Supporting information
for:

Mixed-Valence Nickel-Iron Dithiolates Related to the [NiFe]-Hydrogenases

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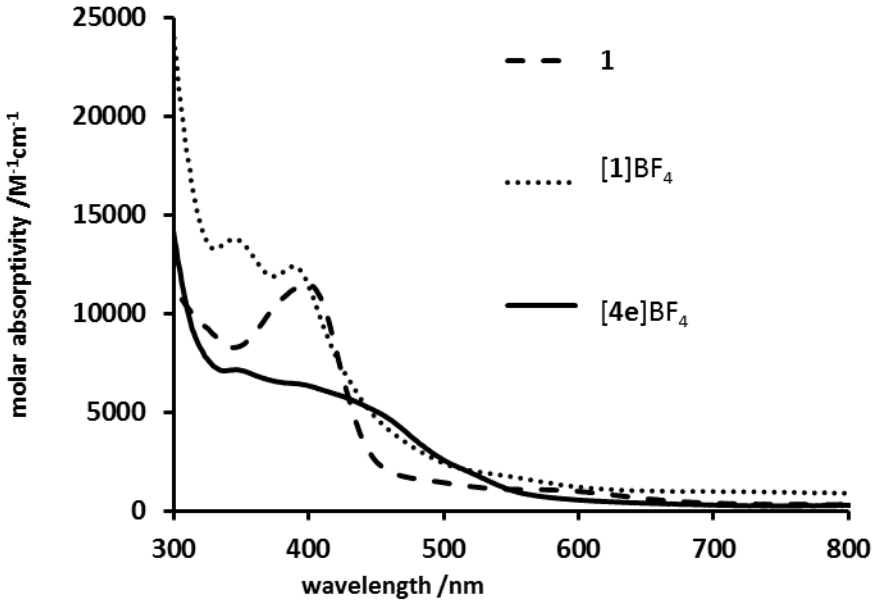

Figure S1: UV-vis spectra of **1**, [**1**]BF_4 and [**4e**]BF_4 (0.5 mM in CH_2Cl_2).

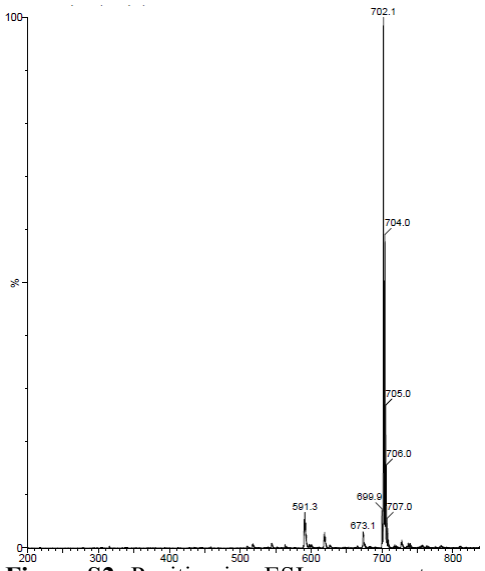

Figure S2: Positive ion ESI mass spectrum of [**1**]BF_4.

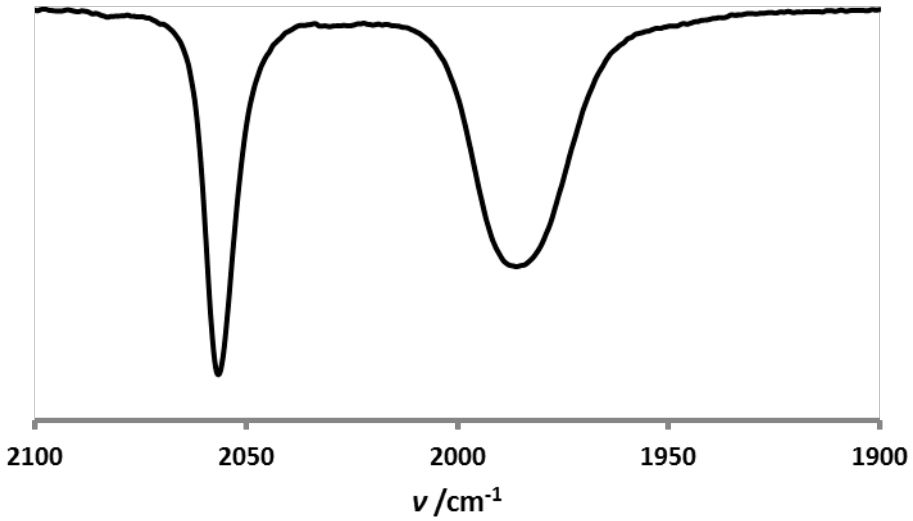

Figure S3: FT-IR spectrum (ν_{CO} region, CH_2Cl_2) of [**1**]BF_4.

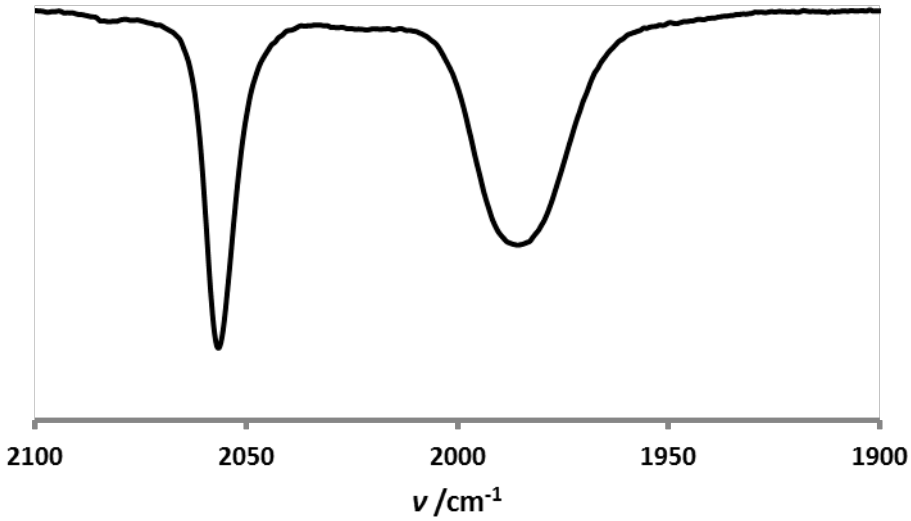

Figure S4: FT-IR spectrum (ν_{CO} region, CH_2Cl_2) of [**1**]PF_6.

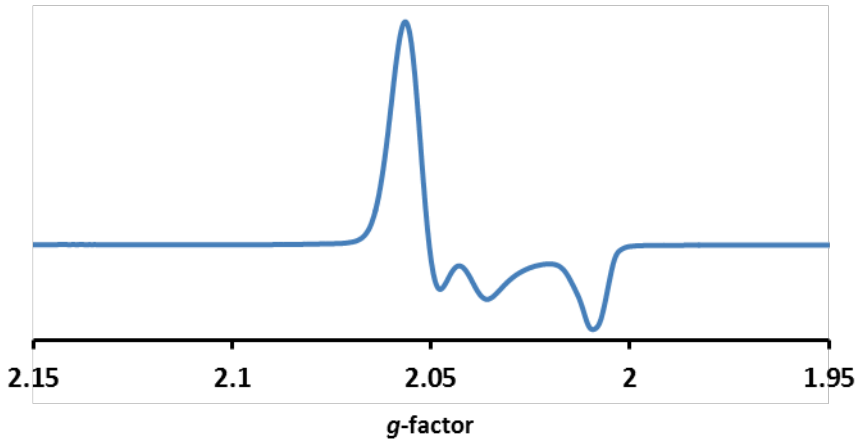

Figure S5: X-band EPR spectrum (CH_2Cl_2/PhMe, 110 K) of [**1**]PF_6.

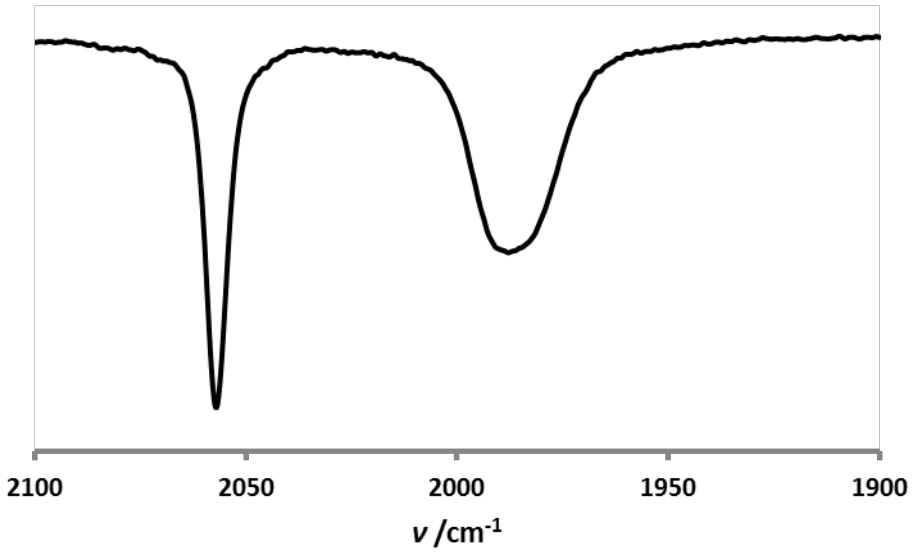

Figure S6: FT-IR spectrum (ν_{CO} region, CH_2Cl_2) of [**1**]$BAr^F{}_4$.

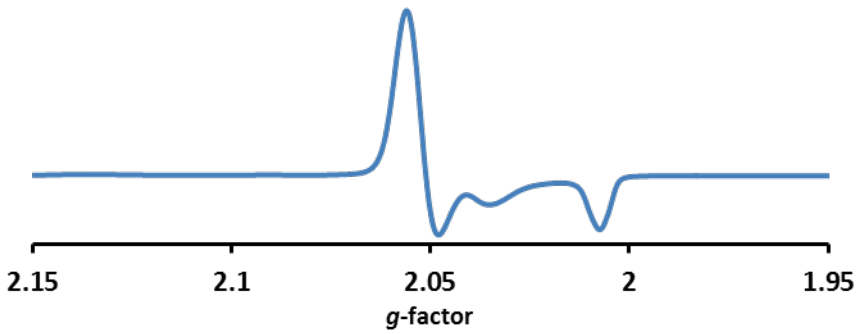

Figure S7: X-band EPR spectrum (CH_2Cl_2/PhMe, 110 K) of [**1**]$BAr^F{}_4$.

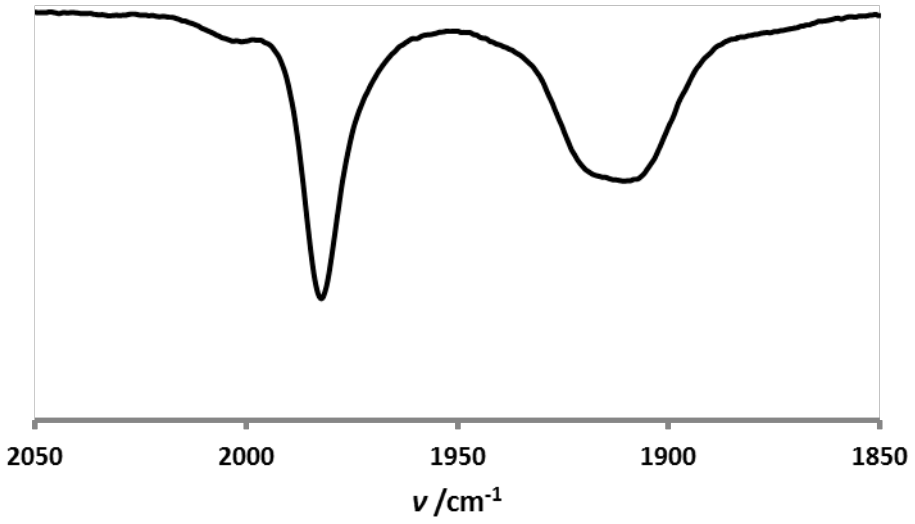

Figure S8: FT-IR spectrum (ν_{CO} region, CH_2Cl_2) of [**1′**].

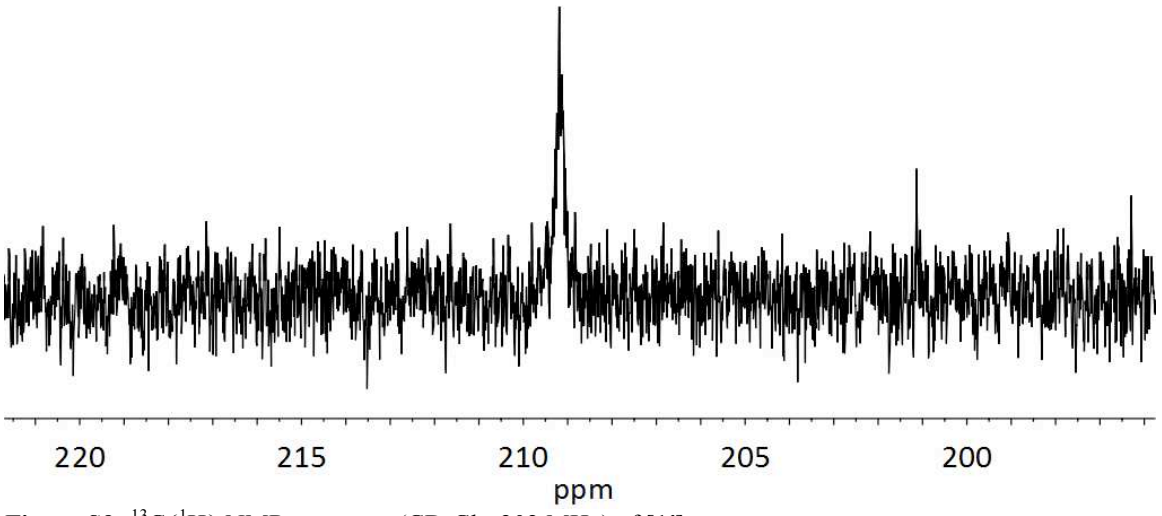

Figure S9: $^{13}C\{^1H\}$ NMR spectrum (CD_2Cl_2, 202 MHz) of [**1′**].

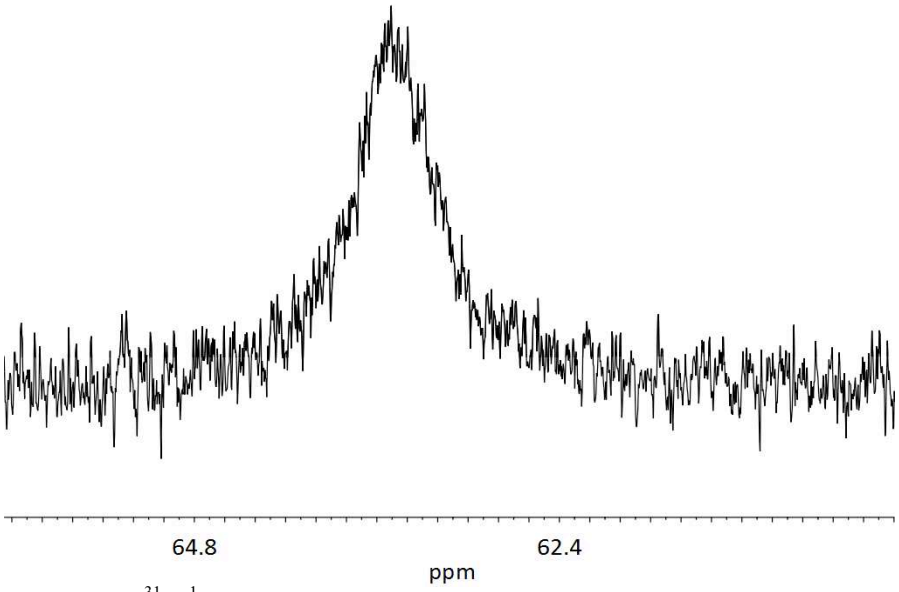

Figure S10: $^{31}P\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 202 MHz) of [**1′**].

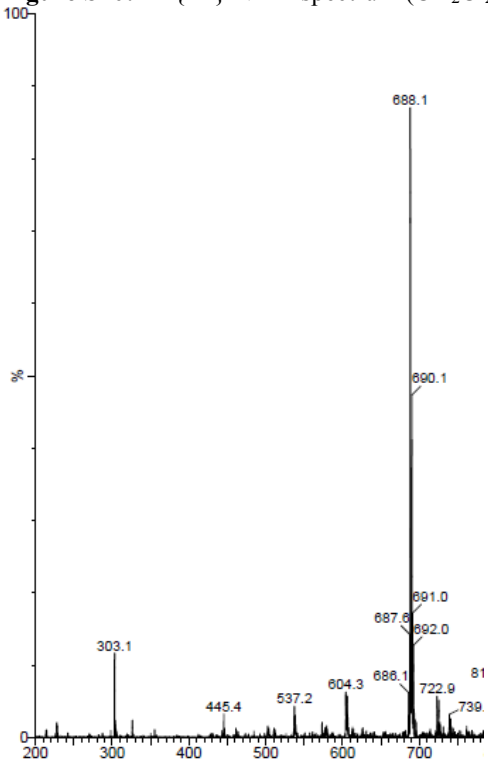

Figure S11: Positive ion ESI mass spectrum of [**2**]BF_4.

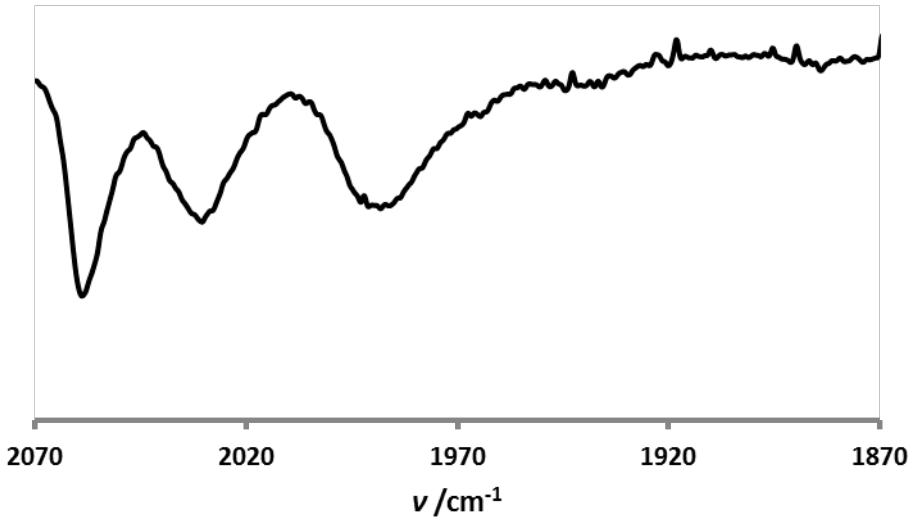

Figure S12: FT-IR spectrum (ν_{CO} region, CH_2Cl_2) of [**2**]BF_4.

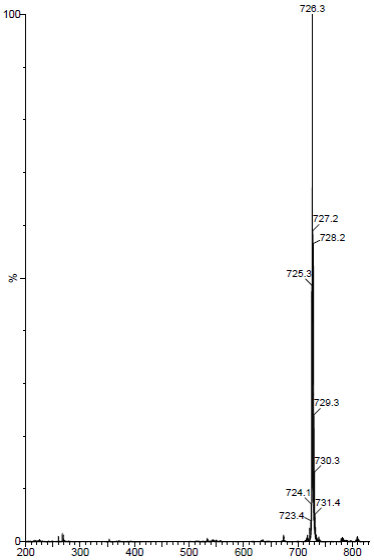

Figure S13: Positive ion ESI mass spectrum of [**3**]BF_4.

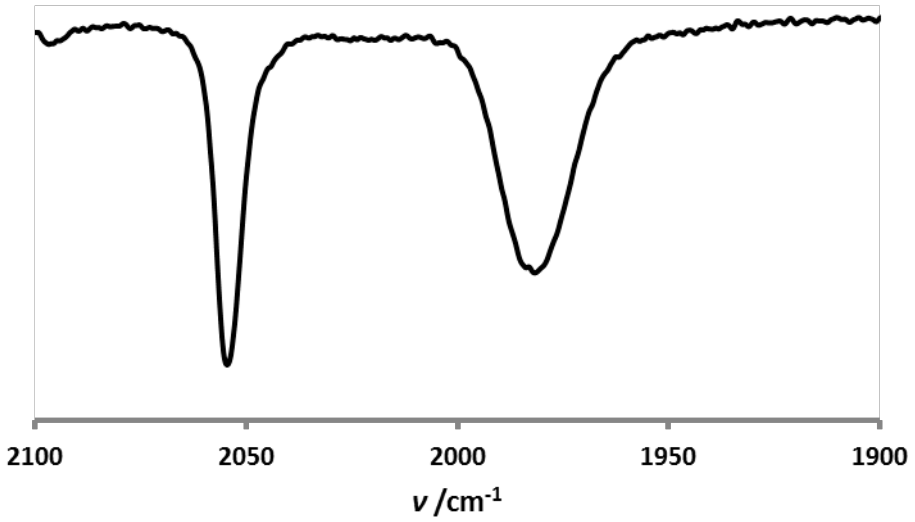

Figure S14: FT-IR spectrum (ν_{CO} region, CH_2Cl_2) of [**3**]BF_4.

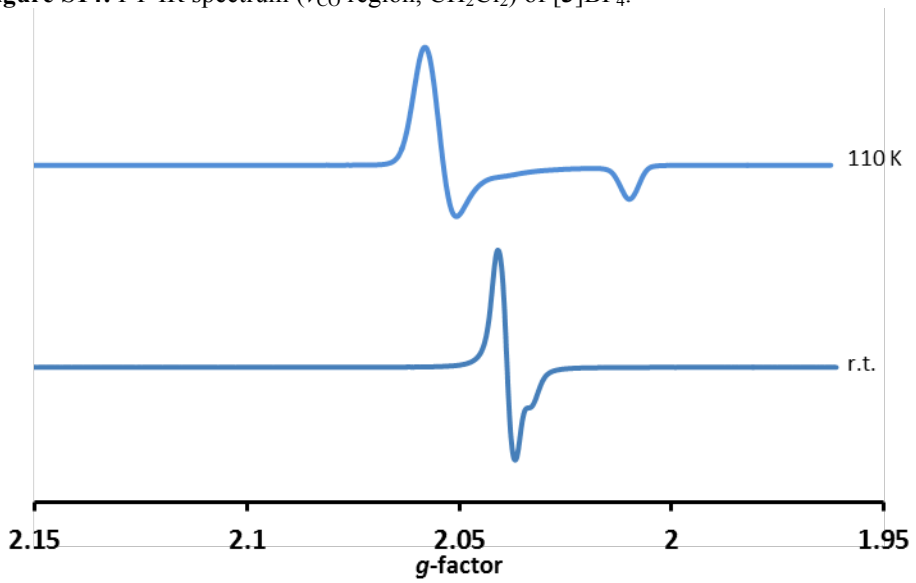

Figure S15: X-band EPR spectra (CH_2Cl_2/PhMe) of [**3**]BF_4 at 110 K and room temperature.

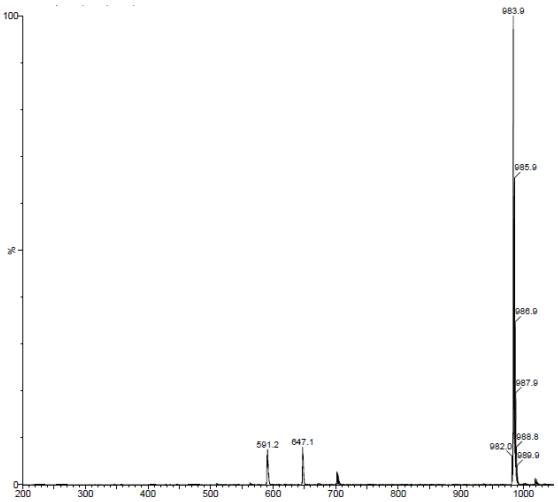

Figure S16: Positive ion ESI mass spectrum of [**4a**]BF_4.

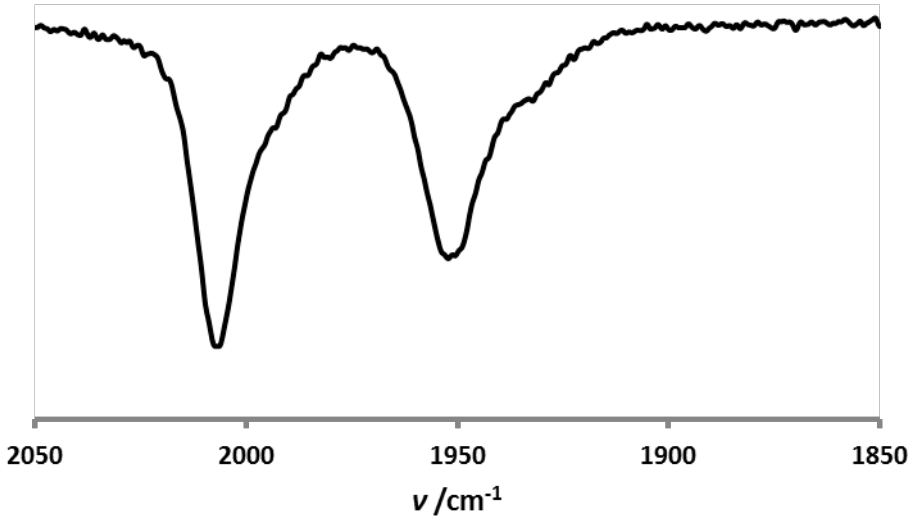

Figure S17: FT-IR spectrum (ν_{CO} region, CH_2Cl_2) of [**4a**]BF_4.

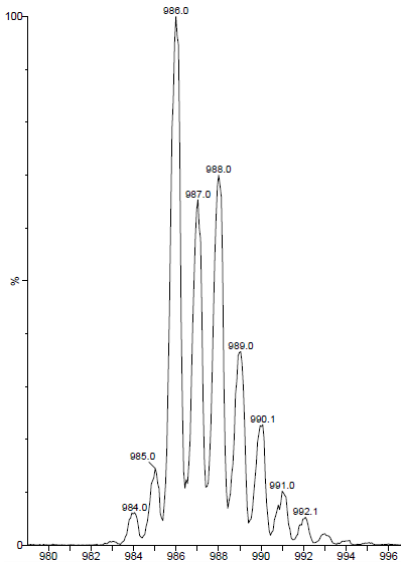

Figure S18: Positive ion ESI mass spectrum of [**4a′**]BF_4.

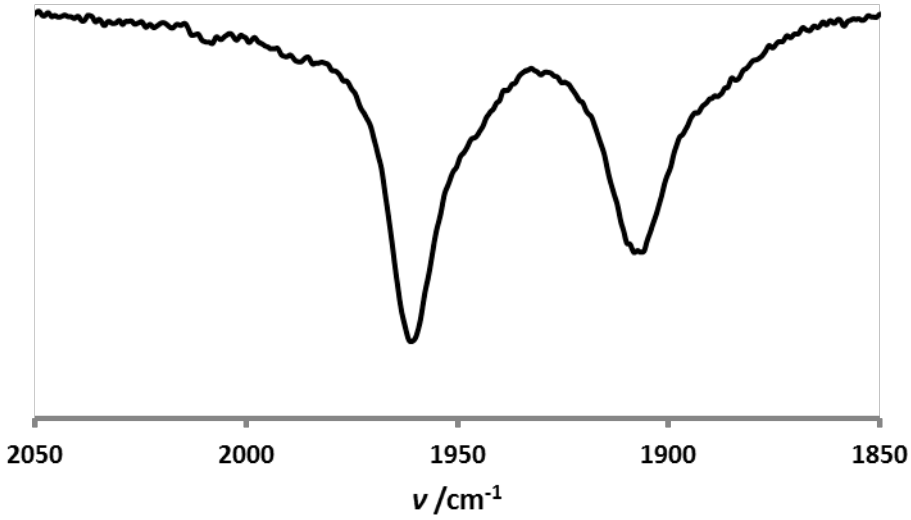

Figure S19: FT-IR spectrum (ν_{CO} region, CH_2Cl_2) of [**4a′**]BF_4.

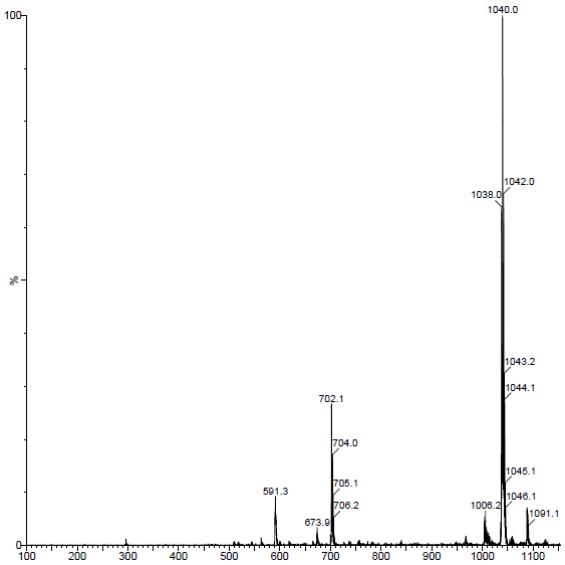

Figure S20: Positive ion ESI mass spectrum of [**4b**]BF_4.

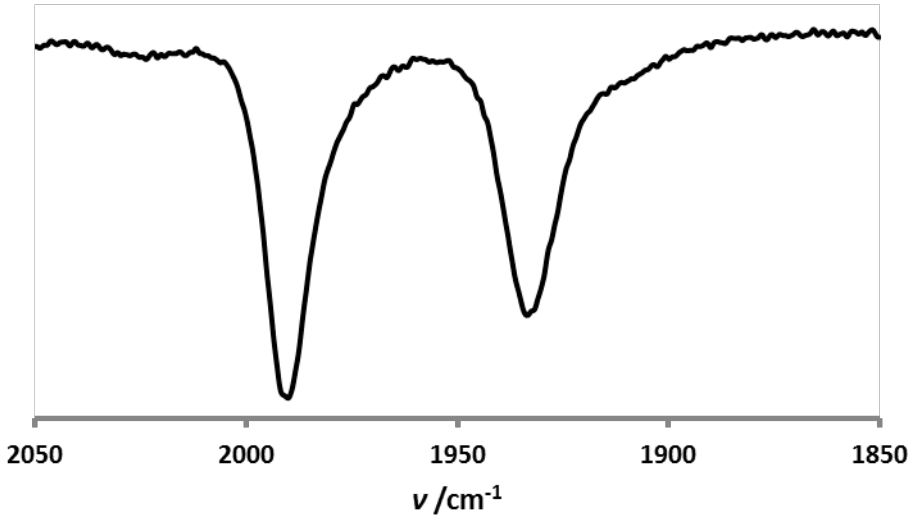

Figure S21: FT-IR spectrum (ν_{CO} region, CH_2Cl_2) of [**4b**]BF_4.

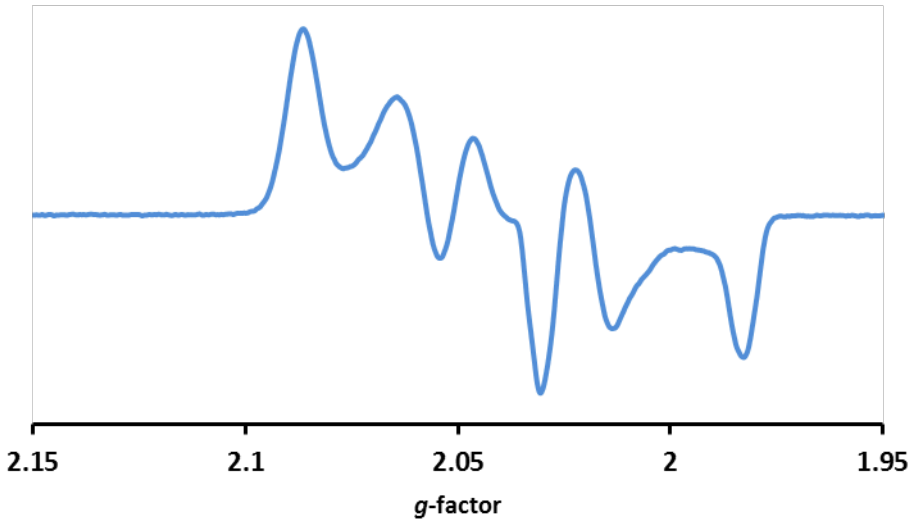

Figure S22: X-band EPR spectrum (CH_2Cl_2/PhMe, 110 K) of [**4b**]BF_4.

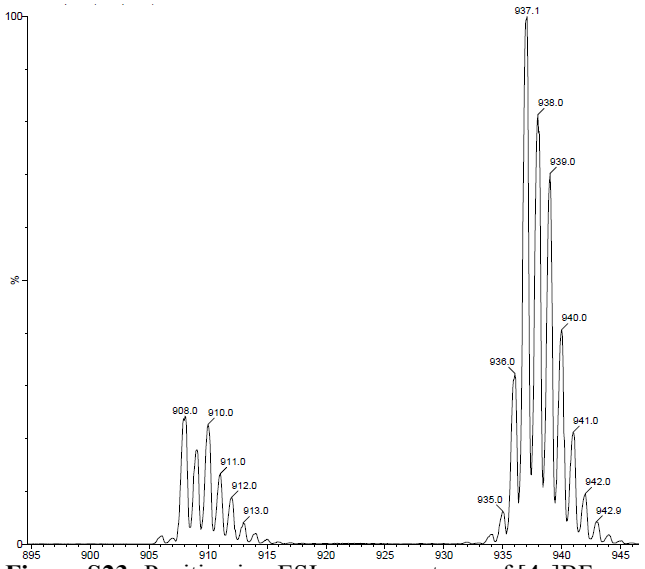

Figure S23: Positive ion ESI mass spectrum of [**4c**]BF_4.

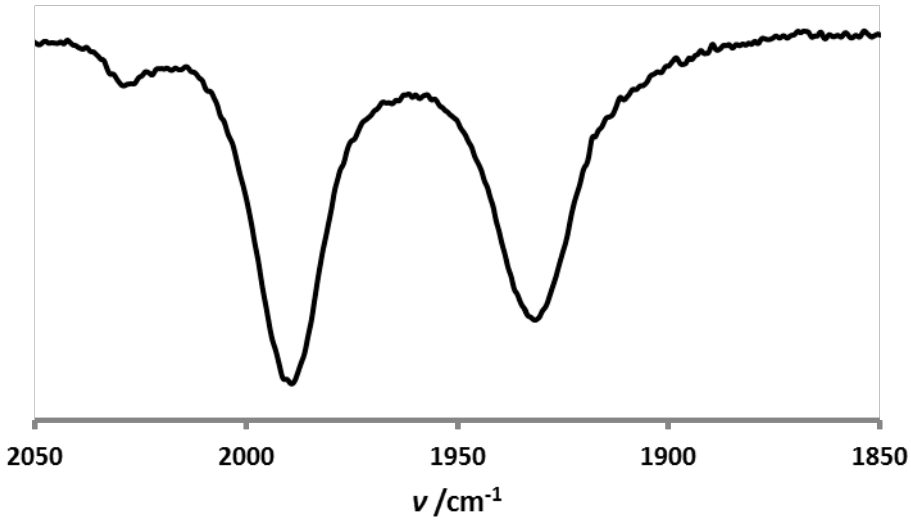

Figure S24: FT-IR spectrum (ν_{CO} region, CH_2Cl_2) of [**4c**]BF_4.

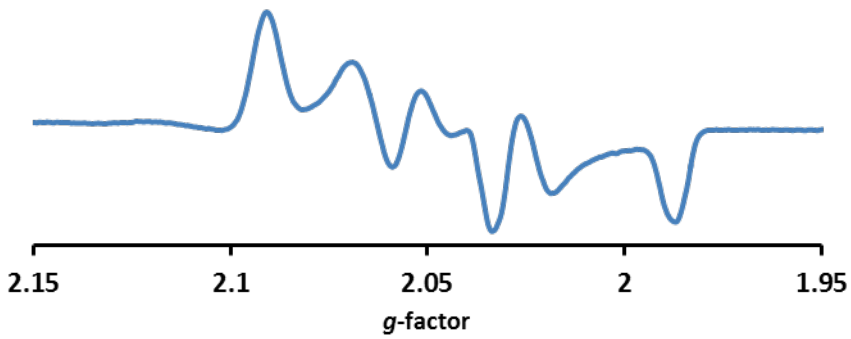

Figure S25: X-band EPR spectrum (CH_2Cl_2/PhMe, 110 K) of [**4c**]BF_4.

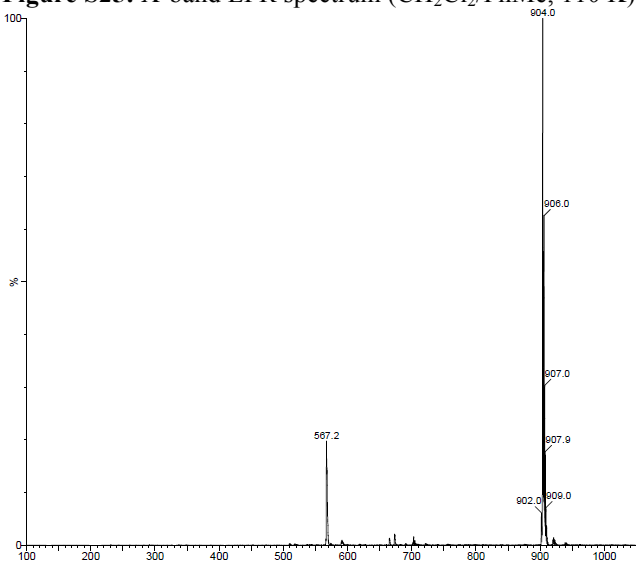

Figure S26: Positive ion ESI mass spectrum of [**4d**]BF_4.

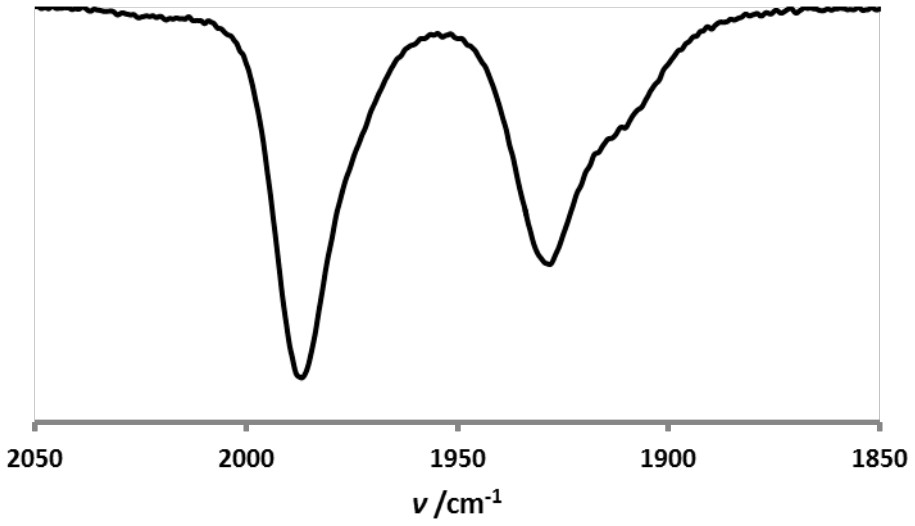

Figure S27: FT-IR spectrum (ν_{CO} region, CH_2Cl_2) of [**4d**]BF_4.

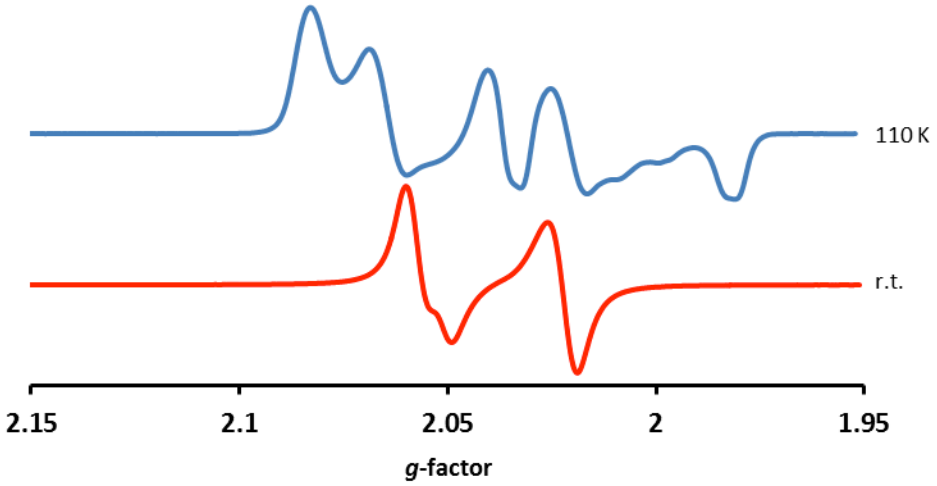

Figure S28: X-band EPR spectra (CH_2Cl_2/PhMe) of [**4d**]BF_4 collected at 110 K and room temperature.

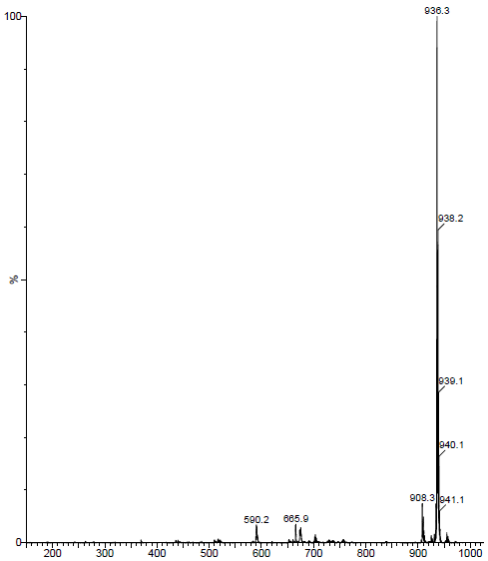

Figure S29: Positive ion ESI mass spectrum of [**4e**]BF_4.

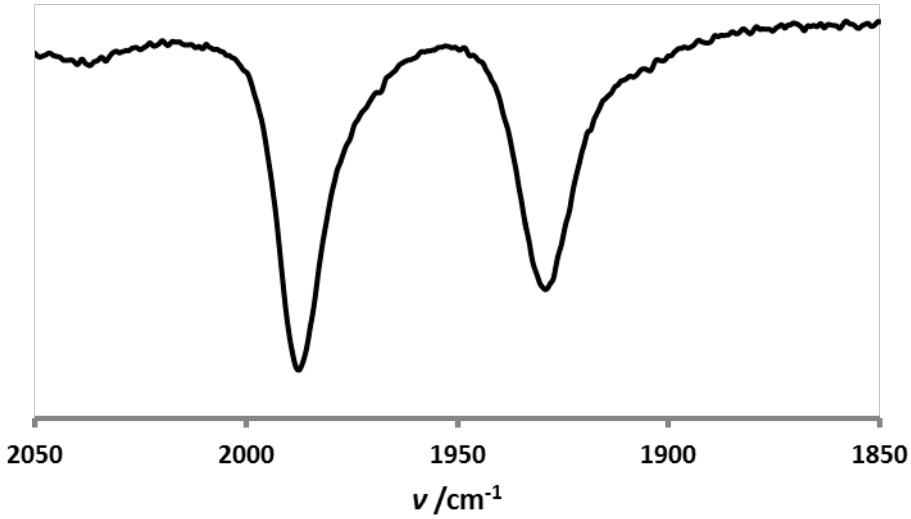

Figure S30: FT-IR spectrum (ν_{CO} region, CH_2Cl_2) of [**4e**]BF_4.

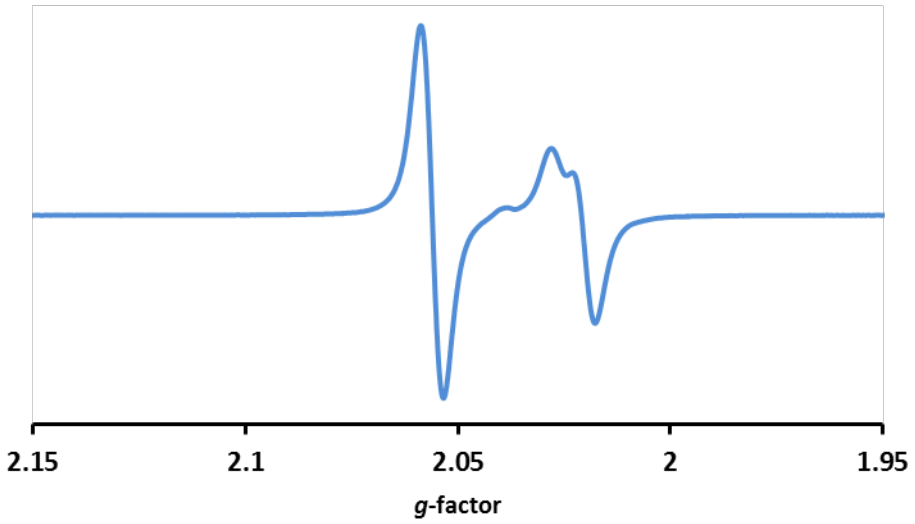

Figure S31: X-band EPR spectrum (CH_2Cl_2/PhMe, rt) of [**4e**]BF_4.

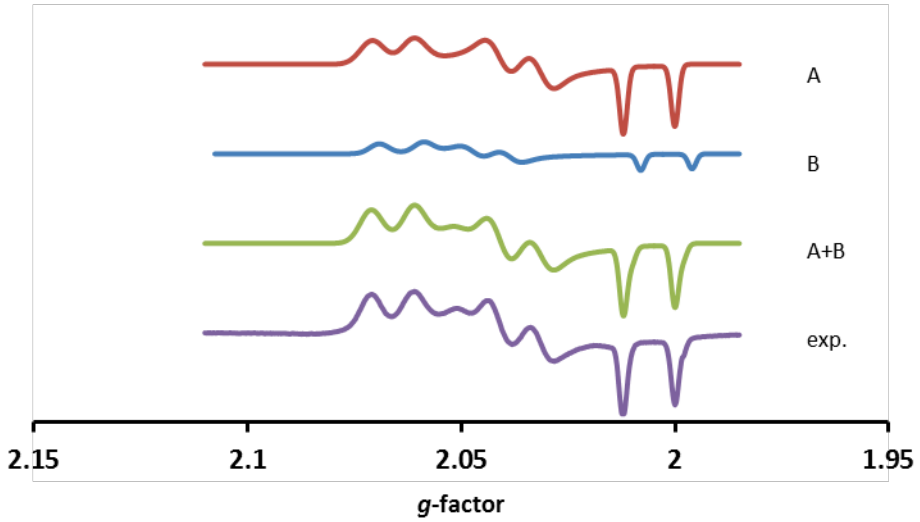

Figure S32: Q-band EPR spectra (CH_2Cl_2/PhMe, 130 K) of [**4e**]BF_4. The experimental spectrum could be simulated as a sum of two components, denoted A and B.

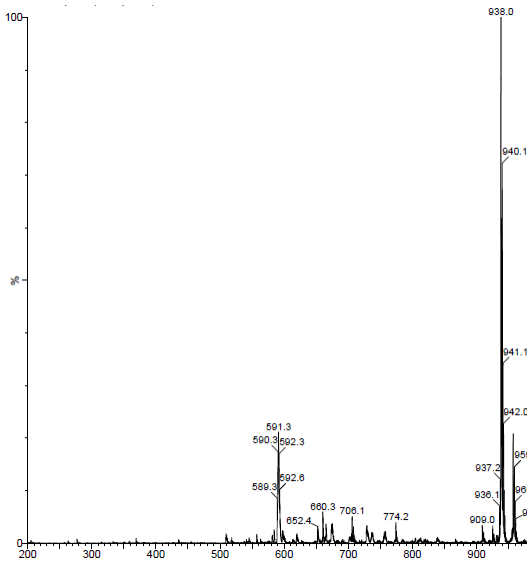

Figure S33: Positive ion ESI mass spectrum of [**4e′**]BF_4.

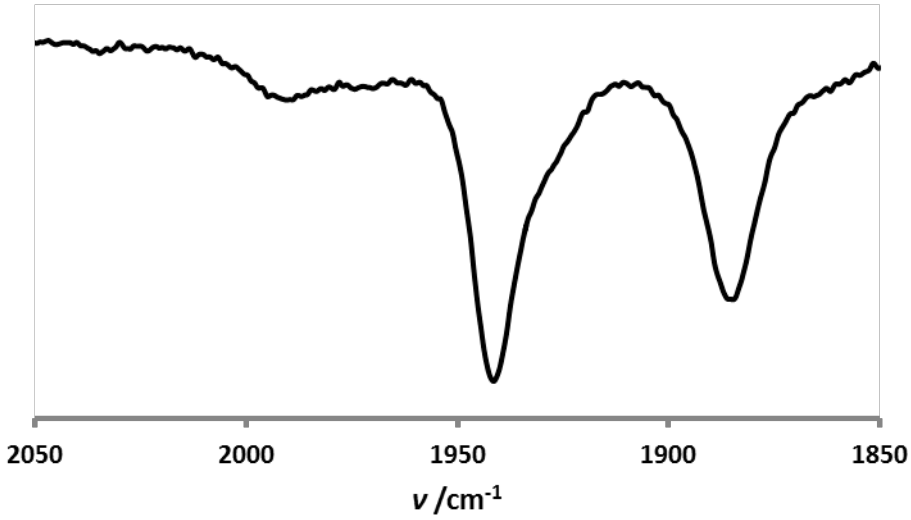

Figure S34: FT-IR spectrum (ν_{CO} region, CH_2Cl_2) of [**4e′**]BF_4.

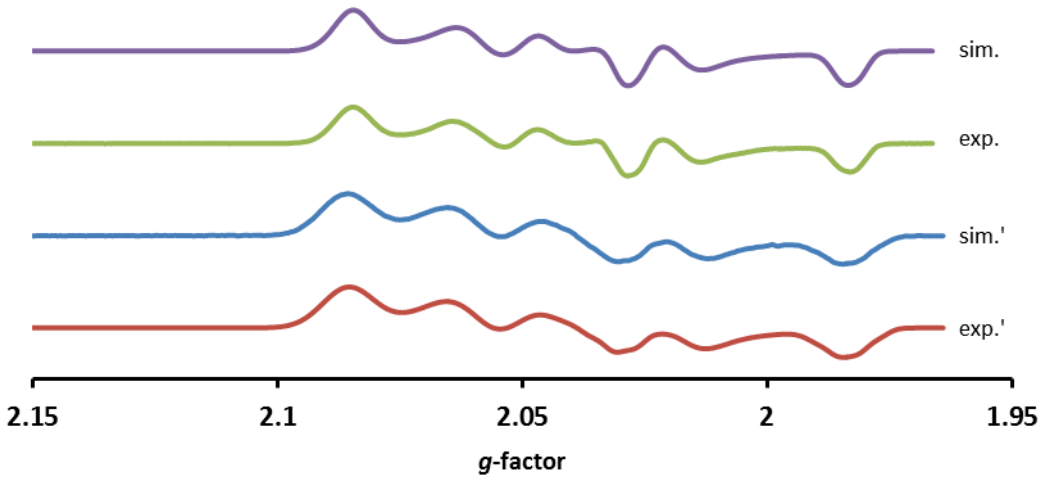

Figure S35: X-band EPR spectrum (CH_2Cl_2/PhMe, 110 K) of [**4e**]BF_4 (exp.) and [**4e′**]BF_4 (exp.′), along with their simulated spectra (sim. and sim.′, respectively).

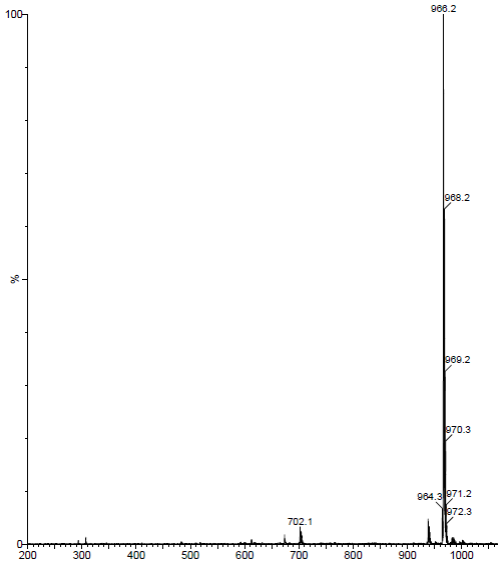

Figure S36: Positive ion ESI mass spectrum of [**4f**]BF_4.

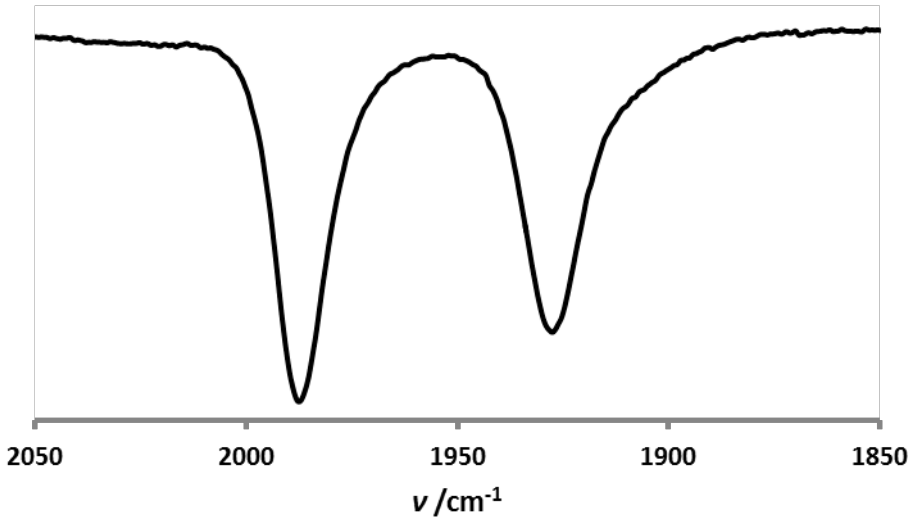

Figure S37: FT-IR spectrum (ν_{CO} region, CH_2Cl_2) of [**4f**]BF_4.

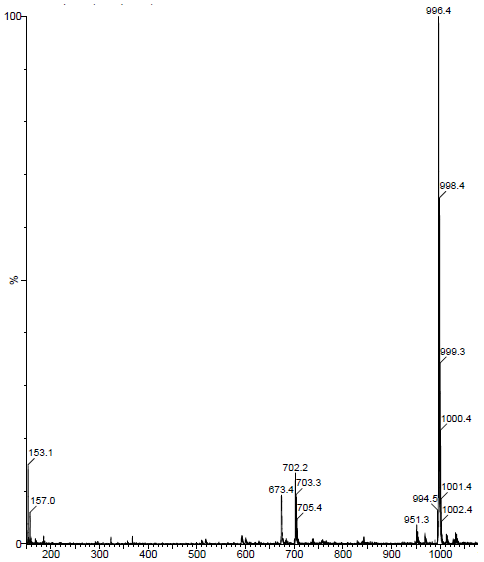

Figure S38: Positive ion ESI mass spectrum of [**4g**]BF_4.

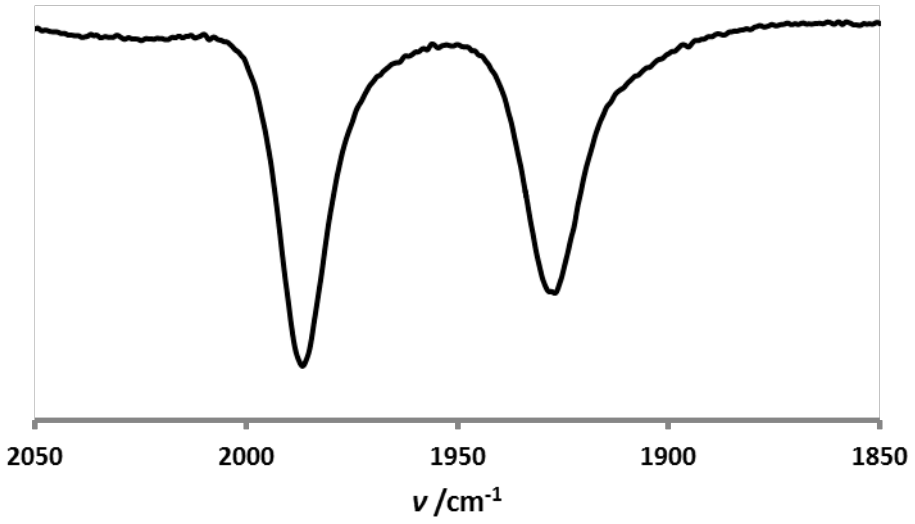

Figure S39: FT-IR spectrum (ν_{CO} region, CH_2Cl_2) of [**4g**]BF_4.

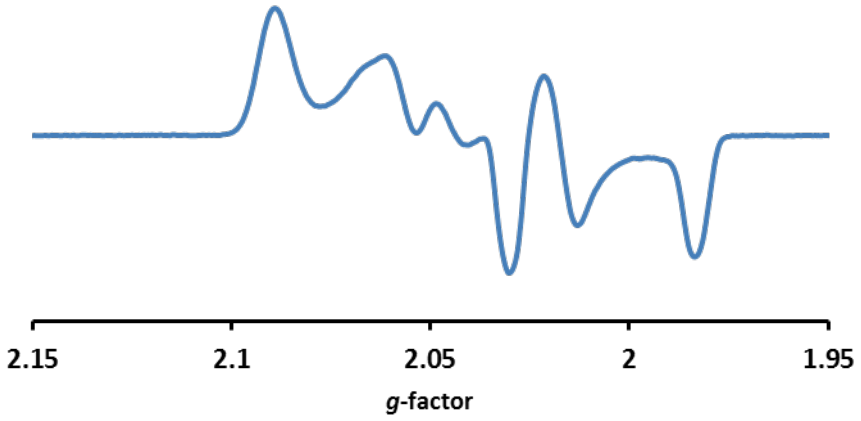

Figure S40: X-band EPR spectrum (CH_2Cl_2/PhMe, 110 K) of [**4g**]BF_4.

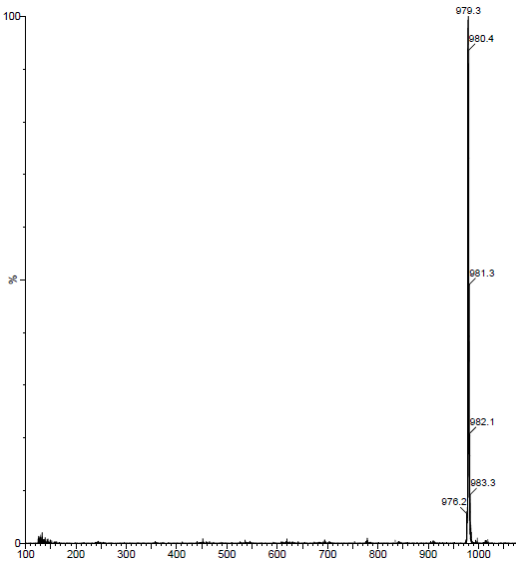

Figure S41: Positive ion ESI mass spectrum of [**4h**]BF_4.

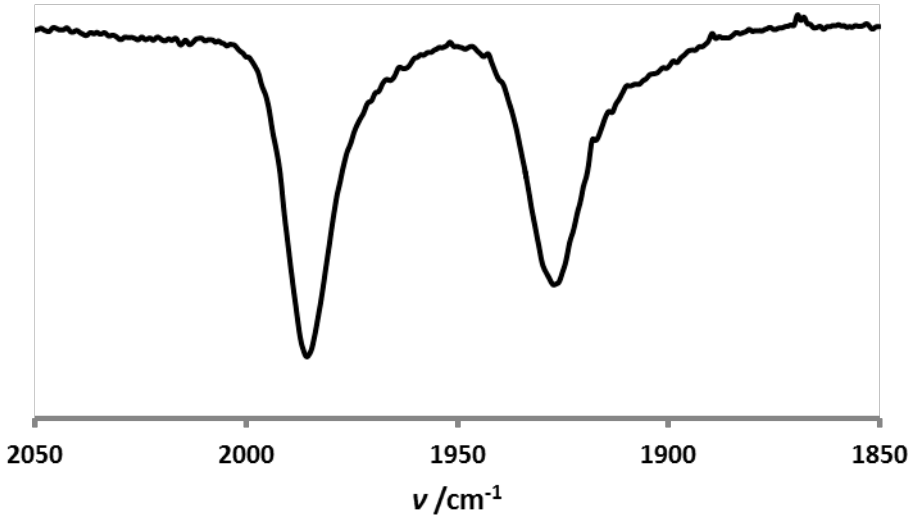

Figure S42: FT-IR spectrum (ν_{CO} region, CH_2Cl_2) of [**4h**]BF_4.

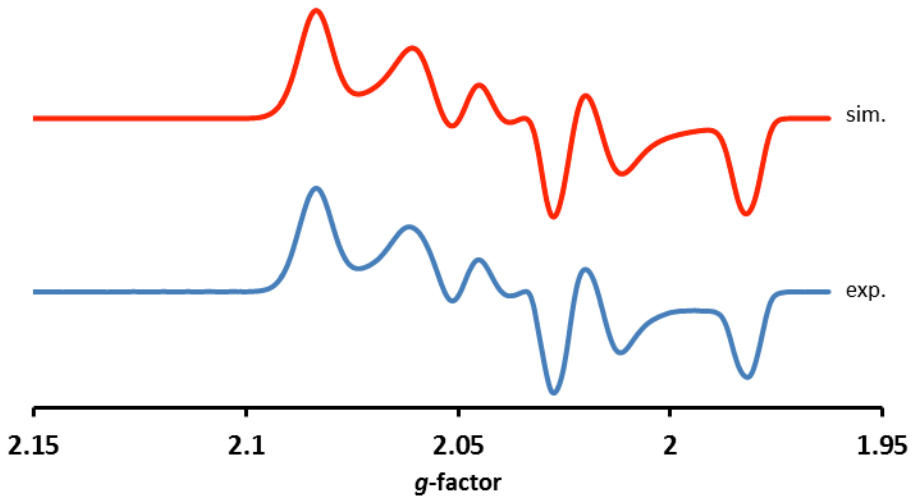

Figure S43: The simulated and experimental X-band EPR spectrum (CH_2Cl_2/PhMe, 110 K) of [**4h**]BF_4.

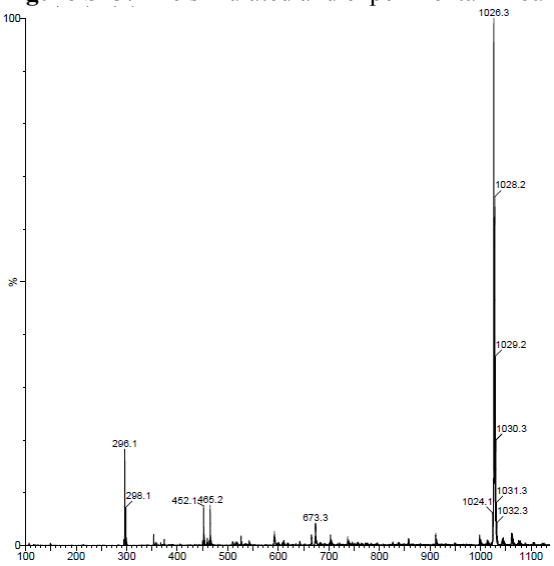

Figure S44: Positive ion ESI mass spectrum of [**4i**]BF_4.

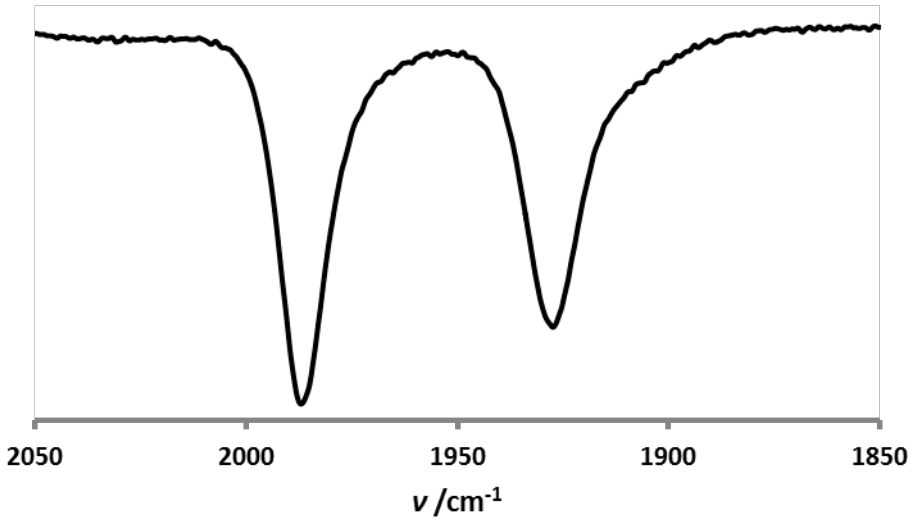

Figure S45: FT-IR spectrum (ν_{CO} region, CH_2Cl_2) of [**4i**]BF_4.

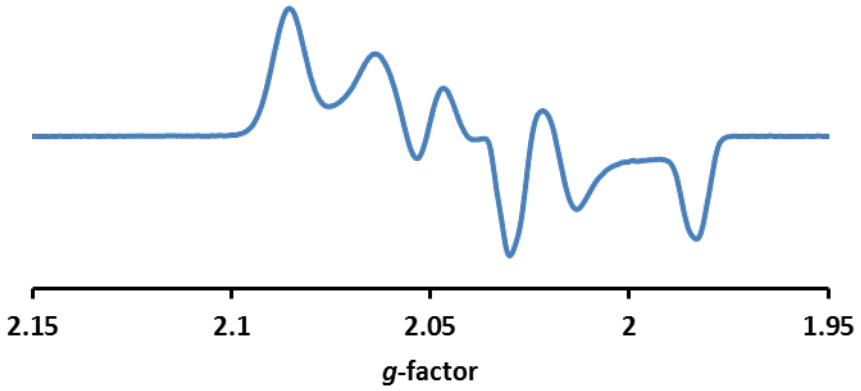

Figure S46: X-band EPR spectrum (CH_2Cl_2/PhMe, 110 K) of [**4i**]BF_4.

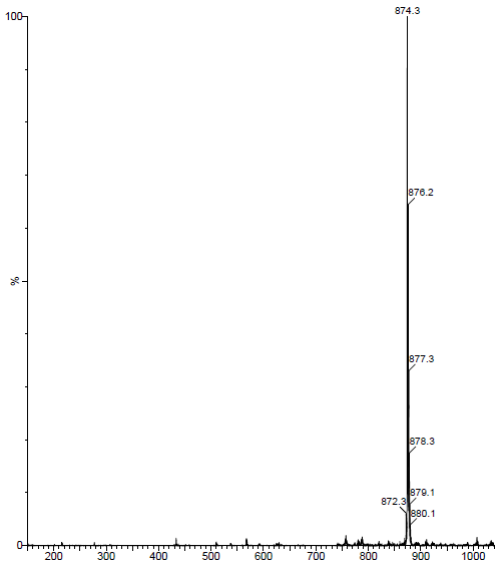

Figure S47: Positive ion ESI mass spectrum of [**4j**]BF_4.

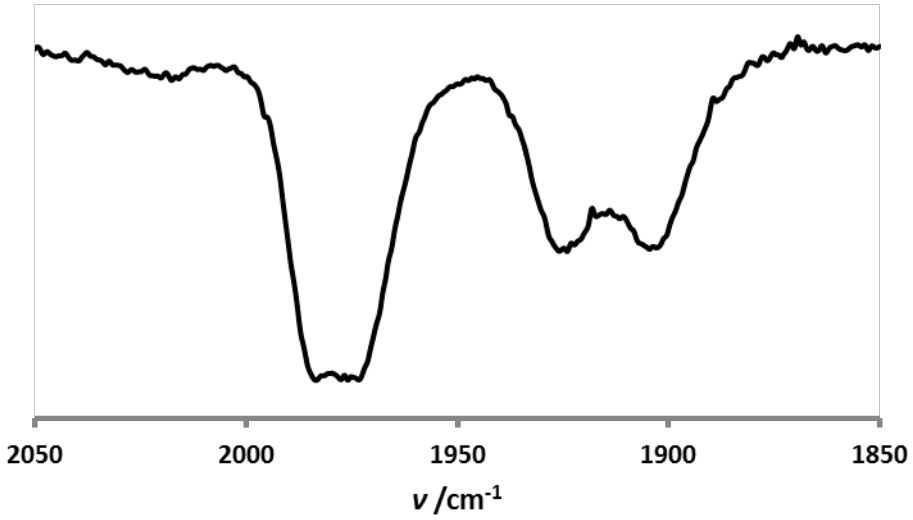

Figure S48: FT-IR spectrum (ν_{CO} region, CH_2Cl_2) of [**4j**]BF_4.

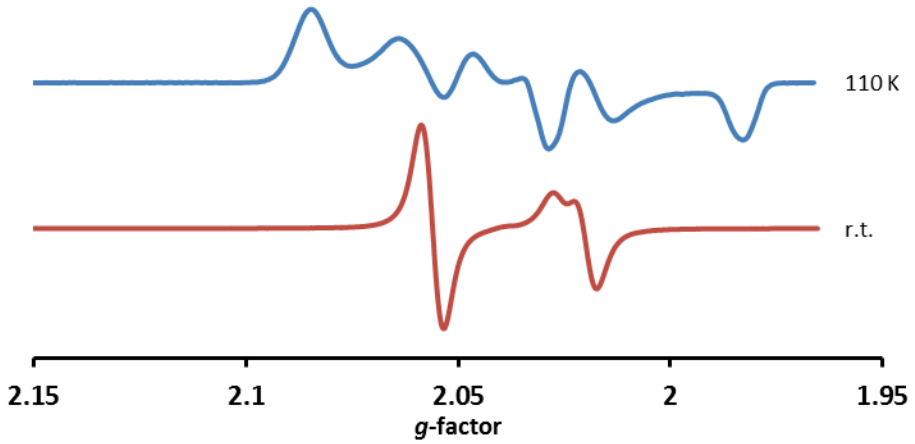

Figure S49: X-band EPR spectra (CH_2Cl_2/PhMe) of [**4j**]BF_4 collected at 110 K and room temperature.

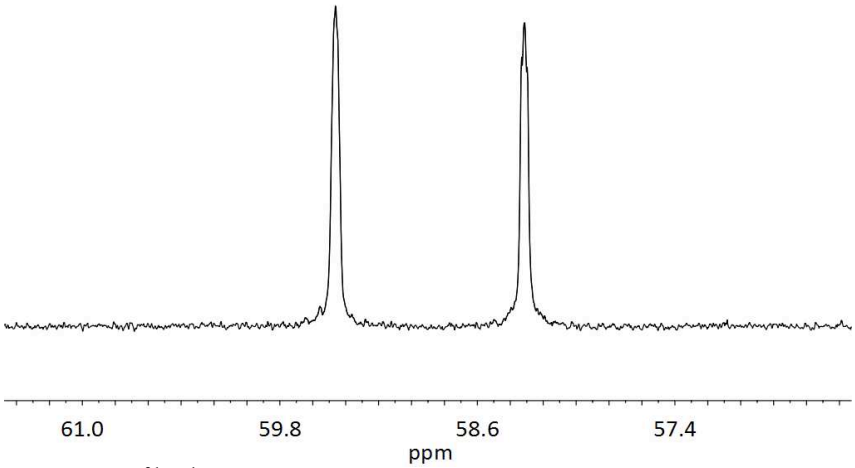

Figure S50: $^{31}P\{^1H\}$ NMR spectrum (CD_2Cl_2, 202 MHz) of [**5**]$(BF_4)_2$.

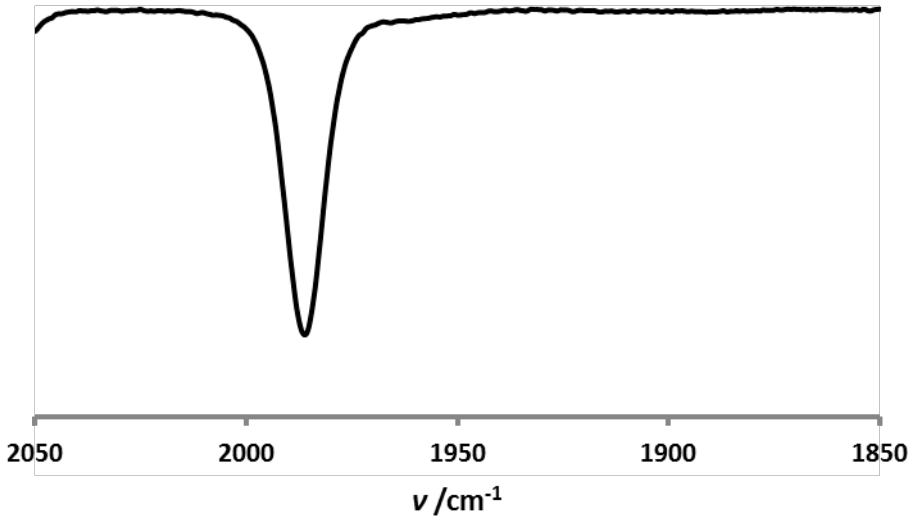

Figure S51: FT-IR spectrum (ν_{CO} region, CH_2Cl_2) of [**5**]$(BF_4)_2$.

Table 1: Calculated *g*-tensor principal values for complexes [**1**]$^{+}$, [**2**]$^{+}$, [**3**]$^{+}$, [**4a**]$^{+}$ and [**4e**]$^{+}$ (superscripts [a] and [b] refer to flipamers of each complex, see Scheme 5).

Complex	**SOMF(1X) TZVP** g_1, g_2, g_3			**ZORA SO ROKS DZ** g_1, g_2, g_3		
	BP	**B3LYP**	**PBE0**	**BP**	**B3LYP**	**PBE0**
[**1**]$^{+a}$	2.033, 2.030, 2.012	2.044, 2.042, 2.005	2.047, 2.044, 2.004	2.041, 2.035, 2.020	2.052, 2.051, 2.006	2.057, 2.055, 2.004
[**1**]$^{+b}$	2.033, 2.027, 2.012	2.044, 2.037, 2.004	2.047, 2.038, 2.003	2.042, 2.030, 2.019	2.051, 2.047, 2.005	2.055, 2.051, 2.004
[**2**]$^{+}$	2.029, 2.026, 2.011	2.041, 2.038, 2.004	2.044, 2.040, 2.003	2.037, 2.029, 2.010	2.049, 2.044, 2.008	2.055, 2.048, 2.003
[**3**]$^{+a}$	2.033, 2.030, 2.016	2.045, 2.041, 2.006	2.048, 2.044, 2.005	2.043, 2.035, 2.026	2.052, 2.047, 2.010	2.057, 2.051, 2.008
[**3**]$^{+b}$	2.033, 2.027, 2.013	2.041, 2.038, 2.004	2.044, 2.040, 2.004	2.042, 2.029, 2.024	2.048, 2.047, 2.008	2.052, 2.051, 2.006
[**4a**]$^{+a}$	2.038, 2.025, 2.014	2.061, 2.037, 2.010	2.065, 2.038, 2.011	2.045, 2.029, 2.018	2.060, 2.043, 2.006	2.065, 2.046, 2.004
[**4a**]$^{+b}$	2.044, 2.026, 2.006	2.064, 2.047, 2.003	2.069, 2.048, 2.003	2.057, 2.024, 2.002	2.072, 2.057, 1.996	2.080, 2.065, 1.993
[**4e**]$^{+a}$	2.045, 2.032, 2.007	2.067, 2.053, 2.004	2.072, 2.056, 2.004	2.059, 2.038, 2.006	2.074, 2.067, 1.997	2.082, 2.076, 1.994
[**4e**]$^{+b}$	2.043, 2.026, 2.006	2.064, 2.047, 2.003	2.068, 2.048, 2.003	2.057, 2.024, 2.002	2.072, 2.057, 1.996	2.080, 2.065, 1.993

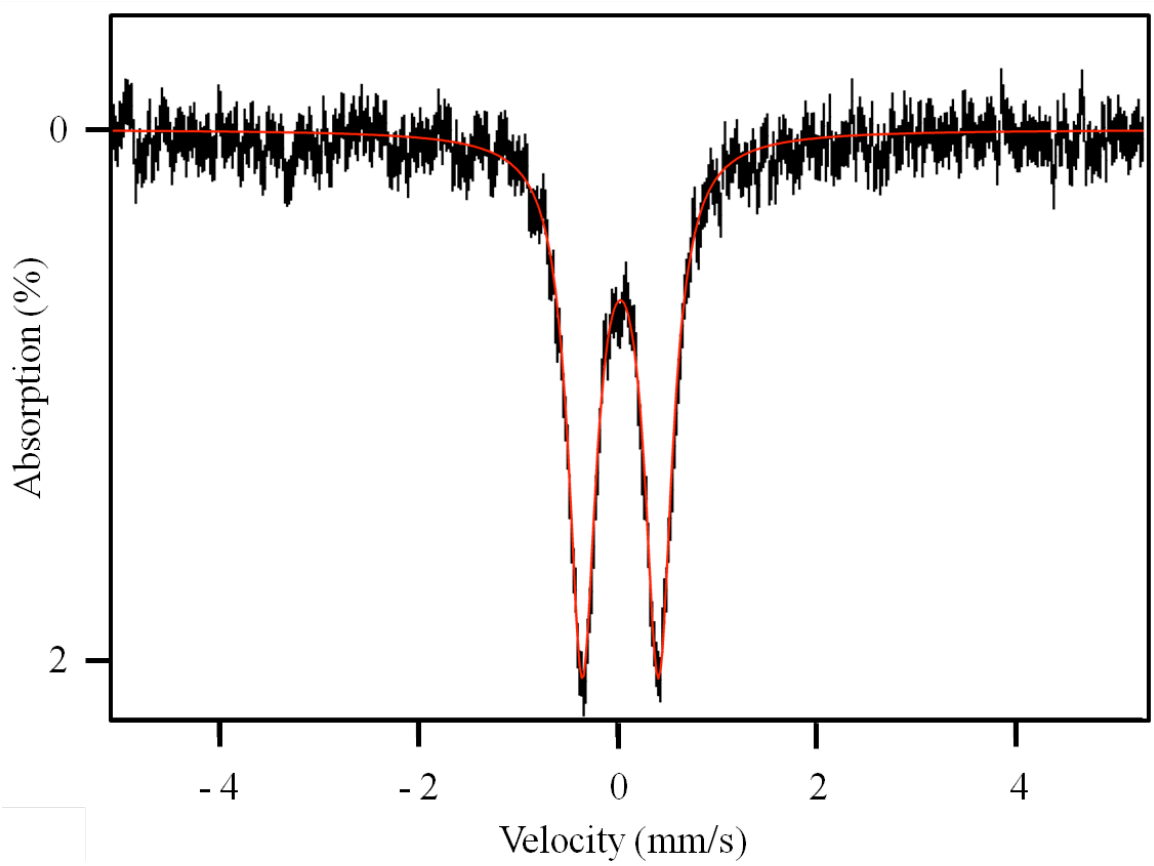

Figure S52: Mössbauer spectrum (5 K, 500 G) of $(CO)_3Fe(pdt)Fe(CO)_3$, and simulated spectrum (solid trace).

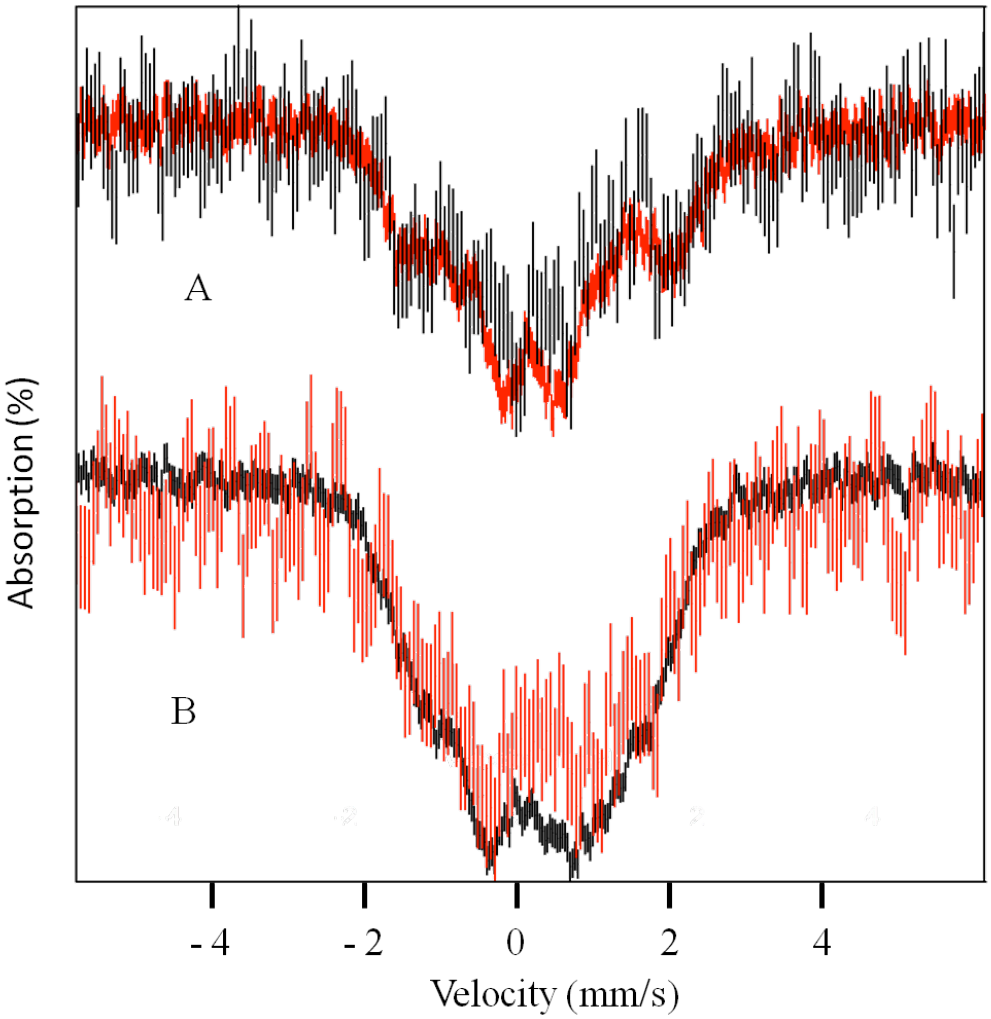

Figure S53: Mössbauer spectra of [**4e**]BF_4. A: 5 K, 500 G, 5 mM sample spectrum (black) overlaid on 40 mM sample spectrum (red). B: 4.2 K, 6 T Mössbauer data for [**4e**]BF_4, solid sample spectrum (black) overlaid on 40 mM sample spectrum (red).