

Supporting Information

Aza-crown Compounds by the Self-condensation of 2-Aminobenzyl alcohol over a Pincer-Ruthenium Catalyst and Applied in Transfer Hydrogenation of Ketones

Shanshan Zhang,^{a,#} Zheng Wang,^{a,b,c,#} Qianrong Cao,^{a,d,#} Erlin Yue,^b Qingbin Liu,^{a,*} Yanping Ma,^b Tongling Liang,^b and Wen-Hua Sun^{b,*}

^aHebei Key Laboratory of Organic Functional Molecules, College of Chemistry and Material Science, Hebei Normal University, Shijiazhuang 050024, China

^bKey Laboratory of Engineering Plastics and Beijing National Laboratory for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

^cCollege of Science, Hebei Agricultural University, Baoding 071001, China

^dHebei Research Institute of Microbiology, Baoding 071051, China

#Shanshan Zhang, Zheng Wang, Qianrong Cao made equal contributions in this work
e-mail: whsun@iccas.ac.cn; liuqingbin@hebtu.edu.cn

Contents:

	Page
1. Experimental section	S1
2. ¹H and ¹³C NMR spectra of aza-crown compounds (1, 2 and 3)	S3
3. HPLC, ESI-MS spectra of aza-crown compounds (1, 2 and 3)	S6
4. X-Ray crystallographic for 1 and 3	S8
5. FT-IR spectra for aza-crown compounds (1, 2 and 3) and iron complexes (Fe1, Fe2 and Fe3)	S9

1 Experimental section

1.1 General Information

All experiments with metal complexes were carried out under nitrogen. All solvents were reagent grade or better and used after being distilled under nitrogen. Most of the chemicals used in the catalytic reactions were re-purified according to standard procedures (vacuum distillation). All ¹H NMR and ¹³C NMR were recorded on a Bruker AVIII-500 NMR spectrometer. GC analyses were carried out on an Agilent 6820 instrument using an OV-1701 column. GC conditions: Injector Temp: 250 °C; Detector Temp: 250 °C; column temp. 120 °C; withdraw time 2 min, then 10 °C/min to 230 °C keeping for 30 min. withdraw time for 5 min. HPLC analysis were carried out on Waters 600 instrument using a column BDS HYPERSIL C18 (250 × 4.6 mm × 5.0 μm), acetonitrile: water (PH = 4, aqueous KH₂PO₄ (0.05 mol/L) solution) = 70:30, flow rate = 1 mL/min, wavelength = 254 nm; ESI-MS analysis were carried out on 3200 QTRAP 1200 infinity series instrument using a column C18, acetonitrile : water = 70:30, flow:1 mL/min, electronic energy = + 40eV, Q1MS scan range = 50 ~ 600.

Table S1 CAS numbers for substrates and products

Products	CAS number	Substrates	CAS number
acetophenone	98-86-2	1-phenylethanol	13323-81-4
2,2-diethoxyacetophenone	6175-45-7	2,2-diethoxy-1-phenylethan-1-ol	38968-67-1
2',4'-dichloroacetophenone	2234-16-4	1-(2,4-dichlorophenyl)ethanol	1475-13-4
4'-chloroacetophenone	99-91-2	1-(4-chlorophenyl)ethanol	3391-10-4
3'-chloroacetophenone	99-02-5	1-(3-chlorophenyl)ethanol	6939-95-3
4'-bromoacetophenone	99-90-1	1-(4-bromophenyl)ethanol	5391-88-8
4'-fluoroacetophenone	403-42-9	1-(4-fluorophenyl)ethanol	403-41-8
4'-methylacetophenone	122-00-9	1-(4-methylphenyl)ethanol	536-50-5
4'-methoxyacetophenone	100-06-1	1-(4-methoxyphenyl)ethanol	3319-15-1
4-methylpropiophenone	5337-93-9	1-(4-methylphenyl)-1-propanol	25574-04-3
4-phenyl-2-butanone	2550-26-7	4-phenyl-2-butanol	2344-70-9
1-phenyl-1-propanone	93-55-0	1-phenyl-1-propanol	93-54-9
benzophenone	119-61-9	benzhydrol	91-01-0

1.2 General procedure for the transfer hydrogenation of ketones under nitrogen

Under a nitrogen atmosphere, the selected ketonic substrate (5.0 mmol) was dissolved in dry and degassed 2-propanol (3 mL) under a nitrogen atmosphere and the solution stirred and heated to 82 °C. On reaching this temperature, a solution of base (5 mmol) in 2-propanol (4 mL) was introduced followed by a solution of catalyst (2 mg) in 2-propanol (3 mL), taking the total volume of solvent to 10 mL. At the specified reaction time (3–48 min), 0.1 mL of the reaction mixture was sampled and immediately diluted with 0.5 mL of 2-propanol precooled to 0 °C, dodecane introduced, before being analyzed by GC. The composition of the reaction mixture was confirmed by running GC of a mixture of pure ketone, alcohol and dodecane.

2. ^1H and ^{13}C NMR spectra of aza-crown compounds (1, 2 and 3)

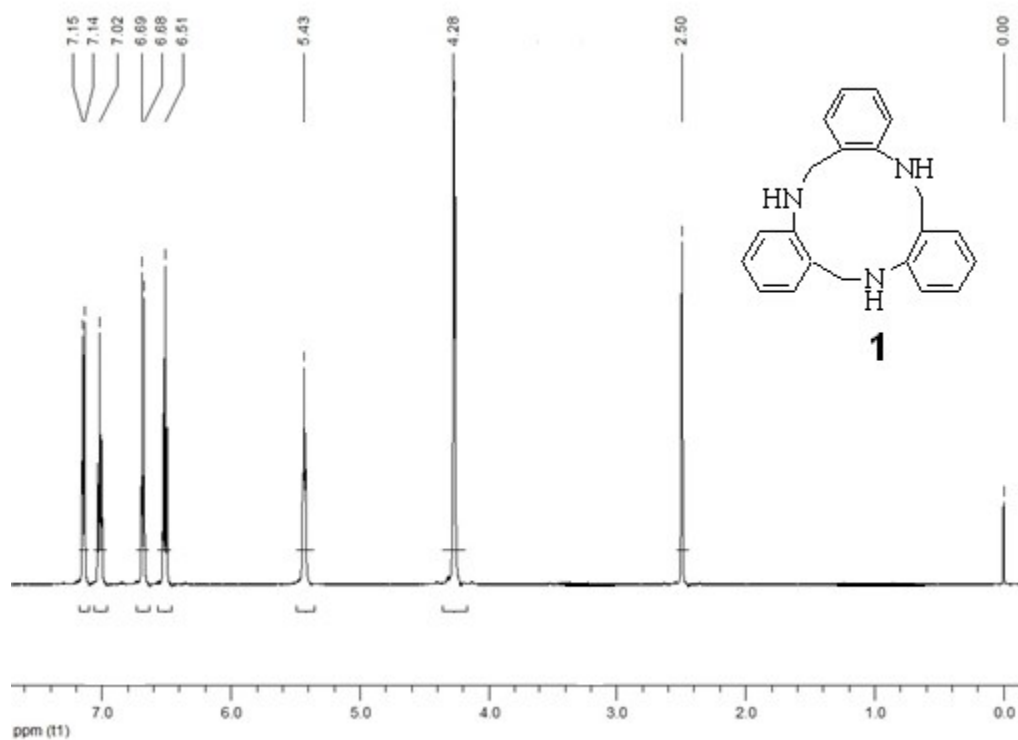


Figure S1 ^1H NMR spectrum of **1** in $\text{DMSO-}d_6$

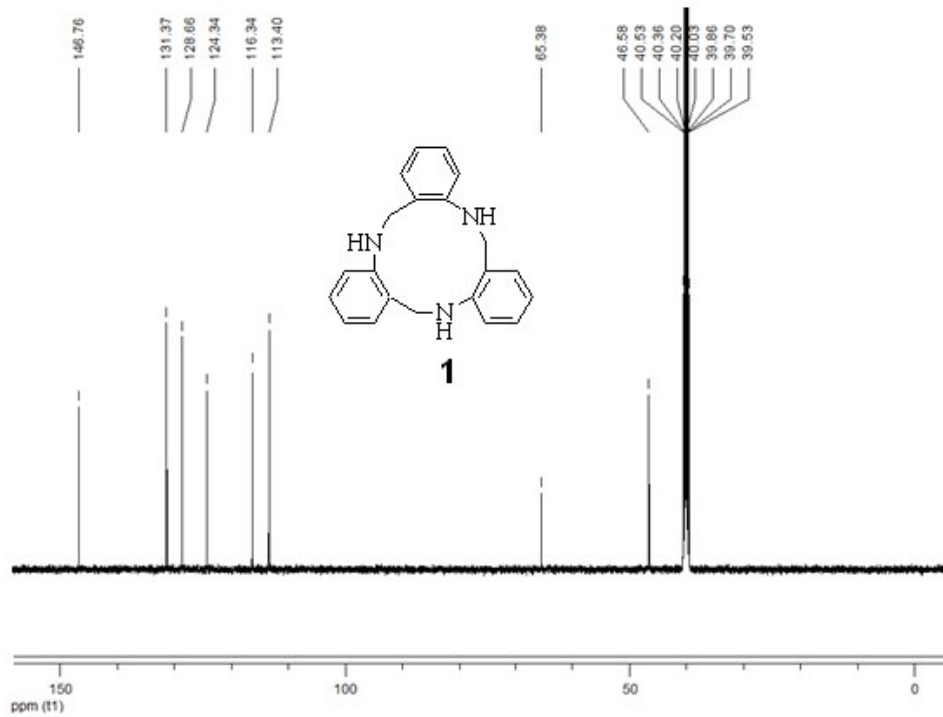


Figure S2 ^{13}C NMR spectrum of **1** in $\text{DMSO-}d$

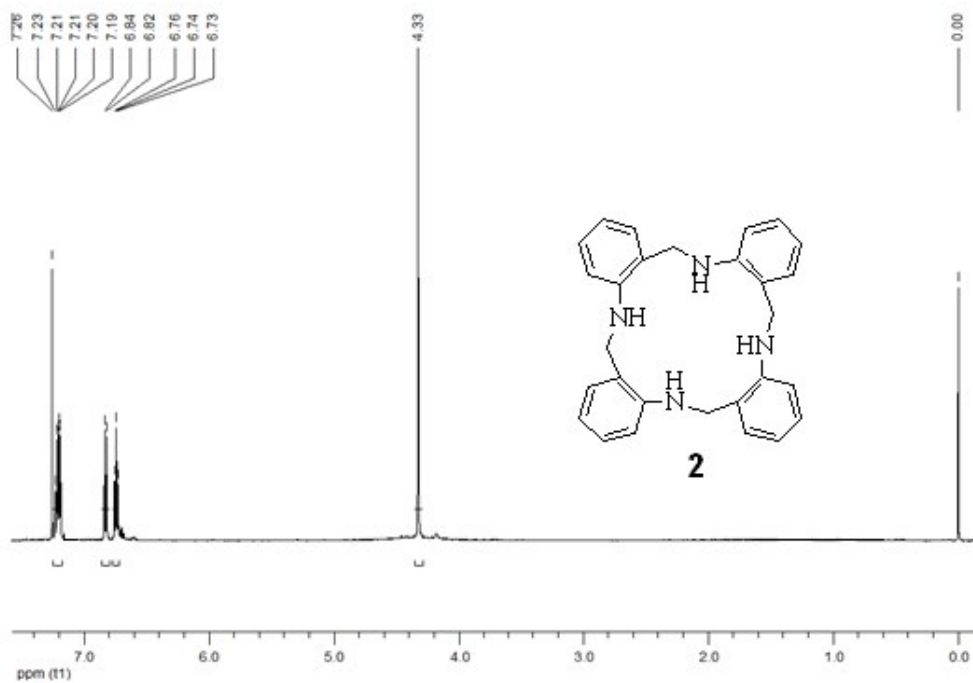


Figure S3 ^1H NMR spectrum of **2** in CDCl_3

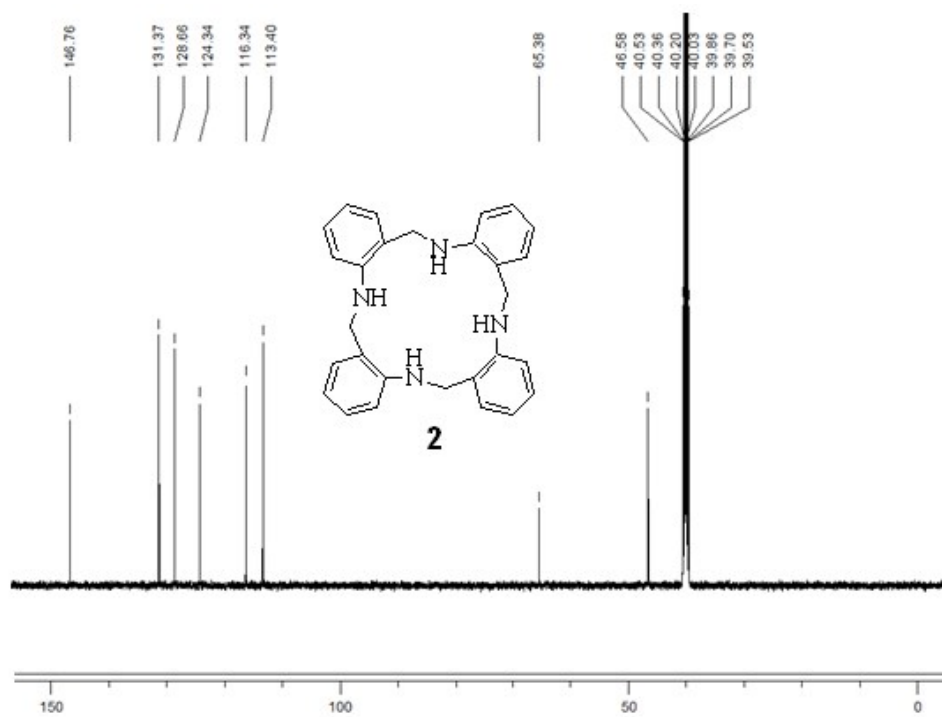


Figure S4 ^{13}C NMR spectrum of **2** in $\text{DMSO-}d$

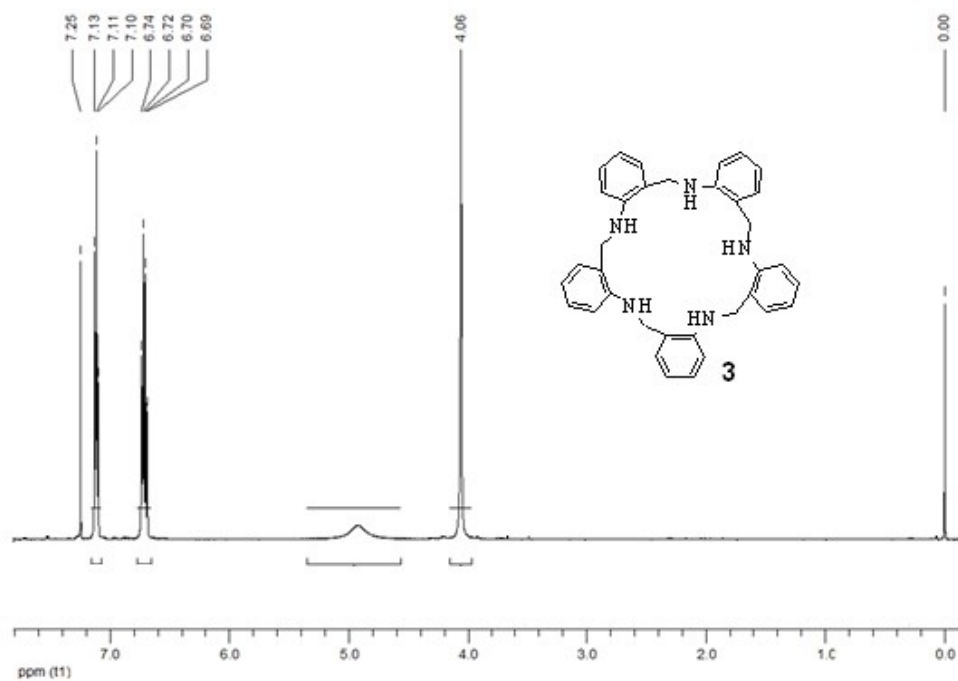


Figure S5 ^1H NMR spectrum of **3** in CDCl_3

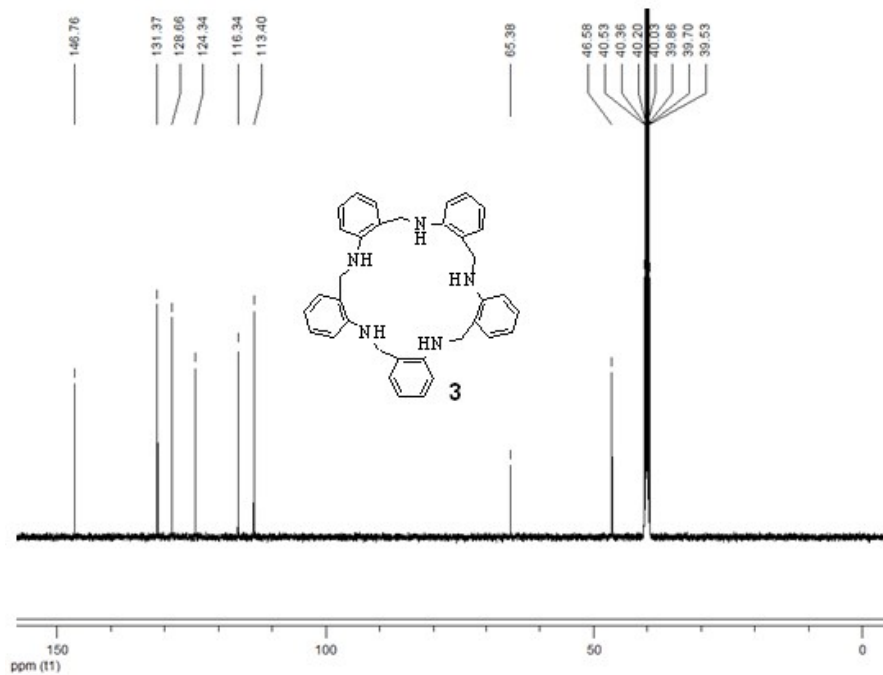


Figure S6 ^{13}C NMR spectrum of **3** in $\text{DMSO}-d_6$

3 HPLC, ESI-MS spectra of aza-crown compounds (1, 2 and 3)

HPLC analysis were carried out on Waters 400 instrument using a column BDS HYPERSIL C18 (250 × 4.6 mm × 5.0 μm), acetonitrile: water [PH = 4, KH₂PO₄ aq (0.05 mol/L)] = 70: 30, flow rate = 1 mL/ min, wave length = 254 nm.

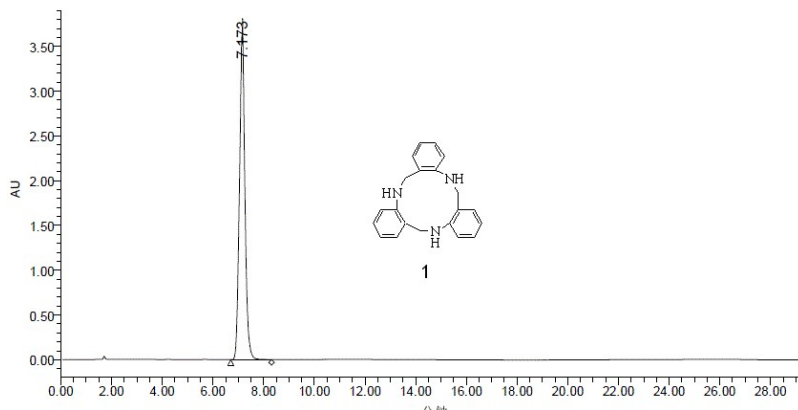


Figure S7 LC spectrum of 1

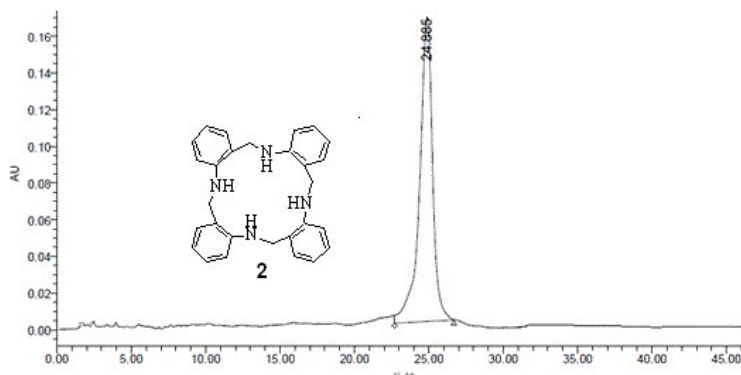


Figure S8 LC spectrum of 2

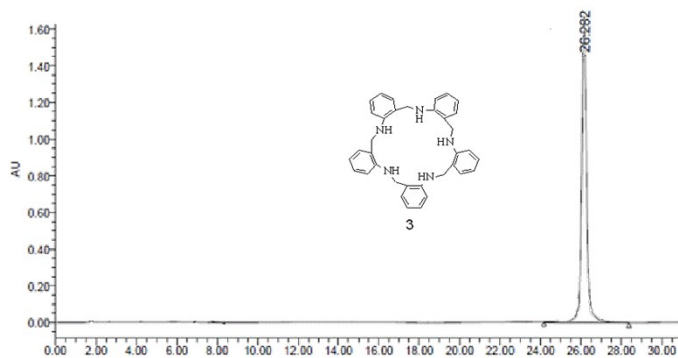


Figure S9 HPLC spectrum of 3

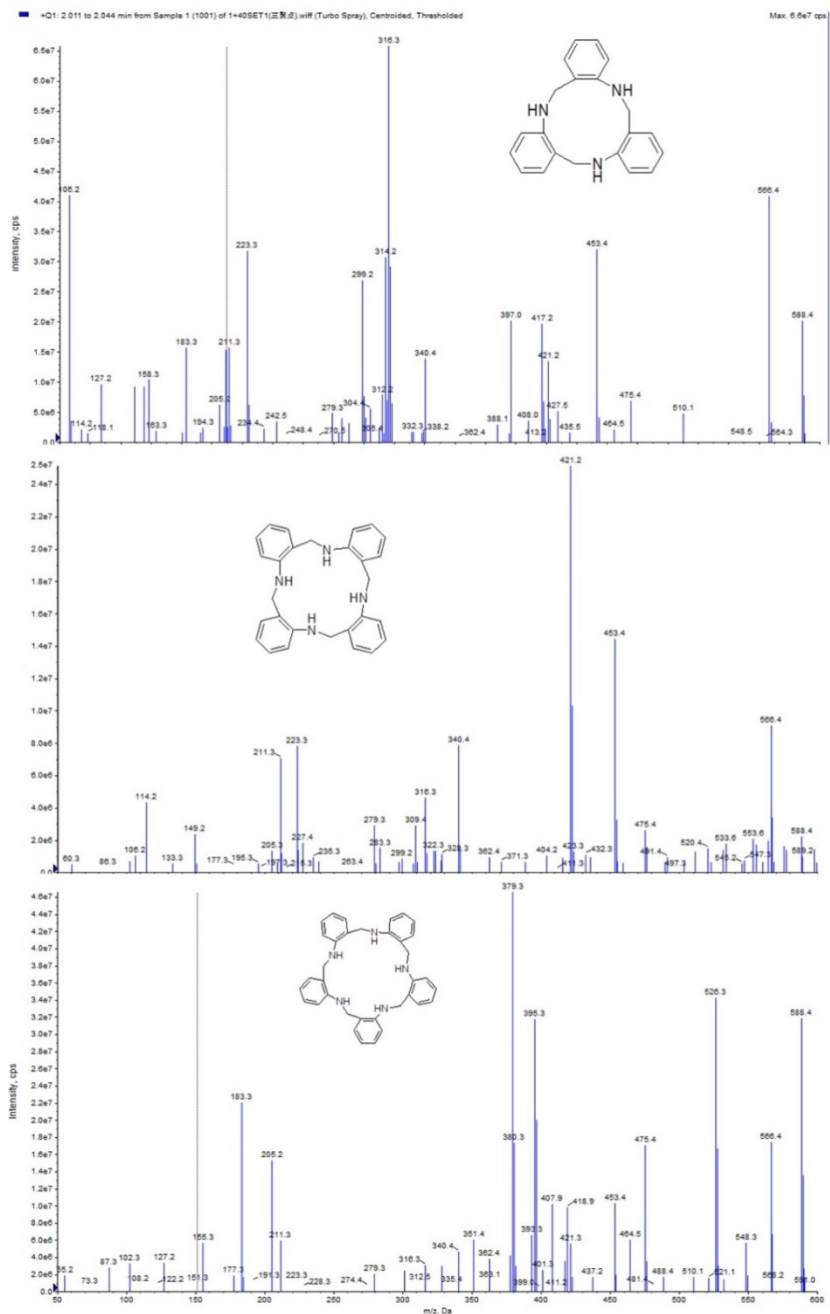


Figure S10 ESI-MS spectrum of 1, 2 and 3

Using the 3200 QTRAP 1200 infinity series instrument, MeCN : H₂O = 70 : 30, flow:1ml/min, electronic energy =+40eV, Q1MS scan range = 50~600. **1**, **2**, and **3** had an [m+1]⁺ peak signal assignable to 316.3, 421.2 and 526.3, respectively.

4. X-Ray crystallographic

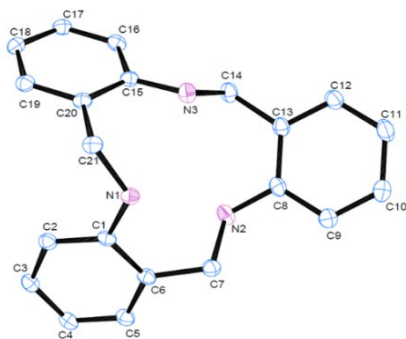


Figure S11. ORTEP representations of **1**. Thermal ellipsoids are shown at 30% probability, and hydrogen atoms have been omitted for clarity

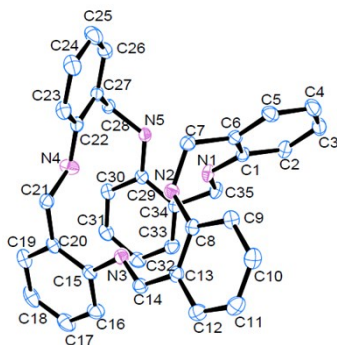


Figure S12. ORTEP representations of **3**. Thermal ellipsoids are shown at 30% probability, and hydrogen atoms have been omitted for clarity

Table S2 Crystal data and structure refinement for **1** and **3**

Identification code	1	3
Empirical formula	C ₂₁ H ₂₁ N ₃	C ₃₅ H ₃₃ N ₅
Formula weight	315.42	523.69
Temperature/K	173.15	173.15
Crystal system	monoclinic	monoclinic
Space group	P2 ₁ /n	P2 ₁ /c
a/Å	4.854(1)	18.000(4)
b/Å	21.542(4)	7.9196(16)
c/Å	15.408(3)	19.361(4)
α/°	90	90
β/°	92.60(3)	93.93(3)
γ/°	90	90
Volume/Å ³	1609.5(6)	2753.4(10)
Z	4	4

$\rho_{\text{calc}}/\text{g}/\text{cm}^3$	1.3016	1.2632
μ/mm^{-1}	0.078	0.076
F(000)	672.2	1112.4
Crystal size/ mm^3	$0.134 \times 0.094 \times 0.077$	$0.198 \times 0.157 \times 0.149$
Radiation	Mo $K\alpha$ ($\lambda = 0.71073$)	Mo $K\alpha$ ($\lambda = 0.71073$)
2θ range for data collection/ $^\circ$	3.26 to 54.96	2.26 to 54.96
Index ranges	$-6 \leq h \leq 6, -27 \leq k \leq 27, -19 \leq l \leq 19$	$-23 \leq h \leq 15, -10 \leq k \leq 10, -25 \leq l \leq 24$
Reflections collected	22322	18851
Independent reflections	3689 [$R_{\text{int}} = 0.0635, R_{\text{sigma}} = 0.0329$]	6284 [$R_{\text{int}} = 0.0761, R_{\text{sigma}} = 0.0653$]
Data/restraints/parameters	3689/0/217	6284/0/361
Goodness-of-fit on F^2	1.029	1.039
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0685, wR_2 = 0.1475$	$R_1 = 0.0791, wR_2 = 0.1652$
Final R indexes [all data]	$R_1 = 0.0715, wR_2 = 0.1497$	$R_1 = 0.0923, wR_2 = 0.1746$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.56/-0.60	0.49/-0.59

5. FT-IR spectra for aza-crown compounds (1, 2 and 3) and iron complexes (Fe1, Fe2, and Fe3)

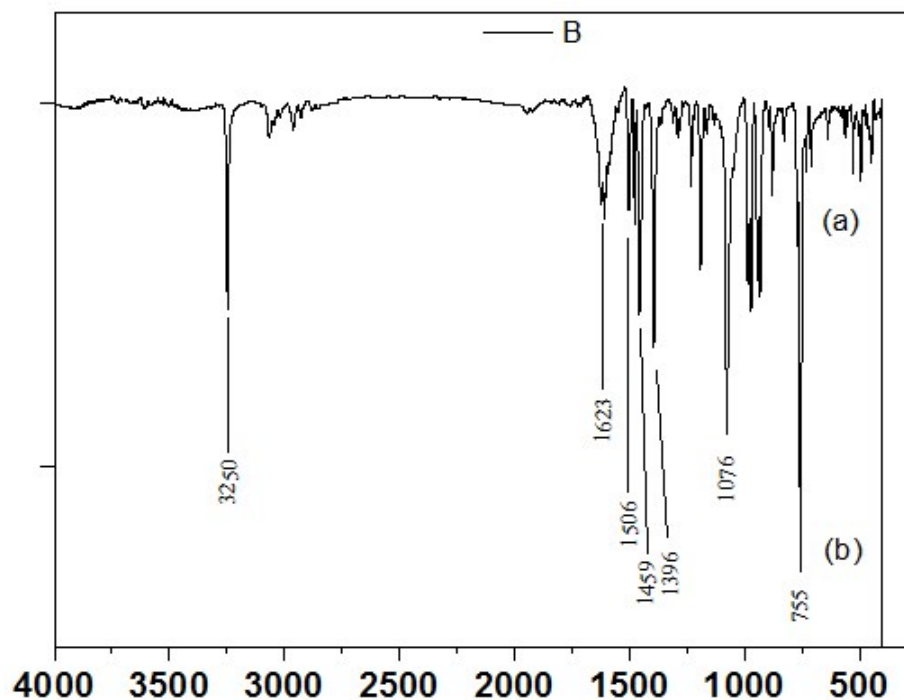


Figure S13. FT-IR spectrum of azacyclo compound 1

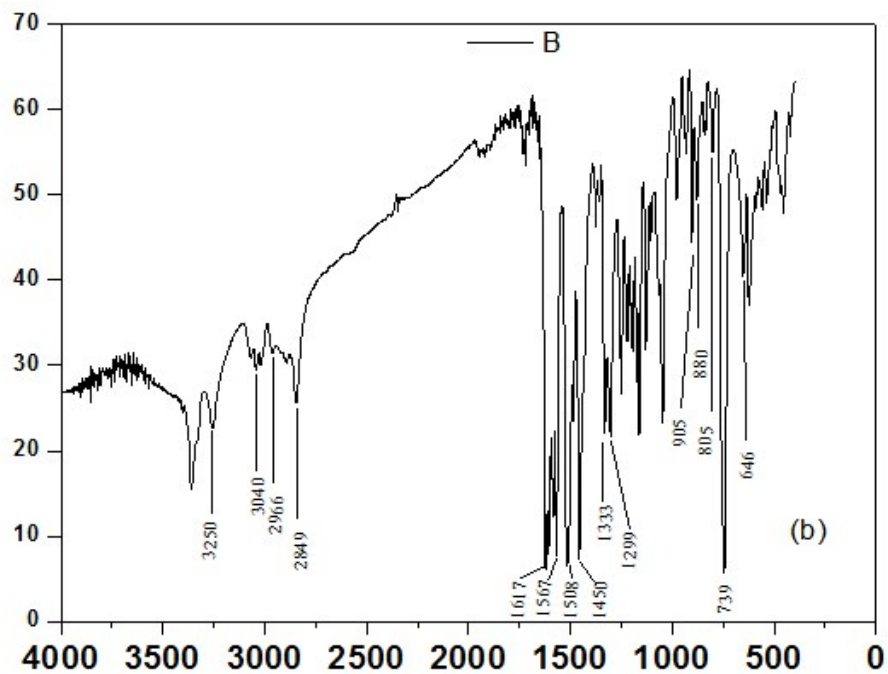


Figure S14. FT-IR spectrum of azacyclo compound 2

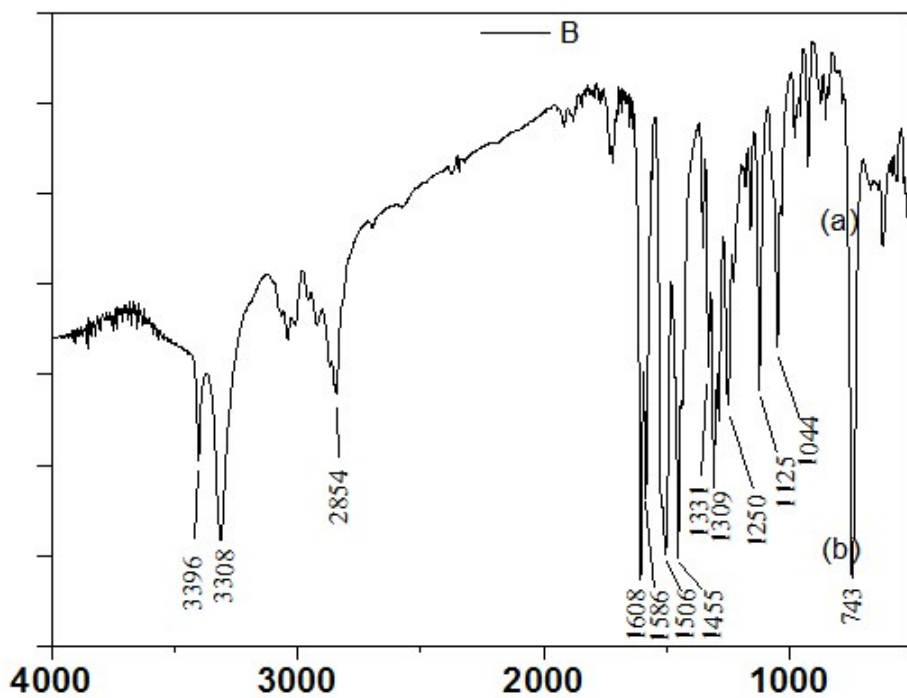


Figure S15. FT-IR spectrum of azacyclo compound 3

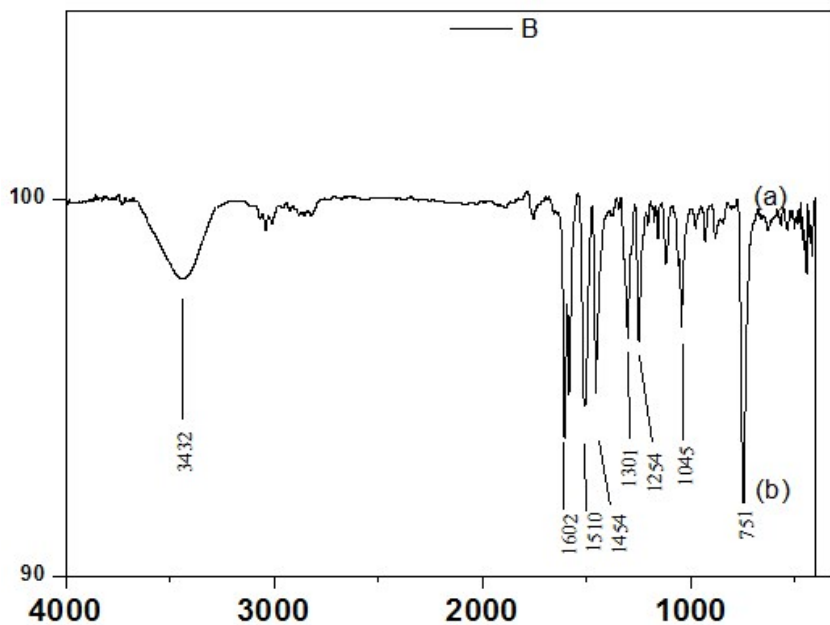


Figure S16. FT-IR spectrum of Fe1

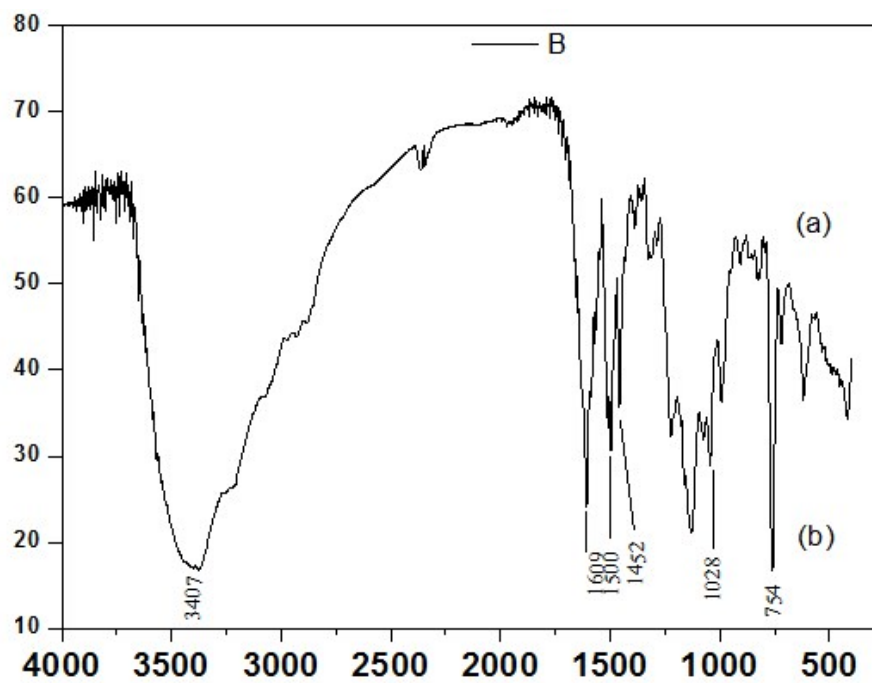


Figure S17. FT-IR spectrum of Fe2

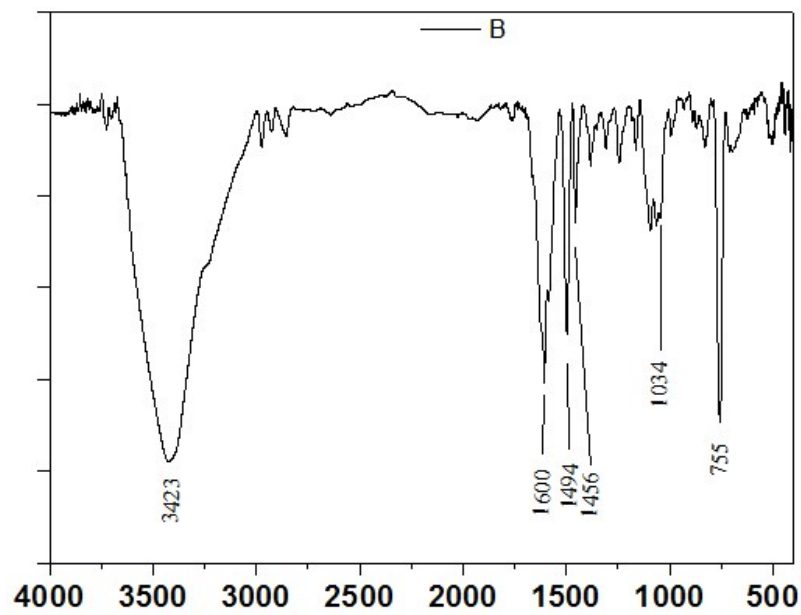


Figure S18. FT-IR spectrum of Fe₃