

Supplementary Material

Three selective and sensitive “off-on” probes based on rhodamine for Fe³⁺ imaging in living cells

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Table S1 X-ray Tables of compounds **3a-c**

Compound	3a
Formula	C ₃₆ H ₃₅ N ₅ O ₂ S
Formula weight	601.25
Temperature (K)	296(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
space group	P2(1)/c
Unit cell dimensions /(Å, °)	a = 16.334 (3) α= 90 b = 12.039(2) β= 109.258(3) c = 16.574(3) γ= 90
Volume (Å ³)	3076.9(10)
Z	40
Calculated density (Mg/m ³)	1.621
Absorption coefficient (mm ⁻¹)	0.775
F(000)	1520
Crystal size (mm ³)	0.35 x 0.33 x 0.24
Theta range for data collection (°)	2.13 - 25.10
Limiting indices	-18<=h<=19 -9<=k<=14 -19<=l<=18
Reflections collected / unique	15110 / 5473 [R(int) = 0.0437]
Completeness to θ = 25.10	99.8 %
Max. and min. transmission	0.9726 and 0.9614
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	5473 / 0 / 401
Goodness-of-fit on F ²	1.049
Final R indices [I>2σ (I)]	R1 = 0.0551, wR2 = 0.1402
R indices (all data)	R1 = 0.0857, wR2 = 0.1607
Largest diff. peak and hole/(e. Å ⁻³)	0.397 and -0.299
CCDC	979338

Compound	3b
Formula	C ₃₇ H ₃₇ N ₅ O ₃ S
Formula weight	631.26
Temperature (K)	296(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
space group	Cc
Unit cell dimensions /(Å, °)	a = 28.380(6) α = 90 b = 17.275(6) β = 129.802(10) c = 19.574(7) γ = 90
Volume (Å ³)	7373(4)
Z	8
Calculated density (Mg/m ³)	1.138
Absorption coefficient (mm ⁻¹)	0.128
F(000)	2672
Crystal size (mm ³)	0.36 x 0.30 x 0.24
Theta range for data collection (°)	1.50 - 25.10
Limiting indices	-33 ≤ h ≤ 32 -20 ≤ k ≤ 15 -23 ≤ l ≤ 23
Reflections collected / unique	18377 / 6565 [R(int) = 0.1492]
Completeness to θ = 25.10	99.9 %
Max. and min. transmission	0.9697 and 0.9557
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	6565 / 0 / 421
Goodness-of-fit on F ²	1.011
Final R indices [I > 2σ (I)]	R1 = 0.1379, wR2 = 0.3309
R indices (all data)	R1 = 0.2844, wR2 = 0.4167
Largest diff. peak and hole/(e. Å ⁻³)	1.094 and -0.462
CCDC	979341

Compound	3c
Formula	C ₃₆ H ₃₄ N ₆ O ₄ S
Formula weight	646.24
Temperature (K)	296(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
space group	P-1
Unit cell dimensions /(Å, °)	a = 9.558(2) α= 74.955(5) b = 12.296(3) β= 82.177(5) c = 14.954(4) γ= 72.016(5)
Volume (Å ³)	1611.3(7)
Z	2
Calculated density (Mg/m ³)	1.333
Absorption coefficient (mm ⁻¹)	0.151
F(000)	680
Crystal size (mm ³)	0.36 x 0.31 x 0.25
Theta range for data collection (°)	1.41 - 26.66
Limiting indices	-11 ≤ h ≤ 11 -15 ≤ k ≤ 14 -18 ≤ l ≤ 14
Reflections collected / unique	9063 / 6470 [<i>R</i> (int) = 0.0417]
Completeness to θ = 25.10	95.2 %
Max. and min. transmission	0.9627 and 0.9473
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	6470 / 0 / 428
Goodness-of-fit on <i>F</i> ²	1.025
Final <i>R</i> indices [<i>I</i> > 2σ (<i>I</i>)]	<i>R</i> 1 = 0.0741, <i>wR</i> 2 = 0.1822
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1530, <i>wR</i> 2 = 0.2351
Largest diff. peak and hole/(e. Å ⁻³)	0.607 and -0.290
CCDC	979339

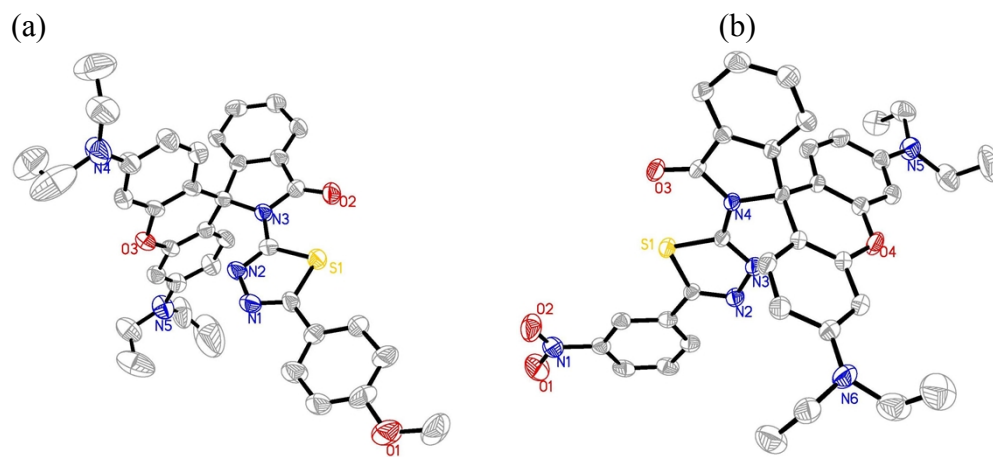


Fig. S1 X-ray crystal structures of **3b** (a) and **3c** (b).

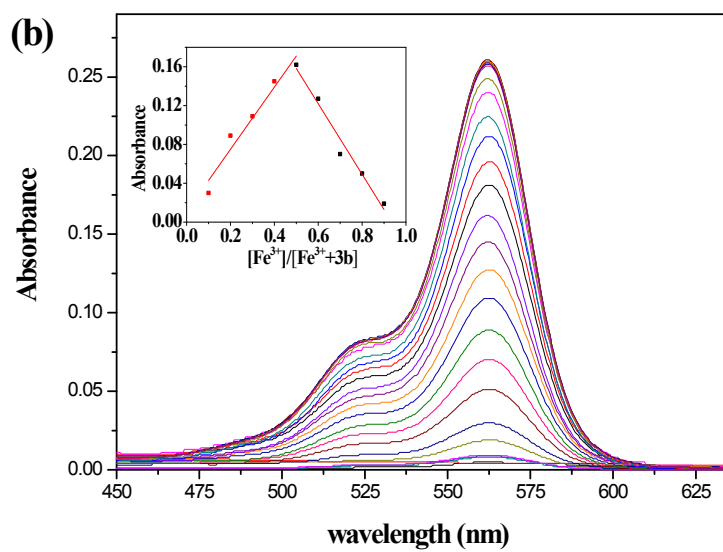
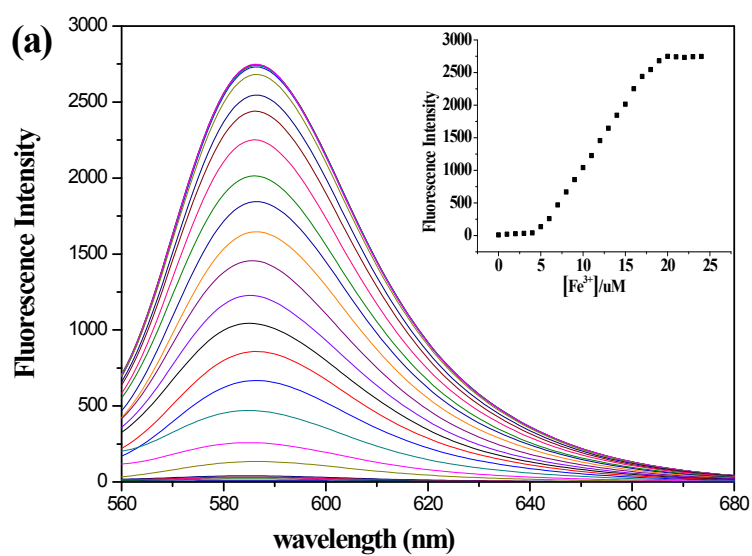


Fig. S2 Fluorescence intensity (a) and absorption (b) changes of **3b** (20 μM) upon addition of Fe^{3+} in methanol-water (4/6, v/v) solution. Inset: (a) Changes of emission intensity at 583 nm. $\lambda_{\text{ex}}=555$ nm. (b) Job's plot of **3b** and Fe^{3+} .

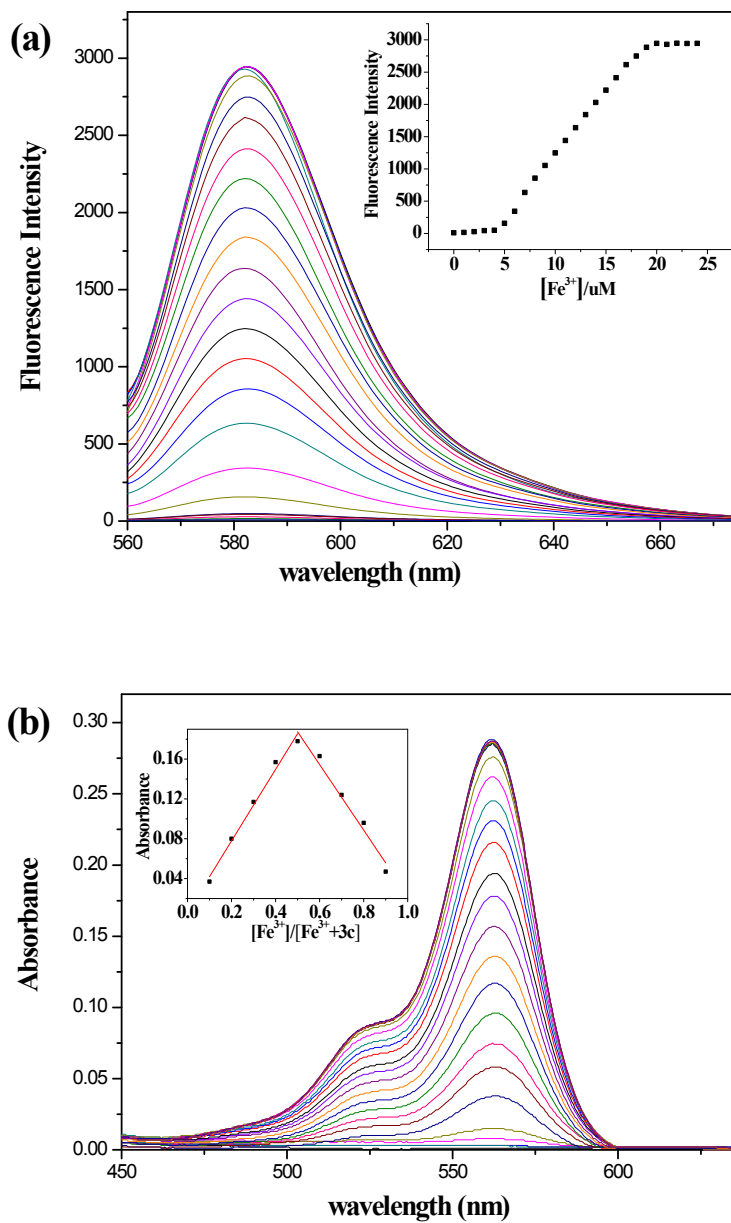
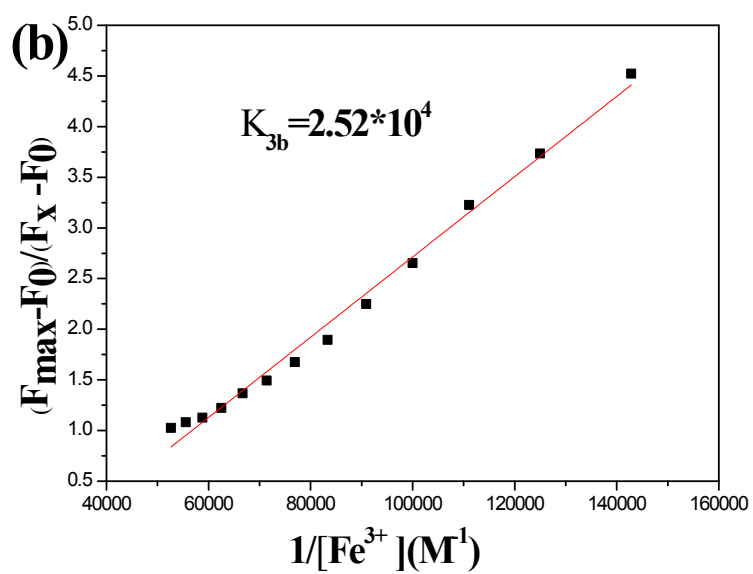
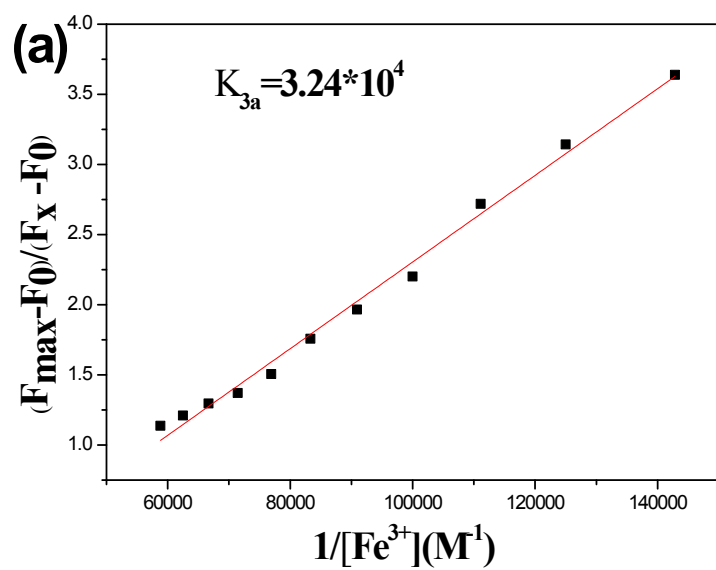


Fig. S3 Fluorescence intensity (a) and absorption (b) changes of **3c** (20 μM) upon addition of Fe³⁺ in methanol-water (4/6, v/v) solution. Inset: (a) Changes of emission intensity at 582 nm, $\lambda_{\text{ex}}=555$ nm. (b) Job's plot of **3c** and Fe³⁺.



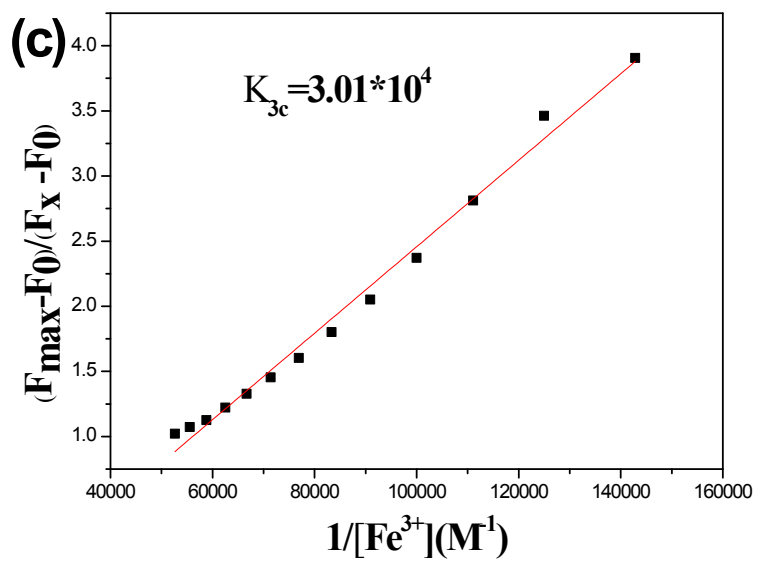


Fig. S4 Determination of binding constant of **3a** (a), **3b** (b) and **3c** (c) (20 μM) with Fe^{3+} (20 μM) using Benesi–Hildebrand equation.

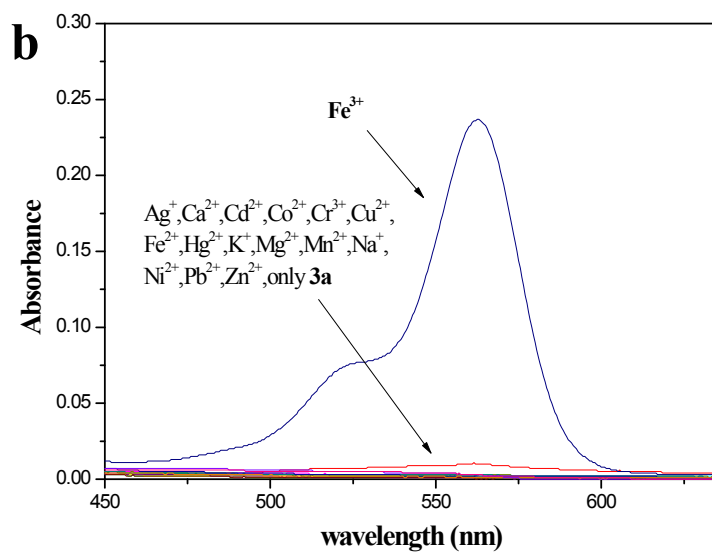
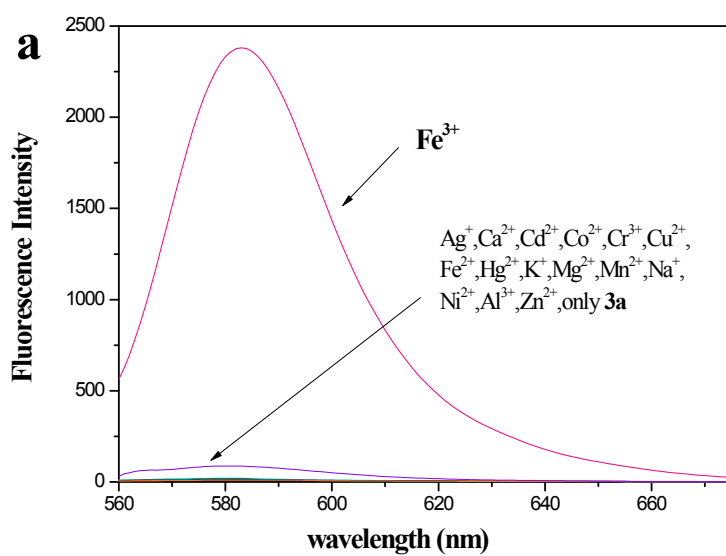


Fig.S5 Fluorescence (a) and absorption (b) spectra of **3a** (20 μM) in methanol-water (4/6, v/v) solution upon addition of various metal ions (20 μM), $\lambda_{\text{ex}}=555$ nm.

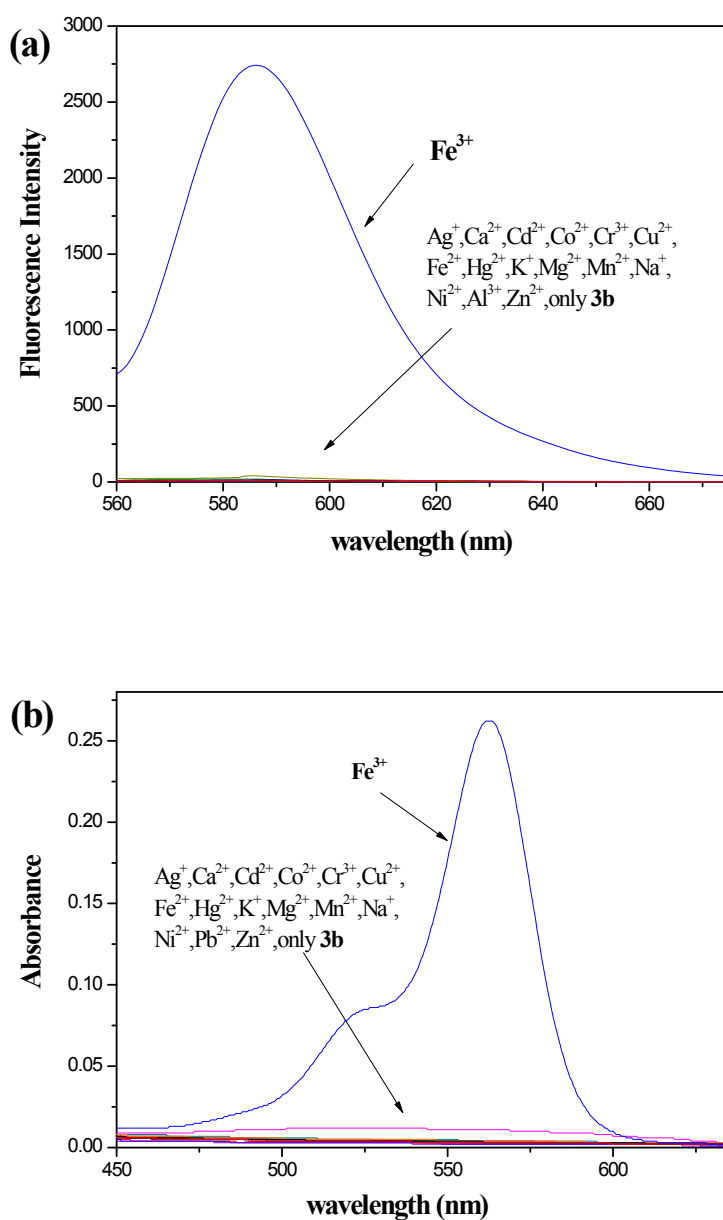


Fig. S6 Fluorescence (a) and absorption (b) spectra of **3b** (20 μM) in methanol-water (4/6, v/v) solution upon addition of various metal ions (20 μM), $\lambda_{\text{ex}}=555$ nm.

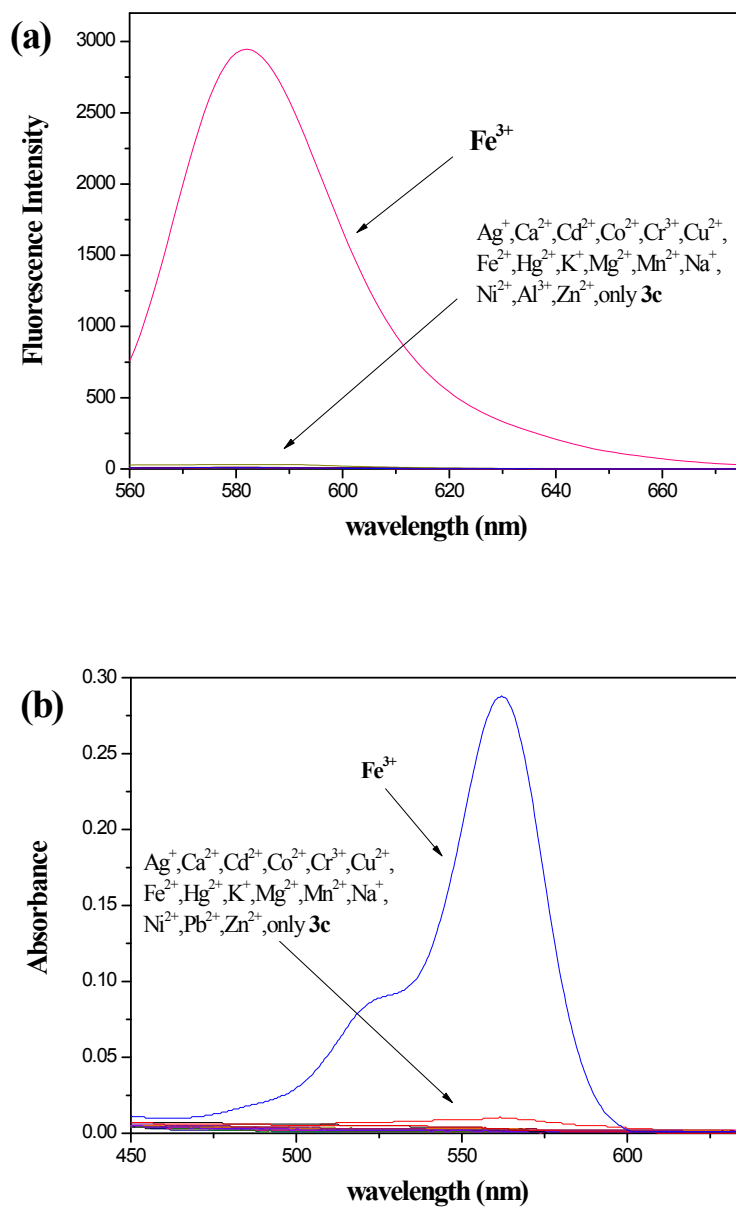


Fig. S7 Fluorescence (a) and absorption (b) spectra of **3c** (20 μM) in methanol-water (4/6, v/v) solution upon addition of various metal ions (20 μM), $\lambda_{\text{ex}}=555$ nm.

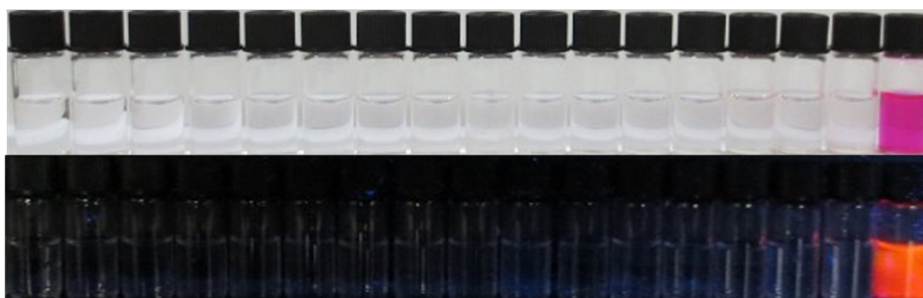


Fig. S8 Pictures of **3b** as a selective naked-eye probe (top) and the visual fluorescence emissions by using a UV lamp (365 nm) (bottom) for Fe³⁺. From the left to right: blank, Ag⁺, Na⁺, K⁺, Ca²⁺, Cd²⁺, Mg²⁺, Co²⁺, Mn²⁺, Cu²⁺, Al³⁺, Zn²⁺, Ni²⁺, Fe²⁺, Hg²⁺, Cr³⁺ and Fe³⁺ ions.



Fig. S9 Pictures of **3c** as a selective naked-eye probe (top) and the visual fluorescence emissions by using a UV lamp (365 nm) (bottom) for Fe³⁺. From the left to right: blank, Ag⁺, Na⁺, K⁺, Ca²⁺, Cd²⁺, Mg²⁺, Co²⁺, Mn²⁺, Cu²⁺, Al³⁺, Zn²⁺, Ni²⁺, Fe²⁺, Hg²⁺, Cr³⁺ and Fe³⁺ ions.

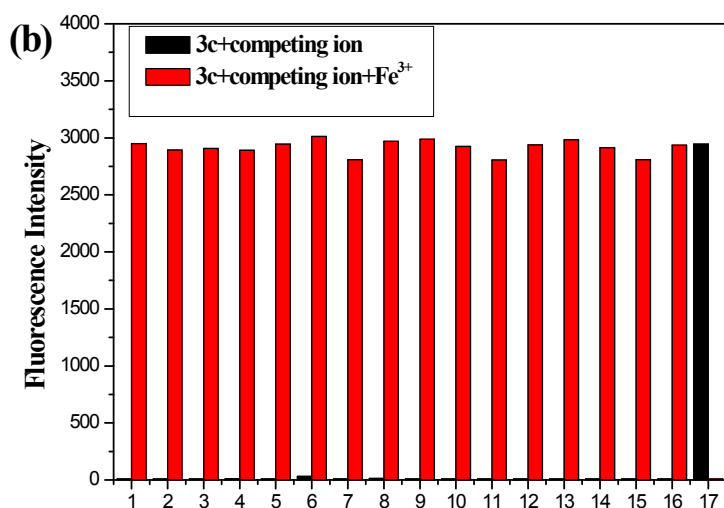
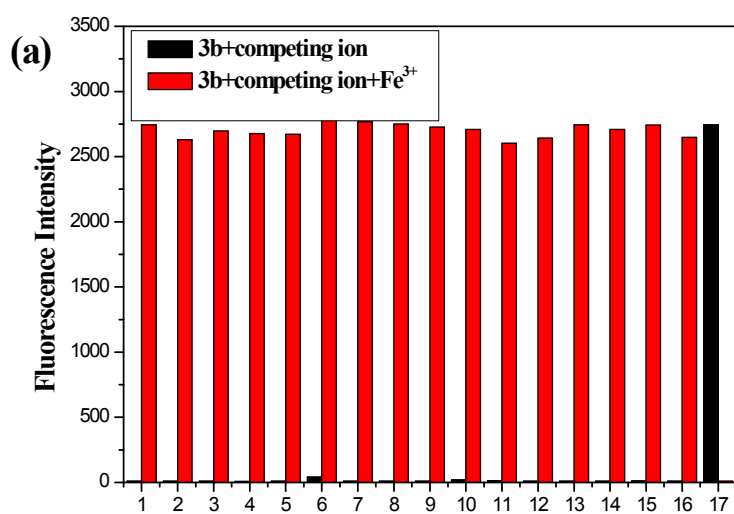


Fig. S10 Fluorescence intensity changes of **3b** (a) and **3c** (b) (20 μM) upon the addition of various metal ions (20 μM) in and without the presence of Fe^{3+} (20 μM) in methanol-water (4/6, v/v) solution. The black bars represent the fluorescence response of **3b/3c** and competing ions: 1.blank, 2. Na^+ , 3. Ca^{2+} , 4. Mg^{2+} , 5. Cd^{2+} , 6. Mn^{2+} , 7. Ni^{2+} , 8. Co^{2+} , 9. Zn^{2+} , 10. Cu^{2+} , 11. Cr^{3+} , 12. Pb^{2+} , 13. Ag^+ , 14. Fe^{2+} , 15. Hg^{2+} , 16. K^+ , 17. Fe^{3+} . The red bars represent the subsequent addition of 20 μM Fe^{3+} to the above solutions.

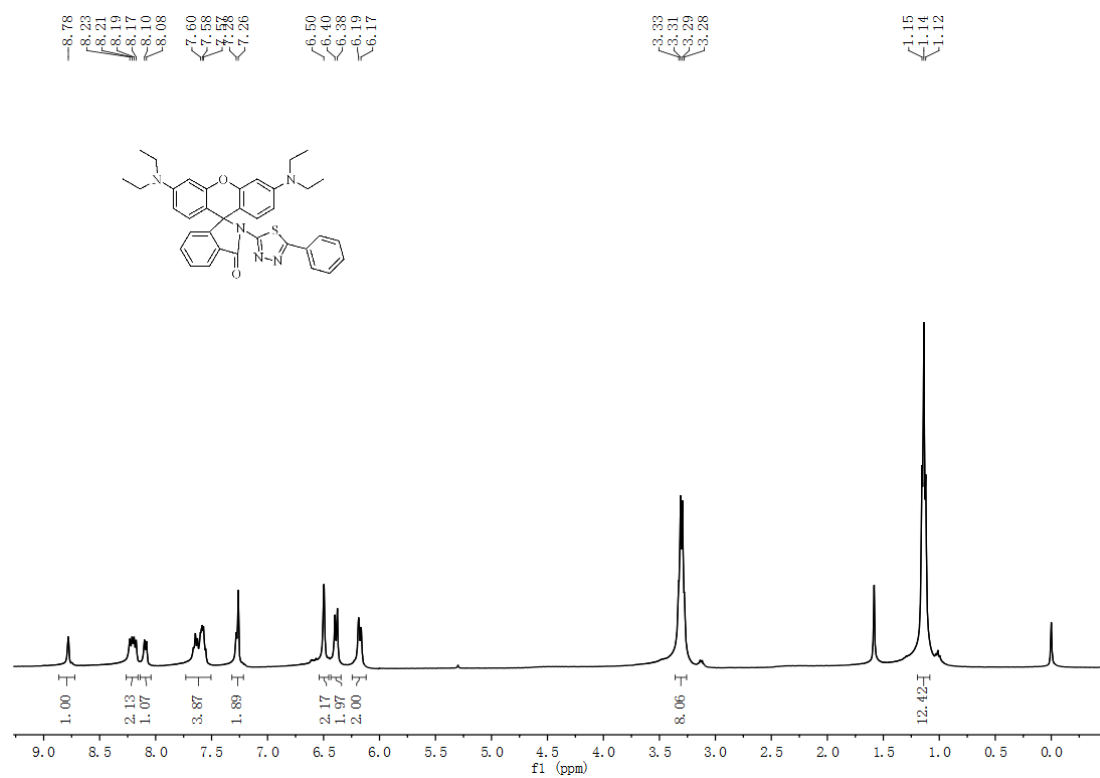


Fig. S11 ¹H NMR spectrum of **3a** in CDCl₃.

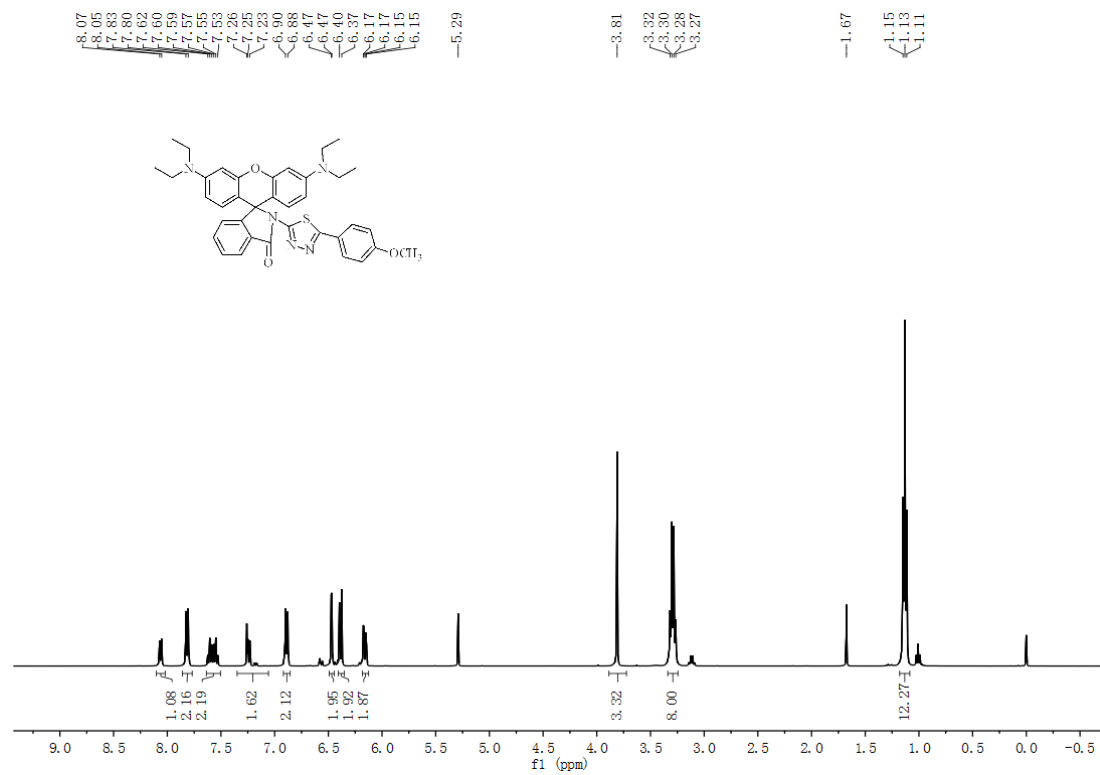


Fig. S12 ¹H NMR spectrum of **3b** in CDCl₃.

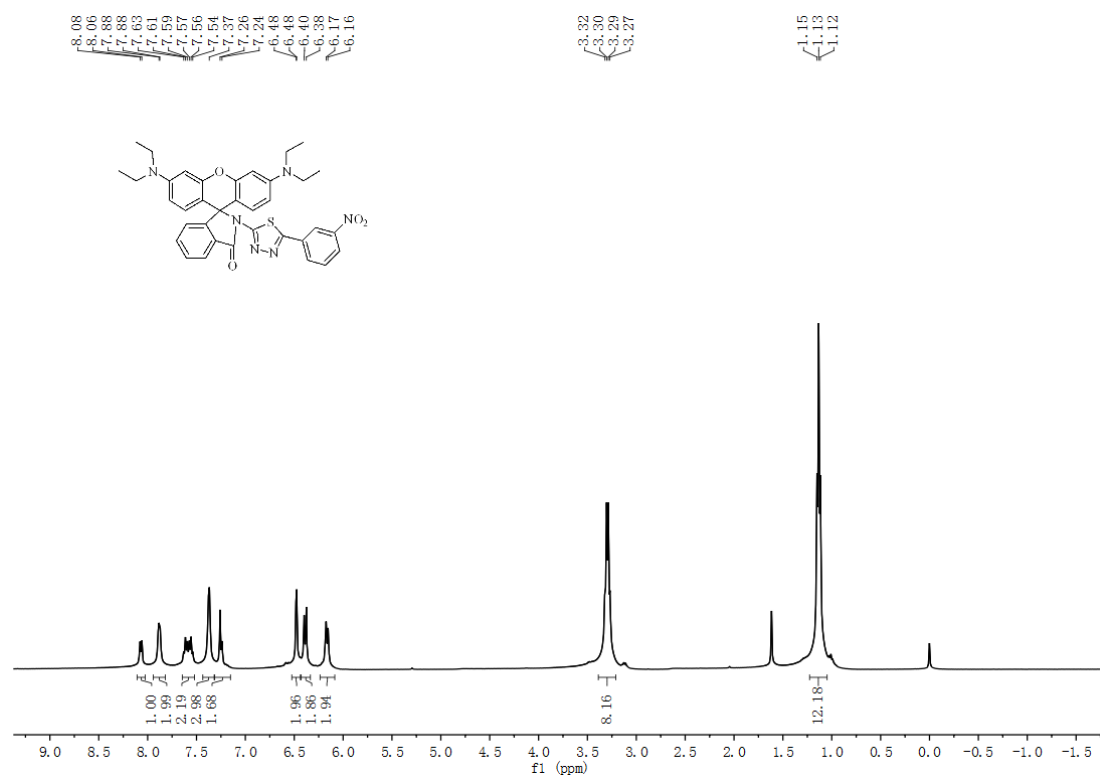


Fig. S13 ¹H NMR spectrum of **3c** in CDCl₃.

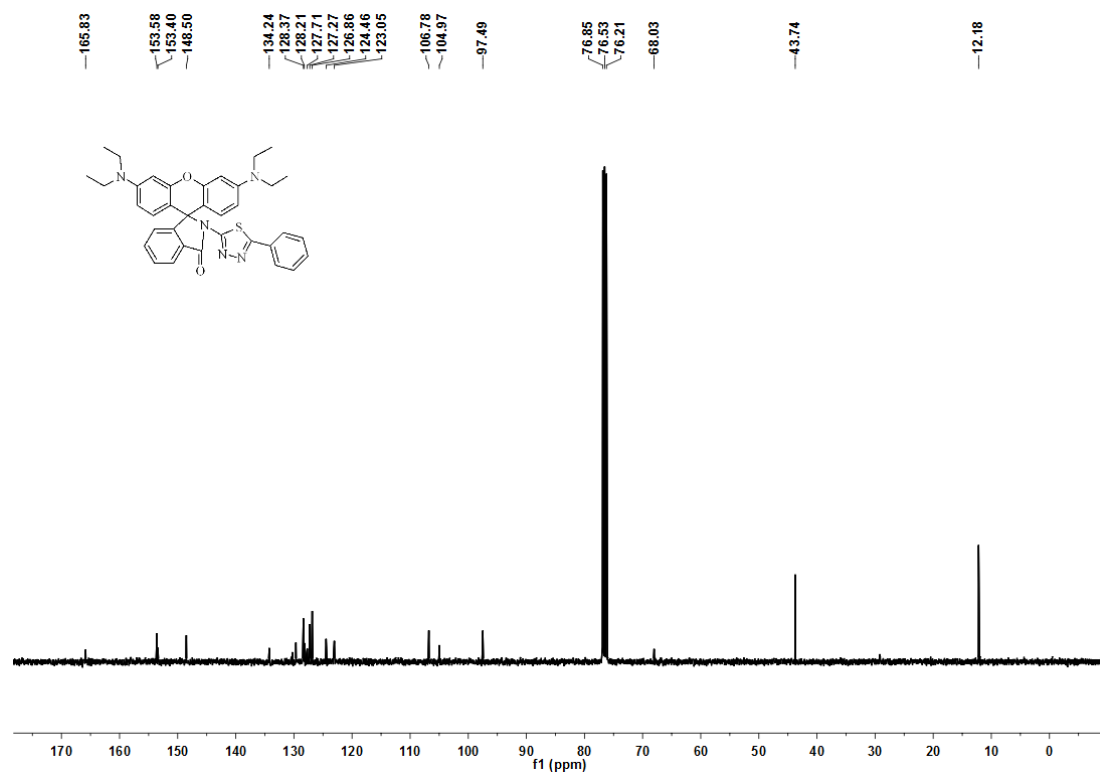


Fig. S14 ^{13}C NMR spectrum of **3a** in CDCl_3 .

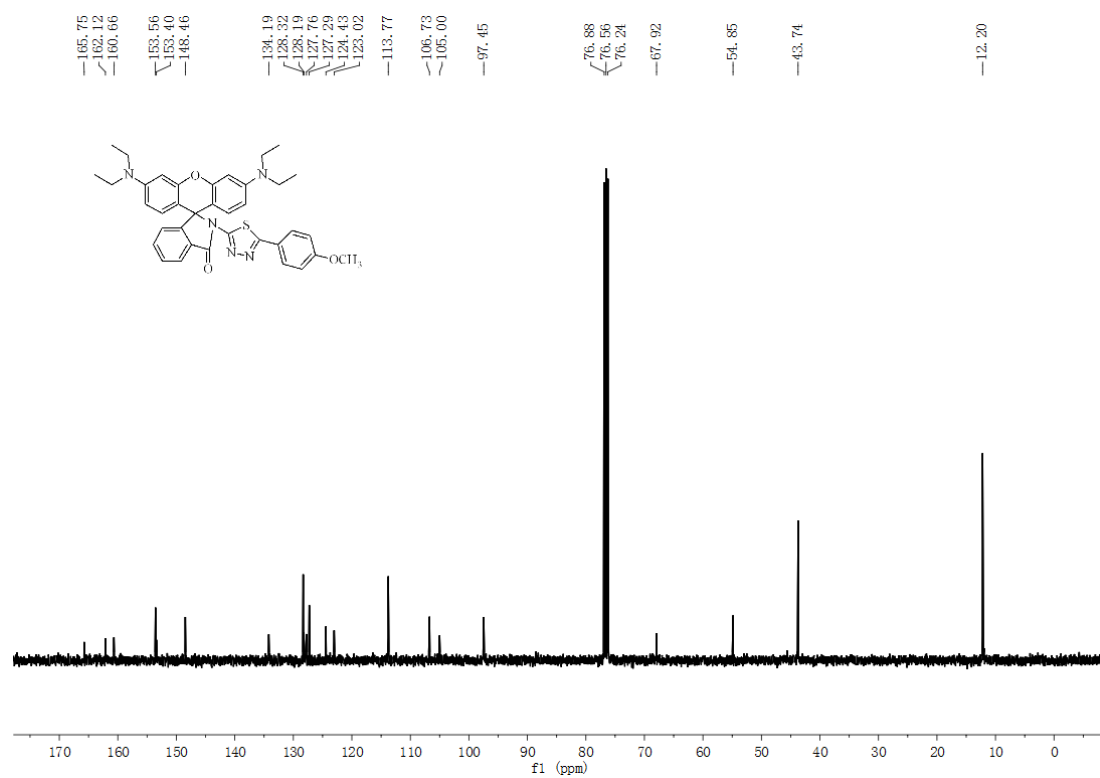


Fig. S15 ¹³C NMR spectrum of **3b** in CDCl₃.

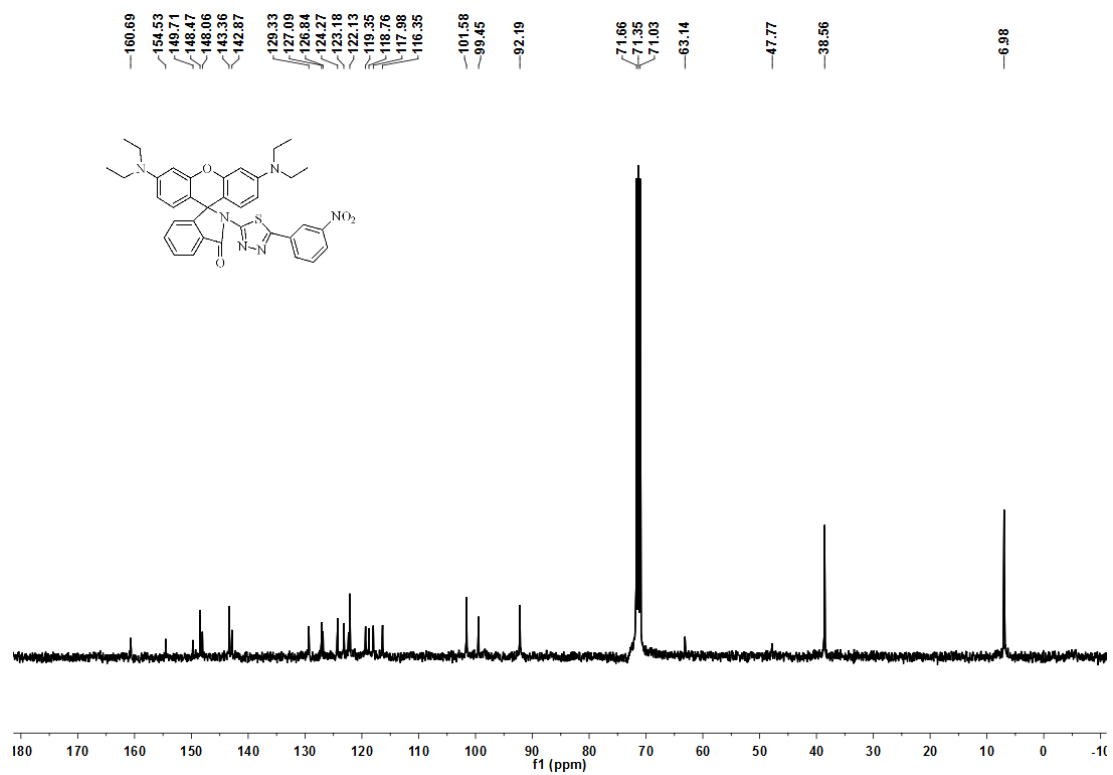


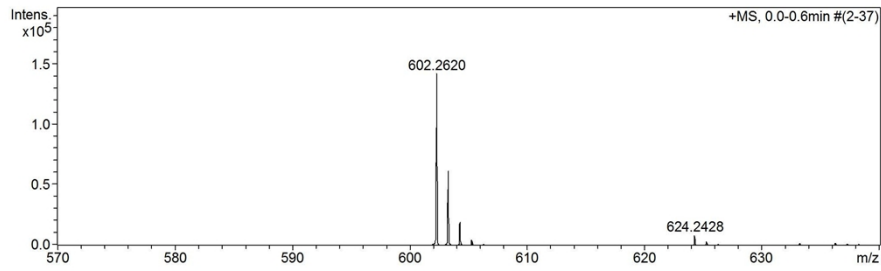
Fig. S16 ¹³C NMR spectrum of **3c** in CDCl₃.

Mass Spectrum SmartFormula Report

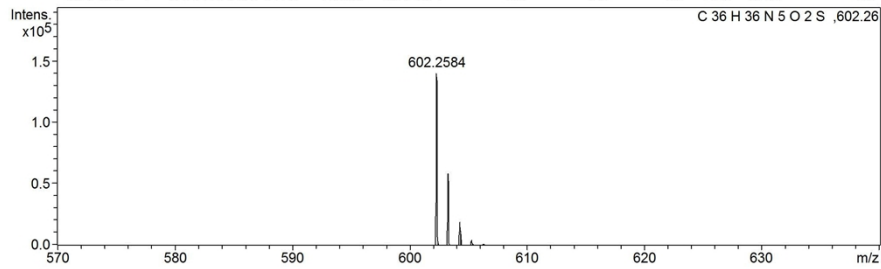
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Method: tune_low 50-500.m
Sample Name:
Comment:
Acquisition Date: 2012/12/18 15:41:14
Operator: NWU
Instrument / Ser#: microTOF-Q II 10280

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	350.0 Vpp	Set Divert Valve	Source



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e ₃ Conf	N-Rule
602.2620	1	C 36 H 36 N 5 O 2 S	100.00	602.2584	-3.6	-5.9	6.7	21.5	even	ok



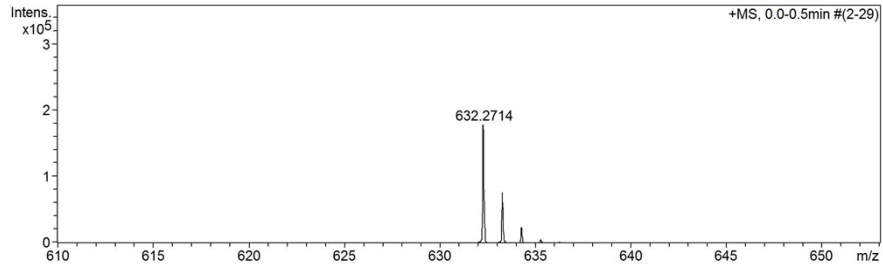
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e ₃ Conf	N-Rule
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Fig. S17 Mass spectrum of **3a**.

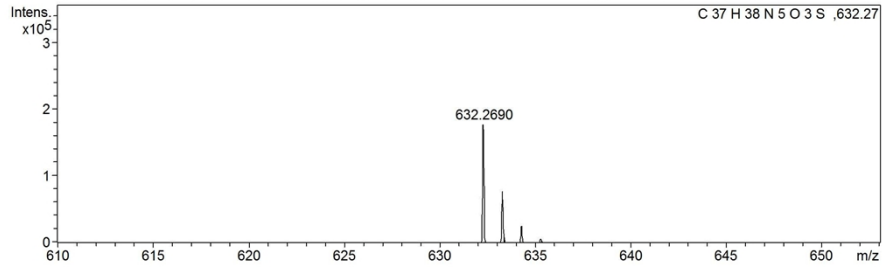
Mass Spectrum SmartFormula Report

Analysis Info
Analysis Name: G:\Ëÿ%4ÿ\ÔËÆ×\2012 1218\Äbμ×Ä+;¶\Ô¼×Ñδ»üBlybq_yangmeipan_2.d
Method: tune_low 50-500.m
Sample Name:
Comment:
Acquisition Date: 2012/12/18 15:43:46
Operator: NWU
Instrument / Ser#: microTOF-Q II 10280

Acquisition Parameter
Source Type: ESI
Focus: Not active
Scan Begin: 50 m/z
Scan End: 3000 m/z
Ion Polarity: Positive
Set Capillary: 4500 V
Set End Plate Offset: -500 V
Set Collision Cell RF: 350.0 Vpp
Set Nebulizer: 0.4 Bar
Set Dry Heater: 180 °C
Set Dry Gas: 4.0 l/min
Set Divert Valve: Source



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	eÿConf	N-Rule
632.2714	1	C 37 H 38 N 5 O 3 S	100.00	632.2690	-2.4	-3.9	6.5	21.5	even	ok



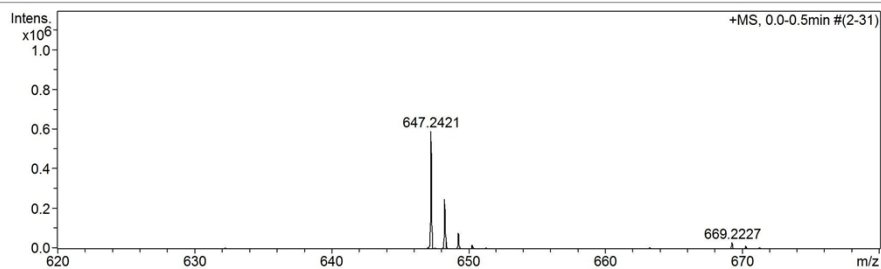
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	eÿConf	N-Rule
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Fig. S18 Mass spectrum of **3b**

Mass Spectrum SmartFormula Report

Analysis Info
Analysis Name C:\Users\Administrator\Desktop\yangmeipan\ÉúÓÐÓÉÆ×Éý¼Ý1218ÁÐµÄ~¼ãlõ»üClybq_yangmeipan_3.d Acquisition Date 2012/12/18 15:48:37
Method tune_low 50-500.m Operator NWU
Sample Name Instrument / Ser# micrOTOF-Q II 10280
Comment

Acquisition Parameter
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Focus Not active Set Capillary 4500 V Set Dry Heater 180 °C
Scan Begin 50 m/z Set End Plate Offset -500 V Set Dry Gas 4.0 l/min
Scan End 3000 m/z Set Collision Cell RF 350.0 Vpp Set Divert Valve Source



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e _i Conf	N-Rule
647.2421	1	C ₃₆ H ₃₅ N ₆ O ₄ S	100.00	647.2435	1.4	2.2	5.3	22.5	even	ok

Intens. x10⁶

C₃₆H₃₅N₆O₄S .647.24

647.2435

m/z

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e _i Conf	N-Rule
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Fig. S19 Mass spectrum of **3c**