Supporting Information:

Reversible H_2 Splitting between Ru(II) and a Remote Carbanion in a Zwitterionic Compound

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1. Synthetic procedures and spectroscopic data.

General. All reactions were handled under argon using standard Schlenk techniques or in a nitrogen-atmosphere glovebox from MBraun. Unless otherwise stated, all chemicals were purchased from commercial sources and used without further purification. Pentane, hexanes, C_6H_6, C_6D_6 and THF were dried over sodium/benzophenone, vacuum transferred and stored over activated 4 Å molecular sieves in the glovebox. 4,5-Diazafluorene (LH),[1] $[RuCl_2(PPh_3)_3]$[2] and $[RuHCl(PPh_3)_3]$[3] were prepared according to literature procedures. CD_2Cl_2 and $CDCl_3$ were purchased from Cambridge Isotope Laboratories, Inc., dried over CaH_2, and vacuum transferred before use. NMR spectra were recorded on a Varian 400 spectrometer working at 400 MHz for ^1H, 162 MHz for ^{31}P and 100 MHz for ^{13}C, or on a Varian 300 spectrometer working at 300 MHz for ^1H and 121 MHz for ^{31}P. Elemental analyses were performed at our Chemistry Department using PE 2400 C/H/N/S analyzer. Due to the air- and moisture-sensitive nature of **2** and **3**, no satisfactory elemental analysis results were obtained for these compounds.

Synthesis of *cis,cis*-$[RuHCl(LH)(PPh_3)_2]$ (1): 1.200 g (1.3 mmol) of $[RuHCl(PPh_3)_3]$ was dissolved in 90 mL of THF and 0.220 g (1.3 mmol) of LH was added as a solid. The solution was stirred overnight in the glovebox. The orange precipitate was collected by filtration, washed several times with THF and dried under vacuum (86 % yield). ^1H NMR ($CDCl_3$, 300 MHz) δ 8.16 (d, 1H, LH), 7.97 (d, 1H, LH), 7.74-7.68 (m, 7H, 6H from PPh_3, 1H from LH), 7.47 (d, 1 H, LH), 7.20-6.99 (m, 13H, 12H from PPh_3, 1H from LH), 6.85-6.83 (m, 6 H, PPh_3), 6.79 (dd, 1H, LH), 3.95 (d, 1H, LH, $^2J_{H-H}$= 15 Hz), 3.74 (d, 1H, LH, $^2J_{H-H}$=15 Hz), -16.32 (t, 1H, $^2J_{H-P}$ =27.8 Hz, Ru-*H*). ^{31}P NMR ($CDCl_3$, 162 MHz) δ 75.37 (dd, $^2J_{P-P}$= 35 Hz, $^2J_{H-P}$= 20 Hz), 65.25 (dd, $^2J_{P-P}$ = 35 Hz, $^2J_{H-P}$ = 20 Hz). Anal. Calcd for $RuP_2N_2ClC_{47}H_{39}$: C, 67.99; H, 4.73; N, 3.37. Found: C, 67.57; H, 4.62; N, 3.51.

Synthesis of *cis,trans*-[RuH(L)(N_2)(PPh_3)$_2$] (2): 0.443 g (0.53 mmol) of **1** was dissolved in 50 mL of THF and 0.063 g (0.56 mmol) of KO^tBu was added as a solid. The solution was stirred overnight under nitrogen. The volume was reduced by vacuum and pentane was added to afford **2** as a purple precipitate (80% yield). Crystals suitable for X-ray crystallographic analysis were obtained from slow diffusion of pentane into a concentrated solution of **2** in THF. ^1H NMR (C_6D_6, 400 MHz) δ 7.96 (d, 1H, $^3J_{H-H}$ = 4 Hz, L), 7.76 (d, 1H, $^3J_{H-H}$ = 8 Hz, L), 7.56 (d, ^1H, $^3J_{H-H}$ = 8 Hz, L), 7.35 (m, 12 H, PPh_3), 6.96 (d, 1H, $^3J_{H-H}$ = 4 Hz, L), 6.85 (m, 18 H, PPh_3), 6.81 (d, 1H, $^3J_{H-H}$ = 4 Hz, L) 6.44 (s, 1 H, C*H* of the C_5 ring of L), 6.16 (dd, 1H, $^3J_{H-H}$ = 4, 8 Hz, L), -12.23 (t, 1H, $^2J_{P-H}$ = 20 Hz, Ru-*H*). ^{31}P NMR (C_6D_6, 162 MHz) δ 49.65 ppm. IR(nujol): ν(Ru-N_2) 2092 (s) cm^{-1}. ^{13}C NMR (C_6D_6, 100 MHz) δ 141.1, 140.6, 137.8, 135.1, 134.0 (t, PPh_3), 133.6 (t, PPh_3), 129.7, 128.2 (t, L), 127.5, 127.4, 125.3, 124.6, 117.9, 117.6, 82.2 (*C*H of the C_5 ring of L).

Synthesis of *cis,cis,trans*-[Ru(H)$_2$(LH)(PPh_3)$_2$] (3): 0.300 g (0.36 mmol) of **1** was dissolved in 25 mL of THF. 0.016 g (0.4 mmol) of NaH (60 wt% dispersion in mineral oil) was added as a solid. The mixture was stirred overnight under nitrogen, filtered through Celite, and concentrated under vacuum. Pentane was added to afford **3** as a purple precipitate (61 % yield). Crystals suitable for X-ray crystallographic analysis were obtained from slow diffusion of hexanes into a concentrated solution of 3 in THF. ^1H NMR (C_6D_6, 300 MHz) δ 8.03 (d, 2 H, $^3J_{H-H}$ = 6 Hz, LH), 7.79 (m, 12 H, PPh_3), 6.97 (m, 18 H, PPh_3), 6.68 (d, 2 H, $^3J_{H-H}$ = 6 Hz, LH), 6.28 (dd, 2 H, $^3J_{H-H}$ = 3, 6 Hz, LH), 2.97 (s, 2 H, CH_2 of LH) -

15.43 (t, 2 H, $^{2}J_{P\text{-}H}$ = 27 Hz, Ru-*H*). $^{31}P\{^{1}H\}$ NMR (C_6D_6, 121 MHz) δ 63.21. ^{13}C NMR (C_6D_6, 100 MHz) δ 162.0, 151.7, 140.9 (t, PPh_3), 133.9(t, PPh_3), 133.4, 127.6, 127.4 (t, LH), 125.7, 123.2, 35.4 (*C*H_2 of LH).

2. NMR spectra of 3 and partially deuterated 3 resulting from the D_2 treatment of 2.

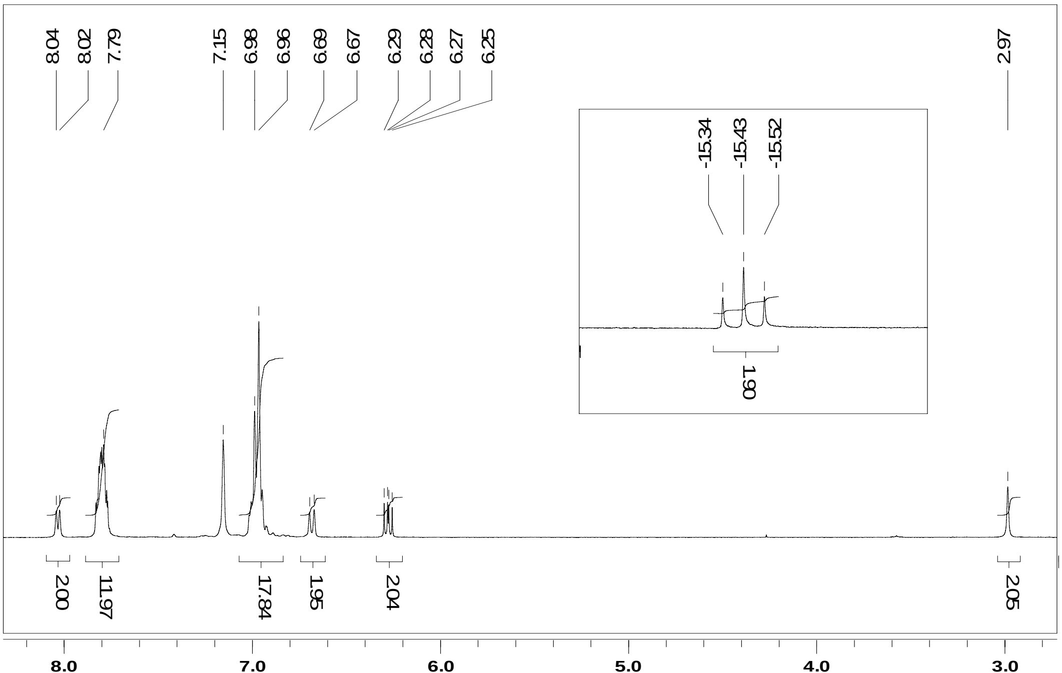


Figure S1. ^{1}H NMR spectrum of compound **3**.

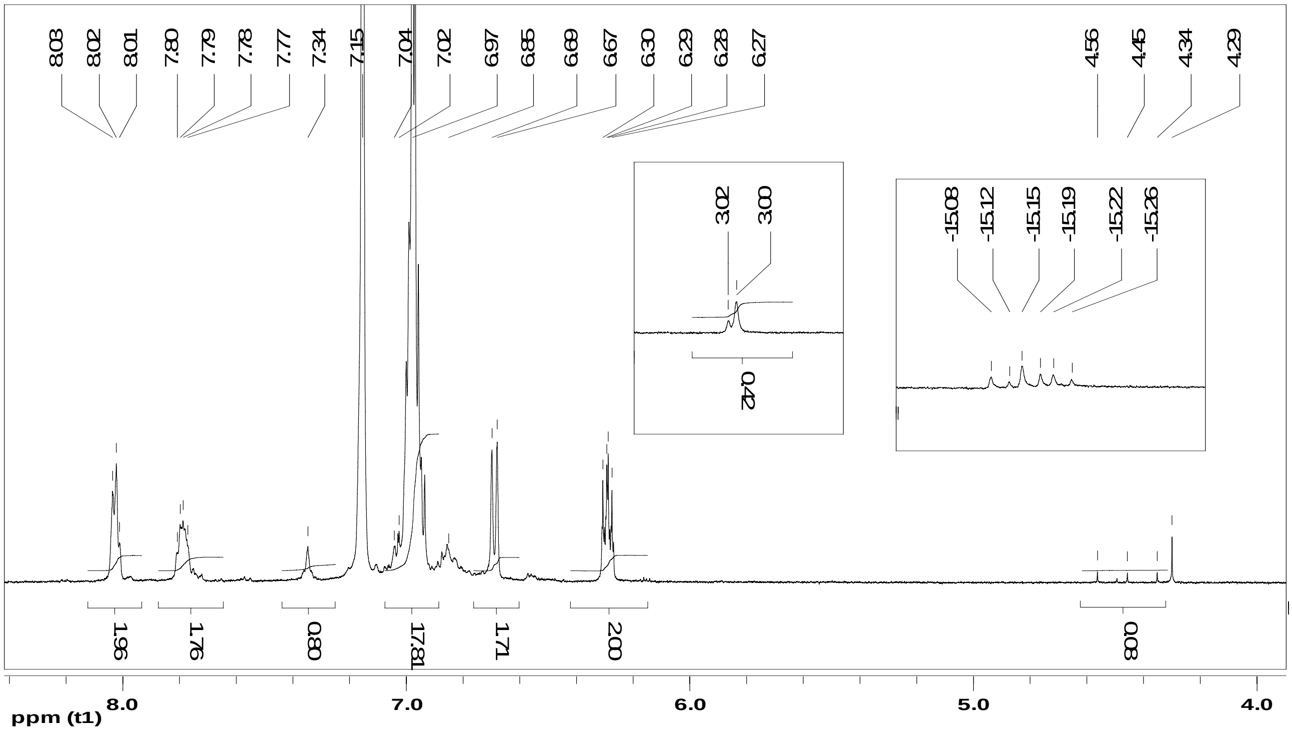
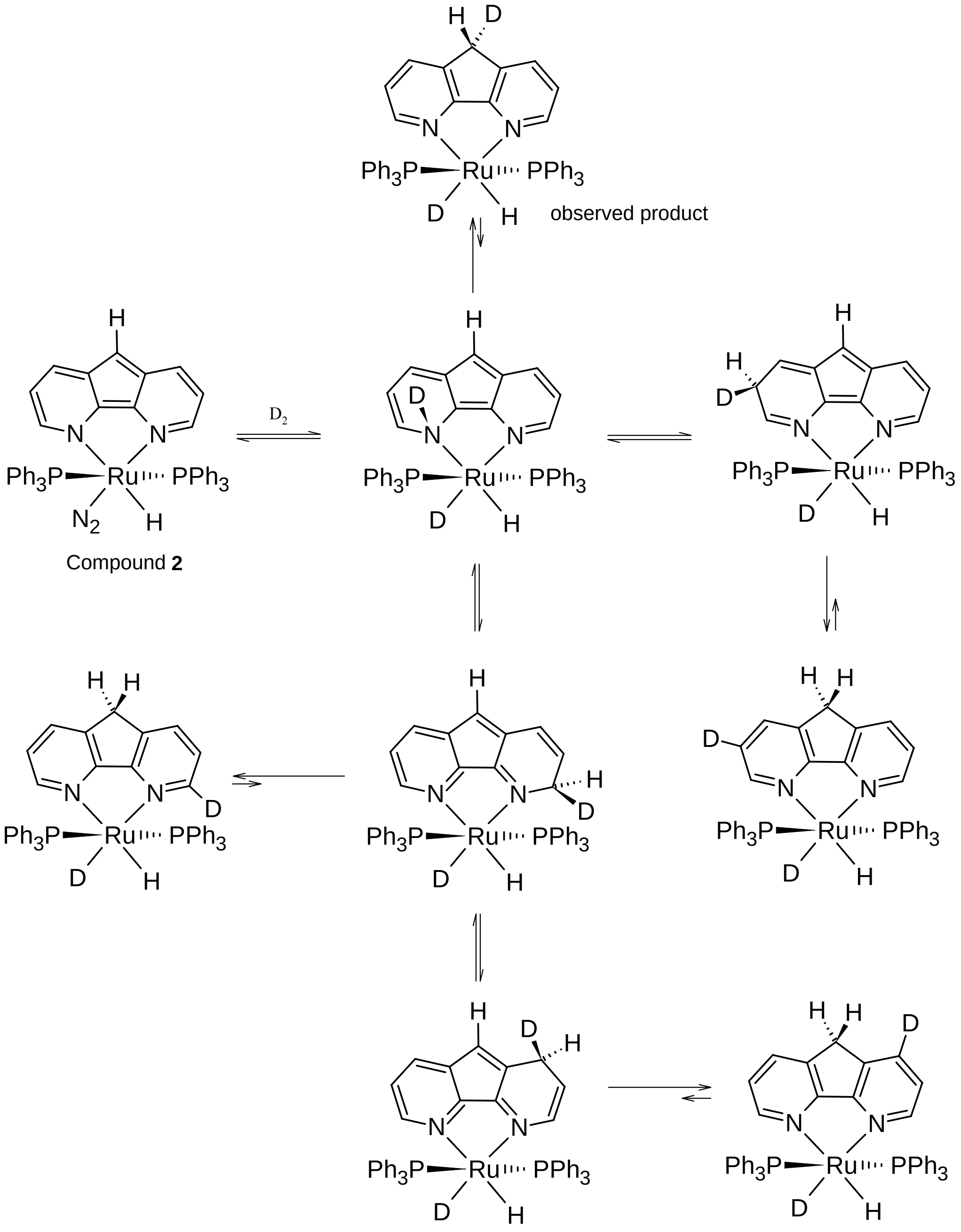


Figure S2. Partially deuterated compound **3**, resulting from the reaction of **2** with D_2.

3. Further mechanistic discussions.

If the initial H_2 splitting was Noyori type followed by isomerization, in addition to the observed deuterium incorporation onto the 9-position of the LH ligand, deuterium scrambling onto the pyridine rings should also be possible (see below). However, no deuterium scrambling onto the pyridine rings was observed.



4. X-ray Diffraction Analyses.

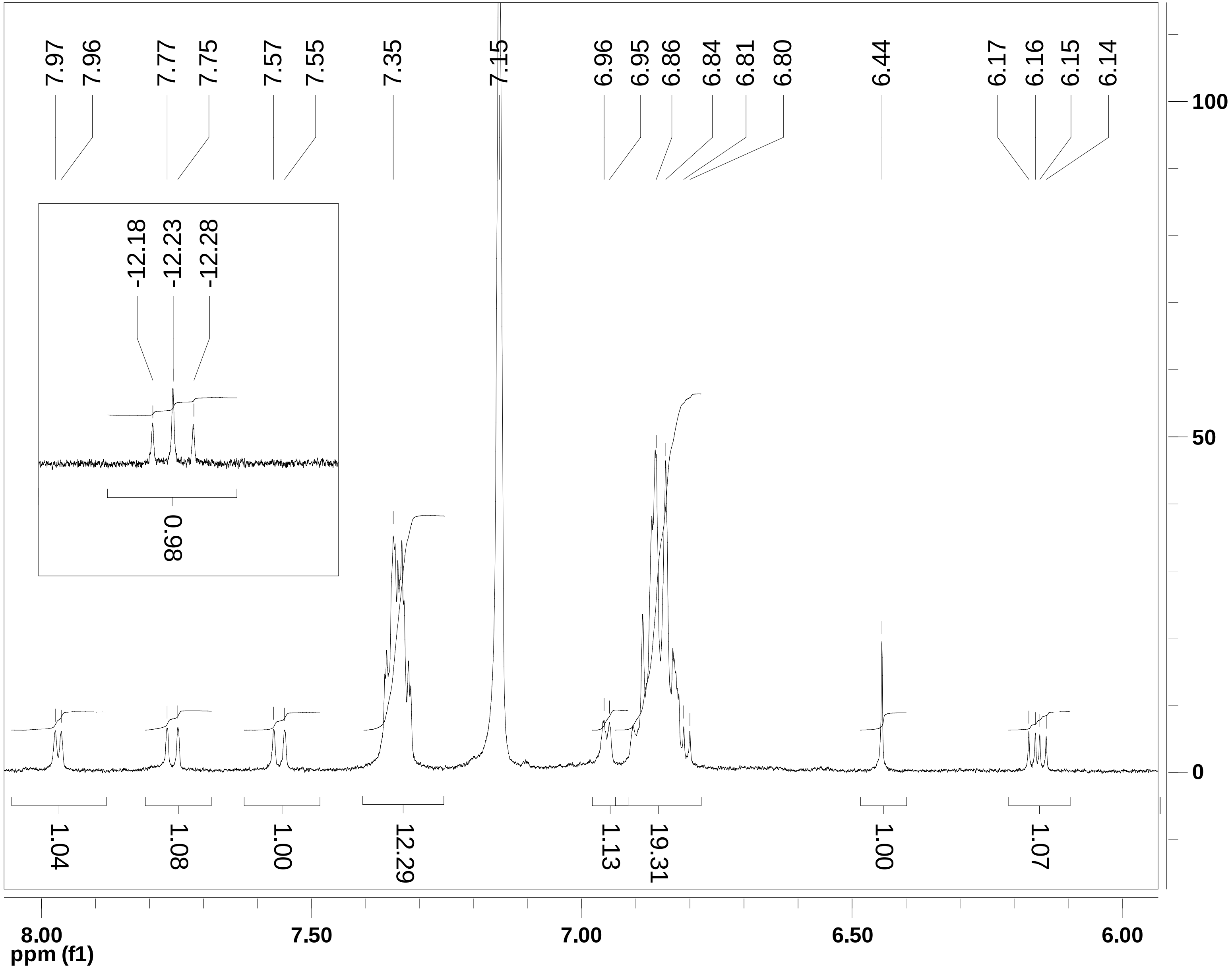
Single-crystal X-ray diffraction data for **2** were collected on a Bruker Kappa Apex II diffractometer and those for **3** were collected on a Nonius Kappa CCD diffractometer. In all cases, the collection conditions are as follows: Mo Kα radiation (λ = 0.71073 Å), 50 kV and 30 mA, 150 K controlled by an Oxford Cryostream 700 series low-temperature system. The diffraction data for **3** were processed with the DENZO-SMN software package,[4] while the data for **2** were processed with the Bruker APEX2 software package.[5] All structures were solved by the direct methods and refined using SHELXTL V6.10.[6] All non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were calculated using the riding model.

References:

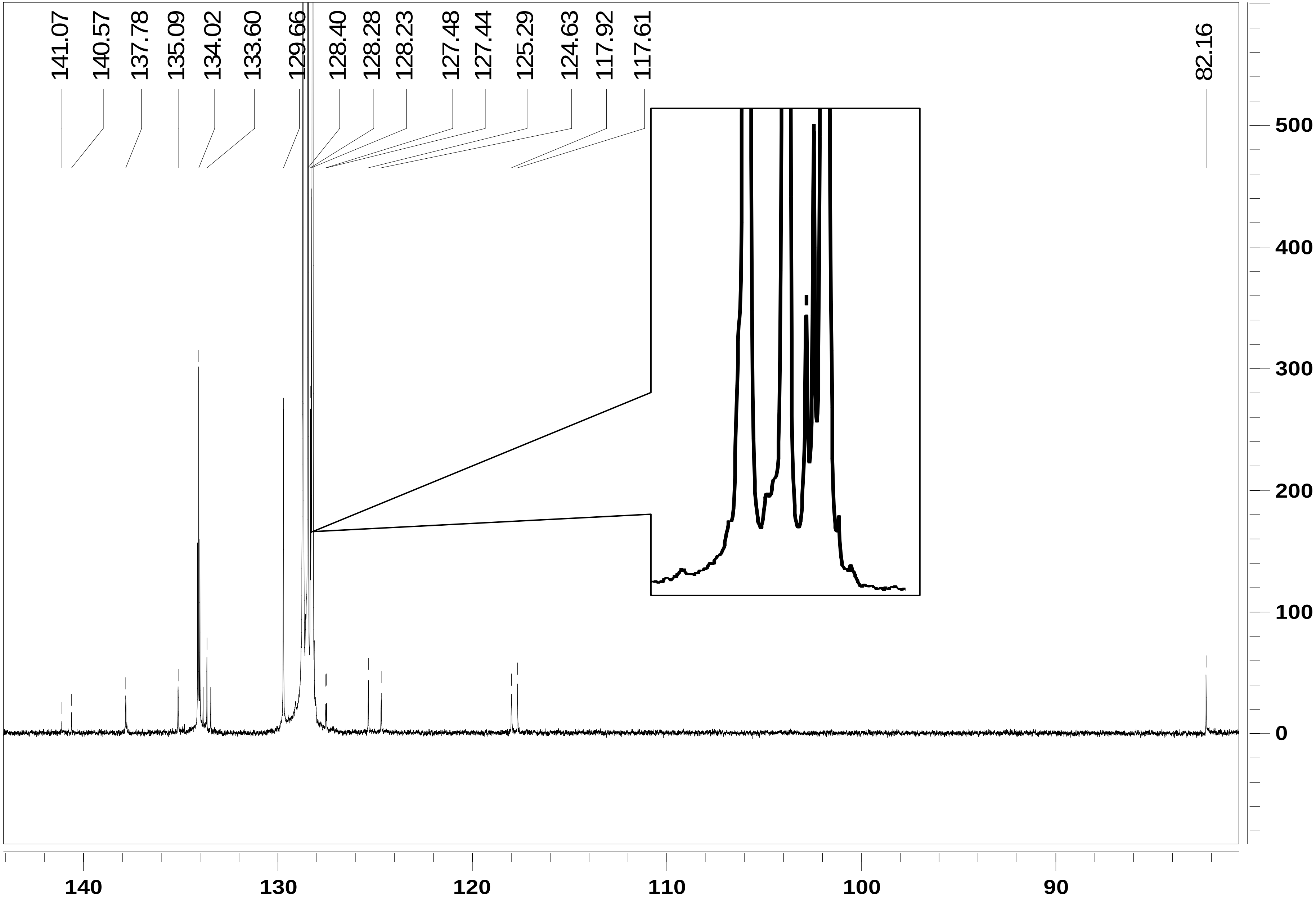
1 a) M. J. Plater, S. Kemp, E. Lattmann, *J. Chem. Soc., Perkin Trans. 1,* 2000, **6**, 971-979. b) R. P. Thummel, F. Lefoulon, R. Mahadevan, *J. Org. Chem.* 1985, **50**, 3824.
2 S. K. Sharma, V. K. Srivastava, R. V. Jasra, *J. Mol. Catal. A: Chem.* 2006, **245**, 200.
3 R. Abbel, K. Abdur-Rashid, M. Faatz, A. Hadzovic, A. J. Lough, R. H. Morris, *J. Am. Chem. Soc.* 2005, **127**, 1870.
4 Z. Otwinowski, W. Minor in *Methods in Enzymology, Macromolecular Crystallography, Part A* (Eds.: C. W. Carter, R. M. Sweet) Academic Press: London, 1997; vol. **276**, pp. 307-326.
5 Apex 2 Software Package; Bruker AXS Inc. 2008.
6 Sheldrick, G. M. Acta Crystallogr., Sect. A: Found. Crystallogr. 2008**, 64**, 112.

Appendix NMR Spectra of Compounds 2 and 3

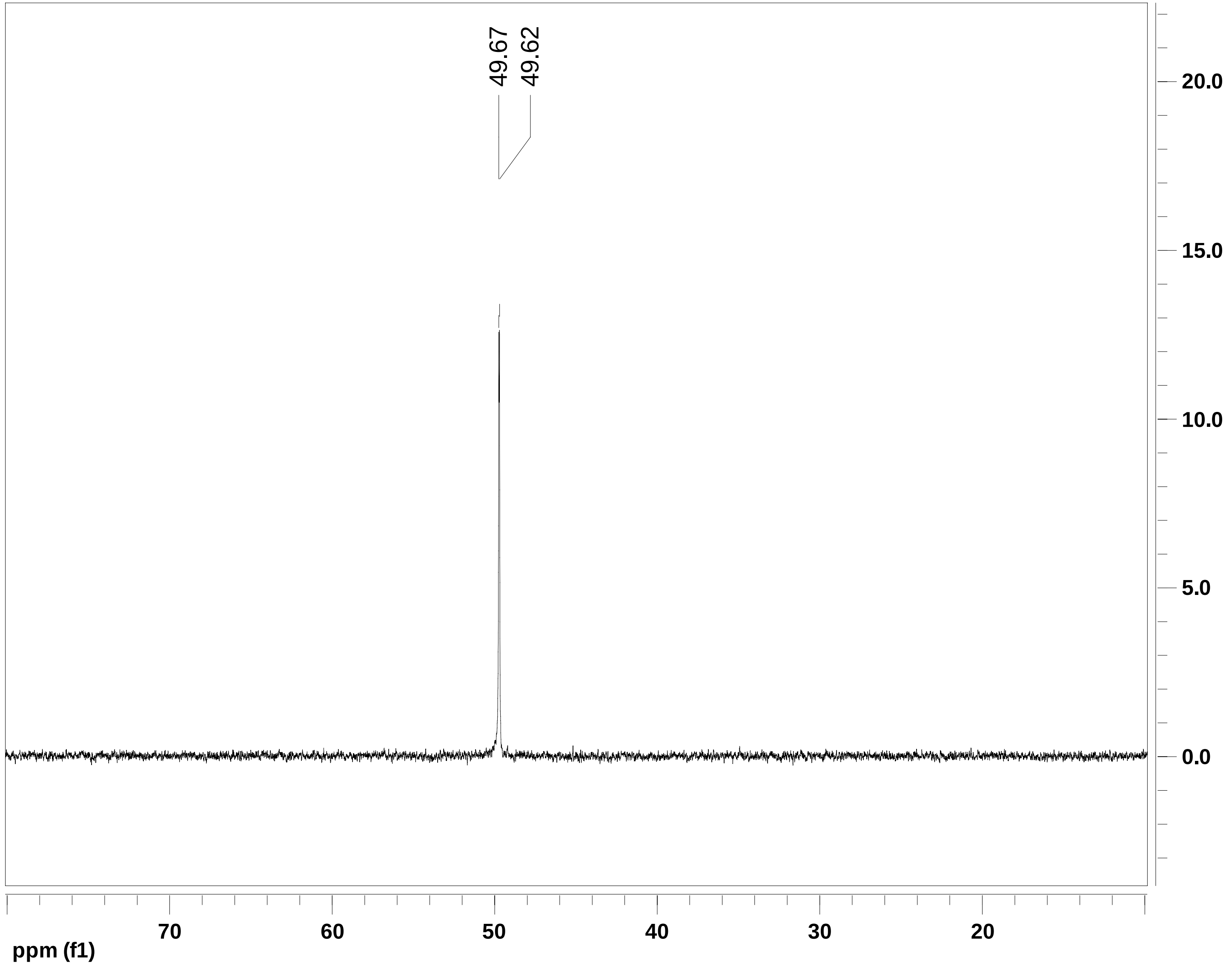
^{1}H NMR spectrum of **2**



^{13}C NMR Spectrum of **2**

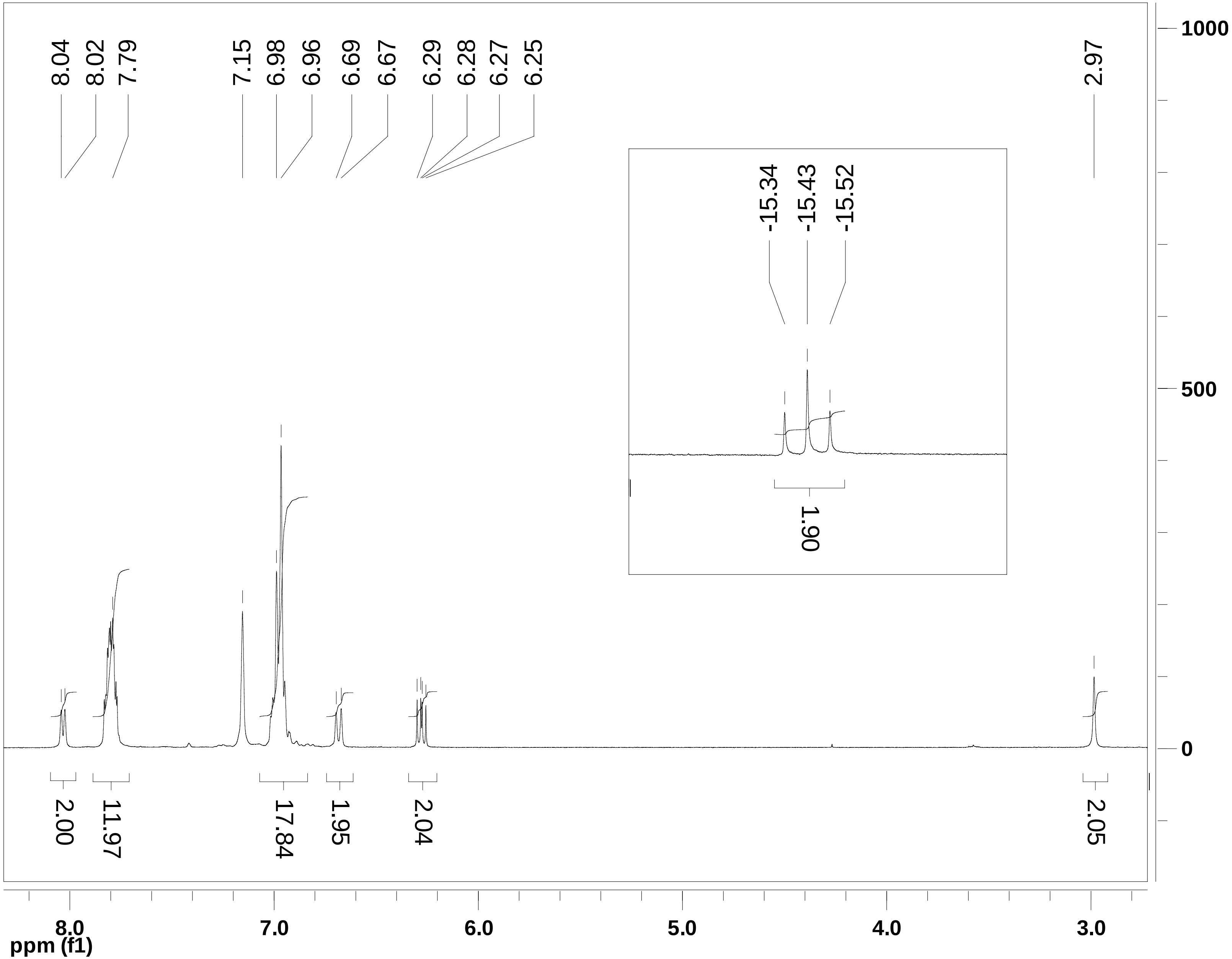


^{31}P NMR Spectrum of **2**

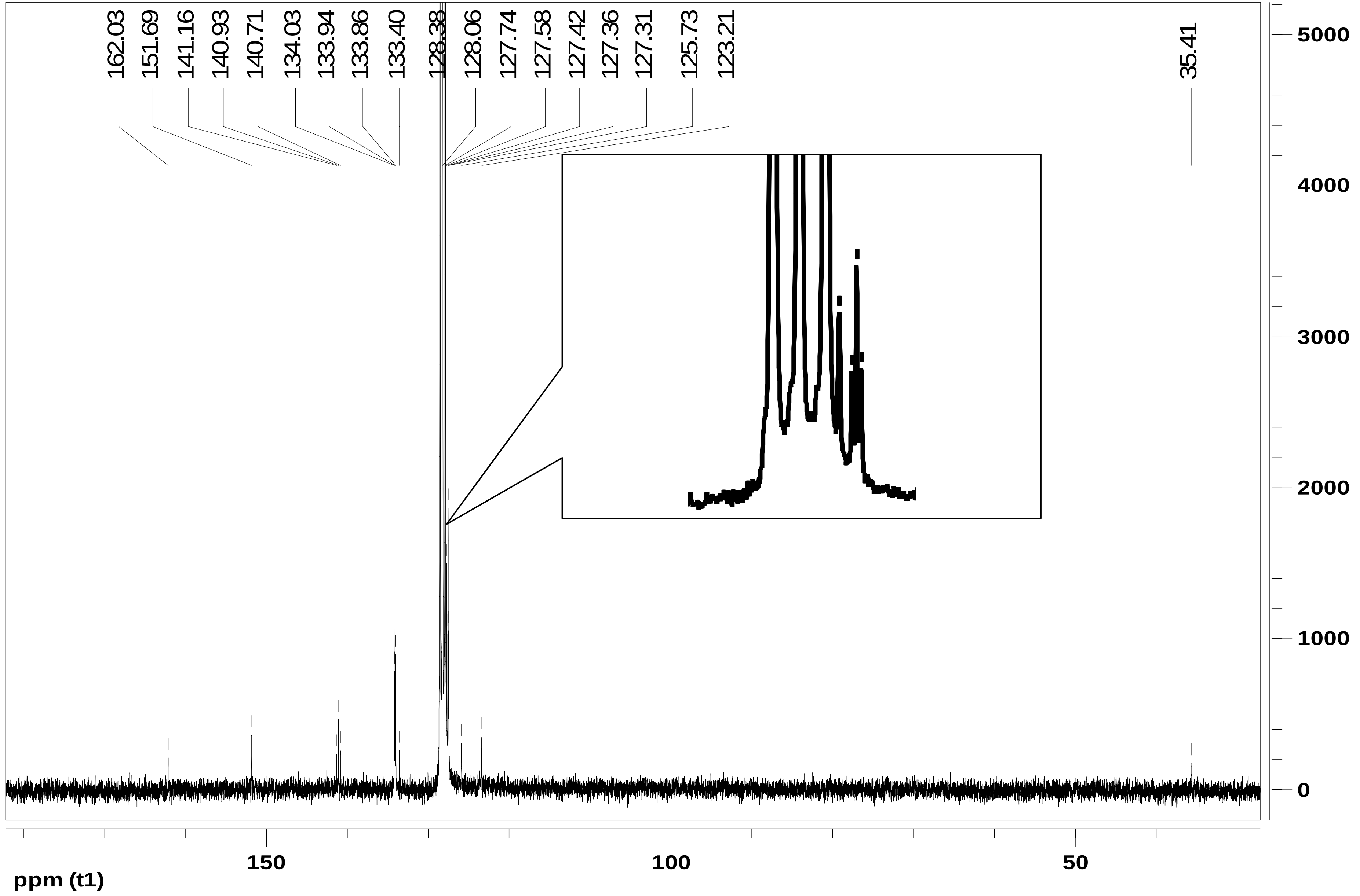


Because of the incomplete decoupling in the hydride region, the ^{31}P signal has some residual splitting pattern.

^{1}H NMR Spectrum of **3**



^{13}C NMR Spectrum of **3**



^{31}P NMR Spectrum of **3**