Planar-Chiral Phosphine-Olefin Ligands Exploiting a (Cyclopentadienyl)manganese (I) Scaffold to Achieve High Robustness and High Enantioselectivity

Ken Kamikawa,[*,†] Ya-Yi Tseng,[†] Jia-Hong Jian,[‡] Tamotsu Takahashi,[‡] and Masamichi Ogasawara[*,‡,§]

[†] Department of Chemistry, Graduate School of Science, Osaka Prefecture University, Sakai, Osaka 599-8531, Japan

[‡] Institute for Catalysis, Hokkaido University, Kita-ku, Sapporo 001-0021, Japan

[§] Department of Natural Science, Graduate School of Science and Technology, Tokushima University, Tokushima 770-8506, Japan

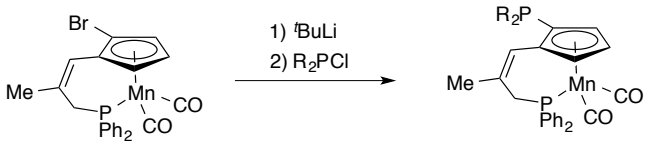
Supporting Information

Table of Contents

Experimental Section.

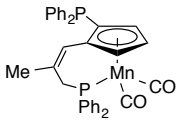
General. All anaerobic and/or moisture sensitive manipulations were carried out with standard Schlenk techniques under predried nitrogen or with glovebox techniques under prepurified argon. ^{1}H NMR (at 400 MHz or 500 MHz) and ^{13}C NMR (at 100 MHz or 125 MHz) chemical shifts are reported in ppm downfield of internal tetramethylsilane. ^{31}P NMR (at 162 MHz or 202 MHz) chemical shifts are externally referenced to 85% H_3PO_4. Tetrahydrofuran, diethyl ether, and benzene were distilled from benzophenone-ketyl under nitrogen prior to use. Dichloromethane was distilled from CaH_2 under nitrogen prior to use. Ph_2P(methallyl)[1] were Grubbs II catalyst[2], $MePPh_3{\cdot}I$[3], Cymantrene carboxaldehyde[4], Cymantrene carboxaldehyde dimethylacetal[5] and [η^5-1-(2*R*,4*R*)-4-(methoxymethyl)-1,3-dioxanyl]cyclopentadienyl]manganese(I) tricarbonyl (**3**)[5] were prepared according to the reported methods. The full characterization data of the following compounds: (η^5-1-Bromo-2-vinylcyclopentadienyl)manganese(I) tricarbonyl (**6**), (η^5-1-bromo-2-vinylcylopentadienyl) (diphenylmetallylphosphine)manganese (I) dicarbonyl (**7**), [(η^5-1-bromo-2-(3-diphenylphosphino-2-methylpropenyl)cylopentadienyl-*P*)]manganese (I) dicarbonyl (**8**) were reported previously.[6] All the other chemicals were obtained from commercial sources and used as received unless otherwise noted.

[η^5-1-(Diarylphosphino)-2-(3-dipneylphosphino-2-methyl-propenyl)cyclopentadienyl-*P*]manganese(I) Dicarbonyl (2a-d).

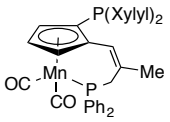


To the THF (6 mL) solution of (*R*)- or (*S*)-[η^5-1-bromo-2-(3-dipneylphosphino-2-methyl-propenyl)cyclopentadienyl-*P*]manganese(I) dicarbonyl **(8)** (170 mg, 0.34 mmol), ^{t}BuLi (1.2 eq, 1.60 M solution in pentane) was added dropwised at –78 °C under a nitrogen atmosphere. The resulting solution was stirred for 30 min at –78 °C and then R_2PCl (1.2 eq) was added. The resulting solution was gradually warmed up to room temperature in 1 h, and quenched with NH_4Cl_{aq}. The mixture was extracted with ethyl acetate and the organic layer was dried over anhydrous $MgSO_4$. After removing $MgSO_4$ by filtration, the solution was concentrated under reduced pressure. The crude product was purified by silica gel chromatography to give the title compound in pure form. The reaction conditions were not optimized. The yields of **2a**-**d** are given in Scheme 3 in a text. The characterization data of chromium complexes **2a**-**d** are given below.

(*S*)-(–)-[(η^5-1-Diphenylphosphino-2-(3-diphenylphosphino-2-methylpropenyl)cyclopentadienyl-*P*)]manganese (I) Dicarbonyl (2a). ^{1}H NMR ($CDCl_3$): δ 1.44 (s, 3H), 3.01 (t, J = 13.0 Hz, 1H), 3.60-3.65(m, 1H), 4.13 (s, 1H), 4.32 (s, 1H), 4.82 (s, 1H), 5.81 (s, 1H), 7.27-7.35 (m, 12H), 7.41-7.43 (m, 4H), 7.52-7.57 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 27.1 (d, J_{PC} = 3.5 Hz), 35.8 (m), 79.9 (s), 82.8 (d, J_{PC} = 26.1 Hz), 87.9 (d, J_{PC} = 10.7 Hz), 106.3 (d, J_{PC} = 23.8 Hz), 117.0 (d, J_{PC} = 10.7 Hz), 128.0 (s), 128.1 (s), 128.3 (s), 128.4 (d, J_{PC} = 6.0 Hz), 129. 4 (s), 129.7 (s), 131.2 (d, J_{PC} = 9.5 Hz), 132.3 (d, J_{PC} = 19.0 Hz), 132.7 (d, J_{PC} = 9.5 Hz), 135.2 (d, J_{PC} = 20.3 Hz), 136.1 (d, J_{PC} = 8.3 Hz), 137.1 (s), 137.5 (s), 138.9 (s), 139.3 (s), 139.7 (d, J_{PC} = 10.7 Hz), 228.7 (d, J_{PC} = 19.0 Hz), 231.0 (d, J_{PC} = 22.5 Hz). ^{31}P NMR ($CDCl_3$): δ –21.2, 106.2. IR ($CHCl_3$): ν 1434, 1873, 1936 cm^{-1}. Anal. Calcd for $C_{35}H_{29}MnO_2P_2$: C, 70.24; H, 4.88. Found: C, 70.25; H, 4.98. $[\alpha]_D^{24}$ –137.84 (*c* 0.5, $CHCl_3$)

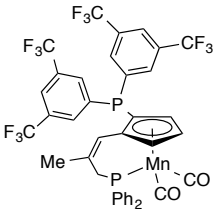


(*R*)-(+)-[(η^5-1-Bis(3,5-dimethylphenyl)phosphino-2-(3-diphenylphosphino-2-methylpropenyl)cyclopentadienyl-*P*)]manganese(I) Dicarbonyl (2b). ^{1}H NMR ($CDCl_3$): δ 1.42



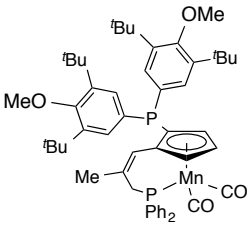
(s, 3H), 2.18 (s, 6H), 2.28 (s, 6H), 2.98 (t, J = 13.2 Hz, 1H), 3.64-3.71 (m, 1H), 4.13 (s, 1H), 4.34 (s, 1H), 4.79 (s, 1H), 5.86 (s, 1H), 6.89 (d, J = 7.6 Hz, 2H), 6.92 (d, J = 4.8 Hz, 2H), 6.99 (d, J = 8.8 Hz, 2H), 7.26-7.35 (m, 4H), 7.39-7.46 (m, 2H), 7.50-7.62 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 21.4 (d, J_{PC} = 25 Hz), 27.1 (d, J_{PC} = 3.5 Hz), 36.2 (m), 77.4 (s), 79.9 (d, J_{PC} = 3.5 Hz), 82.0 (s), 83.6 (d, J_{PC} = 4.8 Hz), 88.3 (d, J_{PC} = 11.9 Hz), 106.6 (d, J_{PC} = 25.0 Hz), 117.2 (d, J_{PC} = 11.9 Hz), 128.0 (d, J_{PC} = 9.5 Hz), 128.3 (d, J_{PC} = 8.3 Hz), 129.3 (s), 129.6 (s), 130.0 (d, J_{PC} = 6.0 Hz), 130.1 (s), 131.1 (s), 131.3 (d, J_{PC} = 9.5 Hz), 132.6 (d, J_{PC} = 8.3 Hz), 132.8 (s), 135.9 (d, J_{PC} = 8.3 Hz), 137.2 (s), 137.4 (s), 137.7 (d, J_{PC} = 6.0 Hz), 137.8 (d, J_{PC} = 8.4 Hz), 139.1 (d, J_{PC} = 7.1 Hz), 139.3 (s), 139.5 (s), 228.6 (d, J_{PC} = 20.2 Hz), 231.2 (d, J_{PC} = 22.6 Hz). ^{31}P NMR ($CDCl_3$): δ –21.7, 106.8. IR ($CHCl_3$): ν 694, 750, 1434, 1873, 1938, 3402 cm^{-1}. Anal. Calcd for $C_{39}H_{37}MnO_2P_2$: C, 71.56; H, 5.70. Found: C, 71.55; H, 5.83. $[\alpha]_D^{26}$ +135.1 (c 0.5, $CHCl_3$).

(*S*)-(–)-[η^5-1-Bis(3,5-di(trifluormethylphenyl)phosphino-2-(3-diphenylphosphino-2-methylpropenyl)cyclopentadienyl-*P*)manganese(I) Dicarbonyl (2c). ^{1}H NMR ($CDCl_3$): δ 1.53

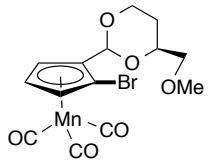


(s, 3H), 3.09 (t, J = 13.8 Hz, 1H), 3.48-3.54 (m, 1H), 4.04 (s, 1H), 4.50 (s, 1H), 4.96 (s, 1H), 5.90 (s, 1H), 7.37-7.53 (m, 10 H), 7.66 (d, J = 5.6 Hz, 2H), 7.80 (d, J = 7.2 Hz, 2H), 7.87 (d, J = 7.6 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ27.3 (d, J_{PC} = 4.1 Hz), 36.2 (m), 77.4 (s), 81.2 (s), 81.9 (s), 83.9 (s), 107.4 (d, J_{PC} = 25.4 Hz), 115.8 (d, J_{PC} = 10.8 Hz), 121.8 (d, J_{PC} = 16.1 Hz), 122.8 (s), 124.5 (d, J_{PC} = 16.1 Hz), 128.2 (d, J_{PC} = 9.4 Hz), 128.7 (d, J_{PC} = 9.4 Hz), 129.7 (s), 130.2 (s), , 131.1 (d, J_{PC} = 8.0 Hz), 131.5 (d, J_{PC} = 16.1 Hz), 132.8 (d, J_{PC} = 10.7 Hz), 135.1 (d, J_{PC} = 22.8 Hz), 138.2 (d, J_{PC} = 13.4 Hz), 139.1 (d, J_{PC} = 13.4 Hz), 142.6 (d, J_{PC} = 18.8 Hz), 227.9 (d, J_{PC} = 17.4 Hz), 229.9 (d, J_{PC} = 22.8 Hz). ^{31}P NMR ($CDCl_3$): δ –18.7, 103.4. IR ($CHCl_3$): ν 899, 1135, 1279, 1354, 1885, 1944 cm^{-1}. Anal. Calcd for $C_{39}H_{25}F_{12}MnO_2P_2$: C, 53.81; H, 2.89. Found: C, 53.81; H, 2.93. $[\alpha]_D^{25}$ –40.9 (c 0.66, $CHCl_3$).

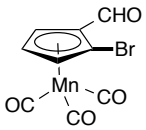
(*S*)-(–)-[η^5-1-Bis(3,5-di(*tert*-butyl-4-methoxyphenyl)phosphino-2-(3-diphenylphosphino-2-methylpropenyl)cylopentadienyl-*P*)] manganese(I) Dicarbonyl (2d). ^{1}H NMR ($CDCl_3$): δ 1.29 (s,



18H), 1.36 (s, 18H), 1.45 (s, 3H), 3.03 (t, J = 13.2 Hz, 1H), 3.60 (s, 3H), 3.65 (s, 4H), 4.10 (s, 1H), 4.31 (s, 1H), 4.82 (t, J = 2.4 Hz, 1H), 5.81 (s, 1H), 7.17–7.22 (m, 4H), 7.34-7.43 (m, 6H), 7.51-7.59 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 27.0 (d, J_{PC} = 3.8 Hz), 32.1 (d, J_{PC} = 21.5 Hz), 35.8 (d, J_{PC} = 13.0 Hz), 64.3 (s), 79.7 (s), 82.2 (s), 82.9 (s), 89.9 (d, J_{PC} = 12.3 Hz), 106.0 (d, J_{PC} = 22.9 Hz), 117.3 (d, J_{PC} = 12.2 Hz), 127.9 (d, J_{PC} = 9.2 Hz), 128.3 (d, J_{PC} = 9.1 Hz), 129.2 (s), 129.4 (d, J_{PC} = 5.4 Hz), 129.6 (s), 130.9 (s), 131.1 (d, J_{PC} = 9.2 Hz), 132.8 (d, J_{PC} = 10.0 Hz), 133.6 (d, J_{PC} = 22.3 Hz), 137.1 (d, J_{PC} = 6.9 Hz), 137.5 (s), 139.2 (s), 139.6 (s), 143.1 (t, J_{PC} = 8.4 Hz) 159.8 (s), 160.9 (s), 228.5 (d, J_{PC} = 19.9 Hz), 231.2 (d, J_{PC} = 22.9 Hz). ^{31}P NMR ($CDCl_3$): δ –22.1, 106.7. IR ($CHCl_3$): ν 758, 1010, 1224, 1878, 1940, 2961 cm^{-1}. Anal. Calcd for $C_{53}H_{65}MnO_4P_2$: C, 72.09; H, 7.42. Found: C, 72.09; H, 7.50. $[\alpha]_D^{23}$ –294.8 (c 0.4, $CHCl_3$).

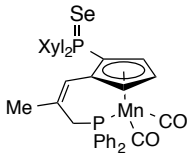


(*S*)-(+)-η^5-1-Bromo-2-[(2*R*,4*R*)-4-(methoxymethyl)-1,3-dioxanyl]cyclopentadienyl]manganese(I) tricarbonyl (4). To an ethereal solution (4 mL) of **3** (240 mg, 0.72 mmol), ^{t}BuLi (1.0 eq, 1.6 M solution in pentane) was added dropwised at –78 °C under argon atmosphere. The resulting solution was stirred for 10 min at –78 °C and then warmed up to room temperature. After 45 min, pale yellow precipitate formed while stirring at room temperature. The solution of 1, 2-dibromotetrachloroethane (350 mg, 1.1 mmol) in THF (2 mL) was added dropwise to the reaction mixture at –78 °C under nitrogen. After stirring for 10 min, cooling bath was removed and stirred at room temperature for 2 h. The resulting reaction mixture was quenched with NH_4Cl_{aq} and extracted with ethyl acetate. The organic layer was dried over anhydrous $MgSO_4$. After removing $MgSO_4$ by filtration, the solution was concentrated under reduced pressure. The crude product was purified by silica gel chromatography via eluting with hexane/EtOAc (5/1) to give the title product **4** as yellow oil (254 mg, 0.617 mmol, 86%). ^{1}H NMR ($CDCl_3$): δ 1.49 (d, *J* = 13.6 Hz, 1H), 1.53 (dq, *J* = 4.4, 12.2 Hz, 1H), 3.4–3.44(m, 4H), 3.49–3.57 (m, 1H), 3.93 (t, *J* = 11.2 Hz, 1H), 4.02 (t, *J* = 5.4, 1H), 4.25 (dd, *J* = 4.8, 11.2 Hz, 1H), 4.62 (s, 1H), 4.84 (s, 1H), 5.00 (s, 1H), 5.28 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 27.6, 59.5, 66.9, 75.3, 76.6, 80.1, 81.0, 83.3, 86.0, 96.3, 100.3, 223.9. IR ($CHCl_3$): ν 1106, 1934, 2025, 2866 cm^{-1}. $[\alpha]_D^{26}$ +7.67 (*c* 0.5, $CHCl_3$). HRMS Calcd for $C_{14}H_{14}BrMnO_6$: 411.9354. Found: 411.9349.



(*S*)-(+)-bromocymantrenecarboxaldehyde (5). The complex **4** (254 mg, 0.617 mmol) was dissolved in THF (10 mL) and HCl_{aq} (10% in water, 10 mL) was added. The mixture was stirred for 2 h at 50 °C and then K_2CO_3 was added to neutralize the acid. The resulting mixture was extracted with ether and the organic layer was washed with brine, dried over anhydrous $MgSO_4$. The mixture was filtrated and concentrated under reduced pressure. The residue was purified by a silica gel chromatography (hexane/EtOAc = 5/1) and desired product (*S*)-**5** was obtained as brown crystals (83%, >99% ee). ^{1}H NMR ($CDCl_3$): δ 4.96 (s, 1H), 5.09 (s, 1H), 5.41 (s, 1H), 9.78 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 83.3, 83.4, 85.5, 88.3, 91.6, 186.6, 221.6. IR ($CHCl_3$): ν 628, 1686, 1847, 1945, 2032 cm^{-1}. HRMS Calcd for $C_9H_4BrMnO_4$: 309.8673. Found: 309.8674. $[\alpha]_D^{23}$ +316.0 (*c* 0.2, $CHCl_3$). HPLC condition: Chiralpak AS, Hexane/^{i}PrOH = 9/1, 1.0 mL/min, 30 °C, 7.58 min (*S* enationmer). 16.83 min (*R* enantiomer), 99.8% ee.

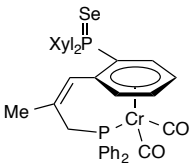
***rac*-[(η^5-1-Bis(3,5-dimethylphenyl)phosphinoseleno-2-(3-diphenylphosphino-2-methylpropenyl)cyclopentadienyl-*P*)]manganese(I) Dicarbonyl (2b-Se).**



To the $CHCl_3$ (4 mL) solution of **2b** (65 mg, 0.1 mmol), the selenium powder (27 mg, 3.3 mmol) was added under nitrogen atmosphere and the resulting suspension was stirred for 2 h at room temperature. The reaction mixture was filtered through Celite, and the filtrate was concentrated under reduced pressure. The residue was purified by silica gel chromatography (hexane/EtOAc = 10/1) to give the tile compound **2b-Se** as yellow crystals (52 mg, 71%). ^{1}H NMR ($CDCl_3$): δ 1.48 (s, 3H), 2.28 (s, 6H), 2.34 (s, 6H), 2.84 (t, *J* = 15.2 Hz, 1H), 3.62-3.67 (m, 1H), 4.0 (s, 1H), 4.34 (s, 1H), 4.96 (s, 1H), 5.64 (s, 1H), 7.05 (s, 1H), 7.11 (s, 1H), 7.36-7.44 (m, 12H), 7.58-7.60 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 21.5 (d, J_{PC} = 7.6 Hz), 27.3 (s), 34.2 (d, J_{PC} = 20.6 Hz), 80.7 (d, J_{PC} = 8.4 Hz), 84.1 (d, J_{PC} = 11.4 Hz), 84.5(d, J_{PC} = 9.2 Hz), 90.0 (s), 90.8 (s), 104.7 (d, J_{PC} = 9.2 Hz), 115.1 (d, J_{PC} = 10.7 Hz), 128.1 (d, J_{PC} = 8.4 Hz), 128.3 (d, J_{PC} = 8.4 Hz), 129.2 (s), 129.9 (s), 130.3 (d, J_{PC} = 10.0 Hz), 130.7 (s), 132.0 (s), 132.4 (s), 132.9 (d, J_{PC} = 9.1 Hz), 133.1 (s), 133.3 (s), 136.8 (s), 137.2 (s), 137.7 (s), 137.8 (d, J_{PC} = 5.4 Hz), 138.0 (s), 138.6 (s), 138.8 (s), 139.3 (s), 228.8 (d, J_{PC} = 18.4 Hz),

231.2 (d, J_{PC} = 24.4 Hz). ^{31}P NMR ($CDCl_3$): δ 27.9 (J_{PSe} = 739.5 Hz), 93.5. IR ($CHCl_3$): ν 1434, 1878, 1940 cm^{-1}. FAB-HRMS Calcd for $C_{39}H_{37}MnO_2P_2Se$: 734.0814. Found: 734.0808.

***rac*-[(η^6-1-Bis(3,5-dimethylphenyl)phosphinoseleno-2-(3-diphenylphosphino-2-methylpropenyl)benzene-*P*)]chromium(0) Dicarbonyl (1b-Se).**



The corresponding phosphinoseleno chromium complex **1b** was also prepared the by the same procedure in complex **2b-Se**. Orange crystals (73%).

^{1}H NMR ($CDCl_3$): δ 1.86 (s, 3H), 2.29 (s, 6H), 2.33 (s, 6H), 2.94 (t, J = 15.8 Hz, 1H), 3.52-3.58 (m, 1H), 3.90 (s, 1H), 4.78 (s, 1H), 4.93 (s, 1H), 5.18 (s, 1H), 5.68 (s, 1H), 7.09 (d, J = 15.2 Hz, 2H), 7.26-7.34 (m, 8H), 7.51-7.7.57 (m, 6H). ^{13}C NMR ($CDCl_3$): δ 21.5 (s), 25.7 (s), 27.5 (s), 34.5 (d, J_{PC} = 16.0 Hz), 68.1 (s), 79.0 (s), 89.3, 90.6 (s), 90.9 (d, J_{PC} = 12.6 Hz), 94.3 (s), 95.1 (s), 105.1 (d, J_{PC} = 6.9 Hz), 120.4 (d, J_{PC} = 8.0 Hz), 128.1 (s), 128.8 (s), 129.4 (s), 130.8 (s), 131.7 (s), 131.9 (s), 132.5 (d, J_{PC} = 9.1 Hz), 133.4 (s), 137.8 (s), 137.9 (s), 138.1 (s), 138.2 (s), 139.5 (s), 139.8 (s), 139.9 (s), 140.1 (s), 236.7 (d, J_{PC} = 20.2 Hz), 239.6 (d, J_{PC} = 21.8 Hz). ^{31}P NMR ($CDCl_3$): δ 35.57 (J_{PSe} = 739.0 Hz), 81.87. IR ($CHCl_3$): ν 1433, 1852, 1904 cm^{-1}. FAB-HRMS Calcd for $C_{45}H_{38}CrO_2P_2Se$: 744.0917 Found: 744.0923.

Rhodium-Catalyzed Asymmetric 1,4-Addition Reaction of Arylboronic Acid to Enones. A solution of $[RhCl(\eta^2\text{-}C_2H_4)_2]_2$ (2.4 mg, 6.3 mmol) and (*R*)- or (*S*)-**2** (13 mmol) in dioxane (1 mL) was stirred at room temperature for 1 h under nitrogen. To this was added aqueous KOH (1.25 M, 0.1 mL, 0.13 mmol) and the solution was stirred for 5 min. Arylboronic acid (0.75 mmol) and enone (0.25 mmol) was added to the solution. After stirring for 7 h at 50 °C, the reaction mixture was concentrated under reduced pressure. The residue was purified by silica gel chromatography via eluting with hexane and EtOAc to give an optically active addition product.
Rhodium-catalyzed asymmetric 1,4-addition reactions of phenylboronic acid to 3-penten-2-one[7], 3-Hepten-2-one[8], 3-Nonen-2-one[7], 3-Decen-2-one[9] and Cyclohexanone[10, 11, 12]: These reactions were performed as above, and the enantiomeric purity and the absolute configuration of the products were determined as reported.

Rhodium-Catalyzed Asymmetric Addition of Phenylboroxine to Arylaldehyde *N*-sulfonyl imines. A solution of $[RhCl(\eta^2\text{-}C_2H_4)_2]_2$ (2.0 mg, 5 μmol) and (*R*)- or (*S*)-**2** (11 μmol) in dioxane (1.0 mL) was stirred at room temperature for 1 h under nitrogen. To this were added *N*-tosylimine (0.100 mmol), phenylboroxine (32 mg, 0.100 mmol), and aqueous KOH (1.0 M, 20 mL, 20 μmol) successively. After stirring for 7 h at 40 °C, then the reaction mixture was concentrated under reduced pressure. The residue was purified by silica gel chromatography (hexane/EtOAc) to give an optically active product as colorless crystals. The enantiomeric purity and the absolute configuration of the product were determined as reported.[10, 13, 14]

Rhodium-Catalyzed Asymmetric Arylation of 1-Naphthylaldehyde with Phenylboronic Acid

To a Schlenk tube charge with $[RhCl(\eta^2\text{-}C_2H_4)_2]_2$ (1.46 mg, 3.8 μmol) and (*S*)-**2d** (7.4 mg, 8.3 μmol) in CH_2Cl_2 (0.5 mL) was stirred at room temperature for 1 h under nitrogen. After removing solvent via vacuum pump, to this were added phenylbronic acid (61mg, 0.500 mmol), powdered KOH (1.46 mg, 0.38 mmol, assay; 85%, pellets) and ^{i}PrOH(1 mL), the reaction mixture was stirred at room temperature for additional 2 min, subsequently1-naphthaldehyde (39 mg, 0.25 mmol) was added into the Schlenk tube. After stirring for 9 h at 40 °C, the mixture was extracted with EtOAc,

then the reaction mixture was concentrated under reduced pressure. The residue was purified by silica gel chromatography (hexane/EtOAc = 9/1) to give an optically active product as pale yellow oil. The enantiomeric purity and the absolute configuration of the product were determined as reported.[15]

X-ray Crystallography of (*S*, S)-12 and (*R*, R**)-SI1.**

The single crystals of **(*S*, S**)-12** and **(*R*, R**)-SI1** were recrystallized from dichloromethane/hexane in vapor diffusion method. A crystal was mounted on a grass fiber with Paratone-N hydrocarbon oil and transferred to a Rigaku Saturn CCD with VariMax. The frame data were processed using CrystalClear. The structures were solved by a direct method (SHELXS 97) and refinement on F^2 by full-matrix least-squares method by using SHELXL.

Figure S1. Ball & stick drawings of **(*S*, S**)-12**. Two xylyl groups on P(3) atom were disordered over two positions.

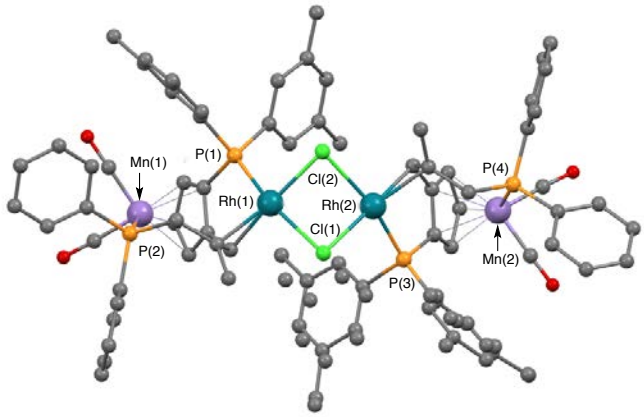
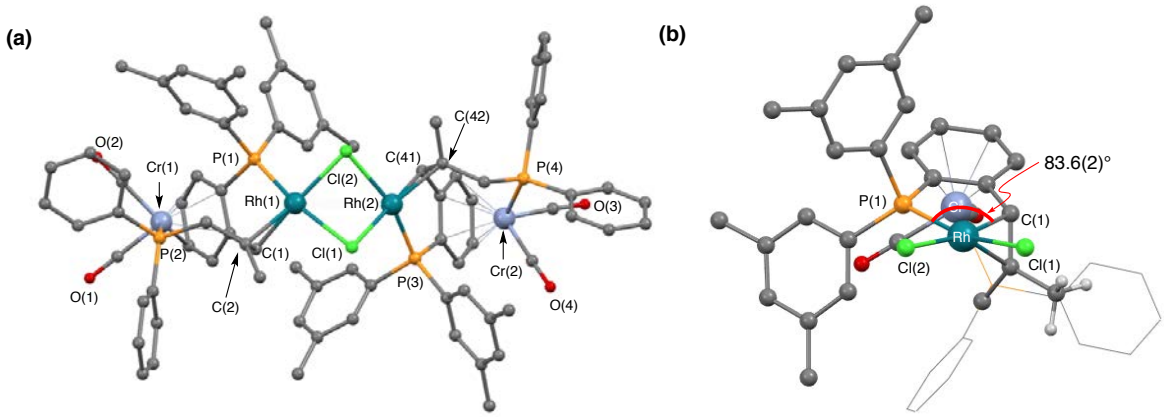
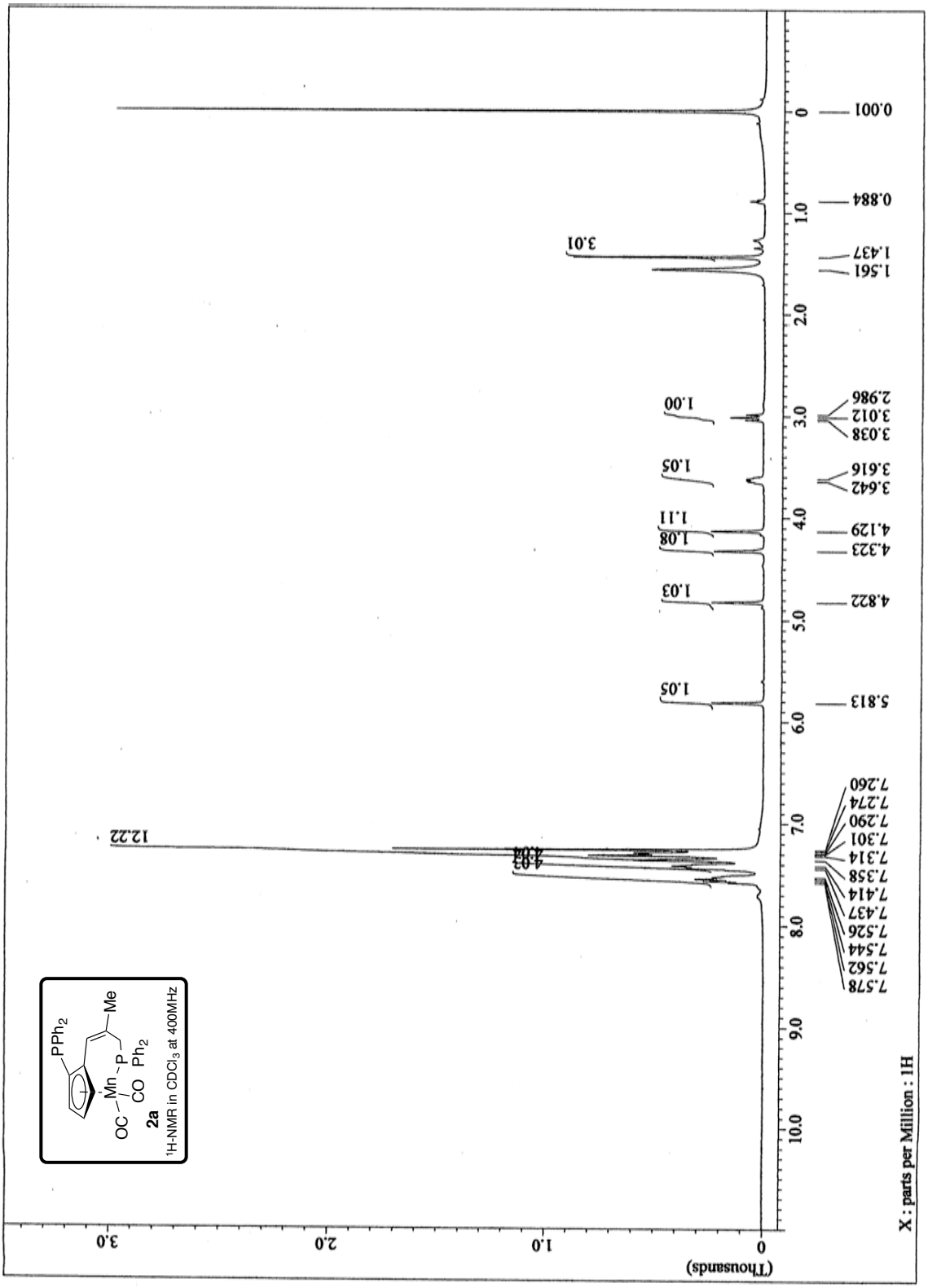
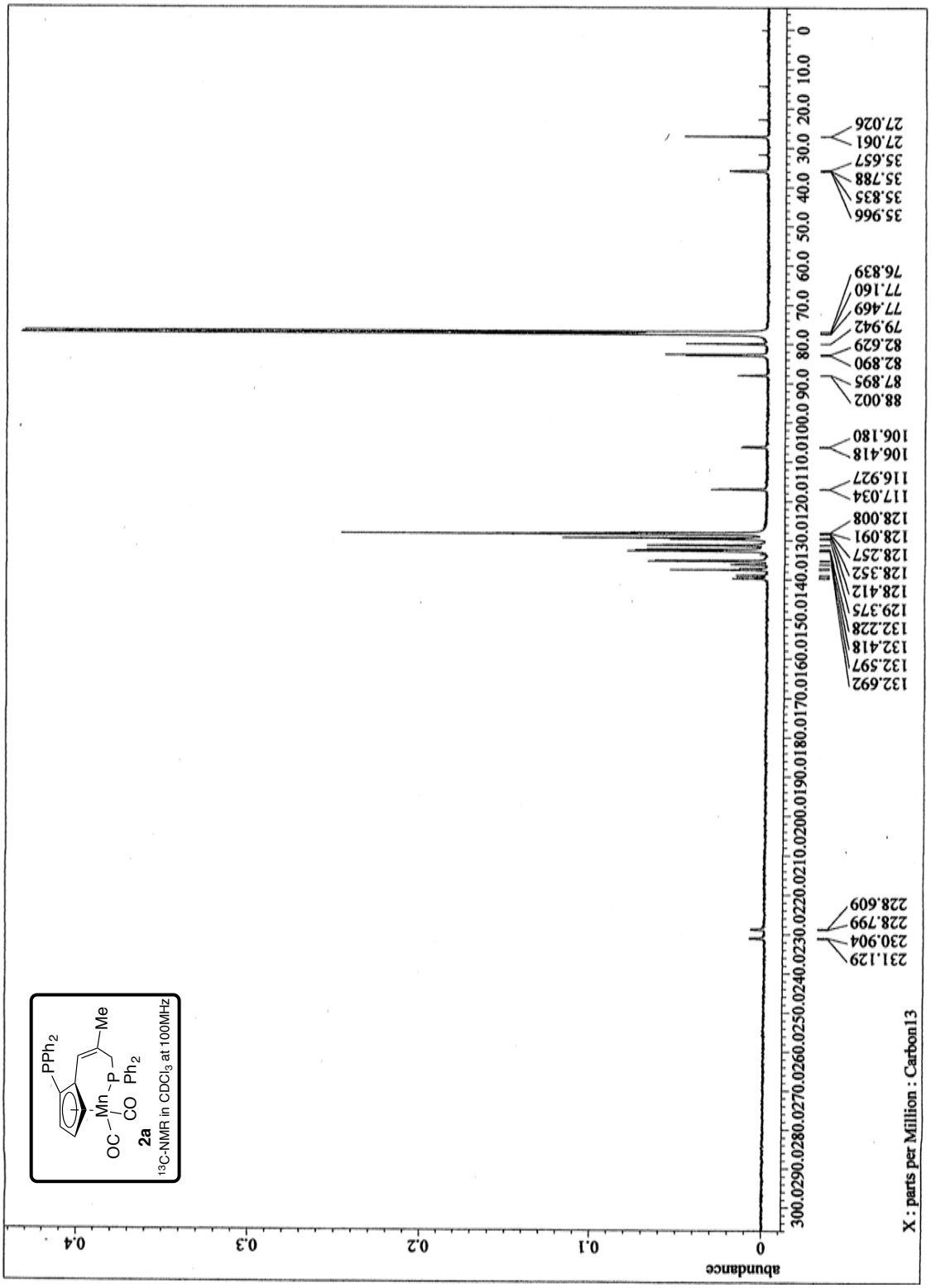
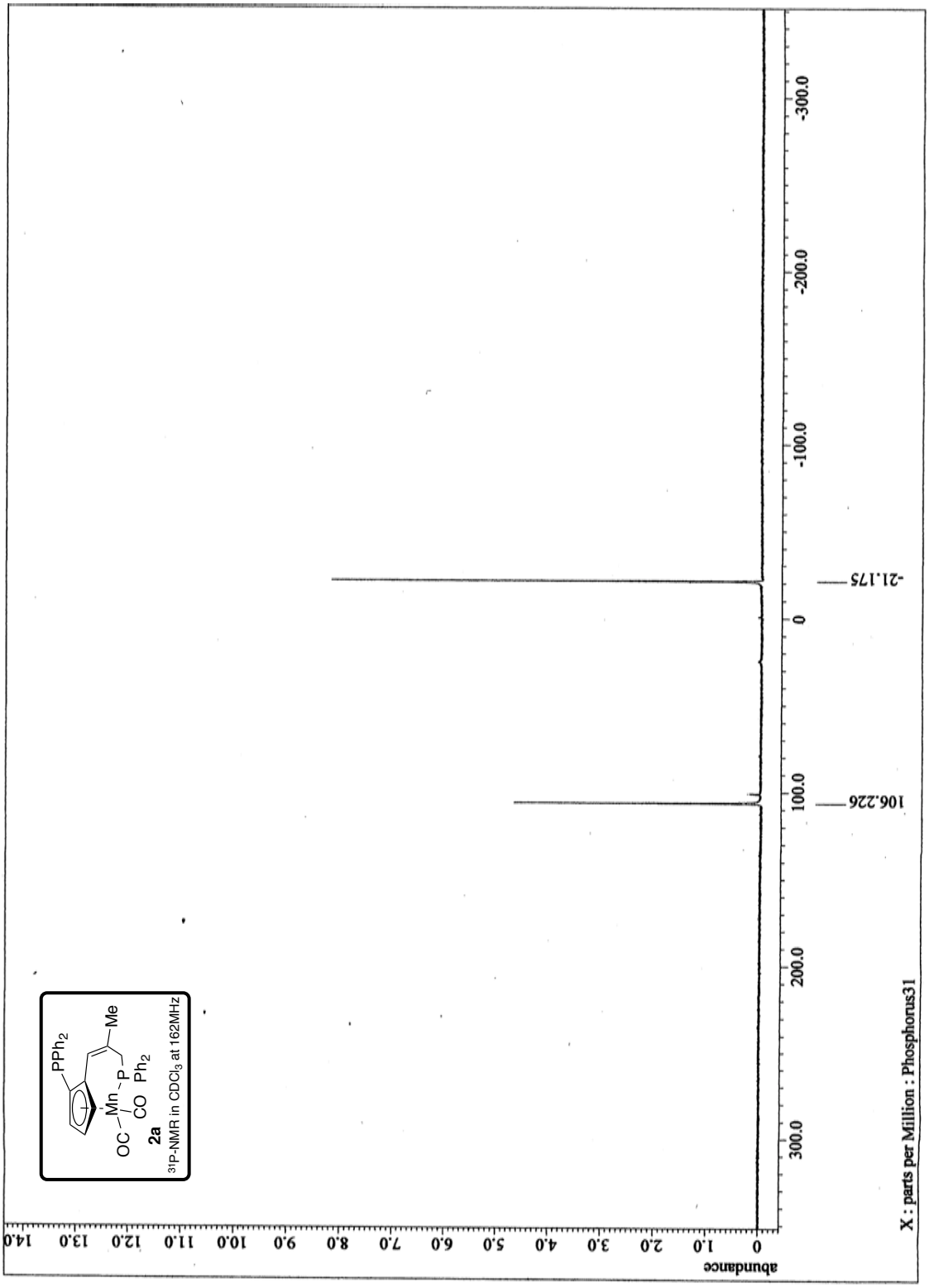


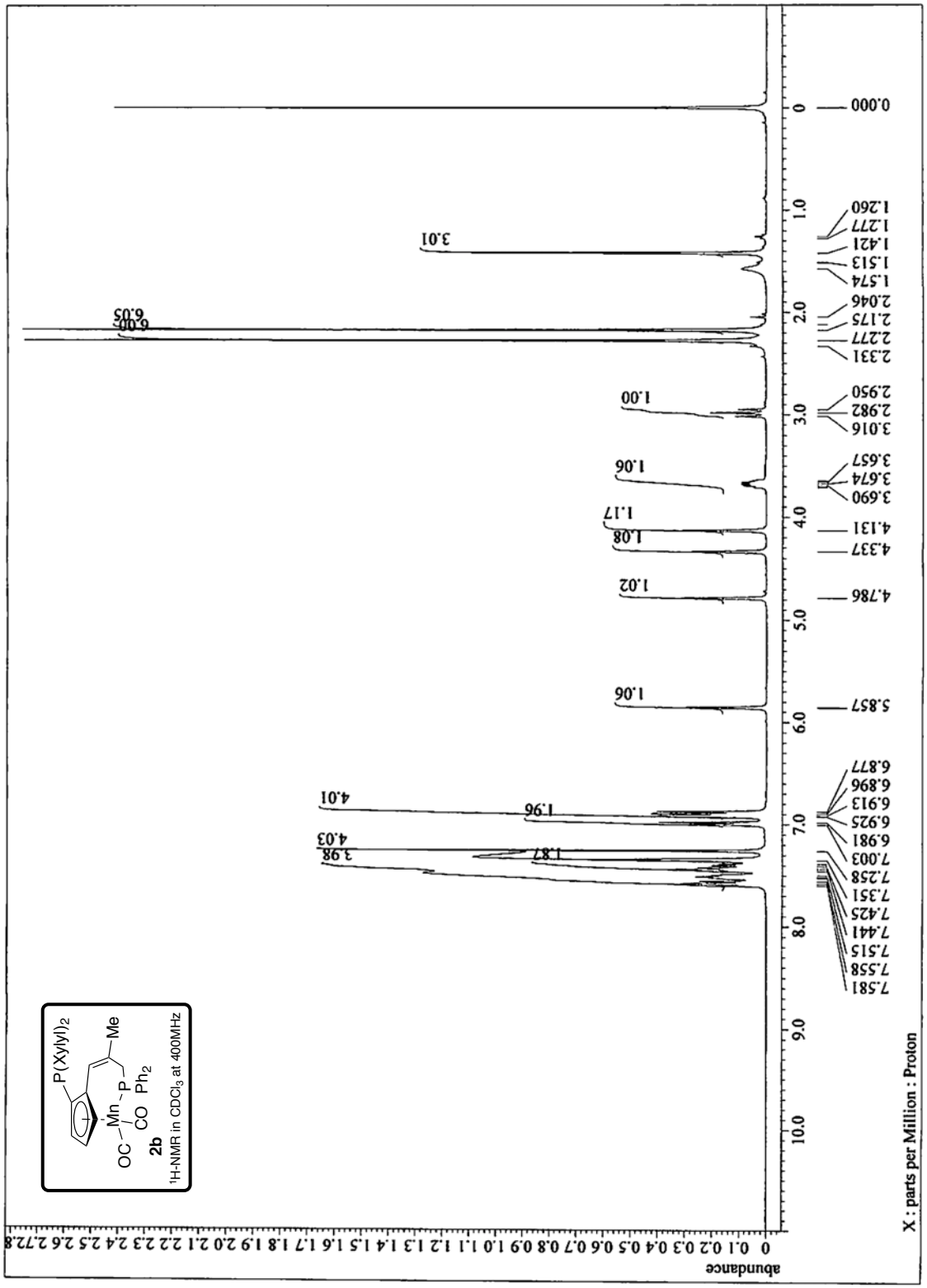
Figure S2. Ball & stick drawings of (a): [RhCl/*rac*-**1b**]$_2$ ((***R*, R****)-SI1** and (b): monomeric substructure of ((***R*, R****)-SI1** with selected atom numbering. All hydrogen atoms and cocrystallized solvent molecules are omitted for clarity

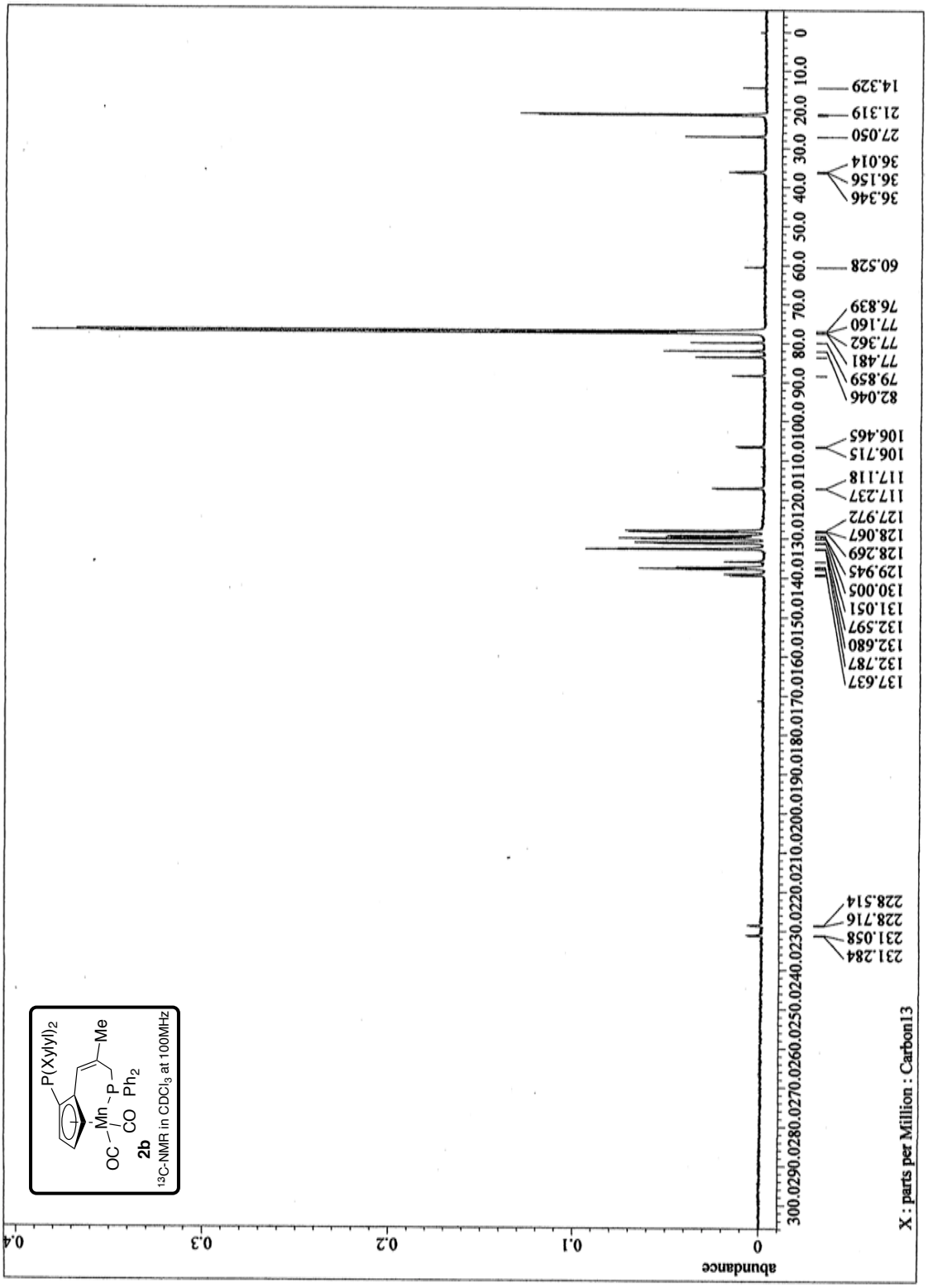


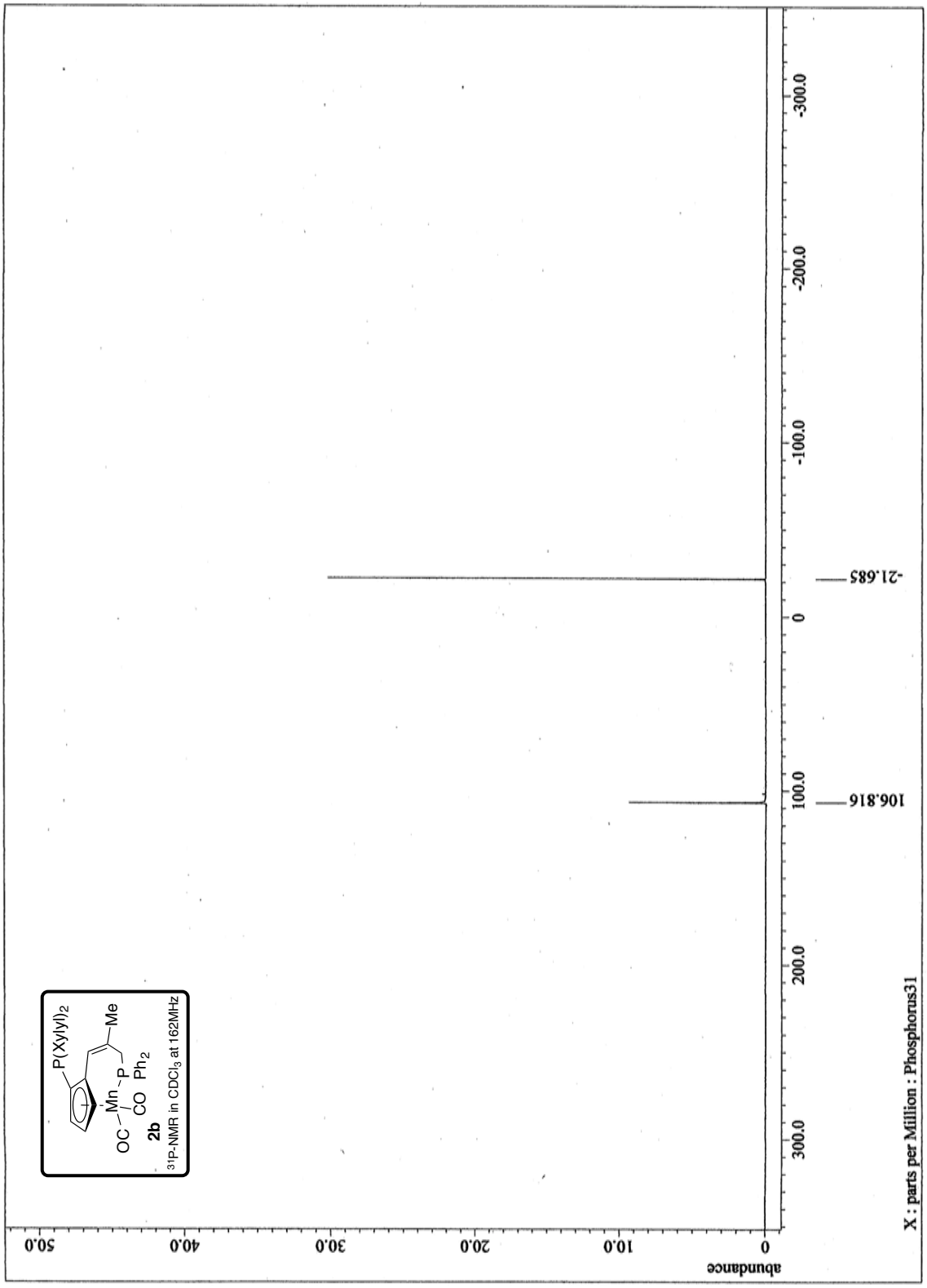

PPh2
Me
Mn
P
OC
CO
Ph2
2a
1H-NMR in CDCl3 at 400MHz
(Thousands)
X : parts per Million : 1H

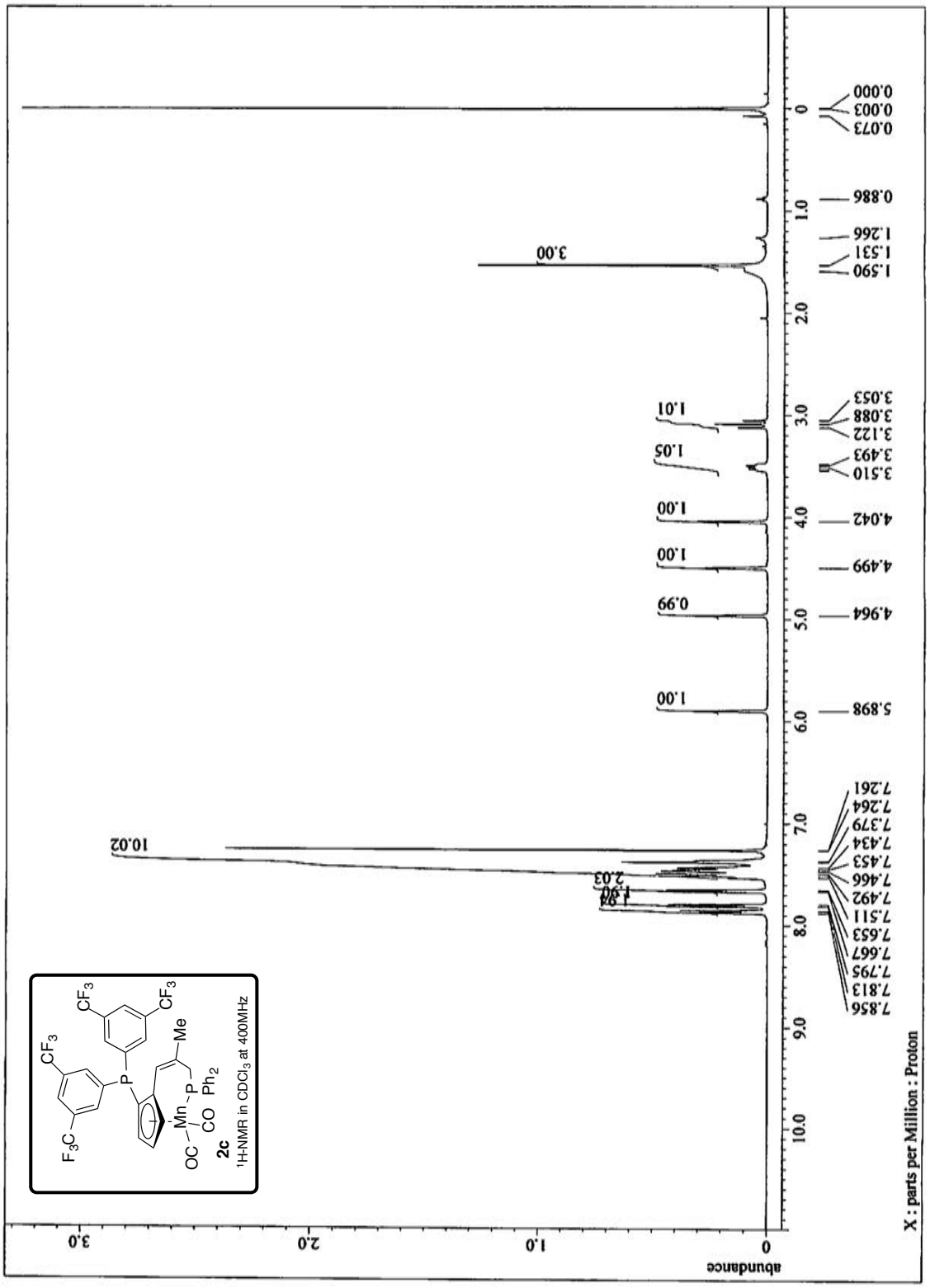

PPh2
Me
Mn
P
OC
CO
Ph2
2a
13C-NMR in CDCl3 at 100MHz
abundance
0
0.1
0.2
0.3
0.4
300.0 290.0 280.0 270.0 260.0 250.0 240.0 230.0 220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
231.129
230.904
228.799
228.609
132.692
132.597
132.418
132.228
129.375
128.412
128.352
128.257
128.091
128.008
117.034
116.927
106.418
106.180
88.002
87.895
82.890
82.629
79.942
77.469
77.160
76.839
35.966
35.835
35.788
35.657
27.061
27.026
X : parts per Million : Carbon13

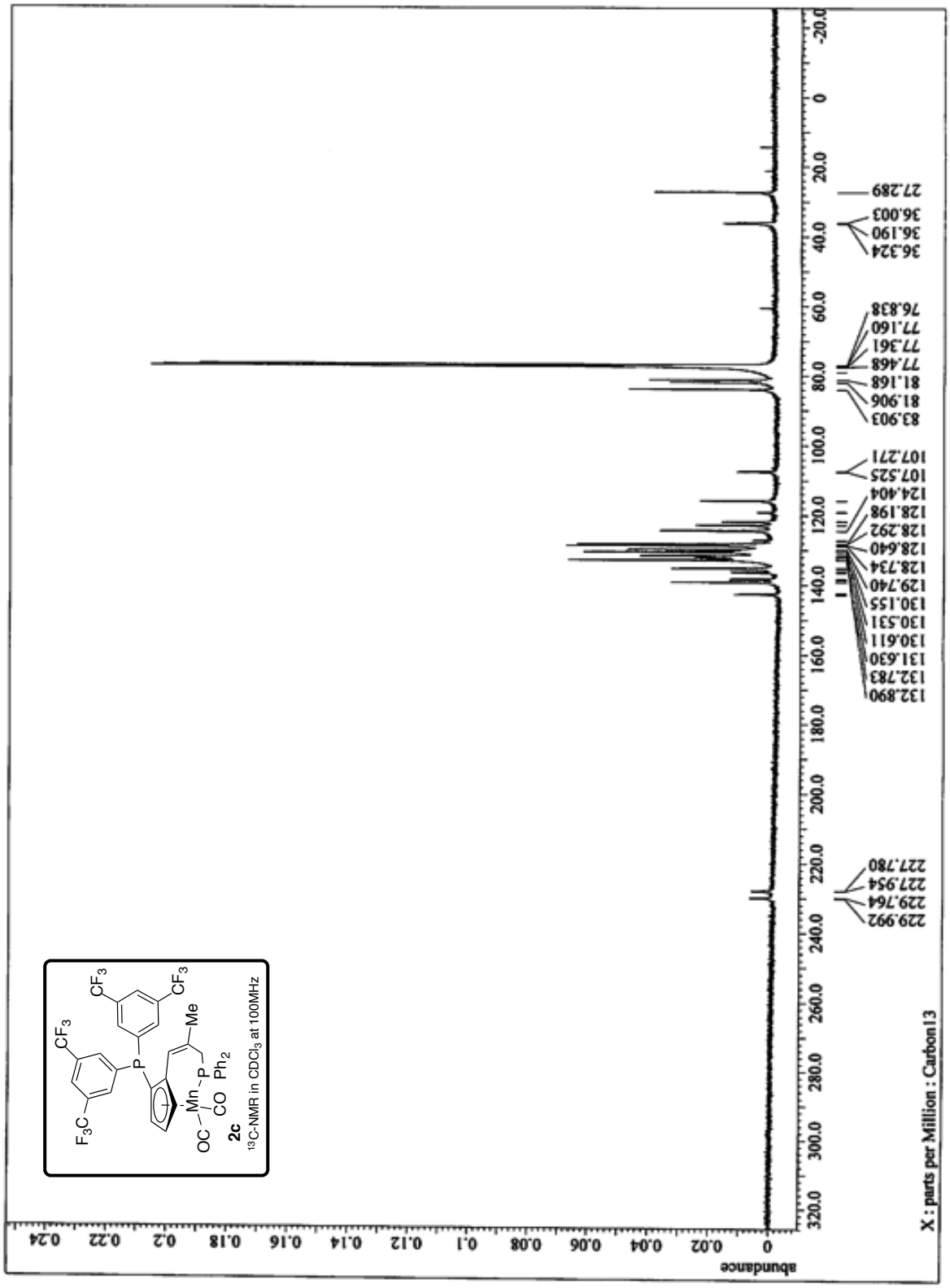

PPh2
Me
OC
Mn
P
CO
Ph2
2a
31P-NMR in CDCl3 at 162MHz
abundance
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
300.0
200.0
100.0
0
-100.0
-200.0
-300.0
106.226
-21.175
X : parts per Million : Phosphorus31

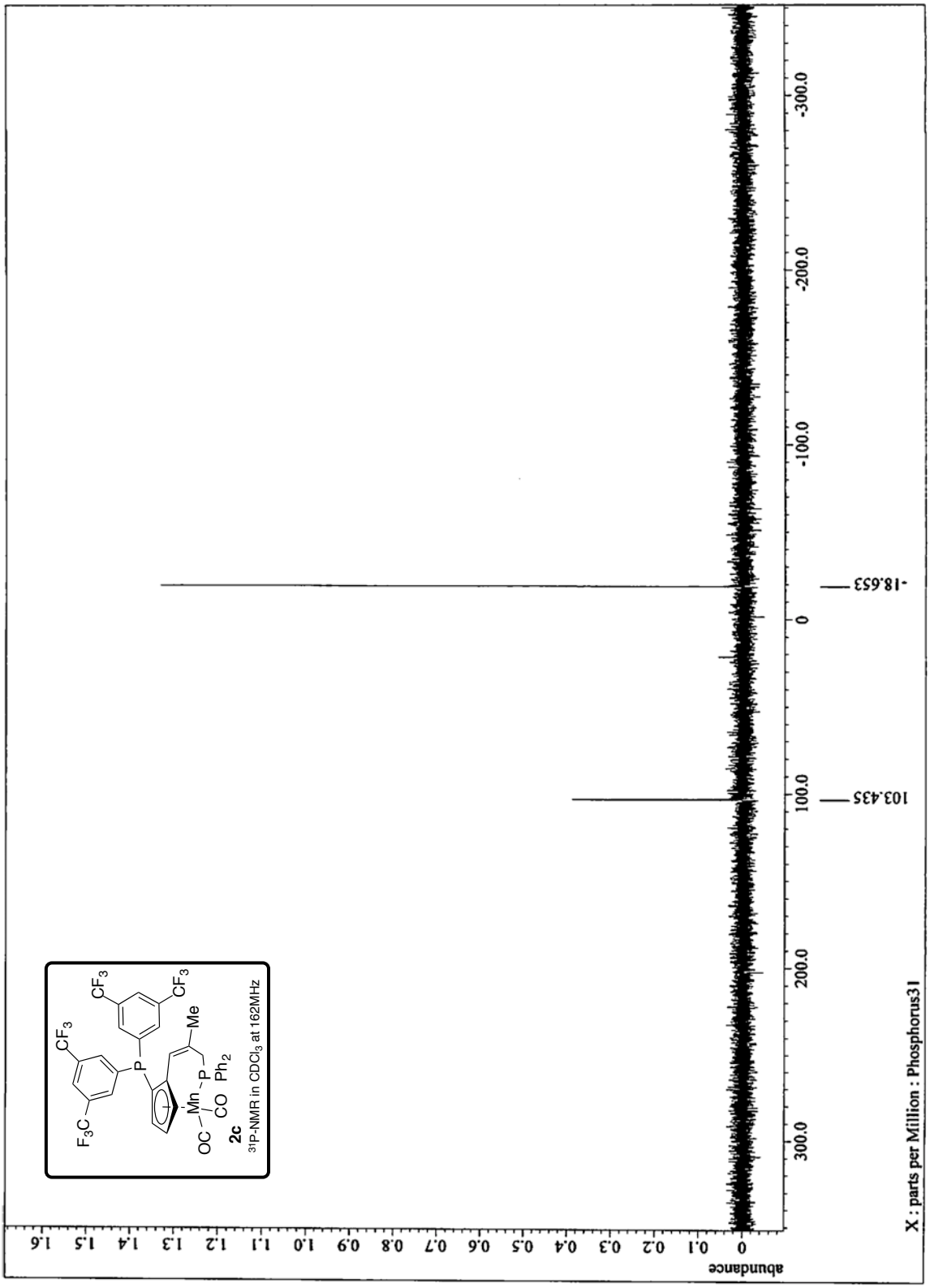

P(Xylyl)2
Me
OC
Mn
P
CO
Ph2
2b
1H-NMR in CDCl3 at 400MHz
X : parts per Million : Proton
abundance

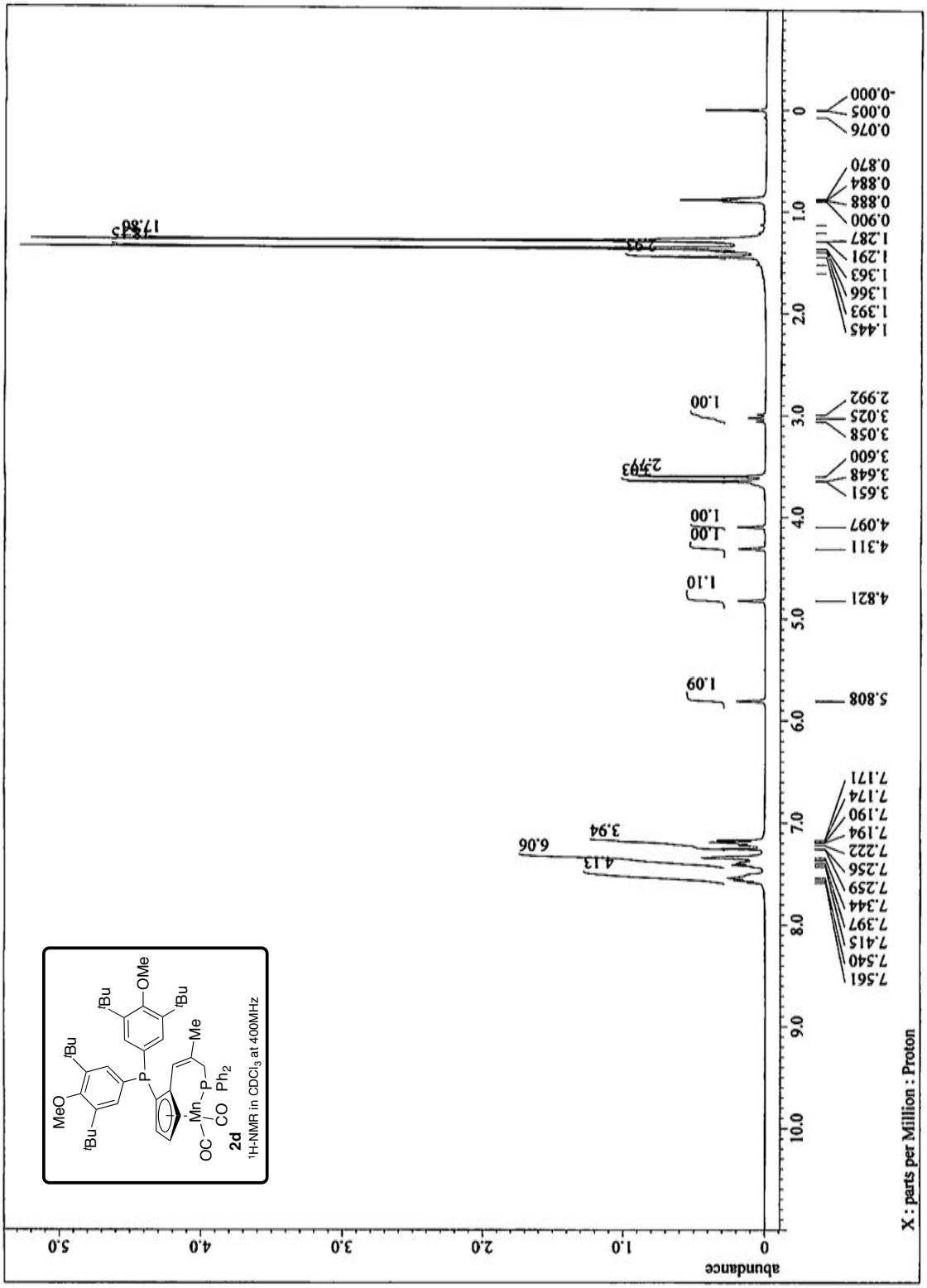

P(Xylyl)2
Me
OC
Mn
P
CO
Ph2
2b
13C-NMR in CDCl3 at 100MHz
abundance
0
0.1
0.2
0.3
0.4
X : parts per Million : Carbon13
231.284
231.058
228.716
228.514
137.637
132.787
132.680
132.597
131.051
130.005
129.945
128.269
128.067
127.972
117.237
117.118
106.715
106.465
82.046
79.859
77.481
77.362
77.160
76.839
60.528
36.346
36.156
36.014
27.050
21.319
14.329

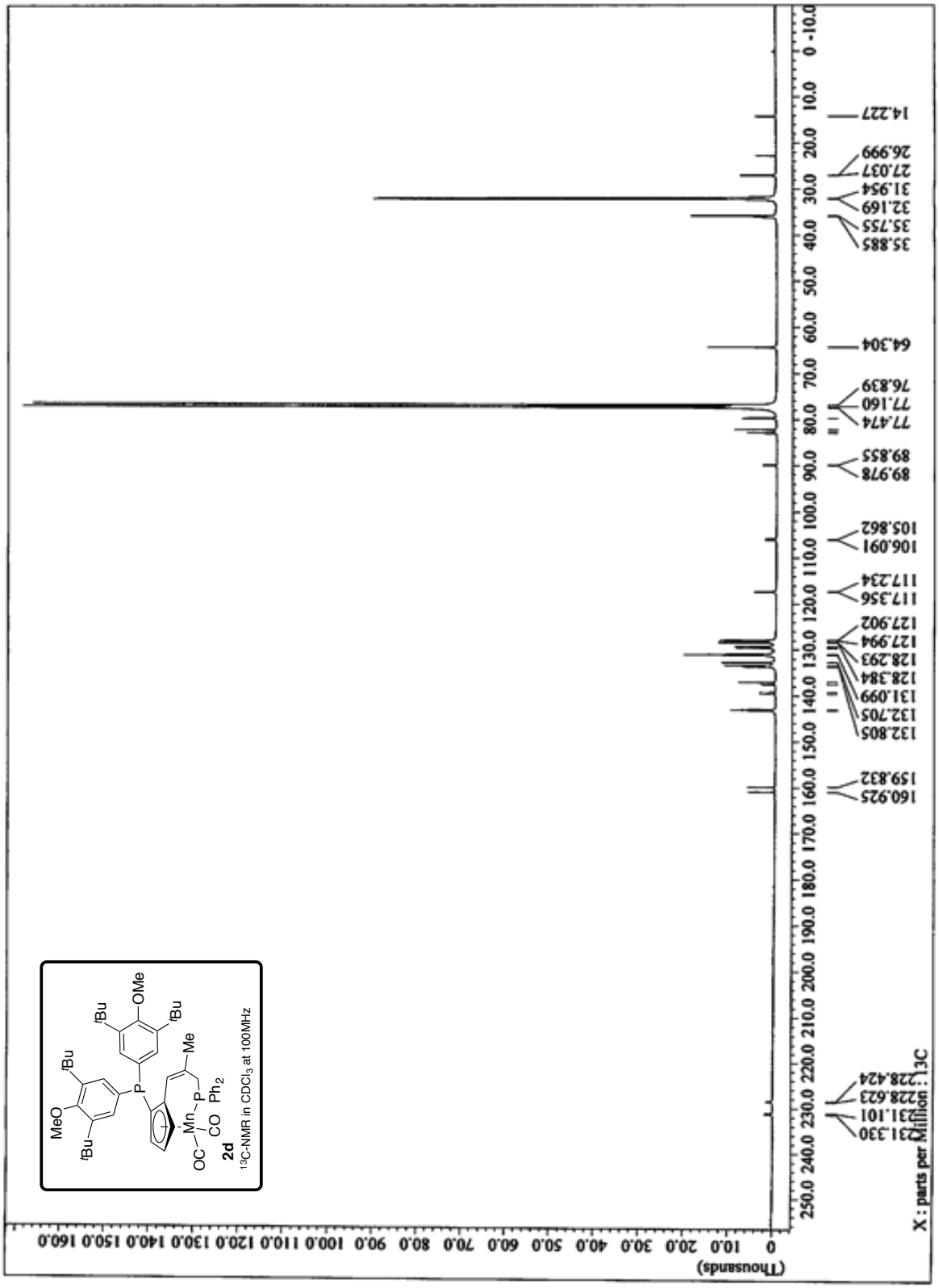

P(Xylyl)2
Me
Mn
P
OC
CO
Ph2
2b
31P-NMR in CDCl3 at 162MHz
abundance
50.0
40.0
30.0
20.0
10.0
0
300.0
200.0
100.0
0
-100.0
-200.0
-300.0
106.816
-21.685
X : parts per Million : Phosphorus31

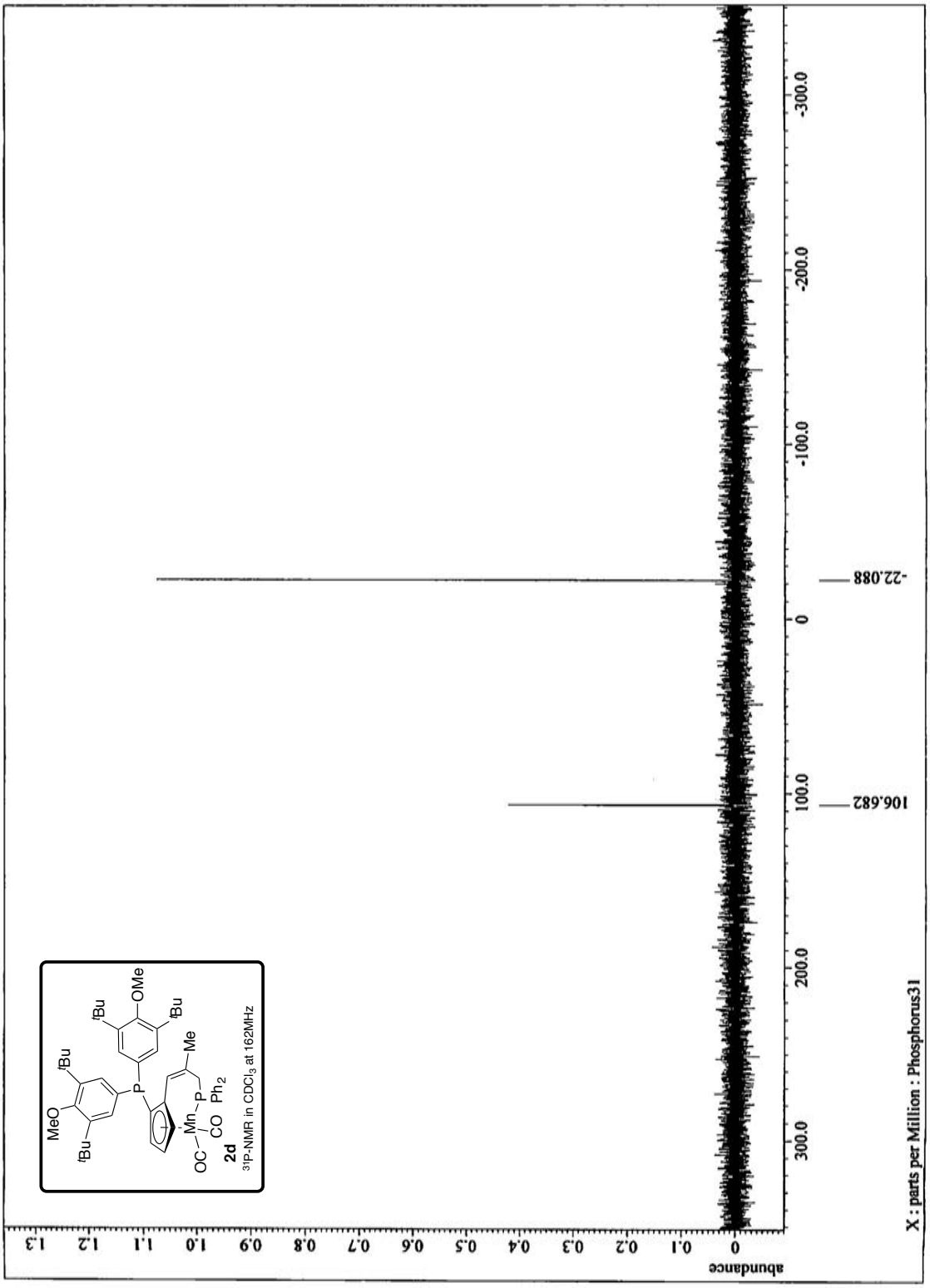

X : parts per Million : Proton
abundance
10.02
3.00
2.03
1.94
1.90
1.05
1.01
1.00
0.99
0.886
0.073
0.003
0.000
2c
^{1}H-NMR in $CDCl_3$ at 400MHz

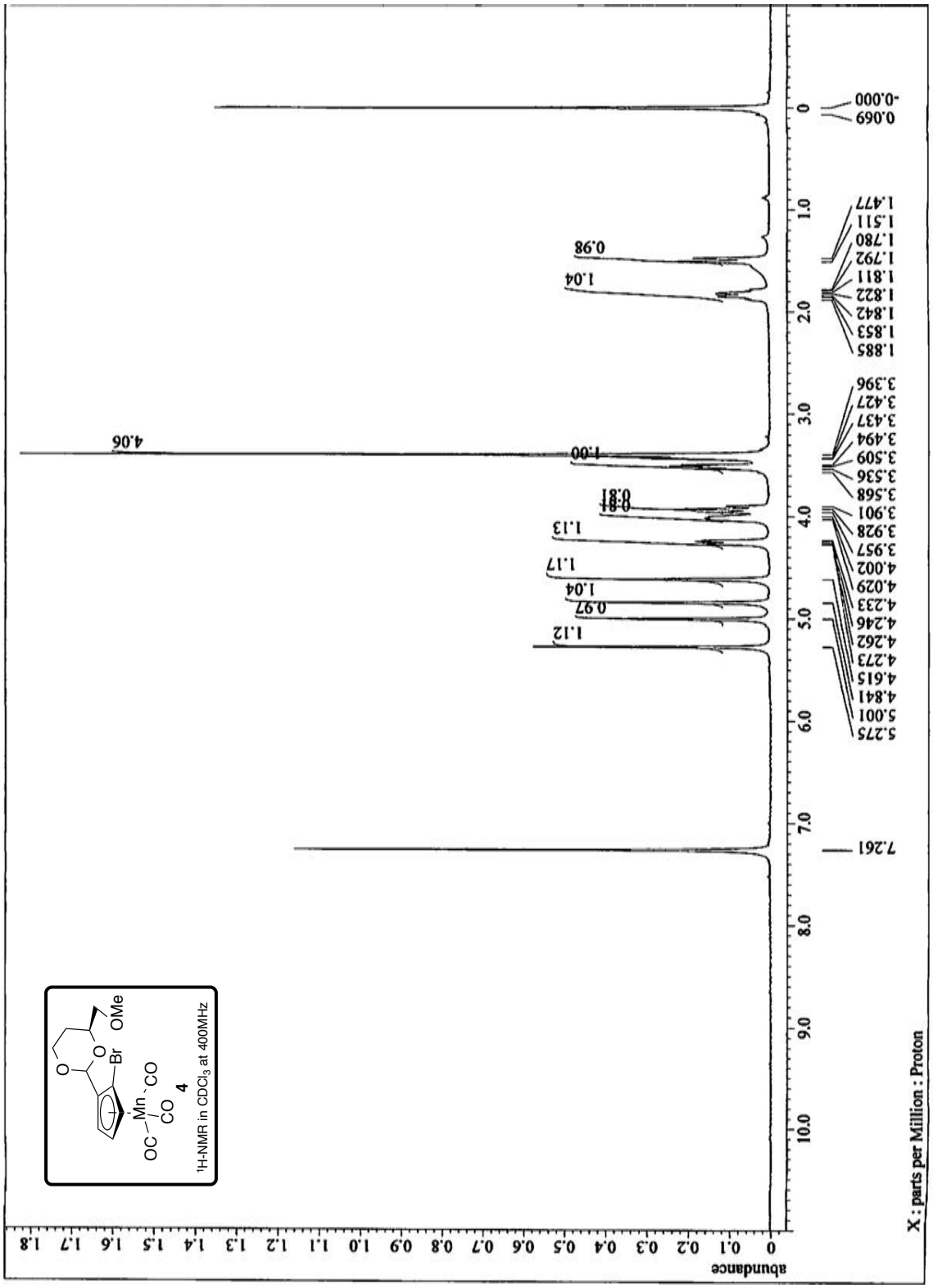

F3C
CF3
CF3
P
Mn
P
Me
OC
CO
Ph2
2c
13C-NMR in CDCl3 at 100MHz
abundance
X : parts per Million : Carbon13
229.992
229.764
227.954
227.780
132.890
132.783
131.630
130.611
130.531
130.155
129.740
128.734
128.640
128.292
128.198
124.404
107.525
107.271
83.903
81.906
81.168
77.468
77.361
77.160
76.838
36.324
36.190
36.003
27.289

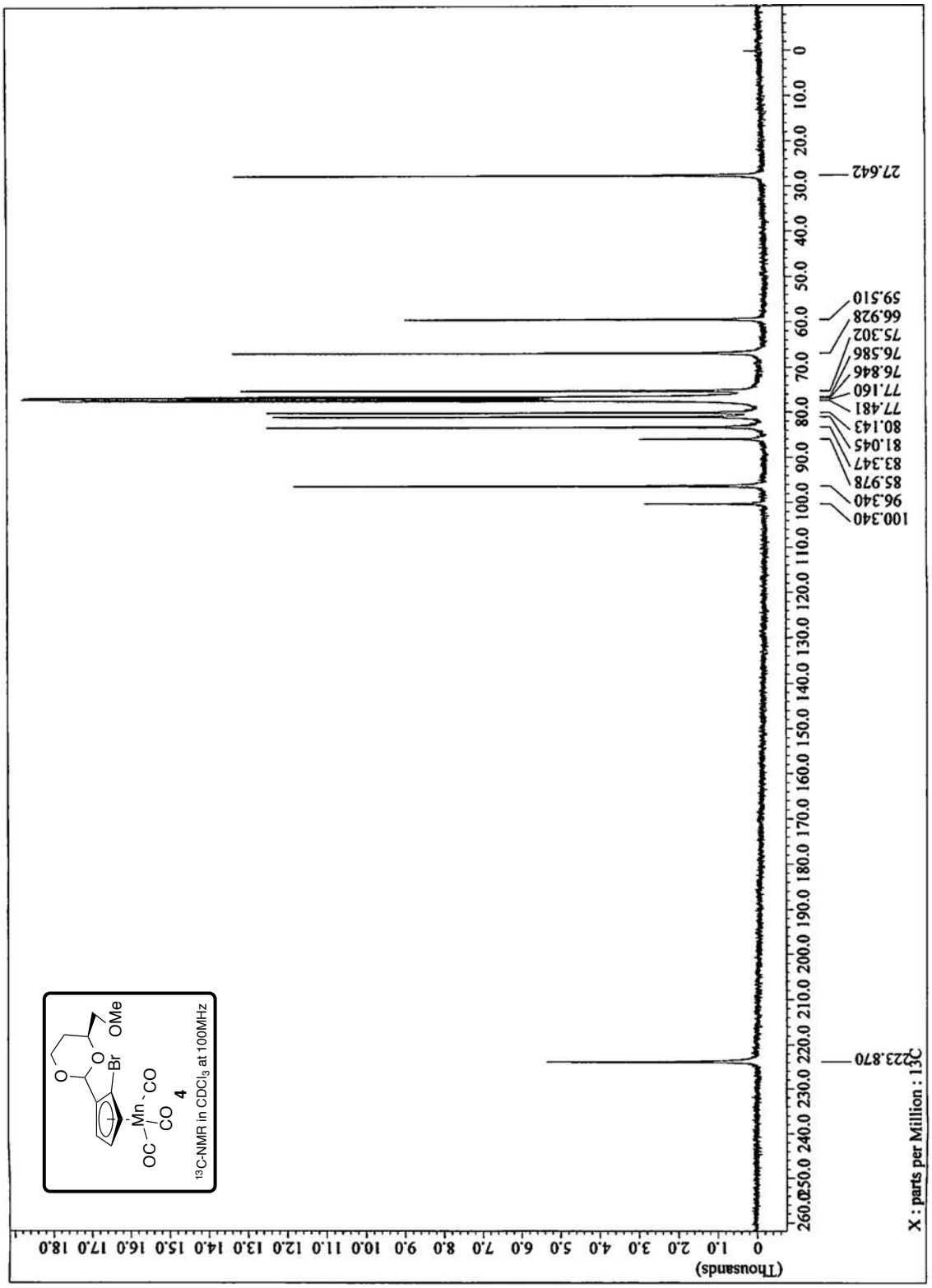

2c
31P-NMR in CDCl3 at 162MHz
103.435
-18.653
X : parts per Million : Phosphorus31
abundance

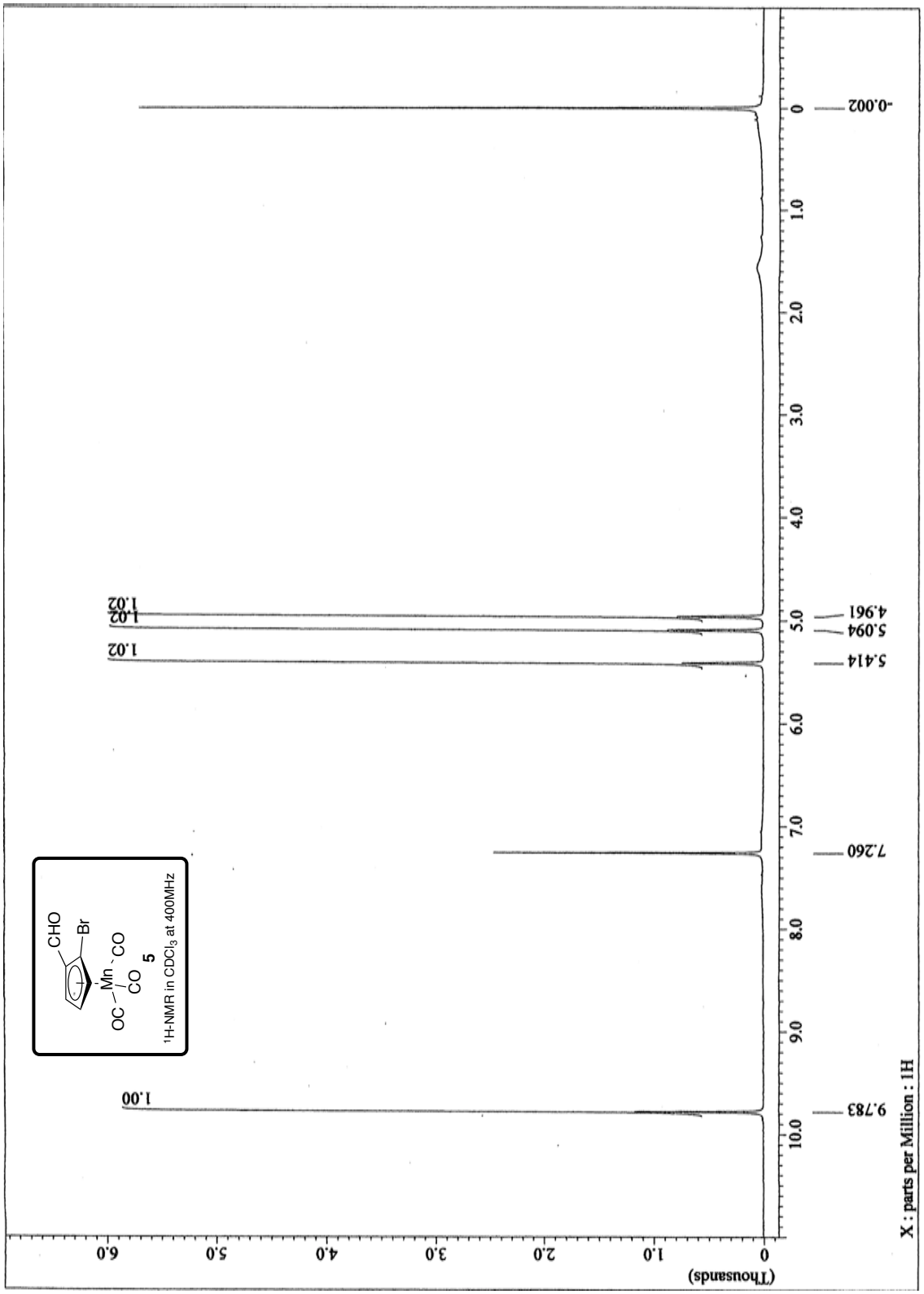

2d
^{1}H-NMR in $CDCl_3$ at 400MHz
X : parts per Million : Proton
abundance

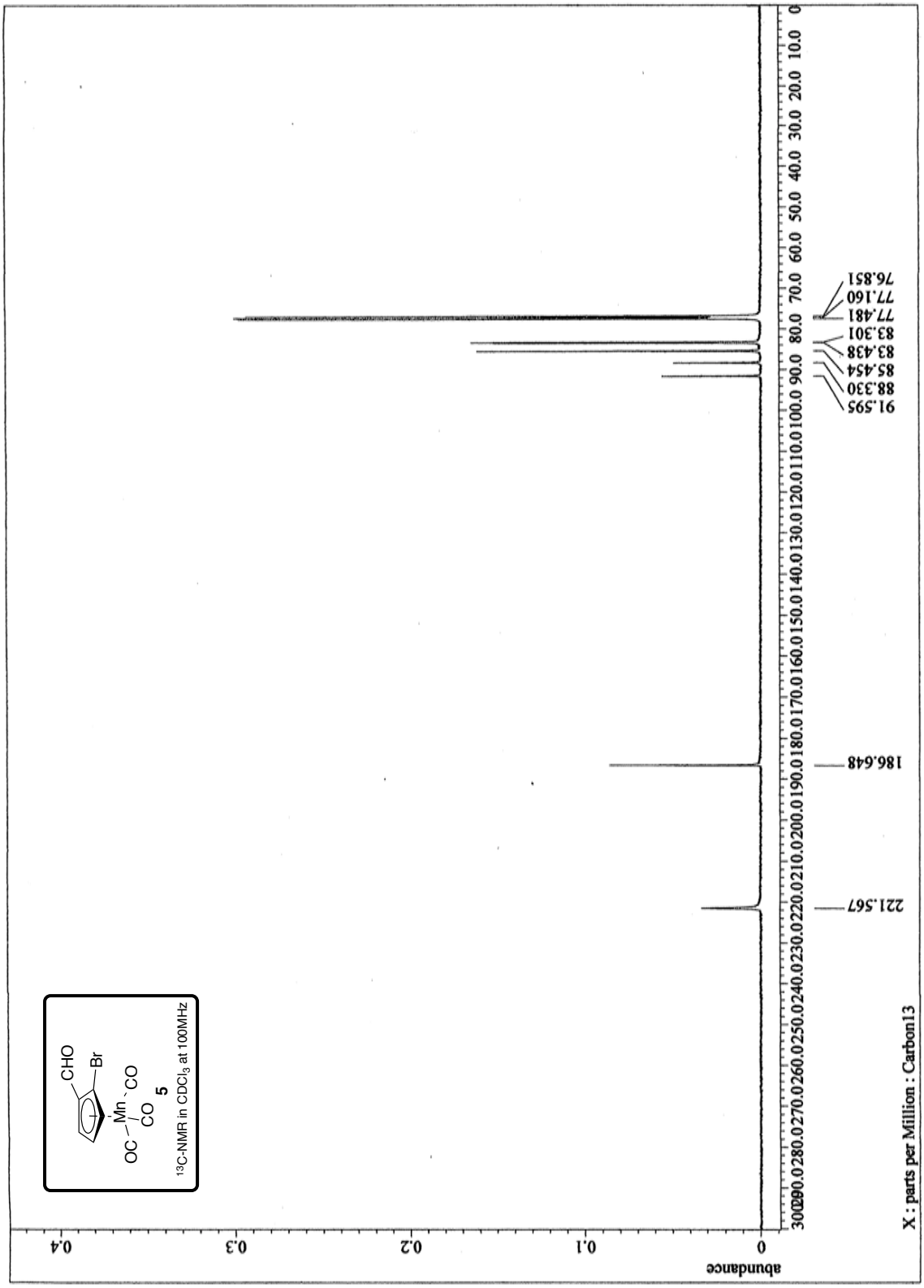

2d
13C-NMR in CDCl3 at 100MHz
X : parts per Million : 13C
(Thousands)

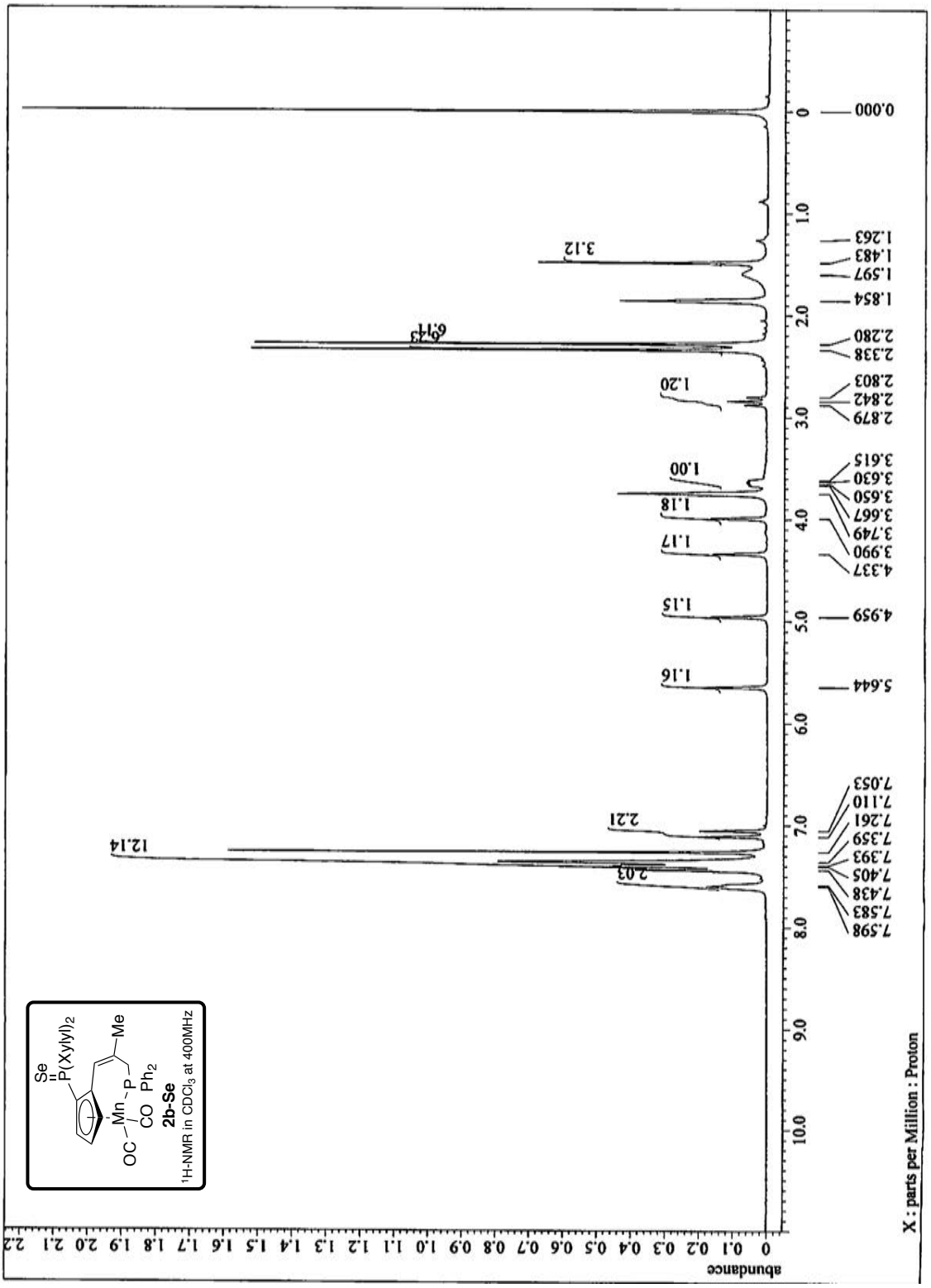

MeO
tBu
tBu
P
tBu
OMe
tBu
Me
Mn
P
OC
CO
Ph2
2d
31P-NMR in CDCl3 at 162MHz
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
300.0
200.0
100.0
0
-100.0
-200.0
-300.0
106.682
-22.088
X : parts per Million : Phosphorus31

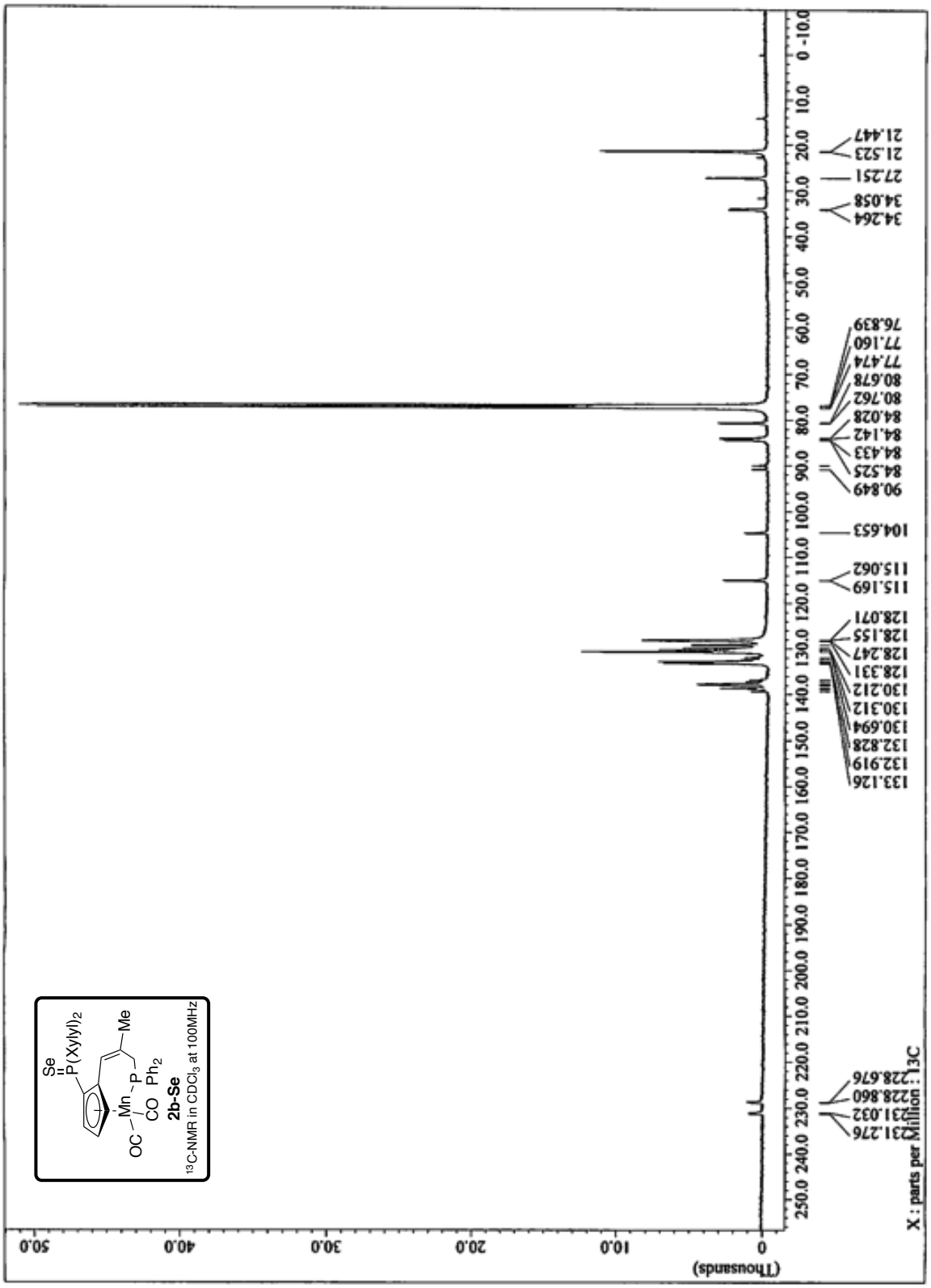

OC
Mn
CO
CO
CO
Br
O
O
O
OMe
4
1H-NMR in CDCl3 at 400MHz
X : parts per Million : Proton
abundance
7.261
5.275
5.001
4.841
4.615
4.273
4.262
4.246
4.233
4.029
4.002
3.957
3.928
3.901
3.568
3.536
3.509
3.494
3.437
3.427
3.396
1.885
1.853
1.842
1.822
1.811
1.792
1.780
1.511
1.477
0.069
-0.000
1.12
0.97
1.04
1.17
1.13
0.81
1.00
4.06
1.04
0.98

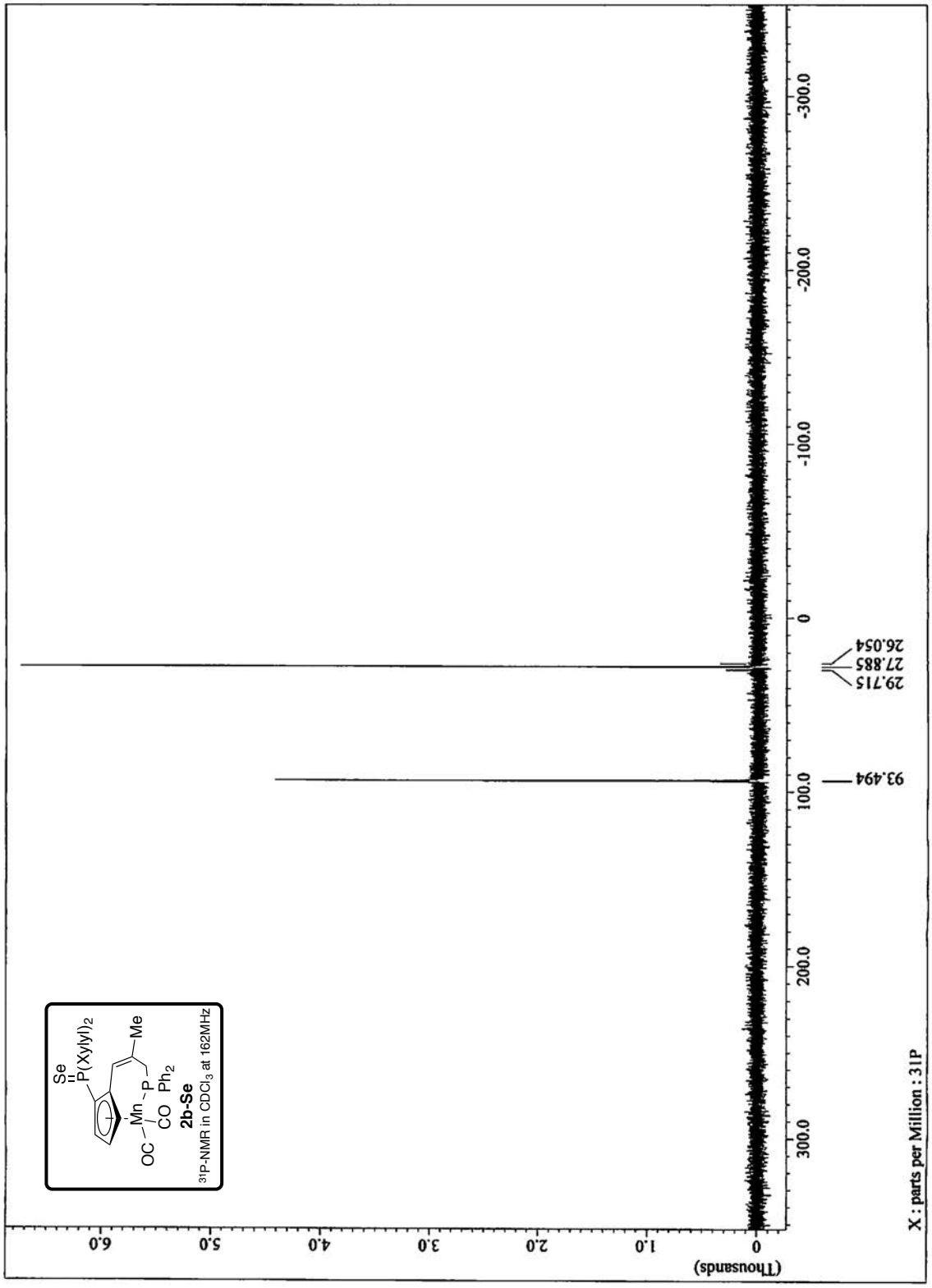

13C-NMR in CDCl3 at 100MHz
4
X : parts per Million : 13C
(Thousands)
223.870
27.642
59.510
66.928
75.302
76.586
76.846
77.160
77.481
80.143
81.045
83.347
85.978
96.340
100.340

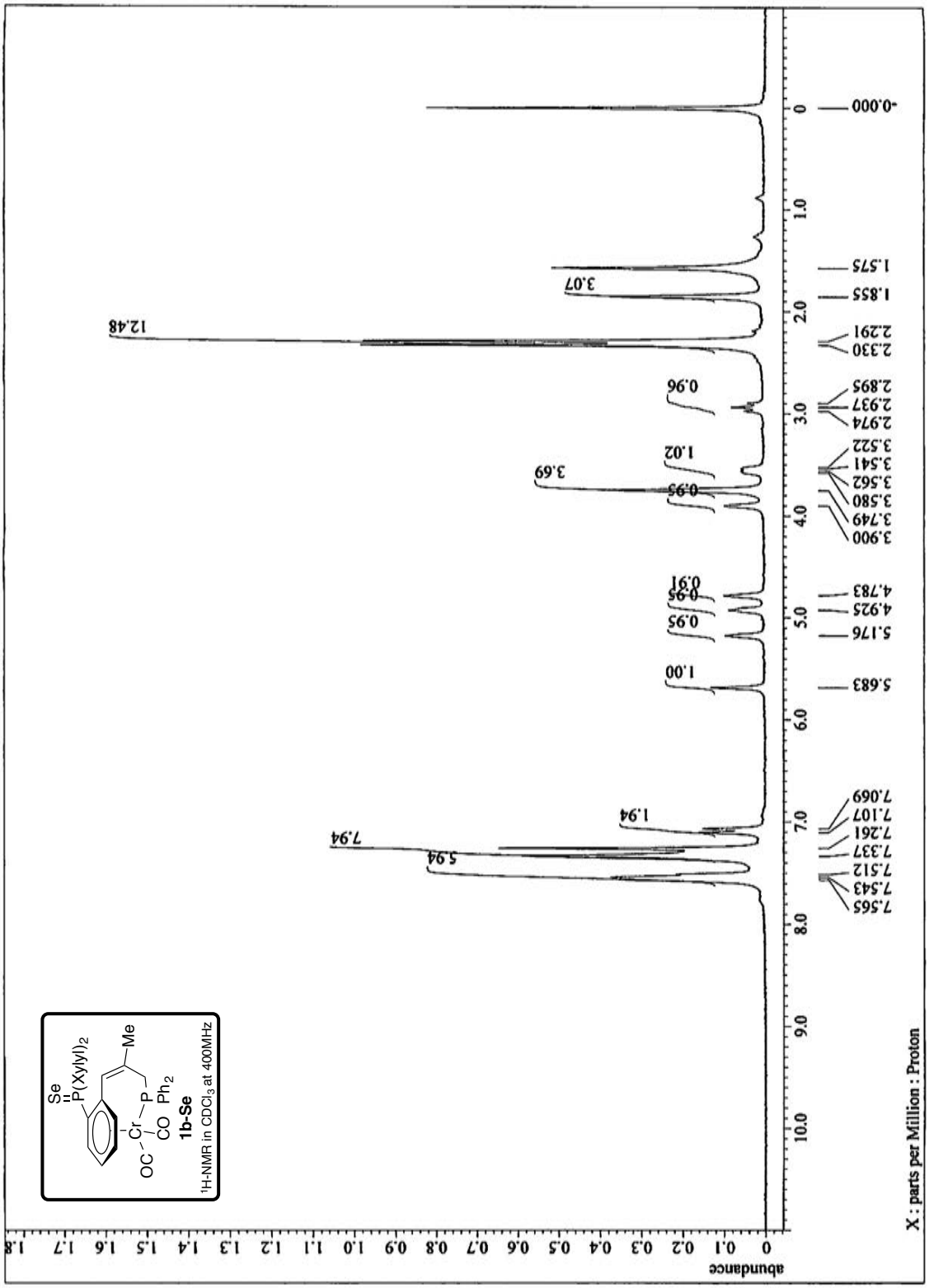

CHO
Br
Mn
OC
CO
CO
5
1H-NMR in CDCl3 at 400MHz
1.00
1.02
1.02
1.02
9.783
7.260
5.414
5.094
4.961
-0.002
X : parts per Million : 1H
(Thousands)

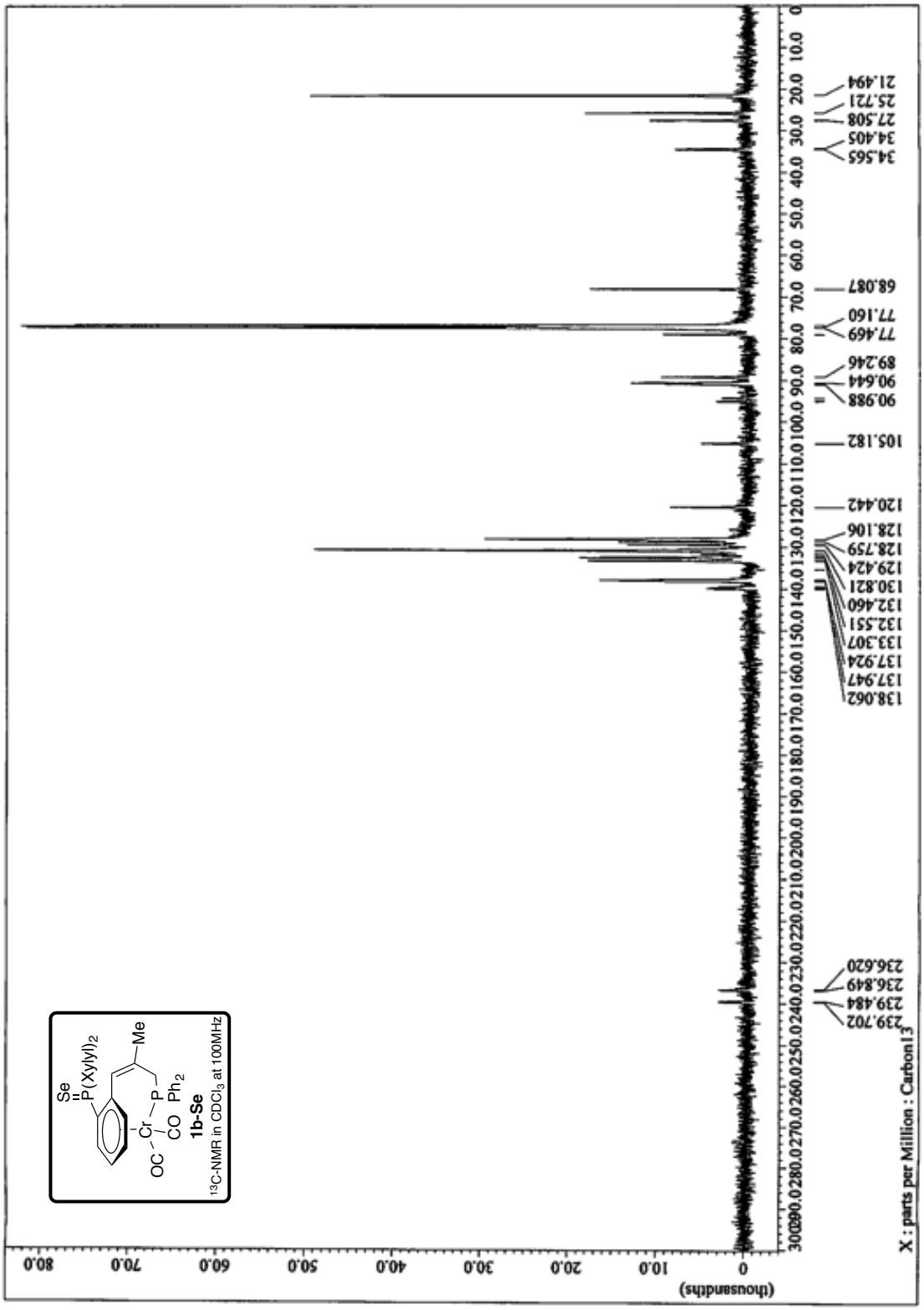

CHO
Br
Mn
CO
OC
CO
5
13C-NMR in CDCl3 at 100MHz
abundance
0.4
0.3
0.2
0.1
0
X : parts per Million : Carbon13
221.567
186.648
91.595
88.330
85.454
83.438
83.301
77.481
77.160
76.851

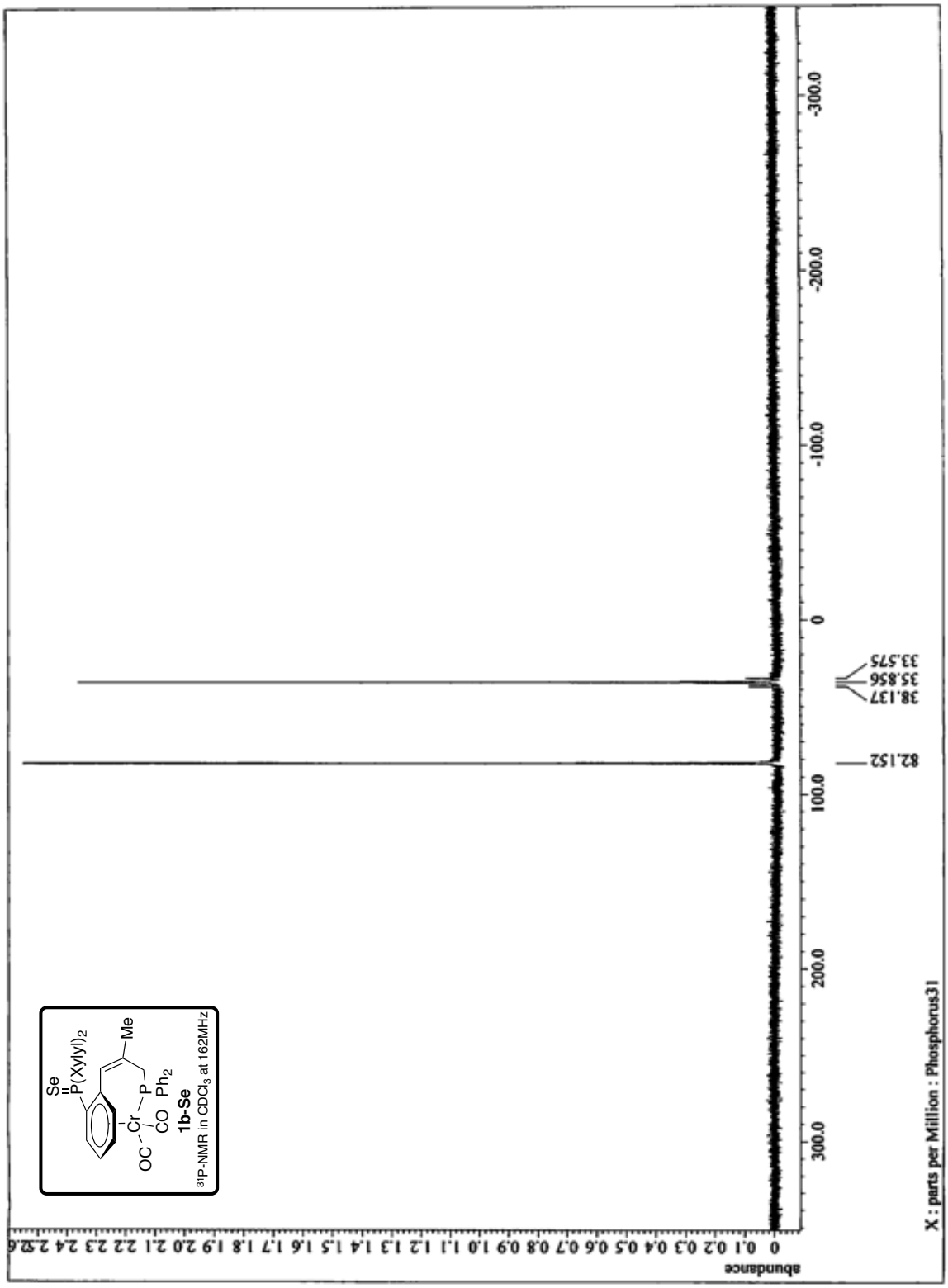

Se
P(Xylyl)2
Mn
P
Me
OC
CO
Ph2
2b-Se
1H-NMR in CDCl3 at 400MHz
X : parts per Million : Proton
abundance

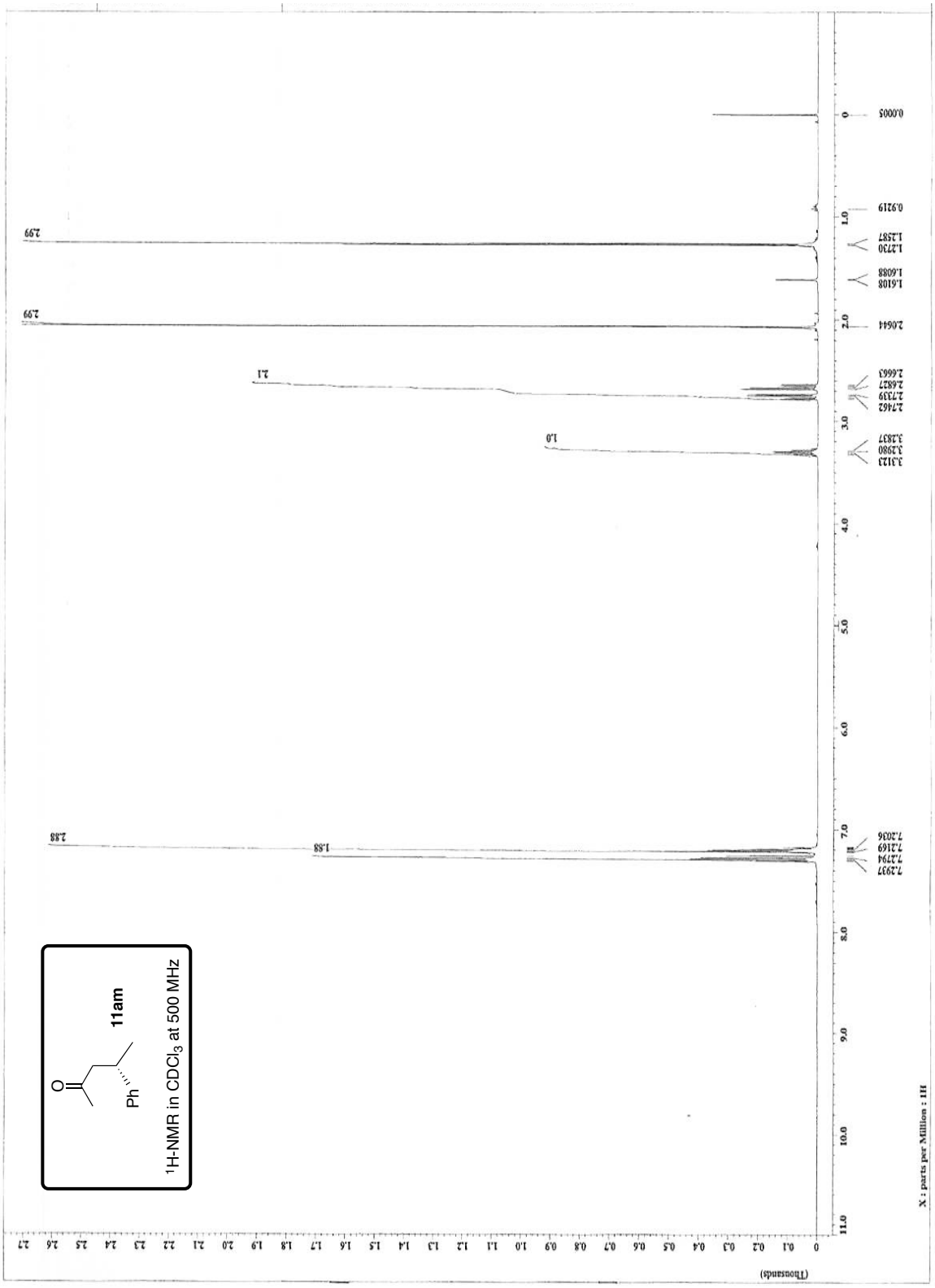

Se
P(Xylyl)2
Me
OC
Mn
P
CO
Ph2
2b-Se
13C-NMR in CDCl3 at 100MHz
(Thousands)
X : parts per Million : 13C
231.276
231.032
228.860
228.676
133.126
132.919
132.828
130.694
130.312
130.212
128.331
128.247
128.155
128.071
115.169
115.062
104.653
90.849
84.525
84.433
84.142
84.028
80.762
80.678
77.474
77.160
76.839
34.264
34.058
27.251
21.523
21.447

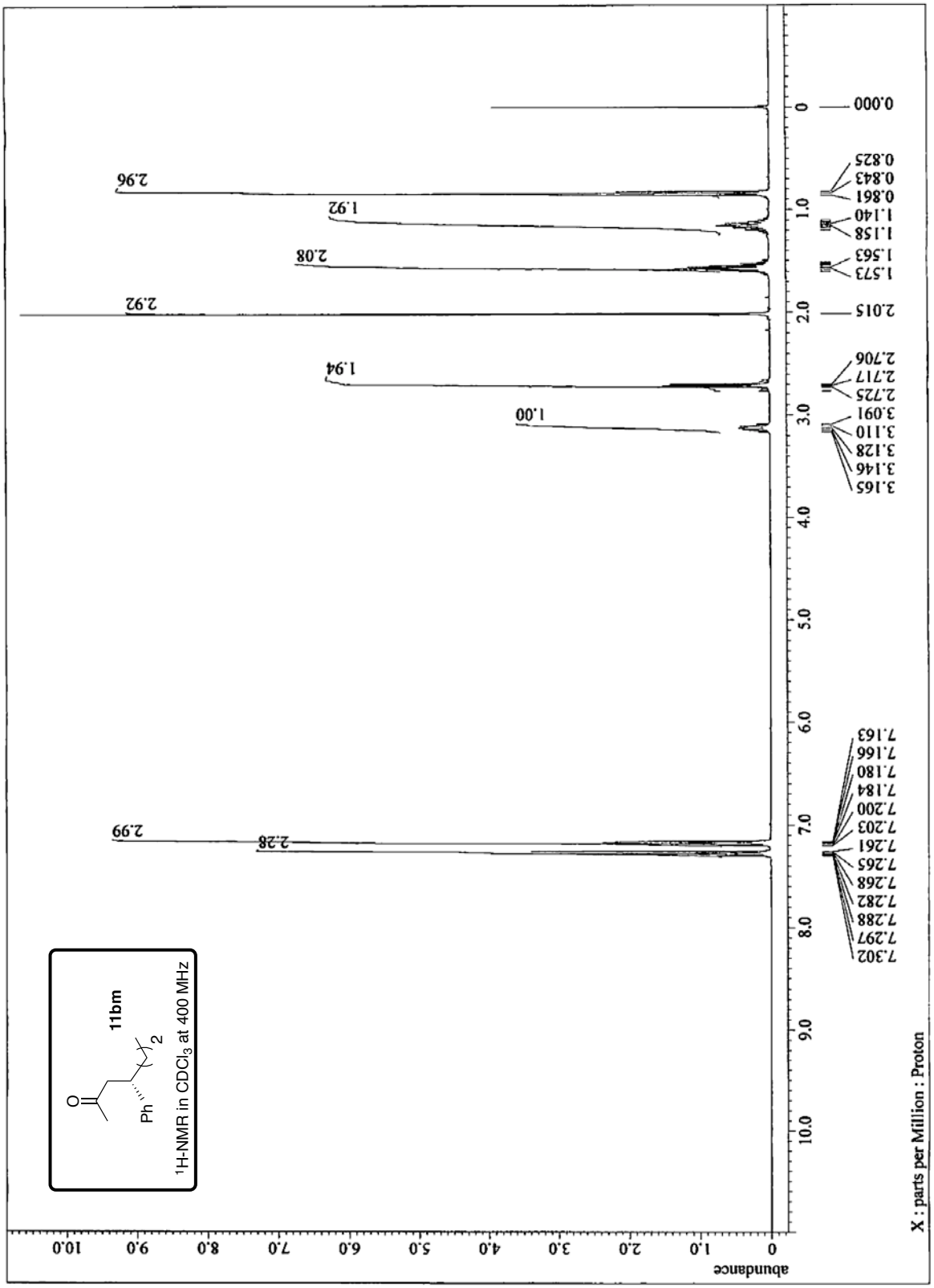

Se
P(Xylyl)2
Me
OC
Mn
P
CO
Ph2
2b-Se
31P-NMR in CDCl3 at 162MHz
(Thousands)
6.0
5.0
4.0
3.0
2.0
1.0
0
300.0
200.0
100.0
0
-100.0
-200.0
-300.0
93.494
29.715
27.885
26.054
X : parts per Million : 31P

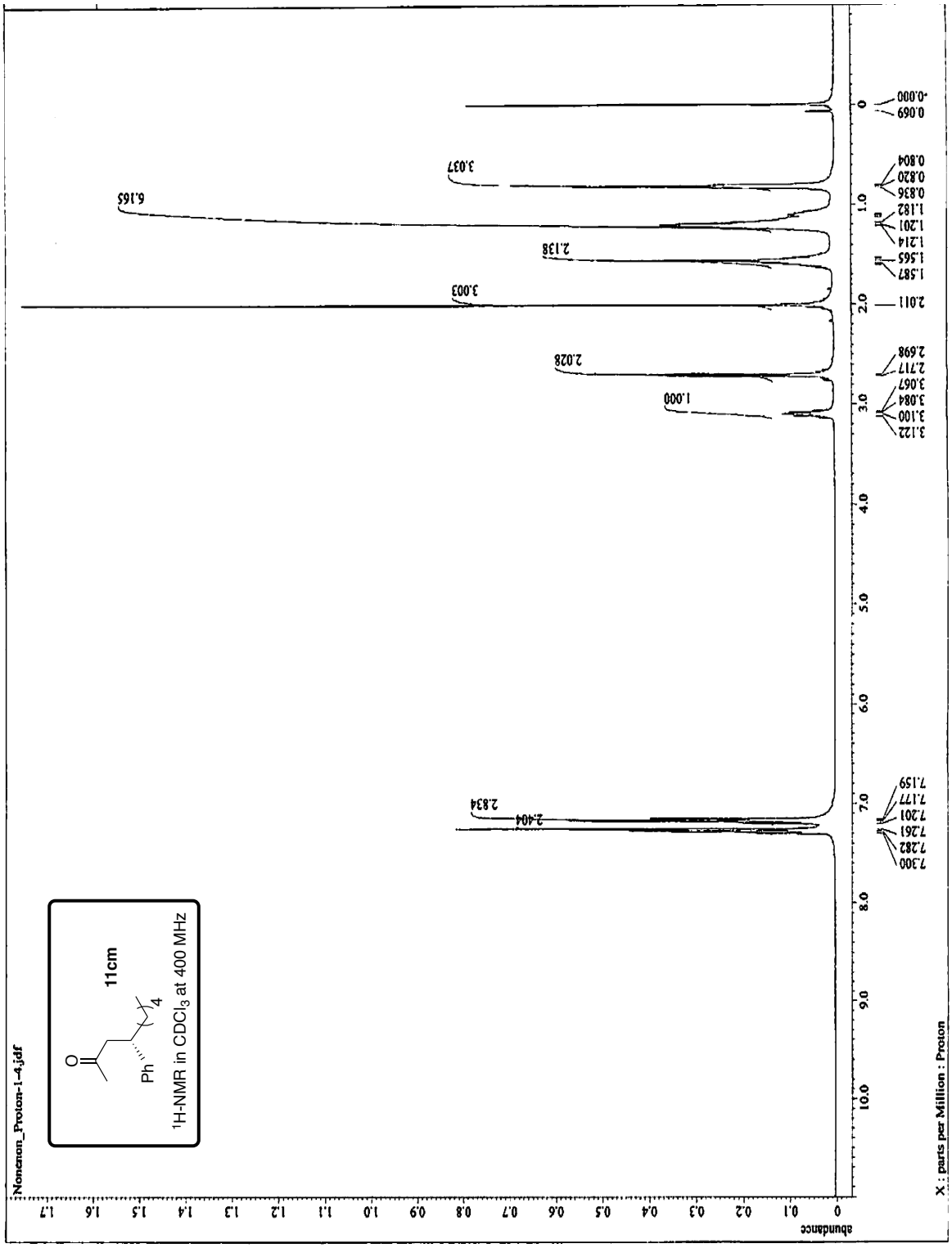

1b-Se
1H-NMR in CDCl3 at 400MHz
X : parts per Million : Proton
abundance

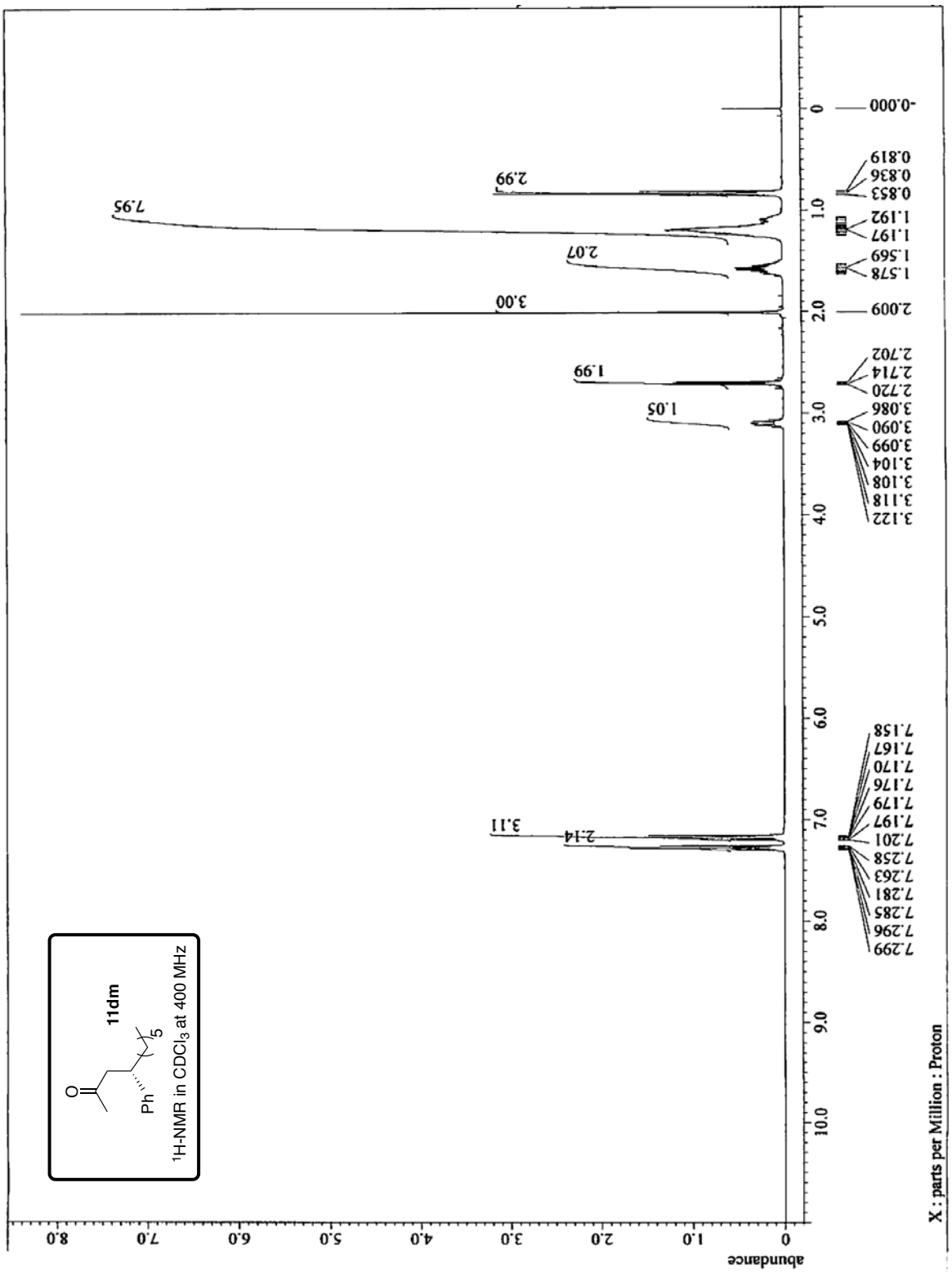

Se
P(Xylyl)2
Me
OC
Cr
P
CO
Ph2
1b-Se
13C-NMR in CDCl3 at 100MHz
(thousandths)
X : parts per Million : Carbon13
239.702
239.484
236.849
236.620
138.062
137.947
137.924
133.307
132.551
132.460
130.821
129.424
128.759
128.106
120.442
105.182
90.988
90.644
89.246
77.469
77.160
68.087
34.565
34.405
27.508
25.721
21.494

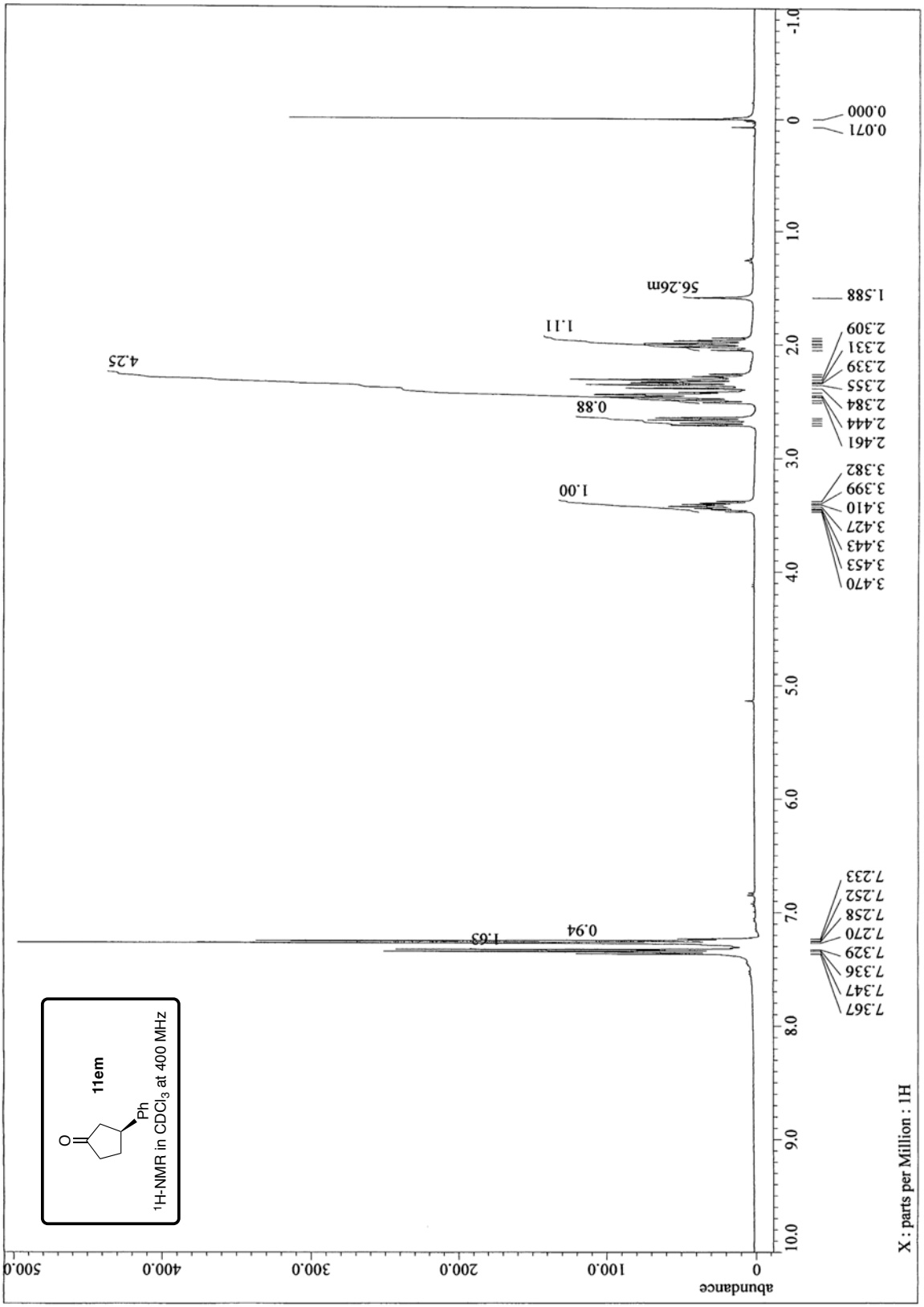

Se
P(Xylyl)2
Me
OC
Cr
P
CO
Ph2
1b-Se
31P-NMR in CDCl3 at 162MHz
82.152
38.137
35.856
33.575
X : parts per Million : Phosphorus31
abundance

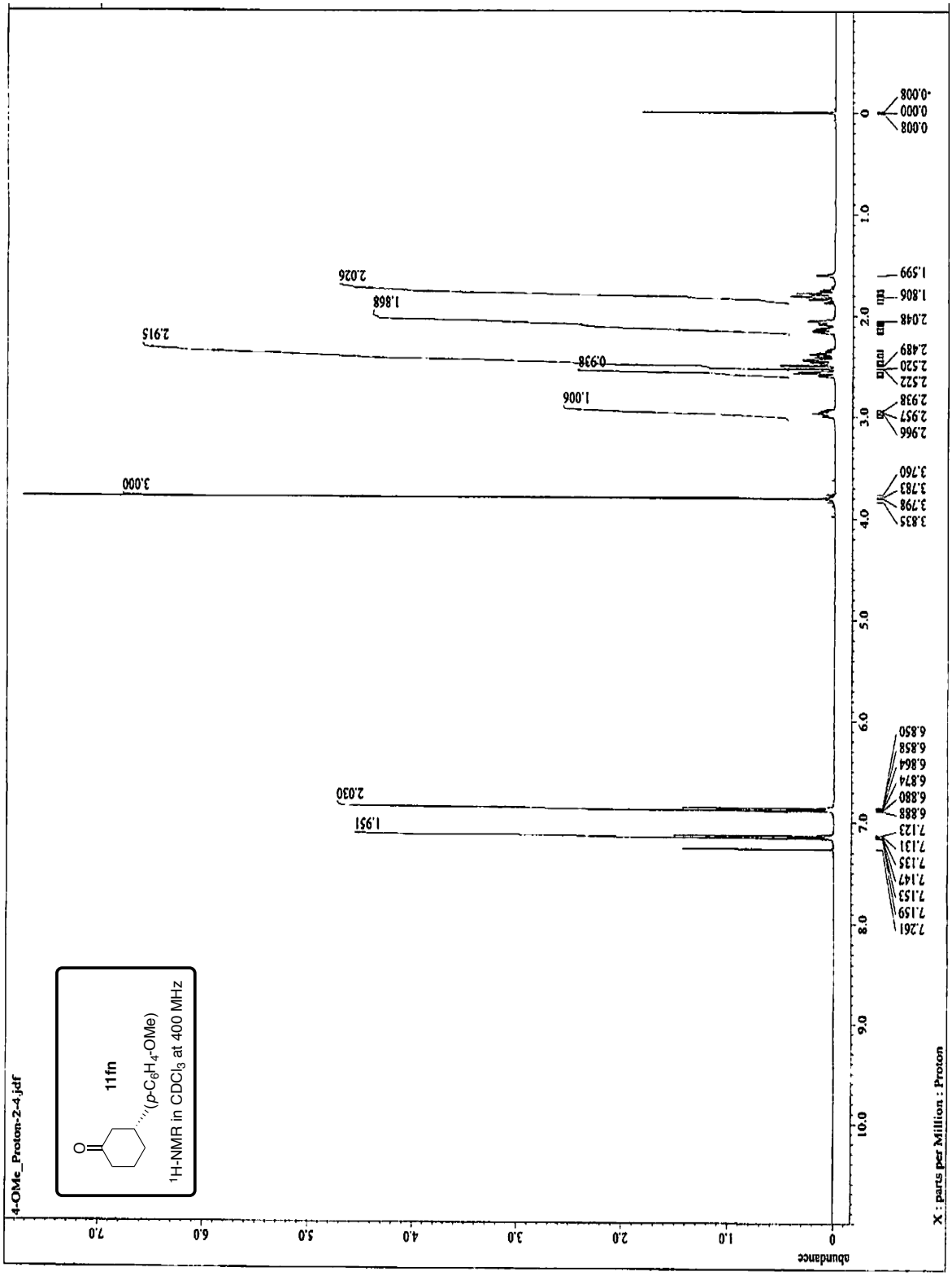

11am
Ph
O
^{1}H-NMR in $CDCl_3$ at 500 MHz
0.0005
0.9219
1.2587
1.2730
1.6088
1.6108
2.0644
2.6663
2.6827
2.7339
2.7462
3.2837
3.2980
3.3123
7.2036
7.2169
7.2794
7.2937
1.88
2.88
1.0
2.1
2.99
2.99
X : parts per Million : 1H
(Thousands)

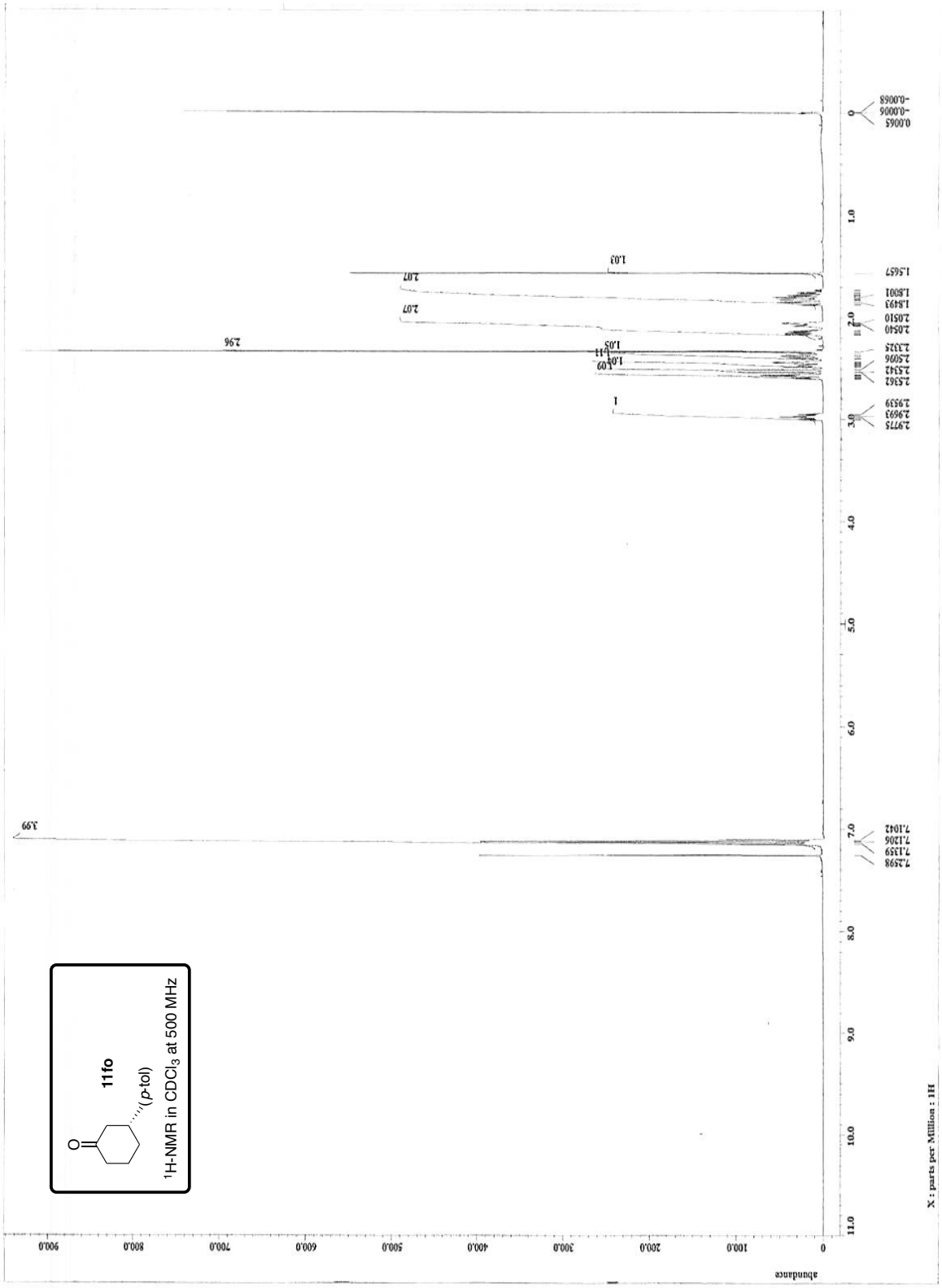

11bm
Ph
O
2
^{1}H-NMR in $CDCl_3$ at 400 MHz
X : parts per Million : Proton
abundance
0.000
2.015
2.99
2.28
2.96
2.92
2.08
1.92
1.94
1.00

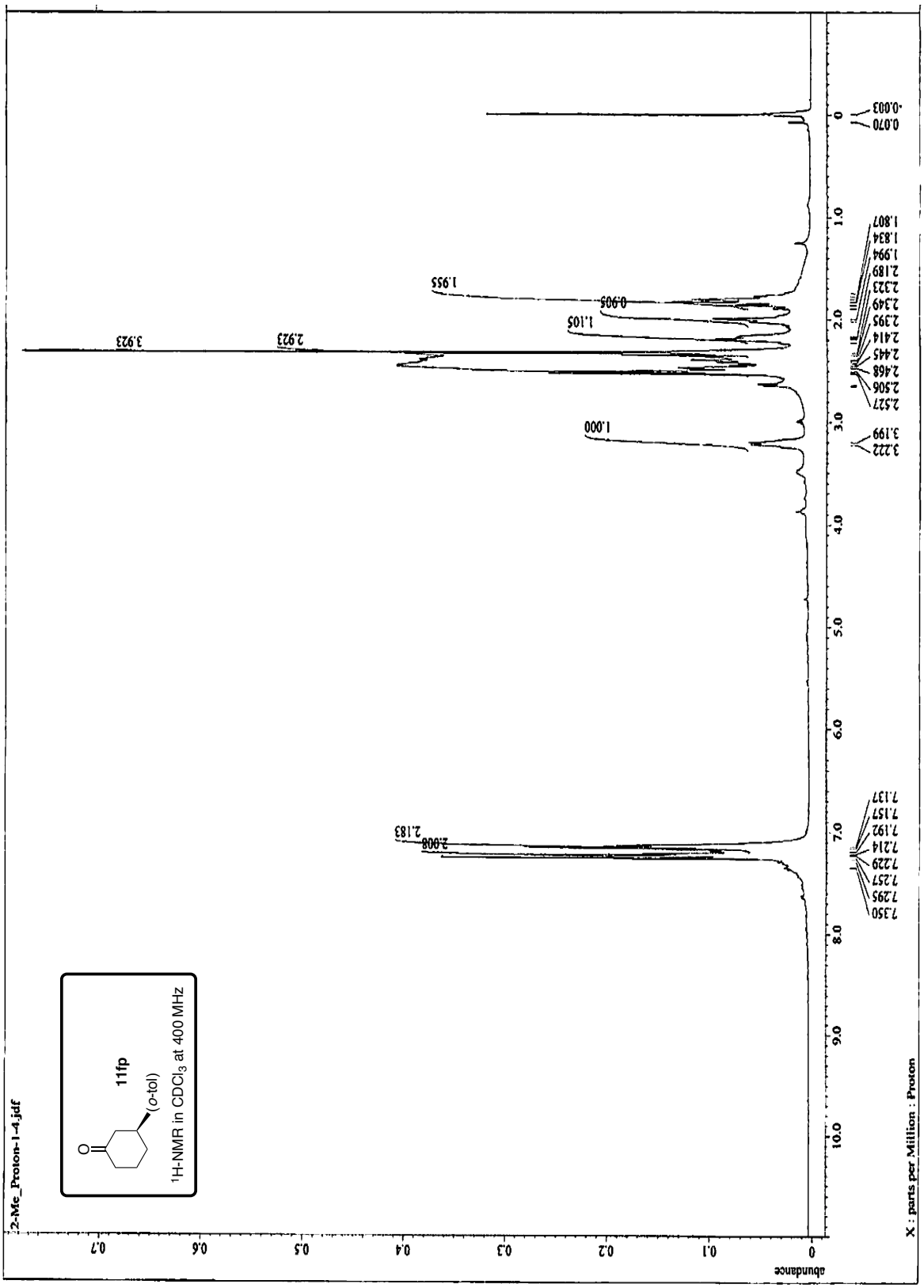

Nonanon_Proton-1-4.jdf
11cm
Ph
4
O
1H-NMR in CDCl3 at 400 MHz
X : parts per Million : Proton
abundance
7.300
7.282
7.261
7.201
7.177
7.159
2.404
2.834
1.000
2.028
3.003
2.138
6.165
3.037
0.069
-0.000
3.122
3.100
3.084
3.067
2.717
2.698
2.011
1.587
1.565
1.214
1.201
1.182
0.836
0.820
0.804

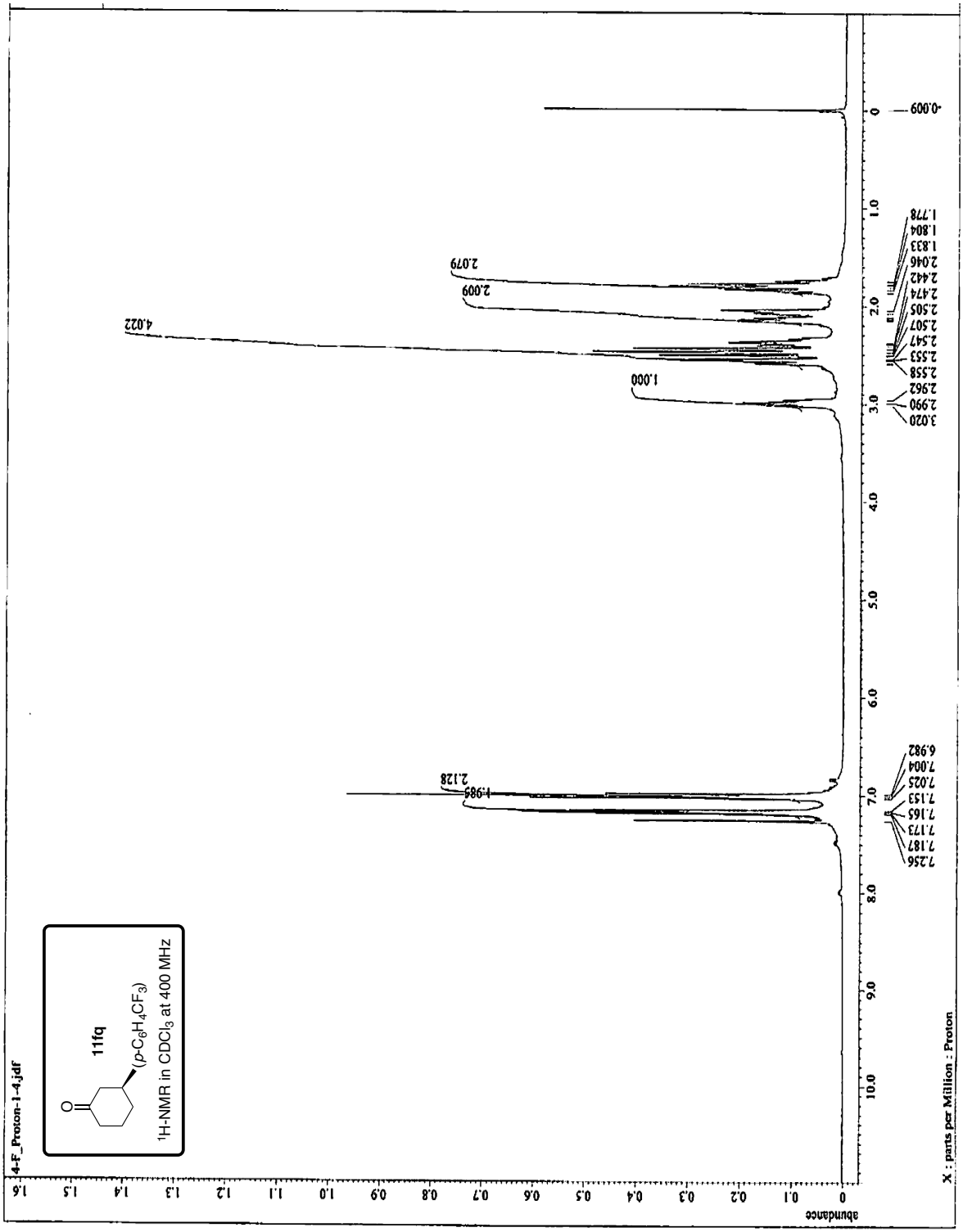

11dm
Ph
O
5
1H-NMR in CDCl3 at 400 MHz
X : parts per Million : Proton
abundance
7.299
7.296
7.285
7.281
7.263
7.258
7.201
7.197
7.179
7.176
7.170
7.167
7.158
3.122
3.118
3.108
3.104
3.099
3.090
3.086
2.720
2.714
2.702
2.009
1.578
1.569
1.197
1.192
0.853
0.836
0.819
-0.000
7.95
2.99
2.07
3.00
1.99
1.05
2.14
3.11

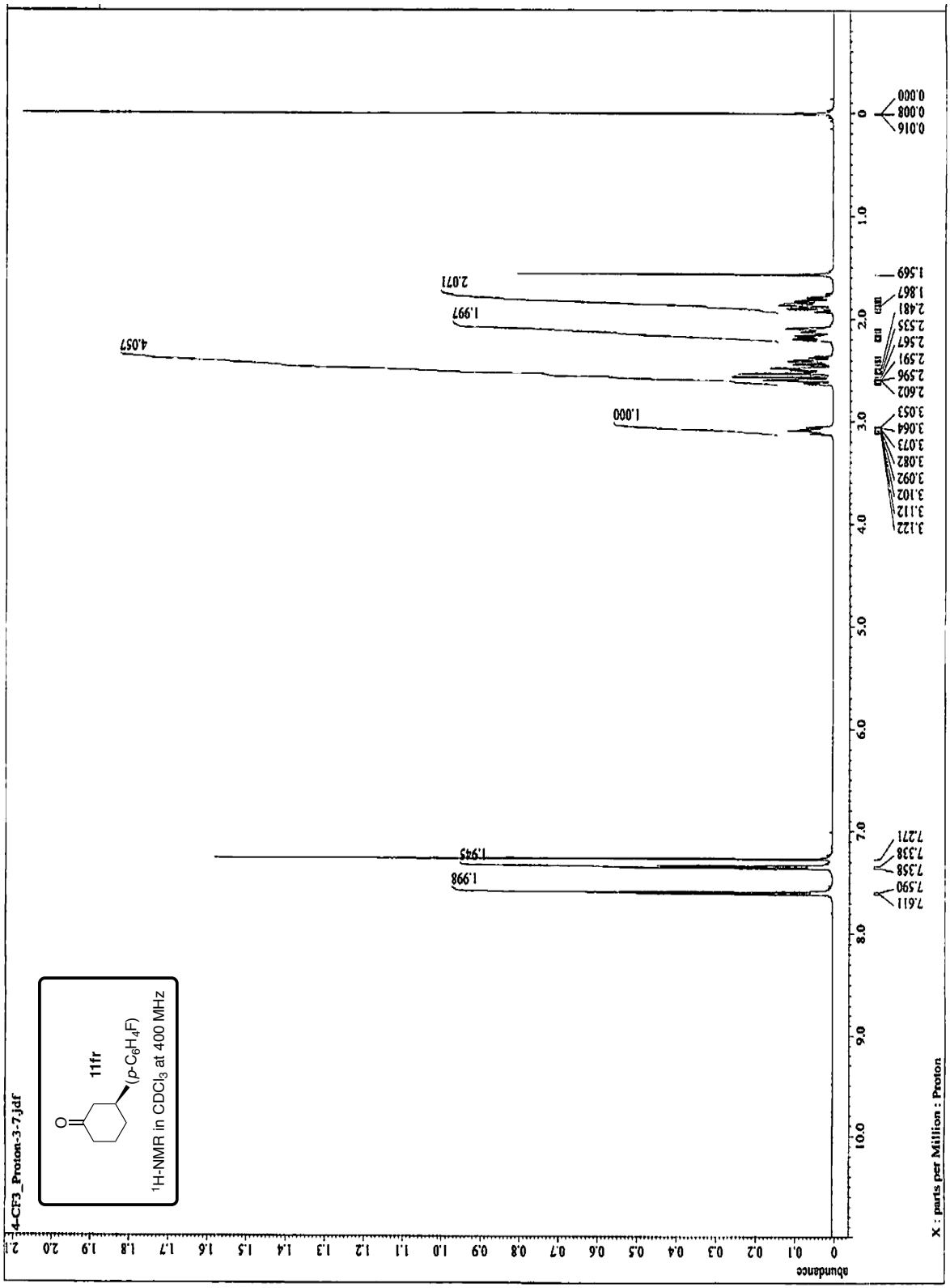

11em
Ph
O
^{1}H-NMR in $CDCl_3$ at 400 MHz
X : parts per Million : 1H
abundance
0.000
0.071
1.588
56.26m
2.309
2.331
2.339
2.355
2.384
2.444
2.461
3.382
3.399
3.410
3.427
3.443
3.453
3.470
1.00
0.88
4.25
1.11
7.233
7.252
7.258
7.270
7.329
7.336
7.347
7.367
0.94
1.63

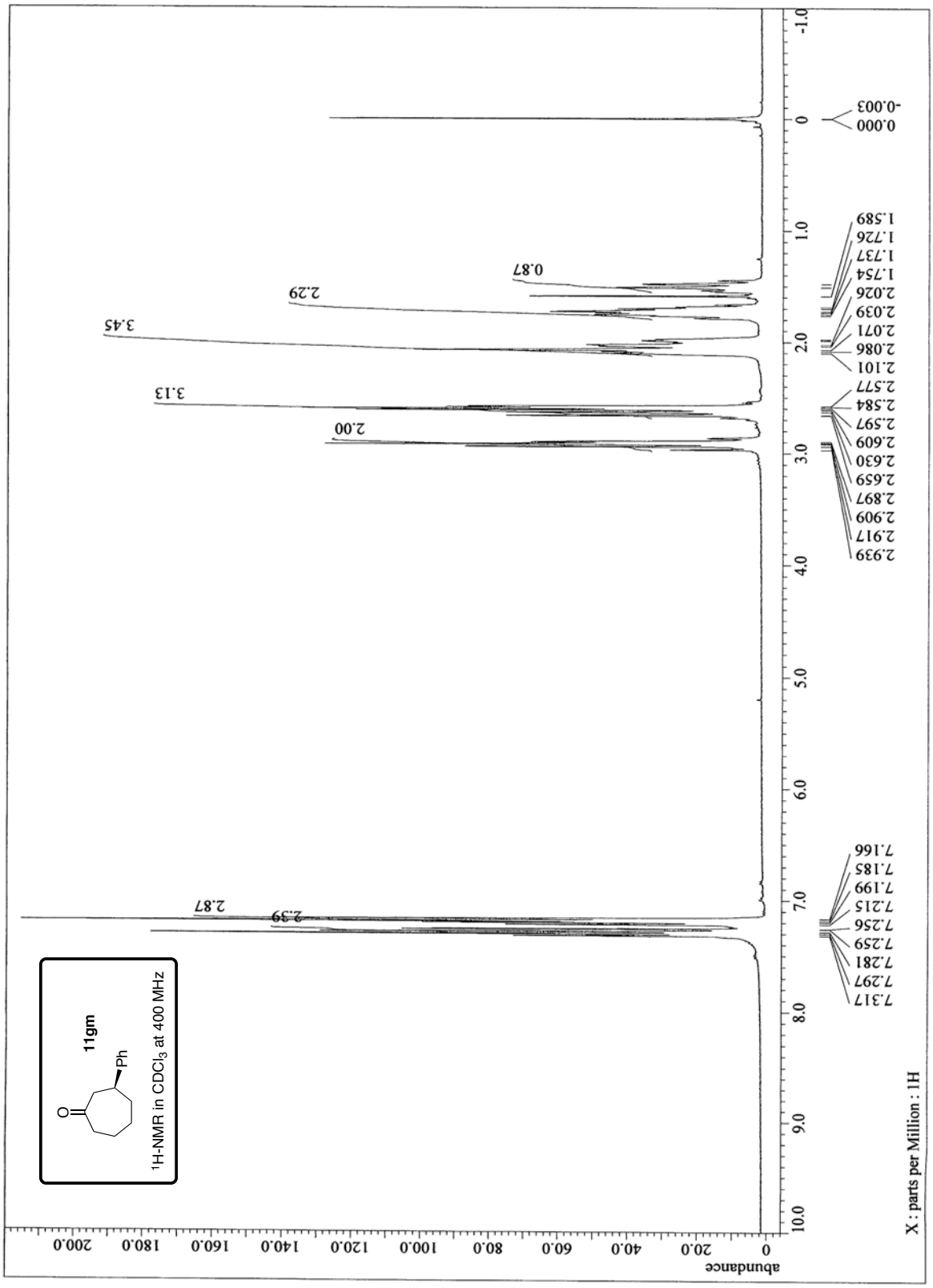

4-OMe_Proton-2-4.jdf
11fn
(p-C6H4-OMe)
1H-NMR in CDCl3 at 400 MHz
X : parts per Million : Proton
abundance

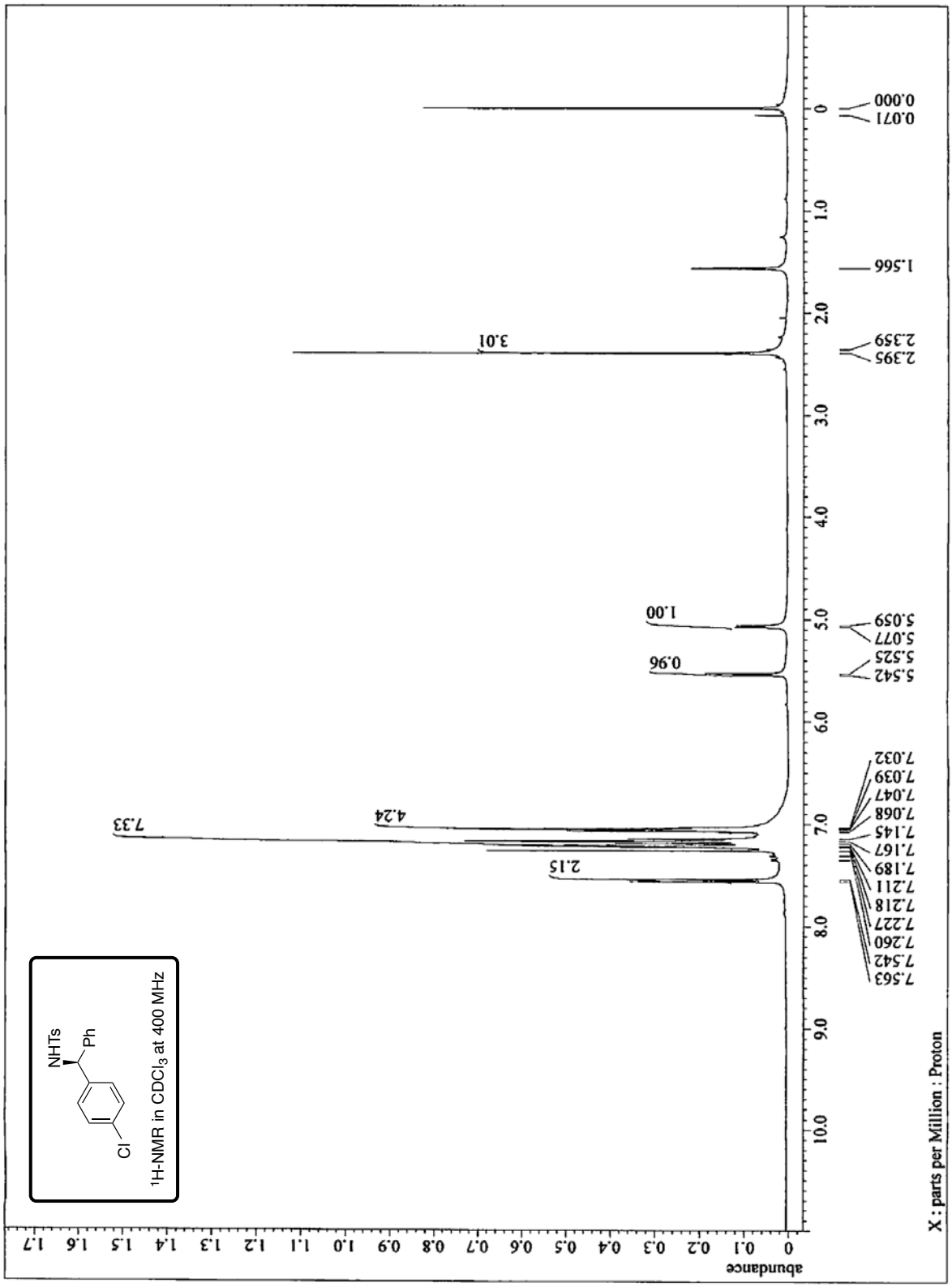

11fo
(p-tol)
^{1}H-NMR in $CDCl_3$ at 500 MHz
X : parts per Million : 1H
abundance

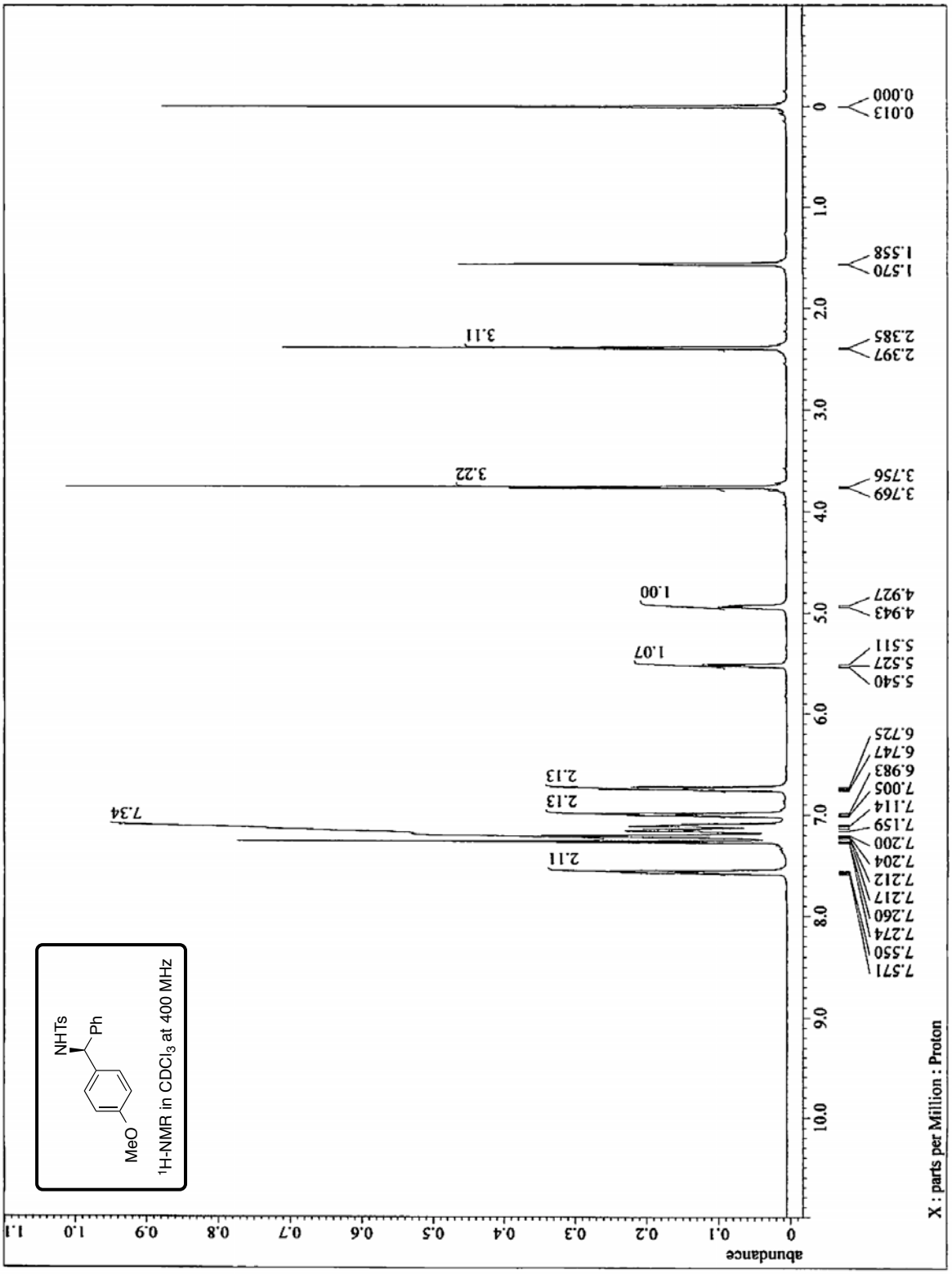

2-Me_Proton-1-4.jdf
11fp
(o-tol)
1H-NMR in CDCl3 at 400 MHz
abundance
X : parts per Million : Proton
7.350
7.295
7.257
7.229
7.214
7.192
7.157
7.137
3.222
3.199
2.527
2.506
2.468
2.445
2.414
2.395
2.349
2.323
2.189
1.994
1.834
1.807
0.070
-0.003
2.008
2.183
1.000
2.923
3.923
1.105
0.905
1.955

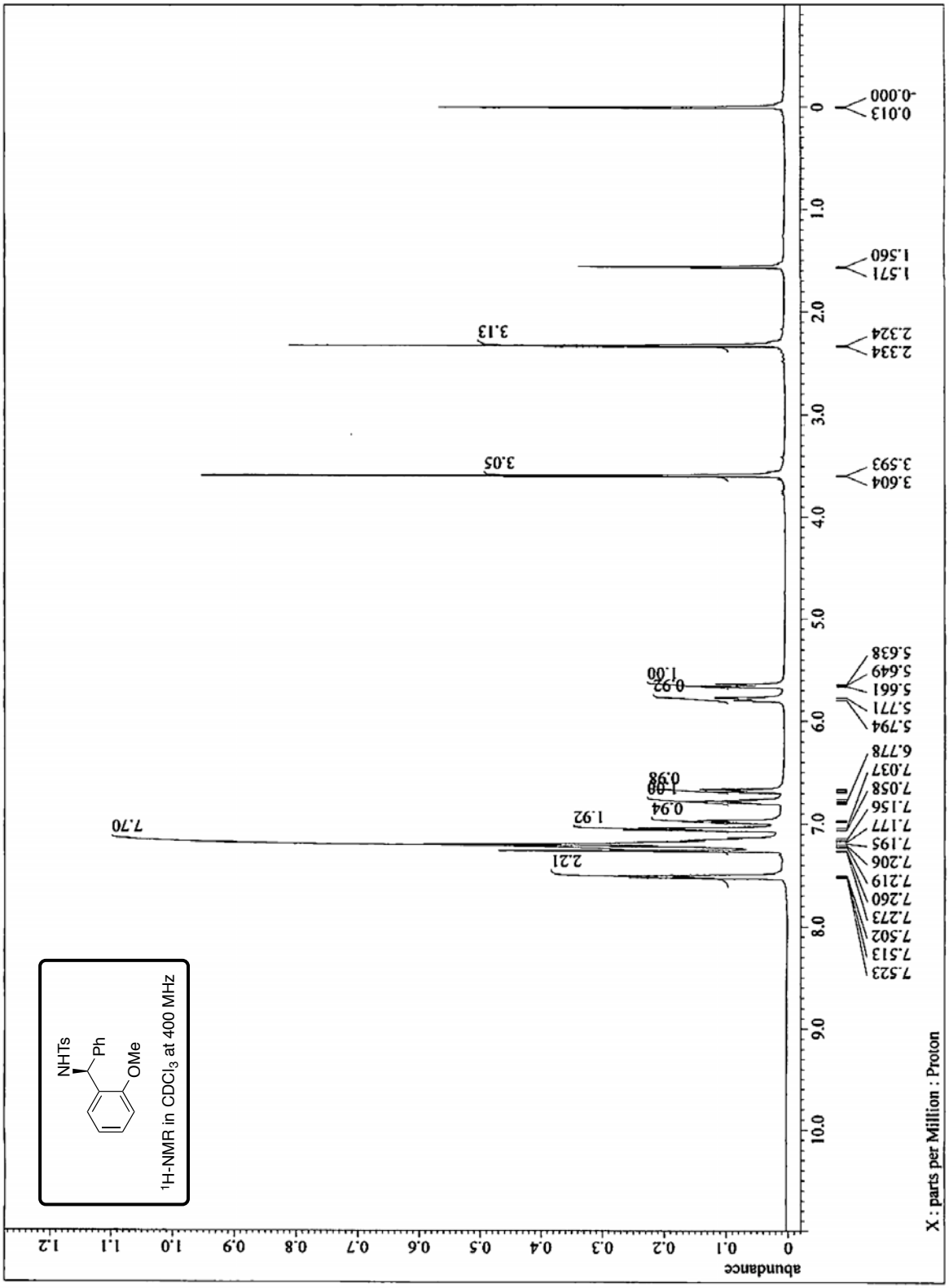

4-F_Proton-1-4.jdf
11fq
(p-C6H4CF3)
1H-NMR in CDCl3 at 400 MHz
X : parts per Million : Proton
abundance
-0.009
7.256
7.187
7.173
7.165
7.153
7.025
7.004
6.982
1.985
2.128
1.000
4.022
3.020
2.990
2.962
2.558
2.553
2.547
2.507
2.505
2.474
2.442
2.046
1.833
1.804
1.778
2.009
2.079

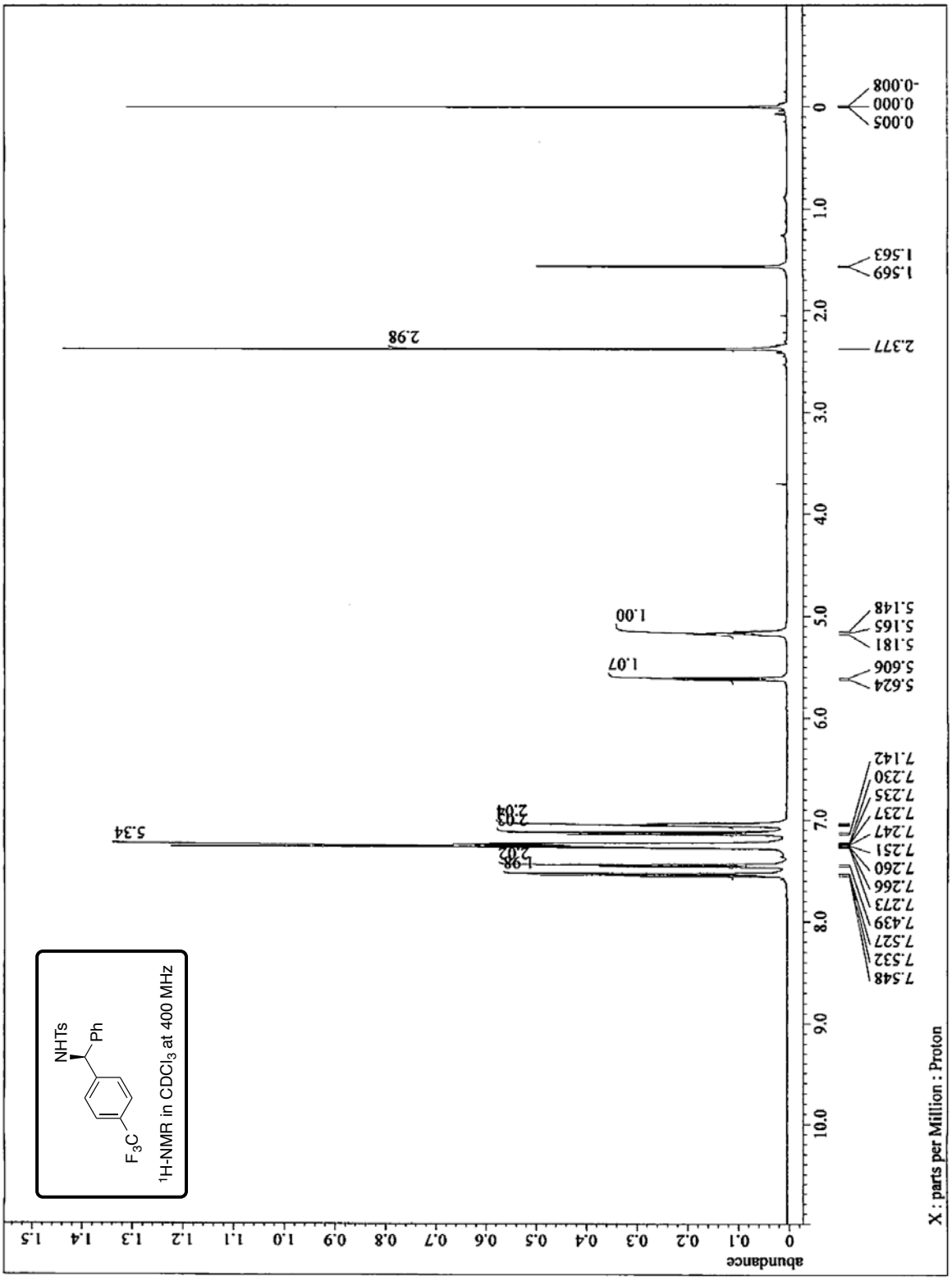

4-CF3_Proton-3-7.jdf
O
11fr
(p-C6H4F)
1H-NMR in CDCl3 at 400 MHz
X : parts per Million : Proton
abundance
0.016
0.008
0.000
1.569
2.071
1.997
1.867
2.481
2.535
2.567
2.591
2.596
2.602
4.057
1.000
3.053
3.064
3.073
3.082
3.092
3.102
3.112
3.122
1.998
1.945
7.611
7.590
7.358
7.338
7.271

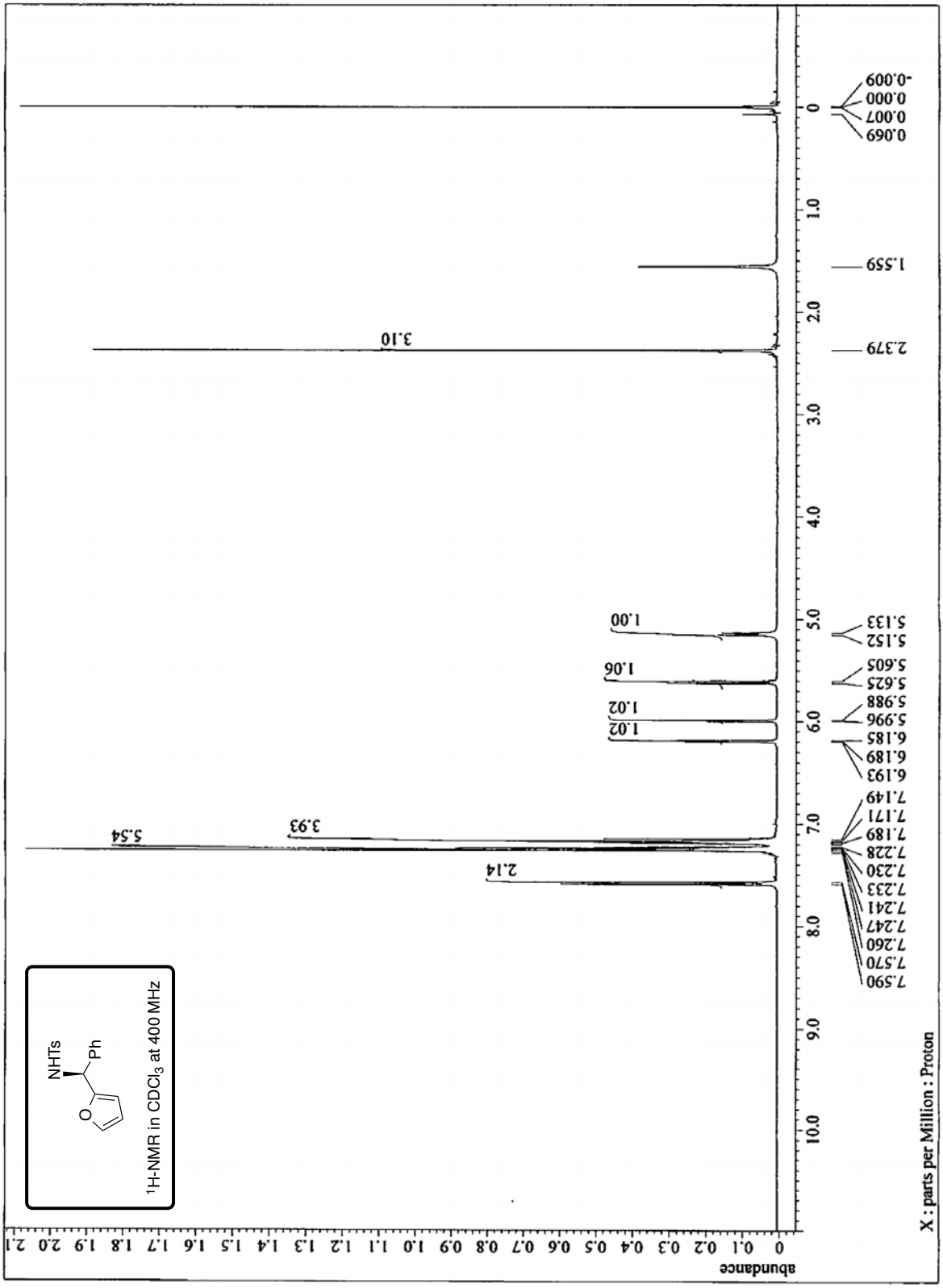

11gm
Ph
O
^{1}H-NMR in $CDCl_3$ at 400 MHz
X : parts per Million : 1H
abundance
7.317
7.297
7.281
7.259
7.256
7.215
7.199
7.185
7.166
2.939
2.917
2.909
2.897
2.659
2.630
2.609
2.597
2.584
2.577
2.101
2.086
2.071
2.039
2.026
1.754
1.737
1.726
1.589
0.000
-0.003
2.39
2.87
2.00
3.13
3.45
2.29
0.87

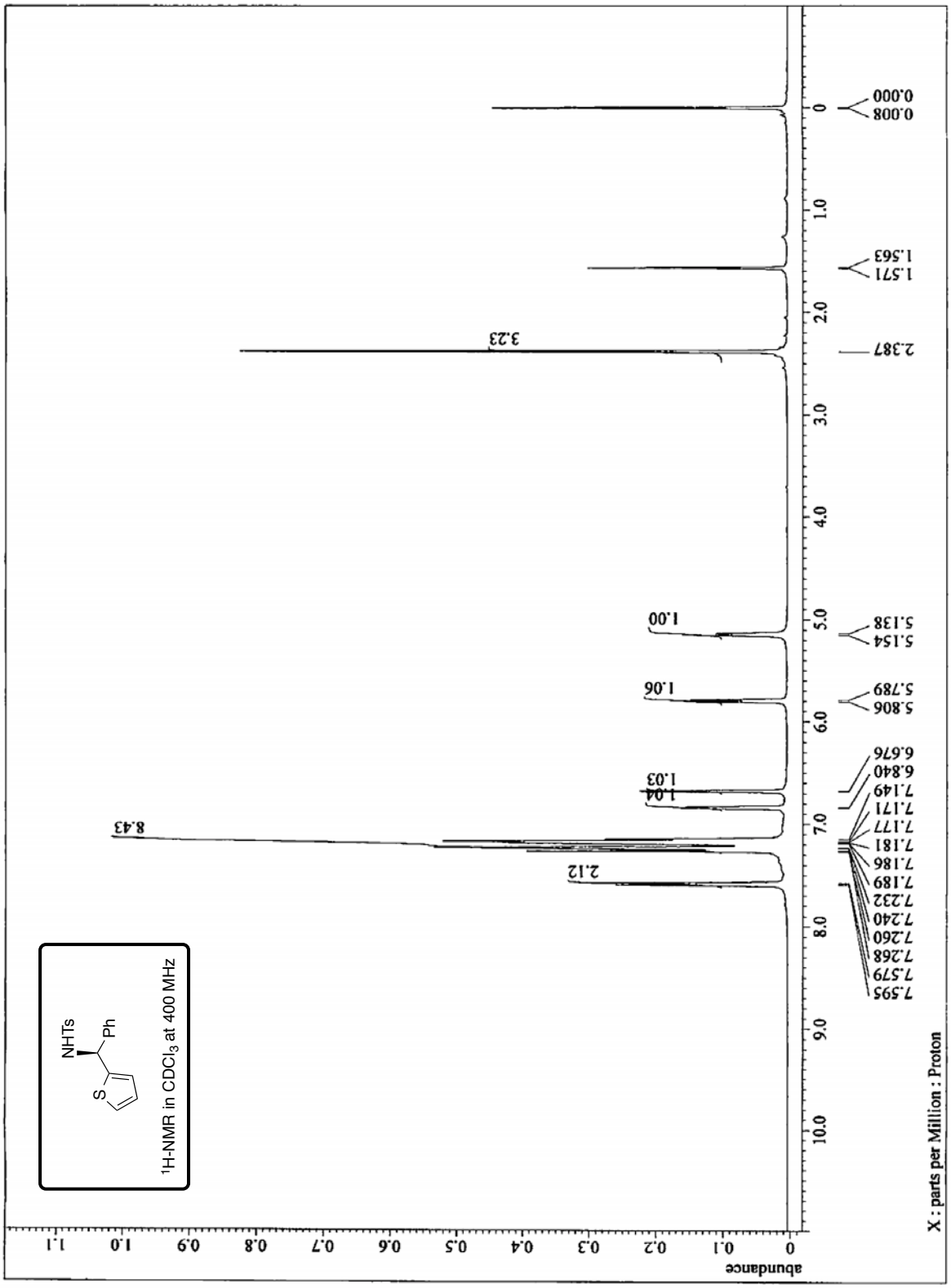

NHTs
Ph
Cl
^{1}H-NMR in $CDCl_3$ at 400 MHz
X : parts per Million : Proton
abundance
7.563
7.542
7.260
7.227
7.218
7.211
7.189
7.167
7.145
7.068
7.047
7.039
7.032
5.542
5.525
5.077
5.059
2.395
2.359
1.566
0.071
0.000
7.33
4.24
2.15
0.96
1.00
3.01

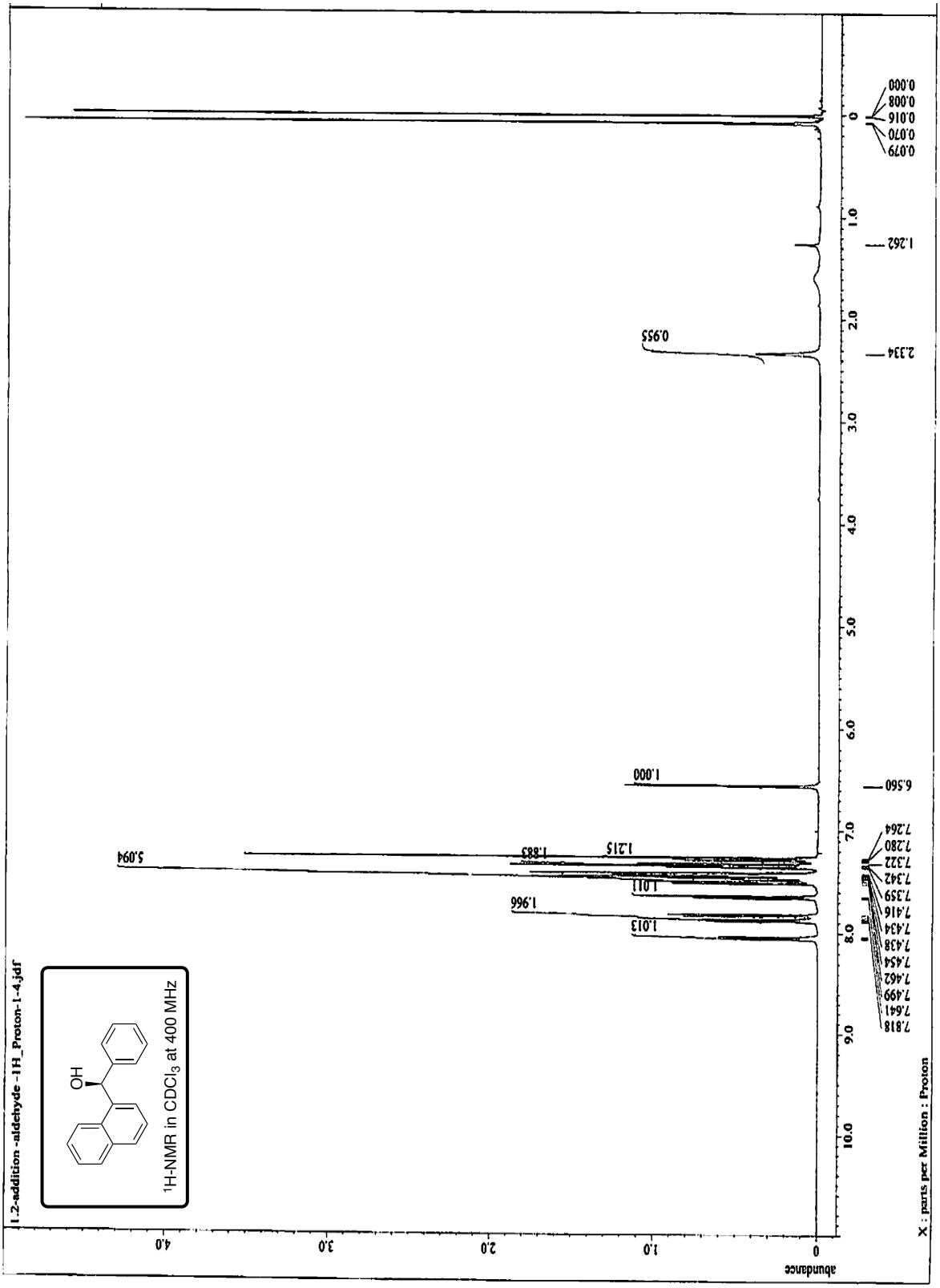

NHTs
Ph
MeO
1H-NMR in CDCl3 at 400 MHz
X : parts per Million : Proton
abundance
7.571
7.550
7.274
7.260
7.217
7.212
7.204
7.200
7.159
7.114
7.005
6.983
6.747
6.725
5.540
5.527
5.511
4.943
4.927
3.769
3.756
2.397
2.385
1.570
1.558
0.013
0.000
7.34
2.11
2.13
2.13
1.07
1.00
3.22
3.11


NHTs
Ph
OMe
1H-NMR in CDCl3 at 400 MHz
X : parts per Million : Proton
abundance
7.523
7.513
7.502
7.273
7.260
7.219
7.206
7.195
7.177
7.156
7.058
7.037
6.778
5.794
5.771
5.661
5.649
5.638
3.604
3.593
2.334
2.324
1.571
1.560
0.013
-0.000
7.70
2.21
1.92
0.94
1.00
0.98
0.92
1.00
3.05
3.13

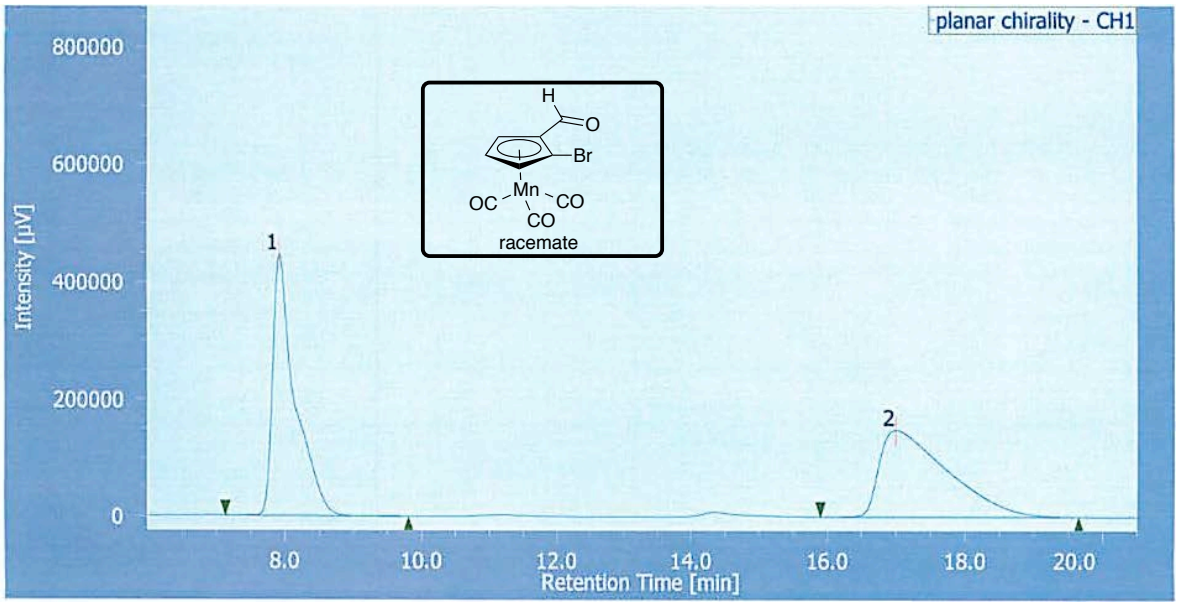

NHTs
Ph
F3C
1H-NMR in CDCl3 at 400 MHz
X : parts per Million : Proton
abundance
5.34
2.98
1.00
1.07
2.03
2.04
1.98
2.02
7.548
7.532
7.527
7.439
7.273
7.266
7.260
7.251
7.247
7.237
7.235
7.230
7.142
5.624
5.606
5.181
5.165
5.148
2.377
1.569
1.563
0.005
0.000
-0.008

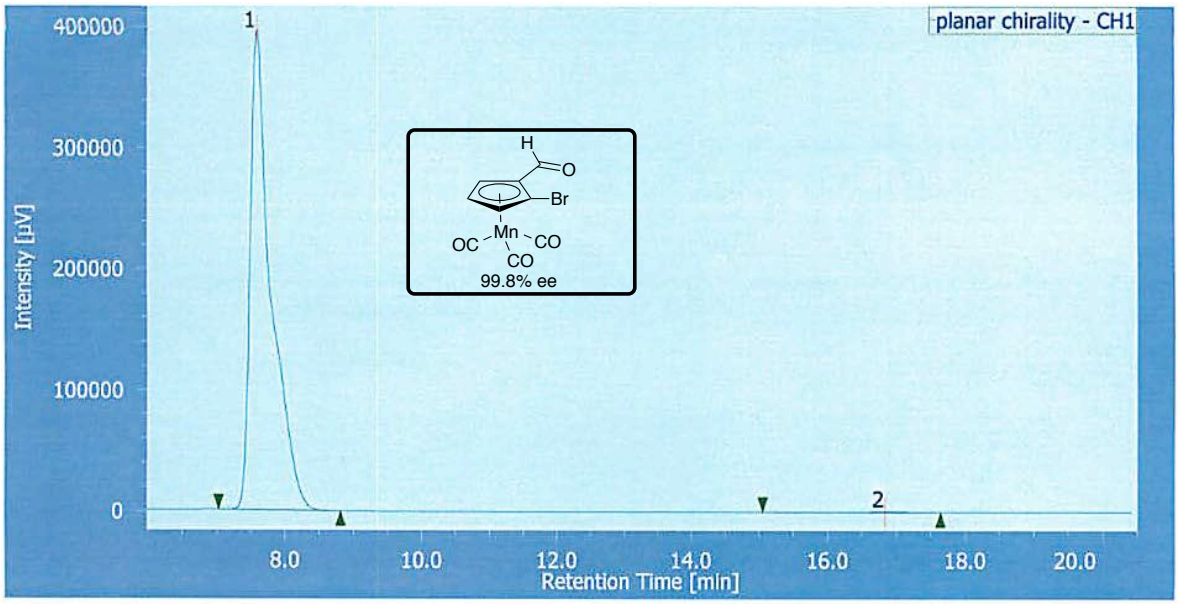

NHTs
Ph
O
1H-NMR in CDCl3 at 400 MHz
X : parts per Million : Proton
abundance
7.590
7.570
7.260
7.247
7.241
7.233
7.230
7.228
7.189
7.171
7.149
6.193
6.189
6.185
5.996
5.988
5.625
5.605
5.152
5.133
2.379
1.559
0.069
0.007
0.000
-0.009
2.14
5.54
3.93
1.02
1.02
1.06
1.00
3.10


NHTs
Ph
S
1H-NMR in CDCl3 at 400 MHz
X : parts per Million : Proton
abundance
8.43
2.12
1.04
1.03
1.06
1.00
3.23
7.595
7.579
7.268
7.260
7.240
7.232
7.189
7.186
7.181
7.177
7.171
7.149
6.840
6.676
5.806
5.789
5.154
5.138
2.387
1.571
1.563
0.008
0.000


1,2-addition-aldehyde-1H_Proton-1-4.jdf
OH
1H-NMR in CDCl3 at 400 MHz
abundance
X : parts per Million : Proton
0.079
0.070
0.016
0.008
0.000
1.262
2.334
6.560
7.264
7.280
7.322
7.342
7.359
7.416
7.434
7.438
7.454
7.462
7.499
7.641
7.818
0.955
1.000
1.013
1.966
1.011
1.215
1.883
5.094

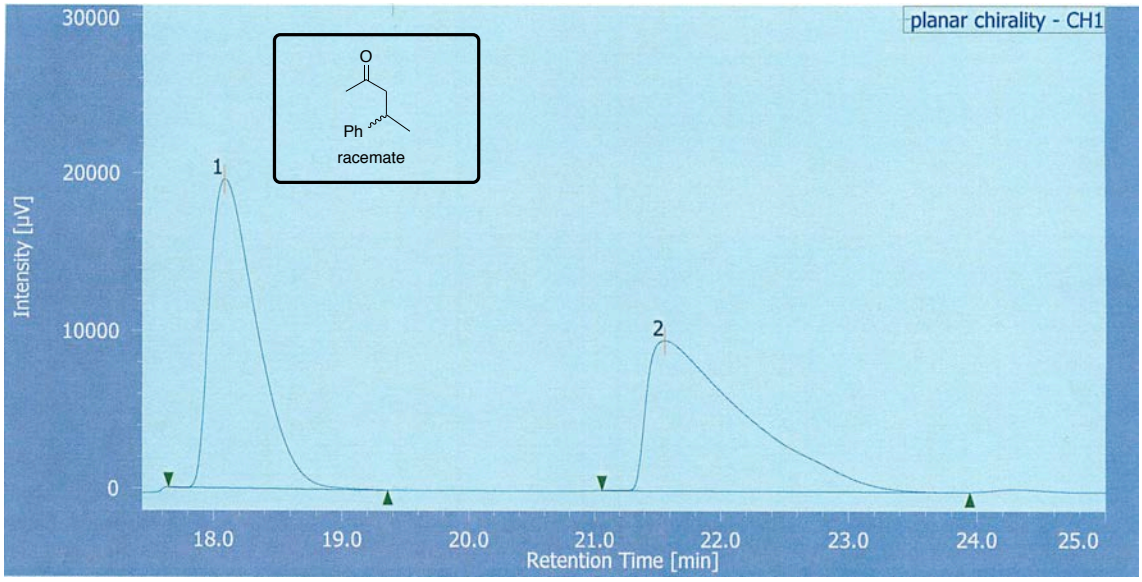
Chiral HPLC Analysis of (*S*)-1-Bromo-2-formyl Cymantrene
chiral column: Chiralpak AS; eluent: hexane/^{i}PrOH = 9/1; flow rate: 1.0 mL/min.
30 °C.

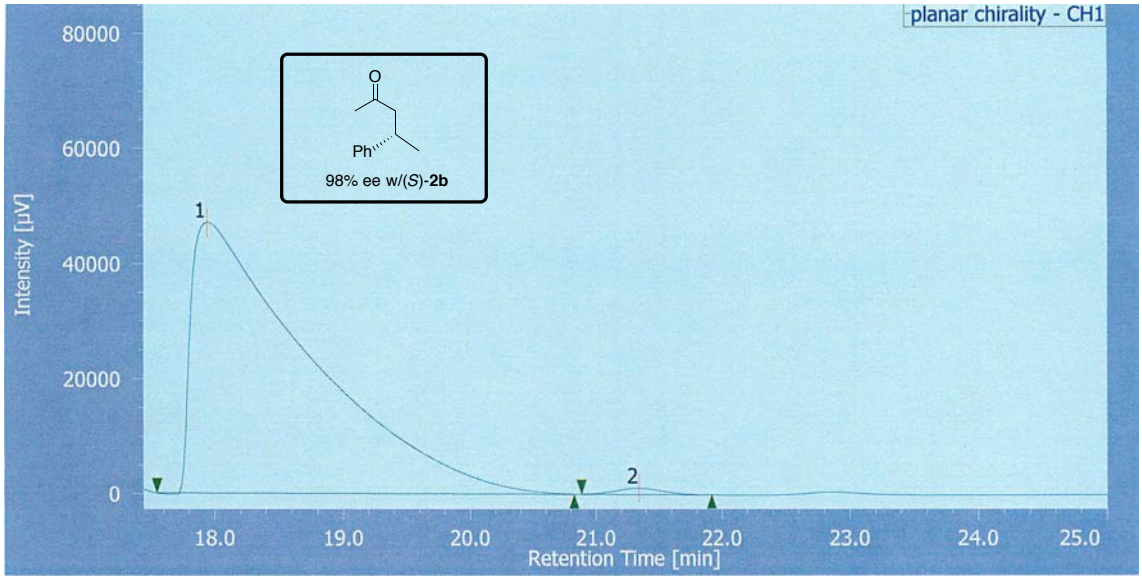




#	peak name	CH	tR[min]	area [µV·sec]	height [µV]	area %	height %	NTP	resolu-tion	symmetry coefficient
1	(*S*)-isomer	1	7.583	8330851	395877	99.907	99.907	4375	13.353	2.071
2	(*R*)-isomer	1	16.833	7750	220	0.056	0.093	5235	N/A	1.357

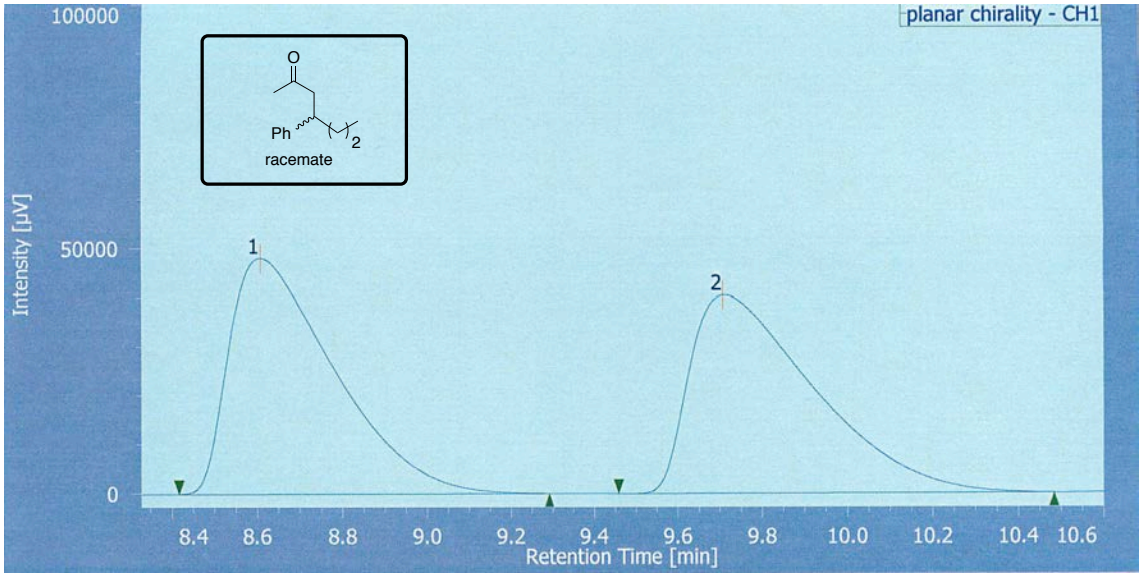
Chiral HPLC Analysis of (*S*)-4-Phenylpentan-2-one.[7]
chiral column: Chiralcel OJ-H; eluent: hexane/^{i}PrOH = 99.5/0.5; flow rate: 0.5 mL/min. 26 °C.

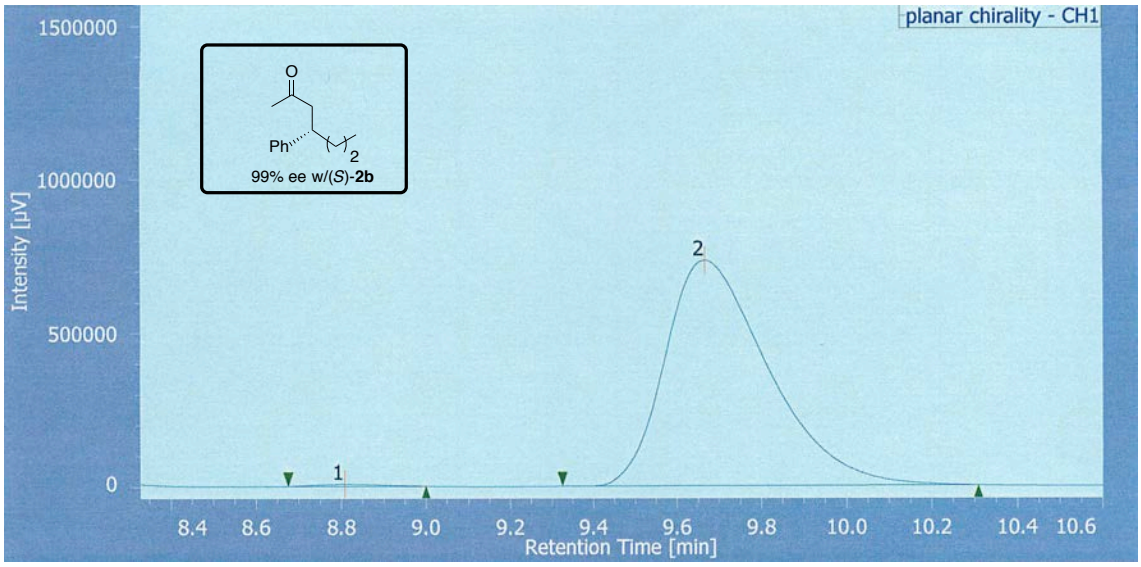




#	peak name	CH	tR[min]	area [µV·sec]	height [µV]	area %	height %	NTP	resolu-tion	symmetry coefficient
1	(*S*)-isomer	1	17.942	3022600	46989	99.071	97.726	1960	2.940	6.015
2	(*R*)-isomer	1	21.342	28343	1093	0.929	2.274	14960	N/A	1.043

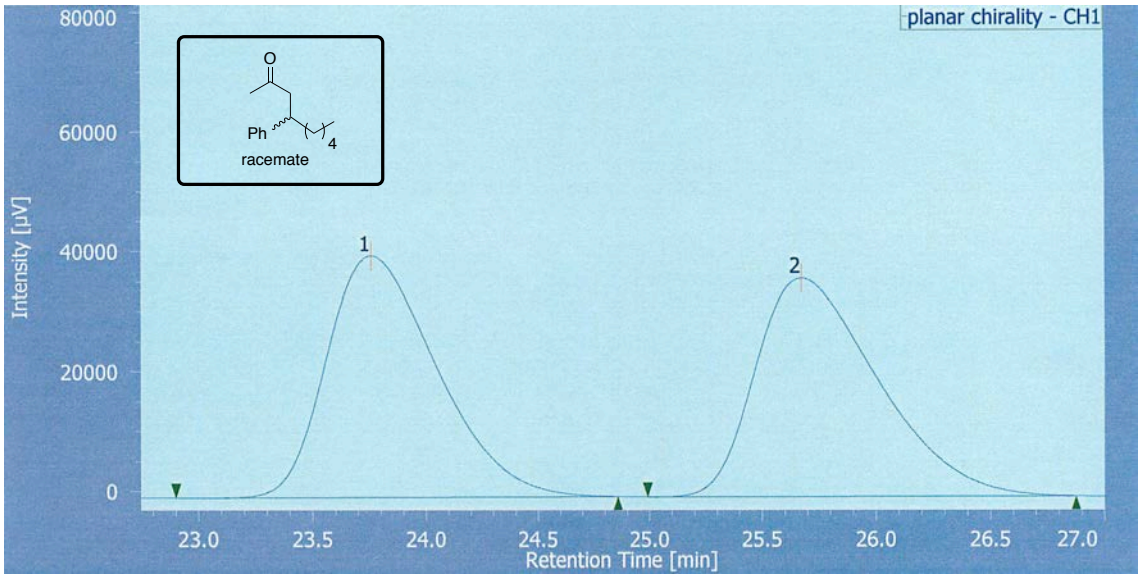
Chiral HPLC Analysis of (*S*)-4-Phenylheptan-2-one.[8]
chiral column: Chiralcel OJ-H; eluent: hexane/^{i}PrOH = 99/1; flow rate: 0.5 mL/min. 26 °C.

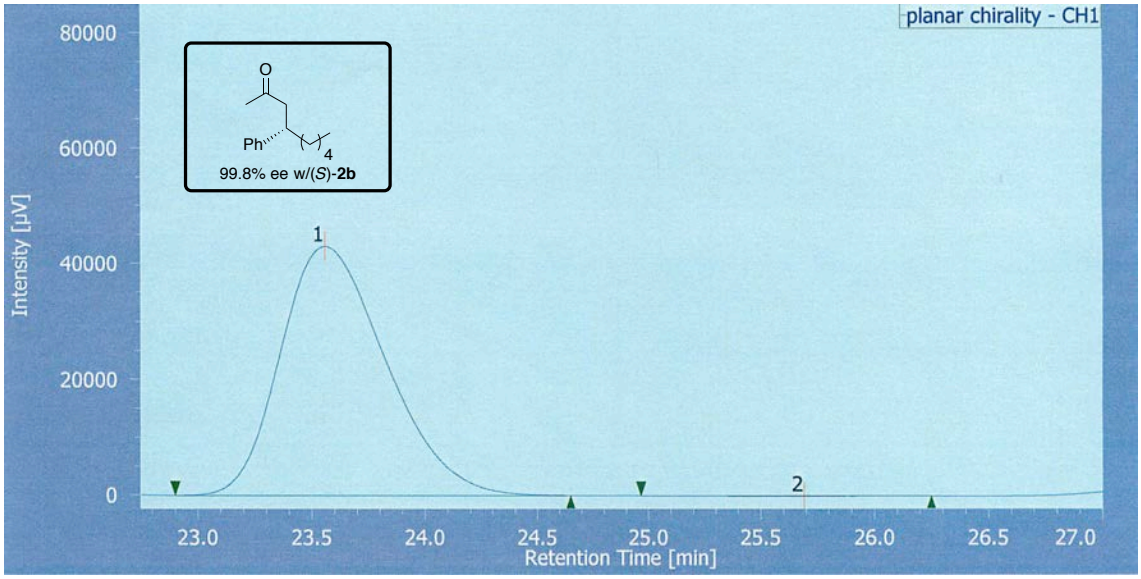




#	peak name	CH	tR[min]	area [µV·sec]	height [µV]	area %	height %	NTP	resolu-tion	symmetry coefficient
1	(*R*)-isomer	1	8.808	70939	6568	0.568	0.891	13149	2.299	1.216
2	(*S*)-isomer	1	9.667	12421609	730285	99.432	99.109	7674	N/A	1.439

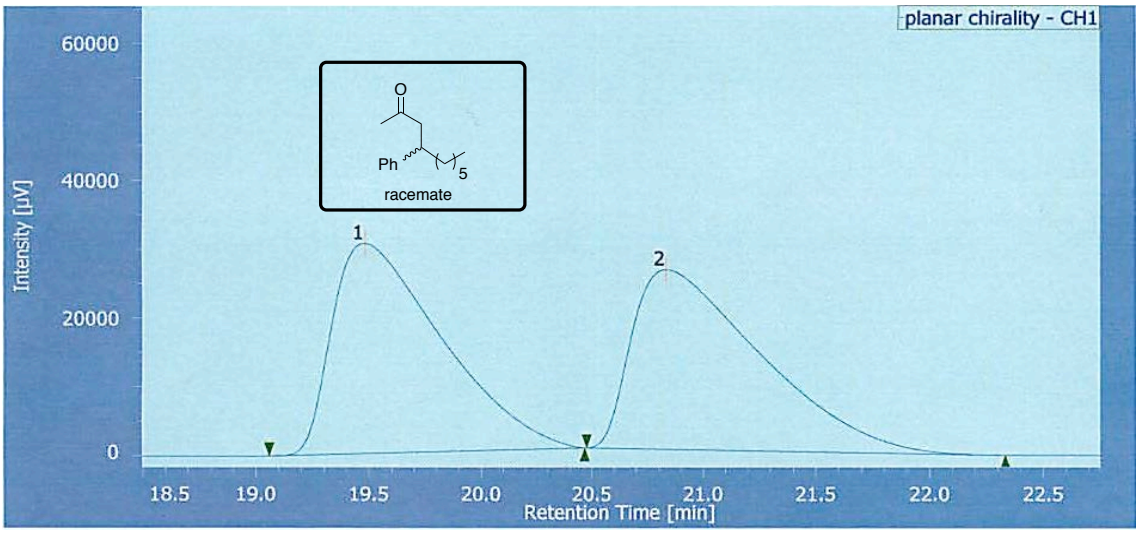
Chiral HPLC Analysis of (*S*)-4-Phenylnonan-2-one.[7]
chiral column: Chiralcel OJ-H; eluent: hexane/^{i}PrOH = 99/1; flow rate: 0.25 mL/min. 26 °C.

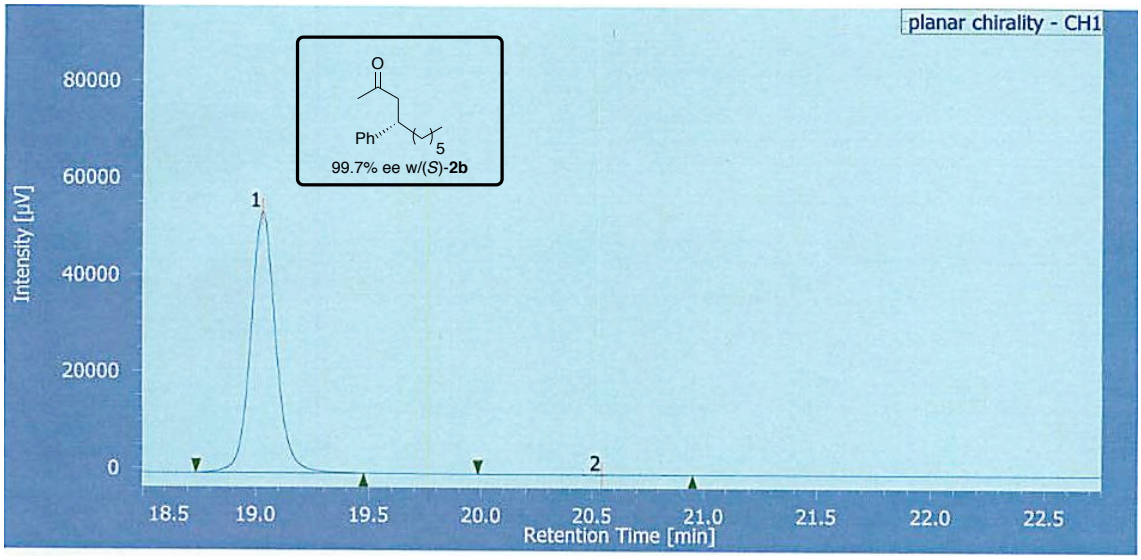




#	peak name	CH	tR[min]	area [µV·sec]	height [µV]	area %	height %	NTP	resolu-tion	symmetry coefficient
1	(*S*)-isomer	1	23.558	1389340	42984	99.886	99.918	12029	2.030	1.281
2	(*R*)-isomer	1	25.692	1589	35	0.114	0.082	6776	N/A	0.817

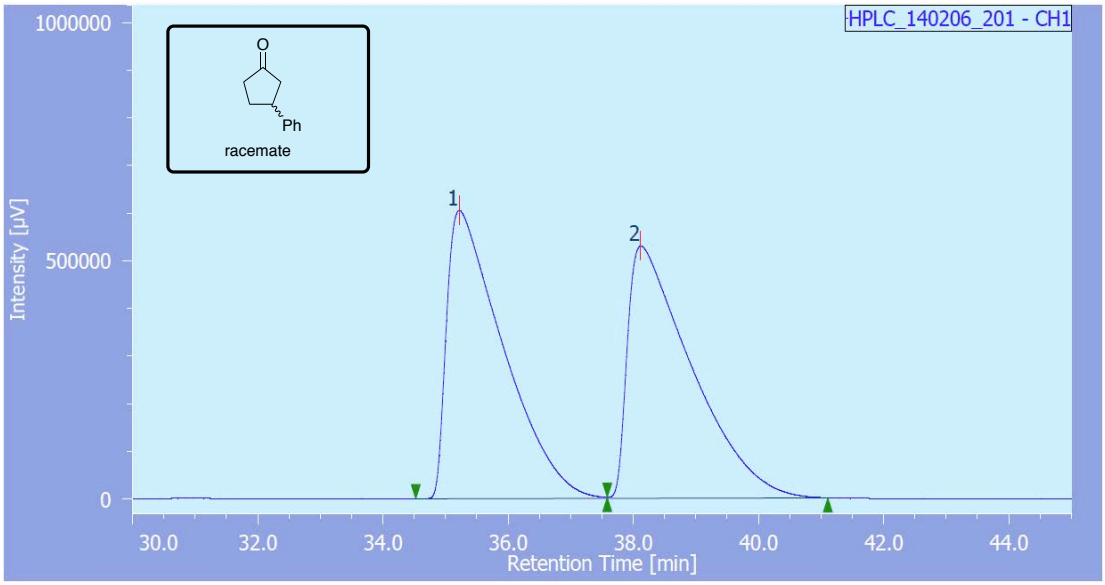
Chiral HPLC Analysis of (*S*)-4-Phenyldecen-2-one.[9]
chiral column: Chiralcel OJ-H; eluent: hexane/^{i}PrOH = 99/1; flow rate: 0.4 mL/min. 26 °C.

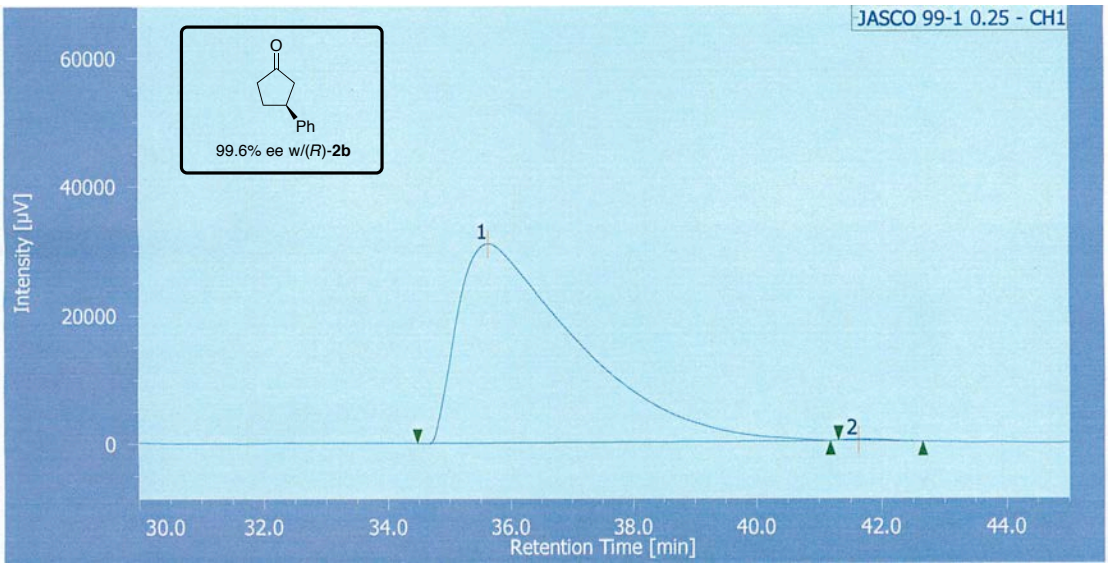




#	peak name	CH	tR[min]	area [µV·sec]	height [µV]	area %	height %	NTP	resolu-tion	symmetry coefficient
1	(*S*)-isomer	1	19.025	414764	53814	99.872	99.973	153499	1.876	1.138
2	(*R*)-isomer	1	20.542	531	15	0.128	0.027	3315	N/A	0.850

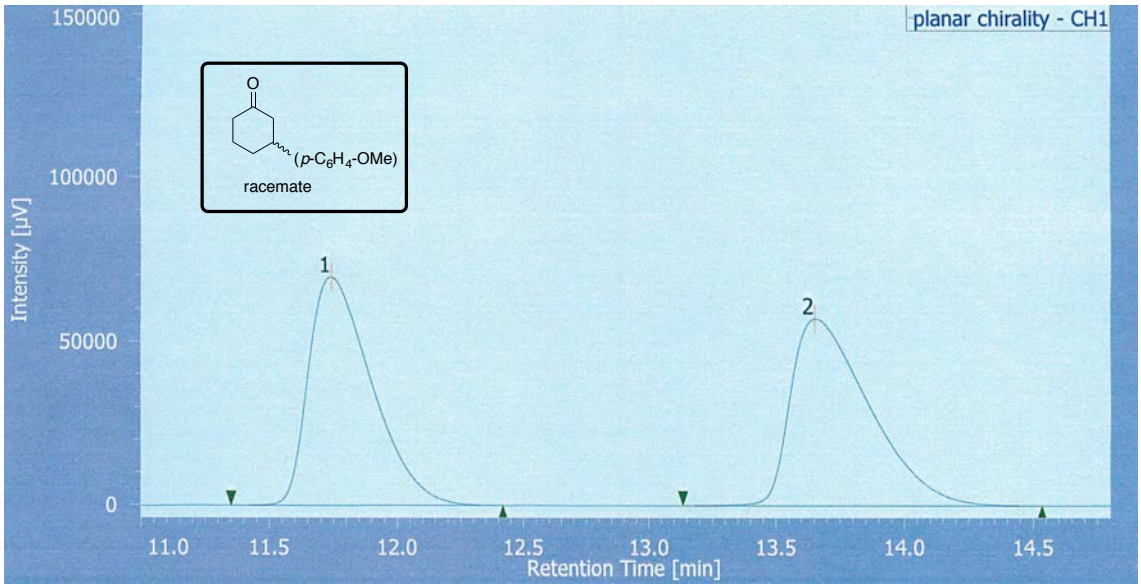
Chiral HPLC Analysis of (*R*)-3-Phenylcyclopentanone.
chiral column: Chiralcel OB-H; eluent: hexane/^{i}PrOH = 99/1; flow rate: 0.7 mL/min; 27 °C.

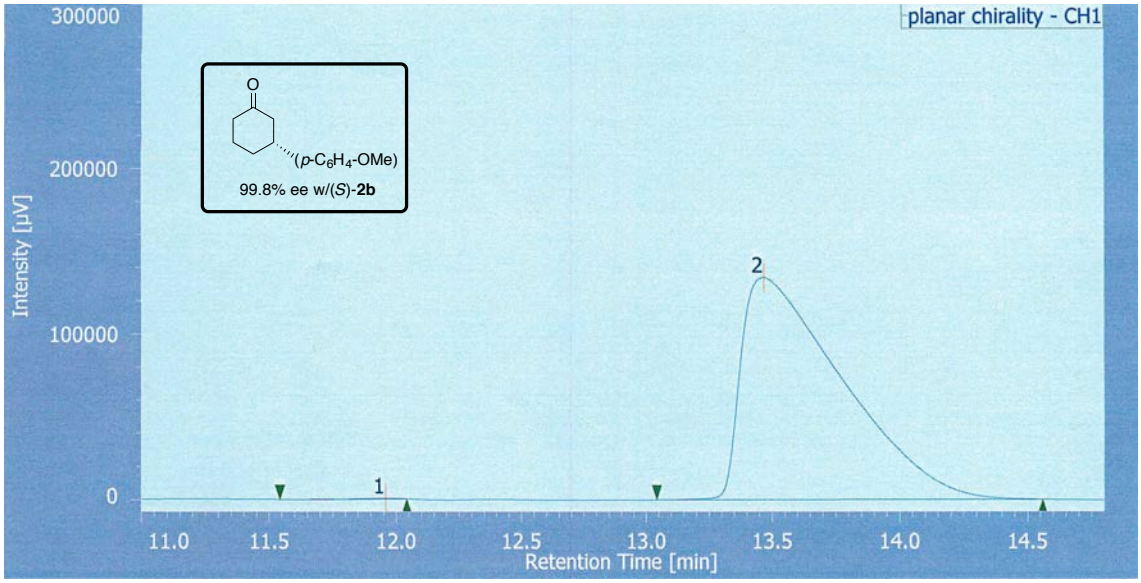




#	peak name	CH	tR[min]	area [µV·sec]	height [µV]	area %	height %	NTP	resolu-tion	symmetry coefficient
1	(*S*)-isomer	1	35.625	4206171	30893	99.808	99.405	1643	2.553	2.795
2	(*R*)-isomer	1	41.625	8103	185	0.192	0.595	19339	N/A	2.051

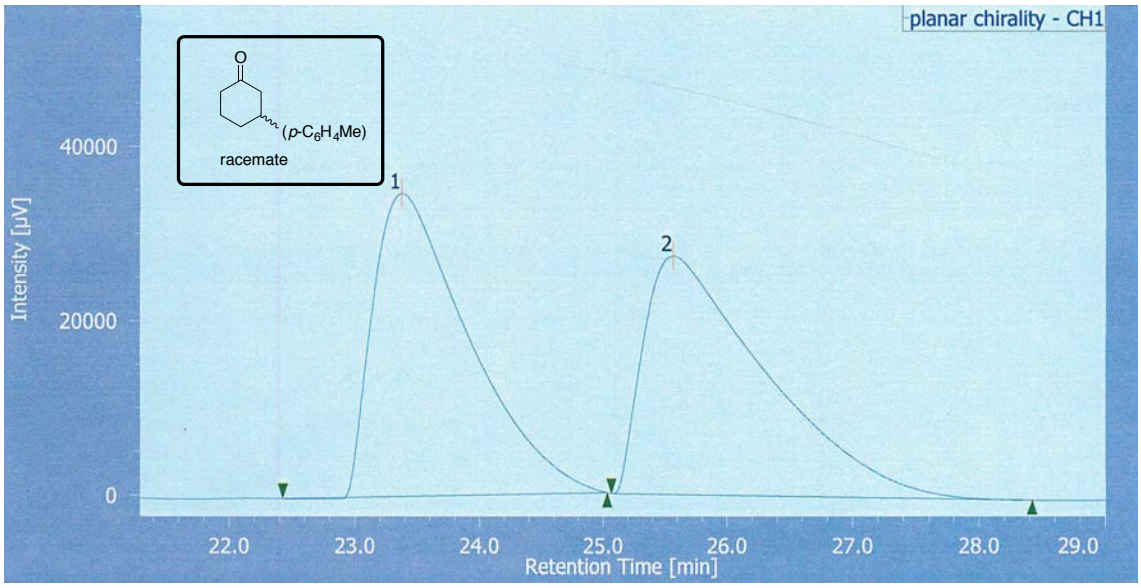
Chiral HPLC Analysis of (*R*)-3-(4-Methoxylphenyl)cyclohexanone.[10]
chiral column: Chiralcel OJ-H; eluent: hexane/^{i}PrOH = 9/1; flow rate: 1.0 mL/min; 40 °C.

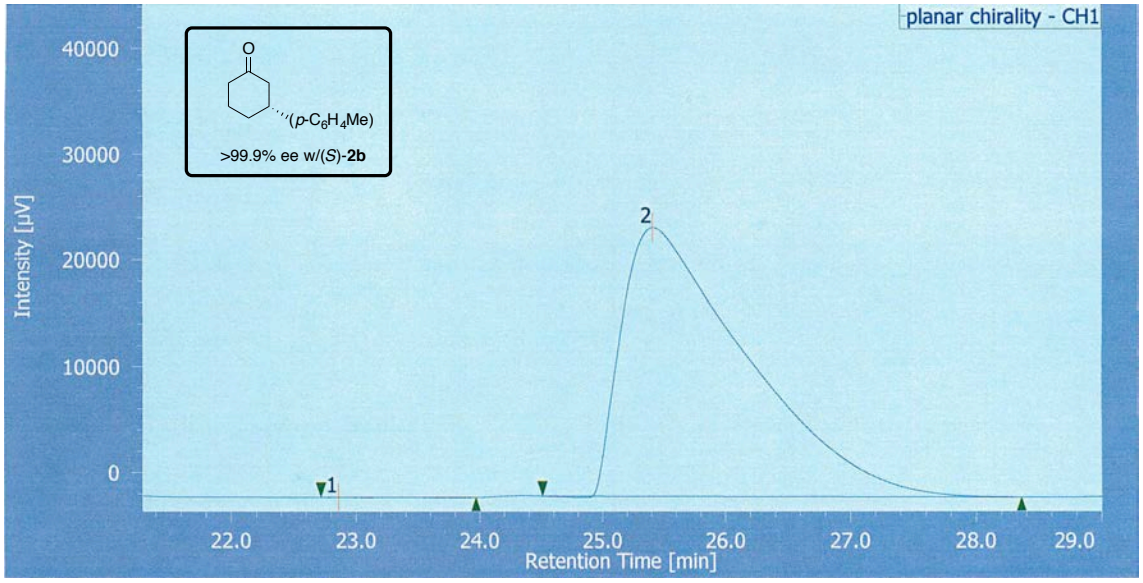




#	peak name	CH	tR[min]	area [µV·sec]	height [µV]	area %	height %	NTP	resolu-tion	symmetry coefficient
1	(*S*)-isomer	1	11.958	3797	445	0.103	0.331	38074	3.066	0.776
2	(*R*)-isomer	1	13.467	3698560	133944	99.897	99.669	5280	N/A	2.869

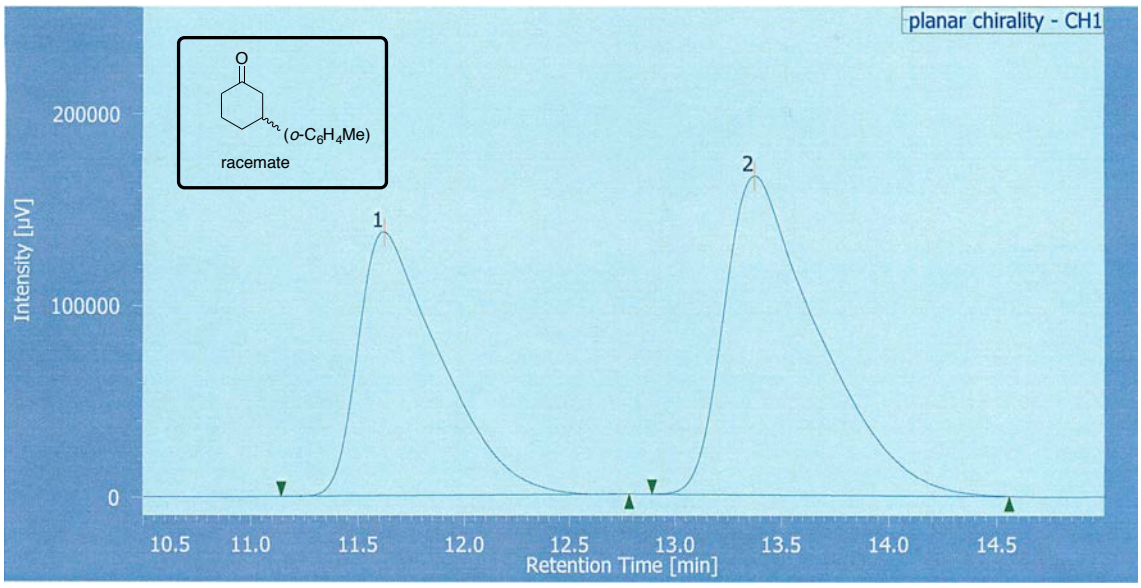
Chiral HPLC Analysis of (*R*)-3-(4-Methylphenyl)cyclohexanone.[10]
chiral column: Chiralcel OJ-H; eluent: hexane/^{i}PrOH = 99.5/0.5; flow rate: 1.0 mL/min; 27 °C.

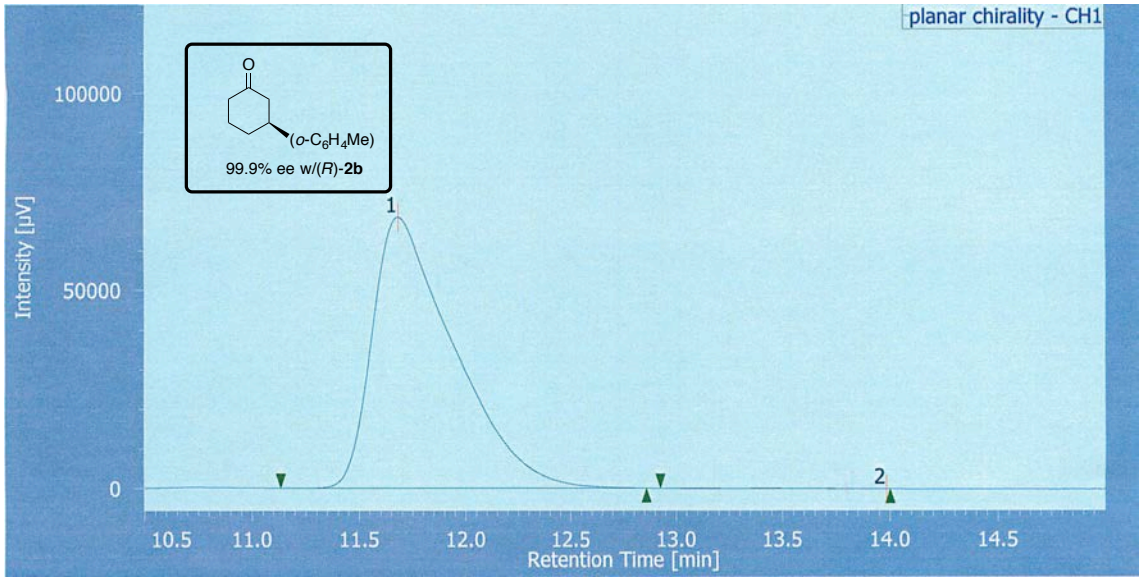




#	peak name	CH	tR[min]	area [µV·sec]	height [µV]	area %	height %	NTP	resolu-tion	symmetry coefficient
1	(*S*)-isomer	1	22.858	17	3	0.001	0.014	11233	1.847	15.276
2	(*R*)-isomer	1	25.408	1769174	25233	99.999	99.986	2969	N/A	2.652

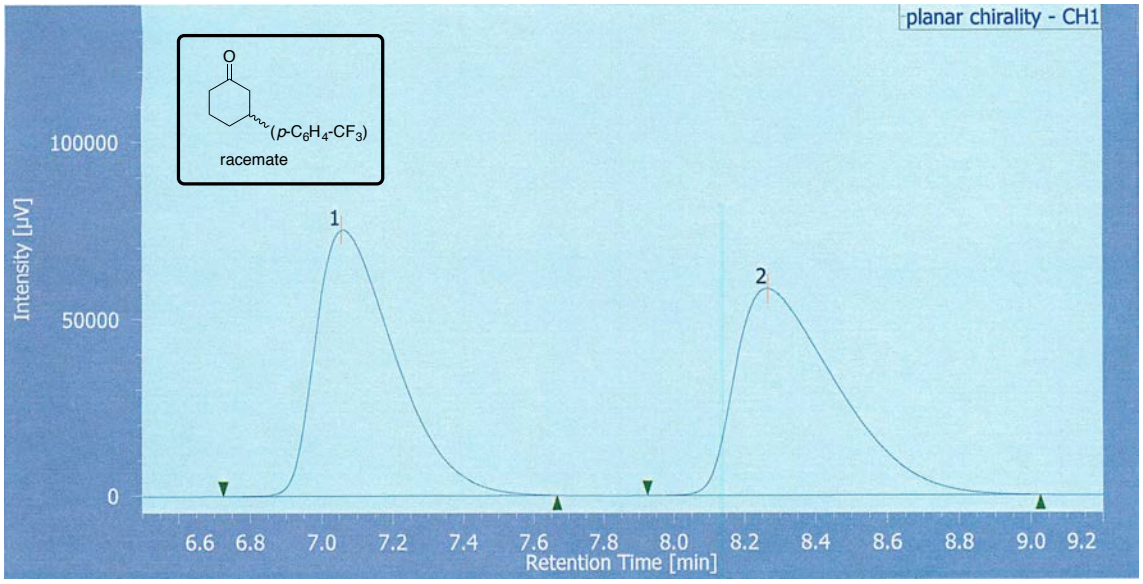
Chiral HPLC Analysis of (*S*)-3-(2-Methylphenyl)cyclohexanone.[11]
chiral column: Chiralpak AD-H; eluent: hexane/^{i}PrOH = 19/1; flow rate: 0.5 mL/min.

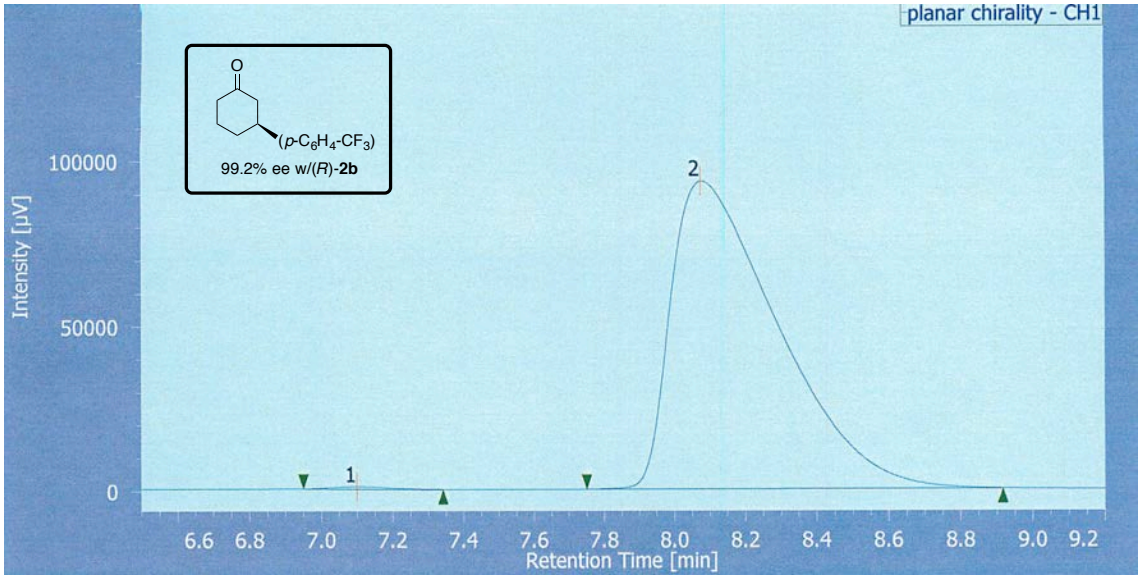




#	peak name	CH	tR[min]	area [µV·sec]	height [µV]	area %	height %	NTP	resolu-tion	symmetry coefficient
1	(*S*)-isomer	1	11.683	1822378	68297	99.968	99.996	4483	1.847	1.837
2	(*R*)-isomer	1	13.983	589	3	0.032	0.004	967	N/A	0.508

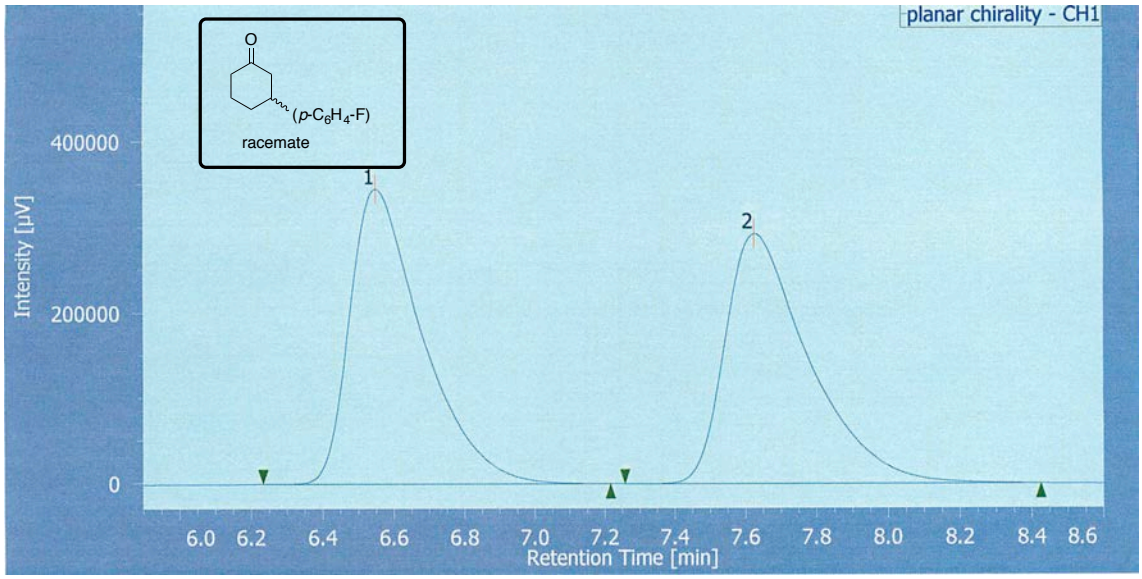
Chiral HPLC Analysis of (*S*)-3-(4-Trifluoromethylphenyl)cyclohexanone.[12]
chiral column: Chiralpak AS; eluent: hexane/^{i}PrOH = 9/1; flow rate: 1.0 mL/min; 40 °C.

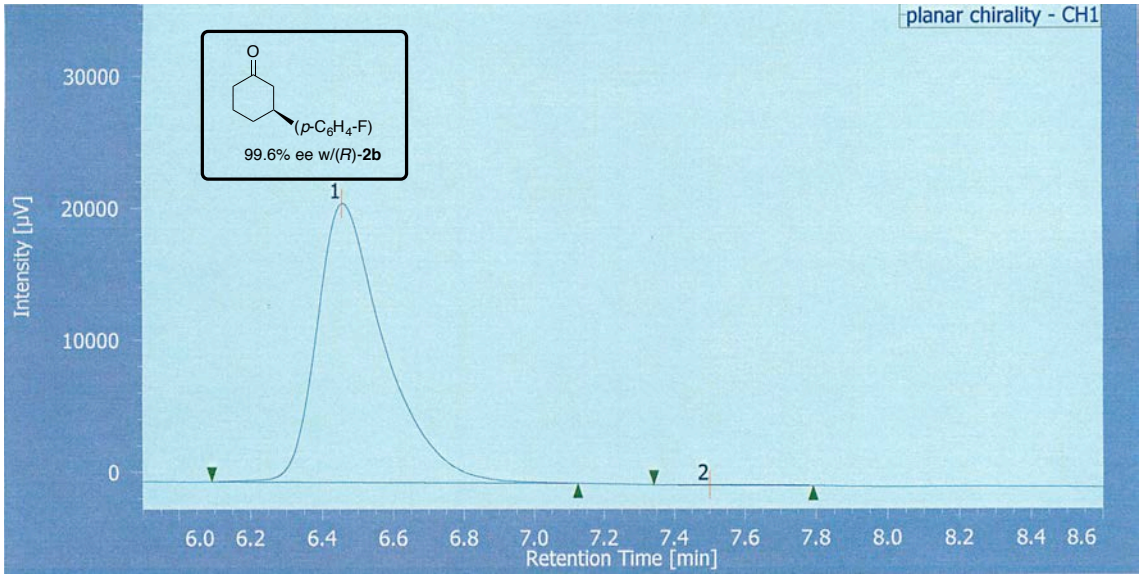




#	peak name	CH	tR[min]	area [µV·sec]	height [µV]	area %	height %	NTP	resolu-tion	symmetry coefficient
1	(*R*)-isomer	1	7.100	7560	711	0.387	0.758	9752	2.321	1.229
2	(*S*)-isomer	1	8.075	1945817	93117	99.613	99.242	3388	N/A	2.140

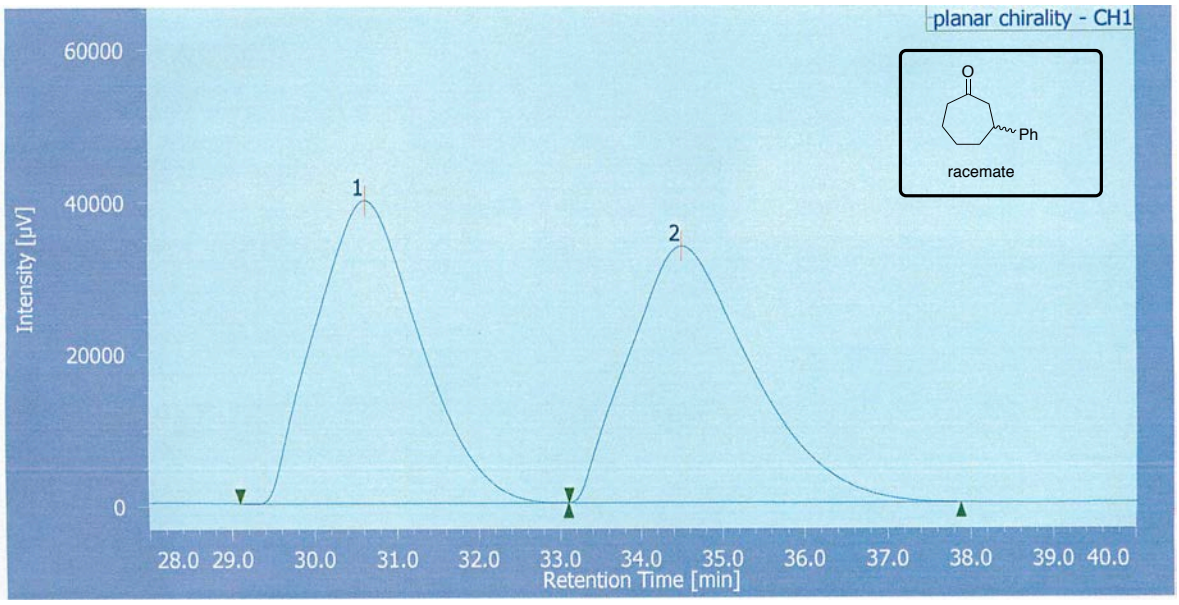
Chiral HPLC Analysis of (*S*)-3-(4-Fluoromethylphenyl)cyclohexanone.
chiral column: Chiralpak AD; eluent: hexane/^{i}PrOH = 9/1; flow rate: 1.0 mL/min; 26 °C.

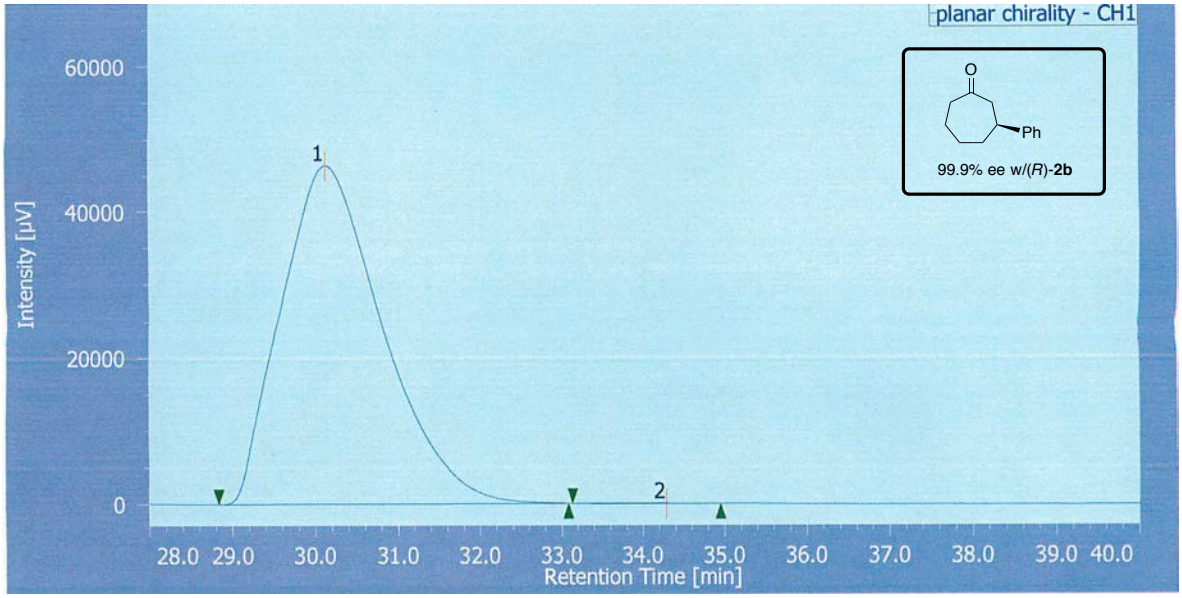




#	peak name	CH	tR[min]	area [µV·sec]	height [µV]	area %	height %	NTP	resolu-tion	symmetry coefficient
1	(*S*)-isomer	1	6.458	279963	21128	99.807	99.869	6219	2.475	1.532
2	(*R*)-isomer	1	7.500	542	28	0.193	0.131	3373	N/A	2.494

Chiral HPLC Analysis of (*S*)-3-Phenylcycloheptanone.[13]
chiral column: Chiralcel OD-H; eluent: hexane/^{i}PrOH = 99/1; flow rate: 0.5 mL/min; 26 °C.

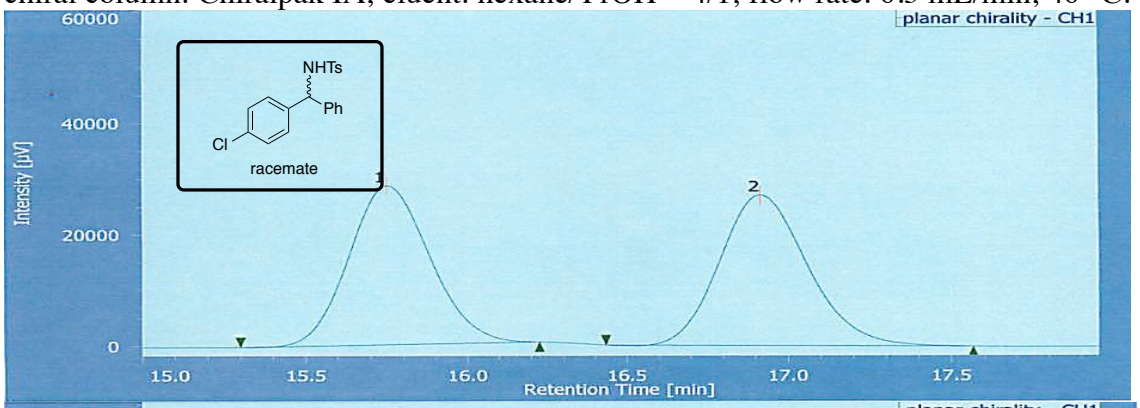


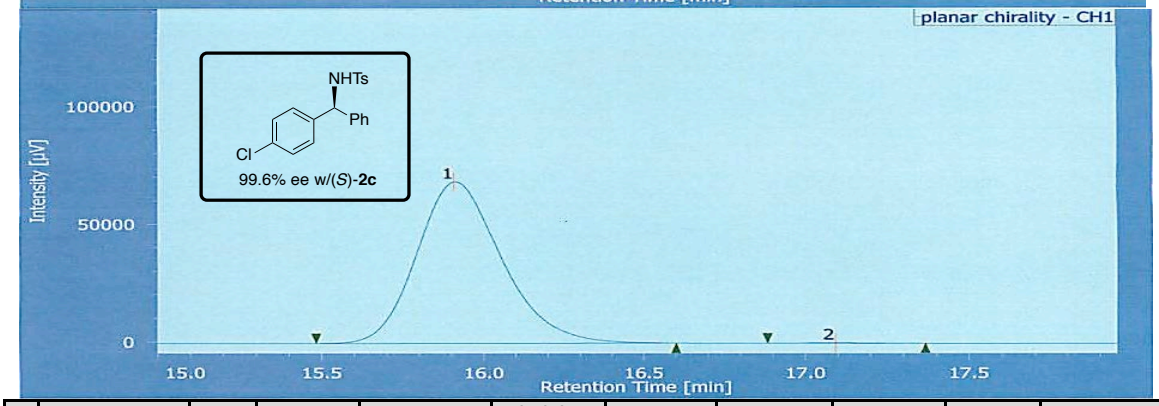


#	peak name	CH	tR[min]	area [µV·sec]	height [µV]	area %	height %	NTP	resolu-tion	symmetry coefficient
1	(*S*)-isomer	1	30.125	3914636	46307	99.933	99.920	2827	1.881	1.347
2	(*R*)-isomer	1	34.283	2635	37	0.067	0.080	4001	N/A	0.785

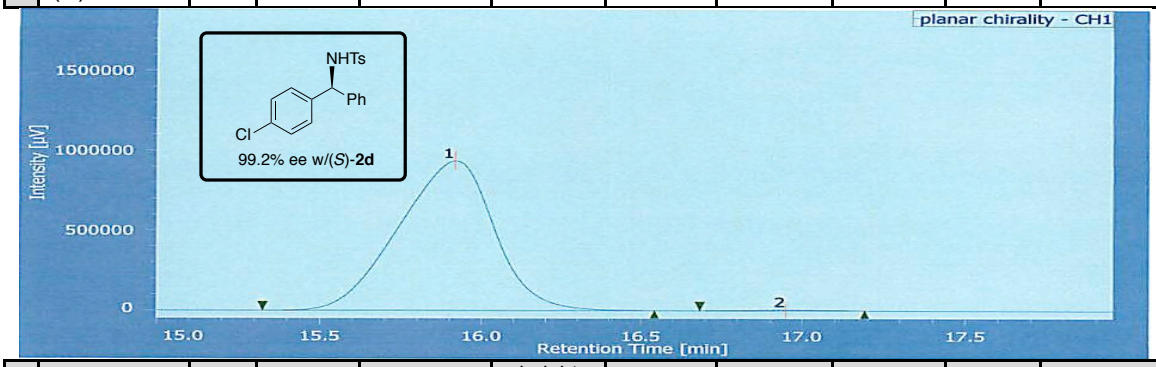
Chiral HPLC Analysis of *N*-[(*S*)-(4-Chlorophenyl)phenylmethyl]-4-methyl benzenesulfonamide.[14]

chiral column: Chiralpak IA; eluent: hexane/^{i}PrOH = 4/1; flow rate: 0.5 mL/min; 40 °C.



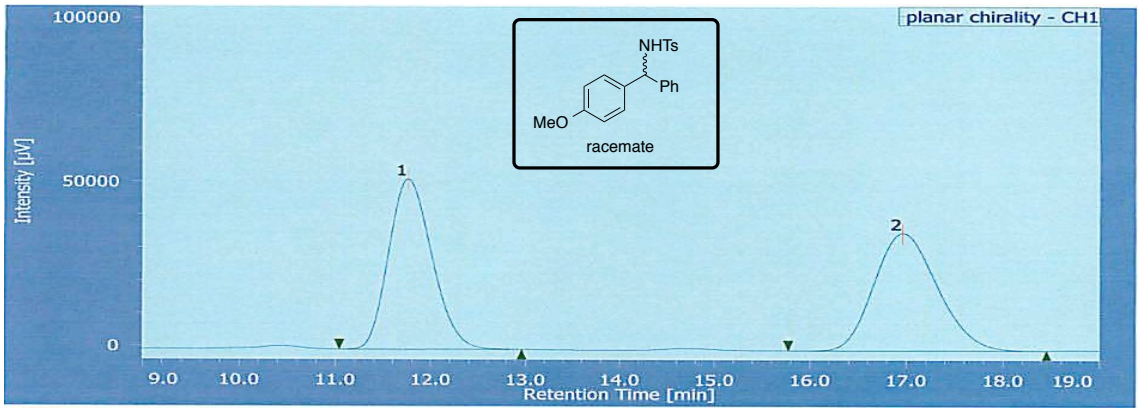


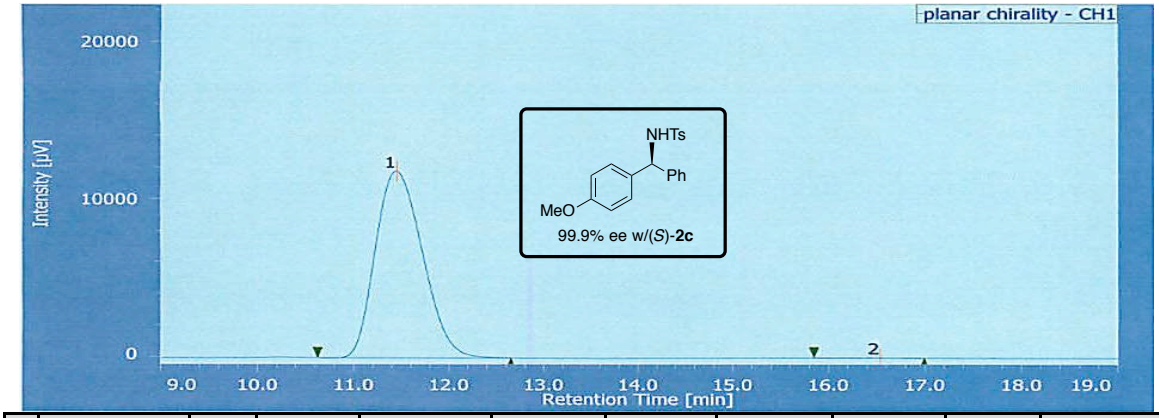
#	peak name	CH	tR[min]	area [µV·sec]	height [µV]	area %	height %	NTP	resolu-tion	symmetry coefficient
1	(*S*)-isomer	1	15.908	1254006	68453	99.821	99.778	18086	2.666	1.224
2	(*R*)-isomer	1	17.092	2246	152	0.179	0.222	26891	N/A	1.187



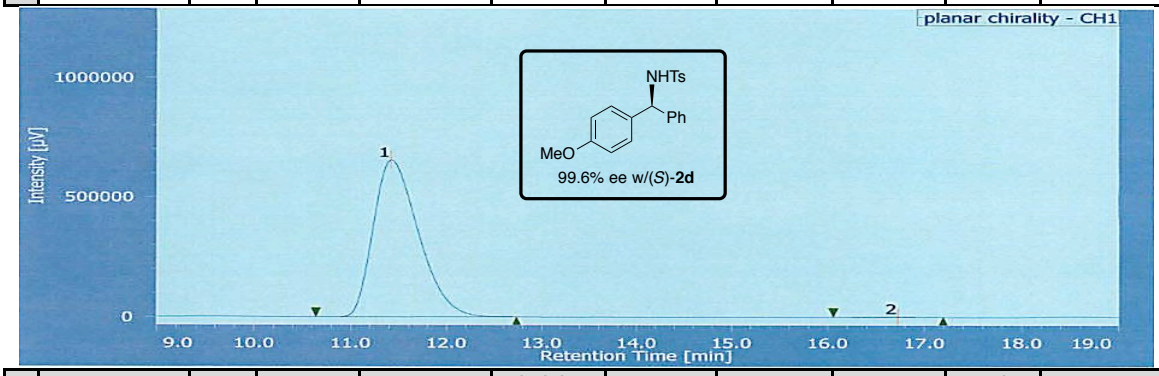
#	peak name	CH	tR[min]	area [µV·sec]	height [µV]	area %	height %	NTP	resolu-tion	symmetry coefficient
1	(*S*)-isomer	1	15.917	19295665	935499	99.608	99.481	13500	2.110	0.906
2	(*R*)-isomer	1	16.950	75871	4882	0.392	0.519	24378	N/A	0.992

Chiral HPLC Analysis of *N*-[(*S*)-(4-Methoxyphenyl)phenylmethyl]tosylamide.[14]
chiral column: Chiralcel OD-H; eluent: hexane/^{i}PrOH = 4/1; flow rate: 0.75 mL/min; 29 °C.



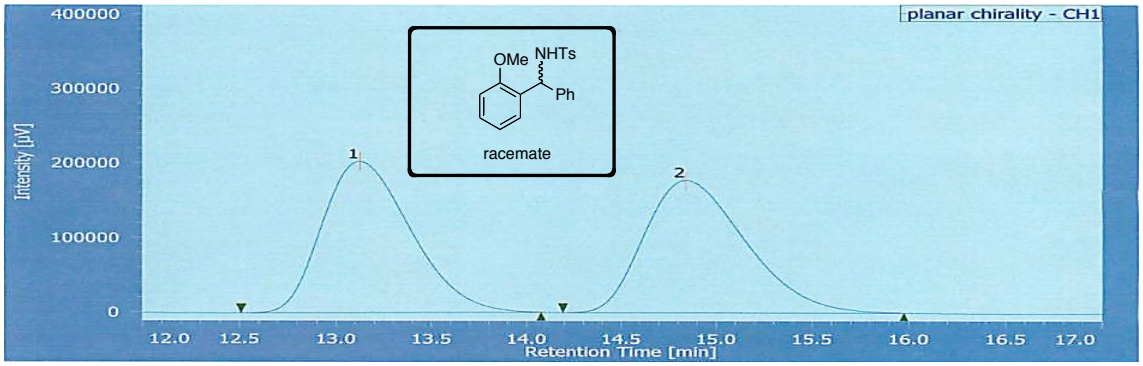


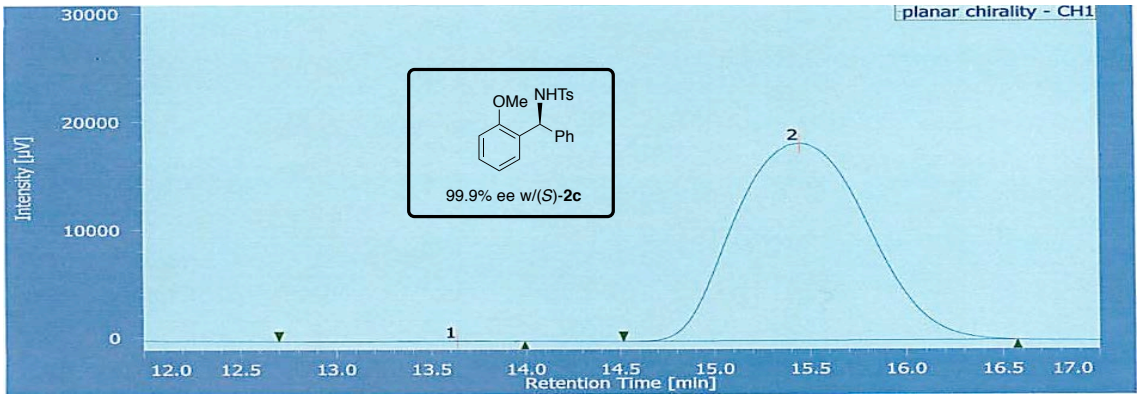
#	peak name	CH	tR[min]	area [µV·sec]	height [µV]	area %	height %	NTP	resolu-tion	symmetry coefficient
1	(*S*)-isomer	1	11.450	403526	11798	99.973	99.921	2426	7.536	1.207
2	(*R*)-isomer	1	16.533	110	9	0.027	0.079	24477	N/A	0.930



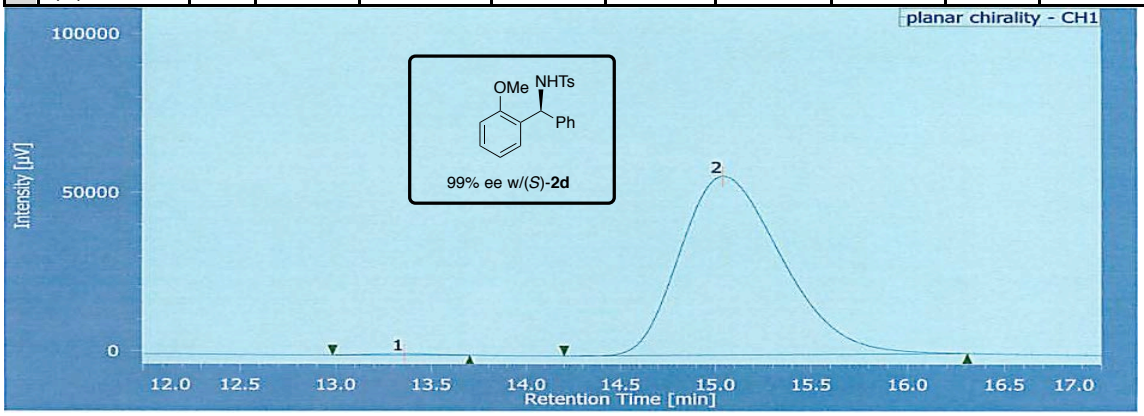
#	peak name	CH	tR[min]	area [µV·sec]	height [µV]	area %	height %	NTP	resolu-tion	symmetry coefficient
1	(*S*)-isomer	1	11.417	21283792	654378	99.811	99.834	2809	5.610	1.425
2	(*R*)-isomer	1	16.725	40212	1089	0.189	0.166	4170	N/A	0.869

Chiral HPLC Analysis of *N*-[(*S*)-(2-Methoxyphenyl)phenylmethyl]tosylamide.[10]
chiral column: Chiralcel OD-H; eluent: hexane/^{i}PrOH = 4/1; flow rate: 0.5 mL/min; 30 °C.





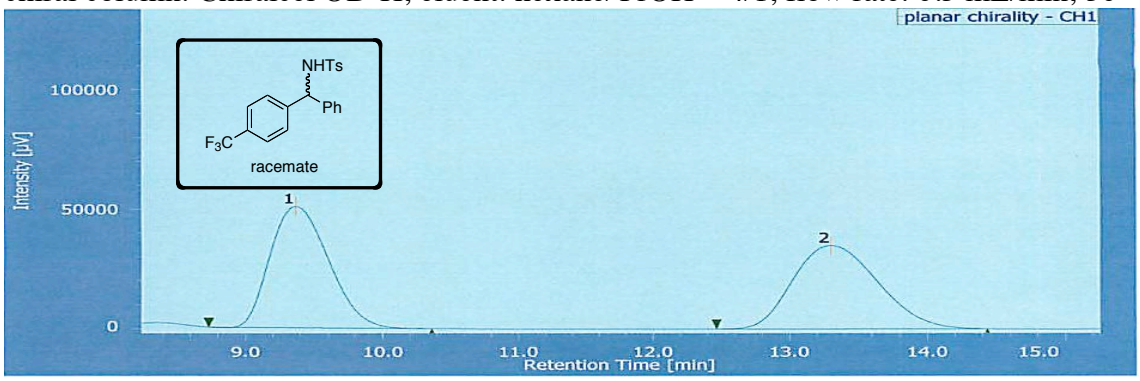
#	peak name	CH	tR[min]	area [µV·sec]	height [µV]	area %	height %	NTP	resolu-tion	symmetry coefficient
1	(*R*)-isomer	1	13.633	346	19	0.039	0.104	5459	1.753	1.430
	(*S*)-isomer	1	15.450	18178	18178	99.961	99.896	2126	N/A	1.106

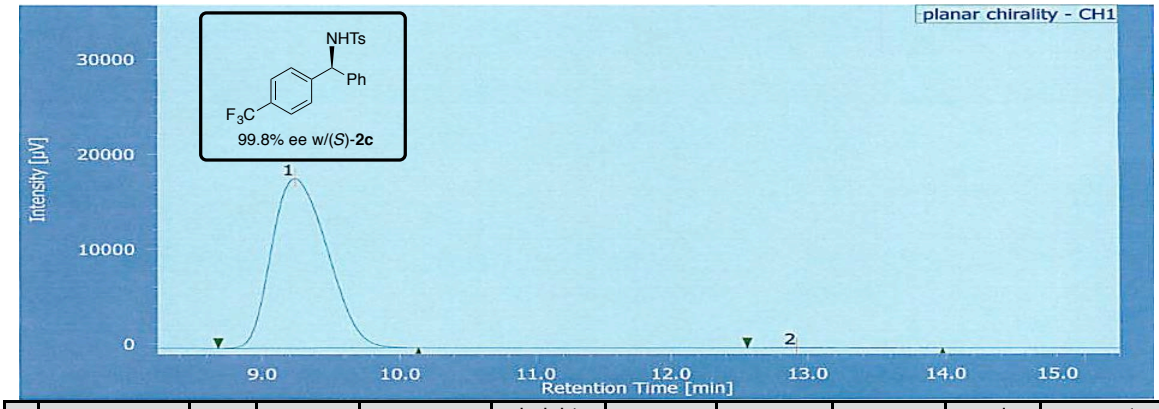


#	peak name	CH	tR[min]	area [µV·sec]	height [µV]	area %	height %	NTP	resolu-tion	symmetry coefficient
1	(*R*)-isomer	1	13.358	10405	426	0.498	0.751	5768	1.998	0.898
2	(*S*)-isomer	1	15.042	2079561	56256	99.502	99.249	3726	N/A	1.291

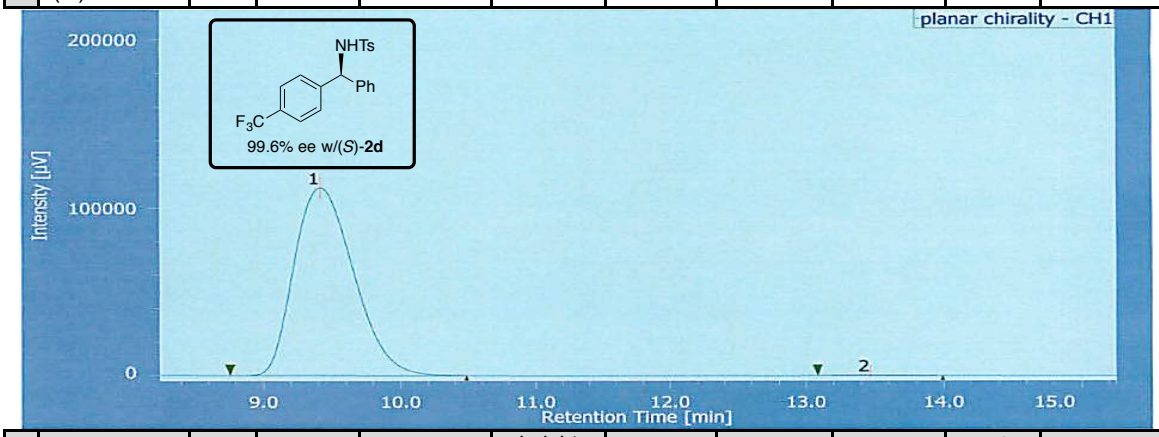
Chiral HPLC Analysis of *N*-[(*S*)-(4-Trifluoromethylphenyl)phenylmethyl]tosylamide.[10]

chiral column: Chiralcel OD-H; eluent: hexane/^{i}PrOH = 4/1; flow rate: 0.5 mL/min; 30 °C.



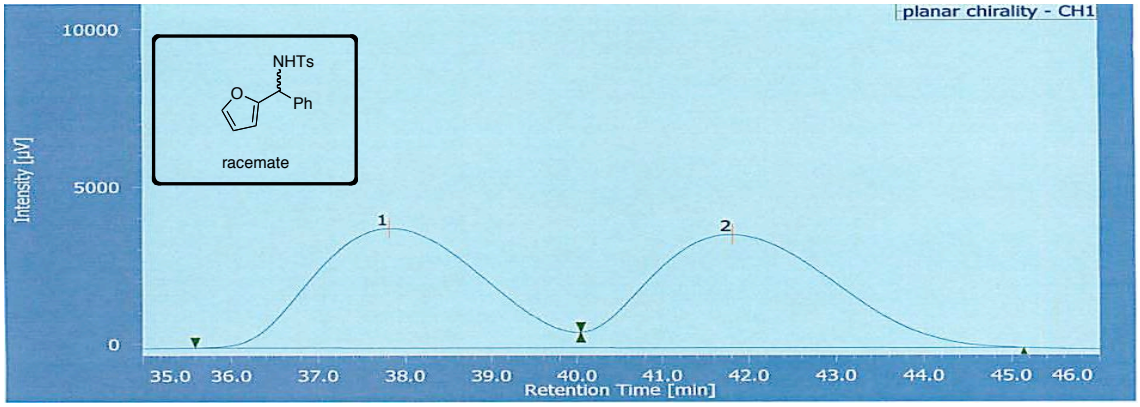


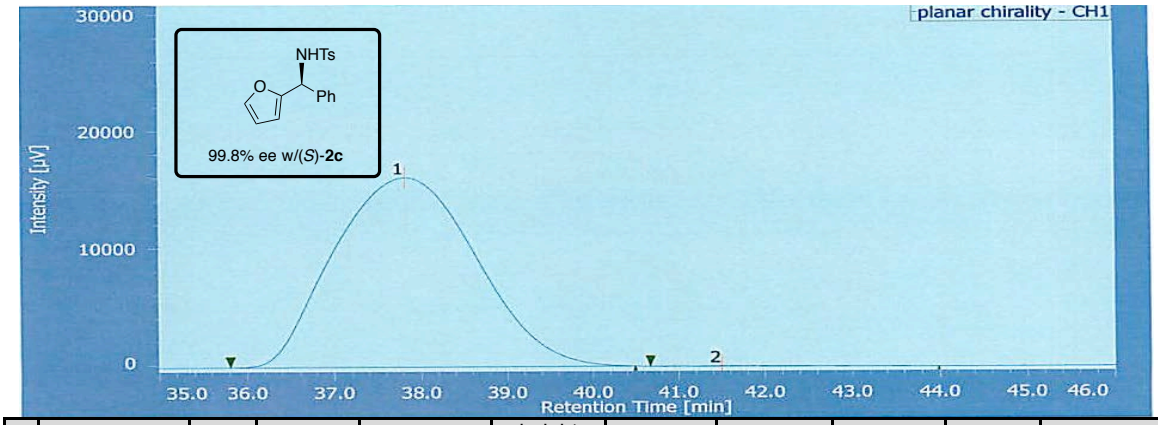
#	peak name	CH	tR[min]	area [µV·sec]	height [µV]	area %	height %	NTP	resolu-tion	symmetry coefficient
1	(*S*)-isomer	1	9.242	501116	17847	99.913	99.910	2286	4.435	1.253
2	(*R*)-isomer	1	12.917	438	16	0.087	0.090	3380	N/A	2.141



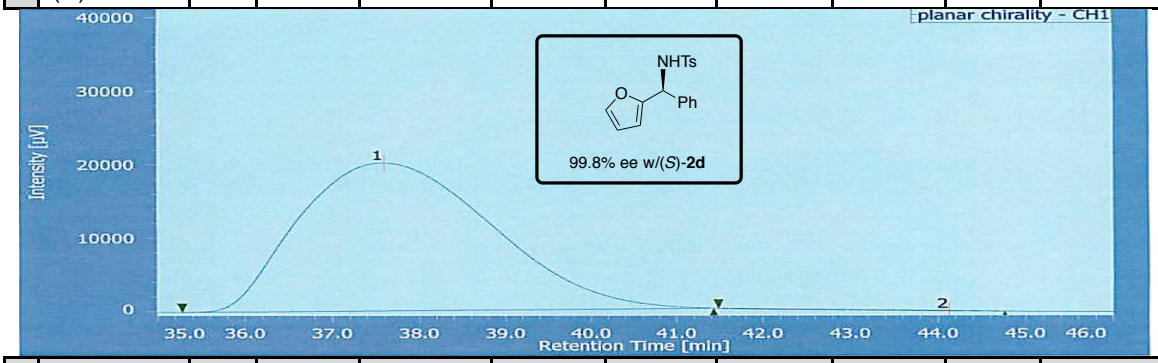
#	peak name	CH	tR[min]	area [µV·sec]	height [µV]	area %	height %	NTP	resolu-tion	symmetry coefficient
1	(*S*)-isomer	1	9.417	3365902	111958	99.792	99.804	2154	4.671	1.269
2	(*R*)-isomer	1	13.467	7018	220	0.208	0.196	3375	N/A	1.186

Chiral HPLC Analysis of *N*-[(*S*)-2-Furanylphenylmethyl] tosylamide.[10]
chiral column: Chiralcel OD-H; eluent: hexane/^{i}PrOH = 19/1; flow rate: 0.5 mL/min; 30 °C.



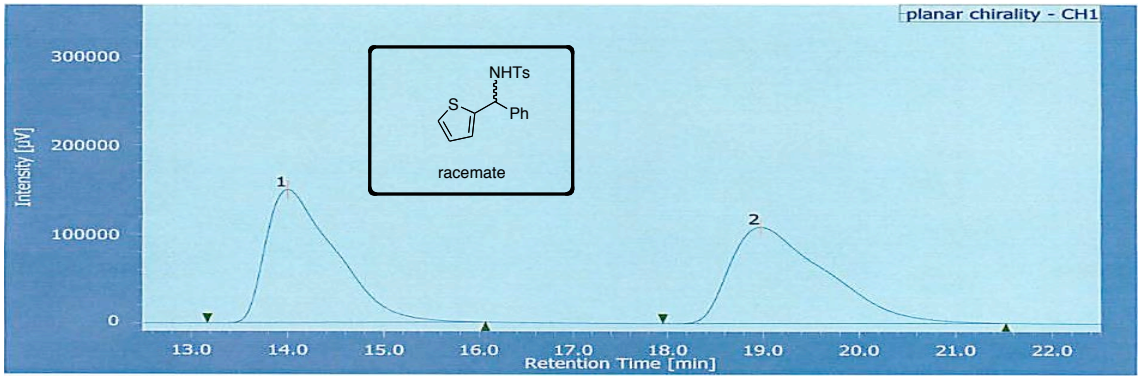


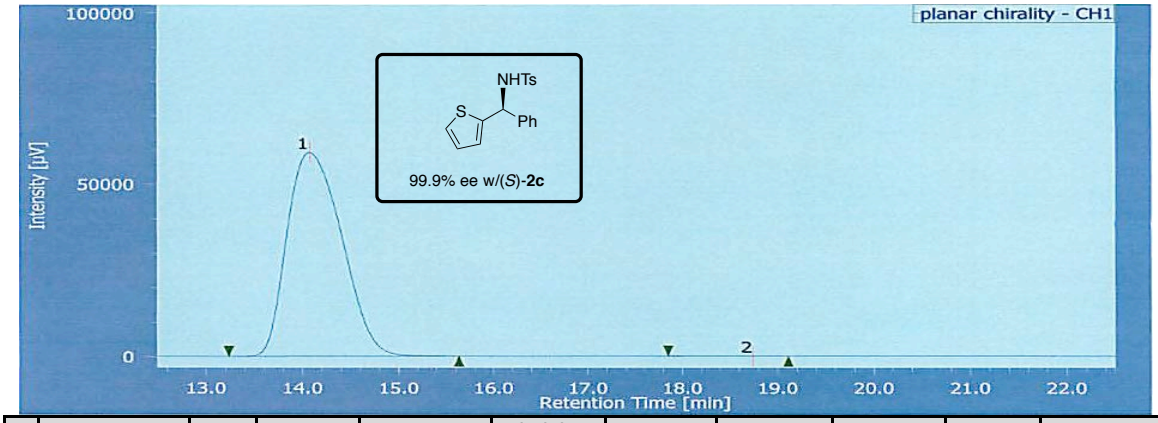
#	peak name	CH	tR[min]	area [µV·sec]	height [µV]	area %	height %	NTP	resolu-tion	symmetry coefficient
1	(*S*)-isomer	1	37.817	1844816	16156	99.909	99.874	2250	1.267	1.113
2	(*R*)-isomer	1	41.500	1673	20	0.091	0.126	3948	N/A	1.823



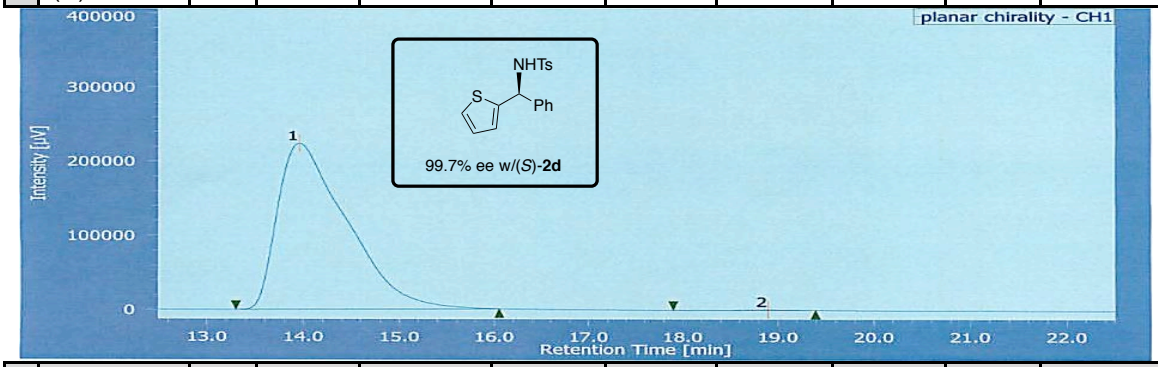
#	peak name	CH	tR[min]	area [µV·sec]	height [µV]	area %	height %	NTP	resolu-tion	symmetry coefficient
1	(*S*)-isomer	1	37.592	3115146	20108	99.900	99.984	1214	N/A	1.325
2	(*R*)-isomer	1	44.267	3108	3	0.100	0.016	3375	N/A	N/A

Chiral HPLC Analysis of *N*-[(*S*)- 2-thienylphenylmethyl]tosylamide.[15]
chiral column: Chiralcel OD-H; eluent: hexane/^{i}PrOH = 4/1; flow rate: 0.5 mL/min; 30 °C.



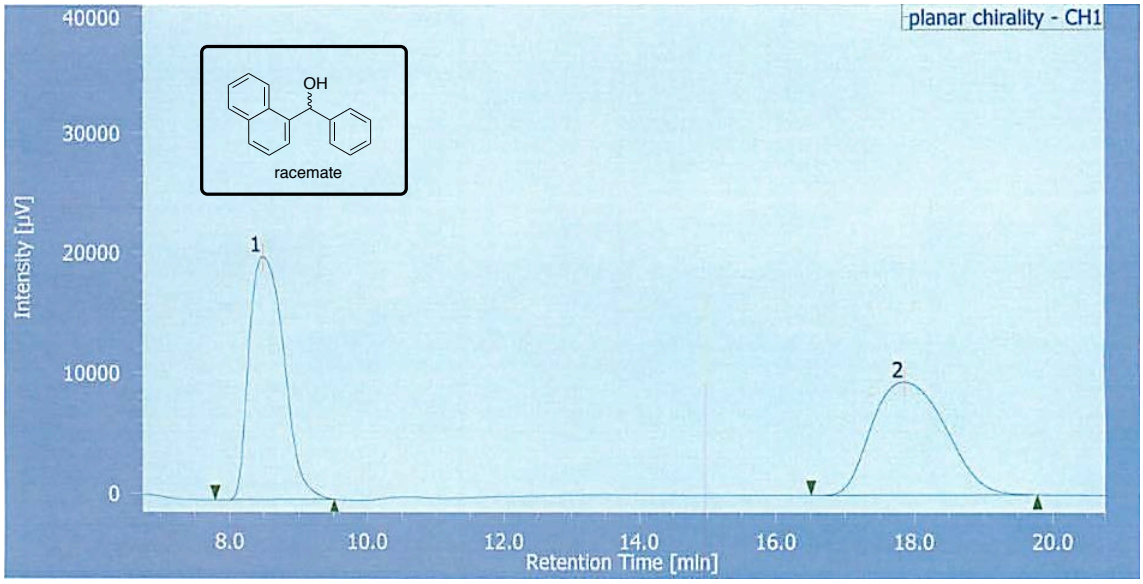


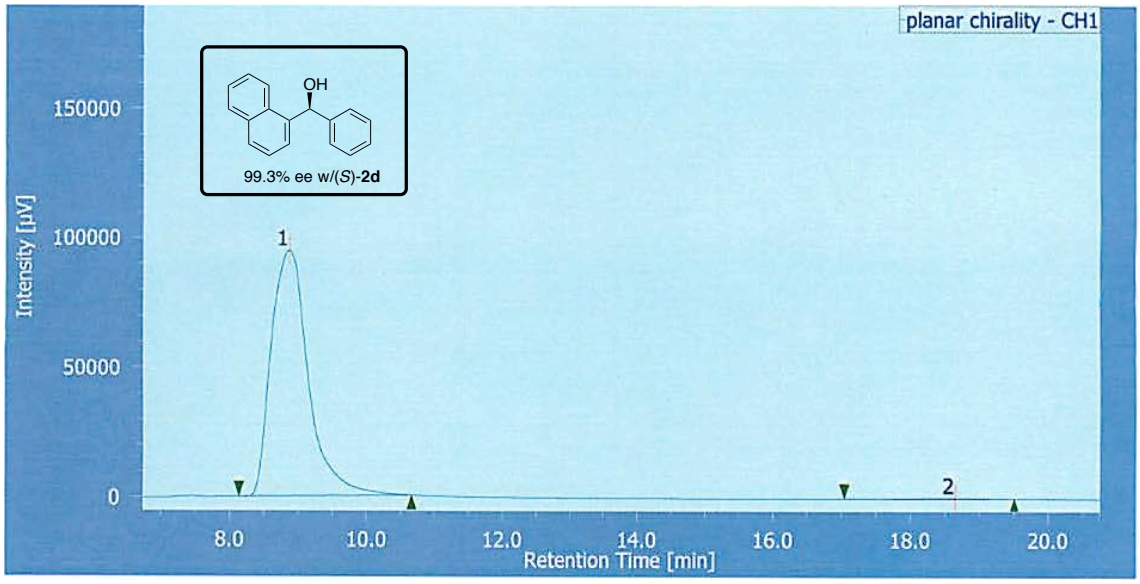
#	peak name	CH	tR[min]	area [µV·sec]	height [µV]	area %	height %	NTP	resolu-tion	symmetry coefficient
1	(*S*)-isomer	1	14.075	2334884	59069	99.959	99.947	2624	4.677	1.287
2	(*R*)-isomer	1	18.742	954	32	0.041	0.053	6909	N/A	0.801



#	peak name	CH	tR[min]	area [µV·sec]	height [µV]	area %	height %	NTP	resolu-tion	symmetry coefficient
1	(*S*)-isomer	1	13.958	11197053	223392	99.864	99.780	1701	4.406	1.943
2	(*R*)-isomer	1	18.900	15233	494	0.136	0.220	7131	N/A	1.137

Chiral HPLC Analysis of α-Phenyl-*2*-naphthalenemethanol.[16]
chiral column: Chiralcel OD-H; eluent: hexane/^{i}PrOH = 4/1; flow rate: 1.0 mL/min; 26 °C.





#	peak name	CH	tR[min]	area [µV·sec]	height [µV]	area %	height %	NTP	resolu-tion	symmetry coefficient
1	(*S*)-isomer	1	8.858	3552699	94602	99.640	99.785	1345	7.005	1.424
2	(*R*)-isomer	1	18.650	12853	204	0.360	0.215	1649	N/A	0.929

References.

(1) Ogasawara, M.; Wu, W.-Y.; Arae, S.; Morita, T.; Takahashi, T.; Kamikawa, K. *Angew. Chem. Int. Ed.* **2012**, *51*, 2951

(2) (a) Trnka, T. M.; Morgan, J. P.; Sanford, M. S.; Wilhelm, T. E.; Scholl, M.; Choi, T.-L.; Ding, S.; Day, M. D.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 2546. (b) Garber, S. B.; Kingsbury, J. S.; Gray, B. L.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2000**, *122*, 8168.

(3) Maercker, A. *Org. React.* **1965**, *14*, 270.

(4) Loim, N. M.; Kondrat'ev, P. V.; Solov'eva, N. P.; Antonovich, V. A.; Petrovskii, P. V.; Parnes, Z. N.; Kursanov, D. N. *J. Organomet. Chem.* **1981**, *209*, 233.

(5) Ferber, B.; Top, S.; Jaouen, G. *J. Organomet. Chem.* **2004**, *689*, 4872.

(6) Tseng, Y.-Y.; Kamikawa, K.; Wu, Q.; Takahashi, T.; Ogasawara, M. *Adv. Synth. Catal.* **2015**, *357*, 2255.

(7) Drinkel, E.; Briceño, A.; Dorta, R.; Dorta, R. *Organometallics*, **2010**, *29*, 2503.

(8) Feng, C.-G.; Wang, Z.-Q.; Shao, C.; Xu, M.-H. *Org. Lett.* **2008**, *10*, 4104.

(9) (a) Pucheault, M.; Darses, S.; Genêt, J.-P. *Eur. J. Org. Chem.* **2002**, 3552, (b) Roth, P. M. C.; Fletcher, S. P. *Org. Lett.* **2015**, *17*, 912.

(10) Yuan, W.-C.; Cun, L.-F.; Mi, A.-Q.; Jiang, Y.-Z.; Gong, L.-Z. *Tetrahedron,* **2009**, *65*, 4130.

(11) Trost, B. M.; Burns, A. C.; Tautz, T. *Org. Lett.* **2011**, *13*, 4566.

(12) Chen, Q.-A.; Dong, X.; Chen, M.-W.; Wang, D.-S.; Zhou, Y.-G.; Li, Y.-X. *Org. Lett.* **2010**, *12*, 1928

(13) Liu, C.-C.; Janmanchi, D.; Chen, C.-C. Wu, H.-L. *Eur. J. Org. Chem.* **2012**, 2503.

(14) Tokunaga, N.; Otomaru, Y.; Okamoto, K.; Ueyama, K.; Shintani, R. Hayashi. T. *J. Am. Chem. Soc.* **2004**, *126*, 13584.

(15) Wang, Z.-Q.; Feng, C.-G.; Xu, M.-H.; Lin, G.-Q. *J. Am. Chem. Soc.* **2007**, *129*, 5336.

(16) Nishimura, T.; Kumamoto, H.; Nagaosa, M.; Hayashi, T. *Chem. Commun.* **2009**, 5713.