Electronic Supplementary Information

Modulation of Coordination Geometry of NCN and NCNC Rh Complexes for Ambidextrous Chiral Catalysts

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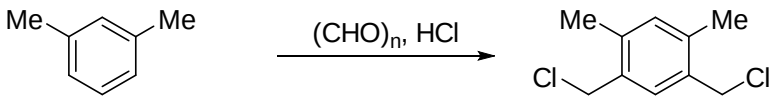
Contents:

1. General Procedure.

All air- and moisture-sensitive compounds were manipulated using standard Schlenk and vacuum line techniques under an argon atmosphere. ^{1}H, ^{13}C and ^{19}F NMR spectra was measured at room temperature on a Varian Mercury 300 spectrometer. ^{1}H NMR chemical shifts are reported in δ units, in ppm relative to the singlet at 7.26 for $CDCl_3$ and 7.16 ppm for C_6D_6 and ^{13}C NMR chemical shifts are reported relative to the triplet at 77.0 ppm for $CDCl_3$ and 128.0 ppm for C_6D_6. ^{19}F NMR spectra are reported in terms of chemical shifts relative to the external signal of CF_3COOH at δ –78.5 ppm. Infrared spectra were recorded on a JASCO FT/IR-230 spectrometer. Mass spectra were recorded on a JEOL JMS-700. Elemental analyses were recorded on a YANACO MT-6 and a PerkinElmer 2400II.

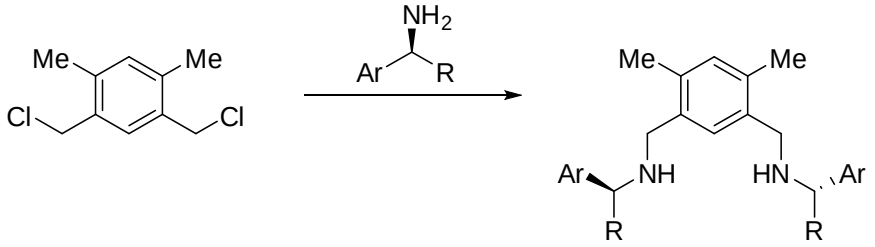
2. Preparation of ligand precursors and Rh complexes.

Preparation of 1,5-bis(chloromethyl)-2,4-dimethylbenzene.[S1]



A mixture of m-xylene (20 mL, 163 mmol) and para-formaldehyde (11.6 g, 400 mmol) in acetic acid (40 mL) and HCl (160 mL) was stirred at 70 °C for 2 days. The resulting suspension was extracted with CH_2Cl_2 (50 mL x 5) and the extract was washed with saturated $NaHCO_3$ solution (50 mL x 4), water (50 mL x 2) and brine (50 mL) and dried over $MaSO_4$. After filtration, the solvent was removed and the residue was crystallized from hexane to give 1,5-bis(chloromethyl)-2,4-dimethylbenzene (21.8 g, 110 mmol, 67%) as colorless crystals. ^{1}H NMR (300 MHz, C_6D_6): δ 6.76 (s, 1H), 6.59 (s, 1H), 4.07 (s, 4H), 2.03 (s, 6H). ^{13}C NMR (75 MHz, C_6D_6): δ 138.2, 134.1, 133.6, 131.9, 44.7, 18.5.

Preparation of 1.



1a (R = Me, Ar = Ph
1b (R = Me, Ar = 2-naphthyl)
1c (R = Et, Ar = Ph)

To a mixture 1,5-bis(chloromethyl)-2,4-dimethylbenzene (2.01 g, 9.9 mmol), (S)-1-phenylethylamine (2.66 g, 22.0 mmol), and K_2CO_3 (5.52 g, 40 mmol) was added DMF (20 ml). The reaction mixture was heated at 100 ºC for 2.5 h. Then, the mixture was diluted with ethyl acetate (100 ml) and the solution was washed with 5% of potassium carbonate and brine. The organic layer was dried with sodium sulfate and was concentrated. The crude product was purified by column chromatography on silica gel (eluent; hexane:ethyl acetate = 4:2 with 2% of NEt_3) to give **1a** (2.41 g, 6.5 mmol, 65 % yield). The use of (*S*)-1-(naphthalene-1-yl)ethylamine (1.02 g, 6.0 mmol) and (S)-1-phenylpropan-1-amine (1.02 g, 5.0 mmol) afforded **1b** (877 mg, 1.97 mmol, 66%) and **1c** (1.71 g, 4.27 mmol, 85%), respectively.

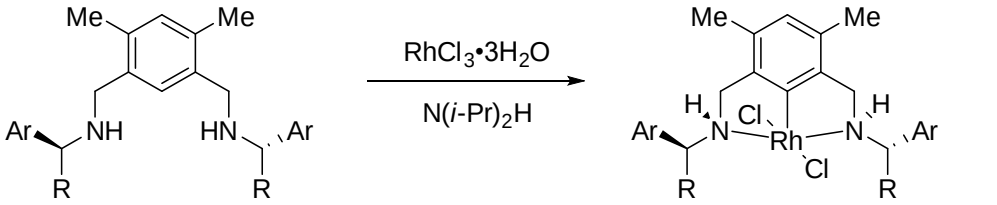
1a: Colorless solid. ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 1.38 (d, *J*= 6.6 Hz, 6H), 2.22 (s, 6H), 3.56 (s, 4H), 3.84 (q, *J* = 6.6 Hz, 2H), 6.92 (s, 1H), 7.10 (s, 1H), 7.27-7.40 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$, rt): δ 18.6, 24.8, 49.5, 58.2, 126.5, 126.7, 128.2, 129.0, 132.1, 134.6, 135.6, 145.5. IR (KBr, cm^{-1}): 3231, 3027, 2964, 2923, 2860, 2802, 1490, 1454, 1377, 1110, 1018, 841. Anal. Calcd for $C_{26}H_{32}N_2$: C, 83.82; H, 8.66; N, 7.52, found: C, 83.63; H, 8.67; N, 7.15. HRMS (FAB, m/z) calcd for $C_{26}H_{32}N_2$ 372.2644[M+H$^+$], found 372.2651. $[\alpha]_D^{18}$ = -44.2 (c 0.99, $CHCl_3$).

1b: Colorless solid. ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 1.58 (d, *J* = 6.6 Hz, 6H), 2.32 (s, 6H), 3.69 (d, *J* = 6.6 Hz, 2H), 3.77 (d, *J* = 6.6 Hz, 2H), 4.75 (q, *J* = 6.6 Hz, 2H), 7.02 (s, 1H), 7.18 (s, 1H), 7.50-7.58 (m, 6H), 7.82 (d, *J* = 7.8 Hz, 4 H), 7.92-7.95 (m, 2H), 8.21-8.24 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, rt): δ 18.5, 23.7, 49.4, 53.3, 122.5, 122.5, 122.6, 124.8, 125.2, 125.3, 126.7, 128.5, 129.0, 130.8, 131.9, 133.5, 134.5, 135.4, 140.6. IR (KBr, cm^{-1}): 3426, 3046, 2965, 2921, 2863, 1735, 1594, 1509, 1450, 1369, 1237, 1172, 1113. Anal. Calcd for $C_{34}H_{36}N_2$: C, 86.40; H, 7.68; N, 5.93, found: C, 86.30; H, 7.72; N, 5.94. HRMS (FAB, m/z) calcd for $C_{34}H_{38}N_2$ 473.2957 [M+H$^+$], found 473.2963.

$[\alpha]_D^{26}$ = -39.2 (c 1.0, $CHCl_3$).

1c: colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, rt): 0.88 (t, *J* = 7.4 Hz, 6 H), 1.52 (br, 2H), 1.64-1.88 (m, 4H), 2.26 (s, 6H), 3.52-3.63 (m, 6H), 6.97 (s, 1H), 7.14 (s, 1H), 7.28-7.40 (m, 10H). ^{13}C NMR (75 Hz, $CDCl_3$, rt): 11.1, 18.6, 31.3, 49.5, 65.0, 126.7, 127.2, 128.0, 129.2, 132.1, 134.7, 135.7, 144.0. IR (KBr, cm^{-1}): 3322, 3060, 2024, 2961, 2926, 2872, 1601, 1454, 1357, 1117, 759, 701. Anal. Calcd for $C_{28}H_{36}N_2$: C, 83.95; H, 9.06; N, 6.99, found: C, 83.66; H, 9.45; N, 6.87. $[\alpha]_D^{25}$ = -47.3 (c 1.0, $CHCl_3$).

Preparation of 2.



2a (R = Me, Ar = Ph
2b (R = Me, Ar = 2-naphthyl)
2c (R = Et, Ar = Ph)

To a mixture of **1a** (373 mg, 1.0 mmol) and $RhCl_3 \cdot 3H_2O$ (263 mg, 1.0 mmol) was added diisopropylamine (5 ml) and then the reaction mixture was refluxed for 24 h. The crude product was purified by column chromatography on silica gel (eluent; chloroform) to give **2a** (355 mg, 0.65 mmol, 65% yield). **1b** (444 mg, 1.0 mmol)/$RhCl_3 \cdot 3H_2O$ (263 mg, 1.0 mmol) and **1c** (409 mg, 1.0 mmol)/$RhCl_3 \cdot 3H_2O$ (296 mg, 1.1 mmol) gave **2b** (447 mg, 0.69 mmol, 69%) and **2c** (228 mg, 0.40 mmol, 40%), respectively.

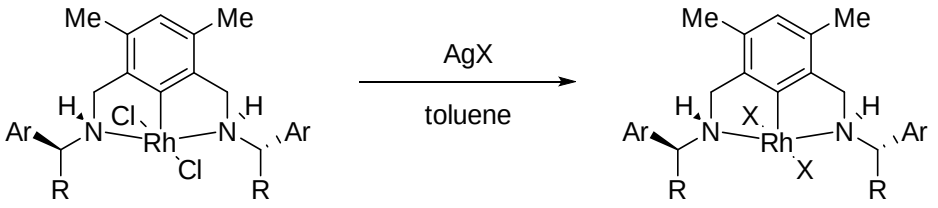
2a: ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 1.97 (d, *J* = 6.9 Hz, 6H), 1.99 (s, 6H), 3.60 (dd, *J* = 5.6, 14.2 Hz, 2H), 3.84 (dd, *J* = 11.1, 14.2 Hz, 2H), 4.39 (dq, *J* = 11.1, 6.9 Hz, 2H), 4.75 (br, 2H, N-*H*)), 6.41 (s, 1H), 7.34-7.49 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$, rt): δ 18.9, 23.5, 55.7, 62.2, 126.3, 127.2, 128.4, 129.1, 131.0, 136.4, 139.9, 145.7 (d, J_{RhC} = 30.8 Hz). IR (KBr, cm^{-1}): 3226 (ν_{NH}), 3000, 2952, 2911, 1604, 1550, 1495, 1455, 1379, 1202, 1078, 1028. Anal. Calcd for $C_{26}H_{31}Cl_2N_2Rh$: C, 57.26; H, 5.73; N, 5.14, found: C, 57.13; H, 5.73; N, 4.86. HRMS (FAB, m/z) calcd for $C_{26}H_{31}Cl_2N_2Rh$ [M^+] 544.0919, found 544.0925. $[\alpha]_D^{18}$ = 27.1 (c 0.3, $CHCl_3$).

2b: ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 1.89 (s, 6H), 2.10 (d, *J* = 6.6 Hz, 6H), 3.71 (dd, *J* = 4.2, 15.0 Hz, 2H), 3.88 (dd, *J* = 9.6, 15.0 Hz, 2H), 5.10 (br, 2H, N-*H*), 5.52 (dq, *J* = 11.1, 6.6 Hz, 2H), 6.37 (s,

1H), 7.56-7.67 (m, 8H), 7.90-7.97 (m, 4H), 8.24 (d, J = 8.7 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, rt): d 19.0, 24.4, 55.6, 55.8, 121.9, 122.1, 125.5, 125.8 126.1, 126.8, 127.3, 128.5, 128.9, 131.0, 133.7, 136.5, 136.6, 146.0 (d, J_{RhC} = 30.8 Hz). IR (KBr, cm^{-1}): 3228 (ν_{NH}), 2916, 2855, 1598, 1557, 1511, 1452, 1377, 1172, 1106, 1065. Anal. Calcd for $C_{34}H_{35}Cl_2N_2Rh$: C, 63.27; H, 5.47; N, 4.34, found: C, 63.40; H, 5.47; N, 4.30. HRMS (FAB, m/z) calcd for $C_{34}H_{35}Cl_2N_2Rh$ 644.1232 [M^+], found 644.1234. $[\alpha]_D^{27}$ = 39.1 (c 0.66, $CHCl_3$).

2c: ^{1}H NMR (300 MHz, $CDCl_3$, rt): 1.05 (t, J= 7.2 Hz, 6H), 1.96 (s, 6H), 2.01-2.14 (m, 2H), 2.61-2.74 (m, 2H), 3.55 (ddd, J = 2.3, 4.3, 14.3 Hz, 2H), 3.82 (dd, J = 10.2, 14.3 Hz, 2H), 4.15 (dt, J = 5.1, 10.8 Hz, 2H), 4.78 (br, 2H), 6.41 (s, 1H), 7.31-7.45 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$, rt): 11.7, 18.9, 30.7, 55.8, 68.4, 127.0, 127.2, 128.3, 129.0, 131.0, 136.8, 138.3, 147.2 (d, J = 30.8 Hz). IR (KBr, cm^{-1}): 3228 (ν_{NH}), 3024, 2965, 2935, 2876, 1606, 1559, 1454, 1178, 1086, 1034, 971, 852, 702. Anal. Calcd for $C_{28}H_{35}Cl_2N_2Rh$: C, 58.65; H, 6.15; N, 4.89, found: C, 58.71; H, 6.22; N, 4.87. $[\alpha]_D^{27}$ = 0.6 (c 0.33, $CHCl_3$).

Preparation of 3.



3a: Ar = Ph, R = Me, X = OAc (88%)
3a': Ar = Ph, R = Me, X = OCO*t*Bu (90%)
3b: Ar = 1-naphthyl, R = Me, X = OAc (75%)
3c: Ar = Ph, R = Et, X = OAc (83%)

To a mixture of **2a** (160 mg, 0.292 mmol) and silver acetate (249 mg, 1.49 mmol) was added toluene and the reaction mixture was stirred at room temperature for 37 h. The crude product was purified by column chromatography on silica gel (eluent: hexane:ethyl acetate = 2:1) to give **3a** (152 mg, 0.256 mmol, 88% yield). Reaction of **2b** (194 mg, 0.30 mmol) and AgOAc (251 mg, 1.5 mmol) at room temperature for 36 h gave **3b** (156 mg, 0.23 mmol, 75%). Reaction of **2c** (114.7 mg, 0.20 mmol) and AgOAc (166.9 mg, 1.0 mmol) at room temperature for 46 h gave **3c** (103.6 mg, 0.17 mmol, 83%). Reaction of **2a** (133 mg, 0.24 mmol) and AgOCO*t*Bu (255 mg, 1.23 mmol) gave **3a'** (143 mg, 0.22

mol, 90%).

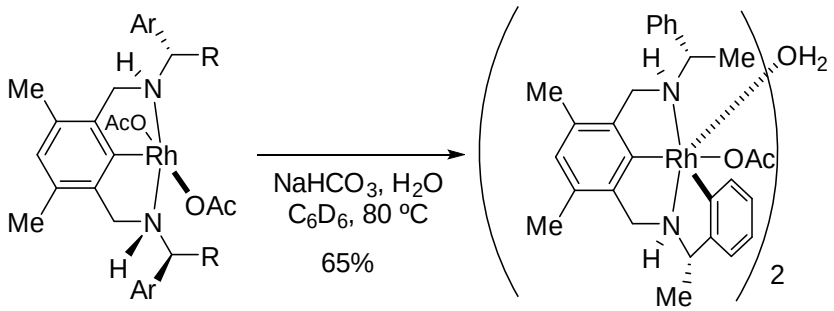
3a: ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 1.97 (d, *J* = 6.8 Hz, 6H), 1.98 (s, 3H), 1.98 (s, 6H), 3.44-3.65 (m, 4H), 3.96 (dq, *J* = 10.1, 6.8 Hz, 2H), 6.41 (s, 1H), 7.31-7.45 (m, 10H), 7.78 (m, 2H, N-*H*). ^{13}C NMR (75 MHz, $CDCl_3$, rt): δ 19.0, 23.5, 24.1, 55.1, 61.2, 126.126.6, 127.0, 127.8, 128.9, 130.1, 138.0, 141.0, 154.2 (J_{RhC} = 31.9 Hz), 183.2. IR (KBr, cm^{-1}): 3030, 2924, 1588 (ν_{CO}), 1495, 1455, 1375, 1321, 1087, 1027. Anal. Calcd for $C_{30}H_{37}N_2O_4Rh$: C, 60.81; H, 6.29; N, 4.73, found: C, 60.24; H, 6.38; N, 4.21. HRMS (FAB, m/z) calcd for $C_{30}H_{37}N_2O_4Rh$ 592.1808 [M^+], found 592.1808. $[\alpha]_D^{18}$ = -210.1 (c 0.35, $CHCl_3$).

3a': ^{1}H NMR (300 MHz, $CDCl_3$, rt): 1.17 (s, 18H), 1.93 (d, *J* = 6.6 Hz, 6H), 1.97 (s, 6H), 3.47-3.61 (m, 4H), 3.96 (dq, *J* = 6.9, 11.0 Hz, 2H), 6.39 (s, 1H), 7.32-7.44 (m, 10H), 7.64 (br, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, rt): 19.0, 23.3, 28.2, 39.6 (J_{RhC} = 1.1 Hz), 55.3, 60.9, 126.5, 126.6, 127.8, 128.9, 129.8, 138.1, 141.0, 156.2 (J_{RhC} = 31.4 Hz), 190.9 (J_{RhC} = 1.1 Hz). IR (KBr, cm^{-1}): 3592, 3063, 2953, 1596, 1479, 1394, 1332, 1214, 1109, 1026, 764, 702. Anal. Calcd for $C_{36}H_{49}N_2O_4Rh$: C, 63.90; H, 7.30; N, 4.14, found: C, 64.07; H, 7.54; N, 4.02. $[\alpha]_D^{24}$ = -187.9 (c 0.76, $CHCl_3$).

3b:^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 1.60 (s, 6H), 2.13 (s, 6H), 2.28 (d, *J* = 6.9 Hz, 6H), 3.68 (dd, *J* = 3.5, 14.1 Hz, 2H), 3.93 (dd, *J* =10.4, 14.1 Hz, 2H), 4.39 (dq, *J* = 10.4, 6.9 Hz, 2H), 6.31 (s, 1H), 7.20-7.30 (m, 4H), 7.54-7.72 (m, 10H), 9.01 (br, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, rt): 19.0, 23.5, 24.1, 55.2, 61.4, 123.6, 126.0, 126.1, 126.3, 127.0, 127.58, 127.63, 129.1, 130.2, 132.9, 133.1, 138.0, 138.3, 154.4 (J_{RhC} = 32.0 Hz), 183.4. IR (KBr, cm^{-1}): 3053, 2927, 1581, 1376, 1324, 1174, 1129, 1082, 858, 749. Anal. Calcd for $C_{38}H_{41}N_2O_4Rh$: C, 65.89; H, 5.97; N, 4.04, found: C, 65.83; H, 5.90; N, 4.01. $[\alpha]_D^{27}$ = -112.4 (c 0.34, $CHCl_3$).

3c: ^{1}H NMR (300 MHz, $CDCl_3$, rt): 0.97 (t, *J* = 7.2 Hz, 6H), 1.89-2.02 (m, 2H), 1.95 (s, 6H), 1.95 (s, 6H), 2.85-2.99 (m, 2H), 3.45-3.57 (m, 4H), 3.71 (dt, *J* = 4.8, 10.5 Hz, 2H), 6.40 (s, 1H), 7.32-7.44 (m, 10H), 8.43 (br, 2H). ^{13}C NMR (75Hz. $CDCl_3$, rt): 11.8, 19.0, 24.2 (J_{RhC} = 1.2 Hz), 30.0, 54.6, 126.9, 127.4, 127.7, 128.7, 130.0, 138.3, 139.1, 153.8 (J_{RhC} = 32.6 Hz), 183.1. IR (KBr, cm^{-1}): 3064, 2965, 2931, 2877, 1584, 1454, 1375, 1322, 1169, 1016, 854, 773, 702. Anal. Calcd for $C_{32}H_{41}N_2O_4Rh$: C, 61.93; H, 6.66; N, 4.51, found: C, 61.45; H, 6.64; N, 4.51. $[\alpha]_D^{27}$ = -214.9 (c 0.38, $CHCl_3$).

Preparation of 4.



3a **4**

To a mixture of **3a** (59.5 mg, 0.10 mmol) and $NaHCO_3$ (84.1 mg, 010 mmol) was added benzene-d_6 (0.7 mL). The solution was heated at 80 ºC for 70 h. After centrifugation of the mixture, the solvent was removed under reduced pressure. The residue was crystallization with hexane and CH_2Cl_2 to give yellow crystals of **4** (35.2 mg, 0.033 mmol, 65% yield).

^{1}H NMR (300 MHz, C_6D_6, rt): δ 1.70 (s, 3H), 1.72 (d, J = 6.9 Hz, 3H), 1.75 (d, J = 7.5 Hz, 3H), 1.76 (s, 3H), 2.38 (s, 3H), 3.40 (d, J = 16.2 Hz, 1H), 3.53-3.69 (m, 2H), 3.93 (dd, J = 10.2, 15.0 Hz, 1H), 4.04-4.19 (m, 2H), 4.60-4.72 (br, 2H), 6.26 (s, 1H), 6.78-6.83 (m, 3H), 6.95-7.08 (m, 5H), 7.32 (d, J 7.8 Hz, 1H). ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 1.66 (d, J = 6.9 Hz,3H), 1.67 (d, J = 6.6 Hz, 3H), 1.90 (s, 3H), 1.96 (s, 3H), 2.08 (s, 3H), 3.68-3.78 (m, 1H), 3.83-3.99 (m, 3H), 4.47 (br, 1H), 4.06-4.24 (m, 2H), 4.63 (dq, J = 8.3, 16.4Hz, 2H), 6.22 (s, 1H), 6.86-6.94 (m, 3H), 7.13 (br, 1H), 7.34-7.48 (m, 5H). ^{13}C NMR (75 MHz, C_6D_6, rt): δ 19.48, 19.51, 24.6, 25.6, 26.1, 60.1, 63.8, 64.2, 72.8, 122.0, 122.9, 125.3, 125.5, 126.7, 128.8, 129.0, 129.1, 135.2, 138.4, 141.6, 142.0, 152.9 (d, J_{RhC} = 37.7 Hz), 154.9, 163.0 (d, J_{RhC} = 32.5 Hz), 183.9. IR (KBr, cm^{-1}): 3253, 3222, 2971, 2920, 1588 (ν_{CO}), 1495, 1455, 1375, 1321, 1087, 1027. Anal. Calcd for $C_{56}H_{68}N_4O_5Rh_2$: C, 62.11; H, 6.33; N, 5.17, found: C, 62.05; H, 6.86; N, 5.08.

The heating reaction of **3a** in benzene-d_6 at 80 °C was monitored by ^{1}H NMR spectroscopy (Figure S1). In the absence of K_2CO_2, equilibrium mixtures of **3a** and **4** were obtained. In contrast, reaction in the presence of K_2CO_3 resulted in the full conversion of **3a**.

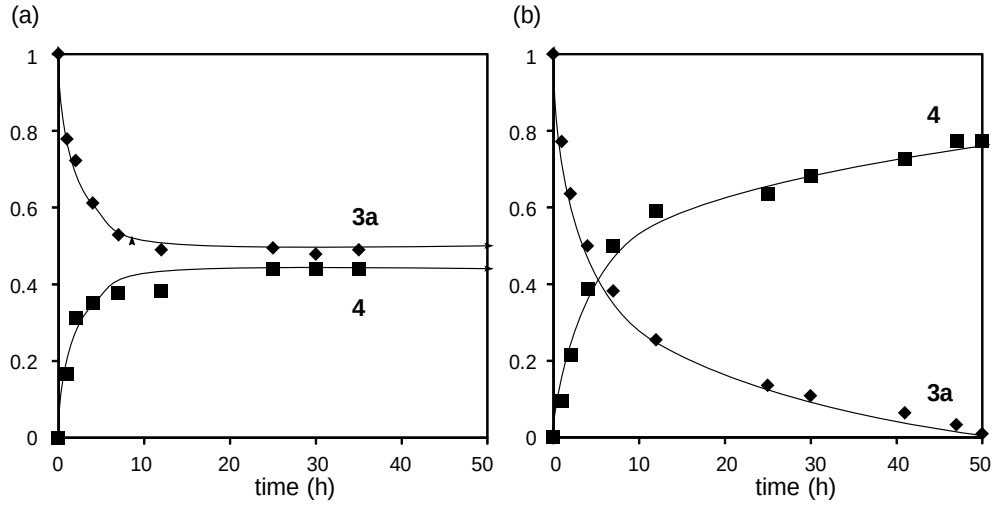
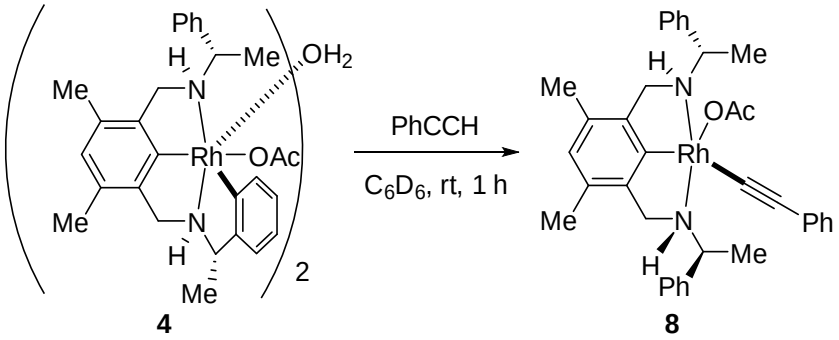


Figure S1. Time conversion curves. Heating of **3a** in benzene-d_6 at 80 ºC (a) in the absence of K_2CO_3 and (b) in the presence of K_2CO_3.

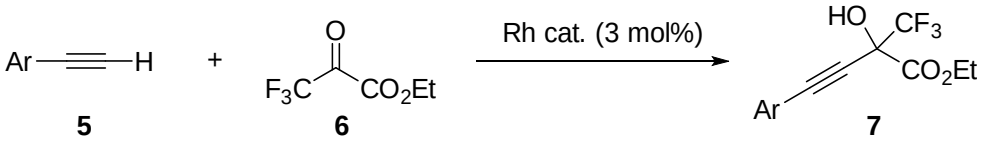
Preparation of 8.



To a solution of **4** (23.6 mg, 0.022 mmol) in toluene (2 mL) was added PhCCH (24 μL, 0.22 mmol). The solution was stirred at room temperature for 3 h and was concentrated in reduced pressure. The residue was washed with hexane to give **8** as a yellow solid (23.7 mg, 0.037 mmol, 86% yield).

^{1}H NMR (300 MHz, C_6D_6, rt): δ 1.20 (d, J = 6.6 Hz, 3H), 1.60 (s, 3H), 1.61 (d, J = 5.1 Hz, 3H), 1.97 (s, 3H), 2.02 (s, 3H), 3.69-3.99 (m, 4H), 4.29-4.51 (m, 2H), 6.00 (brs, 1H), 6.38 (s, 1H), 6.90-7.34 (m, 11H), 7.55-7.58 (m, 2H), 7.83 (d, J = 7.2 Hz, 2H), 8.40 (br, 1H); ^{13}C NMR (75 MHz, C_6D_6, rt): 19.0, 19.3, 19.5, 23.7, 25.8, 57.3, 57.4, 63.4, 64.3, 98.9 (d, J_{RhC} = 58.1 Hz), 105.2 (d, J_{RhC} = 11.4 Hz), 125.2, 126.5, 127.2, 128.6, 129.2, 129.3, 129.8, 130.4, 131.8, 136.9, 138.4, 141.8, 142.3, 154.6 (d, J_{RhC} = 35.3 Hz), 181.2; IR (KBr, cm^{-1}): 3225, 3031, 2930, 2859, 2104 (ν_{CC}), 1571, 1387, 1085, 1027, 757, 701; Anal. Calcd for $C_{36}H_{39}N_2O_2Rh$: C, 68.13; H, 6.19; N, 4.41, found: C, 68.06; H, 6.30; N, 4.18.

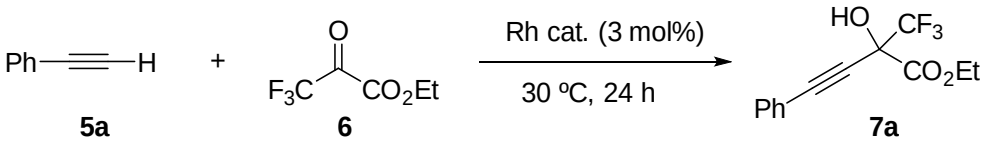
3. Asymmetric alkynylation of ethyl trifluoropyruvate with alkynes



5 **6** **7**

A mixture of alkyne (0.3 mmol) and ketone (0.2 mmol) in the presence of Rh catalysts (3 mol%) was stirred under an argon atmosphere. After removal of the solvent, a crude product was purified by column chromatography on silica gel with hexane/ethyl acetate to give **7**.

Table S1. Asymmetric alkynylation of ethyl trifluoropyruvate with phenylacetylene.[a]

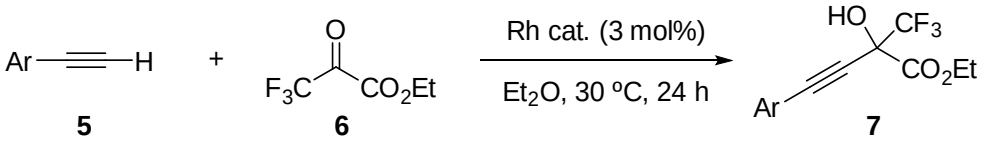


5a **6** **7a**

entry	cat	solvent	temp	yield (%)	ee (%)[b]
1	**3a**	Et_2O	30	72	63 (*R*)
2	**3a**	toluene	30	45	67 (*R*)
3	**3a**	THF	30	3	53 (*R*)
4	**3a**	Et_2O	0	<1	–
5	**3b**	Et_2O	30	75	69 (*R*)
6	**3c**	Et_2O	30	3	40 (*R*)
7	**3a'**	Et_2O	30	<1	–
8	**4**	Et_2O	30	81	36 (*S*)
9	**4**	Et_2O	15	71	42 (*S*)
10	**4**	Et_2O	0	57	66 (*S*)
11	**4**	toluene	0	8	57 (*S*)

[a] Reaction condition: **5a** (0.3 mmol), **6** (0.2 mmol), catalysts (3 mol%), solvent (2 mL), 30 ºC, 24 h. [b] Determined by HPLC.

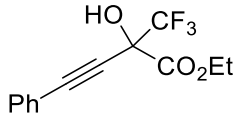
Table S2. Asymmetric alkynylation of ethyl trifluoropyruvate **6** with alkynes **5**.[a]



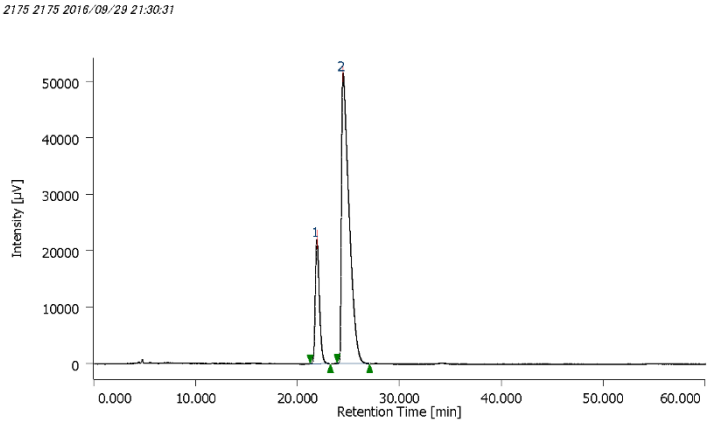
Entry	RCCH	cat	Temp, time	yield (%)	ee (%)[b]
1	4-$CF_3C_6H_4$ (**5b**)	**3a**	30, 24	58	85 (+)
2	4-$CF_3C_6H_4$ (**5b**)	**4**	-20, 48	22	46 (–)
3	4-BrC_6H_4 (**5c**)	**3a**	30, 24	72	79 (+)
4	4-BrC_6H_4 (**5c**)	**4**	-20, 48	8	79 (–)
5	4-BrC_6H_4 (**5c**)	**4**	0, 24	62	9 (–)
6	9-phenanthrene (**5d**)	**3a**	30, 24	67	68 (+)
7	9-phenanthrene (**5d**)	**4**	-20, 48	31	21 (–)
8	4-$CH_3C_6H_4$ (**5e**)	**3a**	30, 24	0	N.D.[d]
9[c]	4-$CH_3C_6H_4$ (**5e**)	**4**	0, 24	54	66 (+)
10	4-$CH_3C_6H_4$ (**5e**)	**4**	0, 45	50	69 (–)
11	4-$CH_3OC_6H_4$ (**5f**)	**3a**	30, 24	0	N.D.[d]
12[c]	4-$CH_3OC_6H_4$ (5**f**)	**4**	0, 24 h	64	75 (+)
13	4-$CH_3OC_6H_4$ (**5f**)	**4**	0, 24 h	23	57 (–)

[a] Reaction condition: **5** (0.3 mmol), **6** (0.3 mmol), catalysts (3 mol%), Et_2O (2 mL), 30 ºC, 24 h. [b] Determined by HPLC. [c] Pretreatment of **4** with **5e, f** at room temperature for 12 h before addition of **6**. [d] Not determined.

Ethyl 2-hydroxy-4-phenyl-2-(trifluoromethyl)but-3-ynoate (7a)[S2]

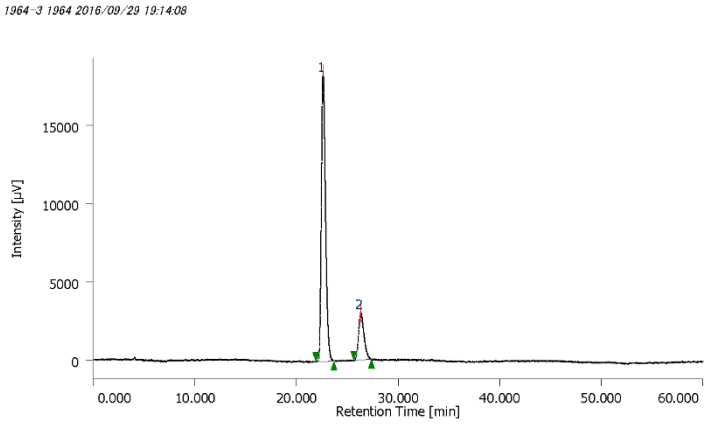


^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 1.40 (t, J = 7.2 Hz, 3H), 4.31 (bs, 1H), 4.38-4.55 (m, 2H), 7.31-7.42 (m,3H), 7.49-7.53 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, rt): δ 13.8, 65.1, 71.7 (q, J_{CF} = 34 Hz), 79.7, 87.2, 120.6 121.7 (J_{CF} = 284 Hz), 128.4, 129.6, 132.2, 166.5. ^{19}F NMR (162 MHz, $CDCl_3$, rt): δ -79.1. HRMS (FAB, m/z) calcd for $C_{13}H_{11}F_3O_3$ 273.0739 [M+H$^+$], found 273.0736.



#	tR [min]	area [μV·sec]	area%
1	21.917	617142	18.891
2	24.480	2649701	81.109

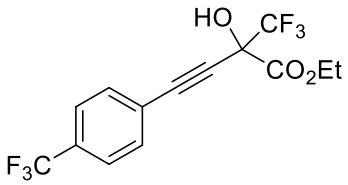
Figure S2. HPLC chart (Daicel CHIRLPAK AD–H, hexane:*i*PrOH = 99:1, 1.0 mL/min, 271 nm) of **7a** (Table 1, entry 1). $[\alpha]_D^{26}$ = –32.1 (c 1.0, $CHCl_3$). (lit.[S2] $[\alpha]_D^{29}$ = –44.6 (c = 1.01, $CHCl_3$, 99 % ee (*R*)).



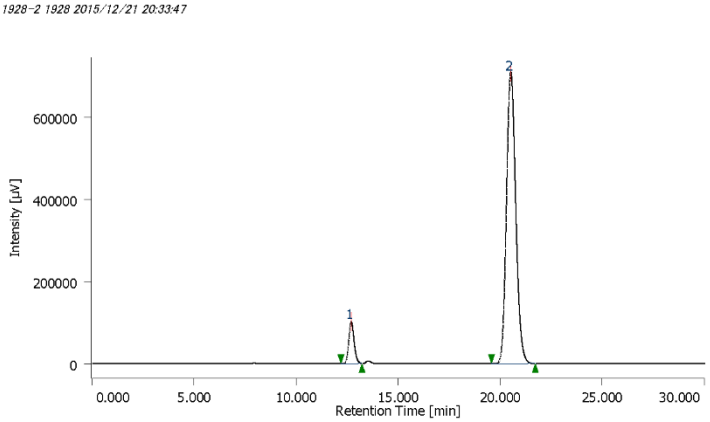
#	tR [min]	area [μV·sec]	area%
1	22.625	525999	82.883
2	26.345	108628	17.117

Figure S3. HPLC chart of **7a** (Table 1, entry 5). $[\alpha]_D^{28}$ = +33.3 (c 1.0, $CHCl_3$).

Ethyl 2-hydroxy-2-(trifluoromethyl)-4-(4-(trifluoromethyl)phenyl)but-3-ynoate (7b)

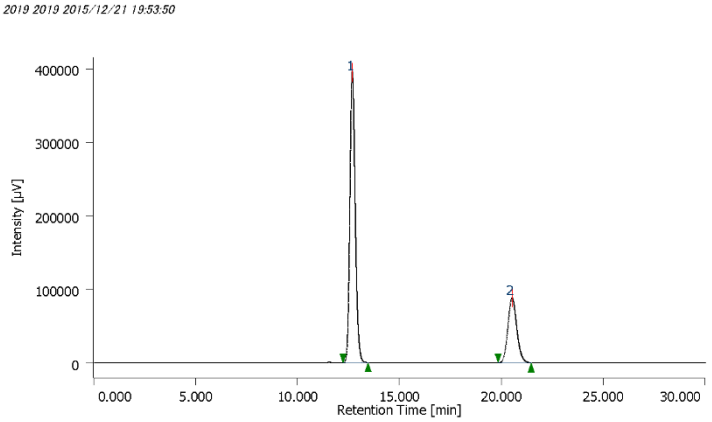


^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 1.41 (t, J = 7.2 Hz, 3H), 4.36 (s, 1H), 4.40-4.57 (m, 2H), 7.61 (s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, rt): δ 14.1, 65.3, 71.7 (q, J_{CF} = 34 Hz), 81.9, 85.5, 121.4 (J_{CF} = 284 Hz), 123.5 (J_{CF} = 270 Hz), 124.2, 125.2 (J_{CF} = 4 Hz), 131.2 (J_{CF} = 33 Hz), 132.3, 165.8. ^{19}F NMR (162 MHz, $CDCl_3$, rt): δ -63.9, -78.9. HRMS (FAB, m/z) calcd for $C_{14}H_{10}F_6O_3$ 341.0612 [M+H$^+$], found 341.0618.



#	tR [min]	area [μV·sec]	area%
1	12.710	1809257	7.491
2	20.515	22343360	92.509

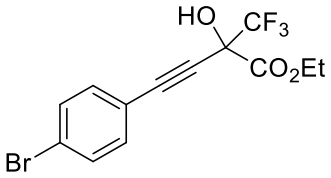
Figure S4. HPLC chart (Daicel CHIRLPAK AD–H, hexane:*i*PrOH = 95:5, 1.0 mL/min, 254 nm) of **7b** (Table 2, entry 1), $[\alpha]_D^{27}$ = –38.0 (c 0.23, $CHCl_3$).



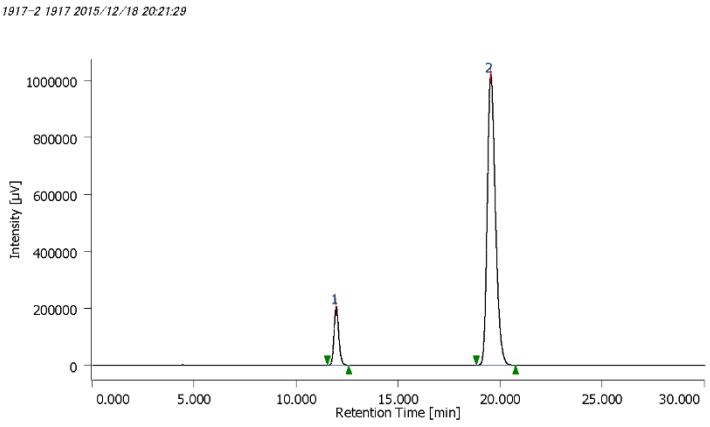
#	tR [min]	area [μV·sec]	area%
1	12.690	7205200	73.028
2	20.527	2661140	26.972

Figure S5. HPLC chart of **7b** (Table 2, entry 2), $[\alpha]_D^{24}$ = +22.8 (c 1.1, $CHCl_3$).

Ethyl 4-(4-bromophenyl)-2-hydroxy-2-(trifluoromethyl)but-3-ynoate (7c) [S2]

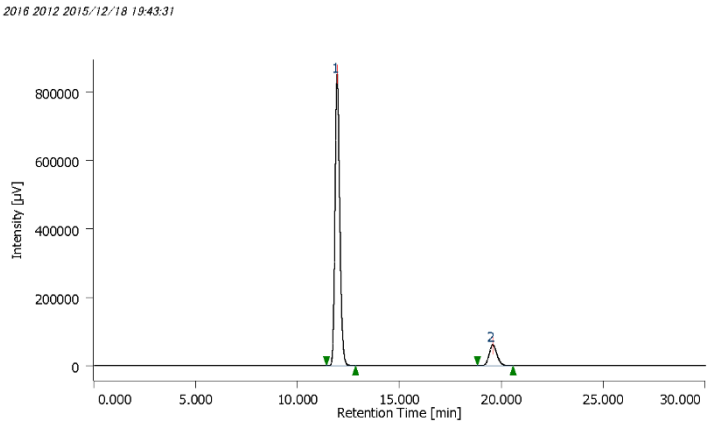


^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 1.40 (t, J = 7.2 Hz, 3H), 4.33 (bs, 1H), 4.39-4.56 (m, 2H), 7.34-7.38 (m,2H), 7.46-7.50 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, rt): δ 14.0, 65.2, 71.7 (q, J_{CF} = 34 Hz), 80.7, 86.0, 115.8, 119.3, 121.4 (J_{CF} = 284 Hz), 124.0 131.5, 133.3, 165.9. ^{19}F NMR (162 MHz, $CDCl_3$, rt): δ -78.9. HRMS (FAB, m/z) calcd for $C_{13}H_{16}BrF_3O_3$ 350.9844 [M+H$^+$], found 350.9847.



#	tR [min]	area [μV·sec]	area%
1	11.967	3293534	10.415
2	19.542	28330947	89.585

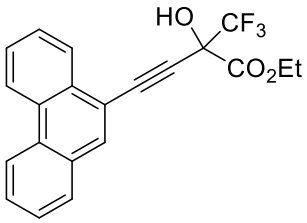
Figure S6. HPLC chart (Daicel CHIRLPAK AD–H, hexane:*i*PrOH = 99:1, 1.0 mL/min, 254 nm) of **7c** (Table 2, entry3), $[\alpha]_D^{26}$ = –34.4 (c 1.1, $CHCl_3$).



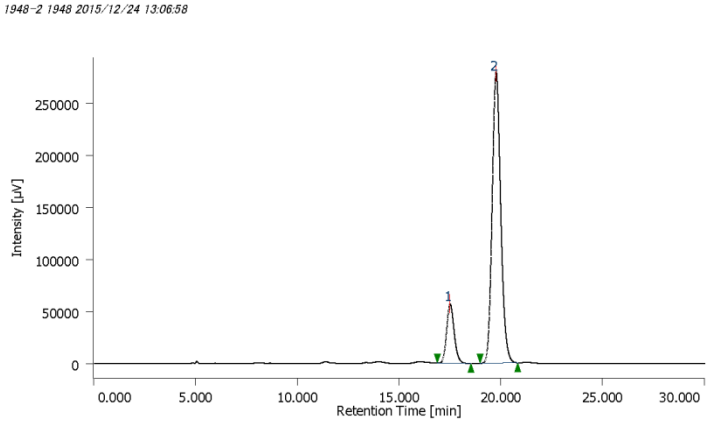
#	tR [min]	area [μV·sec]	area%
1	11.942	13756026	89.288
2	19.583	1650371	10.712

Figure S7. HPLC chart of **7c** (Table 2, entry 4), $[\alpha]_D^{17}$ = +37.2 (c 0.51, $CHCl_3$).

Ethyl 2-hydroxy-4-(phenanthren-9-yl)-2-(trifluoromethyl)but-3-ynoate (7d)

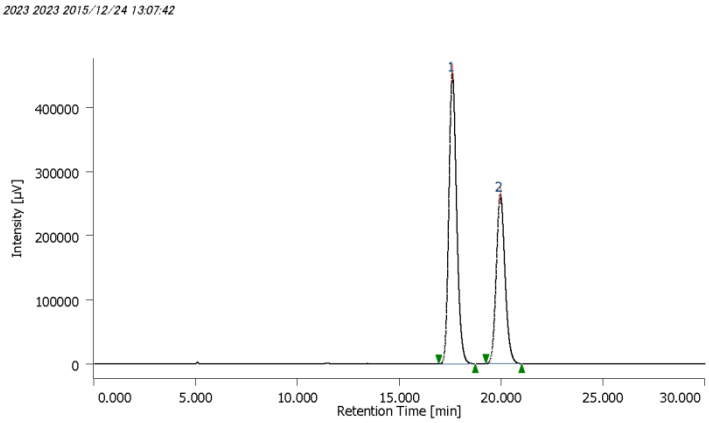


^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 1.48 (t, J = 7.1 Hz, 3H), 4.50 (s, 1H), 4.50-4.59 (m, 2H), 7.58-7.73 (m, 4H), 7.83-7.86 (m, 1H), 8.07 (s, 1H), 8.34-8.37 (m, 1H), 8.61-8.68 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, rt): δ 14.1, 65.2, 72.0 (q, J_{CF} = 34 Hz), 83.9, 85.8, 116.8, 121.7 (J_{CF} = 284 Hz), 122.4, 122.6, 126.2, 126.9, 127.06, 127.08, 128.0, 128.6, 129.7, 130.4, 130.48, 130.52, 133.3, 166.2. ^{19}F NMR (162 MHz, $CDCl_3$, rt): δ -78.7. HRMS (FAB, m/z) calcd for $C_{21}H_{15}F_3O_3$ 372.0973 [M^+], found 372.0963.



#	tR [min]	area [μV·sec]	area%
1	17.508	1459658	15.174
2	19.768	8159608	84.826

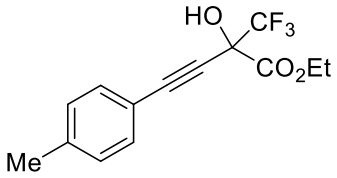
Figure S8. HPLC chart (Daicel CHIRLPAK AD–H, hexane:*i*PrOH = 95:5, 1.0 mL/min, 254 nm) of **7d** (Table 2, etnry 5), $[\alpha]_D^{27}$ = –35.9 (c 1.0, $CHCl_3$).



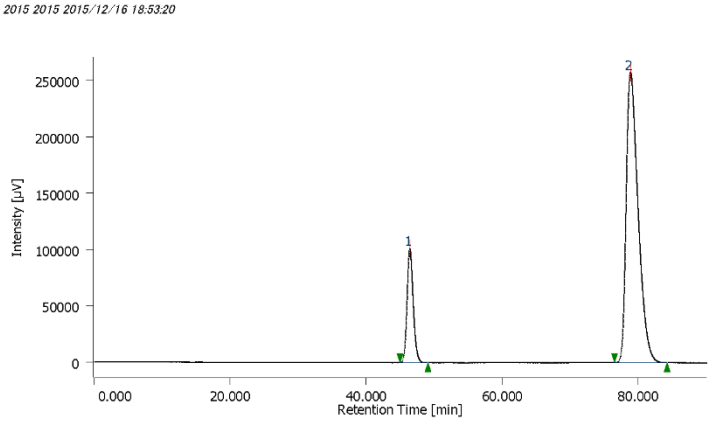
#	tR [min]	area [μV·sec]	area%
1	17.607	12027678	60.408
2	19.958	7883068	39.592

Figure S9. HPLC chart of **7d** (Table 2, entry 6), $[\alpha]_D^{24}$ = +13.1 (c 1.4, $CHCl_3$).

Ethyl 2-hydroxy-4-(p-tolyl)-2-(trifluoromethyl)but-3-ynoate (7e) [S2]

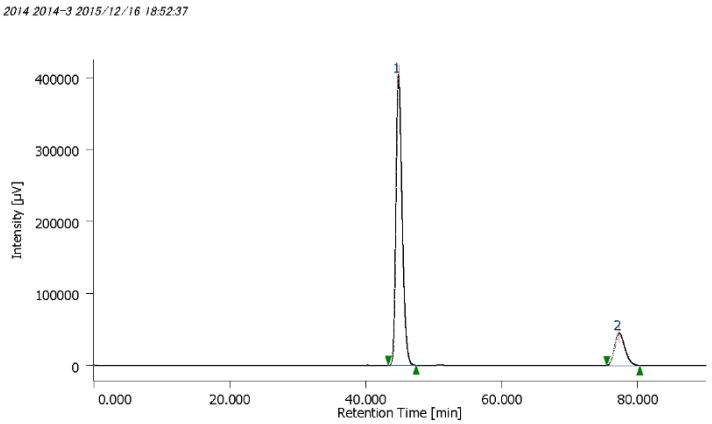


^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 1.41 (t, J = 7.2 Hz, 3H), 2.37 (s, 3H), 4.27 (s, 1H), 4.39-4.55 (m, 2H), 7.14 (d, J = 8.1 Hz, 2H), 7.39 (d, J = 8.1 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, rt): δ 14.1, 21.8, 65.0, 71.7 (q, J_{CF} = 34 Hz), 79.0, 87.3, 117.4, 121.6 (J_{CF} = 283 Hz), 128.9, 131.9, 139.8, 166.2. ^{19}F NMR (162 MHz, $CDCl_3$, rt): δ -79.0. HRMS (FAB, m/z) calcd for $C_{14}H_{13}F_3O_3$ 286.0717 [M^+], found 287.0906.



#	tR [min]	area [μV·sec]	area%
1	46.433	6306719	16.832
2	78.857	31161425	83.168

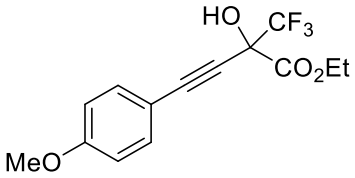
Figure S10. HPLC chart (Daicel CHIRLPAK AD–H, hexane:*i*PrOH = 99:1, 1.0 mL/min, 254 nm) of **7e** (Table 2, entry 7), $[\alpha]_D^{20}$ = –34.2 (c 1.1, $CHCl_3$).



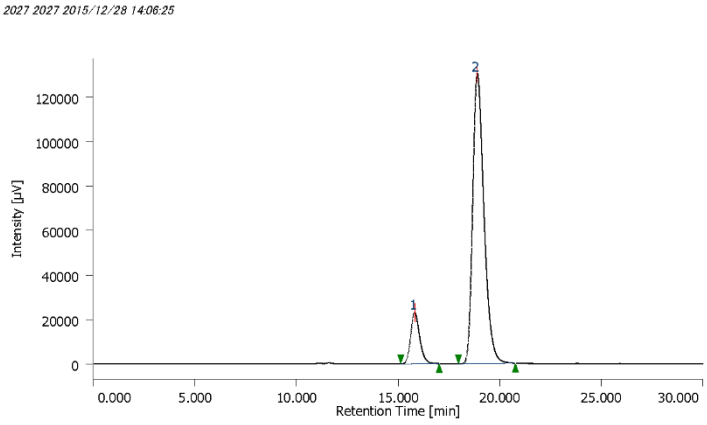
#	tR [min]	area [μV·sec]	area%
1	44.812	25515407	84.441
2	77.267	4701264	15.559

Figure S11. HPLC chart of **7e** (Table 2, entry 8), $[\alpha]_D^{20}$ = +39.5 (c 0.89, $CHCl_3$).

Ethyl 2-hydroxy-4-(4-methoxyphenyl)-2-(trifluoromethyl)but-3-ynoate (7f) [S2]

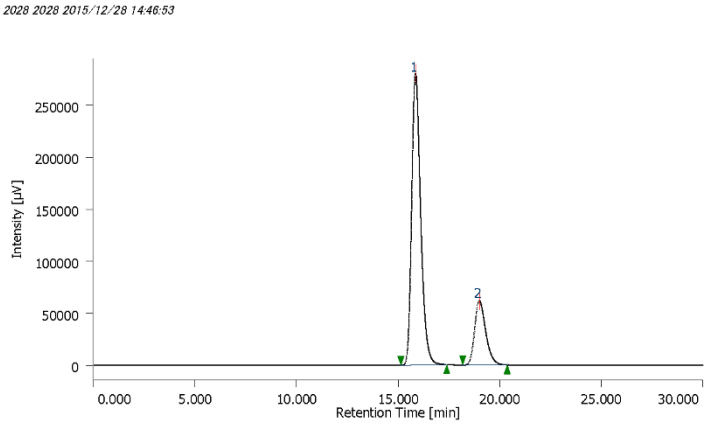


^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 1.39 (t, J = 7.1 Hz, 3H), 3.81 (s, 3H), 4.32 (br, 1H), 4.37-4.54 (m, 2H), 6.82-6.87 (m, 2H), 7.41-7.46 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, rt): δ 13.8, 55.3, 64.9, 71.7 (q, J_{CF} = 34 Hz), 78.4, 87.3, 112.6, 114.0, 121.8 (J_{CF} = 284 Hz), 133.7, 160.5, 166.6. ^{19}F NMR (162 MHz, $CDCl_3$, rt): δ -79.1. HRMS (FAB, m/z) calcd for $C_{14}H_{13}F_3O_4$ 302.0766 [M^+], found 302.0768.



#	tR [min]	area [μV·sec]	area%
1	15.823	699128	12.233
2	18.902	5016151	87.767

Figure S12. HPLC chart of **7f** (Table 2, entry 9), $[\alpha]_D^{21}$ = –37.5 (c 1.1, $CHCl_3$).



#	tR [min]	area [μV·sec]	area%
1	15.858	8589660	78.668
2	19.002	2329206	21.332

Figure S13. HPLC chart of **7f** (Table 2, entry 10), $[\alpha]_D^{21}$ = +29.9 (c 1.2, $CHCl_3$).

4. X-ray analysis of 2a, 2b, 3a, and 4.

The diffraction data of **2b** and **3a** were collected on a Brucker SMART APEX CCD diffractometer with graphite monochromated Mo$K\alpha$ radiation (λ = 0.71073 Å) and the diffraction data of **2a** and **4** were collected on a Bruker D8 QUEST CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). An empirical absorption correction was applied by using SADABS. The structure was solved by direct method and refined by full-matrix least-square on F^2 using SHELXTL. All non-hydrogen atoms were refined with aniotropic displacement parameters. All hydrogen atom were located on calculated positions and refined as rigid groups. CCDC 1507453 (**2a**), CCDC 1507454 (**2b**), CCDC 1507455 (**3a**) and CCDC 1507456 (**4**) contain the supplementary crystallographic data for this paper.

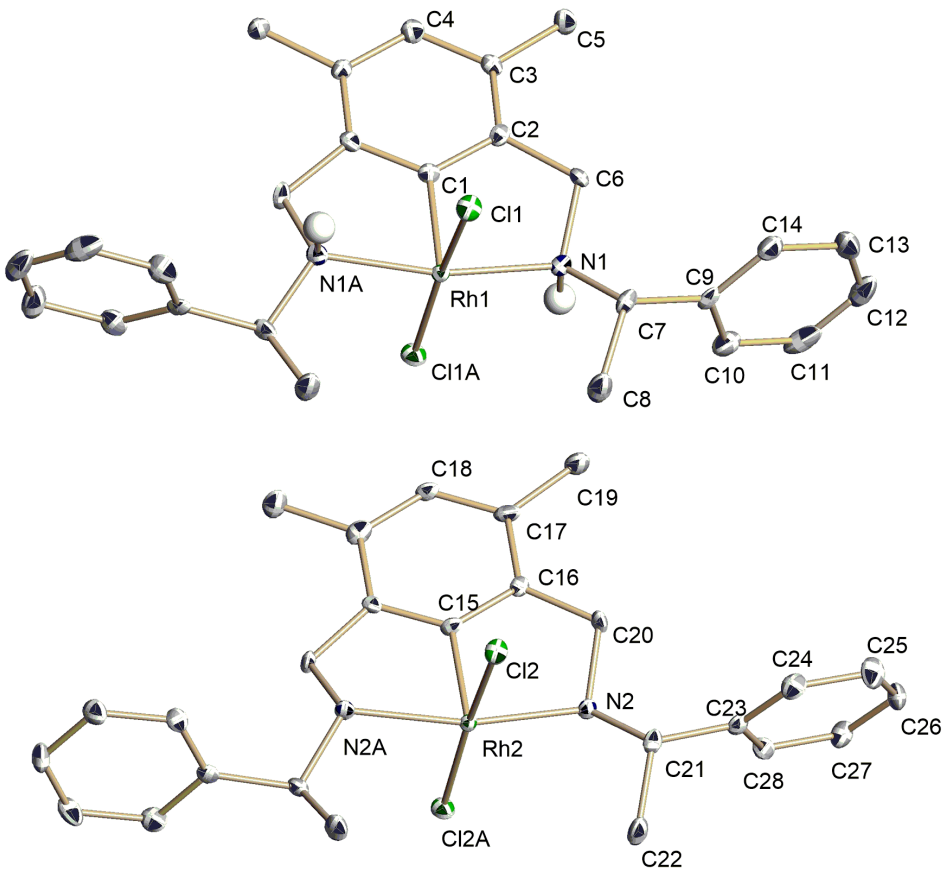


Figure S15. ORTEP diagram of **2a** with 50% probability level. Selected bond lengths (Å) and angles (º). Rh1-C1 1.909(8), Rh1-N1 2.076(4), Rh1-Cl1 2.3117(10), Rh2-C15 1.919(8), Rh2-N2 2.086(4), Rh2-Cl2 2.3092(10), N1-Rh1-N1 166.2(2), Cl1-Rh1-Cl1 172.37(7), C1-Rh1-N1 83.09(11), C1-Rh1-Cl1 93.82(4), N2-Rh2-N2 165.5(2), Cl2-Rh2-Cl2 173.05(8), C15-Rh2-N2 82.74(10), C15-Rh2-Cl2 93.47(4).

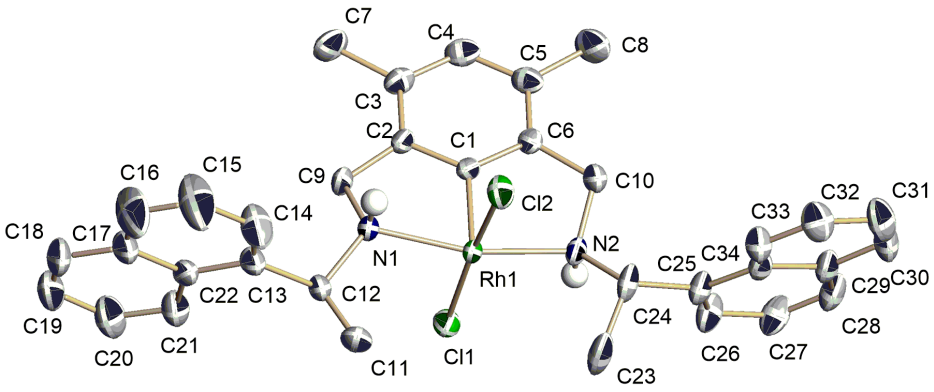


Figure S16. ORTEP diagram of **2b** with 50% probability level. Selected bond lengths (Å) and angles (º). Rh1-C1 1.902(2), Rh1-N1 2.080(2), Rh1-N2 2.0841(17), Rh1-Cl1 2.3254(7), Rh1-Cl2 2.3152(7), N1-Rh1-N2 165.69(8), Cl1-Rh1-Cl2 173.27(3), C1-Rh1-N1 82.89(9), C1-Rh1-N2 82.86(9), C1-Rh1-Cl1 93.09(8), C1-Rh1-Cl2 93.58(8).

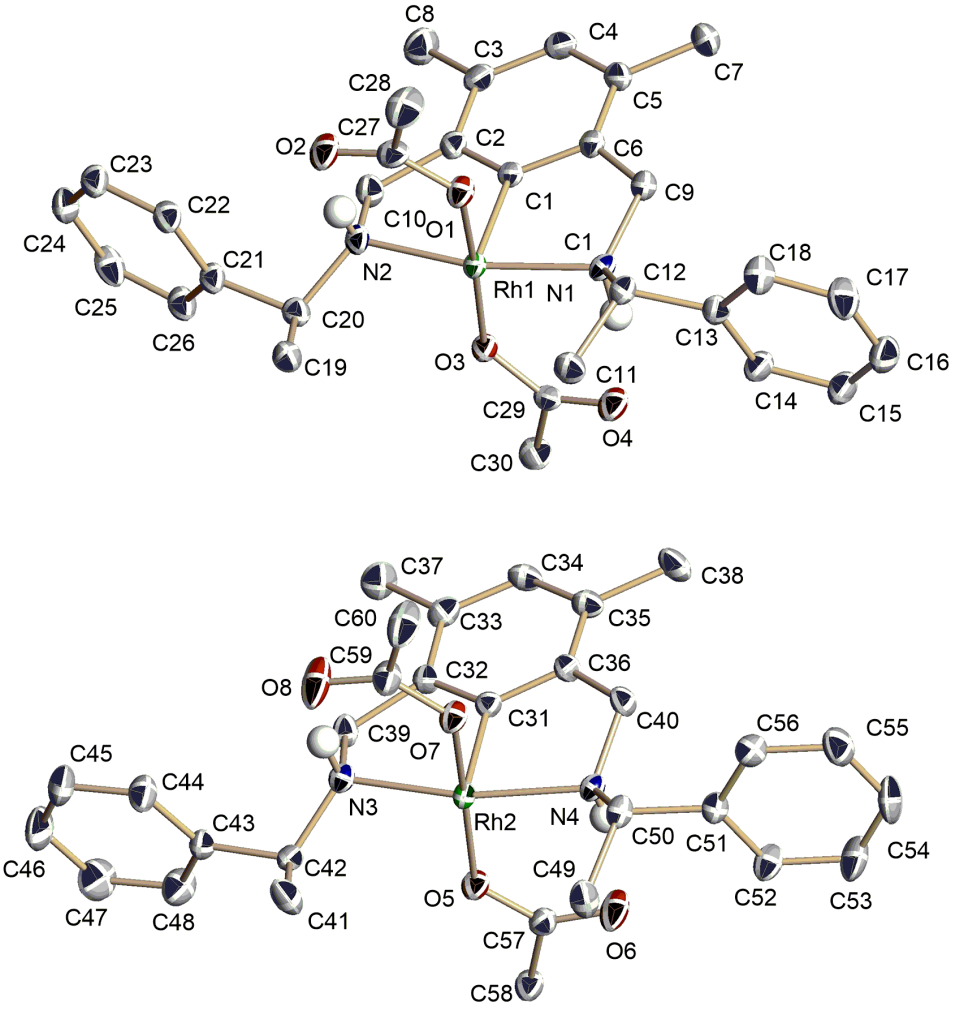


Figure S17. ORTEP diagram of **3a** with 50% probability level. Selected bond lengths (Å) and angles (º). Rh1-C1 1.904(3), Rh1-N1 2.085(3), Rh1-N2 2.072(3), Rh1-O1 2.037(2), Rh1-O3 2.030(2), Rh2-C31 1.901(3), Rh2-N3 2.090(3), Rh2-N4 2.073(3), Rh2-O5 2.037(2), Rh2-O7 2.026(2), N1-Rh1-N2 166.05(11), O1-Rh1-O3 174.80(9), C1-Rh1-N1 82.86(13), C1-Rh1-N2 83.19(13), C1-Rh1-O1 94.71(12), C1-Rh1-O3 90.48(12), N3-Rh2-N4 165.57(12), O5-Rh2-O7 174.06(10), C31-Rh2-N3 82.30(14), C31-Rh2-N4 83.28(13), C31-Rh2-O5 93.49(12), C31-Rh2-O7 92.32(12).

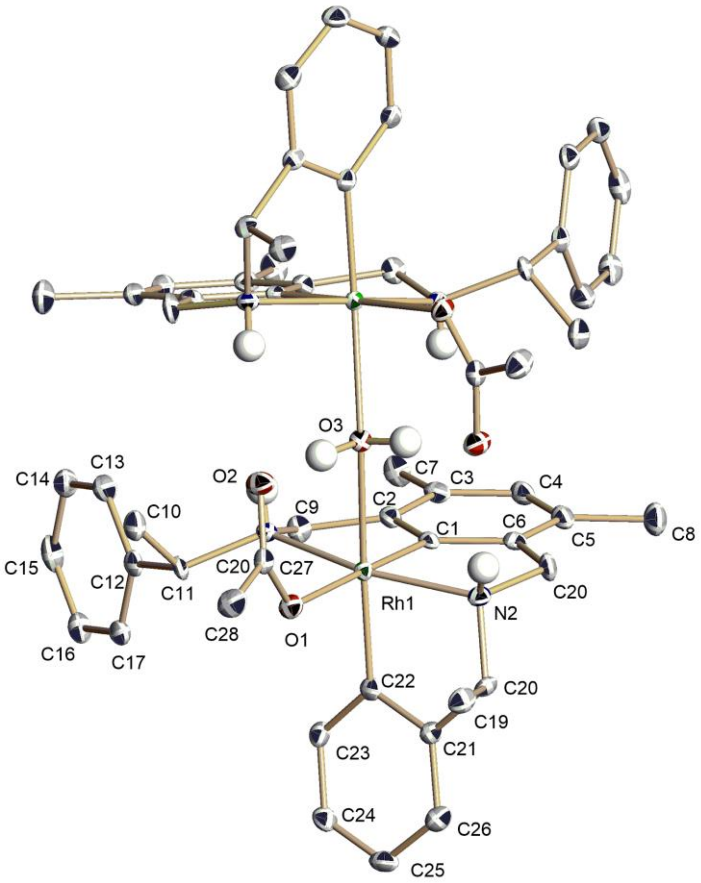


Figure S18. ORTEP diagram of **4** with 50% probability level. Selected bond lengths (Å) and angles (º). Rh1-C1 1.919(3), Rh1-C22 1.985(3), Rh1-N1 2.138(3), Rh1-N2 2.104(3), Rh1-O1 2.234(2), Rh1-O3 2.2807(6), N1-Rh1-N2 163.94(10), C1-Rh1-O1 178.12(10), C22-Rh1-O3 172.26(12), Rh1-O3-Rh1 159.76(15).

Table S3. Crystallographic Data for complexes **2a**, **2b**, **3a** and **4**.

	2a	**2b**
Empirical formula	$C_{26}H_{31}Cl_2N_2Rh$	$C_{34}H_{35}Cl_2N_2Rh$
Formula weight	545.34	645.45
Temperature, K	93	153
Crystal system	Monoclinic	Monoclinic
Space group	*C*2	*C*2
a, Å	16.4067(10)	20.2556(16)
b, Å	17.1103(11)	12.2123(10)
c, Å	10.8096(7)	13.0390(11)
α, deg		
β, deg	127.0881(14)	111.6700(10)
γ, deg		
V, $Å^3$	2420.7(3)	2997.5(4)
Z	4	4
D_{calcd}, g cm^{-3}	1.496	1.430
μ(MoKα), mm^{-1}	0.942	0.774
Reflections collected	8335	11188
Independent reflections	4104 [R(int) = 0.0253]	7310 [R(int) = 0.0238]
parameters	292	364
GOF	1.290	1.045
R1 [$I>2\sigma(I)$]	0.0253	0.0280
wR2 [$I>2\sigma(I)$]	0.0761	0.0669
R1 (all data)	0.0255	0.0295
wR2 (all data)	0.0766	0.0677
Largest diff. peak and hole, $eÅ^{-3}$	0.991 and -0.856	1.029 and -0.267

Table S3. Continued.

	3a	**4**
Empirical formula	$C_{32}H_{42}N_2O_{4.50}$ Rh	$C_{28}H_{34}N_2O_{2.50}Rh$
Formula weight	629.59	541.48
Temperature, K	123	123
Crystal system	Triclinic	Orthorhombic
Space group	*P*1	$P2_12_12$
a, Å	8.797(4)	12.3574(6)
b, Å	12.138(5)	17.1055(8)
c, Å	15.509(6)	11.4148(6)
α, deg	89.798(7)	
β, deg	86.468(7)	
γ, deg	70.434(7)	
V, $Å^3$	1557.2(11)	2412.9(2)
Z	2	2
D_{calcd}, g cm^{-3}	1.343	1.488
μ(MoKα), mm^{-1}	0.587	0.738
Reflections collected	11142	16600
Independent reflections	8980 [R(int) = 0.0361]	4265 [R(int) = 0.0366]
parameters	735	319
GOF	1.042	1.370
R1 [$I>2\sigma(I)$]	0.0348	0.0210
wR2 [$I>2\sigma(I)$]	0.0900	0.0549
R1 (all data)	0.0352	0.0214
wR2 (all data)	0.0905	0.0551
Largest diff. peak and hole, $eÅ^{-3}$	1.259 and -0.470	0.472 and -0.295

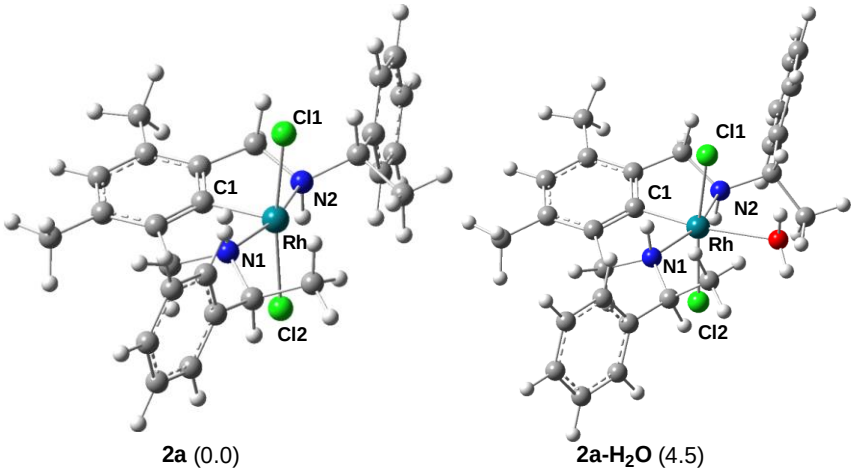
5. DFT calculation.

DFT Calculations of **2a**, **3a** and model complexes [$Me_2C_6H_2(CH_2NRR')RhCl_2$] (**2d**: R=R'=H; **2e**: R=Me, R'=H; **2f**: R=R'=Me) were performed with the Gaussian 09 program package.[S3] Geometries of the ground state were calculated by using density functional theory (DFT) with B3PW91 functional in gas phase. In all geometry optimizations, the 6-311G(d) basis set was used for C, H, N, O and Cl atoms and the SDD basis set was used for the Rh atom. We confirmed that the optimized structure of **2a** reproduced the experimental values in the solid state (Tables S4).

In the case of model complexes **2d-f**, H_2O adducts **2d-f-H_2O** with six-coordinated geometry were more stable than those of H_2O free complex **2d-f** by about 4.5-5.3 kcal/mol (Figures S20-22). In contrast, H_2O adduct **2a-H_2O** was unfavorable than H_2O free complex **2a** by about 4.5 kcal/mol (Figure S19). LUMO level of **2a** was higher than those of other model complexes **2d-f** (Figure S23).

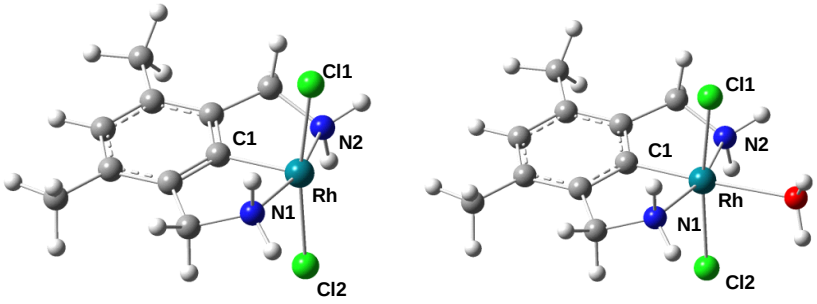
Table S4. Comparison of geometric data of **2a** between the optimized and X-ray structures.

	Optimized structure	XRD Analysis
Rh-C1	1.910	1.909(8)
Rh-N1	2.107	2.076(4)
Rh-N2	2.107	2.076(4)
Rh-Cl1	2.347	2.3117(10)
Rh-Cl2	2.347	2.3117(10)
N1-Rh-N2	164.7	166.2(2)
Cl1-Rh-Cl2	171.4	172.37(7)



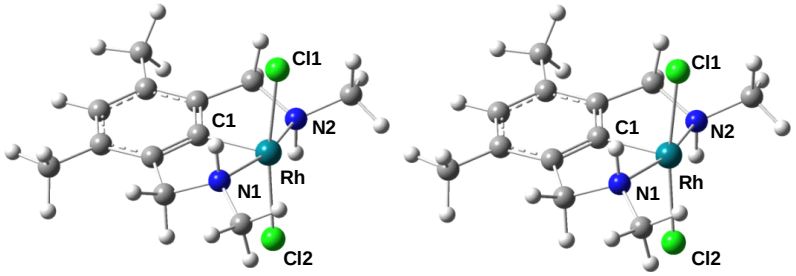
2a (0.0) **2a-H_2O** (4.5)

Figure S19. Optimized structure of **2a** and **2a-H_2O** with the Gibbs energies ΔG^0 (kcal/mol) in parentheses.



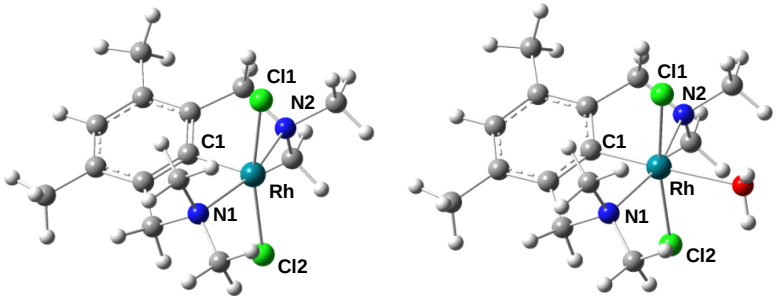
2d (0.0) **2d-H_2O** (-5.3)

Figure S20. Optimized structure of **2d** and **2d-H_2O** with the Gibbs energies ΔG^0 (kcal/mol) in parentheses.



2e (0.0) **2e-H_2O** (-4.5)

Figure S21. Optimized structure of **2e** and **2e-H_2O** with the Gibbs energies ΔG^0 (kcal/mol) in parentheses.



2f (0.0) **2f-H_2O** (-4.5)

Figure S22. Optimized structure of **2e** and **2e-H_2O** with the Gibbs energies ΔG^0 (kcal/mol) in parentheses.

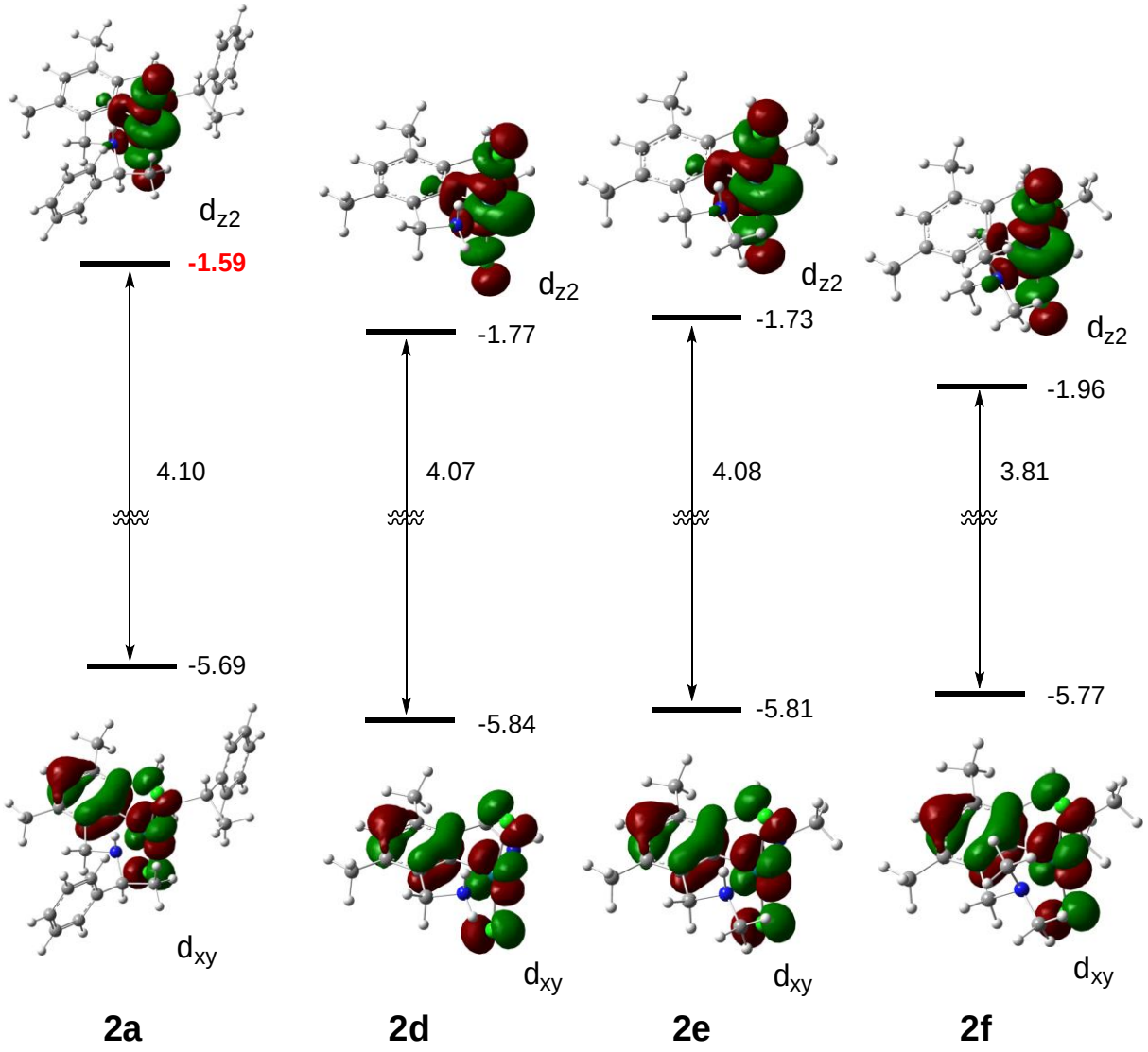


Figure S23. Molecular orbitals of HOMO and LUMO of **3a**, **3d**, **3e** and **3f**. In all complexes, HOMO and LUMO consisted of d_{xy} and d_{z2} orbitals, respectively.

Cartesian coordinates of optimized structures

2a

Rh	4.9508	13.5032	4.3147
Cl	7.2780	13.3329	4.0731
C	4.9507	15.4077	4.3146
N	5.2441	13.7844	6.3903
C	4.8788	16.0556	5.5362
C	4.7338	15.1522	6.7292
H	5.2434	15.5440	7.6153
H	3.6730	15.0338	6.9730
C	4.7580	12.7185	7.3099
H	3.6674	12.7413	7.2257
C	4.8900	17.4493	5.5296
C	4.9506	18.1337	4.3146
H	4.9506	19.2193	4.3146
H	4.8427	18.0080	6.4615
C	5.2589	11.3699	6.8147
H	4.8703	11.1473	5.8169
H	4.9199	10.5734	7.4820
H	6.3518	11.3351	6.7709
H	6.2646	13.8059	6.4310
N	4.6574	13.7843	2.2390
C	5.0226	16.0555	3.0930
C	5.1676	15.1522	1.9001
H	4.6580	15.5439	1.0139
H	6.2285	15.0338	1.6562
C	5.1435	12.7184	1.3195
H	6.2342	12.7415	1.4035
C	5.0113	17.4493	3.0995
H	5.0586	18.0079	2.1677
C	4.6430	11.3698	1.8150
H	5.0318	11.1474	2.8128
H	4.9821	10.5733	1.1478
H	3.5501	11.3348	1.8589
H	3.6369	13.8057	2.1984
Cl	2.6236	13.3327	4.5562
C	5.1716	12.9757	8.7568
H	4.7609	13.9084	9.1502
H	4.8081	12.1681	9.3975
H	6.2621	13.0105	8.8580
C	4.7297	12.9753	-0.1274
H	5.1401	13.9080	-0.5210
H	5.0932	12.1676	-0.7680
H	3.6391	13.0099	-0.2284

2a-H_2O

Rh	4.9321	13.2328	4.3198
Cl	7.2720	13.0991	3.9183
C	4.9060	15.1603	4.3313
C	5.1412	13.0858	8.8664
N	5.3677	13.5989	6.4057
C	4.8356	15.8209	5.5456
C	6.3253	13.5814	9.4209
H	7.2353	13.6153	8.8265
C	4.0261	13.5108	10.9765
H	3.1230	13.4794	11.5788
C	6.3585	14.0418	10.7316
H	7.2863	14.4270	11.1444
C	3.9948	13.0593	9.6600
H	3.0650	12.6828	9.2413
C	5.2080	14.0053	11.5153
H	5.2351	14.3613	12.5407
C	4.7322	14.9174	6.7358
H	5.1884	15.3347	7.6375
H	3.6825	14.7061	6.9648
C	5.0929	12.5574	7.4414
H	4.0723	12.2212	7.2375
C	4.8278	17.2205	5.5547
C	4.8907	17.8814	4.3235
H	4.8836	18.9693	4.3204
C	4.7407	17.9992	6.8394
H	4.7678	19.0750	6.6527
H	5.5698	17.7627	7.5157
H	3.8146	17.7828	7.3831
C	6.0612	11.3913	7.2816
H	6.0360	10.9945	6.2689
H	5.8030	10.5935	7.9813
H	7.0923	11.6916	7.4864
H	6.3759	13.7461	6.3461
C	4.7520	13.0311	-0.1773
N	4.4605	13.5911	2.2665
C	4.9722	15.8149	3.1115
C	3.6313	13.5728	-0.8147
H	2.6847	13.6456	-0.2850
C	6.0262	13.3965	-2.2085
H	6.9663	13.3230	-2.7473
C	3.7073	14.0257	-2.1264
H	2.8266	14.4455	-2.6037
C	5.9475	12.9525	-0.8913
H	6.8295	12.5398	-0.4082
C	4.9061	13.9365	-2.8294
H	4.9643	14.2861	-3.8558
C	5.0922	14.9060	1.9243
H	4.6393	15.3152	1.0173
H	6.1447	14.7013	1.7031
C	4.6858	12.5130	1.2499
H	5.6601	12.0851	1.4987
C	4.9634	17.2143	3.0958
C	5.0420	17.9878	1.8074
H	5.0016	19.0641	1.9889
H	4.2164	17.7376	1.1319
H	5.9710	17.7800	1.2653
C	3.6073	11.4455	1.3965
H	3.5751	11.0661	2.4151
H	3.8168	10.6164	0.7164
H	2.6189	11.8399	1.1421
H	3.4549	13.7441	2.3511
Cl	2.6292	13.0546	4.7714
O	5.1315	10.9077	4.0558
H	6.0929	10.8093	4.0837
H	4.7310	10.3365	4.7171

2d

Rh	4.9742	13.2483	4.3193

Cl	7.2765	13.0975	3.9304
C	4.9304	15.1606	4.3211
N	5.3455	13.5391	6.3568
C	4.9075	15.8061	5.5471
C	4.8488	14.8997	6.7454
H	5.4162	15.2754	7.6031
H	3.8093	14.7705	7.0616
H	4.9337	12.8331	6.9588
C	4.8757	17.2051	5.5552
C	4.8649	17.8686	4.3237
H	4.8387	18.9558	4.3248
C	4.8411	17.9785	6.8450
H	4.8359	19.0548	6.6616
H	5.7113	17.7579	7.4734
H	3.9496	17.7418	7.4361
H	6.3579	13.4849	6.4513
N	4.5899	13.5260	2.2819
C	4.9225	15.8089	3.0963
C	5.0255	14.9082	1.8968
H	4.4445	15.2593	1.0377
H	6.0709	14.8264	1.5843
H	5.0328	12.8403	1.6783
C	4.8862	17.2078	3.0909
C	4.8828	17.9845	1.8026
H	4.8388	19.0595	1.9883
H	4.0226	17.7255	1.1752
H	5.7833	17.7902	1.2097
H	3.5809	13.4269	2.1875
Cl	2.6814	12.9916	4.7080

2d-H_2O

Rh	4.9548	13.2212	4.3144
Cl	7.2867	13.1024	3.9506
C	4.9234	15.1446	4.3270
N	5.3363	13.5400	6.3568
C	4.9003	15.8055	5.5465
C	4.8339	14.8998	6.7449
H	5.3947	15.2727	7.6089
H	3.7924	14.7660	7.0539
H	4.9492	12.8405	6.9819
C	4.8759	17.2041	5.5570
C	4.8719	17.8666	4.3249
H	4.8518	18.9543	4.3239
C	4.8424	17.9801	6.8456
H	4.8434	19.0565	6.6612
H	5.7097	17.7560	7.4771
H	3.9482	17.7495	7.4356
H	6.3514	13.5041	6.4299
N	4.5736	13.5230	2.2878
C	4.9207	15.8035	3.1047
C	5.0188	14.9021	1.9032
H	4.4415	15.2561	1.0422
H	6.0638	14.8130	1.5903
H	5.0105	12.8250	1.6941
C	4.8922	17.2021	3.0936
C	4.8955	17.9780	1.8044
H	4.8575	19.0538	1.9884
H	4.0349	17.7236	1.1753
H	5.7955	17.7779	1.2124
H	3.5645	13.4304	2.1945
Cl	2.6388	13.0112	4.7355
O	4.9515	10.9305	4.1109
H	5.7878	10.5653	4.4169
H	4.2257	10.5688	4.6302

2e

Rh	4.9733	13.2673	4.3193
Cl	7.2815	13.1339	3.9386
C	4.9295	15.1785	4.3212
H	5.3019	12.7906	8.3384
N	5.3968	13.5674	6.3599
C	4.8979	15.8202	5.5479
C	4.8357	14.9018	6.7377
H	5.3629	15.2874	7.6187
H	3.7923	14.7295	7.0222
C	5.0347	12.5098	7.3128
H	3.9620	12.3287	7.2506
C	4.8661	17.2194	5.5563
C	4.8645	17.8823	4.3238
H	4.8387	18.9695	4.3249
C	4.8214	17.9940	6.8450
H	4.8177	19.0702	6.6605
H	5.6863	17.7737	7.4805
H	3.9251	17.7578	7.4289
H	5.5651	11.5951	7.0447
H	6.4128	13.6479	6.3267
H	4.6715	12.7829	0.2988
N	4.5379	13.5514	2.2784
C	4.9303	15.8233	3.0959
C	5.0376	14.9111	1.9046
H	4.4957	15.2736	1.0228
H	6.0888	14.7876	1.6234
C	4.9512	12.5140	1.3243
H	6.0314	12.3851	1.3873
C	4.8946	17.2224	3.0901
C	4.9020	18.0006	1.8027
H	4.8587	19.0756	1.9892
H	4.0460	17.7437	1.1688
H	5.8063	17.8050	1.2163
H	4.4656	11.5742	1.5906
H	3.5192	13.5847	2.3099
Cl	2.6739	13.0291	4.7011

2e-H_2O

Rh	4.9586	13.2341	4.3039
Cl	7.2939	13.1181	3.9493
C	4.9274	15.1579	4.3191
H	5.3022	12.8440	8.3574
N	5.3852	13.5614	6.3555
C	4.8942	15.8136	5.5404
C	4.8243	14.8976	6.7301
H	5.3495	15.2791	7.6149
H	3.7796	14.7261	7.0119
C	5.0467	12.5281	7.3388
H	3.9773	12.3229	7.2830
C	4.8668	17.2122	5.5559
C	4.8692	17.8784	4.3255
H	4.8472	18.9660	4.3278
C	4.8222	17.9846	6.8464
H	4.8234	19.0615	6.6648

H	5.6846	17.7597	7.4841
H	3.9237	17.7512	7.4286
H	5.6019	11.6174	7.1083
H	6.3999	13.6506	6.3034
H	4.6498	12.7960	0.2831
N	4.5350	13.5492	2.2674
C	4.9295	15.8193	3.0995
C	5.0332	14.9133	1.9034
H	4.4907	15.2785	1.0225
H	6.0835	14.7903	1.6177
C	4.9512	12.5243	1.3019
H	6.0352	12.4200	1.3462
C	4.8980	17.2179	3.0919
C	4.9084	17.9986	1.8056
H	4.8684	19.0737	1.9935
H	4.0519	17.7456	1.1704
H	5.8121	17.8013	1.2184
H	4.4974	11.5735	1.5774
H	3.5166	13.5815	2.2963
Cl	2.6381	13.0418	4.7187
O	4.9361	10.9344	4.1536
H	5.7736	10.5737	4.4616
H	4.2164	10.6048	4.7020

2f

Rh	4.9746	13.2377	4.3195
Cl	7.2019	13.0219	3.5897
C	4.9290	15.1492	4.3208
H	5.3568	12.7829	8.3504
N	5.5469	13.5783	6.3918
C	4.8933	15.7896	5.5483
C	4.8331	14.8601	6.7285
H	5.2677	15.2813	7.6436
H	3.7919	14.5975	6.9337
C	5.1308	12.5041	7.3129
H	4.0652	12.3161	7.2033
C	4.8611	17.1891	5.5566
C	4.8652	17.8517	4.3234
H	4.8399	18.9390	4.3245
C	4.8086	17.9660	6.8441
H	4.8204	19.0418	6.6576
H	5.6618	17.7361	7.4916
H	3.9018	17.7414	7.4160
H	5.6820	11.5951	7.0668
H	4.6143	12.7728	0.2865
N	4.3881	13.5547	2.2466
C	4.9350	15.7929	3.0948
C	5.0408	14.8695	1.9132
H	4.5878	15.2715	0.9983
H	6.0935	14.6575	1.7084
C	4.8547	12.5035	1.3232
H	5.9284	12.3674	1.4312
C	4.9006	17.1924	3.0891
C	4.9177	17.9731	1.8030
H	4.8567	19.0470	1.9914
H	4.0762	17.7058	1.1545
H	5.8340	17.7912	1.2311
H	4.3485	11.5684	1.5683
Cl	2.7592	12.9185	5.0504
C	6.9983	13.8026	6.5680
H	7.1984	14.0535	7.6176
H	7.5496	12.9069	6.2930
H	7.3272	14.6162	5.9250
C	2.9278	13.7111	2.0706
H	2.7162	13.9570	1.0220
H	2.4190	12.7894	2.3415
H	2.5613	14.5056	2.7169

2f-H_2O

Rh	4.9629	13.2081	4.2976
Cl	7.2178	13.0334	3.5744
C	4.9321	15.1327	4.3151
H	5.3274	12.8319	8.3672
N	5.5376	13.5731	6.3891
C	4.8978	15.7869	5.5376
C	4.8318	14.8618	6.7196
H	5.2695	15.2796	7.6356
H	3.7894	14.6057	6.9275
C	5.1206	12.5238	7.3337
H	4.0568	12.3262	7.2167
C	4.8670	17.1858	5.5530
C	4.8690	17.8521	4.3223
H	4.8451	18.9398	4.3251
C	4.8175	17.9603	6.8425
H	4.8348	19.0368	6.6589
H	5.6690	17.7252	7.4909
H	3.9093	17.7395	7.4141
H	5.6876	11.6134	7.1289
H	4.5988	12.7893	0.2683
N	4.3924	13.5551	2.2339
C	4.9329	15.7938	3.0951
C	5.0332	14.8785	1.9070
H	4.5709	15.2805	0.9964
H	6.0851	14.6733	1.6904
C	4.8651	12.5182	1.2983
H	5.9441	12.4115	1.3849
C	4.8995	17.1927	3.0879
C	4.9118	17.9759	1.8028
H	4.8516	19.0498	1.9928
H	4.0678	17.7100	1.1566
H	5.8256	17.7951	1.2264
H	4.3937	11.5702	1.5549
Cl	2.7234	12.9401	5.0724
O	4.9098	10.9098	4.1530
H	5.7679	10.5310	4.3686
H	4.2460	10.5981	4.7781
C	6.9890	13.7958	6.5565
H	7.1973	14.0568	7.6026
H	7.5395	12.8979	6.2859
H	7.3149	14.6017	5.9030
C	2.9308	13.6980	2.0681
H	2.7082	13.9476	1.0224
H	2.4347	12.7685	2.3365
H	2.5611	14.4852	2.7214

3a

C	-0.000010	-1.374706	-0.000152
C	1.210111	-2.013725	-0.212373
C	1.215611	-3.414155	-0.210048
C	-0.000022	-4.075321	-0.000439

C	-1.215649	-3.414189	0.209309
C	-1.210136	-2.013758	0.211931
C	2.485309	-4.189676	-0.432976
C	-2.485356	-4.189745	0.432065
C	2.382290	-1.106305	-0.469851
C	-2.382310	-1.106385	0.469596
C	2.542679	2.661926	0.097984
C	2.953447	1.312366	-0.484897
C	4.429390	1.035301	-0.261983
C	4.937938	0.838647	1.026230
C	6.294538	0.605974	1.220865
C	7.165158	0.572378	0.134509
C	6.669535	0.768625	-1.149355
C	5.309567	0.994711	-1.343125
C	-2.542698	2.661971	-0.097410
C	-2.953451	1.312284	0.485186
C	-4.429398	1.035259	0.262245
C	-4.937979	0.838920	-1.026003
C	-6.294580	0.606265	-1.220658
C	-7.165167	0.572373	-0.134285
C	-6.669511	0.768307	1.149615
C	-5.309543	0.994376	1.343402
C	-0.585469	0.577762	-2.965122
C	-0.002544	0.697380	-4.358985
C	0.585497	0.577092	2.965171
C	0.002690	0.696262	4.359119
N	2.090237	0.249329	0.081592
N	-2.090251	0.249369	-0.081551
O	0.296719	0.672227	-2.025394
O	-1.795712	0.389008	-2.815317
O	-0.296690	0.671920	2.025489
O	1.795691	0.388057	2.815289
Rh	-0.000002	0.535414	0.000038
H	3.241424	-3.951962	0.323295
H	2.930591	-3.967861	-1.409069
H	-2.305331	-5.266110	0.389799
H	-3.241429	-3.951931	-0.324216
H	-2.930693	-3.968064	1.408163
H	3.319563	-1.484658	-0.049055
H	2.534941	-0.990121	-1.548612
H	-2.534969	-0.990438	1.548381
H	-3.319583	-1.484645	0.048714
H	1.502734	2.894611	-0.155815
H	3.170982	3.456074	-0.311784
H	2.644543	2.674170	1.185708
H	2.751283	1.319938	-1.559797
H	4.270489	0.858865	1.884003
H	6.673840	0.451385	2.226787
H	8.224834	0.392306	0.289625
H	7.340188	0.741747	-2.003328
H	4.926547	1.143139	-2.349996
H	-2.644593	2.674456	-1.185128
H	-1.502746	2.894597	0.156412
H	-3.170988	3.456029	0.312553
H	-2.751264	1.319624	1.560083
H	-4.270556	0.859370	-1.883790
H	-6.673908	0.451923	-2.226607
H	-8.224844	0.392316	-0.289415
H	-7.340138	0.741197	2.003601
H	-4.926496	1.142556	2.350299
H	0.417432	-0.270535	-4.649847
H	0.804641	1.430912	-4.389215
H	-0.782521	0.961397	-5.072645
H	-0.414978	-0.272470	4.650606
H	-0.806058	1.428052	4.389290
H	0.782344	0.962225	5.072422
H	-0.000026	-5.163179	-0.000553
H	2.305290	-5.266048	-0.390847
H	-2.202973	0.222984	-1.109159
H	2.202940	0.222697	1.109197

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6. References.

[S1] M. Gerisch, J. R. Krumper, R. G. Bergman, T. D. Tilley *Organometallics* **2003**, *22*, 47.

[S2] K. Aikawa, Y. Hioki, K. Mikami, *Org. Lett.* **2010**, *12*, 5716.

[S3] (a) Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2013**.

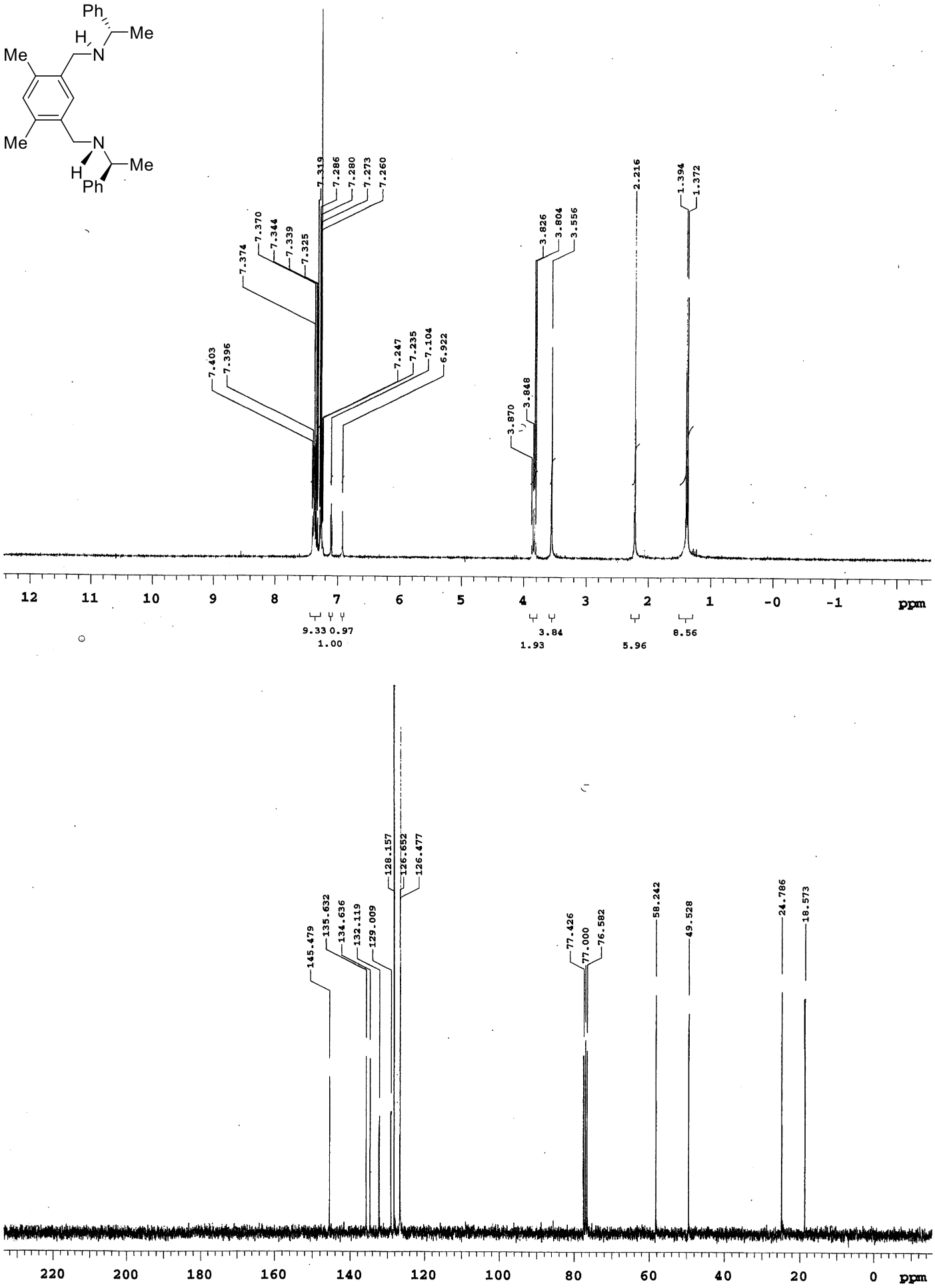


Fig S 24. ^{1}H and ^{13}C NMR spectra of **2a**.

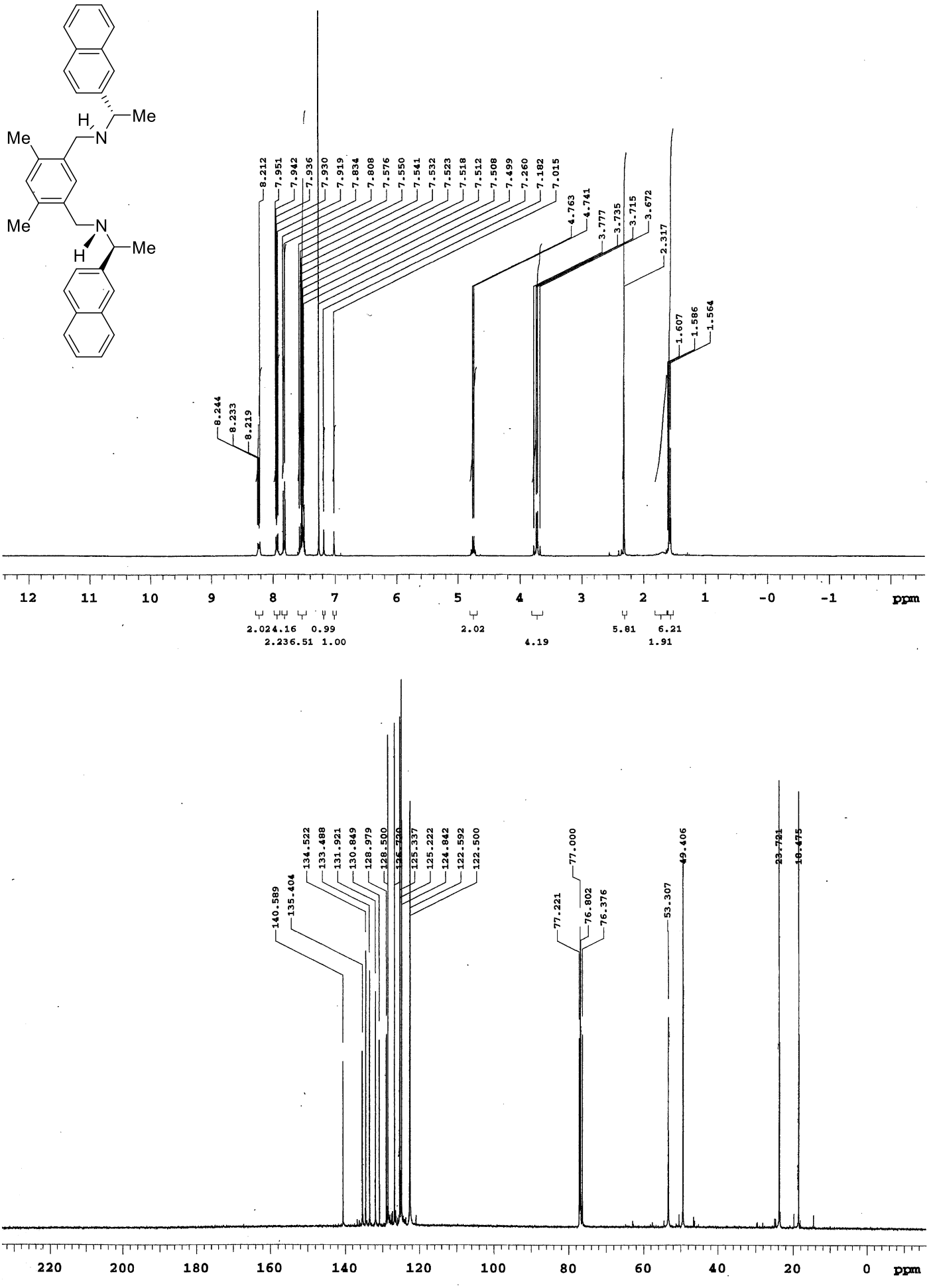


Fig S 25. ^{1}H and ^{13}C NMR spectra of **2b**.

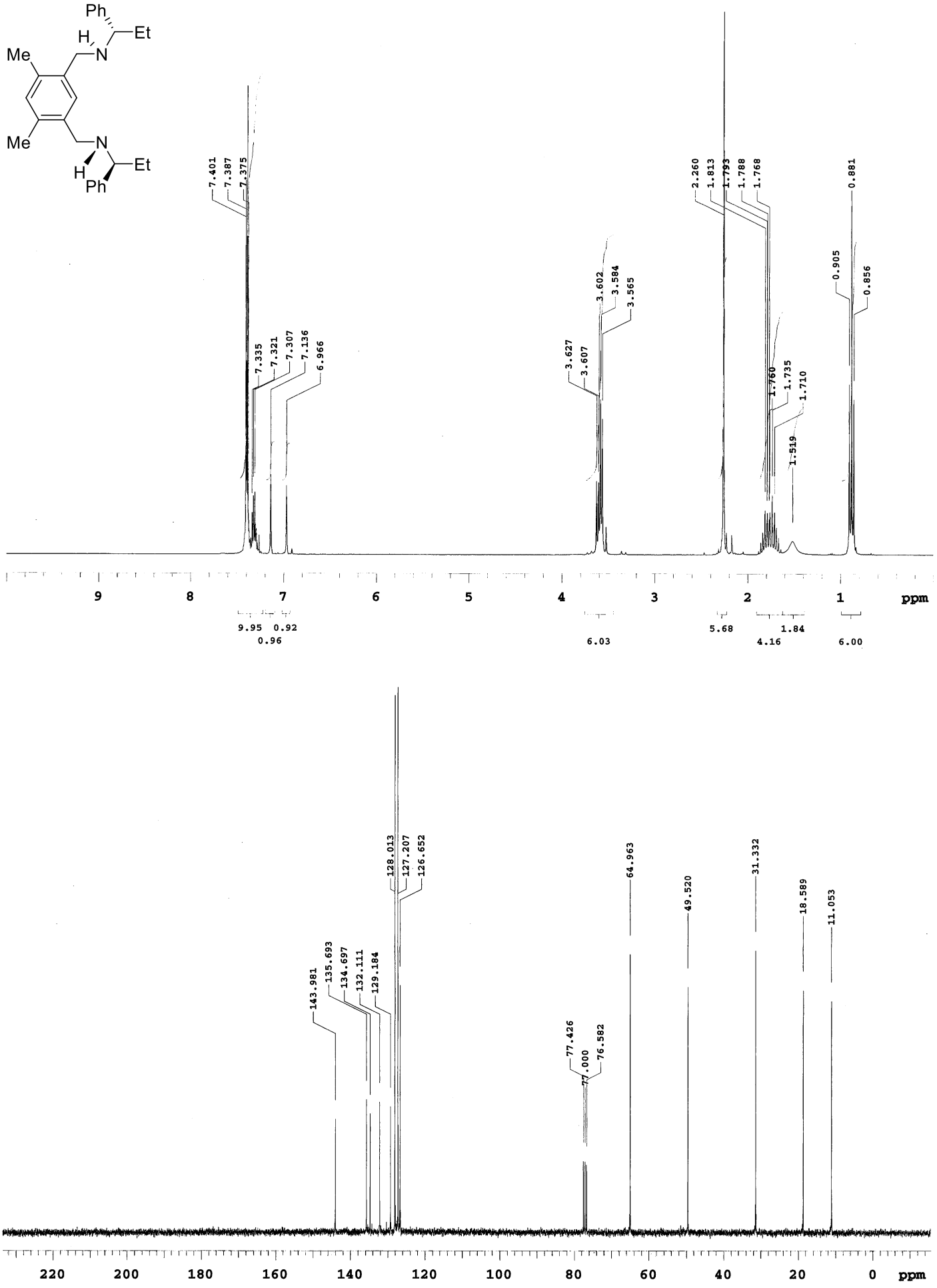


Fig S 26. ^{1}H and ^{13}C NMR spectra of **2c**.

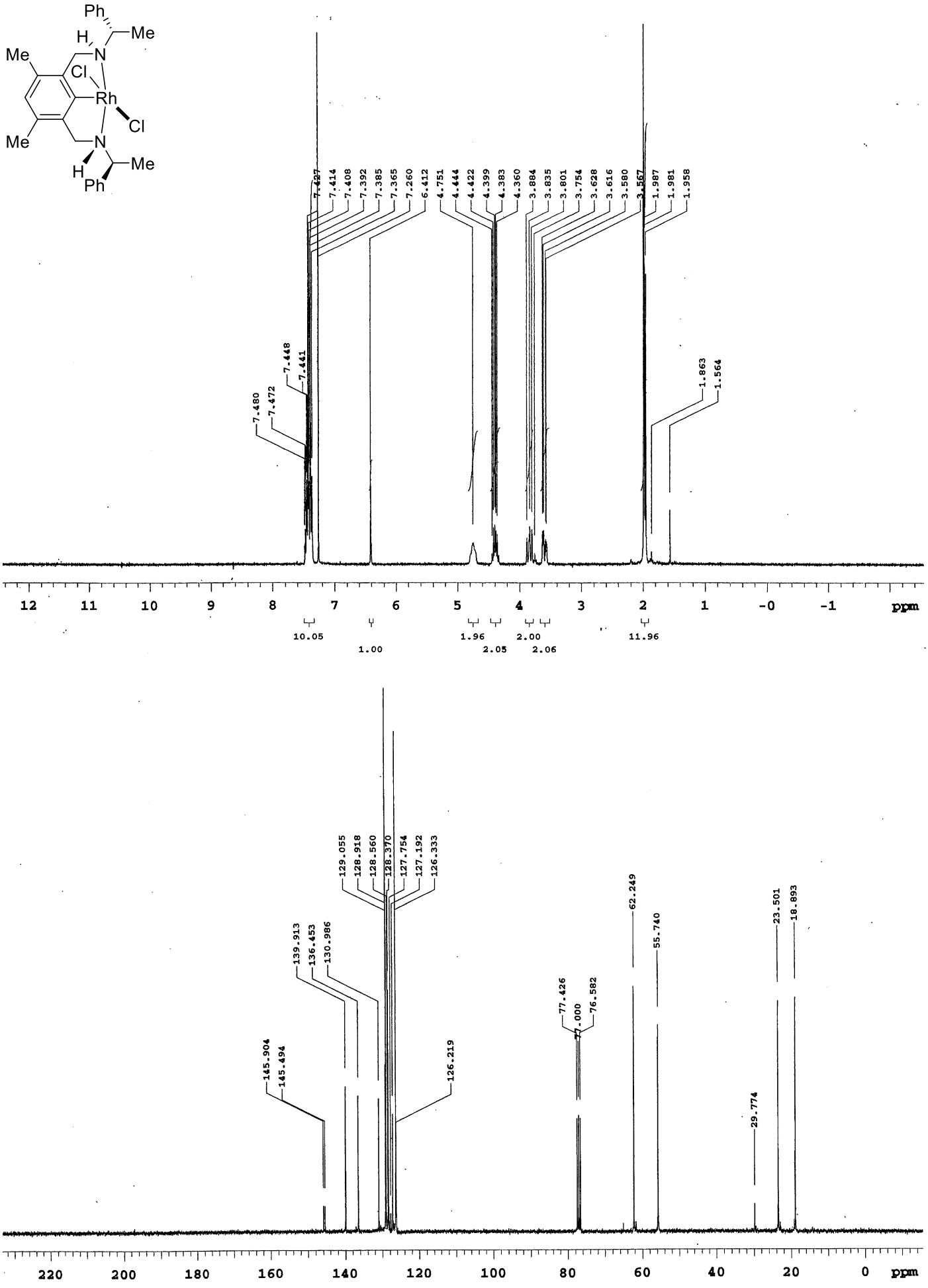


Fig S 27. ^{1}H and ^{13}C NMR spectra of **3a**.

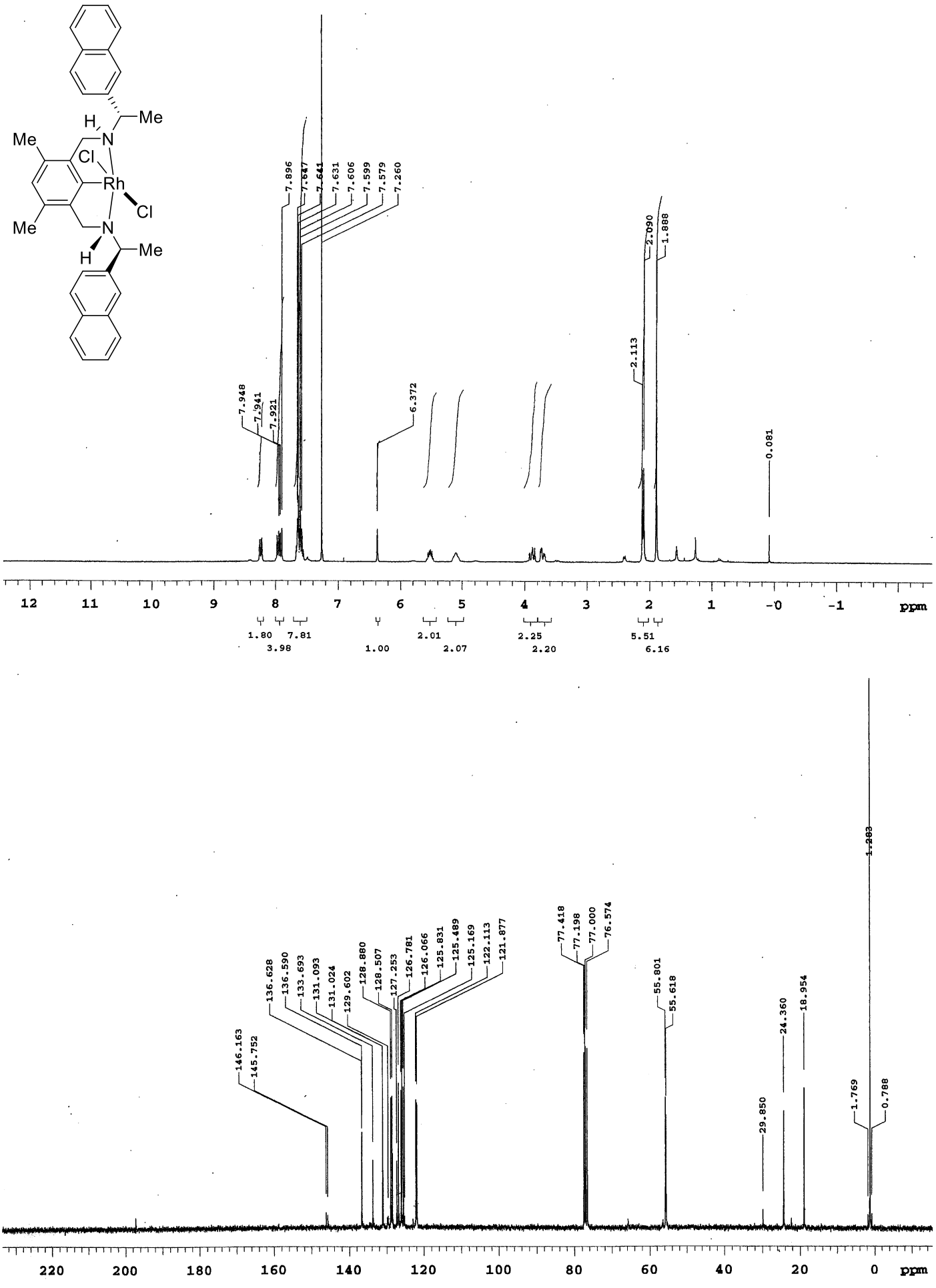


Fig S 28. ^{1}H and ^{13}C NMR spectra of **3b**.

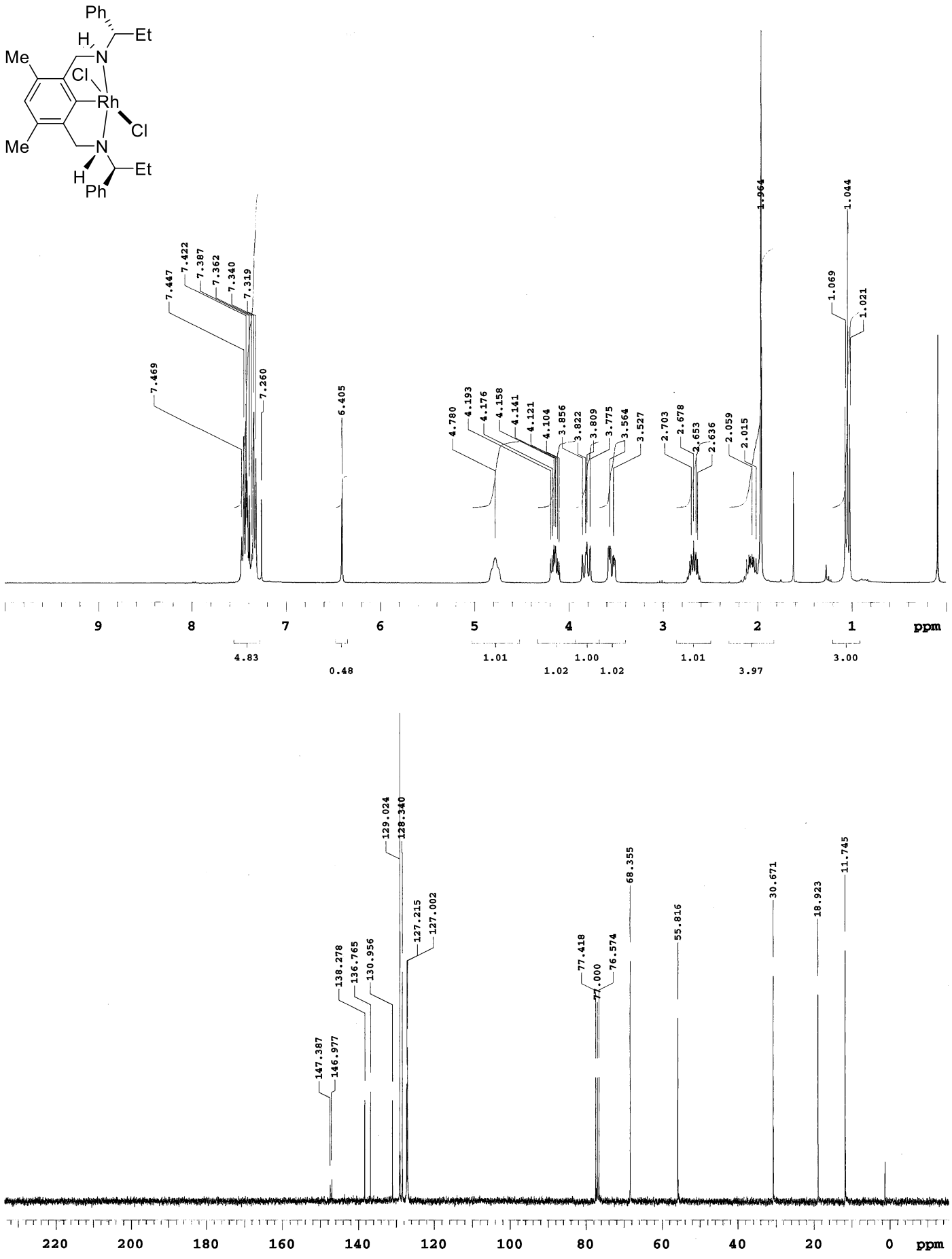


Fig S 29. ^{1}H and ^{13}C NMR spectra of **3c**.

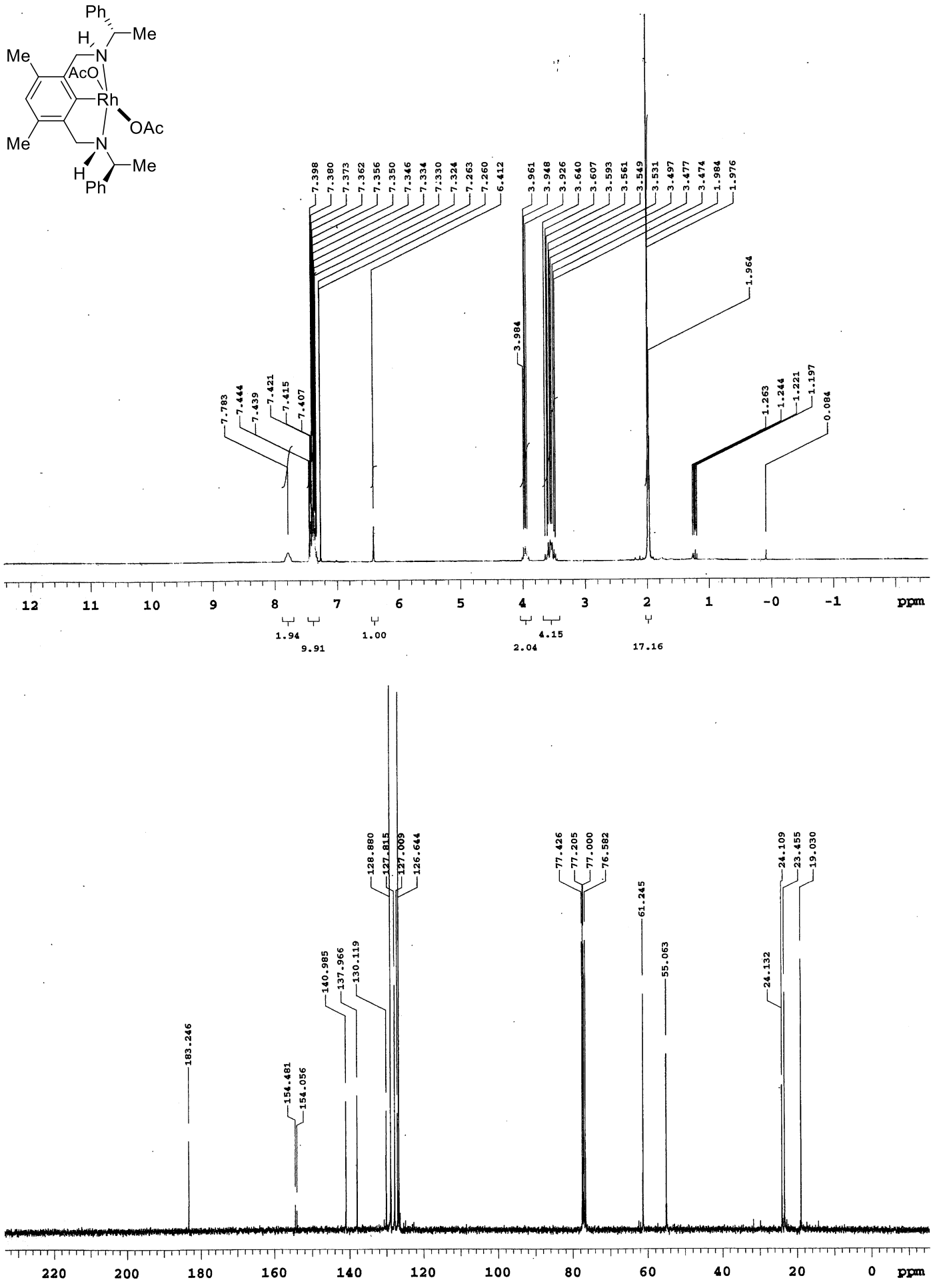


Fig S 30. ^{1}H and ^{13}C NMR spectra of **4a**.

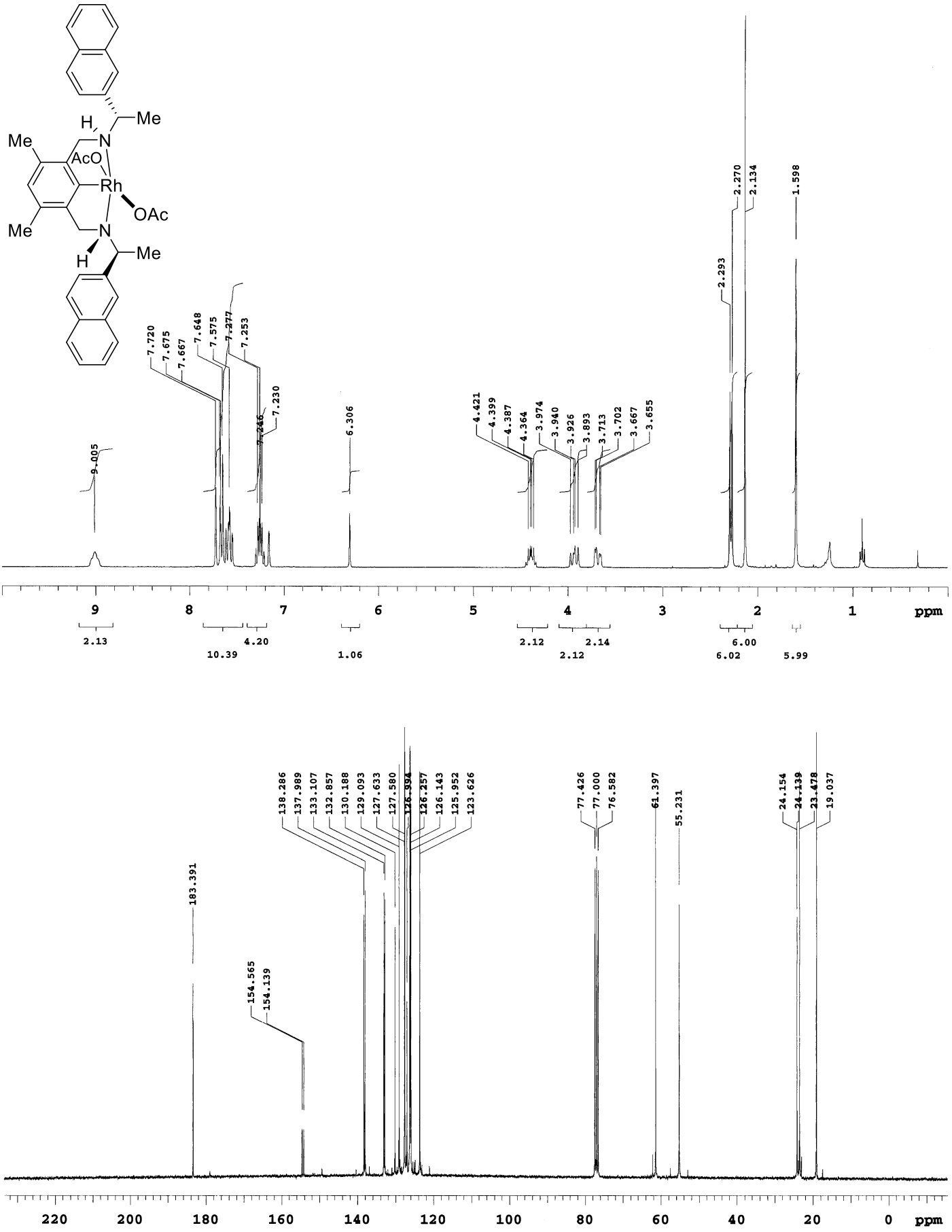


Fig S 31. ^{1}H and ^{13}C NMR spectra of **4b**.

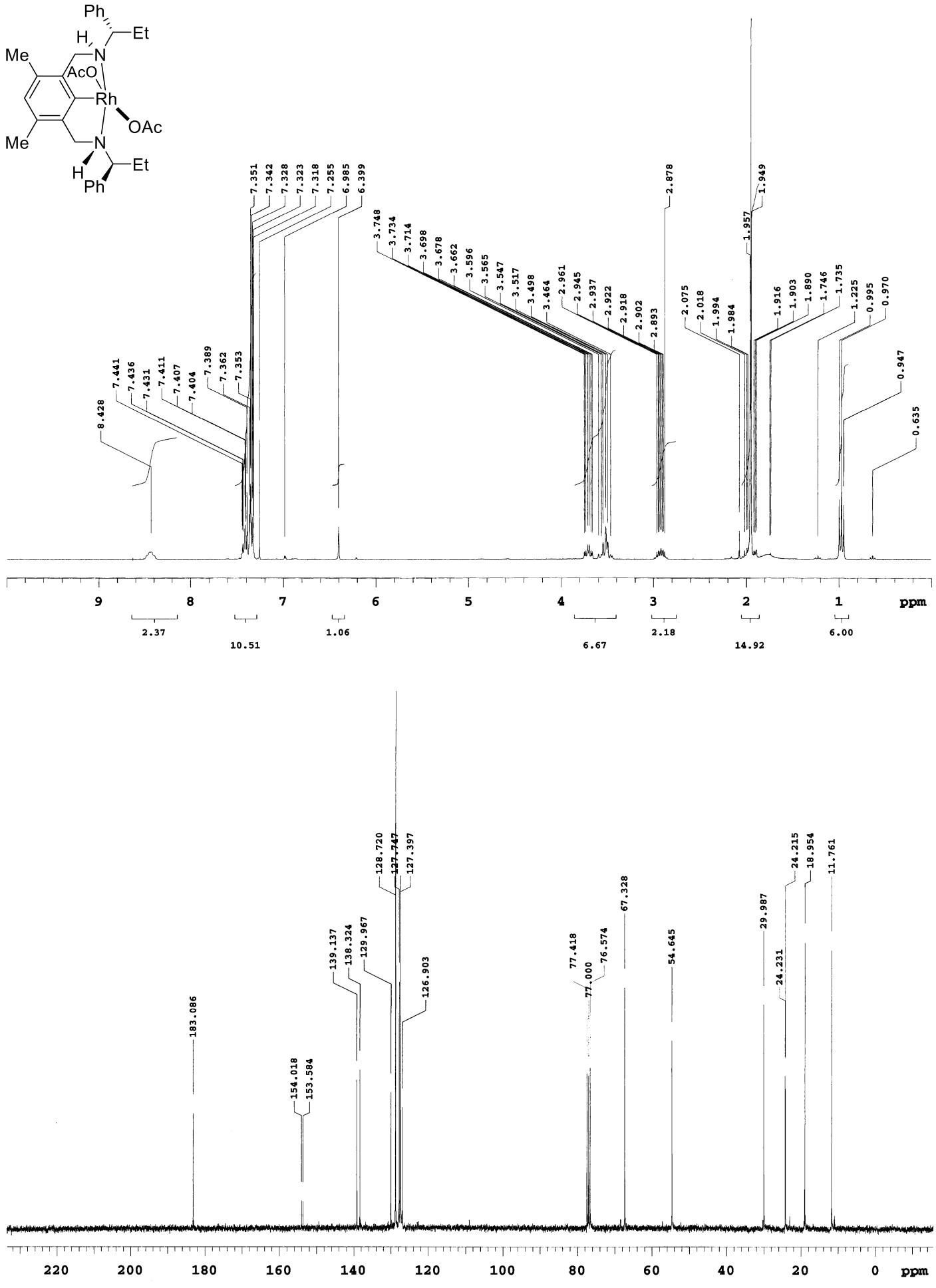


Fig S 32. ^{1}H and ^{13}C NMR spectra of **4c**.

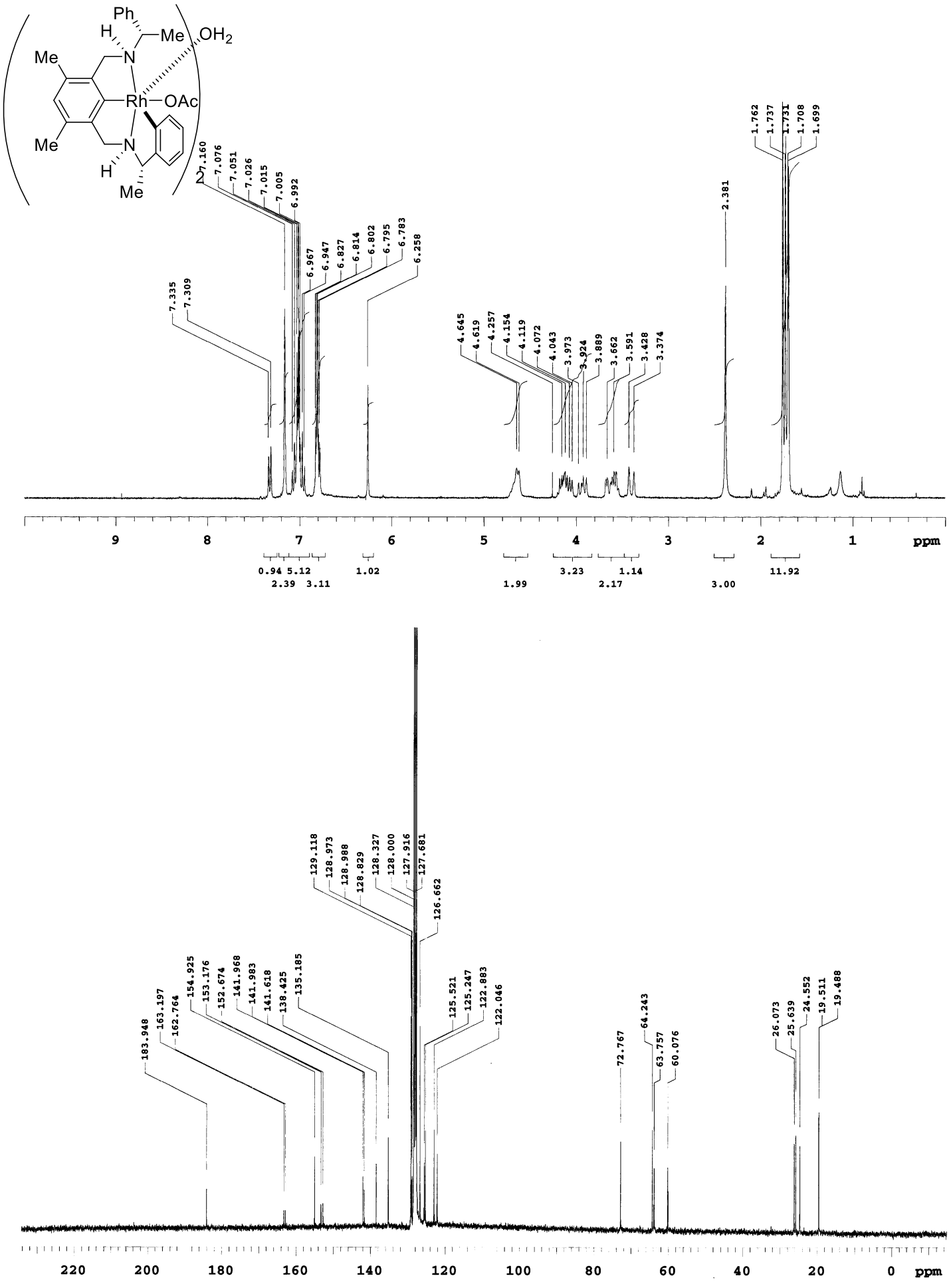


Fig S 33. ^{1}H and ^{13}C NMR spectra of **5**.

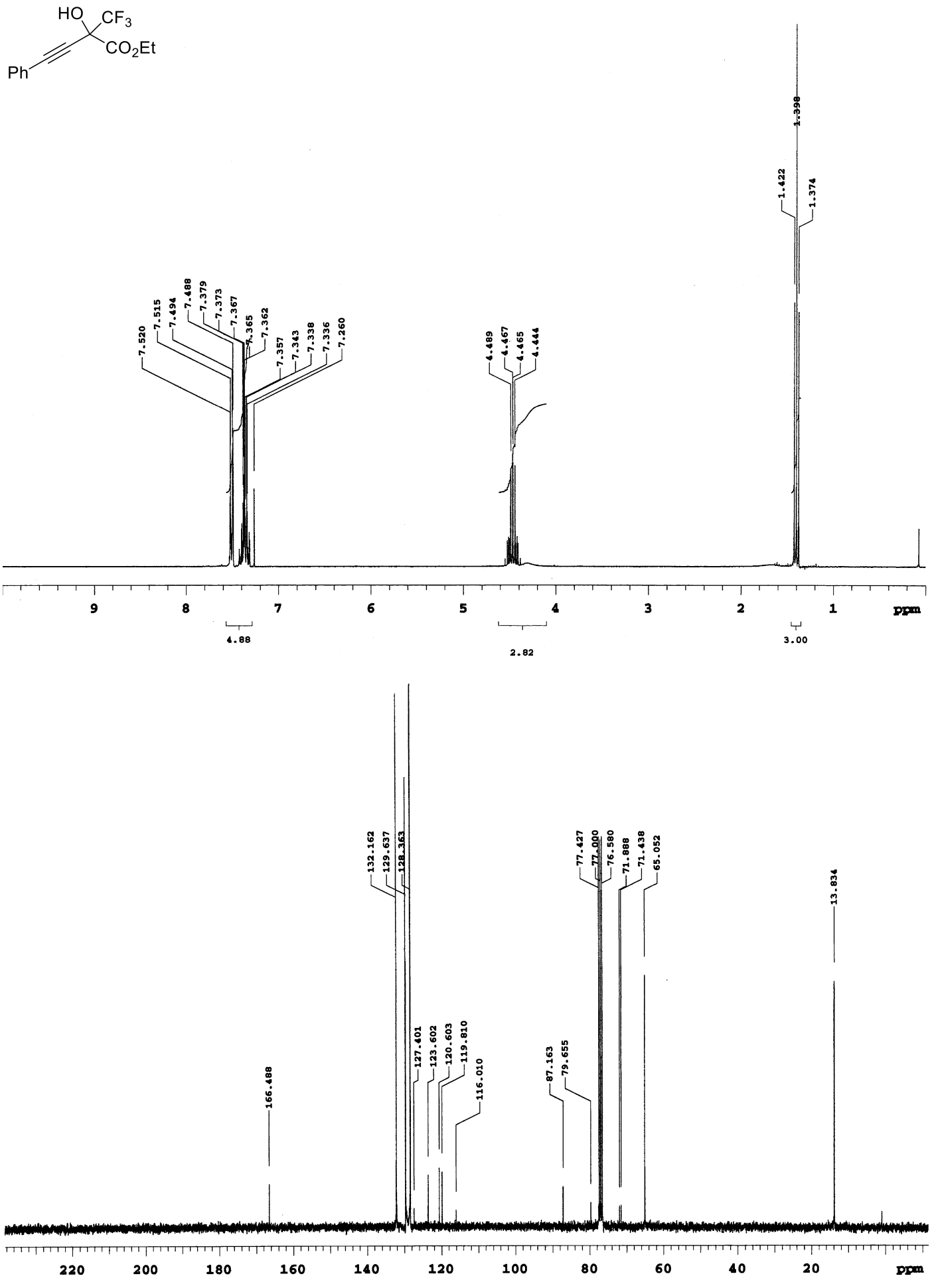


Fig S 34. ^{1}H and ^{13}C NMR spectra of **7a**.

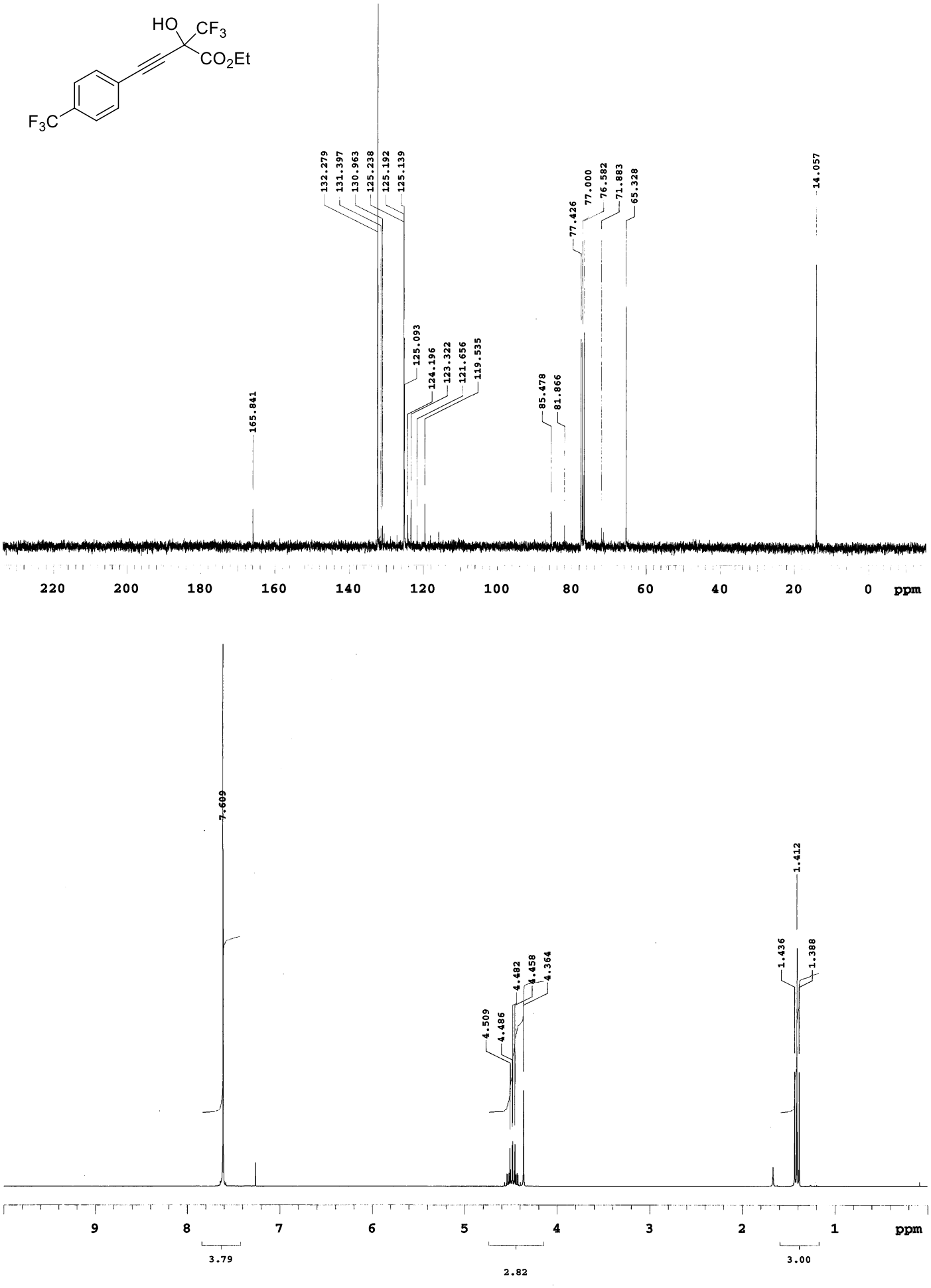
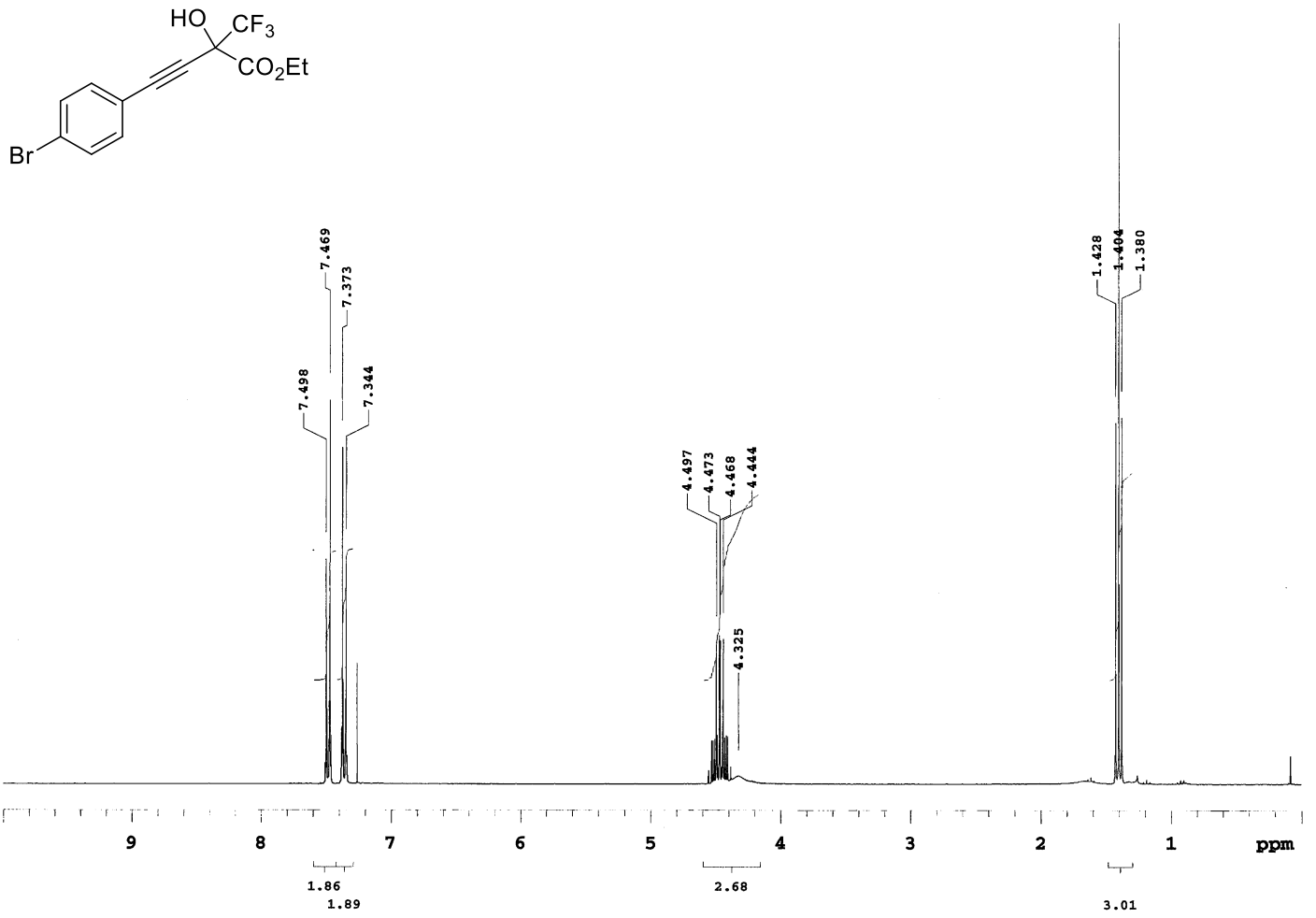


Fig S 35. ^{1}H and ^{13}C NMR spectra of **7b**.



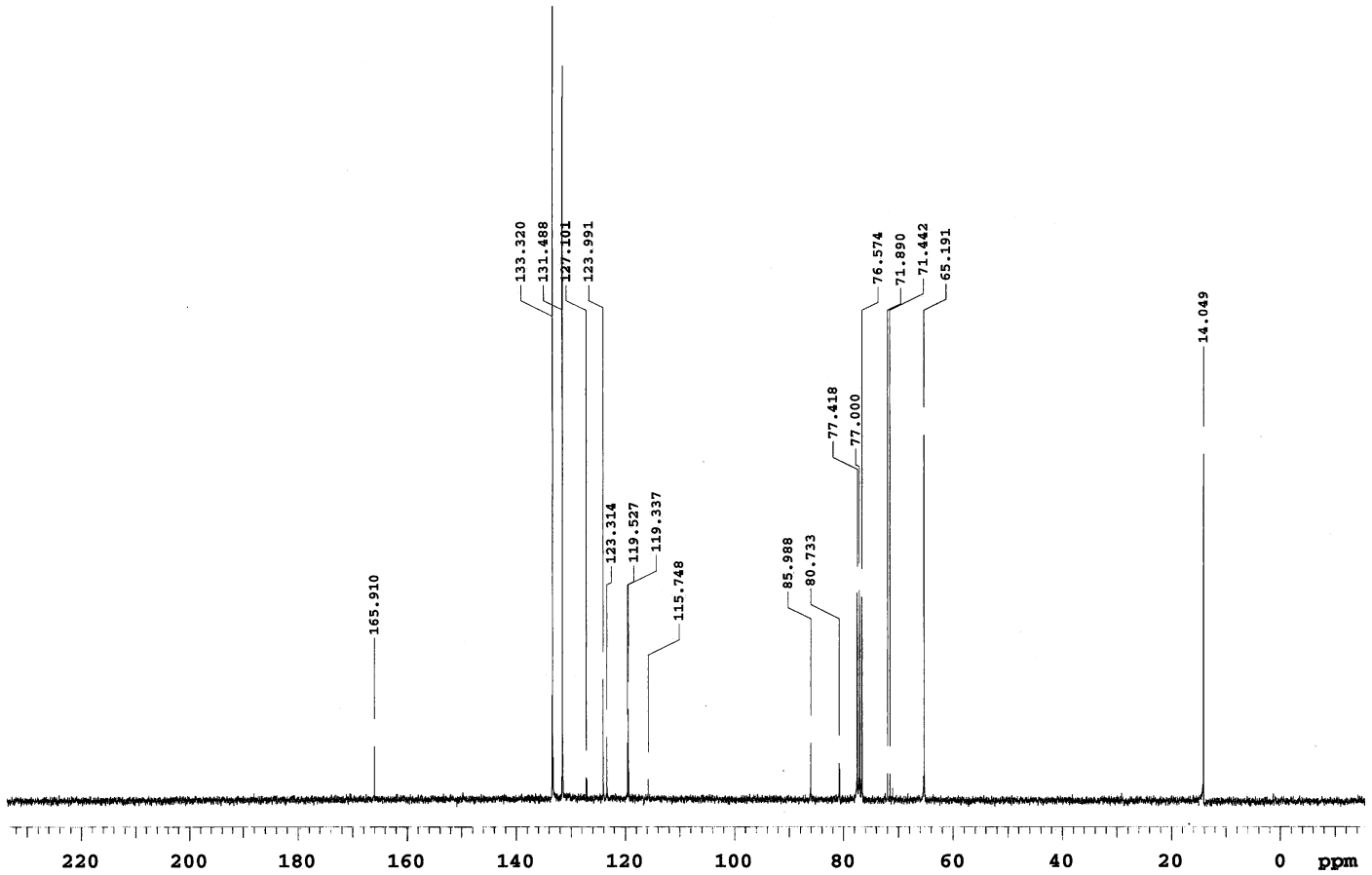


Fig S 36. ^{1}H and ^{13}C NMR spectra of **7c**.

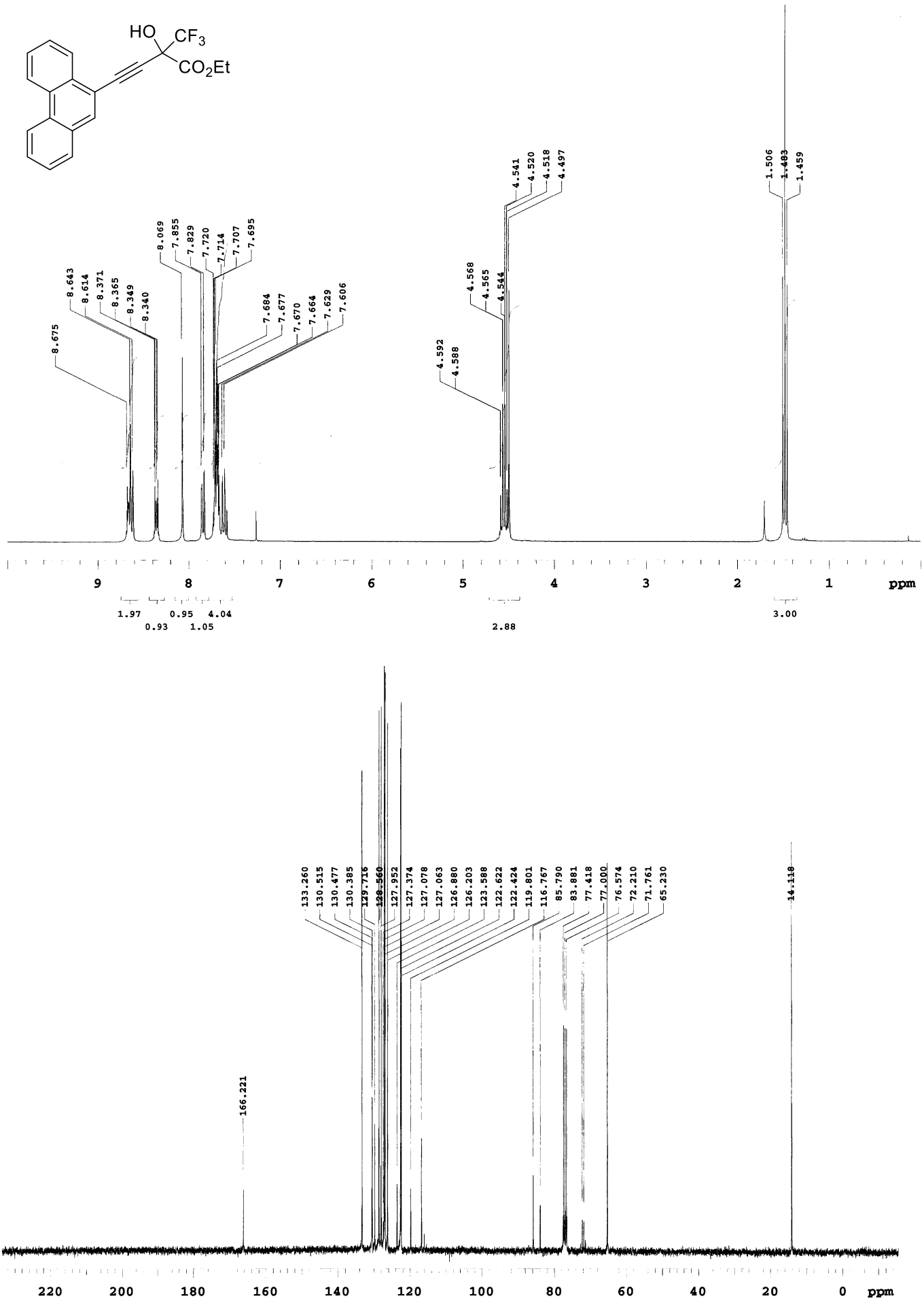


Fig S 37. ^{1}H and ^{13}C NMR spectra of **7d**.

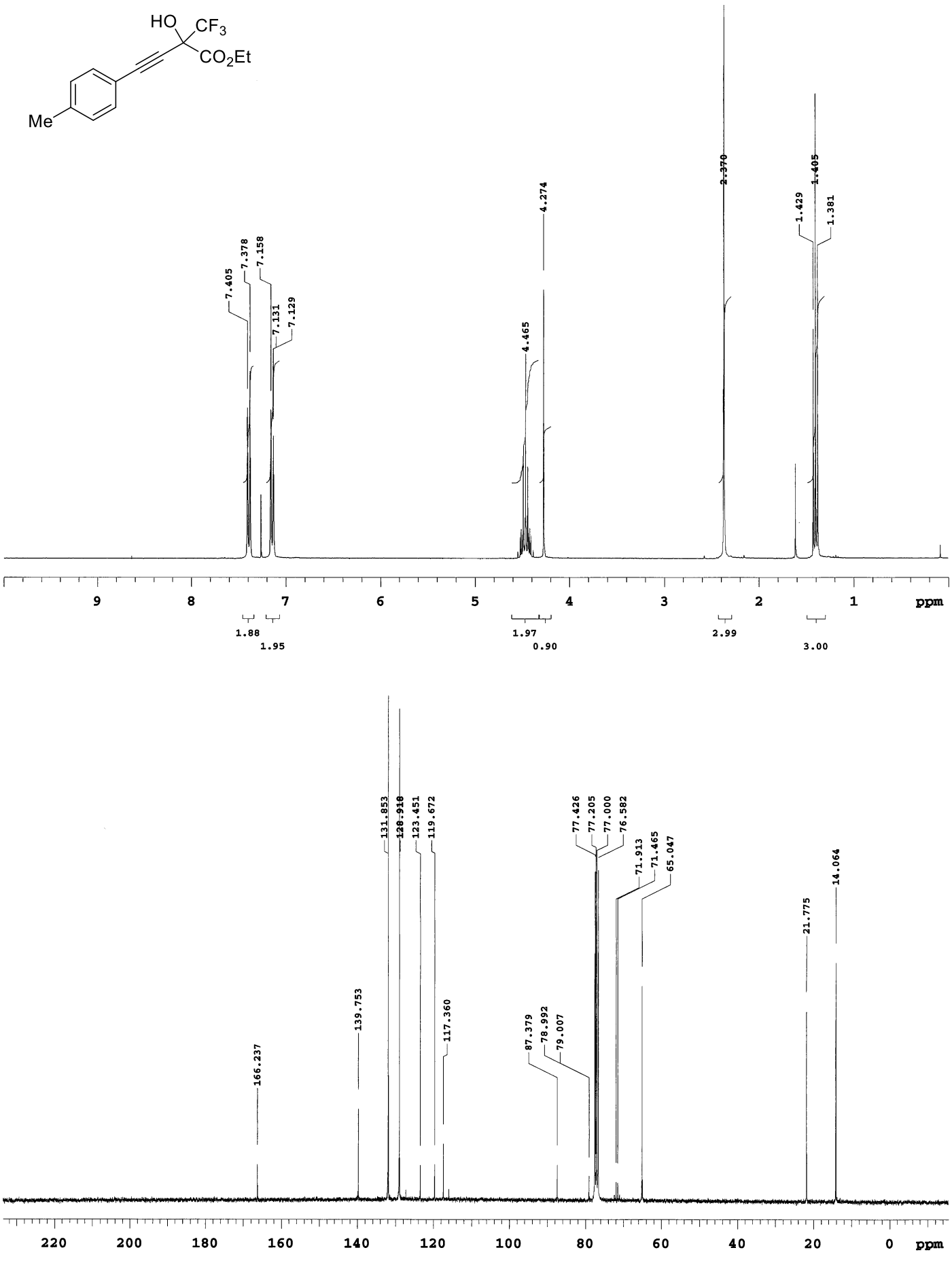


Fig S 38. ^{1}H and ^{13}C NMR spectra of **7e**.

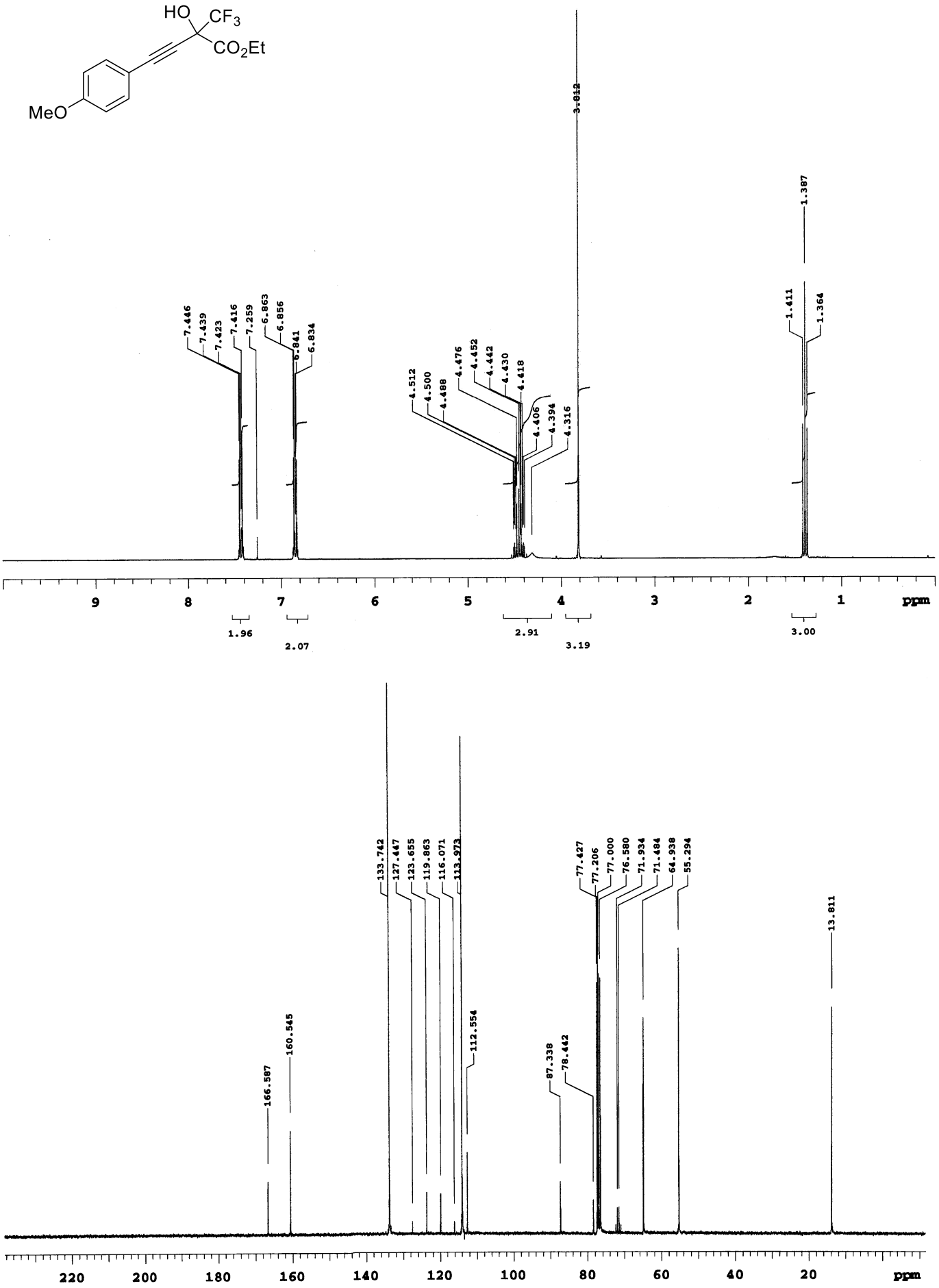


Fig S 39. ^{1}H and ^{13}C NMR spectra of **7f**.

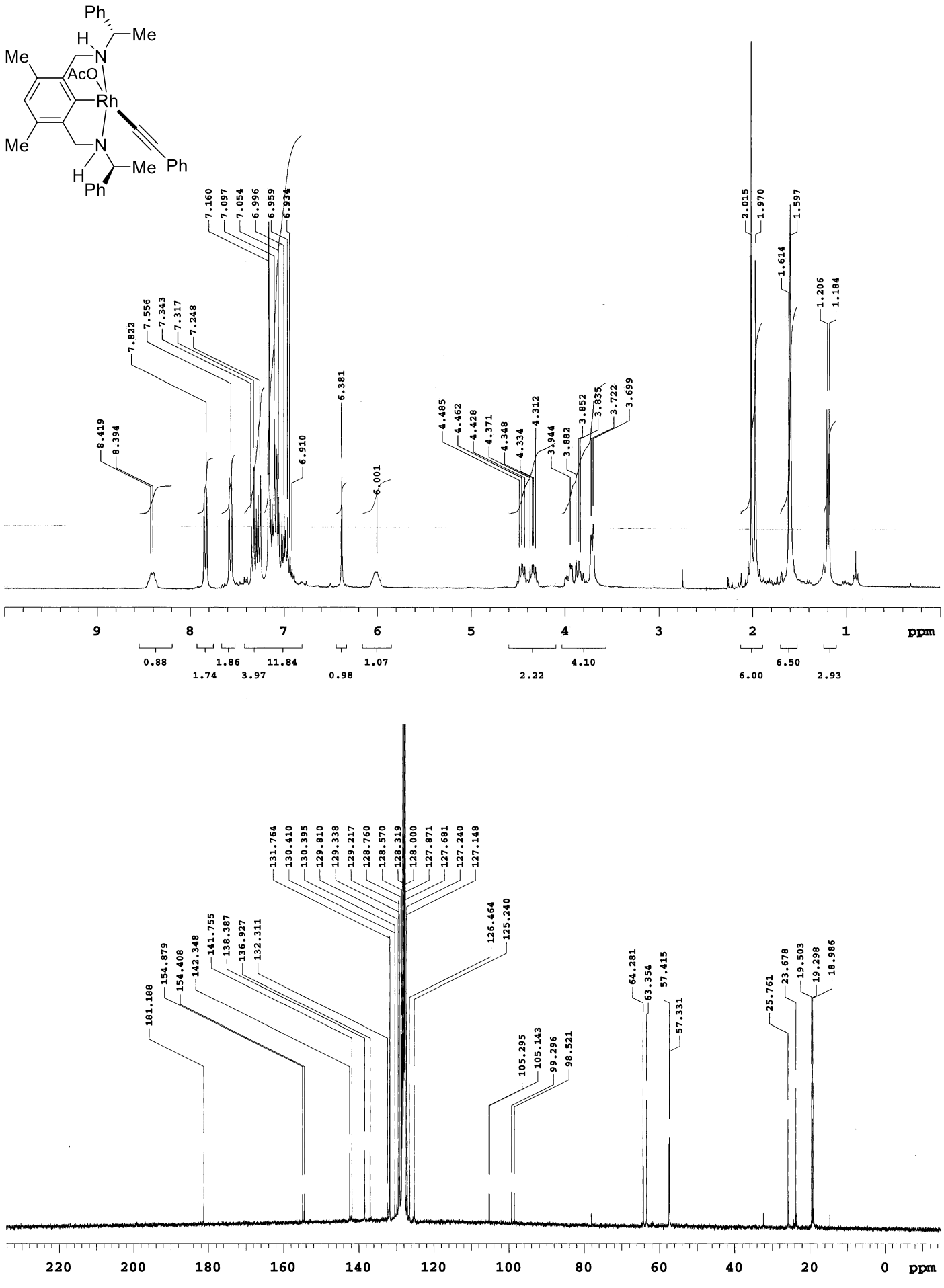


Fig S 40. ^{1}H and ^{13}C NMR spectra of **8**.