



Olefin Dimerization and Isomerization Catalyzed by Pyridylidene Amide Palladium Complexes

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Original

Olefin Dimerization and Isomerization Catalyzed by Pyridylidene Amide Palladium Complexes / Navarro, M., Rosar, V., Montini, T., Milani, B., Albrecht, M.. - In: ORGANOMETALLICS. - ISSN 0276-7333. - ELETTRONICO. - 37:20(2018), pp. 3619-3630. [10.1021/acs.organomet.8b00422]

Availability:

This version is available at: 11368/2929577 since: 2018-10-22T13:26:32Z

Publisher:

Published

DOI:10.1021/acs.organomet.8b00422

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Olefin dimerization and isomerization catalyzed by pyridylideneamide palladium complexes

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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 ₁₅ H ₁₇ F ₆ N ₄ OPPd	
Molecular formula	[C ₁₅ H ₁₇ N ₄ OPd] ⁺ [PF ₆] [−]	
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 ³	
Z	4	
Density (calculated)	1.89 Mg m ^{−3}	
Absorption coefficient	1.174 mm ^{−1}	
F(000)	1032	
Crystal size	0.207 x 0.162 x 0.023 mm ³	
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 ²	
Data / restraints / parameters	4128 / 387 / 320	
Goodness-of-fit on F ²	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 ^{−3}	

2. NMR spectra of all new compounds

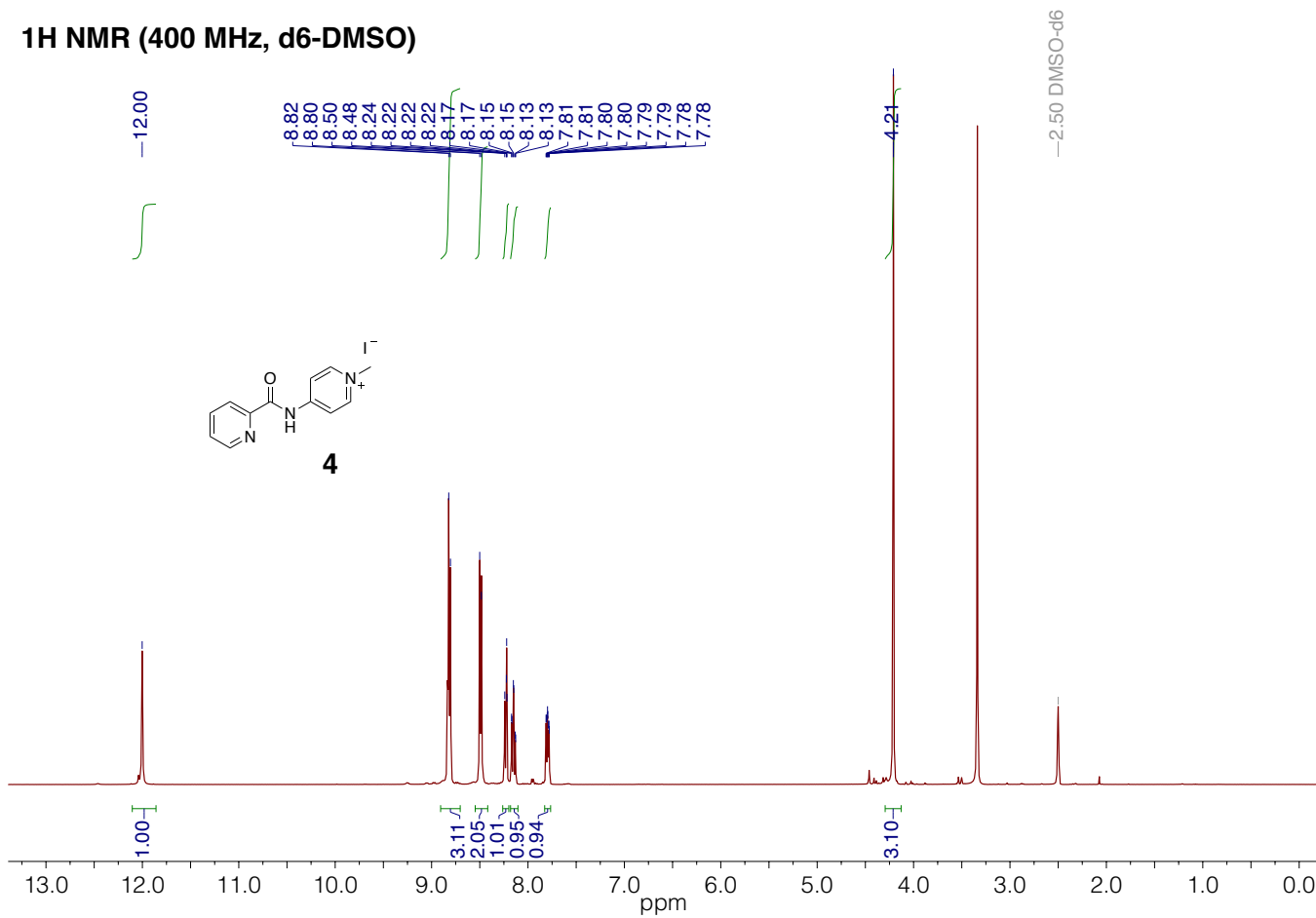


Figure S1. ¹H NMR spectrum of compound **4**.

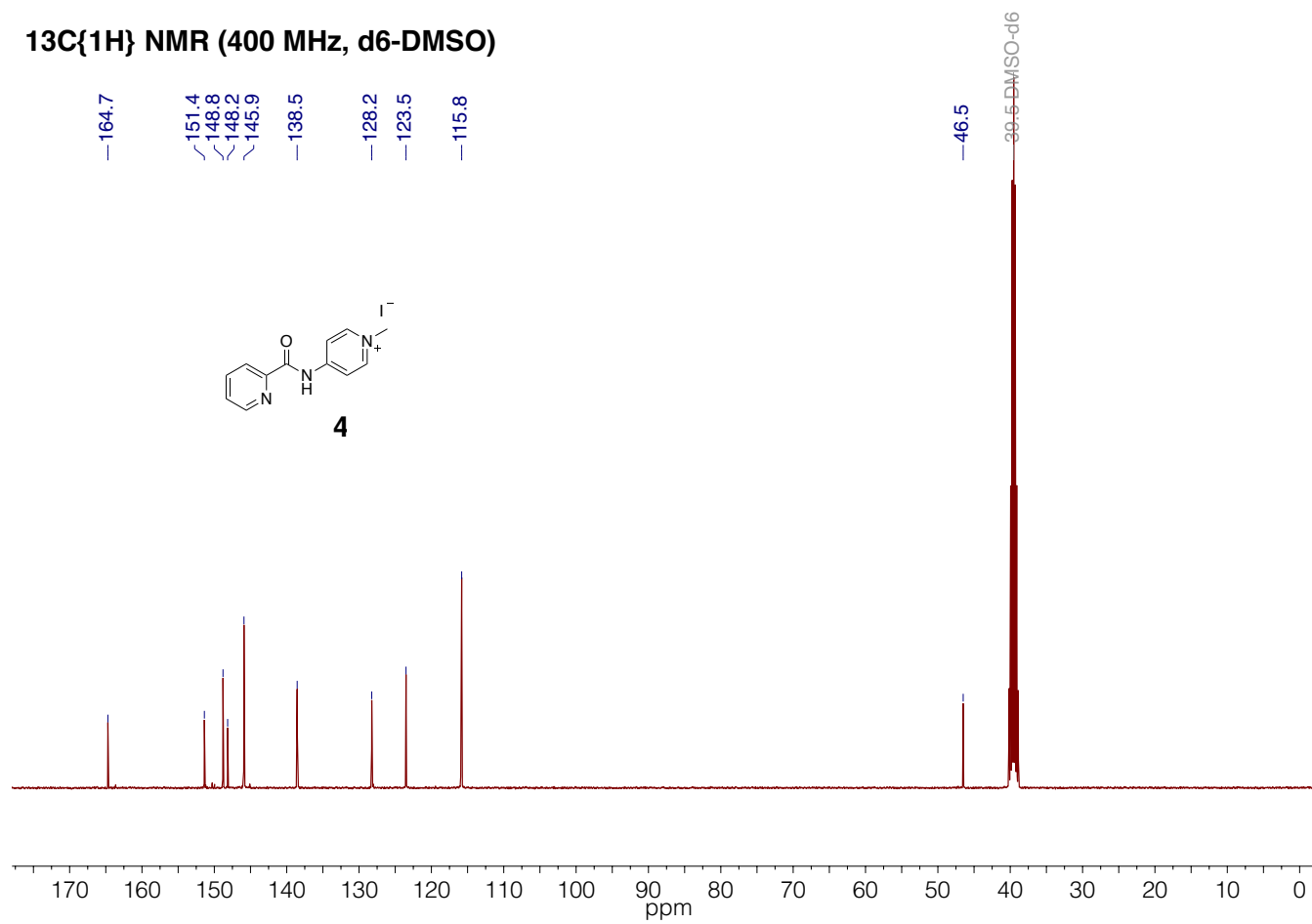


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **4**.

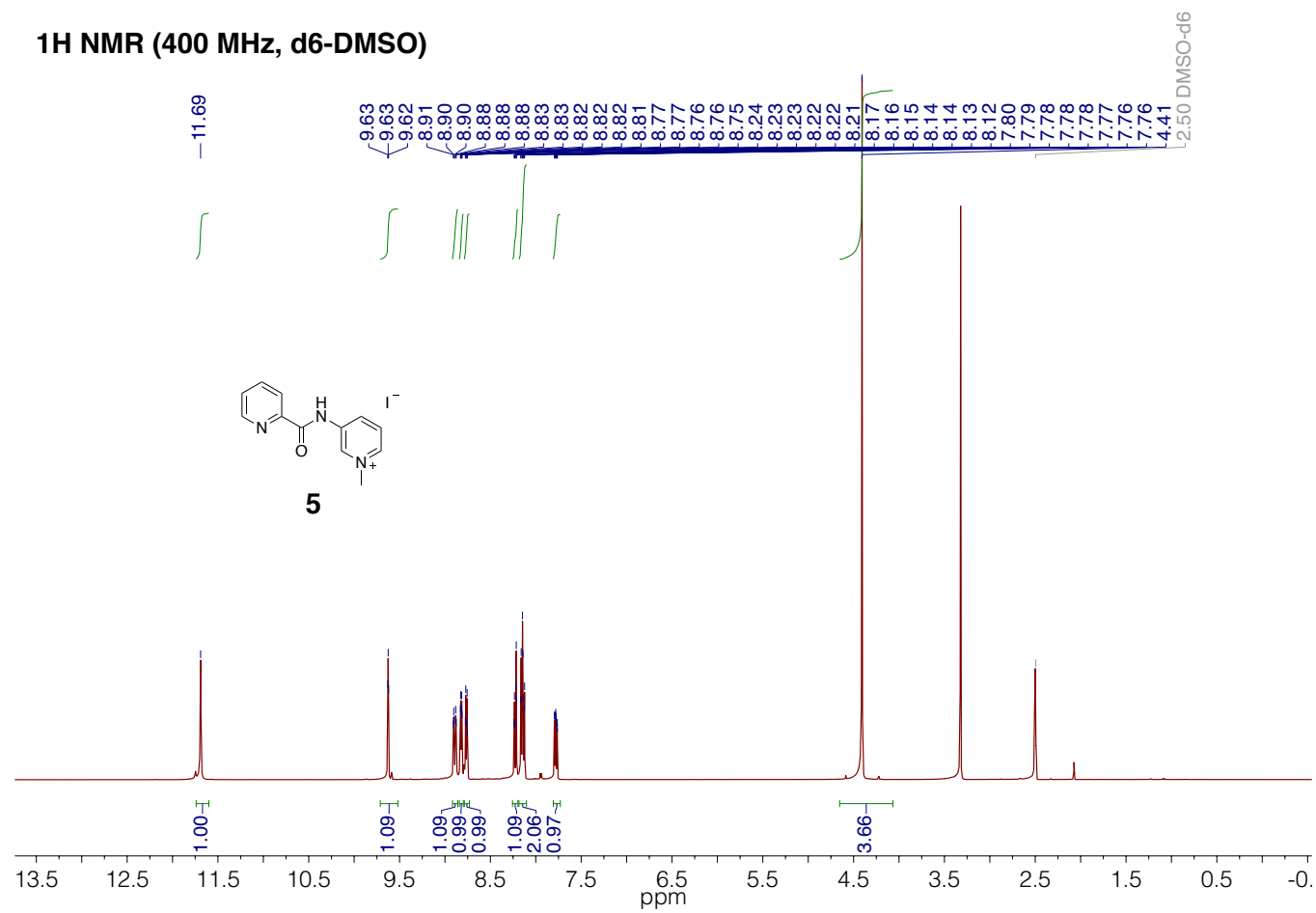


Figure S3. ¹H NMR spectrum of compound **5**.

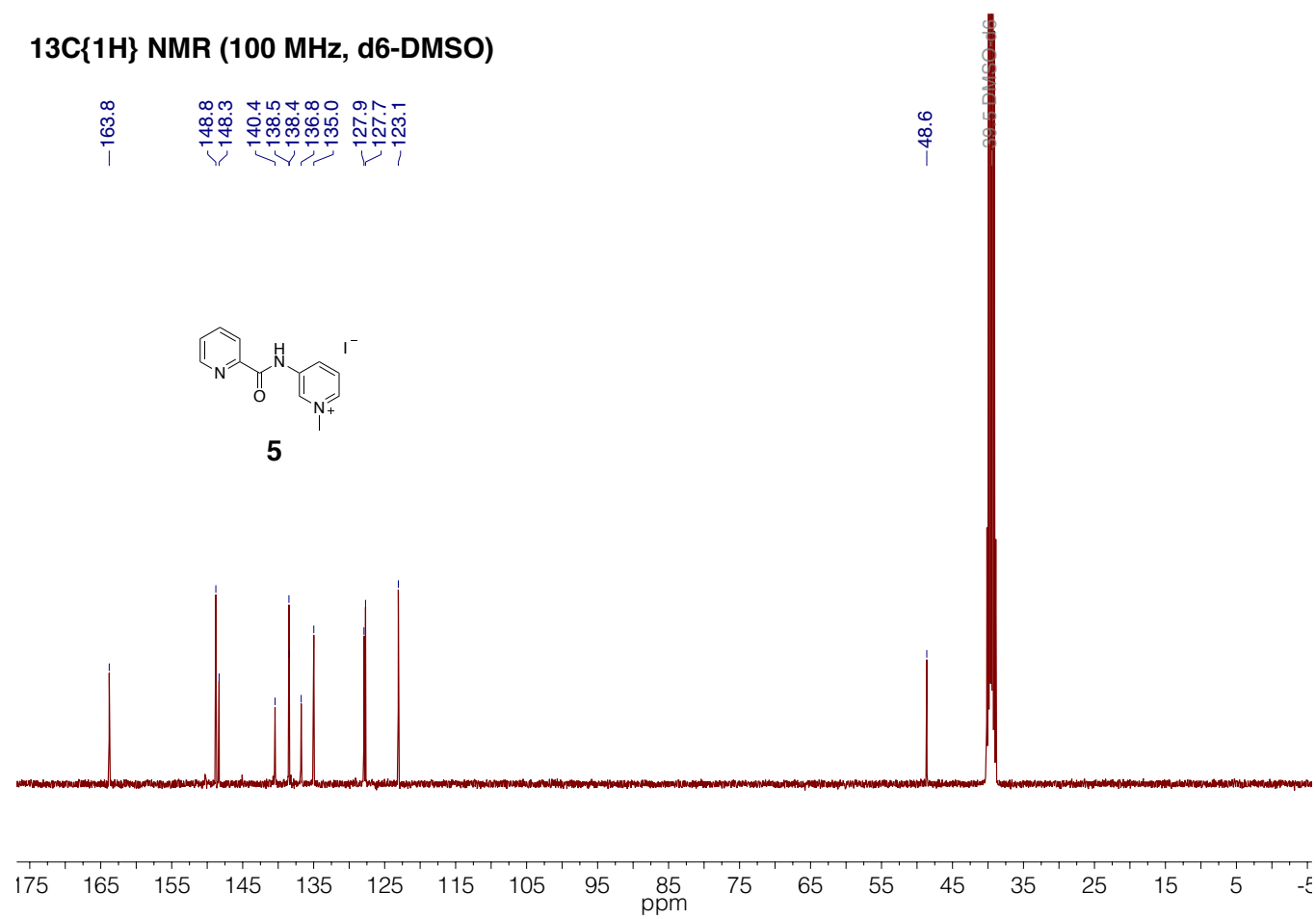


Figure S4. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **5**.

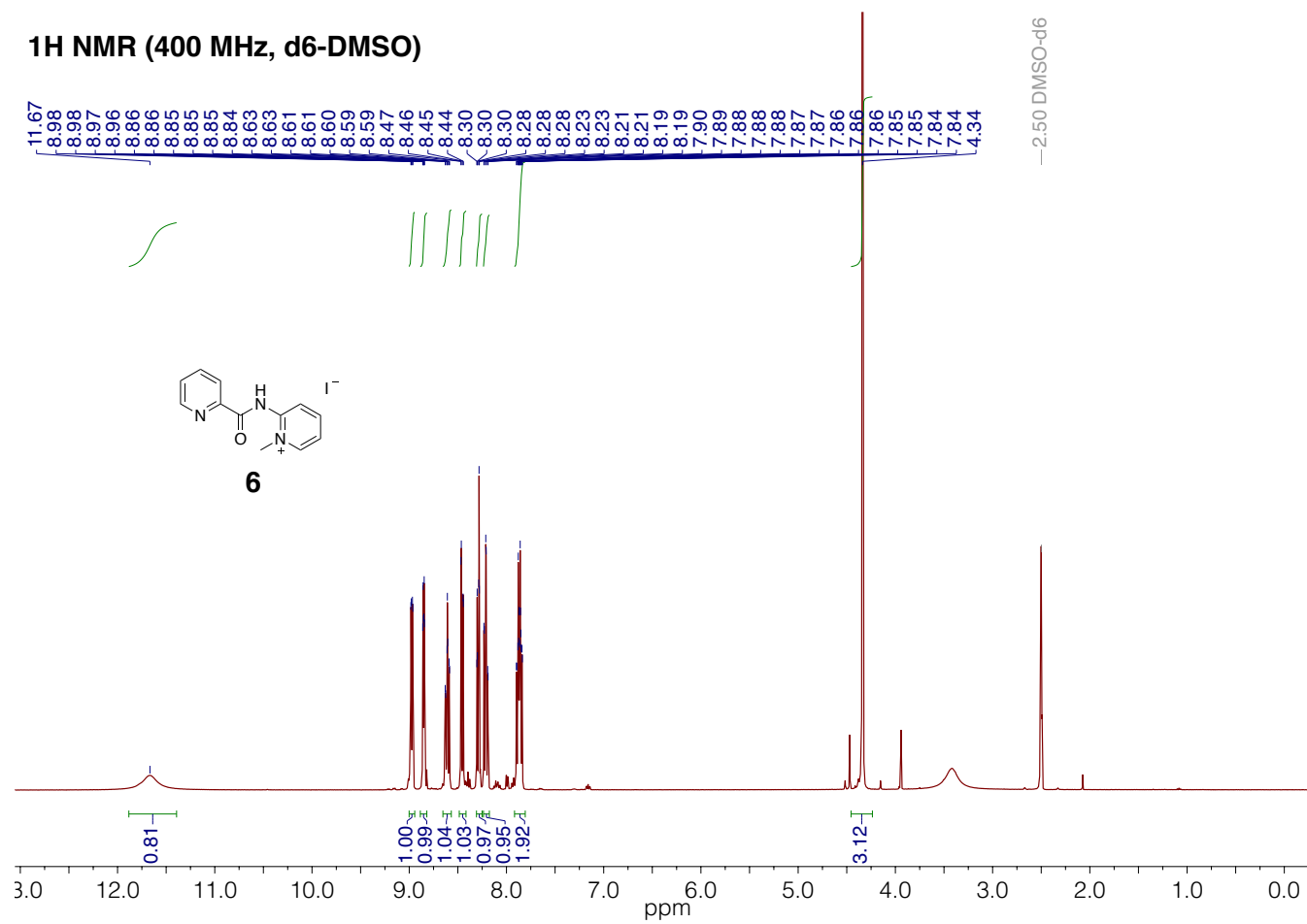


Figure S5. ¹H NMR spectrum of compound **6**.

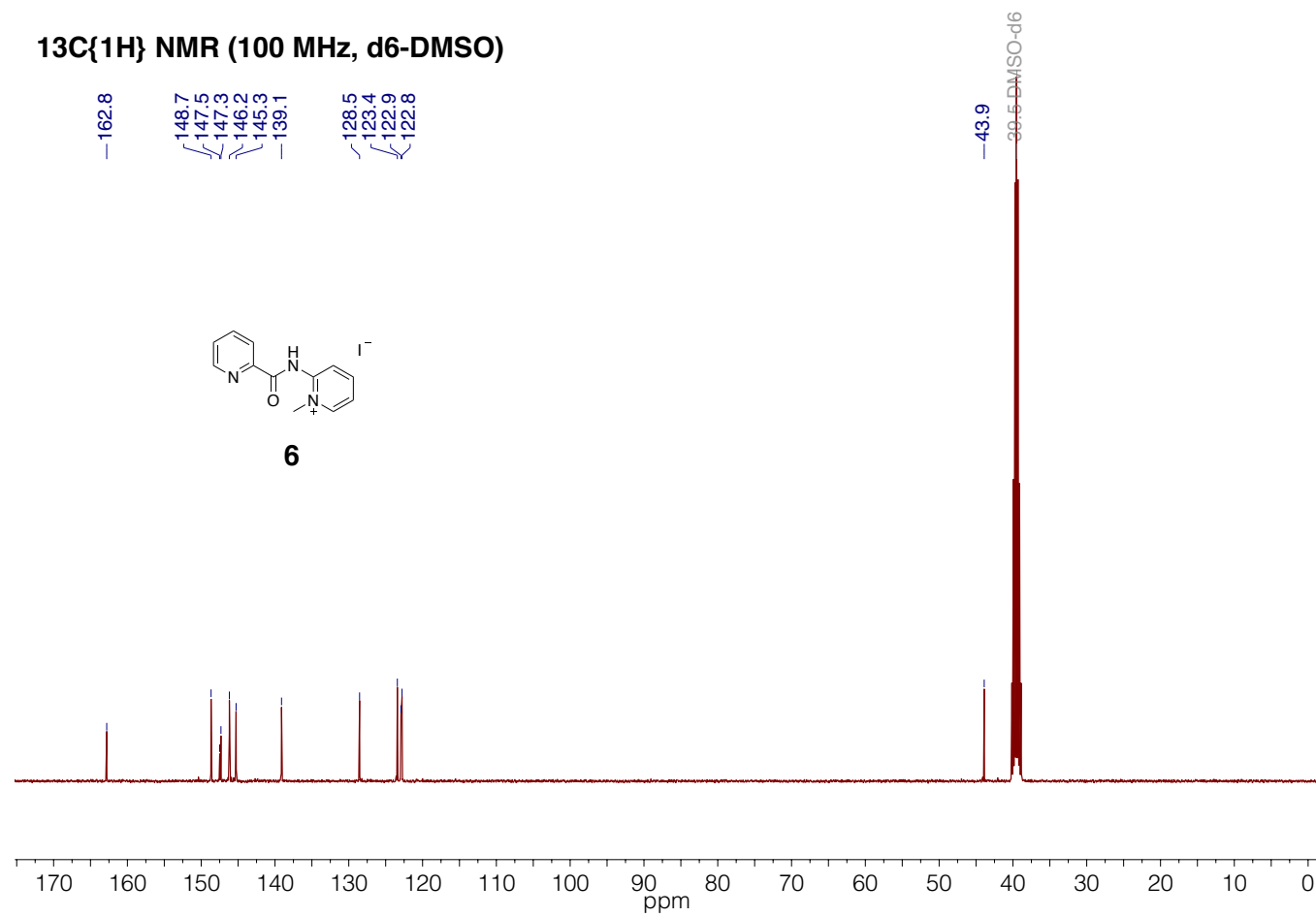


Figure S6. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **6**.

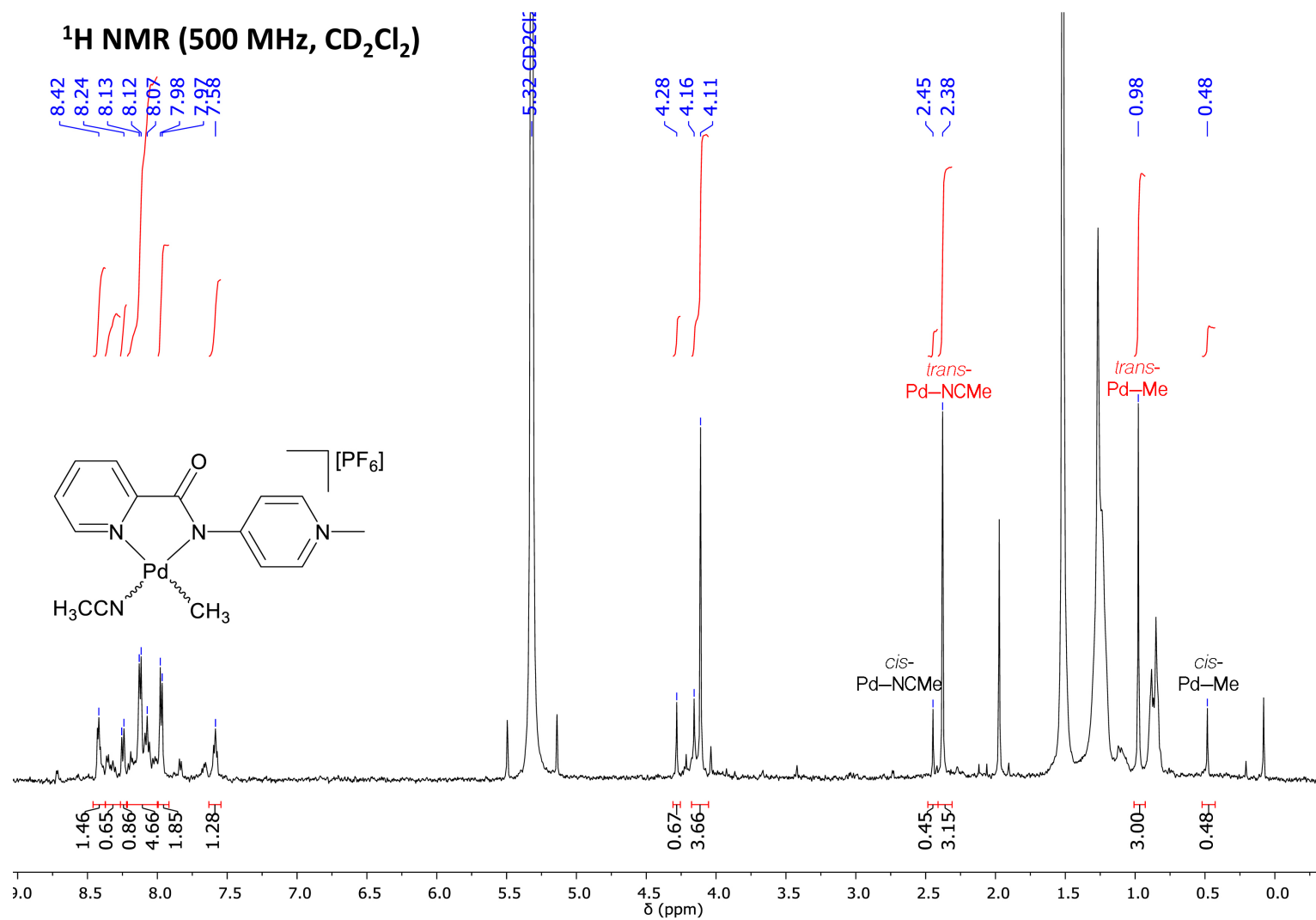


Figure S7. ^1H NMR spectrum of compound 7.

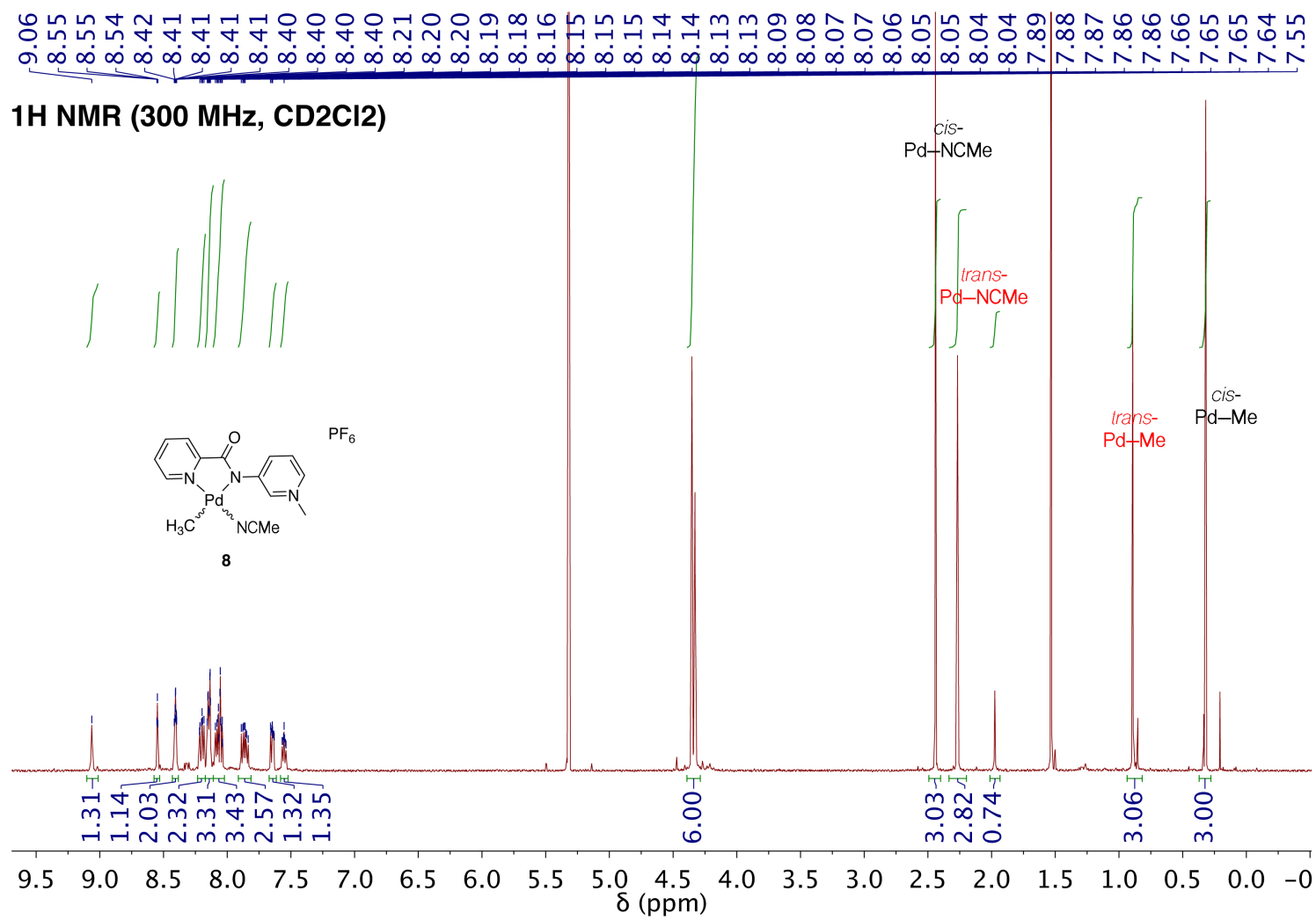


Figure S8. ¹H NMR spectrum of compound **8**.

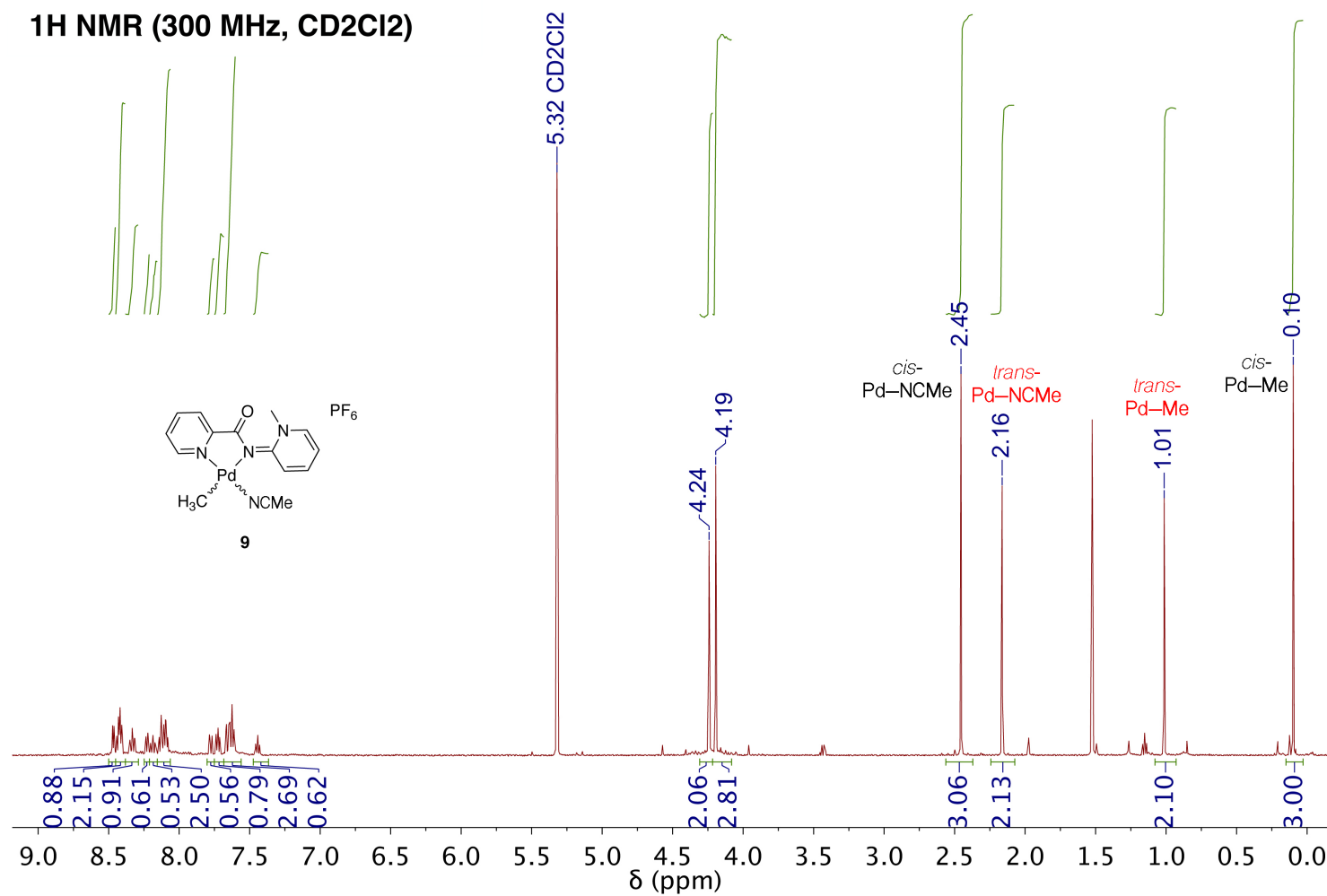


Figure S9. ¹H NMR spectrum of compound **9**.

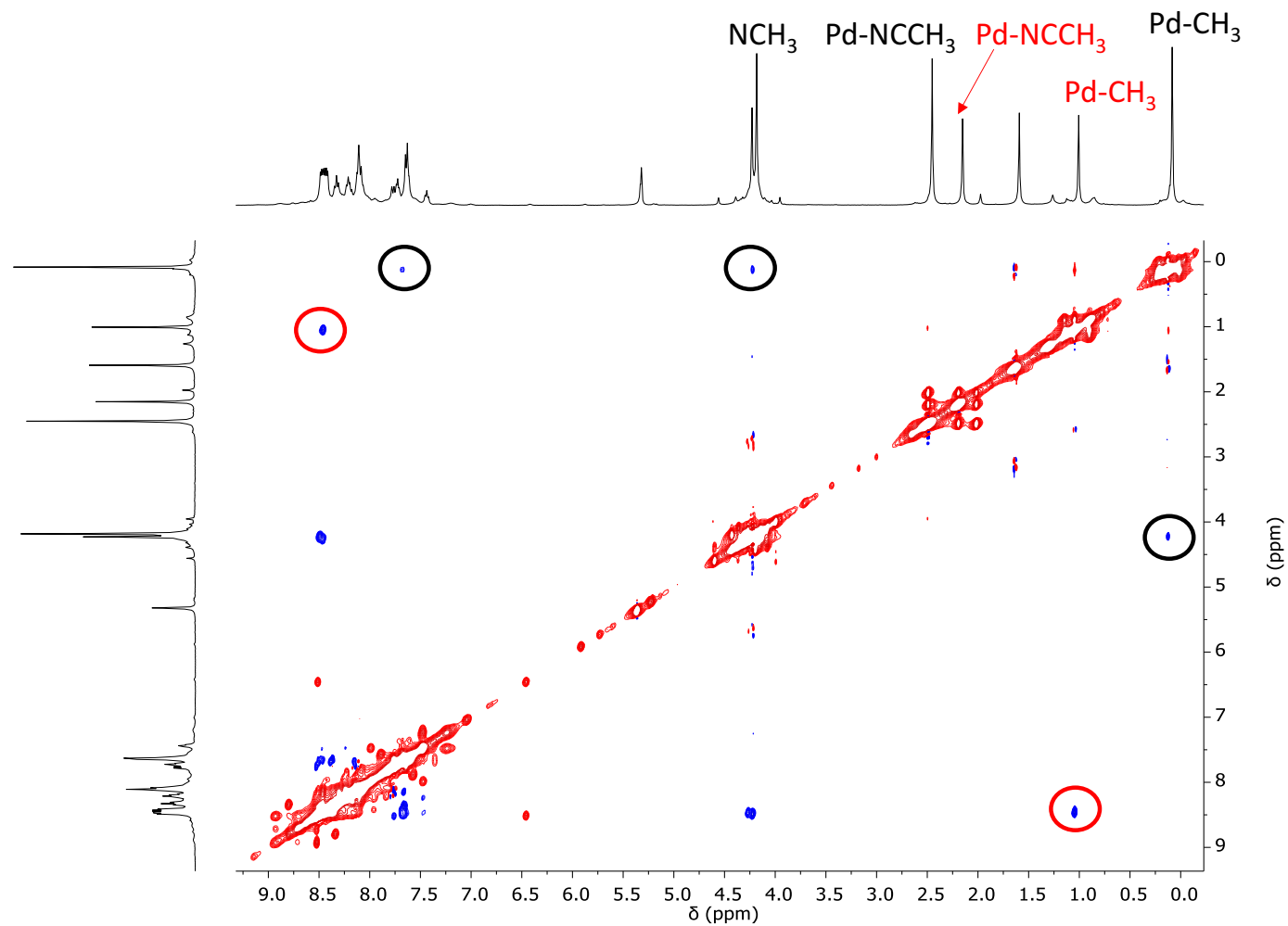


Figure S10. NOESY spectrum of complex **9** showing the presence of the *cis* isomer (black) and the *trans* isomer (red) and the related NOE peaks (circled in the same colors).

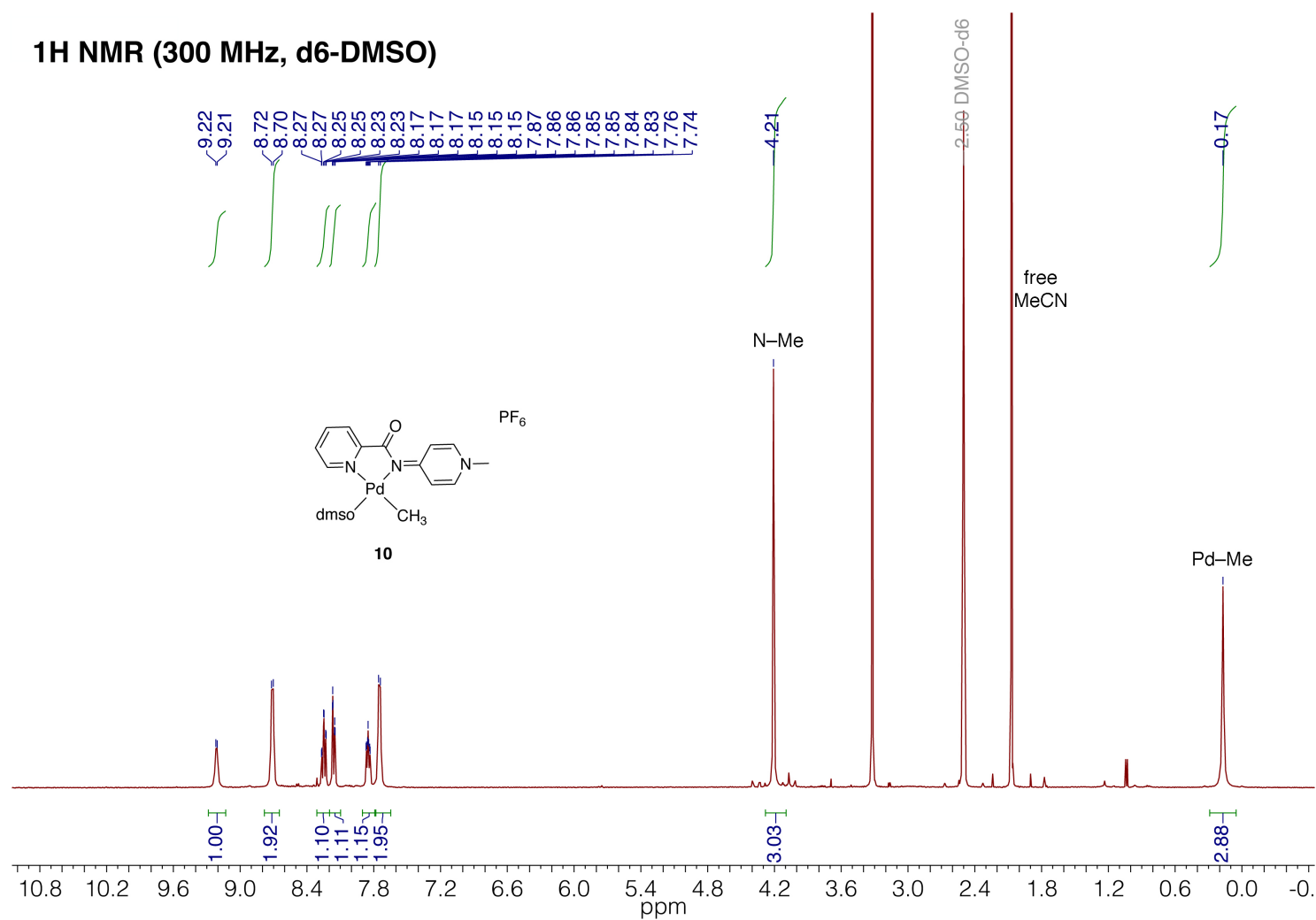


Figure S11. ¹H NMR spectrum of compound **10**.

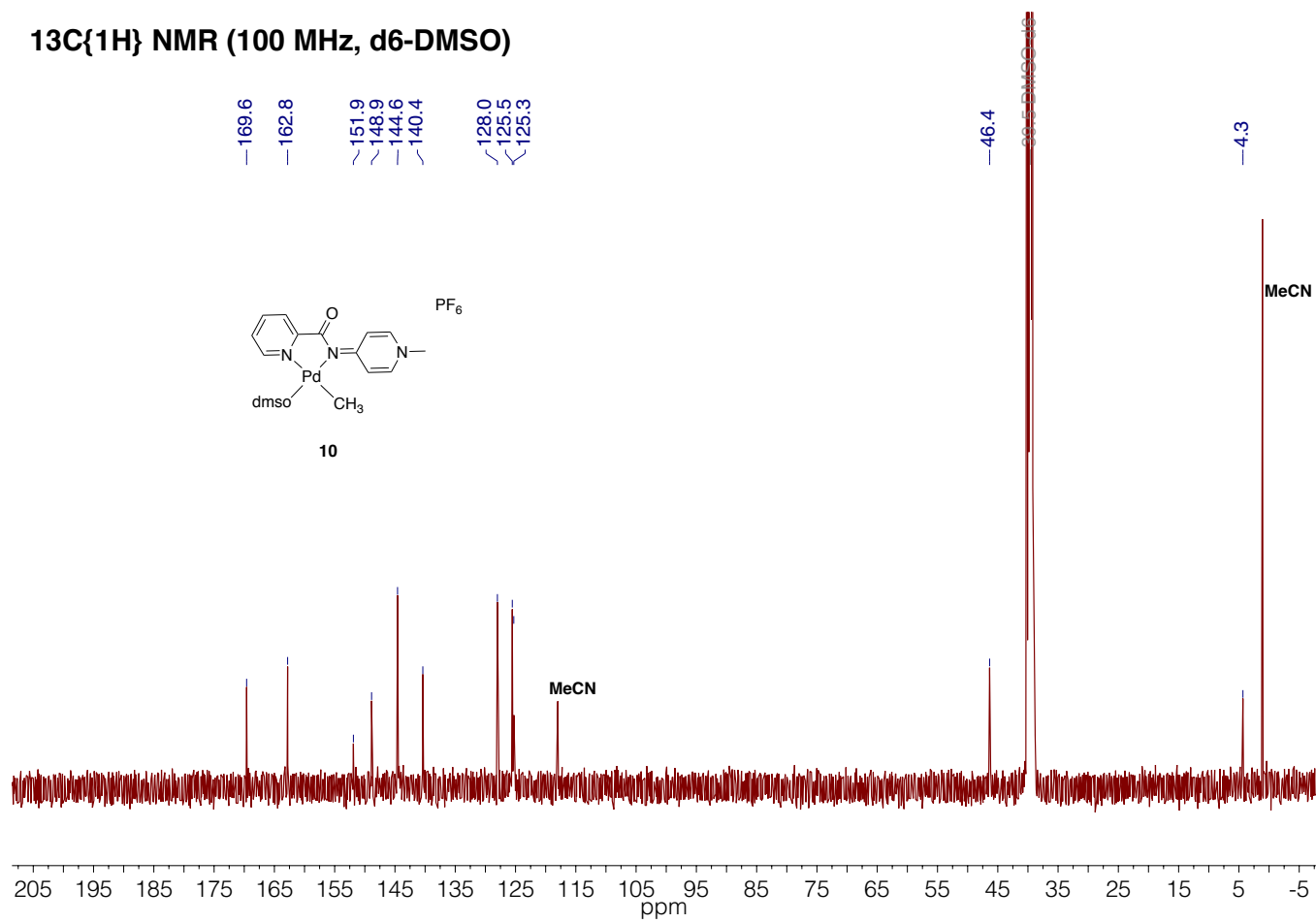


Figure S12. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **10**.

¹H NMR (300 MHz, d6-DMSO)

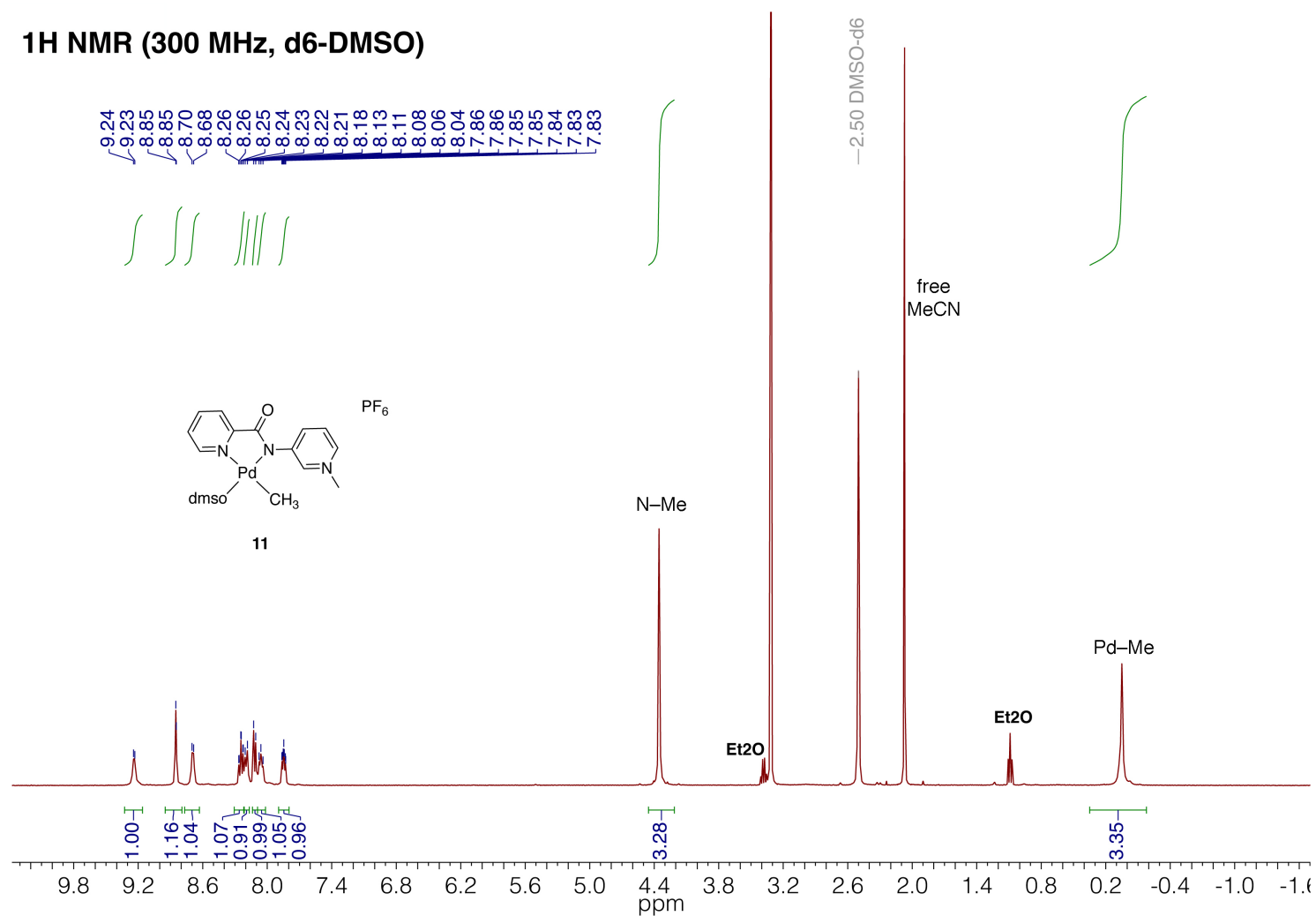


Figure S13. ¹H NMR spectrum of compound **11**.

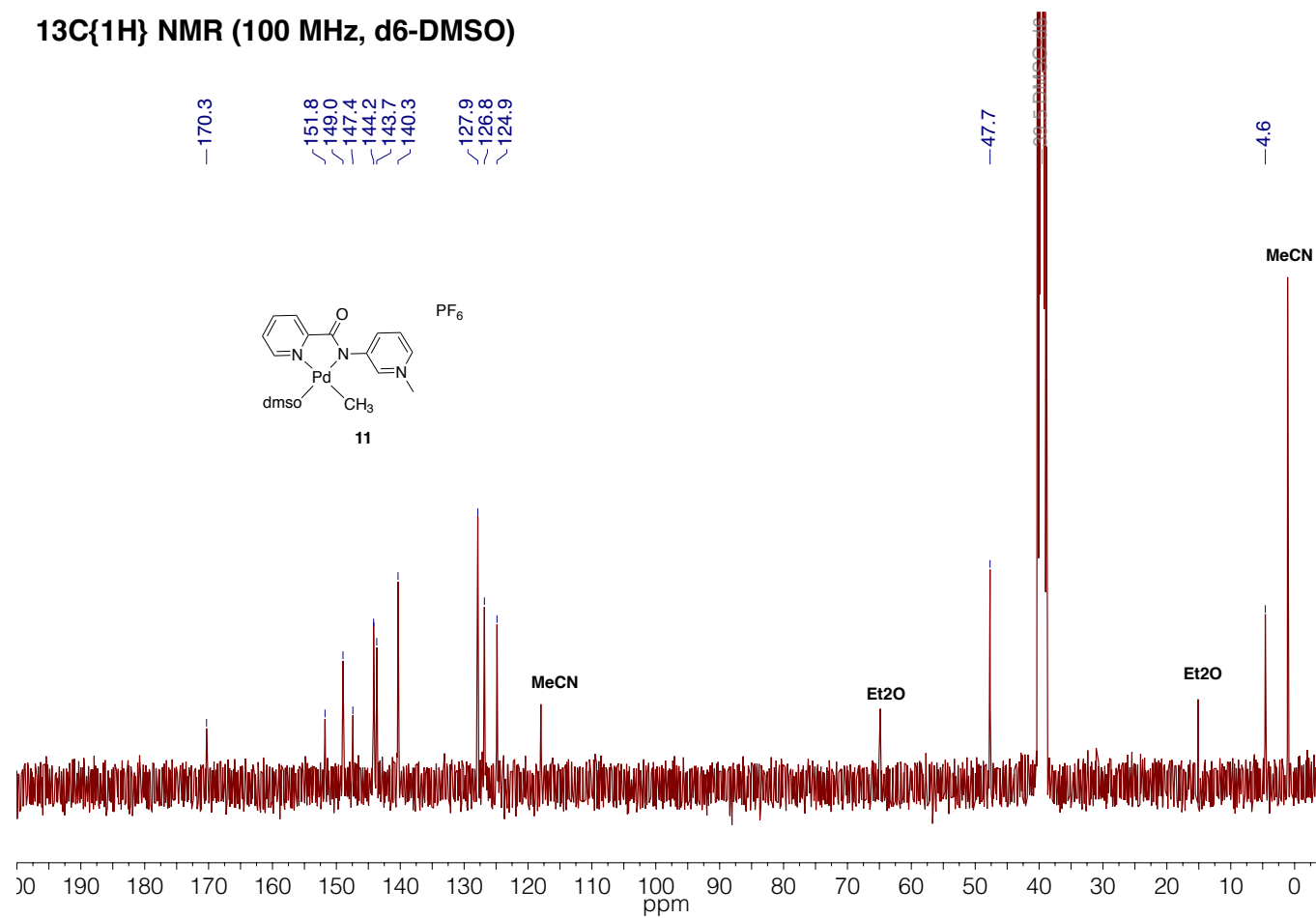


Figure S14. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **11**.

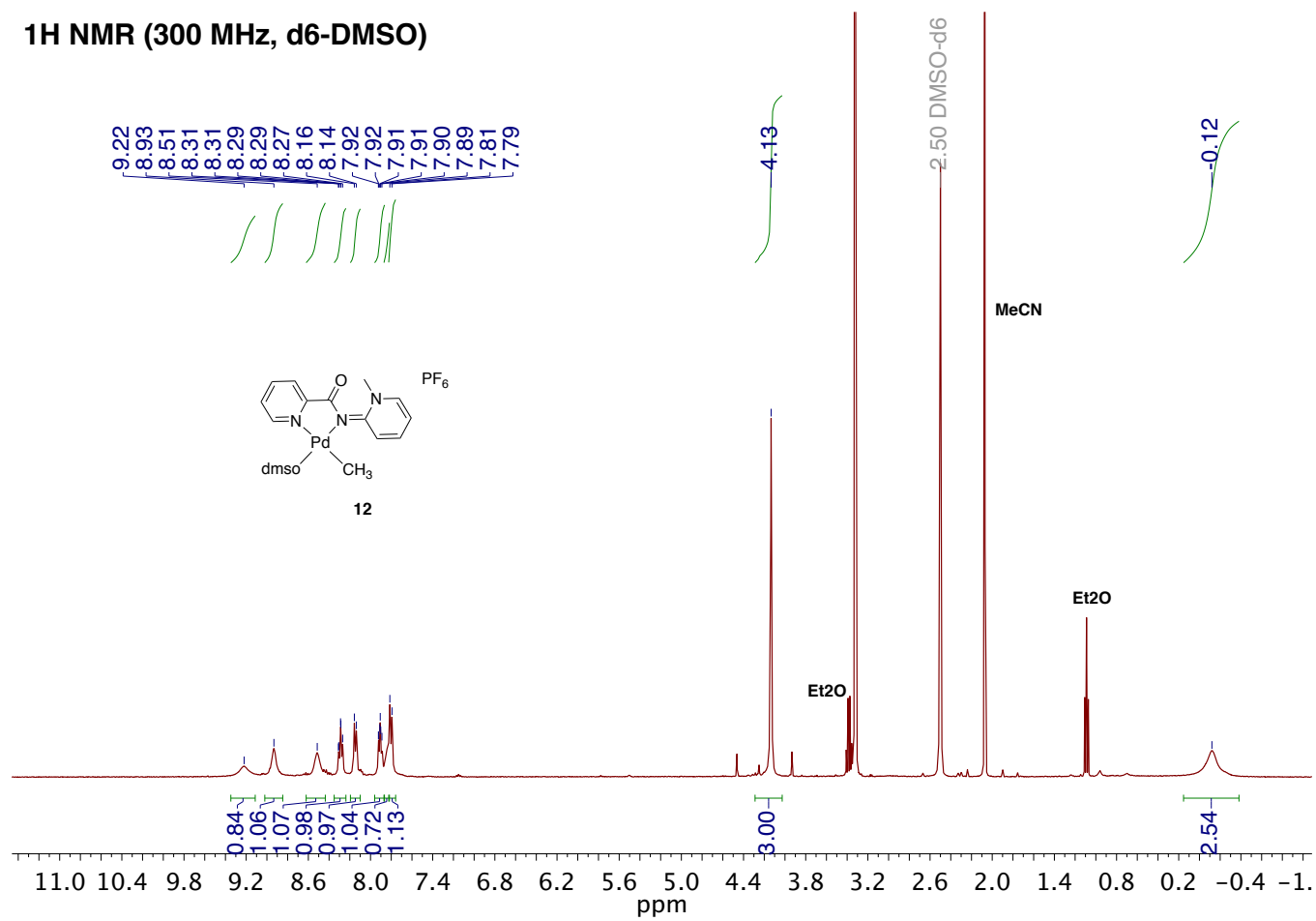


Figure S15. ¹H NMR spectrum of compound **12**.

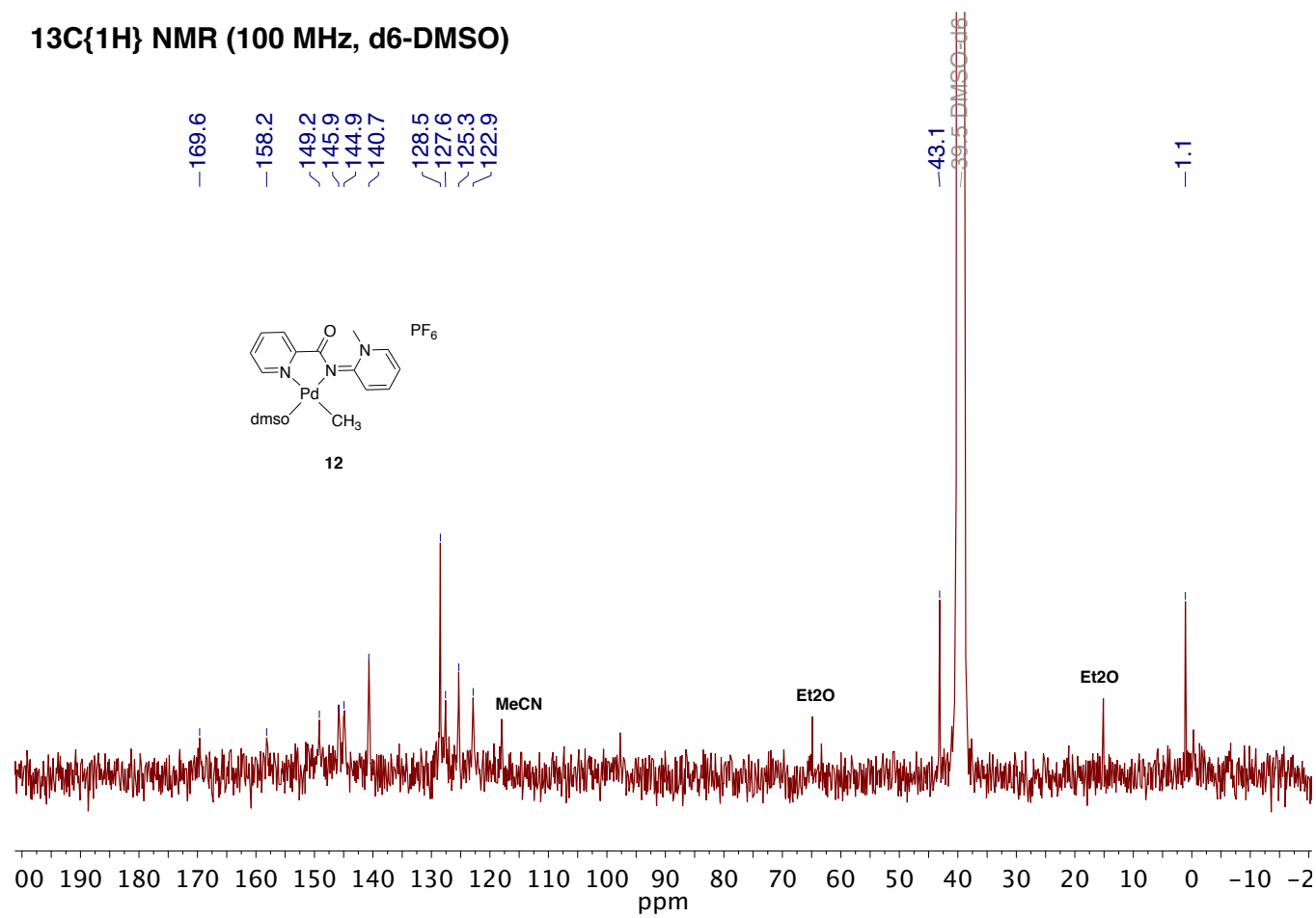


Figure S16. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **12**.

3. Analytical data pertaining to catalytic experiments

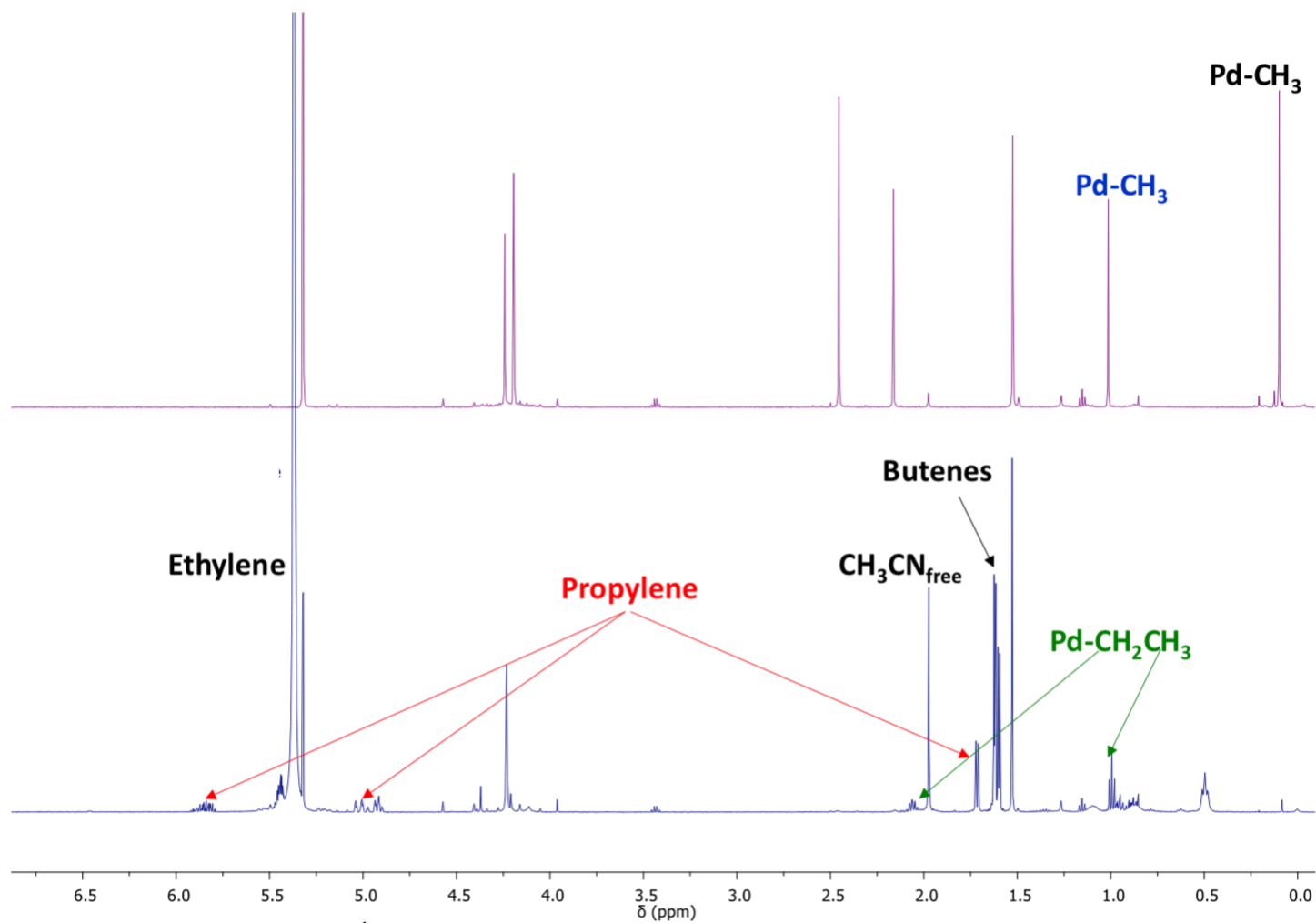


Figure S17. Selected region of ^1H NMR spectrum of complex **7** before addition of ethylene (top) and five minutes after addition (bottom).

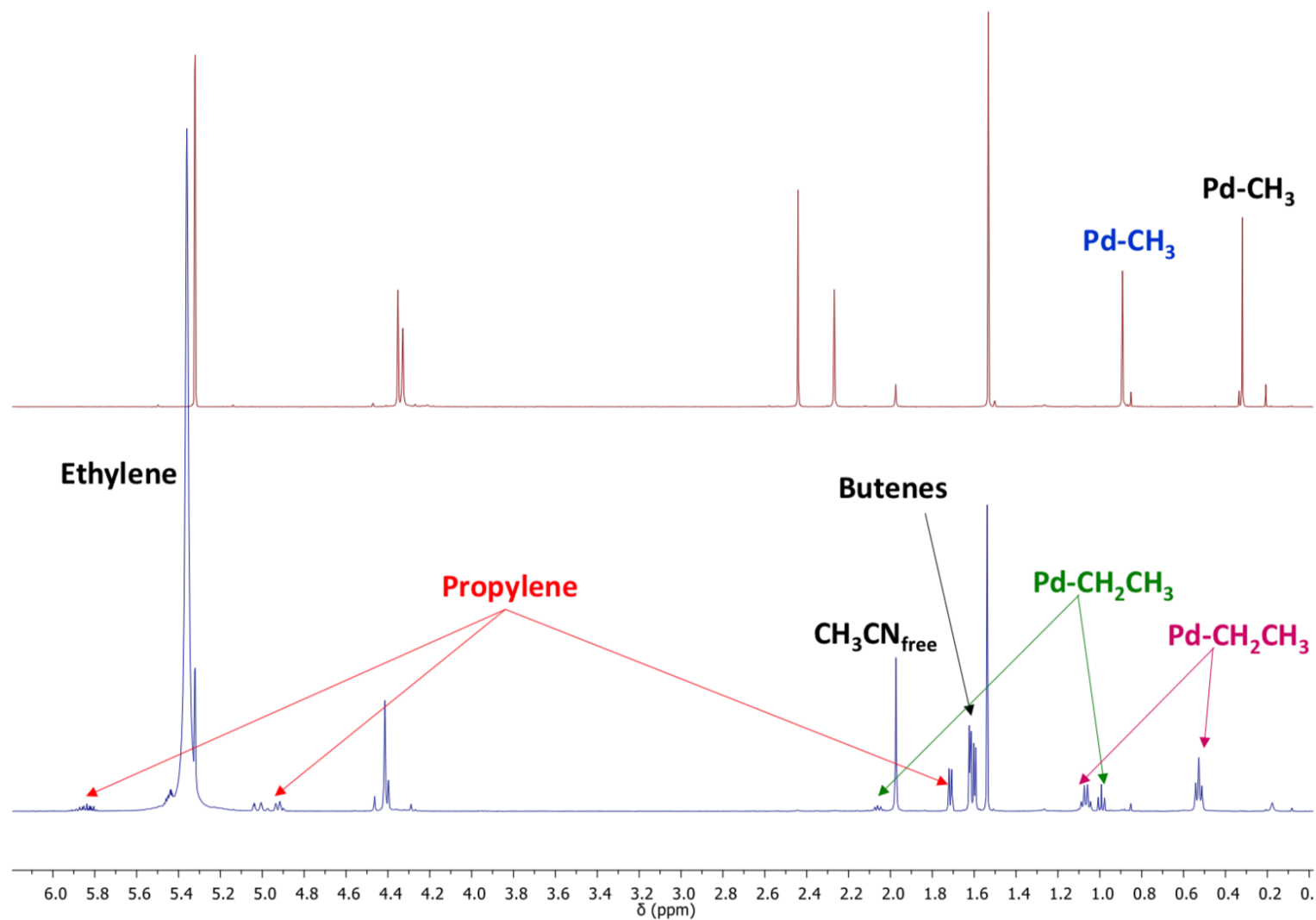


Figure S18. Selected region of ^1H NMR spectrum of complex **8** before addition of ethylene (top) and five minutes after addition (bottom).

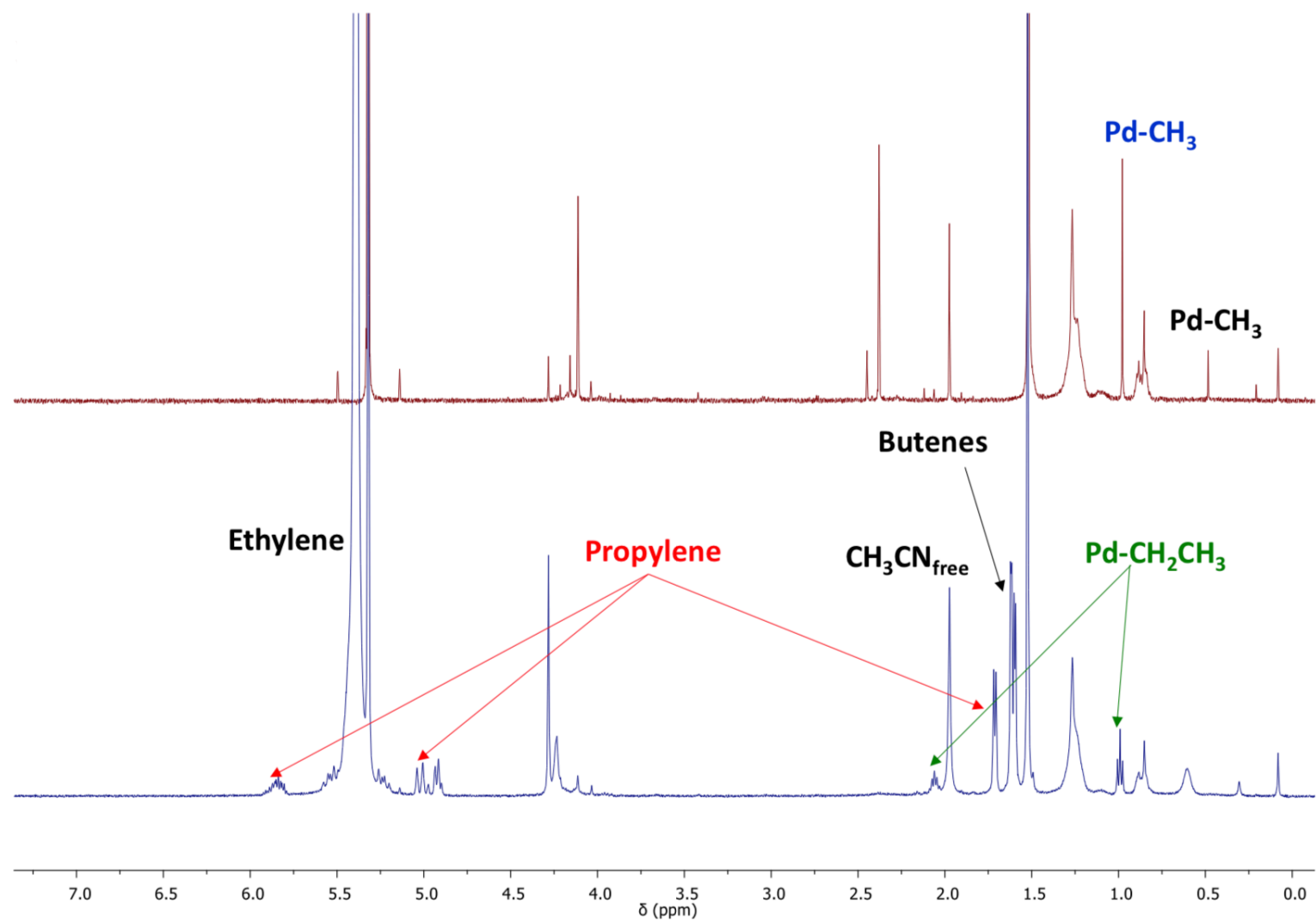


Figure S19. Selected region of ^1H NMR spectrum of complex **9** before addition of ethylene (top) and five minutes after addition (bottom).

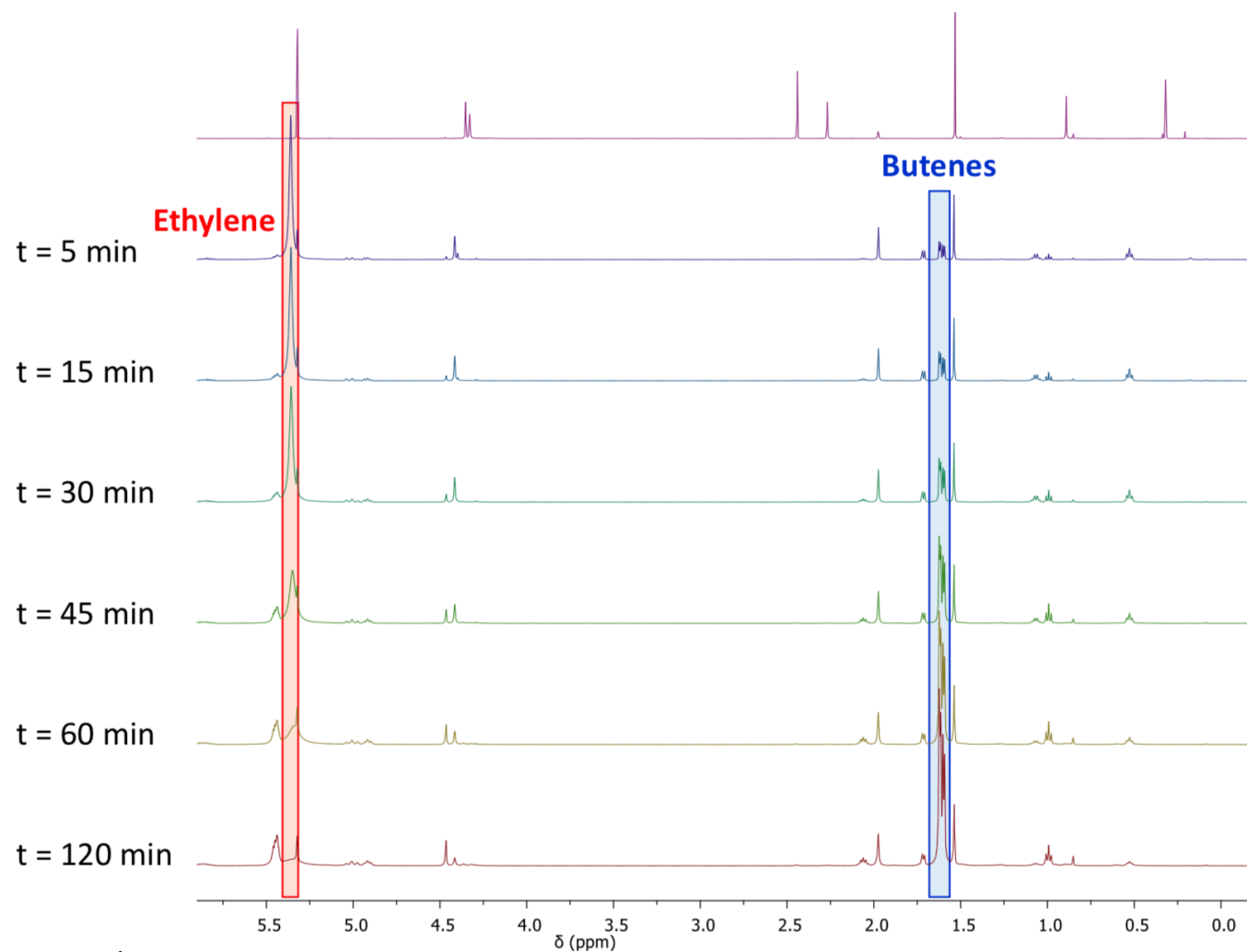


Figure S20. Section of the ^1H NMR spectrum from the catalytic dimerization of ethylene catalyzed by complex **8** in a NMR tube showing the time-dependent consumption of ethylene (red box) and the evolution of butenes (blue box).

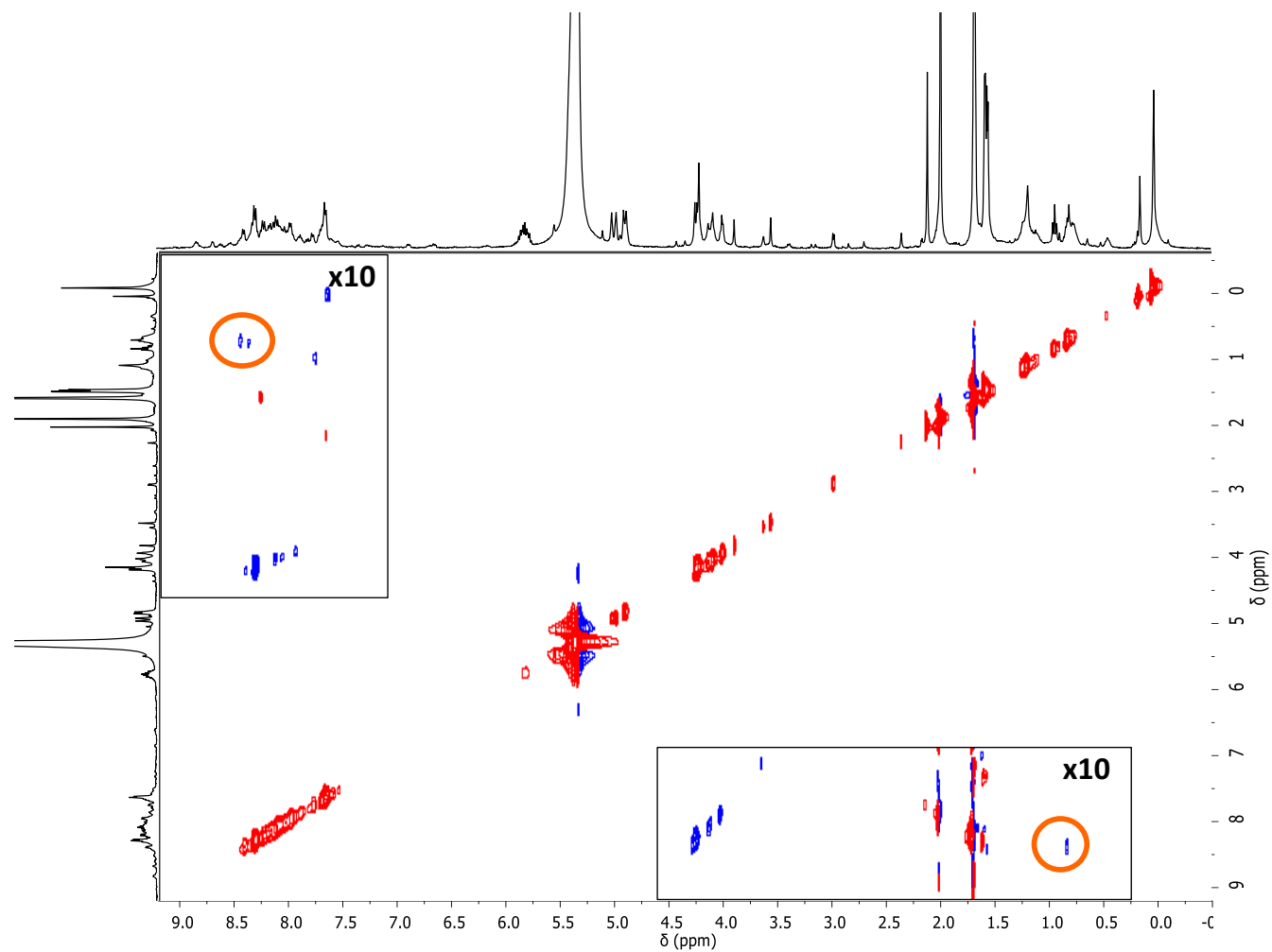


Figure S21. NOESY spectrum of the *in situ* reactivity of complex **7** with ethylene in a NMR tube in CD_2Cl_2 at -50°C . Zoom in of the areas of interest in the boxes.

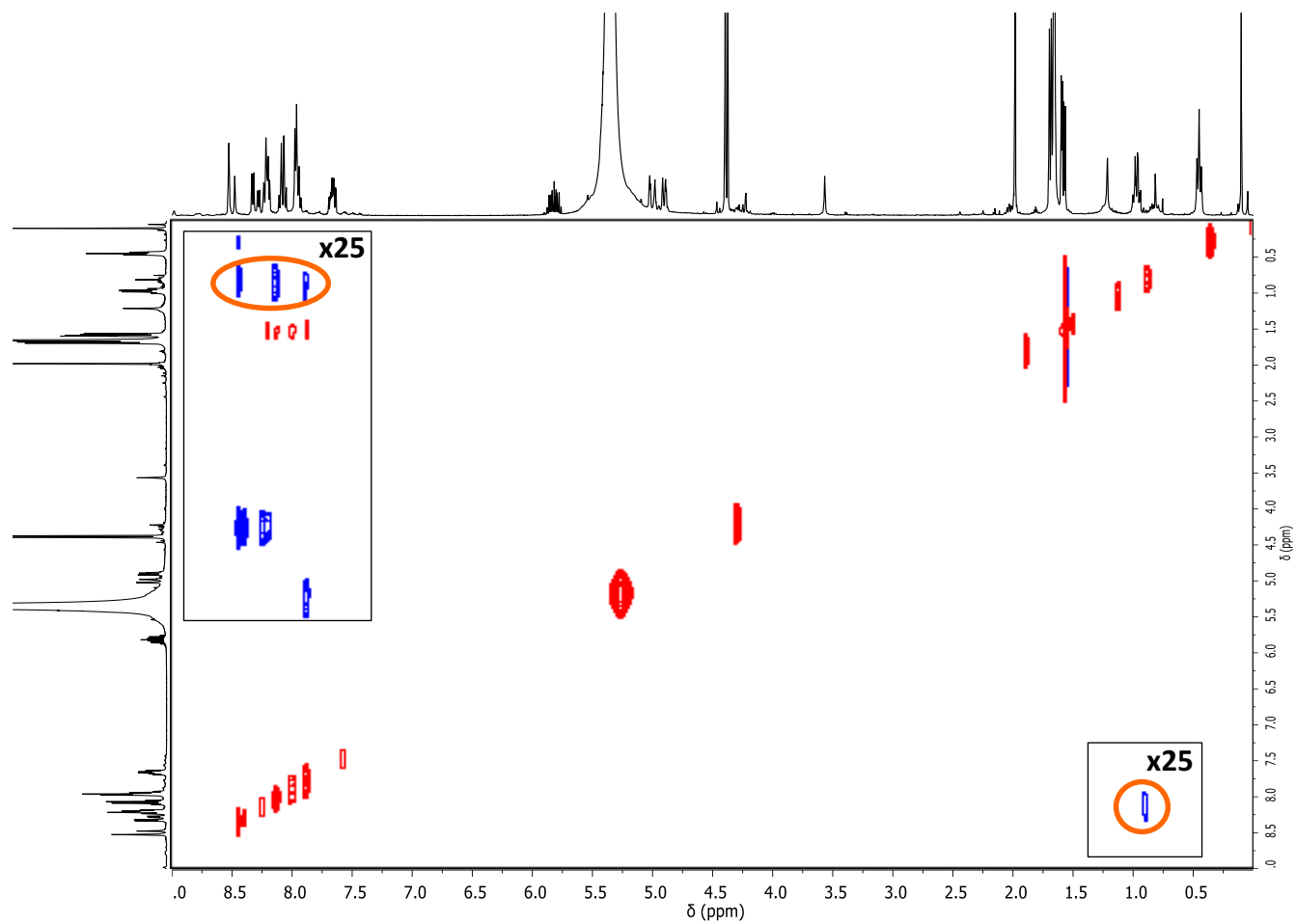


Figure S22. NOESY spectrum of the *in situ* reactivity of complex **8** with ethylene in a NMR tube in CD_2Cl_2 at -30°C . Zoom in of the areas of interest in the boxes.

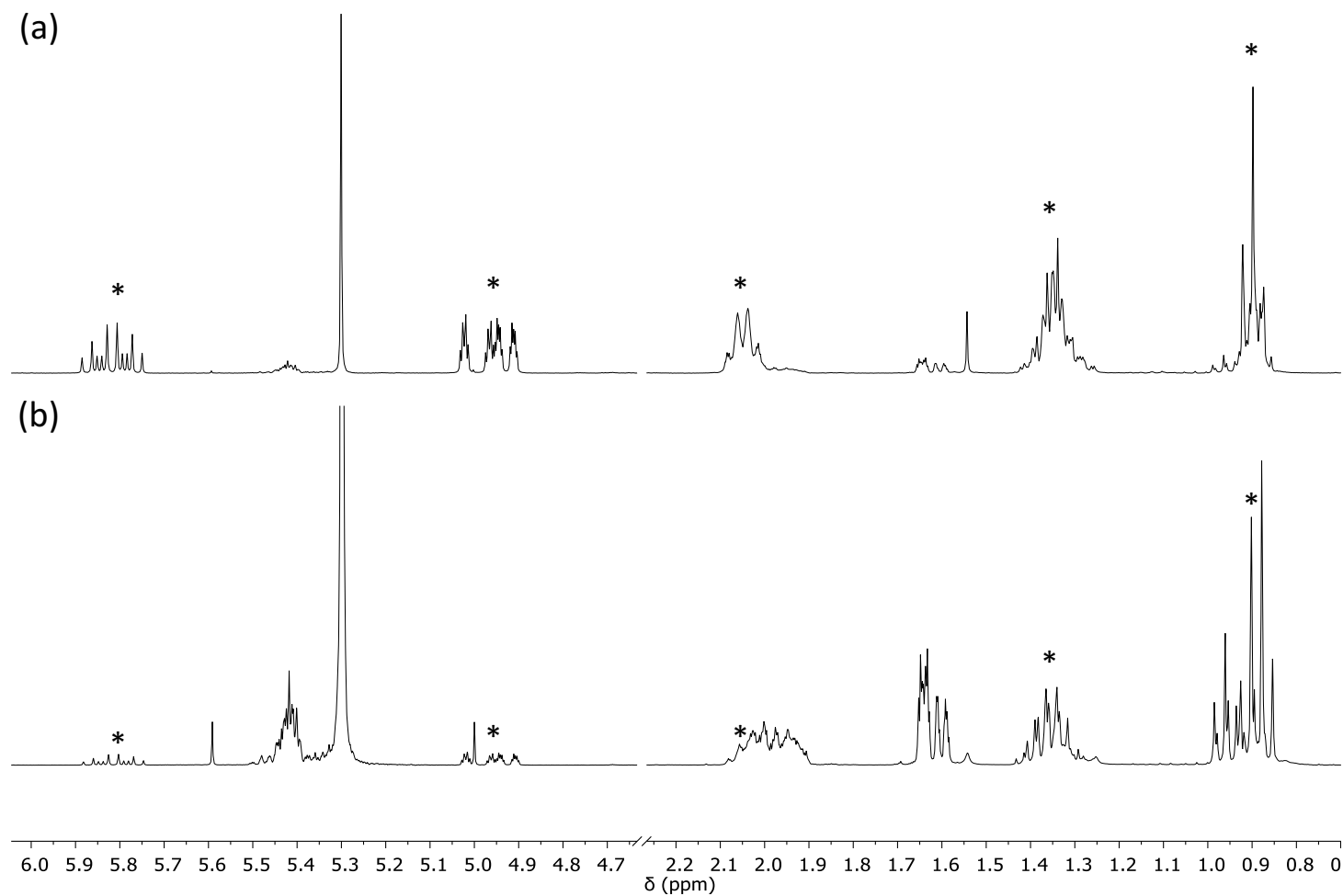


Figure S23. ^1H NMR spectra of crude reaction mixture of 1-hexene dimerization catalysis obtained with complex **9** with 0.01 mol% (a) and 0.1 mol% catalyst loading (b). * 1-hexene.

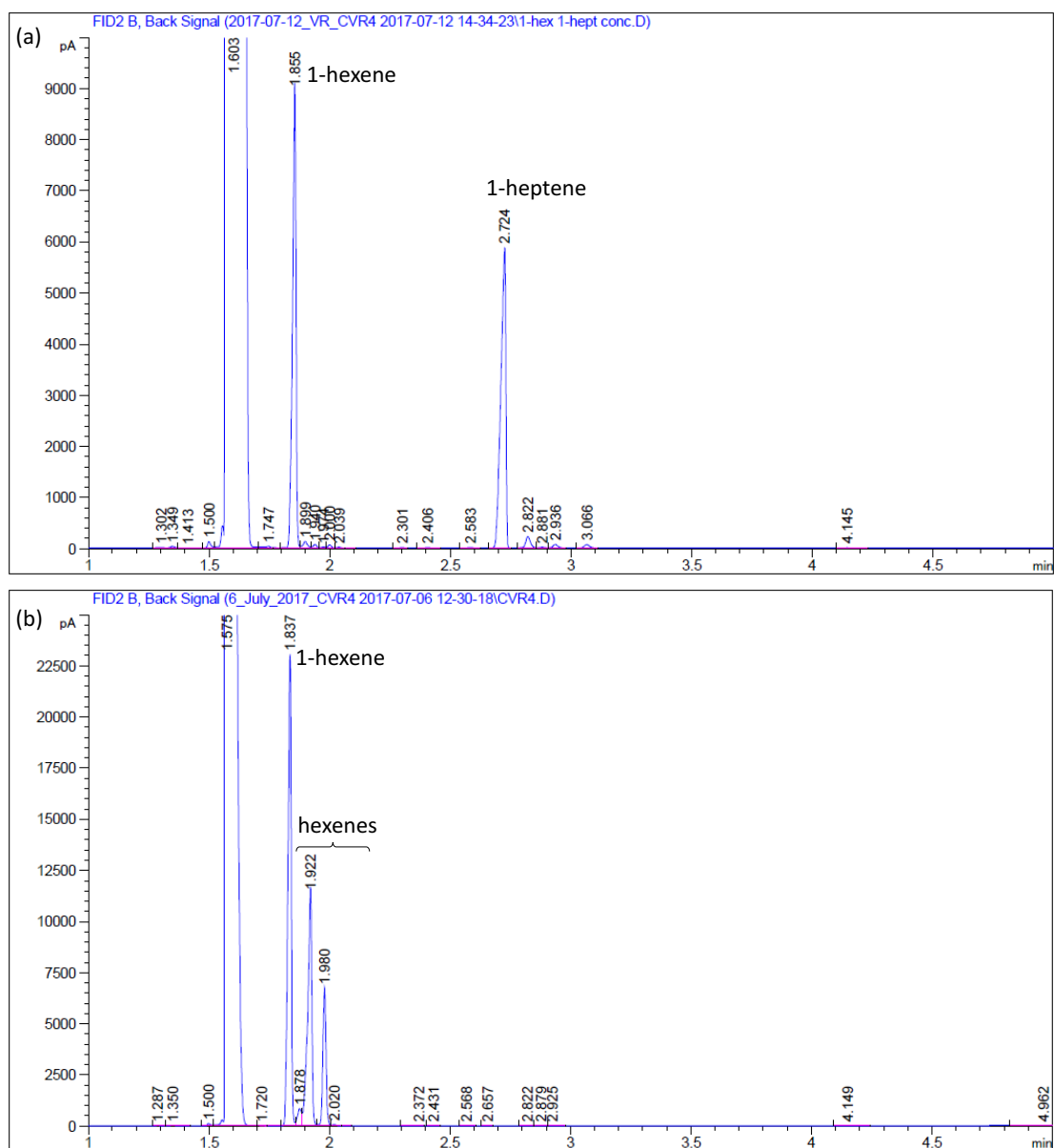


Figure S24. GC analysis of (a) fresh mixture of commercial 1-hexene and 1-heptene; (b) crude reaction mixture of 1-hexene dimerization with 0.1 mol% of precatalyst **9**.

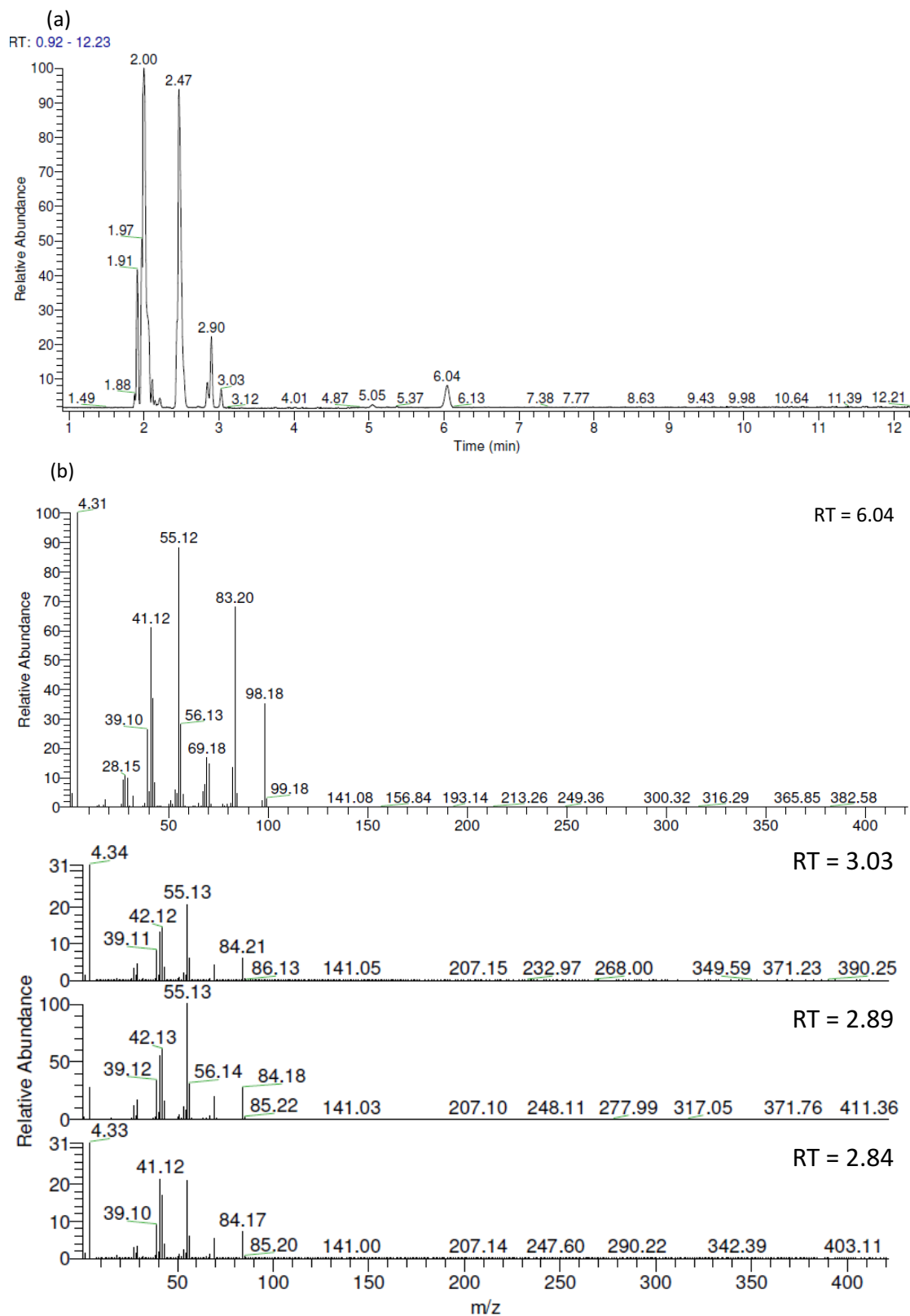


Figure S25. GC-MS analysis of the reaction mixture of 1-hexene dimerization with 10 mol% of precatalyst **9**: (a) full chromatogram; (b) mass spectra of most relevant peaks.