

# Divalent Ytterbium Hydrido Complex Supported by $\beta$ -Diketiminato Based Tetradentate Ligand: Synthesis, Structure and Reactivity

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## Supporting Information

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**General.** All manipulations were performed under an atmosphere of nitrogen using Schlenk techniques or in a nitrogen-filled glovebox. THF, toluene, benzene, hexane, C<sub>6</sub>D<sub>6</sub>, *d*<sub>8</sub>-toluene, *d*<sub>8</sub>-THF and mesitylene were dried over Na/K alloy, transferred under vacuum, and stored in the glovebox. Cyclohexane, PhSiH<sub>3</sub> and pyridine were dried over CaH<sub>2</sub>, transferred under vacuum, degassed by three freeze-pump-thaw cycles, and stored in the glovebox. YbI<sub>2</sub>(THF)<sub>2</sub><sup>1</sup>, KCH<sub>2</sub>SiMe<sub>3</sub><sup>2</sup> and PhSiD<sub>3</sub><sup>3</sup> were synthesized following the literature procedures. The highly pure H<sub>2</sub> (99.999%) was further dried by passing through activated 4 Å molecular sieve. 4-(Dimethylamino)pyridine (DMAP), bipyridine (bpy), triphenylphosphine oxide, triphenylphosphine sulfide and diphenyl disulfide were purified by sublimation before use. <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H} and <sup>31</sup>P{<sup>1</sup>H} spectra were recorded on a Varian 400 MHz, an Agilent 400 MHz, a Bruker 400 MHz or an Agilent 600 MHz spectrometer. <sup>2</sup>H spectra were recorded on a Bruker 400 MHz spectrometer. Chemical shifts  $\delta$  were reported in ppm with references to the residual resonance of the deuterated solvents for proton and carbon spectroscopies, to internal C<sub>6</sub>D<sub>6</sub> for <sup>2</sup>H chemical shifts, and to external H<sub>3</sub>PO<sub>4</sub> (85%) for phosphorus chemical shifts. The assignment of <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} resonances was assisted with gCOSY, gHSQC and gHMBC spectra. Elemental analyses were performed by the Analytical Laboratory of Shanghai Institute of Organic Chemistry.

**LK** (L = [<sup>t</sup>BuC(NDipp)CHC(<sup>t</sup>Bu)NCH<sub>2</sub>CH<sub>2</sub>N(Me)CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>]<sup>-</sup>, Dipp = 2,6-(<sup>i</sup>Pr)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>): LK was synthesized similar to that of LLi.<sup>4</sup> A THF solution (20 mL) of Me(<sup>t</sup>Bu)CNCH<sub>2</sub>CH<sub>2</sub>N(Me)CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub> (5.00 g, 22.0 mmol) was precooled to -78 °C, and then <sup>n</sup>BuLi (22.0 mmol, 9.2 mL of a 2.40 M solution in hexane) was added dropwise. The mixture was allowed to warm to room temperature and stirred for 2 h, resulting in an orange solution. This mixture was precooled to 0 °C, and ClC(<sup>t</sup>Bu)=N(Dipp) (6.16 g, 22.0 mmol) was added dropwise. After stirring at room temperature for 6 h, the volatiles of the reaction mixture were removed under vacuum. After that, water (8 mL) and hexane (50 mL) were added to the residue. The organic phase was collected, dried over Na<sub>2</sub>SO<sub>4</sub>, and filtered. The solvent of the filtration was removed under vacuum. The crude product LH was obtained as a yellow oil (9.80 g, 95% yield). The crude product could not be purified

by distillation due to its high boiling point, and it is also difficult to be purified by column chromatography due to a hydrolysis of the imine unit in LH. However, the obtained crude product can be used for the synthesis of LK without purification. KH (1.32 g, 33.0 mmol) was added to a THF solution (20 mL) of LH (9.80 g, 20.8 mmol) at room temperature, the precipitate was separated by centrifugation after stirring for 12 h. The solvent of the solution was removed under vacuum, the residue was stirred in 10 mL of hexane, and the volatiles were removed again under vacuum. This operation was repeated for three times to remove THF completely. The residue was washed with hexane (15 mL  $\times$  4) and dried under vacuum to give LK as a yellow solid (6.70 g, 63% yield).  $^1\text{H}$  NMR (400 MHz,  $d_8$ -THF, 25 °C):  $\delta$  6.71 (d,  $^3J_{\text{H-H}} = 7.2$  Hz, 2H, *m*-ArH of Dipp), 6.29 (t,  $^3J_{\text{H-H}} = 7.2$  Hz, 1H, *p*-ArH of Dipp), 4.28 (s, 1H,  $^t\text{BuC(N)CH}$ ), 3.67 (sept,  $^3J_{\text{H-H}} = 6.2$  Hz, 2H, ArCHMe<sub>2</sub>), 2.96 (m, 2H, NCH<sub>2</sub>), 2.35 (m, 2H, NCH<sub>2</sub>), 2.26 (m, 2H, NCH<sub>2</sub>), 2.13 (s, 9H, NMe and NMe<sub>2</sub>), 2.10 (m, 2H, NCH<sub>2</sub>), 1.26 (s, 9H, CMe<sub>3</sub>), 1.18 (d,  $^3J_{\text{H-H}} = 6.2$  Hz, 6H, ArCHMe<sub>2</sub>), 1.08 (s, 9H, CMe<sub>3</sub>), 1.01 (d,  $^3J_{\text{H-H}} = 6.2$  Hz, 6H, ArCHMe<sub>2</sub>).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $d_8$ -THF, 25 °C):  $\delta$  180.6, 165.3 (imine C), 152.6 (*i*-ArC of Dipp), 138.2 (*o*-ArC of Dipp), 120.4 (*m*-ArC of Dipp), 113.6 (*p*-ArC of Dipp), 78.8 ( $^t\text{BuC(N)CH}$ ), 63.0, 58.3, 57.6, 53.2 (NCH<sub>2</sub>), 45.8 (NMe<sub>2</sub>), 43.1 (NMe), 41.9, 39.8 (CMe<sub>3</sub>), 32.0, 31.3 (CMe<sub>3</sub>), 28.6 (ArCHMe<sub>2</sub>), 24.4, 22.2 (ArCHMe<sub>2</sub>).

**[LYb( $\mu$ -I)]<sub>2</sub> (1):** To a THF solution (3 mL) of YbI<sub>2</sub>(THF)<sub>2</sub> (571 mg, 1.0 mmol) was added a THF solution (3 mL) of LK (509 mg, 1.0 mmol) at room temperature. The reaction was stirred for 2 h, resulting in a dark brown solution with gray precipitates. After filtration, the solvent of the filtration was removed under vacuum. The residue was stirred in 5 mL of hexane, and the volatiles were removed again under vacuum. This operation was repeated for three times to remove THF completely, and then the residue was extracted with toluene (15 mL). The solvent of the extraction was removed under vacuum, and the residue was washed with hexane (5 mL  $\times$  3) and dried under vacuum to give complex **1** as a dark red solid (400 mg, 52% yield).  $^1\text{H}$  NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  6.98 (m, 1H, *p*-ArH of Dipp), 6.91 (m, 2H, *m*-ArH of Dipp), 5.35 (s, 1H,  $^t\text{BuC(N)CH}$ ), 4.12 (m, 1H, NCH<sub>2</sub>), 3.62 (br, 1H, ArCHMe<sub>2</sub>), 3.15 (br, 2H, NCH<sub>2</sub> and ArCHMe<sub>2</sub>), 2.67 (m, 1H, NCH<sub>2</sub>), 2.25 (s, 3H, NMe), 2.10 – 1.90

(m, 2H,  $\text{NCH}_2$ ), 1.72 (m, 2H,  $\text{NCH}_2$ ), 1.53 (br, 10H,  $\text{NMe}_2$ ,  $\text{NCH}_2$  and  $\text{ArCHMe}_2$ ), 1.46 (s, 9H,  $\text{CMe}_3$ ), 1.33 (d,  $^3J_{\text{H-H}} = 6.5$  Hz, 3H,  $\text{ArCHMe}_2$ ), 1.21 (br, 12H,  $\text{CMe}_3$  and  $\text{ArCHMe}_2$ ), 1.09 (br, 3H,  $\text{ArCHMe}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  172.1, 171.2 (imine C), 147.5 (*i*-ArC of Dipp), 140.3, 139.1 (*o*-ArC of Dipp), 124.0, 123.2 (*m*-ArC of Dipp), 123.0 (*p*-ArC of Dipp), 89.8 ( $^t\text{BuC}(\text{N})\text{CH}$ ), 57.9, 57.2, 55.3, 47.7 ( $\text{NCH}_2$ ), 44.7 ( $\text{NMe}$ ), 44.4 ( $\text{CMe}_3$ ), 43.5 ( $\text{NMe}$ ), 40.8 ( $\text{CMe}_3$ ), 32.4, 31.0 ( $\text{CMe}_3$ ), 29.3 ( $\text{ArCHMe}_2$ ), 27.8 ( $\text{ArCHMe}_2$ ), 26.1, 23.8, 22.8 ( $\text{ArCHMe}_2$ ). Anal. Calcd for  $\text{C}_{60}\text{H}_{106}\text{I}_2\text{N}_8\text{Yb}_2$ : C 46.81; H 6.94; N 7.28. Found: C 46.97; H 6.99; N 7.35.

**LYbCH<sub>2</sub>SiMe<sub>3</sub> (2):** Complex **1** (154 mg, 0.10 mmol) and  $\text{KCH}_2\text{SiMe}_3$  (27.0 mg, 0.20 mmol) were mixed in 4 mL of benzene at room temperature, resulting in a dark brown solution with gray precipitates. The reaction was kept at room temperature for 30 minutes, and then the solvent was removed under vacuum. The residue was extracted with hexane (8 mL). The solvent of the extraction was removed under vacuum to afford complex **2** as a dark red solid (132 mg, 90% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  7.00 (m, 1H, *p*-ArH of Dipp), 6.92 (m, 2H, *m*-ArH of Dipp), 5.34 (s, 1H,  $^t\text{BuC}(\text{N})\text{CH}$ ), 4.16 (m, 1H,  $\text{NCH}_2$ ), 3.78 (sept,  $^3J_{\text{H-H}} = 6.8$  Hz, 1H,  $\text{ArCHMe}_2$ ), 3.15 (m, 1H,  $\text{NCH}_2$ ), 3.12 (sept,  $^3J_{\text{H-H}} = 6.8$  Hz, 1H,  $\text{ArCHMe}_2$ ), 2.65 (m, 1H,  $\text{NCH}_2$ ), 2.06 (s, 3H,  $\text{NMe}$ ), 1.95 (m, 2H,  $\text{NCH}_2$ ), 1.80 (s, 3H,  $\text{NMe}$ ), 1.58 (m, 2H,  $\text{NCH}_2$ ), 1.52 (d,  $^3J_{\text{H-H}} = 6.8$  Hz, 3H,  $\text{ArCHMe}_2$ ), 1.49 (s, 9H,  $\text{CMe}_3$ ), 1.41 (d,  $^3J_{\text{H-H}} = 6.8$  Hz, 3H,  $\text{ArCHMe}_2$ ), 1.35 (m, 1H,  $\text{NCH}_2$ ), 1.26 (s, 9H,  $\text{CMe}_3$ ), 1.20 (d,  $^3J_{\text{H-H}} = 6.8$  Hz, 3H,  $\text{ArCHMe}_2$ ), 1.06 (m, 6H,  $\text{ArCHMe}_2$  and  $\text{NMe}$ ), 0.47 (s, 9H,  $\text{CH}_2\text{SiMe}_3$ ), -1.19 (d, 2H,  $\text{YbCH}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  171.2, 170.6 (imine C), 148.2 (*i*-ArC of Dipp), 140.1, 139.5 (*o*-ArC of Dipp), 124.0 (*p*-ArC of Dipp), 123.1, 122.3 (*m*-ArC of Dipp), 91.9 ( $^t\text{BuC}(\text{N})\text{CH}$ ), 57.3, 56.9, 55.4, 47.4 ( $\text{NCH}_2$ ), 44.6 ( $\text{CMe}_3$ ), 44.5, 43.8, 41.9 ( $\text{NMe}$ ), 41.2 ( $\text{CMe}_3$ ), 32.5, 31.2 ( $\text{CMe}_3$ ), 27.9 ( $\text{ArCHMe}_2$ ), 27.7, 27.5 ( $\text{ArCHMe}_2$ ), 25.9, 24.1, 22.8 ( $\text{ArCHMe}_2$ ), 17.95 ( $\text{YbCH}_2$ ), 5.97 ( $\text{SiMe}_3$ ). Anal. Calcd for  $\text{C}_{34}\text{H}_{64}\text{N}_4\text{SiYb}$ : C 55.94; H 8.84; N 7.67. Found: C 56.04; H 9.04; N 7.77.

**[LYb( $\mu$ -H)]<sub>2</sub> (3):** *Method A.* A hexane solution (3 mL) of **2** (100 mg, 0.14 mmol) was placed in tube

with a Teflon stopcock. The tube was taken out of the glovebox and connected to a Schlenk line. The solution of **2** was degassed at low temperature, and then exposed to 1.0 atm of H<sub>2</sub> at room temperature. After standing at room temperature for 3 h, the resulting solution was concentrated to about 0.5 mL and stood at -35 °C for 12 h. Complex **3** was isolated as dark red crystals (43 mg, 49% yield).

*Method B.* In the glove box, to a hexane solution (3 mL) of **2** (150 mg, 0.21 mmol) was added a hexane solution (131 mg) of PhSiH<sub>3</sub> (22 mg, 0.21 mmol) at room temperature, resulting in a dark red solution. After standing at room temperature for 10 minutes, the solution was concentrated to about 2 mL and stood at -35 °C for 12 h. The resulting dark red crystalline solids were collected, washed with hexane (1 mL × 3), and dried under vacuum to afford **3** (116 mg, 88% yield). There are two isomers in about 4:1 ratio. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): isomer **I**, δ 8.95 (t, <sup>1</sup>J<sub>Yb-H</sub> = 358 Hz, 1.6H, YbH). isomer **II**, δ 9.04 (t, <sup>1</sup>J<sub>Yb-H</sub> = 352 Hz, 0.4H, YbH). Most other signals of two isomers are overlapped. 7.12 (m, 2H, *p*-ArH of Dipp), 7.05 (m, 4H, *m*-ArH of Dipp), 4.95 (s, 2H, <sup>t</sup>BuC(N)CH), 4.16 (m, 2H, NCH<sub>2</sub>), 3.61 (m, 2H, ArCHMe<sub>2</sub>), 3.20 (m, 2H, ArCHMe<sub>2</sub>), 2.83 (m, 4H, NCH<sub>2</sub>), 2.41 (s, 6H, NMe), 2.33 (m, 4H, NCH<sub>2</sub>), 2.18 (m, 6H, NCH<sub>2</sub>), 1.90 (br, 12H, NMe<sub>2</sub>), 1.48-1.44 (m, 30H, ArCHMe<sub>2</sub> and CMe<sub>3</sub>), 1.32-1.28 (m, 30H, ArCHMe<sub>2</sub> and CMe<sub>3</sub>). As some signals in the <sup>1</sup>H NMR spectrum of **3** are overlapped and **3** easily decomposes into another complex in solution, we were failed to determine the specific structure of the isomers by <sup>1</sup>H-<sup>1</sup>H NOESY spectroscopy. The poor solubility and instability of **3** also caused the difficulty in recording the <sup>13</sup>C{<sup>1</sup>H} and <sup>171</sup>Yb NMR spectra of this complex. Anal. Calcd for C<sub>60</sub>H<sub>108</sub>N<sub>8</sub>Yb<sub>2</sub>: C 55.97; H 8.45; N 8.70. Found: C 55.76; H 8.24; N 8.74.

**[LYb(μ-D)]<sub>2</sub> (3-D):** To a hexane solution (3 mL) of **2** (100 mg, 0.14 mmol) was added a hexane solution (86 mg) of PhSiD<sub>3</sub> (16 mg, 0.14 mmol) at room temperature, resulting in a dark red solution. After standing at room temperature for 10 minutes, the solution was concentrated to about 2 mL and stood at -35 °C for 12 h. The resulting dark red crystalline solids were collected, washed with hexane (1 mL × 3), and dried under vacuum to afford **3-D** (78 mg, 88% yield). <sup>2</sup>H NMR (60 MHz, C<sub>6</sub>H<sub>6</sub>, 25 °C): δ 9.03 (br, YbD).

**LYb(NC<sub>5</sub>H<sub>6</sub>) (5):** To a toluene solution (1 mL) of **3** (80 mg, 0.06 mmol) was added a toluene solution (155mg) of pyridine (10 mg, 0.12 mmol) at room temperature, resulting in a dark brown solution. After 10 minutes, the volatiles of the reaction solution were removed under vacuum. The residue was washed with cold hexane (1 mL) and dried under vacuum to afford complex **5** as a dark brown solid (65 mg, 72% yield). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  7.02 (d, <sup>3</sup>J<sub>H-H</sub> = 5.6 Hz, 1H, NCH=CH), 6.97 (m, 1H, *p*-ArH of Dipp), 6.89 (m, 2H, *m*-ArH of Dipp), 6.55 (dd, <sup>3</sup>J<sub>H-H</sub> = 8.4 Hz, <sup>3</sup>J<sub>H-H</sub> = 5.6 Hz, 1H, CH<sub>2</sub>CHCH), 5.39 (m, 2H, <sup>t</sup>BuC(N)CH and NCH=CH), 4.73 (m, 1H, NCH<sub>2</sub>CH), 4.12 (m, 3H, NCH<sub>2</sub> and NCH<sub>2</sub>CH), 3.66 (sept, <sup>3</sup>J<sub>H-H</sub> = 6.5 Hz, 1H, ArCHMe<sub>2</sub>), 3.16 (m, 2H, ArCHMe<sub>2</sub> and NCH<sub>2</sub>), 2.57 (m, 1H, NCH<sub>2</sub>), 2.03 (s, 3H, NMe), 1.85 (m, 2H, NCH<sub>2</sub>), 1.79 – 1.61 (m, 5H, NMe and NCH<sub>2</sub>), 1.46 (s, 10H, CMe<sub>3</sub> and NCH<sub>2</sub>), 1.41 (d, <sup>3</sup>J<sub>H-H</sub> = 6.5 Hz, 3H, ArCHMe<sub>2</sub>), 1.33 (d, <sup>3</sup>J<sub>H-H</sub> = 6.5 Hz, 3H, ArCHMe<sub>2</sub>), 1.24 (s, 9H, CMe<sub>3</sub>), 1.18 (d, <sup>3</sup>J<sub>H-H</sub> = 6.5 Hz, 3H, ArCHMe<sub>2</sub>), 1.07 (d, <sup>3</sup>J<sub>H-H</sub> = 6.5 Hz, 3H, ArCHMe<sub>2</sub>), 1.02 (br, 3H, NMe). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  172.8, 170.5 (imine C), 148.8 (NCH), 147.2 (*i*-ArC of Dipp), 140.4, 139.4 (*o*-ArC of Dipp), 128.5 (CH<sub>2</sub>CHCH), 124.2 (*p*-ArC of Dipp), 123.1, 122.5 (*m*-ArC of Dipp), 92.9 (CH<sub>2</sub>CH), 92.57, 92.52 (NCHCH and <sup>t</sup>BuC(N)CH), 57.8, 56.9, 55.1 (NCH<sub>2</sub>), 48.6 (NCH<sub>2</sub>CH), 47.7 (NCH<sub>2</sub>), 44.4 (CMe<sub>3</sub>), 44.2, 41.3 (NMe), 41.1 (CMe<sub>3</sub>), 32.3, 31.2 (CMe<sub>3</sub>), 27.90, 27.85 (ArCHMe<sub>2</sub>), 27.6, 25.8, 24.0, 22.4 (ArCHMe<sub>2</sub>). Anal. Calcd for C<sub>35</sub>H<sub>59</sub>N<sub>5</sub>Yb: C, 58.15; H, 8.23; N, 9.69. Found: C, 58.43; H, 8.31; N, 9.21.

**L'Yb(DMAP) (6):** To a toluene solution (1 mL) of **3** (80 mg, 0.06 mmol) was added a toluene solution (1 mL) of 4-dimethylamino pyridine (15 mg, 0.12 mmol) at room temperature, resulting in a dark red solution. After standing at room temperature for 10 minutes, the resulting solution was concentrated to about 0.5 mL and stood at -35 °C. Layering hexane (2 mL) on the toluene solution afforded complex **6** as dark red crystals (85 mg, 89% yield). Anal. Calcd for C<sub>37</sub>H<sub>64</sub>N<sub>6</sub>Yb: C, 58.02; H, 8.42; N, 10.97. Found: C, 57.32; H, 8.56; N, 10.78. <sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  4.79 (d, <sup>3</sup>J<sub>H-H</sub> = 6.0 Hz, 1H, <sup>t</sup>BuC(N)CH), 4.29 (m, 2H, NCH<sub>2</sub> and ArCHMe<sub>2</sub>), 3.91 (d, <sup>3</sup>J<sub>H-H</sub> = 6.0 Hz, 1H, <sup>t</sup>BuCH). As complex **6** is unstable in solution and the signals of **6** are overlapped with those of the decomposed complex, the assignment of other signals of **6** is unsuccessful. The <sup>1</sup>H NMR spectral monitoring of **6** in C<sub>6</sub>D<sub>6</sub>

indicated that **6** converted into a new complex **6'** via a ligand redistribution reaction, accompanied by a releasing of 4-dimethylamino pyridine.  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ , 25  $^\circ\text{C}$ ) of **6'**:  $\delta$  7.13 (m, 2H, *m*-ArH of Dipp), 6.96 (m, 1H, *p*-ArH of Dipp), 4.23 (d,  $^3J_{\text{H-H}} = 7.2$  Hz, 1H,  $^t\text{BuC}(\text{N})\text{CH}$ ), 3.84 (d,  $^3J_{\text{H-H}} = 7.2$  Hz, 1H,  $^t\text{BuCH}$ ), 3.57 (m, 2H, ArCHMe<sub>2</sub> and NCH<sub>2</sub>), 3.36 (m, 1H, ArCHMe<sub>2</sub>), 3.11 (m, 2H, NCH<sub>2</sub>), 2.92 (m, 1H, NCH<sub>2</sub>), 2.65 (m, 2H, NCH<sub>2</sub>), 2.22 (s, 3H, NMe), 2.13 (m, 1H, NCH<sub>2</sub>), 2.01 (m, 1H, NCH<sub>2</sub>), 1.90 (s, 6H, NMe<sub>2</sub>), 1.45-1.19 (m, 30H, ArCHMe<sub>2</sub> and CMe<sub>3</sub>). Attempts to grow the single crystals of **6'** did not succeed, complex **6'** might be a dimer or oligomer as  $[\text{L}'\text{Yb}]_n$  ( $\text{L}' = [\text{BuC}(\text{NDipp})\text{CHCH}(\text{Bu})\text{NCH}_2\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2]^{2-}$ ).

**L'Yb(bpy $^{\bullet-}$ ) (7)**: To a toluene solution (1 mL) of **3** (50 mg, 0.04 mmol) was added a toluene solution (1 mL) of bipyridine (12 mg, 0.08 mmol) at room temperature, resulting in an orange solution. After standing for 10 minutes, the volatiles of the reaction solution were removed under vacuum. The residue was washed with cold hexane (1 mL) and dried under vacuum to afford complex **7** as an orange solid (50 mg, 80% yield). This complex is paramagnetic.  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ , 25  $^\circ\text{C}$ ):  $\delta$  253.60, 154.10, 142.25, 105.26, 99.37, 77.30, 53.83, 16.34, 7.16, 2.11, 1.22, 0.70, 0.60, -2.81, -4.90, -5.60, -16.76, -24.72, -33.43, -35.86, -38.78, -40.22, -46.77, -49.37, -79.36, -84.48, -112.08, -136.42, -165.19, -193.82, -203.19, -241.20, -264.07. Anal. Calcd for  $\text{C}_{40}\text{H}_{62}\text{N}_6\text{Yb}$ : C, 60.05; H, 7.81; N, 10.50. Found: C, 59.49; H, 7.84; N, 10.55.

**LYb(OPPh<sub>2</sub>) (8)**: To a toluene solution (1 mL) of **3** (80 mg, 0.06 mmol) was added a toluene solution (1 mL) of triphenylphosphine oxide (35 mg, 0.12 mmol) at room temperature, resulting in a red solution. After standing for 10 minutes, the volatiles of the reaction solution were removed under vacuum. The residue was washed with hexane (1 mL  $\times$  3) and dried under vacuum to afford complex **8** as a red solid (77 mg, 73% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ , 25  $^\circ\text{C}$ ):  $\delta$  7.94 (m, 4H, *o*-PhH of OPPh<sub>2</sub>), 7.32 (m, 4H, *m*-PhH of OPPh<sub>2</sub>), 7.11 (m, 2H, *p*-PhH of OPPh<sub>2</sub>), 6.91 (m, 3H, *m*- and *p*-ArH of Dipp), 5.39 (s, 1H,  $^t\text{BuC}(\text{N})\text{CH}$ ), 4.17 (br, 1H, NCH<sub>2</sub>), 3.57 (br, 1H, ArCHMe<sub>2</sub>), 3.19 (br, 2H, ArCHMe<sub>2</sub> and NCH<sub>2</sub>), 2.61 (m, 1H, NCH<sub>2</sub>), 2.04 (s, 3H, NMe), 1.82 (m, 3H, NCH<sub>2</sub>), 1.70 (m, 2H, NCH<sub>2</sub>), 1.48 (s,

9H,  $\text{CMe}_3$ ), 1.31 (m, 15H,  $\text{CMe}_3$ ,  $\text{ArCHMe}_2$  and  $\text{NMe}$ ), 1.20 (m, 6H,  $\text{ArCHMe}_2$  and  $\text{NMe}$ ), 1.09 (m, 6H,  $\text{ArCHMe}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  172.6, 170.5 (imine C), 155.66 (d,  $^1J_{\text{P-C}} = 36.5$  Hz, *i*-PhC of  $\text{OPPh}_2$ ), 155.62 (d,  $^1J_{\text{P-C}} = 36.9$  Hz, *i*-PhC of  $\text{OPPh}_2$ ), 147.2 (*i*-ArC of Dipp), 140.4, 139.2 (*o*-ArC of Dipp), 129.04 (d,  $^2J_{\text{P-C}} = 20.5$  Hz, *o*-PhC of  $\text{OPPh}_2$ ), 128.99 (d,  $^2J_{\text{P-C}} = 20.8$  Hz, *o*-PhC of  $\text{OPPh}_2$ ), 126.6 (d,  $^4J_{\text{P-C}} = 6.9$  Hz, *p*-PhC of  $\text{OPPh}_2$ ), 124.1, 123.1 (*m*-ArC of Dipp), 122.5 (*p*-ArC of Dipp), 91.9 ( $^t\text{BuC(N)CH}$ ), 57.9, 56.8, 55.2, 47.9 ( $\text{NCH}_2$ ), 44.57, 44.53 ( $\text{CMe}_3$  and  $\text{NMe}_2$ ), 41.8 ( $\text{NMe}$ ), 41.1 ( $\text{CMe}_3$ ), 32.4, 31.3 ( $\text{CMe}_3$ ), 27.8, 27.6 ( $\text{ArCHMe}_2$ ), 27.3, 26.0, 23.9, 22.5 ( $\text{ArCHMe}_2$ ), the signals of *m*-PhC of  $\text{OPPh}_2$  were overlapped with those of  $\text{C}_6\text{D}_6$ .  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  84.05. Anal. Calcd for  $\text{C}_{42}\text{H}_{63}\text{N}_4\text{OPYb}$ : C, 59.77; H, 7.52; N, 6.64. Found: C, 59.38; H, 7.27; N, 6.36.

**[LYb( $\mu$ -SPh)]<sub>2</sub> (9)**: To a toluene solution (1 mL) of **3** (80 mg, 0.06 mmol) was added a toluene solution (1 mL) of diphenyl disulfide (13.5 mg, 0.06 mmol) at room temperature, resulting in a dark brown solution. After standing at room temperature for 10 minutes, the resulting solution was concentrated to about 0.5 mL and stood at -35 °C. Layering hexane (2 mL) on the toluene solution afforded complex **9** as brown crystals (60 mg, 64% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ , 25 °C)  $\delta$  7.83 (d,  $^3J_{\text{H-H}} = 7.6$  Hz, 2H, *o*-PhH of SPh), 7.14 (t,  $^3J_{\text{H-H}} = 7.6$  Hz, 2H, *m*-PhH of SPh), 6.92 (m, 4H, *p*-PhH of SPh, and *m*- and *p*-ArH of Dipp), 5.37 (s, 1H,  $^t\text{BuC(N)CH}$ ), 4.13 (br, 1H,  $\text{NCH}_2$ ), 3.41 (m, 1H,  $\text{ArCHMe}_2$ ), 3.15 (m, 2H,  $\text{NCH}_2$  and  $\text{ArCHMe}_2$ ), 2.67 (br, 1H,  $\text{NCH}_2$ ), 2.17 (s, 3H,  $\text{NMe}$ ), 2.08-1.87 (m, 3H,  $\text{NCH}_2$ ), 1.66 (m, 2H,  $\text{NCH}_2$ ), 1.50 (m, 6H,  $\text{NMe}_2$ ), 1.43 (s, 9H,  $\text{CMe}_3$ ), 1.24 (m, 15H,  $\text{CMe}_3$  and  $\text{ArCHMe}_2$ ), 1.18 (d,  $^3J_{\text{H-H}} = 6.8$  Hz, 3H,  $\text{ArCHMe}_2$ ), 1.07 (d,  $^3J_{\text{H-H}} = 6.8$  Hz, 3H,  $\text{ArCHMe}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  172.0, 171.5 (imine C), 150.2 (*i*-PhC of SPh), 147.4 (*i*-ArC of Dipp), 140.5, 139.3 (*o*-ArC of Dipp), 134.2 (*o*-PhC of SPh), 128.1 (*m*-PhC of SPh), 124.0 (*p*-ArC of Dipp), 123.1, 122.9 (*m*-ArC of Dipp), 120.6 (*p*-PhH of SPh), 91.4 ( $^t\text{BuC(N)CH}$ ), 57.7, 57.2, 55.4, 47.7 ( $\text{NCH}_2$ ), 44.6 ( $\text{NMe}$ ), 44.4 ( $\text{CMe}_3$ ), 42.3 ( $\text{NMe}$ ), 40.9 ( $\text{CMe}_3$ ), 32.4, 31.0 ( $\text{CMe}_3$ ), 28.2, 27.7 ( $\text{ArCHMe}_2$ ), 27.6, 26.1, 23.8, 22.7 ( $\text{ArCHMe}_2$ ). Anal. Calcd for  $\text{C}_{72}\text{H}_{116}\text{N}_8\text{S}_2\text{Yb}_2$ : C, 57.50; H, 7.77; N, 7.45. Found: C, 57.10; H, 7.83; N, 7.37.



**LYb(SPh)<sub>2</sub> (10):** To a toluene solution (1 mL) of **3** (71 mg, 0.055 mmol) was added a toluene solution (1 mL) of diphenyl disulfide (24 mg, 0.11 mmol) at room temperature, resulting in an orange solution. After standing for 10 minutes, the volatiles of the reaction solution were removed under vacuum. The residue was washed with hexane (1 mL  $\times$  3) and dried under vacuum to afford complex **10** as a yellow solid (72 mg, 76% yield). This complex is paramagnetic. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C)  $\delta$  96.53, 38.88, 23.38, 18.51, 17.00, 15.16, 11.04, 7.35, 5.93, 3.68, 1.21, -0.02, -6.23, -11.11, -14.27, -24.84, -81.06, -86.90, -90.17. Anal. Calcd for C<sub>42</sub>H<sub>63</sub>N<sub>4</sub>S<sub>2</sub>Yb: C, 58.58; H, 7.37; N, 6.51. Found: C, 59.19; H, 7.50; N, 6.44. In addition, a <sup>1</sup>H NMR investigation in C<sub>6</sub>D<sub>6</sub> also showed that complex **9** reacts with 1.0 equiv. of PhSSPh to give complex **10** (see Figure S28).

### X-ray Crystallography:

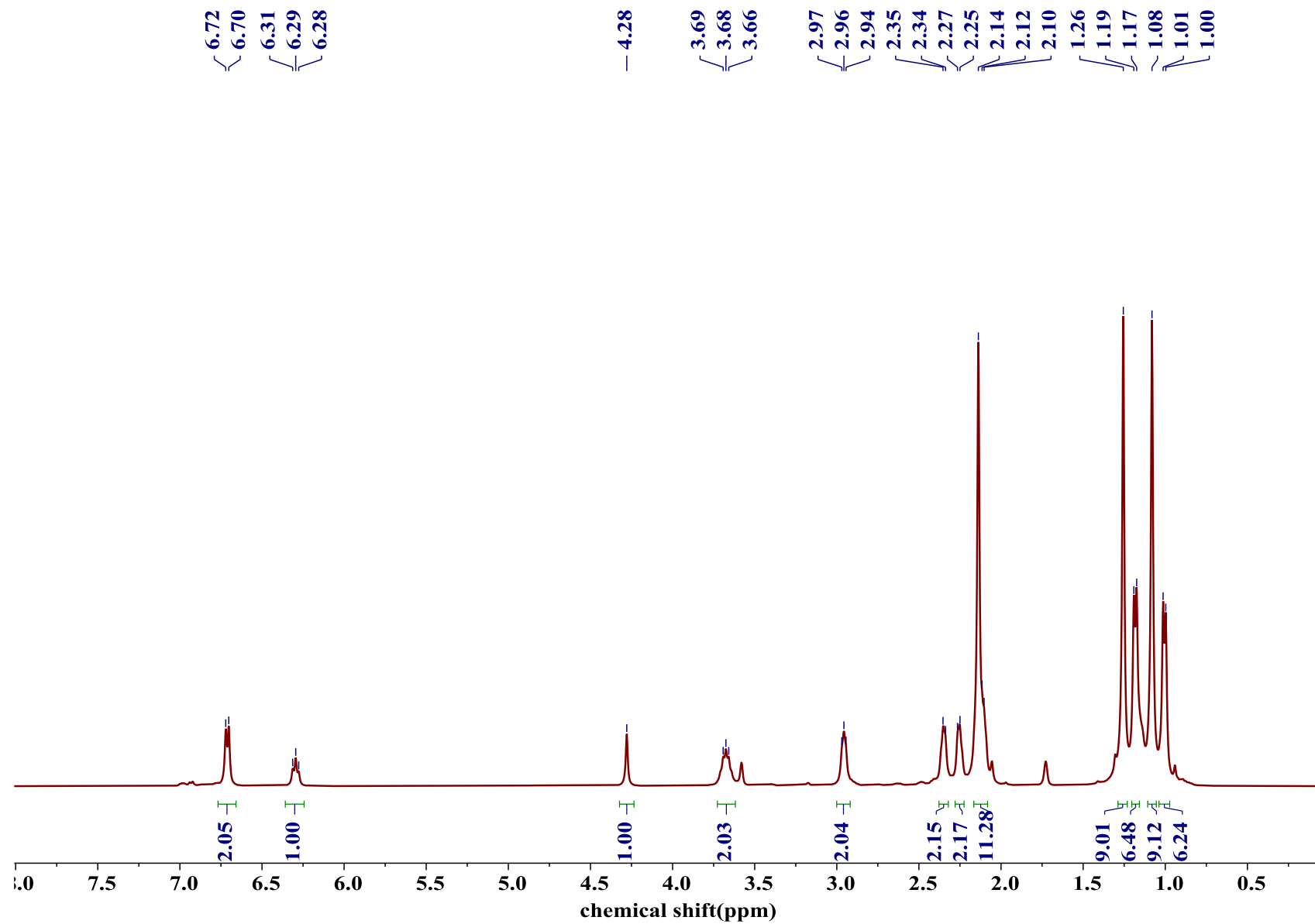
Single crystals of **1** suitable for single-crystal X-ray diffraction were grown from a THF/hexane mixture, those of **2** were from a hexane solution, those of **3** were from a toluene solution, those of **5**, **6**, **8** and **9** were from a toluene/hexane mixture, those of **7** were from a mesitylene solution, and those of **10** were from a toluene/cyclohexane mixture. The crystals were mounted under a nitrogen atmosphere on a glass fiber at low temperature. Data collection of **1**, **3**, **5**, **6**, **7**, **9** and **10** was performed on a Bruker D8 Venture with Ga K $\alpha$  radiation ( $\lambda$  = 1.34139 Å), that of **2** and **8** was performed on a Bruker APEX-II CCD with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å). The SMART program package was used to determine the unit cell parameters. The absorption correction was applied using SADABS program.<sup>5</sup> All structures were solved by direct methods and refined on  $F^2$  by full-matrix least-squares techniques with anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were placed at calculated positions and were included in the structure calculation, except for the hydrogen atoms of Yb–H, which were located in the Fourier different map. Calculations were carried out using the SHELXL-97, SHELXL-2014 or Olex2 program.<sup>6</sup> Crystallographic data and refinement parameters are listed in Table S1.

**Table S1.** Crystallographic data and refinement parameters

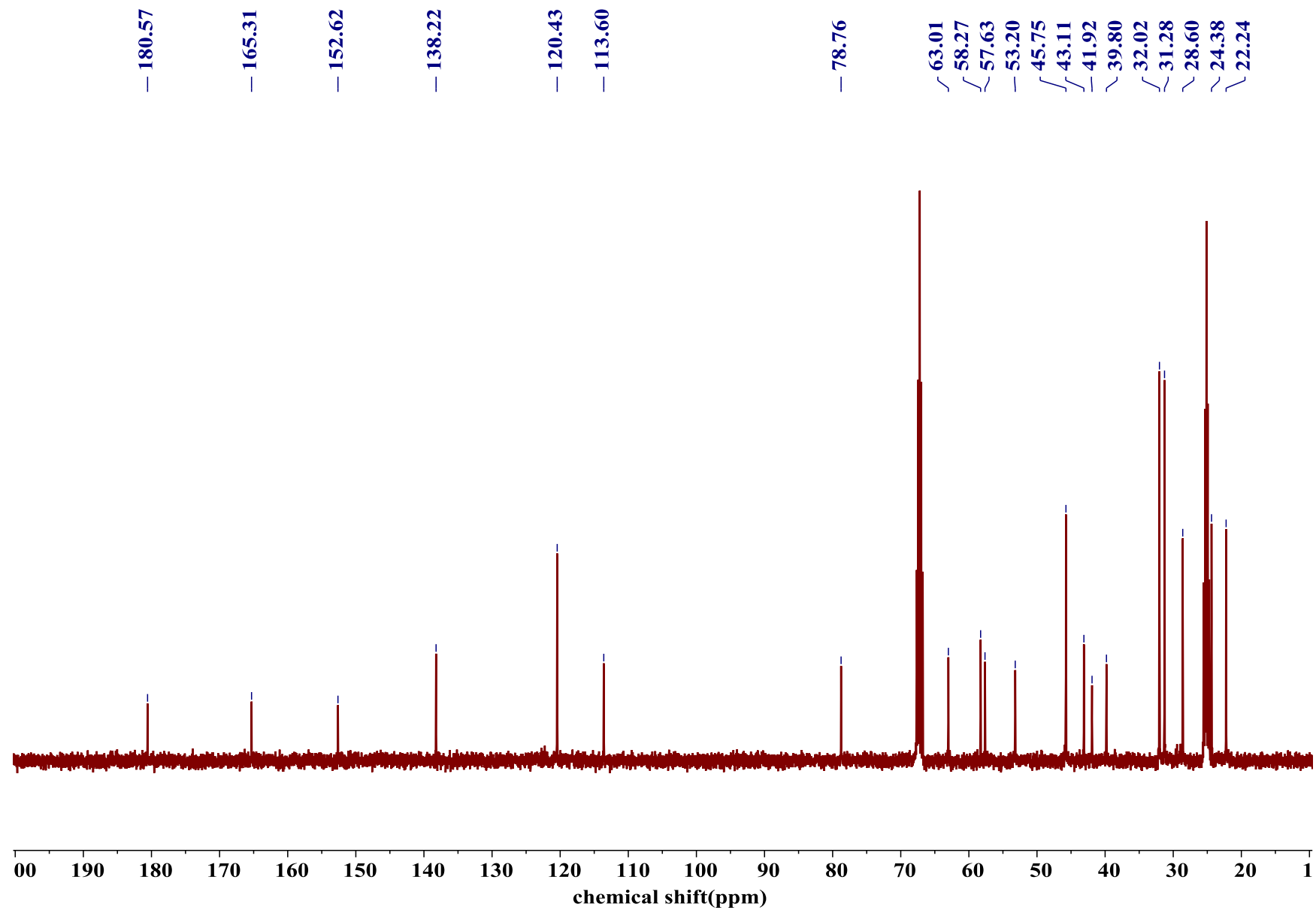
	<b>1</b>	<b>2</b>	<b>0.5(3)</b>
formula	C <sub>60</sub> H <sub>106</sub> I <sub>2</sub> N <sub>8</sub> Yb <sub>2</sub>	C <sub>34</sub> H <sub>64</sub> N <sub>4</sub> SiYb	C <sub>30</sub> H <sub>54</sub> N <sub>4</sub> Yb
fw	1539.40	730.02	643.81
color	red	red	red
crystal system	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> , Å	10.240(1)	11.376(1)	11.917(1)
<i>b</i> , Å	28.616(1)	23.594(1)	20.310(1)
<i>c</i> , Å	11.527(1)	14.219(1)	13.183(1)
$\alpha$ , deg	90	90	90
$\beta$ , deg	109.493(3)	102.100(1)	92.514(2)
$\gamma$ , deg	90	90	90
<i>V</i> , Å <sup>3</sup>	3184.1(3)	3731.6(1)	3187.9(2)
<i>Z</i>	2	4	4
<i>D</i> <sub>calcd</sub> , mg/m <sup>3</sup>	1.606	1.299	1.341
absorption coefficient, mm <sup>-1</sup>	15.071	8.616	9.814
<i>F</i> (000)	1536	1520	1328
<i>T</i> (K)	170(2)	170(2)	173(2)
$\theta$ range, deg	3.786, 54.995	3.210, 54.926	3.787, 54.933
no. of reflns collected	21040	33590	32617
no. of unique reflns	6035	7067	6042
no. of obsd reflns ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	4051	6417	5156
no. of params	338	381	333
final <i>R</i> , <i>wR</i> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.067, 0.168	0.024, 0.056	0.034, 0.085
goodness of fit on <i>F</i> <sup>2</sup>	1.108	1.049	1.026
$\Delta\rho_{\text{max,min}}$ , eÅ <sup>-3</sup>	2.002, -1.594	0.436, -1.037	1.258, -1.129

	<b>5</b>	<b>6</b>	<b>7-mesitylene</b>
formula	C <sub>35</sub> H <sub>59</sub> N <sub>5</sub> Yb	C <sub>37</sub> H <sub>64</sub> N <sub>6</sub> Yb	C <sub>49</sub> H <sub>74</sub> N <sub>6</sub> Yb
fw	722.91	765.98	920.18
color	red	red	orange
crystal system	triclinic	monoclinic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> , Å	9.777(1)	31.728(1)	21.092(1)
<i>b</i> , Å	10.429(1)	12.136(1)	13.185(1)
<i>c</i> , Å	19.793(1)	21.846(1)	16.504(1)
$\alpha$ , deg	78.372(2)	90	90
$\beta$ , deg	77.701(2)	101.593(2)	94.546(2)
$\gamma$ , deg	65.313(2)	90	90
<i>V</i> , Å <sup>3</sup>	1777.2(1)	8239.9(4)	4575.6(3)
<i>Z</i>	2	8	4
<i>D</i> <sub>calcd</sub> , mg/m <sup>3</sup>	1.351	1.235	1.336
absorption coefficient, mm <sup>-1</sup>	8.848	8.307	6.954
<i>F</i> (000)	748	3184	1920
<i>T</i> (K)	170(2)	173(2)	173(2)
$\theta$ range, deg	4.092, 55.173	3.594, 54.884	3.738, 54.944
no. of reflns collected	20165	38830	48464
no. of unique reflns	6737	7815	8668
no. of obsd reflns ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	6239	6589	7415
no. of params	383	412	536
final <i>R</i> , <i>wR</i> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.038, 0.099	0.034, 0.076	0.028, 0.065
goodness of fit on <i>F</i> <sup>2</sup>	1.042	1.053	1.028
$\Delta\rho_{\text{max,min}}$ , eÅ <sup>-3</sup>	1.247, -1.791	0.658, -0.902	0.431, -0.833

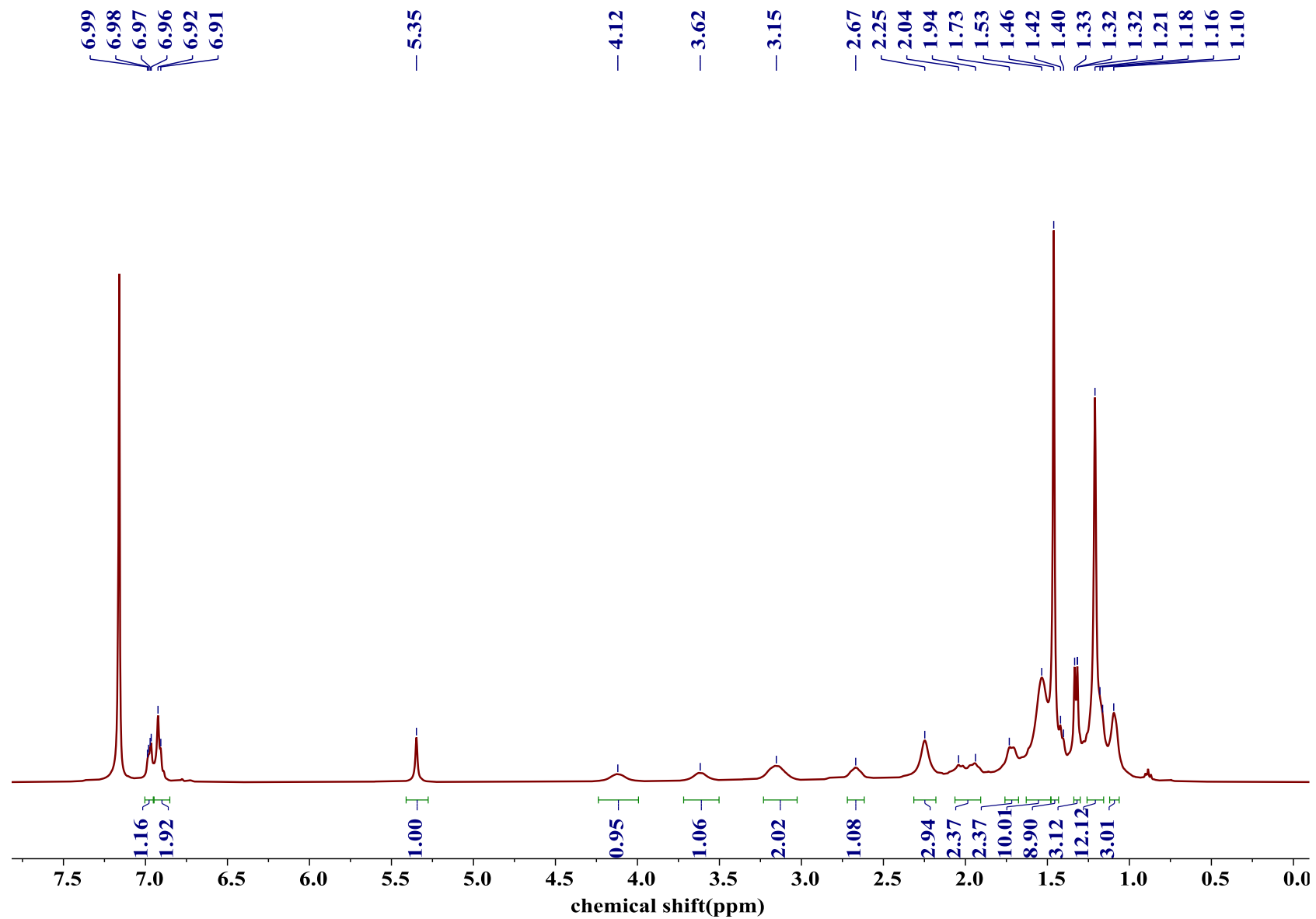
	8	9	10
formula	C <sub>42</sub> H <sub>63</sub> N <sub>4</sub> OPYb	C <sub>72</sub> H <sub>116</sub> N <sub>8</sub> S <sub>2</sub> Yb <sub>2</sub>	C <sub>42</sub> H <sub>63</sub> N <sub>4</sub> S <sub>2</sub> Yb
fw	843.97	1503.92	861.12
color	red	brown	yellow
crystal system	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> , Å	19.463(1)	15.231(1)	19.433(1)
<i>b</i> , Å	11.075(1)	34.584(1)	13.508(1)
<i>c</i> , Å	20.645(1)	21.662(1)	17.331(1)
$\alpha$ , deg	90	90	90
$\beta$ , deg	113.247(3)	95.572(2)	100.930(2)
$\gamma$ , deg	90	90	90
<i>V</i> , Å <sup>3</sup>	4088.6(4)	11356.5(5)	4466.6(3)
<i>Z</i>	4	6	4
<i>D</i> <sub>calcd</sub> , (mg/m <sup>3</sup> )	1.371	1.319	1.281
absorption coefficient, mm <sup>-1</sup>	7.935	8.644	7.648
<i>F</i> (000)	1744	4656	1780
<i>T</i> (K)	173(2)	185(2)	192(1)
$\theta$ range, deg	4.021, 55.010	2.769, 55.001	3.488, 54.987
no. of refns collected	34631	124671	35229
no. of unique refns	7654	21642	8460
no. of obsd refns ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	6347	14445	6217
no. of params	455	1174	455
final <i>R</i> , <i>wR</i> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.066, 0.180	0.053, 0.129	0.067, 0.174
goodness of fit on <i>F</i> <sup>2</sup>	1.109	1.043	1.043
$\Delta\rho_{\text{max, min}}$ , eÅ <sup>-3</sup>	1.806, -2.377	2.276, -1.469	1.807, -2.742



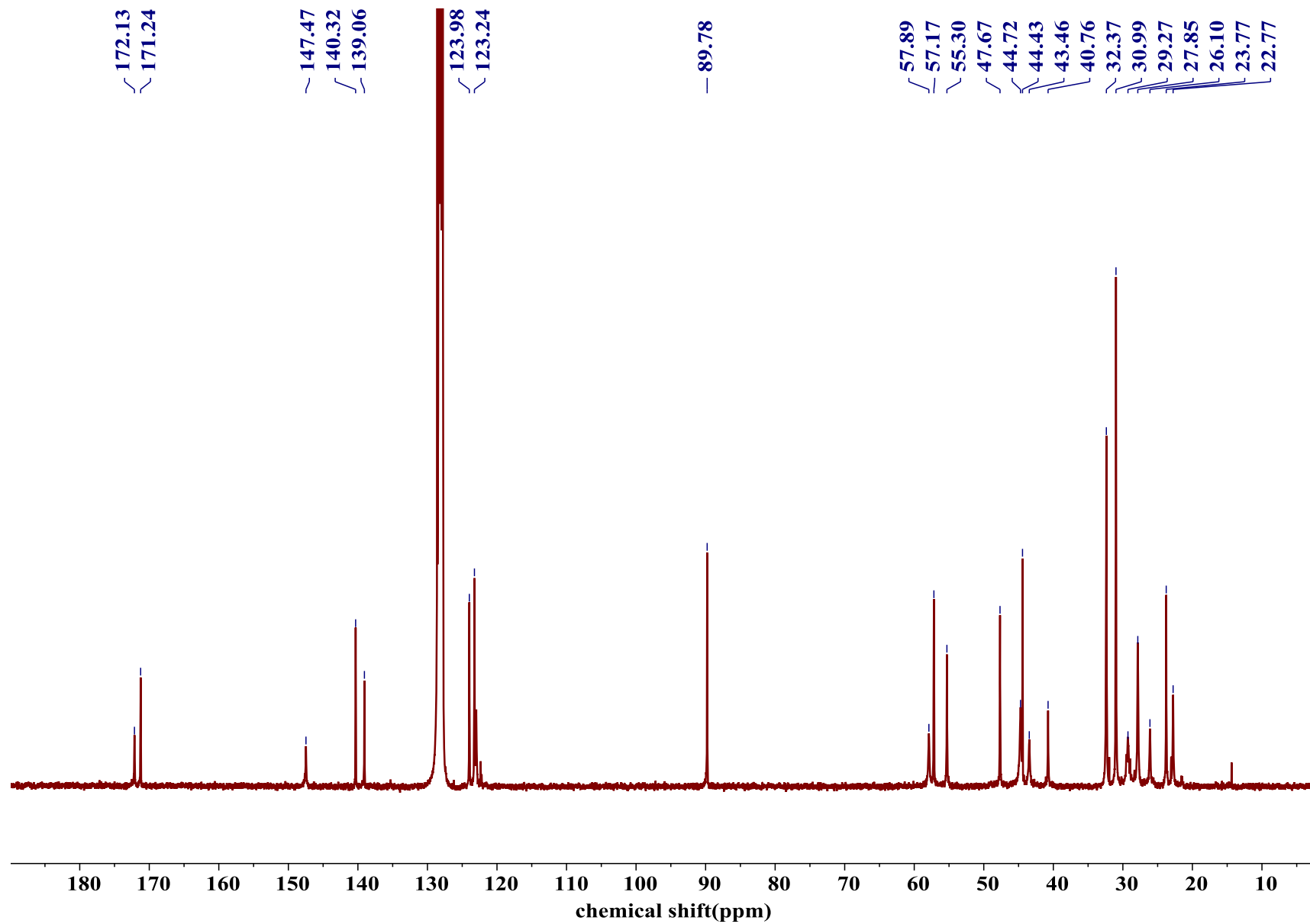
**Figure S1.**  $^1\text{H}$  NMR spectrum of **LK** (400 MHz,  $d_8$ -THF, 25 °C).



**Figure S2.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **LK** (100 MHz,  $d_8$ -THF, 25 °C).

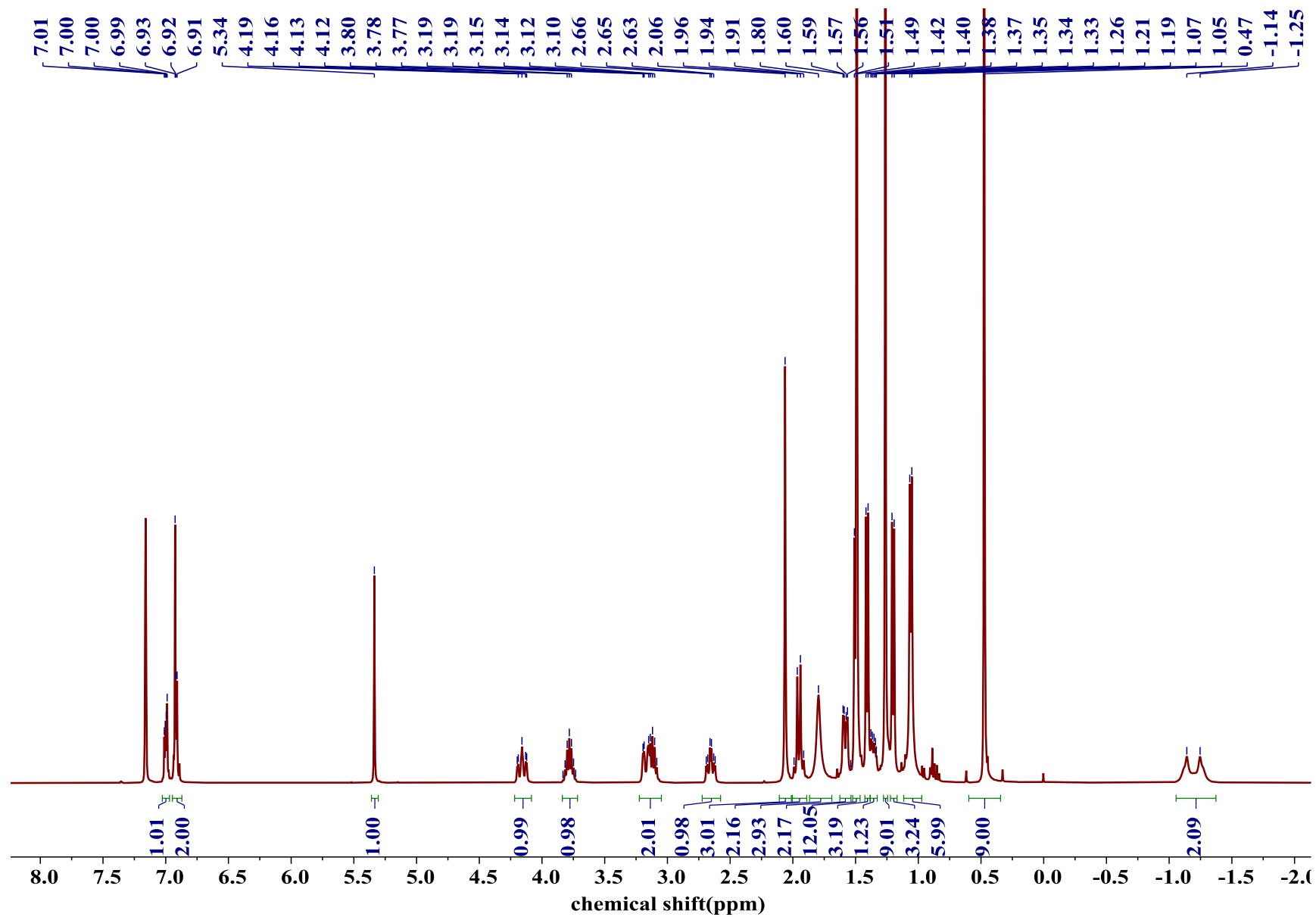


**Figure S3.**  $^1\text{H}$  NMR spectrum of complex **1** (400 MHz,  $\text{C}_6\text{D}_6$ , 25  $^\circ\text{C}$ ).

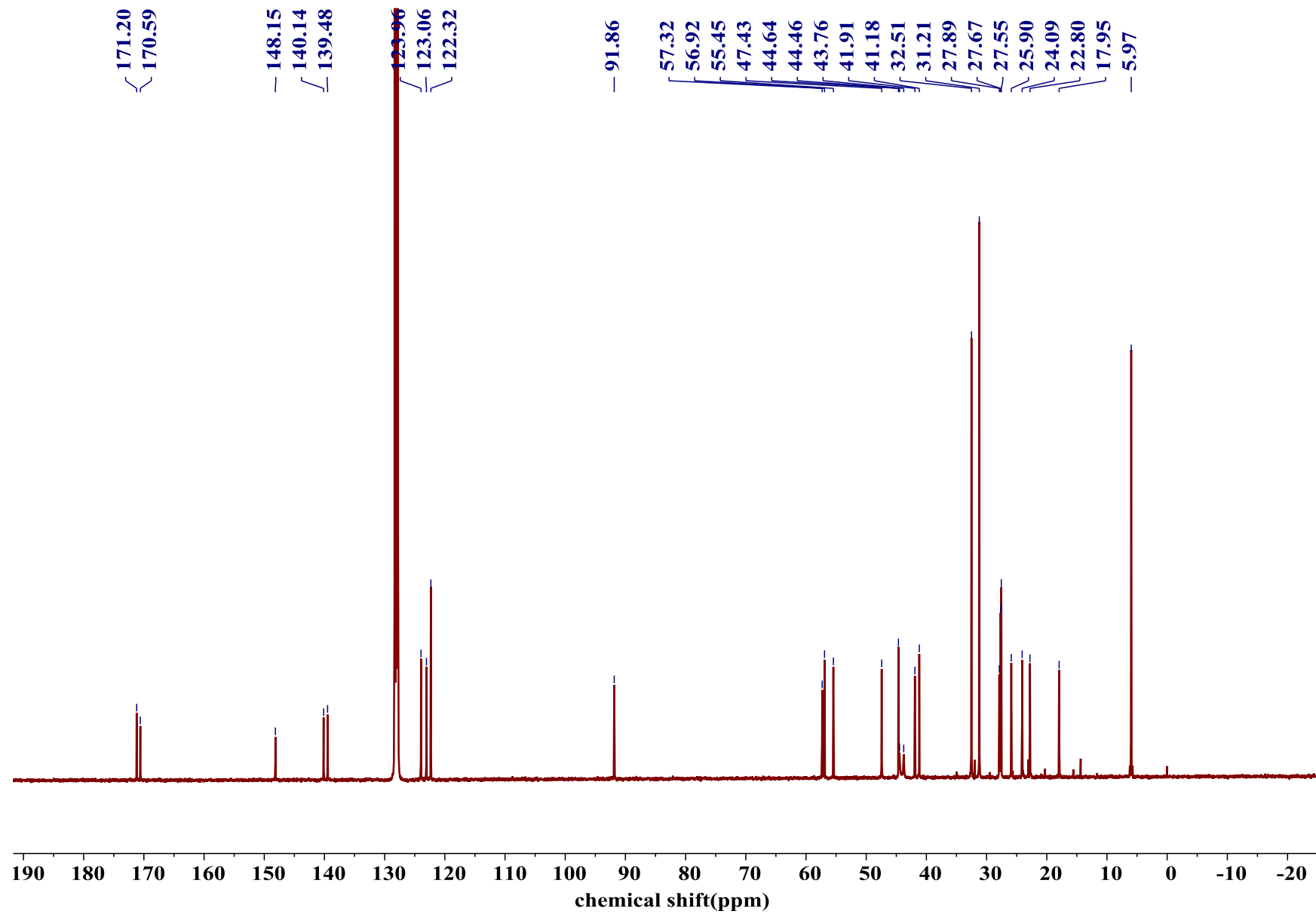


**Figure S4.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of complex **1** (100 MHz,  $\text{C}_6\text{D}_6$ , 25 °C).

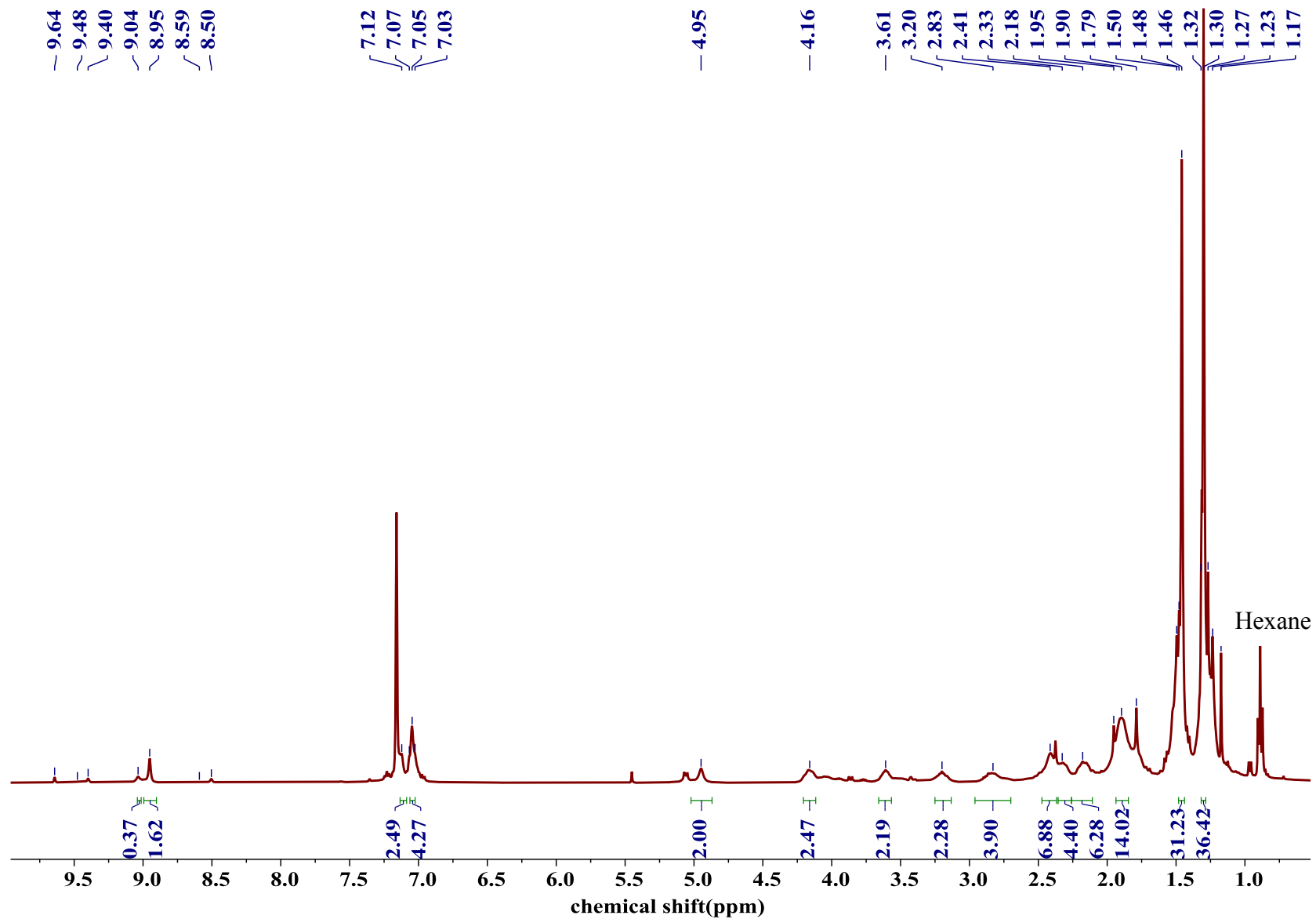




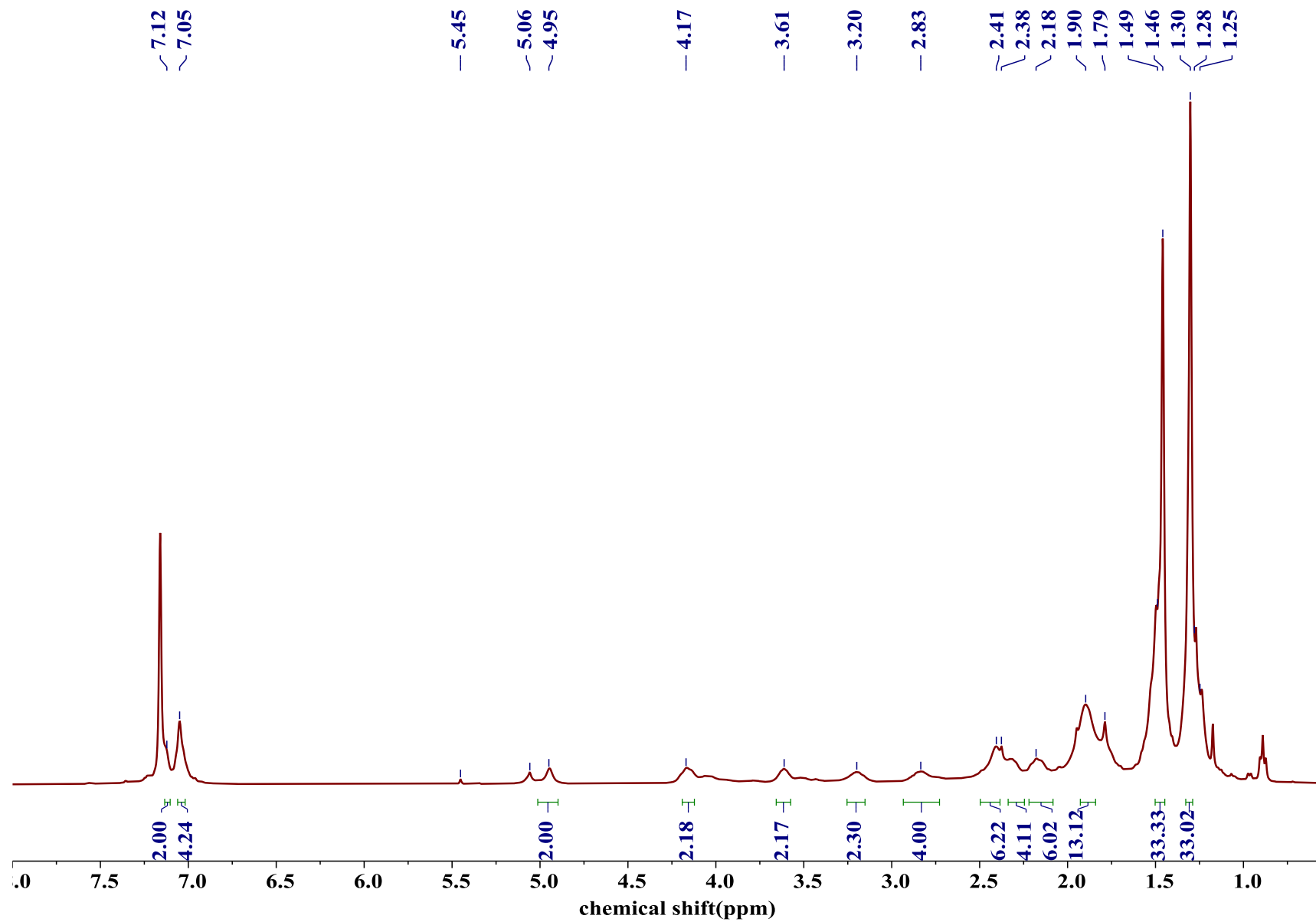
**Figure S5.**  $^1\text{H}$  NMR spectrum of complex **2** (400 MHz,  $\text{C}_6\text{D}_6$ , 25  $^\circ\text{C}$ ).



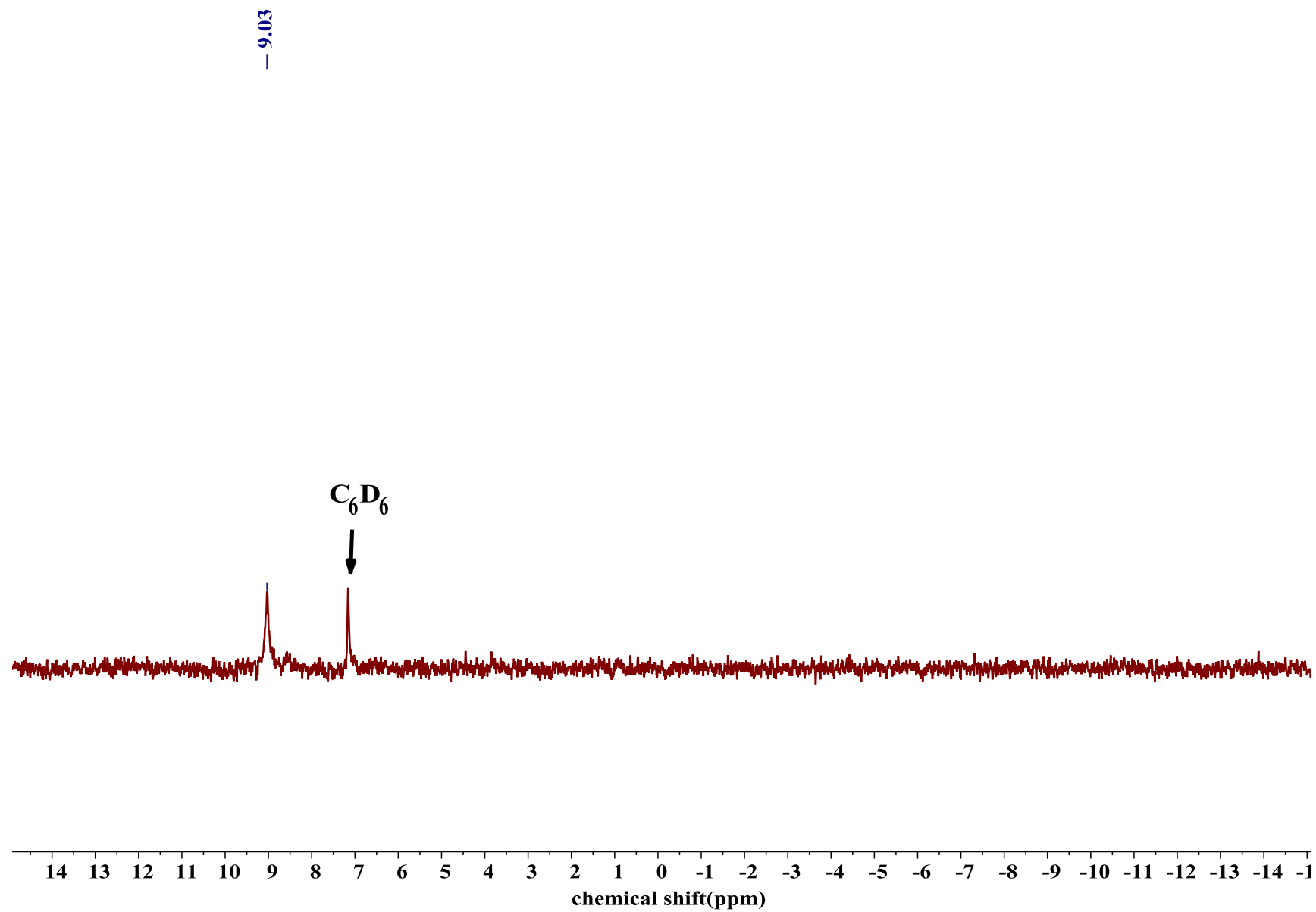
**Figure S6.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of complex **2** (100 MHz,  $\text{C}_6\text{D}_6$ , 25 °C).



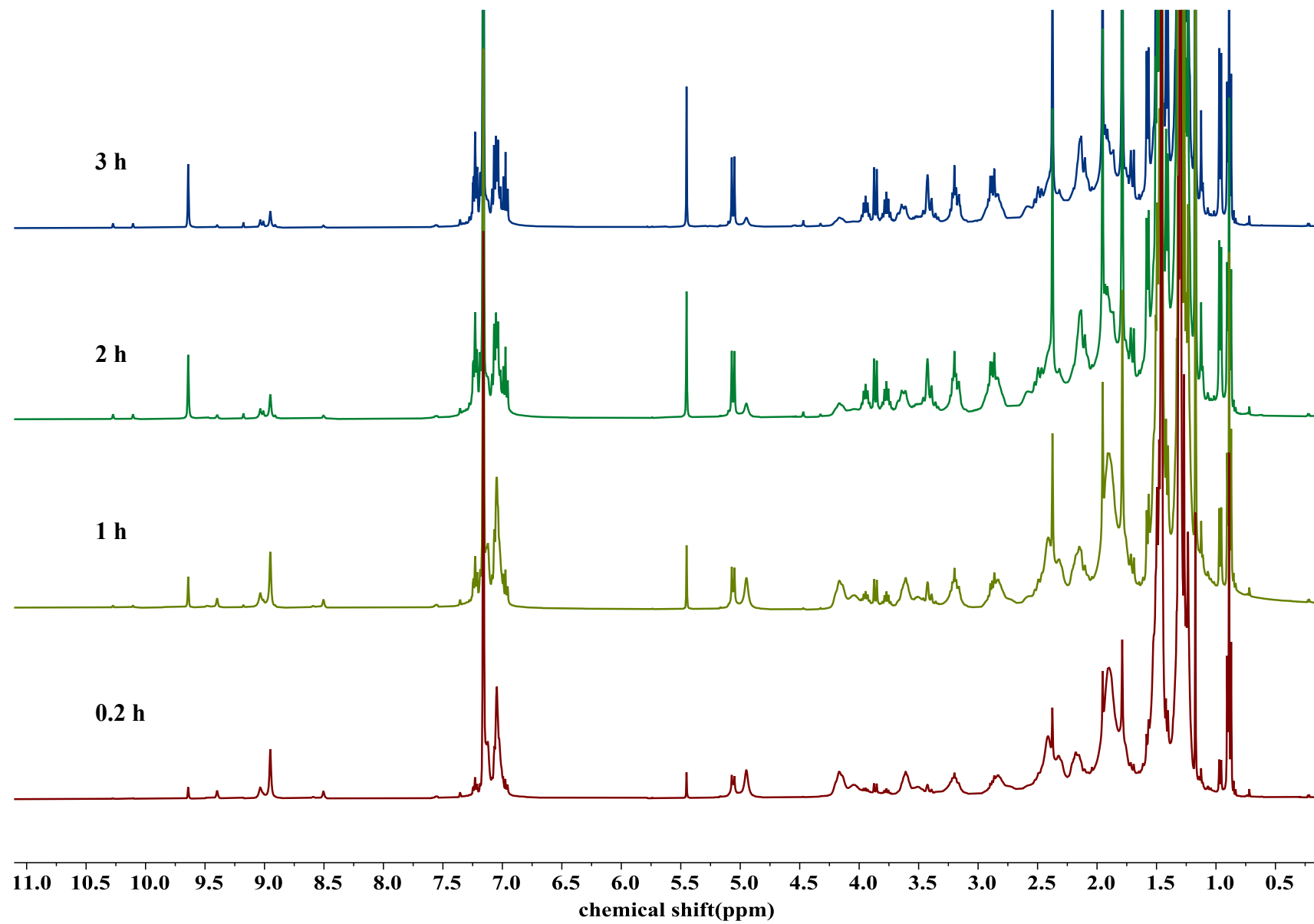
**Figure S7.**  $^1\text{H}$  NMR spectrum of complex **3** (400 MHz,  $\text{C}_6\text{D}_6$ , 25  $^\circ\text{C}$ ). A small amount of complex **3** have decomposed into complex **4**.



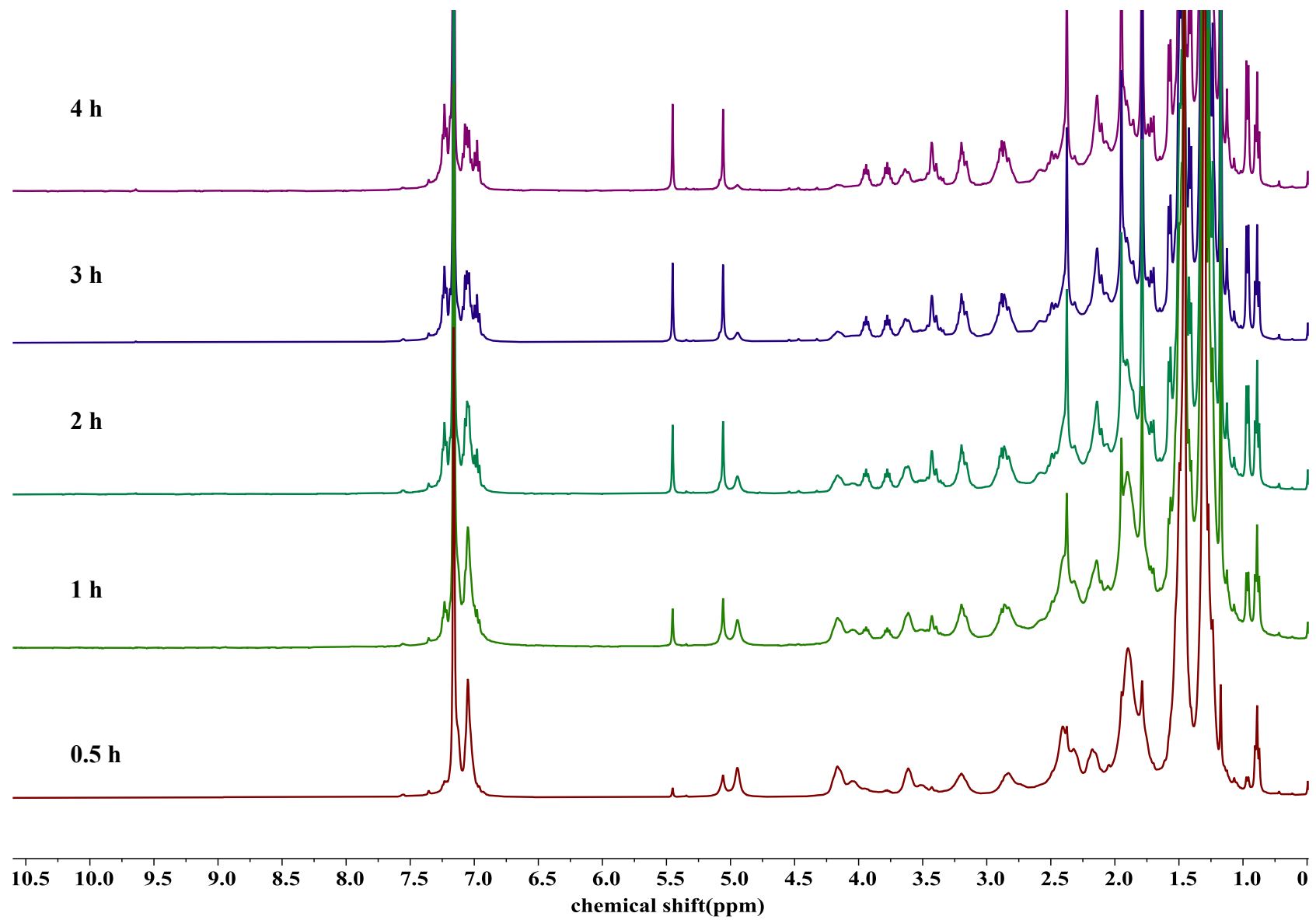
**Figure S8.**  $^1\text{H}$  NMR spectrum of complex **3-D** (400 MHz,  $\text{C}_6\text{D}_6$ , 25  $^\circ\text{C}$ ).



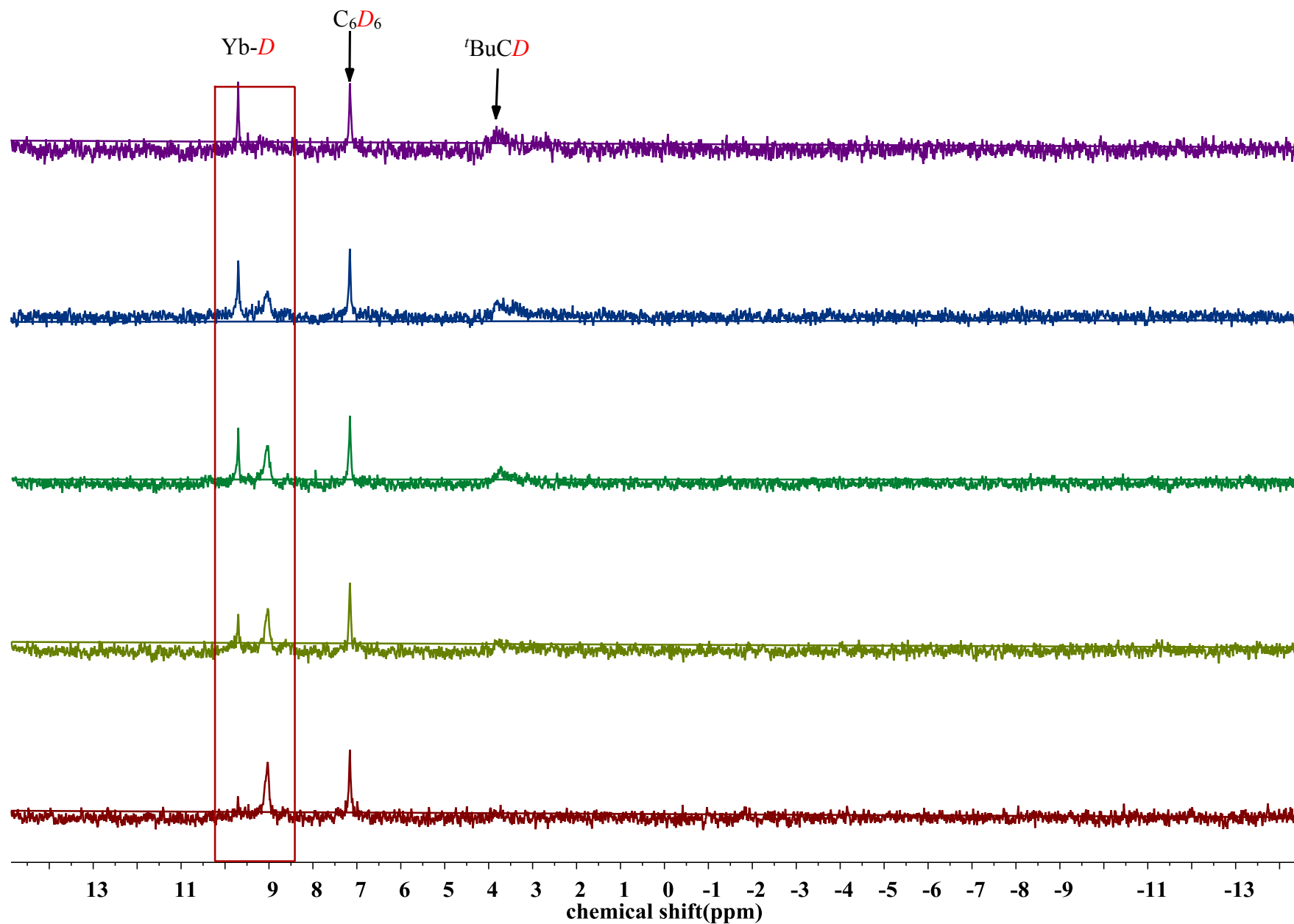
**Figure S9.**  $^2\text{H}$  NMR spectrum of complex **3-D** (60 MHz,  $\text{C}_6\text{H}_6$ , 25  $^\circ\text{C}$ ).  $\text{C}_6\text{D}_6$  as the reference.



**Figure S10.**  $^1\text{H}$  NMR spectral monitoring on transformation of **3** to **4** (400 MHz,  $\text{C}_6\text{D}_6$ , 25  $^\circ\text{C}$ ).

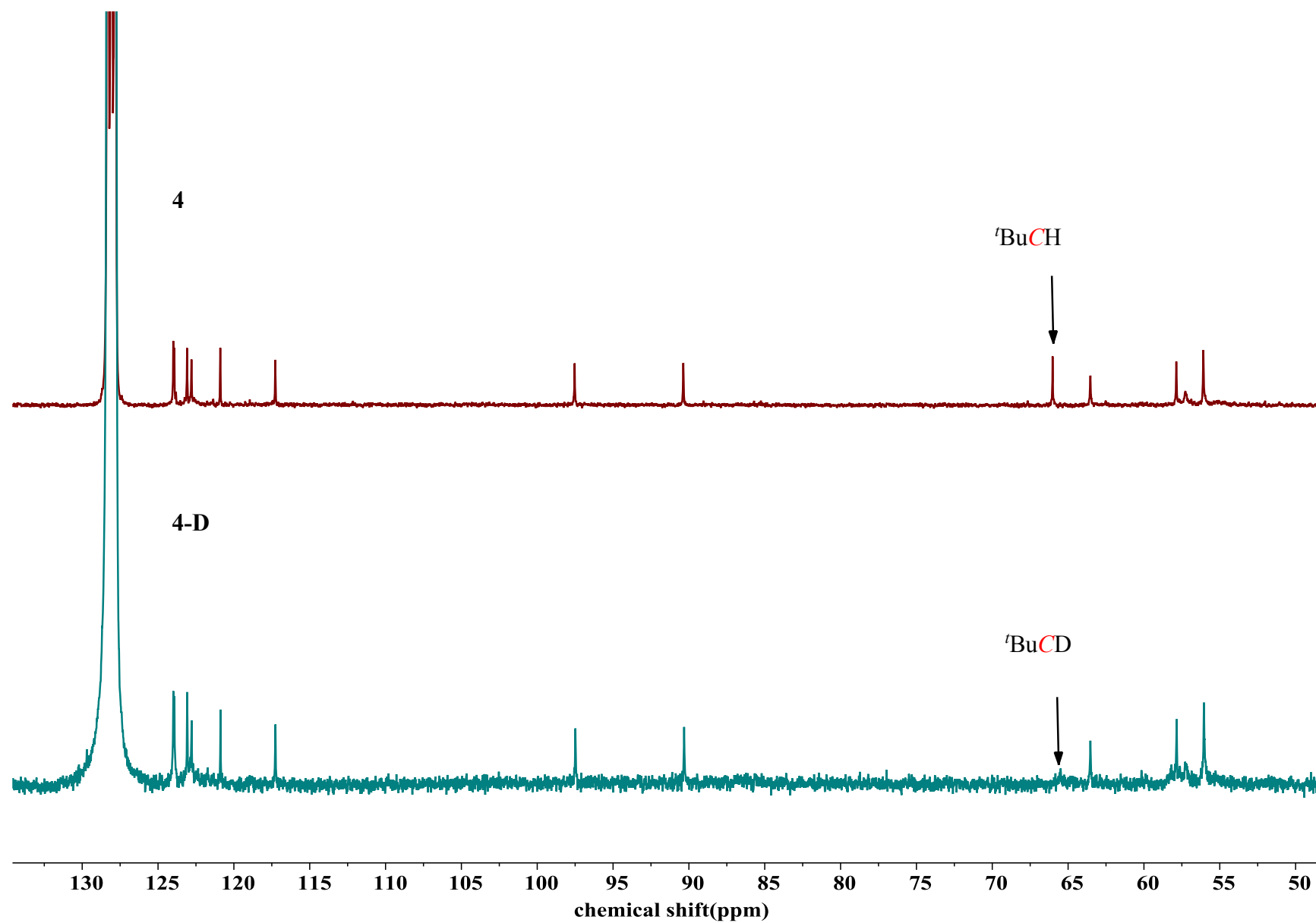


**Figure S11.**  $^1\text{H}$  NMR spectral monitoring on transformation of **3-D** to **4-D** (400 MHz,  $\text{C}_6\text{D}_6$ , 25  $^\circ\text{C}$ ).

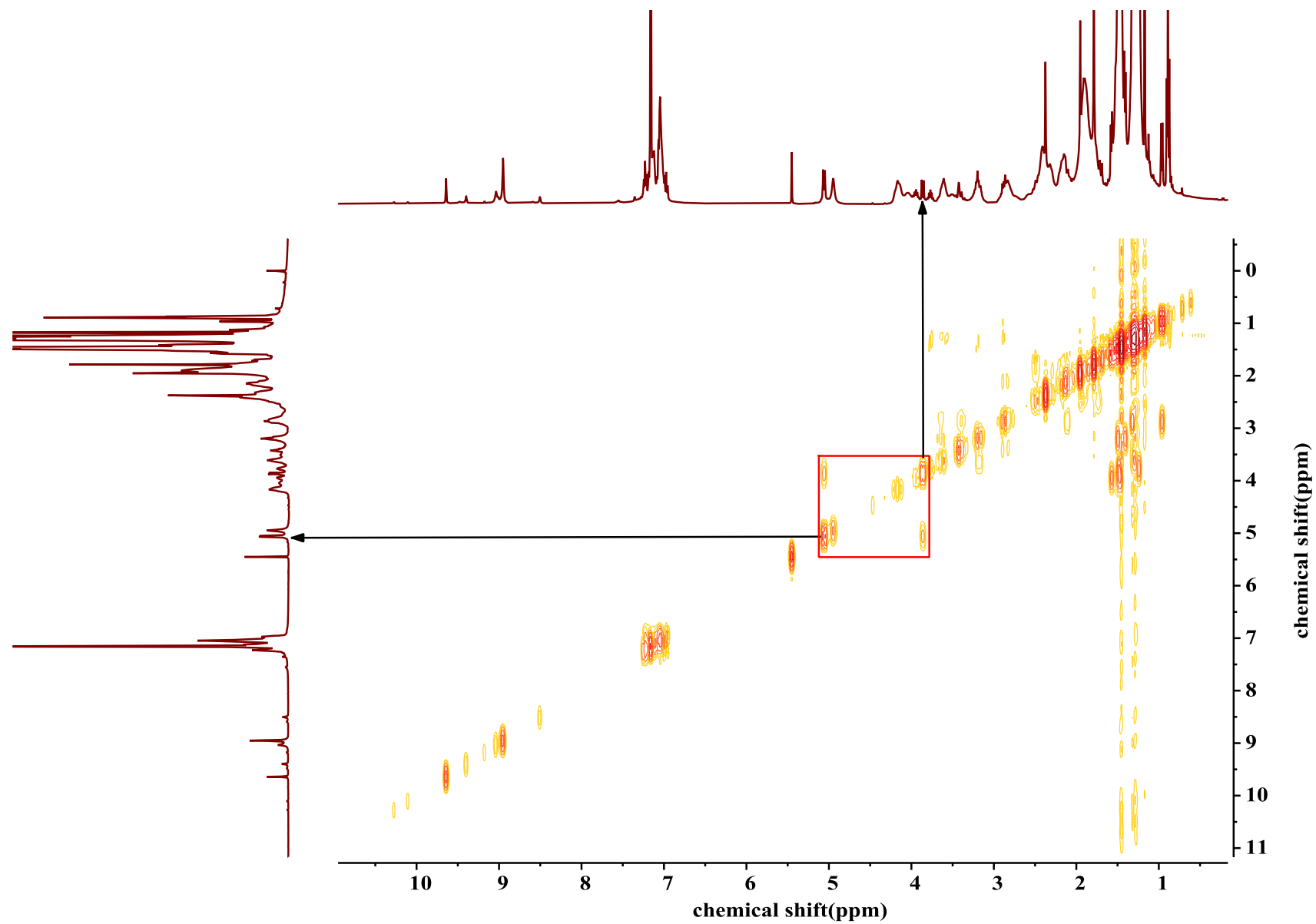


**Figure S12.**  $^2\text{H}$  NMR spectral monitoring on transformation of **3-D** to **4-D** (60 MHz,  $\text{C}_6\text{H}_6$ , 25  $^\circ\text{C}$ ).  $\text{C}_6\text{D}_6$  as the reference.

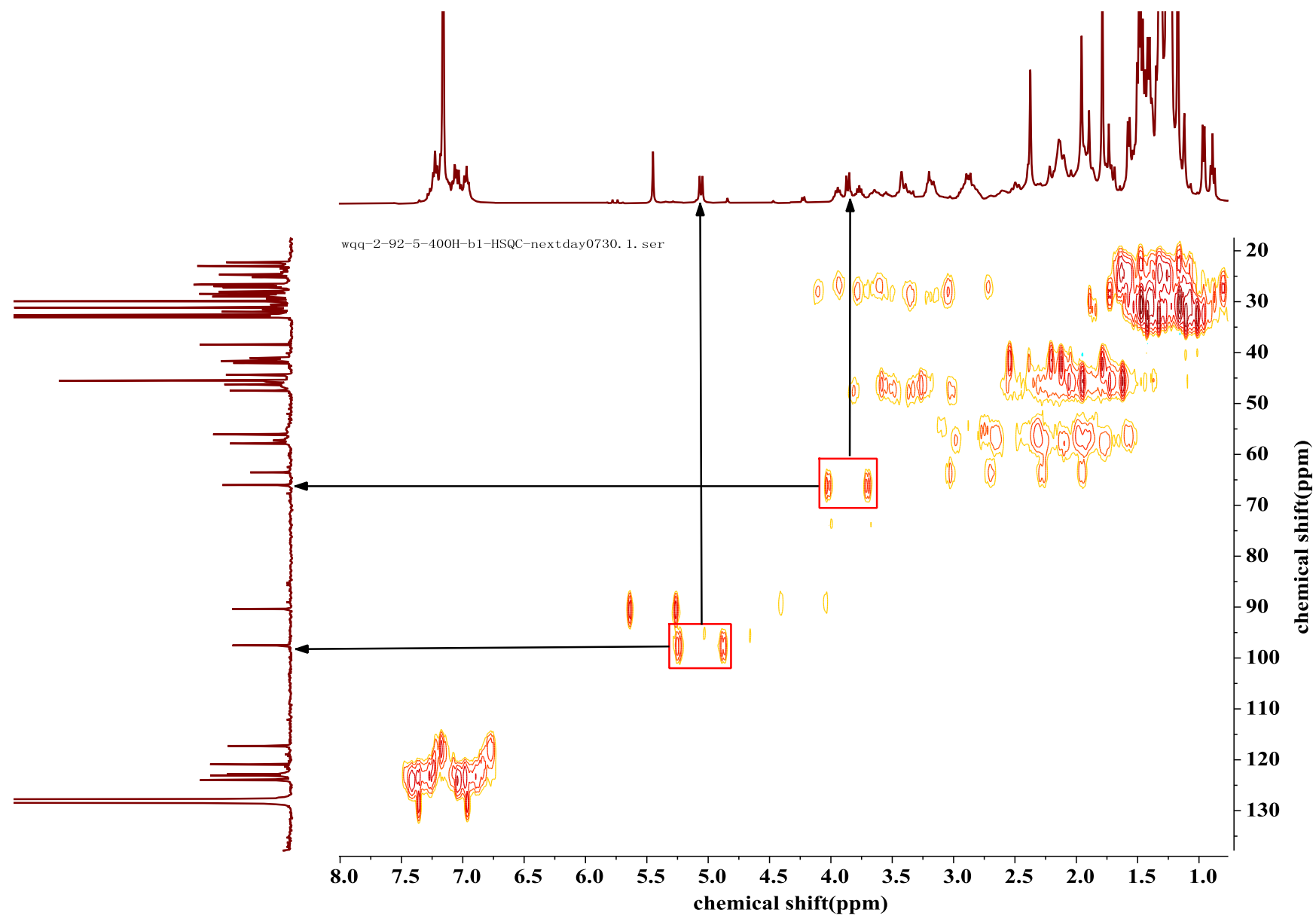




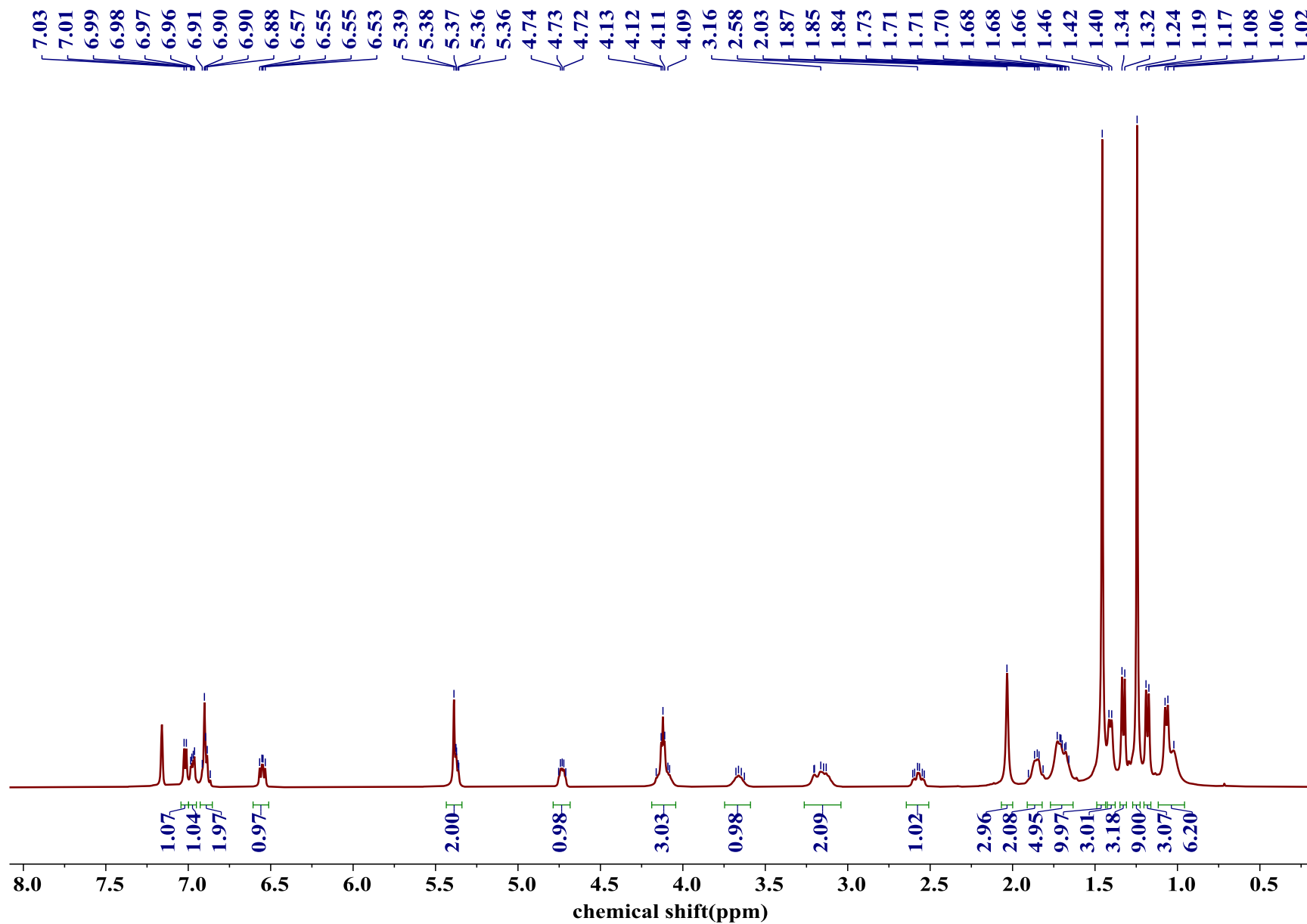
**Figure S13.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of **4** and **4-D**, which indicate the presence of  $^t\text{BuCH}$  in **4** and  $^t\text{BuCD}$  in **4-D** (100 MHz,  $\text{C}_6\text{D}_6$ , 25 °C).



**Figure S14.** gCOSY spectra of the mixture of **3** and **4** (400 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C).



**Figure S15.** gHSQC spectra of **4** (400 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C).



**Figure S16.**  $^1\text{H}$  NMR spectrum of complex **5** (400 MHz,  $\text{C}_6\text{D}_6$ , 25 °C).

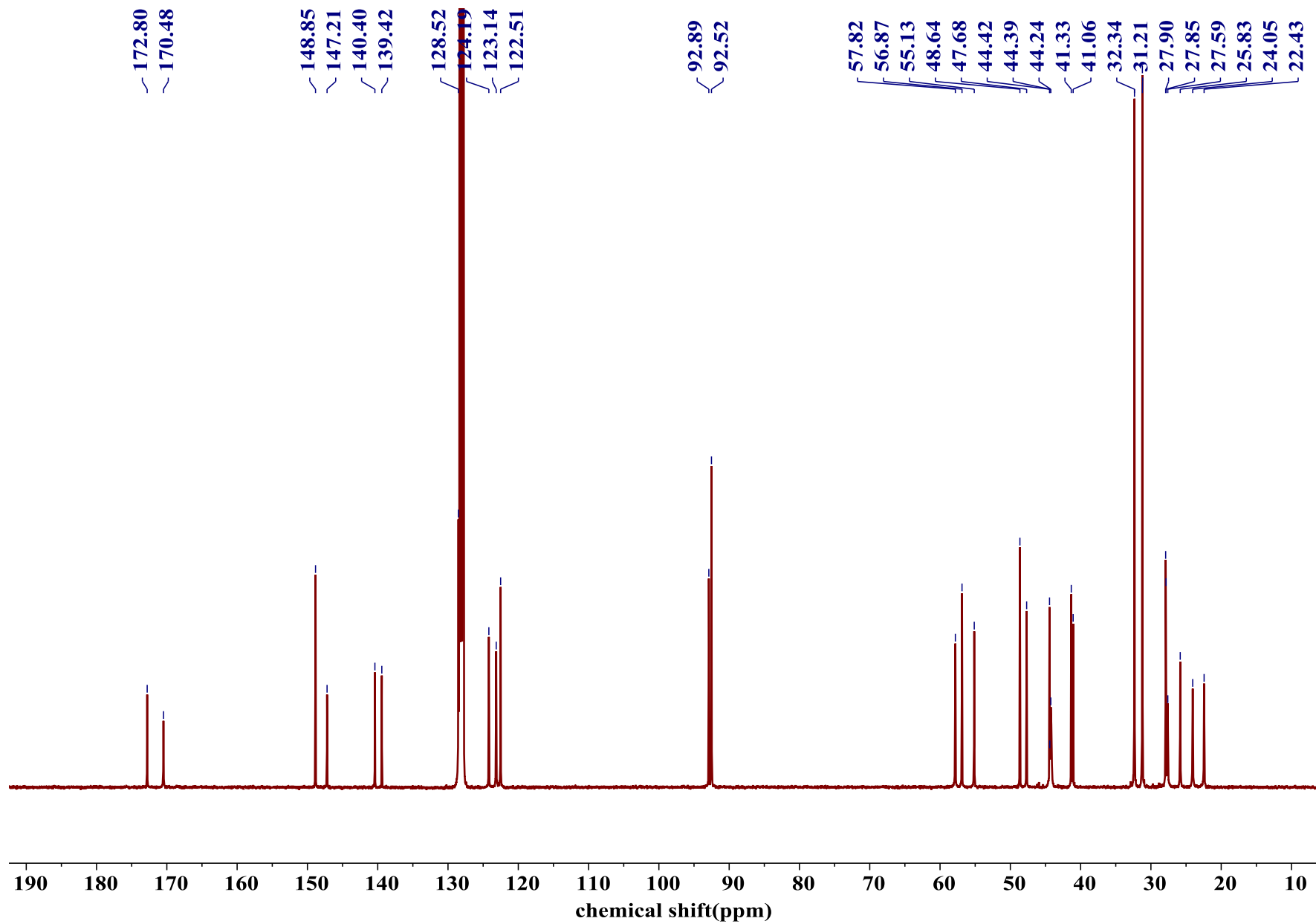
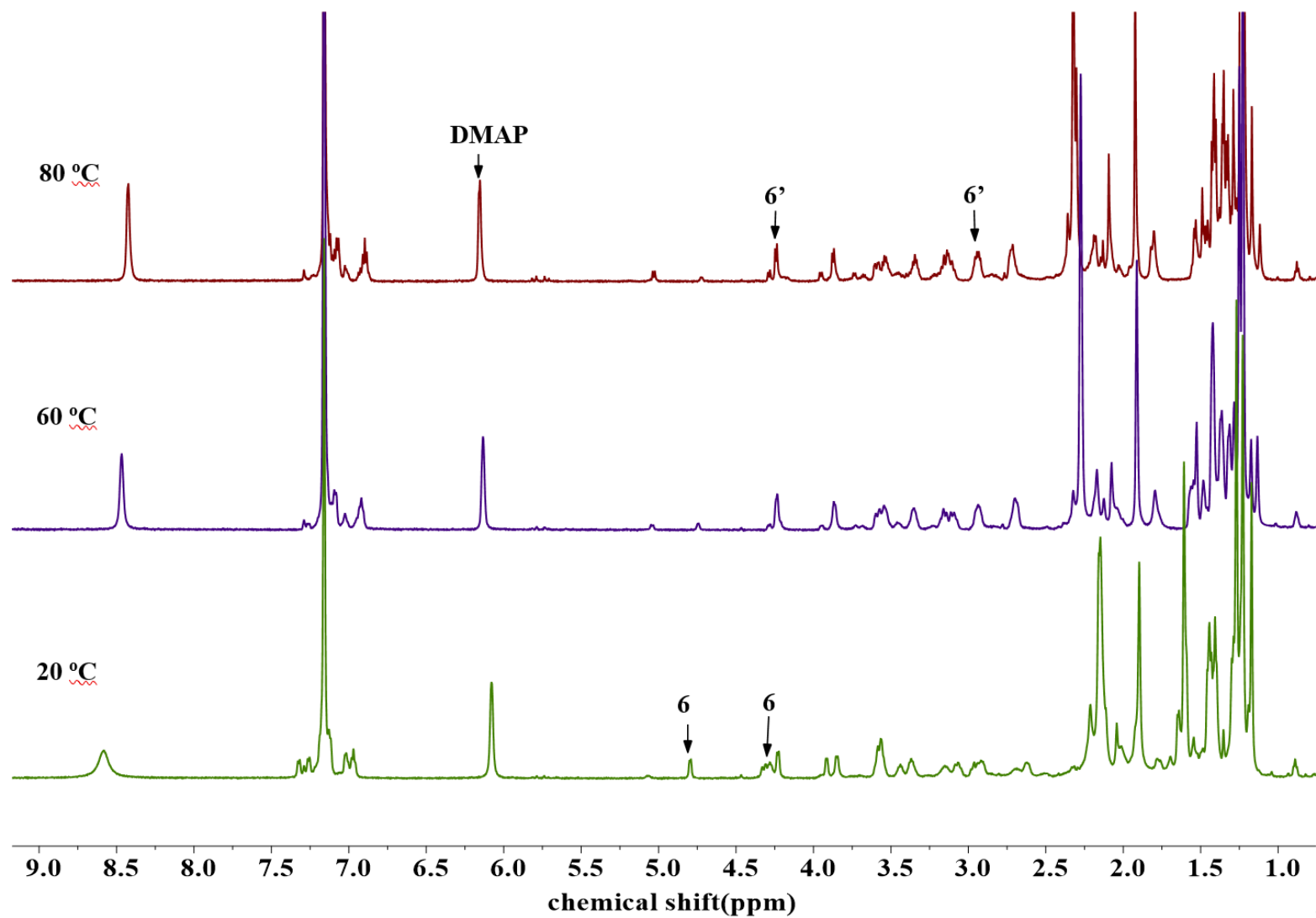


Figure S17.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of complex 5 (100 MHz,  $\text{C}_6\text{D}_6$ , 25  $^\circ\text{C}$ ).



**Figure S18.**  $^1\text{H}$  NMR spectrum showing of the transformation of complex **6** into DMAP and **6'** (600 MHz,  $\text{C}_6\text{D}_6$ )

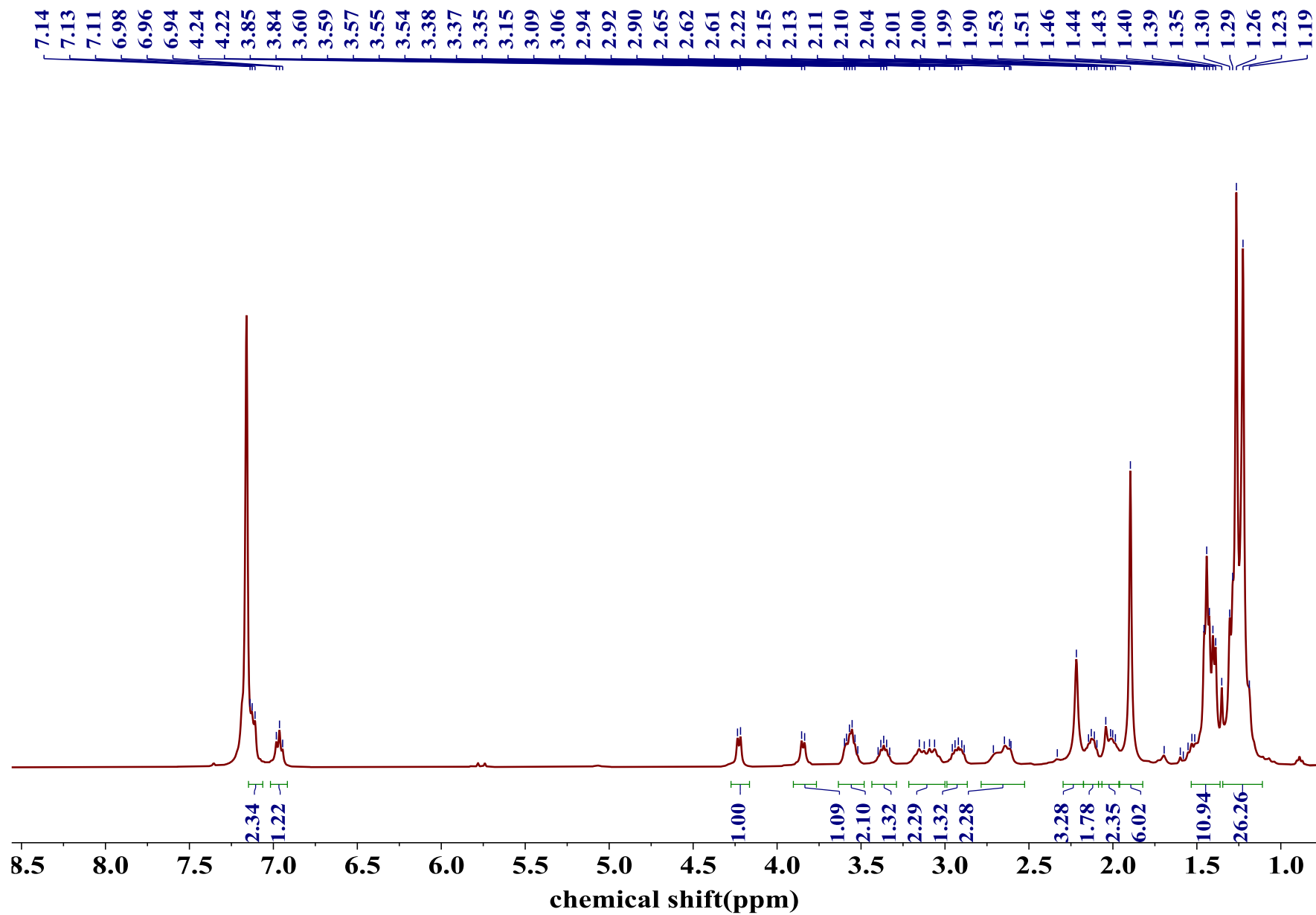


Figure S19.  $^1\text{H}$  NMR spectrum of complex **6'** (400 MHz,  $\text{C}_6\text{D}_6$ , 25 °C).

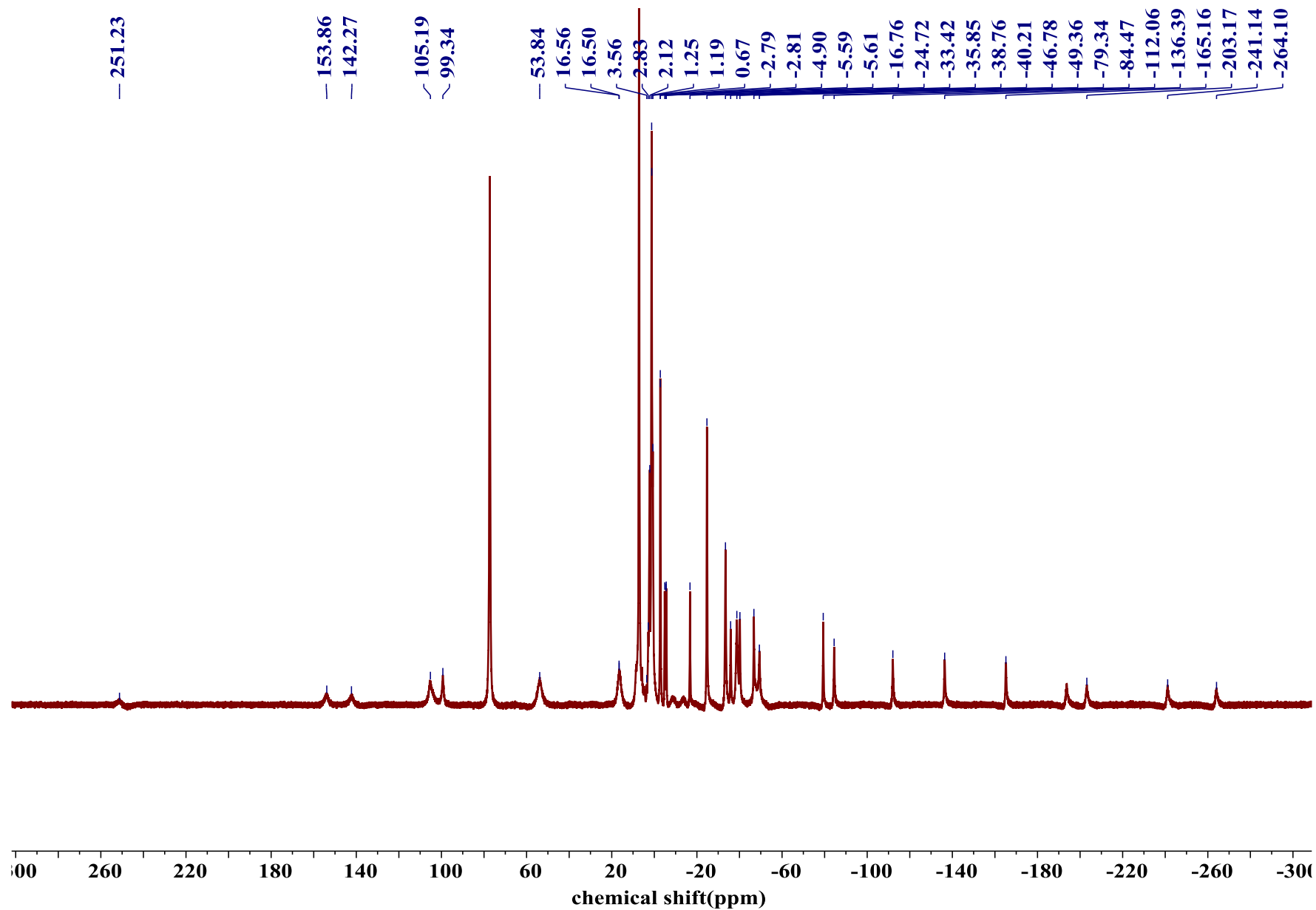


Figure S20.  $^1\text{H}$  NMR spectrum of complex **7** (400 MHz,  $\text{C}_6\text{D}_6$ , 25  $^\circ\text{C}$ ).



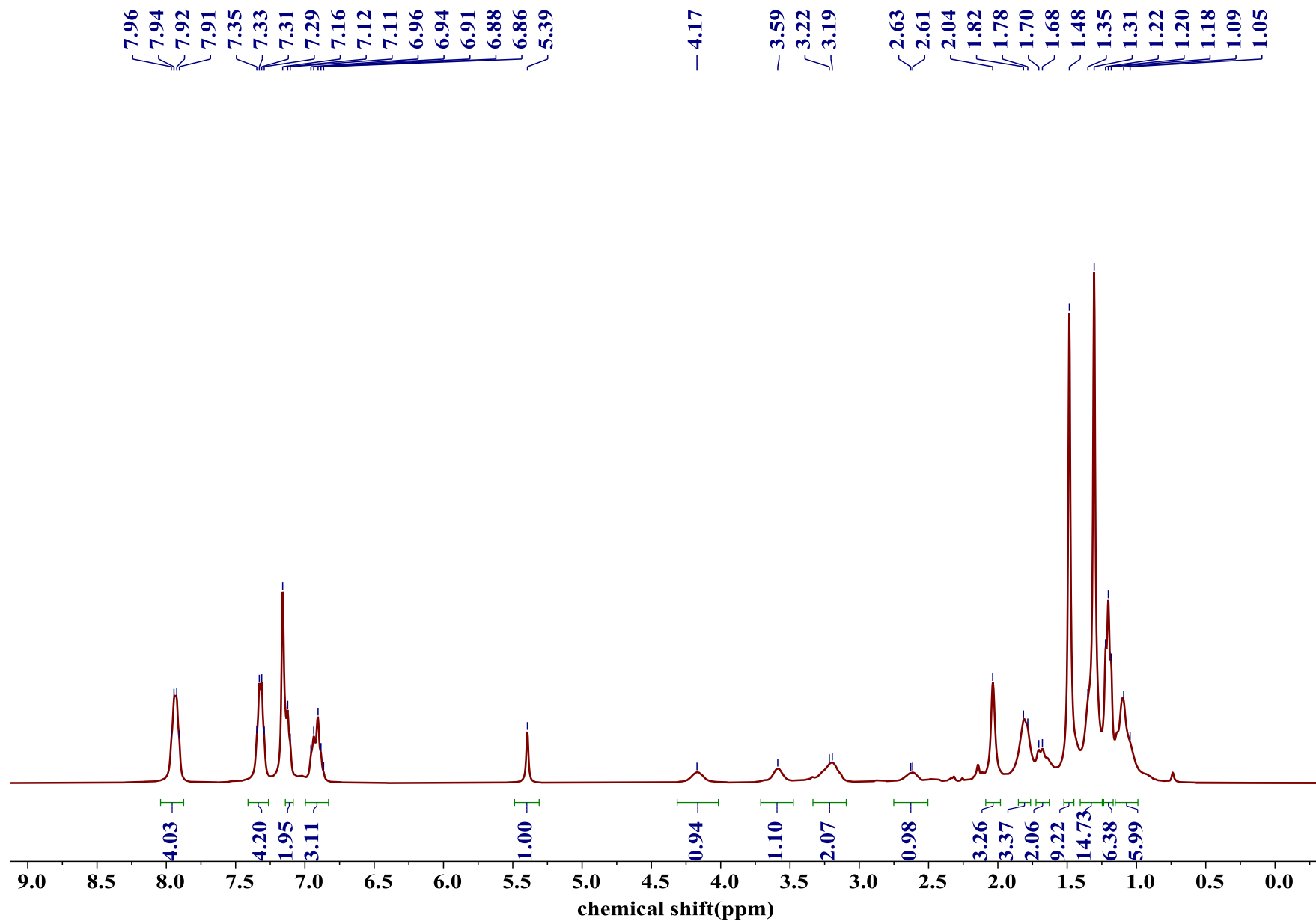


Figure S21.  $^1\text{H}$  NMR spectrum of complex **8** (400 MHz,  $\text{C}_6\text{D}_6$ , 25  $^\circ\text{C}$ ).

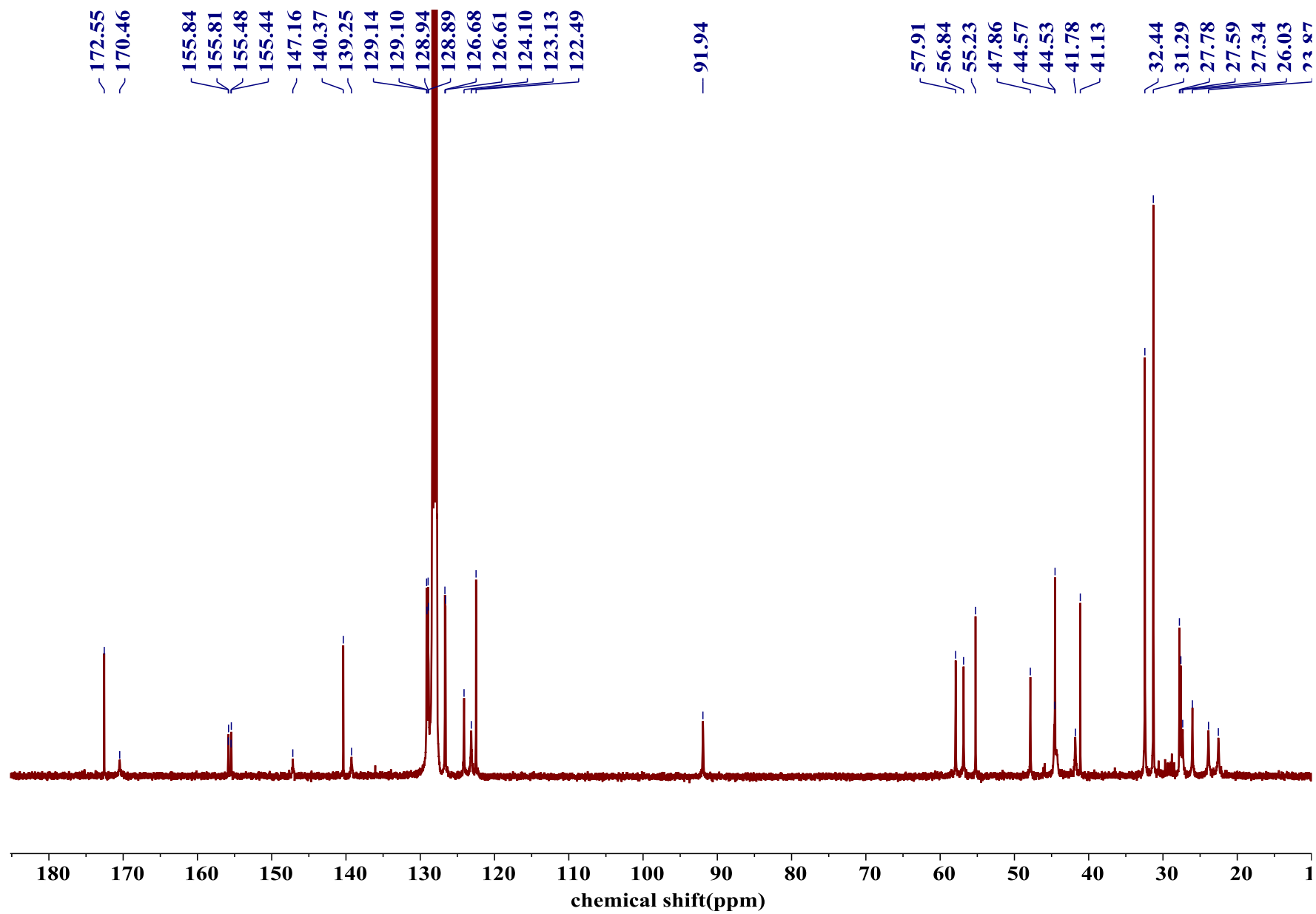
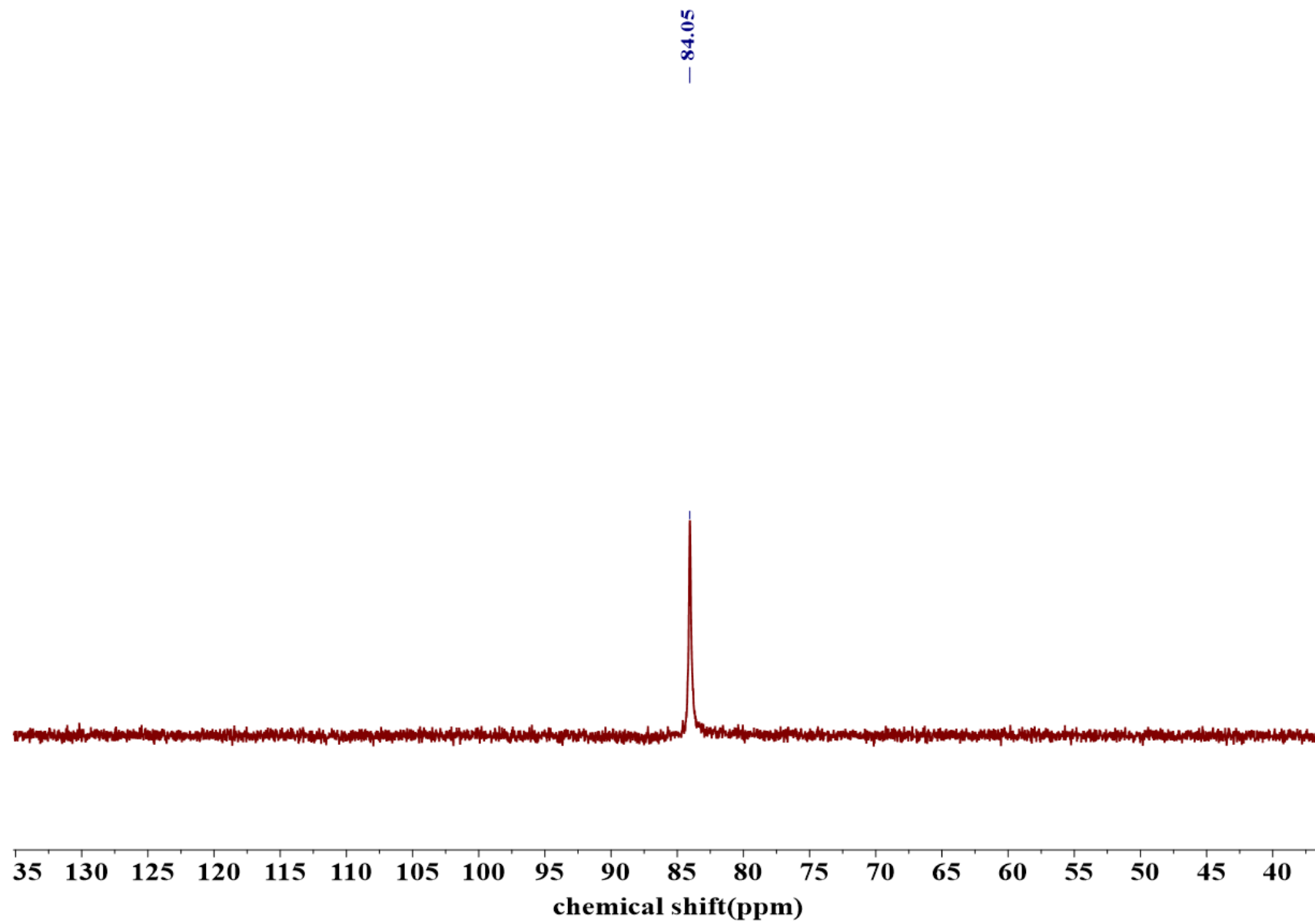
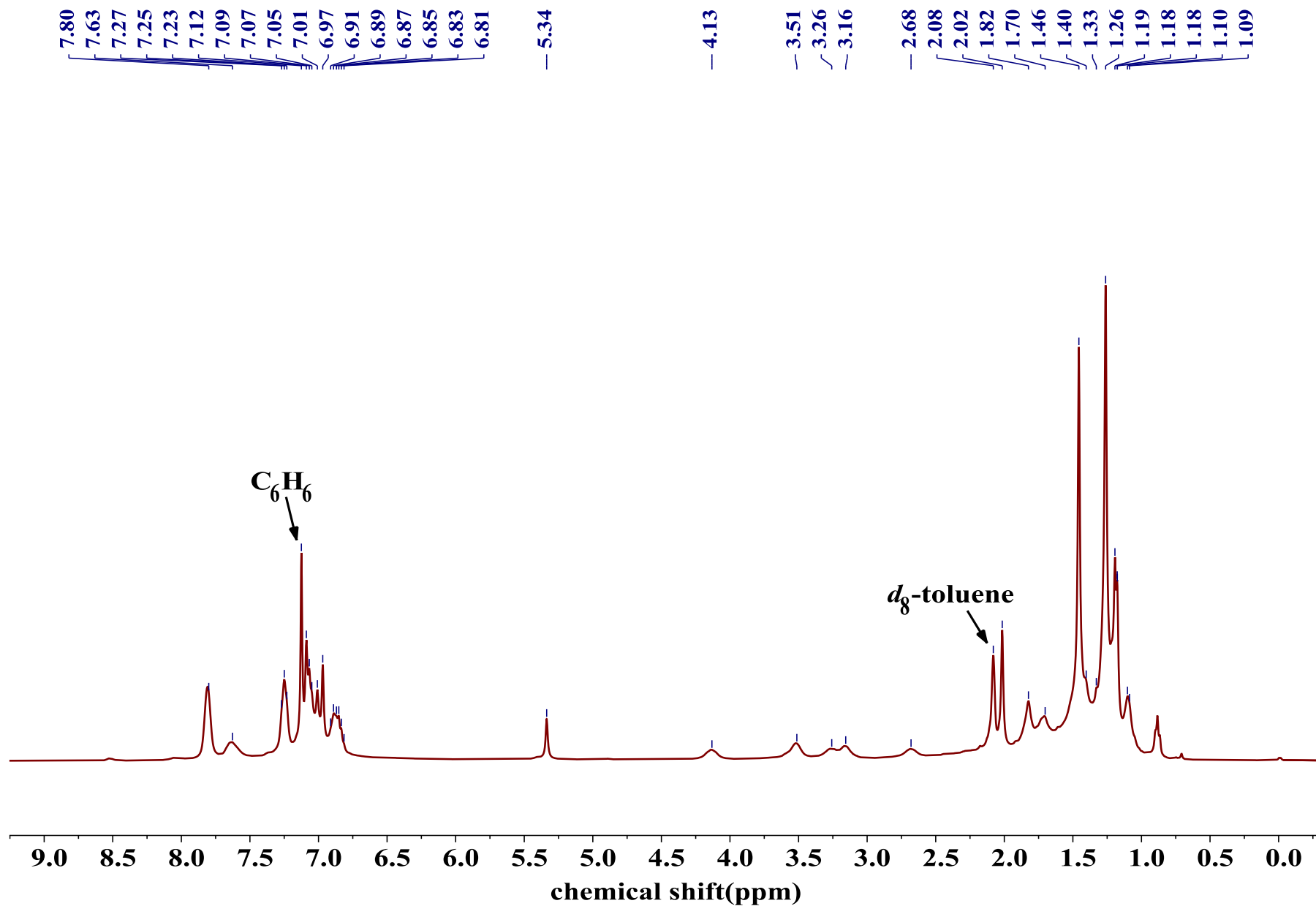


Figure S22.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of complex **8** (100 MHz,  $\text{C}_6\text{D}_6$ , 25  $^\circ\text{C}$ ).



**Figure S23.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of complex **8** (162 MHz,  $\text{C}_6\text{D}_6$ , 25 °C).



**Figure S24.**  $^1\text{H}$  NMR spectrum of the reaction of complex **3** with  $\text{Ph}_3\text{P}=\text{O}$  in  $d_8$ -toluene (400 MHz, 25  $^\circ\text{C}$ ), showing the formation of  $\text{C}_6\text{H}_6$ .

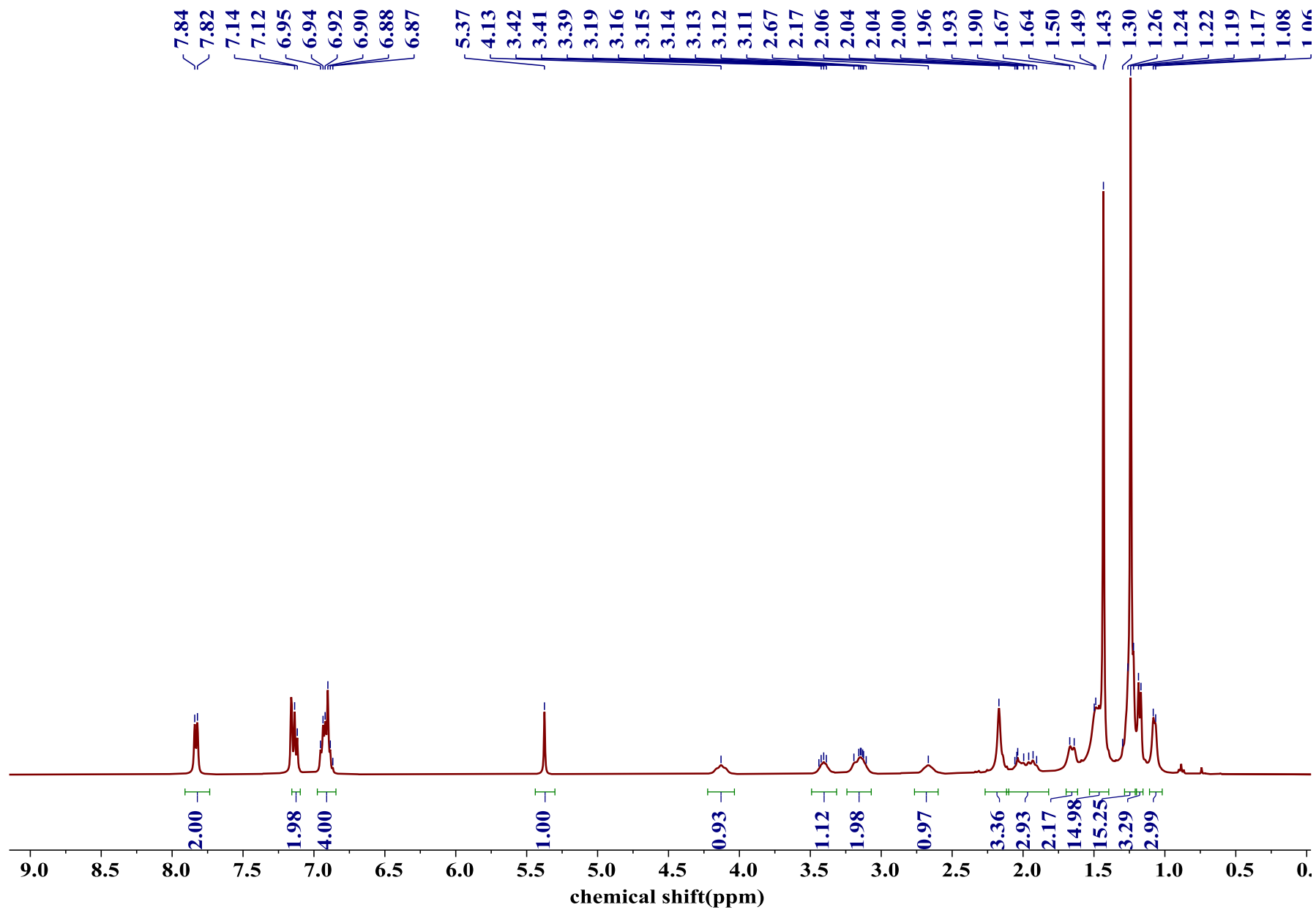


Figure S25.  $^1\text{H}$  NMR spectrum of complex **9** (400 MHz,  $\text{C}_6\text{D}_6$ , 25  $^\circ\text{C}$ ).

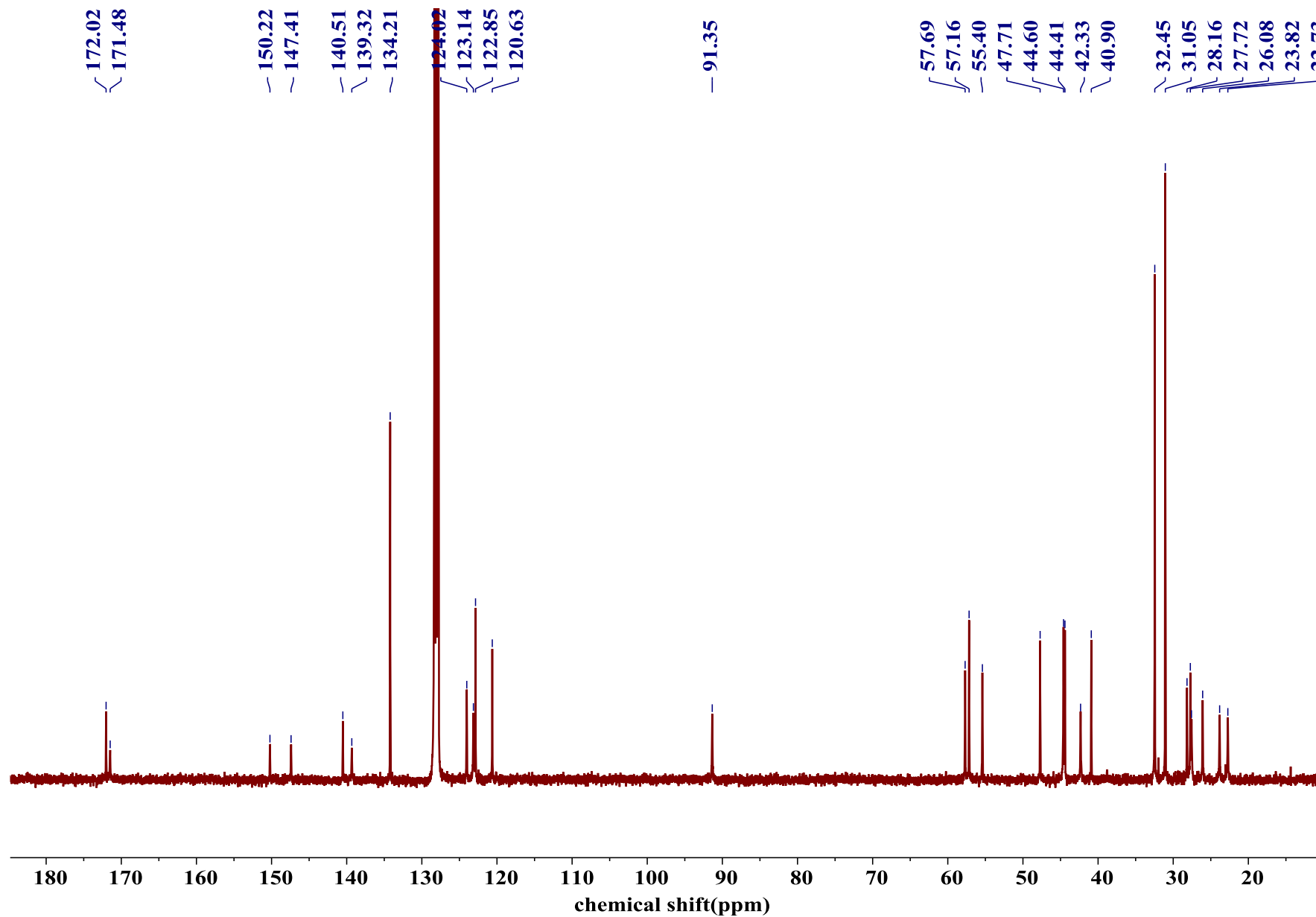
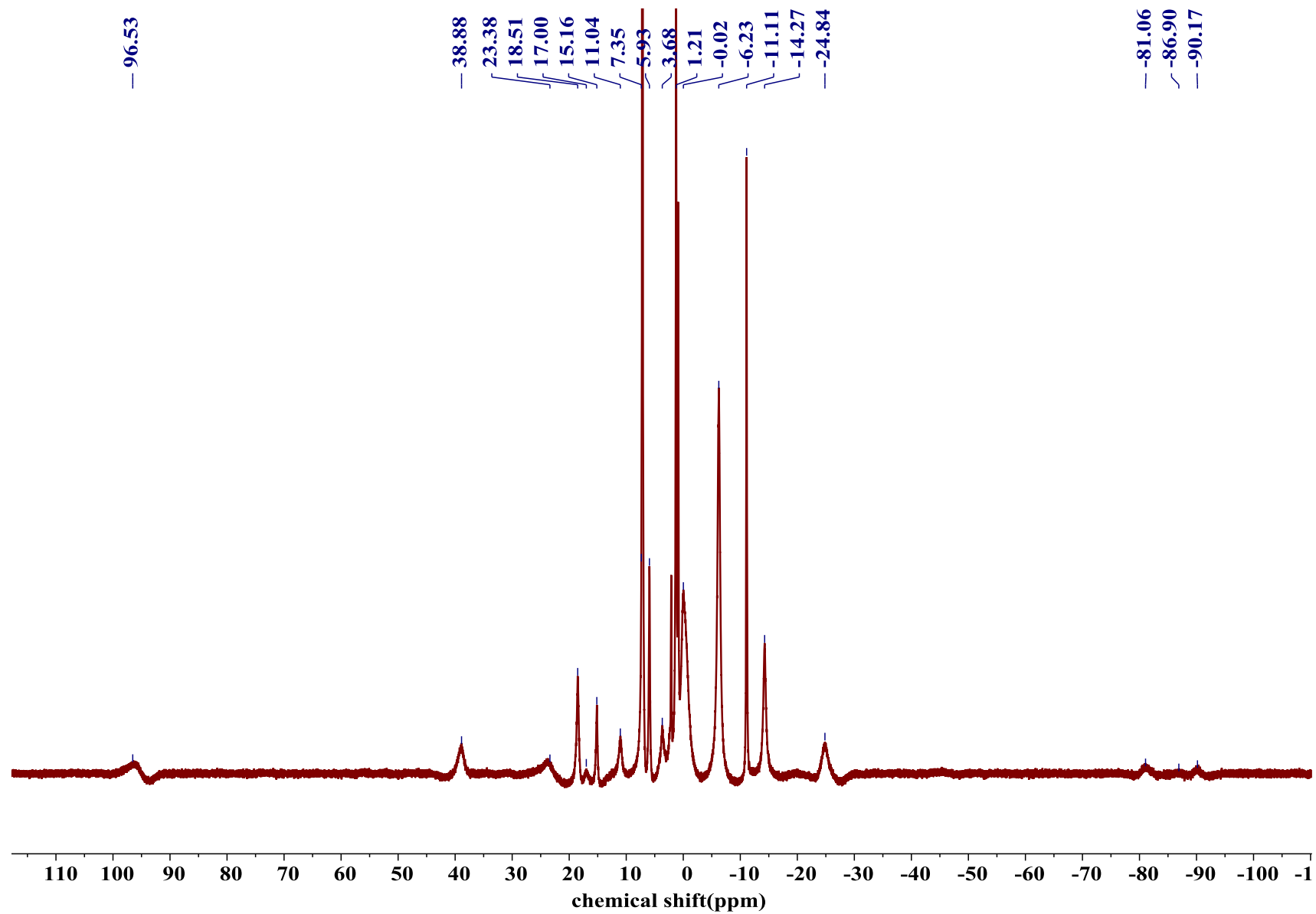
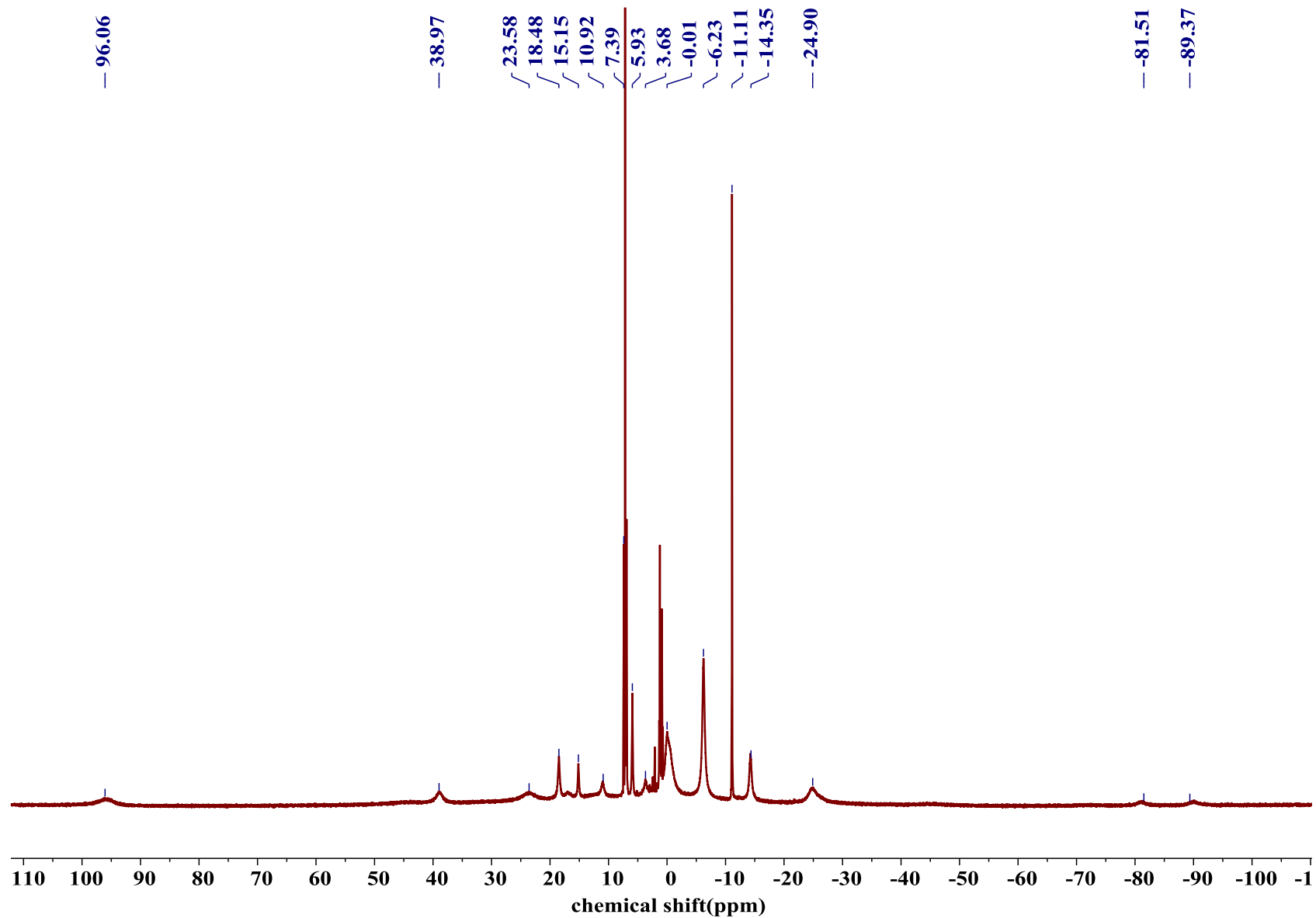


Figure S26.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of complex **9** (100 MHz,  $\text{C}_6\text{D}_6$ , 25  $^\circ\text{C}$ ).



**Figure S27.**  $^1\text{H}$  NMR spectrum of complex **10** (400 MHz,  $\text{C}_6\text{D}_6$ , 25  $^\circ\text{C}$ )



**Figure S28.**  $^1\text{H}$  NMR spectrum of the reaction of complex **9** with 1.0 equiv. PhSSPh in  $\text{C}_6\text{D}_6$  in 20 min (400 MHz, 25  $^\circ\text{C}$ ), showing the formation of complex **10**.



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