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Electronic Supplementary Information (ESI)

Synthesis of Vinylphosphine and Unsymmetric Diphosphine: Iron-catalyzed Selective Hydrophosphination Reaction of Alkynes and Vinylphosphines with Secondary Phosphines

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General considerations: All manipulations were carried out using standard Schlenk techniques under a dry nitrogen atmosphere. Iron complexes Cp*Fe(CO)(py)(Me)[S1], CpFe(CO)$_2$(Me)[S2], Cp*Fe(CO)$_2$(Me)[S3], and secondary phosphines[S4, S5] were prepared according to the literature methods. The other chemicals were commercially available. Solvents were purified employing a two-column solid-state purification system or were distilled from appropriate drying agents under N_2. NMR spectra (^{1}H, ^{13}C{^{1}H}, ^{19}F{^{1}H} and ^{31}P{^{1}H}) were recorded on a JNM AL-400 spectrometer. ^{1}H and ^{13}C{^{1}H} NMR data were referred to residual peaks of solvent as an internal standard, and ^{19}F{^{1}H} and ^{31}P{^{1}H} NMR chemical shifts were referenced to external hexafluorobenzene (–162.7 ppm) and 85% H_3PO_4 (0 ppm) samples. NMR yield and *E/Z* ratio were determined by ^{31}P NMR using triphenylphosphine oxide P(=O)Ph$_3$ as an internal standard. Elemental analysis data were obtained on a Perkin-Elmer 2400 CHN elemental analyzer.

General procedure for vinylphosphines

A toluene solution (1 mL) containing Cp*Fe(CO)(py)(Me) (0.10 mmol, 32 mg, 10 mol% *vs.* secondary phosphine), secondary phosphine (1.0 mmol) and acetylene (1.5 mmol) was heated at 110 °C for 2 days in 7 mL Schlenk tube. After all volatile materials were removed under reduced pressure, the crude product was chromatographed on alumina with 90:10 hexane:CH_2Cl_2 eluent. The yellow-orange band was collected and volatile materials were removed under reduced pressure. The residue was washed with *n*-hexane (1 mL × 4) at –20 °C and dried in *vacuo* to give the title compounds.

[(1*Z*)-2-Phenylethenyl]diphenylphosphine (1a)

The compound **1a** was prepared from *p*-ethynyltoluene and diphenylphosphine by general procedure as a white powder (190 mg, 65%).[S6]

[(1*Z*)-2-(4-Methylphenyl)ethenyl]diphenylphosphine (1b)

The compound **1b** was prepared from *p*-ethynyltoluene and diphenylphosphine by general procedure as a white powder (178 mg, 59%).[S6]

[(1*Z*)-2-(4-Methoxyphenyl)ethenyl]diphenylphosphine (1c)

The compound **1c** was prepared from *p*-ethynylanisole and diphenylphosphine by general procedure and chromatographed on alumina with CH_2Cl_2 eluent. The yellow-orange band was collected and volatile materials were removed under reduced pressure. The residue was washed with *n*-hexane (1 mL × 4) and dried in *vacuo* to give **1c** as a white powder (54 mg, 25%).[S6]

***p*-[(1*Z*)-2-(Diphenylphosphino)ethenyl]aniline (1d)**

The compound **1d** was prepared from *p*-ethynylaniline and diphenylphosphine by general procedure as a pale yellow powder (252 mg, 65%).

^{1}H NMR (400 MHz, C_6D_6, ppm): 2.71 (s, 2H, NH_2), 6.18 (dd, J_{PH} = 21.6 Hz, J_{HH} = 13.1 Hz, 1H, CH=C), 6.23 (dd, J_{PH} = 3.0 Hz, J_{HH} = 13.1 Hz, 1H, C=CHP), 6.96-7.56 (m, 14H, Ph). ^{13}C{^{1}H} NMR (100.4 MHz, $CDCl_3$, ppm): 114.87 (s, *m*-Ph), 125.12 (d, J_{PC} = 14.1 Hz, *o*-Ph), 128.01 (s, C*ipso*), 128.72 (s, *p*-Ph), 128.85 (d, J_{PC} = 6.6 Hz, *o*-Ph), 131.49 (d, J_{PC} = 9.1 Hz,C *ipso*), 133.09 (d, J_{PC} = 19.1 Hz, *m*-Ph), 140.10 (d, J_{PC} = 10.8 Hz, CH), 144.40 (d, J_{PC} = 19.1 Hz, PCH), 146.99 (s, *p*-Ph). ^{31}P{^{1}H} NMR (161.7 MHz, C_6D_6, ppm): –24.25 (s). Elemental Analysis. Calcd. For: $C_{20}H_{18}NP$; C, 79.19; H, 5.98; N, 4.62; Found: C, 79.44; H, 6.11; N, 4.56.

[(1*Z*)-2-(4-Fluoro)ethenyl]diphenylphosphine (1e)

The compound **1e** was prepared from 4-fluorophenylacetylene and diphenylphosphine by general procedure as a white powder (45 mg, 30%).

^{1}H NMR (400 MHz, C_6D_6, ppm): 6.34 (dd, J_{PH} = 2.8 Hz, J_{HH} = 10.4 Hz, 1H, PCH=C), 6.65-7.19 (m, 10H, Ph), 7.35 (dd, J_{PH} = 5.6 Hz, J_{HH} = 10.4 Hz, 1H, PC=CH), 7.36-7.47 (m, 4H, Ph). ^{13}C{^{1}H} NMR (100.4 MHz, C_6D_6, ppm): 115.27 (d, J_{FC} = 21.6 Hz, *m*-Ph), 128.30 (s, *p*-Ph), 128.93 (d, J_{PC} = 6.6 Hz, *o*-Ph), 129.75 (d, J_{FC} = 17.4 Hz, *m*-Ph), 131.78 (t, J_{PC} = 8.3 Hz, PC*ipso*), 133.10 (d, J_{PC} = 19.0 Hz, *o*-Ph), 133.55 (s, C*ipso*), 139.69 (d, J_{PC} = 9.9 Hz, CH), 142.91 (d, J_{PC} = 19.1 Hz, PCH), 162.69 (d, J_{FC} = 249.6 Hz, FC*ipso*). ^{19}F NMR (376 MHz, C_6D_6, ppm): –111.40 (s). ^{31}P{^{1}H} NMR (161.7 MHz, C_6D_6, ppm): –25.33 (s). Elemental Analysis. Calcd. For: $C_{20}H_{16}FP$; C, 78.42; H, 5.27; Found: C, 78.00; H, 5.41.

[(1*Z*)-2-(4-*tert*-Buthylphenyl)ethenyl]diphenylphosphine (1f)

The compound **1f** was prepared from 4-tert-butylphenylacetylene and diphenylphosphine by general procedure as a white powder (189 mg, 42%).

^{1}H NMR (400 MHz, C_6D_6, ppm): 1.13 (s, 9H, CH_3), 6.39 (dd, J_{PH} = 2.8 Hz, J_{HH} = 13.4Hz, 1H, PCH=C), 7.04-7.23 (m, 10H, Ph), 7.24 (dd, J_{PH} = 24.0 Hz, J_{HH} = 13.4 Hz, PC=CH), 7.51-7.61 (m, 4H, Ph). ^{13}C{^{1}H} NMR (100.4 MHz, C_6D_6, ppm): 31.51 (s, CH), 32.24 (s, CH_3), 125.71 (s, *p*-Ph), 128.15 (s, *m*-Ph), 128.44 (s, *o*-Ph), 128.70 (s, C*ipso*), 128.90 (s, *p*-Ph), 129.14 (d, J_{PC} = 6.6 Hz, *m*-Ph), 130.27 (d, J_{PC} = 19.0 Hz, C*ipso*), 133.43 (d, J_{PC} = 19.0 Hz, *o*-Ph), 140.54 (d, J_{PC} = 9.9 Hz, CH), 144.58 (d, J_{PC} = 18.1 Hz, PCH). ^{31}P{^{1}H} NMR (161.7 MHz, C_6D_6, ppm): –24.52 (s). Elemental Anlysis. Calcd. For: $C_{24}H_{25}P$; C, 83.69; H, 7.32; Found: C, 83.32; H, 7.39.

2-[(1*Z*)-2-(Diphenylphosphino)ethenyl]pyridine (1g)

The compound **1g** was prepared from 2-ethynylpyridine and diphenylphosphine by general procedure as a white powder (35 mg, 22%).[S6]

[(1*Z*)-2-(3-Thiophenyl)ethenyl]diphenylphosphine (1h)

The compound **1h** was prepared from 3-ethynylthiophene and diphenylphosphine by general procedure as a white powder (161 mg, 32%).

^{1}H NMR (400 MHz, C_6D_6, ppm): 6.26 (dd, J_{PH} = 12.6 Hz, J_{HH} = 2.7 Hz, 1H, PC=CH), 6.73 (dd, J_{PH} = 4.8 Hz, J_{HH} = 2.7 Hz, 1H, PCH=C), 6.96-7.49 (m, 13H, Ph and thiophenyl). ^{13}C{^{1}H} NMR (100.4 MHz, $CDCl_3$, ppm): 125.01 (s, *p*-Ph), 125.90 (s, thiophenyl), 126.00 (s, thiophenyl), 127.64 (d, J_{PC} = 14.8 Hz, C*ipso*), 128.36 (d, J_{PC} = 7.4 Hz, *m*-Ph), 128.70 (s, thiophenyl), 128.80 (s, thiophenyl), 132.48 (d, J_{PC} = 19.1 Hz, *o*-Ph), 137.29 (d, J_{PC} = 20.7 Hz, PCH), 138.70 (d, J_{PC} = 9.1 Hz, CH). ^{31}P{^{1}H} NMR (161.7 MHz, C_6D_6, ppm): –24.42 (s). Elemental Anlysis. Calcd. For: $C_{18}H_{15}PS$; C, 73.45; H, 5.14; Found: C, 72.95; H, 5.25.

[(1*Z*)-2-Ferrocenylethenyl]diphenylphosphine (1i)

The compound **1i** was prepared from ethynylferrocene and diphenylphosphine by general procedure as an orange powder (183 mg, 46%).

^{1}H NMR (400 MHz, C_6D_6, ppm): 3.91 (s, 5H, Cp), 4.02 (s, 2H, Cp), 4.64 (s, 2H, Cp), 6.21 (dd, J_{PH} = 2.8 Hz, J_{HH} = 12.4 Hz, 1H, PHC=C), 6.89 (dd, J_{PH} = 26.4 Hz, J_{HH} = 12.4 Hz, 1H, PC=CH), 7.05-7.55 (m, 10H, Ph). ^{13}C{^{1}H} NMR (100.4 MHz, C_6D_6, ppm): 69.59 (s, Cp), 79.03 (s, Cp), 70.88 (d, J_{PC} = 10.7 Hz, Cp), 81.80 (s, Cp), 124.93 (d, J_{PC} = 15.8 Hz, C*ipso*), 128.61 (s, *p*-Ph), 128.84 (d, J_{PC} = 6.7 Hz, *m*-Ph), 133.15 (d, J_{PC} = 19.0 Hz, *o*-Ph), 140.50 (d, J_{PC} = 10.7 Hz, CH), 143.20 (d, J_{PC} = 21.6 Hz, PCH). ^{31}P{^{1}H} NMR (161.7 MHz, C_6D_6, ppm): –25.61 (s). Elemental Analysis. Calcd. For $C_{24}H_{21}PFe$; C, 72.75; H, 5.34; Found: C, 72.50; H, 5.42.

***p*-[(1*Z*)-2-{Di(4-methylphenyl)phosphino}ethenyl]aniline (1j)**

The compound **1j** was prepared from *p*-ethynylaniline and bis(4-methylphenyl)phosphine by general procedure and chromatographed on alumina with CH_2Cl_2 eluent. The yellow-orange band was collected and volatile materials were removed under reduced pressure. The residue was washed with EtOH (1 mL × 2) and *n*-hexane (1 mL × 2), and dried in *vacuo* to give **1j** as a pale yellow powder (220 mg, 65%).
^{1}H NMR (400 MHz, C_6D_6, ppm): 2.03 (s, 6H, CH_3), 2.72 (s, 2H, NH_2), 6.20 (d, J_{HH} = 10.5 Hz, 1H, PC=CH), 6.32 (dd, J_{PH} = 2.4 Hz, J_{HH} = 10.5 Hz, 1H, PHC=C), 6.94-6.96 (m, 4H, Ph), 7.20-7.59 (m, 8H, Ph). ^{13}C{^{1}H} NMR (100.4 MHz, $CDCl_3$, ppm): 21.65 (s, CH_3), 114.87 (s, *m*-Ph), 125.87 (d, J_{PC} = 14.1 Hz, *o*-Ph), 128.16 (s, C*ipso*), 129.65 (d, J_{PC} = 6.6 Hz, *o*-Ph), 131.47 (d, J_{PC} = 9.9 Hz, C*ipso*), 133.03 (d, J_{PC} = 19.1 Hz, *m*-Ph), 136.81 (d, J_{PC} = 7.4 Hz, CH), 138.55 (s, *p*-Ph), 143.84 (d, J_{PC} = 18.3 Hz, PCH), 146.85 (s, *p*-Ph). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, ppm): –25.61 (s). Elemental Analysis. Calcd. For $C_{22}H_{22}NP$; C, 79.74; H, 6.69; N, 4.23; Found: C, 79.52; H, 6.80; N, 4.16.

***p*-[(1*Z*)-2-{Di(4-methoxyphenyl)phosphino}ethenyl]aniline (1k)**

The compound **1k** was prepared from *p*-ethynylaniline and bis(4-metoxhyphenyl)phosphine by general procedure and chromatographed on alumina with CH_2Cl_2 eluent. The yellow-orange band was collected and volatile materials were removed under reduced pressure. The residue was washed with EtOH (1 mL × 2) and *n*-hexane (1 mL × 2), and dried in *vacuo* to give **1k** as a pale yellow powder (216 mg, 60%).
^{1}H NMR (400 MHz, C_6D_6, ppm): 2.74 (s, 2H, NH_2), 3.23 (s, 6H, CH_3), 6.23 (d, J_{HH} = 10.5 Hz, 1H, PC=CH), 6.33 (d, J_{HH} = 10.5 Hz, 1H, PCH=C), 6.73-6.75 (m, 4H, Ph), 7.52-7.60 (m, 8H, Ph). ^{13}C{^{1}H} NMR (100.4 MHz, $CDCl_3$, ppm): 55.29 (s, CH_3), 114.27 (d, J_{PC} = 7.4 Hz, *m*-Ph), 114.61 (s, *m*-Ph),126.00 (d, J_{PC} = 13.3 Hz, *o*-Ph), 127.86 (s, *ipso*Ph), 131.03 (d, J_{PC} = 5.8 Hz, *ipso*Ph), 131.23 (d, J_{PC} = 9.1 Hz, *o*-Ph), 134.19 (d, J_{PC} = 19.9 Hz, PCH), 143.12 (d, J_{PC} = 17.4 Hz, CH), 146.61 (s, *p*-Ph), 160.02 (s, *p*-Ph). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, ppm): –26.58 (s). Elemental Analysis. Calcd. For $C_{22}H_{22}NO_2P$; C, 72.71; H, 6.10; N, 3.85; Found: C, 72.40; H, 6.18; N, 3.96.

Preparation of Cp*Fe(CO)(PHPh$_2$)Me (A)

A toluene solution (2 mL) containing Cp*Fe(CO)(py)(Me) (1.62 mmol, 520 mg) and diphenylphosphine (1.62 mmol, 283 μL) was stirred at ambient temperature for 15 minutes. After all volatile materials were removed under reduced pressure, the residue was wash with *n*-hexane (4 mL × 3) at –20 °C and dried in *vacuo* to give **A** as an orange powder (517 mg, 76%).
^{1}H NMR (400 MHz, C_6D_6, ppm): –0.29 (d, J_{PH} = 8.4 Hz, 3H, $FeCH_3$), 1.48 (s, 15H, C_5Me_5), 6.16 (d, J_{PH} = 318.4 Hz, 1H, P-H), 6.99-7.05 (m, 6H, Ph), 7.57 (dt, J_{PH} = 89.6 Hz, J_{HH} = 8.9 Hz, 4H, Ph). ^{13}C{^{1}H} NMR (100.4 MHz, C_6D_6, ppm): –10.89 (d, J_{PC} = 18.27 Hz, $FeCH_3$), 9.51 (s, CCH_3), 90.84 (s, Cp), 128.47 (s, *m*- or *p*-Ph), 128.56 (s, *m*- or *p*-Ph), 129.13 (s, *m*- or *p*-Ph), 129.61 (s, *m*- or *p*-Ph), 132.38 (d, J_{PC} = 7.5 Hz, *o*-Ph), 133.32 (d, J_{PC} = 9.0 Hz, *o*-Ph), 135,24 (d, J_{PC} = 4.29 Hz, C*ipso*), 135.65 (d, J_{PC} = 5.72 Hz, C*ipso*),

223.32 (d, J_{PC} = 26.33 Hz, CO). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, ppm): 77.78 (s). Elemental Analysis. Calcd. For: $C_{24}H_{29}OPFe$: C, 68.58; H, 6.95; Found: C, 68.22; H, 6.87.

Preparation of Cp*Fe(CO)(PPh$_2$)(PHPh$_2$) (G)

A toluene solution (1 mL) containing Cp*Fe(CO)(PHPh$_2$)(Me) (0.5 mmol, 210 mg) and diphenylphosphine (0.5 mmol, 87 μL) was heated at 110 °C for 1 hour. After all volatile materials were removed under reduced pressure, the residue was wash with *n*-hexane (2 mL × 5) at –20 °C and dried in *vacuo* to give **G** as a reddish orange powder (167 mg, 56%).

^1H NMR (400 MHz, C_6D_6, ppm): 1.48 (s, 15H, C_5Me_5), 5.65 (d, J_{PH} = 359.5 Hz, 1H, P-H), 7.38 (m, 20H, Ph). $^{13}C\{^1H\}$ NMR spectra were not observed due to low solubility for organic solvents. ^{31}P NMR (161.7 MHz, C_6D_6, ppm): 44.31 (s, PPh$_2$), 58.46 (d, J_{PH} = 359.5 Hz, PHPh$_2$).[S7] Elemental Analysis. Calcd. For: $C_{35}H_{36}OP_2Fe$: C, 71.20; H, 6.15; Found: C, 70.86; H, 6.19.

Preparation of Cp*Fe(CO){C(Ph)=C(H)PPh$_2$} (E)

A toluene solution (0.6 mL) containing Cp*Fe(CO)(PPh$_2$)(PHPh$_2$) (0.5 mmol, 300 mg) and phenylacetylene (0.5 mmol, 60 μL) was heated at 110 °C for 1 hour. After all volatile materials were removed under reduced pressure, the residue was wash with *n*-hexane (2 mL × 4) at –20 °C and dried in *vacuo* to give **E** as a brown yellow powder (174 mg, 67%).

^1H NMR (400 MHz, $CDCl_3$, ppm): 1.43 (s, 15 H, C_5Me_5), 7.02 (d, J_{PH} = 9.59 Hz, 1H, CH), 7.17 (q, 2H, *o*-CPh), 7.41 (m, 10H, PPh), 7.62 (m, 3H, *m*-, *p*-CPh). $^{13}C\{^1H\}$ NMR (100.4 MHz, $CDCl_3$, ppm): 10.52 (s, CH_3), 90.64 (s, Cp), 123.56 (d, J_{PC} = 50.5 Hz, *o*-Ph), 26.245 (s, *p*-Ph), 126.55 (s, *p*-Ph), 127.91 (s, *p*-Ph), 128.42 (d, J_{PC} = 9.1 Hz, *m*-Ph), 128.49 (d, J_{PC} = 10.4 Hz, *m*-Ph), 129.66 (d, J_{PC} = 40.6 Hz, C*ipso*), 129.69(d, J_{PC} = 40.7 Hz, C*ipso*), 133.09 (d, J_{PC} = 37.3 Hz, *o*-Ph), 133.19 (d, J_{PC} = 39.9 Hz, *o*-Ph), 136.27 (d, J_{PC} = 26.6 Hz, *m*-Ph), 136.36 (d, J_{PC} = 33.2 Hz, C*ipso*), 149.01 (d, J_{PC} = 26.6 Hz, CH), 196.23 (d, J_{PC} = 37.3 Hz, PCH), 223.94 (d, J_{PC} = 21.6 Hz, CO). ^{31}P NMR (161.7 MHz, $CDCl_3$, ppm): –6.83 (d, J_{PH} = 9.59 Hz). Elemental Analysis. Calcd. For $C_{31}H_{31}OPFe$: C, 73.53; H, 6.17; Found: C, 73.29; H, 6.27.

Hydrophosphination promoted by Cp*Fe(CO)(PPh$_2$H)(Me) (A)

A toluene solution (400 μL) containing Cp*Fe(CO)(PPh$_2$H)(Me) (**A**) (0.0056 mmol, 2.2 mg, 10 mol% *vs.* PHPh$_2$), PHPh$_2$ (0.056 mmol) and phenylacetylene (0.084 mmol) was heated at 110 °C for 2 days in an NMR tube. The *E/Z* ratio (20:80) and yield (76%) of formed 2-phenylethenyldiphenylphosphine were determined by ^{31}P NMR.

Hydrophosphination promoted by Cp*Fe(CO){C(Ph)=C(H)PPh$_2$} (E)

A toluene solution (400 μL) containing Cp*Fe(CO){C(Ph)=C(H)PPh$_2$} (**E**) (0.0050 mmol, 2.5 mg, 10 mol% *vs.* PHPh$_2$), PHPh$_2$ (0.050 mmol) and phenylacetylene (0.075 mmol) was heated at 110 °C for 2 days in an NMR tube. The *E/Z* ratio (10:90) and yield (86%) of formed 2-phenylethenyldiphenylphosphine were determined by ^{31}P NMR.

Hydrophosphination promoted by Cp*Fe(CO)(PPh$_2$)(PHPh$_2$) (G)

A toluene solution (400 μL) containing Cp*Fe(CO)(PPh$_2$)(PHPh$_2$) (**G**) (0.010 mmol, 4.2 mg, 10 mol% *vs.* PHPh$_2$), PHPh$_2$ (0.10 mmol) and phenylacetylene (0.15 mmol) was heated at 110 °C for 2 days in an NMR tube. The *E/Z* ratio (13:87) and yield (90%) of formed 2-phenylethenyldiphenylphosphine were determined by ^{31}P NMR.

General procedure for unsymmetric 1,2-bisphosphinoethanes

A mixture containing CpFe(CO)$_2$(Me) (0.018 mmol, 4 mg, 5 mol% *vs.* vinylphosphine), secondary phosphine (0.35 mmol) and vinylphosphine (0.35 mmol) was heated at 110 °C for 1 day in 7 mL Schlenk tube. After all volatile materials were removed under reduced pressure, the crude product was washed with EtOH (1 mL × 2) and *n*-hexane (1 mL × 2) and dried in *vacuo* to give the title compounds.

1,2-Bis(diphenylphosphino)phenylethane (2a)

The compound **2a** was prepared from diphenylphosphine and [(1*Z*)-2-phenylethenyl]-diphenylphosphine (**1a**) by general procedure as a white powder (139 mg, 84%).[S8]

1-Bis(4-methylphenyl)phosphino-2-diphenylphosphinophenylethane (2b)

The compound **2b** was prepared from bis(4-methylphenyl)phosphine and [(1*Z*)-2-phenylethenyl]-diphenylphosphine (**1a**) by general procedure as a white powder (148 mg, 85%).

^{1}H NMR (C$_6$D$_6$, 400 MHz, ppm): 1.87 (s, 3H, CH$_3$), 2.08 (s, 3H, CH$_3$), 2.77 (d, J_{PH} = 26.8 Hz, 2H, CH$_2$), 3.63 (s, 1H, CH), 6.69-7.48 (m, 23H, Ph). ^{13}C{^{1}H} NMR (CDCl$_3$, 100.4 MHz, ppm): 21.69 (d, J_{PC} = 27.4 Hz, CH$_3$), 33.16 (t, J_{PC} = 15.7 Hz, CH$_2$), 42.04 (t, J_{PC} = 12.4 Hz, CH), 126.89 (s, *m*-Ph), 128.22 (s, *p*-Ph), 128. 53 (d, J_{PC} = 2.5 Hz, *m*-Ph), 128.64 (s, *p*-Ph), 128.88 (t, J_{PC} = 7.5 Hz, *m*-Ph), 129.624 (s, *m*-Ph), 129.84 (t, J_{PC} = 6.7 Hz, *m*-Ph), 132.26 (d, J_{PC} = 17.4 Hz, *o*-Ph), 132.81 (d, J_{PC} = 9.9 Hz, *o*-Ph), 133.27 (d, J_{PC} = 17.5 Hz, *o*-Ph), 133.78 (d, J_{PC} = 14.0 Hz, PC*ipso*), 134.68 (dd, J_{PC} = 19.9 Hz, J_{PC} = 5.7 Hz, PC*ipso*), 138.02 (d, J_{PC} = 15.8 Hz, C*ipso*), 138.45 (s, C*ipso*), 139.75 (t, J_{PC} = Hz, C*ipso*), 140.95 (d, J_{PC} = 6.6 Hz, PC*ipso*). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 162 MHz, ppm): –22.17 (d, J_{PP} = 16.5 Hz, PCH$_2$), 0.16 (d, J_{PP} = 16.5 Hz, PCH). Elemental Analysis. Calcd. For C$_{34}$H$_{35}$P$_2$: C, 81.26; H, 6.42; Found: C, 80.84; H, 6.42.

1-Bis(4-methoxyphenyl)phosphino-2-diphenylphosphinophenylethane (2c)

The compound **2c** was prepared from bis(4-methoxyphenyl)phosphine and [(1*Z*)-2-phenylethenyl]-diphenylphosphine (**1a**) by general procedure as a white powder (154 mg, 83%).

^{1}H NMR (400 MHz, C_6D_6, ppm): 2.48 (d, J_{PH} = 12.8 Hz, 2H, CH_2), 3.20 (s, 1H, CH), 3.66 (s, 3H, CH_3), 3.82 (s, 3H, CH_3), 6.54-7.94 (m, 23H, Ph). ^{13}C{^{1}H} NMR spectra were not observed due to low solubility for organic solvents. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, ppm): –22.53 (d, J_{PP} = 18.4 Hz, PCH_2), –0.57 (d, J_{PP} = 18.4 Hz, PCH). Elemental Analysis. Calcd. For $C_{34}H_{32}O_2P_2$: C, 76.39; H, 6.03; Found: C, 75.16; H, 6.01.

1-Bis(4-fluorophenyl)phosphino-2-diphenylphosphinophenylethane (2d)

The compound **2d** was prepared from bis(4-fluorophenyl)phosphine and [(1*Z*)-2-phenylethenyl]-diphenylphosphine (**1a**) by general procedure as a white powder (121 mg, 69%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): 2.64 (d, J_{PH} = 22.5 Hz, 2H, CH_2), 3.38 (s, 1H, CH) 6.48-7.35 (m, 23H, Ph). ^{13}C{^{1}H} NMR (100.4 MHz, $CDCl_3$, ppm): 32.84 (dd, J_{PC} = 15.8 Hz, J_{PC} = 21.6 Hz, CH_2), 42.24 (t, J_{PC} = 14.1 Hz, CH), 115.02 (dd, J_{FC} = 20.7 Hz, J_{PC} = 7.4 Hz, *o*- or *m*-Ph), 116.03 (dd, J_{FC} = 20.7 Hz, J_{PC} = 7.4 HZ, *o*- or *m*- Ph), 126.856 (s, *p*-Ph), 128.10 (s, *p*-Ph), 128.31 (d, J_{PC} = 6.2 Hz, *m*-Ph), 128.50 (s, *p*-Ph), 128.64 (d, J_{PC} = 6.2 Hz, *m*-Ph), 129.39 (t, 7.5 Hz, *m*- or *o*-Ph), 131.40 (d, J_{PC} = 13.3 Hz, PC*ipso*), 131.92 (d, J_{PC} = 17.5 Hz, *o*-Ph), 133.01 (d, J_{PC} = 20.0 Hz, PC*ipso*), 134.32 (d, J_{PC} = 19.9 Hz, *o*-Ph), 134.79 (dd, J_{PC} = 18.7 Hz, J_{PC} = 7.9 Hz, *o*-Ph), 135.98 (dd, J_{PC} = 20.7 Hz, J_{PC} = 8.3 Hz, *o*-Ph), 137.80 (d, J_{PC} = 15.0 Hz, PC*ipso*), 138.91 (d, J_{PC} = 12.5 HZ, PC*ipso*), 140.03 (m, C*ipso*), 163.39 (dd, J_{FC} = 278.5 HZ, J_{PC} = 66.5 Hz, FC*ipso*). ^{19}F NMR (376 MHz, $CDCl_3$, ppm): –151.79 (s), –150.11 (s). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, ppm): –22.38 (d, J_{PP} = 18.1 Hz, PCH_2), –1.65 (d, J_{PP} = 18.1 Hz, PCH). Elemental Analysis. Calcd. For $C_{32}H_{26}F_2P_2$: C, 75.29; H, 5.13; Found: C, 74.66; H, 5.13.

1-Di(*p*-methylphenyl)phosphino-2-diphenylphosphino-2-(*p*-aminophenyl)ethane (2e)

The compound **2e** was prepared from diphenylphosphine and *p*-[(1*Z*)-2-{di(4-methylphenyl)phosphino}ethenyl]aniline (**1j**) by general procedure as a pale yellow powder (160 mg, 88%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.30 (s, 2H, NH_2), 2.34 (s, 3H, CH_3), 2.44 (s, 3H, CH_3), 3.24 (s, 1H, CH), 3.54 (br, 2H, CH_2), 6.57-7.33 (m, 22H, Ph). ^{13}C{^{1}H} NMR (100.4 MHz, $CDCl_3$, ppm). 21.40 (d, J_{PC} = 26.7 Hz, CH_3), 33.28 (dd, J_{PC} = 20.6 Hz, J_{PC} = 10.3 Hz, CH_2), 40.67 (t, J_{PC} = 13.9 Hz, CH), 115.47 (s, *m*-Ph), 127.74 (d, J_{PC} = 6.4 Hz, *p*-Ph), 128.10 (s, *p*-Ph), 128.56 (d, J_{PC} = 7.0 Hz, *m*-Ph), 129.01 (d, J_{PC} = 5.8 Hz, *m*-Ph), 129.32 (d, J_{PC} = 7.7 Hz, *m*-Ph), 130.22 (d, J_{PC} = 4.8 Hz, *o*-Ph), 131.82 (d, *J*PC = 17.6 Hz, *o*-Ph), 133.08 (d, J_{PC} = 17.4 Hz, *o*-Ph), 134.41 (dd, J_{PC} = 10.4 Hz, J_{PC} = 9.4 Hz, *ipso*-Ph), 136.45 (dd, J_{PC} = 8.3 Hz, J_{PC} = 15.8 Hz, *ipso*-Ph), 137.63 (s, *ipso*-Ph), 139.20 (s, *ipso*-Ph), 144.88 (s, *ipso*-Ph). ^{31}P{^{1}H} NMR (162

MHz, $CDCl_3$, ppm): –25.10 (d, J_{PP} = 13.8 Hz, PCH_2), 1.20 (d, J_{PP} = 13.8 Hz, PCH). Elemental Analysis. Calcd. For $C_{34}H_{33}NP_2$: C, 78.90; H, 6.43; N, 2.71; Found: C, 78.23; H, 6.34; N, 2.57.

Crystal structure determination

The single crystals of **1b** and **Cp*Fe(CO)(py)(Me)** were grown by storing at –20 °C of the toluene solution, and the single crystals of **1d**, **1i**, **A**, **G**, and **E** were obtained from the slow diffusion of *n*-hexane into the concentrated toluene solution. The single crystals of **1j** were obtained from the slow evaporation of the acetone solution. The single crystals of **2e** were obtained by diffusion of *n*-hexane vapor into the chloroform solution. All crystals suitable for X-ray diffraction studies were separately mounted in a glass capillary. All of data were collected at 200 K on Rigaku AFC-7/Mercury CCD area-detector diffractometer equipped with monochromated MoKα radiation. All of calculations were performed with the CrystalClear software package of Molecular Structure Corporation. A full-matrix least-squares refinement was used for the non-hydrogen atoms with anisotropic thermal parameters. Hydrogen atoms were located by assuming the ideal geometry and were included in the structure calculation without further refinement of the parameters. CCDC-1441570 for **1b**, -1441571 for **1d**, -1441572 for **1i**, -1441573 for **1j**, -1441575 for **Cp*Fe(CO)(py)(Me)**, -1441673 for **A**, -1441672 for **G**, -1441576 for **E** and -1441574 for **2e** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystallographic data and details of structure refinement of vinylphosphines **1b**, **1d** and **1i**.

	1b	**1d**	**1i**
empirical formula	$C_{21}H_{19}P$	$C_{20}H_{18}NP$	$C_{24}H_{21}FeP$
formula weight	302.33	303.32	396.23
T (K)	200(2)	200(2)	200(2)
crystal system	Triclinic	Monoclinic	Orthorhombic
space group	$P1$	$P2_1/n$	$P2_12_12_1$
a (Å)	5.6674(19)	16.561(6)	9.5281(10)
b (Å)	8.267(3)	5.936(2)	11.4269(12)
c (Å)	9.097(3)	17.511(6)	17.881(2)
α (°)	101.836(8)		
β (°)	101.813(6)	111.673(3)	
γ (°)	92.712(6)		
volume (Å^3)	406.5(2)	1599.8(10)	1946.8(4)
Z	1	4	4
ρ_{calcd} (mg m^{-3})	1.235	1.259	1.352
μ (mm^{-1})	0.163	0.168	0.861
F(000)	160	640	824
crystal size (mm^3)	0.20 × 0.10 × 0.06	0.22 × 0.13 × 0.09	0.25 × 020× 0.15
reflections collected	4016	15615	19332
independent reflections (R(int))	2565 (0.357)	3643 (0.0229)	4416 (0.0609)
$R1$ ($I > 2\sigma(I)$)	0.0439	0.0369	0.0602
w$R2$	0.0984	0.0962	0.1500
Goodness of fit	1.052	1.033	1.057

Table S2. Crystallographic data and details of structure refinement of vinylphosphine **1j**, diphosphine **2e** and iron complex **Cp*Fe(CO)(py)(Me)**.

	1j	**2e**	**Cp*Fe(CO)(py)(Me)**
empirical formula	$C_{22}H_{22}NP$	$C_{34}H_{33}NP_2$	$C_{17}H_{23}FeNO$
formula weight	331.38	517.55	313.21
T (K)	200(2)	200(2)	200(2)
crystal system	Monoclinic	monoclinic	Monoclinic
space group	$P2_1/n$	$P2_1/c$	$P2_1/m$
a (Å)	13.7817(11)	18.2866(7)	7.4495(18)
b (Å)	5.8294(4)	6.0518(2)	13.489(3)
c (Å)	22.8279(17)	25.5425(10)	8.484(2)
α (°)			
β (°)	97.672(4)	94.9633(17)	112.353(4)
γ (°)			
volume (Å^3)	1817.6(2)	2816.11(18)	788.5(3)
Z	4	4	2
ρ_{calcd} (mg m^{-3})	1.211	1.221	1.319
μ (mm^{-1})	0.153	0.178	0.952
F(000)	704	1096	332
crystal size (mm^3)	0.25 × 0.15 × 0.05	0.45 × 0.08 × 0.03	0.40 × 0.20 × 0.04
reflections collected	12917	20552	7239
independent reflections (R(int))	4105 (0.0418)	6233 (0.0327)	1846 (0.0398)
$R1$ ($I > 2\sigma(I)$)	0.0518	0.0486	0.0390
w$R2$	0.1148	0.1013	0.0923
Goodness of fit	1.072	1.086	1.128

Table S3. Crystallographic data and details of structure refinement of iron complexes **A**, **G** and **E**.

	A	**G**	**E**
empirical formula	$C_{24}H_{29}FeOP$	$C_{35}H_{36}FeOP_2$	$C_{31}H_{31}FeOP$
formula weight	420.29	590.43	506.38
T (K)	200(2)	200(2)	200(2)
crystal system	Triclinic	Triclinic	Monoclinic
space group	P-1	P-1	$P2_1/c$
a (Å)	8.282(0)	10.82650(10)	13.439(4)
b (Å)	9.82860(10)	11.986(0)	9.537(3)
c (Å)	14.55090(10)	13.0.692(4)	20.110(5)
α (°)	74.635(7)	81.455(7)	
β (°)	73.740(8)	88.558(7)	91.374(4)
γ (°)	75.570(7)	63.176(4)	
volume (Å^3)	1076.606(13)	1494.99(5)	2576.7(12)
Z	2	2	4
ρ_{calcd} (mg m^{-3})	1.297	1.312	1.305
μ (mm^{-1})	0.785	0.638	0.669
F(000)	444	620	1064
crystal size (mm^3)	0.45 × 0.10 × 0.05	0.35 × 0.35 × 0.30	0.45 × 0.07 × 0.04
reflections collected	12543	16586	19594
independent reflections (R(int))	4765 (0.0252)	6571 (0.0176)	5823 (0.0553)
$R1$ ($I > 2\sigma(I)$)	0.0383	0.0345	0.0760
w$R2$	0.0895	0.0890	0.1397
Goodness of fit	1.061	1.059	1.164

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S7. A P-P coupling is expected to be observed. However, the coupling pattern was not observed at room temperature and even at –55 °C. As the similar no P-P coupling observation between phosphine and phosphide ligands has been reported for a ruthenium complex (M.-A. M. Hoyle, D. A. Pantazis, H. M. Burton, R. McDonald, and L. Rosenberg, *Organometallics*, **2011**, *30*, 6458-6465). Therefore, our observation might be reasonable.

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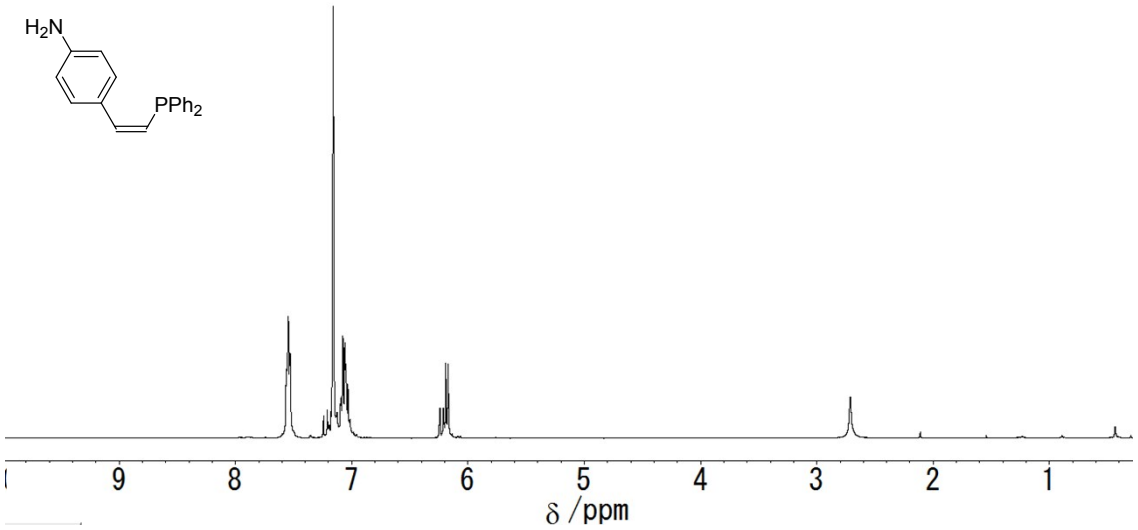
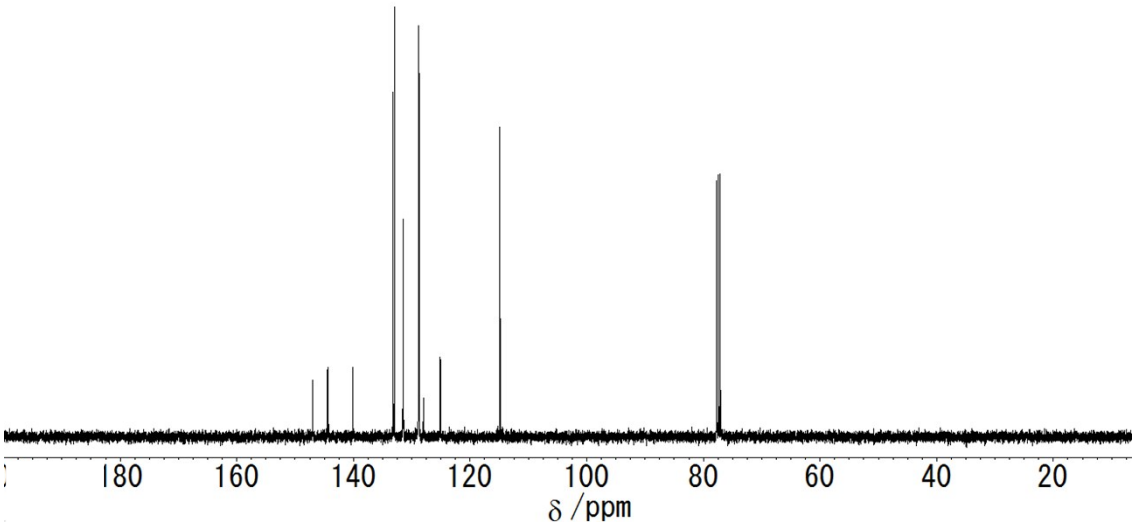
NMR spectra of **1d**

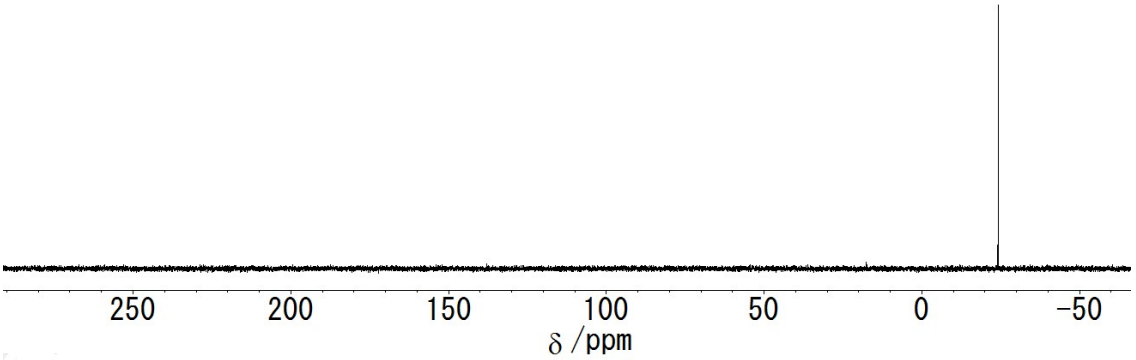
^{1}H NMR



^{13}C{^{1}H} NMR

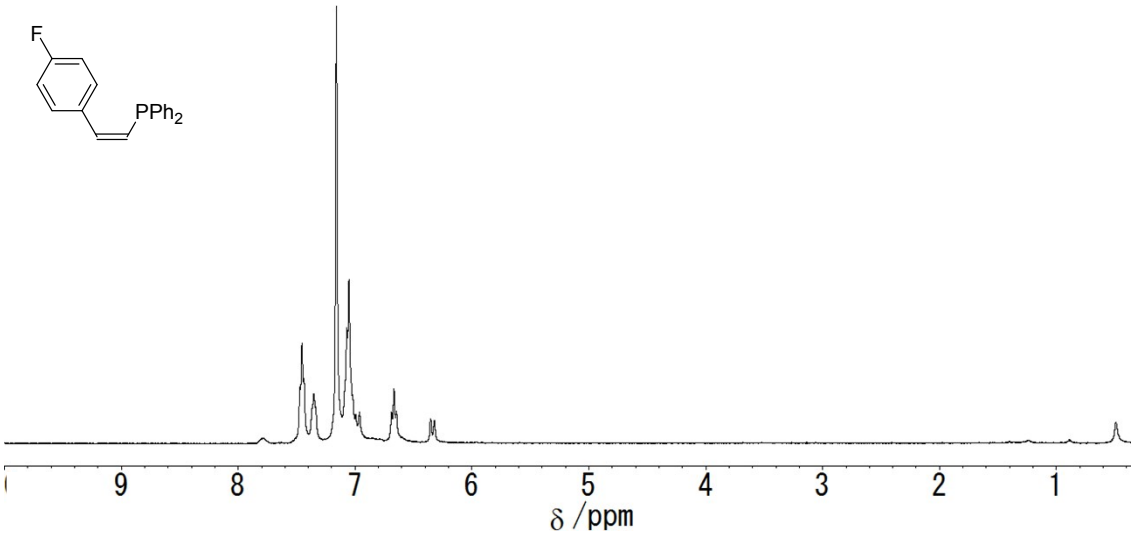


^{31}P{^{1}H} NMR



NMR spectra of **1e**

^{1}H NMR



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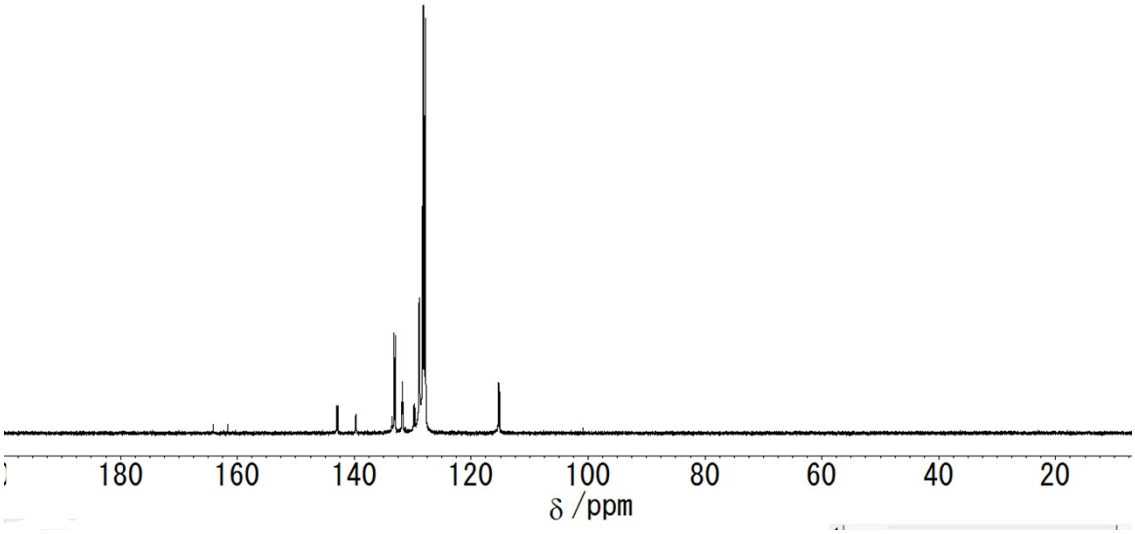

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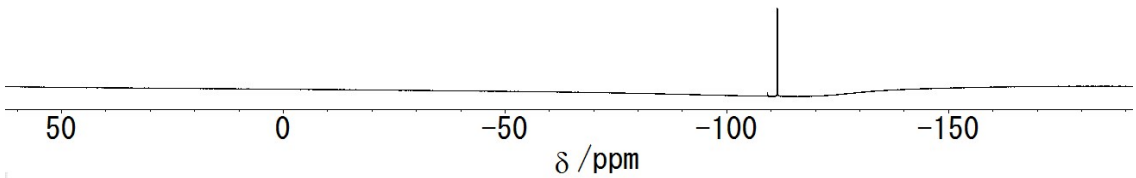

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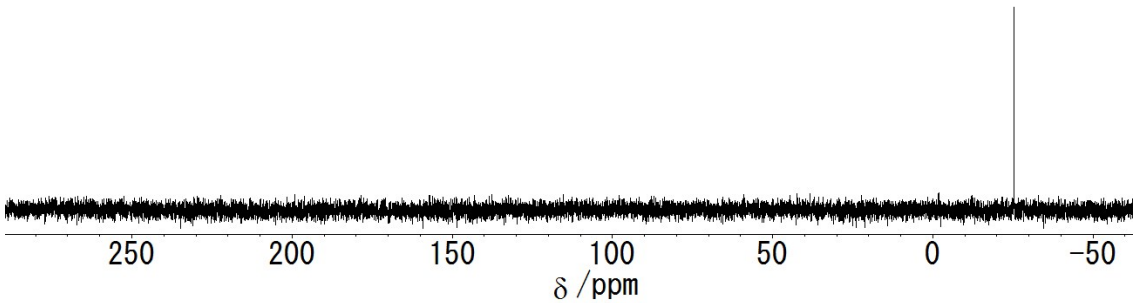
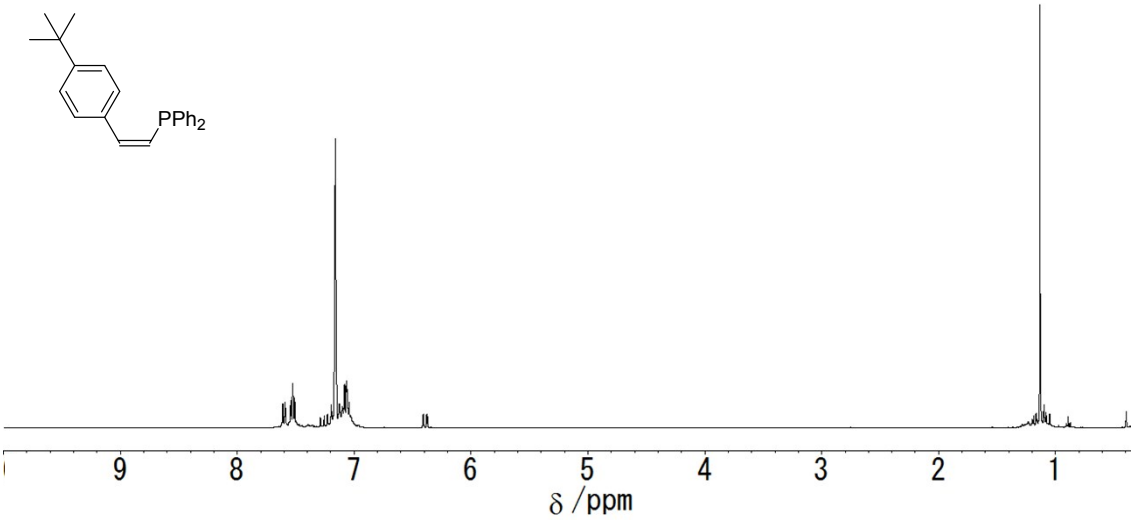


NMR spectra of **1f**

^{1}H NMR



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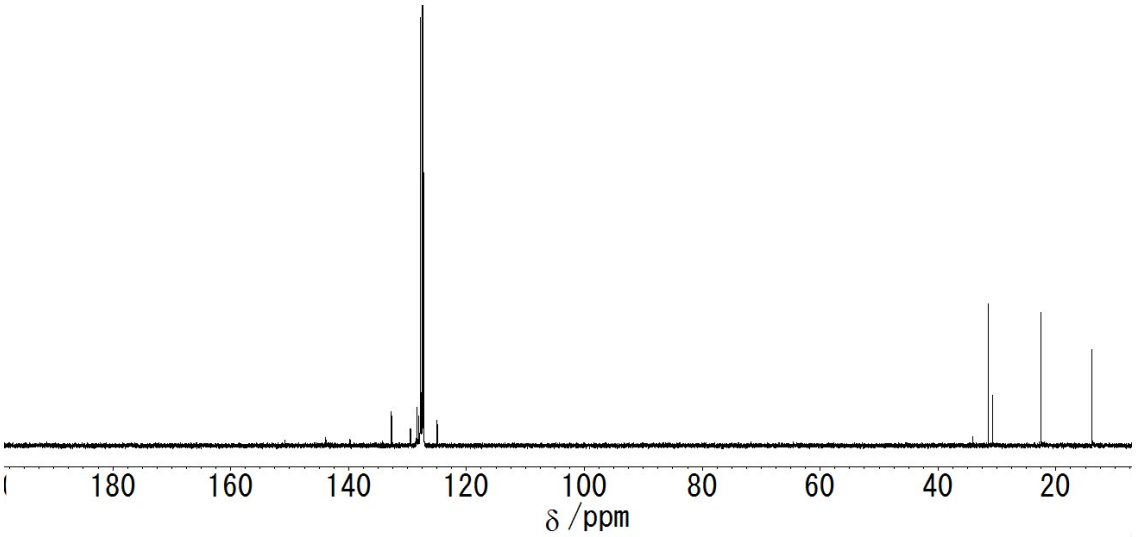

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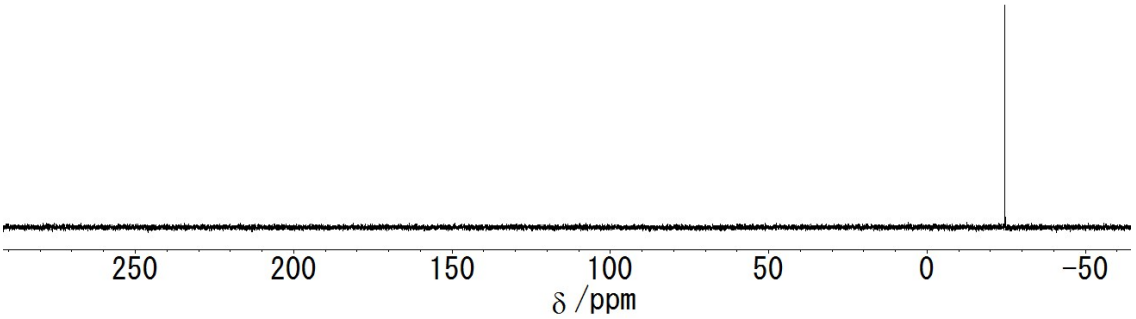
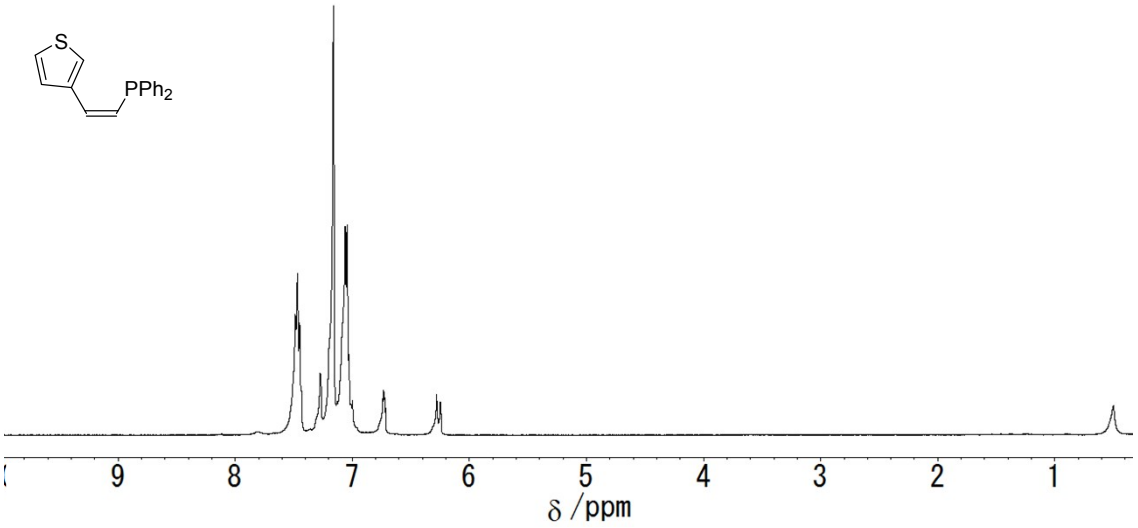


NMR spectra of **1h**

^{1}H NMR



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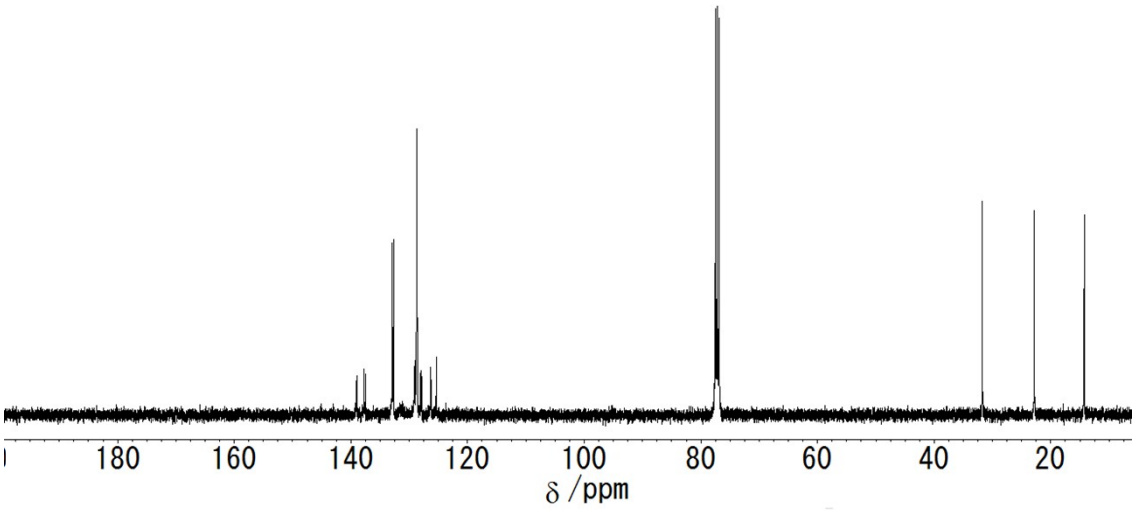

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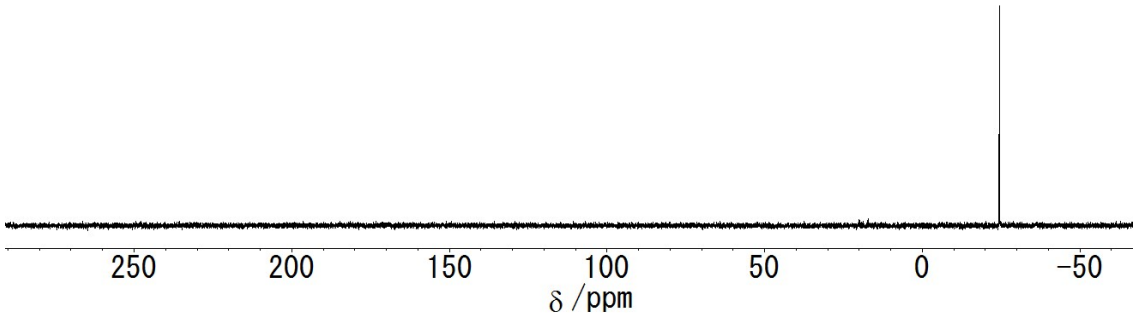
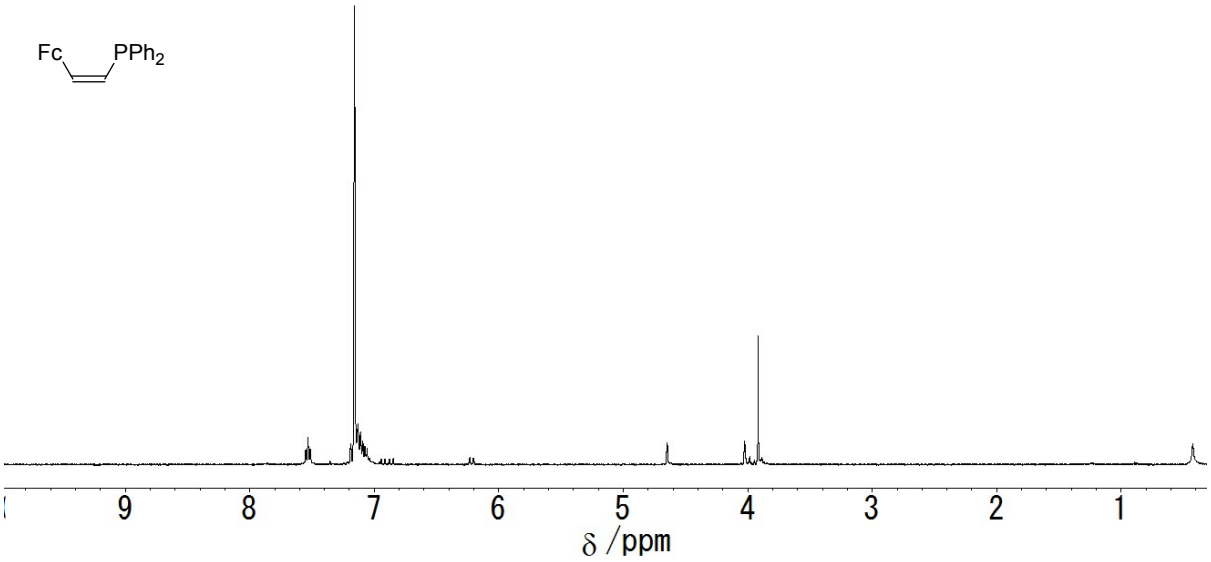
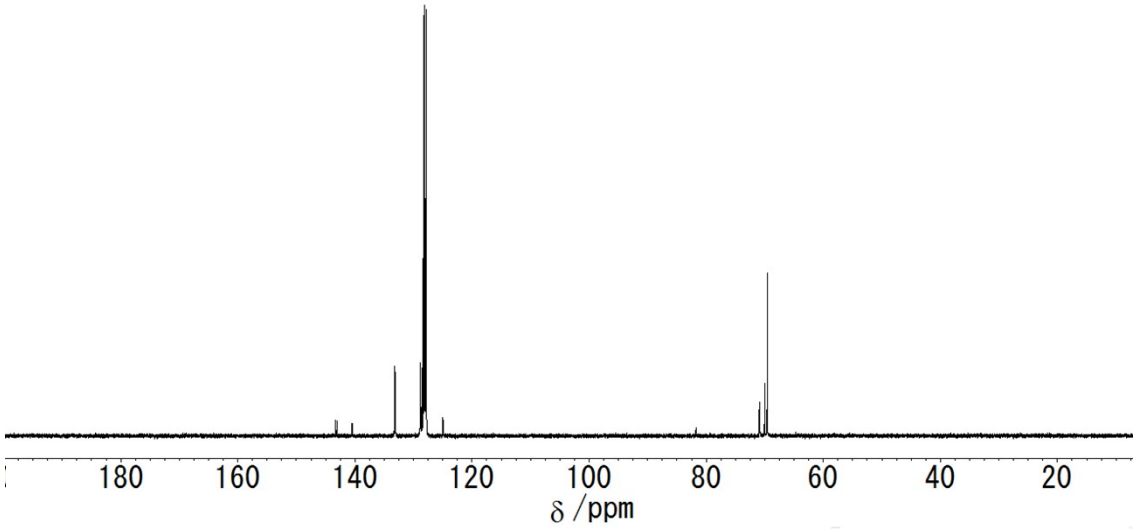


NMR spectra of **1i**

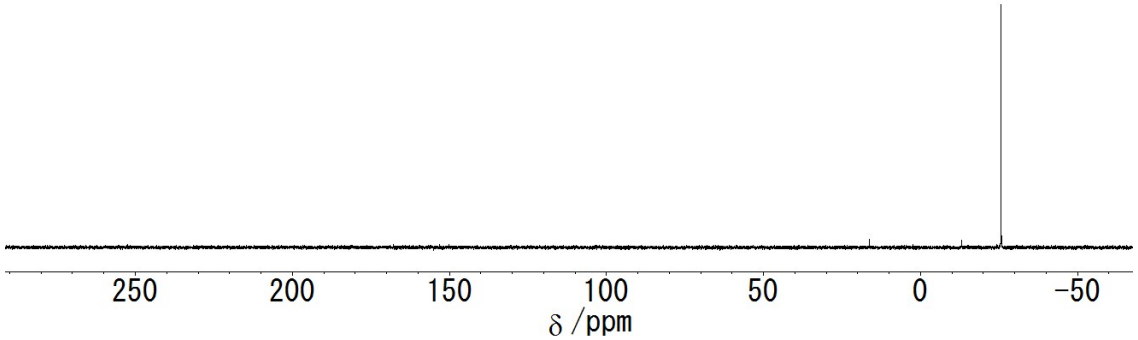
^{1}H NMR



^{13}C{^{1}H} NMR

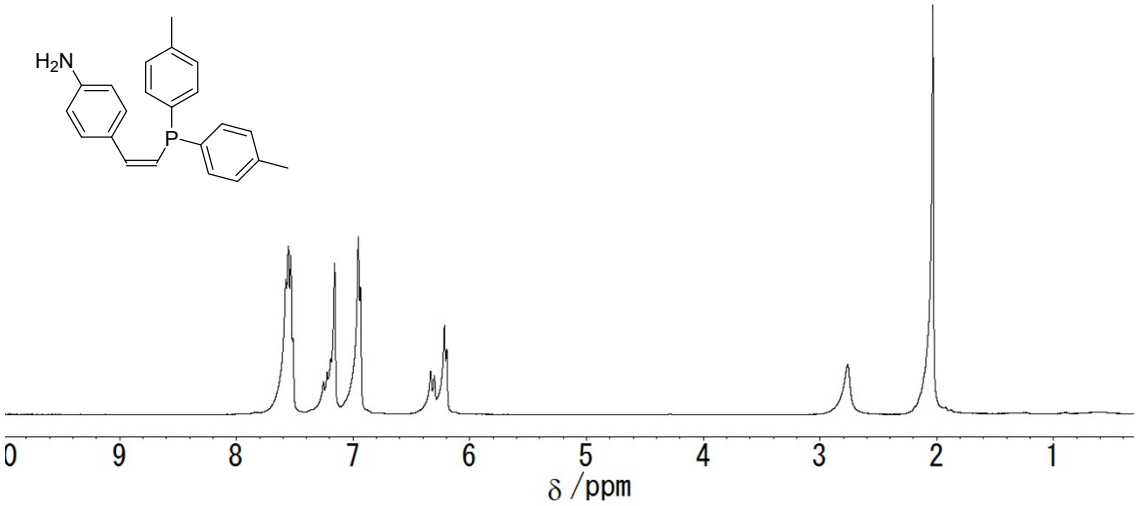


^{31}P{^{1}H} NMR



NMR spectra of **1j**

^{1}H NMR



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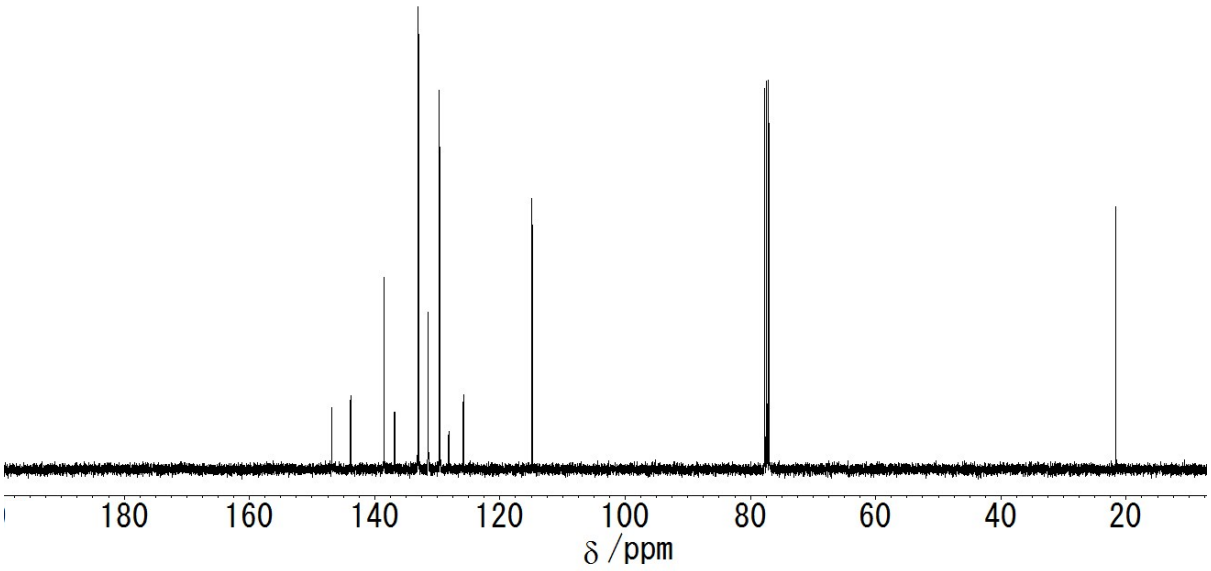

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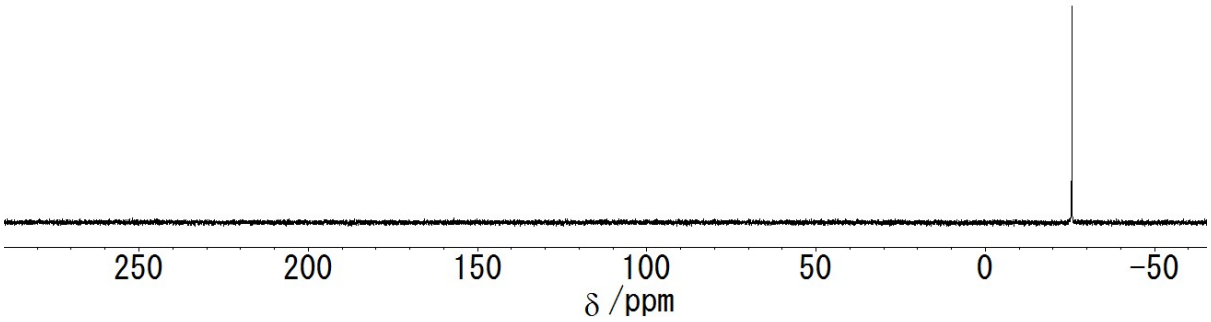

NMR spectra of **1k**

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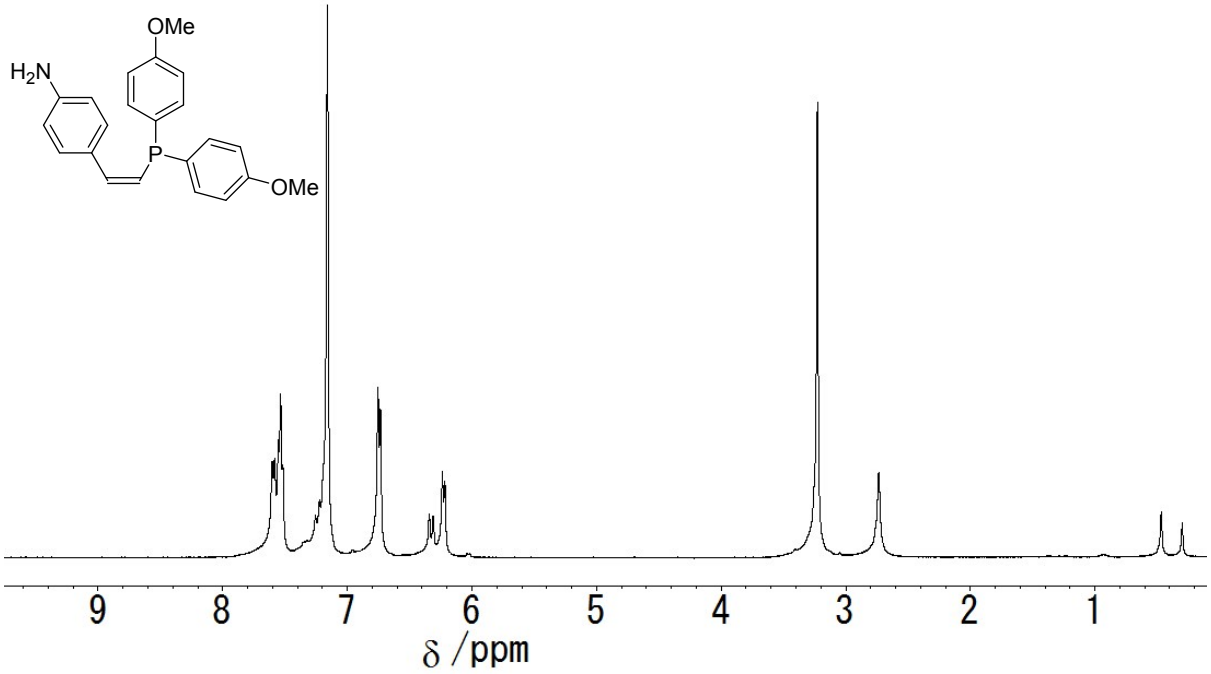

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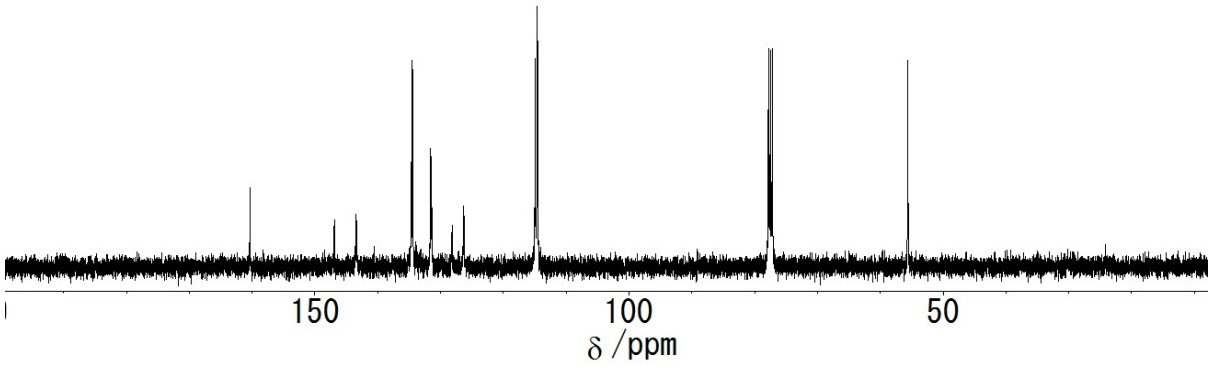
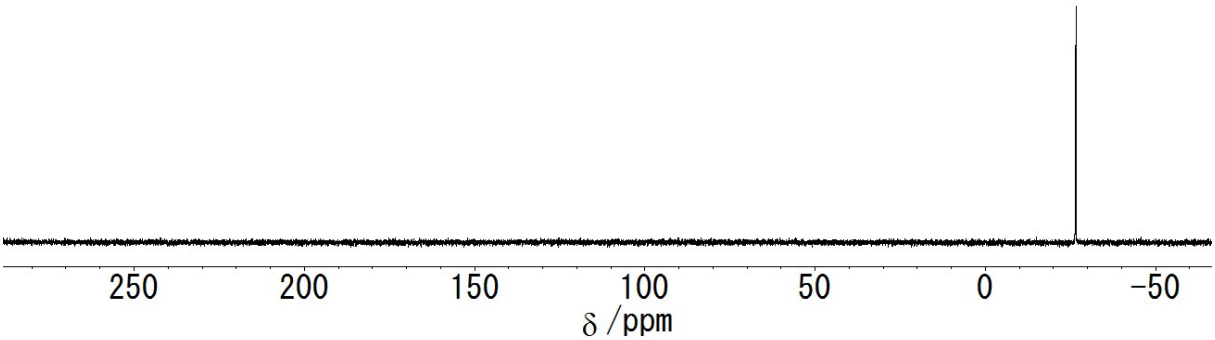
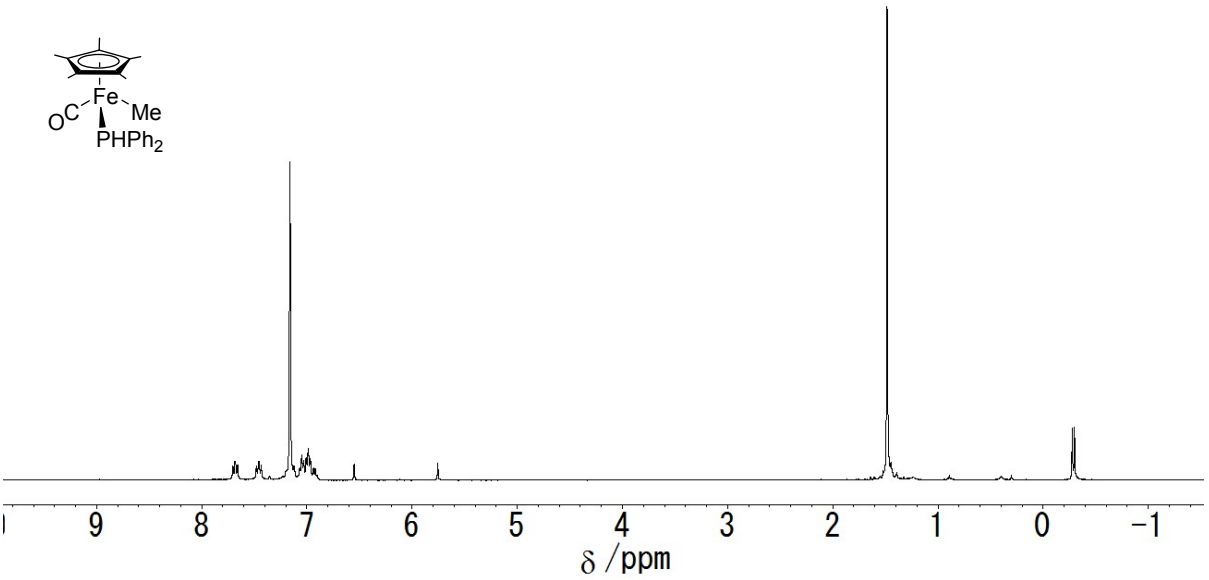


^{31}P{^{1}H} NMR



NMR spectra of **A**

^{1}H NMR



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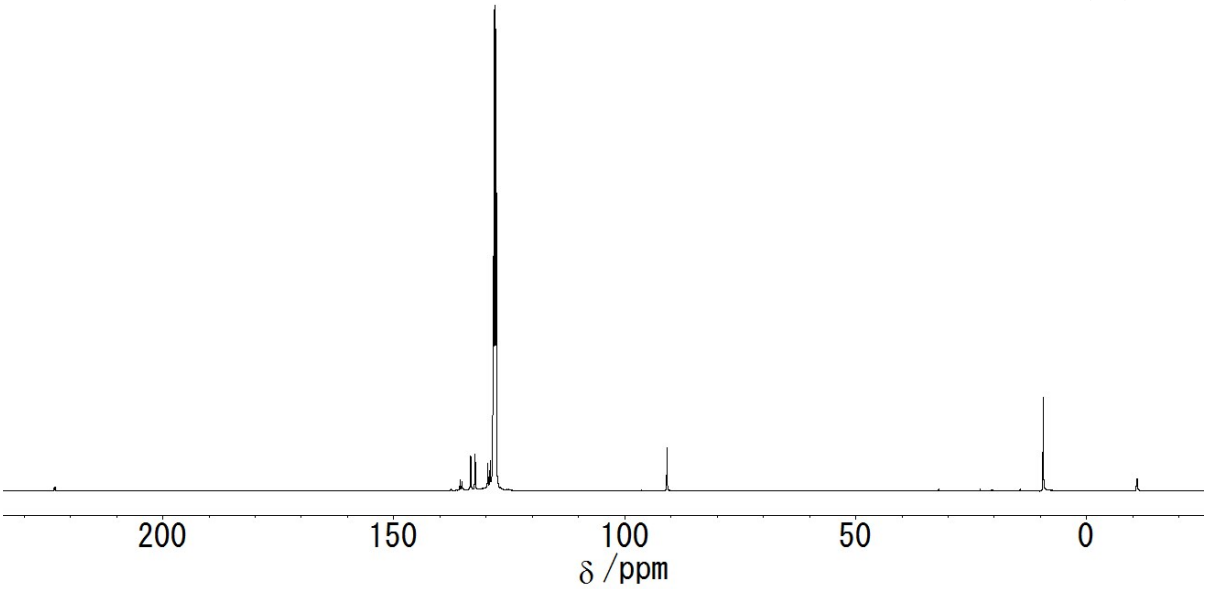
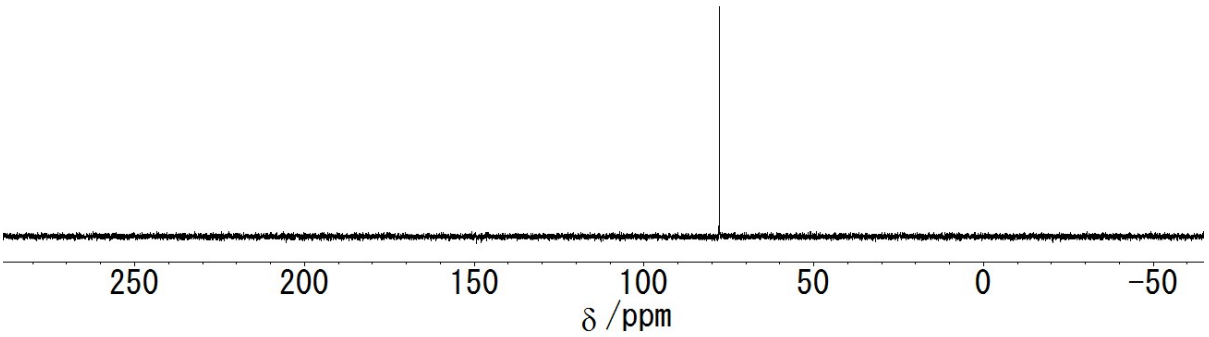
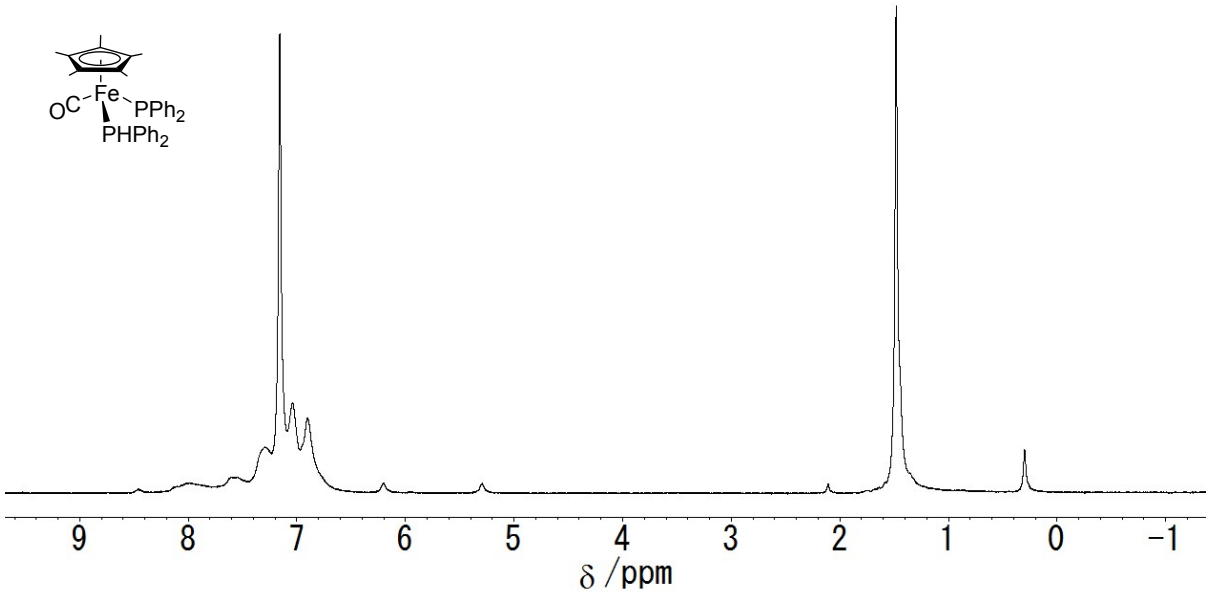


^{31}P{^{1}H} NMR

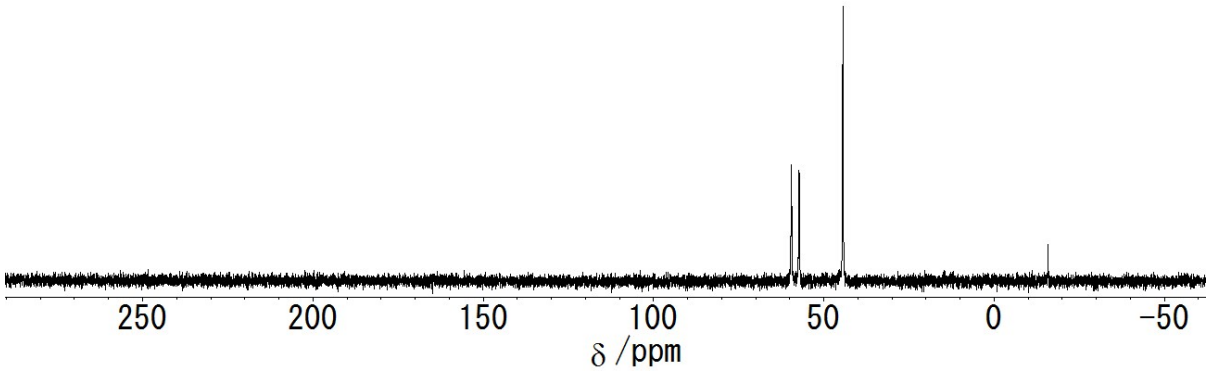


NMR spectra of **G**

^{1}H NMR

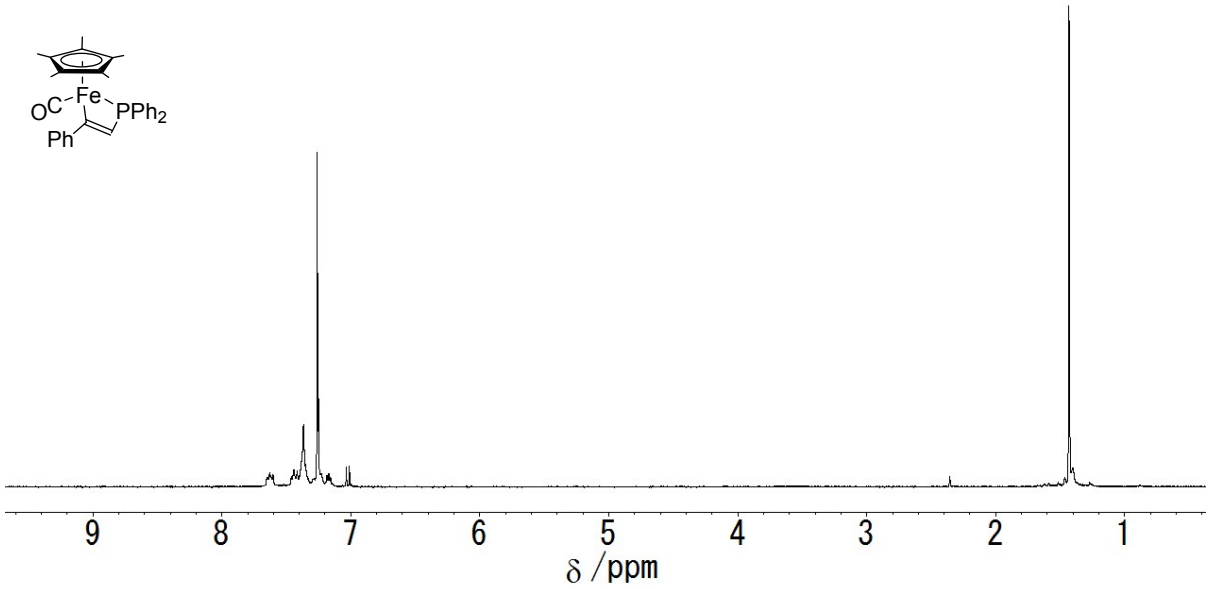


^{31}P NMR

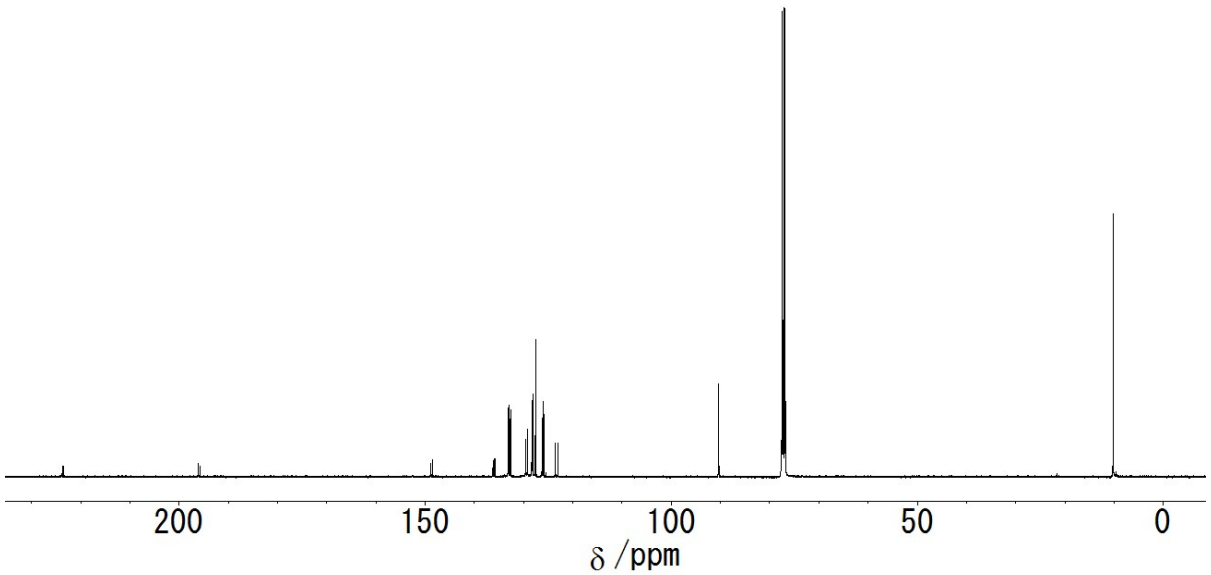


NMR spectra of **E**

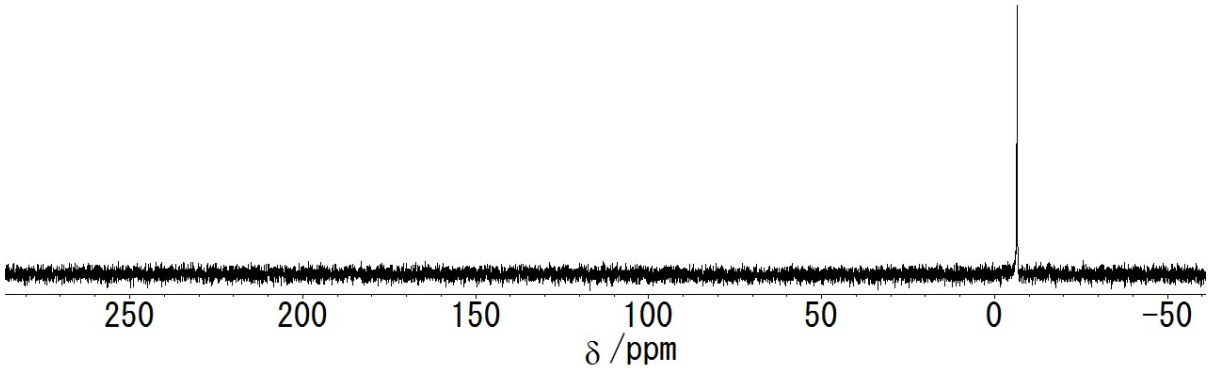
^{1}H NMR



^{13}C{^{1}H} NMR

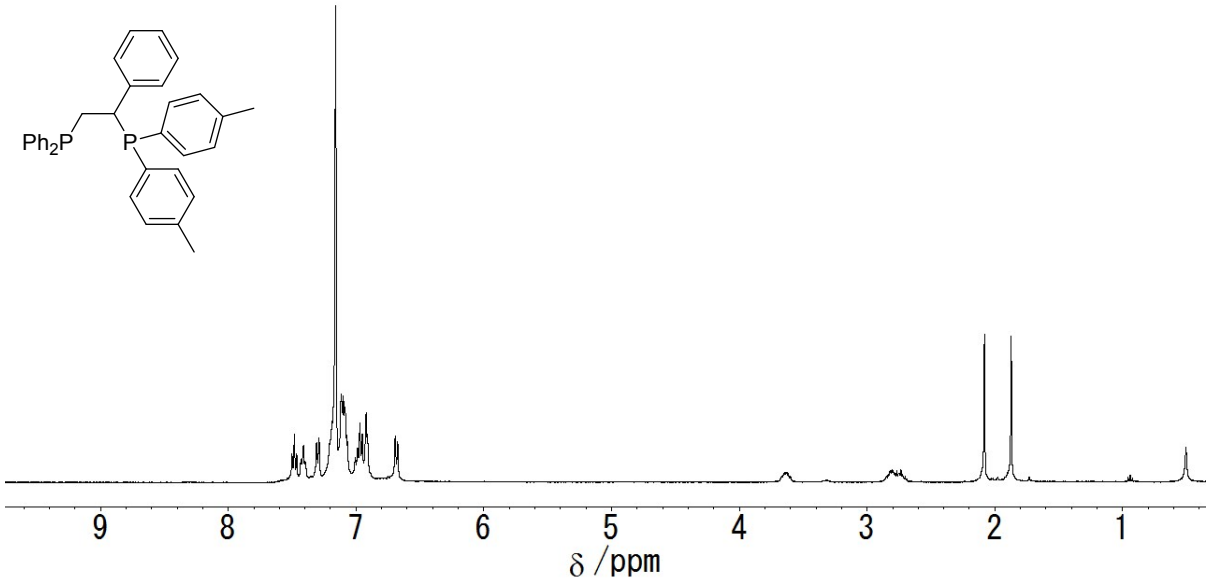


^{31}P{^{1}H} NMR

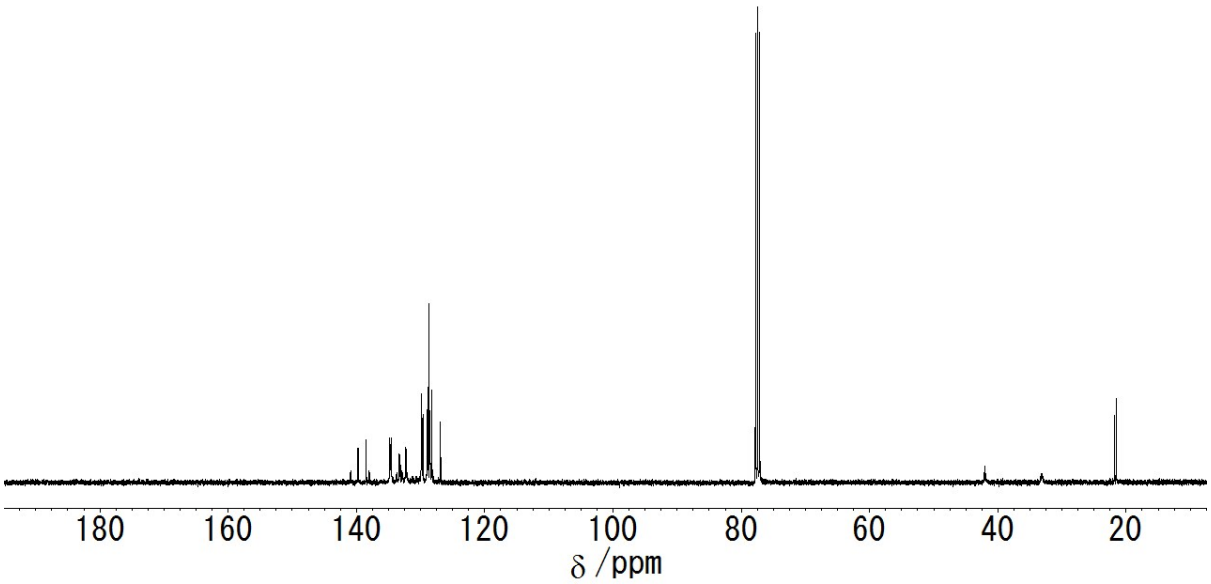


NMR spectra of **2b**

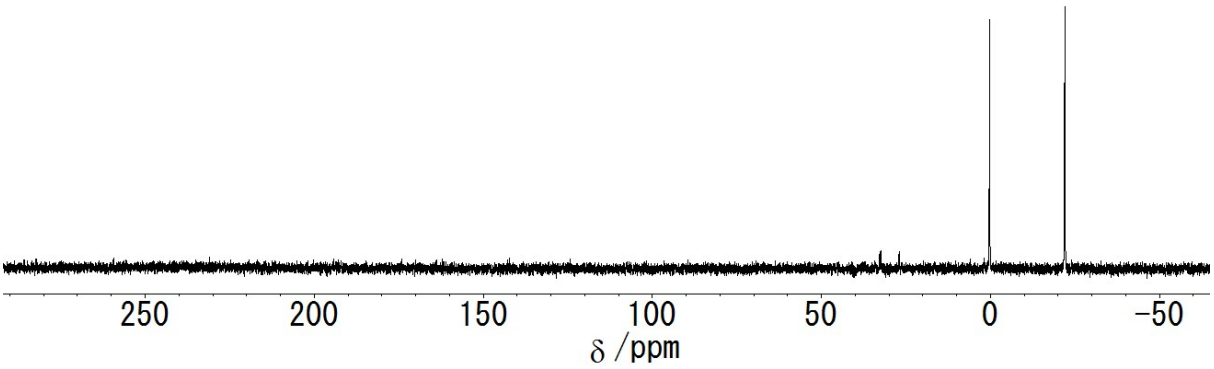
^{1}H NMR



$^{13}C\{^{1}H\}$ NMR

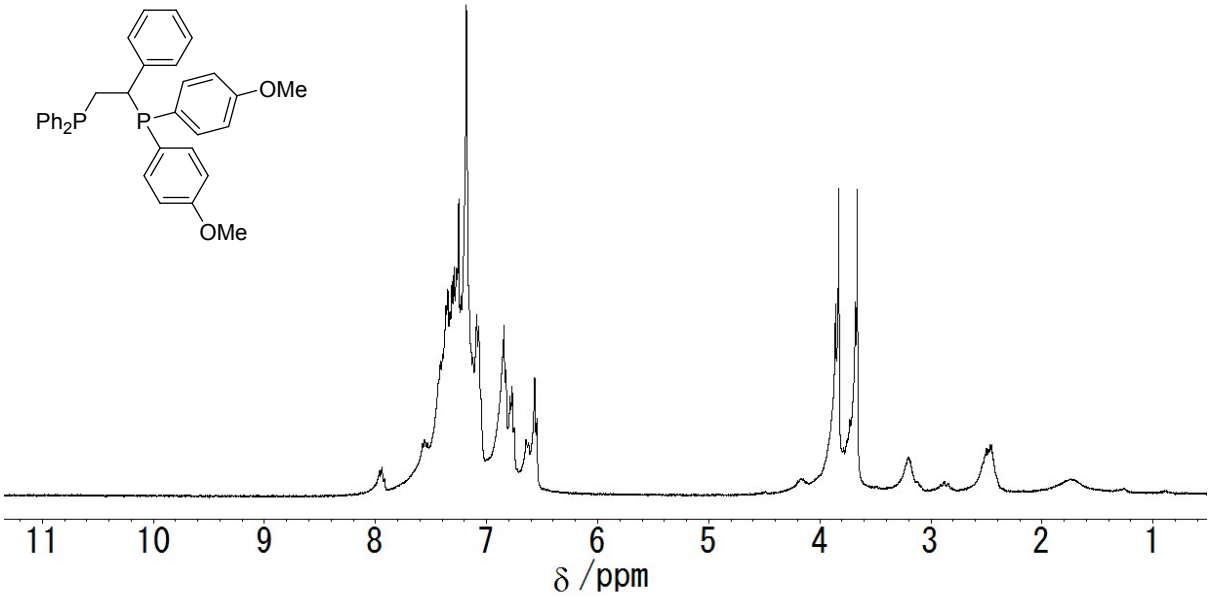


$^{31}P\{^{1}H\}$ NMR

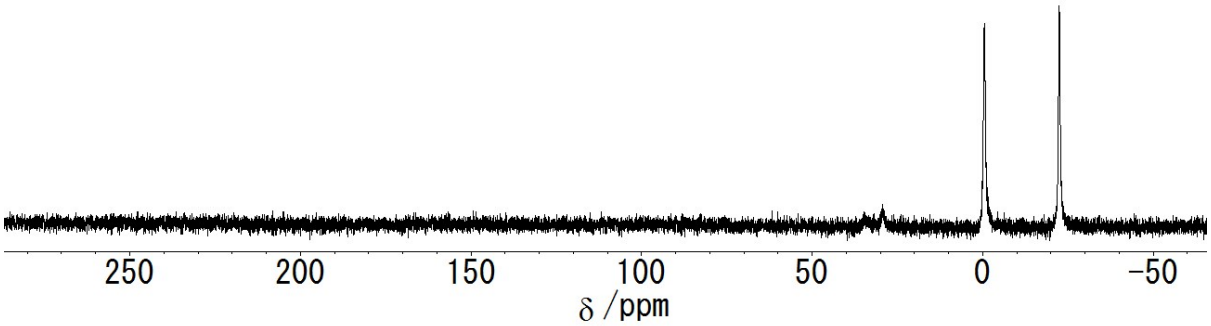


NMR spectra of **2c**

^{1}H NMR

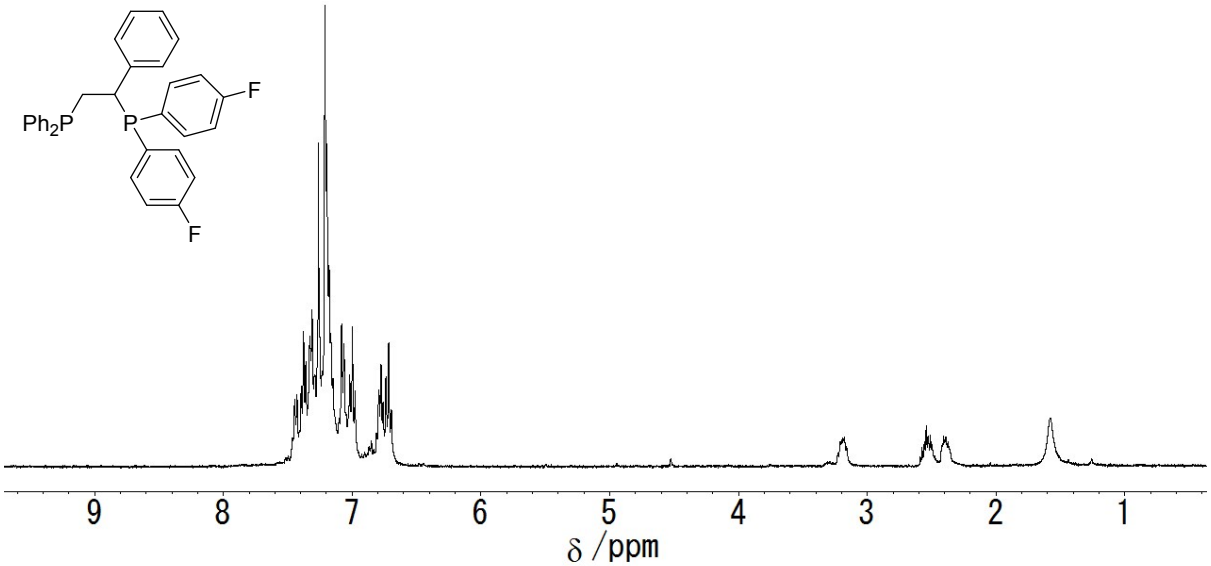


^{31}P{^{1}H} NMR

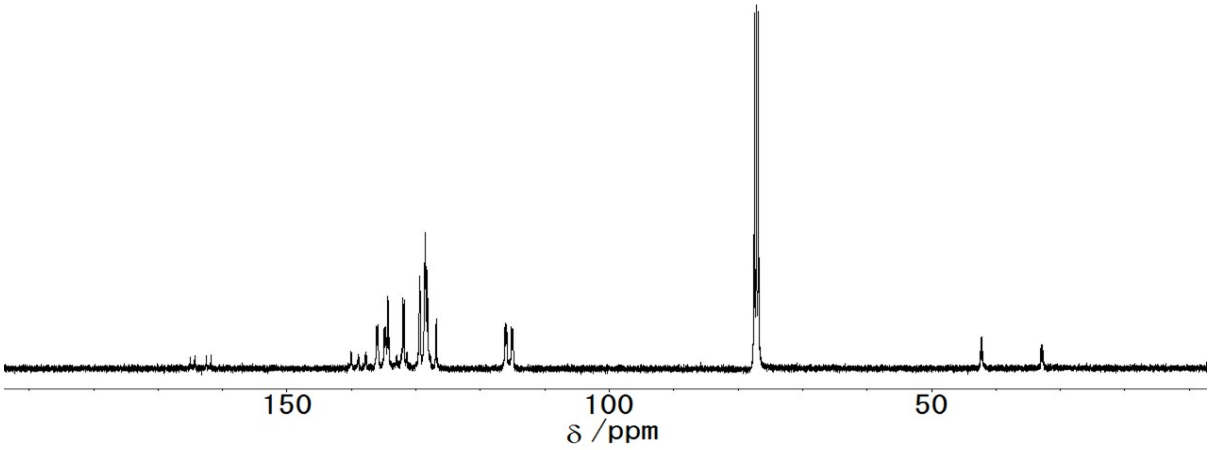


NMR spectra of **2d**

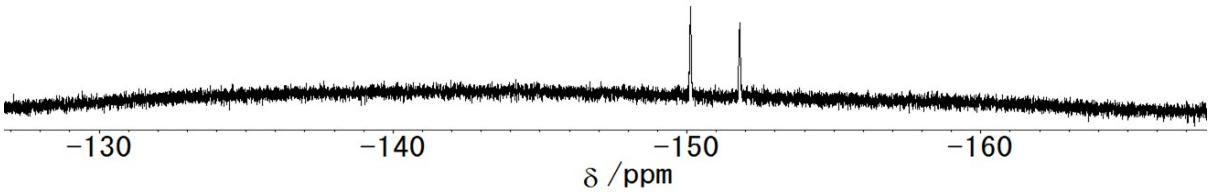
^{1}H NMR



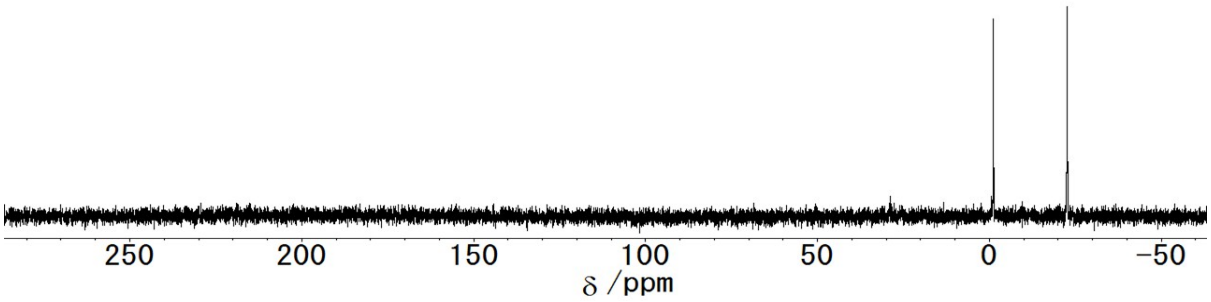
^{13}C{^{1}H} NMR



^{19}F NMR

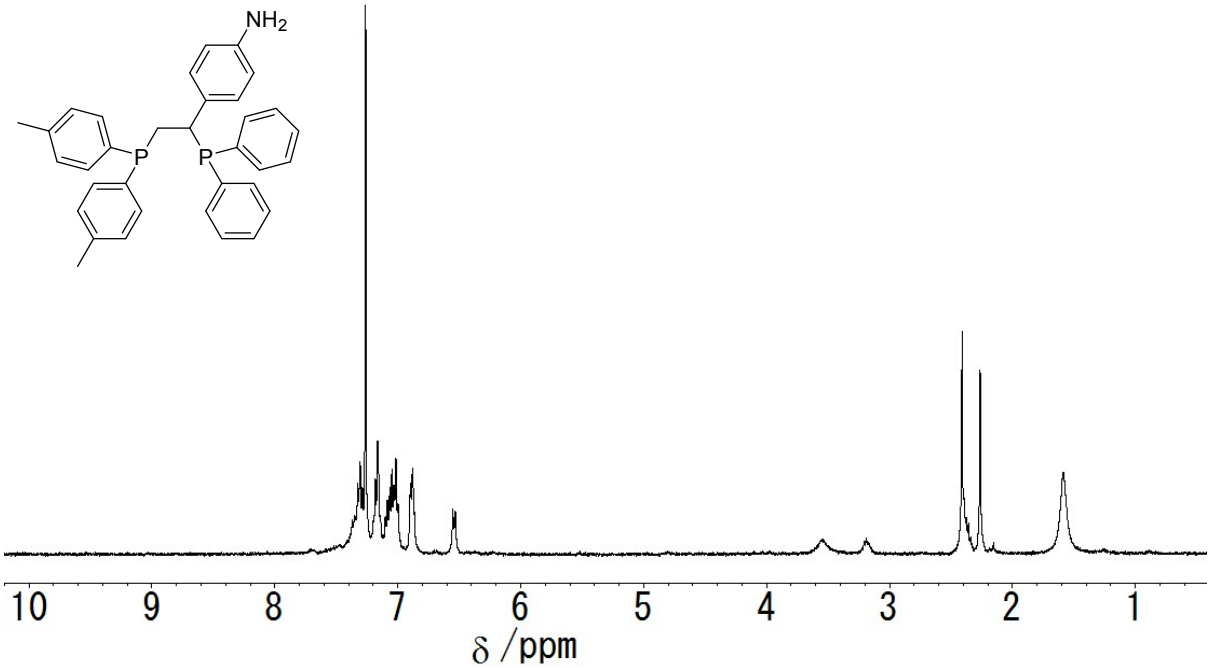


^{31}P{^{1}H} NMR

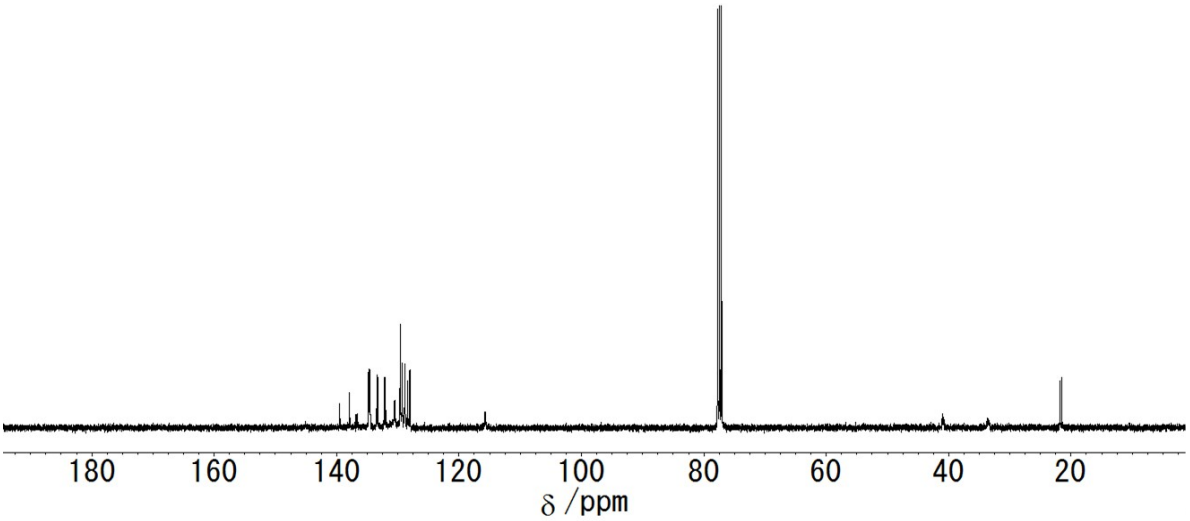
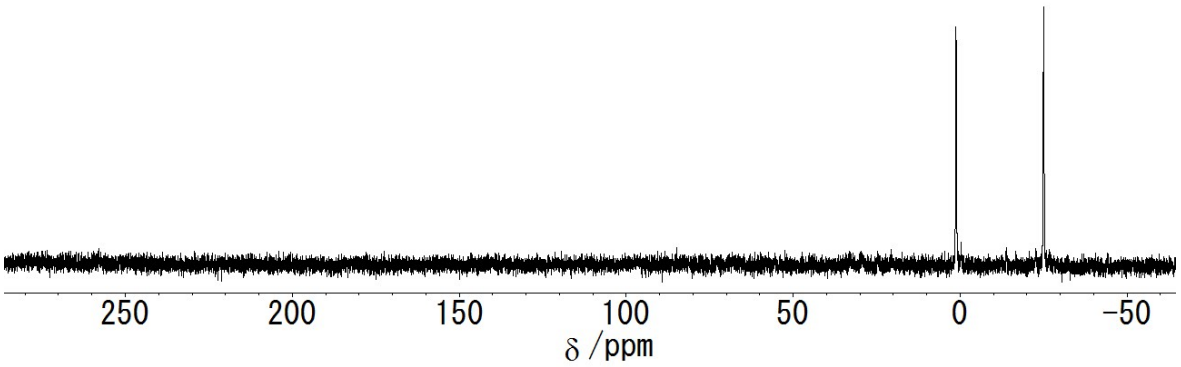


NMR spectra of **2e**

^{1}H NMR



^{13}C{^{1}H} NMR



^{31}P{^{1}H} NMR