Supplementary Material (ESI) for Chemical Communications

Supporting Information

Synthesis and coordination behaviors of P-stereogenic polymers

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Contents:

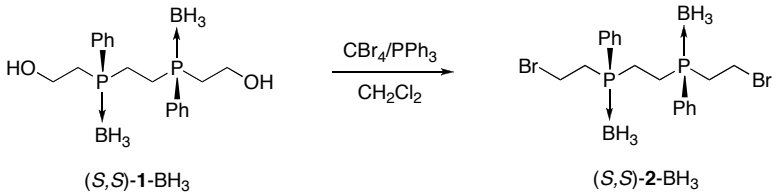
General

^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a JEOL EX 400 spectrometer, and samples were analyzed in $CDCl_3$ or DMF-d_7 using Me_4Si as an internal standard. ^{31}P (161.9 MHz) NMR spectra were also recorded on a JEOL EX 400 spectrometer, and samples were analyzed in $CDCl_3$ or DMF-d_7 using H_3PO_4 as an external standard. The following abbreviations are used; s: singlet, d: doublet, t: triplet, m: multiplet, q: quartet, sep: septet, and br: broad. High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-SX102A spectrometer. Enantiomeric purity was confirmed by a HPLC (TOSOH UV-8020) equipped with a Daicel Chiralcel OD-H column (0.46 cm × 25 cm) using 2-propanol/hexane as an eluent. Optical rotations were measured on a Rudolph Research Analytical AUTOPOL IV instrument using $CHCl_3$ as a solvent. Column chromatography was performed with Wakogel C-300 SiO_2. Elemental analysis was performed at the Microanalytical Center of Kyoto University.

Materials

THF was purchased and purified by passage through purification column under Ar pressure.[1] Dehydrated grade solvents of toluene and $CHCl_3$ were purchased and used without further purification. *N,N,N',N'*-Tetramethylethylenediamine (TMEDA), (–)-sparteine, and 1,4-diazabicyclo[2.2.2]octane (DABCO) were purchased and distilled from KOH under Ar atmosphere. *sec*-BuLi (1.0 M in cyclohexane and *n*-hexane solution), BH_3·THF (1.0 M in THF), CuI, aqueous NH_3 (28%), NaH (60 wt% in mineral oil), triethyleneglycol bis(*p*-toluenesulfonate), $PdCl_2$(cod), and $PtCl_2$(cod) were purchased and used without purification. Compounds (*S,S*)-**1**-BH_3[2] and **4**[3] were prepared by the procedure of the literature. All reactions were performed under Ar atmosphere using standard Schlenk techniques.

Synthesis of (*S,S*)-2-BH_3

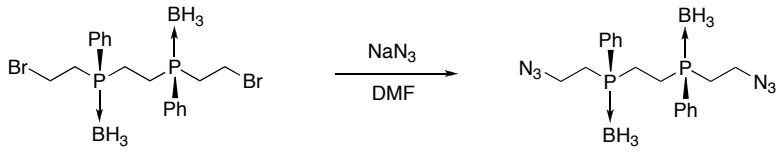


(*S,S*)-**1**-BH_3 (*S,S*)-**2**-BH_3

A solution of (*S,S*)-**1**-BH_3 (1.09 g, 3.0 mmol) and PPh_3 (3.15 g, 12 mmol) in CH_2Cl_2 (30 mL) was cooled to –78 °C under Ar atmosphere. To the stirred solution, CBr_4 (3.58 g, 10.8 mmol) was added in one portion. After 15 minutes, the reaction mixture was allowed to gradually warm to room temperature. After stirring for additional 6 h at room temperature, the reaction mixture was evaporated. The residue was subjected to column chromatography on SiO_2 with hexane/EtOAc (v/v = 1:1). The solvent was removed in vacuo, and recrystallization from toluene and hexane gave (*S,S*)-**2**-BH_3 (1.18 g, 2.4 mmol, 80%) as a colorless solid.

R_f = 0.80 (hexane/EtOAc: v/v = 1:1); $[\alpha]^{26}_D$ 48.4 (*c* 0.5 in $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz δ 0.7 (br q, J_{HB} = 129.8 Hz, -B*H*$_3$, 6H), 1.85 (m, -PC*H*$_2$-, 2H), 2.17 (m, -PC*H*$_2$-, 2H), 2.50 (m, -PC*H*$_2$-, 4H), 3.19 (m, -C*H*$_2$Br, 2H), 3.50 (m, -C*H*$_2$Br, 2H), 7.40-7.51 and 7.54-7.61 (m, -C$_6$*H*$_5$, 10H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.0 (d, J_{CP} = 34.6 Hz, -P*C*H$_2$-), 24.3 (s, -*C*H$_2$Br), 30.2 (d, J_{CP} = 30.5 Hz, -P*C*H$_2$-), 125.1 (d, -*C*$_6$H$_5$, J_{CP} = 50.0 Hz), 129.3 (-*C*$_6$H$_5$), 131.9 (-*C*$_6$H$_5$), 132.3 (-*C*$_6$H$_5$) ppm; ^{31}P{^{1}H}NMR ($CDCl_3$, 161.9 MHz) δ +18.1 ppm. HRMS (FAB) calcd. for $C_{18}H_{28}B_2Br_2P_2$ $[M]^+$: 486.0219, found 486.0204. Anal. calcd. for $C_{18}H_{28}B_2Br_2P_2$: C 44.32; H 5.79; found: C 44.10; H 5.79.

Synthesis of (*S,S*)-3-BH_3

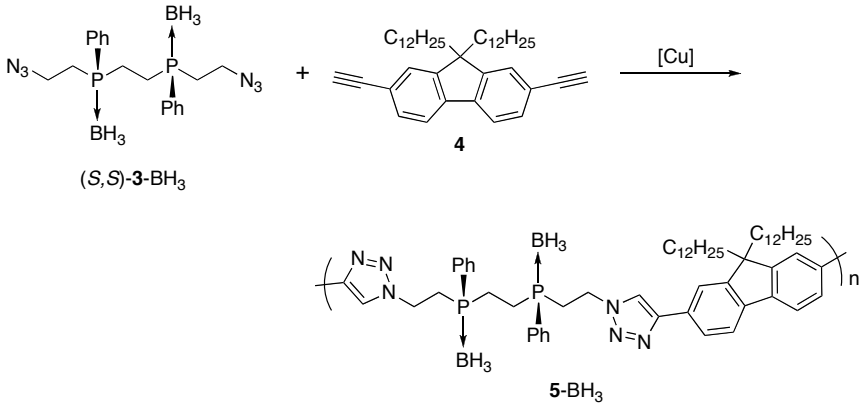


(*S,S*)-**2**-BH_3 (*S,S*)-**3**-BH_3

A solution of (*S,S*)-**2**-BH_3 (732 mg, 1.5 mmol) and NaN_3 (390 mg, 6.0 mmol) in DMF (5.0 mL) was stirred at room temperature under Ar atmosphere. After stirring overnight, the reaction mixture was treated with saturated NH_4Claq and extracted with EtOAc (30 mL × 3). The organic layer was dried over $MgSO_4$. $MgSO_4$ was removed by filtration, and the solvent was removed in vacuo. The residue was subjected to column chromatography on SiO_2 with hexane/EtOAc (v/v = 1:1). The solvent was removed in vacuo, the compound was purified by preparative HPLC ($CHCl_3$) and recrystallization from toluene and hexane to obtain (*S,S*) -**3**-BH_3 (276.0 mg, 0.67 mmol, 45%) as a colorless solid.

R_f = 0.80 (hexane/EtOAc: v/v = 1:1); $[\alpha]^{26}_D$ 42.9 (*c* 0.5 in $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz δ 0.7 (br q, J_{HB} = 122.5 Hz, -B*H*$_3$, 6H), 1.87 (m, -PC*H*$_2$-, 2H), 2.04-2.26 (m, -PC*H*$_2$-, 6H), 3.31 (m, -C*H*$_2$N$_3$, 2H), 3.57 (m, -C*H*$_2$N$_3$, 2H), 7.46-7.51 (m, -C$_6$*H*$_5$, 4H), 7.52-7.67 (m, -C$_6$*H*$_5$, 6H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.3 (d, J_{CP} = 35.4 Hz, -P*C*H$_2$-), 25.8 (d, -P*C*H$_2$- J_{CP} = 33.8 Hz, -P*C*H$_2$-), 45.7 (-*C*H$_2$N$_3$), 125.7 (d, J_{CP} = 55.2 Hz, -*C*$_6$H$_5$), 129.3 (-*C*$_6$H$_5$), 131.9 (-*C*$_6$H$_5$), 132.3 (-*C*$_6$H$_5$) ppm; ^{31}P{^{1}H}NMR ($CDCl_3$, 161.9 MHz) δ +16.0 ppm. HRMS (FAB) calc. for $C_{18}H_{28}N_6P_2B_2$ $[M-H]^+$ 411.1959, found 411.1961. Anal. calcd. for $C_{18}H_{28}N_6P_2B_2$: C 52.47; H 6.85; N 20.40, found: C 52.24; H 6.92; N; 20.11.

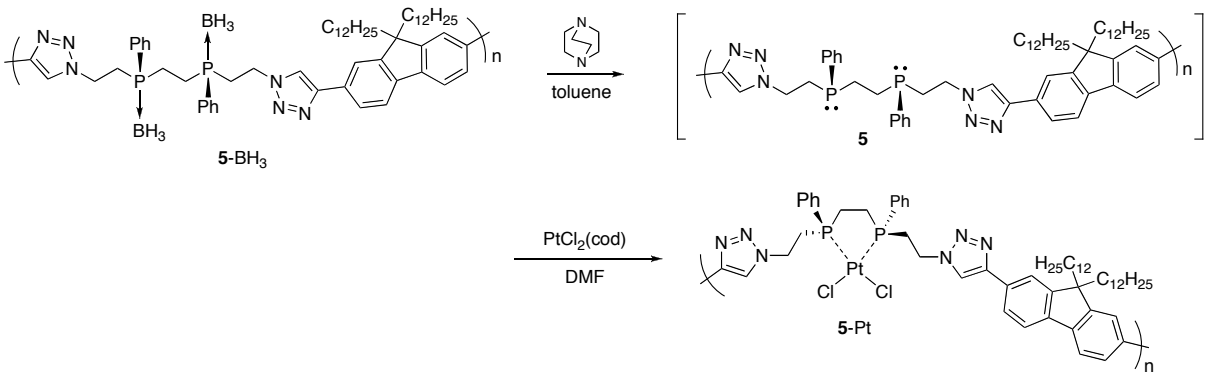
Synthesis of polymer 5-BH_3



A solution of (*S,S*)-**3**-BH_3 (61.8 mg, 0.15 mmol), 9,9-didodecyl-2,7-diehynylfluorene (**4**) (82.6 mg, 0.15 mmol), and $Cu(MeCN)_4PF_6$ (5.6 mg, 0.015 mmol) in DMF (1.5 mL) was stirred at 50 °C under Ar atmosphere. After stirring for 6 h, the reaction mixture was poured into 1% aqeous NH_3 and extracted with $CHCl_3$ (30 mL × 3). The organic layer was washed with 2 N HCl and brine, and then, it was dried over $MgSO_4$. $MgSO_4$ was removed by filtration, and the solvent was dried in vacuo. Reprecipitation from $CHCl_3$ and hexane gave polymer **5**-BH_3 (85.4 mg, 0.089 mmol, 59%) as a pale yellow solid.

$[\alpha]^{26}_D$ 15.9 (*c* 0.5 in $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.24-1.32 (m, -B*H*$_3$ and dodecyl-*H*), 1.78 (br, -PC*H*$_2$-), 1.90-2.18 (br, -PC*H*$_2$-), 2.55 and 2.74 (br, -PC*H*$_2$-), 4.47 and 4.68 (br, -C*H*$_2$-triazole-), 7.30-7.82 (m, -*Ar*) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.1, 19.4 (d, J_{cp} = 37.1 ppm, -P*C*H$_2$-), 22.6, 23.9, 26.8 (d, J_{CP} = 35.5 Hz, -P*C*H$_2$-), 29.2-30.1, 31.8, 40.5, 44.7 (-*C*H$_2$-triazole-), 55.4 (fluorene), 119.9-120.2, 124.3-124.9, 129.0-129.2, 131.9-132.4, 140.8, 148.0, 151.6 ppm; ^{31}P{^{1}H}NMR ($CDCl_3$, 161.9 MHz) δ +16.1 ppm.

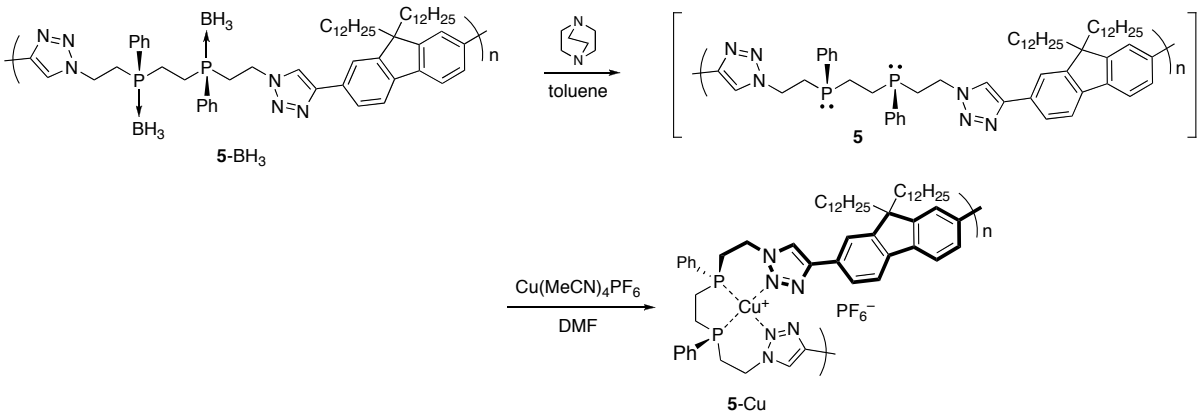
Synthesis of polymer 5-Pt



A solution of polymer **5**-BH_3 (48.1 mg, 0.05 mmol) and DABCO (56.1 mg, 0.50 mmol) in $CHCl_3$ (5.0 mL) was stirred at 50 °C under Ar atmosphere. After stirring for 6 h, the reaction mixture was poured into hexane under Ar atmosphere, and the solvent was removed with a syringe. The residue was solved in $CHCl_3$ (5.0 mL). To the $CHCl_3$ solution was added $PtCl_2$(cod) (18.7 mg, 0.05 mmol) under Ar atmosphere. After stirring for 12 h, the reaction mixture was poured into hexane to obtain polymer complex **5**-Pt as a pale yellow solid (38.0 mg, 0.032 mmol, 63%).

$[\alpha]^{25}_{D}$ 40.2 (*c* 0.5 in $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.64 (br -$C_{12}H_{25}$), 0.82 (br -$C_{12}H_{25}$), 0.94-1.26 (br -$C_{12}H_{25}$), 2.04 (br, -PCH_2-), 3.16 (br, -PCH_2-), 4.98 (br, -CH_2-triazole-), 7.37 (br, -*Ar*), 7.51-7.72 (br, -*Ar*), 7.78 (br, -*Ar*), 7.97 (br, -*Ar*) ppm; ^{31}P{^{1}H}NMR ($CDCl_3$, 161.9 MHz) δ +42.2 ($J_{P\text{-}Pt}$ = 3577 Hz) ppm.

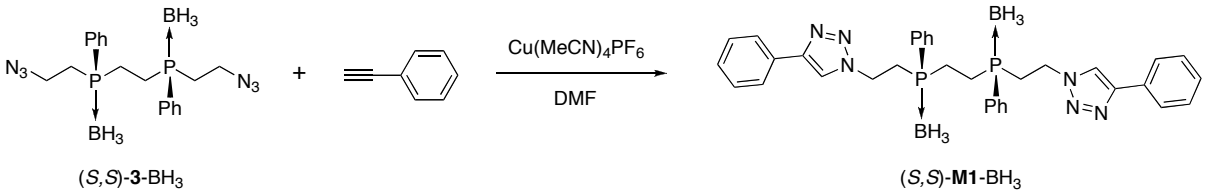
Synthesis of polymer 5-Cu



A solution of polymer **5**-BH_3 (28.9 mg, 0.03 mmol), DABCO (33.6 mg, 0.30 mmol) in $CHCl_3$ (3.0 mL) was stirred at 50 °C. After stirring for 6 h, the reaction mixture was poured into hexane under Ar atmosphere, and the solvent was removed with a syringe. The residue was solved in DMF (3.0 mL), and $Cu(MeCN)_4PF_6$ was added to the DMF solution. After stirring for 12 h, the reaction mixture was poured into toluene to obtain polymer **5**-Cu as a pale yellow solid (25.3 mg, 0.022 mmol, 73%).

$[\alpha]^{25}_{D}$ 8.4 (*c* 0.5 in $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.60-1.45 (br $-C_{12}H_{25}$), 1.93-2.48 (br, -PCH_2-), 4.87 (br, -CH_2-triazole-), 7.11-8.30 (br, -*Ar*), 8.94 (br, -*Ar*) ppm; ^{31}P{^{1}H}NMR ($CDCl_3$, 161.9 MHz) δ –8.1, –145.7 (sep, J_{PF} = 710.7 Hz) ppm.

Synthesis of model compound (*S,S*)-M1-BH_3

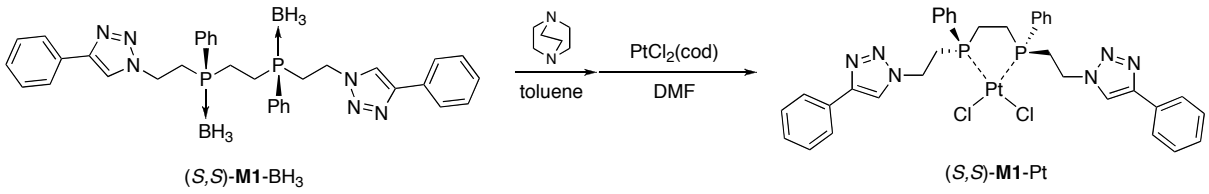


(*S,S*)-**3**-BH_3 (*S,S*)-**M1**-BH_3

A solution of (*S,S*)-**3**-BH_3 (124.0 mg, 0.30 mmol), phenylacetylene (110 mL, 1.0 mmol), and $Cu(MeCN)_4PF_6$ (11.2 mg, 0.03 mmol) in DMF (3.0 mL) was stirred at 50 °C under Ar atmosphere. After stirring for 6 h, the reaction mixture was poured into 1% NH_3aq and extracted with $CHCl_3$ (30 mL × 3). The organic layer was washed with 2 N HCl and brine, and it was dried over $MgSO_4$. $MgSO_4$ was removed by filtration, and the solvent was dried in vacuo. The residure was purified by reprecipitation from $CHCl_3$ and hexane, following recrystallization from toluene and hexane gave (*S,S*)-**M1**-BH_3 (135.1 mg, 0.22 mmol, 73%) as a colorless solid.

$[\alpha]^{26}_D$ 9.9 (*c* 0.5 in $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.75 (br q, J_{HB} = 98.6 Hz, -B*H*$_3$, 6H), 1.61 (m, -PC*H*$_2$-, 2H), 2.00 (m, -PC*H*$_2$-, 2H), 2.52 (m, -PC*H*$_2$-, 2H), 2.69 (m, -PC*H*$_2$-, 2H), 4.43 (m, -C*H*$_2$-triazole, 2H), 4.63 (m, -C*H*$_2$-triazole, 2H), 7.3-7.5 (m, -*Ar*, 18H), 7.61 (s, triazole-*H*, 2H), 7.68 (d, *J* = 7.2 Hz, -*Ar*, 2H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.2 (s, -P*C*H$_2$-), 26.7 (d, J_{CP} = 34.6 Hz, -P*C*H$_2$-), 44.7 (-*C*H$_2$-triazole-), 100.5, 120.3, 125.7, 128.2, 128.8, 129.2, 129.3, 129.3, 130.2, 131.8, 132.4, 147.6 ppm; ^{31}P{^{1}H}NMR ($CDCl_3$, 161.9 MHz) δ +16.1 ppm. HRMS (ESI) calc. for $C_{34}H_{40}N_6P_2B_2$ $[M+H]^+$ 617.3054, found 617.3049.

Synthesis of model compound (*S,S*)-M1-BH_3

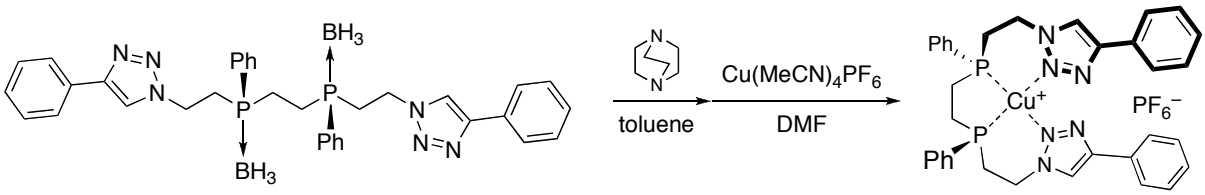


(*S,S*)-**M1**-BH_3 (*S,S*)-**M1**-Pt

A solution of (*S,S*)-**M1**-BH_3 (24.6 mg, 0.04 mmol), DABCO (44.8 mg, 0.40 mmol) in toluene (4.0 mL) was stirred at 50 °C. After stirring for 6 h, the reaction mixture was poured into hexane under Ar atmosphere, and the solvent was removed with a syringe. The residue was solved in CH_2Cl_2 (3.0 mL), and $PtCl_2$(cod) (15.0 mg, 0.04 mmol) was added to the CH_2Cl_2 solution. After stirring for 12 h, the reaction mixture was subjected to reprecipitation from CH_2Cl_2 and hexane to obtain polymer (*S,S*)-**M1**-Pt as a colorless solid (29.8 mg, 0.035 mmol, 87%).

$[\alpha]^{26}_D$ 39.6 (*c* 0.5 in DMF); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.2-2.5 (m, -PCH_2-), 3.16 (m, -PCH_2-, 4H), 4.89 (m, -CH_2-triazole, 4H), 7.35 (m, -*Ar*, 14H), 7.63 (m, -*Ar*, 2H), 7.75 (s, triazole-*H*, 2H), and 7.92 (m, -*Ar*, 4H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.8 (d, J_{CP} = 34.5 Hz, -P*C*H_2-), 26.7 (d, J_{CP} = 34.6 Hz, -P*C*H_2-), 45.7 (-*C*H_2-triazole-), 100.1, 124.7-125.8, 128.3-130.0, 128.2, 132.7-132.9, 147.9 ppm; ^{31}P{^{1}H}NMR ($CDCl_3$, 161.9 MHz) δ +41.3 (J_{PPt} = 3556) ppm. HRMS (ESI) calc. for $C_{34}H_{34}N_6Cl_2P_2Pt$ $[M+Na]^+$ 876.1243, found 876.1230.

Synthesis of model compound (*S,S*)-M1-Cu



(*S,S*)-**M1**-BH_3 (*S,S*)-**M1**-Cu

A solution of (*S,S*)-**M1**-BH_3 (43.1 mg, 0.07 mmol), DABCO (78.4 mg, 0.70 mmol) in toluene (3.0 mL) was stirred at 50 °C. After stirring for 6 h, the reaction mixture was poured into hexane under Ar atmosphere, and the solvent was removed with a syringe. The residue was solved in DMF (3.0 mL), and $Cu(MeCN)_4PF_6$ (26.1 mg, 0.07 mmol) was added to the DMF solution. After stirring for 12 h, the solvent was removed in vacuo. The residue was purified by reprecipitation from $CHCl_3$ and hexane to obtain polymer (*S,S*)-**M1**-Cu as a colorless solid (24.0 mg, 0.030 mmol, 43%).

$[\alpha]^{25}_D$ 39.6 (*c* 0.5 in $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.16 (br, -PCH_2-), 4.85 (m, -CH_2-triazole), 5.06 (m, -CH_2-triazole), 7.3-7.5, 7.75, 7.82, 8.84 (s, triazole-*H*) ppm; ^{31}P{^{1}H}NMR ($CDCl_3$, 161.9 MHz) δ –9.2, –145.8 (sep, J_{PF} = 710.7 Hz) ppm. HRMS (ESI) calc. for $C_{34}H_{34}N_6P_3F_6Cu$ $[M\text{-}PF_6]^+$ 651.1611, found 651.1601.

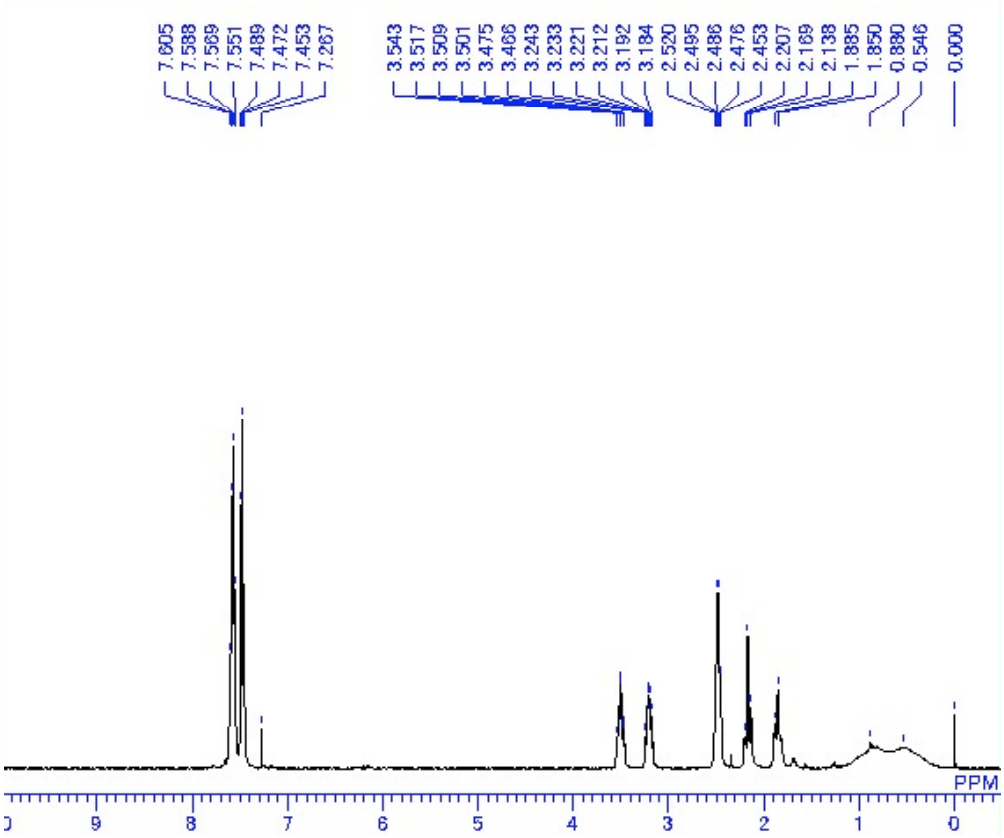


Figure S1. ^{1}H NMR spectrum (400 MHz) of (*S,S*)-**2**-BH_3 in $CDCl_3$.

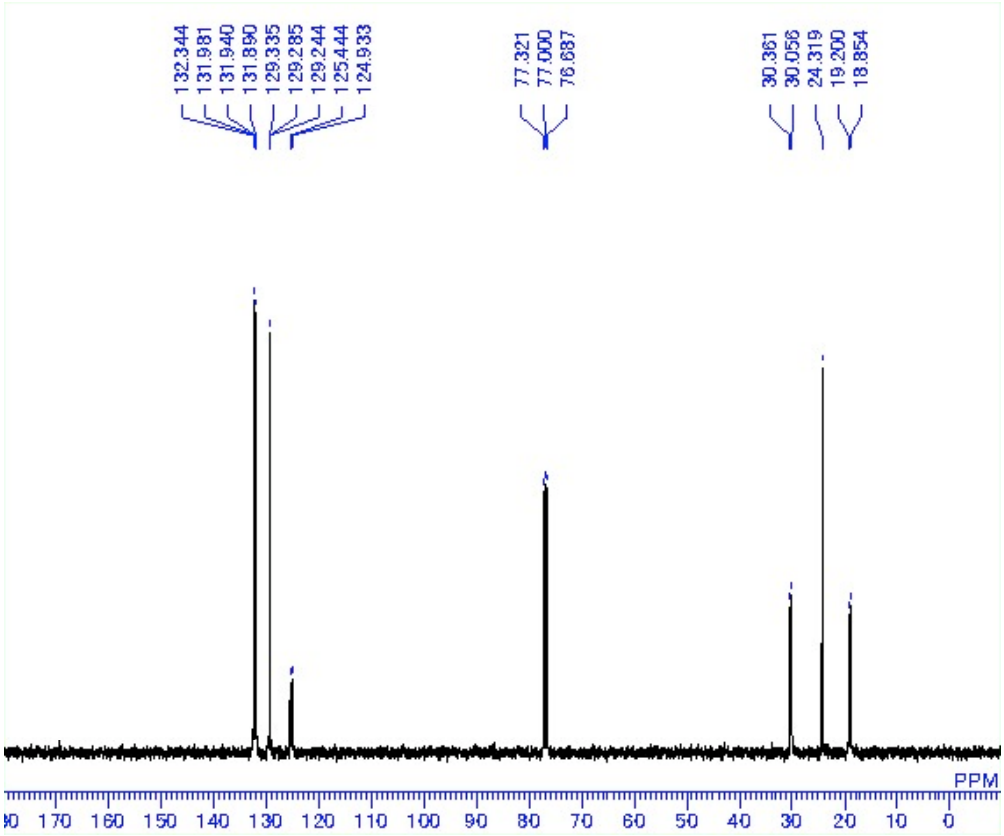


Figure S2. ^{13}C NMR spectrum (100 MHz) of (*S,S*)-**2**-BH_3 in $CDCl_3$.

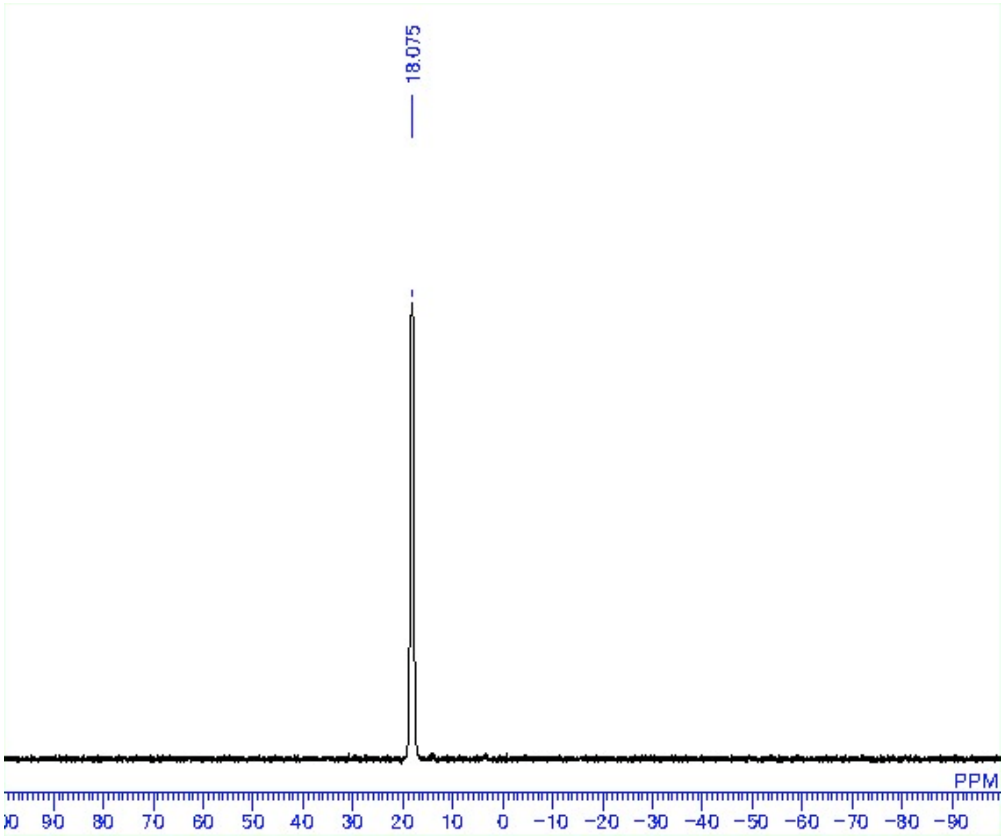


Figure S3. ^{31}P NMR spectrum (161.9 MHz) of (*S,S*)-**2**-BH_3 in $CDCl_3$.

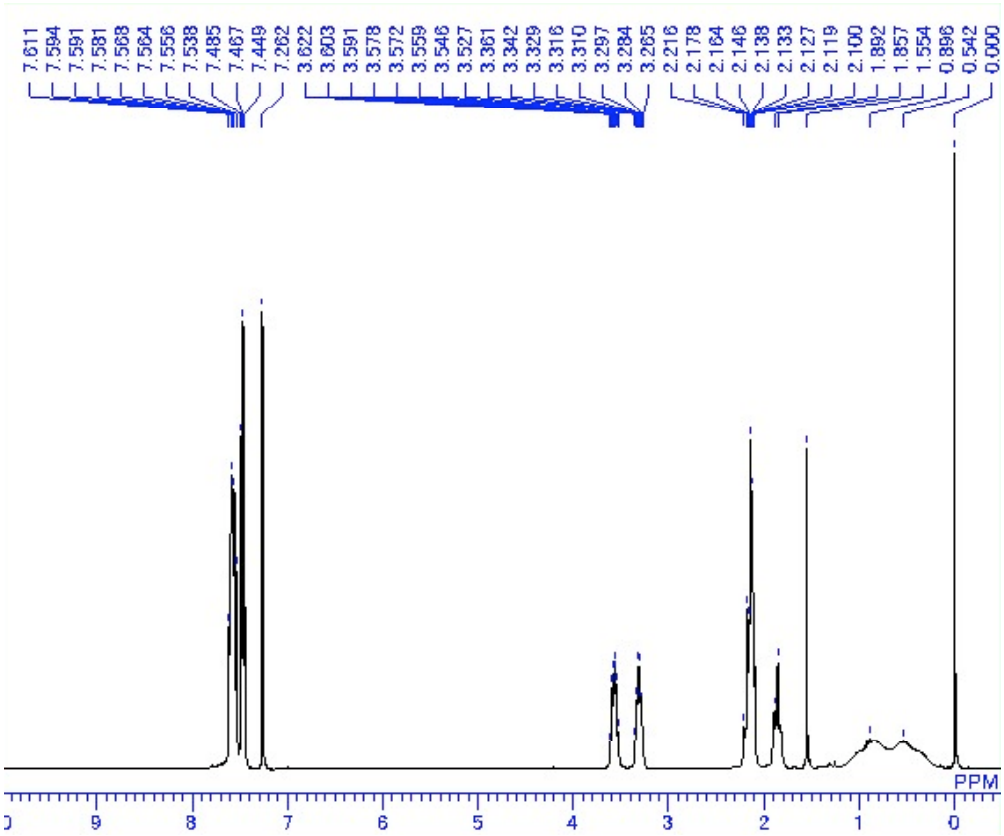


Figure S4. ^{1}H NMR spectrum (400 MHz) of (*S,S*)-**3**-BH_3 in $CDCl_3$.

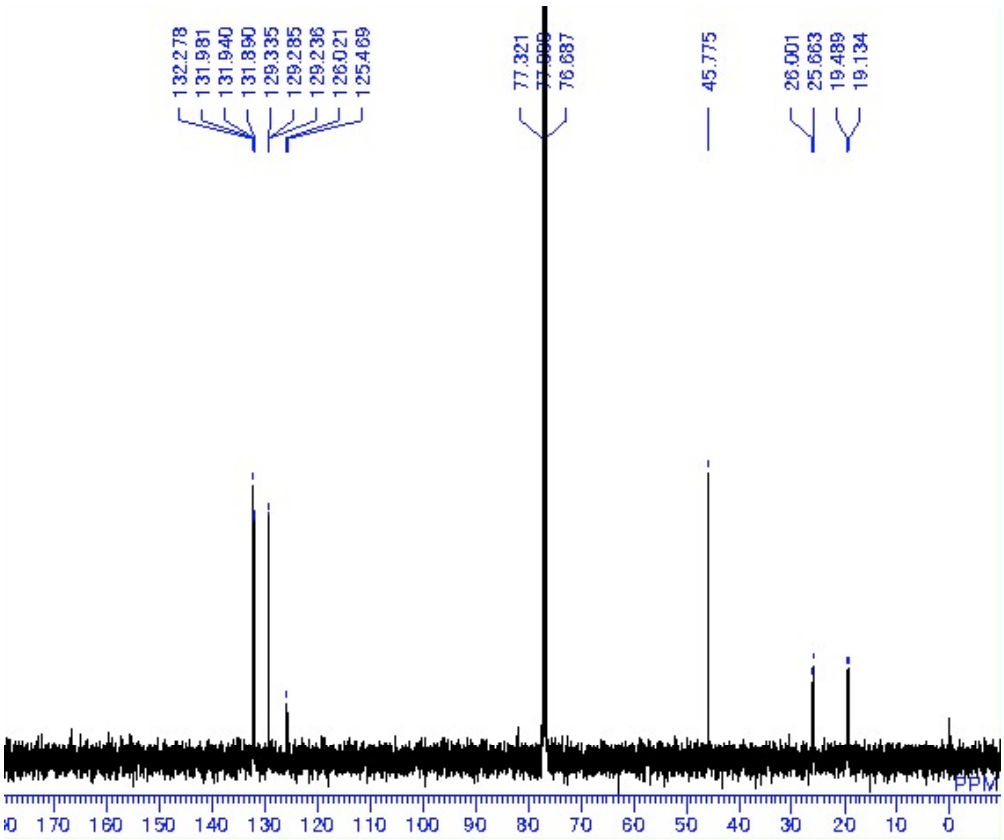


Figure S5. ^{13}C NMR spectrum (100 MHz) of (*S,S*)-**3**-BH_3 in $CDCl_3$.

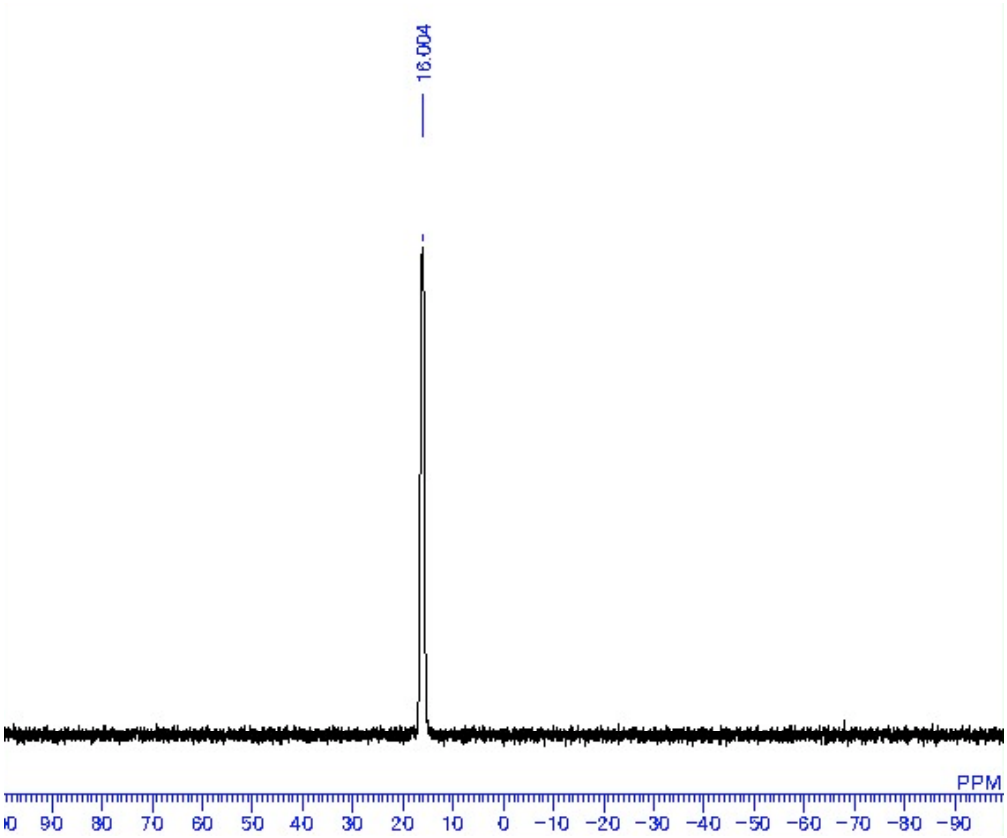


Figure S6. ^{31}P NMR spectrum (161.9 MHz) of (*S,S*)-**3**-BH_3 in $CDCl_3$.

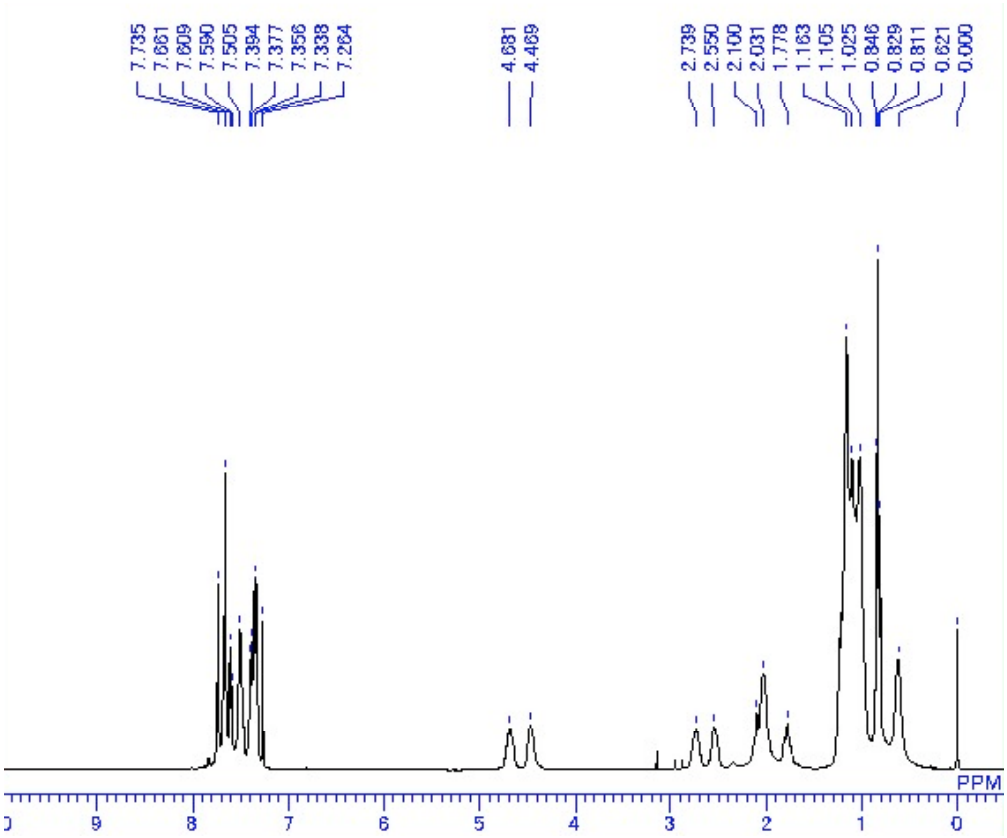


Figure S7. ^{1}H NMR spectrum (400 MHz) of **5**-BH_3 in $CDCl_3$.

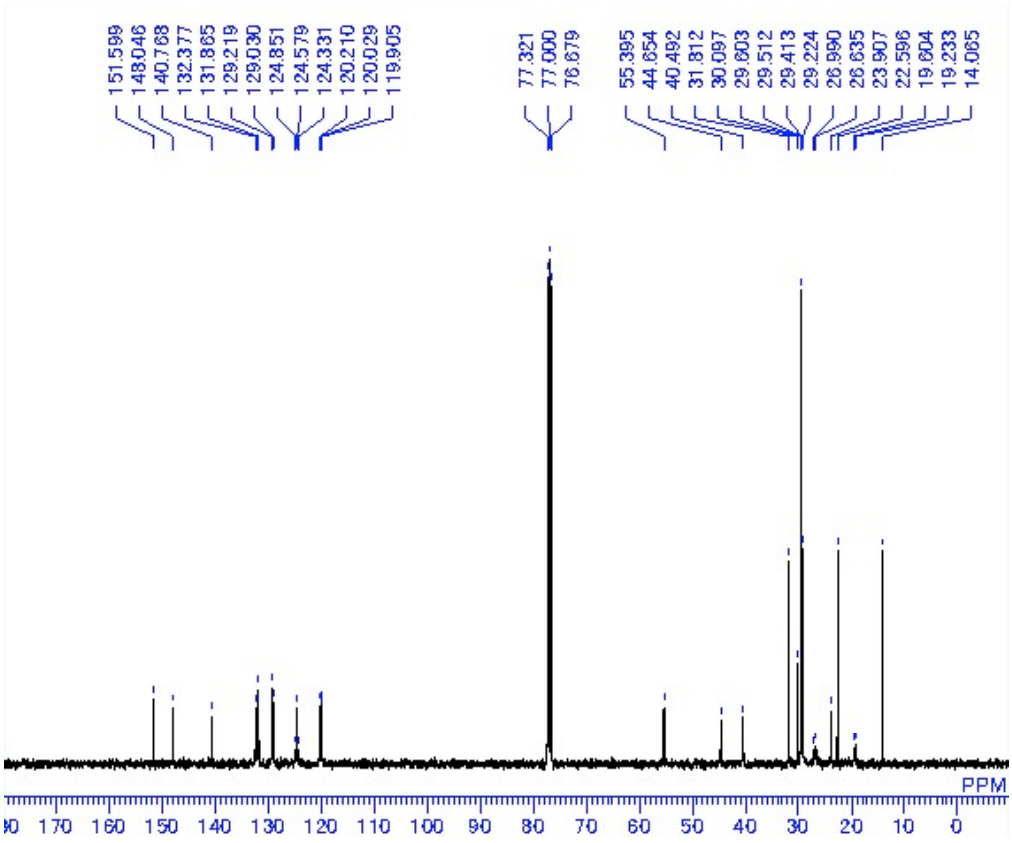


Figure S8. ^{13}C NMR spectrum (100 MHz) of **5**-BH_3 in $CDCl_3$.

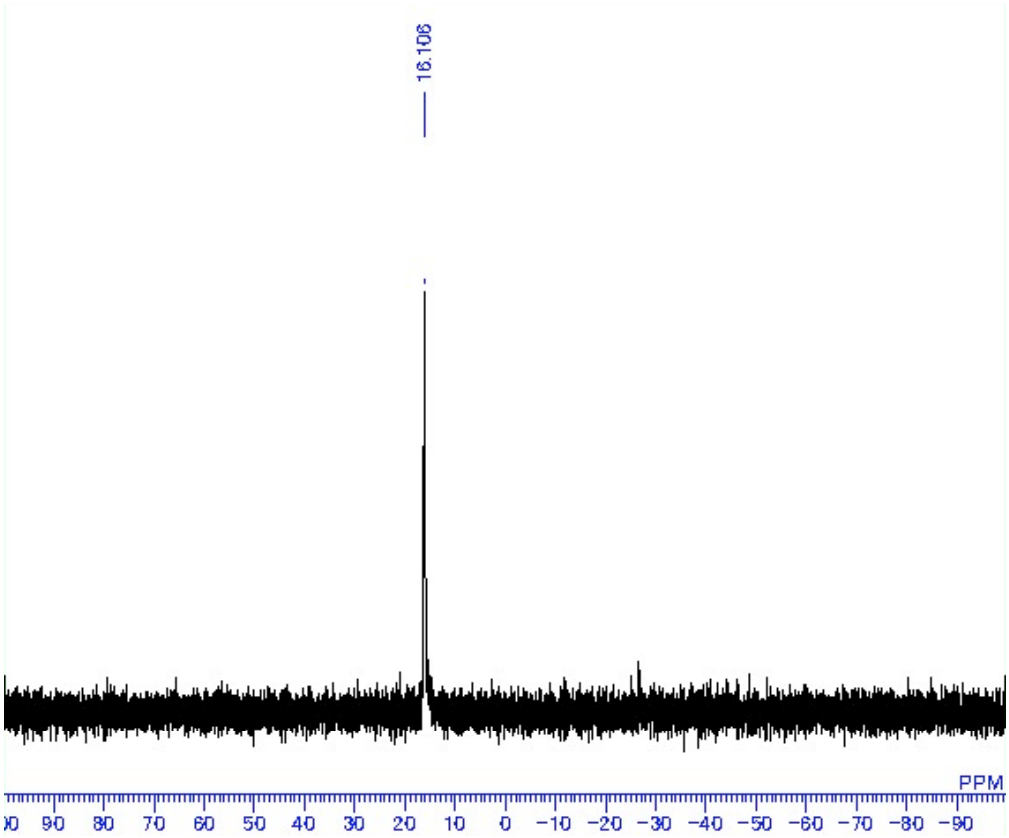


Figure S9. ^{31}P NMR spectrum (161.9 MHz) of **5**-BH_3 in $CDCl_3$.

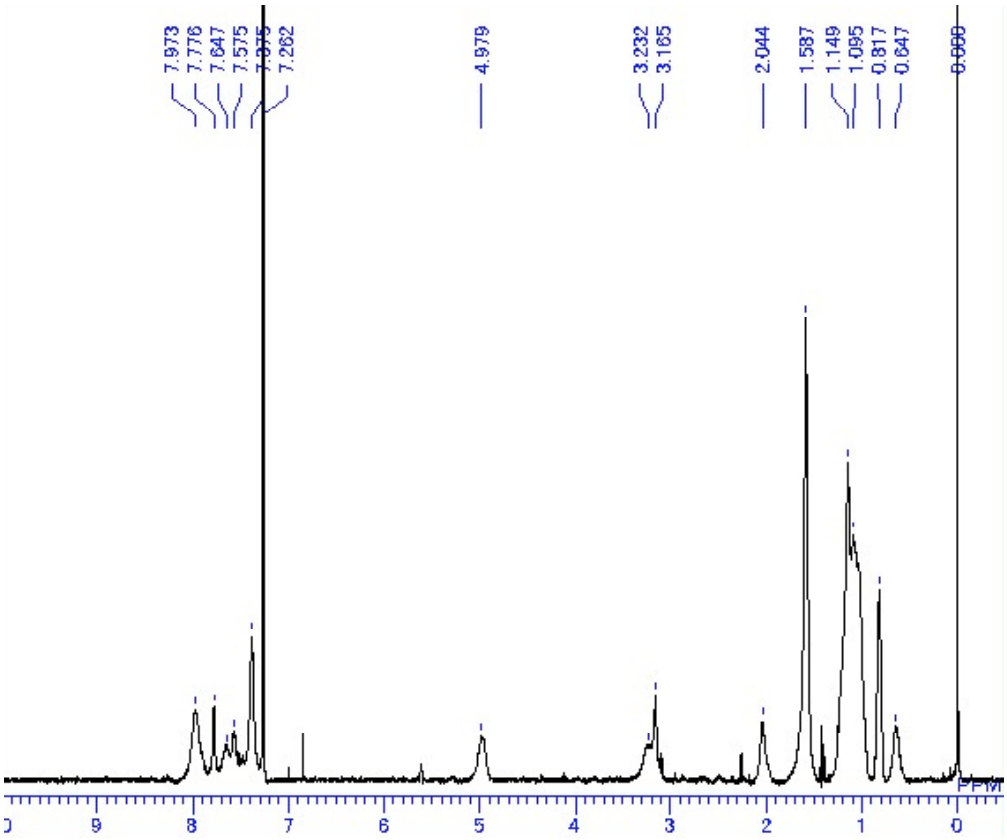


Figure S10. ^{1}H NMR spectrum (400 MHz) of **5**-Pt in $CDCl_3$.

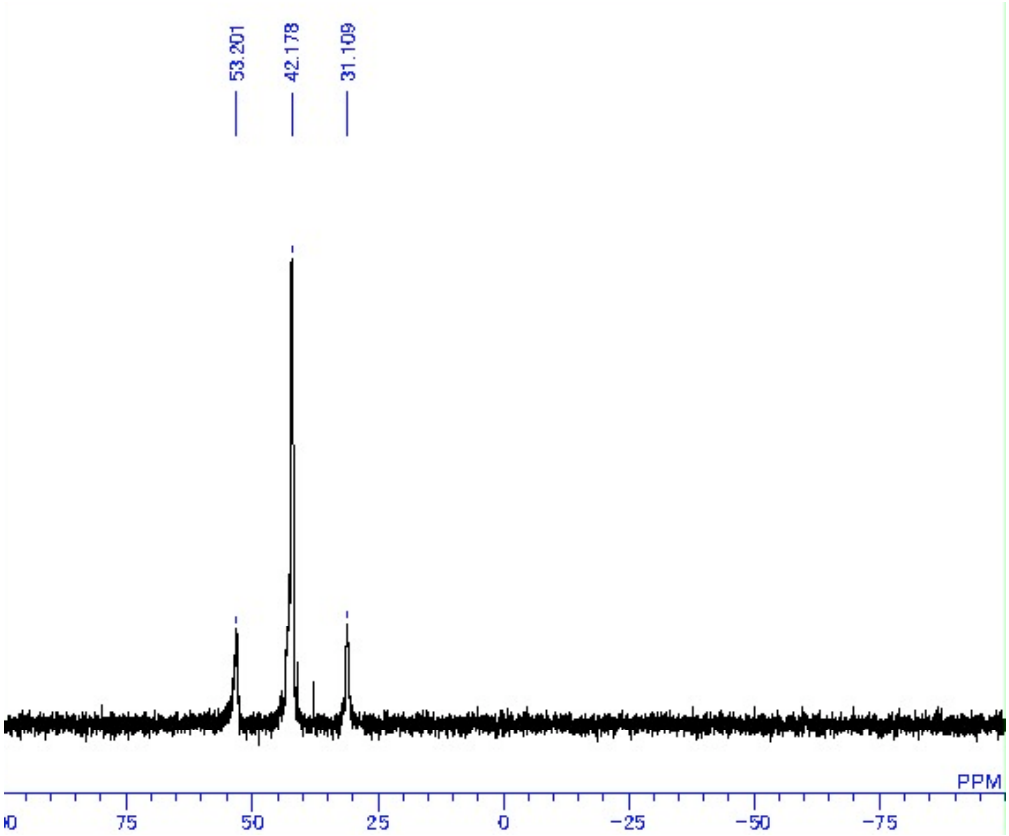


Figure S11. ^{31}P NMR spectrum (161.9 MHz) of **5**-Pt in $CDCl_3$.

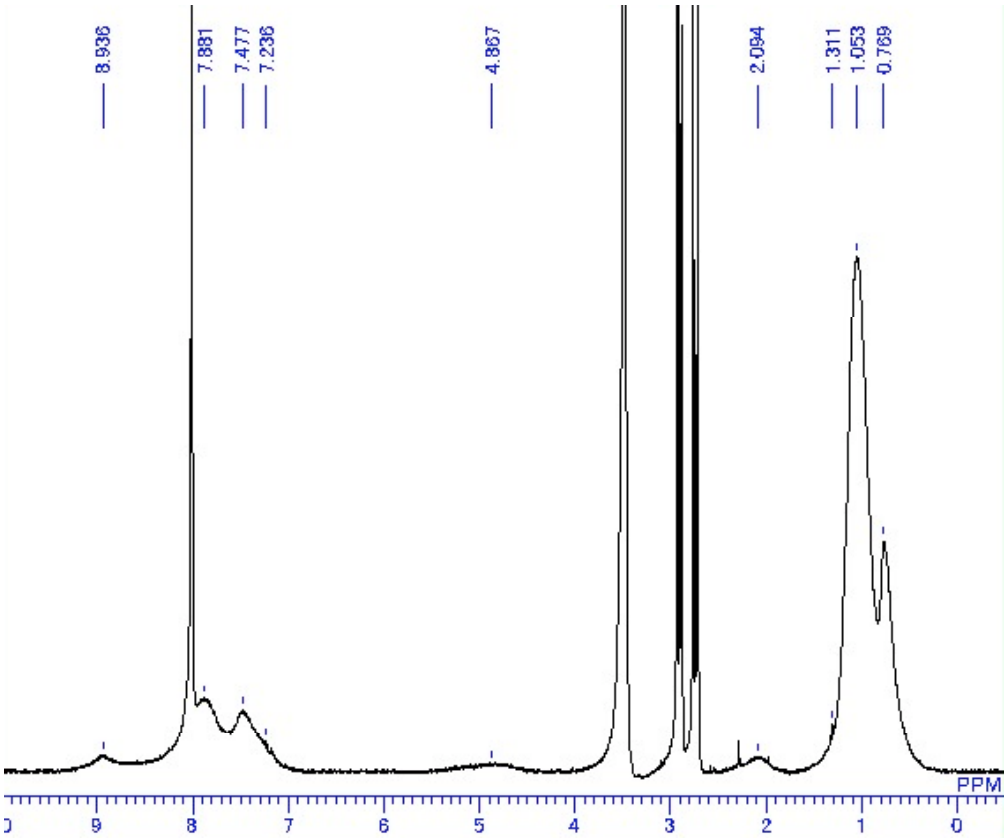


Figure S12. ^{1}H NMR spectrum (400 MHz) of **5**-Cu in DMF-d_7.

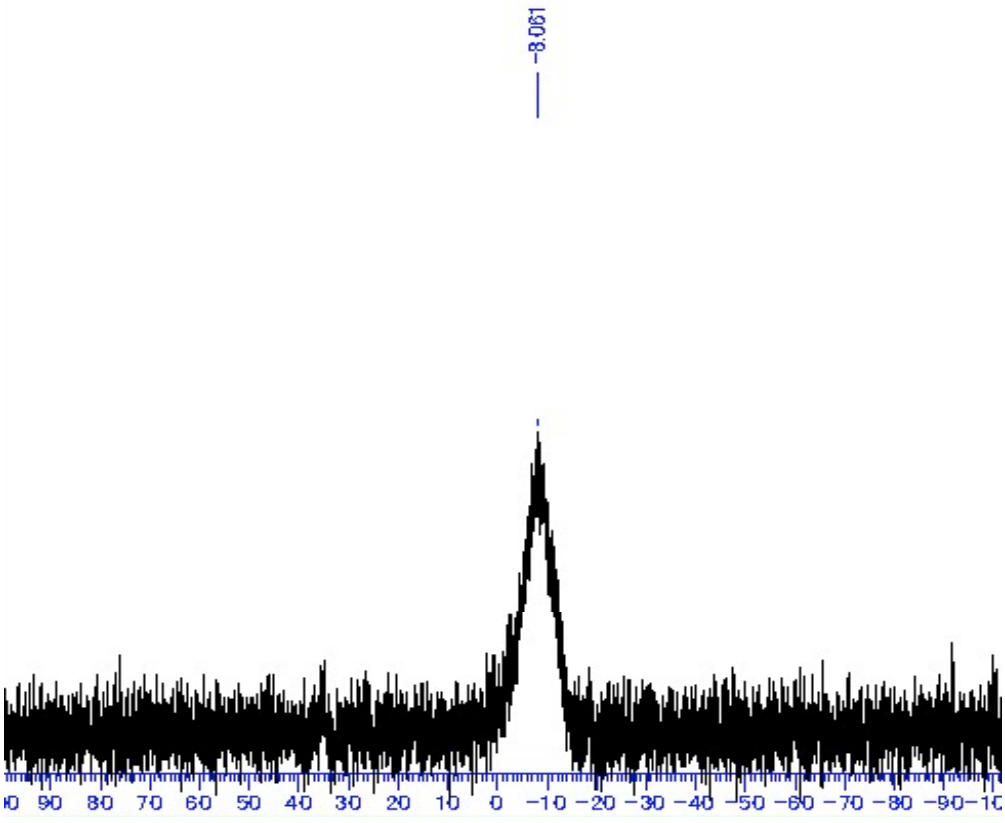


Figure S13. ^{31}P NMR spectrum (161.9 MHz) of **5**-Cu in DMF-d_7.

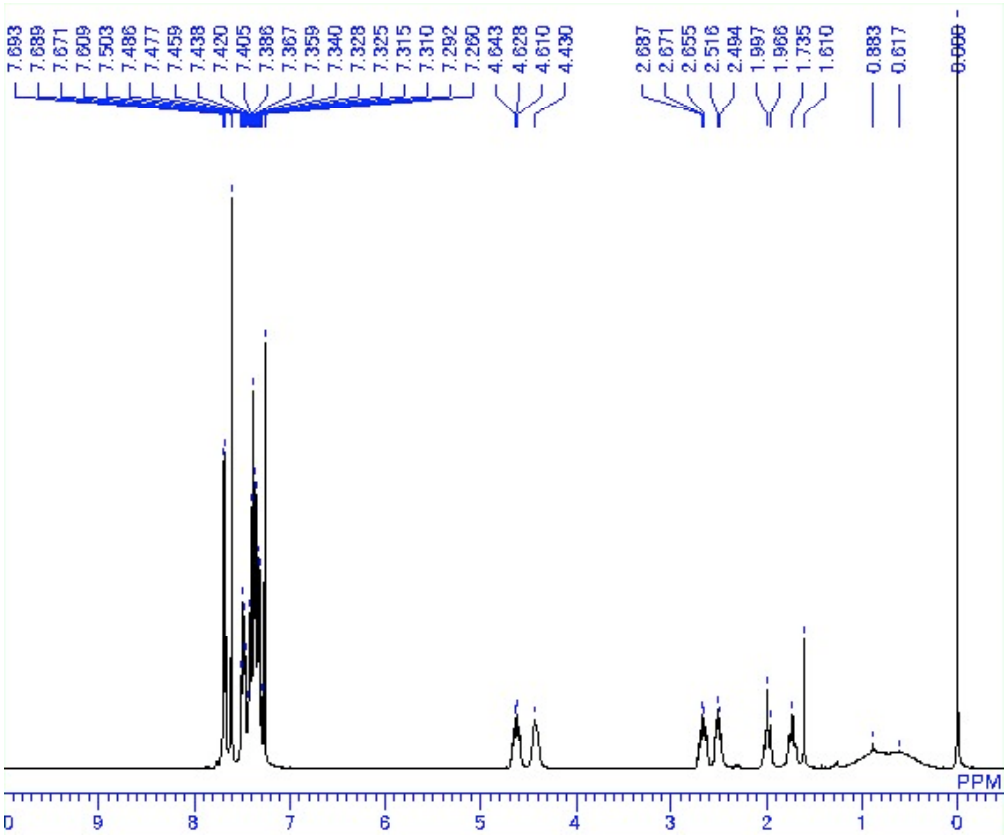


Figure S14. ^{1}H NMR spectrum (400 MHz) of (*S,S*)-**M1**-BH_3 in $CDCl_3$.

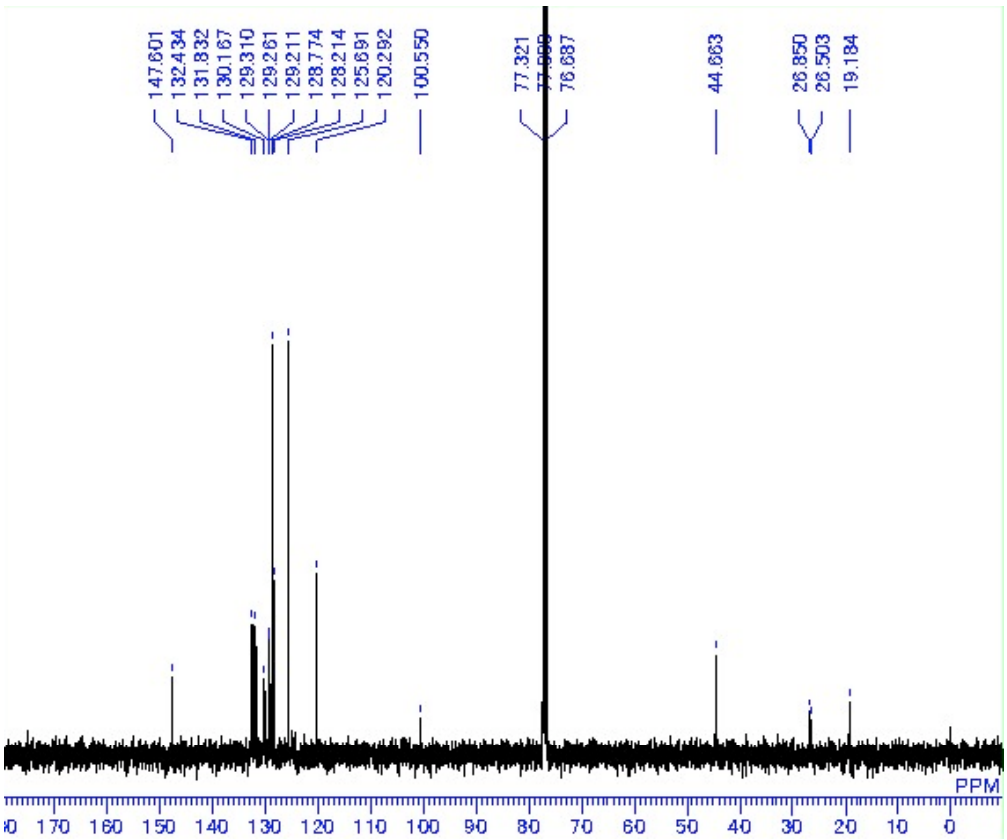


Figure S15. ^{13}C NMR spectrum (100 MHz) of (*S,S*)-**M1**-BH_3 in $CDCl_3$.

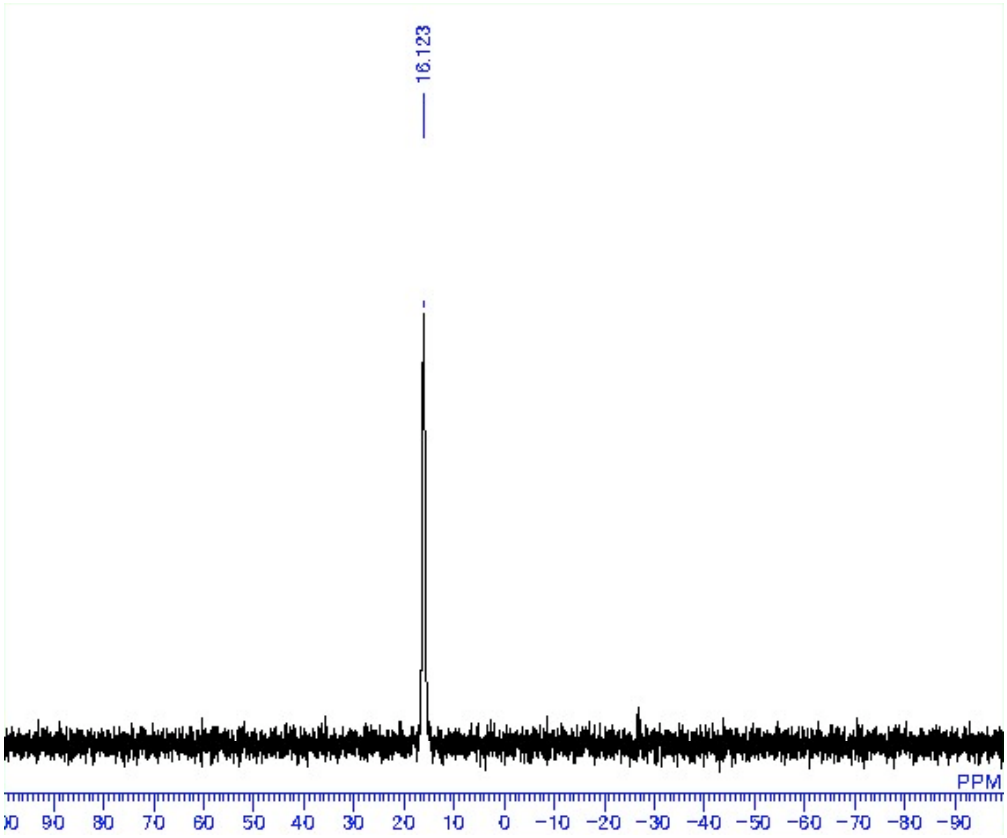


Figure S16. ^{31}P NMR spectrum (161.9 MHz) of (*S,S*)-**M1**-BH_3 in $CDCl_3$.

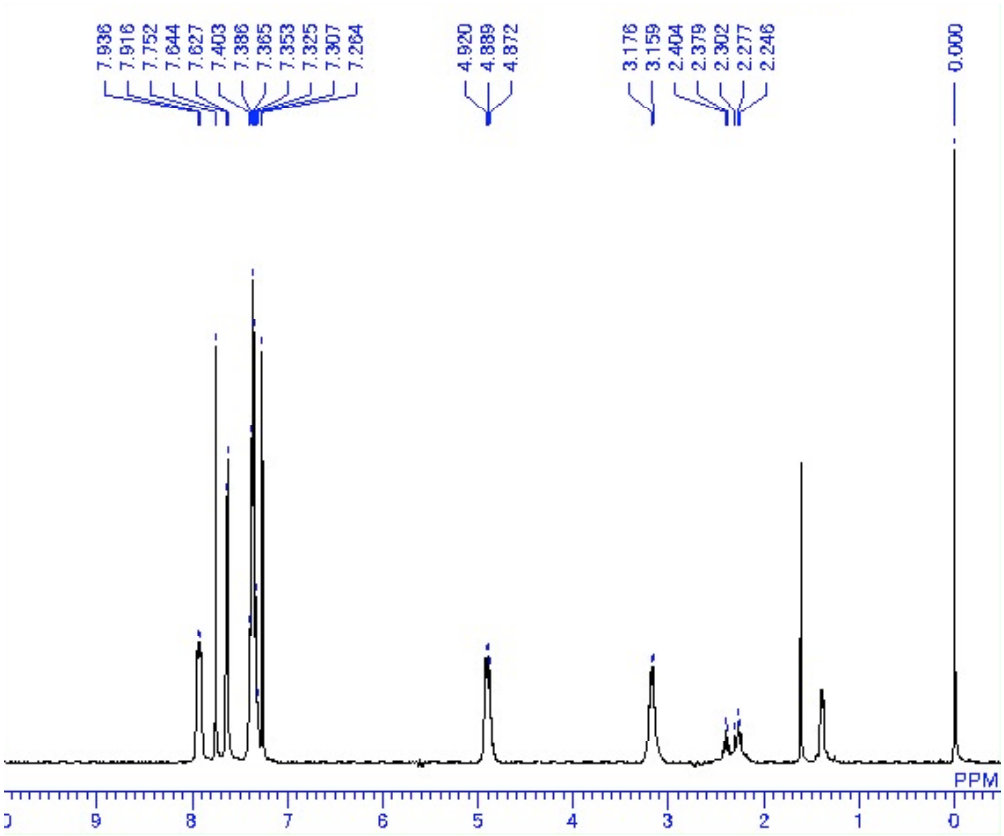


Figure S17. ^{1}H NMR spectrum (400 MHz) of (*S,S*)-**M1**-Pt in $CDCl_3$.

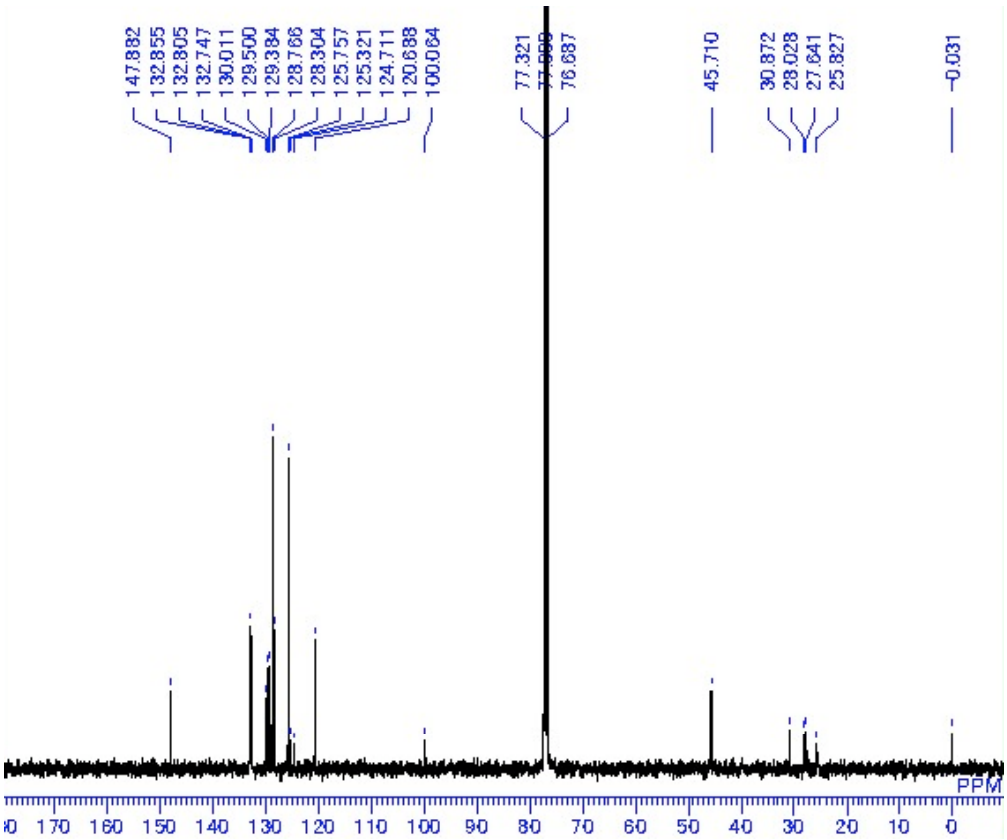


Figure S18. ^{13}C NMR spectrum (100 MHz) of (*S,S*)-**M1**-Pt in $CDCl_3$.

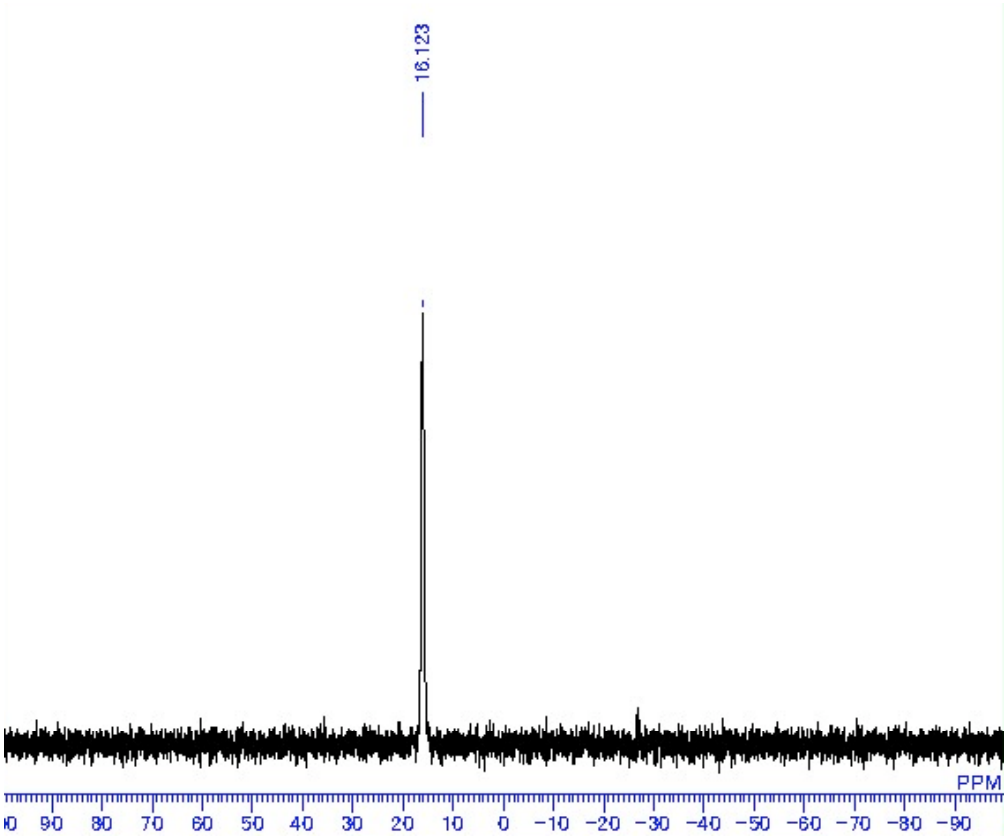


Figure S19. ^{31}P NMR spectrum (161.9 MHz) of (*S,S*)-**M1**-Pt in $CDCl_3$.

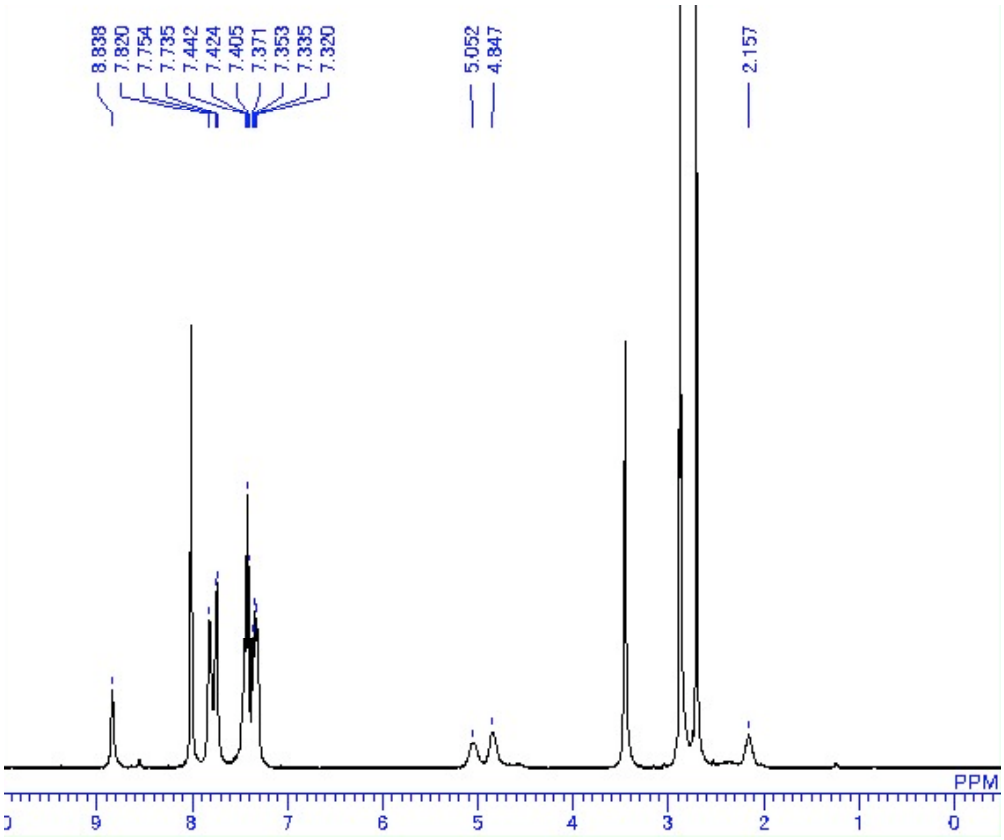


Figure S20. ^{1}H NMR spectrum (400 MHz) of (*S,S*)-**M1**-Cu in DMF-d_7.

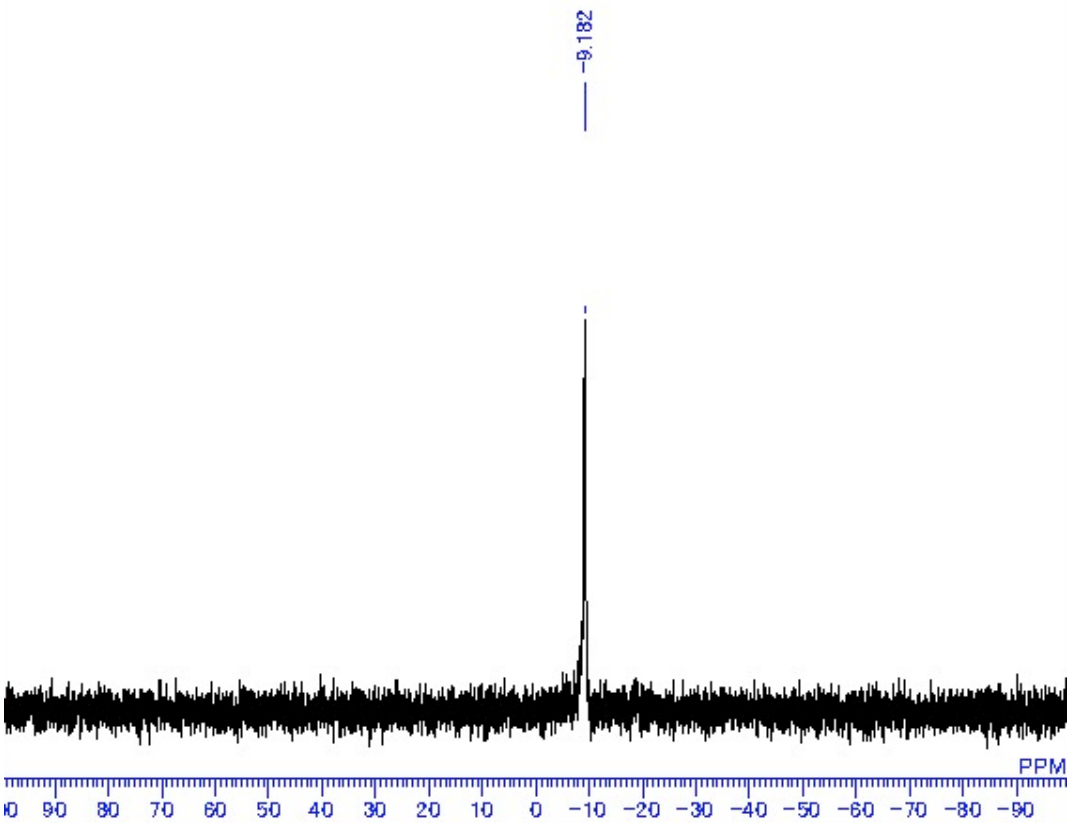


Figure S21. ^{31}P NMR spectrum (161.9 MHz) of (*S,S*)-**M1**-Cu in DMF-d_7.

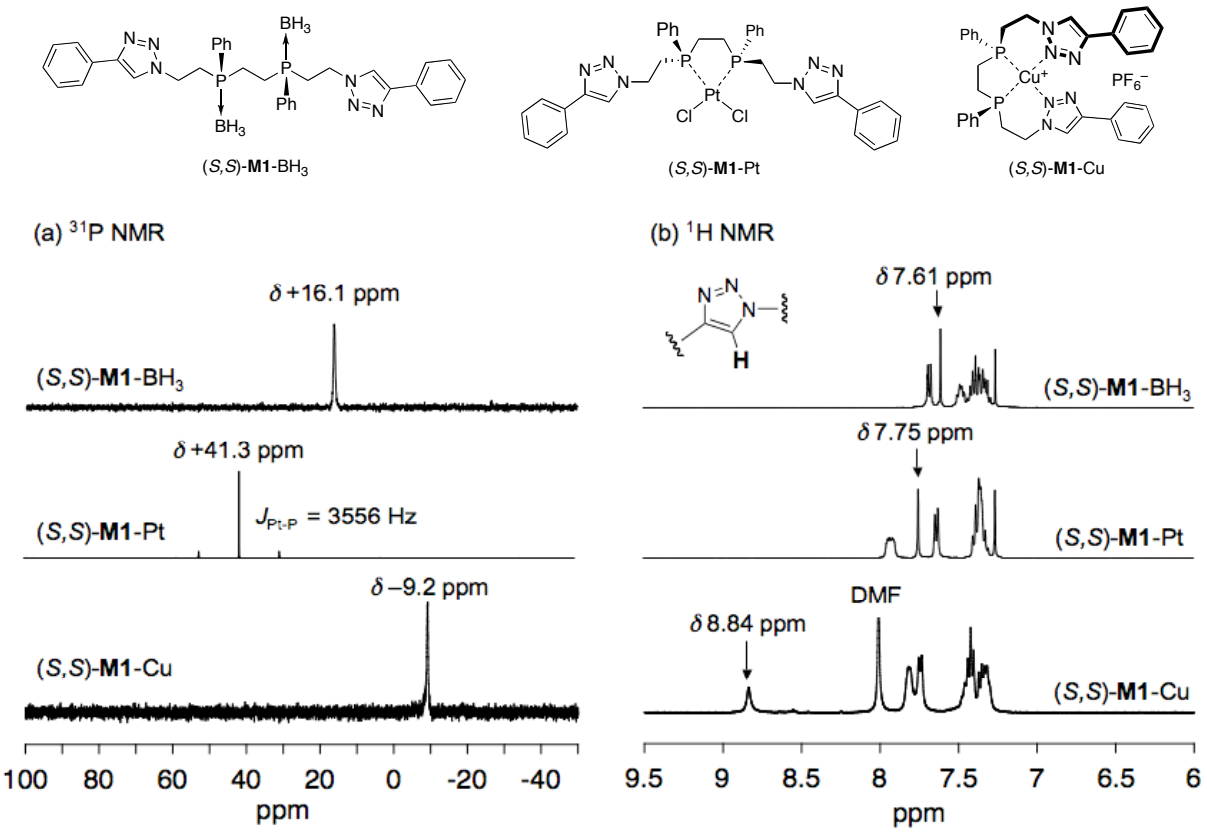


Figure S22. (a) ^{31}P and (b) ^{1}H NMR spectra of (*S,S*)-**M1**-BH_3 (in $CDCl_3$), (*S,S*)-**M1**-Pt (in $CDCl_3$), and (*S,S*)-**M1**-Cu (in DMF-d_7).

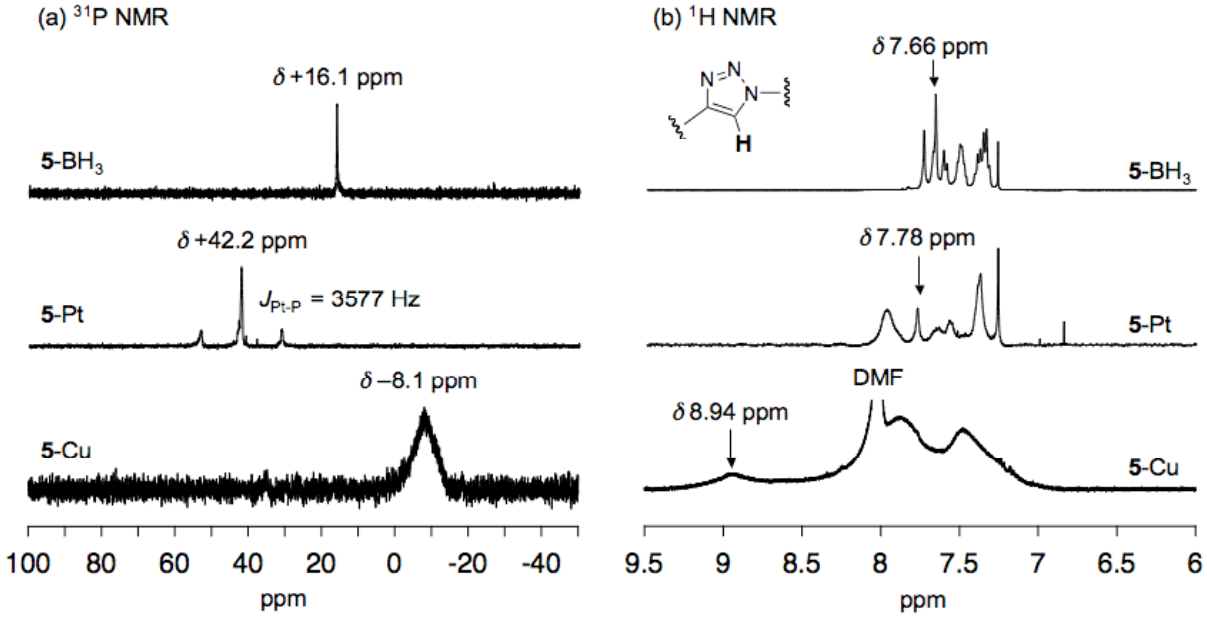


Figure S23. (a) ^{31}P and (b) ^{1}H NMR spectra of **5**-BH_3 (in $CDCl_3$), **5**-Pt (in $CDCl_3$), and **5**-Cu (in DMF-d_7). This is the same figure as "Fig.1" in the manuscript.

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