Design and Synthesis of New Chiral Phosphorus–Olefin Bidentate Ligands and Their Use in the Rhodium-Catalyzed Asymmetric Addition of Organoboroxines to *N*-Sulfonyl Imines

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Supporting Information

I. General

All air- and moisture-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen or in a glove box under argon.

THF and dioxane were purified by passing through neutral alumina columns under nitrogen. DMF was distilled over CaH_2 under vacuum. CH_2Cl_2 was distilled over CaH_2 under nitrogen. Et_3N was distilled over KOH under nitrogen. C_6H_6 was distilled over benzophenone ketyl under nitrogen. Pentane was distilled over benzophenone ketyl in the presence of triglyme under nitrogen.

2-methyl-2-propenyl bromide (Aldrich), NaH (Kanto Chemical; 60 wt% in mineral oil), Grubbs catalyst (Aldrich; 2nd generation), trifluoroacetic acid (Wako Chemicals), chlorodiphenylphosphine (Wako Chemicals), and methanesulfonyl chloride (Wako Chemicals) were used as received.

(*S*)-**2**, [1] (7*R*)-**7**, [2] 2-(benzyloxymethyl)-2-propenol, [3] 2-phenyl-2-propenyl bromide, [4] $Rh(acac)(C_2H_4)_2$,[5] and $[RhCl(C_2H_4)_2]_2$[6] were synthesized following the literature procedures. Imines **5** and **8** were prepared from the corresponding aldehydes and sulfonamides following the literature procedure. [7] Organoboroxines were prepared by dehydration of the corresponding organoboronic acids following the literature procedure.[8]

All other chemicals and solvents were purchased from Aldrich, Wako Chemicals, TCI, or Kanto Chemical and used as received.

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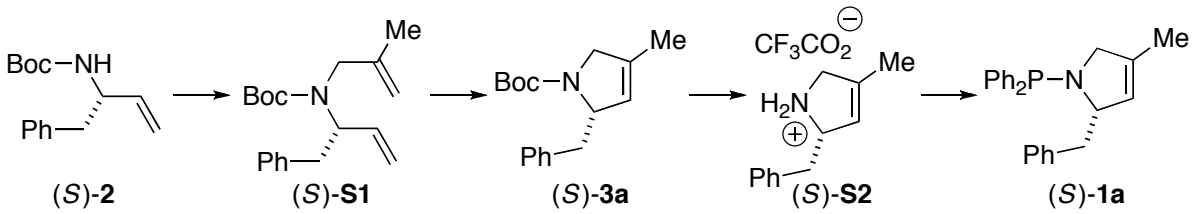
[7] (a) Love, B. E.; Raje, P. S.; Williams II, T. C. *Synlett* **1994**, 493. (b) Brichacek, M.; Lee, D.; Njardarson, J. T. *Org. Lett.* **2008**, *10*, 5023. (c) Chemla, F.; Hebbe, V.; Normant, J.-F. *Synthesis* **2000**, 75.
[8] Chen, F.-X.; Kina, A.; Hayashi, T. *Org. Lett.* **2006**, *8*, 341.

II. Synthesis of Ligands and Complexes

(*S*)-1a



(*S*)-**2** (*S*)-**S1** (*S*)-**3a** (*S*)-**S2** (*S*)-**1a**

2-Methyl-2-propenyl bromide (726 mg, 5.38 mmol) and NaH (256 mg, 6.40 mmol; 60 wt% in mineral oil) were successively added to a solution of (*S*)-**2** (1.01 g, 4.08 mmol) in DMF (9.0 mL) at 0 °C and the mixture was stirred for 1.5 h at room temperature. The reaction was quenched with H_2O at 0 °C and this was extracted with EtOAc/hexane (1/10). The organic layer was dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane = 1/20 to afford compound (*S*)-**S1** as a colorless oil (1.17 g, 3.88 mmol; 95% yield). $[\alpha]^{25}_D$ –55.4 (*c* 1.02, $CHCl_3$).

^{1}H NMR ($CDCl_3$, 50 °C): δ 7.25 (t, $^3J_{HH}$ = 7.5 Hz, 2H), 7.19-7.15 (m, 3H), 6.00 (ddd, $^3J_{HH}$ = 17.0, 10.2, and 6.8 Hz, 1H), 5.06 (d, $^3J_{HH}$ = 10.8 Hz, 1H), 5.04 (d, $^3J_{HH}$ = 18.4 Hz, 1H), 4.77 (s, 1H), 4.73 (s, 1H), 4.34 (bs, 1H), 3.75-3.56 (m, 1H), 3.46 (d, $^2J_{HH}$ = 16.3 Hz, 1H), 3.16-3.04 (m, 1H), 2.91 (dd, $^2J_{HH}$ = 13.6 Hz and $^3J_{HH}$ = 6.8 Hz, 1H), 1.60 (s, 3H), 1.42 (s, 9H). ^{13}C NMR ($CDCl_3$, 50 °C): δ 155.4, 142.8, 139.0, 137.5, 129.5, 128.4, 126.4, 116.2, 111.6, 79.7, 61.5, 52.2, 39.2, 28.6, 20.1. HRMS (ESI-TOF) calcd for $C_{19}H_{27}NO_2Na$ ($M+Na^+$) 324.1934, found 324.1930.

Grubbs catalyst (66.3 mg, 78.1 μmol; 2nd generation) was added to a solution of (*S*)-**S1** (1.16 g, 3.85 mmol) in C_6H_6 (38 mL) and the mixture was stirred for 6 h at 60 °C. The solvent was removed under vacuum, and the residue was chromatographed on silica gel with EtOAc/hexane = 1/20 to afford compound (*S*)-**3a** as a colorless oil (1.03 g, 3.77 mmol; 98% yield, ~6/4 mixture of rotamers). $[\alpha]^{25}_D$ +177 (*c* 1.10, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ 7.28-7.22 (m, 2H), 7.22-7.17 (m, 1H), 7.15 (d, $^3J_{HH}$ = 7.5 Hz, 0.8H), 7.12 (d, $^3J_{HH}$ = 7.5 Hz, 1.2H), 5.26 (s, 0.4H), 5.23 (s, 0.6H), 4.73-4.67 (m, 0.4H), 4.61-4.55 (m, 0.6H), 4.02 (d, $^2J_{HH}$ = 15.0 Hz, 0.6H), 3.89 (d, $^2J_{HH}$ = 14.9 Hz, 0.4H), 3.70 (dd, $^2J_{HH}$ = 14.9 Hz and $^4J_{HH}$ = 4.0 Hz, 0.6H), 3.56 (dd, $^2J_{HH}$ = 15.0 Hz and $^4J_{HH}$ = 4.8 Hz, 0.4H), 3.17 (dd, $^2J_{HH}$ = 12.9 Hz and $^3J_{HH}$ = 3.4 Hz, 0.4H), 3.13 (dd, $^2J_{HH}$ = 13.0 Hz and $^3J_{HH}$ = 3.4 Hz, 0.6H), 2.84 (dd, $^2J_{HH}$ = 13.0 Hz and $^3J_{HH}$ = 8.2 Hz, 0.4H), 2.69 (dd, $^2J_{HH}$ = 12.9 Hz and $^3J_{HH}$ = 8.1 Hz, 0.6H), 1.66 (s, 1.8H), 1.63 (s, 1.2H), 1.55 (s, 5.4H), 1.50 (s, 3.6H). ^{13}C NMR ($CDCl_3$): δ 154.2, 154.0, 138.2, 135.2, 135.1, 129.9, 129.6, 128.2, 127.9, 126.2, 126.0, 123.5, 123.3, 79.5, 79.1, 65.9, 65.6, 56.9, 56.6, 41.3, 39.8, 28.70, 28.66, 14.2, 14.1. HRMS (ESI-TOF) calcd for $C_{17}H_{23}NO_2Na$ ($M+Na^+$) 296.1621, found 296.1617.

Trifluoroacetic acid (7.5 mL) was added to a solution of (*S*)-**3a** (1.03 g, 3.77 mmol) in CH_2Cl_2 (37 mL) and the mixture was stirred for 1.5 h at room temperature. The solvent was removed under vacuum, and the remaining trifluoroacetic acid was further removed by dissolving the residue in C_6H_6 and concentrated under vacuum for three times, followed by the same sequence with hexane for three times. The residue thus obtained was chromatographed on silica gel with MeOH/CH_2Cl_2 = 1/10 to afford compound (*S*)-**S2** as a purple solid (1.03 g, 3.59 mmol; 95% yield). $[\alpha]^{25}_D$ +54.5 (*c* 0.32, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ 10.30 (bs, 1H), 9.23 (bs, 1H), 7.31 (t, $^3J_{HH}$ = 7.5 Hz, 2H), 7.25 (t, $^3J_{HH}$ = 8.1 Hz, 1H), 7.20 (d, $^3J_{HH}$ = 6.8 Hz, 2H), 5.34 (s, 1H), 4.70-4.62 (m, 1H), 3.84 (d, $^2J_{HH}$

= 15.0 Hz, 1H), 3.80 (d, $^2J_{HH}$ = 15.0 Hz, 1H), 3.15 (dd, $^2J_{HH}$ = 13.6 Hz and $^3J_{HH}$ = 6.1 Hz, 1H), 2.95 (dd, $^2J_{HH}$ = 13.6 Hz and $^3J_{HH}$ = 8.9 Hz, 1H), 1.78 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 162.8 (q, $^2J_{CF}$ = 35.9 Hz), 135.8, 135.3, 129.2, 128.8, 127.2, 122.4, 117.0 (q, $^1J_{CF}$ = 293 Hz), 66.9, 53.9, 39.3, 13.6. HRMS (ESI-TOF) calcd for $C_{12}H_{16}N$ ($M–CF_3CO_2^-$) 174.1277, found 174.1278.

1 M NaOH*aq* (15 mL) was added to a solution of (*S*)-**S2** (1.03 g, 3.59 mmol) in Et_2O (5.0 mL) and the mixture was extracted with Et_2O. The organic layer was dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was dissolved in THF (9.0 mL), and Et_3N (2.20 mL, 15.8 mmol) and chlorodiphenylphosphine (710 μL, 3.95 mmol) were successively added to it with additional THF (2.0 mL). The mixture was stirred for 9 h at room temperature, and the volatiles were removed under vacuum. This was chromatographed on silica gel with degassed Et_3N/hexane = 1/2 to afford compound (*S*)-**1a** as a yellow oil (1.06 g, 2.97 mmol; 83% yield). $[\alpha]^{25}_D$ +235 (*c* 1.03, THF).

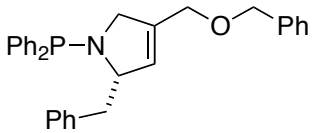
^{1}H NMR (C_6D_6): δ 7.58 (t, ^3J = 7.2 Hz, 2H), 7.48 (t, ^3J = 7.4 Hz, 2H), 7.23-7.19 (m, 2H), 7.18-7.05 (m, 9H), 5.27-5.21 (m, 1H), 4.77-4.68 (m, 1H), 3.60 (bs, 2H), 3.44 (ddd, $^2J_{HH}$ = 12.8 Hz, $^3J_{HH}$ = 3.9 Hz, and $^4J_{HH}$ = 2.8 Hz, 1H), 2.75 (dd, $^2J_{HH}$ = 12.8 Hz and $^3J_{HH}$ = 9.5 Hz, 1H), 1.28 (s, 3H). ^{13}C NMR (C_6D_6): δ 140.2 (d, J_{CP} = 7.7 Hz), 139.5 (d, J_{CP} = 18.1 Hz), 139.4, 137.1, 134.9 (d, J_{CP} = 12.9 Hz), 134.8 (d, J_{CP} = 12.9 Hz), 132.7 (d, J_{CP} = 19.6 Hz), 132.6 (d, J_{CP} = 19.6 Hz), 130.0, 128.61 (d, J_{CP} = 5.7 Hz), 128.59 (d, J_{CP} = 4.7 Hz), 128.5 (d, J_{CP} = 4.1 Hz), 126.3, 125.2 (d, J_{CP} = 6.7 Hz), 73.1 (d, J_{CP} = 30.5 Hz), 57.6 (d, J_{CP} = 9.3 Hz), 45.2 (d, J_{CP} = 5.7 Hz), 14.0. ^{31}P{^{1}H} NMR (C_6D_6): δ 43.5 (s). HRMS (ESI-TOF) calcd for $C_{24}H_{25}NP$ ($M+H^+$) 358.1719, found 358.1717.

2-(Benzyloxymethyl)-2-propenyl methanesulfonate

Et_3N (5.40 mL, 38.7 mmol) and mthanesulfonyl chloride (1.50 mL, 19.4 mmol) were successively added to a solution of 2-(benzyloxymethyl)-2-propenol (2.75 g, 15.4 mmol) in CH_2Cl_2 (25 mL) at 0 °C. The mixture was stirred for 50 min at 0 °C and the reaction was quenched with saturated $NaHCO_3$*aq*. This was extracted with CH_2Cl_2 and the organic layer was washed with saturated NaCl*aq*, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane = 1/4 to afford 2-(benzyloxymethyl)-2-propenyl methanesulfonate as a colorless oil (2.88 g, 11.2 mmol; 73% yield).

^{1}H NMR ($CDCl_3$): δ 7.38-7.28 (m, 5H), 5.40-5.37 (m, 2H), 4.76 (s, 2H), 4.52 (s, 2H), 4.08 (s, 2H), 2.99 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 139.1, 137.8, 128.5, 127.9, 127.8, 118.2, 72.5, 70.2, 70.1, 37.8. HRMS (ESI-TOF) calcd for $C_{12}H_{16}O_4SNa$ ($M+Na^+$) 279.0662, found 279.0663.

(*S*)-1b

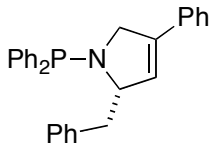


This was synthesized from (*S*)-**2** and 2-(benzyloxymethyl)-2-propenyl methanesulfonate, following the procedure for (*S*)-**1a**. Brown oil. 62% overall yield. $[\alpha]^{25}_D$ +187 (*c* 0.56, THF).

^{1}H NMR (C_6D_6): δ 7.57 (t, ^3J = 7.1 Hz, 2H), 7.46 (t, ^3J = 7.6 Hz, 2H), 7.21-7.11 (m, 13H), 7.09-7.04 (m, 3H), 5.56-5.53 (m, 1H), 4.80-4.73 (m, 1H), 4.15 (d, $^2J_{HH}$ = 12.2 Hz, 1H), 4.11 (d, $^2J_{HH}$ = 12.1 Hz, 1H), 3.86-3.76 (m, 2H), 3.68-3.61 (m, 2H), 3.38 (ddd, $^2J_{HH}$ = 12.7 Hz,

$^3J_{HH}$ = 4.2 Hz, and $^4J_{HH}$ = 2.8 Hz, 1H), 2.80 (ddd, $^2J_{HH}$ = 12.8 Hz, $^3J_{HH}$ = 9.3 Hz, and $^4J_{HH}$ = 0.6 Hz, 1H). ^{13}C NMR (C_6D_6): δ 139.8 (d, J_{CP} = 7.2 Hz), 139.3 (d, J_{CP} = 18.1 Hz), 139.2, 139.0, 138.9, 134.9 (d, J_{CP} = 12.9 Hz), 134.8 (d, J_{CP} = 12.9 Hz), 132.7 (d, J_{CP} = 20.2 Hz), 132.6 (d, J_{CP} = 19.1 Hz), 130.0, 128.64 (d, J_{CP} = 6.2 Hz), 128.59 (d, J_{CP} = 7.2 Hz), 128.5 (d, J_{CP} = 5.2 Hz), 127.9, 127.7, 127.3 (d, J_{CP} = 6.7 Hz), 126.4, 72.9 (d, J_{CP} = 31.5 Hz), 72.0, 66.9, 54.6 (d, J_{CP} = 9.3 Hz), 44.7 (d, J_{CP} = 5.2 Hz). ^{31}P{^{1}H} NMR (C_6D_6): δ 44.8 (s). HRMS (ESI-TOF) calcd for $C_{31}H_{31}NOP$ ($M+H^+$) 464.2138, found 464.2130.

(*S*)-1c



This was synthesized from (*S*)-**2** and 2-phenyl-2-propenyl bromide, following the procedure for (*S*)-**1a**. Pink solid. 85% overall yield. $[\alpha]^{25}_D$ +224 (*c* 0.53, THF).

^{1}H NMR (C_6D_6): δ 7.65-7.61 (m, 2H), 7.54-7.50 (m, 2H), 7.25-7.21 (m, 2H), 7.17-7.05 (m, 9H), 6.99-6.95 (m, 5H), 6.00 (dt, $^3J_{HH}$ = 4.9 Hz and $^4J_{HH}$ = 2.2 Hz, 1H), 4.92-4.85 (m, 1H), 4.24-4.15 (m, 2H), 3.52 (ddd, $^2J_{HH}$ = 12.8 Hz, $^3J_{HH}$ = 4.2 Hz, and ^4J = 2.8 Hz, 1H), 2.80 (dd, $^2J_{HH}$ = 12.8 Hz and $^3J_{HH}$ = 9.5 Hz, 1H). ^{13}C NMR (C_6D_6): δ 139.9 (d, J_{CP} = 8.3 Hz), 139.6, 139.14 (d, J_{CP} = 17.6 Hz), 139.09, 134.9 (d, J_{CP} = 12.9 Hz), 134.8 (d, J_{CP} = 12.9 Hz), 134.2, 132.7 (d, J_{CP} = 20.2 Hz), 132.5 (d, J_{CP} = 19.6 Hz), 130.0, 128.72 (d, J_{CP} = 6.2 Hz), 128.68 (d, J_{CP} = 8.8 Hz), 128.66 (d, J_{CP} = 6.2 Hz), 128.6, 127.8, 126.4, 125.9, 125.5 (d, J_{CP} = 6.7 Hz), 73.6 (d, J_{CP} = 31.0 Hz), 54.5 (d, J_{CP} = 9.3 Hz), 45.1 (d, J_{CP} = 6.2 Hz). ^{31}P{^{1}H} NMR (C_6D_6): δ 44.2 (s). HRMS (ESI-TOF) calcd for $C_{29}H_{27}NP$ ($M+H^+$) 420.1876, found 420.1864.

Rh(acac)((*S*)-1a) (4)

A solution of (*S*)-**1a** (318 mg, 0.890 mmol) in C_6H_6 (4.0 mL) was added slowly over 25 min to a solution of Rh(acac)$(C_2H_4)_2$ (214 mg, 0.829 mmol) in C_6H_6 (1.0 mL) at 30 °C, and the mixture was stirred for 1 h at 30 °C. The reaction mixture was filtered through PTFE membrane with C_6H_6 and the solvent was removed under vacuum. The solid thus obtained was washed with hexane and dried under vacuum to afford complex **4** as a yellow solid (396 mg, 0.708 mmol; 85% yield). $[\alpha]^{25}_D$ –20.5 (*c* 0.52, THF). Recrystallization of this complex from benzene/pentane afforded single crystals suitable for X-ray crystallographic analysis.

^{1}H NMR (C_6D_6): δ 8.25-8.18 (m, 2H), 7.98-7.92 (m, 2H), 7.17-7.07 (m, 3H), 7.06-6.94 (m, 8H), 5.36 (s, 1H), 3.75 (s, 1H), 3.52-3.45 (m, 1H), 2.84 (t, J_{HH} = 14.0 Hz, 1H), 2.63 (dd, $^2J_{HH}$ = 12.8 Hz and $^3J_{HP}$ = 8.8 Hz, 1H), 2.44-2.29 (m, 2H), 1.97 (s, 3H), 1.93 (s, 3H), 1.89 (s, 3H). ^{31}P{^{1}H} NMR (C_6D_6): δ 127.9 (d, $^1J_{PRh}$ = 202 Hz). Anal. Calcd for $C_{29}H_{31}NO_2PRh$: C, 62.26; H, 5.59. Found: C, 62.27; H, 5.52.

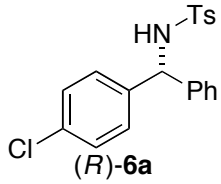
General Procedure for [RhCl((*S*)-1)]$_2$

A solution of (*S*)-**1** (1.0 equiv) in C_6H_6 (ca. 5.0 mL for 1.0 mmol of (*S*)-**1**) was added slowly over 20 min to a solution of $[RhCl(C_2H_4)_2]_2$ (1.1 equiv Rh) in C_6H_6 (ca. 2.5 mL for 1.0 mmol of (*S*)-**1**) at 30 °C, and the mixture was stirred for 1 h at 30 °C. The reaction mixture was filtered through PTFE membrane with C_6H_6 and the solvent was removed under vacuum. The solid thus obtained was washed with hexane and dried under vacuum to afford complex [RhCl((*S*)-**1**)]$_2$, which was directly used as a catalyst for the addition reaction.

III. Catalytic Reactions

General Procedure for Table 1.

4 M KOH*aq* (10 μL, 40 μmol) was added to a solution of [RhCl((*S*)-**1c**)]$_2$ (5.6 mg, 10 μmol Rh), imine **5** (0.200 mmol), and organoboroxine (0.600 mmol B) in dioxane (0.50 mL), and the mixture was stirred for 6 h at 60 °C. This was directly passed through a pad of silica gel with EtOAc and the solvent was removed under vacuum. The residue was purified by silica gel preparative TLC to afford compound **6**.

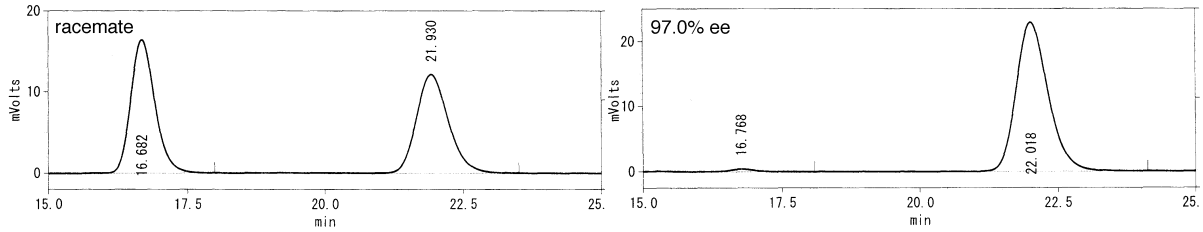


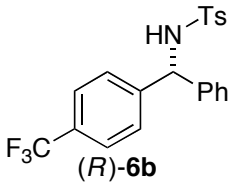
(*R*)-**6a**

Entry 1. (CAS 796966-21-7 for (*R*)-enantiomer) White solid. 90% yield.

The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 80/20, flow = 0.5 mL/min. Retention times: 16.8 min [minor enantiomer], 22.0 min [major enantiomer]. 97% ee. $[\alpha]^{20}_{D}$ +6.1 (*c* 0.93, $CHCl_3$). The absolute configuration was determined by comparison of the optical rotation with the literature value.[9]

^{1}H NMR ($CDCl_3$): δ 7.55 (d, $^3J_{HH}$ = 8.1 Hz, 2H), 7.24-7.14 (m, 7H), 7.07-7.03 (m, 4H), 5.53 (d, $^3J_{HH}$ = 6.8 Hz, 1H), 5.06 (d, $^3J_{HH}$ = 6.8 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 143.5, 140.2, 139.2, 137.4, 133.5, 129.5, 128.9, 128.8, 128.7, 127.9, 127.4, 127.3, 60.9, 21.6.





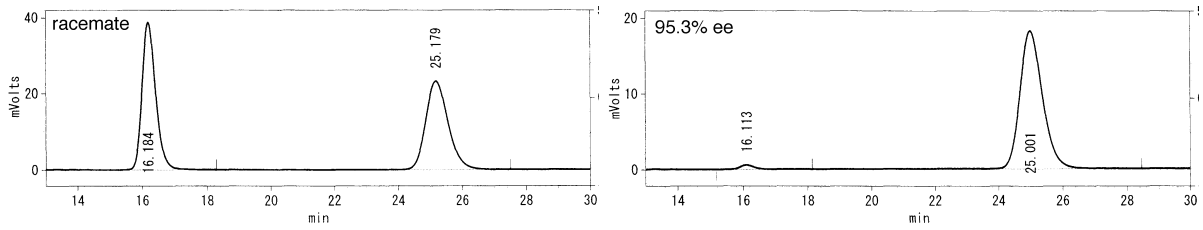
(*R*)-**6b**

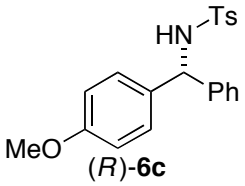
Entry 3. (CAS 831225-96-8 for (*R*)-enantiomer) White solid. 71% yield.

The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 80/20, flow = 0.5 mL/min. Retention times: 16.1 min [minor enantiomer], 25.0 min [major enantiomer]. 95% ee. $[\alpha]^{20}_{D}$ –8.7 (*c* 1.00, $CHCl_3$). The absolute configuration was determined by comparison of the optical rotation with the literature value.[9]

^{1}H NMR ($CDCl_3$): δ 7.54 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 7.45 (d, $^3J_{HH}$ = 8.2 Hz, 2H), 7.28-7.22 (m, 5H), 7.13 (d, $^3J_{HH}$ = 7.9 Hz, 2H), 7.07-7.03 (m, 2H), 5.62 (d, $^3J_{HH}$ = 7.2 Hz, 1H), 5.18 (d, $^3J_{HH}$ = 6.8 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 144.4, 143.7, 139.9, 137.2, 129.8 (q, $^2J_{CF}$ = 31.6 Hz), 129.6, 129.0, 128.2, 127.9, 127.4, 127.3, 125.5, 124.1 (q, $^1J_{CF}$ = 272 Hz), 61.1, 21.5.

[9] Tokunaga, N.; Otomaru, Y.; Okamoto, K.; Ueyama, K.; Shintani, R.; Hayashi, T. *J. Am. Chem. Soc.* **2004**, *126*, 13584.



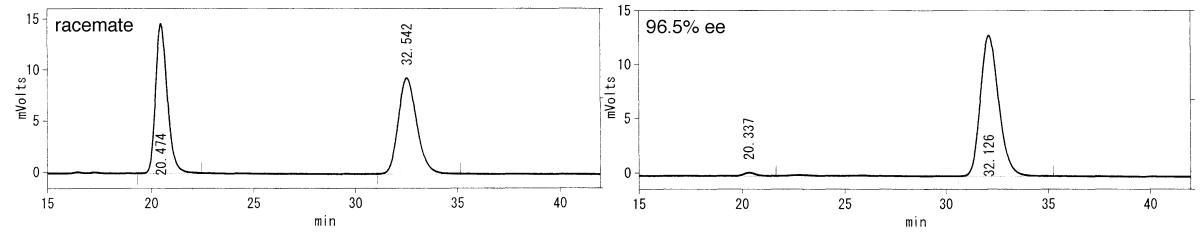


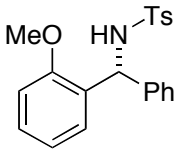
(*R*)-**6c**

Entry 4. (CAS 796966-22-8 for (*R*)-enantiomer) Pale yellow solid. 90% yield.

The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 80/20, flow = 0.5 mL/min. Retention times: 20.3 min [minor enantiomer], 32.1 min [major enantiomer]. 97% ee. $[\alpha]^{20}_{D}$ +20.4 (*c* 1.00, $CHCl_3$). The absolute configuration was determined by comparison of the optical rotation with the literature value.[9]

^{1}H NMR ($CDCl_3$): δ 7.55 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H), 7.23-7.16 (m, 3H), 7.13 (d, $^{3}J_{HH}$ = 8.4 Hz, 2H), 7.12-7.07 (m, 2H), 6.99 (d, $^{3}J_{HH}$ = 8.8 Hz, 2H), 6.72 (d, $^{3}J_{HH}$ = 8.5 Hz, 2H), 5.52 (d, $^{3}J_{HH}$ = 7.1 Hz, 1H), 5.15 (d, $^{3}J_{HH}$ = 7.1 Hz, 1H), 3.74 (s, 3H), 2.37 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 159.1, 143.2, 140.9, 137.6, 132.9, 129.4, 128.7, 128.6, 127.6, 127.4, 127.3, 114.0, 60.9, 55.4, 21.6.



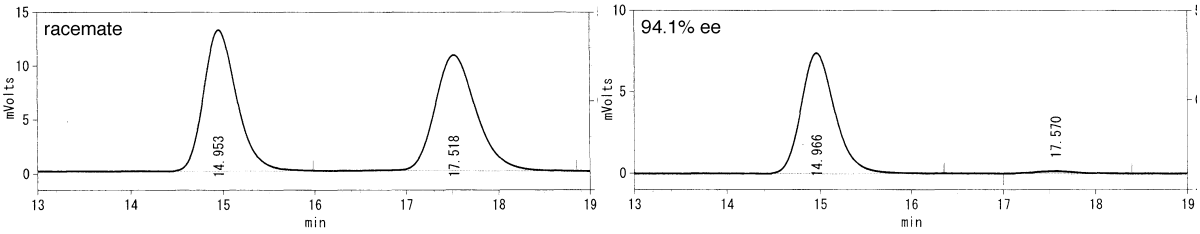


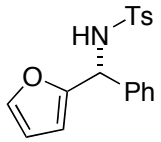
(*R*)-**6d**

Entry 5. (CAS 898269-04-0 for (*R*)-enantiomer) White solid. 95% yield.

The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 80/20, flow = 0.5 mL/min. Retention times: 15.0 min [major enantiomer], 17.6 min [minor enantiomer]. 94% ee. $[\alpha]^{20}_{D}$ +27.5 (*c* 1.01, $CHCl_3$). The absolute configuration was determined by comparison of the optical rotation with the literature value.[9]

^{1}H NMR ($CDCl_3$): δ 7.51 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H), 7.24-7.14 (m, 6H), 7.05 (d, $^{3}J_{HH}$ = 8.1 Hz, 2H), 6.97 (dd, $^{3}J_{HH}$ = 7.5 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 6.78 (td, $^{3}J_{HH}$ = 7.5 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 6.68 (d, $^{3}J_{HH}$ = 8.1 Hz, 1H), 5.76 (d, $^{3}J_{HH}$ = 9.5 Hz, 1H), 5.65 (d, $^{3}J_{HH}$ = 9.6 Hz, 1H), 3.59 (s, 3H), 2.32 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 156.5, 142.9, 140.7, 137.6, 129.7, 129.2, 129.1, 128.2, 127.8, 127.2, 127.1, 126.9, 120.8, 111.2, 59.1, 55.4, 21.5.



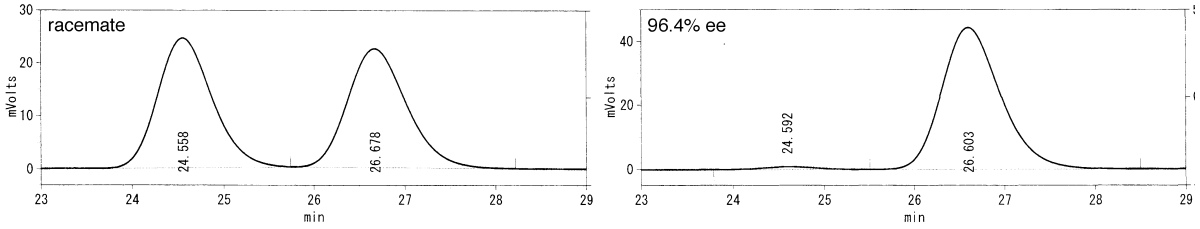


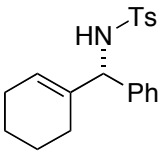
(*R*)-**6e**

Entry 6. (CAS 158568-79-7 for (*R*)-enantiomer) Gray solid. 83% yield.

The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 90/10, flow = 0.5 mL/min. Retention times: 24.6 min [minor enantiomer], 26.6 min [major enantiomer]. 96% ee. $[\alpha]^{20}_{D}$ +14.8 (*c* 1.02, $CHCl_3$). The absolute configuration was determined by comparison of the optical rotation with the literature value.[9]

^{1}H NMR ($CDCl_3$): δ 7.58 (d, $^3J_{HH}$ = 8.1 Hz, 2H), 7.26-7.23 (m, 4H), 7.20-7.17 (m, 2H), 7.16 (d, $^3J_{HH}$ = 8.5 Hz, 2H), 6.19 (dd, $^3J_{HH}$ = 3.3 and 1.8 Hz, 1H), 5.99 (d, $^3J_{HH}$ = 3.2 Hz, 1H), 5.62 (d, $^3J_{HH}$ = 7.7 Hz, 1H), 5.12 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 152.4, 143.3, 142.7, 138.4, 137.5, 129.5, 128.7, 128.1, 127.4, 127.2, 110.4, 108.5, 55.6, 21.6.



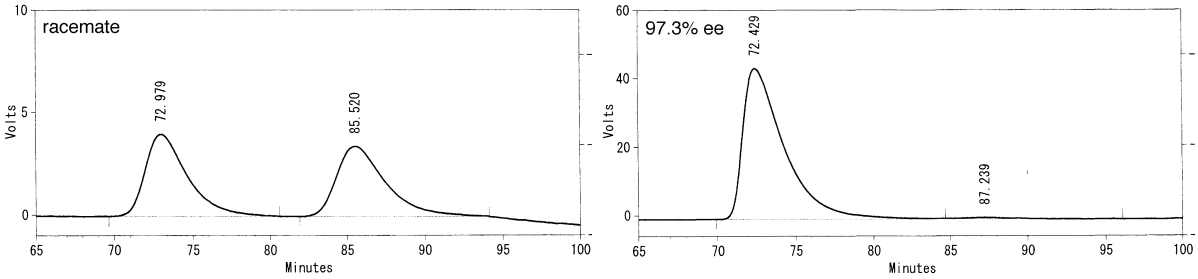


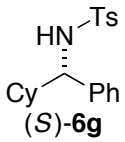
(*S*)-**6f**

Entry 7. The reaction was conducted for 24 h using 0.4 equiv of KOH. White solid. 73% yield.

The ee was determined on a Daicel Chiralcel OJ-H column with hexane/2-propanol = 98/2, flow = 0.5 mL/min. Retention times: 72.4 min [major enantiomer], 87.2 min [minor enantiomer]. 97% ee. $[\alpha]^{20}_{D}$ –11.8 (*c* 1.01, $CHCl_3$). The absolute configuration was assigned by analogy with entry1.

^{1}H NMR ($CDCl_3$): δ 7.63 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 7.23-7.16 (m, 5H), 7.14-7.10 (m, 2H), 5.57-5.53 (m, 1H), 4.86 (d, $^3J_{HH}$ = 7.9 Hz, 1H), 4.83 (d, $^3J_{HH}$ = 7.9 Hz, 1H), 2.39 (s, 3H), 1.98-1.82 (m, 2H), 1.74-1.58 (m, 2H), 1.50-1.32 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 143.2, 139.6, 137.9, 135.7, 129.4, 128.5, 127.5, 127.0, 125.9, 63.4, 25.2, 25.0, 22.4, 22.1, 21.6. Anal. Calcd for $C_{20}H_{23}NO_2S$: C, 70.35; H, 6.79. Found: C, 70.27; H, 6.57.



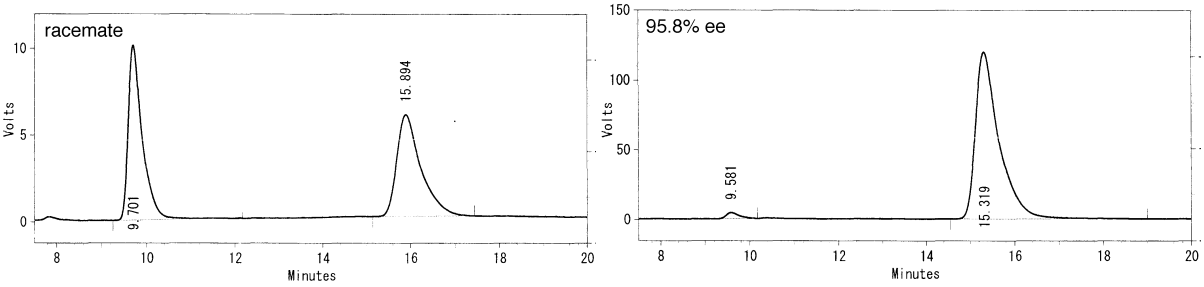


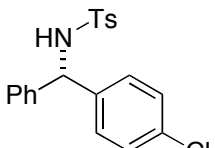
(*S*)-**6g**

Entry 8. (CAS 1112116-79-6 for (*S*)-enantiomer) The reaction was conducted in dioxane/H_2O (100/1). White solid. 73% yield.

The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 80/20, flow = 0.5 mL/min. Retention times: 9.6 min [minor enantiomer], 15.3 min [major enantiomer]. 96% ee. $[\alpha]^{20}_D$ –27.0 (*c* 0.64, $CHCl_3$). The absolute configuration was assigned by analogy with entry 1.

^{1}H NMR ($CDCl_3$): δ 7.45 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 7.11-7.07 (m, 3H), 7.03 (d, $^3J_{HH}$ = 8.0 Hz, 2H), 6.93-6.87 (m, 2H), 4.98 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 4.03 (t, $^3J_{HH}$ = 8.1 Hz, 1H), 2.31 (s, 3H), 1.97-1.91 (m, 1H), 1.77-1.70 (m, 1H), 1.65-1.51 (m, 3H), 1.32-1.25 (m, 1H), 1.20-1.02 (m, 3H), 0.98-0.80 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 142.7, 140.1, 137.9, 129.2, 128.1, 127.14, 127.12, 126.9, 63.6, 43.9, 29.9, 29.6, 26.3, 26.0, 21.5.

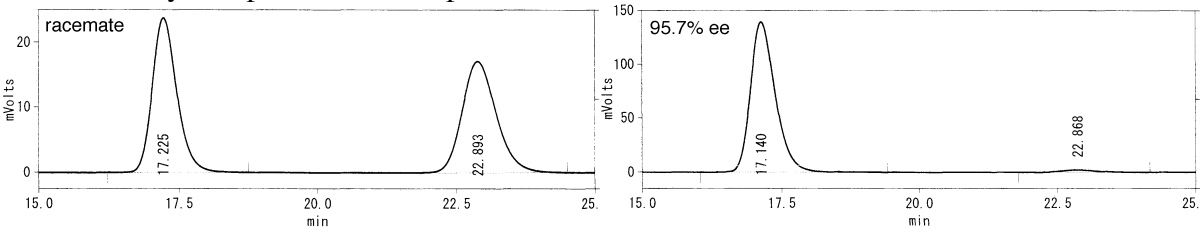


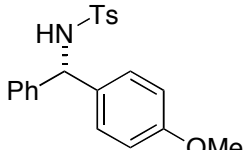


(*S*)-**6a**

Entry 9. (CAS 796966-17-1 for (*S*)-enantiomer) White solid. 83% yield.

The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 80/20, flow = 0.5 mL/min. Retention times: 17.1 min [major enantiomer], 22.9 min [minor enantiomer]. 96% ee. $[\alpha]^{20}_D$ –4.7 (*c* 0.99, $CHCl_3$). The absolute configuration was determined by comparison of the optical rotation with the literature value.[9]

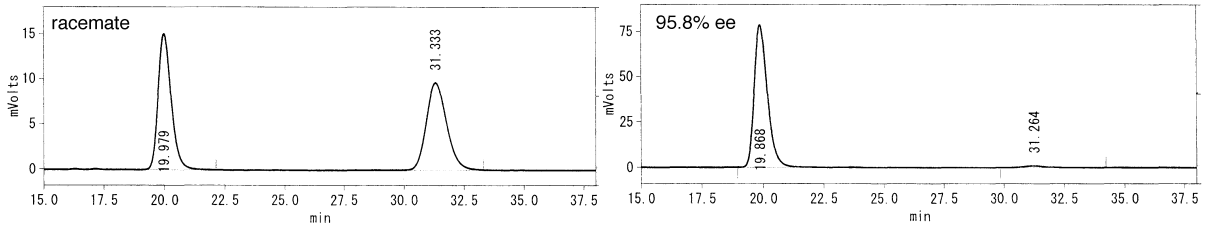


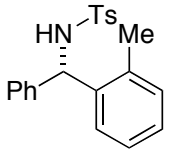


(*S*)-**6c**

Entry 10. (CAS 796966-18-2 for (*S*)-enantiomer) Pale brown solid. 87% yield.

The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 80/20, flow = 0.5 mL/min. Retention times: 19.9 min [major enantiomer], 31.3 min [minor enantiomer]. 96% ee. $[\alpha]^{20}_{D}$ –19.1 (*c* 1.00, $CHCl_3$). The absolute configuration was determined by comparison of the optical rotation with the literature value.[9]



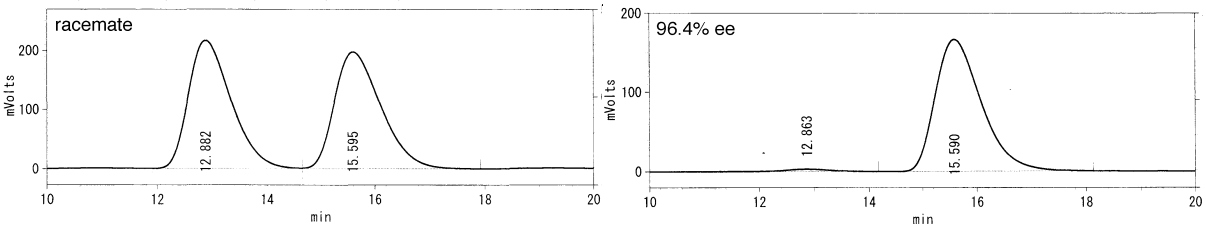


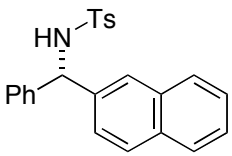
(*S*)-**6h**

Entry 11. (CAS 738626-20-5 for (*S*)-enantiomer) The reaction was conducted for 24 h using 0.4 equiv of KOH. Pale yellow solid. 70% yield.

The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 80/20, flow = 0.5 mL/min. Retention times: 12.9 min [minor enantiomer], 15.6 min [major enantiomer]. 96% ee. $[\alpha]^{20}_{D}$ +10.3 (*c* 0.99, $CHCl_3$). The absolute configuration was determined by comparison of the optical rotation with the literature value.[9]

^{1}H NMR ($CDCl_3$): δ 7.55 (d, $^3J_{HH}$ = 8.0 Hz, 2H), 7.22-7.17 (m, 3H), 7.15-7.09 (m, 4H), 7.08-7.02 (m, 4H), 5.80 (d, $^3J_{HH}$ = 7.1 Hz, 1H), 4.96 (d, $^3J_{HH}$ = 6.5 Hz, 1H), 2.37 (s, 3H), 2.16 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 143.3, 140.1, 138.4, 137.6, 135.6, 130.8, 129.4, 128.7, 127.7, 127.3, 127.2, 126.3, 58.2, 21.6, 19.5.



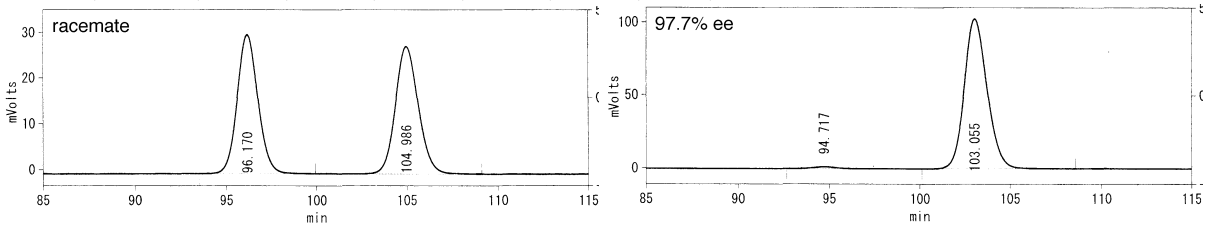


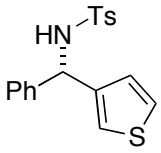
(*S*)-**6i**

Entry 12. (CAS 1171048-75-1 for racemate) White solid. 93% yield.

The ee was determined on two Daicel Chiralpak AD-H columns with hexane/2-propanol = 80/20, flow = 0.3 mL/min. Retention times: 94.7 min [minor enantiomer], 103.1 min [major enantiomer]. 98% ee. $[\alpha]^{20}_{D}$ –14.9 (*c* 0.99, $CHCl_3$). The absolute configuration was assigned by analogy with entry 1.

^{1}H NMR ($CDCl_3$): δ 7.78-7.73 (m, 1H), 7.67 (d, $^3J_{HH}$ = 8.6 Hz, 1H), 7.66-7.64 (m, 1H), 7.55 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 7.50 (s, 1H), 7.47-7.43 (m, 2H), 7.25-7.20 (m, 3H), 7.18-7.14 (m, 3H), 7.03 (d, $^3J_{HH}$ = 8.0 Hz, 2H), 5.74 (d, $^3J_{HH}$ = 7.4 Hz, 1H), 5.29 (bs, 1H), 2.27 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 143.3, 140.5, 137.7, 137.5, 133.1, 132.7, 129.4, 128.7, 128.6, 128.1, 127.7, 127.64, 127.59, 127.3, 126.5, 126.3, 126.2, 125.3, 61.6, 21.5.



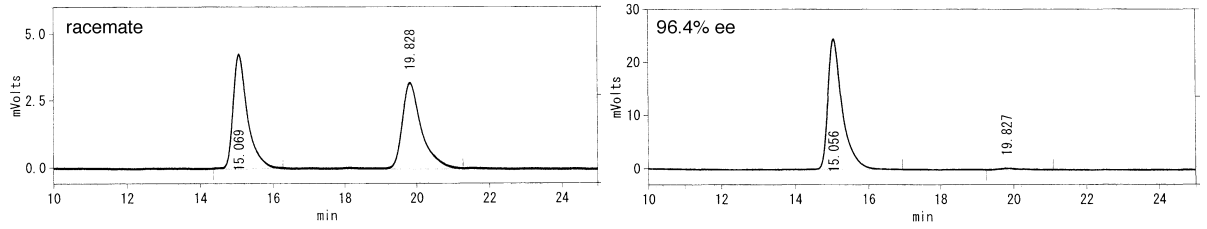


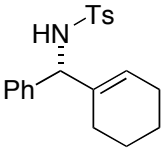
(*S*)-**6j**

Entry 13. (CAS 1032583-00-8 for racemate) Pale brown solid. 88% yield.

The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 80/20, flow = 0.5 mL/min. Retention times: 15.1 min [major enantiomer], 19.8 min [minor enantiomer]. 96% ee. $[\alpha]^{20}_D$ +3.3 (*c* 1.02, $CHCl_3$). The absolute configuration was assigned by analogy with entry 1.

^{1}H NMR ($CDCl_3$): δ 7.56 (d, $^3J_{HH}$ = 8.0 Hz, 2H), 7.23-7.17 (m, 4H), 7.14 (d, $^3J_{HH}$ = 8.1 Hz, 2H), 7.13-7.09 (m, 2H), 6.89-6.86 (m, 1H), 6.77 (d, $^3J_{HH}$ = 5.0 Hz, 1H), 5.62 (d, $^3J_{HH}$ = 7.6 Hz, 1H), 5.03 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 143.3, 142.0, 140.3, 137.6, 129.5, 128.7, 127.8, 127.31, 127.26, 126.8, 126.6, 123.0, 57.7, 21.6.

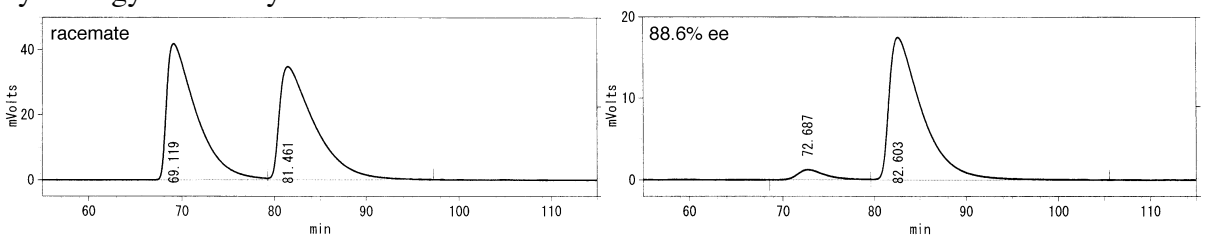


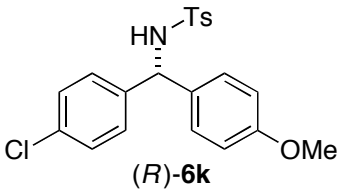


(*R*)-**6f**

Entry 14. White solid. 86% yield.

The ee was determined on a Daicel Chiralcel OJ-H column with hexane/2-propanol = 98/2, flow = 0.5 mL/min. Retention times: 72.7 min [minor enantiomer], 82.6 min [major enantiomer]. 89% ee. $[\alpha]^{20}_D$ +11.2 (*c* 1.00, $CHCl_3$). The absolute configuration was assigned by analogy with entry1.



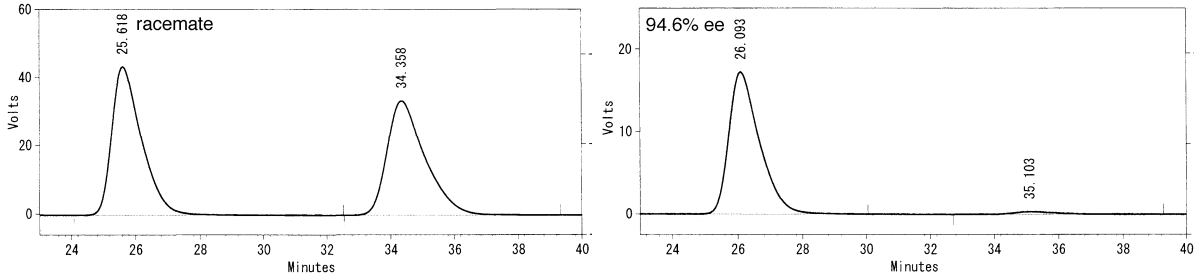


(*R*)-**6k**

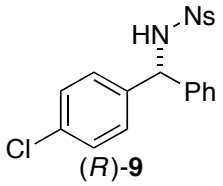
Entry 15. (CAS 796966-23-9 for (*R*)-enantiomer) Pale yellow solid. 91% yield.

The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 80/20, flow = 0.5 mL/min. Retention times: 26.1 min [major enantiomer], 35.1 min [minor enantiomer]. 95% ee. $[\alpha]^{20}_{D}$ –13.7 (*c* 1.03, $CHCl_3$). The absolute configuration was determined by comparison of the optical rotation with the literature value.[9]

^{1}H NMR ($CDCl_3$): δ 7.55 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 7.19-7.14 (m, 4H), 7.06 (d, $^3J_{HH}$ = 8.8 Hz, 2H), 6.94 (d, $^3J_{HH}$ = 8.8 Hz, 2H), 6.73 (d, $^3J_{HH}$ = 8.8 Hz, 2H), 5.49 (d, $^3J_{HH}$ = 6.8 Hz, 1H), 5.02 (d, $^3J_{HH}$ = 6.4 Hz, 1H), 3.75 (s, 3H), 2.40 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 159.2, 143.4, 139.4, 137.4, 133.4, 132.4, 129.5, 128.8, 128.6, 127.3, 114.1, 60.4, 55.4, 21.6.



Procedure for Equation 3.



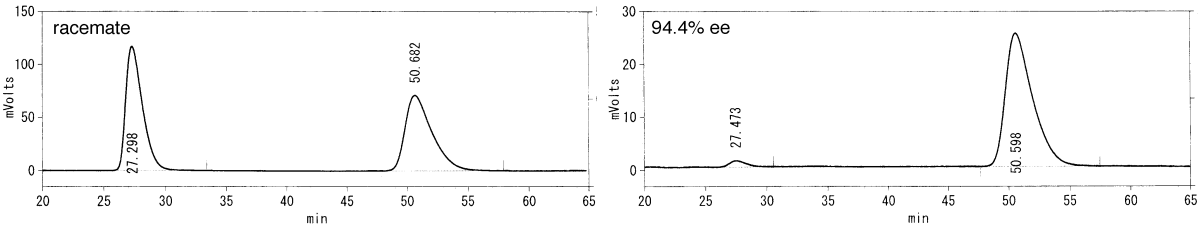
(*R*)-**9**

4 M KOH*aq* (10 μL, 40 μmol) was added to a solution of [RhCl((*S*)-**1c**)]$_2$ (5.6 mg, 10 μmol Rh), imine **8** (64.9 mg, 0.200 mmol), and phenylboroxine (62.3 mg, 0.600 mmol B) in dioxane (0.50 mL), and the mixture was stirred for 6 h at 60 °C. This was directly passed through a pad of silica gel with EtOAc and the solvent was removed under vacuum. The residue was purified by silica gel preparative TLC with EtOAc/hexane/MeOH = 3/16/2 and then with CH_2Cl_2/hexane/MeOH = 100/20/1 to afford compound **9** (CAS 840529-66-0) as a white solid (61.3 mg, 0.152 mmol; 76% yield).

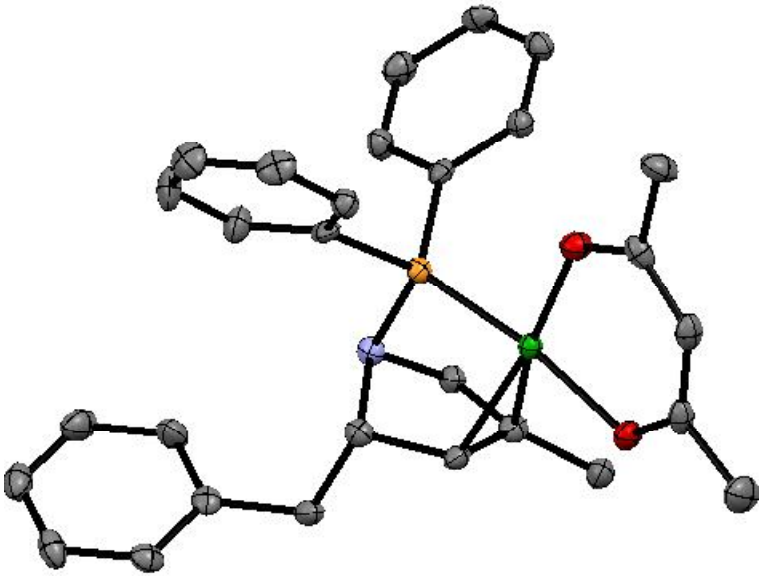
The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 80/20, flow = 0.5 mL/min. Retention times: 27.5 min [minor enantiomer], 50.6 min [major enantiomer]. 94% ee. $[\alpha]^{20}_{D}$ +1.2 (*c* 1.00, $CHCl_3$). The absolute configuration was determined by comparison of the optical rotation with the literature value.[10]

^{1}H NMR ($CDCl_3$): δ 8.14 (d, $^3J_{HH}$ = 8.5 Hz, 2H), 7.78 (d, $^3J_{HH}$ = 8.6 Hz, 2H), 7.24-7.19 (m, 5H), 7.09 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 7.06-7.03 (m, 2H), 5.69 (d, $^3J_{HH}$ = 7.2 Hz, 1H), 5.28 (d, $^3J_{HH}$ = 7.3 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 149.9, 146.2, 139.1, 138.3, 134.2, 129.1, 129.0, 128.9, 128.44, 128.42, 127.4, 124.1, 61.2.

[10] Otomaru, Y.; Tokunaga, N.; Shintani, R.; Hayashi, T. *Org. Lett.* **2005**, *7*, 307.



IV. X-ray Crystal Structure of Rh(acac)((*S*)-1a)



Data Collection

A yellow C_6H_6 solution of Rh(acac)((*S*)-**1a**) was prepared. Crystals suitable for X-ray analysis were obtained by diffusion of pentane at room temperature.

A yellow prism crystal of $C_{29}H_{31}NO_2PRh$ having approximate dimensions of 0.20 x 0.10 x 0.10 mm was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Mo-Kα radiation.

Indexing was performed from 3 oscillations that were exposed for 90 seconds. The crystal-to-detector distance was 127.40 mm.

Cell constants and an orientation matrix for data collection corresponded to a primitive orthorhombic cell with dimensions:

a = 8.270(3) Å
b = 11.652(5) Å
c = 26.490(8) Å
V = 2552.7(15) Å^3

For Z = 4 and F.W. = 559.45, the calculated density is 1.456 g/cm^3. The systematic absences of:

h00: h ± 2n
0k0: k ± 2n
00l: l ± 2n

uniquely determine the space group to be:

$P2_12_12_1$ (#19)

The data were collected at a temperature of –150 ± 1 °C to a maximum 2θ value of 55.0°. A total of 42 oscillation images were collected. A sweep of data was done using ω scans from 130.0 to 190.0° in 5.0° step, at χ = 45.0° and ϕ = 0.0°. The exposure rate was 500.0 [sec./°]. A second sweep was performed using ω scans from 0.0 to 160.0° in 5.0° step, at χ = 45.0°

and ϕ = 180.0°. The exposure rate was 500.0 [sec./°]. The crystal-to-detector distance was 127.40 mm. Readout was performed in the 0.100 mm pixel mode.

Data Reduction

Of the 22742 reflections that were collected, 5782 were unique (R_{int} = 0.102).

The linear absorption coefficient, μ, for Mo-Kα radiation is 7.565 cm^{-1}. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods[11] and expanded using Fourier techniques.[12] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement[13] on F was based on 18345 observed reflections ($I > 2.00\sigma(I)$) and 339 variable parameters and converged (largest parameter shift was 0.01 times its esd) with unweighted and weighted agreement factors of:

$$R = \Sigma \; ||Fo| - |Fc|| \; / \; \Sigma \; |Fo| = 0.0594$$

$$R_W = [\Sigma \; w \; (|Fo| - |Fc|)^2 \; / \; \Sigma \; w \; Fo^2]^{1/2} = 0.0818$$

The standard deviation of an observation of unit weight[14] was 1.00. A Chebychev polynomial weighting scheme was used.[15] Plots of Σ w $(|Fo|-|Fc|)^2$ versus |Fo|, reflection order in data collection, sin θ/λ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 3.06 and –3.34 $e^-/Å^3$, respectively. The absolute structure was deduced based on Flack parameter, 0.04(3), refined using 2473 Friedel pairs.[16]

Neutral atom scattering factors were taken from Cromer and Waber.[17] Anomalous dispersion effects were included in Fcalc;[18] the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[19] The values for the mass attenuation coefficients are those of Creagh and

---

[11] SIR92: Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M.; Polidori, G.; Camalli, M. *J. Appl. Cryst.* **1994**, *27*, 435.

[12] DIRDIF99: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. The DIRDIF-99 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands (1999).

[13] Least Squares function minimized:

$\Sigma w(|F_O|-|F_C|)^2$ where w = Least Squares weights.

[14] Standard deviation of an observation of unit weight:

$[\Sigma w(|F_O|-|F_C|)^2/(N_O-N_V)]^{1/2}$

where: N_O = number of observations, N_V = number of variables

[15] Carruthers, J. R.; Watkin, D. J. *Acta Crystallogr.* **1979**, *A35*, 698.

[16] Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876.

[17] Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

[18] Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.

[19] Creagh, D. C.; McAuley, W. J. "International Tables for Crystallography", Vol C, (A. J. C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219–222 (1992).

Hubbell.[20] All calculations were performed using the CrystalStructure[21,22] crystallographic software package.

The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (deposition number: CCDC 819417). The data can be obtained free of charge via the Internet at www.ccdc.cam.ac.uk/conts/retrieving.html.

[20] Creagh, D. C.; Hubbell, J. H. "International Tables for Crystallography", Vol C, (A. J. C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200–206 (1992).
[21] CrystalStructure 3.8: Crystal Structure Analysis Package, Rigaku and Rigaku Americas (2000-2007). 9009 New Trails Dr. The Woodlands TX 77381 USA.
[22] CRYSTALS Issue 11: Carruthers, J. R.; Rollett, J. S.; Betteridge, P. W.; Kinna, D.; Pearce, L.; Larsen, A.; Gabe, E. Chemical Crystallography Laboratory, Oxford, UK (1999).

Experimental Details

A. Crystal Data

Empirical Formula	$C_{29}H_{31}NO_2PRh$
Formula Weight	559.45
Crystal Color, Habit	yellow, prism
Crystal Dimensions	0.20 X 0.10 X 0.10 mm
Crystal System	orthorhombic
Lattice Type	Primitive
Indexing Images	3 oscillations @ 90.0 seconds
Detector Position	127.40 mm
Pixel Size	0.100 mm
Lattice Parameters	a = 8.270(3) Å b = 11.652(5) Å c = 26.490(8) Å V = 2552.7(15) Å^3
Space Group	$P2_12_12_1$ (#19)
Z value	4
D_{calc}	1.456 g/cm^3
F_{000}	1152.00
μ(MoKα)	7.565 cm^{-1}

B. Intensity Measurements

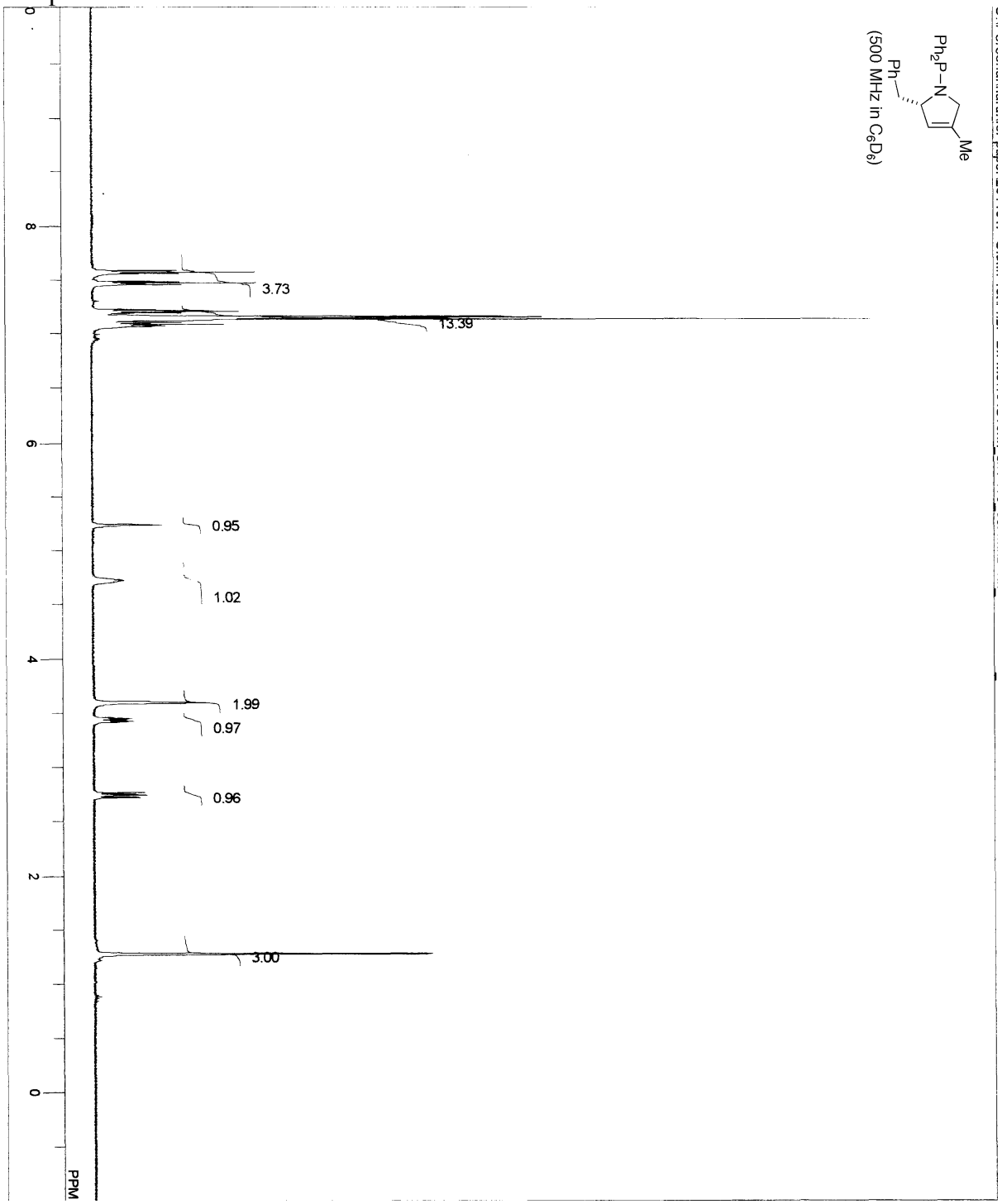
Diffractometer	Rigaku RAXIS-RAPID
Radiation	MoKα (λ = 0.71075 Å) graphite monochromated
Detector Aperture	280 mm x 256 mm
Data Images	42 exposures
ω oscillation Range (χ=45.0, ϕ=0.0)	130.0 - 190.0°
Exposure Rate	500.0 sec./°
ω oscillation Range (χ=45.0, ϕ=180.0)	0.0 - 160.0°
Exposure Rate	500.0 sec./°
Detector Position	127.40 mm
Pixel Size	0.100 mm
$2\theta_{max}$	55.0°
No. of Reflections Measured	Total: 22742 Unique: 5782 (R_{int} = 0.102) Friedel pairs: 2473
Corrections	Lorentz-polarization

C. Structure Solution and Refinement

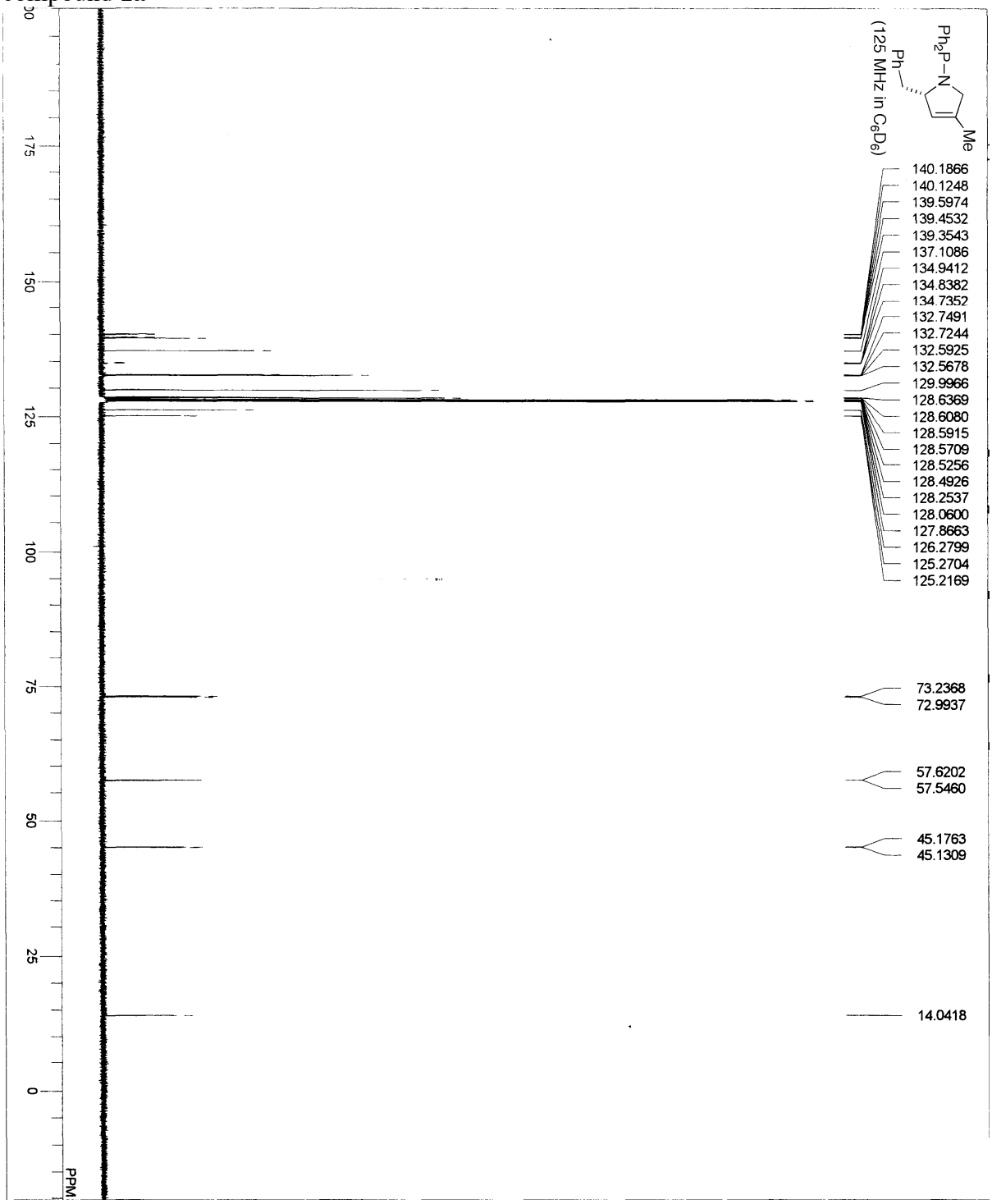
Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares on F
Function Minimized	Σ w (|Fo| –|Fc|)^2
Least Squares Weights	Chebychev polynomial with 3 parameters 63.9849, 68.2451, 17.9686
$2\theta_{max}$ cutoff	55.0°
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>2.00σ(I))	18345
No. Variables	339
Reflection/Parameter Ratio	54.12
Residuals: R (I>2.00σ(I))	0.0594
Residuals: Rw (I>2.00σ(I))	0.0818
Goodness of Fit Indicator	1.003
Flack parameter	0.04(3)
Max Shift/Error in Final Cycle	0.006
Maximum peak in Final Diff. Map	3.06 e^-/Å^3
Minimum peak in Final Diff. Map	–3.34 e^-/Å^3

V. ^{1}H and ^{13}C NMR Spectra

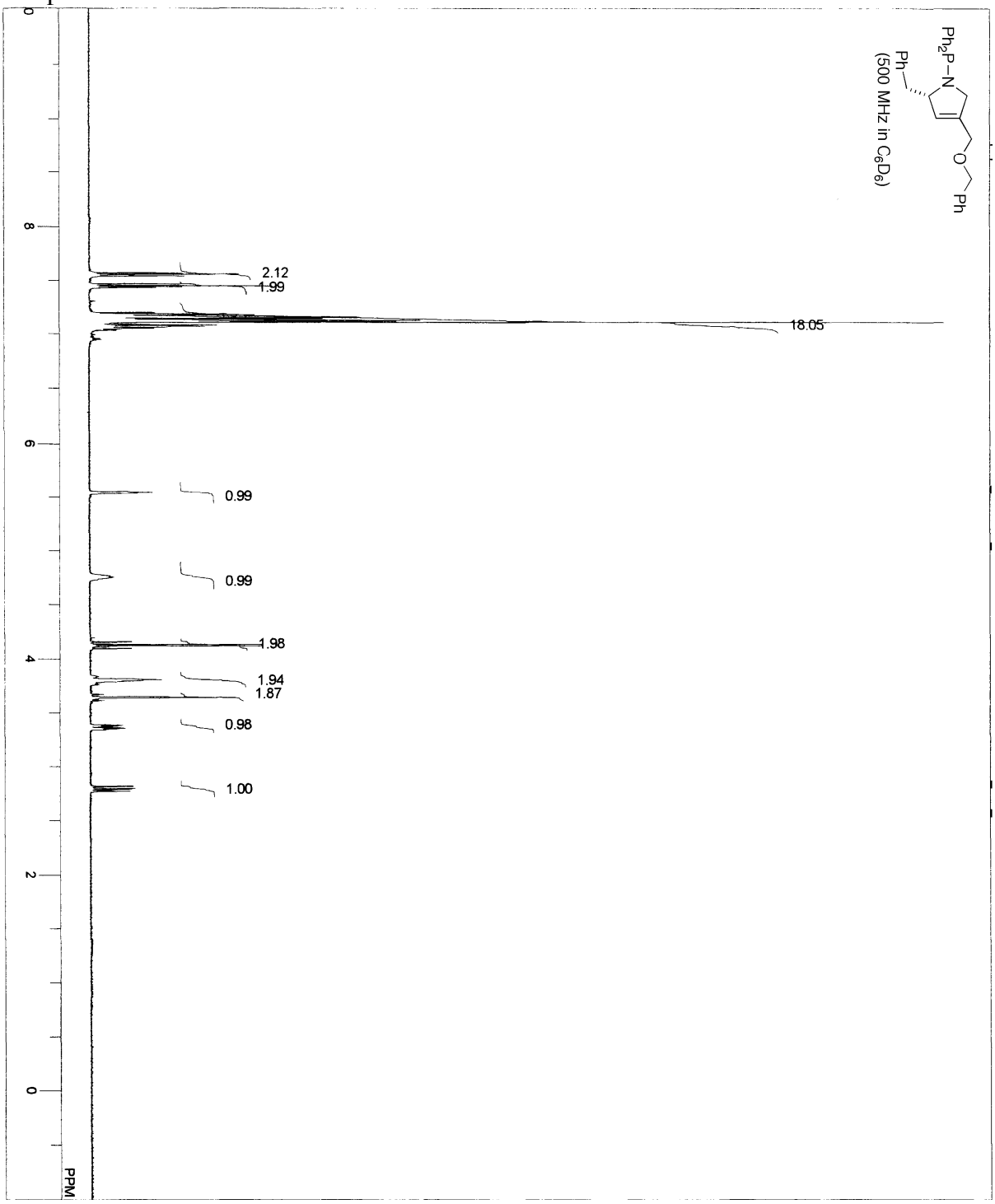
compound **1a**



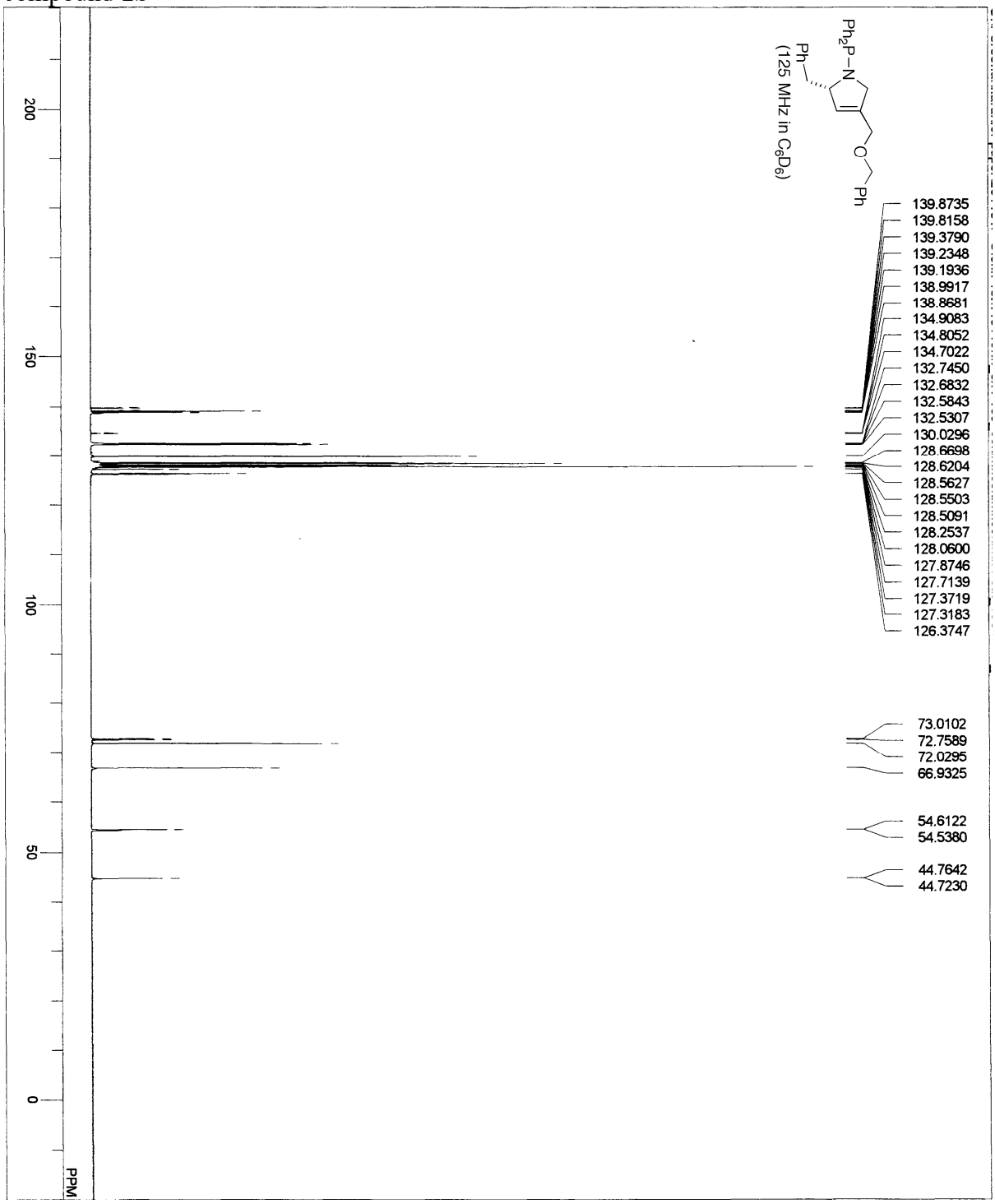
compound **1a**


Ph2P–N
Ph
Me
(125 MHz in C6D6)
140.1866
140.1248
139.5974
139.4532
139.3543
137.1086
134.9412
134.8382
134.7352
132.7491
132.7244
132.5925
132.5678
129.9966
128.6369
128.6080
128.5915
128.5709
128.5256
128.4926
128.2537
128.0600
127.8663
126.2799
125.2704
125.2169
73.2368
72.9937
57.6202
57.5460
45.1763
45.1309
14.0418
PPM

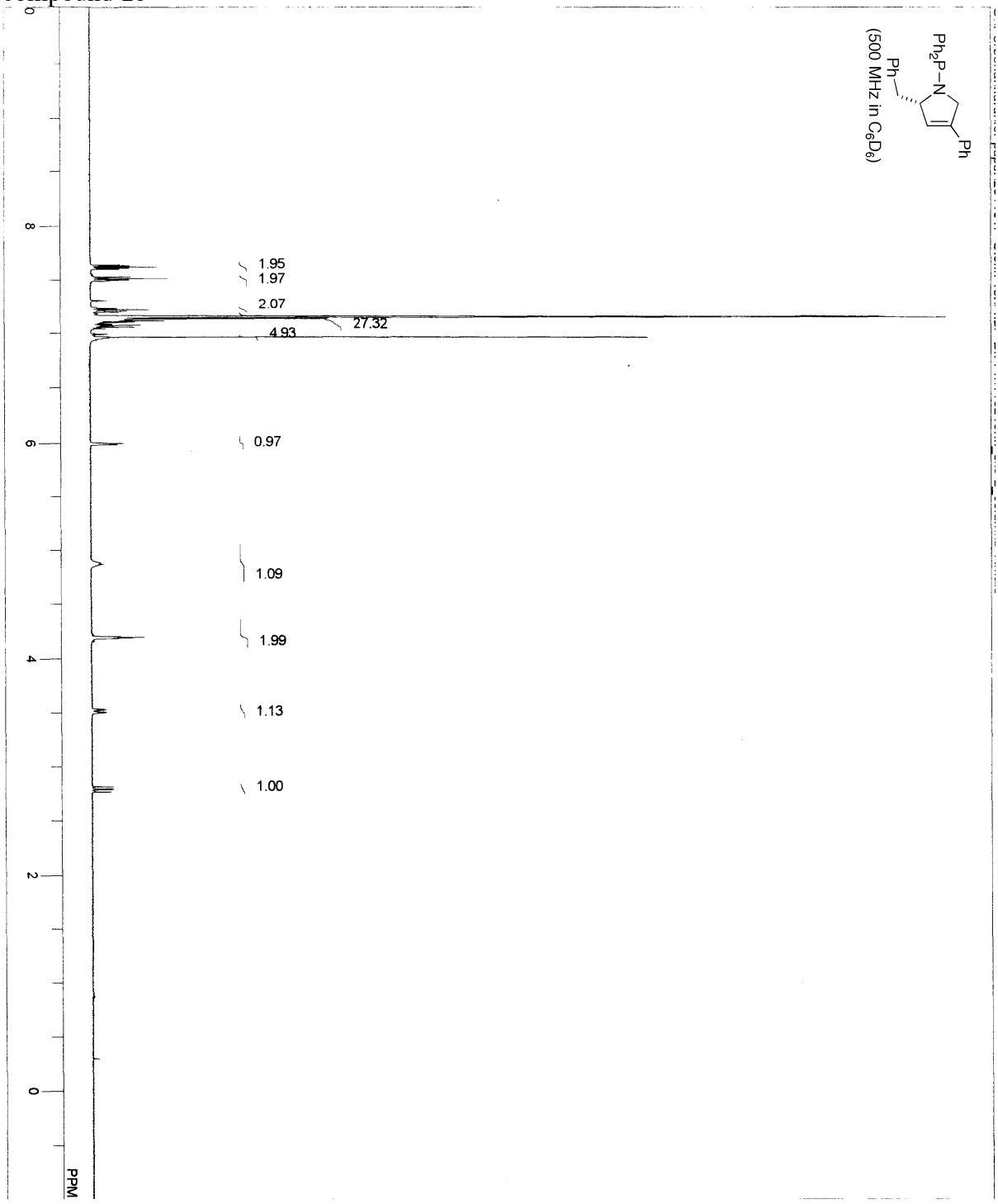
compound **1b**


Ph2P–N
Ph
(500 MHz in C6D6)
O
Ph
2.12
1.99
18.05
0.99
0.99
1.98
1.94
1.87
0.98
1.00
PPM
8
6
4
2
0

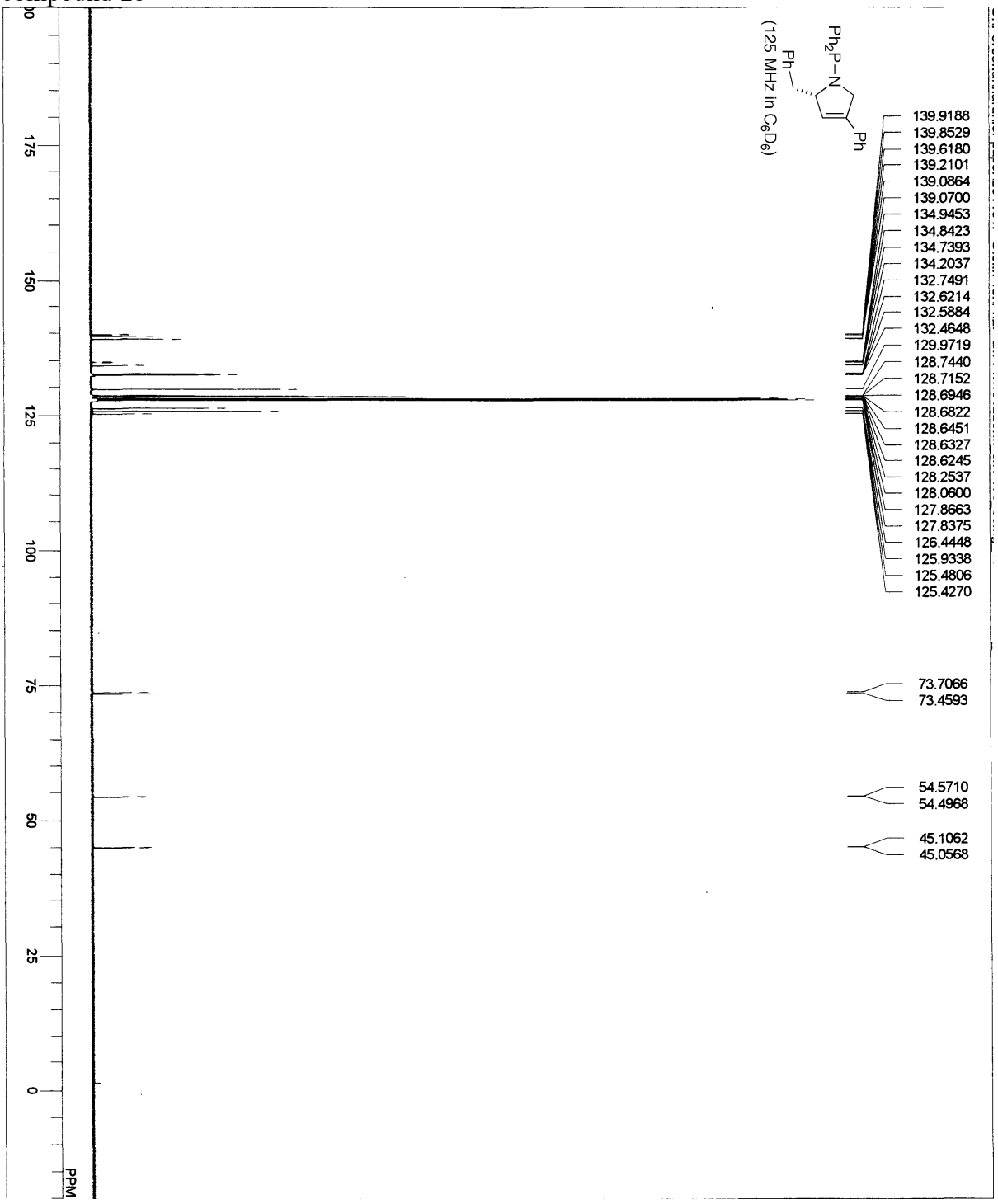
compound **1b**


Ph2P–N
Ph
(125 MHz in C6D6)
O
Ph
139.8735
139.8158
139.3790
139.2348
139.1936
138.9917
138.8681
134.9083
134.8052
134.7022
132.7450
132.6832
132.5843
132.5307
130.0296
128.6698
128.6204
128.5627
128.5503
128.5091
128.2537
128.0600
127.8746
127.7139
127.3719
127.3183
126.3747
73.0102
72.7589
72.0295
66.9325
54.6122
54.5380
44.7642
44.7230
200
150
100
50
0
PPM

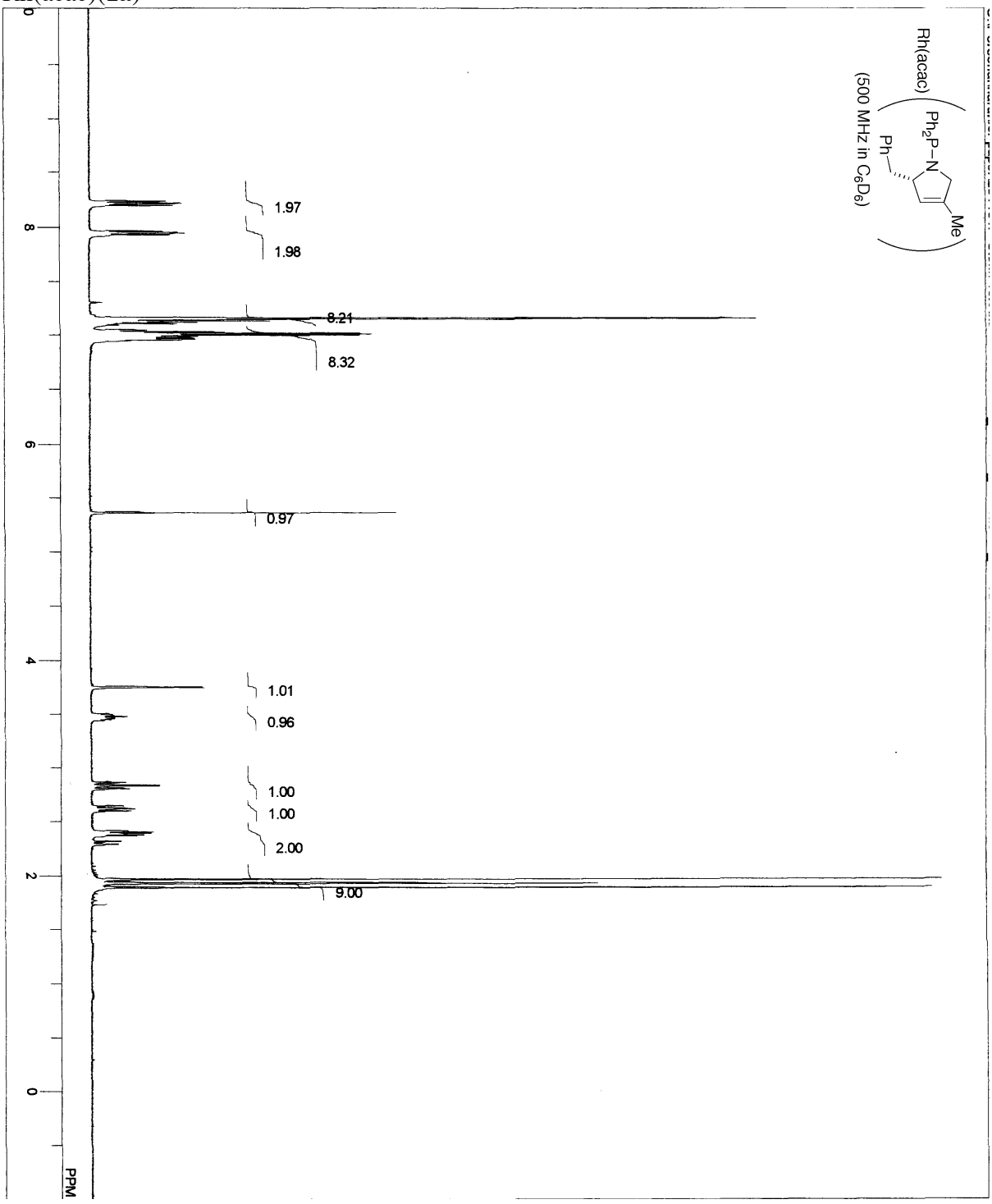
compound **1c**


Ph2P–N
Ph
Ph
(500 MHz in C6D6)
1.95
1.97
2.07
27.32
4.93
0.97
1.09
1.99
1.13
1.00
PPM

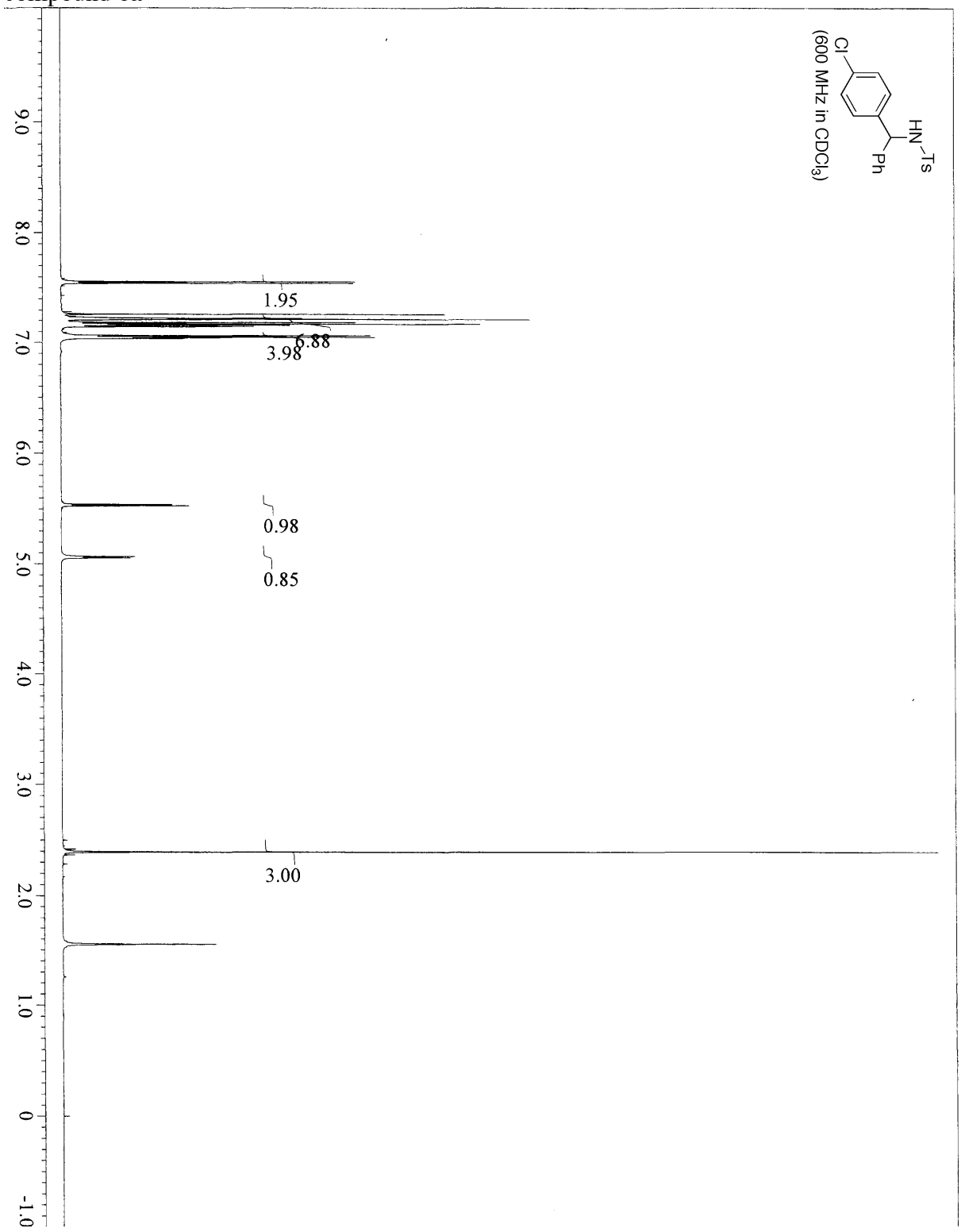
compound **1c**


Ph
(125 MHz in C_6D_6)
Ph_2P-N
Ph
139.9188
139.8529
139.6180
139.2101
139.0864
139.0700
134.9453
134.8423
134.7393
134.2037
132.7491
132.6214
132.5884
132.4648
129.9719
128.7440
128.7152
128.6946
128.6822
128.6451
128.6327
128.6245
128.2537
128.0600
127.8663
127.8375
126.4448
125.9338
125.4806
125.4270
73.7066
73.4593
54.5710
54.4968
45.1062
45.0568
175
150
125
100
75
50
25
0
PPM

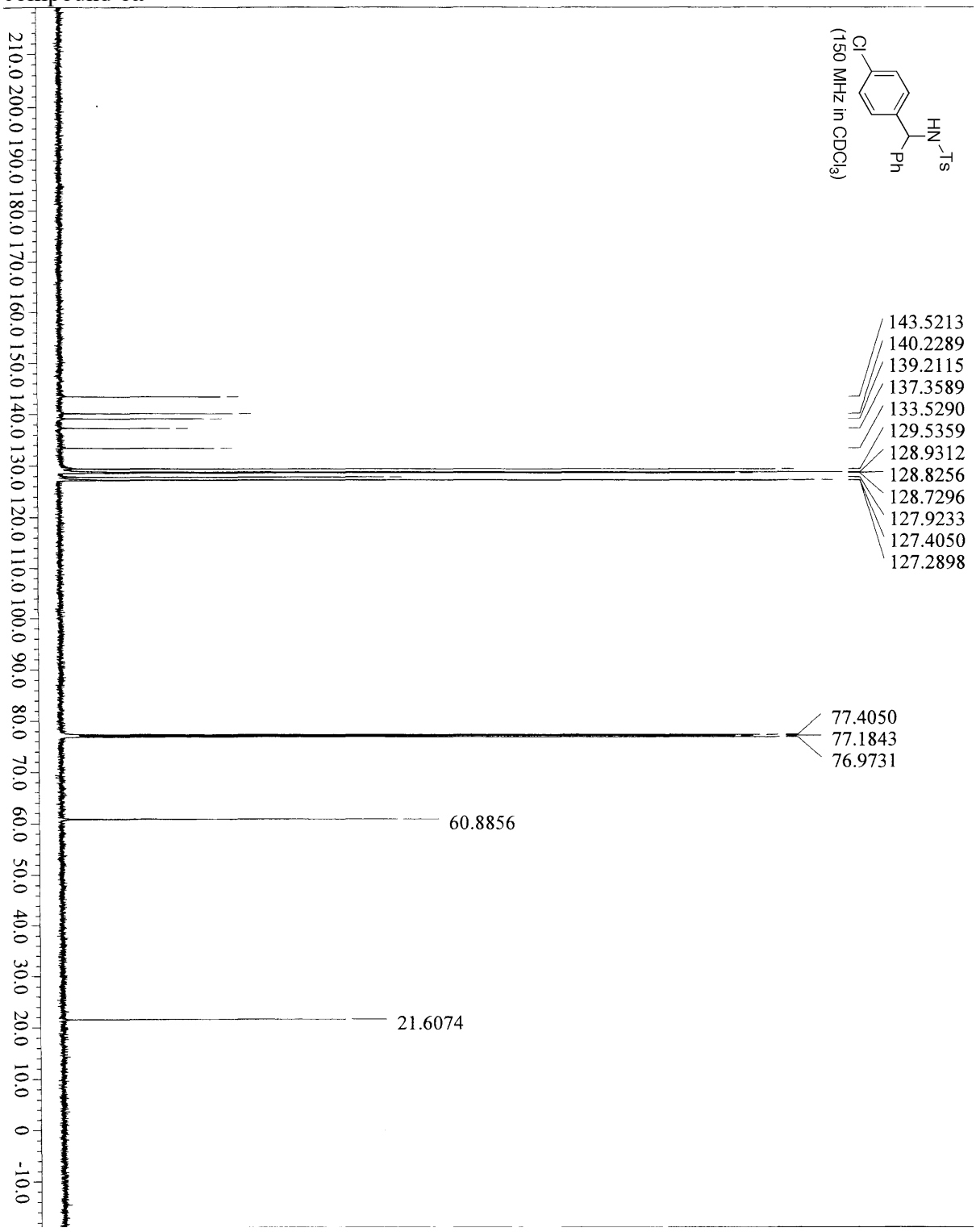
Rh(acac)(**1a**)


Rh(acac)
Ph2P–N
Ph
Me
(500 MHz in C6D6)
1.97
1.98
8.21
8.32
0.97
1.01
0.96
1.00
1.00
2.00
9.00
PPM

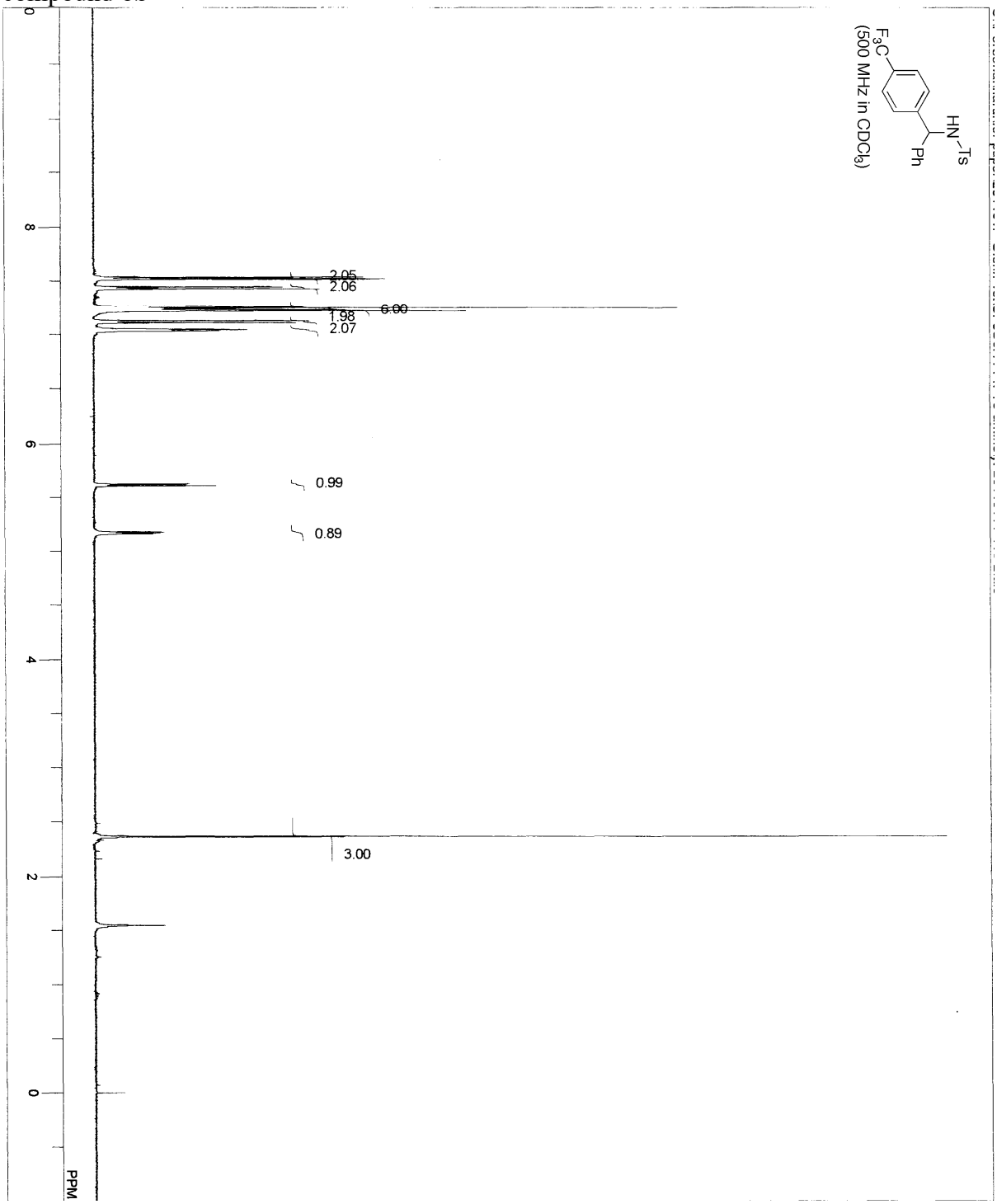
compound **6a**


(600 MHz in CDCl3)
Cl
HN
Ts
Ph
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
1.95
3.98
6.88
0.98
0.85
3.00

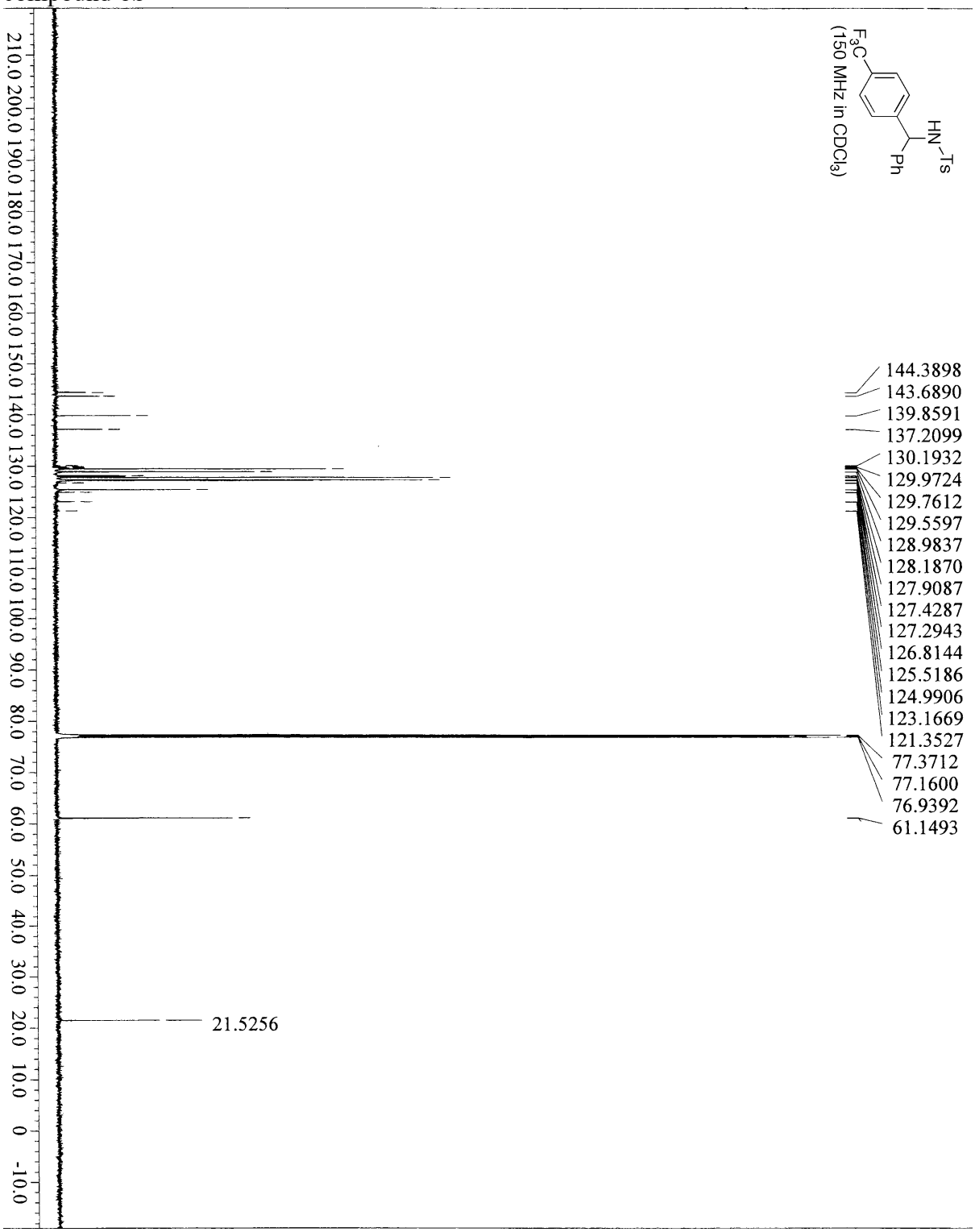
compound **6a**


(150 MHz in CDCl3)
Cl
HN
Ts
Ph
143.5213
140.2289
139.2115
137.3589
133.5290
129.5359
128.9312
128.8256
128.7296
127.9233
127.4050
127.2898
77.4050
77.1843
76.9731
60.8856
21.6074

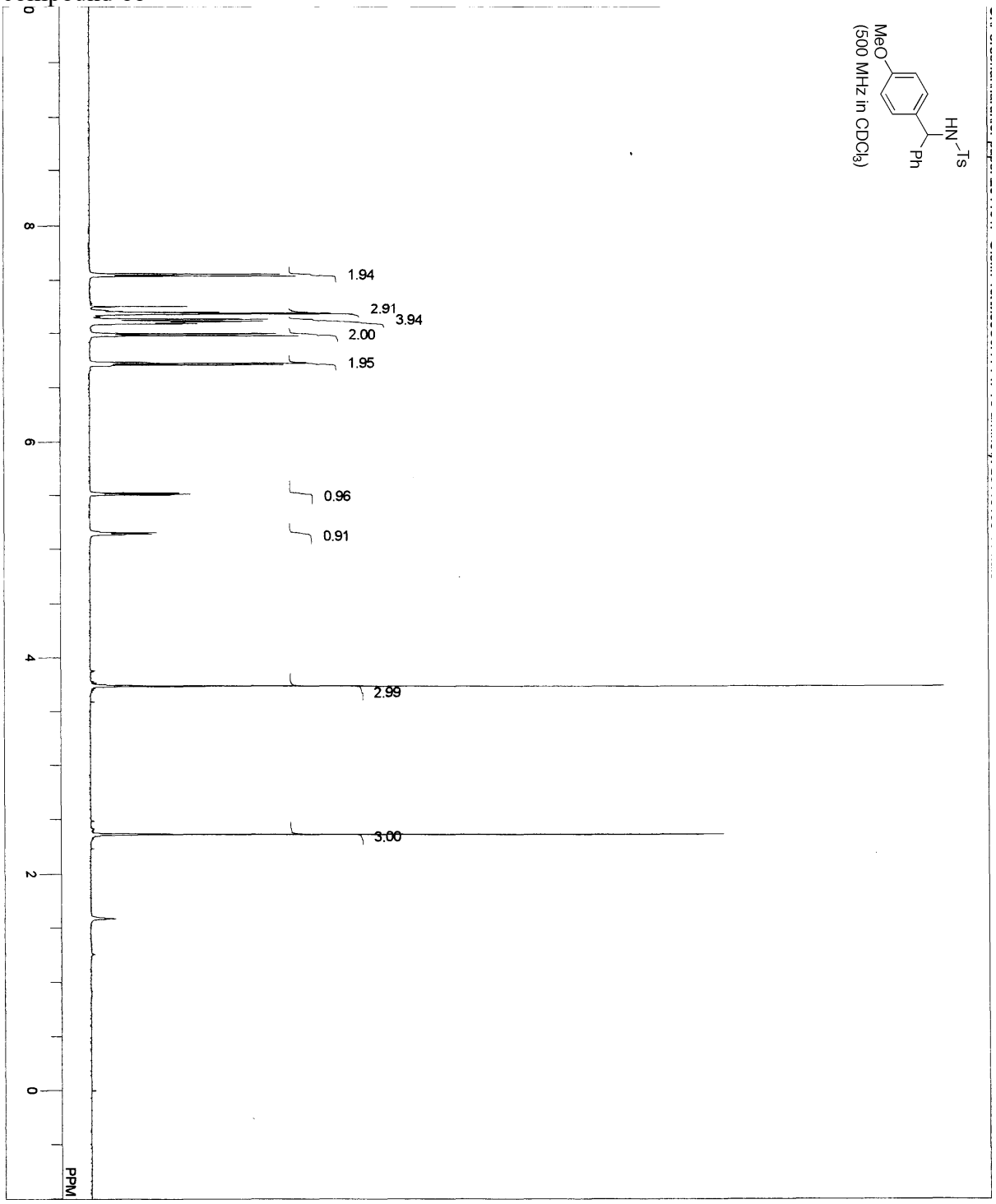
compound **6b**



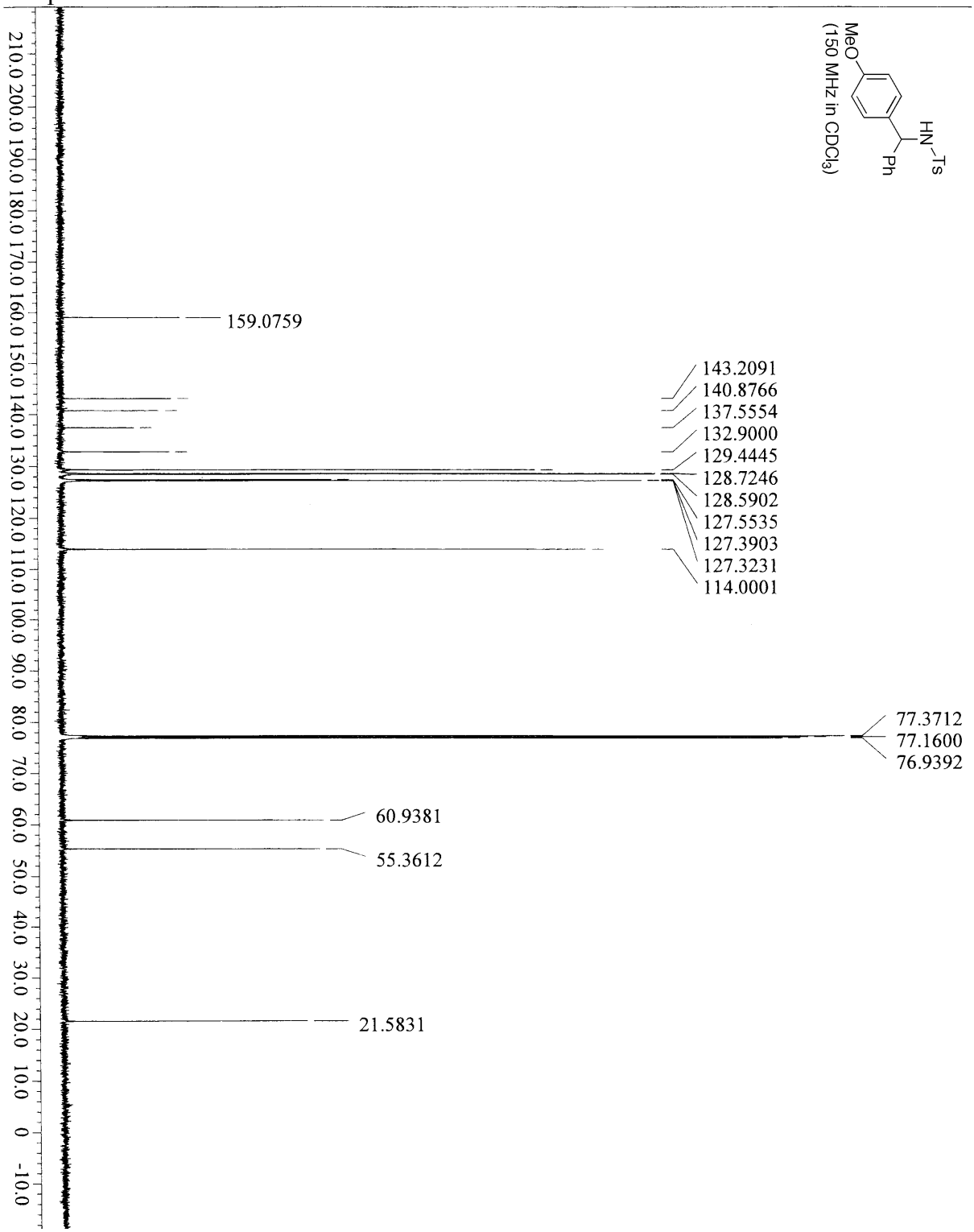
compound **6b**


(150 MHz in CDCl3)
F3C
HN
Ts
Ph
144.3898
143.6890
139.8591
137.2099
130.1932
129.9724
129.7612
129.5597
128.9837
128.1870
127.9087
127.4287
127.2943
126.8144
125.5186
124.9906
123.1669
121.3527
77.3712
77.1600
76.9392
61.1493
21.5256
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 -10.0

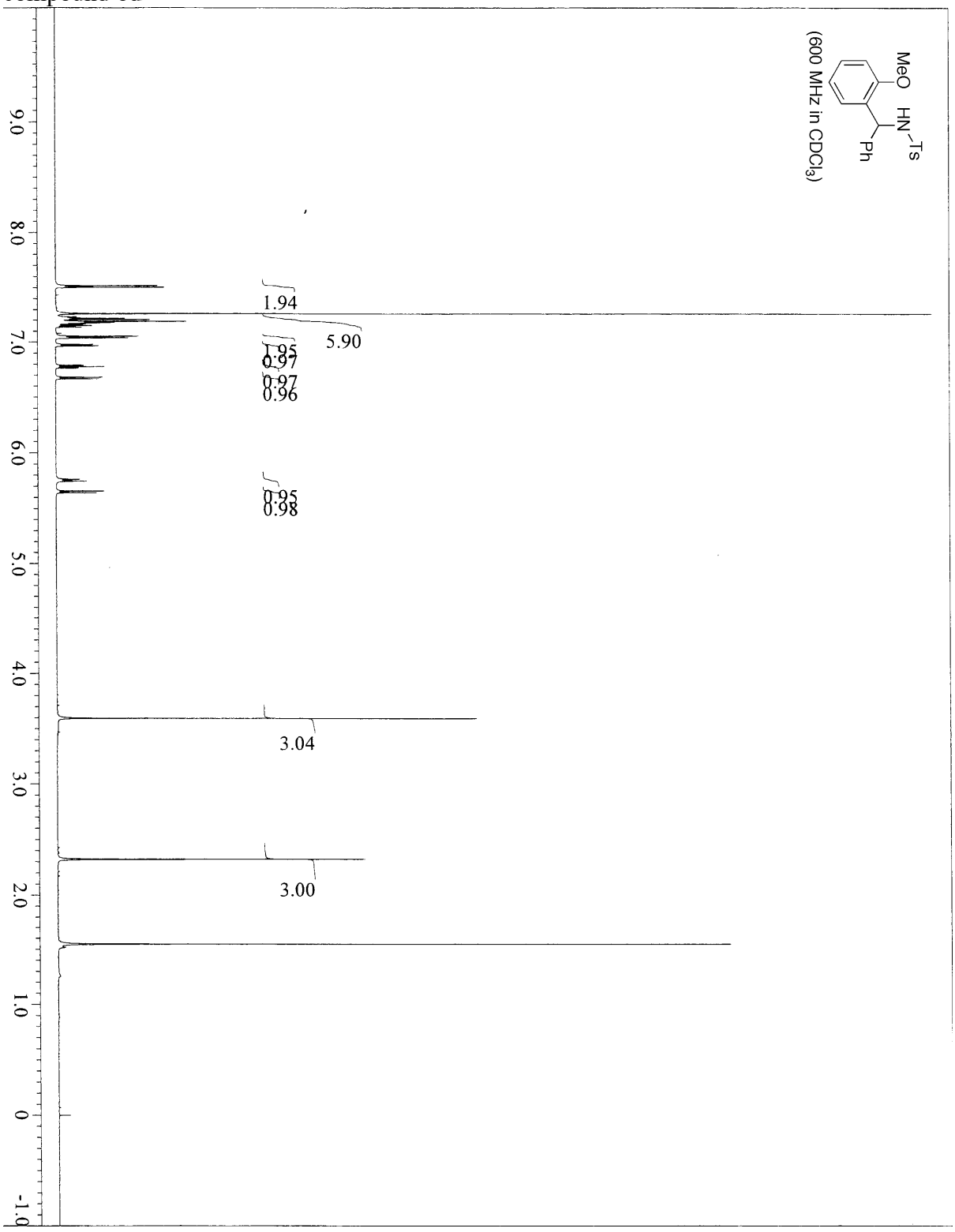
compound **6c**


MeO
(500 MHz in CDCl3)
HN
Ts
Ph
1.94
2.91
3.94
2.00
1.95
0.96
0.91
2.99
3.00
PPM

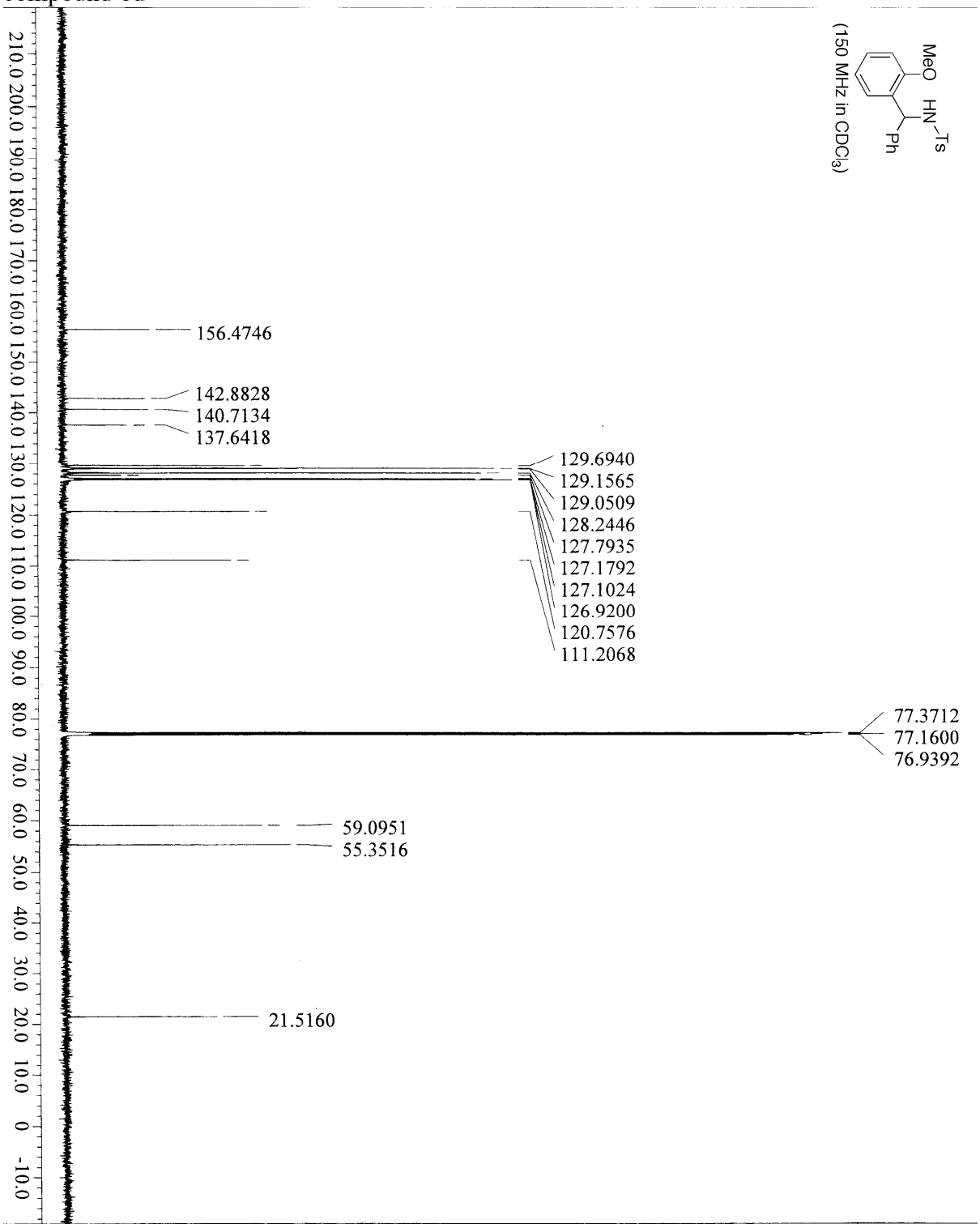
compound **6c**


MeO
(150 MHz in CDCl3)
HN
Ts
Ph
159.0759
143.2091
140.8766
137.5554
132.9000
129.4445
128.7246
128.5902
127.5535
127.3903
127.3231
114.0001
77.3712
77.1600
76.9392
60.9381
55.3612
21.5831
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 -10.0

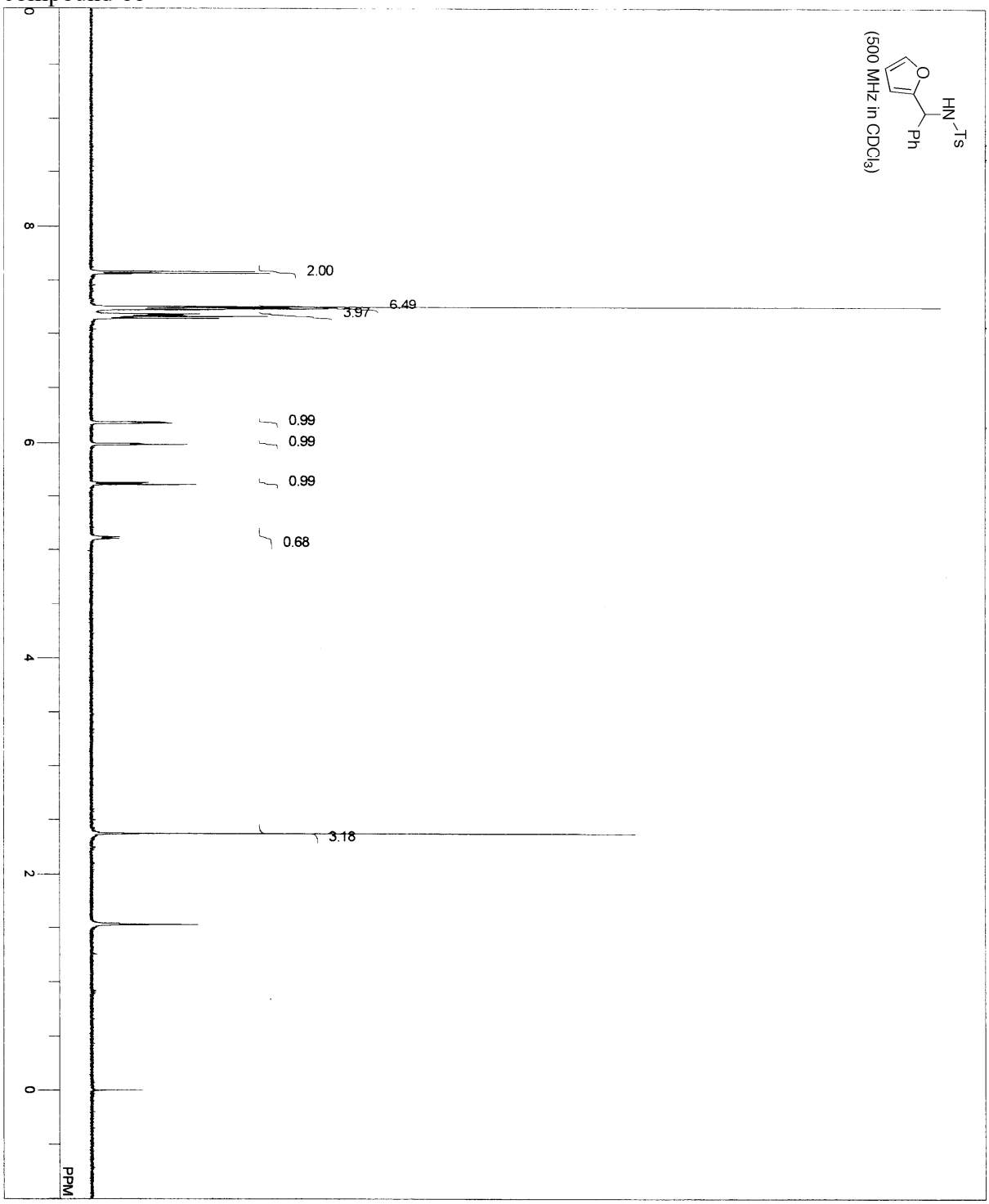
compound **6d**


(600 MHz in CDCl3)
MeO
HN
Ts
Ph
1.94
5.90
1.95
0.97
0.97
0.96
0.95
0.98
3.04
3.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0

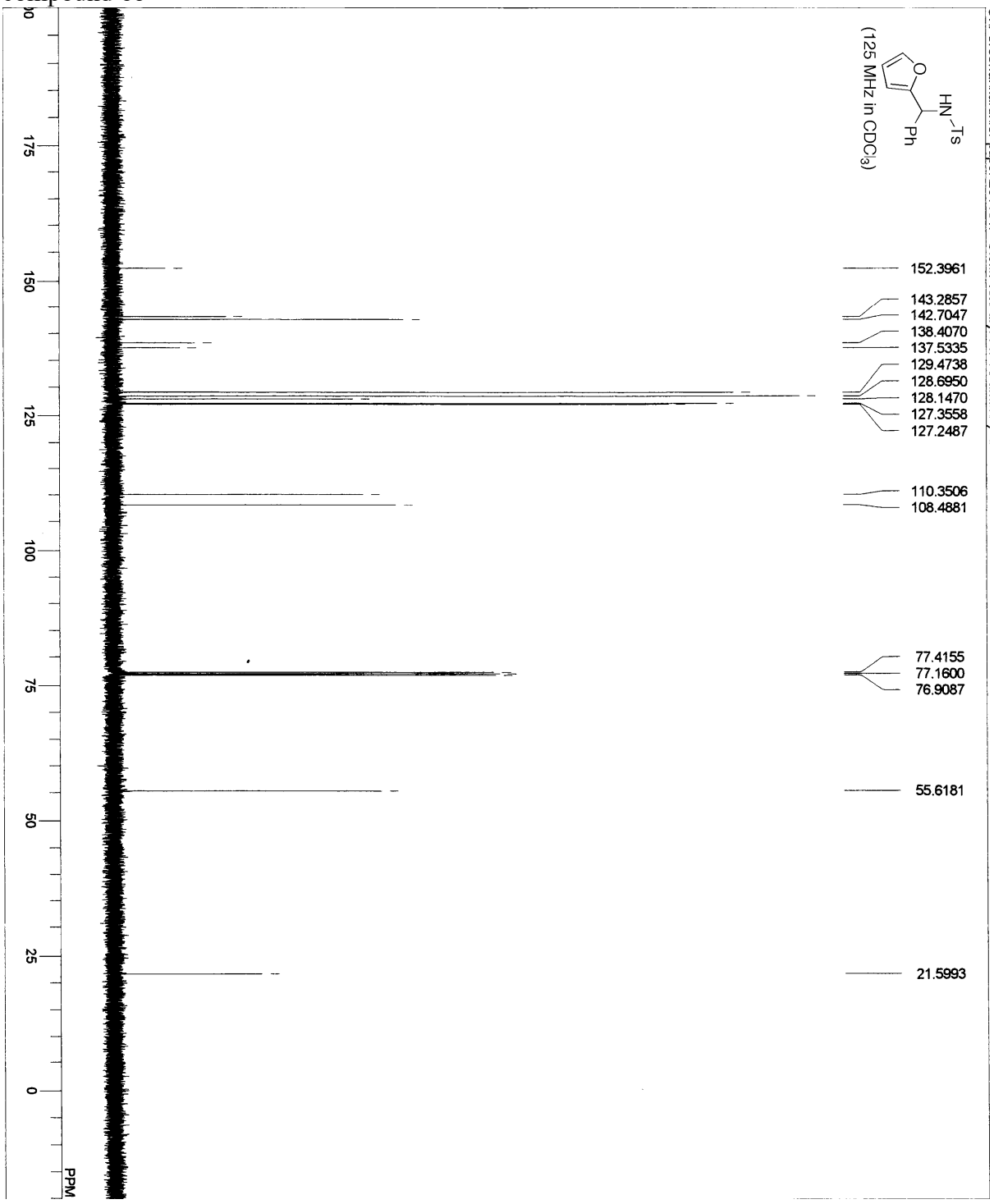
compound **6d**


(150 MHz in CDCl3)
MeO
HN
Ts
Ph
156.4746
142.8828
140.7134
137.6418
129.6940
129.1565
129.0509
128.2446
127.7935
127.1792
127.1024
126.9200
120.7576
111.2068
77.3712
77.1600
76.9392
59.0951
55.3516
21.5160

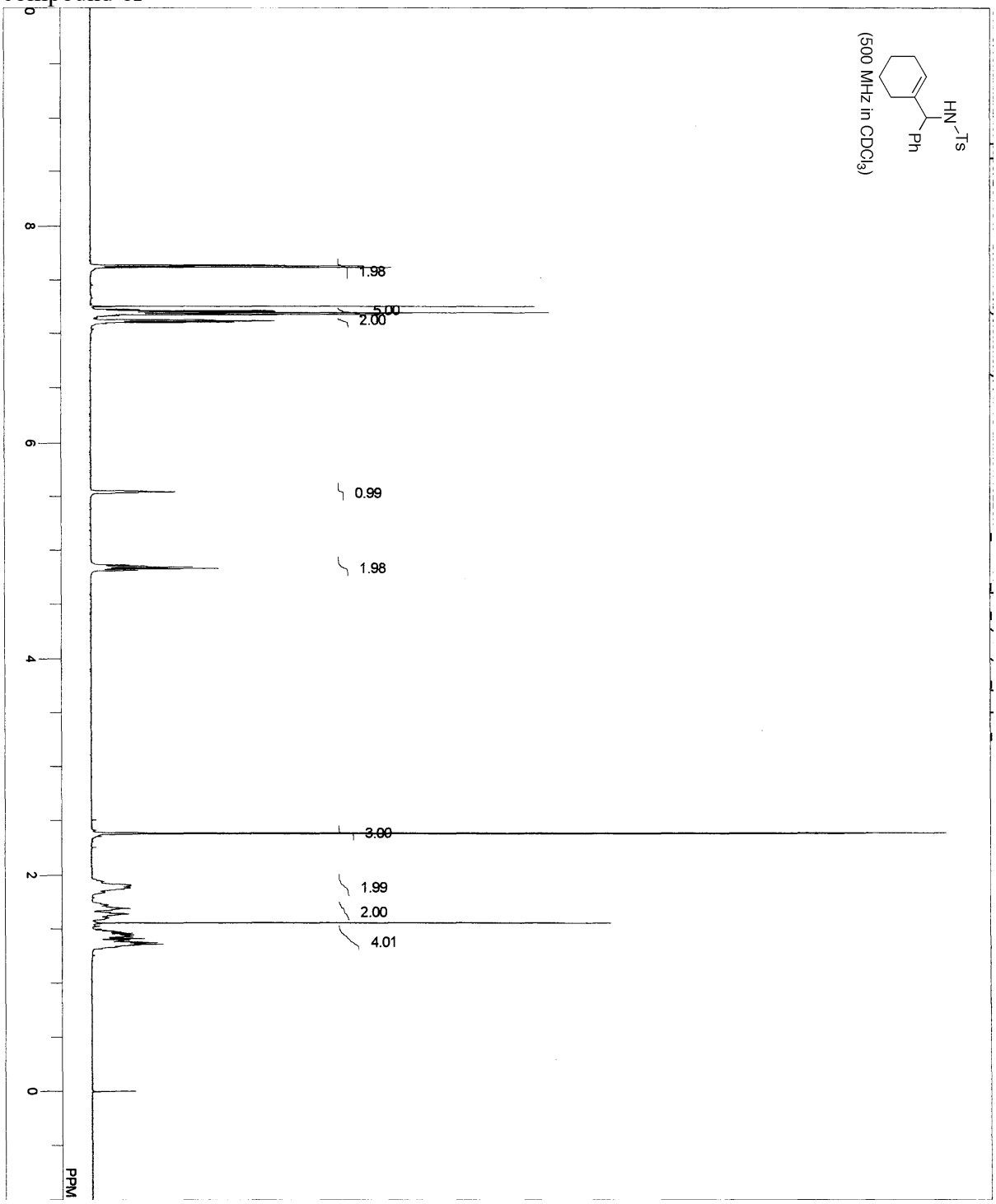
compound **6e**



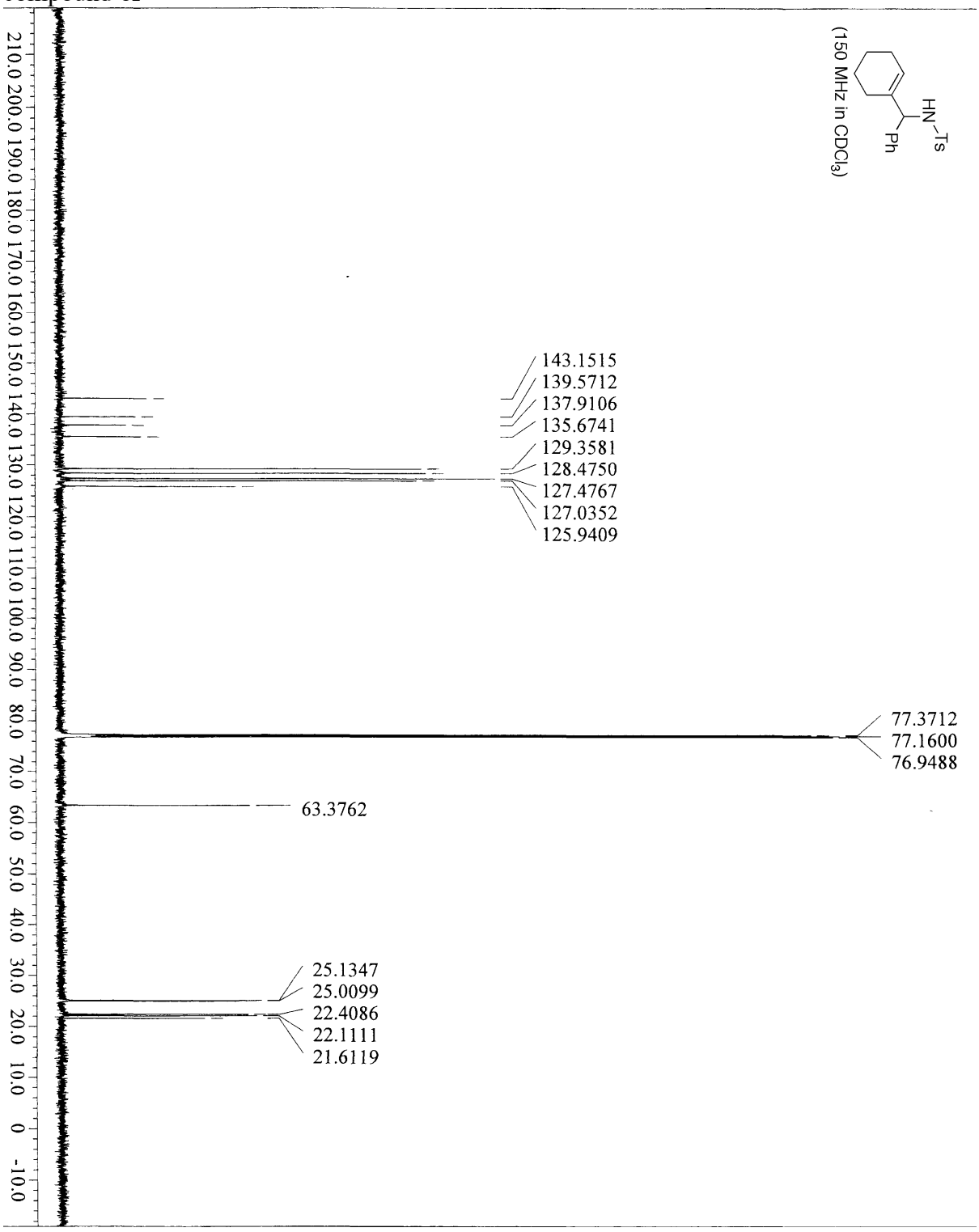
compound **6e**


(125 MHz in CDCl3)
O
HN
Ts
Ph
152.3961
143.2857
142.7047
138.4070
137.5335
129.4738
128.6950
128.1470
127.3558
127.2487
110.3506
108.4881
77.4155
77.1600
76.9087
55.6181
21.5993
175
150
125
100
75
50
25
0
PPM

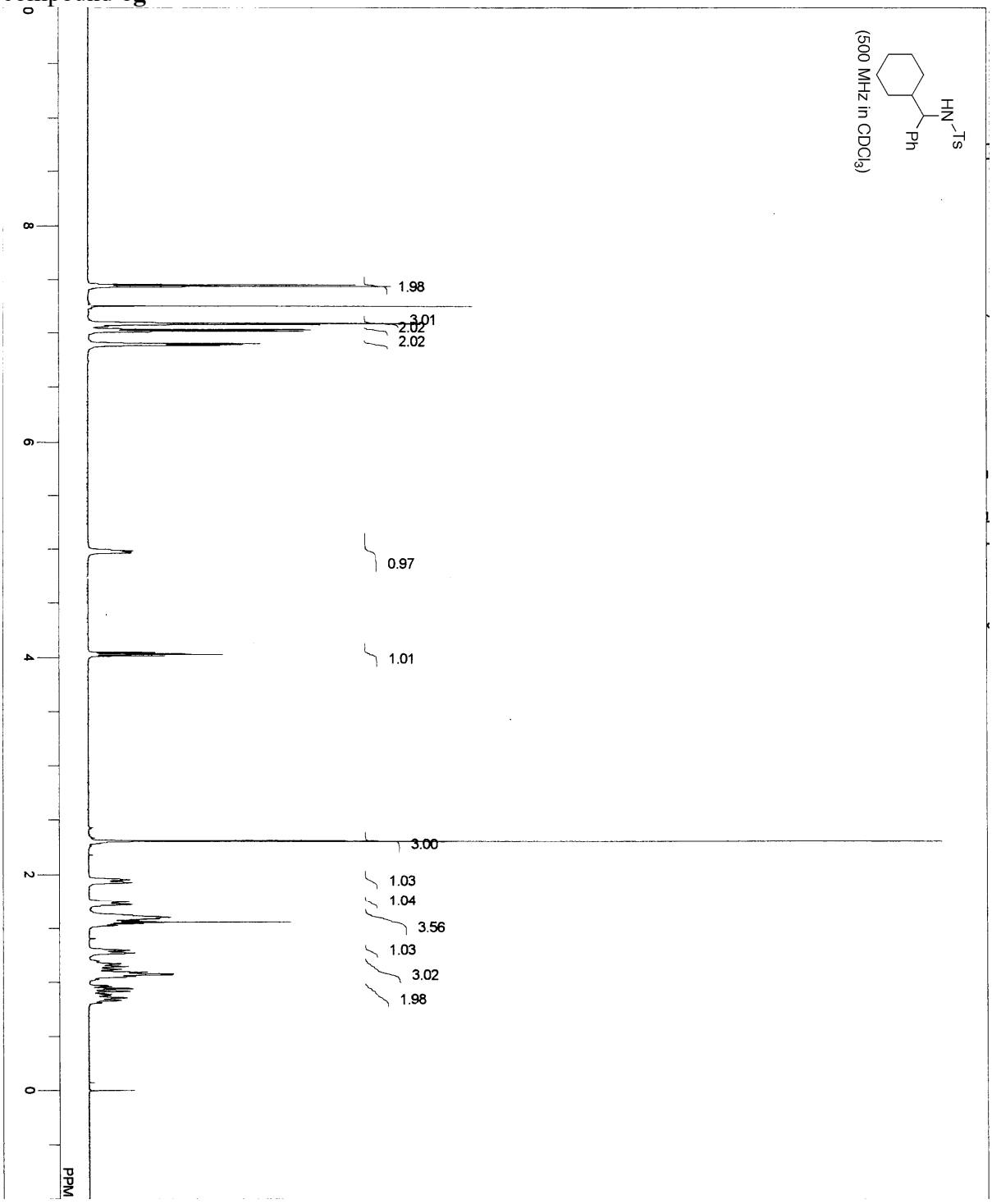
compound **6f**



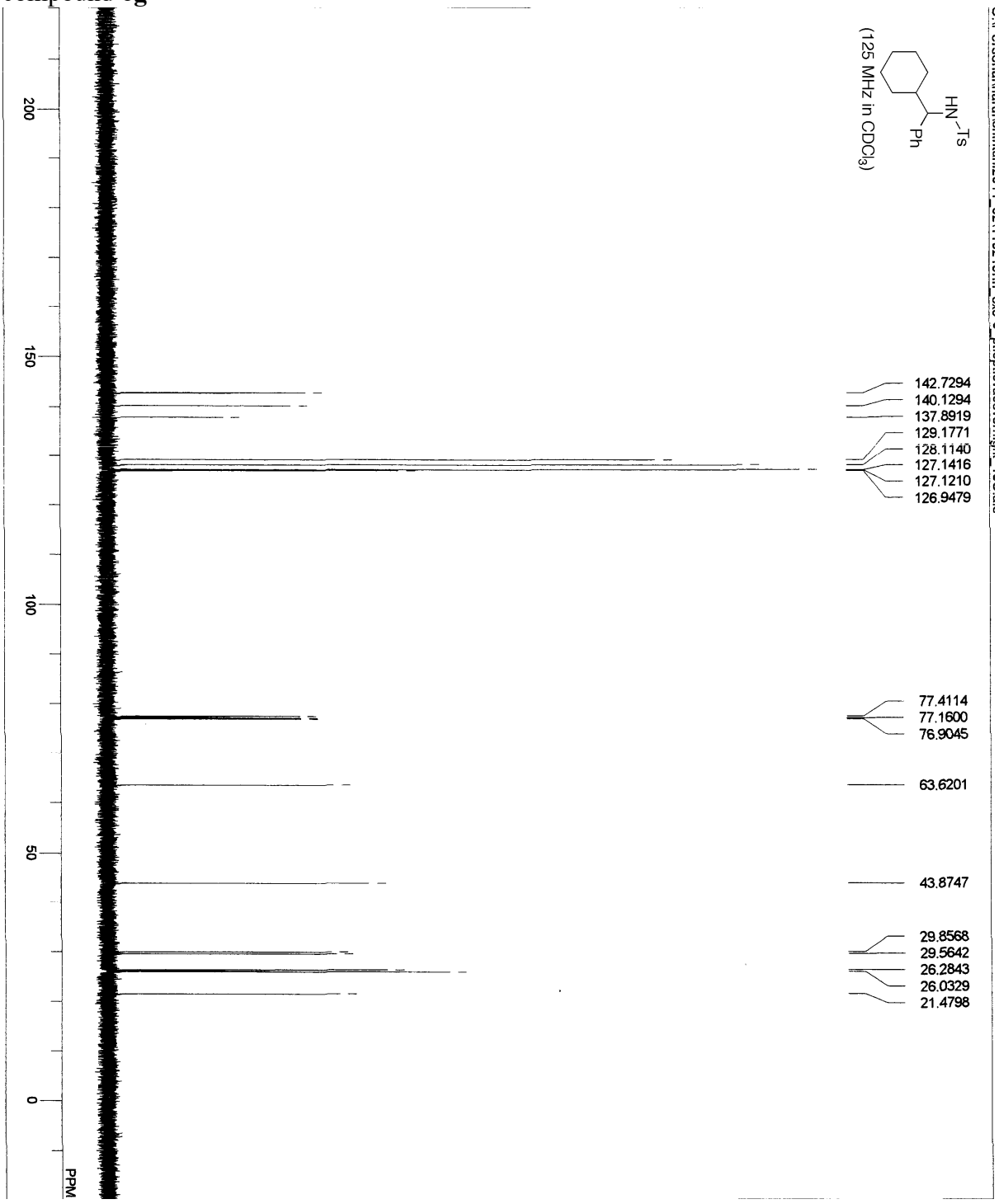
compound **6f**


(150 MHz in CDCl3)
HN
Ts
Ph
143.1515
139.5712
137.9106
135.6741
129.3581
128.4750
127.4767
127.0352
125.9409
77.3712
77.1600
76.9488
63.3762
25.1347
25.0099
22.4086
22.1111
21.6119

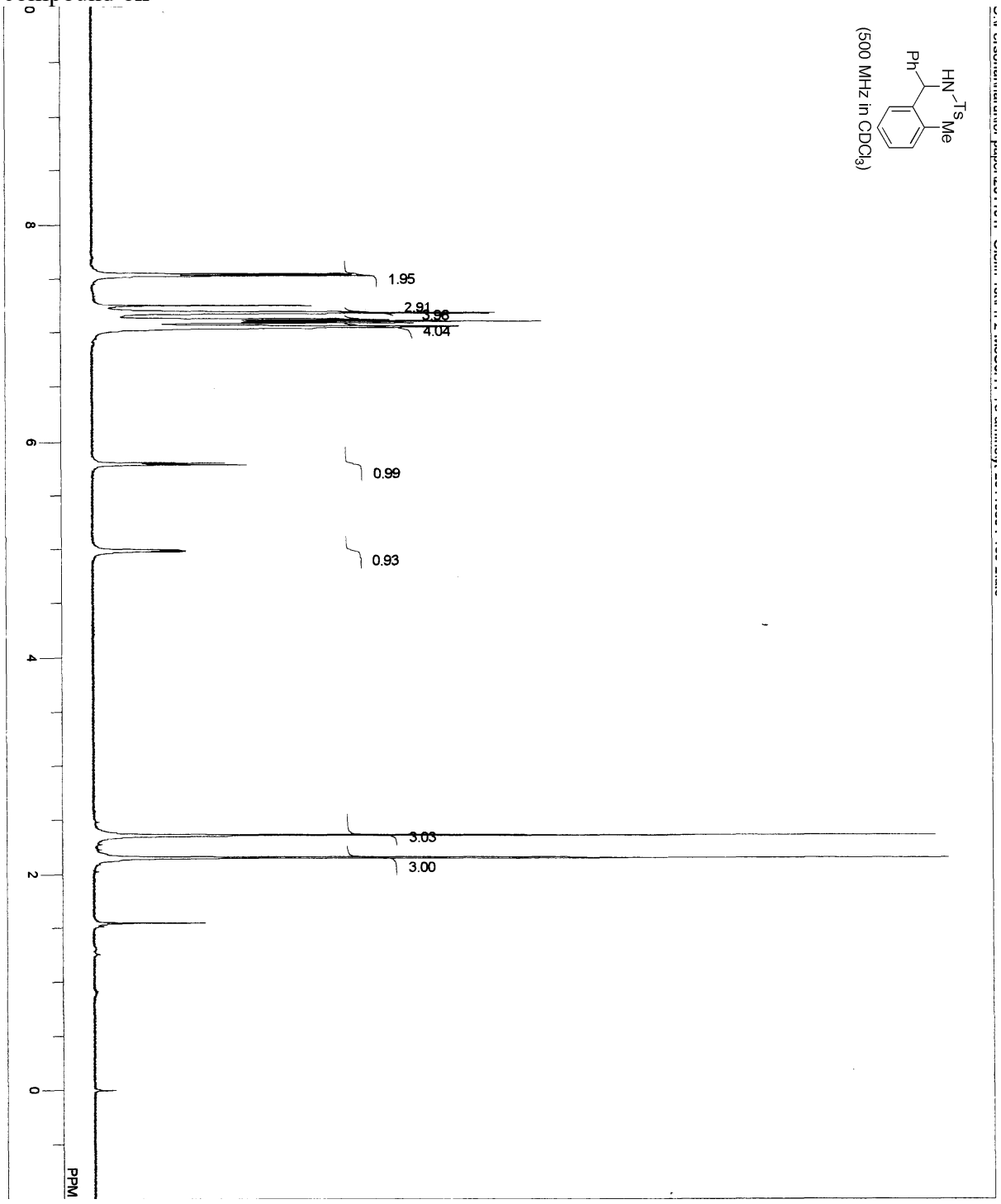
compound **6g**


(500 MHz in CDCl3)
HN
Ts
Ph
1.98
3.01
2.02
2.02
0.97
1.01
3.00
1.03
1.04
3.56
1.03
3.02
1.98
PPM

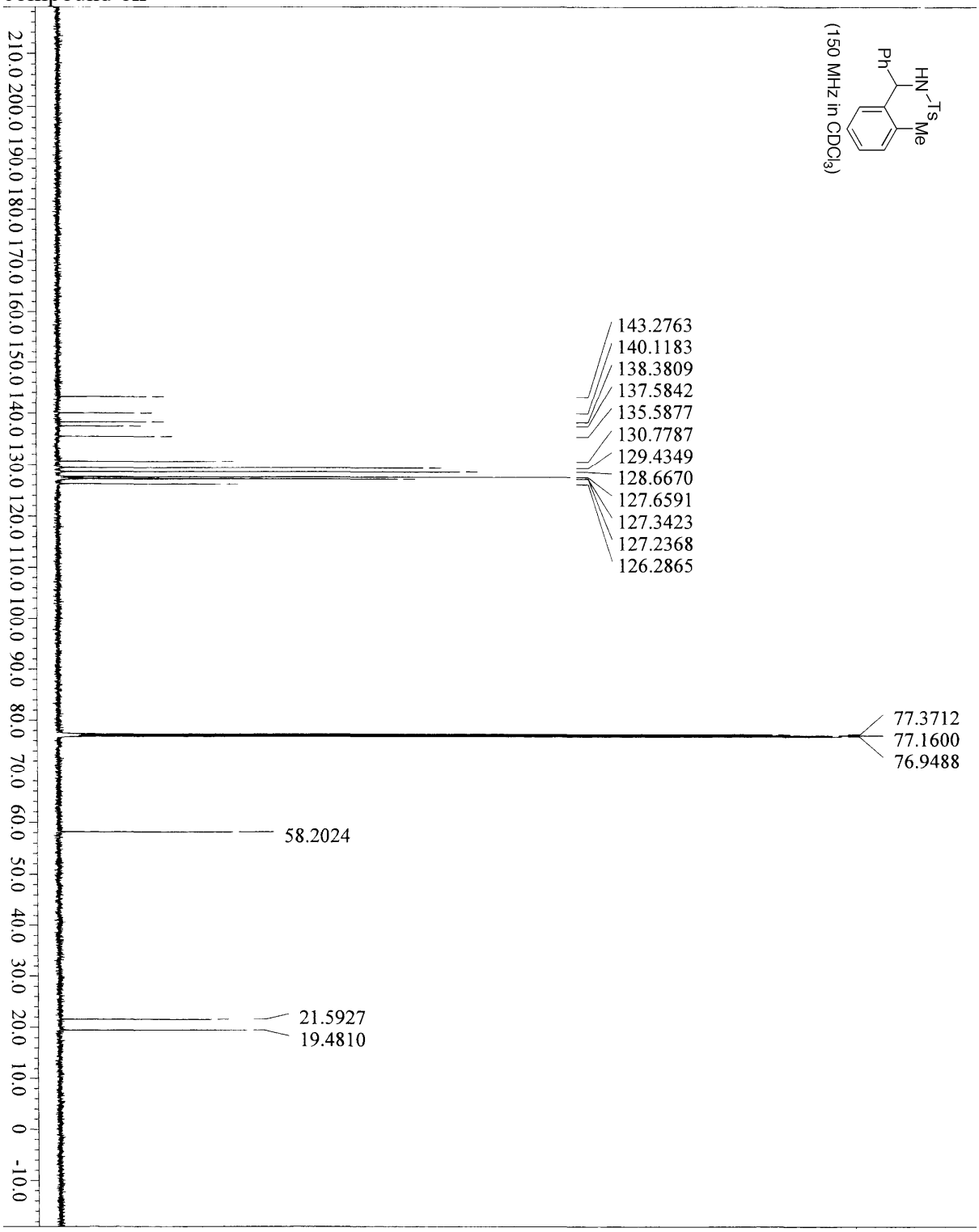
compound **6g**


(125 MHz in CDCl3)
HN
Ts
Ph
142.7294
140.1294
137.8919
129.1771
128.1140
127.1416
127.1210
126.9479
77.4114
77.1600
76.9045
63.6201
43.8747
29.8568
29.5642
26.2843
26.0329
21.4798
200
150
100
50
0
PPM

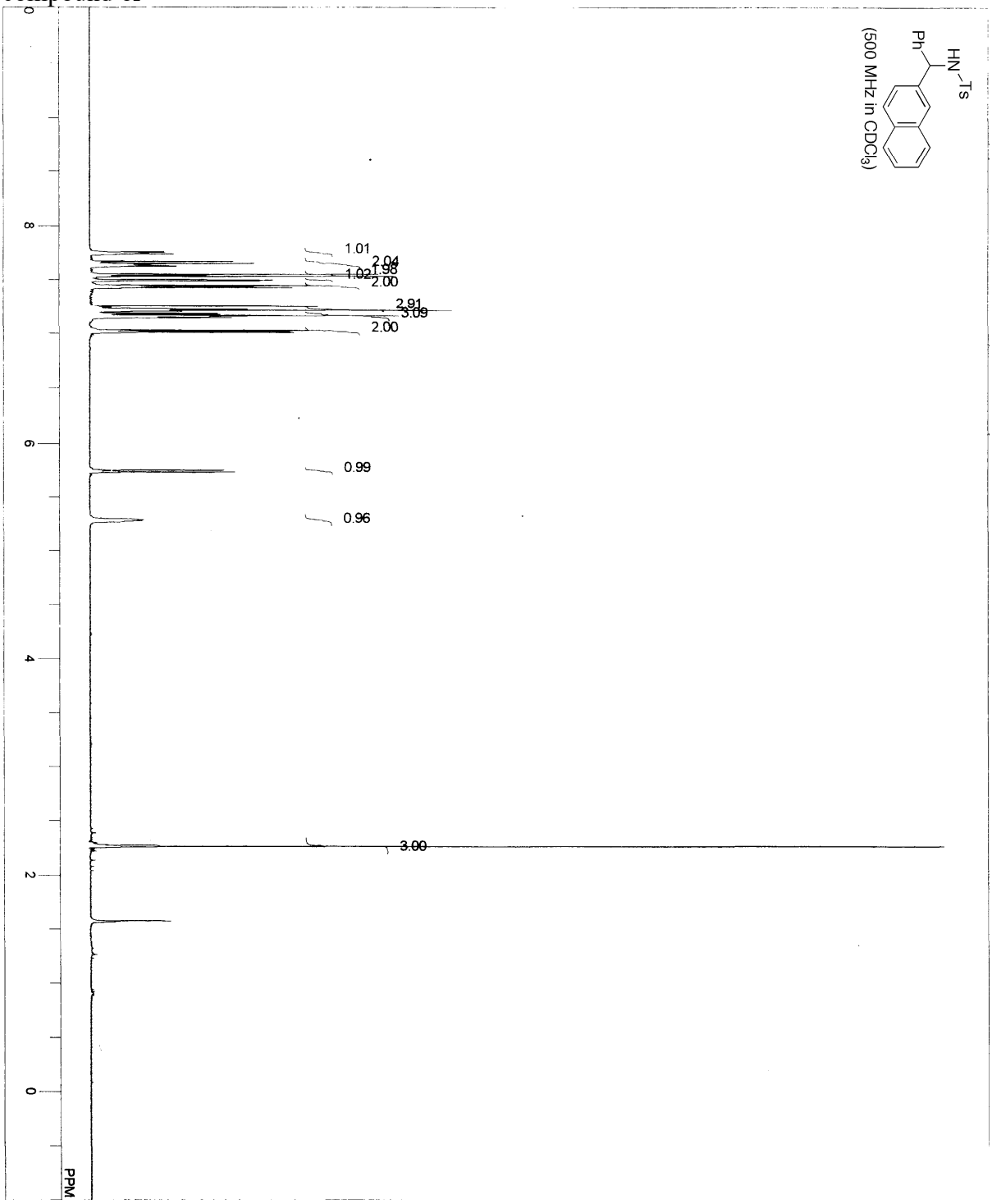
compound **6h**



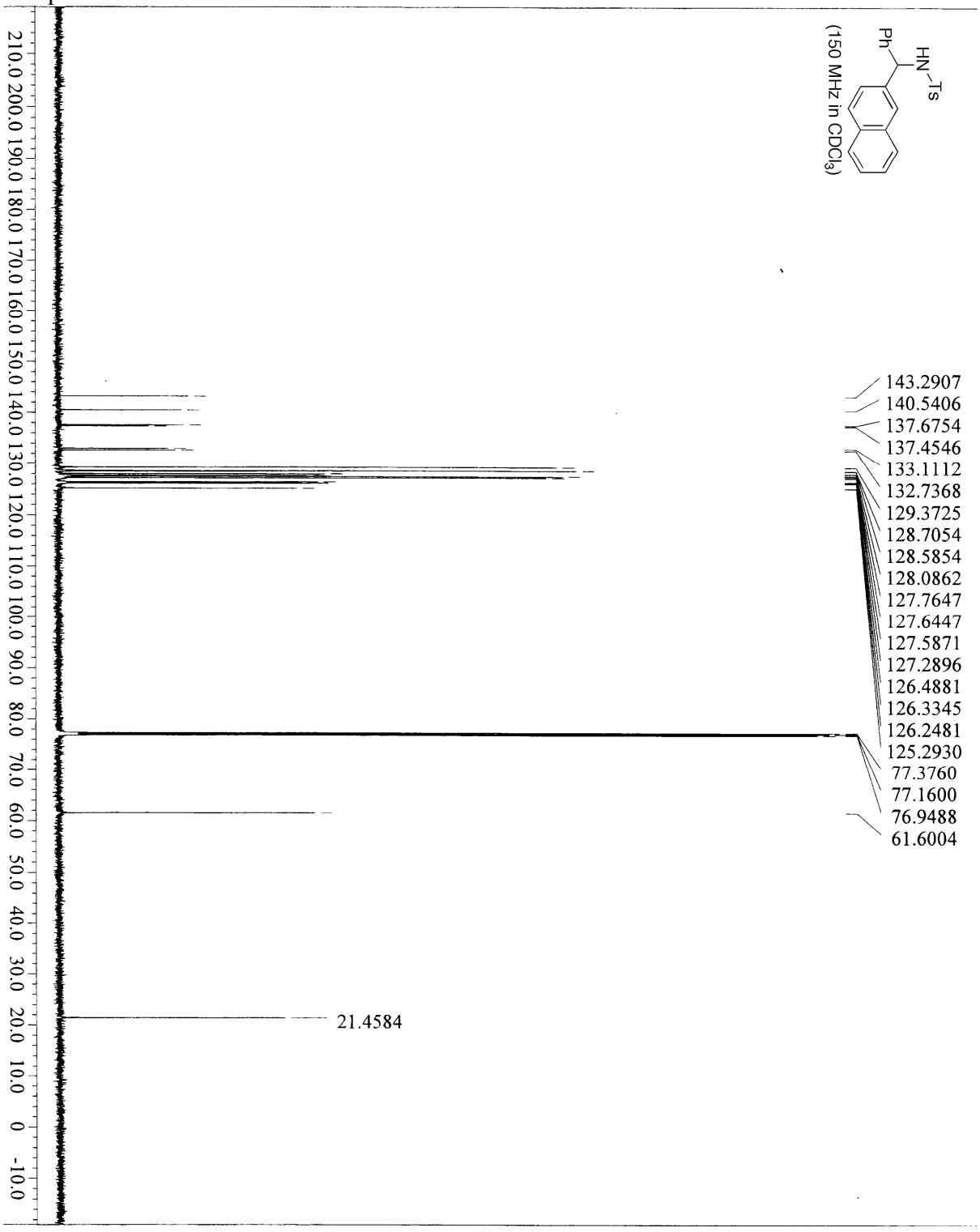
compound **6h**


(150 MHz in CDCl3)
Ph
HN
Ts
Me
143.2763
140.1183
138.3809
137.5842
135.5877
130.7787
129.4349
128.6670
127.6591
127.3423
127.2368
126.2865
77.3712
77.1600
76.9488
58.2024
21.5927
19.4810
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 -10.0

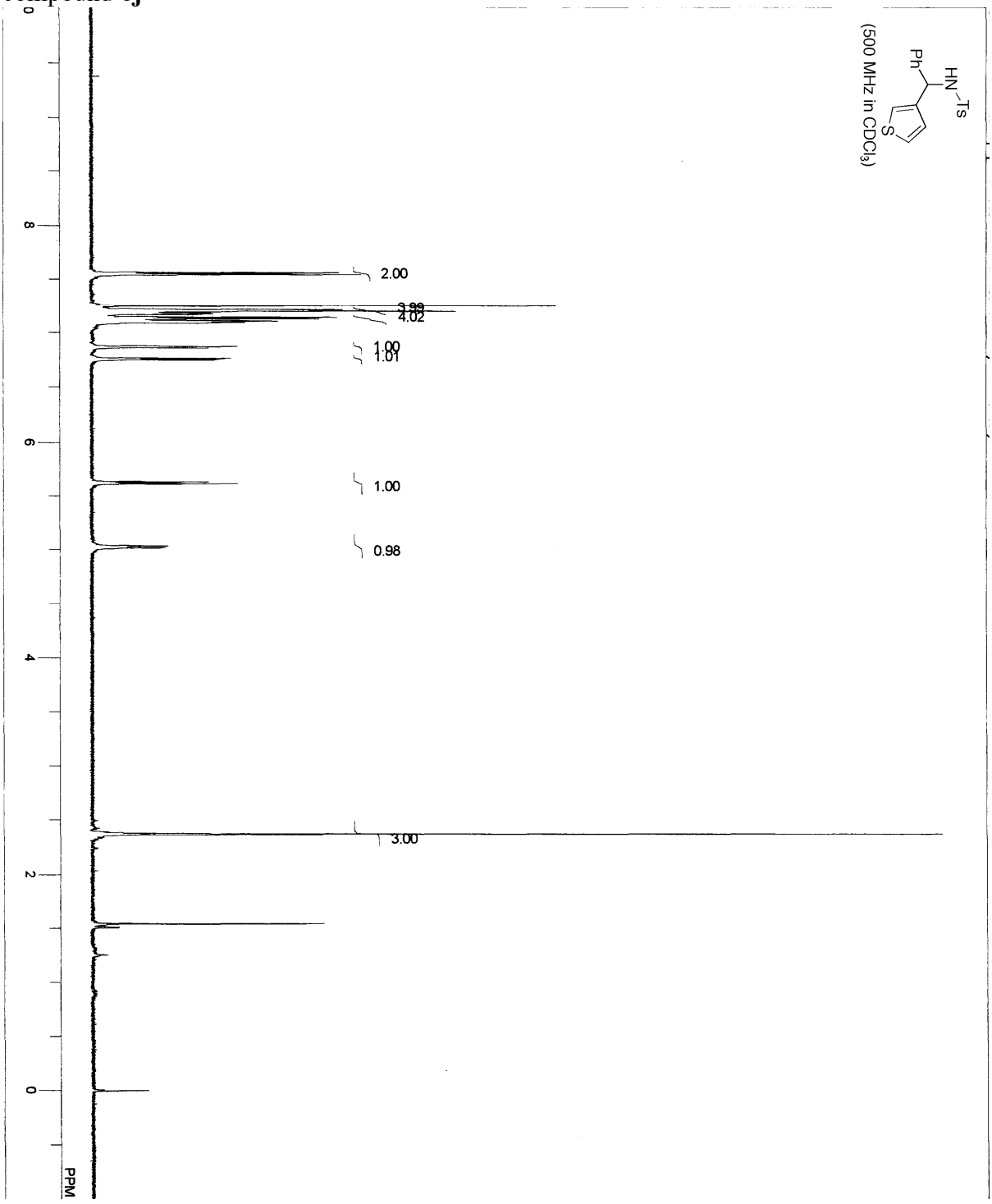
compound **6i**


(500 MHz in CDCl3)
Ph
HN
Ts
1.01
2.04
1.02
1.98
2.00
2.91
3.09
2.00
0.99
0.96
3.00
PPM

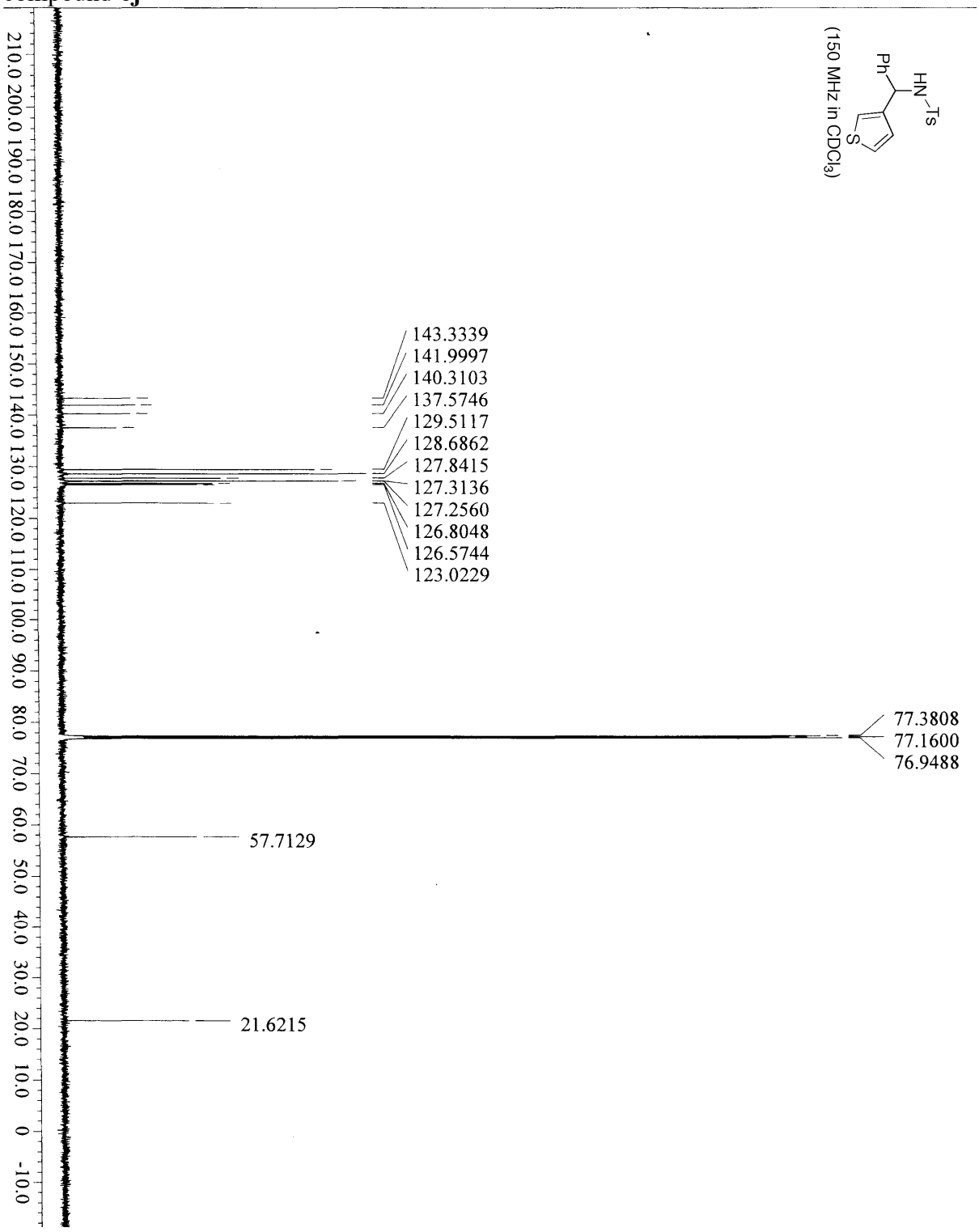
compound **6i**


(150 MHz in CDCl3)
Ph
HN
Ts
143.2907
140.5406
137.6754
137.4546
133.1112
132.7368
129.3725
128.7054
128.5854
128.0862
127.7647
127.6447
127.5871
127.2896
126.4881
126.3345
126.2481
125.2930
77.3760
77.1600
76.9488
61.6004
21.4584
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 -10.0

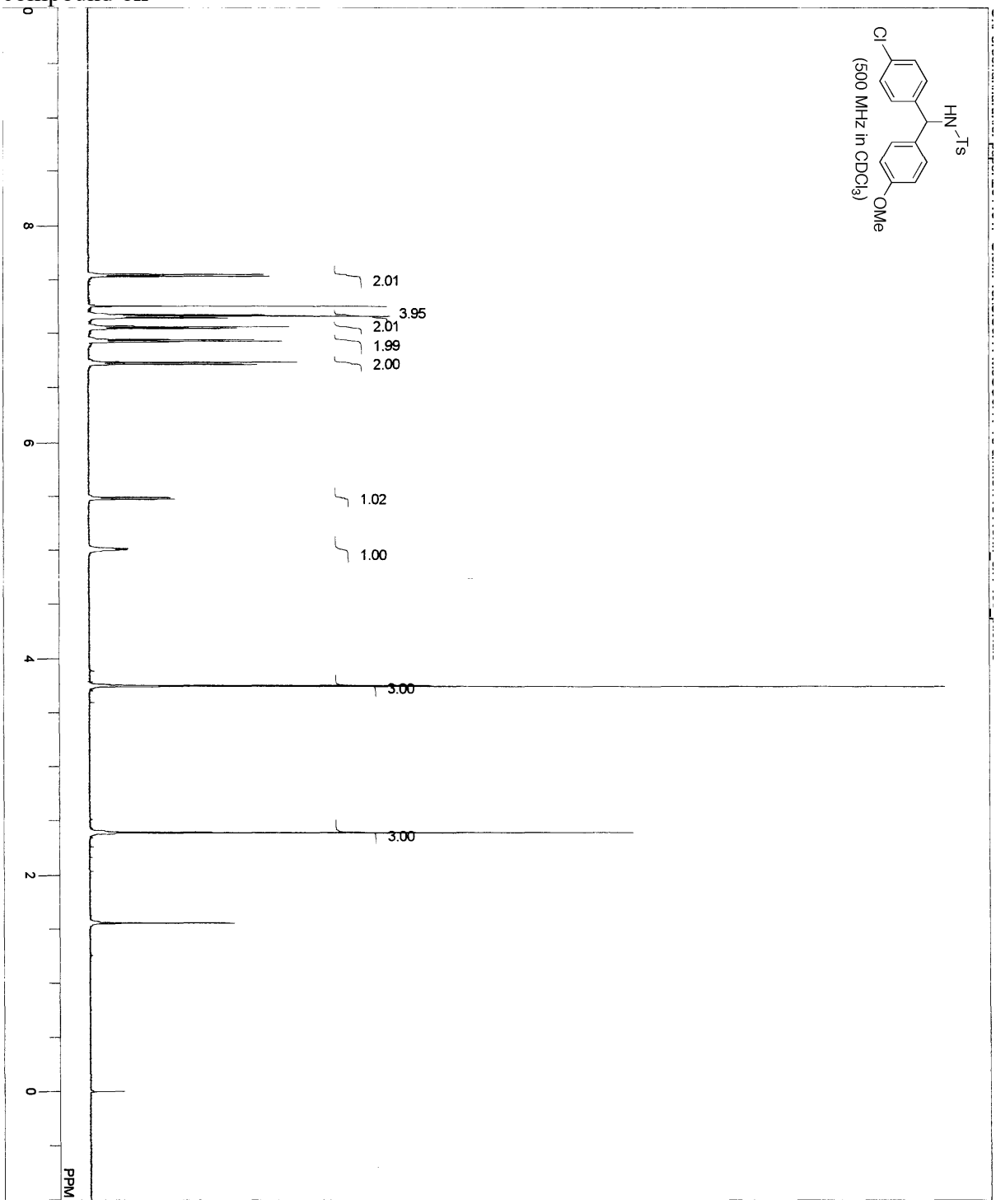
compound **6j**



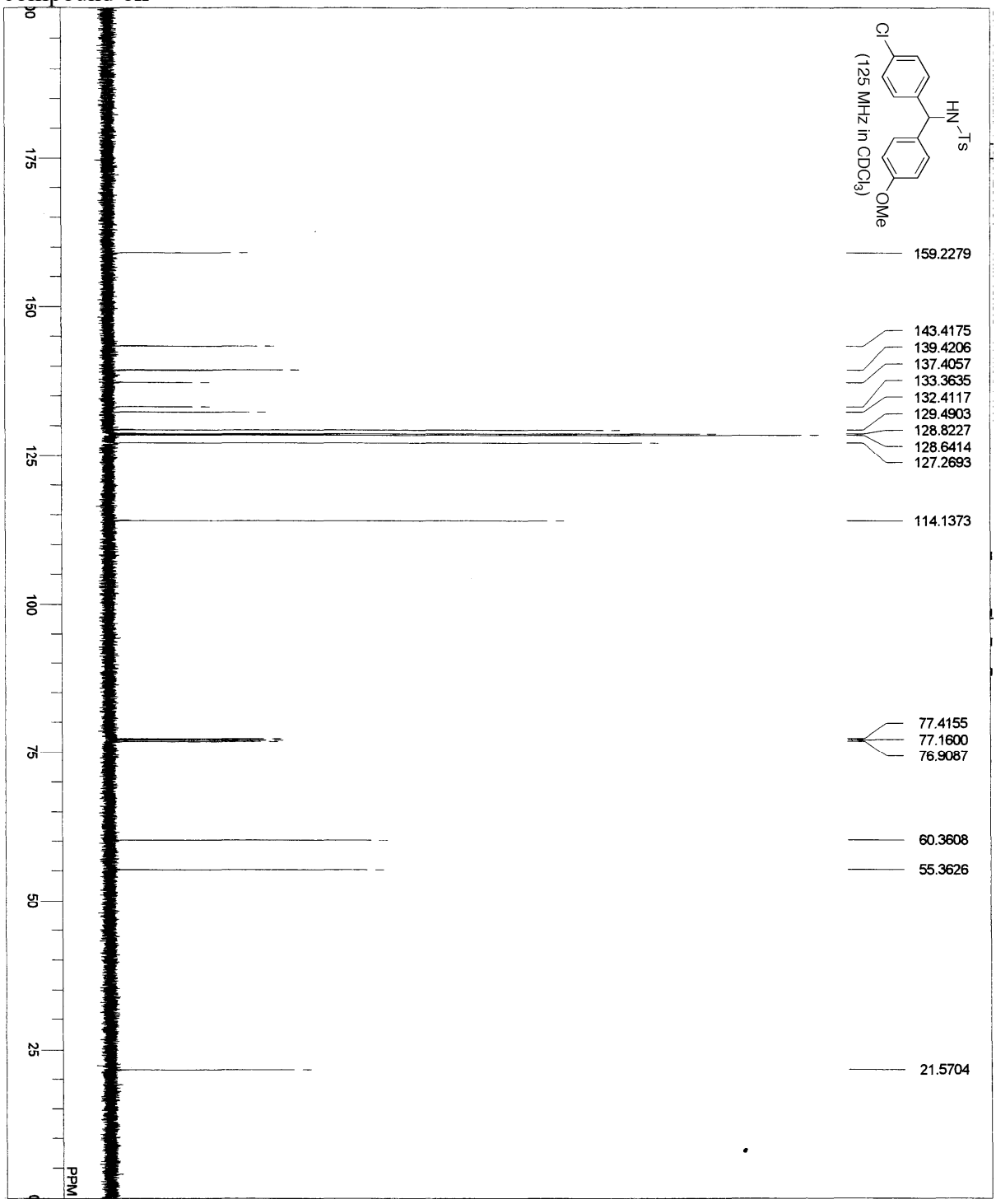
compound **6j**


(150 MHz in CDCl3)
Ph
HN
Ts
S
143.3339
141.9997
140.3103
137.5746
129.5117
128.6862
127.8415
127.3136
127.2560
126.8048
126.5744
123.0229
77.3808
77.1600
76.9488
57.7129
21.6215

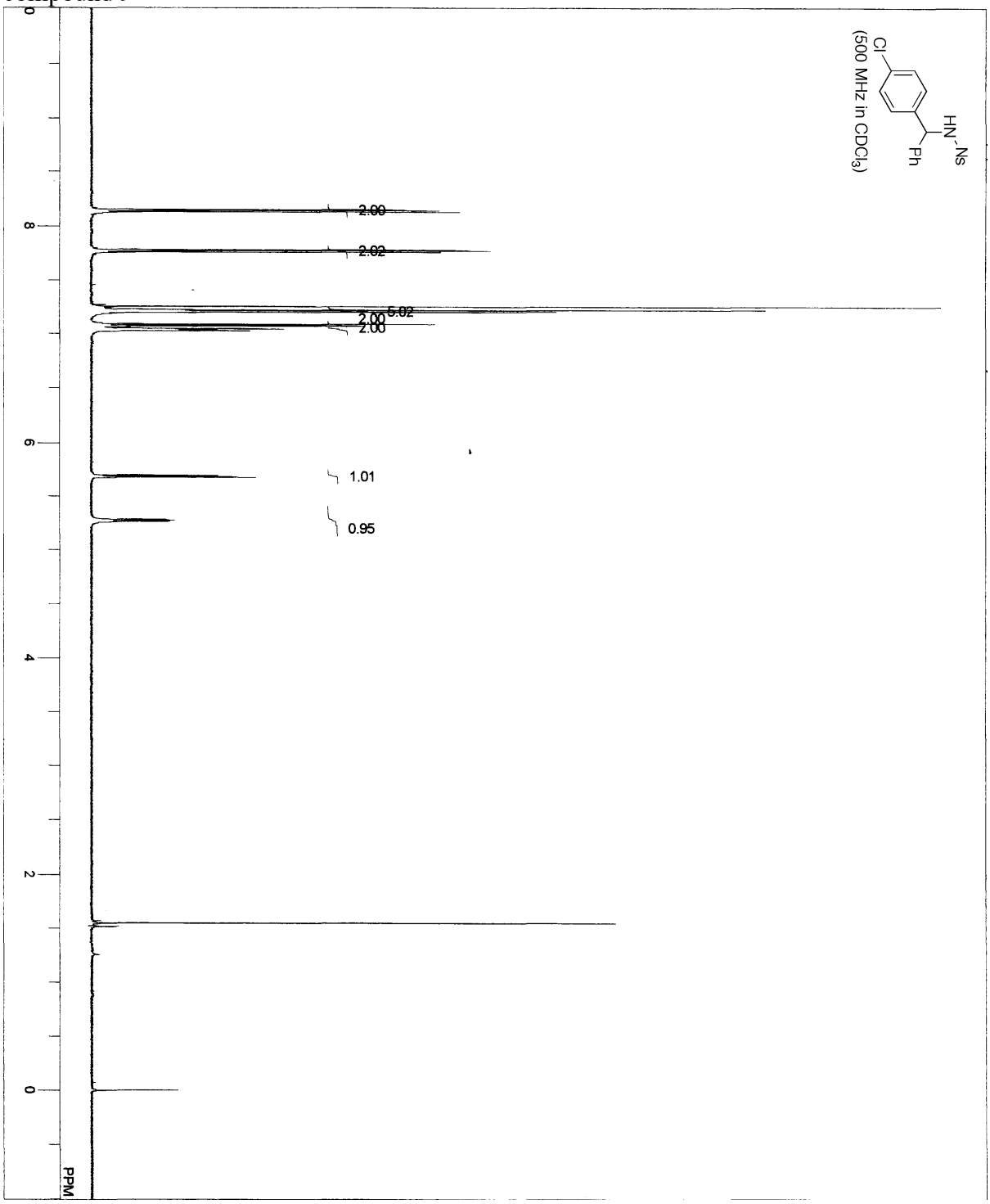
compound **6k**


Cl
HN
Ts
OMe
(500 MHz in CDCl3)
2.01
3.95
2.01
1.99
2.00
1.02
1.00
3.00
3.00
PPM

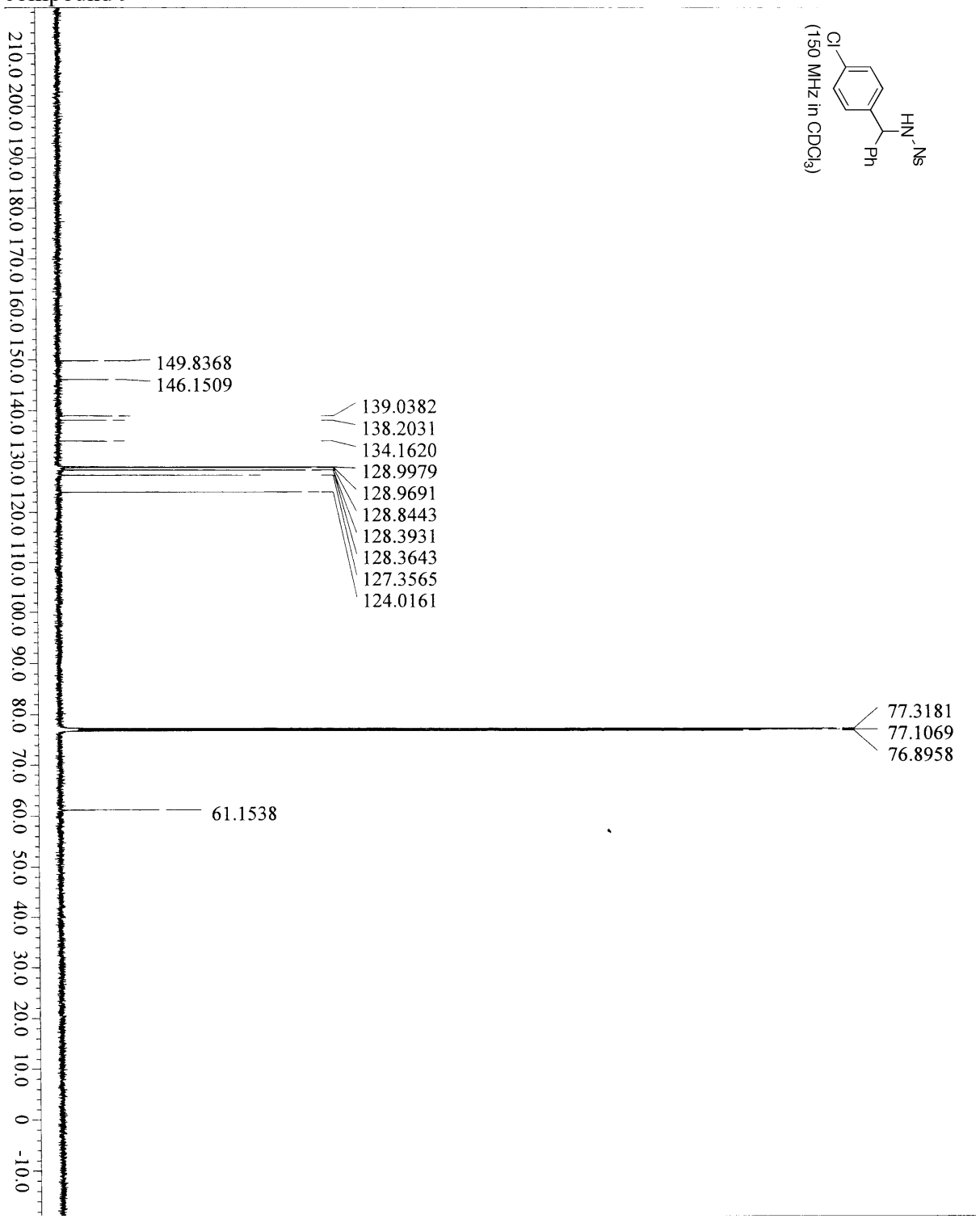
compound **6k**


Cl
HN
Ts
OMe
(125 MHz in CDCl3)
159.2279
143.4175
139.4206
137.4057
133.3635
132.4117
129.4903
128.8227
128.6414
127.2693
114.1373
77.4155
77.1600
76.9087
60.3608
55.3626
21.5704
PPM

compound **9**



compound **9**


(150 MHz in $CDCl_3$)
Cl
HN
Ns
Ph
149.8368
146.1509
139.0382
138.2031
134.1620
128.9979
128.9691
128.8443
128.3931
128.3643
127.3565
124.0161
77.3181
77.1069
76.8958
61.1538
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 -10.0