New five-coordinate Ru(II) phosphoramidite complexes and their catalytic activity in propargylic amination reactions

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Supplementary Information - New Journal of Chemistry

1. Experimental details and characterization data for the catalysis products in Table 3

General. Chemicals were treated as follows: diethyl ether, distilled from Na/benzophenone; CH_2Cl_2, distilled from $CaCl_2$; petroleum ether and ethyl acetate used as received. $[RuCl_2(PPh_3)_3]$ (**5**, Strem), amine substrates for catalytic experiments, Cs_2CO_3, silica (Aldrich), and other materials used as received. "(R)-BINOL-*N*,*N*-dimethyl-phosphoramidite" (R)-**7a** and "(R)-BINOL-*N*,*N*-dibenzyl-phosphoramidite" (R)-**7b** were synthesized with slight modification to literature procedures.[1] The propargylic acetates (**11a**-**d**) were synthesized according to literature procedures.[2] All reactions were carried out under nitrogen employing standard Schlenk techniques; workups and catalytic experiments were carried out in open air.

NMR spectra were obtained at room temperature on a Bruker Avance 300 MHz or a Varian Unity Plus 300 MHz instrument and referenced to a residual solvent signal; all assignments are tentative. GC/MS spectra were recorded on a Hewlett Packard GC/MS System Model 5988A. Exact masses were obtained on a JEOL MStation [JMS-700] Mass Spectrometer. IR spectra were recorded on a Thermo Nicolet 360 FT-IR spectrometer. Elemental analyses were performed by Atlantic Microlab Inc., Norcross, GA, USA.

1,1-Dimethyl-*N*-benzyl-*N*-methyl-2-propyn-1-amine (**13a**):[3a] To a vial containing $[RuCl_2(PPh_3)_2$((R)-**7b**)] (**8b**, 0.019 g, 0.016 mmol) and Cs_2CO_3 (0.209 g, 0.64 mmol), CH_2Cl_2 (0.5 mL) was added to dissolve the metal complex, followed by

1,1-dimethyl-2-propynyl acetate (**11a**, 0.041 g, 0.32 mmol) and *N*-benzyl-*N*-methylamine (0.125 g, 1.10 mmol) under open atmosphere. The mixture was heated at 45 °C for 18 hours. The residue was purified by vacuum filtration through SiO_2 in a fritted funnel with petroleum ether and ethyl acetate (10:1), then concentrated under reduced pressure to give **13a** as a yellow oil (0.043 g, 0.23 mmol; 71%). ^{1}H-NMR δ_H (300.13 MHz; $CDCl_3$; Me_4Si) 7.13-7.29 (m, 5H, Ph), 3.51 (s, 2H, PhCH_2), 2.25 (s, 1H, C≡C*H*), 2.07 (s, 3H, NCH_3), 1.40 (s, 6H, 2CH_3); ^{13}C{^{1}H}-NMR δ_C (75.5 MHz; $CDCl_3$; Me_4Si) 140.6 (Ph), 128.7 (Ph), 128.2 (Ph), 126.7 (Ph), 86.1 (*C*≡CH), 70.8 (C≡*C*H), 56.5 (*C*H_2), 54.3 (N*C*C≡CH), 35.9 (*C*H_3), 28.6 (2*C*H_3). MS (EI) *m*/*z*: 187 (2%), 172 (56), 146 (4), 91 (100). IR (neat oil) ν_{max}/cm^{-1} 3292w (C≡C-H), 3061w, 3027w, 2984m, 2923w, 2846w, 2789w, 1495w, 1453m, 1437m, 1378w, 1355w, 1198s, 1180s, 1119s.

1-Phenyl -*N*,*N*-dibenzyl-2-propyn-1-amine (**13b**):[3b] To a vial containing $[RuCl_2(PPh_3)_2$((R)-**7b**)] (**8b**, 0.014 g, 0.012 mmol) and Cs_2CO_3 (0.150 g, 0.46 mmol), CH_2Cl_2 (0.5 mL) was added to dissolve the metal complex, followed by 1-phenyl-2-propynyl acetate (**11b**, 0.41 g, 0.24 mmol) and dibenzylamine (0.183 g, 0.93 mmol) under open atmosphere. The mixture was shaken for 18 hours at room temperature. The residue was purified by vacuum filtration through SiO_2 in a fritted funnel with hexanes and ethyl acetate (10:1), then concentrated under reduced pressure to give **13b** as a yellow oil (0.053 g, 0.17 mmol; 72%). ^{1}H-NMR δ_H (300.13 MHz; $CDCl_3$; Me_4Si) 7.58 (d, $^3J_{HH}$ = 7.8 Hz, 2H, Ph), 7.11 – 7.33 (m, 13H, Ph), 4.64 (d, $^4J_{HH}$ = 1.9 Hz, 1H, PhC*H*), 3.65 (d, $^2J_{HH}$ = 13.5 Hz, 2H, PhCH_2), 3.36 (d, $^2J_{HH}$ = 13.5 Hz, 2H, PhCH_2),

2.56 (d, $^4J_{HH}$ = 1.9 Hz, 1H, C≡C*H*); $^{13}C\{^1H\}$-NMR δ_C (75.5 MHz; $CDCl_3$; Me_4Si) 139.4 (Ph), 138.5 (Ph), 128.8 (Ph), 128.3 (Ph), 128.11 (Ph), 128.06 (Ph), 127.5 (Ph), 127.0 (Ph), 78.7 (*C*≡CH), 76.1 (C≡*C*H), 55.3 (Ph*C*H), 54.3 (2*C*H_2). MS (EI) *m*/*z* : 311 (3%), 284 (3), 234 (6), 220 (8), 115 (58), 91 (100). IR (neat oil) ν_{max}/cm^{-1} 3293m (C≡C-H), 3085w, 3062w, 3028w, 2927w, 2835w, 2809w, 1602w, 1493s, 1452s, 1364m, 1273m, 1104s, 1070s, 1029s, 965s, 911m.

1-Methyl-1-phenyl-*N*-benzyl-*N*-methyl-2-propyn-1-amine (**13c**):[3c] To a vial containing $[RuCl_2(PPh_3)_2$((R)-**7b**)] (**8b**, 0.014 g, 0.012 mmol) and Cs_2CO_3 (0.145 g, 0.45 mmol), CH_2Cl_2 (0.5 mL) was added to dissolve the metal complex, followed by 1-methyl-1-phenyl-2-propynyl acetate (**11c**, 0.040 g, 0.21 mmol) and *N*-benzyl-*N*-methylamine (0.084 g, 0.74 mmol) under open atmosphere. The mixture was heated at 45 °C for 18 hours. The residue was purified by vacuum filtration through SiO_2 in a fritted funnel with petroleum ether and ethyl acetate (10:1), then concentrated under reduced pressure to give **13c** as a yellow oil (0.040 g, 0.16 mmol; 75%). ^1H-NMR δ_H (300.13 MHz; $CDCl_3$; Me_4Si) 7.75-7.78 (m, 2H, Ph), 7.10-7.30 (m, 8H, Ph), 3.38 (d, $^2J_{HH}$ = 13.6 Hz, 1H, PhC*H*H'), 3.28 (d, $^2J_{HH}$ = 13.6 Hz, 1H, PhCH*H*'), 2.60 (s, 1H, C≡C*H*), 2.10 (s, 3H, NCH_3), 1.61 (s, 3H, CCH_3); $^{13}C\{^1H\}$-NMR δ_C (75.5 MHz; $CDCl_3$; Me_4Si) 145.4 (Ph), 140.3 (Ph), 128.5 (Ph), 128.2 (Ph), 128.1 (Ph), 127.2 (Ph), 126.6 (Ph), 126.3 (Ph), 82.5 (*C*≡CH), 75.2 (C≡*C*H), 63.5 (Ph*C*), 56.8 (PhCH_2), 35.8 (NCH_3), 31.6 (CCH_3). MS (EI) *m*/*z*: 249 (3%), 234 (46), 172 (14), 129 (56), 91 (100). IR (neat oil)

ν_{max}/cm^{-1} 3292w (C≡C-H), 3061w, 3027w, 2987w, 2963w, 2847w, 2793w, 1599w, 1494m, 1447m, 1360w, 1259m, 1085s, 1023s.

1-Phenyl-*N*-benzyl-*N*-methyl-2-propyn-1-amine (**13d**):[3d] To a vial containing $[RuCl_2(PPh_3)_2$((R)-**7b**)] (**8b**, 0.015 g, 0.012 mmol) and Cs_2CO_3 (0.159 g, 0.49 mmol), CH_2Cl_2 (0.5 mL) was added to dissolve the metal complex, followed by 1-phenyl-2-propynyl acetate (**11b**, 0.041 g, 0.23 mmol) and *N*-benzyl-*N*-methylamine (0.111 g, 0.91 mmol) under open atmosphere. The mixture was shaken for 18 hours at room temperature. The residue was purified by vacuum filtration through Al_2O_3 in a fritted funnel with petroleum ether and ethyl acetate (10:1), then concentrated under reduced pressure to give **13d** as a yellow oil (0.042 g, 0.18 mmol; 76%). ^{1}H-NMR δ_H (300.13 MHz; $CDCl_3$; Me_4Si) 7.62 (d, $^3J_{HH}$ = 7.6 Hz, 2H, Ph), 7.22-7.40 (m, 8H, Ph), 4.71 (d, $^4J_{HH}$ = 2.0 Hz, 1H, PhC*H*), 3.67 (d, $^2J_{HH}$ = 13.2 Hz, 1H, PhC*H*H'), 3.54 (d, $^2J_{HH}$ = 13.2 Hz, 1H, PhCH*H*'), 2.59 (d, $^4J_{HH}$ = 2.0 Hz, 1H, C≡C*H*), 2.17 (s, 3H, CH_3); ^{13}C{^{1}H}-NMR δ_C (75.5 MHz; $CDCl_3$; Me_4Si) 139.1 (Ph), 138.4 (Ph), 128.9 (Ph), 128.3 (Ph), 128.15 (Ph), 128.09 (Ph), 127.5 (Ph), 127.1 (Ph), 78.6 (*C*≡CH), 76.1 (C≡*C*H), 58.8, 58.6 (N*C*H_2 and N*C*H), 37.7 (*C*H_3). MS (EI) *m*/*z*: 235 (6%), 158 (44), 144 (23), 115 (100), 91 (100). IR (neat oil) ν_{max}/cm^{-1} 3288w (C≡C-H), 3062w, 3029w, 2927w, 2847w, 2795w, 1712w, 1671s, 1625m, 1549m, 1494m, 1451s, 1398m, 1366m, 1273s, 1121w, 1073w, 1023s.

1,1-Diphenyl-*N*-benzyl-*N*-methyl-2-propyn-1-amine (**13f**):[3c] To a vial containing $[RuCl_2(PPh_3)_2$((R)-**7b**)] (**8b**, 0.010 g, 0.008 mmol) and Cs_2CO_3 (0.104 g, 0.32 mmol), CH_2Cl_2 (0.5 mL) was added to dissolve the metal complex, followed by 1,1-diphenyl-2-propynyl acetate (**11d**, 0.042 g, 0.17 mmol) and *N*-benzyl-*N*-methylamine (0.071 g, 0.63 mmol) under open atmosphere. The mixture was heated at 45 °C for 18 hours. The residue was purified by flash chromatography (1 × 10 cm SiO_2, petroleum ether / EtOAc 10:1 v/v), then concentrated under reduced pressure to obtain **13f** as a yellow oil (0.044 g, 0.14 mmol, 84%). ^{1}H-NMR δ_H (300.13 MHz; $CDCl_3$; Me_4Si) 7.89 – 7.91 (m, 4H, Ph), 7.11 – 7.48 (m, 11H, Ph), 3.56 (s, 2H, C*H*$_2$), 2.91 (s, 1H, C≡C*H*), 2.12 (s, 3H, C*H*$_3$); ^{13}C{^{1}H}-NMR δ_C (75.5 MHz; $CDCl_3$; Me_4Si) 144.2 (Ph), 140.1 (Ph), 128.40 (Ph), 128.36 (Ph), 128.34 (Ph), 127.1 (Ph), 126.7 (Ph), 81.2 (*C*≡CH), 77.4 (*C*C≡*C*H), 72.6 (C≡*C*H), 57.0 (*C*H$_2$), 37.2 (*C*H$_3$). MS (EI) *m*/*z*: 311 (2%), 234 (17), 220 (6), 191 (100), 165 (27), 91 (88).

1-Phenyl -*N,N*-diethyl-2-propyn-1-amine (**13g**):[3b] To a vial containing $[RuCl_2(PPh_3)_2$((R)-**7b**)] (**8b**, 0.015 g, 0.012 mmol) and Cs_2CO_3 (0.160 g, 0.49 mmol), CH_2Cl_2 (0.5 mL) was added to dissolve the metal complex, followed by 1-phenyl-2-propynyl acetate (**11b**, 0.042 g, 0.24 mmol) and diethylamine (0.067 g, 0.92 mmol) under open atmosphere. The mixture was shaken for 18 hours at room temperature. The residue was purified by vacuum filtration through Al_2O_3 in a fritted funnel with petroleum ether and ethyl acetate (10:1), then concentrated under reduced pressure to give **13g** as a yellow oil (0.032 g, 0.17 mmol; 71%). ^{1}H-NMR δ_H (300.13 MHz; $CDCl_3$;

Me_4Si) 7.55 (d, $^3J_{HH}$ = 7.5 Hz, 2H, Ph), 7.16-7.29 (m, 3H, Ph), 4.77 (d, $^4J_{HH}$ = 1.6 Hz, 1H, PhC*H*), 2.31-2.55 (m, 5H, 2CH_2 and C≡C*H*), 0.96 (t, $^3J_{HH}$ = 7.1 Hz, 6H, 2CH_3); $^{13}C\{^1H\}$-NMR δ_C (75.5 MHz; $CDCl_3$; Me_4Si) 139.2 (Ph), 128.1 (Ph), 128.0 (Ph), 127.2 (Ph), 80.0 (*C*≡CH), 74.9 (C≡*C*H), 56.2 (Ph*C*H), 44.4 (2*C*H_2), 13.5 (2*C*H_3). MS (EI) *m*/*z*: 187 (4%), 172 (14), 115 (100), 89 (13). IR (neat oil) ν_{max}/cm^{-1} 3300w (C≡C-H), 3060w, 3029w, 2969m, 2933w, 2872w, 2823w, 1600w, 1492m, 1449s, 1382m, 1266m, 1196s, 1161m, 1118s, 1069m, 1051m.

1-Phenyl -*N*,*N*-diisopropyl-2-propyn-1-amine (**13h**):[3b] To a vial containing $[RuCl_2(PPh_3)_2$((R)-**7b**)] (**8a**, 0.006 g, 0.005 mmol) and Cs_2CO_3 (0.075 g, 0.23 mmol), CH_2Cl_2 (0.5 mL) was added to dissolve the metal complex, followed by 1-phenyl-2-propynyl acetate (**11b**, 0.021 g, 0.12 mmol) and diisopropylamine (0.046 g, 0.46 mmol) under open atmosphere. The mixture was shaken for 18 hours at room temperature. The residue was purified by vacuum filtration through SiO_2 in a fritted funnel with petroleum ether and ethyl acetate (10:1), then concentrated under reduced pressure to give **13h** as a yellow oil (0.012 g, 0.055 mmol; 55%). ^{1}H-NMR δ_H (300.13 MHz; $CDCl_3$; Me_4Si) 7.62 (d, $^3J_{HH}$ = 8.0 Hz, 2H, Ph), 7.13-7.27 (m, 3H, Ph), 4.75 (d, $^4J_{HH}$ = 1.9 Hz, 1H, PhC*H*), 3.09 (sept, $^3J_{HH}$ = 6.6 Hz, 2H, 2C*H*$(CH_3)_2$), 2.40 (d, $^4J_{HH}$ = 1.9 Hz, 1H, C≡C*H*), 1.17 (d, $^3J_{HH}$ = 6.6 Hz, 6H, 2CH_3), 0.94 (d, $^3J_{HH}$ = 6.6 Hz, 6H, 2CH_3); $^{13}C\{^1H\}$-NMR δ_C (75.5 MHz; $CDCl_3$; Me_4Si) 141.6 (Ph), 127.8 (Ph), 127.7 (Ph), 126.8 (Ph), 85.7 (*C*≡CH), 74.0 (C≡*C*H), 49.7 (Ph*C*H), 46.6 (2*C*H$(CH_3)_2$), 23.8 (2*C*H_3), 20.4 (2*C*H_3). MS (EI) *m*/*z*: 215 (2%), 200 (12), 158 (5), 115 (100), 89 (9). IR (neat oil) ν_{max}/cm^{-1} 3305w (C≡C-H),

2961m, 2927m, 2869w, 1491w, 1448m, 1363m, 1207m, 1184s, 1136m, 1118m, 1056m, 1016m.

***N*-Methyl-*N*-(1-phenyl-2-propynyl)cyclohexylamine (13i)**:[3e] To a vial containing $[RuCl_2(PPh_3)_2((R)\text{-}\mathbf{7b})]$ (**8b**, 0.014 g, 0.012 mmol) and Cs_2CO_3 (0.153 g, 0.47 mmol), CH_2Cl_2 (0.5 mL) was added to dissolve the metal complex, followed by 1-phenyl-2-propynyl acetate (**11b**, 0.039 g, 0.23 mmol) and *N*-methylcyclohexylamine (0.104 g, 0.92 mmol) under open atmosphere. The mixture was shaken for 18 hours at room temperature. The residue was purified by vacuum filtration through SiO_2 in a fritted funnel with petroleum ether and ethyl acetate (10:1), then concentrated under reduced pressure to give **13i** as a yellow oil (0.048 g, 0.21 mmol; 94%). ^{1}H-NMR δ_H (300.13 MHz; $CDCl_3$; Me_4Si) 7.51 (d, $^3J_{HH}$ = 7.4 Hz, 2H, Ph), 7.15-7.28 (m, 3H, Ph), 4.83 (d, $^4J_{HH}$ = 2.0 Hz, 1H, PhC*H*), 2.44 (d, $^4J_{HH}$ = 2.0 Hz, 1H, C≡C*H*) 2.42-2.53 (m, 1H, NC*H*$(CH_2)_2$), 2.05 (s, 3H, CH_3), 1.86-1.99 (m, 2H, 2C*H*H), 1.70-1.73 (m, 2H, 2C*H*H), 1.52-1.56 (m, 1H, C*H*H), 1.07-1.34 (m, 5H 5 × C*H*H); ^{13}C{^{1}H}-NMR δ_C (75.5 MHz; $CDCl_3$; Me_4Si) 139.7 (Ph), 128.0 (Ph), 127.2 (Ph), 81.0 (*C*≡CH), 75.5 (C≡*C*H), 61.3 (NC*H*$(CH_2)_2$), 55.9 (Ph*C*H), 33.1 (*C*H_3), 30.9, 30.1, 26.2, 25.6, 25.5. MS (EI) *m*/*z*: 226 (5%), 184 (11), 170 (41), 150 (8), 115 (100), 89 (16). IR (neat oil) ν_{max}/cm^{-1} 3305m (C≡C-H), 2928s, 2853s, 2793w, 1492w, 1449m, 1259m, 1073m, 1028m, 788m, 737m, 697m, 638m.

2. X-ray Structure Determination of **8b**

Crystals of appropriate dimension were obtained by slow diffusion of Et_2O into a solution of complex **8b** in CH_2Cl_2 at –18 °C. A crystal with approximate dimensions 0.21 × 0.19 × 0.17 mm^3 was mounted on a Mitgen cryoloop in a random orientation. Preliminary examination and data collection were performed using a Bruker Kappa Apex II Charge Coupled Device (CCD) Detector system single crystal X-Ray diffractometer equipped with an Oxford Cryostream LT device. All data were collected using graphite monochromated Mo Kα radiation (λ= 0.71073 Å) from a fine focus sealed tube X-Ray source. Preliminary unit cell constants were determined with a set of 36 narrow frame scans. Intensity data were collected using a combinations of ϖ and ϕ scan frames with typical scan width of 0.5° at a crystal to detector distance of 3.5 cm. The collected frames were integrated using an orientation matrix determined from the narrow frame scans. Apex II and SAINT software packages were used for data collection and data integration.[4] Analysis of the integrated data did not show any decay. Final cell constants were determined by global refinement of xyz centroids of 9055 reflections from the complete data set. Collected data were corrected for systematic errors using SADABS based on the Laue symmetry using equivalent reflections.[4]

Crystal data and intensity data collection parameters are listed in Table S1.

Structure solution and refinement were carried out using the SHELXTL- PLUS software package.[5] The structure was solved by direct methods and refined successfully in the space group P-1. Full matrix least-squares refinement was carried out by minimizing $\Sigma w(F_o^2-F_c^2)^2$. The non-hydrogen atoms were refined anisotropically to convergence. All hydrogen atoms were treated using appropriate riding model (AFIX

m3). A disordered molecule of Et_2O was located in the lattice as solvent of crystallization. The disorder was resolved with two orientations for all atoms with 50% occupancies and were refined with geometrical and displacement parameter restraints. The final residual values and structure refinement parameters are listed in Table S1.

Complete listings of positional and isotropic displacement coefficients for hydrogen atoms, anisotropic displacement coefficients for the non-hydrogen atoms are available electronically. Table of calculated and observed structure factors are available in electronic format.

Table S1. Crystallographic parameters.

	Complex **8b**
Empirical formula	$C_{70}H_{56}Cl_2NO_2P_3Ru\cdot(C_4H_{10}O)$
Formula weight	1282.16
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 13.6805(3) Å, α= 77.1170(10)°.
	b = 14.5594(3) Å, β= 71.5080(10)°.
	c = 17.2394(4) Å, γ = 71.6980(10)°.
Volume	3062.57(12) $Å^3$
Z	2
Density (calculated)	1.390 Mg/m^3
Absorption coefficient	0.472 mm^{-1}
F(000)	1328
Crystal size	0.21 x 0.19 x 0.17 mm^3
Theta range for data collection	1.49 to 26.39°
Index ranges	$-17\leq h\leq 17$, $-18\leq k\leq 18$, $-21\leq l\leq 21$
Reflections collected	88454
Independent reflections	12305 [R(int) = 0.0428]
Completeness to theta = 25.00°	98.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9257 and 0.9077
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12305 / 176 / 806
Goodness-of-fit on F^2	1.142
Final R indices [I>2sigma(I)]	R_1 = 0.0459, wR_2 = 0.1271
R indices (all data)	R_1 = 0.0632, wR_2 = 0.1489
Largest diff. peak and hole	1.068 and -0.695 e.$Å^{-3}$

3. References

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[2] R. J. Detz, M. M. E. Delville, H. Hiemstra and J. H. van Maarseveen, *Angew. Chem. Int. Ed.*, 2008, **47**, 3777.

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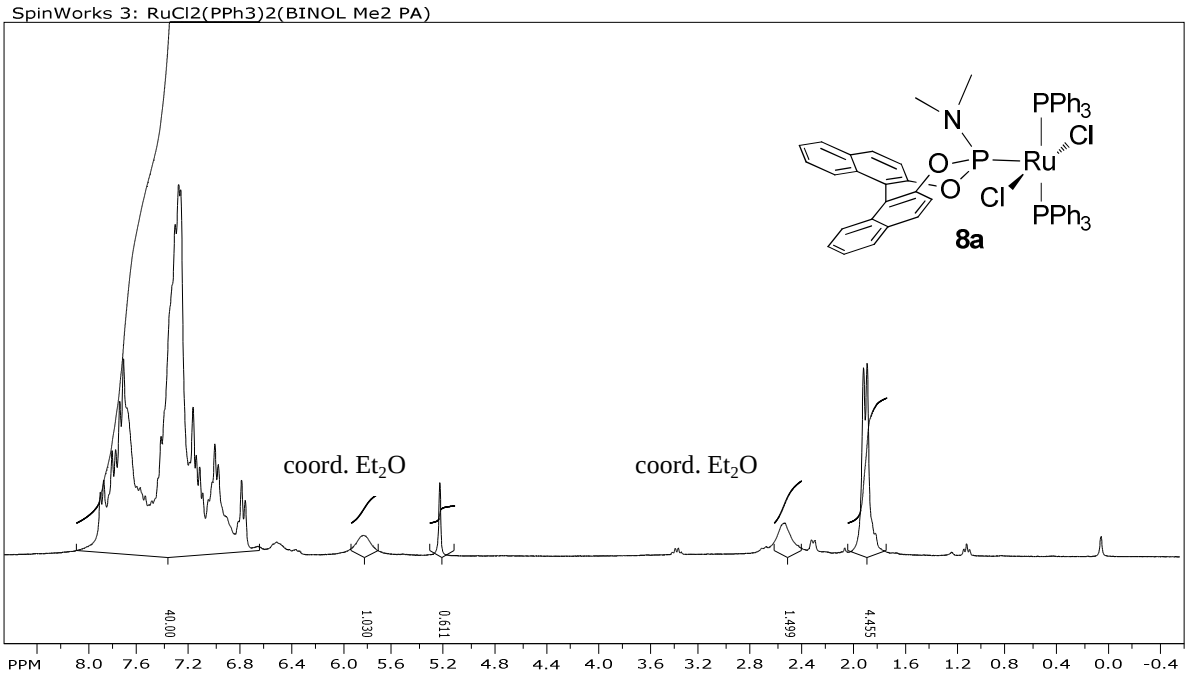
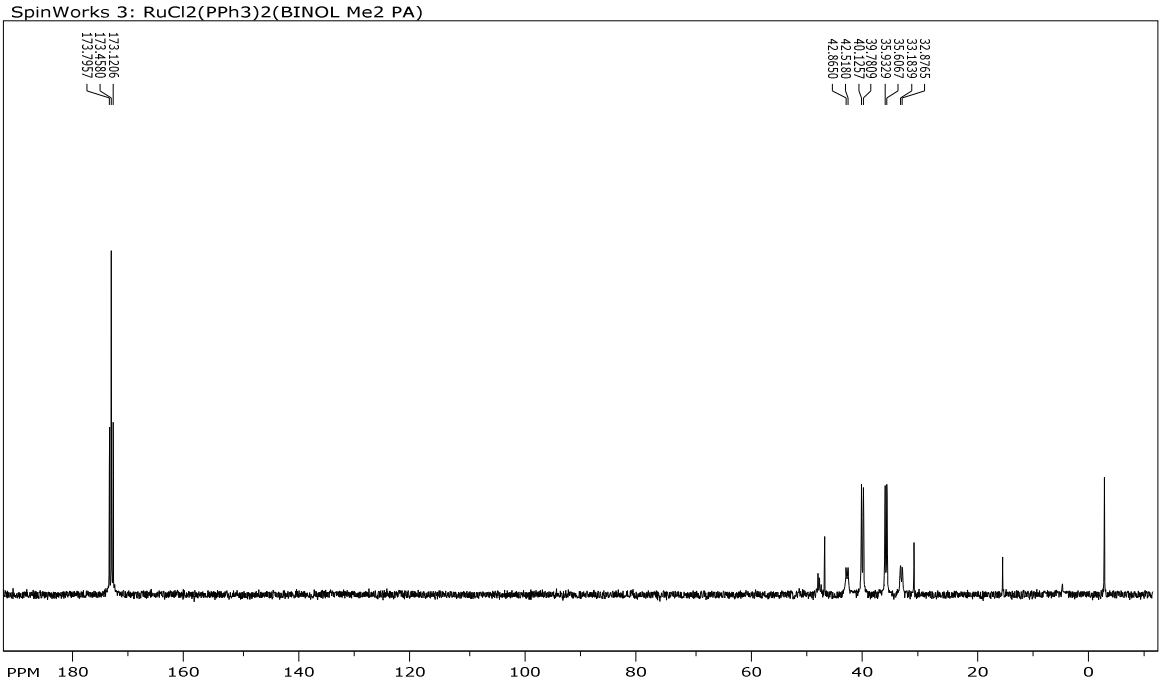
[4] Bruker Analytical X-ray, Madison, WI, 2010.

[5] G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 2008, **64**, 112.

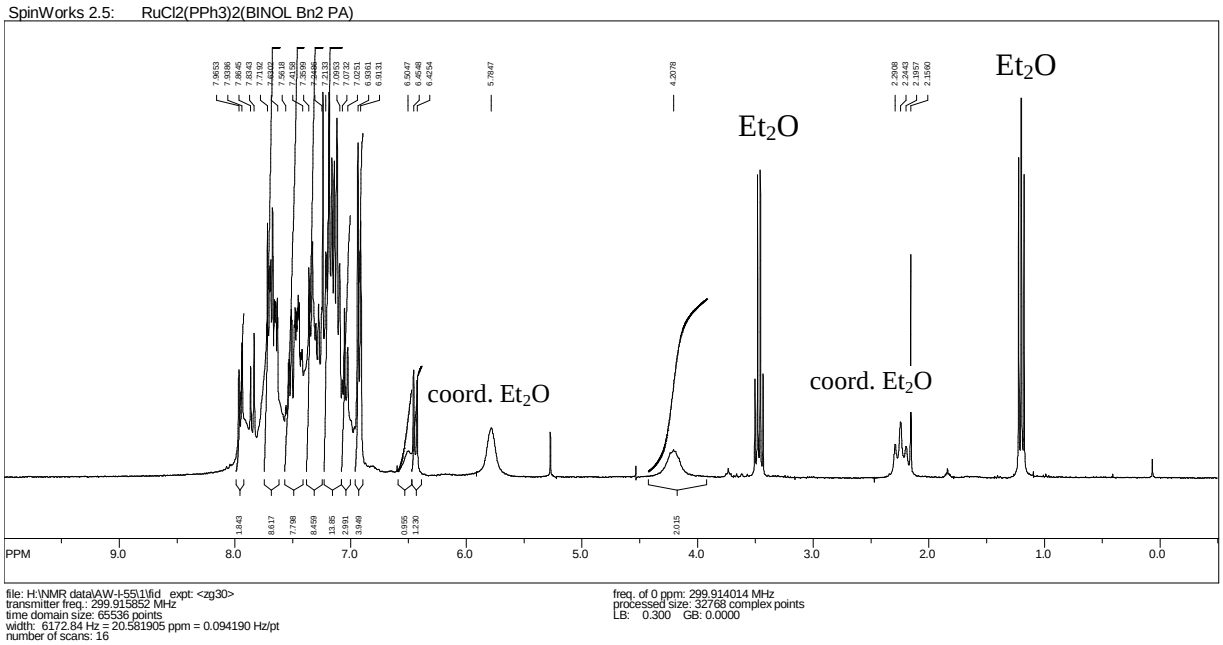
4. ^{1}H NMR and ^{31}P NMR spectra of the complexes **8**

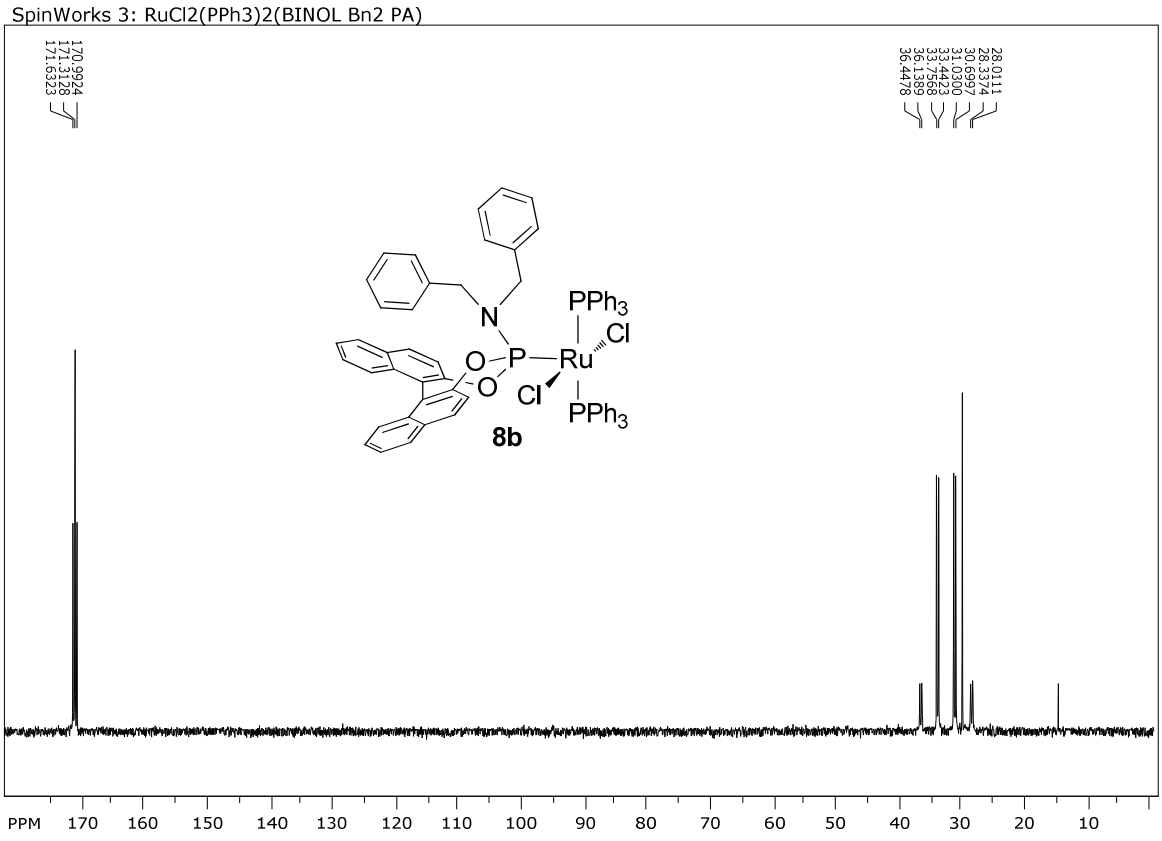
Complex **8a** ^{1}H NMR (top) and ^{31}P{^{1}H} NMR spectra





Complex **8b** ^{1}H NMR (top) and $^{31}P\{^{1}H\}$ NMR spectra





5. ^{1}H and ^{13}C NMR spectra of the catalysis products in Table 2

Table 2, **13a** (entry 1), ^{1}H (top) and $^{13}C\{^{1}H\}$ NMR spectra.

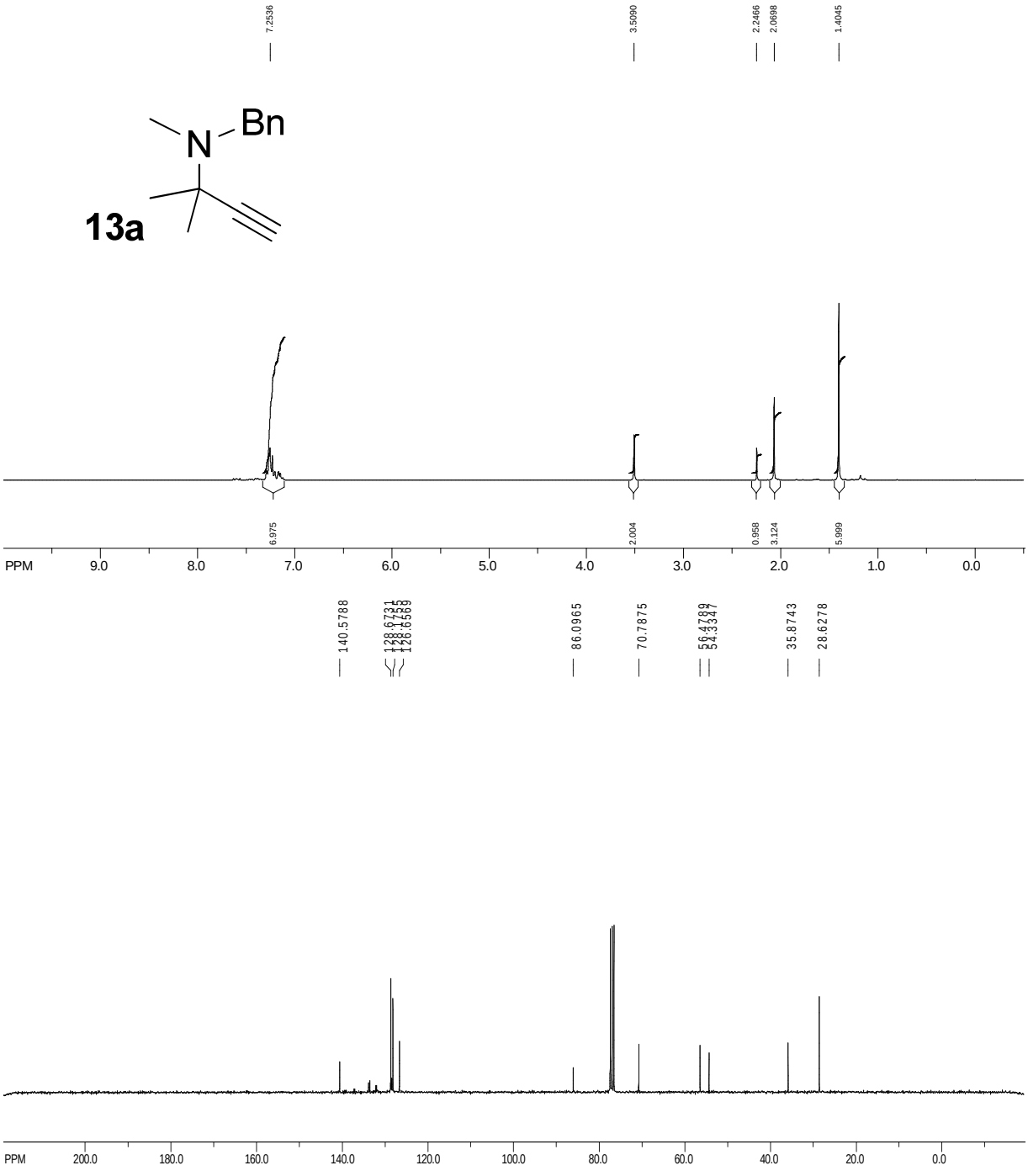


Table 2, **13b** (entry 2), ^{1}H (top) and $^{13}C\{^{1}H\}$ NMR spectra.

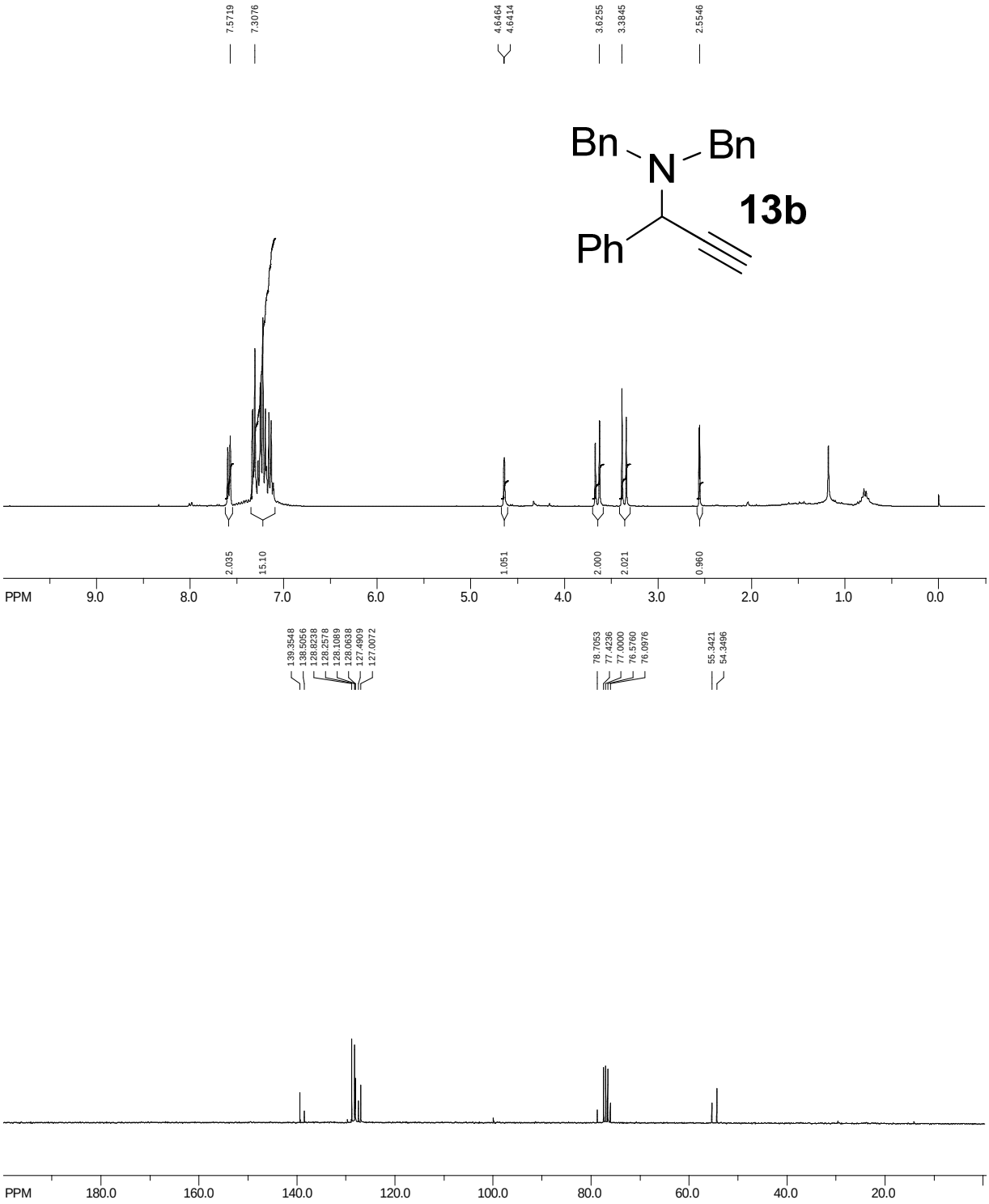


Table 2, **13c** (entry 3), ^{1}H (top) and $^{13}C\{^{1}H\}$ NMR spectra.

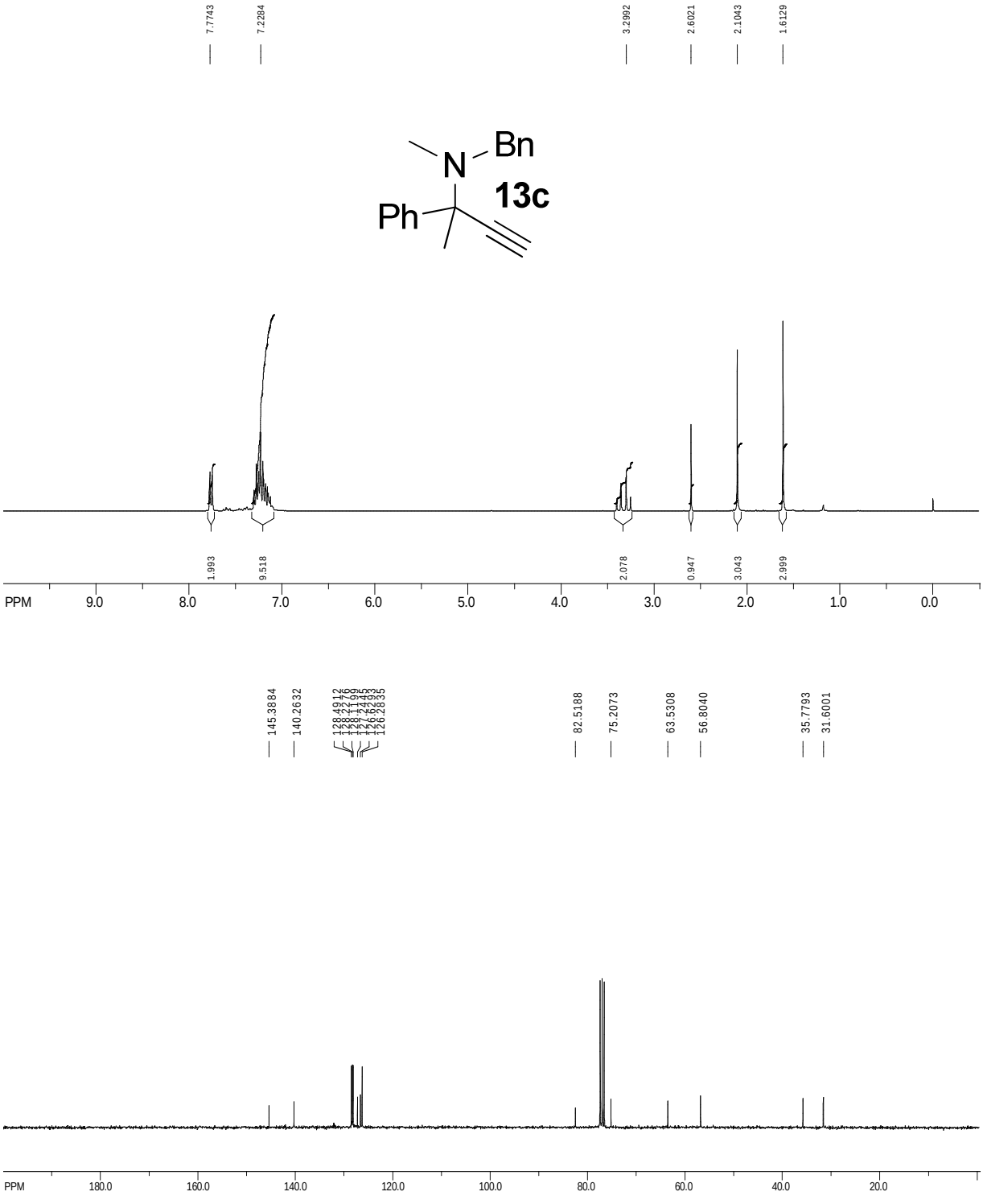
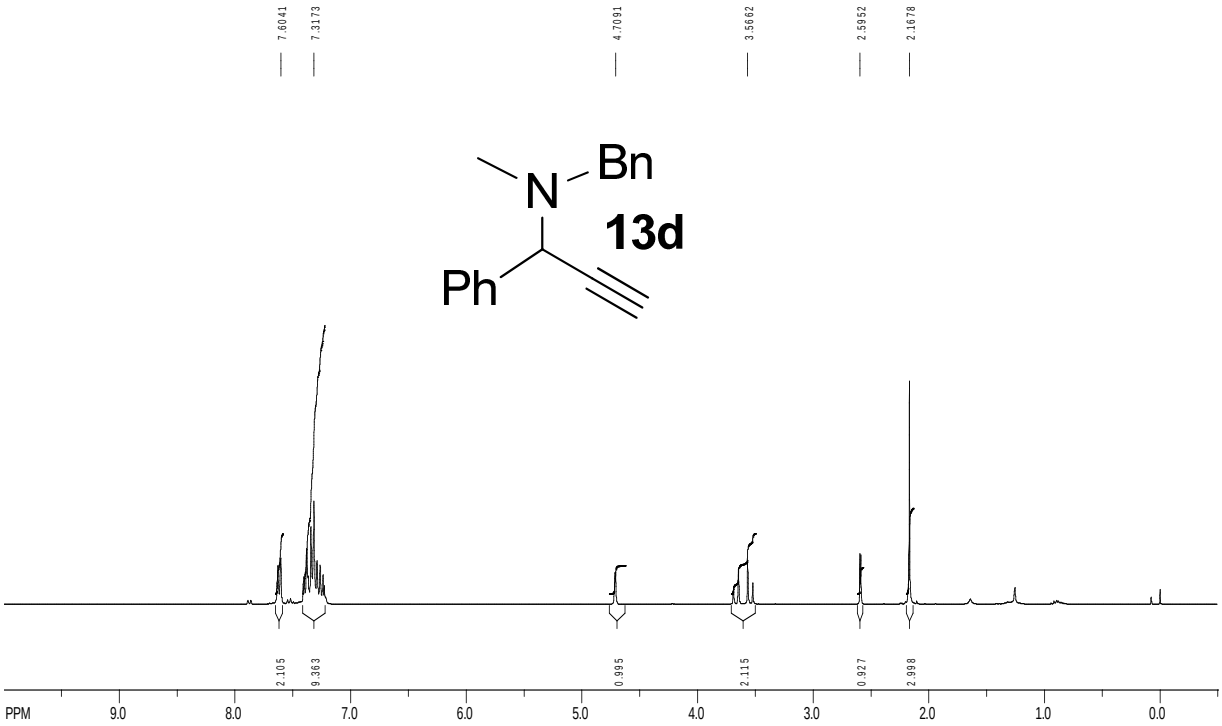
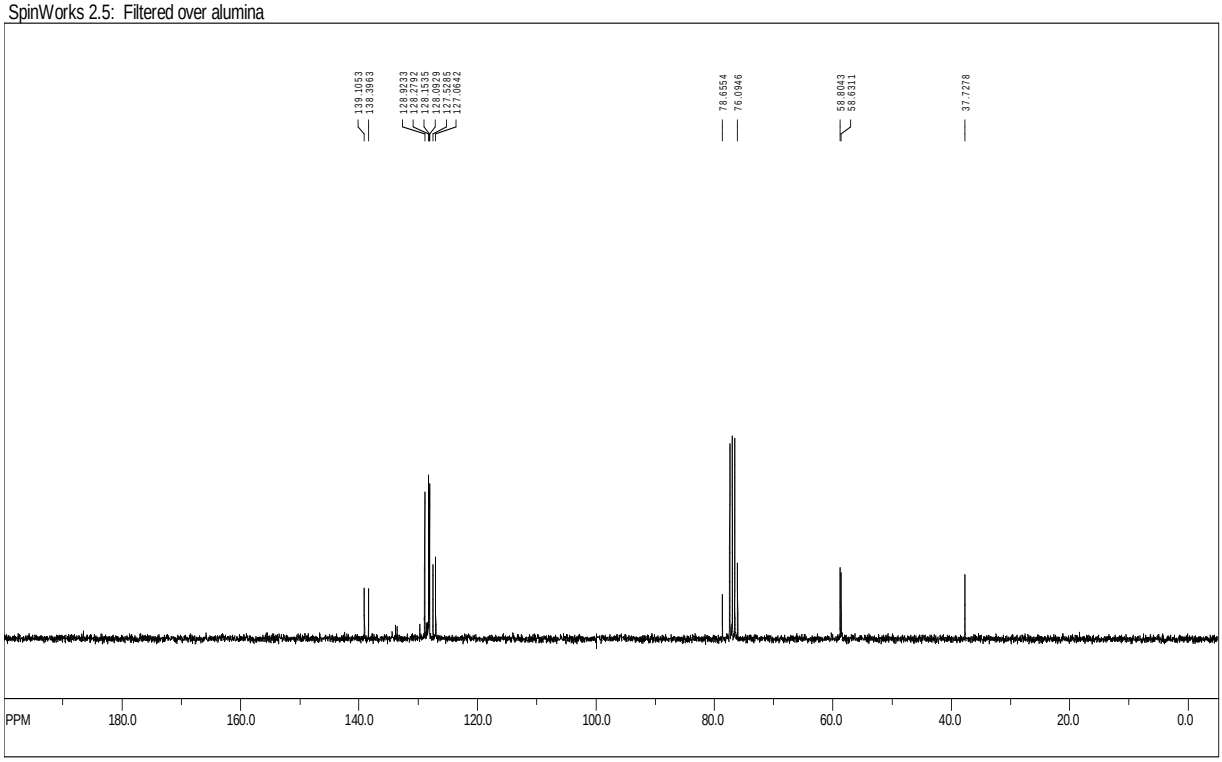


Table 2, **13d** (entry 4), ^{1}H (top) and $^{13}C\{^{1}H\}$ NMR spectra.



SpinWorks 2.5: Filtered over alumina



file: H:\NMR data\AW-III-20B\11\fid expt: <zgpg30>
transmitter freq.: 75.420977 MHz
time domain size: 65536 points
width: 17985.61 Hz = 238.469618 ppm = 0.274439 Hz/pt
number of scans: 105

freq. of 0 ppm: 75.413441 MHz
processed size: 32768 complex points
LB: 1.000 GB: 0.0000

Table 2, **13e** (entry 5), ^{1}H (top) and $^{13}C\{^{1}H\}$ NMR spectra.

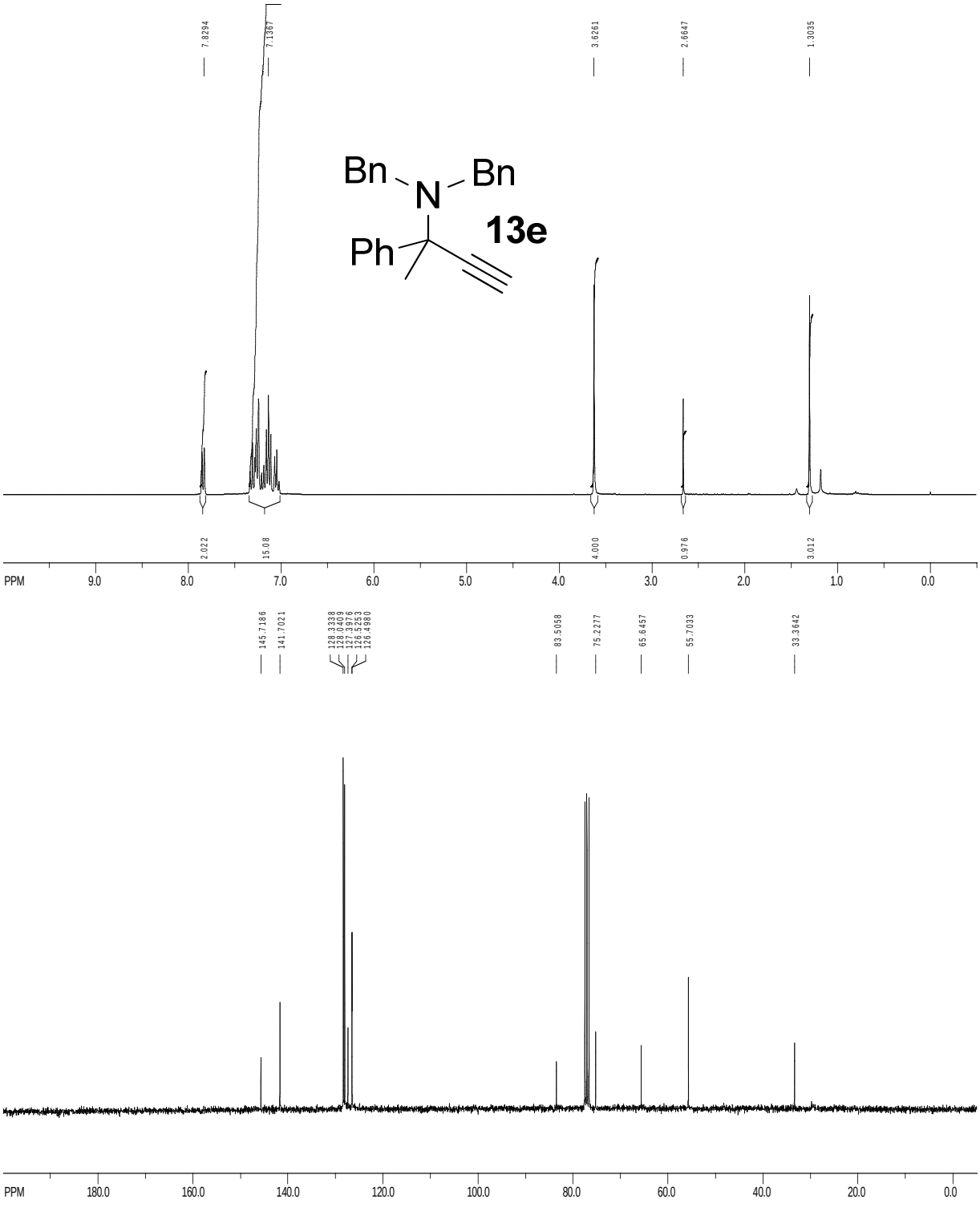
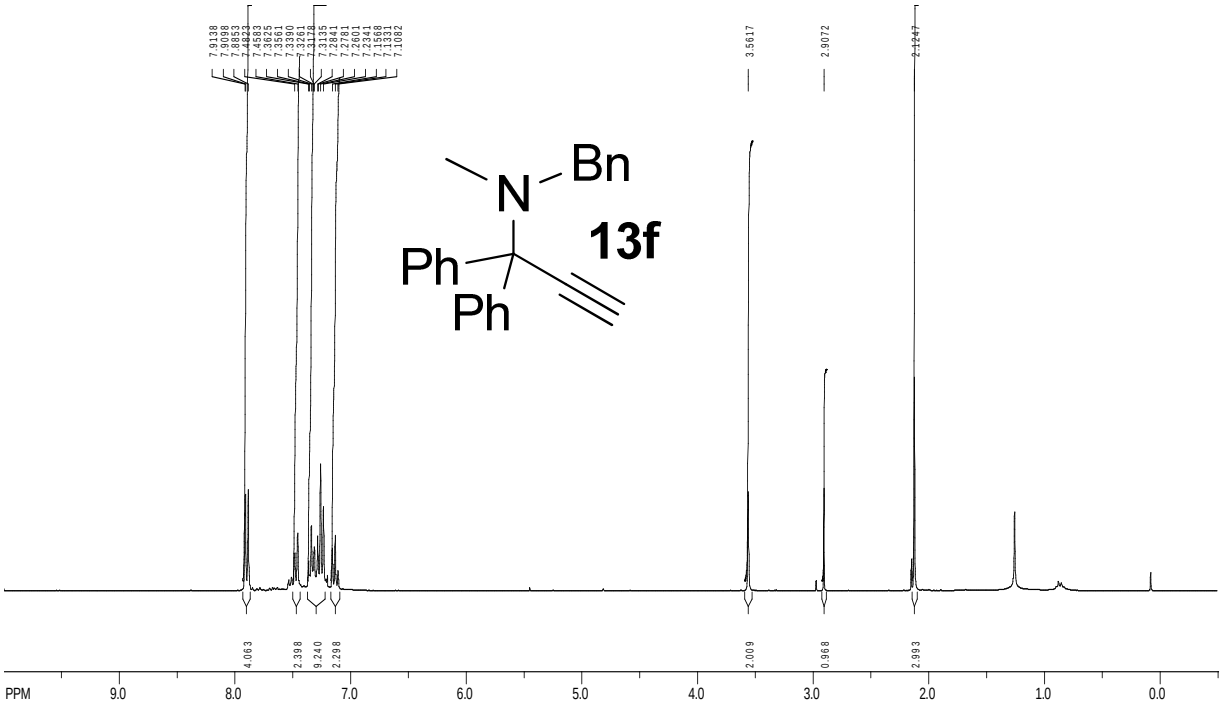


Table 2, **13f** (entry 6), ^{1}H (top) and $^{13}C\{^{1}H\}$ NMR spectra.



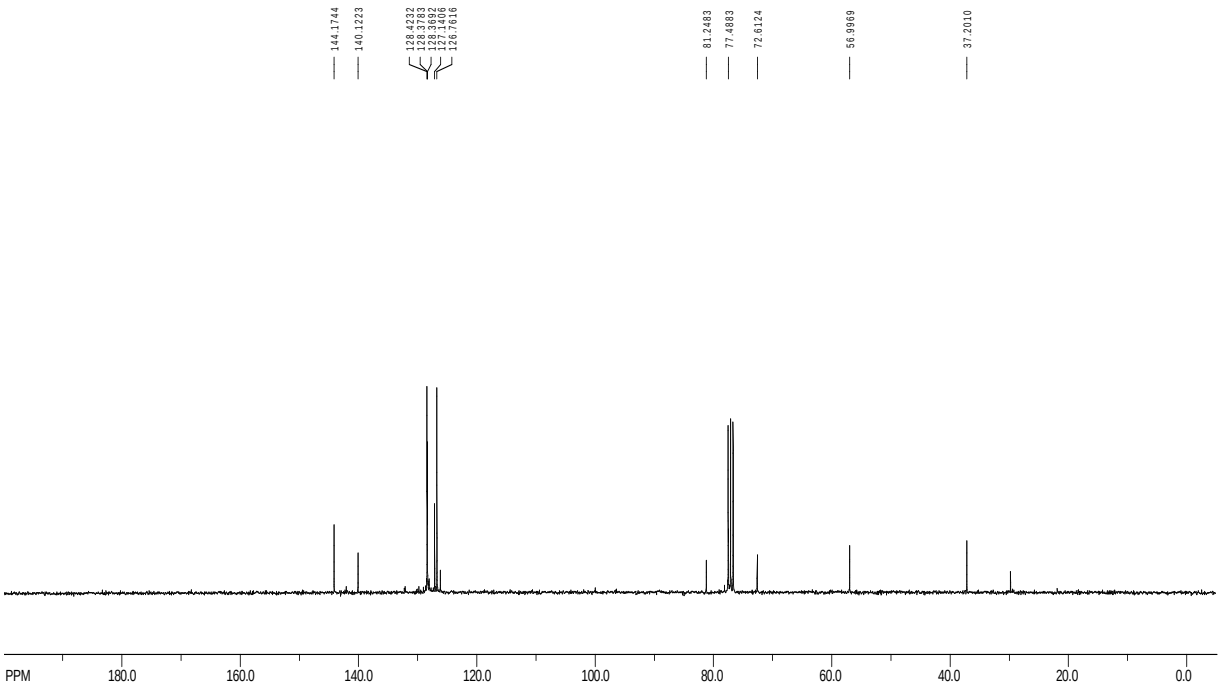


Table 2, **13g** (entry 7), ^{1}H (top) and $^{13}C\{^{1}H\}$ NMR spectra.

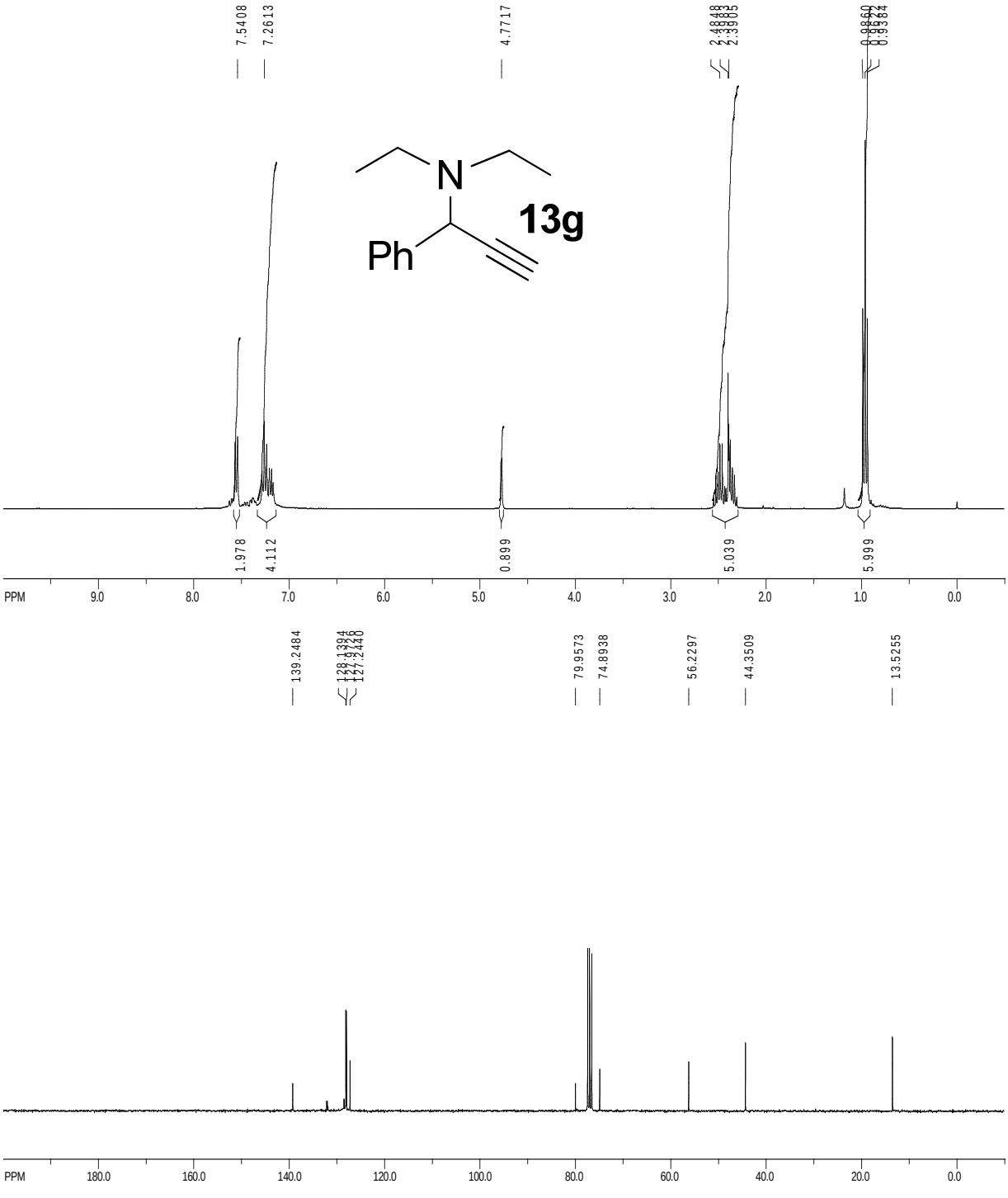


Table 2, **13h** (entry 8), ^{1}H (top) and $^{13}C\{^{1}H\}$ NMR spectra.

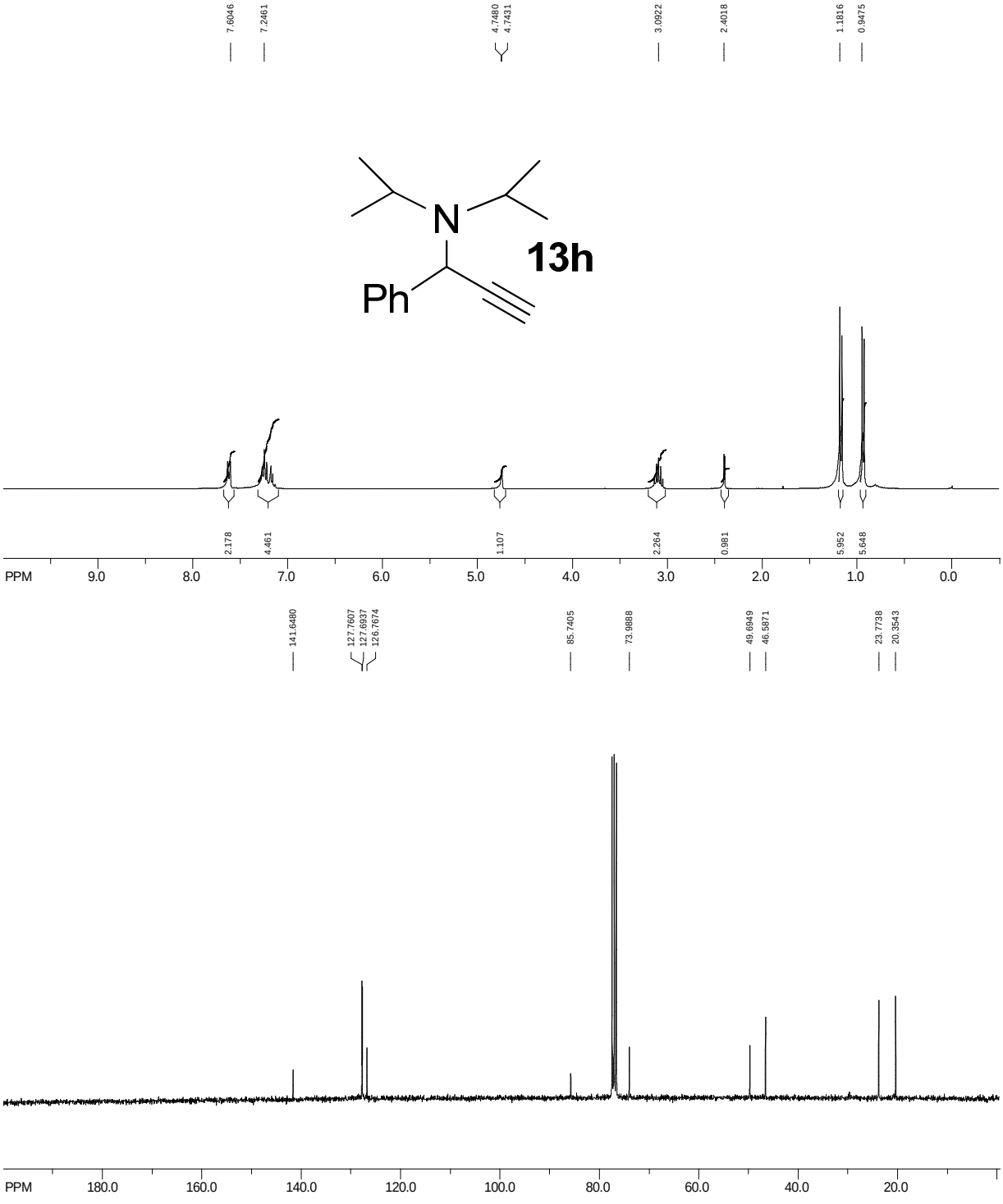


Table 2, **13i** (entry 9), ^{1}H (top) and $^{13}C\{^{1}H\}$ NMR spectra.

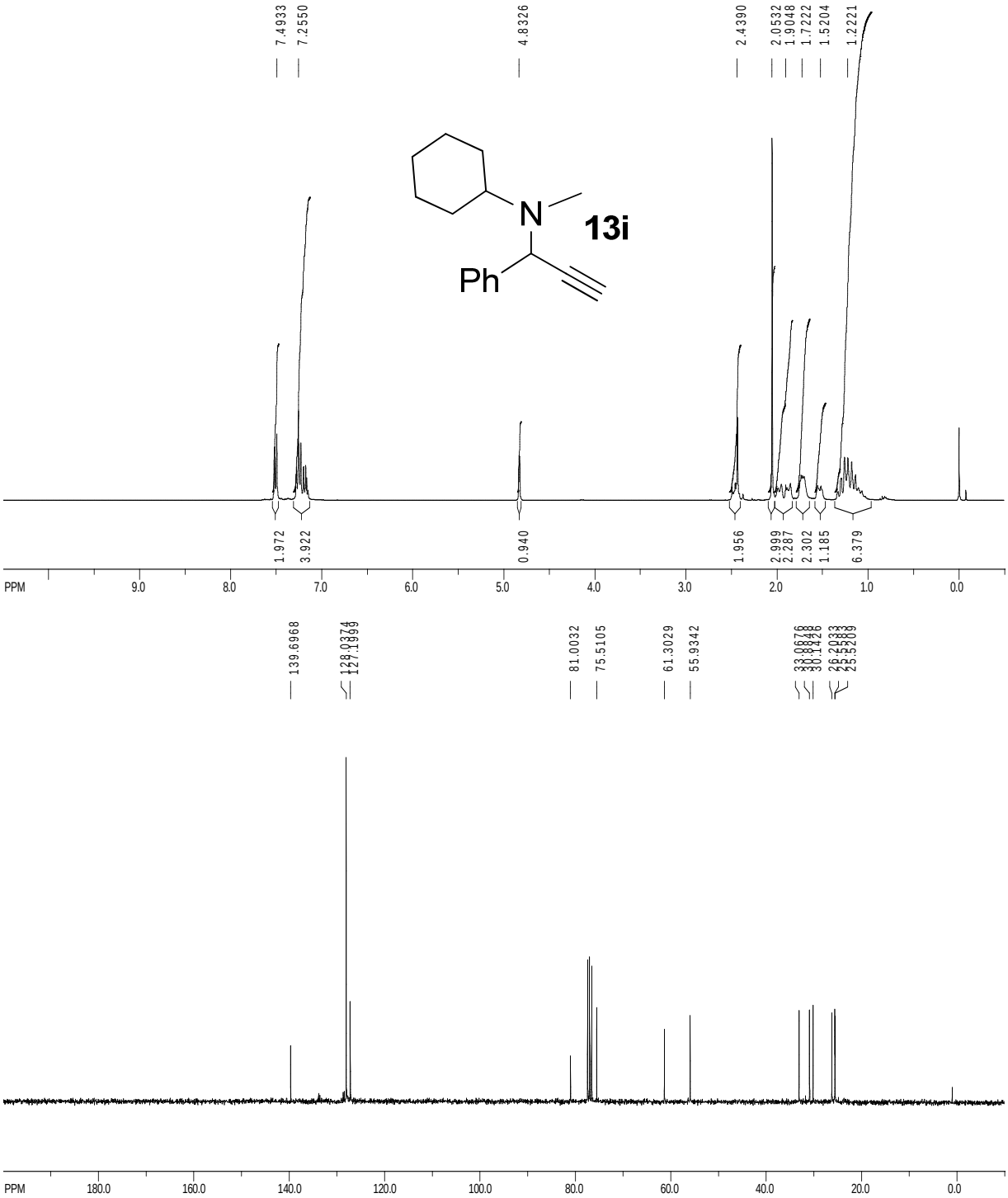


Table 2, **15** (entry 10), ^{1}H (top) and $^{13}C\{^{1}H\}$ NMR spectra.