



## Simple Generation of a Dirhodium $\mu$ -Carbido Complex *via* Thiocarbonyl Reduction

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Harrison J. Barnett, Liam K. Burt and Anthony F. Hill\*

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### General Considerations

All reactions involving air-sensitive compounds were carried out under a dry and oxygen-free nitrogen atmosphere using standard Schlenk and vacuum line techniques, with the use of dried and degassed solvents.

NMR spectra were obtained at 298 K with Bruker Avance 400 ( $^1\text{H}$  at 400.1 MHz,  $^{31}\text{P}$  at 161.9 MHz,  $^{11}\text{B}$  at 128.4 MHz,  $^{19}\text{F}$  at 376.5 MHz and  $^{13}\text{C}$  at 100.5 MHz), Bruker Avance 600 ( $^1\text{H}$  at 600.1 MHz,  $^{31}\text{P}$  at 242.9 MHz, and  $^{13}\text{C}$  at 192.5 MHz) or Bruker Avance 700 ( $^1\text{H}$  at 700.1 MHz,  $^{31}\text{P}$  at 283.5 MHz, and  $^{13}\text{C}$  at 176.1 MHz) spectrometers. Chemical shifts ( $\delta$ ) are reported in ppm and referenced internally to the solvent peak for  $^1\text{H}$  and  $^{13}\text{C}$ , an external  $\text{H}_3\text{PO}_4$  reference for  $^{31}\text{P}$  NMR, an external  $\text{BF}_3\cdot\text{OEt}_2$  reference for  $^{11}\text{B}$  NMR, and an external  $\text{CFCl}_3$  ( $\delta_{\text{F}} = 0.00$  ppm) reference for  $^{19}\text{F}$  NMR. The couplings for multiplicities of the NMR resonances,  $^nJ_{\text{AB}}$ , are reported in Hz. Virtual triplet  $^{13}\text{C}$  resonances characteristic of *trans*-bis( $\text{PPh}_3$ ) ligands are denoted  $t^{\nu}$  with the apparent coupling constant given.

Solution and Nujol Infrared spectra were obtained using a Perkin-Elmer Spectrum One FT-IR spectrometer, and ATR solid state spectra were obtained with a PerkinElmer FT-IR Spectrometer. Elemental microanalysis was performed at the London Metropolitan University. High- and Low-Resolution Electrospray Ionisation Mass Spectrometry (ESI-MS) was performed by the ANU Research School of Chemistry mass spectrometry service, using acetonitrile for the matrix.

Data for the X-ray crystallography analysis were obtained on either an Oxford Diffraction Xcalibur or Oxford Diffraction SuperNova diffractometer and processed using the *Olex* suite of software. The Checkcif-validated .cif files are available on request from the Cambridge Crystallographic Data Centre. The

known compounds  $[\text{RhCl}(\text{PPh}_3)_3]$  and  $[\text{RhCl}(\text{CS})(\text{PPh}_3)_2]$  were prepared as described below in accordance with the literature, and remaining reagents were obtained from commercial sources.

### Synthesis of $[\text{Rh}_2(\mu\text{-C})\text{Cl}_2(\text{PPh}_3)_4]$ (2)

The complex  $\text{RhCl}(\text{CS})(\text{PPh}_3)_2$  (**1**: 550 mg, 0.778 mmol) was partially dissolved in dry benzene (40 mL). A solution of  $\text{HBcat}$  in THF (8.0 mL, 0.30 M, 2.4 mmol) was added and the solution stirred with heating at  $50^\circ\text{C}$  for fifteen hours. The solution was concentrated under reduced pressure and the orange product **2** which precipitated by addition of benzene (20 mL) was isolated *via* cannula filtration and dried *in vacuo*. Yield 214 mg (0.160 mmol, 41%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta_{\text{H}} = 7.13\text{--}7.17$  [m, 24 H,  $\text{H}^{2,6}(\text{C}_6\text{H}_5)$ ], 7.27–7.30 [m, 12 H,  $\text{H}^4(\text{C}_6\text{H}_5)$ ], 7.39–7.44 [m, 24 H,  $\text{H}^{3,5}(\text{C}_6\text{H}_5)$ ].  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 176 MHz)  $\delta_{\text{C}} = 424.4$  (t.br,  $\mu\text{-C}$ ,  $^1J_{\text{RhC}} = 47$ ,  $^2J_{\text{PC}}$  not resolved), 134.9 [ $t^{\nu}$ ,  $\text{C}^4(\text{C}_6\text{H}_5)$ ,  $J = 6$ ], 133.1 [ $t^{\nu}$ ,  $\text{C}^{2,6}(\text{C}_6\text{H}_5)$ ,  $J = 22$ ], 129.4 [ $t^{\nu}$ ,  $\text{C}^{3,5}(\text{C}_6\text{H}_5)$ ,  $J = 5$  Hz], 127.9 [ $\text{C}^4(\text{C}_6\text{H}_5)$ ].  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 162 MHz)  $\delta_{\text{P}} = 21.61$  (dd,  $^1J_{\text{RHP}} = 180$ ,  $^3J_{\text{RHP}} = 7$  Hz). IR (ATR,  $\text{cm}^{-1}$ )  $\nu_{\text{max}} = 1011$  ( $\nu_{\text{Rh=C=Rh}}$ ). MS-ESI(+):  $m/z = 1301.14$  [ $\text{M-Cl}$ ] $^+$ , 1039.05 [ $\text{M-Cl-PPh}_3$ ] $^+$ . Accurate mass: found 1301.1438 [ $\text{M-Cl+H}$ ] $^+$ . Calc. for  $\text{C}_{73}\text{H}_{60}^{35}\text{Cl}_2\text{P}_4\text{Rh}_2$ : 1301.1444. Anal. found: C, 62.90; H, 4.62%. Calcd. for  $\text{C}_{73}\text{H}_{60}\text{Cl}_2\text{P}_4\text{Rh}_2\cdot\text{CH}_2\text{Cl}_2$ : C, 62.47; H, 4.39%. The compound was structurally characterised as a dichloromethane monosolvate through single crystal X-ray crystallography. *Crystal data for*  $\text{C}_{73}\text{H}_{60}\text{Cl}_2\text{P}_4\text{Rh}_2\cdot\text{CH}_2\text{Cl}_2$ :  $M_w = 1422.73$ , triclinic,  $P-1$  (No. 2),  $a = 12.5983(2)$ ,  $b = 13.8742(3)$ ,  $c = 20.5650(4)$  Å,  $\alpha = 85.461(2)$ ,  $\beta = 84.238(1)$ ,  $\gamma = 75.285(1)^\circ$ ,  $V = 3453.74(12)$  Å $^3$ ,  $Z = 2$ ,  $\rho_{\text{calcd}} = 1.368$  Mg m $^{-3}$ ,  $\mu(\text{Cu K}\alpha) = 6.47$  mm $^{-1}$ ,  $T = 150.0(1)$  K, red block  $0.27 \times 0.14 \times 0.09$  mm, 13,963 independent reflections,  $F^2$  refinement,  $R_1 = 0.0345$ ,  $wR_2 = 0.090$  for 12,988 reflections ( $I > 2\sigma(I)$ ),  $2\theta_{\text{max}} = 147.6^\circ$ ), 757 parameters. The asymmetric cell contained one molecule of  $\text{Rh}_2(\mu\text{-C})\text{Cl}_2(\text{PPh}_3)_4$ , a molecule of DCM and what was believed to be an additional two heavily disordered DCM molecules. No sensible disordered model could be formulated for the unknown solvates which would match the observed

<sup>a</sup> Research School of Chemistry, Australian National University, Canberra, Australian Capital Territory, ACT 2601, Australia.

<sup>†</sup> Corresponding author: Email: a.hill@anu.edu.au

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electron density, so the computer program SQUEEZE within PLATON was used to account for the electron density in this region of the unit cell. The program identified solvent accessible voids totalling 454.6 Å<sup>3</sup> and 133.8 electrons per unit cell were recovered. The formula weight, density etc. listed above do not include any correction for the missing solvate.

### Synthesis of [Rh<sub>2</sub>(μ-C)(PPh<sub>3</sub>)<sub>2</sub>{H<sub>2</sub>B(pz)<sub>2</sub>}]<sub>2</sub> (5a)

Complex **2** (116 mg, 0.0867 mmol) and K[H<sub>2</sub>B(pz)<sub>2</sub>] (62 mg, 0.33 mmol) were dissolved in dry dichloromethane (20 mL). The orange solution was stirred with heating at reflux for 12 hours. The red solution was concentrated under reduced pressure then diluted with ethanol (10 mL). Slow removal of dichloromethane under reduced pressure precipitated the orange product, which was isolated *via* vacuum filtration and washed with cold ethanol and dried *in vacuo*. Yield 54 g (0.040 mmol, 46%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> = 3.37 (br. BH), 5.30, 5.96, 6.00 [s x 3, 6 H, H<sup>4</sup>(pz)], 7.03-7.48 [m x 3, 38 H, PPh<sub>3</sub> and H<sup>3,5</sup>(pz)], 8.88 [2, 2 H, H<sup>3,5</sup>(pz)]. <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>) δ<sub>P</sub> = 38.18 (d, <sup>1</sup>J<sub>RhP</sub> = 212 Hz). <sup>11</sup>B{<sup>1</sup>H} NMR (128 MHz, CDCl<sub>3</sub>) δ<sub>B</sub> = -8.49 (br.). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> = 135.4, 135.2 [C<sup>5</sup>(pz)], 134.8 [d, <sup>2</sup>J<sub>PC</sub> = 11, C<sup>2,6</sup>(C<sub>6</sub>H<sub>5</sub>)], 132.9 [d, <sup>1</sup>J<sub>PC</sub> = 41, C<sup>1</sup>(C<sub>6</sub>H<sub>5</sub>)], 132.2 [d, <sup>2</sup>J<sub>RhC</sub> = 9, C<sup>3</sup>(pz)], 129.9 [C<sup>4</sup>(C<sub>6</sub>H<sub>5</sub>)], 128.6 [d, <sup>2</sup>J<sub>RhP</sub> = 11, C<sup>3</sup>(pz)], 128.0 [d, <sup>3</sup>J<sub>PC</sub> = 9, C<sup>3,5</sup>(C<sub>6</sub>H<sub>5</sub>)], 104.0, 103.9 [C<sup>4</sup>(pz)]. IR (ATR, cm<sup>-1</sup>) ν<sub>max</sub> = 2403 (ν<sub>BH</sub>), 2286 (ν<sub>BH</sub>), 1301 (ν<sub>CN</sub>), 1243 (ν<sub>CN</sub>), 1023 (ν<sub>Rh=C=Rh</sub>). MS-ESI(+): *m/z* = 773.25 [M-PPh<sub>3</sub>]<sup>+</sup>. Accurate mass: found 1035.1505 [M-H]<sup>+</sup>. Calc. for C<sub>49</sub>H<sub>45</sub>N<sub>8</sub><sup>11</sup>B<sub>2</sub>P<sub>2</sub>Rh<sub>2</sub>: 1035.1553 Anal. found: C, 52.97; H, 4.81; N, 9.52%. Calcd. for C<sub>49</sub>H<sub>46</sub>B<sub>2</sub>N<sub>8</sub>P<sub>2</sub>Rh<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub>: C, 53.56; H, 4.31; N, 9.99%. The compound was structurally characterised through single crystal X-ray crystallography of a dichloromethane solvate. *Crystal data for* C<sub>49</sub>H<sub>46</sub>B<sub>2</sub>N<sub>8</sub>P<sub>2</sub>Rh<sub>2</sub>·(CH<sub>2</sub>Cl<sub>2</sub>)<sub>1.25</sub>: *M<sub>w</sub>* = 1142.47, monoclinic, *P2<sub>1</sub>/c*, *a* = 23.9780(5), *b* = 18.6930(2), *c* = 23.8266(4) Å, β = 97.097(2)°, γ = 90°, *V* = 10597.8(3) Å<sup>3</sup>, *Z* = 8, ρ<sub>calcd</sub> = 1.432 Mg m<sup>-3</sup>, μ(Mo Kα) = 0.85 mm<sup>-1</sup>, *T* = 150.0(1) K, orange plate, 0.65 × 0.18 × 0.17 mm, 21,633 independent reflections, *F*<sup>2</sup> refinement, *R*<sub>1</sub> = 0.087, *wR*<sub>2</sub> = 0.227 for 17,224 reflections (*I* > 2σ(*I*), 2θ<sub>max</sub> = 52.8°), 1185 parameters, 269 restraints. The asymmetric cell contained two molecules of Rh<sub>2</sub>(μ-C)(Bp)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, with 1.25 solvent molecule of DCM present. One DCM molecule was disordered over two positions with half occupancy in each.

### Synthesis of [Rh<sub>2</sub>(μ-C)(PPh<sub>3</sub>)<sub>2</sub>{H<sub>2</sub>B(pzMe<sub>2</sub>)<sub>2</sub>}]<sub>2</sub> (5b)

The complex **2** (150 mg, 0.112 mmol) and K[H<sub>2</sub>B(pzMe<sub>2</sub>)<sub>2</sub>] (100 mg, 0.413 mmol) were dissolved in dry dichloromethane (20 mL). The solution was stirred with heating at reflux for three hours, turning red in colour. The solution was concentrated under reduced pressure, and ethanol (10 mL) added to precipitate the orange product, which was isolated *via* vacuum filtration and dried *in vacuo*. Yield: 42 mg (0.037 mmol, 33%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> = 1.43, 2.00, 2.31 [s x 3, 23 H, pzCH<sub>3</sub>], 3.33 [br. d, 2 H, BH<sub>2</sub>], 5.02, 5.85 [s x 2, 4 H, H<sup>3</sup>(pz)], 6.93, 7.14, 7.29 [m x 3, 30 H, C<sub>6</sub>H<sub>5</sub>]. <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>) δ<sub>P</sub> =

38.62 (d, <sup>1</sup>J<sub>RhP</sub> = 222 Hz). <sup>11</sup>B{<sup>1</sup>H} NMR (128 MHz, CDCl<sub>3</sub>) δ<sub>B</sub> = -12.5 (br.). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> = 148.6, 148.0, 143.1 [C<sup>3,5</sup>(pz)], 134.7 [d, C<sup>1</sup>(C<sub>6</sub>H<sub>5</sub>)], <sup>1</sup>J<sub>PC</sub> = 12], 132.5 [d, C<sup>2,6</sup>(C<sub>6</sub>H<sub>5</sub>)], <sup>2</sup>J<sub>PC</sub> = 25 Hz], 129.2 [br. d, C<sup>3,5</sup>(C<sub>6</sub>H<sub>5</sub>)], <sup>3</sup>J<sub>PC</sub> = 50 Hz], 127.3 [d, C<sup>4</sup>(C<sub>6</sub>H<sub>5</sub>)], <sup>4</sup>J<sub>PC</sub> = 9 Hz], 106.0, 104.7 [C<sup>4</sup>(pz)], 13.8, 12.9, 12.0 (pzCH<sub>3</sub>). IR (ATR, cm<sup>-1</sup>) ν<sub>max</sub> = 2458 (ν<sub>BH</sub>), 1538 (ν<sub>C=C</sub>), 1373 (ν<sub>CN</sub>), 1159 (ν<sub>CN</sub>), 978 (ν<sub>Rh=C=Rh</sub>). Accurate mass: found 1117.07132 [M-pz\* + MeCN + Na]<sup>+</sup>. Calc. for C<sub>54</sub>H<sub>58</sub><sup>11</sup>B<sub>2</sub>N<sub>7</sub>NaP<sub>2</sub>Rh<sub>2</sub>: 1117.2423. The compound was structurally characterised through single crystal X-ray crystallography of a hexane solvate. *Crystal data for* C<sub>57</sub>H<sub>62</sub>B<sub>2</sub>N<sub>8</sub>P<sub>2</sub>Rh<sub>2</sub>·C<sub>6</sub>H<sub>14</sub>: *M<sub>w</sub>* = 1234.69, monoclinic, *I2/a*, *a* = 18.7605(7), *b* = 13.5447(6), *c* = 23.3266(10) Å, β = 99.155(4)°, *V* = 5851.9(4) Å<sup>3</sup>, *Z* = 4, ρ<sub>calcd</sub> = 1.401 Mg m<sup>-3</sup>, μ(Mo Kα) = 0.67 mm<sup>-1</sup>, *T* = 150.0(1) K, red plate, 0.48 × 0.36 × 0.24 mm, 5,971 independent reflections, *F*<sup>2</sup> refinement, *R*<sub>1</sub> = 0.047, *wR*<sub>2</sub> = 0.128 for 4,551 reflections (*I* > 2σ(*I*), 2θ<sub>max</sub> = 26.4°), 361 parameters, no restraints. The asymmetric cell contained one molecule of Rh<sub>2</sub>(μ-C)(Bp\*)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, with one solvent molecule of n-hexane present.

### Synthesis of [Rh<sub>2</sub>(μ-C)(PPh<sub>3</sub>)<sub>2</sub>{HB(pz)<sub>3</sub>}]<sub>2</sub> (6a)

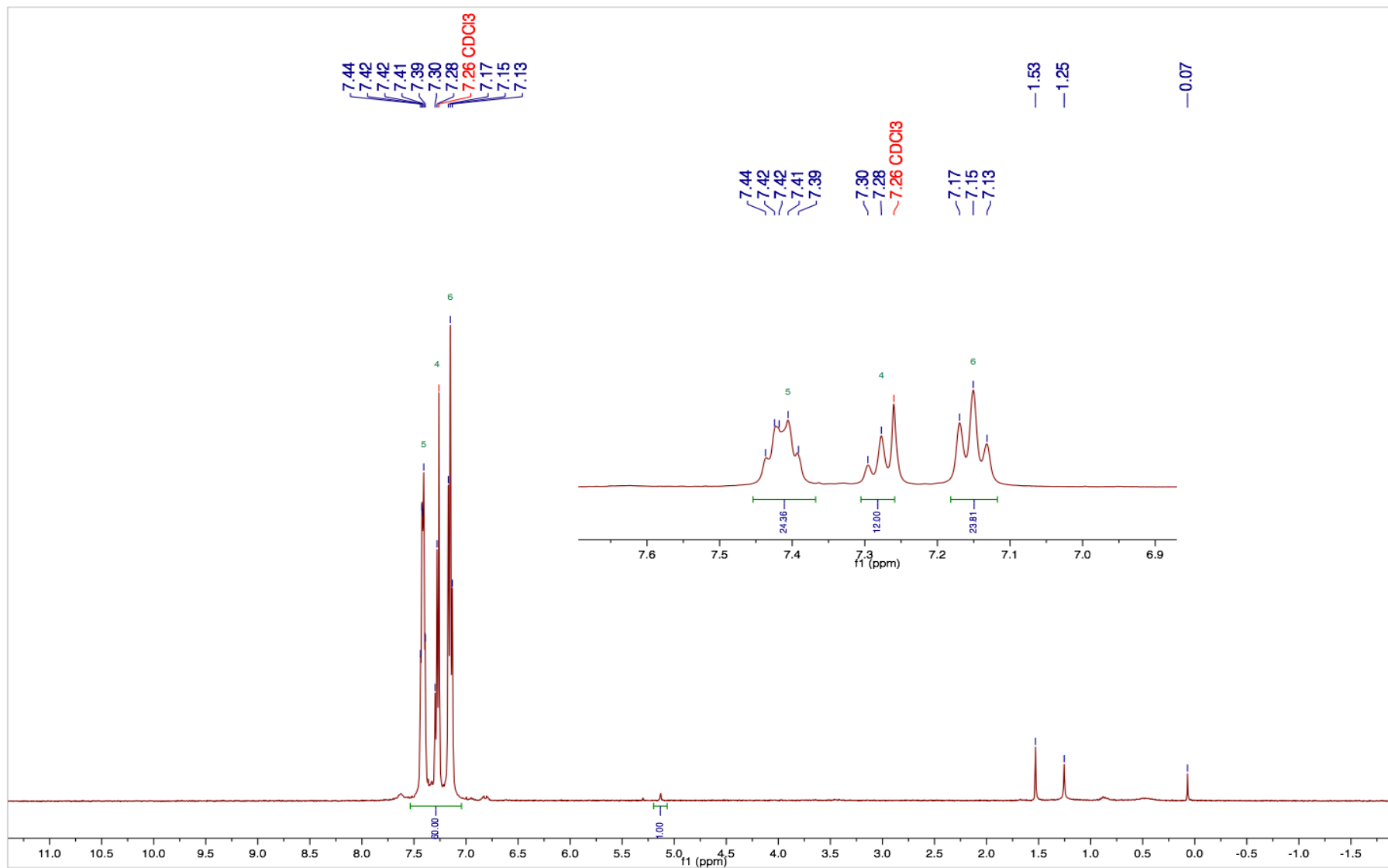
The complex **2** (150 mg, 0.112 mmol) and K[HB(pz)<sub>3</sub>] (102 mg, 0.409 mmol) were dissolved in dry dichloromethane (25 mL). The orange solution was stirred at room temperature for 16 hours, turning red in colour. The solution was concentrated under reduced pressure and then diluted with ethanol (10 mL) before the remaining DCM was removed slowly. The red product precipitated in the ethanol solution, and was isolated *via* vacuum filtration. The product was washed with cold ethanol and dried *in vacuo*. Yield 62 mg (0.053 mmol, 48%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> = 4.53 (br., BH), 5.82 [s, 6 H, H<sup>4</sup>(pz)], 6.88, 7.13, 7.24, 7.51, 7.66 [m x 5, 42 H, C<sub>6</sub>H<sub>5</sub> and H<sup>3,5</sup>(pz)]. <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>) δ<sub>P</sub> = 42.64 [d, <sup>1</sup>J<sub>RhP</sub> = 214 Hz]. <sup>11</sup>B{<sup>1</sup>H} NMR (128 MHz, CDCl<sub>3</sub>) δ<sub>B</sub> = -3.16 (br.). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> = 135.6, 135.5 [C<sup>5</sup>(pz)], 135.2 [d, C<sup>1</sup>(C<sub>6</sub>H<sub>5</sub>)], *J* = 9 Hz], 132.3 [d, C<sup>2,6</sup>(C<sub>6</sub>H<sub>5</sub>)], <sup>2</sup>J<sub>PC</sub> = 10], 132.1, 132.0 [C<sup>3</sup>(pz)], 130.9 [d, C<sup>3,5</sup>(C<sub>6</sub>H<sub>5</sub>)], <sup>3</sup>J<sub>PC</sub> = 14], 128.6 [d, C<sup>4</sup>(C<sub>6</sub>H<sub>5</sub>)], <sup>4</sup>J<sub>PC</sub> = 12 Hz], 106.6, 106.5 [C<sup>4</sup>(pz)]. IR (ATR, cm<sup>-1</sup>): 2458 (ν<sub>BH</sub>), 1303 (ν<sub>CN</sub>), 1260 (ν<sub>CN</sub>), 1011 (ν<sub>Rh=C=Rh</sub>). Accurate mass: found 1169.2139 [M+H]<sup>+</sup>. Calcd. for C<sub>55</sub>H<sub>51</sub><sup>11</sup>B<sub>2</sub>N<sub>12</sub>P<sub>2</sub>Rh<sub>2</sub>·(CH<sub>2</sub>Cl<sub>2</sub>)<sub>1.5</sub>: C, 52.33; H, 4.20; N, 12.96%. The compound was structurally characterised through single crystal X-ray crystallography. *Crystal data for* C<sub>55</sub>H<sub>50</sub>B<sub>2</sub>N<sub>12</sub>P<sub>2</sub>Rh<sub>2</sub>: *M<sub>w</sub>* = 1168.45, orthorhombic, *P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>*, *a* = 18.8404(3), *b* = 13.2630(2), *c* = 11.7030(2) Å, *V* = 2924.35(8) Å<sup>3</sup>, *Z* = 2, ρ<sub>calcd</sub> = 1.327 Mg m<sup>-3</sup>, *T* = 150.0(1) K, red plate, 0.18 × 0.18 × 0.06 mm, 7,607 independent reflections, *F*<sup>2</sup> refinement, *R*<sub>1</sub> = 0.027, *wR*<sub>2</sub> = 0.055 for 6,900 reflections (*I* > 2σ(*I*), 2θ<sub>max</sub> = 30.1°), 330 parameters.

### Synthesis of [Rh<sub>2</sub>(μ-C)H(μ-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>){HB(pzMe<sub>2</sub>)<sub>3</sub>}]<sub>2</sub> (7)

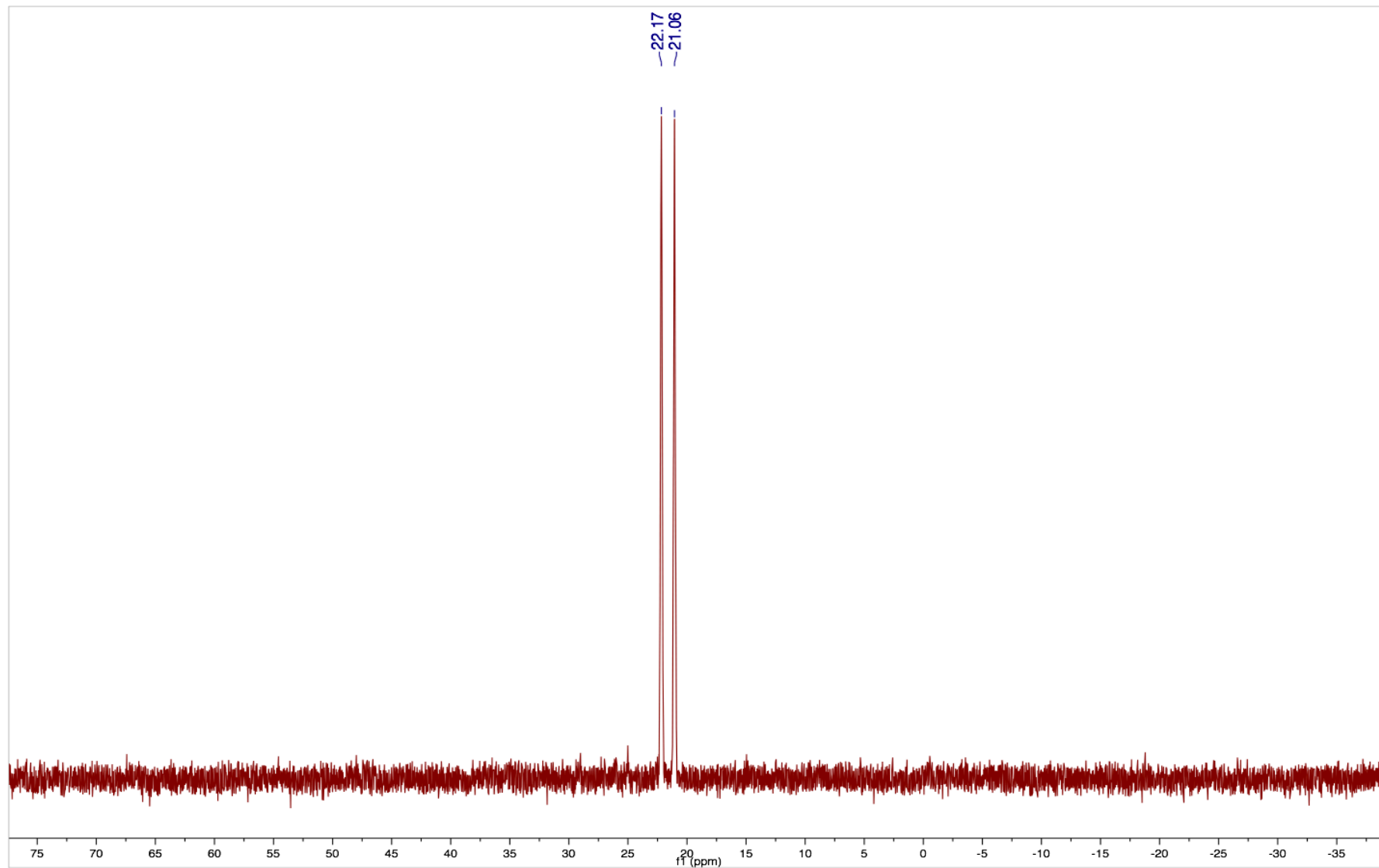
The complex **2** (150 mg, 0.112 mmol) and K[HB(pzMe<sub>2</sub>)<sub>3</sub>] (75 mg, 0.22 mmol) were dissolved in dry dichloromethane (20 mL)

and the solution was stirred at room temperature for three hours, turning dark red in colour. The solution was concentrated under reduced pressure, and dry ethanol added to precipitate the dark red product, which was washed with cold ethanol and dried *in vacuo*. Yield 82 mg (0.061 mmol, 54%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}} = -12.86$  (ddd, 1 H, RhH,  $^1J_{\text{RhH}} = 29$ ,  $^3J_{\text{RhH}} = 25$ ,  $^4J_{\text{PH}} = 3$  Hz), 7.85, 7.47, 7.43, 7.28, 7.09, 7.03, 6.85, 6.73 [m x 8, 14 H,  $\text{C}_6\text{H}_5$  and  $\text{C}_6\text{H}_4$ ], 5.66 (2H), 5.64, 5.60, 5.44, 5.42 [s x 5, 6 H,  $\text{H}^4(\text{pz})$ ], 4.46 (s.v.br, 1 H, BH), 2.69, 2.38, 2.33, 2.29, 2.26, 2.22, 2.19, 2.09, 1.72, 1.67, 1.56, 1.02 (pzCH<sub>3</sub>).  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{P}} = 60.70$  (dd,  $^1J_{\text{RHP}} = 226$ ,  $^3J_{\text{RHP}} = 35$  Hz).  $^{11}\text{B}\{^1\text{H}\}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{B}} = -9.06$  (br. Not resolved).  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}} = ^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) 447.2 [ddd,  $^1J_{\text{RhC}} = 50.3$ , 39.9,  $^2J_{\text{PC}} = 19.6$ , HMBC with  $\delta_{\text{H}} = -12.7$ ; Rh=C=Rh], 165.4 [HMBC with  $\delta_{\text{H}} = -12.7$ ,  $\text{C}^2(\text{PC}_6\text{H}_4\text{Rh})$ ], 151.6, 151.2, 150.4, 149.7, 149.5, 148.8 [ $\text{C}^5(\text{pz})$ ], 145.0, 144.9, 143.4, 143.3, 143.0, 143.0 [ $\text{C}^3(\text{pz})$ ], 140.6 [d,  $^2J_{\text{PC}} = 18.2$ ,  $\text{C}^6(\text{PC}_6\text{H}_4\text{Rh})$ ], 137.1 [d,  $^2J_{\text{PC}} = 11.2$ ,  $\text{C}^{2,6}(\text{C}_6\text{H}_5)$ ], 135.6 [d,  $^2J_{\text{PC}} = 11.2$ ,  $\text{C}^5(\text{PC}_6\text{H}_4\text{Rh})$ ], 132.4 [d,  $^1J_{\text{PC}} = 55.1$ ,  $\text{C}^1(\text{C}_6\text{H}_5)$ ], 131.70 [d,  $^1J_{\text{PC}} = 37.9$ ,  $\text{C}^1(\text{C}_6\text{H}_5)$ ], 131.1 [d,  $^1J_{\text{PC}} = 13.7$ ,  $\text{C}^1(\text{PC}_6\text{H}_4\text{Rh})$ ], 130.4, 129.9 [ $\text{C}^4(\text{C}_6\text{H}_5)$ ], 127.84 [d,  $\text{C}^{3,5}(\text{C}_6\text{H}_5)$ ,  $^3J_{\text{PC}} = 10.0$ ], 127.73, [d,  $\text{C}^{3,5}(\text{C}_6\text{H}_5)$ ,  $^3J_{\text{PC}} = 11.0$ ], 126.7 [ $\text{C}^4(\text{PC}_6\text{H}_4\text{Rh})$ ], 122.3 [d,  $^2J_{\text{PC}} = 8.3$  Hz,  $\text{C}^5(\text{PC}_6\text{H}_4\text{Rh})$ ], 106.3, 106.2, 105.6(2C), 105.3, 105.1 [ $\text{C}^4(\text{pz})$ ], 16.6, 15.7, 15.4, 14.8, 14.7, 14.4, 13.9, 13.1, 12.91, 12.85, 12.8, 12.7 [pzCH<sub>3</sub>]. The quaternary resonance for the *ortho* bridging carbon (expected to be a ddd) was unable to be unambiguously identified in the 1-D  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum due to multiplicity and poor signal/noise. It could however be identified via a HMBC  $^1\text{H}$ - $^{13}\text{C}$  experiment at 165.4 ppm through correlation to the hydride resonance. IR (ATR,  $\text{cm}^{-1}$ ): 2521 ( $\nu_{\text{BH}}$ ), 2076 ( $\nu_{\text{RhH}}$ ), 1544 ( $\nu_{\text{C=C}}$ ), 1382 ( $\nu_{\text{CN}}$ ), 1203 ( $\nu_{\text{CN}}$ ), 1003 ( $\nu_{\text{Rh=C=Rh}}$ ). MS-ESI(+):  $m/z = 1075.31$  [ $\text{M}+\text{H}$ ] $^+$ . Accurate mass: found 1075.3123 [ $\text{M}+\text{H}$ ] $^+$ . Calcd. for  $\text{C}_{49}\text{H}_{60}^{11}\text{B}_2\text{N}_{12}\text{PRh}_2$  1075.4879. Anal. found: C, 45.82; H, 4.25; N, 9.17%. Calcd. for  $\text{C}_{49}\text{H}_{59}\text{B}_2\text{N}_{12}\text{PRh}_2 \cdot (\text{CH}_2\text{Cl}_2)_3$ : C, 46.98; H, 4.93; N, 12.64%. The compound was structurally characterised through single crystal X-ray crystallography. *Crystal data for*  $\text{C}_{49}\text{H}_{59}\text{B}_2\text{N}_{12}\text{PRh}_2$ :  $M_w = 1074.49$ , monoclinic,  $C2/c$ ,  $a = 26.2284(10)$ ,  $b = 10.6335(4)$ ,  $c = 38.1132(13)$  Å,  $\beta = 97.948(4)^\circ$ ,  $V = 10527.6(7)$  Å<sup>3</sup>,  $Z = 8$ ,  $\rho_{\text{calcd}} = 1.356$  Mgm<sup>-3</sup>,  $T = 150.0(1)$  K, red needle,  $0.30 \times 0.09 \times 0.06$  mm, 9,285 independent reflections,  $F^2$  refinement,  $R_1 = 0.059$ ,  $wR_2 = 0.126$  for 6,797 reflections ( $I > 2\sigma(I)$ ),  $2\theta_{\text{max}} = 25.0^\circ$ , 611 parameters, 1 restraint.

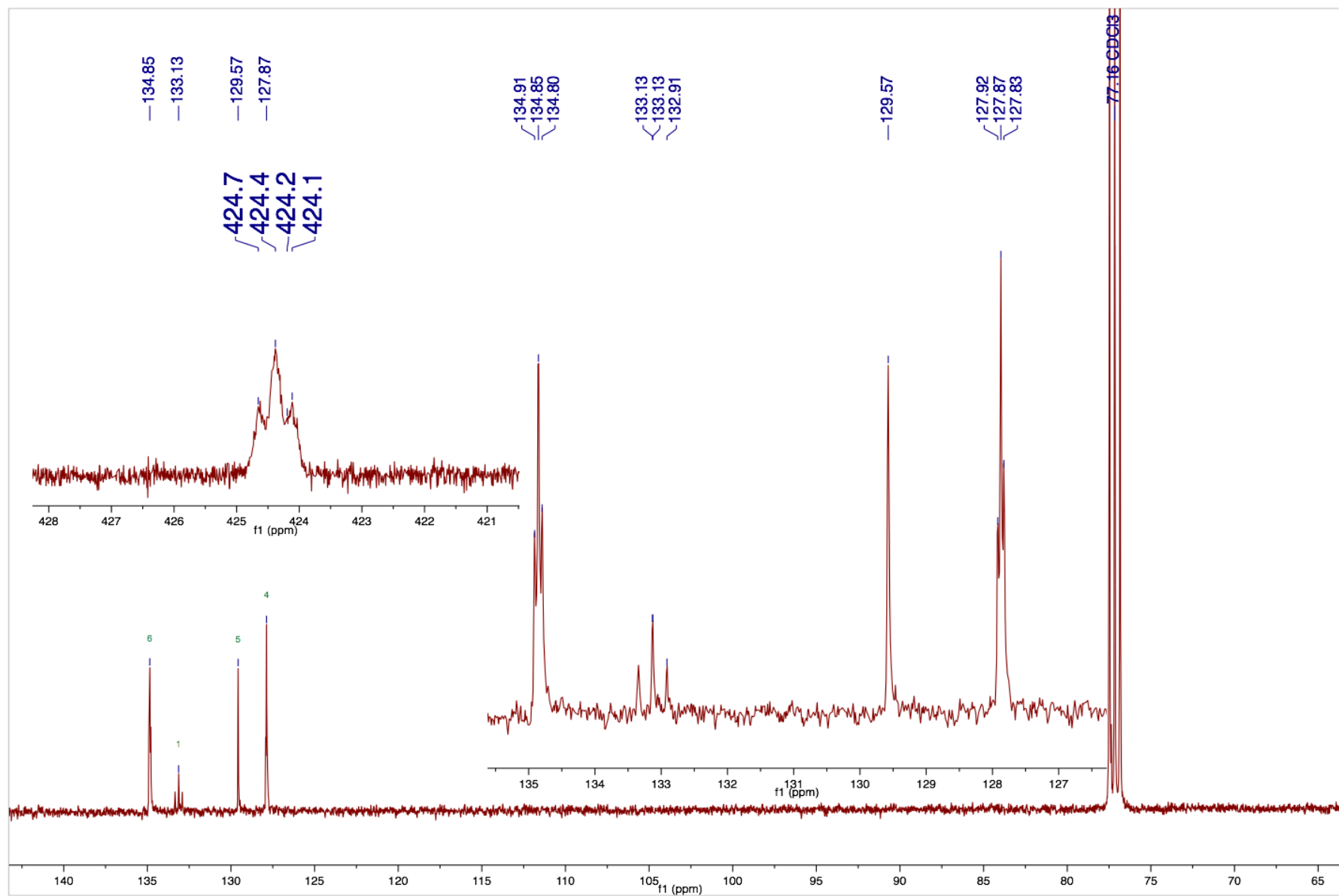
# $^1\text{H}$ NMR Spectrum of $[\text{Rh}_2(\mu\text{-C})\text{Cl}_2(\text{PPh}_3)_4]$ (2)



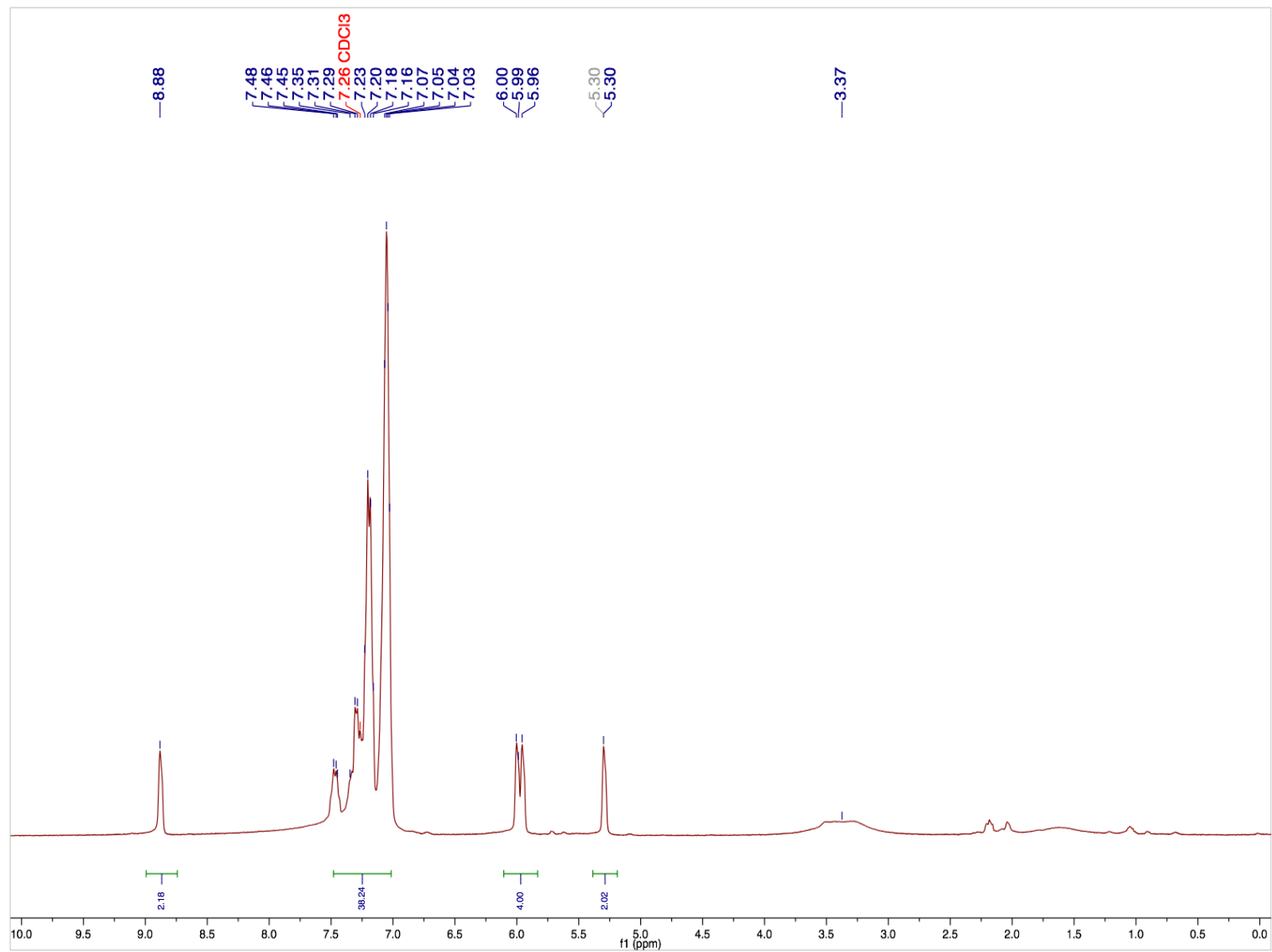
$^{31}\text{P}\{^1\text{H}\}$  NMR Spectrum of  $[\text{Rh}_2(\mu\text{-C})\text{Cl}_2(\text{PPh}_3)_4]$  (2)



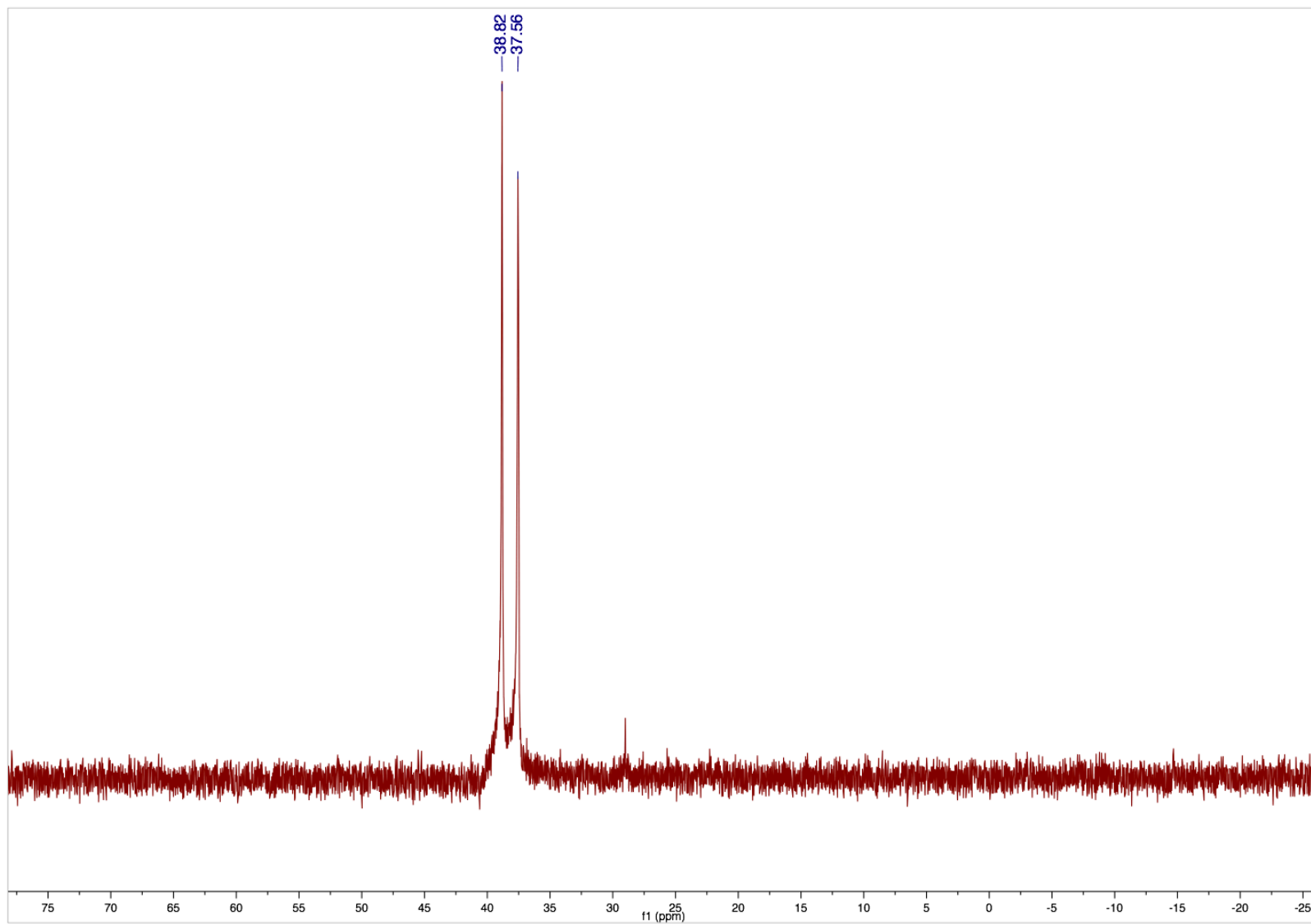
$^{13}\text{C}\{^1\text{H}\}$  NMR Spectrum of  $[\text{Rh}_2(\mu\text{-C})\text{Cl}_2(\text{PPh}_3)_4]$  (2) (Inset: Carbido atom ca 50%  $^{13}\text{C}$  enriched, originating from enriched  $^{13}\text{CS}_2$ )



**$^1\text{H}$  NMR Spectrum of  $[\text{Rh}_2(\mu\text{-C})(\text{Bp})_2(\text{PPh}_3)_2]$  (5a)**

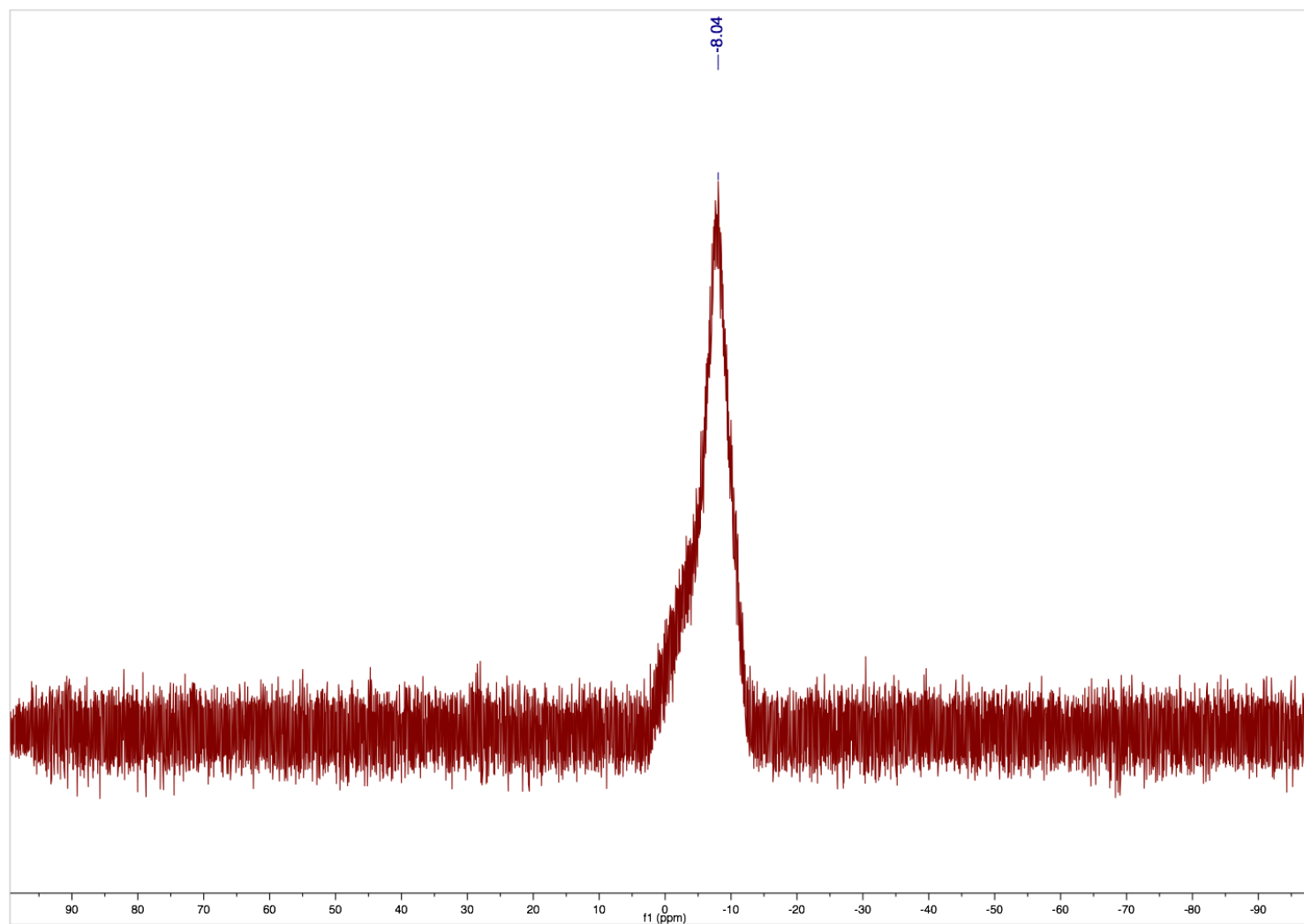


$^{31}\text{P}\{^1\text{H}\}$  NMR Spectrum of  $[\text{Rh}_2(\mu\text{-C})\text{Cl}_2(\text{PPh}_3)_4]$  (5a)

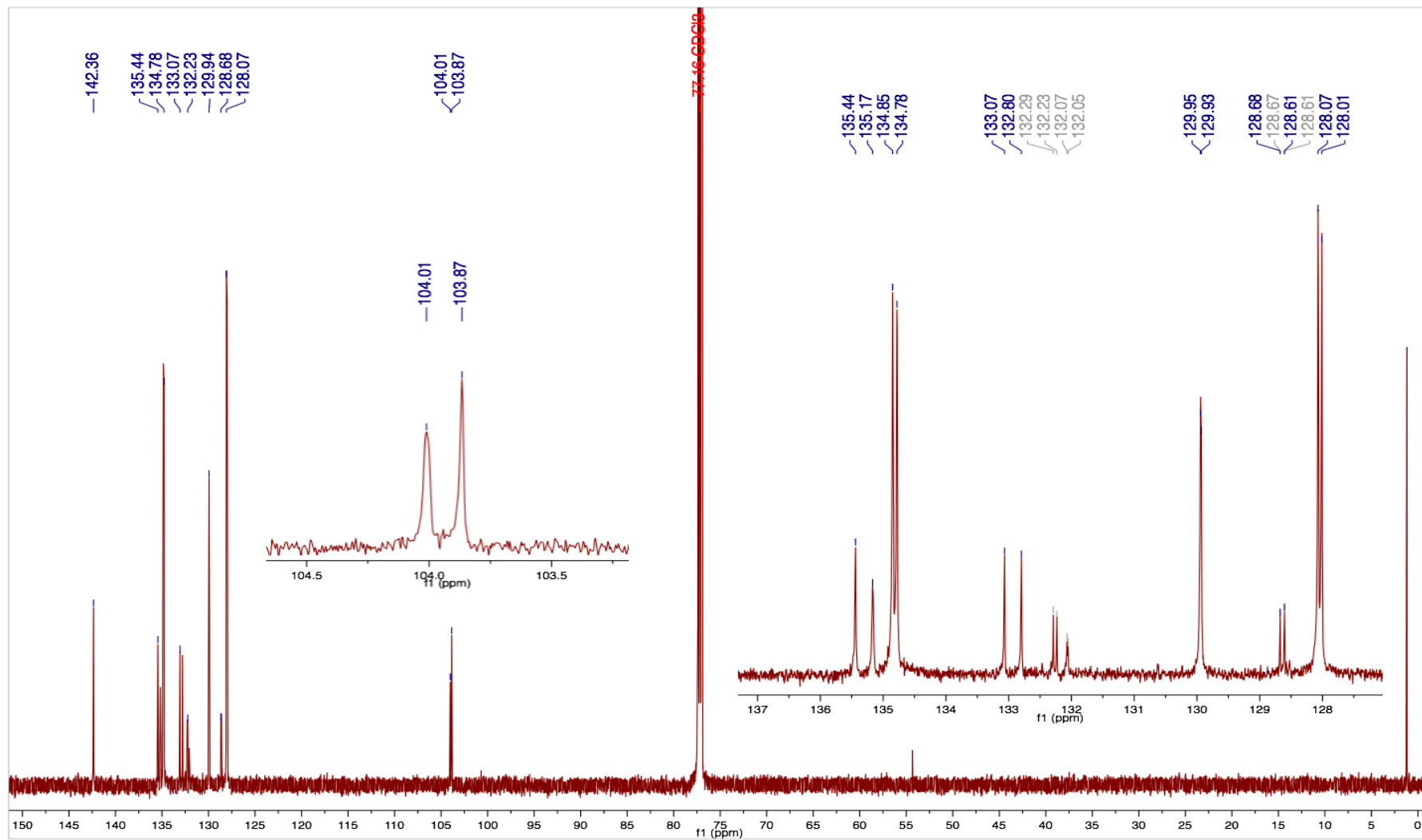




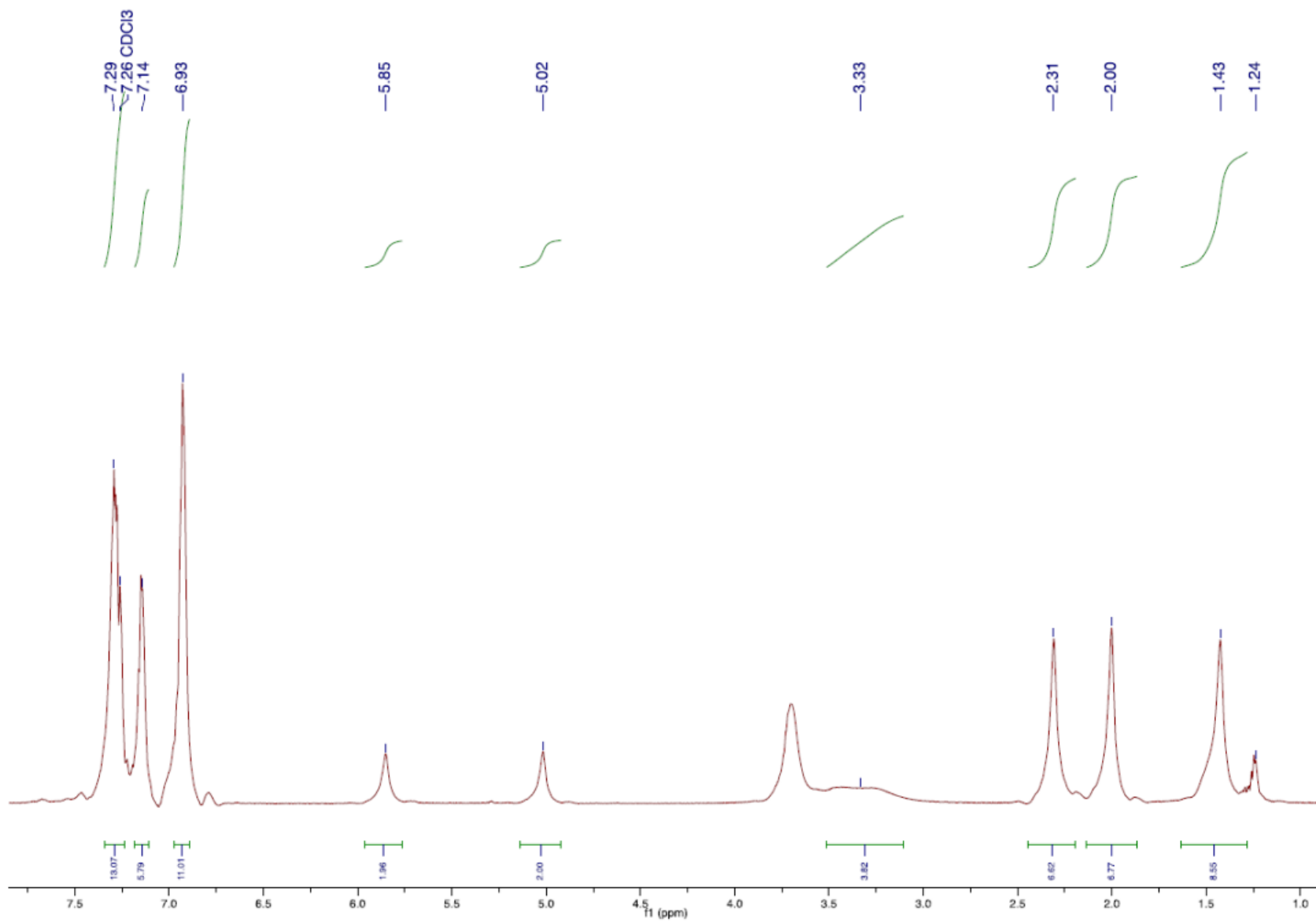
$^{11}\text{B}\{^1\text{H}\}$  NMR Spectrum of  $[\text{Rh}_2(\mu\text{-C})(\text{Bp})_2(\text{PPh}_3)_2]$  (5a)



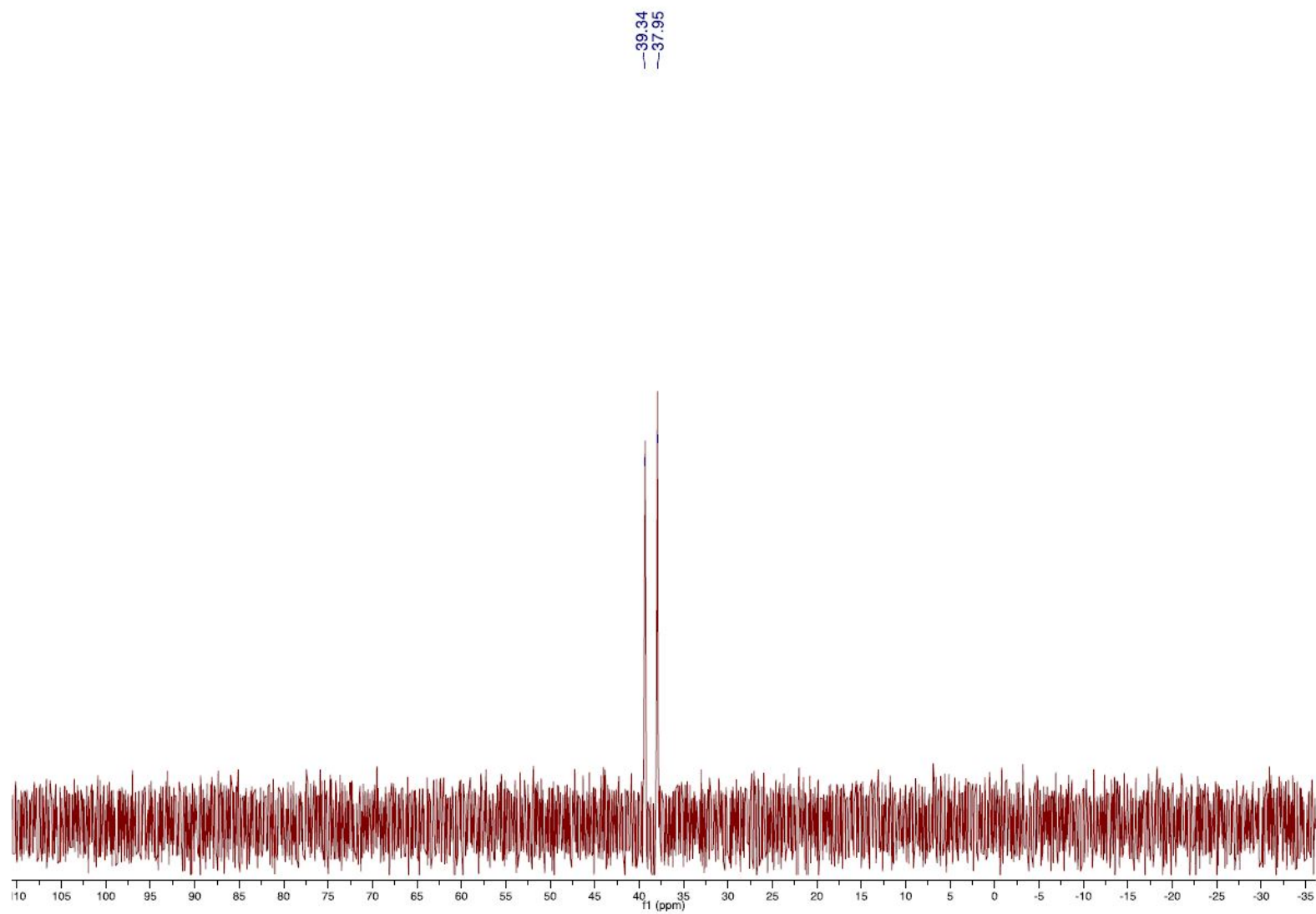
$^{13}\text{C}\{^1\text{H}\}$  NMR Spectrum of  $[\text{Rh}_2(\mu\text{-C})(\text{Bp})_2(\text{PPh}_3)_2]$  (5a)



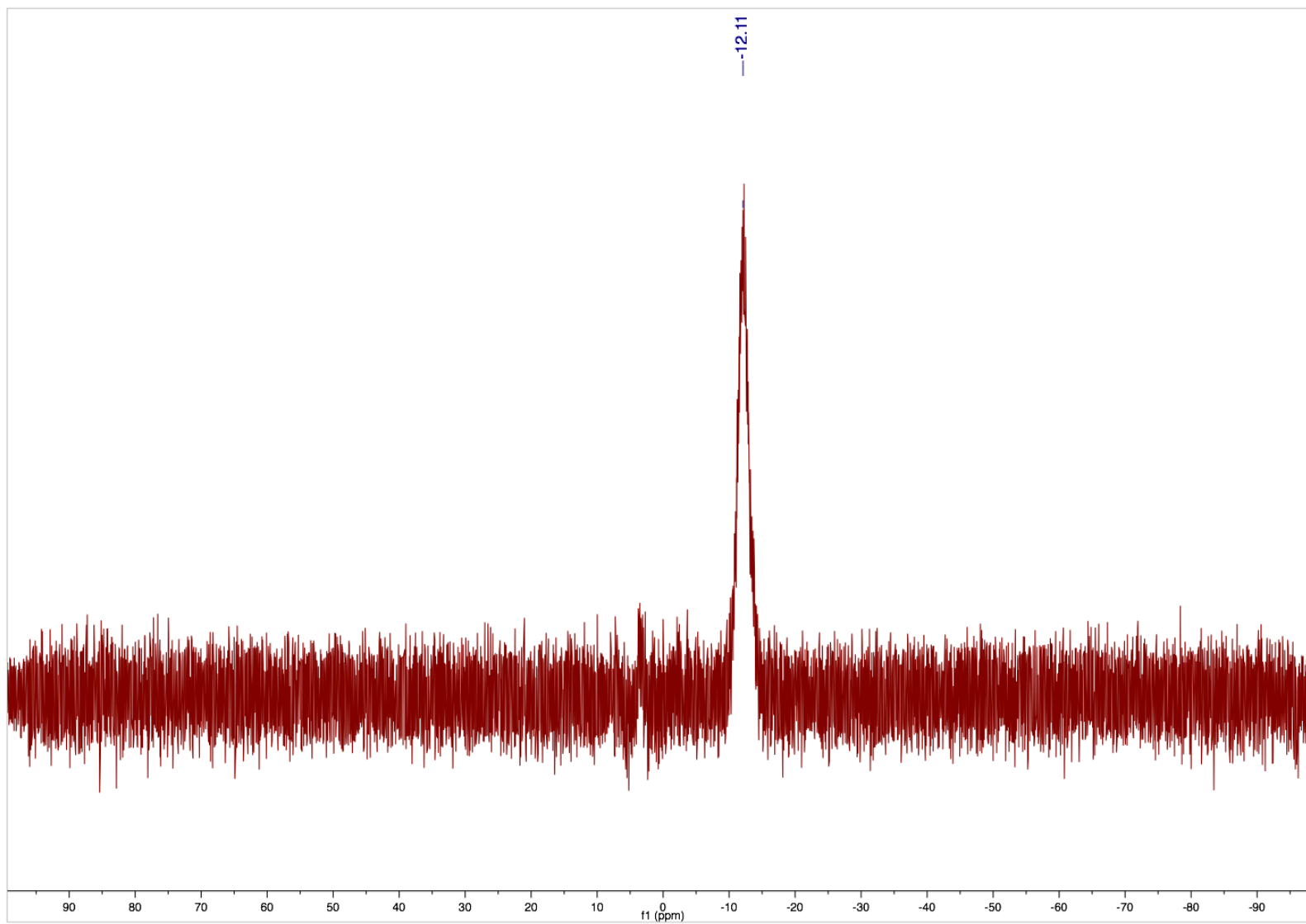
**$^1\text{H}$  NMR Spectrum of  $[\text{Rh}_2(\mu\text{-C})(\text{Bp}^*)_2(\text{PPh}_3)_2]$  (5b)**



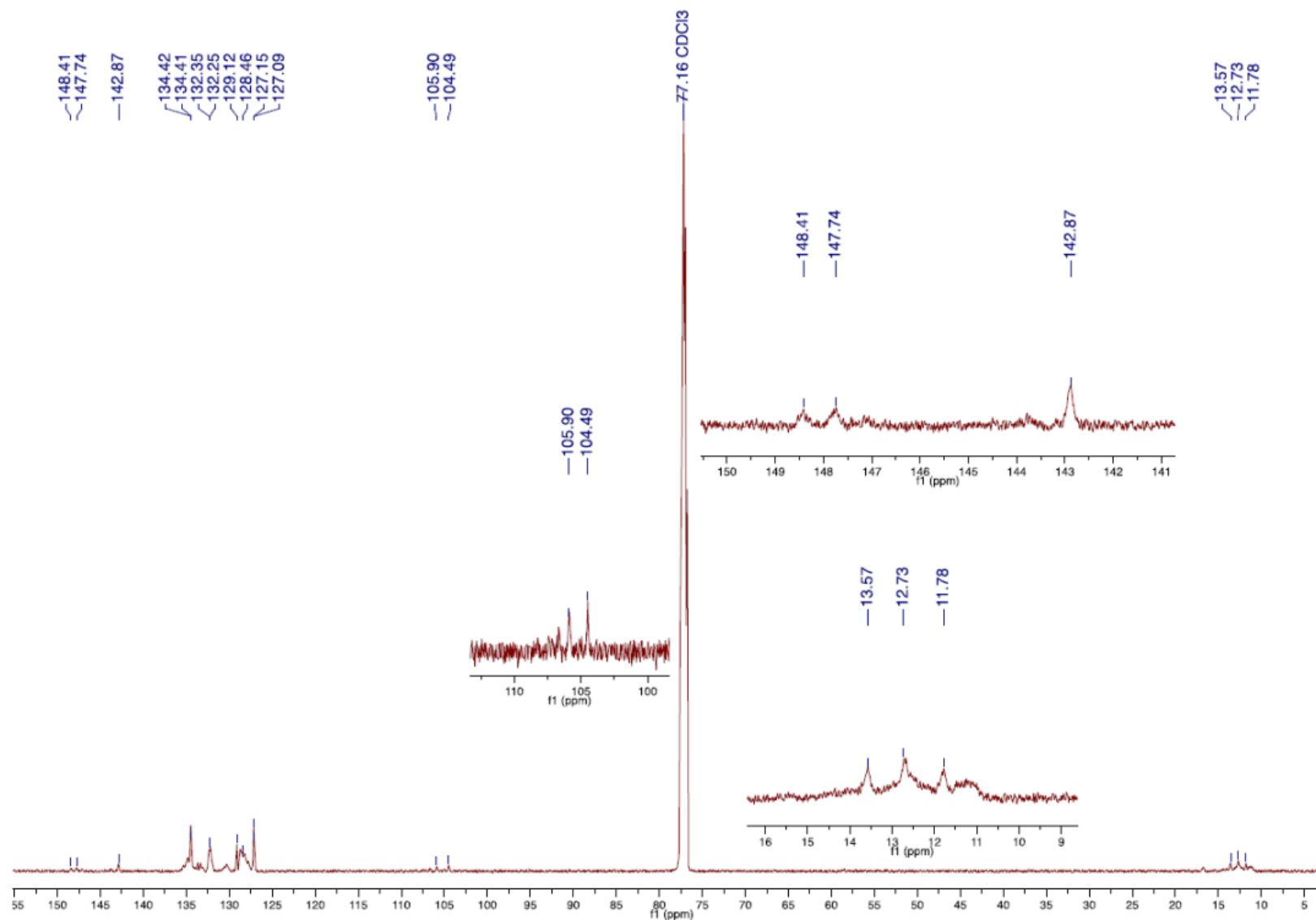
$^{31}\text{P}\{^1\text{H}\}$  NMR Spectrum of  $[\text{Rh}_2(\mu\text{-C})(\text{Bp}^*)_2(\text{PPh}_3)_2]$  (5b)



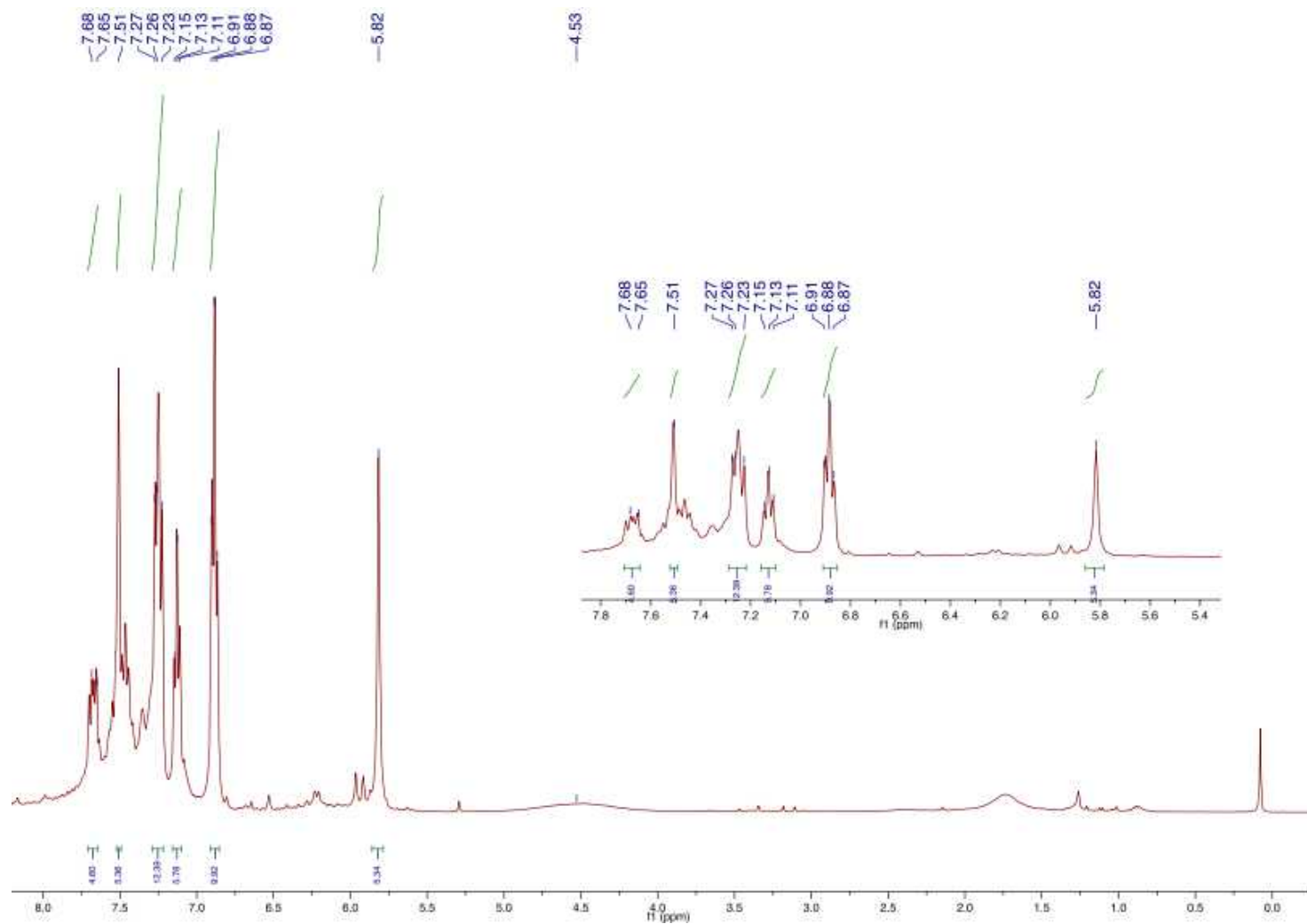
$^{11}\text{B}\{^1\text{H}\}$  NMR Spectrum of  $[\text{Rh}_2(\mu\text{-C})(\text{Bp}^*)_2(\text{PPh}_3)_2]$  (**5b**)



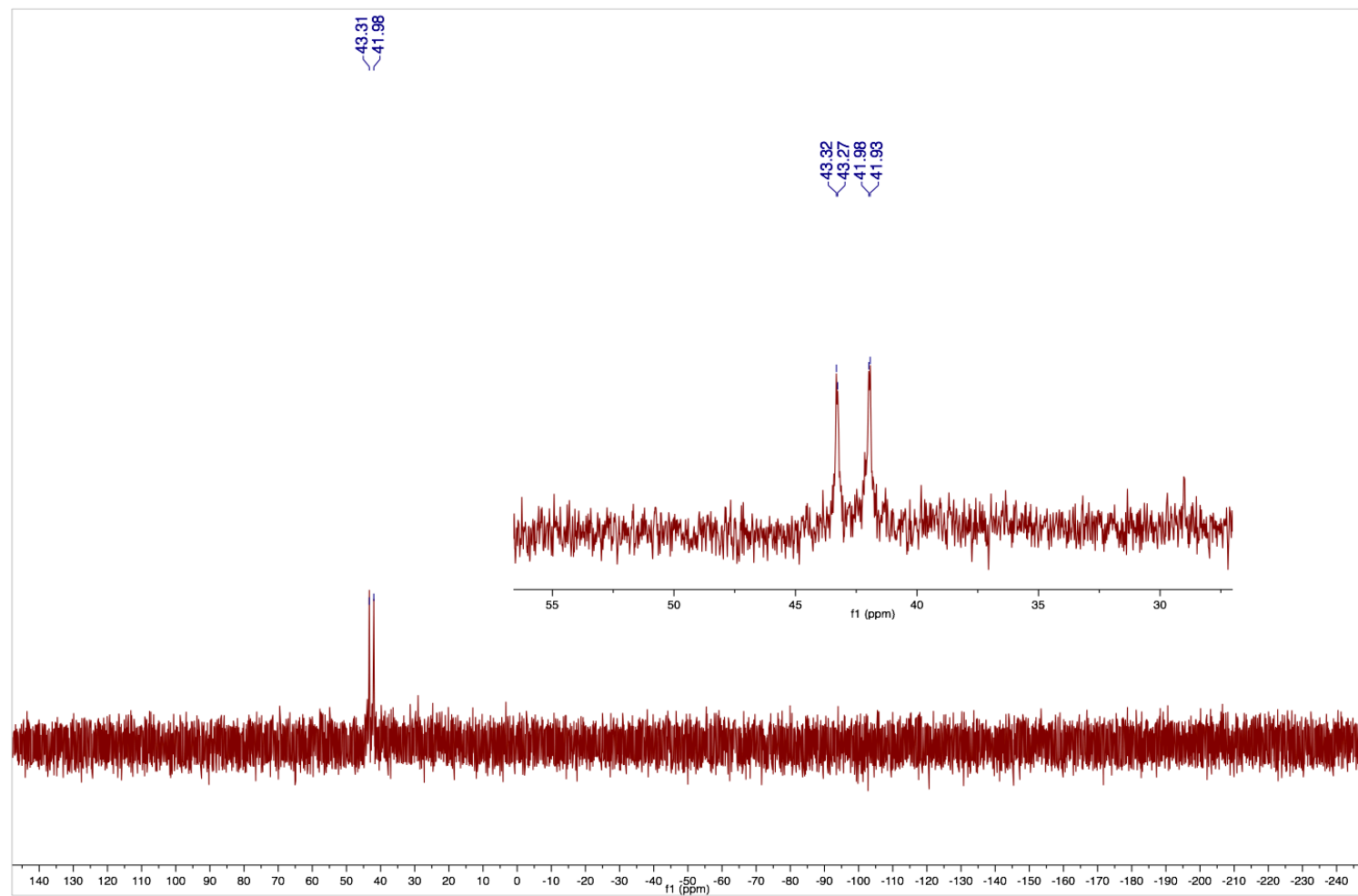
$^{13}\text{C}\{^1\text{H}\}$  NMR Spectrum of  $[\text{Rh}_2(\mu\text{-C})(\text{Bp}^*)_2(\text{PPh}_3)_2]$  (5b) (Poorly soluble)



# $^1\text{H}$ NMR Spectrum of $[\text{Rh}_2(\mu\text{-C})(\text{Tp})_2(\text{PPh}_3)_2]$ (6a)

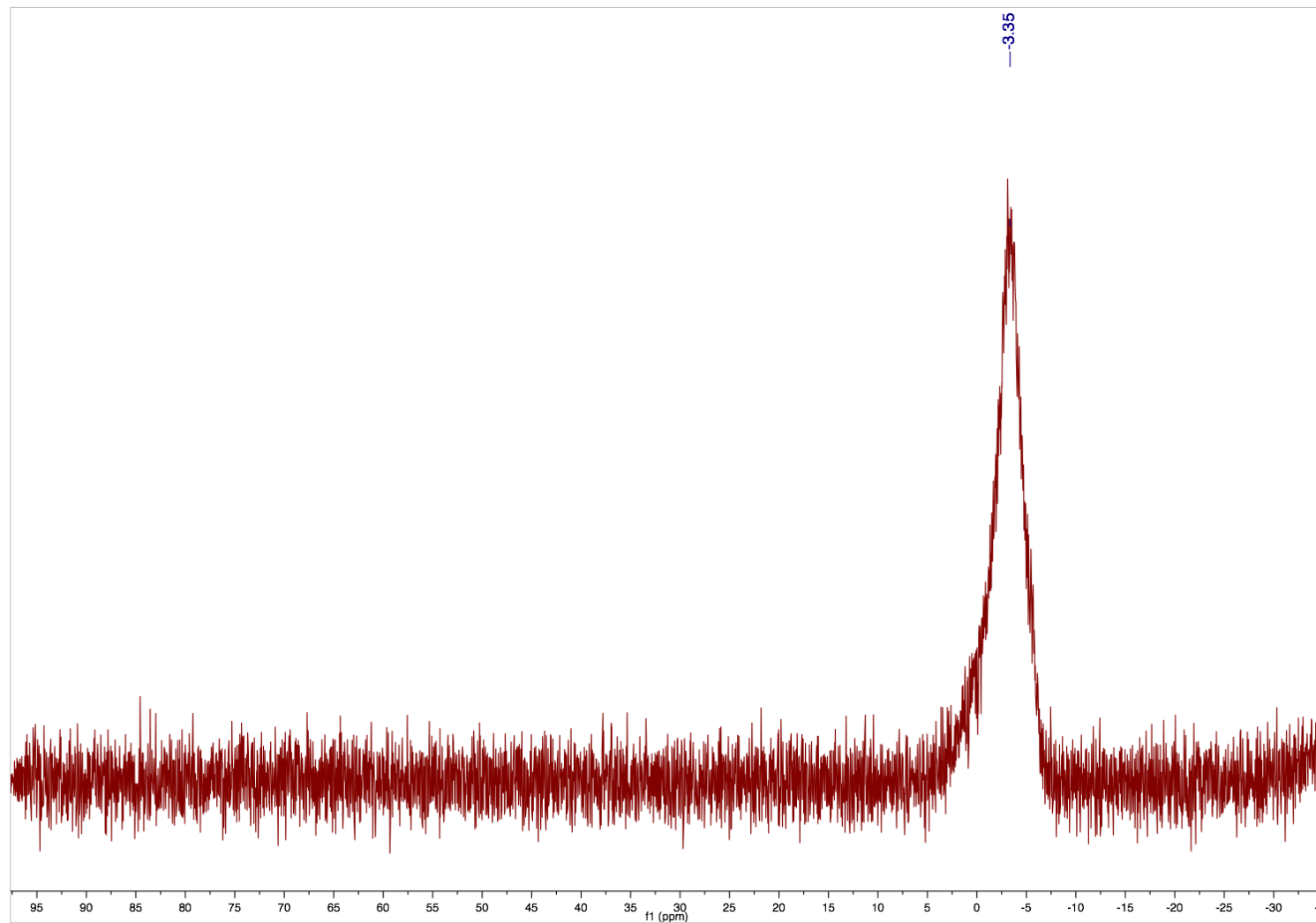


$^{31}\text{P}\{^1\text{H}\}$  NMR Spectrum of  $[\text{Rh}_2(\mu\text{-C})(\text{Tp})_2(\text{PPh}_3)_2]$  (6a)

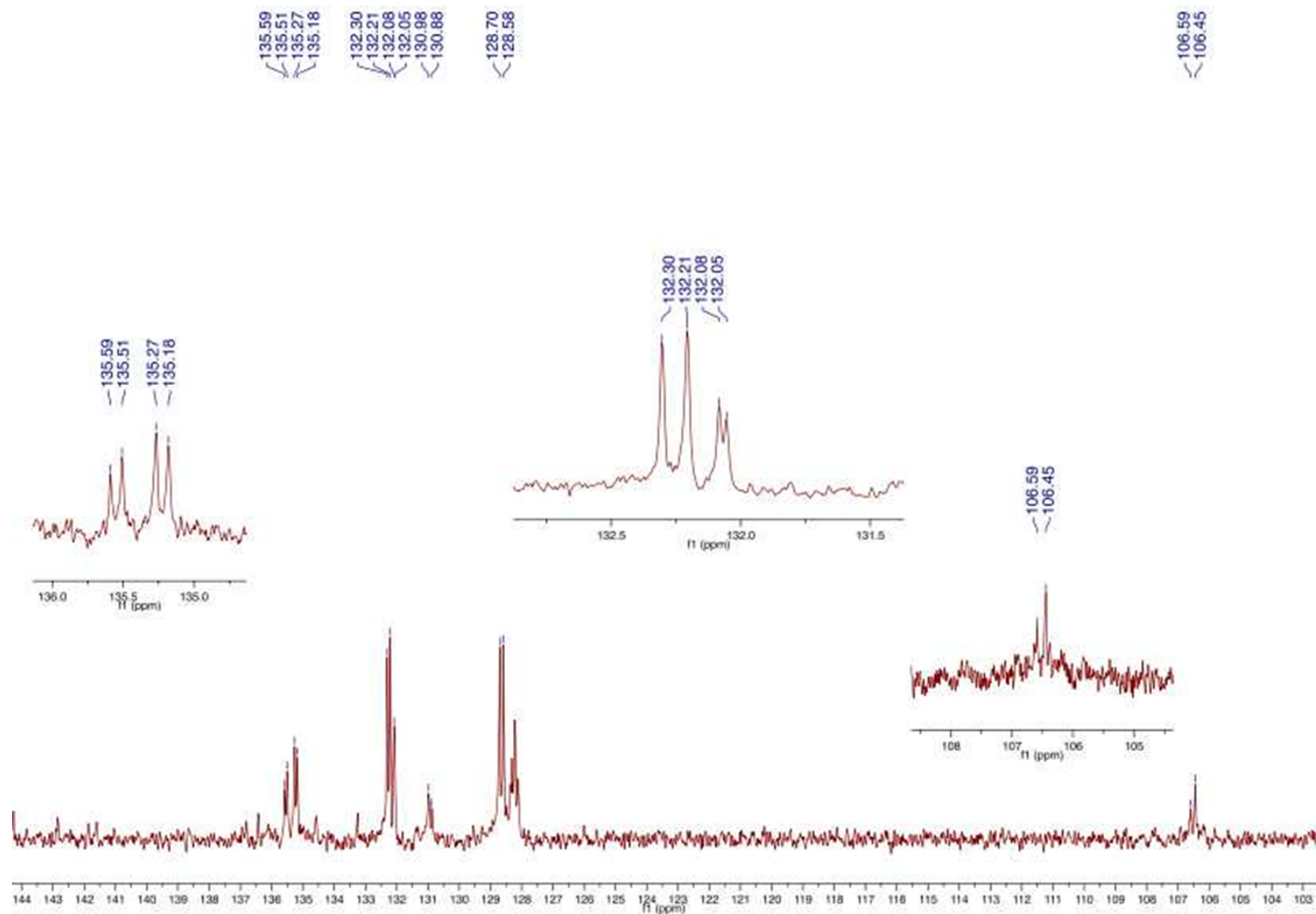




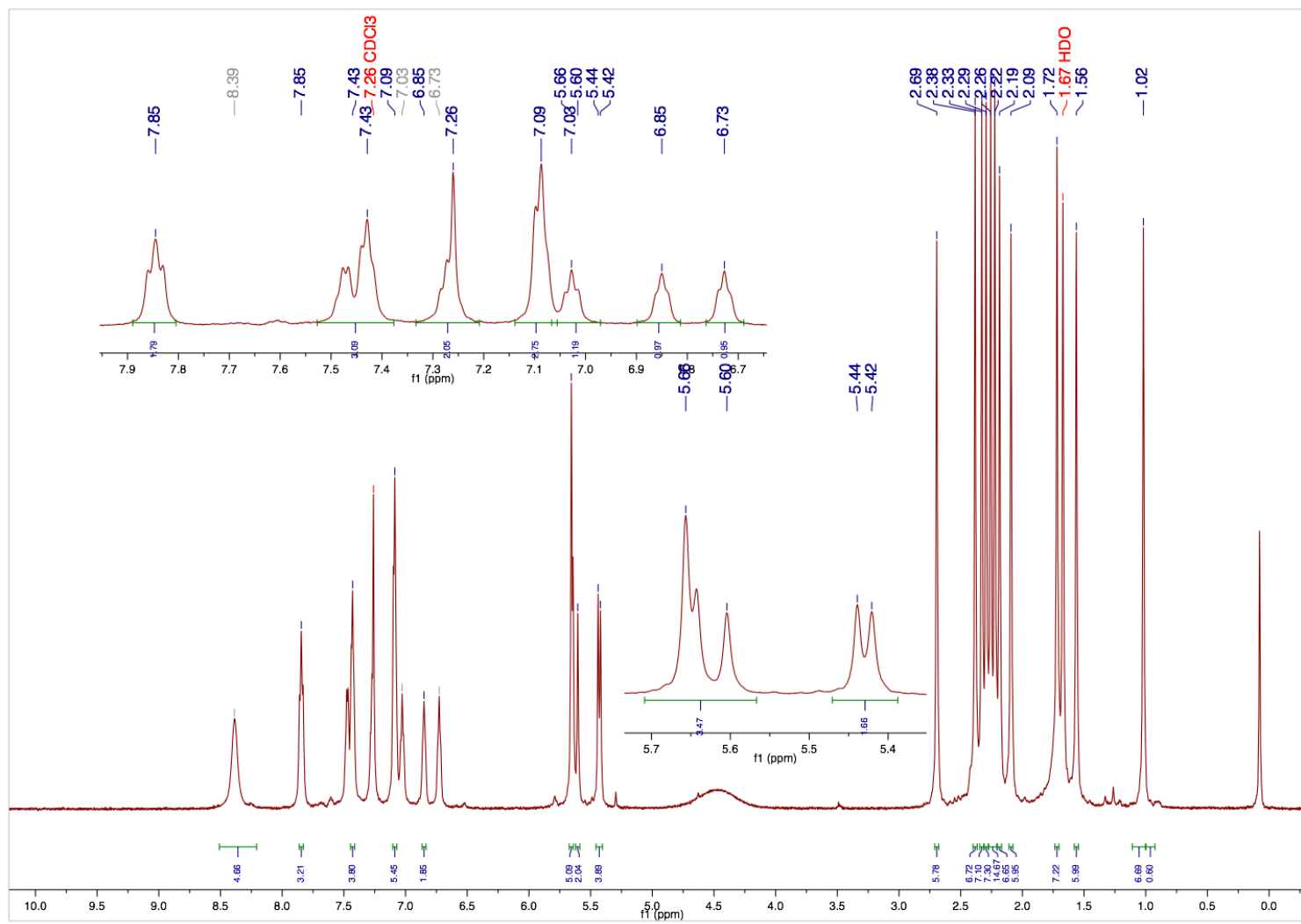
$^{11}\text{B}\{^1\text{H}\}$  NMR Spectrum of  $[\text{Rh}_2(\mu\text{-C})(\text{Tp})_2(\text{PPh}_3)_2]$  (6a)



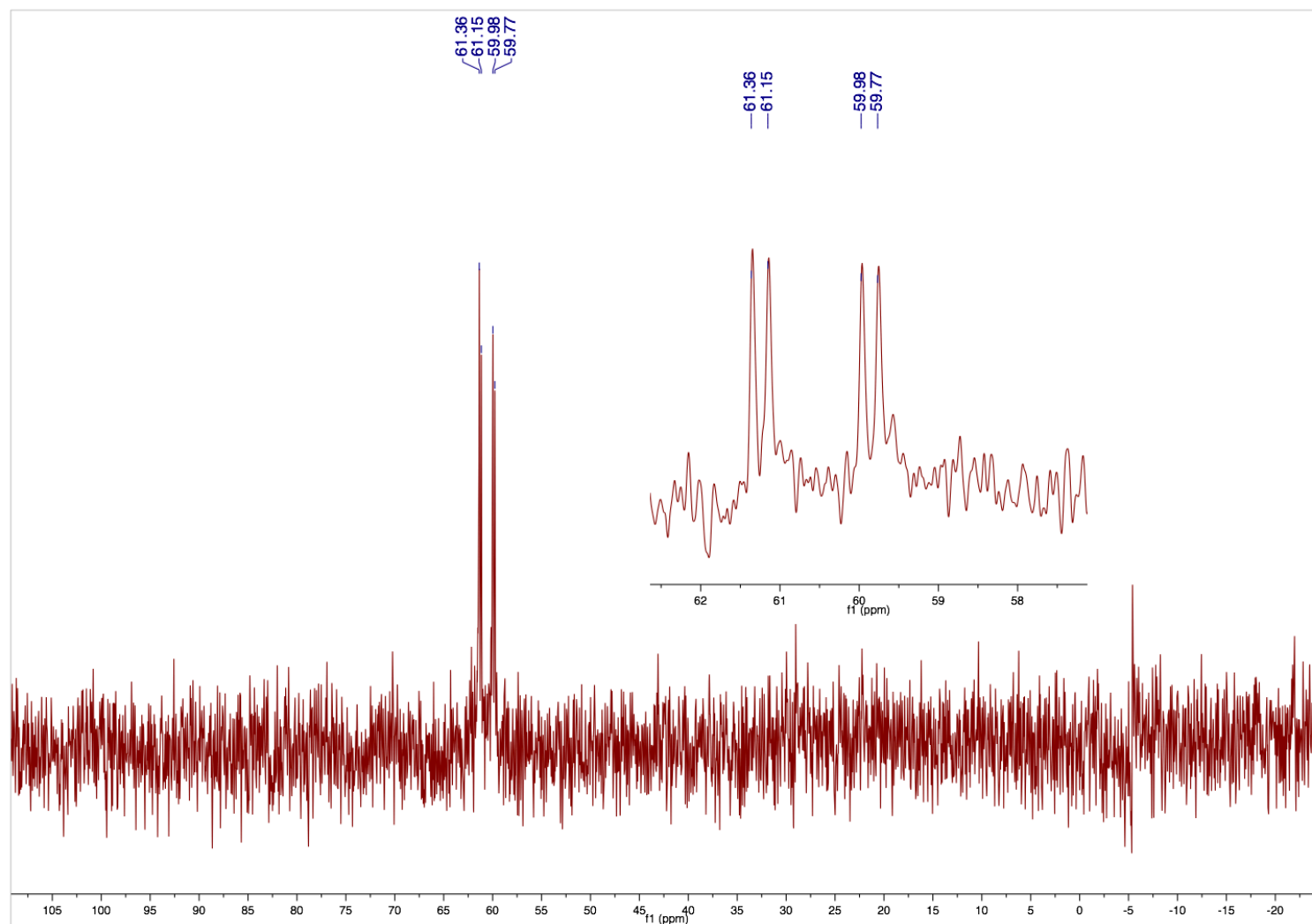
$^{13}\text{C}\{^1\text{H}\}$  NMR Spectrum of  $[\text{Rh}_2(\mu\text{-C})(\text{Tp})_2(\text{PPh}_3)_2]$  (6a) [Poor solubility]



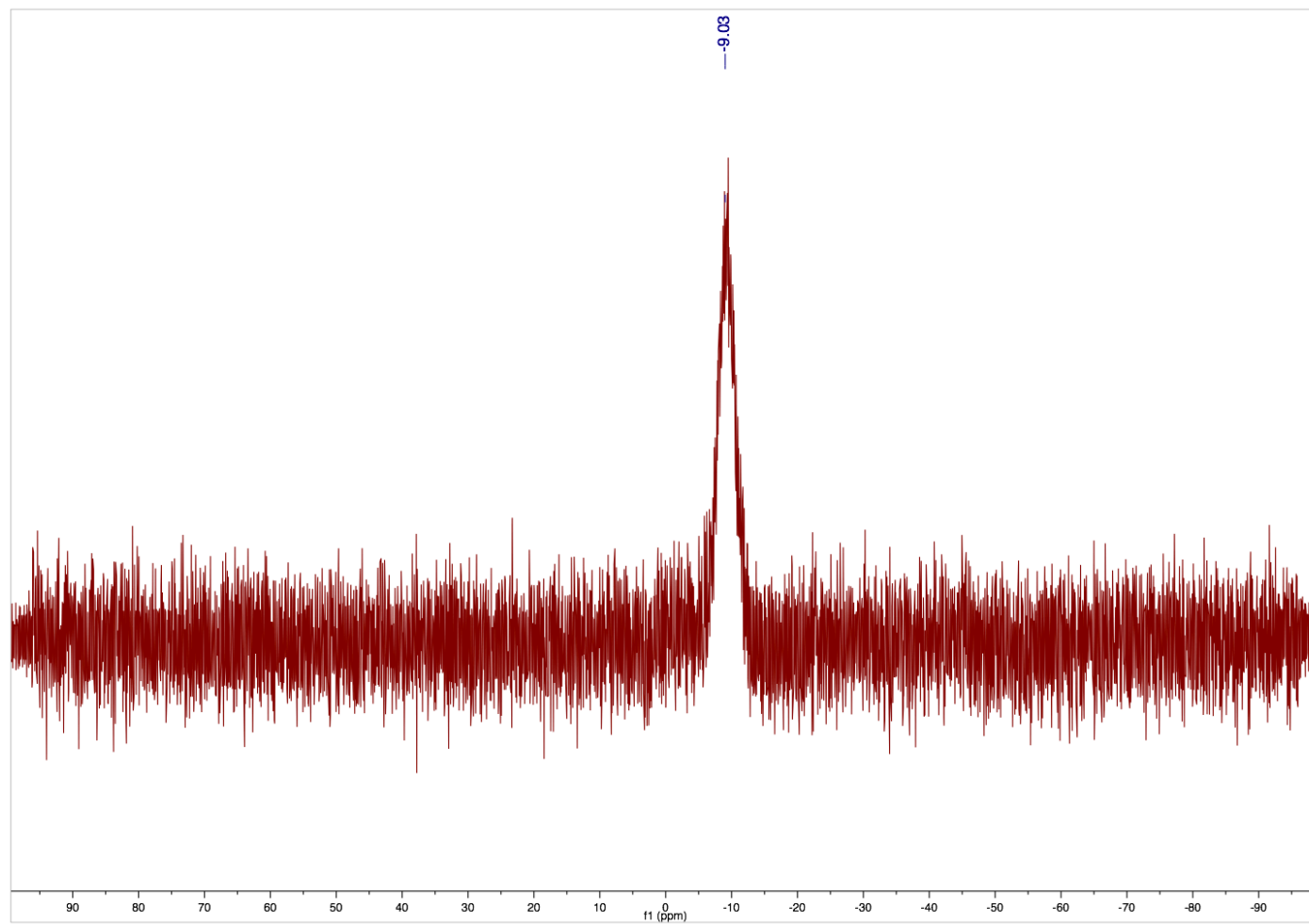
$^1\text{H}$  NMR Spectrum of  $[\text{Rh}_2(\mu\text{-C})\text{H}(\text{Tp}^*)_2(\text{C}_6\text{H}_4\text{PPh}_2\text{-2})]$  (7)



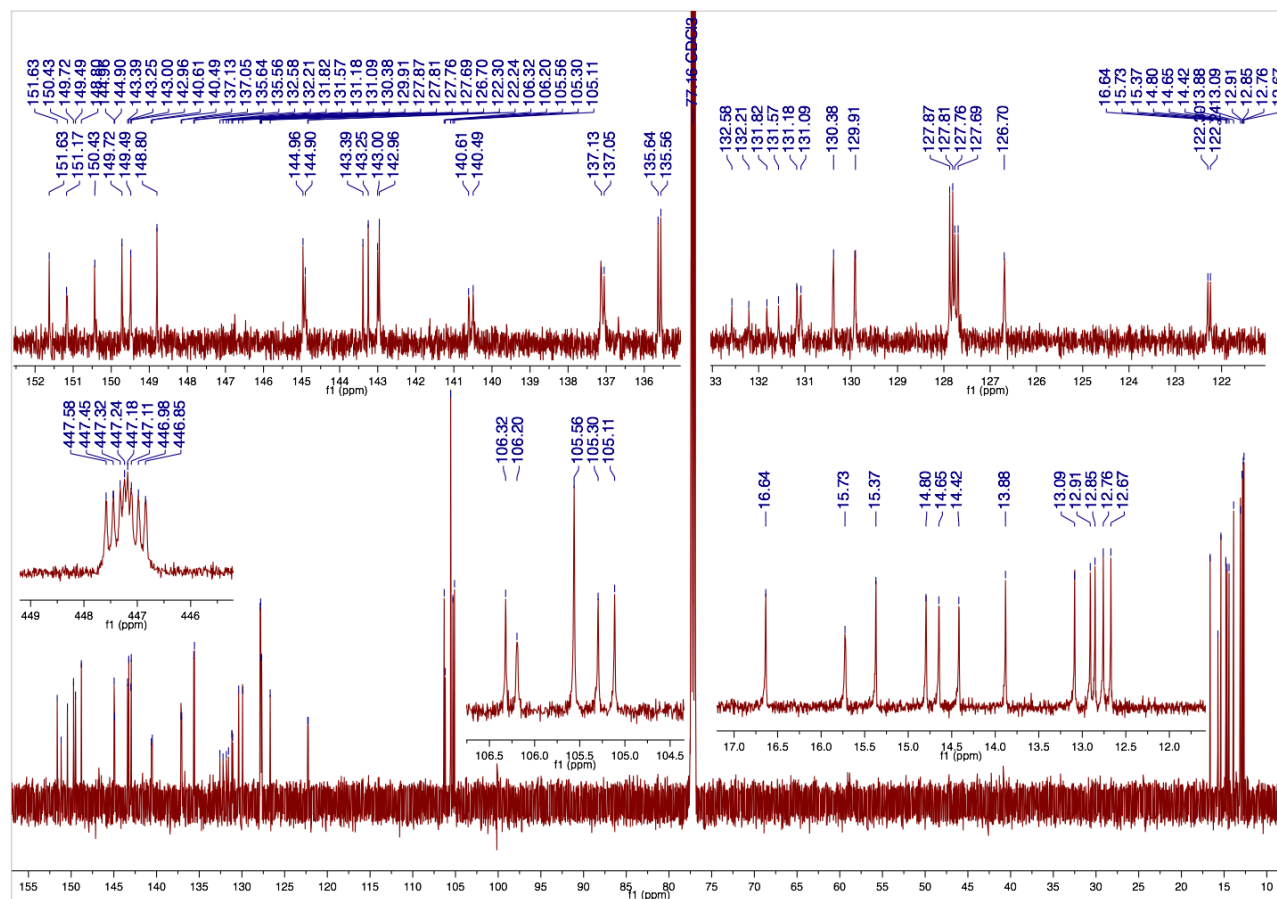
**$^{31}\text{P}\{^1\text{H}\}$  NMR Spectrum of  $[\text{Rh}_2(\mu\text{-C})\text{H}(\text{Tp}^*)_2(\text{C}_6\text{H}_4\text{PPh}_2\text{-2})]$  (7)**



$^{11}\text{B}\{^1\text{H}\}$  NMR Spectrum of  $[\text{Rh}_2(\mu\text{-C})\text{H}(\text{Tp}^*)_2(\text{C}_6\text{H}_4\text{PPh}_2\text{-2})]$  (7)

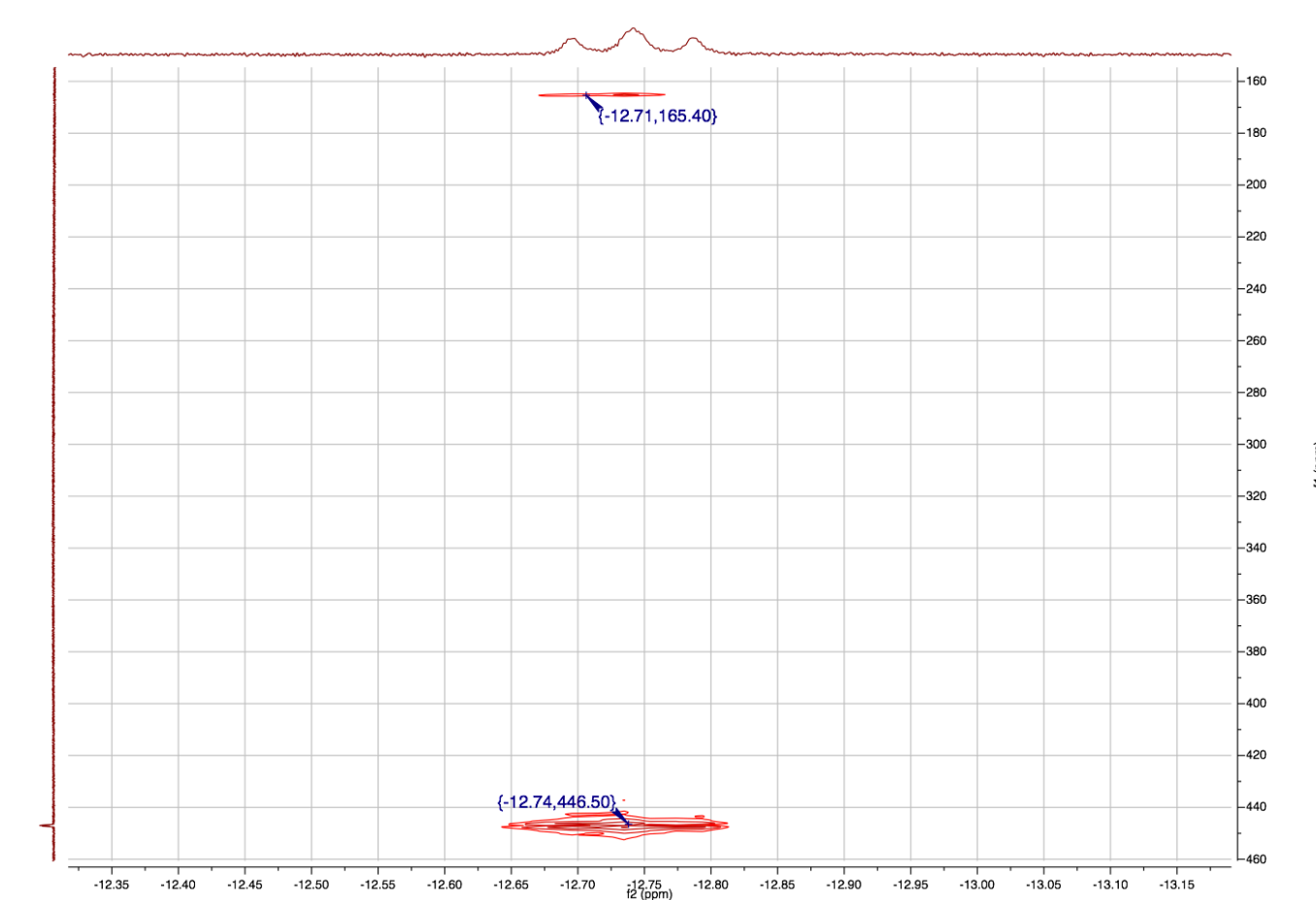


$^{13}\text{C}\{^1\text{H}\}$  NMR Spectrum of  $[\text{Rh}_2(\mu\text{-C})(\text{Tp}^*)_2(\text{C}_6\text{H}_4\text{PPh}_2\text{-2})]$  (7) [50%  $^{13}\text{C}$  enriched at  $\text{Rh}_2\text{C}$ ]



## ELECTRONIC SUPPORTING INFORMATION

$^{13}\text{C}$ - $^1\text{H}$  HMBC NMR Spectrum of  $[\text{Rh}_2(\mu\text{-C})\text{H}(\text{Tp}^*)_2(\text{C}_6\text{H}_4\text{PPh}_2\text{-2})]$  (7) showing weak correlation between hydride and carbide/aryl resonances (magnitude phased, f2).



High frequency (hydride region)  $^1\text{H}$  NMR spectrum of  $[\text{Rh}_2(\mu\text{-C})\text{H}(\text{Tp}^*)_2(\text{C}_6\text{H}_4\text{PPh}_2\text{-2})]$  (7)