Supporting Information

Upper Rim Allyl and Arylazo Coupled Calix[4]arenes as Highly Sensitive Chromogenic Sensors for Hg^{+2} Ion

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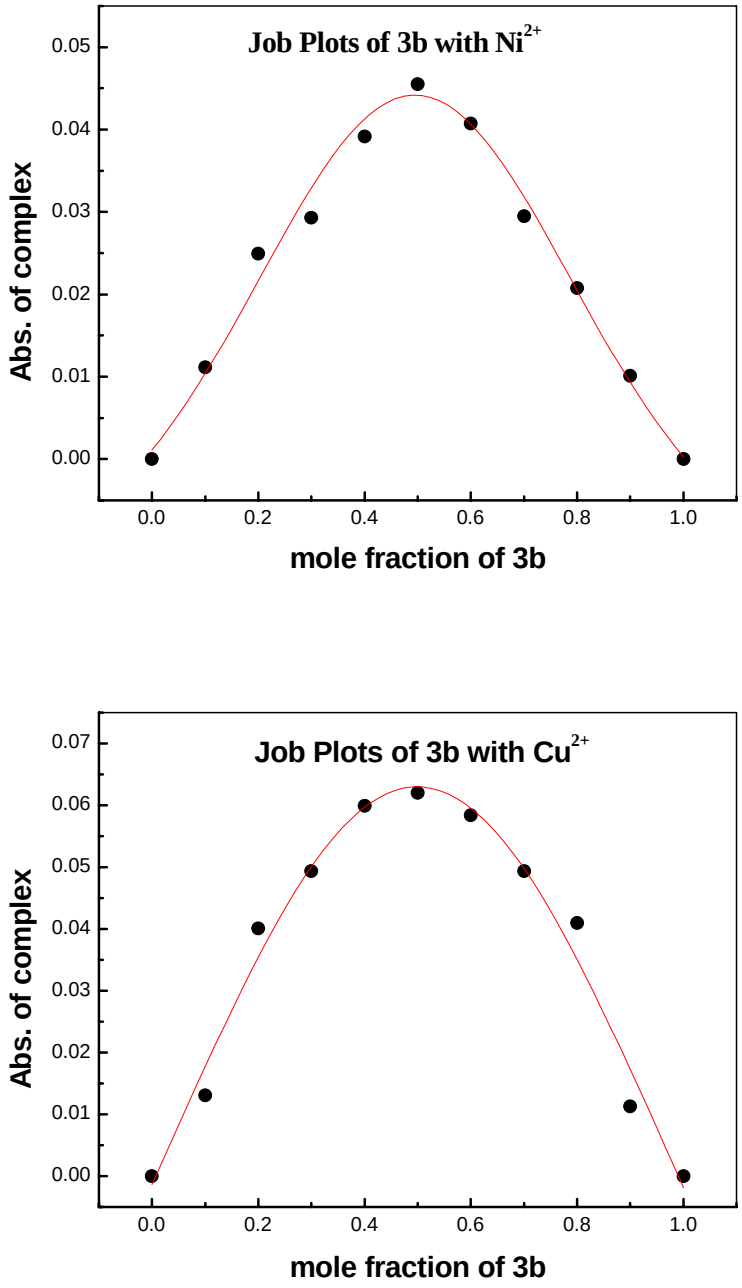


Figure S-1. Job's Plots of **3b** with transition metal perchlorates: (a) Ni^{2+}, and (b) Cu^{2+}.

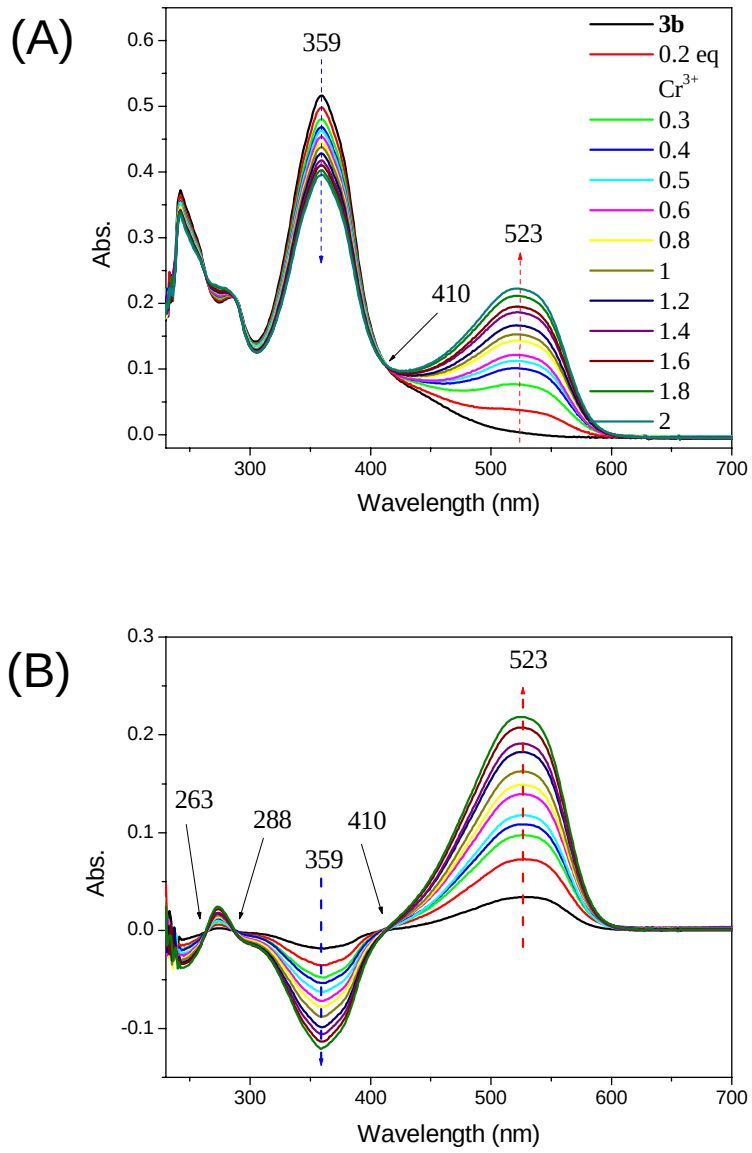


Figure S-2. (A) UV/vis titration spectra of **3b** with $Cr(ClO_4)_3$ in methanol–chloroform (v/v = 1/399) co-solvent. [**3b**] = 0.01 mM, [Cr^{3+}] = 0~2 equiv. of **3b**. (B) Delta absorption plot of (A).

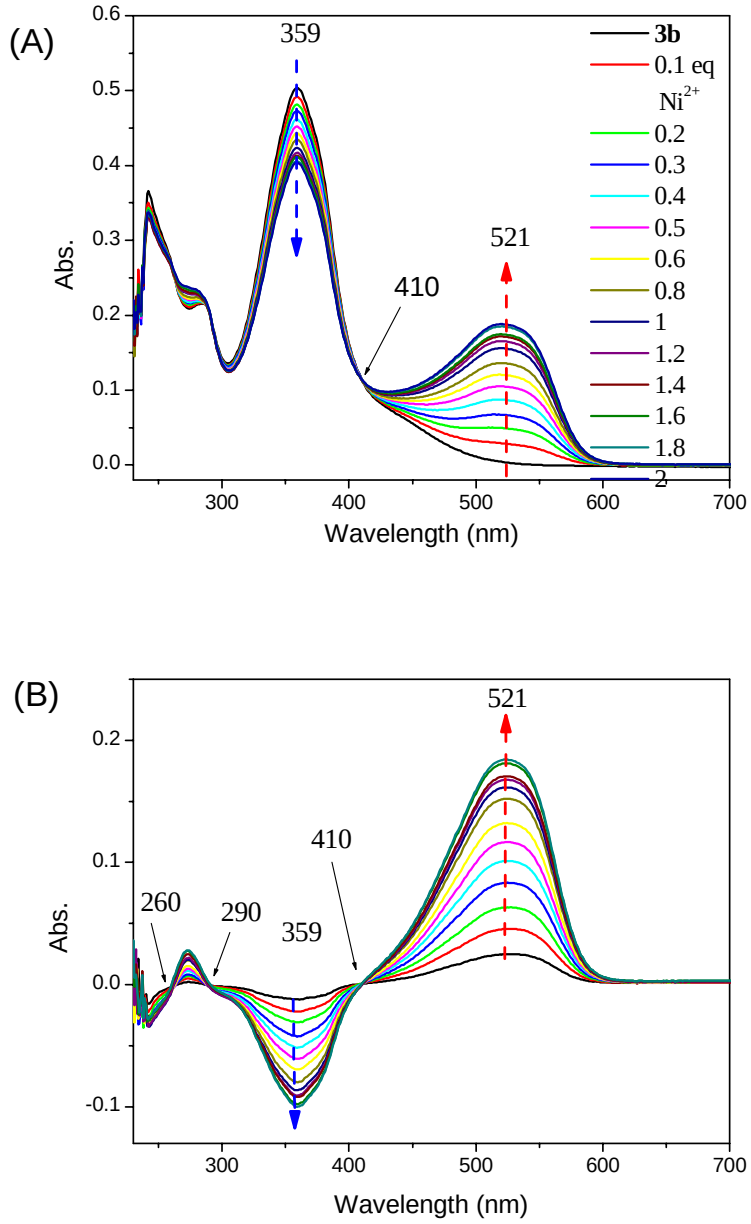


Figure S-3. (A) UV/vis titration spectra of **3b** with $Ni(ClO_4)_2$ in methanol–chloroform (v/v = 1/399) co-solvent. [**3b**] = 0.01 mM, [Ni^{2+}] = 0~2 equiv. of **3b**. (B) Delta absorption plot of (A).

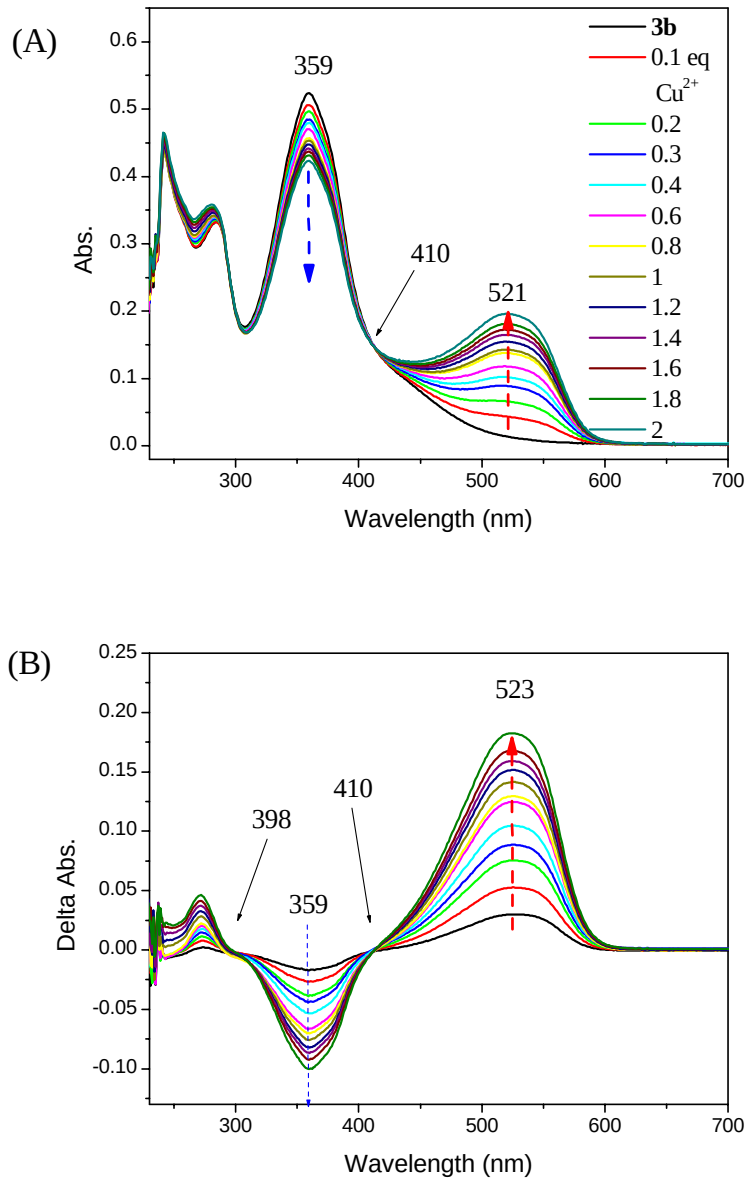


Figure S-4. (A) UV/vis titration spectra of **3b** with $Cu(ClO_4)_2$ in methanol–chloroform (v/v = 1/399) co-solvent. [**3b**] = 0.01 mM, [Cu^{2+}] = 0~2 equiv. of **3b**. (B) Delta absorption plot of (A).

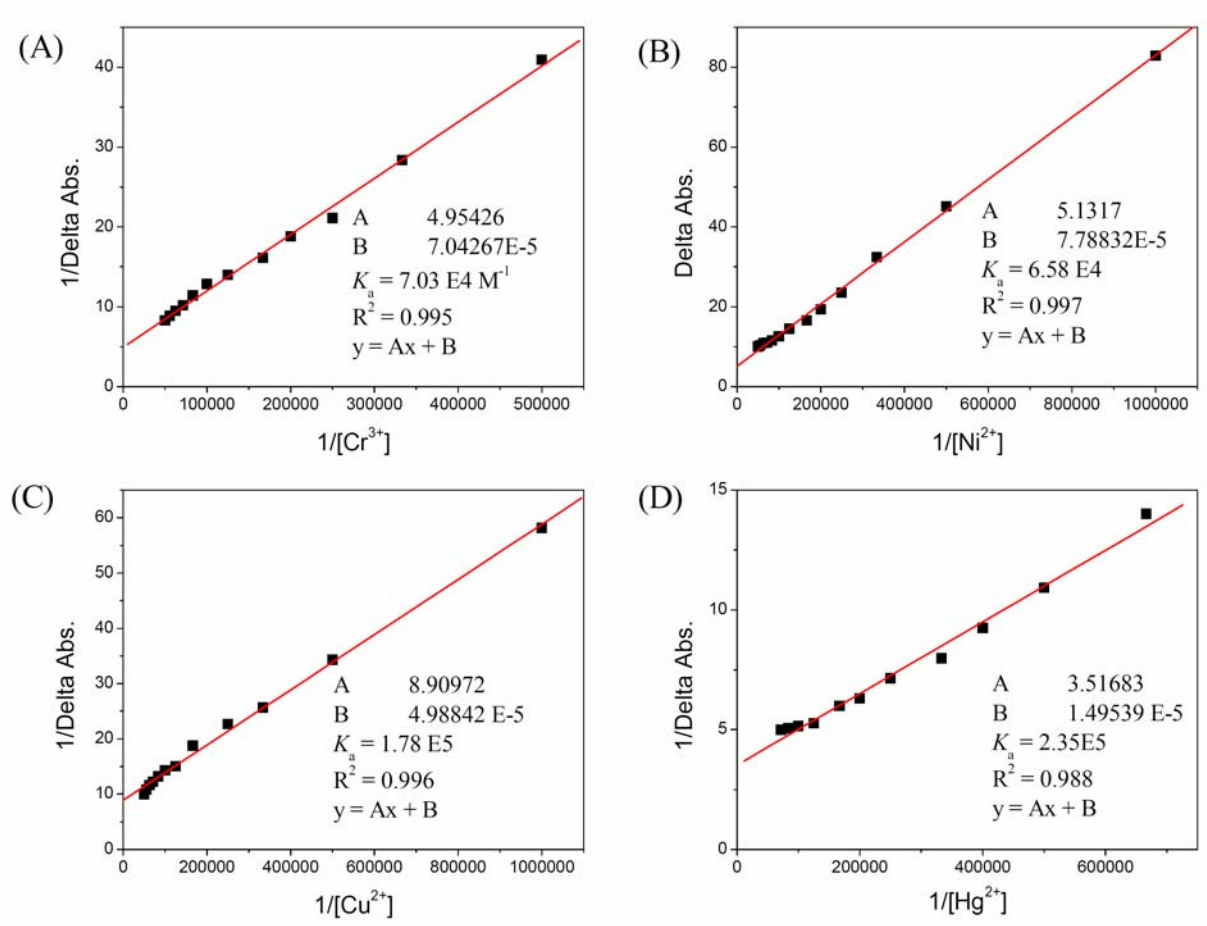


Figure S-5. Benesi-Hilderbrand plots of **3b** with transition metal perchlorates: (a) Cr^{3+}, (b) Ni^{2+}, (c) Cu^{2+} and (d) Hg^{2+}.

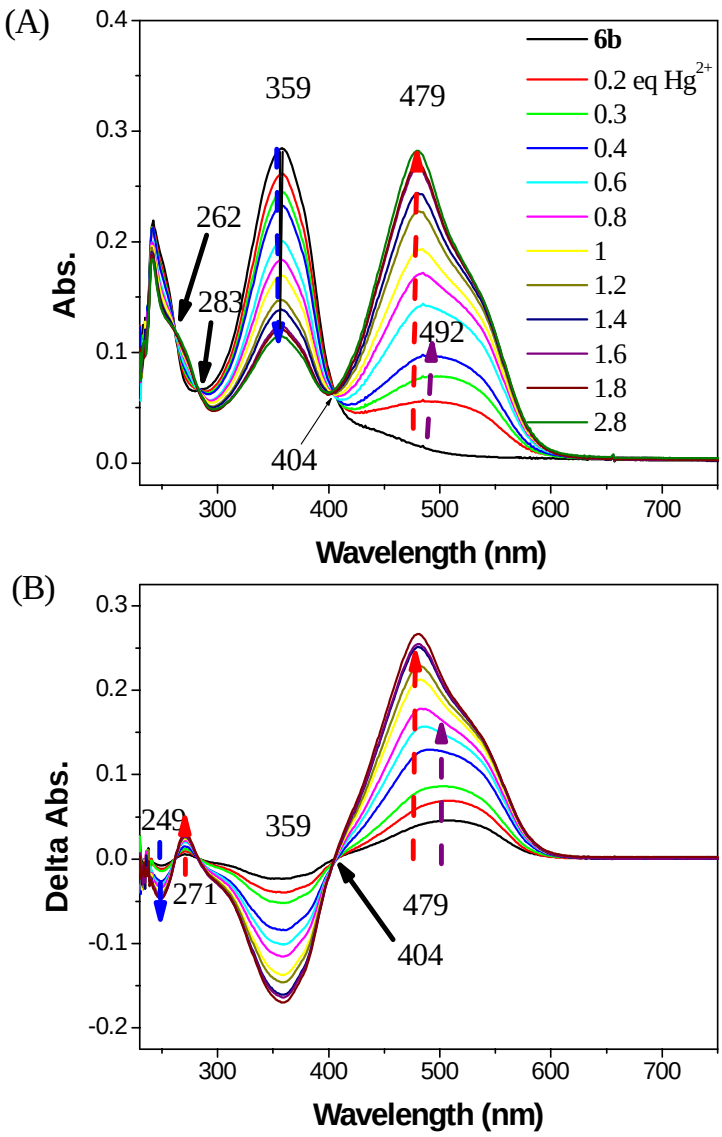


Figure S-6. UV/vis titration spectra of **6b** with $Hg(ClO_4)_2$, in methanol–chloroform (v/v = 1/399) co-solvent. [**6b**] = 10 μM.

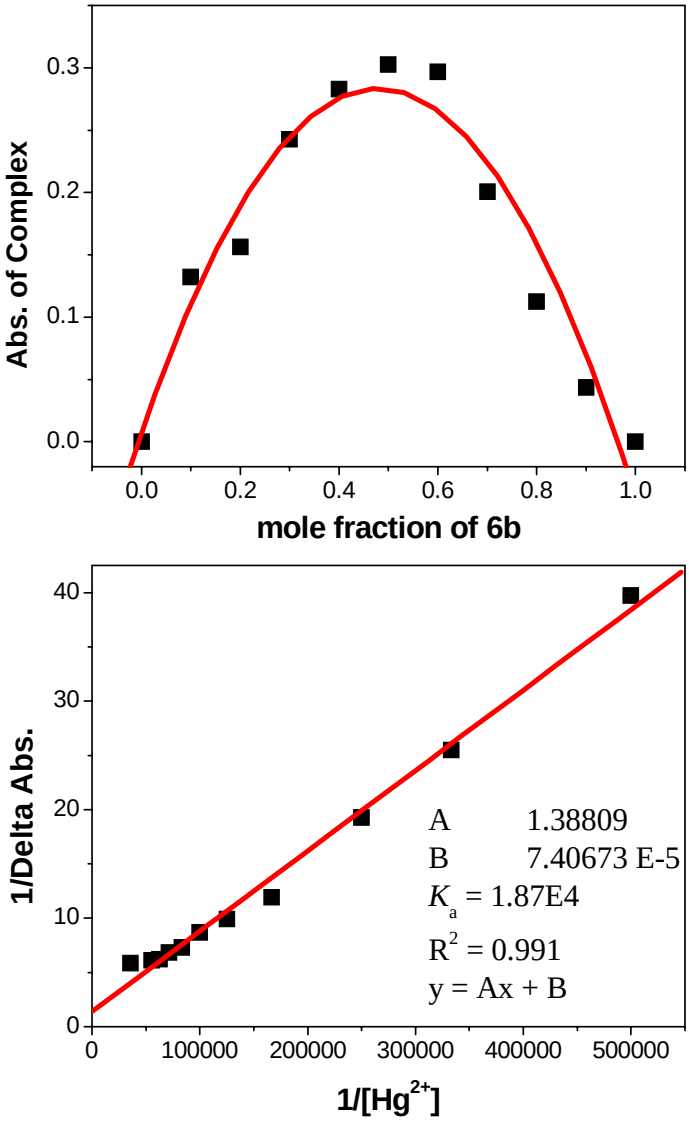


Figure S-7. Job's Plot and Benesi-Hilderbrand Plot of **6b** with $Hg(ClO_4)_2$. Where the absorption at 479 nm was plotted against mole fraction of **6b** at an invariant total concentration of 2 x 10^{-5} M in MeOH/CHCl3 (v/v = 1/19).

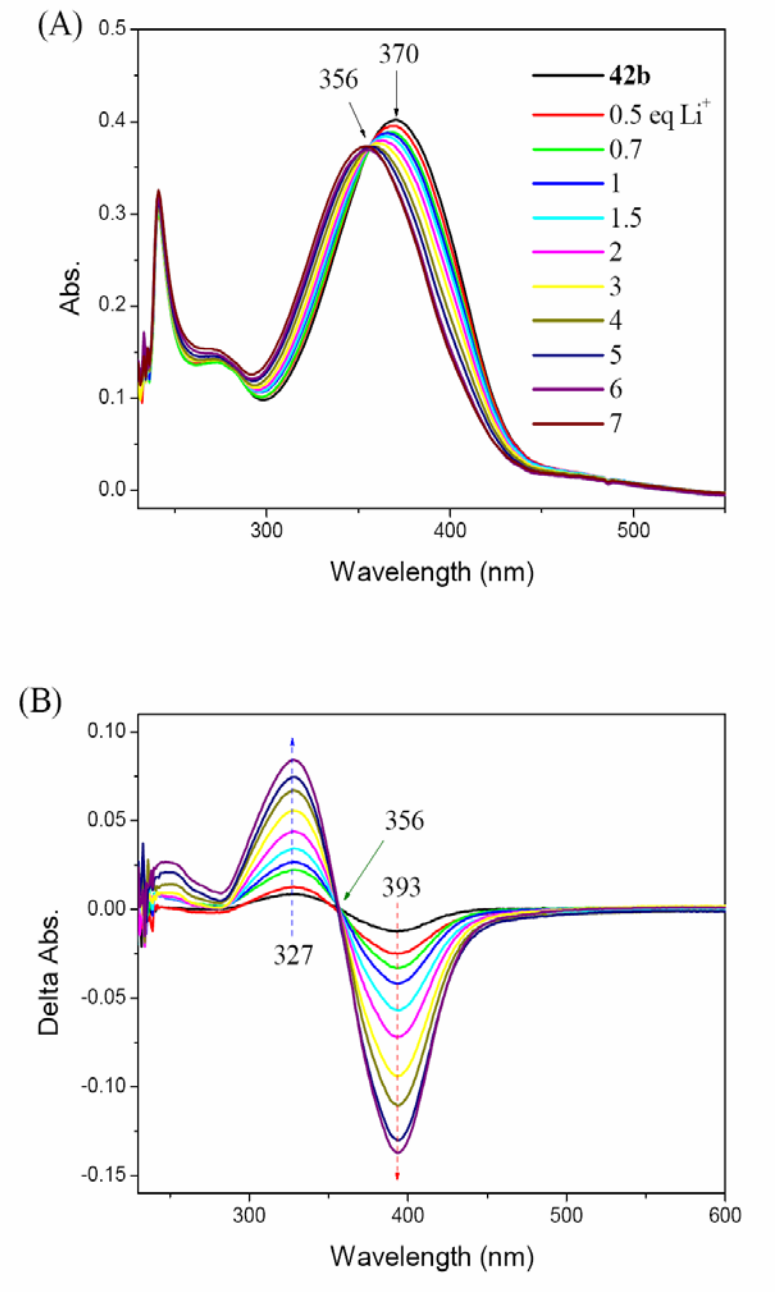


Figure S-8. UV/vis titration spectra of **6c** with $LiClO_4$, in methanol–chloroform (v/v = 1/399) co-solvent, where [**6c**] = 10 μM.

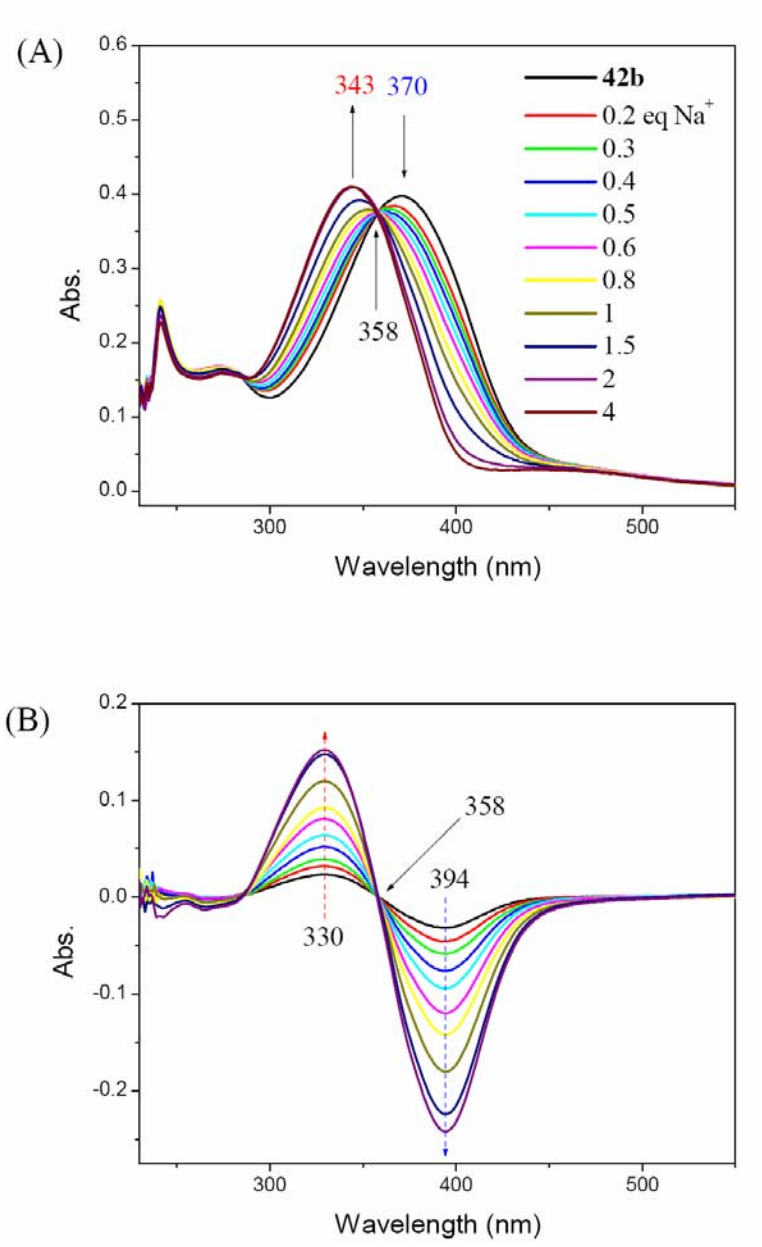
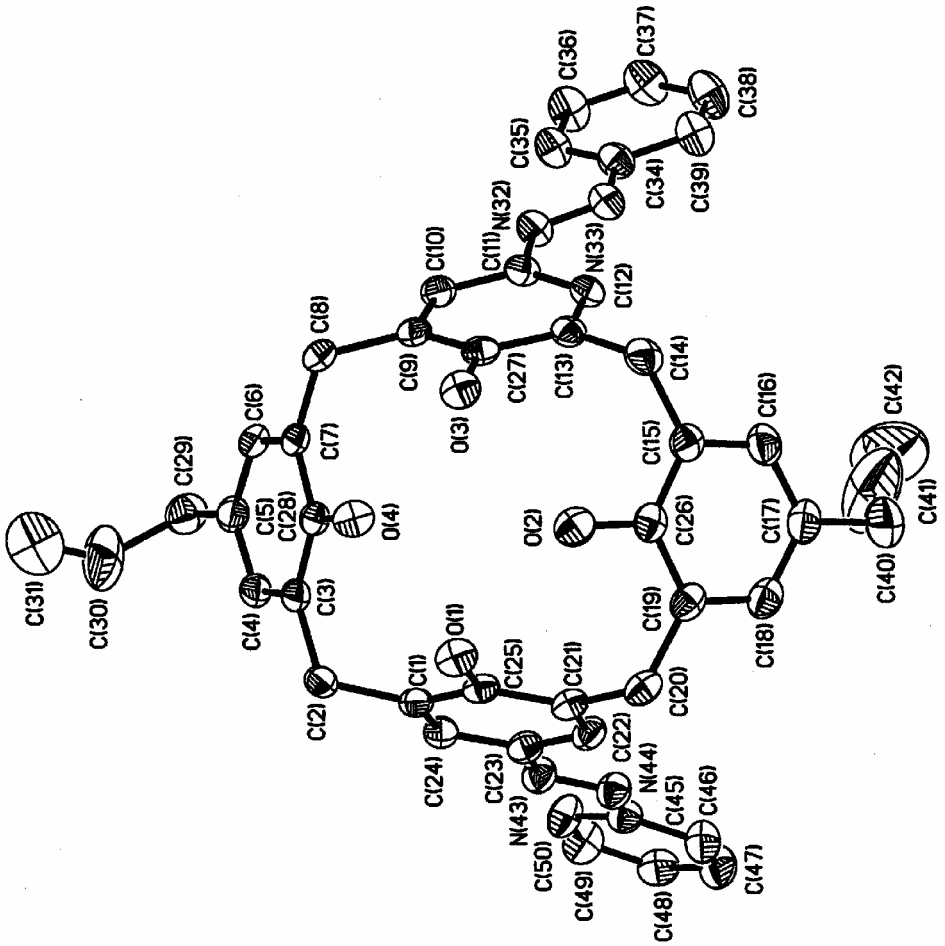


Figure S-9. UV/vis titration spectra of **6c** with $NaClO_4$, in methanol–chloroform (v/v = 1/399) co-solvent, where [**6c**] = 10 μM.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C(38)
C(35)
C(34)
C(39)
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C(8)
C(9)
C(27)
C(13)
C(14)
O(3)
C(6)
C(7)
C(15)
C(16)
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C(29)
C(5)
C(28)
O(4)
O(2)
C(26)
C(17)
C(41)
C(31)
C(30)
C(4)
C(3)
C(19)
C(18)
C(40)
O(1)
C(1)
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C(2)
C(22)
C(24)
C(23)
N(44)
N(43)
C(45)
C(46)
C(50)
C(49)
C(48)
C(47)

3a

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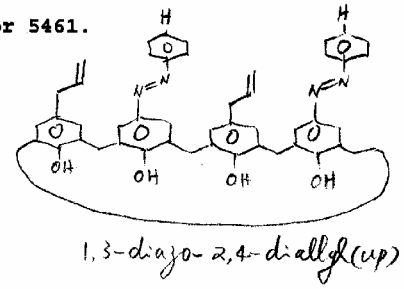
Table 1. Crystal data and structure refinement for 5461.



Identification code	ic5461
Empirical formula	$C_{46}H_{40}N_4O_4$
Formula weight	712.82
Temperature	295(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 10.9387(2) Å alpha = 78.588(1)° b = 11.7439(3) Å beta = 85.163(1)° c = 14.5756(3) Å gamma = 89.702(1)°
Volume, Z	1828.74(7) $Å^3$, 2
Density (calculated)	1.295 Mg/m^3
Absorption coefficient	0.083 mm^{-1}
F(000)	752
Crystal size	0.50 x 0.20 x 0.07 mm
θ range for data collection	1.43 to 25.02°
Limiting indices	$-13 \le h \le 13$, $-13 \le k \le 13$, $-17 \le l \le 17$
Reflections collected	18793
Independent reflections	6425 (R_{int} = 0.0368)
Absorption correction	Sadabs
Max. and min. transmission	0.9280 and 0.7371
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6425 / 0 / 488
Goodness-of-fit on F^2	1.022
Final R indices [I>2σ(I)]	R1 = 0.0601, wR2 = 0.1584
R indices (all data)	R1 = 0.0925, wR2 = 0.1818
Extinction coefficient	0.005(2)
Largest diff. peak and hole	0.402 and -0.323 $eÅ^{-3}$

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Table 2. Bond lengths [Å] and angles [°] for 5461.

O(1)-C(25)	1.386(3)	O(2)-C(26)	1.378(3)
O(3)-C(27)	1.378(3)	O(4)-C(28)	1.374(3)
C(1)-C(25)	1.390(4)	C(1)-C(24)	1.392(4)
C(1)-C(2)	1.517(3)	C(2)-C(3)	1.516(4)
C(3)-C(4)	1.382(4)	C(3)-C(28)	1.397(4)
C(4)-C(5)	1.391(4)	C(5)-C(6)	1.381(4)
C(5)-C(29)	1.515(4)	C(6)-C(7)	1.396(4)
C(7)-C(28)	1.389(4)	C(7)-C(8)	1.519(4)
C(8)-C(9)	1.516(4)	C(9)-C(10)	1.383(4)
C(9)-C(27)	1.402(4)	C(10)-C(11)	1.382(4)
C(11)-C(12)	1.392(4)	C(11)-N(32)	1.433(4)
C(12)-C(13)	1.379(4)	C(13)-C(27)	1.400(4)
C(13)-C(14)	1.534(4)	C(14)-C(15)	1.515(4)
C(15)-C(26)	1.390(4)	C(15)-C(16)	1.394(4)
C(16)-C(17)	1.397(5)	C(17)-C(18)	1.379(5)
C(17)-C(40)	1.518(5)	C(18)-C(19)	1.383(4)
C(19)-C(26)	1.403(4)	C(19)-C(20)	1.513(4)
C(20)-C(21)	1.522(4)	C(21)-C(22)	1.390(4)
C(21)-C(25)	1.402(4)	C(22)-C(23)	1.389(4)
C(23)-C(24)	1.383(4)	C(23)-N(43)	1.436(3)
C(29)-C(30)	1.509(6)	C(30)-C(31)	1.114(7)
N(32)-N(33)	1.239(3)	N(33)-C(34)	1.433(4)
C(34)-C(39)	1.380(4)	C(34)-C(35)	1.388(4)
C(35)-C(36)	1.374(5)	C(36)-C(37)	1.383(5)
C(37)-C(38)	1.365(5)	C(38)-C(39)	1.395(5)
C(40)-C(41)	1.377(8)	C(41)-C(42)	1.106(8)
N(43)-N(44)	1.249(3)	N(44)-C(45)	1.434(3)
C(45)-C(46)	1.376(4)	C(45)-C(50)	1.384(4)
C(46)-C(47)	1.391(4)	C(47)-C(48)	1.358(4)
C(48)-C(49)	1.367(5)	C(49)-C(50)	1.382(4)

C(25)-C(1)-C(24)	117.8(2)	C(25)-C(1)-C(2)	122.3(2)
C(24)-C(1)-C(2)	119.8(2)	C(3)-C(2)-C(1)	112.3(2)
C(4)-C(3)-C(28)	117.7(2)	C(4)-C(3)-C(2)	120.7(2)
C(28)-C(3)-C(2)	121.6(2)	C(3)-C(4)-C(5)	122.4(3)
C(6)-C(5)-C(4)	117.6(3)	C(6)-C(5)-C(29)	122.5(3)
C(4)-C(5)-C(29)	119.9(3)	C(5)-C(6)-C(7)	122.9(3)
C(28)-C(7)-C(6)	117.0(2)	C(28)-C(7)-C(8)	121.5(2)
C(6)-C(7)-C(8)	121.5(2)	C(9)-C(8)-C(7)	113.5(2)
C(10)-C(9)-C(27)	117.1(2)	C(10)-C(9)-C(8)	120.0(2)
C(27)-C(9)-C(8)	122.9(2)	C(11)-C(10)-C(9)	121.9(3)
C(10)-C(11)-C(12)	119.7(3)	C(10)-C(11)-N(32)	115.2(2)
C(12)-C(11)-N(32)	125.2(2)	C(13)-C(12)-C(11)	120.6(3)
C(12)-C(13)-C(27)	118.4(2)	C(12)-C(13)-C(14)	120.0(2)
C(27)-C(13)-C(14)	121.6(2)	C(15)-C(14)-C(13)	113.5(2)
C(26)-C(15)-C(16)	117.4(3)	C(26)-C(15)-C(14)	121.8(3)
C(16)-C(15)-C(14)	120.8(3)	C(15)-C(16)-C(17)	122.3(3)
C(18)-C(17)-C(16)	117.8(3)	C(18)-C(17)-C(40)	120.3(3)
C(16)-C(17)-C(40)	121.8(3)	C(17)-C(18)-C(19)	122.7(3)
C(18)-C(19)-C(26)	117.7(3)	C(18)-C(19)-C(20)	121.2(3)
C(26)-C(19)-C(20)	121.1(2)	C(19)-C(20)-C(21)	112.0(2)
C(22)-C(21)-C(25)	117.3(2)	C(22)-C(21)-C(20)	120.5(2)
C(25)-C(21)-C(20)	122.2(2)	C(23)-C(22)-C(21)	121.4(2)
C(24)-C(23)-C(22)	119.6(2)	C(24)-C(23)-N(43)	115.0(2)
C(22)-C(23)-N(43)	125.4(2)	C(23)-C(24)-C(1)	121.2(3)
O(1)-C(25)-C(1)	117.8(2)	O(1)-C(25)-C(21)	119.6(2)
C(1)-C(25)-C(21)	122.6(2)	O(2)-C(26)-C(15)	120.7(2)
O(2)-C(26)-C(19)	117.1(2)	C(15)-C(26)-C(19)	122.1(3)
O(3)-C(27)-C(13)	117.8(2)	O(3)-C(27)-C(9)	120.0(2)

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C(13)-C(27)-C(9)	122.2(2)	O(4)-C(28)-C(7)	117.3(2)
O(4)-C(28)-C(3)	120.3(2)	C(7)-C(28)-C(3)	122.4(2)
C(30)-C(29)-C(5)	111.7(3)	C(31)-C(30)-C(29)	139.3(7)
N(33)-N(32)-C(11)	114.4(2)	N(32)-N(33)-C(34)	113.8(2)
C(39)-C(34)-C(35)	119.6(3)	C(39)-C(34)-N(33)	116.0(3)
C(35)-C(34)-N(33)	124.4(3)	C(36)-C(35)-C(34)	120.2(3)
C(35)-C(36)-C(37)	120.0(3)	C(38)-C(37)-C(36)	120.3(3)
C(37)-C(38)-C(39)	120.0(3)	C(34)-C(39)-C(38)	119.9(3)
C(41)-C(40)-C(17)	115.6(4)	C(42)-C(41)-C(40)	154.9(13)
N(44)-N(43)-C(23)	114.2(2)	N(43)-N(44)-C(45)	113.3(2)
C(46)-C(45)-C(50)	119.2(3)	C(46)-C(45)-N(44)	115.8(3)
C(50)-C(45)-N(44)	125.0(3)	C(45)-C(46)-C(47)	120.0(3)
C(48)-C(47)-C(46)	120.6(3)	C(47)-C(48)-C(49)	119.6(3)
C(48)-C(49)-C(50)	121.0(3)	C(49)-C(50)-C(45)	119.7(3)

Symmetry transformations used to generate equivalent atoms:

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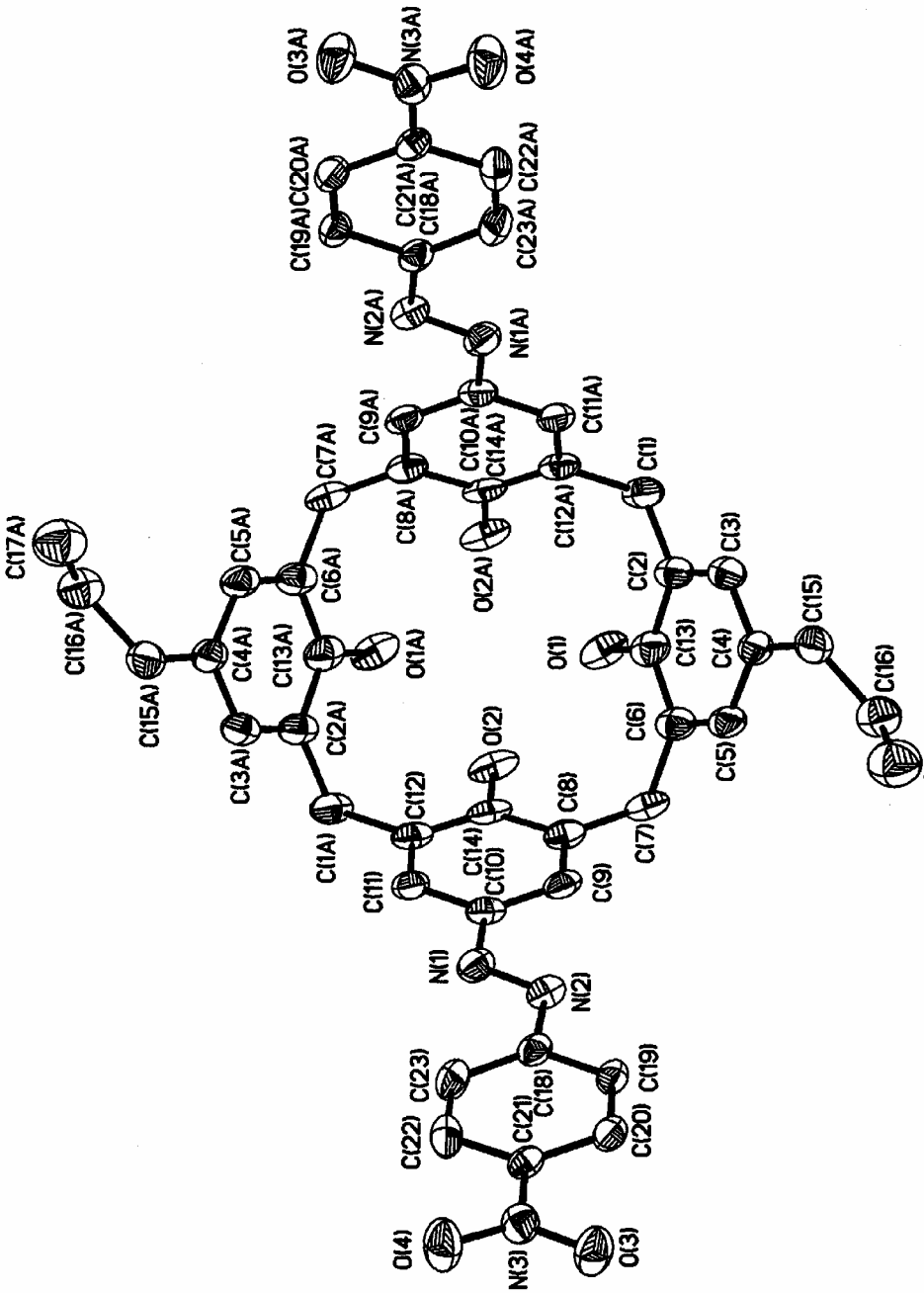

3c

Fig. 1: The molecular structure of IC7695, thermal ellipsoids drawn at the 50% probability level.

S-15

Table 1. Crystal data and structure refinement for ic7695.

Identification code	ic7695
Empirical formula	$C_{48}H_{42}Cl_6N_6O_9$
Formula weight	1059.58
Temperature	150(1) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	a = 34.8369(19) Å alpha = 90° b = 6.1717(3) Å beta = 91.510(1)° c = 22.3919(12) Å gamma = 90°
Volume, Z	4812.7(4) Å^3, 4
Density (calculated)	1.462 Mg/m^3
Absorption coefficient	0.420 mm^{-1}
F(000)	2184
Crystal size	0.40 x 0.15 x 0.01 mm
θ range for data collection	1.17 to 25.00°
Limiting indices	$-41 \le h \le 41$, $-7 \le k \le 7$, $-26 \le l \le 26$
Reflections collected	19651
Independent reflections	4246 (R_{int} = 0.0816)
Completeness to θ = 25.00°	100.0 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4246 / 0 / 309
Goodness-of-fit on F^2	1.113
Final R indices [I>2σ(I)]	R1 = 0.0464, wR2 = 0.0887
R indices (all data)	R1 = 0.1101, wR2 = 0.1175
Largest diff. peak and hole	0.582 and -0.323 eÅ^{-3}

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Table 2. Bond lengths [Å] and angles [°] for ic7695.

O(1)-C(13)	1.383(5)	O(2)-C(14)	1.378(4)
O(3)-N(3)	1.228(4)	O(4)-N(3)	1.226(3)
N(1)-N(2)	1.257(4)	N(1)-C(10)	1.419(5)
N(2)-C(18)	1.430(4)	N(3)-C(21)	1.471(4)
C(1)-C(2)	1.505(5)	C(1)-C(12)#1	1.522(5)
C(2)-C(3)	1.386(5)	C(2)-C(13)	1.400(5)
C(3)-C(4)	1.395(5)	C(4)-C(5)	1.382(5)
C(4)-C(15)	1.508(5)	C(5)-C(6)	1.387(5)
C(6)-C(13)	1.400(5)	C(6)-C(7)	1.536(5)
C(7)-C(8)	1.515(5)	C(8)-C(9)	1.388(5)
C(8)-C(14)	1.398(5)	C(9)-C(10)	1.387(5)
C(10)-C(11)	1.396(5)	C(11)-C(12)	1.385(5)
C(12)-C(14)	1.402(5)	C(12)-C(1)#1	1.522(5)
C(15)-C(16)	1.498(5)	C(16)-C(17)	1.302(5)
C(18)-C(23)	1.387(5)	C(18)-C(19)	1.388(5)
C(19)-C(20)	1.378(5)	C(20)-C(21)	1.377(5)
C(21)-C(22)	1.387(5)	C(22)-C(23)	1.374(5)
C(24)-Cl(3)	1.753(4)	C(24)-Cl(2)	1.758(4)
C(24)-Cl(1)	1.761(4)		

N(2)-N(1)-C(10)	114.8(3)	N(1)-N(2)-C(18)	113.2(3)
O(4)-N(3)-O(3)	123.0(3)	O(4)-N(3)-C(21)	118.4(3)
O(3)-N(3)-C(21)	118.6(3)	C(2)-C(1)-C(12)#1	112.1(3)
C(3)-C(2)-C(13)	117.8(4)	C(3)-C(2)-C(1)	120.4(4)
C(13)-C(2)-C(1)	121.8(4)	C(2)-C(3)-C(4)	122.8(4)
C(5)-C(4)-C(3)	117.0(4)	C(5)-C(4)-C(15)	123.3(4)
C(3)-C(4)-C(15)	119.7(4)	C(4)-C(5)-C(6)	123.4(4)
C(5)-C(6)-C(13)	117.5(4)	C(5)-C(6)-C(7)	120.8(4)
C(13)-C(6)-C(7)	121.7(4)	C(8)-C(7)-C(6)	111.9(3)
C(9)-C(8)-C(14)	117.9(4)	C(9)-C(8)-C(7)	120.0(4)
C(14)-C(8)-C(7)	122.0(4)	C(10)-C(9)-C(8)	121.2(4)
C(9)-C(10)-C(11)	119.6(4)	C(9)-C(10)-N(1)	125.1(3)
C(11)-C(10)-N(1)	115.4(4)	C(12)-C(11)-C(10)	121.2(4)
C(11)-C(12)-C(14)	117.8(4)	C(11)-C(12)-C(1)#1	120.0(4)
C(14)-C(12)-C(1)#1	122.2(4)	O(1)-C(13)-C(6)	118.5(4)
O(1)-C(13)-C(2)	119.8(4)	C(6)-C(13)-C(2)	121.6(4)
O(2)-C(14)-C(8)	117.4(4)	O(2)-C(14)-C(12)	120.3(4)
C(8)-C(14)-C(12)	122.3(4)	C(16)-C(15)-C(4)	115.4(4)
C(17)-C(16)-C(15)	125.0(4)	C(23)-C(18)-C(19)	120.1(4)
C(23)-C(18)-N(2)	124.1(3)	C(19)-C(18)-N(2)	115.7(3)
C(20)-C(19)-C(18)	120.8(3)	C(21)-C(20)-C(19)	118.0(3)
C(20)-C(21)-C(22)	122.4(4)	C(20)-C(21)-N(3)	118.6(3)
C(22)-C(21)-N(3)	119.0(3)	C(23)-C(22)-C(21)	118.9(4)
C(22)-C(23)-C(18)	119.8(3)	Cl(3)-C(24)-Cl(2)	110.9(2)
Cl(3)-C(24)-Cl(1)	110.7(2)	Cl(2)-C(24)-Cl(1)	110.1(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+1/2

S-17

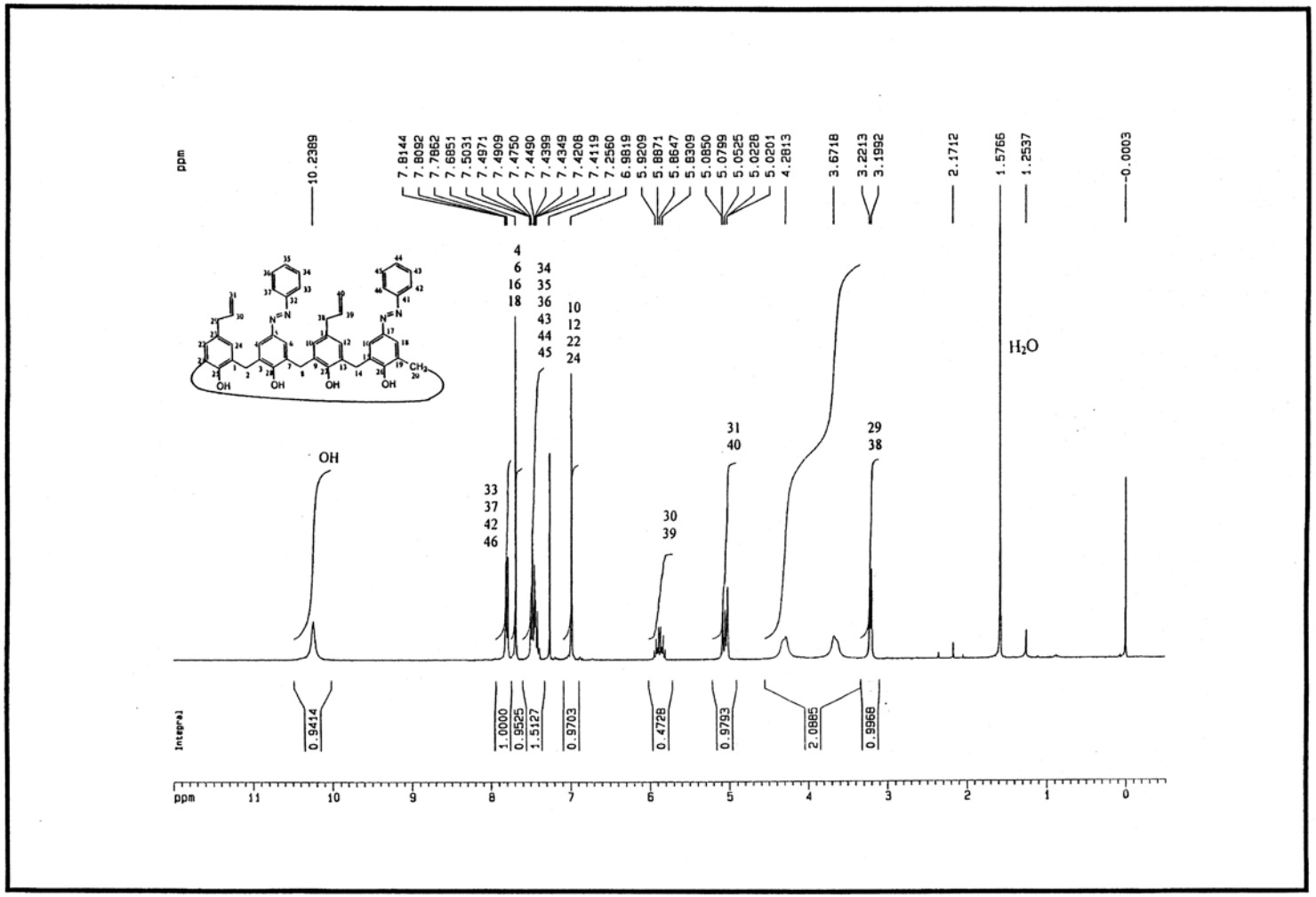


Figure S-10. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of compound **3a**.

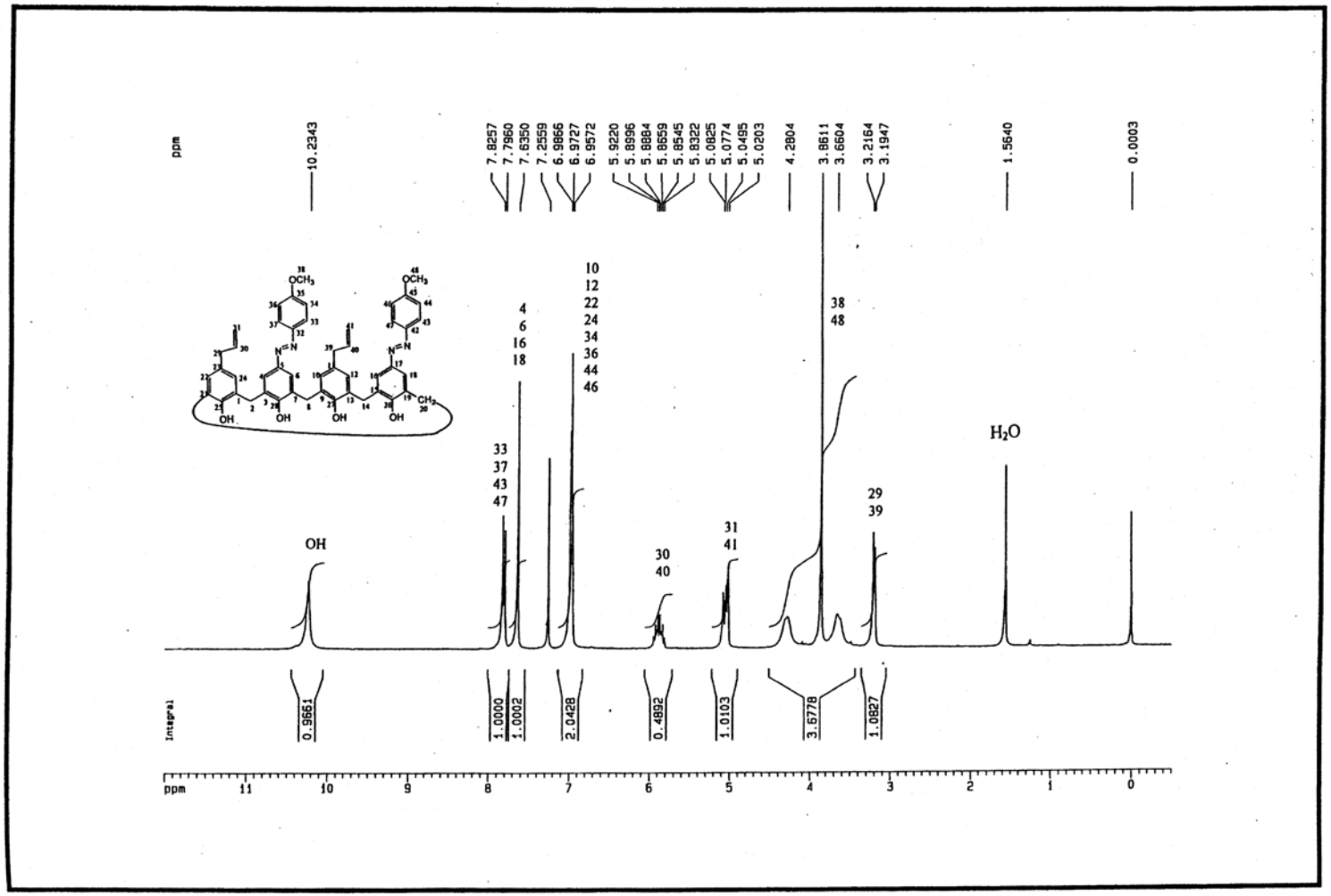


Figure S-11. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of compound **3b**.

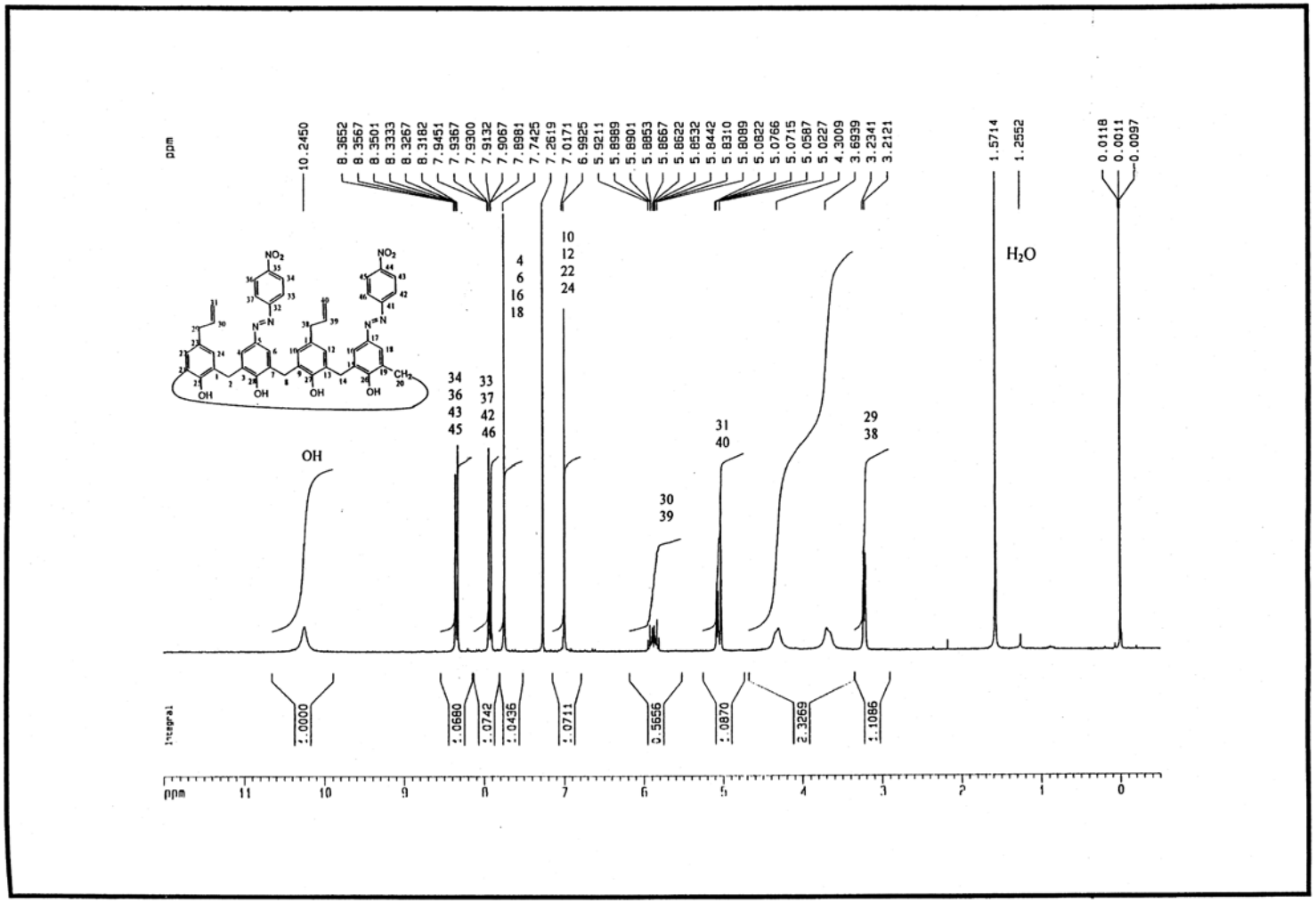


Figure S-12. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of compound **3c**.

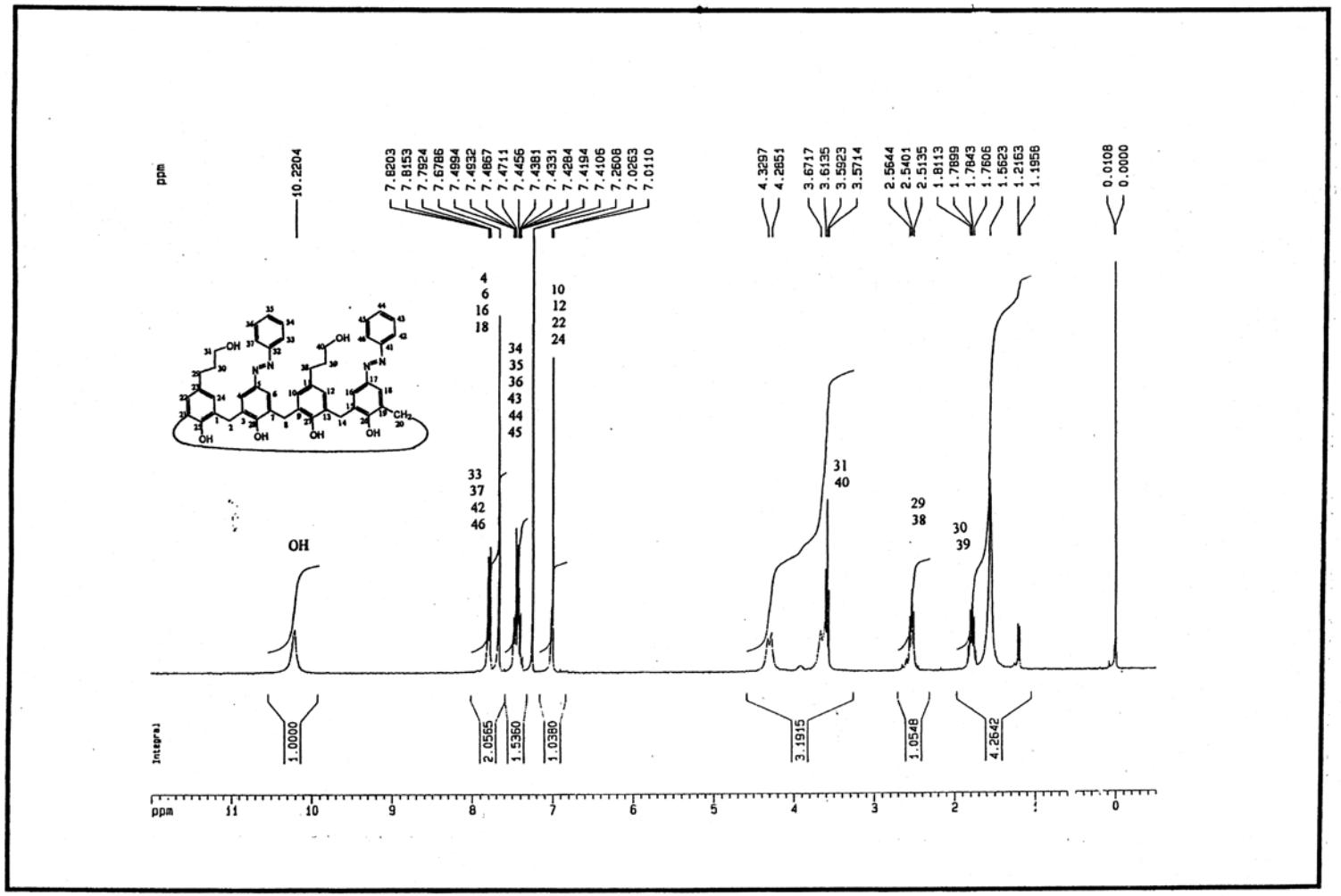


Figure S-13. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of compound **5a**.

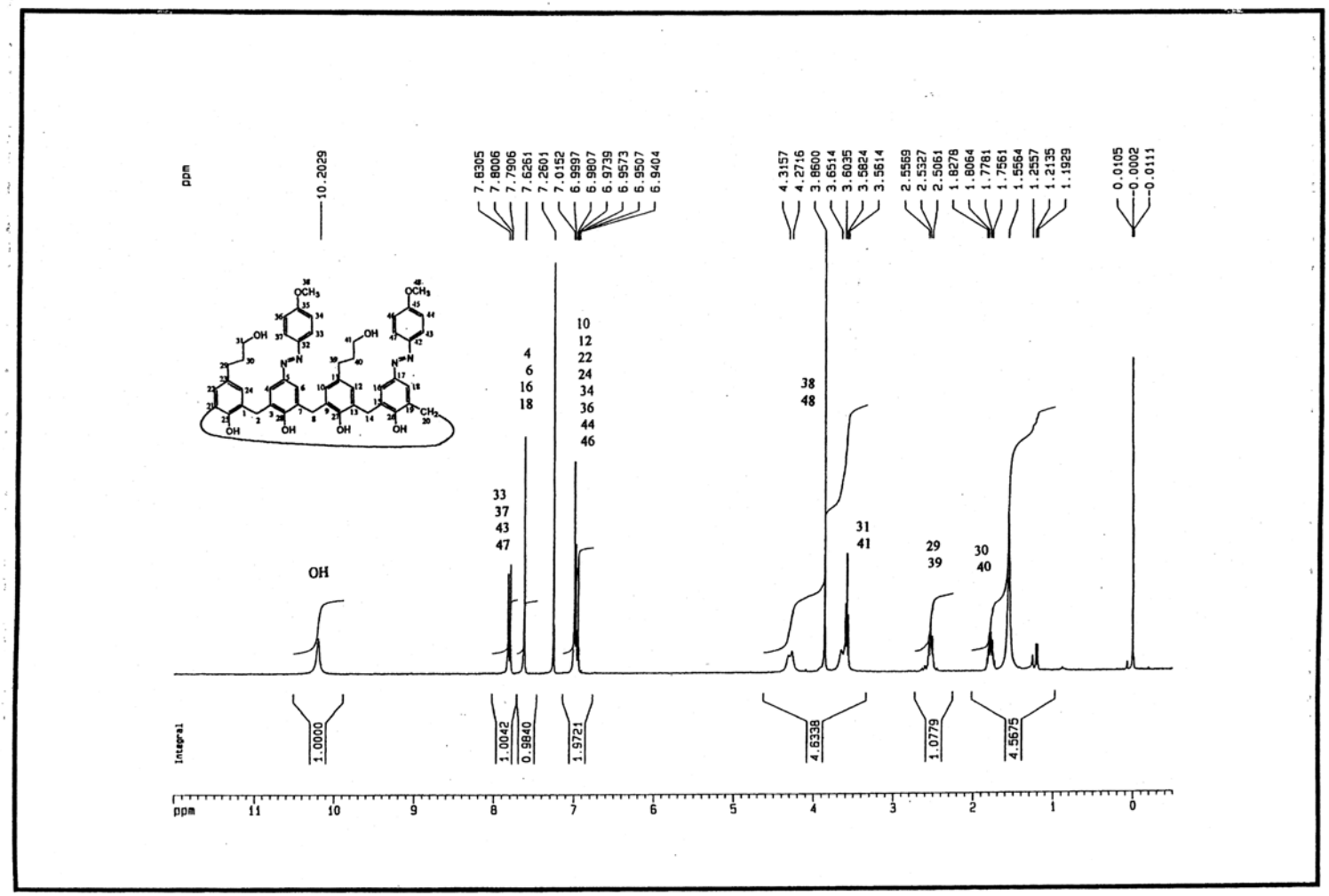


Figure S-14. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of compound **5b**.

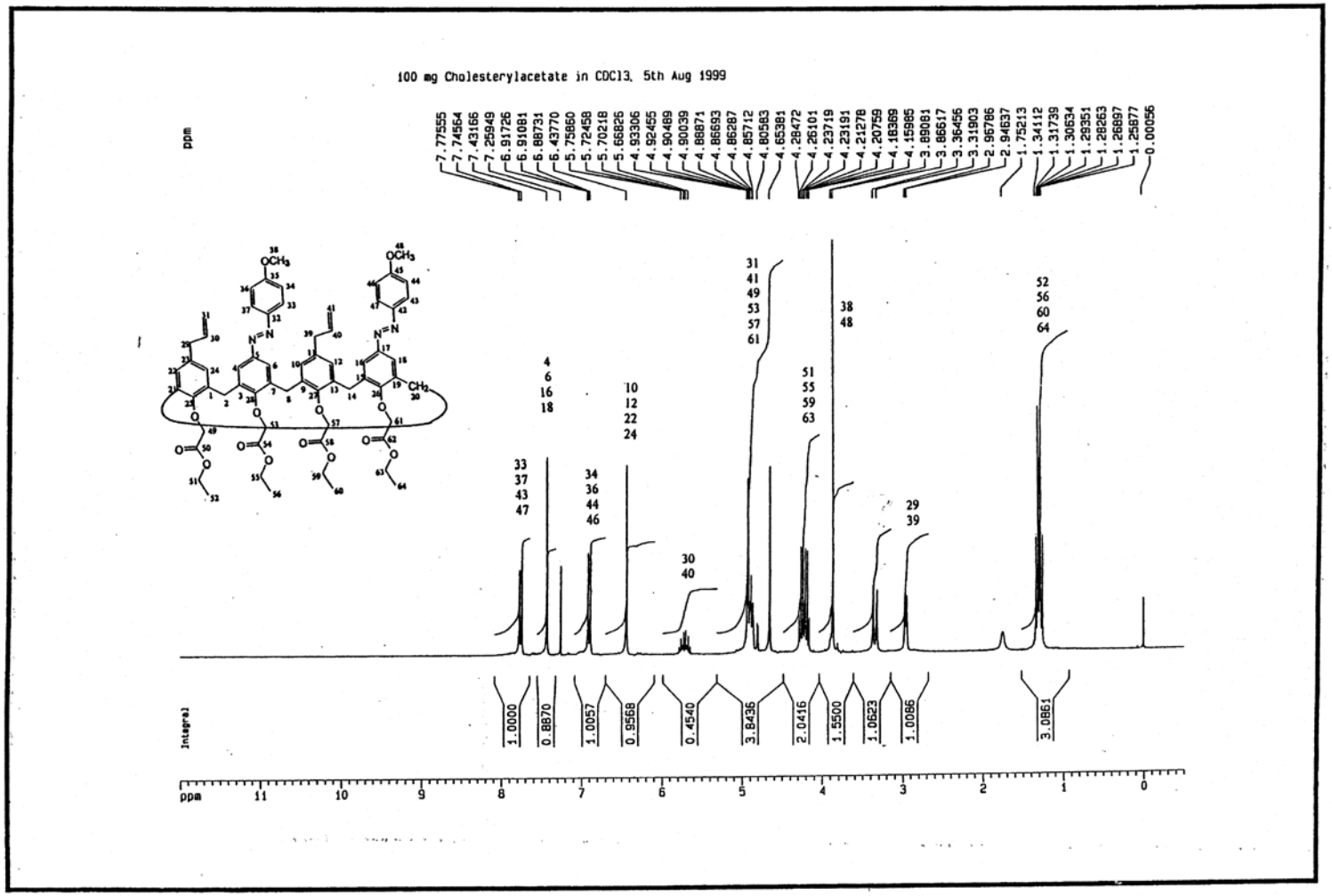


Figure S-15. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of compound **6b**.

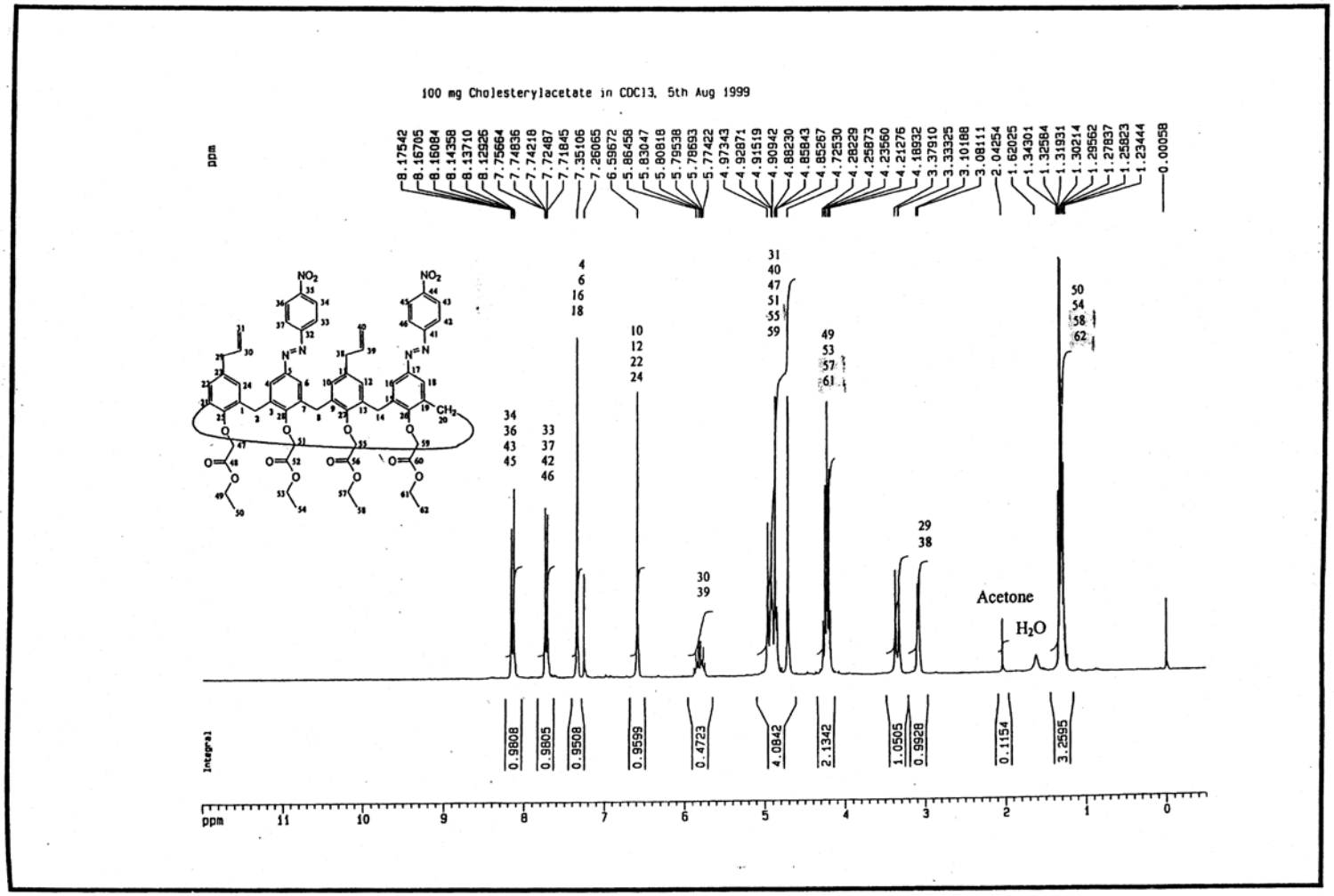


Figure S-16. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of compound **6c**.

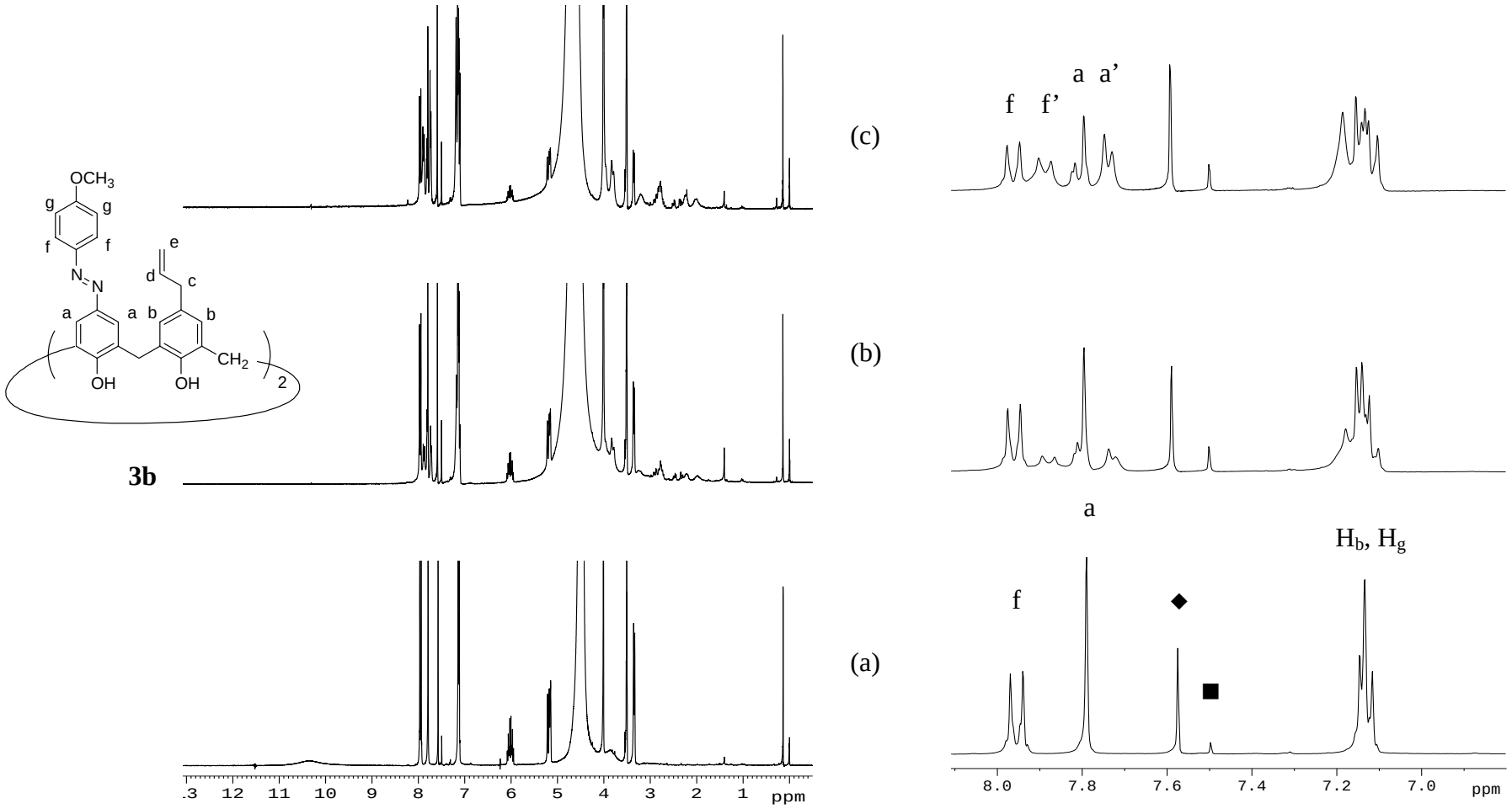
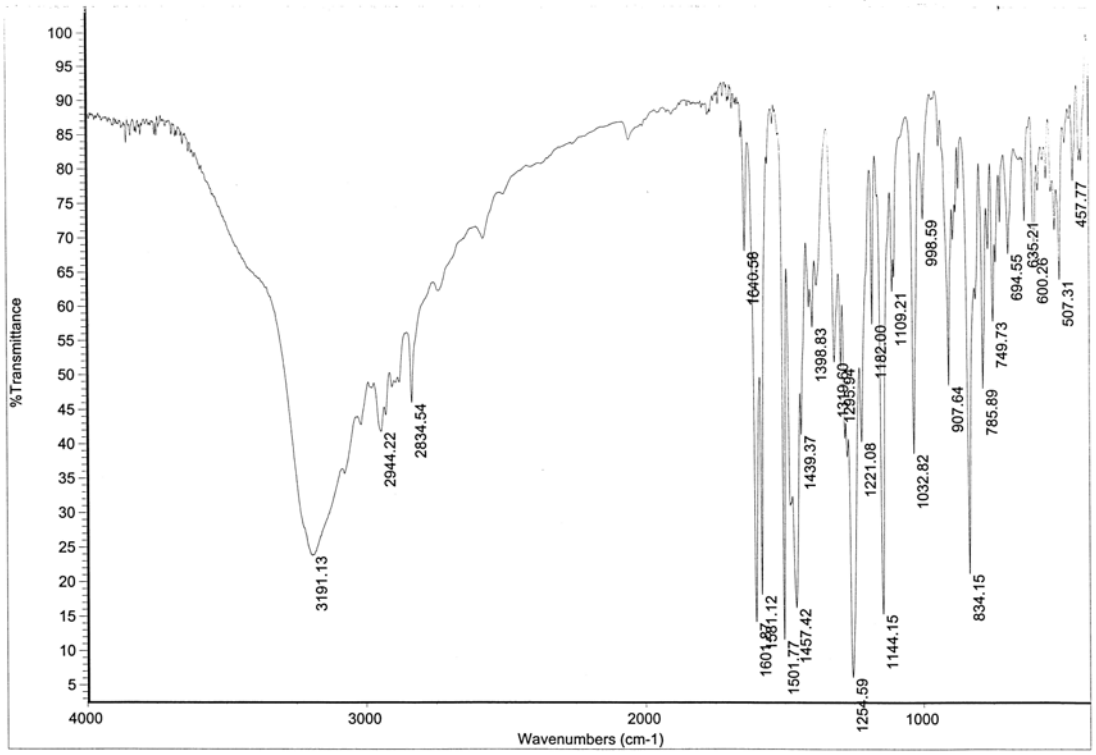


Figure S -17. ^{1}H NMR spectra of compound **3b** (8.35 mM) in $CD_3OH/CDCl_3$ (1:3) solution in the presence of different amounts of $Hg(ClO_4)_2$: (a) 0, (b) 10.14 mM (1.2 equiv.), and (c) 15.77 mM (1.9 equiv.). Spectra on the right are expanded regions of δ 6.8 to δ 8.2, and there were two new signals appeared flanking H_a and $H_{a'}$ when Hg^{2+} ion was added in $CD_3OH/CDCl_3$ (1:3) compared to those in $CD_3OD/CDCl_3$ (Figure 8).

(a)



(b)

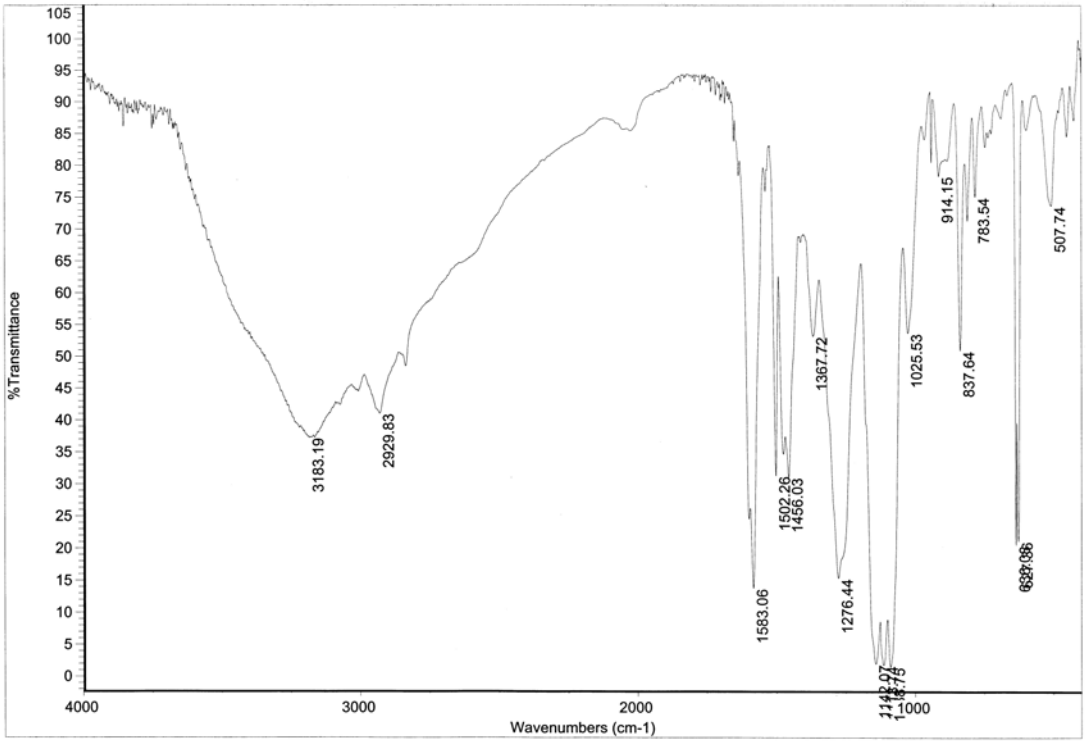


Figure S18. IR (KBr) spectra of compound **3b** in the presence of $Hg(ClO_4)_2$: (a) 0, and (b) 2 equiv.