Exploring the Anticancer Potential of Diiron bis-Cyclopentadienyl Complexes with Bridging Hydrocarbyl Ligands: Behavior in Aqueous Media and in Vitro Cytotoxicity

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Supporting Information

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Table S1. Selected bond distances (Å) and angles (°) for the cation in **11a^{Cl}**.

Fe(1)-Fe(2)	2.5195(4)	Fe(1)-C(1)	1.753(2)
Fe(1)-C(2)	1.979(2)	Fe(2)-C(2)	1.887(2)
Fe(1)-C(3)	1.889(2)	Fe(2)-C(3)	1.857(2)
Fe(2)-P(1)	2.2088(6)	C(1)-O(1)	1.148(3)
C(2)-O(2)	1.173(3)	C(3)-N(1)	1.306(3)
Fe(1)-C(1)-O(1)	177.3(2)	Fe(1)-C(2)-Fe(2)	81.32(9)
Fe(1)-C(3)-Fe(2)	84.55(9)	Fe(1)-C(3)-N(1)	135.51(17)
Fe(2)-C(3)-N(1)	139.91(17)	C(3)-N(1)-C(4)	123.50(19)
C(3)-N(1)-C(5)	123.09(19)	C(4)-N(1)-C(5)	113.35(18)

Table S2. Crystal data and measurement details for **11a^{Cl}·CH$_3$OH**.

	11a^{Cl}·CH$_3$OH
Formula	$C_{22}H_{32}ClFe_2N_4O_3P$
FW	578.63
T, K	100(2)
λ, Å	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
a, Å	9.3113(4)
b, Å	17.3058(8)
c, Å	14.8913(7)
β,°	91.5770(10)
Cell Volume, Å^3	2398.67(19)
Z	4
D_c, g·cm^{-3}	1.602
μ, mm^{-1}	1.420
F(000)	1200
Crystal size, mm	0.22×0.19×0.14
θ limits,°	1.805-27.999
Reflections collected	36322
Independent reflections	5789 [R_{int} = 0.0523]
Data / restraints /parameters	5789 / 0 / 302
Goodness on fit on F^2	1.065
R_1 ($I > 2\sigma(I)$)	0.0361
wR_2 (all data)	0.0825
Largest diff. peak and hole, e Å^{-3}	0.614 / –0.435

Stability studies in D_2O: NMR data

3. ^{1}H NMR (D_2O): δ/ppm = 11.82 (s, 1H), 5.47 (s-br, 10H), 2.10 (s-br, 6H). ^{19}F NMR (D_2O): δ/ppm -150.45, -150.50. Degradation products were already observed in the freshly-prepared solution. *Other species* (0 h). ^{1}H NMR (D_2O): δ/ppm = 5.31 (s-br), 5.08 (s-br), 2.39 (s-br), 2.29 (s), 2.22 (s), 1.95 (s-br).

4. ^{1}H NMR (D_2O): δ/ppm = 5.47 (s, 5H), 5.42 (s, 5H), 4.25–4.14 (m, 1H), 4.06–3.95 (m, 1H), 1.62 (t, J = 7.6 Hz, 3H). ^{19}F NMR: δ/ppm -78.9. *Other species* (72 h). ^{1}H NMR (D_2O): δ/ppm = 6.64-6.60 (m, CpH), 6.57-6.52 (m, CpH), 3.78-3.52 (m), 3.04-3.02 (m, CpH).

5a. ^{1}H NMR (D_2O): δ/ppm = 5.33, *5.22* (s, 10H), *4.26*, 4.19 (s, 6H). Data in italics is related to the *trans* isomer; *cis*/*trans* ratio = 10:1. ^{19}F NMR (D_2O): δ/ppm -78.9. *Other species* (72 h). ^{1}H NMR (D_2O): δ/ppm = 3.7-3.5 (m), 2.72 (s, Me_2NH).

5b. ^{1}H NMR (D_2O): δ/ppm = 7.48–7.35 (m, 3H), 5.49 (s, 5H), 4.88 (s, 5H), 4.45 (s, 3H), 2.66 (s, 3H), 2.16 (s, 3H). ^{19}F NMR (D_2O): δ/ppm -78.9. *Other species* (72 h). ^{1}H NMR (D_2O): δ/ppm = 7.25-7.10 (m), 3.8-3.5 (m), 3.02 (s), 2.85 (s), 2.71 (s), 2.34 (s), 1.91 (s).

5c. ^{1}H NMR (D_2O): δ/ppm = 7.59–7.53 (m, 2H), 7.52–7.46 (m, 3H), 5.85 (d, J = 15.2 Hz, 1H), 5.72 (d, J = 15.4 Hz, 1H), 5.42 (s, 5H), 5.32 (s, 5H), 4.07 (s, 3H). ^{19}F NMR: δ/ppm = -78.9. *Other species* (72 h). ^{1}H NMR (D_2O): δ/ppm = 4.22 (s, 2H, MeNHBn), 3.75-3.50 (m), 2.73 (s, 3H, MeNHBn).

***cis*-11a**. ^{1}H NMR (D_2O): δ/ppm = 5.20 (s, 5H), 5.02 (d, J = 1.5 Hz, 5H), 4.37 (d, J = 13.2 Hz, 3H), 4.27 (d, J = 13.0 Hz, 3H), 4.19 (s, 3H), 4.15 (d, J = 0.8 Hz, 3H), 3.75 (s, 6H). ^{19}F NMR (D_2O): δ/ppm -78.9. ^{31}P{^{1}H} NMR (D_2O): δ/ppm -15.6. *Other species* (72 h). ^{1}H NMR (D_2O): 3.67-3.62 (m), 3.57-3.52 (m), 2.72 (Me_2NH). **O=PTA** (72 h). ^{1}H NMR (D_2O): δ/ppm = 4.44–4.33 (m, 3H), 4.30–4.23 (m, 3H), 4.03 (d, J = 10.3 Hz, 6H). ^{31}P{^{1}H} NMR (D_2O): δ/ppm = -2.9.

Bn = CH_2Ph

Stability studies in D_2O/CD_3OD

A mixture of the selected Fe compound (**4**, **5a-d**, *ca.* 5 mg), CD_3OD (0.2 mL; 0.4 mL for **5d**) and a D_2O solution (0.7 mL; 0.5 mL for **5d**) containing Me_2SO_2 ($9.7 \cdot 10^{-3}$ mol·L^{-1}) was stirred for 30 min then filtered over celite and transferred into an NMR tube. The orange-red solution was analyzed by ^{1}H NMR then heated at 37 °C for 72 hours. After cooling to room temperature, the final solution was separated from an orange-brown solid by filtration over celite and NMR analyses were repeated. The amount of starting material in solution (% with respect to the initial spectrum) was calculated by the relative integral with respect to Me_2SO_2 as internal standard[1] (δ/ppm = 3.08 (s, 6H)) (Table S3). NMR data for the tested compounds are given below; ^{1}H chemical shift values are referenced to the HDO signal as in pure D_2O (δ/ppm = 4.79).

4. ^{1}H NMR (D_2O:CD_3OD 7:2): δ/ppm = 5.43 (s, 5H), 5.38 (s, 5H), 4.20–4.10 (m, 1H), 4.01–3.91 (m, 1H), 1.58 (t, *J* = 7.6 Hz, 3H). *Other species* (72 h). ^{1}H NMR (D_2O:CD_3OD 7:2): δ/ppm = 6.56-6.53 (m, CpH), 6.48-6.45 (m, CpH), 3.70-3.62 (m), 3.59-3.54 (m), 3.51-3.46 (m), 2.96-2.95 (m, CpH).

5a. ^{1}H NMR (D_2O:CD_3OD 7:2): δ/ppm = 5.29, *5.17* (s, 10H), *4.23*, 4.15 (s, 6H). Data in italics is related to the *trans* isomer; *cis*/*trans* ratio *ca*. 30:1. *Other species* (72 h). ^{1}H NMR (D_2O:CD_3OD 7:2): δ/ppm = 3.70-3.62 (m), 3.59-3.54 (m), 3.51-3.47 (m), 2.67 (Me_2NH).

5b. ^{1}H NMR (D_2O:CD_3OD 7:2): δ/ppm = 7.43–7.31 (m, 3H), 5.44 (s, 5H), 4.82* (s), 4.40 (s, 3H), 2.61 (s, 3H), 2.11 (s, 3H). *Superimposed to HDO peak. *Other species* (72 h). ^{1}H NMR (D_2O:CD_3OD 7:2): δ/ppm = 7.17-7.14 (m), 3.67-3.44 (m), 3.17 (s), 2.91 (s, XylMeNH), 2.34 (XylMeNH).

5c. ^{1}H NMR (D_2O:CD_3OD 7:2): δ/ppm = 7.52–7.38 (m, 5H), 5.78 (d, *J* = 15.1 Hz, 1H), 5.68 (d, *J* = 15.1 Hz, 1H), 5.37 (s, 5H), 5.27 (s, 5H), 4.02 (s, 3H). *Other species* (72 h). ^{1}H NMR (D_2O:CD_3OD 7:2): δ/ppm = 7.35-7.25 (m), 5.48 (s), 4.15 (s, MeBnNH), 3.69-3.63 (m), 3.59-3.55 (m), 3.51-3.46 (m), 2.66 (s, MeBnNH).

5d. ^{1}H NMR (D_2O:CD_3OD 5:4): δ/ppm = 8.25 (d, *J* = 8.7 Hz, 1H), 8.19 (s, 1H), 8.12–8.03 (m, 2H), 7.76 (d, *J* = 9.0 Hz, 1H), 7.74–7.68 (m, 2H), 5.49 (s, 5H), 4.70 (s, 5H), 4.64 (s, 3H). *Other species* (72 h). ^{1}H NMR (D_2O:CD_3OD 5:4): δ/ppm = 7.94-7.91 (m), 7.40-7.35 (m), 7.24-7.21 (m), 7.04-7.00 (m), 3.72-3.57 (m), 3.53-3.48 (m), 2.83 (s).

Stability studies in DMSO-d_6/D_2O: NMR data

5d. ^{1}H NMR (DMSO-d_6:D_2O 2:1): δ/ppm = 8.24–8.16 (m, 2H), 8.09–8.00 (m, 2H), 7.74–7.62 (m, 3H), 5.47 (s, 5H), 4.67 (s, 5H), 4.51 (s, 3H). ^{19}F NMR (DMSO-d_6:D_2O 2:1): δ/ppm = - 77.9.

5e. ^{1}H NMR (DMSO-d_6:D_2O 2:1): δ/ppm = 7.64–7.45 (m, 3H), 5.48 (s, 5H); 4.88, 4.84 (s, 5H); 4.34, 4.33 (s, 3H); 2.61, 2.12 (s, 3H). Isomer ratio *ca*. 3:2. ^{19}F NMR (DMSO-d_6:D_2O 2:1): δ/ppm = - 77.9.

6. ^{1}H NMR (DMSO-d_6:D_2O 2:1): δ/ppm = 5.04, 5.03 (s, 10H), 3.94 (s, 3H), 3.87 (s, 3H), 3.61 (s, 3H). ^{19}F NMR (DMSO-d_6:D_2O 2:1): δ/ppm = - 78.0. *Other species* (72 h). ^{1}H NMR (DMSO-d_6:D_2O 2:1): δ/ppm = 5.30 (s), 4.76 (s), 4.72 (s), 4.19 (s), 3.14 (s, MeOH) 1.17-1.11 (m).

7. ^{1}H NMR (DMSO-d_6:D_2O 3:1): δ/ppm = 7.14 (t, *J* = 7.5 Hz, 2H), 7.04 (t, *J* = 7.4 Hz, 1H), 6.92 (d, *J* = 7.2 Hz, 2H), 4.78 (s, 5H), 4.72 (s, 1H), 4.46 (s, 1H), 3.82 (s, 3H), 3.69 (s, 3H), 3.46 (s, 1H), 3.39 (s, 1H). *Other species* (72 h). ^{1}H NMR (DMSO-d_6:D_2O 3:1): δ/ppm = δ 7.82–7.10 (m), 5.31 (s), 5.04–4.98 (m), 3.60 (s), 3.54 (s), 3.51–3.43 (m), 3.42–3.27 (m).

9a. ^{1}H NMR (DMSO-d_6:D_2O 3:1): δ/ppm = 7.40–7.23 (m, 3H), 4.78 (s, 8H), 4.36 (s, 5H), 2.68 (s, 3H), 2.01 (s, 3H). Isomer ratio *ca*. 9:1.

9b. ^{1}H NMR (DMSO-d_6:D_2O 2:1): δ/ppm = 7.33–7.20 (m, 3H); 5.06, 4.86 (s, 5H); 4.44, 4.41 (s, 3H); 4.35*, 4.22* (s); 2.56, 2.55 (s, 3H), 2.43, 2.37 (s, 3H). *Superimposed on HDO peak. Isomer ratio ca. 5:3. *Other species* (72 h). ^{1}H NMR (DMSO-d_6:D_2O 2:1): δ/ppm = 5.27 (s), 3.50-3.28 (m), 2.14 (s).

10. ^{1}H NMR (DMSO-d_6:D_2O 2:1): δ/ppm = 8.25–7.46 (m, 14H, Ar); 5.47 (s), 5.38-5.34 (m, 5H, Cp); 4.67, 4.63 (s), 4.60-4-58 (m, 5H, Cp); 4.57 (s), 4.52–4.49 (m, 3H, Me). Isomer ratio *ca*. 1.3:1:1.3. ^{19}F NMR (DMSO-d_6:D_2O 2:1): δ/ppm = - 77.9. *Other species* (72 h). ^{1}H NMR (DMSO-d_6:D_2O 2:1): δ/ppm = 5.21 (s), 5.05 (s), 4.80 (s), 4.74 (s), 4.69 (s).

11b. ^{1}H NMR (DMSO-d_6:D_2O 2:1): δ/ppm = 7.50–7.28 (m, 10H), 7.25–7.16 (m, 1H), 7.16–7.05 (m, 2H), 6.75–6.67 (m, 1H), 6.62–6.57 (m, 1H), 5.03 (s, 5H), 4.78 (s, 5H), 4.04 (s, 3H), 3.99 (s, 3H). ^{19}F NMR (DMSO-d_6:D_2O 2:1): δ/ppm = - 77.9. ^{31}P{^{1}H} NMR (DMSO-d_6:D_2O 2:1): δ/ppm = 51.6. **O=PPh$_2$(2-C$_6$H$_4$OH)** (72 h). ^{1}H NMR (DMSO-d_6:D_2O 2:1): δ/ppm = 7.63–7.55 (m), 7.52–7.43 (m), 7.02–6.85 (m). ^{31}P{^{1}H} NMR (DMSO-d_6:D_2O 2:1): δ/ppm = 29.6.

Table S3. Stability of selected Fe compounds in D_2O or D_2O/CD_3OD solution at 37 °C.

Compound	% starting material (72 h, 37 °C) [a]		Decomposition products identified in solution [b]
	D_2O	D_2O/CD_3OD	
3	0 %	-	-
4	57 %	66 %	CpH
5a [c]	70 %	83 %	Me_2NH
5b	51 %	80 %	-
5c	75 %	65 %	MeBnNH
5d	-	66 %	-
***cis*-11a**	70 %	-	O=PTA + Me_2NH

[a] Calculated by ^{1}H NMR (Me_2SO_2 internal standard). [b] No additional {FeCp} species was present in solution. [c] Data referred to all isomers collectively

Table S4. Stability of selected Fe compounds in DMSO-d_6/D_2O solution at 37 °C.

Compound	% starting material (72 h, 37 °C) [a]	Decomposition products identified in solution
5d	74 %	**5d^S**
5e [b]	51 %	**5e^S**
6	34 %	**5a^S**, MeOH, other {FeCp} species
7	0 %	-
9a [b]	< 1 %	**5b^S**
9b [b]	42 %	other {FeCp} species
10 [b]	72 %	**5d^S**, other {FeCp} species
11b	78 %	**5a^S**, O=PPh_2(2-C_6H_4OH)

[a] Calculated by ^{1}H NMR (Me_2SO_2 internal standard). [b] Data referred to all isomers collectively.

Reference NMR data

Ferrocene. ^{1}H NMR ($CDCl_3$): δ/ppm = 4.17 (s). ^{1}H NMR (DMSO-d_6:D_2O 2:1): δ/ppm = 4.12 (s).

Cyclopentadiene. ^{1}H NMR (DMSO-d_6): δ/ppm = 6.56 (m, 2H), 6.47 (m, 2H), 2.95 (m, 2H). ^{1}H NMR (CD_3OD:D_2O 8:1): δ/ppm = 6.54 (m, 2H), 6.44 (m, 2H), 2.95 (m, 2H).

Dicyclopentadiene. ^{1}H NMR (DMSO-d_6:D_2O 2:1): δ/ppm = 5.94–5.90 (m, 1H), 5.87–5.82 (m, 1H), 5.47–.43 (m, 1H), 5.42–5.38 (m, 1H), 3.15–3.08 (m, 1H), 2.80 (s, 1H), 2.72 (s, 1H), 2.64 (ddd, *J* = 13.0, 8.6, 4.1 Hz, 1H), 2.12–2.01 (m, 1H), 1.58–1.48 (m, 1H), 1.33 (d, *J* = 7.9 Hz, 1H), 1.23 (d, *J* = 7.9 Hz, 1H).

Dimethylamine hydrochloride. ^{1}H NMR (D_2O): δ/ppm = 2.73.[2]

***N*-methylbenzylamine hydrochloride.** ^{1}H NMR ($CDCl_3$): δ/ppm = 10.5-9.5 (s-br, 2H), 7.52-7.24 (m, 5H), 4.01 (s, 2H), 2.47 (s, 3H).[3]

Stability studies in cell culture medium/DMSO: IR data

4. IR (CH_2Cl_2): ῡ/cm^{-1} = 2038s, 2006m, 1849m. *Other species*. IR (CH_2Cl_2): ῡ/cm^{-1} = 1812m-w, 1712m.

5a. IR (CH_2Cl_2): ῡ/cm^{-1} = 2021s, 1988m, 1835m, 1606m. *Other species*. IR (CH_2Cl_2): ῡ/cm^{-1} = 2199w, 2159w, 1974m, 1711m, 1624m, 1590m, 1577m.

5b. IR (CH_2Cl_2): ῡ/cm^{-1} = 2023s, 1991m, 1839m, 1584w, 1529w. *Other species*. IR (CH_2Cl_2): ῡ/cm^{-1} = 2122w, 1962w-sh, 1793w, 1709w, 1674w.

5c. IR (CH_2Cl_2): ῡ/cm^{-1} = 2022s, 1989m-s, 1835s, 1577w. *Other species*. IR (CH_2Cl_2): ῡ/cm^{-1} = 2214w, 2179w, 1800m, 1601m.

5d. IR (CH_2Cl_2): ῡ/cm^{-1} = 2022s, 1989w, 1837m, 1600w, 1564w, 1540w, 1507w. *Other species*. IR (CH_2Cl_2): ῡ/cm^{-1} = 2127w, 2114w, 1712w, 1633w.

5e. IR (CH_2Cl_2): ῡ/cm^{-1} = 2025s, 1839m-sh, 1541w-sh, 1515w. *Other species*. IR (CH_2Cl_2): ῡ/cm^{-1} = 2118m, 1991s, 1963m-sh, 1950m-sh, 1799s, 1710m-w, 1682m, 1648m.

6. IR (CH_2Cl_2): ῡ/cm^{-1} = 1981s, 1807s, 1605m. *Other species*. IR (CH_2Cl_2): ῡ/cm^{-1} = 2019w.

9a. IR (CH_2Cl_2): ῡ/cm^{-1} = 1983s, 1797s, 1505w. *Other species*. IR (CH_2Cl_2): ῡ/cm^{-1} = 2016w-sh, 1675m, 1639m, 1604w.

9b. IR (CH_2Cl_2): ῡ/cm^{-1} = 2092m, 1981s, 1963s-sh, 1804s, 1504w. *Other species*. IR (CH_2Cl_2): ῡ/cm^{-1} = 2108w, 1723w.

10. IR (CH_2Cl_2): ῡ/cm^{-1} = 2127s, 2115s, 2019m, 1986s, 1822s, 1632w, 1957w, 1527m. *Other species*. IR (CH_2Cl_2): ῡ/cm^{-1} = 1507m.

11a. IR (CH_2Cl_2): ῡ/cm^{-1} = 1966s, 1800s, 1579m.

11b. IR (CH_2Cl_2): ῡ/cm^{-1} = 1900s, 1789s, 1581m. *Other species*. IR (CH_2Cl_2): ῡ/cm^{-1} = 1856w.

Figure S1. Ethidium bromide displacement tests for **5b** (circles); C_{DNA} = 1.30×10^{-4} M, C_{EB} = 5.33×10^{-5} M, NaCl 0.1 M, NaCac 0.01 M, λ_{ex} = 520 nm, λ_{em} = 595 nm, T = 25.0 °C. Open squares are related to blank test (DMSO addition in the absence of **5b**).

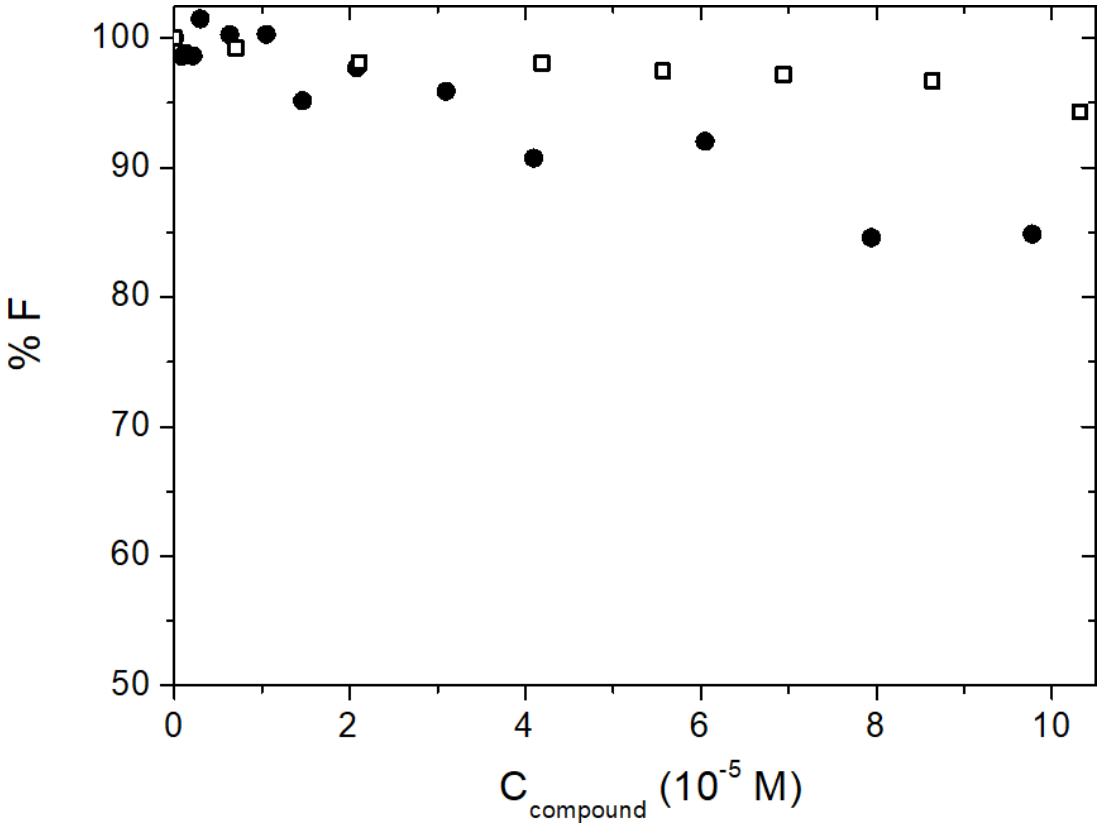
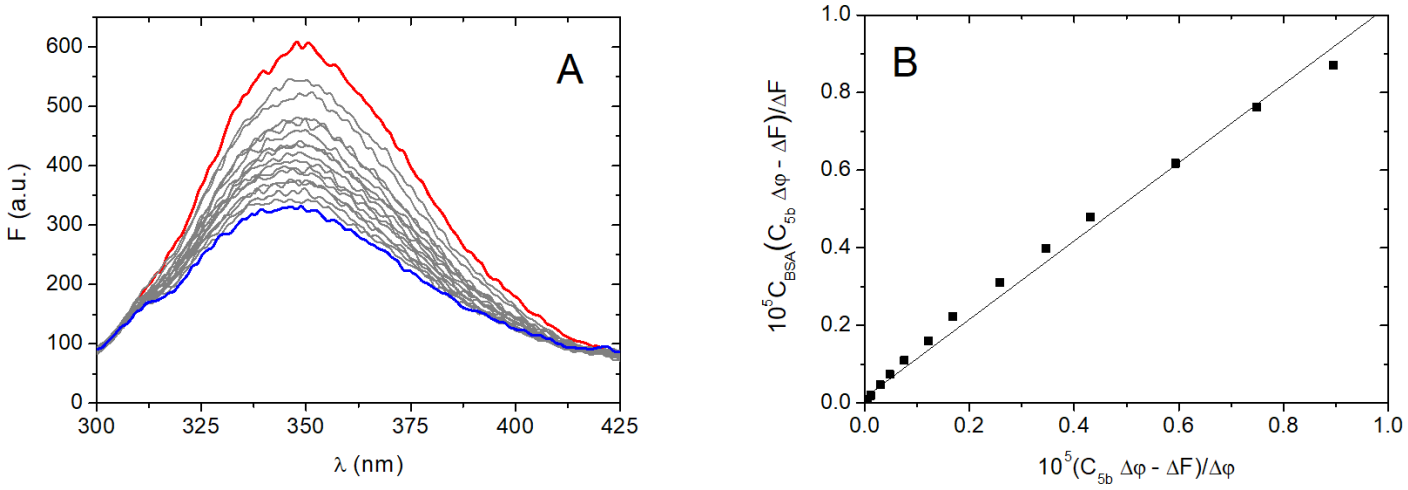


Figure S2. (A) Spectrofluorometric titration of the **5b**/BSA system showing protein quenching upon metal complex addition, and (B) relevant analysis according to Equation S1; C_{BSA} = 3.14×10^{-7} M, $C_{\mathbf{5B}}$ from 0 M (red) to 9.23×10^{-6} M (blue), NaCl 0.1 M, NaCac 0.01 M, λ_{ex} = 280 nm, λ_{em} = 345 nm, T = 25.0 °C.



Equation S1,[4] an alternative form of the Scatchard equation, was used to fit the experimental data and to evaluate the **5b**/BSA binding stoichiometry (*n*) and binding constant (K):

$$\frac{C_{BSA}(C_{5b}\Delta\varphi-\Delta F)}{\Delta F} = \frac{1}{nK} + \frac{(C_{5b}\Delta\varphi-\Delta F)}{\Delta\varphi} \times \frac{1}{n} \qquad \text{(Equation S1)}$$

C_{BSA}, $C_{\mathbf{5b}}$ = total analytical concentrations of BSA and **5b**, respectively

$\Delta\varphi = \varphi_{\mathbf{5b}\text{-BSA}} - \varphi_{BSA}$ (φ: fluorescence analogous of absorptivity)

$\Delta F = F - F°$

n = number of equivalent sites per protein unit

K = binding constant for the **5b**/BSA complex

It comes out that *n* = 1.0 and K is quite high (being the intercept non distinguishable from zero, Figure S2B); the HypSpec® software under *n* = 1.0 reaction conditions was used to estimate log K = 7.30 (Figure S3).

Figure S3. HypSpec analysis (http://www.hyperquad.co.uk) of the fluorescence emission changes observed upon addition of **5b** to BSA. The software enables, through a least square procedure, to fit the data over a wide wavelength range according to multiple equilibria models. Tests for different models and factor analysis of the data confirm that a binding mode according to 1:1 stoichiometry is sufficient to describe the data set. Left: titration curve at 342.5 nm (open diamond = experimental, cross = calculated) and species distribution (green = free BSA, blue = compound/BSA adduct). Right: fluorescence emission spectrum (open diamond = experimental, dashed red line = calculated) and relevant deconvolution (green = free BSA, blue = compound/BSA adduct). Bottom panels: residuals. Other experimental conditions are as for Figure S2.

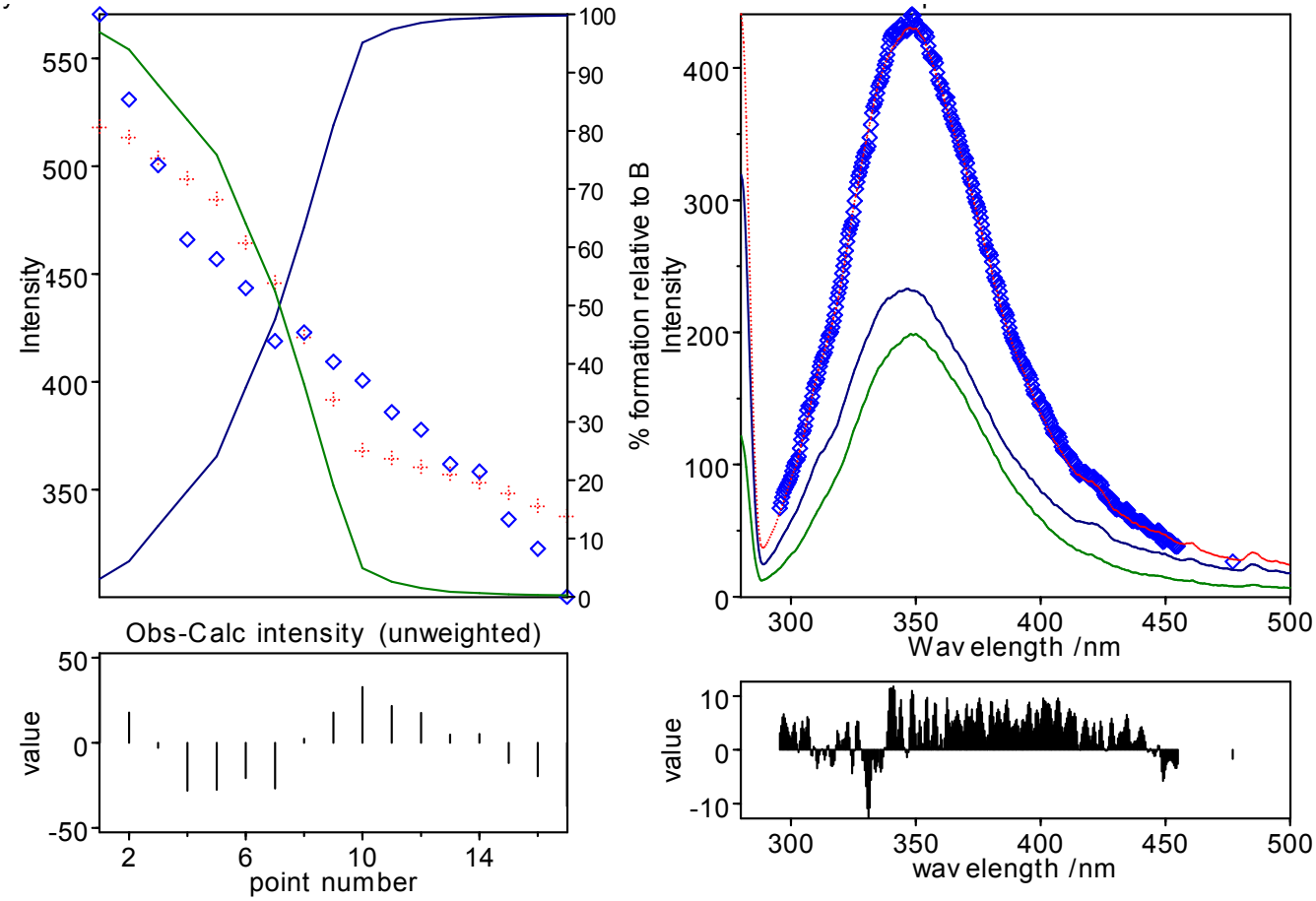


Figure S4. ^{1}H NMR spectrum (401 MHz, acetone-d_6) of *cis*-[$Fe_2Cp_2(CO)(\mu\text{-}CO)\{\mu\text{-}\kappa^1\text{:}\kappa^1\text{-}CNMe_2\}(\kappa P\text{-}PTA)]CF_3SO_3$, ***cis*-11a**.

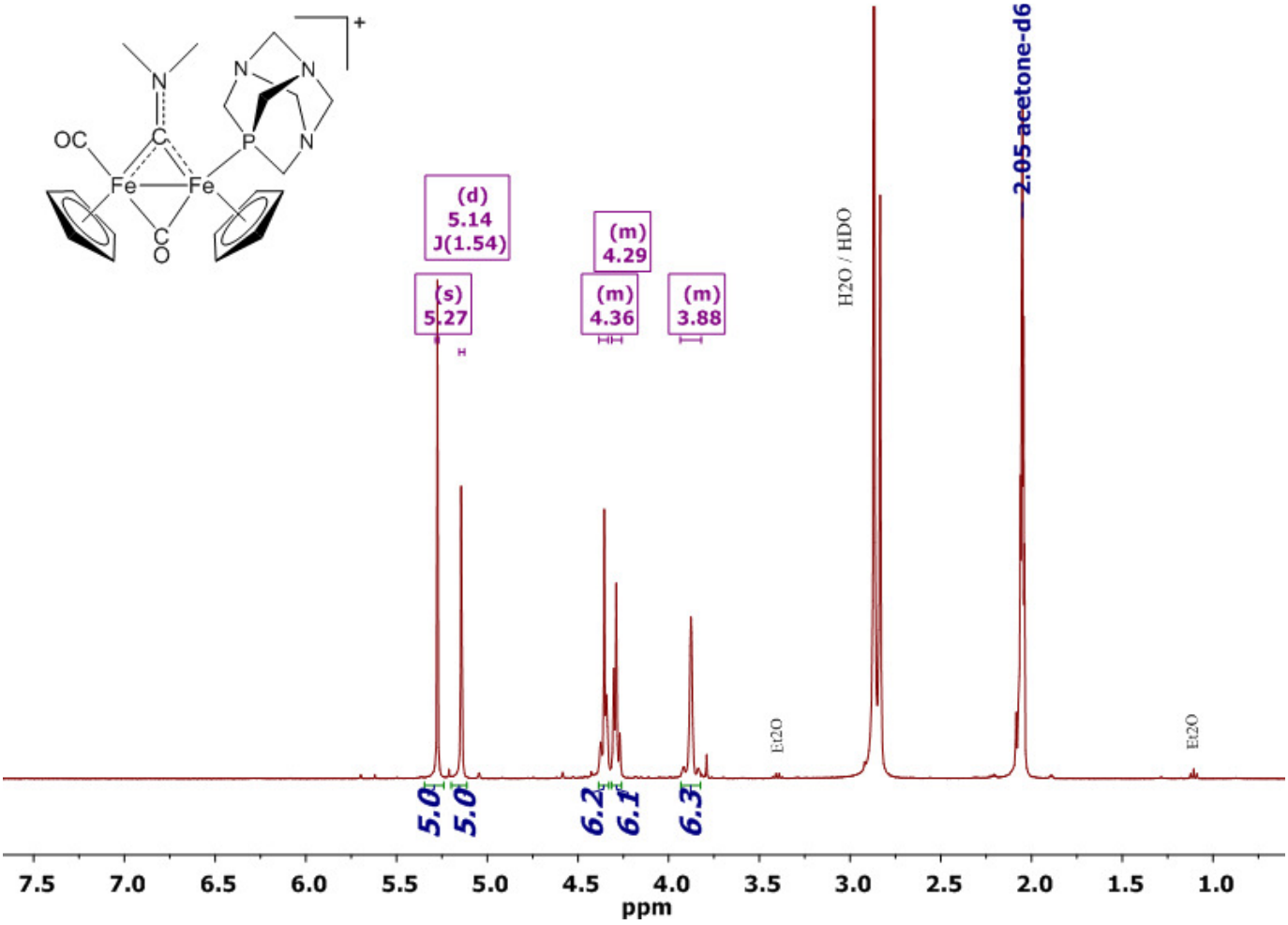


Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, acetone-d_6) of *cis*-[$Fe_2Cp_2(CO)(\mu\text{-}CO)\{\mu\text{-}\eta^1\text{:}\eta^1\text{-}CNMe_2\}(\kappa P\text{-}PTA)]CF_3SO_3$, ***cis*-11a**.

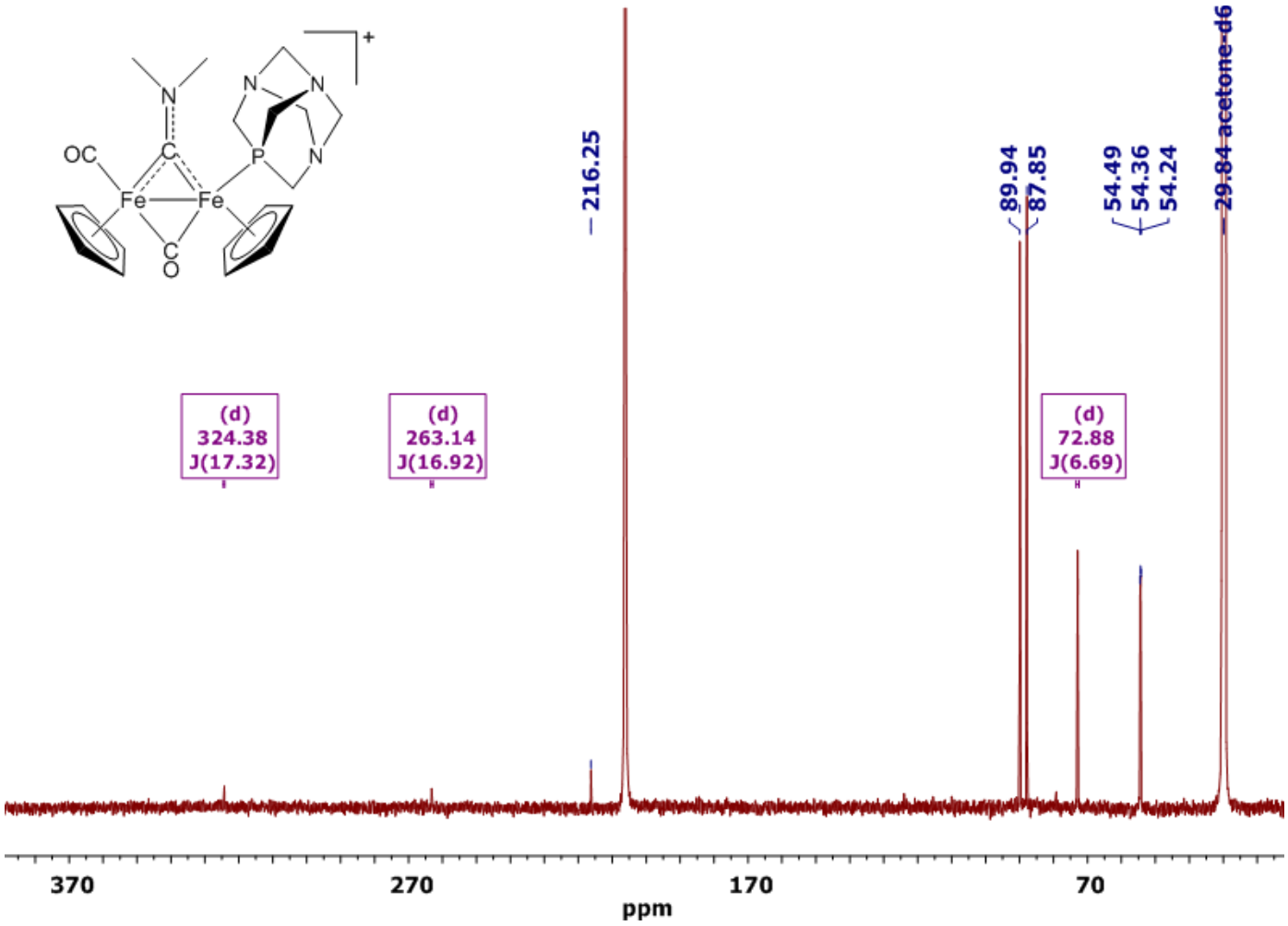


Figure S6. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, acetone-d_6) of *cis*-[$Fe_2Cp_2(CO)(\mu\text{-}CO)\{\mu\text{-}\eta^1\text{:}\eta^1\text{-}CNMe_2\}(\kappa P\text{-}PTA)]CF_3SO_3$, ***cis*-11a**.

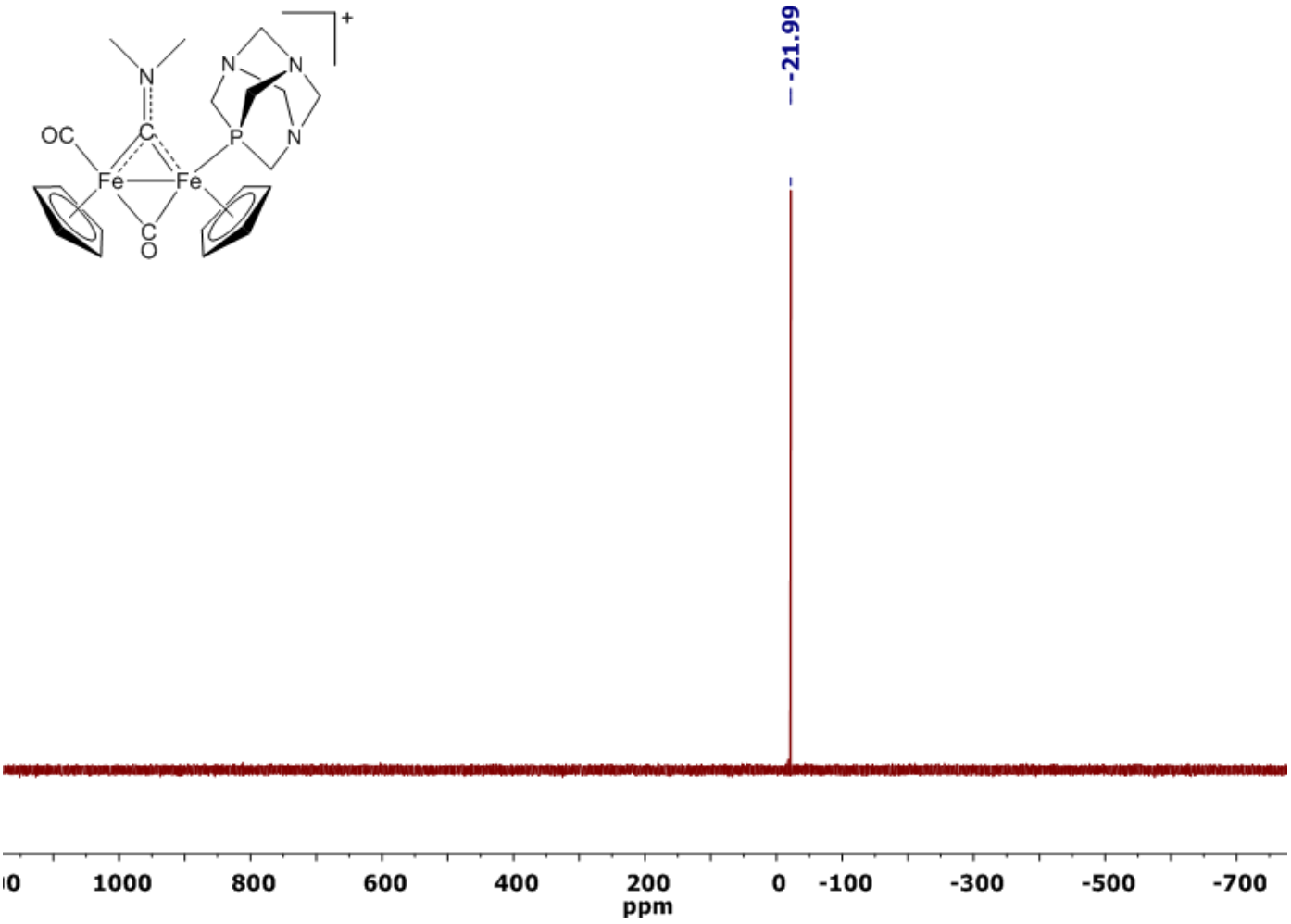


Figure S7. ^{1}H NMR spectrum (401 MHz, acetone-d_6) of $[Fe_2Cp_2(CO)(\mu\text{-}CO)\{\mu\text{-}\eta^1\text{:}\eta^1\text{-}CNMe_2\}\{\kappa P\text{-}Ph_2P(2\text{-}C_6H_4OH)\}]CF_3SO_3$, **11b**. Inset shows the OH resonance.

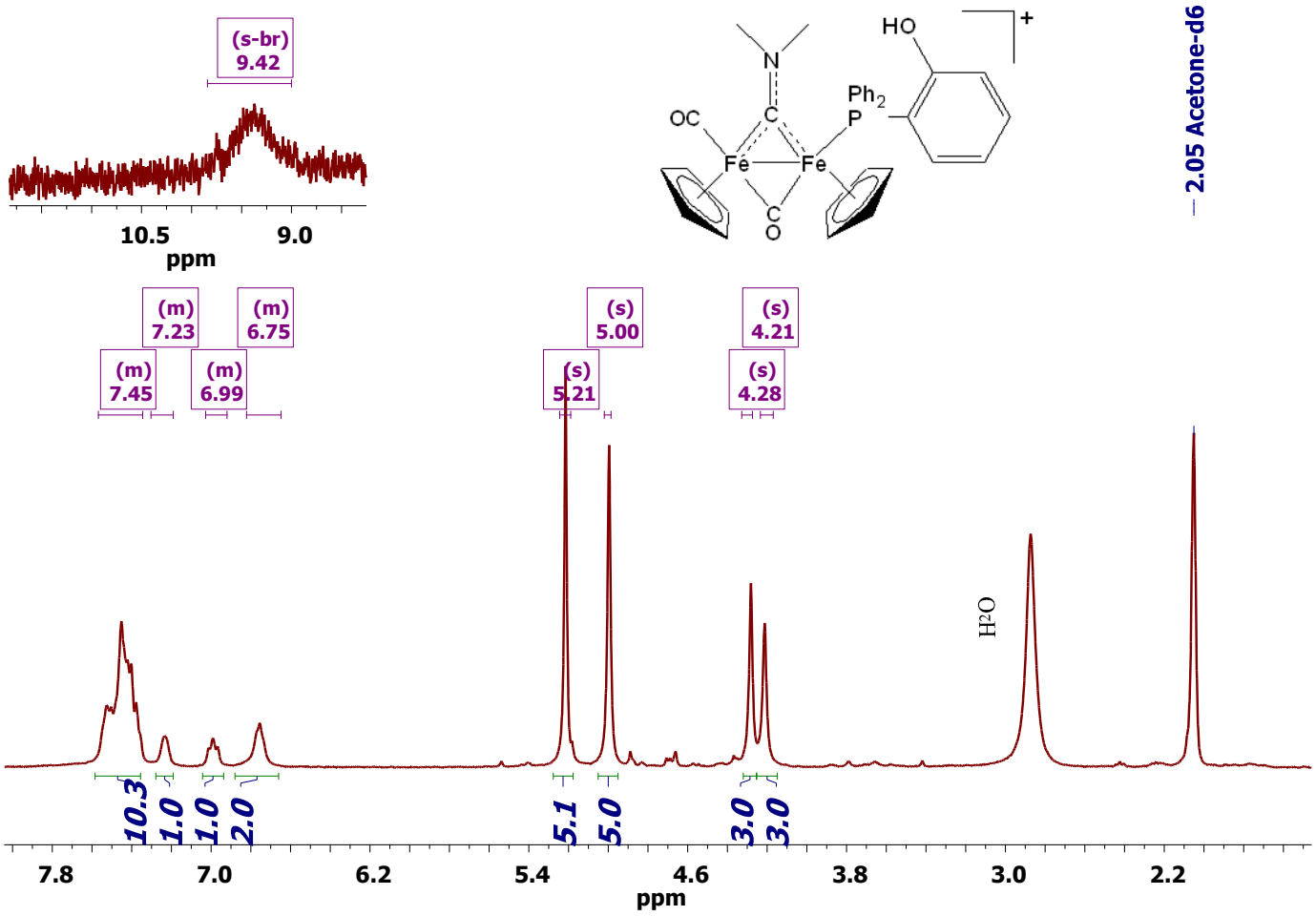


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, acetone-d_6) of $[Fe_2Cp_2(CO)(\mu\text{-}CO)\{\mu\text{-}\eta^1\text{:}\eta^1\text{-}CNMe_2\}\{\kappa P\text{-}Ph_2P(2\text{-}C_6H_4OH)\}]CF_3SO_3$, **11b**. Inset shows the aromatic region.

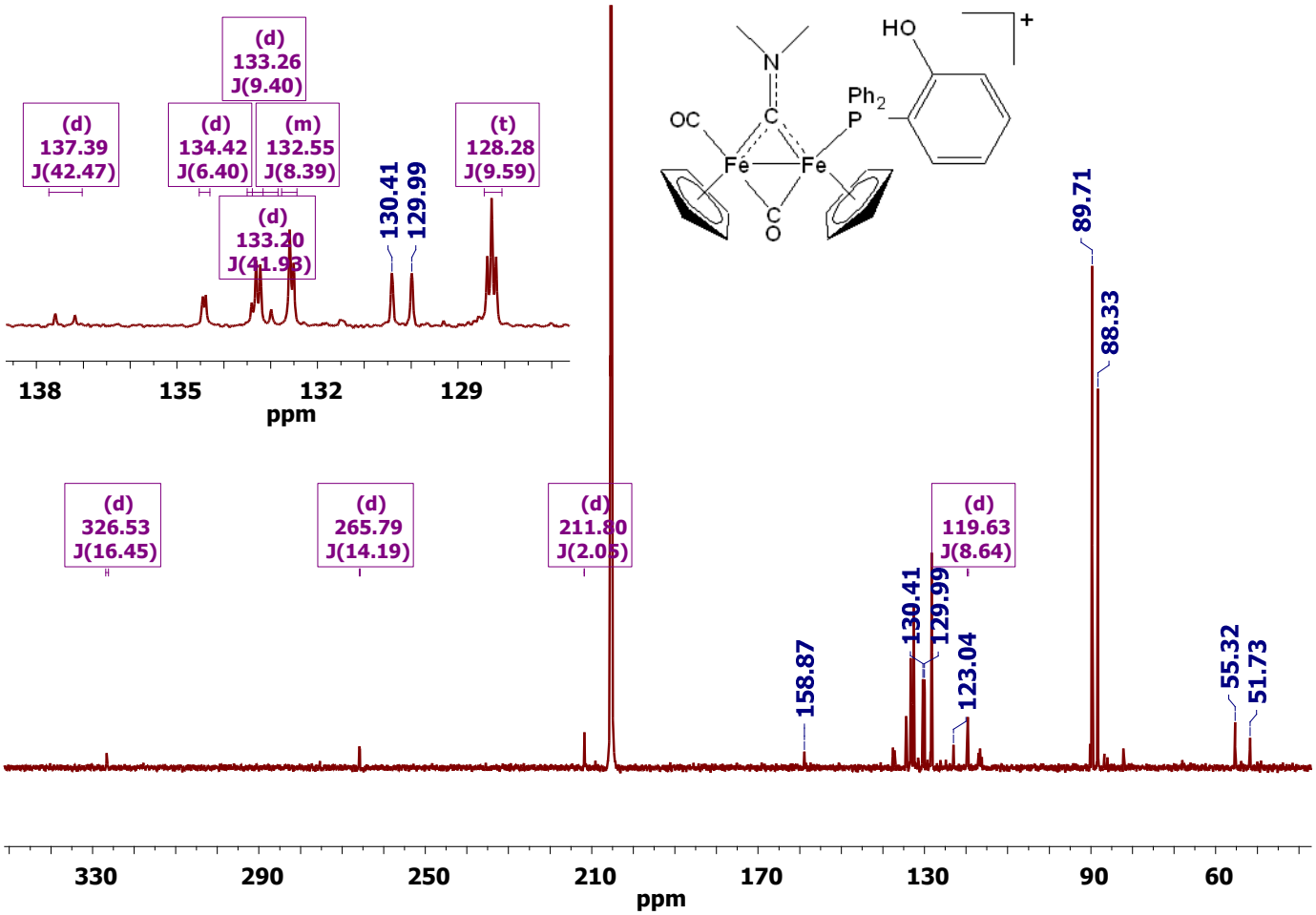


Figure S9. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, acetone-d_6) of $[Fe_2Cp_2(CO)(\mu\text{-}CO)\{\mu\text{-}\eta^1\text{:}\eta^1\text{-}CNMe_2\}\{\kappa P\text{-}Ph_2P(2\text{-}C_6H_4OH)\}]CF_3SO_3$, **11b**.

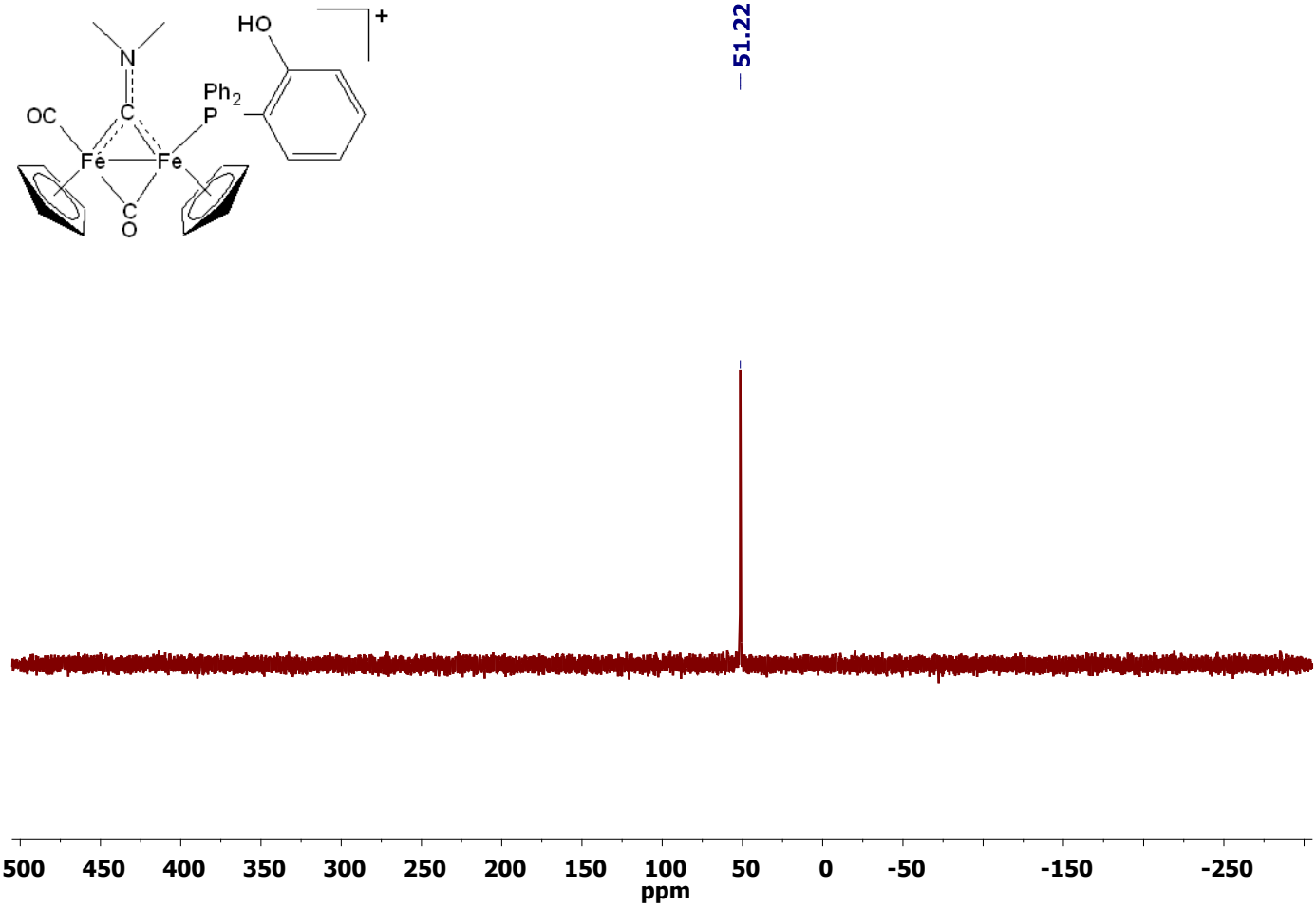
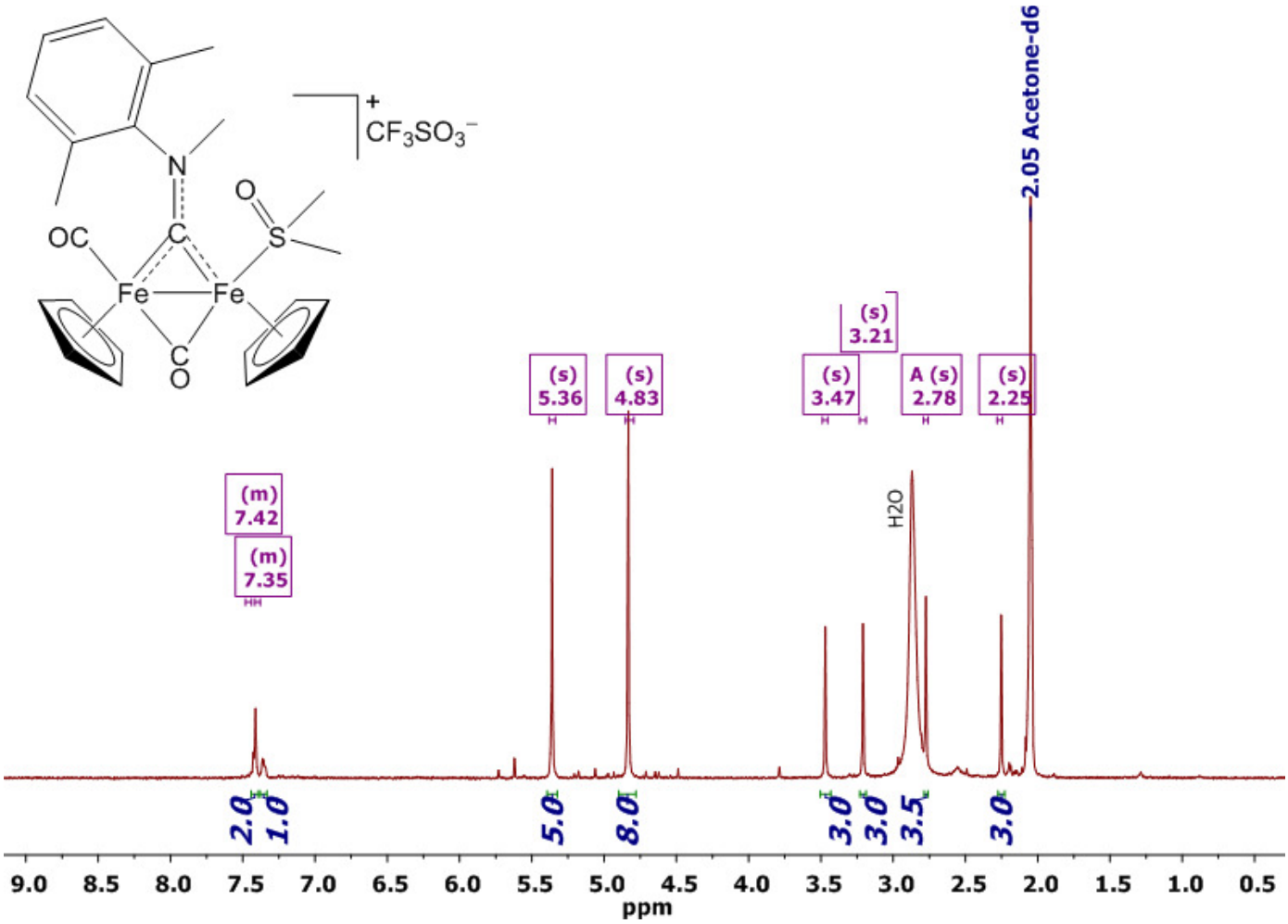


Figure S10. ^{1}H NMR spectrum (401 MHz, acetone-d_6) of $[Fe_2Cp_2(CO)(\mu\text{-}CO)\{\mu\text{-}\eta^1\text{:}\eta^1\text{-}CNMeXyl\}(\kappa S\text{-}DMSO)]CF_3SO_3$, **5b^{S}**.



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