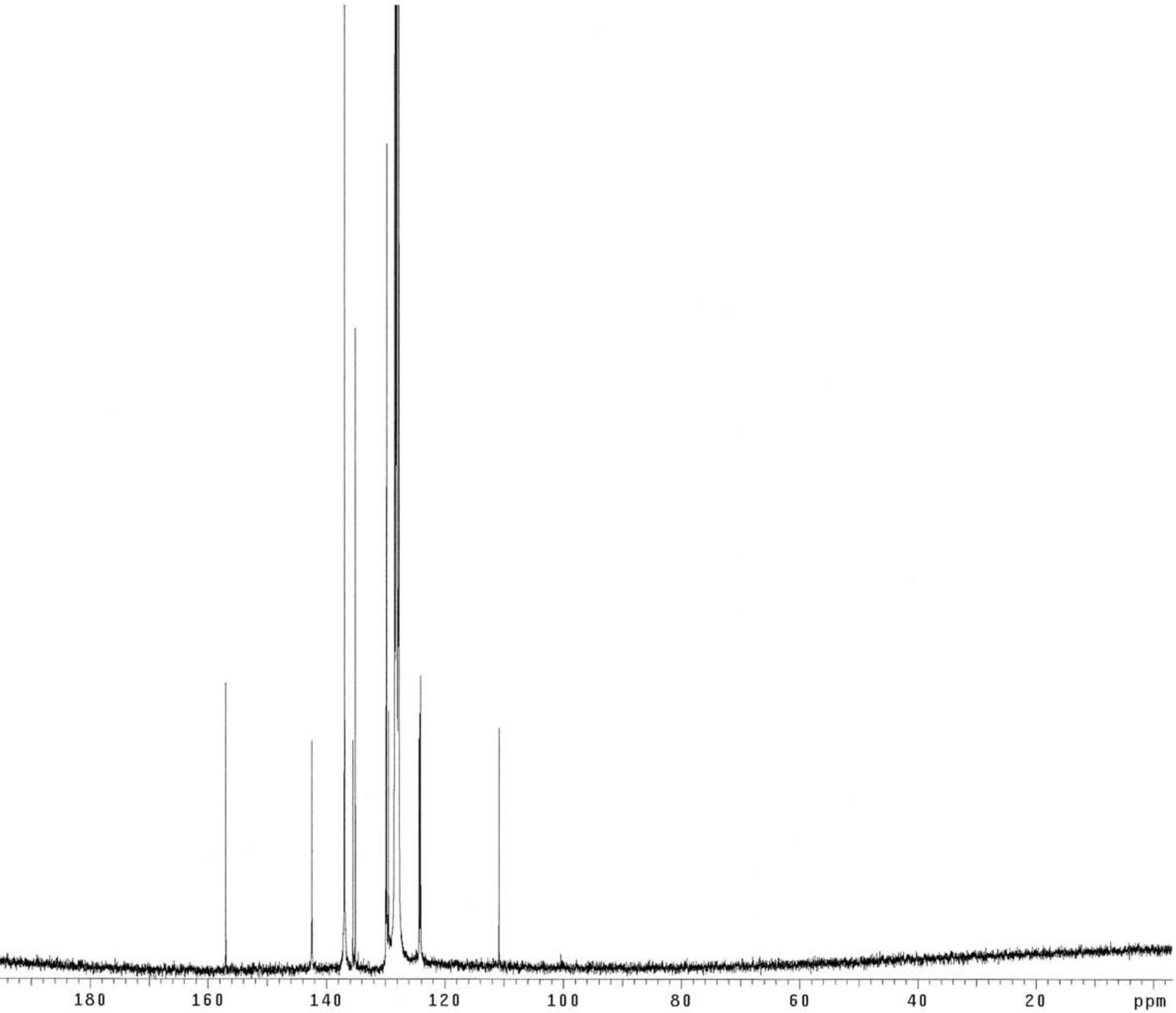
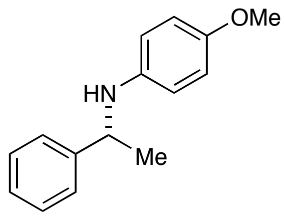
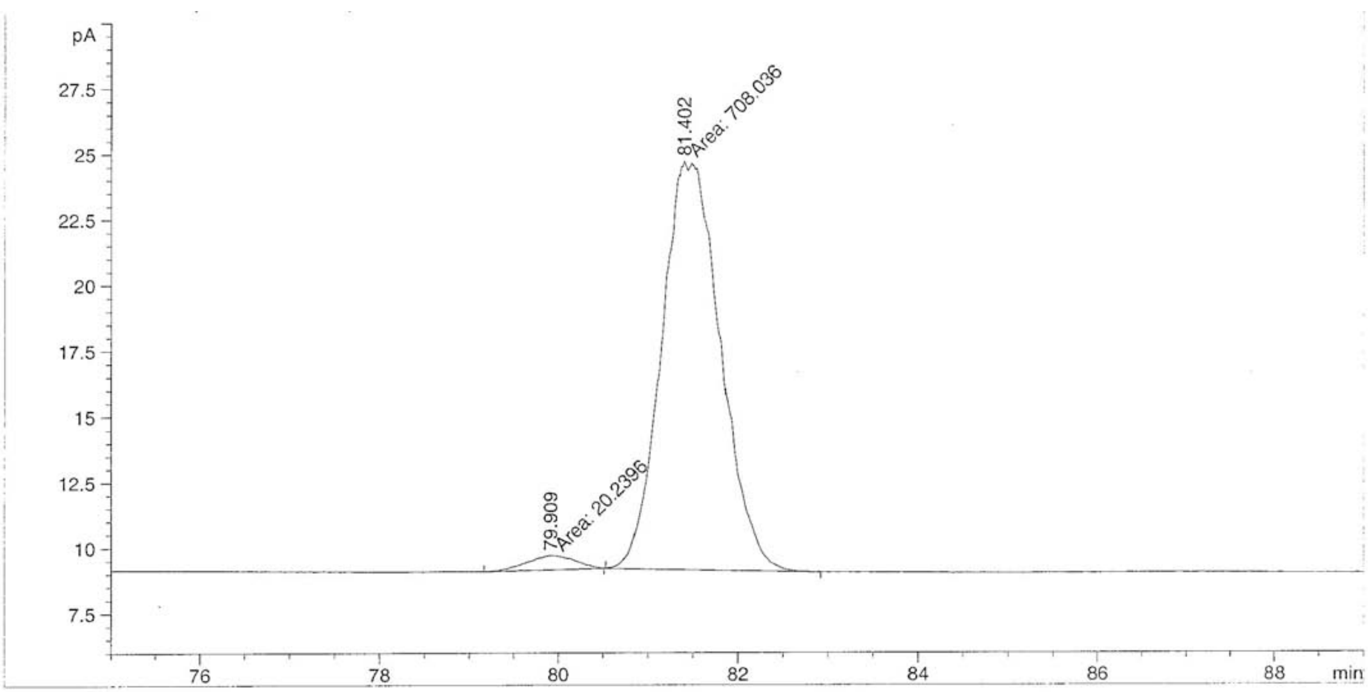


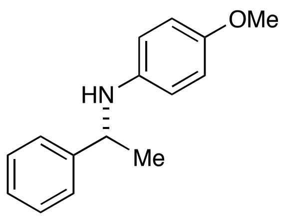
Table 2, Entry 1



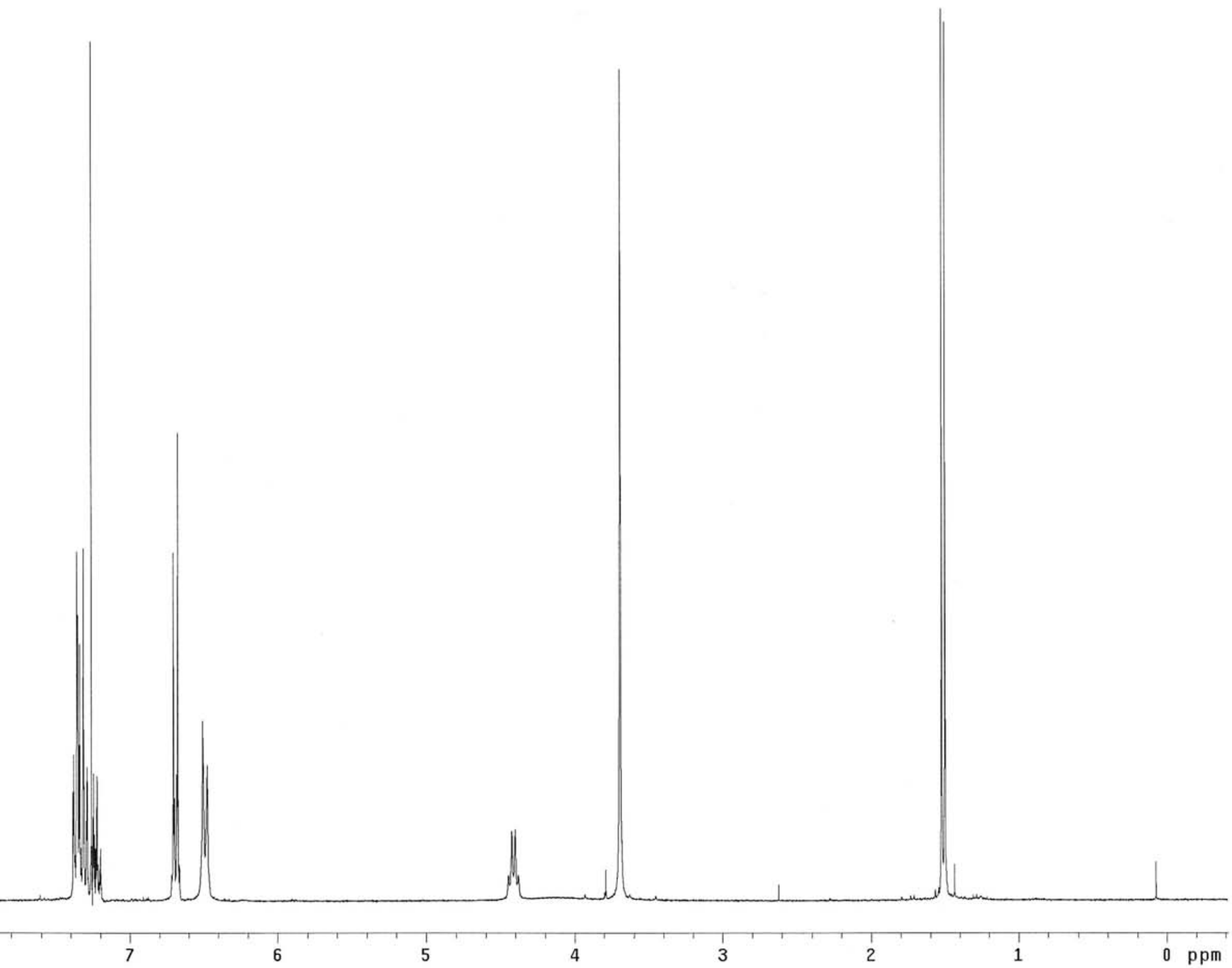
GLC (Varian CP-chirasil-dex-CB)
150 ˚C isotherm

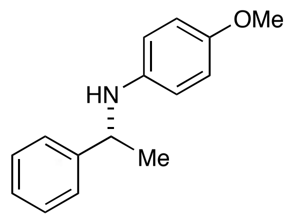



```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height      Area
  #   [min]        [min]   [pA*s]       [pA]         %
----|-------|----|-------|----------|----------|--------|
   1  79.909 MM    0.6157   20.23964 5.47899e-1  2.77912
   2  81.402 MM    0.7596  708.03607   15.53460 97.22088

Totals :                   728.27571   16.08250
```



300 MHz, $CDCl_3$





75 MHz, $CDCl_3$

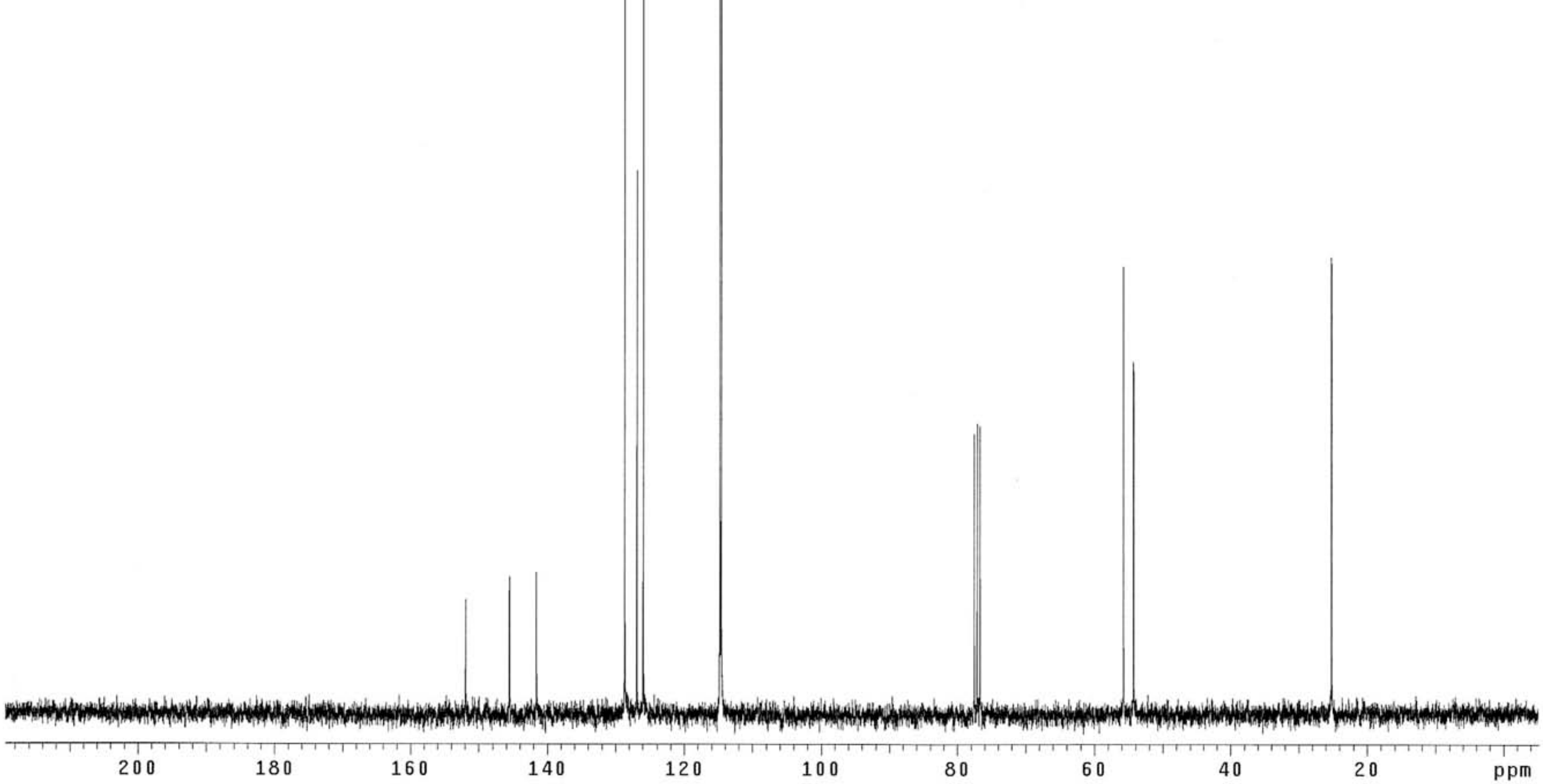
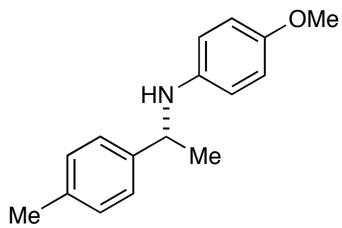
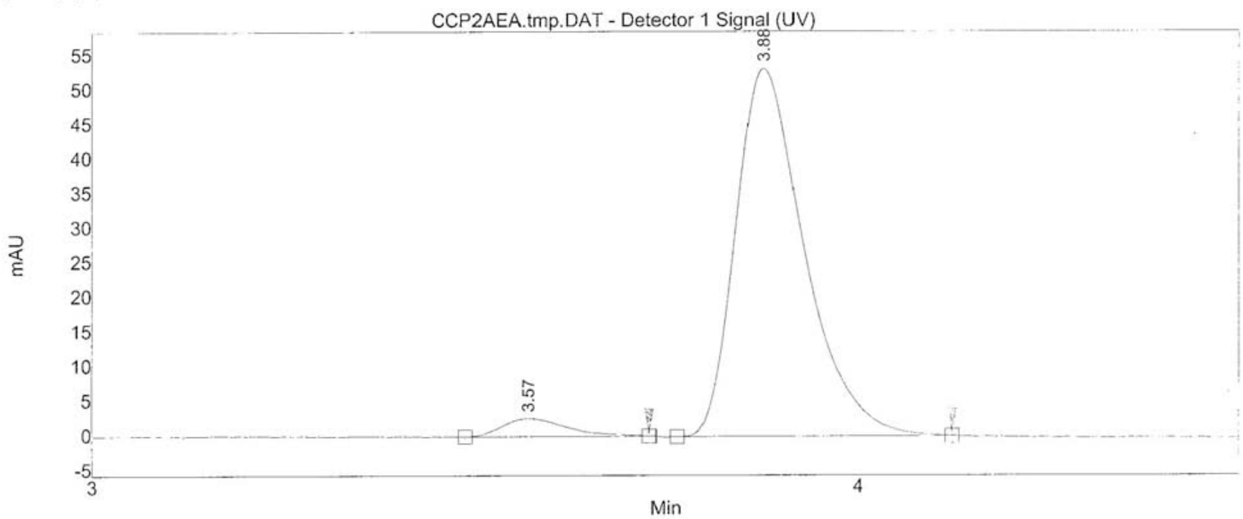


Table 2, Entry 2



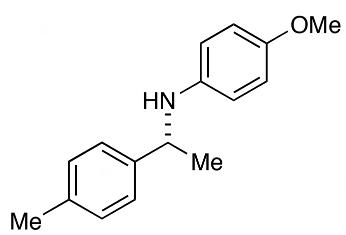
SFC (Daicel Chiracel ADH)
MeOH 5-50% ramp



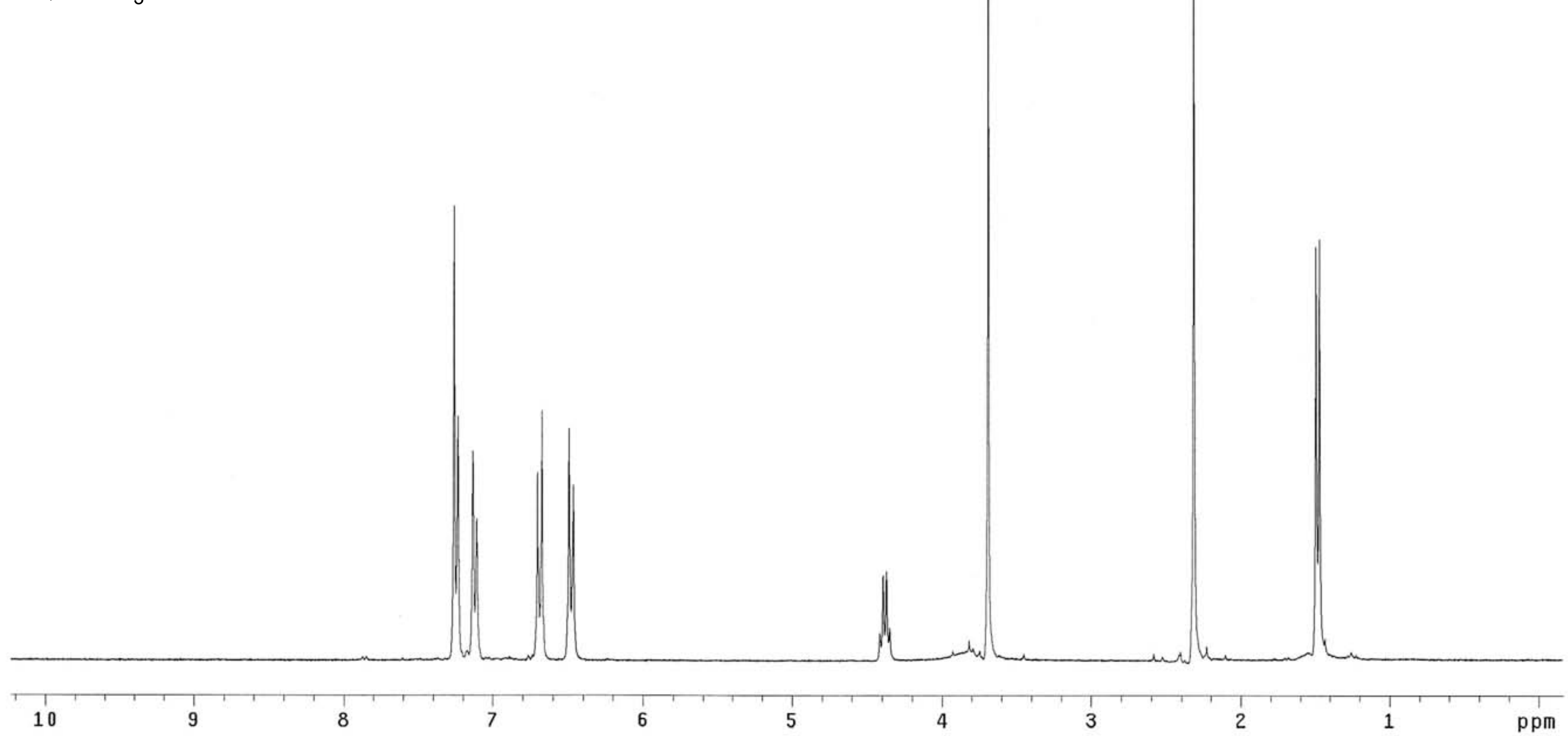
The Chromatogram Noise is 0

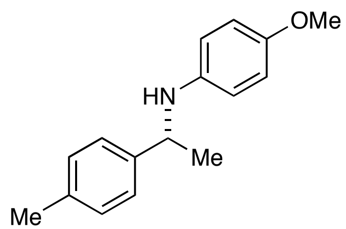
Results Table:

Index	Name	Time	Width USP	Quantity	Height	Area	Area
		[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
2	UNKNOWN	3.57	0.15	4.38	2.6	0.3	4.380
1	UNKNOWN	3.88	0.16	95.62	53.1	5.5	95.620
Total				100.00	55.7	5.7	100.000



300 MHz, $CDCl_3$





75 MHz, $CDCl_3$

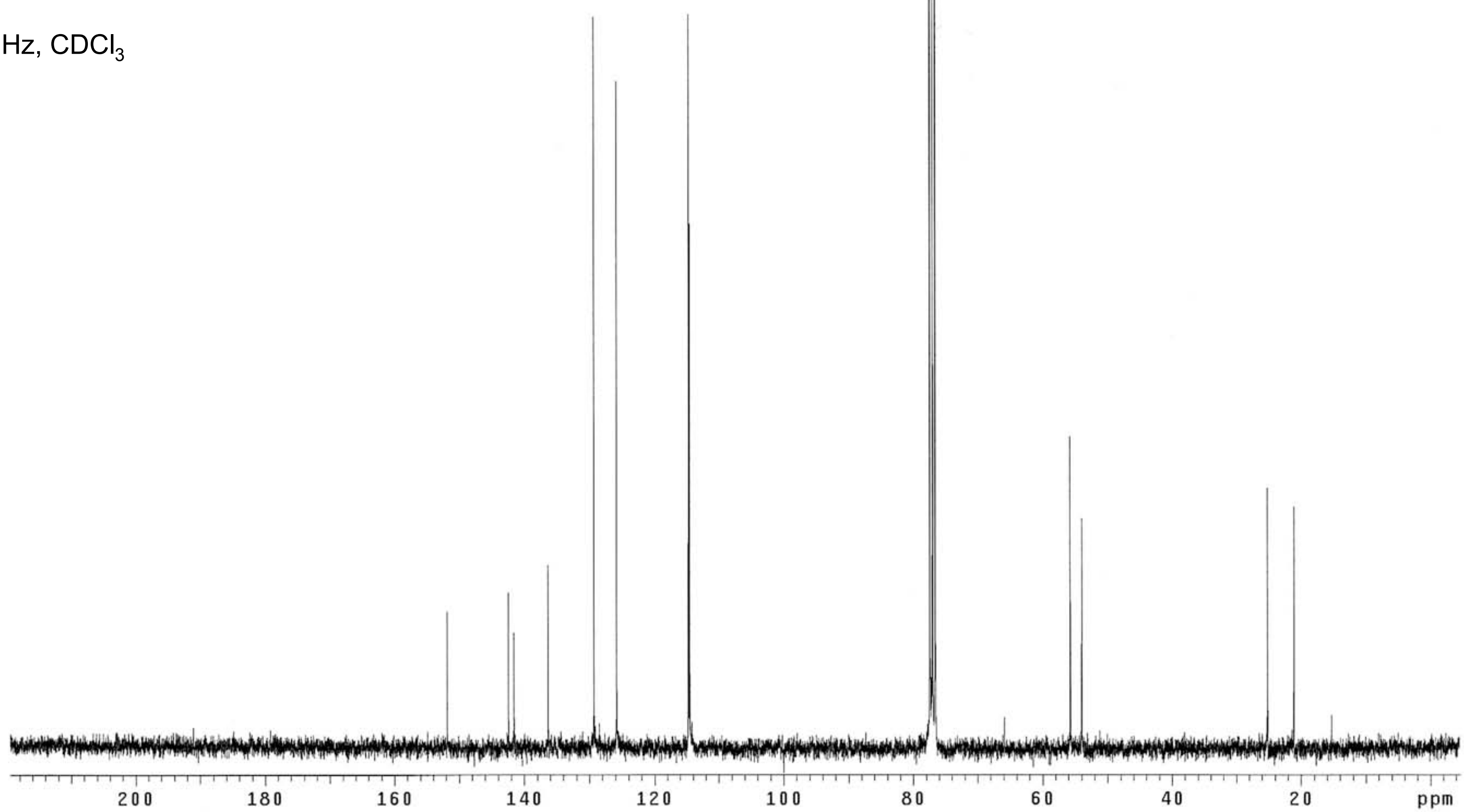
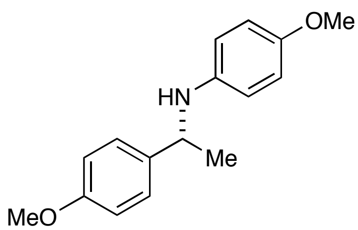
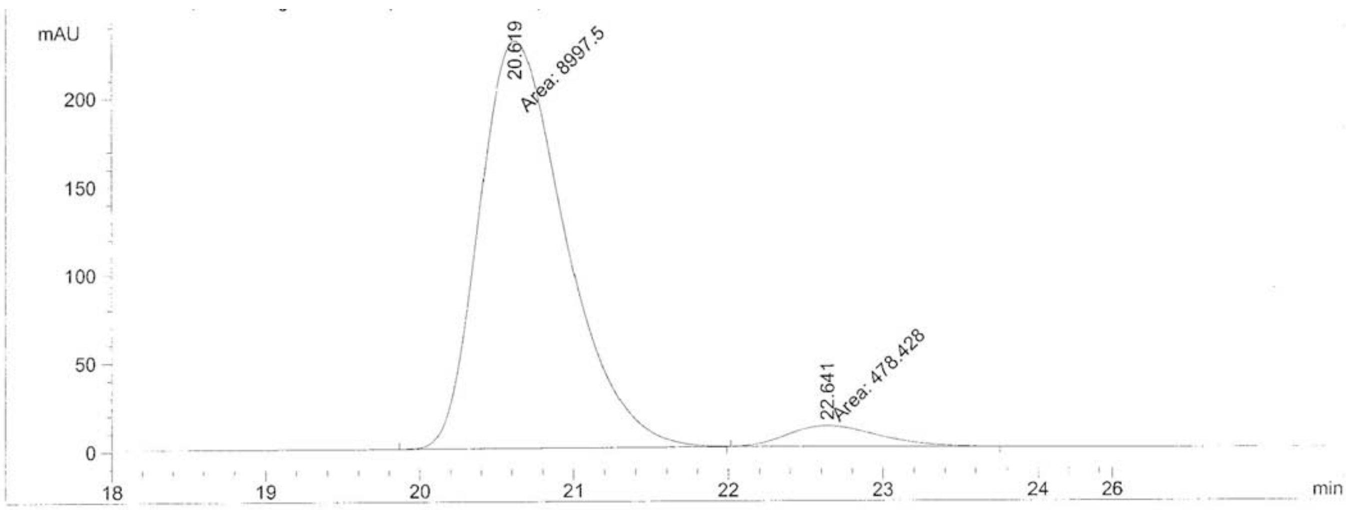


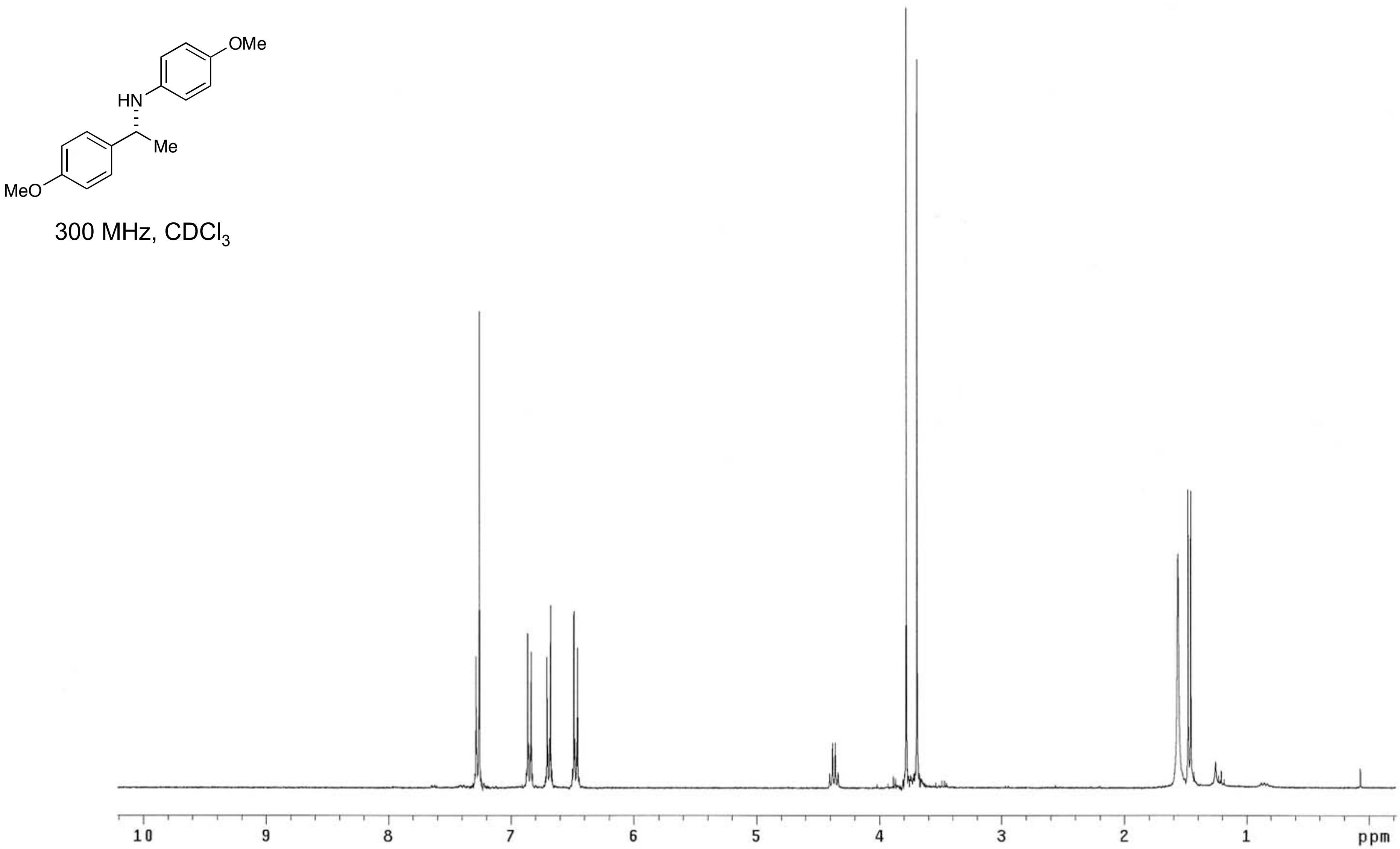
Table 2, Entry 3



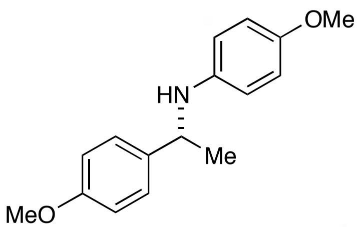
HPLC (Daicel Chiracel ODH)
5% ^{i}PrOH / hexane




```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU    *s  [mAU    ]      %
----|-------|----|-------|----------|----------|--------|
   1  20.619 MM    0.6507 8997.49805  230.44293  94.9511
   2  22.641 MM    0.6793  478.42844   11.73816   5.0489

Totals :                  9475.92648  242.18109
```



300 MHz, $CDCl_3$



75 MHz, $CDCl_3$

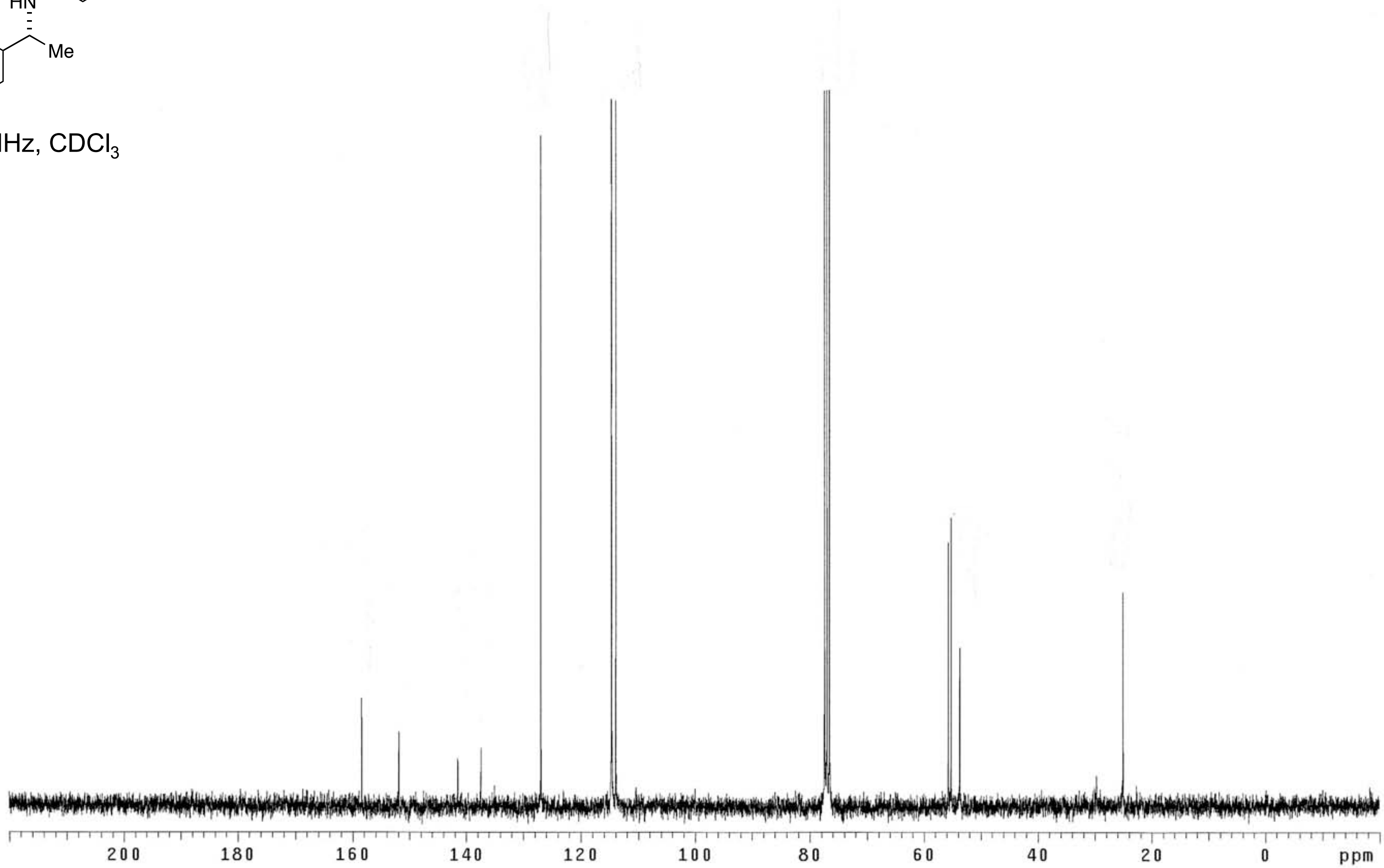
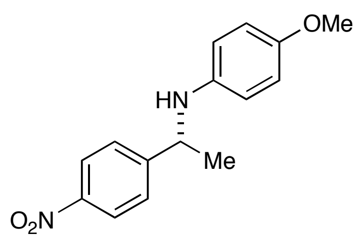
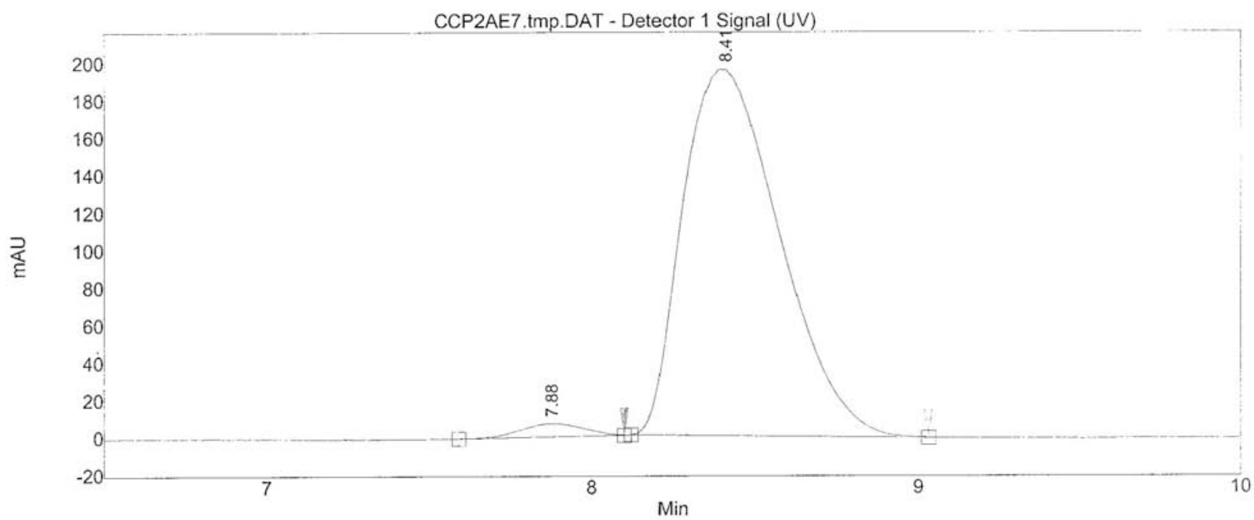


Table 2, Entry 4



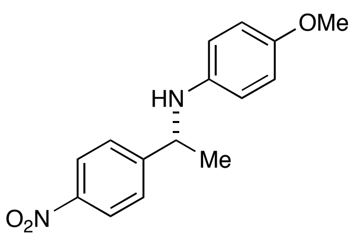
SFC (Daicel Chiracel ODH)
MeOH 5-10% ramp



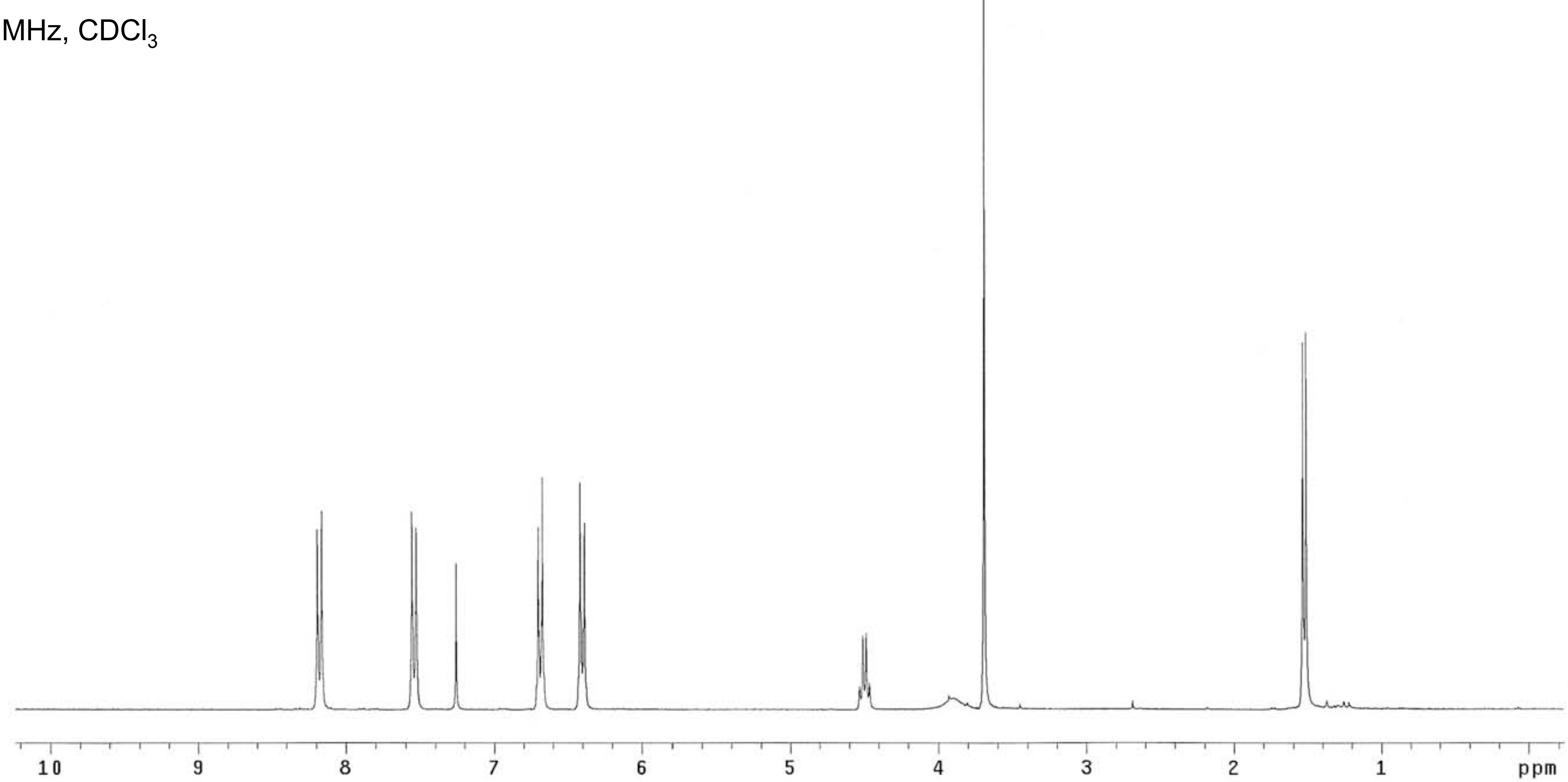
The Chromatogram Noise is 0

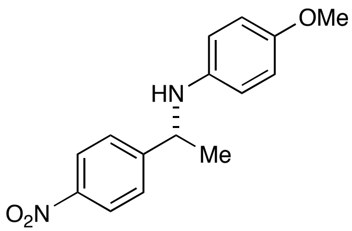
Results Table:

Index	Name	Time	Height	Width USP	Area	Area
		[Min]	[µV]	[Min]	[µV.Min]	[%]
1	UNKNOWN	7.88	7.1	0.37	1.6	2.275
2	UNKNOWN	8.41	195.6	0.54	67.2	97.725
Total			202.6		68.7	100.000



300 MHz, $CDCl_3$





75 MHz, $CDCl_3$

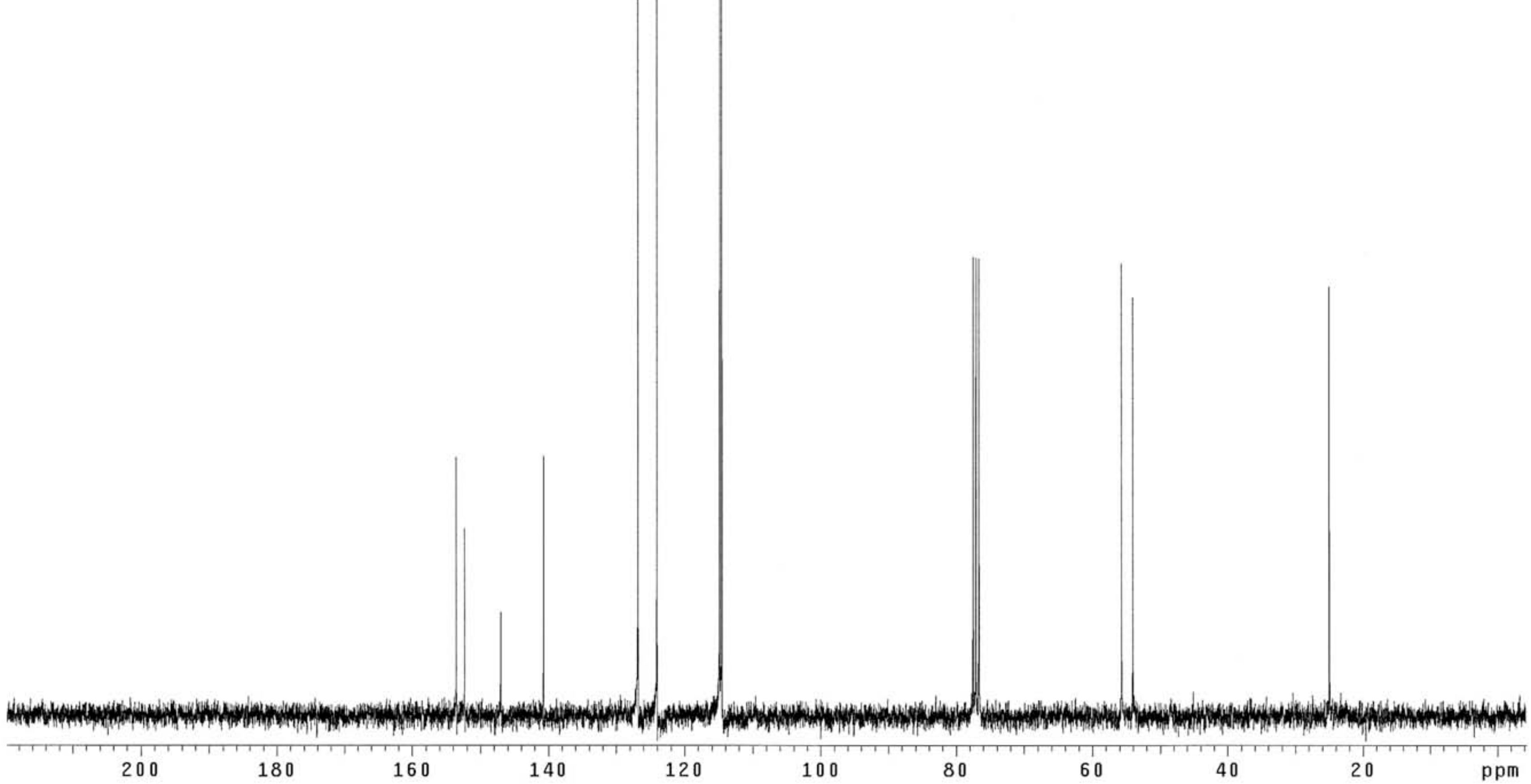
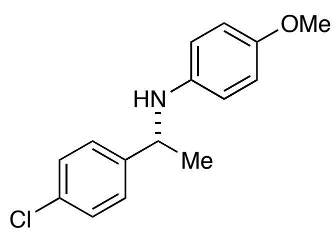
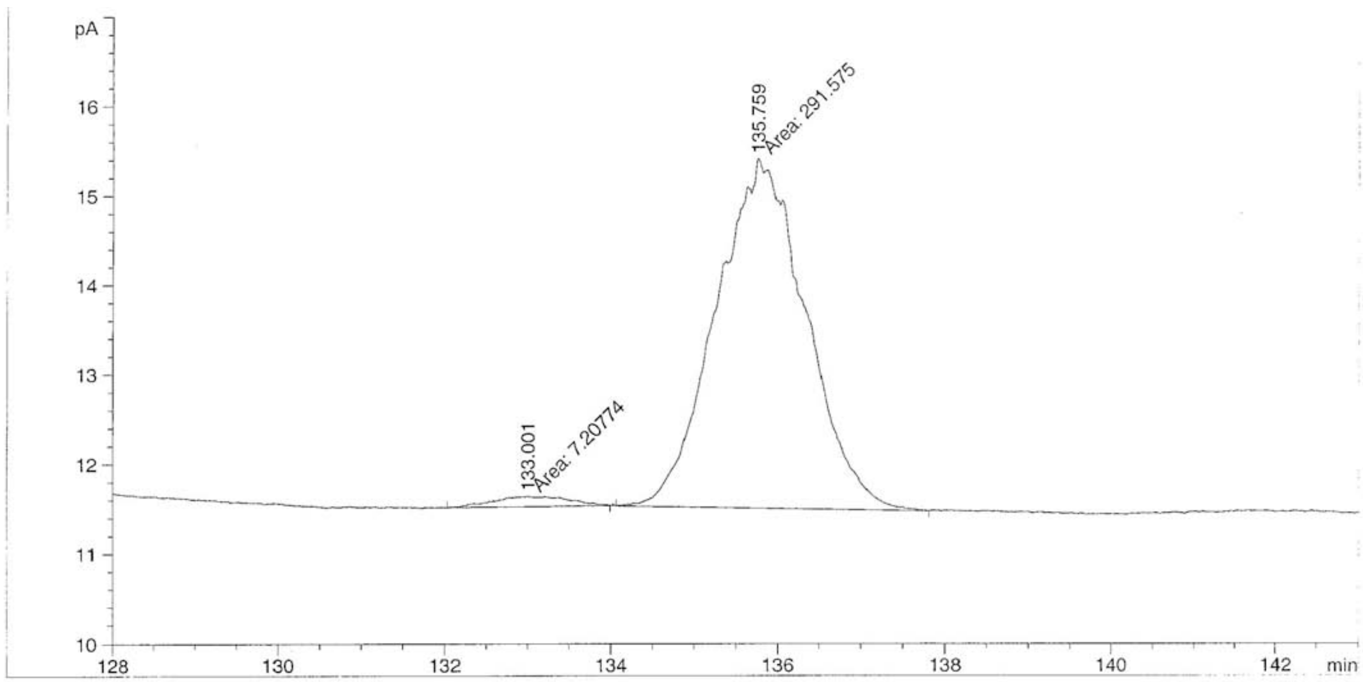


Table 2, Entry 5



GLC (Varian CP-chirasil-dex-CB)
160 ˚C isotherm



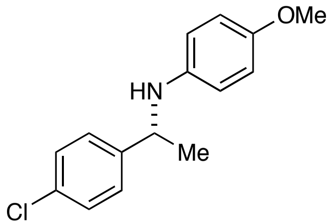
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

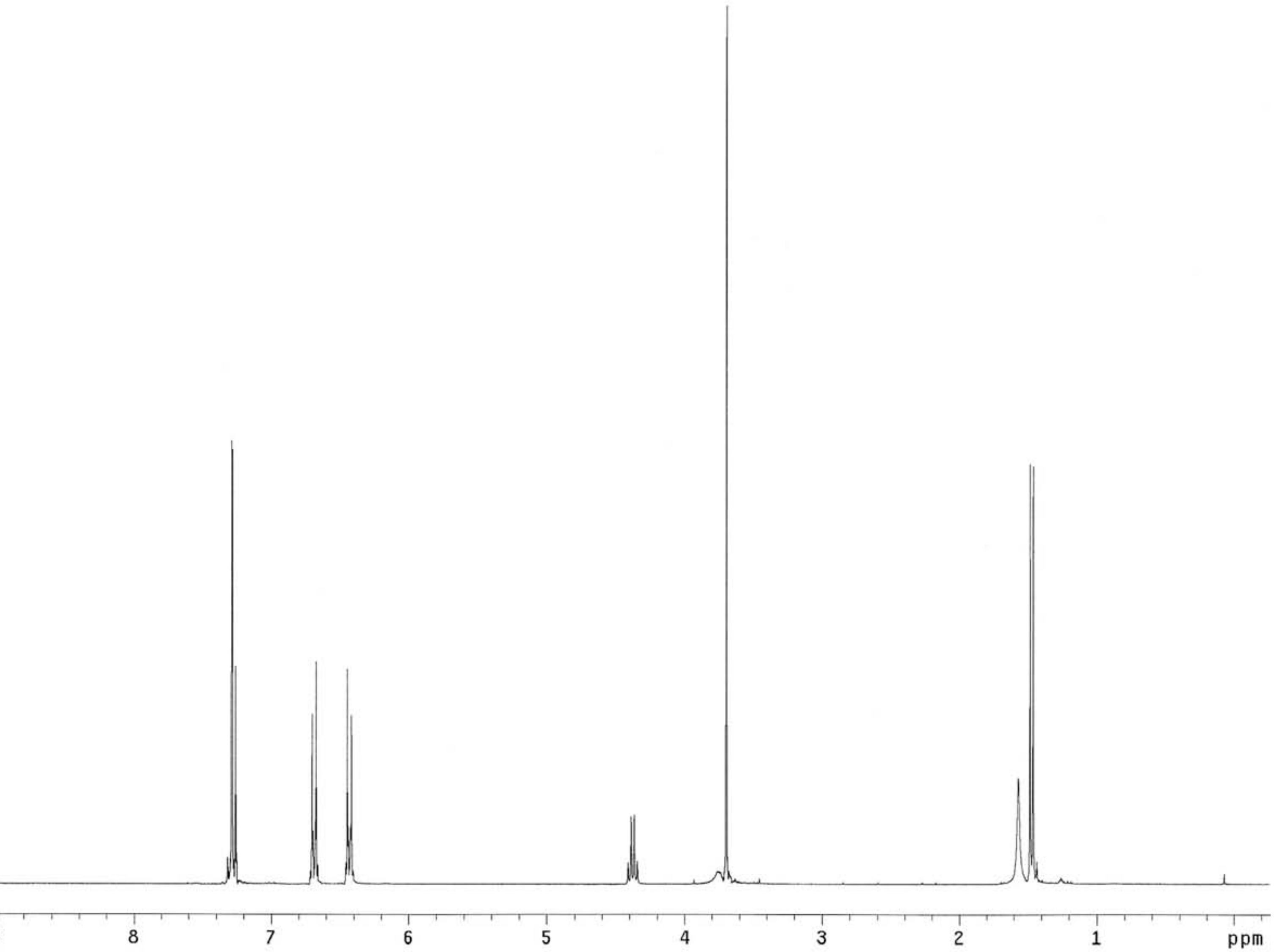
Signal 1: FID1 A,

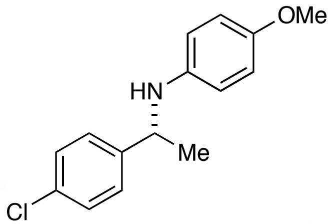
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	133.001	MM	1.0256	7.20774	1.17130e-1	2.41237
2	135.759	MM	1.2465	291.57526	3.89868	97.58763

Totals : 298.78300 4.01581



300 MHz, $CDCl_3$





75 MHz, $CDCl_3$

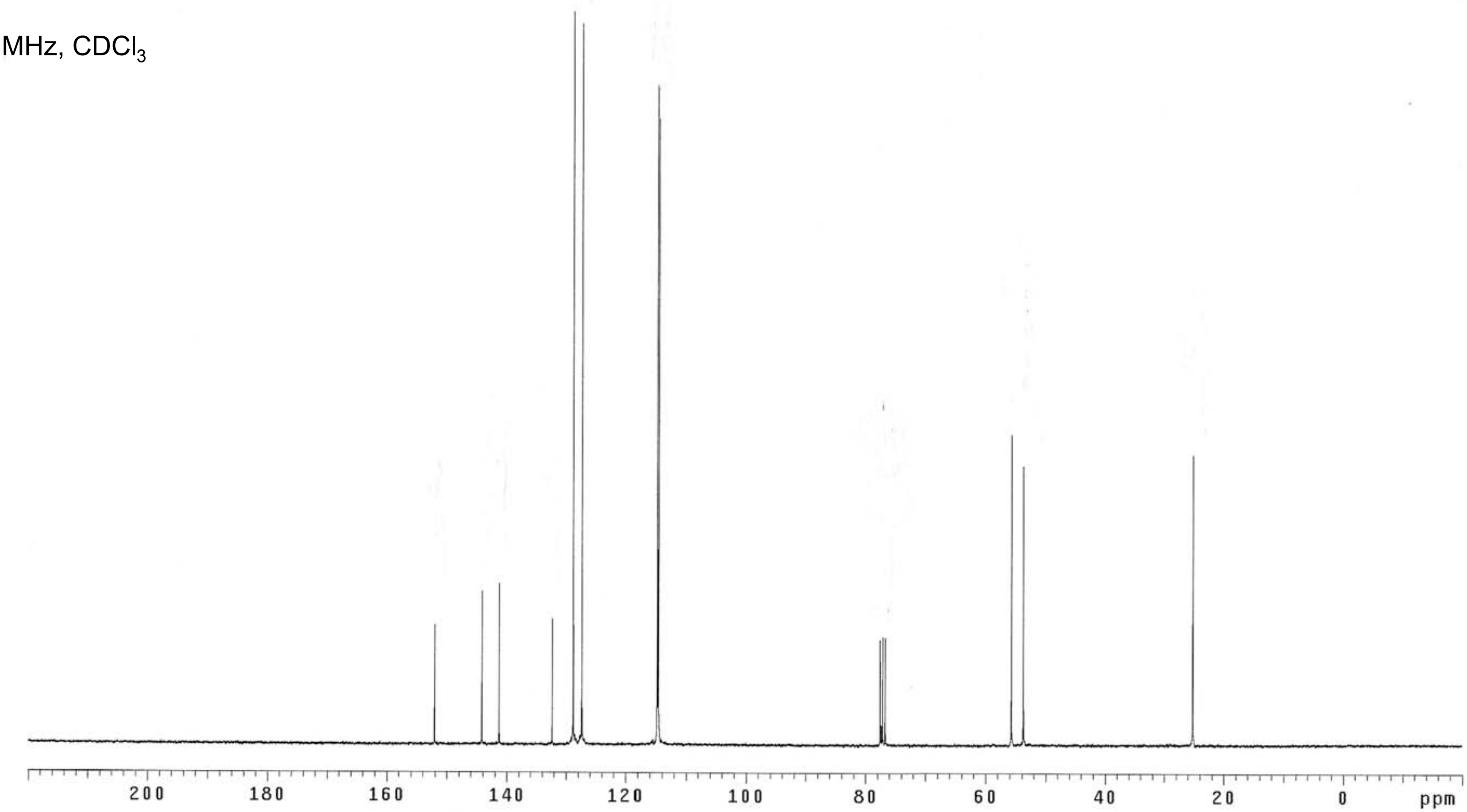
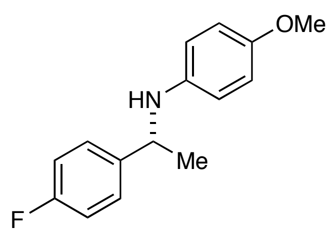
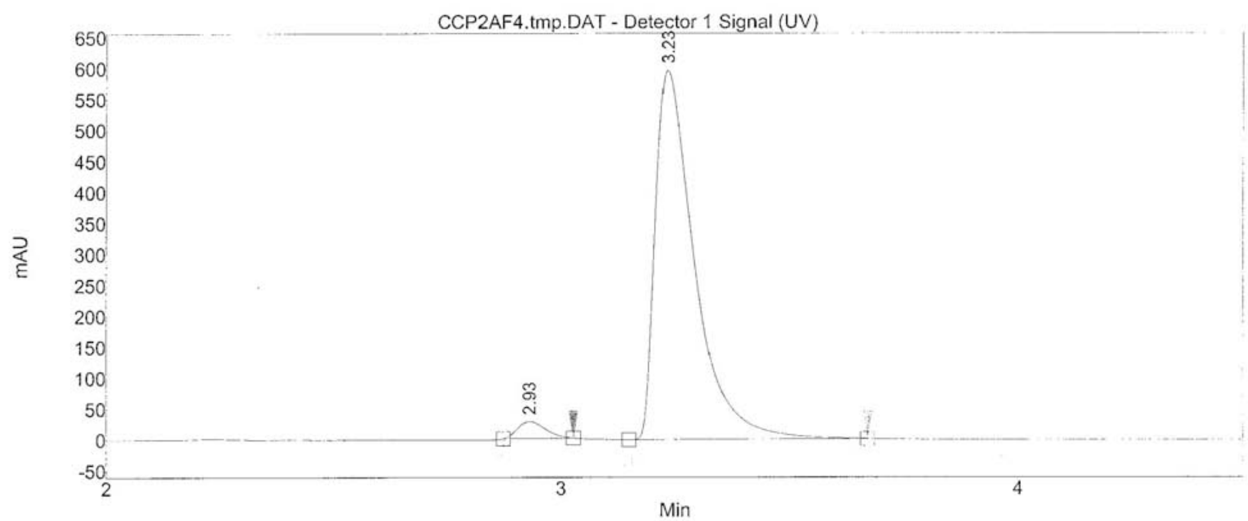


Table 2, Entry 6



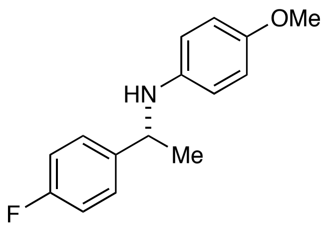
SFC (Daicel Chiracel ADH)
MeOH 5-50% ramp



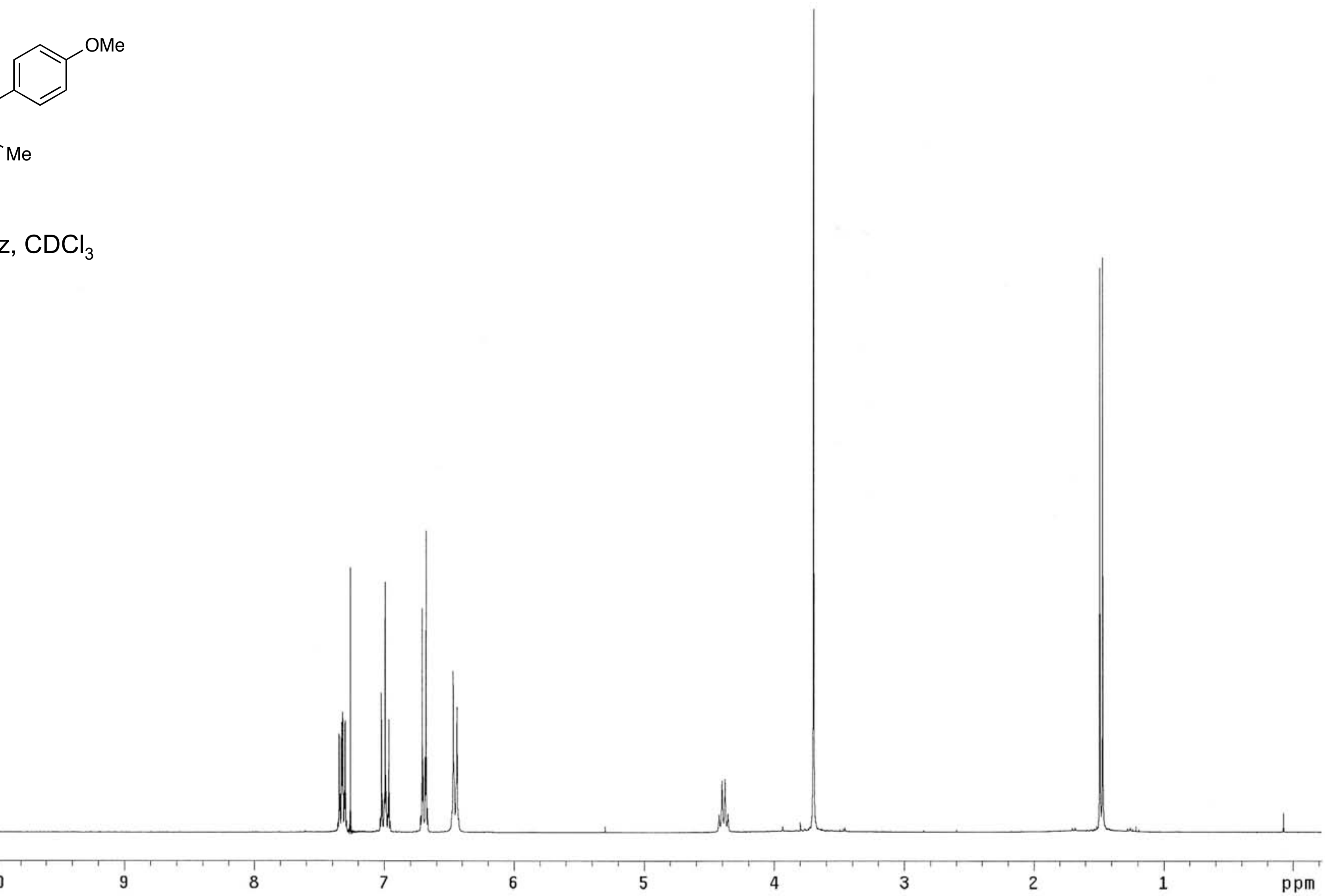
The Chromatogram Noise is 0

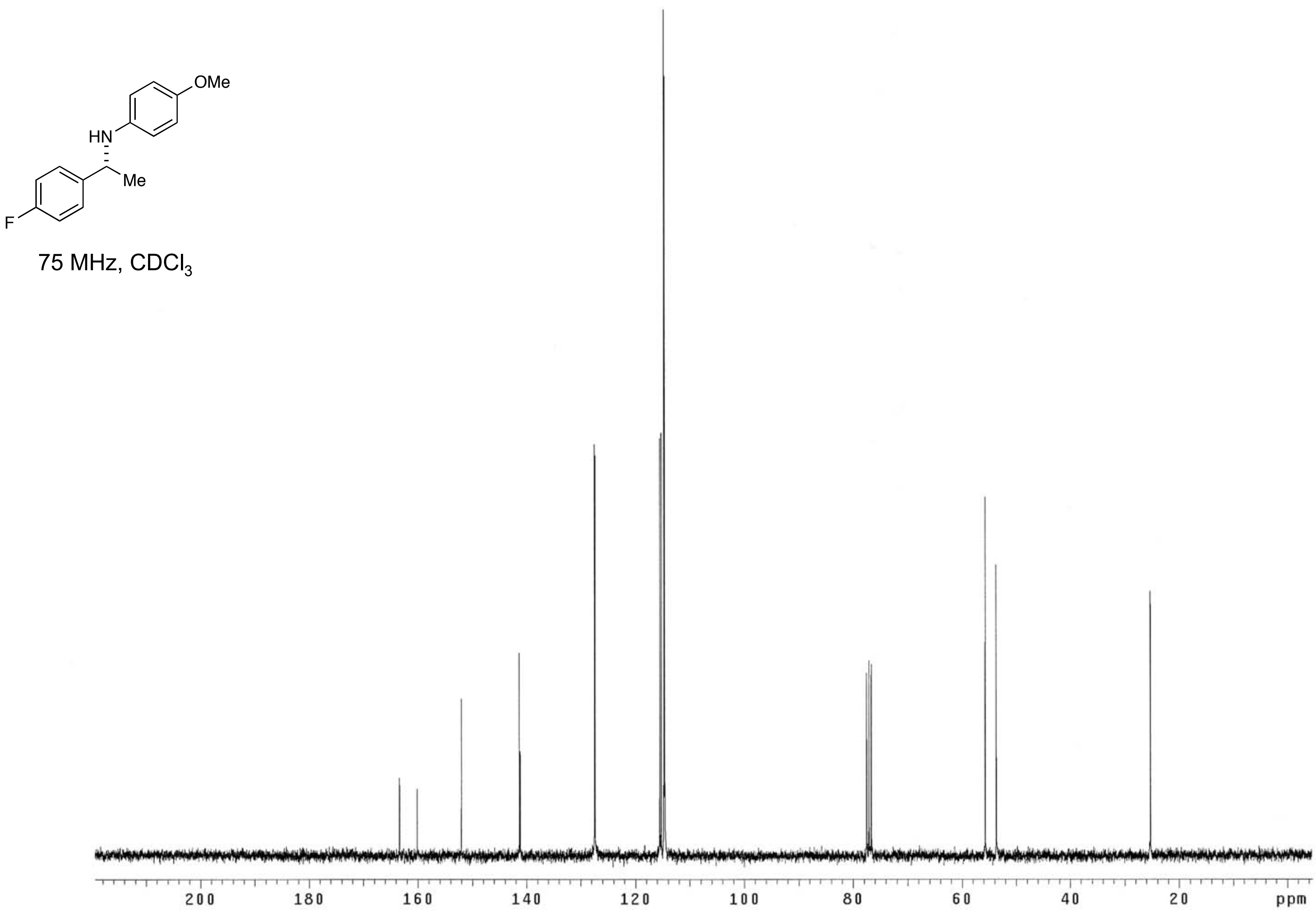
Results Table:

Index	Name	Time	Width USP	Quantity	Height	Area	Area
		[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	2.93	0.11	3.15	27.5	1.9	3.148
2	UNKNOWN	3.23	0.15	96.85	596.3	59.2	96.852
Total				100.00	623.9	61.1	100.000



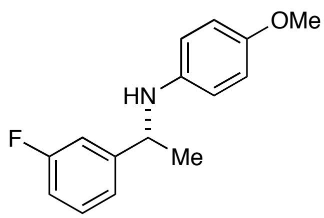
300 MHz, $CDCl_3$



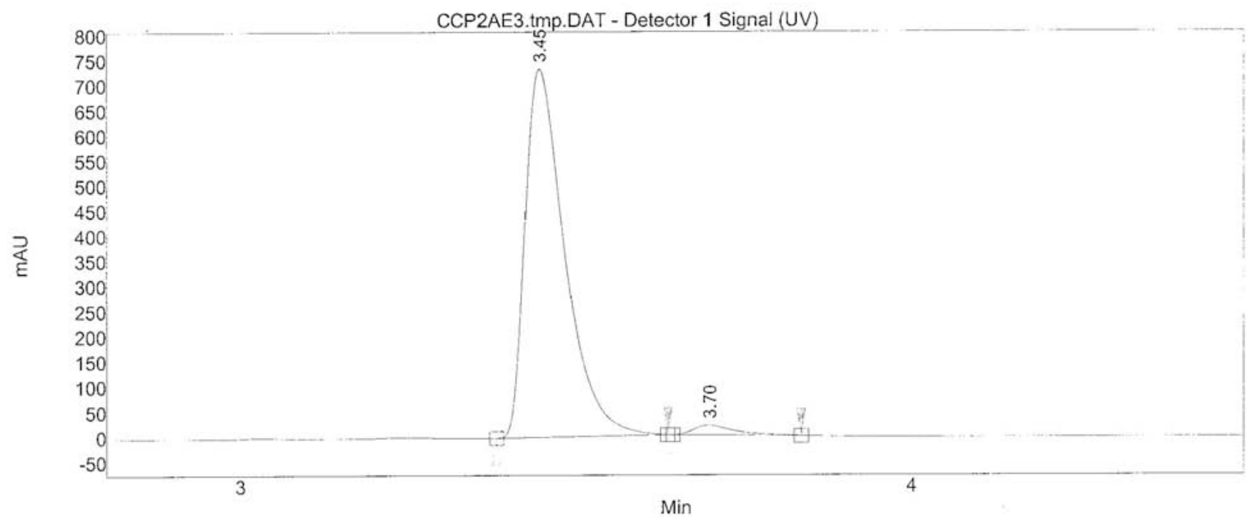


OMe
HN
Me
F
75 MHz, $CDCl_3$
200
180
160
140
120
100
80
60
40
20
ppm

Table 2, Entry 7



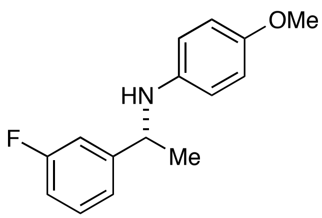
SFC (Daicel Chiracel ADH)
^{i}PrOH 5-50% ramp



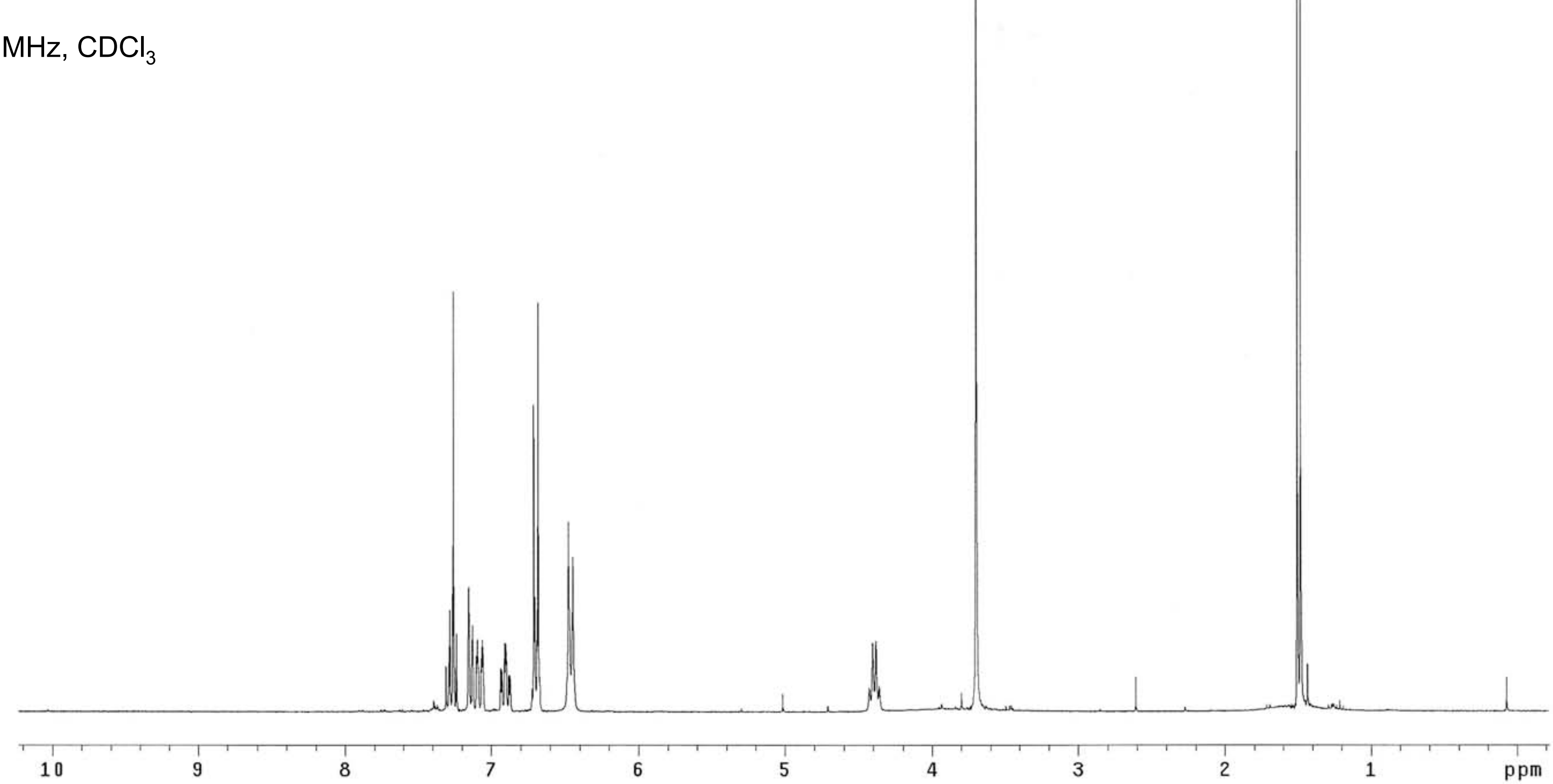
The Chromatogram Noise is 0

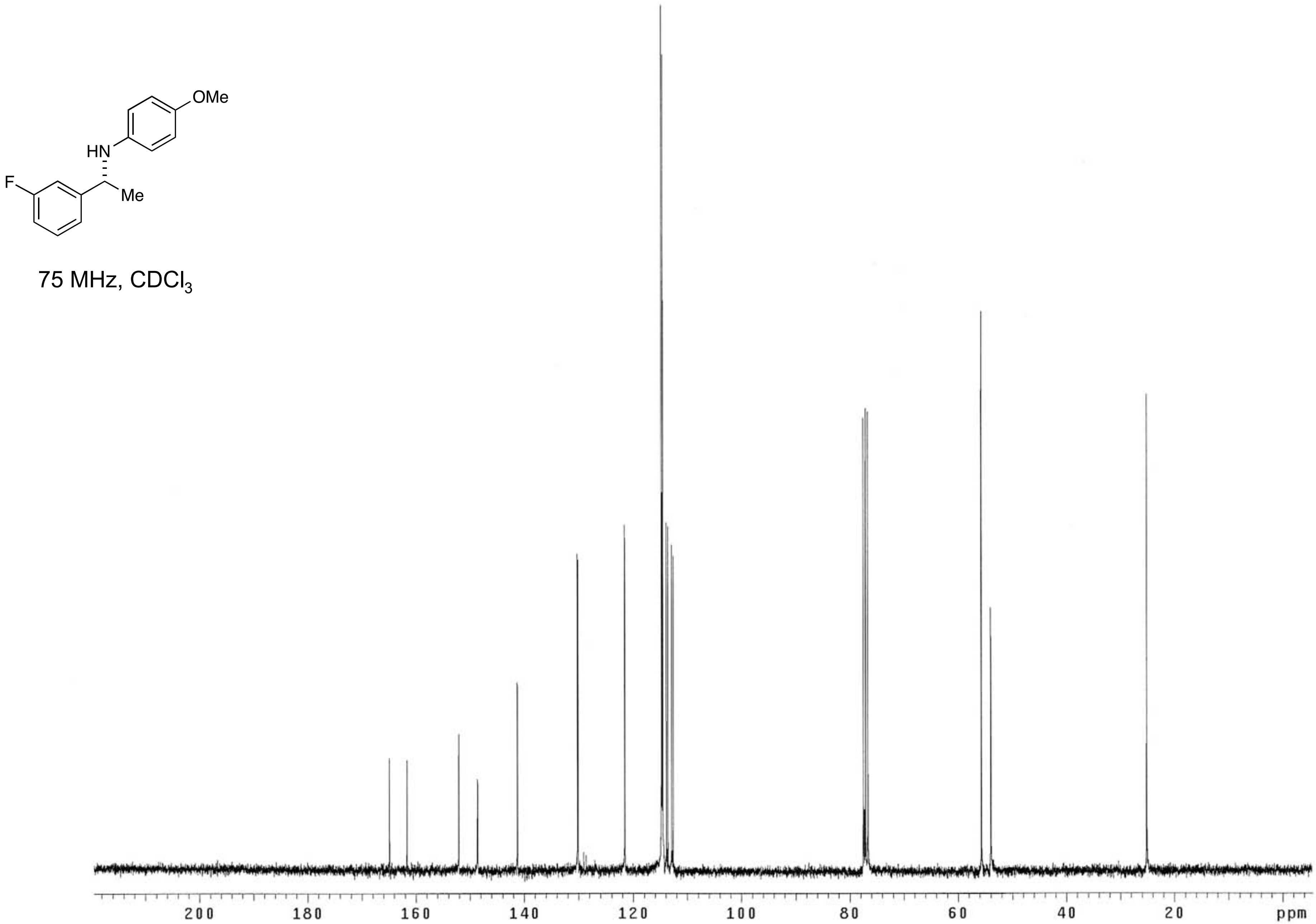
Results Table:

Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	3.38	3.45	3.64	0.00	97.38	732.7	50.1	97.384
2	UNKNOWN	3.65	3.70	3.84	0.00	2.62	19.3	1.3	2.616
Total						100.00	752.0	51.5	100.000



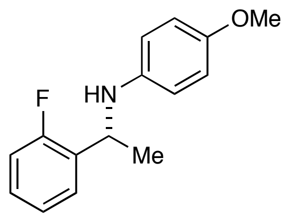
300 MHz, $CDCl_3$



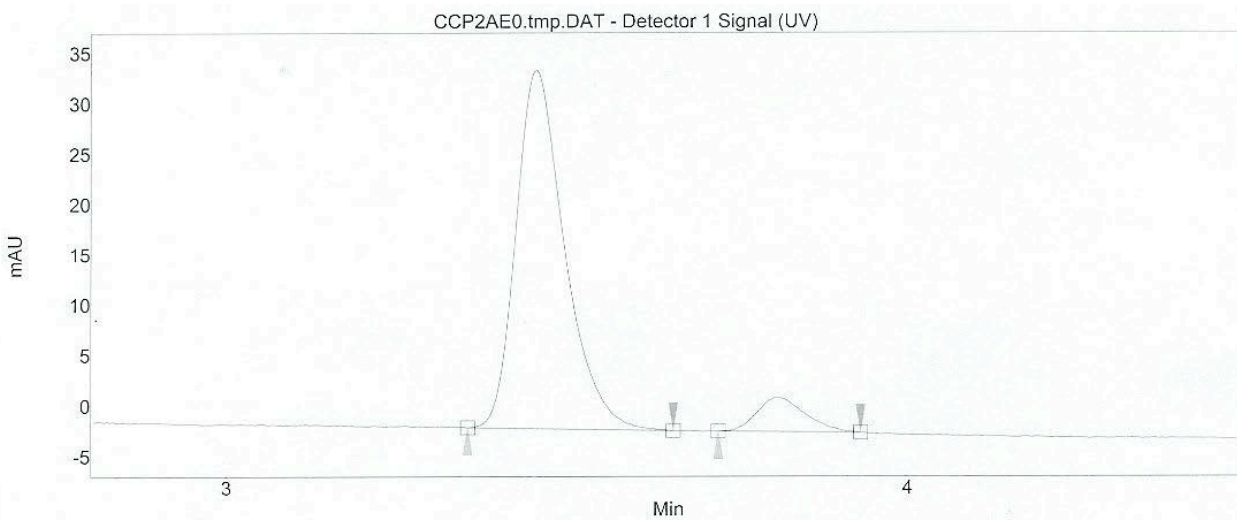


75 MHz, $CDCl_3$

Table 2, Entry 8



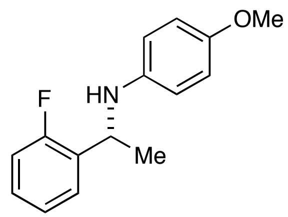
SFC (Daicel Chiracel OJH)
MeOH 5-50% ramp



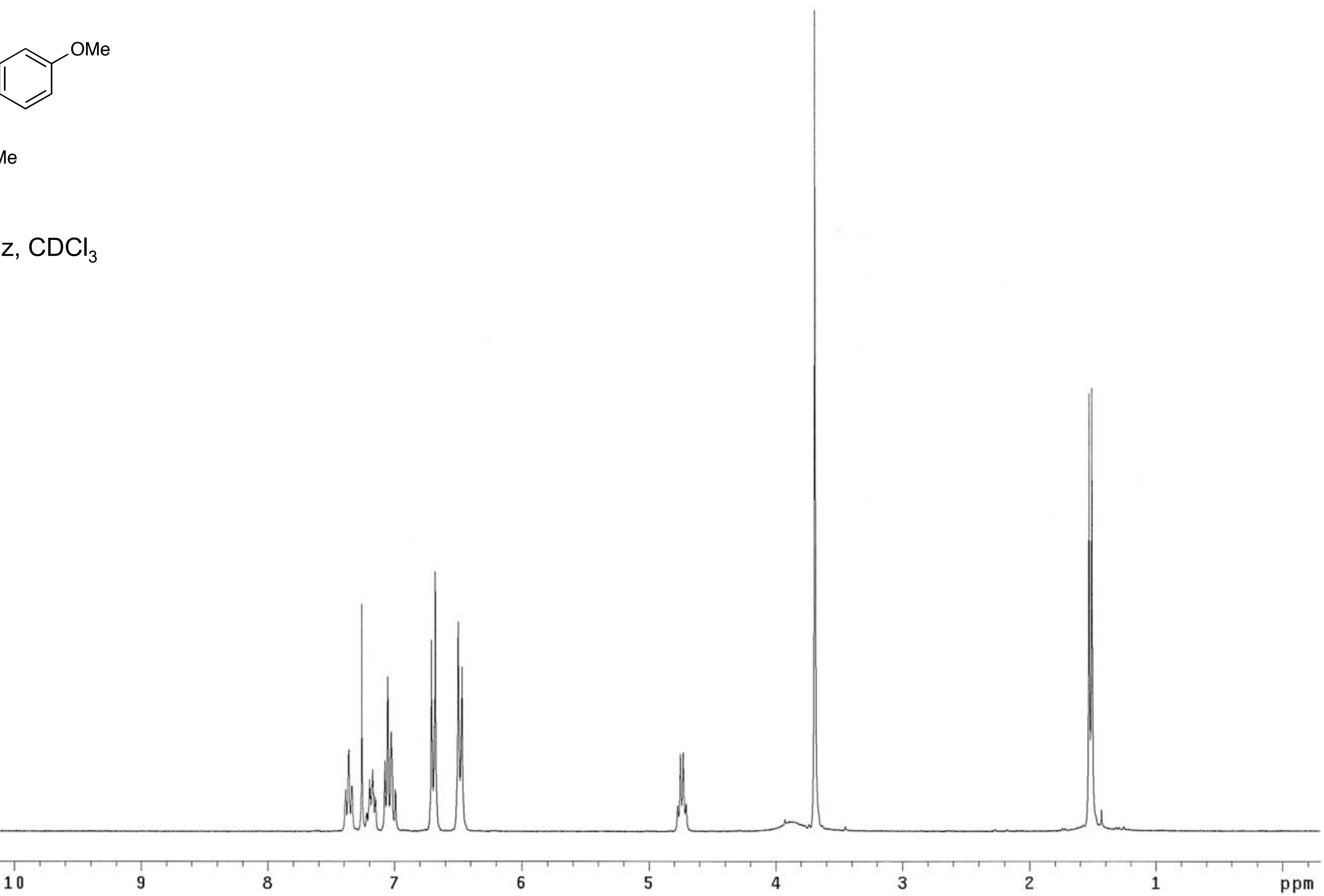
The Chromatogram Noise is 0

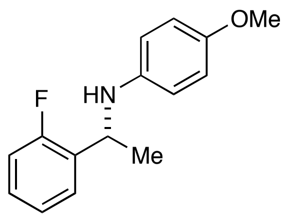
Results Table:

Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[μV]	[μV.Min]	[%]
1	UNKNOWN	3.35	3.46	3.66	0.00	91.50	35.6	2.9	91.505
2	UNKNOWN	3.72	3.81	3.93	0.00	8.50	3.4	0.3	8.495
Total						100.00	39.0	3.2	100.000



300 MHz, $CDCl_3$





75 MHz, $CDCl_3$

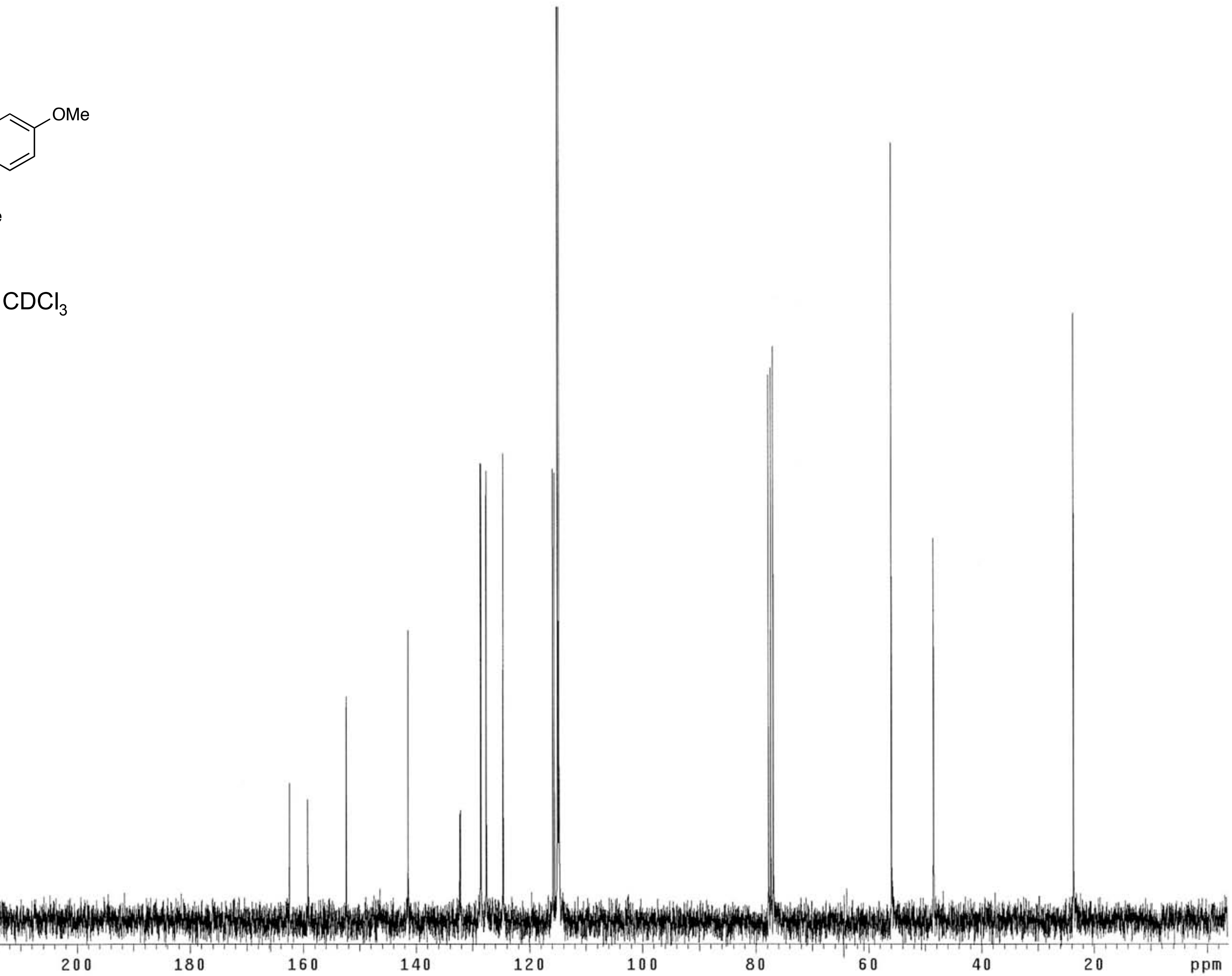
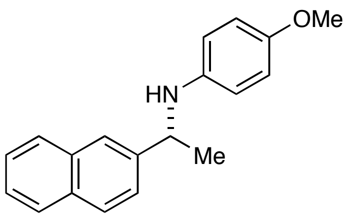
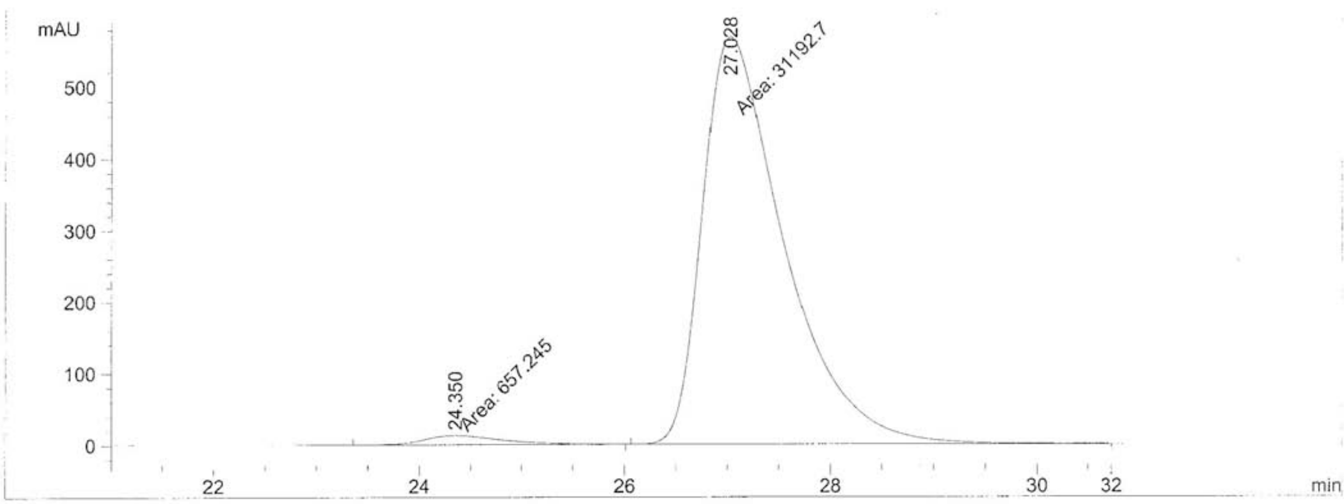


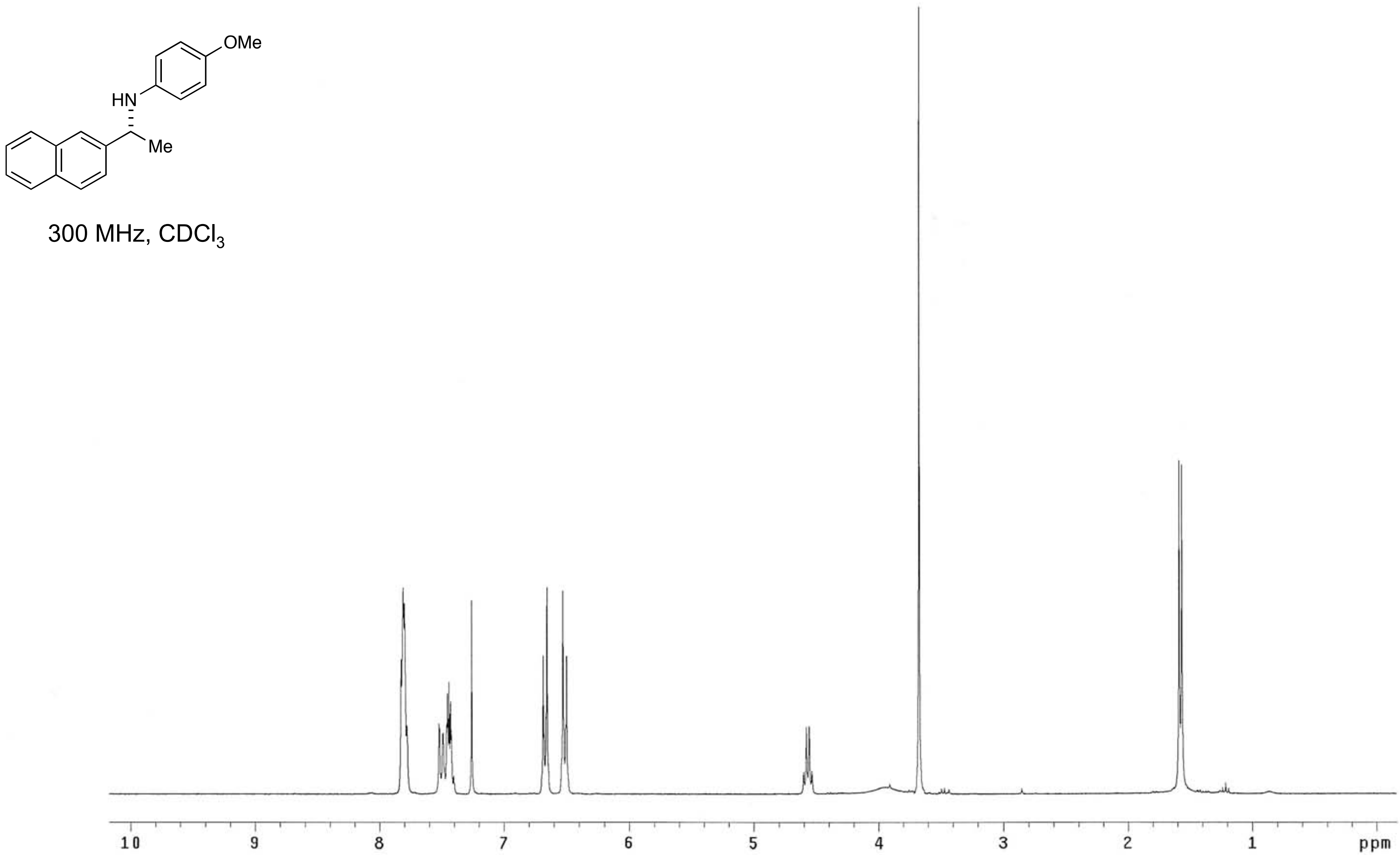
Table 2, Entry 9



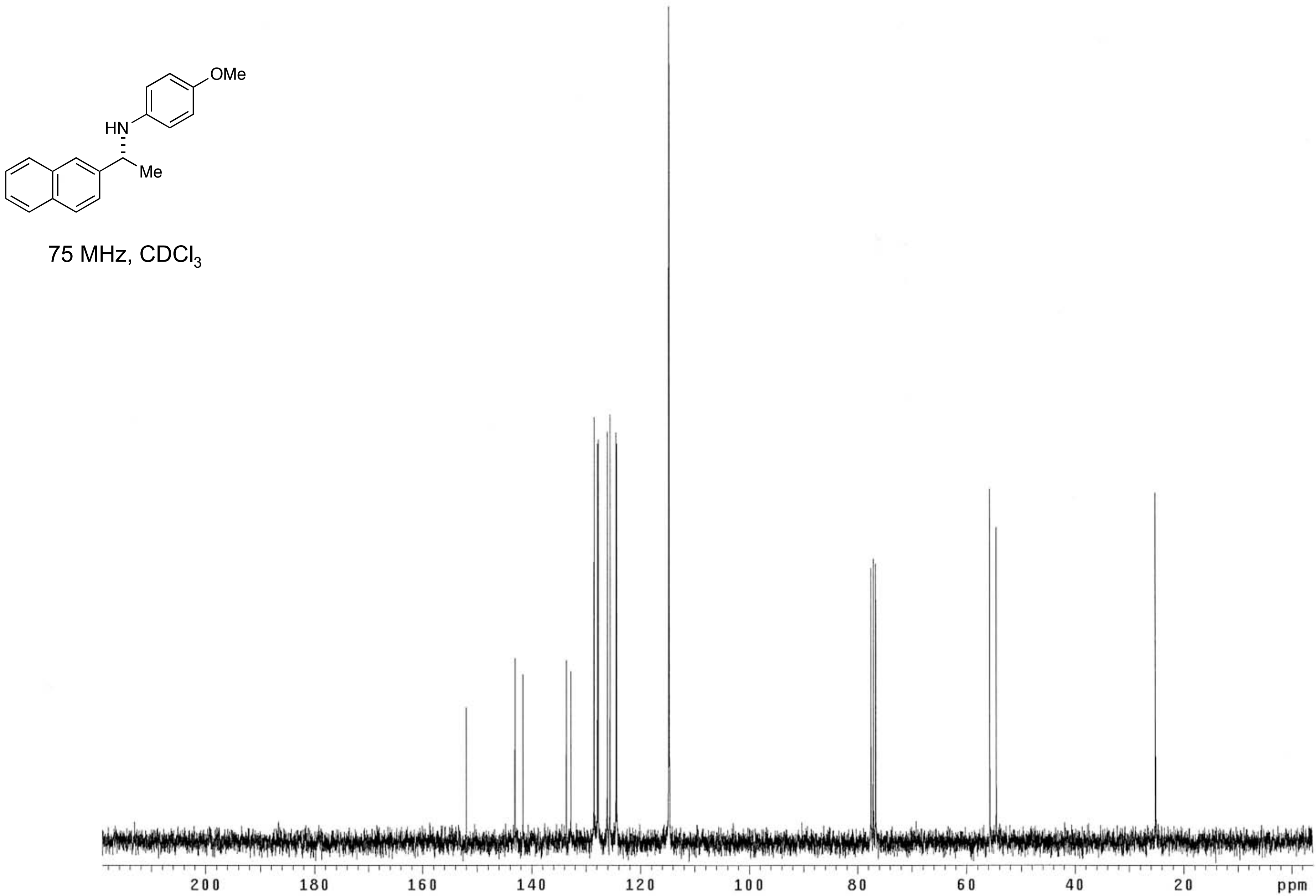
HPLC (Daicel Chiracel ODH)
2% ^{i}PrOH / hexane




```
=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]     %
----|-------|----|-------|----------|----------|--------|
   1  24.350 MM    0.8621  657.24451   12.70683   2.0636
   2  27.028 MM    0.9156 3.11927e4   567.80847  97.9364

Totals :                  3.18499e4   580.51530
```

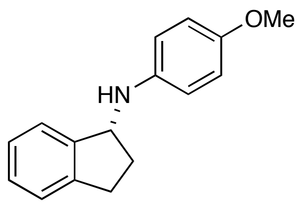


300 MHz, $CDCl_3$

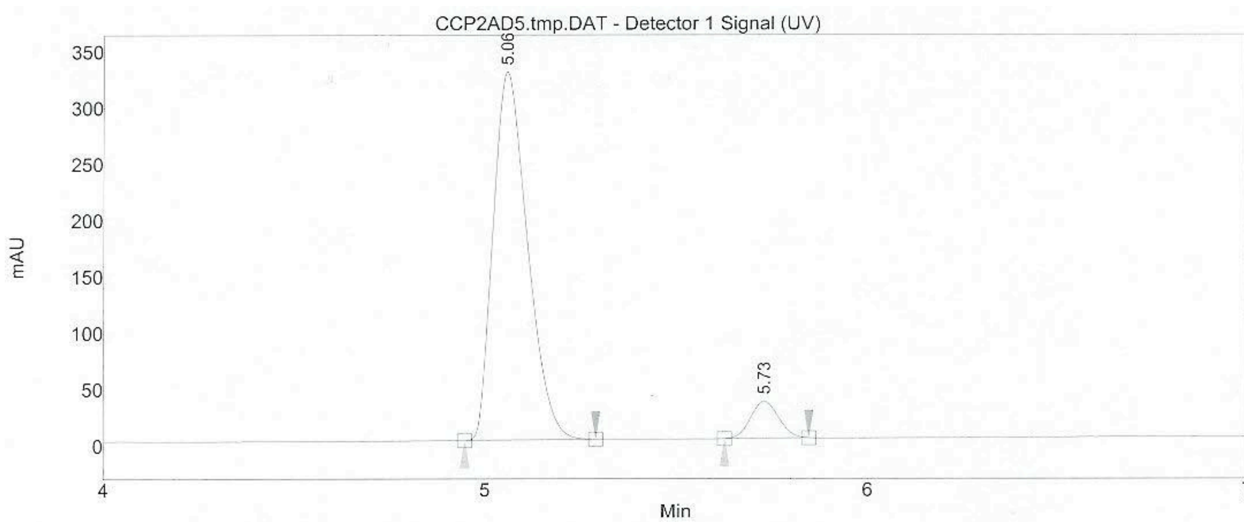


75 MHz, $CDCl_3$

Table 2, Entry 10



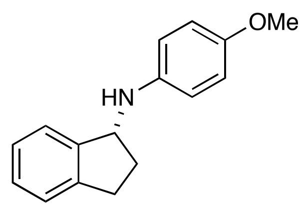
SFC (Daicel Chiracel ADH)
MeOH 5-50% ramp



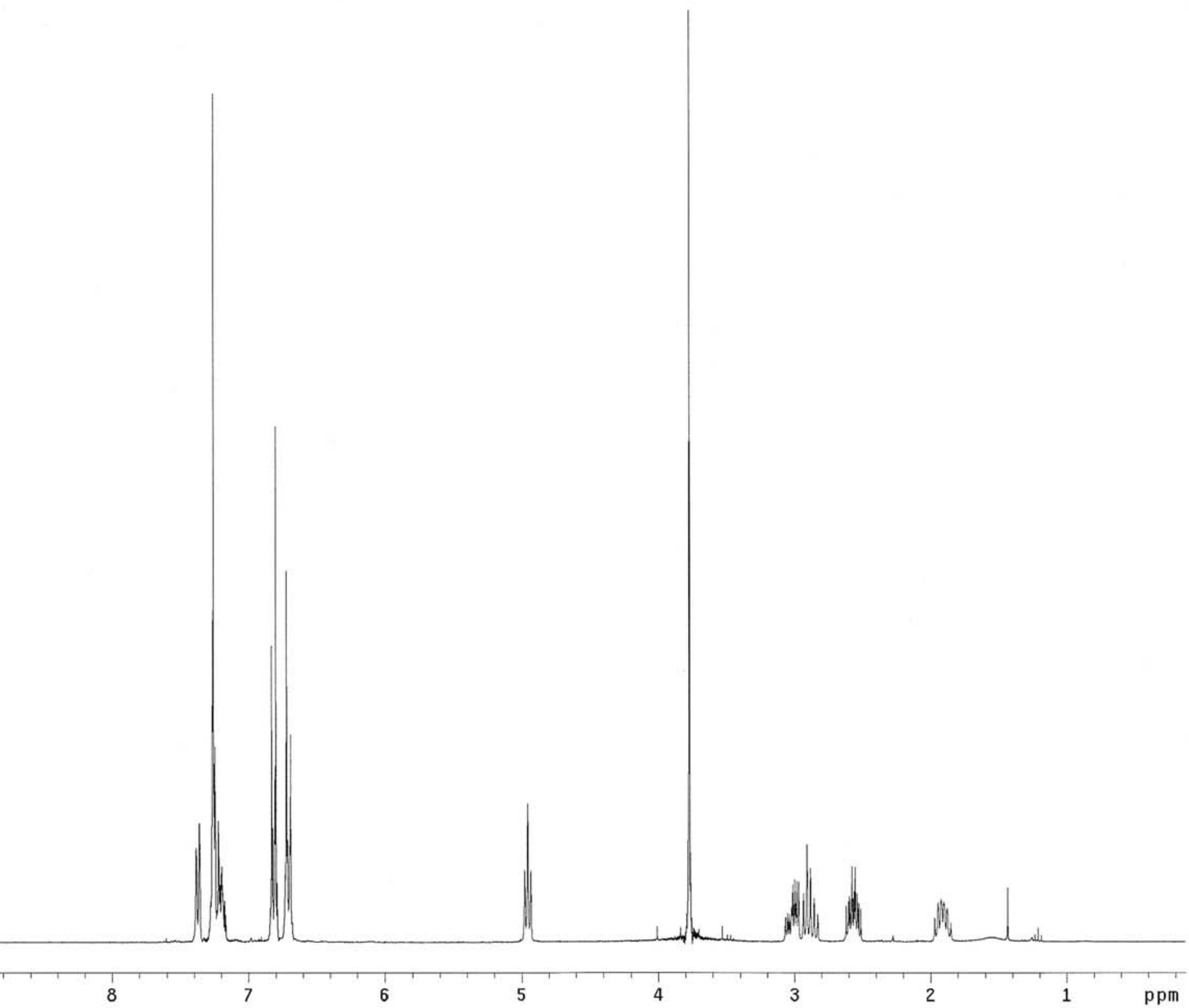
The Chromatogram Noise is 0

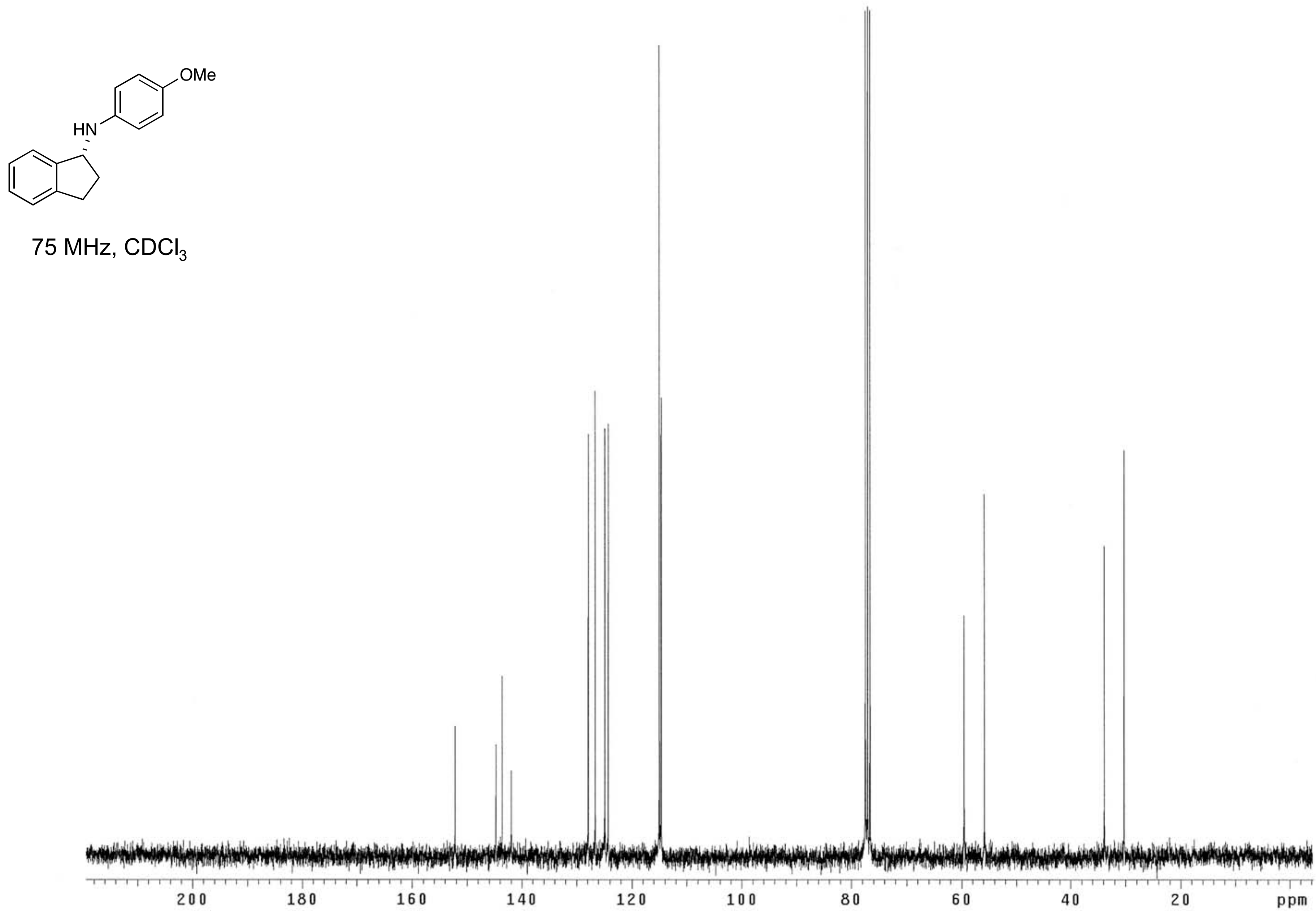
Results Table:

Index	Name	Time	Width USP	Quantity	Height	Area	Area
		[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	5.06	0.17	92.50	326.6	34.0	92.501
2	UNKNOWN	5.73	0.14	7.50	32.5	2.8	7.499
Total				100.00	359.2	36.8	100.000



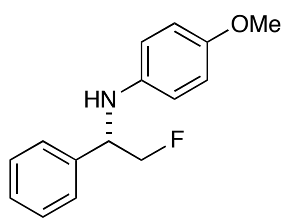
300 MHz, $CDCl_3$



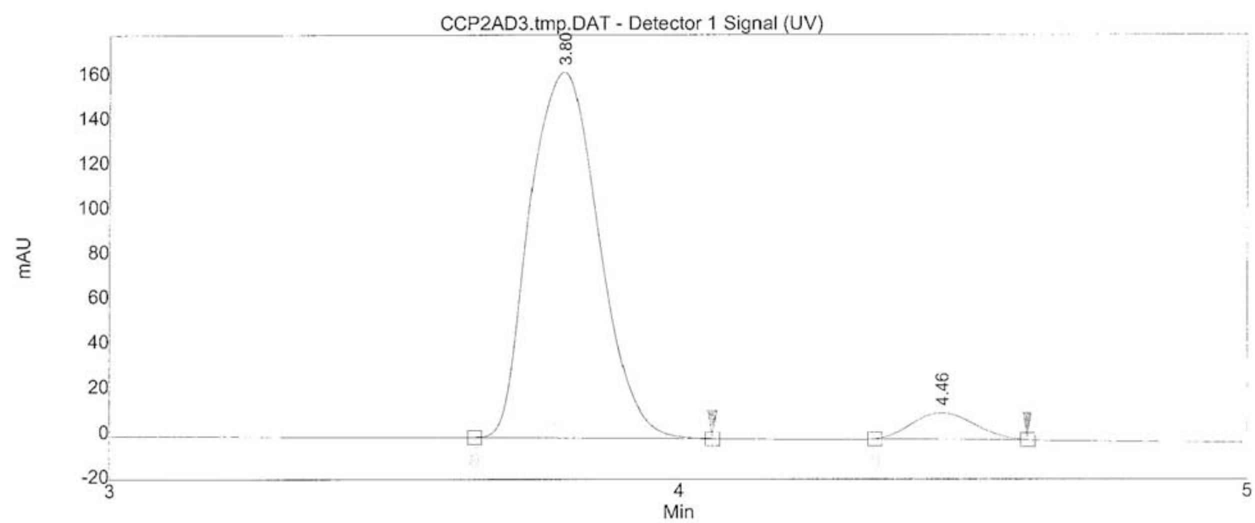


75 MHz, $CDCl_3$

Table 2, Entry 11



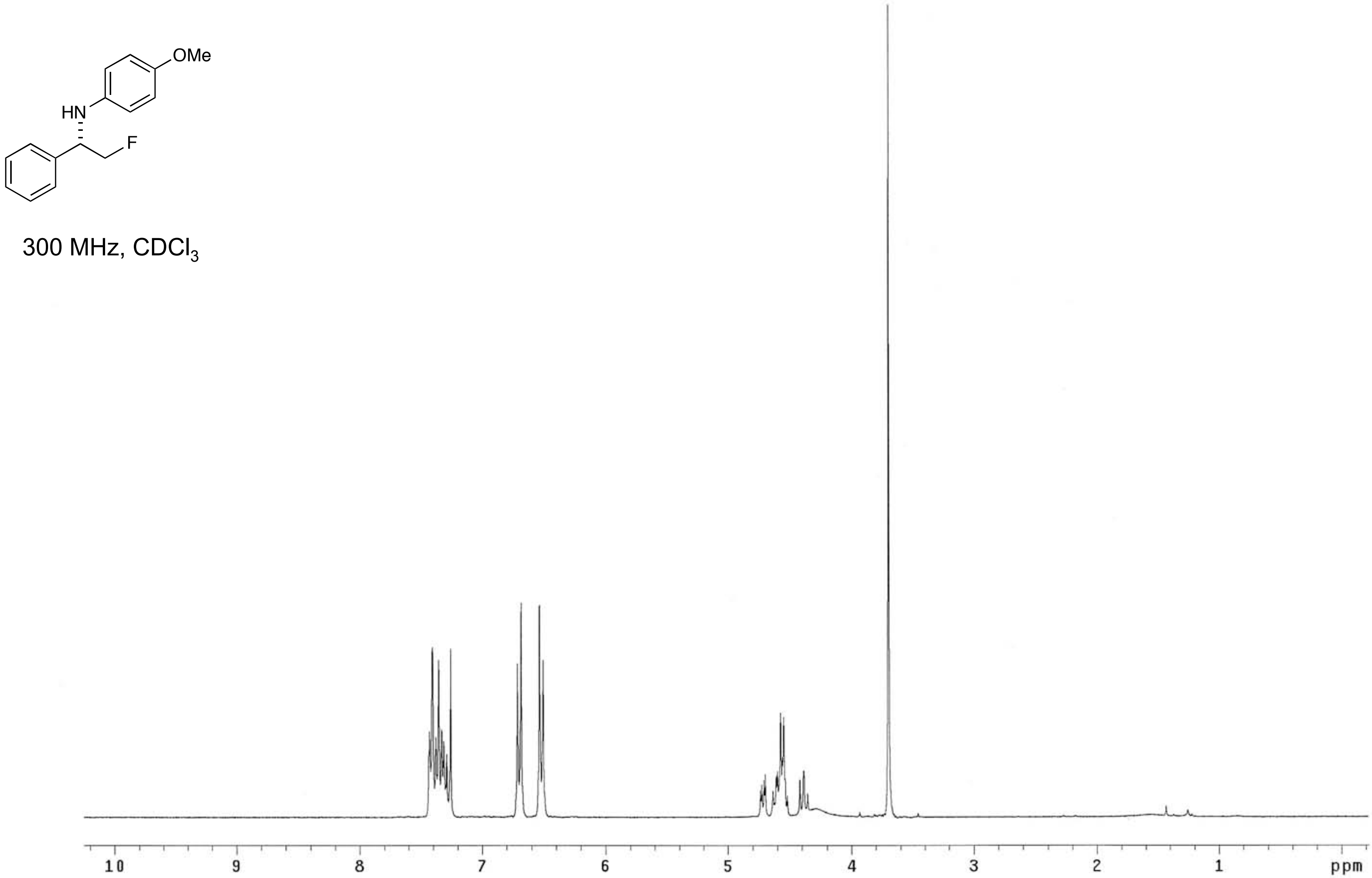
SFC (Daicel Chiracel ADH)
MeOH 5-50% ramp



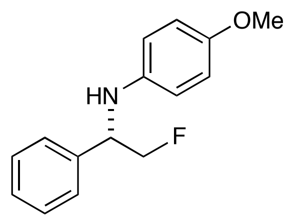
The Chromatogram Noise is 0

Results Table:

Index	Name	Time	Width USP	Quantity	Height	Area	Area
		[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	3.80	0.22	93.90	163.3	22.8	93.904
2	UNKNOWN	4.46	0.20	6.10	11.7	1.5	6.096
Total				100.00	175.0	24.3	100.000



300 MHz, $CDCl_3$



75 MHz, $CDCl_3$

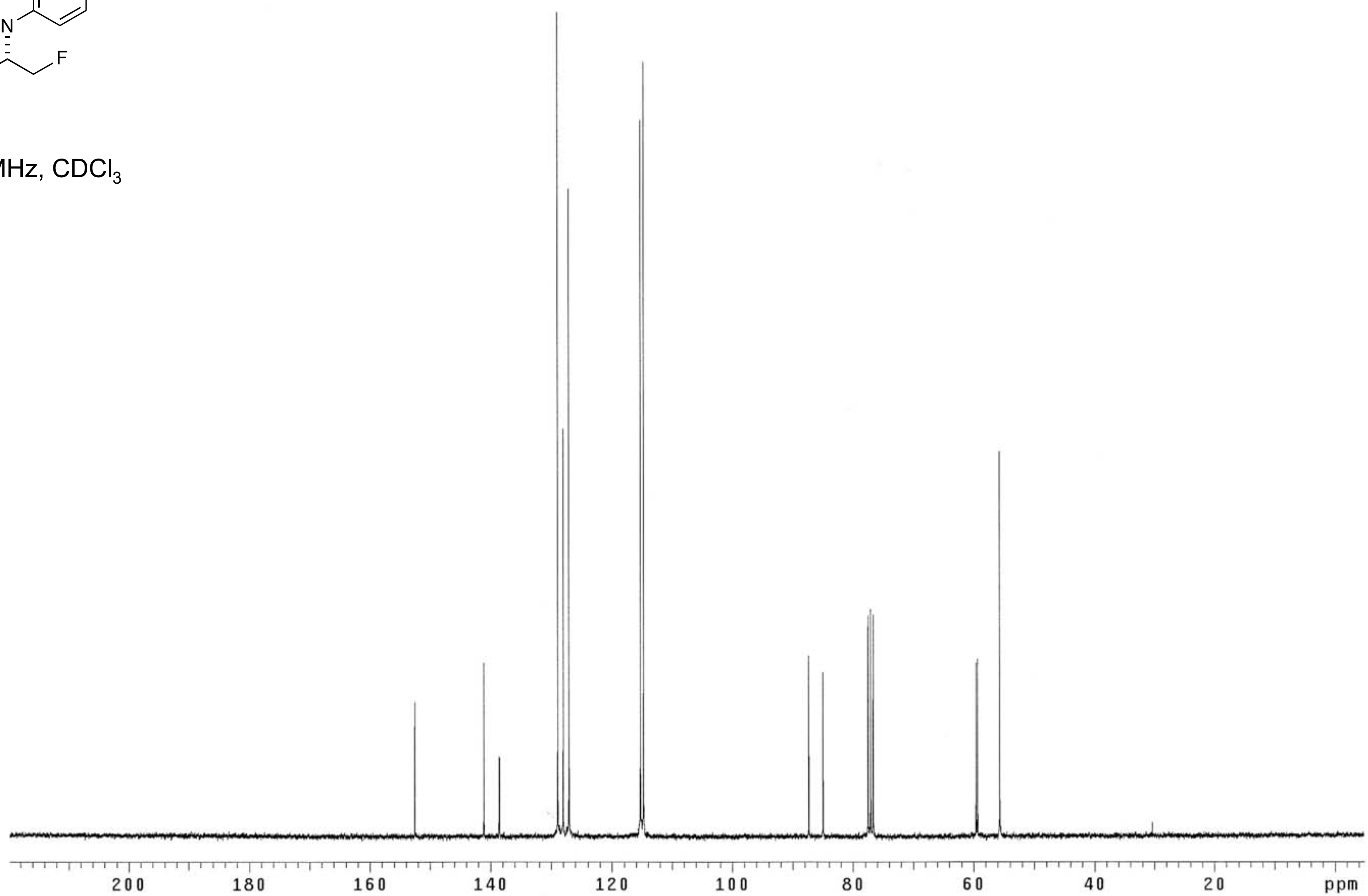
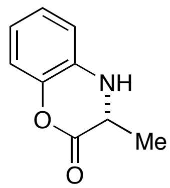
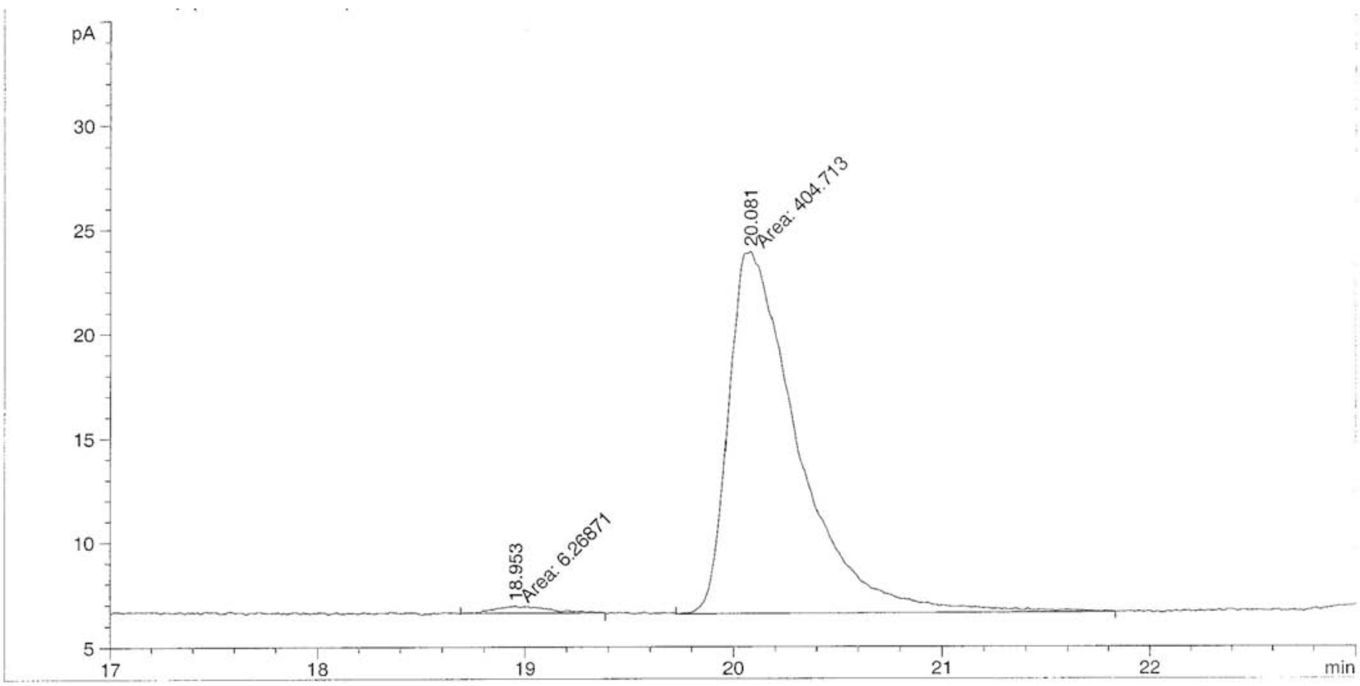


Table 2, Entry 12



GLC (Bodman Chiraldex Γ-TA)
150 ˚C isotherm

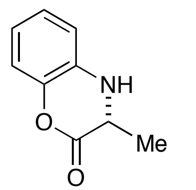


Area Percent Report

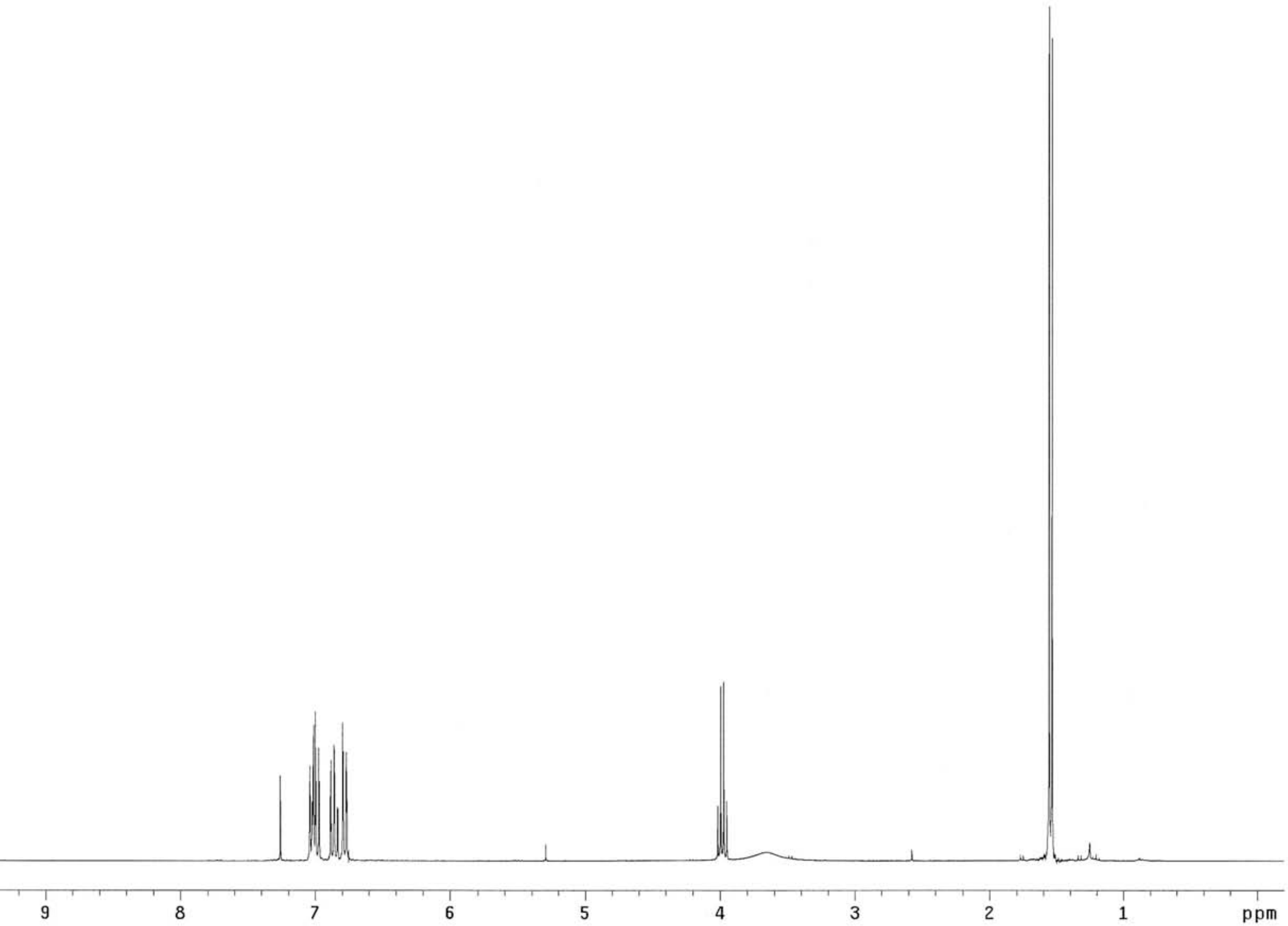
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

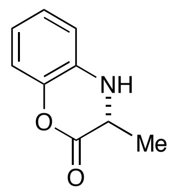
Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	18.953	MM	0.3085	6.26871	3.38634e-1	1.52530
2	20.081	MM	0.3888	404.71326	17.34952	98.47470
Totals :				410.98196	17.68815	



300 MHz, $CDCl_3$





75 MHz, $CDCl_3$

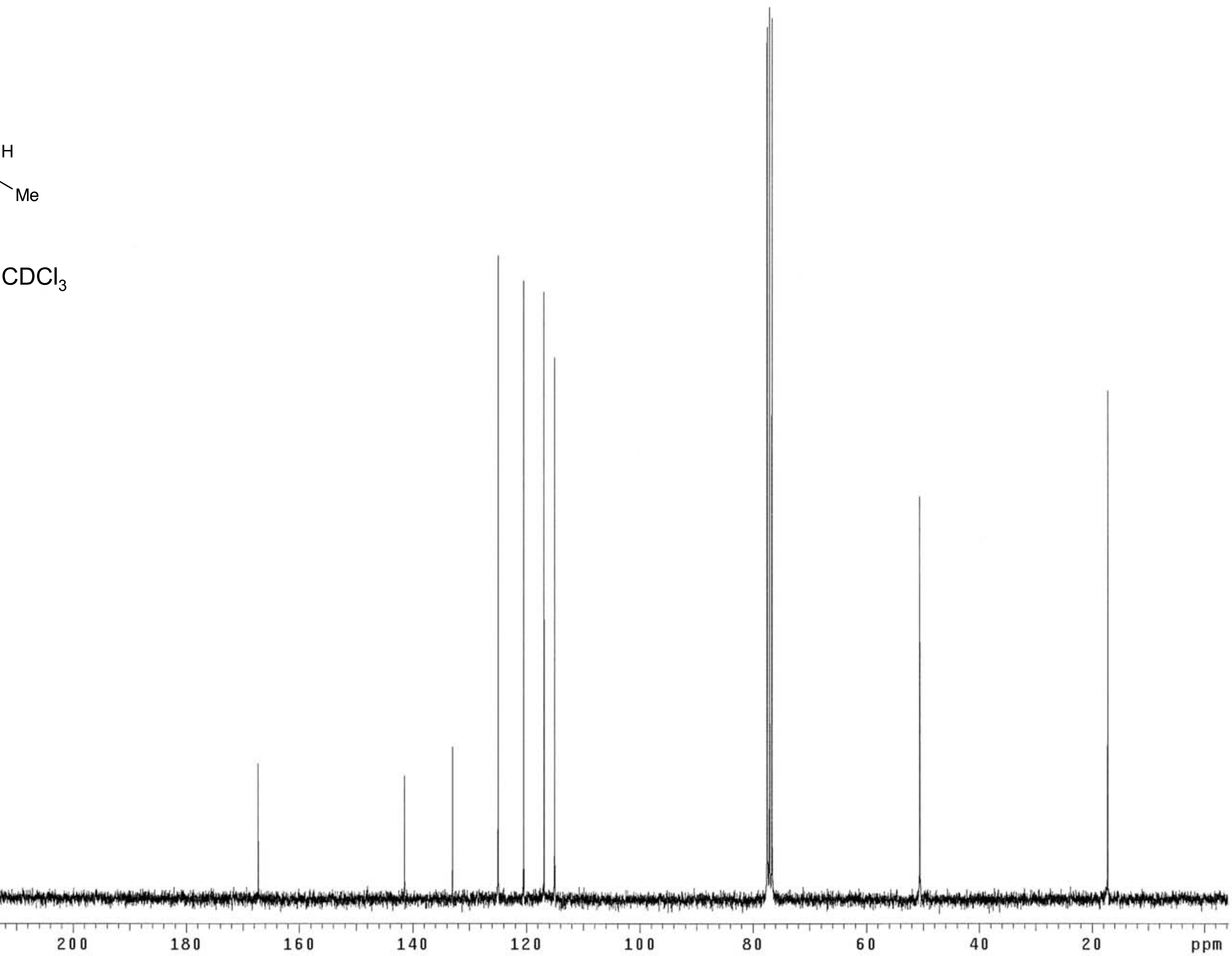
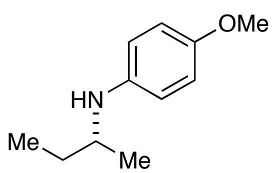
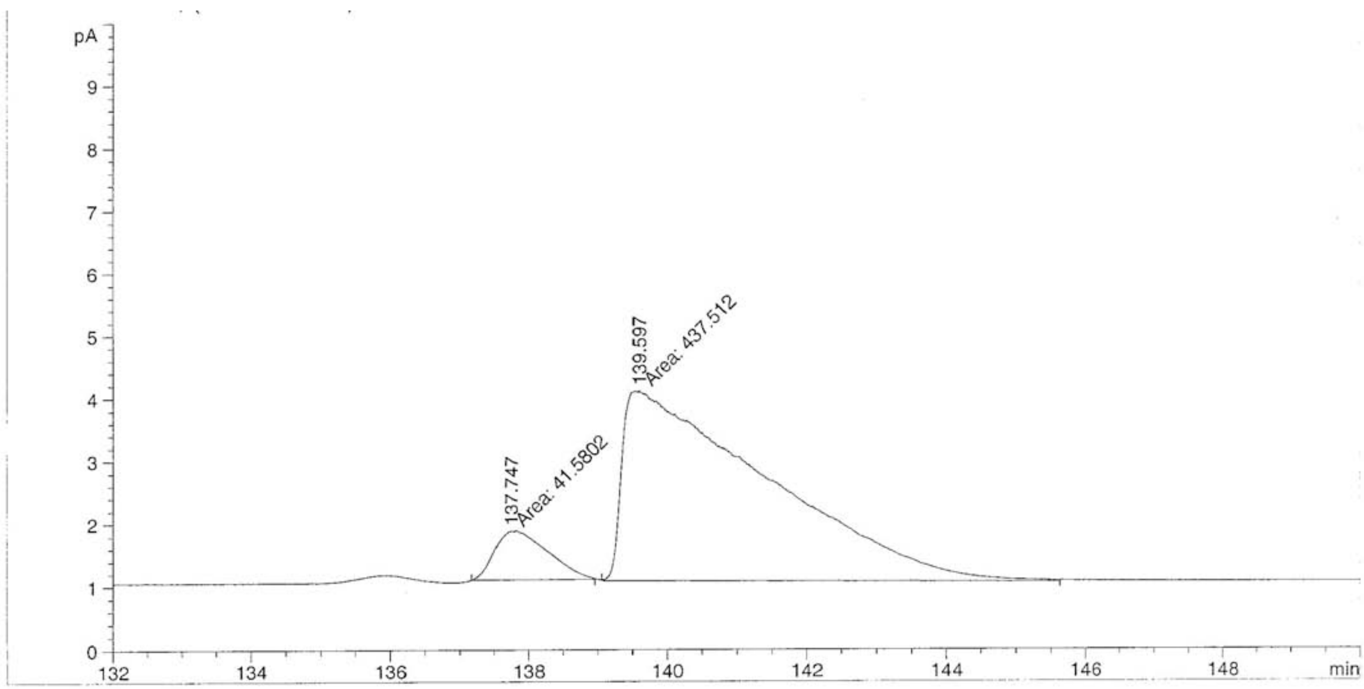


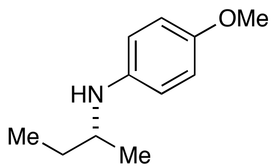
Table 3, Entry 1



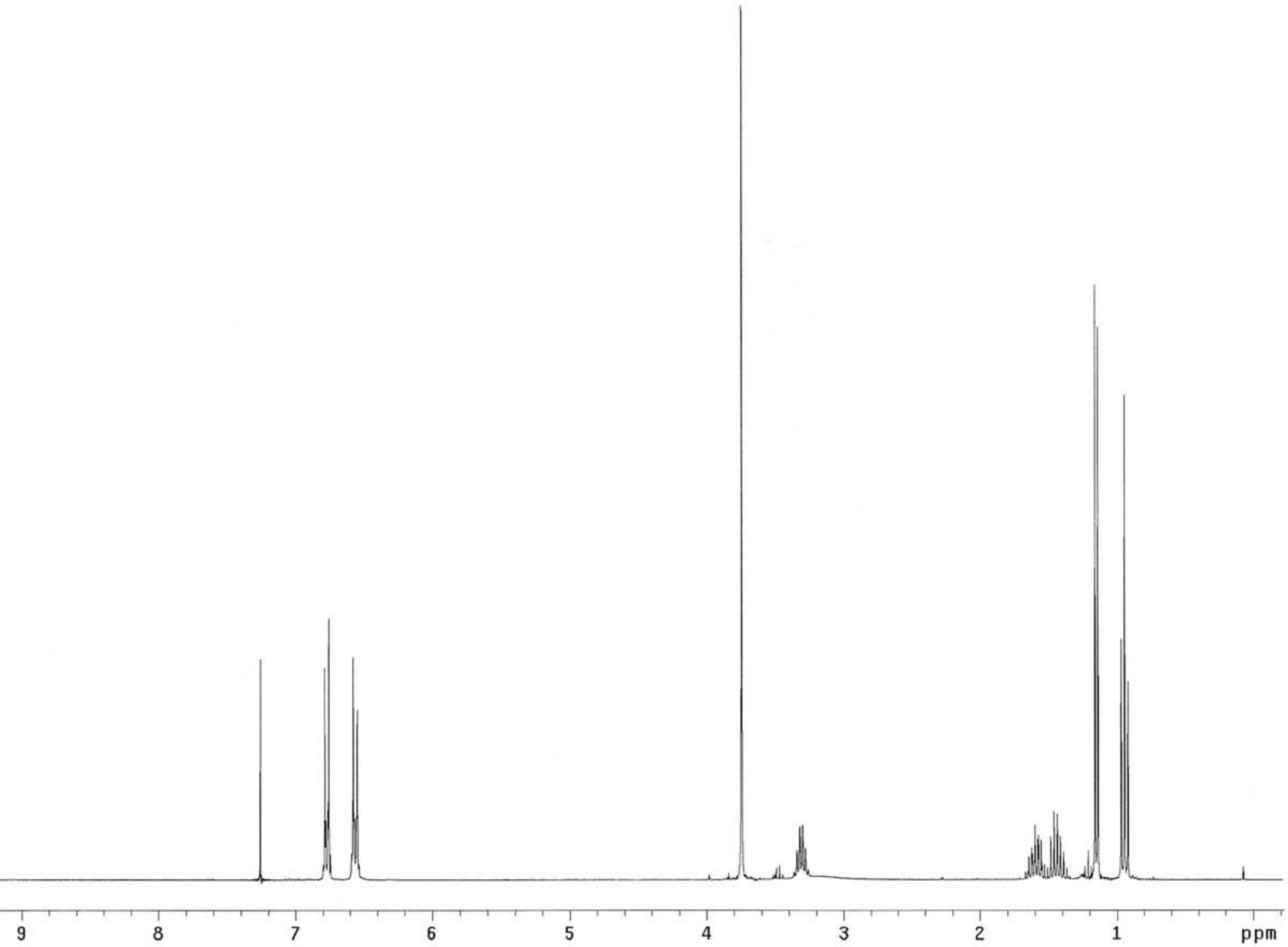
GLC (Varian CP-chirasil-dex-CB)
100 ˚C isotherm

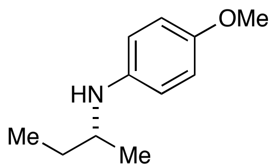



```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height      Area
  #   [min]        [min]   [pA*s]      [pA]         %
----|-------|----|-------|----------|----------|--------|
   1 137.747 MM     0.8885   41.58017 7.79946e-1  8.67895
   2 139.597 MM     2.4091  437.51208    3.02684 91.32105

Totals :                    479.09225    3.80679
```



300 MHz, $CDCl_3$





75 MHz, $CDCl_3$

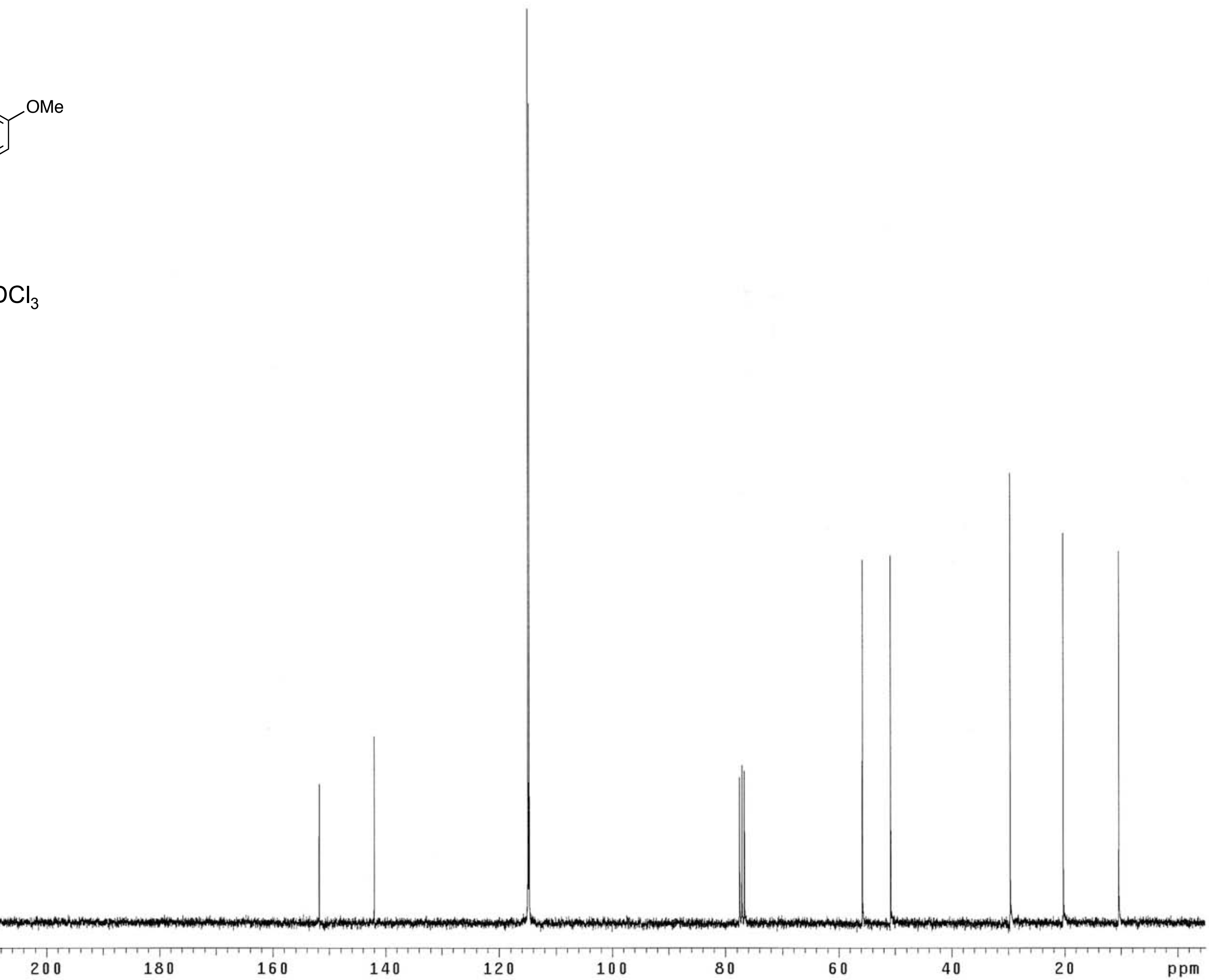
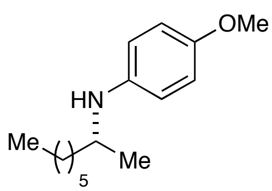
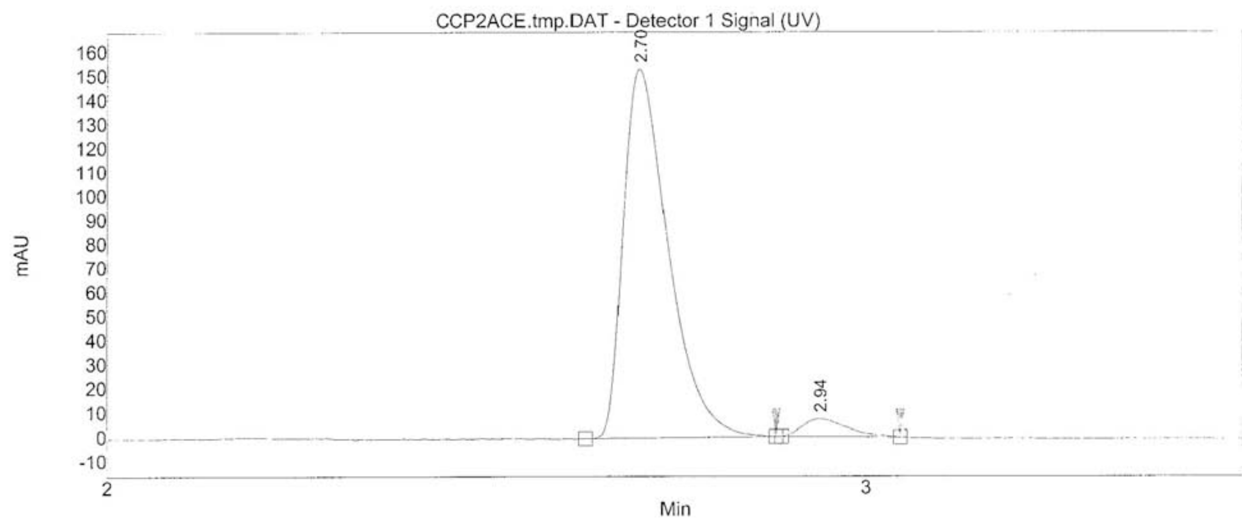


Table 3, Entry 2



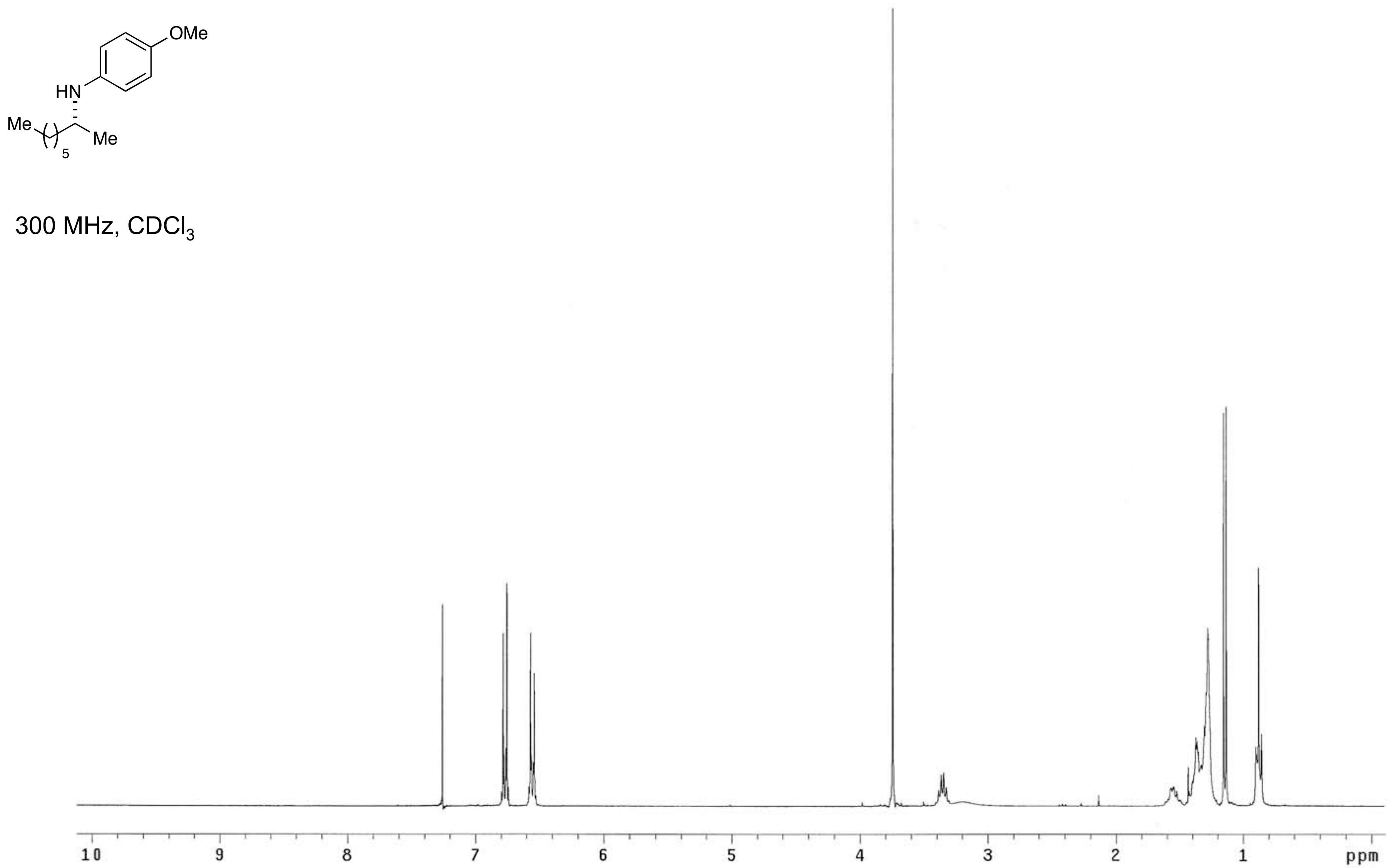
SFC (Daicel Chiracel OJH)
MeOH 5-10% ramp



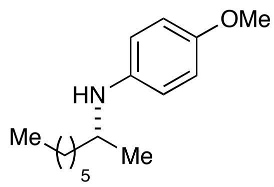
The Chromatogram Noise is 0

Results Table:

Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	2.63	2.70	2.88	0.00	95.64	153.1	10.5	95.641
2	UNKNOWN	2.89	2.94	3.04	0.00	4.36	7.1	0.5	4.359
Total						100.00	160.1	10.9	100.000



OMe
HN
Me
Me
5
300 MHz, $CDCl_3$
10
9
8
7
6
5
4
3
2
1
ppm



75 MHz, $CDCl_3$

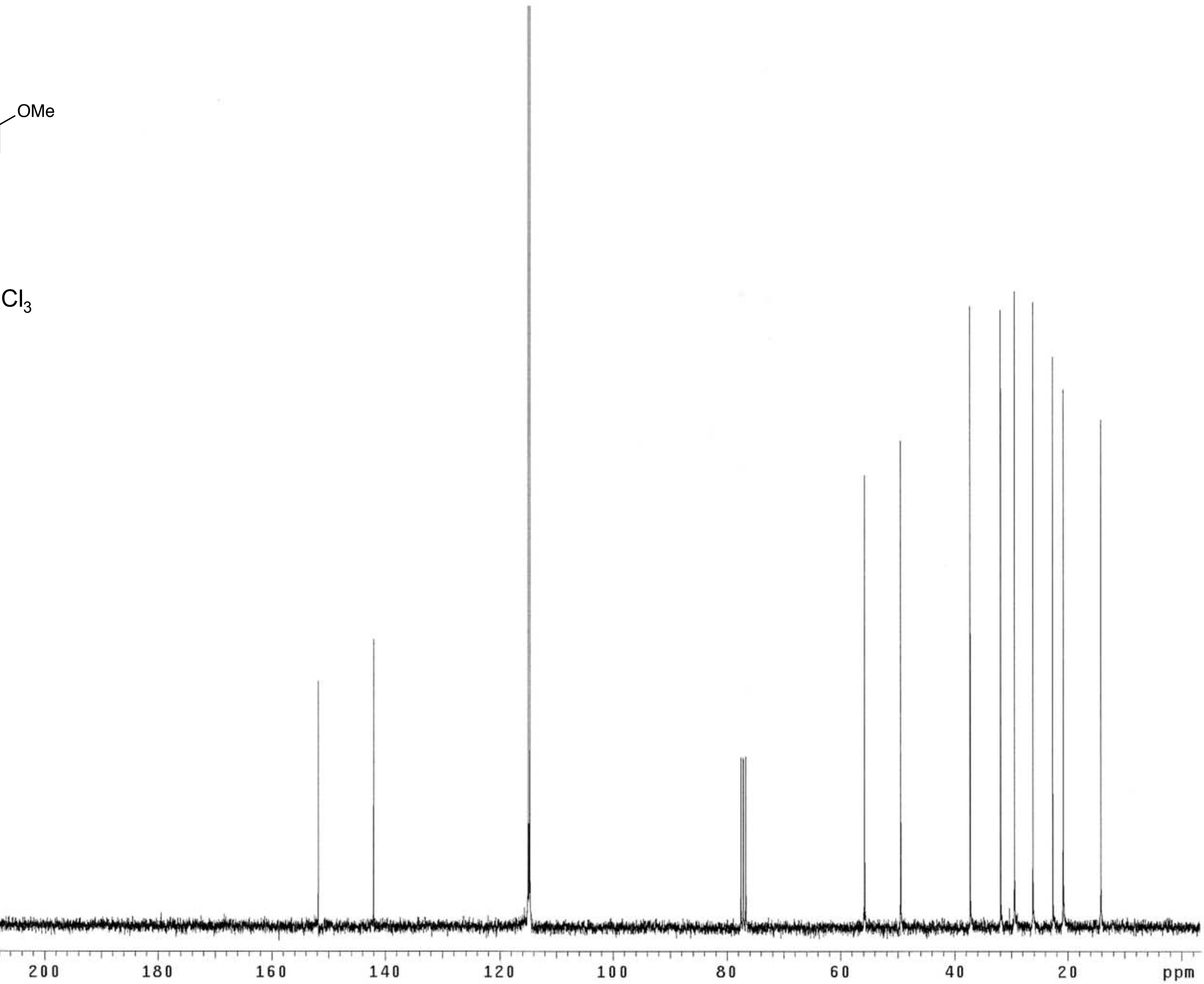
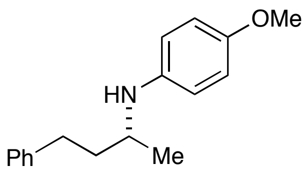
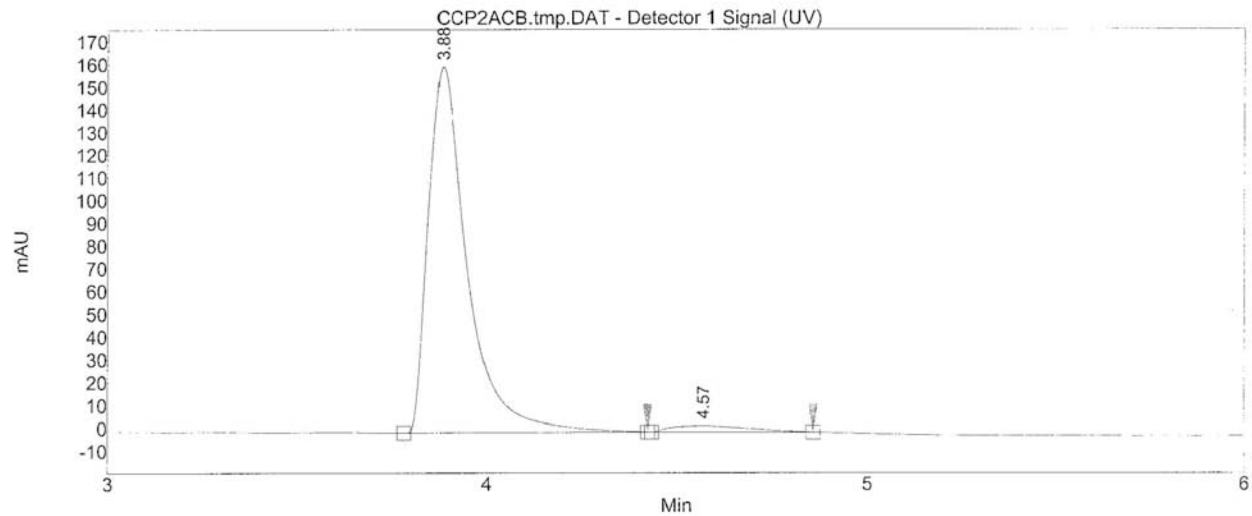


Table 3, Entry 3



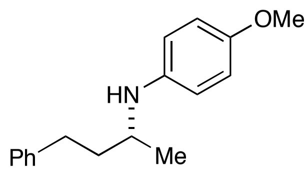
SFC (Daicel Chiracel ADH)
MeOH 5-50% ramp



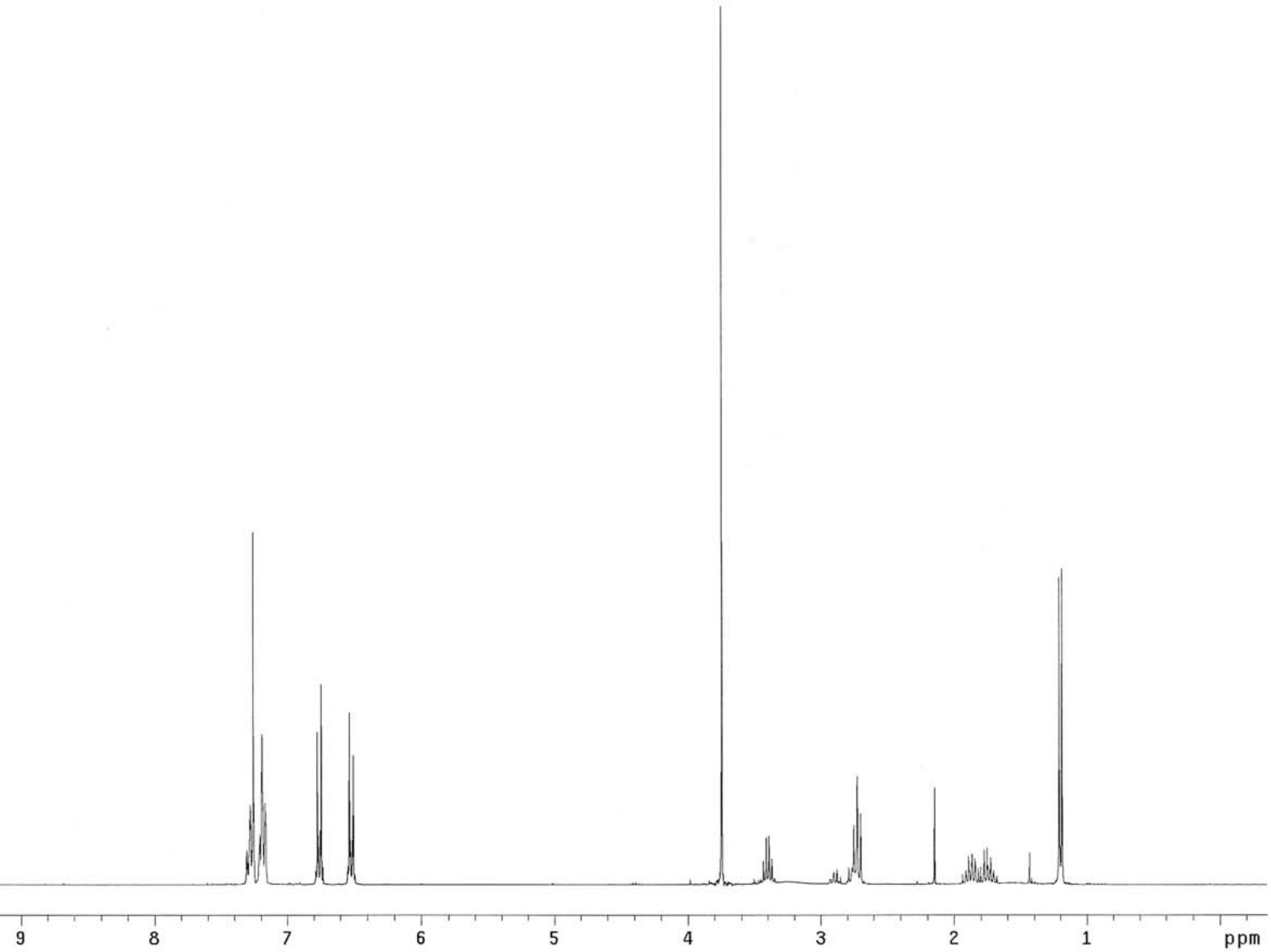
The Chromatogram Noise is 0

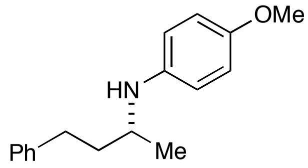
Results Table:

Index	Name	Time	Width USP	Quantity	Height	Area	Area
		[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	3.88	0.18	96.89	160.8	19.3	96.885
2	UNKNOWN	4.57	0.37	3.11	2.7	0.6	3.115
Total				100.00	163.6	19.9	100.000



300 MHz, $CDCl_3$





75 MHz, $CDCl_3$

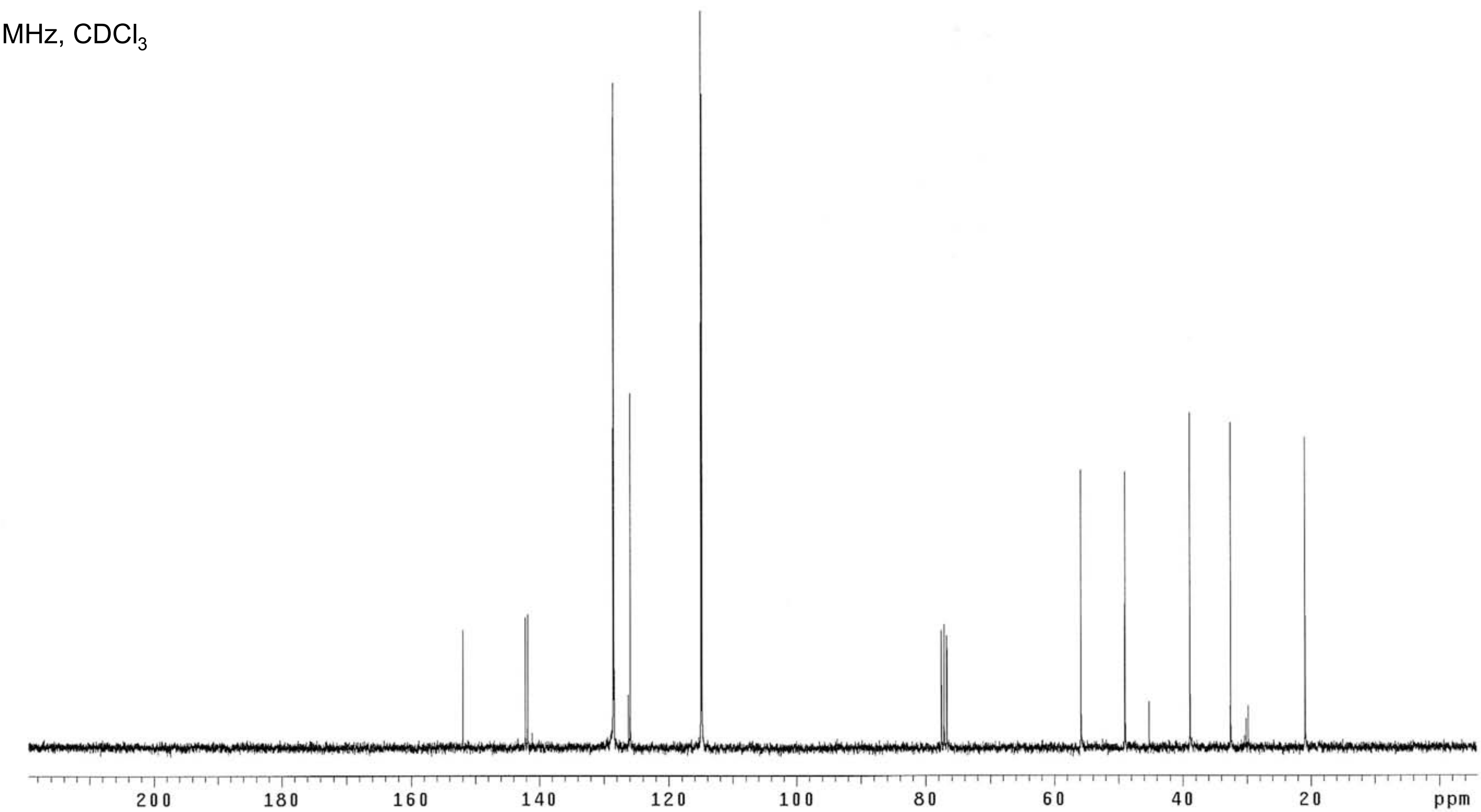
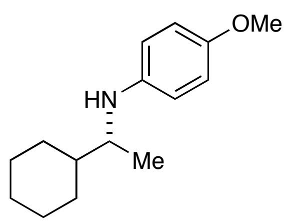
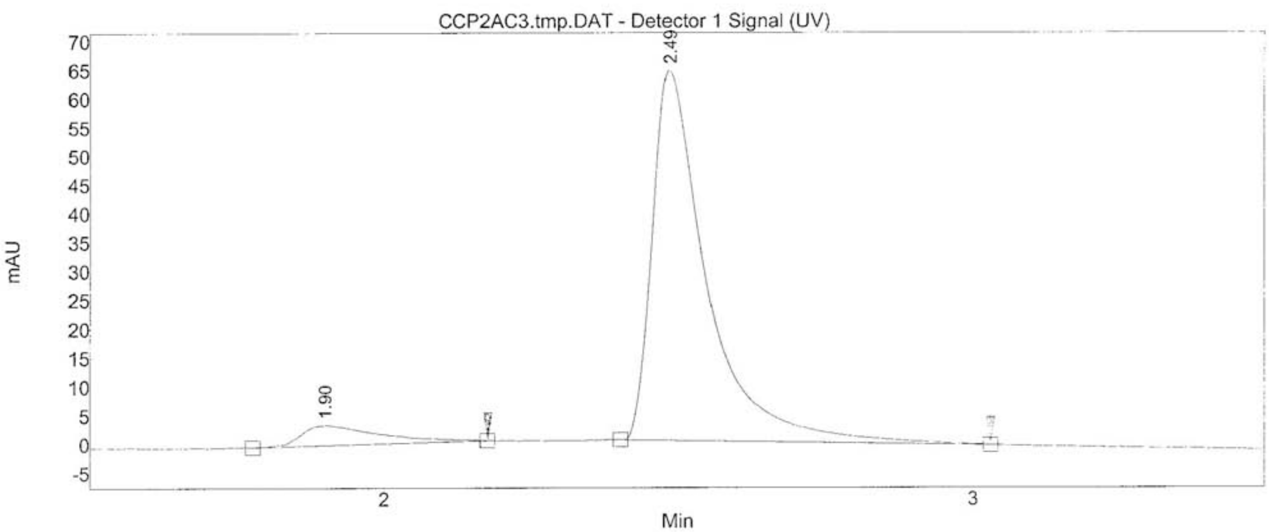


Table 3, Entry 4



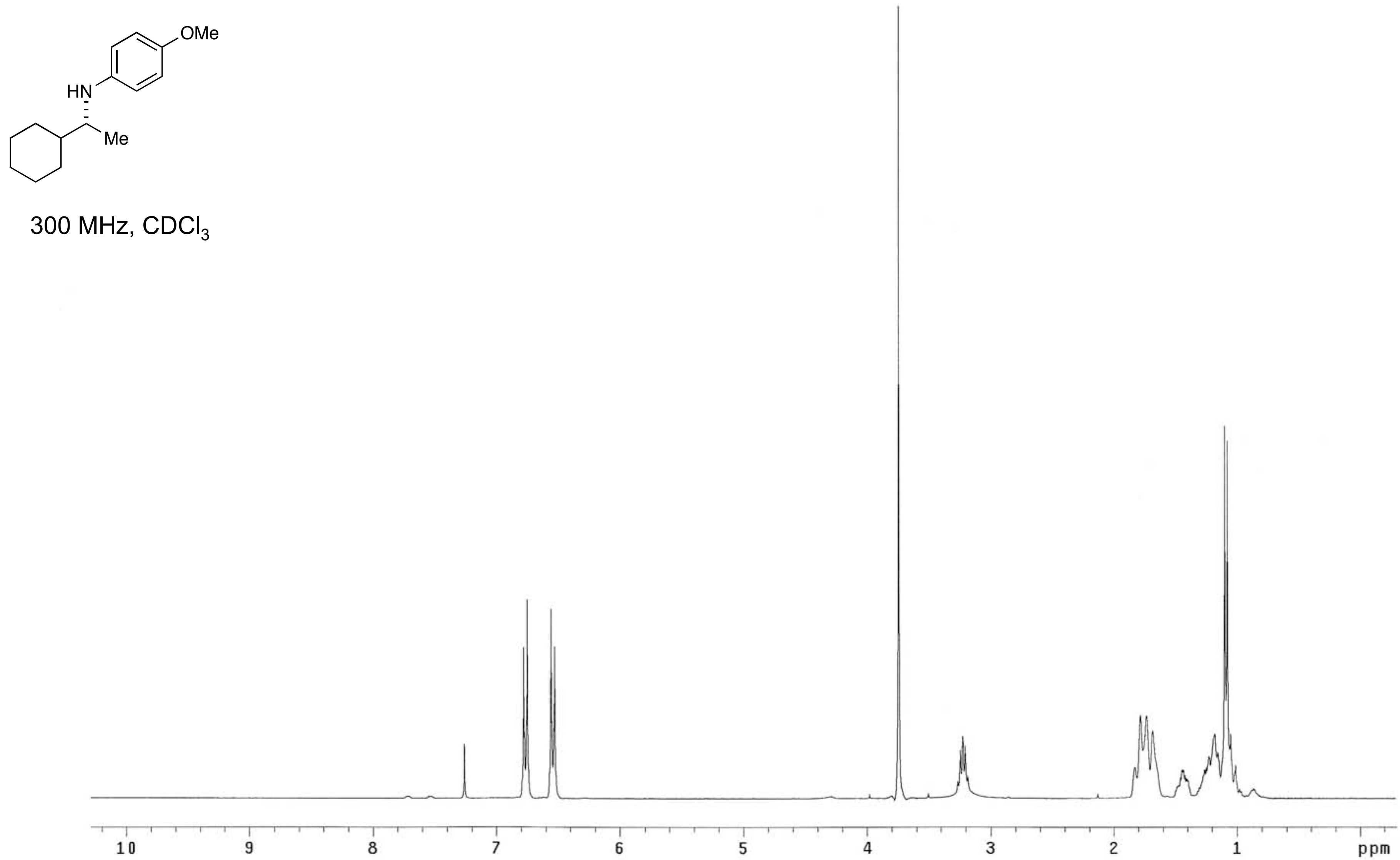
SFC (Daicel Chiracel ASH)
MeOH 5-25% ramp



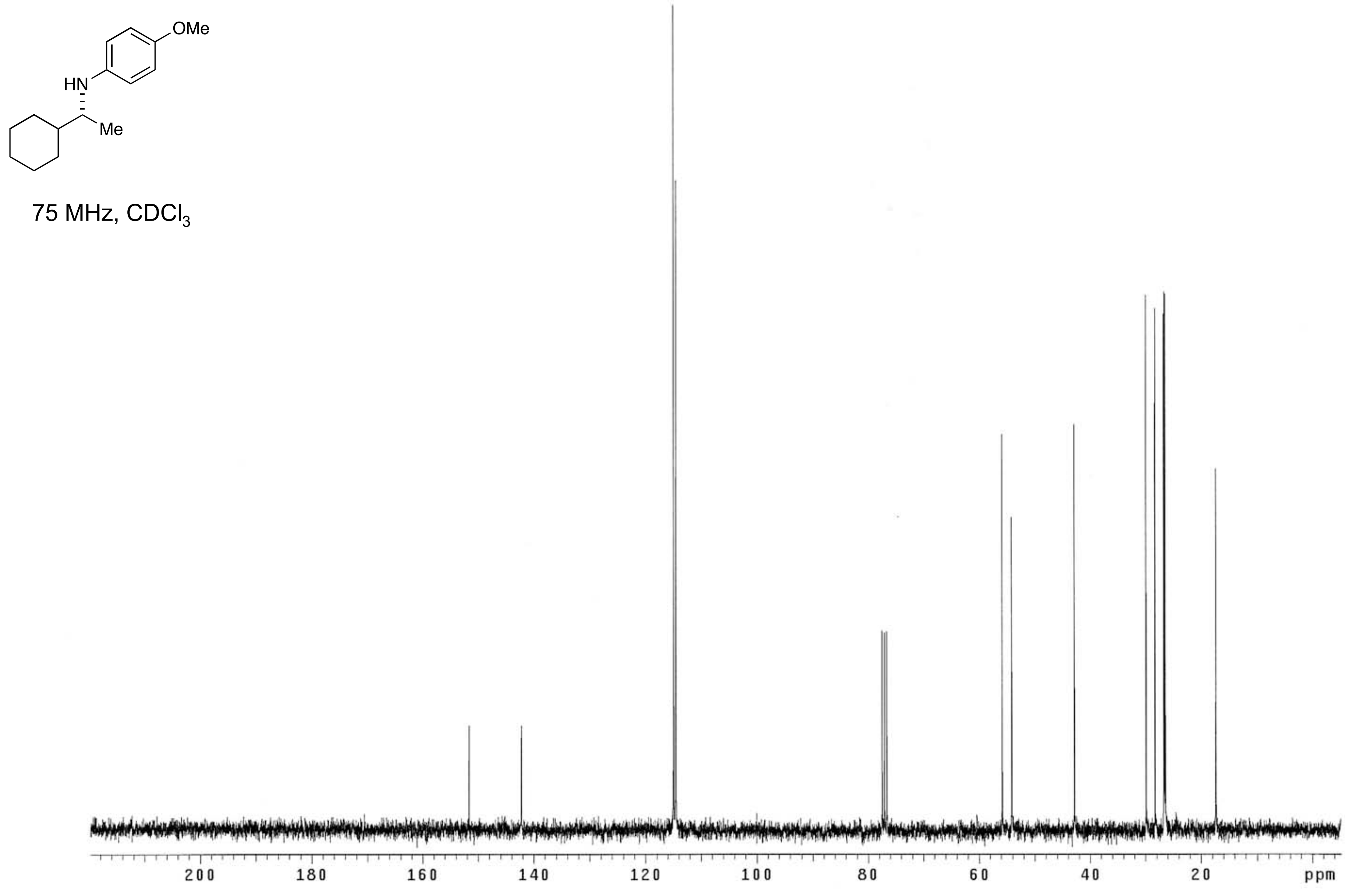
The Chromatogram Noise is 0

Results Table:

Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[μV]	[μV.Min]	[%]
2	UNKNOWN	1.78	1.90	2.18	0.00	7.20	3.4	0.5	7.196
1	UNKNOWN	2.40	2.49	3.03	0.00	92.80	64.2	6.9	92.804
Total						100.00	67.6	7.4	100.000

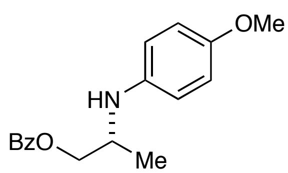


300 MHz, $CDCl_3$

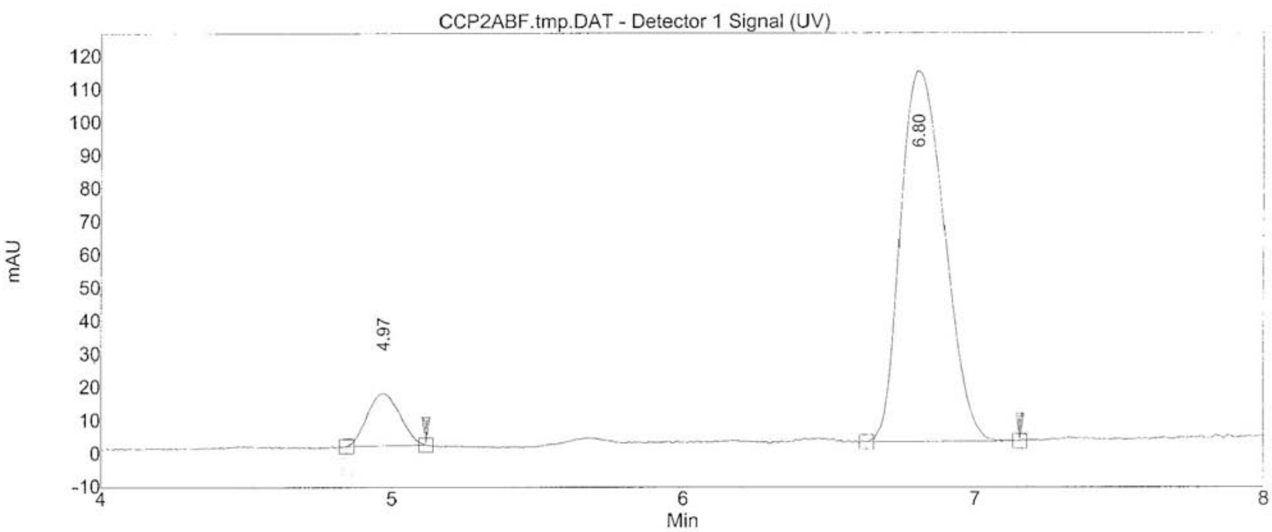


75 MHz, $CDCl_3$

Table 3, Entry 5



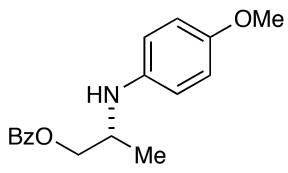
SFC (Daicel Chiracel ADH)
MeOH 5-50% ramp



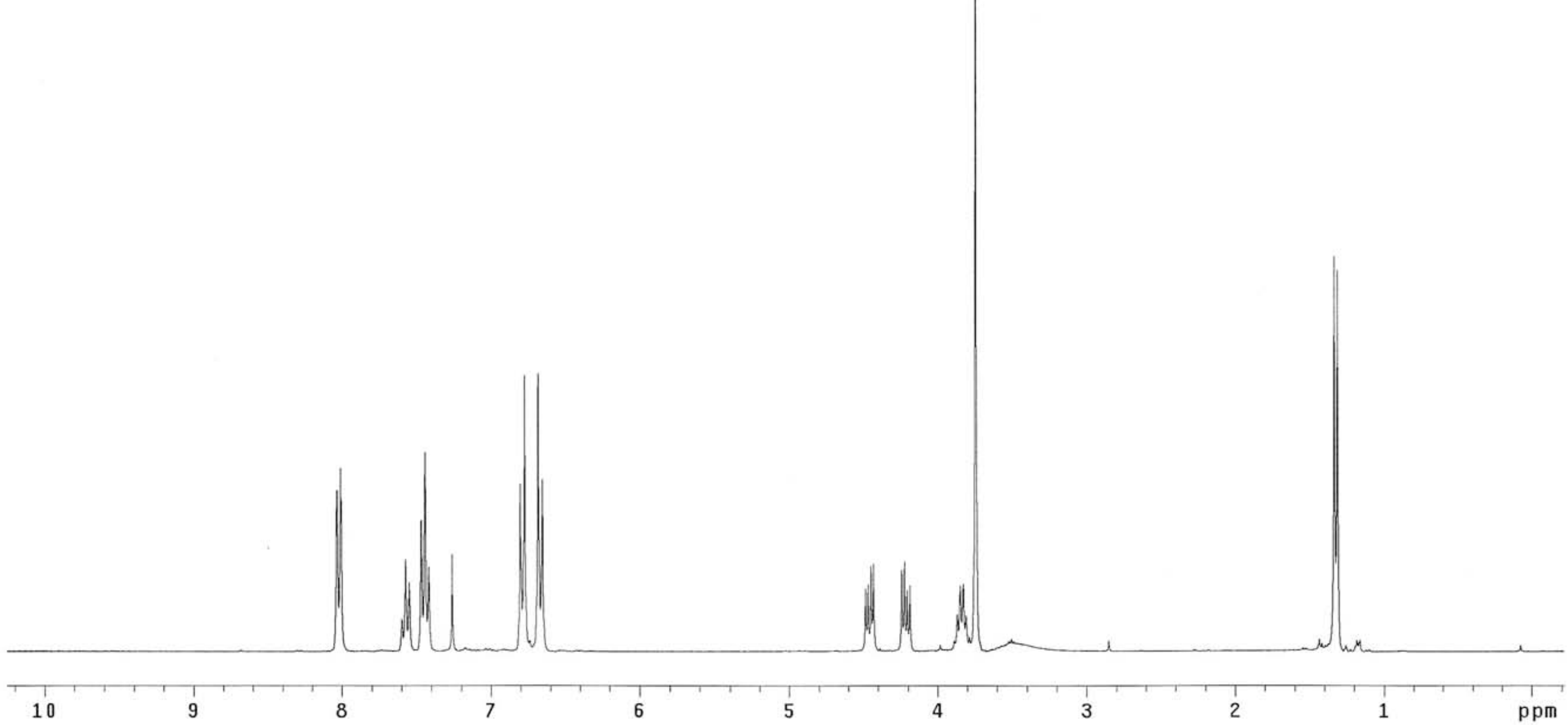
The Chromatogram Noise is 0

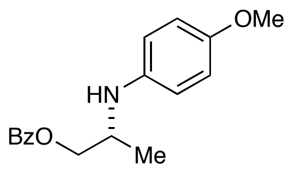
Results Table:

Index	Name	Time	Width USP	Quantity	Height	Area	Area
		[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
2	UNKNOWN	4.97	0.21	9.47	15.8	2.0	9.474
1	UNKNOWN	6.80	0.27	90.53	111.6	19.5	90.526
Total				100.00	127.4	21.5	100.000



300 MHz, $CDCl_3$





75 MHz, $CDCl_3$

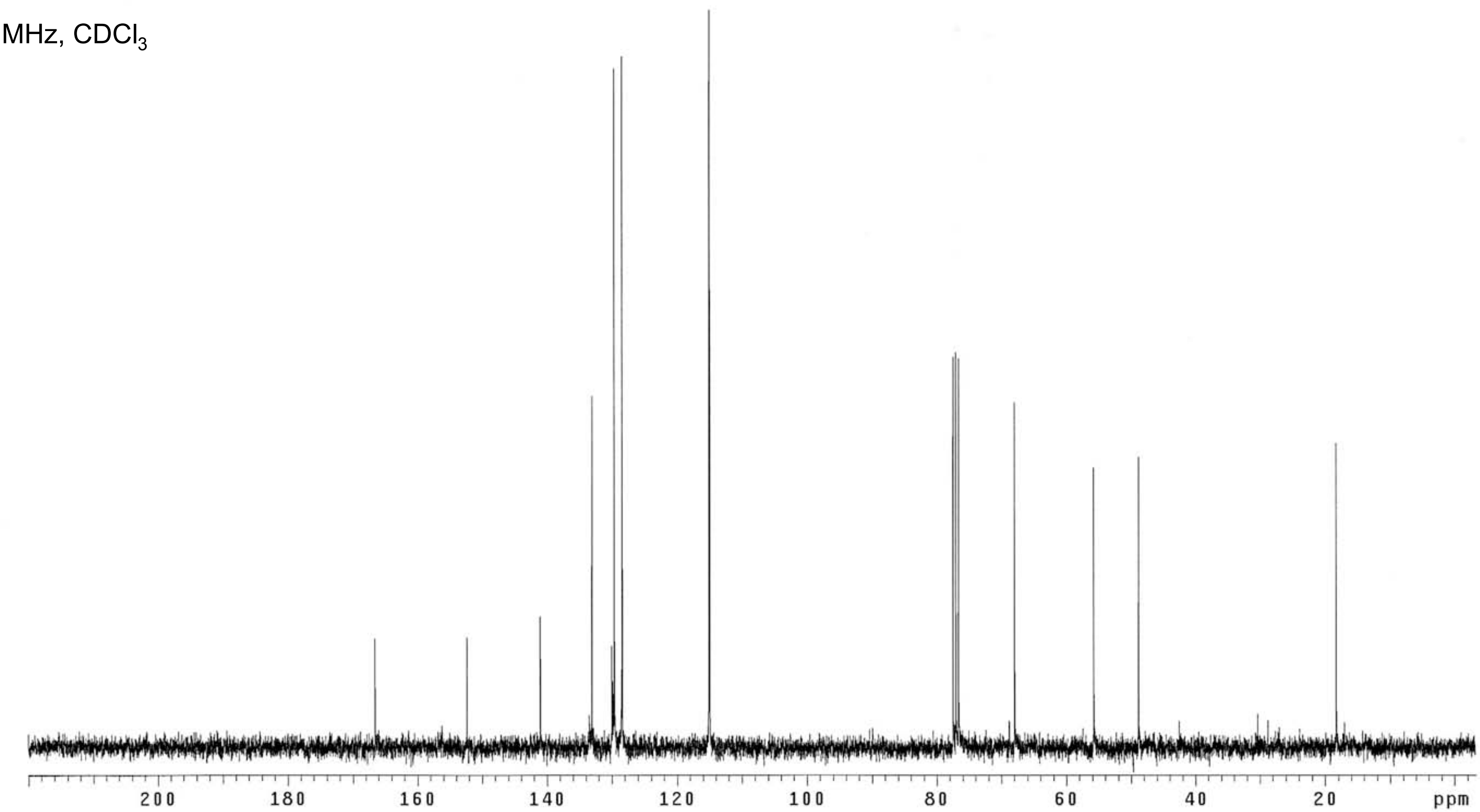
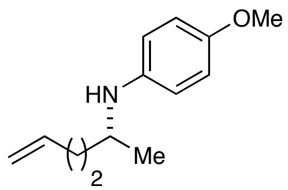
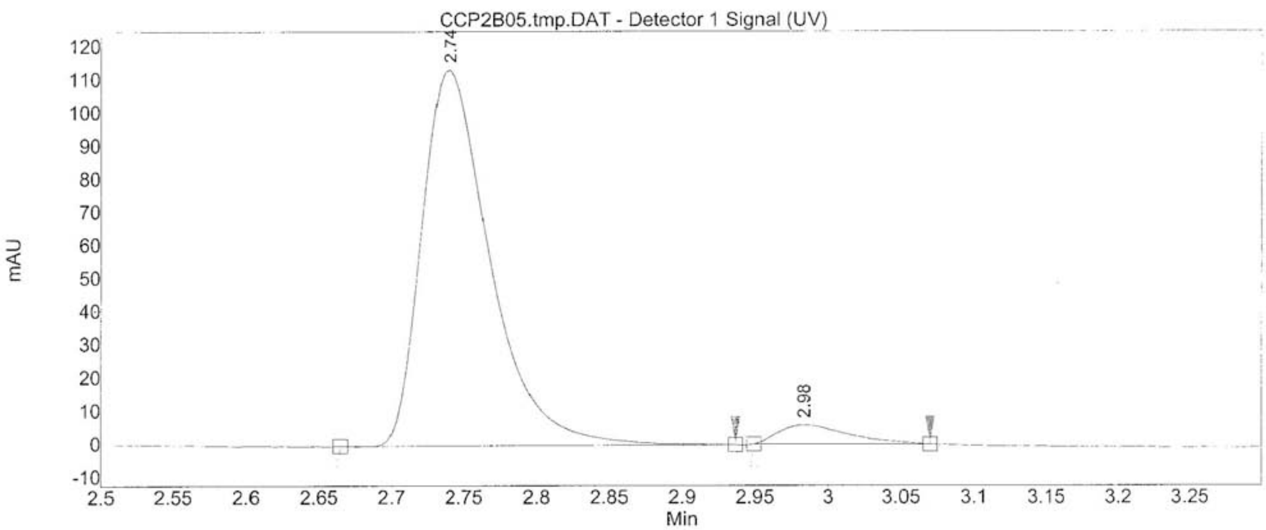


Table 3, Entry 6



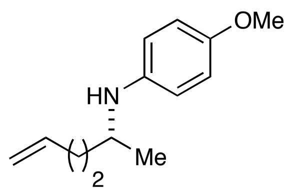
SFC (Daicel Chiracel OJH)
iPrOH 5-50% ramp



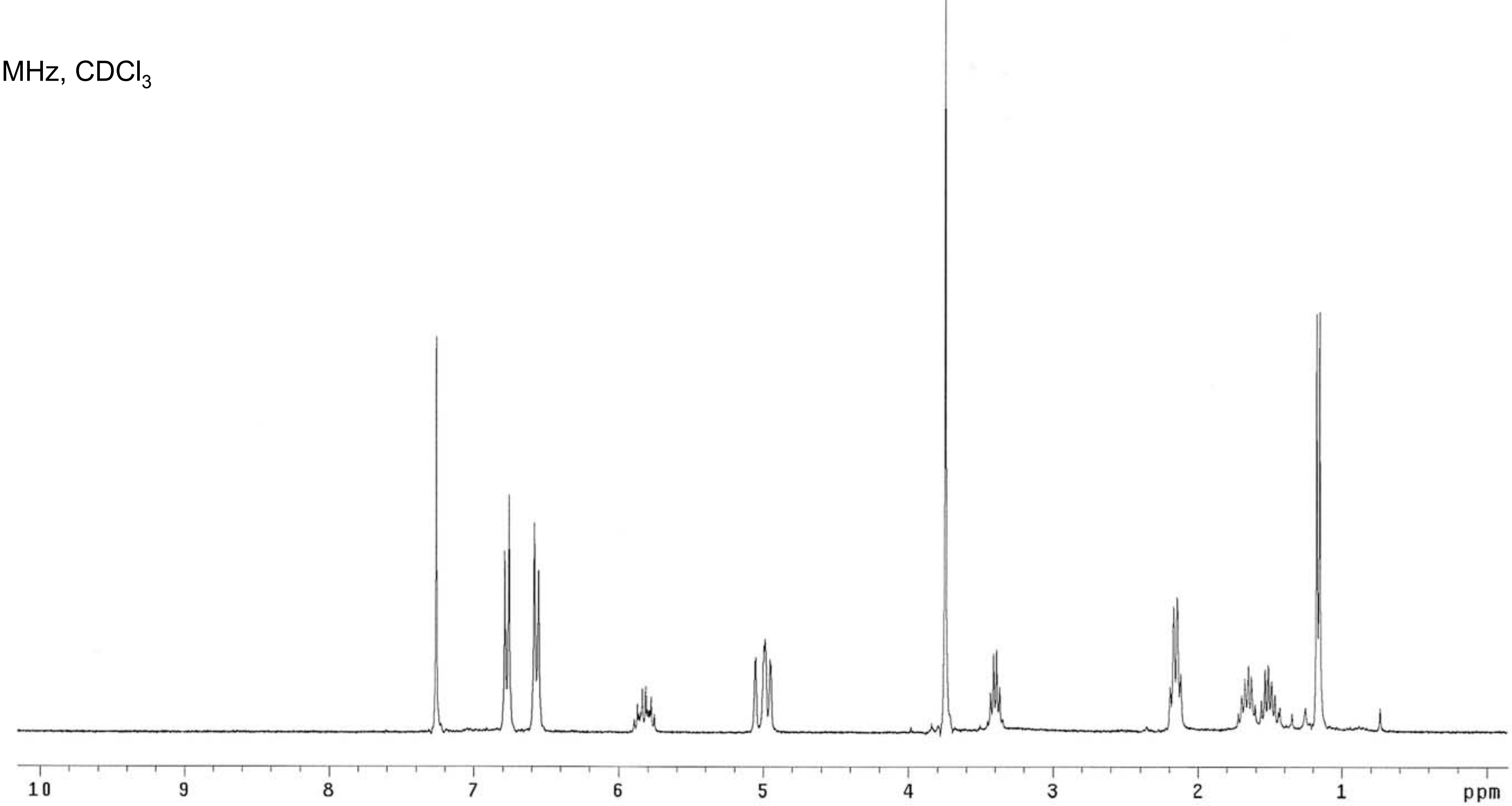
The Chromatogram Noise is 0

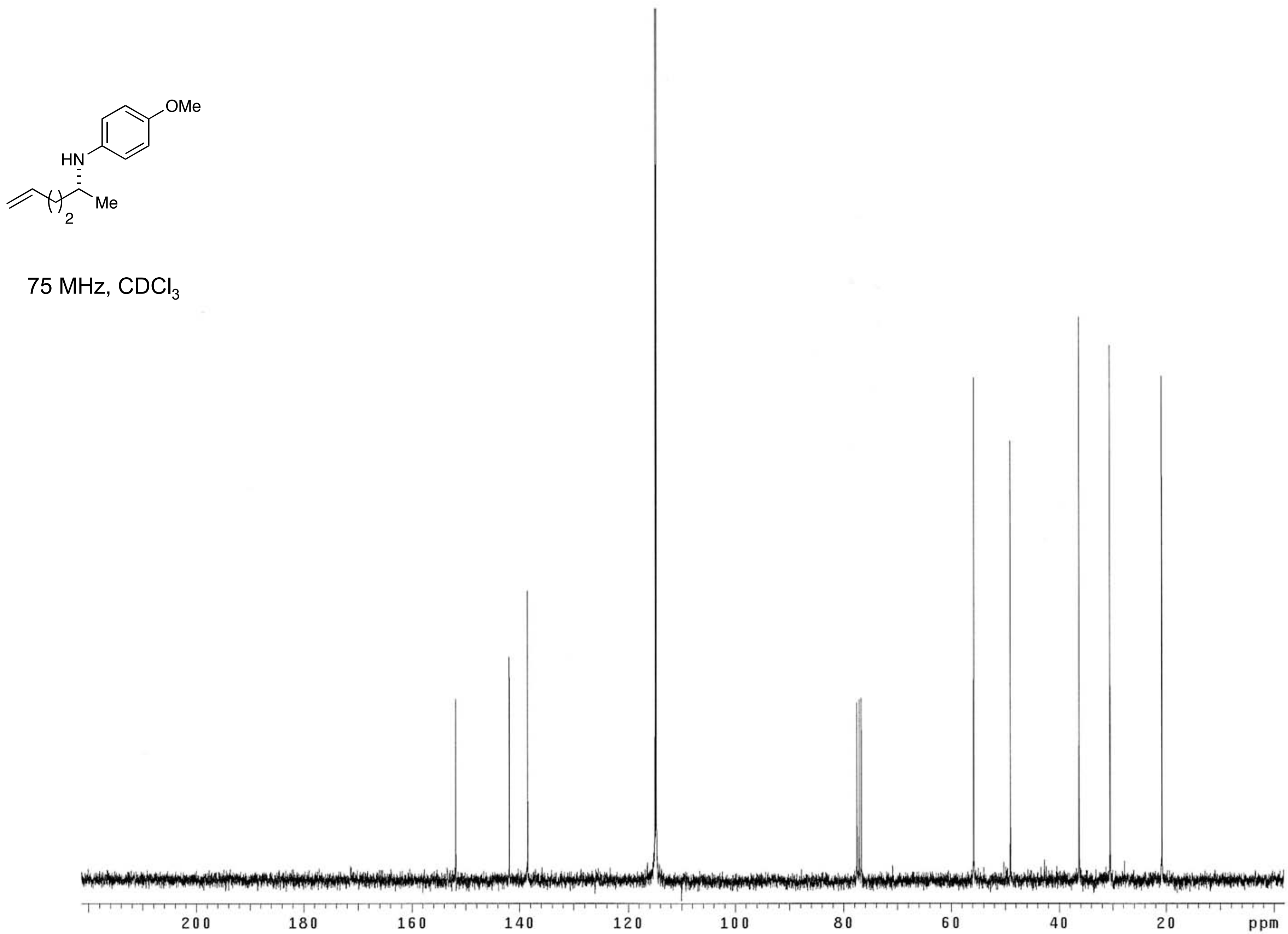
Results Table:

Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	2.66	2.74	2.94	0.00	95.19	113.5	6.2	95.191
2	UNKNOWN	2.95	2.98	3.07	0.00	4.81	5.7	0.3	4.809
Total						100.00	119.2	6.5	100.000



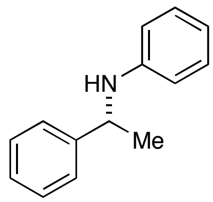
300 MHz, $CDCl_3$



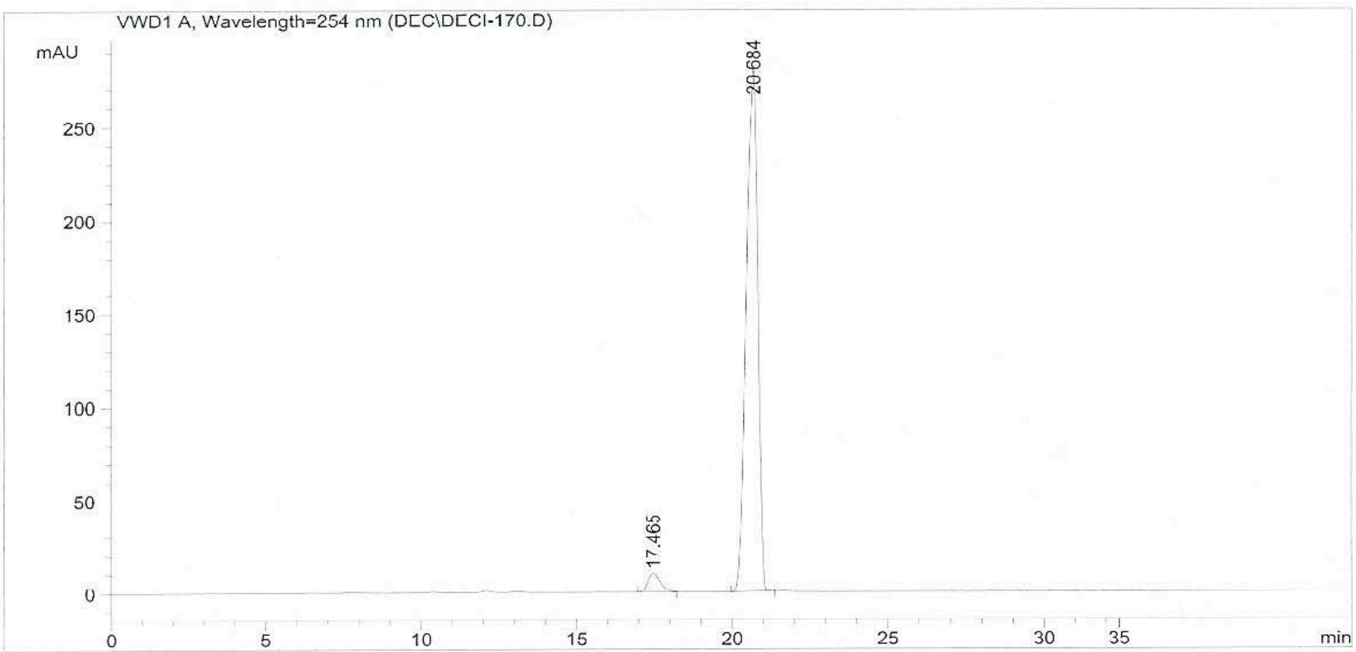


75 MHz, $CDCl_3$

Table 4, Entry 1



HPLC (Daicel Chiracel OD)
5% iPrOH in hexanes



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

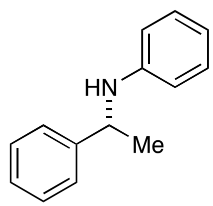
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.465	BB	0.4278	271.14349	9.79589	3.6212
2	20.684	PB	0.3253	7216.62256	281.46823	96.3788

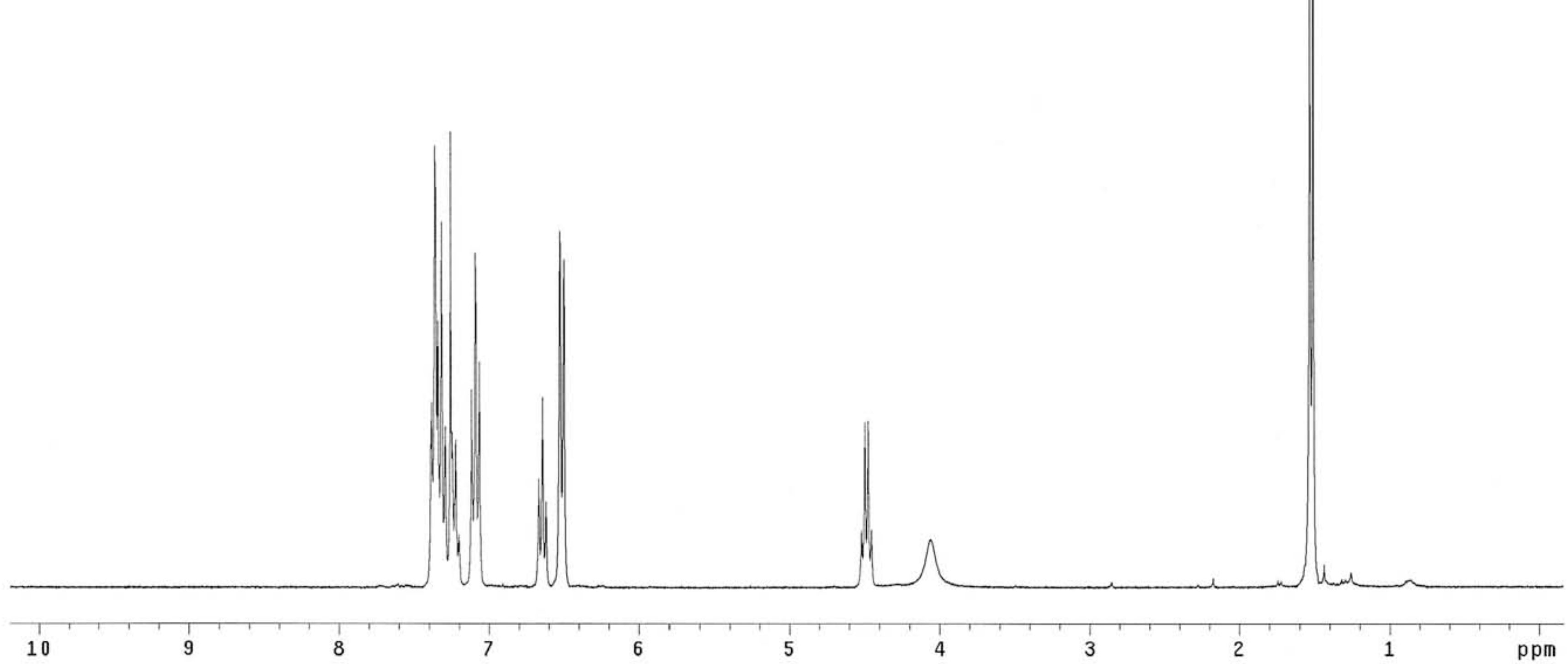
Totals : 7487.76605 291.26412

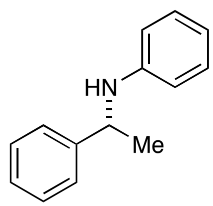
Results obtained with enhanced integrator!

*** End of Report ***



300 MHz, $CDCl_3$





75 MHz, $CDCl_3$

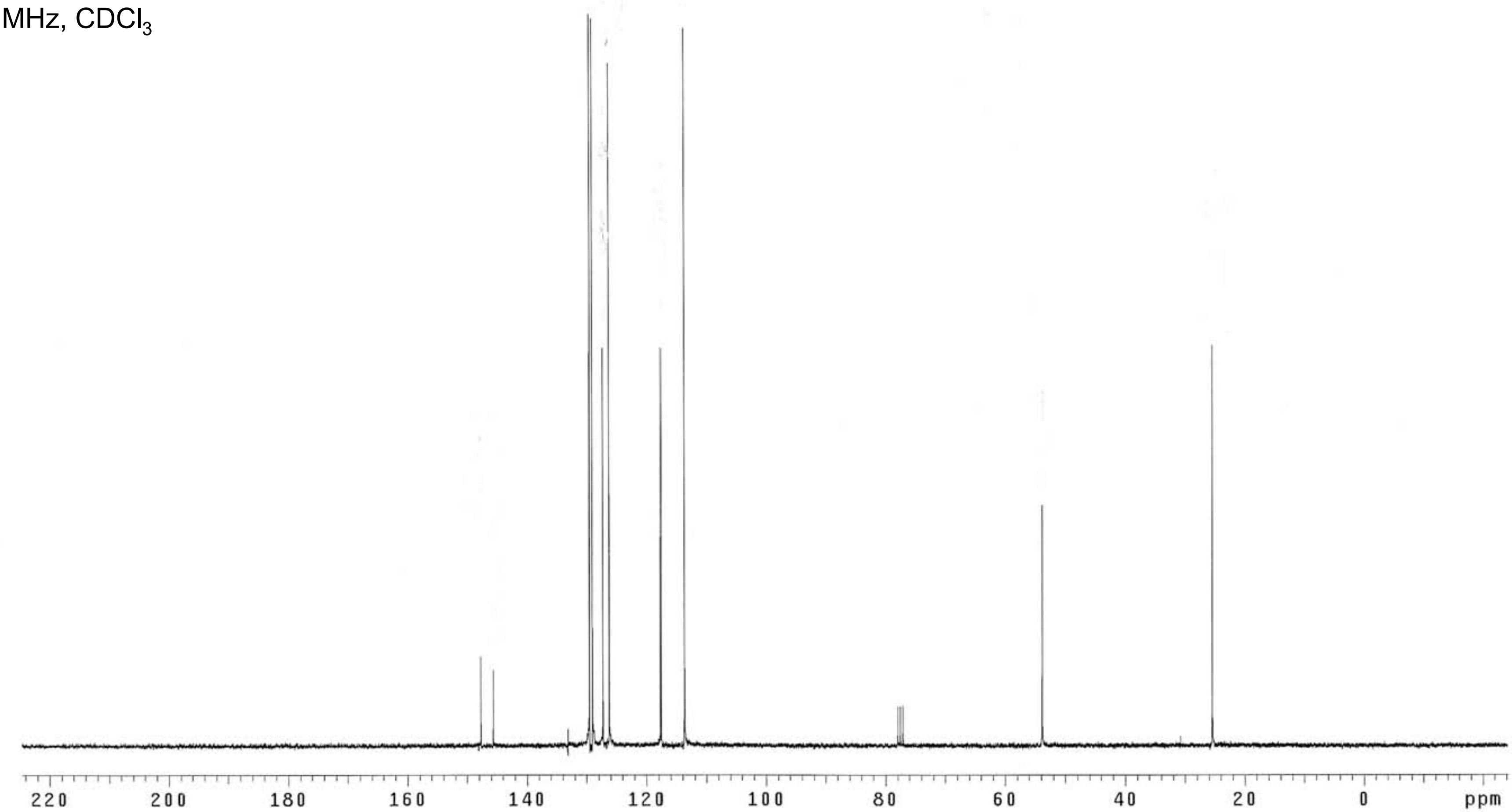
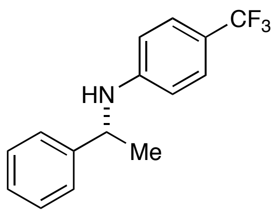
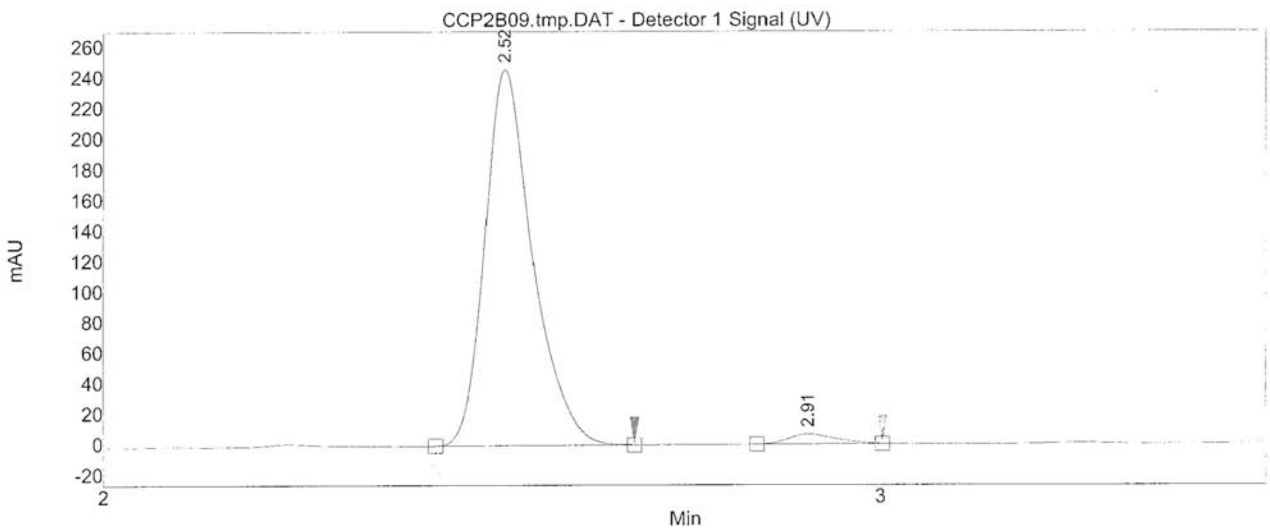


Table 4, Entry 2



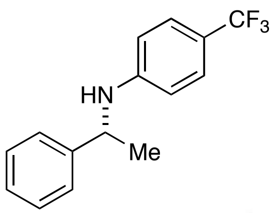
SFC (Daicel Chiracel ADH)
^{i}PrOH 5-50% ramp



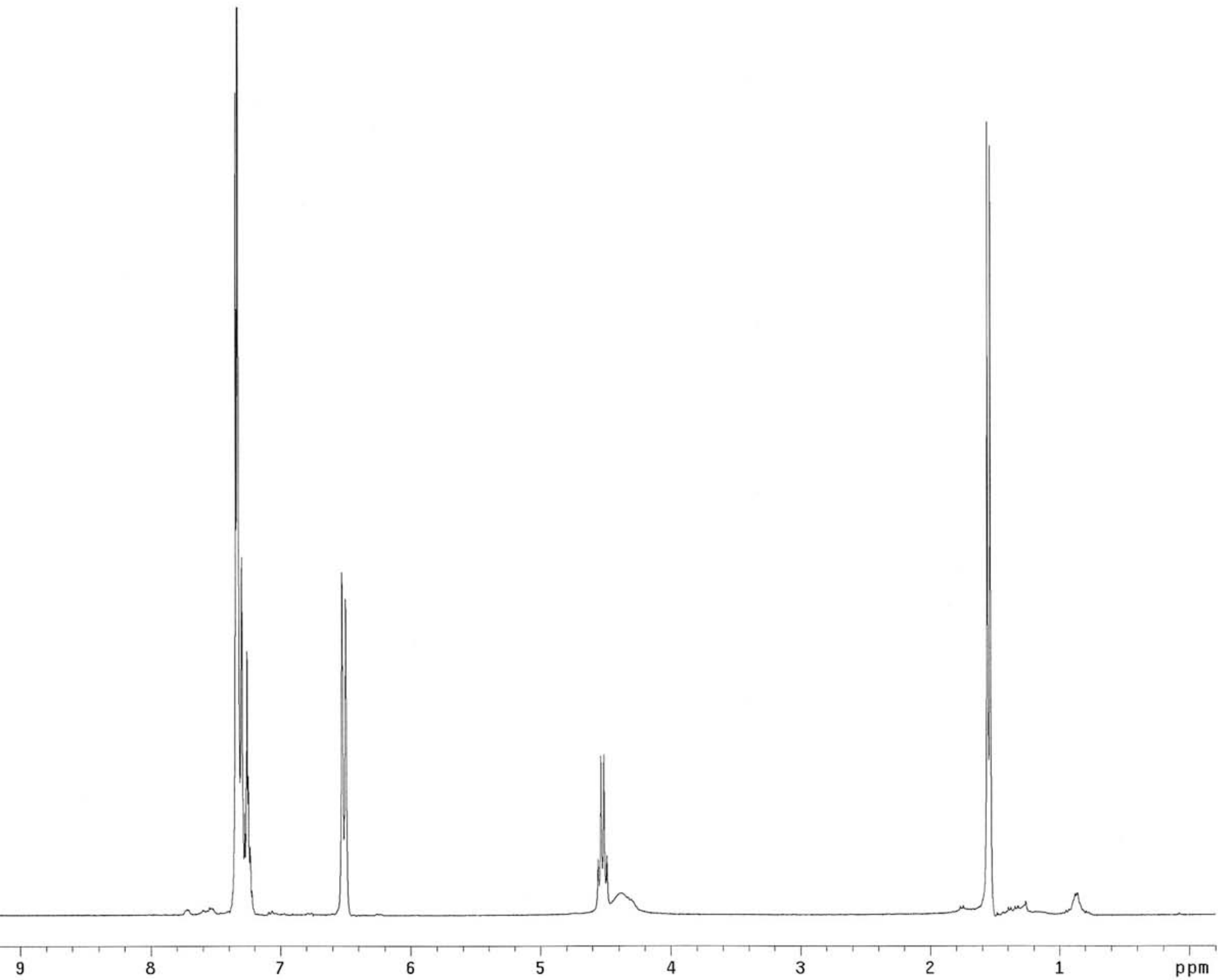
The Chromatogram Noise is 0

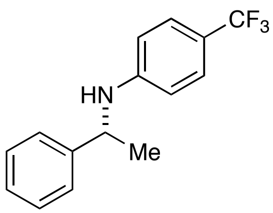
Results Table:

Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	2.43	2.52	2.68	0.00	97.58	246.0	17.6	97.579
2	UNKNOWN	2.84	2.91	3.00	0.00	2.42	6.4	0.4	2.421
Total						100.00	252.5	18.0	100.000



300 MHz, $CDCl_3$





75 MHz, $CDCl_3$

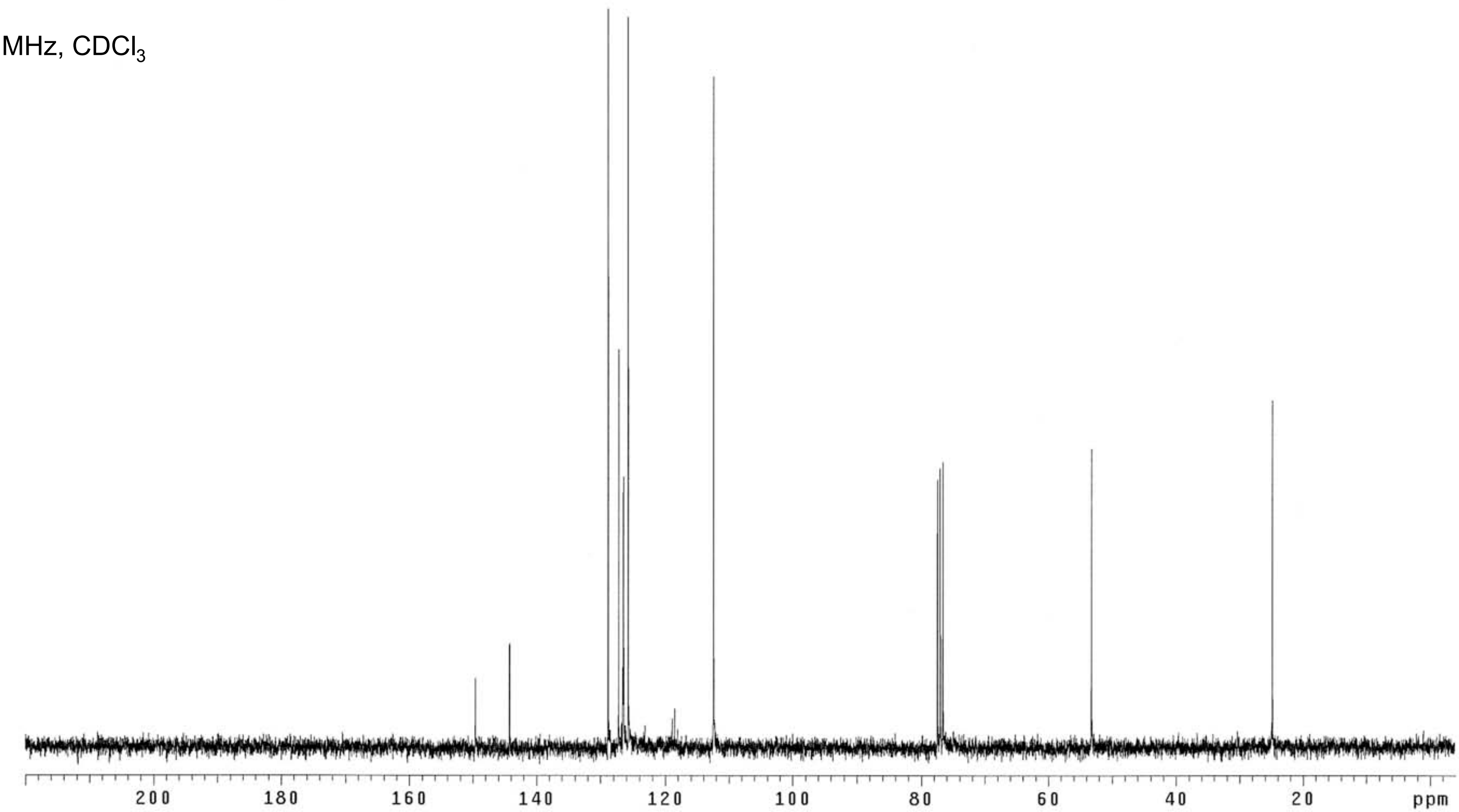
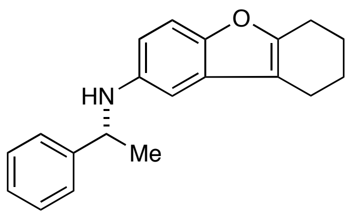
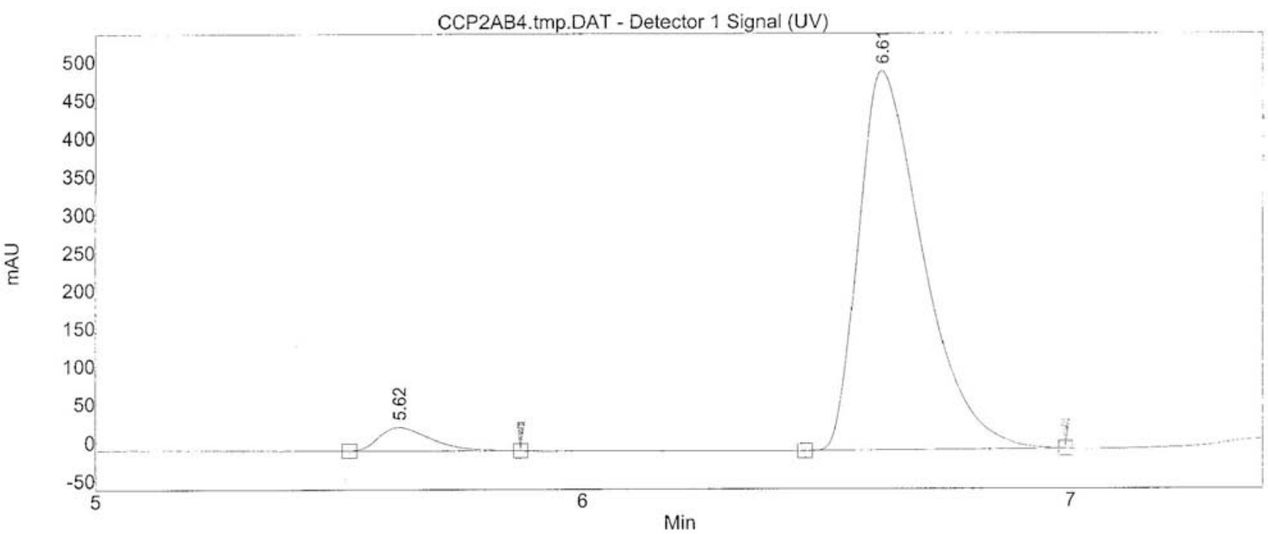


Table 4, Entry 3



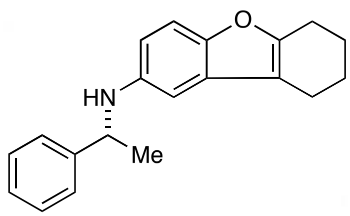
SFC (Daicel Chiracel ADH)
MeOH 5-50% ramp



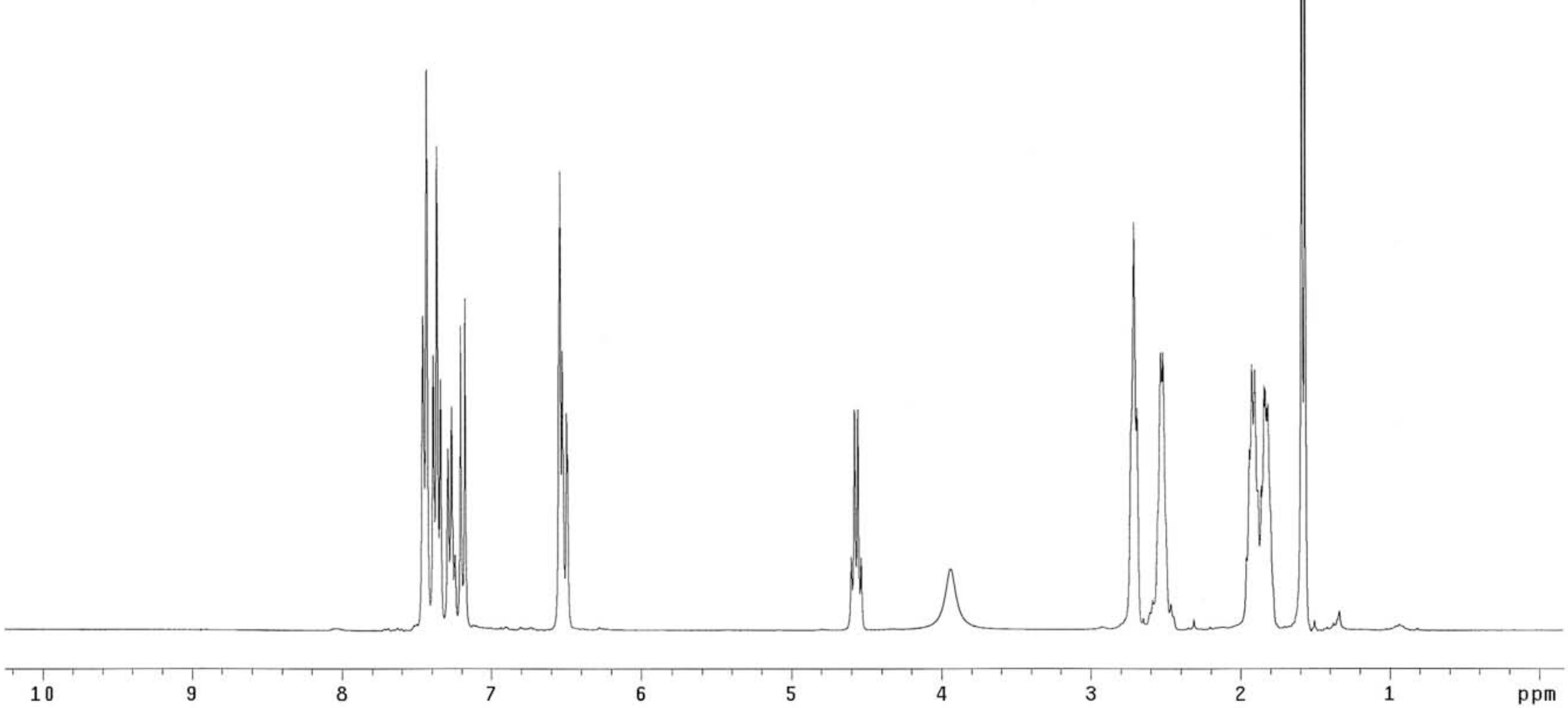
The Chromatogram Noise is 0

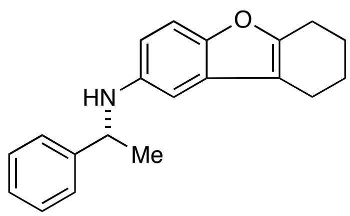
Results Table:

Index	Name	Time	Width USP	Quantity	Height	Area	Area
		[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	5.62	0.19	4.62	29.7	3.7	4.621
2	UNKNOWN	6.61	0.24	95.38	497.4	75.5	95.379
Total				100.00	527.1	79.2	100.000



300 MHz, $CDCl_3$





75 MHz, $CDCl_3$

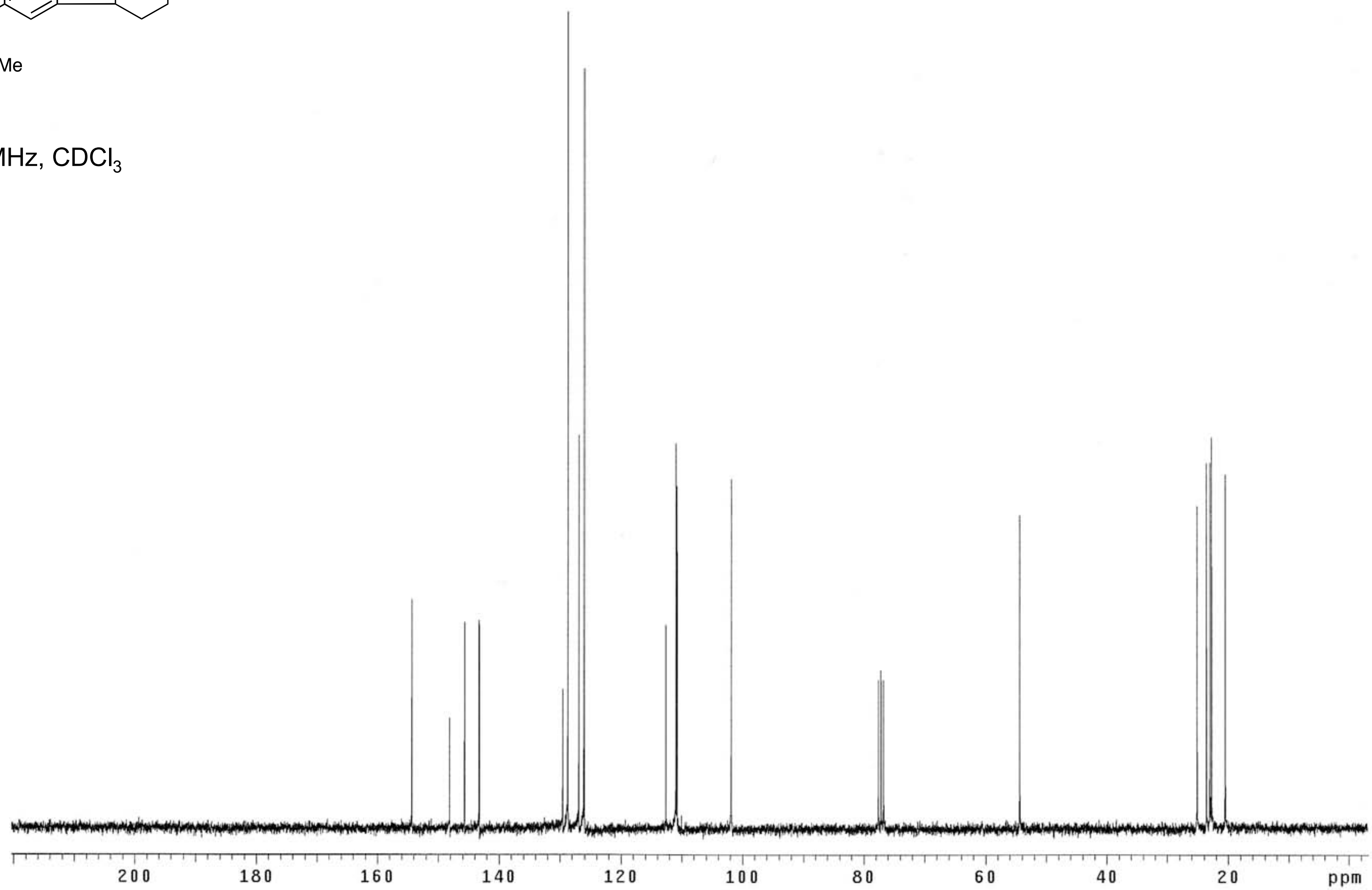
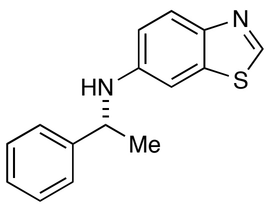
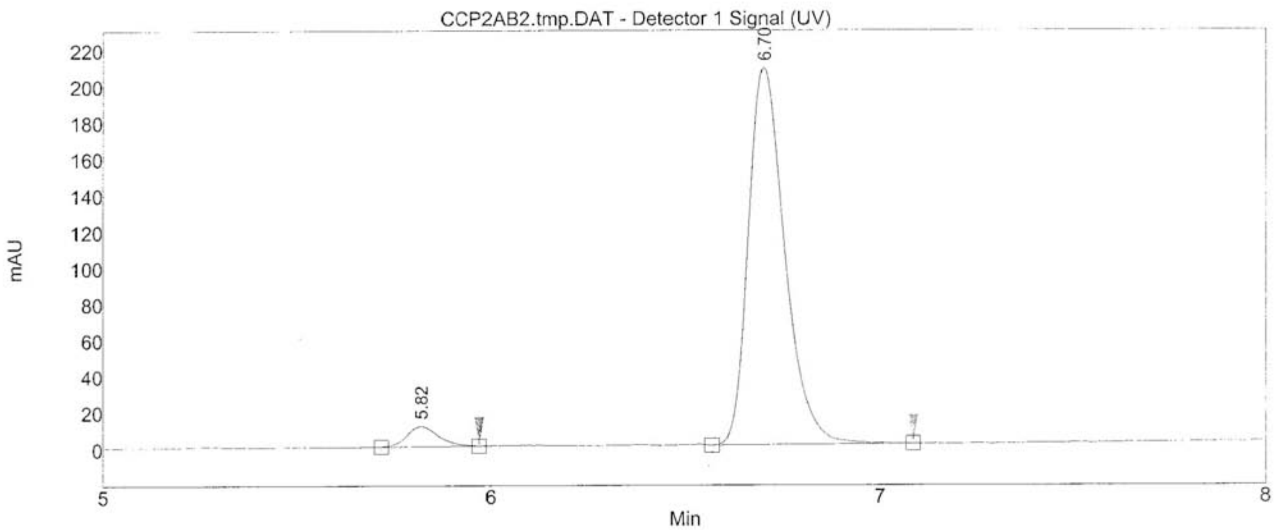


Table 4, Entry 4



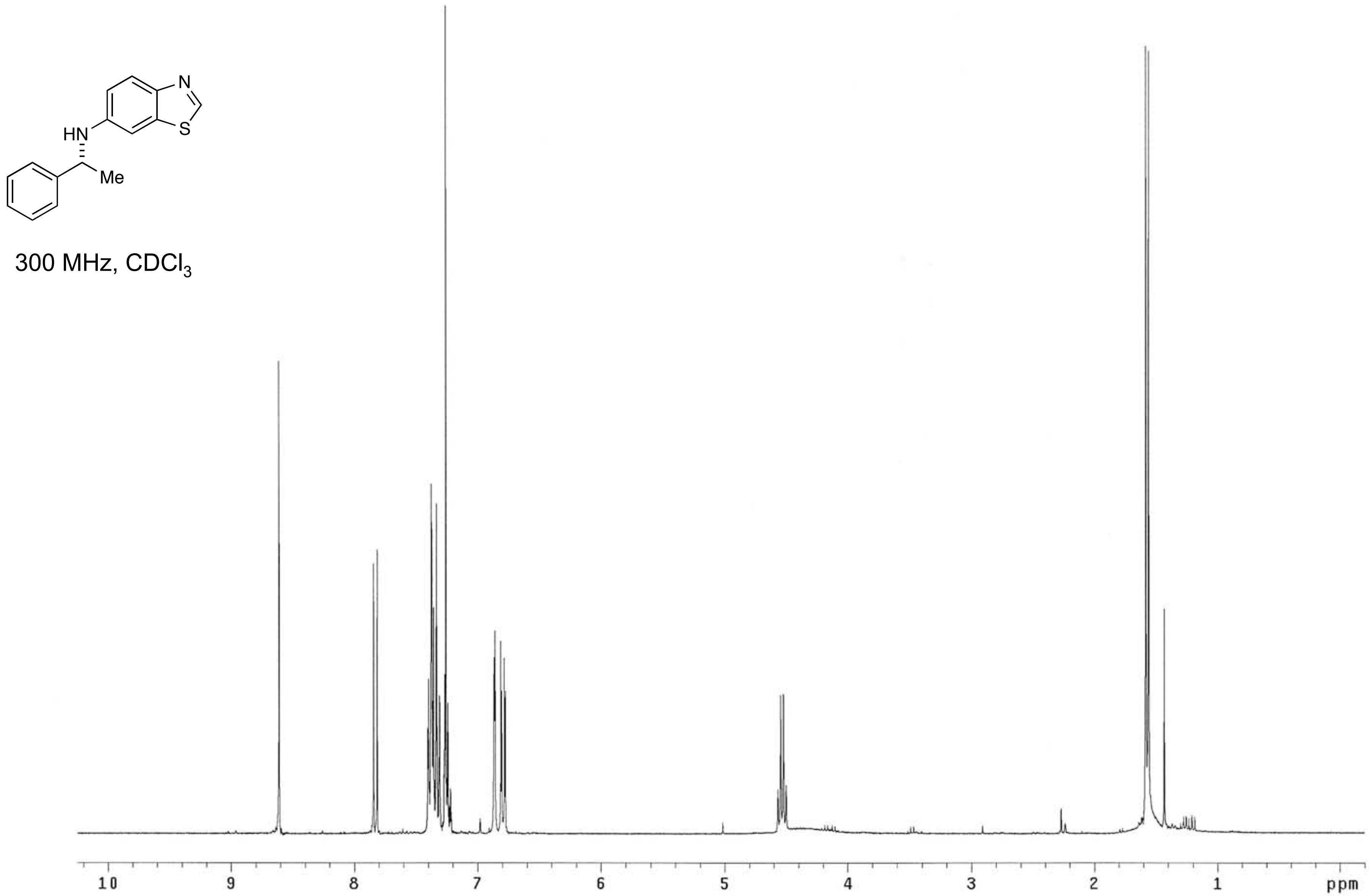
SFC (Daicel Chiracel OJH)
MeOH 5-50% ramp



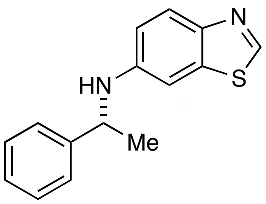
The Chromatogram Noise is 0

Results Table:

Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	5.72	5.82	5.97	0.00	4.39	10.9	1.0	4.394
2	UNKNOWN	6.57	6.70	7.09	0.00	95.61	207.7	22.4	95.606
Total						100.00	218.6	23.5	100.000



300 MHz, $CDCl_3$



75 MHz, $CDCl_3$

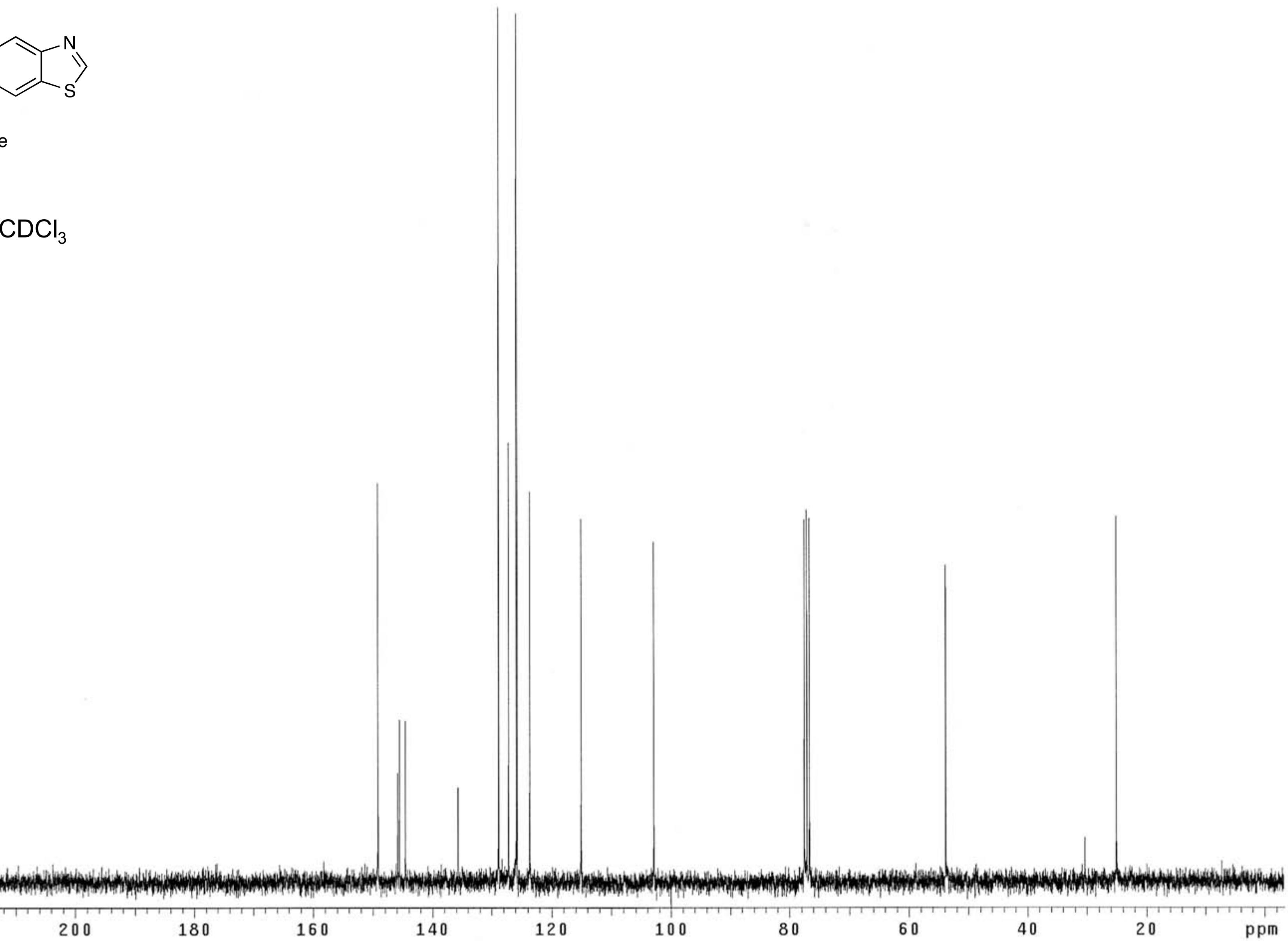
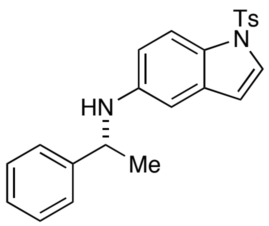
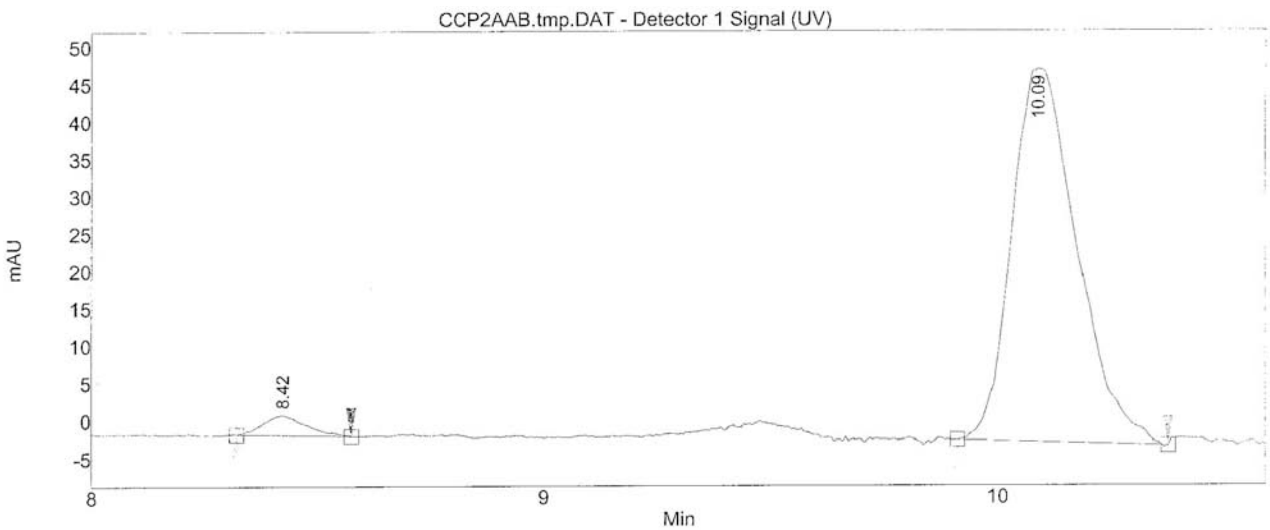


Table 4, Entry 5



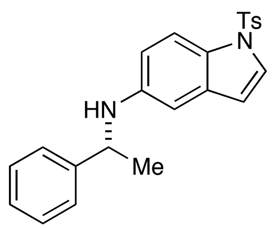
SFC (Daicel Chiracel OJH)
*i*PrOH 5-55% ramp



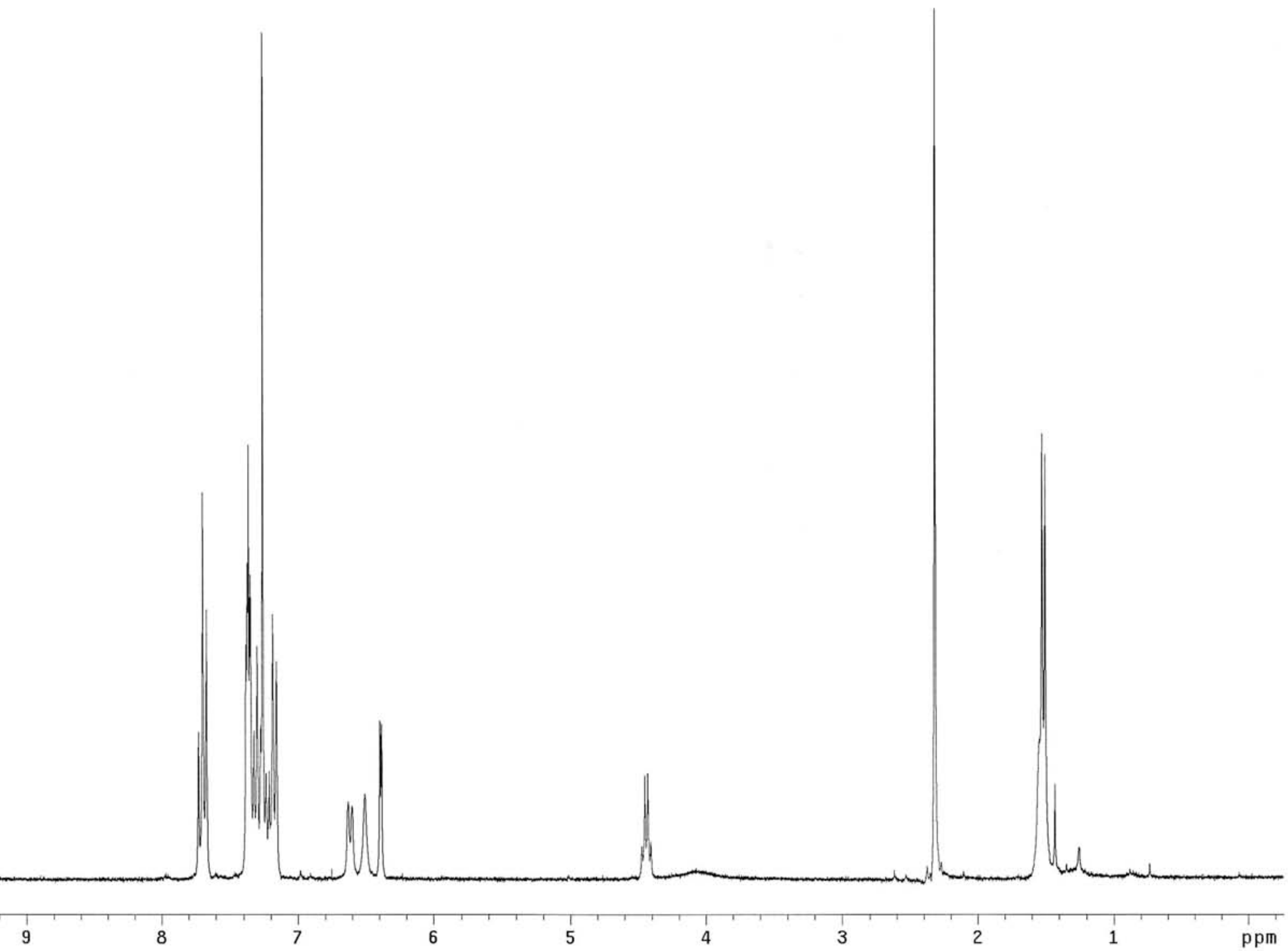
The Chromatogram Noise is 0

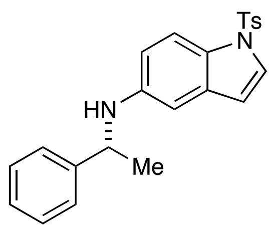
Results Table:

Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	8.32	8.42	8.58	0.00	3.33	2.6	0.3	3.327
2	UNKNOWN	9.91	10.09	10.38	0.00	96.67	49.9	8.4	96.673
Total						100.00	52.5	8.6	100.000



300 MHz, $CDCl_3$





75 MHz, $CDCl_3$

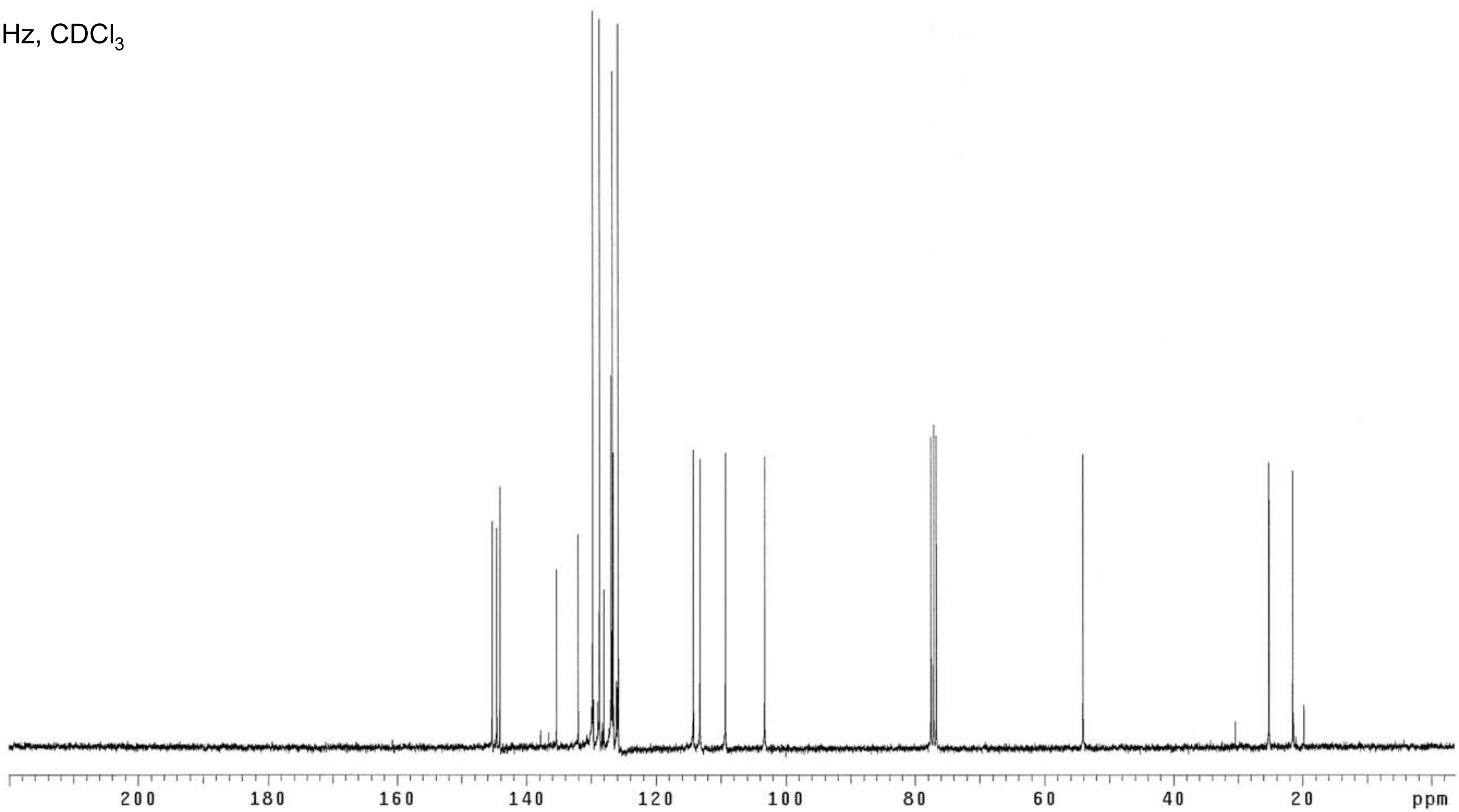
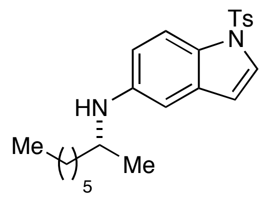
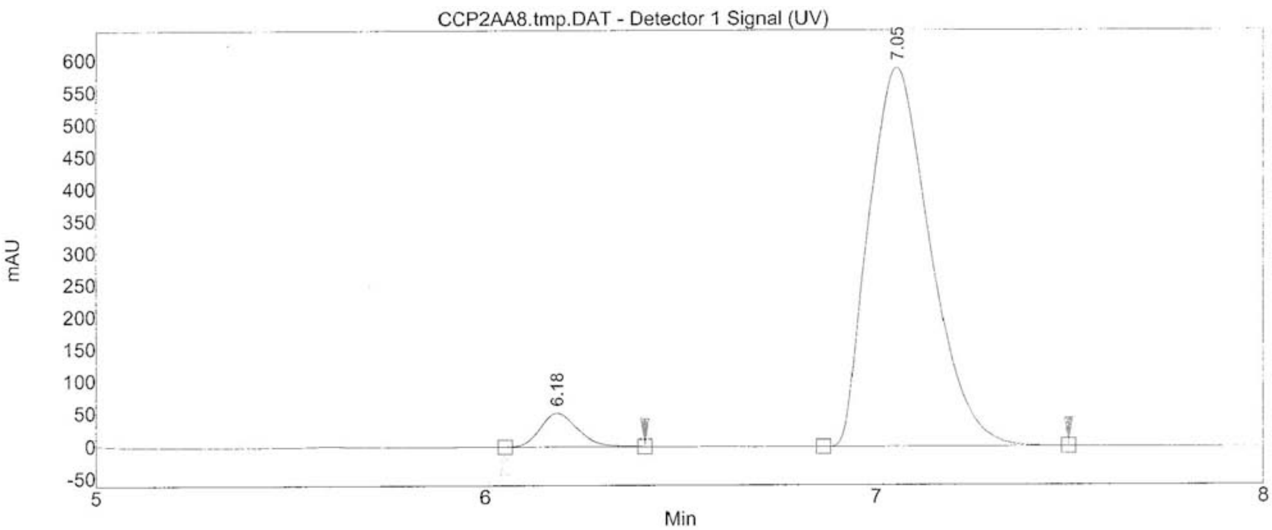


Table 4, Entry 6



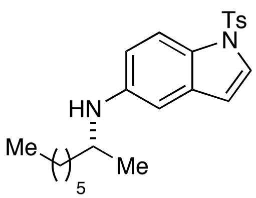
SFC (Daicel Chiracel ADH)
MeOH 5-50% ramp



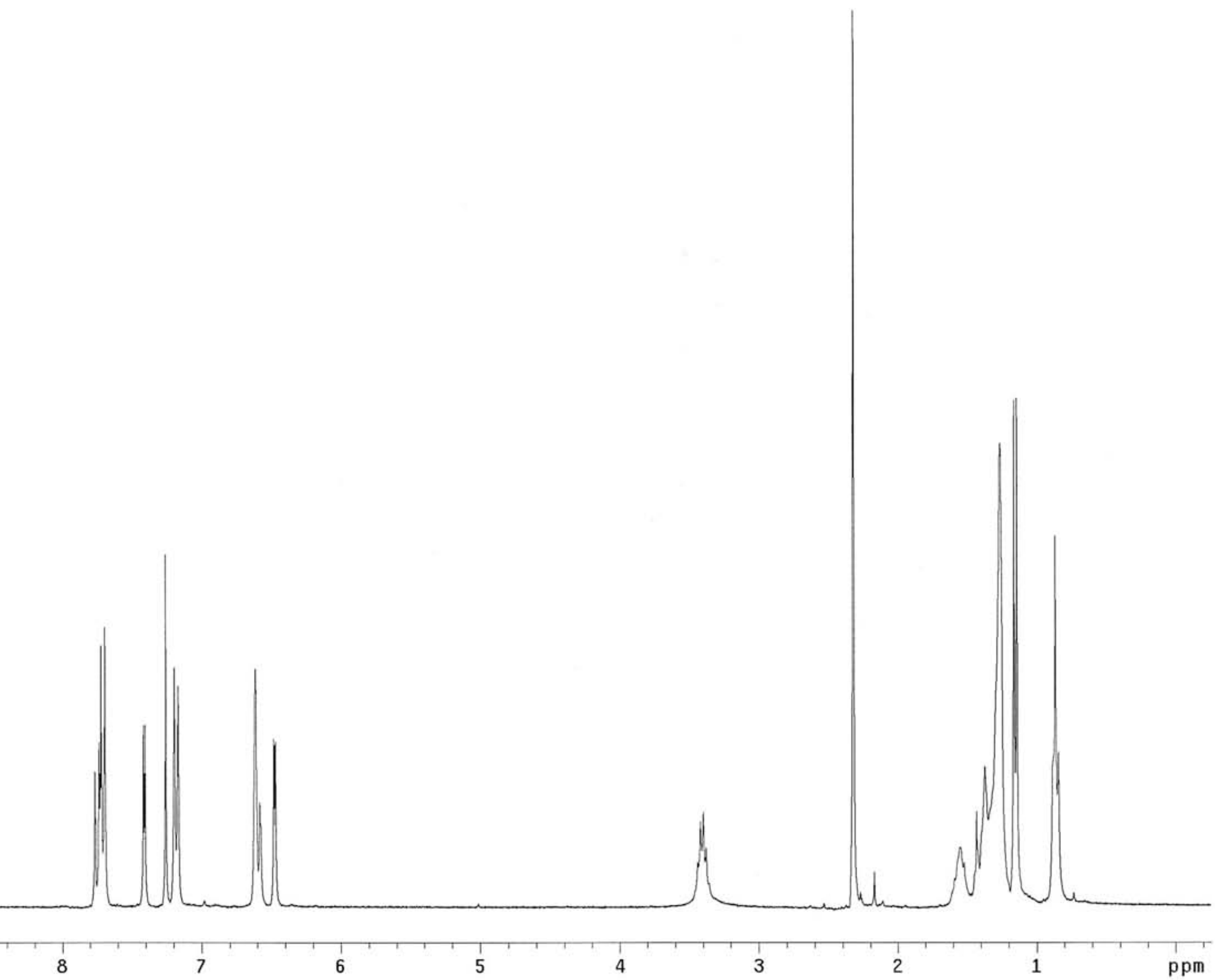
The Chromatogram Noise is 0

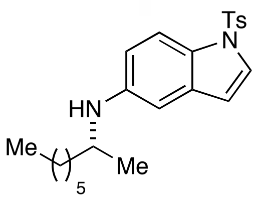
Results Table:

Index	Name	Time	Width USP	Quantity	Height	Area	Area
		[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
2	UNKNOWN	6.18	0.17	5.02	51.0	5.6	5.022
1	UNKNOWN	7.05	0.29	94.98	588.8	106.4	94.978
Total				100.00	639.7	112.0	100.000

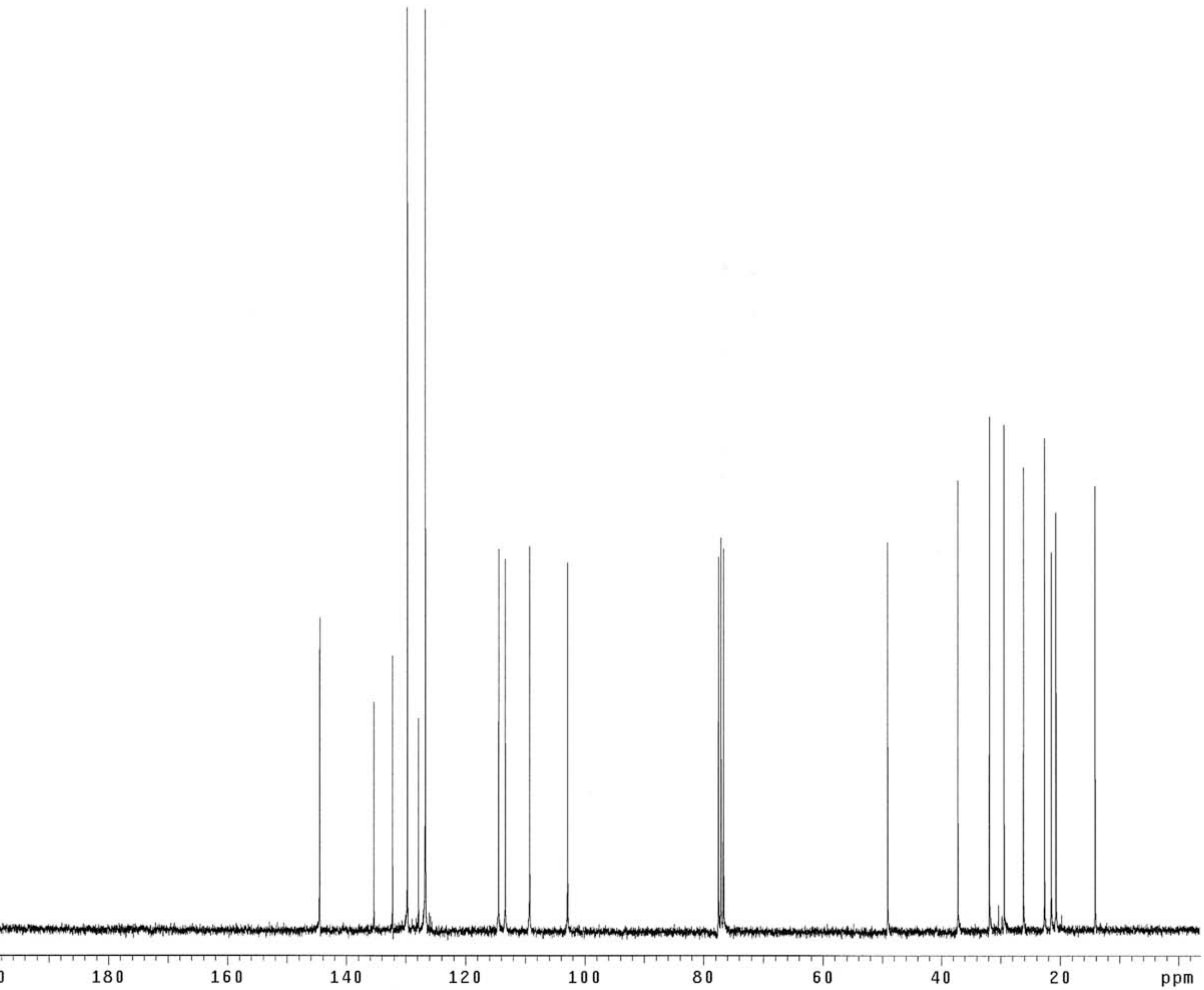


300 MHz, $CDCl_3$

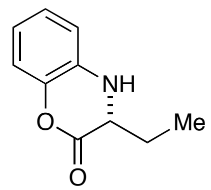




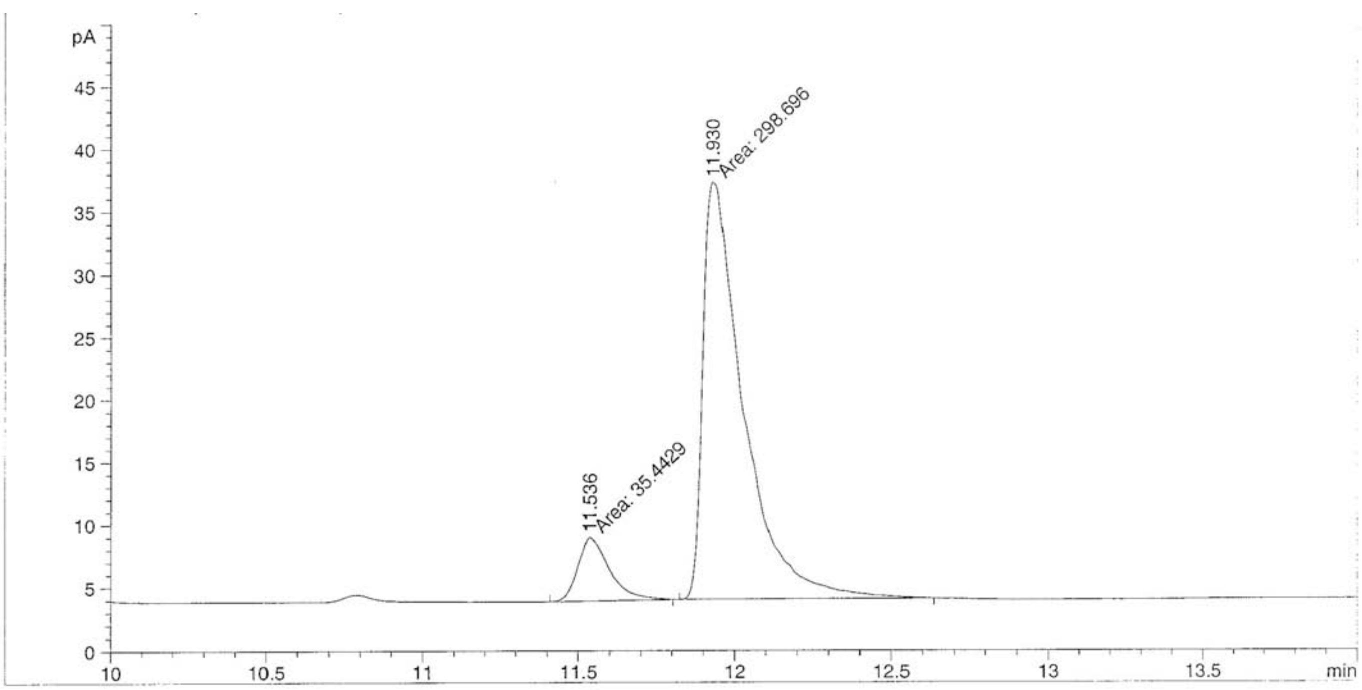
75 MHz, $CDCl_3$



Eq. 3, compound **7**



GLC (Varian CP-chirasil-dex-CB)
170 ˚C isotherm



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Area Percent Report

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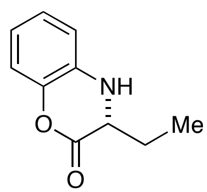
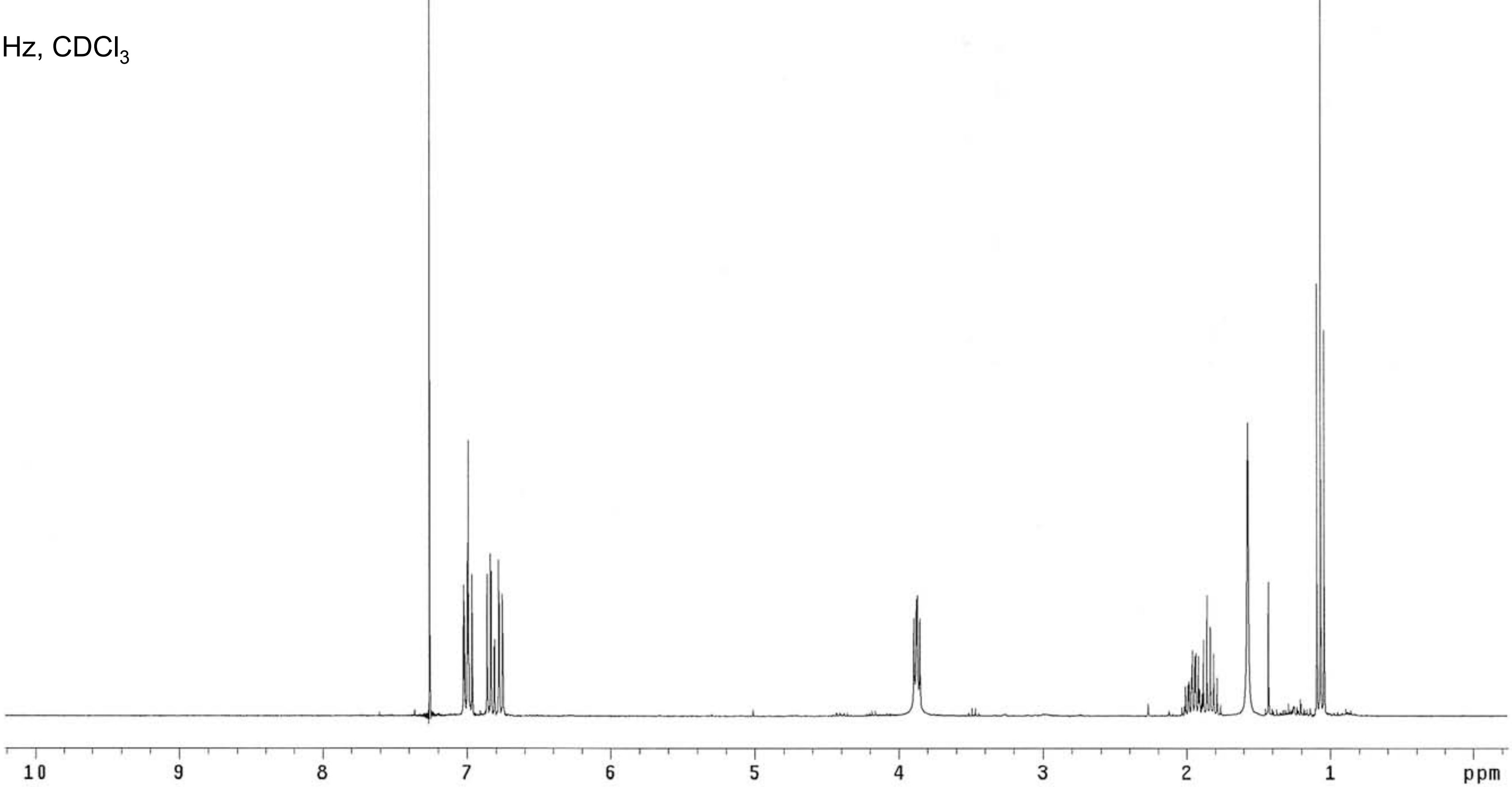
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

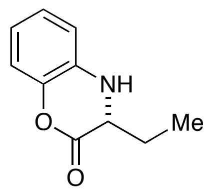
Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	11.536	MM	0.1162	35.44292	5.08437	10.60723
2	11.930	MM	0.1500	298.69623	33.19915	89.39277
Totals :				334.13915	38.28353	

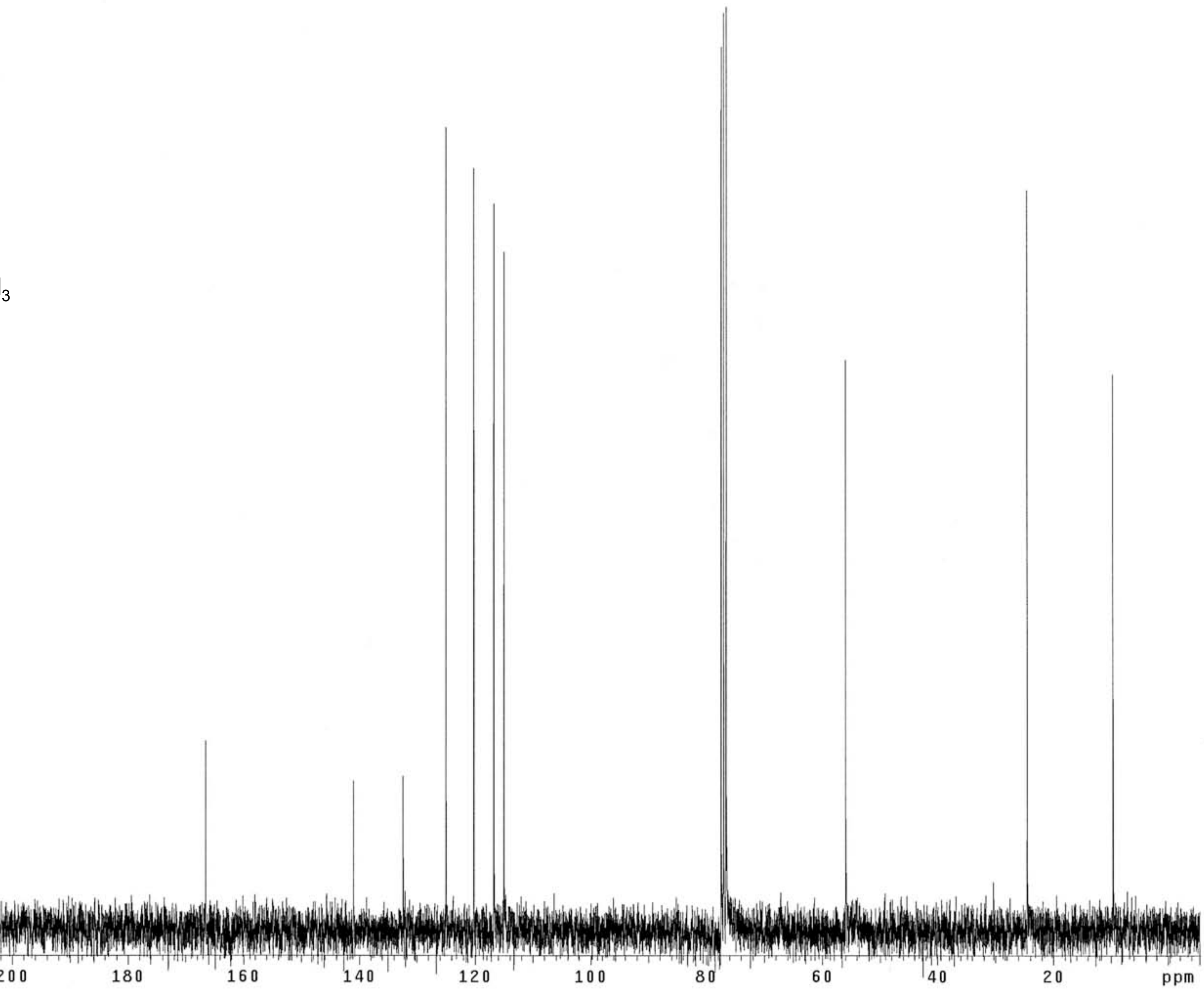


300 MHz, $CDCl_3$

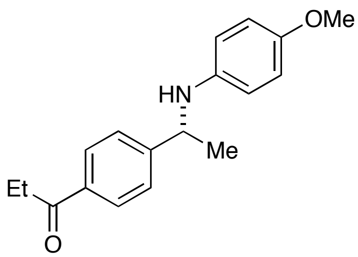




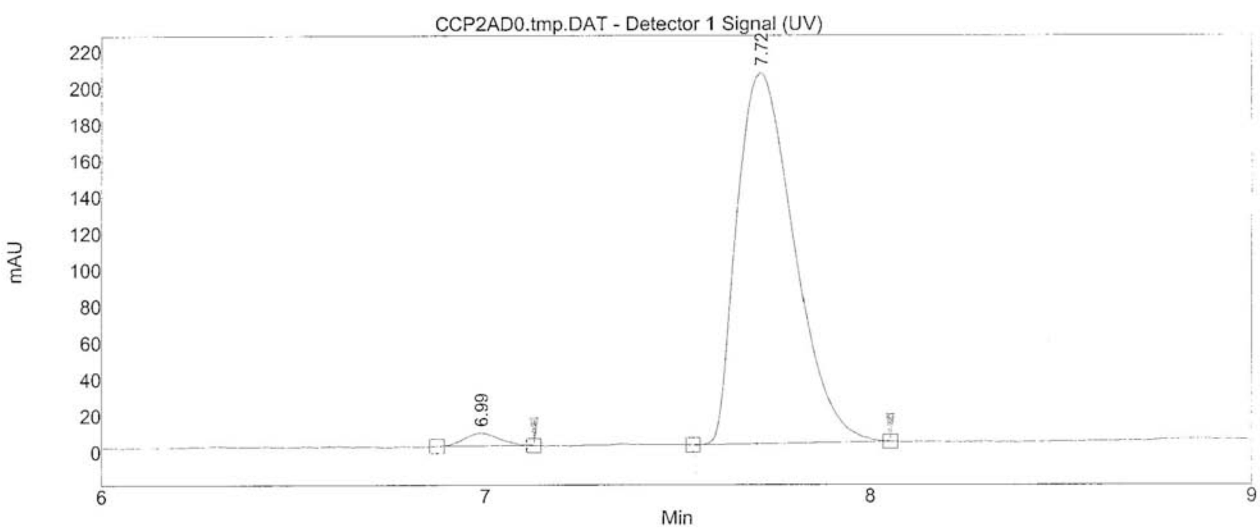
75 MHz, $CDCl_3$



Eq. 4, compound **9**



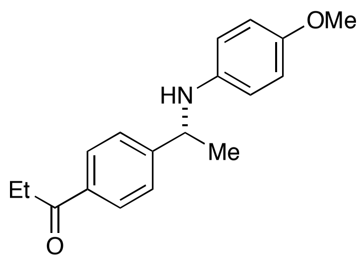
SFC (Daicel Chiracel ADH)
MeOH 5-50% ramp



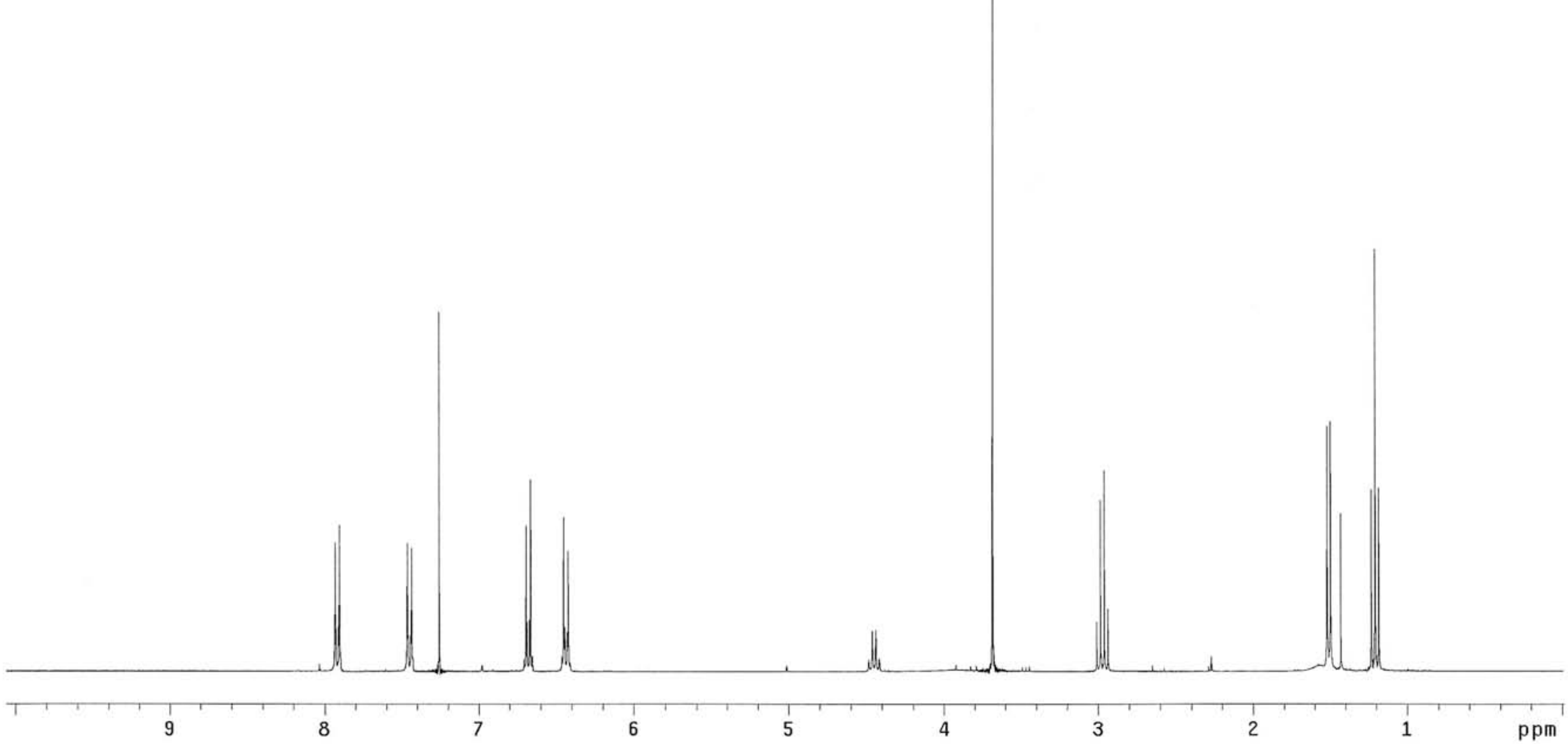
The Chromatogram Noise is 0

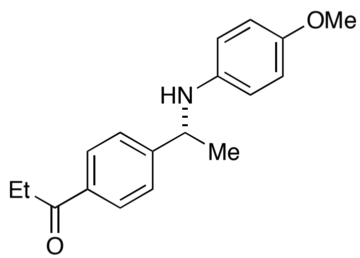
Results Table:

Index	Name	Time	Width USP	Quantity	Height	Area	Area
		[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	6.99	0.17	2.06	6.9	0.7	2.062
2	UNKNOWN	7.72	0.27	97.94	203.6	34.9	97.938
Total				100.00	210.5	35.7	100.000

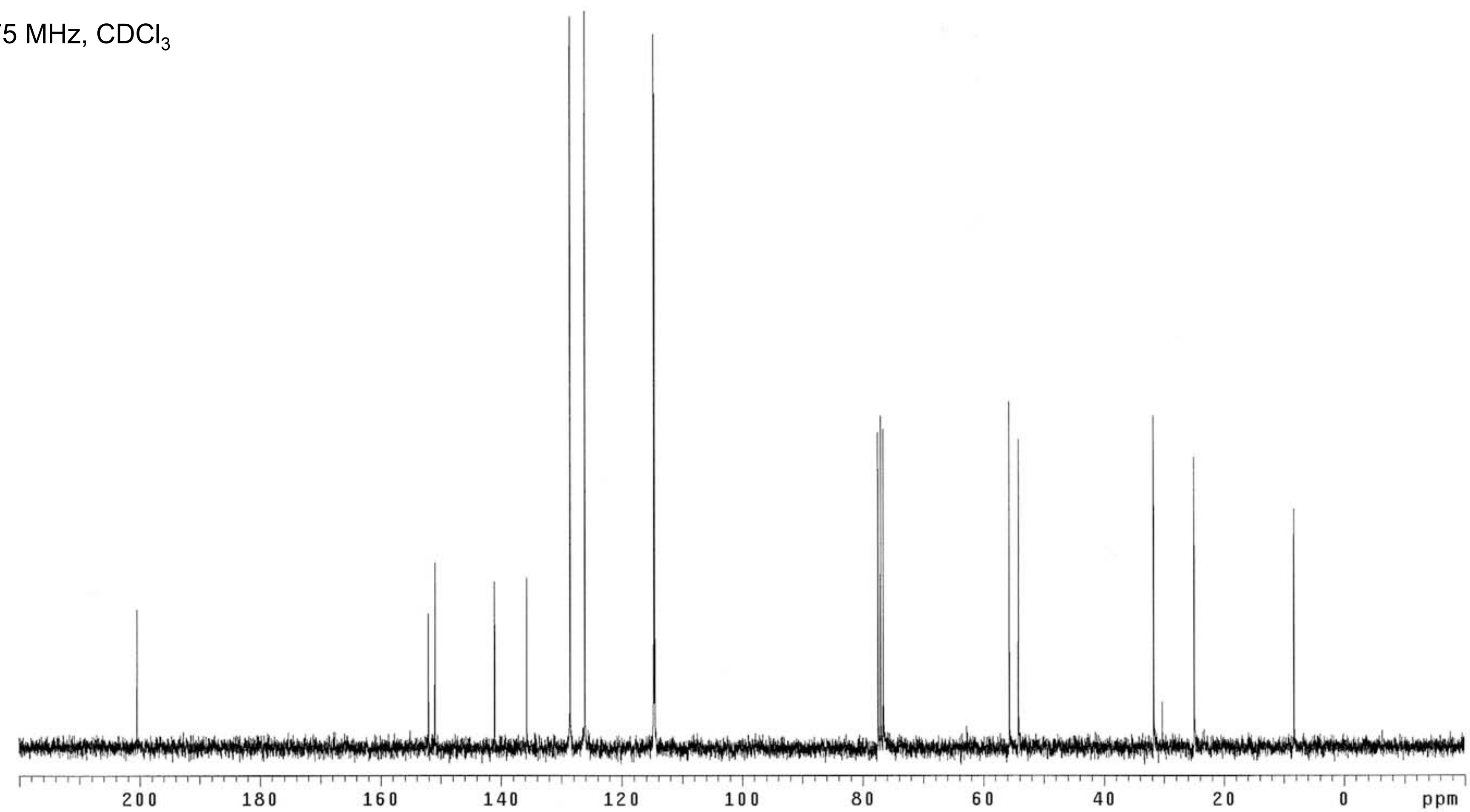


300 MHz, $CDCl_3$





75 MHz, $CDCl_3$



CALIFORNIA INSTITUTE OF TECHNOLOGY

BECKMAN INSTITUTE

X-RAY CRYSTALLOGRAPHY LABORATORY

Crystal Structure Analysis of:

RIS06

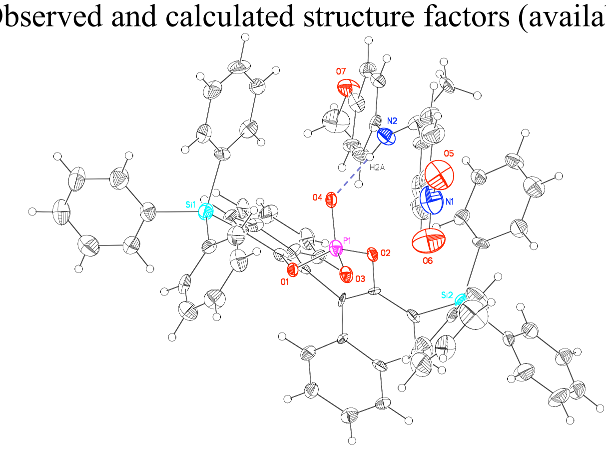
(shown below)

For Investigator: Ian Storer

Advisor: D. W. C. MacMillan

By Michael W. Day e-mail: mikeday@caltech.edu

Contents



RIS06

Note: The crystallographic data have been deposited in the Cambridge Database (CCDC) and has been placed on hold pending further instructions from me. The deposition number is 287655. Ideally the CCDC would like the publication to contain a footnote of the type: "Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 287655."

Table 1. Crystal data and structure refinement for RIS06 (CCDC 287655).

Empirical formula	$[C_{56}H_{40}O_4PSi_2]^-$ $[C_{15}H_{15}N_2O_3]^+$ • 4(C7 H8) • O
Formula weight	1519.86
Crystallization Solvent	Toluene
Crystal Habit	Fragment
Crystal size	0.15 x 0.15 x 0.11 mm^3
Crystal color	Yellow

Data Collection

Type of diffractometer	Bruker SMART 1000
Wavelength	0.71073 Å MoKα
Data Collection Temperature	100(2) K
θ range for 7276 reflections used in lattice determination	2.22 to 18.24°
Unit cell dimensions	a = 9.8819(5) Å b = 16.0655(8) Å c = 50.192(3) Å
Volume	7968.3(7) $Å^3$
Z	4
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Density (calculated)	1.267 Mg/m^3
F(000)	3208
θ range for data collection	1.33 to 20.86°
Completeness to θ = 20.86°	94.9 %
Index ranges	-9 ≤ h ≤ 9, -16 ≤ k ≤ 15, -47 ≤ l ≤ 49
Data collection scan type	ω scans at 3 ϕ settings
Reflections collected	46009
Independent reflections	7765 [R_{int}= 0.1370]
Absorption coefficient	0.127 mm^{-1}
Absorption correction	None
Max. and min. transmission	0.9862 and 0.9813

Table 1 (cont.)

Structure solution and Refinement

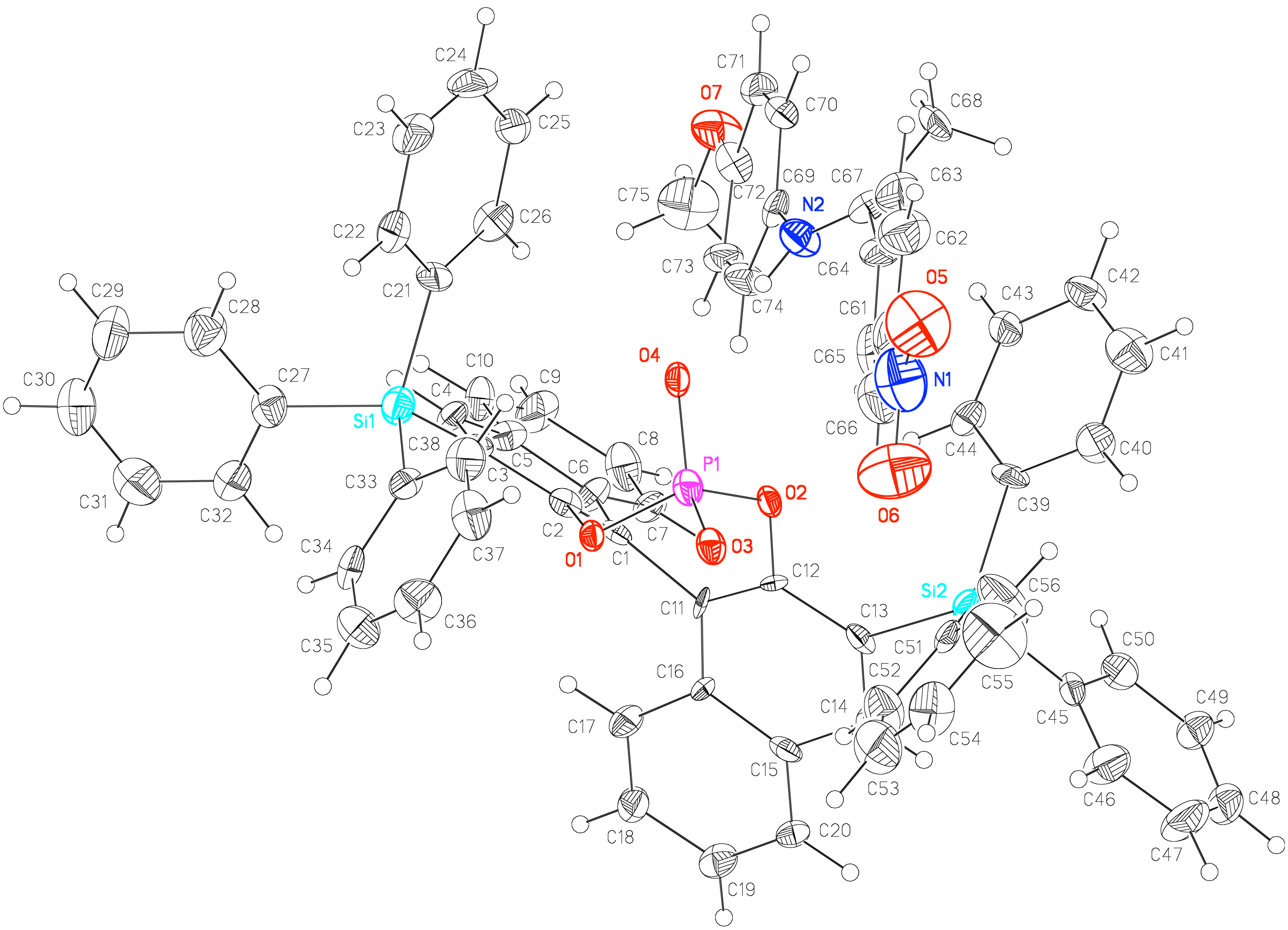
Structure solution program	Bruker XS v6.12
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	Bruker XS v6.12
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	7765 / 960 / 1047
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	1.419
Final R indices [$I>2\sigma(I)$, 4963 reflections]	R1 = 0.0601, *w*R2 = 0.0835
R indices (all data)	R1 = 0.1161, *w*R2 = 0.0913
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.006
Average shift/error	0.000
Absolute structure parameter	-0.05(15)
Largest diff. peak and hole	0.324 and -0.376 e.Å^{-3}

Special Refinement Details

The crystals contain toluene as a solvent of crystallization with four molecules in each asymmetric unit. Three of these toluene molecules are disordered. The geometries of the toluene molecules were restrained to be similar and the six-member rings of these molecules were constrained to be regular hexagons with C-C distances of 1.39Å. For each of the disordered toluene sites the total occupancy of the disordered pair was restrained to sum to one. For two of these sites the minor component was refined with isotropic displacement parameters (see Table 2). The anisotropic displacement parameters of ALL other atoms were restrained to approximate isotropic behavior. Additionally, the asymmetric unit contains a lone atom which was modeled as oxygen.

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors ® are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.



C24
C71
C70
C68
O7
C23
C25
C67
C63
C75
C72
C69
N2
C22
C26
C62
C73
C64
C29
C28
C21
C74
O5
C43
C42
C61
C30
C27
C10
O4
C65
C41
C9
N1
Si1
C4
C66
C38
C5
C8
P1
C44
C40
C33
C3
C6
O2
C31
C32
C2
C7
O6
C39
C34
C37
O1
C1
O3
C12
C35
C36
C11
C13
Si2
C56
C51
C50
C16
C52
C55
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C54
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C49
C15
C53
C46
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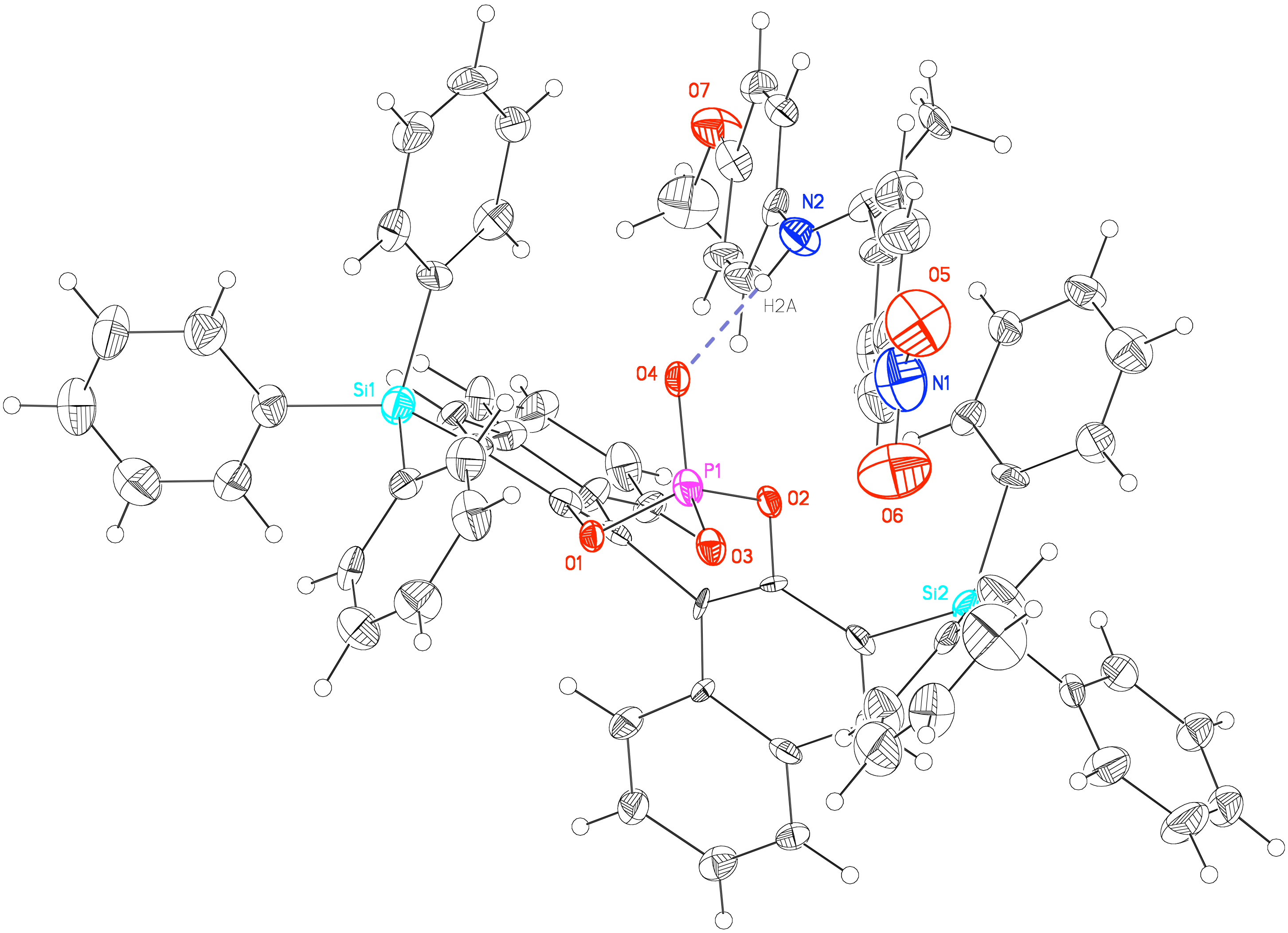
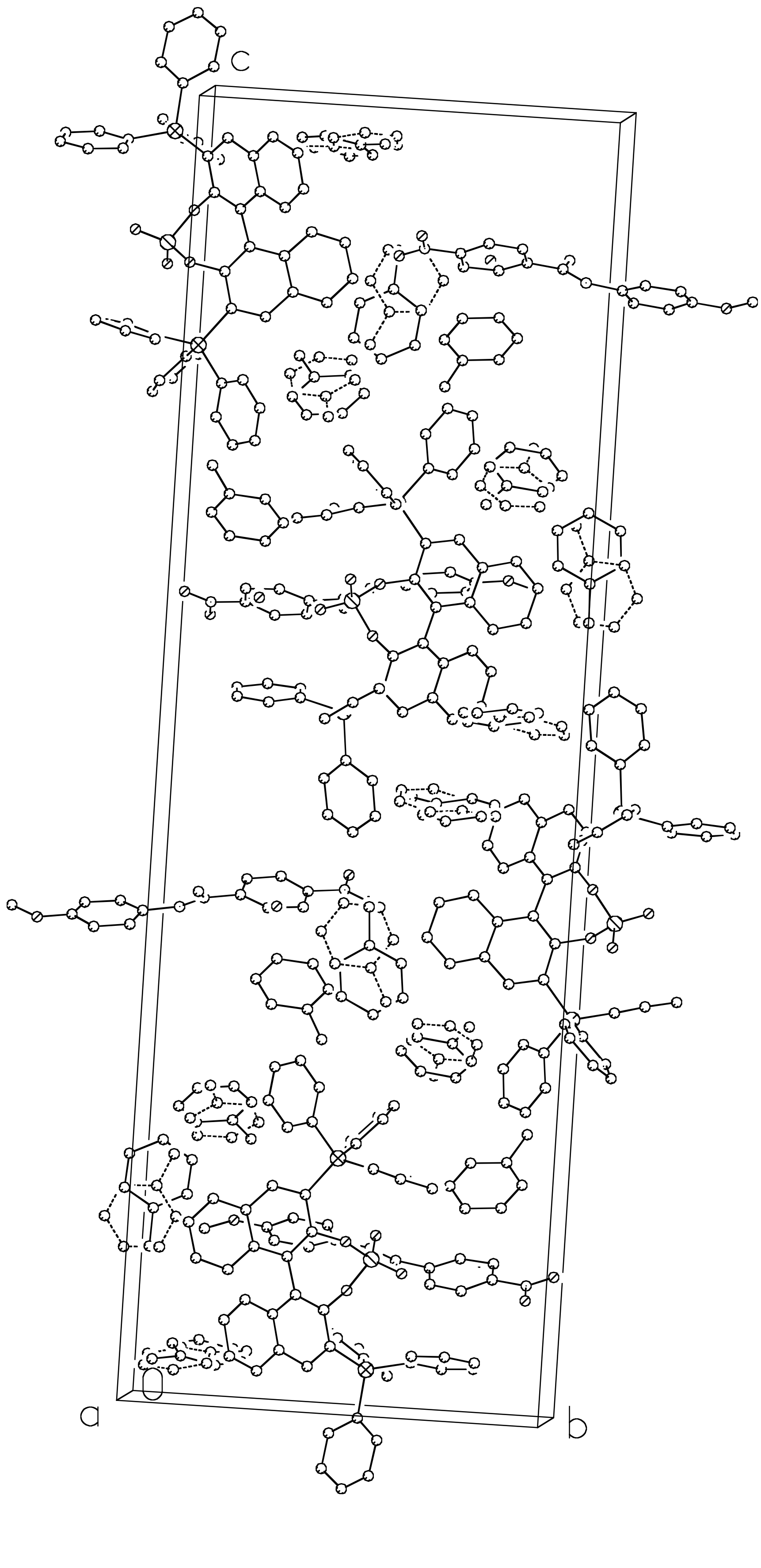
C18
C20
C47
C19


O7
N2
O5
H2A
O4
Si1
N1
P1
O2
O6
O1
O3
Si2


c
0
a
b

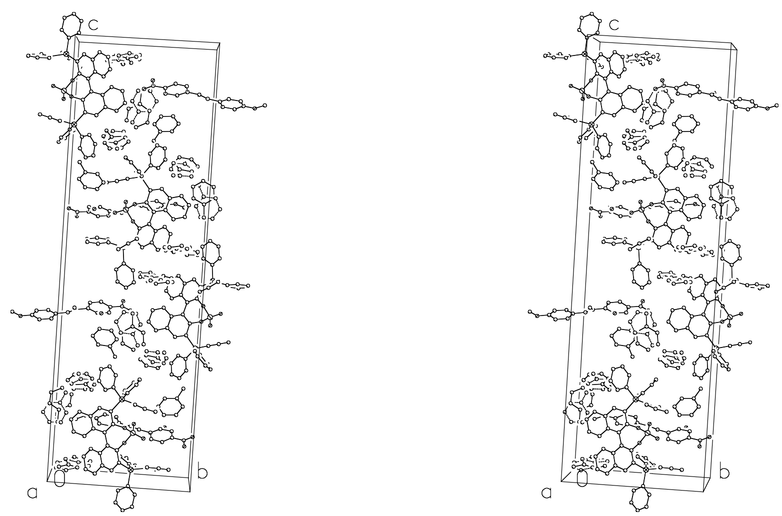

c
a
0
b
c
a
0
b

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for RIS06 (CCDC 287655). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}	Occ
P(1)	3582(2)	-762(1)	8811(1)	22(1)	1
Si(1)	4479(2)	146(1)	8049(1)	26(1)	1
Si(2)	3030(2)	-777(1)	9660(1)	23(1)	1
O(1)	4738(4)	-169(3)	8679(1)	16(1)	1
O(2)	3077(4)	-206(3)	9065(1)	17(1)	1
O(3)	4261(4)	-1523(3)	8899(1)	21(1)	1
O(4)	2357(4)	-785(3)	8637(1)	20(1)	1
C(1)	4282(6)	1207(5)	8823(2)	13(2)	1
C(2)	4379(7)	658(5)	8623(2)	21(2)	1
C(3)	4298(6)	868(5)	8342(2)	17(2)	1
C(4)	3952(7)	1674(5)	8294(2)	25(2)	1
C(5)	3697(7)	2274(5)	8493(2)	22(2)	1
C(6)	3840(7)	2027(5)	8767(2)	20(2)	1
C(7)	3485(7)	2622(5)	8959(2)	26(2)	1
C(8)	3049(7)	3412(5)	8891(2)	34(2)	1
C(9)	2955(7)	3641(5)	8620(2)	36(2)	1
C(10)	3300(7)	3080(5)	8427(2)	26(2)	1
C(11)	4576(7)	943(4)	9109(1)	13(2)	1
C(12)	3945(7)	277(5)	9217(2)	13(2)	1
C(13)	4044(6)	70(5)	9492(2)	19(2)	1
C(14)	4916(7)	550(4)	9648(1)	19(2)	1
C(15)	5704(7)	1210(5)	9531(2)	19(2)	1
C(16)	5522(7)	1420(5)	9260(2)	16(2)	1
C(17)	6342(7)	2062(4)	9157(1)	22(2)	1
C(18)	7219(7)	2501(5)	9315(2)	26(2)	1
C(19)	7331(7)	2315(5)	9587(2)	25(2)	1
C(20)	6592(7)	1678(4)	9693(1)	19(2)	1
C(21)	2728(7)	-194(5)	7942(2)	27(2)	1
C(22)	2575(8)	-787(5)	7743(2)	35(2)	1
C(23)	1296(9)	-986(5)	7646(2)	35(2)	1
C(24)	186(8)	-581(5)	7747(2)	40(3)	1
C(25)	323(8)	15(5)	7943(1)	29(2)	1
C(26)	1569(8)	200(5)	8036(1)	33(2)	1
C(27)	5286(8)	785(5)	7776(2)	29(2)	1
C(28)	4855(8)	684(5)	7512(2)	44(3)	1
C(29)	5459(9)	1142(5)	7312(2)	46(3)	1
C(30)	6492(9)	1702(5)	7364(2)	47(3)	1
C(31)	6948(8)	1786(5)	7619(2)	52(3)	1
C(32)	6346(8)	1320(5)	7821(2)	35(2)	1
C(33)	5536(8)	-811(5)	8113(1)	22(2)	1
C(34)	6935(8)	-798(5)	8093(1)	30(2)	1
C(35)	7720(8)	-1482(5)	8149(1)	34(2)	1
C(36)	7116(8)	-2224(5)	8212(2)	38(2)	1
C(37)	5709(9)	-2264(5)	8224(1)	37(2)	1
C(38)	4951(8)	-1546(5)	8180(1)	32(2)	1
C(39)	1141(7)	-633(5)	9592(2)	21(2)	1
C(40)	239(8)	-1187(5)	9720(1)	31(2)	1

C(41)	-1130(8)	-1059(5)	9686(2)	40(3)	1
C(42)	-1629(8)	-399(5)	9543(2)	30(2)	1
C(43)	-744(8)	172(5)	9432(1)	29(2)	1
C(44)	624(8)	35(5)	9453(1)	24(2)	1
C(45)	3284(7)	-658(5)	10031(1)	18(2)	1
C(46)	4039(7)	-1177(5)	10185(2)	40(3)	1
C(47)	4142(8)	-1037(6)	10460(2)	45(3)	1
C(48)	3545(8)	-396(5)	10577(2)	34(2)	1
C(49)	2771(7)	141(5)	10438(2)	28(2)	1
C(50)	2614(7)	24(5)	10166(2)	31(2)	1
C(51)	3739(8)	-1848(5)	9579(1)	19(2)	1
C(52)	5082(8)	-1907(5)	9519(1)	37(2)	1
C(53)	5718(9)	-2715(6)	9503(2)	54(3)	1
C(54)	5005(9)	-3407(5)	9539(2)	42(3)	1
C(55)	3661(10)	-3340(6)	9598(2)	65(3)	1
C(56)	3044(8)	-2563(6)	9621(2)	50(3)	1
C(61)	763(10)	6449(6)	8931(2)	49(3)	1
C(62)	-541(9)	6489(5)	8819(2)	49(3)	1
C(63)	-1116(8)	7307(6)	8802(2)	42(3)	1
C(64)	-390(8)	7998(5)	8882(2)	25(2)	1
C(65)	870(9)	7916(5)	8995(2)	38(3)	1
C(66)	1514(9)	7138(6)	9026(2)	46(3)	1
C(67)	-1008(8)	8832(5)	8845(2)	22(2)	1
C(68)	-2506(6)	8919(4)	8903(1)	29(2)	1
N(1)	1417(9)	5611(5)	8955(2)	59(2)	1
N(2)	-255(6)	9425(4)	8759(1)	31(2)	1
O(5)	730(6)	4997(4)	8882(1)	72(2)	1
O(6)	2574(7)	5570(4)	9060(1)	81(2)	1
O(7)	-1548(5)	12736(3)	8622(1)	39(2)	1
C(69)	-589(8)	10282(5)	8714(1)	21(2)	1
C(70)	-1829(7)	10520(5)	8615(1)	27(2)	1
C(71)	-2105(7)	11360(5)	8580(1)	27(2)	1
C(72)	-1137(8)	11929(5)	8656(2)	24(2)	1
C(73)	128(7)	11692(5)	8743(1)	26(2)	1
C(74)	380(7)	10855(5)	8772(2)	28(2)	1
C(75)	-577(7)	13386(5)	8692(2)	54(3)	1
C(1A)	4195(8)	4255(5)	9672(2)	55(4)	0.822(9)
C(2A)	3052(6)	3630(4)	9645(1)	35(3)	0.822(9)
C(3A)	1773(7)	3884(3)	9563(1)	29(3)	0.822(9)
C(4A)	744(5)	3301(5)	9533(1)	30(3)	0.822(9)
C(5A)	994(6)	2465(4)	9585(2)	48(4)	0.822(9)
C(6A)	2272(8)	2212(3)	9668(1)	27(3)	0.822(9)
C(7A)	3301(5)	2795(5)	9698(1)	29(5)	0.822(9)
C(1B)	1240(40)	2138(19)	9591(11)	25(18)	0.178(9)
C(2B)	1980(30)	2964(16)	9611(8)	80(20)	0.178(9)
C(3B)	3330(30)	2990(18)	9688(8)	20(20)	0.178(9)
C(4B)	3940(30)	3750(20)	9747(8)	60(20)	0.178(9)
C(5B)	3190(40)	4480(18)	9730(8)	120(30)	0.178(9)
C(6B)	1840(40)	4454(16)	9653(8)	110(30)	0.178(9)
C(7B)	1230(30)	3696(19)	9594(8)	9(16)	0.178(9)

C(1C)	5854(10)	4796(8)	8883(2)	40(4)	0.756(8)
C(2C)	6222(8)	4745(5)	8586(1)	50(4)	0.756(8)
C(3C)	6611(9)	5443(4)	8441(2)	65(6)	0.756(8)
C(4C)	6977(8)	5363(5)	8175(2)	74(5)	0.756(8)
C(5C)	6956(9)	4586(6)	8054(1)	84(6)	0.756(8)
C(6C)	6567(9)	3888(4)	8199(2)	45(4)	0.756(8)
C(7C)	6201(7)	3967(4)	8465(2)	57(4)	0.756(8)
C(1D)	6990(40)	4300(20)	8158(6)	73(18)	0.244(8)
C(2D)	6440(30)	4686(14)	8413(5)	97(19)	0.244(8)
C(3D)	6220(30)	5538(13)	8430(5)	29(14)	0.244(8)
C(4D)	5890(20)	5897(14)	8673(6)	68(15)	0.244(8)
C(5D)	5790(30)	5400(20)	8900(4)	90(20)	0.244(8)
C(6D)	6020(40)	4550(20)	8883(5)	450(90)	0.244(8)
C(7D)	6350(40)	4193(14)	8640(6)	110(20)	0.244(8)
C(1E)	-157(9)	5868(6)	7814(2)	121(4)	1
C(2E)	672(5)	6282(4)	8030(1)	64(3)	1
C(3E)	1601(6)	5853(3)	8187(1)	66(3)	1
C(4E)	2417(5)	6283(4)	8365(1)	60(3)	1
C(5E)	2304(5)	7143(4)	8388(1)	44(3)	1
C(6E)	1376(6)	7572(3)	8231(1)	52(3)	1
C(7E)	560(5)	7142(4)	8053(1)	59(3)	1
C(1F)	60(15)	2395(10)	7980(4)	81(7)	0.582(10)
C(2F)	1225(10)	2816(7)	7836(2)	40(5)	0.582(10)
C(3F)	2131(12)	2361(5)	7682(2)	50(9)	0.582(10)
C(4F)	3214(11)	2760(8)	7559(2)	70(7)	0.582(10)
C(5F)	3390(10)	3612(8)	7591(2)	63(8)	0.582(10)
C(6F)	2483(13)	4067(5)	7744(2)	50(6)	0.582(10)
C(7F)	1401(11)	3669(6)	7867(2)	44(7)	0.582(10)
C(1G)	3720(20)	3300(16)	7561(6)	74(11)	0.418(10)
C(2G)	2376(14)	3162(10)	7702(3)	56(8)	0.418(10)
C(3G)	1733(17)	3806(8)	7837(4)	73(13)	0.418(10)
C(4G)	541(17)	3654(10)	7976(3)	88(10)	0.418(10)
C(5G)	-9(14)	2858(12)	7979(3)	85(12)	0.418(10)
C(6G)	633(18)	2214(9)	7845(4)	71(10)	0.418(10)
C(7G)	1826(17)	2365(9)	7706(3)	76(15)	0.418(10)
O(1A)	5426(6)	-3028(4)	8846(1)	100(2)	1

Table 3. Bond lengths [Å] and angles [°] for RIS06 (CCDC 287655).

P(1)-O(3)	1.463(5)	C(34)-C(35)	1.375(9)
P(1)-O(4)	1.492(4)	C(35)-C(36)	1.369(9)
P(1)-O(1)	1.628(5)	C(36)-C(37)	1.393(9)
P(1)-O(2)	1.633(4)	C(37)-C(38)	1.392(9)
Si(1)-C(3)	1.883(7)	C(39)-C(44)	1.380(9)
Si(1)-C(21)	1.892(7)	C(39)-C(40)	1.413(9)
Si(1)-C(33)	1.886(8)	C(40)-C(41)	1.379(9)
Si(1)-C(27)	1.889(8)	C(41)-C(42)	1.370(9)
Si(2)-C(45)	1.888(7)	C(42)-C(43)	1.384(9)
Si(2)-C(13)	1.889(7)	C(43)-C(44)	1.373(8)
Si(2)-C(51)	1.902(7)	C(45)-C(46)	1.359(9)
Si(2)-C(39)	1.912(7)	C(45)-C(50)	1.449(9)
O(1)-C(2)	1.403(8)	C(46)-C(47)	1.405(9)
O(2)-C(12)	1.387(7)	C(47)-C(48)	1.324(9)
C(1)-C(2)	1.344(8)	C(48)-C(49)	1.347(9)
C(1)-C(6)	1.416(9)	C(49)-C(50)	1.387(8)
C(1)-C(11)	1.524(9)	C(51)-C(52)	1.364(9)
C(2)-C(3)	1.448(9)	C(51)-C(56)	1.355(10)
C(3)-C(4)	1.361(9)	C(52)-C(53)	1.443(10)
C(4)-C(5)	1.410(9)	C(53)-C(54)	1.330(10)
C(5)-C(10)	1.393(9)	C(54)-C(55)	1.366(10)
C(5)-C(6)	1.438(9)	C(55)-C(56)	1.394(10)
C(6)-C(7)	1.404(9)	C(61)-C(62)	1.407(10)
C(7)-C(8)	1.383(9)	C(61)-C(66)	1.416(10)
C(8)-C(9)	1.415(8)	C(61)-N(1)	1.500(11)
C(9)-C(10)	1.366(9)	C(62)-C(63)	1.435(10)
C(11)-C(12)	1.352(9)	C(63)-C(64)	1.381(9)
C(11)-C(16)	1.425(9)	C(64)-C(65)	1.374(9)
C(12)-C(13)	1.420(9)	C(64)-C(67)	1.484(9)
C(13)-C(14)	1.399(9)	C(65)-C(66)	1.410(10)
C(14)-C(15)	1.440(9)	C(67)-N(2)	1.284(8)
C(15)-C(20)	1.412(8)	C(67)-C(68)	1.515(8)
C(15)-C(16)	1.414(8)	N(1)-O(5)	1.252(8)
C(16)-C(17)	1.409(8)	N(1)-O(6)	1.260(8)
C(17)-C(18)	1.369(8)	N(2)-C(69)	1.435(8)
C(18)-C(19)	1.404(8)	O(7)-C(72)	1.369(8)
C(19)-C(20)	1.364(9)	O(7)-C(75)	1.461(8)
C(21)-C(26)	1.392(9)	C(69)-C(74)	1.359(9)
C(21)-C(22)	1.387(9)	C(69)-C(70)	1.378(9)
C(22)-C(23)	1.391(9)	C(70)-C(71)	1.387(9)
C(23)-C(24)	1.373(9)	C(71)-C(72)	1.376(9)
C(24)-C(25)	1.378(9)	C(72)-C(73)	1.379(9)
C(25)-C(26)	1.350(9)	C(73)-C(74)	1.375(9)
C(27)-C(32)	1.374(9)	C(1A)-C(2A)	1.517(7)
C(27)-C(28)	1.399(9)	C(2A)-C(3A)	1.3900
C(28)-C(29)	1.383(9)	C(2A)-C(7A)	1.3900
C(29)-C(30)	1.385(10)	C(3A)-C(4A)	1.3900
C(30)-C(31)	1.366(10)	C(4A)-C(5A)	1.3900
C(31)-C(32)	1.391(9)	C(5A)-C(6A)	1.3900
C(33)-C(38)	1.358(9)	C(6A)-C(7A)	1.3900
C(33)-C(34)	1.386(9)	C(1B)-C(2B)	1.519(8)

C(2B)-C(3B)	1.3900
C(2B)-C(7B)	1.3900
C(3B)-C(4B)	1.3900
C(4B)-C(5B)	1.3900
C(5B)-C(6B)	1.3900
C(6B)-C(7B)	1.3900
C(1C)-C(2C)	1.536(7)
C(2C)-C(3C)	1.3900
C(2C)-C(7C)	1.3900
C(3C)-C(4C)	1.3900
C(4C)-C(5C)	1.3900
C(5C)-C(6C)	1.3900
C(6C)-C(7C)	1.3900
C(1D)-C(2D)	1.518(7)
C(2D)-C(3D)	1.3900
C(2D)-C(7D)	1.3900
C(3D)-C(4D)	1.3900
C(4D)-C(5D)	1.3900
C(5D)-C(6D)	1.3900
C(6D)-C(7D)	1.3900
C(1E)-C(2E)	1.514(6)
C(2E)-C(3E)	1.3900
C(2E)-C(7E)	1.3900
C(3E)-C(4E)	1.3900
C(4E)-C(5E)	1.3900
C(5E)-C(6E)	1.3900
C(6E)-C(7E)	1.3900
C(1F)-C(2F)	1.520(8)
C(2F)-C(3F)	1.3900
C(2F)-C(7F)	1.3900
C(3F)-C(4F)	1.3900
C(4F)-C(5F)	1.3900
C(5F)-C(6F)	1.3900
C(6F)-C(7F)	1.3900
C(1G)-C(2G)	1.527(8)
C(2G)-C(3G)	1.3900
C(2G)-C(7G)	1.3900
C(3G)-C(4G)	1.3900
C(4G)-C(5G)	1.3900
C(5G)-C(6G)	1.3900
C(6G)-C(7G)	1.3900
O(3)-P(1)-O(4)	121.9(3)
O(3)-P(1)-O(1)	106.8(3)
O(4)-P(1)-O(1)	110.2(3)
O(3)-P(1)-O(2)	111.2(3)
O(4)-P(1)-O(2)	102.8(3)
O(1)-P(1)-O(2)	102.2(2)
C(3)-Si(1)-C(21)	108.3(4)
C(3)-Si(1)-C(33)	114.9(3)
C(21)-Si(1)-C(33)	108.6(4)
C(3)-Si(1)-C(27)	105.8(3)
C(21)-Si(1)-C(27)	109.7(4)
C(33)-Si(1)-C(27)	109.4(3)

C(45)-Si(2)-C(13)	107.3(3)
C(45)-Si(2)-C(51)	104.7(3)
C(13)-Si(2)-C(51)	111.1(3)
C(45)-Si(2)-C(39)	107.0(3)
C(13)-Si(2)-C(39)	110.6(3)
C(51)-Si(2)-C(39)	115.5(4)
C(2)-O(1)-P(1)	117.3(4)
C(12)-O(2)-P(1)	123.2(4)
C(2)-C(1)-C(6)	118.9(7)
C(2)-C(1)-C(11)	120.7(7)
C(6)-C(1)-C(11)	120.4(7)
C(1)-C(2)-O(1)	119.3(7)
C(1)-C(2)-C(3)	124.8(7)
O(1)-C(2)-C(3)	115.5(7)
C(4)-C(3)-C(2)	114.1(7)
C(4)-C(3)-Si(1)	118.1(6)
C(2)-C(3)-Si(1)	127.6(6)
C(3)-C(4)-C(5)	124.7(7)
C(10)-C(5)-C(4)	121.1(8)
C(10)-C(5)-C(6)	120.8(7)
C(4)-C(5)-C(6)	118.1(7)
C(7)-C(6)-C(1)	125.0(8)
C(7)-C(6)-C(5)	116.4(7)
C(1)-C(6)-C(5)	118.6(7)
C(8)-C(7)-C(6)	122.2(7)
C(7)-C(8)-C(9)	119.8(8)
C(10)-C(9)-C(8)	119.7(8)
C(9)-C(10)-C(5)	121.0(7)
C(12)-C(11)-C(16)	121.1(7)
C(12)-C(11)-C(1)	120.6(7)
C(16)-C(11)-C(1)	118.3(7)
C(11)-C(12)-O(2)	120.4(7)
C(11)-C(12)-C(13)	122.8(7)
O(2)-C(12)-C(13)	116.6(7)
C(14)-C(13)-C(12)	117.3(7)
C(14)-C(13)-Si(2)	118.2(6)
C(12)-C(13)-Si(2)	124.5(6)
C(13)-C(14)-C(15)	120.6(7)
C(20)-C(15)-C(16)	120.3(7)
C(20)-C(15)-C(14)	119.5(7)
C(16)-C(15)-C(14)	120.1(7)
C(17)-C(16)-C(15)	117.0(7)
C(17)-C(16)-C(11)	125.3(7)
C(15)-C(16)-C(11)	117.7(7)
C(18)-C(17)-C(16)	122.0(7)
C(17)-C(18)-C(19)	120.2(7)
C(20)-C(19)-C(18)	119.6(7)
C(19)-C(20)-C(15)	120.7(7)
C(26)-C(21)-C(22)	117.8(7)
C(26)-C(21)-Si(1)	121.6(6)
C(22)-C(21)-Si(1)	120.2(6)
C(23)-C(22)-C(21)	120.6(7)
C(24)-C(23)-C(22)	119.2(8)
C(23)-C(24)-C(25)	121.0(8)

C(26)-C(25)-C(24)	119.2(7)	C(64)-C(67)-C(68)	117.5(7)
C(25)-C(26)-C(21)	122.2(7)	O(5)-N(1)-O(6)	125.0(9)
C(32)-C(27)-C(28)	117.3(8)	O(5)-N(1)-C(61)	116.7(8)
C(32)-C(27)-Si(1)	122.9(7)	O(6)-N(1)-C(61)	118.2(9)
C(28)-C(27)-Si(1)	119.6(7)	C(67)-N(2)-C(69)	129.2(7)
C(29)-C(28)-C(27)	119.7(8)	C(72)-O(7)-C(75)	116.8(6)
C(28)-C(29)-C(30)	121.8(8)	C(74)-C(69)-C(70)	121.1(7)
C(31)-C(30)-C(29)	119.0(9)	C(74)-C(69)-N(2)	117.1(8)
C(30)-C(31)-C(32)	119.2(9)	C(70)-C(69)-N(2)	121.8(8)
C(27)-C(32)-C(31)	123.0(8)	C(69)-C(70)-C(71)	119.3(7)
C(38)-C(33)-C(34)	117.2(8)	C(72)-C(71)-C(70)	118.4(7)
C(38)-C(33)-Si(1)	121.0(6)	C(73)-C(72)-O(7)	124.8(8)
C(34)-C(33)-Si(1)	121.8(7)	C(73)-C(72)-C(71)	122.3(8)
C(35)-C(34)-C(33)	122.3(8)	O(7)-C(72)-C(71)	112.9(7)
C(36)-C(35)-C(34)	119.8(8)	C(72)-C(73)-C(74)	117.9(8)
C(35)-C(36)-C(37)	119.0(8)	C(69)-C(74)-C(73)	120.8(8)
C(38)-C(37)-C(36)	119.5(8)	C(3A)-C(2A)-C(7A)	120.0
C(33)-C(38)-C(37)	122.0(8)	C(3A)-C(2A)-C(1A)	120.7(6)
C(44)-C(39)-C(40)	119.1(7)	C(7A)-C(2A)-C(1A)	119.3(6)
C(44)-C(39)-Si(2)	123.1(6)	C(4A)-C(3A)-C(2A)	120.0
C(40)-C(39)-Si(2)	117.4(6)	C(5A)-C(4A)-C(3A)	120.0
C(41)-C(40)-C(39)	117.9(8)	C(6A)-C(5A)-C(4A)	120.0
C(42)-C(41)-C(40)	122.2(8)	C(7A)-C(6A)-C(5A)	120.0
C(41)-C(42)-C(43)	119.6(8)	C(6A)-C(7A)-C(2A)	120.0
C(44)-C(43)-C(42)	119.1(8)	C(3B)-C(2B)-C(7B)	120.00(6)
C(43)-C(44)-C(39)	121.8(7)	C(3B)-C(2B)-C(1B)	120.5(10)
C(46)-C(45)-C(50)	116.7(7)	C(7B)-C(2B)-C(1B)	118.7(10)
C(46)-C(45)-Si(2)	124.8(6)	C(2B)-C(3B)-C(4B)	120.0
C(50)-C(45)-Si(2)	118.5(6)	C(5B)-C(4B)-C(3B)	120.00(6)
C(45)-C(46)-C(47)	120.0(8)	C(4B)-C(5B)-C(6B)	120.00(7)
C(48)-C(47)-C(46)	121.9(8)	C(7B)-C(6B)-C(5B)	120.0
C(47)-C(48)-C(49)	121.5(8)	C(6B)-C(7B)-C(2B)	120.0
C(48)-C(49)-C(50)	119.1(8)	C(3C)-C(2C)-C(7C)	120.0
C(49)-C(50)-C(45)	120.8(7)	C(3C)-C(2C)-C(1C)	122.0(6)
C(52)-C(51)-C(56)	117.9(8)	C(7C)-C(2C)-C(1C)	118.0(6)
C(52)-C(51)-Si(2)	118.0(6)	C(4C)-C(3C)-C(2C)	120.0
C(56)-C(51)-Si(2)	123.1(7)	C(5C)-C(4C)-C(3C)	120.0
C(51)-C(52)-C(53)	119.9(8)	C(4C)-C(5C)-C(6C)	120.0
C(54)-C(53)-C(52)	120.9(8)	C(7C)-C(6C)-C(5C)	120.0
C(53)-C(54)-C(55)	118.6(9)	C(6C)-C(7C)-C(2C)	120.0
C(54)-C(55)-C(56)	120.9(9)	C(3D)-C(2D)-C(7D)	120.0
C(51)-C(56)-C(55)	121.7(8)	C(3D)-C(2D)-C(1D)	120.4(6)
C(62)-C(61)-C(66)	125.4(9)	C(7D)-C(2D)-C(1D)	119.1(6)
C(62)-C(61)-N(1)	117.9(9)	C(2D)-C(3D)-C(4D)	120.0
C(66)-C(61)-N(1)	116.7(9)	C(5D)-C(4D)-C(3D)	120.0
C(61)-C(62)-C(63)	115.3(8)	C(6D)-C(5D)-C(4D)	120.0
C(64)-C(63)-C(62)	120.9(8)	C(5D)-C(6D)-C(7D)	120.0
C(63)-C(64)-C(65)	120.9(8)	C(6D)-C(7D)-C(2D)	120.0
C(63)-C(64)-C(67)	118.4(8)	C(3E)-C(2E)-C(7E)	120.0
C(65)-C(64)-C(67)	120.7(8)	C(3E)-C(2E)-C(1E)	122.9(5)
C(64)-C(65)-C(66)	122.7(8)	C(7E)-C(2E)-C(1E)	116.8(5)
C(65)-C(66)-C(61)	114.7(8)	C(2E)-C(3E)-C(4E)	120.0
N(2)-C(67)-C(64)	118.2(7)	C(5E)-C(4E)-C(3E)	120.0
N(2)-C(67)-C(68)	124.2(7)	C(4E)-C(5E)-C(6E)	120.0

C(7E)-C(6E)-C(5E)	120.0	C(6F)-C(7F)-C(2F)	120.0
C(6E)-C(7E)-C(2E)	120.0	C(3G)-C(2G)-C(7G)	120.0
C(3F)-C(2F)-C(7F)	120.0	C(3G)-C(2G)-C(1G)	121.1(9)
C(3F)-C(2F)-C(1F)	121.3(8)	C(7G)-C(2G)-C(1G)	118.8(9)
C(7F)-C(2F)-C(1F)	118.7(8)	C(4G)-C(3G)-C(2G)	120.0
C(2F)-C(3F)-C(4F)	120.0	C(3G)-C(4G)-C(5G)	120.0
C(5F)-C(4F)-C(3F)	120.0	C(6G)-C(5G)-C(4G)	120.0
C(4F)-C(5F)-C(6F)	120.0	C(5G)-C(6G)-C(7G)	120.0
C(5F)-C(6F)-C(7F)	120.0	C(6G)-C(7G)-C(2G)	120.0

Table 4. Anisotropic displacement parameters ($Å^2$x 10^4) for RIS06 (CCDC 287655). 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}
P(1)	227(13)	208(15)	214(15)	16(13)	37(13)	-35(13)
Si(1)	285(15)	270(16)	215(15)	21(14)	8(13)	-27(13)
Si(2)	244(14)	220(15)	212(15)	33(13)	-14(12)	17(13)
O(1)	160(30)	190(30)	130(30)	10(30)	40(20)	10(30)
O(2)	150(30)	190(30)	160(30)	0(30)	40(30)	-40(30)
O(3)	230(30)	170(30)	220(30)	0(30)	40(30)	-60(30)
O(4)	210(30)	260(30)	140(30)	-10(30)	50(30)	-50(30)
C(1)	80(40)	130(50)	190(50)	-110(50)	20(40)	-10(40)
C(2)	150(40)	160(50)	320(60)	180(50)	-20(40)	-30(40)
C(3)	140(40)	170(50)	200(50)	-50(40)	-30(40)	60(40)
C(4)	260(50)	350(50)	160(50)	80(50)	-60(40)	-60(40)
C(5)	240(50)	160(50)	260(50)	10(50)	-70(40)	-20(40)
C(6)	300(50)	170(50)	150(50)	-10(50)	-40(40)	20(40)
C(7)	240(50)	310(50)	220(50)	130(50)	-50(40)	0(40)
C(8)	390(50)	260(50)	370(60)	0(50)	110(40)	-50(40)
C(9)	480(50)	240(50)	350(60)	190(50)	-110(50)	-60(40)
C(10)	360(50)	190(50)	240(50)	70(50)	70(40)	-40(40)
C(11)	190(50)	150(50)	50(50)	40(40)	50(40)	130(40)
C(12)	90(40)	190(40)	120(40)	20(30)	-50(30)	10(30)
C(13)	110(50)	190(50)	260(50)	30(40)	40(40)	-20(40)
C(14)	140(40)	290(50)	130(50)	100(40)	30(40)	40(40)
C(15)	90(40)	240(50)	240(50)	-50(40)	0(40)	-20(40)
C(16)	140(50)	240(50)	90(50)	40(40)	-20(40)	10(40)
C(17)	280(50)	210(50)	150(50)	-50(40)	-40(40)	-20(40)
C(18)	270(50)	330(50)	180(50)	0(40)	0(40)	-70(40)
C(19)	300(50)	250(50)	210(50)	-80(40)	-40(40)	10(40)
C(20)	190(50)	190(50)	200(50)	30(40)	-50(40)	40(40)
C(21)	190(50)	390(50)	230(50)	-80(50)	-40(40)	-140(40)
C(22)	370(60)	480(60)	200(50)	-20(50)	40(40)	-20(50)
C(23)	450(60)	350(60)	240(50)	-50(40)	-70(50)	-150(50)
C(24)	320(50)	550(60)	340(60)	-100(50)	-170(50)	-60(50)
C(25)	230(50)	430(60)	230(50)	-50(50)	20(40)	70(50)
C(26)	390(50)	390(50)	200(50)	-180(40)	-10(50)	-50(50)
C(27)	330(50)	280(50)	250(50)	-90(50)	60(40)	0(50)
C(28)	510(60)	460(60)	370(60)	30(50)	0(50)	-140(50)
C(29)	610(60)	500(60)	290(50)	40(50)	80(50)	-80(50)
C(30)	560(60)	440(60)	420(60)	70(50)	140(50)	-60(50)
C(31)	400(60)	610(60)	560(60)	70(60)	10(50)	-80(50)
C(32)	360(50)	410(60)	270(50)	50(50)	-10(50)	-20(50)
C(33)	240(50)	230(50)	190(50)	10(40)	-30(40)	-10(40)
C(34)	400(50)	350(50)	150(50)	80(40)	50(40)	-10(50)
C(35)	290(50)	300(50)	420(60)	-50(50)	50(40)	40(50)
C(36)	390(60)	320(60)	440(60)	0(50)	-10(50)	120(50)
C(37)	440(60)	290(60)	370(50)	-90(50)	100(50)	-70(50)
C(38)	370(50)	320(50)	280(50)	-100(50)	40(40)	40(50)
C(39)	120(40)	260(50)	260(50)	-110(40)	-40(40)	-60(40)
C(40)	300(50)	280(50)	360(50)	70(50)	20(50)	50(40)

C(41)	380(60)	330(60)	490(60)	-70(50)	20(50)	-70(40)
C(42)	190(50)	300(50)	420(50)	40(40)	0(40)	30(40)
C(43)	210(50)	370(50)	280(50)	80(50)	20(40)	40(50)
C(44)	300(50)	200(50)	210(50)	60(40)	-30(40)	50(40)
C(45)	190(50)	200(50)	170(50)	-40(40)	50(40)	-60(40)
C(46)	410(50)	460(60)	330(60)	0(50)	-90(50)	80(40)
C(47)	520(60)	510(60)	330(60)	140(50)	-150(50)	100(50)
C(48)	370(50)	430(60)	210(50)	-90(50)	10(50)	-100(50)
C(49)	330(50)	300(50)	220(50)	-60(50)	-10(40)	0(40)
C(50)	280(50)	340(50)	300(50)	20(50)	-10(40)	-110(40)
C(51)	250(50)	210(50)	110(50)	60(40)	0(40)	70(40)
C(52)	370(60)	290(50)	460(60)	70(50)	110(50)	10(50)
C(53)	460(60)	640(60)	510(60)	-30(60)	140(50)	230(60)
C(54)	580(60)	210(50)	470(60)	80(50)	70(50)	90(50)
C(55)	780(70)	230(60)	950(70)	10(50)	50(60)	-40(50)
C(56)	310(50)	390(60)	790(60)	20(50)	170(50)	70(50)
C(61)	570(60)	460(60)	450(60)	220(50)	60(50)	80(60)
C(62)	490(60)	480(60)	510(60)	70(50)	-90(50)	-30(50)
C(63)	380(50)	500(60)	380(50)	120(50)	-50(50)	110(50)
C(64)	240(50)	240(50)	260(50)	-30(40)	-90(40)	-100(50)
C(65)	480(60)	300(60)	360(50)	80(50)	180(50)	-20(50)
C(66)	480(60)	420(60)	480(60)	10(50)	70(50)	-80(50)
C(67)	320(50)	150(50)	190(50)	-50(40)	-80(40)	50(40)
C(68)	140(50)	400(50)	340(50)	30(40)	80(40)	50(40)
N(1)	640(50)	460(60)	670(60)	-40(50)	180(50)	80(50)
N(2)	230(40)	290(50)	400(50)	40(40)	10(40)	-30(40)
O(5)	810(50)	480(50)	860(50)	-70(40)	40(40)	-30(40)
O(6)	770(50)	780(50)	870(50)	0(40)	-240(40)	130(40)
O(7)	340(30)	280(40)	560(40)	10(30)	-70(30)	-150(30)
C(69)	300(50)	200(50)	140(50)	60(40)	30(40)	40(50)
C(70)	180(50)	350(60)	280(50)	60(40)	10(40)	-30(40)
C(71)	260(50)	290(50)	250(50)	10(50)	-40(40)	-40(50)
C(72)	270(50)	120(50)	330(50)	-50(40)	60(40)	0(40)
C(73)	210(50)	290(50)	290(50)	40(40)	-60(40)	50(40)
C(74)	220(50)	240(50)	390(50)	40(50)	-50(40)	-80(50)
C(75)	570(60)	320(50)	730(60)	20(50)	-70(50)	140(50)
C(1A)	610(70)	280(60)	760(80)	40(60)	-170(60)	-120(60)
C(2A)	450(70)	480(70)	130(60)	-100(60)	100(50)	-130(60)
C(3A)	260(60)	430(70)	170(60)	80(50)	0(60)	210(60)
C(4A)	300(60)	210(60)	390(60)	-10(60)	10(50)	-50(60)
C(5A)	390(70)	470(80)	590(80)	-100(70)	-20(60)	-90(70)
C(6A)	340(60)	260(60)	210(60)	-60(50)	80(50)	90(50)
C(7A)	290(80)	260(70)	310(80)	-70(50)	110(50)	170(50)
C(1C)	310(60)	450(80)	430(70)	-120(60)	-160(50)	30(50)
C(2C)	170(60)	560(80)	760(80)	-120(70)	10(60)	180(60)
C(3C)	720(90)	540(90)	700(90)	230(70)	90(70)	10(70)
C(4C)	970(80)	530(80)	730(90)	-10(70)	0(70)	-40(70)
C(5C)	1140(90)	690(90)	690(80)	-100(80)	60(70)	150(70)
C(6C)	450(70)	450(80)	450(80)	-180(60)	110(60)	-80(60)
C(7C)	390(70)	490(80)	820(80)	-80(70)	-40(70)	-10(60)

C(1E)	1280(80)	1210(80)	1130(70)	-480(70)	-520(70)	-60(70)
C(2E)	640(60)	610(60)	660(60)	-150(60)	-40(60)	-40(60)
C(3E)	720(60)	700(60)	550(60)	110(60)	-200(50)	-90(60)
C(4E)	740(60)	540(60)	500(60)	40(50)	-140(50)	-20(50)
C(5E)	460(60)	520(60)	340(60)	-20(50)	110(50)	-50(50)
C(6E)	390(50)	590(60)	560(60)	-240(50)	180(50)	-10(50)
C(7E)	550(60)	610(60)	620(60)	-80(60)	110(50)	40(60)
C(1F)	780(100)	830(100)	800(110)	-40(90)	-160(80)	120(80)
C(2F)	440(90)	430(90)	330(80)	90(70)	-80(70)	30(70)
C(3F)	510(100)	540(120)	450(110)	-10(80)	-240(80)	120(80)
C(4F)	710(100)	770(100)	630(100)	60(80)	-10(80)	70(80)
C(5F)	580(110)	770(110)	550(100)	160(80)	-210(80)	-50(80)
C(6F)	600(90)	500(90)	410(90)	140(70)	-130(70)	150(80)
C(7F)	490(100)	440(100)	400(100)	-50(80)	-210(80)	30(80)
C(1G)	760(140)	810(140)	670(140)	50(90)	-60(90)	0(100)
C(2G)	490(110)	720(120)	480(110)	70(90)	-90(90)	80(90)
C(3G)	780(150)	780(150)	630(150)	60(90)	-50(90)	130(90)
C(4G)	810(130)	910(130)	930(130)	-10(90)	-90(90)	-150(90)
C(5G)	870(140)	810(140)	870(140)	110(100)	-150(90)	30(90)
C(6G)	720(130)	670(130)	750(130)	90(90)	40(90)	-40(90)
C(7G)	780(170)	790(170)	710(170)	0(90)	-70(90)	280(90)
O(1A)	1170(50)	920(50)	910(50)	30(40)	90(40)	140(40)

Table 5. Hydrogen bonds for RIS06 (CCDC 287655) [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(2A)...O(4)#1	0.88	1.81	2.674(7)	168.7

Symmetry transformations used to generate equivalent atoms:
#1 x,y+1,z