

# CHEMISTRY

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### Supporting Information

#### **Structural Mimics of Acetylene Hydratase: Tungsten Complexes Capable of Intramolecular Nucleophilic Attack on Acetylene**

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# Supporting Information

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## ***TABLE OF CONTENTS:***

Table of contents: .....	1
Experimental Section:.....	2
NMR spectra .....	9
Labelling Experiments: .....	27
X-ray Crystallography: .....	28

## **EXPERIMENTAL SECTION:**

**General Procedures:** All operations were carried out under N<sub>2</sub> atmosphere using standard Schlenk and glovebox techniques. Silica gel was washed with NEt<sub>3</sub> and dried *in vacuo* prior to use. Solvents were dried via a Pure Solv Solvent Purification System and stored over activated molecular sieve (3 Å). Acetylene 2.6 was purified by bubbling it through water and conc. H<sub>2</sub>SO<sub>4</sub> and then dried by passing it through KOH and CaCl<sub>2</sub>.<sup>[1]</sup> Pyridine-2-thione was recrystallized from toluene prior to use. 6-*Tert*-butylpyridazine-3-thione<sup>[2]</sup> was synthesized according to literature. All other chemicals were purchased from commercial sources and were used without further purification.

**NMR spectra** were measured on a Bruker Avance III 300 MHz spectrometer at 25 °C. Chemical shifts of <sup>1</sup>H and <sup>13</sup>C NMR spectra are given in ppm. <sup>1</sup>H NMR spectra are referenced to residual protons of the NMR solvent. <sup>13</sup>C NMR spectra are referenced to the deuterated solvent peak. Coupling constants *J* are given in Hertz. The prefix b is used to identify broad signals.

**Solid state IR spectra** were recorded on a Bruker ALPHA-P Diamant ATR-FTIR spectrometer at a resolution of 2 cm<sup>-1</sup>. Absorption bands were assigned to their relative intensities as strong (s) or medium (m). Most medium and weak (w) resonances were omitted.

**Mass spectra** were obtained on an Agilent Technologies 5975C inert XL MSD instrument using the direct insertion technique.

**Elemental analyses** were performed at the Graz University of Technology using a Heraeus Vario Elementar automatic analyzer.

### **Sodium pyridine-2-thionate (NaSPy)**

In a 150 mL Schlenk tube 3.280 g HSPy (29.5 mmol, 1.0 equiv.) were dissolved in 50 mL THF. NaH (707 mg (100%), 29.5 mmol, 1.0 equiv.) was added portionwise over 20 min and the suspension was stirred for another 2 h before its volume was reduced to 50 mL. The off-white precipitate was isolated by filtration, washed with diethyl ether (2 x 15 mL) and dried at 100 °C for approx. 45 min and subsequently in vacuo giving 3.115 g (23.4 mmol) of NaSPy as an off-white microcrystalline solid (79%). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN) δ = 7.82 (ddd, *J* = 5.1, 2.1, 1.0, 1H, CH), 7.14 (td, *J* = 8.1, 1.1, 1H, CH), 7.02 (ddd, *J* = 8.1, 7.0, 2.1, 1H, CH), 6.50 (ddd, *J* = 7.1, 5.0, 1.2, 1H, CH). <sup>13</sup>C NMR (75 MHz, CD<sub>3</sub>CN) δ = 180.41 (C-S), 148.32 (C=N), 134.68, 129.14, 114.04.

### **Sodium *tert*-butylpyridazine-3-thionate (NaSPn)**

In a 250 mL Schlenk flask 13.59 g HSPn (80.83 mmol, 1.0 equiv.) were dissolved in 150 mL diethyl ether. NaH (3.892 g (50% in oil), 80.83 mmol, 1.0 equiv.) was added portionwise and the suspension was stirred for 16 h, and subsequently allowing the solvent to evaporate. The residue was washed with pentane (3 x 50 mL) and dried in vacuo to give 13.07 g (68.70 mmol) of NaPn as an off-white powder (85%). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN) δ = 7.30 (d, *J* = 9.1, 1H, CH), 6.97 (d, *J* = 9.1, 1H, CH), 1.27 (s, 9H, *t*Bu). <sup>13</sup>C NMR (75 MHz, CD<sub>3</sub>CN) δ = 180.75 (C=S), 161.89 (C=N), 134.83, 122.87, 36.53 (CMe<sub>3</sub>), 30.05 (CMe<sub>3</sub>).

### **[W(CO)<sub>3</sub>(MeCN)<sub>2</sub>Br<sub>2</sub>]**

[W<sub>2</sub>(CO)<sub>7</sub>Br<sub>4</sub>] (20.791 g, 23.54 mmol) was cooled to 0 °C and 200 mL of MeCN were added. After stirring for 2 h, the suspension was filtered over a pad of Celite and the solvent was concentrated in vacuo to approx. 50 mL. The precipitated wine red crystals were isolated by filtration in 64 % yield (15.412 g, 30.23 mmol). Single crystals suitable for X-ray diffraction analysis were obtained by crystallization from acetonitrile at -35 °C. IR: 2319 (m, C≡N), 2291 (m, C≡N), 2024 (s, C≡O), 1910 (s, C≡O), 1897 (sh). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN) δ = 1.96 (s, 6H). Equals free, de-coordinated acetonitrile. EI-MS: No assignable signals. The compound was previously prepared by another synthetic procedure.<sup>[3]</sup>

### **[W(CO)<sub>3</sub>(SPy)<sub>2</sub>] (1)**

To a 100 mL Schlenk flask charged with [W(CO)<sub>3</sub>(MeCN)<sub>2</sub>Br<sub>2</sub>] (1.004 g, 1.97 mmol, 1.0 equiv.) and 40 mL CH<sub>2</sub>Cl<sub>2</sub>, NaSPy (527 mg, 3.96 mmol, 2.0 equiv.) was added in one portion. The reaction mixture was stirred for 1 h before the solution was filtered through a pad of Celite. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/heptane gave cherry-red crystals in 67% yield (623mg, 1.28 mmol). <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ = 8.43 (ddd, *J* = 5.6, 1.7, 0.9, 2H), 7.46 (ddd, *J* = 8.2, 7.5, 1.7, 2H), 6.90 (ddd, *J* = 7.4, 5.6, 1.2, 2H), 6.83 (td, *J* = 8.2, 1.0, 2H). <sup>13</sup>C NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ = 235.08 (*J*<sub>W-C</sub> = 118.8 Hz, CO), 177.22 (C-S), 145.81 (C=N), 138.30, 127.99, 119.18. IR (cm<sup>-1</sup>): 2013 (s, C≡O), 1933 (m, C≡O), 1899 (vs, C≡O). EI-MS: *m/z* 488.1 [M]<sup>+</sup>, 460.0 [M-C≡O]<sup>+</sup>, 404.0 [M-3 C≡O]<sup>+</sup>. This compound was previously prepared by different synthetic procedures leading to lower yield and different signals in the <sup>1</sup>H NMR spectrum.<sup>[4]</sup>

### **Spectroscopic data of [W(CO)<sub>3</sub>(SPn)<sub>2</sub>] (2) derived from single crystals from CH<sub>2</sub>Cl<sub>2</sub>/heptane**

<sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ = 7.27 (d, *J* = 9.1, 1H), 6.99 (d, *J* = 9.1, 1H), 1.19 (s, 9H, *t*Bu). <sup>13</sup>C NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ = 233,98 (CO), 179.37 (C=S), 166,60 (C=N), 133,09, 125,08, 37,08 (CMe<sub>3</sub>), 29,76 (CMe<sub>3</sub>). IR (cm<sup>-1</sup>): 2014 (s, C≡O), 1918 (vs, C≡O).

### **[W<sub>2</sub>(CO)<sub>4</sub>(SPn)<sub>4</sub>] (3)**

[W(CO)<sub>3</sub>(MeCN)<sub>2</sub>Br<sub>2</sub>] (404 mg, 0.79 mmol, 1.0 equiv.) was suspended in 5 mL of cold CH<sub>2</sub>Cl<sub>2</sub> (-35 °C) to which NaSPn (304mg, 1.60 mmol, 2.0 equiv), suspended in 7 mL CH<sub>2</sub>Cl<sub>2</sub>, was added in three portions. The reaction mixture was stirred for 20 min before the solvent was evaporated to dryness. The dark red residue was dissolved in 10 mL CH<sub>2</sub>Cl<sub>2</sub> and filtered over a pad of Celite. After washing with 10 mL CH<sub>2</sub>Cl<sub>2</sub> and the combined filtrate was cooled with liq. N<sub>2</sub> during filtration. The solution was evaporated to dryness and redissolved in approx. 15 mL MeCN. After crystallization overnight the mixture was stored at -25 °C for two days. The supernatant solution was filtered off and the dark red crystals were washed with MeCN (2x 2–3 mL). Drying in vacuo gave analytically pure [W<sub>2</sub>(CO)<sub>4</sub>SPn<sub>4</sub>] in 31% yield (143 mg, 0.12 mmol). Single crystals suitable for X-ray diffraction analysis were obtained from CH<sub>2</sub>Cl<sub>2</sub>/heptane. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ = 7.12 (bd, *J* = 9.1, 2H,CH), 6.92 (d, *J* = 2.7, 2H, CH), 6.89 (d, *J* = 2.6, 2H, CH), 6.63 (bd, *J* = 8.6, 2H, CH), 1.29 (bs, 18H, *t*Bu), 1.20 (bs, 18H, *t*Bu). <sup>13</sup>C NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ = 170.13 (b), 166.81 (b), 133.23 (b, CH), 132.13 (b, CH),

124.00 (b, 2CH), 122.59 (2 CH), 37.33 (CMe<sub>3</sub>), 37.13 (CMe<sub>3</sub>), 30.16 (CMe<sub>3</sub>), 29.92 (CMe<sub>3</sub>). IR (cm<sup>-1</sup>): 1944(s, C≡O), 1846 (s, C≡O). MS: m/z 1,036.3 [M-4 C≡O]<sup>+</sup>, 574.8 [M-2 C≡O-W(SP<sub>2</sub>)<sub>2</sub>]<sup>+</sup>, 518.1 [M-4 C≡O-W(SP<sub>2</sub>)<sub>2</sub>]<sup>+</sup>. elemental analysis calcd (%) for C<sub>36</sub>H<sub>44</sub>N<sub>8</sub>O<sub>4</sub>S<sub>4</sub>W: C 37.64, H 3.86, N 9.75, S 11.17; found: C 37.69, H 3.69, N 9.87, S 10.78.

#### **[W(CO)(C<sub>2</sub>H<sub>2</sub>)(CHCH-SPy)(SPy)] (4)**

[W(CO)<sub>3</sub>(SPy)<sub>2</sub>] (1) (595 mg, 1.22 mmol) was suspended in 50 mL toluene and acetylene was purged through the flask for 45 min while the mixture was heavily stirred. After stirring for another 12 h under acetylene atmosphere the reaction was evaporated to dryness. The residue was dissolved in 50 mL CH<sub>2</sub>Cl<sub>2</sub> and filtrated through a silica gel pad. Heptane (40 mL) was added to the magenta solution and the product was precipitated by subsequent removal of CH<sub>2</sub>Cl<sub>2</sub>. The dark purple solid was isolated by filtration and dried in vacuo to give 436 mg of **4** (0.90 mmol, 74%). Single crystals suitable for X-ray diffraction analysis were obtained from a saturated MeCN solution at -35 °C. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ = 12.94 (bs, 1H, η<sup>2</sup>-C<sub>2</sub>H<sub>2</sub>), 12.00 (bs, 1H, η<sup>2</sup>-C<sub>2</sub>H<sub>2</sub>), 8.20 (ddd, *J* = 5.4, 1.8, 1.0, 1H), 7.86 – 7.68 (m, 3H, η<sup>1</sup>-C<sub>2</sub>H<sub>2</sub>, SPy), 7.49 (ddd, *J* = 8.2, 7.5, 1.8, 1H), 7.16 (ddd, *J* = 8.5, 7.0, 1.5, 1H), 6.96 – 6.85 (m, 2H), 6.82 (td, *J* = 8.2, 1.1, 1H), 6.58 (d, *J*<sub>H-H</sub> = 11.0, *J*<sub>W-H</sub> = 11, 1, 1H, η<sup>1</sup> C<sub>2</sub>H<sub>2</sub>). <sup>13</sup>C NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ = 231.44, 197.53 (b, η<sup>2</sup>-C<sub>2</sub>H<sub>2</sub>), 192.55 (b, η<sup>2</sup>-C<sub>2</sub>H<sub>2</sub>), 179.58, 168.83 (*J*<sub>W-C</sub> = 102.5, η<sup>1</sup>-C<sub>2</sub>H<sub>2</sub>), 160.64, 148.33, 140.29, 136.65, 134.11, 132.62, 132.47, 127.57, 118.37, 117.32. IR (cm<sup>-1</sup>): 1899 (sh, C≡O), 1890 (s, C≡O), EI-MS: m/z 457.9 [M-C<sub>2</sub>H<sub>2</sub>]<sup>+</sup>, 430.9 [M-C<sub>2</sub>H<sub>2</sub>-C≡O]<sup>+</sup>, 404.9 [M-2 C<sub>2</sub>H<sub>2</sub>-C≡O]<sup>+</sup>. elemental analysis calcd (%) for C<sub>15</sub>H<sub>12</sub>N<sub>2</sub>OS<sub>2</sub>W · 0.45 CH<sub>2</sub>Cl<sub>2</sub>: C 35.52, H 2.49, N 5.36, S 12.27; found: C 35.37, H 2.69, N 5.21, S 12.10.

#### **[W(CO)(C<sub>2</sub>H<sub>2</sub>)(CHCH-SPn)(SPn)] (5)**

In a 50 mL Schlenk flask, equipped with a bubbler, 1.303 g [W(CO)<sub>3</sub>(MeCN)<sub>2</sub>Br<sub>2</sub>] (2.56 mmol, 1.0 equiv.) were dissolved in 25 mL MeCN. Upon the portionwise addition of NaSPn (981 mg, 5.17 mmol, 2.0 equiv.) the solution turned cherry red. While the mixture was heavily stirred acetylene was purged through the flask for 20 min. The deep purple suspension was stirred for another 10 min during which the acetylene atmosphere was refreshed three times. The mixture was dried in vacuo after CO evolution had ceased. The residue was dissolved in 80 mL toluene and filtrated over a pad of silica gel. The flask was washed with 5 mL toluene.

Removal of the solvent in vacuo gave 846 mg (1.41 mmol, 55%) of analytically pure bright purple microcrystalline solid. Single crystals suitable for X-ray diffraction analysis were obtained from MeCN/diethyl ether.  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  = 12.99 (bs, 1H,  $\eta^2\text{-C}_2\text{H}_2$ ), 12.02 (bs, 1H,  $\eta^2\text{-C}_2\text{H}_2$ ), 8.07 (dd,  $J_{\text{H-H}} = 11.3, 0.7$ ,  $J_{\text{W-H}} = 9.1$ , 1H,  $\eta^1\text{-C}_2\text{H}_2$ ), 7.90 (dd,  $J = 9.1, 0.7$ , 1H), 7.35 (d,  $J = 9.1$ , 1H), 7.01 (d,  $J = 9.0$ , 1H), 6.98 (d,  $J = 9.0$ , 1H), 6.73 (d,  $J_{\text{H-H}} = 11.3$ ,  $J_{\text{W-H}} = 14.5$ , 1H,  $\eta^1\text{-C}_2\text{H}_2$ ), 1.31 (s, tBu, 9H), 1.30 (s, tBu, 9H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  = 230.05 (CO), 196.24 ( $\eta^2\text{-C}_2\text{H}_2$ ), 191.60 ( $\eta^2\text{-C}_2\text{H}_2$ ), 179.05 (C=S), 173.94 ( $J_{\text{W-C}} = 105.6$ ,  $\eta^1\text{-C}_2\text{H}_2$ ), 166.07, 163.98, 155.85, 136.00, 132.01, 124.73, 120.56, 37.25 (CMe<sub>3</sub>), 37.11 (CMe<sub>3</sub>), 30.07 (CMe<sub>3</sub>), 29.16 (CMe<sub>3</sub>). IR ( $\text{cm}^{-1}$ ): 1918 (s, C $\equiv$ O). MS:  $m/z$  598.2 [M]<sup>+</sup>, 572.2 [M-C<sub>2</sub>H<sub>2</sub>]<sup>+</sup>, 544.1 [M-C<sub>2</sub>H<sub>2</sub>-C $\equiv$ O]<sup>+</sup>, 518.1 [M-2 C<sub>2</sub>H<sub>2</sub>-C $\equiv$ O]<sup>+</sup>. elemental analysis calcd (%) for C<sub>21</sub>H<sub>26</sub>N<sub>4</sub>OS<sub>2</sub>W: C 42.15, H 4.38, N 9.36, S 10.72; found: C 42.44, H 4.34, N 9.44, S 10.59.

### **[W(CO)(C<sub>2</sub>H<sub>2</sub>)(SPy)<sub>2</sub>] (6)**

In a 150 mL Schlenk tube equipped with a bubbler, [W(CO)<sub>3</sub>(MeCN)<sub>2</sub>Br<sub>2</sub>] (3.132 g, 6.14 mmol, 1.0 equiv.) were dissolved in 40 mL MeCN. While the solution was heavily stirred acetylene-gas was purged through the tube for 10 min. The reaction mixture was stirred under acetylene atmosphere for another 55 min until CO evolution had ceased. The volume of the solvent was reduced to ½ and the solid was isolated by filtration. Washing with CH<sub>2</sub>Cl<sub>2</sub> (2 x 5 mL) and drying in vacuo gave 2.323 g of an olive-green powder consisting of a mixture of [W(CO)(C<sub>2</sub>H<sub>2</sub>)(MeCN)<sub>2</sub>Br<sub>2</sub>] (**7a**) and [W(CO)(C<sub>2</sub>H<sub>2</sub>)<sub>2</sub>(MeCN)Br<sub>2</sub>] (**7b**). Crystallization from CH<sub>2</sub>Cl<sub>2</sub> at -35 °C gave single crystals suitable for X-ray diffraction analysis of [W(CO)(C<sub>2</sub>H<sub>2</sub>)(MeCN)<sub>2</sub>Br<sub>2</sub>] (**7a**) and from MeCN at -35 °C [W(CO)(C<sub>2</sub>H<sub>2</sub>)<sub>2</sub>(MeCN)Br<sub>2</sub>] (**7b**).  $^1\text{H}$  NMR (300 MHz, CD<sub>3</sub>CN)  $\delta$  = 11.50 (t,  $J_{\text{W-H}} = 9.3$ , 2H,  $\equiv\text{-H}$ ), 11.00 (t,  $J_{\text{W-H}} = 8.2$ , 2H,  $\equiv\text{-H}$ ). IR ( $\text{cm}^{-1}$ ): 2324 (w, C $\equiv$ N), 2296 (w, C $\equiv$ N); 2069 (s, C $\equiv$ O), 2006 (m, C $\equiv$ O). Signals of **7a** in the  $^1\text{H}$  NMR spectrum and  $^{13}\text{C}$  NMR spectra were not accessible due to extremely low solubility.

The obtained olive-green powder (489 mg) was suspended in 15 mL CH<sub>2</sub>Cl<sub>2</sub> in a 100 mL Schlenk flask and cooled to -70 °C (EtOH/liq. N<sub>2</sub>). NaSPy (303 mg, 2.28 mmol) was dissolved in 15 mL MeCN, cooled to -45 °C and added to the stirring suspension with the help of a cannula. After addition of 5 mL CH<sub>2</sub>Cl<sub>2</sub>, the mixture was cooled to -60 °C and stirred for 25 min under a gentle N<sub>2</sub> stream. The dark green suspension was filtrated at approx. -40 °C over a pad of silica gel which was subsequently eluted with 40 mL CH<sub>2</sub>Cl<sub>2</sub>. The solvent was removed in vacuo and the residue was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/heptane. The grey powder

was washed with MeCN (2 x 2 mL) and recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/heptane to give 111 mg (0.24 mmol, 23%) of a dark grey microcrystalline solid of [W(CO)(C<sub>2</sub>H<sub>2</sub>)(SPy)<sub>2</sub>]. Single crystals suitable for X-ray diffraction analysis were obtained from a saturated MeCN solution. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>) two isomers (61:39): δ = 13.77 (bs, 1H, C<sub>2</sub>H<sub>2</sub>), 13.66 (bs, 1H, C<sub>2</sub>H<sub>2</sub>), 12.36 (bs, 1H, C<sub>2</sub>H<sub>2</sub>), 12.24 (bs, 1H, C<sub>2</sub>H<sub>2</sub>), 8.89 (ddd, *J* = 5.3, 1.8, 0.9, 1H, SPy), 8.61 (ddd, *J* = 5.6, 1.8, 1.0, 1H, SPy), 7.95 (ddd, *J* = 5.3, 1.7, 1.0, 1H, SPy), 7.69 (m, 2H, SPy), 7.33 (ddd, *J* = 8.2, 7.4, 1.8, 1H, SPy), 7.10 (m, 3H, SPy), 6.95 (m, 2H, SPy), 6.89 (dt, *J* = 8.1, 1.1, 1H, SPy), 6.82 (ddd, *J* = 7.4, 5.6, 1.2, 1H, SPy), 6.71 (m, 2H, SPy), 6.58 (ddd, *J* = 7.2, 5.7, 1.2, 1H, SPy). <sup>13</sup>C NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ = 240.73 (CO), 238.81 (CO), 207.58 (b, C<sub>2</sub>H<sub>2</sub>, 2C) 206.41 (b, C<sub>2</sub>H<sub>2</sub>, 2C), 178.63 (CS), 178.50 (CS), 171.74 (C=N), 170.75 (C=N), 147.05, 146.28, 146.03, 145.82, 139.49, 138.92, 137.32, 135.92, 127.59, 127.33, 126.83, 126.64, 120.48, 117.64. Isomeric ratio in: CDCl<sub>3</sub> (71:29) and CD<sub>3</sub>CN (45:55). IR (cm<sup>-1</sup>): 1911 (s, C≡O), 1901 (s, C≡O), EI-MS: *m/z* 458.0 [M<sup>+</sup>]. elemental analysis calcd (%) for C<sub>13</sub>H<sub>10</sub>N<sub>2</sub>OS<sub>2</sub>W: C 34.08, H 2.20, N 6.11, S 14.00; found: C 34.25, H 2.36, N 6.02, S 13.66. MS: *m/z* 458.1 [M]<sup>+</sup>, 430.1 [M-C≡O]<sup>+</sup>, 404.1 [M-C<sub>2</sub>D<sub>2</sub>-C≡O]<sup>+</sup>.

### [W(CO)(C<sub>2</sub>D<sub>2</sub>)(SPy)<sub>2</sub>] (9)

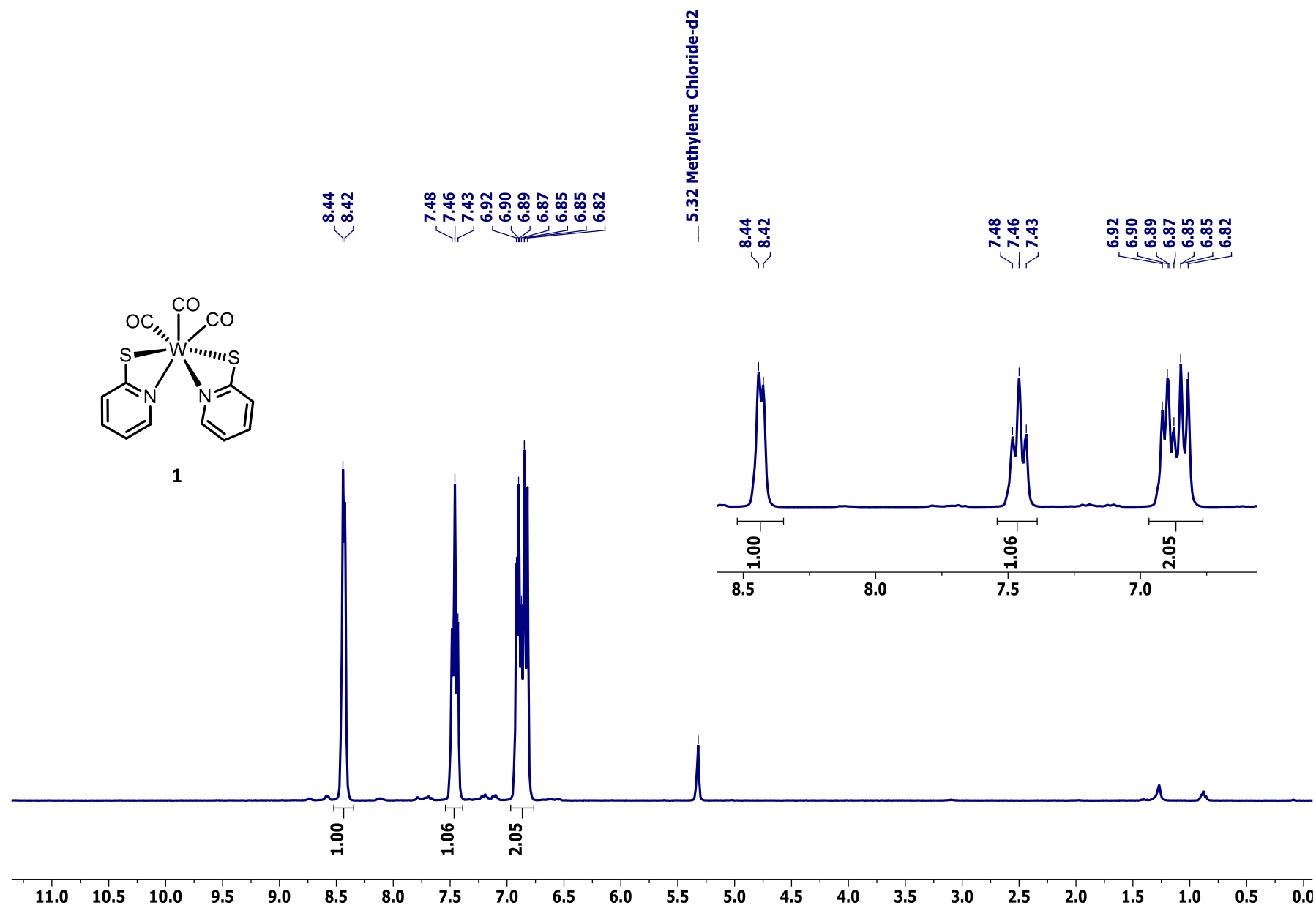
In a 150 mL Schlenk tube equipped with a bubbler, [W(CO)<sub>3</sub>(MeCN)<sub>2</sub>Br<sub>2</sub>] (3.035 g, 5.95mmol, 1.0 equiv.) were dissolved in 50 mL MeCN. While the solution was heavily stirred deuterated acetylene was portionwise purged through the tube for 1.5 h (C<sub>2</sub>D<sub>2</sub> was generated from 3.203 g CaC<sub>2</sub> (80%) and 2.5 mL D<sub>2</sub>O and was passed through CaCl<sub>2</sub> prior to use). The precipitated pale olive green solid was isolated by filtration and washed with CH<sub>2</sub>Cl<sub>2</sub> (2 x 6 mL). Drying in vacuo gave 2.285 g of [W(CO)(C<sub>2</sub>D<sub>2</sub>)(MeCN)<sub>2</sub>Br<sub>2</sub>] and [W(CO)(C<sub>2</sub>D<sub>2</sub>)<sub>2</sub>(MeCN)Br<sub>2</sub>] (**8a** and **8b**) as pale olive green powder.

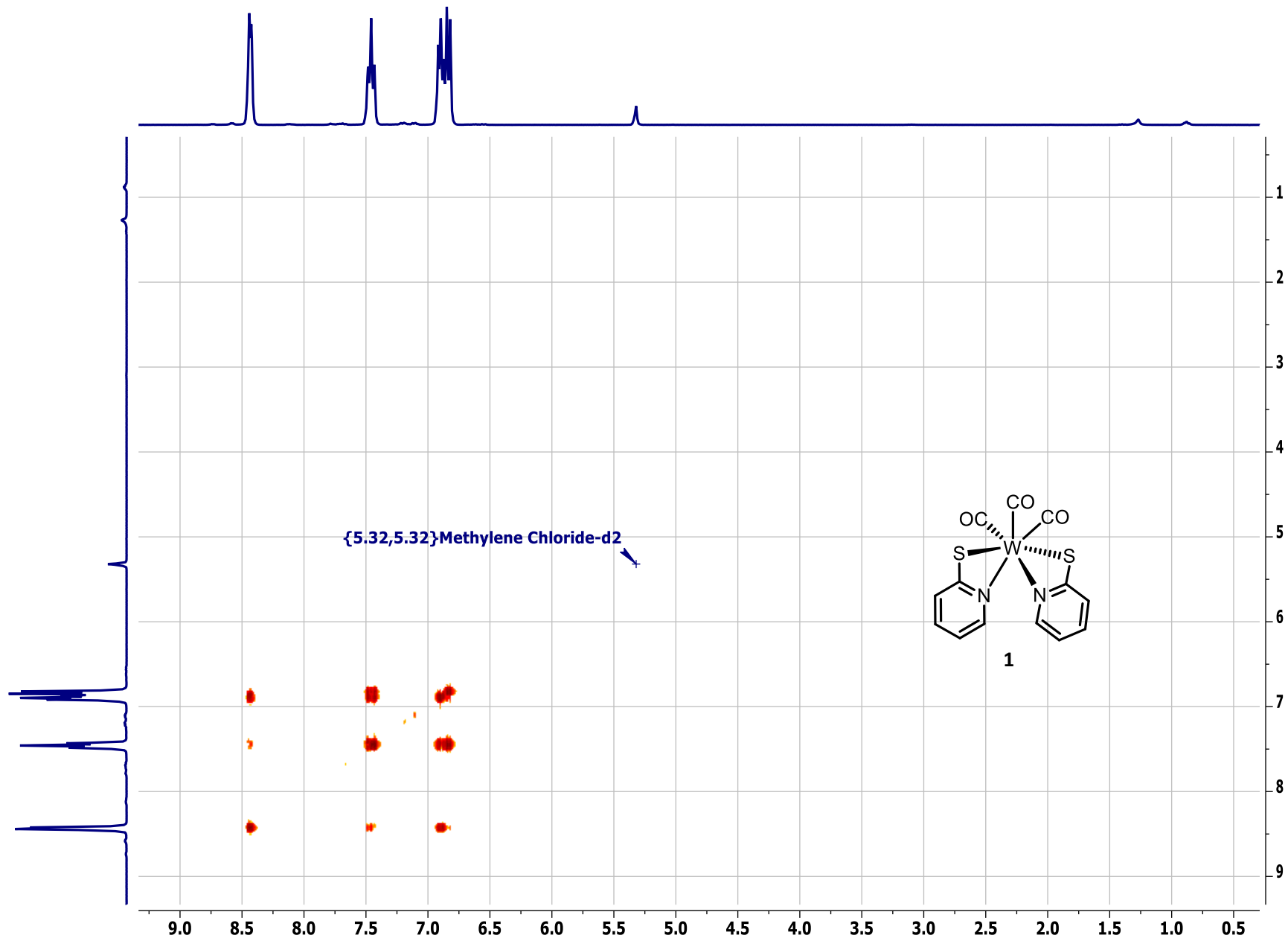
In a 150 mL Schlenk tube 995 mg of the olive green mixture were suspended in 35 mL CH<sub>2</sub>Cl<sub>2</sub> and cooled to -80 °C (EtOH/liq. N<sub>2</sub>). NaSPy (595 mg, 4.47 mmol) was dissolved in 30 mL MeCN, cooled to -45 °C and added to the stirring suspension with the help of a cannula. The mixture was stirred at -70 °C for 35 min under a gentle N<sub>2</sub> stream before it was filtered at approx. -40 °C over a pad of silica gel. After addition of 5 mL CH<sub>2</sub>Cl<sub>2</sub>, the product was eluted from the silica gel with 50 mL CH<sub>2</sub>Cl<sub>2</sub>. The solvent was removed in vacuo and the residue was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/heptane. The grey powder was isolated by filtration and drying in vacuo gave 351 mg (0.76 mmol, 36%) of [W(CO)(C<sub>2</sub>D<sub>2</sub>)(SPy)<sub>2</sub>]. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ =

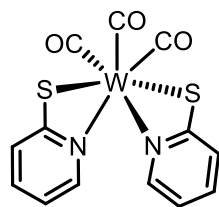


8.89 (ddd,  $J = 5.3, 1.8, 1.0$ , 1H, SPy), 8.61 (ddd,  $J = 5.6, 1.8, 1.0$ , 1H, SPy), 7.95 (ddd,  $J = 5.3, 1.8, 1.0$ , 1H, SPy), 7.69 (m, 2H, SPy), 7.33 (ddd,  $J = 8.2, 7.4, 1.8$ , 1H, SPy), 7.10 (m, 3H, SPy), 6.95 (m, 2H, SPy), 6.89 (dt,  $J = 8.1, 1.1$ , 1H, SPy), 6.82 (ddd,  $J = 7.4, 5.6, 1.2$ , 1H, SPy), 6.71 (m, 2H, SPy), 6.58 (ddd,  $J = 7.1, 5.7, 1.2$ , 1H, SPy). IR ( $\text{cm}^{-1}$ ): 1911 (s,  $\text{C}\equiv\text{O}$ ), 1901 (s,  $\text{C}\equiv\text{O}$ ). MS:  $m/z$  460.1  $[\text{M}]^+$ , 432.1  $[\text{M}-\text{C}\equiv\text{O}]^+$ , 404.1  $[\text{M}-\text{C}_2\text{H}_2-\text{C}\equiv\text{O}]^+$ .

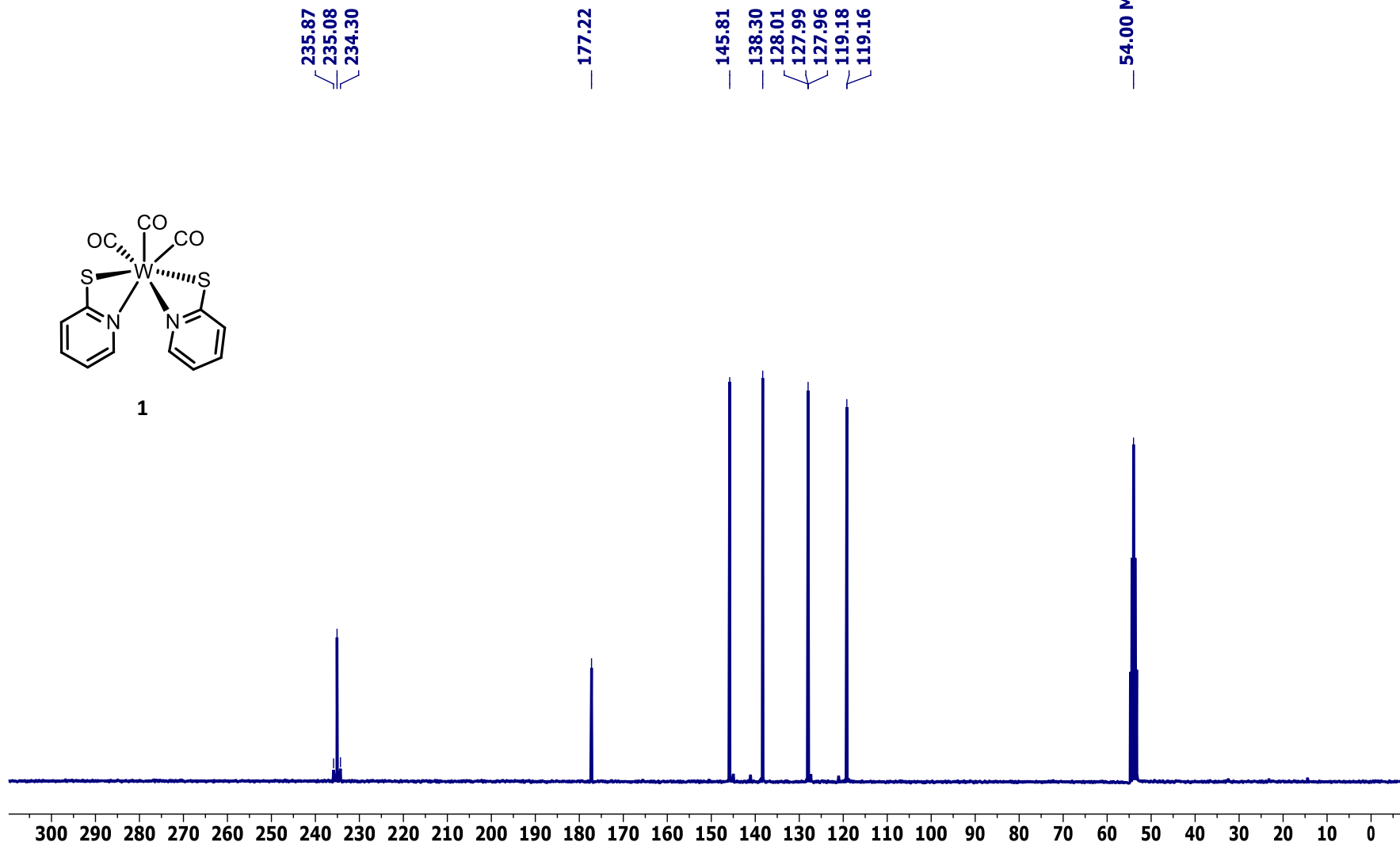
# NMR SPECTRA

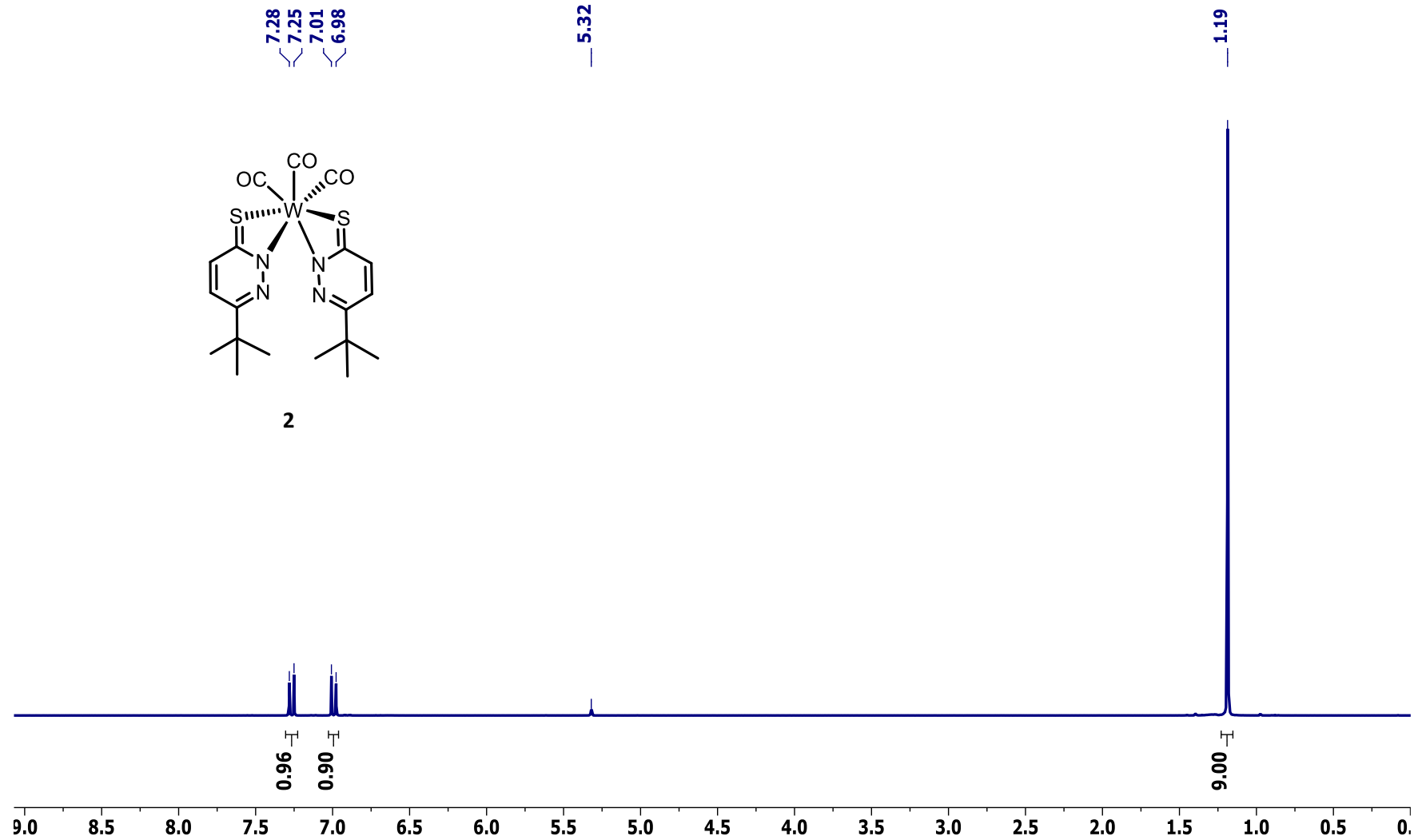




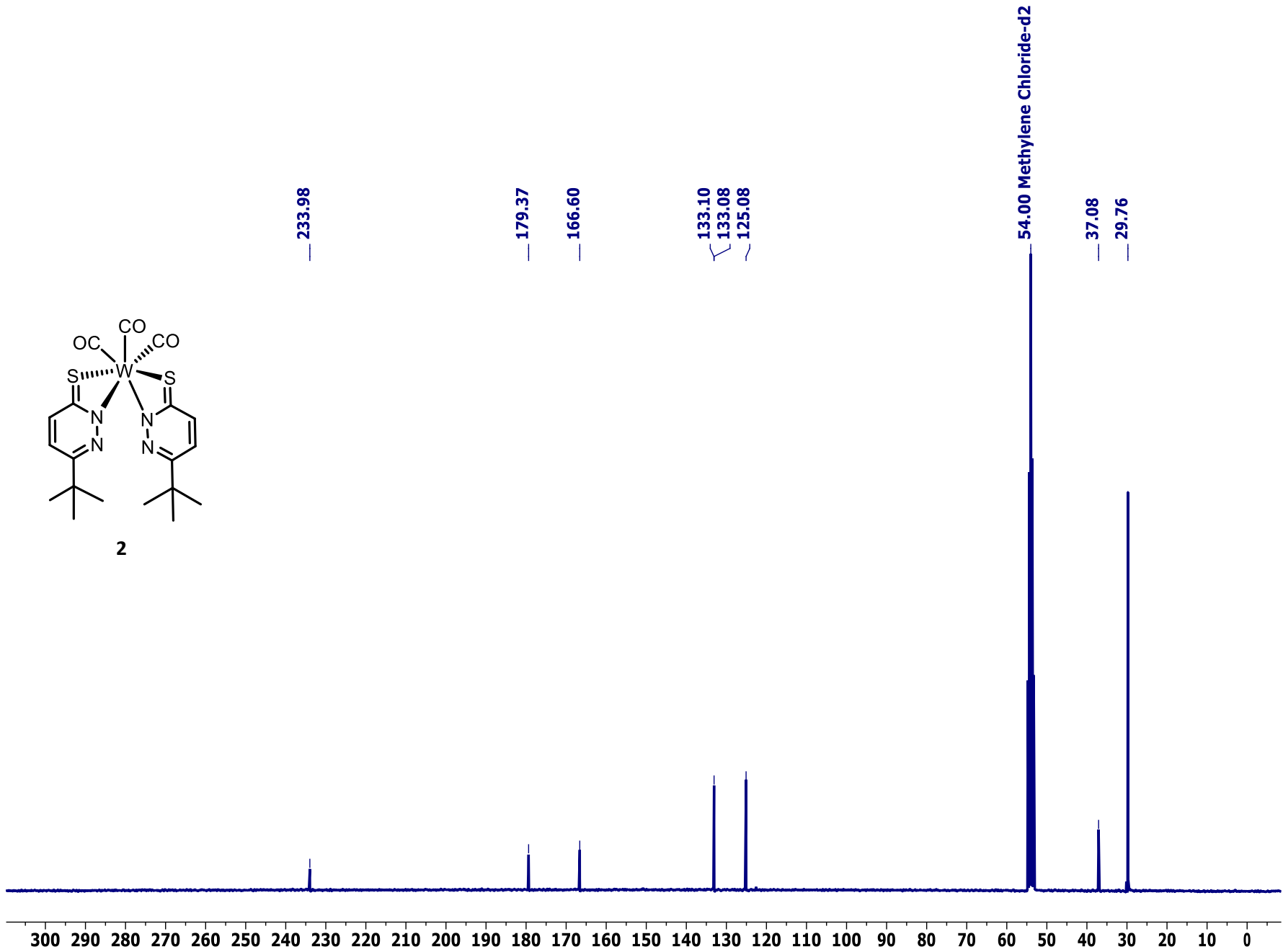


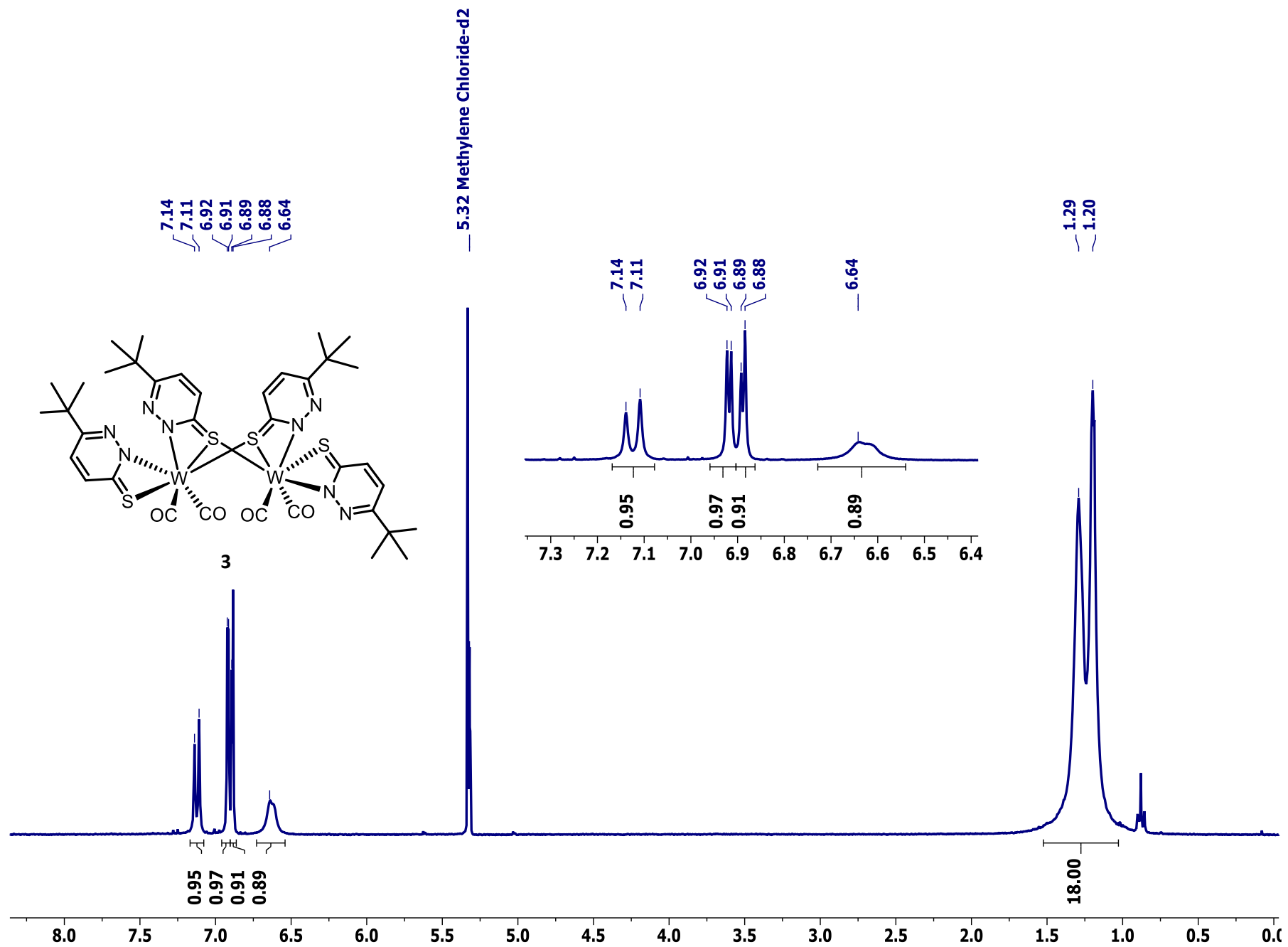
1

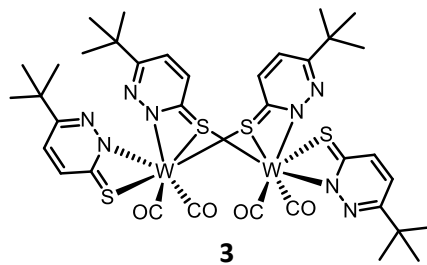




— 5.32 Methylene Chloride-d2







-54°C



-40°C



-30°C



-20°C



-10°C



0°C



10°C

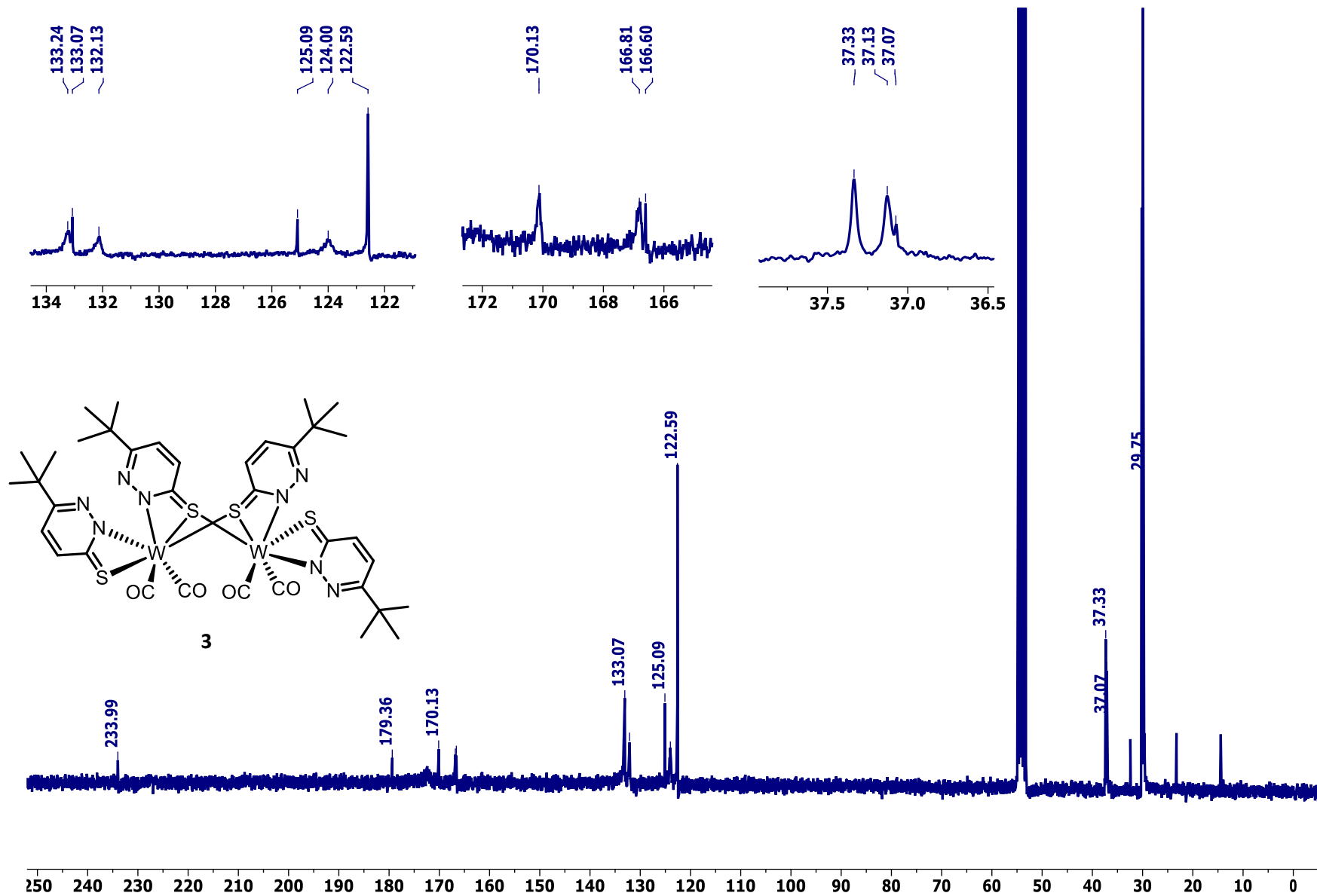


23°C

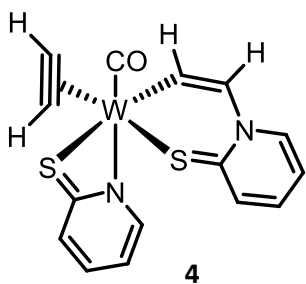
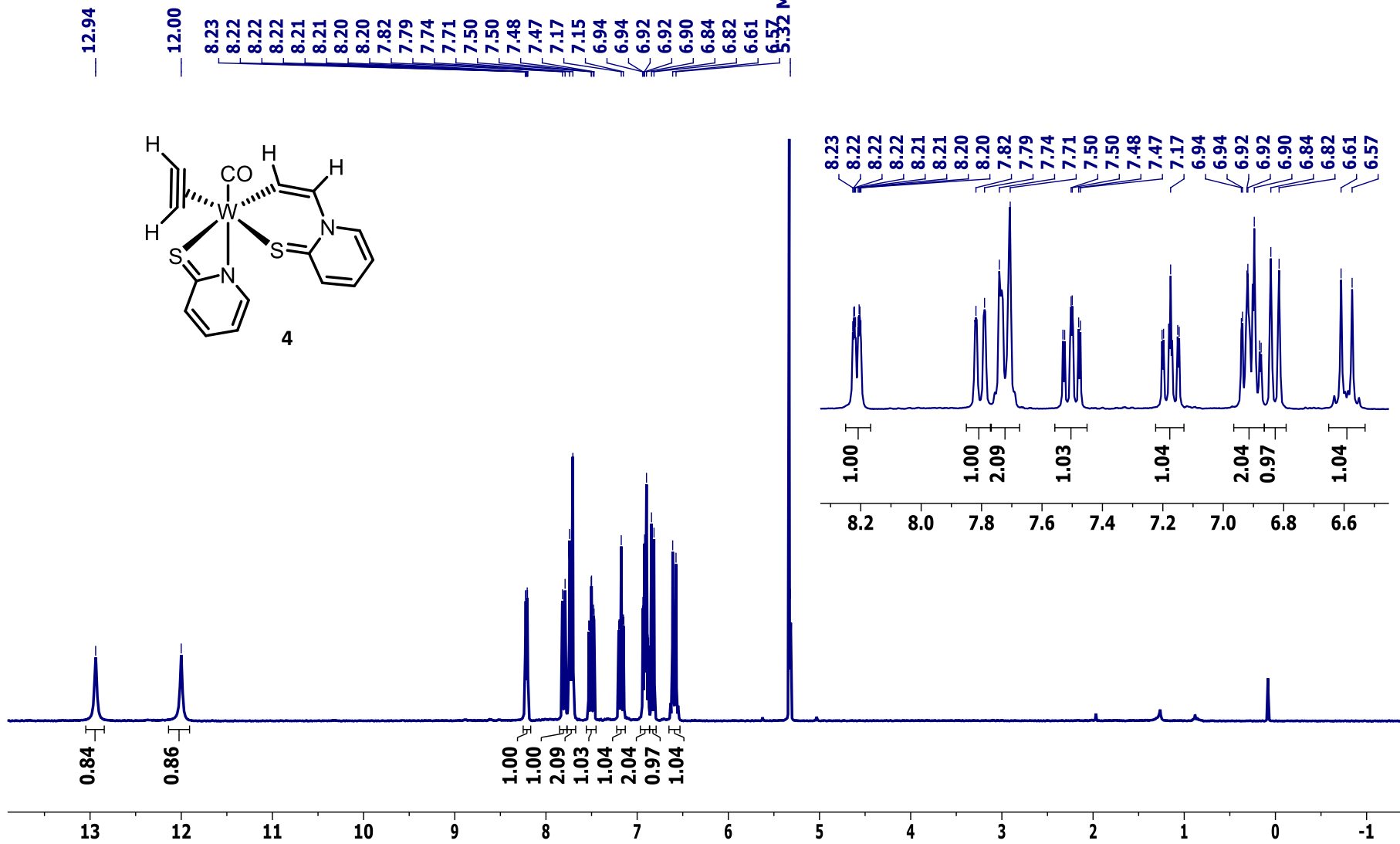


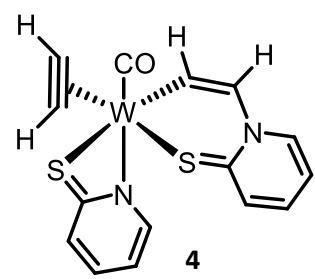
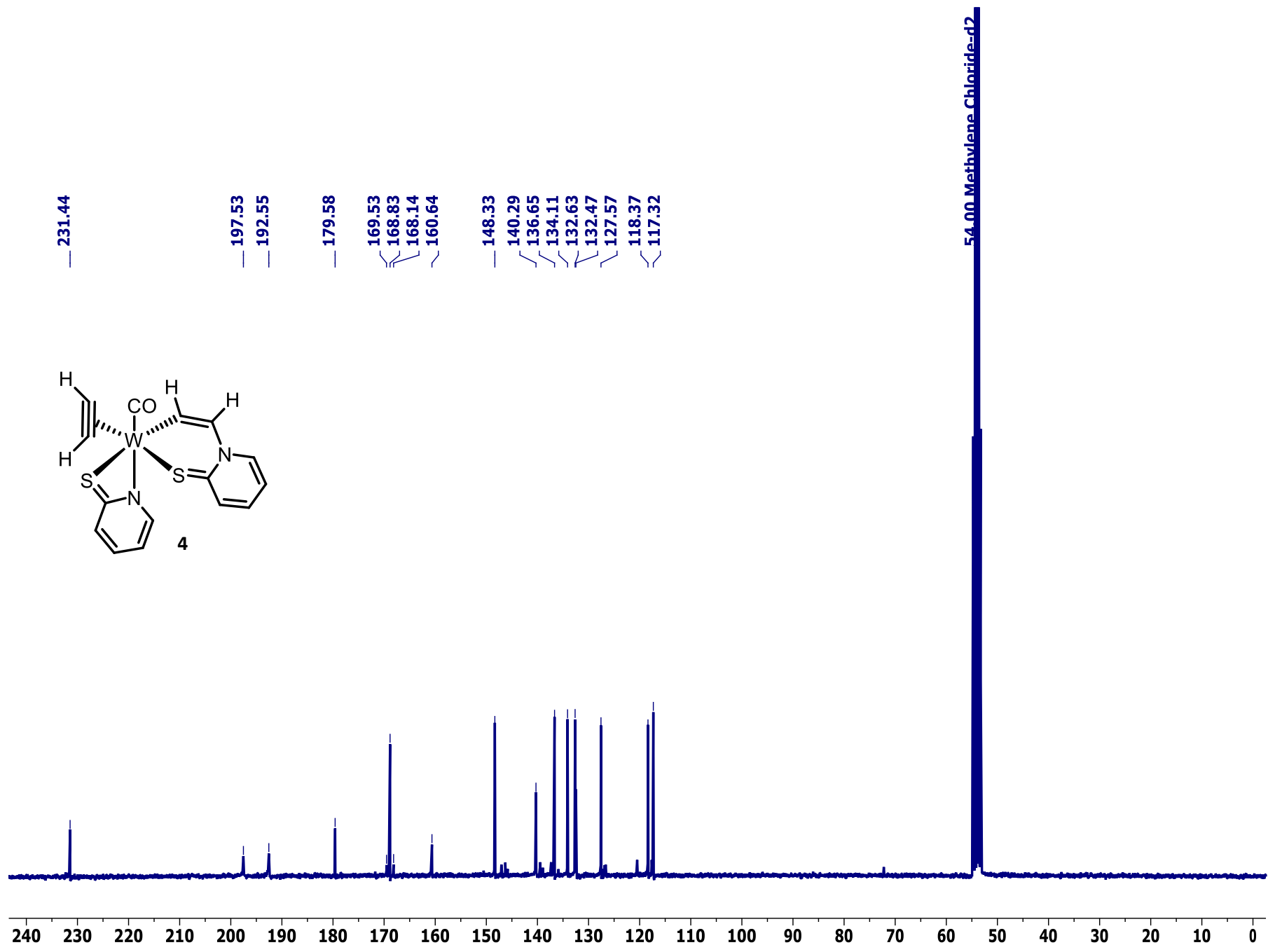
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9 0.8 0.7 0.6 0.5

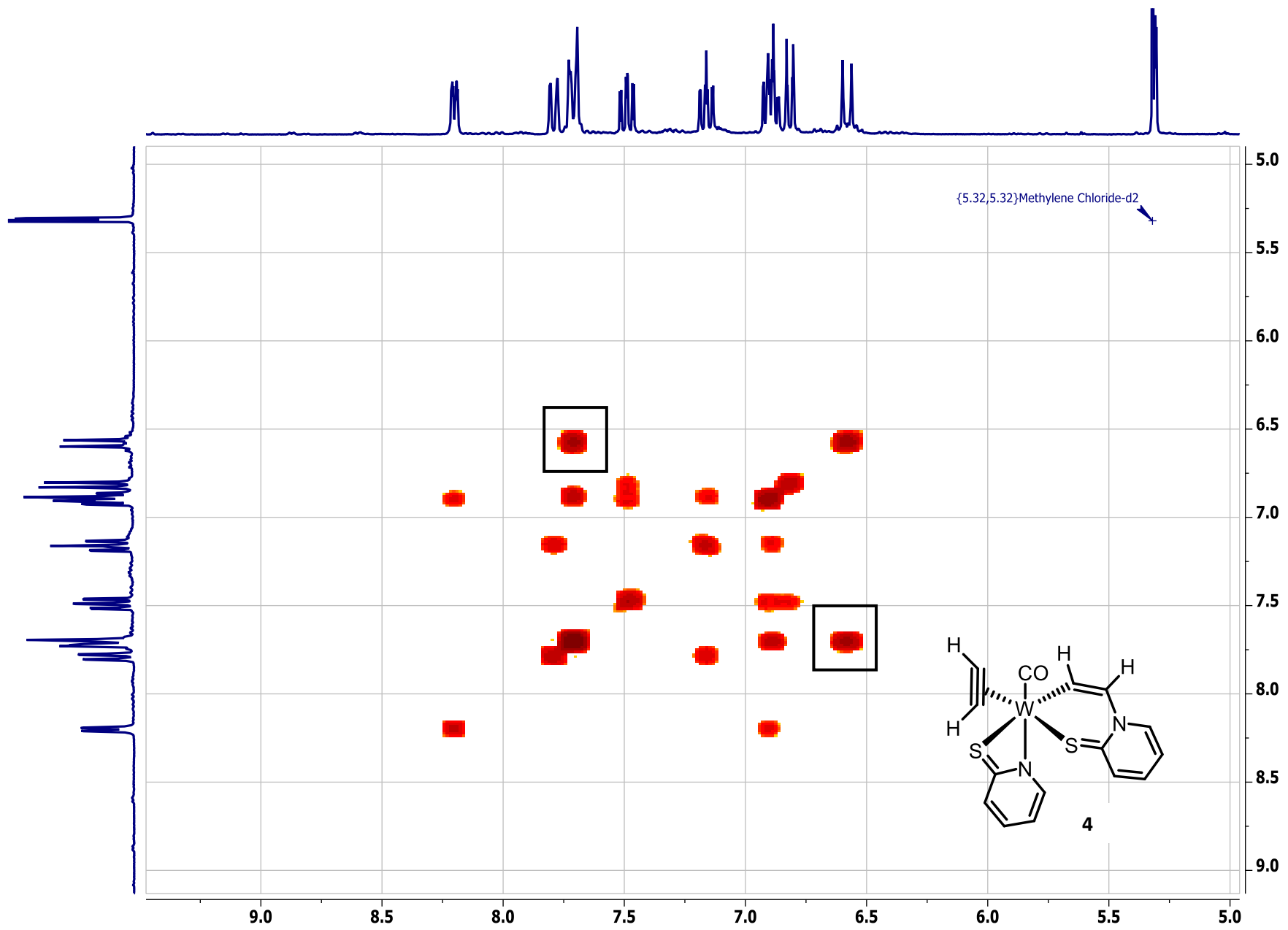


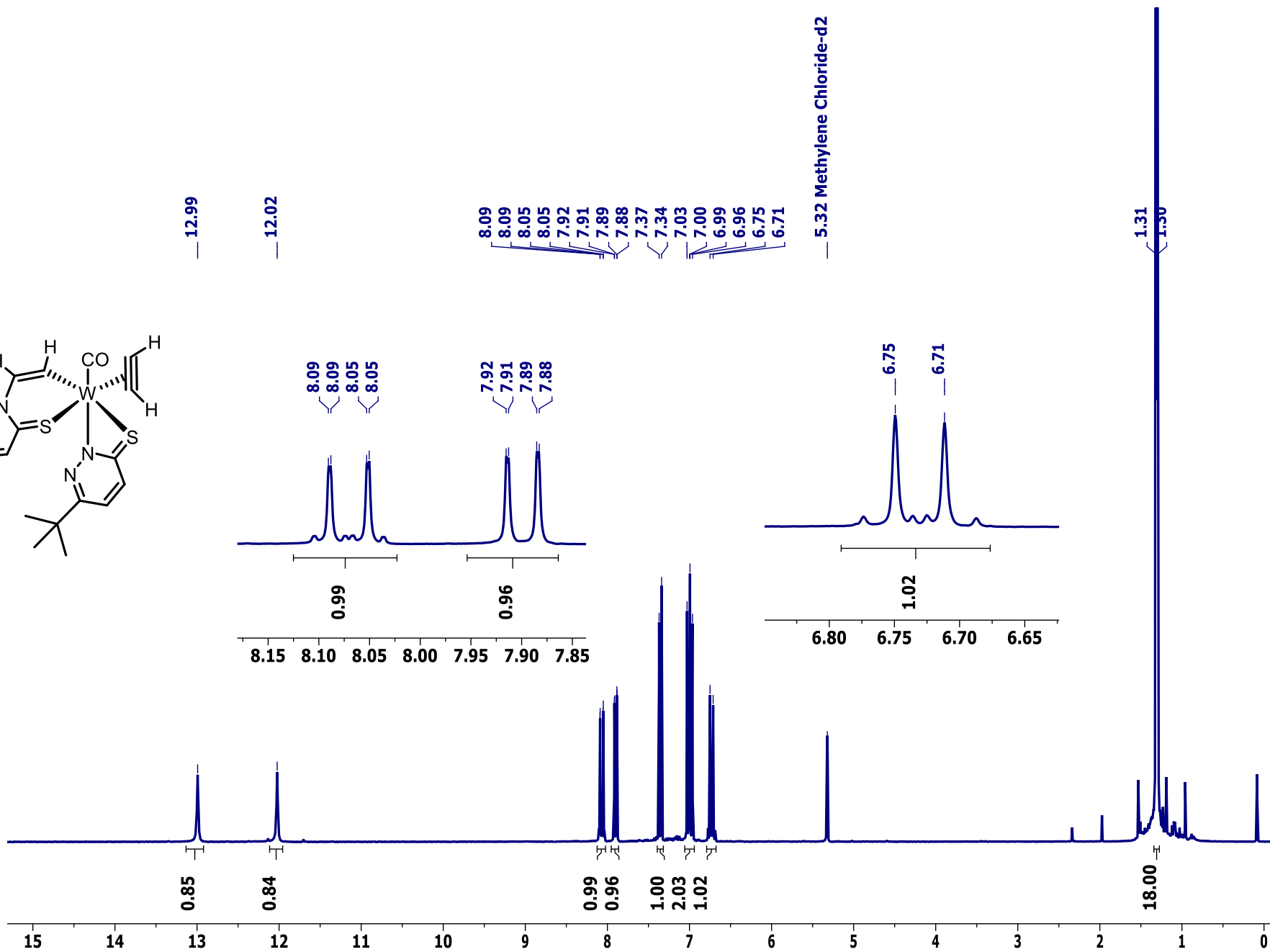
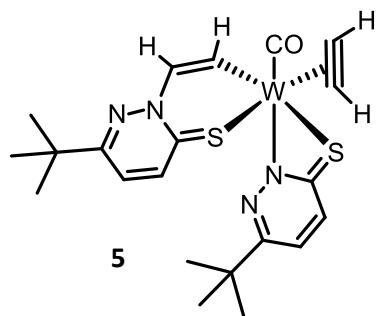


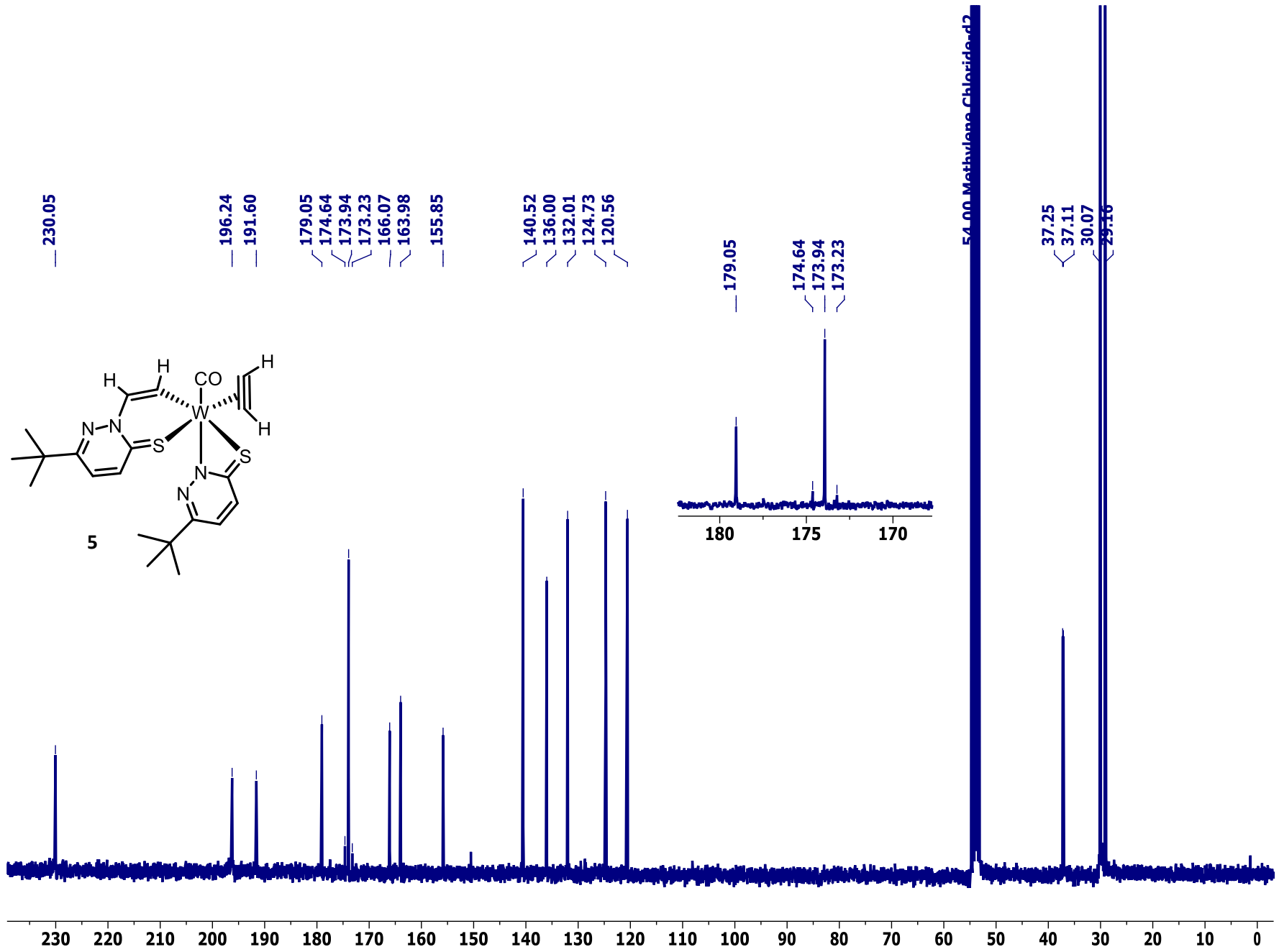
Dynamic complex  $[W_2(CO)_4(Pn)_4]$  (**3**) measured with 12,750 scans, due to its fluxional behavior the CO-signal was not detected. The complex also decomposes to complex  $[W(CO)_3(Pn)_2]$  (**2**) in solution over time.

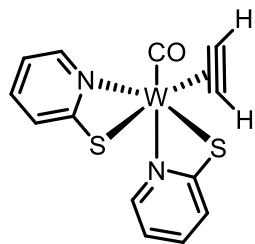






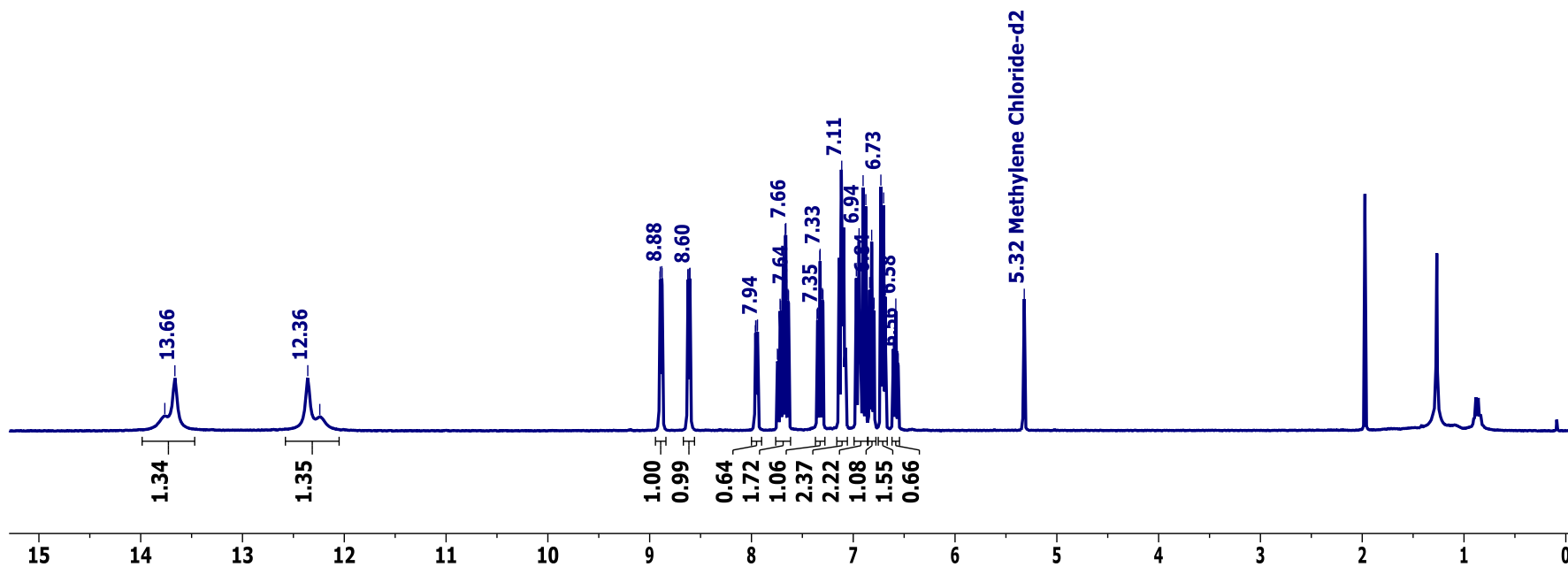
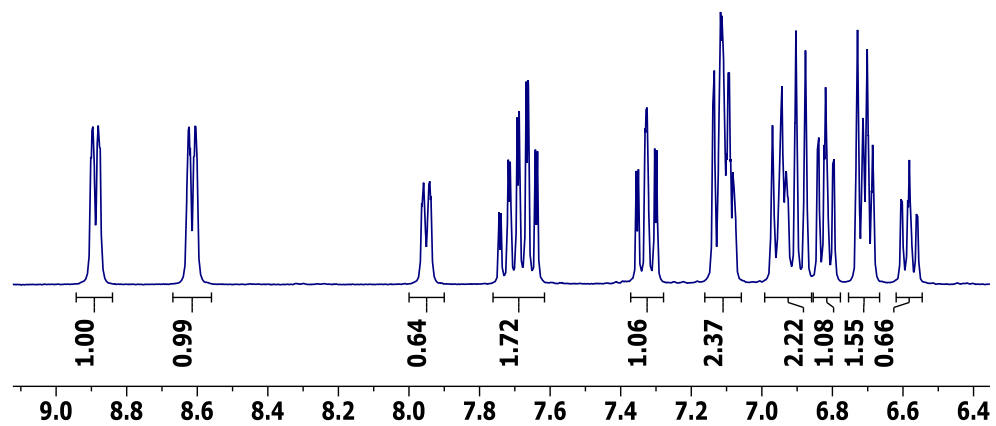


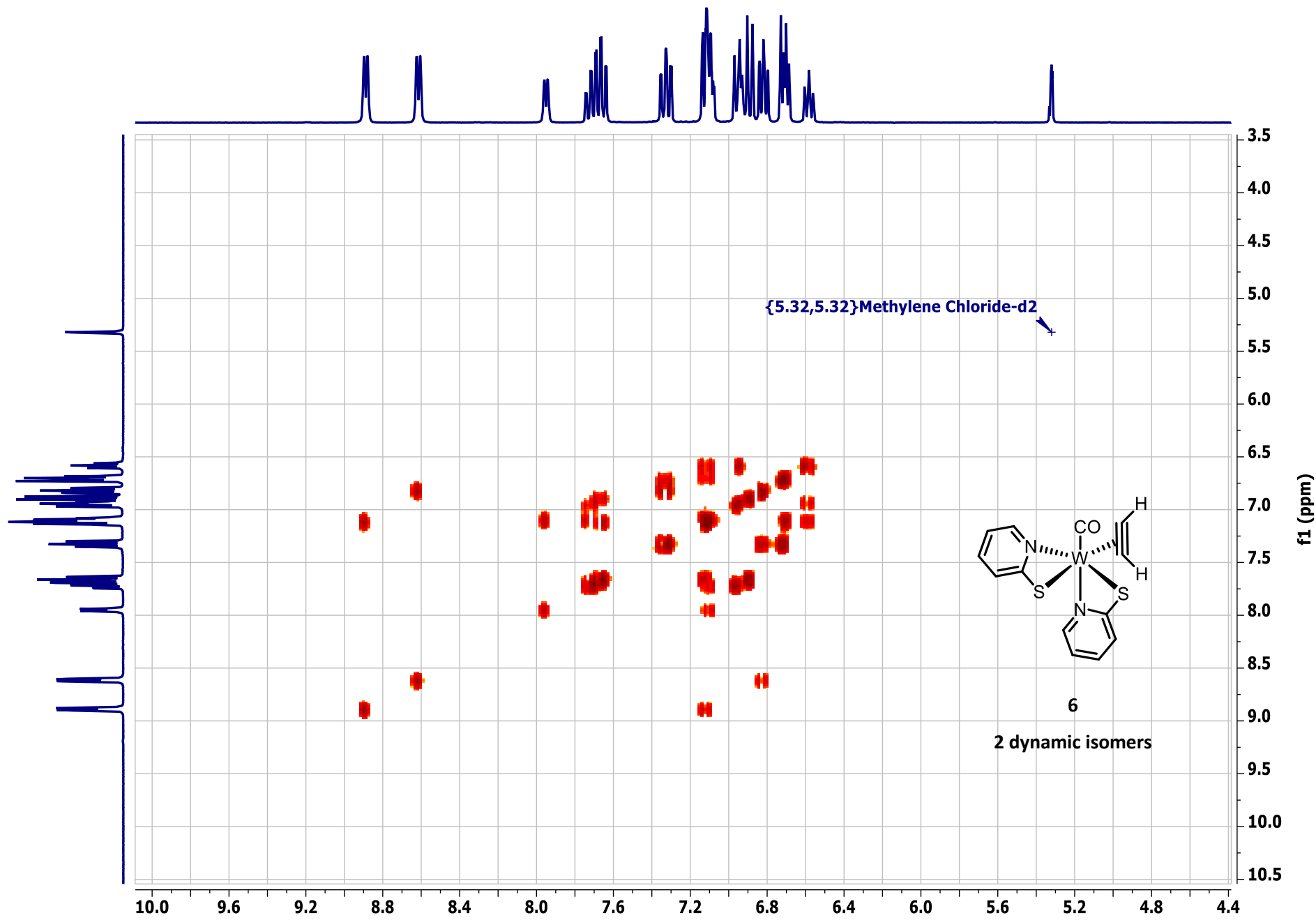




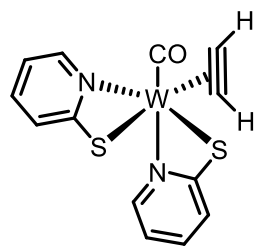
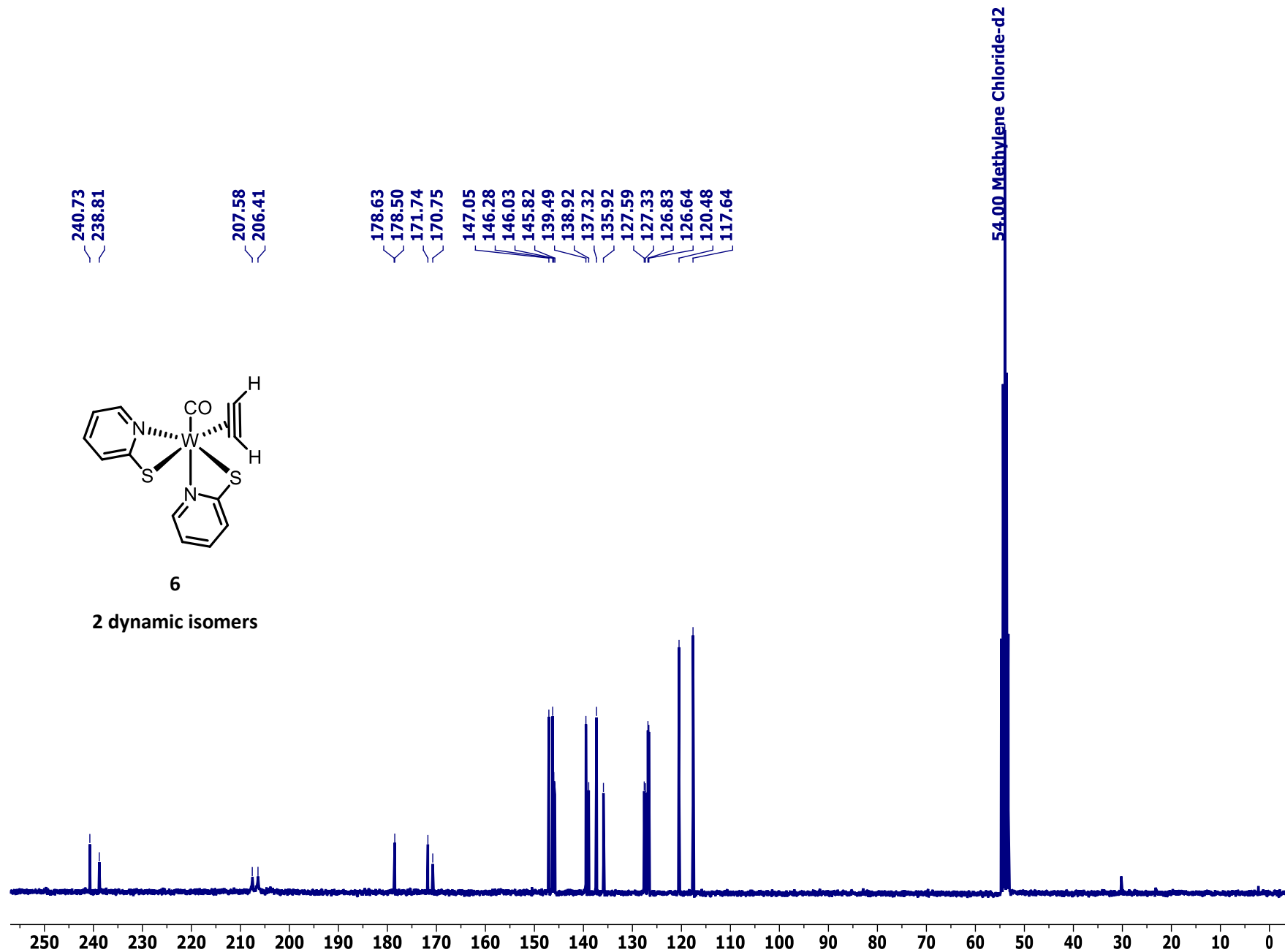
6

2 dynamic isomers



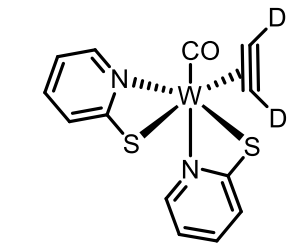






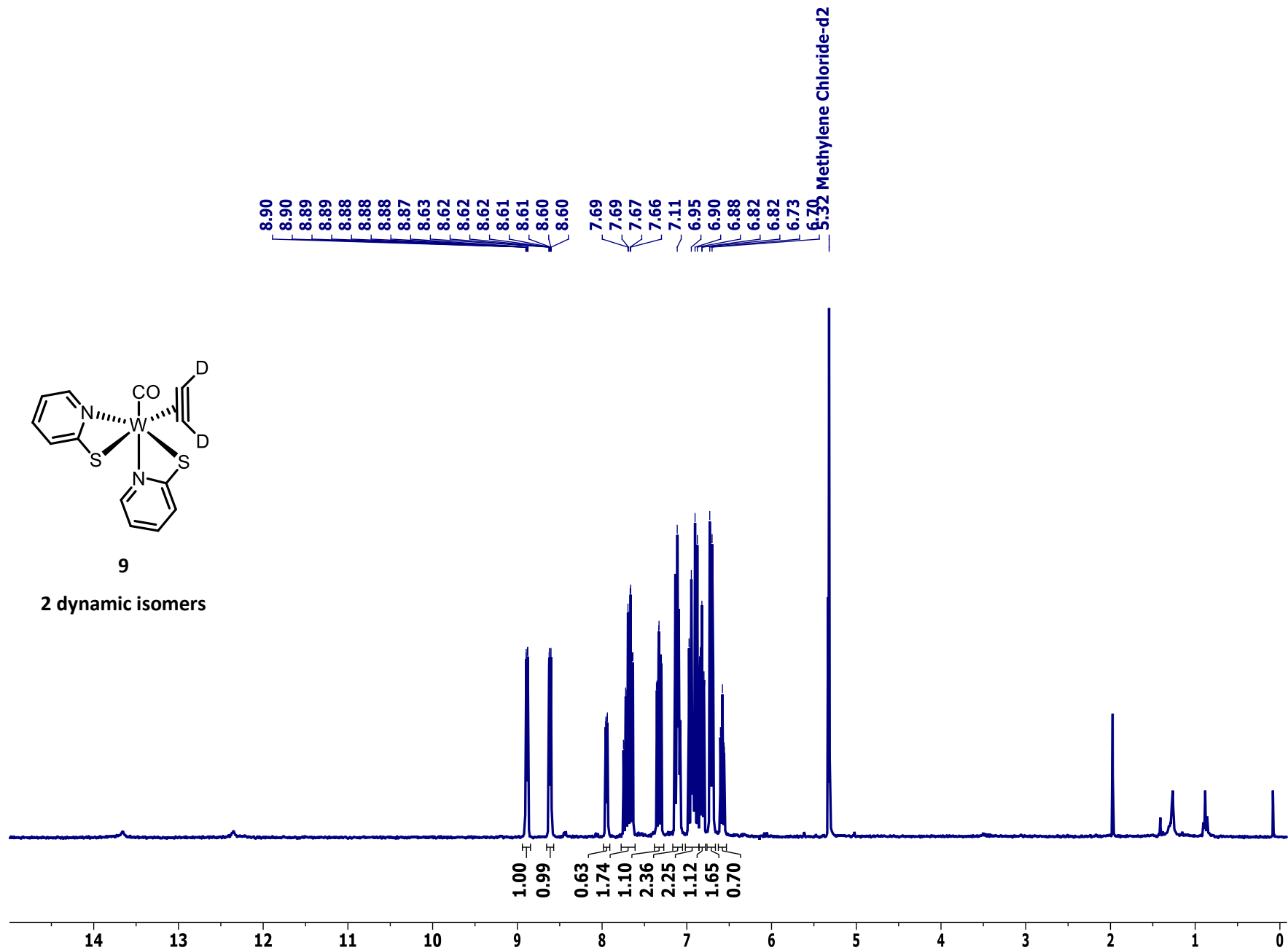
6

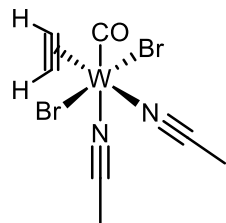
2 dynamic isomers



9

2 dynamic isomers

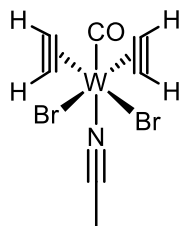
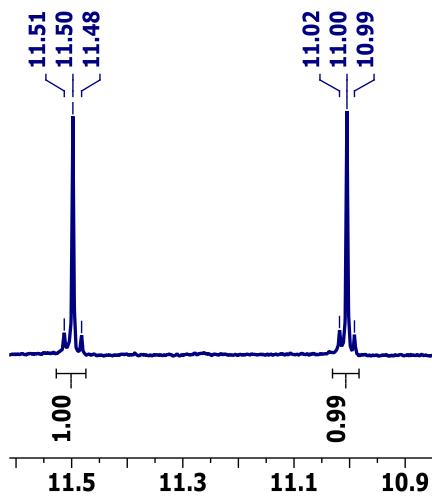




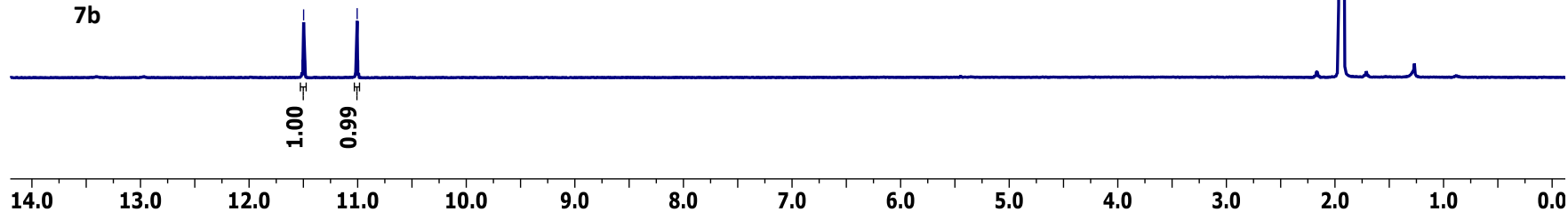
7a

(not detected due to very bad solubility of the obtained crude mixture)

11.51  
11.50  
11.48  
11.02  
11.00  
10.99

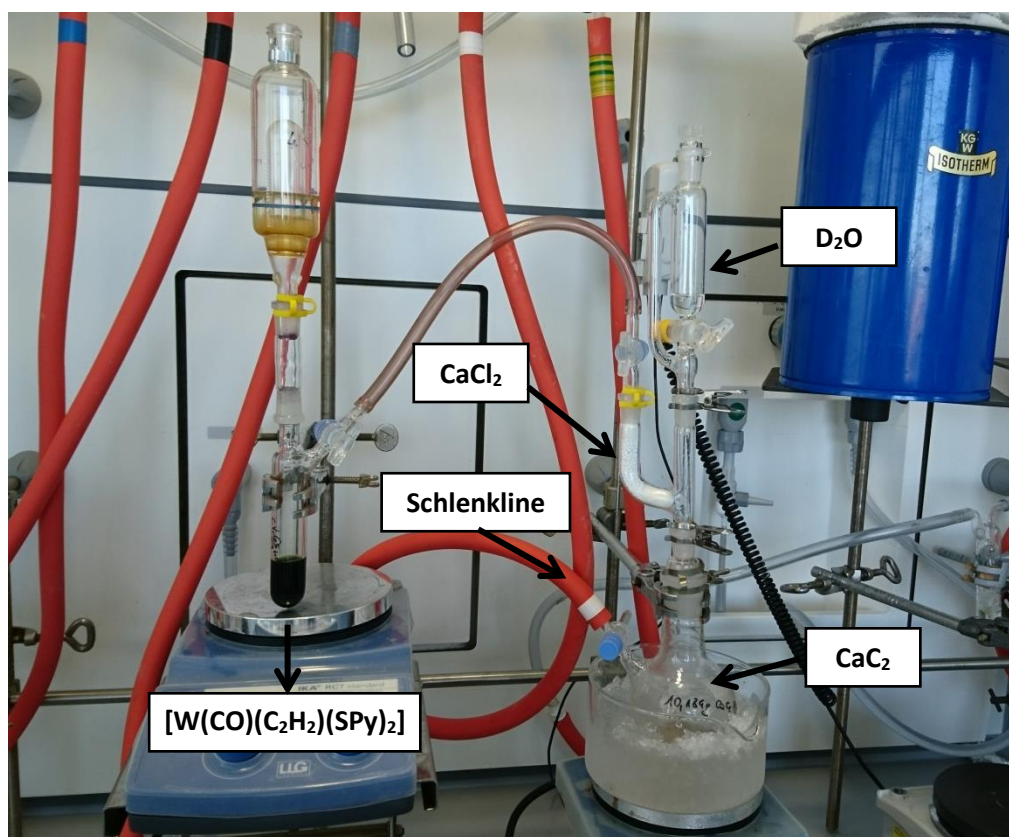


7b



## **LABELLING EXPERIMENTS:**

For the experiments, approx. 45 mg of  $[\text{W}(\text{CO})(\text{C}_2\text{H}_2)(\text{SPy})_2]$  (**6**) or  $[\text{W}(\text{CO})(\text{C}_2\text{D}_2)(\text{SPy})_2]$  (**9**) were dissolved in approx. 8 mL of toluene and purged with the  $\text{C}_2\text{D}_2$  or  $\text{C}_2\text{H}_2$ , respectively, for 10 min and thereafter stirred for 4 h. Deuterated acetylene was prepared by the addition of  $\text{D}_2\text{O}$  to  $\text{CaC}_2$  and dried by passing through a glass tube packed with  $\text{CaCl}_2$  (Figure S1). The solvent was removed in vacuo, the residue was dissolved in  $\text{CH}_2\text{Cl}_2$ , filtered through silica gel and recrystallized from  $\text{CH}_2\text{Cl}_2$ /heptane. In order to evaluate the  $^1\text{H}$  NMR spectra they have been recorded using a  $T_1$  of 10 sec as in an *Inversion Recovery Experiment* the  $\eta^2$ -acetylene protons were found to have a  $T_1$  of 8.8 seconds.



**Figure S1.** Technical set up for  $\text{C}_2\text{D}_2$ -addition.

## **X-RAY CRYSTALLOGRAPHY:**

**Crystallographic Details.** X-ray measurements ( $\phi$  and  $\omega$  scans) were performed on a Bruker APEX-II CCD diffractometer using monochromated Mo-K $\alpha$  radiation at 100 K. Crystallographic data (including structure factors) for the compounds reported in this article were deposited with the Cambridge Crystallographic Data Center as supplementary publication numbers. The following CCDC deposition numbers have been assigned: 1918473-1918484.

**Crystal Structure Determination – General.** The structures were solved by direct methods (SHELXS-97)<sup>[5]</sup> and refined by full-matrix least-squares techniques against  $F^2$  [semi-empirical absorption correction from equivalents, no correction for extinction, weighting scheme  $w = 1/[\sigma^2(F_o^2)+(aP)^2+bP]$ , where  $P = (F_o^2+2F_c^2)/3$ ] using SHELXL-2014/6.<sup>[5]</sup> The non-hydrogen atoms of the metal complex were refined with anisotropic displacement parameters without any constraints. The H atoms of the pyridazine and pyridine rings were put at the external bisectors of the X–C–C angles at C–H distances of 0.95 Å and common isotropic displacement parameters were refined for the H atoms of the same ring. The H atoms of the *tert*-butyl groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometries with tetrahedral angles, enabling rotation around the C–C bonds, and C–H distances of 0.98 Å. The H atoms of the acetonitrile ligands were refined with a common isotropic displacement parameter and idealized geometry with tetrahedral angles, enabling rotation around the C–C bond, and C–H distances of 0.98 Å. The positions of the H atoms of the ethenidyl groups and of the ethyne ligands were taken from difference Fourier maps. These H atoms were refined with isotropic displacement parameters common to each C<sub>2</sub>H<sub>2</sub> unit without any positional constraints. The handling of disordered *tert*-butyl groups or solvent molecules is described in the CIF file. Crystal data, data collection and refinement parameters and results are given in Tables S1-S3.

**Crystal Structure Determination of another modification of [W(CO)<sub>3</sub>(SPn)<sub>2</sub>] (2').** The data show a superstructure corresponding to a pseudo-symmetric A centering: whereas for reflections with  $k+l = 2n$  the mean intensity  $I_{\text{mean}} = 29.5$  [82.0% had  $I/\sigma(I) > 3$ ], for reflections with  $k+l = 2n+1$  the value of  $I_{\text{mean}}$  is only 8.7, but still 71.1% had  $I/\sigma(I) > 3$ . The two

complexes have similar bonding parameters but distinctly different packing surroundings [e.g. W-W distances below 8.5Å: W1···W1' 6.2989(5)Å, W1···W1'' 7.5660(5)Å, W1'···W1···W1'' 84.81(1)° vs. W2···W2' 6.4054(5)Å, W2···W2'' 8.0482(5)Å, W2'···W2···W2'' 80.23(1)°].

**Crystal Structure Determination of [W(CO)(C<sub>2</sub>H<sub>2</sub>)(MeCN)<sub>2</sub>Br<sub>2</sub>] (7a).** Since racemic twinning was detected a twin matrix (-1 0 0 / 0 -1 0 / 0 0 -1) was applied. As the refined scale factor between the two components did not deviate significantly from 0.5, the structure was refined as a 2-component perfect inversion twin. The structure is not centrosymmetric: In the centrosymmetric space group *P n m* the complex would lie with its W atom on a mirror plane through W1, Br1 and bisecting the N–W–N angle but this would make Br2 and the carbonyl ligand equivalent (s. Fig. S13). This is not the case: There is some disorder but the two disordered Br positions have very different site occupation values [e.g. 0.848(4) for Br2 vs. 0.152(4) for Br9].

**Crystal Structure Determination of [W(CO)(C<sub>2</sub>H<sub>2</sub>)<sub>2</sub>(MeCN)Br<sub>2</sub>] (7b).** Since racemic twinning was detected a twin matrix (-1 0 0 / 0 -1 0 / 0 0 -1) was applied. As the refined scale factor between the two components did not deviate significantly from 0.5, the structure was refined as a 2-component perfect inversion twin. The structure is not centrosymmetric: In *C 2/c* the complex would lie with its W atom on a two-fold rotation axis bisecting the Br-W-Br angle but this is not possible since it would interchange the acetonitrile and the carbonyl ligands (s. Fig. S15). In the crystal these two ligands of the complexes are parallel-arranged in the direction [-2 0 1] in a head-to-tail manner. Because of their different space requirements they can not interchange.

**Table S1:** Crystallographic data and structure refinement details of  $[\text{W}(\text{CO})_3(\text{MeCN})_2\text{Br}_2]$ , **1**, **2** and **2'**.

<b>Crystal data</b>	$[\text{W}(\text{CO})_3(\text{MeCN})_2\text{Br}_2]$	$[\text{W}(\text{CO})_3(\text{SPy})_2]$ ( <b>1</b> )	$[\text{W}(\text{CO})_3(\text{SPn})_2]$ ( <b>2</b> )	$[\text{W}(\text{CO})_3(\text{SPn})_2]$ ( <b>2'</b> )
Empirical formula	$\text{C}_7\text{H}_6\text{Br}_2\text{N}_2\text{O}_3\text{W}$	$\text{C}_{13}\text{H}_8\text{N}_2\text{O}_3\text{S}_2\text{W}$	$\text{C}_{19}\text{H}_{22}\text{N}_4\text{O}_3\text{S}_2\text{W}$	$\text{C}_{19}\text{H}_{22}\text{N}_4\text{O}_3\text{S}_2\text{W}$
Formula weight	509.81	488.18	602.37	602.37
Crystal description	block, red	block, red	block, red	block, red
Crystal size	0.20 x 0.18 x 0.15mm	0.28 x 0.12 x 0.09mm	0.30 x 0.27 x 0.25mm	0.31 x 0.28 x 0.16mm
Crystal system	triclinic	monoclinic	triclinic	triclinic
Space group	P -1	P 2 <sub>1</sub> /n	P -1	P -1
a	6.3226(3)Å	9.0949(2)Å	10.0288(11)Å	9.3971(4)Å
b	8.1953(4)Å	12.8526(3)Å	11.2836(13)Å	12.8912(6)Å
c	12.0188(6)Å	13.1355(3)Å	11.5408(12)Å	19.4842(8)Å
$\alpha$	95.8122(13)°		73.138(4)°	71.8943(16)°
$\beta$	91.0953(11)°	108.6344(6)°	64.695(4)°	82.6578(18)°
$\gamma$	91.7895(11)°		88.149(5)°	80.3723(19)°
Volume	619.10(5)Å <sup>3</sup>	1454.96(6)Å <sup>3</sup>	1123.5(2)Å <sup>3</sup>	2204.59(17)Å <sup>3</sup>
Z	2	4	2	4
Calc. density	2.735Mg/m <sup>3</sup>	2.229Mg/m <sup>3</sup>	1.781Mg/m <sup>3</sup>	1.815Mg/m <sup>3</sup>
F(000)	460	920	588	1176
Linear absorption coefficient $\mu$	15.772mm <sup>-1</sup>	8.235mm <sup>-1</sup>	5.353mm <sup>-1</sup>	5.456mm <sup>-1</sup>
Max. and min. transmission	0.747 and 0.393	1.000 and 0.861	1.000 and 0.453	1.000 and 0.495
Unit cell determination	2.50° < $\Theta$ < 36.04°	2.28° < $\Theta$ < 35.41°	2.72° < $\Theta$ < 30.80°	2.38° < $\Theta$ < 35.97°
Reflections used at 100K	7586	8036	9042	9699
<b>Data collection</b>				
Monochromator	graphite	graphite	multilayer	multilayer
$\Theta$ range for data collection	2.50 to 35.00°	2.28 to 35.00°	1.90 to 30.00°	1.71 to 35.00°
Reflections collected/ unique	10585 / 5398	12603 / 6399	29007 / 6551	55740 / 19425
Significant unique reflections	5001 with $I > 2\sigma(I)$	5749 with $I > 2\sigma(I)$	5815 with $I > 2\sigma(I)$	16265 with $I > 2\sigma(I)$
R(int), R(sigma)	0.0241, 0.0329	0.0118, 0.0177	0.0620, 0.0518	0.0490, 0.0474
Completeness to $\Theta_{\text{max}}$	99.0%	99.9%	99.9%	100.0%
<b>Refinement</b>				
Data/ parameters/ restraints	5398 / 140 / 0	6399 / 192 / 0	6551 / 272 / 0	19425 / 543 / 0
Goodness-of-fit on $F^2$	1.044	1.025	1.087	1.043
Final R indices [ $I > 2\sigma(I)$ ]	R1 = 0.0220, wR2 = 0.0507	R1 = 0.0177, wR2 = 0.0427	R1 = 0.0341, wR2 = 0.0813	R1 = 0.0284, wR2 = 0.0625
R indices (all data)	R1 = 0.0252, wR2 = 0.0517	R1 = 0.0218, wR2 = 0.0444	R1 = 0.0416, wR2 = 0.0852	R1 = 0.0387, wR2 = 0.0666
Weighting scheme param. a, b	0.0214, 0.3559	0.0270, 0.2898	0.0392, 1.7196	0.0140, 1.8594
Largest $\Delta/\sigma$ in last cycle	0.002	0.004	0.001	0.002
Largest diff. peak and hole	2.680 and -1.963e/Å <sup>3</sup>	3.388 and -1.508e/Å <sup>3</sup>	2.529 and -2.092e/Å <sup>3</sup>	3.361 and -2.676e/Å <sup>3</sup>
<b>CCDC no.</b>	<b>1918473</b>	<b>1918474</b>	<b>1918475</b>	<b>1918476</b>

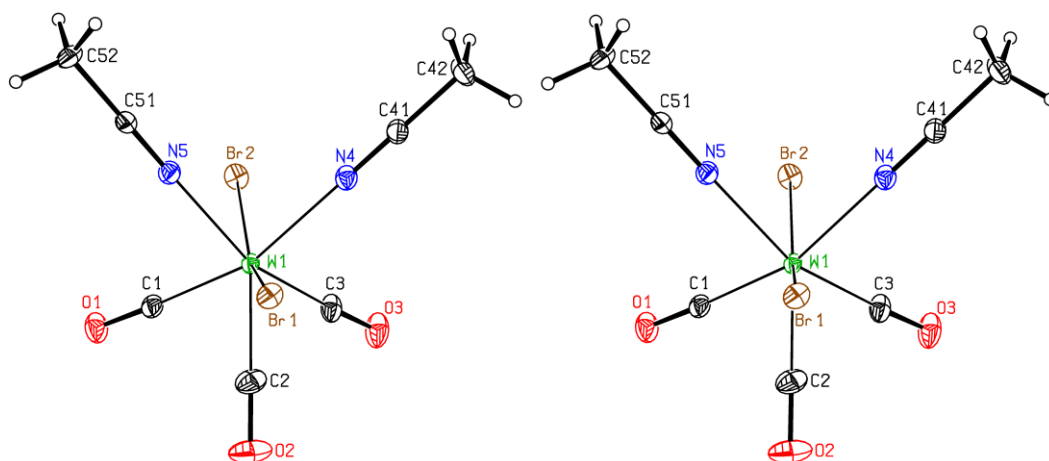
**Table S2:** Crystallographic data and structure refinement details of **3**, **3'**, **4** and **4'**.

<b>Crystal data</b>	<b>[W<sub>2</sub>(CO)<sub>4</sub>(SPn)<sub>4</sub>] (3)</b>	<b>[W<sub>2</sub>(CO)<sub>4</sub>(SPn)<sub>4</sub>] (3')</b>	<b>[W(CO)(C<sub>2</sub>H<sub>2</sub>)(CHCH-SPy)(SPy)] (4)</b>	<b>[W(CO)(C<sub>2</sub>H<sub>2</sub>)(CHCH-SPy)(SPy)] (4')</b>
Empirical formula	2C <sub>36</sub> H <sub>44</sub> N <sub>8</sub> O <sub>4</sub> S <sub>4</sub> W <sub>2</sub> · 3CH <sub>2</sub> Cl <sub>2</sub>	C <sub>36</sub> H <sub>44</sub> N <sub>8</sub> O <sub>4</sub> S <sub>4</sub> W <sub>2</sub>	C <sub>15</sub> H <sub>12</sub> N <sub>2</sub> OS <sub>2</sub> W · 2(C <sub>2</sub> H <sub>3</sub> N)	2C <sub>15</sub> H <sub>12</sub> N <sub>2</sub> OS <sub>2</sub> W · CH <sub>2</sub> Cl <sub>2</sub>
Formula weight	2552.24	1148.73	566.34	1053.40
Crystal description	plate, red	plate, red	plate, red	block, red
Crystal size	0.30 x 0.16 x 0.005mm	0.20 x 0.11 x 0.03mm	0.29 x 0.15 x 0.08mm	0.30 x 0.27 x 0.22mm
Crystal system	monoclinic	monoclinic	triclinic	monoclinic
Space group	P 2 <sub>1</sub> /c	I 2/a	P -1	C 2/c
a	23.7689(9)Å	14.0861(18)Å	7.7743(3)Å	26.297(5)Å
b	10.0758(4)Å	13.5780(17)Å	11.4232(5)Å	9.0378(18)Å
c	20.3891(7)Å	22.564(3)Å	13.0148(5)Å	14.184(3)Å
α			66.2069(13)°	
β	92.496(2)°	92.631(13)°	80.7594(14)°	95.545(4)°
γ			70.7022(13)°	
Volume	4878.4(3)Å <sup>3</sup>	4311.2(9)Å <sup>3</sup>	997.66(7)Å <sup>3</sup>	3355.2(12)Å <sup>3</sup>
Z	2	4	2	4
Calc. density	1.738Mg/m <sup>3</sup>	1.770Mg/m <sup>3</sup>	1.885Mg/m <sup>3</sup>	2.085Mg/m <sup>3</sup>
F(000)	2492	2240	548	2008
Linear absorption coefficient μ	5.093mm <sup>-1</sup>	5.572mm <sup>-1</sup>	6.015mm <sup>-1</sup>	7.296mm <sup>-1</sup>
Max. and min. transmission	1.000 and 0.574	1.000 and 0.358	1.000 and 0.455	0.747 and 0.251
Unit cell determination	2.40° < Θ < 26.58°	2.72° < Θ < 26.40°	2.78° < Θ < 35.38°	2.75° < Θ < 35.56°
Reflections used at 100K	9895	4517	9546	9714
<b>Data collection</b>				
Monochromator	multilayer	multilayer	multilayer	multilayer
Θ range for data collection	2.20 to 26.00°	2.71 to 26.00°	2.78 to 35.00°	1.56 to 35.00°
Reflections collected/ unique	43839 / 9594	22681 / 4232	53318 / 8798	44340 / 7392
Significant unique reflections	7063 with I > 2σ(I)	2670 with I > 2σ(I)	8562 with I > 2σ(I)	6782 with I > 2σ(I)
R(int), R(sigma)	0.0655, 0.0750	0.0931, 0.0804	0.0473, 0.0252	0.0568, 0.0375
Completeness to Θ <sub>max</sub>	99.9%	99.8%	99.9%	99.9%
<b>Refinement</b>				
Data/ parameters/ restraints	9594 / 563 / 26	4232 / 253 / 0	8798 / 264 / 0	7392 / 221 / 0
Goodness-of-fit on F <sup>2</sup>	1.014	1.013	1.098	1.066
Final R indices [I > 2σ(I)]	R1 = 0.0400, wR2 = 0.0824	R1 = 0.0367, wR2 = 0.0636	R1 = 0.0148, wR2 = 0.0385	R1 = 0.0267, wR2 = 0.0724
R indices (all data)	R1 = 0.0654, wR2 = 0.0898	R1 = 0.0905, wR2 = 0.0743	R1 = 0.0155, wR2 = 0.0388	R1 = 0.0290, wR2 = 0.0737
Weighting scheme param. a, b	0.0280, 3.6369	0.0270, 0.0000	0.0133, 0.3206	0.0415, 3.3558
Largest Δ/σ in last cycle	0.002	0.001	0.004	0.005
Largest diff. peak and hole	2.138 and -1.980e/Å <sup>3</sup>	1.069 and -0.919e/Å <sup>3</sup>	1.610 and -0.790e/Å <sup>3</sup>	2.287 and -2.358e/Å <sup>3</sup>
<b>CCDC no.</b>	<b>1918477</b>	<b>1918478</b>	<b>1918479</b>	<b>1918480</b>

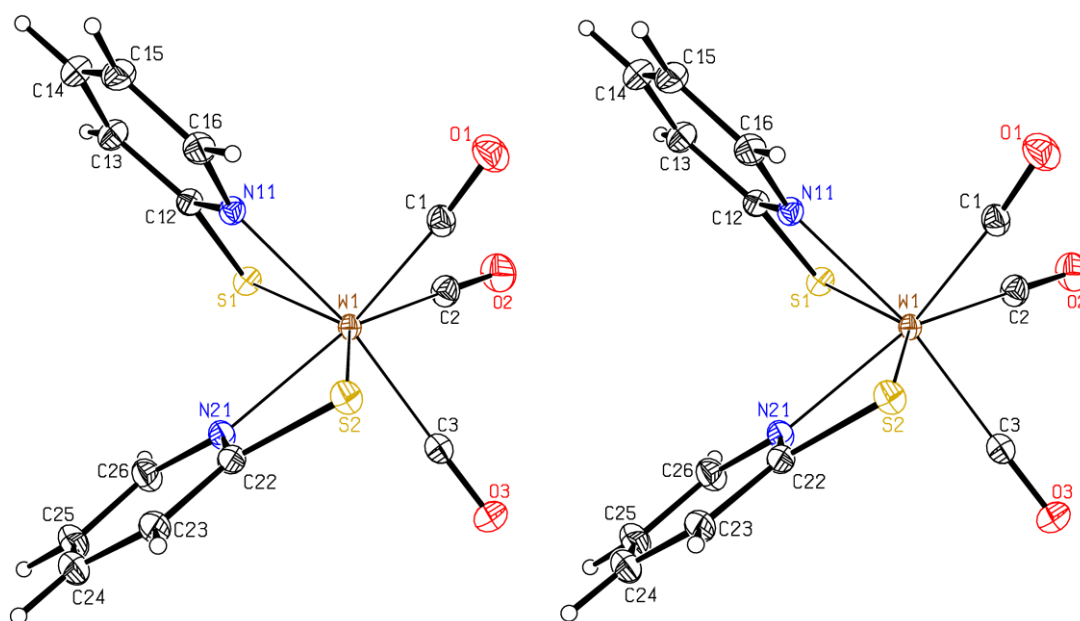


**Table S3:** Crystallographic data and structure refinement details of **5**, **6**, **7a** and **7b**.

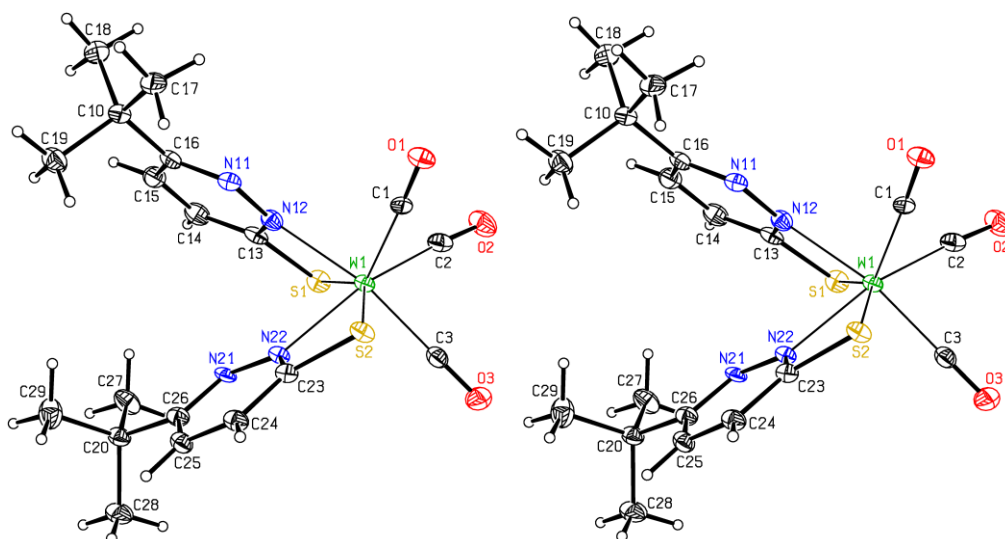
<b>Crystal data</b>	[W(CO)(C <sub>2</sub> H <sub>2</sub> )(CHCH-SPn)(SPn)] ( <b>5</b> )	[W(CO)(C <sub>2</sub> H <sub>2</sub> )(SPy) <sub>2</sub> ] ( <b>6</b> )	[W(CO)(C <sub>2</sub> H <sub>2</sub> )(MeCN) <sub>2</sub> Br <sub>2</sub> ] ( <b>7a</b> )	[W(CO)(C <sub>2</sub> H <sub>2</sub> ) <sub>2</sub> (MeCN)Br <sub>2</sub> ] ( <b>7b</b> )
Empirical formula	C <sub>21</sub> H <sub>26</sub> N <sub>4</sub> OS <sub>2</sub> W	C <sub>13</sub> H <sub>10</sub> N <sub>2</sub> OS <sub>2</sub> W	C <sub>7</sub> H <sub>8</sub> Br <sub>2</sub> N <sub>2</sub> OW	C <sub>7</sub> H <sub>7</sub> Br <sub>2</sub> NOW
Formula weight	598.43	458.20	479.82	464.81
Crystal description	board, violet	plate, red	plate, blue	block, yellow
Crystal size	0.33 x 0.24 x 0.08mm	0.23 x 0.20 x 0.13mm	0.26 x 0.17 x 0.07mm	0.12 x 0.12 x 0.07mm
Crystal system	monoclinic	monoclinic	orthorhombic	monoclinic
Space group	C 2/c	P 2 <sub>1</sub> /n	P n a 2 <sub>1</sub>	C c
a	38.888(17)Å	8.2942(6)Å	6.2536(8)Å	7.9484(5)Å
b	6.531(3)Å	10.9825(9)Å	12.7478(15)Å	10.2942(6)Å
c	18.958(9)Å	15.2984(12)Å	13.8998(17)Å	12.9186(8)Å
β	109.875(5)°	93.028(3)°		97.9796(12)°
Volume	4528(4)Å <sup>3</sup>	1391.60(19)Å <sup>3</sup>	1108.1(2)Å <sup>3</sup>	1046.80(11)Å <sup>3</sup>
Z	8	4	4	4
Calc. density	1.756Mg/m <sup>3</sup>	2.187Mg/m <sup>3</sup>	2.876Mg/m <sup>3</sup>	2.949Mg/m <sup>3</sup>
F(000)	2352	864	864	832
Linear absorption coefficient μ	5.306mm <sup>-1</sup>	8.592mm <sup>-1</sup>	17.600mm <sup>-1</sup>	18.623mm <sup>-1</sup>
Max. and min. transmission	1.000 and 0.645	1.000 and 0.470	1.000 and 0.348	1.000 and 0.421
Unit cell determination	2.59° < Θ < 29.92°	2.73° < Θ < 40.98°	2.93° < Θ < 35.85°	3.18° < Θ < 40.82°
Reflections used at 100K	5554	9901	9950	9706
<b>Data collection</b>				
Monochromator	multilayer	multilayer	multilayer	multilayer
Θ range for data collection	2.59 to 30.00°	2.73 to 40.00°	2.93 to 29.99°	3.18 to 30.00°
Reflections collected/ unique	11662 / 6610	26559 / 8601	16776 / 3217	9092 / 2980
Significant unique reflections	5610 with I > 2σ(I)	7232 with I > 2σ(I)	2906 with I > 2σ(I)	2741 with I > 2σ(I)
R(int), R(sigma)	0.0307, 0.0463	0.0433, 0.0465	0.0663, 0.0640	0.0363, 0.0410
Completeness to Θ <sub>max</sub>	99.9%	99.9%	99.9%	99.6%
<b>Refinement</b>				
Data/ parameters/ restraints	6610 / 290 / 0	8601 / 181 / 2	3217 / 84 / 2	2980 / 82 / 2
Goodness-of-fit on F <sup>2</sup>	1.046	1.020	1.073	1.042
Final R indices [I > 2σ(I)]	R1 = 0.0375, wR2 = 0.0968	R1 = 0.0264, wR2 = 0.0549	R1 = 0.0357, wR2 = 0.0797	R1 = 0.0222, wR2 = 0.0549
R indices (all data)	R1 = 0.0465, wR2 = 0.1013	R1 = 0.0366, wR2 = 0.0592	R1 = 0.0413, wR2 = 0.0818	R1 = 0.0263, wR2 = 0.0563
Weighting scheme param. a, b	0.0625, 0.9610	0.0110, 1.0901	0.0186, 3.1138	0.0186, 3.9476
Largest Δ/σ in last cycle	0.001	0.004	0.001	0.001
Largest diff. peak and hole	2.017 and -2.269e/Å <sup>3</sup>	2.096 and -1.931e/Å <sup>3</sup>	2.419 and -2.398e/Å <sup>3</sup>	2.022 and -1.542e/Å <sup>3</sup>
<b>CCDC no.</b>	<b>1918481</b>	<b>1918482</b>	<b>1918484</b>	<b>1918483</b>



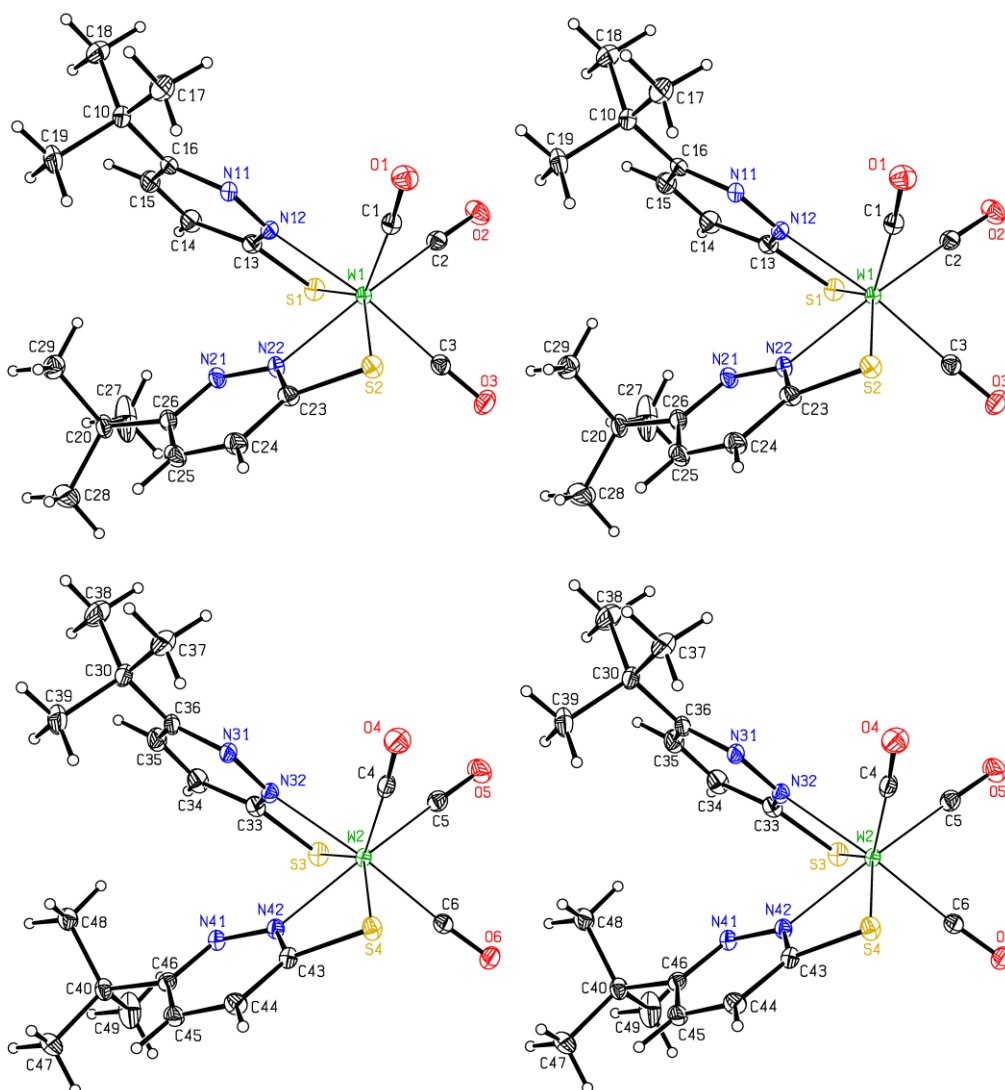
**Figure S2.** Stereoscopic ORTEP plot of  $[\text{W}(\text{CO})_3(\text{MeCN})_2\text{Br}_2]$  showing the atomic numbering scheme. The probability ellipsoids are drawn at the 50% probability level. The H atoms are drawn with arbitrary radii.



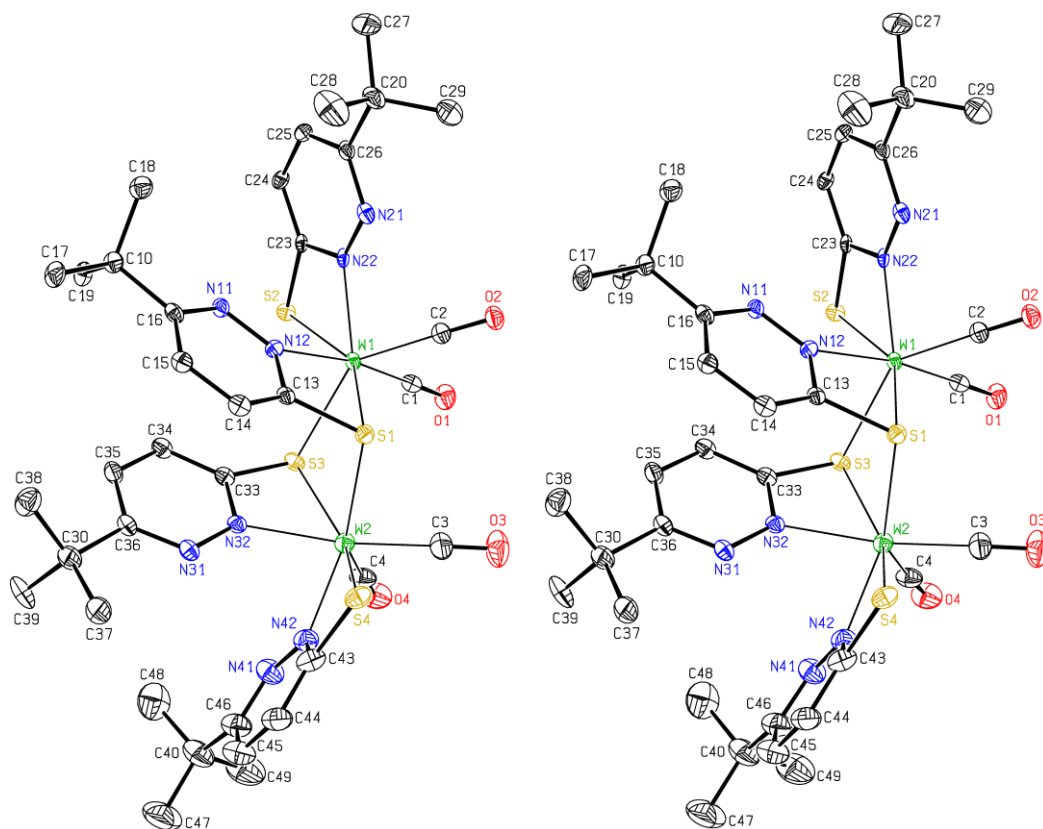
**Figure S3.** Stereoscopic ORTEP plot of  $[\text{W}(\text{CO})_3(\text{SPy})_2]$  (**1**) showing the atomic numbering scheme. The probability ellipsoids are drawn at the 50% probability level. The H atoms are drawn with arbitrary radii.



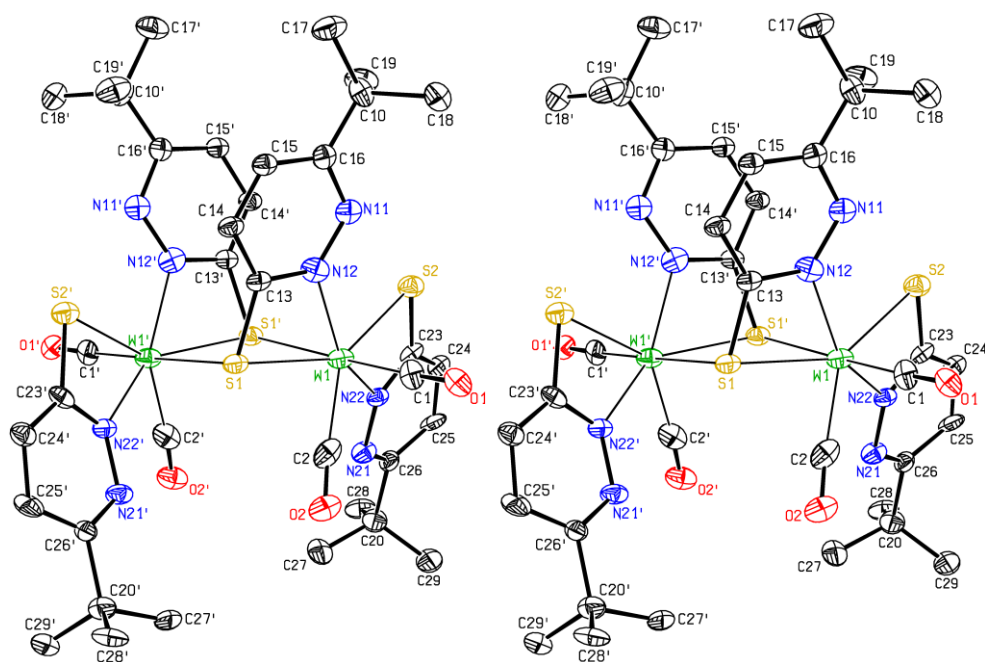
**Figure S4.** Stereoscopic ORTEP plot of  $[\text{W}(\text{CO})_3(\text{SPn})_2]$  (**2**) showing the atomic numbering scheme. The probability ellipsoids are drawn at the 50% probability level. The H atoms are drawn with arbitrary radii.



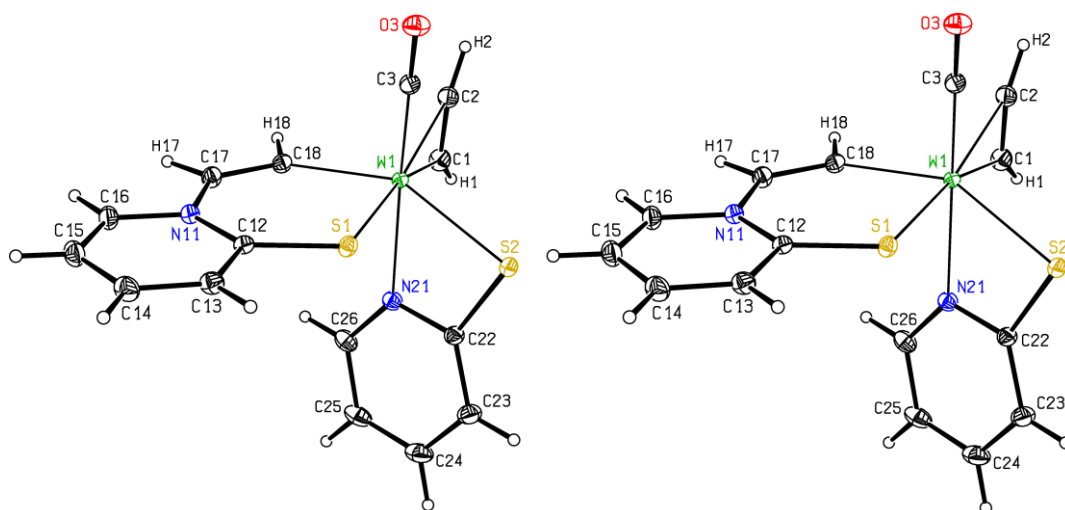
**Figure S5.** Stereoscopic ORTEP plot of the two complexes of the asymmetric unit of  $[\text{W}(\text{CO})_3(\text{SPn})_2]$  (**2'**) showing the atomic numbering scheme. The probability ellipsoids are drawn at the 50% probability level. The H atoms are drawn with arbitrary radii.



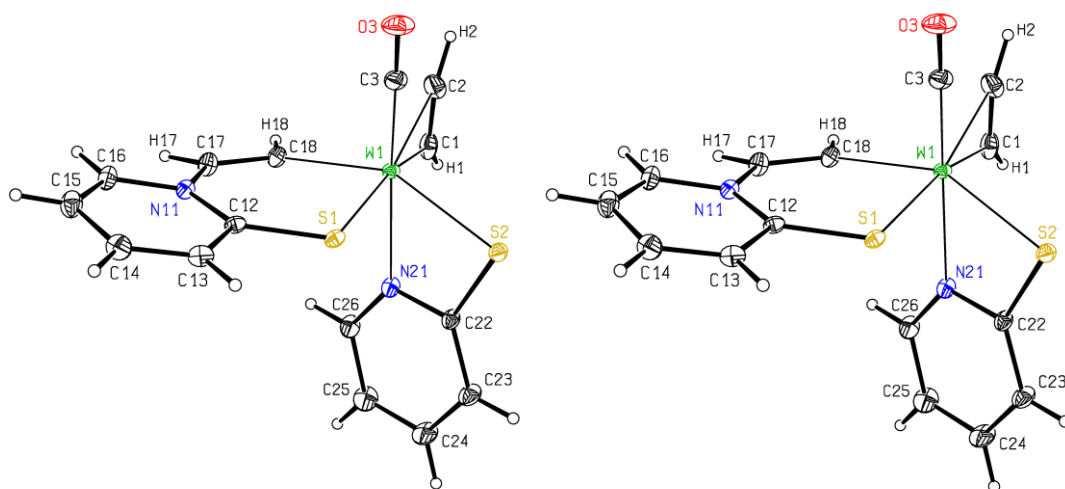
**Figure S6.** Stereoscopic ORTEP plot of the metal complex of  $[W_2(CO)_4(SPn)_4]$  (**3**) showing the atomic numbering scheme. The probability ellipsoids are drawn at the 30% probability level. The H atoms as well as the dichloromethane solvent molecules were omitted for clarity.



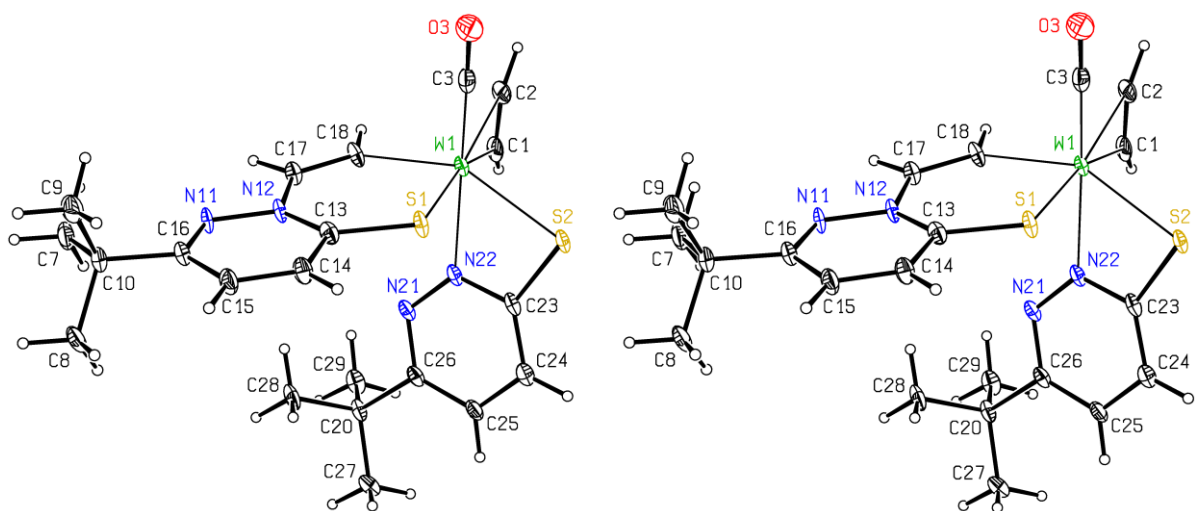
**Figure S7.** Stereoscopic ORTEP plot of  $[W_2(CO)_4(SPn)_4]$  (**3'**) showing the atomic numbering scheme. The probability ellipsoids are drawn at the 30% probability level. The H atoms were omitted for clarity reasons.



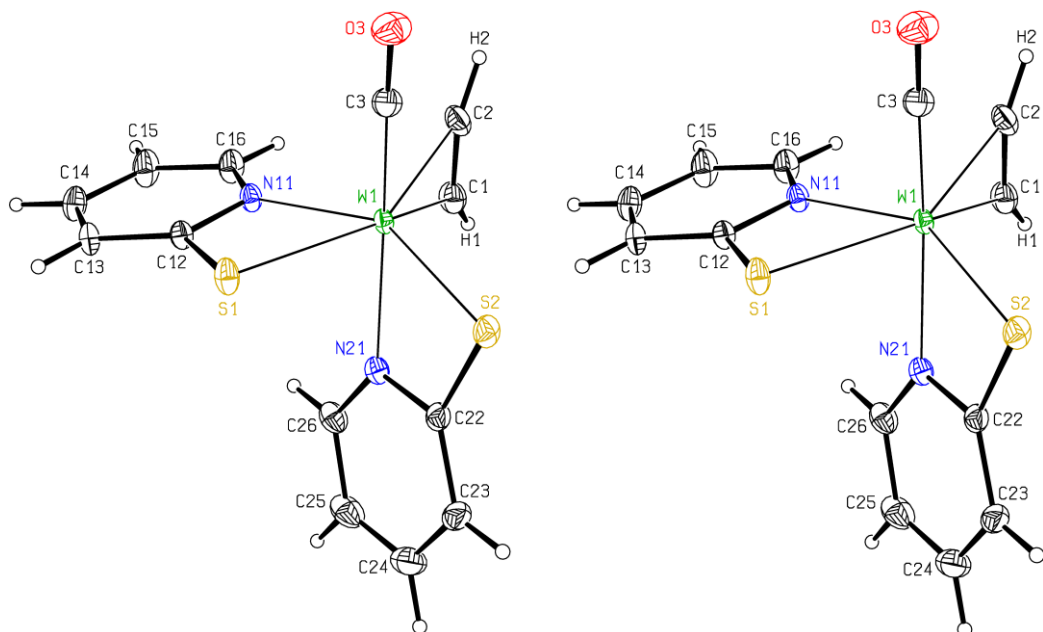
**Figure S8.** Stereoscopic ORTEP plot of  $[W(CO)(C_2H_2)(CHCH-SPy)(SPy)]$  (**4**) showing the atomic numbering scheme. The probability ellipsoids are drawn at the 50% probability level. The H atoms are drawn with arbitrary radii. The acetonitrile solvent molecules were omitted for clarity.



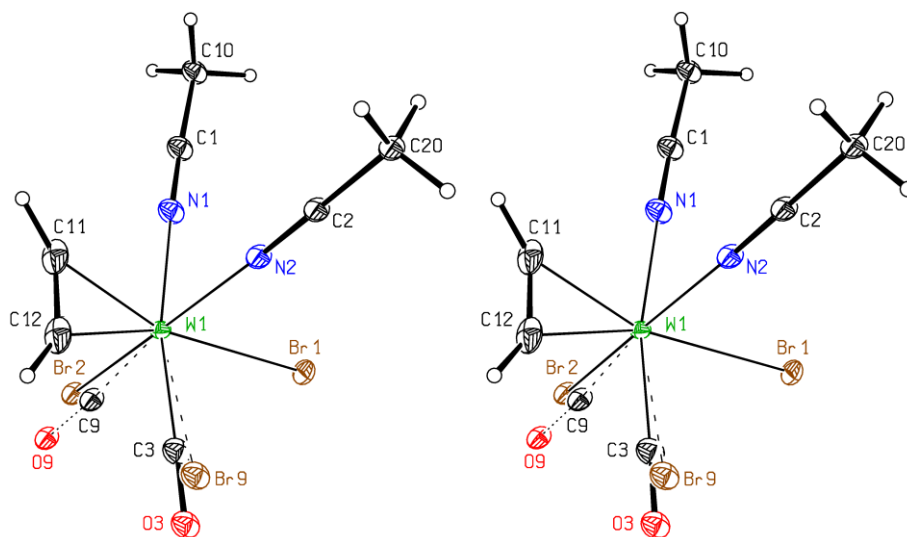
**Figure S9.** Stereoscopic ORTEP plot of another modification of  $[W(CO)(C_2H_2)(CHCH-SPy)(SPy)]$  (**4'**) showing the atomic numbering scheme. The probability ellipsoids are drawn at the 50% probability level. The H atoms are drawn with arbitrary radii. The dichloromethane solvent molecule was omitted for clarity.



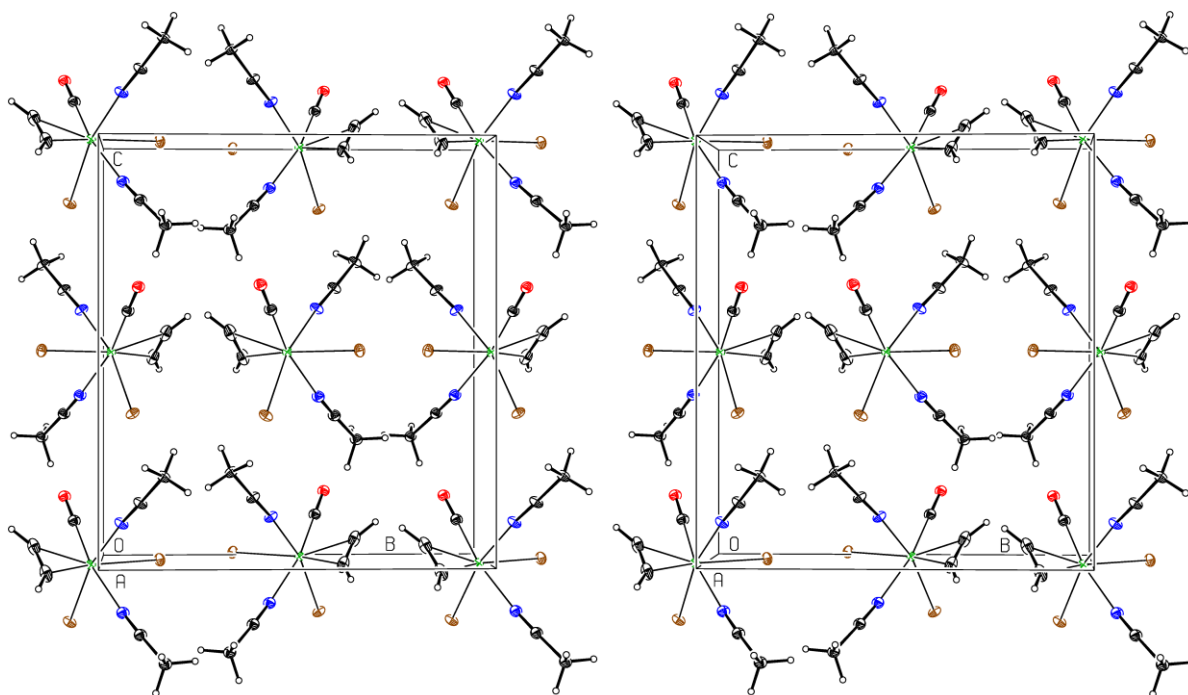
**Figure S10.** Stereoscopic ORTEP plot of  $[W(CO)(C_2H_2)(CHCH-SPn)(SPn)]$  (**5**) showing the atomic numbering scheme. The probability ellipsoids are drawn at the 50% probability level. The H atoms are drawn with arbitrary radii.



**Figure S11.** Stereoscopic ORTEP plot of  $[W(CO)(C_2H_2)(SPy)_2]$  (**6**) showing the atomic numbering scheme. The probability ellipsoids are drawn at the 50% probability level. The H atoms are drawn with arbitrary radii.

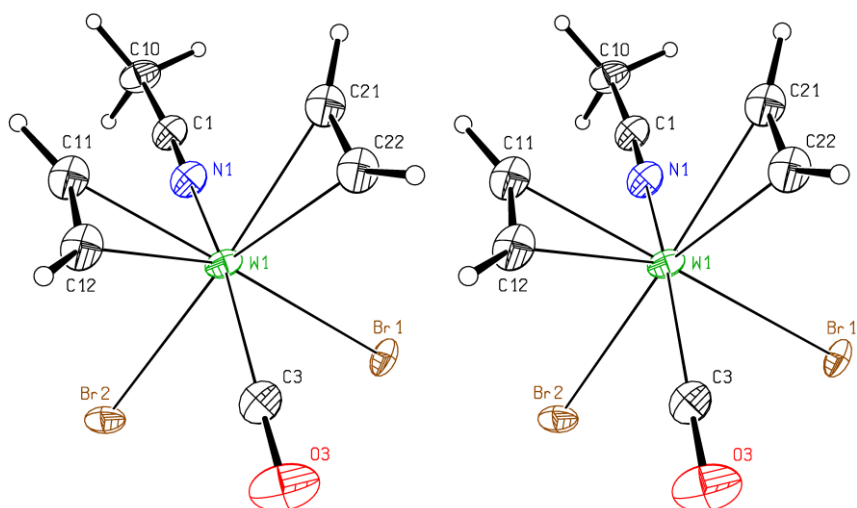


**Figure S12.** Stereoscopic ORTEP plot of  $[\text{W}(\text{CO})(\text{C}_2\text{H}_2)(\text{MeCN})_2\text{Br}_2]$  (**7a**) showing the atomic numbering scheme. The probability ellipsoids are drawn at the 50% probability level. The H atoms are drawn with arbitrary radii. The bonds to the atoms of the disordered parts of the complex in the orientations with low site occupation factors of 0.152(4) were plotted with dashed lines.

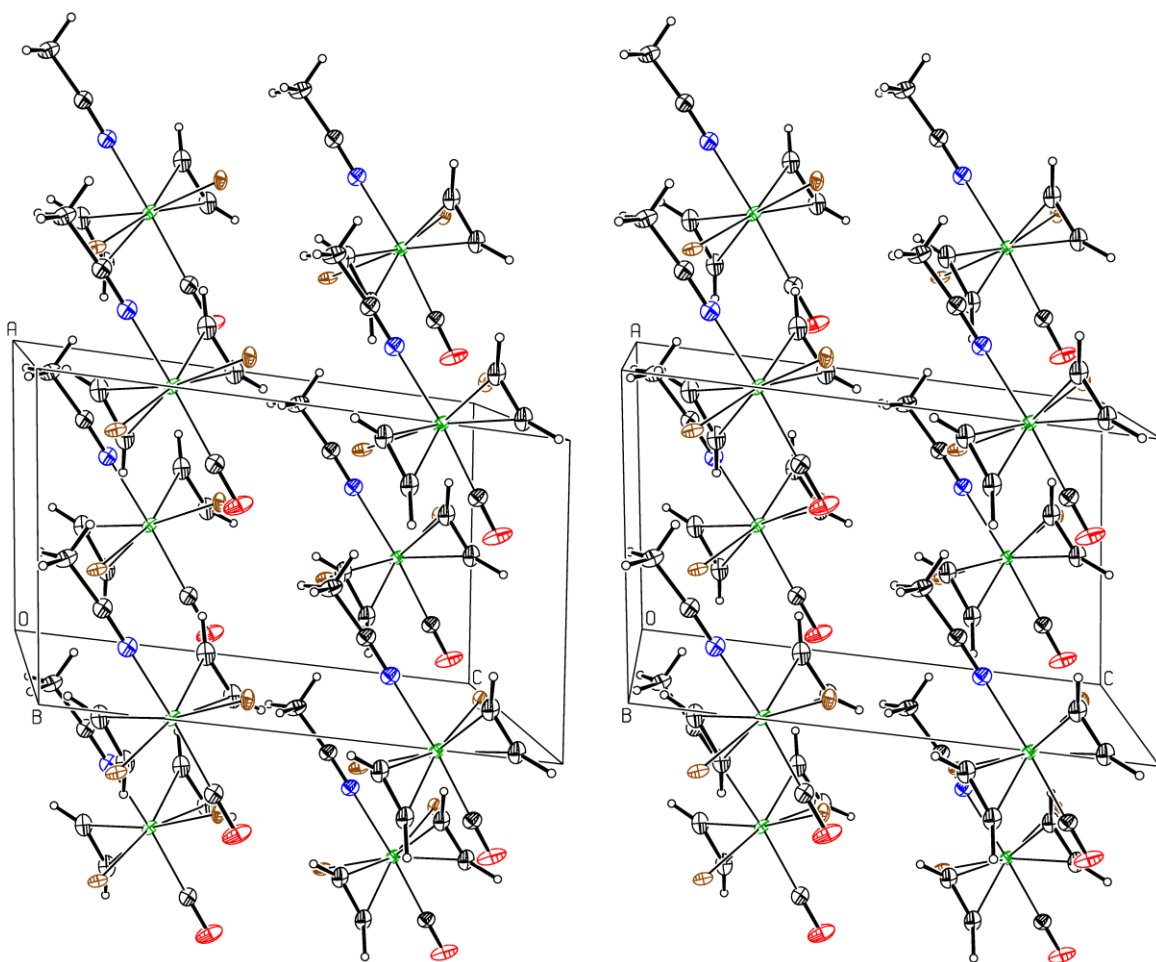


**Figure S13.** Stereoscopic ORTEP plot of the packing of  $[\text{W}(\text{CO})(\text{C}_2\text{H}_2)(\text{MeCN})_2\text{Br}_2]$  (**7a**). The probability ellipsoids are drawn at the 50% probability level. The H atoms are drawn with arbitrary radii. The disordered parts of the complexes in the orientations with low site occupation factors of 0.152(4) were omitted for clarity.





**Figure S14.** Stereoscopic ORTEP plot of  $[\text{W}(\text{CO})(\text{C}_2\text{H}_2)_2(\text{MeCN})\text{Br}_2]$  (**7b**) showing the atomic numbering scheme. The probability ellipsoids are drawn at the 50% probability level. The H atoms are drawn with arbitrary radii.



**Figure S15.** Stereoscopic ORTEP plot of the packing of  $[\text{W}(\text{CO})(\text{C}_2\text{H}_2)_2(\text{MeCN})\text{Br}_2]$  (**7b**). The probability ellipsoids are drawn at the 50% probability level. The H atoms are drawn with arbitrary radii.



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