SUPPORTING INFORMATION

for

Asymmetric Hydrogenation of Bicyclic Ketones Catalyzed by BINAP/IPHAN–Ru(II) Complex

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(A) Preparation and Physical Data of *trans*-$RuCl_2$(binap)(1,4-diamine) complexes (3a–e)

The preparative method for these complexes was previously described.[1] Their physical properties are as follows:

***trans*-$RuCl_2$[(*R*)-binap][(*S*)-ipban] [(*R*,*S*)-3a].** IR (ATR) 3326, 3053, 1433, 1087, 1075, 1021, 741, 697 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 1.27 (s, 6H), 2.43–2.47 (br m, 2H), 2.57–2.75 (m, 4H), 2.93 (br s, 2H), 3.67–3.70 (m, 2H), 6.27 (d, 2H, *J* = 8.2 Hz), 6.47 (br m, 6H), 6.67–6.72 (t-like m, 2H), 7.12–7.17 (t-like m, 2H), 7.39 (br m, 6H), 7.52 (d, 2H, *J* = 8.0 Hz), 7.62 (br m, 4H), 7.73 (d, 2H, *J* = 8.5 Hz), 7.91 (br, m, 4H), 8.25–8.30 (m, 2H). ^{31}P NMR (121 MHz, $CDCl_3$) δ 46.5 (s). HRMS (ESI^+) *m*/*z* 954.1606 (M^+), calcd for $C_{51}H_{48}{}^{35}Cl_2N_2O_2P_2{}^{102}Ru$: 954.1612.

***trans*-$RuCl_2$[(*S*)-binap][(*S*)-ipban] [(*S*,*S*)-3a].** IR (ATR) 3323, 3054, 1434, 1087, 1023, 741, 697 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 1.29 (s, 6H), 2.07 (br m, 2H), 2.67–2.70 (br m, 2H), 2.85 (br m, 2H), 3.06–3.08 (br m, 2H), 3.72–3.74 (m, 2H), 6.28 (d, 2H, *J* = 8.7 Hz), 6.48 (br m, 6H), 6.68–6.73 (t-like m, 2H), 7.13–7.17 (t-like m, 2H), 7.39 (br m, 6H), 7.52 (d, 2H, *J* = 8.0 Hz), 7.61 (br m, 4H), 7.71 (d, 2H, *J* = 8.7 Hz), 7.89 (br, m, 4H), 8.23–8.27 (m, 2H). ^{31}P NMR (121 MHz, $CDCl_3$) δ 46.5 (s). HRMS (ESI^+) *m*/*z* 954.1617 (M^+), calcd for $C_{51}H_{48}{}^{35}Cl_2N_2O_2P_2{}^{102}Ru$: 954.1612.

***trans*-$RuCl_2$[(*S*)-binap][(*R*)-iphan] [(*S*,*R*)-3b].** IR (KBr-disk) 3311, 3055, 1569, 1482, 1433, 1370, 1057, 1035, 741, 697 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 0.54 (d, 6H, *J* = 6.4 Hz), 1.24 (s, 6H), 2.66–2.75 (br m, 4H), 3.04 (br m, 2H), 3.47–3.51 (m, 2H), 6.25 (d, 2H, *J* = 8.4 Hz), 6.45–6.47 (br m, 6H), 6.64–6.70 (t-like m, 2H), 7.10–7.16 (t-like m, 2H), 7.39–7.41 (br m, 6H), 7.51 (d, 2H, *J* = 8.0 Hz), 7.63 (br m, 4H), 7.72 (d, 2H, *J* = 8.5 Hz), 7.96 (br, m, 4H), 8.28–8.34 (m, 2H). ^{31}P NMR (121 MHz, $CDCl_3$) δ 45.7 (s). HRMS (ESI^+) *m*/*z* 982.1918 (M^+), calcd for $C_{53}H_{52}{}^{35}Cl_2N_2O_2P_2{}^{102}Ru$: 982.1925. Found: C, 64.62%, H, 5.55%; N, 2.70%. Calcd for $C_{53}H_{52}Cl_2N_2O_2P_2Ru$: C, 64.76%; H, 5.33%; N, 2.85%.

***trans*-RuCl$_2$[(*S*)-tolbinap][(*R*)-iphan] [(*S*,*R*)-3c].** IR (ATR) 3309, 2989, 1500, 1223, 1194, 1053, 1038, 808, 756, 744 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.53 (d, 6H, *J* = 6.4 Hz), 1.24 (s, 6H), 1.77 (s, 6H), 2.35 (s, 6H), 2.63–2.73 (m, 4H), 3.01 (br m, 2H), 3.46–3.51 (m, 2H), 6.20–6.24 (m, 6H), 6.65–6.69 (t-like m, 2H), 7.12–7.16 (t-like m, 2H), 7.21 (d, 4H, *J* = 8.0 Hz), 7.46 (br m, 4H), 7.50 (d, 2H, *J* = 7.9 Hz), 7.72 (d, 2H, *J* = 8.7 Hz), 7.87 (br, m, 4H), 8.28–8.33 (m, 2H). ^{31}P NMR (161 MHz, $CDCl_3$) δ 44.5 (s). HRMS (ESI$^+$) *m*/*z* 1038.2580 (M$^+$), calcd for $C_{57}H_{60}{}^{35}Cl_2N_2O_2P_2{}^{102}Ru$: 1038.2551. Found: C, 61.34%, H, 5.34%; N, 2.40%. Calcd for $C_{57}H_{60}Cl_2N_2O_2P_2Ru$•0.67$CHCl_3$: C, 61.92%; H, 5.47%; N, 2.50%.

***trans*-RuCl$_2$[(*S*)-binap][(*R*,*R*)-2,5-hexanediamine] [(*S*,*R*)-3d].** IR (ATR) 3320, 3054, 2960, 1574, 1482, 1432, 1260, 1085, 1027, 806, 738, 696 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.44 (d, 6H, *J* = 6.4 Hz), 1.25–1.31 (br m, 2H), 1.52 (br m, 2H), 2.73–2.74 (br m, 4H), 2.99 (br m, 2H), 6.25 (d, 2H, *J* = 8.4 Hz), 6.45–6.47 (br m, 6H), 6.65–6.70 (t-like m, 2H), 7.10–7.15 (t-like m, 2H), 7.38 (br m, 6H), 7.52 (d, 2H, *J* = 7.8 Hz), 7.64 (br m, 4H), 7.72 (d, 2H, *J* = 8.5 Hz), 7.98 (br, m, 4H), 8.26–8.32 (m, 2H). ^{31}P NMR (121 MHz, $CDCl_3$) δ 45.7 (s). HRMS (ESI$^+$) *m*/*z* 910.1706 (M$^+$), calcd for $C_{50}H_{48}{}^{35}Cl_2N_2O_2P_2{}^{102}Ru$: 910.1713. Found: C, 65.93%, H, 5.31%; N, 3.08%. Calcd for $C_{50}H_{48}Cl_2N_2O_2P_2Ru$•0.25$CHCl_3$: C, 64.16%; H, 5.17%; N, 2.98%.

***trans*-RuCl$_2$[(*R*)-tolbinap][(*S*,*S*)-2,5-hexanediamine] [(*R*,*S*)-3e].** IR (ATR) 3316, 3053, 2919, 1499, 1191, 1089, 1037, 804 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.43 (d, 6H, *J* = 6.4 Hz), 1.21–1.30 (m, 2H), 1.51 (br m, 2H), 1.78 (s, 6H), 2.33 (s, 6H), 2.71 (br m, 4H), 2.96 (br m, 2H), 6.20–6.24 (m, 6H), 6.63–6.69 (t-like m, 2H), 7.09–7.19 (m, 6H), 7.48–7.52 (m, 6H), 7.72 (d, 2H, *J* = 8.5 Hz), 7.90 (br m, 4H), 8.26–8.32 (m, 2H). ^{31}P NMR (121 MHz, $CDCl_3$) δ 43.9 (s). HRMS (ESI$^+$) *m*/*z* 966.2343 (M$^+$), calcd for $C_{54}H_{56}{}^{35}Cl_2N_2O_2P_2{}^{102}Ru$: 966.2339.

(B) Asymmetric Hydrogenation of 3-Quinuclidinone (1a) (S/C = 50,000)

Solid (*S*,*R*)-**3b** (3.0 mg, 0.0031 mmol) and 3-quinuclidinone (**1a**) (18.78 g, 150 mmol) were placed in a 200 mL SUS autoclave with a Teflon-coated magnetic stirring bar. Air present in the autoclave was replaced by argon. 2-Propanol (49 mL) was added to the autoclave and degassed. A solution of *t*-C_4H_9OK in 2-propanol (1 M, 1.0 mL, 1.0 mmol) which had been degassed was added to the autoclave. Hydrogen was initially introduced into the autoclave at a pressure of 5 atm, before being reduced to 1 atm by carefully releasing the stop valve. After this procedure was repeated 5 times, the vessel was pressurized to 50 atm. The reaction mixture was vigorously stirred at 25 °C. After stirring for 24 h and carefully venting the hydrogen gas, the solvent was removed under reduced pressure. The residue was purified by silica-gel (Fuji silysia, Chromatorex NH) column chromatography giving (*R*)-3-quinuclidinol[2,3] [(*R*)-**2a**] (colorless powder, 18.9 g, 99% yield, 97% ee). The enantiomeric excess of **2a** was determined by HPLC analysis of acetylated derivative. Column, CHIRALCEL AD-H; eluent, hexane:ethanol:2-propanol = 90:5:5; flow, 0.5 mL min^{-1}; column temp, 25 °C; retention time (t_R) of Ac-(*S*)-**2a**, 18.3 min (1.5%); t_R of Ac-(*R*)-**2a**, 24.6 min (98.5%). $[\alpha]_D^{28}$ –42.5 (*c* 1.06, 1M HCl) (lit.[2] $[\alpha]_D^{25}$ –44.9 (*c* 2.0, 1 M HCl), 96% ee (*R*)). IR (KBr-disk) 3109 (br), 2941, 2871, 1456, 1346, 1309, 1116, 1045, 988, 817, 795, 773 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.31–1.40 (m, 1H), 1.41–1.51 (m, 1H), 1.64–1.72 (m, 1H), 1.79–1.83 (m, 1H), 1.90–1.98 (m, 1H), 2.58–2.69 (m, 2H), 2.72–2.82 (m, 2H), 2.87–2.95 (m including a broad signal, 2H), 3.13 (ddd, *J*=14.1, 8.2, 2.3 Hz, 1H), 3.83–3.87 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.9 (CH_2), 24.8 (CH_2), 28.3 (CH), 46.3 (CH_2), 47.3 (CH_2), 57.9 (CH_2), 67.5 (CH). HRMS(EI^+), *m*/*z* 127.0997 (M^+), calcd $C_7H_{13}NO$: 127.0997. Found: C, 65.81%, H, 10.32%; N, 10.94%. Calcd for $C_7H_{13}NO$: C, 66.10%; H, 10.30%; N, 11.01%.

(C) Asymmetric Hydrogenation of Bicyclo[2.2.2]octan-2-one (1b) (S/C = 1,000)

Solid (*S*,*R*)-**3b** (1.3 mg, 1.3 μmol), *t*-C_4H_9OK (14.9 mg, 0.133 mmol), and bicyclo[2.2.2]octan-2-one (**1b**) (167.9 mg, 1.35 mmol) were placed in a 100-mL glass

autoclave with a Teflon-coated magnetic stirring bar under Ar. A degassed (three freeze–thaw cycles) mixture of 2-propanol (4.8 mL) and *tert*-butylalcohol (1.6 mL) was added to the autoclave. Hydrogen was initially introduced into the autoclave at a pressure of 10 atm, before being reduced to 1 atm by carefully releasing the stop valve. After this procedure was repeated several times, the vessel was pressurized to 20 atm, and then the reaction mixture was vigorously stirred at 20 °C for 2 h. After venting the hydrogen gas, the solvent was carefully removed under reduced pressure. The residue was purified by silica-gel column chromatography eluted with a hexane–ethyl acetate (7:1 then 4:1) giving (*S*)-bicyclo[2.2.2]octan-2-ol[4] [(*S*)-**2b**] (colorless crystals, 153.4 mg, 90% yield, 98% ee). The enantiomeric excess of **2b** was determined by GC analysis. Column, BETA DEX-120 (0.25x30, DF = 0.25); carrier, He (100 kPa); oven temp, 80 °C, 2 min hold, 1 °C/min to 140 °C; t_R of (*R*)-**2b**, 47.98 min (1%); t_R of (*S*)-**2b**, 48.34 min (99%). $[\alpha]_D^{28}$ +33.0 (*c* 1.01, $CHCl_3$). (lit.[4] $[\alpha]_D^{27}$ +31.3 (*c* 1.4, $CHCl_3$), 97.8% ee (*S*)). IR (KBr-disk) 3357, 2932, 2861, 1456, 1362, 1092, 1034 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.30–1.51 (m, 6H), 1.53–1.65 (m, 4H), 1.84–1.92 (m, 1H), 1.97–2.05 (m, 1H), 3.95 (br d, 1H, *J*=9.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.5 (CH_2), 23.7 (CH_2), 24.4 (CH_2), 24.7 (CH), 25.6 (CH_2), 31.7 (CH), 37.5 (CH_2), 69.6 (CH). HRMS(EI$^+$), *m*/*z* 126.1045 (M^+), calcd for $C_8H_{14}O$: 126.1045. Found: C, 76.14%, H, 11.37%. Calcd for $C_8H_{14}O$: C, 76.14%; H, 11.18%.

(D) Asymmetric Hydrogenation of (±)-Benzobicyclo[2.2.2]octen-2-one [(±)-4]

Solid (*S*,*R*)-**3b** (1.3 mg, 1.3 μmol), *t*-C_4H_9OK (16.6 mg, 0.148 mmol), and (±)-**4**[5] (224.0 mg, 1.30 mmol) were placed in a 100-mL glass autoclave with a Teflon-coated magnetic stirring bar under Ar. A degassed (three freeze–thaw cycles) mixture of 2-propanol (4.9 mL) and *tert*-butylalcohol (1.5 mL) was added to the autoclave. Hydrogen was initially introduced into the autoclave at a pressure of 10 atm, before being reduced to 1 atm by carefully releasing the stop valve. After this procedure was repeated several times, the vessel was pressurized to 20 atm, and then the reaction mixture was vigorously stirred at 20 °C for 2 h. After venting the hydrogen gas, the

solvent was carefully removed under reduced pressure. The residue was purified on silica-gel preparative thin-layer chromatography developed with a toluene–ethyl acetate (10:1) giving (1*R*,2*S*,4*R*)-benzobicyclo[2.2.2]octen-2-ol[4,5] (**5**, *exo*-alcohol) (colorless crystals, 94.2 mg, 42% yield, 99% ee), and (1*S*,2*S*,4*S*)-benzobicyclo[2.2.2]octen-2-ol[4,5] (**6**, *endo*-alcohol) (colorless crystals, 103.5 mg, 46% yield, 96% ee). The enantiomeric excess of **5** and **6** was determined by HPLC analysis. For **5**: Column, CHIRALCEL OD-H; eluent, hexane:2-propanol = 95:5; flow, 0.5 mL min^{-1}; column temp, 40 °C; retention time (t_R) of (1*S*,2*R*,4*S*)-**5**, 13.7 min (0.3%); t_R of (1*R*,2*S*,4*R*)-**5**, 16.0 min (99.7%). For **6**: Column, CHIRALCEL OJ-H; eluent, hexane:2-propanol = 90:10; flow, 0.5 mL min^{-1}; column temp, 40 °C; retention time (t_R) of (1*S*,2*S*,4*S*)-**6**, 23.8 min (97.9%); t_R of (1*R*,2*R*,4*R*)-**6**, 31.5 min (2.1%). *exo*-alcohol (1*R*,2*S*,4*R*)-**5**: $[\alpha]_D^{28}$ +7.3 (*c* 1.03, $CHCl_3$), lit.[4] $[\alpha]_D$ +7.7 ($CHCl_3$, (*S*)-config., extrapolated). IR (KBr-disk) 3319 (br), 2945, 1482, 1460, 1077, 1051, 1012, 750 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.23–1.31 (m, 1H), 1.37–1.48 (m, 2H), 1.61 (br d, 1H), 1.86–1.94 (m, 1H), 1.95–2.03 (m, 1H), 2.26–2.34 (m, 1H), 2.96–2.99 (m, 1H), 3.01–3.03 (m, 1H), 3.91–3.94 (m, 1H), 7.11–7.14 (m, 1H), 7.17–7.21 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.0 (CH_2), 26.4 (CH_2), 34.6 (CH), 36.8 (CH_2), 42.2 (CH), 69.5 (CH), 123.5 (CH), 124.7 (CH), 126.0 (CH), 126.4 (CH), 141.4 (C), 143.8 (C). *endo*-alcohol (1*S*,2*S*,4*S*)-**6**: $[\alpha]_D^{28}$ –20.0 (*c* 1.04, $CHCl_3$), lit.[4] $[\alpha]_D^{27}$ –18.55 (*c* 0.9, $CHCl_3$), 85% ee (*S*)). IR (KBr, disk) 3281 (br), 3211 (br), 2941, 2864, 1485, 1330, 1080, 1035, 754 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.02 (d, *J*=8.6 Hz, 1H), 1.19 (m, 1H), 1.26–1.34 (m, 1H), 1.42–1.50 (m, 1H), 1.57–1.72 (m, 2H), 2.26 (ddd, *J*=14.0, 8.8, 2.5 Hz, 1H), 3.03–3.06 (m, 1H), 3.09–3.11 (m, 1H), 4.09–4.14 (m, 1H), 7.15–7.18 (m, 1H), 7.21–7.24 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.5 (CH_2), 24.6 (CH_2), 34.1 (CH), 39.5 (CH_2), 42.0 (CH_2), 69.7 (CH), 123.5 (CH), 126.2 (CH), 126.65 (CH), 126.72 (CH), 138.4 (C), 144.0 (C).

(E) Asymmetric Hydrogenation of (±)-Norcamphor [(±)-7] (S/C = 1,000)

Solid (*S*,*R*)-**3b** (1.4 mg, 1.4 μmol), *t*-C_4H_9OK (16.0 mg, 0.143 mmol), and (±)-norcamphor [(±)-**7**] (158.0 mg, 1.43 mmol) were placed in a 100-mL glass autoclave with a Teflon-coated magnetic stirring bar under Ar. A degassed (three freeze–thaw cycles) mixture of 2-propanol (4.8 mL) and *tert*-butylalcohol (1.6 mL) was added to the autoclave. Hydrogen was initially introduced into the autoclave at a pressure of 10 atm, before being reduced to 1 atm by carefully releasing the stop valve. After this procedure was repeated several times, the vessel was pressurized to 10 atm, and then the reaction mixture was vigorously stirred at 20 °C for 2 h. After venting the hydrogen gas, the solvent was carefully removed under reduced pressure. The residue was purified by silica-gel thin layer chromatography developed with a 7:1 hexane–ethyl acetate to give a diastereomeric mixture of norborneol [**8** (exo) and **9** (endo), **8**:**9** = 11:89] (colorless crystals, 115.1 mg, 72% yield). This sample contained a small amount of ethyl acetate (4%(w/w)). The ratio of diastereomers was determined by GC analysis. Column, BETA DEX-325 (0.25x30, DF = 0.25); carrier, He (100 kPa); oven temp, 100 °C isothernal, t_R of (1*R*,2*R*,4*S*)-**8**, 17.14 min (0.28%); t_R of (1*S*,2*S*,4*R*)-**8**, 17.59 min (11.3%), t_R of (1*S*,2*R*,4*R*)-**9**, 18.19 min (38.5%); t_R of (1*R*,2*S*,4*S*)-**9**, 18.65 min (49.9%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.84 (dt, *endo*-1H, J_d=12.7, J_t=3.4 Hz), 0.98–1.05 (m, *exo*-2H), 1.10–1.14 (m, *exo*-1H), 1.26–1.70 (m, *endo*-6H and *exo*-6H), 1.84–1.99 (m, *endo*-2H), 2.14–2.26 (m, *endo*-2H and *exo*-2H), 3.76 (br d, *exo*-1H, *J*=6.8 Hz), 4.23 (br m, *endo*-1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.8 (*endo*, CH_2), 24.3 (*exo*, CH_2), 28.0 (*exo*, CH_2), 29.8 (*endo*, CH_2), 34.3 (*exo*, CH_2), 35.3 (*exo*, CH), 37.1 (*endo*, CH), 37.5 (*endo*, CH_2), 39.3 (*endo*, CH_2), 42.1 (*exo*, CH_2), 42.4 (*endo*, CH), 44.1 (*exo*, CH), 72.8 (*endo*, CH), 74.7 (*exo*, CH).

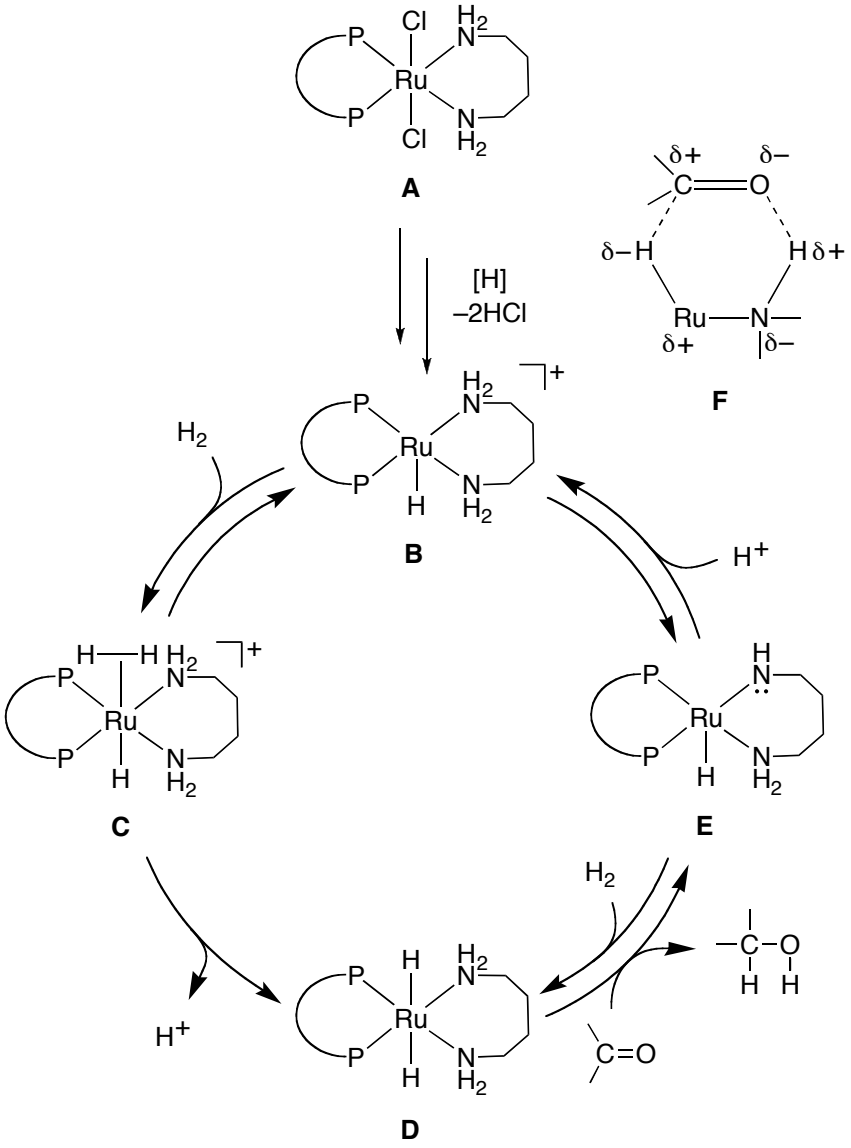
(F) Asymmetric Hydrogenation of (±)-2-Diphenylmethyl-3-quinuclidinone [(±)-10]

Solid (*S*,*R*)-**3b** (2.6 mg, 0.0027 mmol) and (±)-2-diphenylmethyl-3-quinuclidinone[6,7] [(±)-**10**] (7.71 g, 26.5 mmol) were placed in a 200 mL SUS autoclave with a Teflon-

coated magnetic stirring bar. Air present in the autoclave was replaced by argon. 2-Propanol (108 mL) and dimethylacetamide (18 mL) were added to the autoclave. Argon was introduced into the autoclave at a pressure of 5 atm, then released to 1 atm. This procedure was repeated 5 times. A solution of *t*-C_4H_9OK in 2-propanol (1 M, 2.6 mL, 2.6 mmol) which had been degassed was added to the autoclave. Hydrogen was initially introduced into the autoclave at a pressure of 5 atm, before being reduced to 1 atm by carefully releasing the stop valve. After this procedure was repeated 5 times, the vessel was pressurized to 50 atm. The reaction mixture was vigorously stirred at 25 °C. After stirring for 24 h and carefully venting the hydrogen gas, the solvent was removed under reduced pressure. The residue was purified by silica-gel (Fuji silysia, Chromatorex NH) column chromatography giving (2*S*,3*S*)-2-diphenylmethyl-3-quinuclidinol[8] [(*S*,*S*)-**11**] (colorless powder, 7.73 g, 99% yield, >99% ee) as a single diastereomer. The enantiomeric excess of **11** was determined by HPLC analysis. Column, CHIRALCEL OD-RH; eluent, CH_3CN : 0.1 M aq. KPF_6 = 70 : 30; flow, 0.5 mL min^{-1}; column temp, 25 °C; retention time (t_R) of (*R*,*R*)-**11**, 33.7 min (t_R of racemic **11**) (<0.5% not detected); t_R of (*S*,*S*)-**11**, 41.1 min (>99.5%). $[\alpha]_D^{26}$ +11.6 (*c* 1.0, $CHCl_3$) (lit.[8] $[\alpha]_D$ +11.6 (*c* 1, $CDCl_3$), 99.5% ee (*S*,*S*)). IR (KBr-disk) 3430 (br), 3024, 2935, 2869, 1597, 1495, 1450, 1066, 1042, 755, 741, 702 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 1.12–1.32 (m, 1H), 1.35 (d, 1H, *J* = 3.3 Hz), 1.47–1.69 (m, 2H), 1.88–1.96 (m, 2H), 1.61–1.69 (m, 1H), 2.77–2.83 (m, 2H), 3.14–3.25 (m, 1H), 3.61–3.67 (m, 1H), 3.94–3.99 (m, 1H), 4.48 (d, 1H, *J* = 12.0 Hz), 7.07–7.34 (m, 8H), 7.42–7.46 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.2 (CH_2), 24.8 (CH_2), 28.4 (CH), 41.5 (CH_2), 49.0 (CH_2), 49.2 (CH), 63.3 (CH), 68.9 (CH), 126.1 (CH), 126.7 (CH), 127.6 (CH), 127.7 (CH), 128.4 (CH), 129.3 (CH), 143.6 (C), 144.3 (C). HRMS (EI^+) *m*/*z* 293.1778 (M^+), calcd for $C_{20}H_{23}NO$: 293.1780. Found: C, 81.36%, H, 8.01%; N, 4.67%. Calcd for $C_{20}H_{23}NO$: C, 81.87%; H, 7.90%; N, 4.77%.

(G) Comment on the Catalytic Cycle

A plausible catalytic cycle for the hydrogenation of ketones with BINAP/1,4-diamine–Ru complexes **3** in 2-propanol is shown in Scheme S1 by analogy with the mechanism of BINAP/DPEN–Ru catalyzed hydrogenation.[9] The excellent activity of this catalyst is rationalized by a non-classical "*metal-ligand cooperative mechanism*" using the NH functionality. The precatalyst dichloride complex **A** is converted to the cationic species **B** by releasing two HCl molecules with the assistance of a base, followed by hydride donation from 2-propanol or H_2. Then, **B** reacts with an H_2 molecule to form a cationic intermediate **C**, which undergoes deprotonation with a solvent molecule to afford the active RuH_2 species **D**. This process is promoted by a base. Ketone is promptly reduced by **D**, resulting in the alcoholic product and the 16-electron Ru–amide complex **E**. This species is easily protonated in an alcoholic solvent to regenerate the cationic amino complex **B**, while it partially returns to **D** by reaction with H_2. The active species **D** has a *fac*-structure for the hydride and two nitrogen atoms of the diamine, so that this species and a ketonic substrate react smoothly through the six-membered pericyclic transition state **F**. Ketone is hydrogenated in the outer coordination sphere of **D**, where neither ketone/Ru nor alkoxy/Ru interaction is involved.



SCHEME S1. Plausible Catalytic Cycle for BINAP/1,4-diamine–Ru-catalyzed Hydrogenation of Ketones. P—P = (*S*)-BINAP. NH_2—NH_2 = 1,4-diamine.

(H) References

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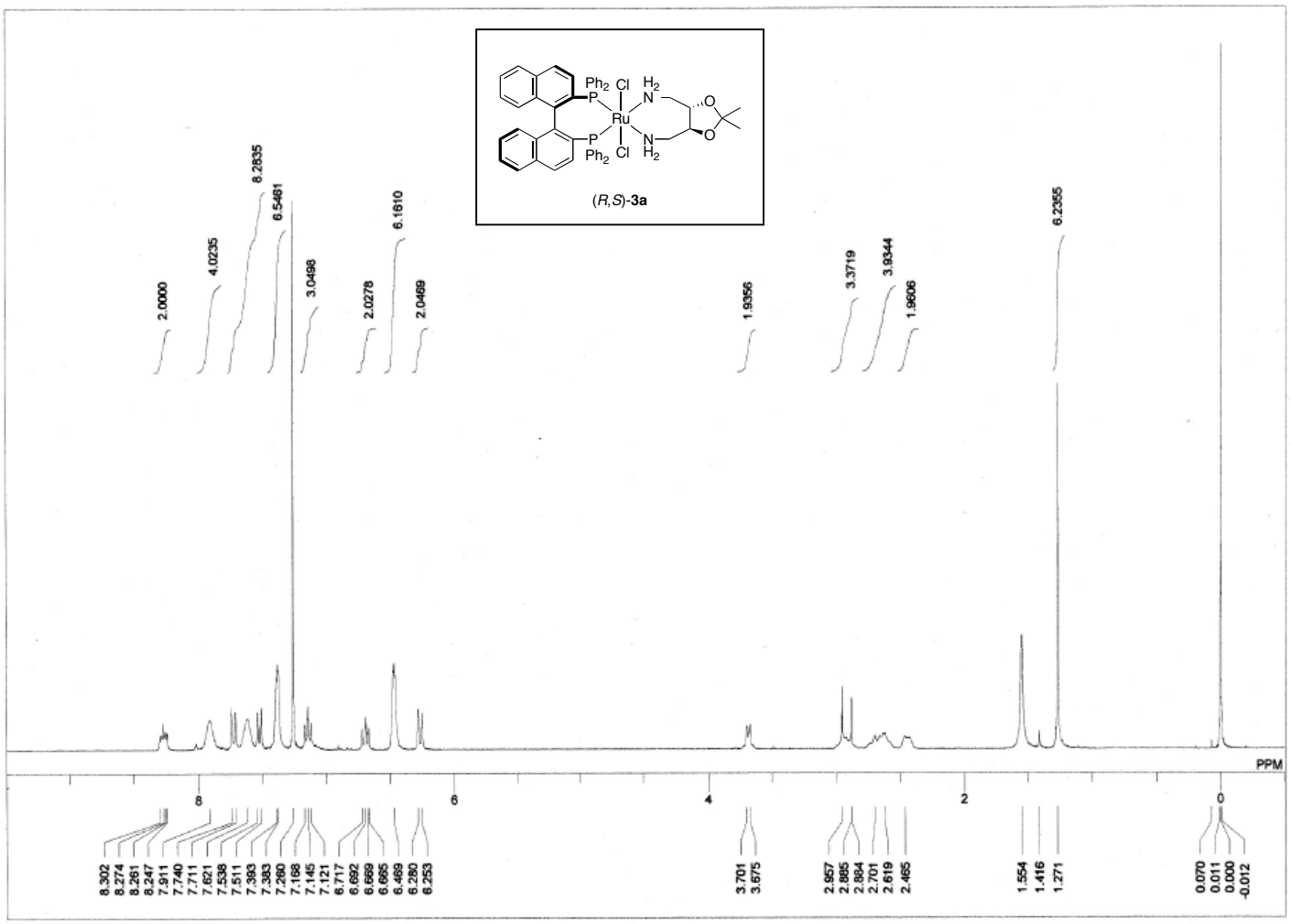
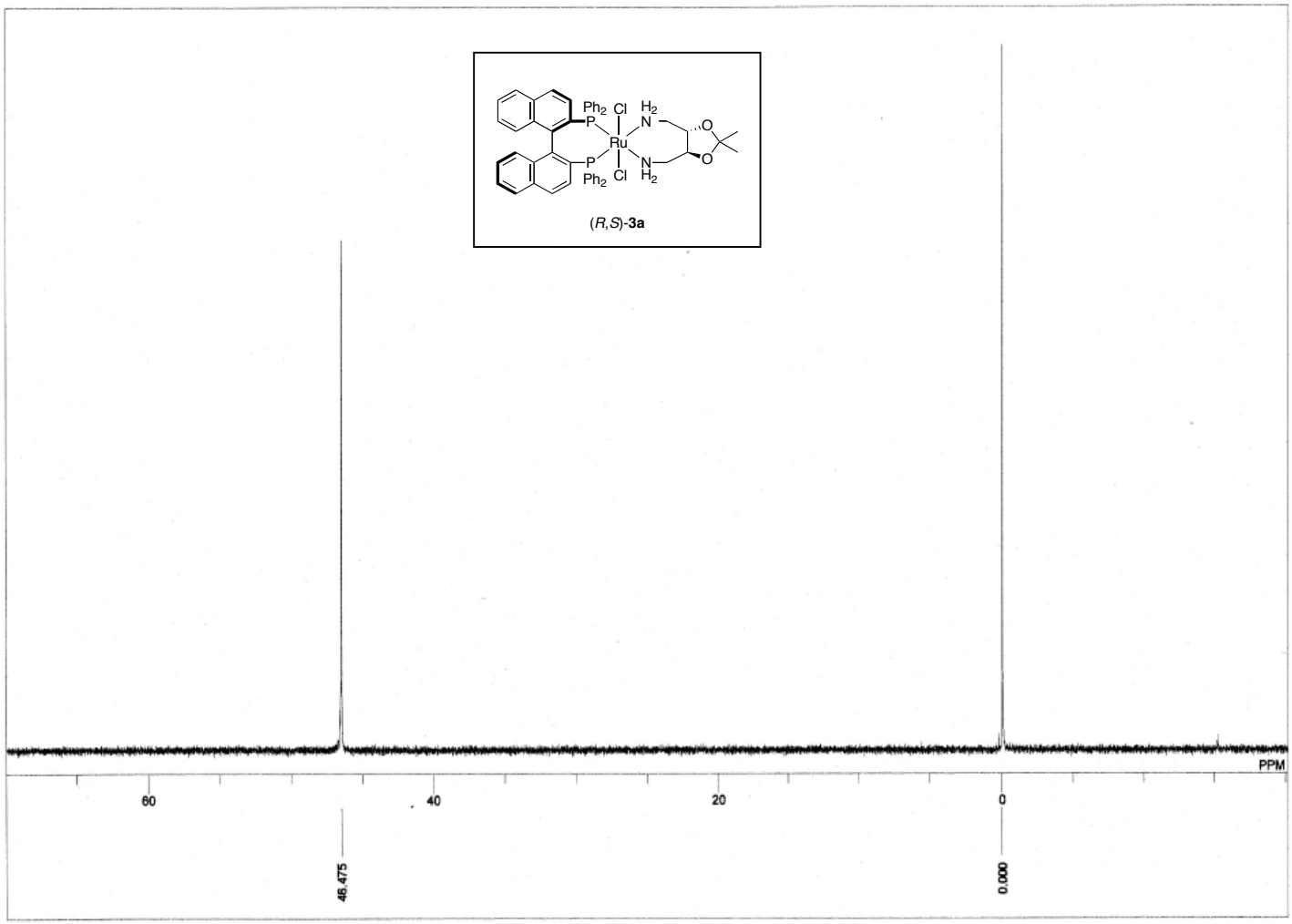
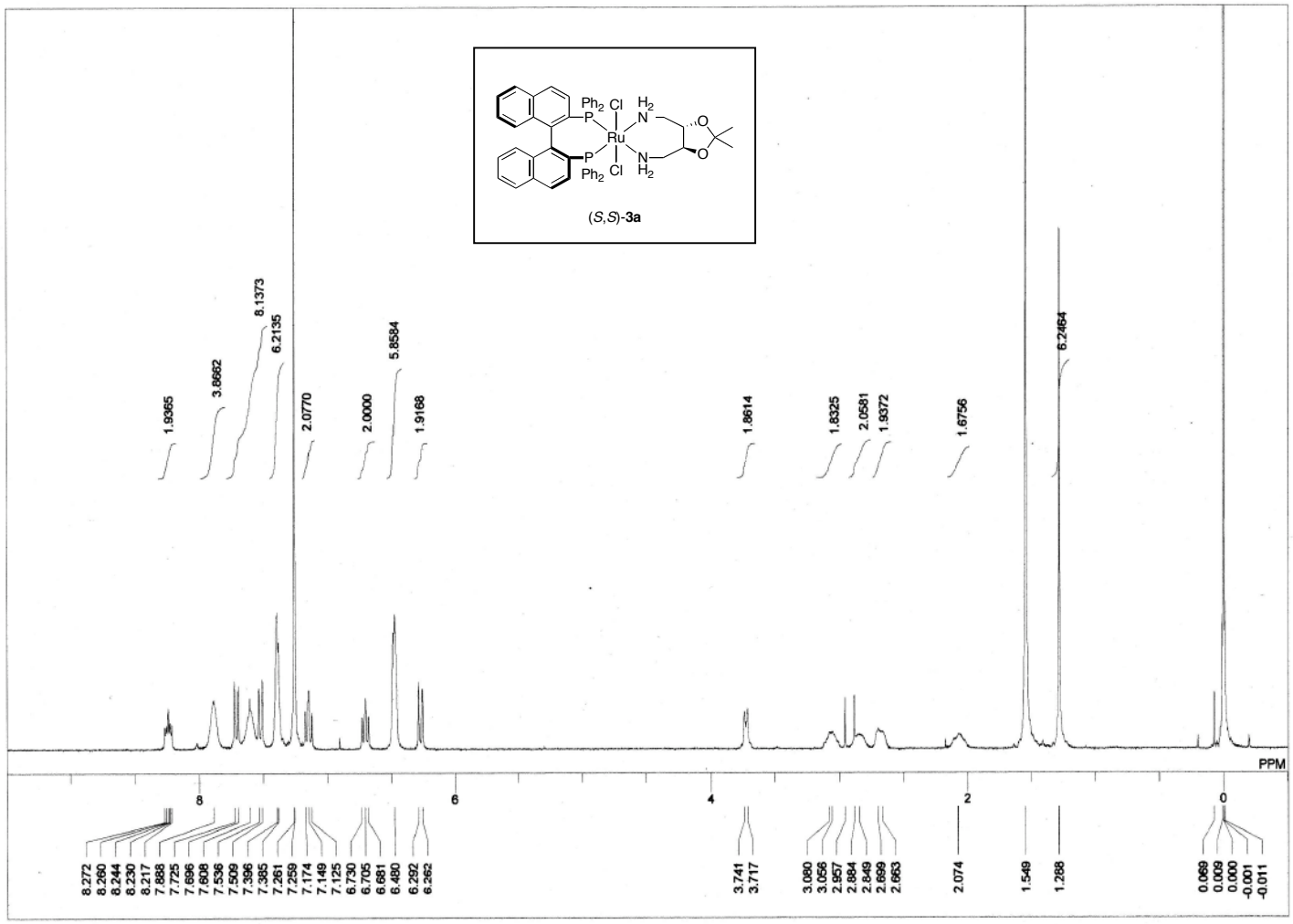
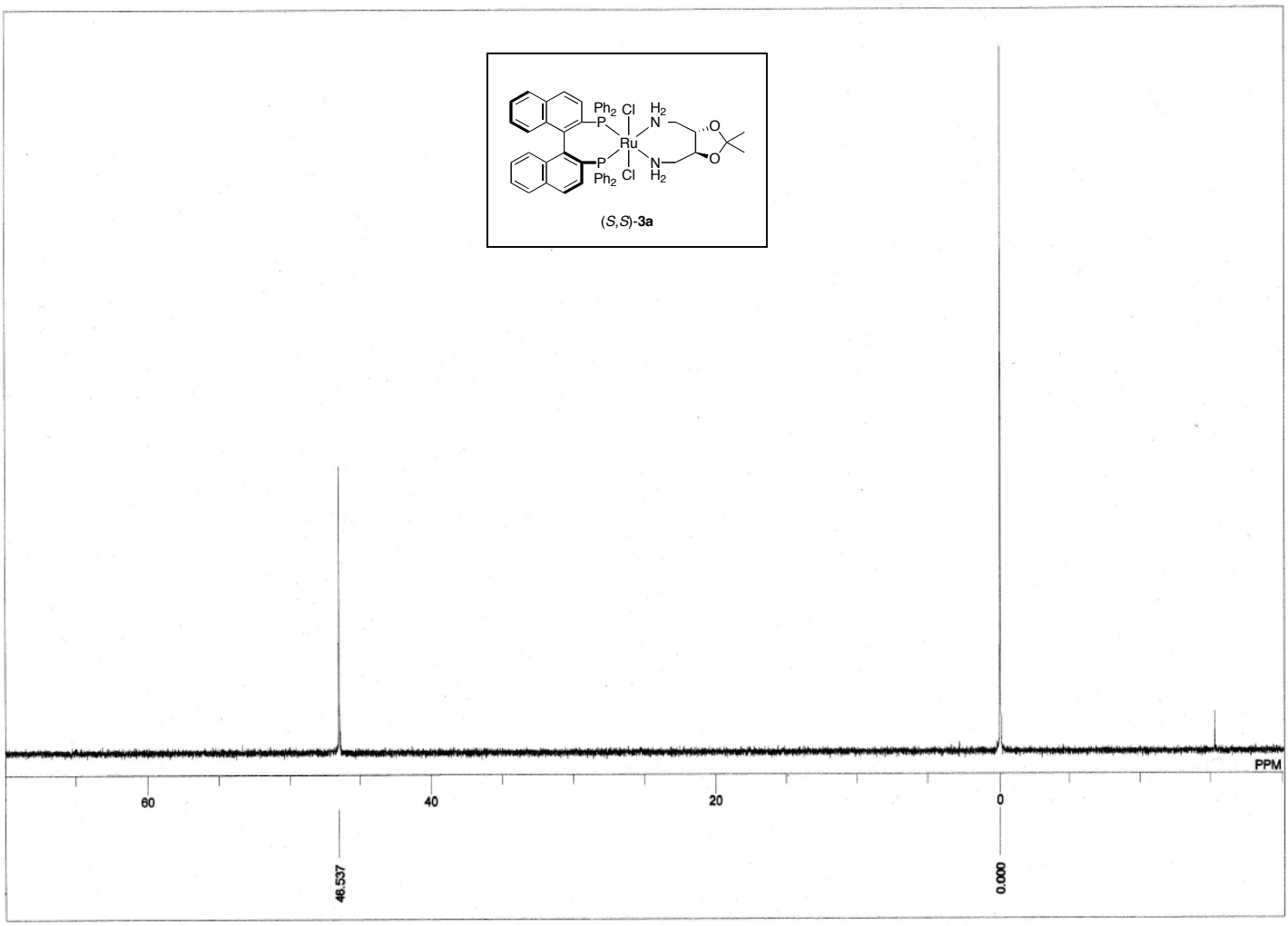
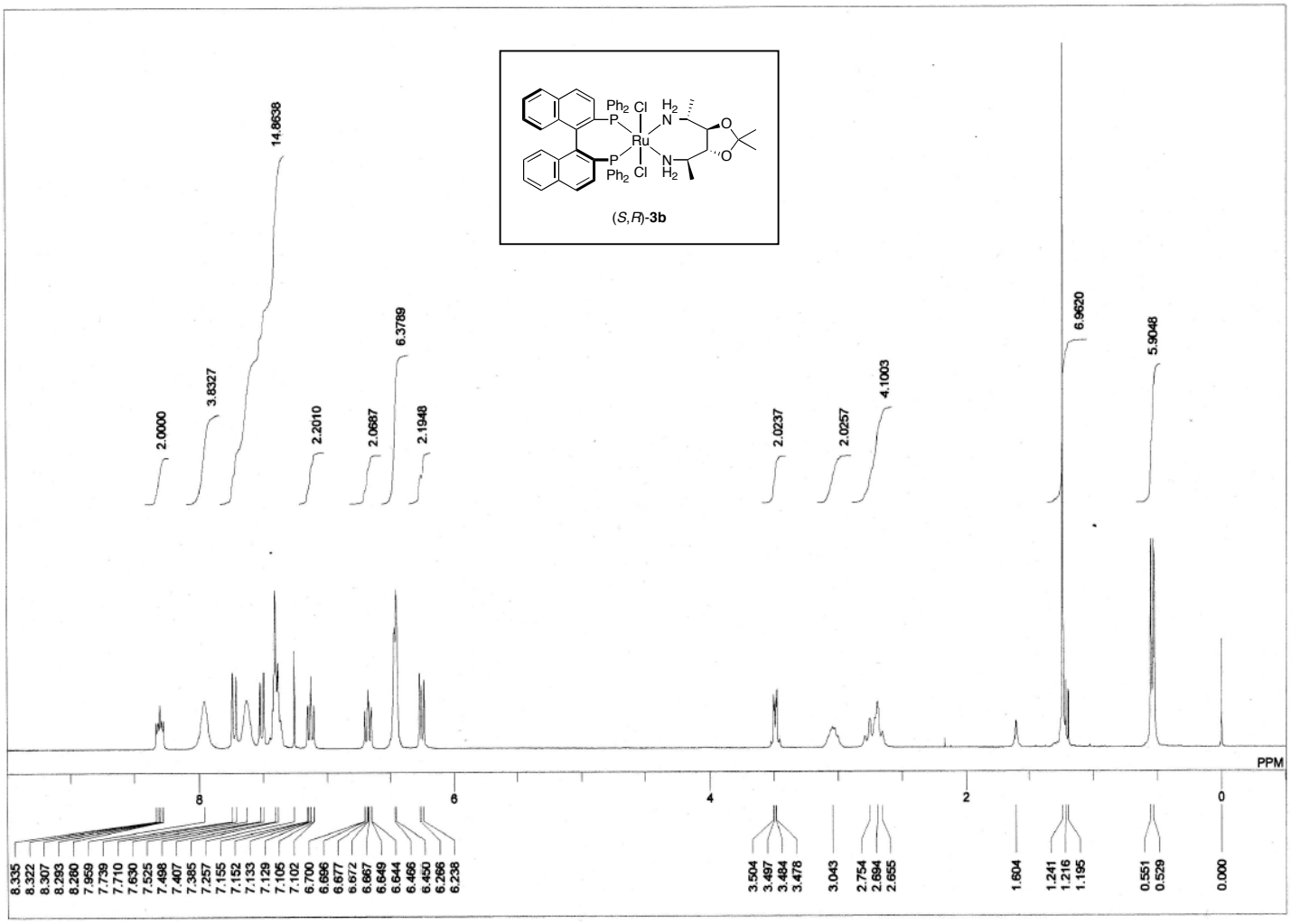
(I) Spectral Charts

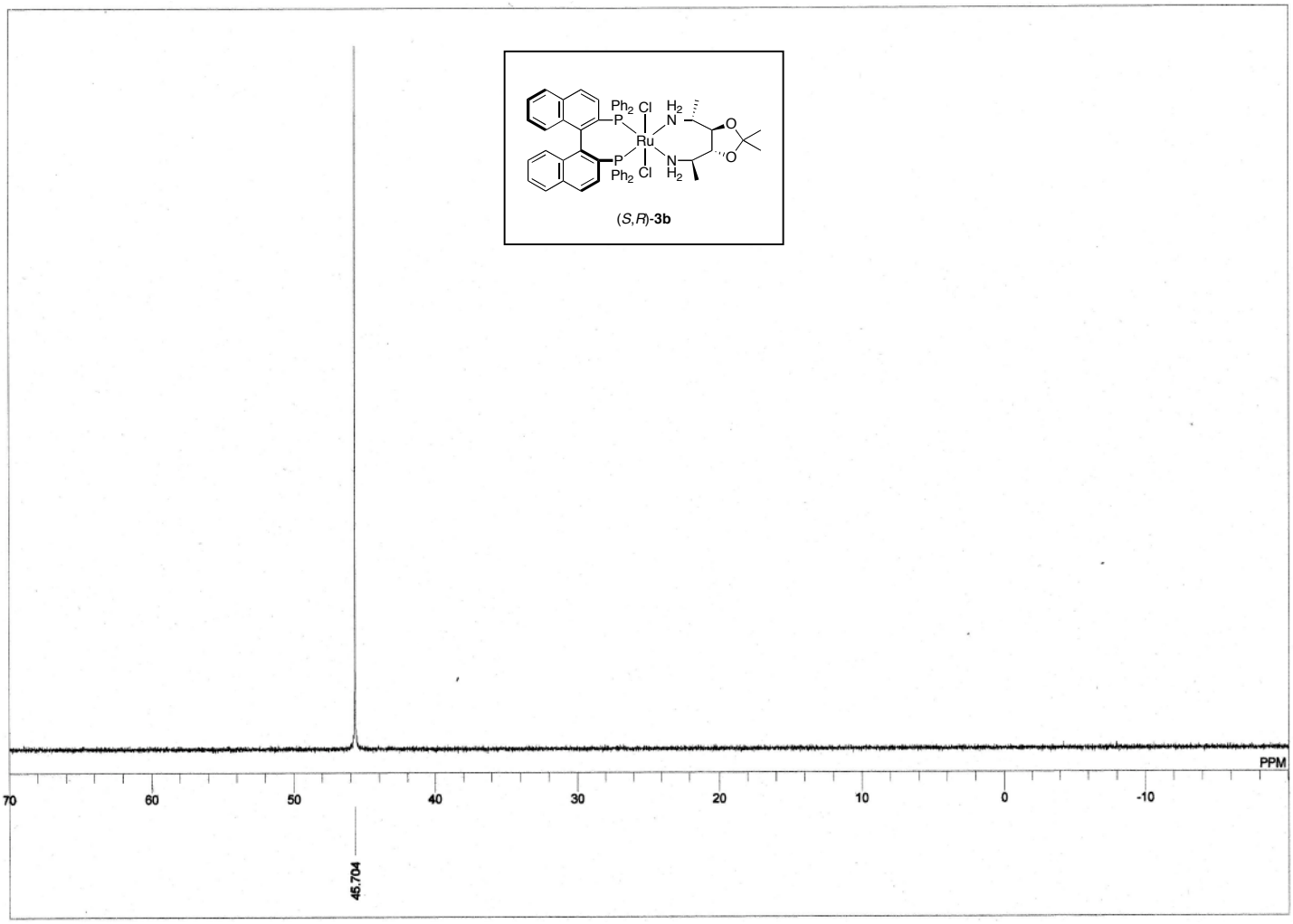

(R,S)-3a
2.0000
4.0235
8.2835
6.5461
3.0498
2.0278
6.1610
2.0489
1.9356
3.3719
3.9344
1.9606
6.2355
PPM
8
6
4
2
0
8.302
8.274
8.261
8.247
7.911
7.740
7.711
7.621
7.538
7.511
7.393
7.383
7.260
7.168
7.145
7.121
6.717
6.692
6.669
6.665
6.469
6.280
6.253
3.701
3.675
2.857
2.885
2.884
2.701
2.619
2.465
1.554
1.416
1.271
0.070
0.011
0.000
-0.012

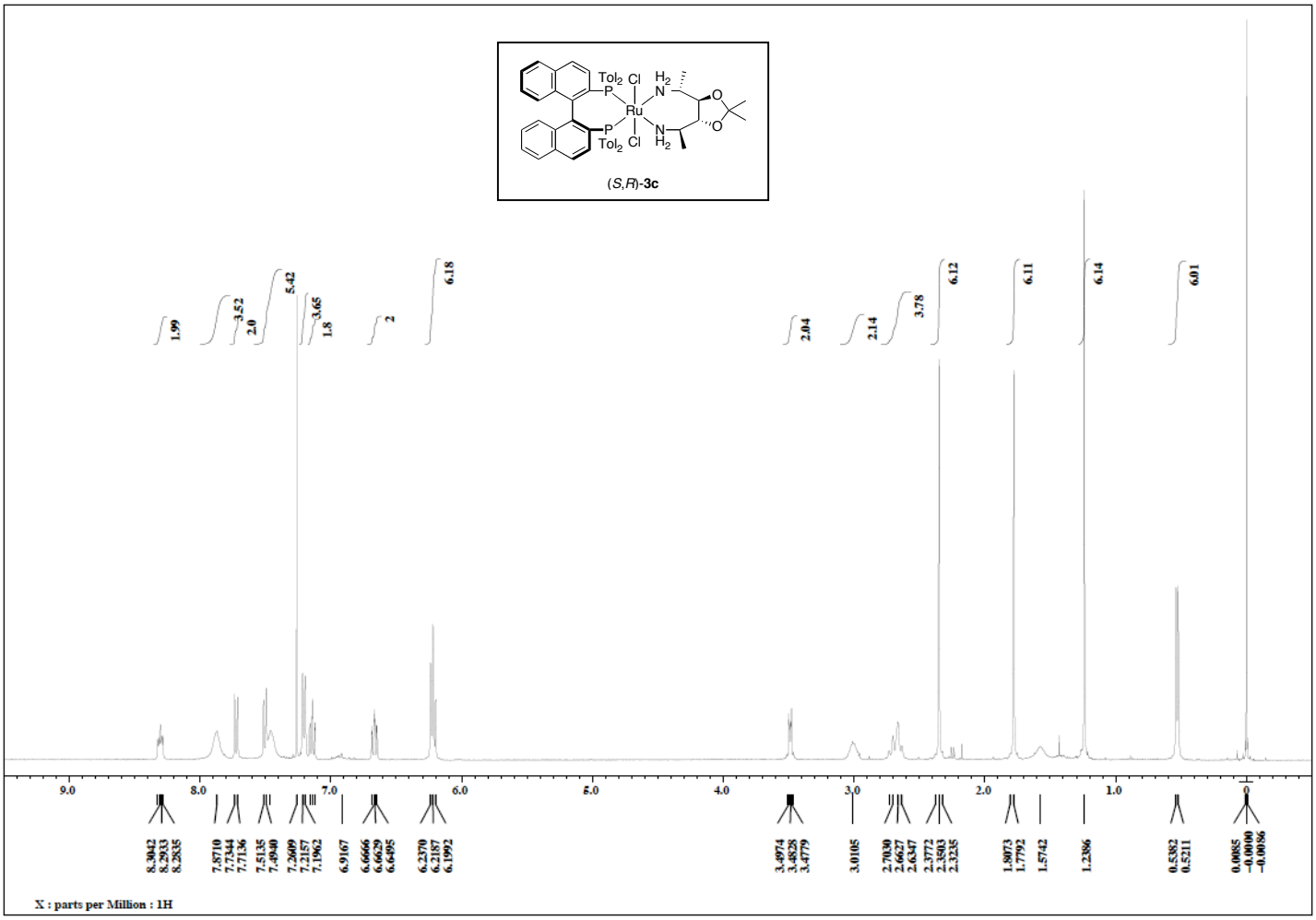

(R,S)-3a
PPM
60
40
20
0
45.475
0.000

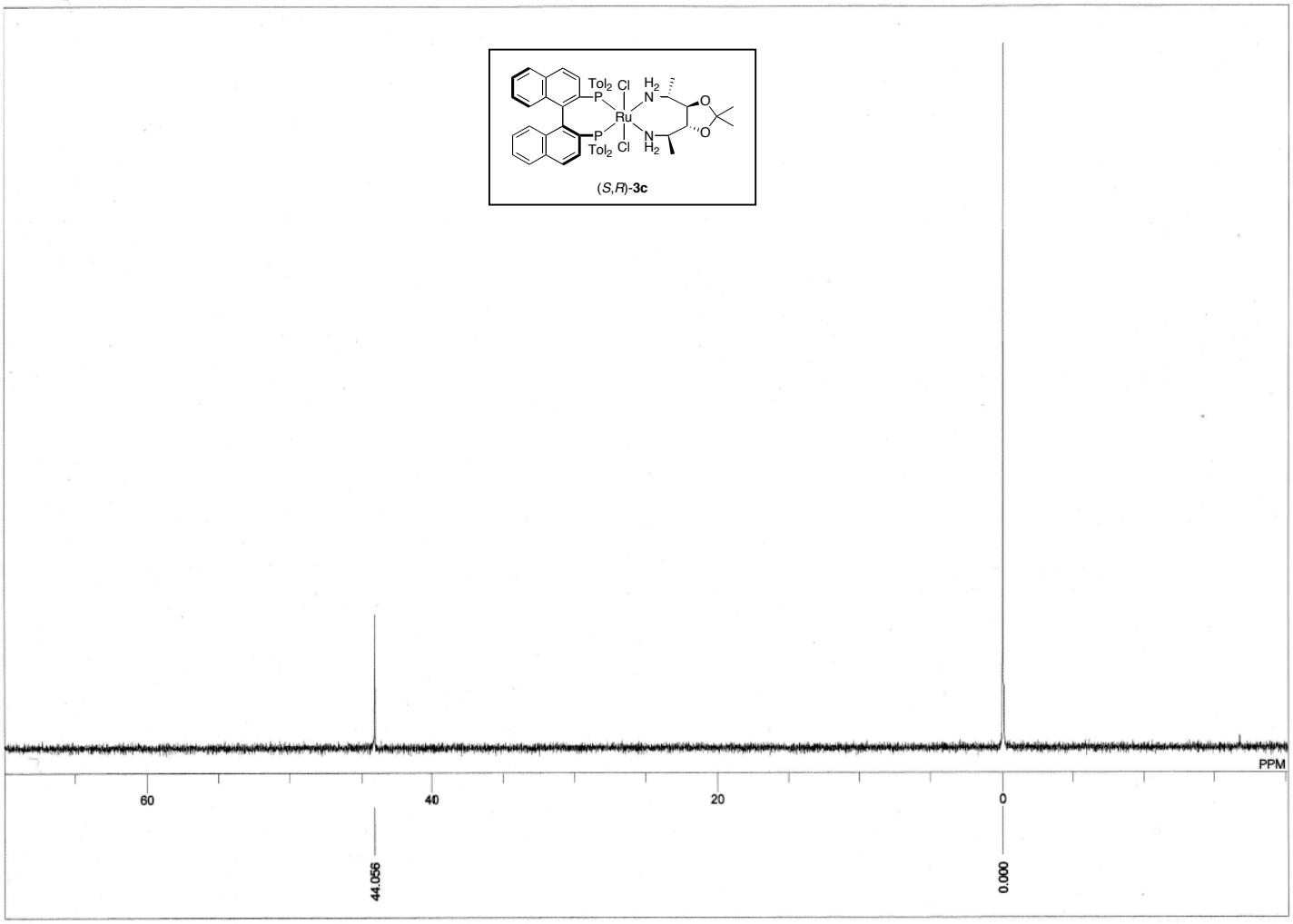

(S,S)-3a
1.9365
3.8662
8.1373
6.2135
2.0770
2.0000
5.8584
1.9168
1.8614
1.8325
2.0581
1.9372
1.6756
6.2464
PPM
8
6
4
2
0
8.272
8.260
8.244
8.230
8.217
7.888
7.725
7.696
7.608
7.536
7.509
7.396
7.385
7.261
7.259
7.174
7.149
7.125
6.730
6.705
6.681
6.480
6.292
6.262
3.741
3.717
3.080
3.056
2.957
2.884
2.849
2.699
2.663
2.074
1.549
1.288
0.069
0.009
0.000
-0.001
-0.011

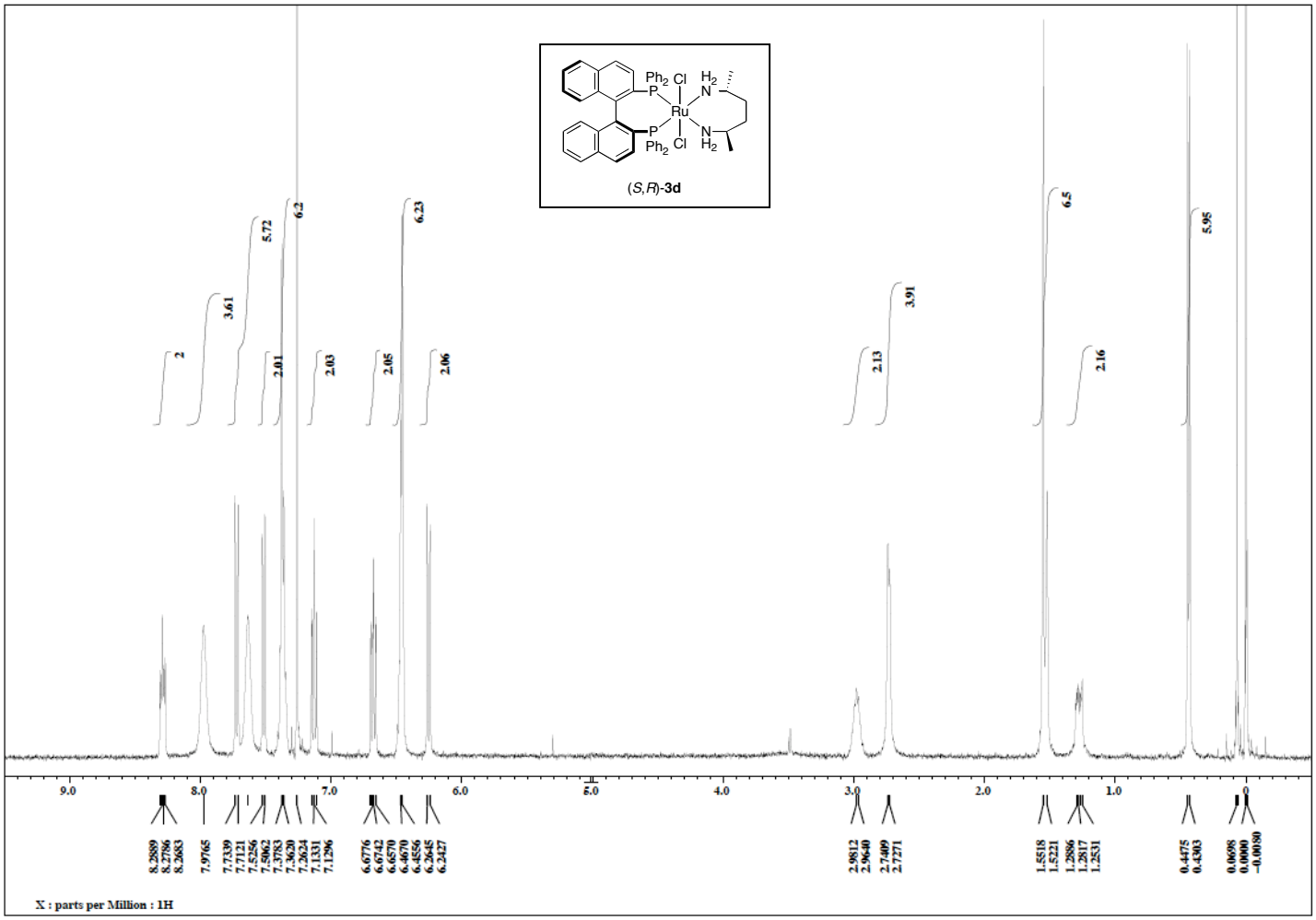

(S,S)-3a
PPM
60
40
20
0
46.537
0.000

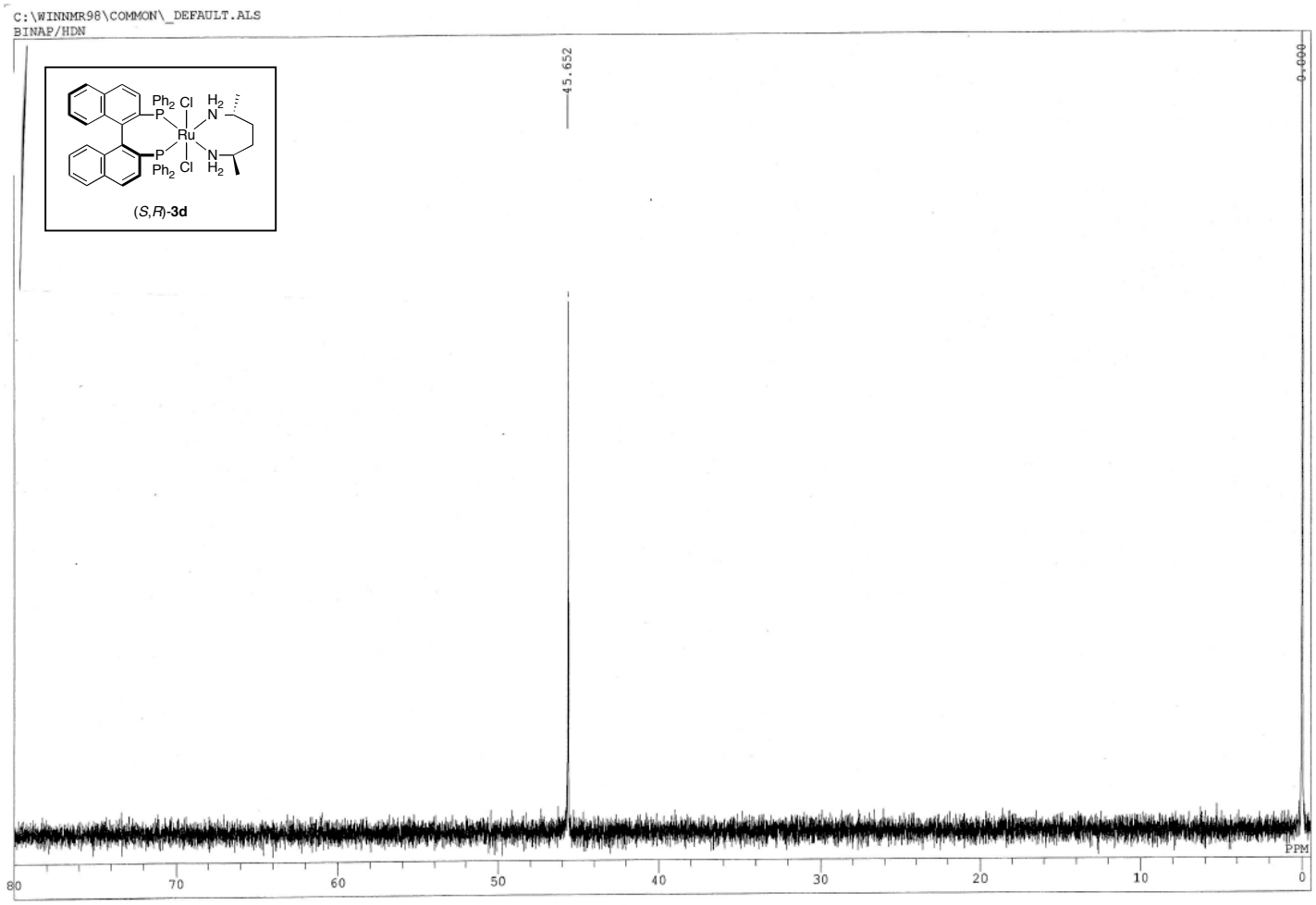

(S,R)-3b
2.0000
3.8327
14.8638
2.2010
2.0687
6.3789
2.1948
2.0237
2.0257
4.1003
6.9620
5.9048
PPM
8
6
4
2
0
8.335
8.322
8.307
8.293
8.280
7.959
7.739
7.710
7.630
7.525
7.498
7.407
7.385
7.257
7.155
7.152
7.133
7.129
7.105
7.102
6.700
6.696
6.677
6.672
6.667
6.649
6.644
6.466
6.450
6.266
6.238
3.504
3.497
3.484
3.478
3.043
2.754
2.694
2.655
1.604
1.241
1.216
1.195
0.551
0.529
0.000

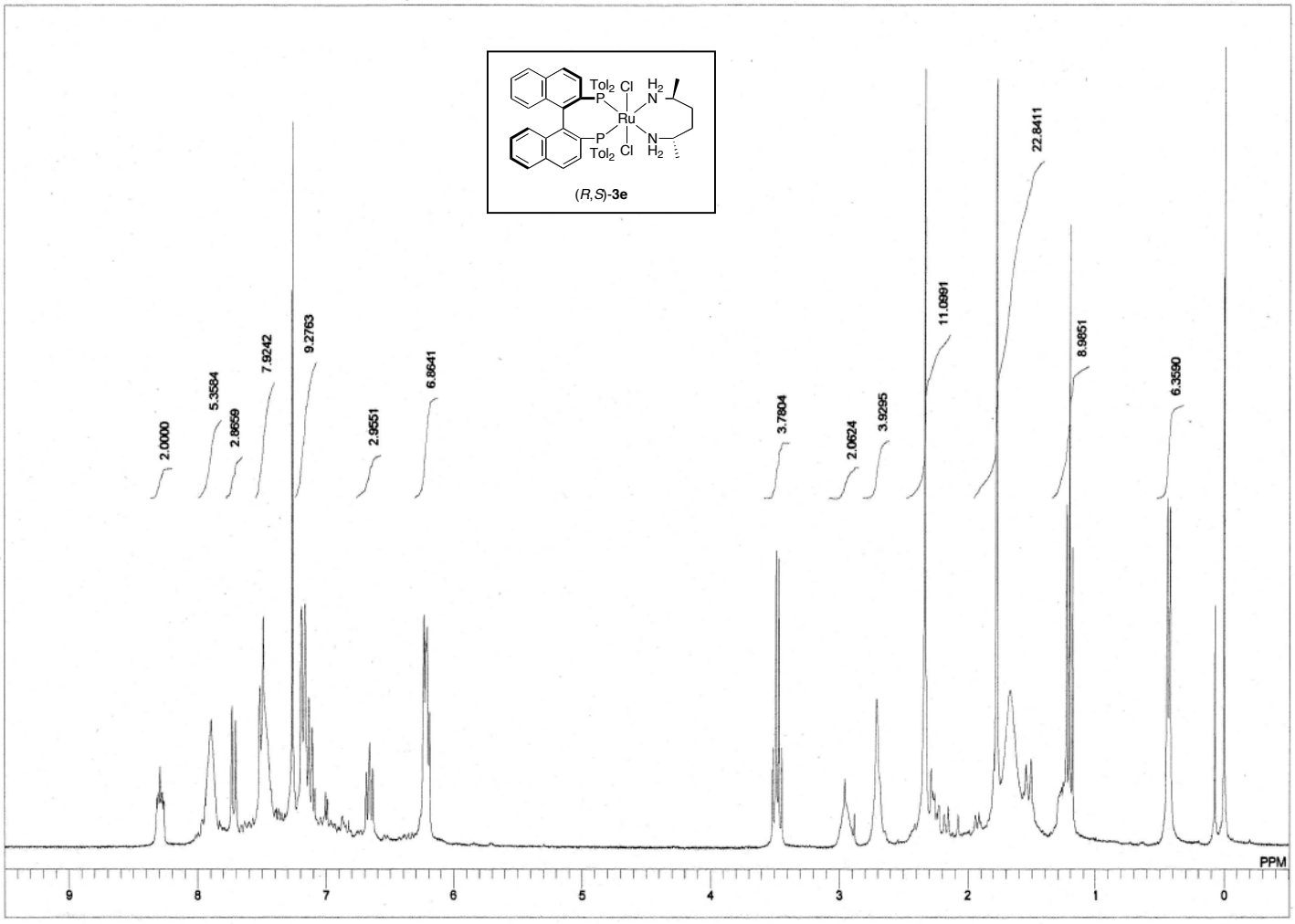

(S,R)-3b
PPM
70
60
50
40
30
20
10
0
-10
45.704

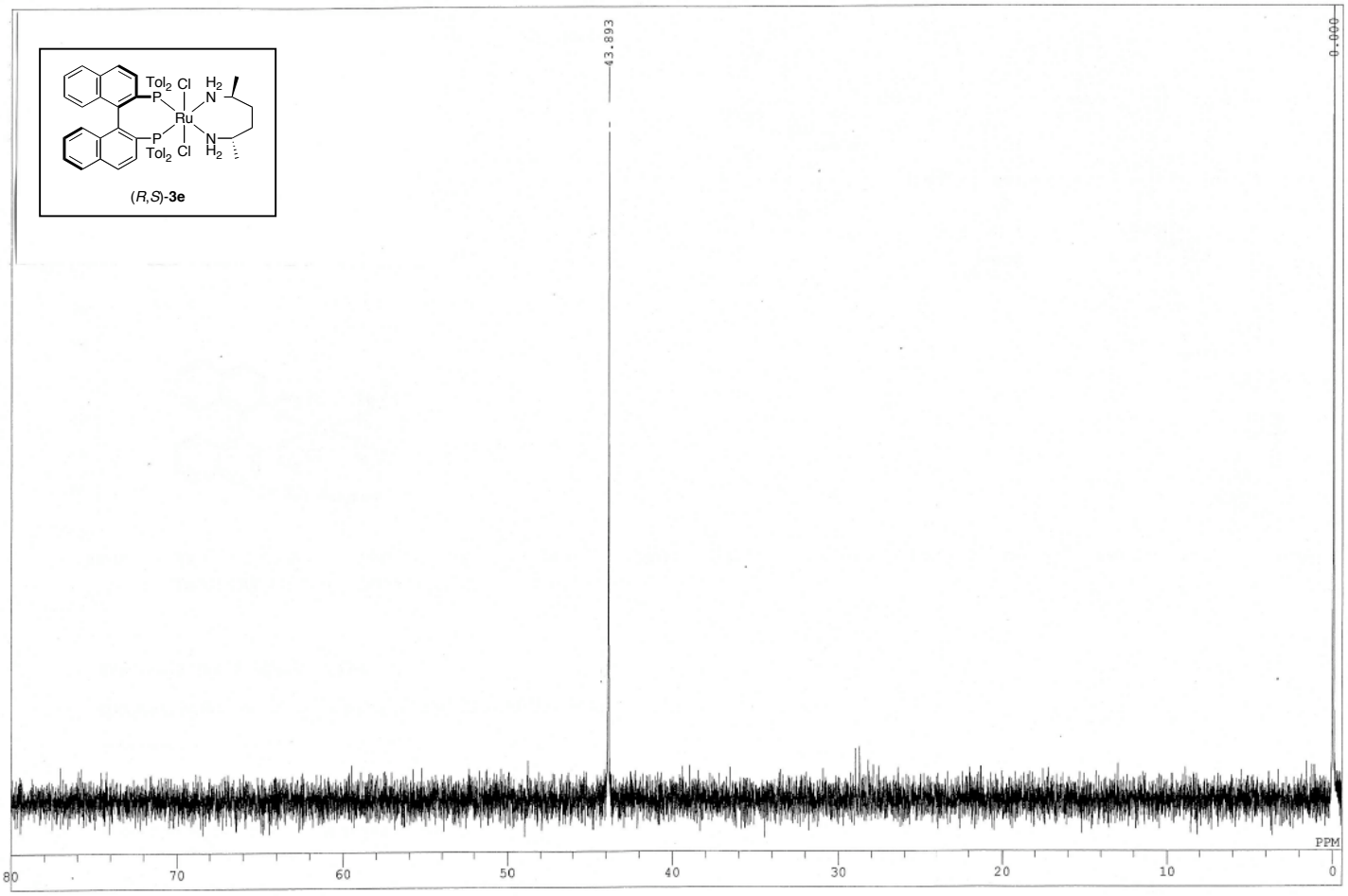

(S,R)-3c
1.99
3.52
2.0
5.42
3.65
1.8
2
6.18
2.04
2.14
3.78
6.12
6.11
6.14
6.01
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.3042
8.2933
8.2835
7.8710
7.7344
7.7136
7.5135
7.4940
7.2669
7.2157
7.1962
6.9167
6.6666
6.6629
6.6495
6.2370
6.2187
6.1992
3.4974
3.4828
3.4779
3.0105
2.7030
2.6627
2.6347
2.3772
2.3503
2.3235
1.8073
1.7792
1.5742
1.2366
0.5382
0.5211
0.0085
-0.0000
-0.0086
X : parts per Million : 1H

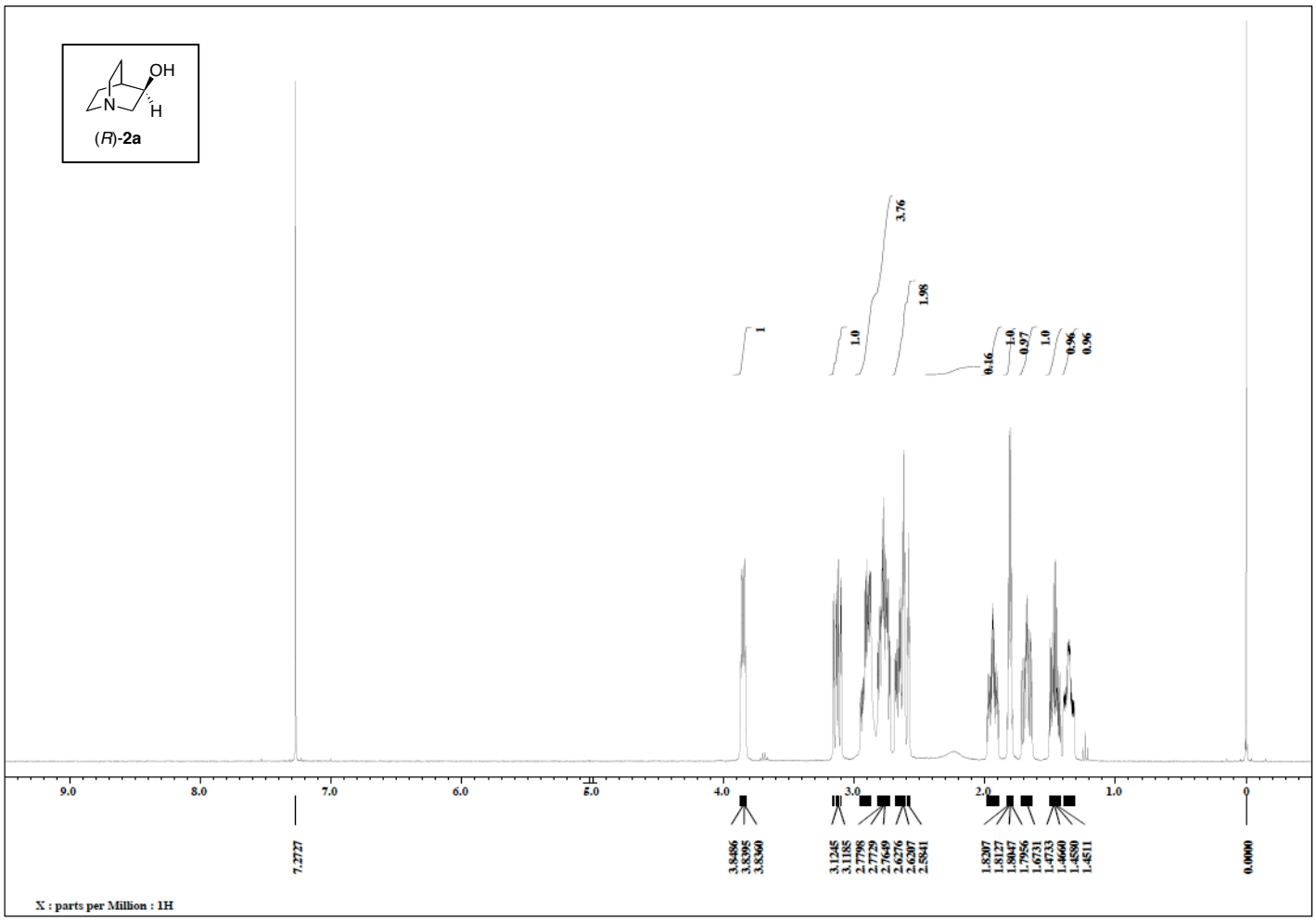

(S,R)-3c
PPM
60
40
20
0
44.056
0.000

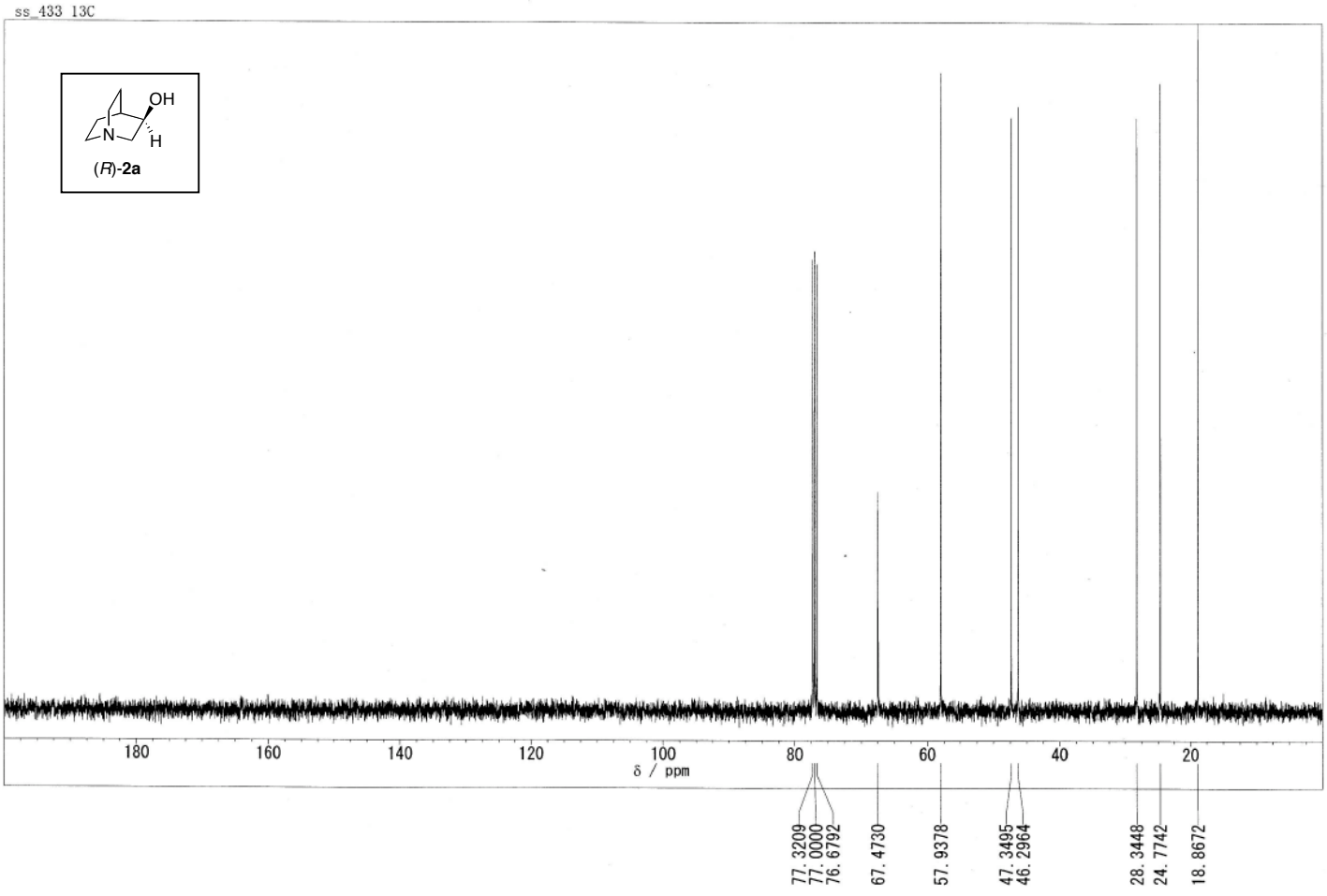

(S,R)-3d
2
3.61
5.72
6.2
2.01
2.03
2.05
6.23
2.06
2.13
3.91
6.5
2.16
5.95
X : parts per Million : 1H

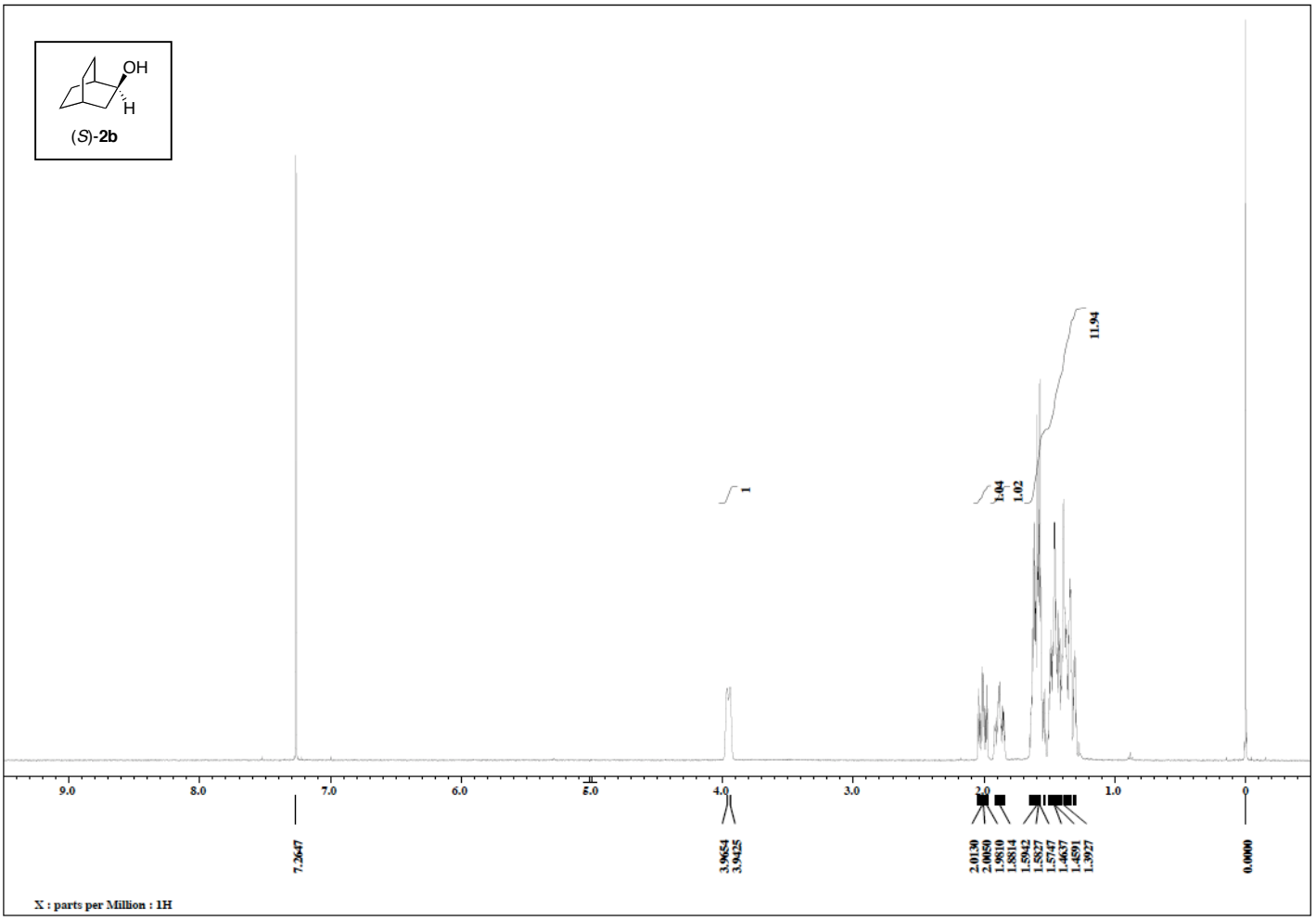

C:\WINNMR98\COMMON_DEFAULT.ALS
BINAP/HDN
(S,R)-3d
45.652
PPM

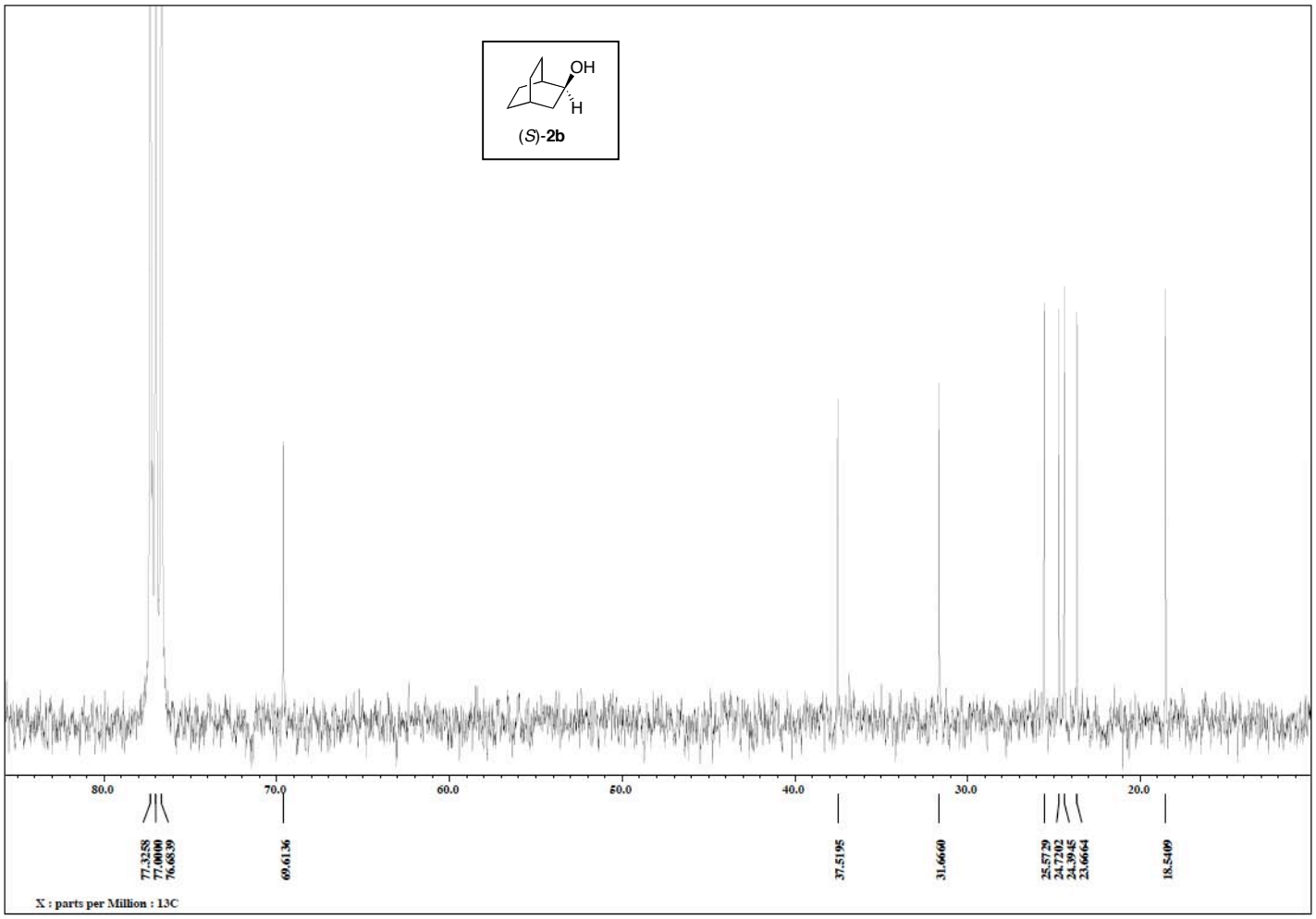

(R,S)-3e
2.0000
5.3584
2.8659
7.9242
9.2763
2.9551
6.8641
3.7804
2.0624
3.9295
11.0991
22.8411
8.9851
6.3590
PPM
9
8
7
6
5
4
3
2
1
0

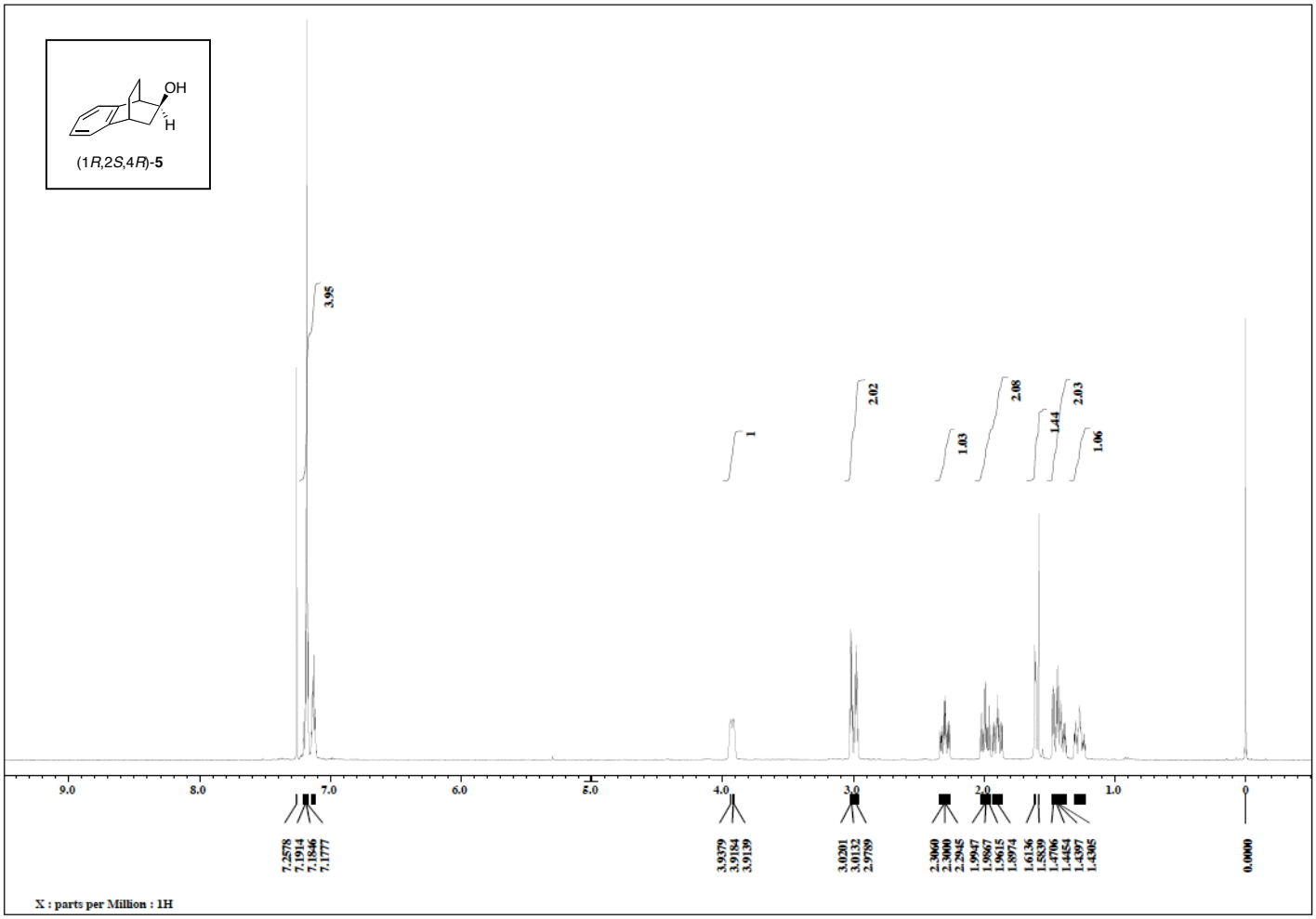

(R,S)-3e
43.893
0.000
PPM
80
70
60
50
40
30
20
10
0

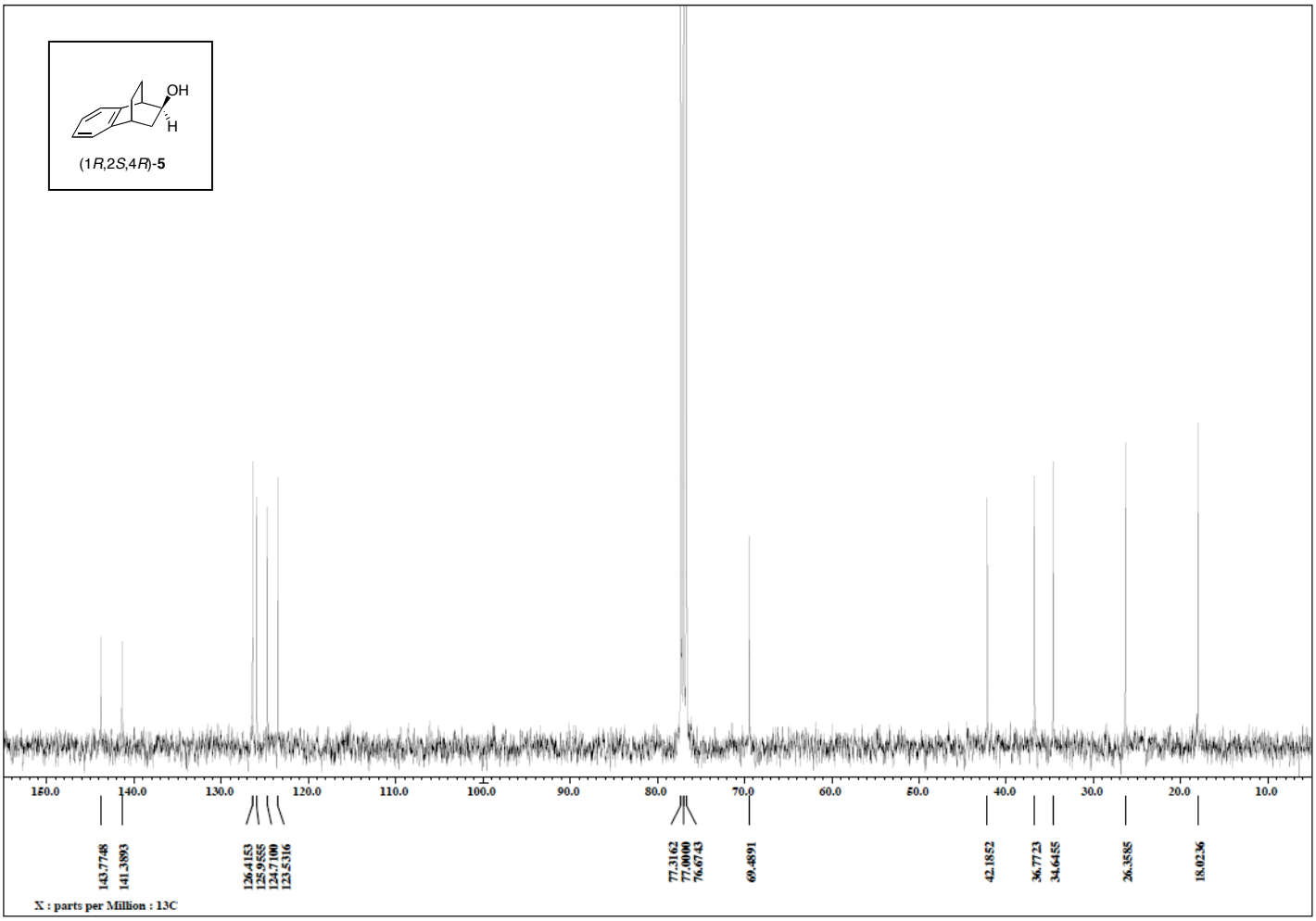

OH
N
H
(R)-2a
3.76
1.98
1
1.0
0.16
1.0
0.97
1.0
0.96
0.96
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.2727
3.8486
3.8395
3.8360
3.1245
3.1185
2.7798
2.7729
2.7649
2.6276
2.6207
2.5941
1.8307
1.8127
1.8047
1.7956
1.6731
1.4733
1.4660
1.4580
1.4511
0.0000
X : parts per Million : 1H

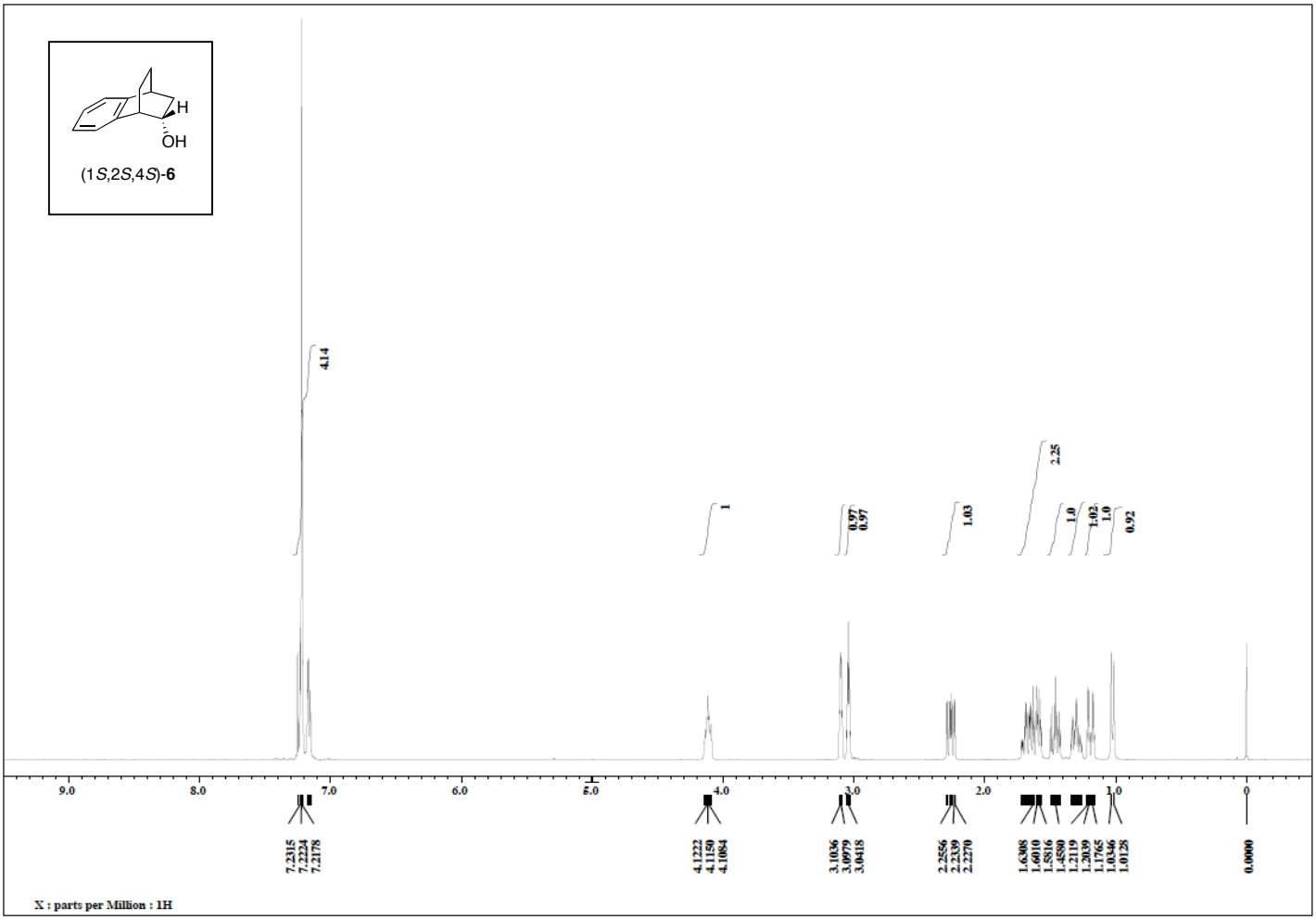

ss_433 13C
OH
N
H
(R)-2a
180
160
140
120
100
80
60
40
20
δ / ppm
77.3209
77.0000
76.6792
67.4730
57.9378
47.3495
46.2964
28.3448
24.7742
18.8672

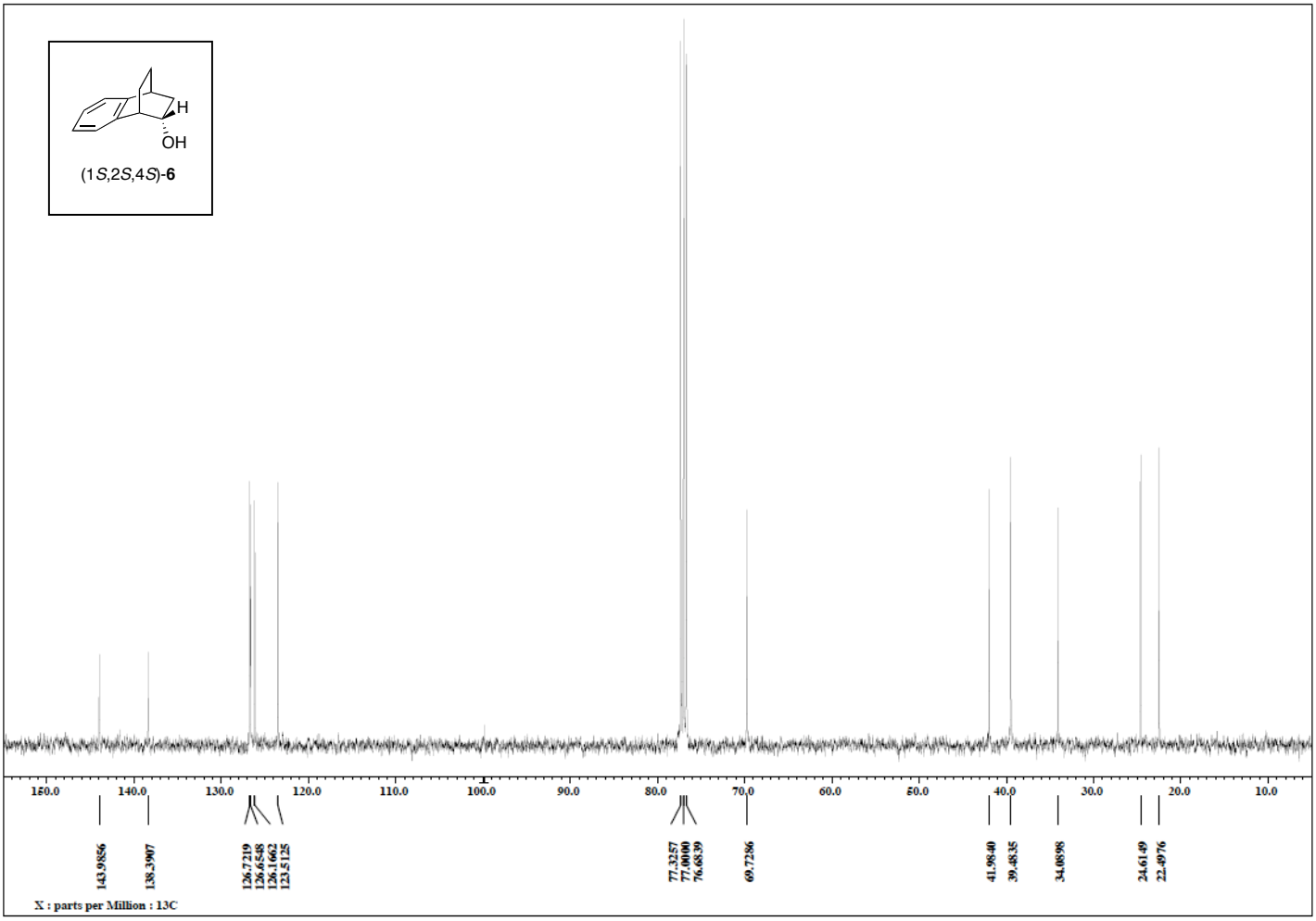

OH
H
(S)-2b
11.94
1
1.04
1.02
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.2647
3.9654
3.9425
2.0130
2.0069
1.9810
1.5814
1.5942
1.5827
1.5747
1.4637
1.4591
1.3927
0.0000
X : parts per Million : 1H

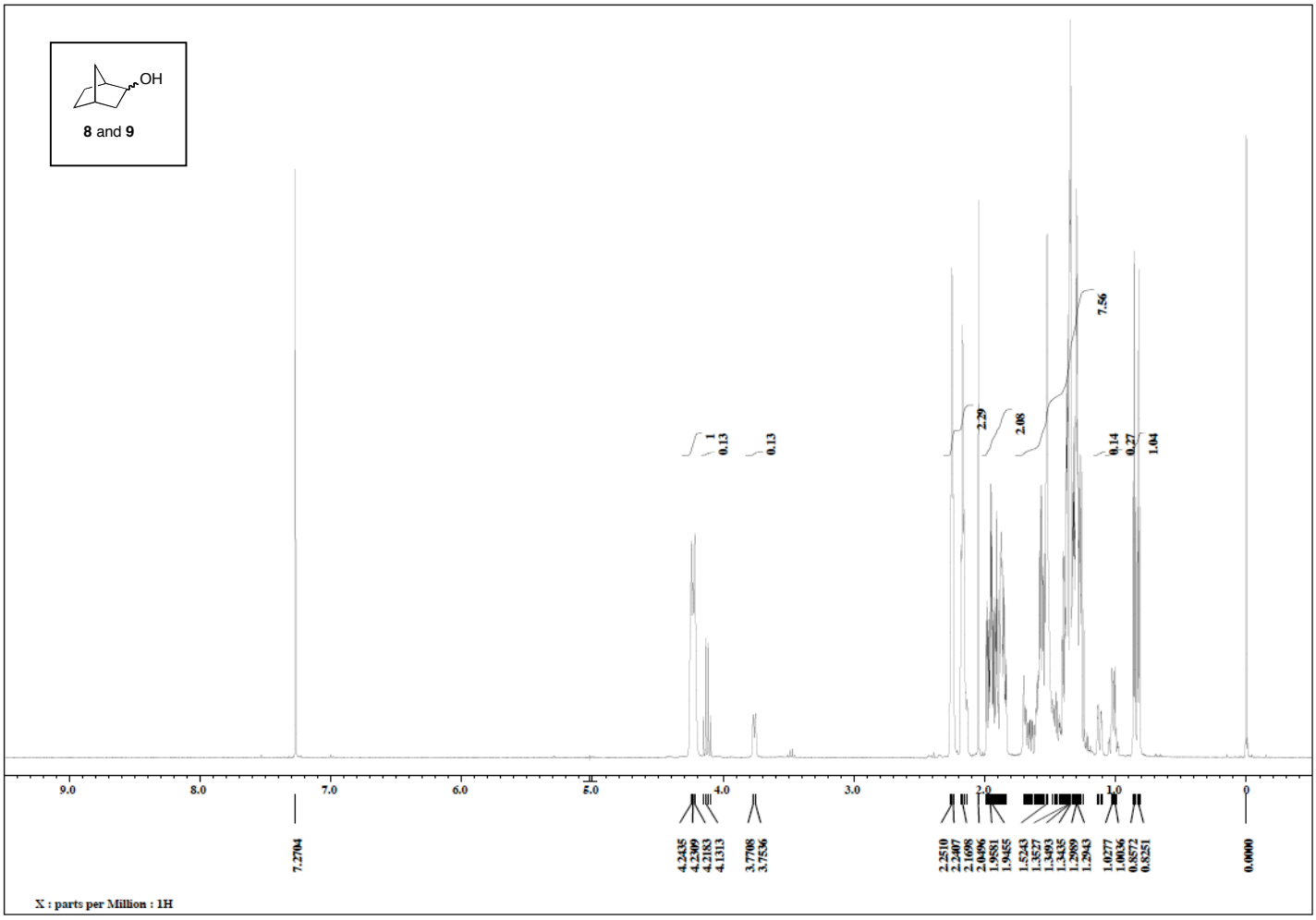

OH
H
(S)-2b
80.0
70.0
60.0
50.0
40.0
30.0
20.0
77.3258
77.0000
76.6839
69.6136
37.5195
31.6660
25.5729
24.7202
24.3945
23.6664
18.5409
X : parts per Million : 13C

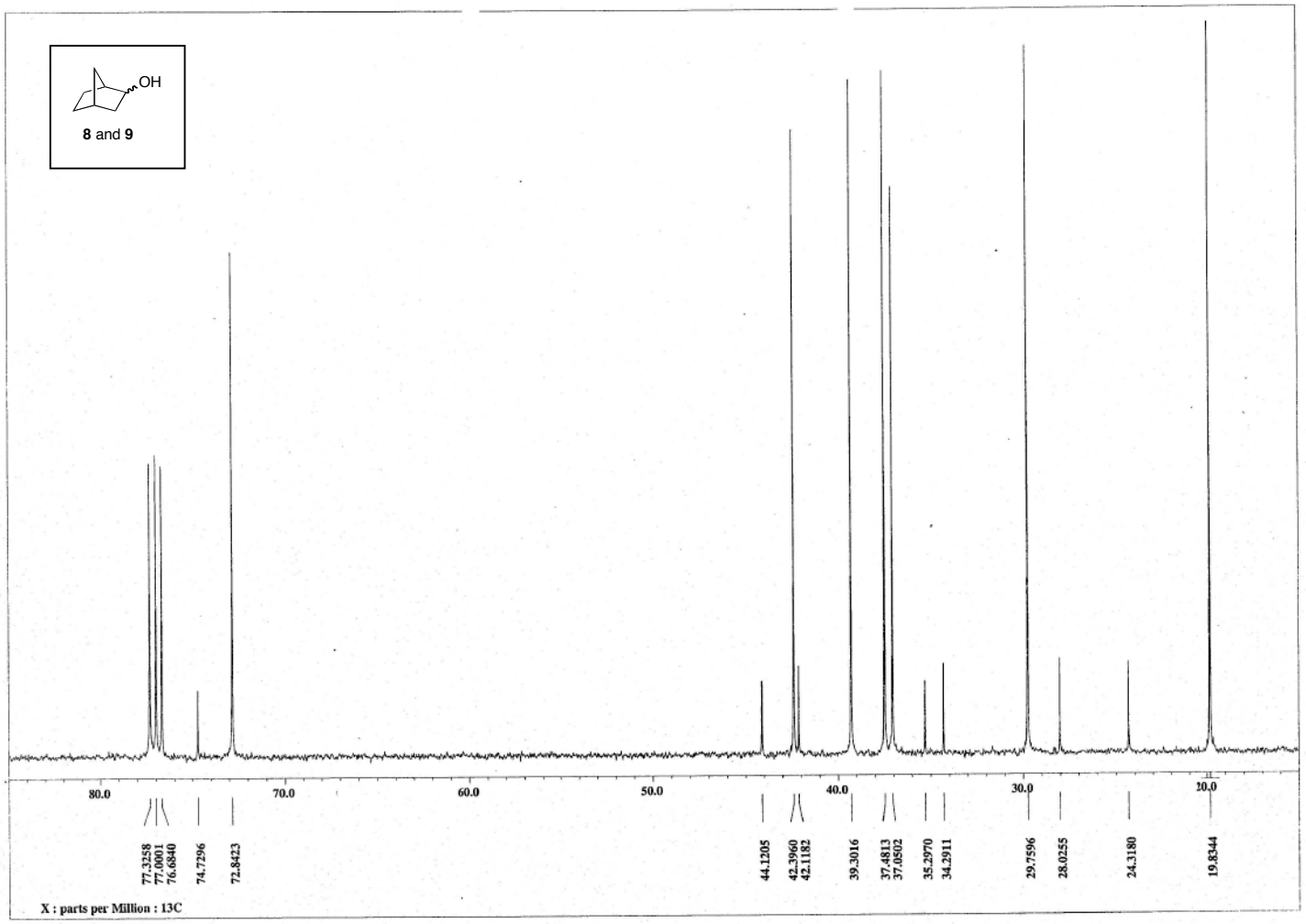

OH
H
(1R,2S,4R)-5
3.95
1
2.02
1.03
2.08
1.44
2.03
1.06
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.2578
7.1914
7.1846
7.1777
3.9379
3.9184
3.9139
3.0201
3.0132
2.9789
2.3060
2.3000
2.2945
1.9947
1.9867
1.9615
1.8974
1.6136
1.5839
1.4706
1.4454
1.4397
1.4085
0.0000
X : parts per Million : 1H

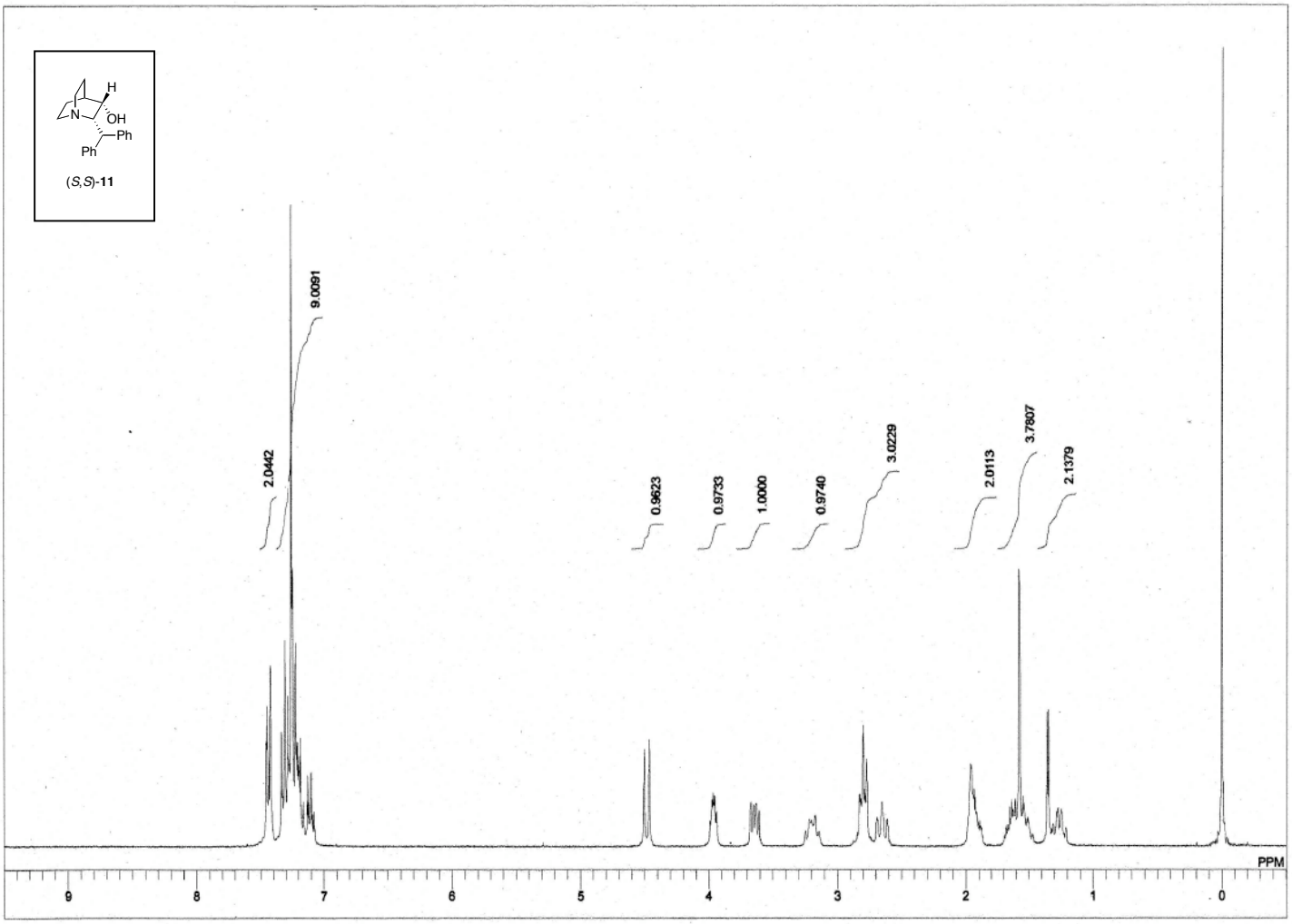

OH
H
(1R,2S,4R)-5
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
143.7748
141.3893
126.4153
125.9555
124.7100
123.5316
77.3162
77.0000
76.6743
69.4891
42.1852
36.7723
34.6455
26.3585
18.0236
X : parts per Million : 13C

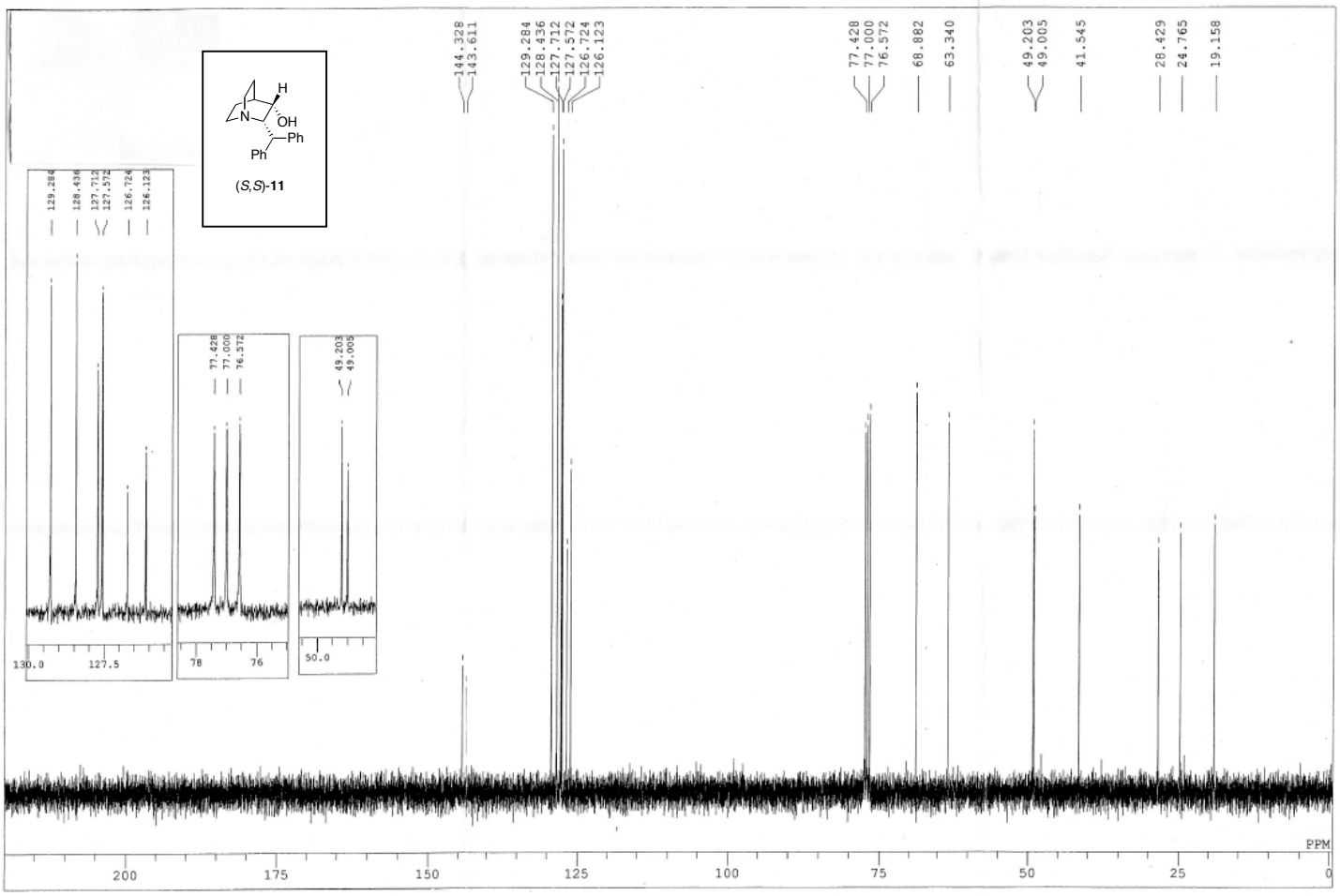

H
OH
(1S,2S,4S)-6
4.14
1
0.97
0.97
1.03
2.25
1.0
1.02
1.0
0.92
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.2315
7.2224
7.2178
4.1222
4.1150
4.1084
3.1036
3.0979
3.0418
2.2556
2.2339
2.2270
1.6308
1.6010
1.5816
1.4580
1.2119
1.2039
1.1765
1.0346
1.0128
0.0000
X : parts per Million : 1H


H
OH
(1S,2S,4S)-6
160.0
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
143.9856
138.3907
126.7219
126.6548
126.1662
123.5125
77.3257
77.0000
76.6839
69.7286
41.9840
39.4835
34.0898
24.6149
22.4976
X : parts per Million : 13C


OH
8 and 9
7.56
2.29
2.08
1
0.13
0.13
0.14
0.27
1.04
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.2704
4.2435
4.2309
4.2183
4.1313
3.7708
3.7536
2.2510
2.2407
2.1698
2.0496
1.9581
1.9455
1.5243
1.3527
1.3493
1.3435
1.2989
1.2943
1.0277
1.0036
0.8572
0.8251
0.0000
X : parts per Million : 1H


OH
8 and 9
80.0
70.0
60.0
50.0
40.0
30.0
20.0
77.3258
77.0001
76.6840
74.7296
72.8423
44.1205
42.3960
42.1182
39.3016
37.4813
37.0502
35.2970
34.2911
29.7596
28.0255
24.3180
19.8344
X : parts per Million : 13C


(S,S)-11
2.0442
9.0091
0.9623
0.9733
1.0000
0.9740
3.0229
2.0113
3.7807
2.1379
PPM


(S,S)-11
144.328
143.611
129.284
128.436
127.712
127.572
126.724
126.123
77.428
77.000
76.572
68.882
63.340
49.203
49.005
41.545
28.429
24.765
19.158
PPM