Supplementary information

Redox Activation of Halogen-Bonding Catalysts for Organic Synthesis

Sihem Groni,[a†] Sercan Akbaba,[b†] Uchral Otgonbayar,[a] Jérémy Forté,[a] Stefan M. Huber,[c] Sitthichok Kasemthaveechok,*[a] Bernd Schöllhorn*[d] and Claire Fave*[a]

a. Sorbonne Université, CNRS, Institut Parisien de Chimie Moléculaire, IPCM, 75005 Paris, France
b. Université Paris Cité, CNRS, 75005 Paris, France
c. Fakultät für Chemie und Biochemie, Ruhr-Universität Bochum Universitätsstraβe 150, 44801 Bochum, Germany
d. ITODYS UMR 7086, Université Paris Cité, CNRS, 75013 Paris, France

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1. General Information

All manipulations unless stated otherwise were performed using Schlenk or glovebox techniques under dry argon or nitrogen atmosphere, respectively. THF was dried over Na/benzophenone, freshly distilled prior to use and stored under nitrogen atmosphere over molecular sieves (4Å). All commercial chemicals were purchased from suppliers and used as received.

NMR spectra (^{1}H and ^{13}C) were recorded on a Bruker AM 300 MHz or a Bruker AVANCE 400 MHz or a Bruker AVANCE 600 MHz spectrophotometer. Chemical shifts δ are given in ppm and coupling constants *J* in Hz. Chemical shifts for ^{1}H NMR spectra are referenced relative to residual protium in the deuterated solvent (^{1}H δ = 7.26 ppm, $CDCl_3$, δ = 5.32 ppm, CD_2Cl_2, δ = 2.50 ppm, DMSO-d_6, δ = 2.05 ppm, acetone-d_6). ^{13}C shifts are referenced to deuterated solvent (δ = 77.2 ppm for $CDCl_3$, δ = 53.8 ppm for CD_2Cl_2, δ = 39.5 ppm, DMSO-d_6, δ = 206.7 ppm, acetone-d_6). The following abbreviations are used for describing NMR spectra: s (singlet), d (doublet), t (triplet), td (triplet of doublets), ddd (doublet of doublets of doublets), vd (virtual doublet), vt (virtual triplet), br (broad). Thin-layer chromatography (TLC) was performed on aluminum sheets precoated with Merck 5735 Kieselgel 60F254. Column chromatography was carried out with Merck 5735 Kieselgel 60F (0.040-0.063 mm mesh).

High resolution mass spectra (HRMS) were obtained using a mass spectrometer MicroTOF from Bruker with an electron spray source (ESI) or an atmospheric pressure chemical ionization (APCI) source and a TOF detector at Institut Parisien de Chimie Moléculaire (FR 2769).

Electrochemical measurement: Cyclic voltammetry experiments were performed using a AUTOLAB potentiostat from Metronohm. The measurements were performed in a standard one-compartment three electrode cell containing 0.1 M solution of $TBABF_4$ in anhydrous MeCN/DCM mixture (1:1) at room temperature. Mechanically polished glassy carbon electrodes (carbon/platinum rod of 3 mm diameter, embedded in an insoluble polymer matrix) were employed as WEs for CV measurements and a platinum wire was used as the CE. A salt bridge containing the electrolyte was used to connect the electrochemical cell with a SCE.

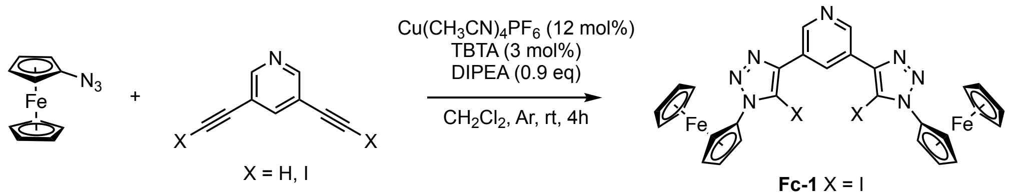
UV-vis spectroscopy experiment was measured using a Agilent Technology Cary 60 UV-Vis spectrometer; the light source used for sample irradiation during spectrophotochemistry is a LED Kessil PR160L (λmax = 390 nm, 52W).

Single crystals of each compound were selected, mounted on a cryoloop, and transferred into a cold nitrogen gas stream. Intensity data were collected on a Bruker Kappa APEX2 CCD diffractometer or a Rigaku XtaLAB Synergy diffractometer (for **(Fc-2)I**) using micro-focused Cu Kα radiation, or graphite-monochromated Mo Kα radiation (for **(Fc-2)OTf)** . Data collection, unit-cell parameter determination, integration, and data reduction were performed using the Bruker APEX/SAINT[1] software suite at 200 K, or the CrysAlisPro[2] software suite at 170 K (for **(Fc-2)I**). The structures were solved using SHELXT[3] and refined by full-matrix least-squares methods on F^2 using SHELXL[4] within the Olex2[5] software package or the WinGX[6] program suite. Non-hydrogen atoms were refined anisotropically.
The crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under deposition numbers 2536425–2536429 and can be obtained free of charge via www.ccdc.cam.ac.uk

2. Synthesis and characterization

Azidoferrocene[7] and 3,5-bis(iodoethynyl)pyridine[8] was synthesized using reported synthetic methods in literature.

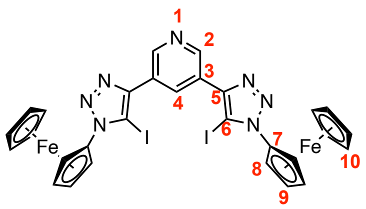
A. Synthesis procedure of Huisgen Click Addition



Fc-1 X = I
Fc-3 X = H

Synthesis was optimized according to the literature procedure.[9] In a round-bottom flask, the 3,5-diethynylpyridine (1.0 eq) and azidoferrocene (2.2 eq) was dissolved in dichloromethane (2 mL). To this solution was added a degassed dichloromethane solution (3 mL) containing $Cu(CH_3CN)_4PF_6$ (12 mol%), *N*,*N*-diisopropylethylamine (DIPEA, 0.9 eq), and tris(benzyltriazolylmethyl)amine (TBTA, 3 mol%). The reaction mixture was stirred at RT for 45 min. Upon completion, the mixture was diluted with dichloromethane (20 mL) and the organic phase was washed with 2 × 10 mL of 10% aqueous NH_3 containing 0.02 M EDTA, followed by several washes with distilled water. The product was purified by silica gel column chromatography using ethyl acetate/dichloromethane (30:70) as the eluent.

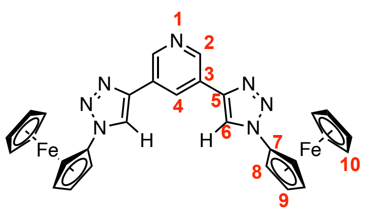
3,5-bis(1-ferrocenyl-5-iodo-1H-1,2,3-triazol-4-yl)pyridine Fc-1



Synthesis with the above procedure from 200 mg of 3,5-bis(iodoethynyl)pyridine, an orange powder was obtained in 56 % yield (231 mg).

^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 4.44 (s, 10H^{10}); 4.47 (t, ^3J(H,H) = 2.0 Hz, 4H^9); 4.90 (t, ^3J(H,H) = 1.60 Hz, 4H^8); 8.87 (t, ^4J(H,H) = 2.0 Hz, 1H^4); 9.18 (d, ^4J(H,H) = 2.0 Hz, 2H^2).
^{13}C NMR ($CDCl_3$, 101 MHz): δ (ppm) = 147.3 (s, C^5), 146.6 (s, C^2), 132.3 (s, C^4), 126.3 (s, C^3), 94.1 (s, C^7), 86.3 (s, C^6), 70.2 (s, C^{10}), 66.9 (s, C^9), 66.4 (s, C^8)
HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{29}H_{21}Fe_2I_2N_7H$ 833.8720. Found 833.8711; (Δ = -1.0 ppm).

3,5-bis(1-ferrocenyl-1H-1,2,3-triazol-4-yl)pyridine Fc-3



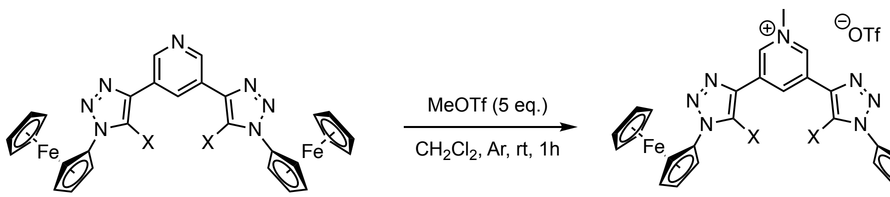
From 38 mg of 3,5-diethynylpyridine, an orange yellow powder was obtained in 70.5% yield (122 mg).

^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 4.27 (s, 10H^{10}); 4.34 (t, ^3J(H,H) = 2.0 Hz, 4H^9); 4.93 (t, ^3J(H,H) = 2.0 Hz, 4H^8); 8.18 (s, 2H^6); 8.72 (t, ^4J(H,H) = 2.0 Hz, 1H^4); 9.12 (d, ^4J(H,H) = 2.0 Hz, 2H^2).

^{13}C NMR ($CDCl_3$, 101 MHz): δ (ppm) = 146.6 (s, C-H^2), 144.5 (s, C-H^5), 130.0 (s, C-H^4), 126.8 (s, C-H^3), 120.0 (s, C-H^6), 93.6 (s, C-H^7), 70.4 (s, C-H^{10}), 67.0 (s, Cp-H^9), 62.3 (s, Cp-H^8).

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{29}H_{23}Fe_2N_7Na$ 604.0606. Found 604.0606; (Δ = 0.0 ppm).

B. General procedure for methylation of pyridine

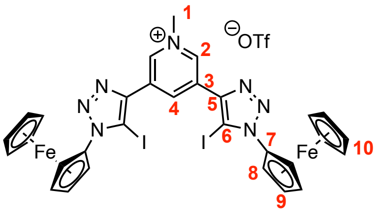


Fc-1 X = I
Fc-3 X = H

(Fc-2)OTf X = I
(Fc-4)OTf X = H

The procedure is adopted from literature.[10] Under an inert atmosphere, the ferrocene derivative (1.0 eq.) was dissolved in anhydrous dichloromethane, and alkylation agent was added. Methyl trifluoromethanesulfonate (5.0 eq.) was added. The reaction mixture was stirred at RT for 1 h. Upon formation of a fine precipitate, diethyl ether was added, and the mixture was centrifuged at 10,000 rpm and allow to precipitate at 15 °C for 30 min. The precipitate was collected.

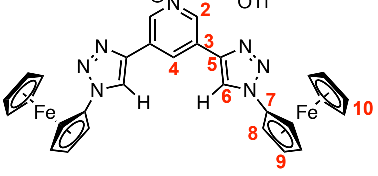
3,5-bis(1-ferrocenyl-5-iodo-1H-1,2,3-triazol-4-yl)-1-methylpyridin-1-ium trifluoromethanesulfonate (Fc-2)OTf



A red orange powder was obtained in 92 % yield.

^{1}H NMR (DMSO-d_6, 400 MHz): δ (ppm) = 4.44 (s, $10H^{10}$); 4.51 (t, ^3J(H,H) = 2.0 Hz, $4H^9$); 4.58 (s, $3H^1$) ; 4.94 (t, ^3J(H,H) = 2.0 Hz, $4H^8$); 9.58 (d, ^4J(H,H) = 1.70 Hz, $2H^2$); 9.61 (t, ^4J(H,H) = 1.70 Hz, $1H^4$).
^{13}C NMR (DMSO-d_6, 101 MHz): δ (ppm) = 143.8 (s, C^3), 142.7 (s, C^2), 137.6 (s, C^4), 130.3 (s, C^5), 93.8 (s, C^7), 88.6 (s, C^6), 70.3 (s, C^{10}), 67.2 (s, C^9), 66.2 (s, C^8), 48.8 (s, C^1).
^{19}F NMR (DMSO-d_6, 125 MHz): δ (ppm) = -78.7
HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{30}H_{24}Fe_2I_2N_7$ 847.8876. Found 847.8878; (Δ = 0.2 ppm).

3,5-bis(1-ferrocenyl-1H-1,2,3-triazol-4-yl)-1-methylpyridin-1-ium trifluoromethanesulfonate (Fc-4)OTf

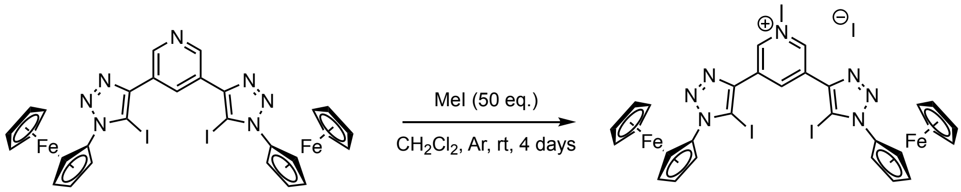


A red orange powder was obtained in 89 % yield.

^{1}H NMR (Acetone-d_6, 400 MHz): δ (ppm) = 4.29 (s, $10H^{10}$); 4.44 (t, ^3J(H,H) = 2.0 Hz, $4H^9$); 4.84 (s, $3H^1$) ; 5.14 (t, ^3J(H,H) = 2.0 Hz, $4H^8$); 9.40 (s, $2H^6$); 9.46 (t, ^4J(H,H) = 2.0 Hz, $1H^4$), 9.59 (d, ^4J(H,H) = 2.0 Hz, $2H^2$).
^{13}C NMR (Acetone-d_6, 101 MHz): δ (ppm) = 141.8 (s, C^5), 141.4 (s, C^2), 136.7 (s, C^4), 133 (s, C^3), 124.4 (s, C^6), 94.3 (s, C^7), 71.1 (s, C^{10}), 68.0 (s, C^9), 63.0 (s, C^8), 49.8 (s, C^1).

^{19}**F NMR** (Acetone-d_6, 125 MHz): δ (ppm) = -79.8
HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{30}H_{26}Fe_2N_7$ 596.0944. Found 596.0943; (Δ = -0.2 ppm).

3,5-bis(1-ferrocenyl-5-iodo-1H-1,2,3-triazol-4-yl)-1-methylpyridin-1-ium iodide (Fc-2)I



Under an inert atmosphere, 100 mg **Fc-1** (0.12 mmol) was dissolved in anhydrous dichloromethane 3 mL, and alkylation agent was added. For the alkylation with iodomethane, 370 mL (50 eq.) of the methyl iodide were added and allowed to stir for 4 days at room temperature. The precipitate was washed twice by dichloromethane and centrifuged at 10,000 rpm and stored at 15 °C for 30 min. A product was obtained as red orange powder (90 mg, 77 % yield).

^{1}**H NMR** (DMSO-d_6, 400 MHz): δ (ppm) = 4.44 (s, $10H^{10}$); 4.51 (t, $^3J(H,H)$ = 2.0 Hz, $4H^9$); 4.58 (s, $3H^1$) ; 4,94 (t, $^3J(H,H)$ = 2.0 Hz, $4H^8$); 9.58 (d, $^4J(H,H)$ = 1.70 Hz, $2H^2$), 9.62 (t, $^4J(H,H)$ = 1.70 Hz, $1H^4$).
^{13}**C NMR** (DMSO-d_6, 101 MHz): δ (ppm) = 143.8 (s, C^5), 130.3 (s, C^3), 93.9 (s, C^7), 70.3 (s, C^{10}), 64.9 (s, C^6), 67.2 (s, C^9), 66.2 (s, C^8), 48.8 (s, C^1).

3. Crystal data and X-ray structure determination process

A. Single-crystal growth conditions for X-ray analysis

- For **Fc-1**, dark orange crystals were obtained by slow evaporation of an ethyl acetate/dichloromethane solution (3:7). The samples were stored at 4 °C for less than one week to control crystal growth.
- For **(Fc-2)OTf**, red-orange crystals were obtained by slow diffusion of diethyl ether into an acetonitrile solution. The samples were stored at 4 °C for less than one week.
- For **(Fc-2)I**, dark brown crystals were obtained by slow evaporation of a DMF solution at room temperature.
- For **Fc-3**, yellow crystals were obtained at room temperature by slow evaporation of the column eluent (ethyl acetate/petroleum ether, 80:20).
- For **(Fc-4)OTf**, orange crystals were obtained by slow diffusion of diethyl ether into an acetone solution. The samples were stored at 4 °C for one week to control crystal growth.

B. Crystal structures of Fc-1, (Fc-2)OTf, (Fc-2)I, Fc-3 and (Fc-4)OTf

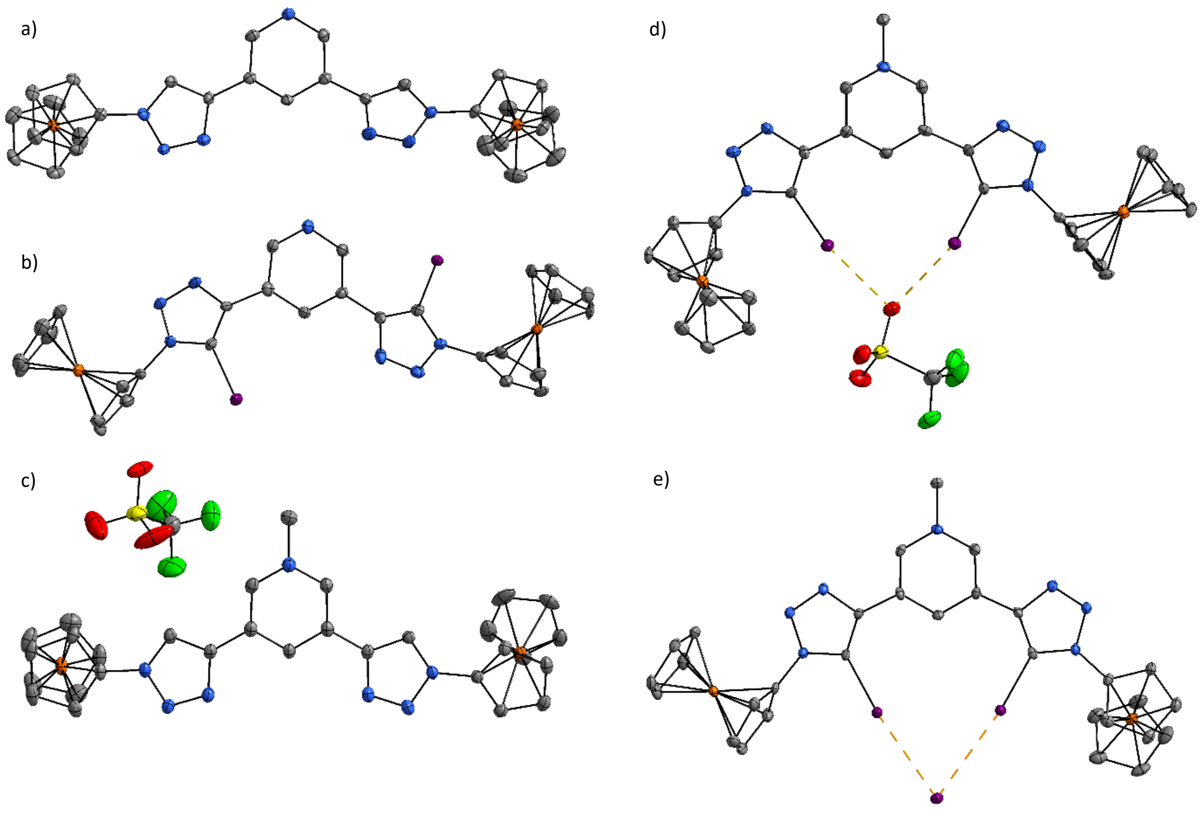


Figure S1. Crystal structures (ORTEP representations) of (a) **Fc-3**, (b) **Fc-1**, (c) **(Fc-4)OTf**, (d) **(Fc-2)OTf** and (e) **(Fc-2)I**. Thermal ellipsoids are drawn at the 30% probability level. Atom colour code: purple (I), red (O), yellow (S), green (F), orange (Fe), blue (N), and grey (C). Halogen bonding interactions in [d] and [e] are shown as orange dotted lines. Hydrogen atoms, solvent molecules (DCM for [a], acetone for [c], acetonitrile for [d] and DMF for [e]), the second molecule in the asymmetric unit of [c], and the second position of the disordered Cp group in [d] are omitted for clarity.

C. Crystal and refinement data for Fc-1, (Fc-2)OTf, (Fc-2)I, Fc-3 and (Fc-4)OTf

Table S1:

	Fc-1	**(Fc-2)OTf**	**(Fc-2)I**	**Fc-3**	**(Fc-4)OTf**
CCDC deposit number	*2536426*	*2536428*	*2536429*	*2536425*	*2536427*
Empirical formula[a]	$C_{29}H_{21}Fe_2I_2N_7$	$C_{35}H_{30}F_3Fe_2I_2N_9O_3S$	$C_{33}H_{31}N_8OFe_2I_3$	$C_{30}H_{25}Cl_2Fe_2N_7$	$C_{32.5}H_{29}N_7O_{3.5}F_3SFe_2$
Moiety Formula	$C_{29}H_{21}Fe_2I_2N_7$	$C_{30}H_{24}Fe_2I_2N_7{}^+$, $CF_3O_3S^-$, $2(C_2H_3N)$	$C_{30}H_{24}Fe_2I_2N_7{}^+$, I^-, C_3H_7NO	$C_{29}H_{23}Fe_2N_7$, CH_2Cl_2	$C_{30}H_{26}Fe_2N_7{}^+$, $CF_3O_3S^-$, $0.5(C_3H_6O)$
Formula weight (g/mol)	833.03	1079.24	1048.06	666.17	774.39
Temperature (K)	200	200	170	200	200
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	P-1
a (Å)	19.7188(10)	8.2870(5)	7.67655(14)	5.7498(3)	10.1900(2)
b (Å)	7.3791(3)	25.7120(14)	24.6328(4)	16.4645(8)	14.7294(2)
c (Å)	20.4086(12)	17.9654(10)	18.0523(3)	28.9636(12)	22.1574(3)
α (°)	90	90	90	90	79.1450(10)
β (°)	110.565(3)	98.175(2)	94.4505(15)	94.275(3)	81.1440(10)
γ (°)	90	90	90	90	82.0860(10)
Volume (Å^3)	2780.4(2)	3789.1(4)	3403.32(10)	2734.3(2)	3206.91(9)
Z	4	4	4	4	4
ρ_{calc} (g/cm^3)	1.990	1.892	2.045	1.618	1.604
Absorption coefficient μ (mm^{-1})	26.073 (CuKα)	2.515 (MoKα)	28.534 (CuKα)	10.592 (CuKα)	8.442 (CuKα)
F(000)	1608	2112	2016	1360	1584
Crystal size (mm²)	0.21 × 0.04 × 0.04	0.26 × 0.04 × 0.04	0.09 × 0.02 × 0.01	0.18 × 0.03 × 0.02	0.15 × 0.09 × 0.04
Wavelength λ (Å)	1.54178	0.71073	1.54178	1.54178	1.54178
2Θ range (°)	4.786 - 124.998	4.582 - 50.09	6.082 - 132.946	6.12 - 125.468	6.148 - 133.19
Miller indexes ranges	-22 ≤ h ≤ 22, -8 ≤ k ≤ 8, -23 ≤ l ≤ 23	-9 ≤ h ≤ 9, -30 ≤ k ≤ 30, -21 ≤ l ≤ 21	-9 ≤ h ≤ 9, -29 ≤ k ≤ 28, -20 ≤ l ≤ 21	-6 ≤ h ≤ 6, -18 ≤ k ≤ 18, -30 ≤ l ≤ 33	-10 ≤ h ≤ 12, -17 ≤ k ≤ 17, -26 ≤ l ≤ 26
Measured reflections	23543	34719	21204	21021	42765
Unique reflections	4434	6699	5981	4354	11327
R_{int} / R_{sigma}	0.1193 / 0.0793	0.1091 / 0.0915	0.0573 / 0.0505	0.1452 / 0.1032	0.0666 / 0.0621
Reflections [I ≥ 2σ(I)]	3152	4129	5203	2917	8947
Restraints	60	171	0	30	53
Parameters	361	544	427	388	887
Goodness-of-fit F²	0.973	1.004	1.028	1.006	1.032
Final R indexes[b c] **[all data]**	R_1 = 0.0832, wR_2 = 0.1272	R_1 = 0.1020, wR_2 = 0.0937	R_1 = 0.0449, wR_2 = 0.1099	R_1 = 0.1051, wR_2 = 0.1616	R_1 = 0.0733, wR_2 = 0.1563
Final R indexes[b c] **[I ≥ 2σ(I)]**	R_1 = 0.0526, wR_2 = 0.1178	R_1 = 0.0449, wR_2 = 0.0769	R_1 = 0.0386, wR_2 = 0.1058	R_1 = 0.0621, wR_2 = 0.1394	R_1 = 0.0566, wR_2 = 0.1442
Largest diff. peak/hole (e/Å^3)	2.20 / -0.94	0.79 / -0.57	1.16 / -0.82	0.56 / -0.71	0.99 / -0.95

[a] Including solvent molecules (if presence)

[b] $R1 = \sum \big||F_o| - |F_c|\big| / \sum |F_o|$

[c] $wR2 = \sqrt{\sum\left(w(F_o^2 - F_c^2)\right)/\sum\left(w(F_o^2)^2\right)}$

4. Steady-state physical characterizations

A. Neutral state characterization

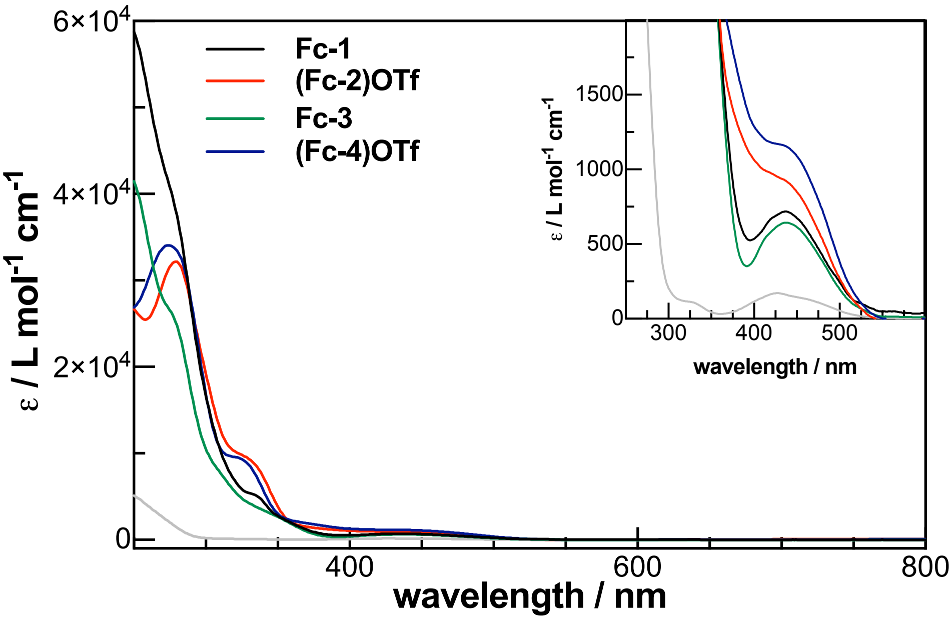


Figure S2. UV-vis spectra of compound **Fc-1** (black), **(Fc-2)OTf** (red), **Fc-3** (green), **(Fc-4)OTf** (blue), and Ferrocene (grey) in 1:1 dichloromethane/acetonitrile (ca. 10^{-5} M) at 298 K.

Table S2: UV-Vis characterization of Fc derivatives in 1:1 dichloromethane/acetonitrile (ca. 10^{-5} M) at 298 K.

Compound	λ_{max} [a]	ε [b]
Fc	427	170
Fc-1	437	718
Fc-2⁺	436	1157
Fc-3	437	635
Fc-4⁺	441	900

[a] = nm ; [b] = L mol^{-1} cm^{-1}

Table S3: Redox potential of Fc derivatives

Compound	E_p^1 (C-I) [a]	E_p^2 (N^+) [a]	E_p^3 (Fc->Fc^+) [a]	D [b]
Fc	-	-	0.53	-
Fc-1	-1.40	-	0.70	3.62 x 10^{-5}
$Fc\text{-}2^+$	-1.55	-1.09	0.75	2.52 x 10^{-5}
Fc-3	-	-	0.68	2.92 x 10^{-5}
$Fc\text{-}4^+$	-	-1.07	0.72	3.86 x 10^{-5}

[a] = V vs SCE; [b] = cm^2 s^{-1}

B. Ferrocenium state characterization

Table S4: UV-Vis characterization of ferrocenium derivatives in in 1:1 dichloromethane/acetonitrile (ca. 10^{-5} M) at 298 K in presence of 1.2 equiv of $NOBF_4$ (per ferrocene).

Compound	λ max [a]	ε [b]	$t_{1/2}$ [c]
Fc^+	617	641	-
$Fc\text{-}1^{2+}$	642	1341	15
$(Fc\text{-}2)^{3+}$	642	1421	200
$Fc\text{-}3^{2+}$	690	851	8
$(Fc\text{-}4)^{3+}$	688	984	6.7

[a] = nm ; [b] = L mol^{-1} cm^{-1}; [c] = min

C. Half-lives determination

All ferrocenium species were prepared by oxidation with $NOBF_4$ (2.2 eq per ferrocene). The kinetic stabilities of the cationic ferrocenium were followed by UV-vis measurement under Ar.

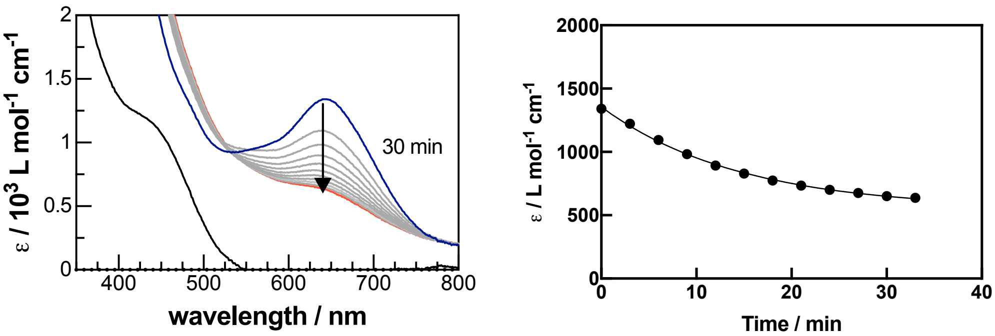


Figure S3. Left) Time-dependent UV-vis absorption spectra of **$Fc\text{-}1^{2+}\cdot 2BF_4^-$** in 1:1 dichloromethane/acetonitrile under Ar at 298 K (blue trace). For comparison UV spectrum of **Fc-1** has been added (black curve). **Right**) Exponential decay fitting plot as a function of time at 642 nm.

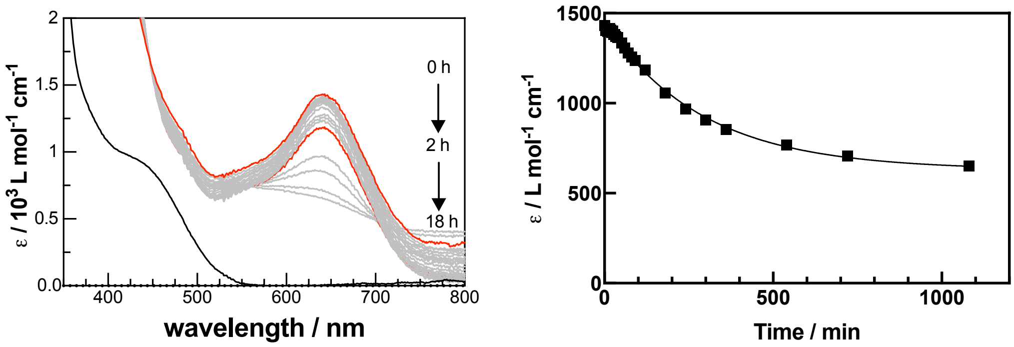


Figure S4. Left) Time-dependent UV-vis absorption spectra of **$(Fc\text{-}2)^{3+}\cdot 2BF_4^- OTf^-$** in 1:1 dichloromethane /acetonitrile under Ar at 298 K (blue trace). For comparison UV spectrum of **$Fc\text{-}2^+$** has been added (black curve).. **Right**) Exponential decay fitting plot as a function of time at 642 nm.

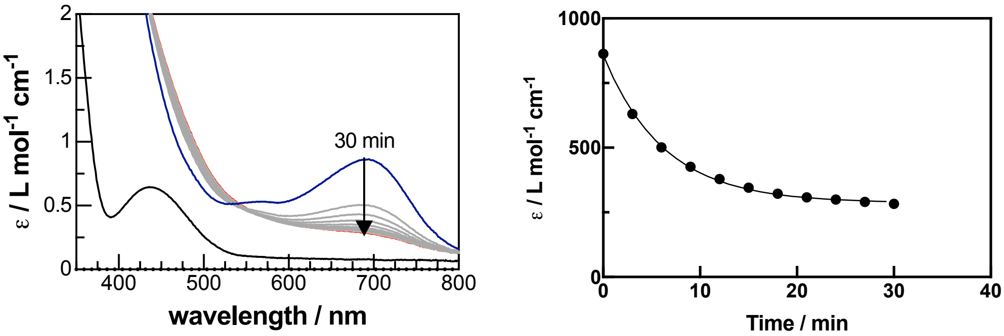


Figure S5. Left) Time-dependent UV-vis absorption spectra of **Fc-3^{2+}·2BF$_4^-$** in 1:1 dichloromethane/acetonitrile under Ar at 298 K (blue trace). For comparison UV spectrum of **Fc-3** has been added (black curve). **Right**) Exponential decay fitting plot as a function of time at 690 nm.

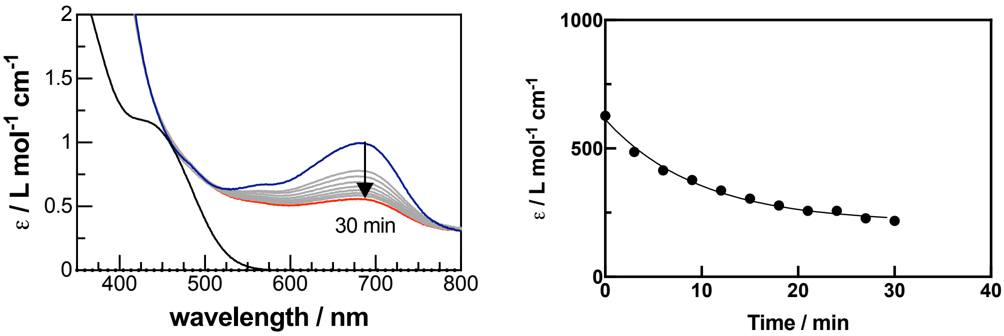


Figure S6. Left) Time-dependent UV-vis absorption spectra of **(Fc-4)$^{3+}$·2BF$_4^-$OTf$^-$** in 1:1 dichloromethane /acetonitrile under Ar at 298 K (blue trace). For comparison UV spectrum of **Fc-4$^+$** has been added (black curve).. **Right**) Exponential decay fitting plot as a function of time at 688 nm.

5. Electrochemical Characterization

A. Fc derivatives in solution

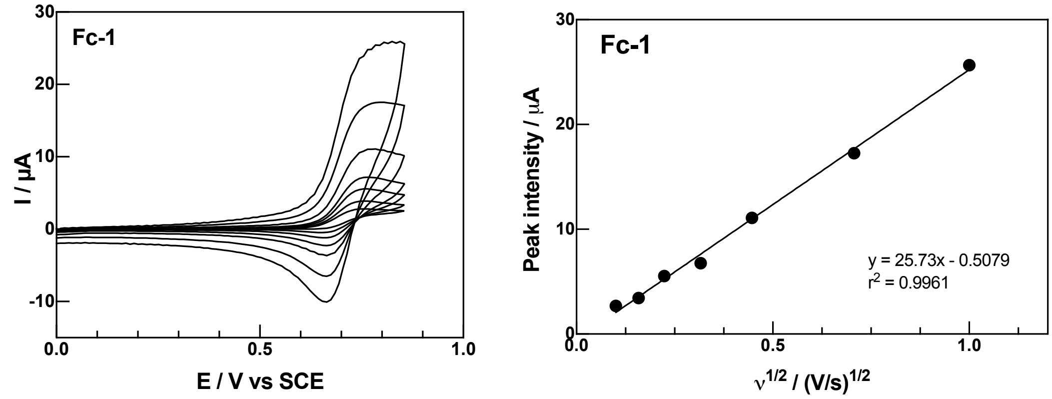


Figure S7. **Left)** CVs of compound **Fc-1** (c = 0.25 mM) in a solution of 0.1M TBABF$_4$ CH_2Cl_2/ACN (1/1) at various scan rate from 25 mV.s^{-1} to 1 V.s^{-1}; **Right)** Plot of the peak current versus the square root of the scan rate. Right) WE = GC electrode, RE = SCE.

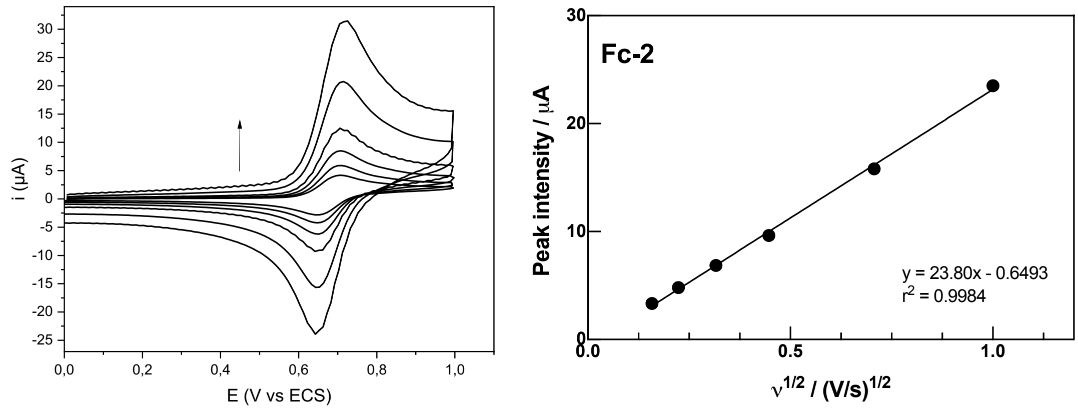


Figure S8. **Left)** CVs of compound **Fc-2** (c = 0.25 mM) in a solution of 0.1M TBABF$_4$ CH$_2$Cl$_2$/ACN (1/1) at various scan rate from 25 mV.s^{-1} to 1 V.s^{-1}; **Right)** Plot of the peak current versus the square root of the scan rate. Right) WE = GC electrode, RE = SCE.

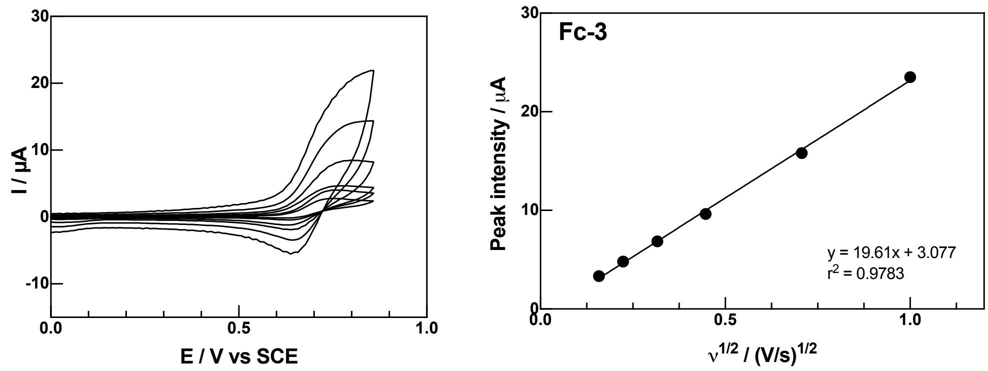


Figure S9. **Left)** CVs of compound **Fc-3** (c = 0.25 mM) in a solution of 0.1M TBABF$_4$ CH$_2$Cl$_2$/ACN (1/1) at various scan rate from 25 mV.s^{-1} to 1 V.s^{-1}; **Right)** Plot of the peak current versus the square root of the scan rate. Right) WE = GC electrode, RE = SCE.

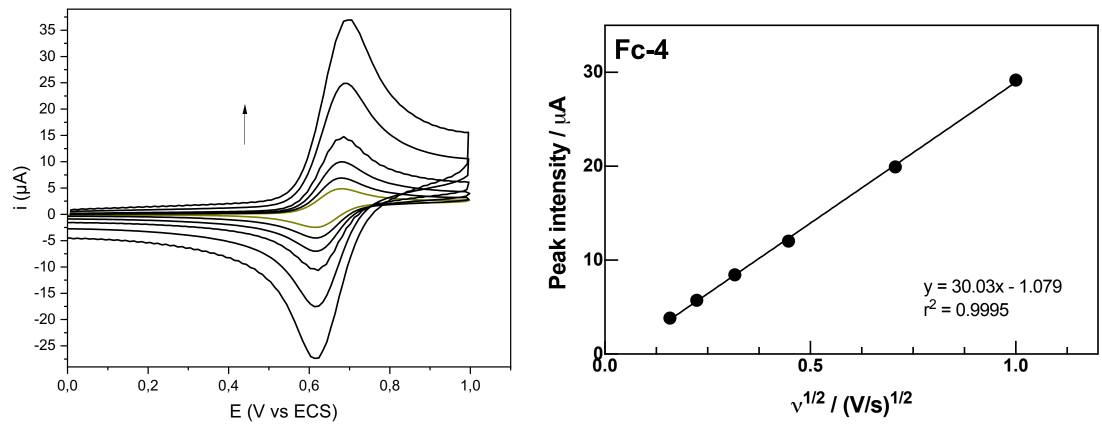


Figure S10. **Left)** CVs of compound **Fc-4** (c = 0.25 mM) in a solution of 0.1M TBAPF$_6$ CH$_2$Cl$_2$/ACN (1/1) at various scan rate from 25 mV.s^{-1} to 1 V.s^{-1}; **Right)** Plot of the peak current versus the square root of the scan rate. WE = GC electrode, RE = SCE.

B. Fc derivatives in solution in presence of various LB

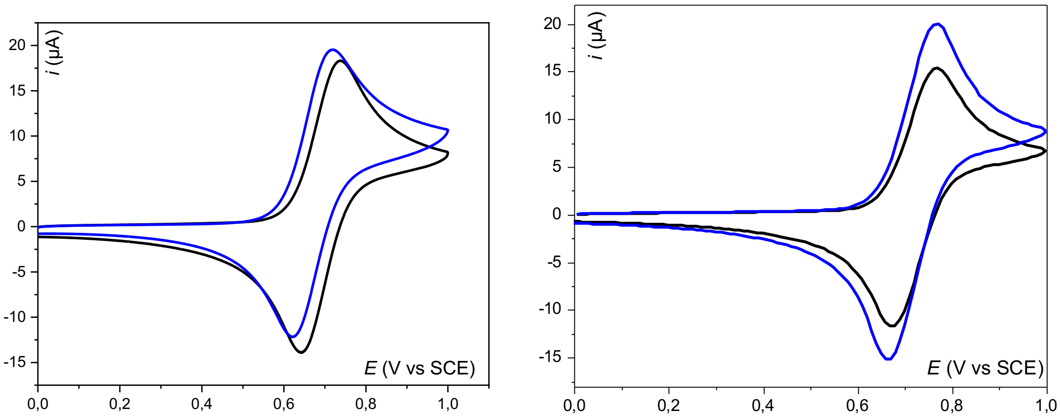


Figure S11. CV of compound **Fc-1** (C = 0.5 mM) in a solution of 0.1M $TBAPF_6$ / dichloromethane, ν = 100 mV/s, WE = GC electrode, RE = SCE. **left**) without (black trace) and with 5 equiv of TBACl (blue trace); **right**) without (black trace) and with 5 equiv of TBAOTf (blue trace).

C. Fc derivatives in solution in presence of the substrates

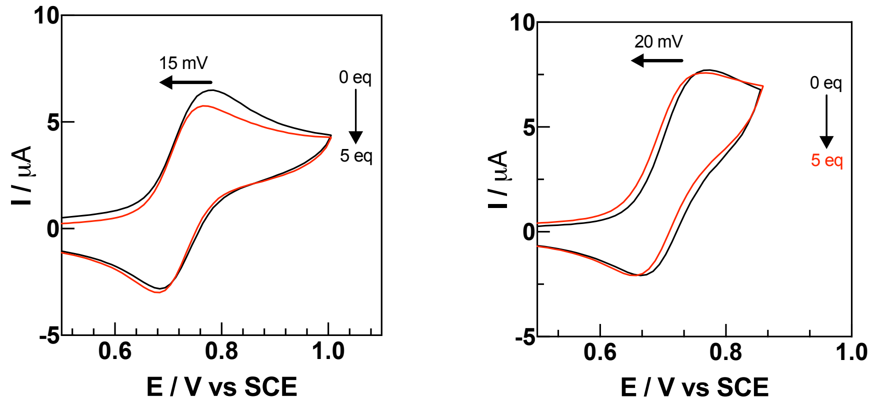


Figure S12. CV of compound **Fc-1** (c = 0.25 mM) in a solution of 0.1M $TBABF_4$ / 1:1 dichloromethane/acetonitrile, ν = 100 mV/s, WE = GC electrode, RE = SCE). **left**) without (black trace) and with 5 equiv of benzyhydril chloride (red trace); **right**) without (black trace) and with 5 equiv of benzyhydril bromide (red trace).

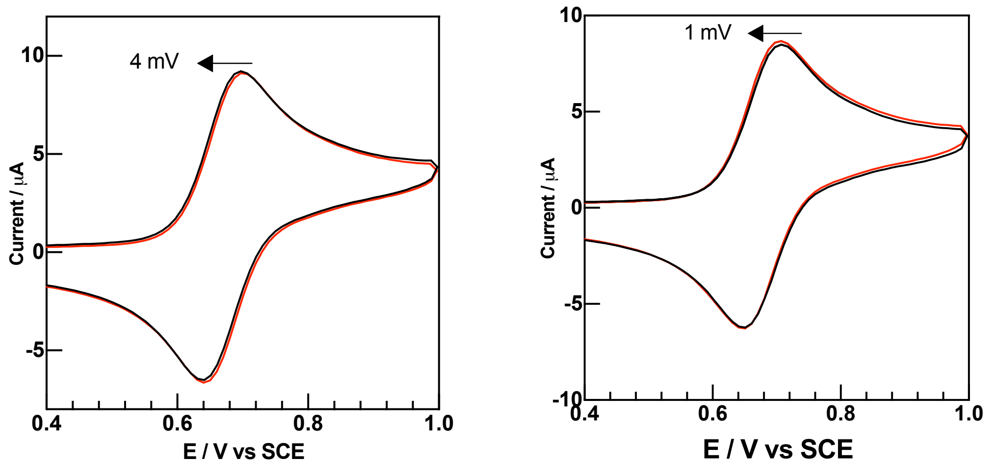


Figure S13. CV of compound **Fc-2** (c = 0.25 mM) in a solution of 0.1M $TBABF_4$ / 1:1 dichloromethane/acetonitrile, ν = 100 mV/s, WE = GC electrode, RE = SCE). **left**) without (black trace) and with 5 equiv of benzyhydril chloride (red trace); **right**) without (black trace) and with 5 equiv of benzyhydril bromide (red trace).

6. Activation of XB donor for Freidel-Craft Alkylation

A. General Procedure for stoichiometric condition

A solution of XB donor (8.33 mM in solvent) was added to $NOBF_4$ (2.2 eq) under argon and store for 5 minutes. Then, this solution was transfer to an NMR tube containing a solution of benzyhydril halide (0.005 mmol), 1,3,5-trimethoxymethane (0.005 mmol), *t*-amyl methyl ether (0.005 mmol) and cesium carbonate (0.010 mmol) in solvent (0.1 mL). The resulting mixture was shaken manually for 5 min before being monitored by ^{1}H NMR. The ^{1}H NMR yields were calculated using the following formula:

yield (%) = 100% • [ν (product) / ν (standard)] • n • N, where [ν (product) / ν (standard)] is the integral ratio of the corresponding ^{1}H NMR peaks, n is the ratio of the standard to starting material (in mol) and N +
is the ratio of the number of protons of the standard to the number of protons of the starting material.

B. General Procedure for catalysis

A solution of XB donor (x mM in 500 μL 1:1 CD_2Cl_2/CD_3CN) was added to $NOBF_4$ (2.2 eq) under argon and store for 5 minutes. Then, this solution was transfer to an NMR tube containing a solution of benzyhydril chloride (0.005 mmol), 1,3,5-trimethoxymethane (0.005 mmol), *t*-amyl methyl ether (0.005 mmol) and cesium carbonate (0.010 mmol) in solvent (0.1 mL). The resulting mixture was shaken manually for 5 min before being monitored by ^{1}H NMR. The ^{1}H NMR yields were calculated using the following formula:

yield (%) = 100% • [ν (product) / ν (standard)] • n • N, where [ν (product) / ν (standard)] is the integral ratio of the corresponding ^{1}H NMR peaks, n is the ratio of the standard to starting material (in mol) and N is the ratio of the number of protons of the standard to the number of protons of the starting material.

C. Procedure for substrate concentration

A solution of XB donor (8.33 mM in 0.5 mL 1:1 CD_2Cl_2/CD_3CN) was added to $NOBF_4$ (2.2 eq) under argon and store for 5 minutes. Then, this solution was transfer to an NMR tube containing a solution of benzyhydril chloride (x mmol), 1,3,5-trimethoxymethane (0.005 mmol), *t*-amyl methyl ether (0.005 mmol) and cesium carbonate (0.010 mmol) in solvent (0.1 mL). The resulting mixture was shaken manually for 5 min before being monitored by ^{1}H NMR. The ^{1}H NMR yields were calculated using the following formula:

yield (%) = 100% • [ν (product) / ν (standard)] • n • N, where [ν (product) / ν (standard)] is the integral ratio of the corresponding ^{1}H NMR peaks, n is the ratio of the standard to starting material (in mol) and N is the ratio of the number of protons of the standard to the number of protons of the starting material.

7. Reproducibility experiment

The reproducibility of the experiments with BHC and the freshly generated XB donor (**Fc-2)$^{3+}$** in a 1:1 mixture of CD_2Cl_2/CD_3CN (**Figure S14**). The experiments were repeated 4 times and similar results were obtained with a standard deviation of solely 1.25 % for the average final yield of 63.25 % (**Table S5**). However, with regards to the kinetic curves, significant differences in the initial reaction rate v_{ini} could be identified. The values were compared relative to the experiment that exhibited the highest exponential growth (**Figure S14**, black curve). By determining the initial slope within the 0-2 h time interval and with the fastest kinetic curve normalized v_{rel}, the lowest v_{rel} was calculated to be 0.75. Despite the differences in v_{ini} the reaction was regarded to be reproducible, due to the overall high similarity of the yields after 24 h and overall the curve´s progression.

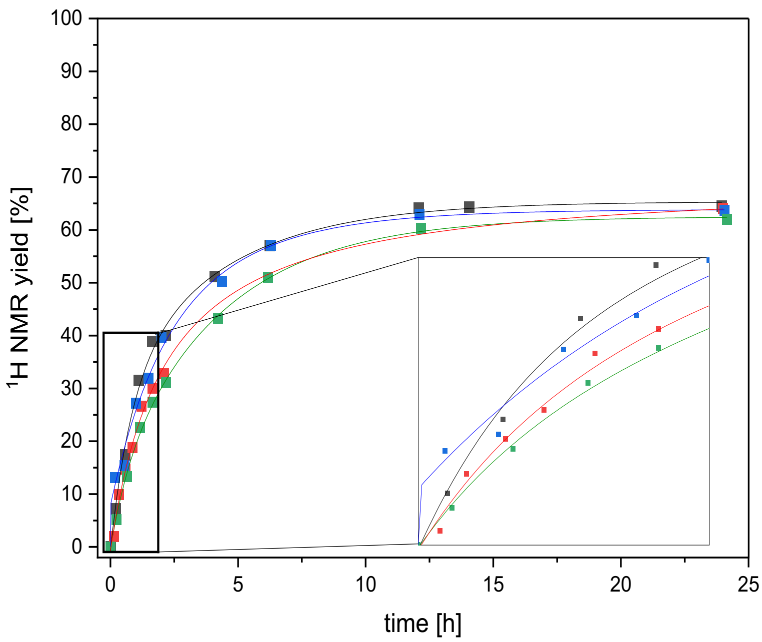


Figure S14. Time-yield plot of the TMPMDB between BHC and TMB using **(I-Fc)$_2$Py^{2+}(BF$_4^-$)$_2$** as activator species, obtained in 1:1 CD_2Cl_2/CD_3CN over 4 separate experiments.

Table S5. Friedel-Crafts reaction yields after 24 h of 4 experiments at the same reaction conditions. (stoichiometric reaction cond.: **(Fc-2)$^{3+}$**, BHC, TMB, Cs_2CO_3 in CD_2Cl_2/CD_3CN; c = 8.33 mM; rt).
[a] = in % determined via ^{1}H NMR spectroscopy; [b] = mol/s.

Entry	NMR Yield after 24 h [a]	v_{ini} [b]	v_{rel}
1	64.5	$2.80 \cdot 10^{-10}$	1.00
2	64.1	$2.60 \cdot 10^{-10}$	0.93
3	63.7	$2.31 \cdot 10^{-10}$	0.82
4	62.0	$2.10 \cdot 10^{-10}$	0.75
average	63.25 ± 1.25	$2.45 \cdot 10^{-10}$	-

8. UV-vis analysis in the presence of substrate

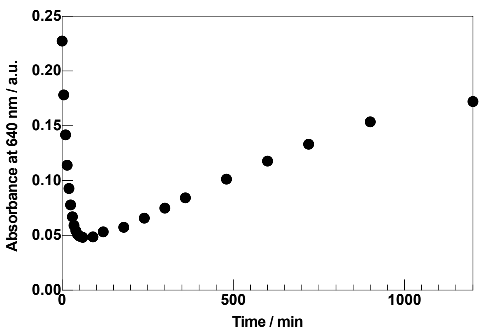


Figure S15. UV-vis absorbance at 640 nm over time of the reaction mixture at 10 mol% **Fc-2**$^{3+}$ in the presence of 8.33 mM **2** and **4.**

9. NMR spectra

A. NMR spectra of Fc-1

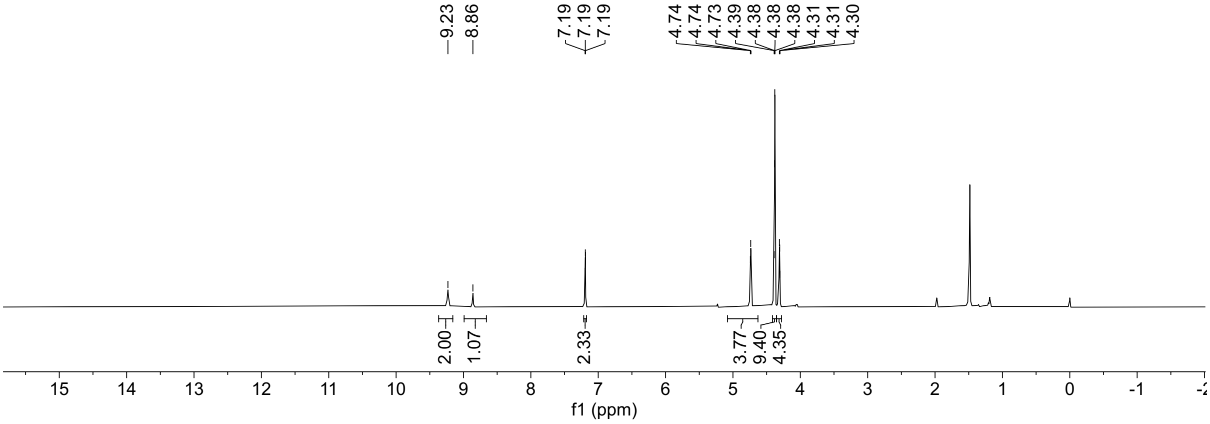


Figure S16. [1]H NMR spectrum of **Fc-1** in $CDCl_3$ at 298K (400 MHz)

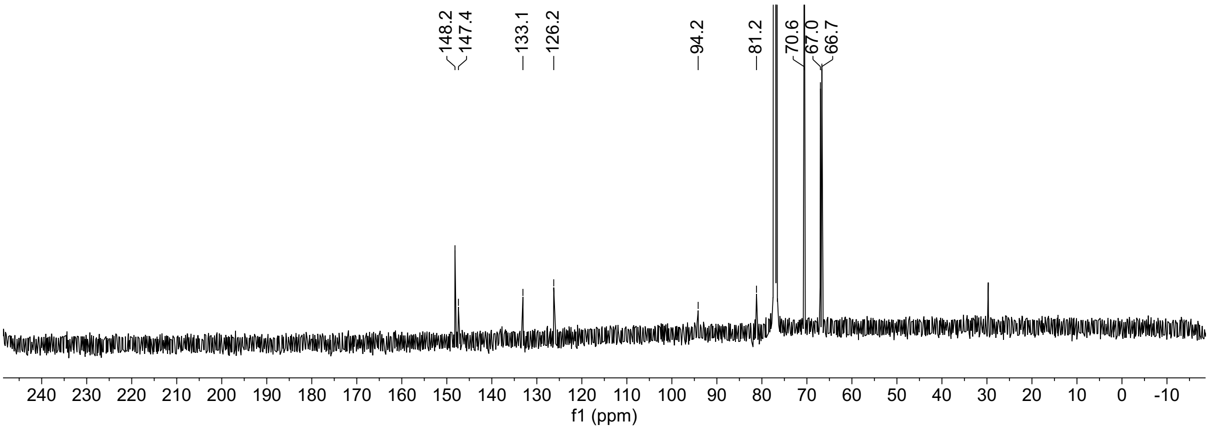


Figure S17. [13]C NMR spectrum of **Fc-1** in DMSO at 298K (101 MHz)

B. NMR spectra of (Fc-2)OTf

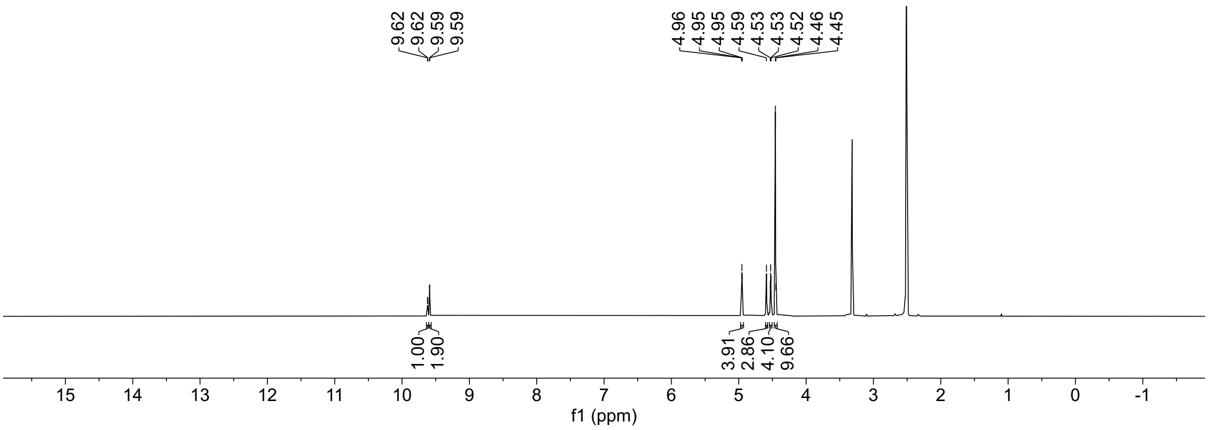


Figure S18. [1]H NMR spectrum of **(Fc-2)OTf** in DMSO at 298K (400 MHz)

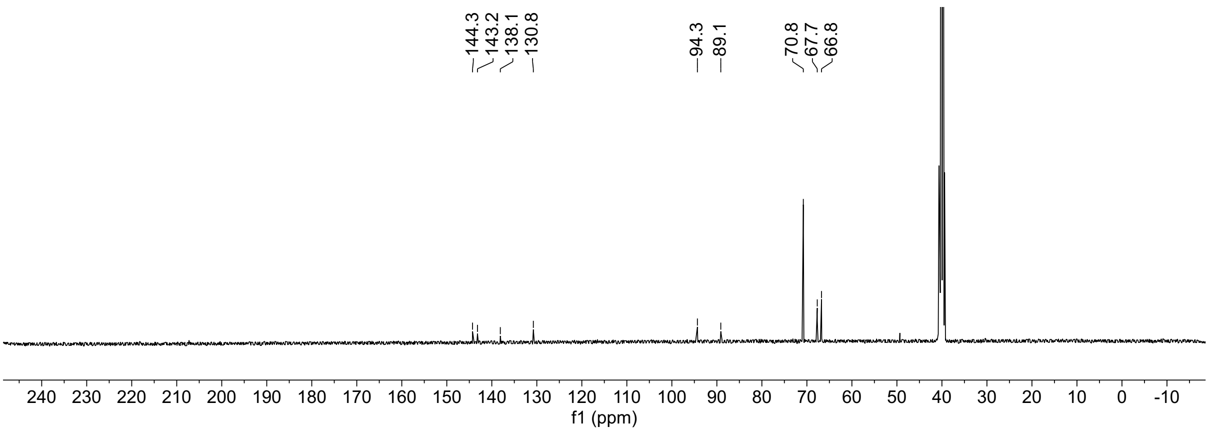


Figure S19. [13]C NMR spectrum of **(Fc-2)OTf** in DMSO at 298K (400 MHz)

C. NMR spectra of Fc-3

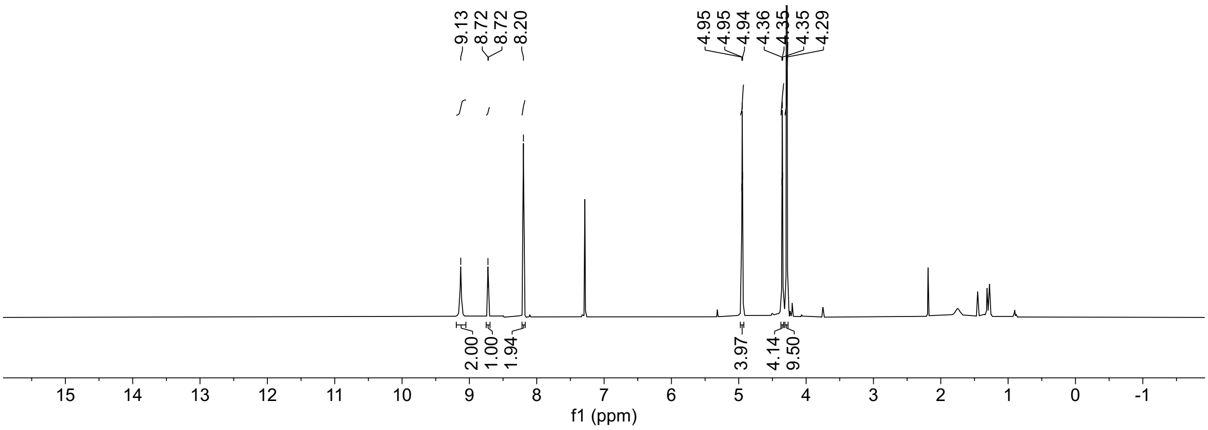


Figure S20. [1]H NMR spectrum of **Fc-3** in $CDCl_3$ at 298K (400 MHz)

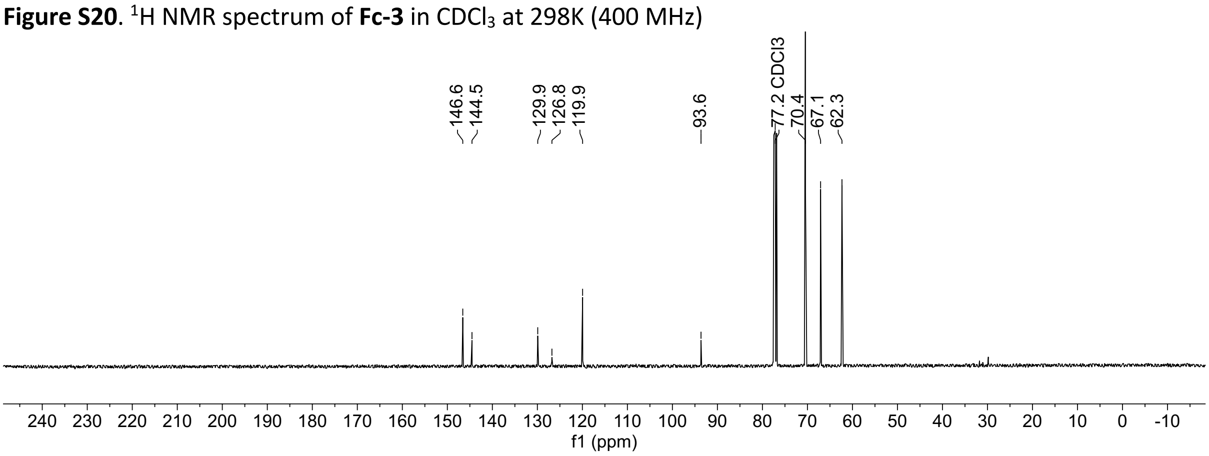


Figure S21. [13]C NMR spectrum of **Fc-3** in $CDCl_3$ at 298K (400 MHz)

D. NMR spectra of (Fc-4)OTf

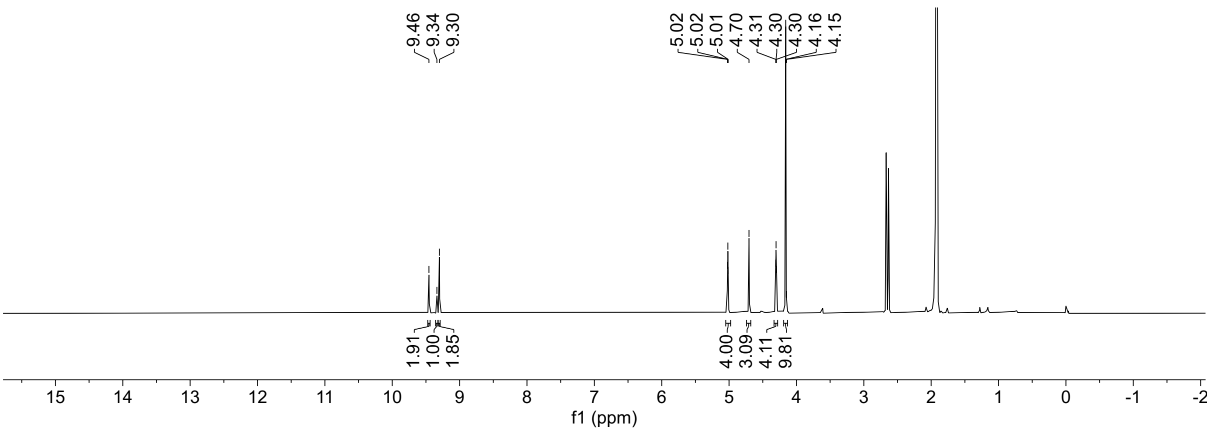


Figure S22. ^{1}H NMR spectrum of **(Fc-4)OTf** in acetone at 298K (400 MHz)

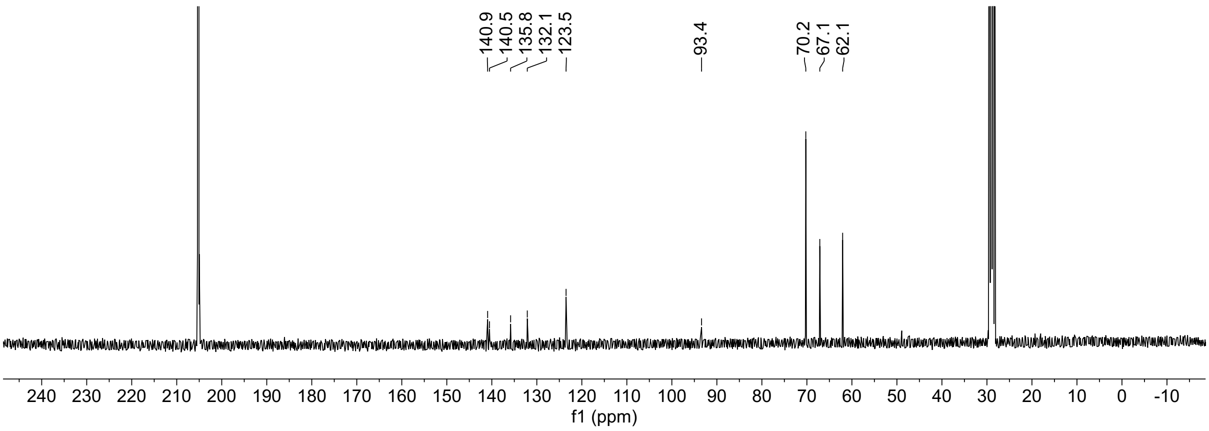


Figure S23. ^{13}C NMR spectrum of **(Fc-4)OTf** in acetone at 298K (400 MHz)

E. NMR spectra of (Fc-2)I

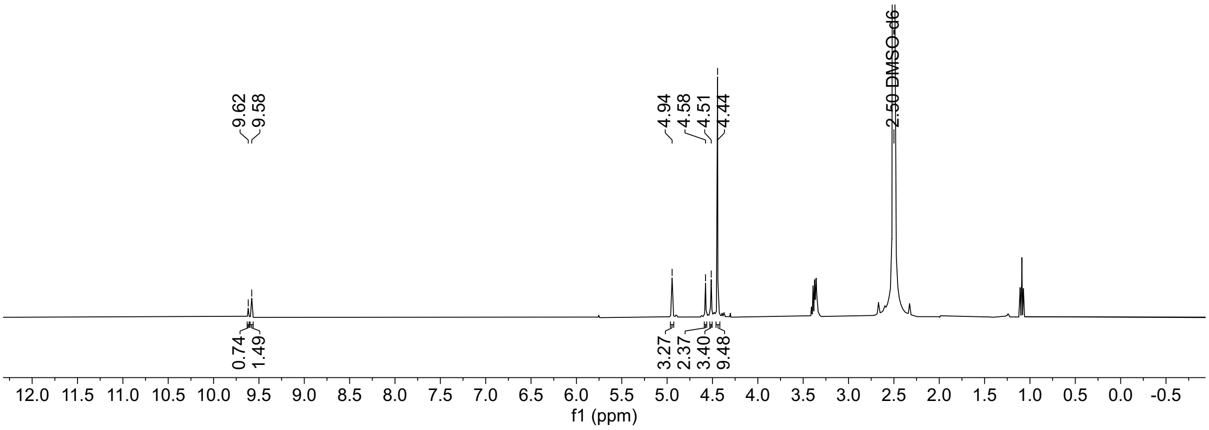


Figure S24. ^{1}H NMR spectrum of **(Fc-2)I** in DMSO at 298K (400 MHz)

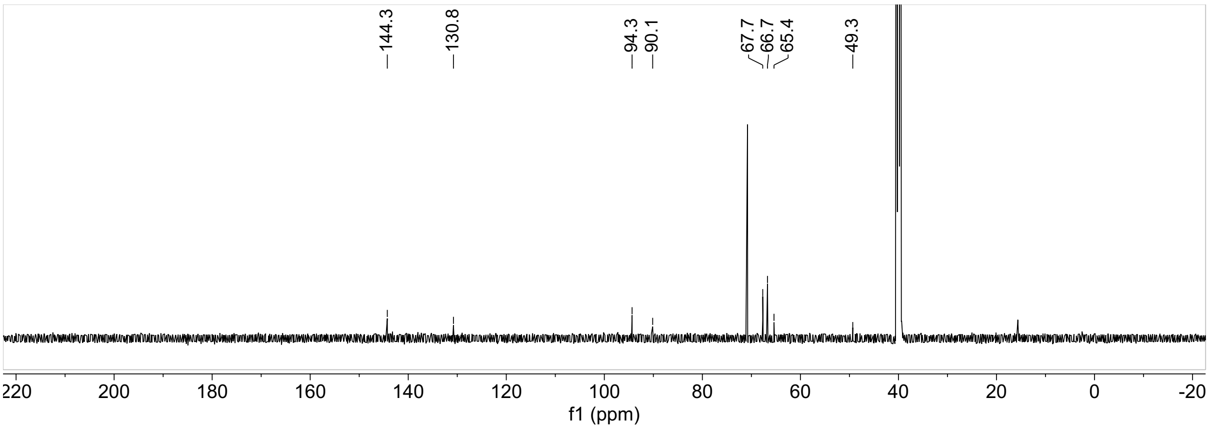
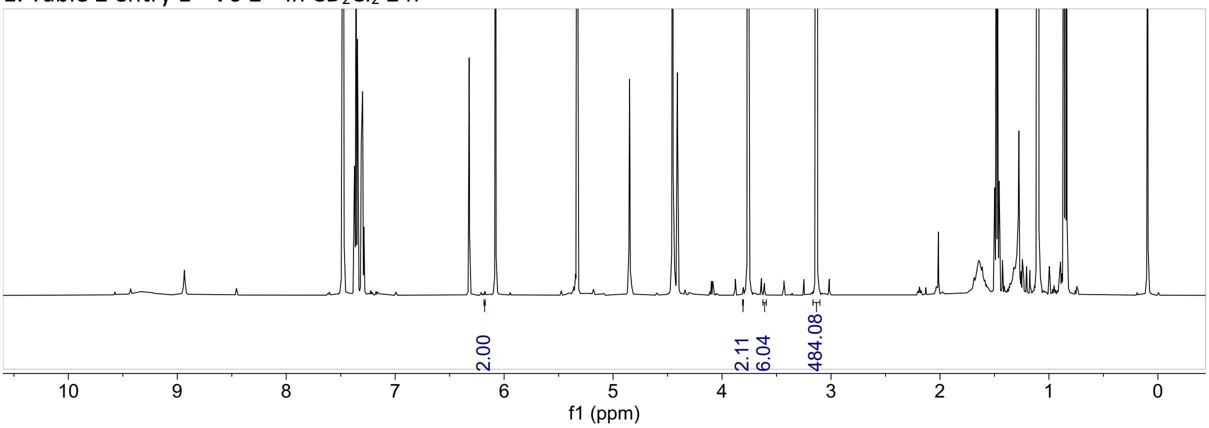


Figure S25. ^{13}C NMR spectrum of **(Fc-2)I** in DMSO at 298K (400 MHz)

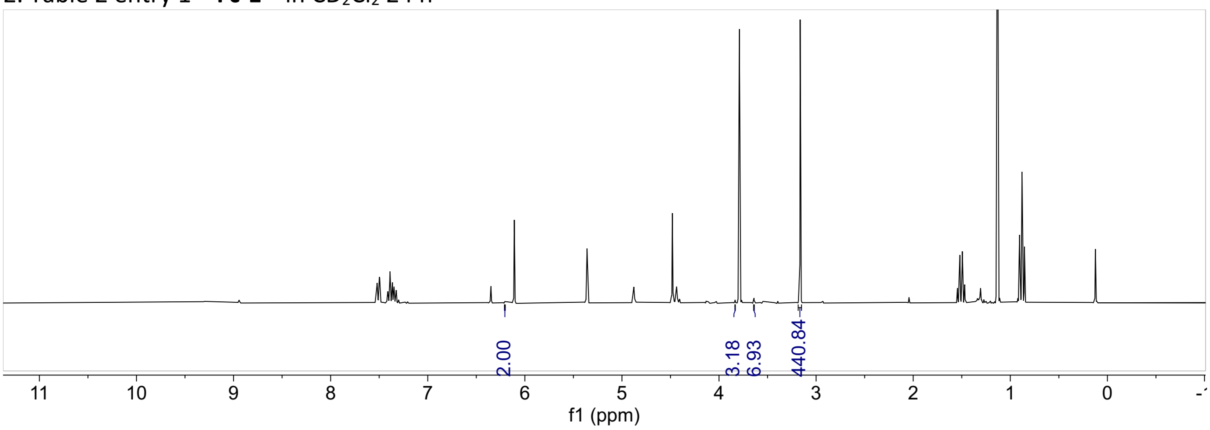
10. NMR spectra of catalysis experiment

A. Reactivity with BHB – stoichiometric condition

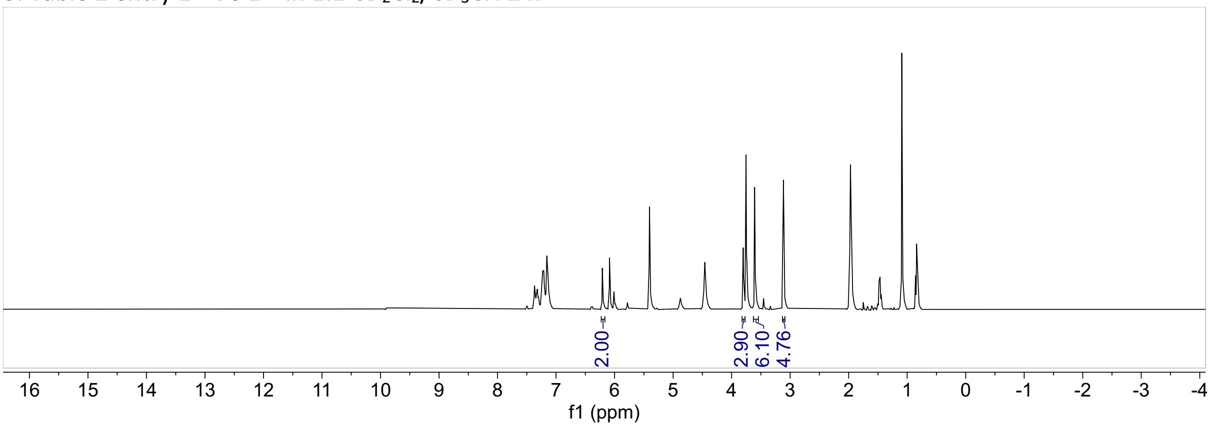
1. Table 2 entry 1 – **Fc-1^{2+}** in CD_2Cl_2 2 h



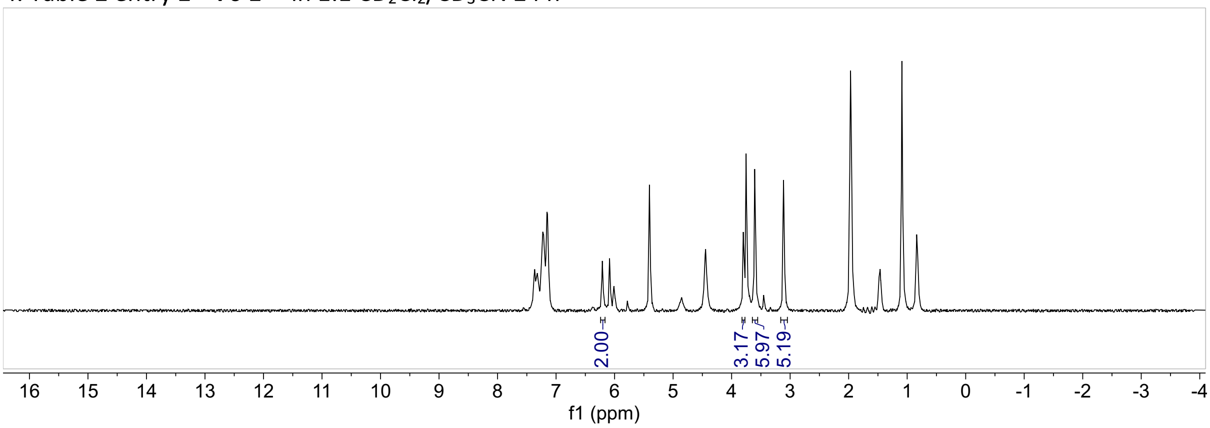
2. Table 2 entry 1 – **Fc-1^{2+}** in CD_2Cl_2 24 h



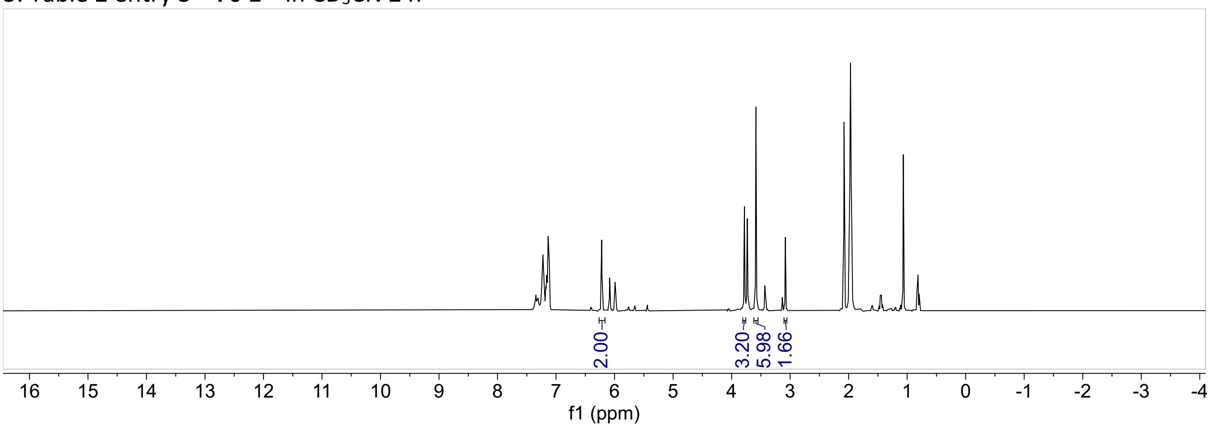
3. Table 2 entry 2 – **Fc-1^{2+}** in 1:1 CD_2Cl_2/CD_3CN 2 h



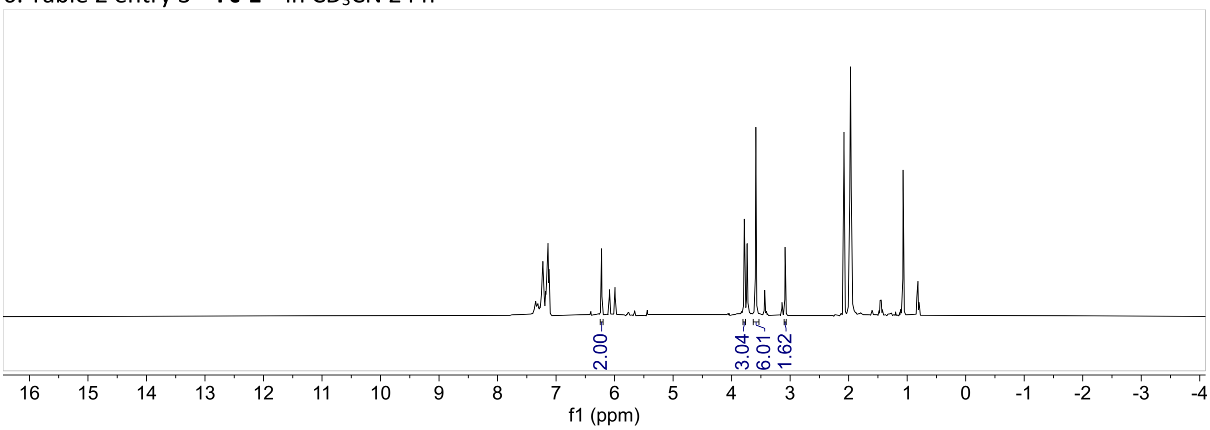
4. Table 2 entry 2 – **Fc-1^{2+}** in 1:1 CD_2Cl_2/CD_3CN 24 h



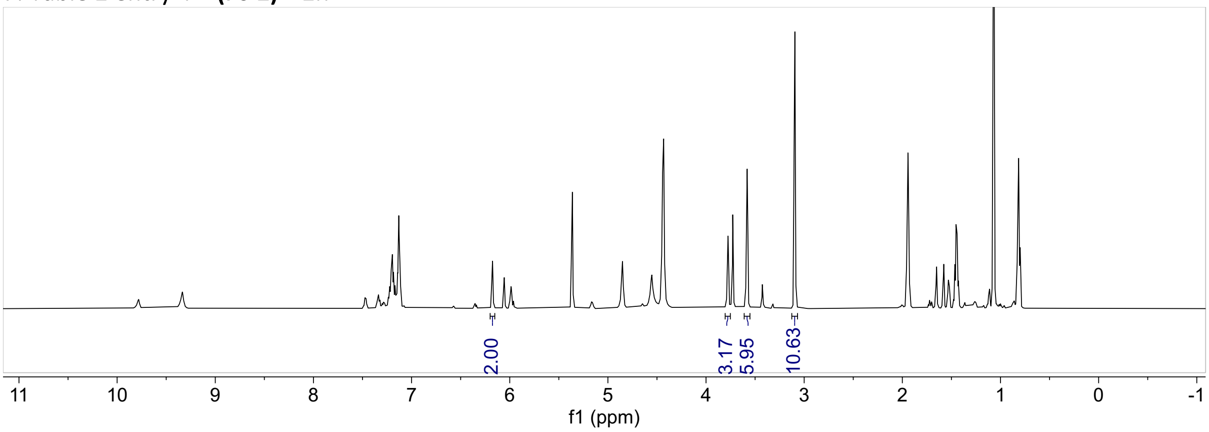
5. Table 2 entry 3 – **Fc-1^{2+}** in CD_3CN 2 h



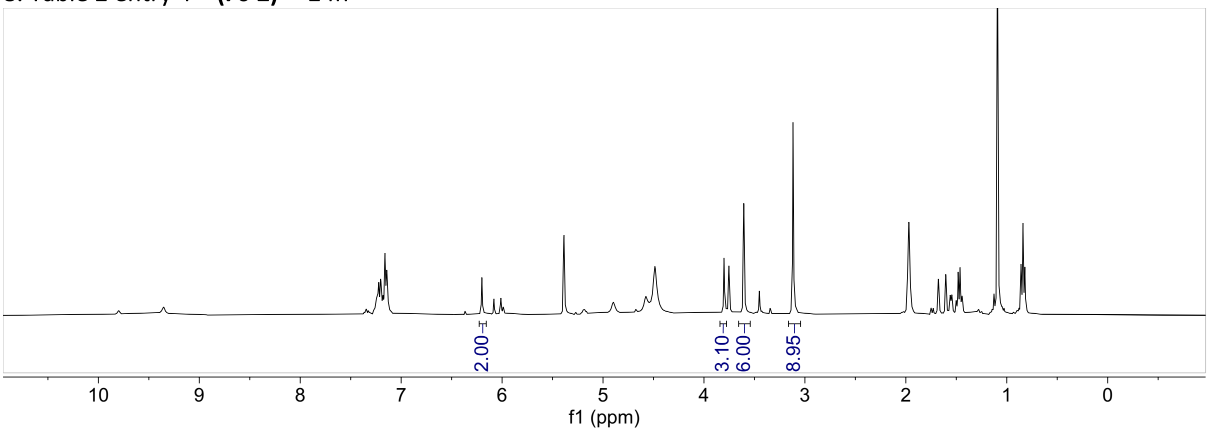
6. Table 2 entry 3 – **Fc-1^{2+}** in CD_3CN 24 h



7. Table 2 entry 4 – **(Fc-2)$^{3+}$** 2h

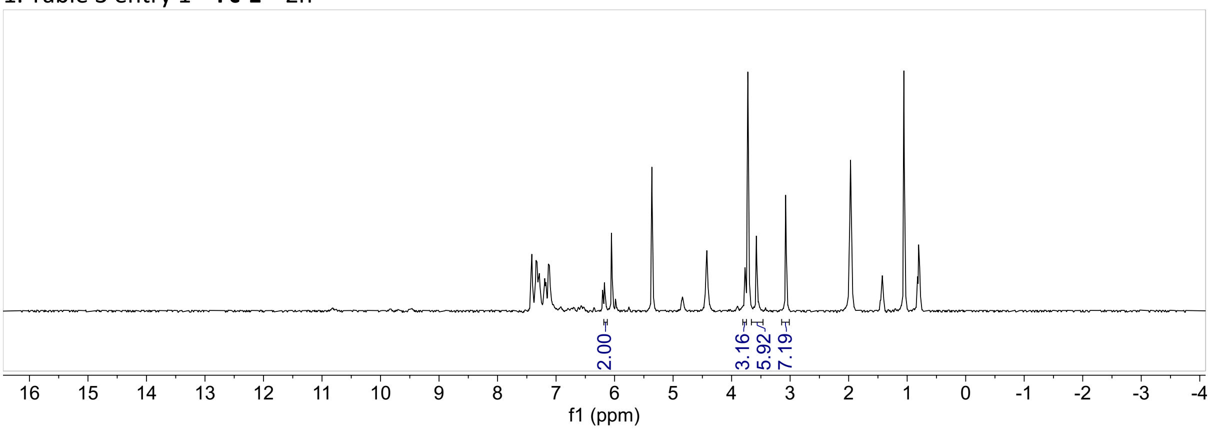


8. Table 2 entry 4 – **(Fc-2)$^{3+}$** 24h

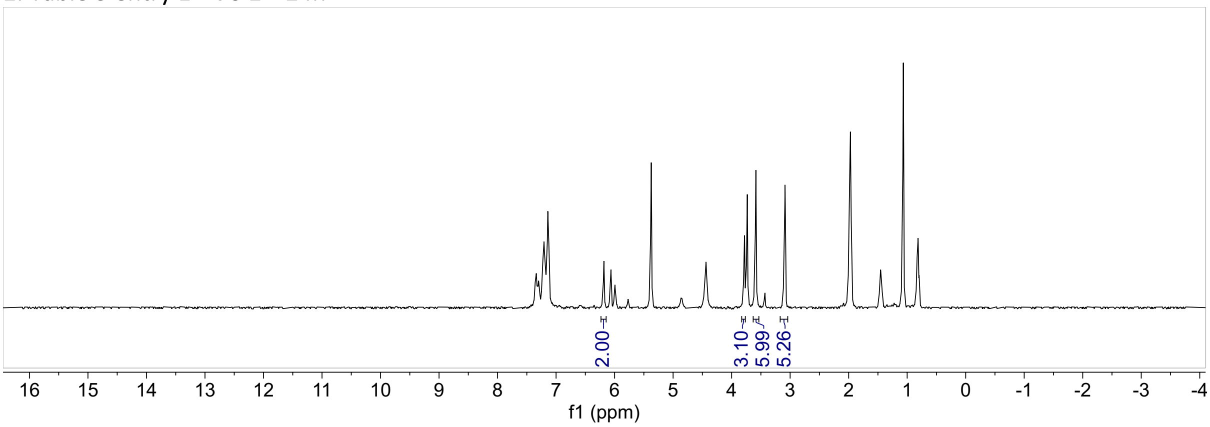


B. Reactivity with BHC – stoichiometric condition

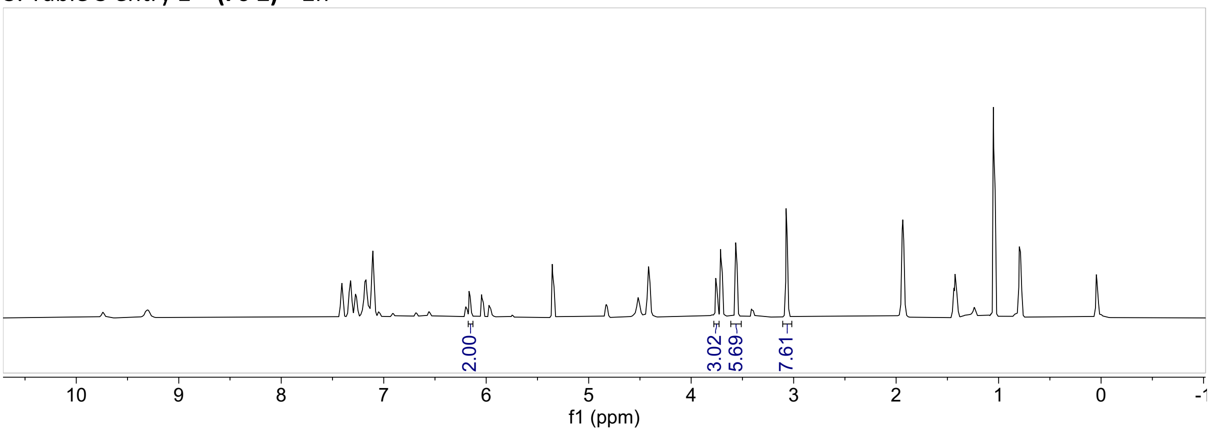
1. Table 3 entry 1 – **Fc-1^{2+}** 2h



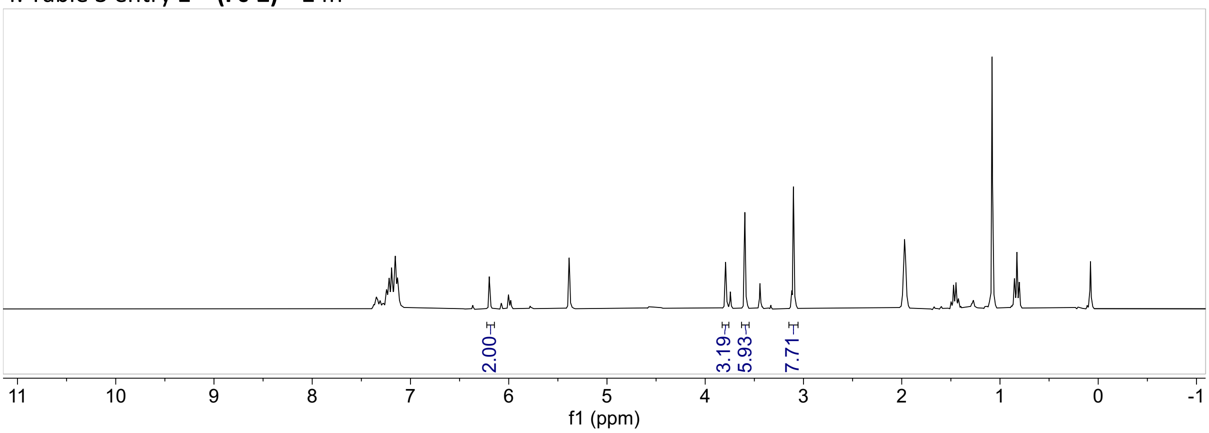
2. Table 3 entry 1 – **Fc-1**$^{2+}$ 24h



3. Table 3 entry 2 – **(Fc-2)**$^{3+}$ 2h

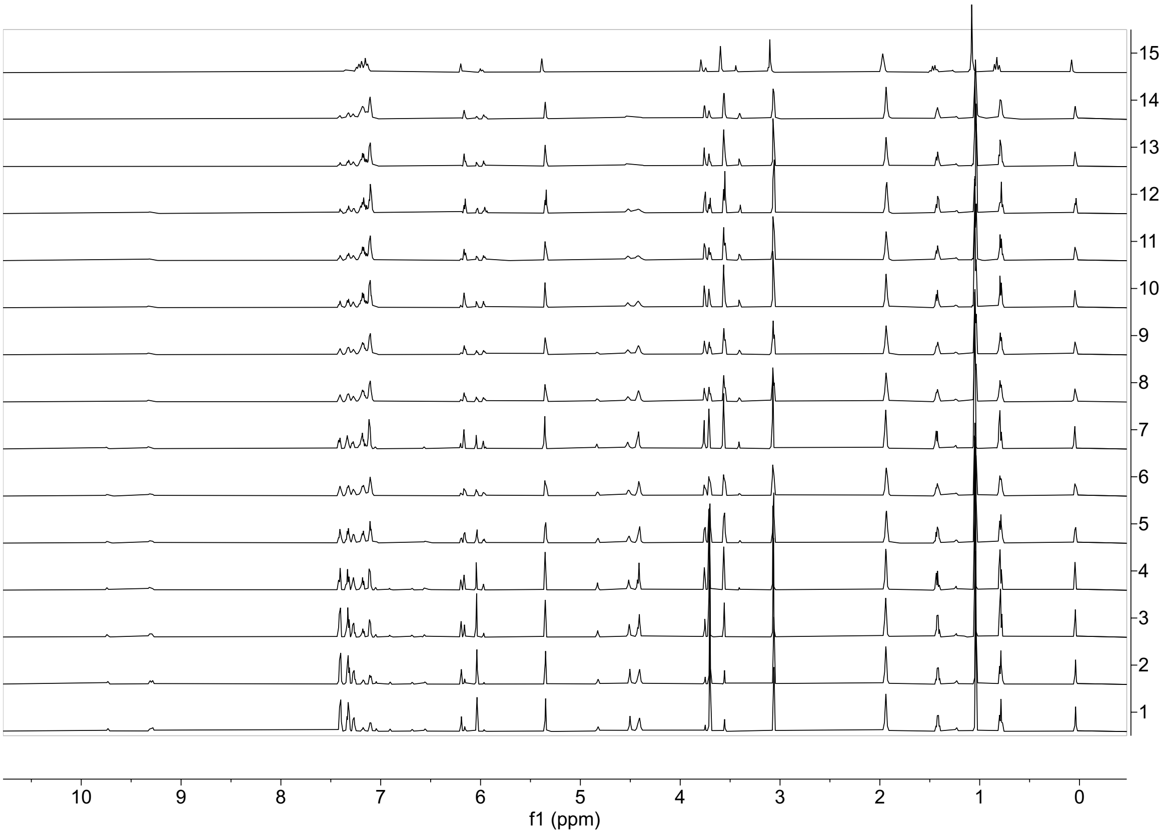


4. Table 3 entry 2 – **(Fc-2)**$^{3+}$ 24h

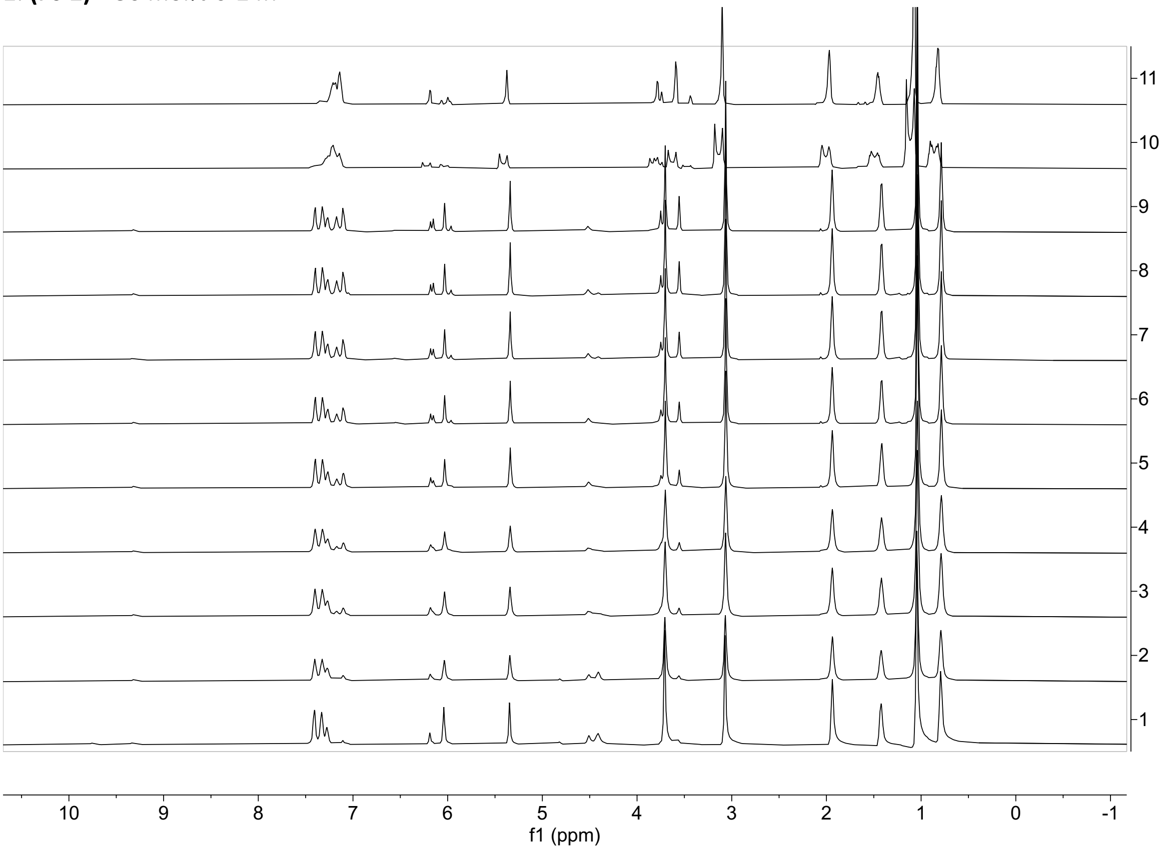


C. Reactivity with BHC – catalytic condition

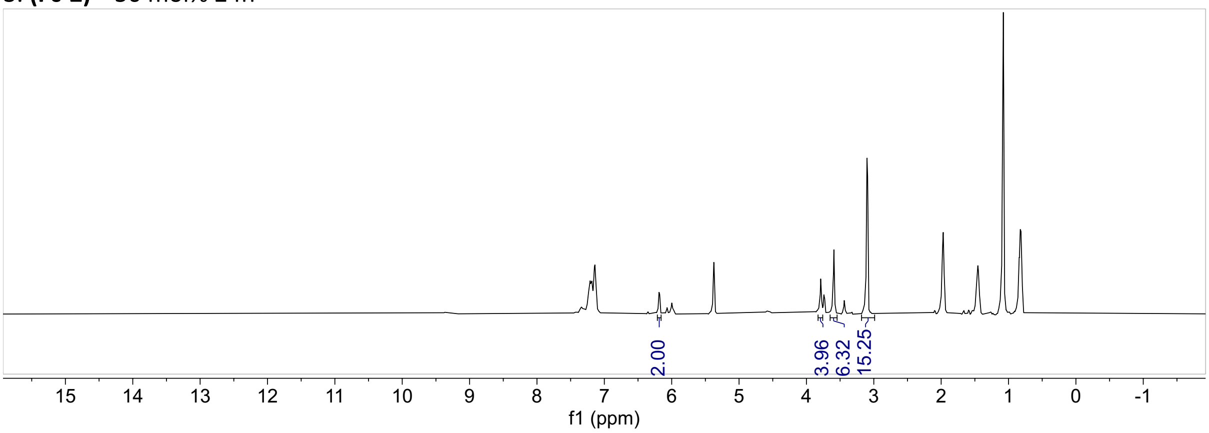
1. **(Fc-2)$^{3+}$** 100 mol% 0-24h



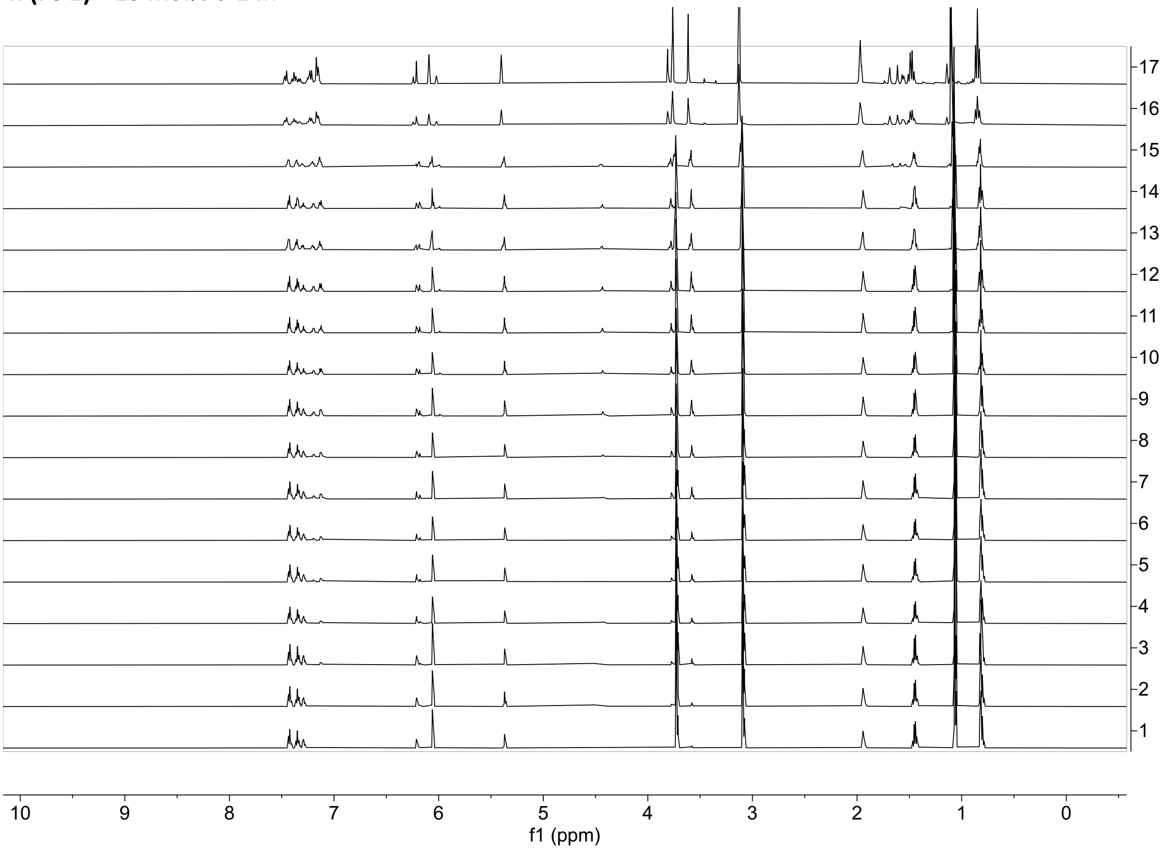
2. **(Fc-2)**$^{3+}$ 50 mol% 0-24h



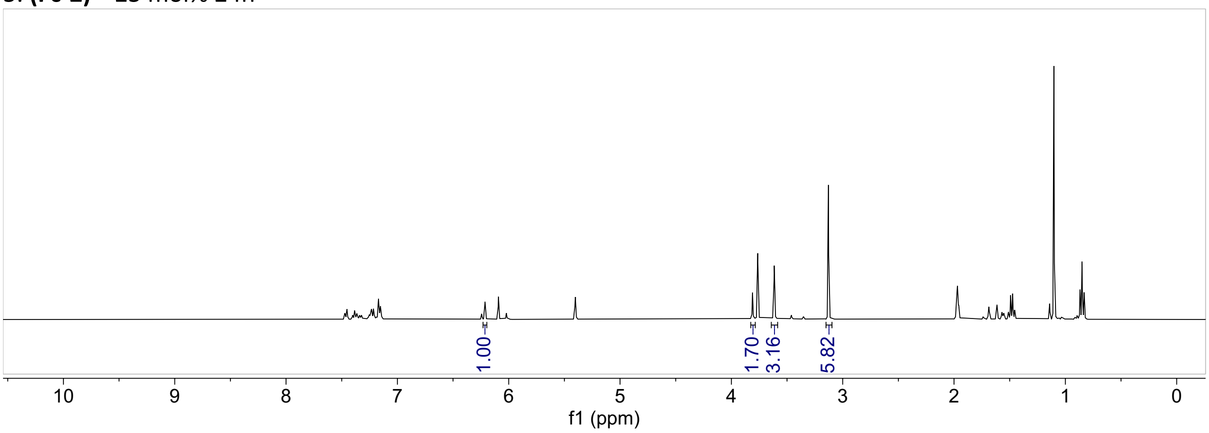
3. **(Fc-2)**$^{3+}$ 50 mol% 24h



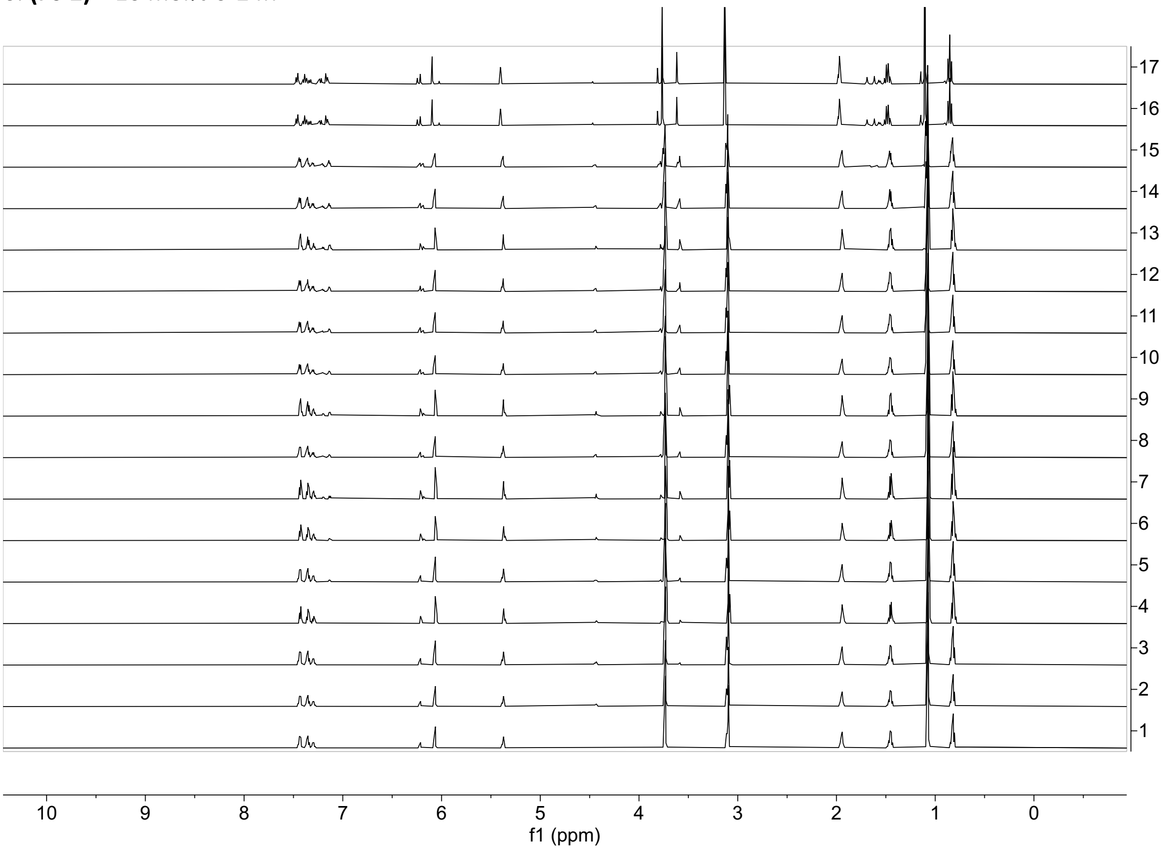
4. **(Fc-2)$^{3+}$** 25 mol% 0-24h



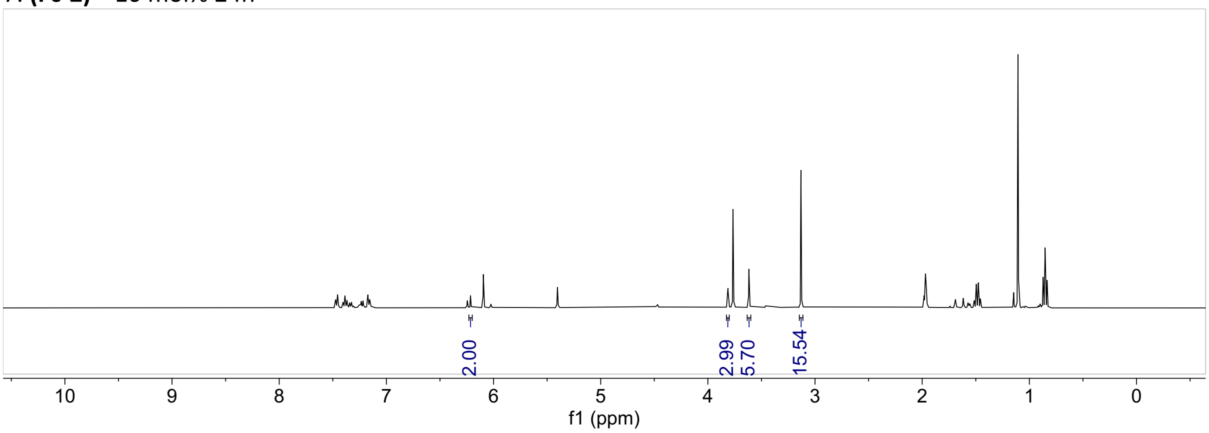
5. **(Fc-2)$^{3+}$** 25 mol% 24h



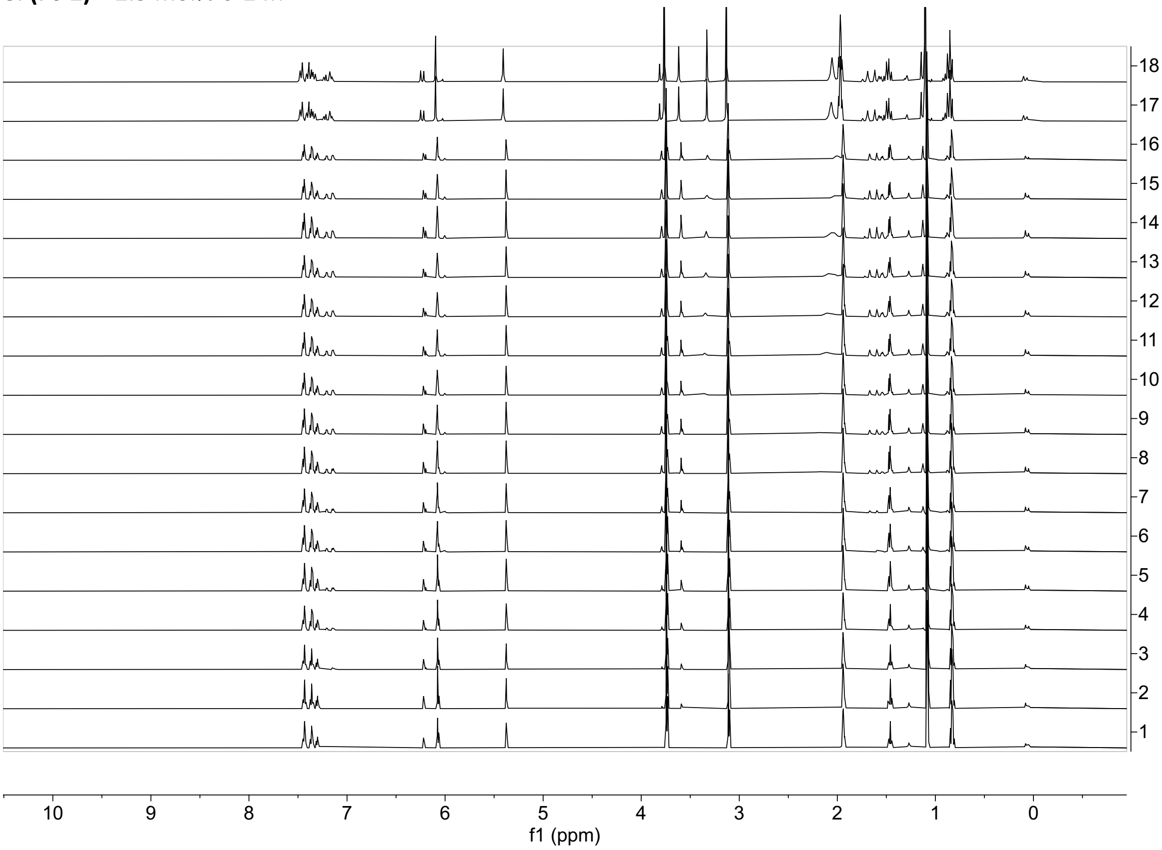
6. **(Fc-2)**$^{3+}$ 10 mol% 0-24h



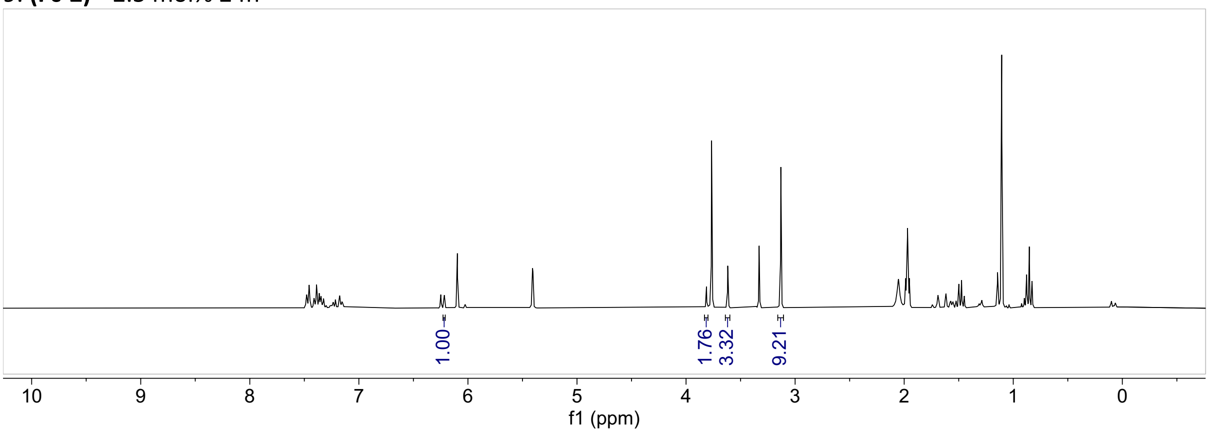
7. **(Fc-2)**$^{3+}$ 10 mol% 24h



8. **(Fc-2)**$^{3+}$ 2.5 mol% 0-24h

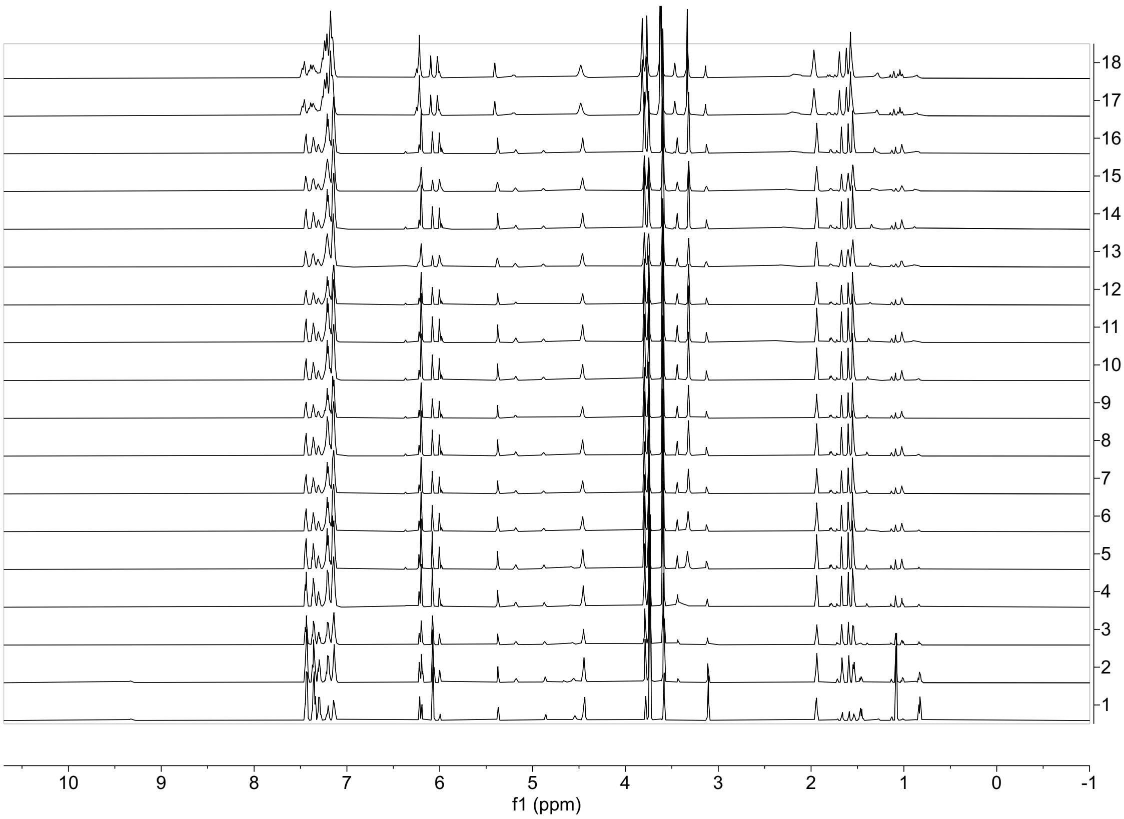


9. **(Fc-2)**$^{3+}$ 2.5 mol% 24h

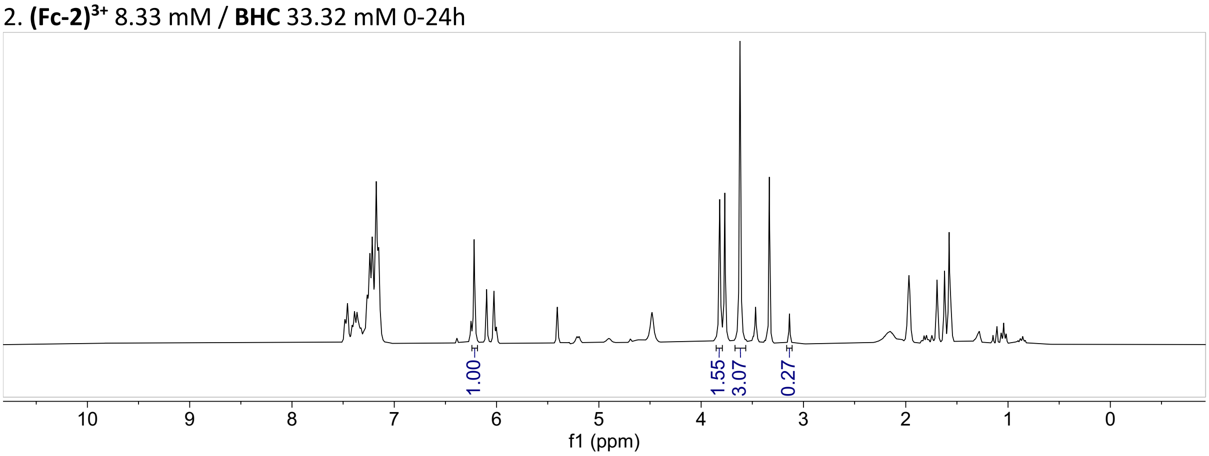


D. Reactivity with BHC – catalyst/substrate concentration

1. **(Fc-2)$^{3+}$** 8.33 mM / **BHC** 33.32 mM 0-24h



2. **(Fc-2)$^{3+}$** 8.33 mM / **BHC** 33.32 mM 0-24h



11. Cartesian coordinates of the optimized structures

^{1}Fc-1^{2+}

Charge: 2, Multiplicity: 1, NImag: 0

E = -4623.96276439 ht

G = -4623.61603196 ht

H	1.39767000	-0.11737700	-0.13915900
C	1.92088700	0.82676200	-0.07290000
C	2.27018200	1.34672800	1.16908900
C	2.26946000	1.51945200	-1.22868100
C	2.95711600	2.73126100	-1.07218100
C	2.96868500	2.56015100	1.19180800
H	3.24603200	3.29718700	-1.95118400
H	3.26243300	2.98943100	2.14412400
N	2.40821700	0.23685800	4.52691800
N	2.81995300	0.87883800	3.49910000
C	1.97570200	0.69782200	2.43804900
C	0.93432100	-0.10771400	2.86656900
N	1.23292200	-0.38636400	4.17089000
C	1.98706200	1.05882500	-2.57992600
C	1.71184100	-0.18789500	-3.12140100
N	1.63179900	0.03659500	-4.46770900
N	1.83996900	1.36889000	-4.73735400
N	2.03726900	1.95192600	-3.61601300
N	3.29641200	3.23702900	0.10270800
C	0.57156900	-1.13104700	5.14621000
C	-0.80775300	-1.07439700	5.47481500
C	1.24803600	-1.93970500	6.10159300
C	-1.00104600	-1.90984400	6.60302400
H	-1.56097700	-0.49904700	4.96144300
C	0.26226300	-2.44397600	6.99134600
H	2.30809800	-2.13546100	6.11462200
H	-1.94514700	-2.08507800	7.09443700
H	0.44766800	-3.11247300	7.81700500
C	1.40742200	-0.82228600	-5.54312100
C	2.11804200	-0.73790200	-6.77234300
C	0.35988200	-1.77029900	-5.67207900
C	1.54097500	-1.69265100	-7.65145100
H	2.94921700	-0.08011100	-6.96958900
C	0.45991100	-2.32628000	-6.97118000
H	-0.37054500	-2.01556700	-4.91809300
H	1.86948400	-1.89516500	-8.65847900
H	-0.19239900	-3.08282700	-7.37820800
Fe	0.14145100	-0.30095800	-7.16245900
Fe	0.31222800	-0.41603300	7.12751900
C	-1.49875800	-0.02860500	-8.39649100
C	-0.34385700	0.62618700	-8.91486300
C	-1.79564000	0.53313400	-7.13008900
H	-2.03481400	-0.83824600	-8.86749900
C	0.07319600	1.59128000	-7.95631300
H	0.13450100	0.42221900	-9.85975600
C	-0.83499000	1.53338800	-6.86483400
H	-2.59580900	0.22901700	-6.47412600
H	0.92888400	2.24318500	-8.03322000
H	-0.74775800	2.10181400	-5.95105800
C	-0.44302000	0.51935800	8.81043500

C	-0.34508000	1.48036700	7.77363400
C	0.85840400	-0.01055800	9.05073400
H	-1.35321800	0.21793200	9.30573400
C	1.00792300	1.55080300	7.37606700
H	-1.16379300	2.03685200	7.34559700
C	1.75789700	0.62572200	8.15052400
H	1.11543300	-0.76427500	9.77814300
H	1.39815000	2.14261800	6.56163900
H	2.81573900	0.43632900	8.06012600
I	1.61213600	-2.07905000	-2.30600200
I	-0.73453800	-0.82773800	1.89628900

^{3}Fc-1^{2+}

Charge: 2, Multiplicity: 3, NImag: 0

E = -4623.96895200 ht

G = -4623.61009250 ht

H	0.58240400	-0.52448500	0.00000000
C	-0.26340700	0.15128800	-0.00000000
C	-0.81305000	0.58662200	1.20181500
C	-0.81305000	0.58662200	-1.20181500
C	-1.88484300	1.48133600	-1.13555000
C	-1.88484300	1.48133600	1.13555000
H	-2.31979600	1.88486900	-2.04464600
H	-2.31979600	1.88486900	2.04464600
N	1.36030900	-0.58503500	3.74652900
N	1.07265000	-0.18926400	2.56279700
C	-0.25172200	0.13651200	2.46658200
C	-0.83199100	-0.07557600	3.70623600
N	0.19818900	-0.52483600	4.48542000
C	-0.25172200	0.13651200	-2.46658200
C	-0.83199100	-0.07557600	-3.70623600
N	0.19818900	-0.52483600	-4.48542000
N	1.36030900	-0.58503500	-3.74652900
N	1.07265000	-0.18926400	-2.56279700
N	-2.40483600	1.92303900	-0.00000000
C	0.25658900	-0.89214800	5.82651500
C	-0.37534600	-0.24227500	6.91889600
C	1.12948700	-1.89940200	6.32372200
C	0.05285400	-0.89970300	8.09906400
H	-1.05380200	0.59300100	6.85678700
C	0.97950000	-1.92042000	7.73586400
H	1.75946800	-2.53164800	5.71942100
H	-0.25744400	-0.64645400	9.10059100
H	1.48585400	-2.59411500	8.40866800
C	0.25658900	-0.89214800	-5.82651500
C	1.12948700	-1.89940200	-6.32372200
C	-0.37534600	-0.24227500	-6.91889600
C	0.97950000	-1.92042000	-7.73586400
H	1.75946800	-2.53164800	-5.71942100
C	0.05285400	-0.89970300	-8.09906400
H	-1.05380200	0.59300100	-6.85678700
H	1.48585400	-2.59411500	-8.40866800
H	-0.25744400	-0.64645400	-9.10059100
Fe	1.70398000	-0.10805400	-7.17031500
Fe	1.70398000	-0.10805400	7.17031500
C	2.68984400	1.08607200	-8.54267000

C	3.54140600	0.05733800	-8.04362500
C	2.28950800	1.89730300	-7.45184100
H	2.37396500	1.20842300	-9.56728000
C	3.65924300	0.23713300	-6.63706700
H	4.00799300	-0.72206200	-8.62503200
C	2.89297400	1.37987000	-6.28452600
H	1.61997000	2.74133800	-7.50164400
H	4.21756400	-0.38554000	-5.95624000
H	2.73135100	1.73700800	-5.27823300
C	2.68984400	1.08607200	8.54267000
C	2.28950800	1.89730300	7.45184100
C	3.54140600	0.05733800	8.04362500
H	2.37396500	1.20842300	9.56728000
C	2.89297400	1.37987000	6.28452600
H	1.61997000	2.74133800	7.50164400
C	3.65924300	0.23713300	6.63706700
H	4.00799300	-0.72206200	8.62503200
H	2.73135100	1.73700800	5.27823300
H	4.21756400	-0.38554000	5.95624000
I	-2.79957300	-0.03584300	-4.31597400
I	-2.79957300	-0.03584300	4.31597400

^{1}Fc-1

Charge: 0, Multiplicity: 1, NImag: 0

E = -4624.49729479 ht

G = -4624.13514320 ht

H	0.00001300	0.81310600	-0.02693300
C	0.00001200	1.88549900	-0.18296900
C	-1.20278500	2.58386100	-0.24559800
C	1.20281500	2.58385100	-0.24556800
C	1.13499700	3.97506000	-0.36946700
C	-1.13494600	3.97507000	-0.36950200
H	2.05720200	4.54564500	-0.41049500
H	-2.05714300	4.54566300	-0.41056200
N	-4.61660200	1.90359200	0.43625200
N	-3.54785500	2.63373200	0.43876500
C	-2.51190700	1.95765300	-0.12928800
C	-2.99391400	0.72102900	-0.52243700
N	-4.30275400	0.71974300	-0.14748200
C	2.51192000	1.95761500	-0.12922800
C	2.99392900	0.72102900	-0.52249000
N	4.30274000	0.71967000	-0.14744100
N	4.61657000	1.90343900	0.43646500
N	3.54783900	2.63360600	0.43898200
N	0.00002900	4.65802000	-0.43070500
C	-5.29506900	-0.26502000	-0.33884400
C	-6.58009400	-0.01746200	-0.90299600
C	-5.18387500	-1.65267400	-0.02581100
C	-7.26236100	-1.26191000	-0.94929300
H	-6.94566500	0.94739200	-1.21539200
C	-6.40536600	-2.26572800	-0.41631300
H	-4.33022500	-2.13349900	0.42435100
H	-8.26838400	-1.41435600	-1.30645200
H	-6.64801800	-3.31009700	-0.30182000
C	5.29503600	-0.26511400	-0.33881200
C	5.18383100	-1.65274900	-0.02571000

C	6.58004700	-0.01759900	-0.90300300
C	6.40531100	-2.26583200	-0.41619600
H	4.33018600	-2.13354500	0.42449200
C	7.26230200	-1.26205100	-0.94924300
H	6.94562200	0.94723400	-1.21545500
H	6.64795600	-3.31019600	-0.30165300
H	8.26831700	-1.41452600	-1.30641300
Fe	6.73187300	-0.80838600	0.95060000
Fe	-6.73190200	-0.80835600	0.95056000
C	7.73513100	-1.64780900	2.49908300
C	6.45853100	-1.18675200	2.92524200
C	8.45316800	-0.53360800	1.98237800
H	8.08758500	-2.66644100	2.53863100
C	6.38692400	0.20932800	2.66931100
H	5.67187800	-1.79591300	3.34183200
C	7.61828700	0.61381400	2.08649500
H	9.44495000	-0.56102000	1.55938200
H	5.53425300	0.84811300	2.83576600
H	7.85348700	1.60975400	1.74635200
C	-7.73495100	-1.64797400	2.49906100
C	-8.45321500	-0.53389800	1.98238700
C	-6.45841800	-1.18668000	2.92518500
H	-8.08721200	-2.66667300	2.53861200
C	-7.61854100	0.61368200	2.08648300
H	-9.44500700	-0.56149200	1.55942600
C	-6.38708000	0.20942300	2.66925900
H	-5.67163300	-1.79569400	3.34174100
H	-7.85396500	1.60958300	1.74637900
H	-5.53452200	0.84836300	2.83569500
I	2.12796900	-0.78467100	-1.63273000
I	-2.12791200	-0.78482000	-1.63244400

^{1}Fc-2^{+}

Charge: 1, Multiplicity: 1, NImag: 0

E = -4664.21486560 ht

G = -4663.81812507 ht

H	-0.04663900	0.54595100	-0.28129000
C	-0.00991400	1.62589000	-0.31036300
C	-1.20170900	2.35351200	-0.29424000
C	1.22627400	2.27191500	-0.34024200
C	1.22682100	3.66566700	-0.34897200
C	-1.11749200	3.74062400	-0.29380400
H	2.14646300	4.22995700	-0.37388700
H	-1.99719600	4.36600900	-0.26394000
N	-4.66464600	1.87576500	0.13527500
N	-3.56914600	2.55474200	0.15819700
C	-2.52929800	1.77709200	-0.24868800
C	-3.03708300	0.52512200	-0.56894400
N	-4.36523200	0.62478300	-0.30852200
C	2.52129200	1.62165200	-0.35498500
C	2.94251700	0.30178100	-0.24354300
N	4.29658600	0.37272100	-0.31175600
N	4.69194200	1.66429000	-0.47398000
N	3.63280300	2.39584400	-0.49630500
N	0.07732000	4.35334700	-0.31924100
C	-5.38889100	-0.33464500	-0.48662700

C	-6.59713900	-0.10122200	-1.20960800
C	-5.37249500	-1.68465000	-0.01962600
C	-7.32320400	-1.32057400	-1.19941600
H	-6.88335200	0.83283600	-1.66565200
C	-6.57490100	-2.28951600	-0.47482200
H	-4.59485300	-2.14600000	0.56818800
H	-8.29326700	-1.47559300	-1.64364700
H	-6.87965100	-3.30437500	-0.27633500
C	5.25318500	-0.67030300	-0.29955900
C	5.37360400	-1.69978100	0.68376200
C	6.23289700	-0.87474900	-1.31748600
C	6.42592600	-2.55309200	0.25553600
H	4.77995000	-1.79968700	1.57844900
C	6.95174200	-2.04653900	-0.96549400
H	6.38096700	-0.24441800	-2.17959900
H	6.78394300	-3.42052700	0.78622000
H	7.77714900	-2.46490600	-1.51874700
Fe	7.08151400	-0.65033900	0.49884000
Fe	-6.96441000	-0.67566000	0.68903300
C	8.62968200	-0.74642400	1.80853000
C	7.56607100	0.02175300	2.35582000
C	9.03827000	-0.12813800	0.59535600
H	9.03804000	-1.65261800	2.22679800
C	7.31642400	1.11172300	1.48013400
H	7.02689000	-0.20047000	3.26306300
C	8.22450500	1.02017200	0.39090500
H	9.81046100	-0.48486800	-0.06747400
H	6.54665500	1.85828400	1.59357600
H	8.26339300	1.68783500	-0.45501600
C	-8.15735800	-1.33078200	2.19538300
C	-8.78165800	-0.26635000	1.48928300
C	-6.92466300	-0.84929300	2.71469700
H	-8.54017800	-2.33371400	2.29768500
C	-7.93282800	0.87197400	1.56921900
H	-9.72042000	-0.32213700	0.96157500
C	-6.78664900	0.51022000	2.32738800
H	-6.20907100	-1.42417800	3.28093500
H	-8.10710000	1.83186400	1.10979500
H	-5.94337400	1.15033400	2.53278700
C	0.11025200	5.82191600	-0.34023900
H	1.12971700	6.15839100	-0.19161500
H	-0.25538500	6.17804800	-1.30012400
H	-0.52296800	6.20722500	0.45342000
I	1.93382200	-1.48580500	-0.07167100
I	-2.18396100	-1.12282600	-1.46232300

^{1}Fc-2^{3+}

Charge: 3, Multiplicity: 1, NImag: 0

E = -4663.53695544 ht

G = -4663.14159591 ht

H	-0.01702800	0.35113500	-0.18471500
C	0.00442800	1.43214200	-0.21077600
C	1.23257900	2.09668400	-0.25366500
C	-1.19351000	2.14657800	-0.20761400
C	-1.12153000	3.53716000	-0.23709700
C	1.21839100	3.48588700	-0.29093000

H	-2.00846500	4.15284000	-0.22789400
H	2.12786500	4.06673300	-0.33748000
N	4.68490000	1.50441800	-0.66065700
N	3.61528900	2.20946000	-0.66532900
C	2.54097700	1.45629200	-0.29225400
C	2.99629600	0.17395000	-0.01838000
N	4.33768700	0.24518000	-0.25591900
C	-2.52968400	1.56752900	-0.17718400
C	-3.03495500	0.29772200	-0.41977200
N	-4.38158000	0.44488100	-0.26215800
N	-4.68745000	1.73913100	0.05185000
N	-3.58309800	2.38819000	0.09982700
N	0.06057400	4.16474300	-0.27845700
C	5.32345500	-0.76177500	-0.23112000
C	5.68379800	-1.56293200	0.88146900
C	6.15481000	-1.09567300	-1.34324200
C	6.71553300	-2.42515500	0.44915200
H	5.25943200	-1.50831600	1.87172300
C	7.01334400	-2.14233200	-0.91210000
H	6.10824500	-0.64984600	-2.32440800
H	7.23088000	-3.13870500	1.07432600
H	7.75840600	-2.63436400	-1.51734300
C	-5.41853800	-0.48810100	-0.47332100
C	-6.42305000	-0.37341600	-1.47773400
C	-5.62057400	-1.70851900	0.23037400
C	-7.23823800	-1.53771700	-1.38325100
H	-6.52165500	0.44381900	-2.17527100
C	-6.74163200	-2.35215900	-0.33548800
H	-5.04935900	-2.04702900	1.08230400
H	-8.10365100	-1.75398100	-1.99089600
H	-7.16484600	-3.28735300	-0.00393100
Fe	-7.30448400	-0.43543300	0.36870100
Fe	7.34582200	-0.43691300	0.18915300
C	-9.05921900	-0.55838200	1.54155400
C	-9.20488400	0.42454000	0.53582800
C	-7.94443800	-0.20232700	2.33568400
H	-9.66773800	-1.44178400	1.65850000
C	-8.17311100	1.39174600	0.69513400
H	-9.93821000	0.40620700	-0.25698500
C	-7.39000300	1.00388300	1.81644000
H	-7.55927800	-0.77453200	3.16636600
H	-8.00292200	2.25737300	0.07452300
H	-6.52611800	1.53053400	2.18929400
C	9.28328300	-0.18003400	0.98406100
C	8.33159100	0.51529100	1.76991100
C	9.21869600	0.30865900	-0.34380500
H	9.90271000	-0.99767300	1.32316900
C	7.67572800	1.44775900	0.92815900
H	8.13233900	0.34938200	2.81703600
C	8.22422400	1.31939500	-0.38503500
H	9.80393100	-0.04401000	-1.17876000
H	6.88560100	2.12151500	1.21982000
H	7.91814300	1.87495500	-1.25788700
C	0.10800700	5.63878000	-0.32032500
H	-0.90201000	6.02908800	-0.27994700
H	0.67682000	6.00211400	0.53101200
H	0.58808000	5.95420700	-1.24281300

I	-2.18431300	-1.47723700	-1.02414400
I	2.06882500	-1.55269100	0.61157600

^{3}Fc-2^{3+}

Charge: 3, Multiplicity: 3, NImag: 0

E = -4663.53720158 ht

G = -4663.14238038 ht

H	0.02380100	0.34925400	-0.19888800
C	0.00280600	1.43010300	-0.23053500
C	1.20100600	2.14398700	-0.23789600
C	-1.22532700	2.09511600	-0.26793500
C	-1.21032700	3.48429900	-0.30982900
C	1.12989200	3.53441600	-0.27147600
H	-2.11978600	4.06551800	-0.35205800
H	2.01707600	4.14979900	-0.26986500
N	4.69452400	1.73381100	0.01153600
N	3.59077800	2.38207000	0.07116000
C	2.53708600	1.56405600	-0.21305100
C	3.04103800	0.29644000	-0.47108200
N	4.38814200	0.44258700	-0.31644000
C	-2.53441900	1.45560000	-0.29463300
C	-2.98757900	0.17185800	-0.02319200
N	-4.33157300	0.24551800	-0.24454900
N	-4.68245400	1.50728500	-0.63791900
N	-3.61245900	2.21153800	-0.65101700
N	-0.05217300	4.16257100	-0.30691700
C	5.43259400	-0.47834600	-0.53698900
C	5.61941800	-1.71667400	0.12946500
C	6.49626100	-0.28280100	-1.47224100
C	6.78002600	-2.30600900	-0.41752600
H	4.99638100	-2.11924200	0.91272700
C	7.32702000	-1.43175800	-1.39370100
H	6.61798500	0.56778300	-2.12456100
H	7.21501200	-3.23919400	-0.09218400
H	8.21808000	-1.60562300	-1.97623700
C	-5.31753300	-0.76132200	-0.21431800
C	-6.15684100	-1.09370000	-1.32106100
C	-5.66915100	-1.56521200	0.89920200
C	-7.01166000	-2.14155000	-0.88562900
H	-6.11781800	-0.64603300	-2.30173300
C	-6.70354500	-2.42704200	0.47262400
H	-5.23746900	-1.51265600	1.88642500
H	-7.76121000	-2.63257000	-1.48614000
H	-7.21431800	-3.14179800	1.10019300
Fe	-7.33582800	-0.43743600	0.22149700
Fe	7.27889600	-0.43002800	0.41385800
C	-9.26928700	-0.18234700	1.02667800
C	-9.21147100	0.31379800	-0.29853500
C	-8.31196200	0.50710900	1.81121600
H	-9.88808200	-1.00100400	1.36449600
C	-8.21579600	1.32311700	-0.33967300
H	-9.80147500	-0.03372300	-1.13230100
C	-7.65938200	1.44345900	0.97096500
H	-8.10744500	0.33536500	2.85638200
H	-7.91335400	1.88248800	-1.21137800
H	-6.86719700	2.11503700	1.26198700

C	8.98165000	-0.59290500	1.64788600
C	7.82001700	-0.33910300	2.42144600
C	9.14939800	0.46412400	0.72263800
H	9.59534500	-1.48023000	1.70489800
C	7.26621700	0.88897100	1.97727300
H	7.42571000	-0.97366100	3.19953400
C	8.09098200	1.38538600	0.92165100
H	9.92634800	0.53742100	-0.02243900
H	6.37206600	1.35945700	2.35426000
H	7.91841200	2.28640200	0.35340000
C	-0.09901300	5.63650700	-0.35453400
H	-0.67204800	6.00309700	0.49251600
H	0.91090300	6.02672700	-0.31053400
H	-0.57433900	5.94858600	-1.28066900
I	-2.05508900	-1.56041000	0.58328400
I	2.18341800	-1.46604800	-1.10047800

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