Oxidative cyclization of thiosemicarbazide: chemo-dosimetric approach for highly selective fluorescence detection of cerium(IV)

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Experimental

Apparatus and reagents

Hydrazine hydrate, 9-anthracenecarboxaldehyde, phenyliso-thiocyanate, 2-thiophenecarboxaldehyde, thiosemicarbazide and salicaldehyde are purchased from Sigma-Aldrich (USA). Solvents used are of spectroscopic grade. Other chemicals are analytical reagent grade and used without further purification, unless specified otherwise. Milli-Q Millipore 18.2 MΩ cm^{-1} water is used where needed. A Shimadzu Multi Spec 2450 spectrophotometer was used for recording UV-vis spectra. FTIR spectra are recorded on a Shimadzu FTIR spectrophotometer (Shimadzu). Mass spectra are recorded with a QTOF 60 Micro YA 263 mass spectrometer in ES positive mode. ^{1}H NMR spectra of A12 and A12i and ^{13}C NMR spectrum of A12 were performed with a Bruker Advance 600 (600 MHz) NMR. ^{1}H NMR spectra of A12a and A12b are recorded with a Bruker Advance 300 (300 MHz). Elemental analyses are performed on a Perkin-Elmer 2400 CHN analyzer. The steady state emission and excitation spectra are recorded with a Hitachi F-4500 spectro-fluorimeter. All spectra are recorded at room temperature.

General method of UV-Vis and fluorescence titration

The cell path length for absorption and emission measurement is 1 cm. Stock solutions of A12, A12a, A12b and Ce^{4+} are prepared in aqueous-methanol (1: 4, v/v, 0.1 M HEPES, pH 7.4). Working solutions of A12, A12a, A12b and Ce^{4+} are prepared from respective stock solutions. Fluorescence measurement has been performed using 2.5 × 2.5 nm slit width.

Determination of detection limit

From fluorescence titration experiment, emission intensities at λ_{em} = 508 nm at low Ce^{4+} concentration regions are normalized between the minimum and maximum values $\frac{I_x - I_0}{I_{max} - I_0}$.

Linear regression curve is then fitted to the normalized data, and the point at which the line crosses the ordinate axes have been considered as the detection limit.[1]

Synthesis of anthracen-9-ylmethylene-hydrazine (X3, Scheme 1)

10 mL (~ 200 mmol) hydrazine hydrate is taken in a 50 mL round bottom flask and placed over a magnetic stirrer. Another solution containing 9-anthracenecarboxaldehyde (3.0 g, ~14.55 mmol) dissolved in minimum methanol is added drop wise with continuous stirring. After stirring for 6h, the solution is filtered off. The filtrate is then poured in 50 mL water whereby a precipitate appeared which is collected by filtration and dried in air. ESI-MS(+) m/z, Calculated for $C_{15}H_{12}N_2$: 221.10; found: 221.20 $[M+H]^+$ (Fig. S1, ESI†).

Synthesis of 5-(anthracen-9-yl)-N-phenyl-1, 3, 4-thiadiazol-2-amine (A12) (Scheme 1)

Phenyl isothiocyanate (135 mg, ~1 mmol) was added drop wise to a solution of X3 (220 mg, ~1 mmol) in THF and stirred magnetically at room temperature. After 10 minutes the round bottom flask was transferred to an oil bath and the stirring was continued to further 4h at 80 °C. The resulting yellow color solution was kept for slow evaporation to get a deep yellow colored crystalline solid suitable for single crystal X-ray diffraction. The yield was 90%. Anal. calcd. (%): C, 74.34; H, 4.82; N, 11.82 and S, 9.02 found: C, 74.19; H, 4.90; N, 11.75 and S, 9.06. ^{1}H NMR [600 MHz, DMSO-d_6, TMS, J (Hz), δ (ppm)]: 12.03 (1H, s), 9.99 (1H, s), 9.39 (1H, s), 8.72 (1H, s), 7.72 (2H, d, J = 13.2), 8.15 (2H, d, J = 11.4), 7.59 (6H, m, J = 3.6),7.34 (2H, m, J = 11.4), 7.18 (1H, m, J = 10.8) (Fig. S2, ESI†).^{13}C NMR [600 MHz, DMSO-d_6,, TMS, δ (ppm)]: 176.40, 142.97, 139.48, 131.31, 130.12, 129.93, 129.39, 128.51, 127.76, 126.07, 125.64 , 125.57 , 125.28 (Fig. S3, ESI†). ESI-MS (+), m/z, calculated for $C_{22}H_{15}N_3S$: 356.11. found: 356.35 $[M+H]^+$ (Fig. S4, ESI†). FT-IR (Fig. S5, ESI†).

Synthesis of 1-(anthracen-9-ylmethylene)-2-(thiophen-2-ylmethylene)hydrazine (A12a) (Scheme 1)

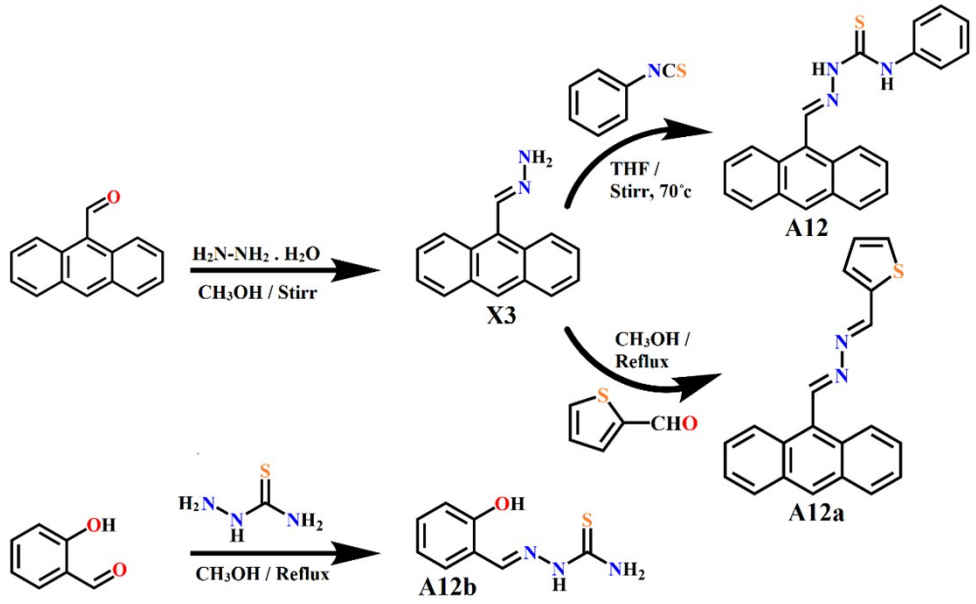
A methanol solution of X3 (220 mg, 1 mmol) and 2-thiophenecarboxaldehyde (112 mg, ~1 mmol) is refluxed for 6h. The resulting pale yellow solution is kept for slow evaporation to get a red solid which upon crystallization from 1:1 methanol-methylene chloride yielded plate shape X-ray quality crystals. The yield is 85%. Anal. calcd. (%): C, 76.40; H, 4.49 and N, 8.91; found: C, 76.46; H, 4.43 and N, 8.88. ^{1}H NMR [300 MHz, $CDCl_3$, TMS, J (Hz), δ (ppm)]: 13.30 (1H, s), 9.74 (1H, s), 8.88 (1H, s), 8.25 (1H, d, J = 9.0), 7.94 (2H, q, J = 8.4), 7.62 (3H,d, J = 5.7), 7.55 (1H, s), 7.48 (1H, d, J = 8.1), 7.33 (2H, t, J = 13.8) (Fig. S6, ESI†). ESI-MS (+), m/z, calcd. for $C_{20}H_{14}N_2S$: 315.09, found: 315.08 $[M+H]^+$ (Fig. S7, ESI†). FT-IR (Fig. S8, ESI†).

Synthesis of 2-(2-hydroxybenzylidene)hydrazine-1-carbothioamide (A12b) (Scheme 1)

A methanol solution of thiosemicarbazide (91 mg, ~1 mmol) and salicaldehyde (122 mg, ~1 mmol) is refluxed for 4 h to get a green-yellow solution. The solution is allowed to slow evaporation. After several days, X-ray quality rod shape yellow crystals appeared. Yield: 87%. Anal. calcd (%): C, 49.22; H, 4.65; and N, 21.52; found: C, 49.18; H, 4.63 and N, 21.55. ^{1}H NMR [300 MHz, $CDCl_3$, TMS, J (Hz), δ (ppm)]: 11.32 (1H, s), 9.60 (1H, s), 8.32 (1H, s), 7.66 (2H, s), 7.44 (1H, s), 7.24 (1H,d, J = 7.2), 6.93 (2H, q J = 7.8) (Fig. S9, ESI†). ESI-MS(+) m/z, calcd. for $C_8H_9N_3OS$: 196.05; found: 196.08 $[M+H]^+$, (Fig. S10, ESI†). FT-IR (Fig. S11, ESI†).

Synthesis of 5-(anthracen-9-yl)-4-phenyl-4,5-dihydro-3H-1,2,4-triazole-3-thione (A12i)

A methanol solution of CAN (0.5 g, ~0.91 mmol) was added drop wise to a magnetically stirred solution of A12 (0.2 g, ~0.56 mmol) in methanol. After addition the stirring was continued for further 10 minutes. After filtration the solution was kept for evaporation at room temperature. After removal of the solvent, a solid product was obtained which was used for MASS (**Fig. S12**, ESI†) and FT-IR (**Fig. S13**, ESI†) spectroscopy. The absorption and emission spectra of an arbitrary concentration of A12i in aqueous ethanol is shown in **Fig. S14**, ESI†).



Scheme S1 Synthetic protocol of the probes

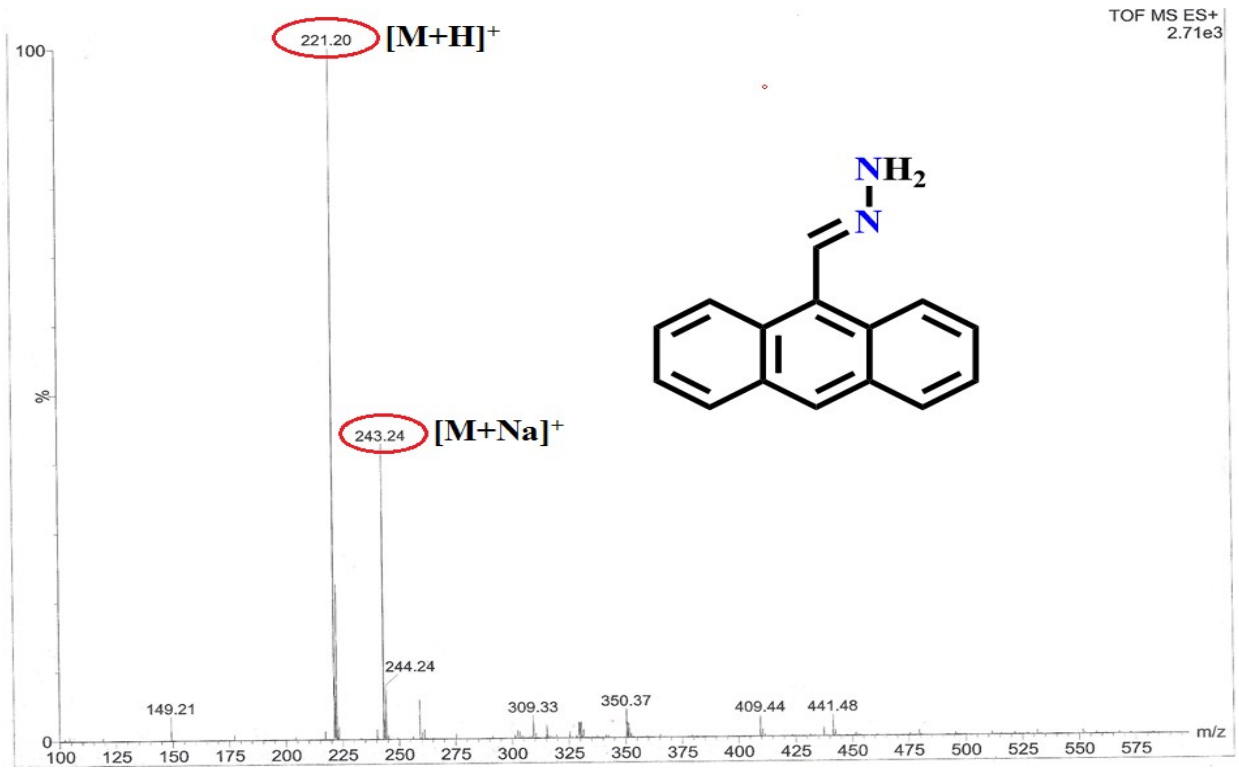


Fig.S1 Mass spectrum of X3

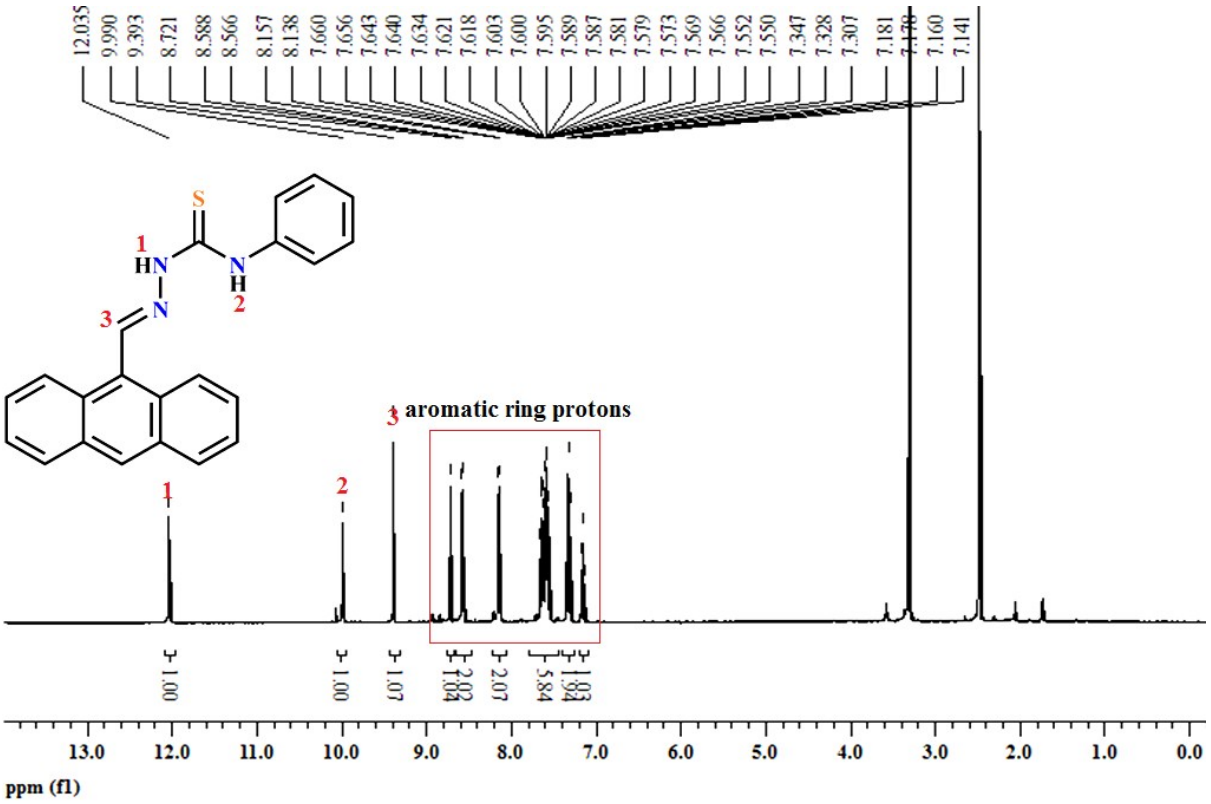


Fig.S2 ^{1}H NMR spectrum of A12 in DMSO-d_6

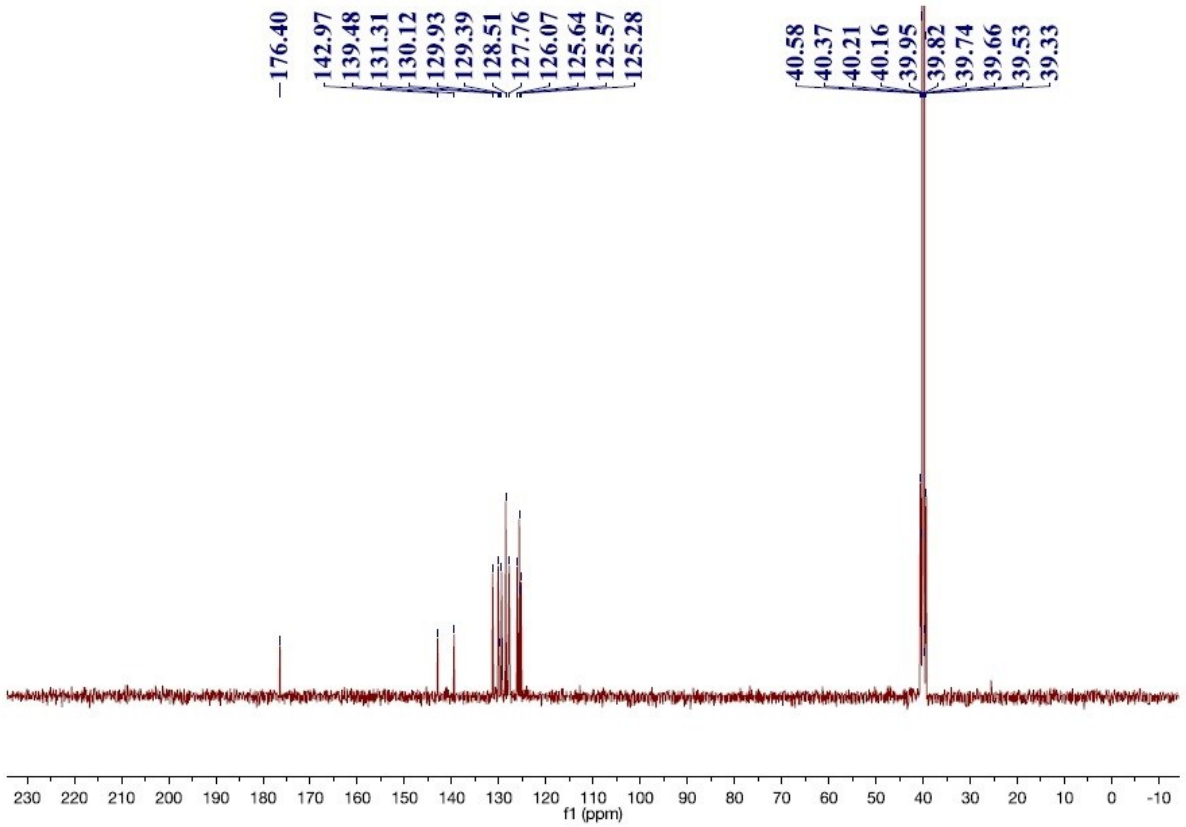


Fig.S3 ^{13}C NMR spectrum of A12 in DMSO-d_6

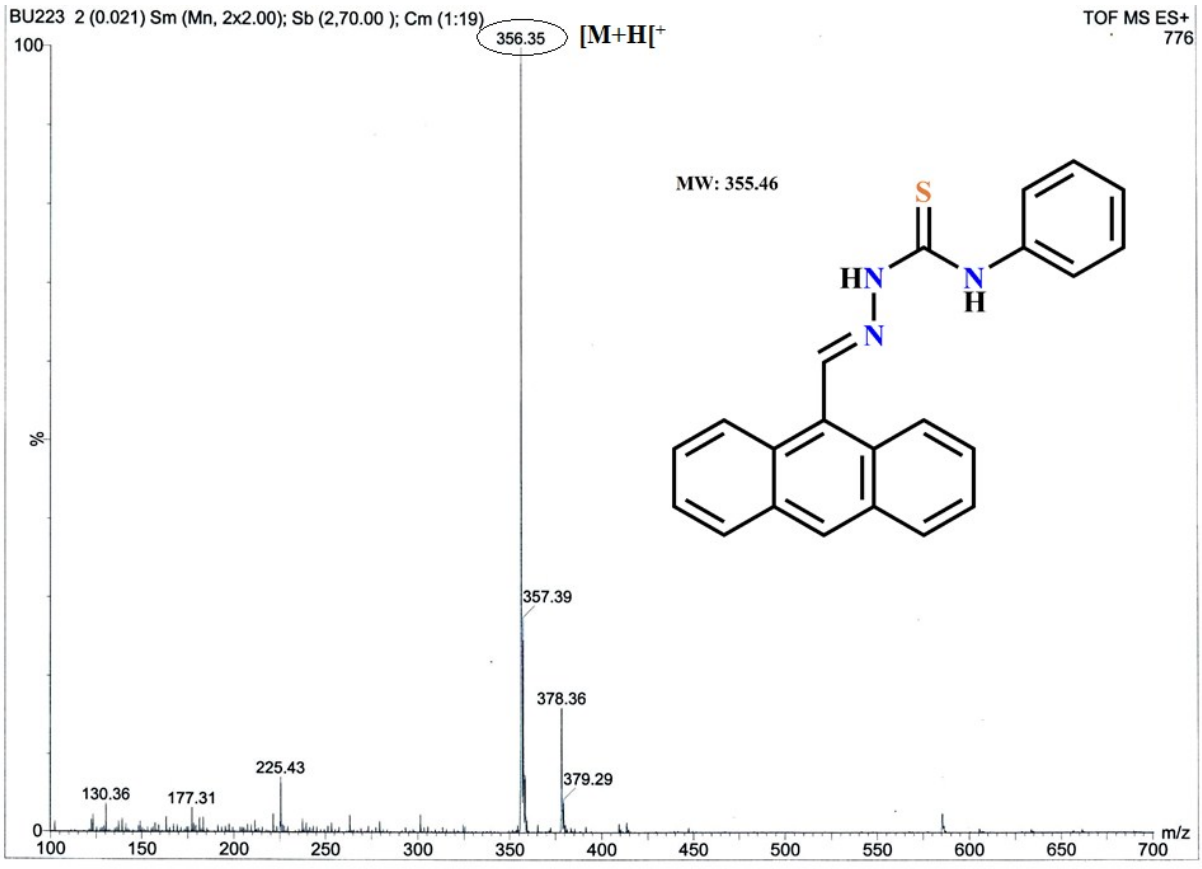


Fig.S4 Mass spectrum of A12

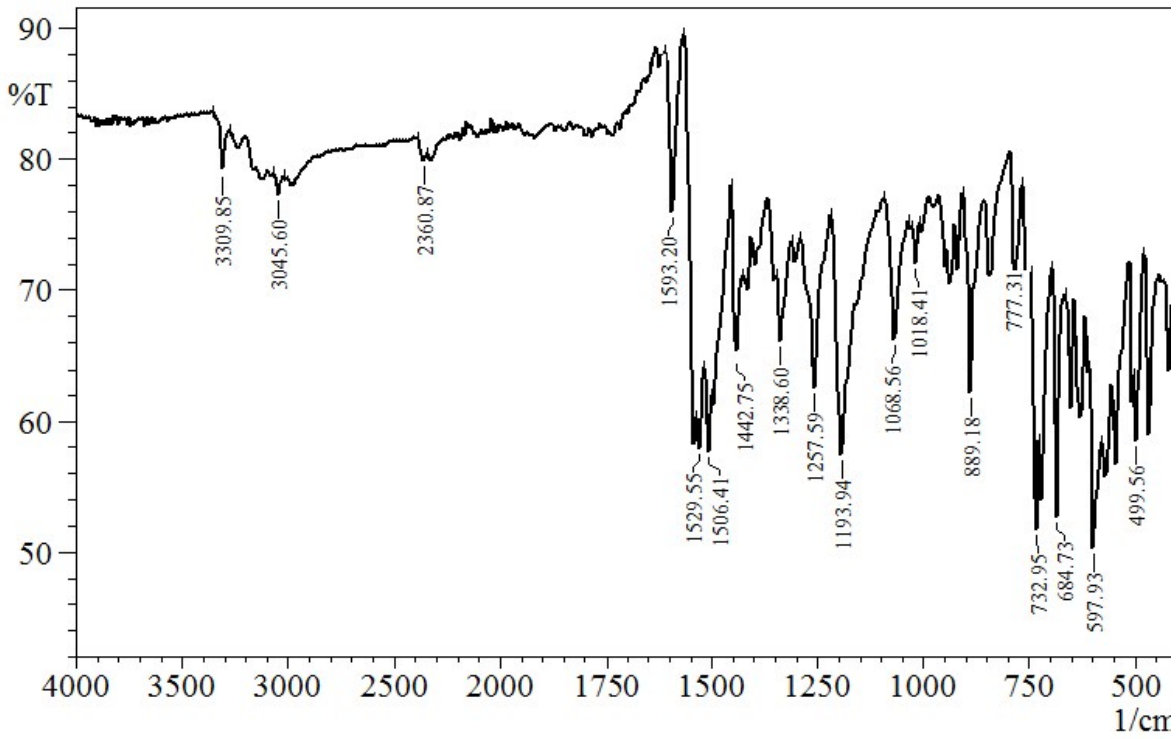


Fig.S5 FTIR spectrum of A12

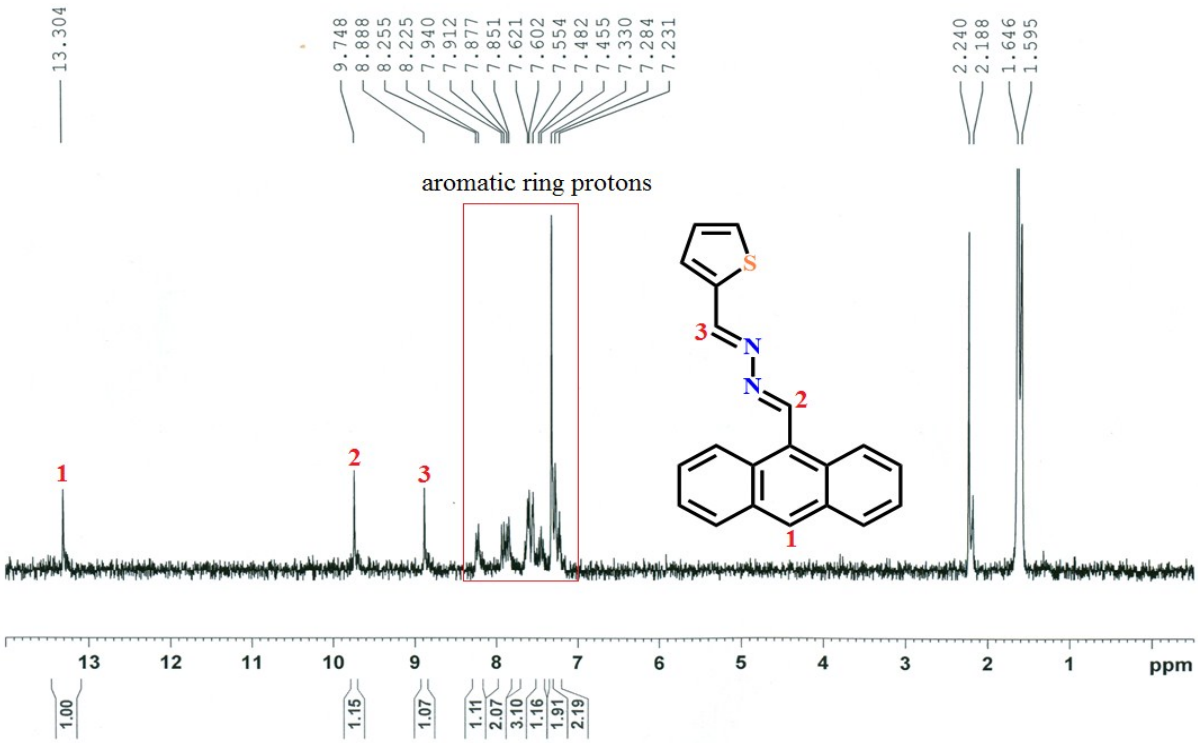


Fig.S6 ^{1}H NMR spectrum of A12a in $CDCl_3$

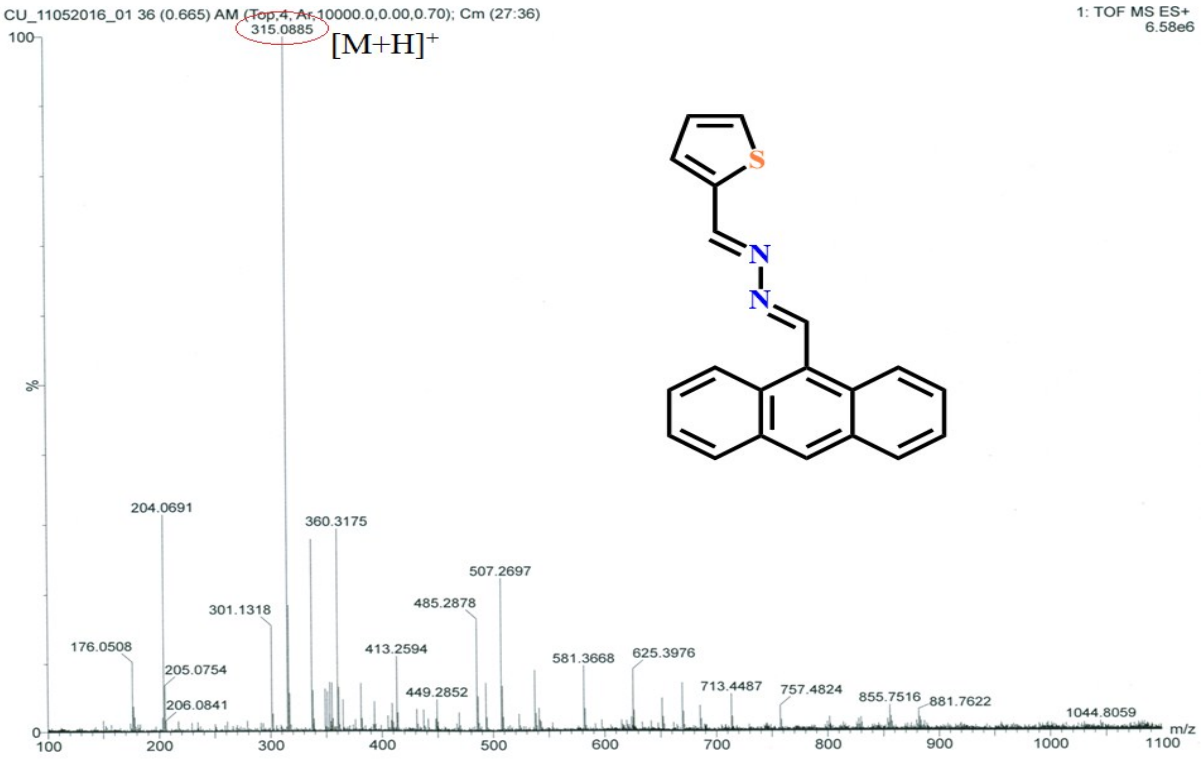


Fig.S7 Mass spectrum of A12a

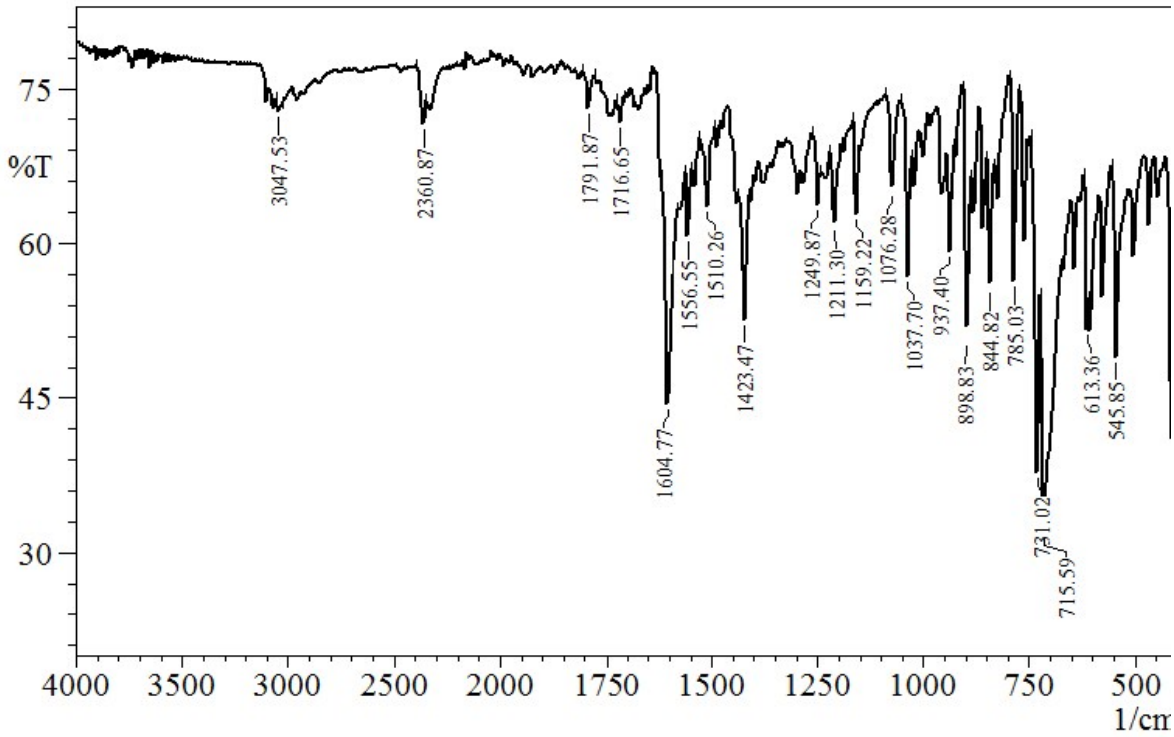


Fig.S8 FTIR spectrum of A12a

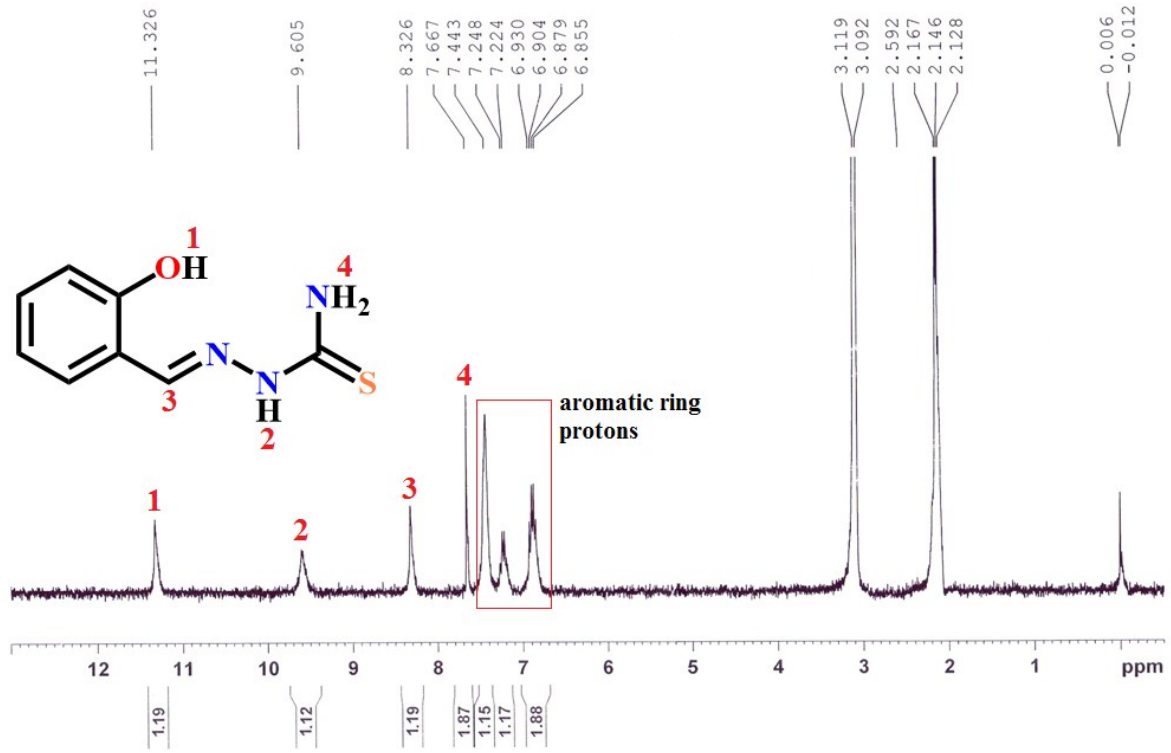


Fig.S9 ^{1}H NMR spectrum of A12b in $CDCl_3$

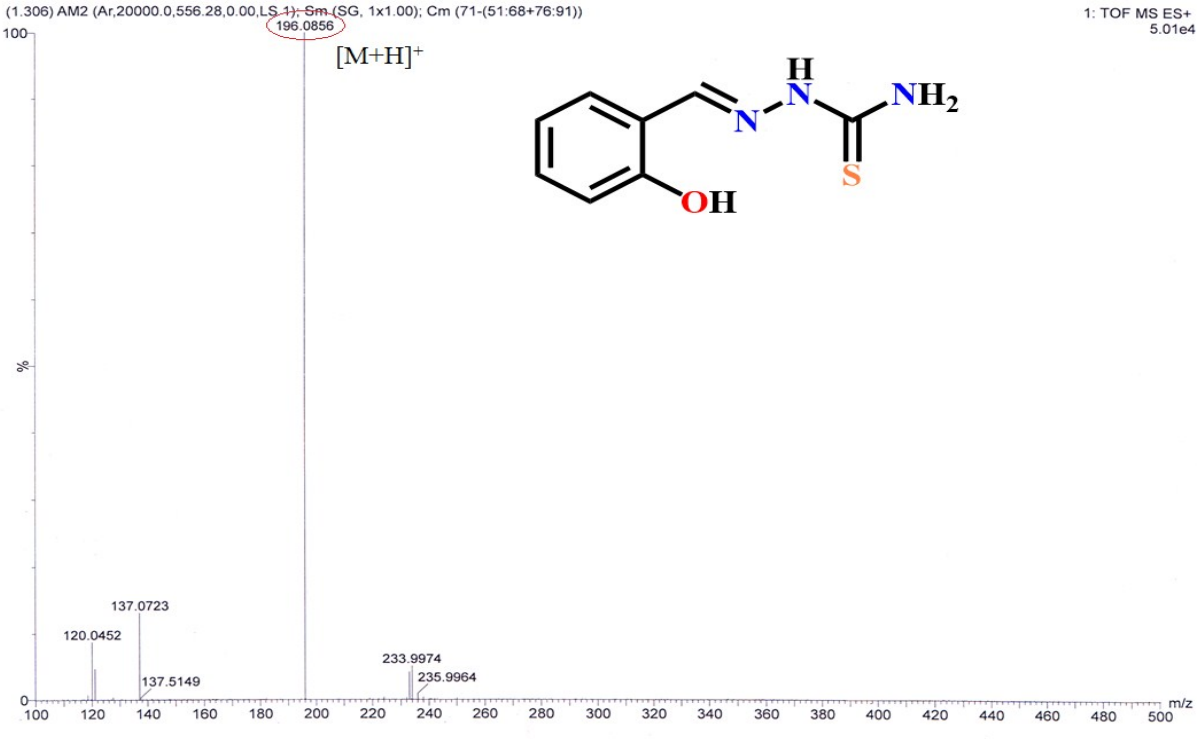


Fig.S10 Mass spectrum of A12b

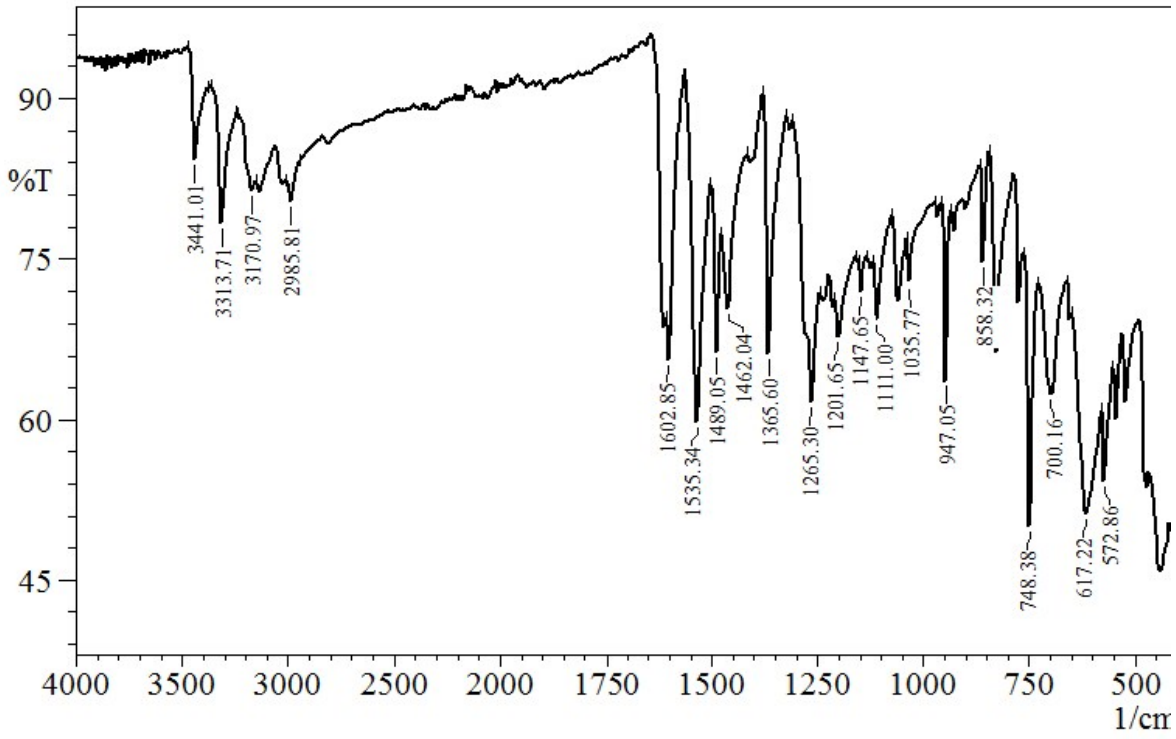


Fig.S11 FTIR spectrum of A12b

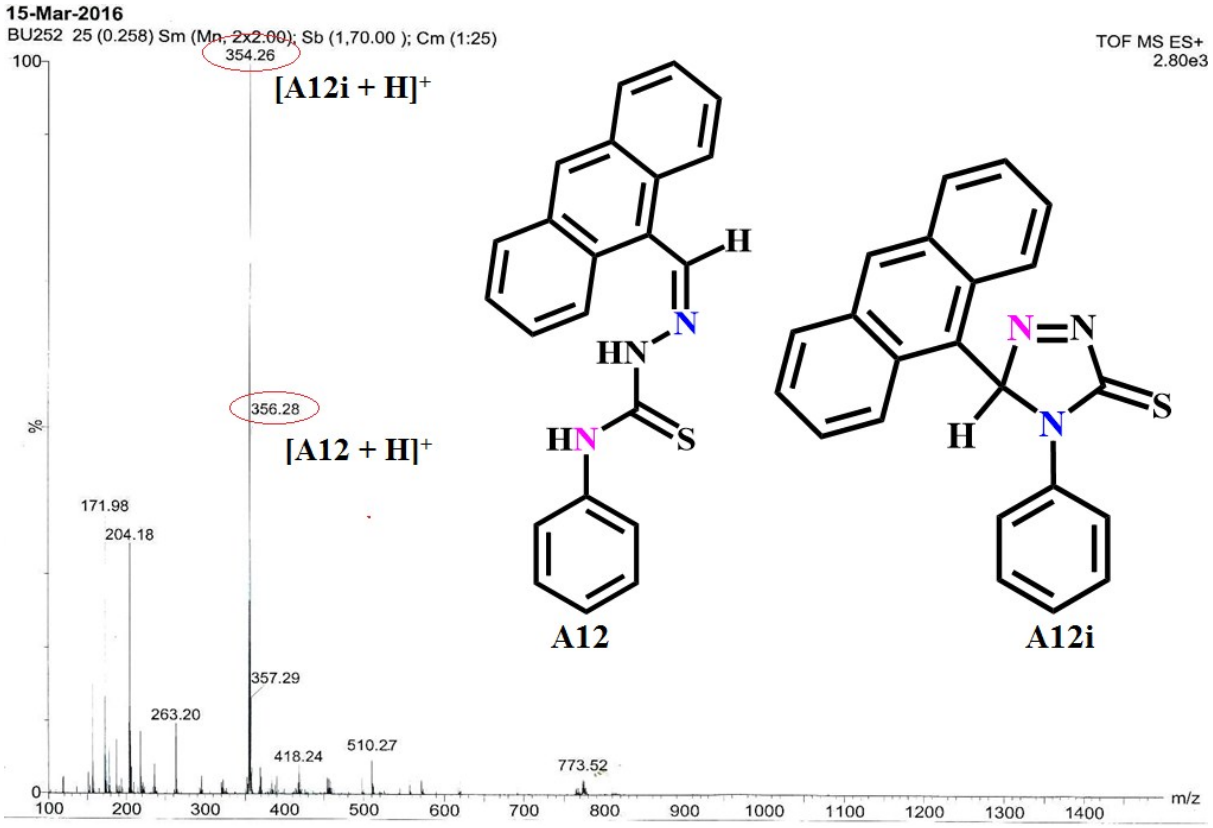


Fig.S12 Mass spectrum of A12i

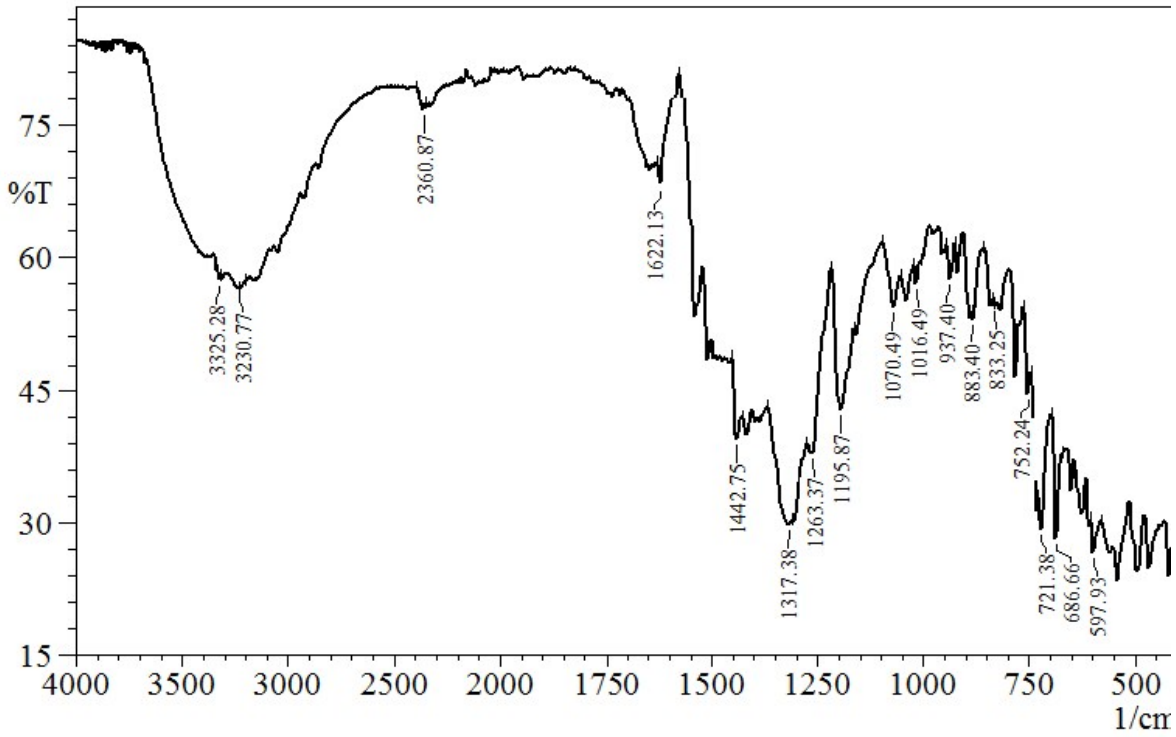


Fig.S13 FTIR spectrum of A12i

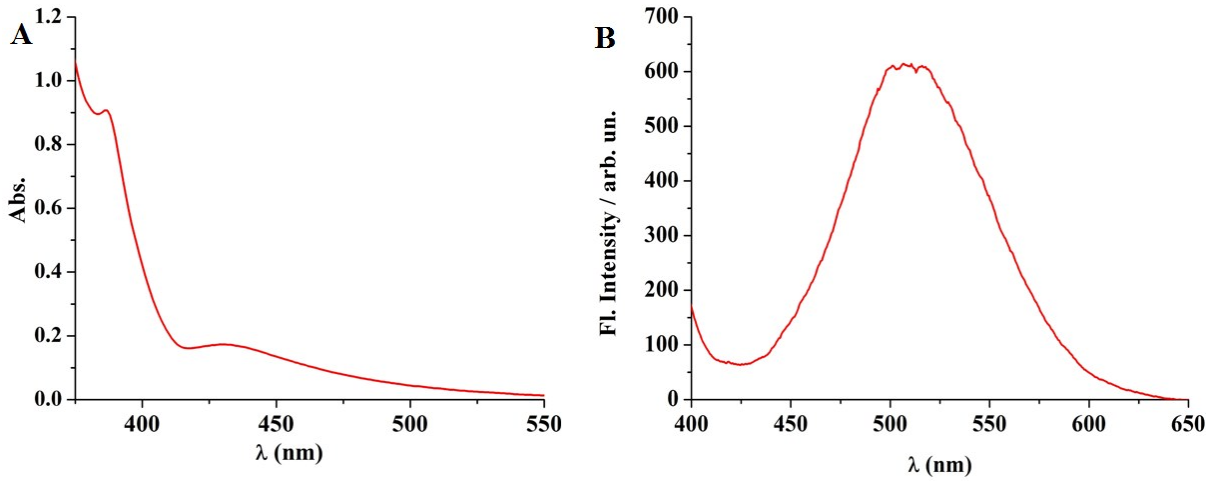


Fig.S14 (A) Absorption and (B) emission (λ_{ex}, 375 nm) spectra of A12i (ethanol-water, 4: 1, v/v)

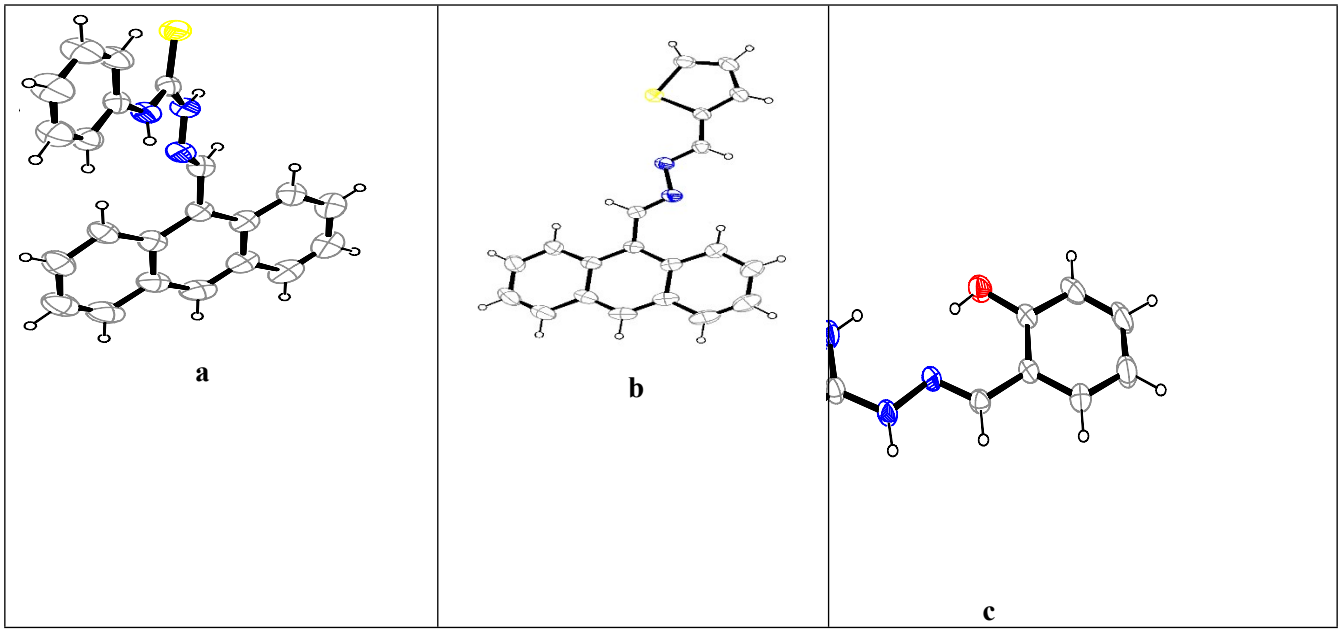


Fig.S15 ORTEP view of (a) A12 (b) A12a (c) A12b

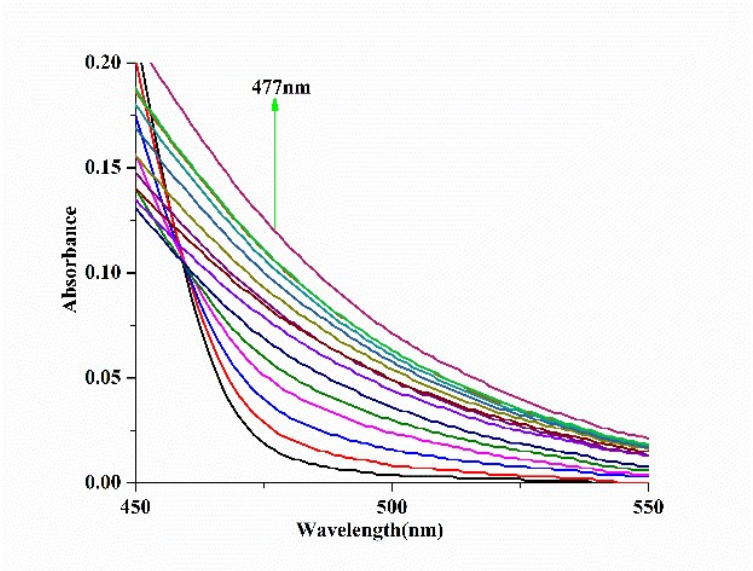


Fig.S16 Expanded view of the new weak band that appeared at 477 nm in the absorption spectra of A12 (10 μM, ethanol-water, 4: 1, v/v, 1 M HEPES buffer, pH 7.4) upon gradual addition of Ce^{4+} (0-200 μM).

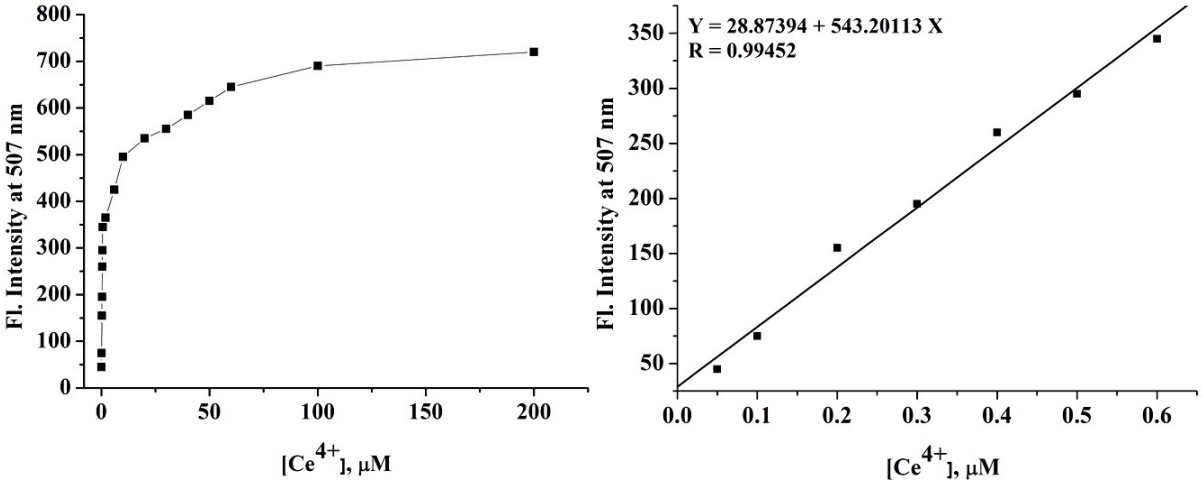


Fig.S17 Emission intensities of A12 (10 μM, ethanol– water, 4 : 1, v/v, 1 M HEPES buffer, pH 7.4, λ_{ex}, 375 nm; λ_{em}, 508 nm) as a function of added Ce^{4+} (0- 200 μM). Linear region of the plot (right)

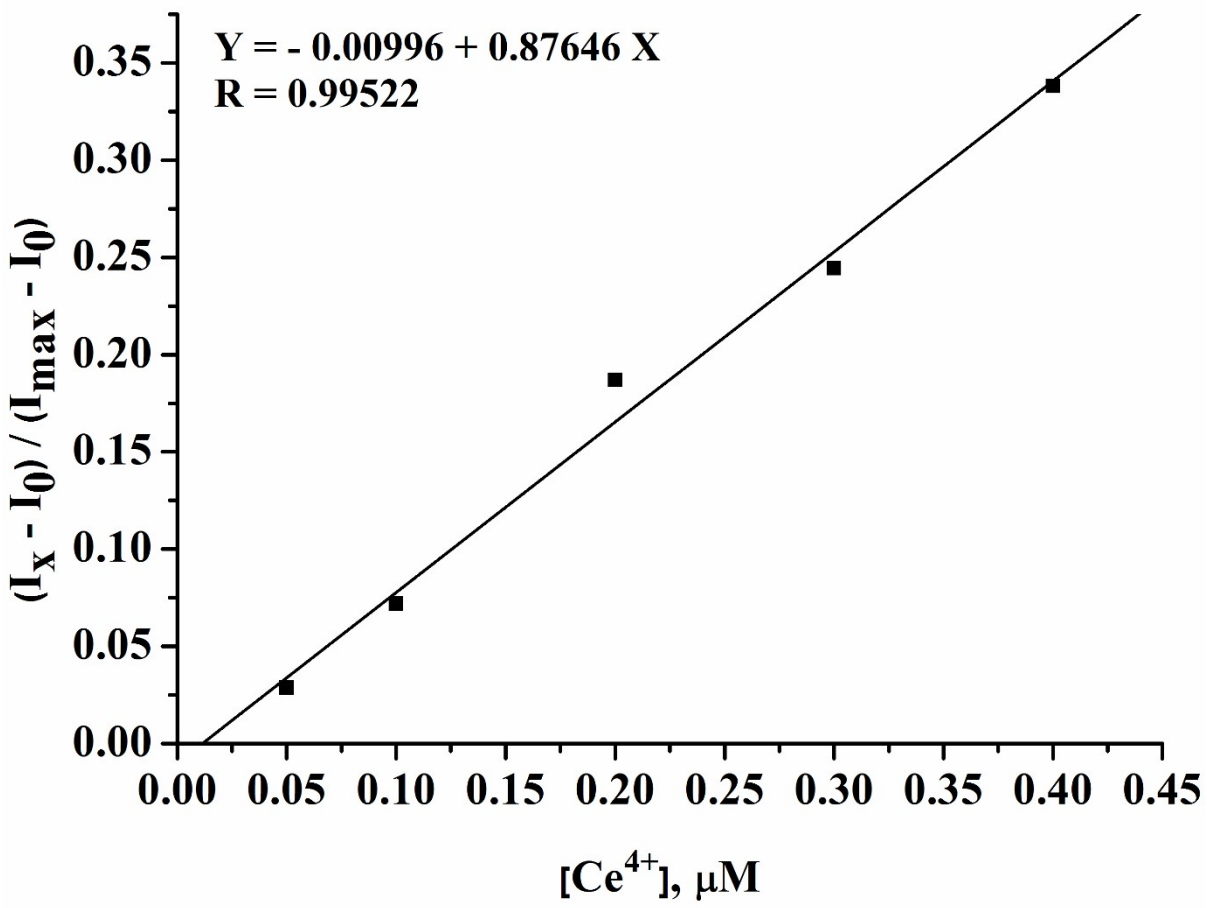


Fig.S18 Emission intensities of A12 (10 μM, λ_{ex}, 375 nm; λ_{em}, 508 nm (from Fig. 4) as a function of added Ce^{4+} in ethanol– water (4 : 1, v/v), 1 M HEPES buffer, pH 7.4

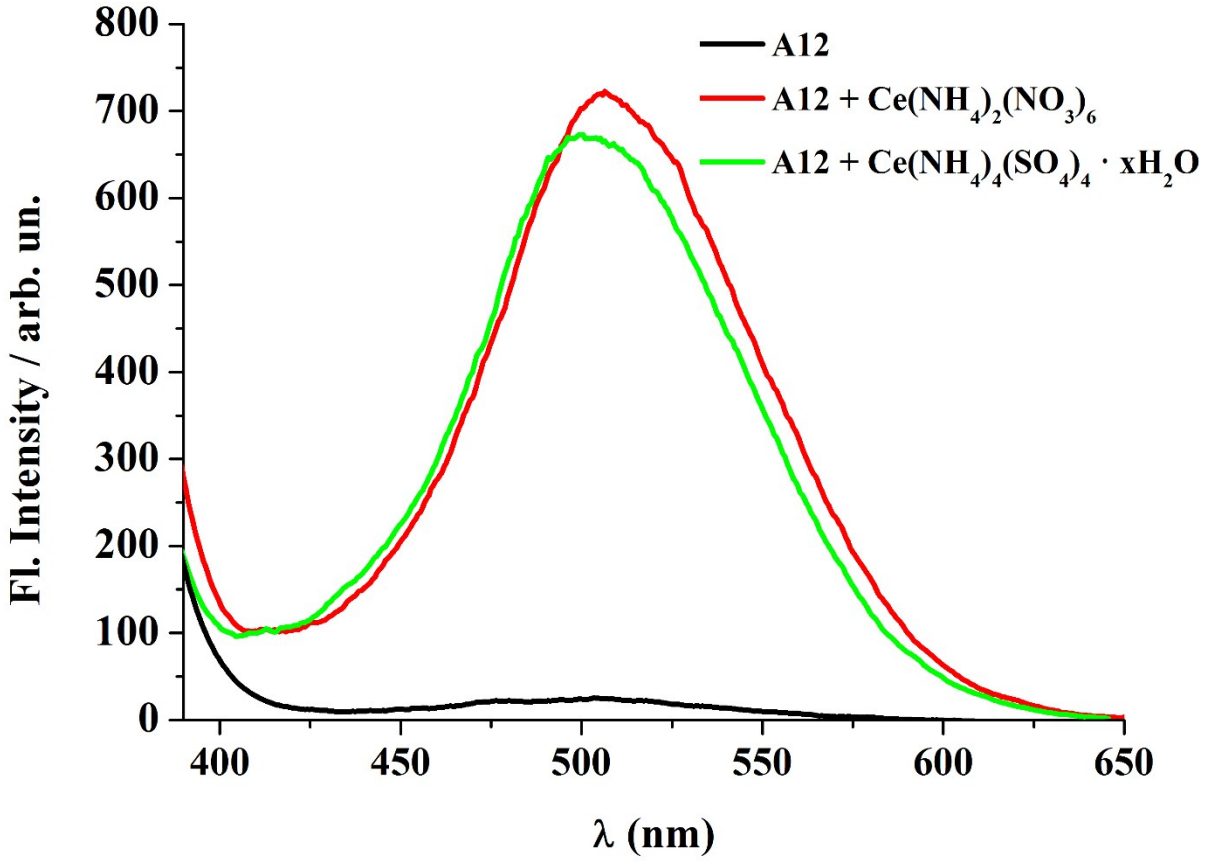


Fig.S19 Effect of Ce^{4+} (200 µM) on the emission spectra of A12 (10 µM, λ_{ex}, 375 nm; λ_{em}, 508 nm) in ethanol-water (4: 1, v/v).

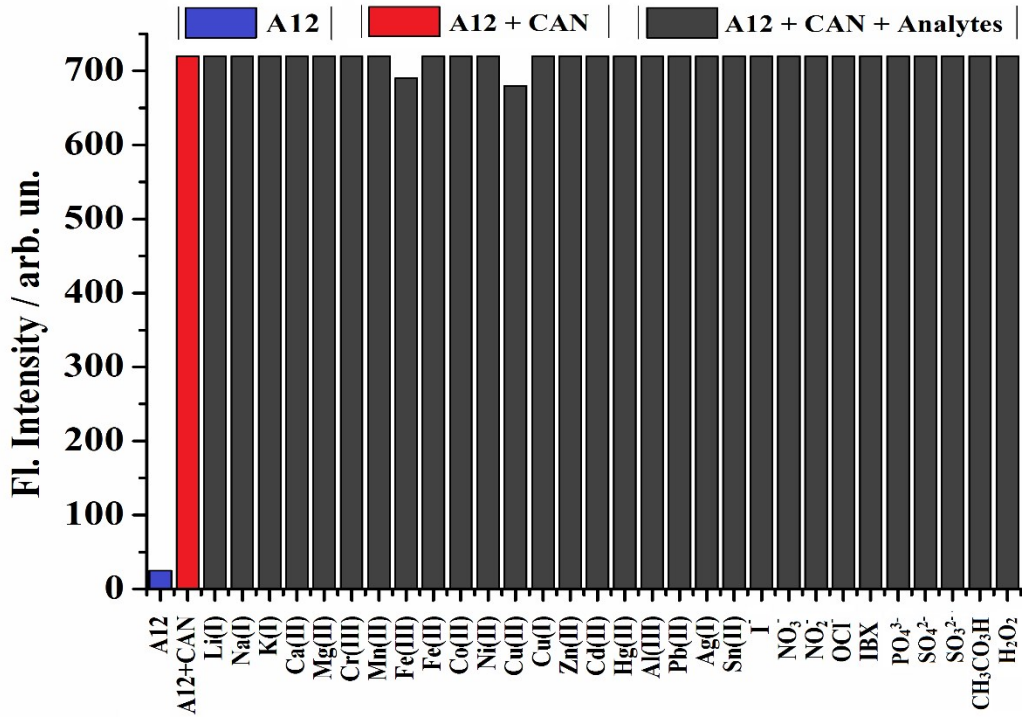


Fig.S20 Effect of different analyte on the emission intensities of [A12+ Ce^{4+}] system (λ_{ex}, 375 nm; λ_{em}, 508 nm).

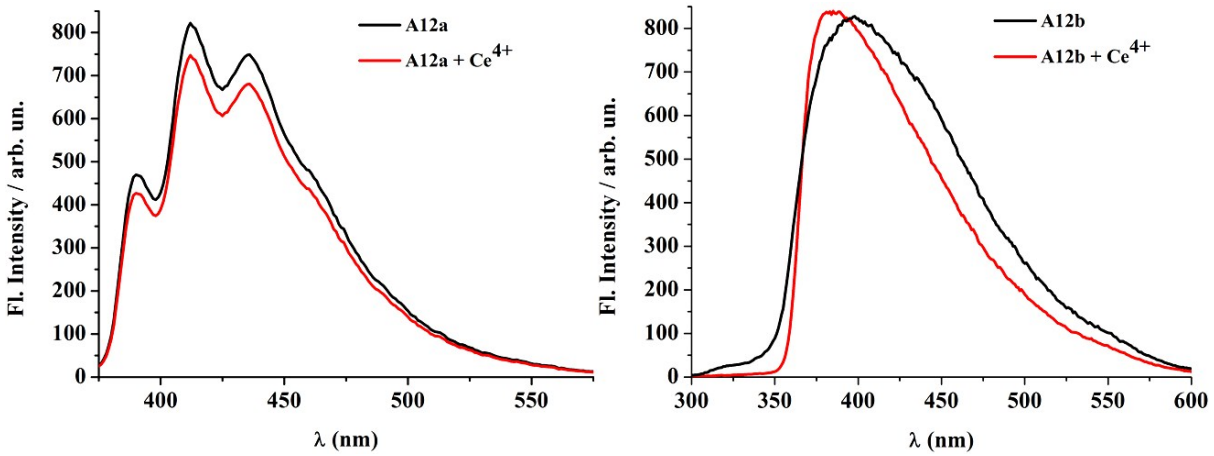


Fig.S21 Effect of Ce^{4+} (200 μM) on the emission spectra of A12a (10 μM, λ_{ex}, 349 nm) and A12b (10 μM, λ_{ex}, 360 nm) in ethanol-water (4: 1, v/v).

Table S1 Crystallographic parameters of the A12 and A12a

	A12	**A12a**
CCDC	1450504	1458041
System	Orthorhombic	Triclinic
Space Group	P n/a 21	P -1
a/Å	8.2558	10.1560
b/Å	24.884	14.3840
c/Å	17.450	17.1787
α/°	90	103.925
β/°	90	99.209
γ/°	90	93.100
Volume/Å3	3584.8	2393.13
Z	8	6
T/K	296	296
Dx/ gm cm^{-3}	1.317	1.309
Mu (mm-1)	0.191	0.203
F000	1488.0	984.0
F000′	1489.45	985.05
h, k, l max	9, 29, 20	13, 19, 23
N_{ref}	6398	12058
Tmin, Tmax	0.977, 0.992	0.976, 0.988
Data completeness	1.91/0.99	0.981
Theta max	25.218	28.627
R(reflections)	0.0512(4026)	0.0563(5900)
wR2(reflection)	0.1298(6398)	0.2040(12058)
S	1.009	0.971
N_{par}	470	623

Table S2 Selected bond angles and lengths of A12

Atoms	Angles	Atoms	Distances
C15 N1 N2	115.0(5)	S1 C16	1.676(6)
C37 N4 N5	114.8(5)	S2 C38	1.670(6)
C16 N3 C17	128.4(5)	N5 C38	1.355(7)
C16 N2 N1	120.4(5)	N5 N4	1.374(6)
C38 N6 C39	131.2(5)	N1 C15	1.275(7)
C1 C14 C13	123.4(5)	N1 N2	1.389(6)
C1 C14 C9	119.2(5)	N4 C37	1.294(7)
C13 C14 C9	117.4(6)	N3 C16	1.341(7)
C40 C39 C44	119.1(5)	N3 C17	1.431(7)
C40 C39 N6	116.0(5)	N2 C16	1.355(7)
C44 C39 N6	124.9(5)	N6 C38	1.352(7)
C25 C24 C23	123.6(6)	N6 C39	1.425(7)
C25 C24 C29	117.5(6)	C14 C1	1.417(8)
C23 C24 C29	118.9(6)	C14 C13	1.423(8)
N5 C38 N6	114.2(5)	C14 C9	1.435(8)
N5 C38 S2	117.5(4)	C39 C40	1.372(8)
N6 C38 S2	128.3(4)	C39 C44	1.385(8)
C35 C36 C31	118.7(6)	C24 C25	1.419(9)
C35 C36 C23	123.4(6)	C24 C23	1.427(8)
C31 C36 C23	117.8(6)	C24 C29	1.432(9)
C30 C29 C24	119.0(6)	C36 C35	1.425(9)
C30 C29 C28)	121.6(7	C36 C31	1.432(9)
C24 C29 C28	119.4(8)	C36 C23	1.431(8)
N3 C16 N2	114.3(5)	C29 C30	1.388(10)
N3 C16 S1	126.1(4)	C29 C28	1.433(11)
N2 C16 S1	119.6(5)	C17 C18	1.373(9)
C18 C17 C22	120.1(6)	C17 C22	1.372(9)
C18 C17 N3	121.5(6)	C1 C2	1.424(8)
C22 C17 N3	118.3(6)	C23 C37	1.472(8)
N1 C15 C1	120.9(6)	C35 C34	1.362(9)
N1 C15 H15	119.6	C9 C8	1.386(9)
C1 C15 H15	119.6	C9 C10	1.436(9)
C14 C1 C2	120.5(5)	C13 C12	1.350(9)
C14 C1 C15	117.6(5)	C7 C8	1.385(9)
C2 C1 C15	121.8(5)	C7 C6	1.441(10)
C24 C23 C36	121.2(5)	C7 C2	1.448(9)
C24 C23 C37	115.6(6)	C40 C41	1.377(9)
C36 C23 C37	123.0(5)	C12 C11	1.391(10)
C34 C35 C36	120.9(7)	C2 C3	1.432(8)

C14 C1 C15	117.6(5)	C31 C30	1.388(10)
C2 C1 C15	121.8(5)	C31 C32	1.438(10)
C8 C9 C14	119.5(6)	C28 C27	1.335(11)
C8 C9 C10	121.8(6)	C25 C26	1.356(9)
C14 C9 C10	118.7(6)	C18 C19	1.376(10)
C12 C13 C14	121.2(6)	C10 C11	1.343(9)
N4 C37 C23	125.7(6)	C4 C5	1.404(11)
C8 C7 C6	122.3(7)	C22 C21	1.390(11)
C8 C7 C2	119.2(6)	C26 C27	1.414(11)
C6 C7 C2	118.5(7)	C41 C42	1.373(10)
C39 C40 C41	120.6(6)	C34 C33	1.412(11)
C13 C12 C11	121.4(7)	C42 C43	1.362(10)
C1 C2 C3	123.4(6)	C21 C20	1.378(12)
C1 C2 C7	118.7(6)	C19 C20	1.347(11)
C3 C2 C7	117.8(6)	C6 C5	1.323(11)
C30 C31 C36	120.0(7)	C33 C32	1.339(11)
C30 C31 C32	122.3(7)		
C36 C31 C32	117.6(7)		
C27 C28 C29	121.0(8)		
C26 C25 C24	120.7(7)		
C4 C3 C2	120.1(7)		
C17 C18 C19	119.8(7)		
C43 C44 C39	119.6(6)		
C29 C30 C31	123.0(7)		
C11 C10 C9	120.6(7)		
C3 C4 C5	120.7(8)		
C9 C8 C7	122.6(6)		
C17 C22 C2	119.7(7)		
C25 C26 C27	121.7(8)		
C10 C11 C12	120.8(7)		
C42 C41 C40	120.5(7)		
C28 C27 C26	119.8(7)		
C35 C34 C33	120.4(8)		
C43 C42 C41	119.0(7)		
C20 C21 C22	119.1(8)		
C20 C19 C18	120.5(8)		
C5 C6 C7	121.2(8)		
C19 C20 C21	120.8(8)		
C42 C43 C44	121.3(7)		
C32 C33 C34	120.7(8)		
C33 C32 C31	121.6(8)		
C6 C5 C4	121.5(8)		

Table S3 Selected bond angles and bond lengths of A12a

Atoms	Angles	Atoms	Distances
C01M S001 C00K	90.67(14)	S001 C01M	1.711(3)
C01T S002 C00S	91.54(16)	S001 C00K	1.724(3)
C00W S003 C01U	91.46(14	S002 C01T	1.703(3)
C00N N004 N006	111.6(2)	S002 C00S	1.710(3)
C00X N005 N1	112.1(2)	S003 C00W	1.698(3)
C00M N006 N004	112.4(2)	S003 C01U	1.707(3)
C00Y N007 N008	111.9(2)	N004 C00N	1.270(3)
C00R N008 N007	112.6(2)	N004 N006	1.414(3)
C00Q N1 N005	114.4(2)	N005 C00X	1.276(3)
C00G C00A C00B	120.2(2)	N005 N1	1.410(3)
C00G C00A C00R	122.7(2)	N006 C00M	1.268(3)
C00B C00A C00R	116.9(2)	N007 C00Y	1.272(3)
C00A C00B C010	123.7(2)	N007 N008	1.410(3)
C00A C00B C00E	119.4(2)	N008 C00R	1.270(3)
C010 C00B C00E	116.9(2)	N1 C00Q	1.235(3)
C00D C00C C00U	124.2(2)	C00A C00G	1.416(3)
C00D C00C C00P	118.5(2)	C00A C00B	1.423(3)
C00U C00C C00P	117.3(2)	C00A C00R	1.456(3)
C00C C00D C00I	120.7(2)	C00B C010	1.427(3)
C00C C00D C00N	122.0(2)	C00B C00E	1.437(3)
C00I C00D C00N	117.1(2)	C00C C00D	1.417(3)
C00L C00E C012	121.3(2)	C00C C00U	1.428(3)
C00L C00E C00B	119.0(2)	C00C C00P	1.440(3)
C012 C00E C00B	119.7(2)	C00D C00I	1.418(3)
C00L C00F C00G	120.2(2)	C00D C00N	1.477(3)
C00L C00F C00Z	121.2(2)	C00E C00L	1.386(3)
C00G C00F C00Z	118.5(2)	C00E C012	1.433(3)
C00A C00G C00F	118.8(2)	C00F C00L	1.387(3)
C00A C00G C00T	123.5(2)	C00F C00G	1.428(3)
C00F C00G C00T	117.7(2)	C00F C00Z	1.431(3)
C00O C00H C00J	120.3(2)	C00G C00T	1.430(3)
C00O C00H C00Q	117.2(2)	C00H C00O	1.424(4)
C00J C00H C00Q	122.5(2)	C00H C00J	1.424(4)
C00D C00I C016	123.5(2)	C00H C00Q	1.469(3)
C00D C00I C00V	119.8(2)	C00I C016	1.430(4)
C016 C00I C00V	116.7(2)	C00I C00V	1.429(3)
C00H C00J C01D	124.1(2)	C00J C01D	1.429(4)
C00H C00J C01B	119.2(3)	C00J C01B	1.432(4)
C01D C00J C01B	116.7(3)	C00K C011	1.376(3)
C011 C00K C00X	126.4(2)	C00K C00X	1.433(3)
C011 C00K S001	111.28(19)	S001 C01M	1.711(3)
C00X C00K S001	122.30(19)	S001 C00K	1.724(3)
C00F C00L C00E	122.1(2)	S002 C01T	1.703(3)
C00H C00O C01J	124.1(2)	S002 C00S	1.710(3)
C00H C00O C018	119.2(3)	S003 C00W	1.698(3)
C01J C00O C018	116.7(3)	S003 C01U	1.707(3)
C013 C00P C01C	121.2(2)	N004 C00N	1.270(3)
C013 C00P C00C	119.8(2)	N004 N006	1.414(3)
C01C C00P C00C	119.0(2)	N005 C00X	1.276(3)
N004 C00N C00D	125.2(2)	N005 N1	1.410(3)

N006 C00M C00S	123.1(2)	N006 C00M	1.268(3)
N1 C00Q C00H	126.5(2)	N007 C00Y	1.272(3)
N008 C00R C00A	123.5(2)	N007 N008	1.410(3)
C01L C00S C00M	125.7(3)	N008 C00R	1.270(3)
C01L C00S S002	110.8(2)	N1 C00Q	1.235(3)
C00M C00S S002	123.41(19)	C00A C00G	1.416(3)
C014 C00T C00G	121.3(2)	C00A C00B	1.423(3)
C01A C00U C00C	121.6(2)	C00A C00R	1.456(3)
C013 C00V C00I	119.2(2)	C00B C010	1.427(3)
C013 C00V C01I	121.3(3)	C00B C00E	1.437(3
C00I C00V C01I	119.5(3)	C00C C00D	1.417(3)
C019 C00W C00Y	127.7(2)	C00C C00U	1.428(3)
C019 C00W S003	110.86(19)	C00C C00P	1.440(3)
C00Y C00W S003	121.39(19)	C00D C00I	1.418(3)
N005 C00X C00K	121.7(2)	C00D C00N	1.477(3)
N007 C00Y C00W	121.8(2)	C00E C00L	1.386(3)
C015 C00Z C00F	121.7(2)	C00E C012	1.433(3)
C01K C010 C00B	121.1(3)	C00F C00L	1.387(3)
C00K C011 C01H	112.3(3)	C00F C00G	1.428(3)
C01E C012 C00E	120.8(3)	C00F C00Z	1.431(3)
C00V C013 C00P	122.1(2)	C00G C00T	1.430(3)
C00T C014 C015	121.2(2)	C00H C00O	1.424(4)
C00Z C015 C014	119.6(2)	C00H C00J	1.424(4)
C01O C016 C00I	121.3(3)	C00H C00Q	1.469(3)
C018 C017 C01B	122.8(3)	C00I C016	1.430(4)
C017 C018 C00O	119.3(3)	C00I C00V	1.443(3)
C017 C018 C01Q	121.8(3)	C00J C01D	1.429(4)
C00O C018 C01Q	118.9(3)	C00J C01B	1.432(4)
C00W C019 C01F	112.5(2)	C00K C011	1.376(3)
C00U C01A C01G	120.3(3)	C00K C00X	1.433(3)
C017 C01B C00J	119.3(3)	C00M C00S	1.429(3)
C017 C01B C01N	121.7(3)	C00O C01J	1.422(4)
C00J C01B C01N	119.0(3)	C00O C018	1.435(4)
C01G C01C C00P	121.7(3)	C00P C013	1.399(4)
C01S C01D C00J	121.6(3)	C00P C01C	1.419(4)
C012 C01E C01K	119.8(2)	C00S C01L	1.362(4)
C01U C01F C019	112.3(2)	C00T C014	1.353(4)
C01C C01G C01A	120.0(3)	C00U C01A	1.360(4)
C01M C01H C011	112.6(3)	C00V C013	1.351(4)
C01P C01I C00V	120.9(3)	C00V C01I	1.433(4)
C01W C01J C00O	122.0(3)	C00W C019	1.382(3)
C00S C01L C01R	112.7(3)	C00W C00Y	1.442(3)
C01H C01M S001	113.1(2)	C00Z C015	1.387(4)
C01X C01N C01B	121.6(3)	C010 C01K	1.366(4)
C016 C01O C01P	121.2(3)	C011 C01H	1.406(4)
C01I C01P C01O	120.3(3)	C012 C01E	1.352(4)
C01V C01Q C018)	121.7(3	C014 C015	1.408(4)
C01T C01R C01L	112.6(3)	C016 C01O	1.360(4)
C01D C01S C01X	121.1(4)	C017 C018	1.385(4)
C01R C01T S002	112.3(2)	C017 C01B	1.389(4)
C01F C01U S003	112.8(2)	C018 C01Q	1.436(4)
C01Q C01V C01W	119.9(3)	C019 C01F	1.398(5

C01J C01W C01V	120.7(4)	C01A C01G	1.425(4)
C01N C01X C01S	120.0(3)	C01D C01S	1.356(4)
		C01B C01N	1.430(4)
		C01C C01G	1.344(4)
		C01E C01K	1.404(4)
		C01F C01U	1.333(4)
		C01H C01M	1.338(4)
		C01I C01P	1.341(5)
		C01J C01W	1.354(4)
		C01N C01X	1.339(5)
		C01O C01P	1.394(5)
		C01Q C01V	1.326(5)
		C01R C01T	1.334(4)
		C01S C01X	1.403(4)
		C01V C01W	1.415(5)

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