

*Supporting Information*

## Olefin dimerization and isomerization catalyzed by pyridylideneamide palladium complexes

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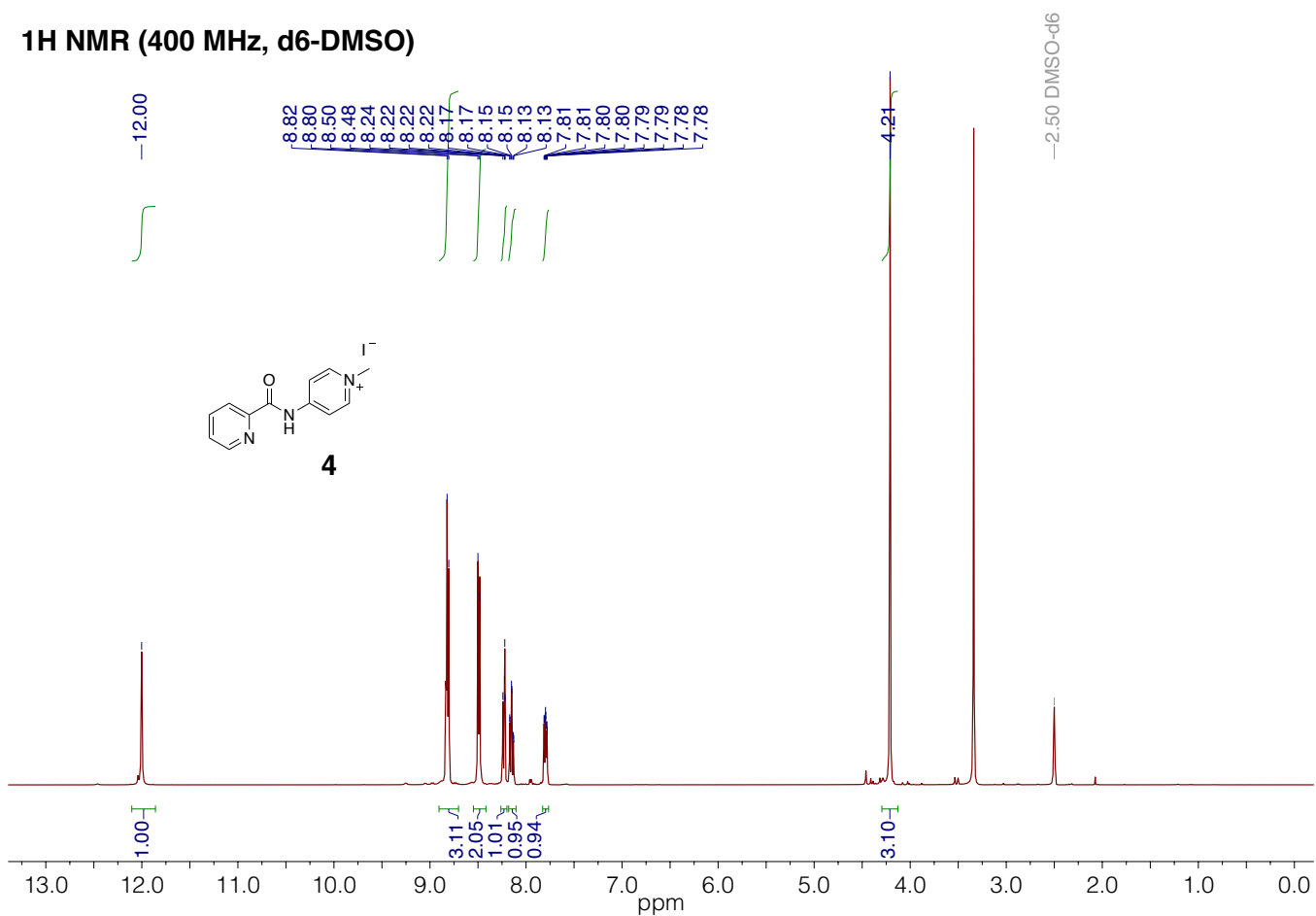
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## 1. Crystal structure determinations

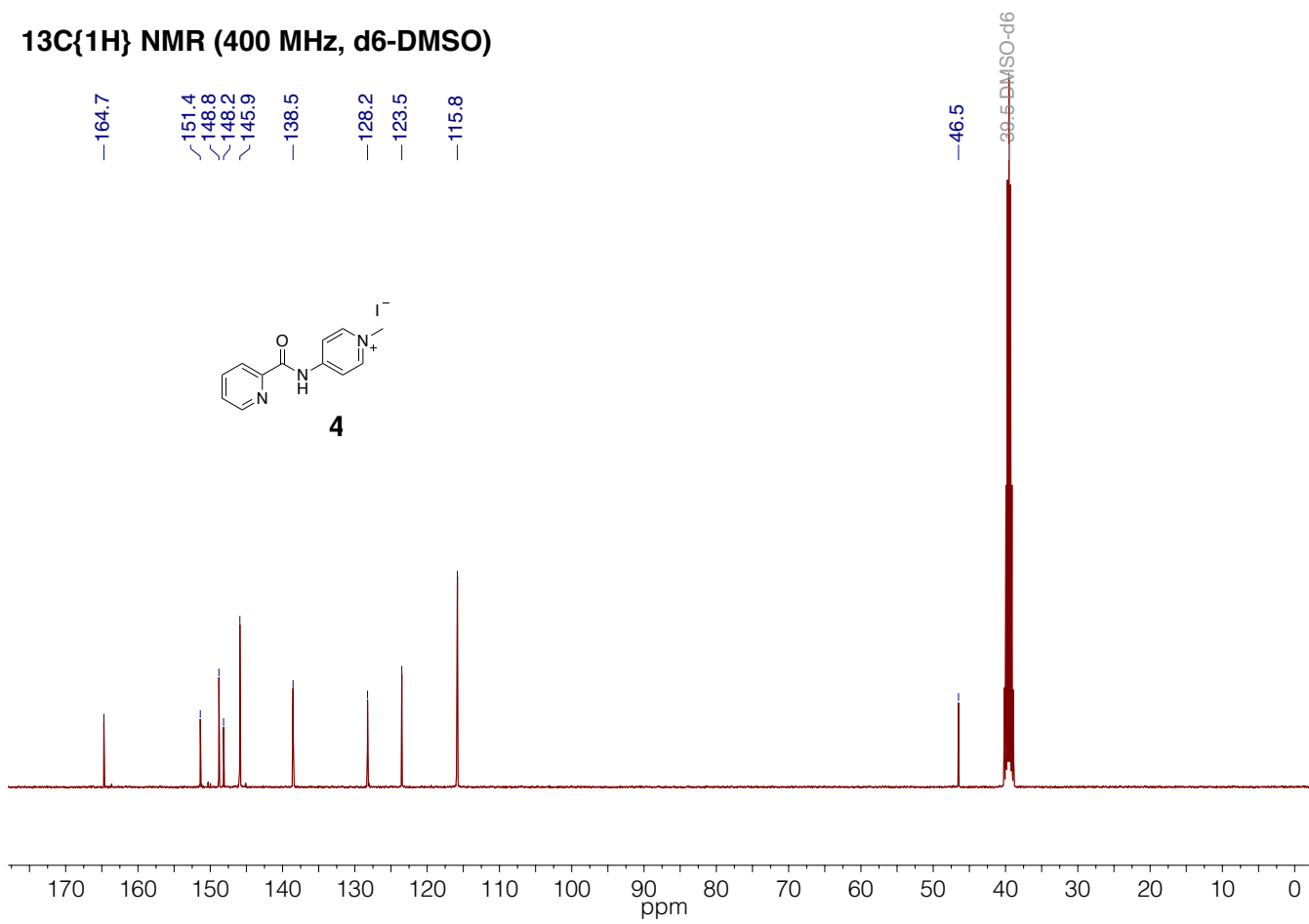
**Table S1.** Crystal data and structure refinement for compound *trans-7*

CCDC No.	1841366
Empirical formula	C <sub>15</sub> H <sub>17</sub> F <sub>6</sub> N <sub>4</sub> OPPd
Molecular formula	[C <sub>15</sub> H <sub>17</sub> N <sub>4</sub> OPd] <sup>+</sup> [PF <sub>6</sub> ] <sup>-</sup>
Formula weight	520.7
Temperature	123(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 21/n
Unit cell dimensions	a = 8.3940(2) Å      α = 90° b = 25.6728(9) Å      β = 90.782(2)° c = 8.4924(2) Å      γ = 90°
Volume	1829.92(9) Å <sup>3</sup>
Z	4
Density (calculated)	1.89 Mg m <sup>-3</sup>
Absorption coefficient	1.174 mm <sup>-1</sup>
F(000)	1032
Crystal size	0.207 x 0.162 x 0.023 mm <sup>3</sup>
Theta range for data collection	2.526 to 28.277°
Index ranges	-10 ≤ h ≤ 10, -33 ≤ k ≤ 33, -10 ≤ l ≤ 10
Reflections collected	16772
Independent reflections	4128 [R(int) = 0.0395]
Completeness to theta = 32.00°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.91259 and 0.91259
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	4128 / 387 / 320
Goodness-of-fit on F <sup>2</sup>	1.281
Final R indices [I > 2σ(I)]	R1 = 0.0511, wR2 = 0.094
R indices (all data)	R1 = 0.0612, wR2 = 0.0968
Largest diff. peak and hole	1.004 and -1.353 e Å <sup>-3</sup>

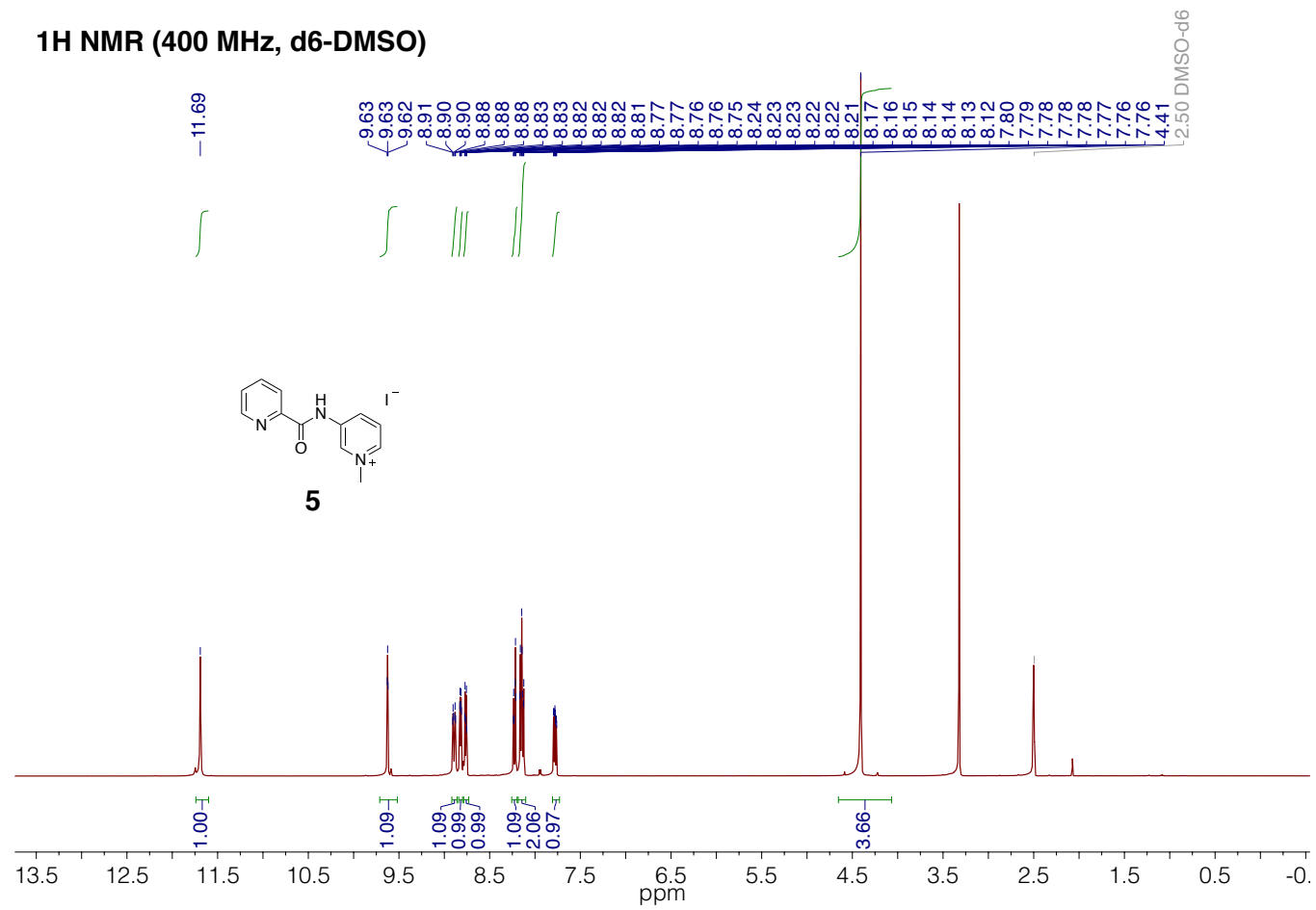
## 2. NMR spectra of all new compounds



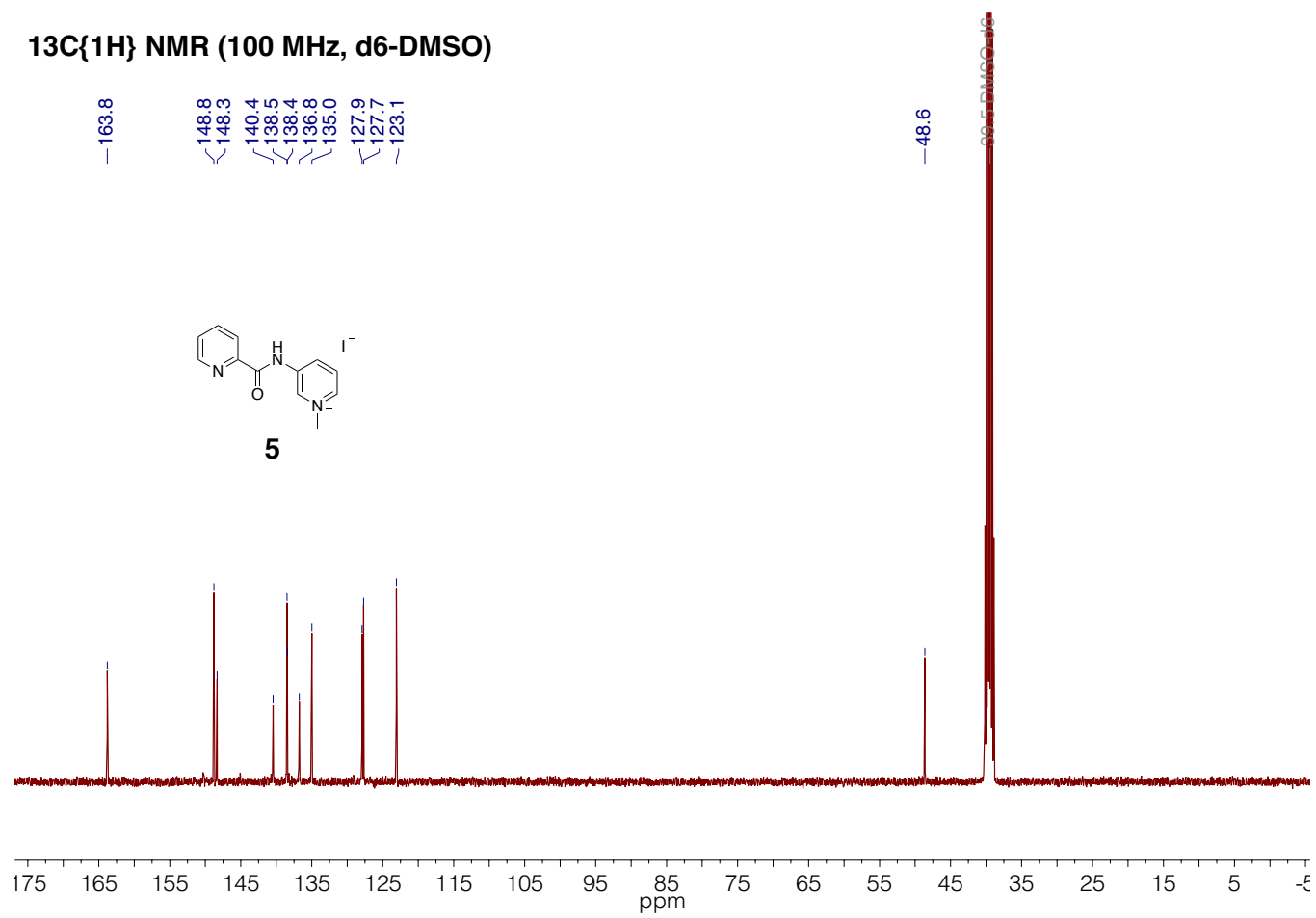
**Figure S1.** <sup>1</sup>H NMR spectrum of compound **4**.



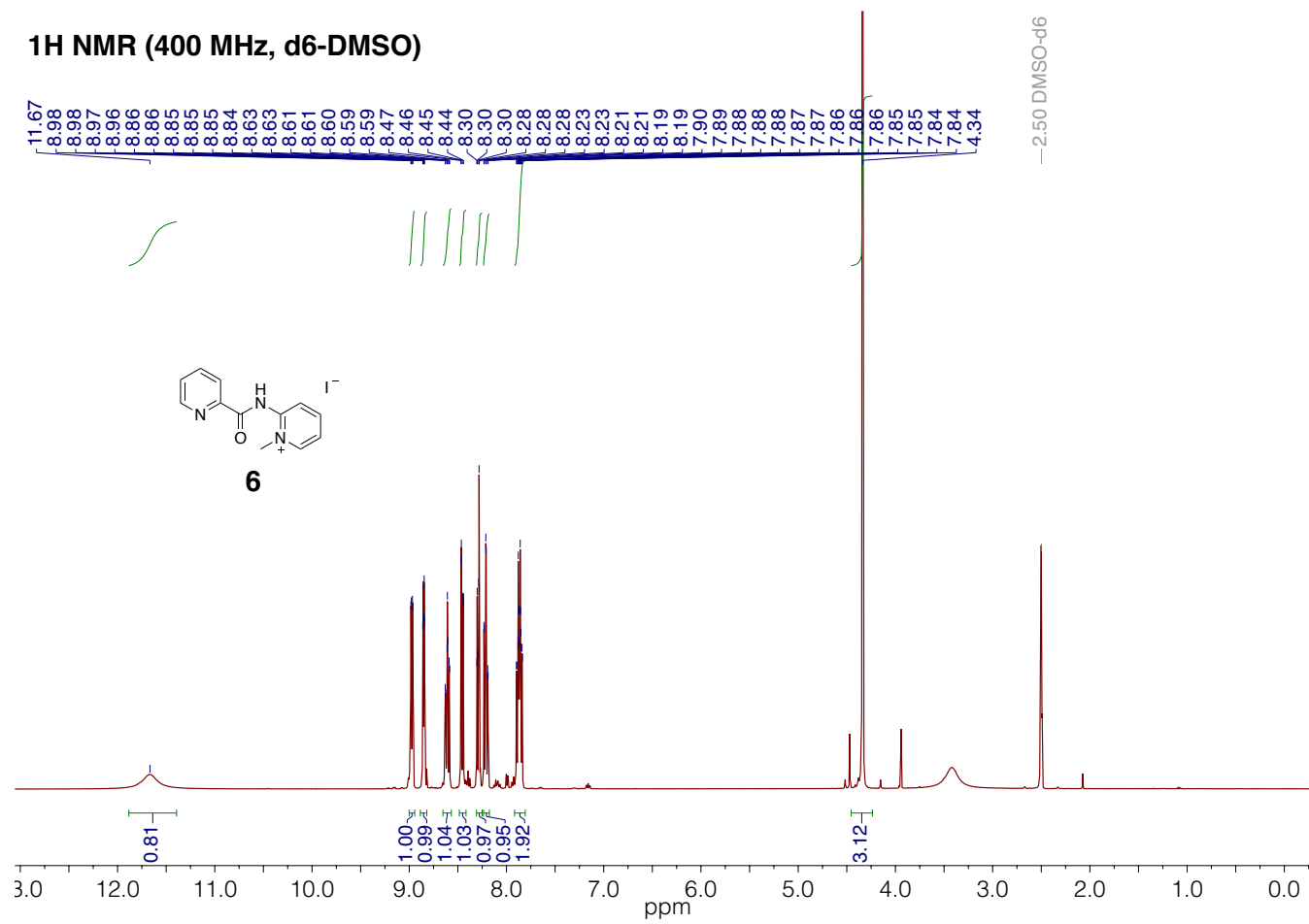
**Figure S2.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **4**.



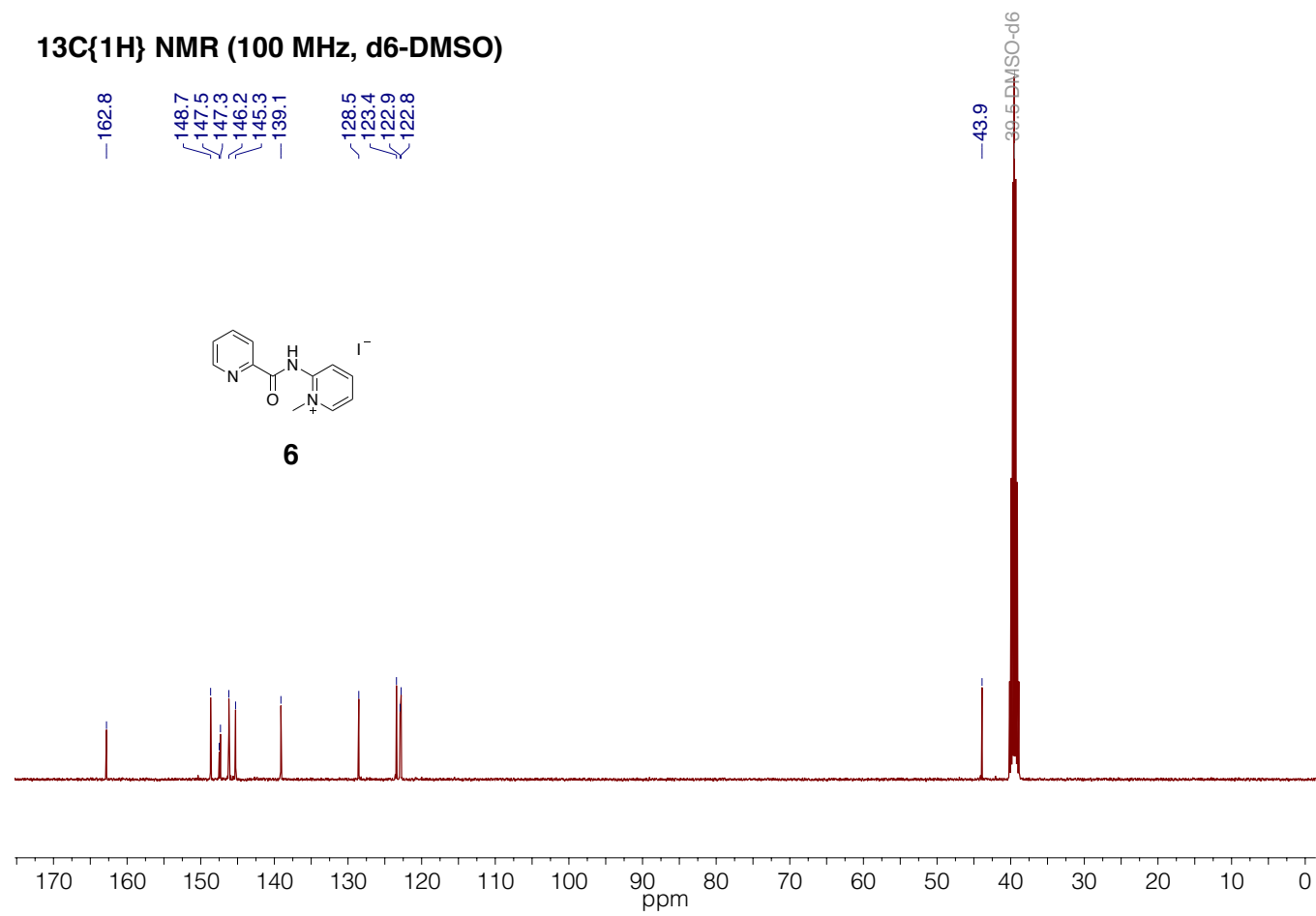
**Figure S3.** <sup>1</sup>H NMR spectrum of compound **5**.



**Figure S4.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **5**.

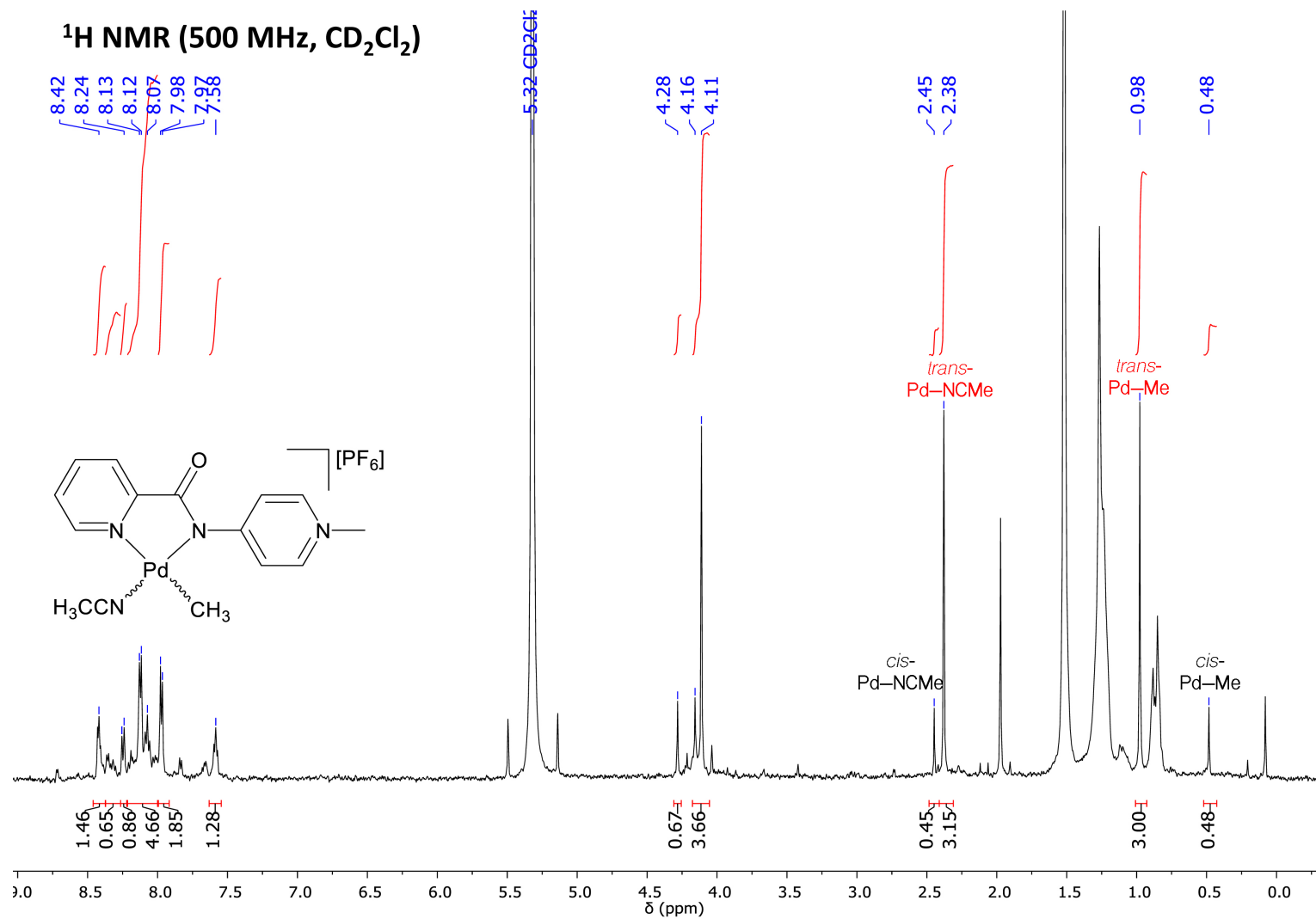


**Figure S5.** <sup>1</sup>H NMR spectrum of compound **6**.

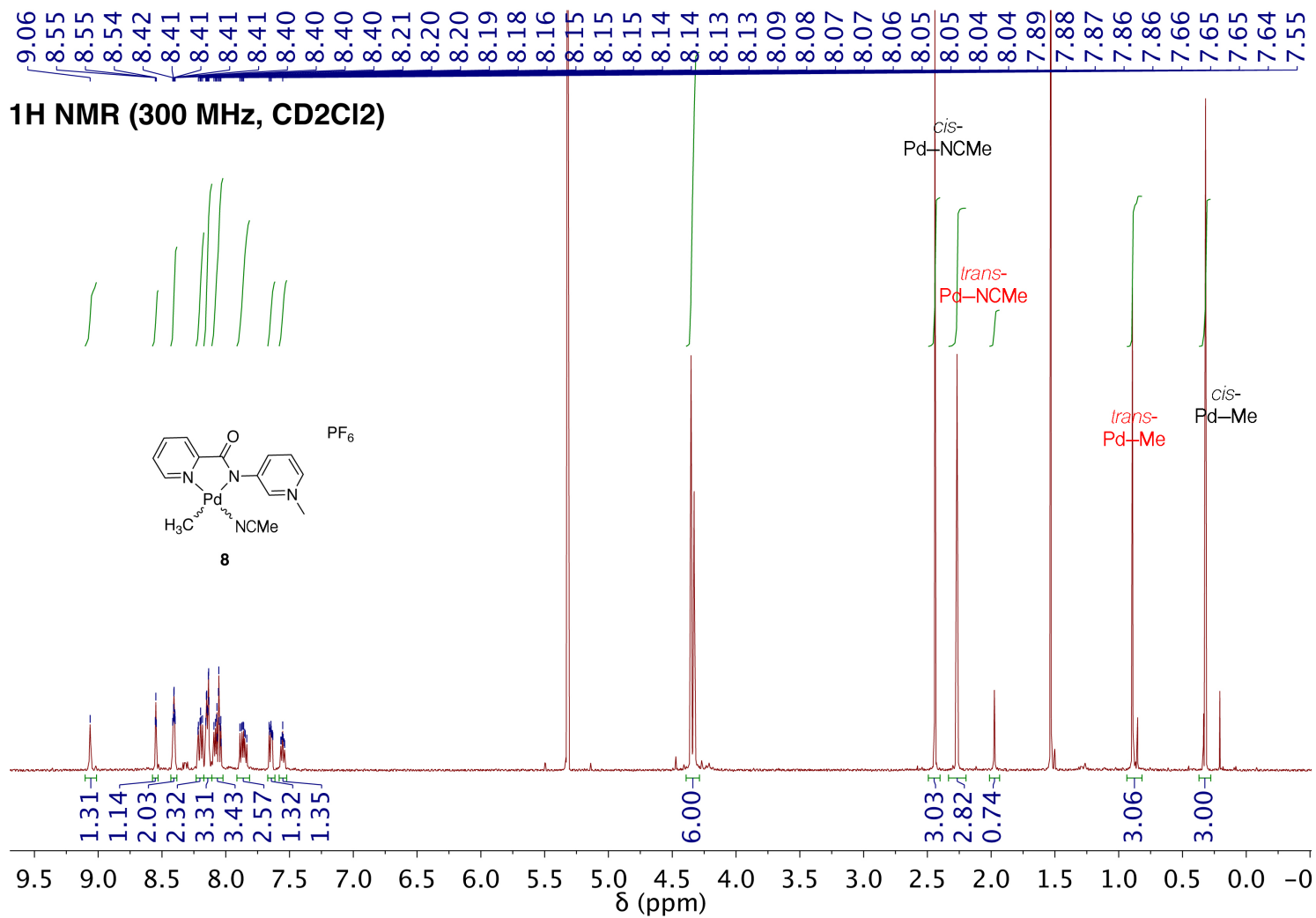


**Figure S6.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **6**.



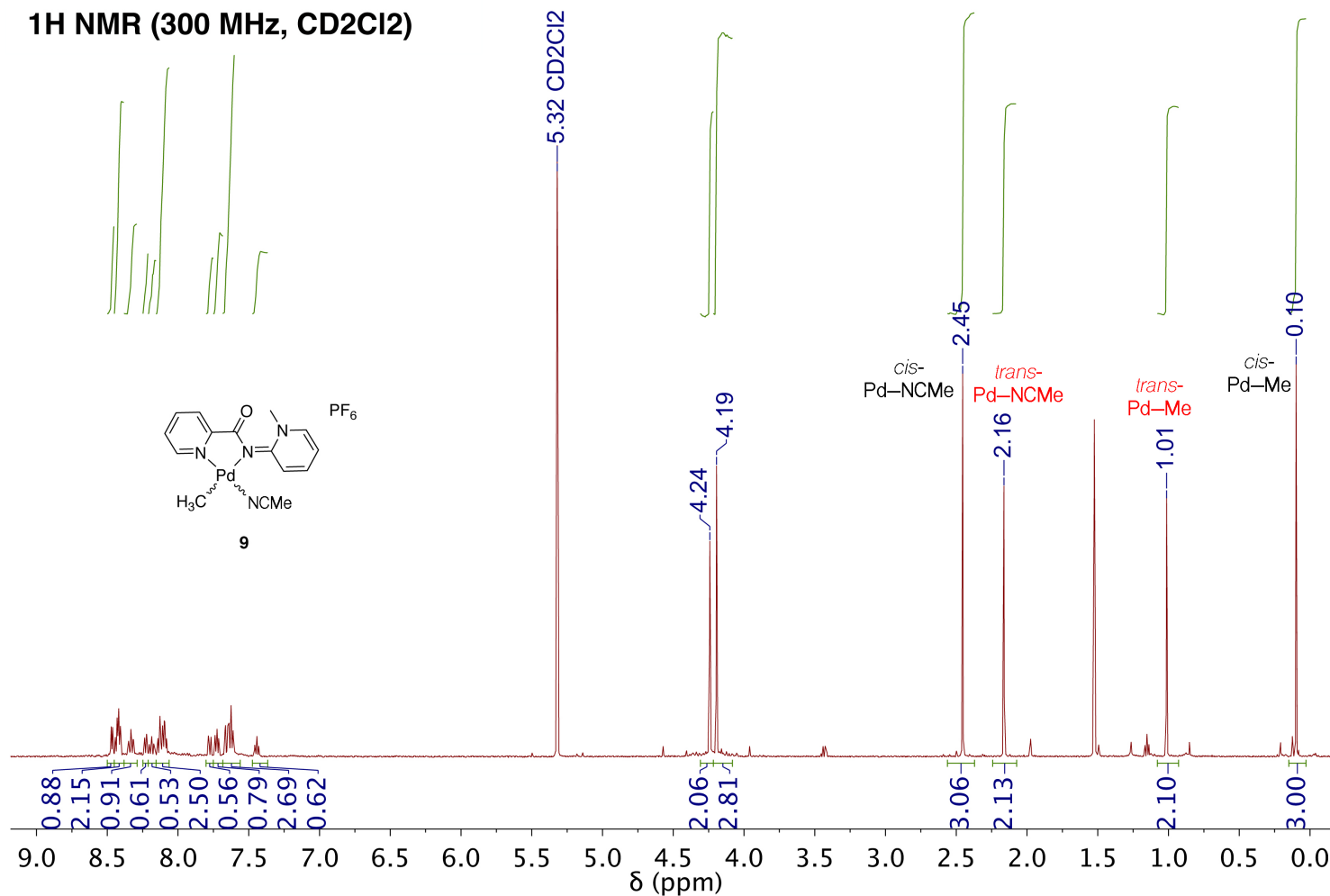


**Figure S7.**  $^1\text{H}$  NMR spectrum of compound 7.

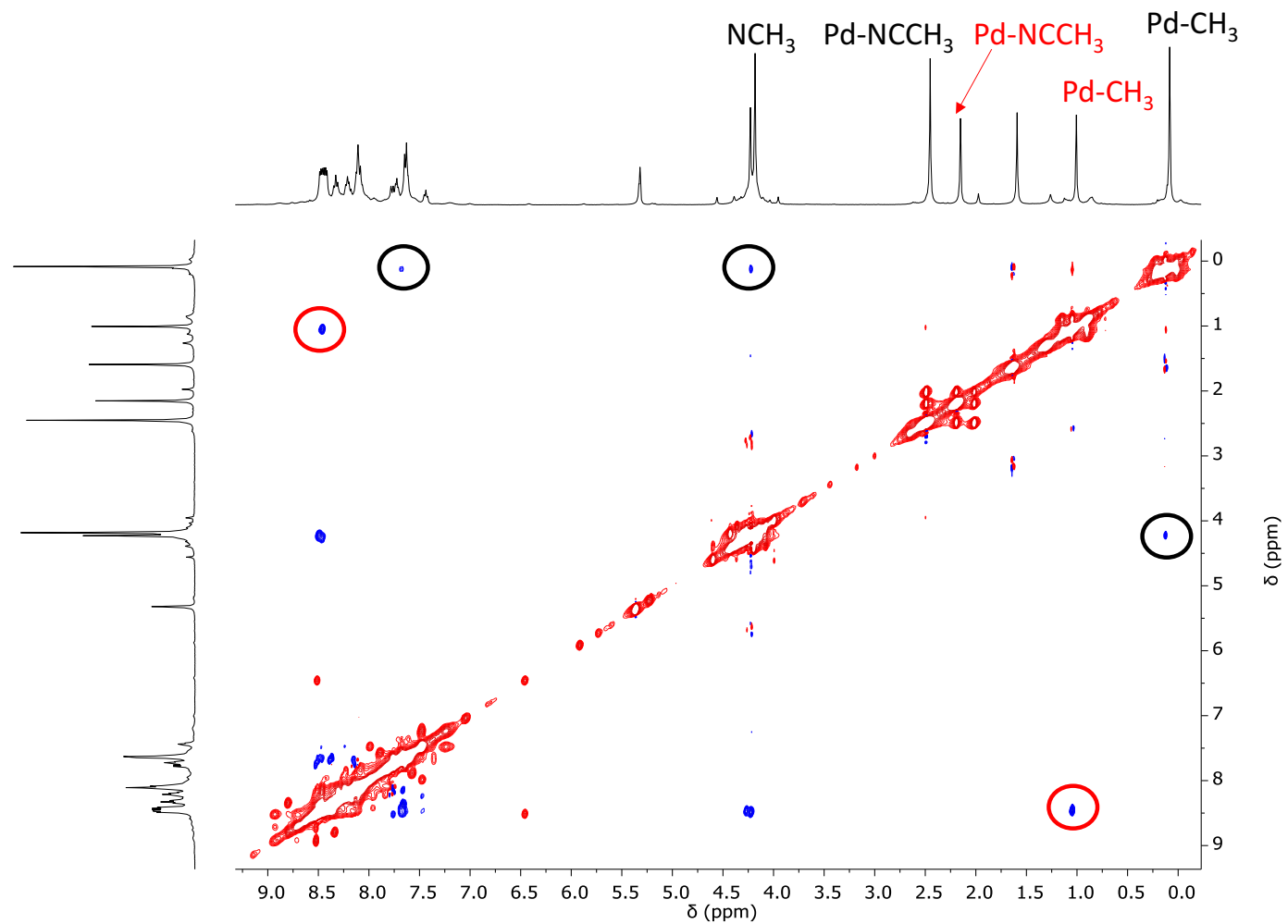


**Figure S8.** <sup>1</sup>H NMR spectrum of compound **8**.

**<sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>)**

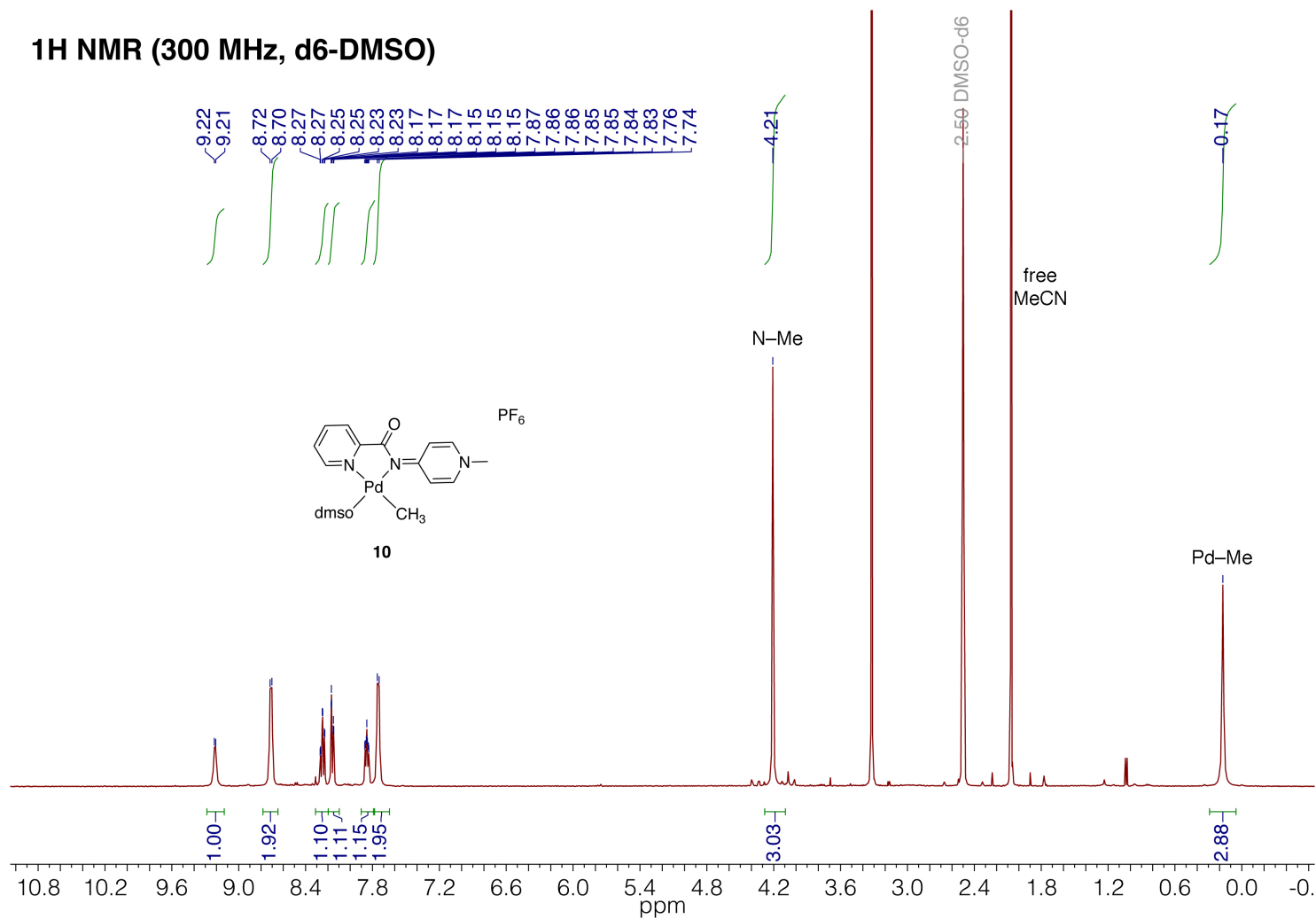


**Figure S9.** <sup>1</sup>H NMR spectrum of compound **9**.



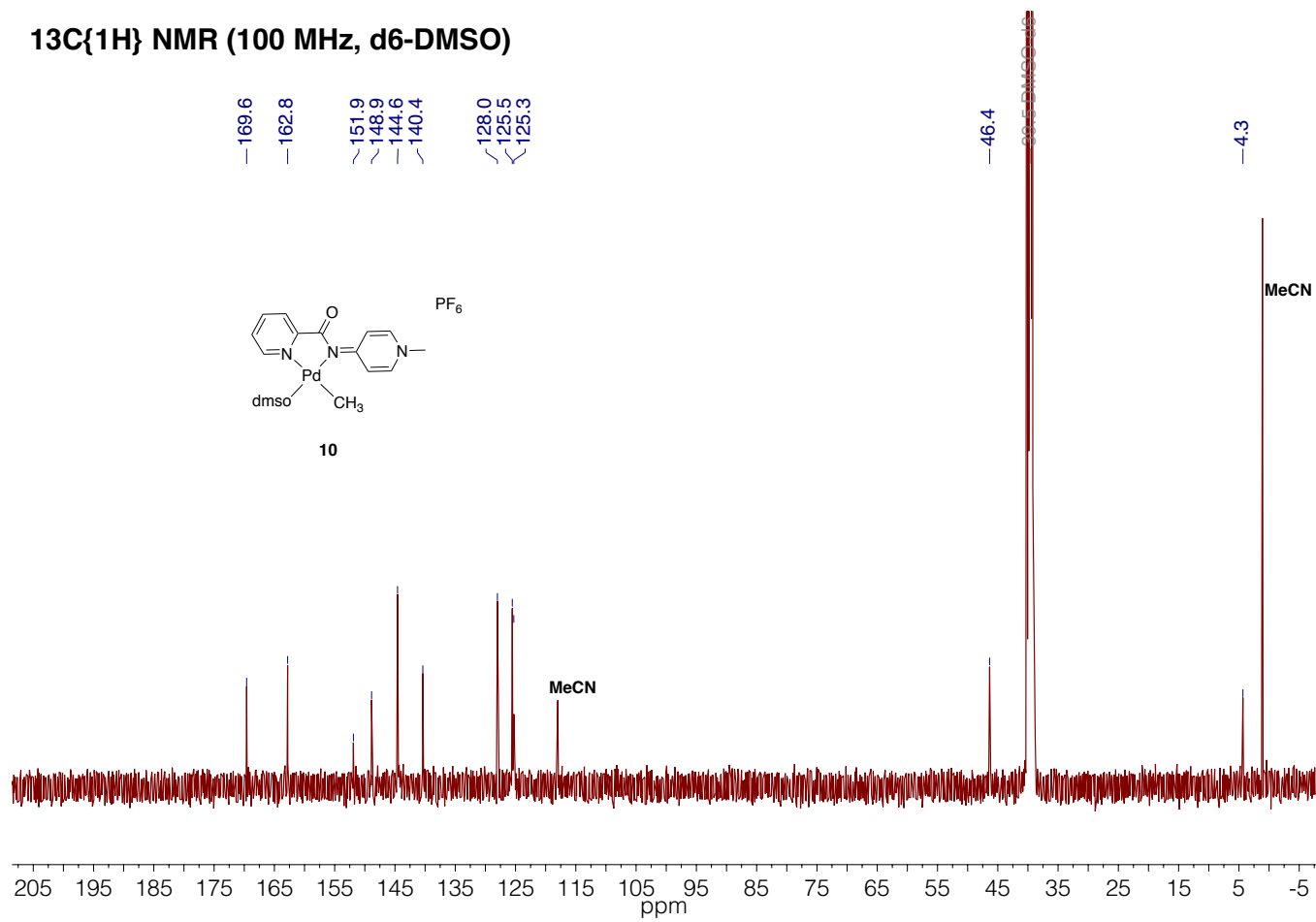
**Figure S10.** NOESY spectrum of complex **9** showing the presence of the *cis* isomer (black) and the *trans* isomer (red) and the related NOE peaks (circled in the same colors).

**<sup>1</sup>H NMR (300 MHz, d6-DMSO)**



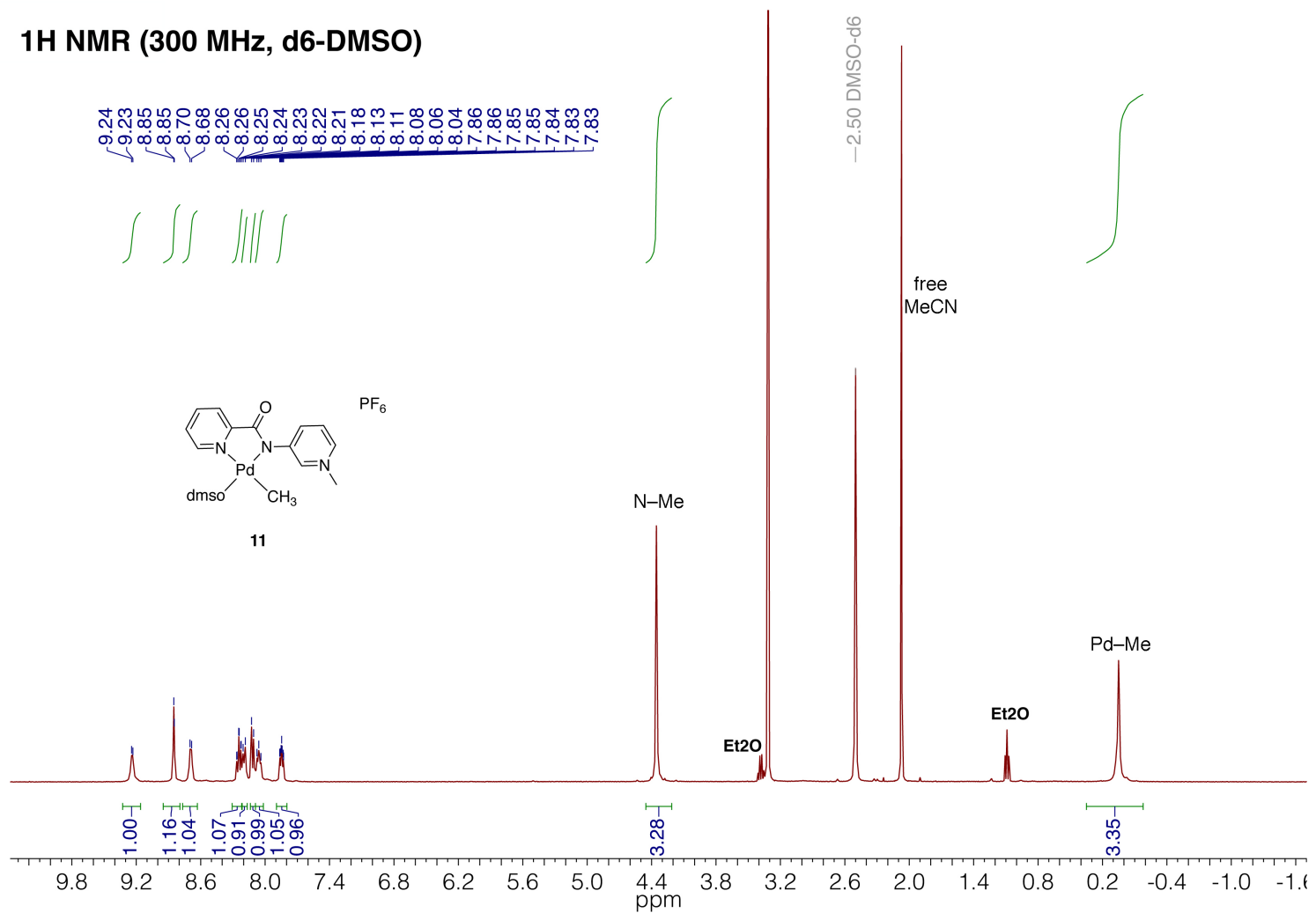
**Figure S11.** <sup>1</sup>H NMR spectrum of compound **10**.

**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{d}_6\text{-DMSO}$ )**



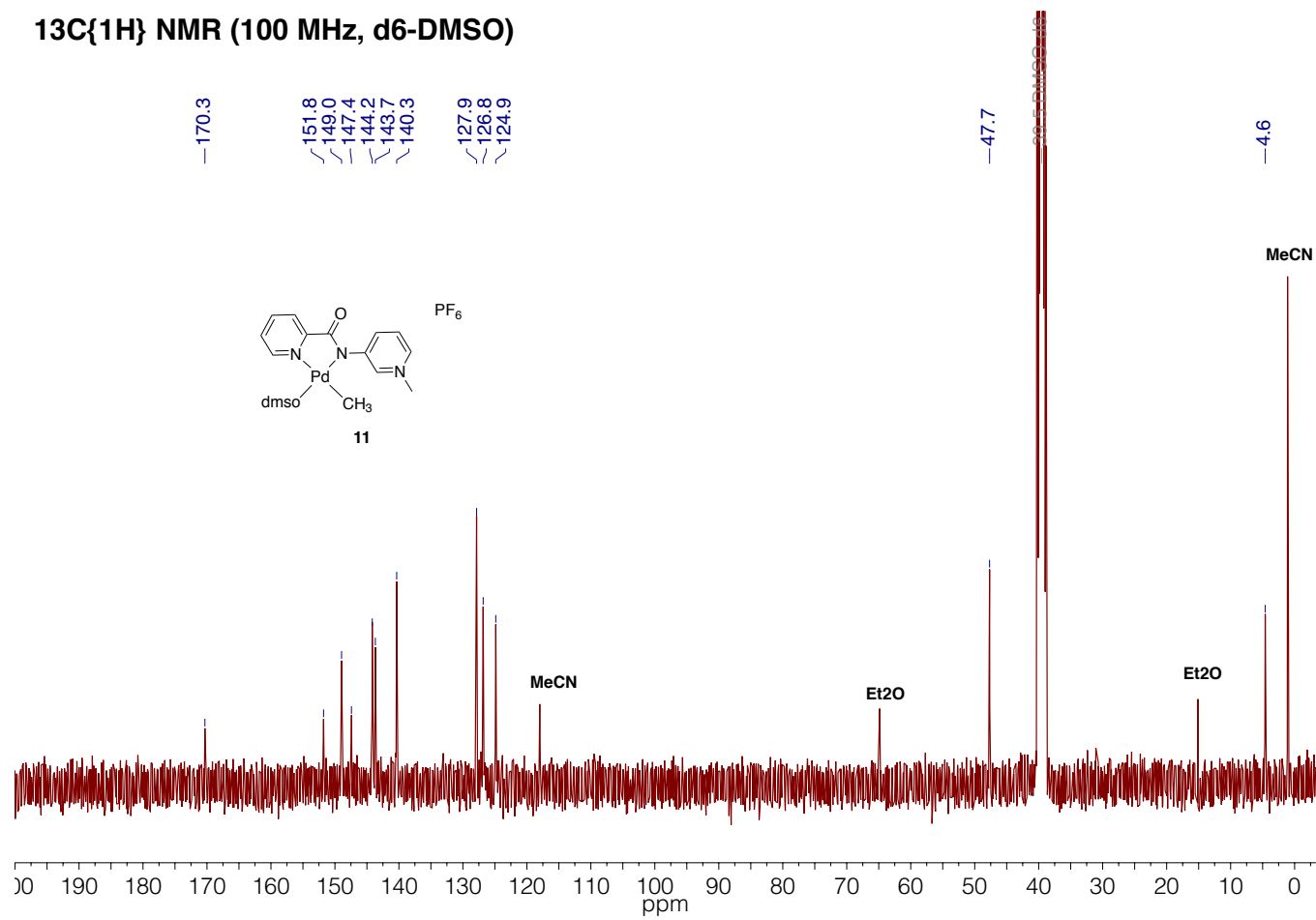
**Figure S12.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **10**.

**<sup>1</sup>H NMR (300 MHz, d6-DMSO)**



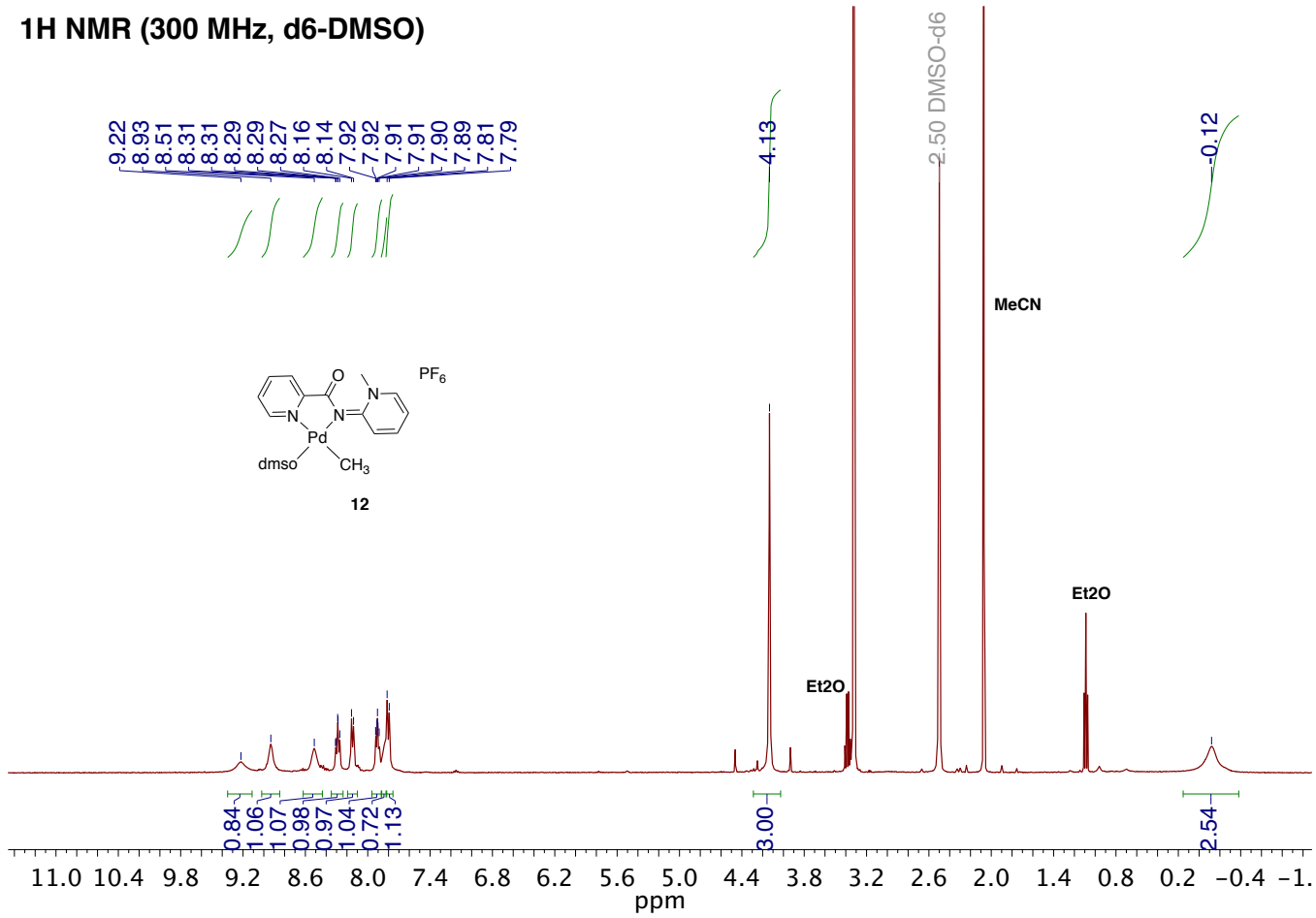
**Figure S13.** <sup>1</sup>H NMR spectrum of compound **11**.

**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{d}_6\text{-DMSO}$ )**



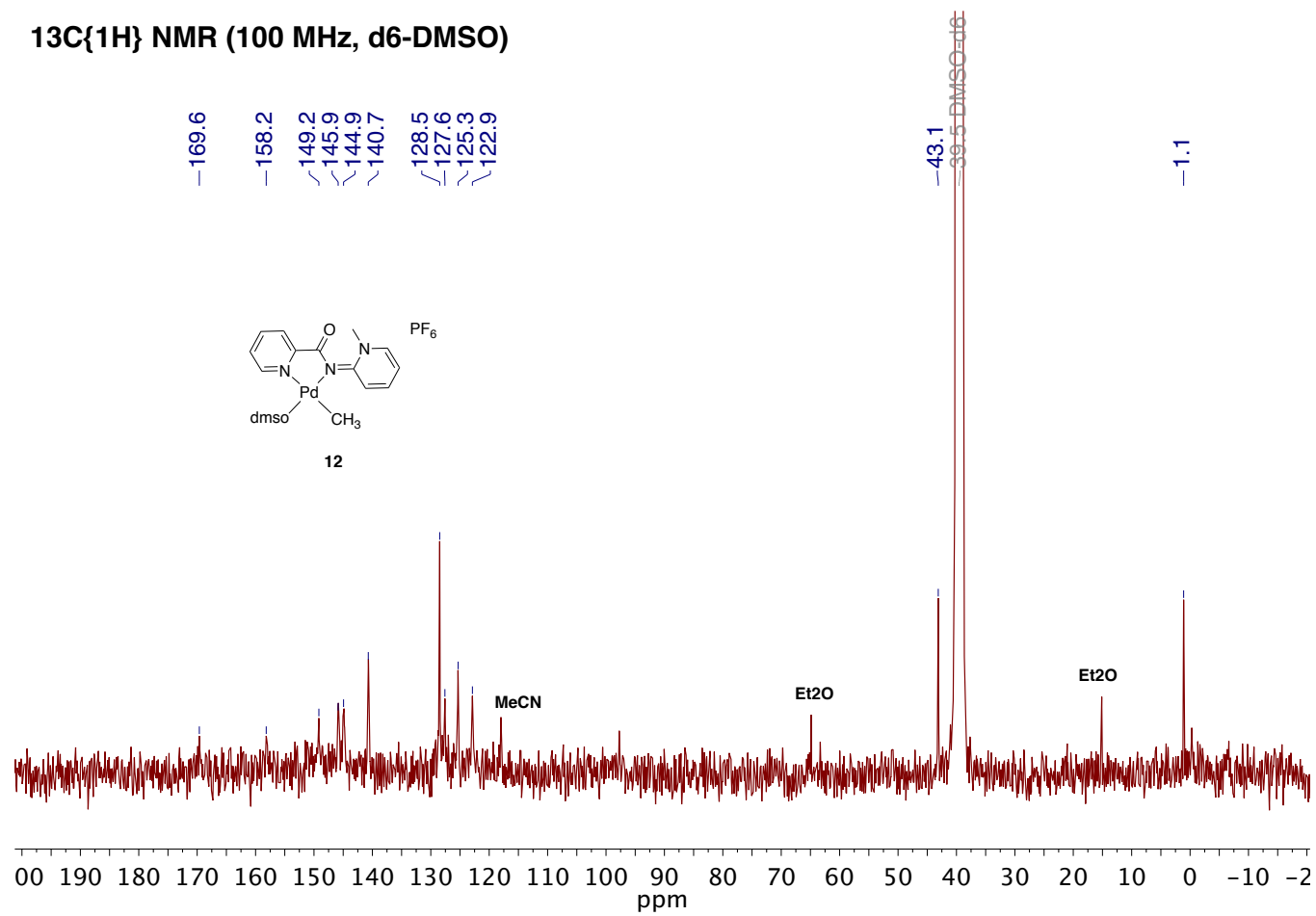
**Figure S14.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **11**.





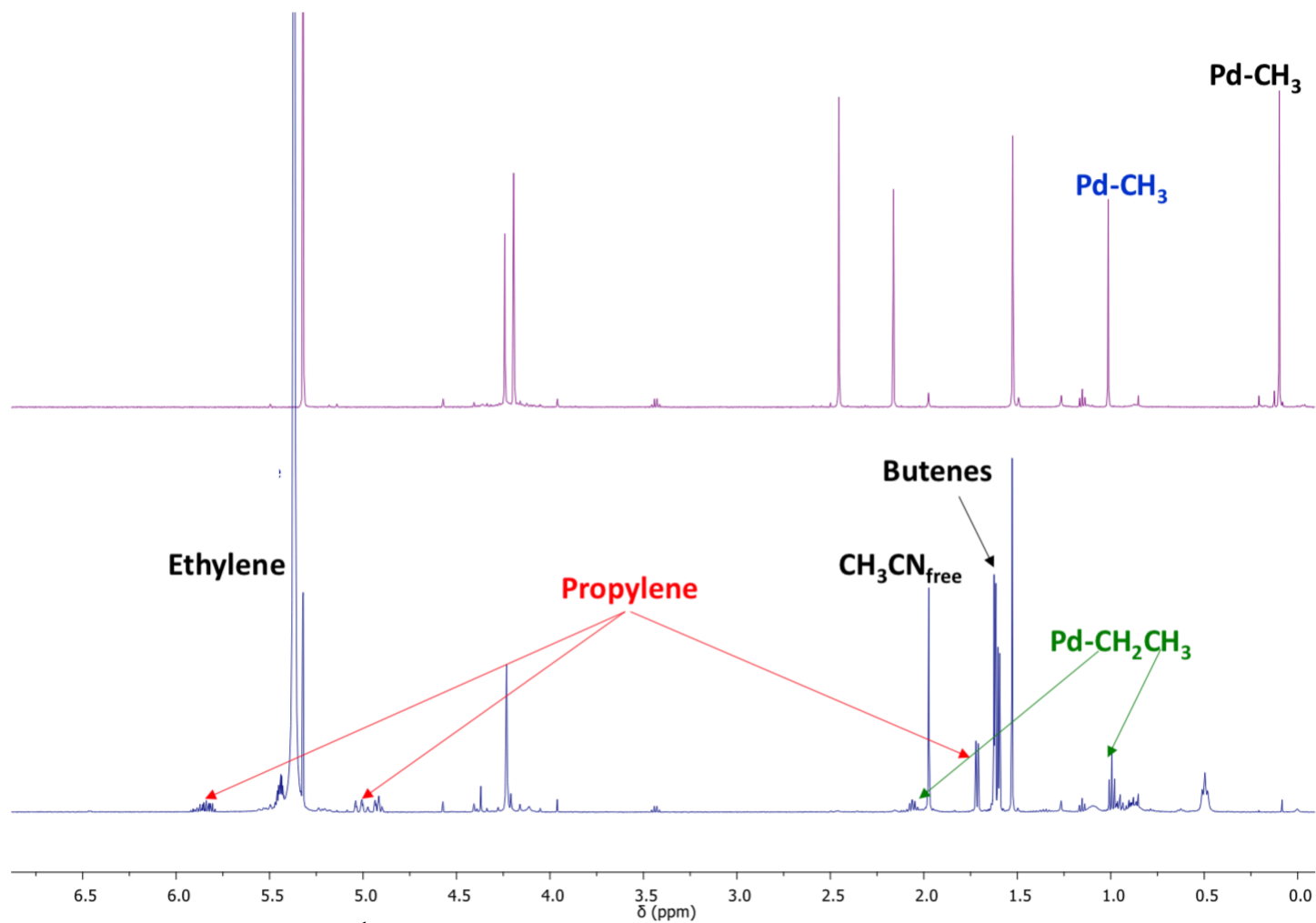
**Figure S15.** <sup>1</sup>H NMR spectrum of compound **12**.

**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{d}_6\text{-DMSO}$ )**

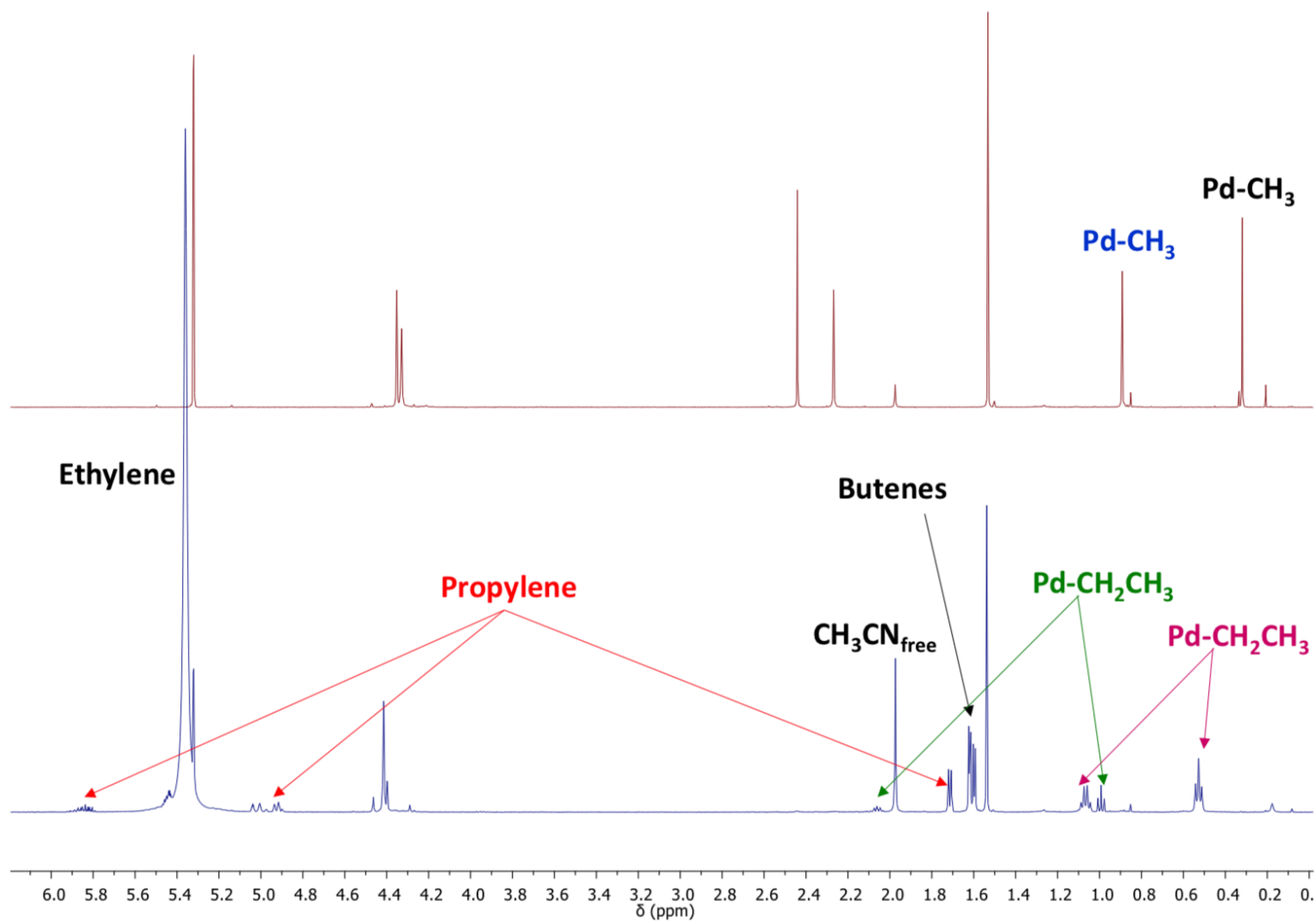


**Figure S16.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound 12.

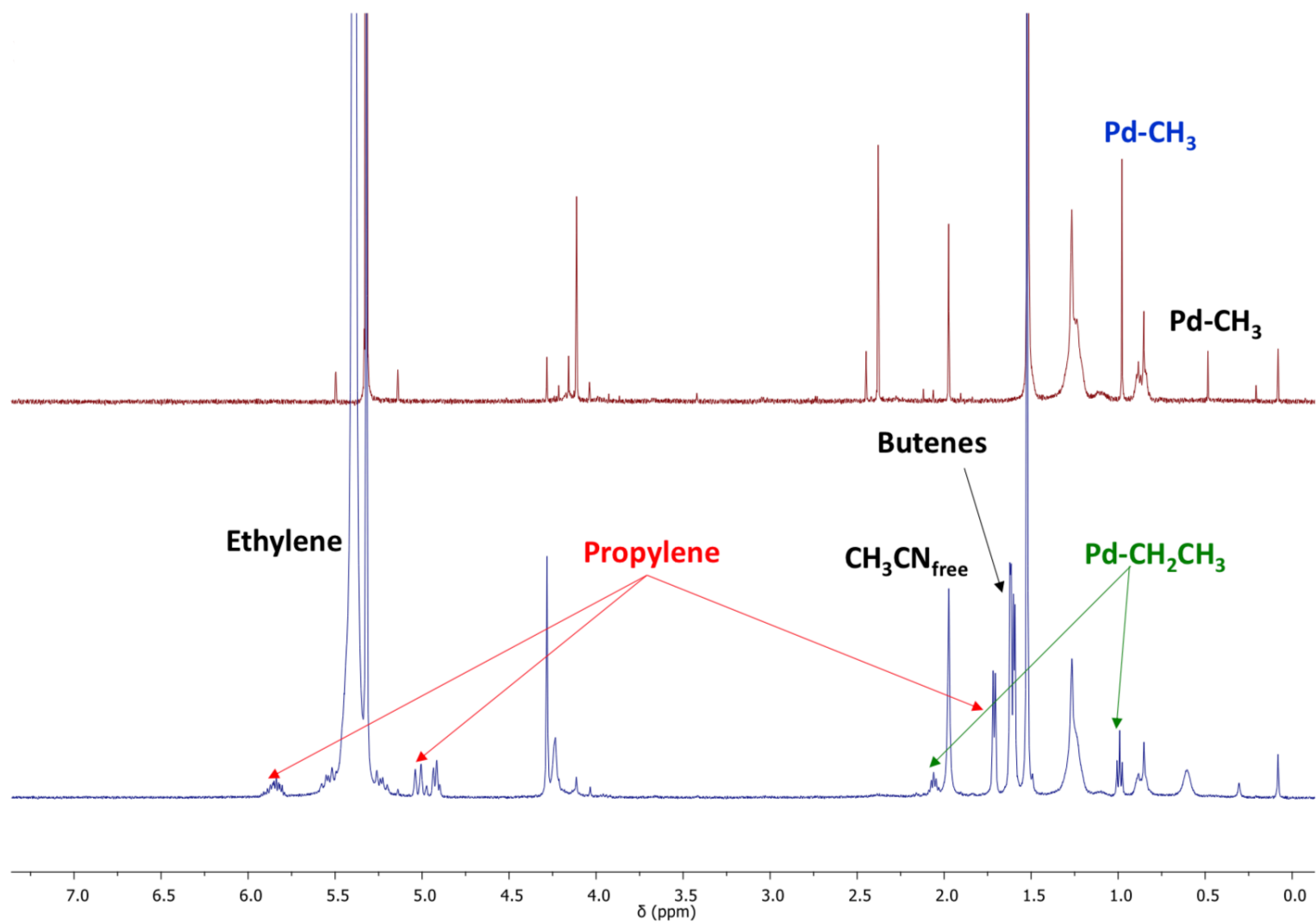
### 3. Analytical data pertaining to catalytic experiments



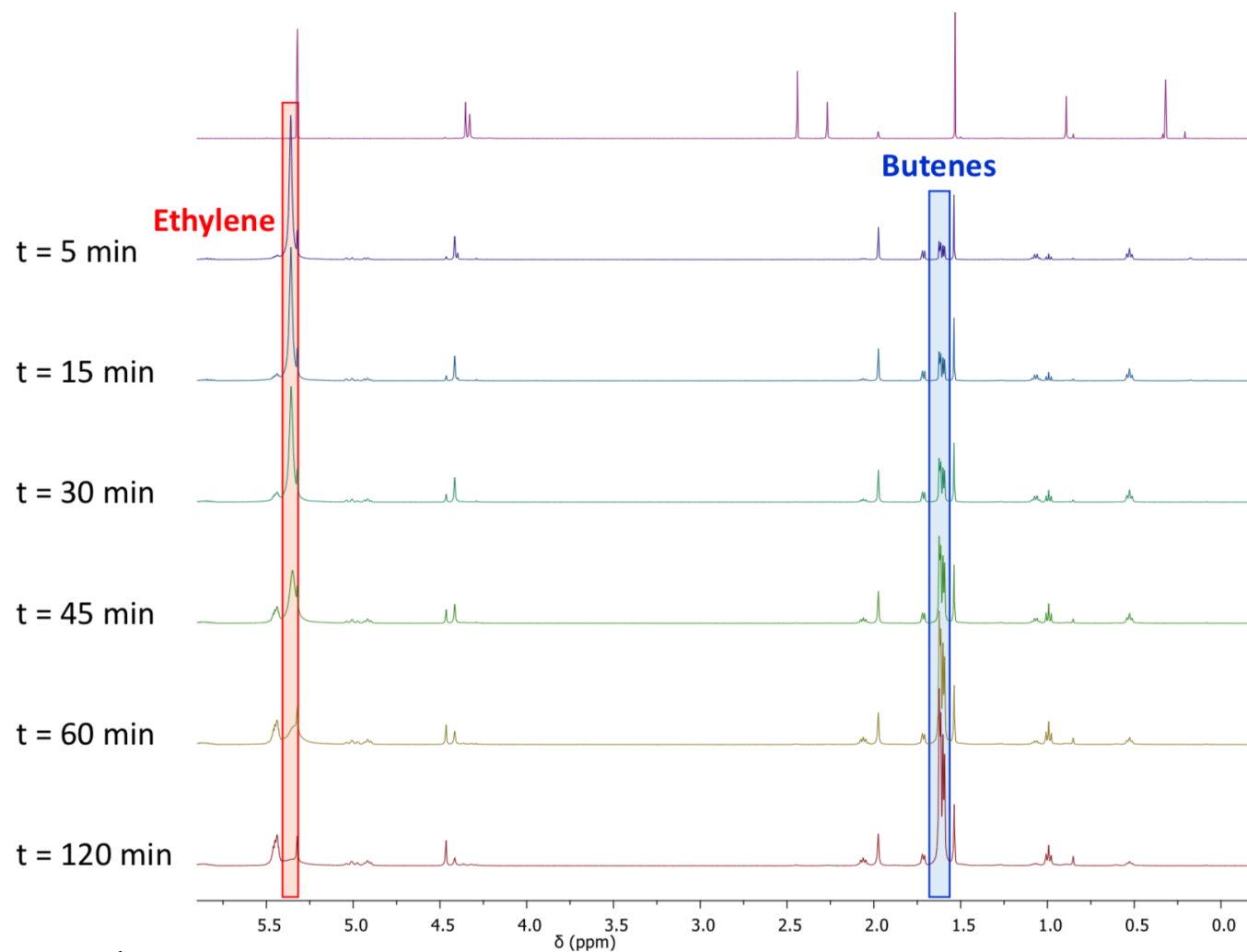
**Figure S17.** Selected region of  $^1\text{H}$  NMR spectrum of complex **7** before addition of ethylene (top) and five minutes after addition (bottom).



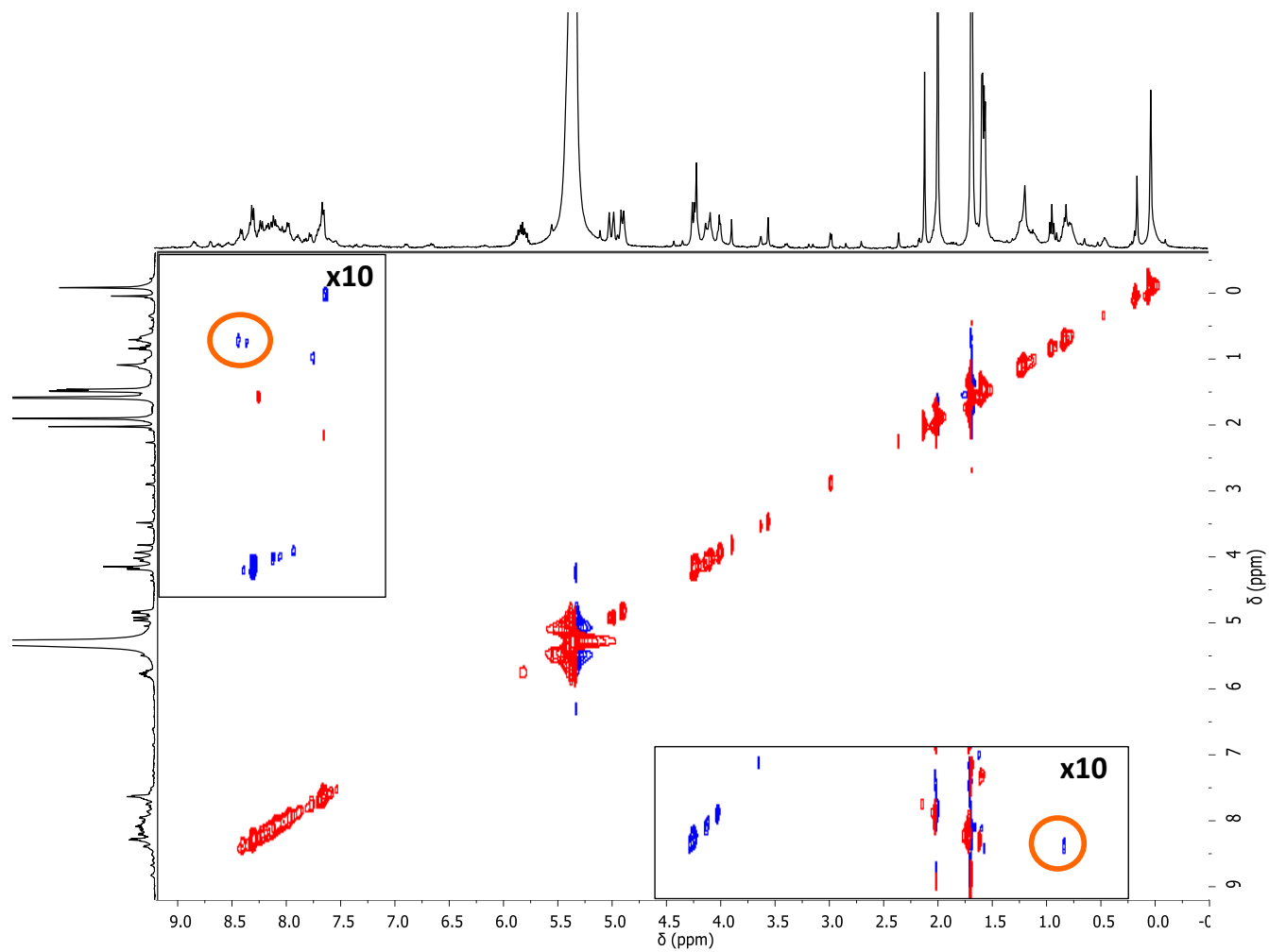
**Figure S18.** Selected region of  $^1\text{H}$  NMR spectrum of complex **8** before addition of ethylene (top) and five minutes after addition (bottom).



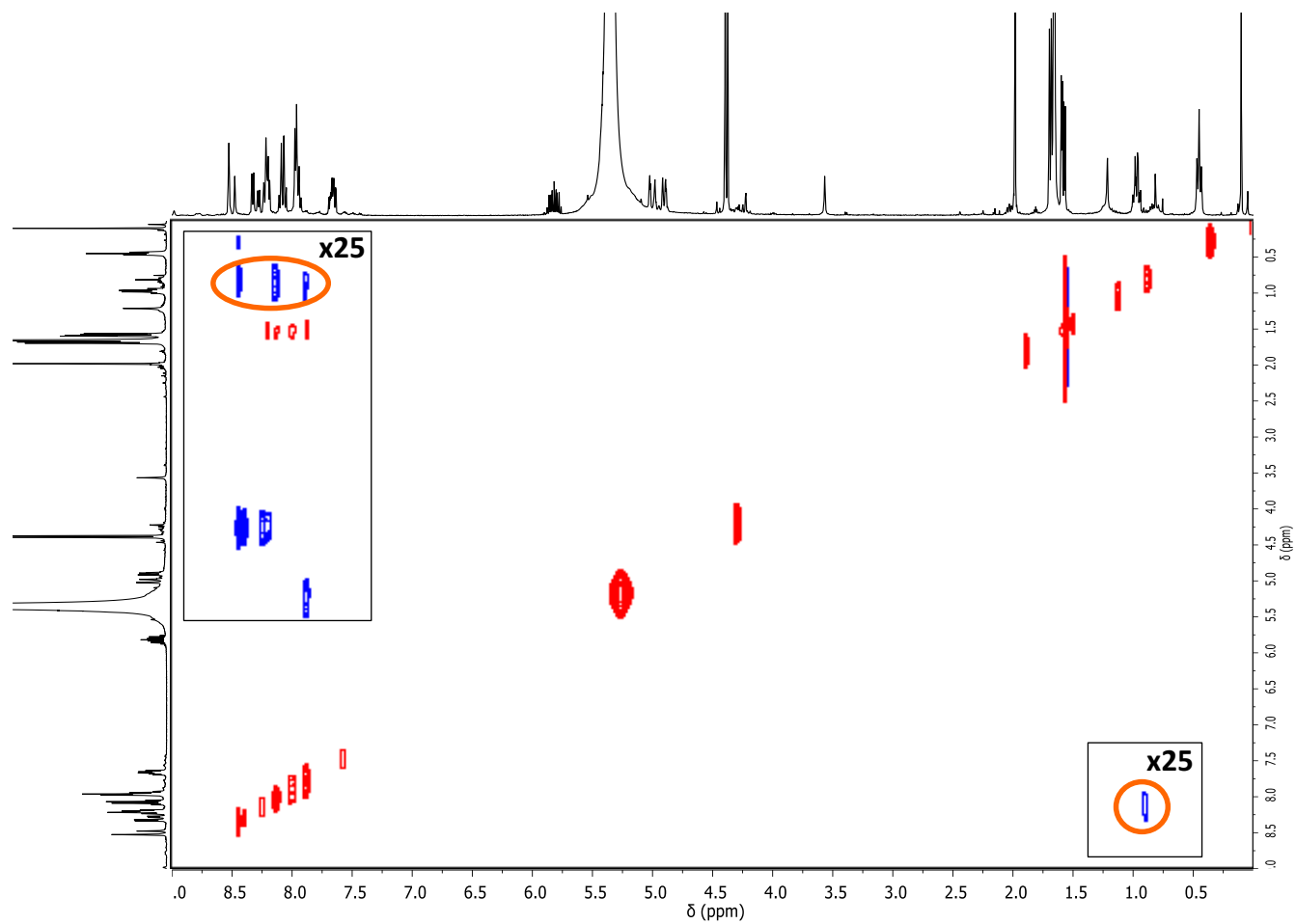
**Figure S19.** Selected region of <sup>1</sup>H NMR spectrum of complex 9 before addition of ethylene (top) and five minutes after addition (bottom).



**Figure S20.** Section of the  $^1\text{H}$  NMR spectrum from the catalytic dimerization of ethylene catalyzed by complex **8** in a NMR tube showing the time-dependent consumption of ethylene (red box) and the evolution of butenes (blue box).

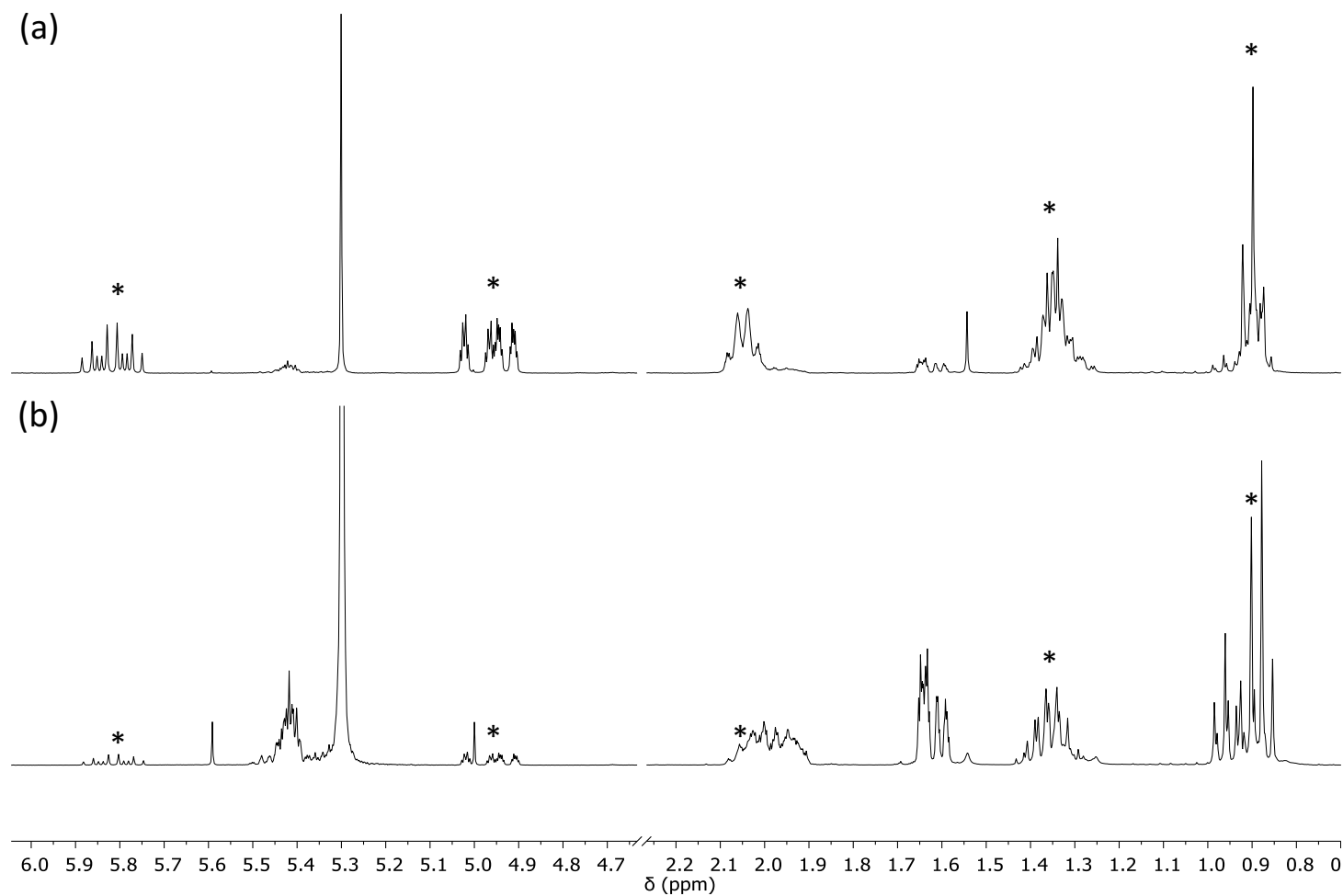


**Figure S21.** NOESY spectrum of the *in situ* reactivity of complex **7** with ethylene in a NMR tube in CD<sub>2</sub>Cl<sub>2</sub> at -50°C. Zoom in of the areas of interest in the boxes.

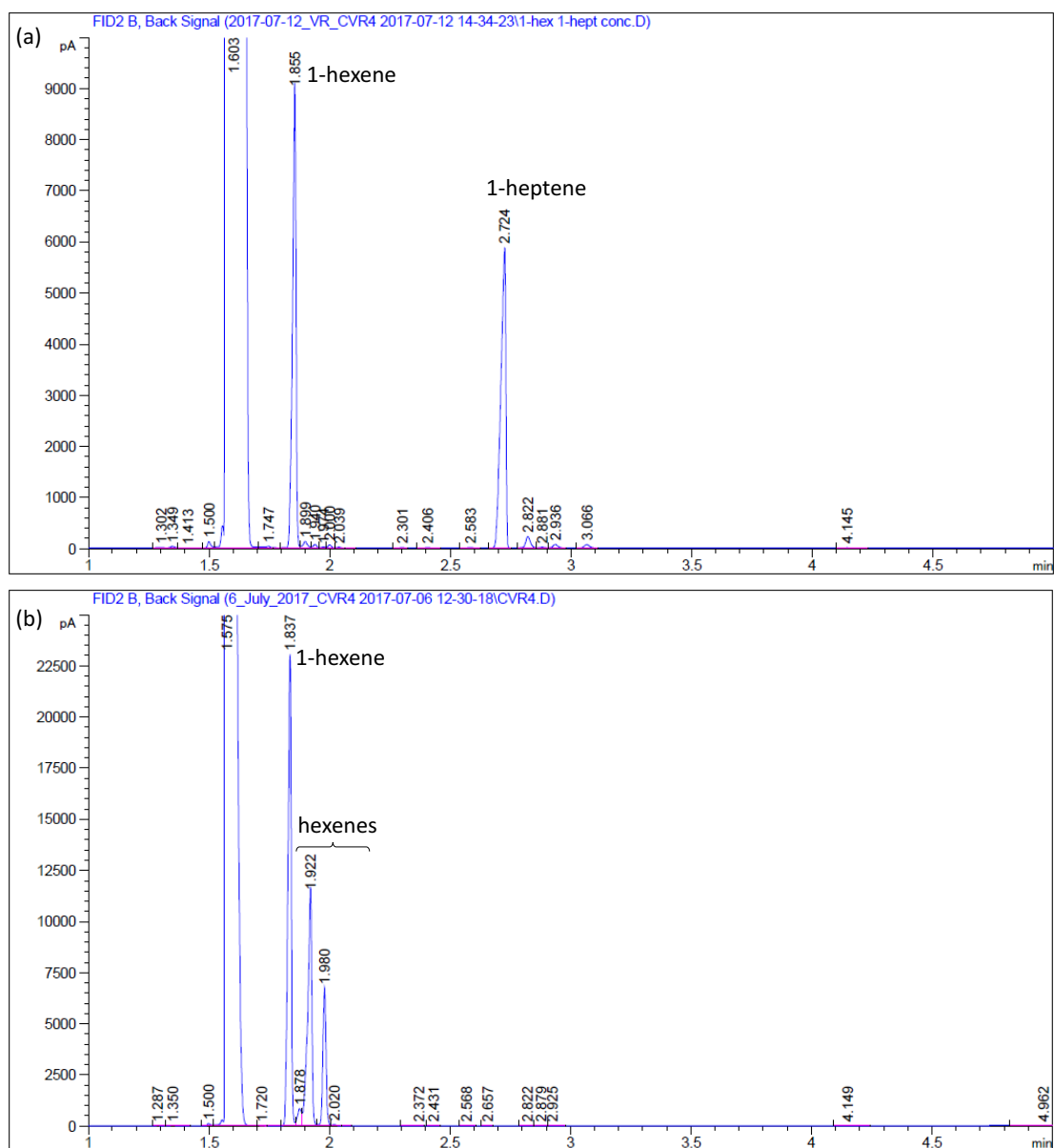


**Figure S22.** NOESY spectrum of the *in situ* reactivity of complex **8** with ethylene in a NMR tube in  $\text{CD}_2\text{Cl}_2$  at  $-30^\circ\text{C}$ . Zoom in of the areas of interest in the boxes.

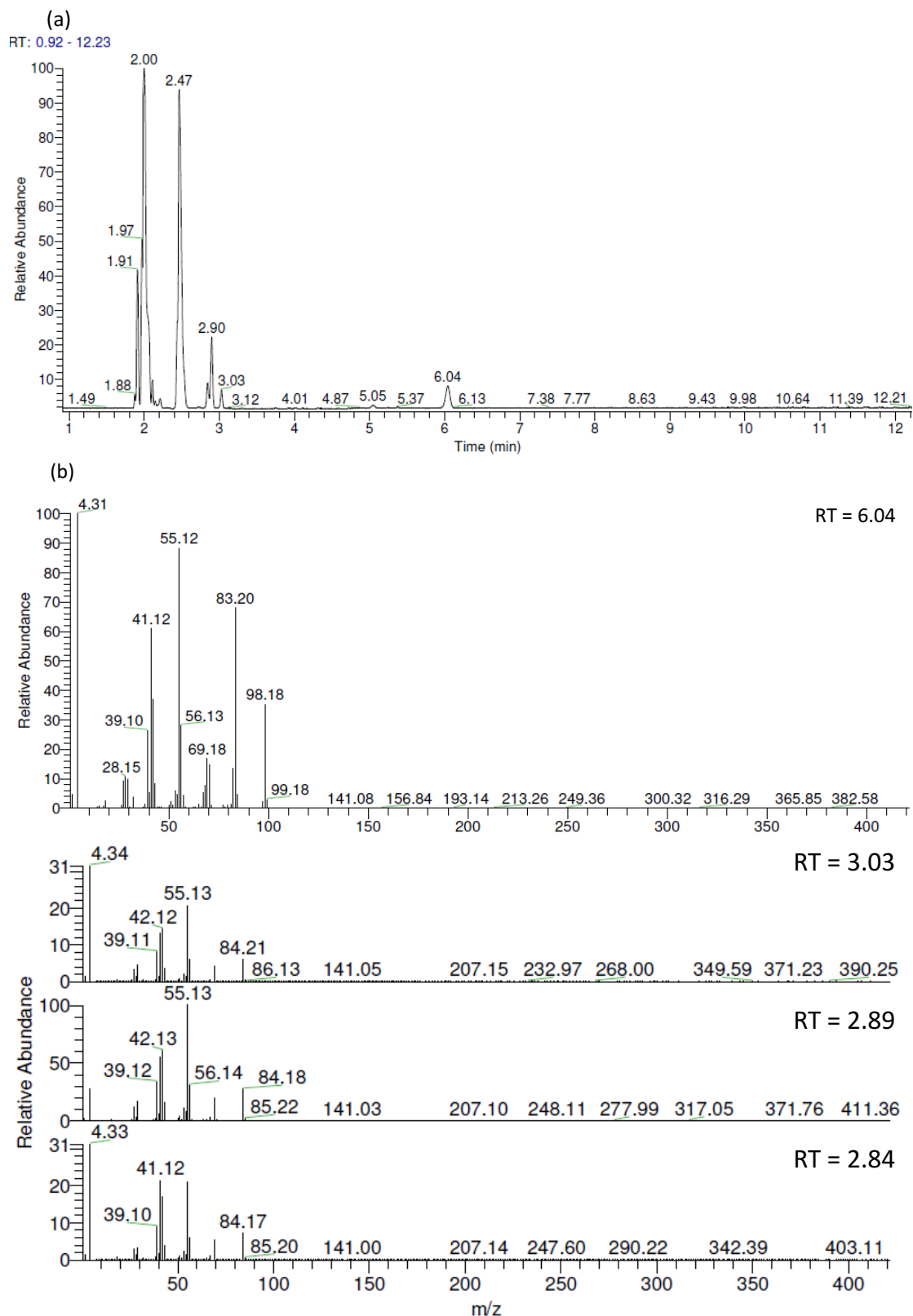




**Figure S23.**  $^1\text{H}$  NMR spectra of crude reaction mixture of 1-hexene dimerization catalysis obtained with complex **9** with 0.01 mol% (a) and 0.1 mol% catalyst loading (b). \* 1-hexene.



**Figure S24.** GC analysis of (a) fresh mixture of commercial 1-hexene and 1-heptene; (b) crude reaction mixture of 1-hexene dimerization with 0.1 mol% of precatalyst **9**.



**Figure S25.** GC-MS analysis of the reaction mixture of 1-hexene dimerization with 10 mol% of precatalyst **9**: (a) full chromatogram; (b) mass spectra of most relevant peaks.