Supporting Information

for

Manganese Corrole Catalyzed Selective Oxidation of Styrene to Benzaldehyde: Sodium Nitrite Functions as Oxidant and Cocatalyst

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1. Optimization of Reaction Conditions

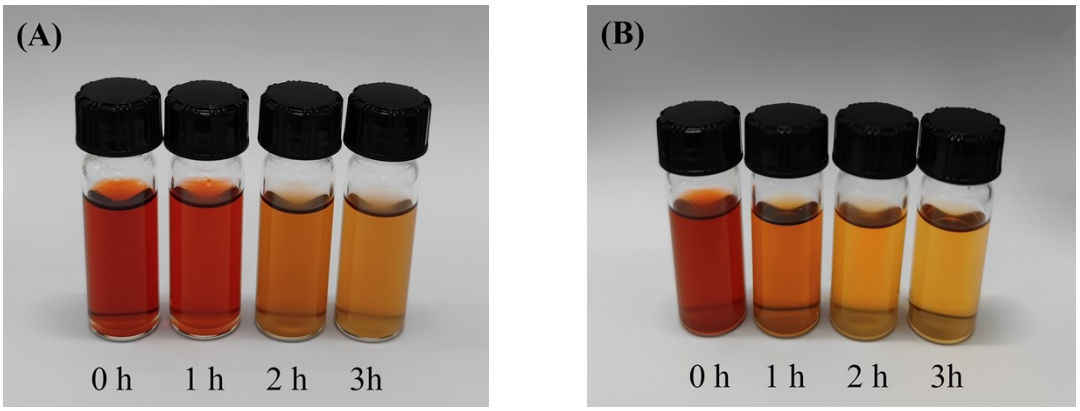


Figure S1 The color reaction of sodium nitrite/ aniline α-naphthol for monitoring sodium nitrite consuming in the catalytic reaction. (A) Open to the air, (B) Under the nitrogen atmosphere.

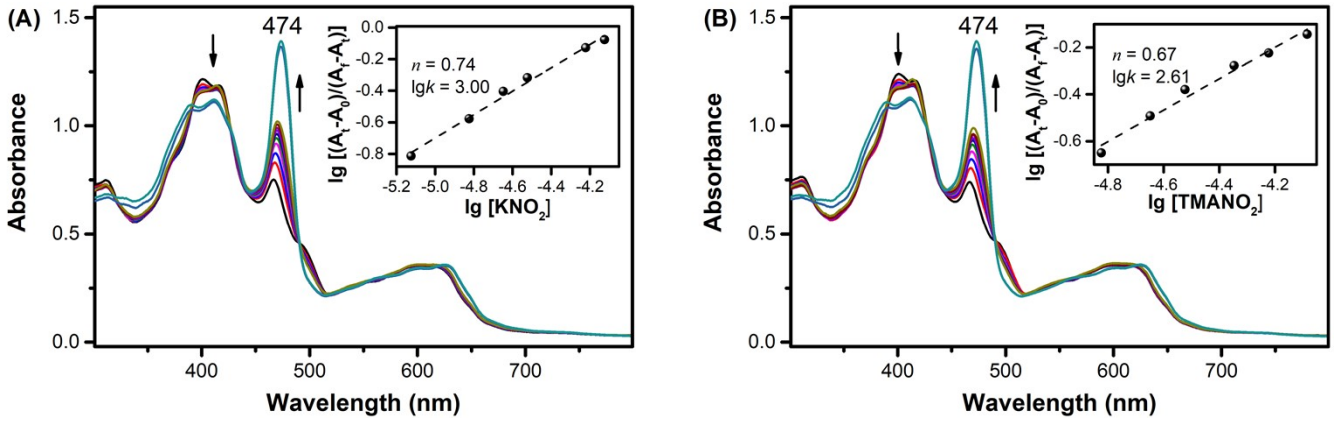


Figure S2 UV-vis spectral changes of [(F_{15}TPC) Mn^{III}] upon the addition of KNO_2 (A) and $TMANO_2$ (B) in CH_3CN solution at 25±0.1 °C.

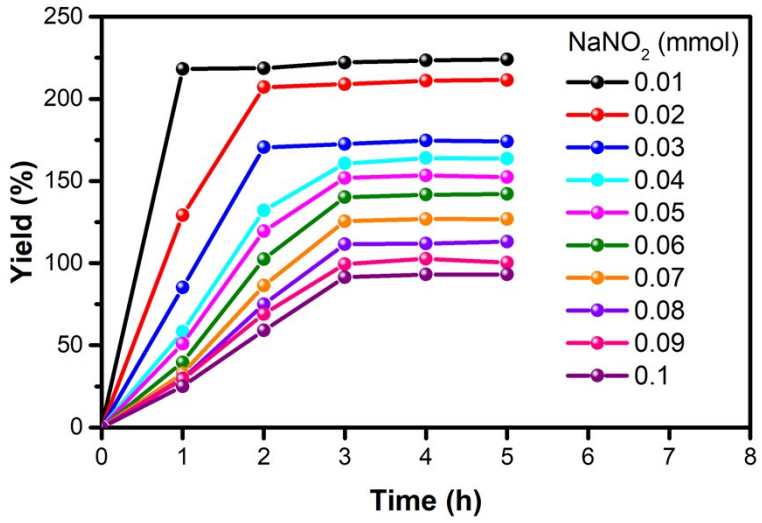


Figure S3 Time courses of the yield of produced benzaldehyde for oxidation of styrene (1 mmol) by [(F_{15}TPC)Mn^{III}] (1 μmol) with different concentrations of aqueous solution of 5 M $NaNO_2$ (0.01-0.1 mmol) in 2 mL CH_3CN at room temperature.

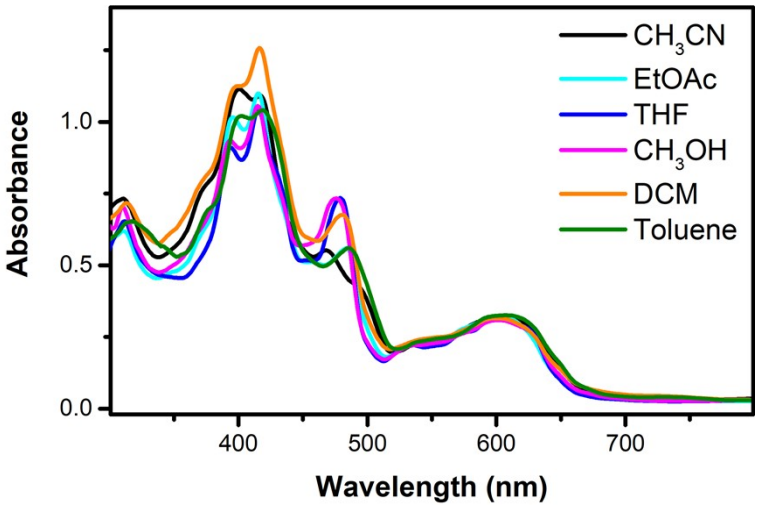


Figure S4 UV-vis spectral of [(F_{15}TPC)Mn^{III}] in different solvents.

Table S1 Effect of different catalysts and solvents on the selective oxidation of styrene.

			Yield (%)[b]			Total	TON	Select(%)
Entry[a]	Catalyst	Solvent	BA	PA	SO			BA
1	$[(F_{15}TPC)Mn^{III}]$	EtOAc	55	N.D.	0.4	55.4	27.7	99.3
2[c]	$[(F_{15}TPC)Mn^{III}]$	Toluene	45.8	N.D.	1.3	47.1	23.6	97.2
3	$[(F_{15}TPC)Mn^{III}]$	CH_3OH	N.D.	N.D.	N.D.			
4	$[(F_{15}TPC)Mn^{III}]$	THF	N.D.	N.D.	N.D.			
5	$[(F_{15}TPC)Mn^{III}]$	DCM	N.D.	N.D.	N.D.			
6	$[(F_{10}TPC)Mn^{III}]$	CH_3CN	78.2	N.D.	Trace	78.2	39.1	> 99
7	$[(F_5TPC)Mn^{III}]$	CH_3CN	15.4	N.D.	Trace	15.4	7.7	> 99
8	$[(F_0TPC)Mn^{III}]$	CH_3CN	3.2	N.D.	Trace	3.2	1.6	> 99
9	$[(F_{20}TPP)Mn^{III}]$	CH_3CN	N.D.	N.D.	N.D.			
10	MnO_2	CH_3CN	N.D.	N.D.	N.D.			
11	K_2MnO_4	CH_3CN	N.D.	N.D.	N.D.			
12	$KMnO_4$	CH_3CN	N.D.	N.D.	N.D.			
13	Mn $(OAc)_2$	CH_3CN	N.D.	N.D.	N.D.			

[a] Reaction conditions: catalyst (1 μmol), 0.05 mmol $NaNO_2$ (5 M aqueous solution, 10 μL) and 1 mmol styrene were mixed in 2 mL CH_3CN and stirred for 3 h at room temperature open to air. [b] Yields are determined by GC based on the amount of $NaNO_2$ used. [c] 12 h. N.D.= Not detected.

2. Characterization of Intermediate

Intermediate Na[(F_{15}TPC)$Mn^{III}(NO_2)$] (**1**)

Na[(F_{15}TPC)$Mn^{III}(NO_2)$] (**1**) intermediate was generated by adding Sodium nitrite ($NaNO_2$, 2 equiv, 0.060 mM) into a UV−vis cuvette containing a CH_3CN solution of [(F_{15}TPC)Mn^{III}] (0.030 mM) under air atmosphere at 25 °C. Formation of **1** with an absorption band at 474 nm. UV-vis (CH_3CN)**:** λ_{max} [nm] (lg ε) = 390 (4.42), 412 (4.44), 474 (3.53), 600 nm (3.89).

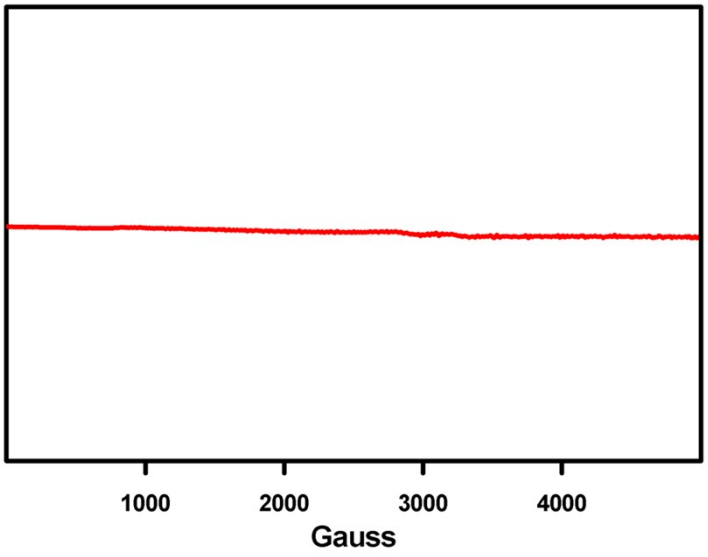


Figure S5 1 was EPR X-band EPR spectrum of Na[(F_{15}TPC)$Mn^{III}(NO_2)$](**1**) produced by mixed [(F_{15}TPC)Mn^{III}] (0.5 mmol) with $NaNO_2$ (10 mmol) in 5 mL CH_3CN, confirm the formation of **1** by UV-vis, and then remove excess $NaNO_2$. Spectrum was recorded at 5 K.

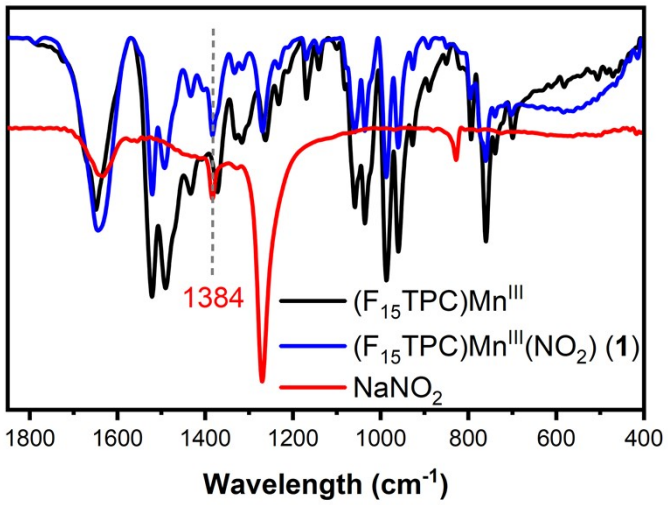


Figure S6 FT-IR of [(F_{15}TPC)Mn^{III}], [(F_{15}TPC)Mn^{III}(NO_2)] (**1**) and $NaNO_2$.

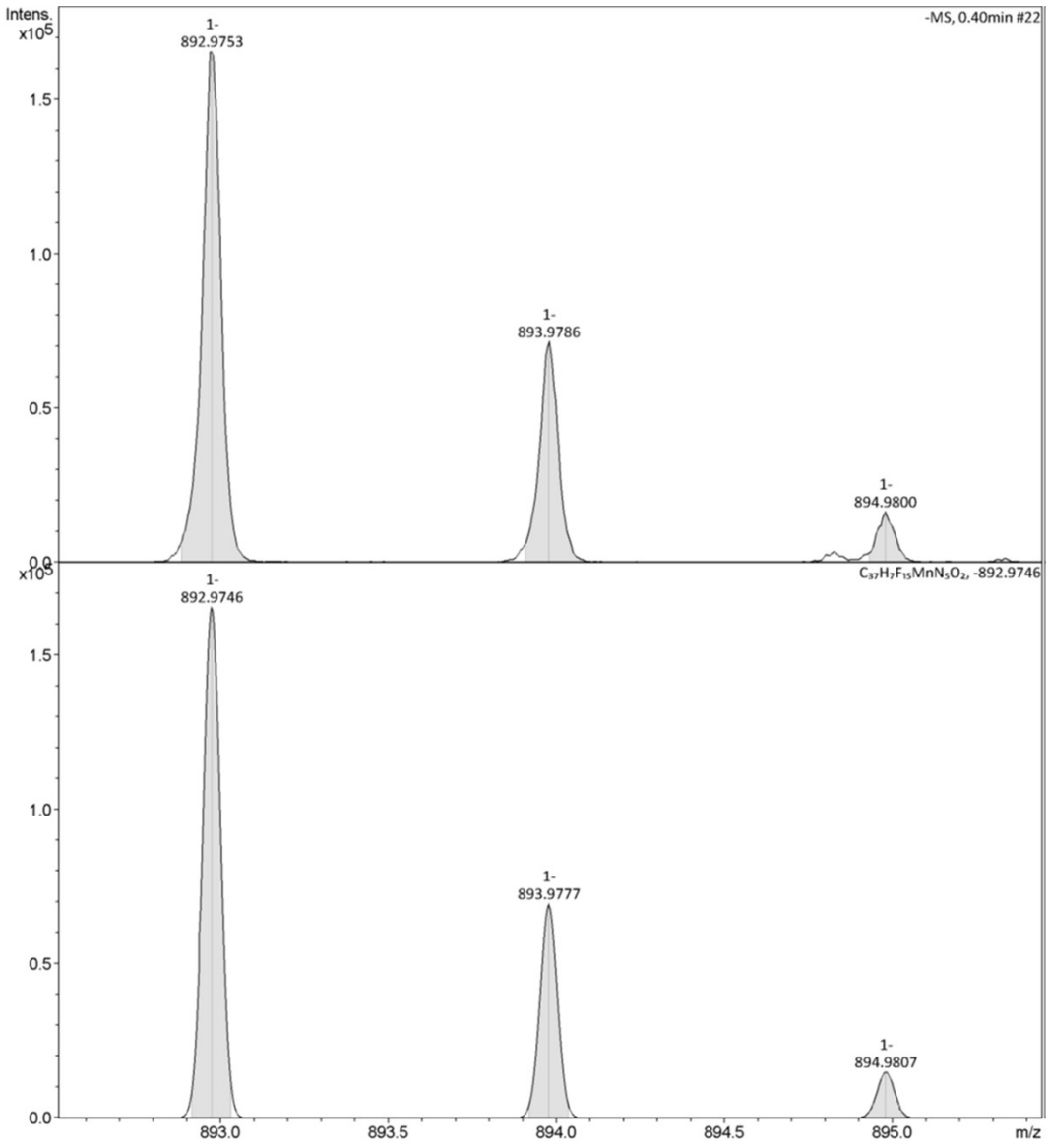


Figure S7 HRMS spectrum of $[(F_{15}TPC)Mn^{III}(NO_2)]$ in mixed CH_3CN solution of $[(F_{15}TPC)Mn^{III}]$(30 μM) with $NaNO_2$ (2 eq).

Intermediate [(F_{15}TPC)Mn^{V}(O)] (2)

[(F_{15}TPC)Mn^{V}(O)] (**2**) was produced by adding $NaNO_2$ (2 equiv, 0.060 mM) and a small amount of styrene into a CH_3CN solution of [(F_{15}TPC)Mn^{III}] (0.030 mM) under air at 25 °C. Formation of **2** was confirmed by monitoring UV−vis spectral changes at 472 and 600 nm due to the decay of [(F_{15}TPC)Mn^{III}] and at 346 and 406 nm due to the formation of **2**. UV-vis (CH_3CN)**:** λ_{max} [nm] (lg ε) = 346 (4.53), 406 (4.54), 520 (3.92). HRMS(ESI):m/z calcd for $C_{37}H_8F_{15}N_4MnO+H^+$: 864.9912 $[M+H]^+$; found: 864.9903.

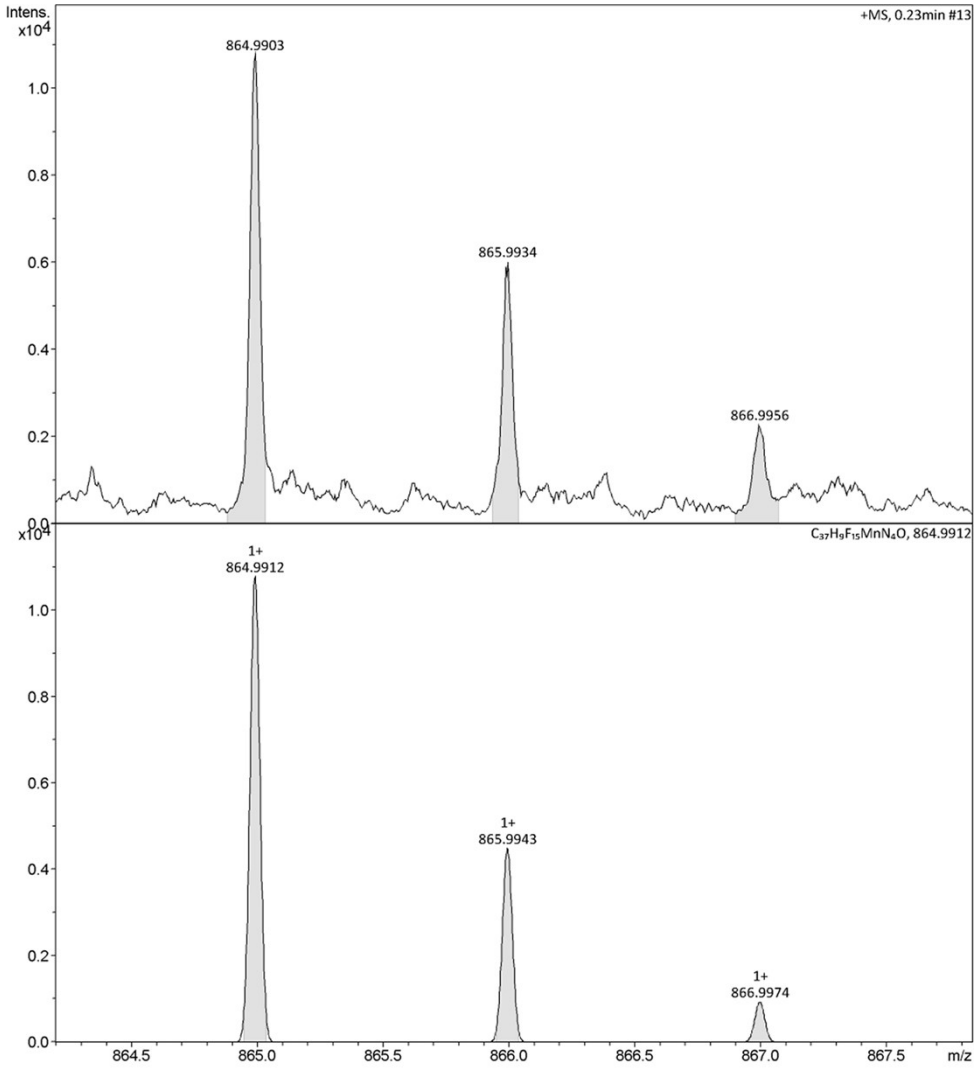


Figure S8 Situ HRMS spectrum of [(F_{15}TPC)Mn^{V}(O)] species in the reaction mixture.

Intermediate [(F_{15}TPC)$Mn^{V}(O_2)$]

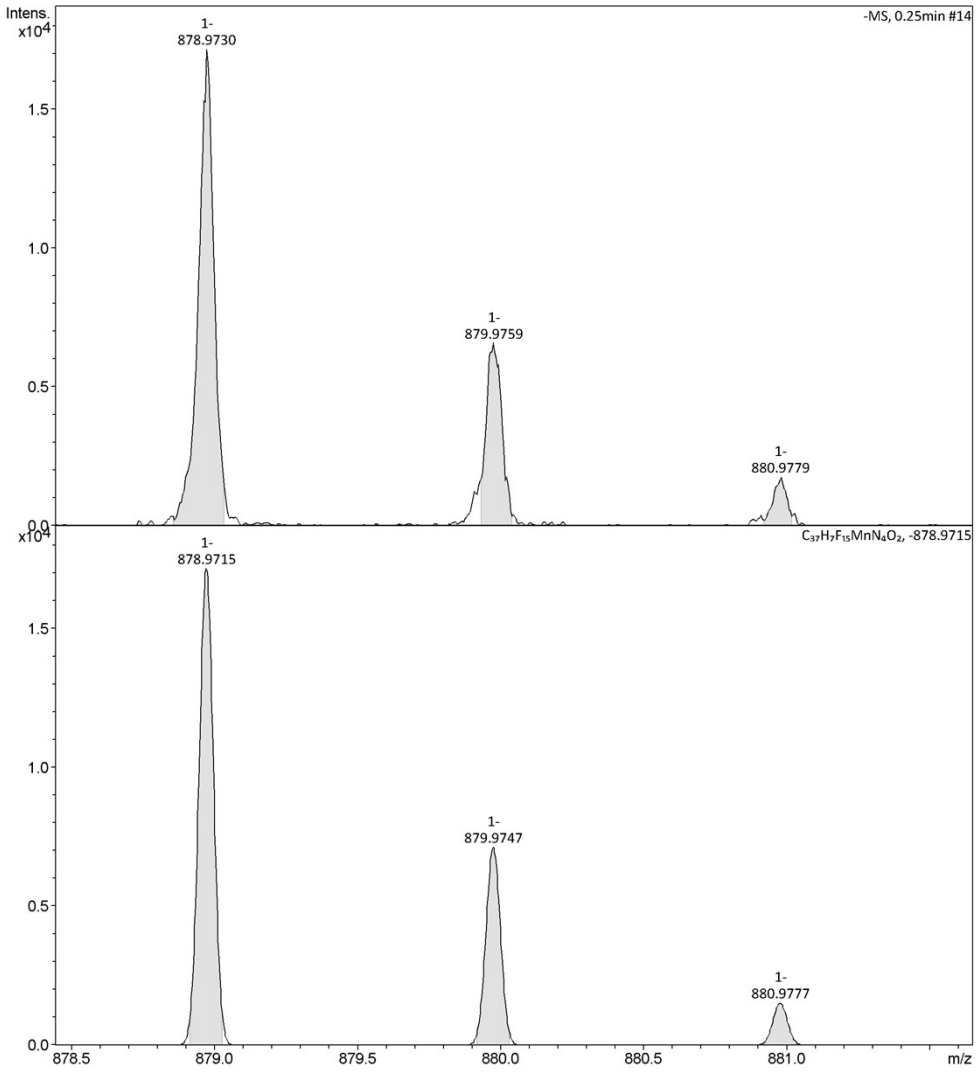


Figure S9 Situ HRMS spectrum of [(F_{15}TPC)$Mn^{V}(O_2)$] species in the reaction mixture.

3. Mechanism Exploration

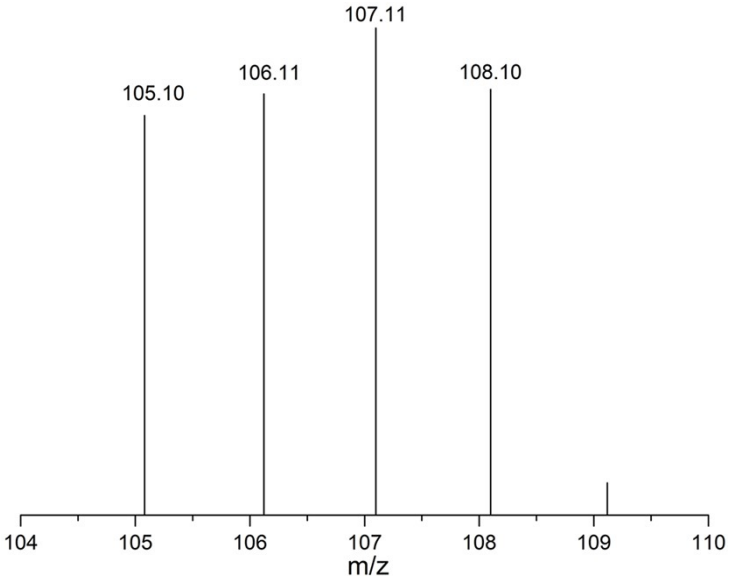


Figure S10 GC-MS spectrum of product of catalytic reaction of styrene with [(F_{15}TPC)Mn^{III}] using $NaNO_2$ as oxidant in the presence of $H_2{}^{18}O$.

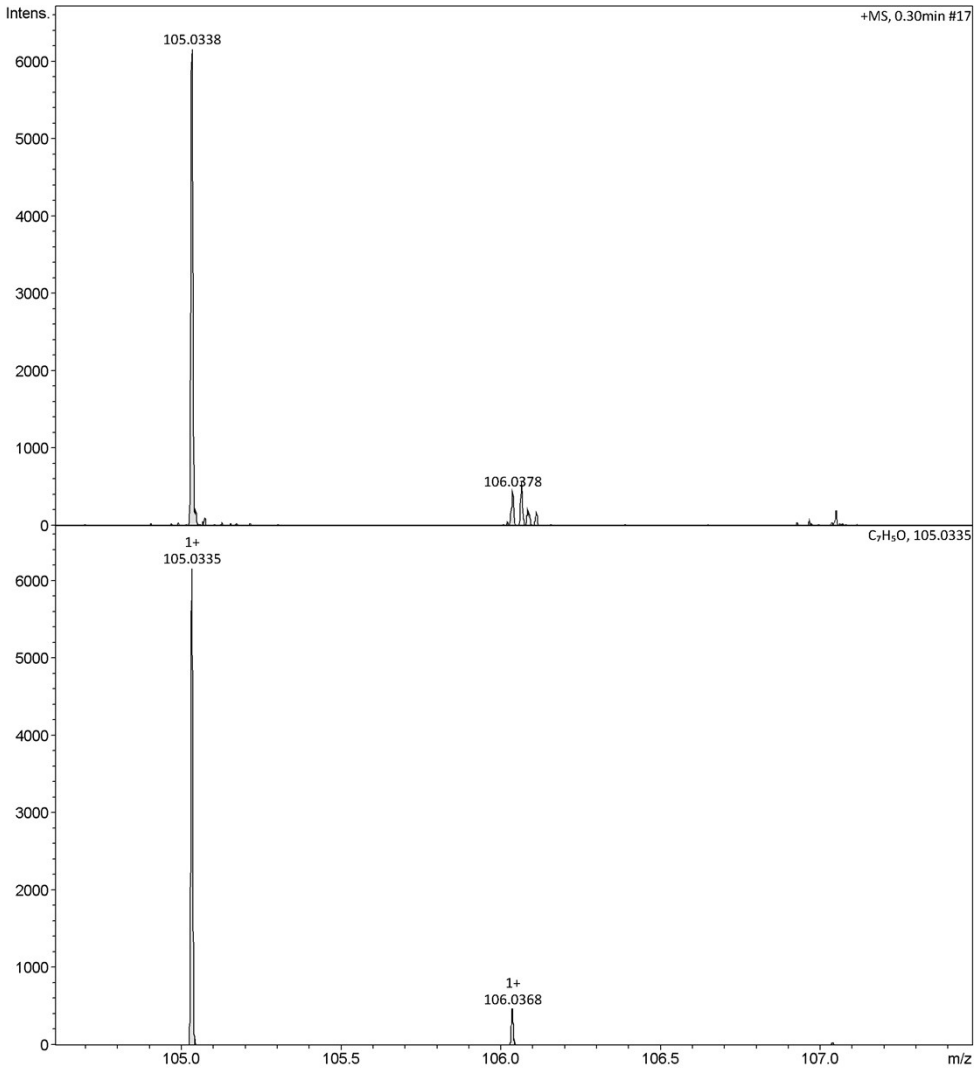


Figure S11 HRMS spectrum of benzaldehyde: CH_3CN (2 mL) solution containing 100 μL $H_2{}^{18}O$, benzaldehyde (400 μmol) and [(F_{15}TPC)Mn^{III}] (1 μmol).

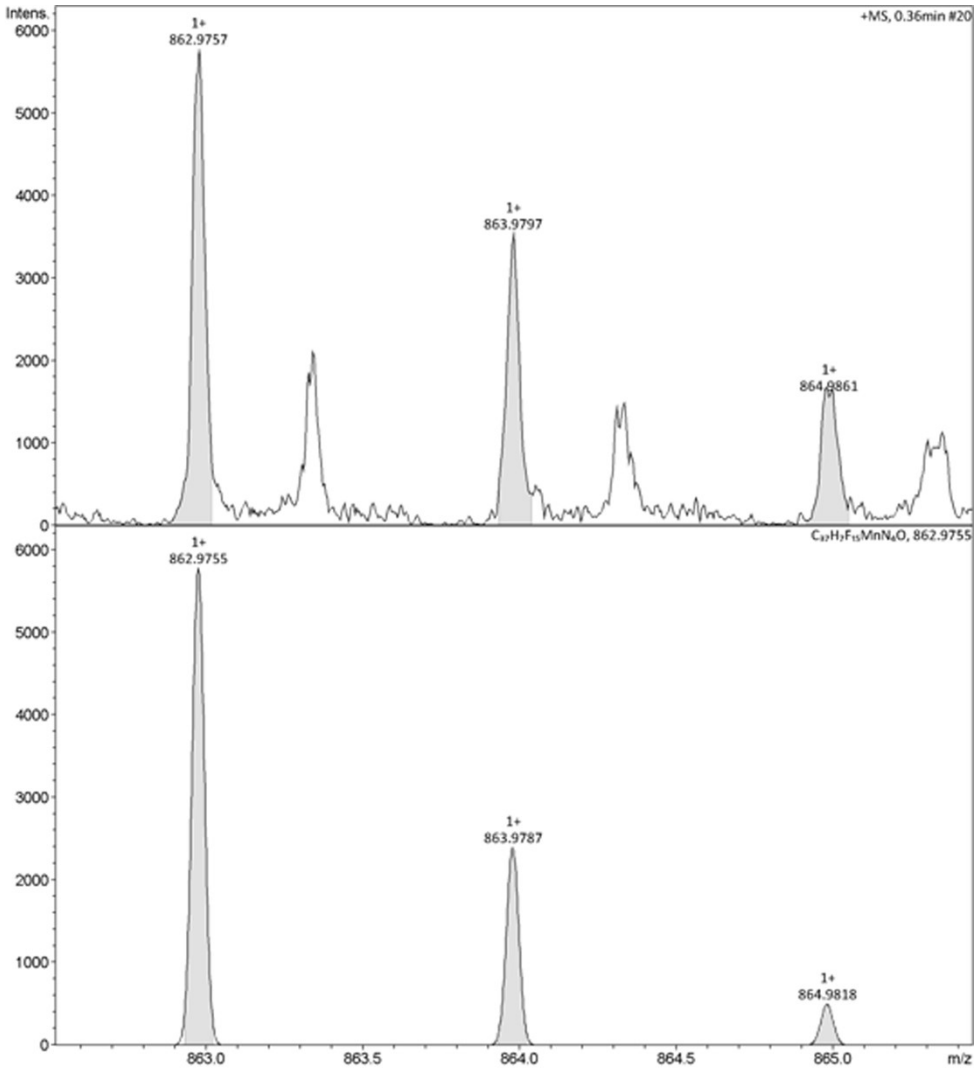


Figure S12 Situ HRMS spectrum of [(F_{15}TPC)Mn^{V}(O)] (**2**) after added 50 μL $H_2{}^{18}O$ in CH_3CN.

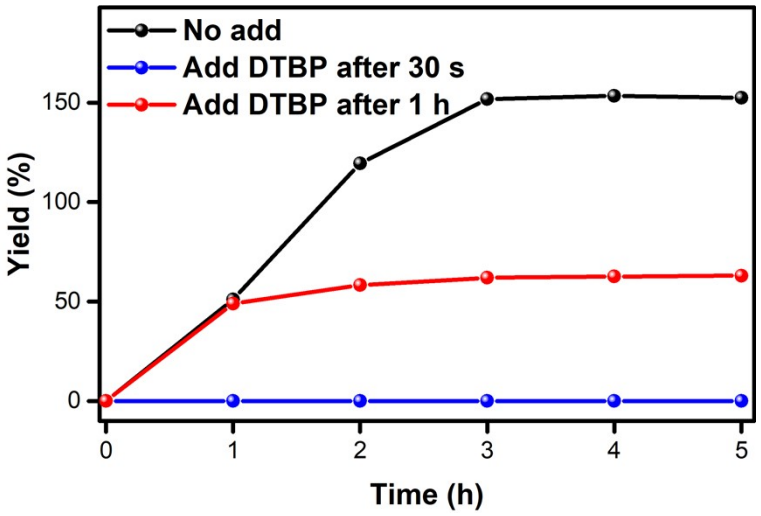


Figure S13 The product yields changes with time, DTBP was added after the manganese corrole catalyzed reaction proceeded for 30 s and 1 h. Reaction conditions: catalyst (1 μmol), 0.05 mmol nitrite (5 M aqueous solution, 10 μL) and 1 mmol styrene were mixed in 2 mL CH_3CN and stirred at room temperature open to air.

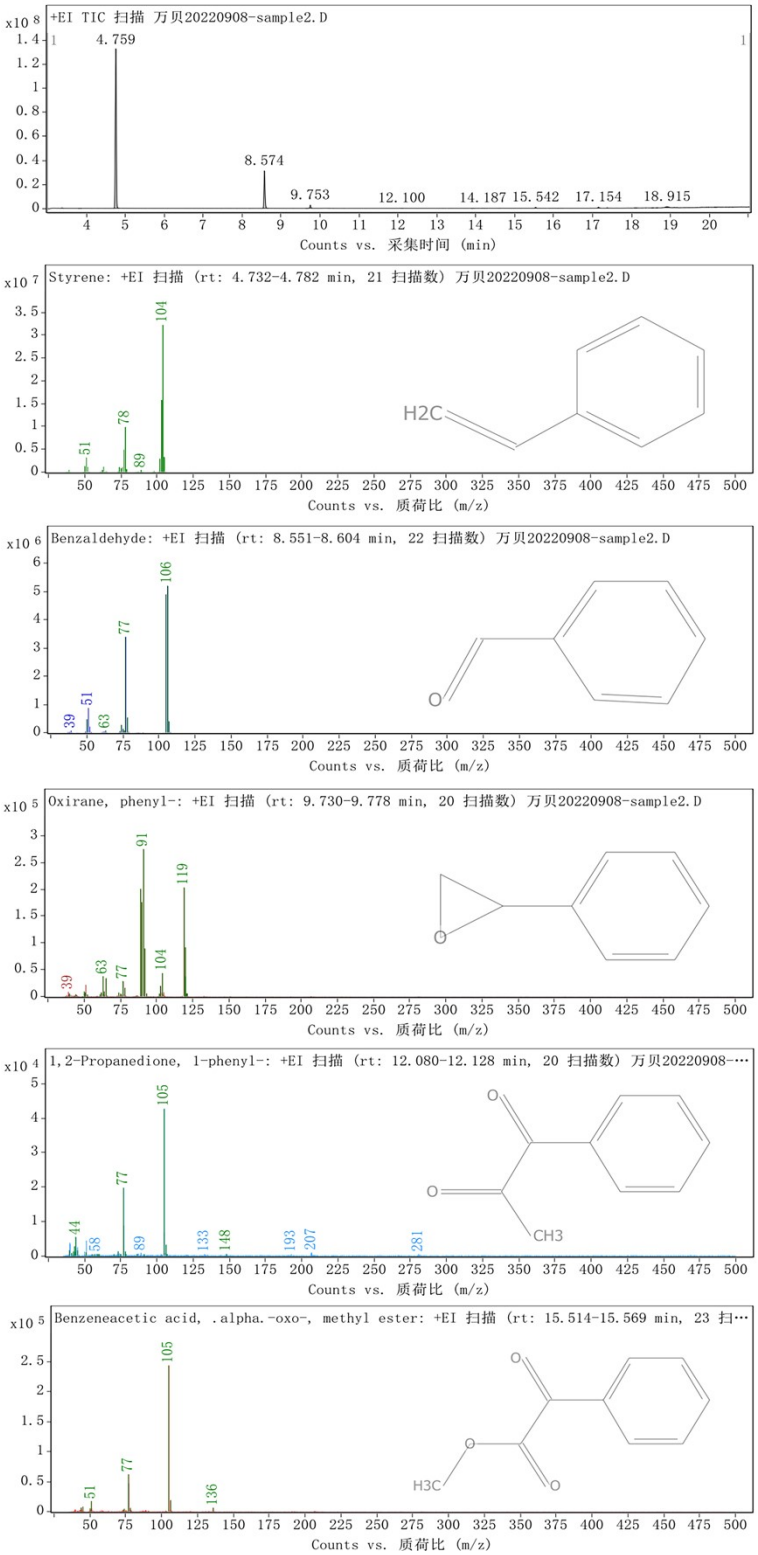
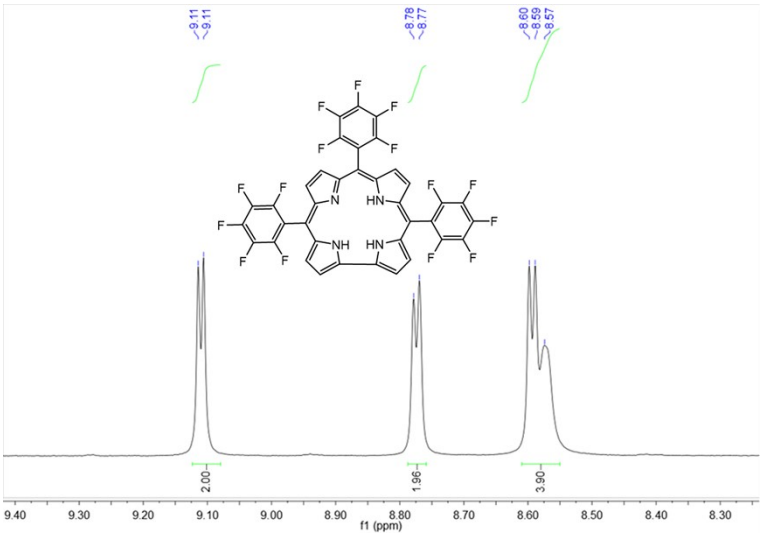
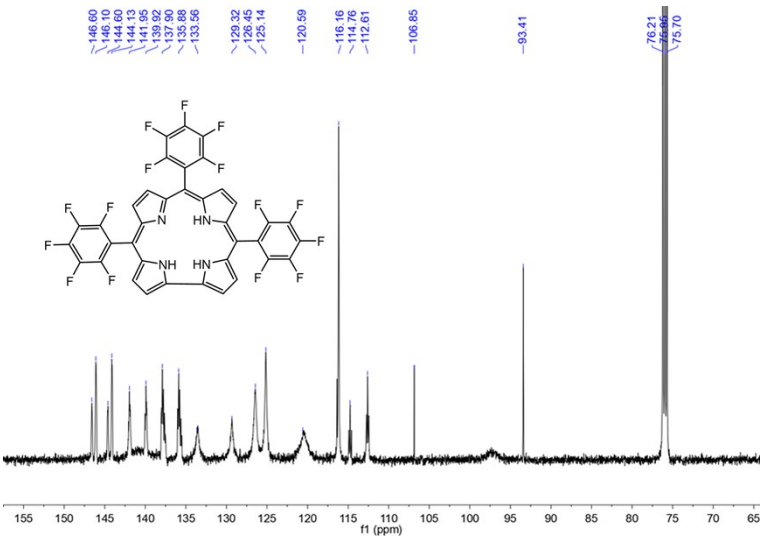


Figure S14 GC-MS results of reaction mixture progressed 2 hours.

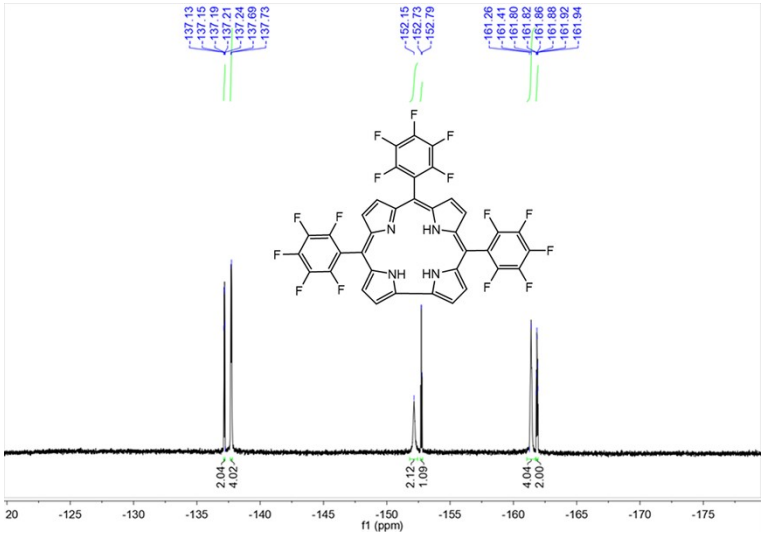
4.^{1} H, ^{13}C and ^{19}F NMR Spectrum



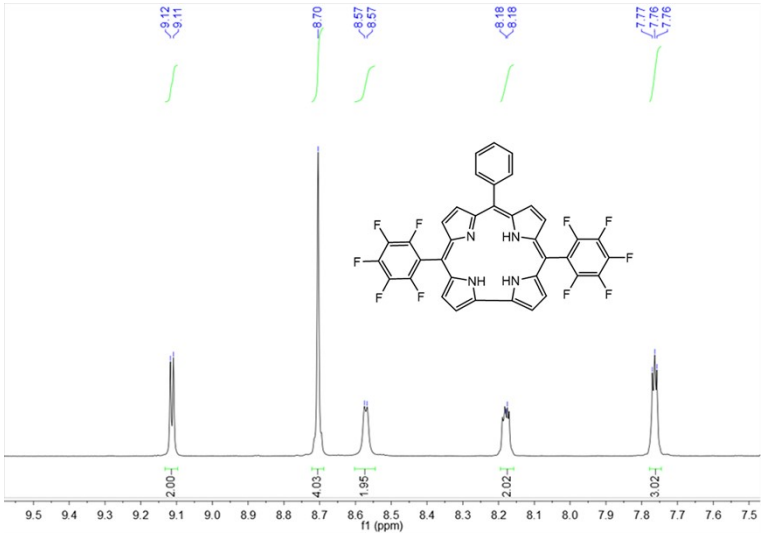
^{1}H NMR spectrum of [F_{15}TPC] (500 MHz, $CDCl_3$)



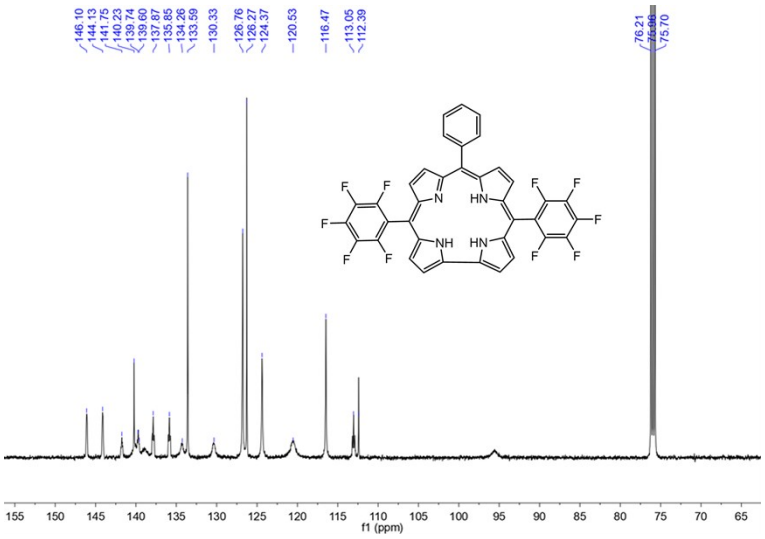
^{13}C NMR spectrum of [F_{15}TPC] (126 MHz, $CDCl_3$)



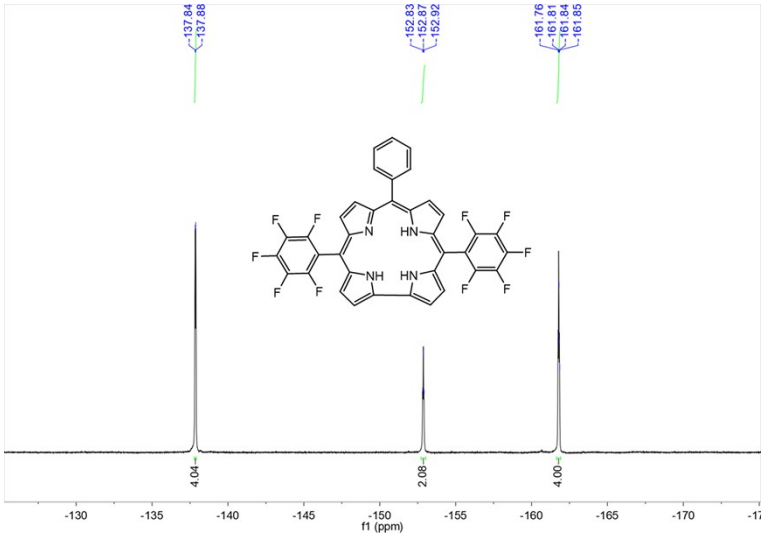
^{19}F NMR spectrum of [F_{15}TPC] (376 MHz, $CDCl_3$)



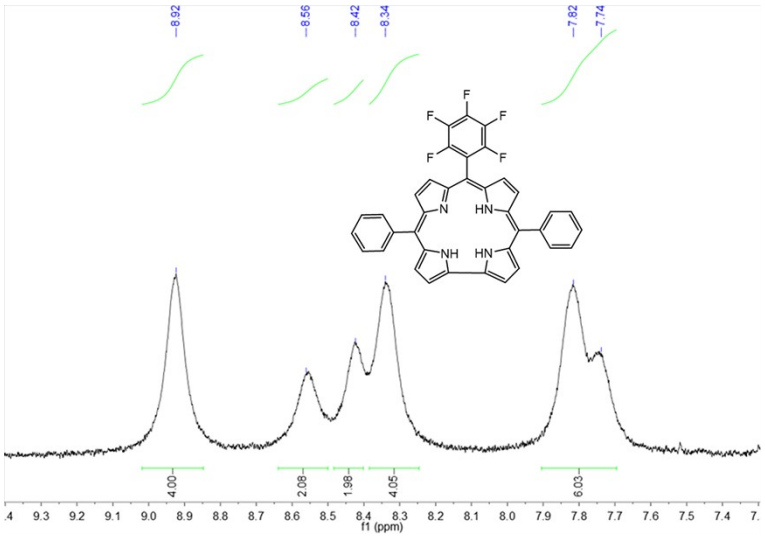
^{1}H NMR spectrum of [F_{10}TPC] (500 MHz, $CDCl_3$)



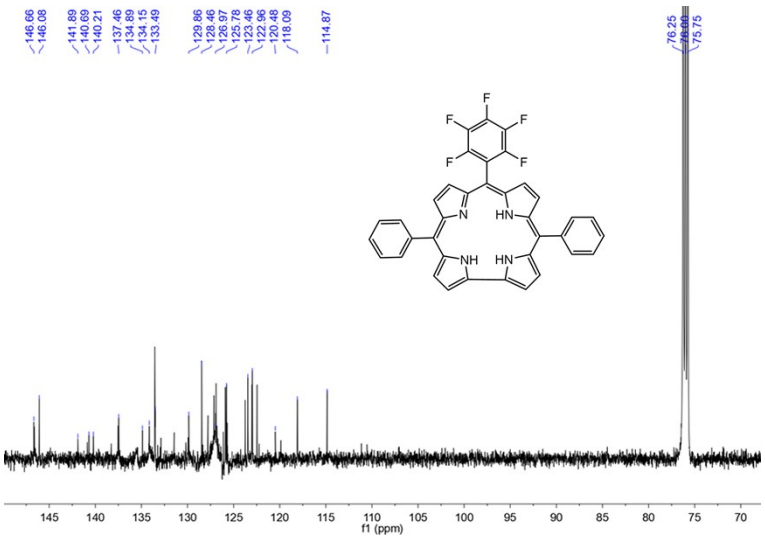
^{13}C NMR spectrum of [F_{10}TPC] (126 MHz, $CDCl_3$)



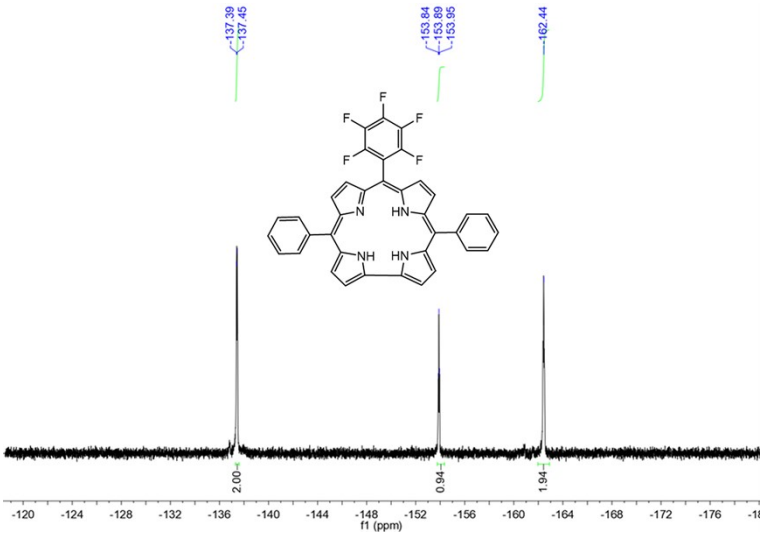
^{19}F NMR spectrum of [F_{10}TPC] (471 MHz, $CDCl_3$)



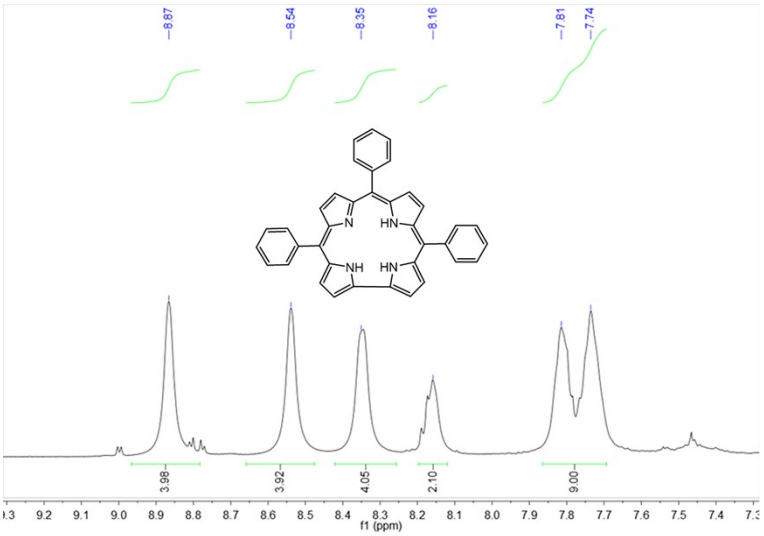
^{1}H NMR spectrum of [F_5TPC] (400 MHz, $CDCl_3$)



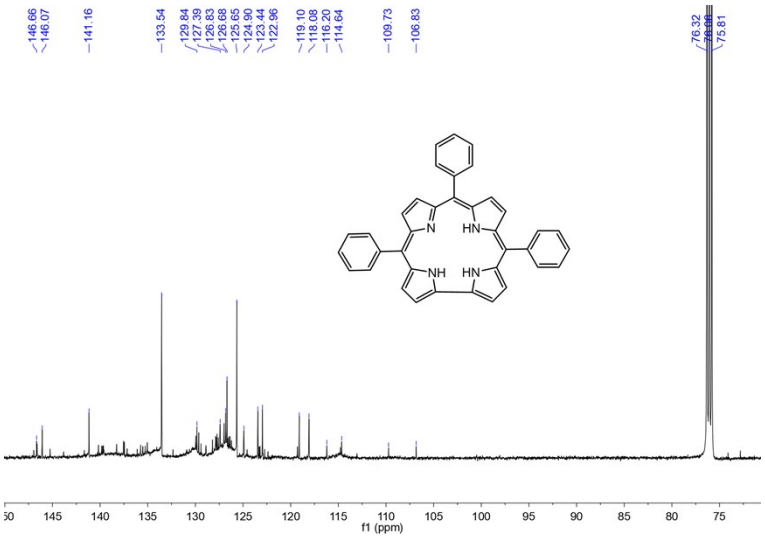
^{13}C NMR spectrum of [F_5TPC] (126 MHz, $CDCl_3$)



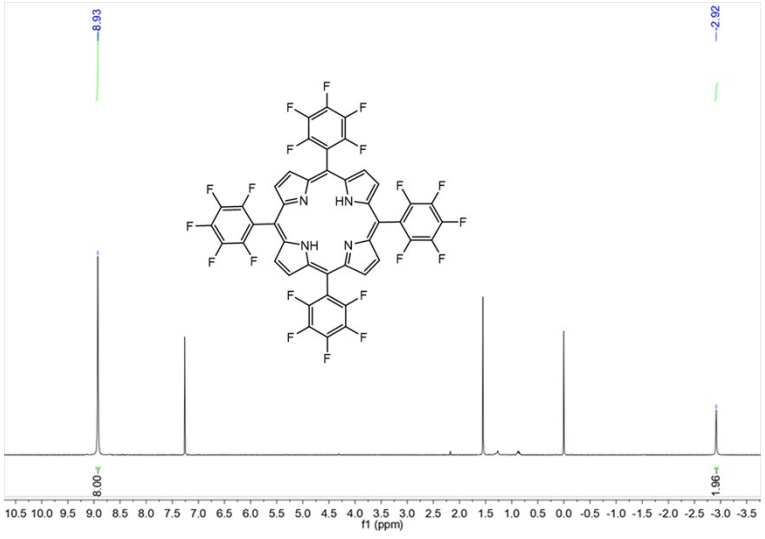
^{19}F NMR spectrum of [F_5TPC] (376 MHz, $CDCl_3$)



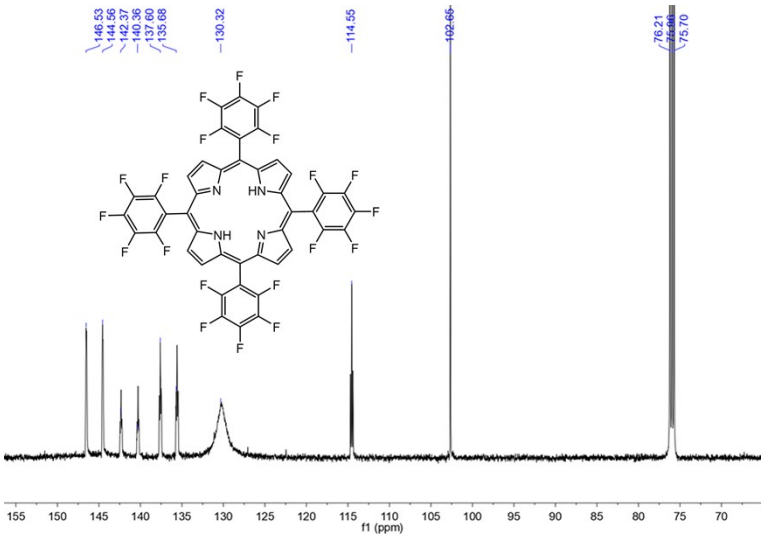
^{1}H NMR spectrum of [F_0TPC] (500 MHz, $CDCl_3$)



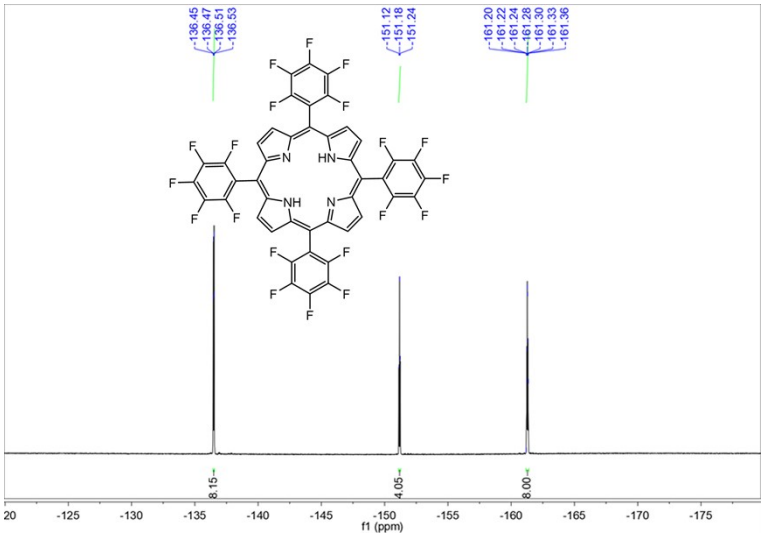
^{13}C NMR spectrum of [F_0TPC] (126 MHz, $CDCl_3$)



^{1}H NMR spectrum of [F_{20}TPP] (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of [F_{20}TPP] (126 MHz, $CDCl_3$)



^{19}F NMR spectrum of [F_{20}TPP] (376 MHz, $CDCl_3$)