Electronic Supplementary Information for

Halide-Bridged Tetranuclear Organocopper(I) Clusters Supported by the Indolyl-based *NCN* Pincer Ligands and Their Catalytic Activities towards Hydrophosphination of Alkenes

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I. Preliminary mechanistic study

The complex **1b** (24.3 mg, 0.02 mmol.) and C_6D_6 (500 uL) were added to a dried glass tube, forming a deep red solution. Then Ph_2PH (11.2 mg, 10.5uL, 0.06 mmol, 3.0 equiv.) was added to above solution. The mixture was stirred at room temperature for 12 h, and the color of the reaction mixture was changed from red to yellow. After that, the mixed solution (100 uL) was syringed into a J-Young NMR tube, diluted with C_6D_6 (400 uL) and sealed for the ^{1}H NMR probing. Comparative ^{1}H NMR spectra of **L^{1}H** and this reaction mixture, it could be observed that the tetranuclear Cu(I) cluster **1b** was dissociated by Ph_2PH to give the species that similar to **L^{1}H**.

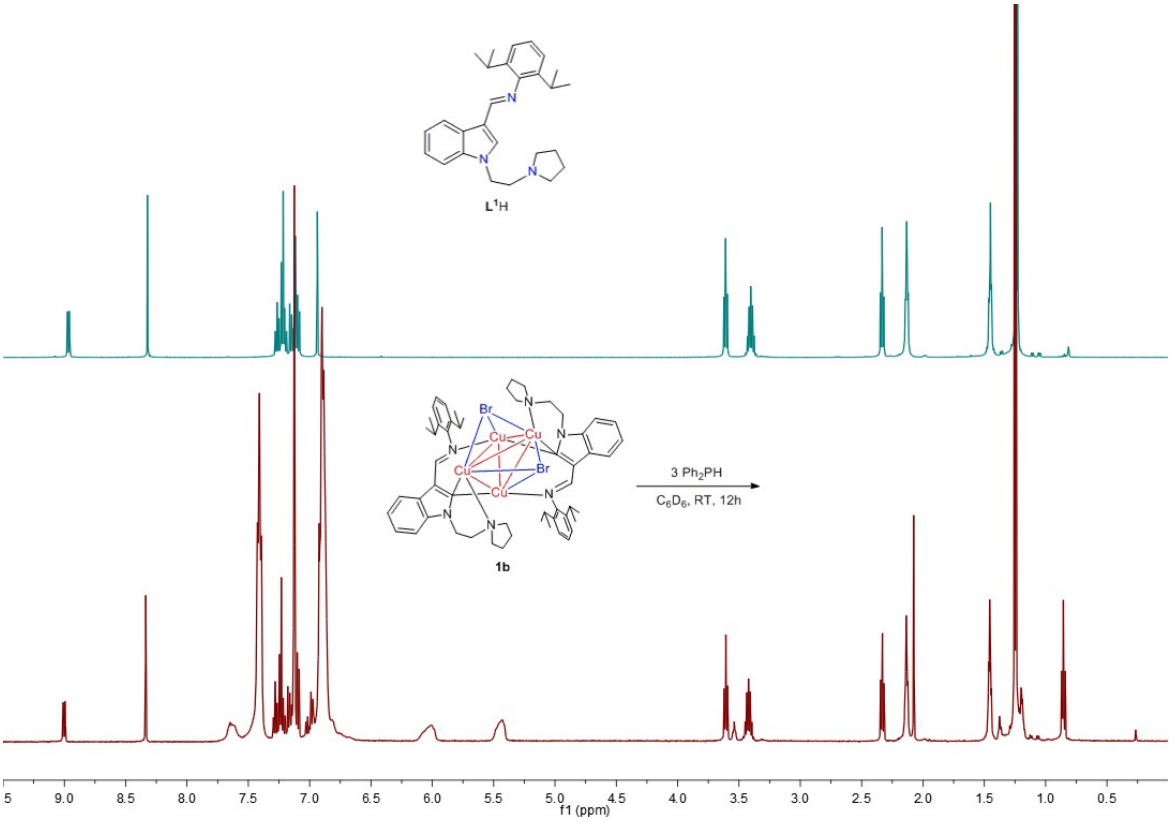


Figure S1. Comparative ^{1}H NMR spectra of **L^{1}H** and **1b** reaction with Ph_2PH in C_6D_6.

II. ^{1}H & ^{13}C NMR spectra of the complex 1a-2c

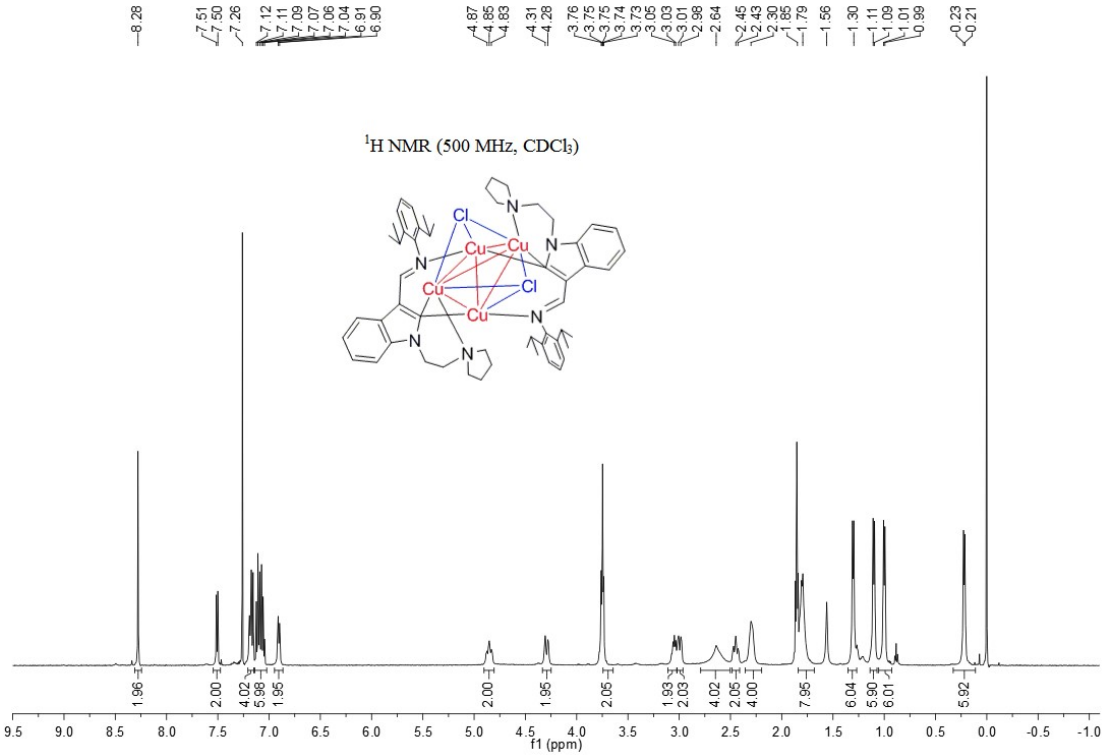


Figure S2. ^{1}H NMR spectra of **1a**

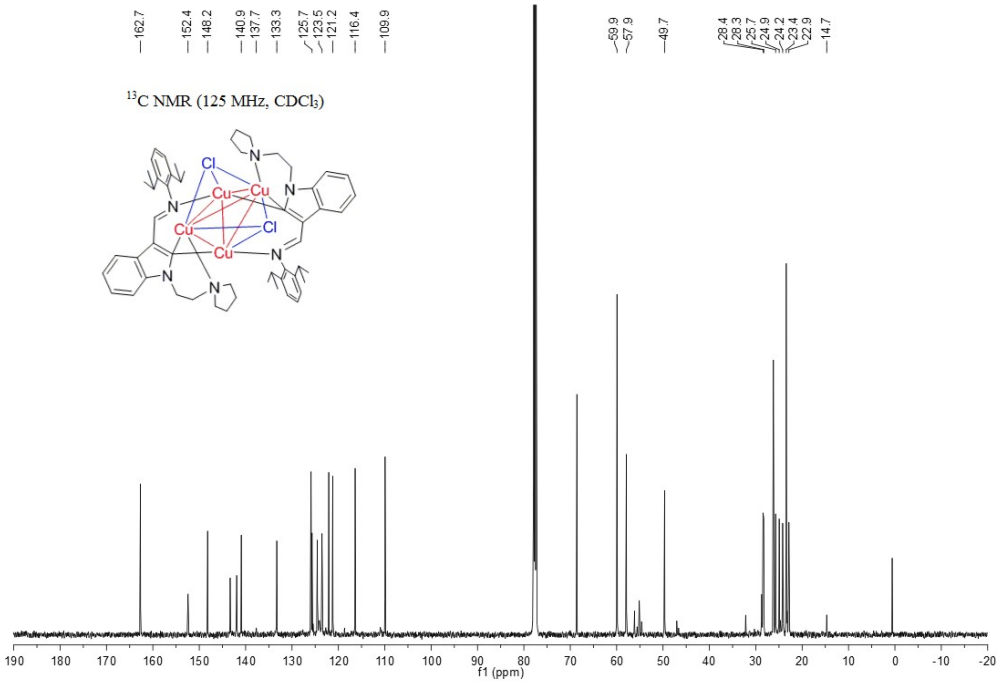


Figure S3. ^{13}C NMR spectra of **1a**

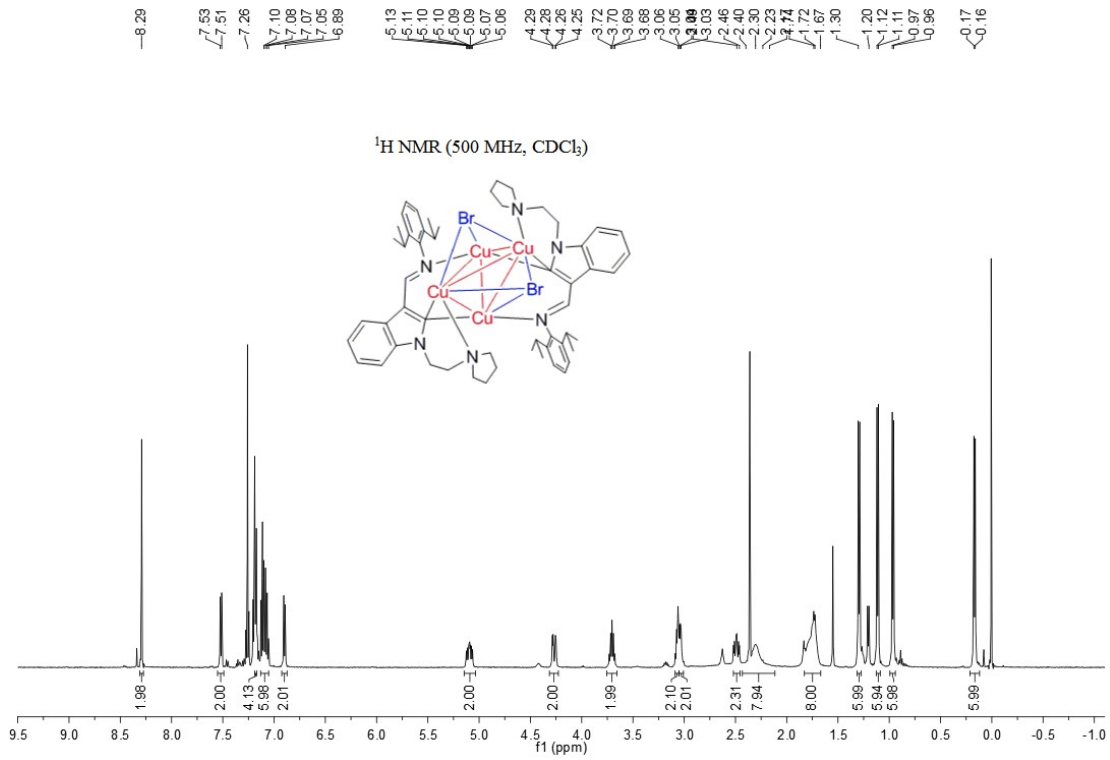


Figure S4. ^{1}H NMR spectra of **1b**

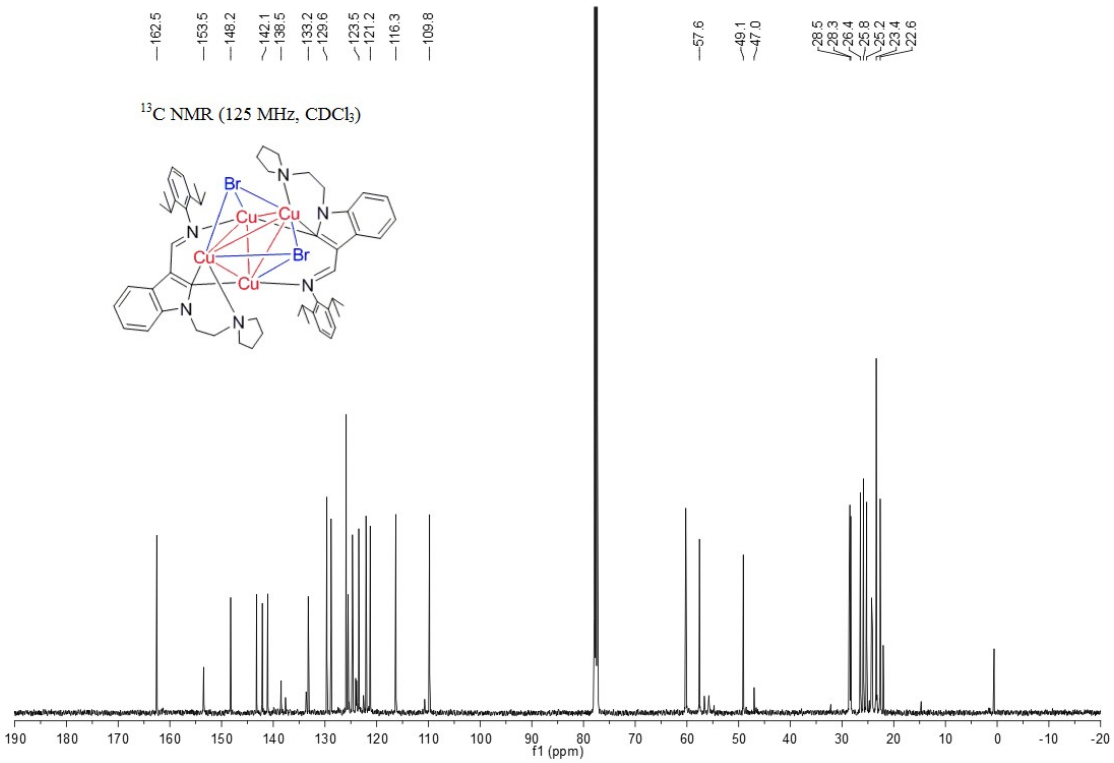


Figure S5. ^{13}C NMR spectra of **1b**

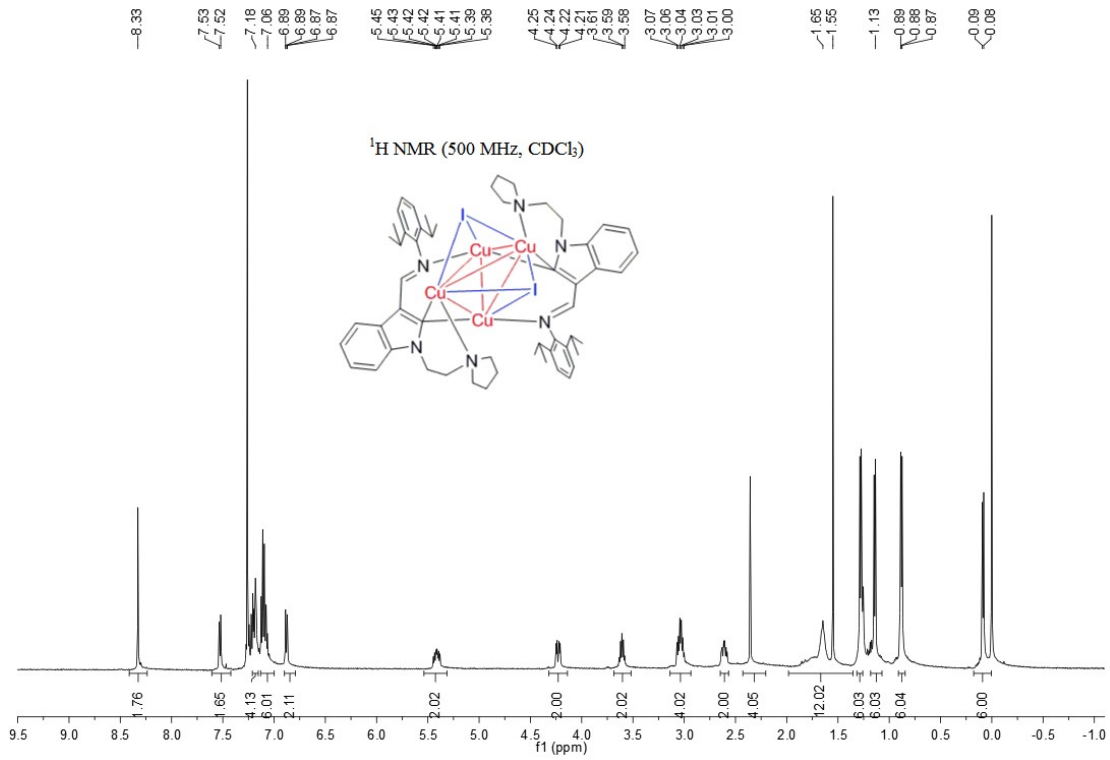


Figure S6. ^{1}H NMR spectra of **1c**

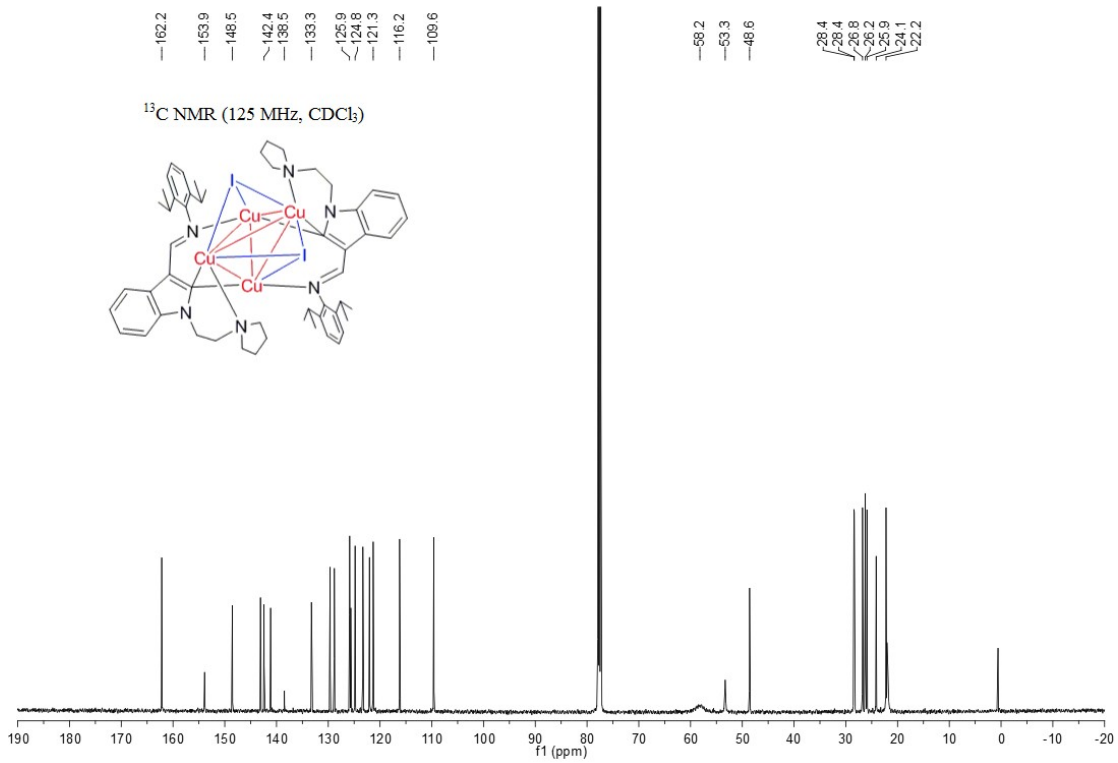


Figure S7. ^{13}C NMR spectra of **1c**

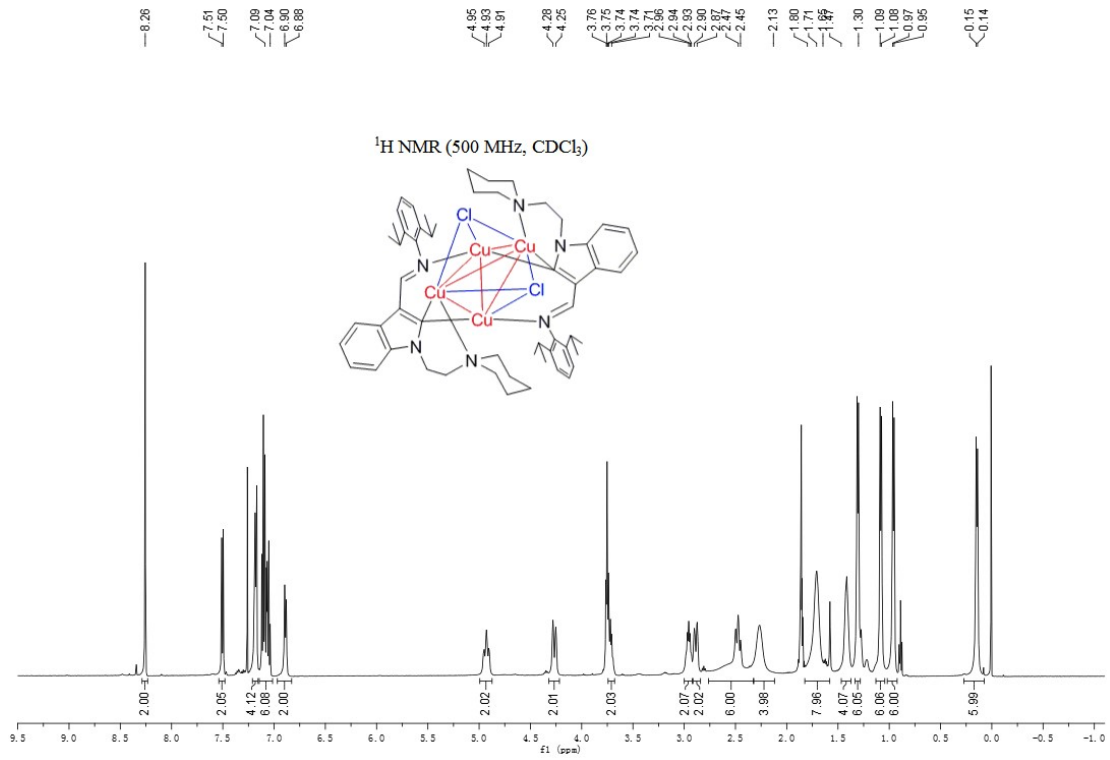


Figure S8. ^{1}H NMR spectra of **2a**

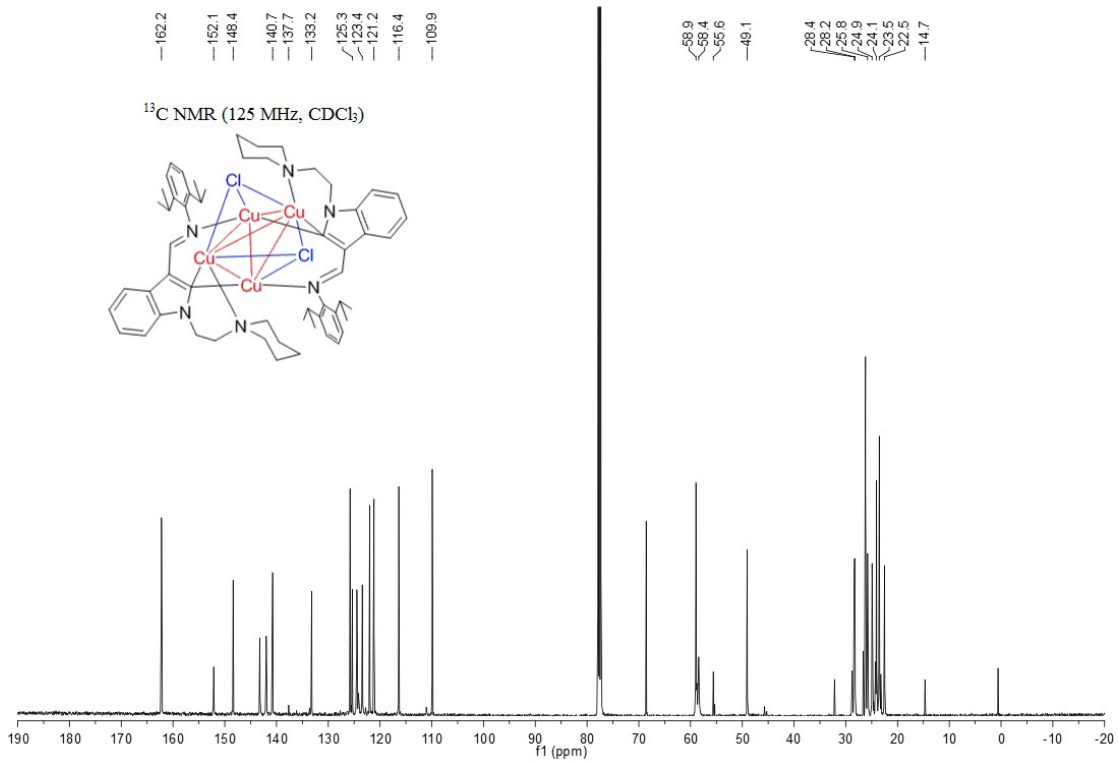


Figure S9. ^{13}C NMR spectra of **2a**

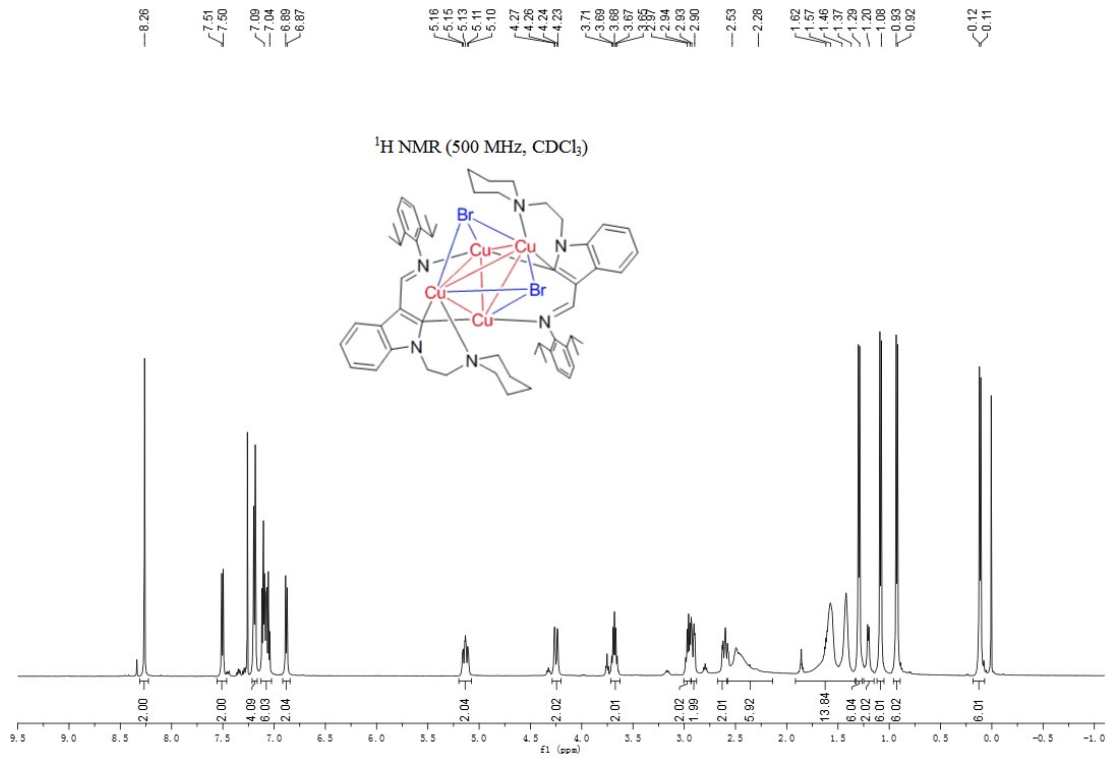


Figure S10. ^{1}H NMR spectra of **2b**

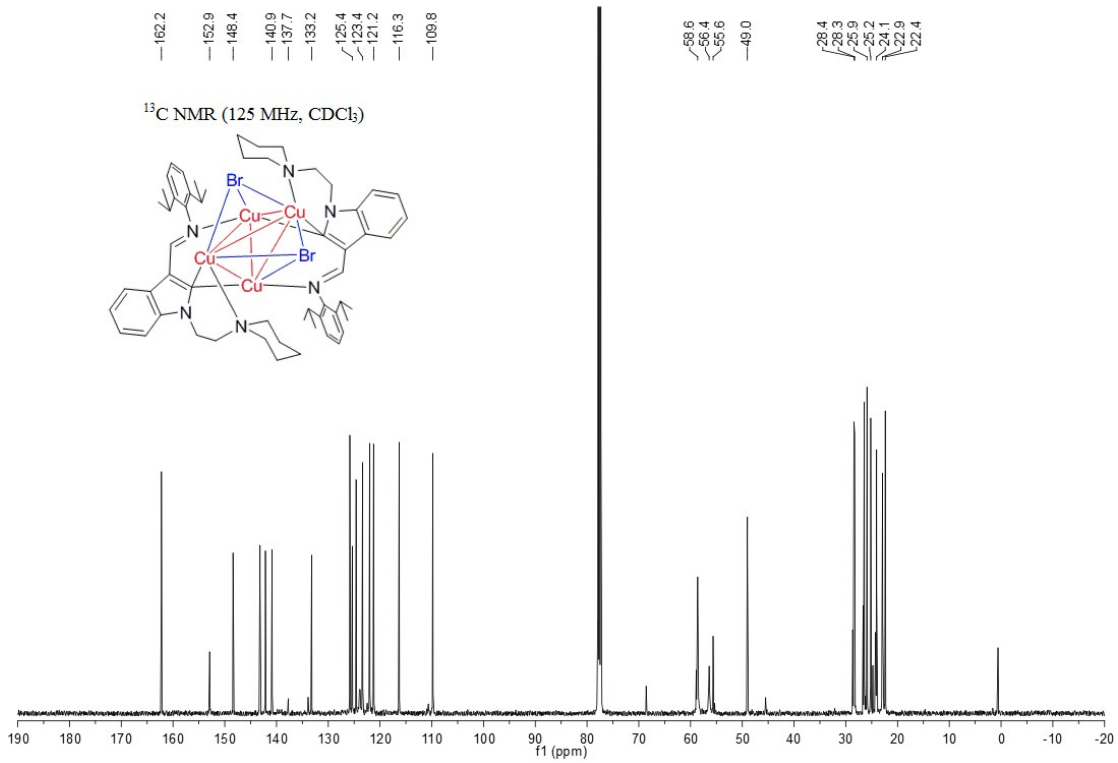


Figure S11. ^{13}C NMR spectra of **2b**

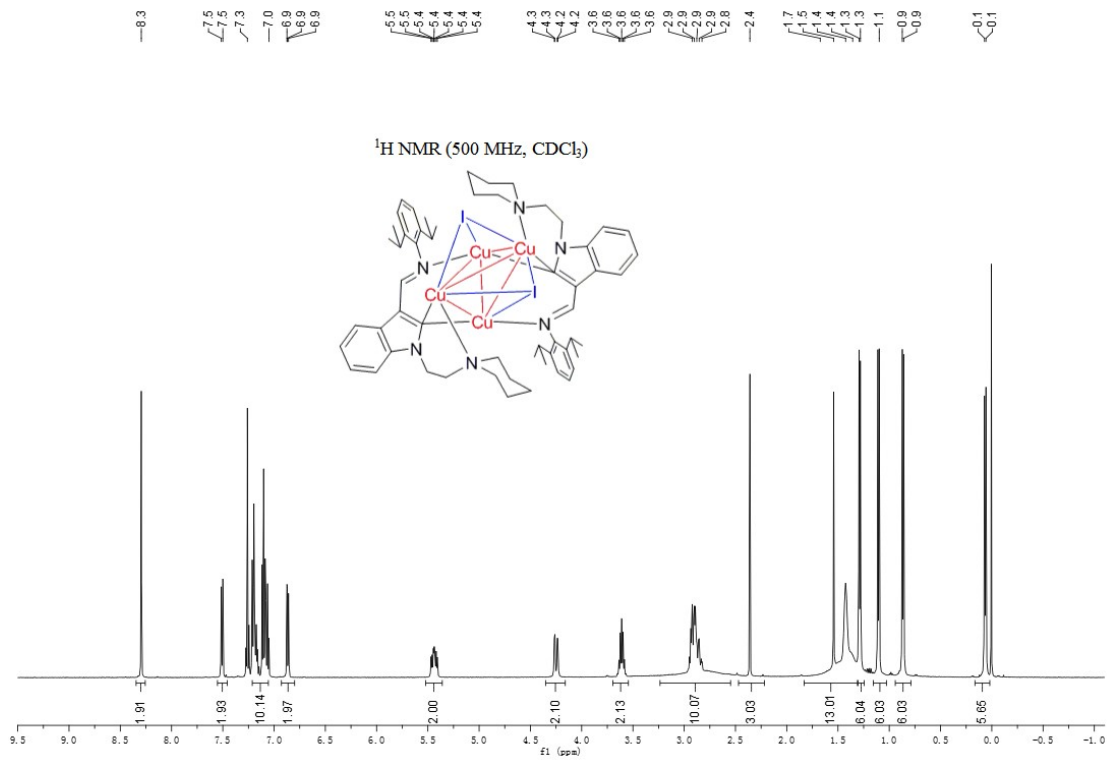


Figure S12. ^{1}H NMR spectra of **2c**

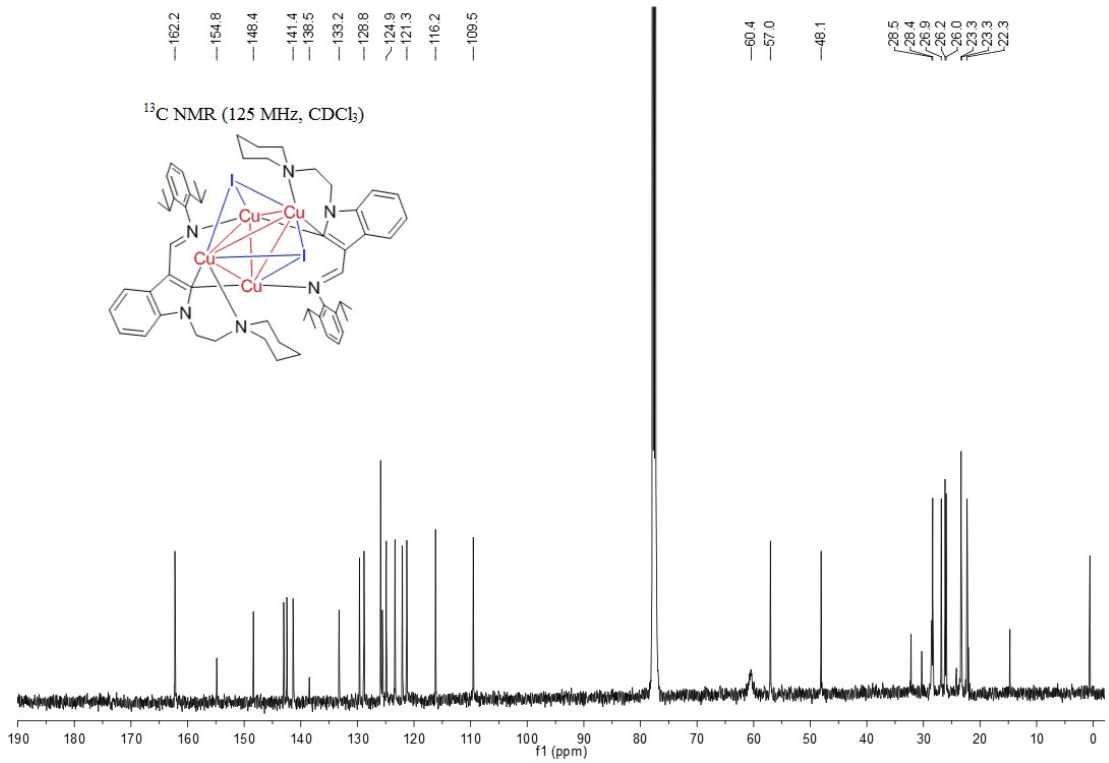
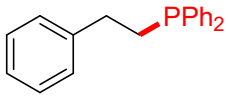
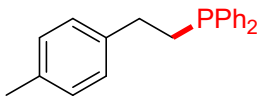


Figure S13. ^{13}C NMR spectra of **2c**

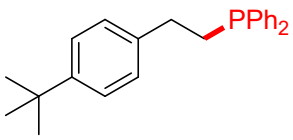
III. Spectral data of the hydrophosphination products 3a-4j



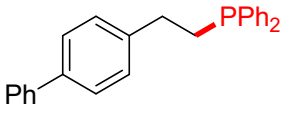
Phenethyldiphenylphosphine (3a). Light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$, 298K): δ 7.49-7.47 (m, 4H, Ph*H*), 7.37-7.36 (m, 6H, Ph*H*), 7.32-7.27 (m, 2H, Ph*H*), 7.23-7.20 (m, 3H, Ph*H*), 2.78-2.73 (m, 2H, PCH_2CH_2), 2.42-2.39 (m, 2H, PCH_2). ^{13}C NMR (125 MHz, $CDCl_3$, 298K): δ 143.0 (d, J = 12.5 Hz), 138.8 (d, J = 11.3 Hz), 133.2 (d, J = 18.8 Hz), 129.1, 128.9, 128.8, 128.6, 126.4, 32.6 (d, J = 17.5 Hz), 30.6 (d, J = 11.3 Hz). ^{31}P NMR (202 MHz, $CDCl_3$ 298K): δ –15.8. Unknown impurity present at –20.8 ppm.[5,6] Spectroscopic data are in accordance with those described in the literature.[5]



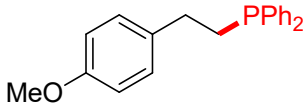
(4-methylphenethyl)diphenylphosphane (3b). Light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$, 298K): δ 7.50-7.47 (m, 4H, Ph*H*), 7.37-7.34 (m, 6H, Ph*H*), 7.21-7.00 (m, 4H, Ph*H*), 2.74-2.70 (m, 2H, PCH_2CH_2), 2.41-2.37 (m, 2H, PCH_2), 2.35(s, 3H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, 298K): δ 143.0 (d, J = 13.8 Hz), 138.9 (d, J = 12.5 Hz), 138.4, 133.2 (d, J = 18.8 Hz), 129.4, 129.0, 128.9 (d, J = 7.5 Hz), 128.8, 127.2, 125.6, 32.5 (d, J = 17.5 Hz), 30.6 (d, J = 12.5 Hz), 21.8. ^{31}P NMR (202 MHz, $CDCl_3$ 298K): δ –15.7. Spectroscopic data are in accordance with those described in the literature.[5] Unknown impurity present at –20.9 ppm.[5,6]



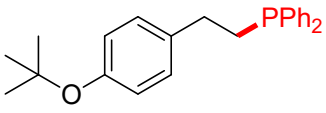
(4-tert-butylphenethyl)diphenylphosphane (3c). Light yellow oil. Yield 333 mg, 96%. ^{1}H NMR (500 MHz, $CDCl_3$, 298K): δ 7.47-7.44 (m, 4H, Ph*H*), 7.37-7.32 (m, 6H, Ph*H*), 7.30 (d, J = 8.0 Hz, 2H, Ph*H*), 7.12 (d, J = 8.5 Hz, 2H, Ph*H*), 2.73-2.68 (m, 2H, PCH_2CH_2), 2.40-2.36 (m, 2H, PCH_2). ^{13}C NMR (125 MHz, $CDCl_3$, 298K): δ 149.2, 139.9 (d, J = 13.8 Hz), 138.7 (d, J = 11.3 Hz), 133.1 (d, J = 17.5 Hz), 129.0, 128.8 (d, J = 6.3 Hz), 128.2, 125.7, 34.8, 31.9 (d, J = 18.8 Hz), 31.8, 30.4 (d, J = 11.3 Hz), 29.2. ^{31}P NMR (202 MHz, $CDCl_3$ 298K): δ –15.7. Spectroscopic data are in accordance with those described in the literature.[7] Unknown impurity present at –20.3 ppm.[5,6]



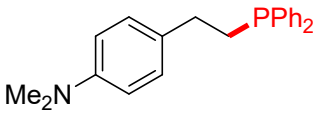
{2-[(1,1'-Biphenyl)-4-yl]ethyl}diphenylphosphane (3d). Light yellow oil. Yield 355 mg, 97%. ^{1}H NMR (500 MHz, $CDCl_3$, 298K): δ 7.61-7.58 (m, 2H, Ph*H*), 7.57-7.44 (m, 8H, Ph*H*), 7.42-7.32 (m, 7H, Ph*H*), 7.29-7.26 (m, 2H, Ph*H*), 2.82-2.78 (m, 2H, PCH_2CH_2), 2.46-2.43 (m, 2H, PCH_2). ^{13}C NMR (125 MHz, $CDCl_3$, 298K): δ 142.2 (d, J = 12.5 Hz), 141.5, 139.5, 138.9 (d, J = 11.3 Hz), 133.2 (d, J = 17.5 Hz), 129.2, 129.1, 129.0, 128.9 (d, J = 7.5 Hz), 127.6, 127.5, 127.5, 32.2 (d, J = 17.5 Hz), 30.6 (d, J = 11.3 Hz). ^{31}P NMR (202 MHz, $CDCl_3$ 298K): δ –15.8. Spectroscopic data are in accordance with those described in the literature.[5] Unknown impurity present at –20.6 ppm.[5,6]



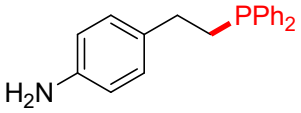
(4-methoxyphenethyl)diphenylphosphane (3e). Light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$, 298K): δ 7.47-7.44 (m, 6H, Ph*H*), 7.35-7.34 (m, 4H, Ph*H*), 7.10-7.09 (m, 2H, Ph*H*), 6.84-6.82 (m, 2H, Ph*H*), 3.79 (s, 3H, CH_3), 2.70-2.65 (m, 2H, PCH_2CH_2), 2.37-2.33 (m, 2H, PCH_2). ^{13}C NMR (125 MHz, $CDCl_3$, 298K): δ 158.3, 138.9 (d, J = 11.3 Hz), 135.1 (d, J = 13.8 Hz), 133.2 (d, J = 18.8 Hz), 129.5, 129.0, 129.9 (d, J = 7.5 Hz), 114.3, 55.7, 31.6 (d, J = 16.3 Hz), 30.9 (d, J = 12.5 Hz). ^{31}P NMR (202 MHz, $CDCl_3$ 298K): δ –16.1. Spectroscopic data are in accordance with those described in the literature.[5]



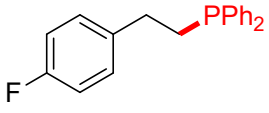
(4-tert-butoxyphenethyl)diphenylphosphane (3f). Light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$, 298K): δ 7.47-7.44 (m, 4H, Ph*H*), 7.34-7.33 (m, 6H, Ph*H*), 7.06 (d, J = 8.5 Hz, 2H, Ph*H*), 6.89 (d, J = 8.5 Hz, 2H, Ph*H*), 2.71-2.66 (m, 2H, PCH_2CH_2), 2.38-2.34 (m, 2H, PCH_2), 1.33 (s, 9H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, 298K): δ 153.8, 138.9 (d, J = 12.5 Hz), 137.9 (d, J = 13.8 Hz), 134.3 (d, J = 16.3 Hz), 133.2 (d, J = 18.8 Hz), 129.0, 128.9 (d, J = 6.3 Hz), 124.6, 78.6, 31.9 (d, J = 17.5 Hz), 30.6 (d, J = 12.5 Hz), 29.2. ^{31}P NMR (202 MHz, $CDCl_3$ 298K): δ –15.6. HRMS: m/z (ESI) calcd. for (4-tert-butoxyphenethyl)diphenylphosphane oxide $C_{24}H_{27}O_2P$ $[M+H]^+$: 379.1821, found: 379.1815.



(4-dimethylaminophenethyl)diphenylphosphane (3g). Light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$, 298K): δ 7.46-7.44 (m, 4H, Ph*H*), 7.34-7.33 (m, 6H, Ph*H*), 7.06 (d, J = 10.0 Hz, 2H, Ph*H*), 6.89 (d, J = 10.0 Hz, 2H, Ph*H*), 2.92 (s, 6H, CH_3), 2.67-2.62 (m, 2H, PCH$_2$CH_2), 2.36-2.33 (m, 2H, PCH_2). ^{13}C NMR (125 MHz, $CDCl_3$, 298K): δ 149.6, 139.1 (d, J = 11.3 Hz), 134.4 (d, J = 16.3 Hz), 133.2 (d, J = 17.5 Hz), 129.2, 128.9, 128.8 (d, J = 6.3 Hz), 113.5, 41.3, 31.5 (d, J = 17.5 Hz), 30.9 (d, J = 12.5 Hz). ^{31}P NMR (202 MHz, $CDCl_3$ 298K): δ –16.0. HRMS: m/z (ESI) calcd. for (4-dimethylaminophenethyl)diphenylphosphane oxide $C_{22}H_{24}NOP$ $[M+H]^+$: 350.1688, found: 350.1682.

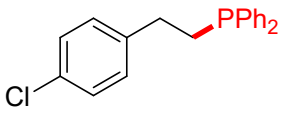


(4-aminophenethyl)diphenylphosphane (3h). White solid. Yield ^{1}H NMR (500 MHz, $CDCl_3$, 298K): δ 7.49-7.43 (m, 4H, Ph*H*), 7.36-7.33 (m, 6H, Ph*H*), 6.96 (d, J = 8.0 Hz, 2H, Ph*H*), 6.61 (d, J = 8.0 Hz, 2H, Ph*H*), 3.58 (s, 2H, CH_3), 2.64-2.59 (m, 2H, PCH$_2$CH_2), 2.34-2.30 (m, 2H, PCH_2). ^{13}C NMR (125 MHz, $CDCl_3$, 298K): δ 144.9, 139.0 (d, J = 12.5 Hz), 134.4 (d, J = 16.3 Hz), 133.2 (d, J = 18.8 Hz), 129.4, 129.0, 128.9 (d, J = 6.3 Hz), 115.7, 31.7 (d, J = 17.5 Hz), 30.9 (d, J = 12.5 Hz). ^{31}P NMR (202 MHz, $CDCl_3$ 298K): δ –16.0. HRMS: m/z (ESI) calcd. for (4-aminophenethyl)diphenylphosphane oxide $C_{20}H_{20}NOP$ $[M+H]^+$: 322.1355, found: 322.1363.

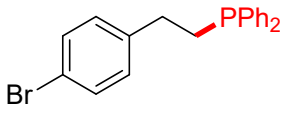


(4-fluorophenethyl)diphenylphosphane (3i). Light yellow oil. Yield ^{1}H NMR (500 MHz, $CDCl_3$, 298K): δ 7.46-7.42 (m, 4H, Ph*H*), 7.35-7.32 (m, 6H, Ph*H*), 7.13-7.10 (m, 2H, Ph*H*), 6.97-6.93 (m, 2H, Ph*H*), 2.72-2.67 (m, 2H, PCH$_2$CH_2), 2.36-2.32 (m, 2H, PCH_2). ^{13}C NMR (125 MHz, $CDCl_3$, 298K): δ 161.7 (d, J = 242.1 Hz), 138.6 (d, J = 12.8 Hz), 134.4 (d, J = 16.6 Hz), 133.2 (d, J = 18.1 Hz), 130.0 (d, J = 7.6 Hz), 129.1, 128.9 (d, J = 6.6 Hz), 115.6 (d, J = 20.9 Hz), 31.7 (d, J = 16.3 Hz), 30.7 (d, J = 11.3 Hz). ^{31}P NMR (202 MHz, $CDCl_3$ 298K): δ –16.1. ^{19}F NMR (470 MHz, $CDCl_3$ 298K): δ –117.3

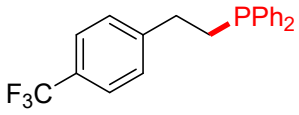
(dd, J =13.2, 8.5 Hz). Spectroscopic data are in accordance with those described in the literature.[5]



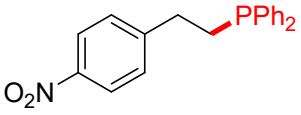
(4-chlorophenethyl)diphenylphosphane (3j). Light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$, 298K): δ 7.49-7.44 (m, 4H, Ph*H*), 7.38-7.32 (m, 6H, Ph*H*), 7.23 (d, J = 7.0 Hz, 2H, Ph*H*), 7.09 (d, J = 7.5 Hz, 2H, Ph*H*), 2.71-2.66 (m, 2H, PCH_2CH_2), 2.37-2.33 (m, 2H, PCH_2). ^{13}C NMR (125 MHz, $CDCl_3$, 298K): δ 141.4 (d, J = 12.5 Hz), 138.6 (d, J = 11.3 Hz), 134.3 (d, J = 17.5 Hz), 133.1 (d, J = 18.8 Hz), 132.1, 129.9, 129.1, 128.9 (d, J = 6.3 Hz), 31.9 (d, J = 17.5 Hz), 30.5 (d, J = 12.5 Hz). ^{31}P NMR (202 MHz, $CDCl_3$ 298K): δ –16.2. Spectroscopic data are in accordance with those described in the literature.[5]



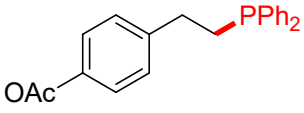
(4-bromophenethyl)diphenylphosphane (3k). White solid. Yield ^{1}H NMR (500 MHz, $CDCl_3$, 298K): δ 7.46-7.45 (m, 4H, Ph*H*), 7.39 (d, J = 8.0 Hz, 2H, Ph*H*), 7.35-7.34 (m, 6H, Ph*H*), 7.04 (d, J = 8.5 Hz, 2H, Ph*H*), 2.70-2.65 (m, 2H, PCH_2CH_2), 2.37-2.33 (m, 2H, PCH_2). ^{13}C NMR (125 MHz, $CDCl_3$, 298K): δ 141.9 (d, J = 12.5 Hz), 138.6 (d, J = 11.3 Hz), 133.1 (d, J = 18.8 Hz), 131.9, 130.4, 129.1, 128.9 (d, J = 17.5 Hz), 120.2, 32.0 (d, J = 17.5 Hz), 30.4 (d, J = 12.5 Hz). ^{31}P NMR (202 MHz, $CDCl_3$ 298K): δ –16.2. Spectroscopic data are in accordance with those described in the literature.[5]



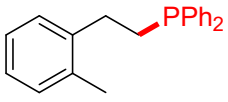
(4-trifluoromethylphenethyl)diphenylphosphane (3l). White solid. ^{1}H NMR (500 MHz, $CDCl_3$, 298K): δ 7.52 (d, J = 7.5 Hz, 2H, Ph*H*), 7.45-7.43 (m, 4H, Ph*H*), 7.36-7.34 (m, 6H, Ph*H*), 7.27 (d, J = 7.5 Hz, 2H, Ph*H*), 2.80-2.75 (m, 2H, PCH_2CH_2), 2.38-2.35 (m, 2H, PCH_2). ^{13}C NMR (125 MHz, $CDCl_3$, 298K): δ 147.1 (d, J = 12.5 Hz), 138.6 (d, J = 11.3 Hz), 134.4 (d, J = 16.3 Hz), 133.2 (d, J = 16.3 Hz), 129.3, 129.1, 129.0, 125.8 (d, J = 3.8 Hz), 124.9 (q, J = 270.0 Hz), 32.5 (d, J = 17.5 Hz), 30.3 (d, J = 13.8 Hz). ^{31}P NMR (202 MHz, $CDCl_3$ 298K): δ –16.1. ^{19}F NMR (470 MHz, $CDCl_3$ 298K): δ –62.1. Spectroscopic data are in accordance with those described in the literature.[8]



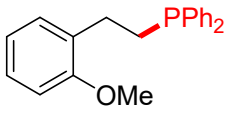
(4-nitrylphenethyl)diphenylphosphane (3m). Light yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$, 298K): δ 8.12-8.11 (m, 2H, Ph*H*), 7.55-7.29 (m, 12H, Ph*H*), 2.84-2.79 (m, 2H, PCH_2CH_2), 2.39-2.36 (m, 2H, PCH_2). ^{13}C NMR (125 MHz, $CDCl_3$, 298K): δ 150.6 (d, J = 12.5 Hz), 146.9, 138.2 (d, J = 13.8 Hz), 133.1 (d, J = 18.8 Hz), 129.5, 129.3, 129.0 (d, J = 6.3 Hz), 124.1, 32.5 (d, J = 18.8 Hz), 30.1 (d, J = 13.8 Hz). ^{31}P NMR (202 MHz, $CDCl_3$ 298K): δ –16.2. HRMS: m/z (ESI) calcd. for (4-nitrylphenethyl)diphenylphosphane oxide $C_{20}H_{18}NO_3P$ $[M+H]^+$: 352.1097, found: 352.1093.



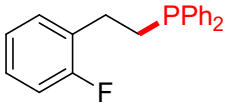
4-[2-(Diphenylphosphanyl)ethyl]phenyl acetate (3n). Light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$, 298K): δ 7.48-7.45 (m, 4H, Ph*H*), 7.36-7.35 (m, 6H, Ph*H*), 7.18 (d, J = 8.5 Hz, 2H, Ph*H*), 7.00 (d, J = 8.5 Hz, 2H, Ph*H*), 2.75-2.70 (m, 2H, PCH_2CH_2), 2.39-2.36 (m, 2H, PCH_2), 2.30 (s, 3H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, 298K): δ 170.1, 149.3, 140.6 (d, J = 13.8 Hz), 138.7 (d, J = 12.5 Hz), 132.1 (d, J = 13.8 Hz), 129.5, 129.1, 128.9 (d, J = 6.3 Hz), 121.97, 32.0 (d, J = 17.5 Hz), 30.5 (d, J = 12.5 Hz), 21.6. ^{31}P NMR (202 MHz, $CDCl_3$ 298K): δ –16.0. Spectroscopic data are in accordance with those described in the literature.[9]



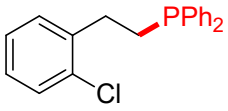
(2-methylphenethyl)diphenylphosphane (3o). Light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$, 298K): δ 7.54-7.49 (m, 4H, Ph*H*), 7.46-7.37 (m, 6H, Ph*H*), 7.17-7.14 (m, 4H, Ph*H*), 2.75-2.70 (m, 2H, PCH_2CH_2), 2.36-2.32 (m, 2H, PCH_2), 2.21(s, 3H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, 298K): δ 141.3 (d, J = 13.8 Hz), 138.9 (d, J = 11.3 Hz), 136.1, 133.2 (d, J = 17.5 Hz), 130.7, 129.0, 128.9 (d, J = 7.5 Hz), 126.6, 126.5, 30.0 (d, J = 17.5 Hz), 29.4 (d, J = 12.5 Hz), 19.6. ^{31}P NMR (202 MHz, $CDCl_3$ 298K): δ –15.3. Spectroscopic data are in accordance with those described in the literature.[5]



(2-methoxyphenethyl)diphenylphosphane (3p). White solid. ^{1}H NMR (500 MHz, $CDCl_3$, 298K): δ 7.51-7.49 (m, 4H, Ph*H*), 7.36-7.35 (m, 6H, Ph*H*), 7.20 (t, J = 7.8 Hz, 1H, Ph*H*), 7.14 (d, J = 7.0 Hz, 1H, Ph*H*), 6.90 (t, J = 7.3 Hz, 1H, Ph*H*), 6.85 (d, J = 8.5 Hz, 1H, Ph*H*), 3.81(s, 3H, CH_3), 2.78-2.75 (m, 2H, PCH$_2$CH_2), 2.39-2.35 (m, 2H, PCH_2). ^{13}C NMR (125 MHz, $CDCl_3$, 298K): δ 157.7, 139.0 (d, J = 11.3 Hz), 133.2 (d, J = 18.8 Hz), 131.4 (d, J = 12.5 Hz), 130.0, 128.9, 128.8 (d, J = 6.3 Hz), 127.7, 120.8, 110.6, 55.5, 28.8 (d, J = 12.5 Hz), 27.6 (d, J = 17.5 Hz). ^{31}P NMR (202 MHz, $CDCl_3$ 298K): δ –15.3. Spectroscopic data are in accordance with those described in the literature.[7] Unknown impurity present at –20.1 ppm.[5,6]

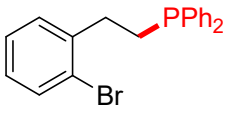


(2-fluorophenethyl)diphenylphosphane (3q). Light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$, 298K): δ 7.44-7.42 (m, 4H, Ph*H*), 7.33-7.32 (m, 6H, Ph*H*), 7.18-7.13 (m, 2H, Ph*H*), 7.05-6.96 (m, 2H, Ph*H*), 2.73-2.70 (m, 2H, PCH$_2$CH_2), 2.38-2.35 (m, 2H, PCH_2). ^{13}C NMR (125 MHz, $CDCl_3$, 298K): δ 161.4 (d, J = 243.8 Hz), 138.1 (d, J = 10.0 Hz), 133.1 (d, J = 17.5 Hz), 130.8 (d, J = 5.0 Hz), 129.8 (d, J = 2.1 Hz), 129.1, 128.8 (d, J = 6.3 Hz), 128.1 (d, J = 7.5 Hz), 124.4 (d, J = 3.8 Hz), 115.6 (d, J = 22.5 Hz), 29.0 (d, J = 10.0 Hz), 26.0 (d, J = 17.5 Hz). ^{31}P NMR (202 MHz, $CDCl_3$ 298K): δ –15.4. ^{19}F NMR (470 MHz, $CDCl_3$ 298K): δ –118.5 (dd, J =14.1, 8.5 Hz). Spectroscopic data are in accordance with those described in the literature.[5] Unknown impurity present at –20.8 ppm.[5,6]

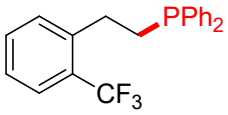


(2-chlorophenethyl)diphenylphosphane (3r). Light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$, 298K): δ 7.50-7.47 (m, 4H, Ph*H*), 7.37-7.32 (m, 7H, Ph*H*), 7.21-7.12 (m, 3H, Ph*H*), 2.87-2.82 (m, 2H, PCH$_2$CH_2), 2.39-2.36 (m, 2H, PCH_2). ^{13}C NMR (125 MHz, $CDCl_3$, 298K): δ 140.6 (d, J = 13.8 Hz), 138.6 (d, J = 11.3 Hz), 134.1, 133.2 (d, J = 18.8 Hz), 130.7, 129.9, 129.1, 128.9 (d, J = 6.3 Hz), 128.0, 127.3, 30.7 (d, J = 17.5 Hz), 28.8 (d, J = 7.5 Hz). ^{31}P NMR (202 MHz, $CDCl_3$ 298K): δ –15.6. Spectroscopic data are in accordance with those described in the literature.[5] Unknown impurity present at –21.2

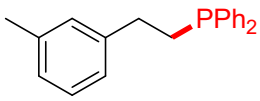
ppm.[5,6]



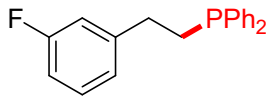
(2-bromophenethyl)diphenylphosphane (3s). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$, 298K): δ 7.52-7.48 (m, 5H, Ph*H*), 7.38-7.32 (m, 6H, Ph*H*), 7.24-7.20 (m, 2H, Ph*H*), 7.07-7.04 (m, 1H, Ph*H*), 2.88-2.83 (m, 2H, PCH_2CH_2), 2.40-2.36 (m, 2H, PCH_2). ^{13}C NMR (125 MHz, $CDCl_3$, 298K): δ 142.4 (d, J = 13.8 Hz), 133.6 (d, J = 11.3 Hz), 133.3 (d, J = 18.8 Hz), 133.3, 130.8, 129.1, 128.9 (d, J = 6.3 Hz), 128.2, 128.0, 124.6, 33.2 (d, J = 18.8 Hz), 29.0 (d, J = 12.5 Hz). ^{31}P NMR (202 MHz, $CDCl_3$ 298K): δ –15.4. Spectroscopic data are in accordance with those described in the literature.[5] Unknown impurity present at –21.4 ppm.[5,6]



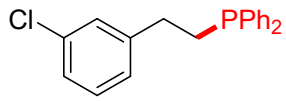
(2-trifluoromethylphenethyl)diphenylphosphane (3t). White solid. ^{1}H NMR (500 MHz, $CDCl_3$, 298K): δ 7.60 (d, J = 8.0 Hz, 1H, Ph*H*), 7.48-7.44 (m, 5H, Ph*H*), 7.36-7.26 (m, 8H, Ph*H*), 2.98-2.83 (m, 2H, PCH_2CH_2), 2.38-2.34 (m, 2H, PCH_2). ^{13}C NMR (125 MHz, $CDCl_3$, 298K): δ 142.0 (d, J = 13.8 Hz), 138.7 (d, J = 11.3 Hz), 133.3 (d, J = 18.8 Hz), 132.4, 131.6, 129.3, 128.9 (d, J = 21.3 Hz), 128.5 (d, J = 30.0 Hz), 126.7, 126.5 (d, J = 6.3 Hz), 125.1 (q, J = 272.1 Hz), 31.1 (d, J = 13.8 Hz), 29.7 (d, J = 18.8 Hz). ^{31}P NMR (202 MHz, $CDCl_3$ 298K): δ –14.9. ^{19}F NMR (470 MHz, $CDCl_3$ 298K): δ –59.6. Spectroscopic data are in accordance with those described in the literature.[10]



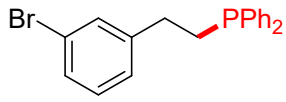
(3-methylphenethyl)diphenylphosphane (3u). Light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$, 298K): δ 7.50-7.47 (m, 4H, Ph*H*), 7.37-7.36 (m, 6H, Ph*H*), 7.21-7.18 (m, 1H, Ph*H*), 7.04-7.00 (m, 3H, Ph*H*), 2.75-2.70 (m, 2H, PCH_2CH_2), 2.41-2.38 (m, 2H, PCH_2), 2.35(s, 3H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, 298K): δ 143.0 (d, J = 13.8 Hz), 138.9 (d, J = 12.5 Hz), 138.4, 133.2 (d, J = 18.8 Hz), 129.4, 129.0, 128.9 (d, J = 7.5 Hz), 128.8, 127.2, 125.6, 32.5 (d, J = 17.5 Hz), 30.6 (d, J = 12.5 Hz), 21.8. ^{31}P NMR (202 MHz, $CDCl_3$ 298K): δ –15.7. Spectroscopic data are in accordance with those described in the literature.[5] Unknown impurity present at –20.6 ppm.[5,6]



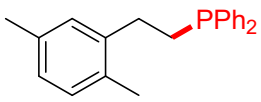
(3-fluorophenethyl)diphenylphosphane (3v). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$, 298K): δ 7.48-7.45 (m, 4H, Ph*H*), 7.37-7.34 (m, 6H, Ph*H*), 7.26-7.22 (m, 1H, Ph*H*), 6.97-6.95 (m, 1H, Ph*H*), 6.90-6.88 (m, 2H, Ph*H*), 2.76-2.71 (m, 2H, PCH_2CH_2), 2.40-2.36 (m, 2H, PCH_2), 2.35(s, 3H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, 298K): δ 163.3 (d, J = 243.8 Hz), 145.5 (dd, J = 10.0, 5.0 Hz), 138.4 (d, J = 7.5 Hz), 133.1 (d, J = 17.5 Hz), 130.2 (d, J = 8.8 Hz), 129.2, 128.9 (d, J = 6.3 Hz), 124.2 (d, J = 2.5 Hz), 115.4 (d, J = 21.3 Hz), 113.3 (d, J = 21.3 Hz), 32.2 (d, J = 17.5 Hz), 30.2 (d, J = 11.3 Hz). ^{31}P NMR (202 MHz, $CDCl_3$ 298K): δ –15.9. ^{19}F NMR (470 MHz, $CDCl_3$ 298K): δ –113.5 (dd, J =15.0, 8.5 Hz). Spectroscopic data are in accordance with those described in the literature.[5] Unknown impurity present at –20.9 ppm.[5,6]



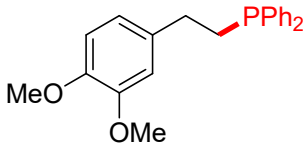
(3-chlorophenethyl)diphenylphosphane (3w). White solid. ^{1}H NMR (500 MHz, $CDCl_3$, 298K): δ 7.46-7.43 (m, 4H, Ph*H*), 7.35-7.34 (m, 6H, Ph*H*), 7.21-7.15 (m, 3H, Ph*H*), 7.04 (d, J = 18.8 Hz, 1H, Ph*H*), 2.72-2.67 (m, 2H, PCH_2CH_2), 2.36-2.33 (m, 2H, PCH_2). ^{13}C NMR (125 MHz, $CDCl_3$, 298K): δ 145.0 (d, J = 12.5 Hz), 138.6 (d, J = 12.5 Hz), 134.6, 133.1 (d, J = 18.8 Hz), 130.1, 129.1, 128.9 (d, J = 6.3 Hz), 128.7, 126.8, 126.6, 32.3 (d, J = 17.5 Hz), 30.3 (d, J = 12.5 Hz). ^{31}P NMR (202 MHz, $CDCl_3$ 298K): δ –16.1. Spectroscopic data are in accordance with those described in the literature.[5]



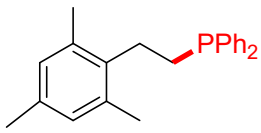
(3-bromophenethyl)diphenylphosphane (3x). White solid. ^{1}H NMR (500 MHz, $CDCl_3$, 298K): δ 7.47-7.43 (m, 4H, Ph*H*), 7.38-7.34 (m, 6H, Ph*H*), 7.32-7.31 (m, 2H, Ph*H*), 7.15-7.08 (m, 2H, Ph*H*), 2.72-2.67 (m, 2H, PCH_2CH_2), 2.37-2.34 (m, 2H, PCH_2). ^{13}C NMR (125 MHz, $CDCl_3$, 298K): δ 145.3 (d, J = 12.5 Hz), 138.5 (d, J = 12.5 Hz), 133.1 (d, J = 17.5 Hz), 131.6, 130.4, 129.5, 129.2, 128.9 (d, J = 6.3 Hz), 127.3, 122.9, 32.3 (d, J = 17.5 Hz), 30.3 (d, J = 13.8 Hz). ^{31}P NMR (202 MHz, $CDCl_3$ 298K): δ –16.2. Spectroscopic data are in accordance with those described in the literature.[5] Unknown impurity present at –20.9 ppm.[5,6]



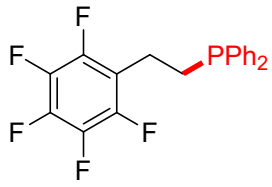
(2,5-dimethylphenethyl)diphenylphosphane (4a). Light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$, 298K): δ 7.53-7.47 (m, 4H, Ph*H*), 7.39-7.37 (m, 6H, Ph*H*), 7.05-6.95 (m, 3H, Ph*H*), 2.72-2.68 (m, 2H, PCH_2CH_2), 2.36-2.34 (m, 2H, PCH_2), 2.34 (s, 3H, CH_3), 2.18 (s, 3H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, 298K): δ 141.1 (d, J = 13.8 Hz), 139.0 (d, J = 12.5 Hz), 135.9, 133.2 (d, J = 17.5 Hz), 132.9, 130.6, 129.7, 129.1, 128.9 (d, J = 6.3 Hz), 127.2, 29.9 (d, J = 18.8 Hz), 29.4 (d, J = 12.5 Hz), 21.4, 19.1. ^{31}P NMR (202 MHz, $CDCl_3$ 298K): δ –15.2. Unknown impurity present at –20.3 ppm.[5,6] HRMS: m/z (ESI) calcd. for (2,5-dimethylphenethyl)diphenylphosphane oxide $C_{22}H_{23}OP$ $[M+H]^+$: 335.1559, found: 335.1562.



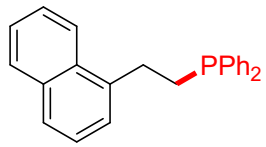
(3,4-dimethoxyphenethyl)diphenylphosphane (4b). Light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$, 298K): δ 7.47-7.45 (m, 4H, Ph*H*), 7.37-7.31 (m, 6H, Ph*H*), 6.79-6.67 (m, 3H, Ph*H*), 3.85(s, 3H, CH_3), 3.85(s, 3H, CH_3), 2.71-2.66 (m, 2H, PCH_2CH_2), 2.38-2.35 (m, 2H, PCH_2). ^{13}C NMR (125 MHz, $CDCl_3$, 298K): δ 149.3, 147.7, 138.9 (d, J = 12.5 Hz), 135.6 (d, J = 13.8 Hz), 133.2 (d, J = 18.8 Hz), 129.0, 128.9 (d, J = 6.3 Hz), 120.4, 112.0, 111.7, 56.3, 56.2, 32.2 (d, J = 17.5 Hz), 30.7 (d, J = 12.5 Hz). ^{31}P NMR (202 MHz, $CDCl_3$ 298K): δ –15.9. Spectroscopic data are in accordance with those described in the literature.[11] Unknown impurity present at –20.4 ppm.[5,6]



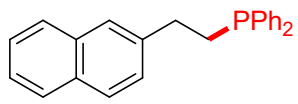
(2,4,6-trimethylphenethyl)diphenylphosphane (4c). White solid. ^{1}H NMR (500 MHz, $CDCl_3$, 298K): δ 7.50-7.47 (m, 4H, Ph*H*), 7.37-7.35 (m, 6H, Ph*H*), 6.82 (s, 2H, Ph*H*), 2.66-2.61 (m, 2H, PCH_2CH_2), 2.24 (s, 3H, CH_3), 2.18-2.15 (m, 2H, PCH_2), 2.14 (s, 6H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, 298K): δ 139.0 (d, J = 12.5 Hz), 136.9 (d, J = 15.0 Hz), 136.1, 135.6, 133.2 (d, J = 17.5 Hz), 129.3, 129.1, 128.8 (d, J = 6.3 Hz), 28.0 (d, J = 12.5 Hz), 25.8 (d, J = 18.8 Hz), 21.2, 19.9. ^{31}P NMR (202 MHz, $CDCl_3$ 298K): δ –14.9. Spectroscopic data are in accordance with those described in the literature.[11]



(2,3,4,5,6-pentafluorophenethyl)diphenylphosphane (4d). White solid. ^{1}H NMR (500 MHz, $CDCl_3$, 298K): δ 7.44-7.42 (m, 4H, Ph*H*), 7.35-7.34 (m, 6H, Ph*H*), 2.85-2.80 (m, 2H, PCH_2CH_2), 2.35-2.32 (m, 2H, PCH_2). ^{13}C NMR (125 MHz, $CDCl_3$, 298K): δ 146.3 (t, J = 9.6 Hz), 144.3 (t, J = 9.6 Hz), 141.2-141.0 (m), 139.2-138.7 (m), 137.9 (d, J = 10.6 Hz), 137.0-136.7 (m), 134.4 (d, J = 16.8 Hz), 133.1 (d, J = 19.0 Hz), 129.3, 129.0 (d, J = 6.6 Hz), 115.7 (dd, J = 30.4, 15.8 Hz), 28.1 (d, J = 13.8 Hz), 19.5 (d, J = 21.3 Hz). ^{31}P NMR (202 MHz, $CDCl_3$ 298K): δ –16.4. ^{19}F NMR (470 MHz, $CDCl_3$ 298K): δ –143.7 (d, J =20.4 Hz, 2F), –157.6 (t, J =20.4 Hz, 1F) –162.7- –162.8(m, 2F). HRMS: m/z (ESI) calcd. for (2,3,4,5,6-pentafluorophenethyl)diphenylphosphane oxide $C_{20}H_{14}F_5OP$ $[M+H]^+$: 397.0775, found: 397.0782.

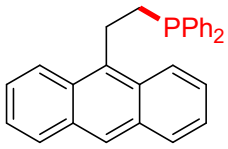


[2-(naphthalen-1-yl)ethyl]diphenylphosphane (4e). White solid. ^{1}H NMR (500 MHz, $CDCl_3$, 298K): δ 7.86-7.84 (m, 1H, Ph*H*), 7.78-7.76 (m, 1H, Ph*H*), 7.73-7.71 (m, 1H, Ph*H*), 7.52-7.32 (m, 14H, Ph*H*), 3.20-3.15 (m, 2H, PCH_2CH_2), 2.51-2.47 (m, 2H, PCH_2). ^{13}C NMR (125 MHz, $CDCl_3$, 298K): δ 171.5, 139.2 (d, J = 12.5 Hz), 138.7 (d, J = 12.5 Hz), 134.3, 133.2 (d, J = 17.5 Hz), 131.9, 129.2, 129.2, 128.9 (d, J = 6.3 Hz), 127.3, 126.3, 126.1, 126.0, 125.9, 124.0, 30.0 (d, J = 11.3 Hz), 29.7 (d, J = 17.5 Hz). ^{31}P NMR (202 MHz, $CDCl_3$ 298K): δ –15.3. Spectroscopic data are in accordance with those described in the literature.[11]

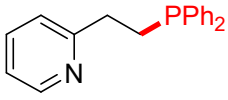


[2-(naphthalen-2-yl)ethyl]diphenylphosphane (4f). White solid. ^{1}H NMR (500 MHz, $CDCl_3$, 298K): δ 7.82-7.76 (m, 3H, Ph*H*), 7.62 (s, 1H, Ph*H*), 7.50-7.47 (m, 6H, Ph*H*), 7.36-7.33 (m, 7H, Ph*H*), 2.93-2.88 (m, 2H, PCH_2CH_2), 2.49-2.46 (m, 2H, PCH_2). ^{13}C NMR (125 MHz, $CDCl_3$, 298K): δ 140.4 (d, J = 13.8 Hz), 138.8 (d, J = 12.5 Hz), 130.4, 133.2 (d, J = 18.8 Hz), 132.5, 129.1, 128.9 (d, J = 6.3 Hz), 128.4, 128.0, 127.9, 127.5, 126.5, 126.4, 125.7, 32.7 (d, J = 17.5 Hz), 30.5 (d, J = 12.5 Hz). ^{31}P NMR (202 MHz,

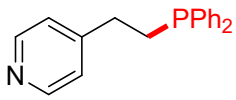
$CDCl_3$ 298K): δ –15.8. Spectroscopic data are in accordance with those described in the literature.[9]



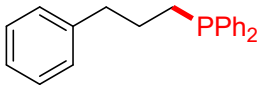
[2-(anthracen-9-yl)ethyl]diphenylphosphane (4g). White solid. ^{1}H NMR (500 MHz, $CDCl_3$, 298K): δ 7.60 (s, 1H, Ph*H*), 7.40-7.38 (m, 5H, Ph*H*), 7.35-7.29 (m, 8H, Ph*H*), 7.25-7.17 (m, 5H, Ph*H*), 3.77-3.68 (m, 2H, PCH_2CH_2), 3.43-3.33 (2H, PCH_2). ^{13}C NMR (125 MHz, $CDCl_3$, 298K): δ 140.2, 137.8 (d, J = 11.3 Hz), 134.3 (d, J = 17.5 Hz), 133.1 (d, J = 18.8 Hz), 129.5, 129.1 (d, J = 6.3 Hz), 126.7, 126.1, 123.5, 120.8, 119.4, 108.9, 40.3 (d, J = 26.3 Hz), 28.0 (d, J = 13.8 Hz). ^{31}P NMR (202 MHz, $CDCl_3$ 298K): δ –21.9. HRMS: m/z (ESI) calcd. for [2-(anthracen-9-yl)ethyl]diphenylphosphane oxide $C_{28}H_{23}OP$ $[M+H]^+$: 407.1559, found: 407.1564.



2-(2-(diphenylphosphino)ethyl)pyridine (4h). White solid. ^{1}H NMR (500 MHz, $CDCl_3$, 298K): δ 8.52 (dd, J = 1.5 Hz, J = 4.5 Hz, 1H, Ph*H*), 7.57-7.54 (m, 1H, Ph*H*), 7.47-7.44 (m, 4H, Ph*H*), 7.37-7.32 (m, 6H, Ph*H*), 7.08 (d, J = 6.0 Hz, 2H, Ph*H*), 2.93-2.87 (m, 2H, PCH_2CH_2), 2.53-2.49 (m, 2H, PCH_2). ^{13}C NMR (125 MHz, $CDCl_3$, 298K): δ 151.7, 151.6, 150.2, 138.3 (d, J = 12.5 Hz), 134.3 (d, J = 16.3 Hz), 133.1 (d, J = 18.8 Hz), 129.3, 129.0 (d, J = 6.3 Hz), 124.0, 31.8 (d, J = 18.8 Hz), 29.3 (d, J = 12.5 Hz). ^{31}P NMR (202 MHz, $CDCl_3$ 298K): δ –16.0. Spectroscopic data are in accordance with those described in the literature.[5]



4-(2-(diphenylphosphino)ethyl)pyridine (4i). Light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$, 298K): δ 8.47 (d, J = 4.5 Hz, 2H, Ph*H*), 7.46-7.43 (m, 4H, Ph*H*), 7.34-7.30 (m, 6H, Ph*H*), 7.08 (d, J = 4.5 Hz, 2H, Ph*H*), 2.73-2.68 (m, 2H, PCH_2CH_2), 2.37-2.34 (m, 2H, PCH_2). ^{13}C NMR (125 MHz, $CDCl_3$, 298K): δ 162.2 (d, J = 13.8 Hz), 149.8, 138.7 (d, J = 11.3 Hz), 136.7, 133.2 (d, J = 18.8 Hz), 129.0, 128.9 (d, J = 7.5 Hz), 123.1, 121.6, 31.9 (d, J = 17.5 Hz), 28.3 (d, J = 11.3 Hz). ^{31}P NMR (202 MHz, $CDCl_3$ 298K): δ –15.4. Spectroscopic data are in accordance with those described in the literature.[5]



Phenpropyldiphenylphosphine (4j). Light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$, 298K): δ 7.41-7.38 (m, 4H, Ph*H*), 7.33-7.26 (m, 8H, Ph*H*), 7.22-7.16 (m, 3H, Ph*H*), .2.76 (t, J = 7.5 Hz, 2H, Ph*H*), 2.11-2.06 (m, 2H, PCH_2CH_2), 1.88-1.72 (m, 2H, PCH_2). ^{13}C NMR (125 MHz, $CDCl_3$, 298K): δ 142.1, 139.0 (d, J = 13.8 Hz), 133.1 (d, J = 18.8 Hz), 128.9, 128.8 (d, J = 7.5 Hz), 128.7, 126.2, 37.5 (d, J = 13.8 Hz), 28.0, 27.8 (d, J = 10.0 Hz). ^{31}P NMR (202 MHz, $CDCl_3$ 298K): δ –16.6. Spectroscopic data are in accordance with those described in the literature.[11]

IV. ^{1}H & ^{13}C & ^{31}P & ^{19}F NMR spectra of the hydrophosphination products 3a-4j

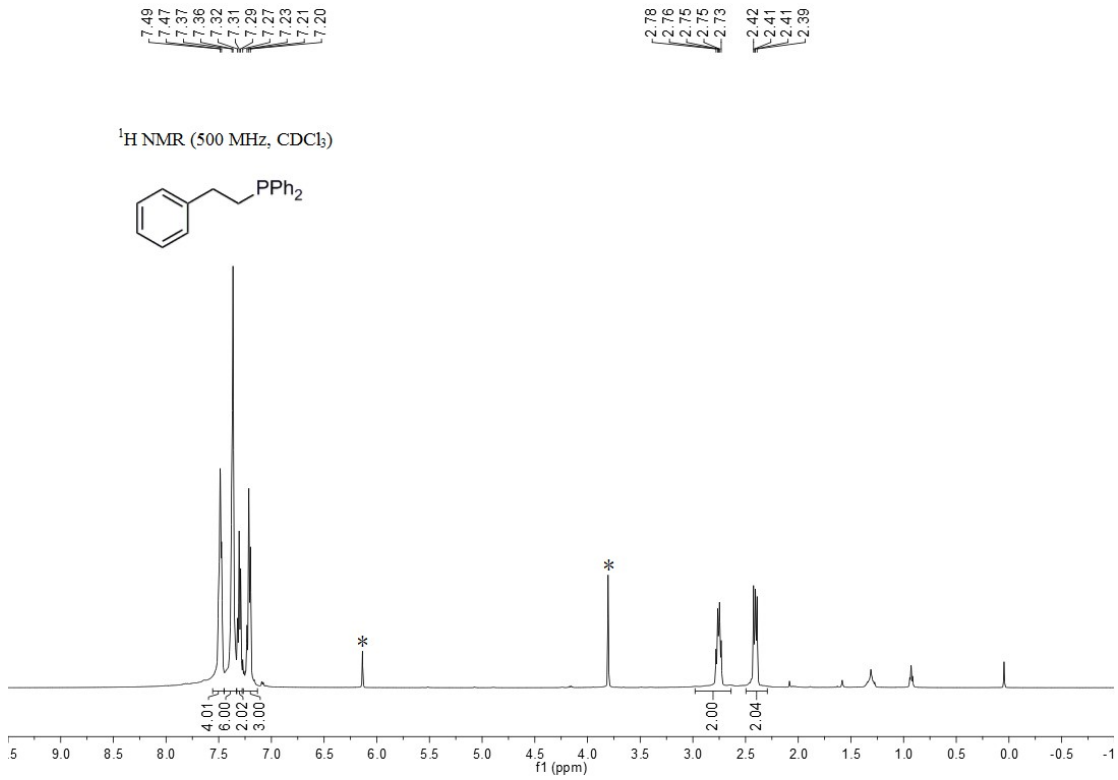


Figure S14. ^{1}H NMR spectra of **3a** (* represents 1,3,5-trimethoxybenzene)

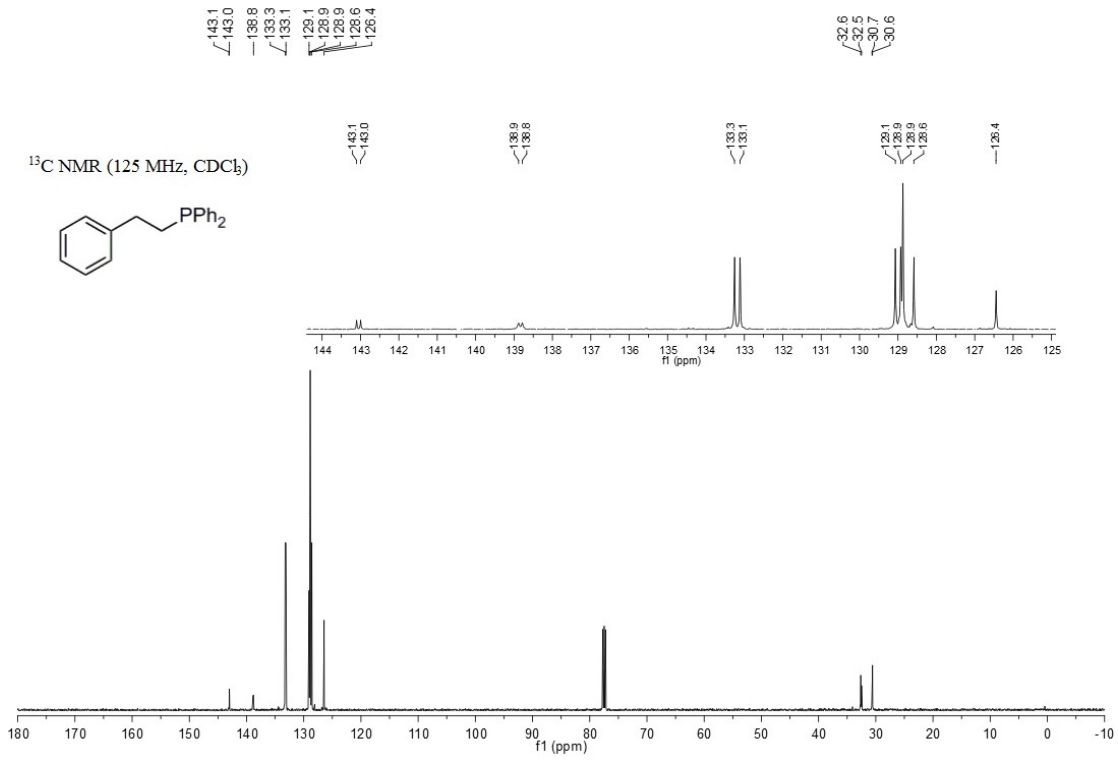


Figure S15. ^{13}C NMR spectra of **3a**

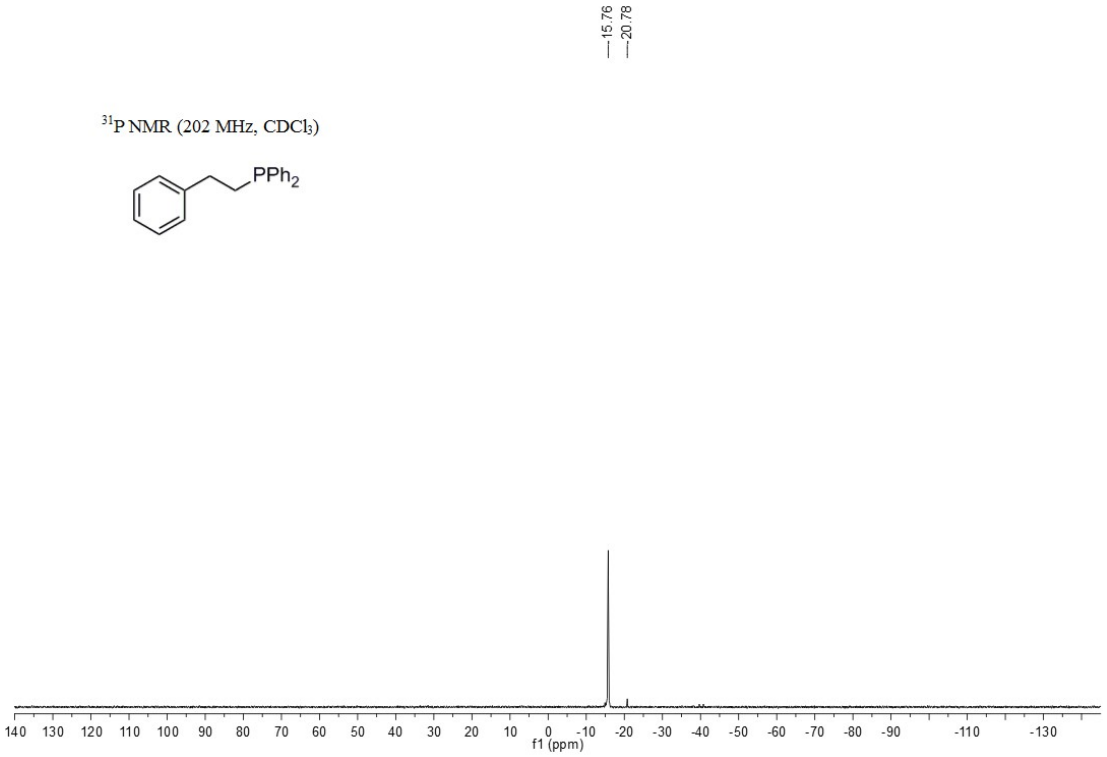


Figure S16. ^{31}P NMR spectra of **3a**

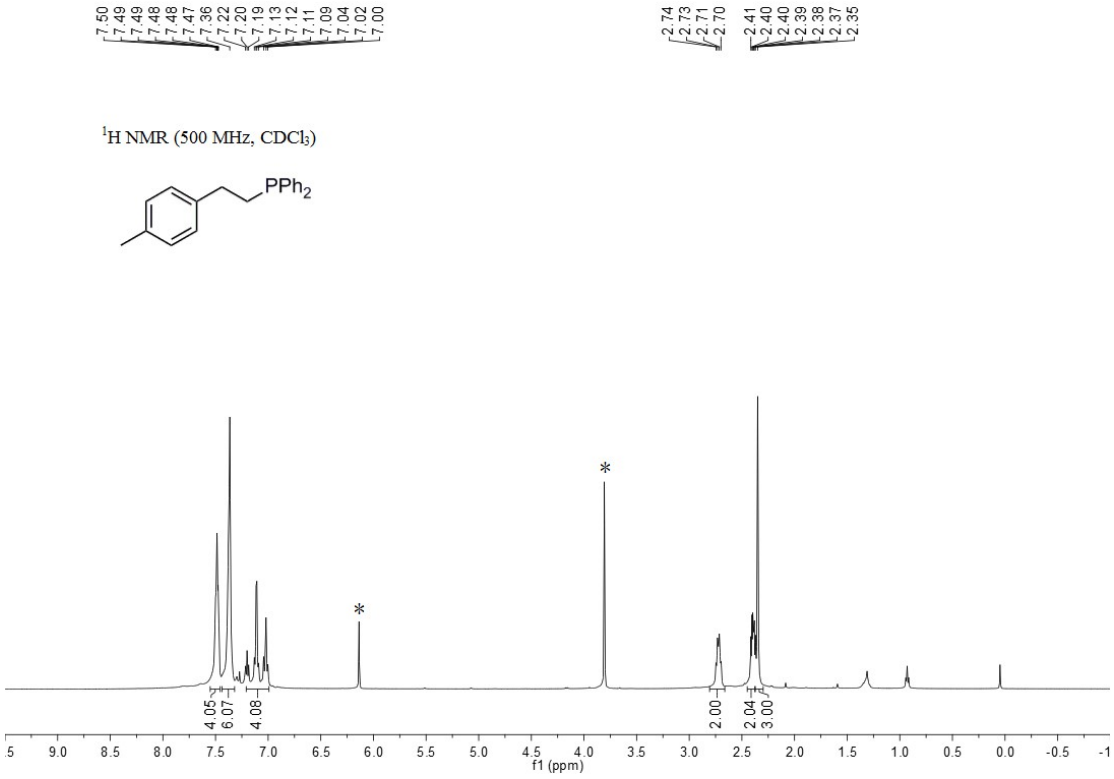


Figure S17. ^{1}H NMR spectra of **3b** (* represents 1,3,5-trimethoxybenzene)

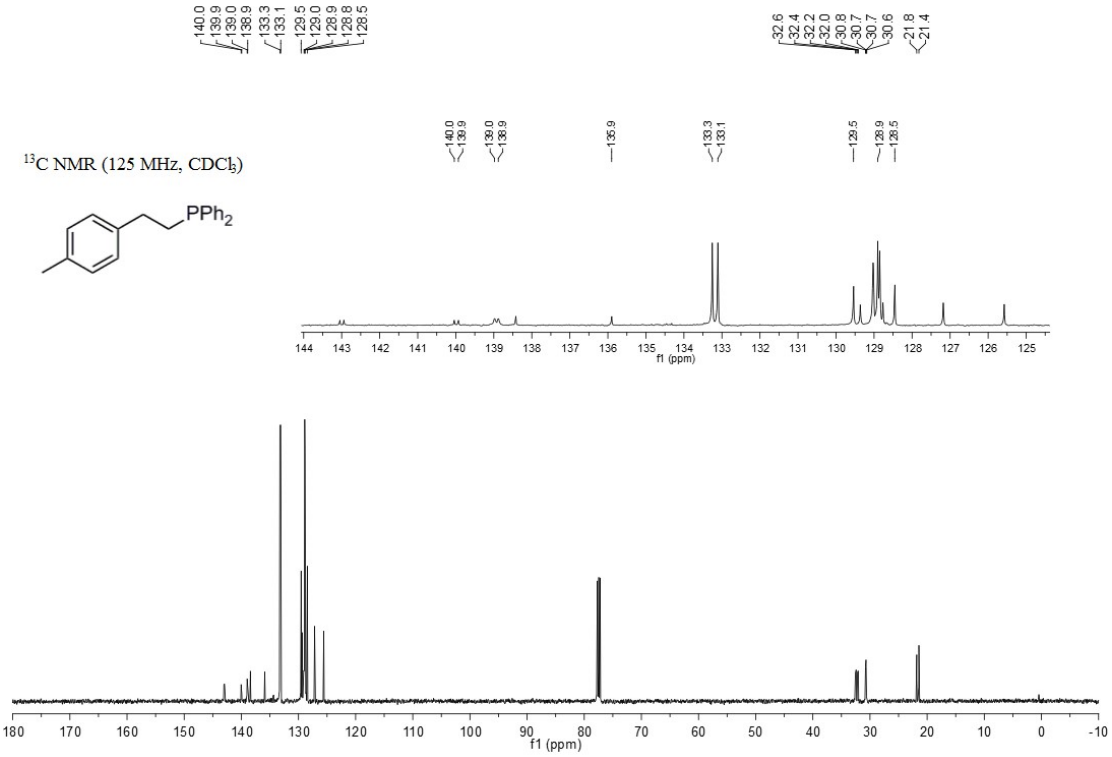


Figure S18. ^{13}C NMR spectra of **3b**

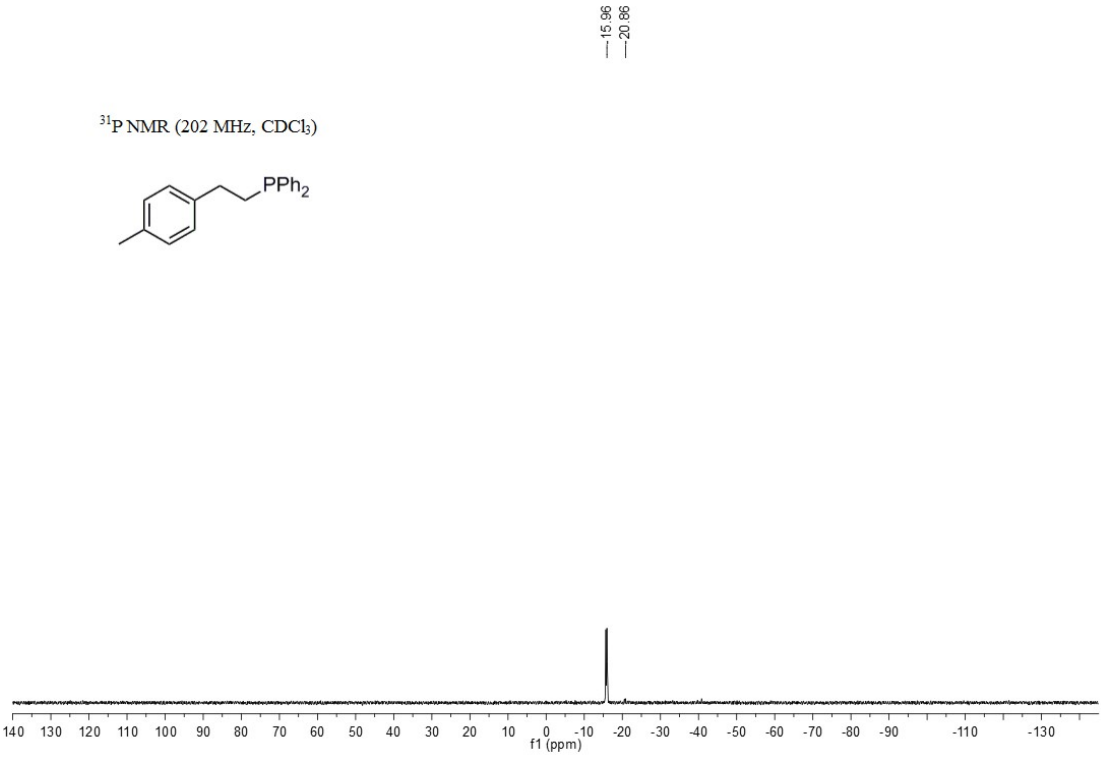


Figure S19. ^{31}P NMR spectra of **3b**

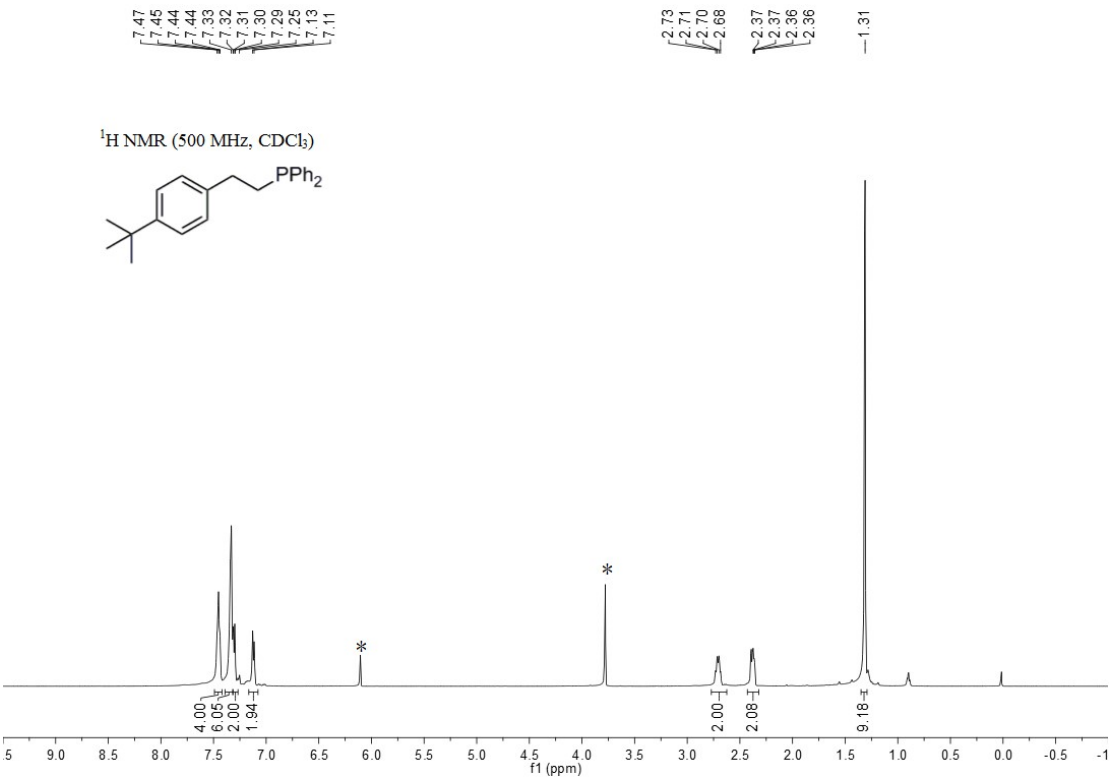


Figure S20. ^{1}H NMR spectra of **3c** (* represents 1,3,5-trimethoxybenzene)

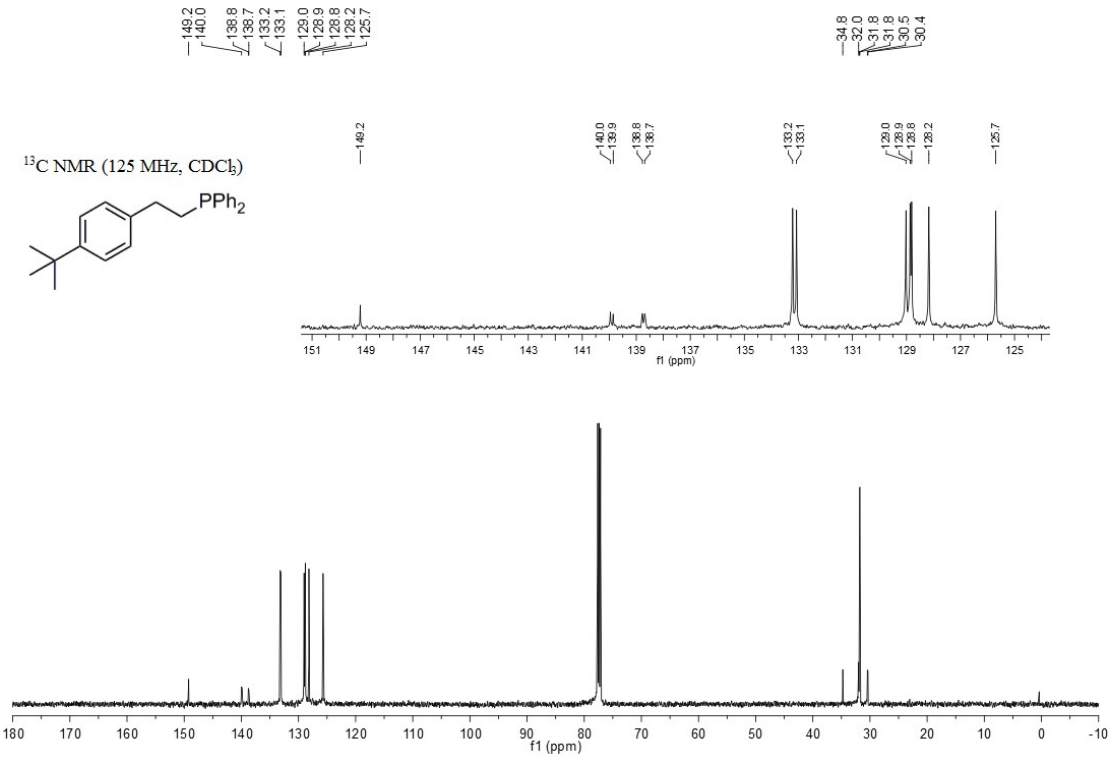


Figure S21. ^{13}C NMR spectra of **3c**

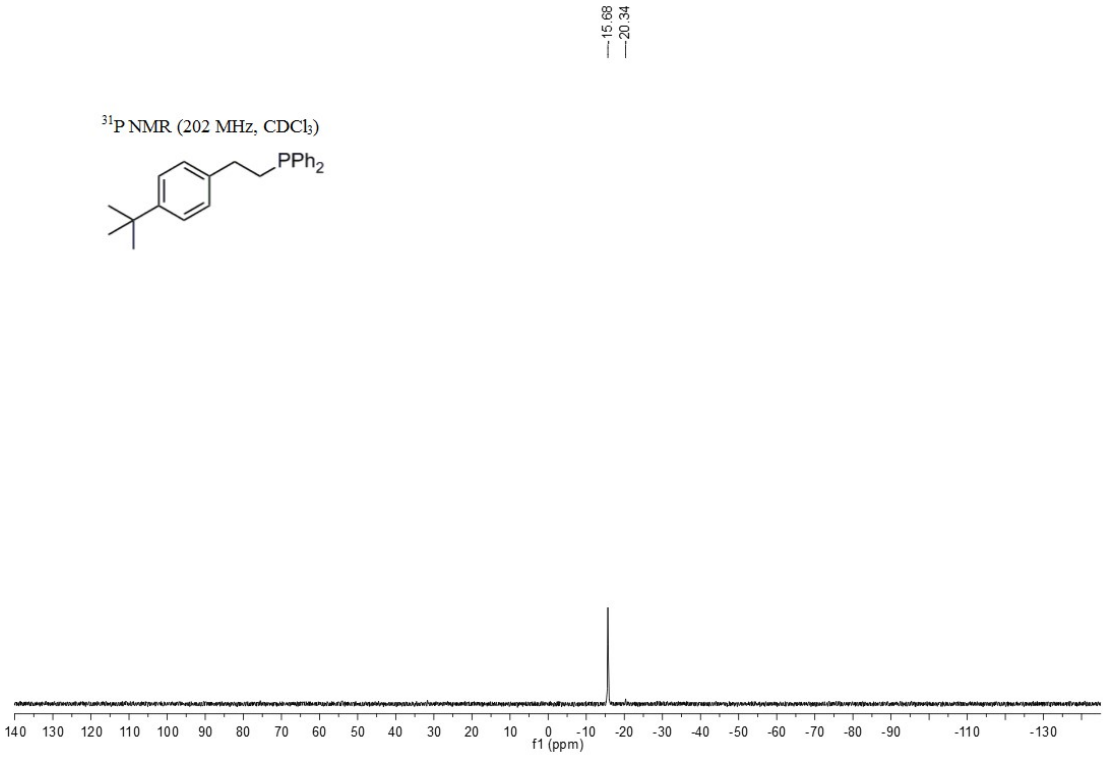


Figure S22. ^{31}P NMR spectra of **3c**

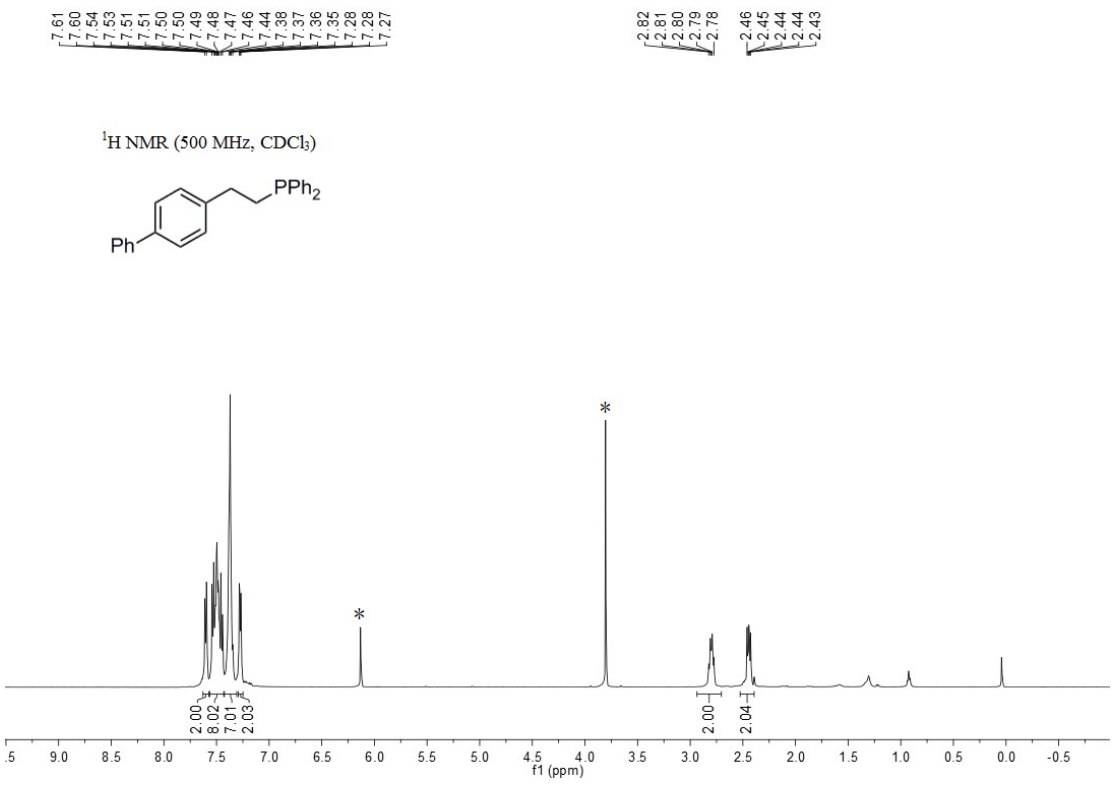


Figure S23. ^{1}H NMR spectra of **3d** (* represents 1,3,5-trimethoxybenzene)

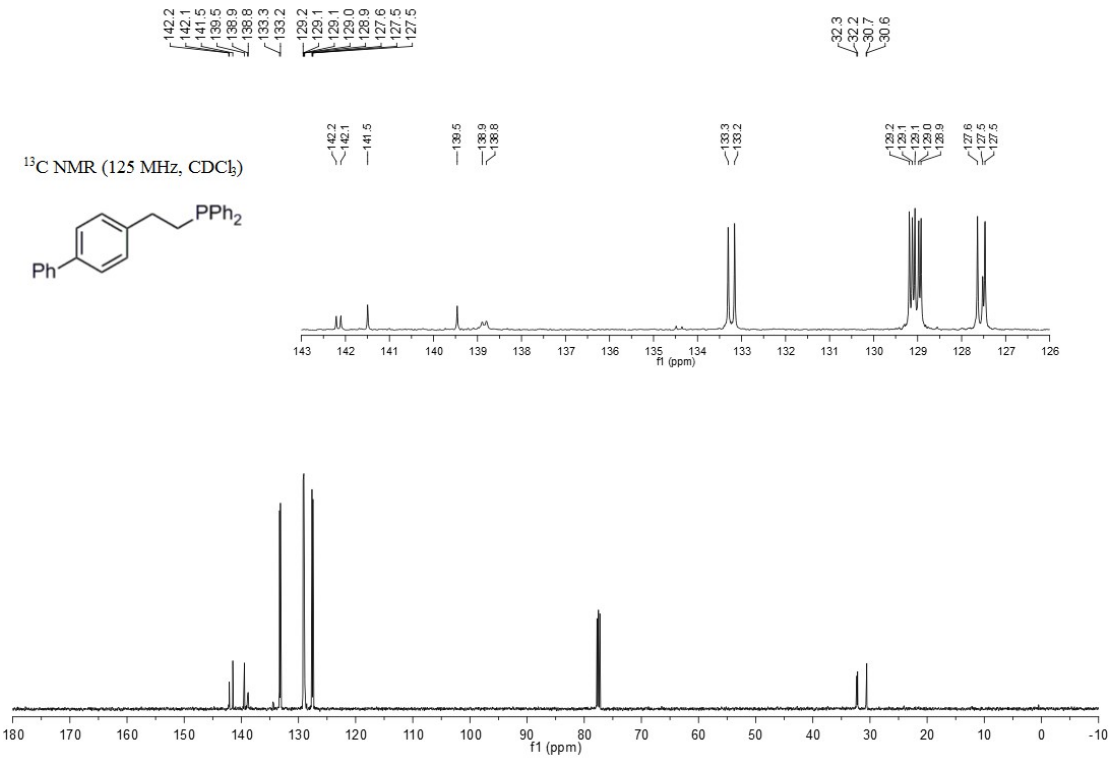


Figure S24. ^{13}C NMR spectra of **3d**

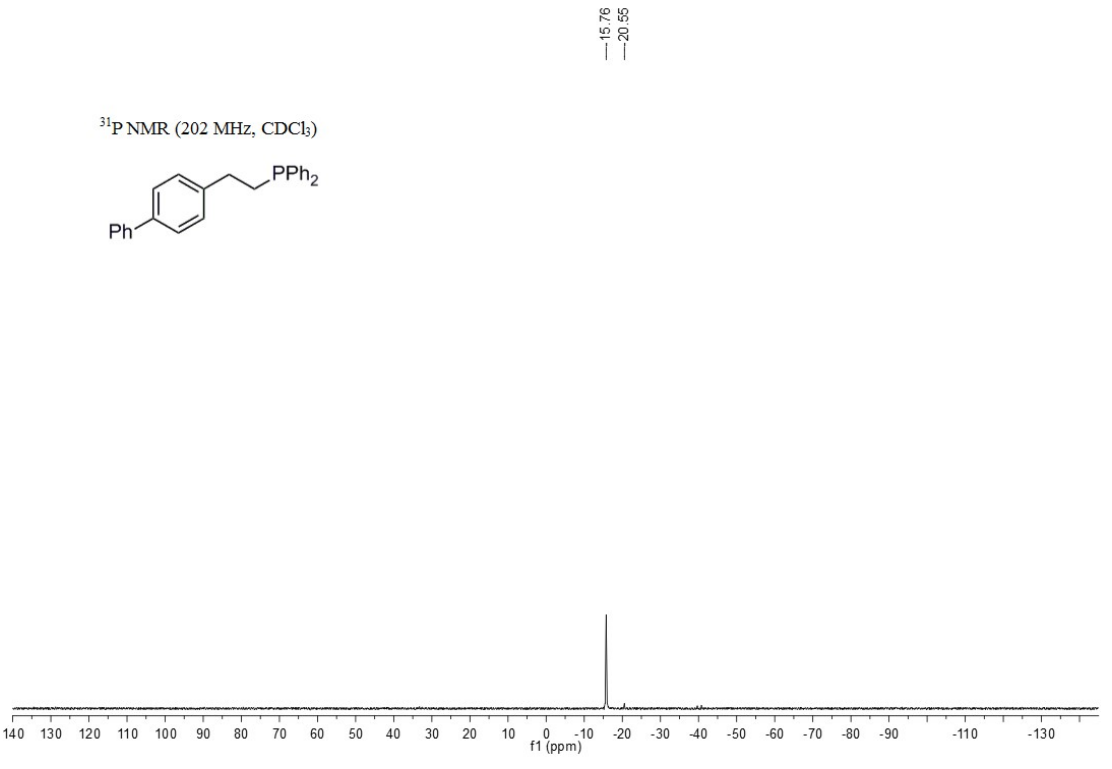


Figure S25. ^{31}P NMR spectra of **3d**

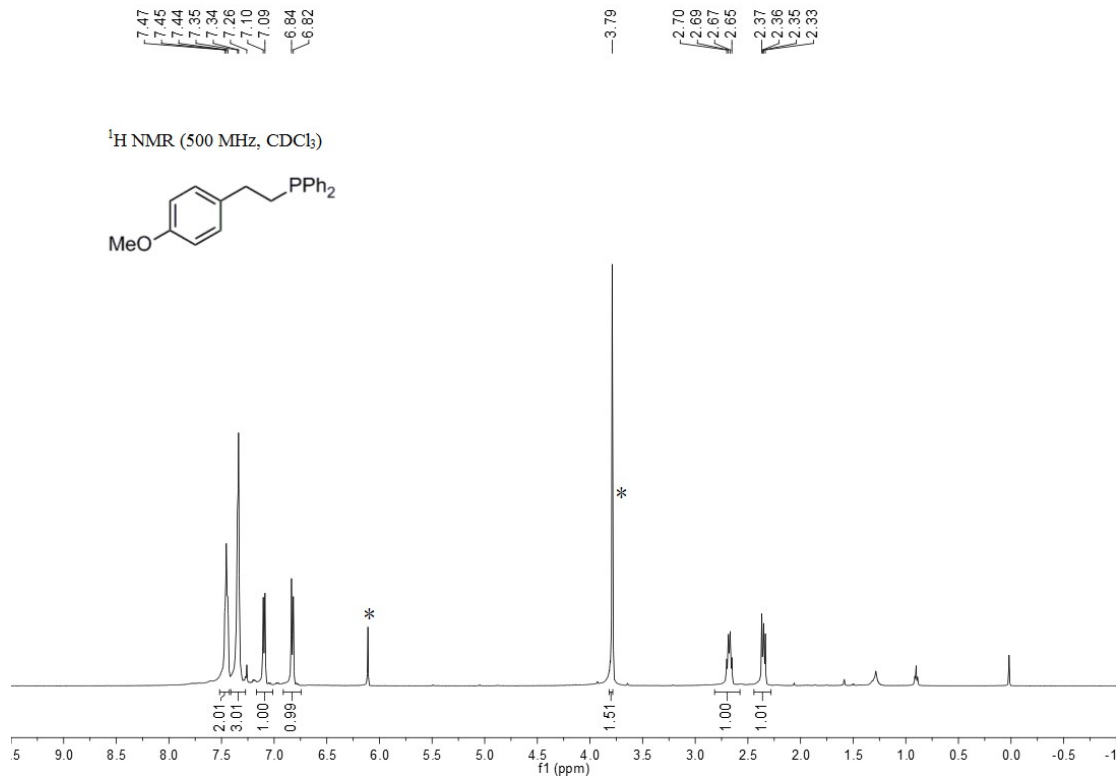


Figure S26. ^{1}H NMR spectra of **3e** (* represents 1,3,5-trimethoxybenzene)

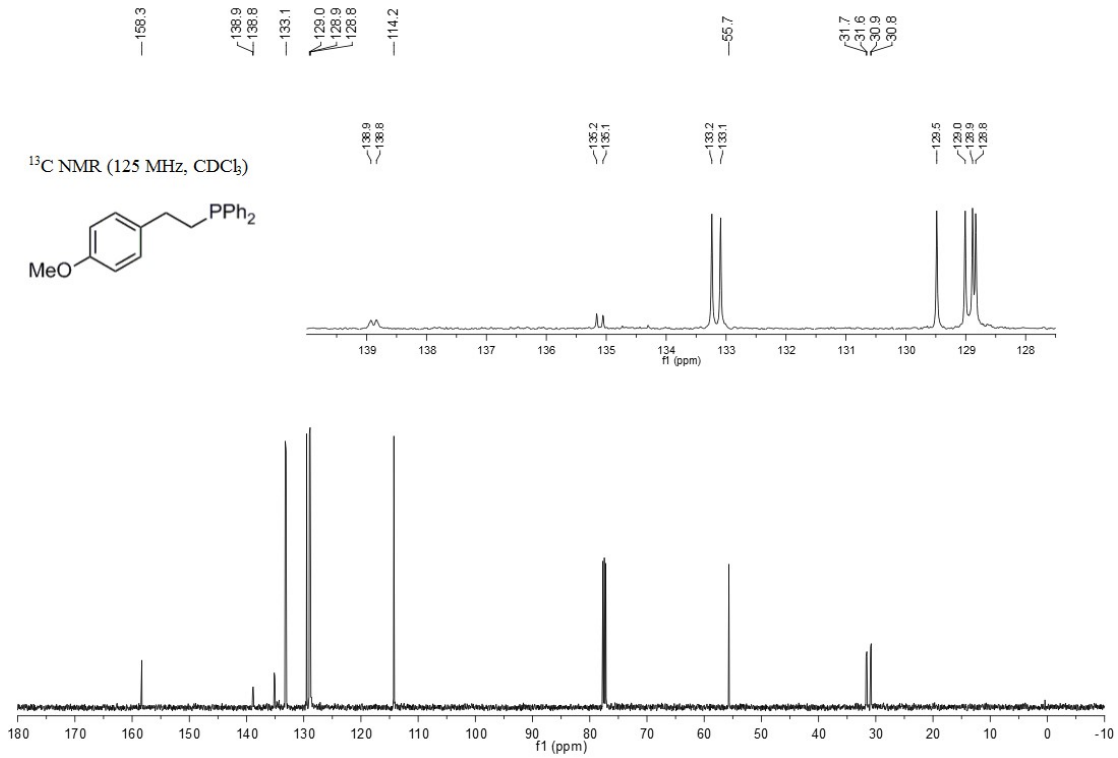


Figure S27. ^{13}C NMR spectra of **3e**

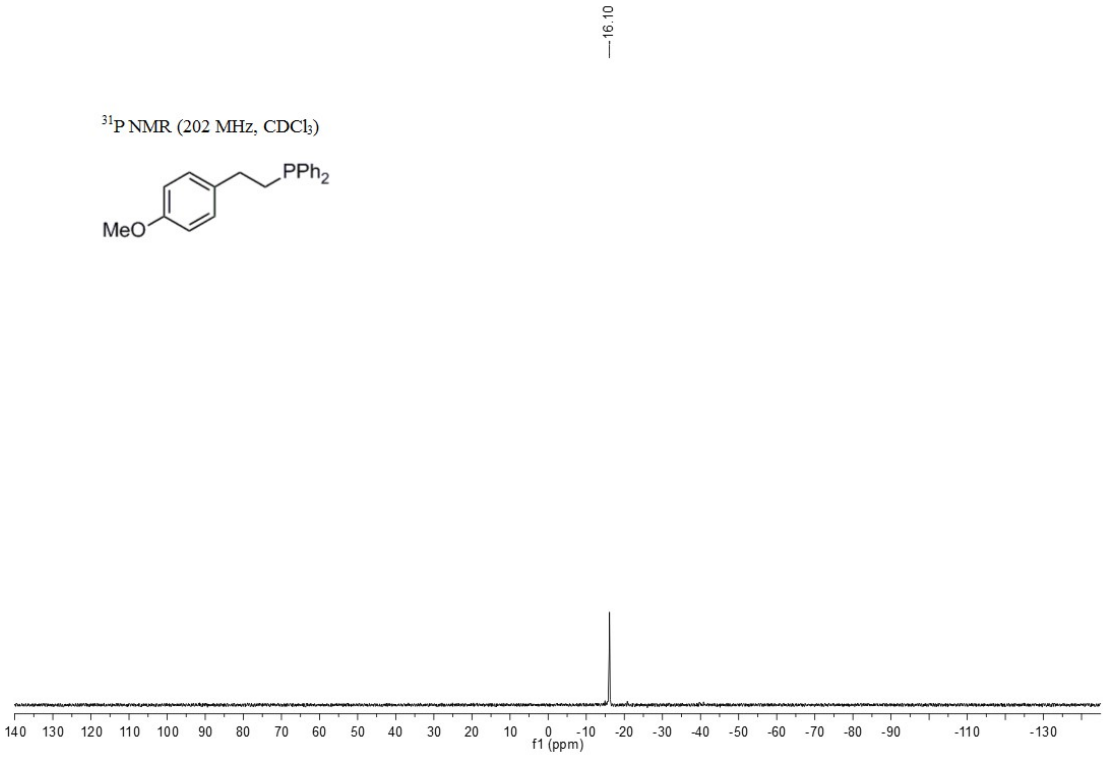


Figure S28. ^{31}P NMR spectra of **3e**

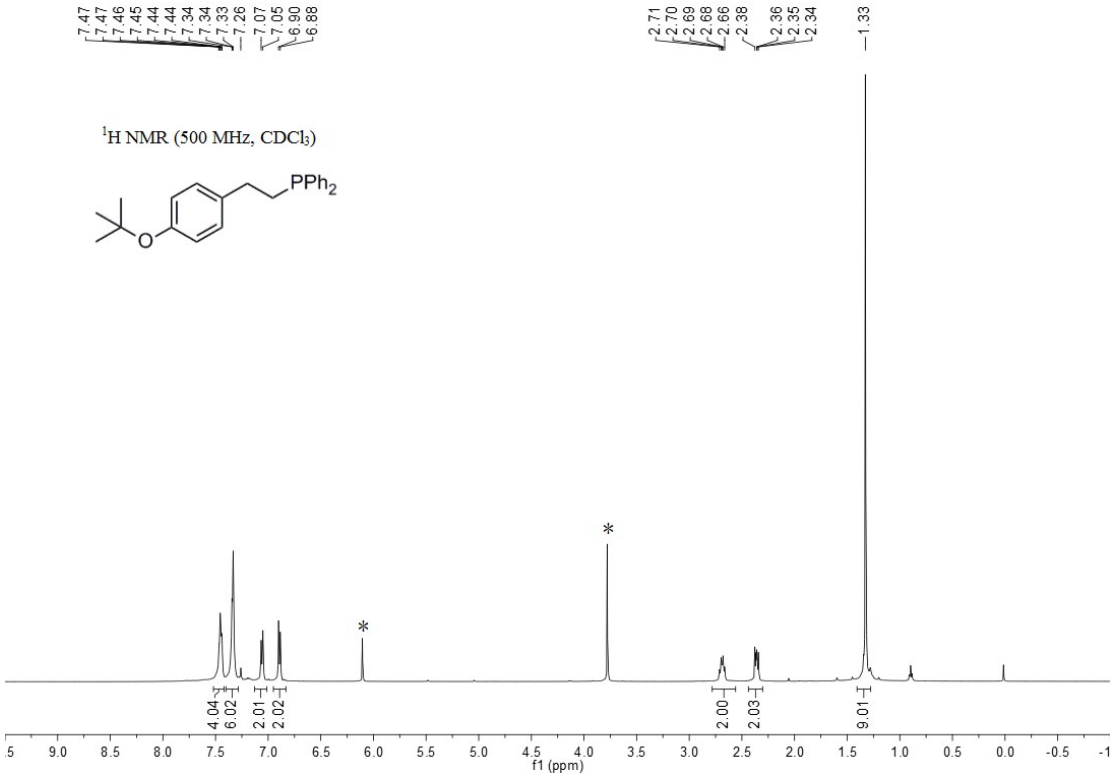


Figure S29. ^{1}H NMR spectra of **3f** (* represents 1,3,5-trimethoxybenzene)

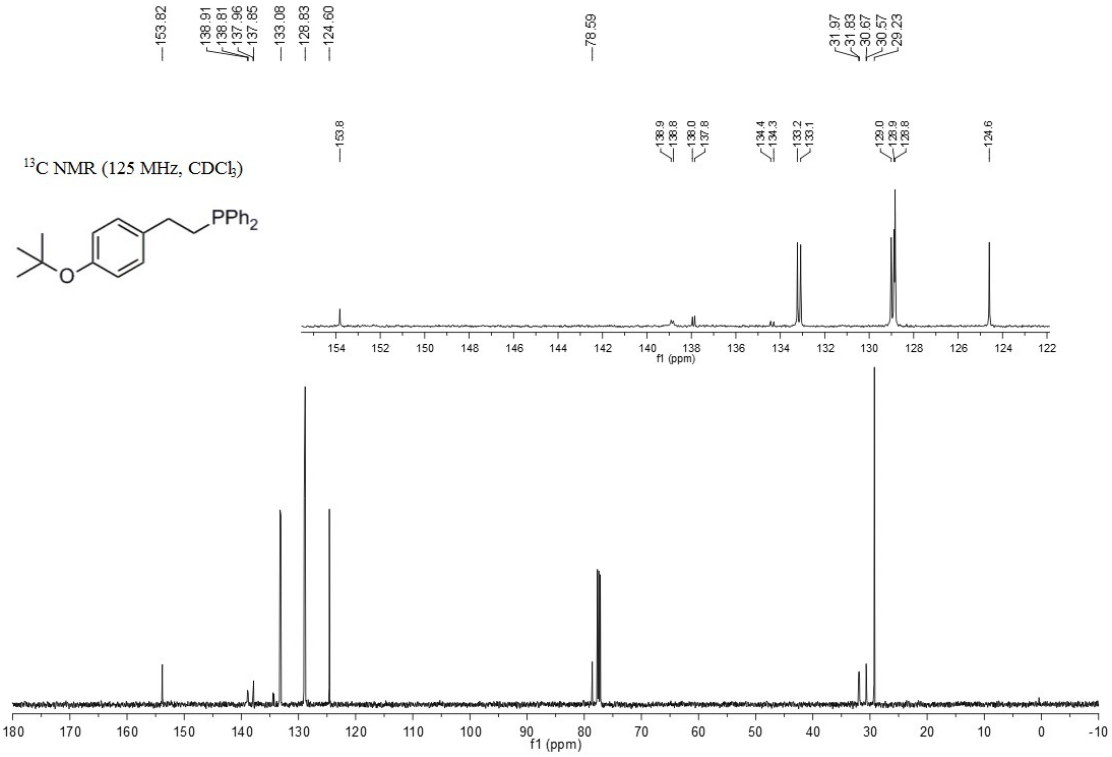


Figure S30. ^{13}C NMR spectra of **3f**

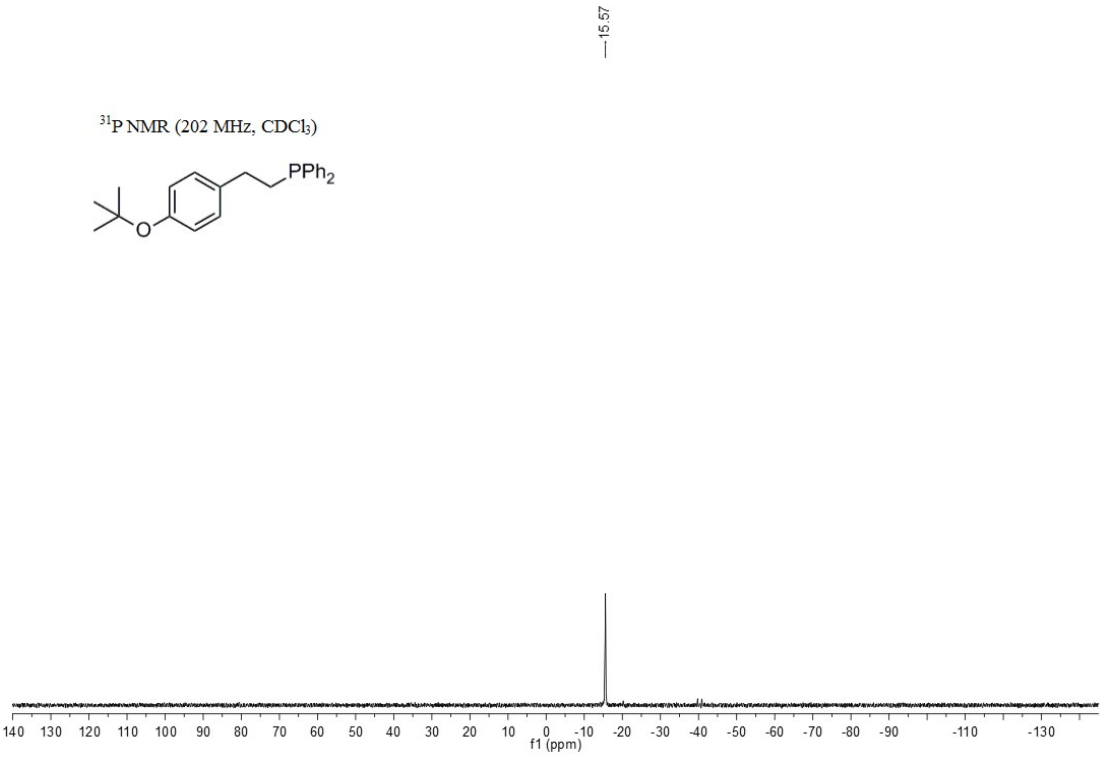


Figure S31. ^{31}P NMR spectra of **3f**

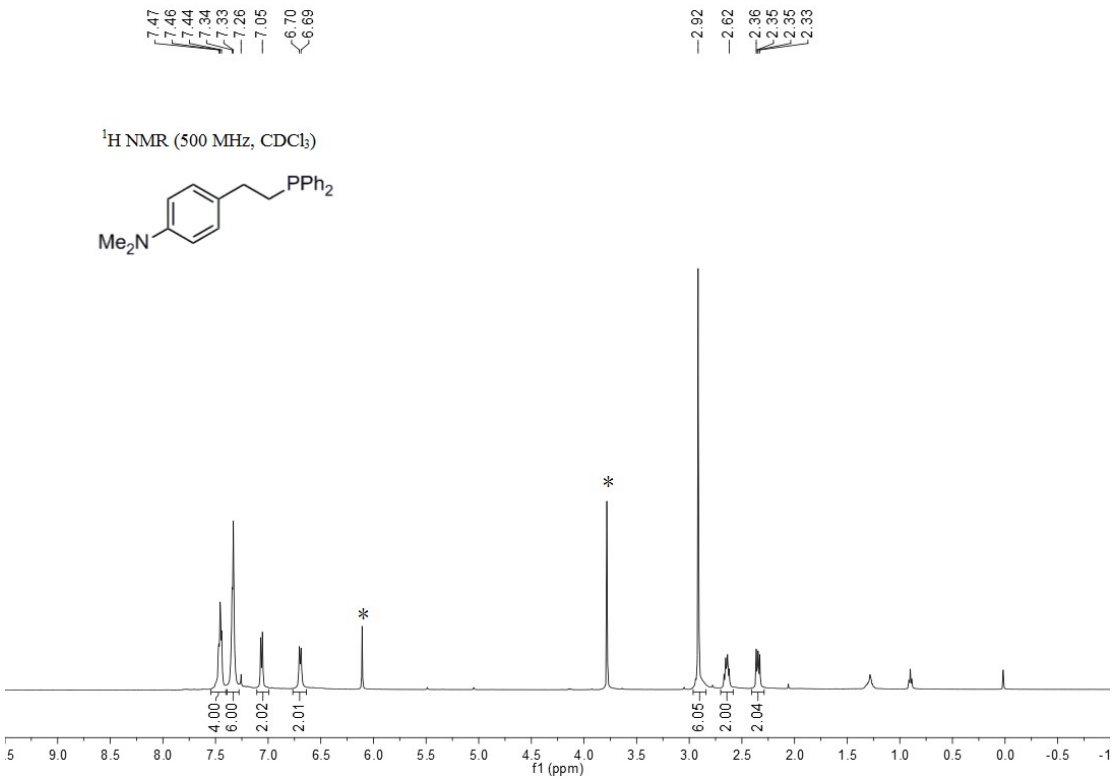


Figure S32. ^{1}H NMR spectra of **3g** (* represents 1,3,5-trimethoxybenzene)

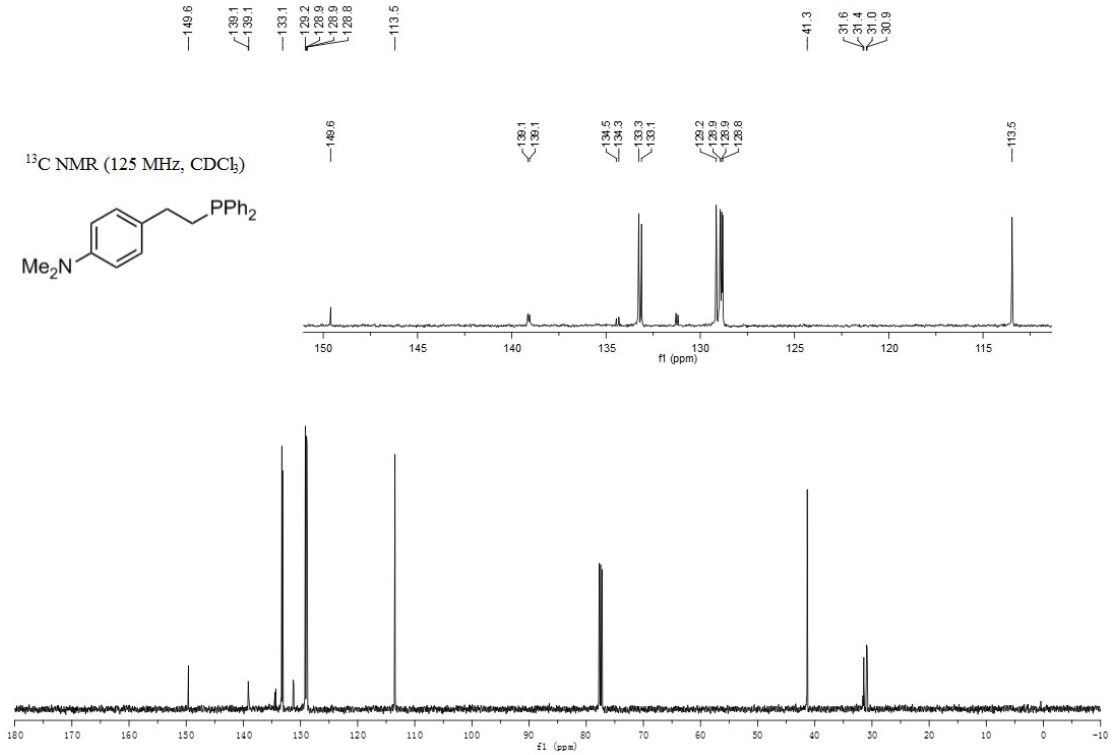


Figure S33. ^{13}C NMR spectra of **3g**

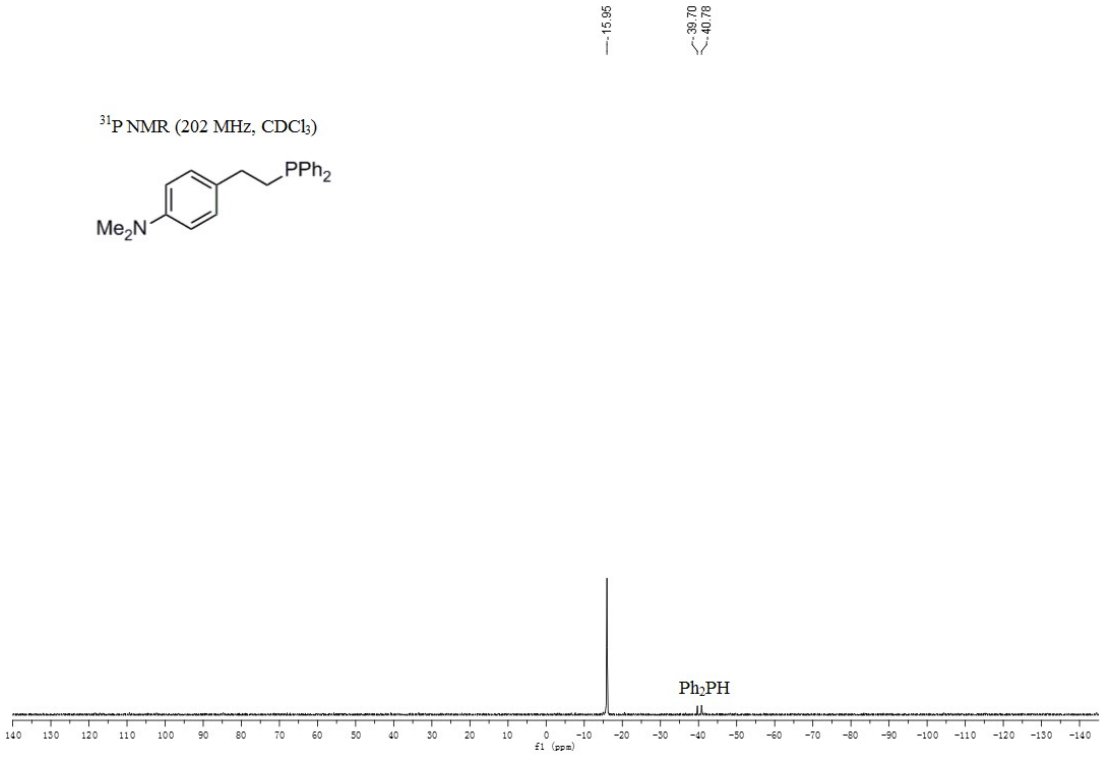


Figure S34. ^{31}P NMR spectra of **3g**

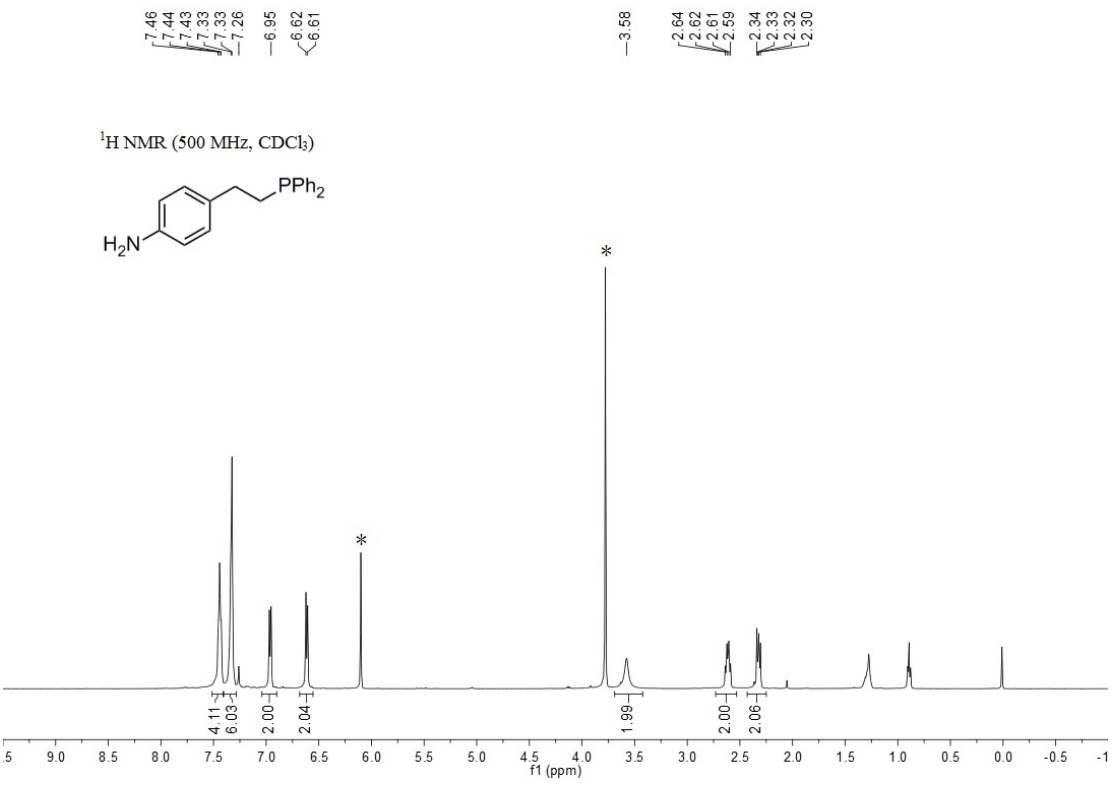


Figure S35. ^{1}H NMR spectra of **3h** (* represents 1,3,5-trimethoxybenzene)

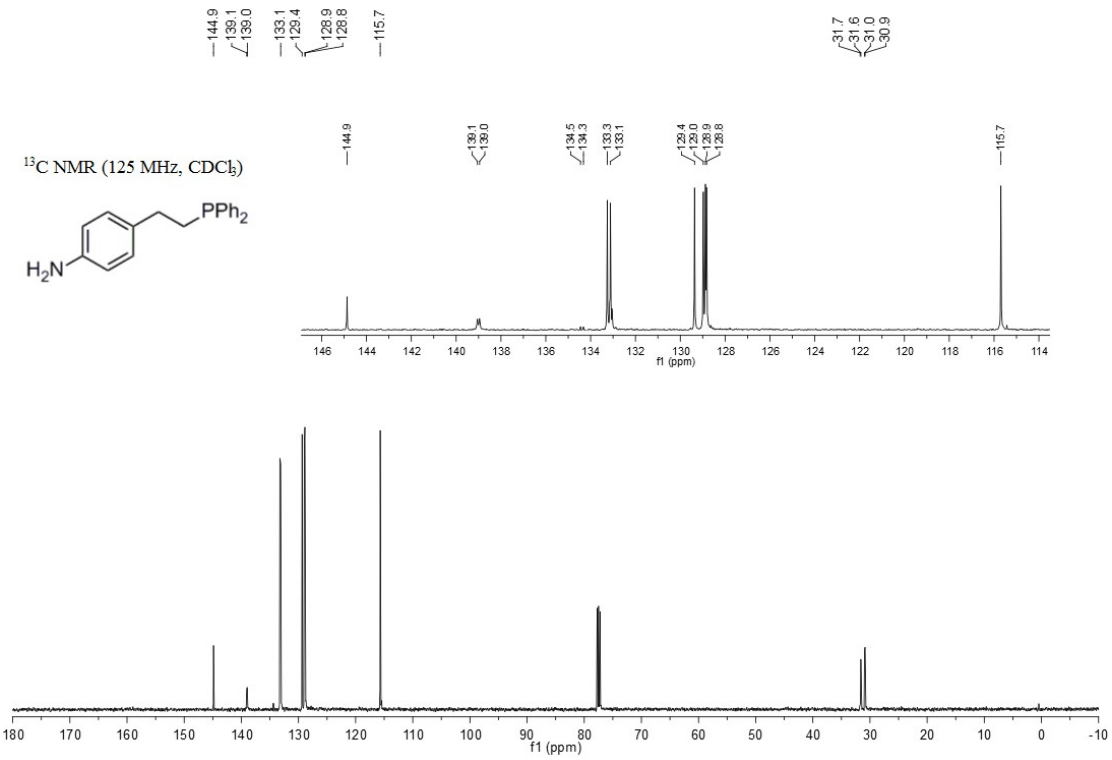


Figure S36. ^{13}C NMR spectra of **3h**

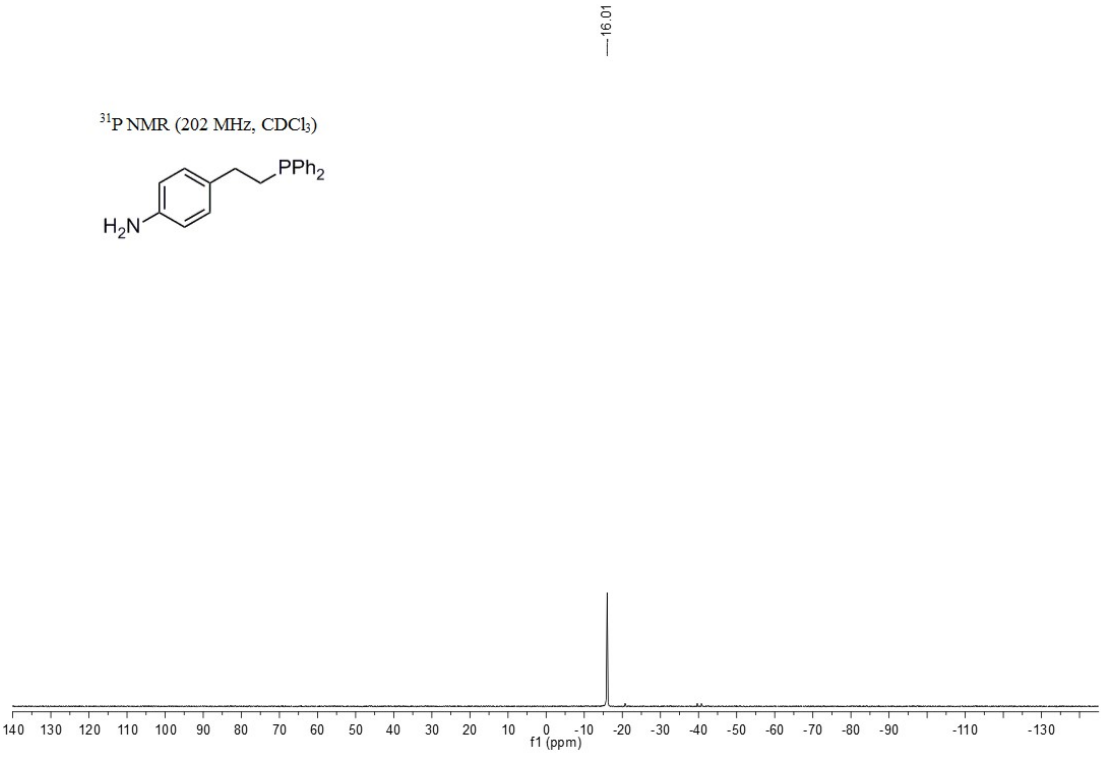


Figure S37. ^{31}P NMR spectra of **3h**

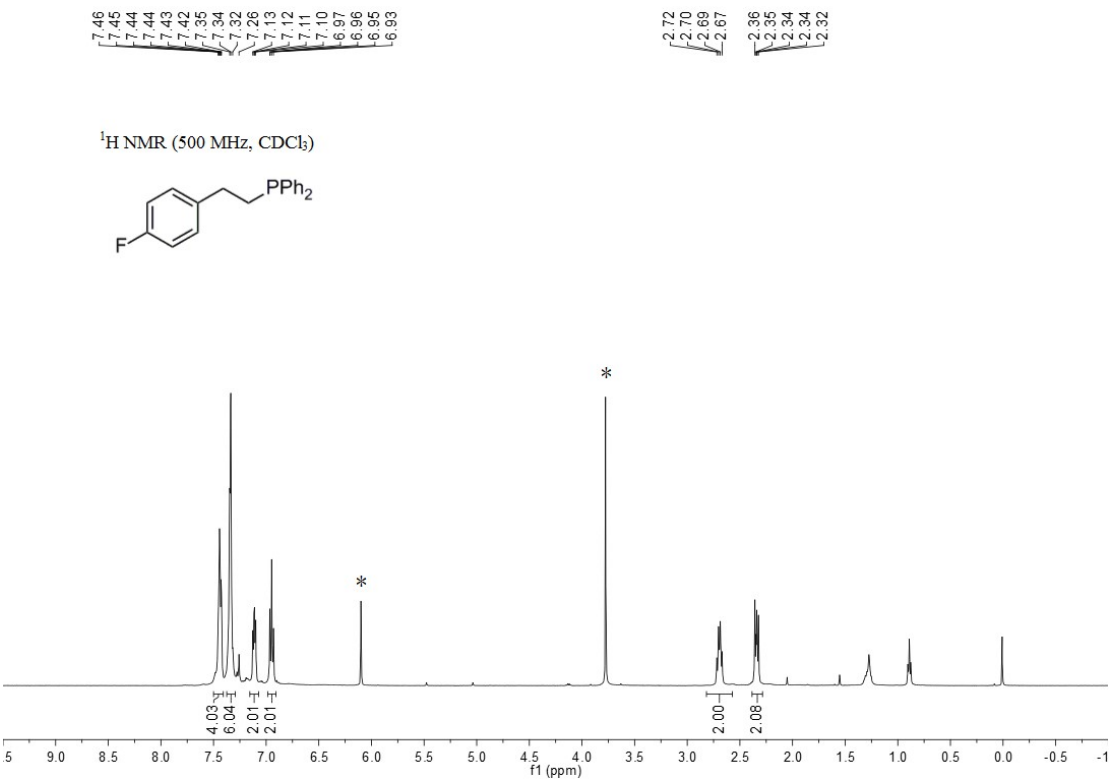


Figure S38. ^{1}H NMR spectra of **3i** (* represents 1,3,5-trimethoxybenzene)

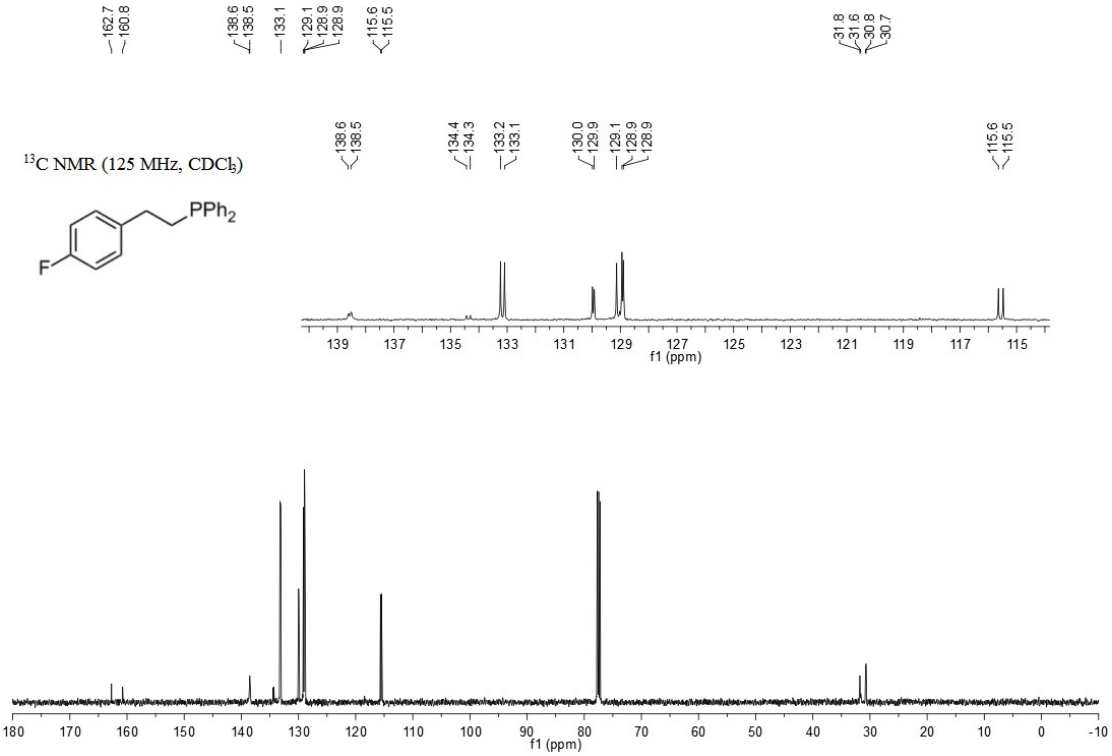


Figure S39. ^{13}C NMR spectra of **3i**

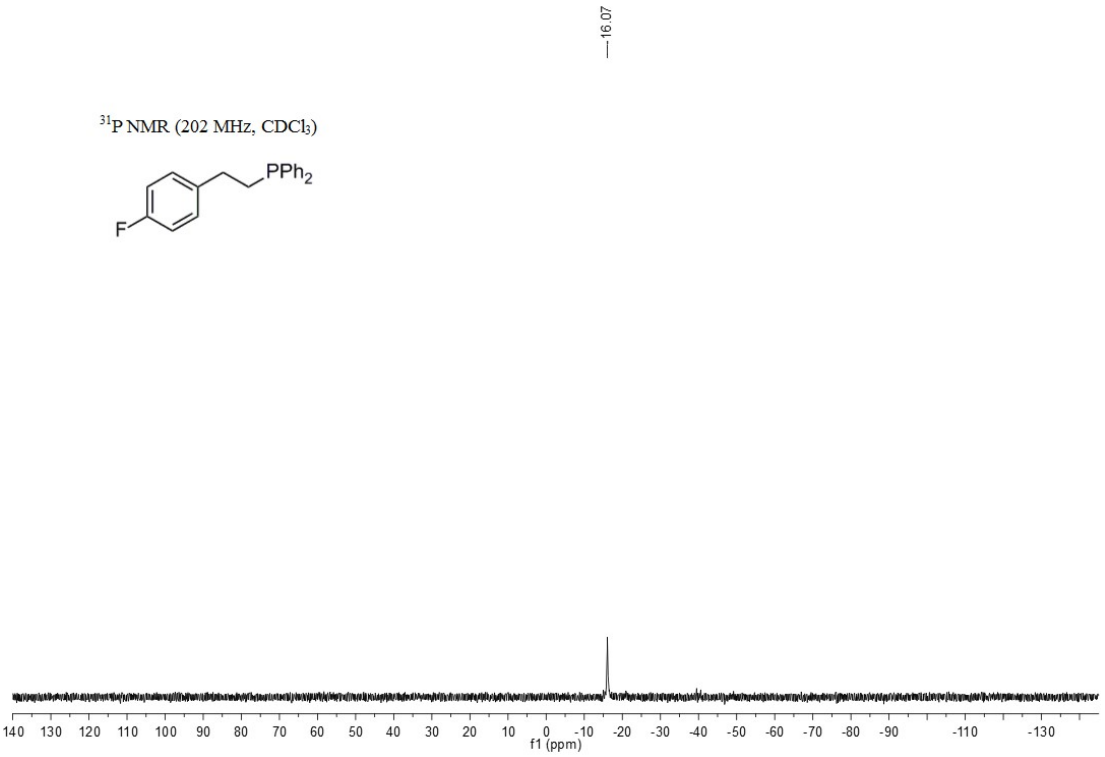


Figure S40. ^{31}P NMR spectra of **3i**

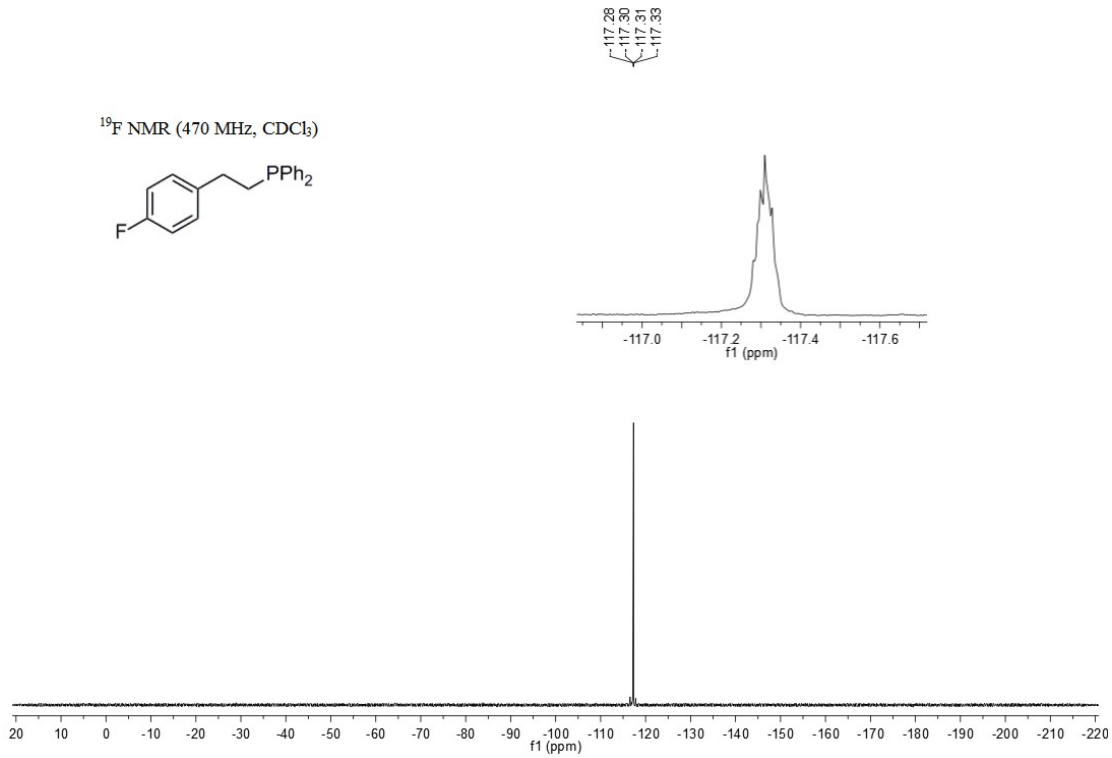


Figure S41. ^{19}F NMR spectra of **3i**

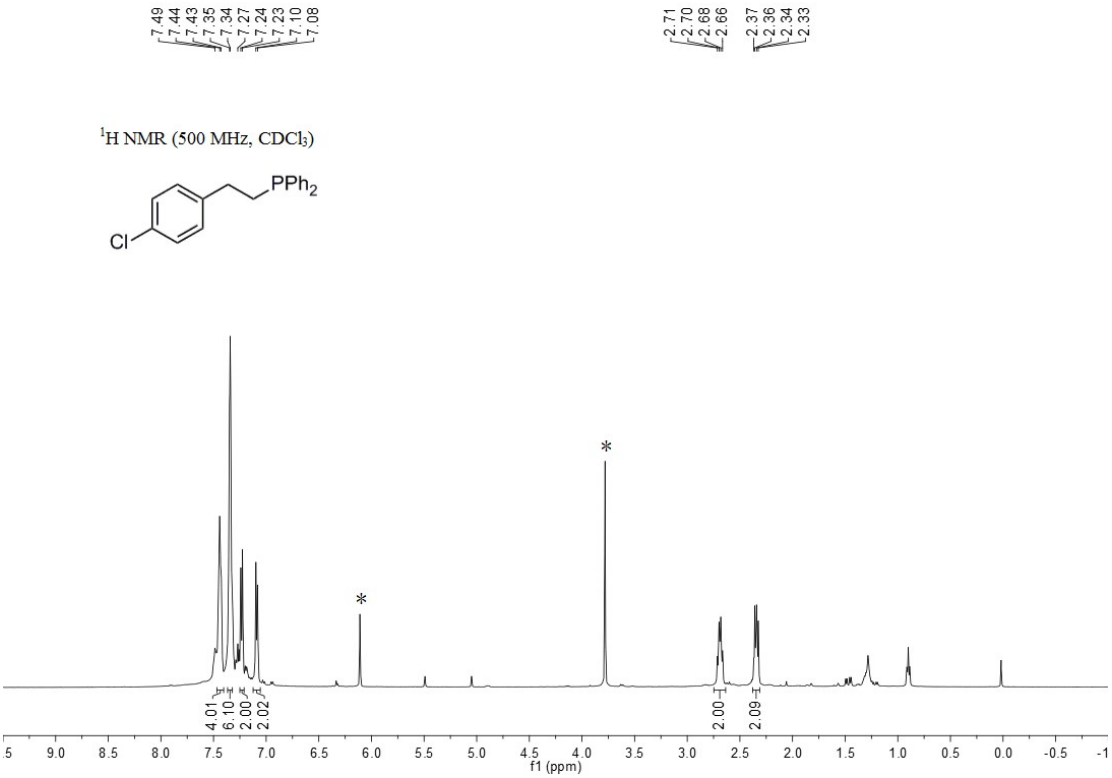


Figure S42. ^{1}H NMR spectra of **3j** (* represents 1,3,5-trimethoxybenzene)

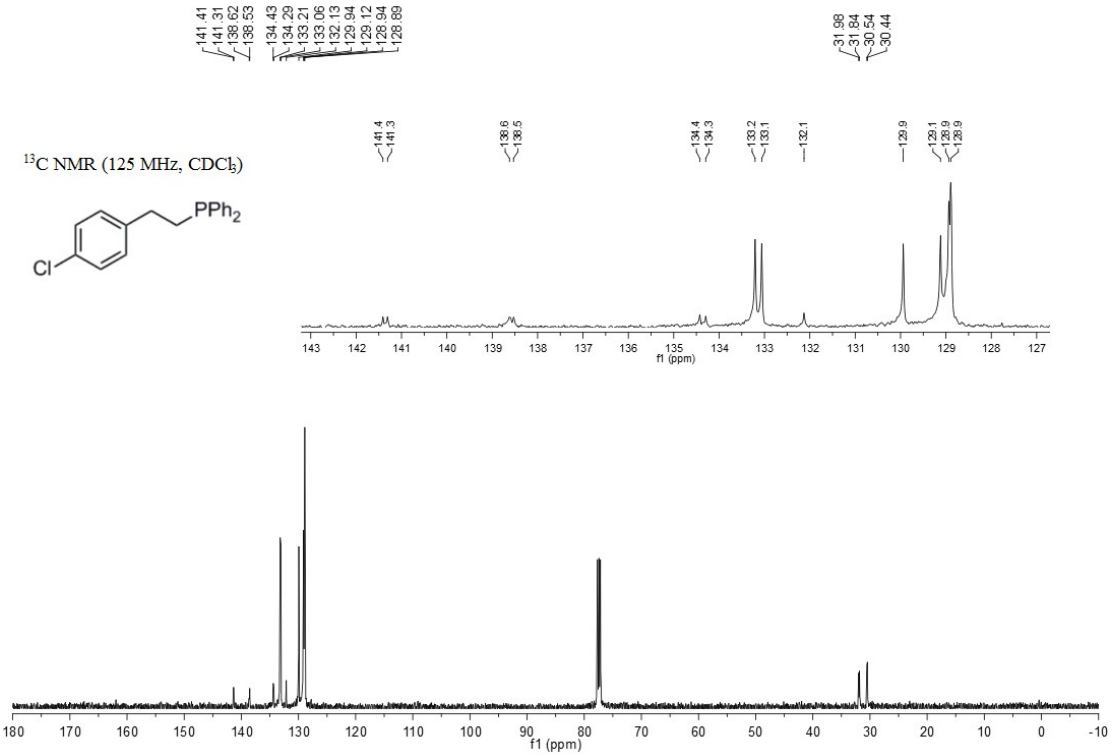


Figure S43. ^{13}C NMR spectra of **3j**

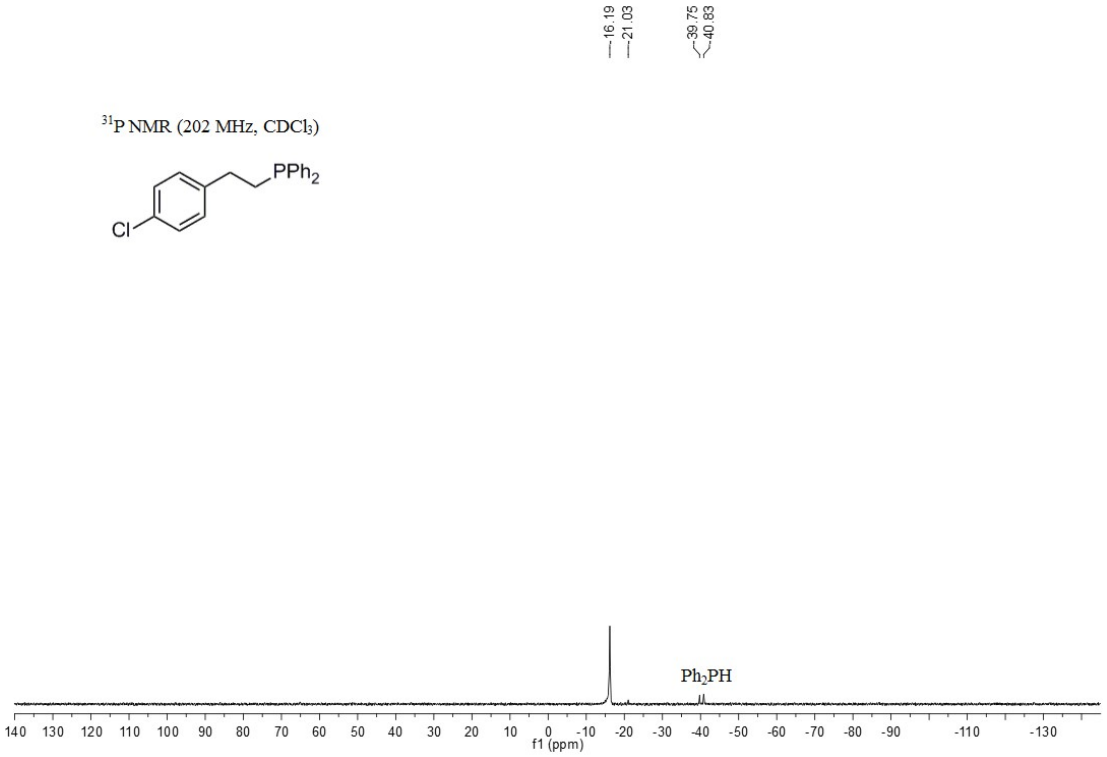


Figure S44. ^{31}P NMR spectra of **3j**

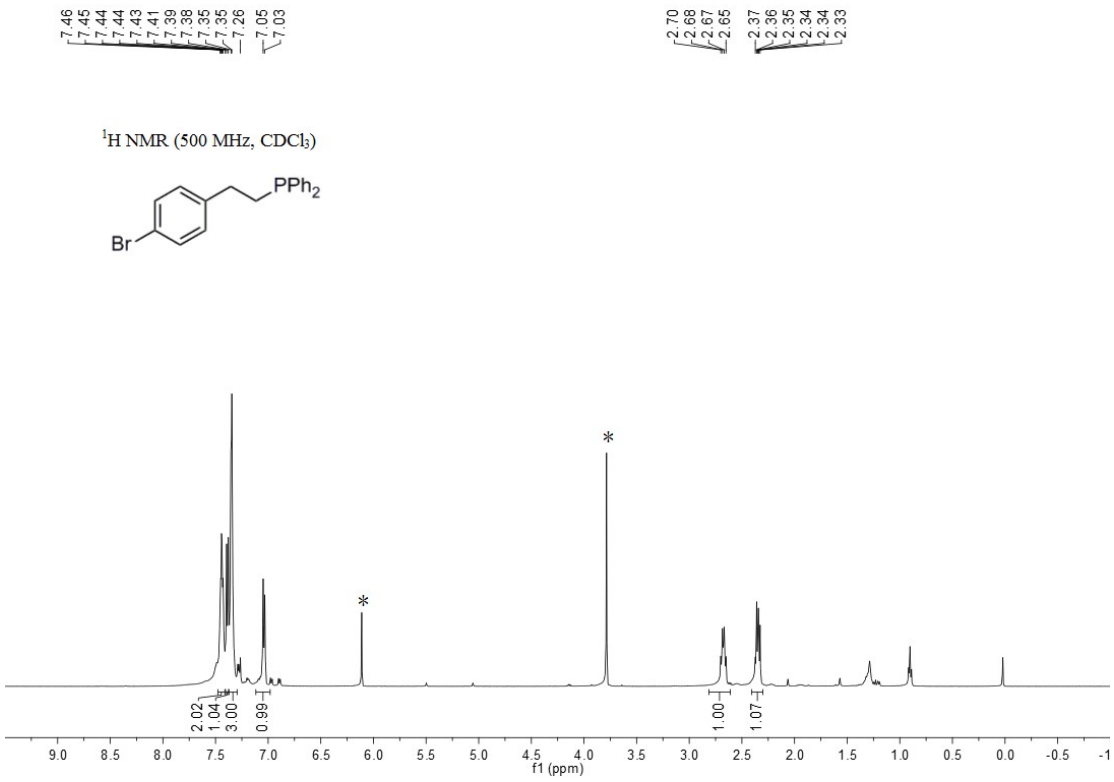


Figure S45. ^{1}H NMR spectra of **3k** (* represents 1,3,5-trimethoxybenzene)

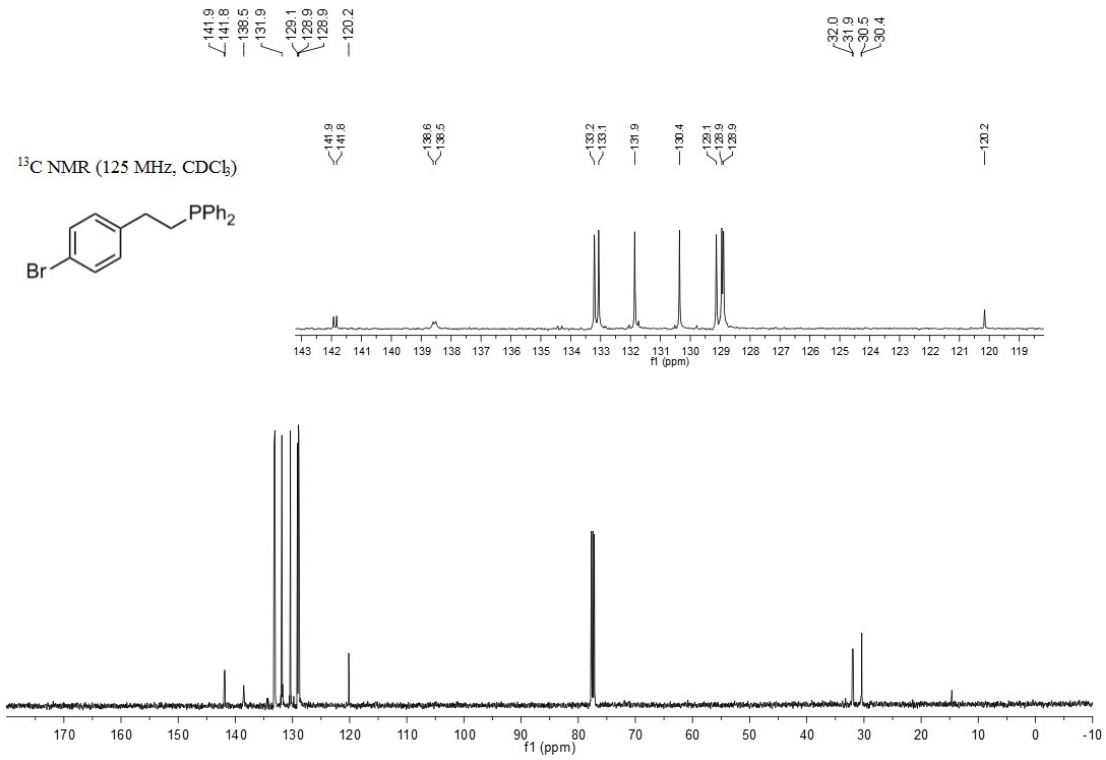


Figure S46. ^{13}C NMR spectra of **3k**

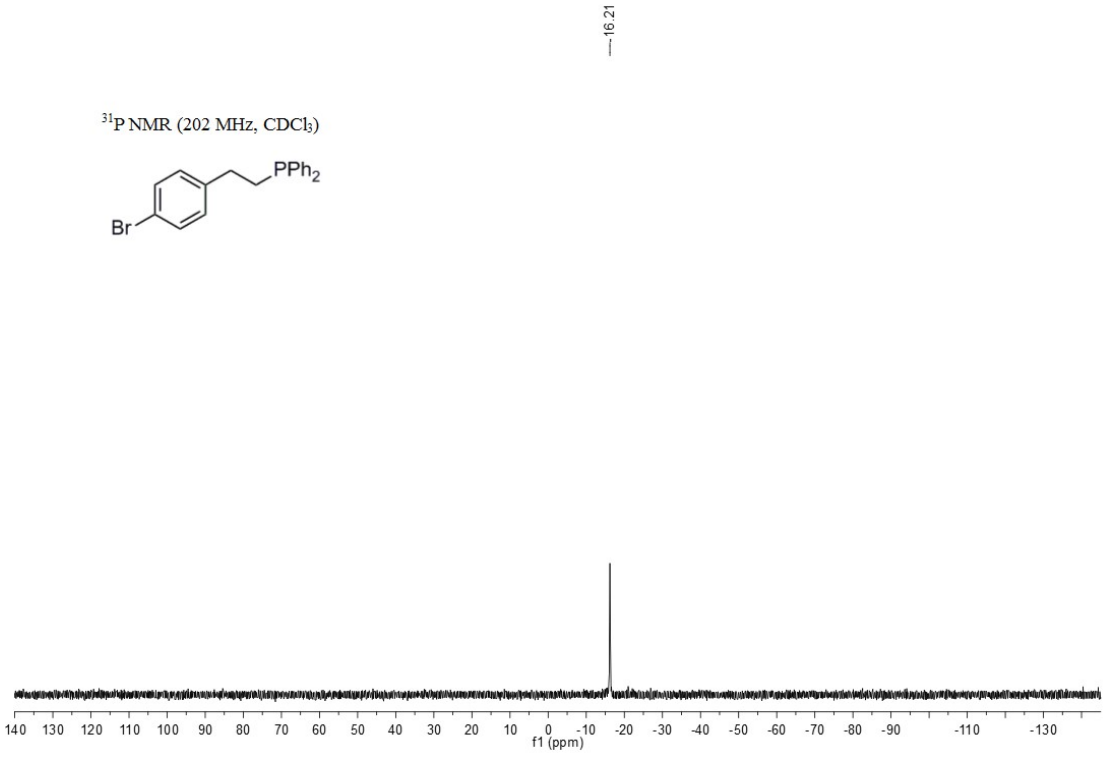


Figure S47. ^{31}P NMR spectra of **3k**

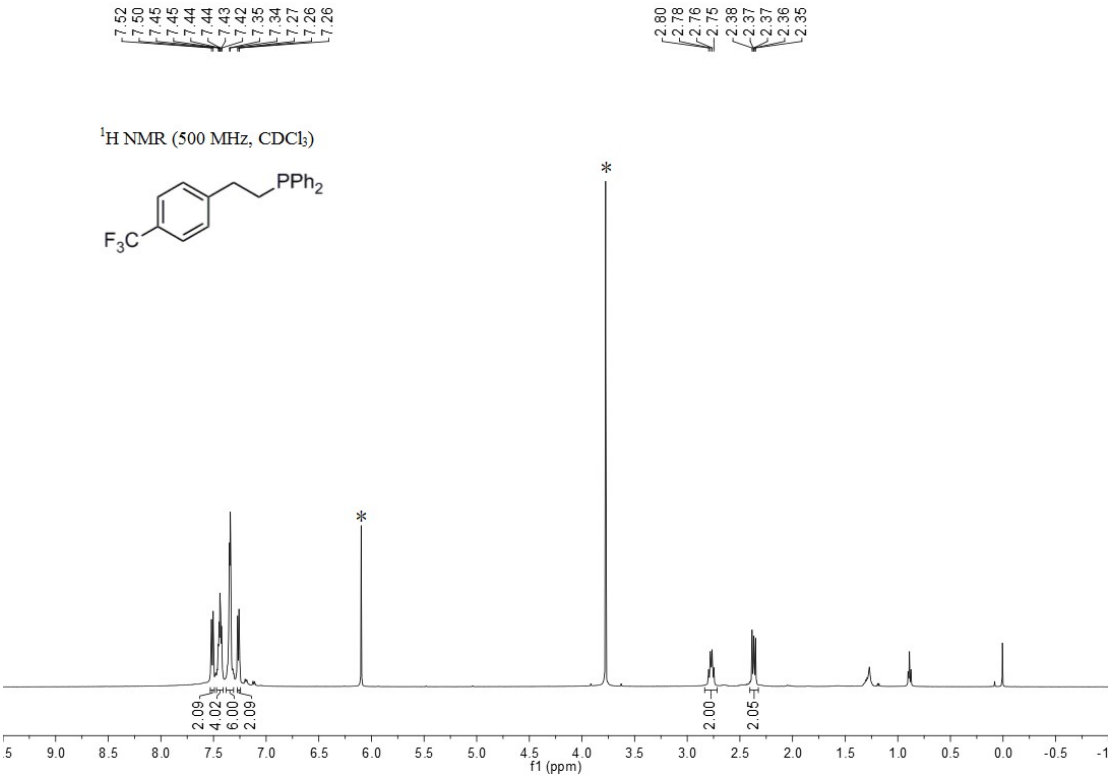


Figure S48. ^{1}H NMR spectra of **3l** (* represents 1,3,5-trimethoxybenzene)

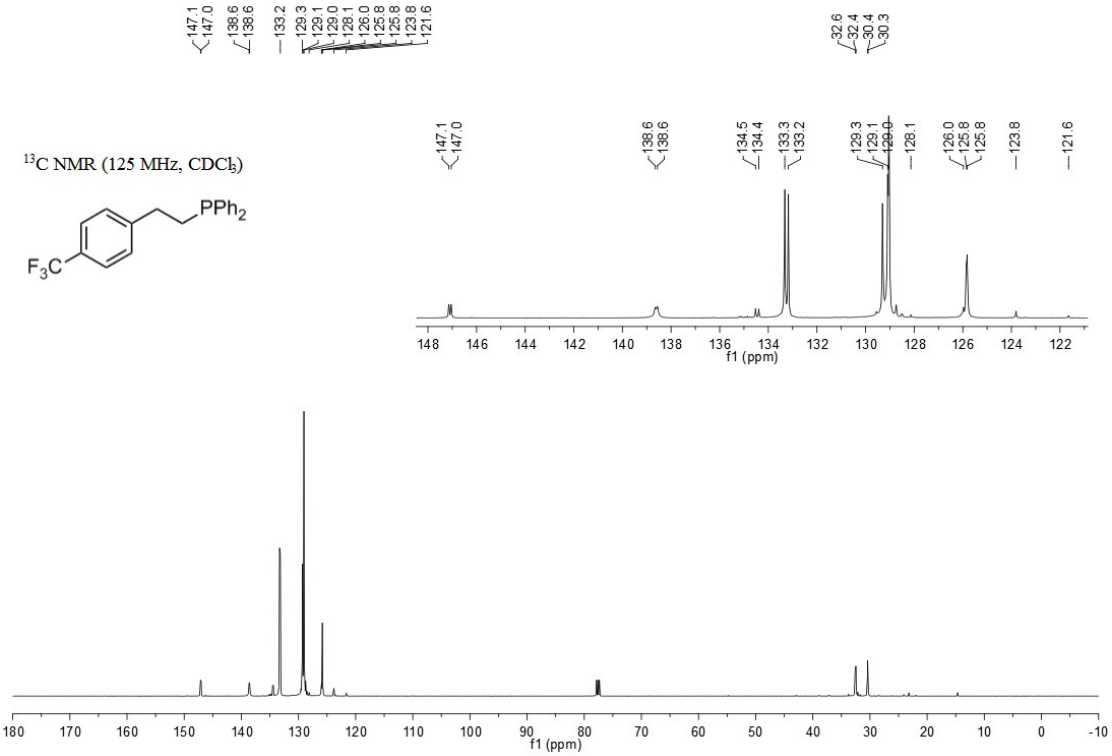


Figure S49 ^{13}C NMR spectra of **3l**

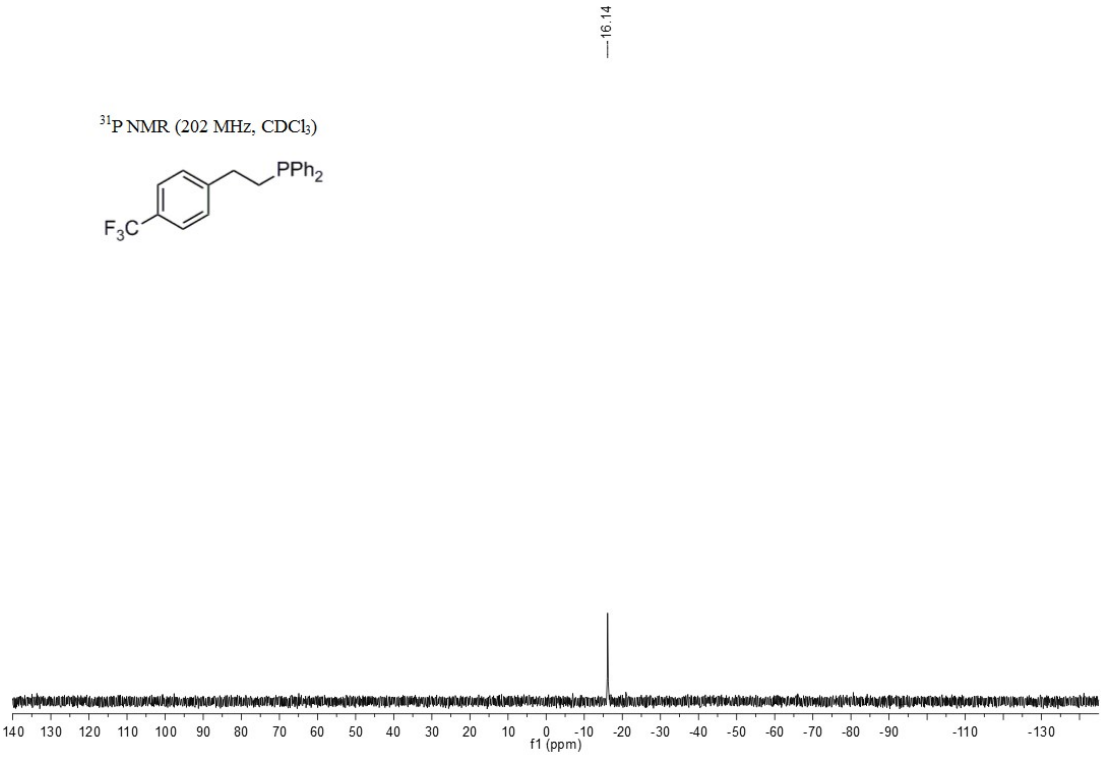


Figure S50. ^{31}P NMR spectra of **3l**

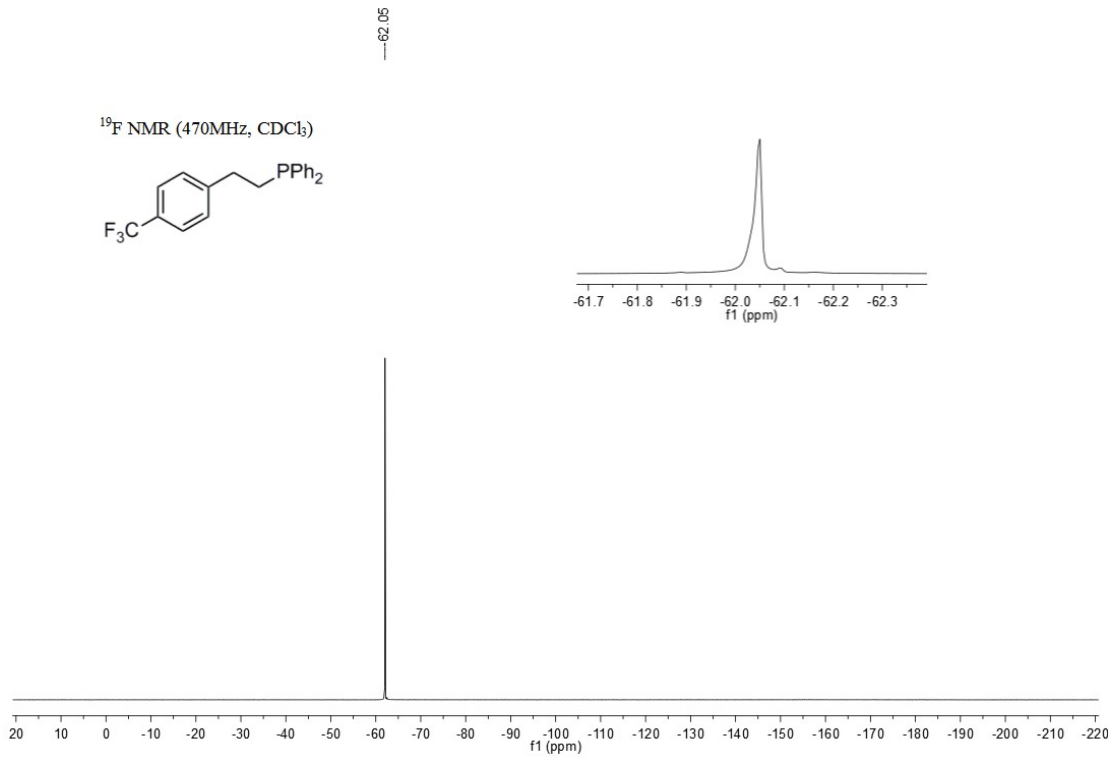


Figure S51. ^{19}F NMR spectra of **3l**

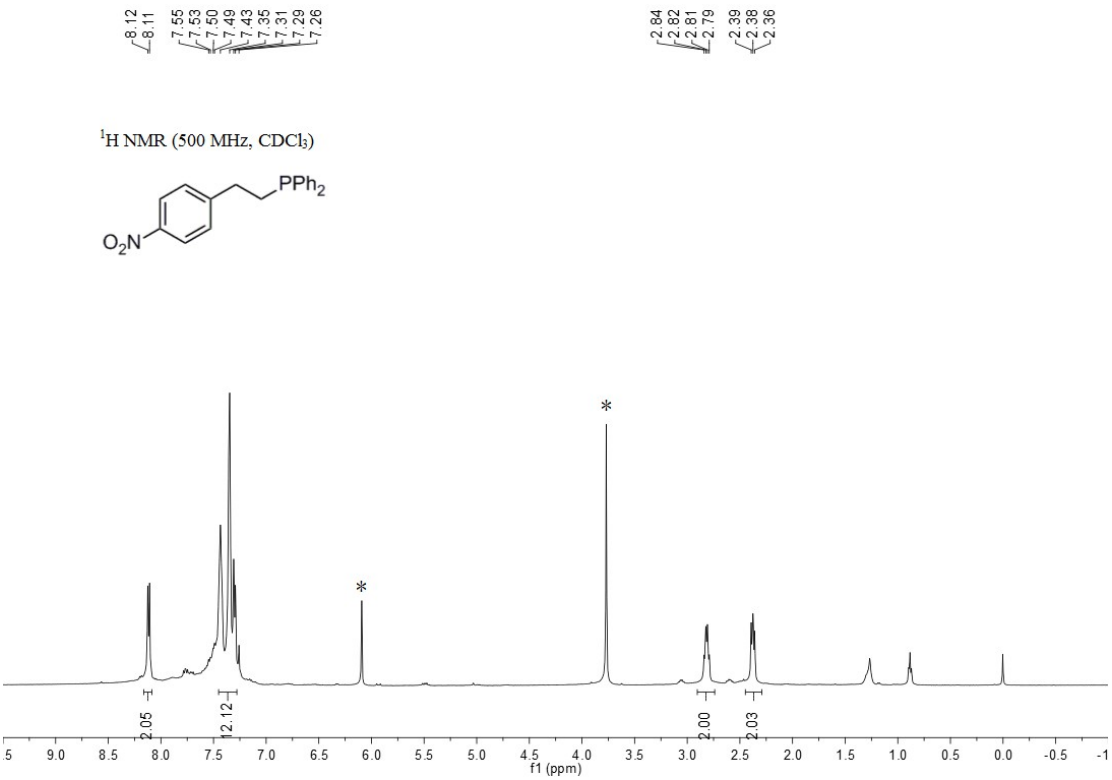


Figure S52. ^{1}H NMR spectra of **3m** (* represents 1,3,5-trimethoxybenzene)

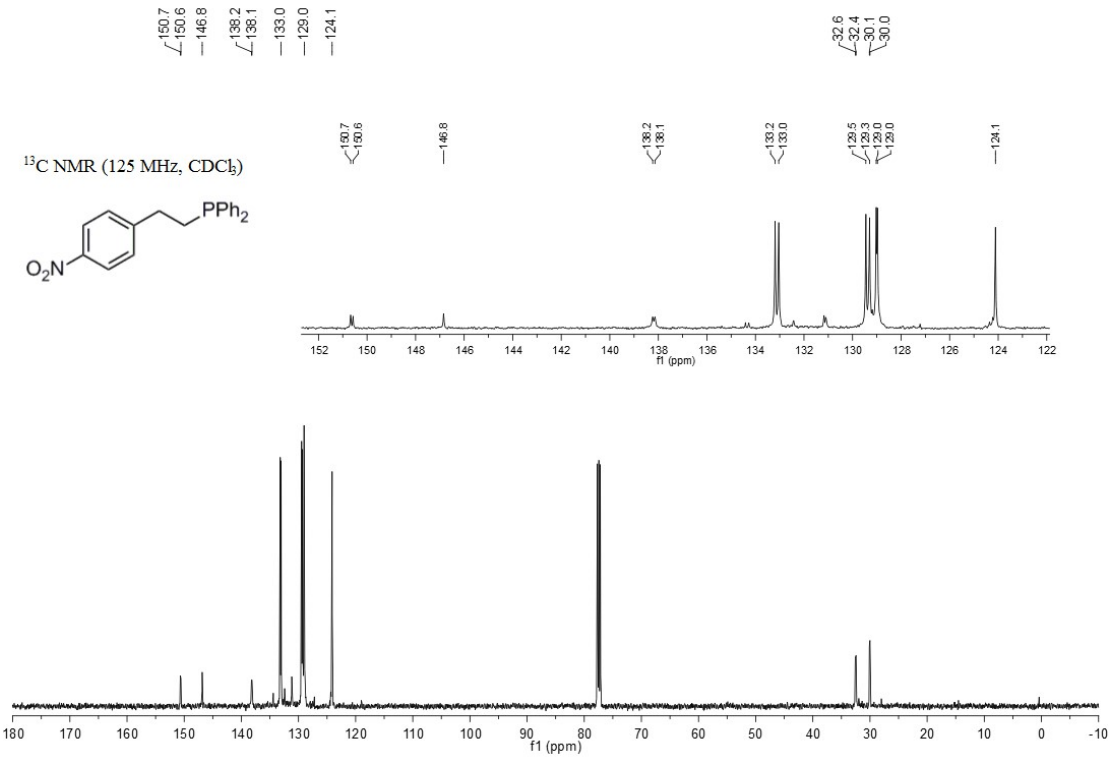


Figure S53. ^{13}C NMR spectra of **3m**

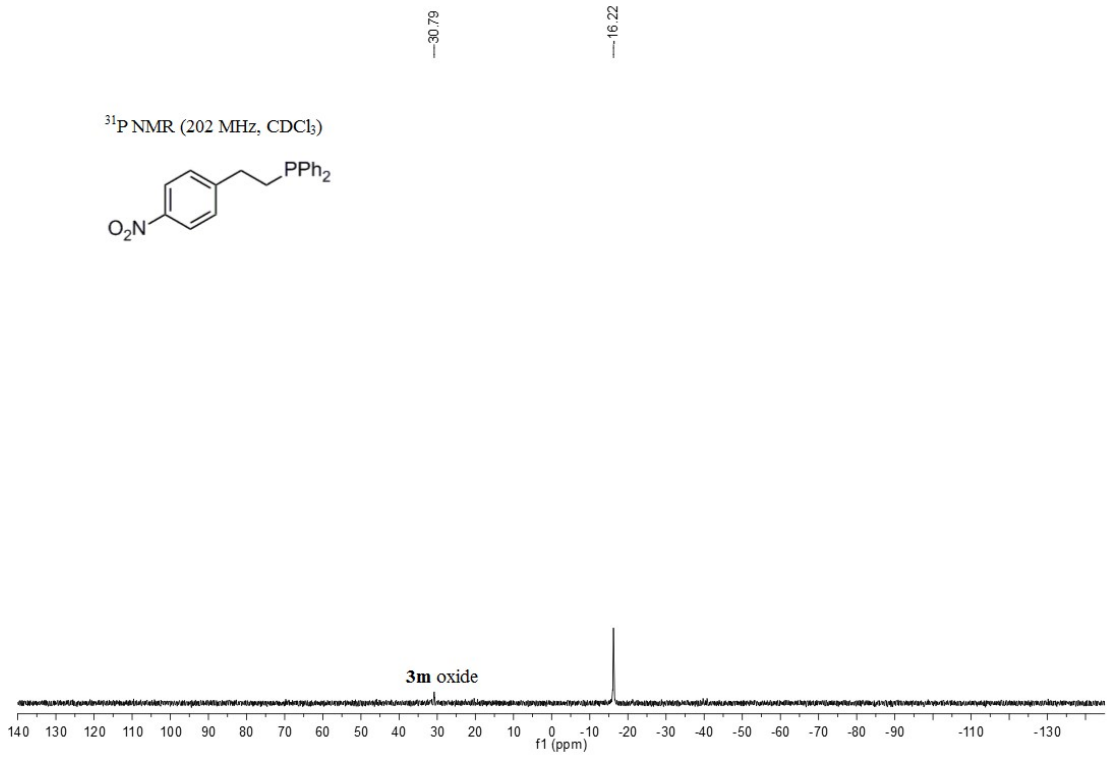


Figure S54. ^{31}P NMR spectra of **3m**

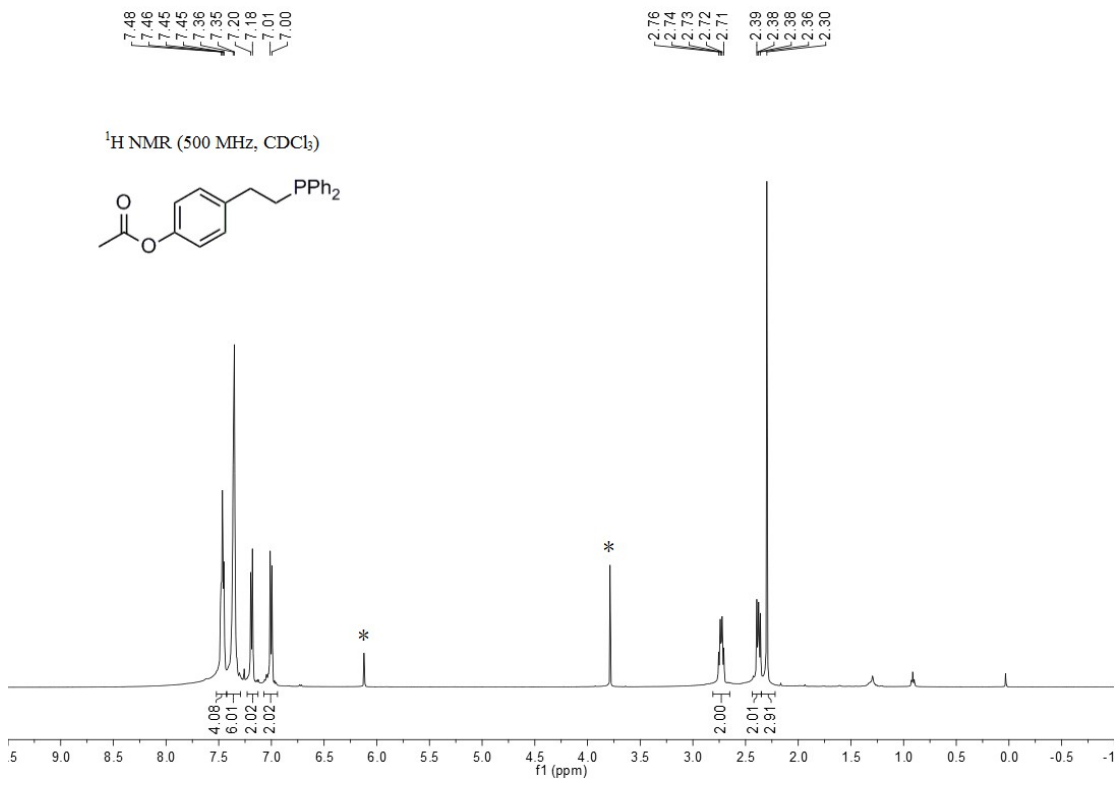


Figure S55. ^{1}H NMR spectra of **3n** (* represents 1,3,5-trimethoxybenzene)

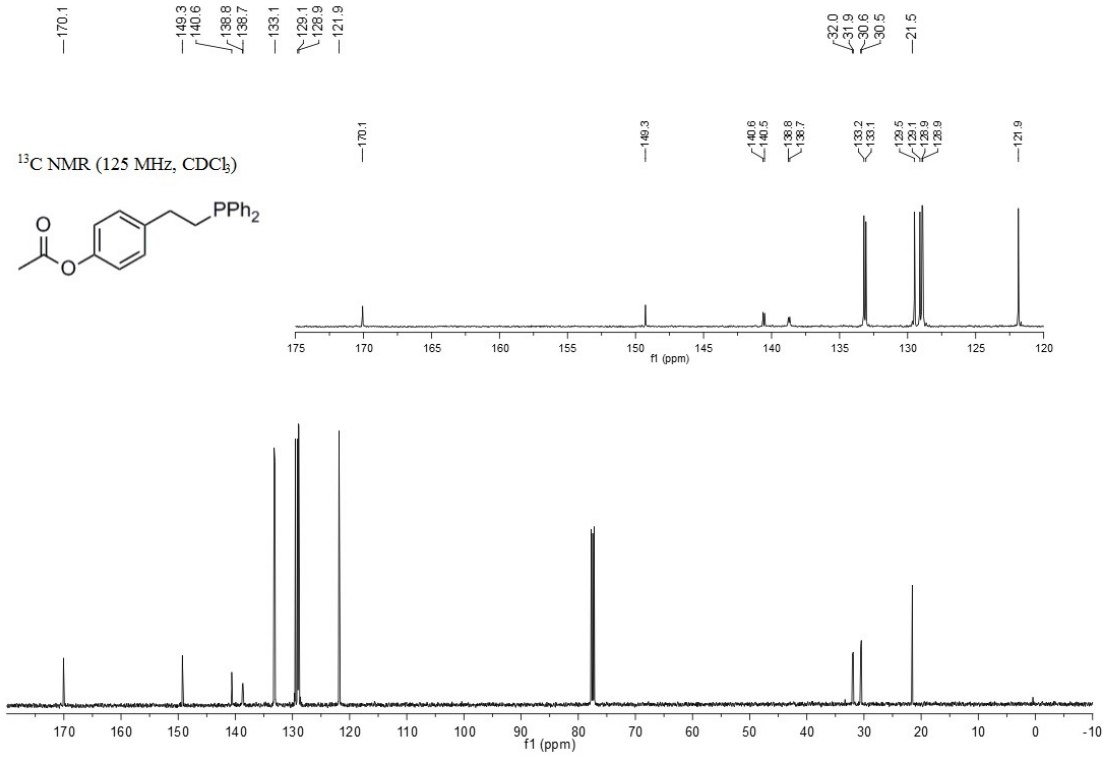


Figure S56. ^{13}C NMR spectra of **3n**

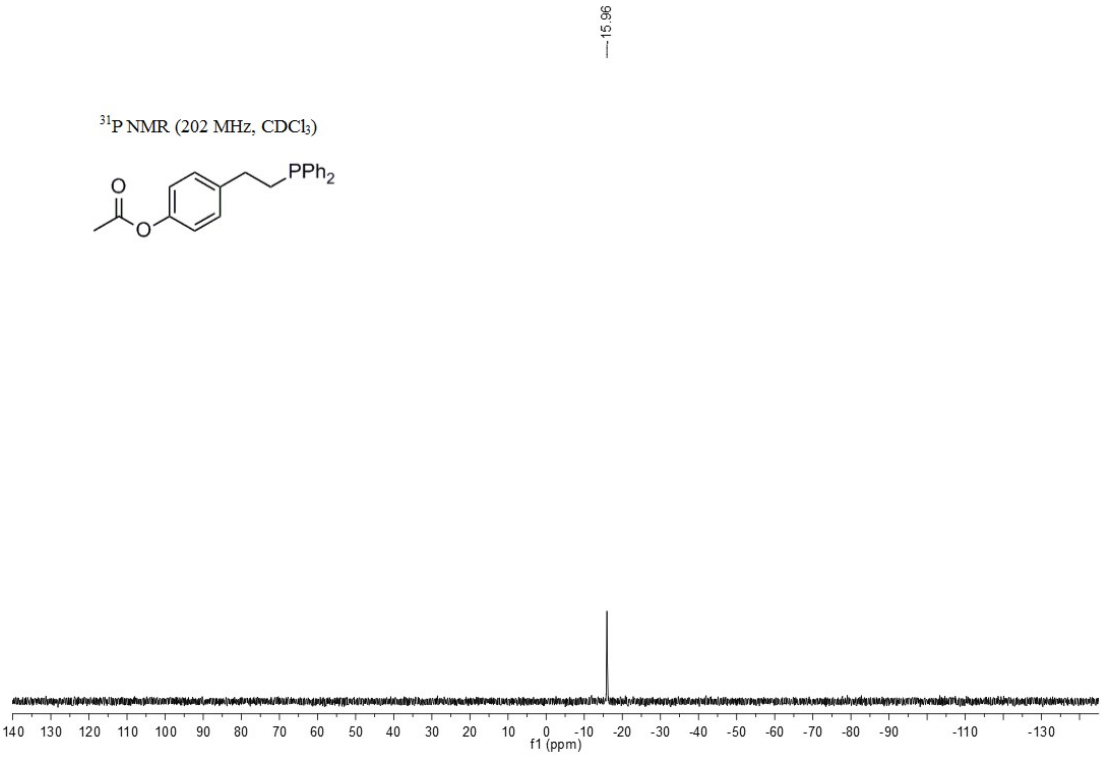


Figure S57. ^{31}P NMR spectra of **3n**

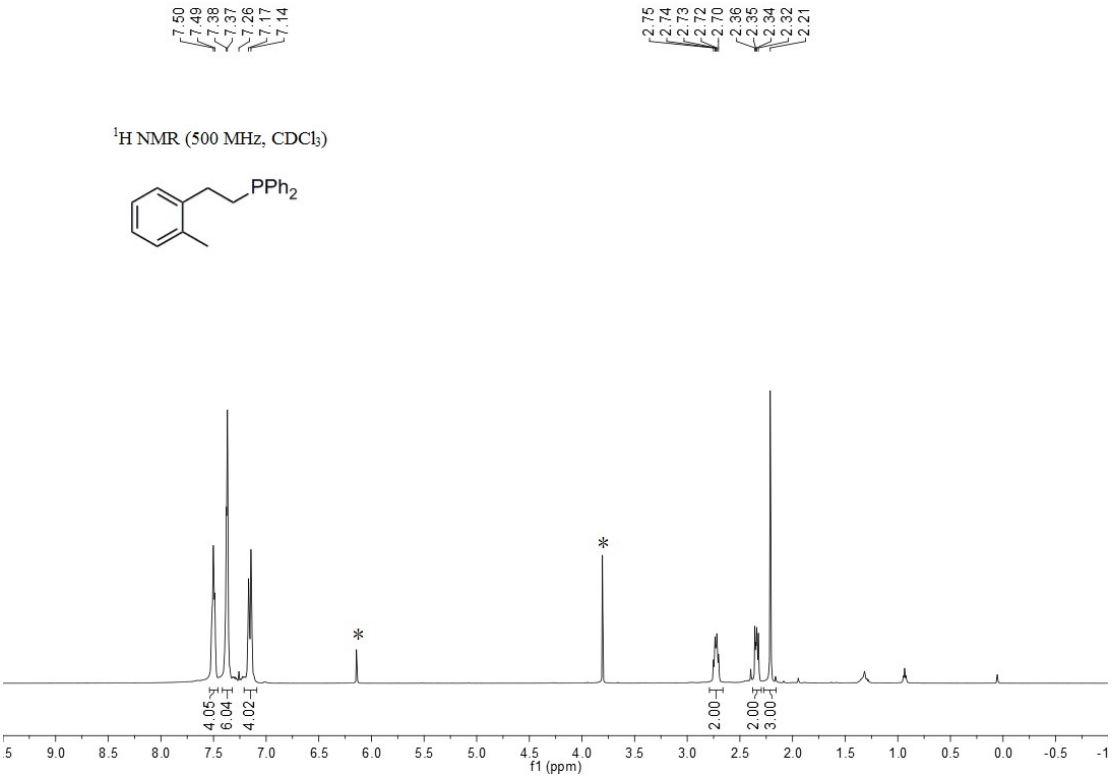


Figure S58. ^{1}H NMR spectra of **3o** (* represents 1,3,5-trimethoxybenzene)

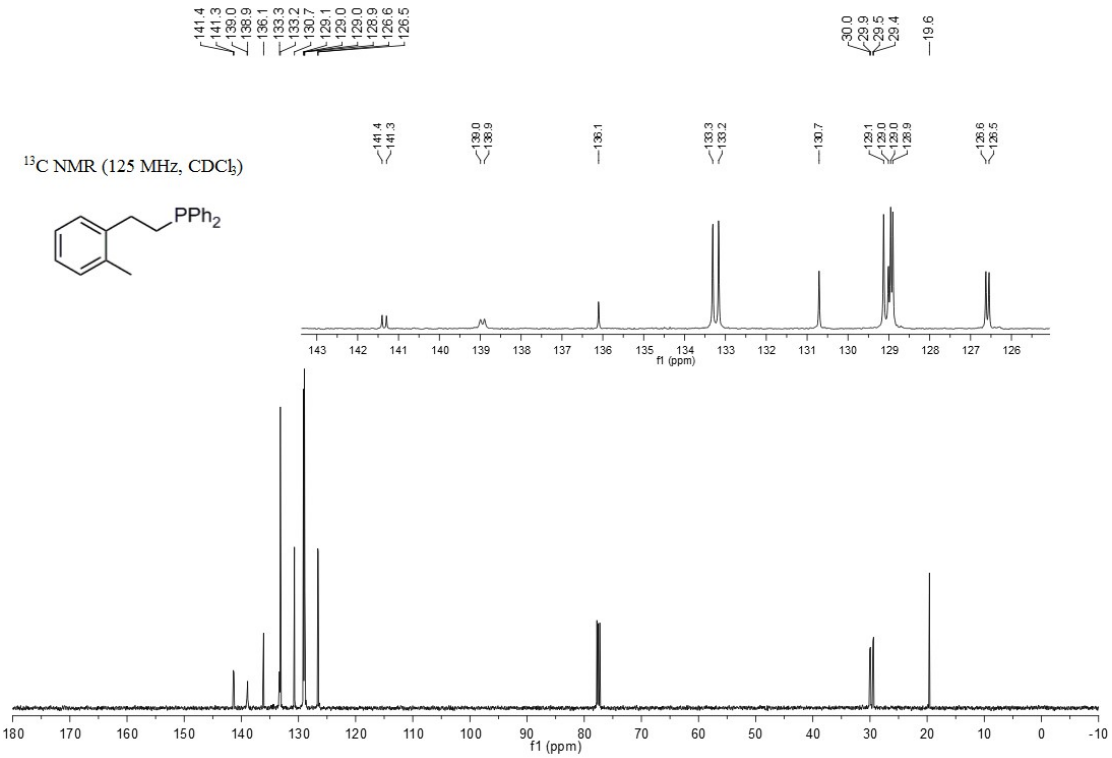


Figure S59. ^{13}C NMR spectra of **3o**

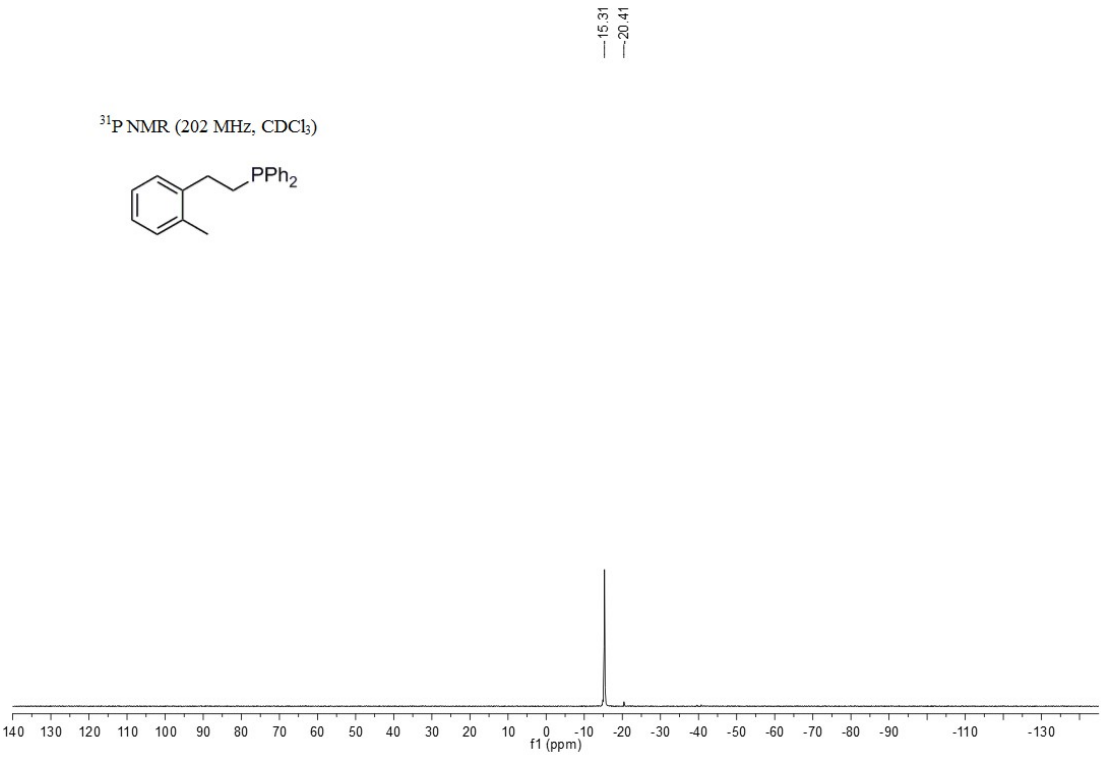


Figure S60. ^{31}P NMR spectra of **3o**

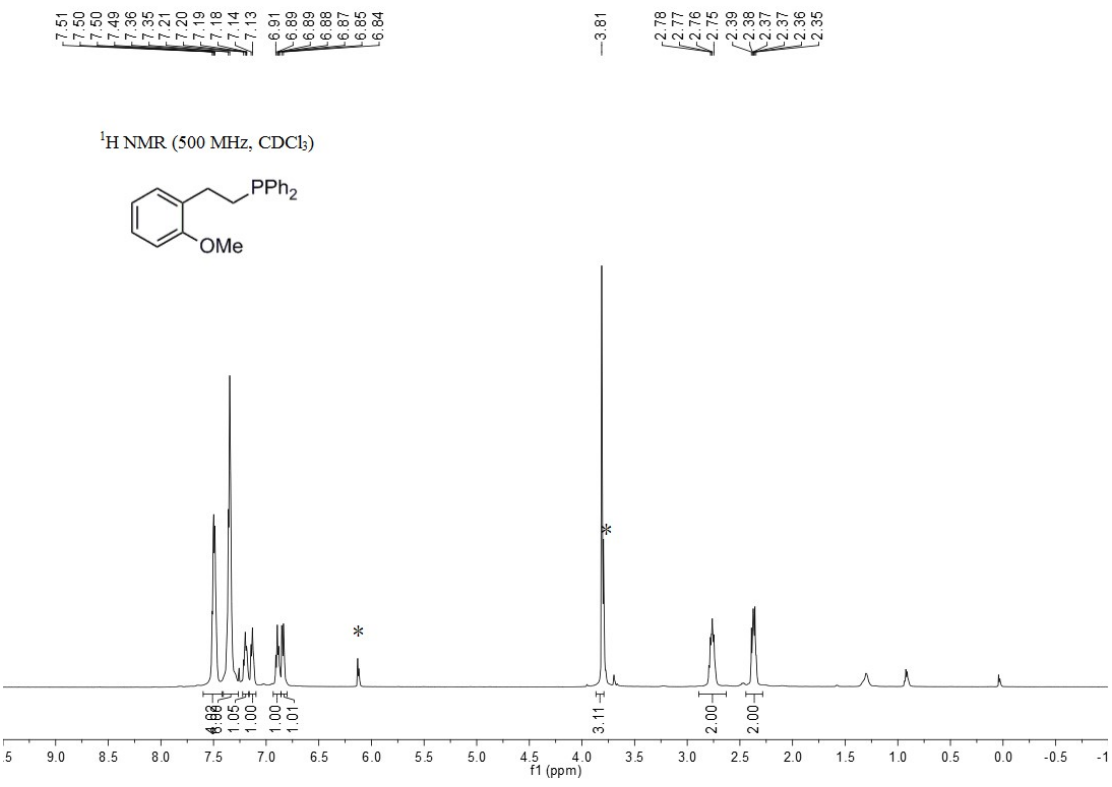


Figure S61. ^{1}H NMR spectra of **3p** (* represents 1,3,5-trimethoxybenzene)

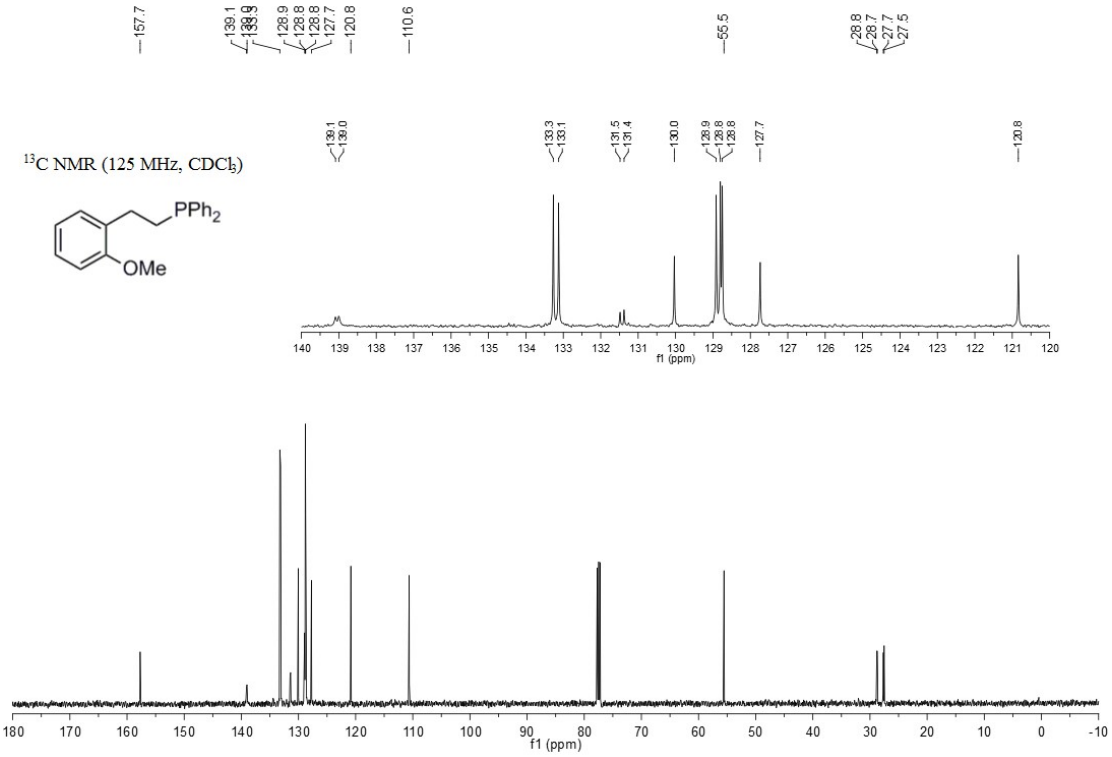


Figure S62. ^{13}C NMR spectra of **3p**

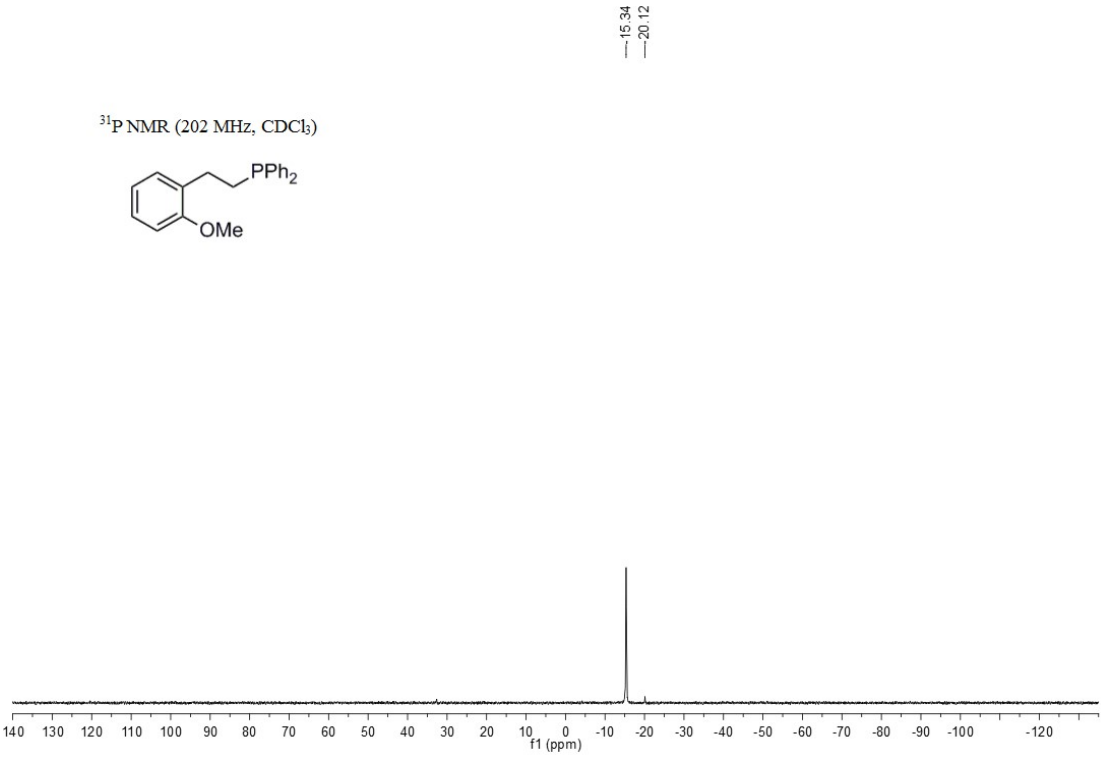


Figure S63. ^{31}P NMR spectra of **3p**

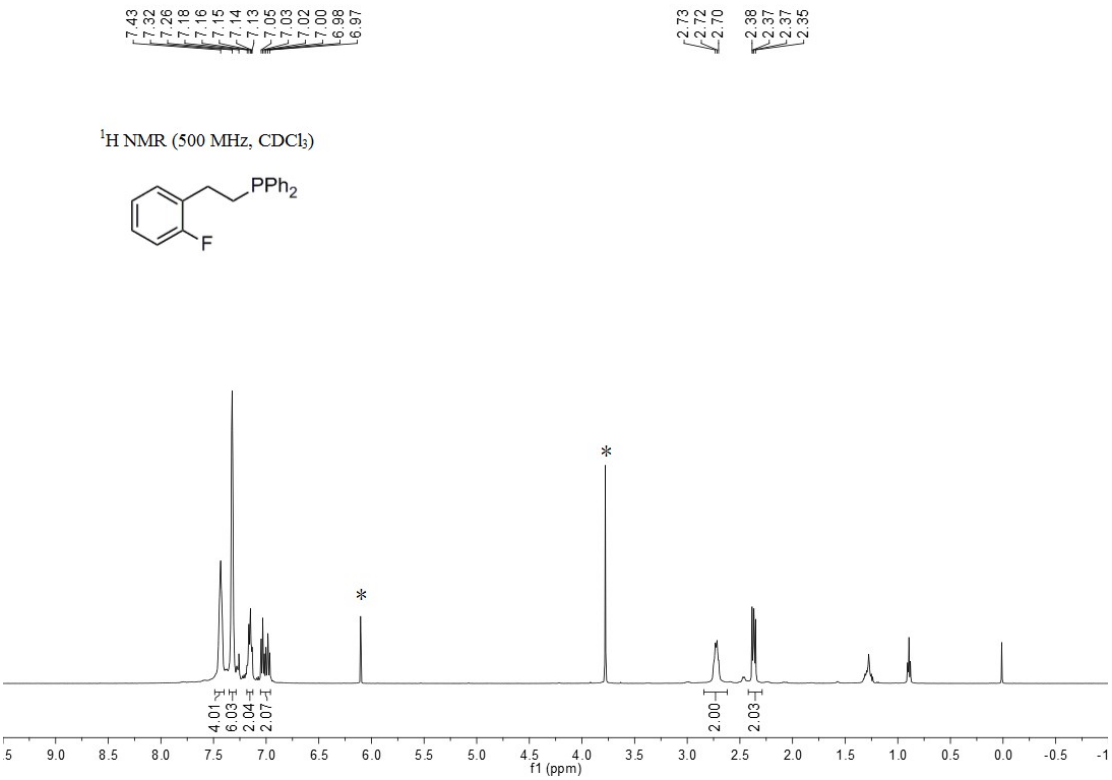


Figure S64. ^{1}H NMR spectra of **3q** (* represents 1,3,5-trimethoxybenzene)

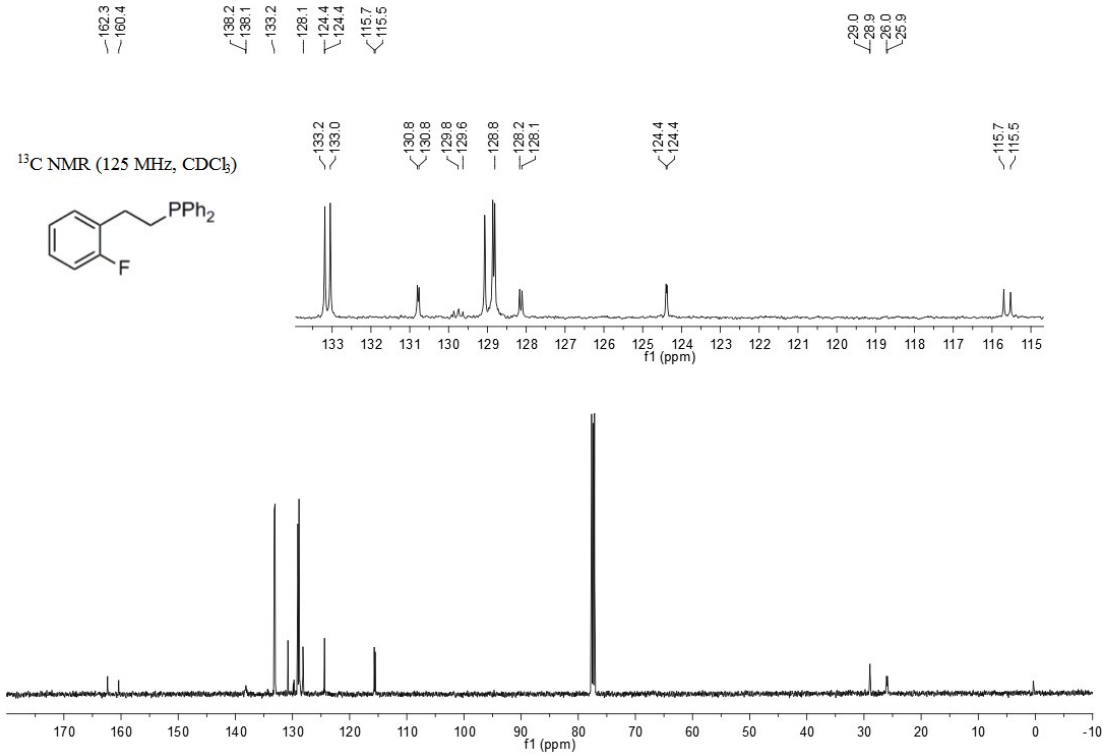


Figure S65. ^{13}C NMR spectra of **3q**

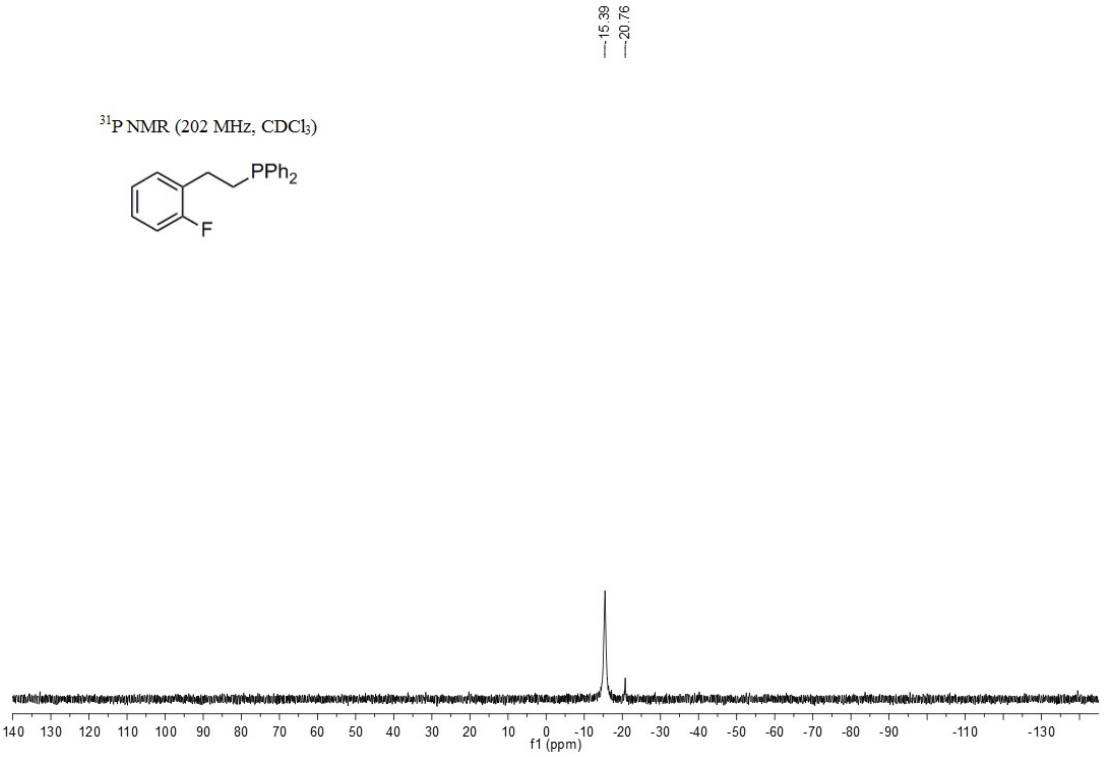


Figure S66. ^{31}P NMR spectra of **3q**

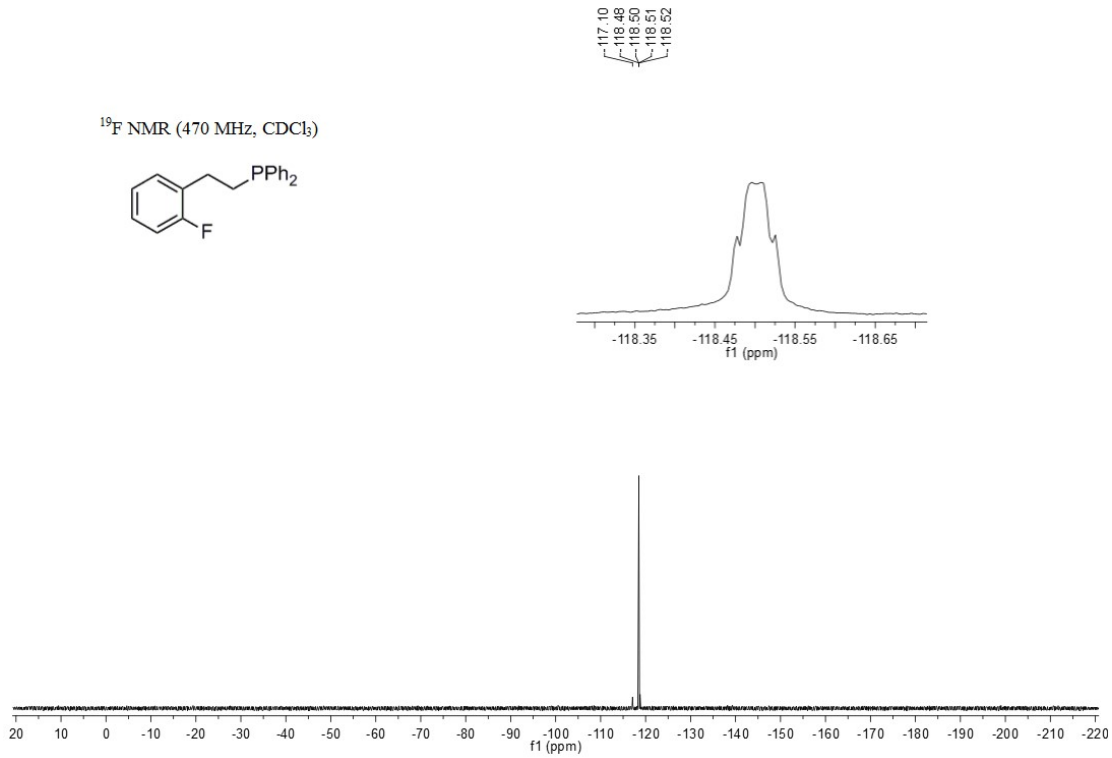


Figure S67. ^{19}F NMR spectra of **3q**

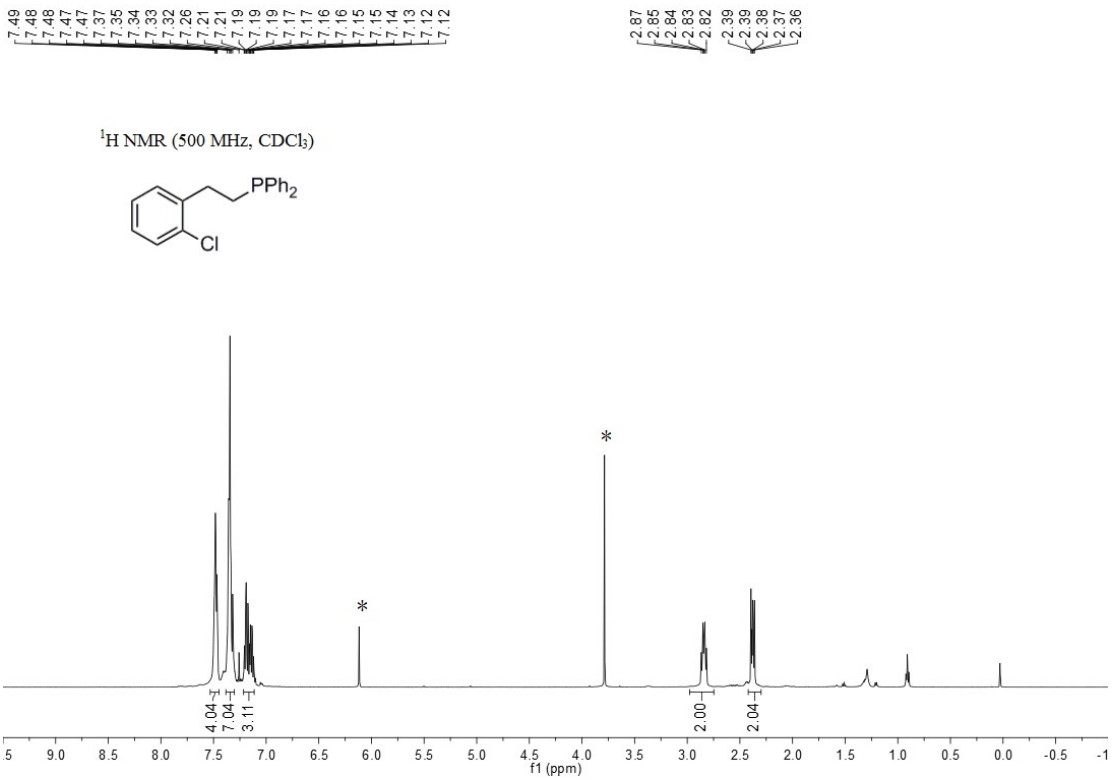


Figure S68. ^{1}H NMR spectra of **3r** (* represents 1,3,5-trimethoxybenzene)

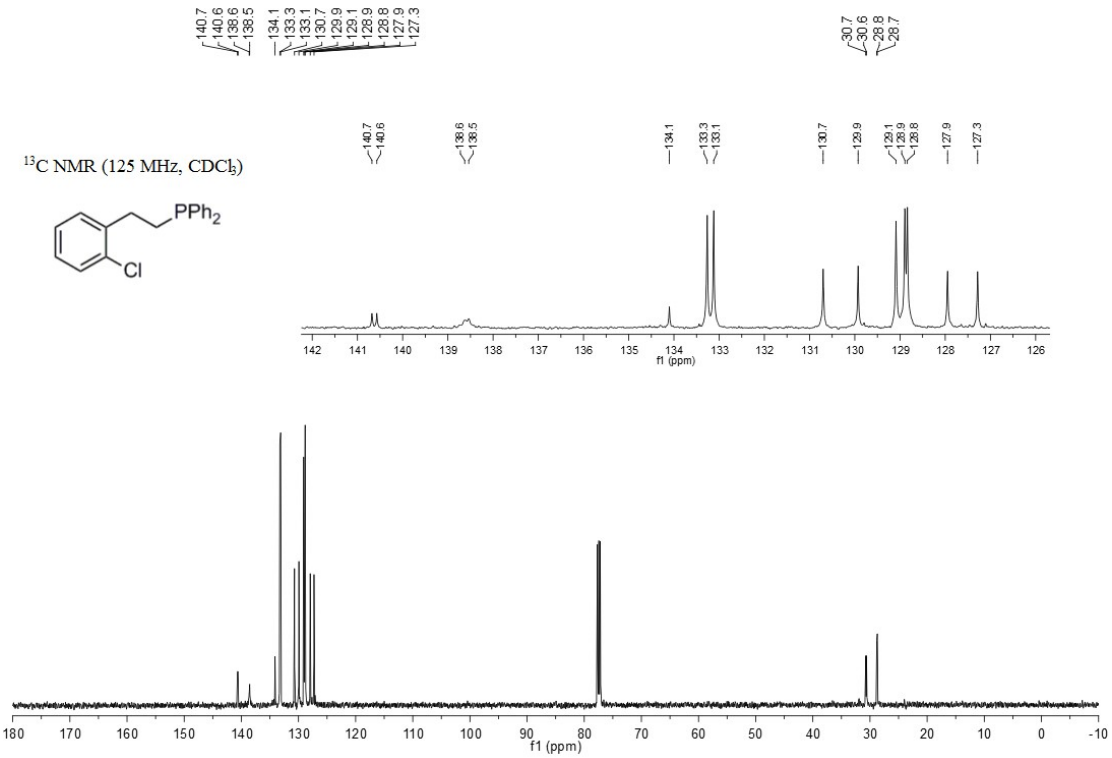


Figure S69. ^{13}C NMR spectra of **3r**

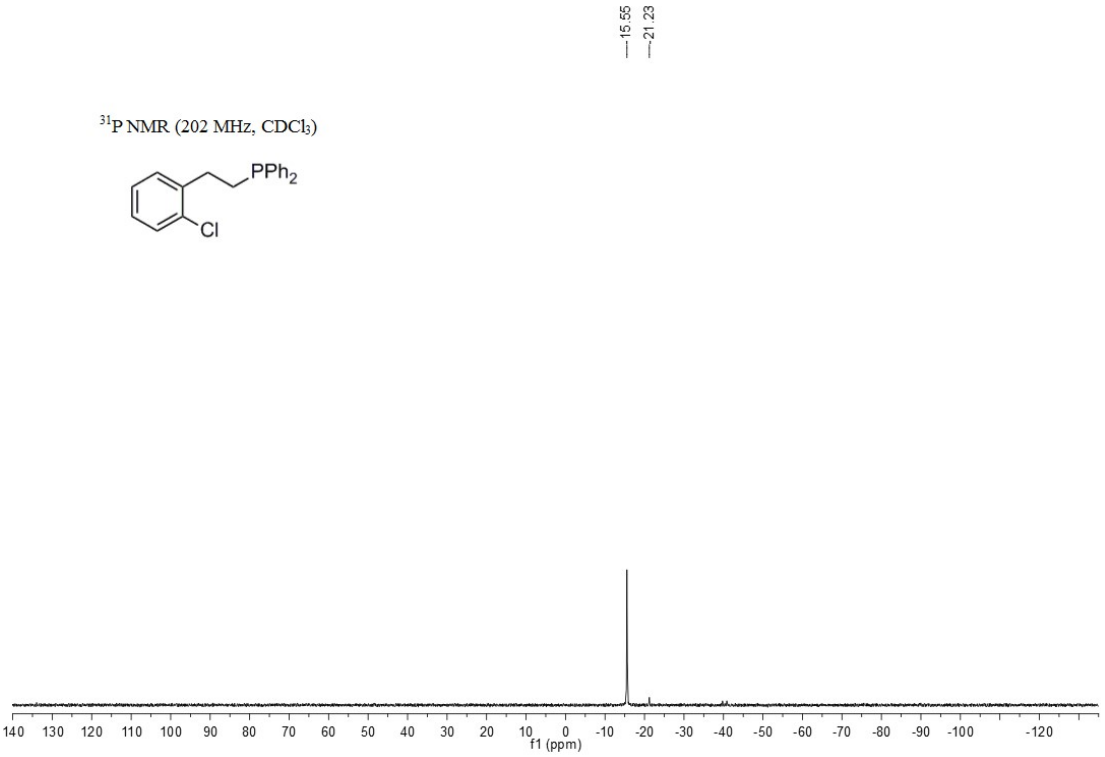


Figure S70. ^{31}P NMR spectra of **3r**

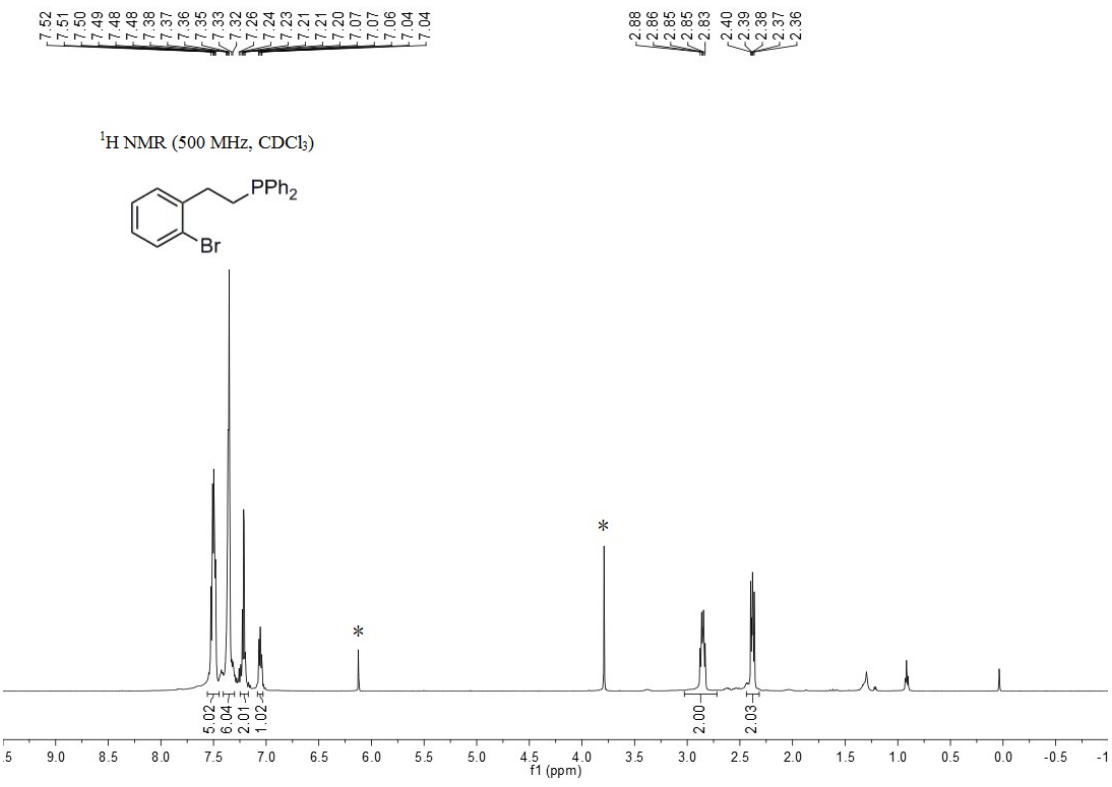


Figure S71. ^{1}H NMR spectra of **3s** (* represents 1,3,5-trimethoxybenzene)

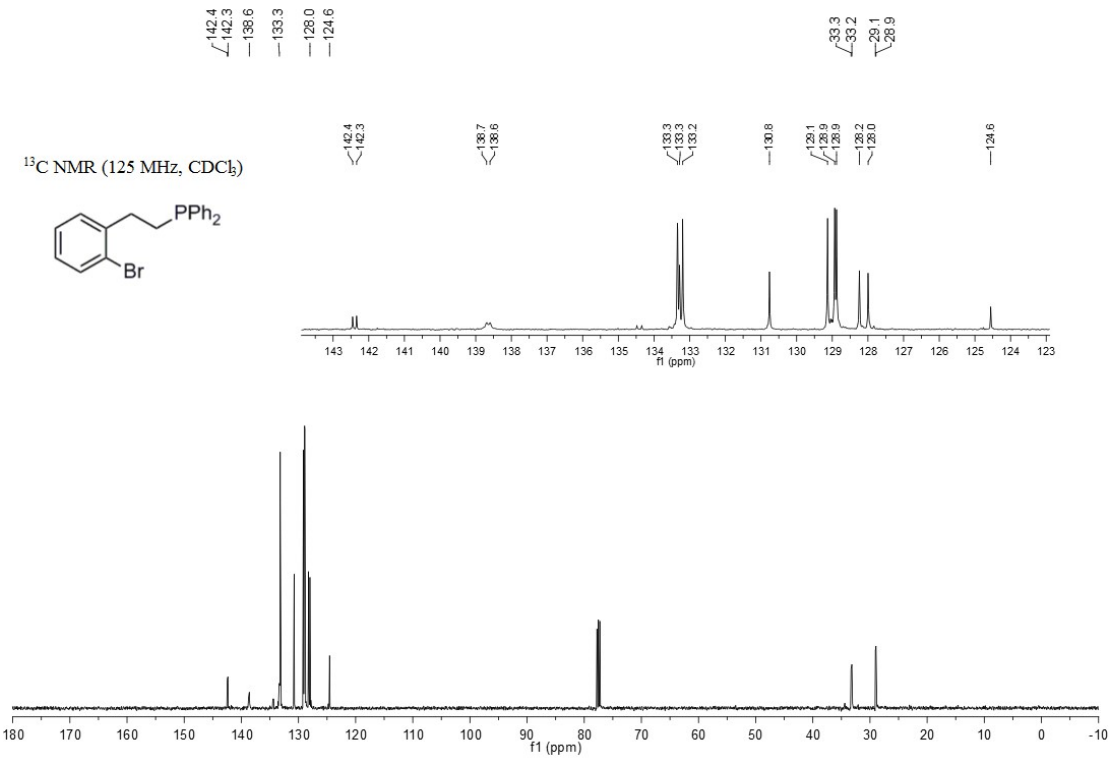


Figure S72. ^{13}C NMR spectra of **3s**

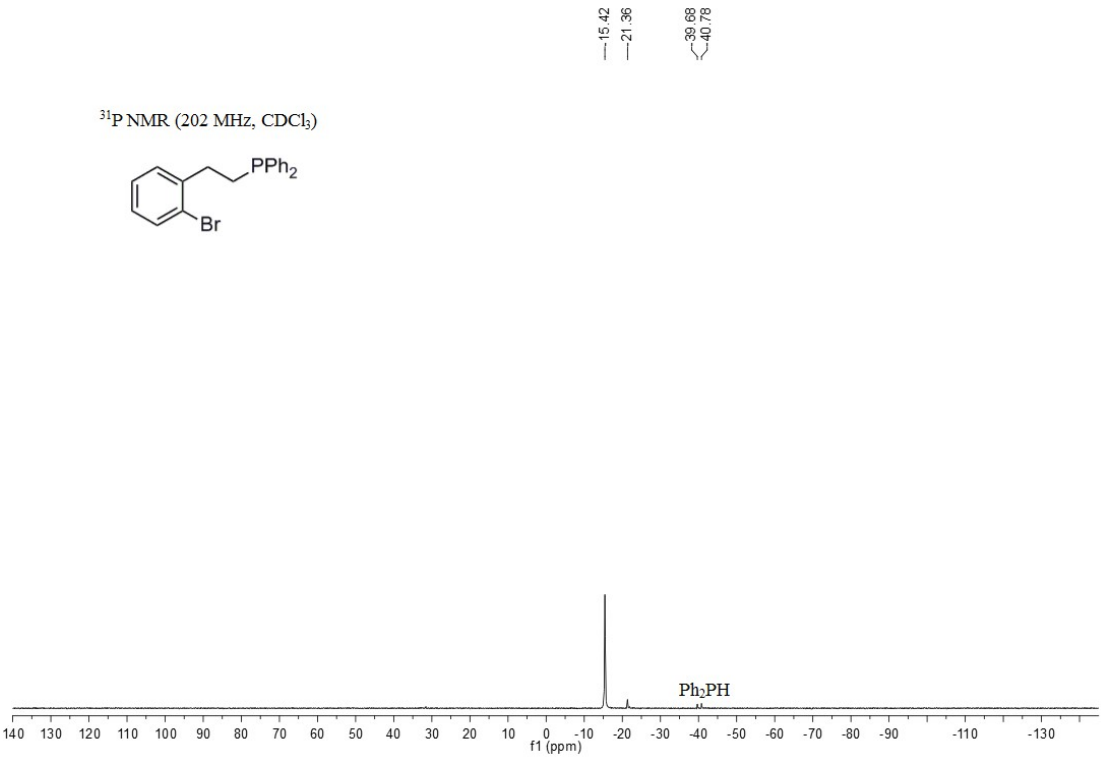


Figure S73. ^{31}P NMR spectra of **3s**

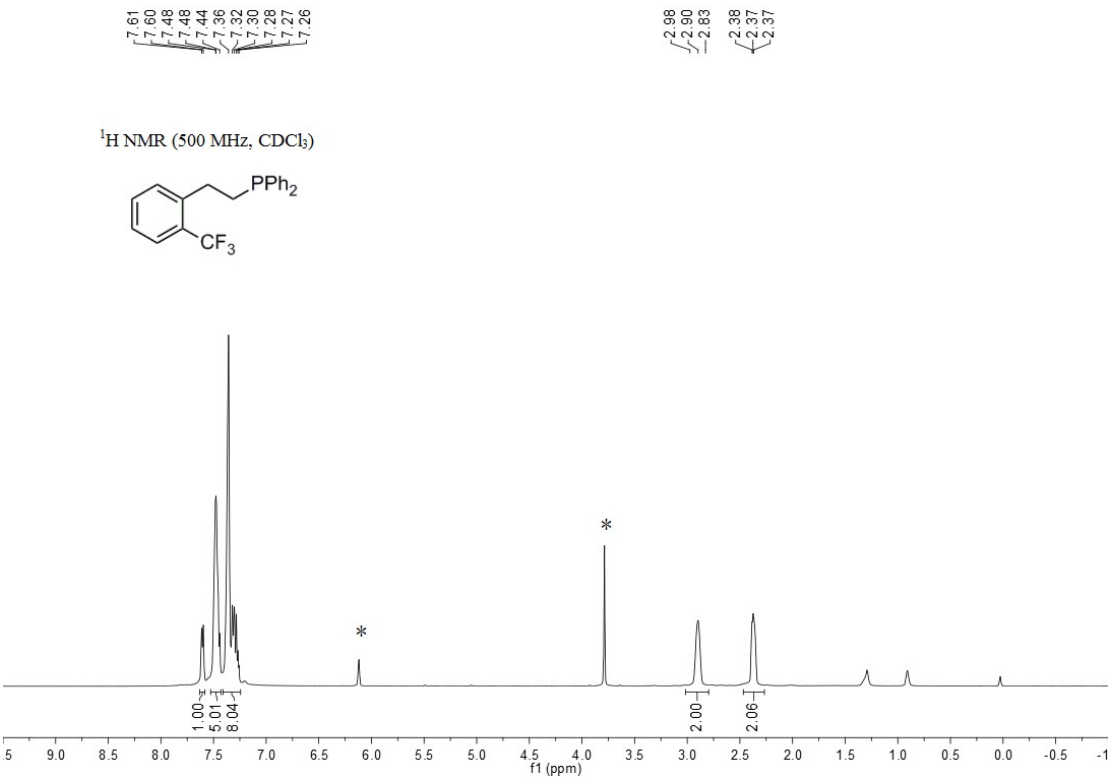


Figure S74. ^{1}H NMR spectra of **3t** (* represents 1,3,5-trimethoxybenzene)

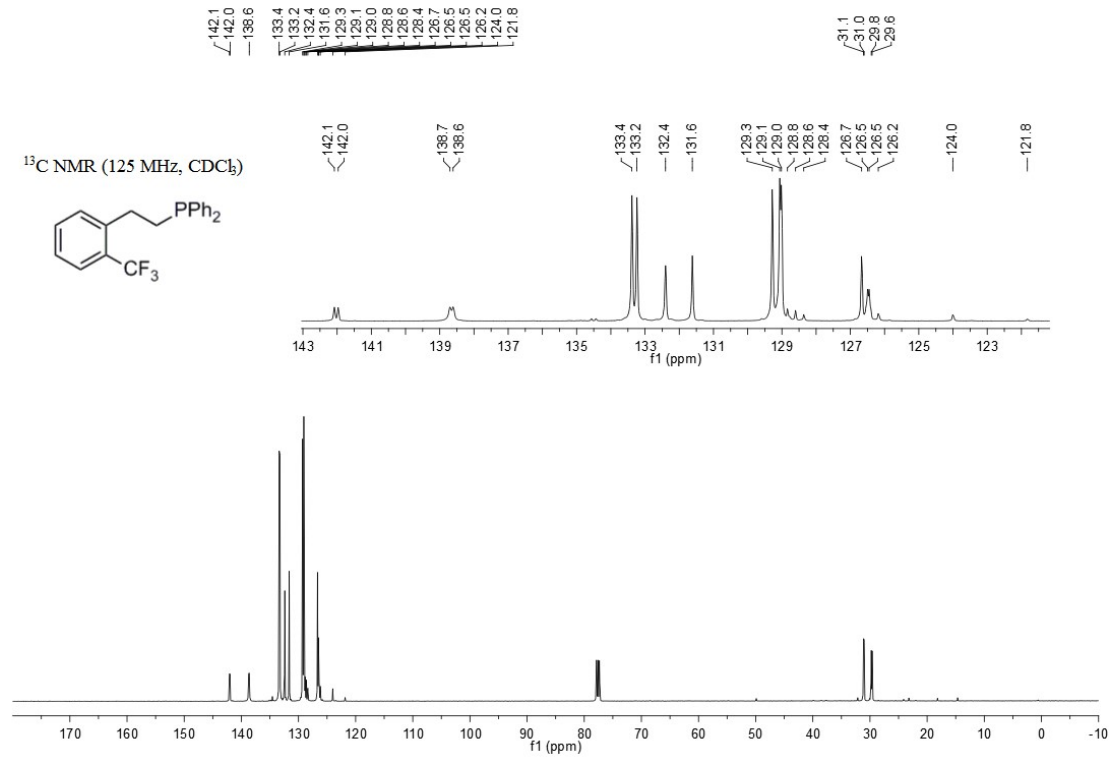


Figure S75. ^{13}C NMR spectra of **3t**

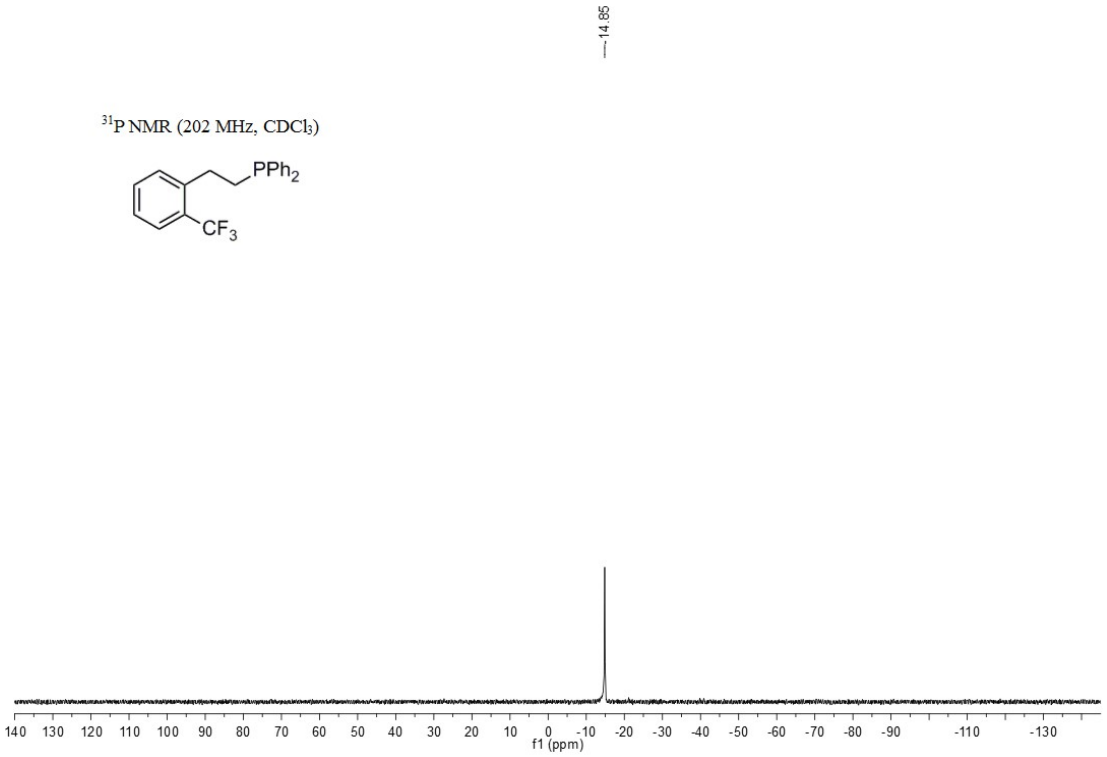


Figure S76. ^{31}P NMR spectra of **3t**

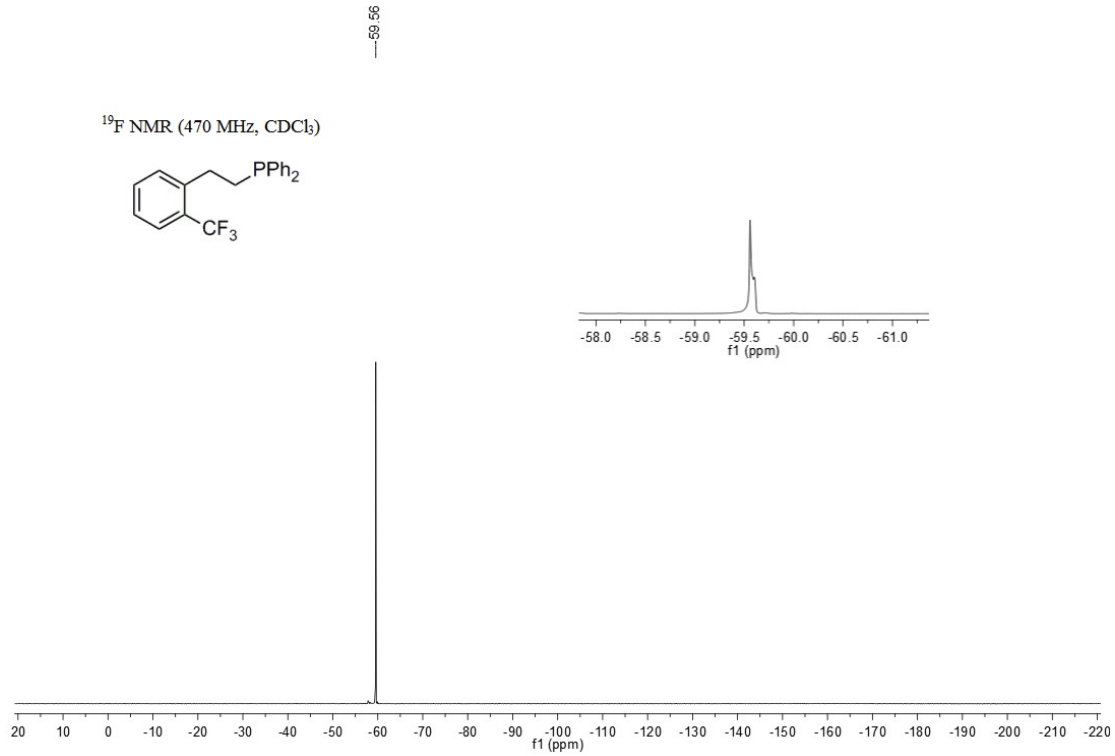


Figure S77. ^{19}F NMR spectra of **3t**

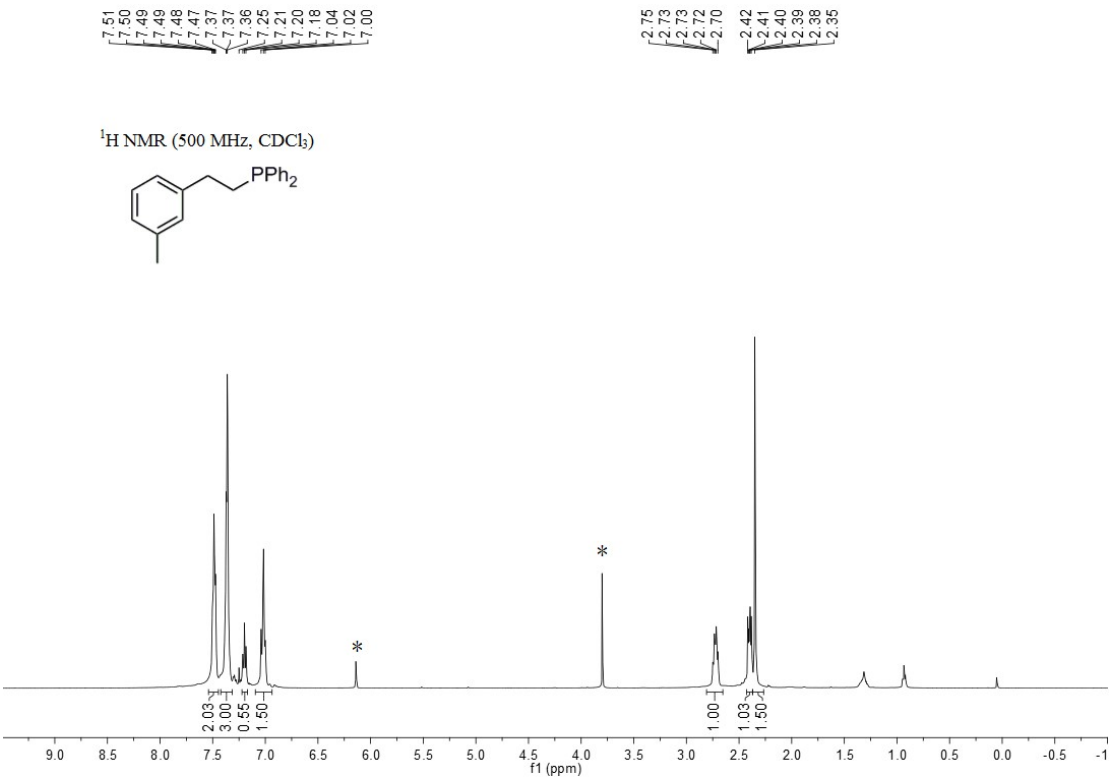


Figure S78. ^{1}H NMR spectra of **3u** (* represents 1,3,5-trimethoxybenzene)

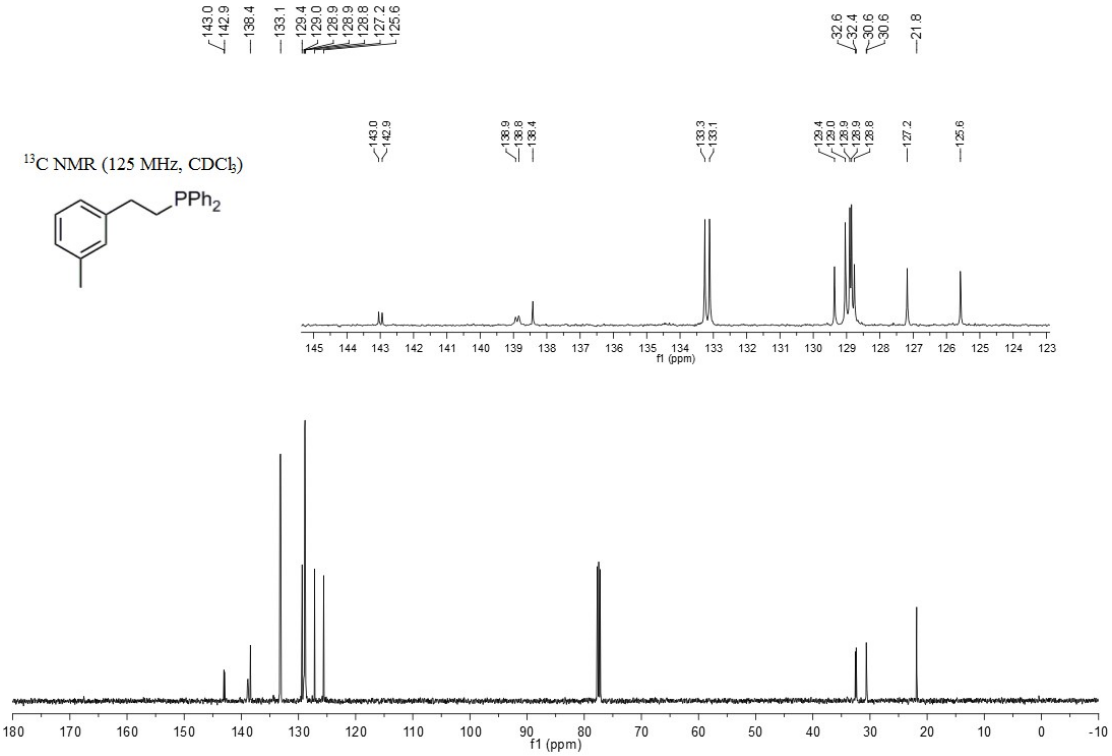


Figure S79. ^{13}C NMR spectra of **3u**

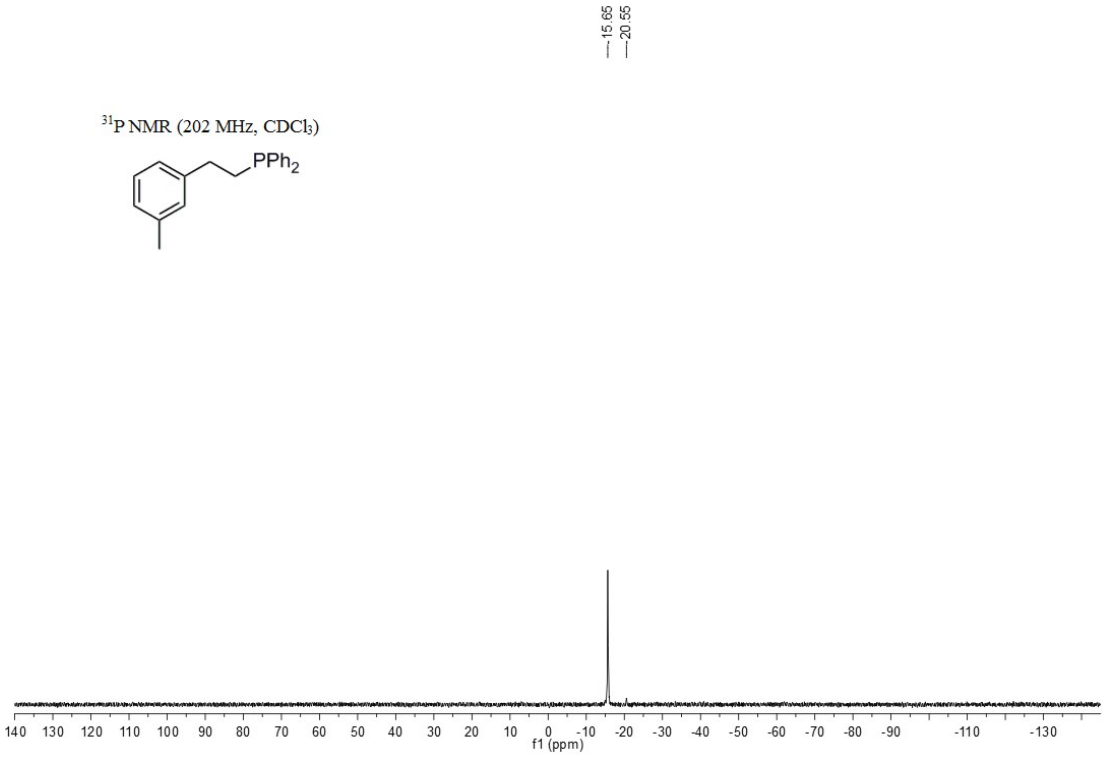


Figure S80. ^{31}P NMR spectra of **3u**

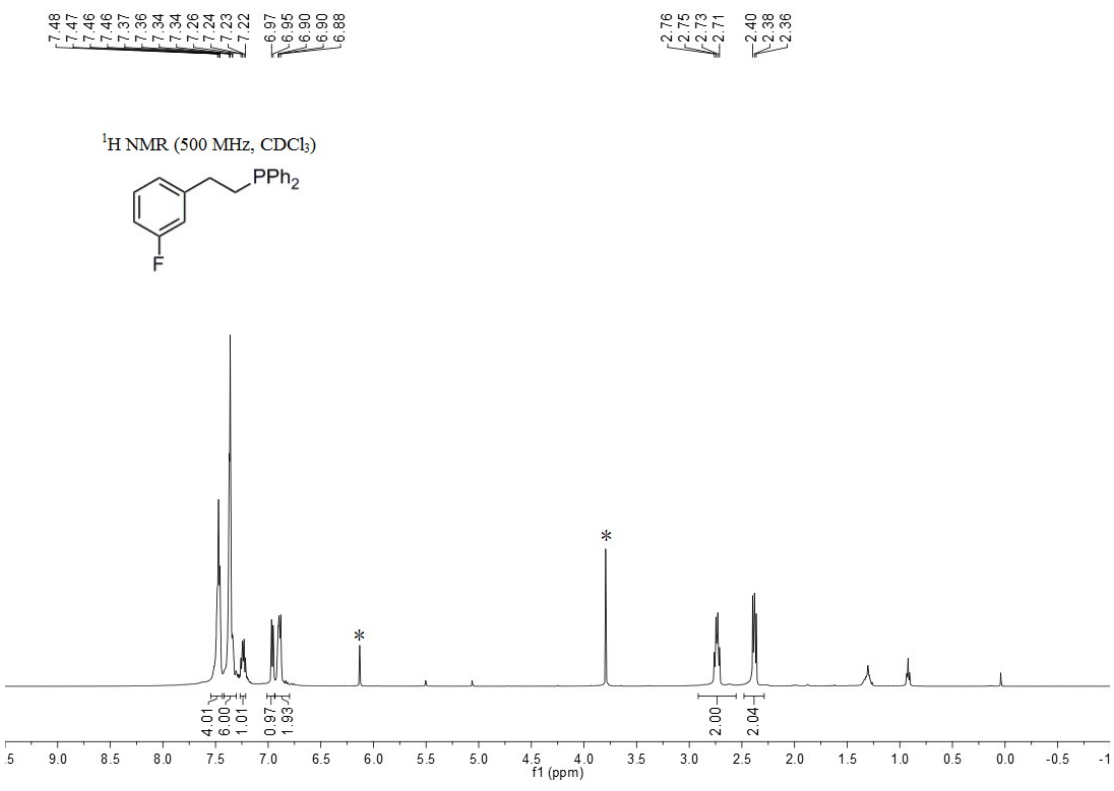


Figure S81. ^{1}H NMR spectra of **3v** (* represents 1,3,5-trimethoxybenzene)

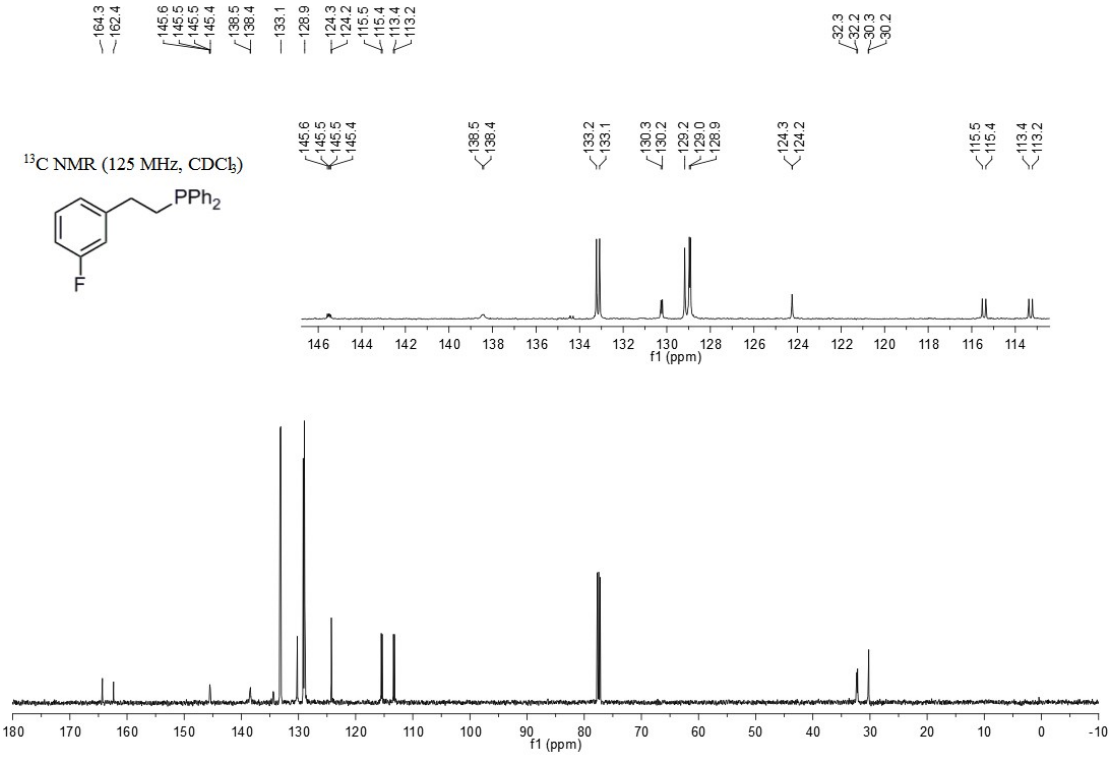


Figure S82. ^{13}C NMR spectra of **3v**

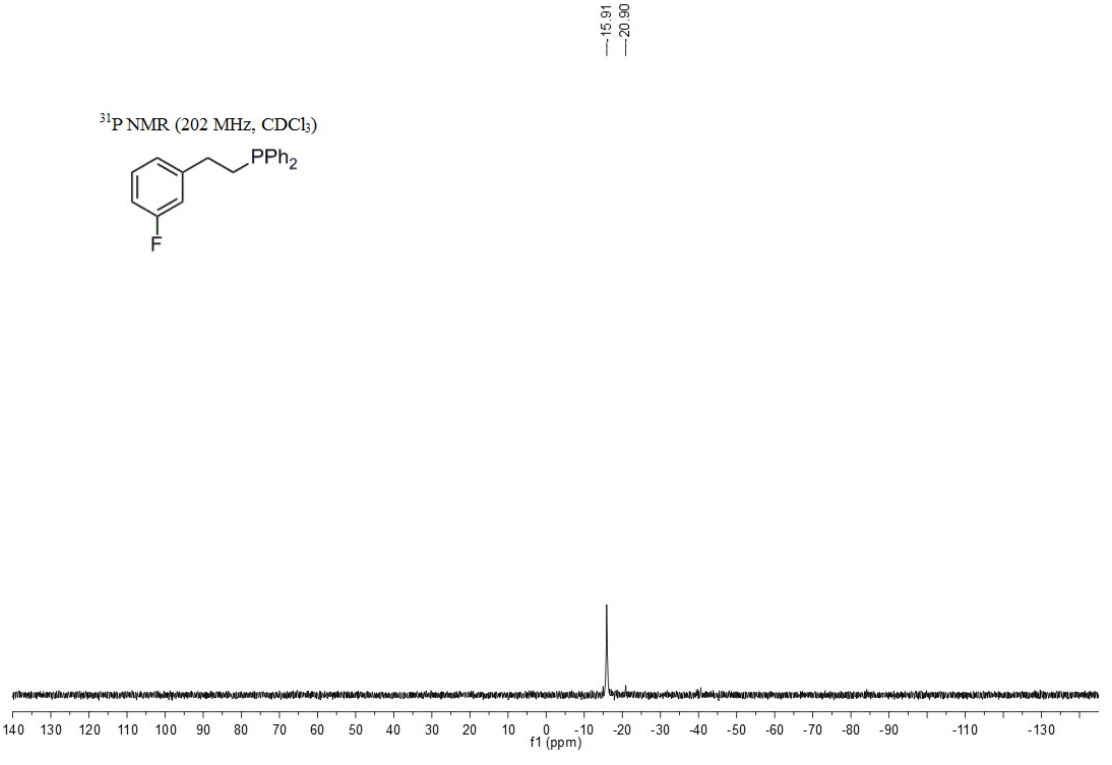


Figure S83. ^{31}P NMR spectra of **3v**

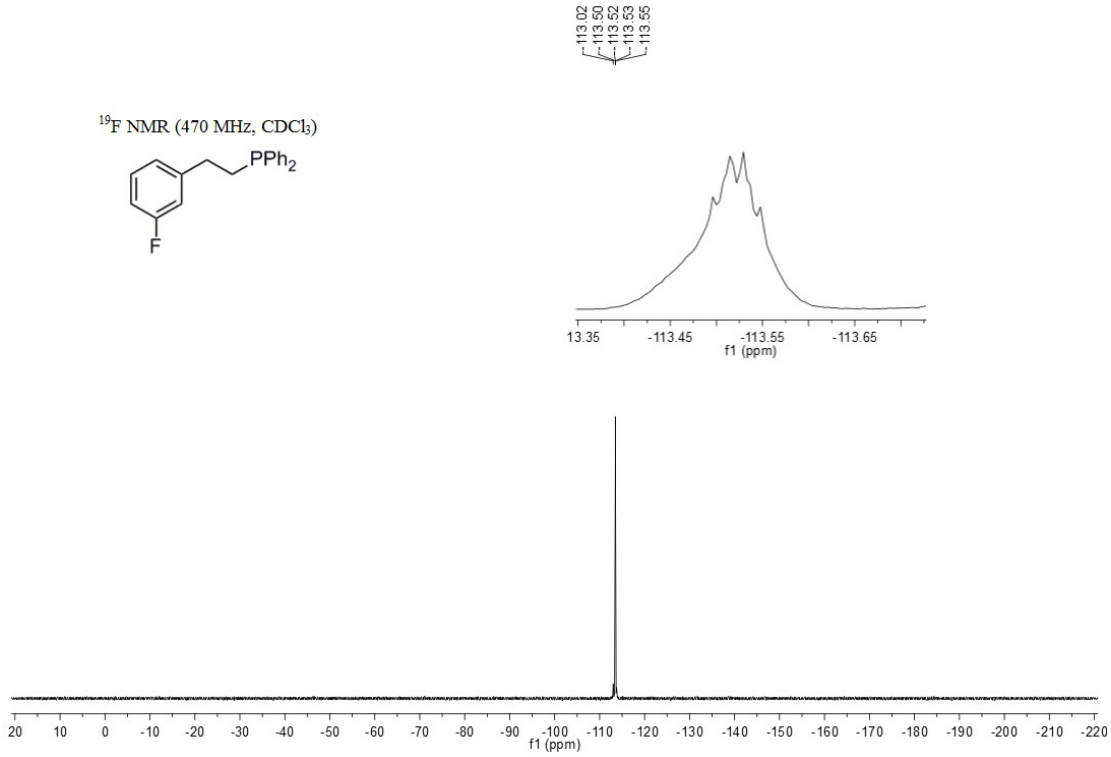


Figure S84. ^{19}F NMR spectra of **3v**

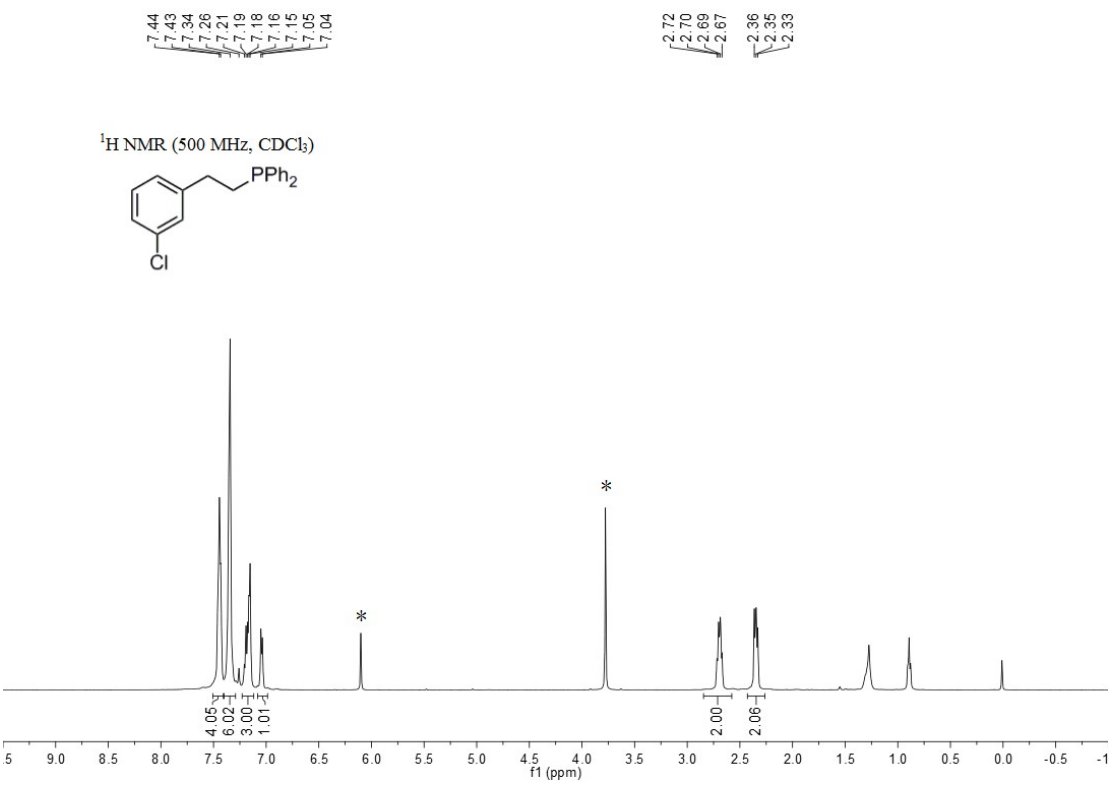


Figure S85. ^{1}H NMR spectra of **3w** (* represents 1,3,5-trimethoxybenzene)

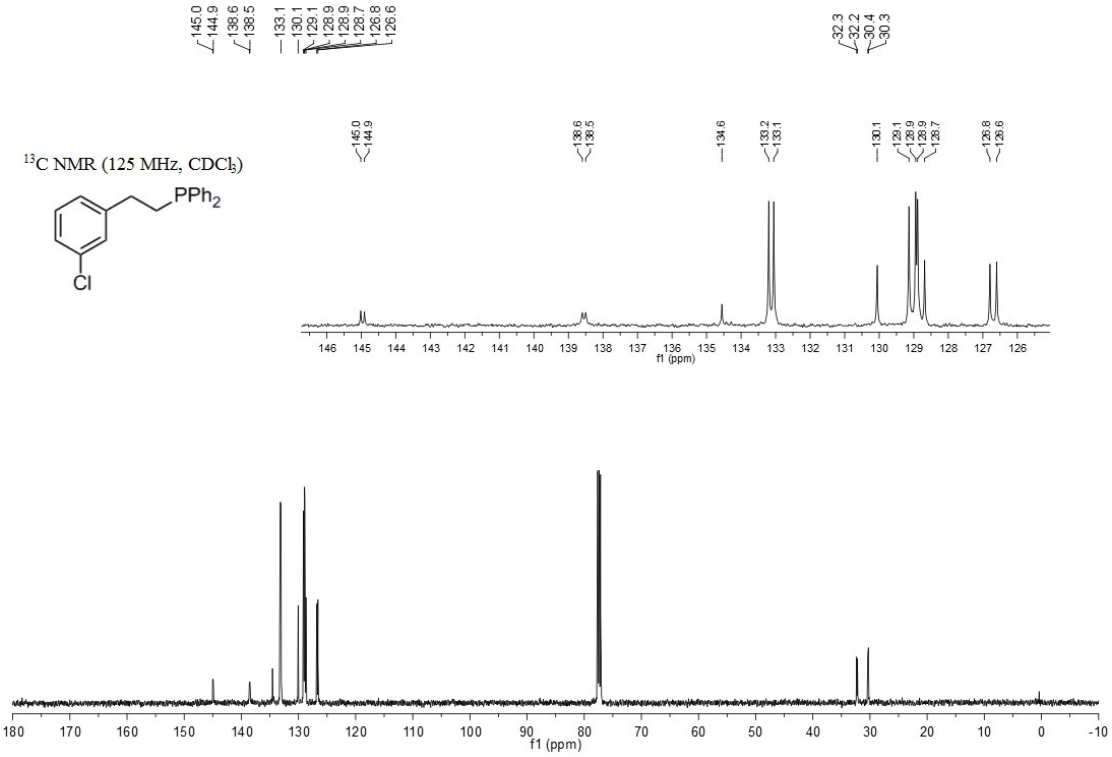


Figure S86. ^{13}C NMR spectra of **3w**

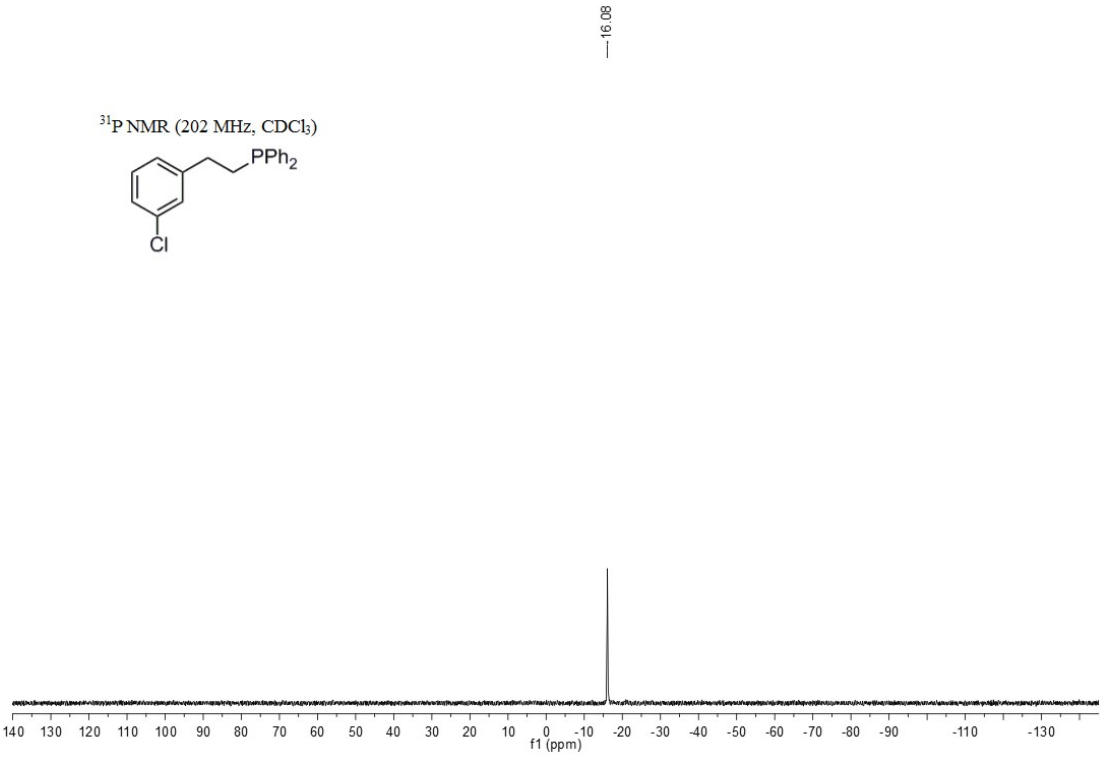


Figure S87. ^{31}P NMR spectra of **3w**

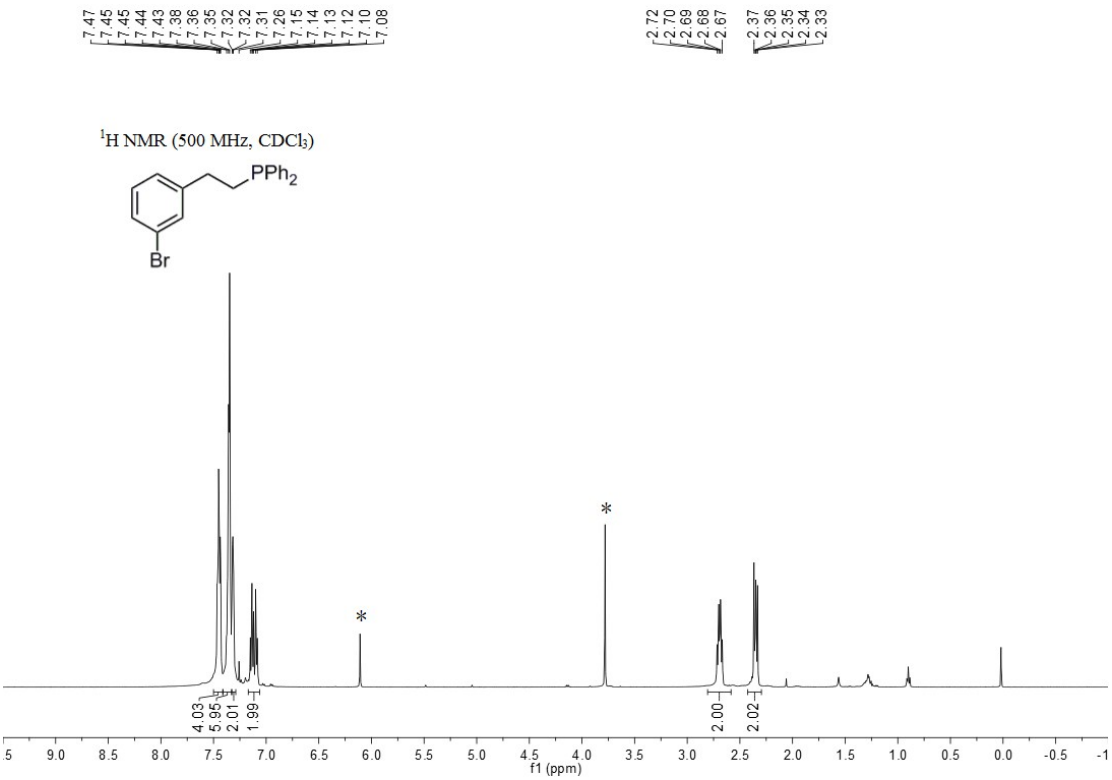


Figure S88. ^{1}H NMR spectra of **3x** (* represents 1,3,5-trimethoxybenzene)

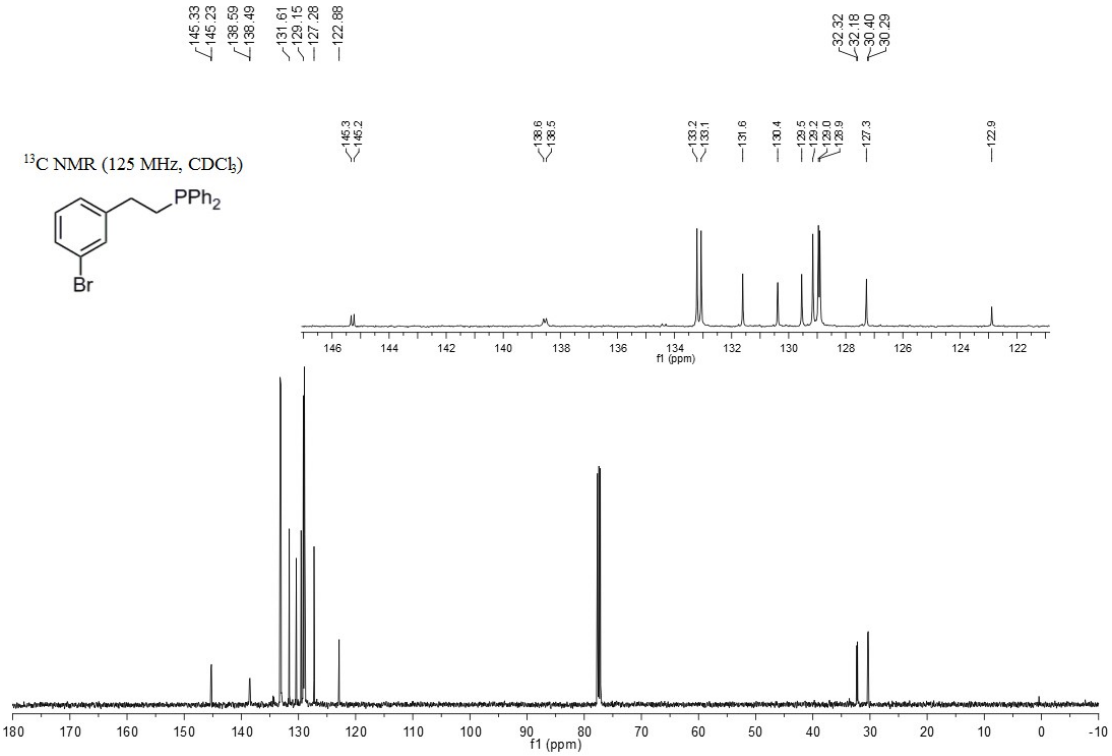


Figure S89. ^{13}C NMR spectra of **3x**

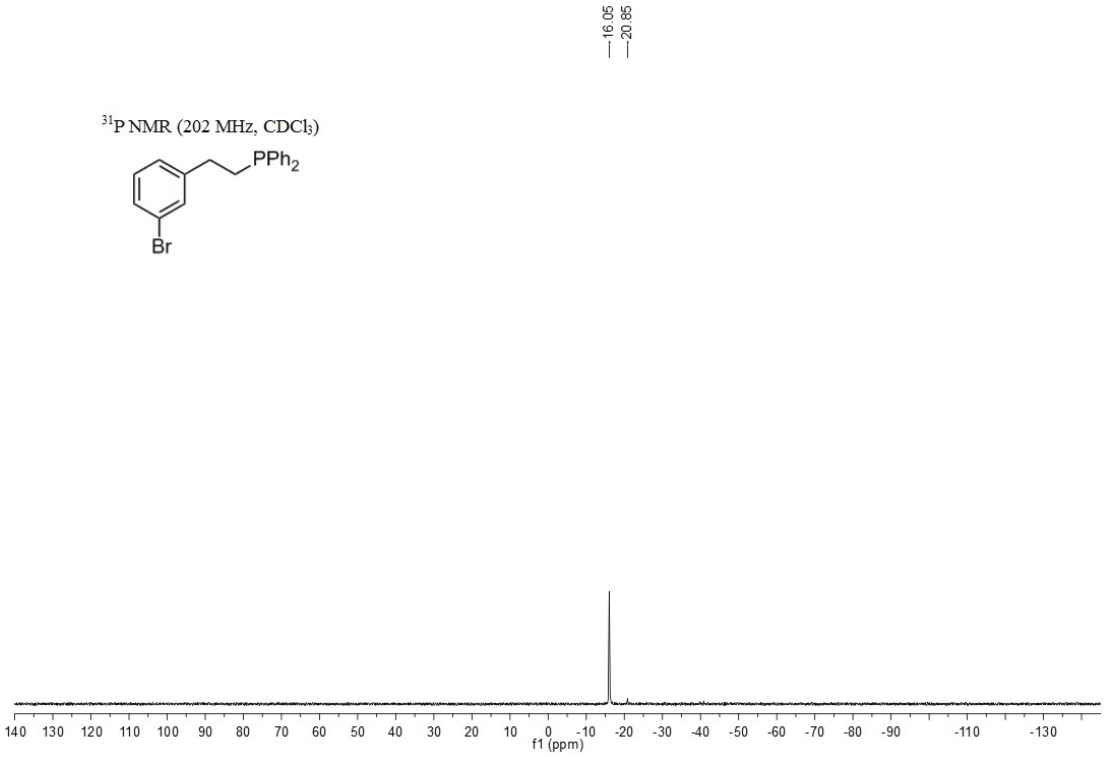


Figure S90. ^{31}P NMR spectra of **3x**

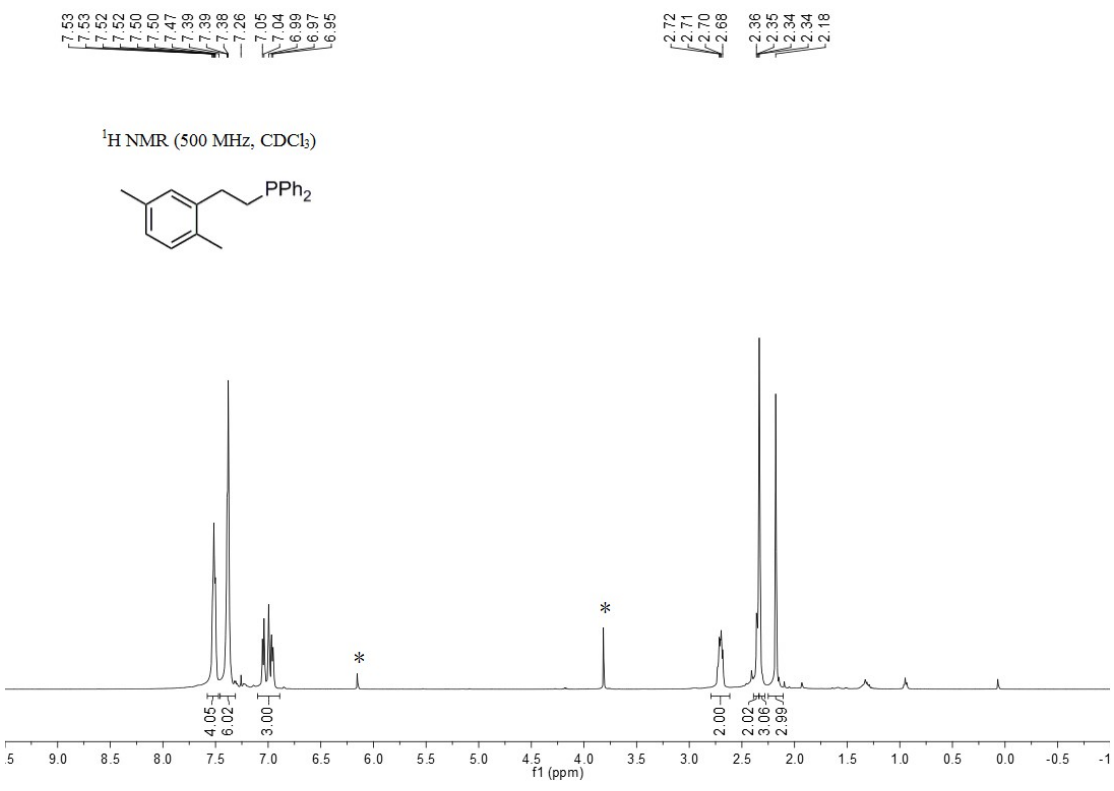


Figure S91. ^{1}H NMR spectra of **4a** (* represents 1,3,5-trimethoxybenzene)

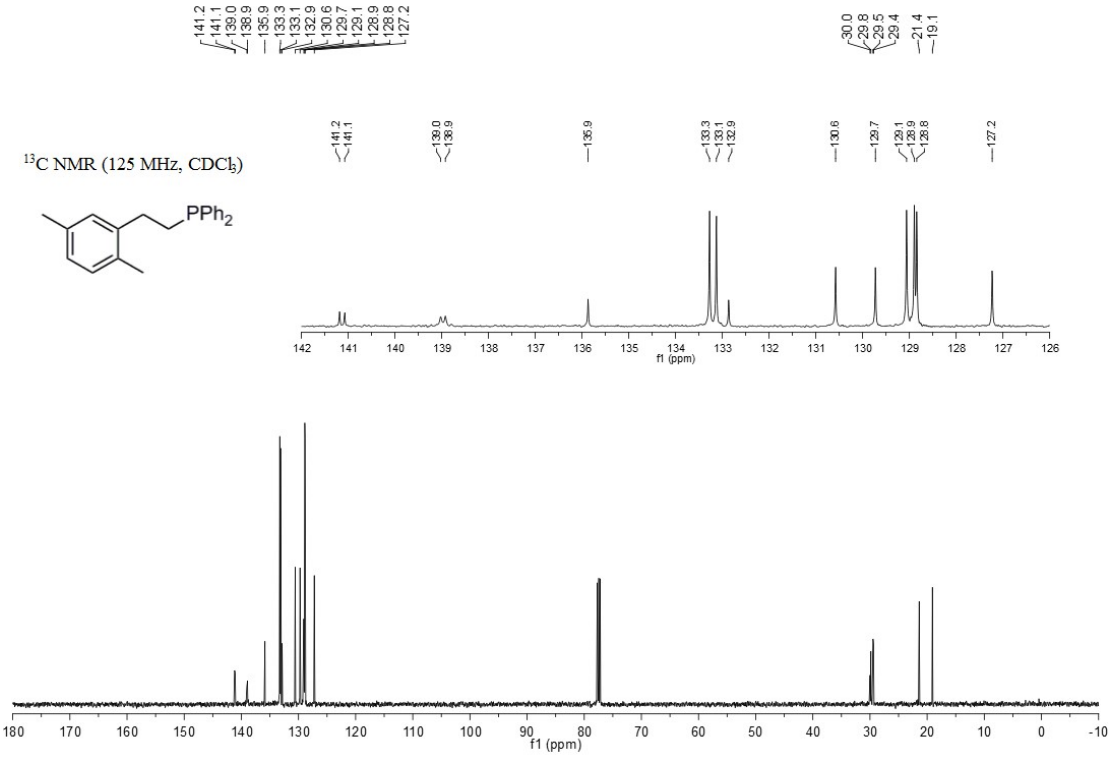


Figure S92. ^{13}C NMR spectra of **4a**

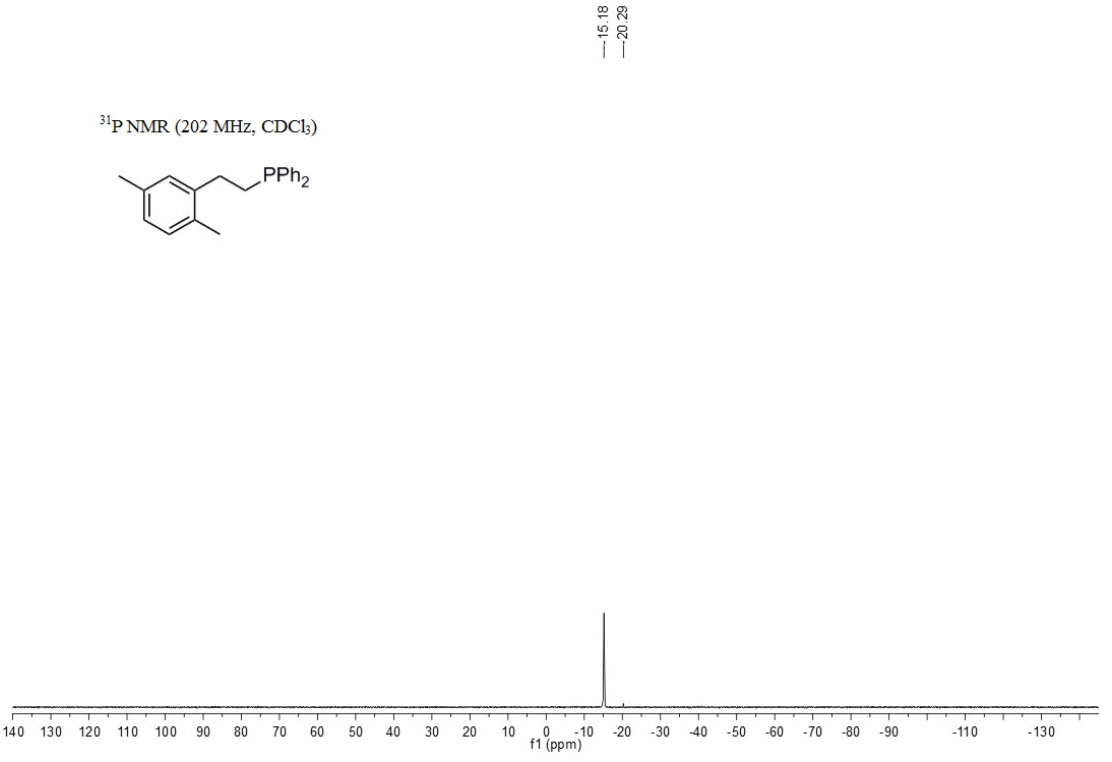


Figure S93. ^{31}P NMR spectra of **4a**

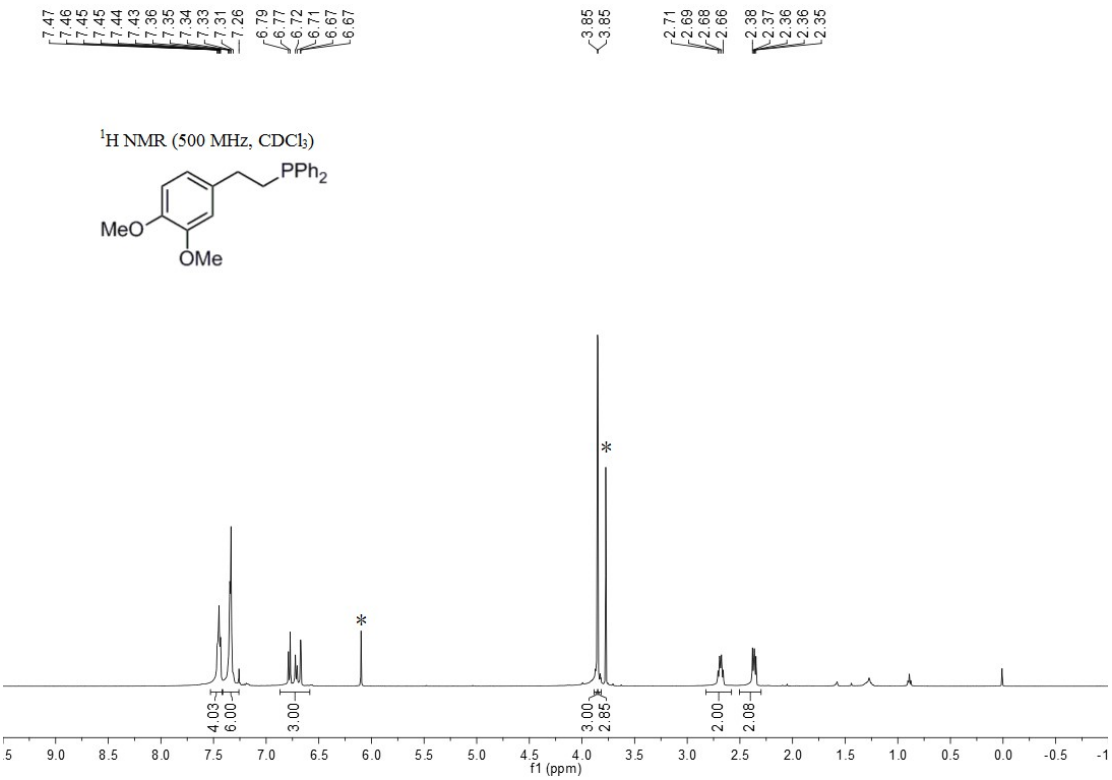


Figure S94. ^{1}H NMR spectra of **4b** (* represents 1,3,5-trimethoxybenzene)

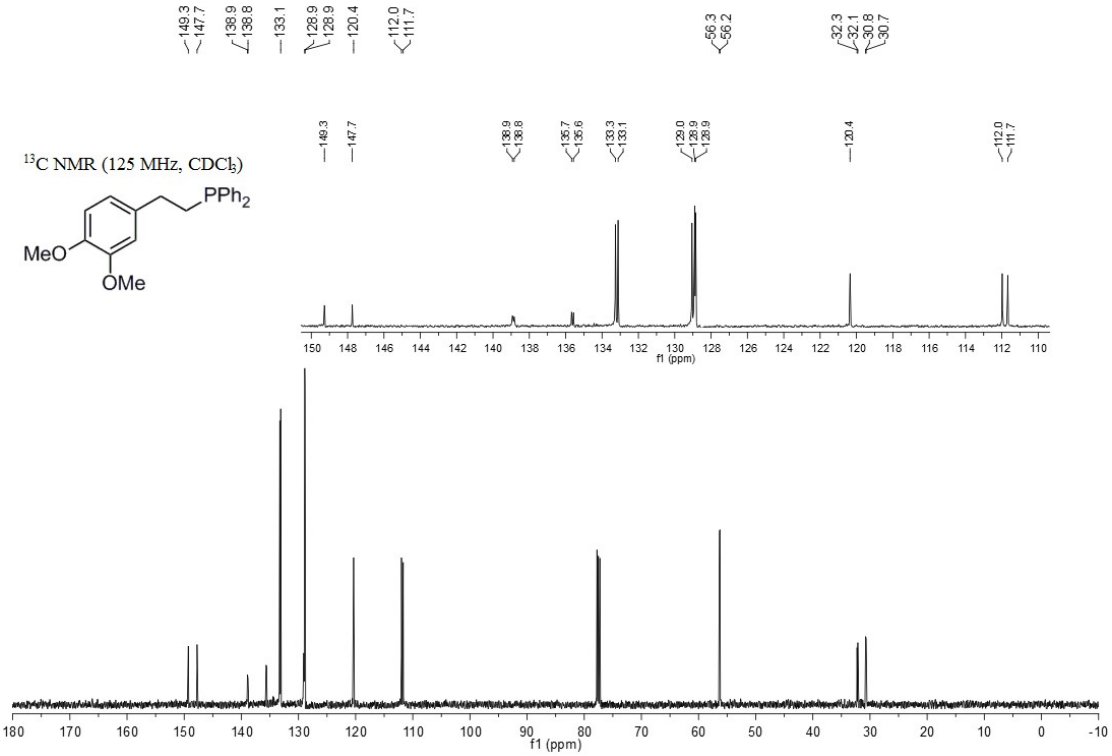


Figure S95. ^{13}C NMR spectra of**4b**

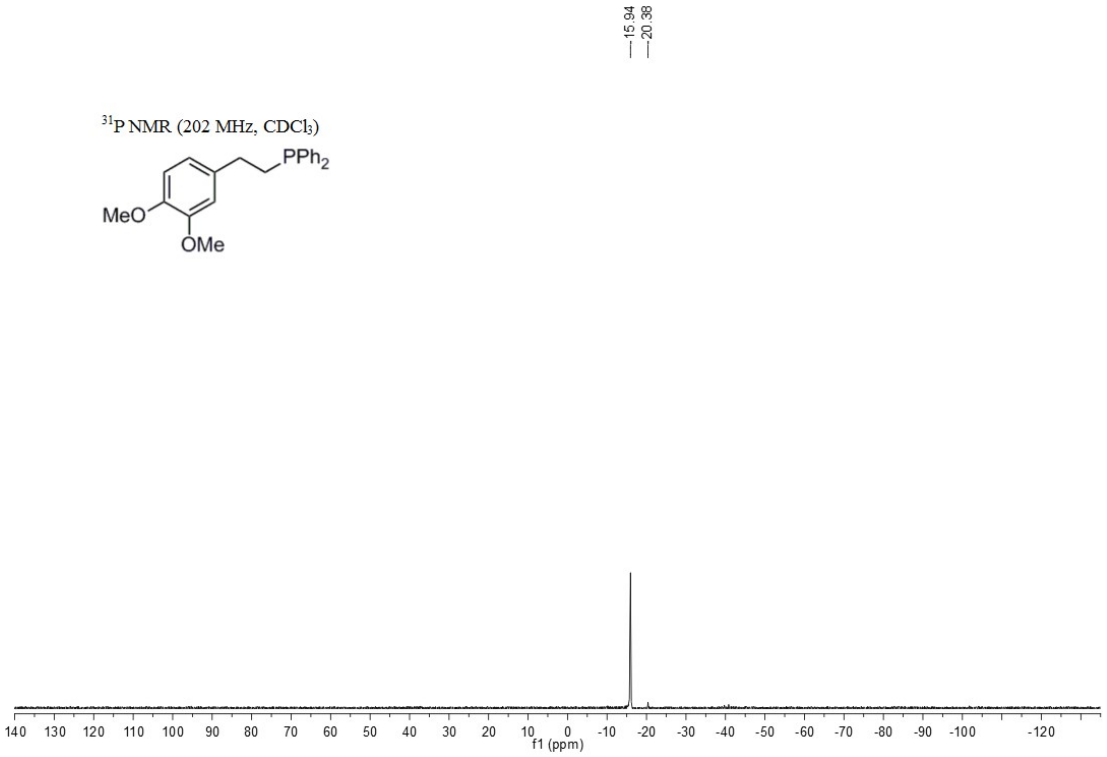


Figure S96. ^{31}P NMR spectra of **4b**

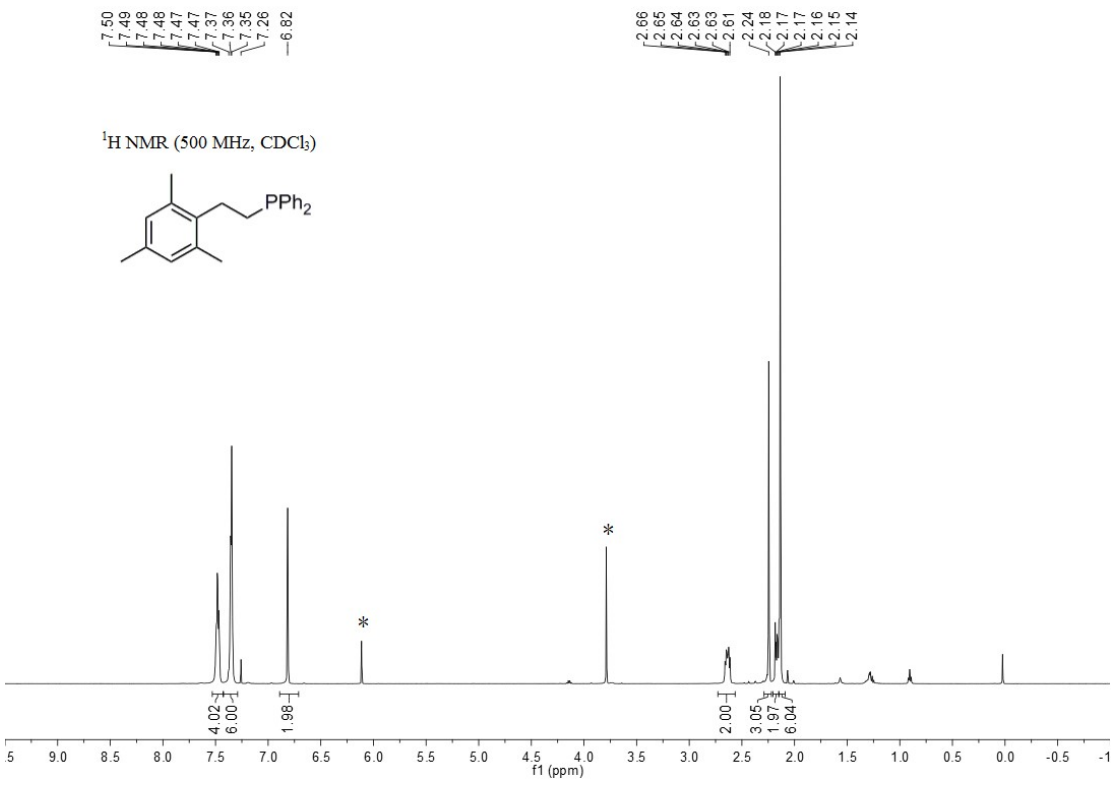


Figure S97. ^{1}H NMR spectra of **4c** (* represents 1,3,5-trimethoxybenzene)

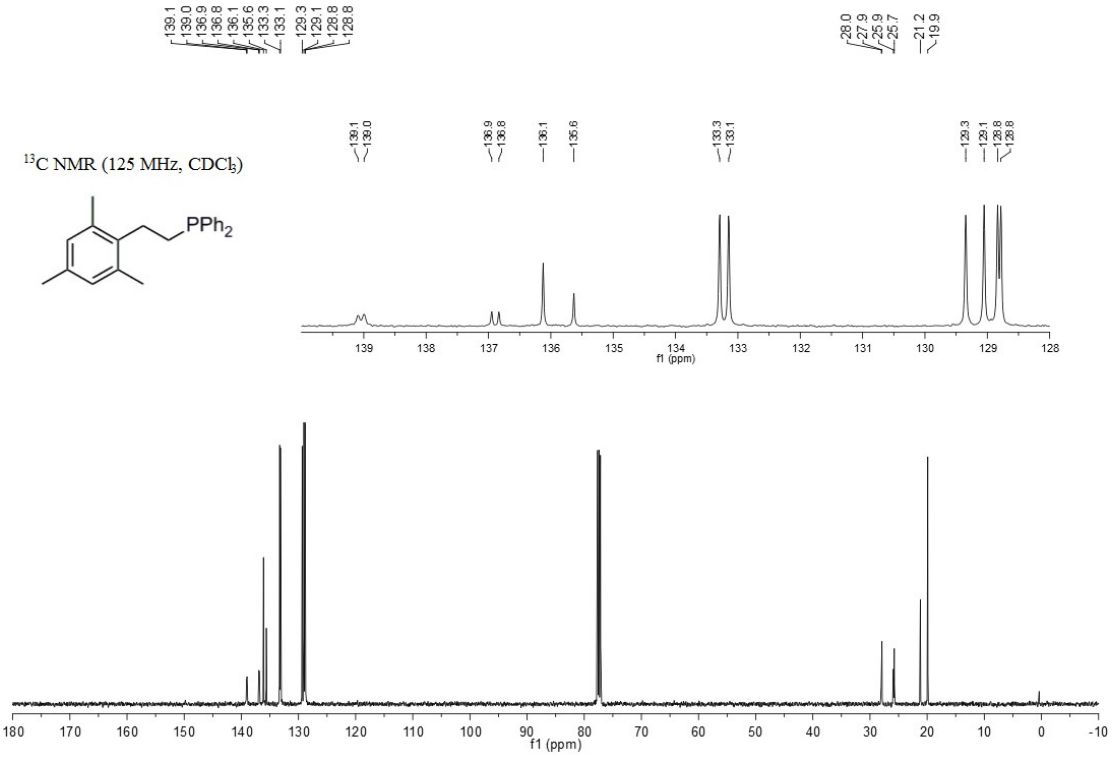


Figure S98. ^{13}C NMR spectra of **4c**

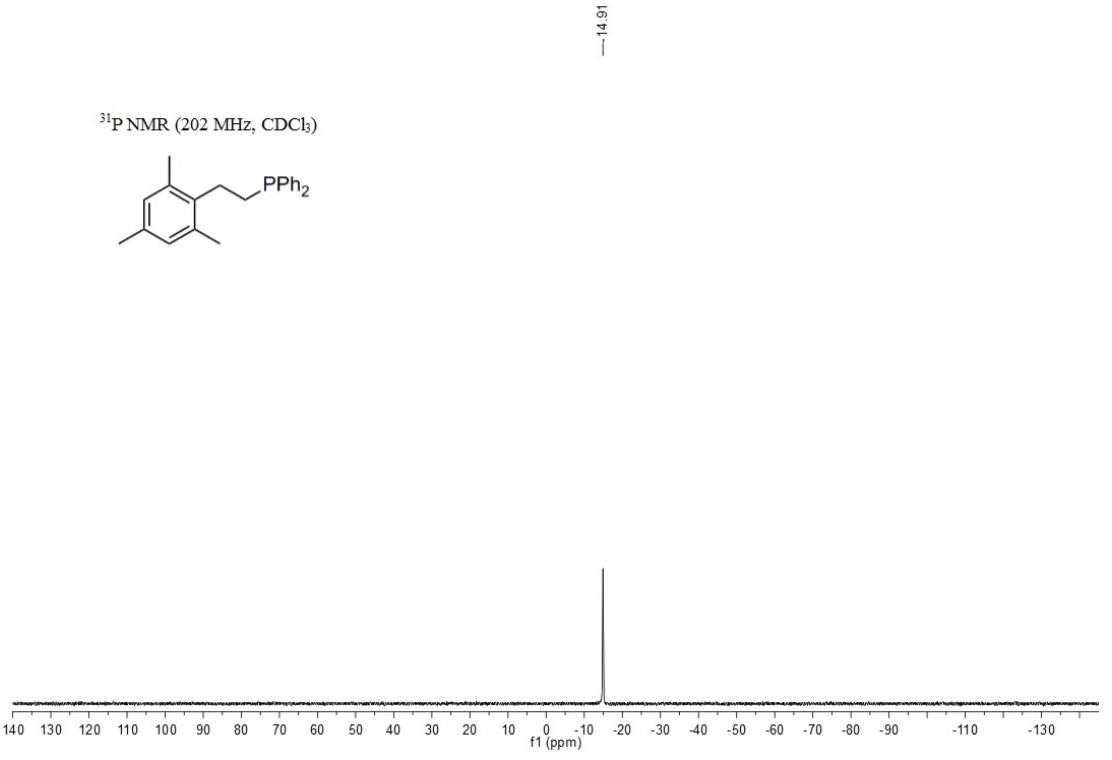


Figure S99. ^{31}P NMR spectra of **4c**

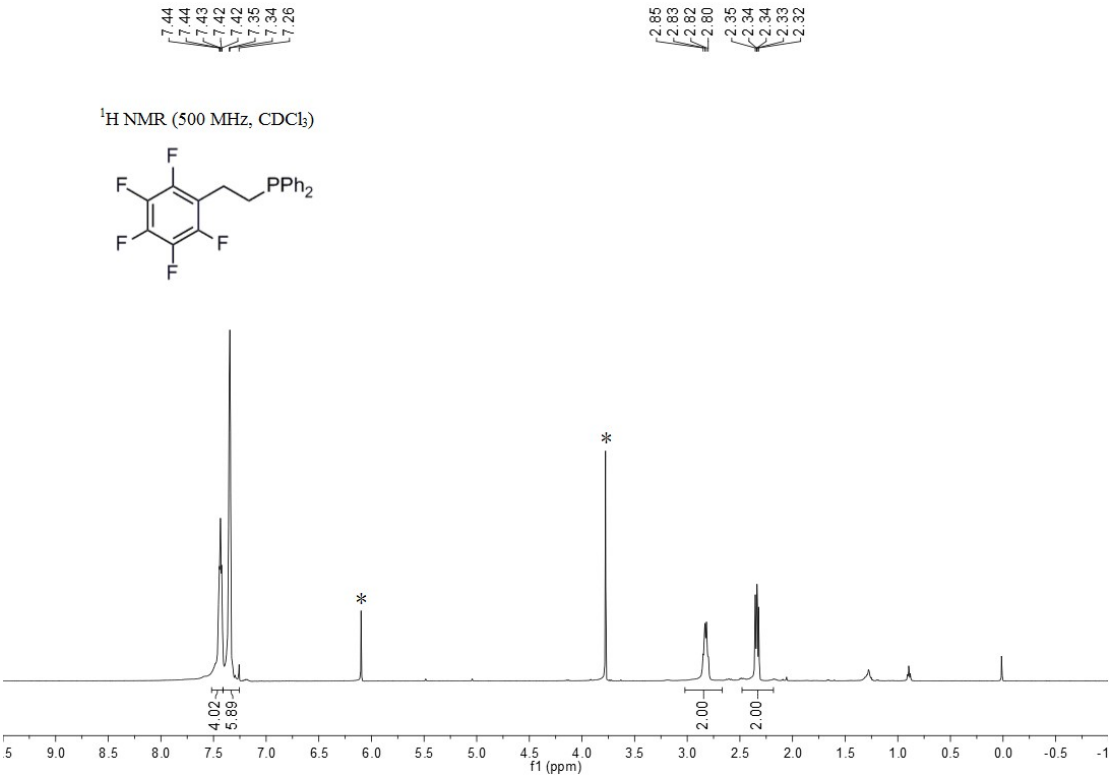


Figure S100. ^{1}H NMR spectra of **4d** (* represents 1,3,5-trimethoxybenzene)

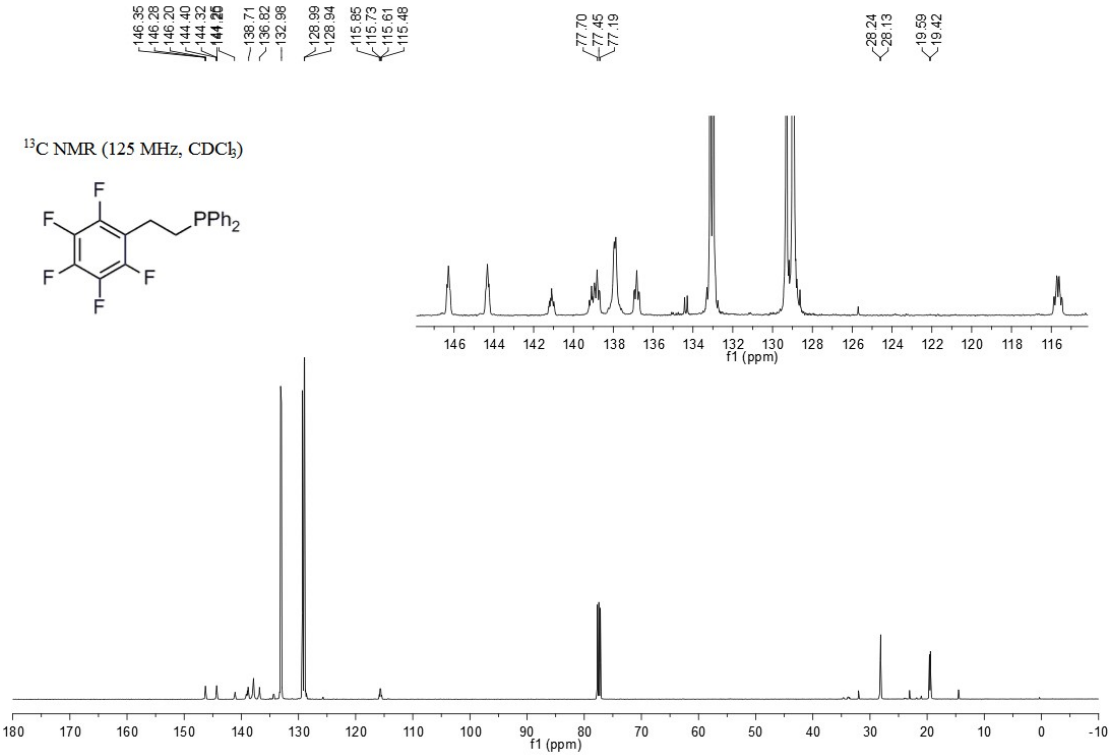


Figure S101. ^{13}C NMR spectra of **4d**

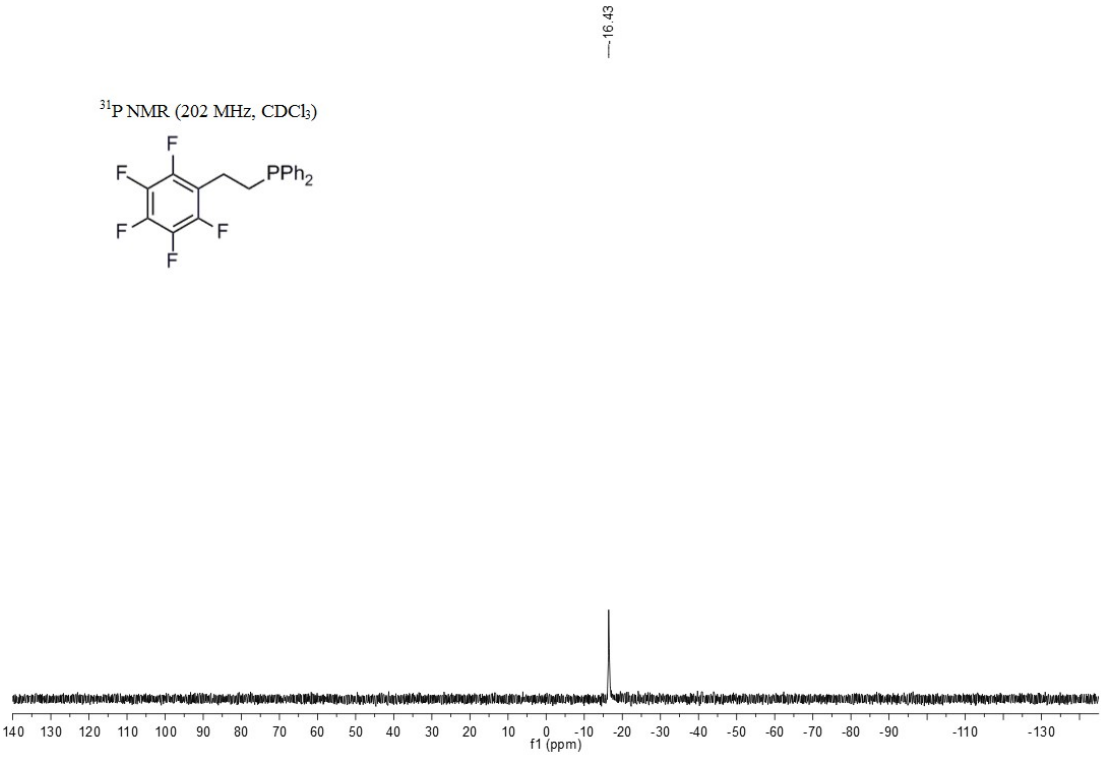


Figure S102. ^{31}P NMR spectra of **4d**

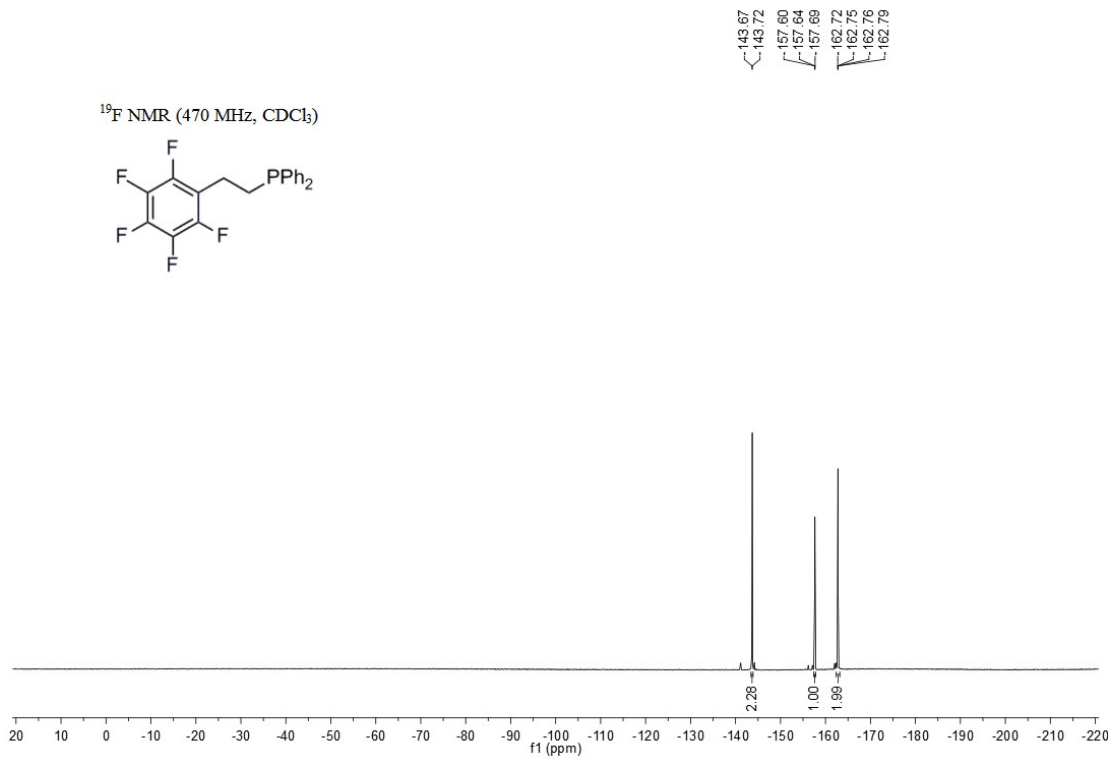


Figure S103. ^{19}F NMR spectra of **4d**

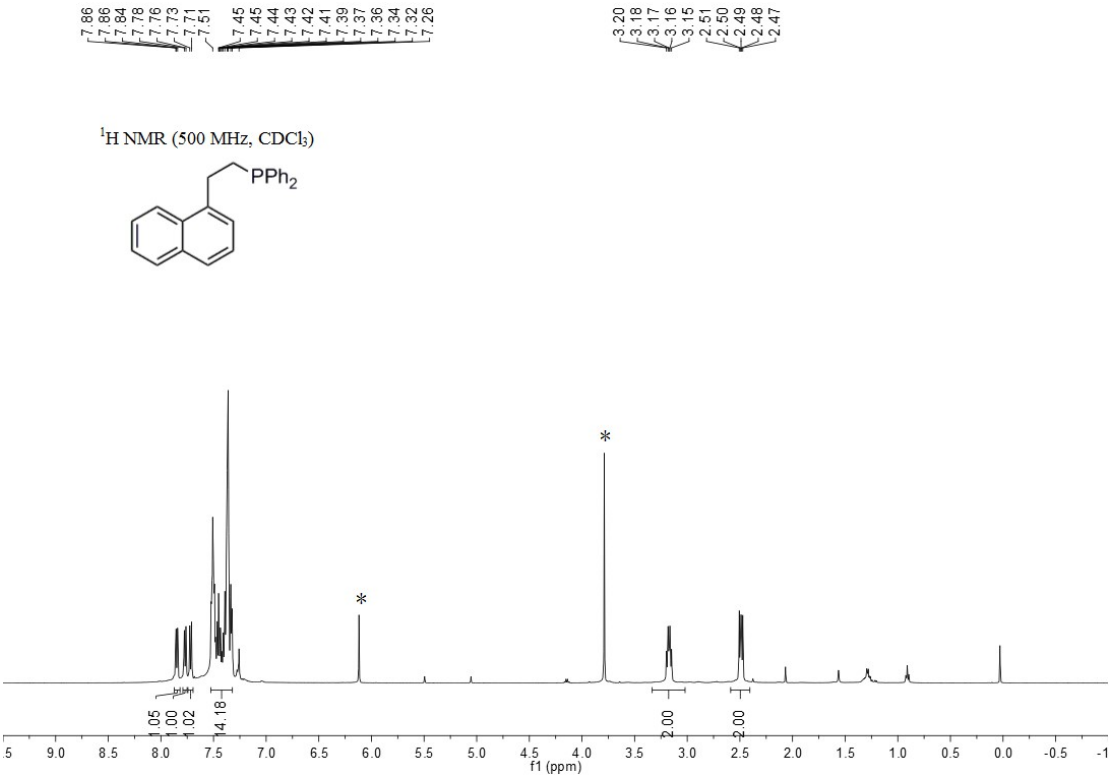


Figure S104. ^{1}H NMR spectra of **4e** (* represents 1,3,5-trimethoxybenzene)

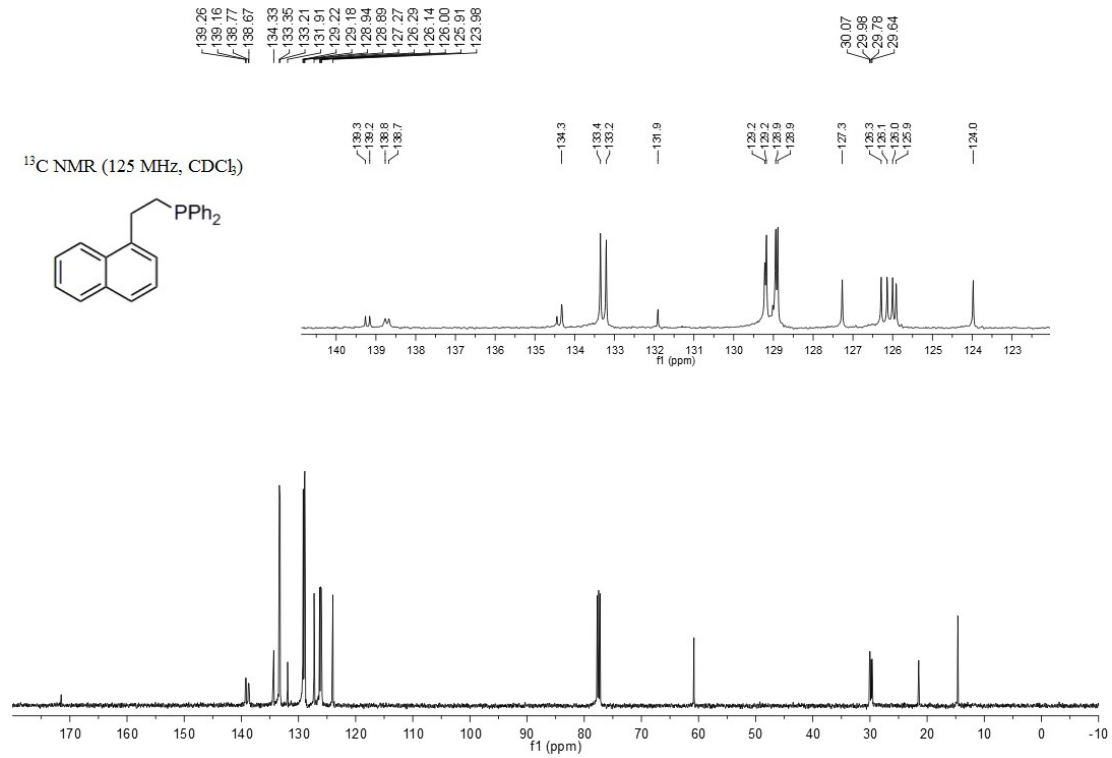


Figure S105. ^{13}C NMR spectra of **4e**

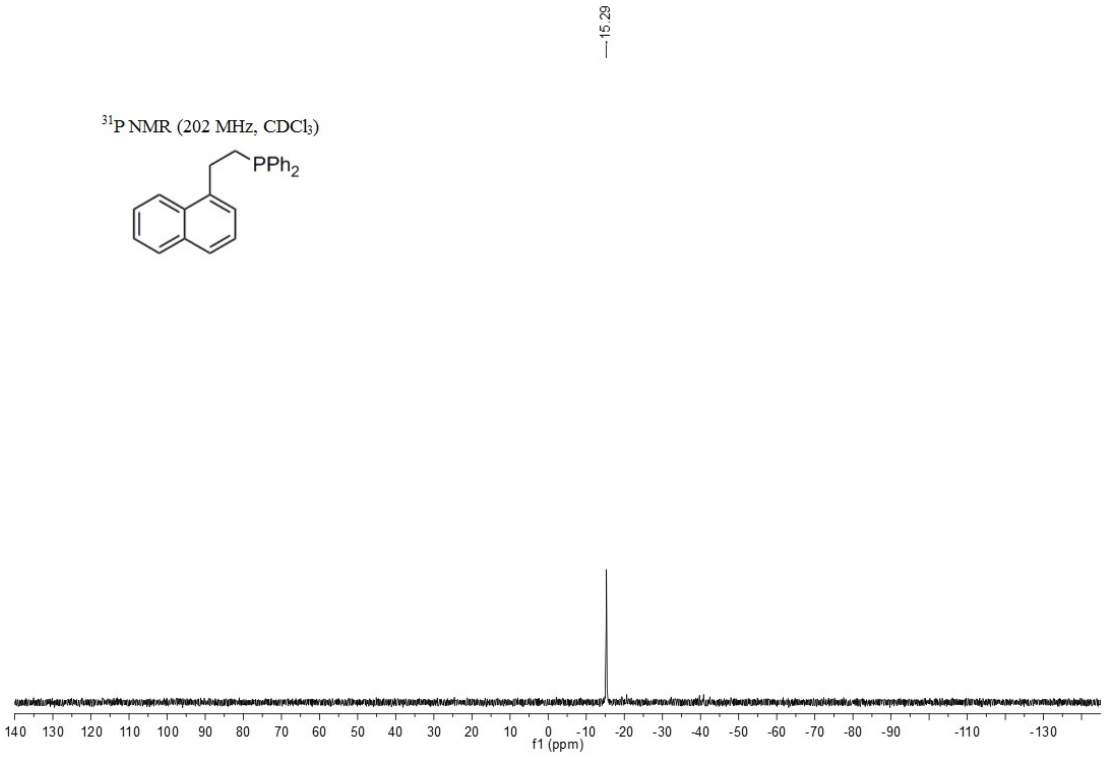


Figure S106. ^{31}P NMR spectra of **4e**

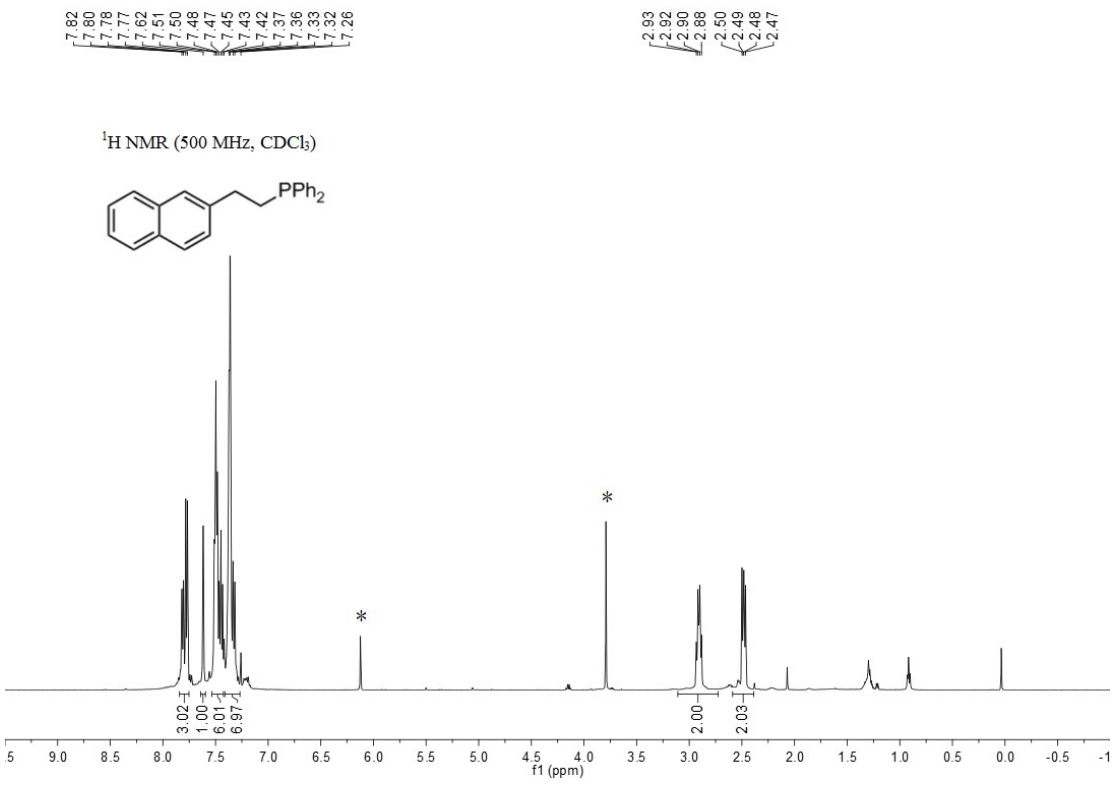


Figure S107. ^{1}H NMR spectra of **4f** (* represents 1,3,5-trimethoxybenzene)

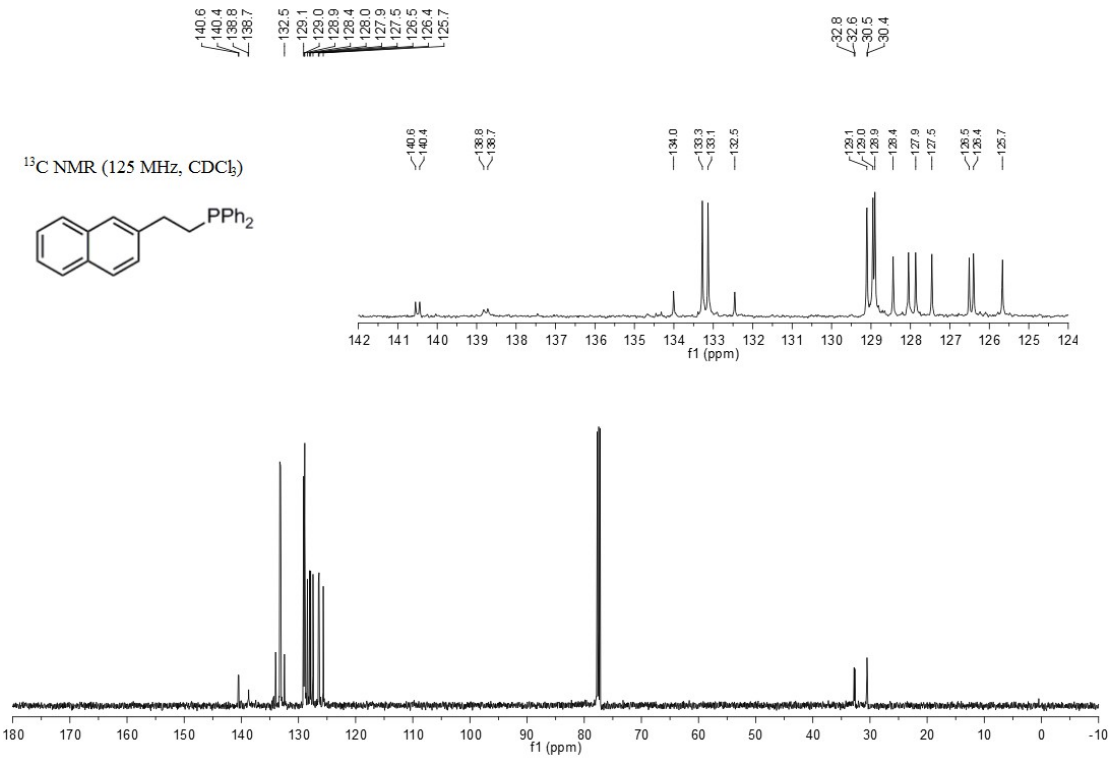


Figure S108. ^{13}C NMR spectra of **4f**

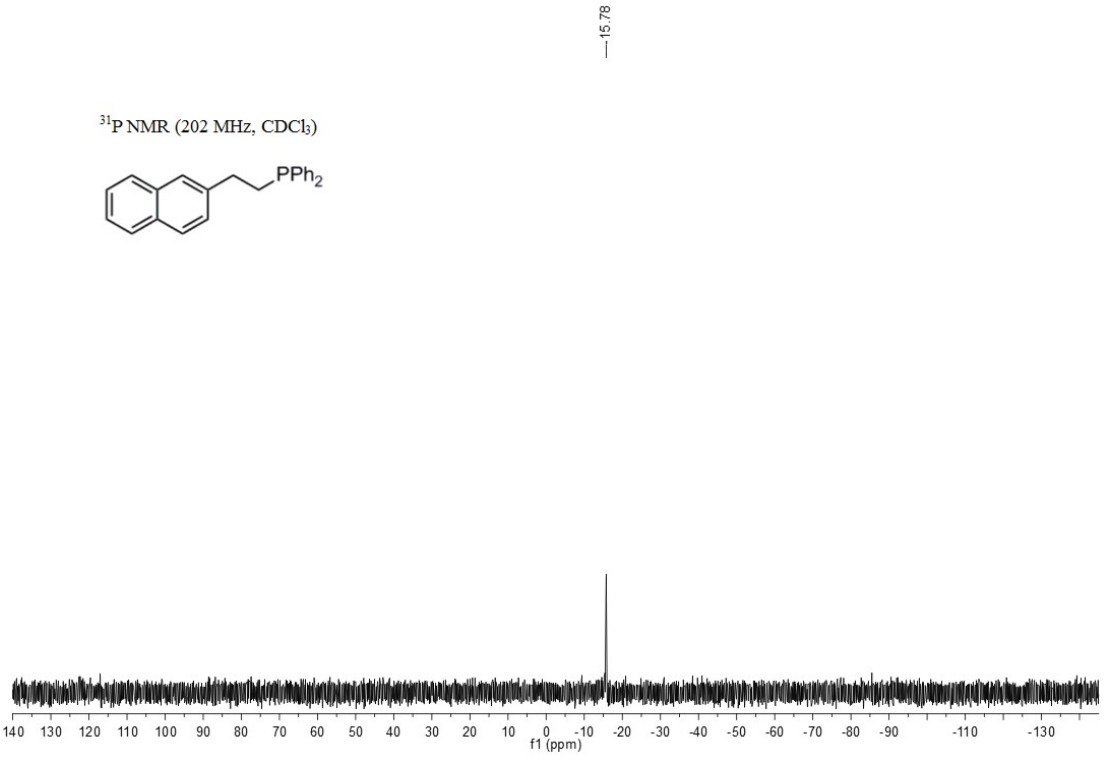


Figure S109. ^{31}P NMR spectra of **4f**

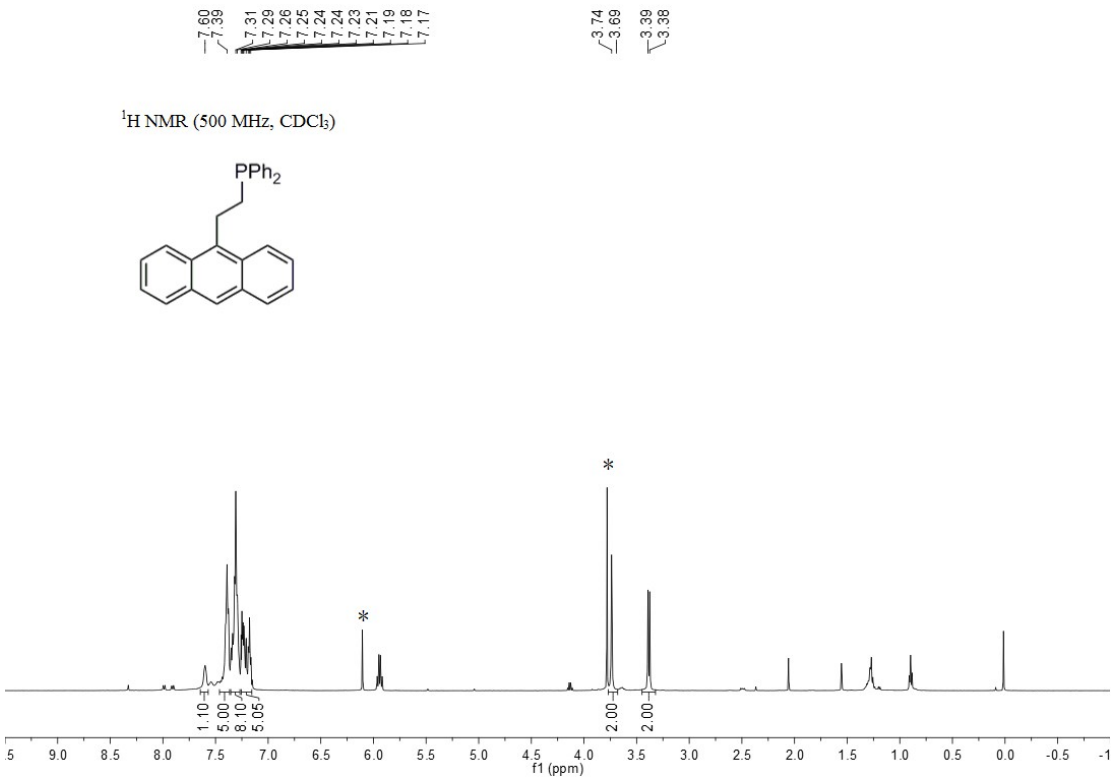


Figure S110. ^{1}H NMR spectra of **4g** (* represents 1,3,5-trimethoxybenzene)

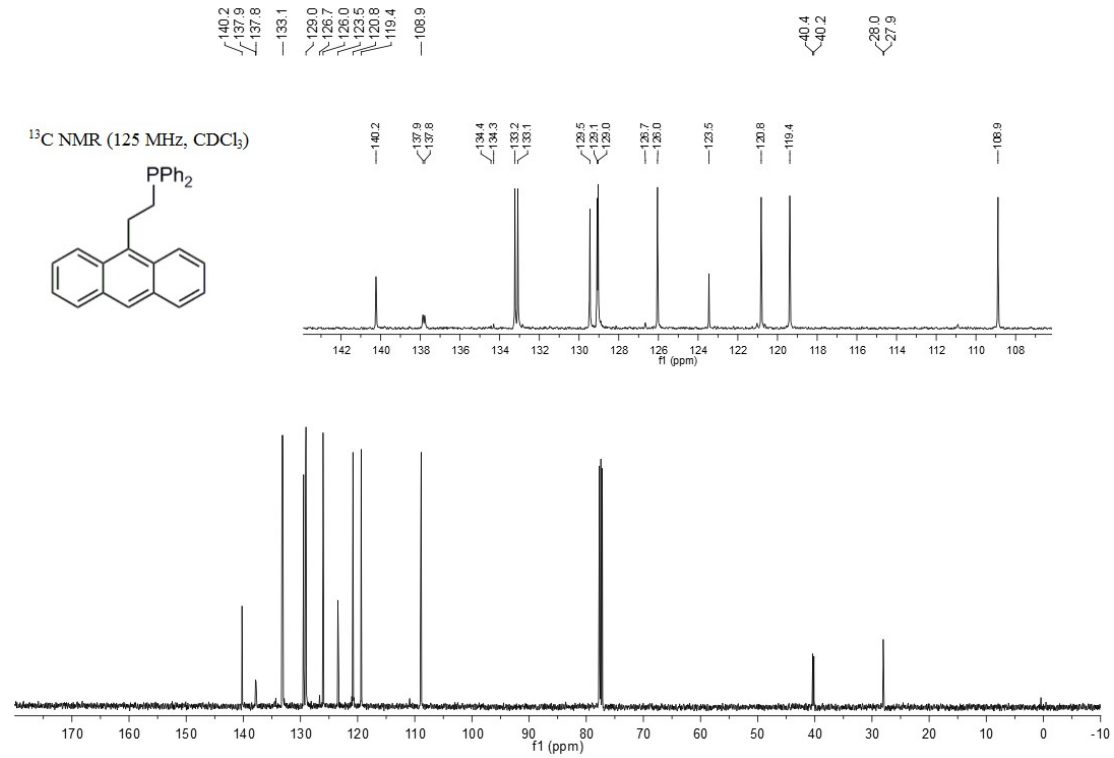


Figure S111. ^{13}C NMR spectra of **4g**

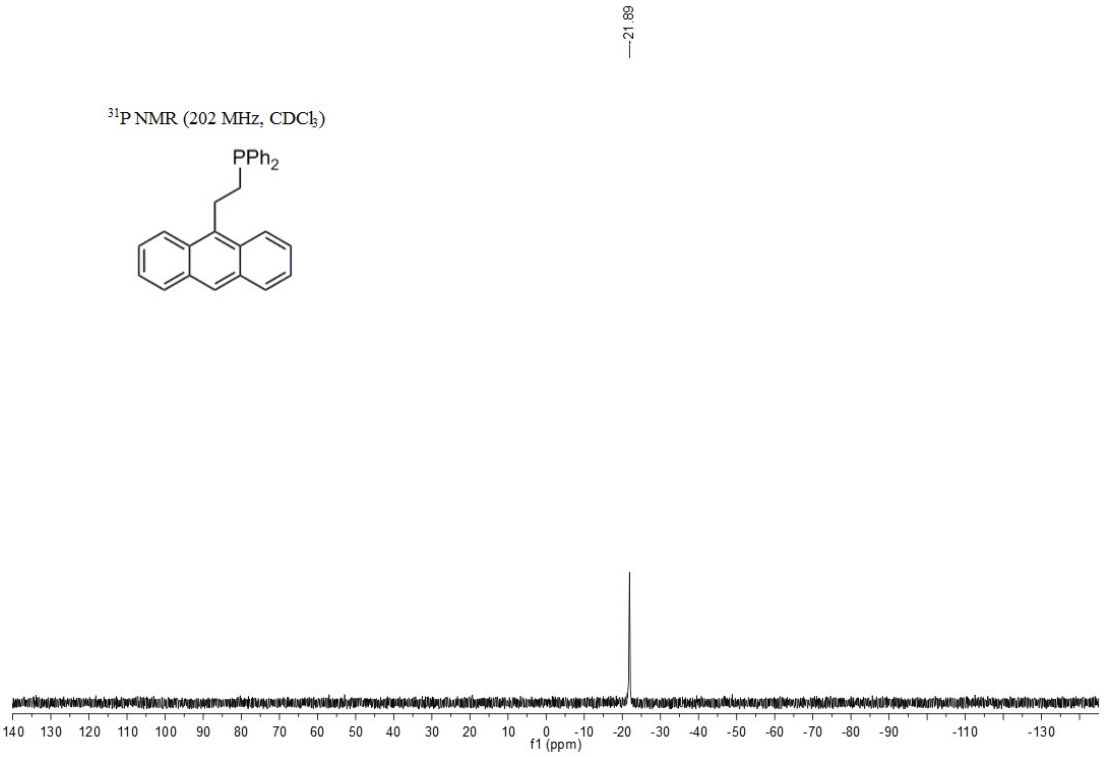


Figure S112. ^{31}P NMR spectra of **4g**

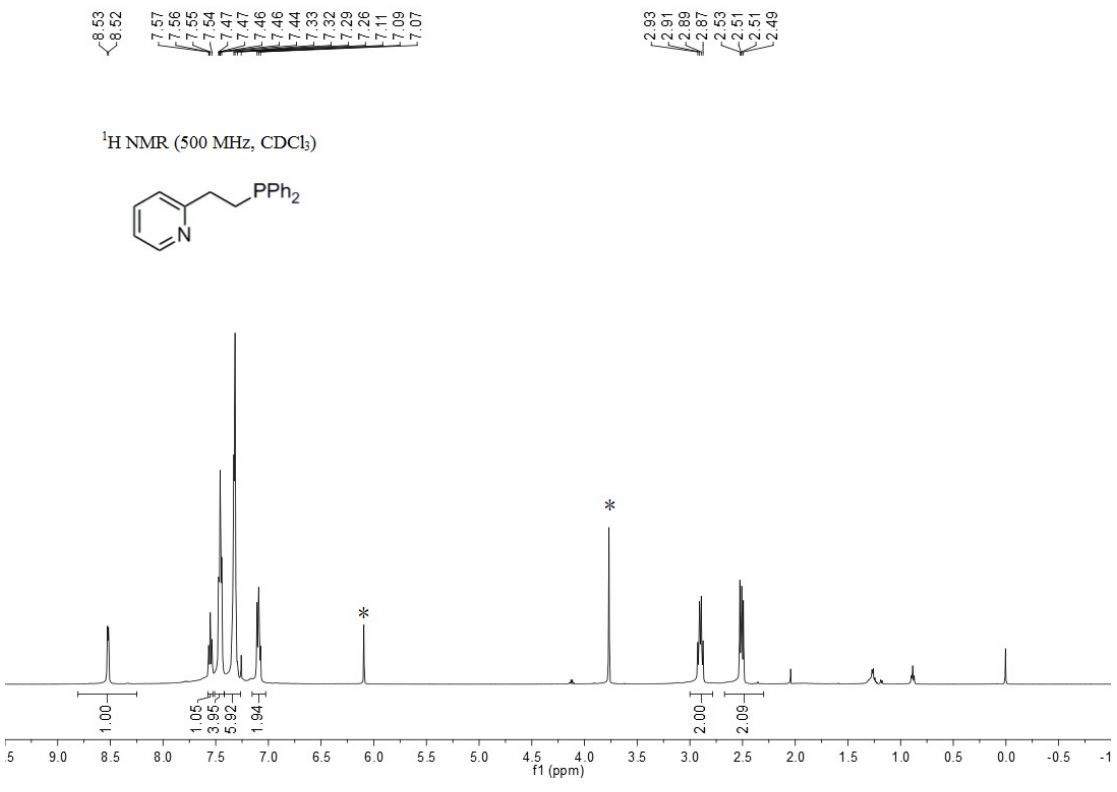


Figure S113. ^{1}H NMR spectra of **4h** (* represents 1,3,5-trimethoxybenzene)

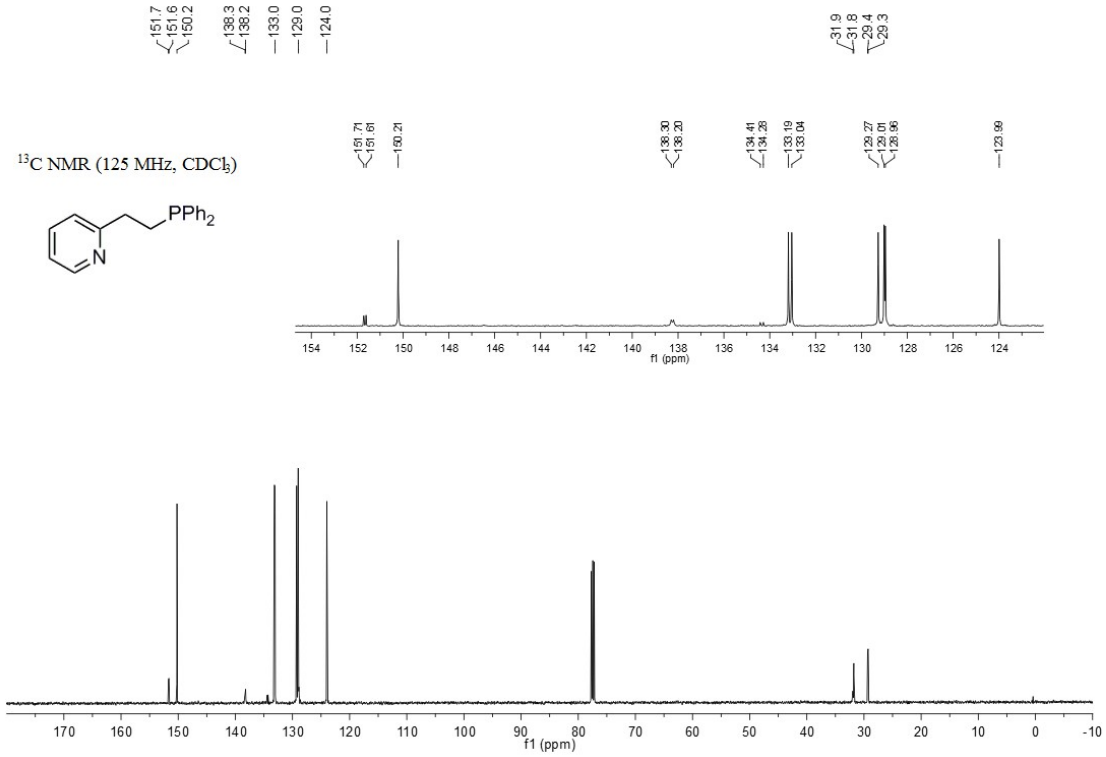


Figure S114. ^{13}C NMR spectra of **4h**

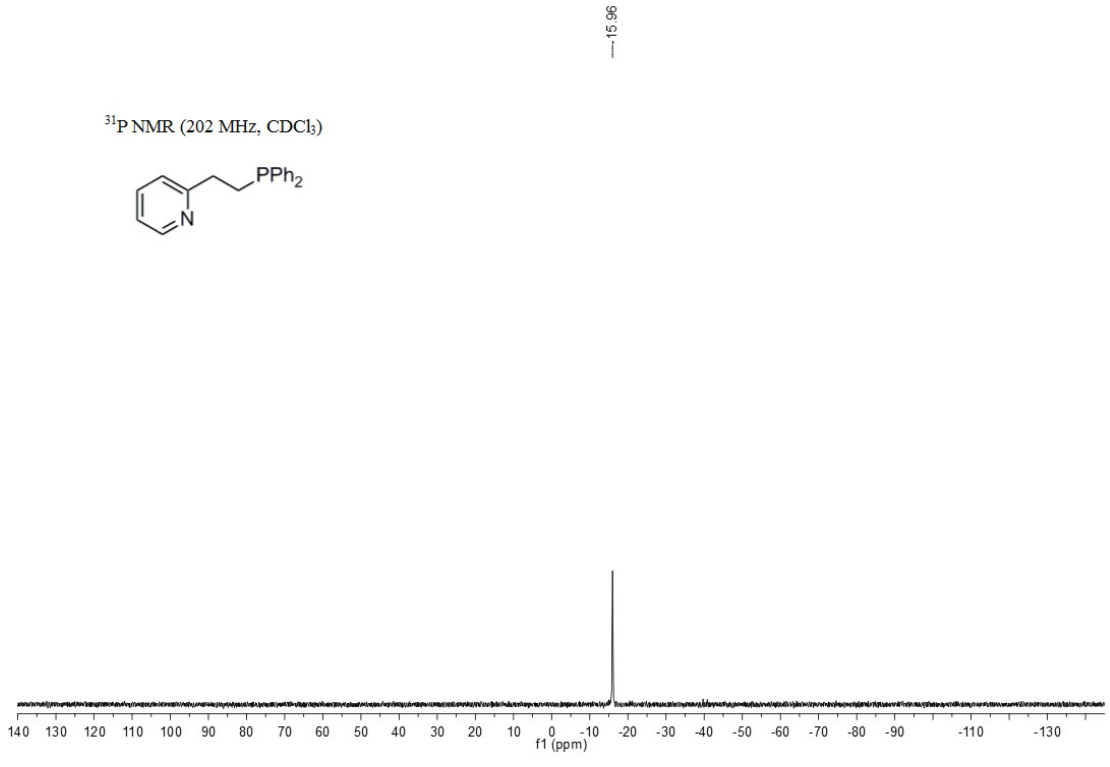


Figure S115. ^{31}P NMR spectra of **4h**

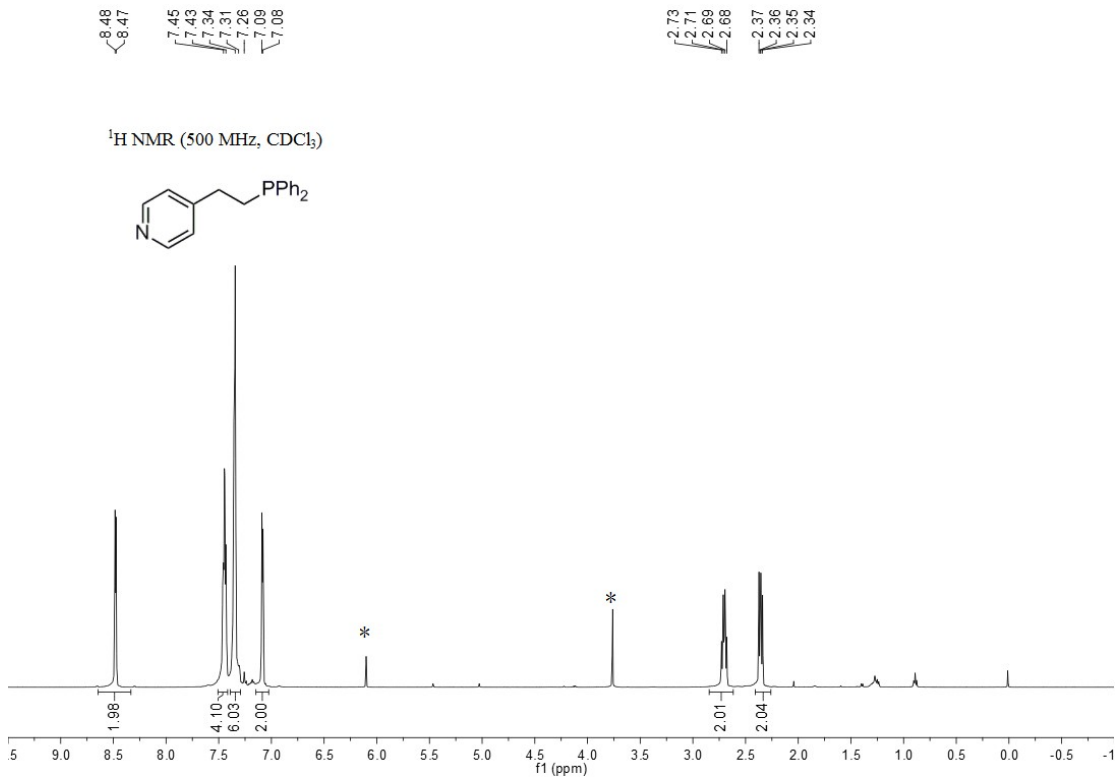


Figure S116. ^{1}H NMR spectra of **4i** (* represents 1,3,5-trimethoxybenzene)

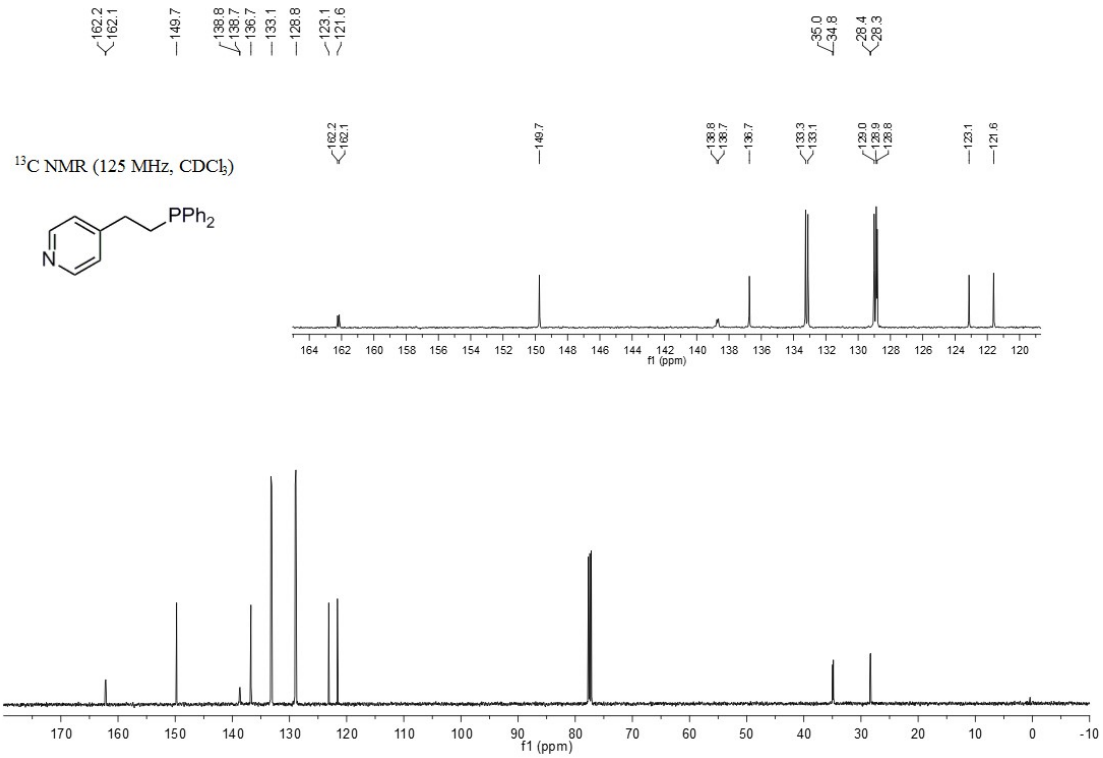


Figure S117. ^{13}C NMR spectra of **4i**

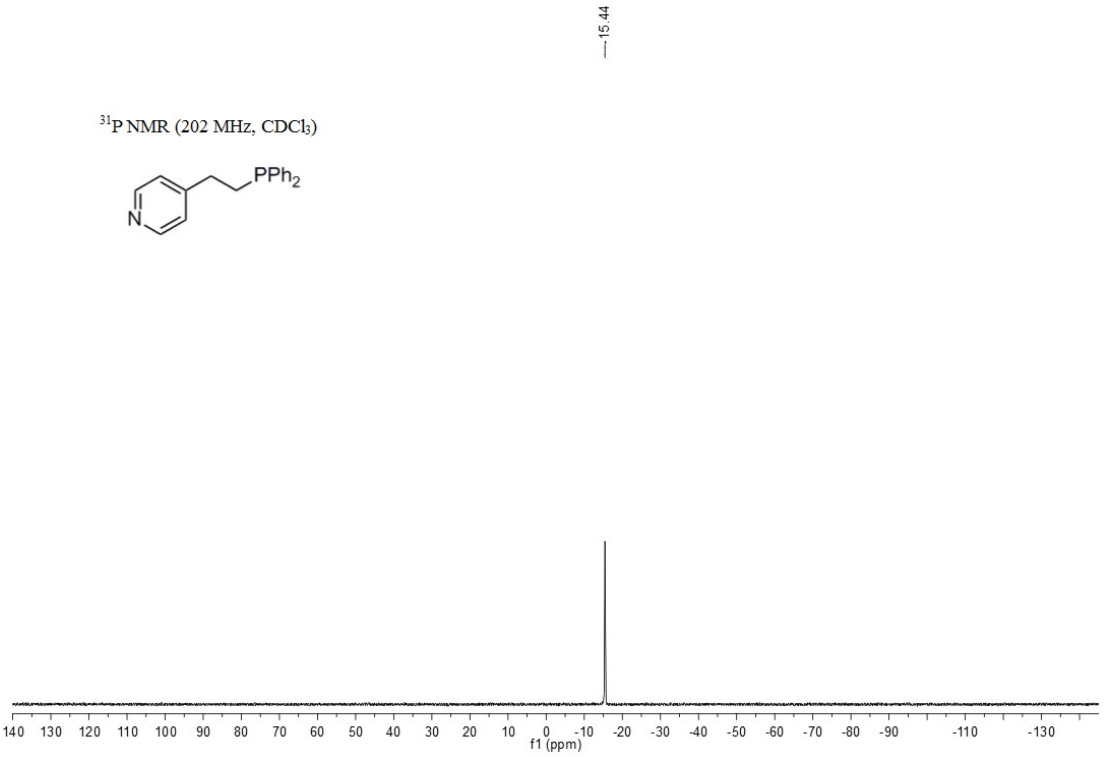


Figure S118. ^{31}P NMR spectra of **4i**

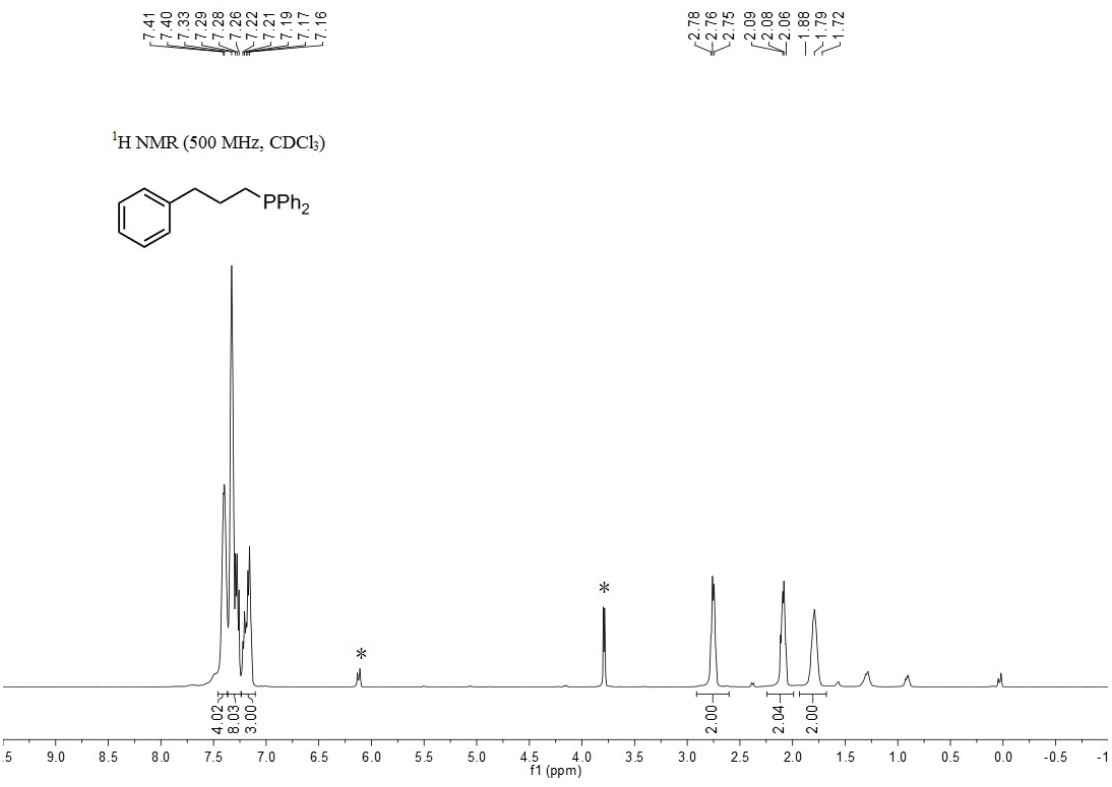


Figure S119. ^{1}H NMR spectra of **4j** (* represents 1,3,5-trimethoxybenzene)

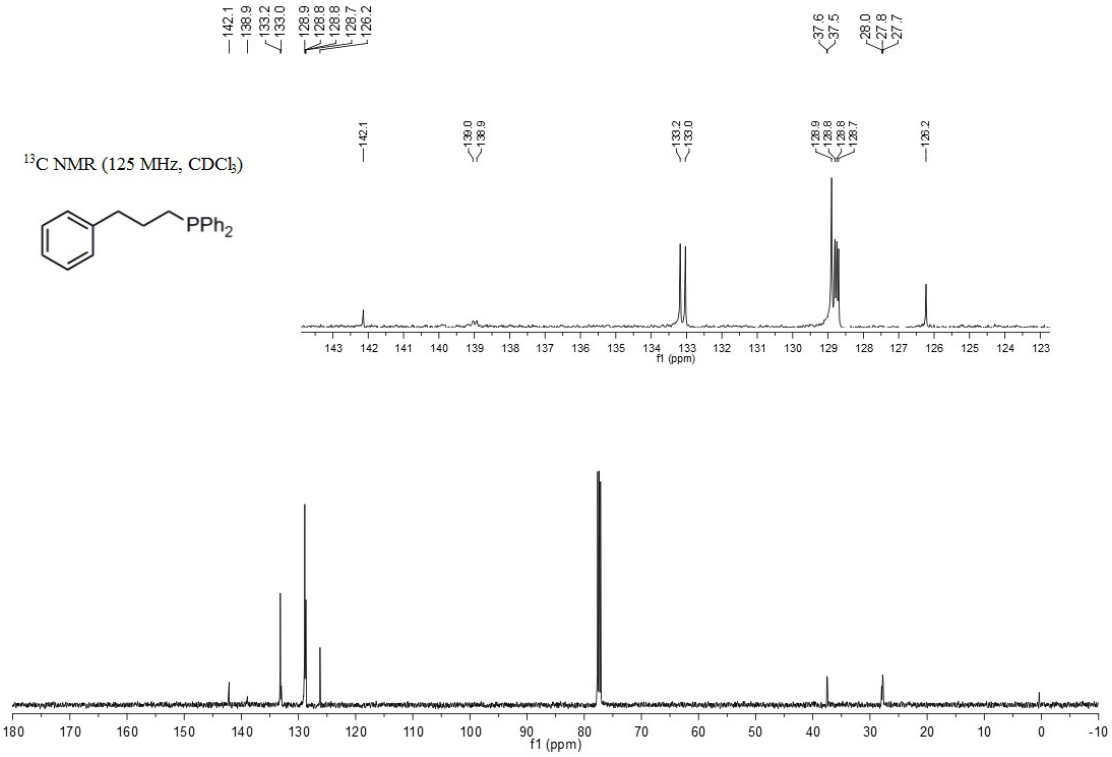


Figure S120. ^{13}C NMR spectra of **4j**

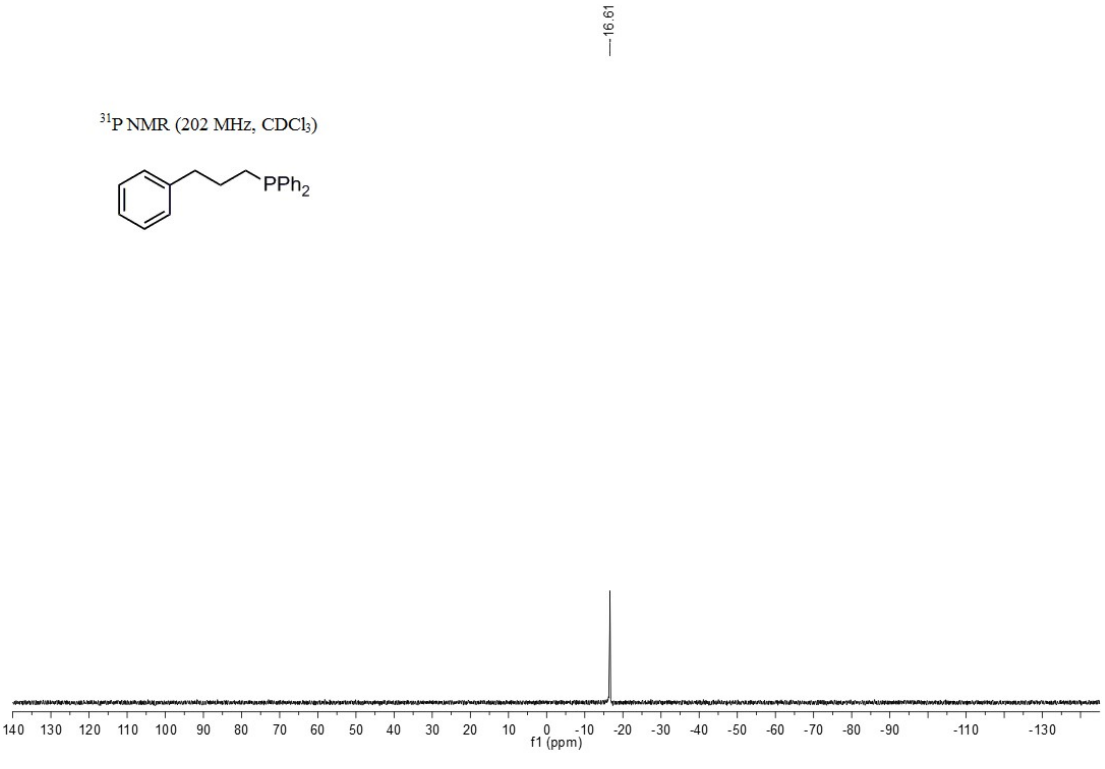


Figure S121. ^{31}P NMR spectra of **4j**

V. X-Ray Structure Determination

Suitable single crystals of clusters **1a-2c** were mounted in a sealed capillary respectively. Diffraction was performed on a Bruker SMART APEX II CCD area detector diffractometer using graphite-monochromated Mo *Kα* radiation (λ = 0.71073 Å) at 293(2) K, φ and ω scan technique. An empirical absorption correction was applied using the SADABS program.[1] All structures were solved by direct methods, completed by subsequent difference Fourier syntheses, and refined anisotropically for all nonhydrogen atoms by full-matrix least-squares calculations based on F^2 using the SHELXTL program package.[2] The hydrogen atom coordinates were calculated with SHELXTL by using an appropriate riding model with varied thermal parameters. The residual electron densities of solvent were squeezed by using PLATON.[3] All crystal structural pictures drawn by *OLEX* 2 program.[4] The crystal data for the complexes were deposited in Cambridge Crystal Data Centre with CCDC nos. 2142862 (**1a**), 2142863 (**1b**), 2142864 (**1c**), 2142865 (**2a**), 2142866 (**2b**), 2142867 (**2c**).

VI. Molecular structure of complexes 1a-2c.

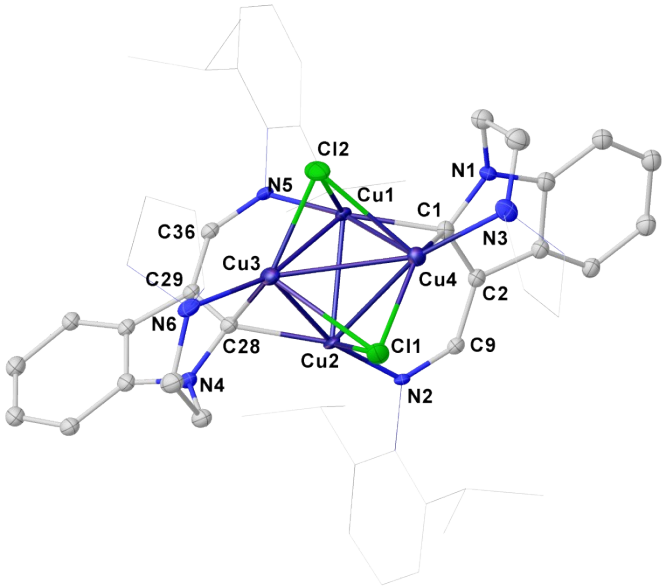


Figure S122. Molecular structure of complex **1a**. The hydrogen atoms were omitted, the pyrrolidinyl carbon atoms and 2,6-diisopropyl-phenyl groups were drawn as wireframe for clarity.

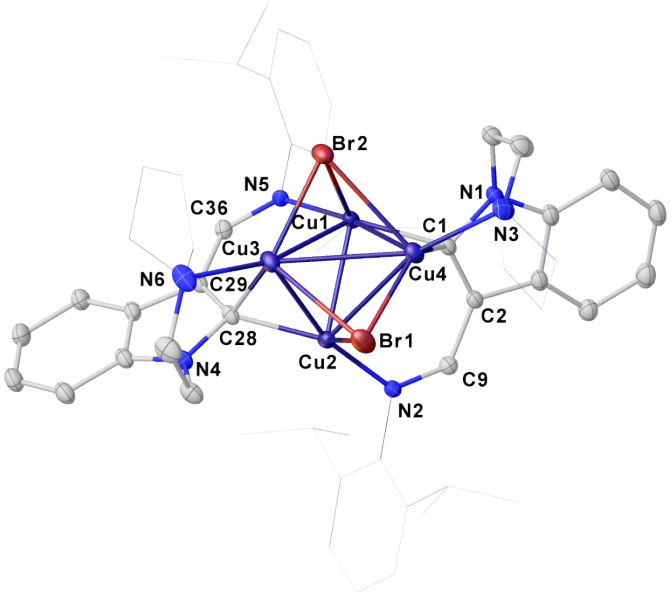


Figure S123. Molecular structure of complex **1b**. The hydrogen atoms were omitted, the pyrrolidinyl carbon atoms and 2,6-diisopropyl-phenyl groups were drawn as wireframe for clarity.

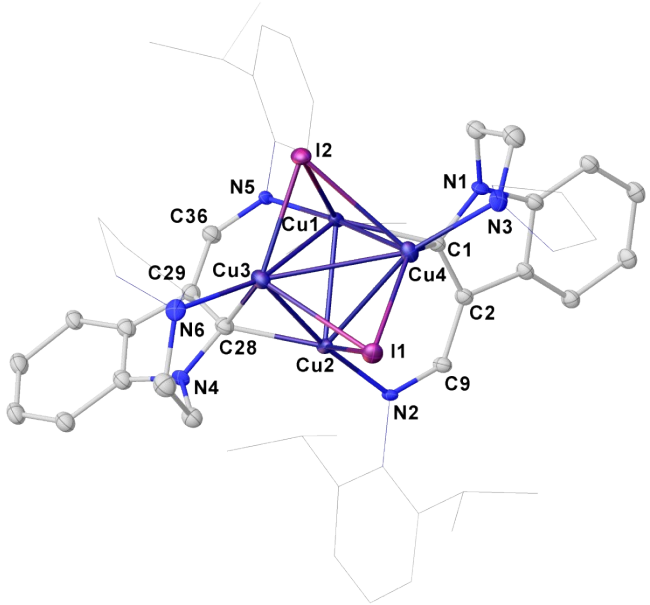


Figure S124. Molecular structure of complex **1c**. The hydrogen atoms were omitted, the pyrrolidinyl carbon atoms and 2,6-diisopropyl-phenyl groups were drawn as wireframe for clarity.

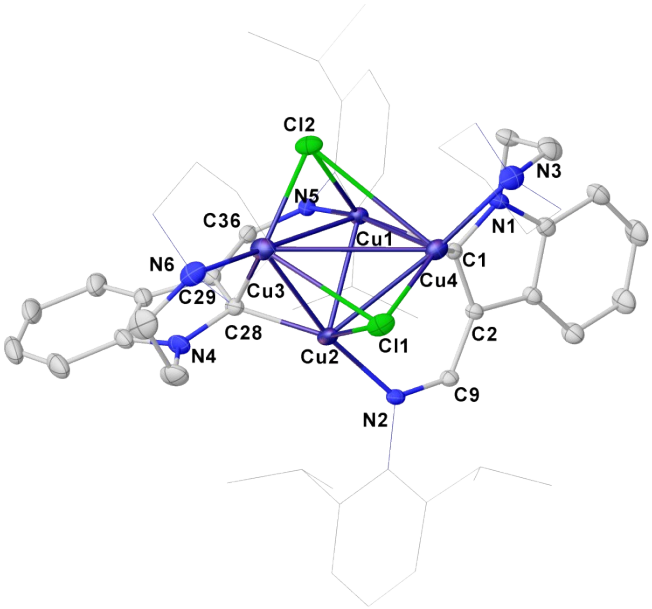


Figure S125. Molecular structure of complex **2a**. The hydrogen atoms were omitted, the piperidyl carbon atoms and 2,6-diisopropyl-phenyl groups were drawn as wireframe for clarity.

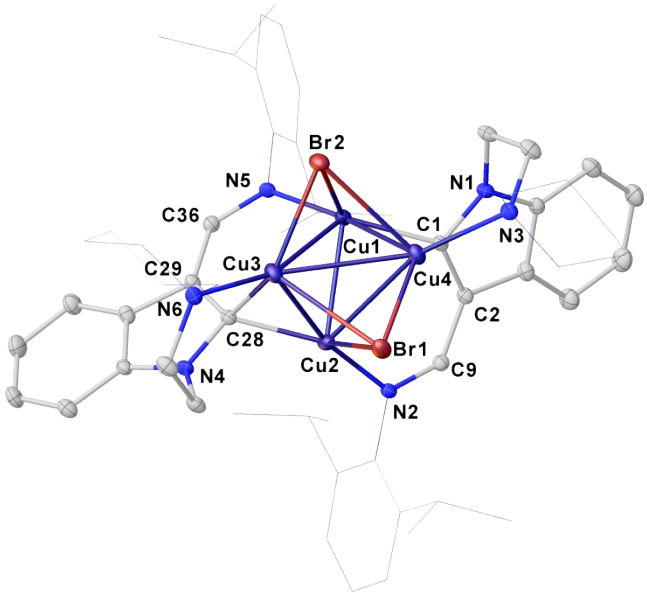


Figure S126. Molecular structure of complex **2b**. The hydrogen atoms were omitted, the piperidyl carbon atoms and 2,6-diisopropyl-phenyl groups were drawn as wireframe for clarity.

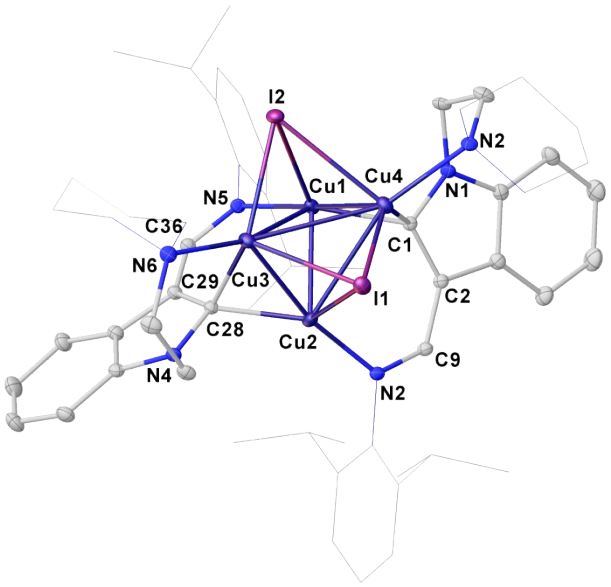


Figure S127. Molecular structure of complex **2c**. The hydrogen atoms were omitted, the piperidyl carbon atoms and 2,6-diisopropyl-phenyl groups were drawn as wireframe for clarity.

VII. Crystallographic data and refinements for complexes 1a-2c

Table S1. Crystallographic data for complexes **1a-1c**

	1a	**1b**	**1c**
Empirical formula	$C_{54}H_{68}Cl_2Cu_4N_6$	$C_{54}H_{68}Br_2Cu_4N_6$	$C_{54}H_{68}Cu_4I_2N_6$
Formula weight	1126.2	1215.12	1309.1
Temperature/K	293.15	293.15	273.15
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$
a/Å	12.697(4)	12.8172(7)	12.426(11)
b/Å	20.986(6)	20.8740(11)	11.631(13)
c/Å	23.210(7)	23.2383(12)	44.05(4)
α/°	90	90	90
β/°	103.848(4)	104.3130(10)	95.409(16)
γ/°	90	90	90
Volume/Å^3	6005(3)	6024.3(6)	6338(11)
Z	4	4	4
ρ_{calc}g/cm^3	1.246	1.34	1.372
μ/mm^{-1}	1.523	2.756	2.333
F(000)	2336	2480	2624
Crystal size/mm^3	0.22 × 0.21 × 0.2	0.22 × 0.21 × 0.2	0.22 × 0.21 × 0.2
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.652 to 50	2.66 to 55.014	5.818 to 55.294
Index ranges	-15 ≤ h ≤ 15, -24 ≤ k ≤ 24, -27 ≤ l ≤ 27	-16 ≤ h ≤ 16, -27 ≤ k ≤ 27, -29 ≤ l ≤ 29	-14 ≤ h ≤ 16, -15 ≤ k ≤ 15, -57 ≤ l ≤ 57
Reflections collected	56373	70071	103003
Independent reflections	10557 [R_{int} = 0.1512, R_{sigma} = 0.1092]	13768 [R_{int} = 0.0738, R_{sigma} = 0.0657]	14523 [R_{int} = 0.0909, R_{sigma} = 0.0926]
Data/restraints/parameters	10557/1244/603	13768/1218/603	14523/1255/603
Goodness-of-fit on F^2	1.037	1.019	1.067
Final R indexes [I>=2σ (I)]	R_1 = 0.1039, wR_2 = 0.2565	R_1 = 0.0545, wR_2 = 0.1192	R_1 = 0.1039, wR_2 = 0.2178
Final R indexes [all data]	R_1 = 0.1642, wR_2 = 0.3020	R_1 = 0.1122, wR_2 = 0.1409	R_1 = 0.1568, wR_2 = 0.2387
Largest diff. peak/hole / e Å^{-3}	1.58/-1.28	0.89/-0.65	1.39/-1.98

Table S2. Crystallographic data for complexes **2a-2c**

	2a	**2b**	**2c**
Empirical formula	$C_{56}H_{72}Cl_2Cu_4N_6$	$C_{56}H_{72}Br_2Cu_4N_6$	$C_{56}H_{72}Cu_4I_2N_6$
Formula weight	1154.25	1243.17	1337.15
Temperature/K	293.15	293.15	293.15
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	C2	C2
a/Å	22.1754(12)	21.510(3)	21.7379(12)
b/Å	12.3278(7)	11.7559(14)	11.7973(6)
c/Å	44.251(2)	12.4242(14)	12.4396(7)
α/°	90	90	90
β/°	102.2010(10)	100.044(2)	100.382(2)
γ/°	90	90	90
Volume/Å^3	11823.9(11)	3093.6(7)	3137.9(3)
Z	8	2	2
ρ_{calc}g/cm^3	1.297	1.335	1.415
μ/mm^{-1}	1.548	2.685	2.357
F(000)	4800	1272	1344
Crystal size/mm^3	0.22 × 0.2 × 0.19	0.22 × 0.21 × 0.2	0.15 × 0.11 × 0.1
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.272 to 54.934	3.33 to 54.938	5.494 to 64.706
Index ranges	-28 ≤ h ≤ 28, -15 ≤ k ≤ 15, -57 ≤ l ≤ 57	-27 ≤ h ≤ 27, -15 ≤ k ≤ 15, -15 ≤ l ≤ 16	-32 ≤ h ≤ 32, -17 ≤ k ≤ 14, -18 ≤ l ≤ 18
Reflections collected	136059	17740	61272
Independent reflections	26767 [R_{int} = 0.0719, R_{sigma} = 0.0651]	7002 [R_{int} = 0.0337, R_{sigma} = 0.0517]	9825 [R_{int} = 0.0577, R_{sigma} = 0.0468]
Data/restraints/parameters	26767/0/1241	7002/44/312	9825/559/415
Goodness-of-fit on F^2	1.019	1.015	1.031
Final R indexes [I>=2σ (I)]	R_1 = 0.0479, wR_2 = 0.1004	R_1 = 0.0412, wR_2 = 0.0984	R_1 = 0.0350, wR_2 = 0.0716
Final R indexes [all data]	R_1 = 0.0967, wR_2 = 0.1152	R_1 = 0.0594, wR_2 = 0.1061	R_1 = 0.0610, wR_2 = 0.0797
Largest diff. peak/hole / e Å^{-3}	0.34/-0.44	0.48/-0.35	0.47/-0.69

VIII. References

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