Supporting Information for

Selective C–C Bond Cleavage of Cyclopentadiene Rings Assisted by Ferric Chloride to Synthesize Water-Soluble Pyrylium Salts

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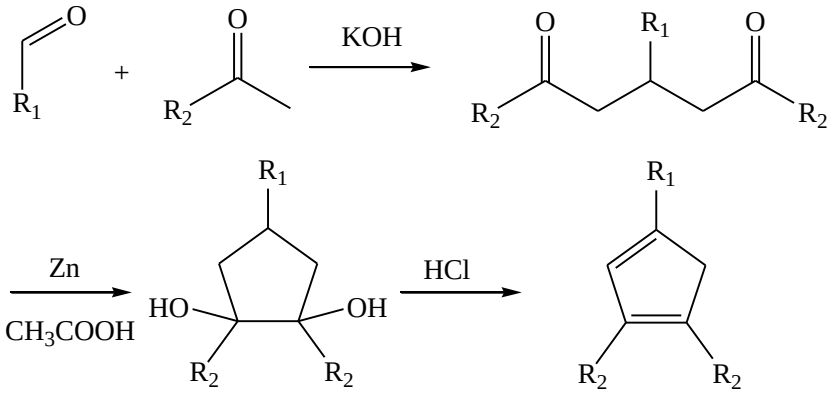
Experimental section

1) Materials and methods

The solvents were purified with standard methods and dried as needed. Elemental analysis was performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. Absorption spectra were determined on HITACHI U-4100 UV-vis Spectrophotometer. The photoluminescence (PL) studies were conducted with a JASCO FP-6300 Spectrofluorimeter with a 150 W Xe lamp. All spectra were measured at room temperature. The reflection data were collected on a Rigaku R-AXIS RAPID diffractometer (Mokα radiation, graphite monochromator).

2) Synthesis

The raw materials Cpds were synthesized according reported strategy and the chemical structures of Cpds were checked according with reference (S. S. Hirseh, W. J. Beiley, *J. Org. Chem.*, 1978, **43(21)**, 4090-4094.):



Cpd-**a**. $R_1 = R_2 =$ Ph

Cpd-**b**. $R_1 =$ *p*-MeOPh $R_2 =$ Ph

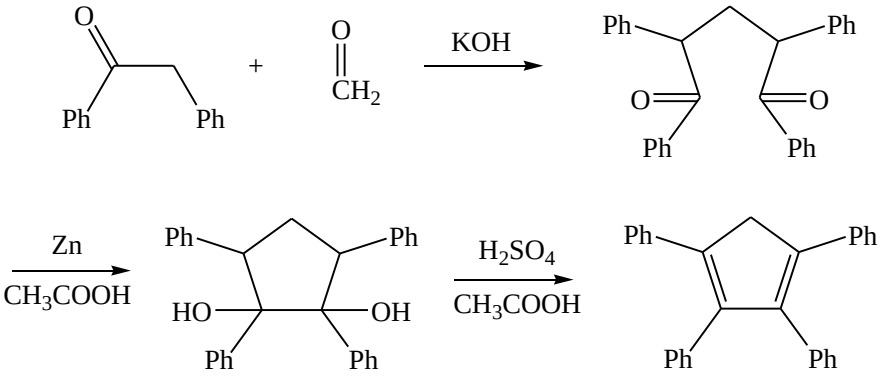
Cpd-**c**. $R_1 =$ Ph $R_2 =$ *p*-MeOPh

Cpd-**d**. $R_1 = R_2 =$ *p*-MeOPh

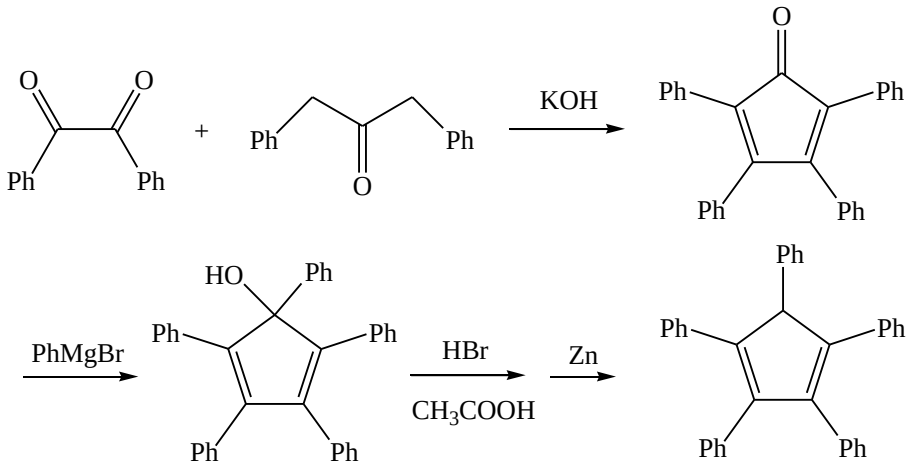
1,2-bis-(*p*-methoxylphenyl)-4-phenyl cyclopentadiene. ^{1}H-NMR (25°C, CD_3CN, 400MHz, δ in ppm): 7.627(d, *J*=8Hz, 2H), 7.346(t, *J*=7.6Hz, 2H), 7.304(d, *J*=8.8Hz, 2H), 7.254(m, 3H), 7.073(s, 1H), 6.893(d, *J*=8.8Hz, 2H), 6.808(d, *J*=8.8Hz, 2H), 3.922(s, 2H), 3.784(s, 3H), 3.752 (s, 3H). ^{13}C-NMR(25°C, $CDCCl_3$, 100MHz, δ in ppm): 158.811(s), 158.401(s), 144.214(s),

140.392(s), 138.277(s), 136.075(s), 132.196(s), 129.924(s), 129.723(d), 129.038(d), 128.836(d), 126.885(s), 124.972(d), 114.067(d), 113.881(d), 55.386(q), 45.021(t). MS (API-ES), calcd for $C_{25}H_{22}O_2$, M: 354.4; found, $(M+1)^+$/Z: 355.1. Yields: 69.6%.

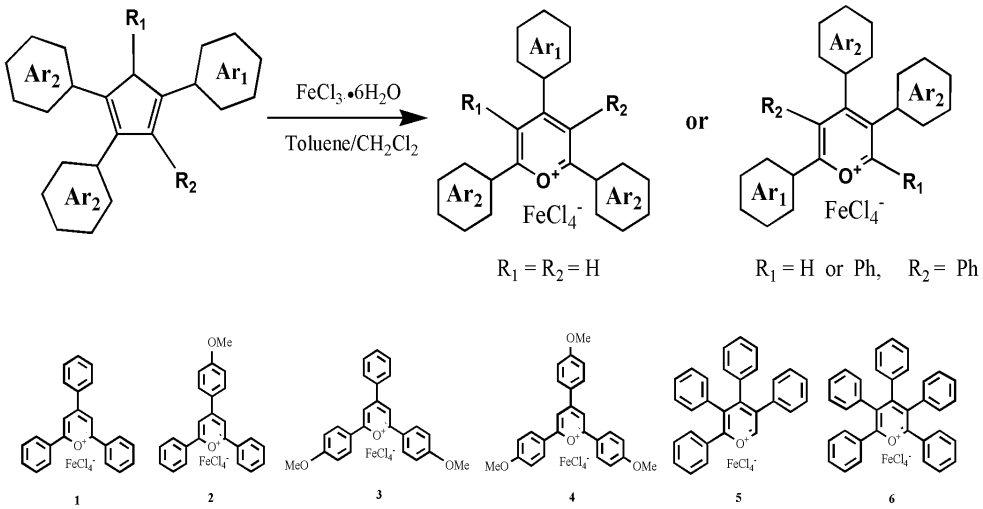
1,2,3,4-tetraphenyl cyclopentadiene was synthesized according reported strategy as below and the structure is checked according with reference (]L. Mehr, E. I. Becker, P. E. Spoerri, *J. Am. Chem. Soc.*, 1952, **77(4)**, 984-989.):



1,2,3,4,5-pentaphenyl cyclopentadiene was synthesized according reported strategy as below and the structure is checked according with reference (L. D. Field, K. M .Ho, C. M. Lindall. *Austr. J. Chem.*, 1990, **43(2)**, 281-291.):



Synthesis of pyrylium tetrachloroferrates: stirring $FeCl_3.6H_2O$ with Cpds in a mixture of toluene and dichloromethane at room temperature for 48 h, a dark precipitate was isolated by filtration. After purification by washing with ether and multiple recrystallizations from a mixture of toluene and dichloromethane, the pure pyrylium salt could be obtained.



The anion exchange reaction: 1 mmol pyrylium tetrachloroferrates and 5 mmol perchlorate were added in 15 mL acetonitrile, stirring for 8 h. When finished, 40 mL dichloromethane were added, and the system was washed with 40 mL water for 3 times, dried with $MgSO_4$ and evaporating the solvents in reduced pressure. After recrystallizing, the pyrylium perchlorates **1'-6'** were obtained, respectively.

2,4,6-triphenyl pyrylium tetrachloroferrate (1). IR (KBr), ν(cm^{-1}): 1631, 1594, 1497, 1253. MS (API-ES), cation calcd for $C_{23}H_{17}O^+$, M^+: 309.1, found, M^+/Z: 309.2; anion calcd for $FeCl_4^-$, M^-: 197.7; found, M^-/Z: 197.9. Anal. Calcd for $C_{23}H_{17}Cl_4FeO$: C, 54.48; H, 3.38; Found: C, 54.29; H, 3.36. Yields: 41.5%.

2,4,6-triphenyl pyrylium perchlorates (1'). ^{1}H-NMR analysis (25°C, CD_3CN, 400M, δ ppm)：8.71 (s, 2H), 8.43 (m, 4H), 8.31 (m, 2H), 7.86 (m, 3H), 7.78 (m, 6H). ^{13}C-NMR analysis (25°C, CD_3CN, 100M, δ ppm): 170.93, 166.45, 135.41, 135.28, 132.91, 130.06, 129.63, 129.02, 128.75, 115.82.

2,6-diphenyl-4-(*p*-methoxylphenyl) pyrylium tetrachloroferrate (2). IR (KBr), ν(cm^{-1}): 1638, 1594, 1491 1246, 1179. MS (API-ES), cation calcd for $C_{24}H_{19}O_2^+$, M^+: 339.14, found, M^+/Z: 339.1; anion calcd for $FeCl_4^-$, M^-: 197.7; found, M^-/Z: 197.9. Anal. Calcd for $C_{24}H_{19}Cl_4FeO_2$: C, 53.67; H, 3.57; Found: C, 53.63; H, 3.58. Yields: 45.3%.

2,6-diphenyl-4-(*p*-methoxyphenyl) pyrylium perchlorates (2') ^{1}H-NMR analysis (25°C, CD_3CN, 400M, δ ppm): 8.59 (s, 2H), 8.38 (m, 6H), 7.84 (m, 2H), 7.75 (m, 4H), 7.28 (d, 2H),

3.99 (s, 3H). ^{13}C-NMR analysis (25°C, CD_3CN, 100M, δ ppm): 169.67, 166.66, 164.51, 134.94, 132.59, 129.94, 129.23, 128.42, 124.44, 115.86, 113.65, 56.10.

2,6-bis-(*p*-methoxylphenyl)-4-phenyl pyrylium tetrachloroferrate (3). IR (KBr), ν(cm^{-1}): 1638, 1601, 1497, 1268, 1173. MS (API-ES), cation calcd for $C_{25}H_{21}O_3^+$, M^+: 369.2, found, M^+/Z: 369.0; anion calcd for $FeCl_4^-$, M^-: 197.7; found, M^-/Z: 197.9. Anal. Calcd for $C_{25}H_{21}Cl_4FeO_3$: C, 52.95; H, 3.73; Found: C, 52.79; H, 3.75. Yields: 47.4%.

2,6-bis-(*p*-methoxyphenyl)-4-phenyl pyrylium perchlorates (3'). ^{1}H-NMR analysis (25°C, CD_3CN, 400M, δ ppm): 8.41 (s, 2H), 8.35 (m, 4H), 8.21 (d, 2H), 7.83-7.70(m, 3H), 7.24(m, 4H), 3.97(s, 6H).^{13}C-NMR analysis (25°C, CD_3CN, 100M, δ ppm): 169.70, 165.68, 164.34, 134.51, 133.31, 130.95, 129.90, 129.11, 121.21, 115.63, 113.20, 55.95.

2,4,6-tri-(*p*-methoxylphenyl) pyrylium tetrachloroferrate (4). IR (KBr), ν(cm^{-1}): 1638, 1594, 1497, 1268.4, 1174. MS (API-ES), cation calcd for $C_{26}H_{23}O_4^+$, M^+: 399.2, found, M^+/Z: 399.2; anion calcd for $FeCl_4^-$, M^-: 197.7; found, M^-/Z: 197.9. Anal. Calcd for $C_{26}H_{23}Cl_4FeO_4$: C, 52.30; H, 3.88. Found: C, 52.47; H, 3.86. Yields: 42.6%.

2,4,6-tri-(*p*-methoxyphenyl) pyrylium perchlorates (4'). ^{1}H-NMR analysis (25°C, CD_3CN, 400M, δ ppm): 8.21 (m, 8H), 7.17 (m, 6H), 3.94 (d, J=4 Hz,9H). ^{13}C-NMR analysis (25°C, CD_3CN, 100M, δ ppm) 168.46, 165.85, 165.29, 162.49, 131.83, 130.52, 124.57, 121.19, 115.54, 115.46, 110.99, 55.94, 55.86.

2,3,4,5,-tetraphenyl pyrylium tetrachloroferrate (5). IR (KBr), ν(cm^{-1}): 1604.0, 1597, 1434.3, 399.3. MS (API-ES): calcd for $C_{23}H_{17}O^+$, M^+: 385.48, found, M^+/Z: 385.0; anion calcd for $FeCl_4^-$, M^-: 197.66; found, M^-/Z: 197.8. Anal. Calcd for $C_{29}H_{21}Cl_4FeO$: C, 59.73; H, 3.63; Found: C, 59.80; H, 3.71. Yields: 59.5%.

2,4,5,6-tetraphenyl pyrylium perchlorates (5'). ^{1}H-NMR analysis (25°C, CD_3CN, 400M, δ ppm): 9.49 (s, 1H), 7.62 -7.55(m, 3H), 7.47-7.30 (m, 6H), 7.28-7.13(m, 9H), 6.97 (m, 2H). ^{13}C-NMR analysis (25°C, CD_3CN, 100M, δ ppm): 172.64, 169.74, 162.47, 138.01, 137.77, 133.70, 133.21, 131.82, 130.74, 130.62, 130.50, 129.90, 129.85, 129.82, 129.70, 129.32, 129.03, 128.81, 128.77, 128.54, 127.99.

2,3,4,5,6-pentaphenyl pyrylium tetrachloroferrate (6). IR (KBr), ν(cm^{-1}): 1646, 1565, 1424, 1179. MS (API-ES), cation calcd for $C_{35}H_{25}O^+$, M^+: 461.2, found, M^+/Z: 461.5; anion

calcd for $FeCl_4^-$, M^-: 197.7; found, M^-/Z: 197.9. Anal. Calcd for $C_{35}H_{25}Cl_4FeO$: C, 63.77; H, 3.82; Found: C, 63.68; H, 3.84. Yields: 56.7%.

2,3,4,5,6-pentaphenyl pyrylium perchlorates (6'). ^{1}H-NMR analysis (25°C, CD_3CN, 400M, δ ppm): 7.62 (m, 6H), 7.45 (m, 4H), 7.27 (m, 6H), 7.18-7.07 (m,7H), 6.95 (d, 2H). ^{13}C-NMR analysis (25°C, CD_3CN, 100M, δ ppm): 170.99, 170.72, 135.83, 134.25, 133.41, 132.27, 130.72, 130.54, 130.18, 129.10, 129.02, 128.96, 128.69, 128.33, 127.64.

3) NaOH titration experiments of 3

Six copies of 5 mL aqueous solution of 10^{-4}M **3** were prepared in six conical flasks (10 mL-scale). Another six copies of 5mL NaOH aqueous solution with concentration from 0 to 5×10^{-4}M (10^{-4}M alternation) were subsequently added, respectively. Then the solutions were dissolved by assistant ultrasonic vibration for 3 minutes, and then characterized by Fluorescence and UV-vis absorption.

4) The Hela cells staining

The HeLa cells were seeded in 24 well plates at concentration of 5×10^5 cells/cm^2 and cultured for 24h in DMEM supplemented with 10% fetal bovine serum at 37 ℃ in an atmosphere of 5% CO_2. For experiments, the cells were rinsed 2 times with PBS buffer and incubated 4h in the **4**, which were dissolved in PBS at various concentrations. After rinsing 2 times with PBS buffer, fluorescence images were acquired using a phase -contrast microscope (OLYMPUS IX70, Japan).

5) X-ray crystal structure

X-ray crystal structure determinations were performed on a Bruker SMART APEX CCD diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) using the SMART and SAINT programs. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares methods with SHELXTL version 5.1. All non-hydrogen atoms

were refined anisotropically. The hydrogen atoms were calculated by geometrical models. Crystallographic data has been deposited in the Cambridge Crystallographic Data Centre with reference numbers 825996-825999 and 873588. A summary of the crystallographic data and structure refinements are tabulated in Table S1 and Table S3. The selected bond lengths and angles are listed in Table S2 and Table S4.

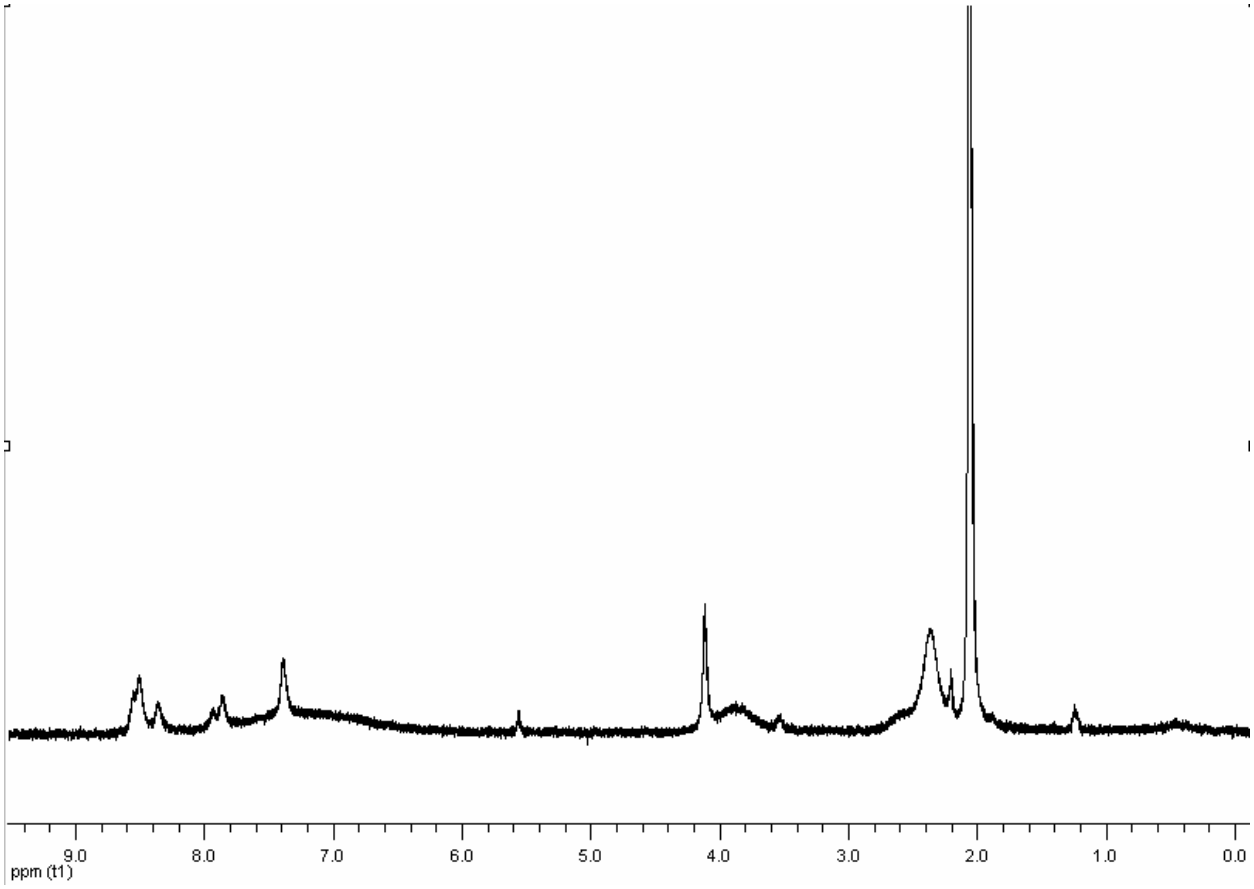


Fig. S1 ^{1}HNMR spectrum of **1** in CD_3CN.

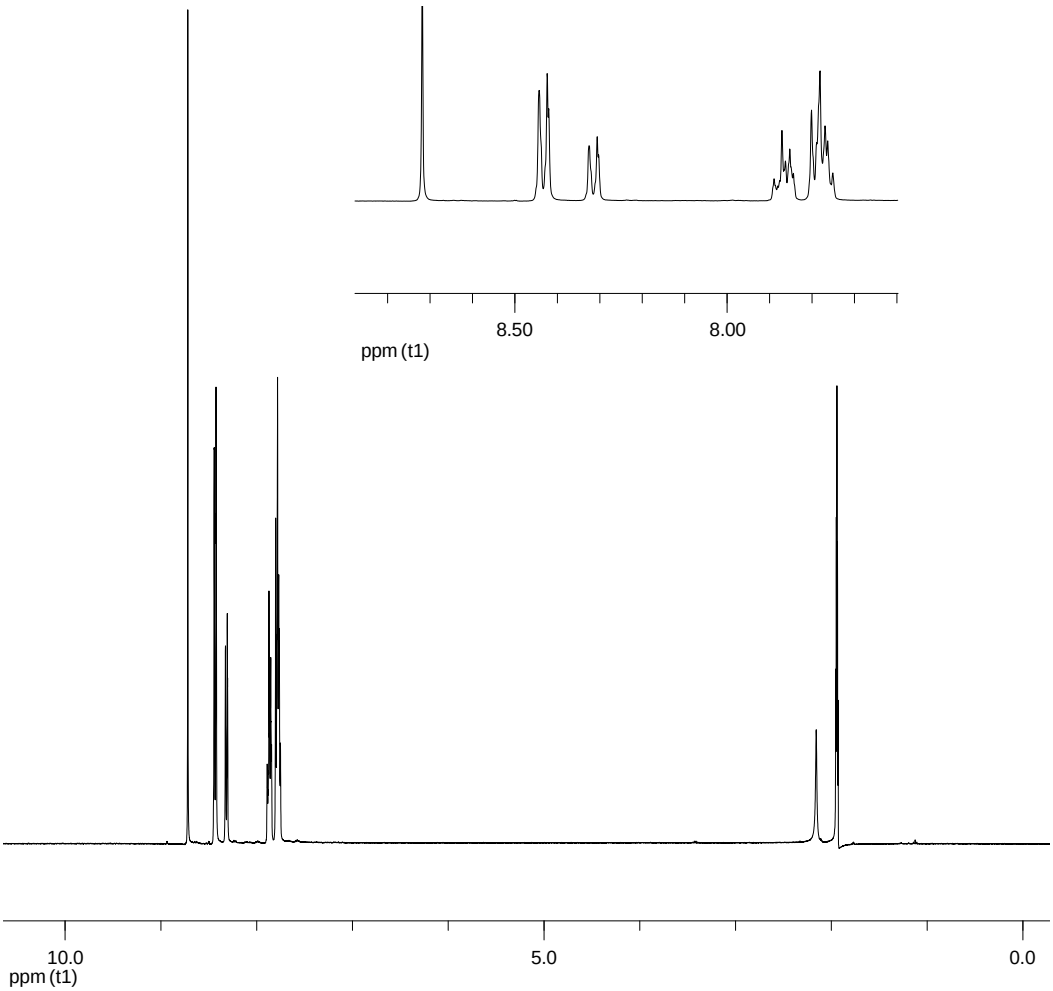


Fig. S2 ^{1}HNMR spectrum of **1'** in CD_3CN.

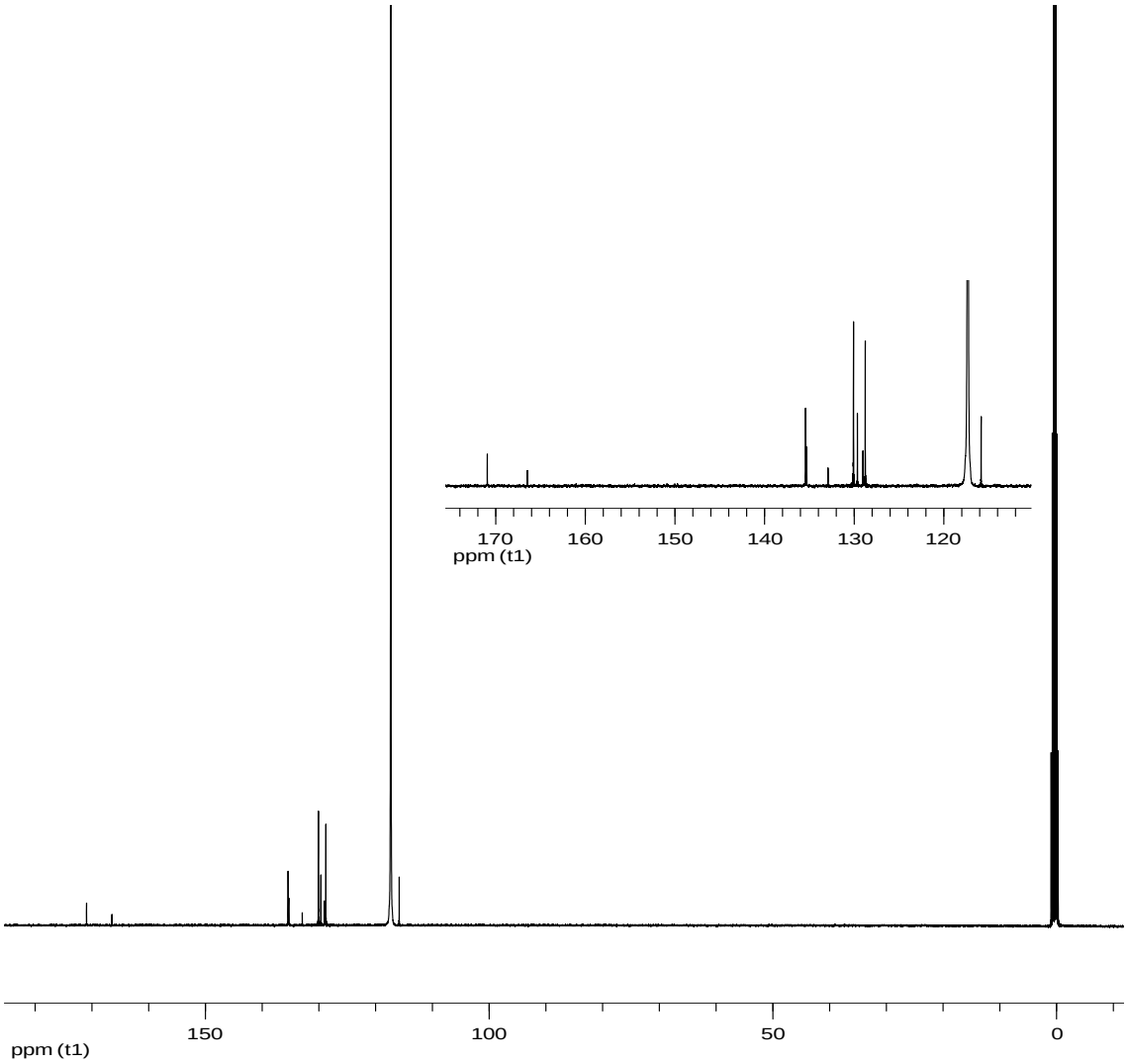


Fig. S3 ^{13}C-NMR spectrum of **1'** in CD_3CN.

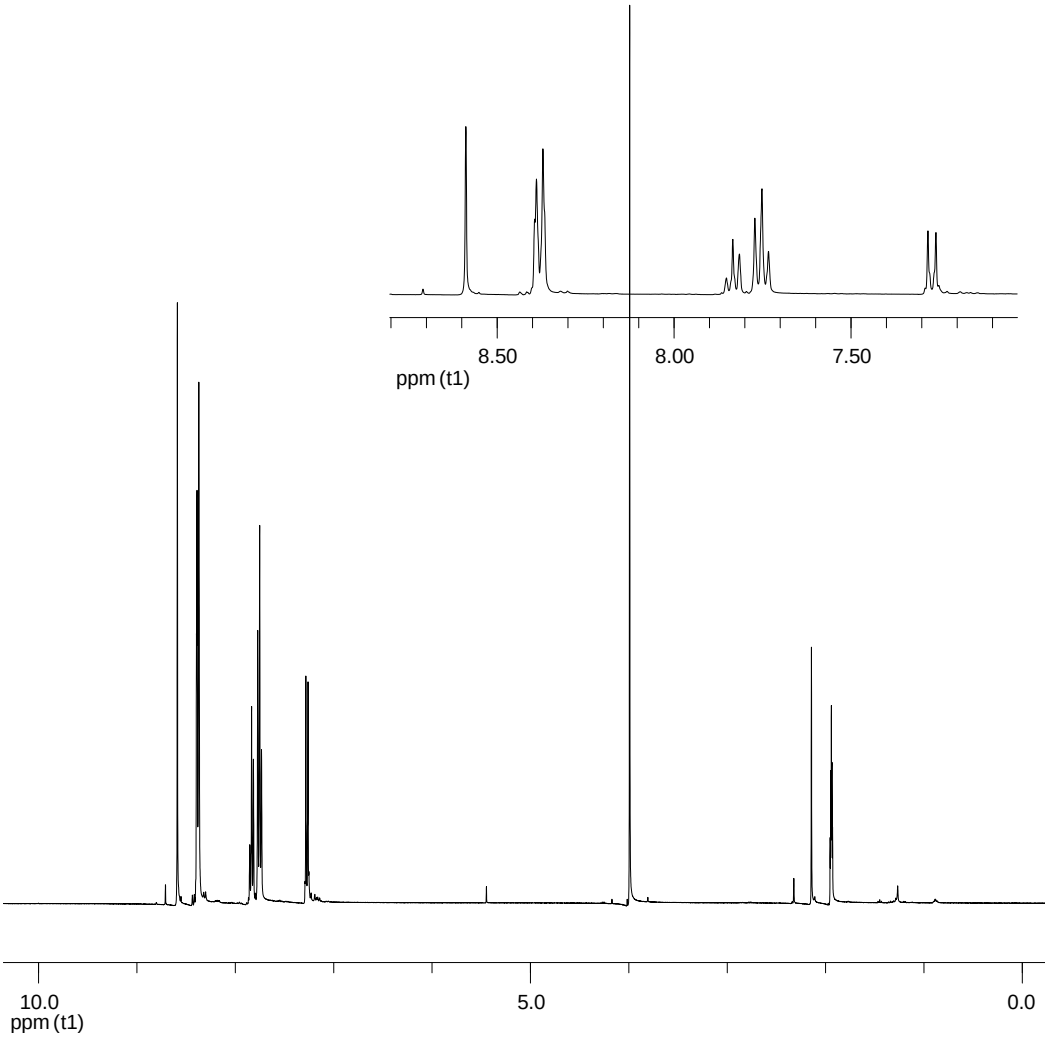


Fig. S4 ^{1}HNMR spectrum of **2'** in CD_3CN.

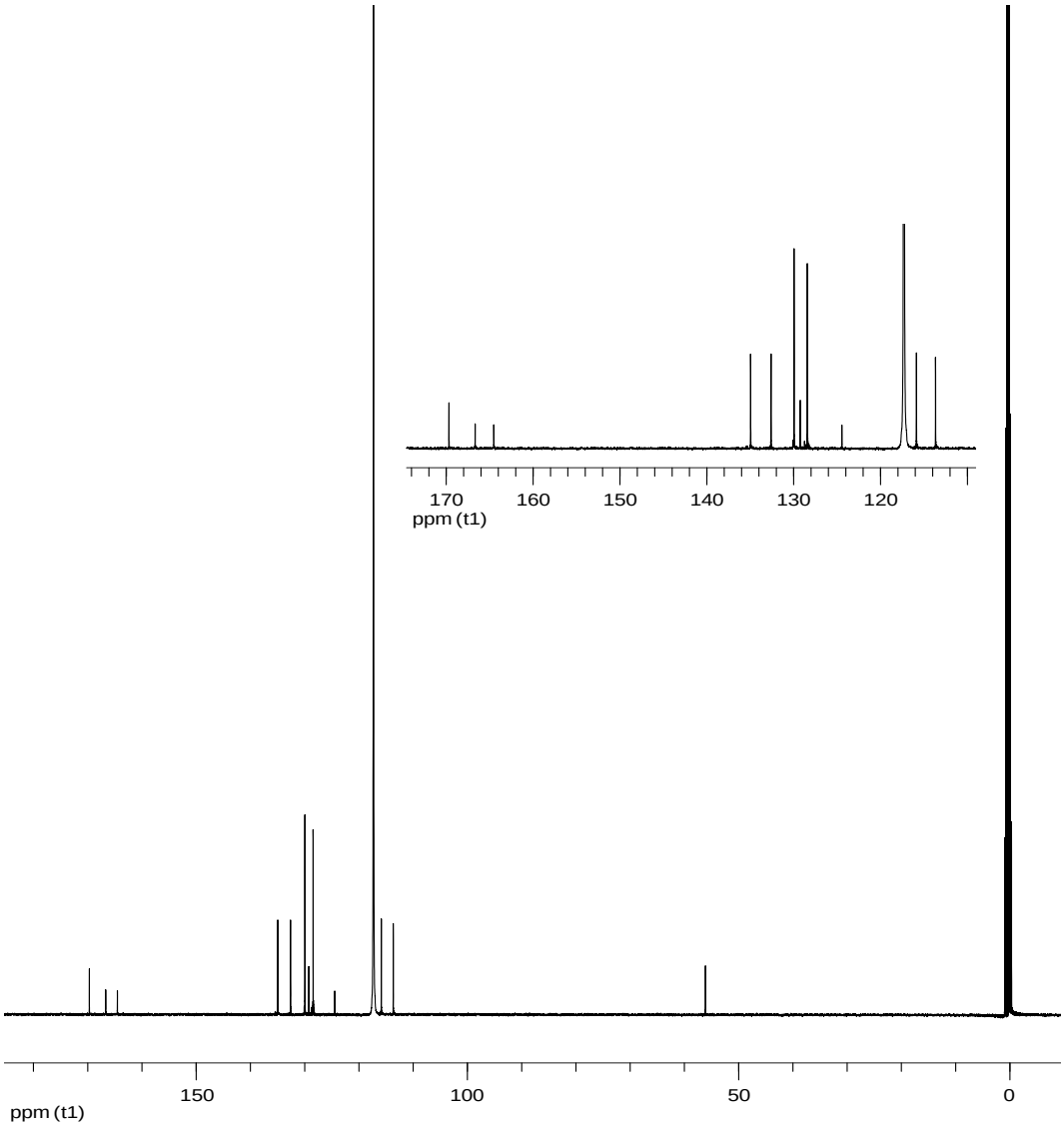


Fig. S5 ^{13}C-NMR spectrum of **2'** in CD_3CN.

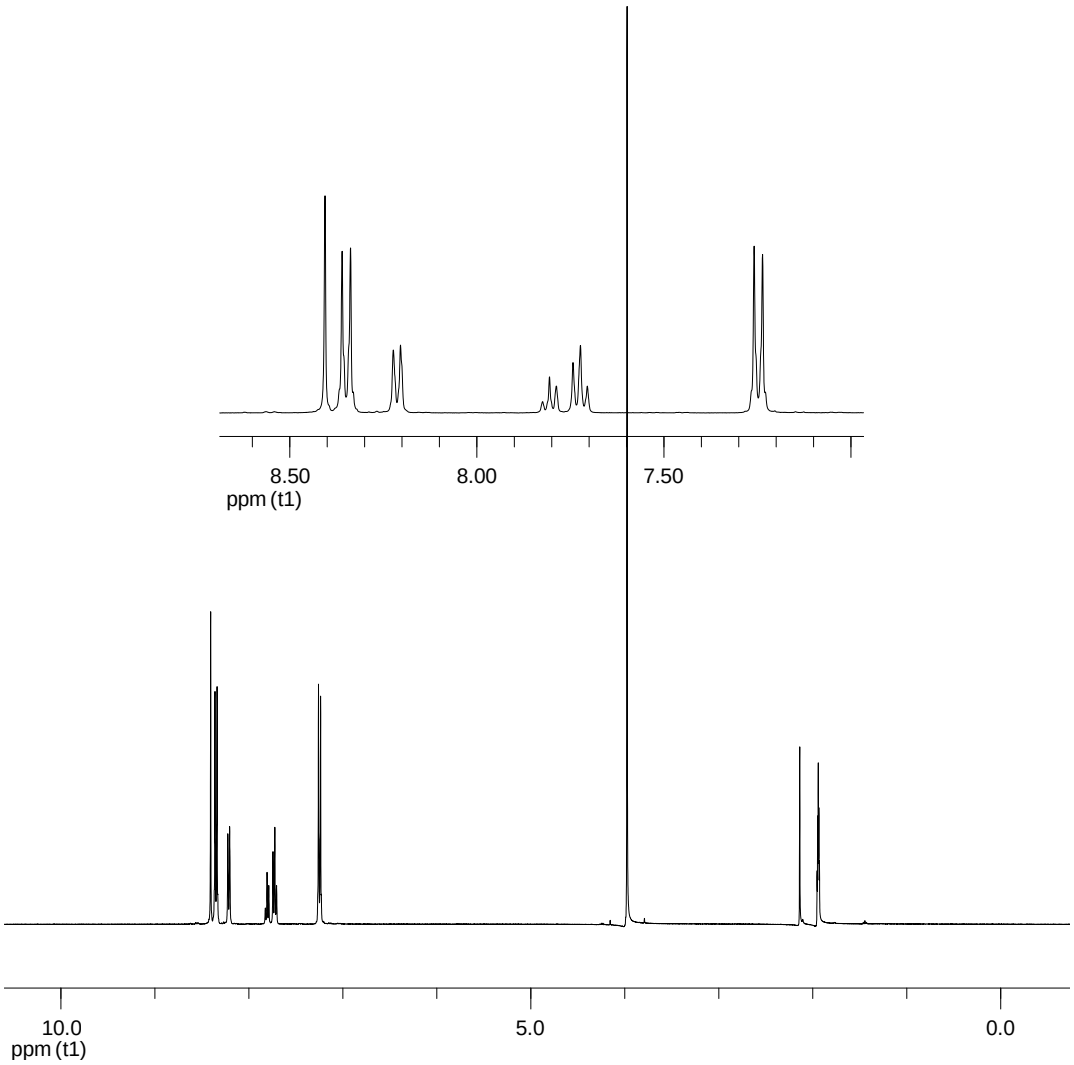


Fig. S6 ^{1}HNMR spectrum of **3'** in CD_3CN.

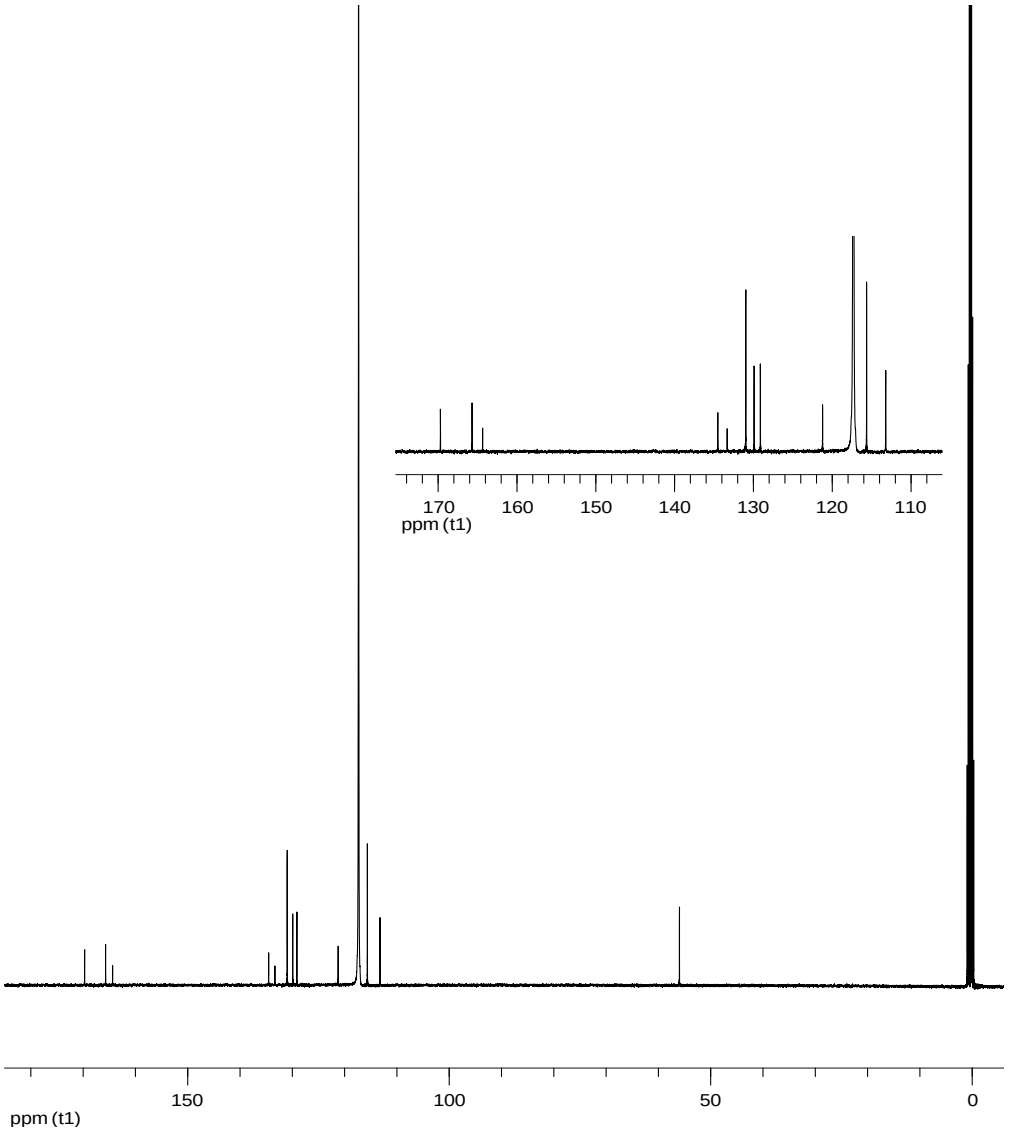


Fig. S7 ^{13}C-NMR spectrum of **3'** in CD_3CN.

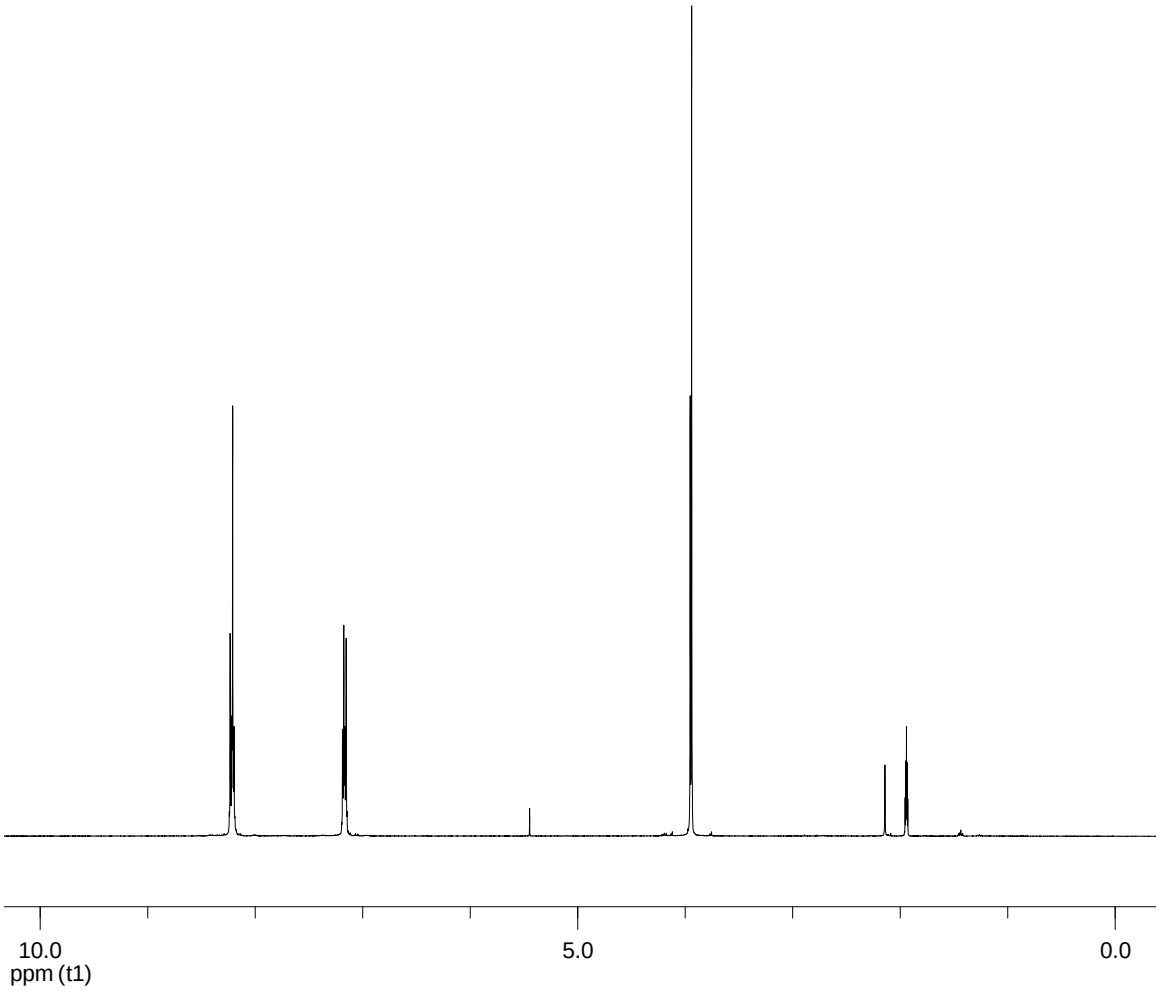


Fig. S8 ^{1}HNMR spectrum of **4'** in CD_3CN.

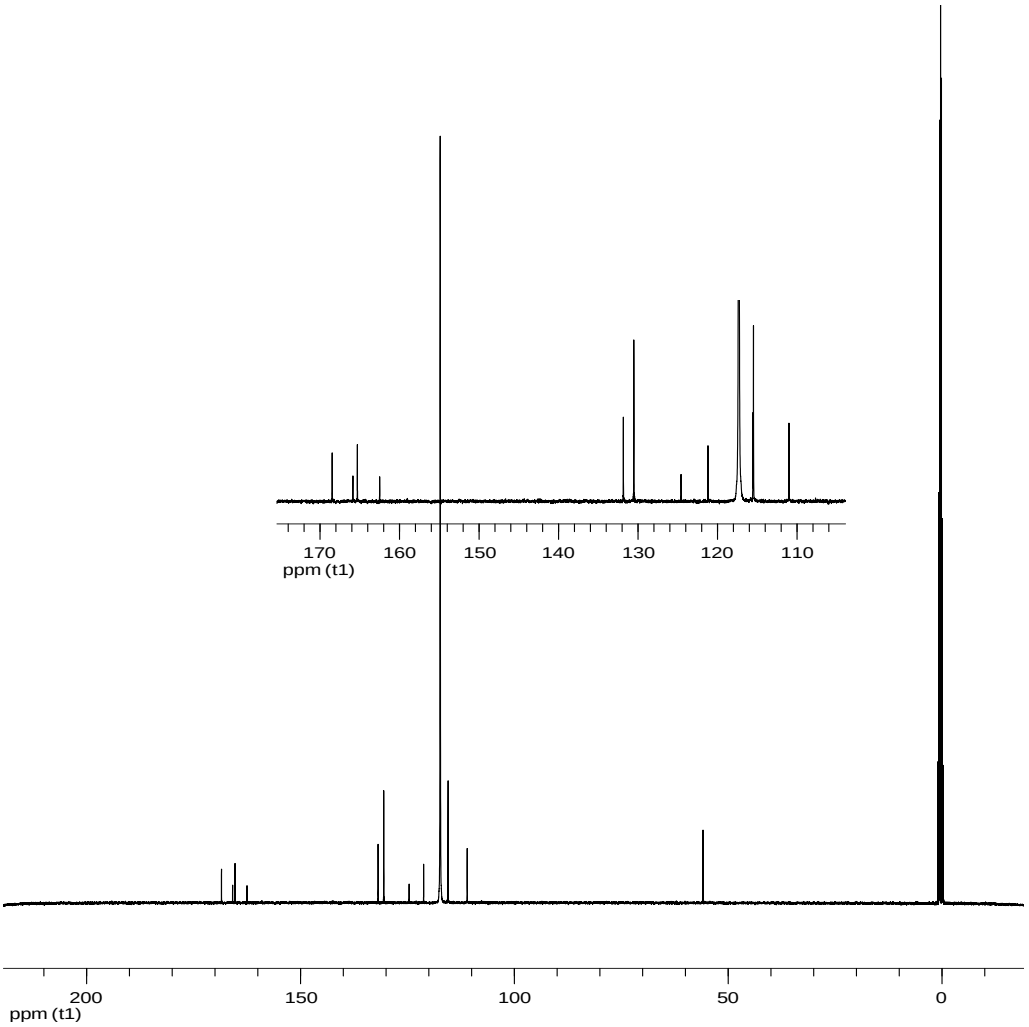


Fig. S9 ^{13}C-NMR spectrum of **4'** in CD_3CN.

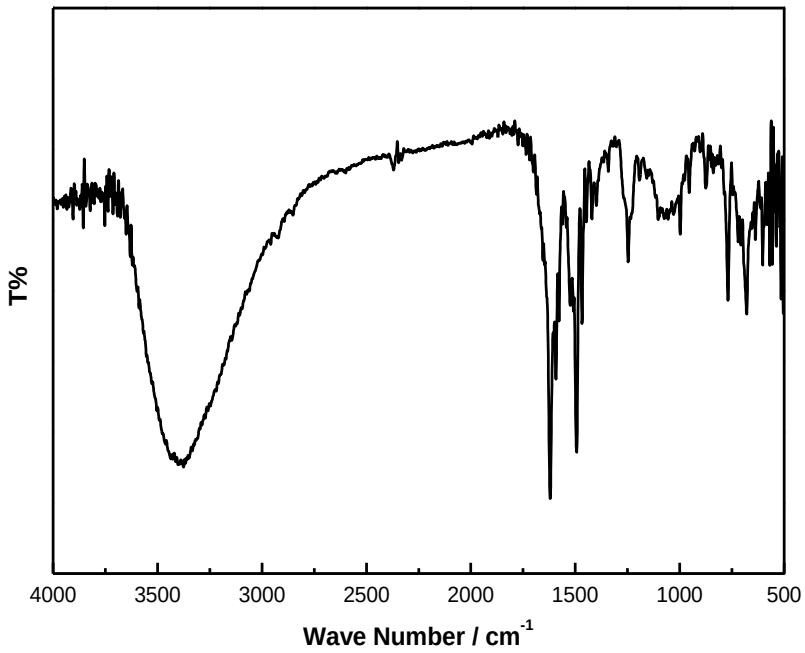


Fig. S10 IR spectrum of **1**.

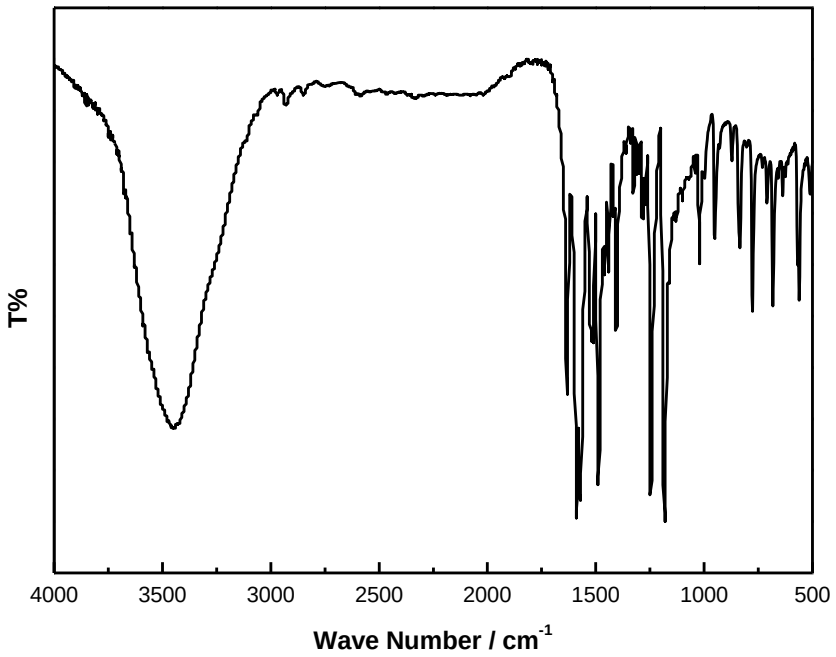


Fig. S11 IR spectrum of **2**.

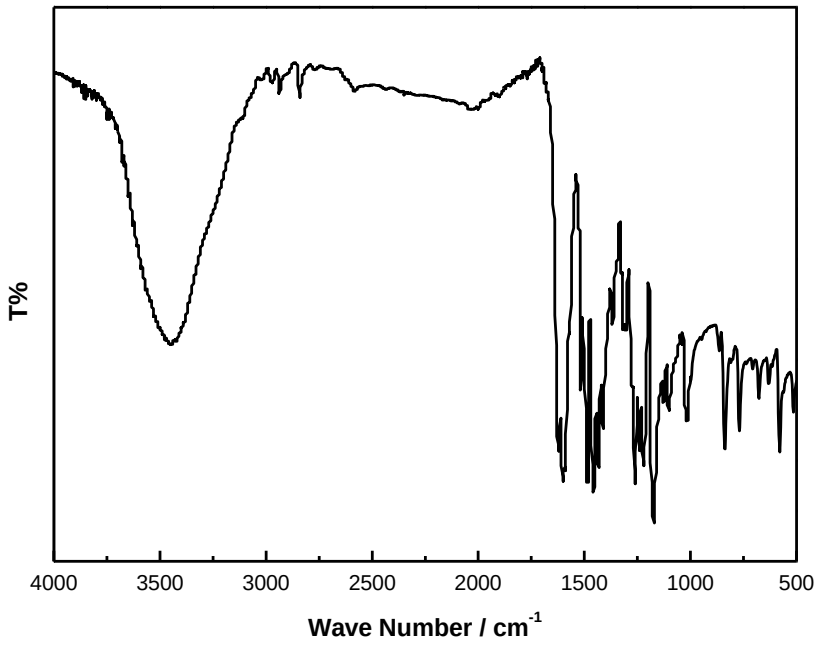


Fig. S12 IR spectrum of **3**.

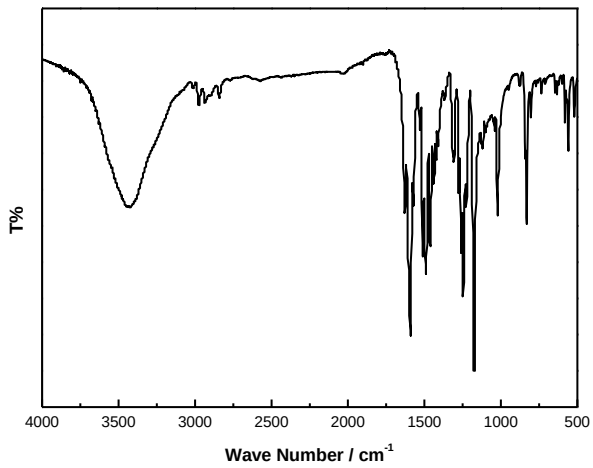
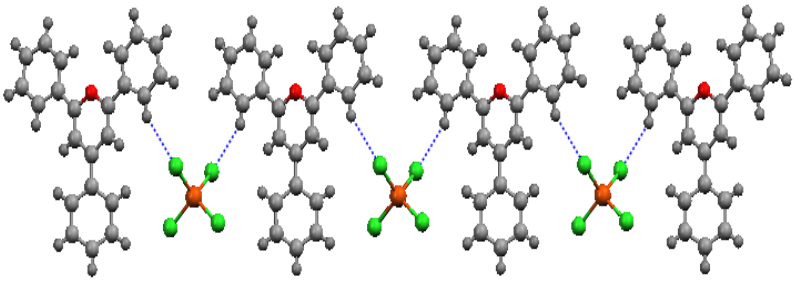
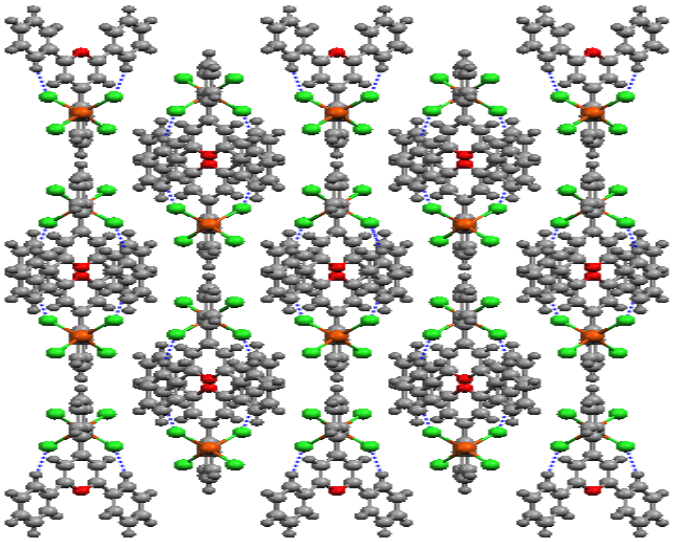


Fig. S13 IR spectrum of **4**.



(a)



(b)

Fig. S14 The schematic C–H···Cl interactions in **1**.

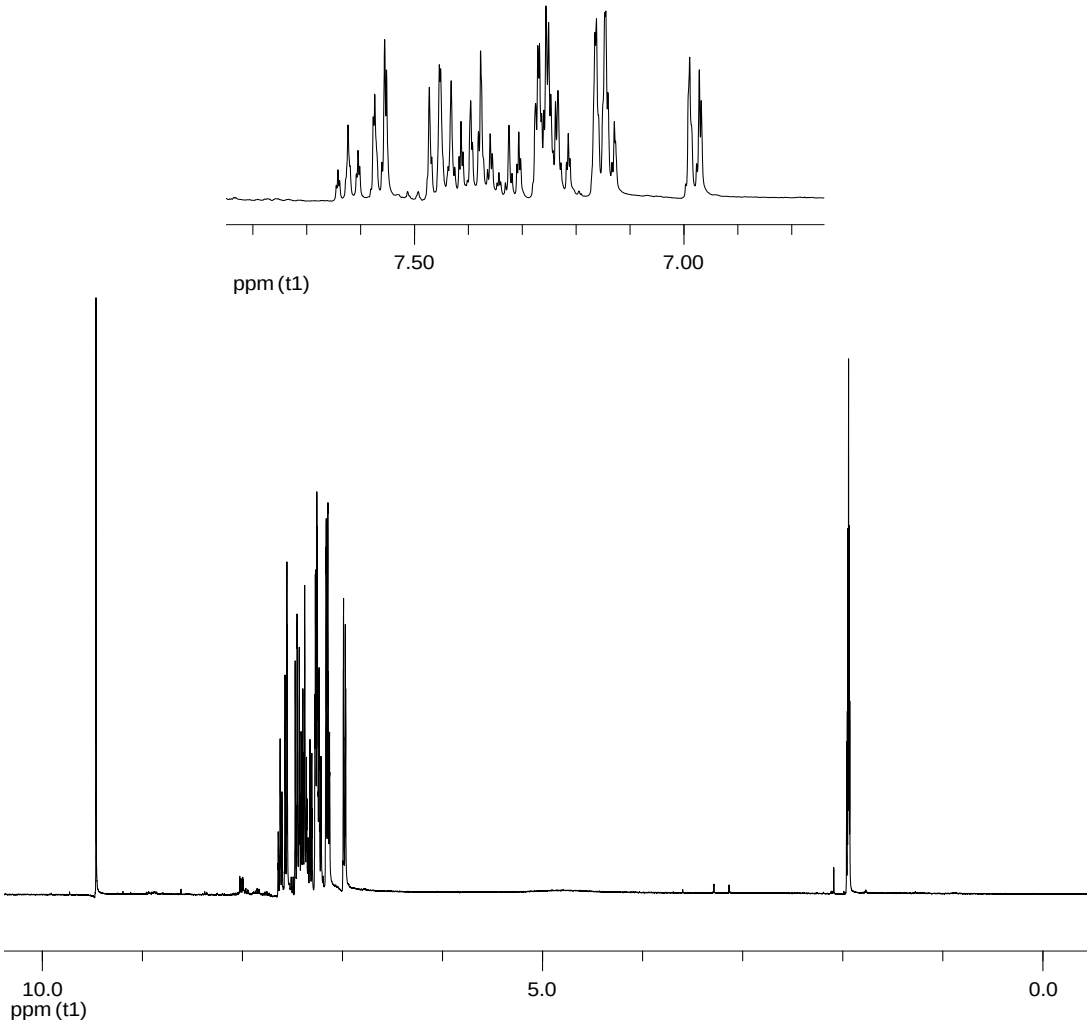


Fig. S15 ^{1}HNMR spectrum of **5'** in CD_3CN.

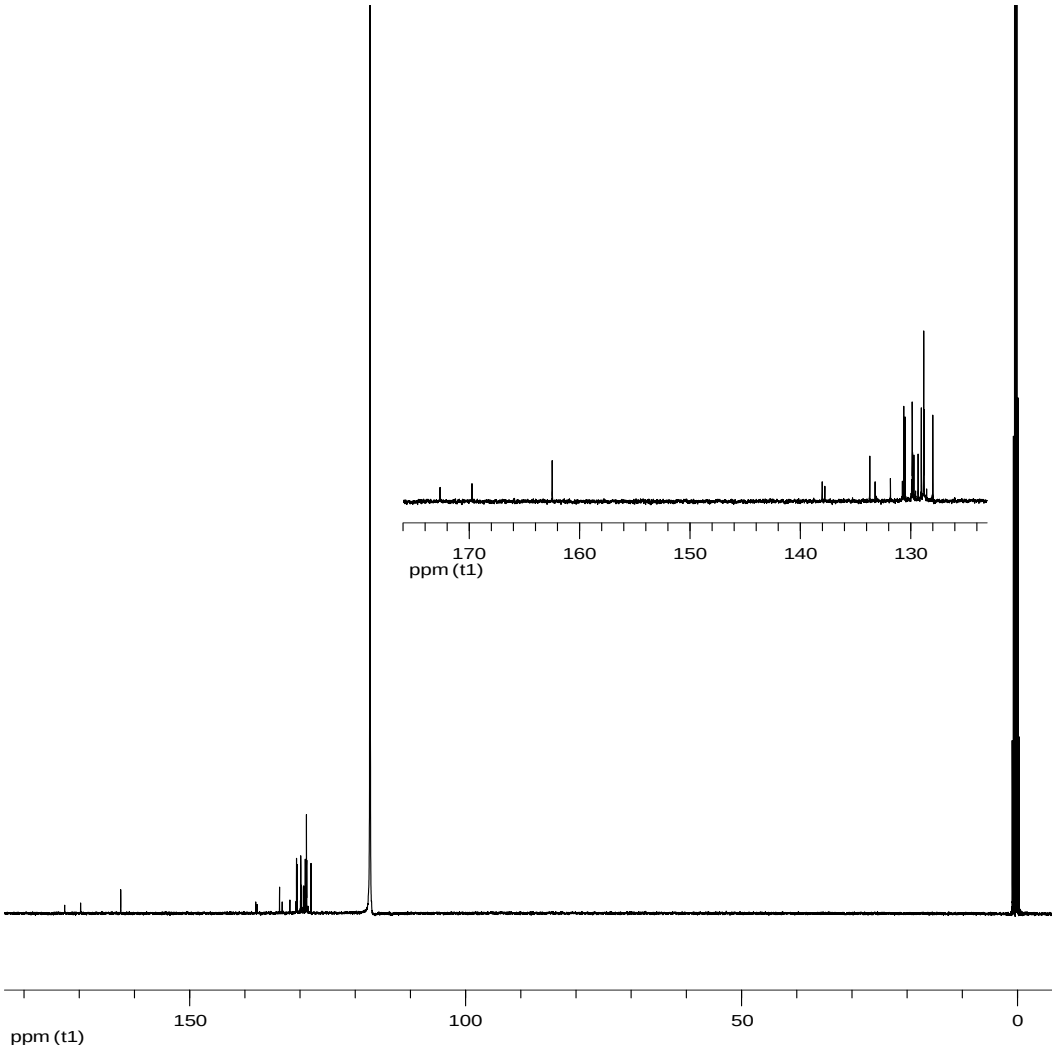


Fig. S16 ^{13}C-NMR spectrum of **5'** in CD_3CN.

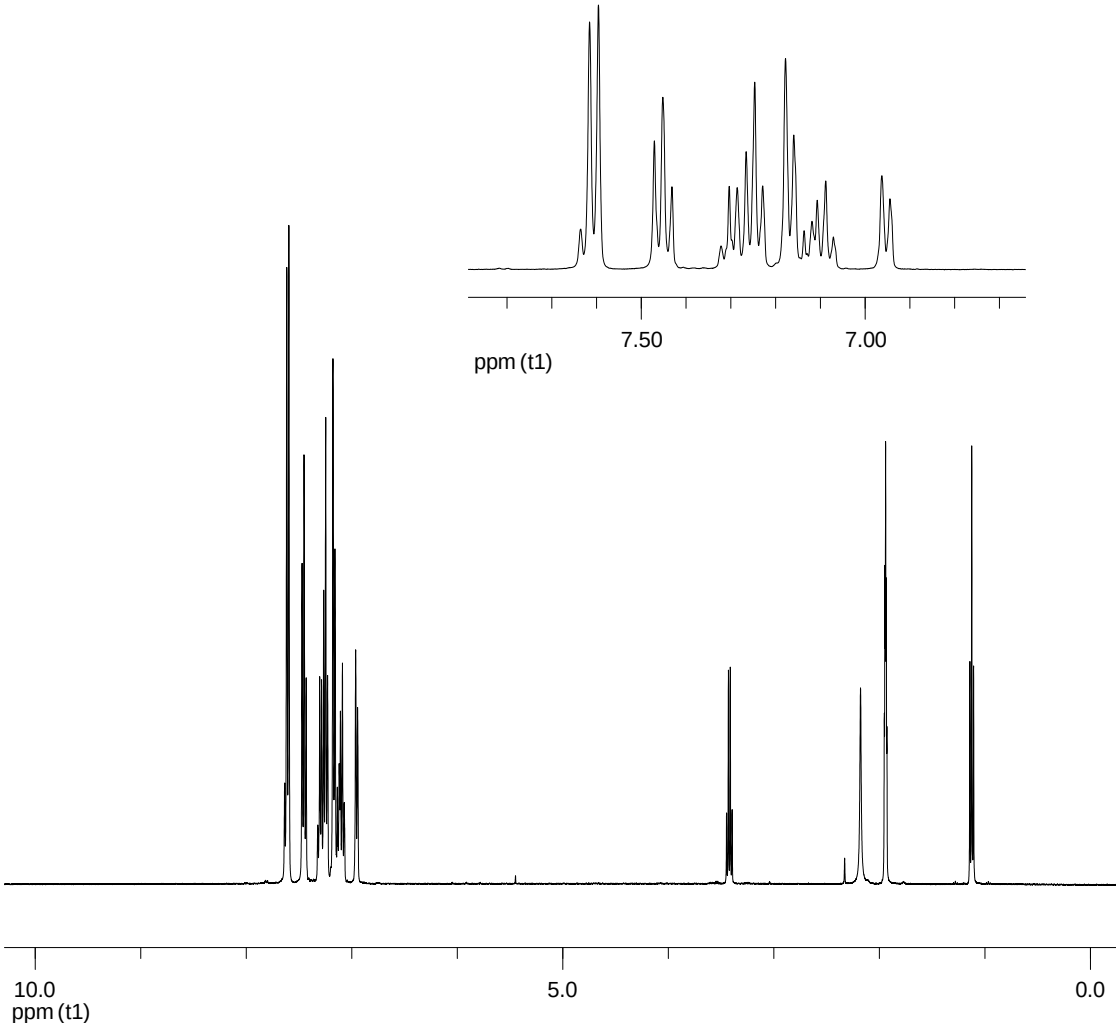


Fig. S17 ^{1}HNMR spectrum of **6'** in CD_3CN.

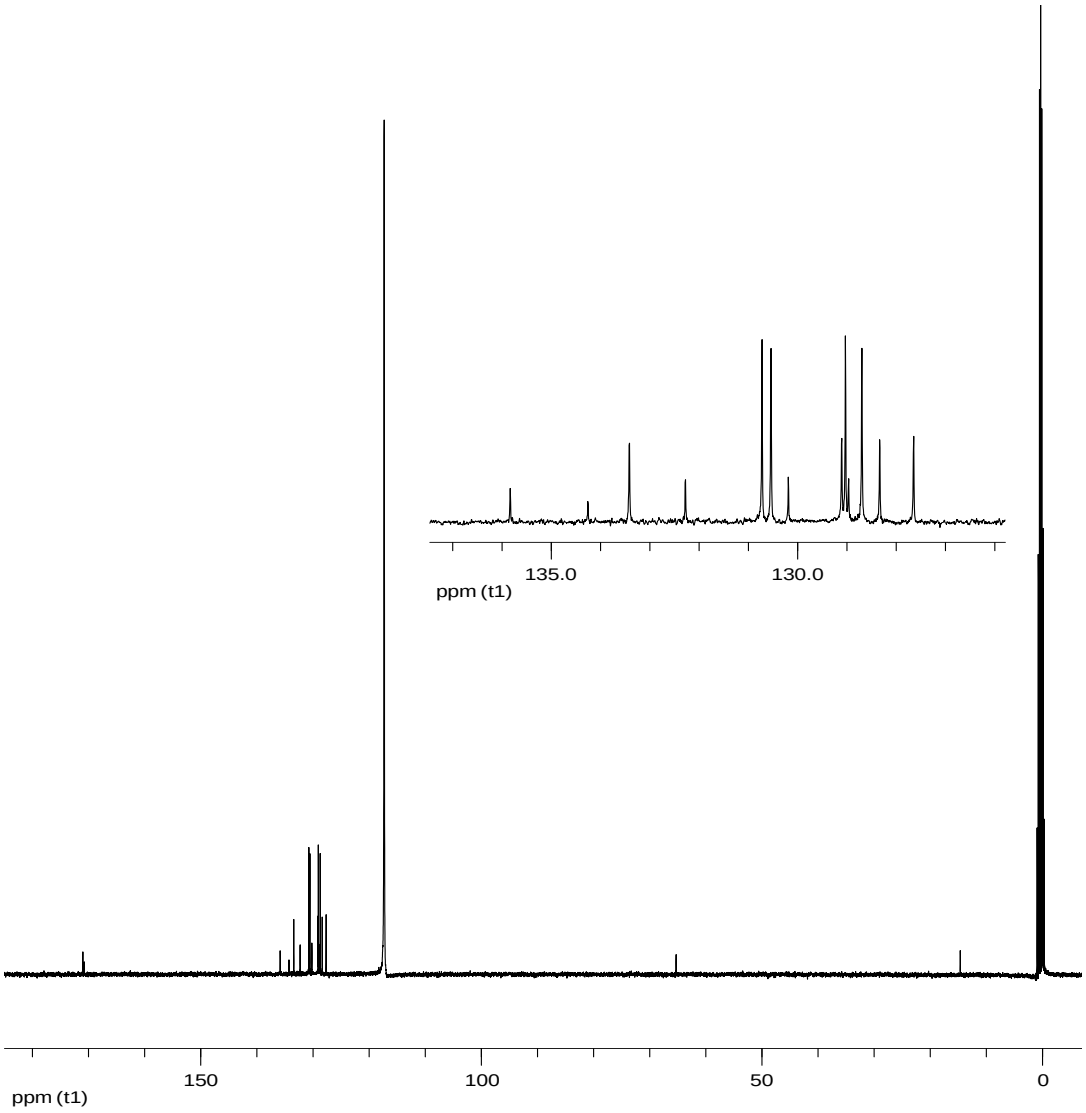


Fig. S18 ^{13}C-NMR spectrum of **6'** in CD_3CN.

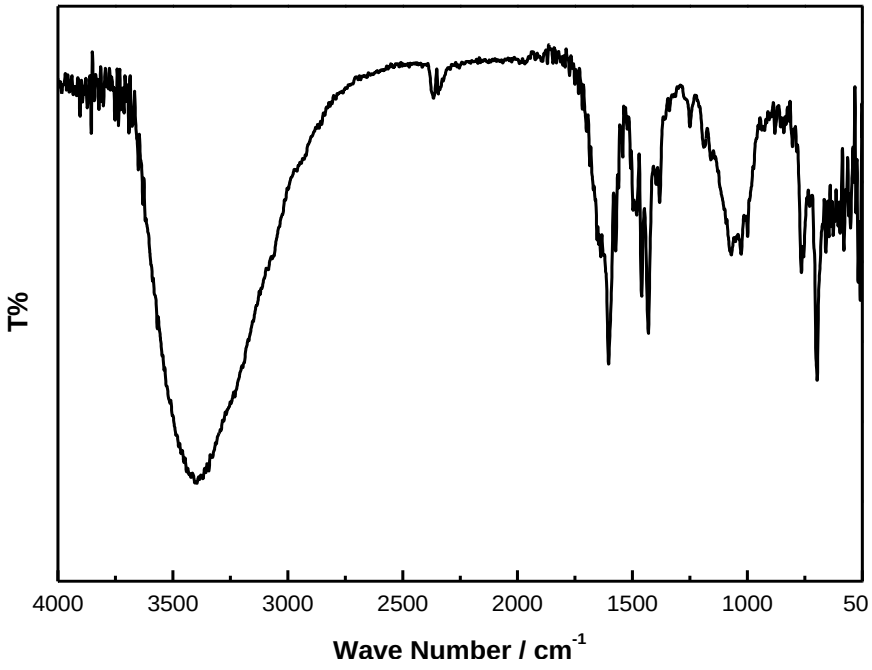


Fig. S19 IR spectrum of **5**.

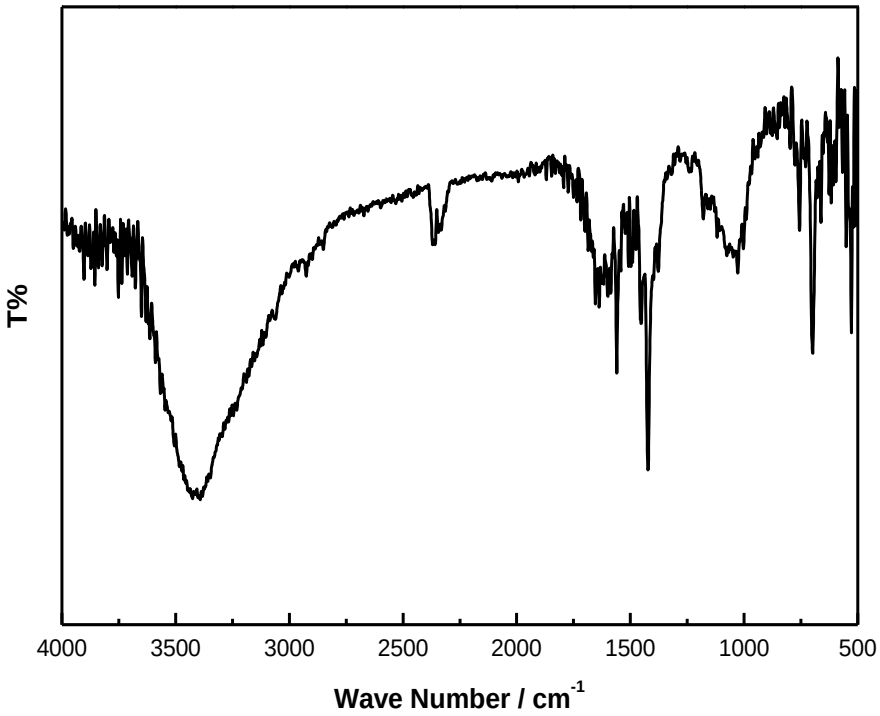


Fig. S20 IR spectrum of **6**.

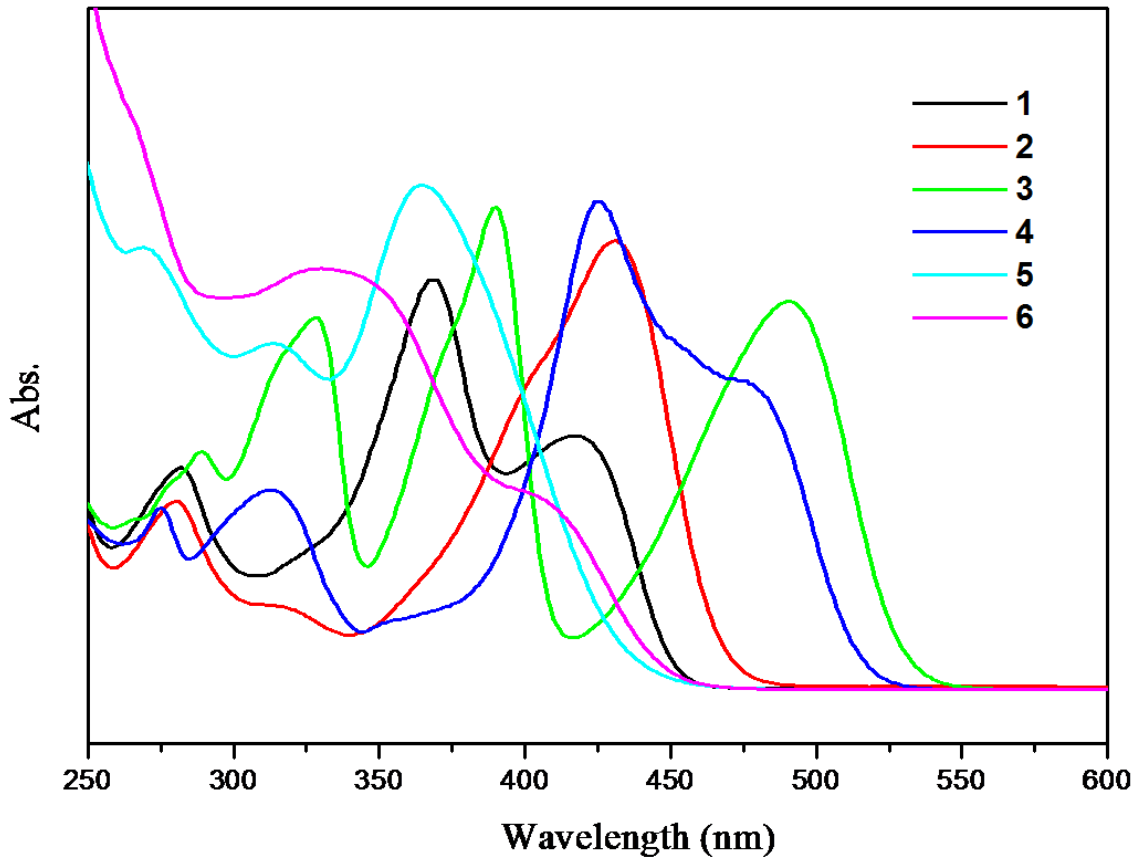


Fig. S21 The UV-vis absorption spectra of **1-6** in CH_2Cl_2 solution

Table S1 Crystallographic data and structure refinements for **1-4**

	1	**2**	**3**	**4**
Empirical formula	$C_{23}H_{17}Cl_4FeO$	$C_{24}H_{19}Cl_4FeO_2$	$C_{25}H_{21}Cl_4FeO_3$	$C_{26}H_{23}Cl_4FeO_4$
Formula weight	507.02	537.04	567.07	597.09
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic
Space group	*P*bcn	*P*bca	*P*2(1)/n	*P*2(1)/c
a (Å)	10.949(2)	13.319(6)	7.542(12)	7.772(6)
b (Å)	17.190(3)	18.375(7)	18.02(3)	19.769(16)
c (Å)	12.099(2)	19.555(8)	19.28(3)	17.515(14)
β (º)	90	90	96.98(2)	92.980(10)
Volume ($Å^3$)	2277.2(8)	4786(3)	2601 (7)	2688(4)
Z	4	8	4	4
D_{Calc}（mg/m^{-3}）	1.479	1.491	1.448	1.476
μ (mm^{-1})	1.143	1.096	1.015	0.989
F(000)	1028	2184	1156	1220
R_{int}	0.1030	0.0658	0.1139	0.0380
Data/restraints/par	2600 / 0 / 134	3818 / 0 / 281	5353 / 0 / 300	6088 / 0 / 319
GOF on F^2	1.000	1.021	1.006	0.999
R_1 [I>2σ(I)]*	0.0765	0.0413	0.0847	0.0479
wR_2 [I>2σ(I)]*	0.1697	0.0863	0.1500	0.1068
R_1 (all data) *	0.1538	0.0819	0.2712	0.0981
wR_2 (all data)*	0.2092	0.1038	0.1981	0.1264

* $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)]^2\}^{1/2}$

Table S2 Selected bond lengths [Å] and angles [°] for **1-4**

1			
Fe(1)-Cl(1)	2.1603(17)	Fe(1)-Cl(2)$^{\#1}$	2.1861(17)
Fe(1)-Cl(1)$^{\#1}$	2.1603(17)	Fe(1)-Cl(2)	2.1861(17)
O(1)-C(1)	1.359(5)	C(4)-C(5)	1.360(7)
O(1)-C(1)$^{\#2}$	1.359(5)	C(4)-C(9)	1.395(7)
C(3)-C(2)$^{\#2}$	1.390(7)	C(9)-C(8)	1.407(8)
C(3)-C(2)	1.390(7)	C(8)-C(7)	1.379(10)
C(3)-C(10)	1.443(11)	C(5)-C(6)	1.347(9)
C(2)-C(1)	1.331(7)	C(13)-C(12)$^{\#2}$	1.359(8)
C(1)-C(4)	1.446(7)	C(13)-C(12)	1.359(8)
C(10)-C(11)	1.399(7)	C(7)-C(6)	1.346(10)
C(10)-C(11)$^{\#2}$	1.399(7)	C(11)-C(12)	1.378(8)
Cl(1)-Fe(1)-Cl(1)$^{\#1}$	108.29(13)	Cl(1)-Fe(1)-Cl(2)$^{\#1}$	109.44(8)
Cl(1)$^{\#1}$-Fe(1)-Cl(2)$^{\#1}$	109.26(8)	Cl(1)-Fe(1)-Cl(2)	109.26(8)
Cl(1)$^{\#1}$-Fe(1)-Cl(2)	109.44(8)	Cl(2)$^{\#1}$-Fe(1)-Cl(2)	111.11(10)
C(1)-O(1)-C(1)$^{\#2}$	123.4(6)	C(2)$^{\#2}$-C(3)-C(2)	114.0(7)
C(2)$^{\#2}$-C(3)-C(10)	123.0(4)	C(2)-C(3)-C(10)	123.0(4)
C(1)-C(2)-C(3)	124.3(5)	C(2)-C(1)-O(1)	117.0(5)
C(2)-C(1)-C(4)	128.2(5)	O(1)-C(1)-C(4)	114.8(5)
C(11)-C(10)-C(11)$^{\#2}$	117.3(8)	C(11)-C(10)-C(3)	121.3(4)
C(11)$^{\#2}$-C(10)-C(3)	121.3(4)	C(5)-C(4)-C(9)	118.4(5)
C(5)-C(4)-C(1)	122.0(5)	C(9)-C(4)-C(1)	119.5(5)
C(4)-C(9)-C(8)	119.8(6)	C(7)-C(8)-C(9)	118.0(6)

C(6)-C(5)-C(4)	122.3(7)	C(6)-C(7)-C(8)	121.5(7)
C(12)$^{\#2}$-C(13)-C(12)	120.6(9)	C(7)-C(6)-C(5)	120.0(7)
C(12)-C(11)-C(10)	120.7(6)	C(13)-C(12)-C(11)	120.3(7)

Symmetry codes: #1 -x,y,-z+1/2; #2 -x+2,y,-z+1/2.

2

Fe(1)-Cl(3)	2.1748(13)	Fe(1)-Cl(1)	2.1826(14)
Fe(1)-Cl(2)	2.1844(12)	Fe(1)-Cl(4)	2.2039(15)
O(1)-C(5)	1.353(4)	O(1)-C(1)	1.355(4)
O(2)-C(15)	1.351(4)	O(2)-C(24)	1.422(4)
C(5)-C(4)	1.350(4)	C(5)-C(18)	1.457(5)
C(1)-C(2)	1.349(4)	C(1)-C(6)	1.464(4)
C(3)-C(2)	1.402(4)	C(3)-C(4)	1.404(4)
C(3)-C(12)	1.455(5)	C(12)-C(17)	1.385(5)
C(12)-C(13)	1.386(4)	C(18)-C(23)	1.376(5)
C(18)-C(19)	1.387(5)	C(6)-C(11)	1.382(5)
C(6)-C(7)	1.382(5	C(15)-C(16)	1.376(5)
C(15)-C(14)	1.377(5)	C(8)-C(9)	1.366(5)
C(8)-C(7)	1.372(5)	C(14)-C(13)	1.377(5)
C(9)-C(10)	1.369(5)	C(23)-C(22)	1.390(5)
C(16)-C(17)	1.367(5)	C(19)-C(20)	1.377(5)
C(20)-C(21)	1.367(5)	C(10)-C(11)	1.382(5)
C(21)-C(22)	1.368(5)	C(6)-C(11)-C(10)	120.1(4)
Cl(3)-Fe(1)-Cl(1)	107.22(5)	Cl(3)-Fe(1)-Cl(2)	109.30(5)
Cl(1)-Fe(1)-Cl(2)	112.85(5)	Cl(3)-Fe(1)-Cl(4)	112.25(5)
Cl(1)-Fe(1)-Cl(4)	108.70(5)	Cl(2)-Fe(1)-Cl(4)	106.62(5)

C(5)-O(1)-C(1)	121.5(3)	C(15)-O(2)-C(24)	119.1(3)
C(4)-C(5)-O(1)	119.6(3)	C(4)-C(5)-C(18)	127.7(3)
O(1)-C(5)-C(18)	112.6(3)	C(2)-C(1)-O(1)	119.8(3)
C(2)-C(1)-C(6)	127.5(3)	O(1)-C(1)-C(6)	112.7(3)
C(2)-C(3)-C(4)	116.2(3)	C(2)-C(3)-C(12)	122.0(3)
C(4)-C(3)-C(12)	121.8(3)	C(17)-C(12)-C(13)	116.7(3)
C(17)-C(12)-C(3)	121.2(3)	C(13)-C(12)-C(3)	122.1(3)
C(5)-C(4)-C(3)	121.5(3)	C(23)-C(18)-C(19)	118.2(4)
C(23)-C(18)-C(5)	121.1(3)	C(19)-C(18)-C(5)	120.7(3)
C(1)-C(2)-C(3)	121.4(3)	C(11)-C(6)-C(7)	118.9(3)
C(11)-C(6)-C(1)	120.3(3)	C(7)-C(6)-C(1)	120.8(3)
O(2)-C(15)-C(16)	115.6(3)	O(2)-C(15)-C(14)	124.7(4)
C(16)-C(15)-C(14)	119.7(3)	(9)-C(8)-C(7)	120.3(4)
C(13)-C(14)-C(15)	119.3(3)	C(8)-C(9)-C(10)	120.0(4)
C(18)-C(23)-C(22)	120.9(4)	C(14)-C(13)-C(12)	122.2(3)
C(17)-C(16)-C(15)	120.0(4)	C(20)-C(19)-C(18)	120.5(4)
C(21)-C(20)-C(19)	120.8(4)	C(16)-C(17)-C(12)	122.0(4)
C(9)-C(10)-C(11)	120.1(4)	C(8)-C(7)-C(6)	120.4(4)
C(20)-C(21)-C(22)	119.5(4)	C(21)-C(22)-C(23)	120.0(4)

3

Fe(1)-Cl(1)	2.154(3)	Fe(1)-Cl(3)	2.163(3)
Fe(1)-Cl(4)	2.181(4)	Fe(1)-Cl(2)	2.198(3)
O(1)-C(1)	1.333(7)	O(1)-C(5)	1.370(8)
C(6)-C(7)	1.369(8)	C(6)-C(11)	1.393(9)
C(6)-C(1)	1.495(9)	C(3)-C(4)	1.395(9)

C(3)-C(2)	1.422(8)	C(3)-C(12)	1.460(9)
O(2)-C(24)	1.358(8)	O(2)-C(9)	1.373(7)
C(1)-C(2)	1.363(8)	C(5)-C(4)	1.342(9)
C(5)-C(18)	1.469(10)	C(11)-C(10)	1.358(8)
C(7)-C(8)	1.426(8)	C(9)-C(10)	1.364(9)
C(9)-C(8)	1.420(9)	C(17)-C(16)	1.419(11)
C(17)-C(12)	1.424(9)	C(12)-C(13)	1.363(9)
C(15)-C(14)	1.333(10)	C(15)-C(16)	1.349(12)
C(18)-C(23)	1.362(9)	C(18)-C(19)	1.419(9)
O(3)-C(25)	1.361(9)	O(3)-C(21)	1.419(10)
C(22)-C(23)	1.370(10)	C(22)-C(21)	1.385(13)
C(20)-C(21)	1.368(12)	C(20)-C(19)	1.377(11)
C(14)-C(13)	1.401(10)		
Cl(1)-Fe(1)-Cl(3)	108.18(12)	Cl(1)-Fe(1)-Cl(4)	111.27(18)
Cl(3)-Fe(1)-Cl(4)	110.32(17)	Cl(1)-Fe(1)-Cl(2)	111.15(14)
Cl(3)-Fe(1)-Cl(2)	111.04(13)	Cl(4)-Fe(1)-Cl(2)	104.88(14)
C(1)-O(1)-C(5)	120.5(6)	C(7)-C(6)-C(11)	119.2(7)
C(7)-C(6)-C(1)	119.3(7)	C(11)-C(6)-C(1)	121.4(7)
C(4)-C(3)-C(2)	113.9(7)	C(4)-C(3)-C(12)	125.1(7)
C(2)-C(3)-C(12)	121.0(7)	C(24)-O(2)-C(9)	119.1(7)
O(1)-C(1)-C(2)	120.9(7)	O(1)-C(1)-C(6)	111.6(6)
C(2)-C(1)-C(6)	127.4(7)	C(4)-C(5)-O(1)	119.2(7)
C(4)-C(5)-C(18)	131.2(8)	O(1)-C(5)-C(18)	109.5(7)
C(10)-C(11)-C(6)	119.7(7)	C(6)-C(7)-C(8)	122.7(7)
C(10)-C(9)-O(2)	114.6(7)	C(10)-C(9)-C(8)	121.2(7)

O(2)-C(9)-C(8)	124.2(7)	C(9)-C(8)-C(7)	115.1(7)
C(16)-C(17)-C(12)	115.9(8)	C(13)-C(12)-C(17)	118.8(8)
C(13)-C(12)-C(3)	123.0(8)	C(17)-C(12)-C(3)	118.2(8)
C(1)-C(2)-C(3)	121.5(7)	C(14)-C(15)-C(16)	117.5(9)
C(5)-C(4)-C(3)	124.1(7)	C(23)-C(18)-C(19)	118.1(8)
C(23)-C(18)-C(5)	123.0(8)	C(19)-C(18)-C(5)	118.9(8)
C(11)-C(10)-C(9)	122.0(7)	C(25)-O(3)-C(21)	115.3(9)
C(23)-C(22)-C(21)	117.0(9)	C(21)-C(20)-C(19)	119.9(9)
C(15)-C(14)-C(13)	122.2(9)	C(15)-C(16)-C(17)	124.7(10)
C(18)-C(23)-C(22)	123.5(8)	C(12)-C(13)-C(14)	121.0(8)
C(20)-C(21)-C(22)	122.2(8)	C(20)-C(21)-O(3)	125.4(12)
C(22)-C(21)-O(3)	112.5(12)	C(20)-C(19)-C(18)	119.3(8)
4			
Fe(1)-Cl(4)	2.1807(15)	Fe(1)-Cl(3)	2.1886(15)
Fe(1)-Cl(2)	2.1965(17)	Fe(1)-Cl(1)	2.2043(16)
O(1)-C(1)	1.353(3)	O(1)-C(5)	1.366(3)
O(2)-C(9)	1.364(3)	O(2)-C(12)	1.432(4)
O(4)-C(23)	1.359(3)	O(4)-C(26)	1.427(4)
C(5)-C(4)	1.368(4)	C(5)-C(20)	1.446(4)
C(3)-C(4)	1.393(4)	C(3)-C(2)	1.407(4)
C(3)-C(13)	1.457(4)	C(13)-C(18)	1.395(4)
C(13)-C(14)	1.404(4)	C(7)-C(6)	1.386(4)
C(7)-C(8)	1.387(4)	C(6)-C(11)	1.403(4)
C(6)-C(1)	1.458(4)	C(20)-C(21)	1.399(4)
C(20)-C(25)	1.405(4)	C(2)-C(1)	1.357(4)

C(24)-C(25)	1.364(4)	C(24)-C(23)	1.385(4)
O(3)-C(16)	1.354(4)	O(3)-C(19)	1.418(4)
C(8)-C(9)	1.388(4)	C(22)-C(21)	1.393(4)
C(22)-C(23)	1.399(4)	C(17)-C(18)	1.380(4)
C(17)-C(16)	1.390(4)	C(11)-C(10)	1.375(4)
C(14)-C(15)	1.373(4)	C(16)-C(15)	1.394(4)
Cl(4)-Fe(1)-Cl(3)	110.11(7)	Cl(4)-Fe(1)-Cl(2)	112.27(5)
Cl(3)-Fe(1)-Cl(2)	106.98(5)	Cl(4)-Fe(1)-Cl(1)	106.42(6)
Cl(3)-Fe(1)-Cl(1)	111.57(5)	Cl(2)-Fe(1)-Cl(1)	109.55(7)
C(1)-O(1)-C(5)	123.1(2)	(9)-O(2)-C(12)	117.5(3)
C(23)-O(4)-C(26)	119.1(3)	O(1)-C(5)-C(4)	118.1(2)
O(1)-C(5)-C(20)	113.7(2)	C(4)-C(5)-C(20)	128.2(3)
C(4)-C(3)-C(2)	116.8(3)	C(4)-C(3)-C(13)	122.0(3)
C(2)-C(3)-C(13)	121.1(3)	C(5)-C(4)-C(3)	121.7(3)
C(18)-C(13)-C(14)	117.7(3)	C(18)-C(13)-C(3)	120.9(3)
C(14)-C(13)-C(3)	121.4(3)	C(6)-C(7)-C(8)	121.3(3)
C(7)-C(6)-C(11)	118.3(3)	C(7)-C(6)-C(1)	121.7(3)
C(11)-C(6)-C(1)	120.0(3)	C(21)-C(20)-C(25)	117.8(3)
C(21)-C(20)-C(5)	121.9(2)	C(25)-C(20)-C(5)	120.3(3)
C(1)-C(2)-C(3)	121.6(3)	C(25)-C(24)-C(23)	120.4(3)
C(16)-O(3)-C(19)	118.4(3)	C(7)-C(8)-C(9)	119.6(3)
O(1)-C(1)-C(2)	118.6(3)	O(1)-C(1)-C(6)	114.3(2)
C(2)-C(1)-C(6)	127.0(3)	C(21)-C(22)-C(23)	118.4(3)
C(22)-C(21)-C(20)	121.6(3)	O(4)-C(23)-C(24)	116.0(3)
O(4)-C(23)-C(22)	123.5(3)	C(24)-C(23)-C(22)	120.5(3)

C(18)-C(17)-C(16)	120.1(3)	C(24)-C(25)-C(20)	121.2(3)
C(10)-C(11)-C(6)	120.1(3)	C(15)-C(14)-C(13)	121.3(3)
C(11)-C(10)-C(9)	121.1(3)	C(17)-C(18)-C(13)	121.3(3)
O(3)-C(16)-C(17)	124.6(3)	O(3)-C(16)-C(15)	116.0(3)
C(17)-C(16)-C(15)	119.4(3)	O(2)-C(9)-C(10)	115.6(3)
O(2)-C(9)-C(8)	124.9(3)	C(10)-C(9)-C(8)	119.5(3)
C(14)-C(15)-C(16)	120.1(3)		

Table S3 Crystal data and structure refinement for **5·H_2O.**

Empirical formula	$C_{29}H_{23}Cl_4FeO_2$
Formula weight	601.12
Crystal system	monoclinic
Space group	P2(1)/c
a (Å)	10.4870(6)
b (Å)	32.446(2)
c (Å)	9.5526(5)
β (º)	107.715(4)
Volume ($Å^3$)	3096.3(3)
Z	4
D_{Calc}（mg/m^{-3}）	1.290
μ (mm^{-1})	0.855
$F_{(000)}$	1228
R_{int}	0.0338
Data / restraints / parameters	7103 / 0 / 334
GOF on F^2	1.056
R_1 [$I>2\sigma(I)$]*	0.0737
wR_2 [$I>2\sigma(I)$]*	0.2357
R_1 (all data) *	0.1210
wR_2 (all data)*	0.2744

*$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)]^2\}^{1/2}$

Table S4 Selected bond lengths [Å] and angles [°] for **5·H$_2$O**.

O(1)-C(5)	1.336(4)	C(18)-C(23)	1.377(5)
O(1)-C(1)	1.339(4)	C(18)-C(19)	1.390(5)
C(1)-C(2)	1.383(5)	C(19)-C(20)	1.376(6)
C(1)-C(6)	1.462(5)	C(20)-C(21)	1.351(8)
C(2)-C(3)	1.403(4)	C(21)-C(22)	1.376(8)
C(2)-C(12)	1.483(5)	C(22)-C(23)	1.394(7)
C(3)-C(4)	1.409(5)	C(24)-C(25)	1.384(5)
C(3)-C(18)	1.480(5)	C(24)-C(29)	1.384(5)
C(4)-C(5)	1.346(5)	C(25)-C(26)	1.383(6)
C(4)-C(24)	1.487(5)	C(26)-C(27)	1.353(8)
C(6)-C(11)	1.386(5)	C(27)-C(28)	1.363(9)
C(6)-C(7)	1.391(5)	C(28)-C(29)	1.381(7)
C(7)-C(8)	1.381(6)	Fe(1)-Cl(4)	2.1658(14)
C(8)-C(9)	1.360(7)	Fe(1)-Cl(1)	2.1649(13)
C(9)-C(10)	1.364(7)	Fe(1)-Cl(2)	2.1852(12)
C(10)-C(11)	1.370(6)	Fe(1)-Cl(3)	2.1860(16)
C(12)-C(13)	1.376(6)	C(14)-C(15)	1.344(9)
C(12)-C(17)	1.385(6)	C(15)-C(16)	1.369(10)
C(13)-C(14)	1.381(7)	C(16)-C(17)	1.390(7)
C(5)-O(1)-C(1)	122.0(3)	C(23)-C(18)-C(3)	120.1(3)
O(1)-C(1)-C(2)	119.2(3)	C(19)-C(18)-C(3)	120.8(3)
O(1)-C(1)-C(6)	112.2(3)	C(20)-C(19)-C(18)	120.5(4)
C(2)-C(1)-C(6)	128.6(3)	C(21)-C(20)-C(19)	120.2(5)
C(1)-C(2)-C(3)	119.4(3)	C(20)-C(21)-C(22)	120.6(5)
C(1)-C(2)-C(12)	119.8(3)	C(21)-C(22)-C(23)	119.9(5)
C(3)-C(2)-C(12)	120.8(3)	C(18)-C(23)-C(22)	119.7(5)
C(2)-C(3)-C(4)	119.1(3)	C(25)-C(24)-C(29)	119.3(4)
C(2)-C(3)-C(18)	121.5(3)	C(25)-C(24)-C(4)	120.1(3)
C(4)-C(3)-C(18)	119.4(3)	C(29)-C(24)-C(4)	120.4(4)
C(5)-C(4)-C(3)	117.9(3)	C(24)-C(25)-C(26)	120.2(4)
C(5)-C(4)-C(24)	116.7(3)	C(27)-C(26)-C(25)	119.9(5)
C(3)-C(4)-C(24)	125.3(3)	C(26)-C(27)-C(28)	120.8(5)
O(1)-C(5)-C(4)	122.5(3)	C(27)-C(28)-C(29)	120.5(5)
C(11)-C(6)-C(7)	118.5(4)	C(28)-C(29)-C(24)	119.4(5)

C(11)-C(6)-C(1)	122.0(3)	Cl(4)-Fe(1)-Cl(1)	111.20(8)
C(7)-C(6)-C(1)	119.5(3)	Cl(4)-Fe(1)-Cl(2)	107.88(6)
C(8)-C(7)-C(6)	119.6(4)	Cl(1)-Fe(1)-Cl(2)	108.99(6)
C(9)-C(8)-C(7)	121.1(5)	Cl(4)-Fe(1)-Cl(3)	109.99(9)
C(10)-C(9)-C(8)	119.4(5)	Cl(1)-Fe(1)-Cl(3)	108.94(7)
C(9)-C(10)-C(11)	120.8(5)	Cl(2)-Fe(1)-Cl(3)	109.82(6)
C(10)-C(11)-C(6)	120.5(4)	C(15)-C(14)-C(13)	119.5(6)
C(13)-C(12)-	119.6(4)	C(14)-C(15)-C(16)	121.7(6)
C(13)-C(12)-C(2)	121.5(4)	C(15)-C(16)-C(17)	119.5(6)
C(17)-C(12)-C(2)	118.9(4)	C(12)-C(17)-C(16)	119.2(5)
C(12)-C(13)-	120.5(5)	C(23)-C(18)-C(19)	119.1(4)