Supporting Information

Solvent-Responsive Metalloporphyrins: Binding and Catalysis

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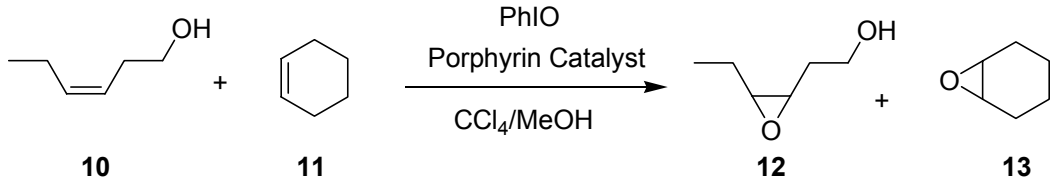
Synthesis of compound 3.[1] Cholic acid (1.07 g, 2.62 mmol), DCC (590 mg, 2.86 mmol), and N-hydroxysuccinimide (430 mg, 3.78 mmol) were dissolved in anhydrous THF (50 mL) and CH_3CN (5 mL). After 8 h at room temperature, the white solid formed was filtered out and the filtrate was concentrated in vacuo to give a white foam (1.19 g, 91% yield). A portion of this solid (350 mg, 0.700 mmol) was dissolved in anhydrous DMF (5 mL). NH_4OH (42 mg, 27% aqueous solution) was added. After 12 h at 50 °C, the mixture was poured into brine (50 mL). The precipitate was collected by suction filtration, washed with water (2 × 10 mL), and purified with Precipitate was filtered, washed with water (2 x 10 mL), and purified with column chromatography over silica gel using CH_2Cl_2/CH_3OH (8/1) as the eluent to give a white powder (215 mg, 78% yield). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.21 (s, 1H), 6.61 (s, 1H), 4.31 (d, 1H, J = 4.2 Hz), 4.09 (d, 1H, J = 3.6 Hz), 4.00 (d, 1H, J = 3.3 Hz), 3.76 (s, 1H), 3.59 (s, 1H), 3.16 (m, 1H), 2.20–0.79 (m, 28H), 0.56 (s, 3H).

Synthesis of compound 4.[1] Compound **3** (305 mg, 0.763 mmol) was dissolved in anhydrous THF (20 mL) under N_2. $LiAlH_4$ (15.2 mL, 0.5 M in diglyme, 7.60 mmol) was added slowly via a syringe. The reaction mixture was heated to reflux for 12 h. A small amount of ethyl acetate was added slowly and the solvent was concentrated in vacuo. The residue was purified with column chromatography over silica gel using CH_2Cl_2/CH_3OH (10/1) and CH_3OH/Et_3N (50/1) as the eluents to give a white solid (168 mg, 56% yield). ^{1}H NMR (300 MHz, CD_3OD, δ): 4.30 (d, 1H, J = 4.2 Hz), 4.08 (d, 1H, J = 3.3 Hz), 3.99 (d, 1H, J = 3.0 Hz), 3.59 (s, 1H), 3.38 (s, 1H), 3.15 (m, 2H), 3.05 (m, 1H), 2.21–0.76 (m, 30H), 0.57 (s, 3H).

[1] Bellini, A. M.; Quaglio, M. P.; Guarneri, M.; Cavazzini, G. *Eur. J. Med. Chem.* **1983**, *18*, 185–190.

Table 1S. Competitive Epoxidation of *cis*-3-Hexen-1-ol and Cyclohexene by Fe(CFTPP)Cl and Fe(TPP)Cl.[a,b]



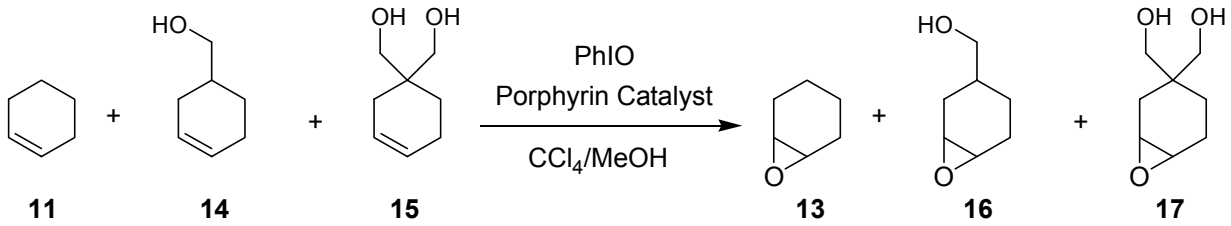
10 **11** **12** **13**

CCl_4:MeOH	Fe(CFTPP)Cl	Fe(TPP)Cl
	Yield (%**12**/%**13**)	Yield (%**12**/%**13**)
90/10	36%/5%	17%/8%
	38%/7%	17%/9%
	37%/8%	17%/9%
	Average: **37%/7%**	Average: **17%/9%**
80/20	22%/5%	15%/15%
	25%/7%	16%/15%
	23%/7%	15%/15%
	Average: **23%/6%**	Average:**15%/15%**
70/30	17%/8%	10%/14%
	22%/8%	11%/15%
	20%/8%	10%/15%
	Average: **20%/8%**	Average: **10%/15%**
60/40	14%/8%	17%/21%
	15%/11%	15%/22%
	16%/13%	14%/19%
	Average: **15%/11%**	Average: **15%/21%**
40/60	8%/10%	7%/17%
	9%/11%	7%/14%
	10%/9%	9%/20%
	Average: **9%/10%**	Average: **8%/17%**
20/80	8%/9%	5%/14%
	8%/11%	5%/14%
	9%/13%	6%/17%
	Average: **8%/11%**	Average: **5%/15%**

[a] Reactions were carried out at room temperature for 3 hours under N_2. [Catalyst] = 1 mM. [Catalyst]/[PhIO] /[**11**]/[**14**]/[**15**] = 0.05/1/5/5/5.

[b] Yields are based on iodosylbenzene and were determined by GC analysis.

Table 2S. Competitive Epoxidation of Cyclohexene Derivatives by Fe(CFTPP)Cl and Fe(TPP)Cl.[a,b]



11 **14** **15** **13** **16** **17**

CCl_4:MeOH	Fe(CFTPP)Cl	Fe(TPP)Cl
	Yield (%**13**/%**16**/%**17**)	Yield (%**13**/%**16**/%**17**)
90/10	1%/14%/7%	8%/9%/3%
	3%/15%/8%	9%/9%/4%
	3%/16%/9%	10%/10%/4%
	Average: **2%/15%/8%**	Average: **9%/9%/4%**
80/20	3%/13%/6%	9%/8%/4%
	4%/15%/7%	9%/8%/4%
	4%/13%/7%	8%/10%/6%
	Average:**4%/14%/7%**	Average: **9%/9%/5%**
60/40	4%/14%/5%	8%/6%/2%
	5%/13%/5%	9%/6%/3%
	5%/15%/6%	7%/8%/3%
	Average: **5%/14%/5%**	Average: **8%/7%/3%**
20/80	6%/12%/4%	7%/7%/3%
	7%/13%/3%	6%/6%/3%
	9%/14%/4%	4%/6%/4%
	Average: **7%/13%/4%**	Average: **6%/6%/3%**

[a] Reactions were carried out at room temperature for 3 hours under N_2. [Catalyst] = 1 mM. [Catalyst]/[PhIO] /[**11**]/[**14**]/[**15**] = 0.05/1/5/5/5.

[b] Yields are based on iodosylbenzene and were determined by GC analysis.

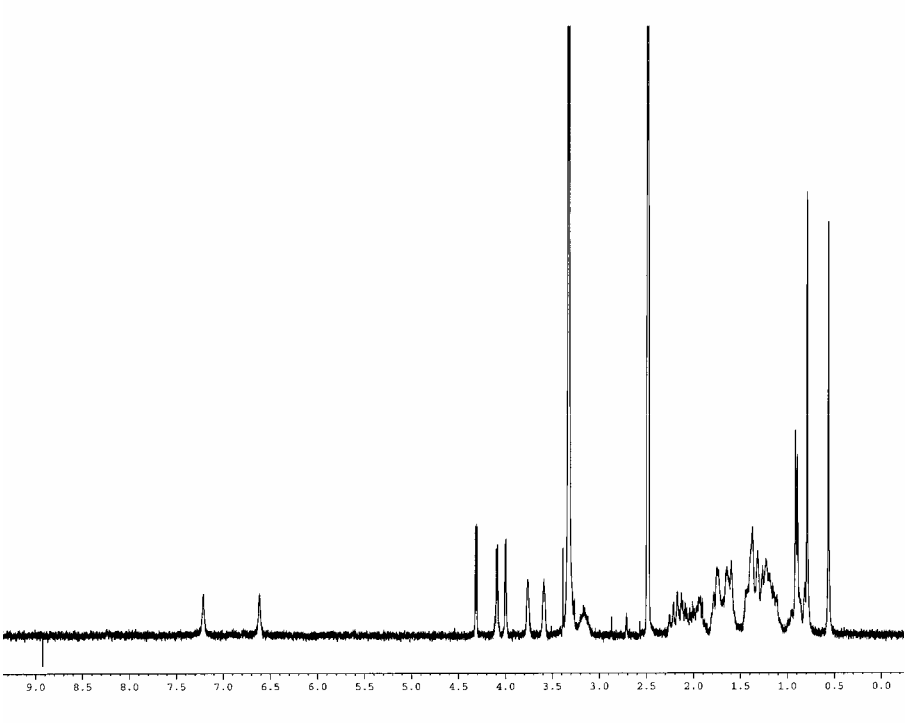


Figure 1S. ^{1}H NMR spectrum (400 MHz) of **3** in DMSO-d_6.

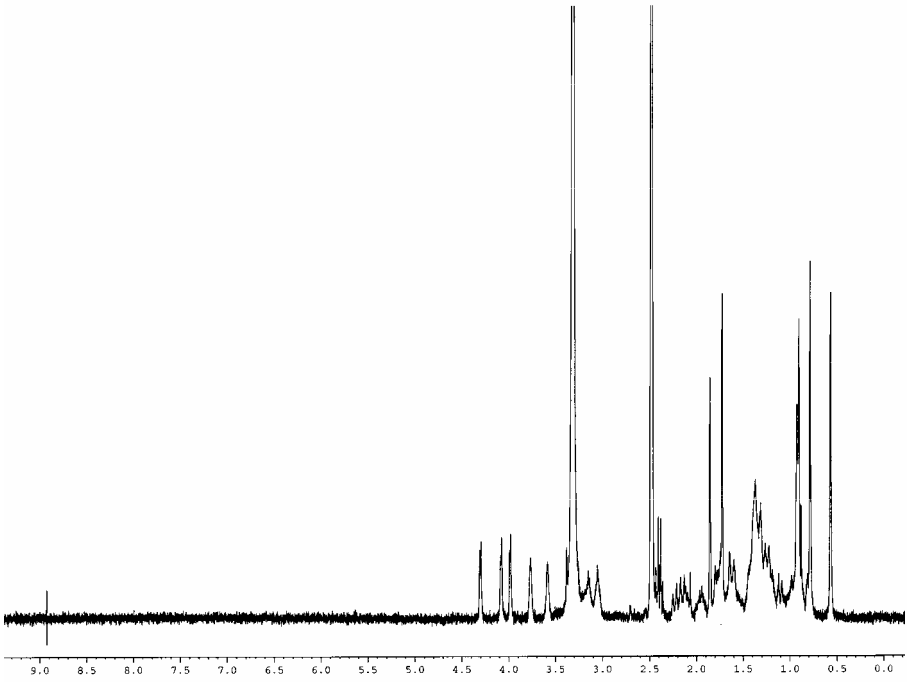


Figure 2S. ^{1}H NMR spectrum (400 MHz) of **4** in DMSO-d_6.

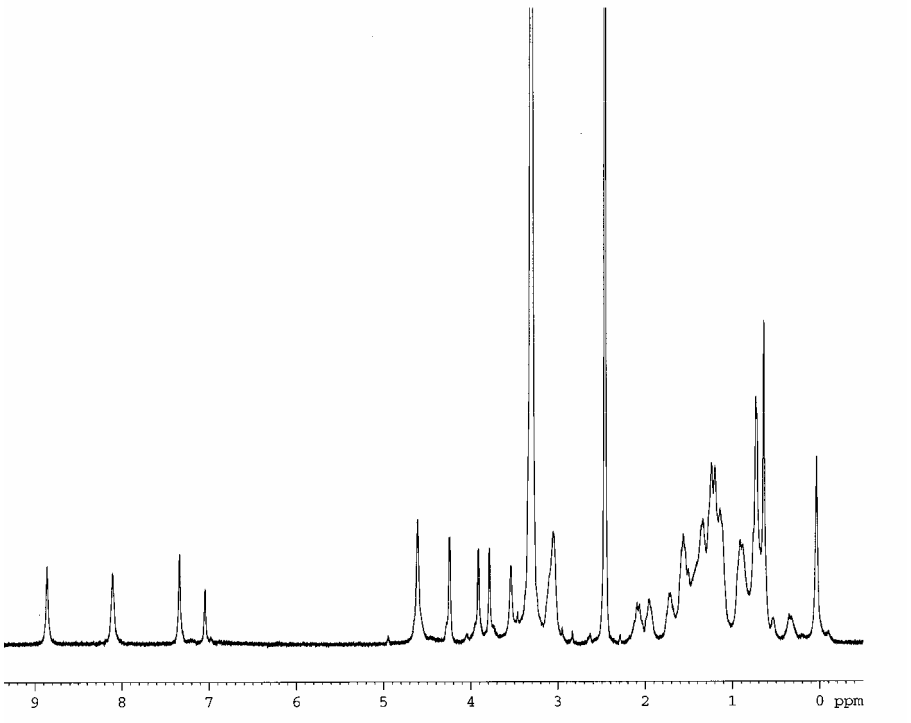


Figure 3S. ^{1}H NMR spectrum (400 MHz) of **2** in DMSO-d_6.

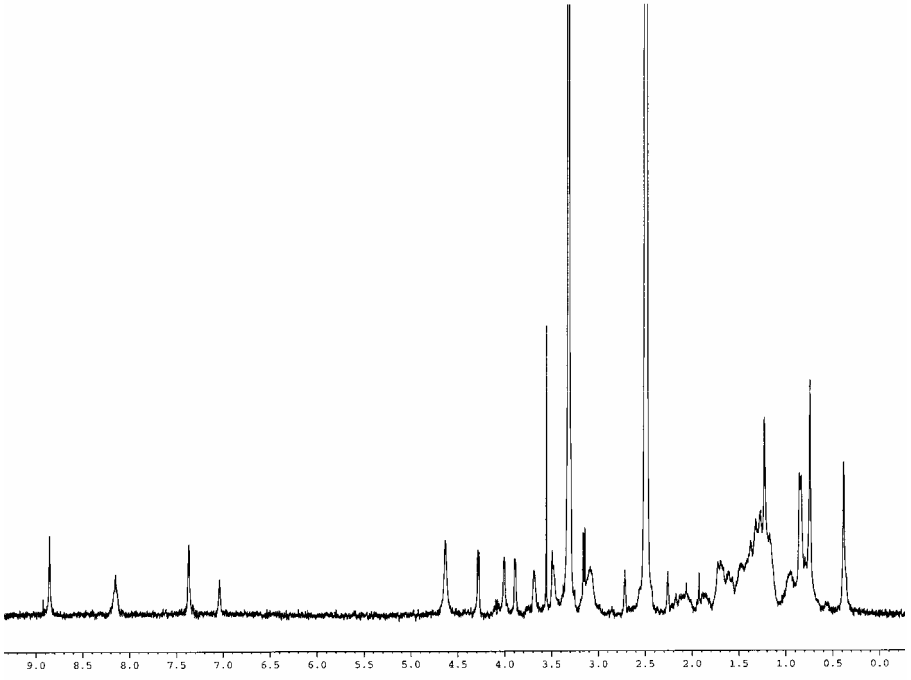


Figure 4S. ^{1}H NMR spectrum (400 MHz) of Zn(CFTPP) in DMSO-d_6.

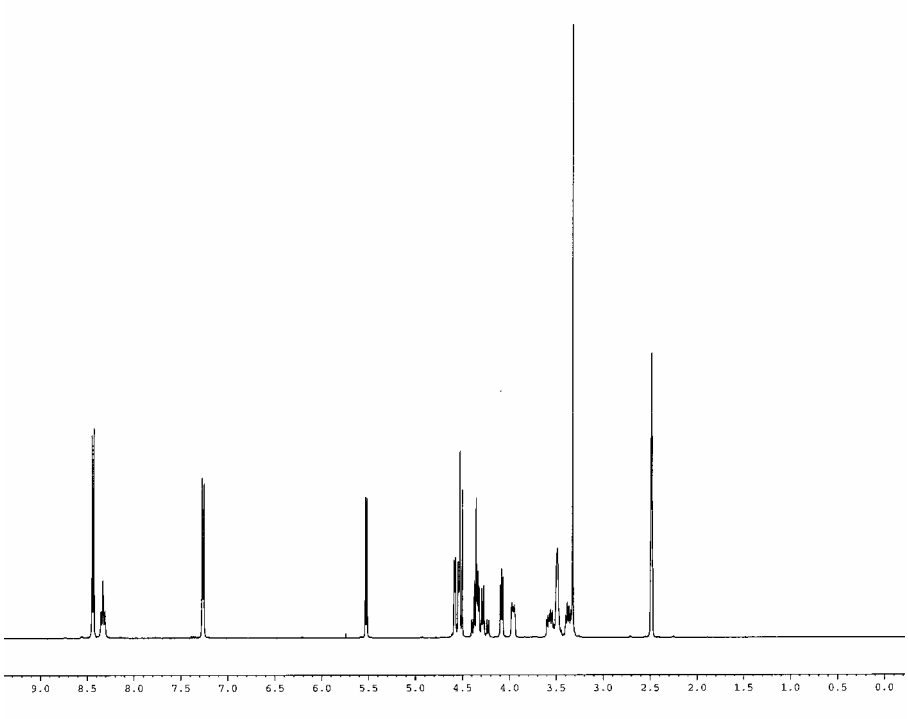


Figure 5S. ^{1}H NMR spectrum (400 MHz) of **7** in DMSO-d_6.

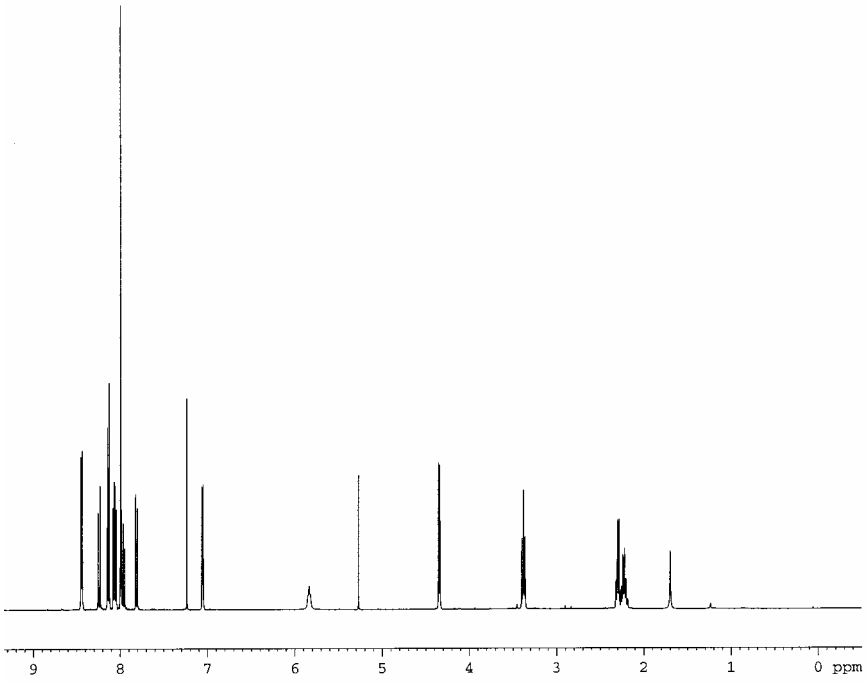


Figure 6S. ^{1}H NMR spectrum (400 MHz) of **9** in $CDCl_3$.