

## SUPPORTING INFORMATION

for

Stable Mixed-Valence Diphenylphosphanido Bridged Platinum(II)- Platinum(IV) Complexes

by

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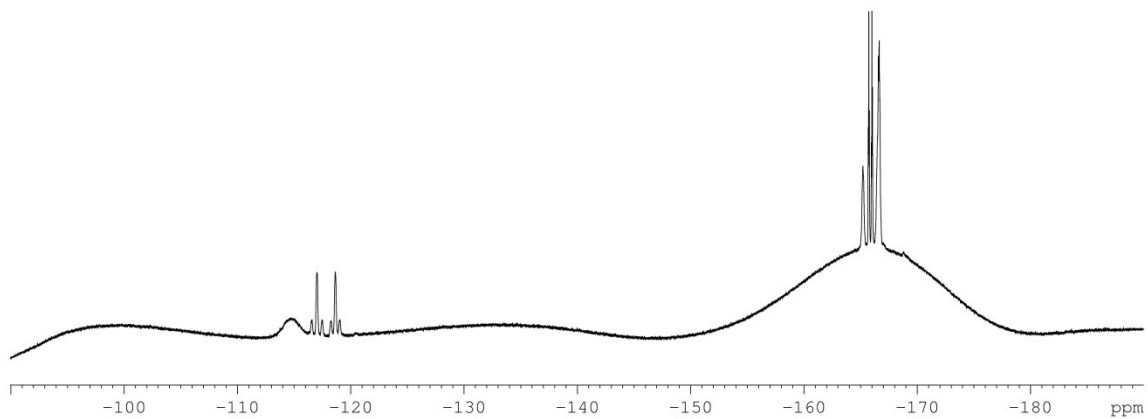


Figure S1:  $^{19}\text{F}$  spectrum of **4** ( $\text{C}_3\text{D}_6\text{O}$ , 376 MHz, 298 K).

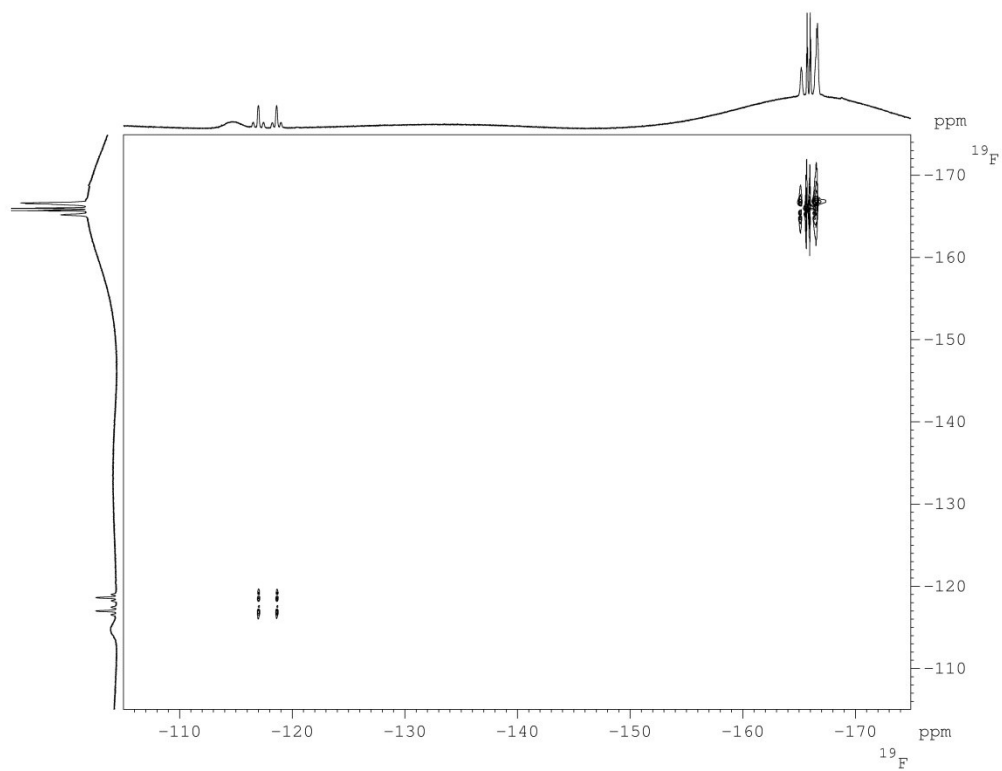


Figure S2:  $^{19}\text{F}$  EXSY spectrum of **4** ( $\text{C}_3\text{D}_6\text{O}$ , 376 MHz, 298 K).

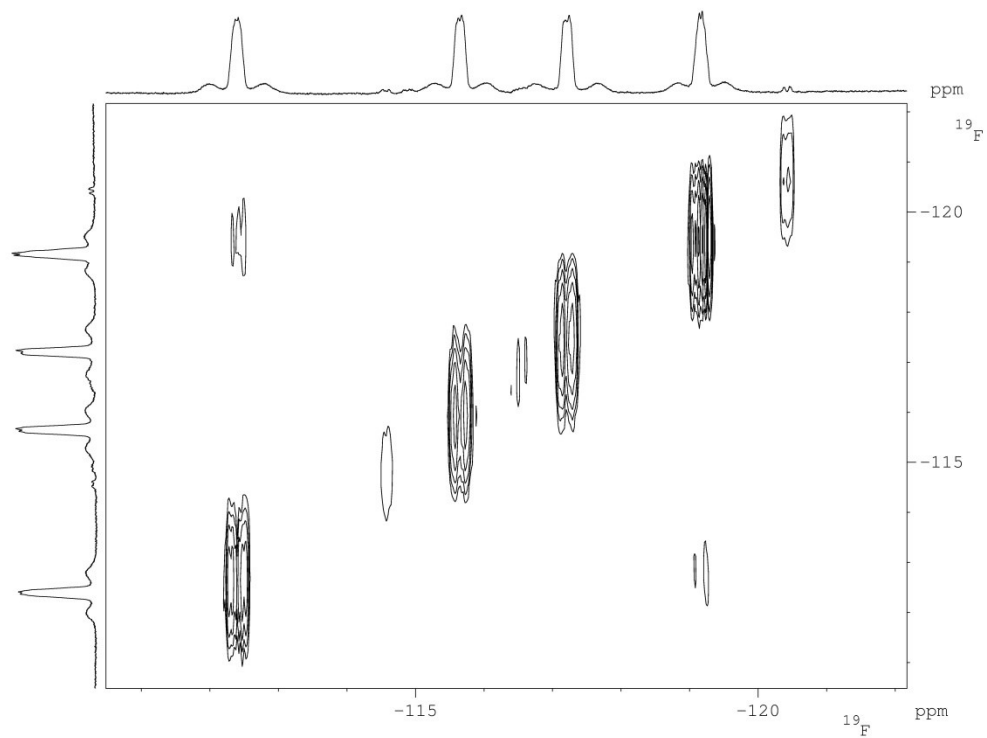


Figure S3: Portion of the  $^{19}\text{F}$  COSY spectrum of **4** ( $\text{C}_3\text{D}_6\text{O}$ , 376 MHz, 198 K).

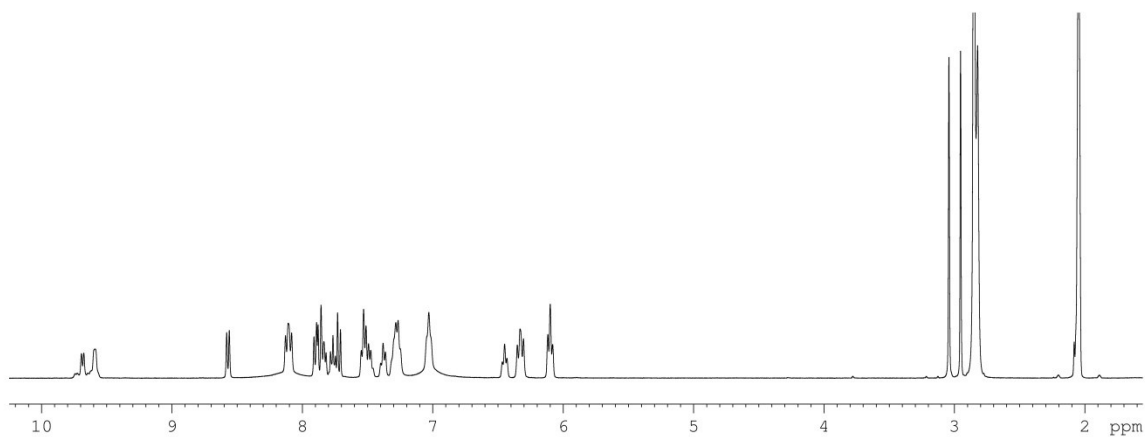


Figure S4:  $^1\text{H}$  spectrum of **4** ( $\text{C}_3\text{D}_6\text{O}$ , 400 MHz, 298 K).

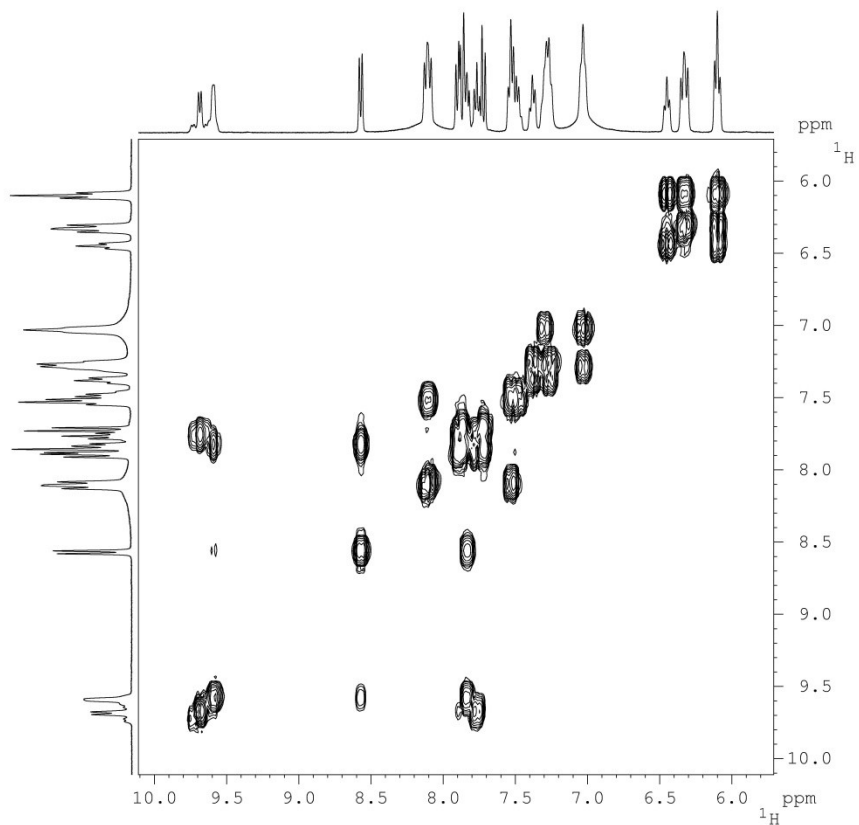


Figure S5: Portion of the  $^1\text{H}$  COSY spectrum of **4** ( $\text{C}_3\text{D}_6\text{O}$ , 400 MHz, 298 K).

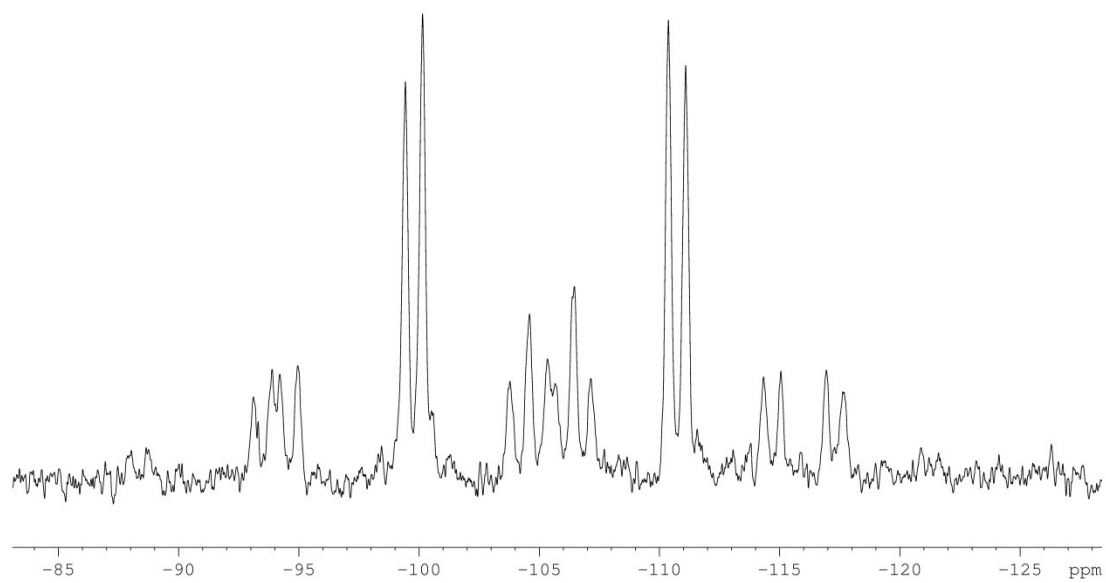


Figure S6:  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **4** ( $\text{C}_3\text{D}_6\text{O}$ , 162 MHz, 298 K).

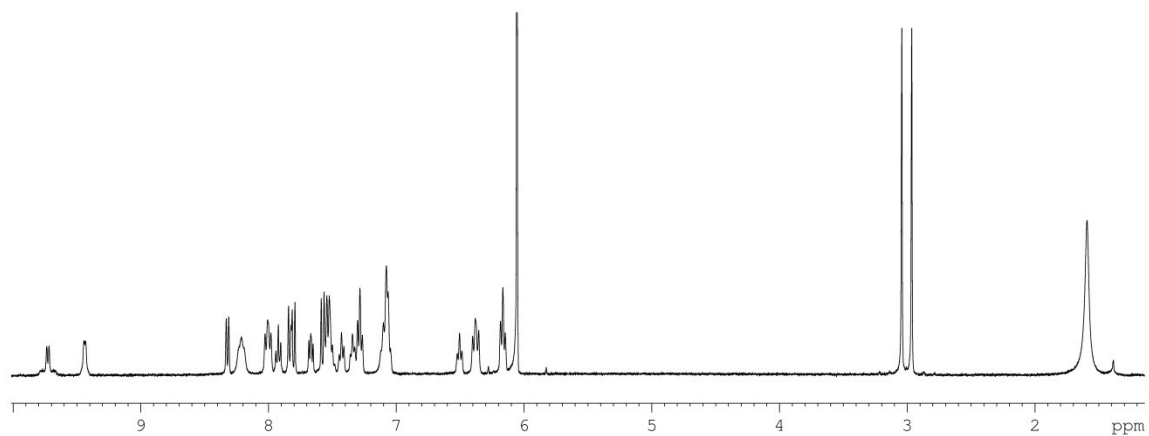


Figure S7:  $^1\text{H}$  NMR spectrum of **4** (348 K, 400 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ).

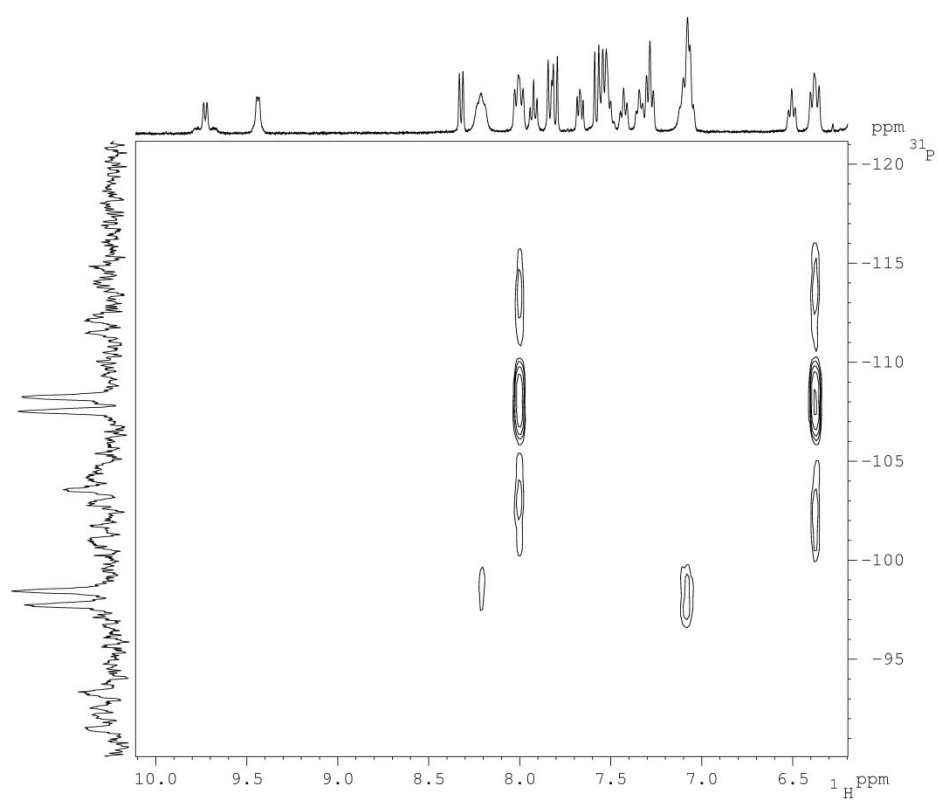


Figure S8: Low-field portion of the  $^1\text{H}$ - $^{31}\text{P}$  HMQC spectrum of **4** ( $\text{C}_2\text{D}_2\text{Cl}_4$ , 348 K).

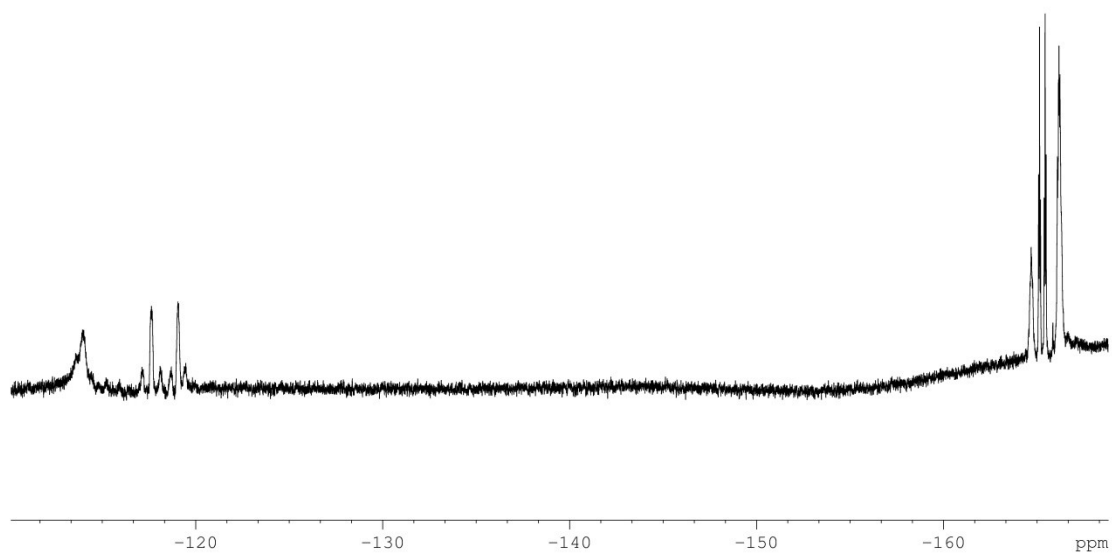


Figure S9:  $^{19}\text{F}$  NMR spectrum of **2** ( $\text{C}_3\text{D}_6\text{O}$ , 376 MHz, 298 K)

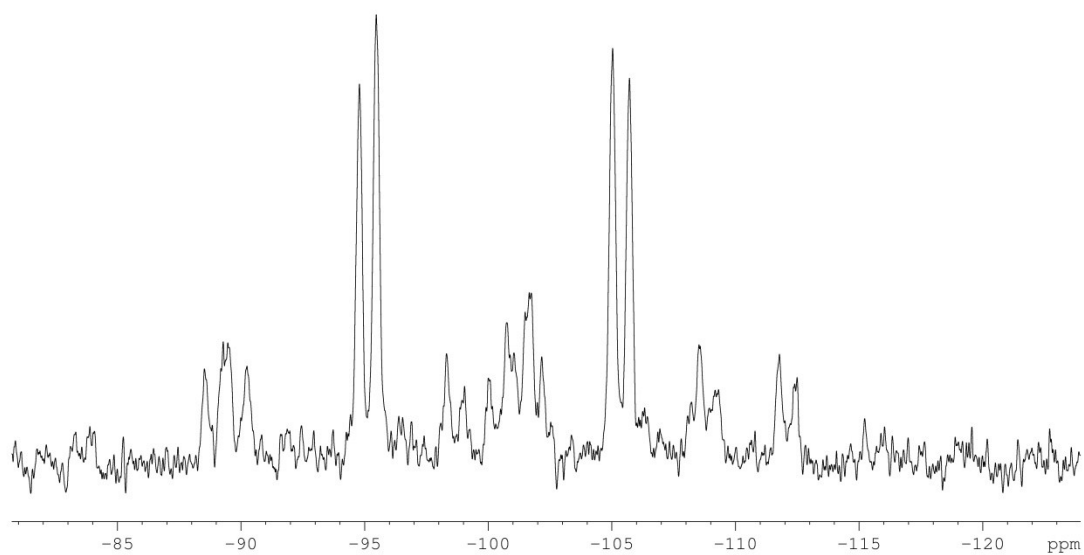


Figure S10:  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **2** ( $\text{C}_3\text{D}_6\text{O}$ , 162 MHz, 298 K)

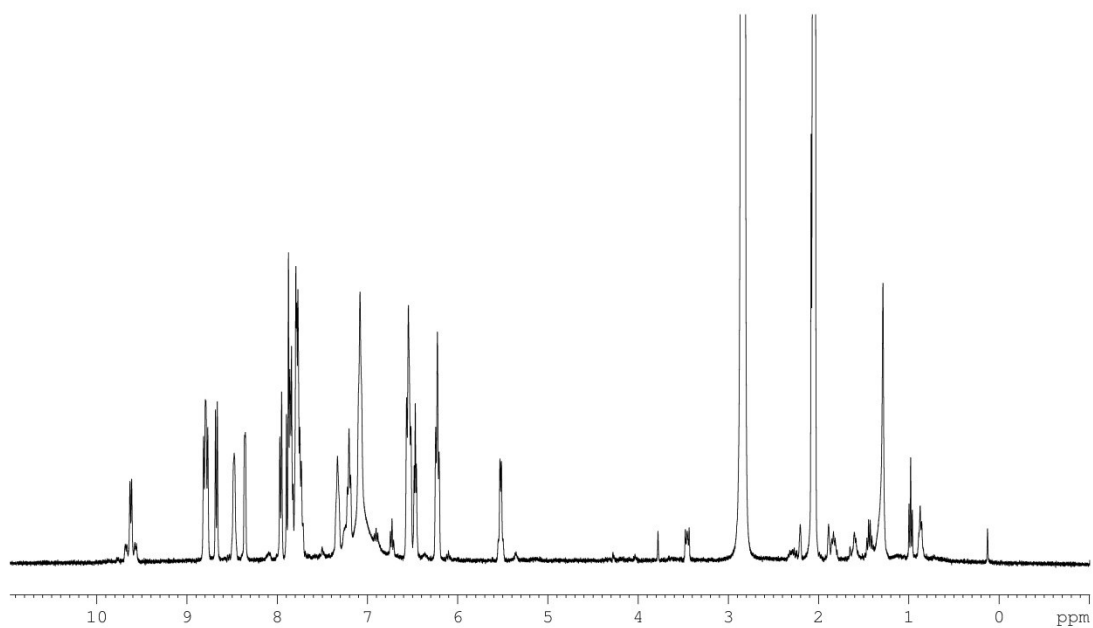


Figure S11:  $^1\text{H}$  NMR spectrum of **2** ( $\text{C}_3\text{D}_6\text{O}$ , 400 MHz, 298 K)

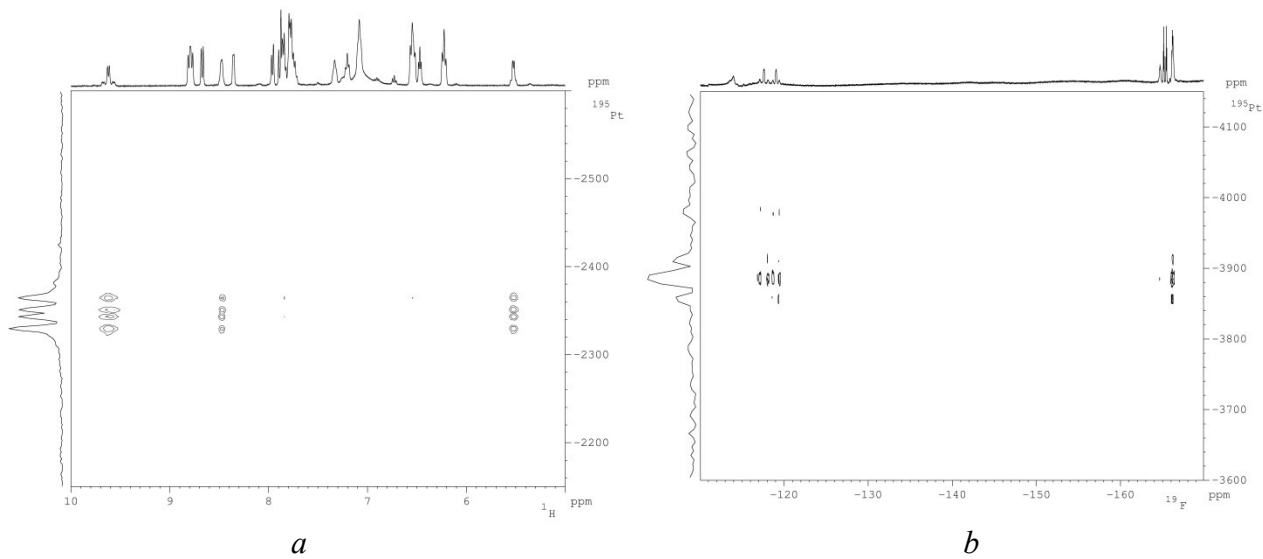


Figure S12 *a*:  $^1\text{H}$ - $^{195}\text{Pt}$  HMQC and *b*)  $^{19}\text{F}$ - $^{195}\text{Pt}$  HMQC spectra of **2** ( $\text{C}_3\text{D}_6\text{O}$ , 298 K).



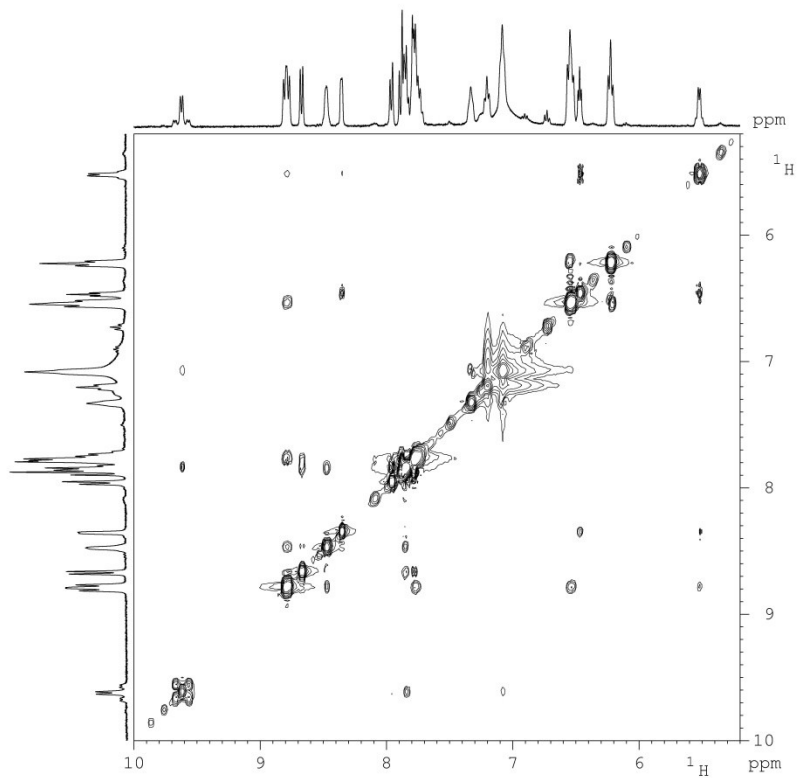


Figure S13. Low-field portion of the  $^1\text{H}$  NOESY spectrum of **2** ( $\text{C}_3\text{D}_6\text{O}$ , 400 MHz, 298 K).

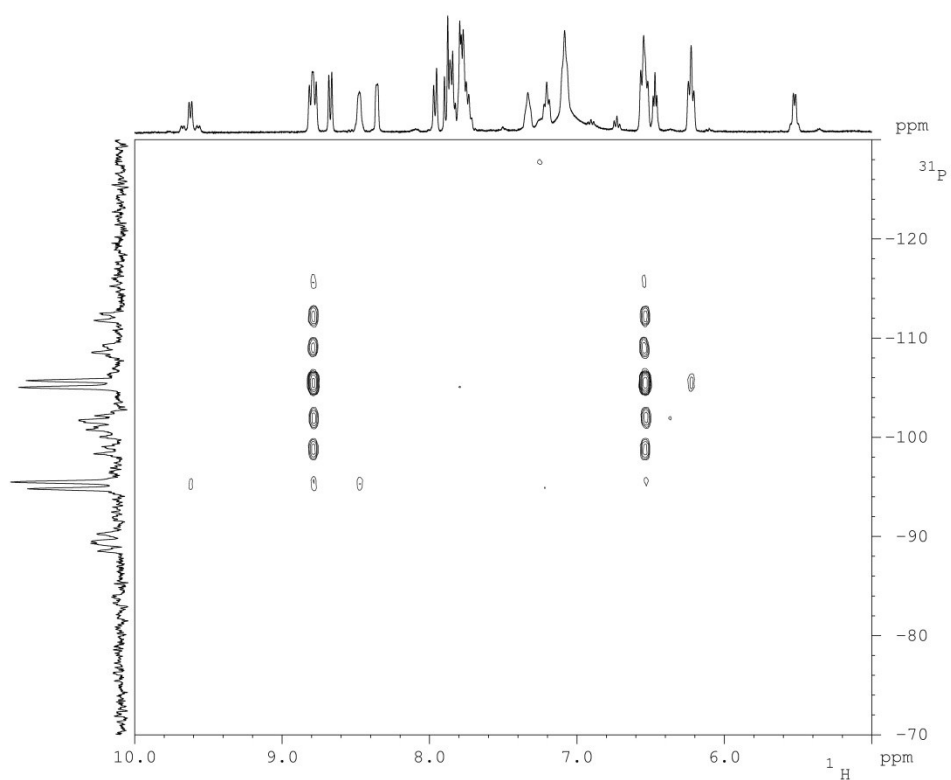


Figure S14. Portion of the  $^1\text{H}$ - $^{31}\text{P}$  HMQC spectrum of **2** ( $\text{C}_3\text{D}_6\text{O}$ , 298 K).

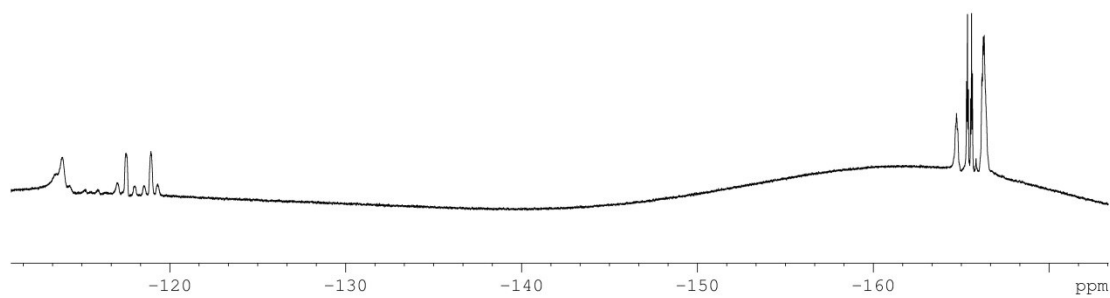


Figure S15:  $^{19}\text{F}$  NMR spectrum of **3** ( $\text{C}_3\text{D}_6\text{O}$ , 376 MHz, 298 K)

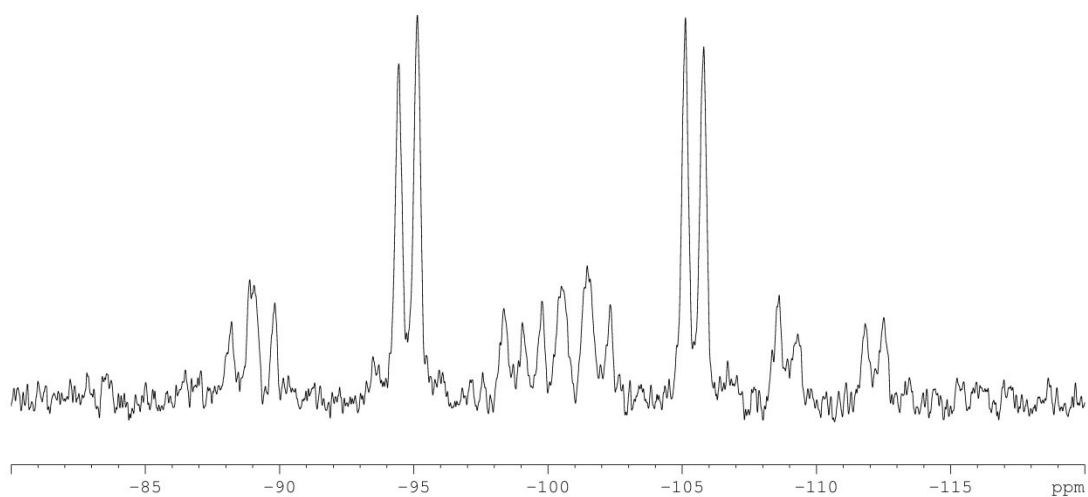


Figure S16:  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **3** ( $\text{C}_3\text{D}_6\text{O}$ , 162 MHz, 298 K)

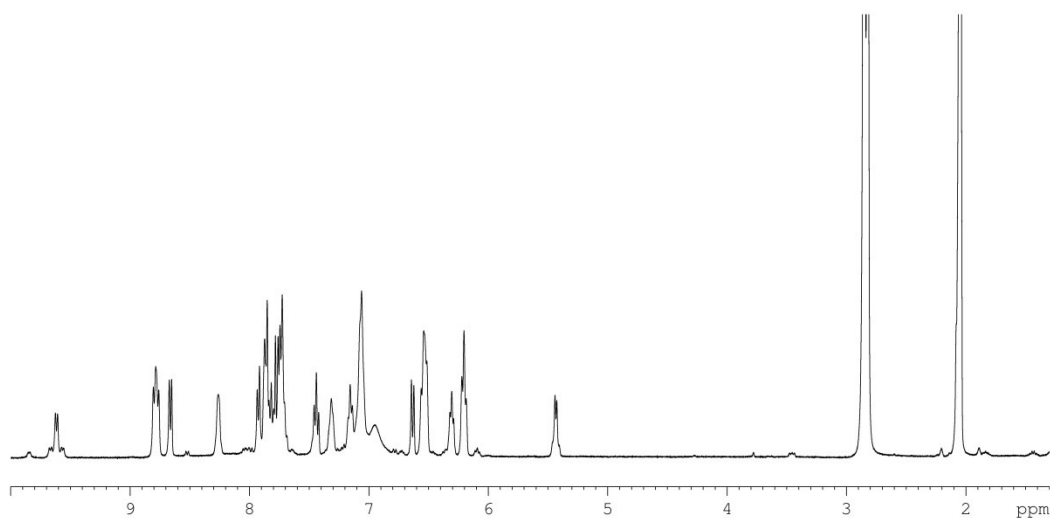


Figure S17:  $^1\text{H}$  NMR spectrum of **3** ( $\text{C}_3\text{D}_6\text{O}$ , 400 MHz, 298 K)

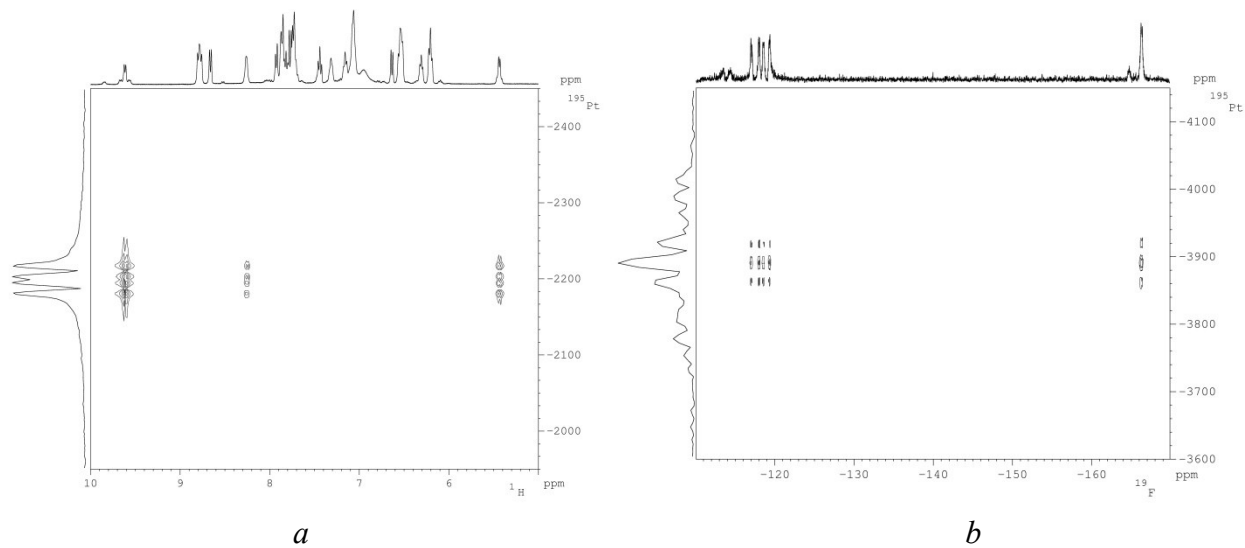


Figure S18 a:  $^1\text{H}$ - $^{195}\text{Pt}$  HMQC and b)  $^{19}\text{F}$ - $^{195}\text{Pt}$  HMQC spectra of **3** ( $\text{C}_3\text{D}_6\text{O}$ , 298 K).

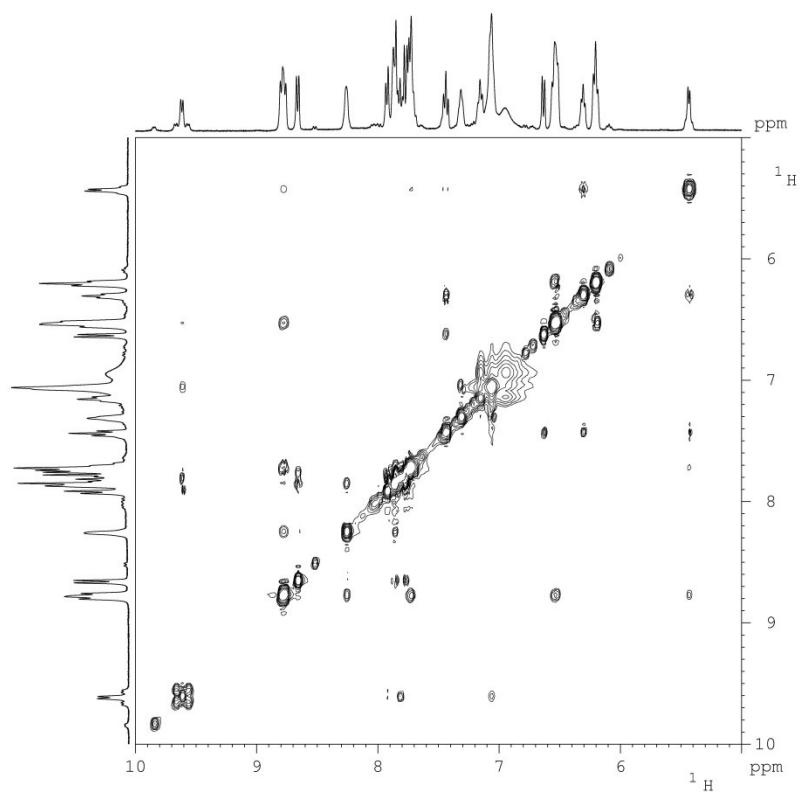


Figure S19: Low-field portion of the  $^1\text{H}$  NOESY spectrum of **3** ( $\text{C}_3\text{D}_6\text{O}$ , 400 MHz, 298 K).

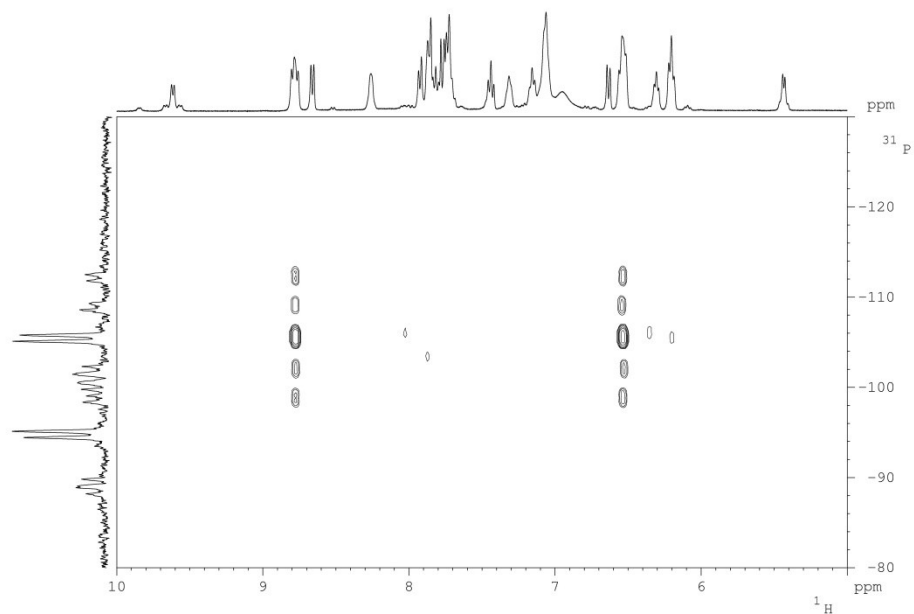


Figure S20: Portion of the  $^1\text{H}$ - $^{31}\text{P}$  HMQC spectrum of **3** ( $\text{C}_3\text{D}_6\text{O}$ , 298 K).

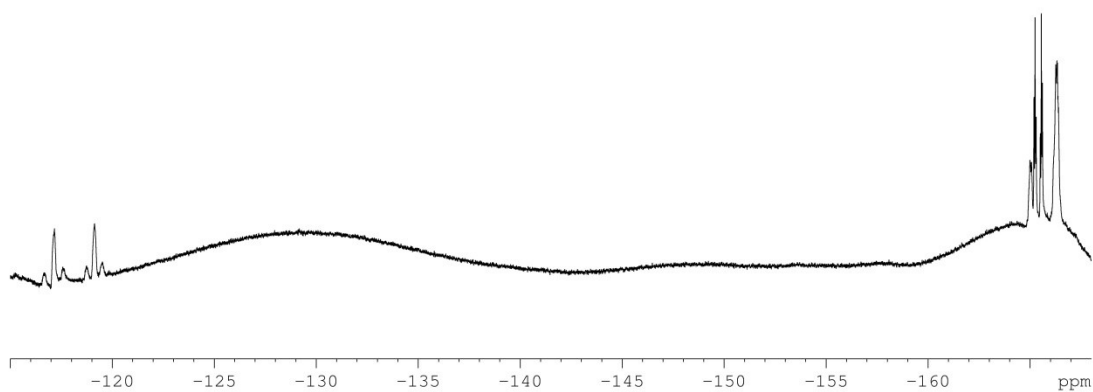


Figure S21:  $^{19}\text{F}$  NMR spectrum of **5** ( $\text{C}_3\text{D}_6\text{O}$ , 376 MHz, 298 K)

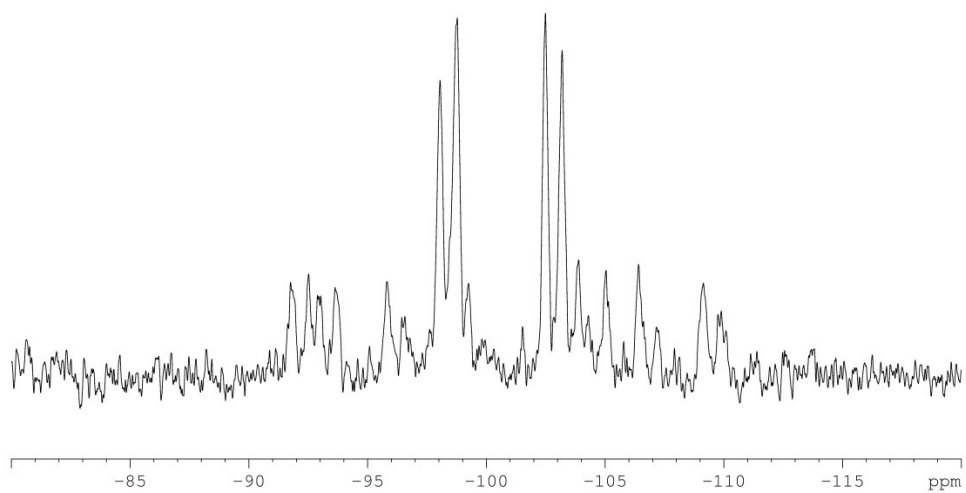


Figure S22:  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **5** ( $\text{C}_3\text{D}_6\text{O}$ , 162 MHz, 298 K)

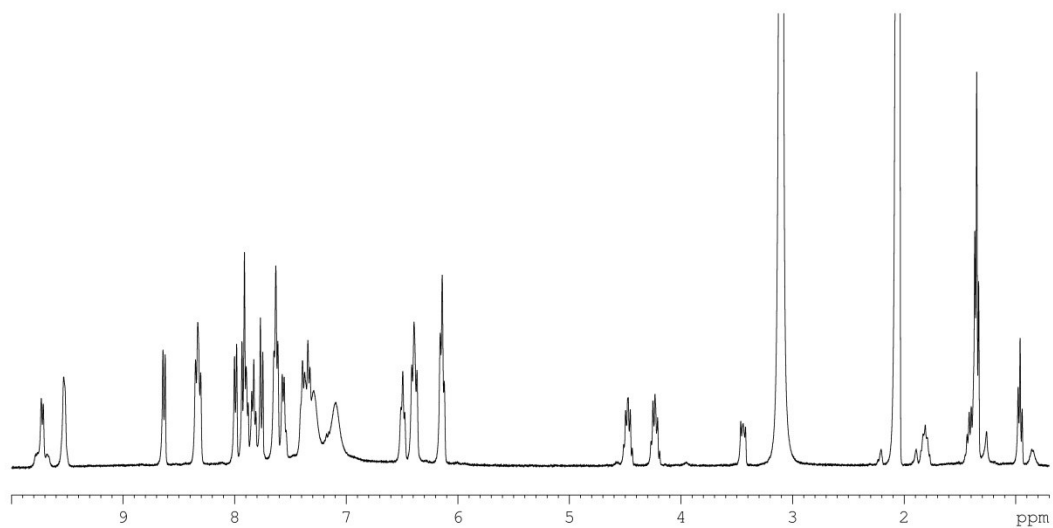


Figure S23:  $^1\text{H}$  NMR spectrum of **5** ( $\text{C}_3\text{D}_6\text{O}$ , 400 MHz, 298 K)

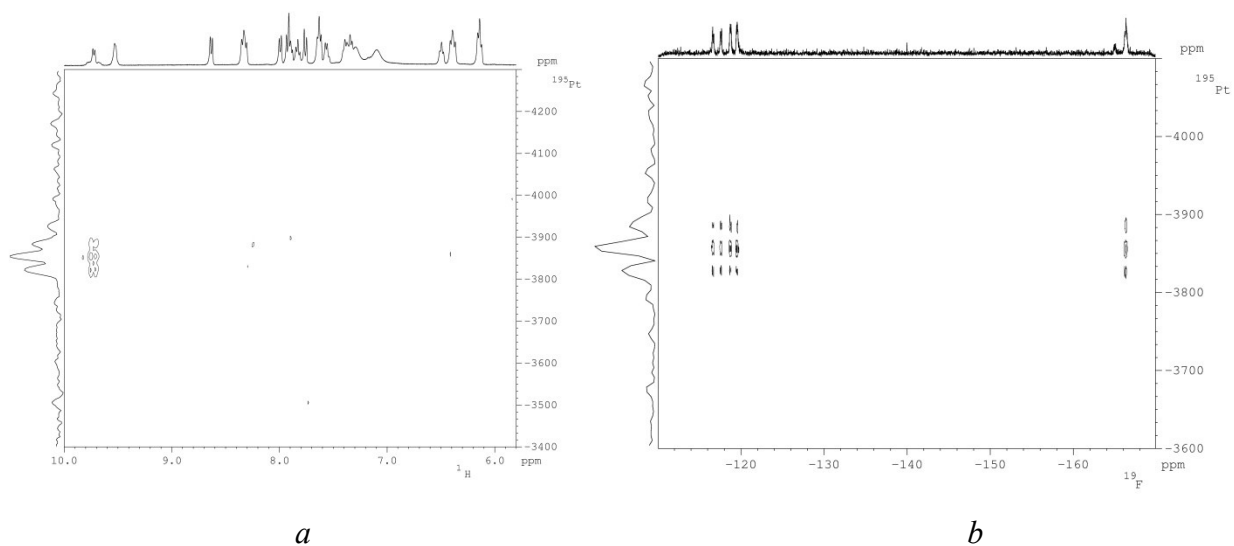


Figure S24 a:  $^1\text{H}$ - $^{195}\text{Pt}$  HMQC and b)  $^{19}\text{F}$ - $^{195}\text{Pt}$  HMQC spectra of **5** ( $\text{C}_3\text{D}_6\text{O}$ , 298 K).

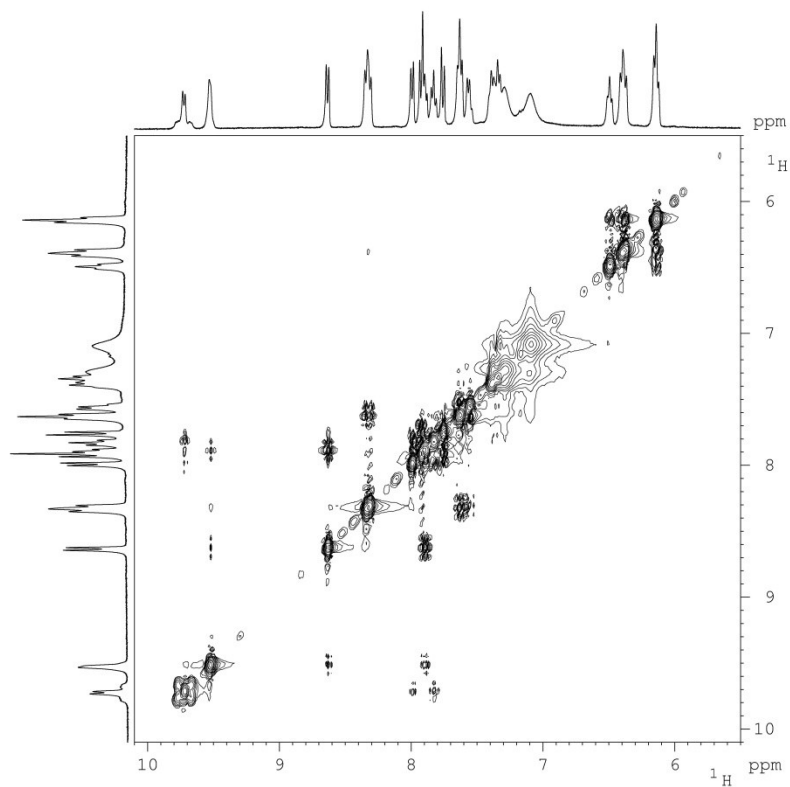


Figure S25: Low-field portion of the  $^1\text{H}$  NOESY spectrum of **5** ( $\text{C}_3\text{D}_6\text{O}$ , 400 MHz, 298 K)

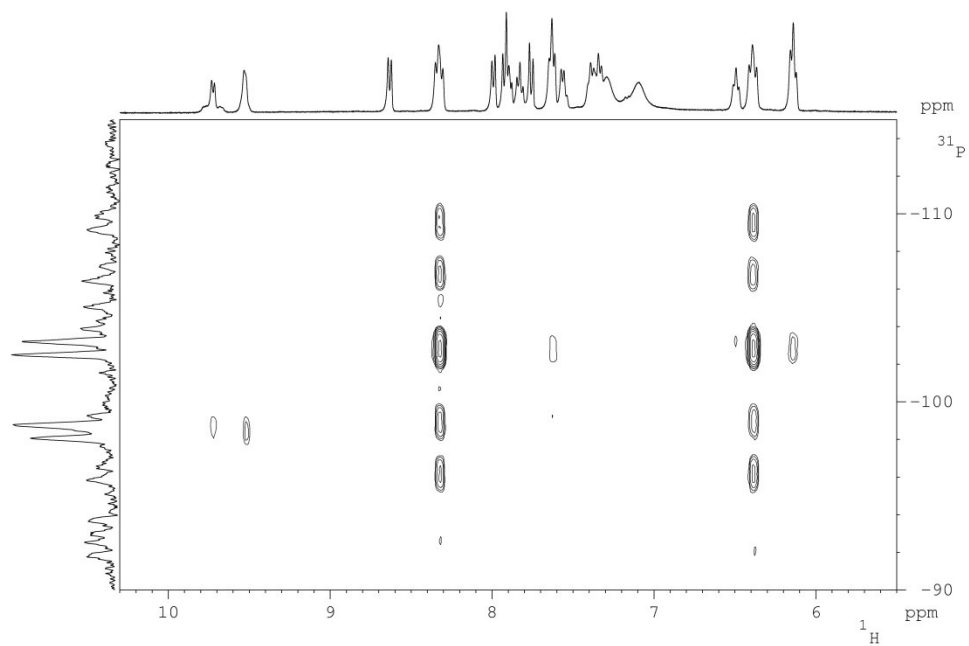


Figure S26: Portion of the  $^1\text{H}$ - $^{31}\text{P}$  HMQC spectrum of **5** ( $\text{C}_3\text{D}_6\text{O}$ , 298 K).

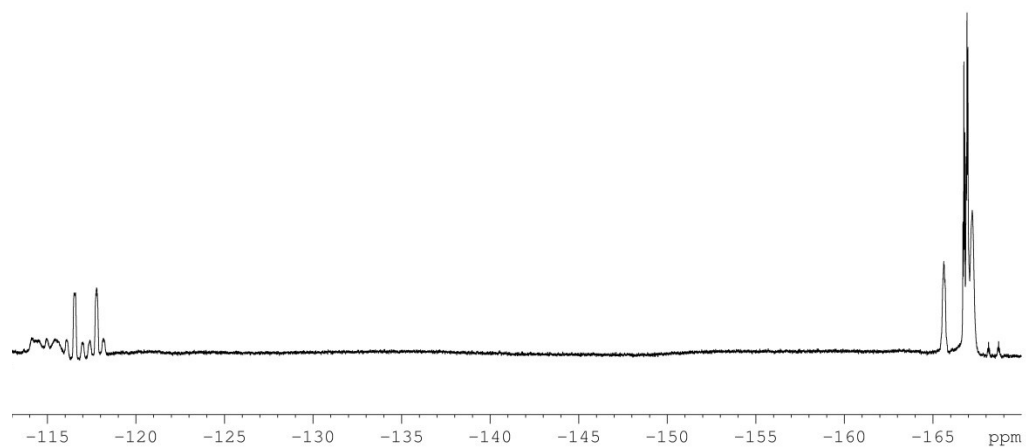


Figure S27:  $^{19}\text{F}$  NMR spectrum of **6** ( $\text{C}_3\text{D}_6\text{O}$ , 376 MHz, 298 K)

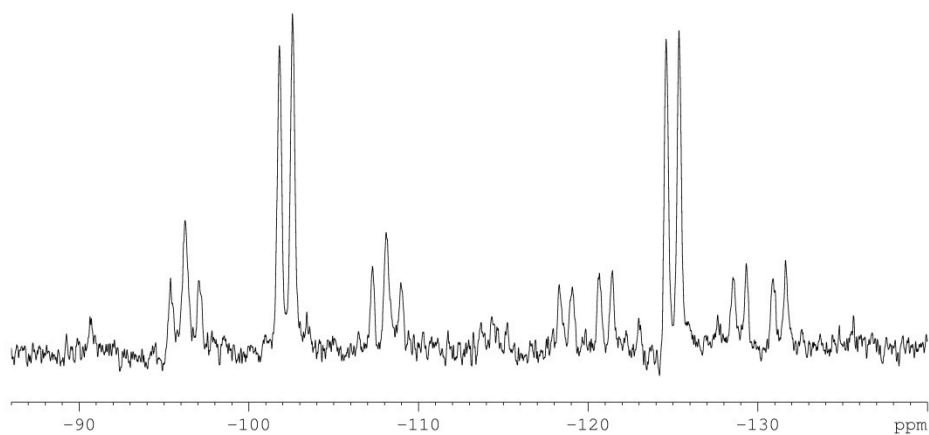


Figure S28:  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **6** ( $\text{C}_3\text{D}_6\text{O}$ , 162 MHz, 298 K)

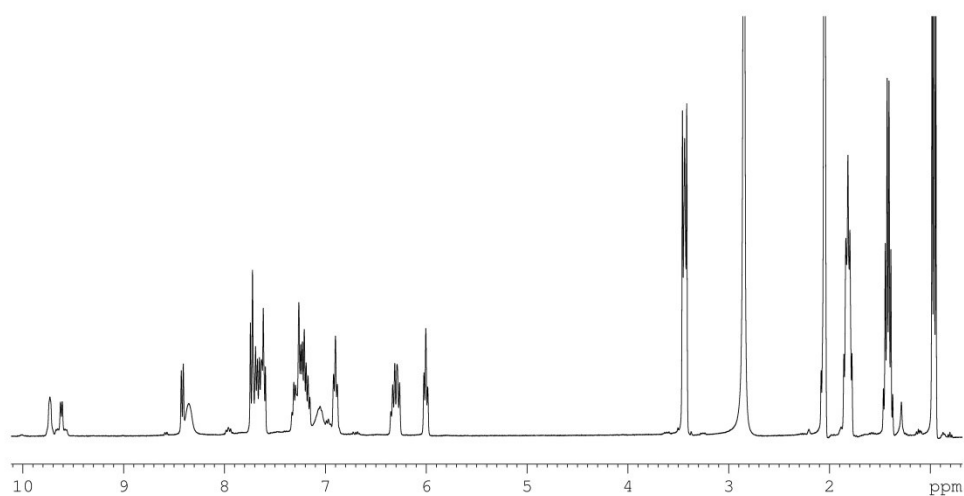


Figure S29:  $^1\text{H}$  NMR spectrum of **6** ( $\text{C}_3\text{D}_6\text{O}$ , 400 MHz, 298 K)

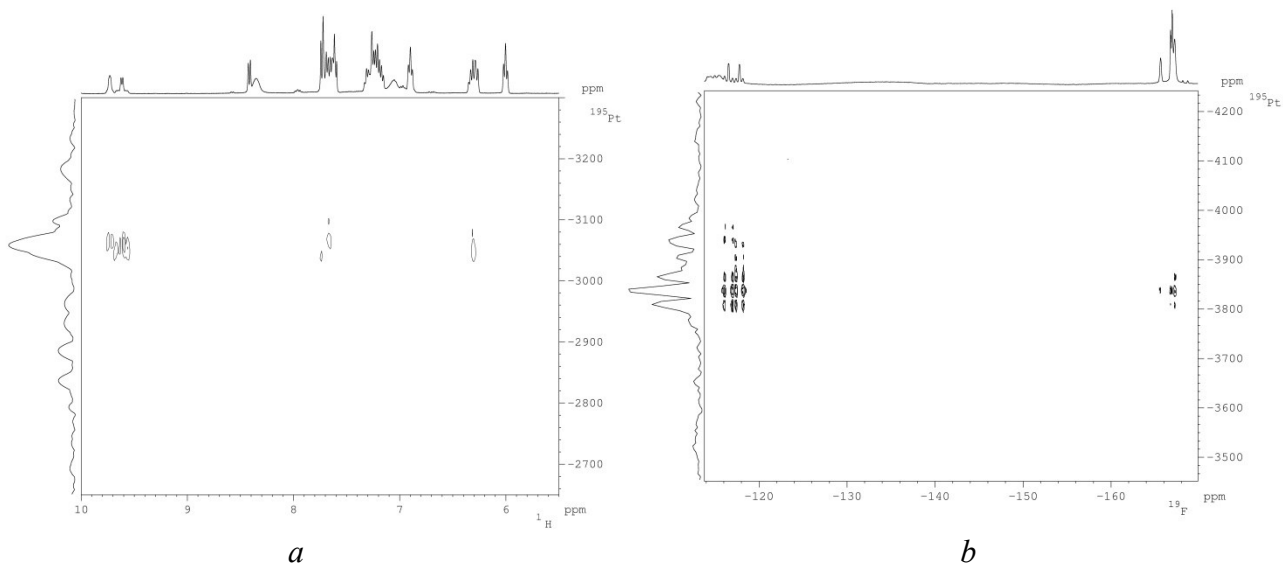


Figure S30 a:  $^1\text{H}$ - $^{195}\text{Pt}$  HMQC and b)  $^{19}\text{F}$ - $^{195}\text{Pt}$  HMQC spectra of **6** ( $\text{C}_3\text{D}_6\text{O}$ , 298 K).

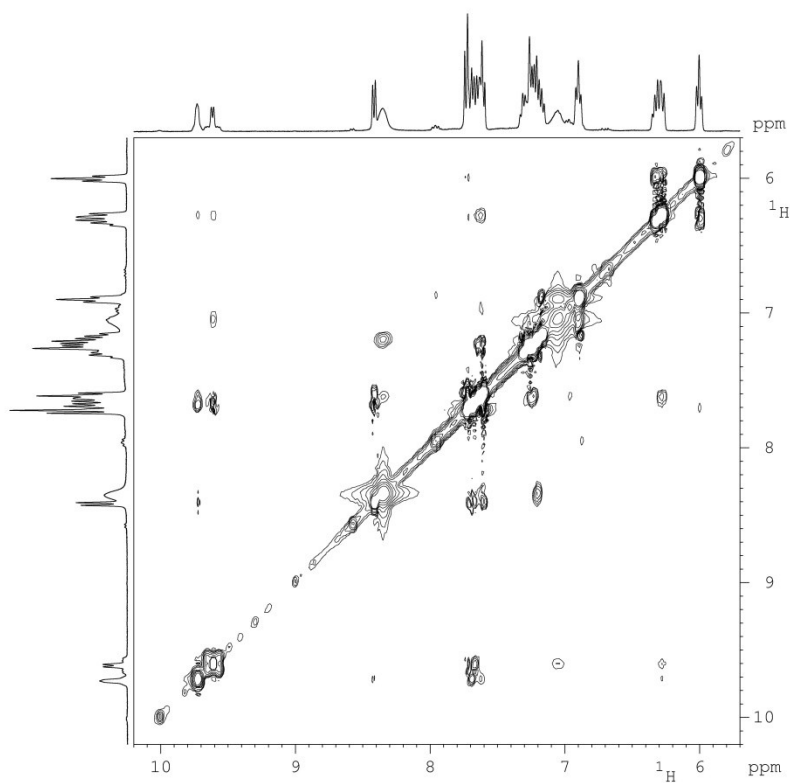


Figure S31: Low-field portion of the  $^1\text{H}$  NOESY spectrum of **6** ( $\text{C}_3\text{D}_6\text{O}$ , 400 MHz, 298 K).



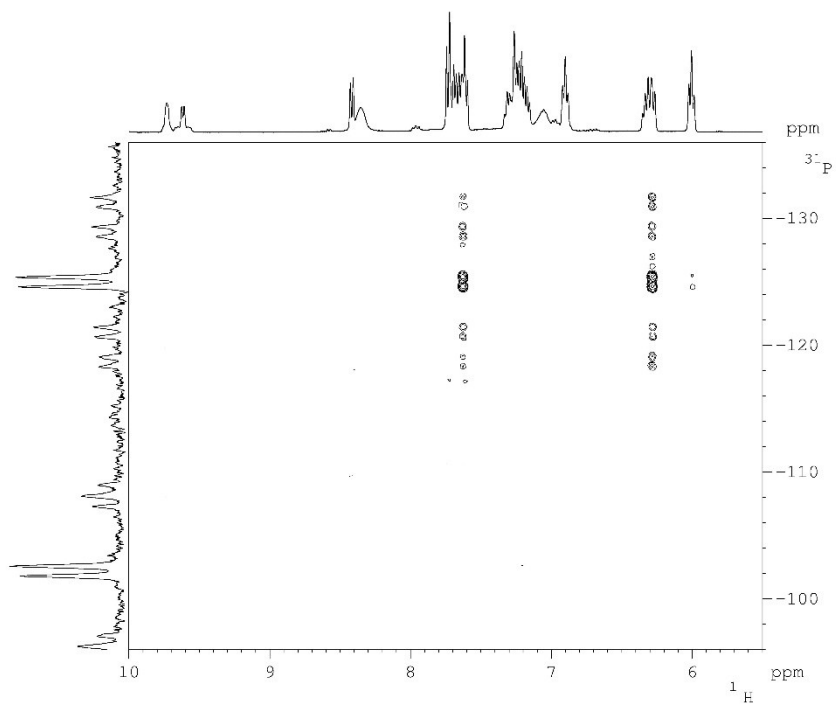


Figure S32: Portion of the  $^1\text{H}$ - $^{31}\text{P}$  HMQC spectrum of **6** ( $\text{C}_3\text{D}_6\text{O}$ , 298 K).

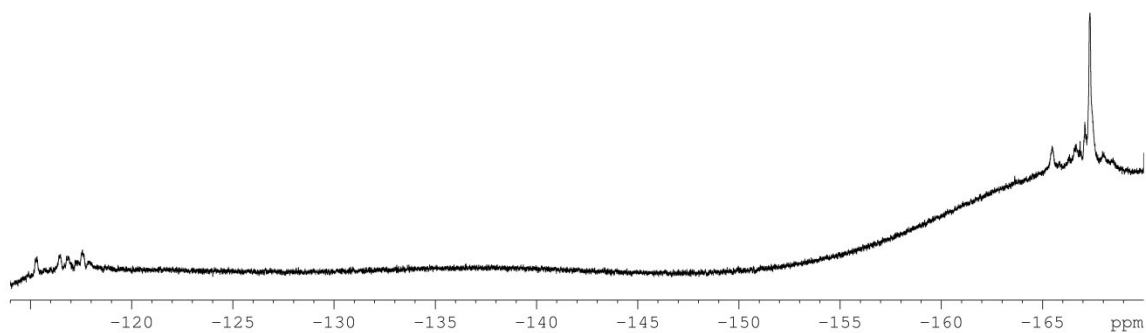


Figure S33:  $^{19}\text{F}$  NMR spectrum of **7** ( $\text{C}_3\text{D}_6\text{O}$ , 376 MHz, 298 K)

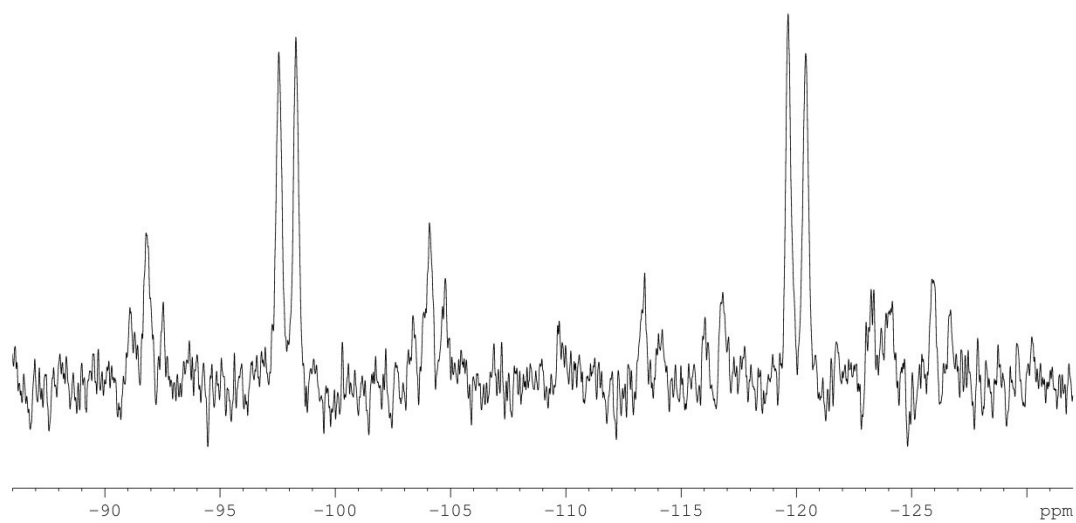


Figure S34:  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **7** ( $\text{C}_3\text{D}_6\text{O}$ , 162 MHz, 298 K)

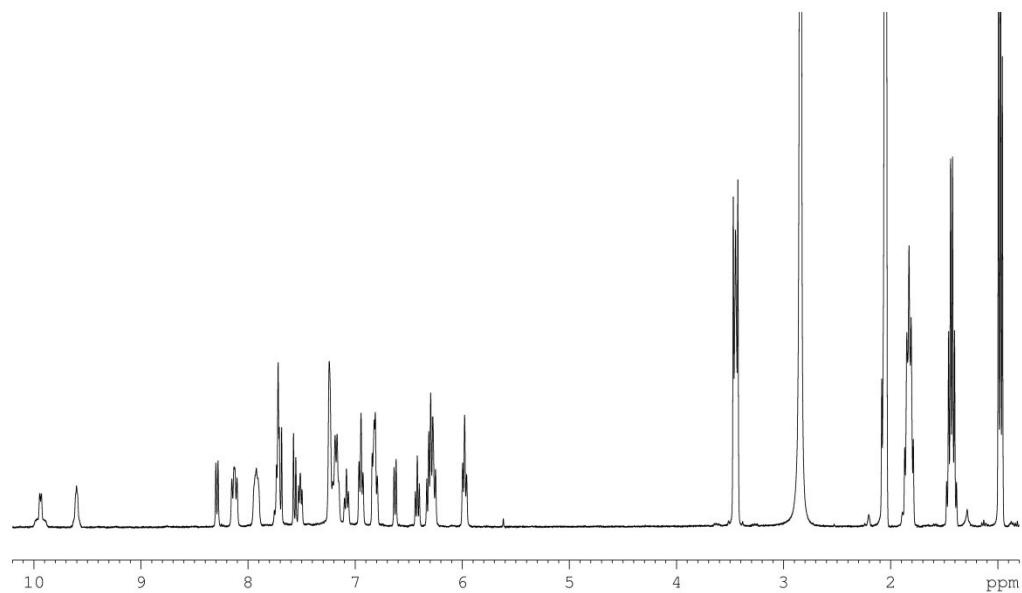


Figure S35:  $^1\text{H}$  NMR spectrum of **7** ( $\text{C}_3\text{D}_6\text{O}$ , 400 MHz, 298 K)

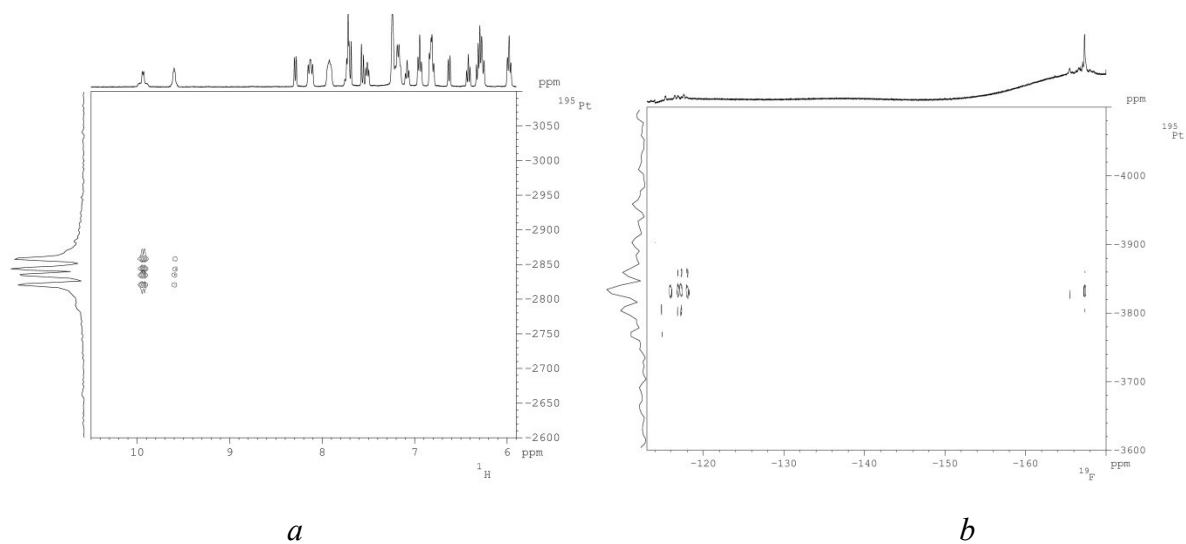


Figure S36 a:  $^1\text{H}$ - $^{195}\text{Pt}$  HMQC and b)  $^{19}\text{F}$ - $^{195}\text{Pt}$  HMQC spectra of **7** ( $\text{C}_3\text{D}_6\text{O}$ , 298 K).

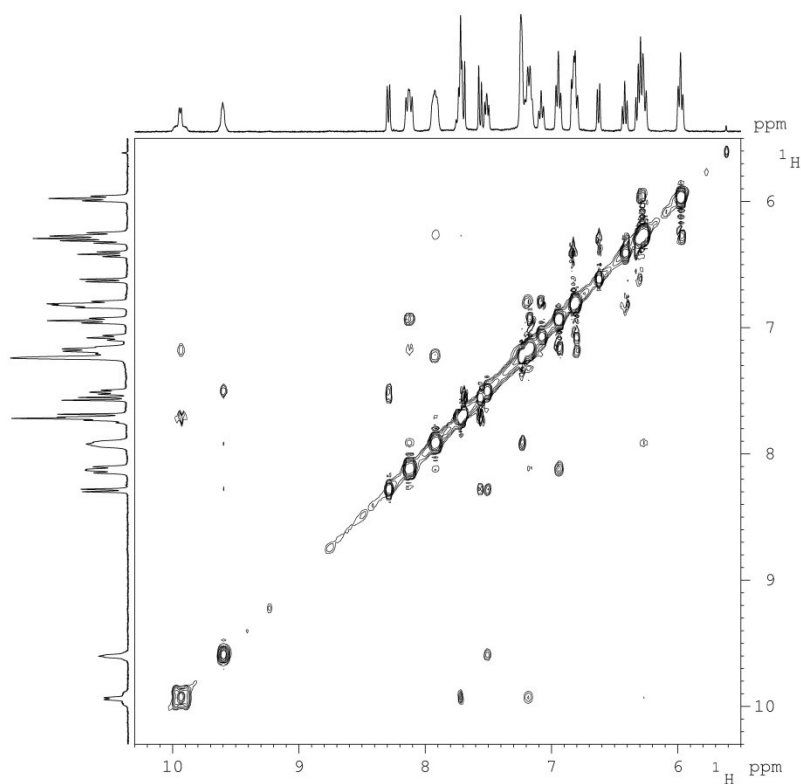


Figure S37: Low-field portion of the  $^1\text{H}$  NOESY spectrum of **7** ( $\text{C}_3\text{D}_6\text{O}$ , 400 MHz, 298 K).

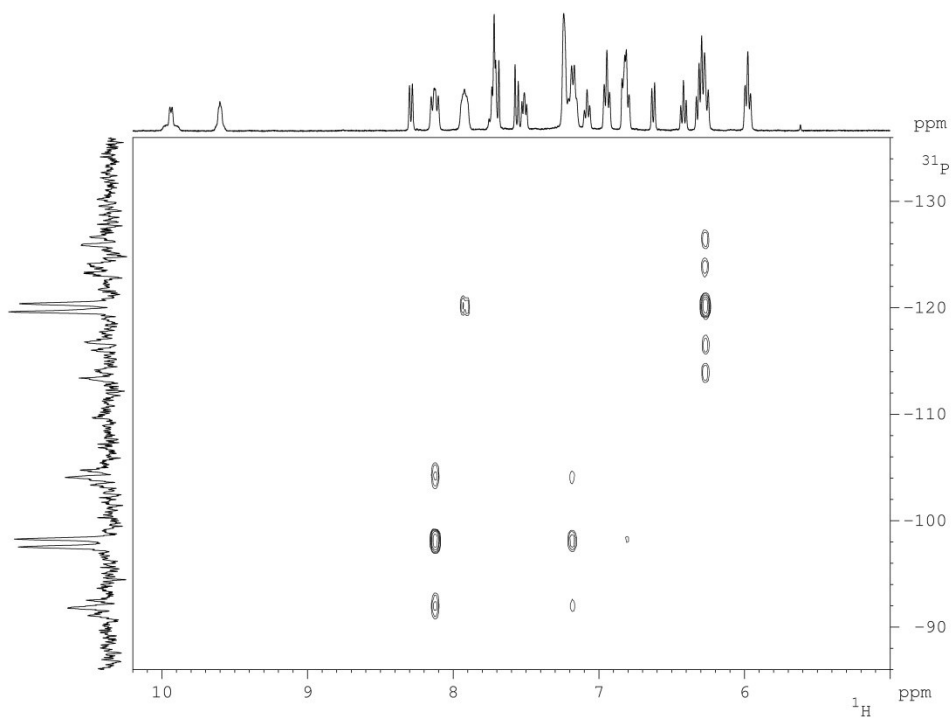


Figure S38. Portion of the  $^1\text{H}$ - $^{31}\text{P}$  HMQC spectrum of **7** ( $\text{C}_3\text{D}_6\text{O}$ , 298 K).

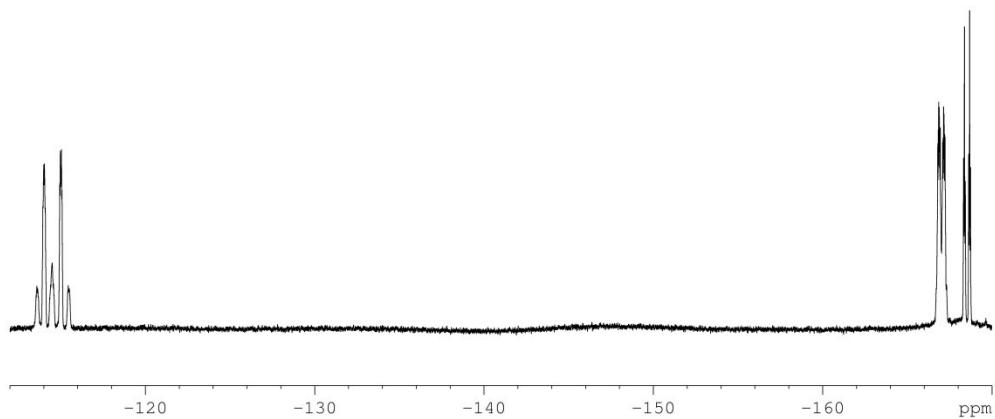


Figure S39:  $^{19}\text{F}$  NMR spectrum of **8** ( $\text{C}_3\text{D}_6\text{O}$ , 376 MHz, 298 K)

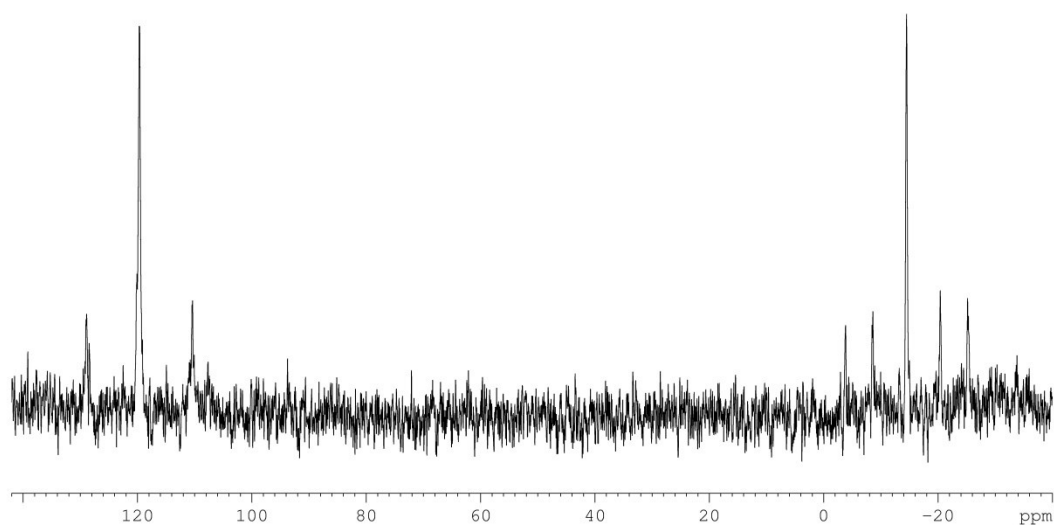


Figure S40:  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **8** ( $\text{C}_3\text{D}_6\text{O}$ , 162 MHz, 298 K)

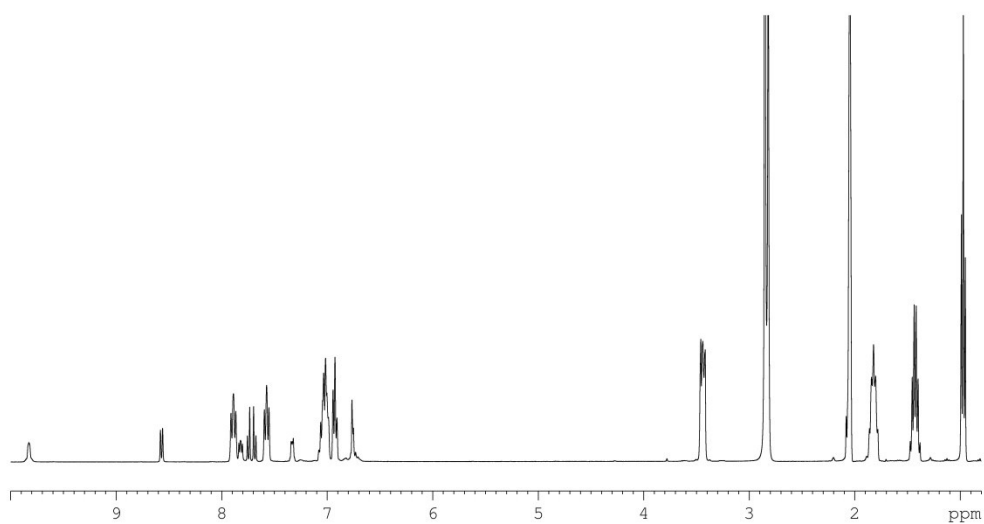


Figure S41:  $^1\text{H}$  NMR spectrum of **8** ( $\text{C}_3\text{D}_6\text{O}$ , 400 MHz, 298 K).

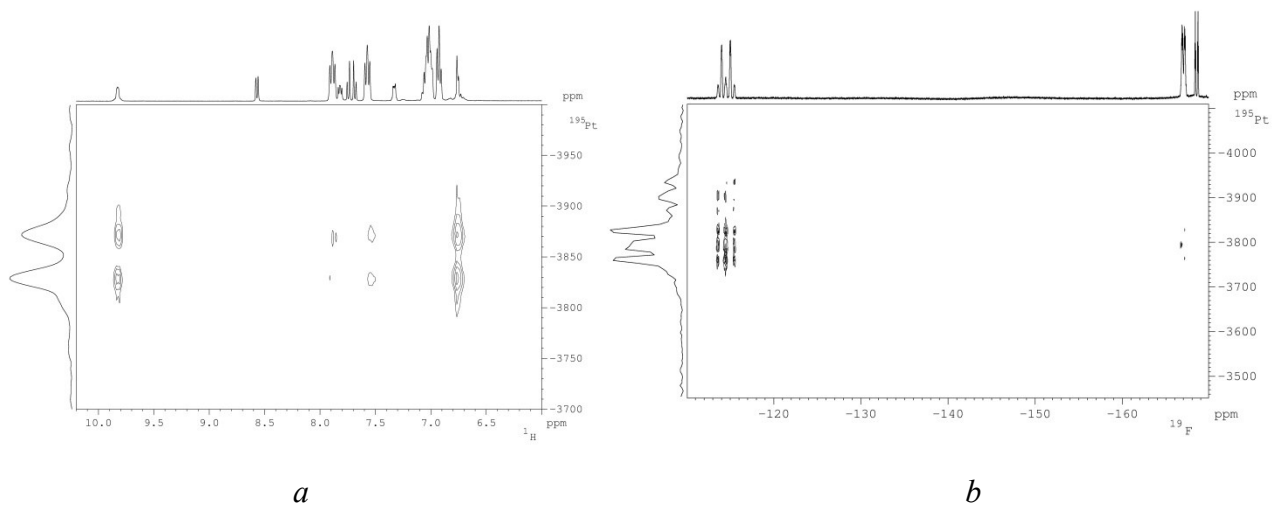


Figure S42 a:  $^1\text{H}$ - $^{195}\text{Pt}$  HMQC and b)  $^{19}\text{F}$ - $^{195}\text{Pt}$  HMQC spectra of **8** ( $\text{C}_3\text{D}_6\text{O}$ , 298 K).

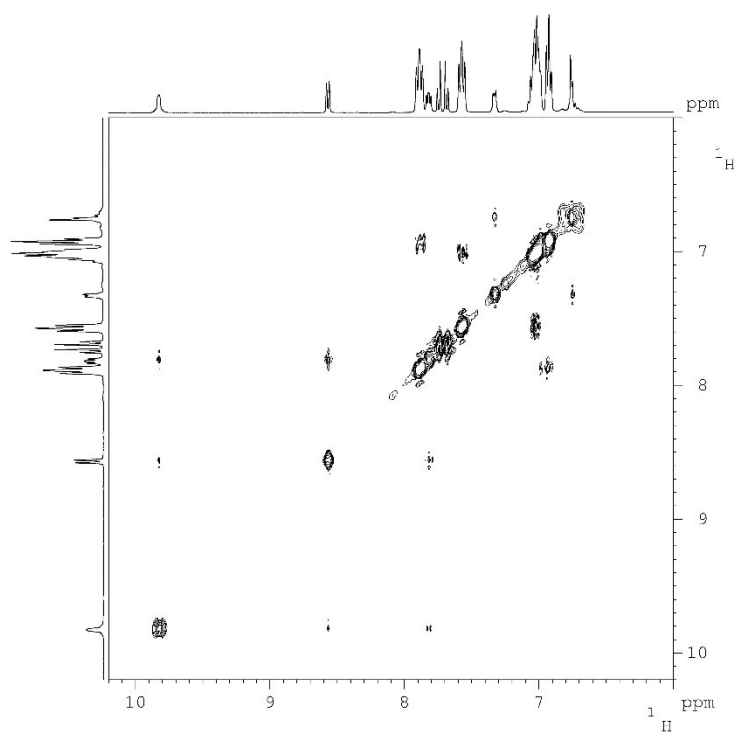


Figure S43: Low-field portion of the  $^1\text{H}$  NOESY spectrum of **8** ( $\text{C}_3\text{D}_6\text{O}$ , 400 MHz, 298 K).

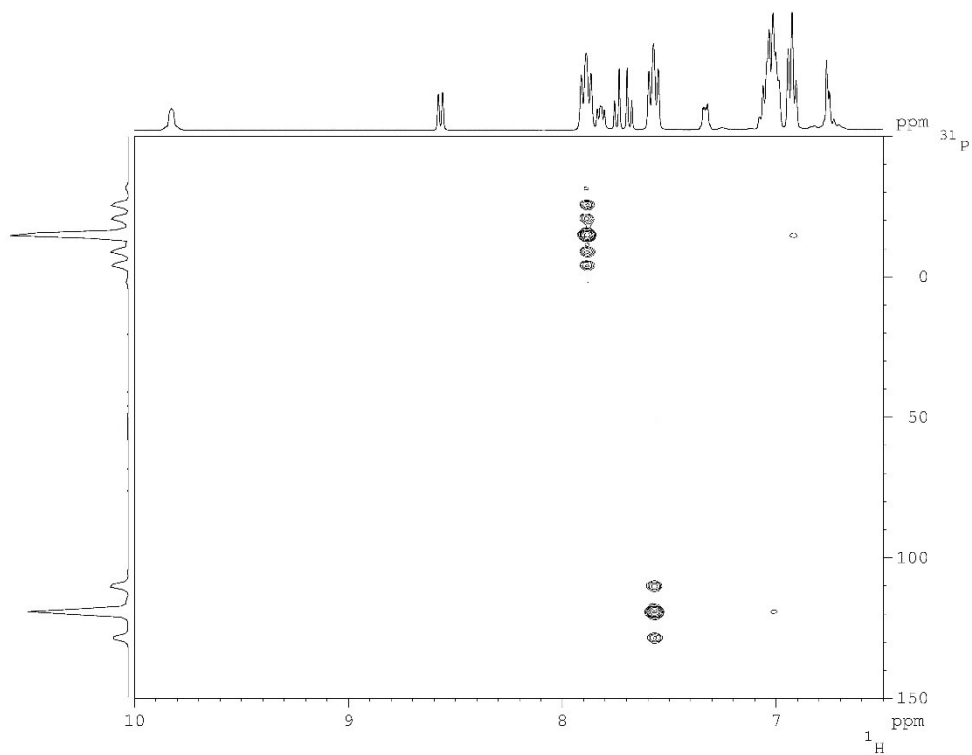


Figure S44: Portion of the  $^1\text{H}$ - $^{31}\text{P}$  HMQC spectrum of **8** ( $\text{C}_3\text{D}_6\text{O}$ , 298 K).

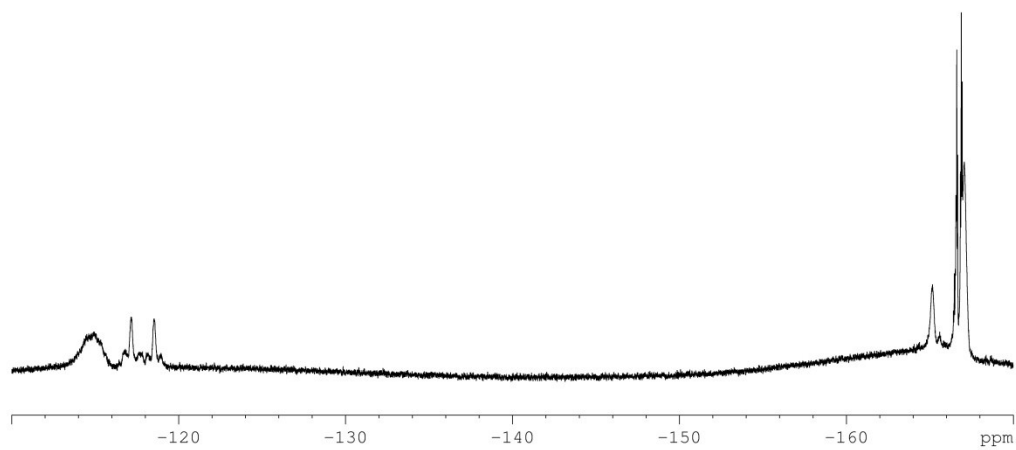


Figure S45:  $^{19}\text{F}$  NMR spectrum of **10** ( $\text{C}_3\text{D}_6\text{O}$ , 376 MHz, 298 K)

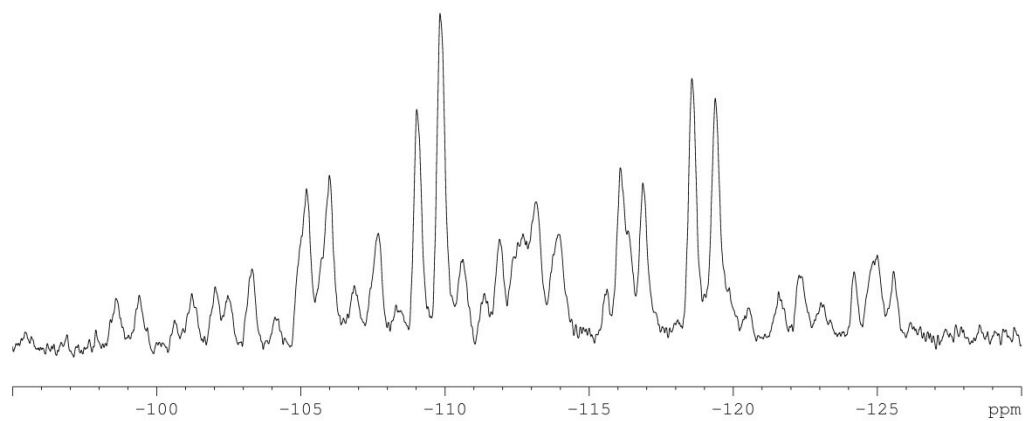


Figure S46:  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **10** ( $\text{C}_3\text{D}_6\text{O}$ , 162 MHz, 298 K)

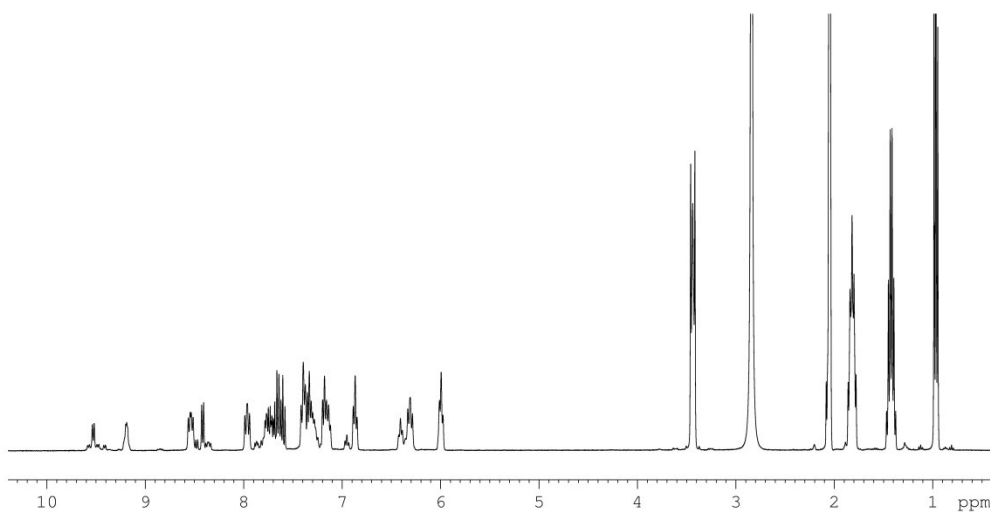


Figure S47:  $^1\text{H}$  NMR spectrum of **10** ( $\text{C}_3\text{D}_6\text{O}$ , 400 MHz, 298 K)

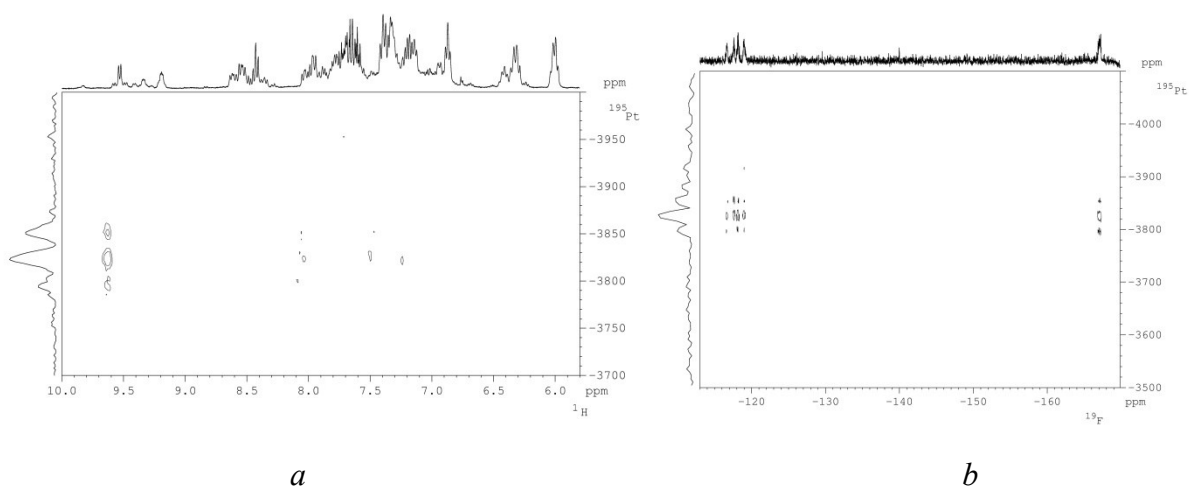


Figure S48 a:  $^1\text{H}$ - $^{195}\text{Pt}$  HMQC and b)  $^{19}\text{F}$ - $^{195}\text{Pt}$  HMQC spectra of **10** ( $\text{C}_3\text{D}_6\text{O}$ , 298 K).

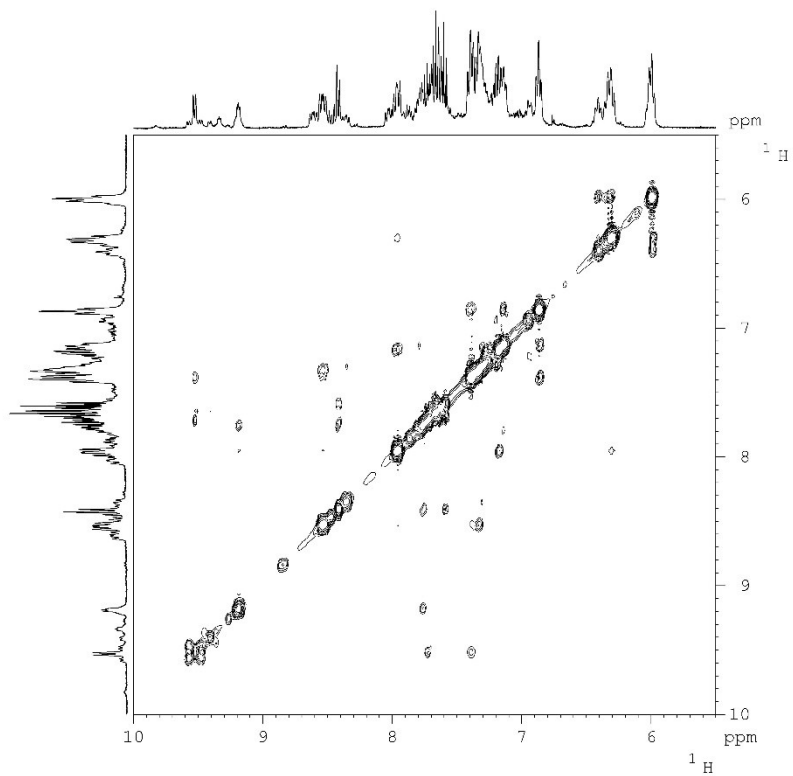


Figure S49: Low-field portion of the  $^1\text{H}$  NOESY spectrum of **10** ( $\text{C}_3\text{D}_6\text{O}$ , 400 MHz, 298 K).

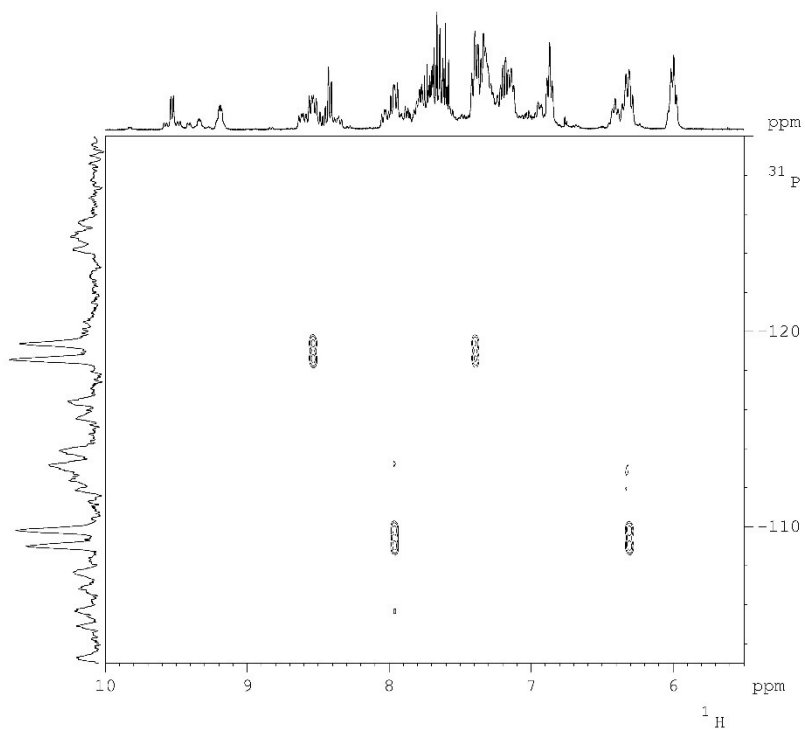


Figure S50: Portion of the  $^1\text{H}$ - $^{31}\text{P}$  HMQC spectrum of **10** ( $\text{C}_3\text{D}_6\text{O}$ , 298 K).



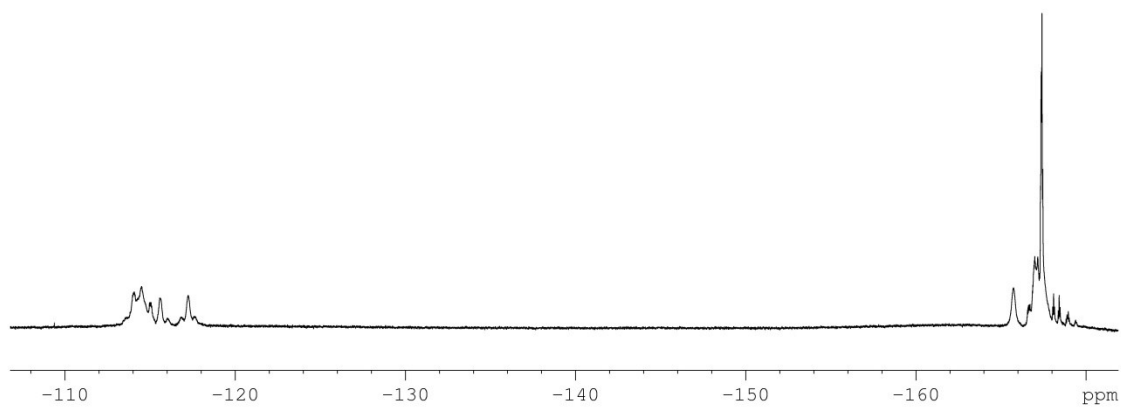


Figure S51:  $^{19}\text{F}$  NMR spectrum of **11** ( $\text{C}_3\text{D}_6\text{O}$ , 376 MHz, 298 K)

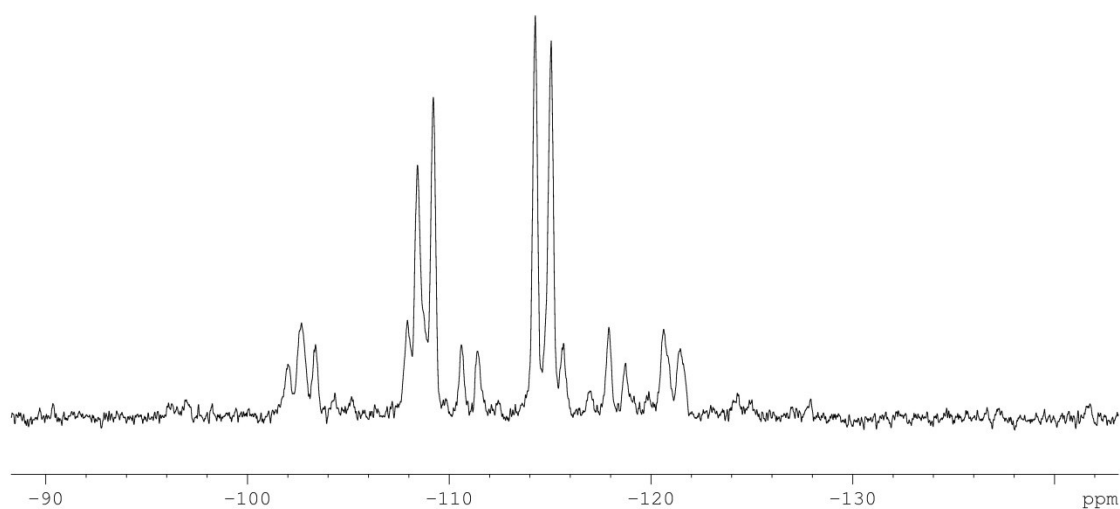


Figure S52:  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **11** ( $\text{C}_3\text{D}_6\text{O}$ , 162 MHz, 298 K)

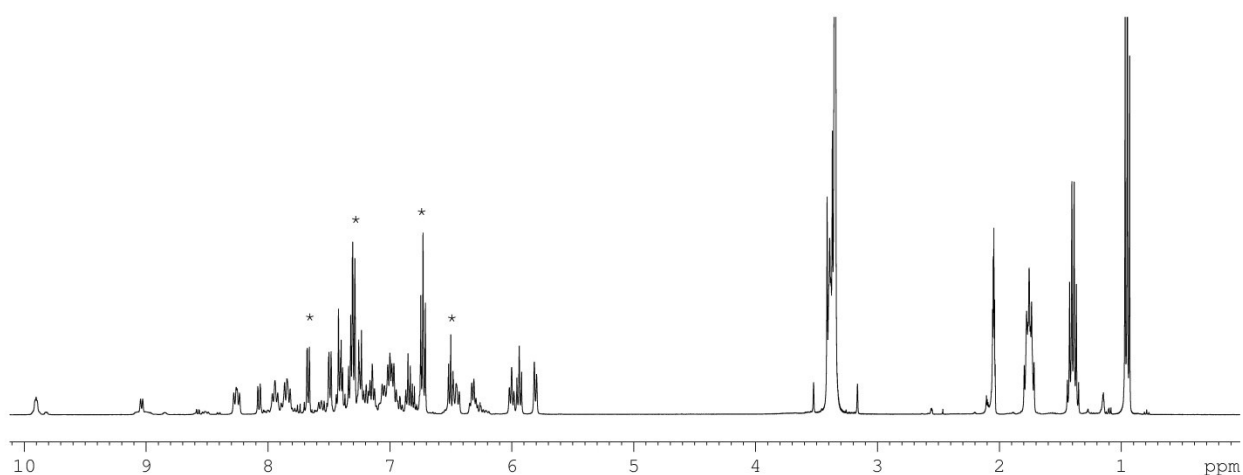


Figure S53:  $^1\text{H}$  NMR spectrum of **11** ( $\text{C}_3\text{D}_6\text{O}$ , 400 MHz, 298 K). Asterisked peaks belong to free  $\text{NBu}_4\text{PhS}$ .

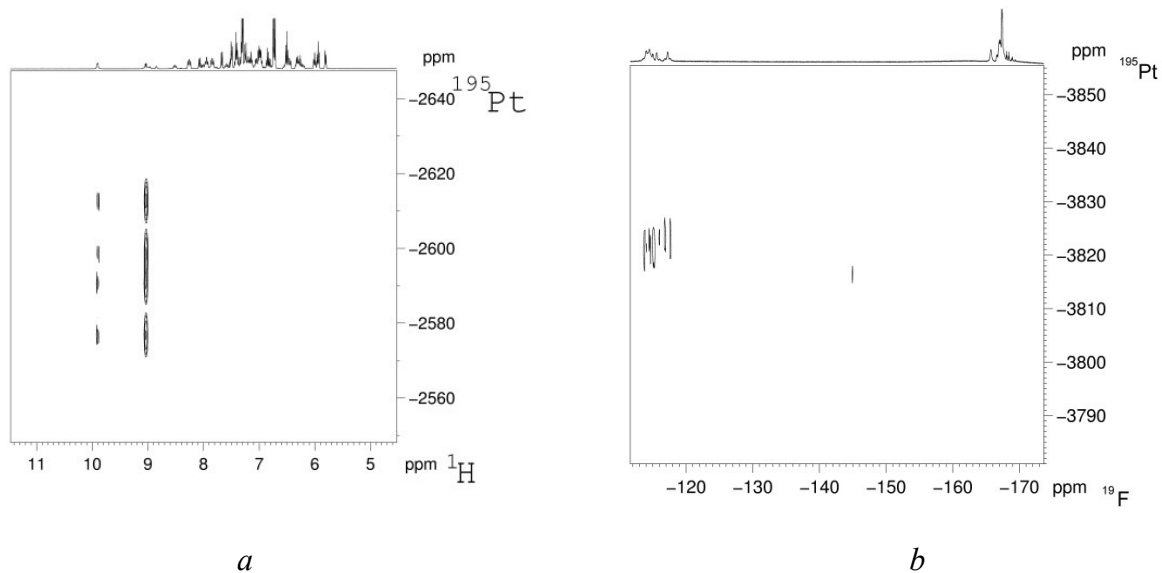


Figure S54 a:  $^1\text{H}$ - $^{195}\text{Pt}$  HMQC and b)  $^{19}\text{F}$ - $^{195}\text{Pt}$  HMQC spectra of **11** ( $\text{C}_3\text{D}_6\text{O}$ , 298 K).

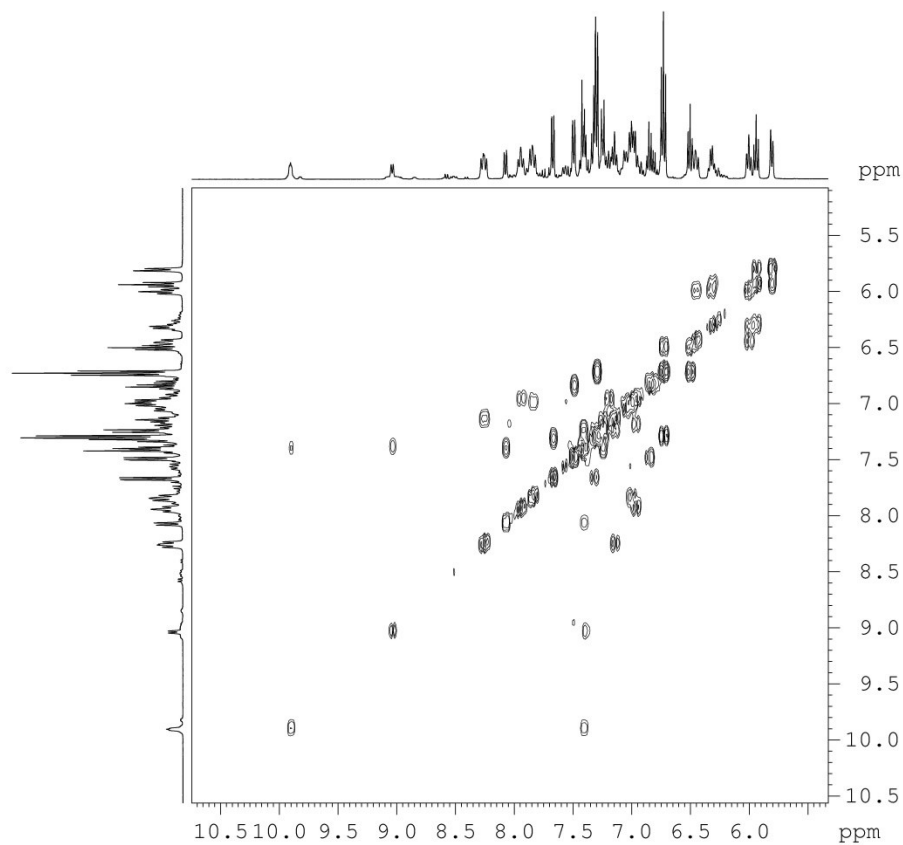


Figure S55: Low-field portion of the  $^1\text{H}$  COSY spectrum of **11** ( $\text{C}_3\text{D}_6\text{O}$ , 400 MHz, 298 K).

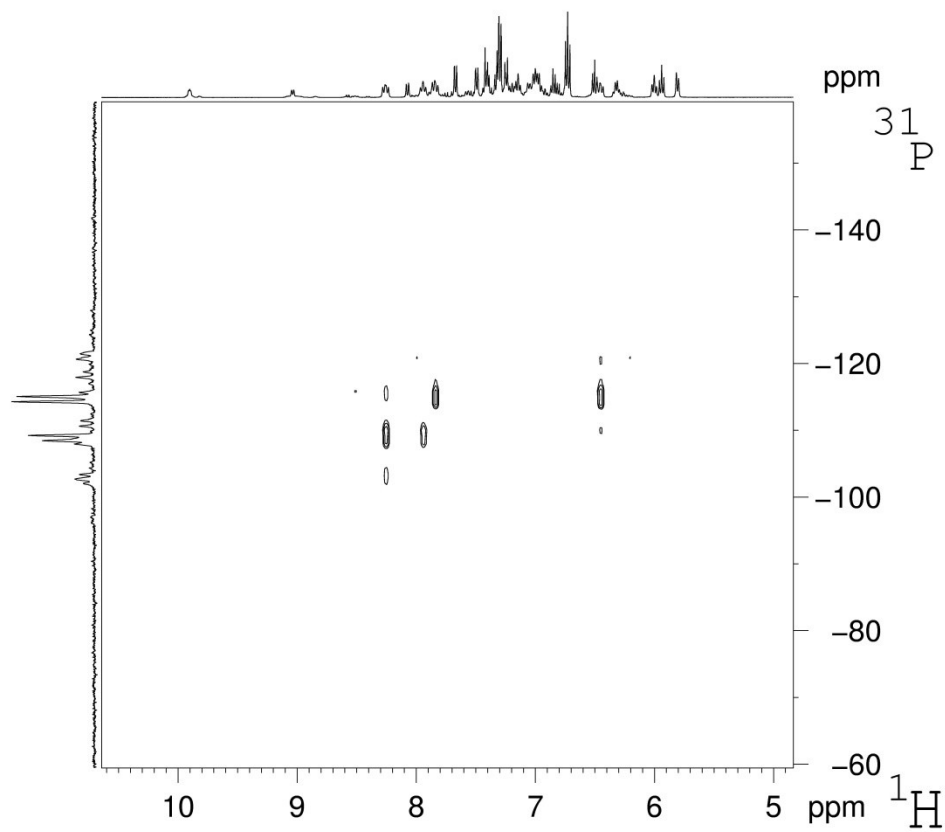


Figure S56: Portion of the  $^1\text{H}$ - $^{31}\text{P}$  HMQC spectrum of **11** ( $\text{C}_3\text{D}_6\text{O}$ , 298 K).

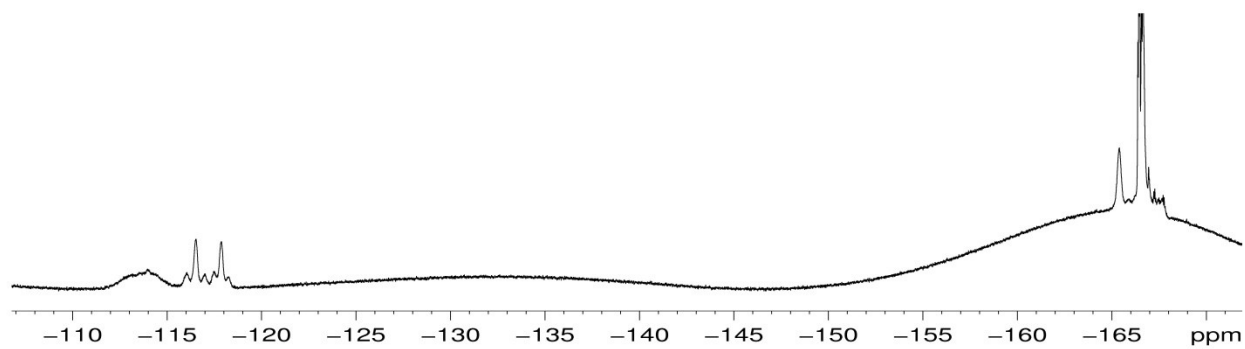


Figure S57:  $^{19}\text{F}$  NMR spectrum of *cis*-**12** ( $\text{C}_3\text{D}_6\text{O}$ , 376 MHz, 298 K)

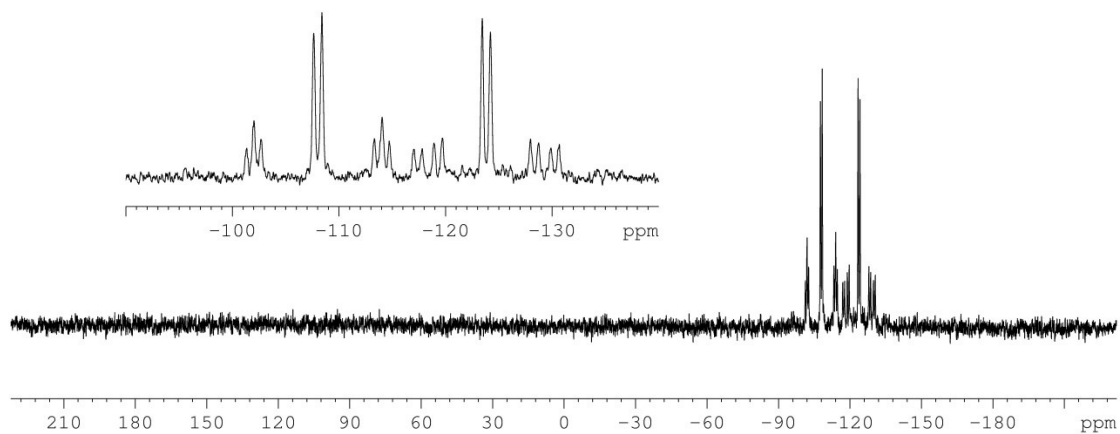


Figure S58:  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of *cis*-**12** ( $\text{C}_3\text{D}_6\text{O}$ , 162 MHz, 298 K)

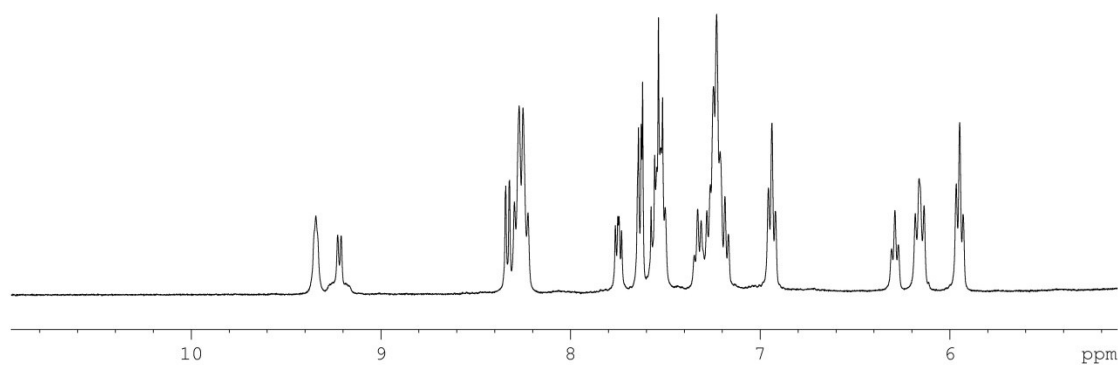


Figure S59: Lowfield part of the  $^1\text{H}$  NMR spectrum of *cis*-**12** ( $\text{C}_3\text{D}_6\text{O}$ , 400 MHz, 298 K).

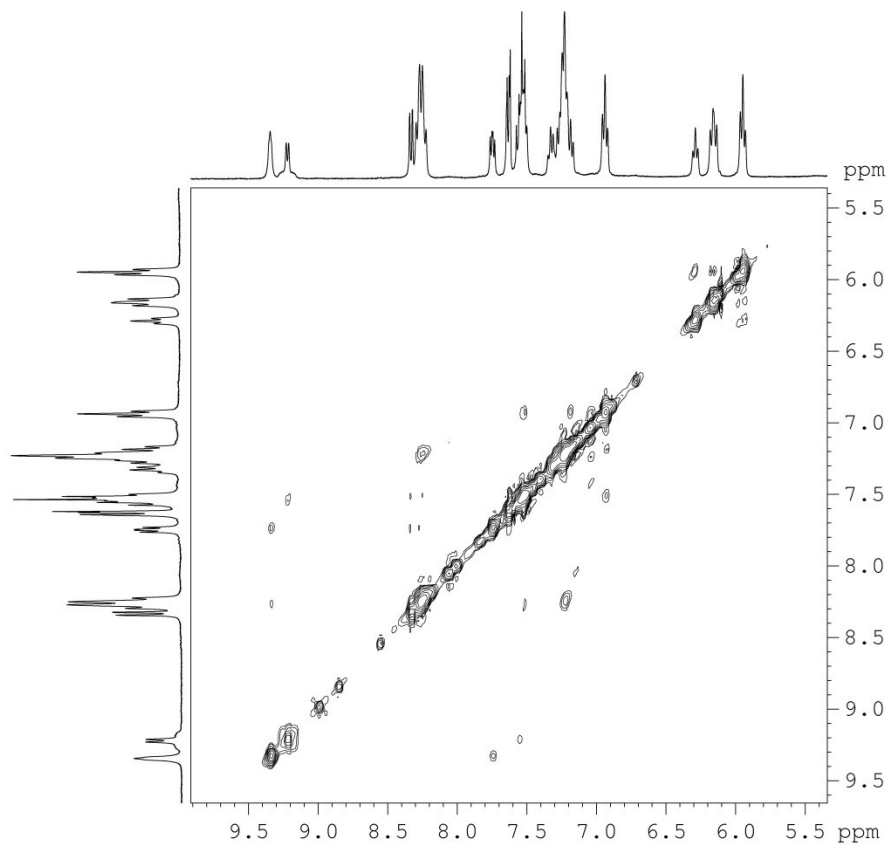


Figure S60: Low-field portion of the  $^1\text{H}$  NOESY spectrum of *cis*-**12** ( $\text{C}_3\text{D}_6\text{O}$ , 400 MHz, 298 K).