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1,4-Difluoro-2,5-dimethyl-3,6-bis(diphenylphosphoryl)benzene: regioselective synthesis and coordination with Mn^{2+} cation

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Experimental

Organic solvents used in the work were purified by standard procedures. $CDCl_3$ (99.8% D, Sigma-Aldrich) was used as received.

Multinuclear ^{1}H, ^{13}C, ^{31}P and ^{19}F NMR spectra were recorded on a Bruker Avance 400 spectrometer (operating at 400.23, 100.61 and 161.98 MHz, respectively), and a Bruker Avance 300 instrument (operating at 300.13, 75.47, 121.49 and 282.40 MHz, respectively) at ambient temperature using $CDCl_3$ solutions. Chemical shifts (ppm) refer to the residual protic solvent peaks (for ^{1}H and ^{13}C), and 85% H_3PO_4 (for ^{31}P) as external standards and coupling constants are expressed in hertz (Hz). IR spectra were obtained on a Bruker Tensor 37 FTIR spectrometer in the region 400–4000 cm^{-1} for solid samples. The solid samples were KBr pellets. Raman spectra of the crystalline samples were obtained in the region 100–3500 cm^{-1} on a Jobin-Ivon LabRAM 300 spectrometer, equipped with a microscope and laser CCD detector. The He–Ne laser emission line at 632.8 nm was used for excitation at a power not higher than 2 mW. HPLC-MS was performed using a Shimadzu LCMS-2020 instrument (Japan) by means of electrospray ionization (ESI). The range of detected masses was of *m/z* 50 to 2000, the measurements were performed in the positive ions mode (voltage at the interface 4500 V and voltage at the detector 1000 V). V). Acetonitrile (high-purity grade) was used as the mobile phase.
The content of C, H, and N was determined on a Carlo Erba 1106 instrument. The content of P was determined according to the published procedures [*Gel'man NE, Terent'eva EA, Shanina TM, Kiparenko LM, Rezl V (1987) Methods of Quantitative Organic Elemental Microanalysis. Khimiya, Moscow*]. Melting points were determined in open capillary tubes on a Stanford Research Systems MPA120 EZ-melt automated melting point apparatus and were not corrected.

Reagents: diphenylphosphine, 1,2,4,5-tetrafluoro-3,6-dimethylbenzene, $MnBr_2 \cdot 4H_2O$ were purchased from Aldrich.

1,4-Difluoro-2,5-dimethyl-3,6-bis(diphenylphosphino)benzene **2**.
Found (%): C 75.06, H 5.33, F 7.11, P 12.05. Calcd. For $C_{32}H_{26}F_2P_2$: C 75.29, H 5.13, F 7.44, P 12.13. Mass spectrum, *m/z* (I_{rel}, %): 511.30 (10) $[M+H]^+$, 334.30 (10), 613.30 (5). ^{1}H NMR (400.13 MHz, $CDCl_3$) δ, ppm: 7.47–7.39 (m, 20H, C_6H_5–P), 2.46 (s, 6H, CH_3). ^{13}C{^{1}H} NMR (100.61 MHz, $CDCl_3$) δ, ppm, *J*, Hz: 158.79 (ddd, $^1J_{C\text{-}F}$ = 244.8, $^2J_{P\text{-}C}$ = 9.4, $^3J_{P\text{-}C}$ = 9.0, C–F), 135.27 (d, $^1J_{P\text{-}C}$ = 10.0, *ipso*-C), 132.71 (d, $^2J_{P\text{-}C}$ = 20.1, *o*-C), 129.90–129.36 (m, <u>C</u>–P–C_6H_5), 128.29 (s, *p*-C), 128.28 (d, $^3J_{P\text{-}C}$ = 13.3, *m*-C), 126.27–125.75 (m, <u>C</u>-CH_3), 14.00 (ddd, $^3J_{C\text{-}F}$ = 27.9, $^3J_{P\text{-}C}$ = $^4J_{P\text{-}C}$ = 3.3, CH_3). ^{31}P NMR (161.97 MHz, $CDCl_3$) δ, ppm, *J*, Hz : –19.30 (dd, $^3J_{P\text{-}F}$ = 21.3, $^4J_{P\text{-}F}$ = 4.4). ^{19}F NMR (282.40 MHz, $CDCl_3$) δ, ppm, *J*, Hz : –101.92 (dd, $^3J_{P\text{-}F}$ = 28.0, $^4J_{P\text{-}F}$ = 7.9). IR, ν, sm^{-1} (KBr): 3071, 1475, 1433, 1411, 1394, 1370, 1215, 1089, 740, 693, 507, 493.

1,4-Difluoro-2,5-dimethyl-3,6-bis(diphenylphosphoryl)benzene **3**.
Found (%):C 70.65, H 4.84, F 6.94, P 11.11. Calcd. For $C_{32}H_{26}F_2O_2P_2$: C 70.85, H 4.83, F 7.00, P 11.42. Mass spectrum, *m/z* (I_{rel}, %): 543.35 (10) $[M+H]^+$, 341.15 (10), 432.40 (3), 602.50 (5), 650.35 (5). MALDI : 542.85.^{1}H NMR (400.13 MHz, $CDCl_3$) δ, ppm, *J*, Hz: 7.72 (dd, $^2J_{P\text{-}H}$ = 12.8, $^3J_{H\text{-}H}$ = 7.8, 8H, *o*-CH), 7.59 (dd, $^5J_{P\text{-}H}$ = 1.6, $^3J_{H\text{-}H}$ = 7.8, 4H, *p*-CH), 7.50 (td, $^4J_{P\text{-}H}$ = 3.0, $^3J_{H\text{-}H}$ = 7.8, 8H, *m*-CH), 2.43 (s, 6H, CH_3). ^{13}C{^{1}H} NMR (125.77 MHz, $CDCl_3$) δ, ppm, *J*, Hz: 158.32–158.16 and 156.36–156.20 (both m, C–F), 133.10 (d, $^1J_{P\text{-}C}$ = 86.2, *ipso*-C); 132.16 (d, $^4J_{P\text{-}C}$ = 2.4, *p*-CH), 131.28 (d, $^2J_{P\text{-}C}$ = 9.6, *o*-CH), 130.46–130.01 (m, <u>C</u>-CH_3), 128.63 (d, $^3J_{P\text{-}C}$ = 10.3, *m*-CH), 124.93–124.65 and 124.18–123.99 (both m, <u>C</u>–P–C_6H_5), 12.53 (dd, $^3J_{P\text{-}C}$ = $^3J_{F\text{-}C}$ = 4.5, CH_3); ^{31}P NMR (161.97 MHz, $CDCl_3$) δ, ppm: 26.43 s. ^{19}F{^{1}H} NMR (282.40 MHz, $CDCl_3$) δ, ppm: –101.86 s. IR, ν, sm^{-1} (KBr): 3057, 1437, 1417, 1367, 1225, 1191 (P=O), 1118, 1102, 774, 726, 693, 551, 506.

Complex 4.
The transparent colorless crystals suitable for X-ray diffraction that formed after the reaction were separated by decantation, washed with MeCN and dried at 62 °C in a vacuum (0.1 Torr). Found (%): C 43.41; H 3.75; P 6.95. Calcd. for $C_{32}H_{26}F_2O_2P_2 \cdot MnBr_2 \cdot CHCl_3 \cdot 2H_2O$ (%): C 43.43; H 3.43; P 6.79. Principal IR and Raman spectra data (cm^{-1}): IR – ν(P=O) 1159(s), 1145(s)*;* Raman – ν(Mn–Br) 265, 234. The Raman spectral data are consistent with the tetrahedral structure of the Mn^{2+} polyhedron found in XRD. Complex **4** is insoluble in common organic solvents, so NMR spectra could not be obtained.

^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectra for 2, 3 in $CDCl_3$

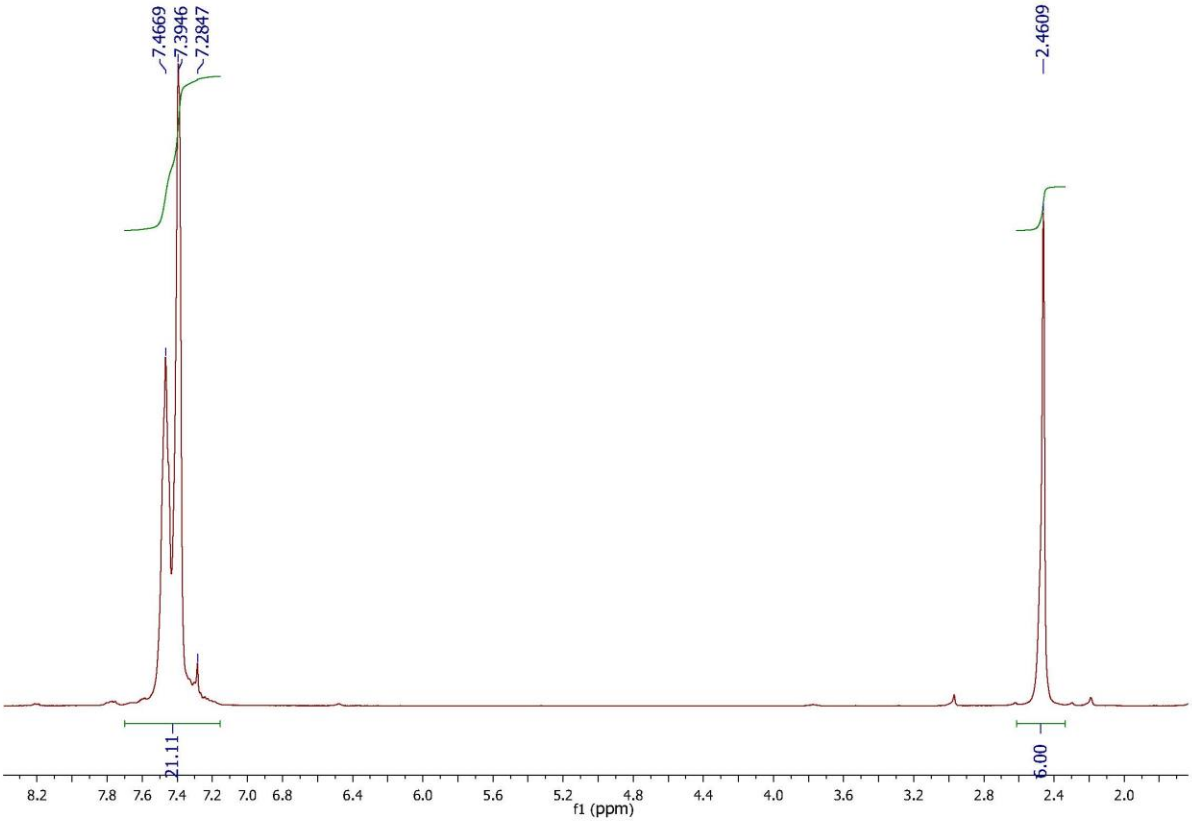

Figure S1. ^{1}H NMR spectrum for phosphine **2** ($CDCl_3$, 400.13 MHz).

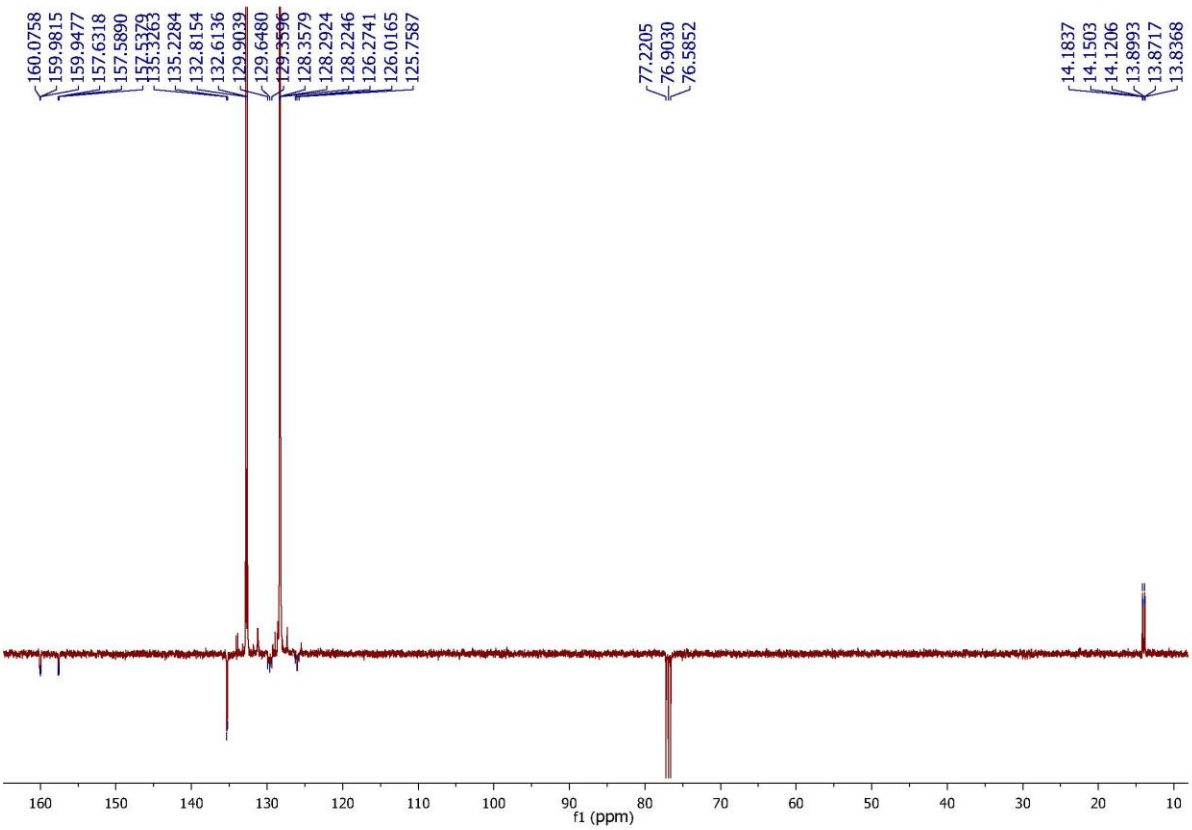

Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum for phosphine **2** ($CDCl_3$, 100.61 MHz)

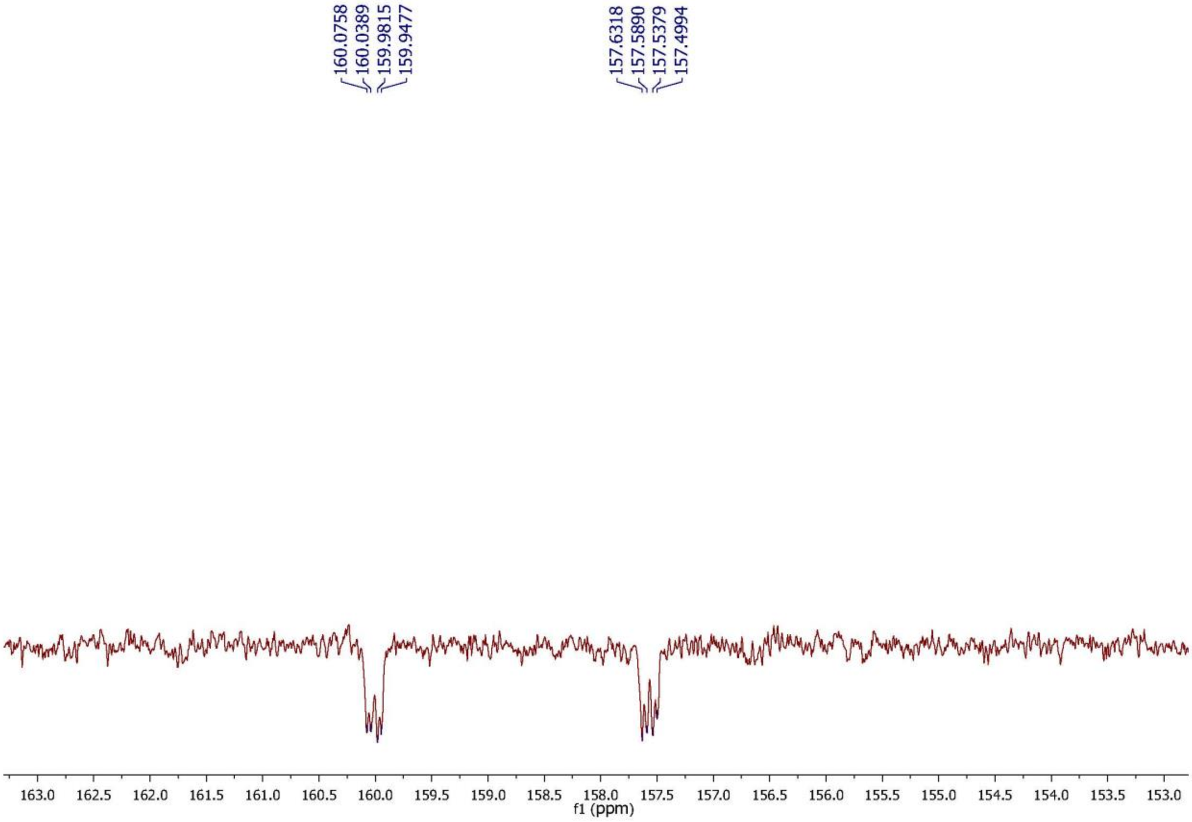

Figure S3. Fragment of $^{13}C\{^1H\}$ NMR spectrum for phosphine **2** ($CDCl_3$, 100.61 MHz)

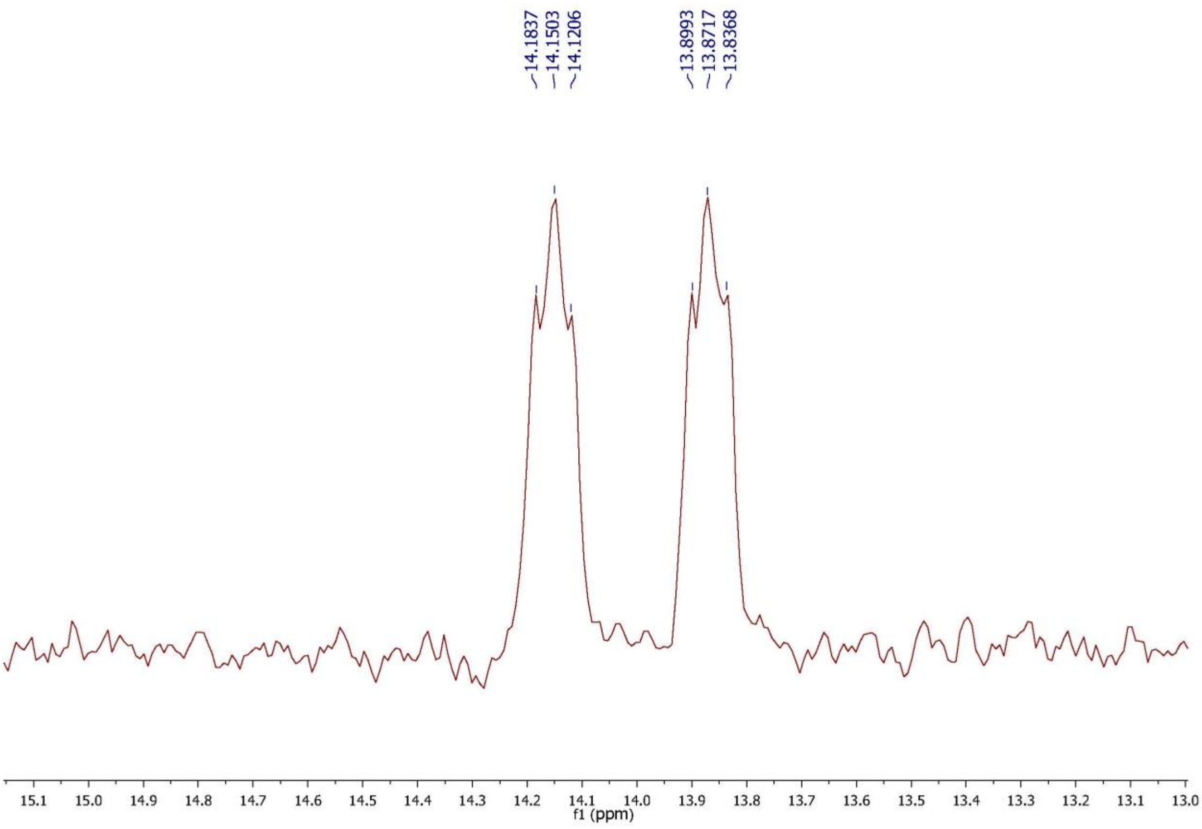

Figure S4. Fragment of $^{13}C\{^1H\}$ NMR spectrum for phosphine **2** ($CDCl_3$, 100.61 MHz)

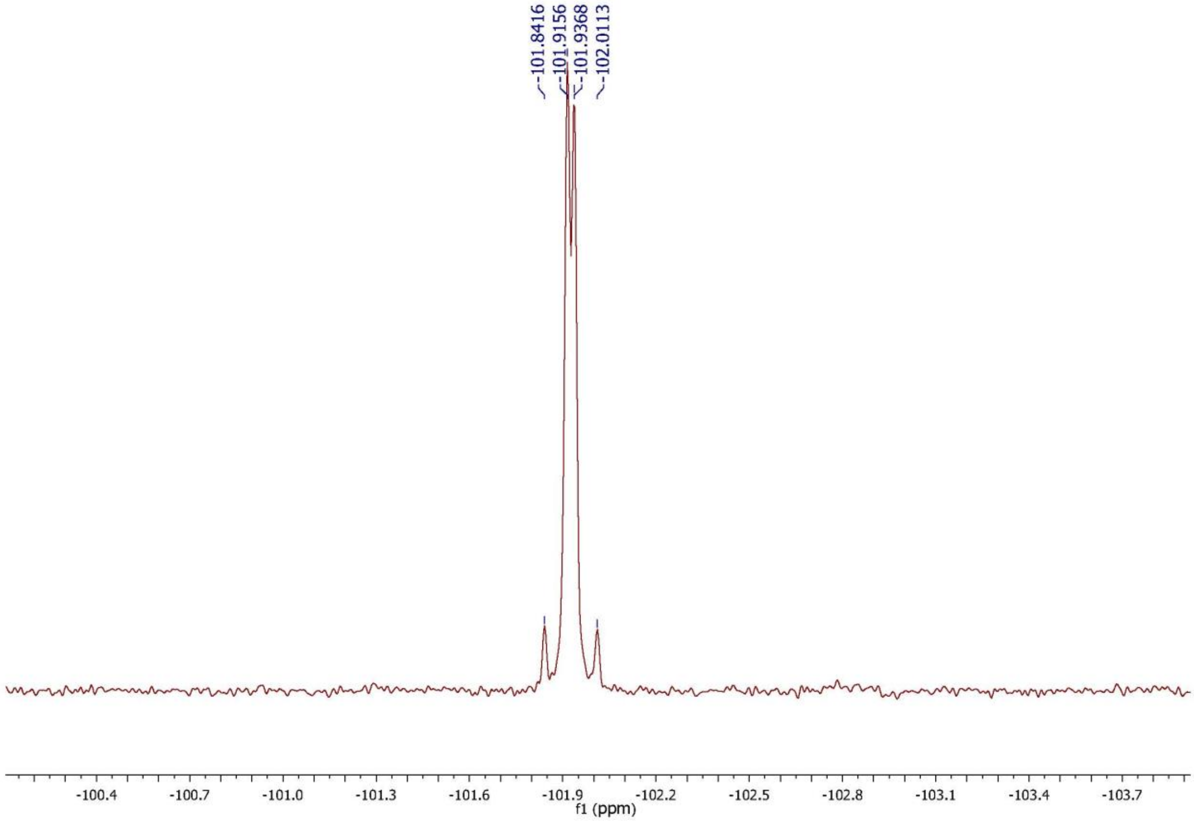

Figure S5. ^{19}F NMR spectrum for phosphine **2** ($CDCl_3$, 282.40 MHz)

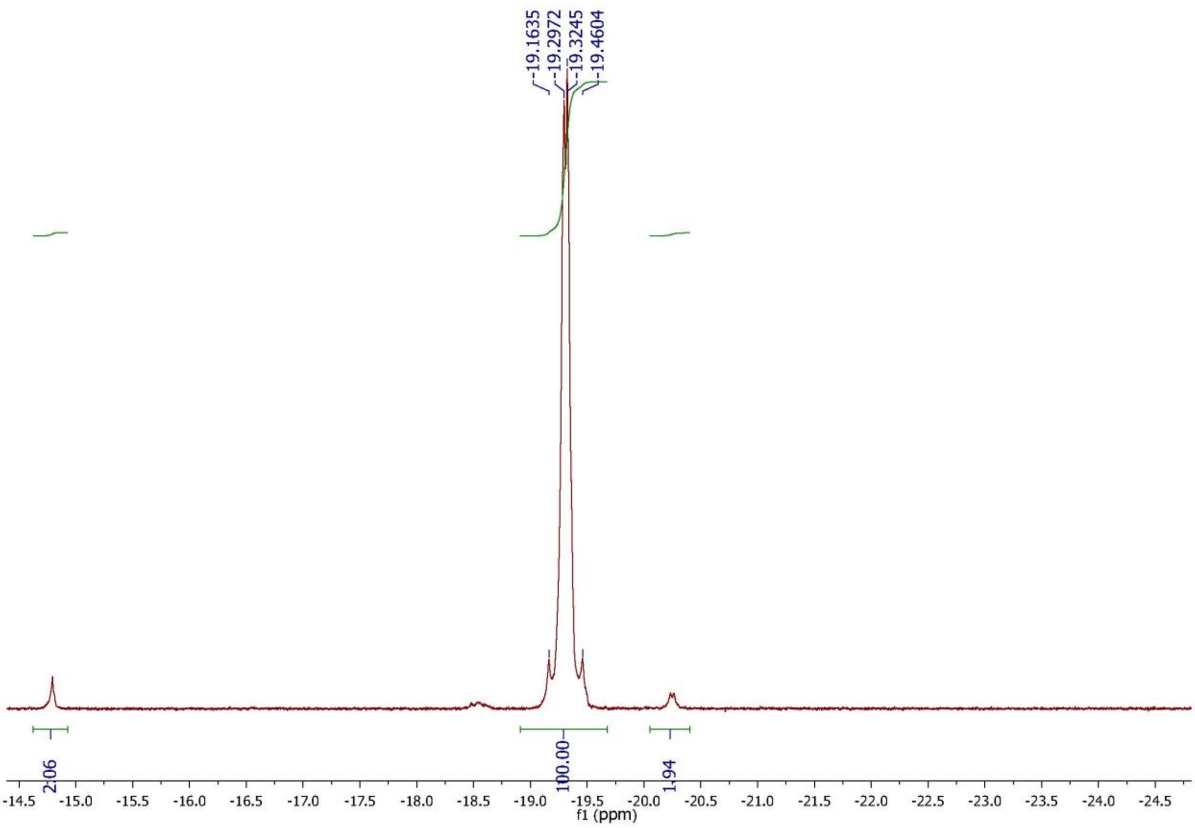

Figure S6. ^{31}P NMR spectrum for phosphine **2** ($CDCl_3$, 161.98 MHz).

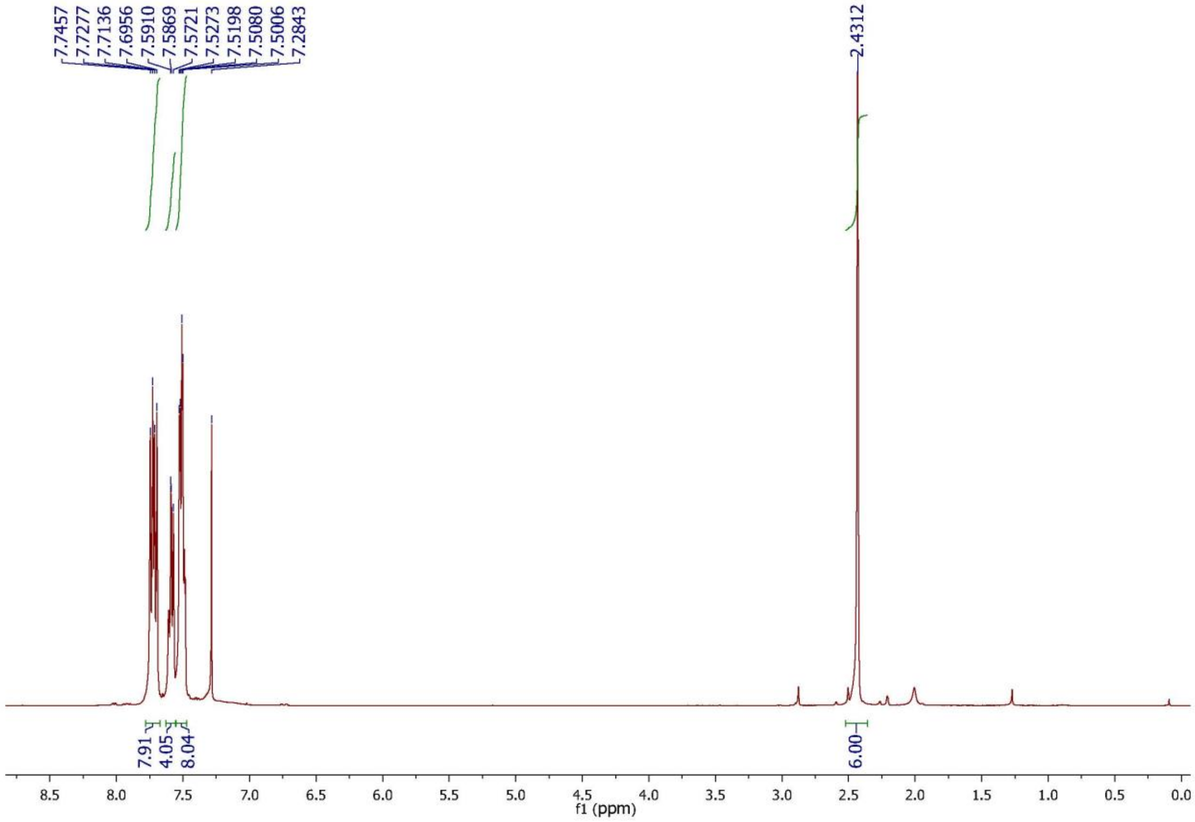

Figure S7. ^{1}H NMR spectrum for phosphine oxide **3** ($CDCl_3$, 400.13 MHz).

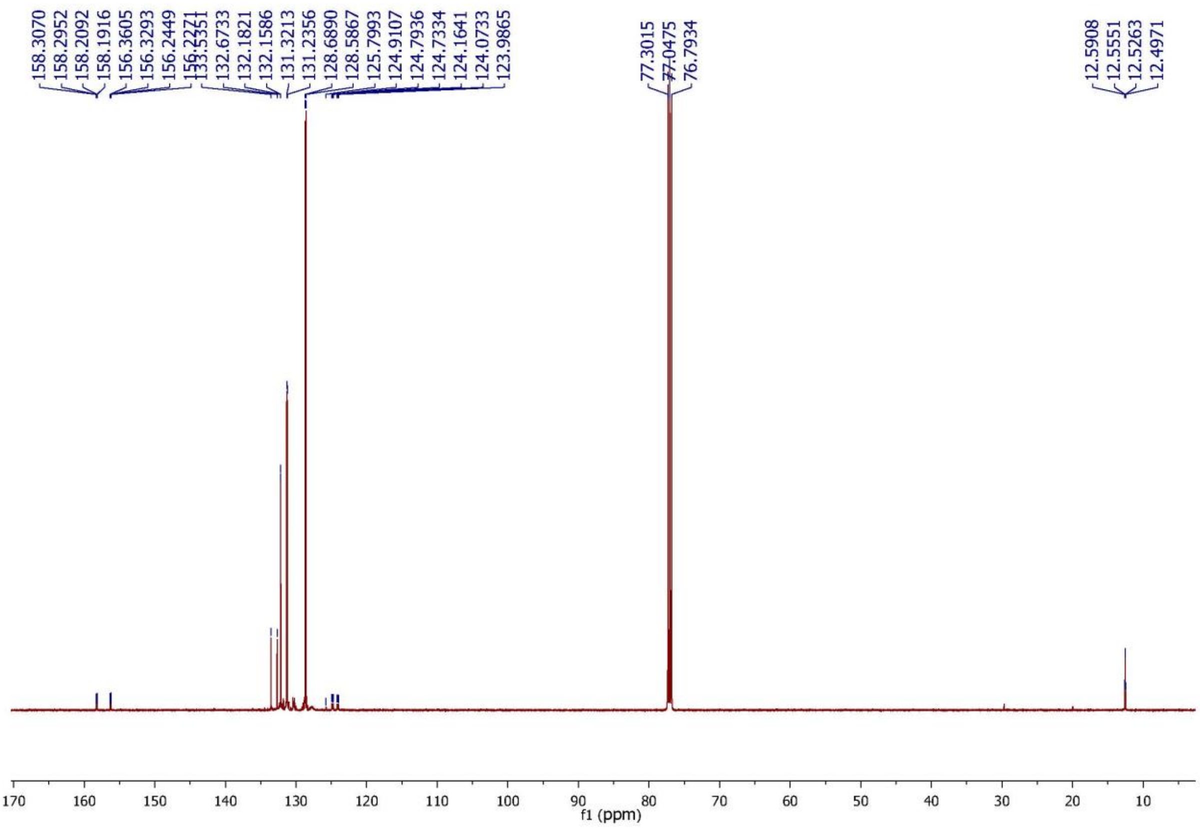

Figure S8. ^{13}C{^{1}H} NMR spectrum for phosphine oxide **3** ($CDCl_3$, 100.61 MHz)

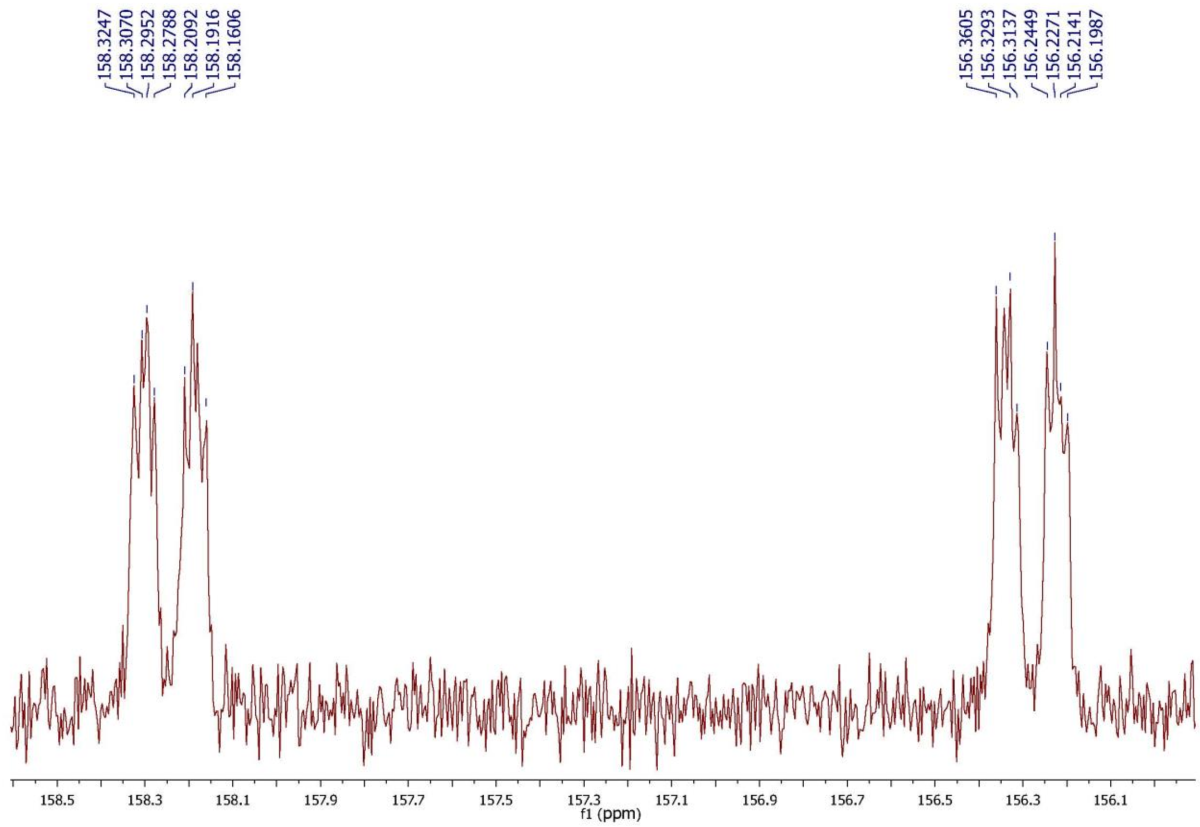

Figure S9. Fragment of $^{13}C\{^{1}H\}$ NMR spectrum for phosphine oxide **3** ($CDCl_3$, 100.61 MHz)

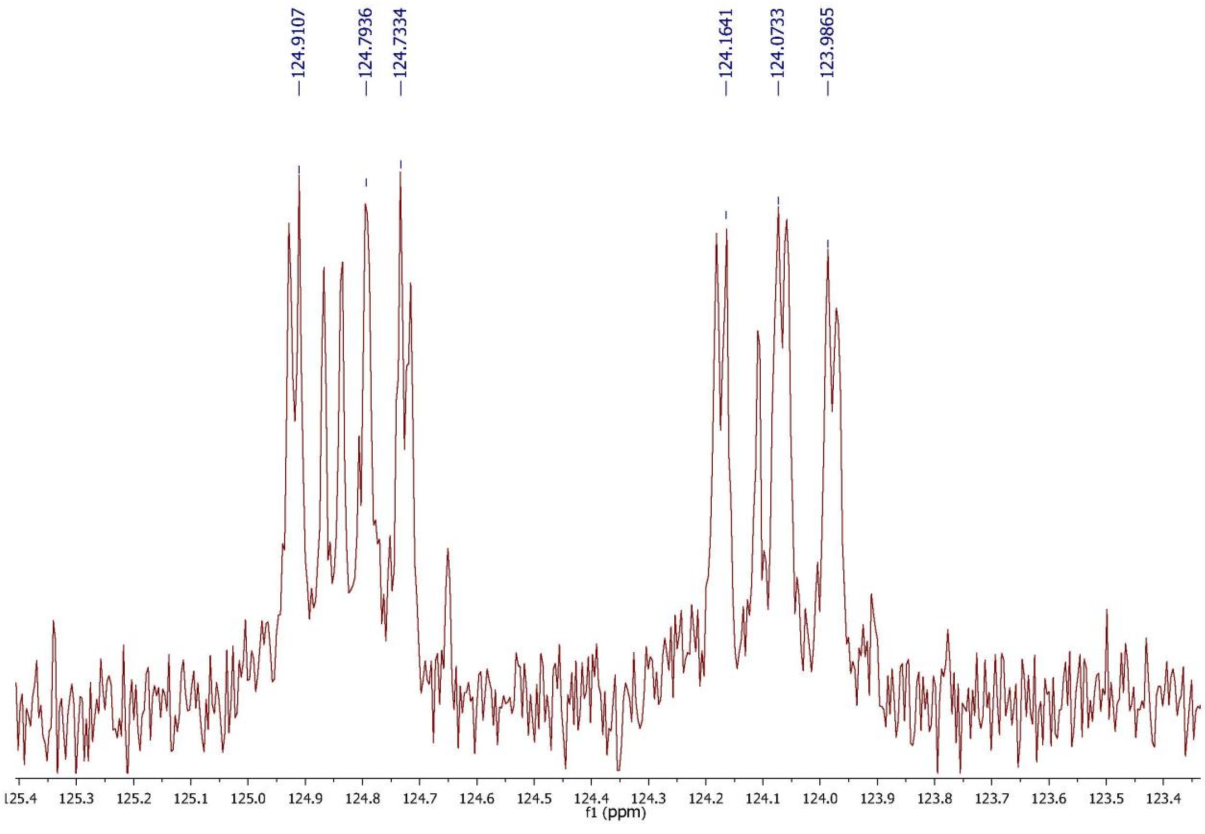

Figure S10. Fragment of $^{13}C\{^{1}H\}$ NMR spectrum for phosphine oxide **3** ($CDCl_3$, 100.61 MHz)

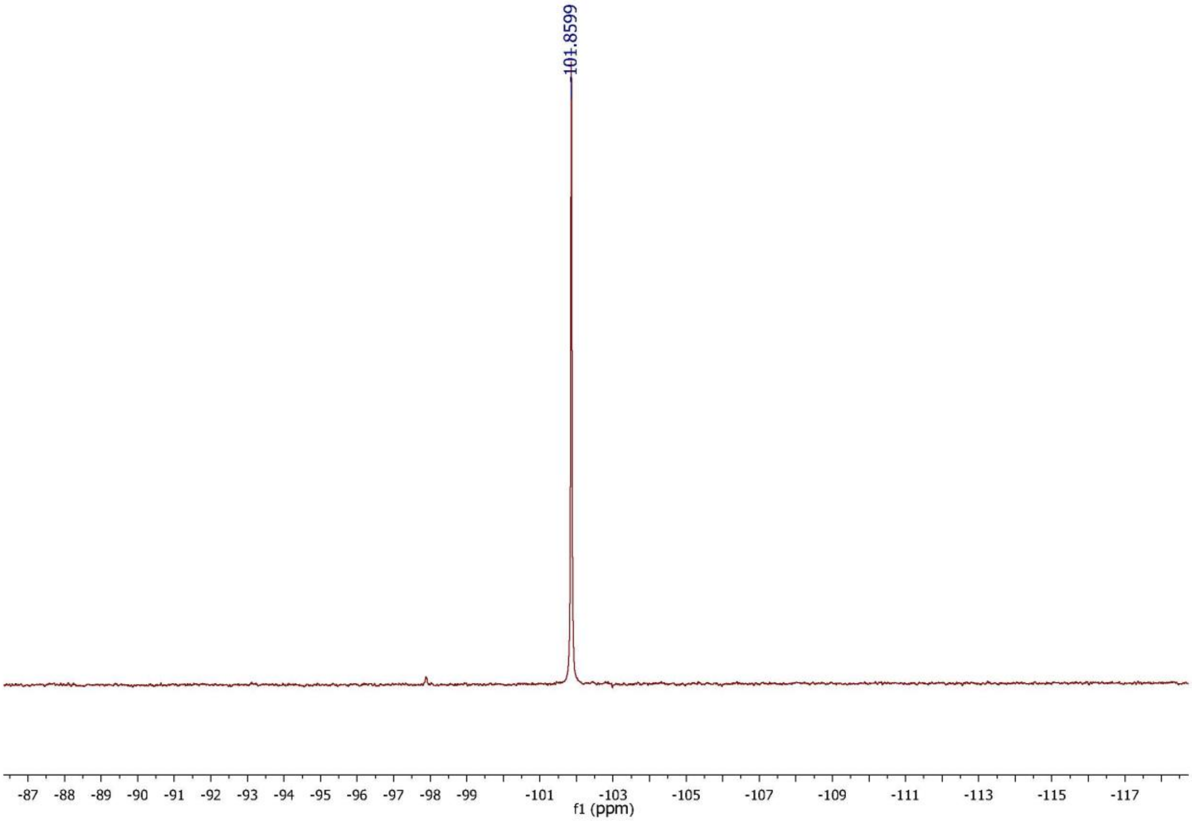

Figure S11. ^{19}F NMR spectrum for phosphine oxide **3** ($CDCl_3$, 282.40 MHz)

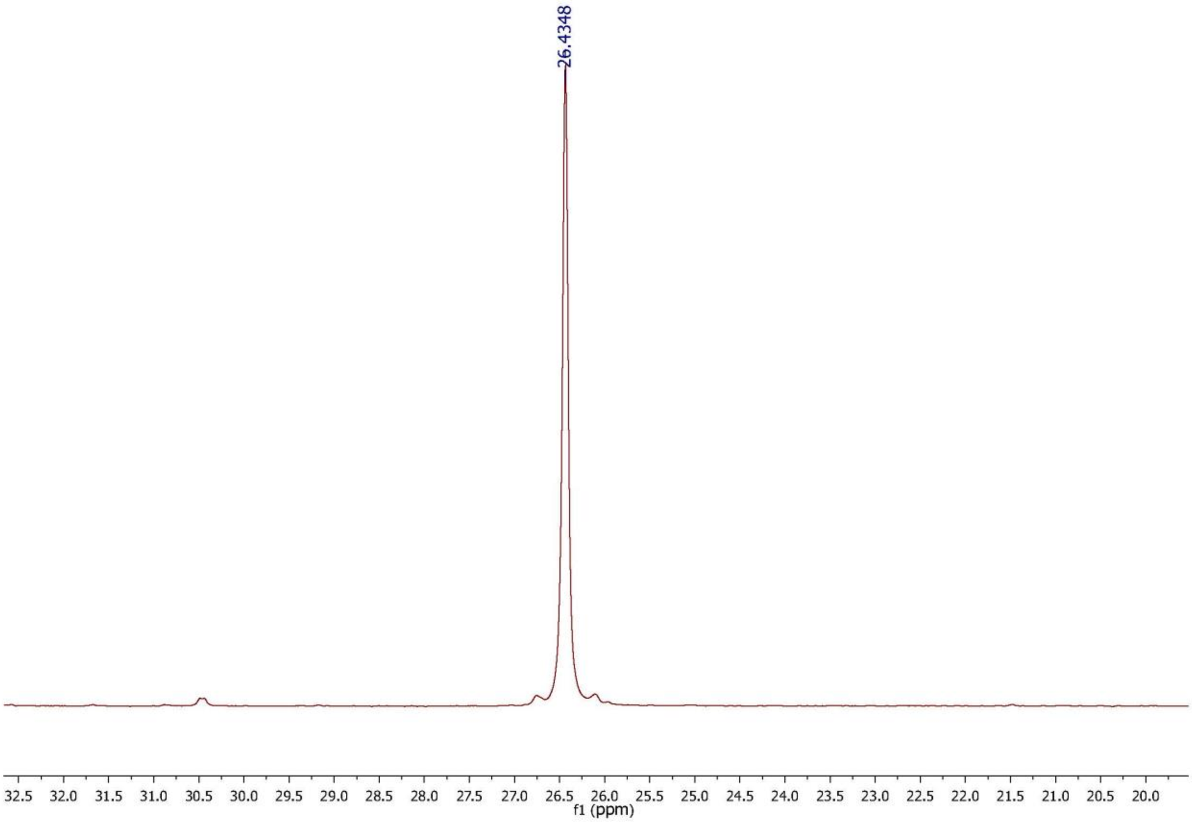

Figure S12. ^{31}P NMR spectrum for phosphine oxide **3** ($CDCl_3$, 161.98 MHz).