Electronic Supplementary Information

Catalytic O_2 activation with synthetic models of a-ketoglutarate dependent oxygenases based in triazacyclononane ligands

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1. Experimental Section

Materials and methods. Reagents and solvents used were of commercially available reagent quality unless otherwise stated. Preparation and handling of air-sensitive materials were performed under an inert atmosphere in a glove box. Acetonitrile and $^{18}O_2$ (99%) were purchased from Sigma-Aldrich and acetone from Scharlau. $H_2{}^{18}O$ (95% ^{18}O-enriched) was received from ICON Isotopes. 1,4,7-tris(*p*-toluenesulfonyl)-1,4,7-triazacyclononane (Ts_3tacn) was obtained from Catexel.

Instrumentation
Infrared spectra were collected on a Nicolet Avatar 360 FTIR spectrometer. UV-Visible spectroscopy was performed in a 1 cm quartz cell using an Agilent Technology 8453 UV-Vis spectrophotometer equipped with a diode-array detector. NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer in $CDCl_3$ or CD_3CN solvent using standard conditions and were referenced to the residual proton signal of the solvent. Elemental analysis was performed on a 4.1 Vario EL 3-elemental analyzer from Elementar. The ESI-MS experiments were performed with a Bruker esquire 6000 LC/MS chromatograph, using acetonitrile as a mobile phase. The product analyses after catalysis experiments were carried out on an Agilent Technology 7820A gas chromatograph with 16-sample automatic liquid sampler, flame ionization detector and EzChrom Elite Compact software. GC-MS analyses were performed on an Agilent Technology 7890A GC system equipped with 5975C inert XL EI/CI MSD with Triple-Axis Detector. The products were identified by comparison of their GC retention times and GC/MS with those of authentic compounds.

Synthesis and characterization of ligands

1,4,7-Triazacyclononane hexahydrochloride ($H_3tacn{\cdot}6HCl$) was prepared following a similar procedure to that described in the literature.[1]
In a 250 mL round bottomed flask with a stirrer, Ts_3tacn (25 g, 0.041 mol) was dissolved in concentrated H_2SO_4 (50 mL). The resulting solution was heated at 170 °C for 30 min. After this period the solution was poured into cold ethanol (180 mL) which led to the formation of a white-brown solid. After dropwise addition of diethylether (270 mL) the resulting mixture was stored in the fridge overnight. The resulting brown solid was filtered off and dissolved in water (75 mL) and refluxed at 120°C for 30 min. The resulting solution was filtered through Celite® to remove impurities. Water evaporation from the filtrates afforded a brown oil, to which HCl conc. (18 mL) was added together with ethanol (75 mL). This caused the immediate precipitation of a yellowish solid, which was filtered and washed with ethanol affording 12.5 g of $H_3tacn{\cdot}6HCl$. Yield: 86%. ^1H NMR (D_2O, 300 MHz, 25°C) δ, ppm: 3.49 (s, 12H). ^{13}C NMR (D_2O, 400 MHz, 25 °C) δ, ppm: 51. Anal. Calcd. for $C_6H_{15}N_3$: C, 20.71; H, 6.08; N, 12.08. Found: C, 22.86; H, 5.82; N, 11.98.

1,4,7-tris(isopropyl)-1,4,7-triazacyclononane (*i*Pr_3tacn) was prepared following a similar procedure to that described in the literature.[2] In a 100 mL round bottomed flask $H_3tacn{\cdot}6HCl$ (2.35 g, 6.75 mmol), isopropylbromide (1.99 mL, 0.0212 mol) and K_2CO_3 (23.5 g, 0.170 mol) were dissolved in 50 mL of acetonitrile. The mixture was refluxed for 24 h at 90 °C. The resulting solution was filtered, and the acetonitrile from the filtrates was removed under reduced pressure. Afterwards NaOH 1 M (30 mL) was added to the resulting solid and the mixture was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic phases were dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. 1.23 g of a yellowish oil corresponding to *i*Pr_3tacn were obtained. Yield = 71 %. ^1H

NMR ($CDCl_3$, 400 MHz, 25°C) δ, ppm: 0.94 (d, 18H), 2.61 (s, 12H), 2.85 (hept, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, 25°C) δ, ppm: 18.49, 52.97, 54.56. ESI-MS (m/z): 256.2 $[M+H]^+$..

Ligand *i*Bu_3tacn was prepared following a modified literature protocol.[3]

N,N',N''-tri(isopropylcarbonyl)-1,4,7-triazacyclononane ((*i*PrCO)$_3$tacn). In a 500 mL two-necked round-bottomed flask H_3tacn·6HCl (3.23 g, 9.28 mmol) was dissolved in acetonitrile (250 mL). To this solution 18 equiv of triethylamine were added (23 mL, 167 mmol) and the reaction mixture was stirred at room temperature for 15 min. Then 3 equiv of isobutyryl chloride (3 mL, 27.8 mmol) were added dropwise. The resulting solution was stirred overnight at 70 °C. After addition of water (100 mL) the acetonitrile solvent was removed under reduced pressure. The resulting aqueous mixture was extracted with CH_2Cl_2 (3 x 20 mL) and the combined organic phases were dried over $MgSO_4$. Filtration and solvent evaporation under reduced pressure afforded 2.81 g of (*i*PrCO)$_3$tacn as a white solid. Yield: 89 %. ^1H NMR ($CDCl_3$, 400 MHz, 25 °C) δ, ppm: 1.1 (d, 18H), 2.71 (hept, 3H), 3.39 (m, 6H), 3.69 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C) δ, ppm: 19.69, 30.66, 48.44, 51.50, 178.49. ESI-MS (m/z): 362.24 $[M+Na]^+$, 701.49 $[2M+Na]^+$.

1,4,7-tris(isobutyl)-1,4,7-triazacyclononane (*i*Bu$_3$tacn). In a 250 mL round-bottomed schlenck flask, (iPrCO)$_3$tacn (2.81 g, 8.3 mmol) was dissolved in CH_2Cl_2 (50 mL) and the solution was cooled down in an ice bath. Under a N_2 atmosphere 6 equiv $LiAlH_4$ (49 mL of a 1 M solution in diethylether, 49 mmol) were added dropwise and the resulting solution was stirred overnight at room temperature. After this period, ethyl acetate (50 mL) was slowly added at 0 °C under N_2. Evaporation of the solvents under reduced pressure afforded a white solid, which was stirred in 100 mL of CH_2Cl_2 for 2 h. The solid was filtered off and washed with CH_2Cl_2 (2 x 20 mL). The organic filtrates were extracted with NaOH 1 M (100 mL) and the aqueous phase was further extracted with CH_2Cl_2 (2 x 20 mL). The combined organic fractions were dried over $MgSO_4$ and filtered. Solvent evaporation under reduced pressure afforded 1.94 g of *i*Bu_3tacn as a white solid. Yield: 79%. ^1H NMR ($CDCl_3$, 400 MHz, 25 °C) δ, ppm: 0.9 (d, 18H), 1.65 (hept, 3H), 2.20 (d, 6H), 2.7 (s, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C) δ, ppm: 1.16, 21.24, 27.05, 29.85, 56.60, 68.06. ESI-MS (m/z): 298.32 $[M+H]^+$.

Sodium benzoylformate (NaBF). In a 25 mL round-bottomed flask NaOH (262 mg, 6.55 mmol) was dissolved in methanol (5 mL) and to this solution benzoylformic acid (990 mg, 6.55 mmol) was added directly as a solid. The resulting mixture was stirred at room temperature for 2h. After this time the solvent was evaporated and the resulting white solid was dried in the vacuum line at 40 °C for 2 h. 1.07 g of NaBF were obtained as a white solid. Yield: 95%. ^1H NMR (D_2O, 400 MHz, 25°C)□□, ppm: 7.63 (t, 2H), 7.78 (t, 1H), 7.97 (d, 2H). ESI-MS (m/z): 148.7 $[M-Na]^+$. Anal. Calcd. for $C_8H_5NaO_3$: C, 55.83; H, 2.93. Found: C, 55.37; H, 2.56.

Synthesis and characterization of complexes

[Fe(BF)(CF_3SO_3)(*i*Pr$_3$tacn)] (1BF). Inside the glove box *i*Pr$_3$tacn (212 mg, 0.83 mmol) was dissolved in CH_3CN (250 μL). In a separate vial an equimolar amount of $[Fe(CF_3SO_3)_2(CH_3CN)_2]$ (362 mg, 0.83 mmol) was solubilized in CH_3CN (500 μL). The colorless iron salt solution was poured onto the ligand solution which caused the immediate color change to pale yellow. After stirring for 5 min sodium benzoylformate (143 mg, 0.83 mmol) was added directly as a solid. The solution turned deep purple immediately. The reaction was stirred for 1 h at room temperature and filtered through a Celite® plug. Slow diethyl ether over the resulting solution afforded 387 mg of nice square purple crystals corresponding to **1BF**. Yield: 76%. ^1H NMR (CD_3CN, 400 MHz, 25 °C) δ, ppm: -14.55 (s, 6H), 11.07 (s, *m*-2H), 13.08 (s, *p*-1H), 23.95 (s, *o*-2H); 46.85 (s, 1H); 132.08 (s, 4H). ESI-MS (CH_3CN): m/z = 256.2757

[*i*Pr$_3$tacn]$^+$, 460.2260 [Fe(BF)(*i*Pr$_3$TACN)]$^+$. UV-Vis (1.3 mM, CH_3CN, 25 °C) λ, nm: 370 (390 $M^{-1}cm^{-1}$), 540 (390 $M^{-1}cm^{-1}$), 568 (390 $M^{-1}cm^{-1}$). μ_{eff} (CD_3CN, 25°C): 5.25 μ_B.

[Fe(Bz)(*i*Pr$_3$tacn)(CH_3CN)](CF_3SO_3) (1Bz). In a vial inside the glovebox *i*Pr$_3$tacn (50 mg, 0.19 mmol) was dissolved in acetonitrile (500 μL). An equimolar amount of [Fe(OTf)$_2$(CH_3CN)$_2$] (84.7 mg, 0.19 mmol) was solubilized in acetonitrile (500 μL) in a separate vial and added dropwise onto the *i*Pr$_3$tacn solution, affording a pale yellow mixture. After stirring for 5 min, sodium benzoate (28 mg, 0.19 mmol) was added as a solid. The resulting solution was filtered through a Celite® plug. 113 mg of pale yellow crystals were isolated from diethyl ether diffusion over the solution of **1Bz**. Yield: 92%. ^{1}H NMR (CD_3CN, 400 MHz, 25°C) δ, ppm: -20.32 (s, 6H), 11.45 (s, *m*-2H), 18.08 (s, *p*-1H), 29.34 (s, *o*-2H); 44.65 (s, 1H); 130.49 (s, 4H). ESI-MS (CH_3CN): m/z = 256.2753 [*i*Pr$_3$tacn]$^+$, 432.2322 [Fe(BZ)(*i*Pr$_3$tacn)]$^+$. UV-Vis (1.3 mM, CH_3CN, 25°C) λ, nm: 324 (330 $M^{-1}cm^{-1}$), 378 (200 $M^{-1}cm^{-1}$). μ_{eff} (CD_3CN, 25°C): 5.03 μ_B.

[Fe$_2$(BF)$_2$(μ-Cl)(*i*Bu$_3$tacn)$_2$](ClO_4) (2BF-ClO_4). In the glove box, *i*Bu$_3$tacn (34 mg, 0.11 mmol) was dissolved in CH_3CN (500 μL) and under stirring $FeCl_2$ (14 mg, 0.11 mmol) suspended in CH_3CN (1 mL) was added dropwise. To the resulting pale-yellow solution 2 equiv $AgClO_4$ (25 mg, 0.22 mmol) were added directly as a solid, causing the immediate precipitation of a white solid corresponding to AgCl. After stirring for 10 min, 1 equiv sodium benzoylformate (19 mg, 0.11 mmol) was added directly as a solid and the reaction was stirred for 1 h. Then the mixture was filtered using an Acrodisc obtaining a dark green solution. Slow diffusion of diethyl ether over this solution afforded 89 mg of orange crystals suitable for X-ray diffraction. Yield: 74%. ESI-MS (m/z): 1039.5204 [M-ClO_4]$^+$.

Reactivity tests. Inside the glovebox, complexes **1BF**, **1Bz** or **2BF-ClO_4** (6.56 μmol) were dissolved in anhydrous solvent (5 mL acetonitrile or acetone) and 100 equiv methyl *p*-tolyl sulfide (656 μmol) were added to the mixture. The vial was capped with a rubber cap and taken out of the glovebox. A balloon filled with O_2 was gently bubbled through the solution. Different treatments were followed depending on the final compound to be analyzed. For *sulfoxide quantification*, the reaction was stopped after 4 hours and a known amount of biphenyl was added as an internal standard; the solution was filtered through a silica plug and washed with ethyl acetate. The resulting solution was analyzed by GC. For *benzoic acid* quantification, after 4 h of reaction half equivalent of 1,3,5-trimethoxybenzene (TMB) was added as an internal standard, the solution was evaporated under vacuum and then HCl 3 M (10 mL) was added. The mixture was extracted 3 times with diethyl ether and the combined organic phases were washed twice with brine and finally dried over $MgSO_4$. After filtration, the resulting solution was concentrated and analyzed by ^{1}H NMR. Quantification of benzoic acid was carried out by comparison of the integrals of the aromatic protons of the TMB and the α-protons of the benzoic acid.

Isotope labeling experiments. Following the procedure described above but using $^{18}O_2$ instead of $^{16}O_2$, the incorporation of ^{18}O into sulfoxide and benzoic acid products was determined by GC-MS and ESI-MS in negative mode, respectively. ^{18}O-labeled water exchange experiments were carried out following the procedure described above but adding different amounts of $H_2{}^{18}O$ (10-80 equiv with respect to the Fe complex) prior to oxygenation. Analysis of the amount of ^{18}O incorporated into the sulfoxide products was performed by GC-MS.

Catalytic tests. Inside the glovebox **1BF** (6.56 μmol) was dissolved in acetone (5 mL). Then the appropriate amounts of methyl *p*-tolyl sulfide (20 – 100 equiv with respect to **1BF**) and HBF (3 – 100 equiv with respect to **1BF**) were added to the reaction mixture. The vial was capped with a rubber cap and taken outside of the glovebox. A balloon filled with O_2 gas was gently bubbled to the solution for 5 min and an O_2 atmosphere was kept for 4 hours under stirring. After this period, a known amount of biphenyl was added to the solution as an internal standard. The resulting mixture was filtered through a silica plug that was afterwards washed with ethyl acetate. The resulting solution was analyzed by GC and the amount of sulfoxide produced was determined.

Hammett plot analysis. Inside the glovebox **1BF** (6.56 μmol) was dissolved in acetone (5 mL) and different amounts of pairs of p-X-thioanisoles were mixed until a total amount of 200 equiv of substrate were added. The vial was capped with a rubber cap and taken outside of the glovebox. A balloon filled with O_2 gas was gently bubbled to the solution for 5 min and an O_2 atmosphere was kept for 2 hours under stirring. After this period, biphenyl was added as an internal standard and the resulting solution was analyzed by GC.

2. Compounds characterization

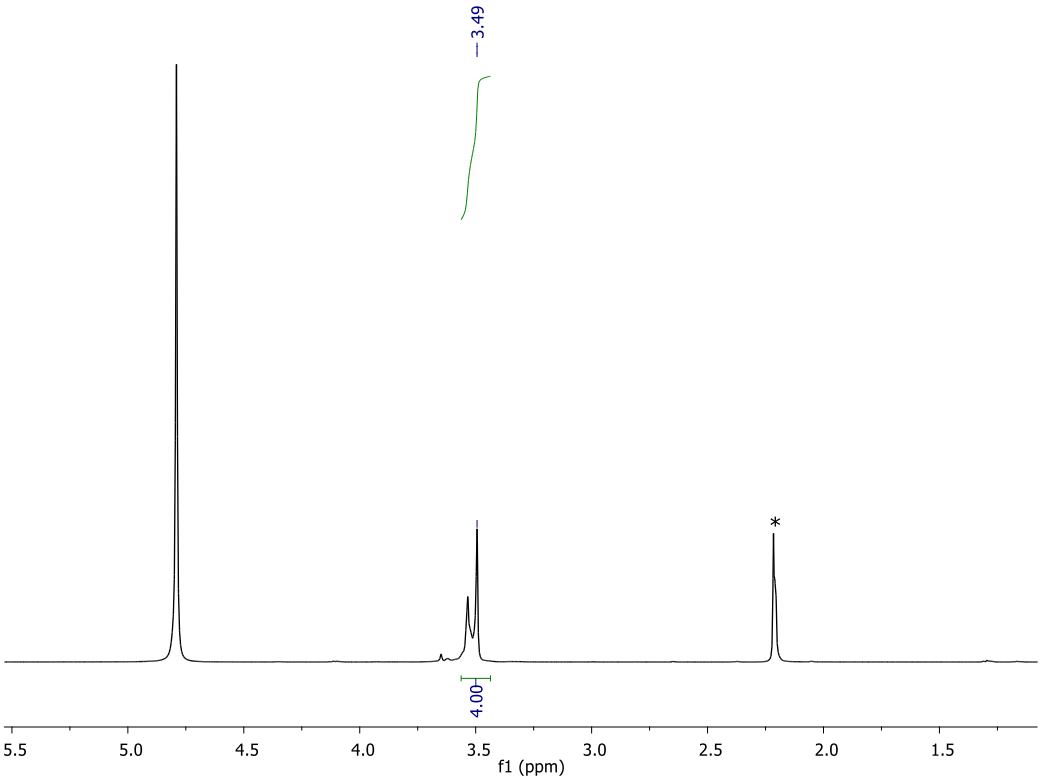


Figure S1. ^{1}H NMR spectrum of $H_3tacn \cdot 6HCl$ in D_2O at 25°C. *acetone

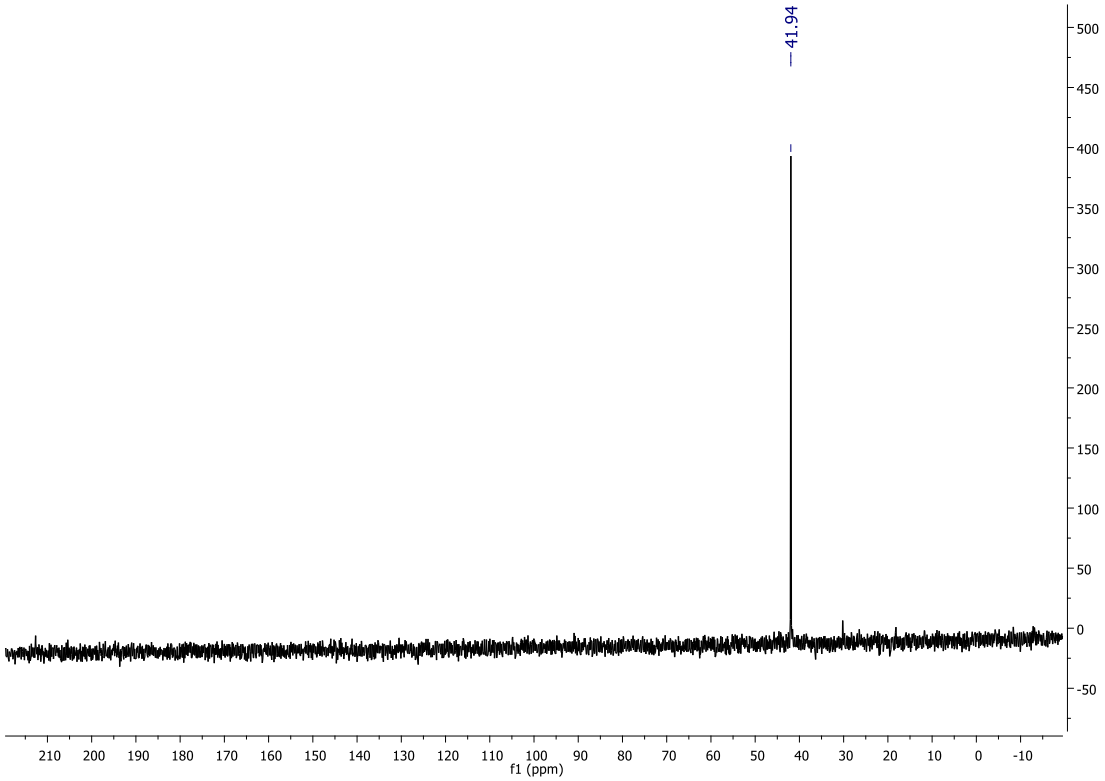


Figure S2. ^{13}C NMR spectrum of $H_3tacn \cdot 6HCl$ in D_2O at 25°C

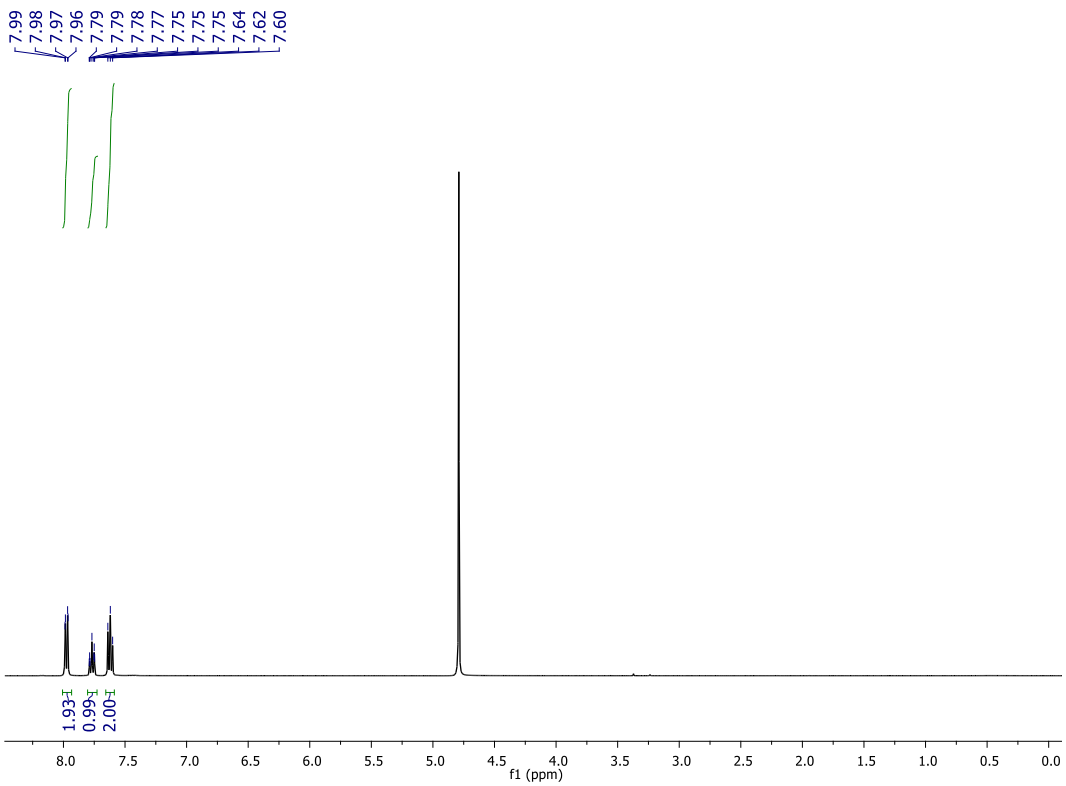


Figure S3. ^{1}H NMR spectrum of **NaBF** in D_2O at 25°C

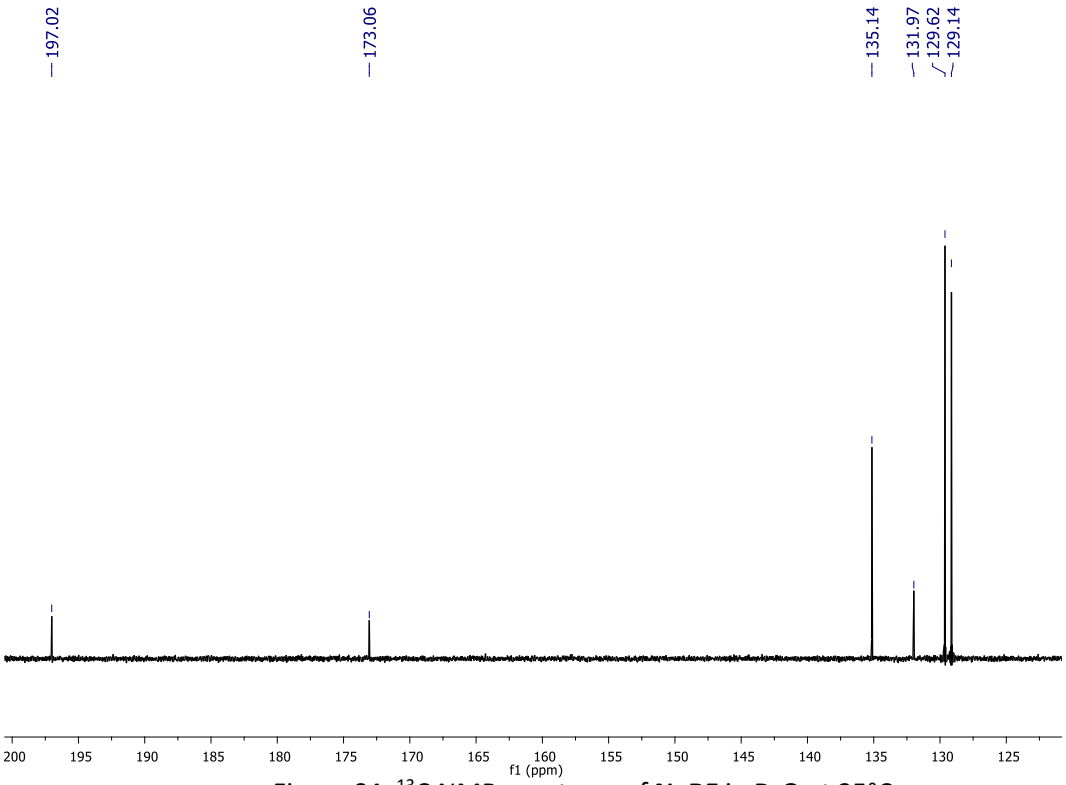


Figure S4. ^{13}C NMR spectrum of **NaBF** in D_2O at 25°C

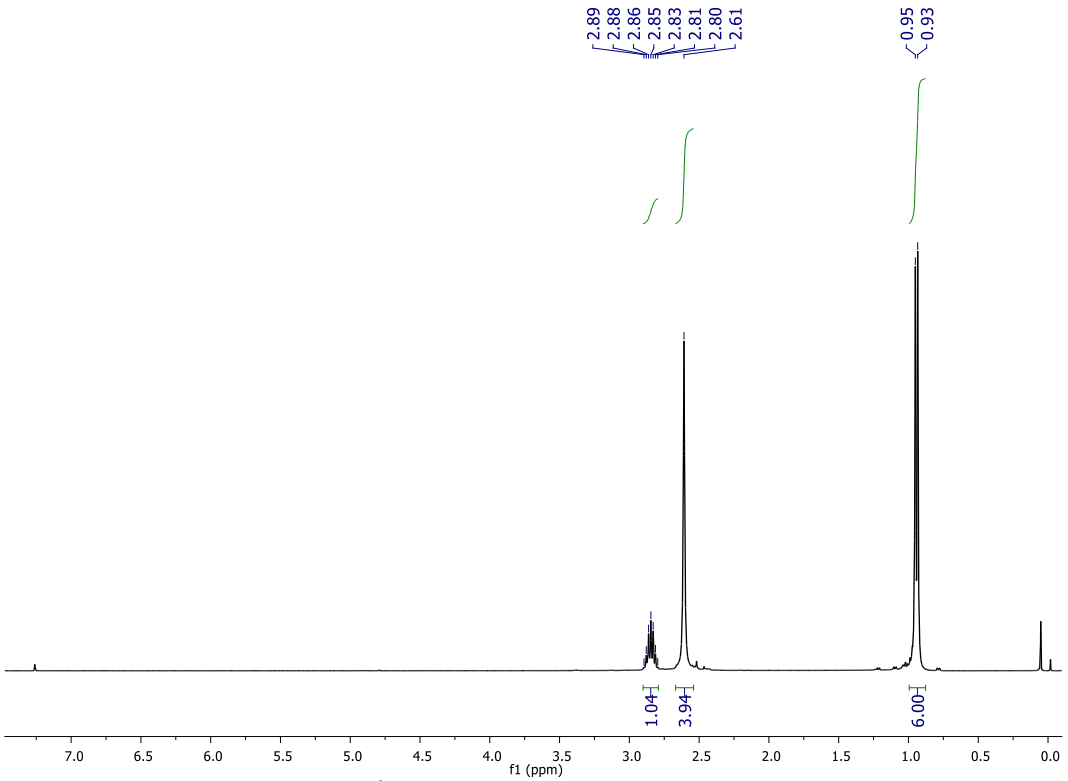


Figure S5. ^{1}H NMR spectrum of *i*Pr$_3$tacn in $CDCl_3$ at 25°C

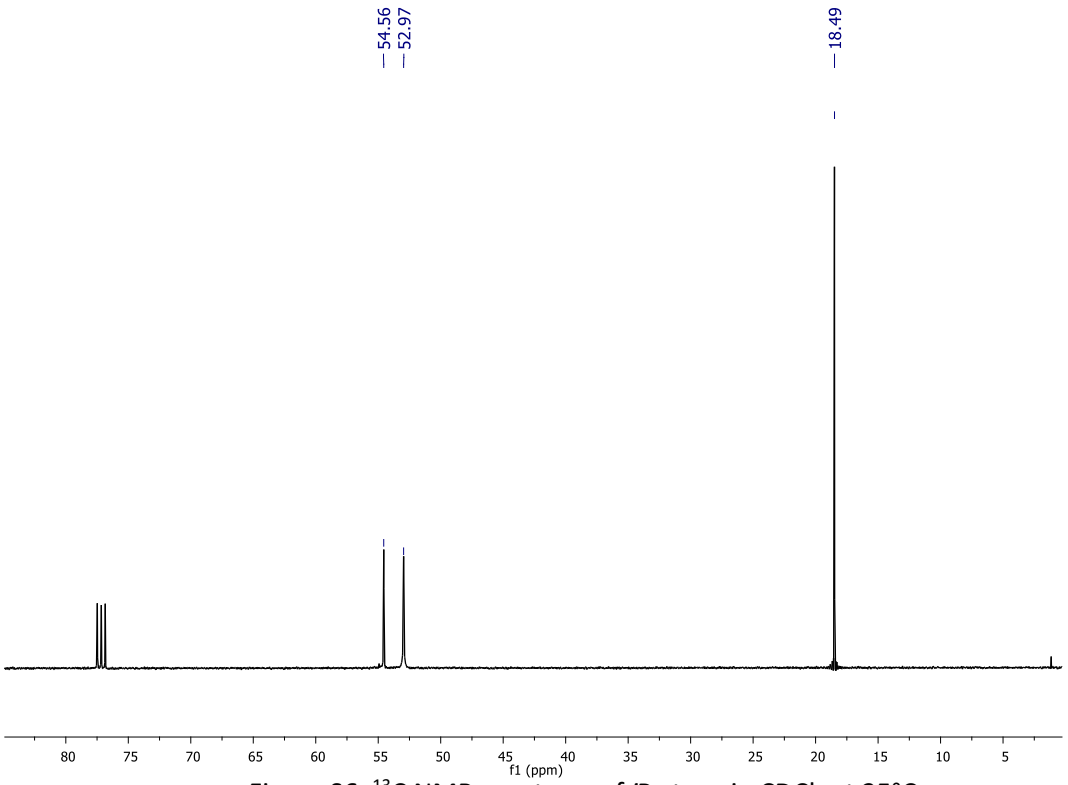


Figure S6. ^{13}C NMR spectrum of *i*Pr$_3$tacn in $CDCl_3$ at 25°C

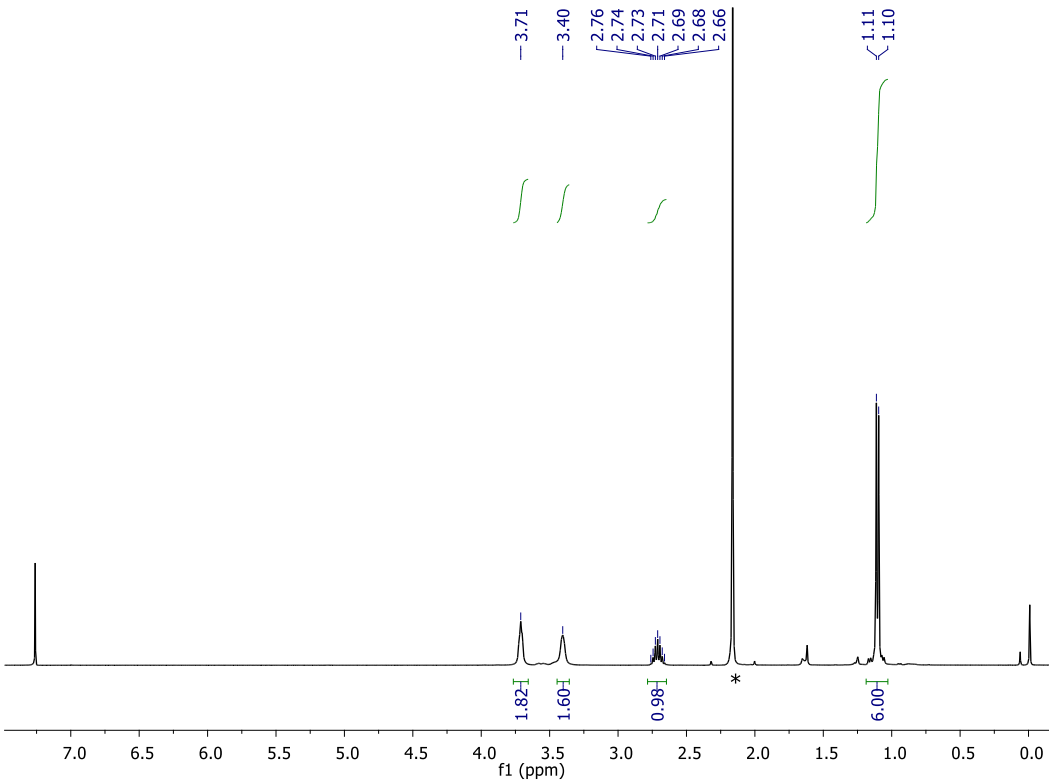


Figure S7. ^{1}H NMR spectrum of (*i*PrCO)$_3$tacn in $CDCl_3$ at 25°C. *acetone

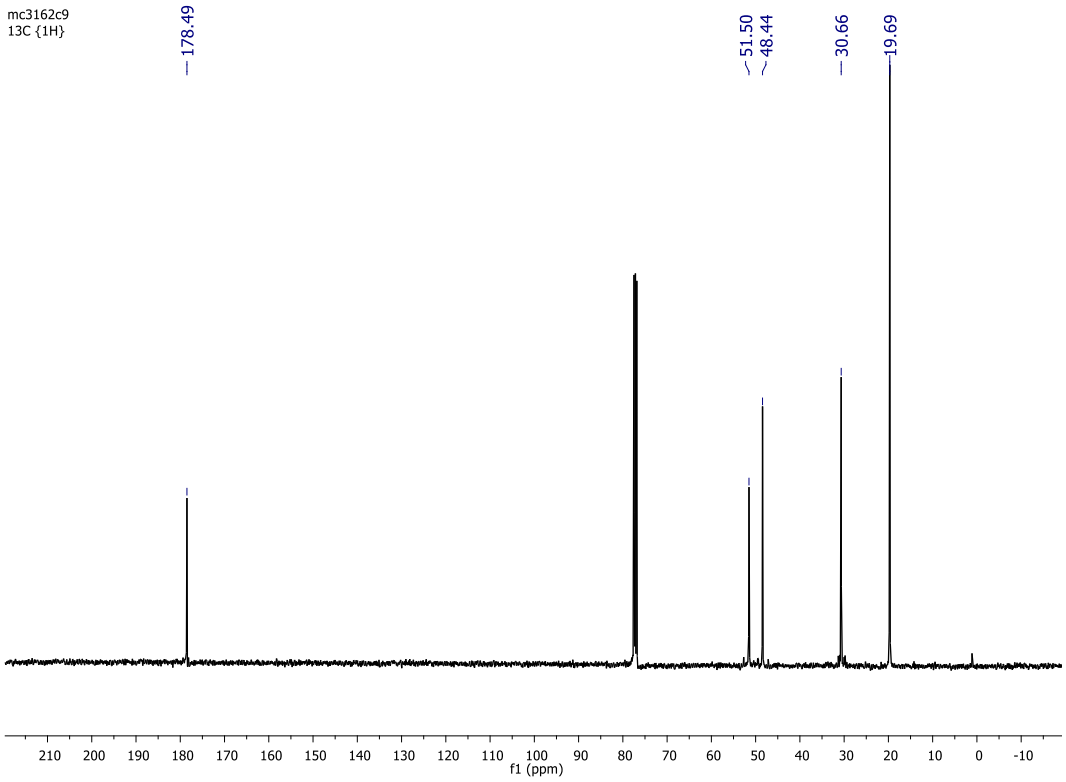


Figure S8. ^{13}C NMR spectrum of (*i*PrCO)$_3$tacn in $CDCl_3$ at 25°C

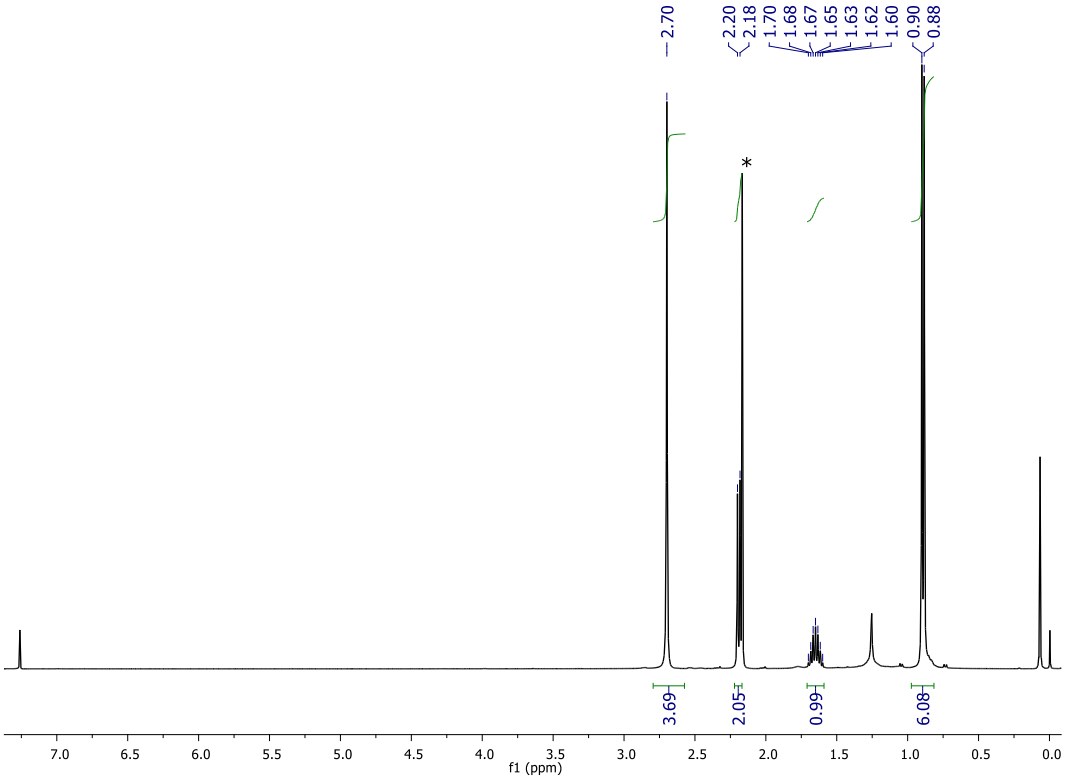


Figure S9. ^{1}H NMR spectrum of *i*Bu$_3$tacn in $CDCl_3$ at 25°C. * acetone

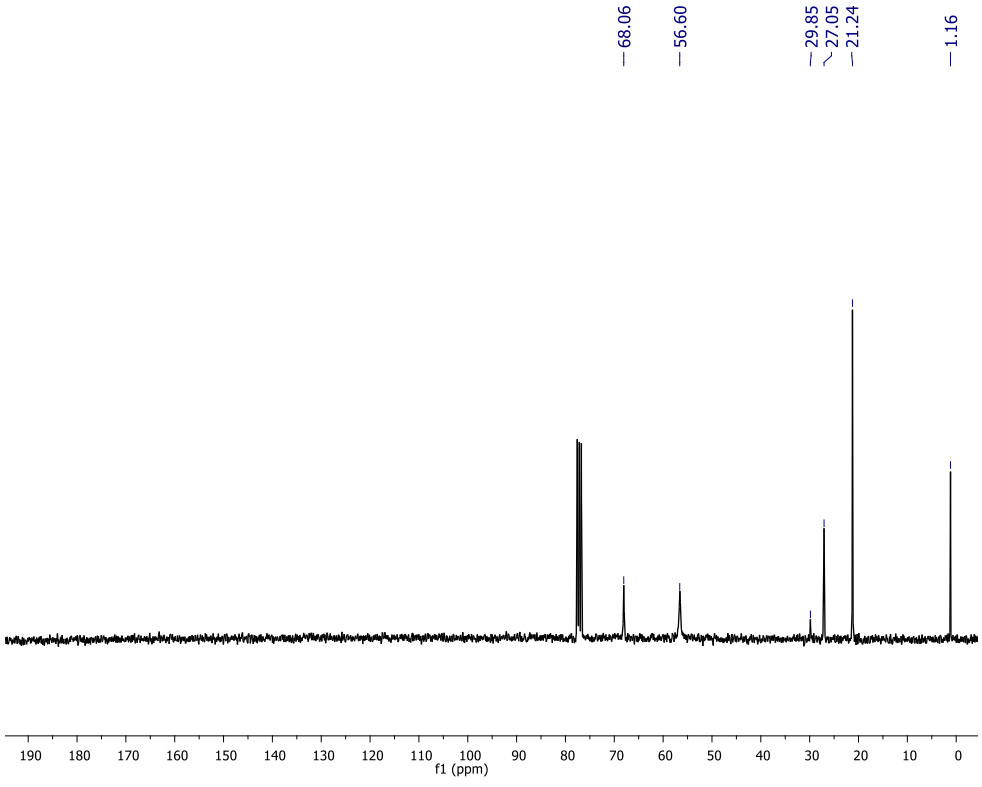


Figure S10. ^{13}C NMR spectrum of *i*Bu$_3$tacn in $CDCl_3$ at 25°C.

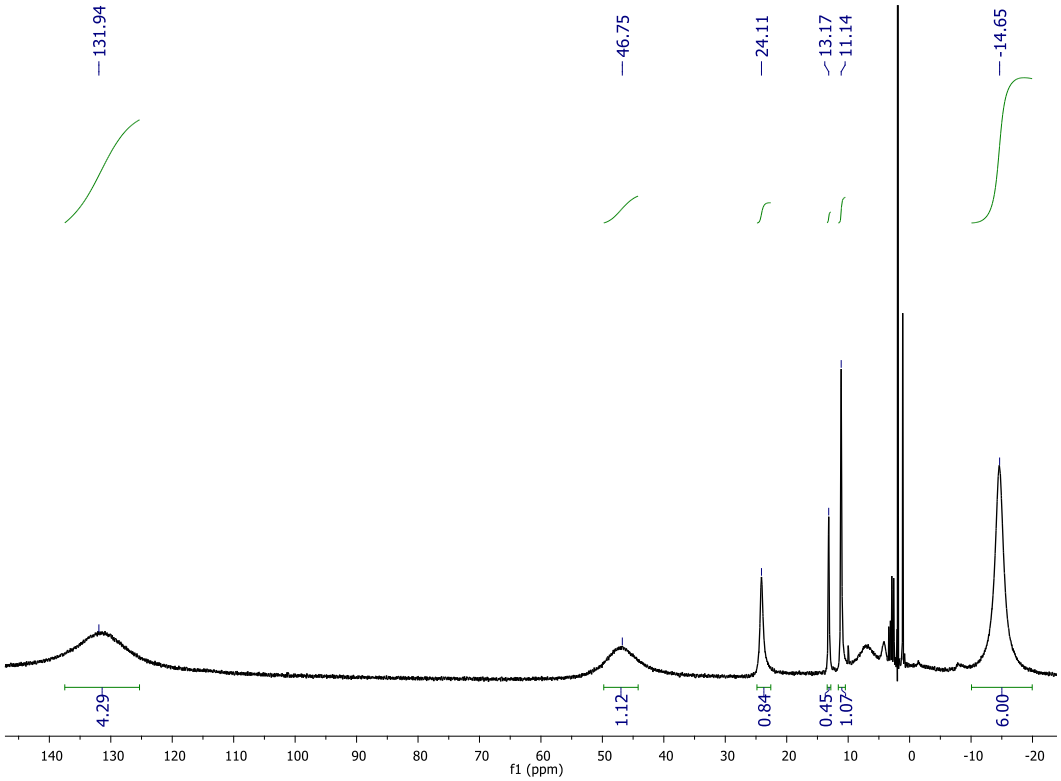


Figure S11. ^{1}H NMR spectrum of **1BF** in CD_3CN at 25°C.

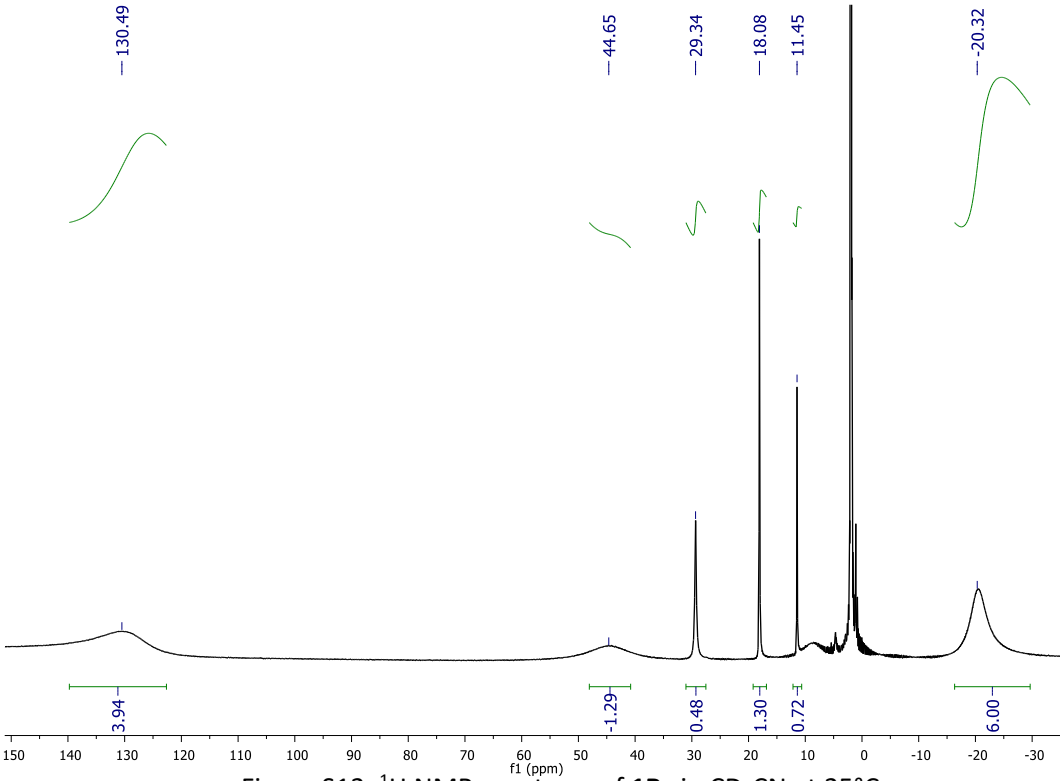


Figure S12. ^{1}H NMR spectrum of **1Bz** in CD_3CN at 25°C

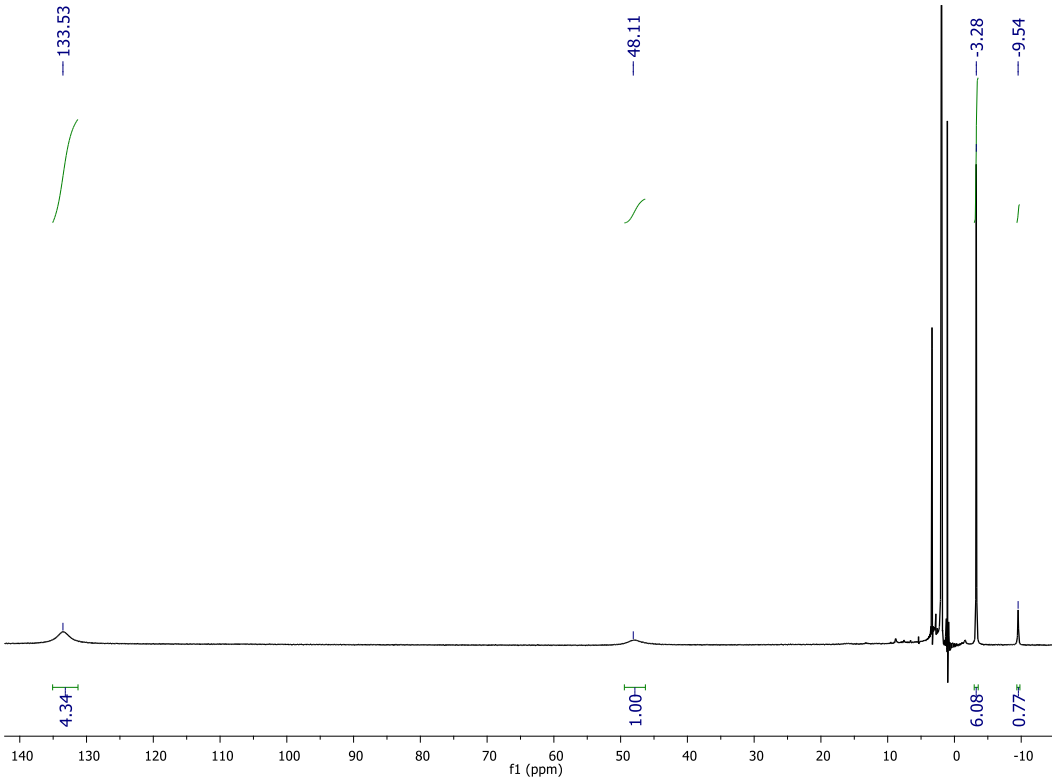


Figure S13. ^{1}H NMR spectrum of **2BF-ClO$_4$** in CD_3CN at 25°C

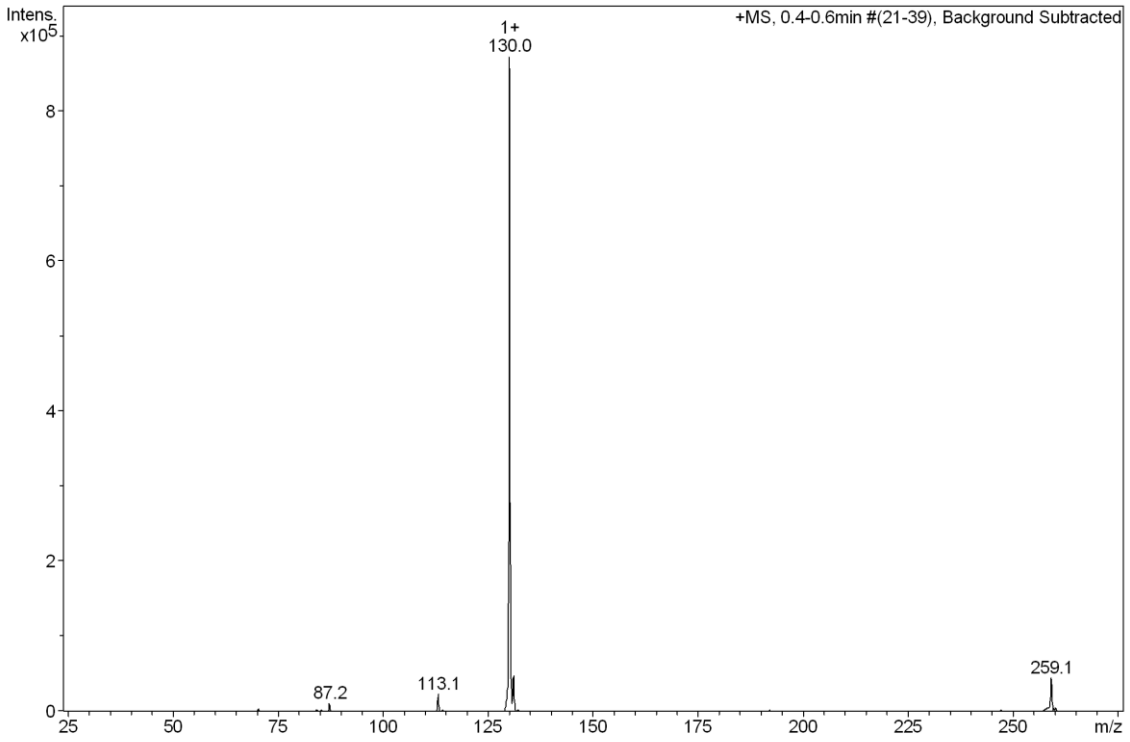


Figure S14. ESI-MS spectrum of tacn 6HCl.

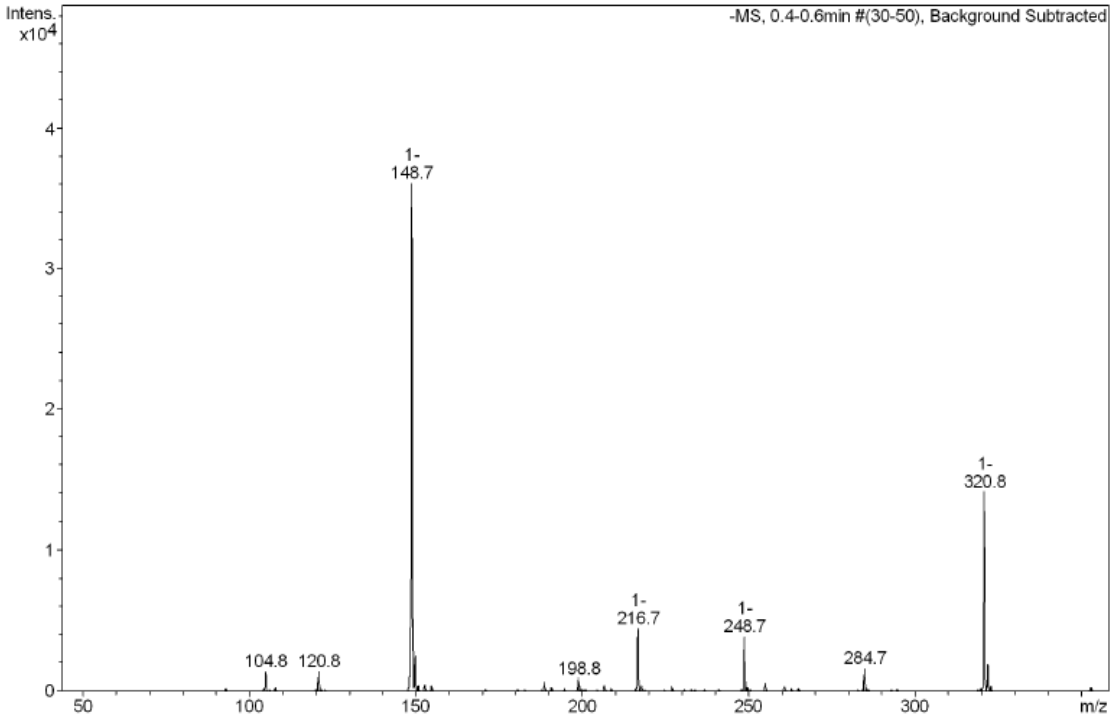


Figure S15. ESI-MS spectrum of **NaBF**.

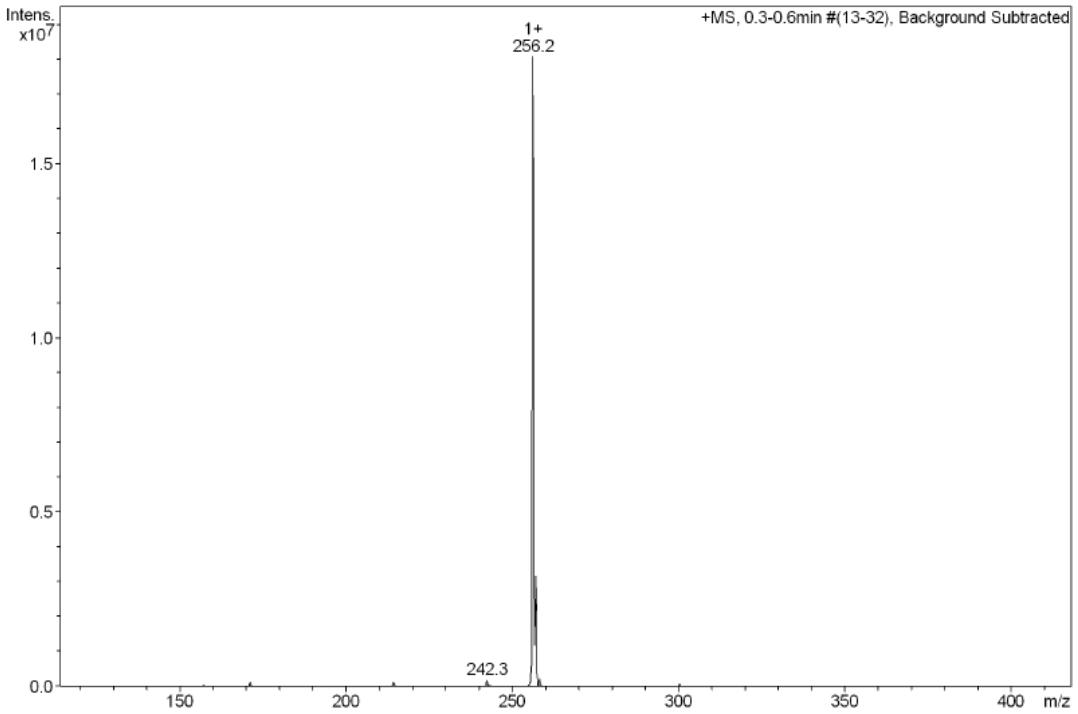


Figure S16. ESI-MS spectrum of of *i*Pr$_3$tacn.

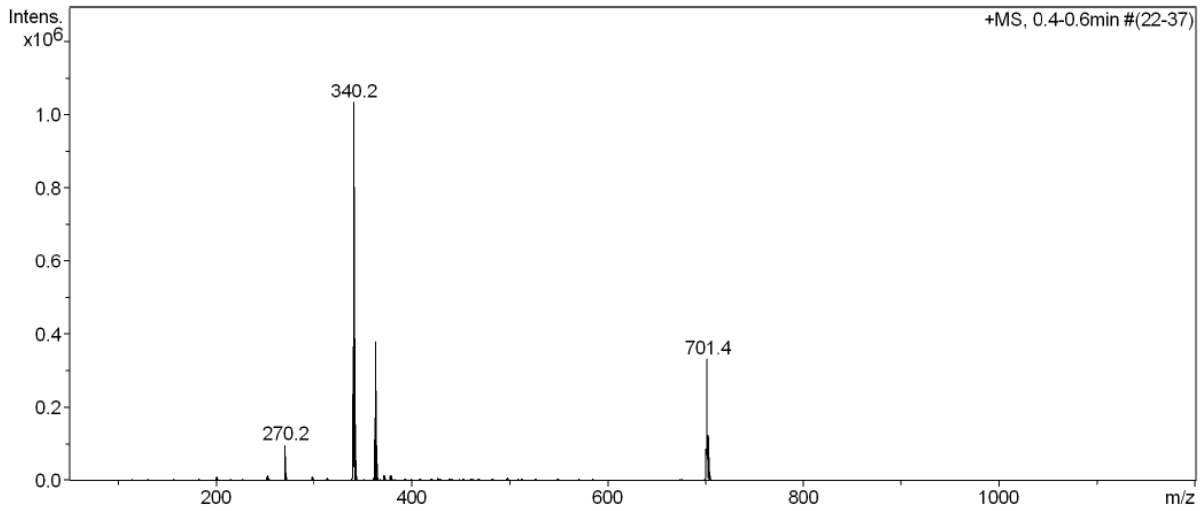


Figure S17. ESI-MS spectra of (*i*PrCO)$_3$tacn.

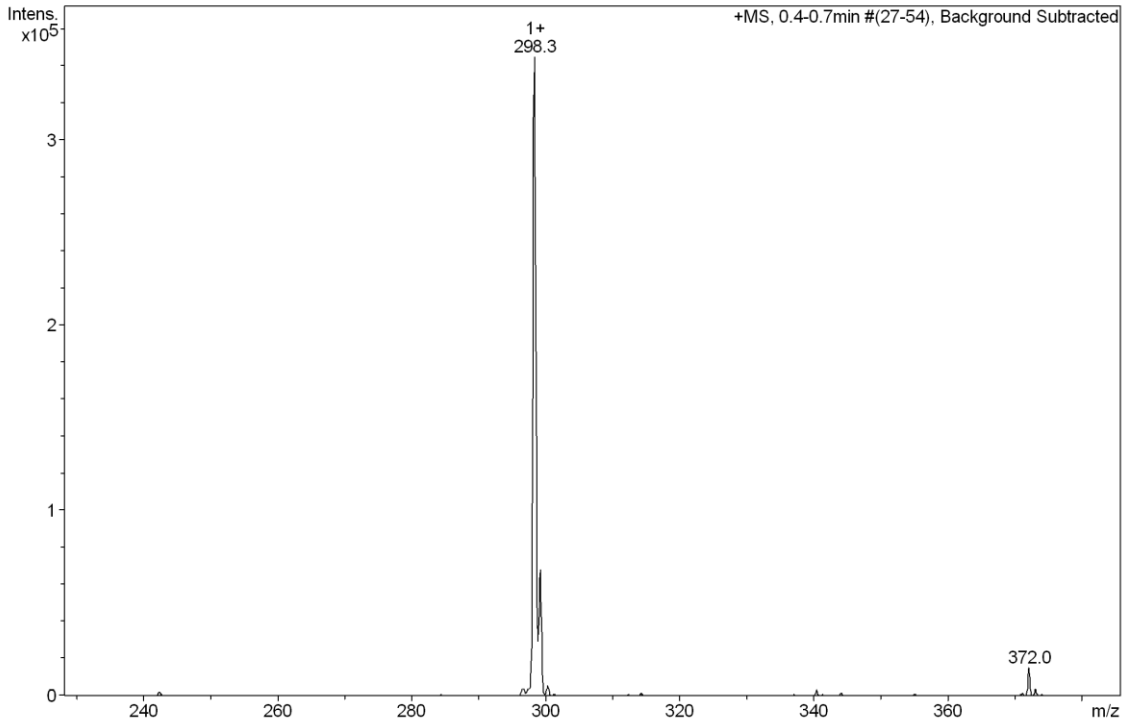


Figure S18. ESI-MS spectrum of of *i*Bu$_3$tacn.

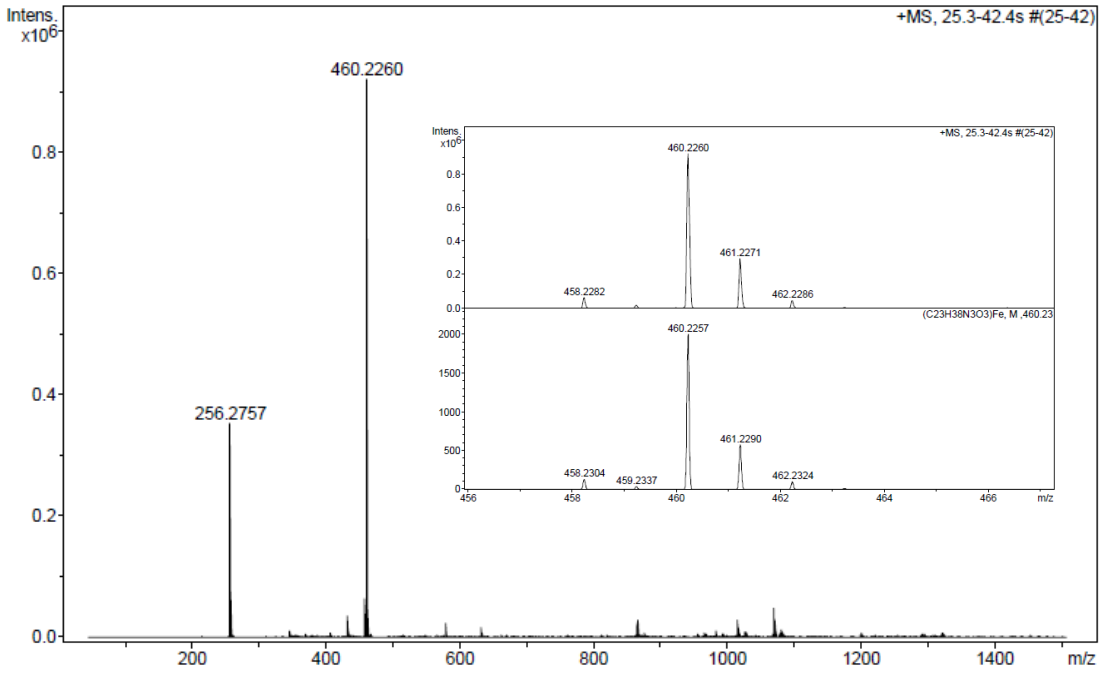


Figure S19. ESI-MS spectrum of **1BF** in CH_3CN. Inset: Isotopic distribution comparison between experimental and simulated data.

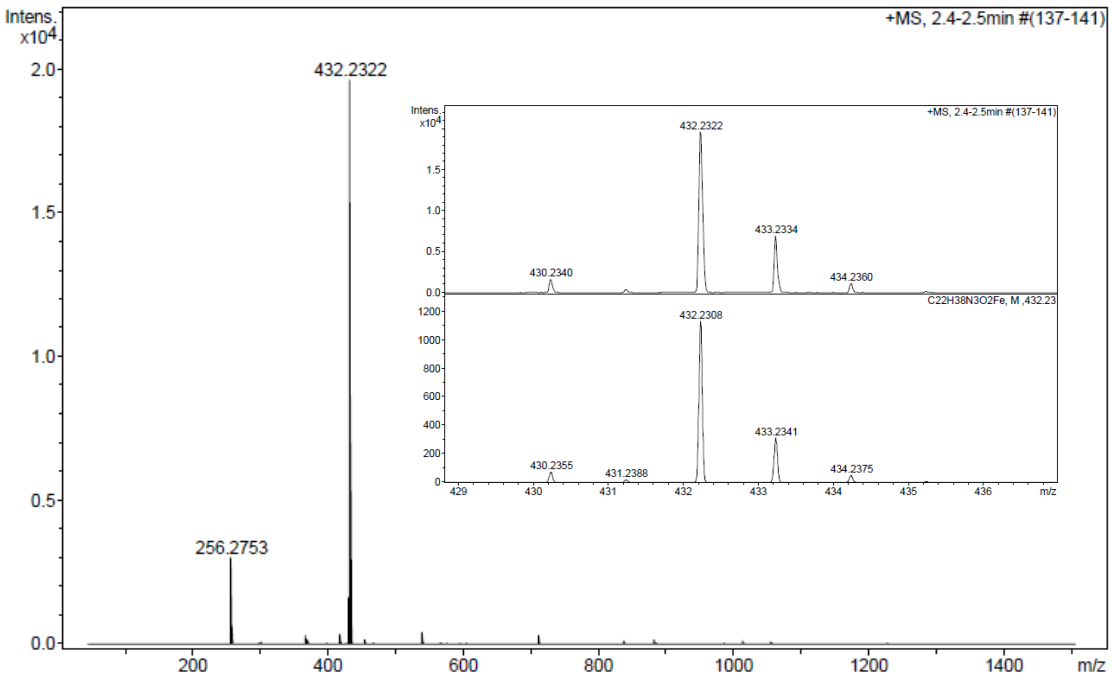


Figure S20. ESI-MS spectrum of **1Bz** in CH_3CN. Inset: Isotopic distribution comparison between experimental and simulated data.

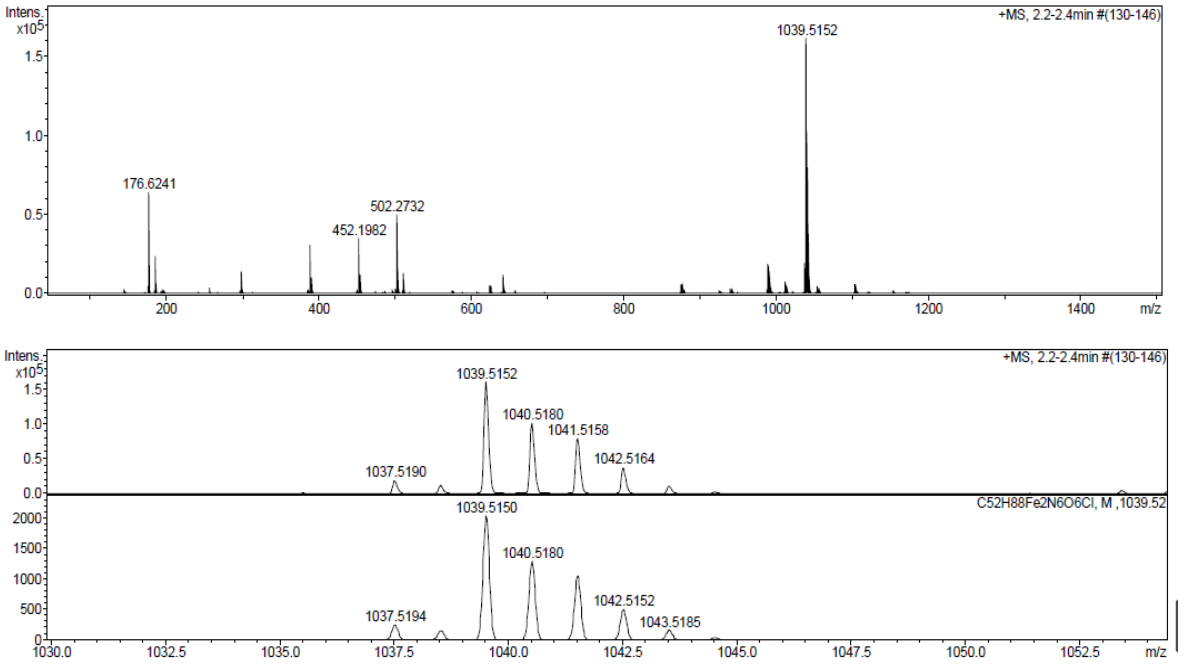


Figure S21. ESI-MS spectrum of **2BF-ClO$_4$** in CH_3CN. Inset: Isotopic distribution comparison between experimental and simulated data.

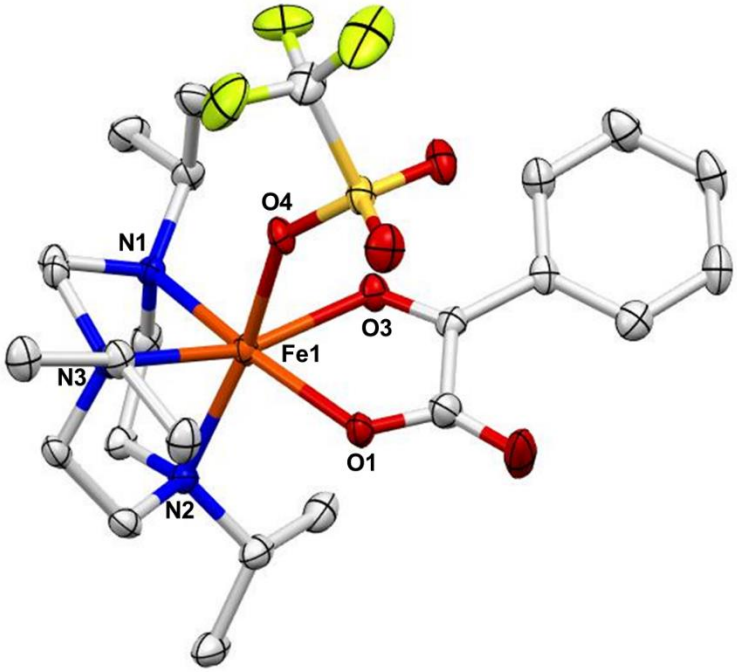
3. Crystallographic data

Table S1. Selected bond distances (Å) for **1BF**, **1Bz** and **2BF-ClO$_4$**.

1BF		**1Bz**		**2BF-ClO$_4$**	
Fe1-N1	2.247(2)	Fe1-N1	2.203(2)	Fe1-N1	2.261(3)
Fe1-N2	2.248(2)	Fe1-N1	2.2127(18)	Fe1-N2	2.252(3)
Fe1-N3	2.239(2)	Fe1-N4	2.159(2)	Fe1-N3	2.212(3)
Fe1-O1	2.0389(2)	Fe1-O1	2.0868(18)	Fe1-O1	2.105(2)
Fe1-O3	2.215(2)	Fe1-O2	2.3366(19)	Fe1-O4	2.101(2)
Fe1-O4	2.195(2)	Fe1-N3	2.203(2)	Fe1-Cl1	2.4513(10)
				Fe2-N4	2.220(3)
				Fe2-N5	2.220(3)
				Fe2-N6	2.243(3)
				Fe2-O2	2.112(2)
				Fe2-O5	2.093(3)
				Fe2-Cl1	2.4696(10)

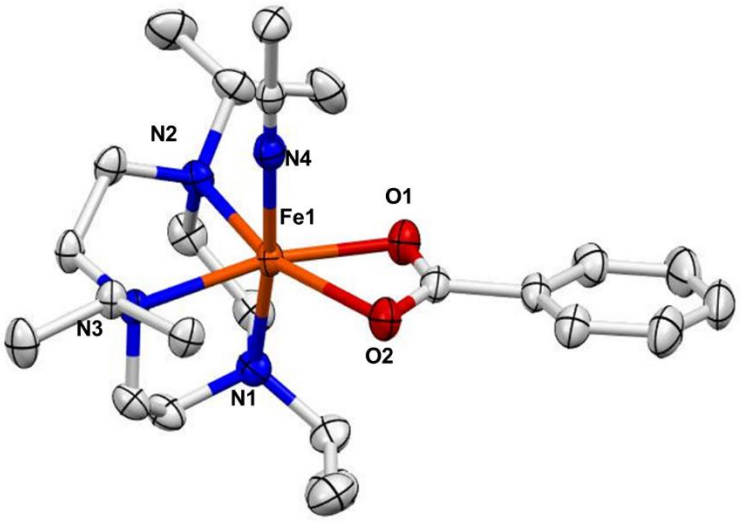
Table S2. Selected crystallographic data for **1BF**, **1Bz** and **2BF-ClO$_4$**

	1BF	**1Bz**	**2BF-ClO$_4$**
Formula	$C_{24}H_{38}F_3FeN_3O_6S$	$C_{27}H_{44}F_3FeN_5O_5S$	$C_{56}H_{98}Cl_2Fe_2N_6O_{11}$
Molecular weight	609.48	663.58	1214.00
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	P-1	P-1	P2(1)/n
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal color	Purple	Colourless-yellow	Orange
T (K)	293(2)	180.(2)	100(2) K
Size (mm)		0.1 x 0.1 x 0.1	0.25 x 0.14 x 0.14
a (Å)	9.1103(9)	10.8333(8)	12.832(3)
b (Å)	9.9440(10)	12.2736(8)	15.977(3)
c (Å)	15.5023(16)	13.0120(9)	30.509(6)
α (°)	77.338(2)	79.726(2)	90
β (°)	89.422(2)	74.064(2)	98.773(4)
γ (°)	88.622(2)	81.746(2)	90
V (Å^3)	1369.8(2)	1628.8(2)	6182(2)
hkl ranges	-12 ≤ h ≤ 12 -12 ≤ k ≤ 12 -8 ≤ l ≤ 19	-14 ≤ h ≤ 14 -16 ≤ k ≤ 16 -17 ≤ 1 ≤ 17	-16 ≤ h ≤ 16 -20 ≤ k ≤ 20 -39 ≤ l ≤ 39
ρ_{calc} (g cm^{-3})	1.478	1.353	1.304
Z	2	2	4
F(000)	640	700	2600
μ (mm^{-1})	0.691	0.586	0.616
θ range (°)	1.346 to 28.297	3.35 to 28.24	1.64 to 27.50
Absorption corr.		Multi-scan	Empirical
T_{max}, T_{min}	0.989, 0.886	0.94, 0.53	1.0, 0.896233
Refinement	Fsqd	Fsqd	Full-matrix least-squares on F^2
Reflections	6023	7986	14176
Data/restr./param.	6023 / 0 / 349	7986 / 0 / 445	14176 / 0 / 713
Goodness-of-fit	1.008	1.094	1.110
R	0.0777	0.0704	0.0965
R_w	0.1030	0.1385	0.1564
Peak, hole (e Å^3)	0.479, -0.352	0.648, -0.576	1.063, -0.514



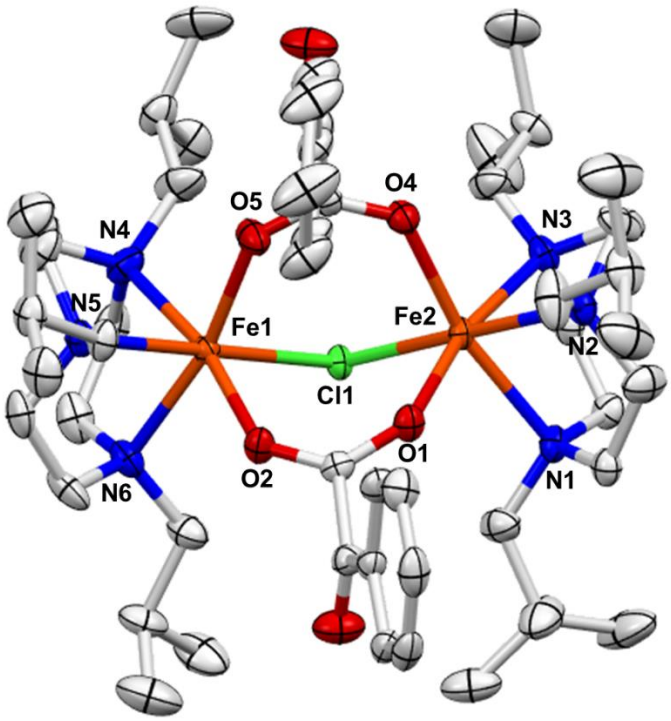
1BF

Figure S22. Mercury diagram at 30% of probability level of **1BF**. Hydrogens and counteranion CF_3SO_3 were removed for clarity.



1Bz

Figure S23. Mercury diagram at 30% of probability level of **1Bz**. Hydrogens and counteranion CF_3SO_3 were removed for clarity.



2BF·ClO$_4$

Figure S24. Mercury diagram at 30% of probability level of **2BF·ClO$_4$**. Hydrogens and counteranion ClO$_4$ were removed for clarity.

4. O_2 reactivity

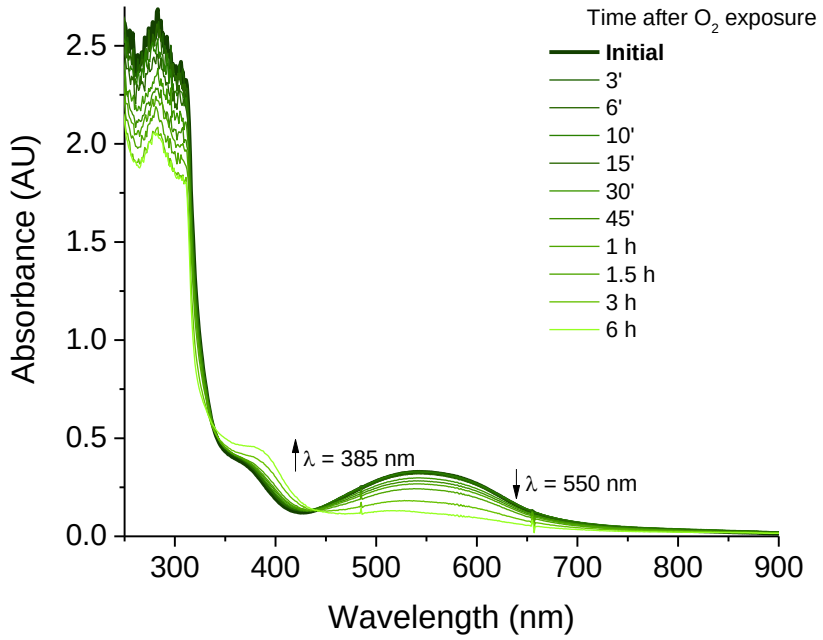


Figure S25. UV-Vis spectra of the reaction of **1BF** with O_2 ([Fe] = 1.3 mM) in CH_3CN at 25°C

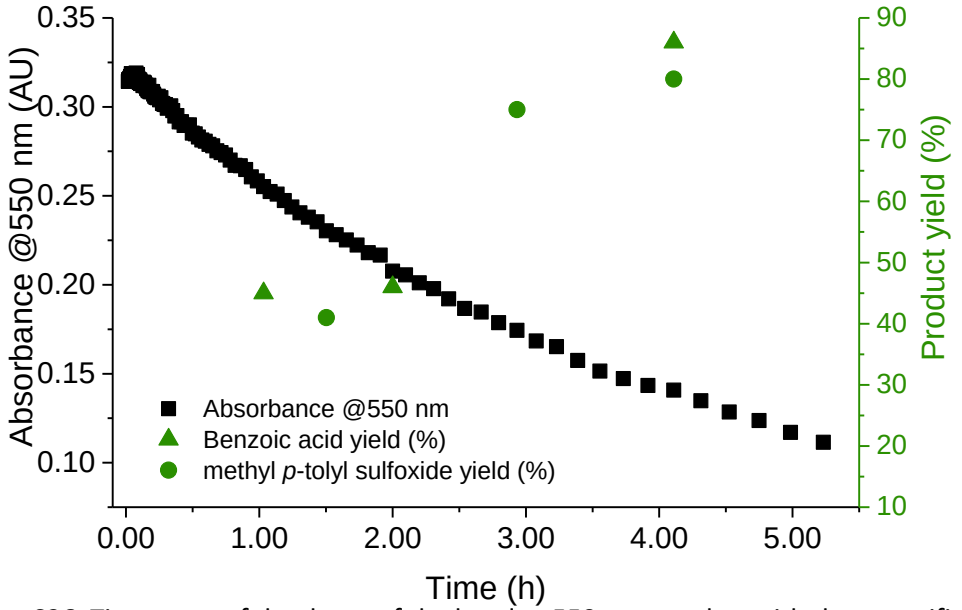


Figure S26. Time trace of the decay of the band at 550nm together with the quantification over time of the production of HBz and methyl *p*-tolyl sulfoxide for the reaction of **1BF** and O_2 in CH_3CN at 25°C. k_{obs} = (6.3 ± 0.1) x 10^{-5} s^{-1} (τ = 183 min)

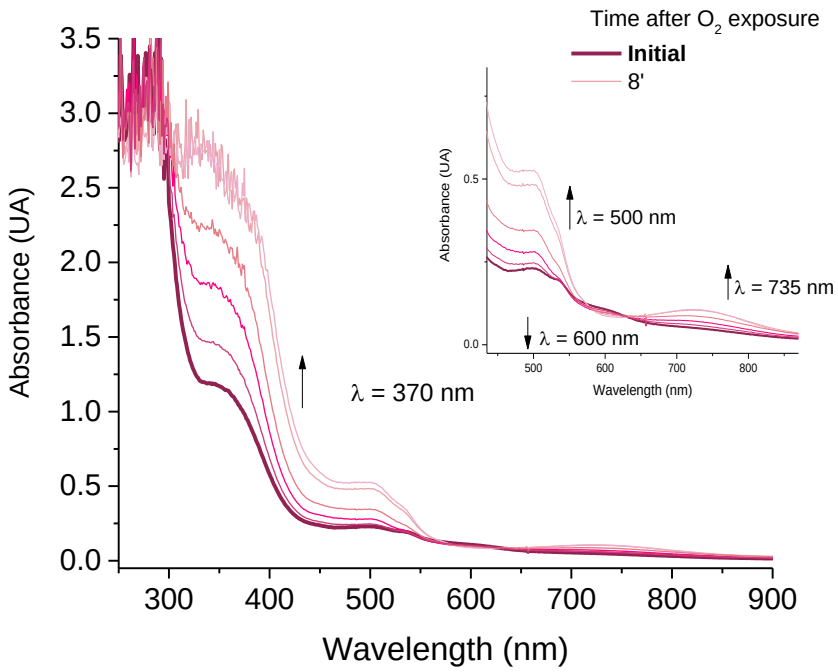


Figure S27. UV-vis spectra of the reaction of **2BF-ClO$_4$** with O_2 ([Fe] = 1.3 mM) in CH_3CN at 25°C.

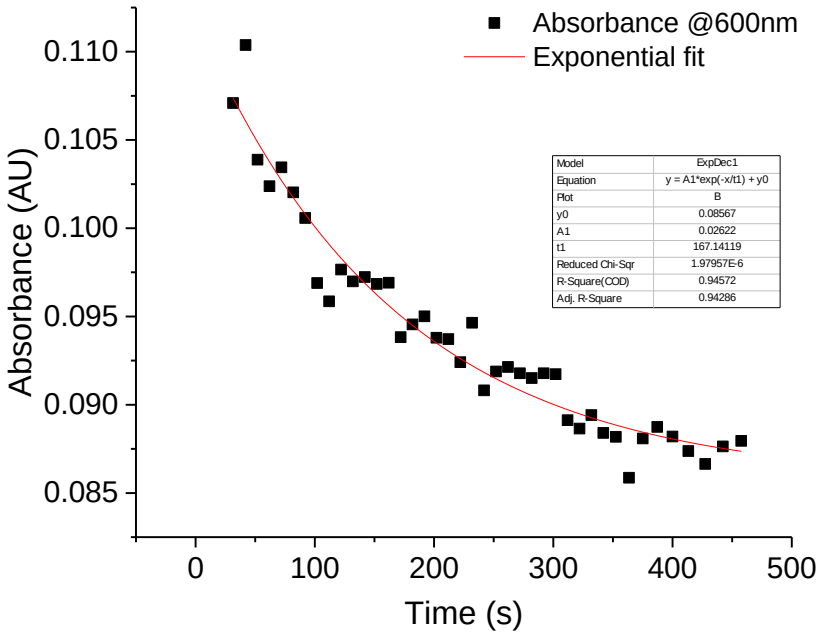


Figure S28. Time trace of the decay of the band at 600 nm from the reaction of **2BF-ClO$_4$** with O_2 in CH_3CN at 25°C. k_{obs} = (5.9 ± 0.1) x 10^{-3} s^{-1} (τ = 1.9 min)

5. Mechanistic studies

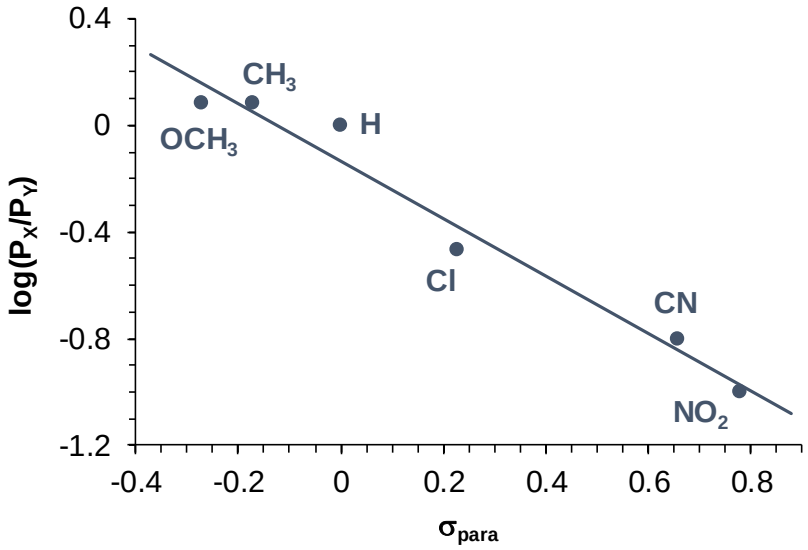


Figure S29. Hammett plot for the oxygenation of **1BF** in the presence of *p*-X-thioanisoles obtained in competition experiments by analysis of the final product mixtures.

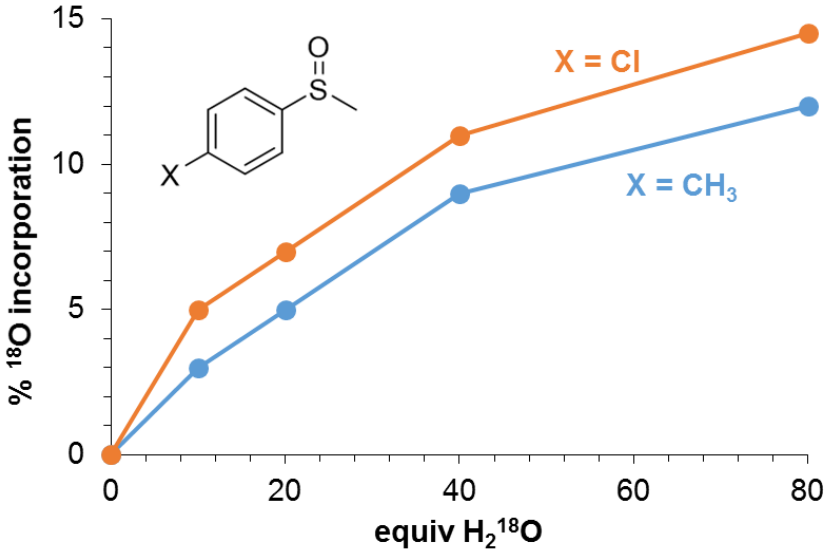


Figure S30. Incorporation of ^{18}O into the sulfoxide product obtained in the oxygenation of **1BF** in the presence of 100 equiv *p*-Cl-thioanisole or *p*-CH_3-thioanisole and variable amounts of $H_2{}^{18}O$ (from 0 to 80 equiv).

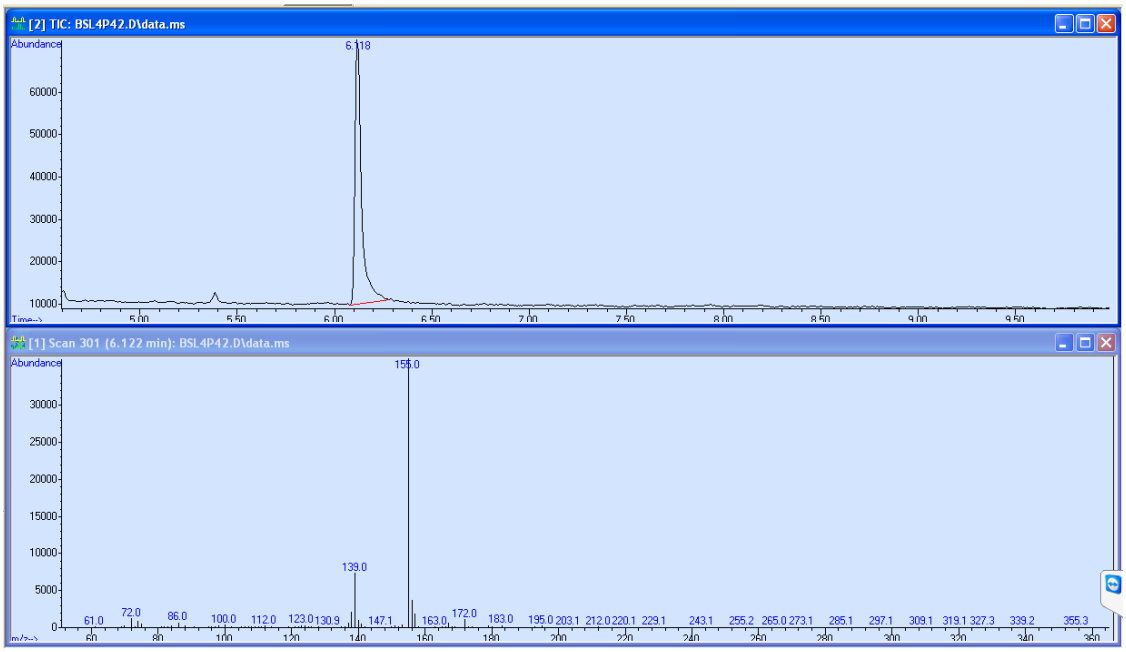


Figure S31. GC-MS spectrum of methyl *p*-tolyl sulfoxide formed from the oxidation of methyl *p*-tolyl sulfide in the reaction of **1BF** with $^{16}O_2$.

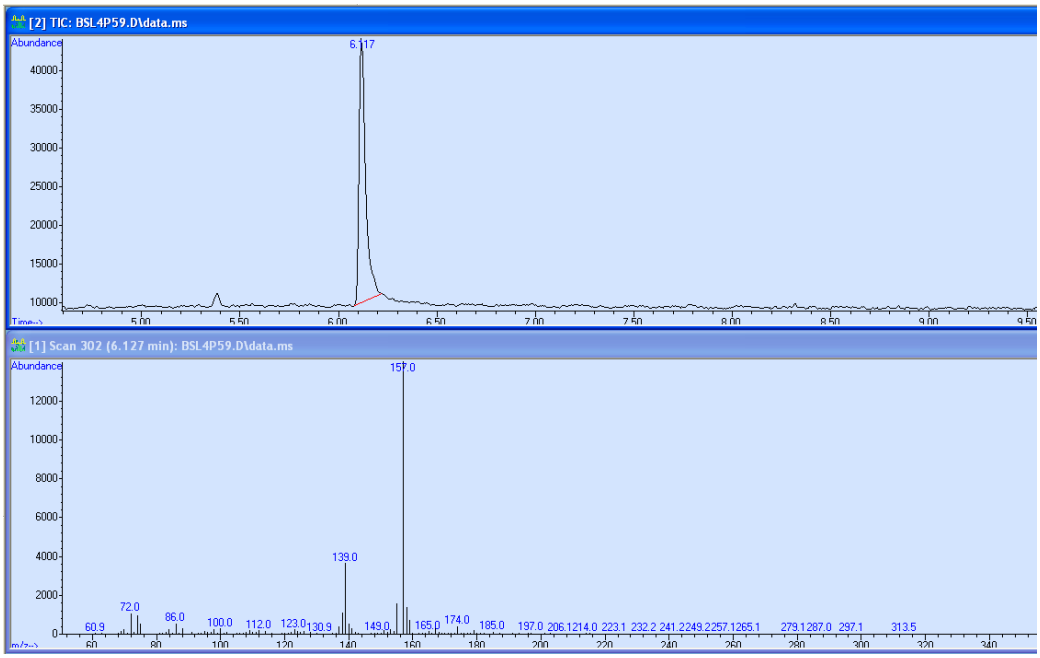


Figure S32. GC-MS spectrum of methyl *p*-tolyl sulfoxide formed from the oxidation of methyl *p*-tolyl sulfide in the reaction of **1BF** with $^{18}O_2$, exhibiting 90% ^{18}O-incorporation.

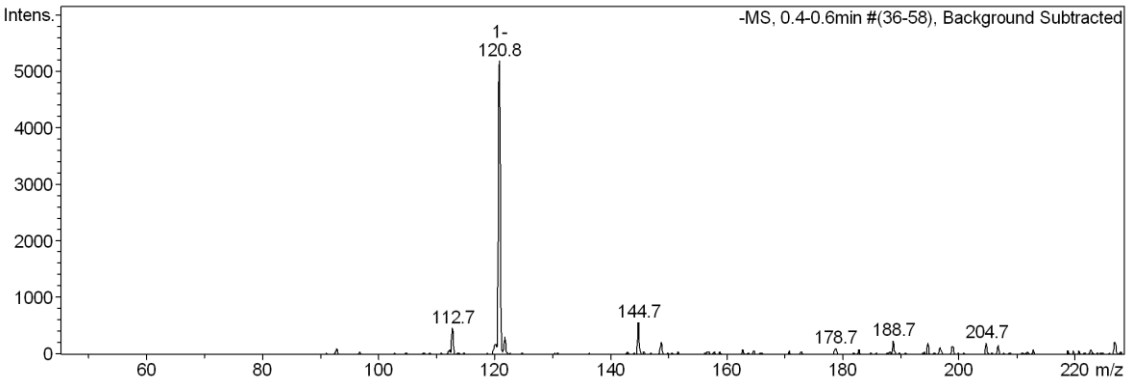


Figure S33. ESI-MS spectrum of benzoic acid formed after the oxidation of methyl *p*-tolyl sulfide in the reaction of **1BF** with $^{16}O_2$.

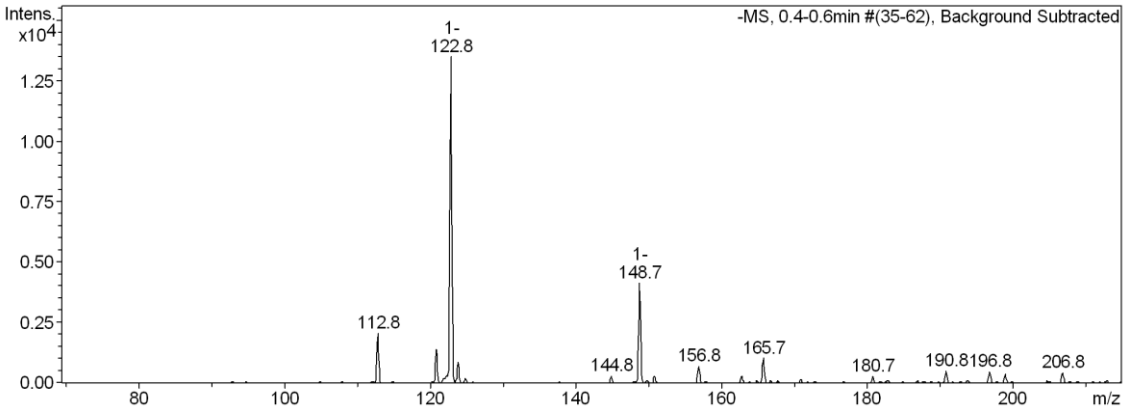


Figure S34. ESI-MS spectrum of benzoic acid formed after the oxidation of methyl *p*-tolyl sulfide in the reaction of **1BF** with $^{18}O_2$, exhibiting 90% ^{18}O-incorporation.

6. Catalytic studies

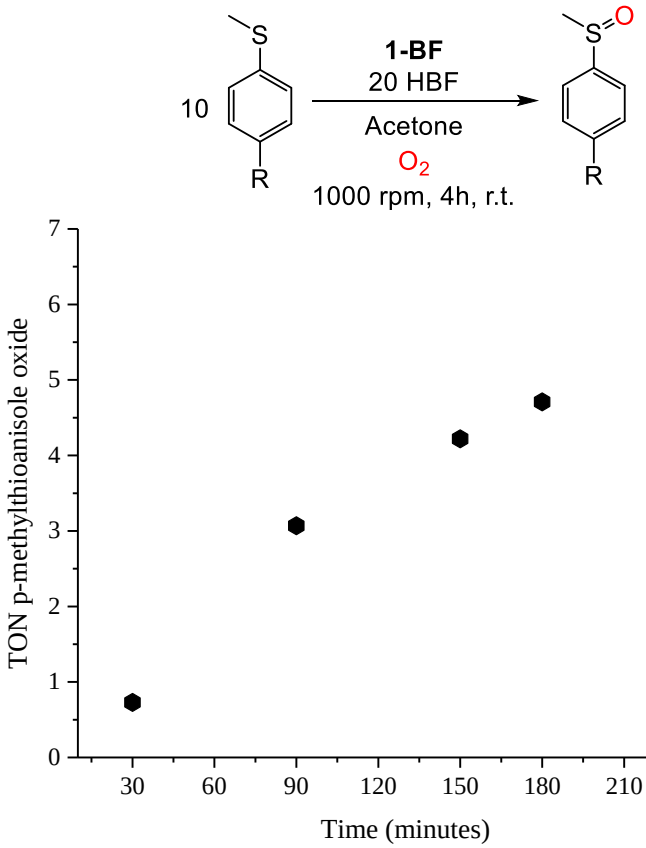


Figure S35. Formation of methyl *p*-tolyl sulfoxide over time in the oxygenation of methyl *p*-tolyl sulfide catalyzed by **1BF**.

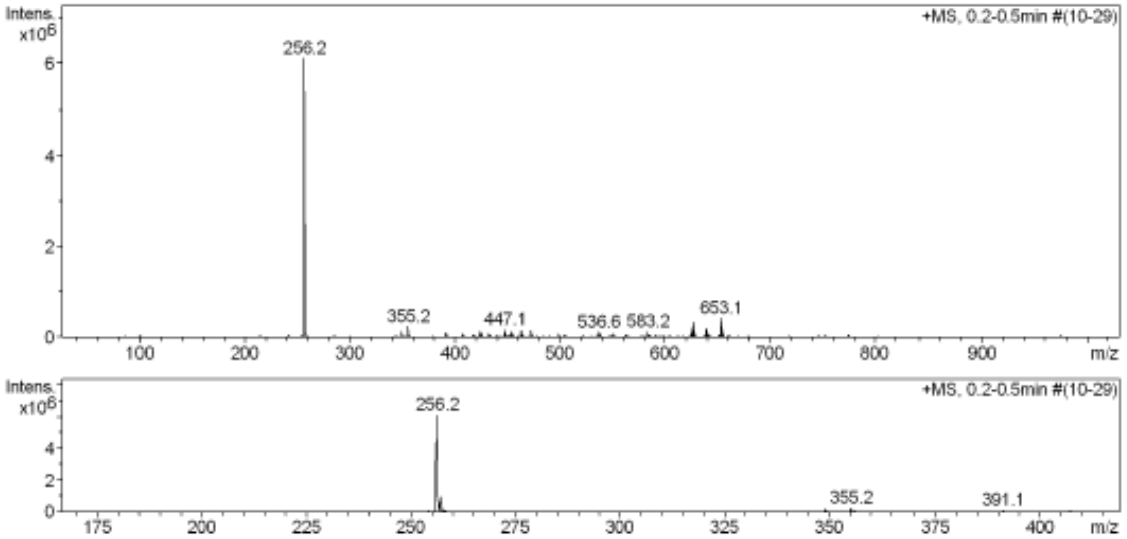
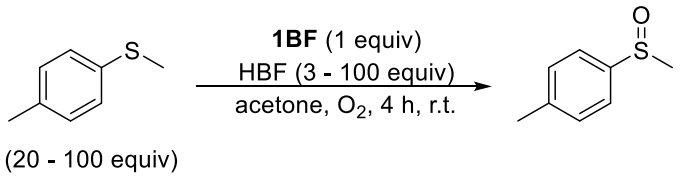


Figure S36. ESI-MS spectrum after the reaction of **1BF** with O_2. Peak at m/z = 256.2 corresponds to the protonated form of *i*Pr$_3$tacn.

Table S3. Screening of catalytic conditions



entry	HBF (equiv)	sulfide (equiv)	sulfoxide (TN)	Observations/hypothesis
1	20	20	8	**Reference reaction**
				Addition of reducing agents aiming at restoring deactivated ferric species
2	10	20	8	1 equiv. ascorbic acid (0.5 equiv added after 2h and 4h).
3	20	20	3	0.5 equiv. DDT added after 2 h
				Addition of sulfoxide to test possible product inhibition
4	10	20	7	Reaction run in the presence of 10 equiv thioanisole sulfoxide
				Addition of Fe(II) aiming at restoring activity by binding to the demetallated ligand
5	10	20	7	0.5 equiv $[Fe(CF_3SO_3)_2(CH_3CN)_2]$ and 0.5 equiv NaBF added after 2h
6	20	20	9	0.5 equiv $[Fe(CF_3SO_3)_2(CH_3CN)_2]$ and 0.5 equiv NaBF added after 2h
7	10	20	7	0.5 equiv $[Fe(CF_3SO_3)_2(CH_3CN)_2]$ added after 2h
8	20	20	7	0.5 equiv $[Fe(CF_3SO_3)_2(CH_3CN)_2]$ added after 2h
				Addition of HBF using syringe pump
9	20	20	5	HBF added by syringe pump during 2h
10	15	20	6	HBF added by syringe pump during 4h

7. References

1.- Kang, J.; Jo, J. H. *Bull. Korean Chem. Soc.* **2003**, *24* , 1403.

2.- Nakanishi, S. I.; Kawamura, M.; Kai, H.; Jin, R. H.; Sunada, Y.; Nagashima, H. *Chem. - A Eur. J.* **2014**, *20*, 5802.

3.- Sessler, J. L.; Sibert, W. J.; Lynch, V. *Inorganica Chim. Acta* **1994**, *216*, 89.