Electronic Supplementary Information

Oxidative Addition of Bi-C Bonds to Pt(0): Reaction of Pt(PEt_3)$_3$ with 12-Phenyl- and 12-Chloro-5,6,7,12-tetrahydrodibenz[c,f][1,5]azabismocines

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1. General.

All manipulations of air-sensitive materials were carried out under a nitrogen atmosphere using standard Schlenk techniques or in a glovebox. Anhydrous toluene, hexane and THF were purchased from Kanto Chemicals and degassed before use. C_6D_6, THF-d_8, and CD_2Cl_2 were dried over molecular sieves and degassed. NMR spectra were recorded on Jeol LA500, JNM-ECX400P spectrometers, or Bruker AVANCE III HD 600 spectrometer with a CryoProbe. Chemical shifts are reported in δ (ppm) and are referenced to the (residual) solvent signals for ^{1}H and ^{13}C[S1] or to the external standard (85% H_3PO_4 (0 ppm)) for ^{31}P. Coupling constants were reported in Hertz. 5,6,7,12-Tetrahydrodibenz[c,f][1,5]azabismocines **1**,[S2] **2a**,[S2] and **2b**[S3] and $Pt(PEt_3)_4$[S4] were prepared according to literature procedures.

Safety Caution: $Pt(PEt_3)_4$ and PEt_3 are pyrophoric and should be handled with great care.

2. Reaction of 12-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][1,5]azabismocine 1 with Pt(PEt$_3$)$_3$.

Monitoring of the reaction of 1 and Pt(PEt$_3$)$_3$ by NMR. $Pt(PEt_3)_4$ (35.6 mg, 0.066 mmol) was placed in a Schlenk tube and heated at 60 ºC for 10 min under vacuum to form $Pt(PEt_3)_3$ as an orange oil. Compound **1** (43.8 mg, 0.066 mmol) and C_6D_6 (0.8 mL) were added to the Schlenk tube to form an orange solution. Ca. 0.5 mL of the solution was transferred to an NMR tube and the tube was sealed with a PTFE valve. The reaction progress at room temperature was periodically monitored by NMR. After 91 h, volatiles were removed under vacuum and the residue was dissolved again in C_6D_6. The reaction was further monitored by NMR.

The progress of the reaction was shown in Fig. S1 (^{31}P{^{1}H} NMR) and Fig. S2 (^{1}H NMR).

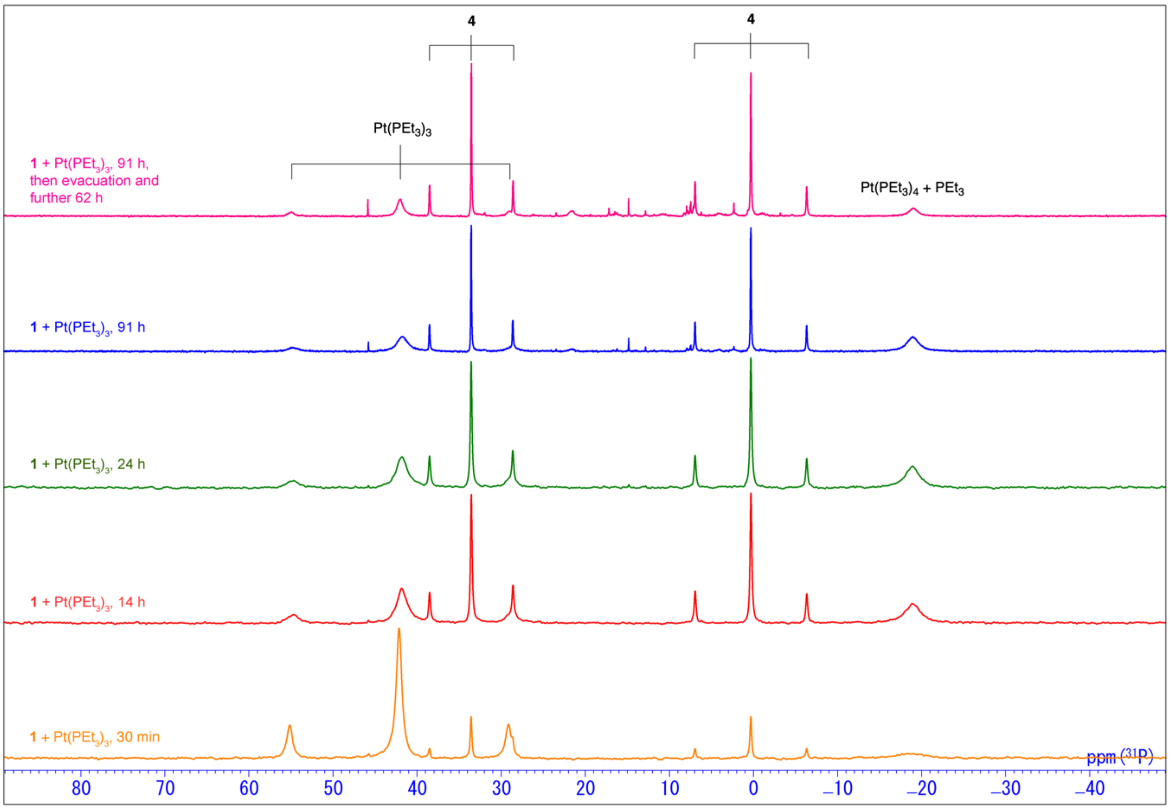


Fig. S1 ^{31}P{^{1}H} NMR spectra (161 MHz, C_6D_6) of the reaction mixture of **1** and $Pt(PEt_3)_3$ after 30 min (orange), 14 h (red), 24 h (green), 91 h (blue) and 91 h + evacuation + 62 h (pink).

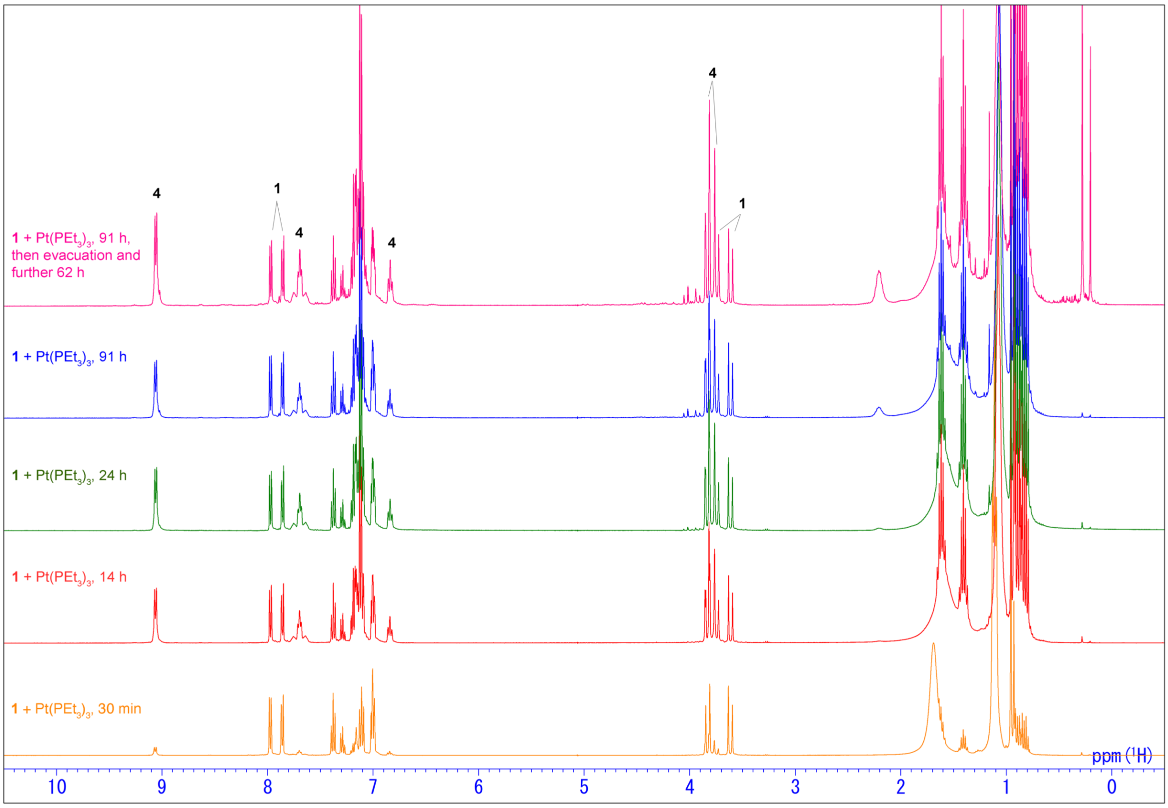
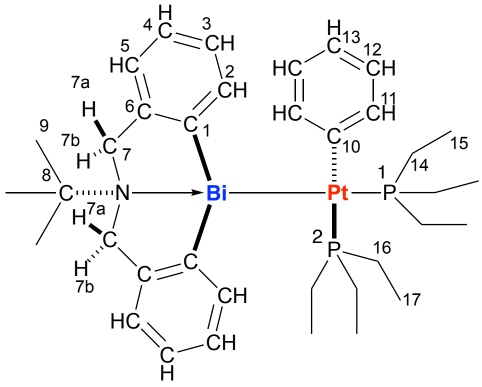


Fig. S2 ^{1}H NMR spectra (400 MHz, C_6D_6) of the reaction mixture of **1** and $Pt(PEt_3)_3$ after 30 min (orange), 14 h (red), 24 h (green), 91 h (blue) and 91 h + evacuation + 62 h (pink).

Synthesis of complex 4. A mixture of $Pt(PEt_3)_3$ (0.378 mmol, prepared from 203 mg of $Pt(PEt_3)_4$ by heating at 60 ºC under vacuum) and **1** (254 mg, 0.380 mmol) in benzene (5 mL) was stirred at room temperature for 43 h. The color of the mixture changed from light orange to brown. A small aliquot of the mixture was taken for ^{1}H NMR analysis, which showed the molar ratio of **1**:**4** = ca 43:57. After the volatiles were removed under vacuum, the residue was again dissolved in benzene (6 mL) and stirred at room temperature for further 24 h. After the volatiles were removed under vacuum, the residue was dissolved in hexane (10 mL) and the hexane solution was kept at –32 ºC for 4 days, resulting the formation of orange crystals. The supernatant was removed and the crystals were washed with cold hexane (cooled at –32 ºC, 3 × 0.7 mL) and dried under vacuum to give **4** (151 mg, 41% yield). The stability of **4** in deuterated solvents was checked and found to be C_6D_6 > THF-d_8 (more than 2/3 of **4** changed to unknown species after 24 h) >> CD_2Cl_2 (immediate (partial) change to unknown species). However, signal separation was better in THF-d_8 than in C_6D_6. Therefore, full NMR characterization was done in THF-d_8. ^{1}H NMR (499 MHz, C_6D_6, Fig. S11) δ 0.78-0.93 (m, 18H), 0.92 (s, 9H), 1.40 (quint, J = 7.6 Hz, 6H), 1.61 (quint, J = 7.5 Hz, 6H), 3.76 (d, J = 15.1 Hz, 2H), 3.84 (d, J = 15.1 Hz, 2H), 6.86 (dt, J = 1.1, 7.3 Hz, 1H), 7.11-7.24 (m, 8H), 7.72 (dt, J = 1.1, 5.9 Hz, $^3J_{\text{Pt-H}}$ = 45 Hz, 2H), 9.09 (d, J = 6.6 Hz, 2H). ^{13}C NMR (126 MHz, C_6D_6) δ 8.46 ($J_{\text{Pt-C}}$ = 12 Hz), 9.83 ($J_{\text{Pt-C}}$ = 21 Hz), 15.5-16.1 (m), 20.6-21.3 (m), 28.04, 56.54, 57.28, 121.51, 126.27, 128.35, 128.76 (br, $J_{\text{Pt-C}}$ = ca. 60 Hz), 139.50 (d, $J_{\text{P-C}}$ = 2 Hz, $J_{\text{Pt-C}}$ = ca. 28 Hz), 143.96 ($J_{\text{Pt-C}}$ = ca. 33 Hz), 149.36, 150.27 (br). ^{31}P NMR (202 MHz, C_6D_6) δ –0.22 (s, $^1J_{\text{Pt-P}}$ = 2149 Hz), 32.98 (s, $^1J_{\text{Pt-P}}$ = 1605 Hz).



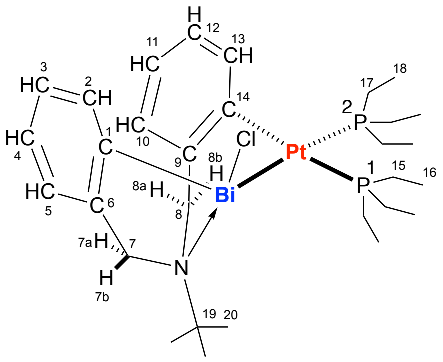
Atomic numbering of complex **4** for the NMR signal assignment

^{1}H NMR (600 MHz, THF-d_8, Fig. S13) δ 0.86-0.96 (m, 9H, H-17), 0.96 (s, 9H, H-9), 1.09-1.16 (m, 9H, H-15), 1.64 (quint, J = 7.6 Hz, 6H, H-14), 1.72 (quint, J = 7.5 Hz, 6H, H-16), 3.61 (d, J = 15.0 Hz, 2H, H-7a), 3.80 (d, J = 15.0 Hz, 2H, H-7b), 6.55 (t, J = 7.1 Hz, 1H, H-13), 6.81-6.88 (m, 4H, H-3 & H-12), 6.96-7.02 (m, 4H, H-4 & H-5), 7.37 (t with Pt satellites, J = 6.1 Hz, $^3J_{\text{Pt-H}}$ = 44 Hz, 2H, H-11), 8.69 (d, J = 6.9 Hz, 2H, H-2). ^{13}C{^{1}H} NMR (151 MHz, THF-d_8, Figs. S14-S18) δ 8.6 (s with Pt satellites, $^3J_{\text{Pt-C}}$ = 12 Hz, C-15), 9.9 (s with Pt satellites, $^3J_{\text{Pt-C}}$ = 21 Hz, C-17), 15.8-16.2 (m, C-14), 20.9-21.5 (m, C-16), 28.1 (s, C-9), 56.7 (s, C-8), 57.3 (s, C-7), 121.1 (s, C-13), 126.1 (s, C-4), 128.0 (s, C-5), 128.1 (s, C-3), 128.4 (dd with Pt satellites, $^4J_{\text{P-C}}$ = 2, 6 Hz, $^3J_{\text{Pt-C}}$ = 58 Hz, C-12), 139.7 (dd with Pt satellites, $^3J_{\text{P-C}}$ = 1, 3 Hz, $^2J_{\text{Pt-C}}$ = 28 Hz, C-11), 143.9 (s with Pt satellites, $^3J_{\text{Pt-C}}$ = 33 Hz, C-2), 149.2 (s, C-6), 149.9 (br, C-1), 162.3 (d with Pt satellites, $^2J_{\text{P-C}}$ = 101 Hz, $^1J_{\text{Pt-C}}$ = 721 Hz, C-10). ^{31}P{^{1}H} NMR (243 MHz, THF-d_8, Fig. S19) δ –0.9 (s with Pt satellites, $^1J_{\text{Pt-P}}$ = 2147 Hz, P-2), 32.6 (s with

Pt satellites, ${}^{1}J_{\text{Pt-P}}$ = 1650 Hz, P-1).
Anal. Calcd for $C_{36}H_{56}BiNP_2Pt$: C, 44.63%; H, 5.83%; N, 1.45%. Found: C, 44.95%; H, 5.78%; N, 1.38%.

3. Reaction of 12-chloro-5,6,7,12-tetrahydrodibenzo[*c,f*][1,5]azabismocine 2a or 2b with Pt(PEt$_3$)$_3$.

Synthesis of complex 5a. A mixture of Pt(PEt$_3$)$_3$ (0.30 mmol, prepared from 200 mg of Pt(PEt$_3$)$_4$ by heating at 60 ºC under vacuum) and **2a** (149 mg, 0.30 mmol) in THF (20 mL) was stirred for 30 h at room temperature and then 60 h at 40 ºC. After the volatiles were removed under vacuum, the residue was washed with hexane (2 × 20 mL) and then with hexane/THF (1/2, 15 mL). The residual yellow powder was dried under vacuum to give **5a** (144 mg, 52%). Because NMR signal separation was better in CD_2Cl_2 than in C_6D_6, full NMR characterization was done in CD_2Cl_2. ^{1}H NMR (499 MHz, C_6D_6, Fig. S25) δ 0.63 (dt, $J_{\text{P-H}}$ = 15 Hz, $J_{\text{H-H}}$ = 7.6 Hz, 9H), 1.07-1.30 (m, 6H), 1.08 (dt, $J_{\text{P-H}}$ = 15 Hz, $J_{\text{H-H}}$ = 7.6 Hz, 9H), 1.18 (s, 9H), 1.98 (quasi sept, J = 7.3 Hz, 3H), 2.27 (quasi sept, J = 7.6 Hz, 3H), 3.40 (d, J = 9.8 Hz, 2H), 3.73 (d, J = 15.8 Hz, 2H), 4.09 (d, J = 15.6 Hz, 2H), 4.63 (d, J = 9.9 Hz, 2H), 6.39 (t, J = 7.3 Hz, 1H), 6.72 (t, J = 7.3 Hz, 1H), 6.85-6.94 (m, 2H), 6.98-7.28 (m, 3H), 8.99 (d, J = 7.5 Hz, 1H). ^{31}P NMR (202 MHz, C_6D_6) δ 0.54 (d, ${}^{2}J_{\text{P-P}}$ = 11, ${}^{1}J_{\text{Pt-P}}$ = 2063 Hz), 58.08 (d, ${}^{2}J_{\text{P-P}}$ = 11, ${}^{1}J_{\text{Pt-P}}$ = 2036 Hz).

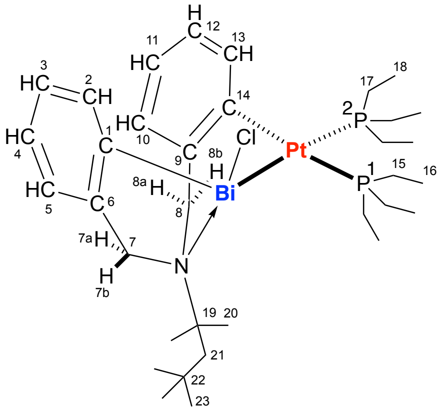


Atomic numbering of complex **5a** for the NMR signal assignment

^{1}H NMR (600 MHz, CD_2Cl_2, Fig. S26) δ 0.92-0.98 (m, 9H, H-18), 1.20-1.27 (m, 9H, H-16), 1.46 (s, 9H, H-20), 1.43-1.52 (m, 3H, H-17), 1.57-1.65 (m, 3H, H-17), 2.12 (quasi septet, J = 7.4 Hz, 3H, H-15), 2.34 (quasi septet, J = 7.6 Hz, 3H, H-15), 3.61 (d, J = 10.2 Hz, 1H, H-8a), 3.98 (d, J = 15.9 Hz, 1H, H-7a), 4.31 (d, J = 15.9 Hz, 1H, H-7b), 4.69 (d, J = 10.2 Hz, 1H, H-8b), 6.08 (tt, J = 1.4, 7.3 Hz, 1H, H-11), 6.43 (t, J = 7.3 Hz, 1H, H-12), 6.71 (t, J = 7.2 Hz, 1H, H-3), 6.81 (t, J = 7.5 Hz, 1H, H-5), 6.83 (t, J = 7.5 Hz, 1H, H-4), 6.87 (td, J = 1.7, 7.4 Hz, 1H, H-10), 6.90-6.94 (m, 1H, H-13), 7.91 (d, J = 7.4 Hz, 1H, H-2). ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, Figs. S27-S31) δ 8.5 (d with Pt satellites, $J_{\text{P-C}}$ = 1 Hz, ${}^{3}J_{\text{Pt-C}}$ = 15 Hz, C-18), 9.2 (s with Pt satellites, ${}^{3}J_{\text{Pt-C}}$ = 14 Hz, C-16), 16.2-16.7 (m, C-17), 18.8-19.2 (m, C-15), 29.8 (br, C-20), 59.7 (s, C-7), 60.5 (s, C-19), 65.8 (s with Pt satellites, ${}^{3}J_{\text{Pt-C}}$ = 82 Hz, C-8), 121.3 (d, ${}^{5}J_{\text{P-C}}$ = 3 Hz, C-11), 124.3 (s, C-4), 125.59 (s, C-5), 125.66 (dd with Pt satellites, ${}^{4}J_{\text{P-C}}$ = 2, 5 Hz, ${}^{3}J_{\text{Pt-C}}$ = 49 Hz, C-12), 126.9 (s, C-3), 132.3 (dd with Pt satellites, ${}^{4}J_{\text{P-C}}$ = 2, 6 Hz, ${}^{3}J_{\text{Pt-C}}$ = 41 Hz, C-10), 139.0 (d, ${}^{3}J_{\text{P-C}}$ = 5 Hz, C-13), 139.5 (s, C-2), 143.2 (t with Pt satellites, ${}^{3}J_{\text{P-C}}$ = 2

Hz, $^{2}J_{\text{Pt-C}}$ = 26 Hz, C-9), 151.3 (s, C-6), 161.6 (dd with Pt satellites, $^{2}J_{\text{P-C}}$ = 9, 93 Hz, $^{1}J_{\text{Pt-C}}$ = 693 Hz, C-14), 169.2 (br, C-1). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, Fig. S32) δ 0.3 (d with Pt satellites, $^{2}J_{\text{P-P}}$ = 12 Hz, $^{1}J_{\text{Pt-P}}$ = 2029 Hz, P-1), 62.2 (d with Pt satellites, $^{2}J_{\text{P-P}}$ = 12 Hz, $^{1}J_{\text{Pt-P}}$ = 2154 Hz, P-2).
Anal. Calcd for $C_{30}H_{51}BiClNP_2Pt$: C, 38.86%; H, 5.54%; N, 1.51%. Found: C, 39.06%; H, 5.46%; N, 1.42%.

Synthesis of complex 5b. A mixture of $Pt(PEt_3)_3$ (0.33 mmol, prepared from 222 mg of $Pt(PEt_3)_4$ by heating at 60 °C under vacuum) and **2b** (183 mg, 0.33 mmol) in C_6H_6 (11 mL) was stirred for 92 h at room temperature and then for 23 h at 40 °C. After the volatiles were removed under vacuum, the residue was extracted with hexane (10 mL) and then with hexane/C_6H_6 (3/1, 8 mL). Cooling the hexane/C_6H_6 extract at –35 °C afforded **5b** as a yellow powder, which was separated and dried under vacuum (107 mg, 33%).



Atomic numbering of complex **5b** for the NMR signal assignment

^{1}H NMR (600 MHz, CD_2Cl_2) δ 0.92-0.98 (m, 9H, H-18), 1.07 (s, 9H, H-23), 1.21-1.28 (m, 9H, H-16), 1.43-1.73 (m, 13H, H-17, H-20 & one of H-21), 1.85 (d, J = 13.9 Hz, 1H, one of H-21), 2.12 (quasi septet, J = 7.4 Hz, 3H, H-15), 2.34 (quasi septet, J = 7.6 Hz, 3H, H-15), 3.66 (br s, 1H, H-8a), 4.00 (d, J = 16.0 Hz, 1H, H-7a), 4.30 (d, J = 16.0 Hz, 1H, H-7b), 4.68 (d, J = 9.7 Hz, 1H, H-8b), 6.08 (t, J = 7.1 Hz, 1H, H-11), 6.43 (t, J = 7.3 Hz, 1H, H-12), 6.71 (dt, J = 1.0, 7.2 Hz, 1H, H-3), 6.80-6.86 (m, 2H, H-4 & H-5), 6.87-6.93 (m, 2H, H-10 & H-13), 7.93 (d, J = 6.5 Hz, 1H, H-2). ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2) δ 8.5 (d with Pt satellites, $J_{\text{P-C}}$ = 1 Hz, $^{3}J_{\text{Pt-C}}$ = 15 Hz, C-18), 9.3 (s, C-16), 16.2-16.7 (m, C-17), 18.8-19.2 (m, C-15), 33.2 (br), 32.1 (s, C-23), 36.4 (br), 44.2 (br), 58.9 (s, C-7), 64.5 (s with Pt satellites, $^{3}J_{\text{Pt-C}}$ = 81 Hz, C-8), 64.7 (s, C-19), 121.3 (d, $^{5}J_{\text{P-C}}$ = 3 Hz, C-11), 124.3 (s, C-4), 125.7 (dd with Pt satellites, $^{4}J_{\text{P-C}}$ = 1, 5 Hz, $^{3}J_{\text{Pt-C}}$ = ca. 50 Hz, C-12), 125.9 (s, C-5), 126.9 (s, C-3), 132.4 (br s with Pt satellites, $^{3}J_{\text{Pt-C}}$ = ca. 39 Hz, C-10), 139.0 (d, $^{3}J_{\text{P-C}}$ = 5 Hz, C-13), 139.5 (s, C-2), 143.6 (br, C-9), 151.9 (s, C-6), 161.5 (d with Pt satellites, $^{2}J_{\text{P-C}}$ = ca. 94 Hz, $^{1}J_{\text{Pt-C}}$ = ca. 673 Hz, C-14), 169.5 (br, C-1). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ 0.3 (br s with Pt satellites, $^{1}J_{\text{Pt-P}}$ = 2052 Hz, P-1), 63.5 (d with Pt satellites, $^{2}J_{\text{P-P}}$ = 10 Hz, $^{1}J_{\text{Pt-P}}$ = 2152 Hz, P-2). Anal. Calcd for $C_{34}H_{59}BiClNP_2Pt$: C, 41.53%; H, 6.05%; N, 1.42%. Found: C, 41.64%; H, 6.07%; N, 1.53%.

Monitoring of the reaction of 2b and Pt(PEt_3)$_3$ by NMR. Pt(PEt_3)$_4$ (26.5 mg, 0.048 mmol) was placed in a Schlenk tube and heated at 60 ºC for 10 min under vacuum to form Pt(PEt_3)$_3$ as an orange oil. Compound **2b** (32.1 mg, 0.048 mmol) and C_6D_6 (1.2 mL) were added to the Schlenk tube to form an almost homogeneous orange mixture. The mixture was transferred to an NMR tube and the tube was sealed with a PTFE valve. The reaction progress at room temperature was periodically monitored by NMR.

The progress of the reaction was shown in Figs. S3 and S7 ($^{31}P\{^1H\}$ NMR) and Figs. S4-S6 (^1H NMR).

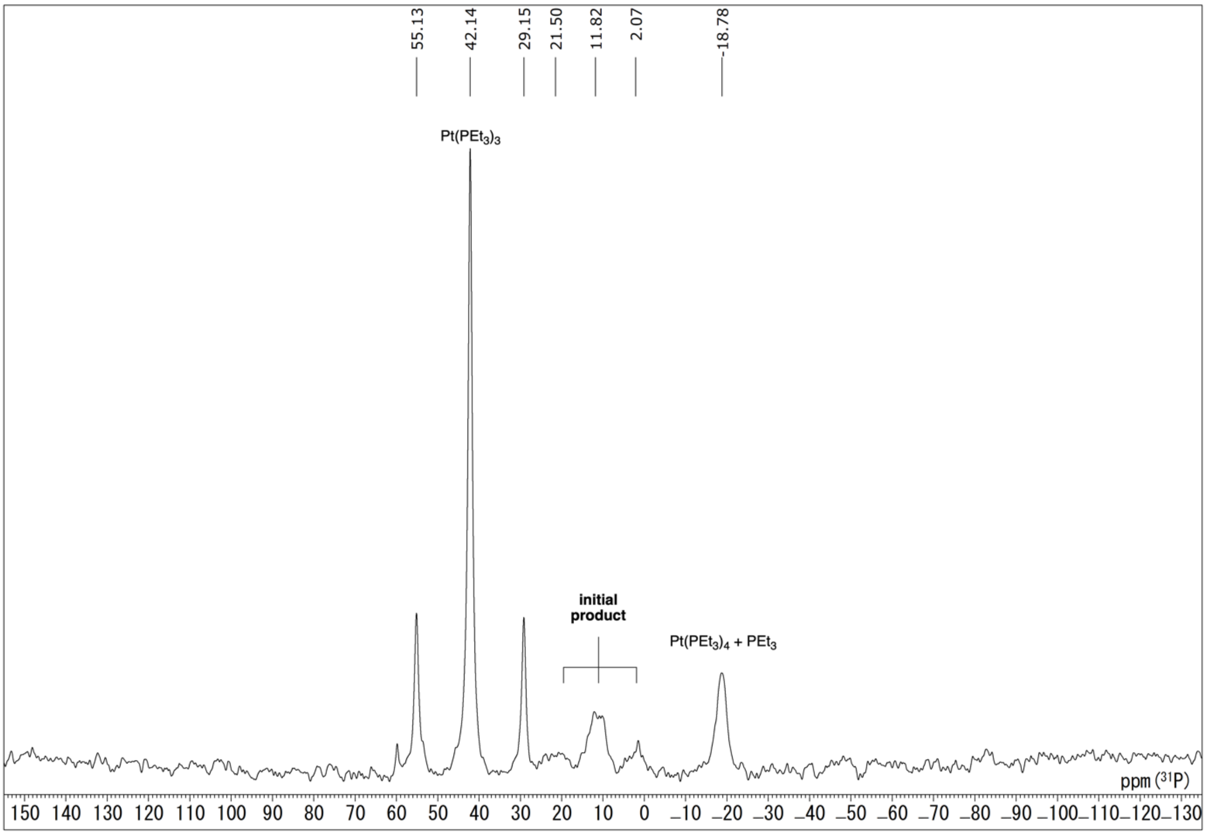


Fig. S3 $^{31}P\{^1H\}$ NMR spectrum (161 MHz, C_6D_6) of the reaction mixture of **2b** and Pt(PEt_3)$_3$ in C_6D_6 after 30 min

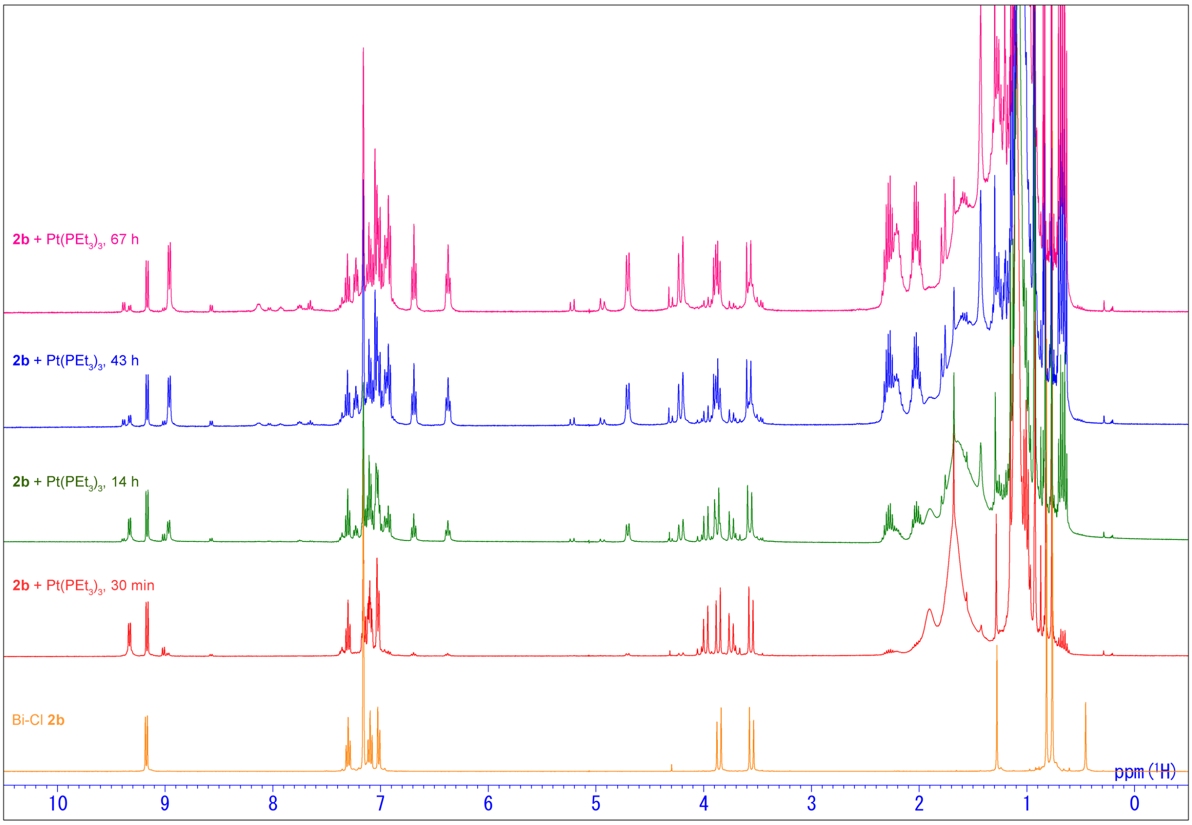


Fig. S4 ^{1}H NMR spectra (400 MHz, C_6D_6) of bismocine chloride **2b** (orange) and the reaction mixture of **2b** and $Pt(PEt_3)_3$ after 30 min (red), 14 h (green), 43 h (blue) and 67 h (pink).

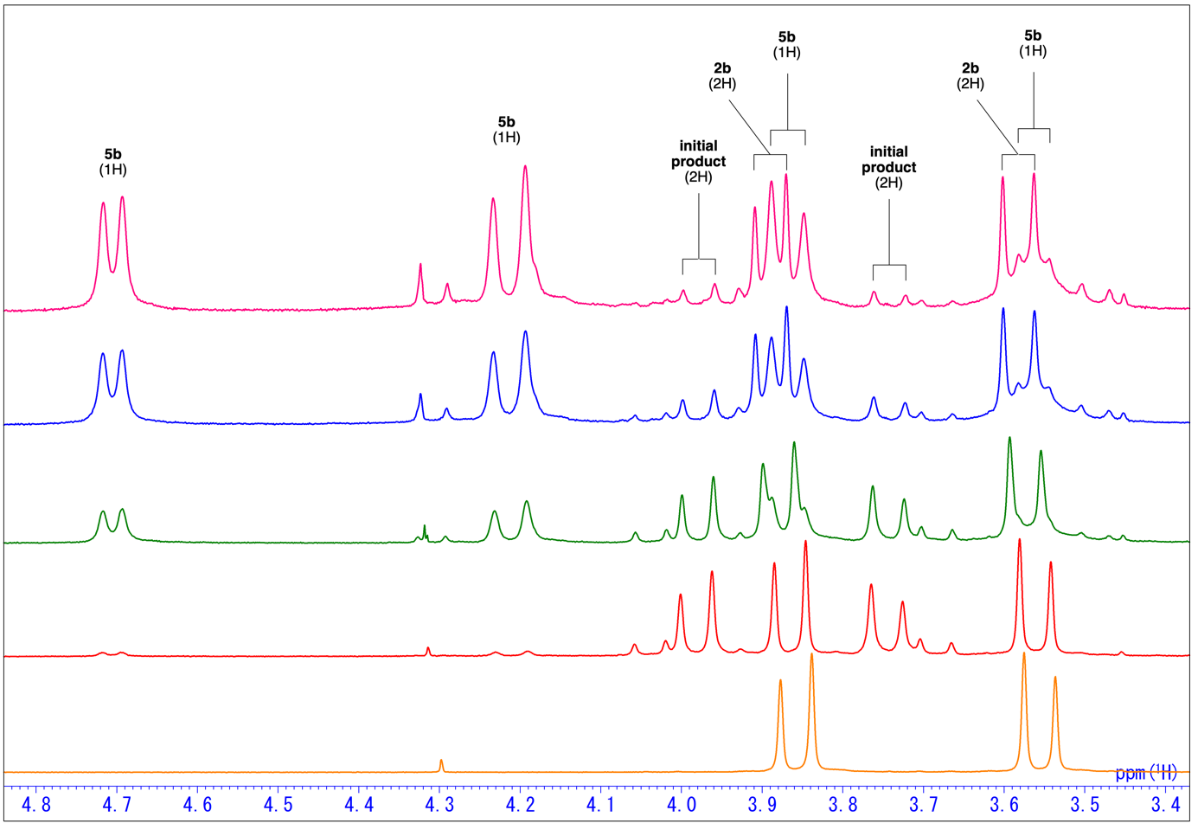


Fig. S5 Expansion (3.4 - 4.8 ppm region) of Fig. S4

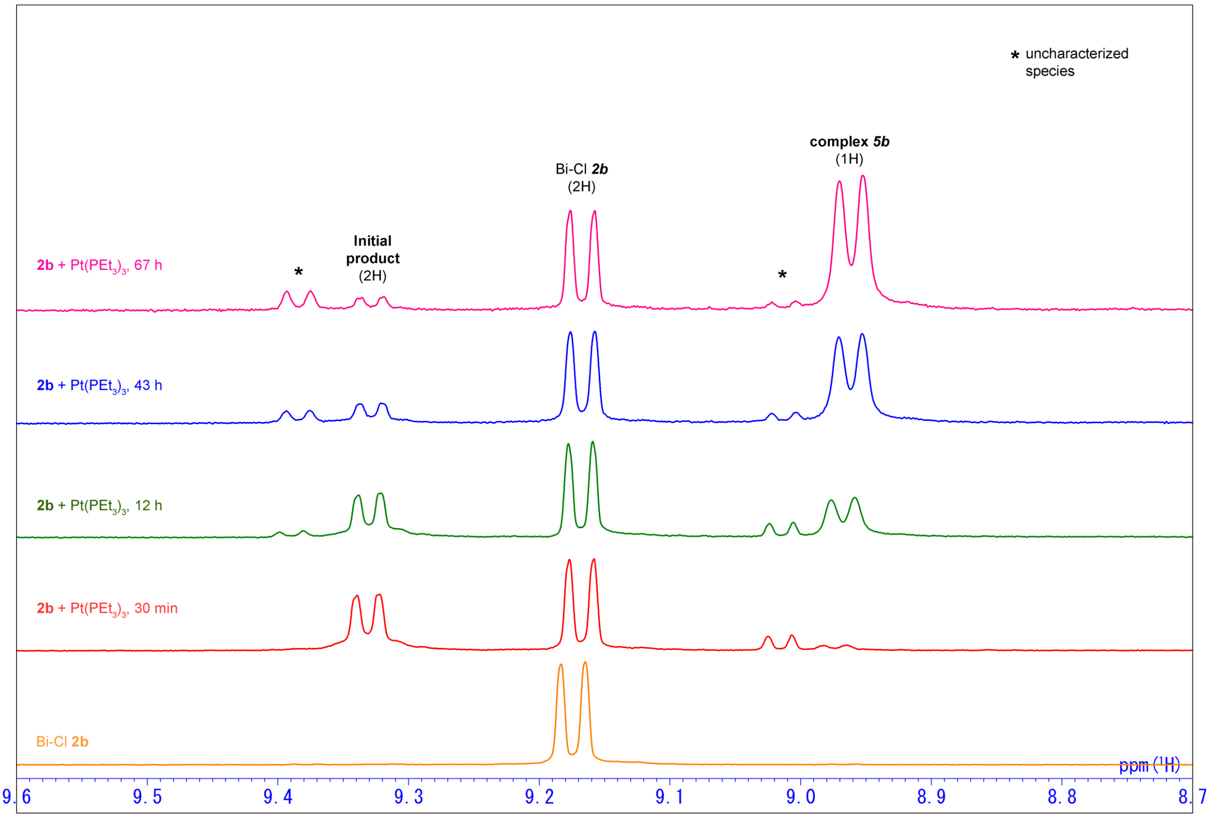


Fig. S6 Expansion (8.7 - 9.6 ppm region) of Fig. S4

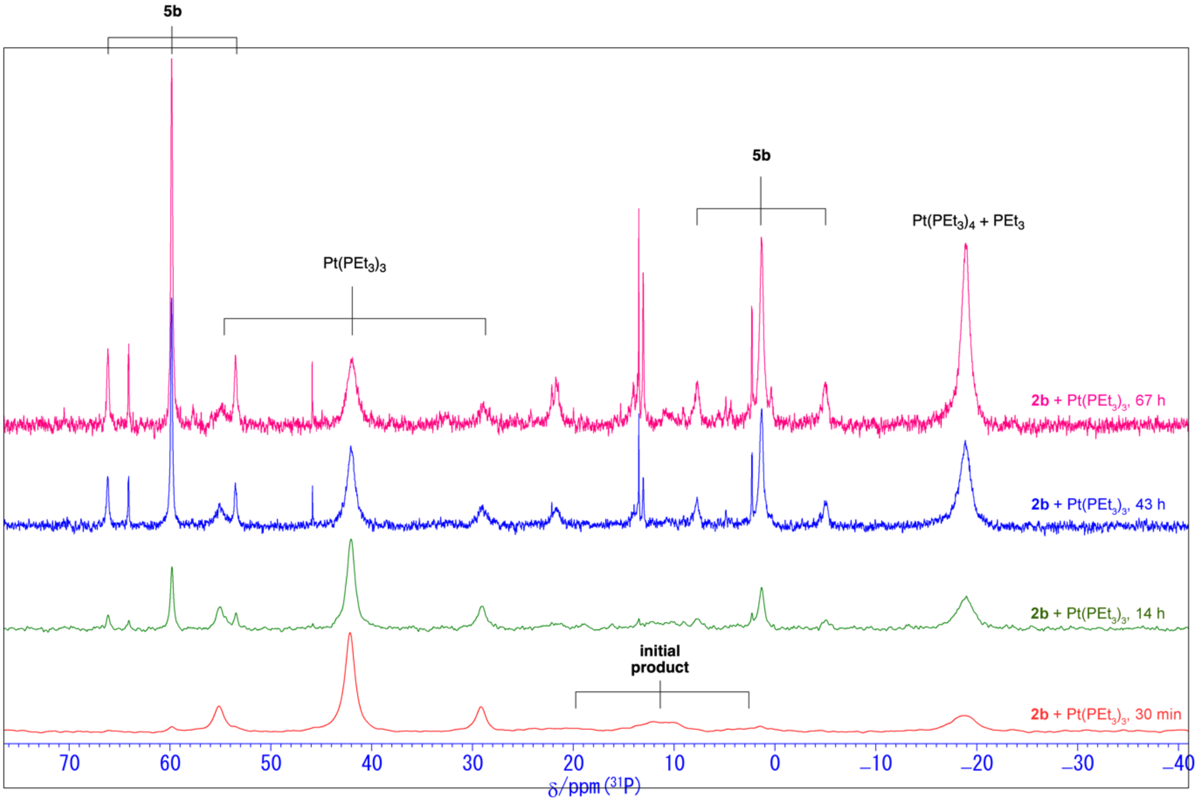
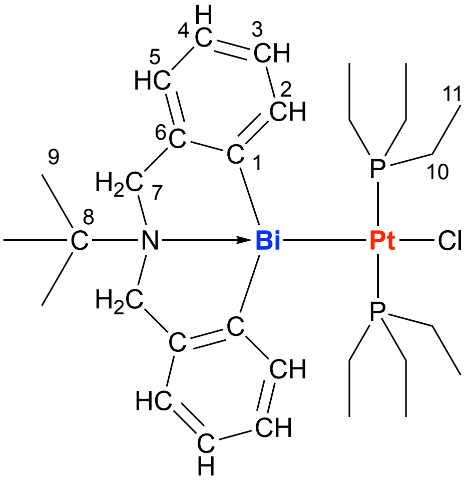


Fig. S7 ^{13}P{^{1}H} NMR spectra (161 MHz, C_6D_6) of the reaction mixture of **2b** and $Pt(PEt_3)_3$ after 30 min (red), 14 h (green), 43 h (blue) and 67 h (pink).

4. Synthesis of complex 6a

Synthesis of complex 6a. To a Schlenk tube containing $Pt(PEt_3)_3$ (0.24 mmol, prepared from 159 mg of $Pt(PEt_3)_4$ by heating at 60 ºC under vacuum) was added a THF (12 mL) solution **2a** (90 mg, 0.18 mmol). The clear light orange solution was stirred for 30 min at room temperature. Then the volatiles were removed under vacuum to leave brown-yellow residue. The residue was extracted with hexane (1 × 10 mL, 3 × 5 mL). Each extract was kept in a freezer at –35 ºC. From the first extract, **6a** was obtained as yellow crystals (42 mg, 25% yield). ^{1}H NMR (600 MHz, C_6D_6, Fig. S38) δ 0.93-1.06 (m, 27H, H-9 & H-11), 1.89 (very broad s, 12H, H-10), 3.69 (d, J = 15.4 Hz, 2H, H-7), 3.85 (d, J = 15.4 Hz, 2H, H-7), 6.98 (dd, J = 1.0, 7.3 Hz, 2H, H-5), 7.10 (dt, J = 1.5, 7.2 Hz, 2H, H-3), 7.15 (dt, J = 1.6, 7.2 Hz, 2H, H-4), 9.34 (dd, J = 1.5, 7.0 Hz, 2H, H-2). ^{13}C{^{1}H} NMR (151 MHz, C_6D_6, Figs. S39-S41) δ 9.3 (br s, C-11), 17.0 (br s, C10), 27.9 (s, C-9), 57.1 (s, C-8), 57.3 (s, C-7), 127.25 (C-5), 127.33 (C-4), 128.8 (C-3), 142.4 (br s, C-1), 145.8 (s with Pt satellites, $^{3}J_{\text{Pt-C}}$ = 46 Hz, C-2), 148.6 (C-6). ^{31}P NMR (243 MHz, C_6D_6, Fig. S42) δ 0-21 (very broad multiplet). Anal. Calcd for $C_{30}H_{51}BiClNP_2Pt$: C, 38.86%; H, 5.54%; N, 1.51%. Found: C, 38.73%; H, 5.59%; N, 1.51%.



Atomic numbering of complex **6a** for the NMR signal assignment

5. Monitoring the change of complex 6a in C_6D_6 or THF-d_8 by ^{1}H NMR

Complex **6a** (ca. 2 mg) was dissolved in C_6D_6 or THF-d_6 (0.5 mL). ^{1}H NMR spectra of the solution were measured periodically during 4 days (Fig. S8 (C_6D_6) and Fig. S9 (THF-d_6)). Another sample containing **6a** (ca. 2 mg) and PEt_3 (20 wt% toluene solution, 2.5 µL, ca. 2 equiv) was also prepared and monitored by ^{1}H NMR (Fig. S10).

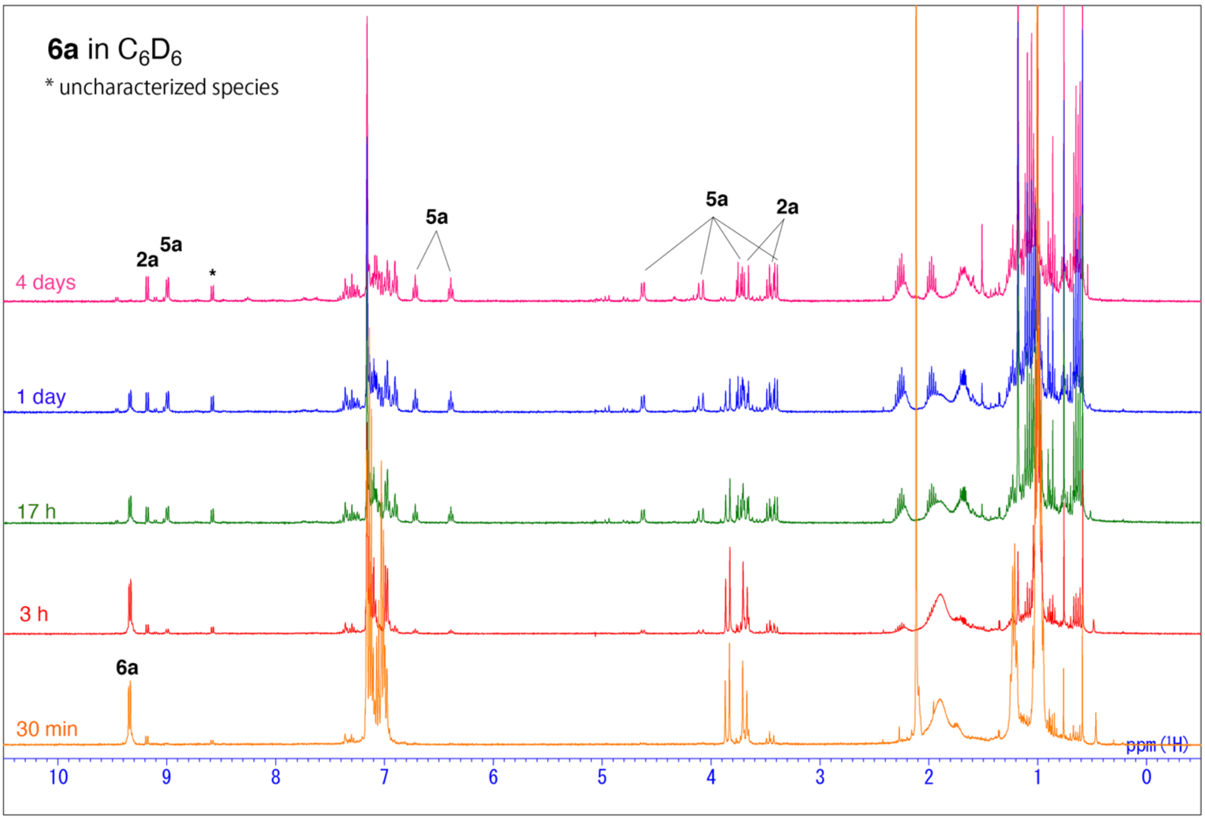


Fig. S8 Change of ^{1}H NMR spectra (400 MHz) of the C_6D_6 solution of **6a** after 30 min (orange), 3 h (red), 17 h (green), 1 day (blue) and 4 days (pink).

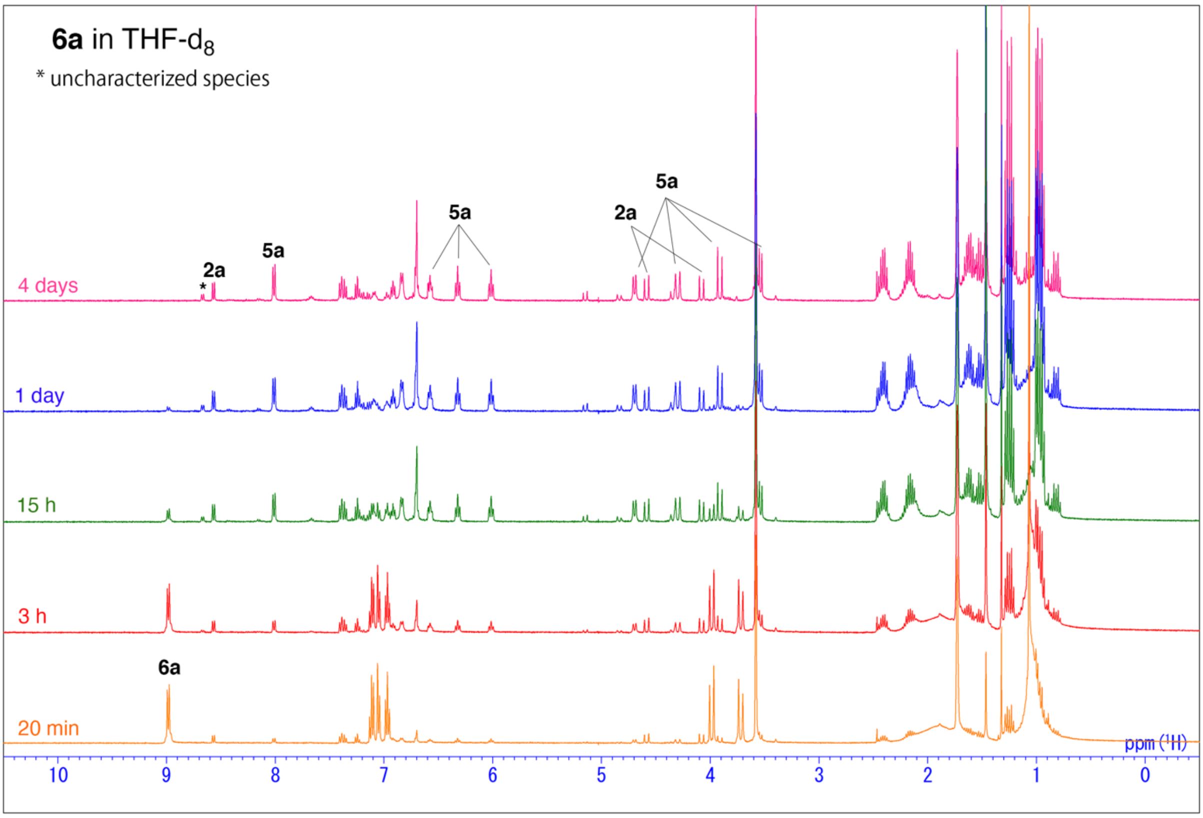


Fig. S9 Change of ^{1}H NMR spectra (400 MHz) of the THF-d_8 solution of **6a** after 20 min (orange), 3 h (red), 15 h (green), 1 day (blue) and 4 days (pink).

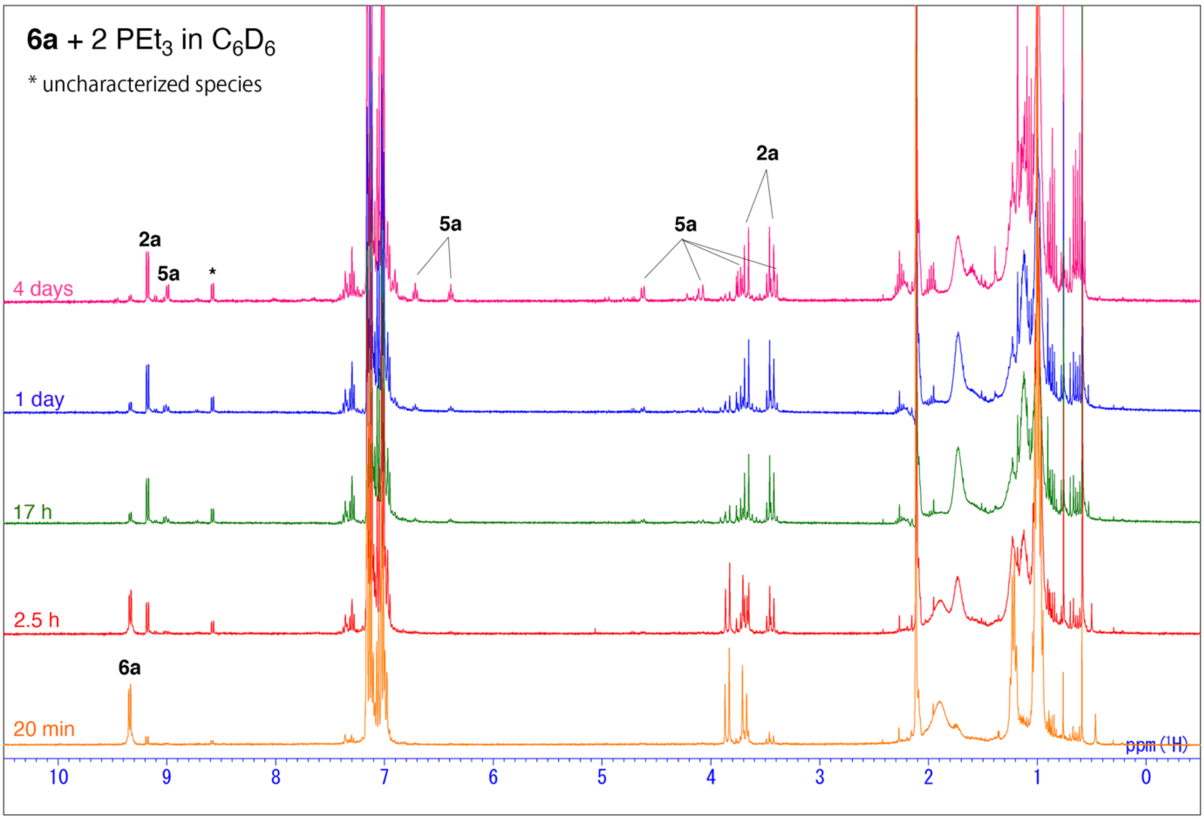


Fig. S10 Change of ^{1}H NMR spectra (400 MHz) of the C_6D_6 solution of **6a** and PEt_3 (ca. 2 equiv) after 20 min (orange), 2.5 h (red), 17 h (green), 1 day (blue) and 4 days (pink).

6. Single crystal X-ray structure analysis

Data collection of complexes **4** and **5a** was performed at –120 °C on a Bruker APEX II diffractometer using graphite monochromated Mo Kα radiation. The determination of crystal class and unit cell parameters was carried out with the APEX2 program package.[S5] The raw frame data were processed using SAINT[S6] and SADABS[S7] to yield the reduction data file. Structure solution and refinement were performed using CrystalStructure software package[S8] with PATTY[S9] and SHELXL[S10] programs.

The crystals of **6a** was obtained directly from the hexane extract of the crude reaction mixture. Although the crystals were very small and their quality was not very good, recrystallization could not be attained due to the instability of **6a** in solution. Data collection of complex **6a** was performed at –180 °C on a Rigaku XtaLAB P200 diffractometer using multi-layer mirror optics monochromated Mo Kα radiation. The determination of crystal class and unit cell parameters was carried out with the CrysAlisPro program package.[S11] The raw frame data were processed using CrysAlisPro to yield the reduction data file. Structure solution and refinement were performed using Olex2 software package[S12] with SHELXT and SHELXL programs.[S10]

CCDC 1991384, 1991385 and 2043453 contain the supplementary crystallographic data for complexes **4**, **5a** and **6a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.

7. References:

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S2 S. Shimada, O. Yamazaki, T. Tanaka, Y. Suzuki and M. Tanaka, *J. Organomet. Chem.*, 2004, **689**, 3012-3023.

S3 S. Shimada, J. Maruyama, Y.-K. Choe and T. Yamashita, *Chem. Commun.*, 2009, 6168-6170.

S4 T. Yoshida, T. Matsuda, S. Otsuka, G. W. Parshall and W. G. Peet, *Inorg. Synth.*, 1979, **19**, 110-111.

S5 APEX2 Version 2009.9 ; Bruker AXS Inc., Madison, WI 2009.

S6 SAINT Version 7.68A; Bruker AXS Inc., Madison, WI 2009.

S7 G. M. Sheldrick, SADABS. University of Göttingen, Germany, 2007.

S8 CrystalStructure 4.3: Crystal Structure Analysis Package, Rigaku Corporation (2000-2018). Tokyo 196-8666, Japan.

S9 P. T. Beurskens, G. Admiraal, H. Behm, G. Beurskens, J. M. M. Smits and C. Smykalla, Z. Kristallogr. 1991, Suppl.4, 99.

S10 Shelxl Version 2018/3: G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *64*, 112.

S11 CrysAlisPro 1.171.40.67a. Rigaku OD, 2019.

S12 Olex2 1.3: O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339.

8. NMR spectra of complexes 4, 5a and 6a

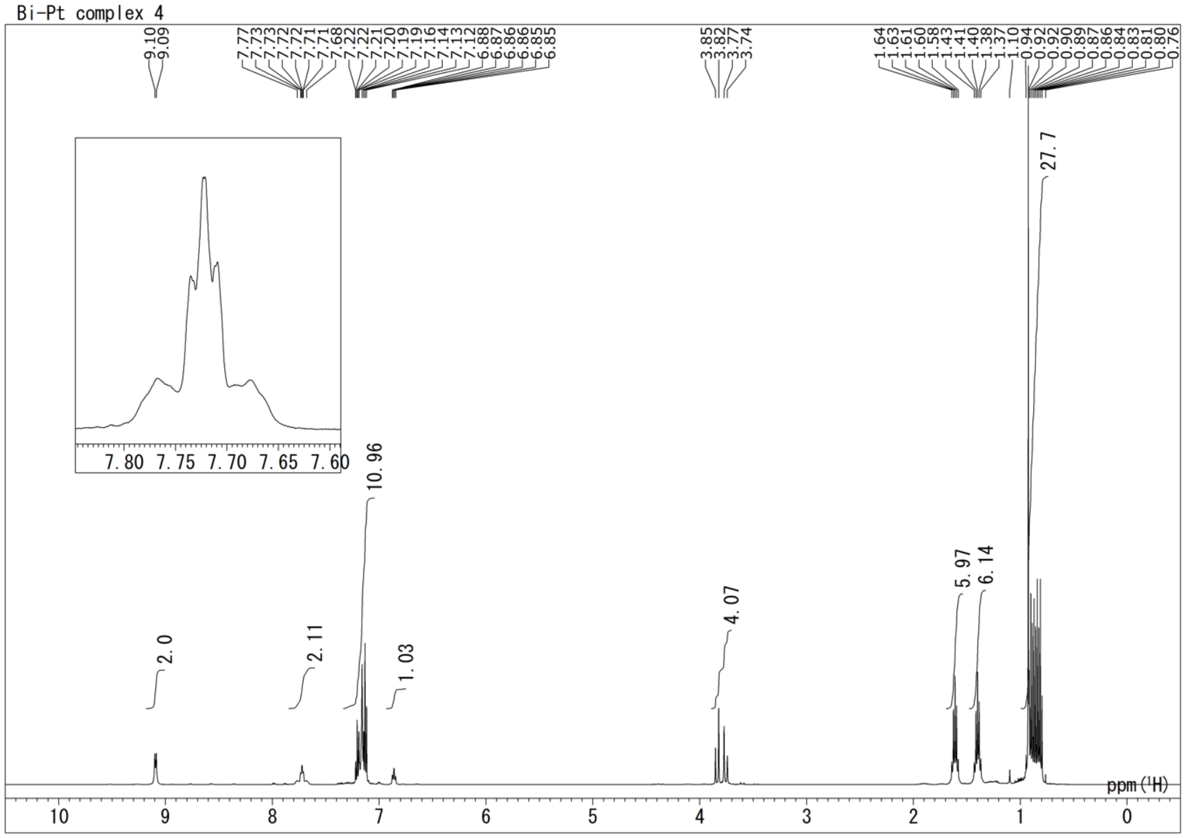


Fig. S11 ^{1}H NMR spectrum (499 MHz) of complex **4** in C_6D_6.

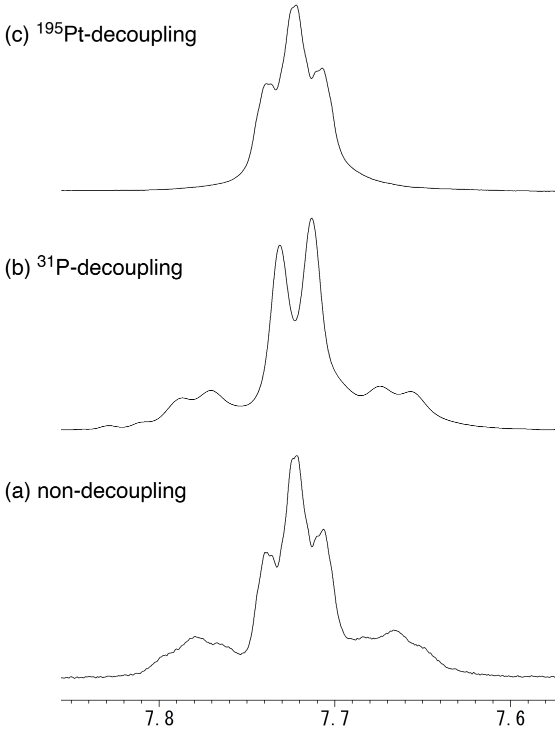
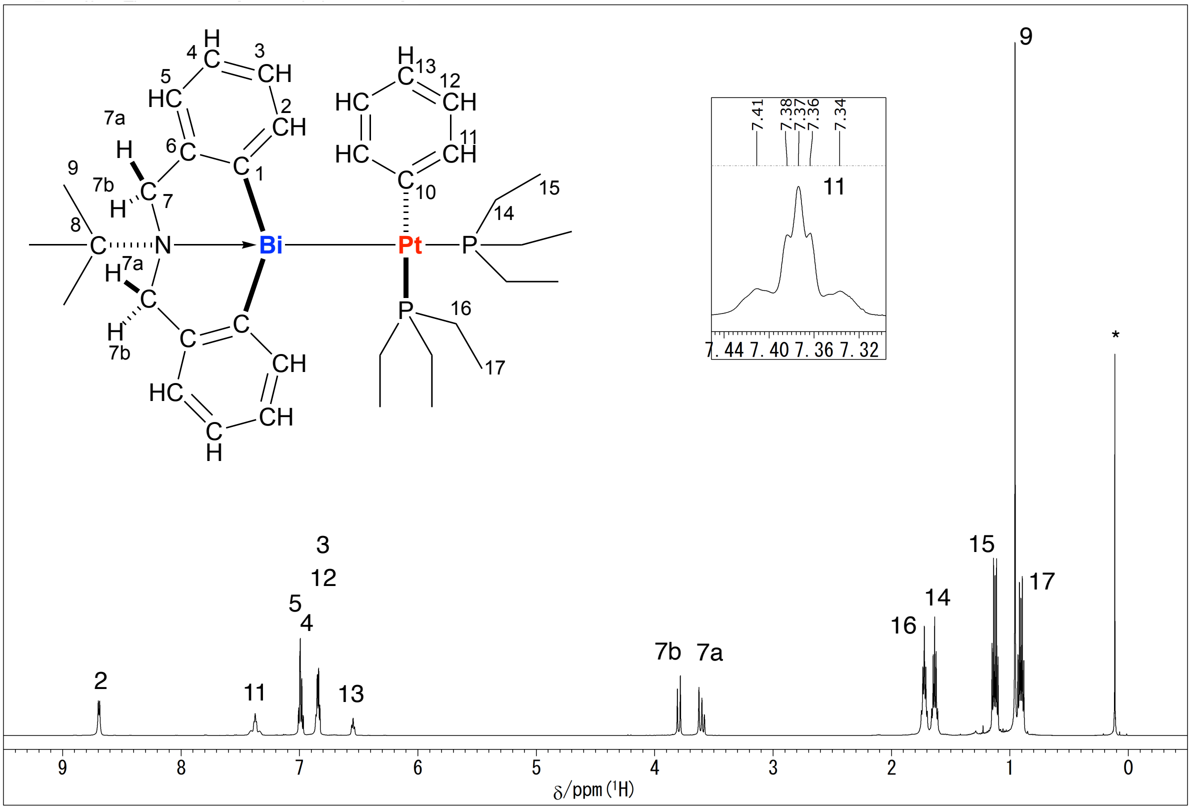
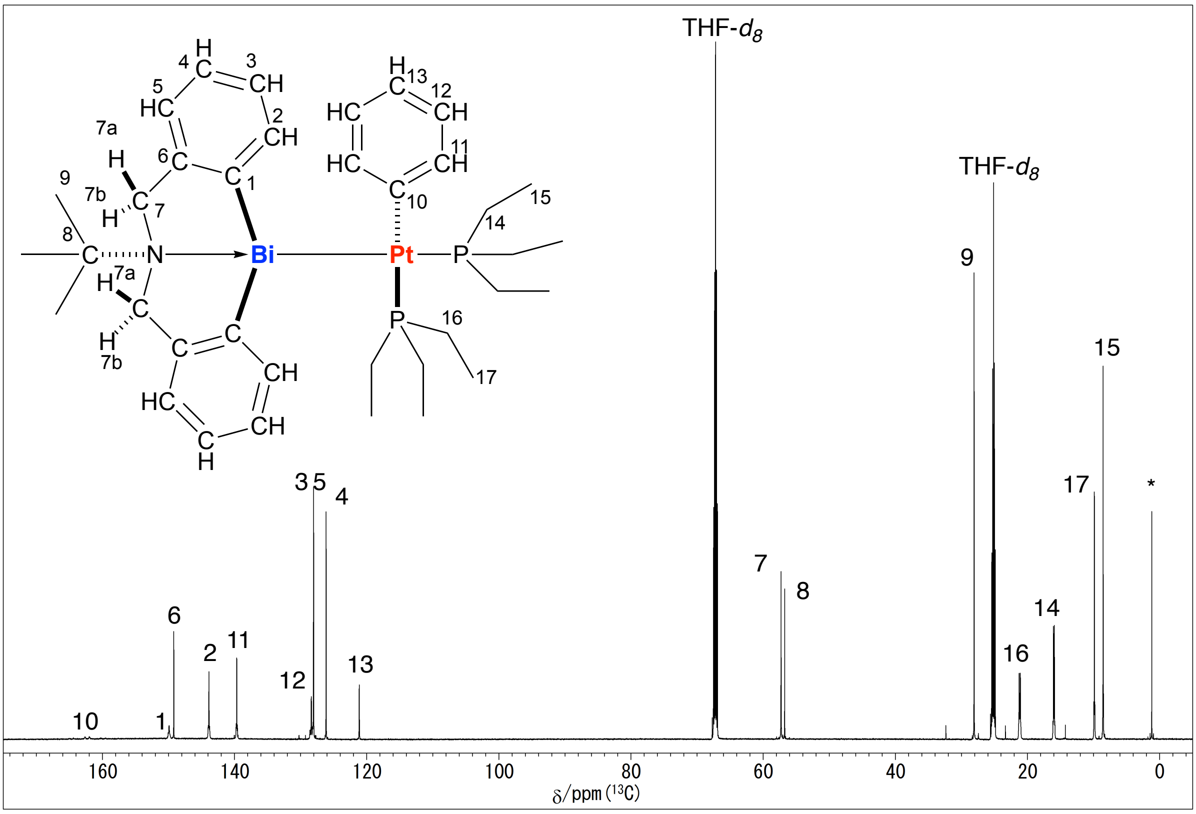


Fig. S12 Change of the shape of ^{1}H NMR (C_6D_6, 400 MHz) signal at 7.72 ppm by the ^{31}P and ^{195}Pt decoupling.



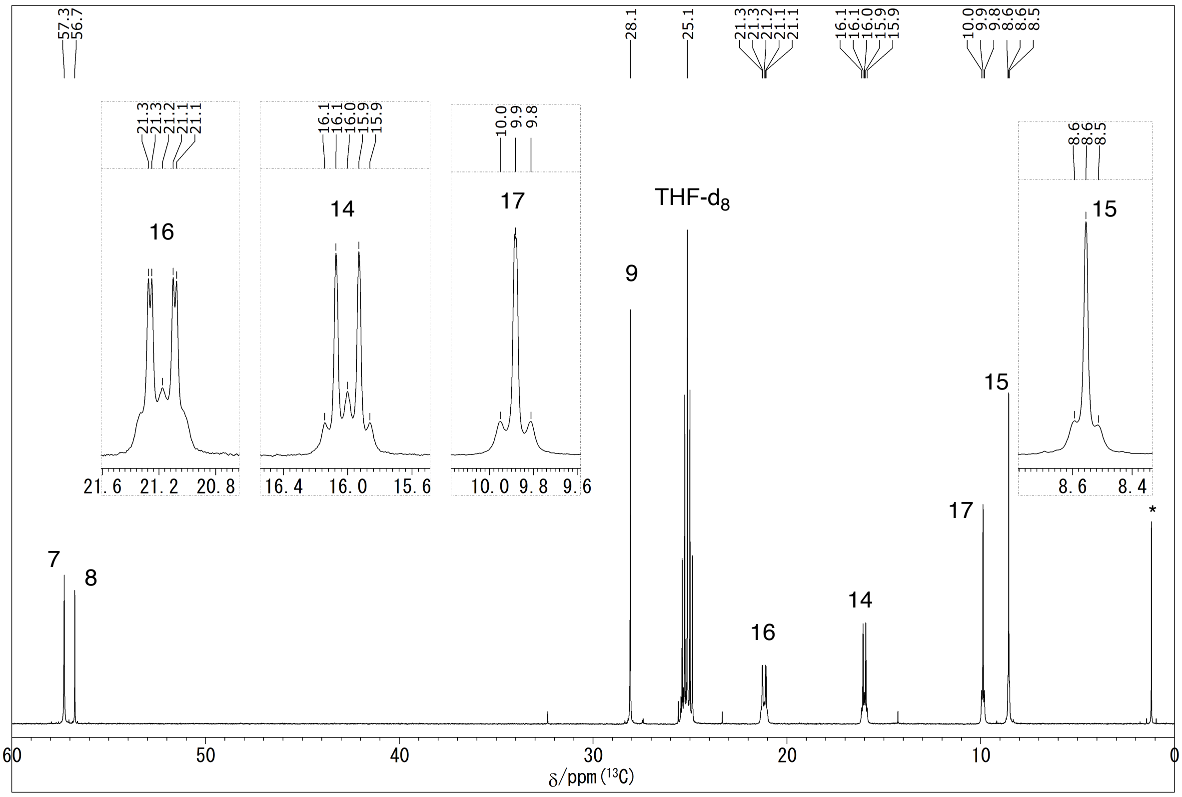
*silicone grease

Fig. S13 ^{1}H NMR spectrum (600 MHz) of complex **4** in THF-d_8.



*silicone grease

Fig. S14 ^{13}C{^{1}H} NMR spectrum (151 MHz) of complex **4** in THF-d_8.



*silicone grease

Fig. S15 A part (0–60 ppm region) of $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz) of complex **4** in THF-d_8.

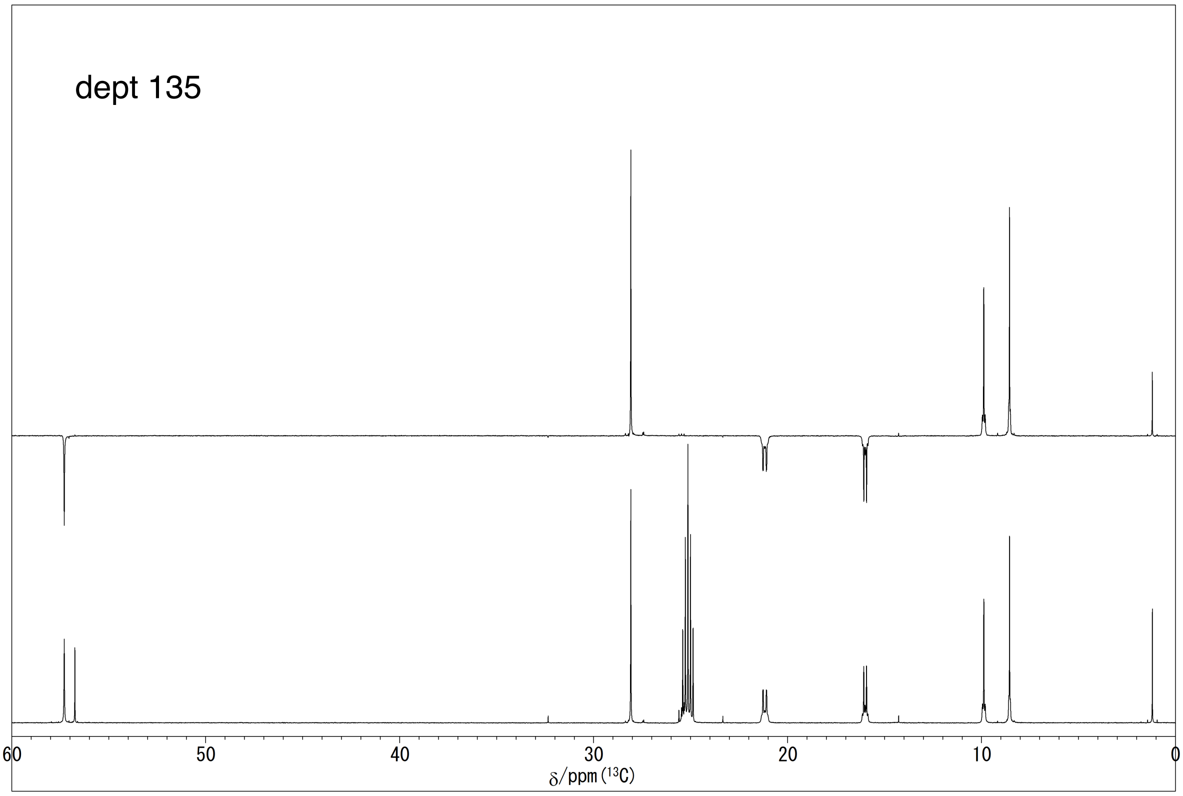


Fig. S16 A part (0–60 ppm region) of $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz) with dept 135 spectrum (upper) of complex **4** in THF-d_8.

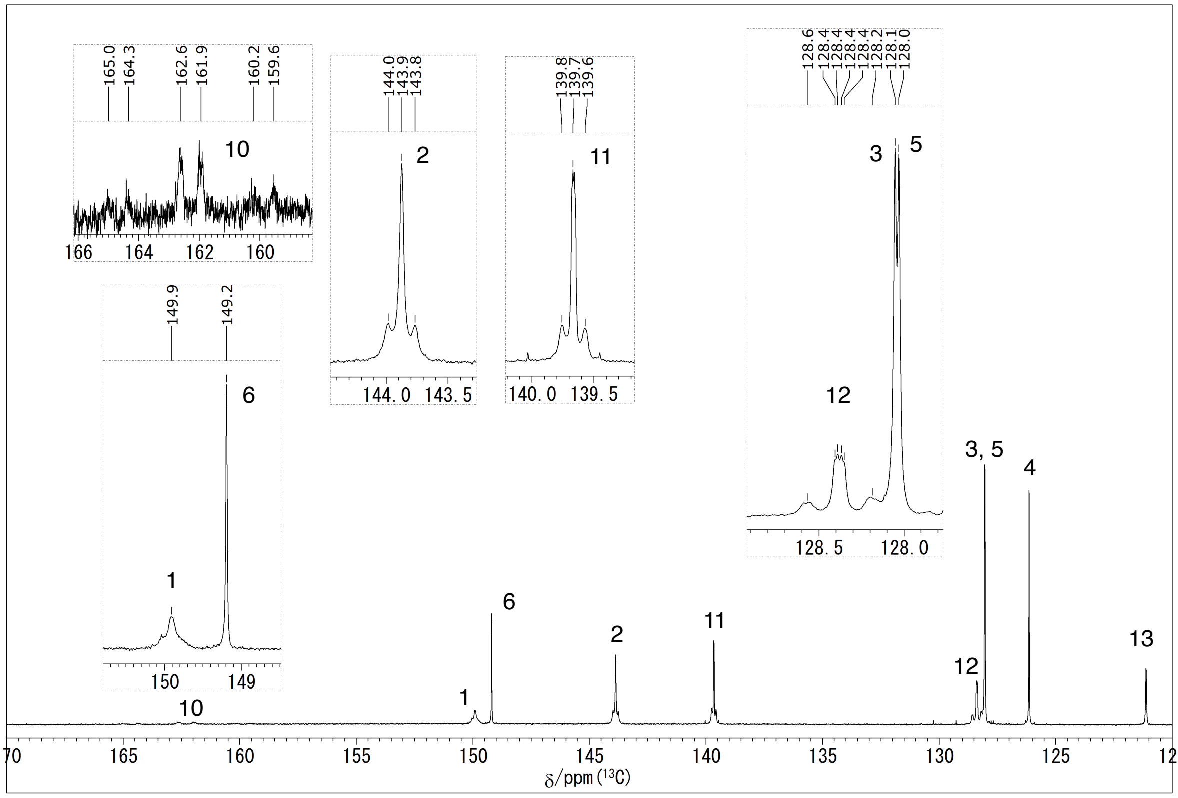


Fig. S17 A part (120–170 ppm region) of $^{13}C\{^1H\}$ NMR spectrum (151 MHz) of complex **4** in THF-d_8.

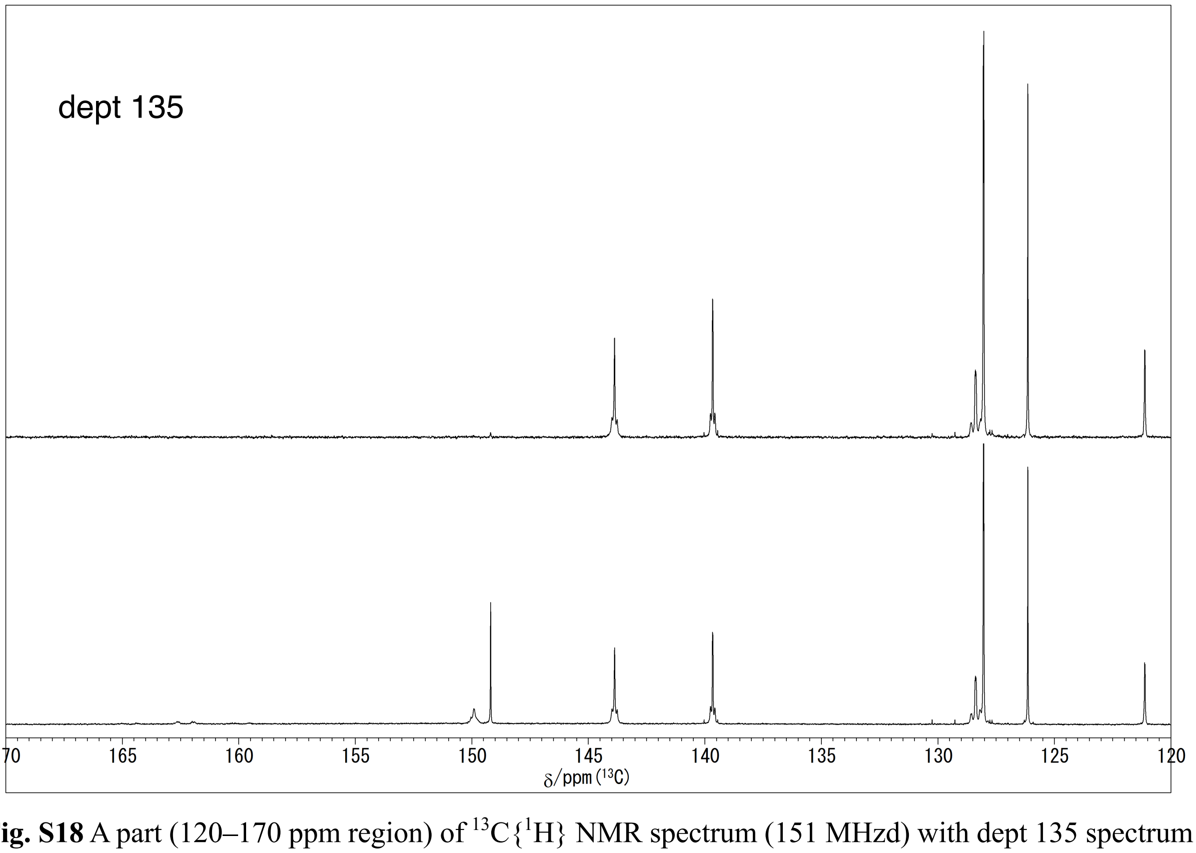


Fig. S18 A part (120–170 ppm region) of $^{13}C\{^1H\}$ NMR spectrum (151 MHzd) with dept 135 spectrum (upper) of complex **4** in THF-d_8.

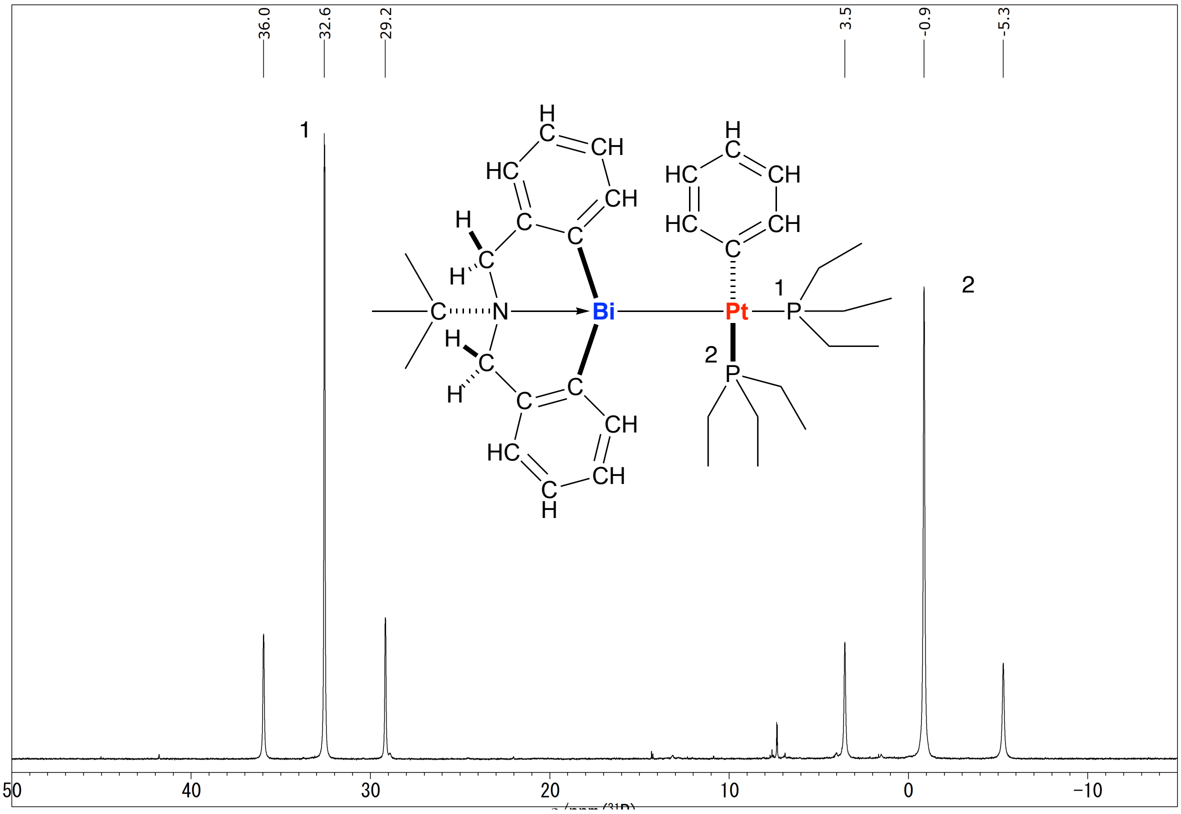


Fig. S19 ^{13}P{^{1}H} NMR spectrum (243 MHz) of complex **4** in THF-d_8.

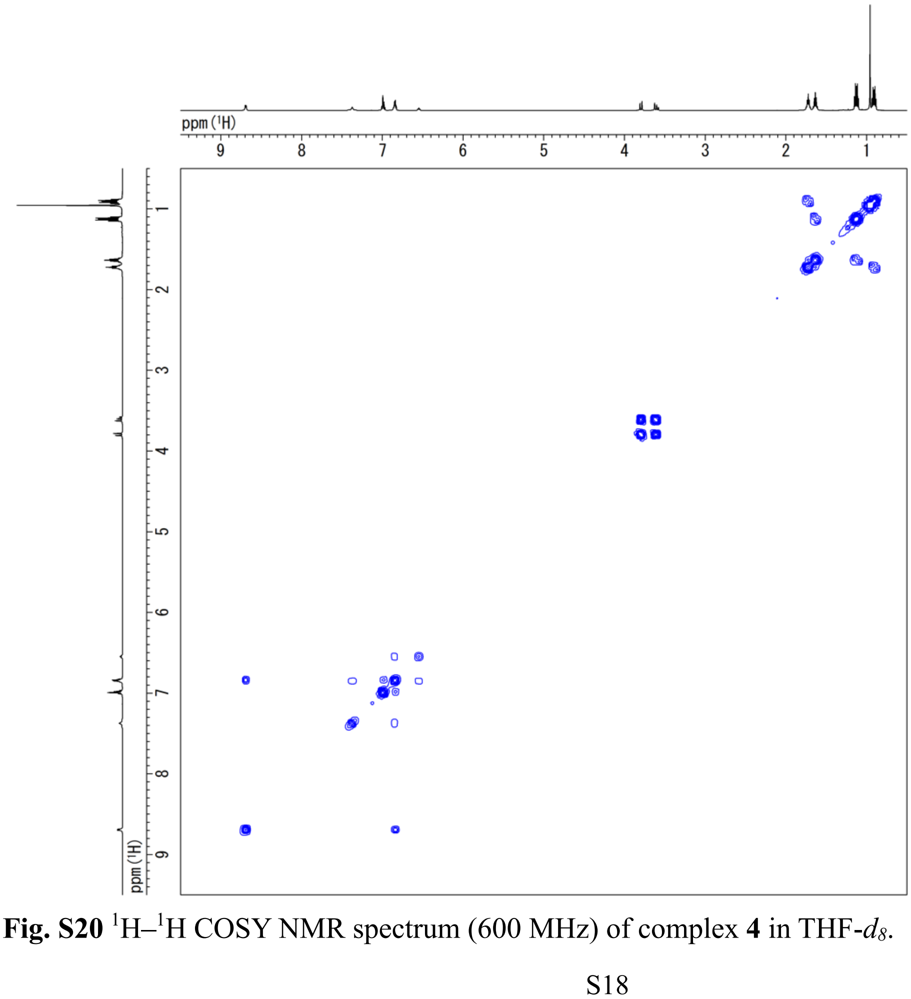


Fig. S20 ^{1}H–^{1}H COSY NMR spectrum (600 MHz) of complex **4** in THF-d_8.

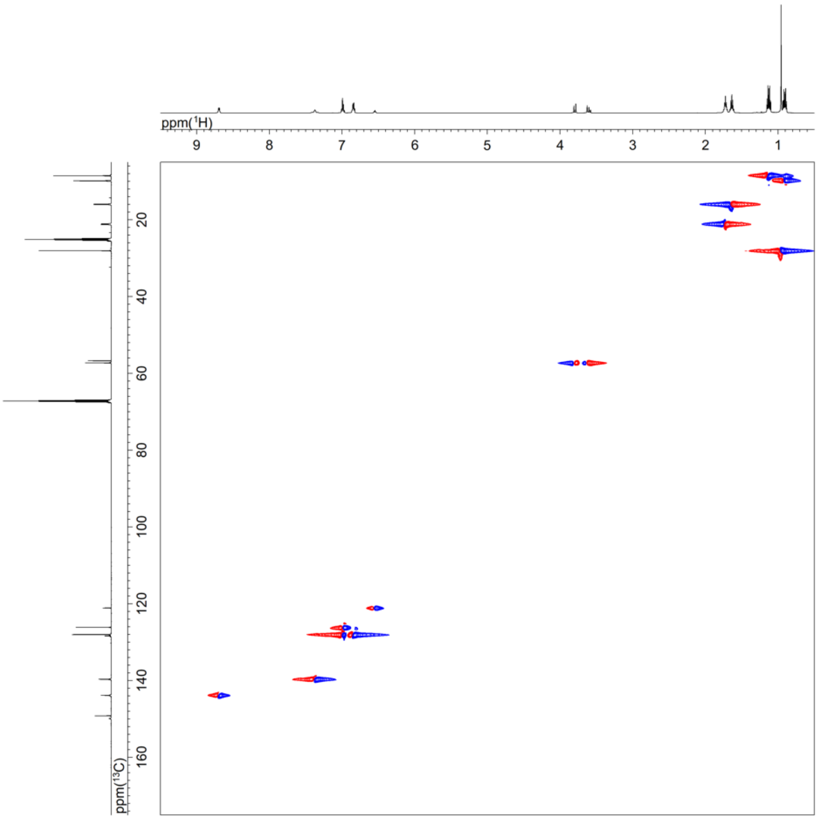


Fig. S21 ^{1}H–^{13}C HSQC NMR spectrum (600 MHz for ^{1}H, 151 MHz for ^{13}C) of complex **4** in THF-d_8.

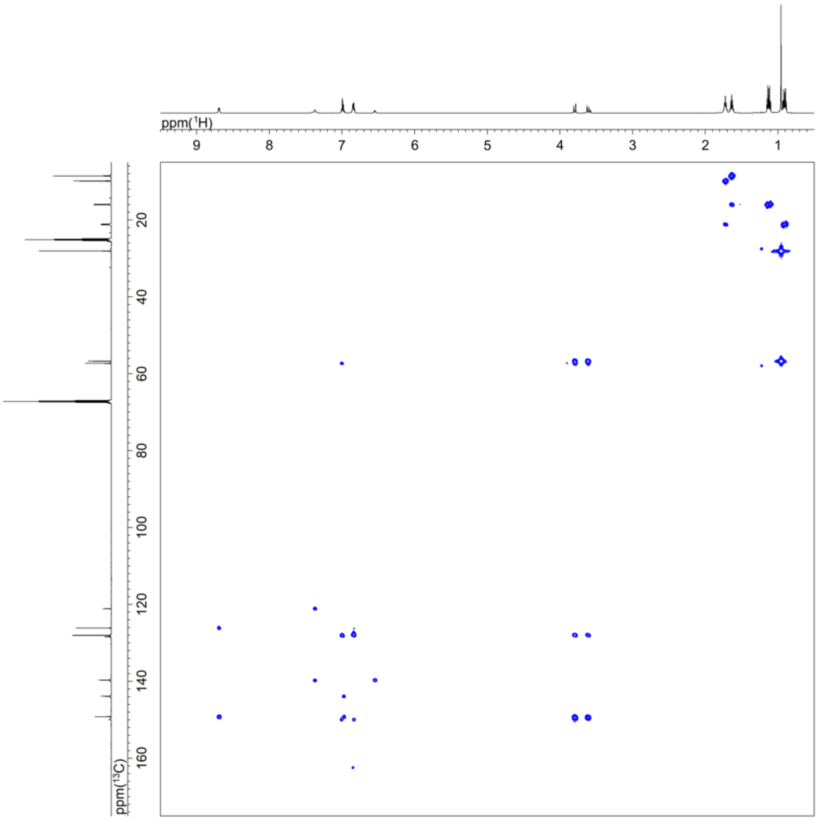


Fig. S22 ^{1}H–^{13}C HMBC NMR spectrum (600 MHz for ^{1}H, 151 MHz for ^{13}C) of complex **4** in THF-d_8.

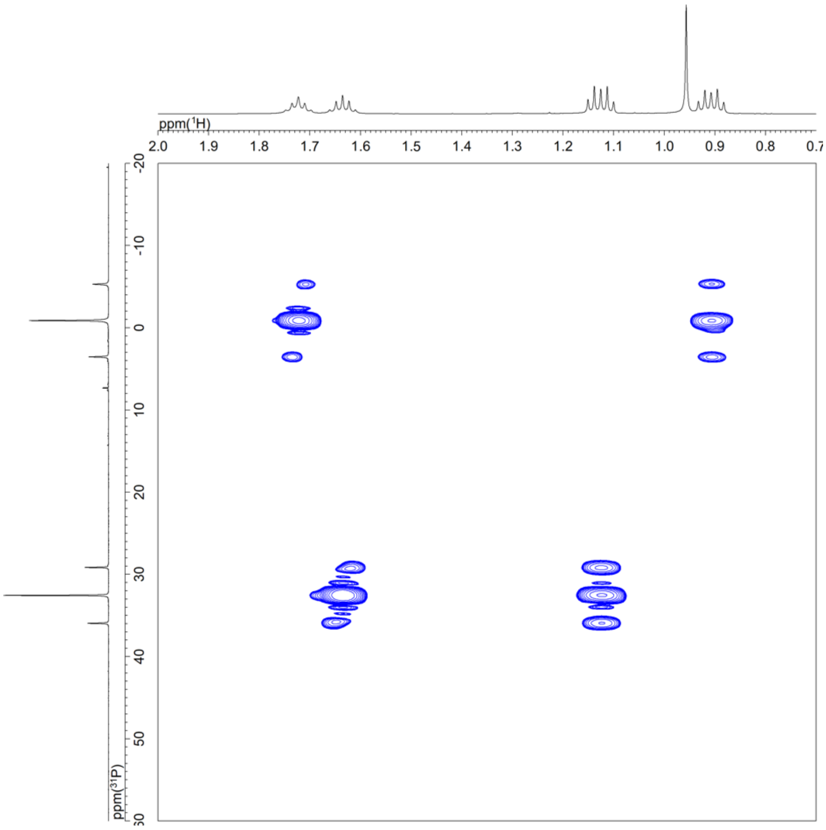


Fig. S23 ^{1}H–^{31}P HMBC NMR spectrum (600 MHz for ^{1}H, 243 MHz for ^{31}P) of complex **4** in THF-d_8.

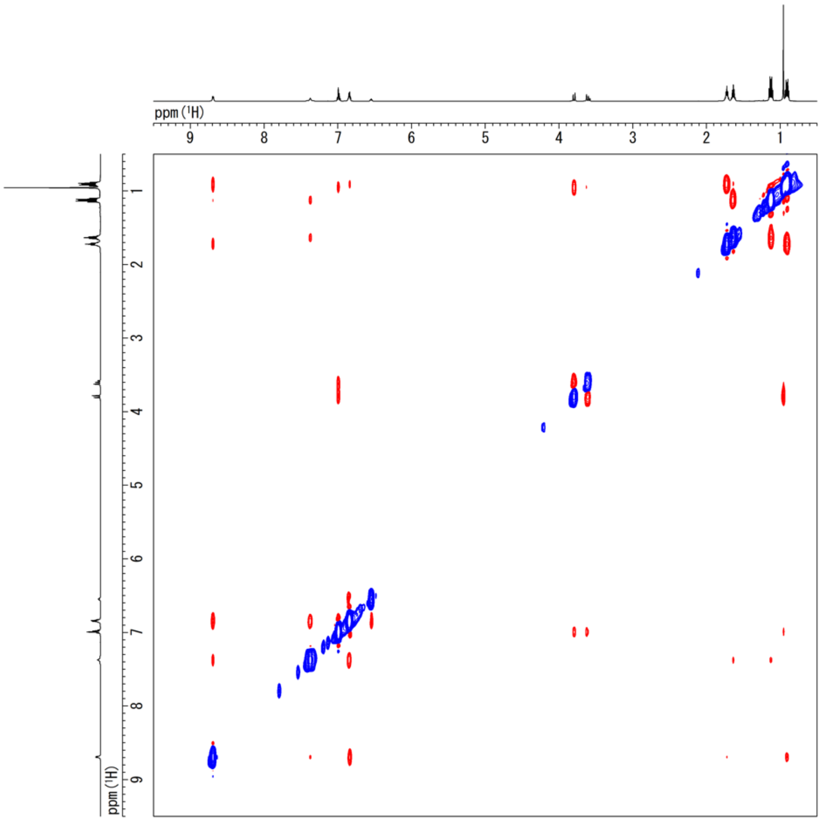


Fig. S24 NOESY NMR spectrum (600 MHz for ^{1}H) of complex **4** in THF-d_8.

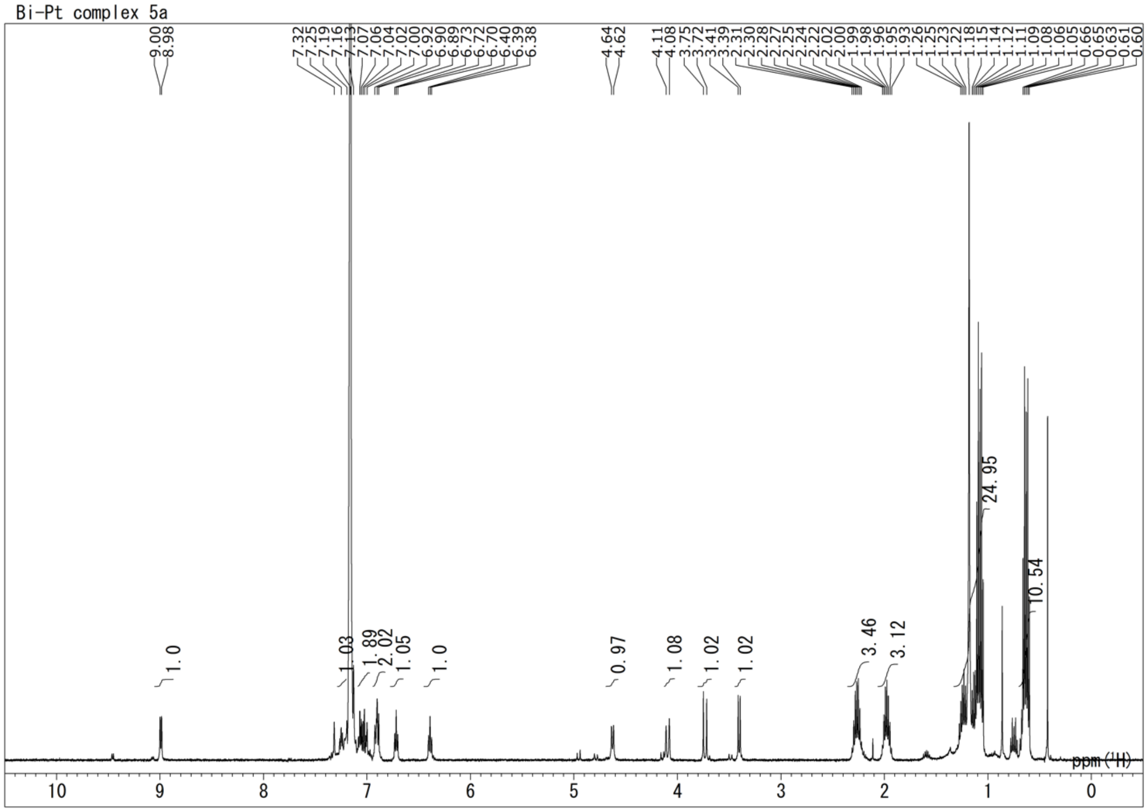
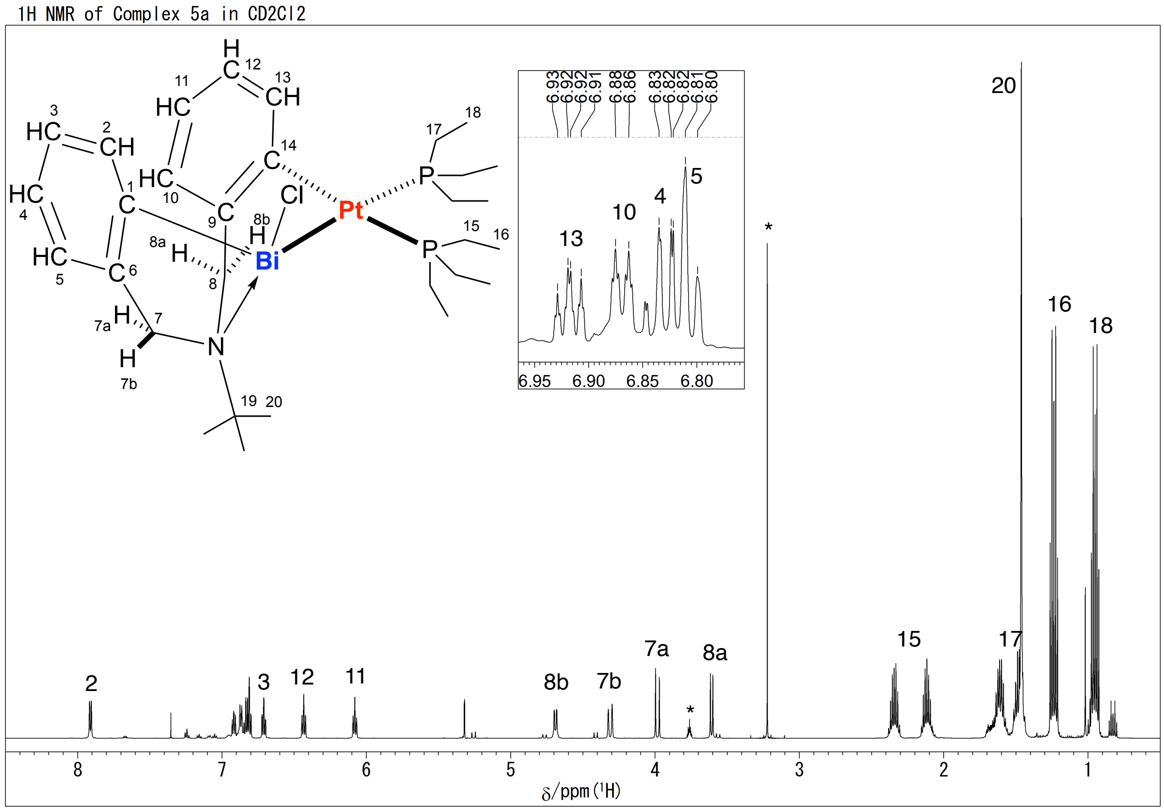
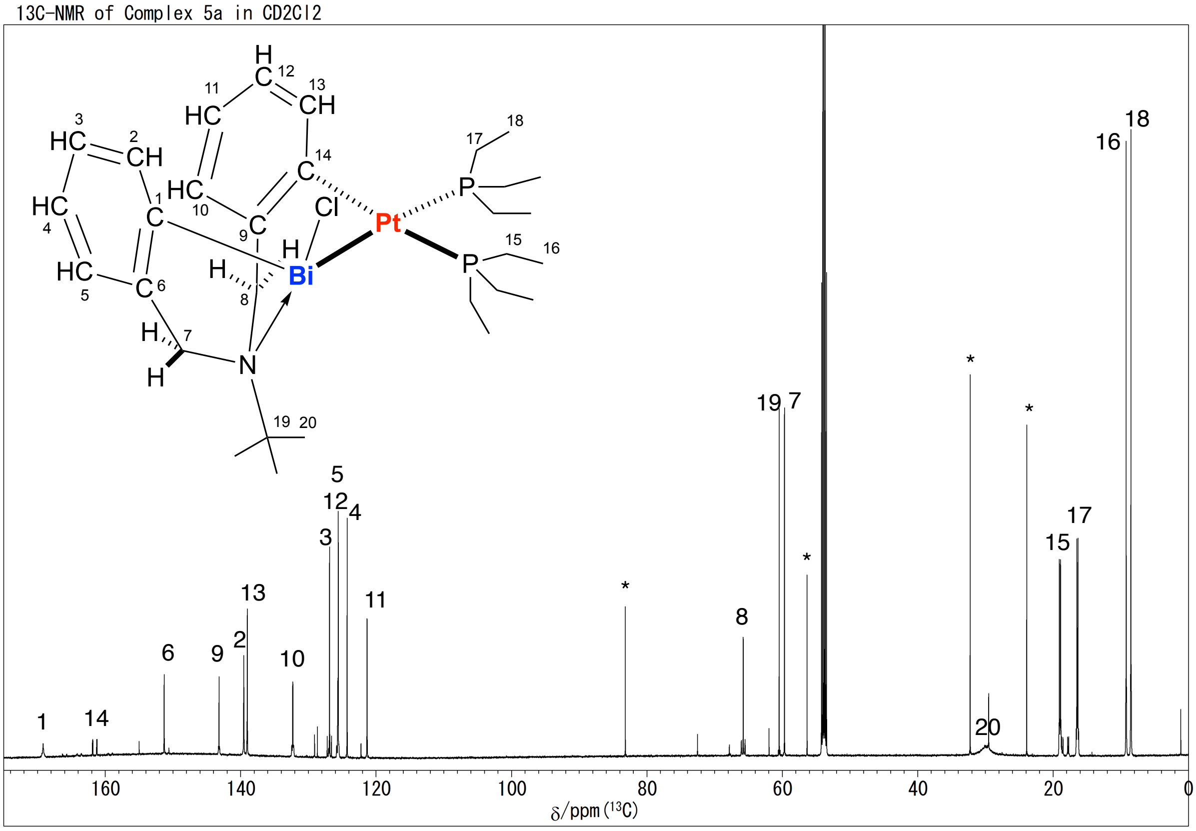


Fig. S25 ^{1}H NMR spectrum (499 MHz) of complex **5a** in C_6D_6.



* cyclopentyl methyl ether

Fig. S26 ^{1}H NMR spectrum (600 MHz) of complex **5a** in CD_2Cl_2.



* cyclopentyl methyl ether

Fig. S27 $^{13}C\{^1H\}$ NMR spectrum (151 MHz) of complex **5a** in CD_2Cl_2.

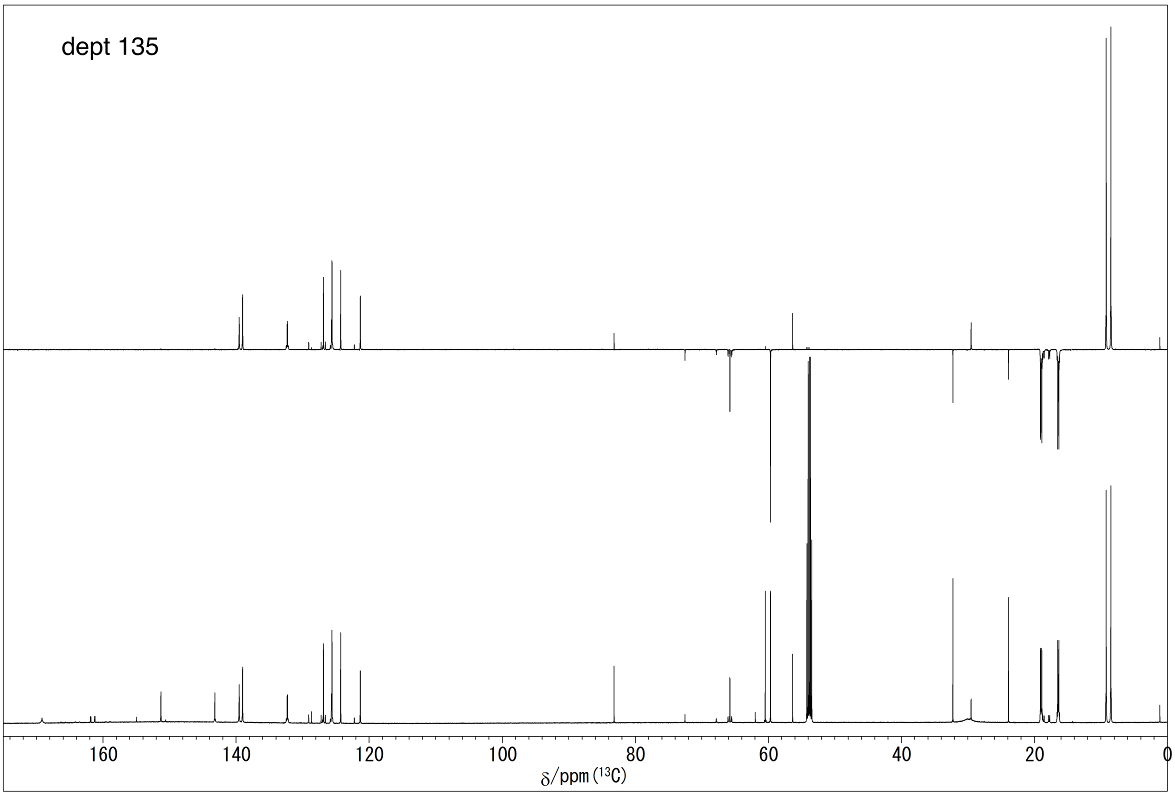
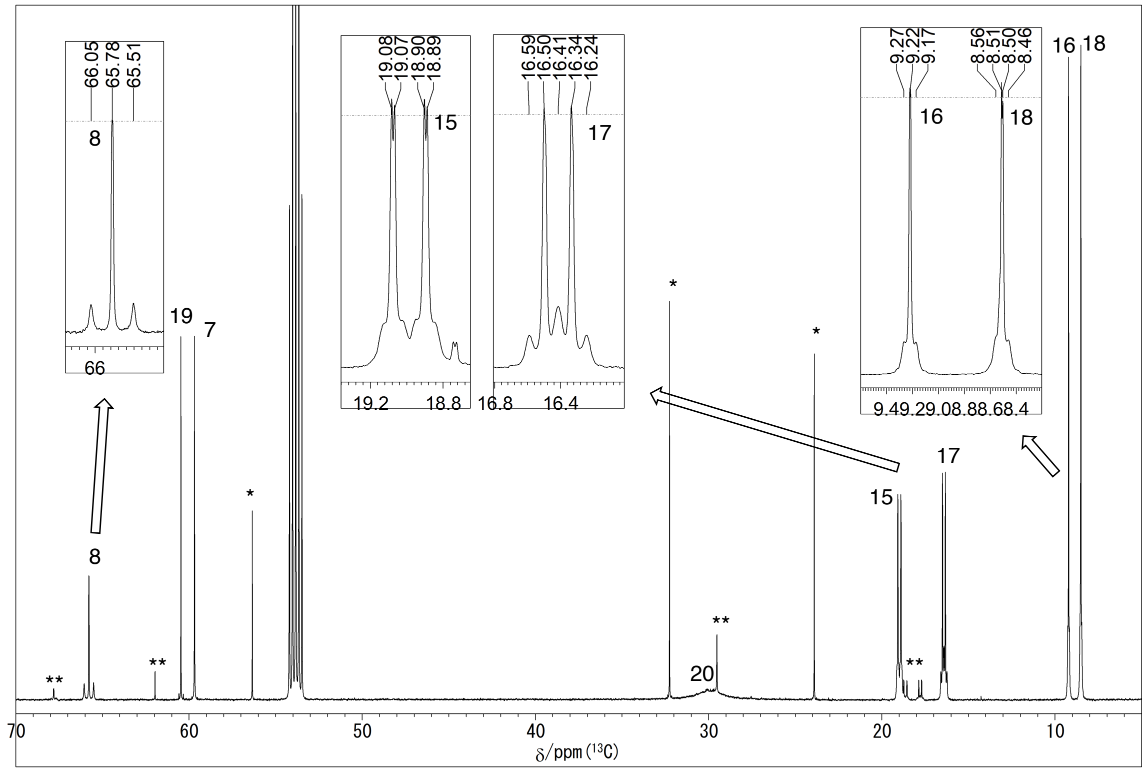
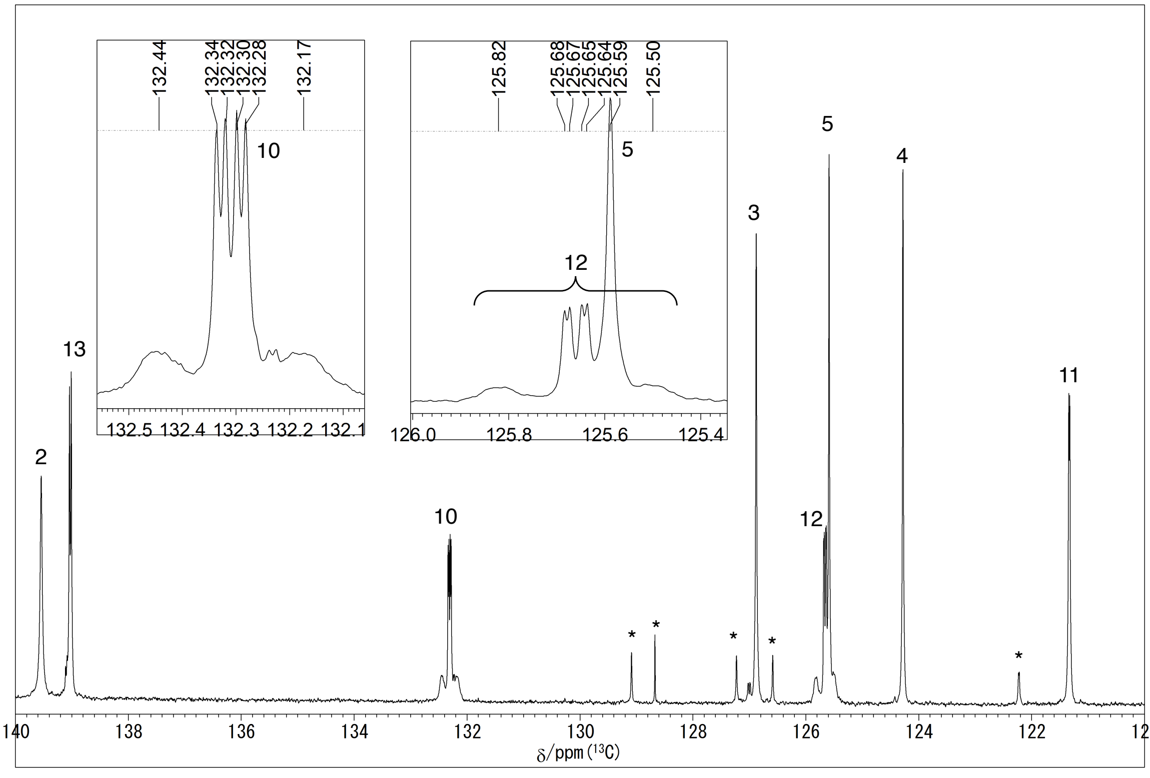


Fig. S28 $^{13}C\{^1H\}$ NMR spectrum (151 MHz) with dept 135 spectrum (upper) of complex **5a** in CD_2Cl_2.



* cyclopentyl methyl ether
** other impurity

Fig. S29 A part (120–140 ppm region) of $^{13}C\{^1H\}$ NMR spectrum (151 MHz) of complex **5a** in CD_2Cl_2.



* impurity

Fig. S30 A part (120–140 ppm region) of $^{13}C\{^1H\}$ NMR spectrum (151 MHz) of complex **5a** in CD_2Cl_2.

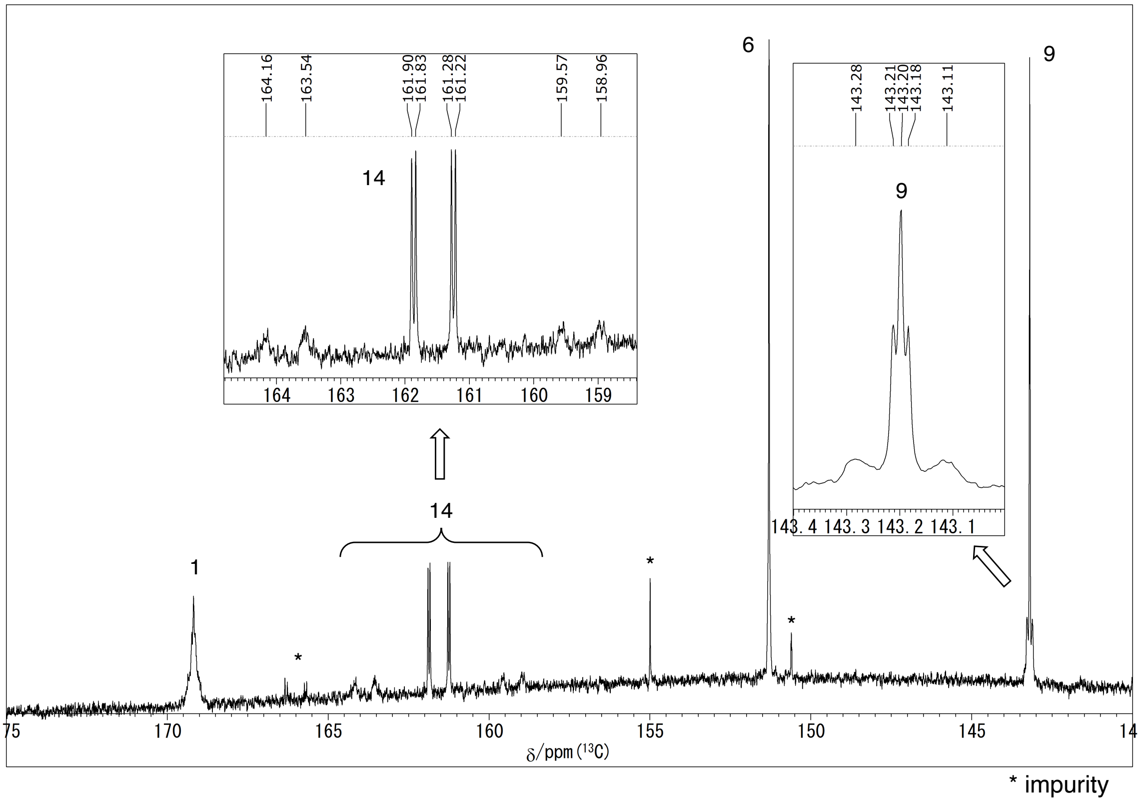


Fig. S31 A part (140–175 ppm region) of ^{13}C{^{1}H} NMR spectrum (151 MHz) of complex **5a** in CD_2Cl_2.

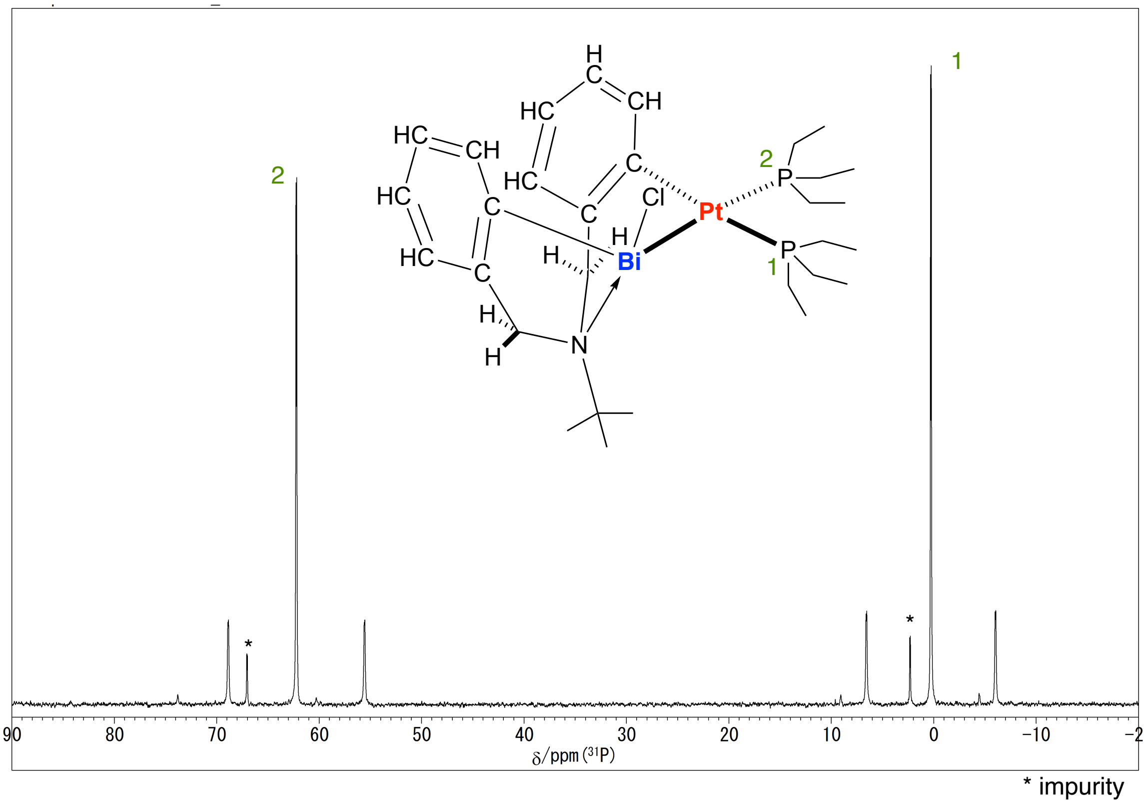


Fig. S32 ^{13}P{^{1}H} NMR spectrum (162 MHz) of complex **5a** in CD_2Cl_2.

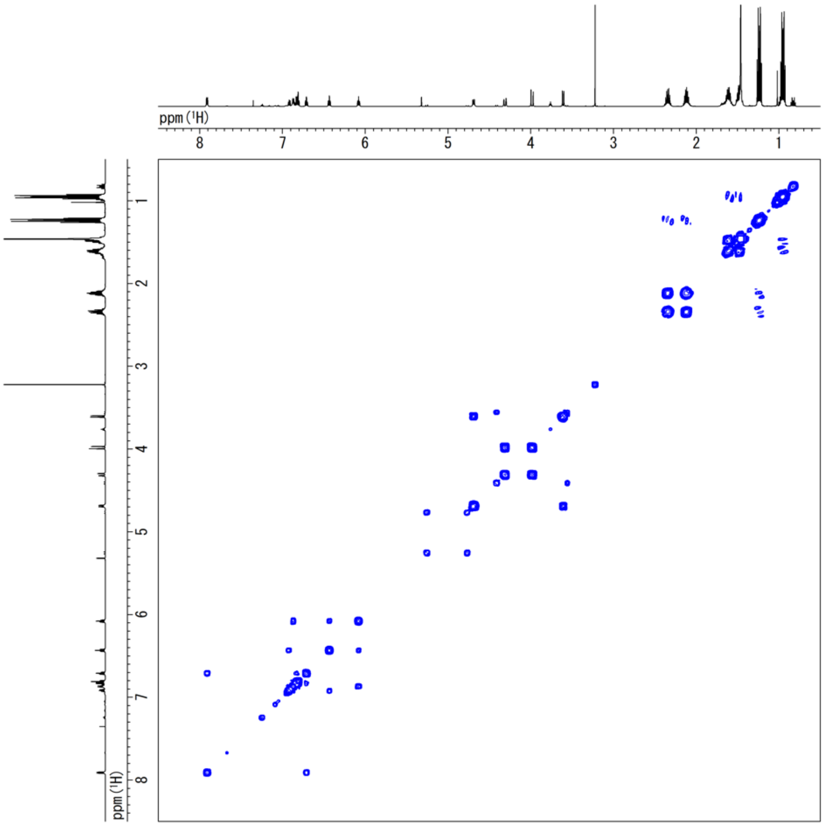


Fig. S33 ^{1}H–^{1}H COSY NMR spectrum (600 MHz) of complex **5a** in CD_2Cl_2.

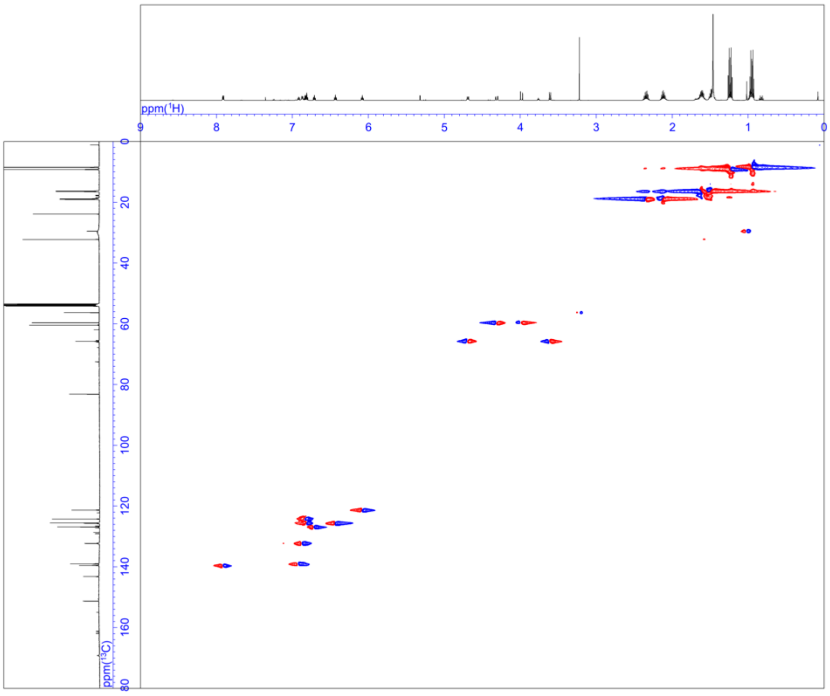


Fig. S34 ^{1}H–^{13}C HSQC NMR spectrum (600 MHz for ^{1}H, 151 MHz for ^{13}C) of **5a** in CD_2Cl_2.

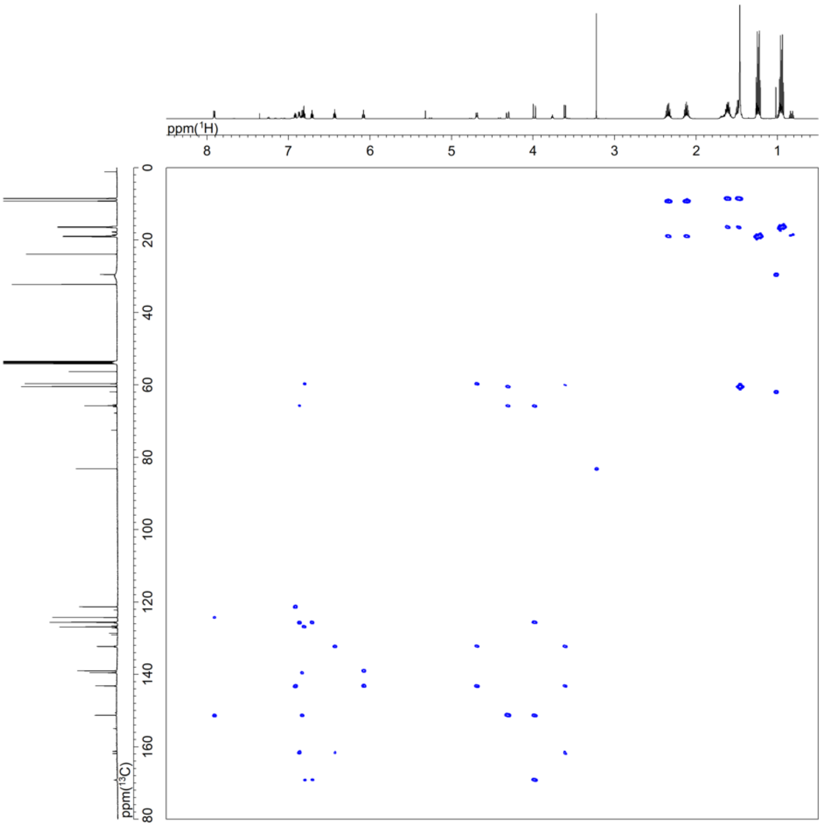


Fig. S35 ^{1}H–^{13}C HMBC NMR spectrum (600 MHz for ^{1}H, 151 MHz for ^{13}C) of complex **5a** in CD_2Cl_2.

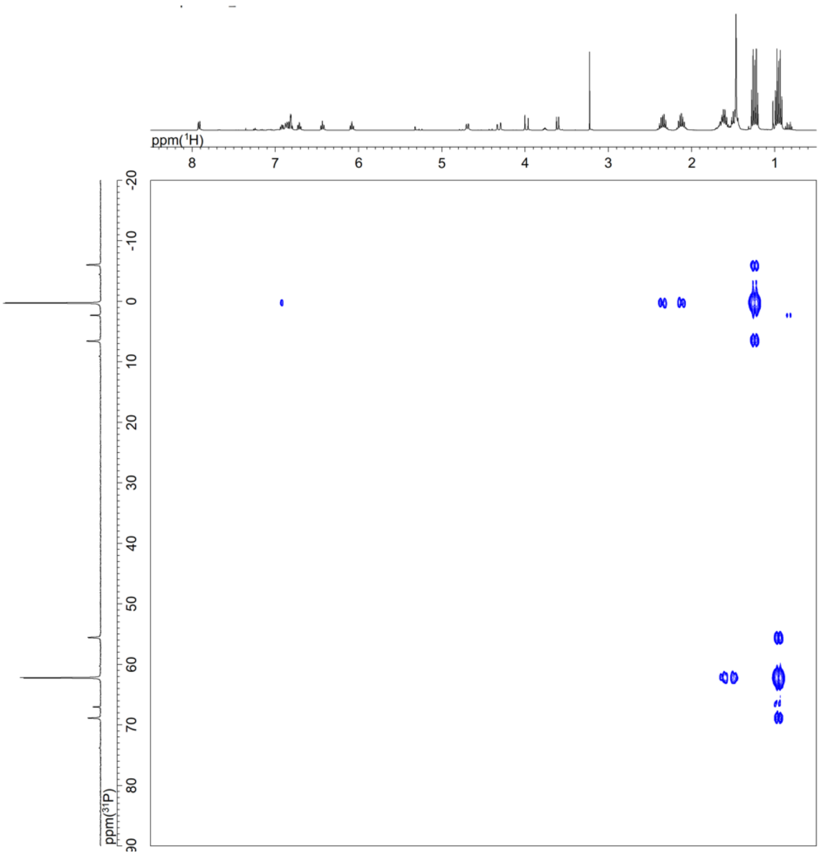


Fig. S36 ^{1}H–^{31}P HMBC NMR spectrum (400 MHz for ^{1}H, 162 MHz for ^{31}P) of complex **5a** in CD_2Cl_2.

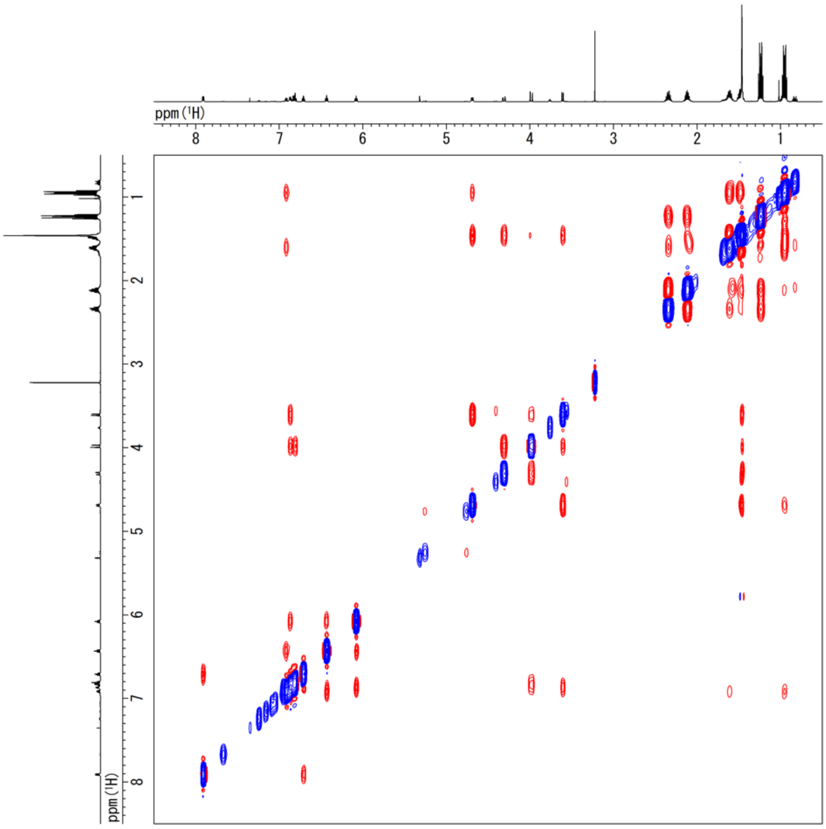


Fig. S37 NOESY NMR spectrum (600 MHz for ^{1}H) of complex **5a** in CD_2Cl_2.

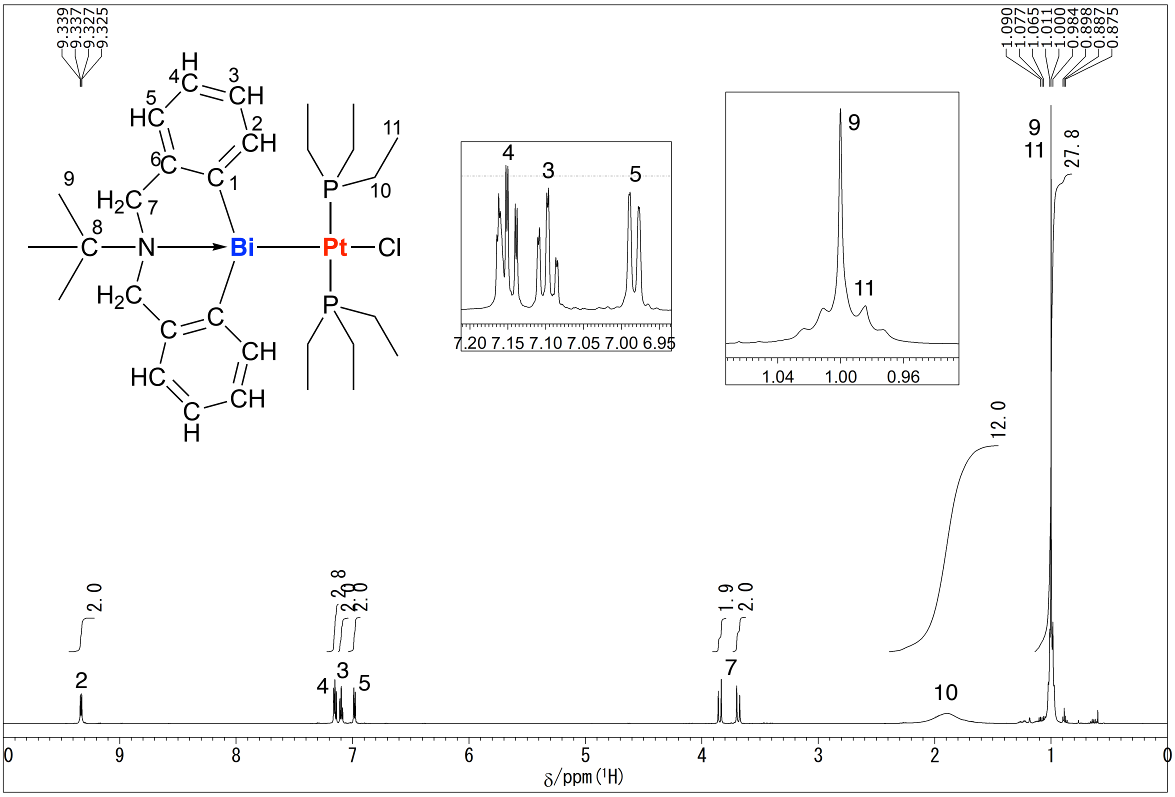


Fig. S38 ^{1}H NMR spectrum (600 MHz) of complex **6a** in C_6D_6.

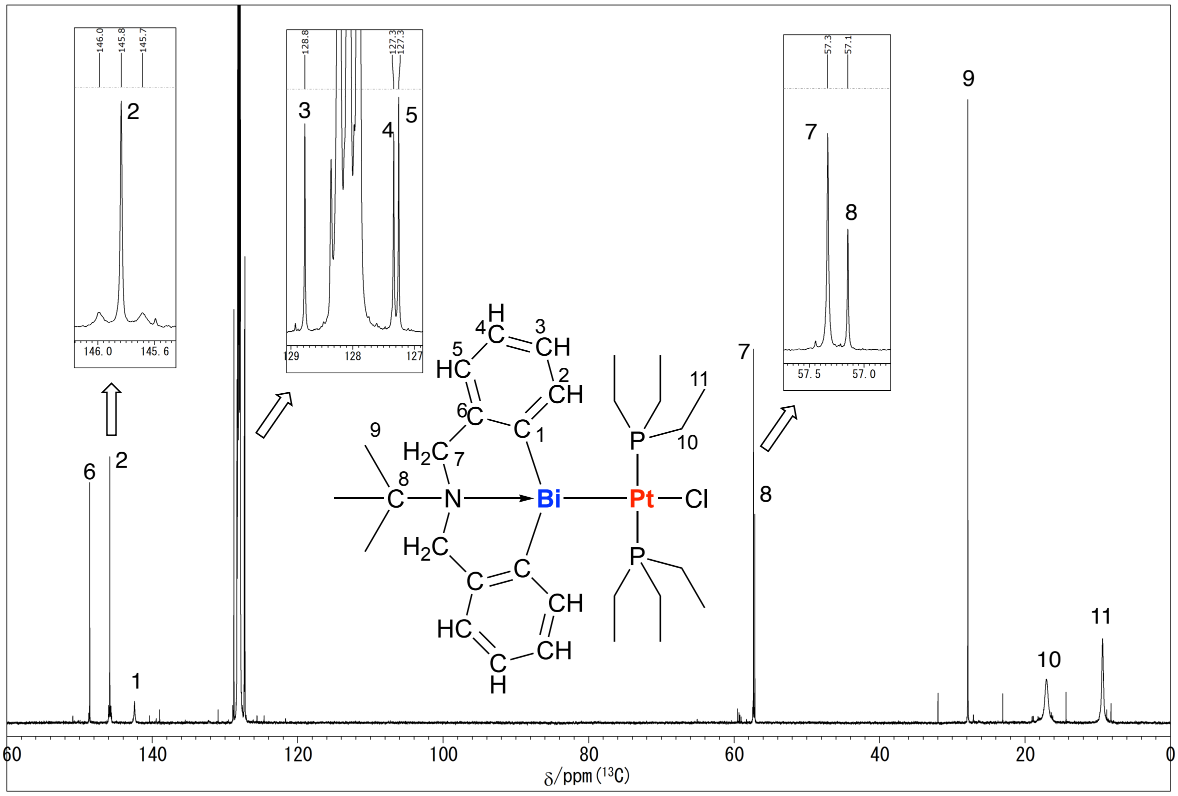


Fig. S39 ^{13}C{^{1}H} NMR spectrum (151 MHz) of complex **6a** in C_6D_6.

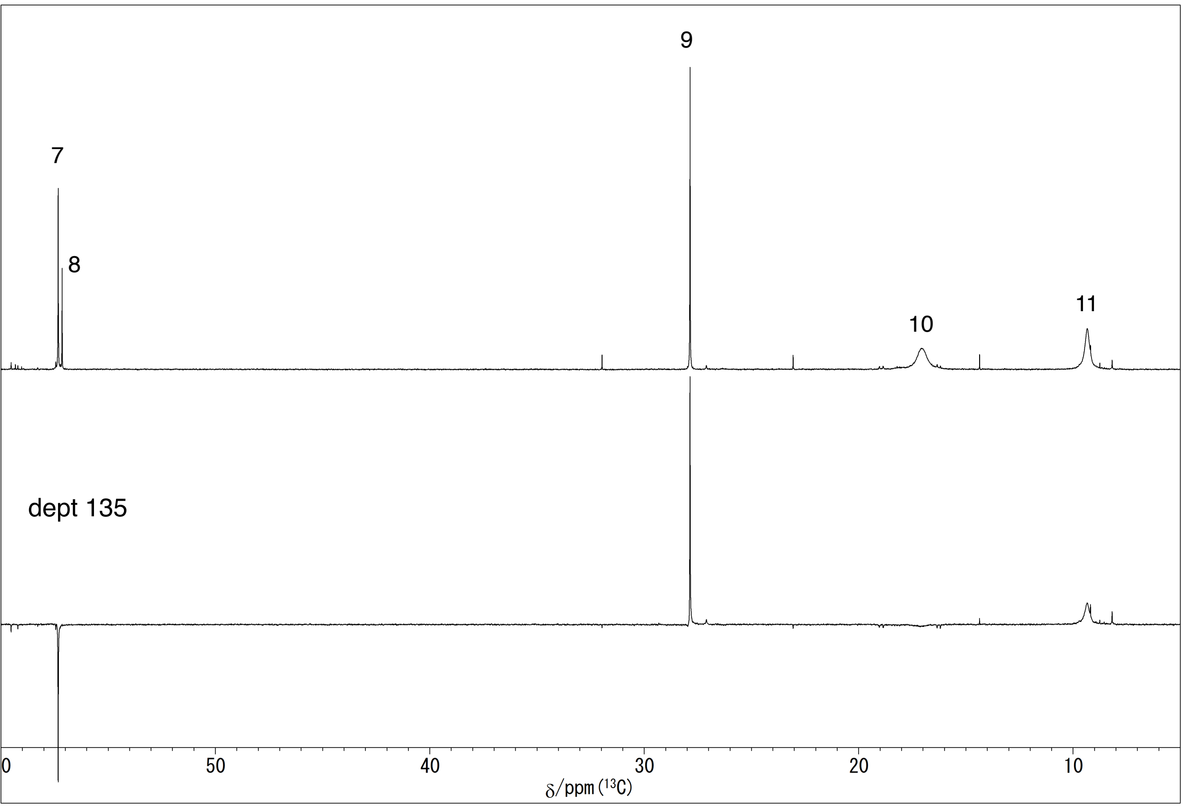


Fig. S40 A part (5–60 ppm region) of $^{13}C\{^1H\}$ NMR spectrum (151 MHz) with dept 135 spectrum (lower) of complex **6a** in C_6D_6.

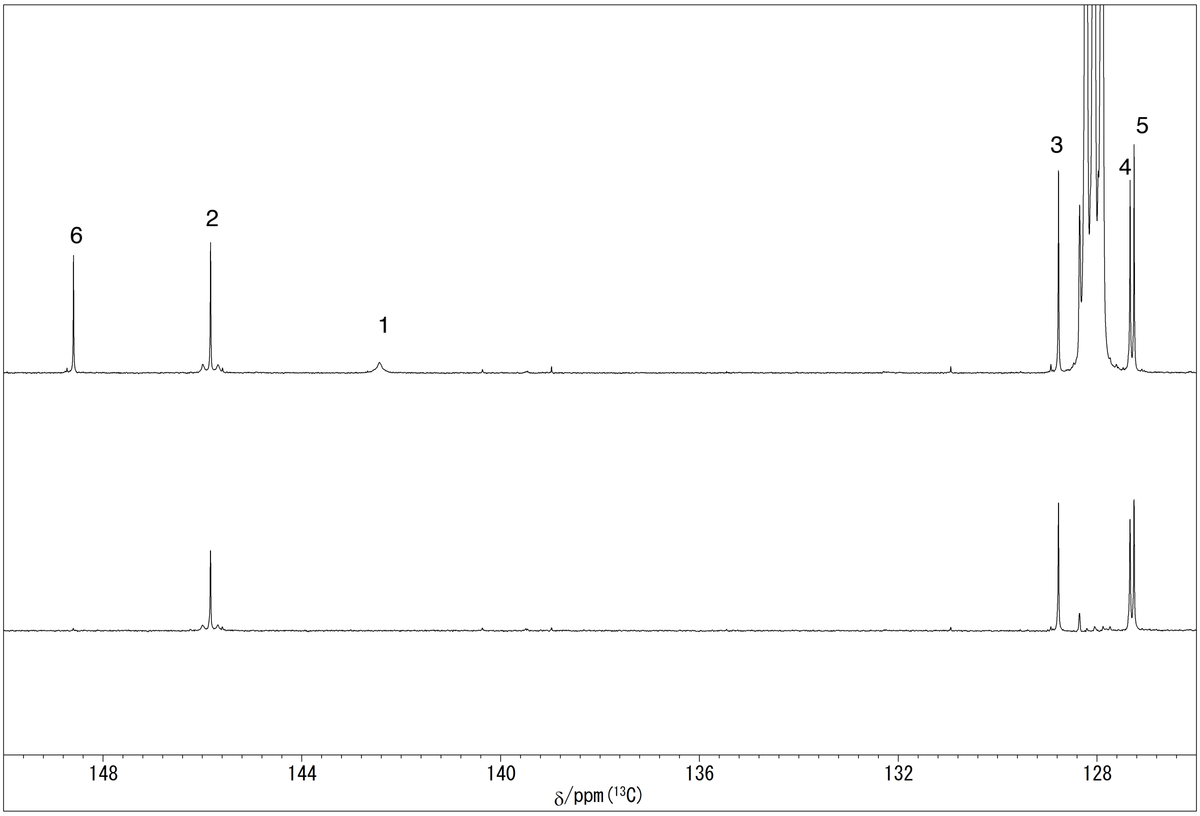


Fig. S41 A part (126–150 ppm region) of $^{13}C\{^1H\}$ NMR spectrum (151 MHz) with dept 135 spectrum (lower) of complex **6a** in C_6D_6.

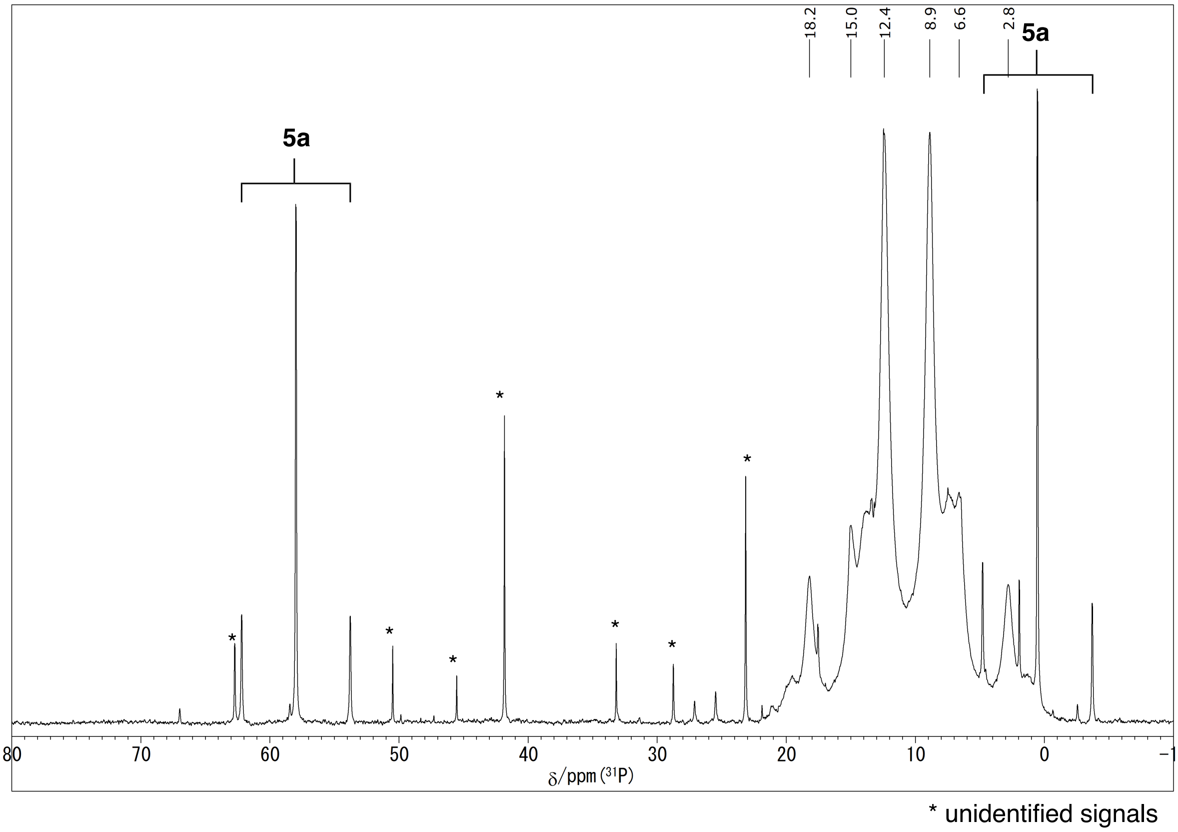


Fig. S42 ^{13}P{^{1}H} NMR spectrum (243 MHz) of complex **6a** in C_6D_6. The spectrum was obtained 2 h after the sample preparation and contained weak signals of **5a** and unidetified species.

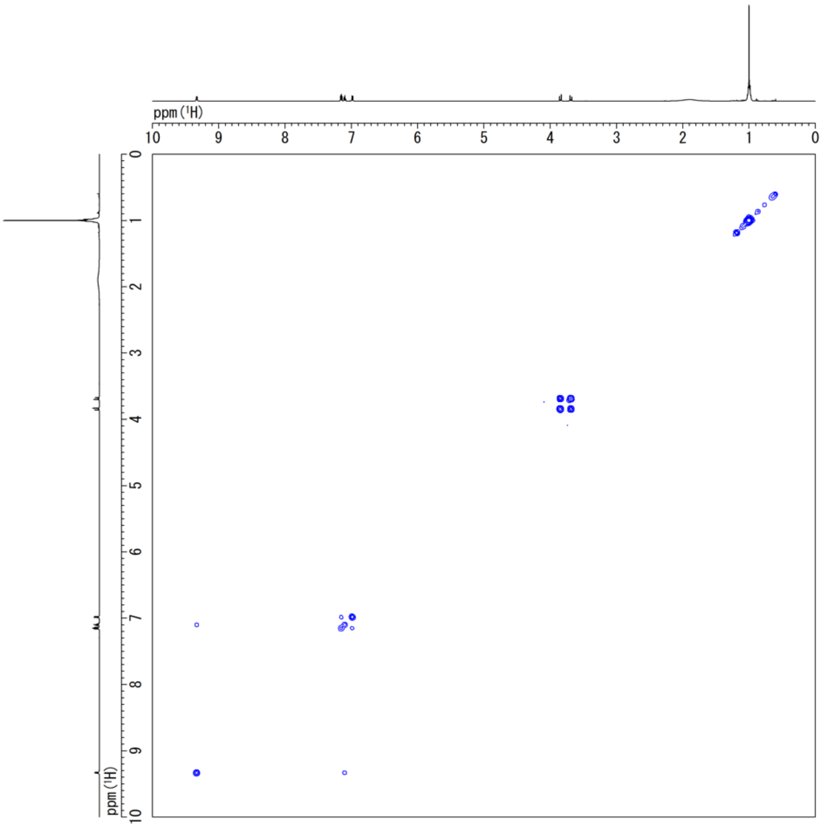


Fig. S43 ^{1}H–^{1}H COSY NMR spectrum (600 MHz) of complex **6a** in C_6D_6.

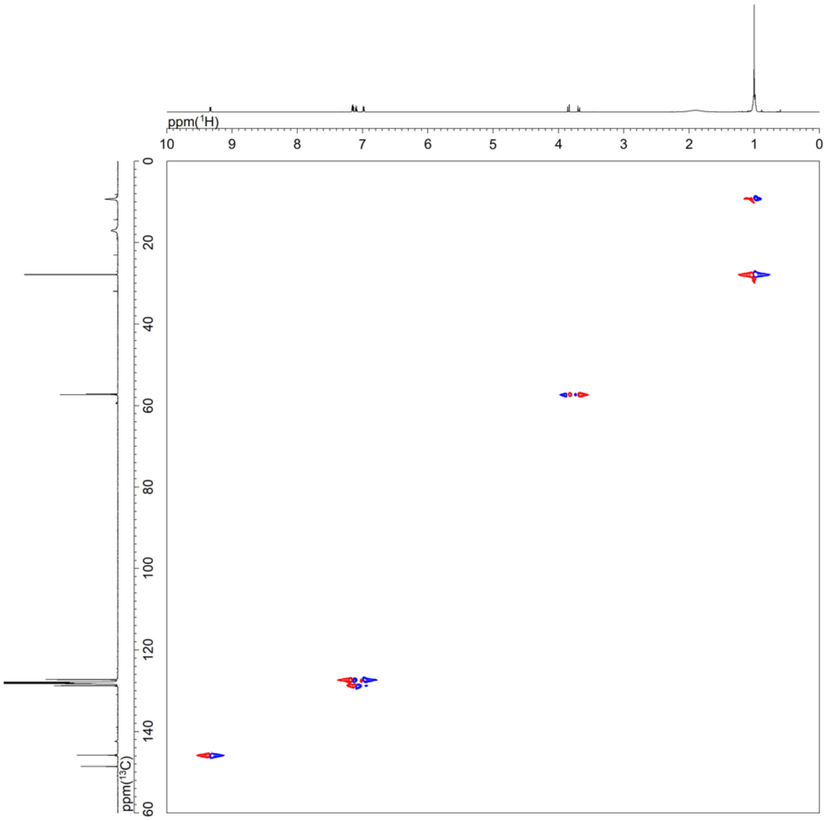


Fig. S44 ^{1}H–^{13}C HSQC NMR spectrum (600 MHz for ^{1}H, 151 MHz for ^{13}C) of complex **6a** in C_6D_6.

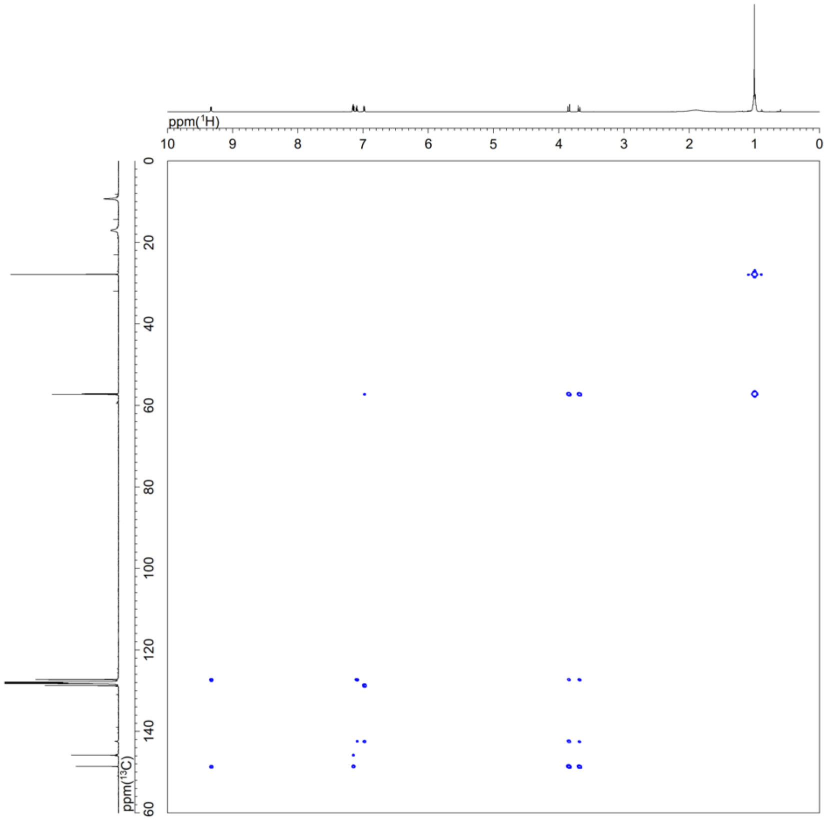


Fig. S45 ^{1}H–^{13}C HMBC NMR spectrum (600 MHz for ^{1}H, 151 MHz for ^{13}C) of complex **6a** in C_6D_6.