Mixed Valence Triiron Complexes from the Conjugation of Dinuclear [$CpFe^{I}$-$Fe^{I}Cp$] and [Fe^{II}] Complexes via Intermolecular Carbyne/Diyne Coupling

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Supporting Information

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Figure S1. ^{1}H NMR spectrum (401 MHz, acetone-d_6) of **[2a1]CF_3SO_3**

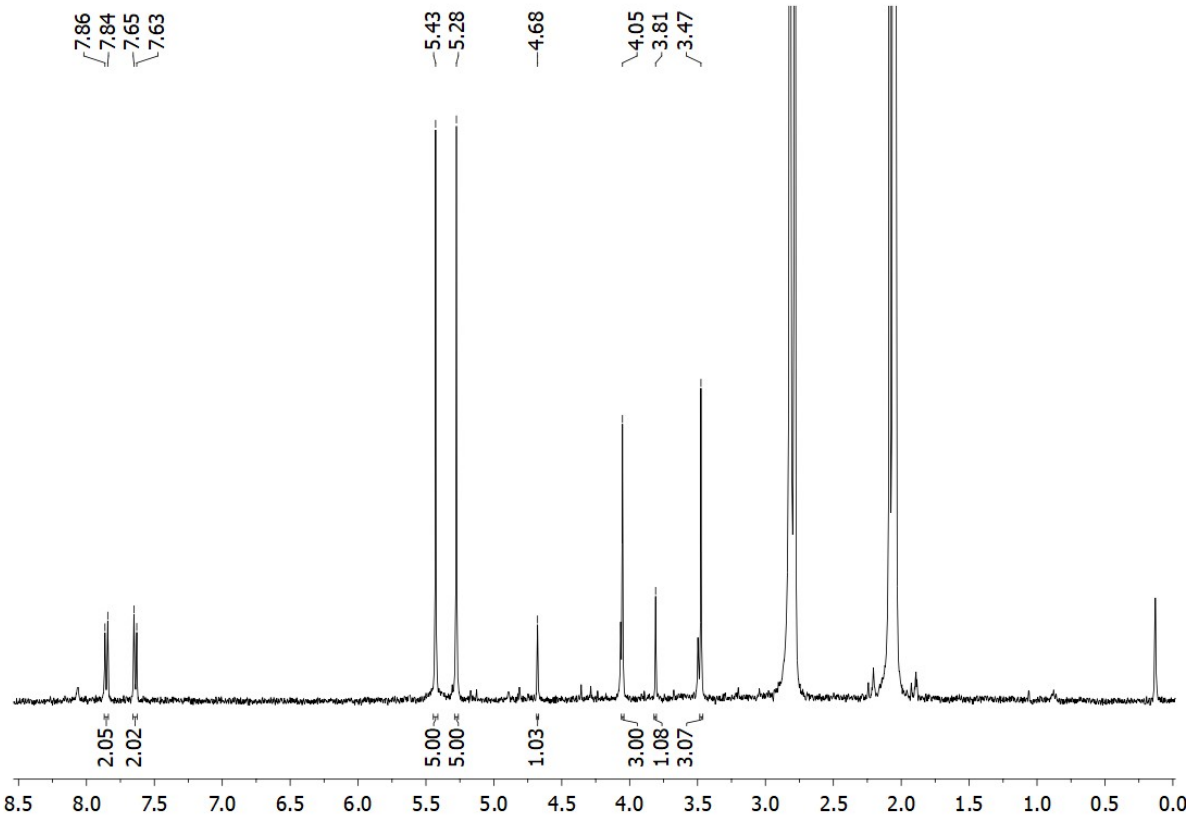


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, acetone-d_6) of **[2a1]CF_3SO_3**.

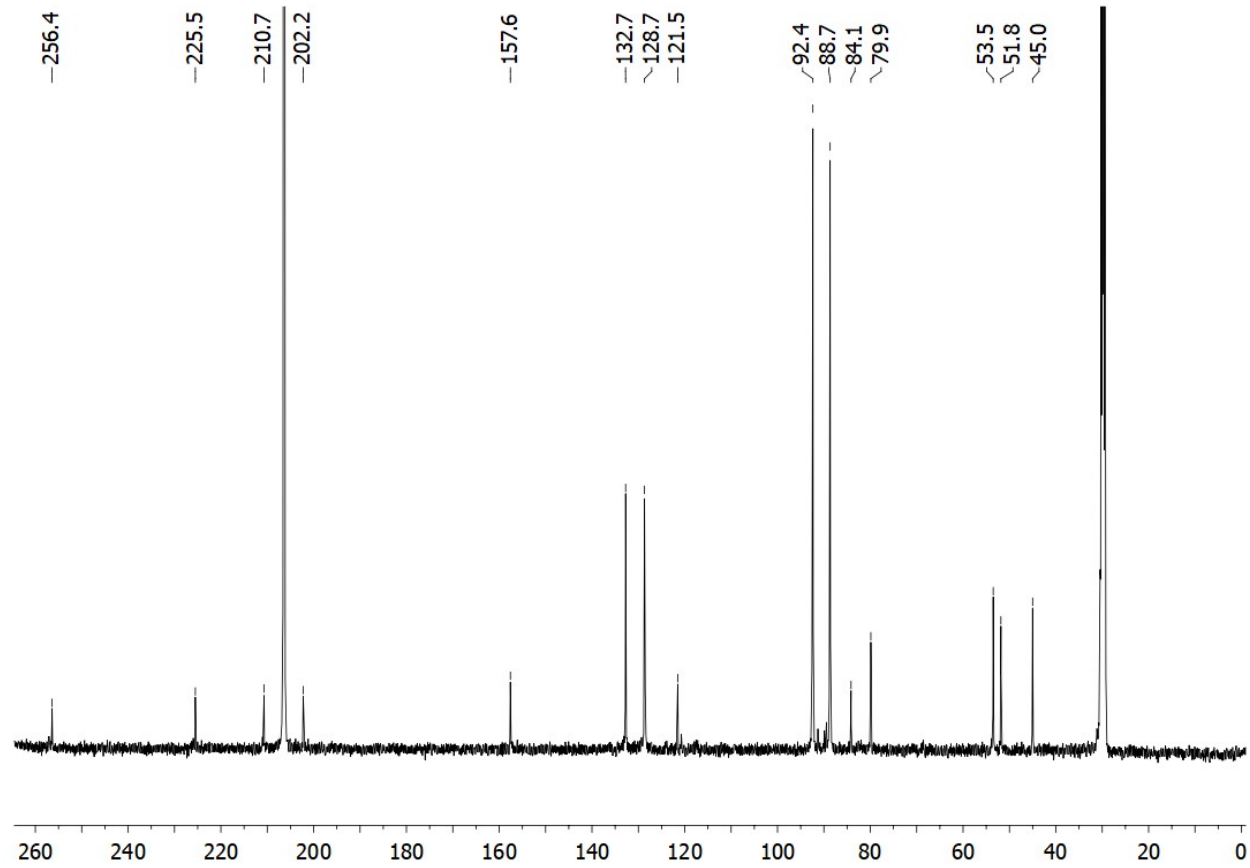


Figure S3. ^{1}H NMR spectrum (401 MHz, acetone-d_6) of **[2a2]CF_3SO_3**

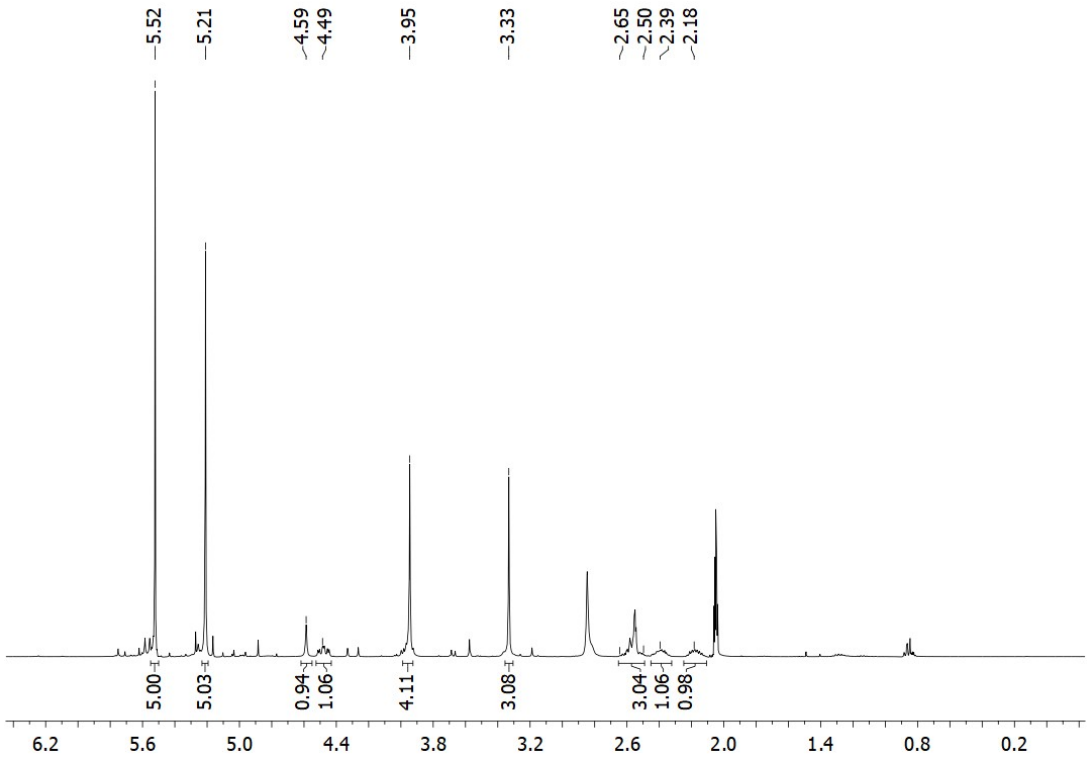


Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, acetone-d_6) of **[2a2]CF_3SO_3**.

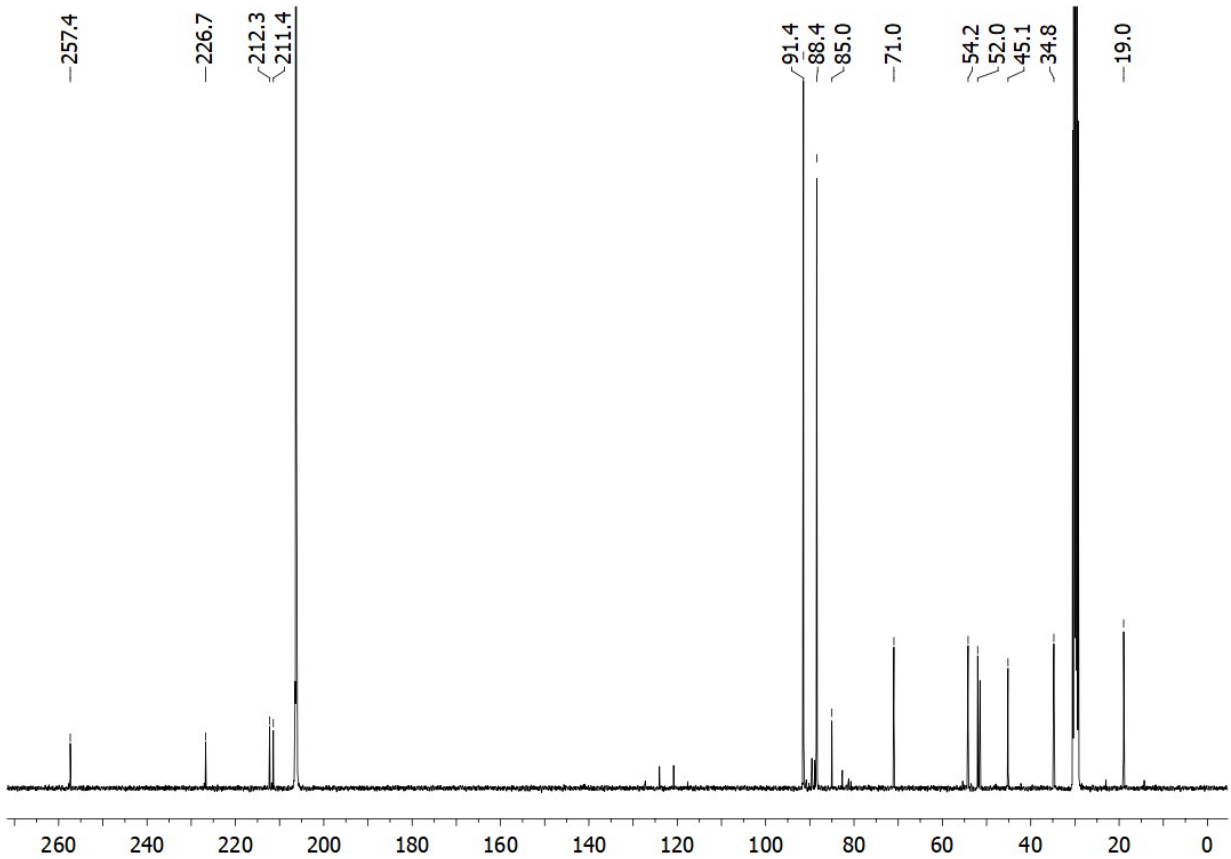


Figure S5. ^{1}H NMR spectrum (401 MHz, $CDCl_3$) of **3a1**.

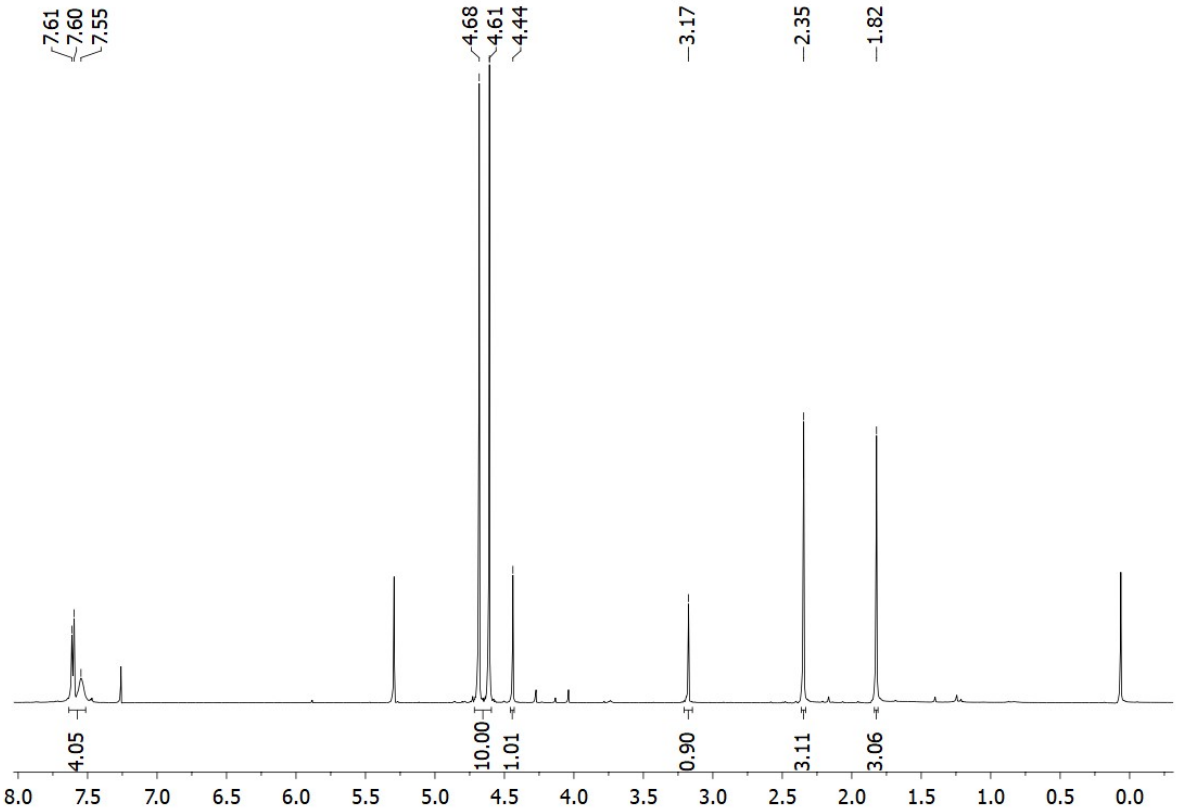


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **3a1**.

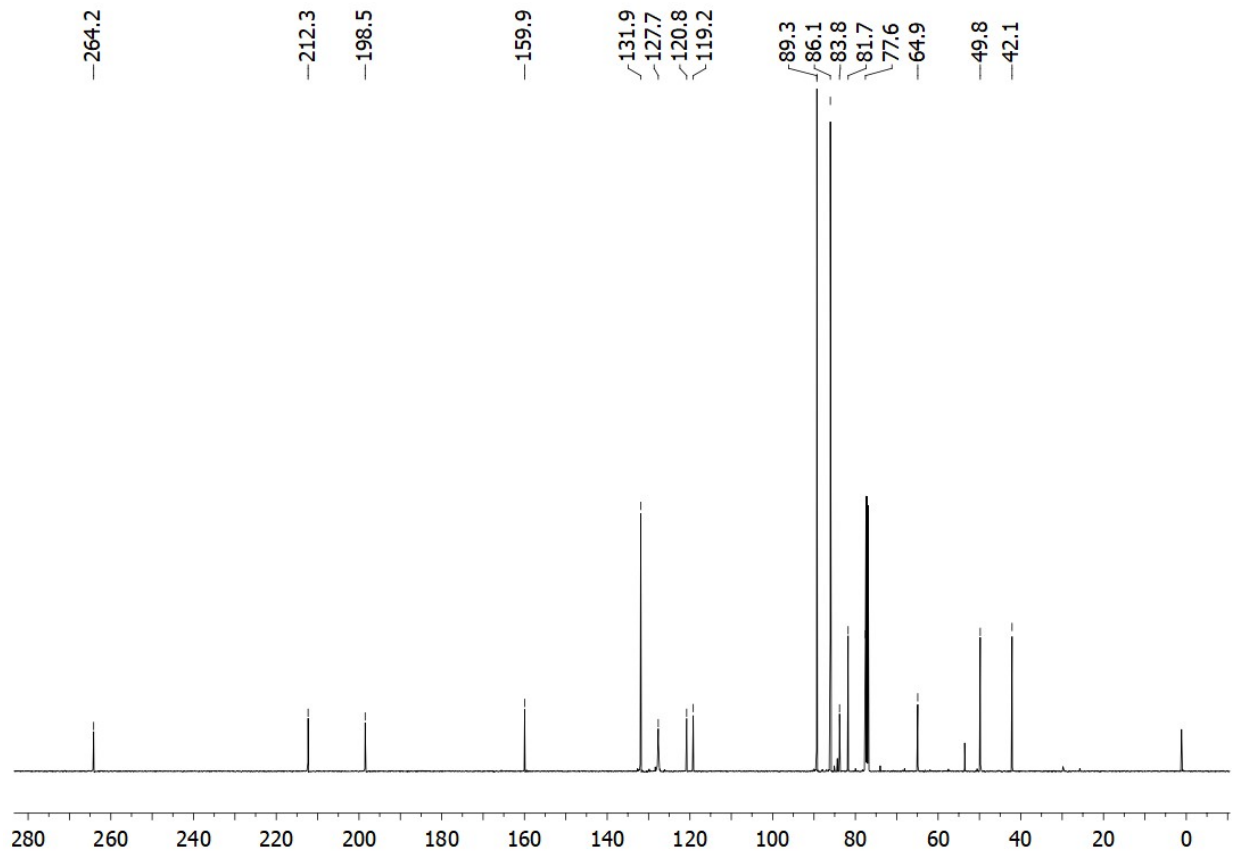


Figure S7. ^{1}H NMR spectrum (401 MHz, $CDCl_3$) of **3a2**.

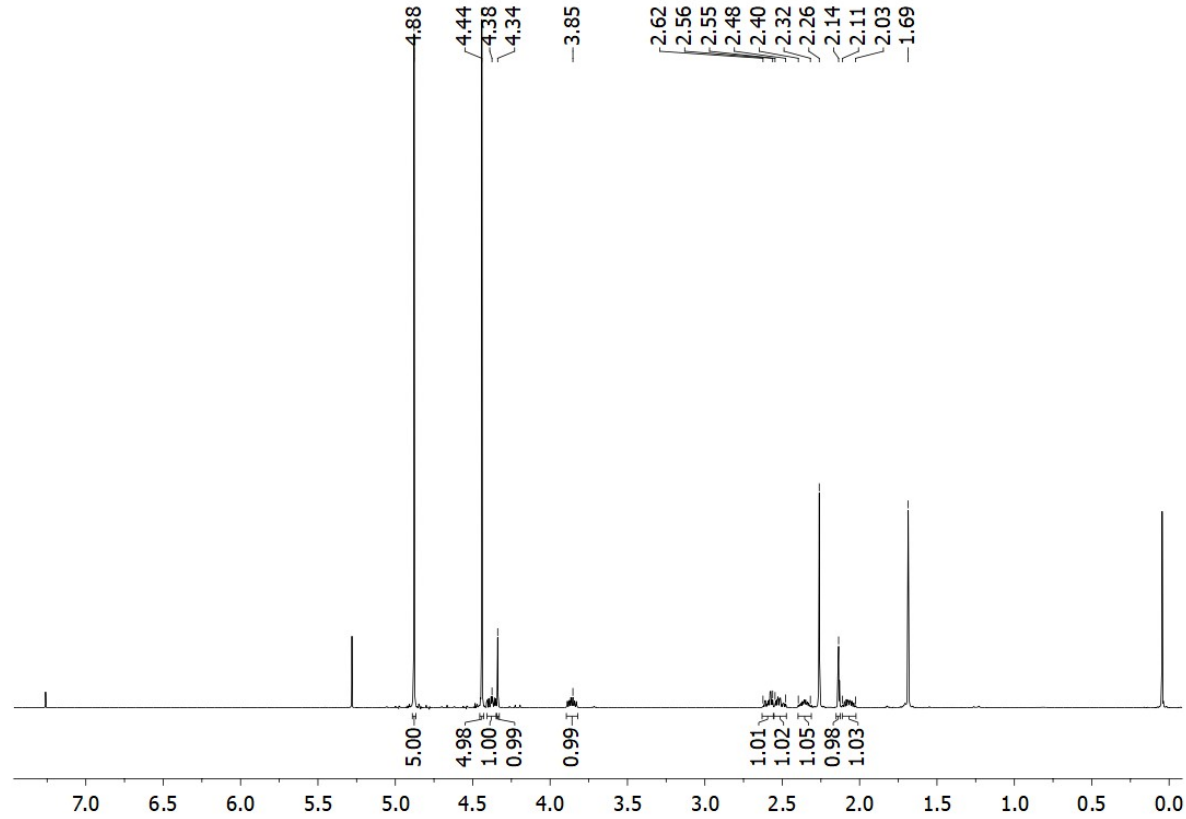


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **3a2**.

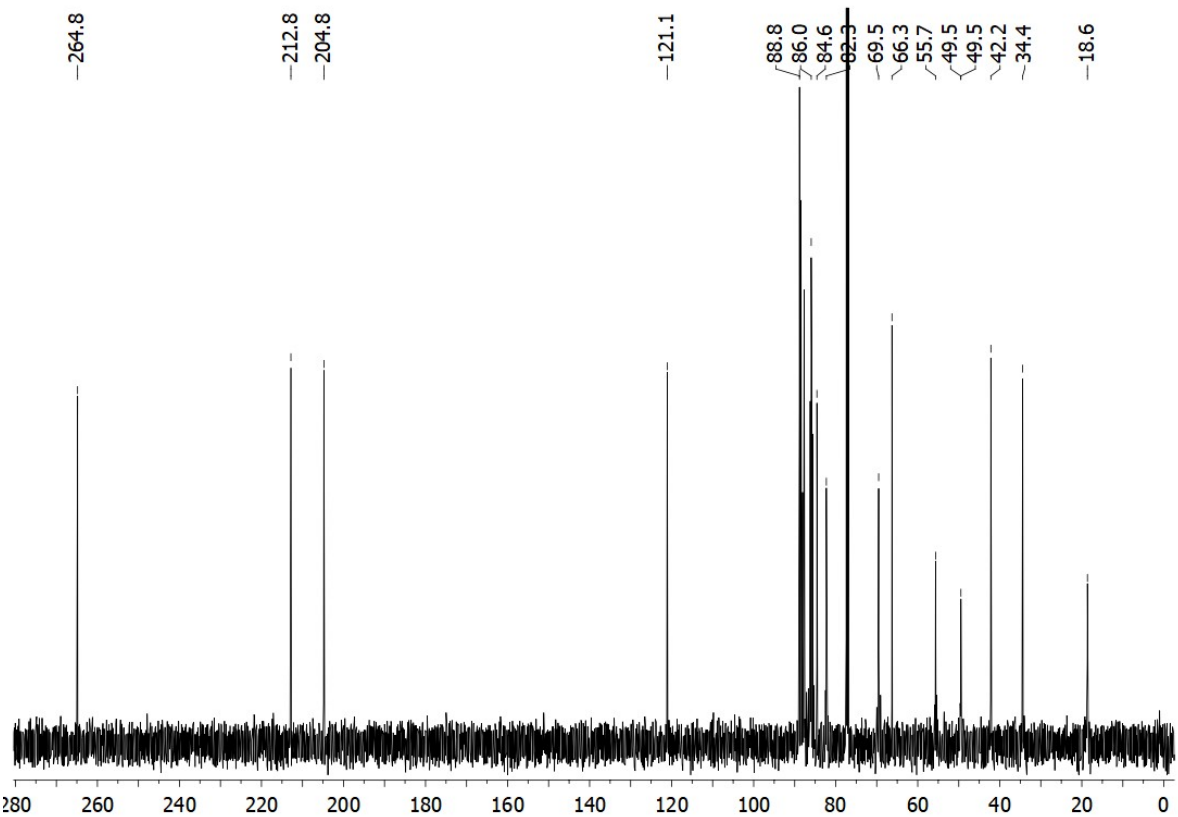


Figure S9. ^{1}H NMR spectrum (401 MHz, $CDCl_3$) of **4a1**.

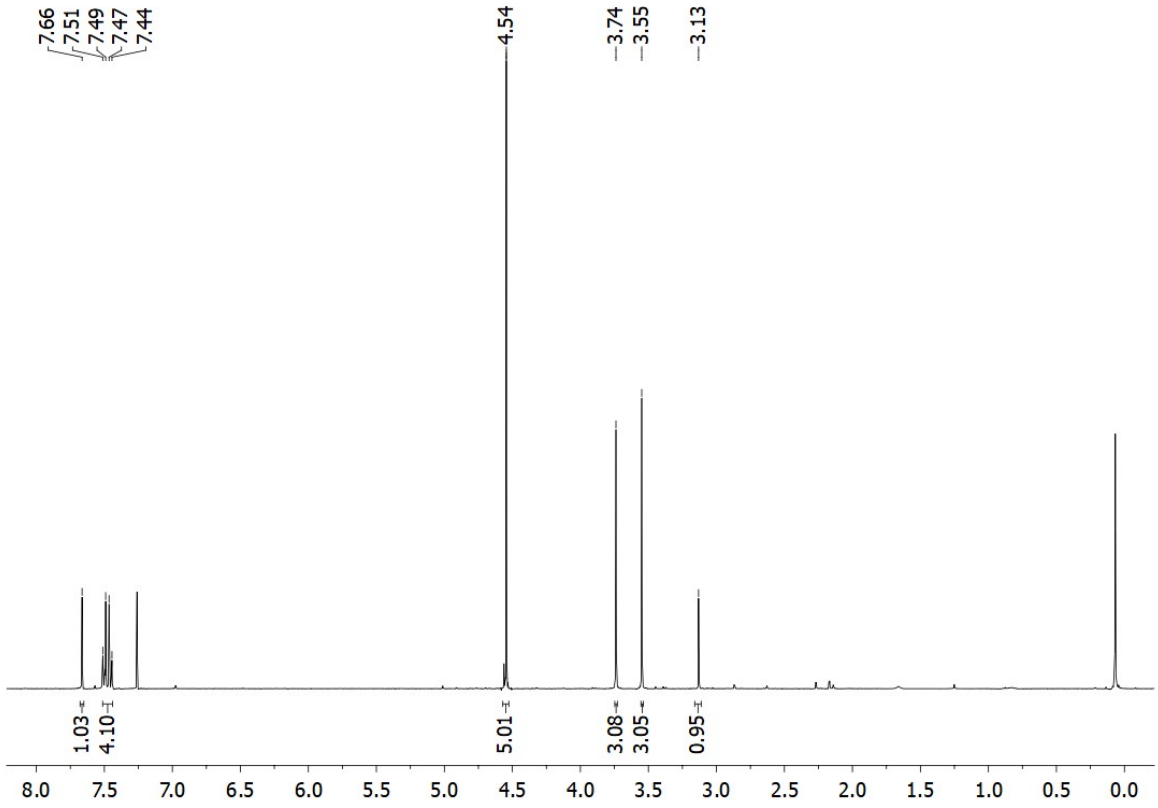


Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **4a1**.

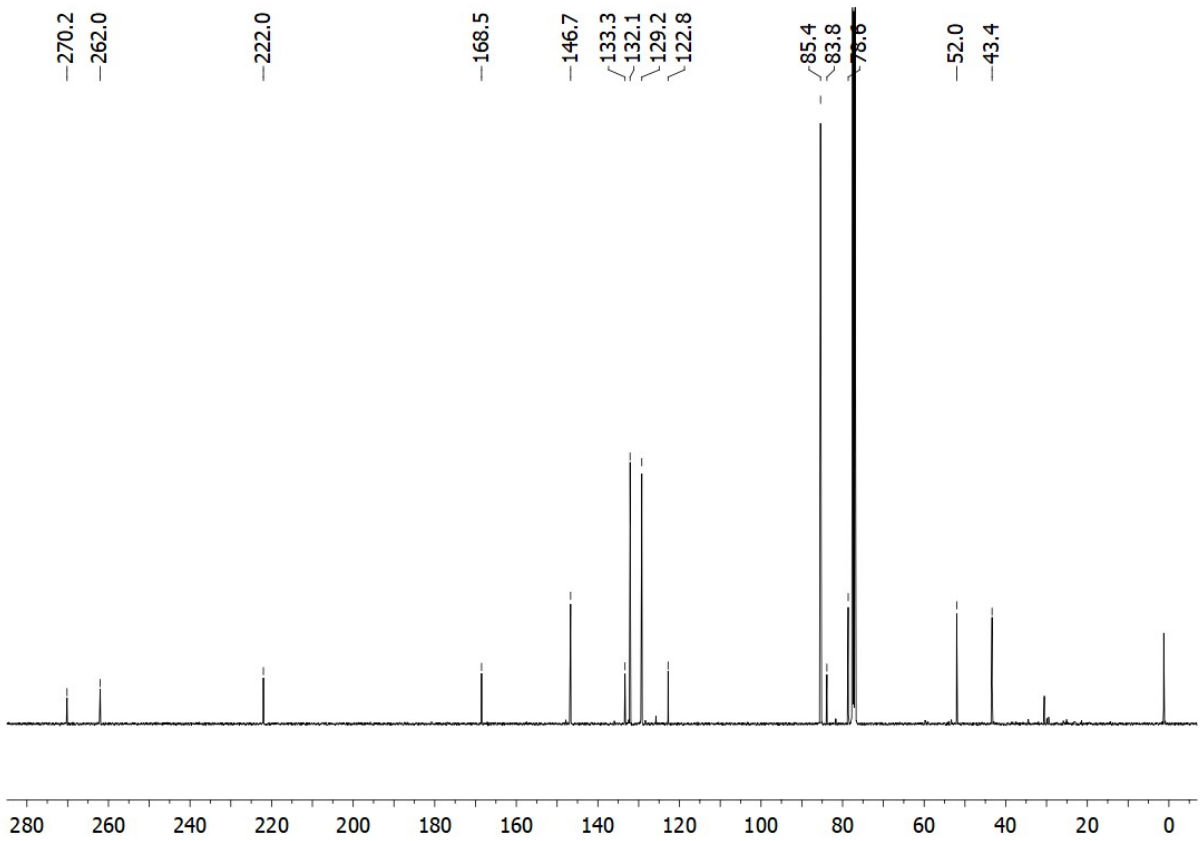


Figure S11. ^{1}H NMR spectrum (401 MHz, acetone-d_6) of **[5a1]CF_3SO_3**.

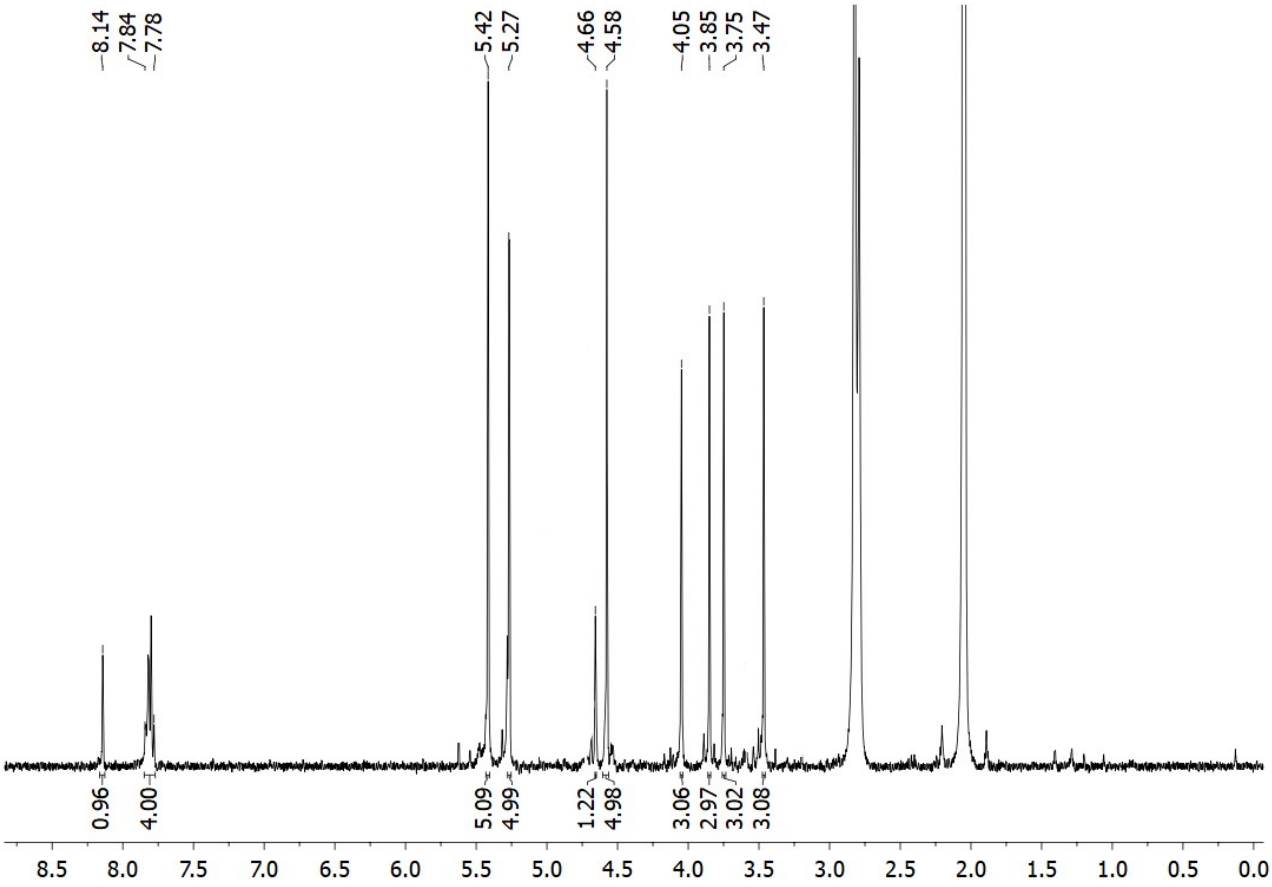


Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, acetone-d_6) of **[5a1]CF_3SO_3**.

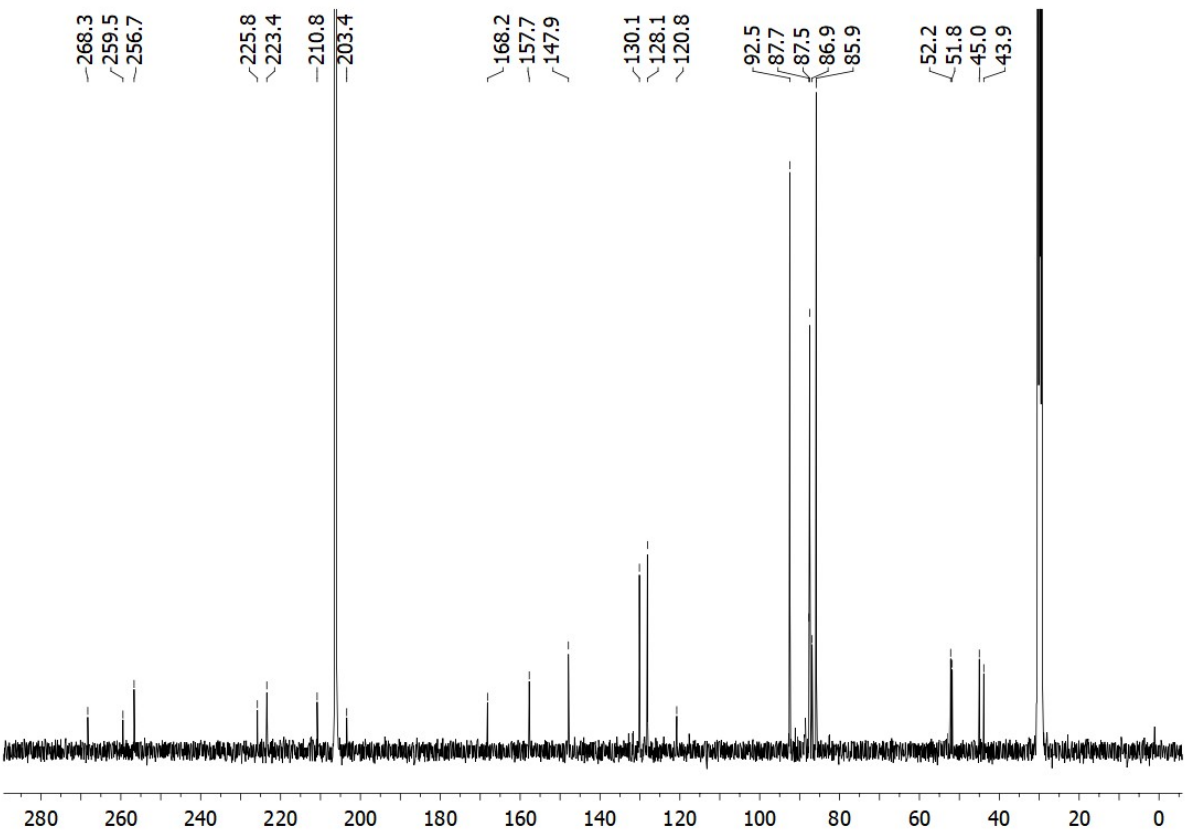


Figure S13. ^{1}H NMR spectrum (401 MHz, acetone-d_6) of **[5b1]CF_3SO_3**.

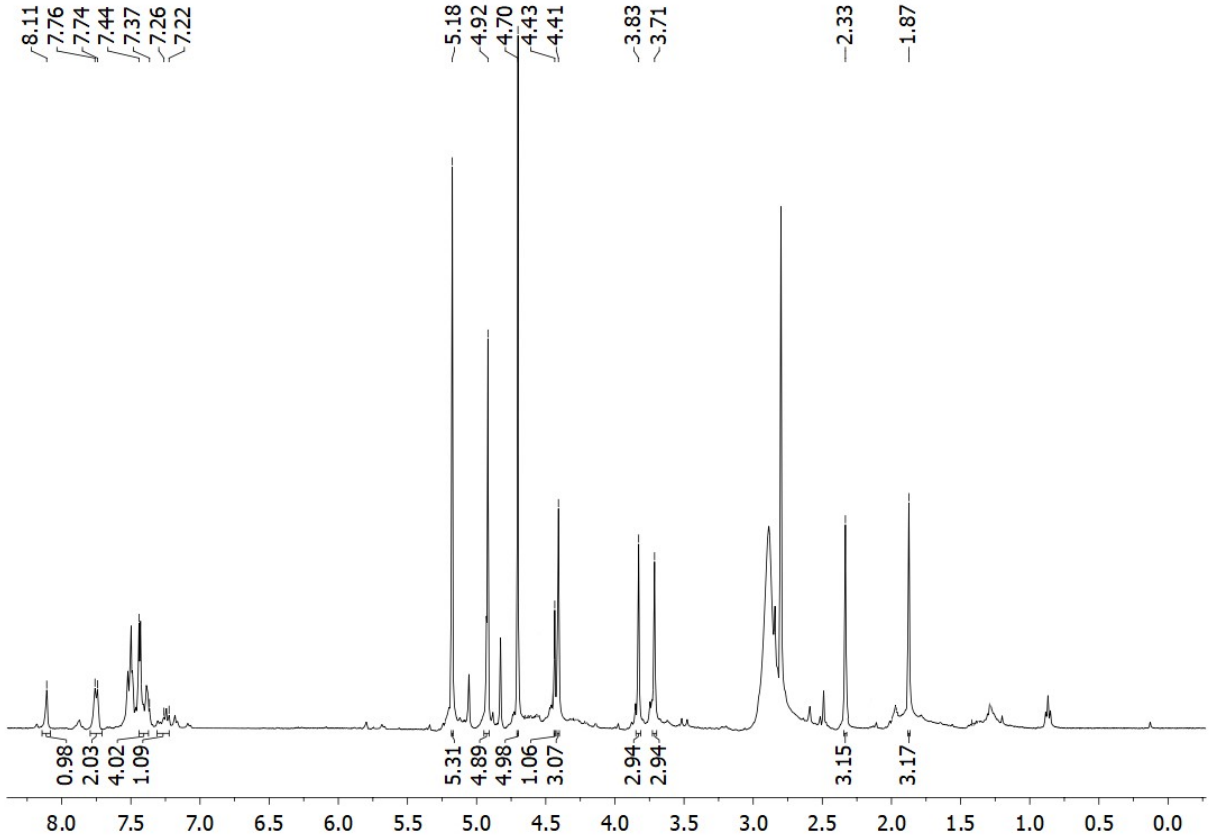


Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, acetone-d_6) of **[5b1]CF_3SO_3**.

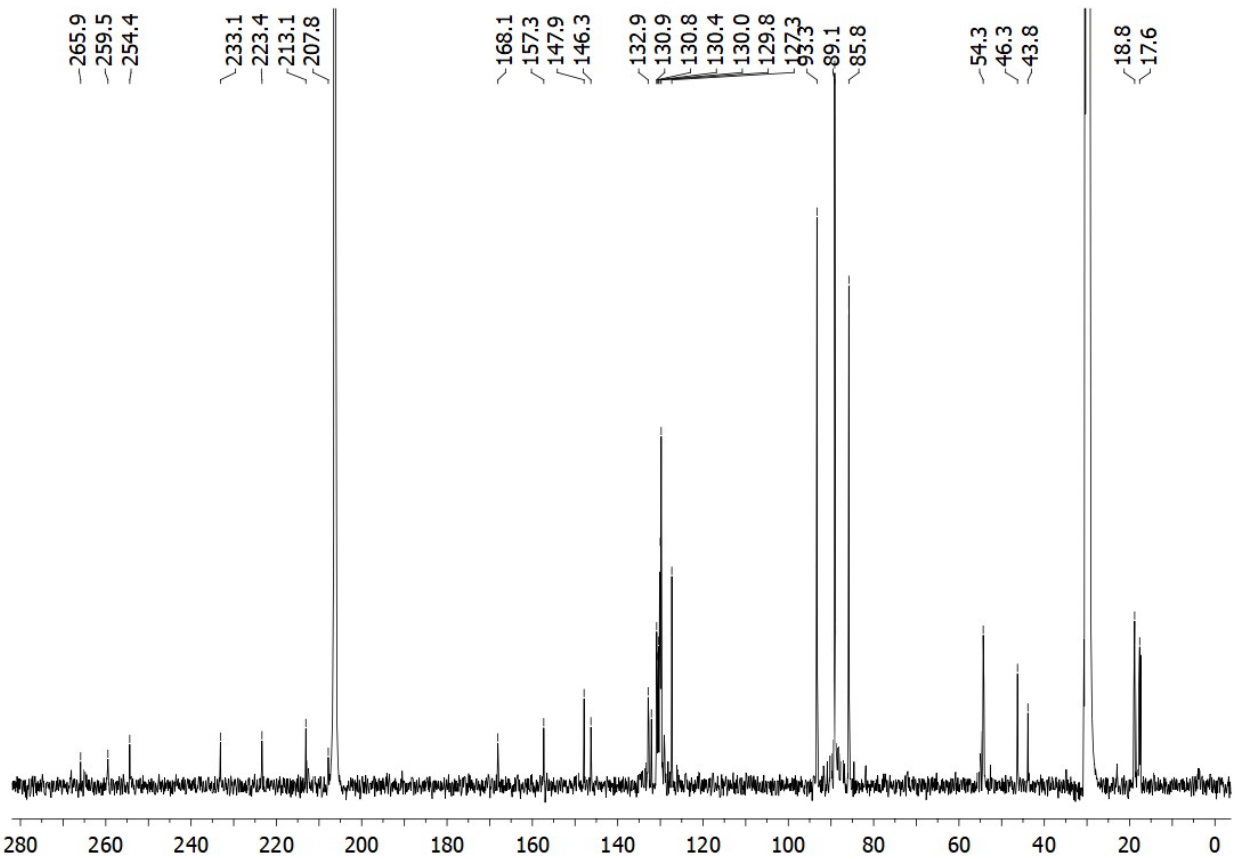


Figure S15. View of the DFT-optimized structure of [**5a1**]$^{2+}$ (doublet state). Calculated bond distances (Å) and angles (°): Fe(1)-C(1) 1.769, Fe(1)-C(2) 1.946, Fe(1)-C(5) 2.006, C(1)-O(1) 1.154, C(2)-N(1) 1.326, C(5)-O(2) 1.201, C(11)-C(12) 1.479, C(12)-C(13) 1.428, C(13)-C(14) 1.426, Fe(2)-C(12) 2.040, Fe(2)-C(13) 2.048, Fe(2)-C(14) 1.843, C(14)-N(2) 1.303, Fe(2)-C(18) 1.951, Fe(3)-C(12) 1.960, Fe(3)-C(18) 1.890, C(18)-O(3) 1.180, Fe(3)-C(17) 1.749, C(17)-O(2) 1.159, Fe(2)-Fe(3) 2.560, Fe(1)-C(1)-O(1) 178.9, C(2)-Fe(1)-C(5) 84.8, sum at N(1) 359.9, Fe(2)-C(12)-Fe(3) 79.6, Fe(3)-C(17)-O(2) 178.7, Fe(2)-C(18)-Fe(3) 88.6, sum at N(2) 360.0. Hydrogens atoms are omitted for clarity.

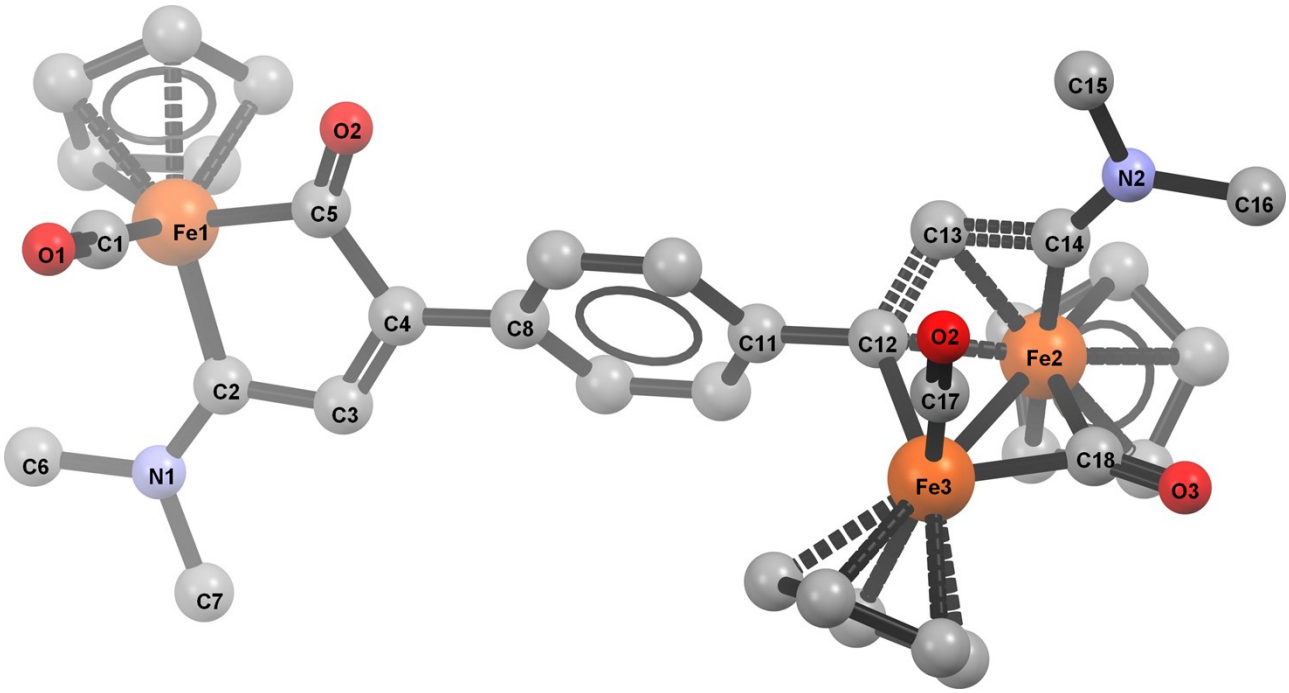


Figure S16. IR spectra of a CH_2Cl_2 solution of **4a1** recorded in an OTTLE cell during the progressive increase of the potential from –0.1 to +0.3 V (*vs*. Ag pseudoreference electrode). Scan rate 1.0 mV s^{-1}; spectra collected every minute. $[N^nBu_4]PF_6$ (0.2 mol dm^{-3}) as the supporting electrolyte. The absorptions of the solvent and supporting electrolyte have been subtracted.

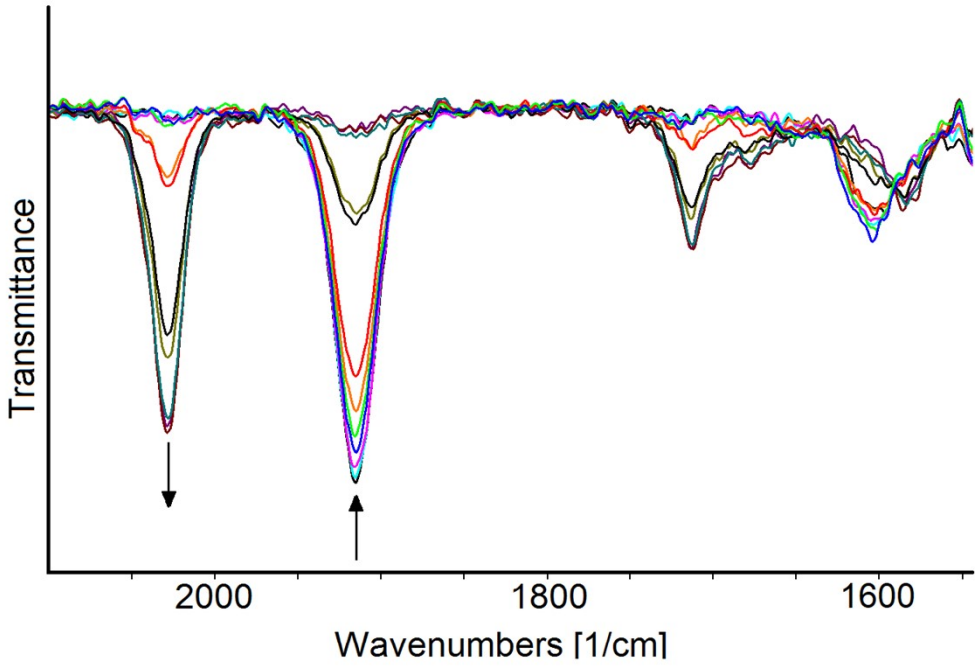


Figure S17. IR spectra of a CH_2Cl_2 solution of **[5a1]CF_3SO_3** recorded in an OTTLE cell before (black line) and after (red line) a cyclic voltammetry between –0.6 and –1.2 V (*vs*. Ag pseudoreference electrode) at the scan rate of 2 mV s^{-1}. The green line is the difference spectrum (red minus black). $[N^nBu_4]PF_6$ (0.2 mol dm^{-3}) as the supporting electrolyte. The absorptions of the solvent and supporting electrolyte have been subtracted.

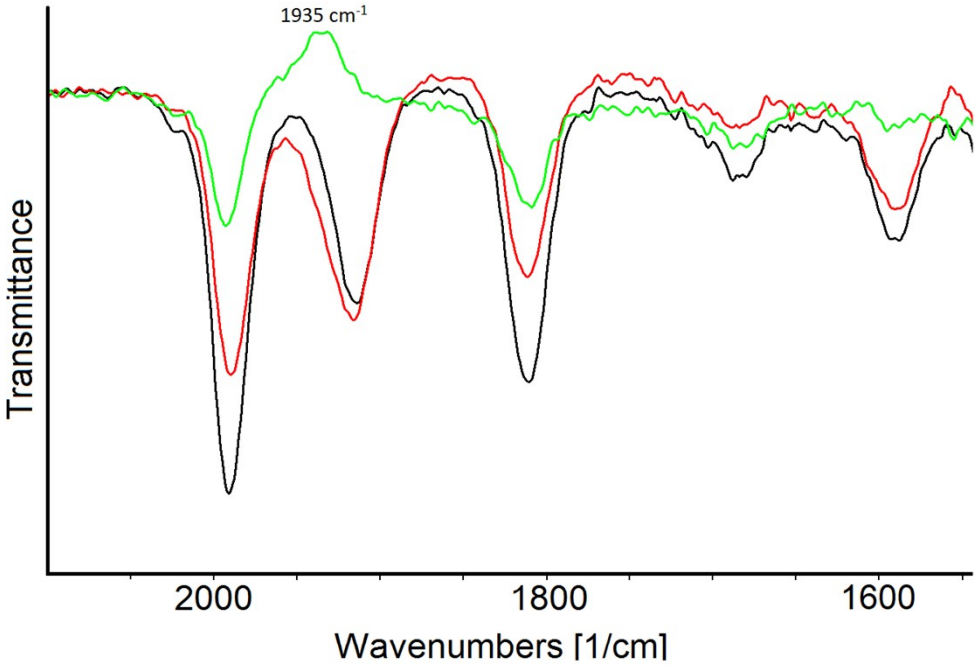
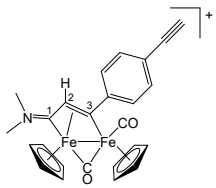
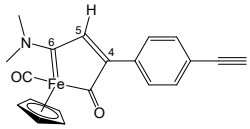
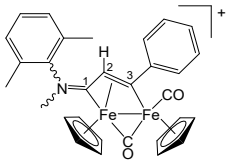
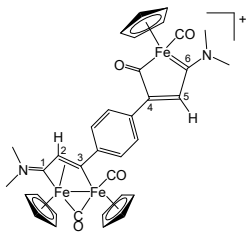
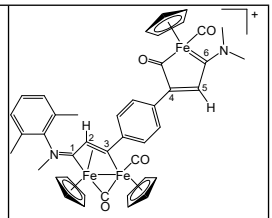


Table S1. Comparative view of ^{1}H and ^{13}C NMR data (solvent for analysis indicated in parentheses).

	 **[2a1]CF_3SO_3** (acetone-d_6)	 **4a1** ($CDCl_3$)	 ($CDCl_3$) [a]	 **[5a1]CF_3SO_3** (acetone-d_6)	 **[5b1]CF_3SO_3** (acetone-d_6)
^{1}H NMR (δ/ppm)					
$Fe_2\underline{Cp_2}$	5.43, 5.28		5.37, 5.14, *5.08, 4.88*	5.42, 5.27	5.18, 4.92
C^1-$N\underline{Me_x}$	4.05, 3.47		4.25, *3.58*	4.05, 3.47	4.41
C^2-$\underline{H}$	4.68		*4.97*, 3.94	4.66	4.43
$Fe\underline{Cp}$		4.54		4.58	4.70
C^5-$\underline{H}$		7.66		8.14	8.11
C^6-$N\underline{Me_2}$		3.74, 3.55		3.85, 3.75	3.83, 3.71
Me^{Xyl}			*2.51*, *2.01*, 2.20, 1.79		2.33, 1.87
^{13}C NMR (δ/ppm)					
$Fe_2\underline{Cp_2}$	92.4, 88.7		92.2, *92.1*, 88.0, *87.9*	92.5, 87.5	93.3, 90.1
$Fe_2\underline{C}O$	210.7		*210.3*, 209.6	210.8	213.1
μ-$\underline{C}O$	256.4		253.2	256.7	254.4
C^1-$N\underline{Me_x}$	51.8, 45.0		*52.5*, 45.9	52.2, 45.0	43.8
C^1	225.5		231.9, *230.4*	225.8	233.1
C^2	53.5		53.6, *53.4*	53.8	54.3
C^3	202.2		207.6, *207.1*	203.4	207.8
$Fe\underline{Cp}$		85.4		85.9	85.8
Fe-$\underline{C}O$		222.0		223.4	223.4
$\underline{C}O^{acyl}$		270.2		268.3	265.0
C^4		168.5		168.2	168.1
C^5		146.7		147.9	147.9
C^6-$N\underline{Me_2}$		52.0, 43.4		51.8, 43.9	54.3, 46.3
C^6		262.2		259.5	259.5
Me^{Xyl}			*18.7*, 18.0, *17.9*, 17.2		18.8, 17.6
ipso-Xyl			145.1, *140.8*		146.3

[a] From: Albano, V. G.; Busetto, L.; Marchetti, F.; Monari, M.; Zacchini, S.; Zanotti, V. Diiron μ-Vinyliminium Complexes from Acetylene Insertion into a Metal - Aminocarbyne Bond, *Organometallics* **2003**, *22*, 1326-1331. E/Z ratio = 3. Signals related to Z isomer are italicized.

DFT optimized coordinates (XYZ)

[5a1]$^{+}$

Fe	1.643700	0.331640	-0.937586
Fe	0.099891	-1.681147	-1.352072
O	1.541529	-0.645812	-3.658015
O	0.085730	2.577295	-1.911682
C	0.697428	1.667802	-1.528107
C	-1.201039	-0.534668	-1.941659
C	-1.204402	-0.335389	-0.531334
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C	-0.711541	0.702085	2.265402

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H	2.826440	-1.983974	7.739233
H	3.426512	-1.884650	9.411980
H	3.887820	-0.616891	8.234435

[5a1]$^{2+}$

Fe	1.629325	0.254879	-0.885039
Fe	0.066443	-1.733528	-1.283328
O	1.522307	-0.741913	-3.605964
O	0.119281	2.521848	-1.900051
C	0.713530	1.608591	-1.506381
C	-1.229988	-0.577317	-1.899074
C	-1.234581	-0.366067	-0.488893
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C	0.705472	-1.178260	2.436227
C	-0.579608	0.867963	2.258704
C	-0.581709	0.999746	3.647726
C	0.708737	-1.052029	3.824621
H	1.188000	-2.042547	1.974878
H	-1.071529	1.631339	1.645392
H	-1.083885	1.854861	4.104771
H	1.179564	-1.835218	4.428933
C	0.118479	0.168135	5.928071
C	1.145149	-0.279484	6.722885
H	2.055300	-0.687236	6.269114
C	-1.024813	0.821065	6.697222
O	-1.924013	1.434424	6.189846
C	1.004983	-0.101410	8.155845
N	2.029543	-0.322078	8.968623
C	1.950246	-0.008951	10.398992
H	2.025870	-0.934104	10.998002
H	0.997633	0.495354	10.611715
H	2.783794	0.660358	10.675338
C	3.344192	-0.820020	8.512186
H	3.219416	-1.698495	7.860229
H	3.936483	-1.119444	9.388892
H	3.888399	-0.027948	7.968452