Supporting Information for

Development of rhodamine-based fluorescent probes for sensitive detection of Fe^{3+} in water: Spectroscopic and computational investigations†

Zi-ying Wu[1], Zhong-yong Xu[1], Jin-wu Yan[1,2 *], Yafang Li[3], Qiuye Kou[3] and Lei Zhang[1, 2 *]

[1] *School of Biology and Biological Engineering, South China University of Technology, Guangzhou 510006, P. R. China.*

[2] *Guangdong Provincial Engineering and Technology Research Center of Biopharmceuticals, South China University of Technology, Guangzhou 510006, PR China..*

[3] *The Sixth Affiliated Hospital of Sun Yat-Sen University, 26th Yuancun Road II, Guangzhou 510655, P. R. China.*

* Corresponding Authors.

School of Biology and Biological Engineering,

South China University of Technology

Guangzhou 510006, P. R. China.

Tel: +86 20 39380678.

E-mail address: yjw@scut.edu.cn *(J.-W. Yan); lzhangce@scut.edu.cn *(L. Zhang).

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(I) Supporting figures

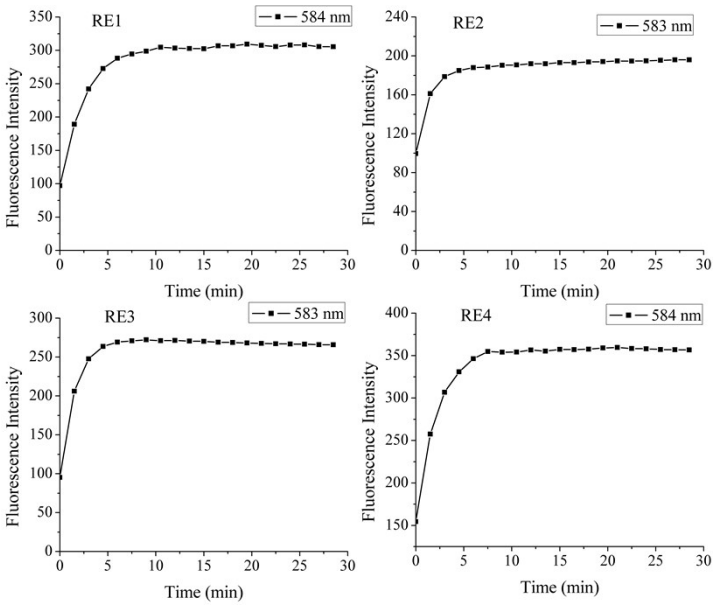


Fig. S1 The fluorescence intensity of probes **RE1-RE4** (10 μM) at the maximum emission with immersion time in Fe^{3+} water solution of 20 μM，λ_{ex} = 530 nm.

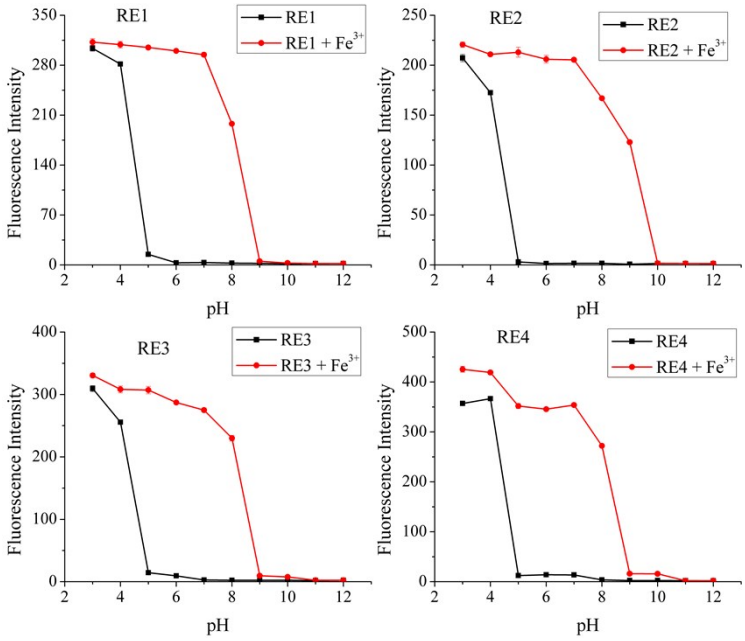


Fig. S2 Effect of pH studies on fluorescence intensity at 581 nm of probes (**RE1- RE4**) and probes-Fe^{3+}.

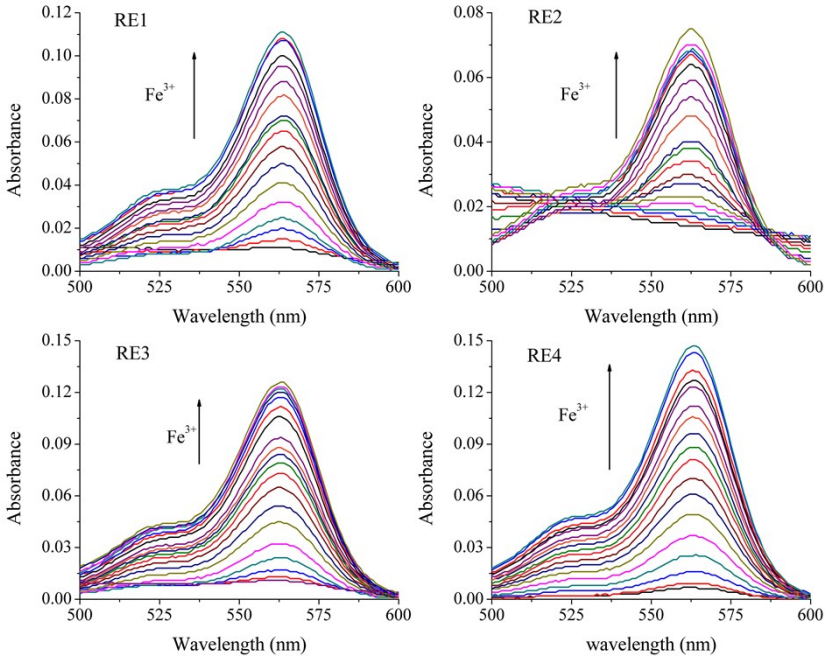


Fig. S3 UV-vis absorbance titration spectra of probes (**RE1-RE4**) with Fe^{3+} in water solution.

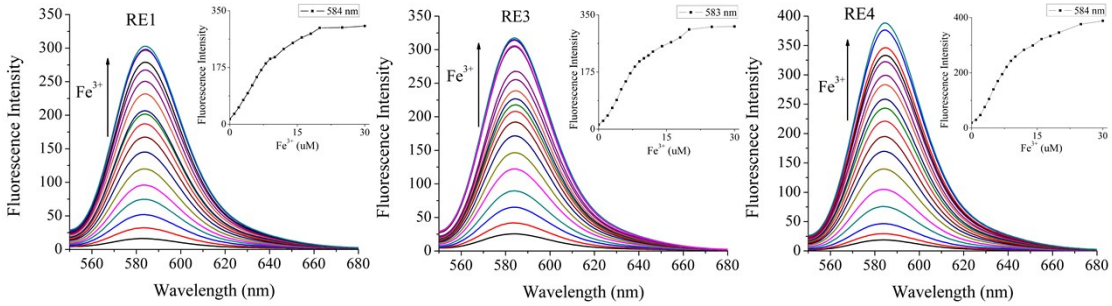


Fig. S4 Fluorescence emission spectra of **RE1**, **RE3** and **RE4** with 0-2 equiv. Fe^{3+} in water solutions. Inset: Emission intensity changes of **RE1**, **RE3** and **RE4** (λ_{ex} = 530 nm).

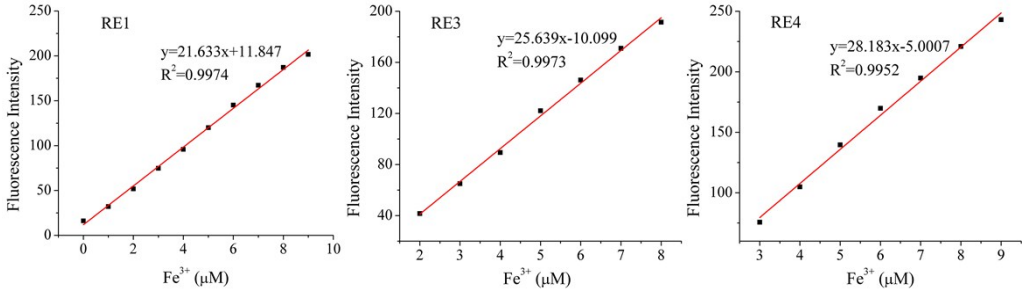


Fig. S5 Detection limits of **RE1**, **RE3** and **RE4** with Fe^{3+}. The fluorescence intensity at maximum emission wavelength of **RE1**, **RE3** and **RE4** (10 μM) with different concentrations of Fe^{3+} in water solutions (λ_{ex} = 530 nm, slit: 10/10 nm).

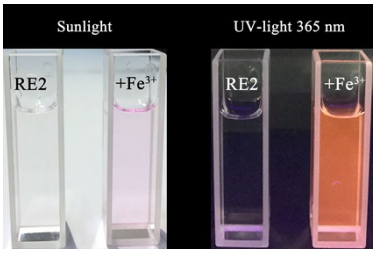


Fig. S6 Digital photograph of **RE2** with Fe^{3+} (2 equiv.) or without Fe^{3+} under sunlight and UV-light (365 nm).

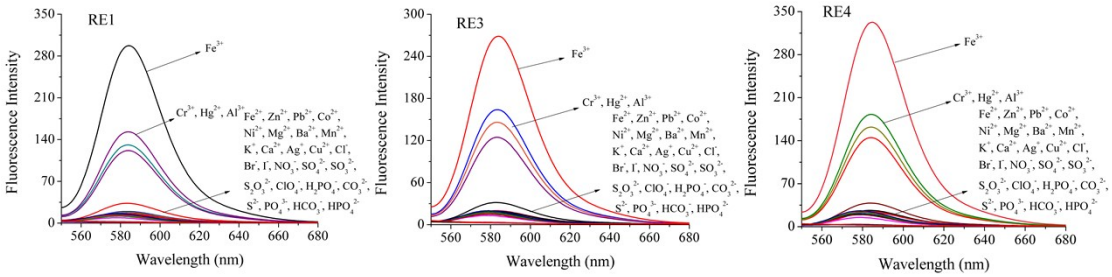


Fig. S7 Fluorescence spectra of **RE1**, **RE3** and **RE4** upon addition of 2 equiv. various ions in water solutions (λ_{ex} = 530 nm).

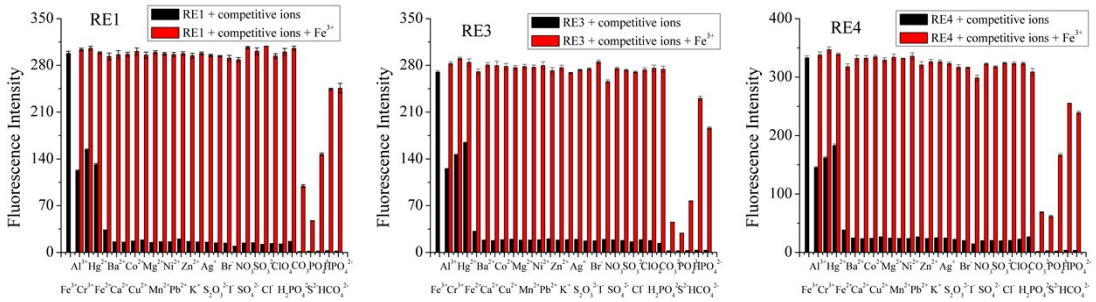


Fig. S8 The competitive selectivity of **RE1**, **RE3** and **RE4** were examined with 2 equiv. Fe^{3+} in the presence of various ions in water solutions (λ_{ex} = 530 nm).

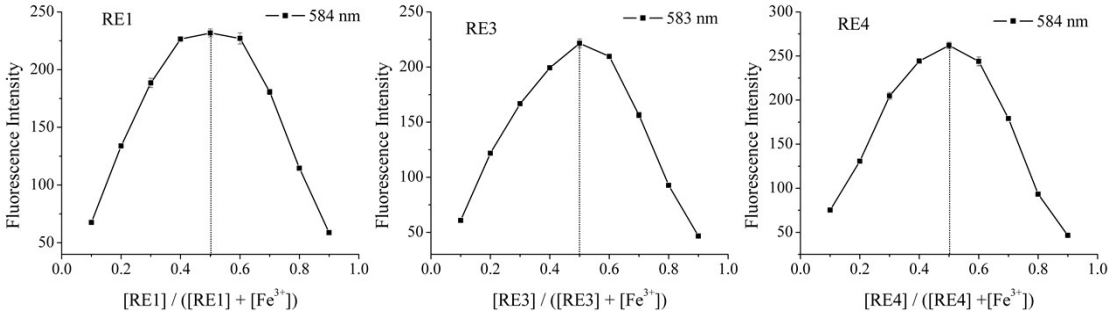


Fig. S9 Job's plots of **RE1**, **RE3** and **RE4** with Fe^{3+} (λ_{ex} = 530 nm). The total concentrations of probes (**RE1**, **RE3** and **RE4**) with Fe^{3+} are 10 μM. The experiments were measured at room temperature in water solutions.

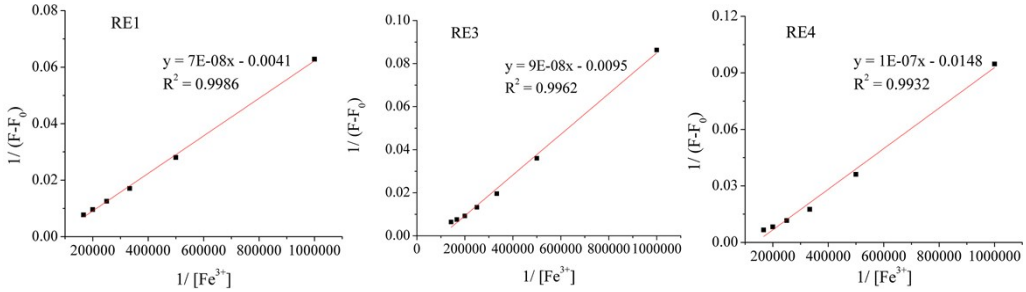


Fig. S10 The binding association constants of **RE1**, **RE3** and **RE4** with Fe^{3+} were based on a Benesi-Hildebrand plot.

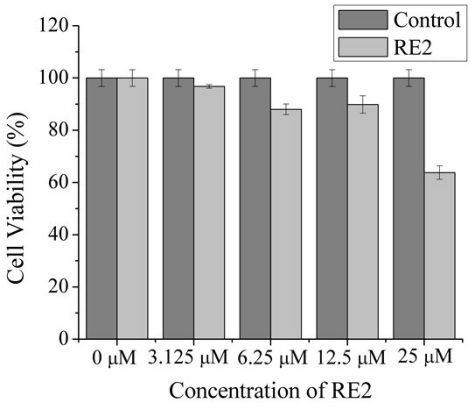


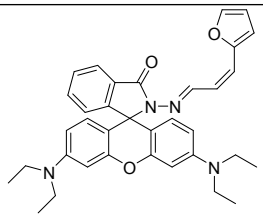
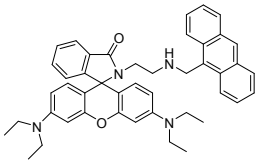
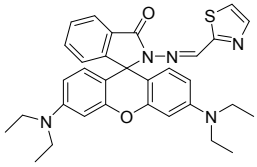
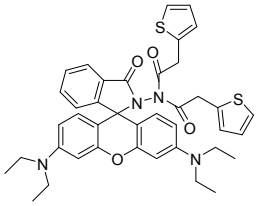
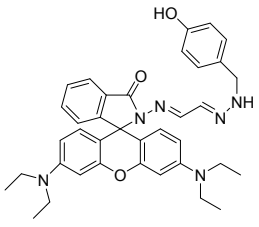
Fig. S11 Cytotoxicity of **RE2** in Hela cells. Cells were treated with different concentrations of **RE2** for 12 h and cell viability assay was determined by MTT assay. Data were expressed as means ± SD.

(II) Supporting tables

Table S1 The fluorescence quantum yields of probes before and after the addition of Fe^{3+}

Probes	Φ_{probe}	Probes + Fe^{3+}	$\Phi_{(Probes + Fe^{3+})}$
RE1	0.06	**RE1** + Fe^{3+}	0.25
RE2	0.02	**RE2** + Fe^{3+}	0.20
RE3	0.06	**RE3** + Fe^{3+}	0.26
RE4	0.08	**RE4** + Fe^{3+}	0.29

Table S2 Comparison of **RE2** with other reported Fe^{3+} fluorescent probes

Name	Structure	Medium	Ka (M^{-1})	LOD (nM)	Ref.
R1		EtOH-H_2O (1:1, v/v)	7.66×10^4	28.1	*Spectrochim. Acta, Part A*, 2018, **191**, 566-572
1		C_2H_5OH-Tris - HCl buffer (1/9, v/v, pH = 7.0)	8.11×10^4	42	*Sens. Actuators, B*, 2017, **247**, 461-468
1		HEPES buffer solution (1.0 mM, pH 7.0).	2.88×10^5	92	*J. Lumin.*, 2018, **196**, 379-386
RTT		C_2H_5OH-H_2O (1/4, v/v)	2.95×10^4	130	*Sens. Actuators, B*, 2017, **252**, 1140-1145
HL		MeOH	1.14×10^4	140	*J. Photoch. Photobio. A*, 2018, **351**, 1-7

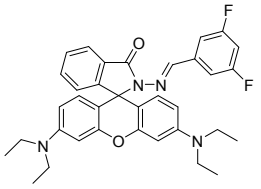
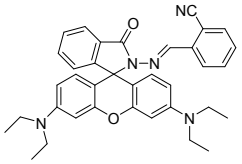
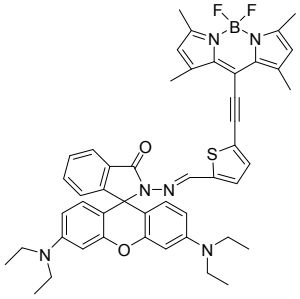
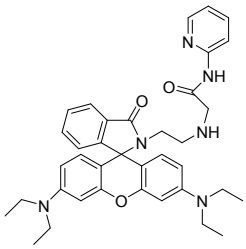
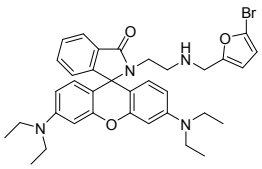
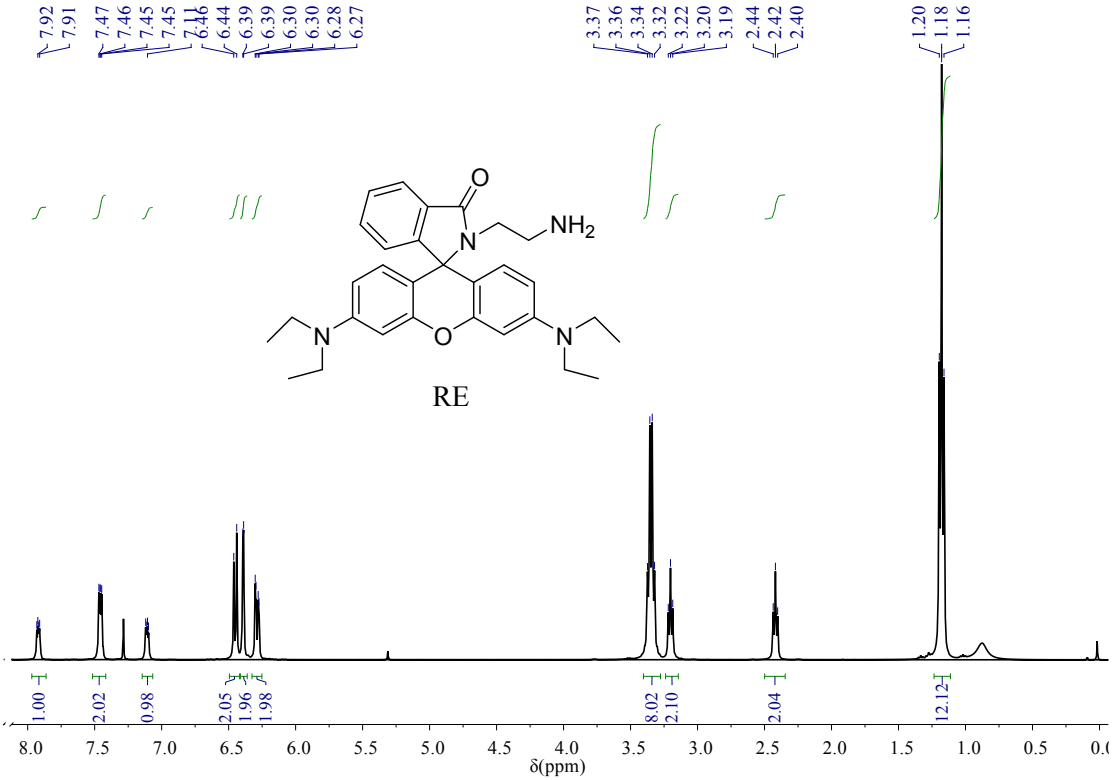
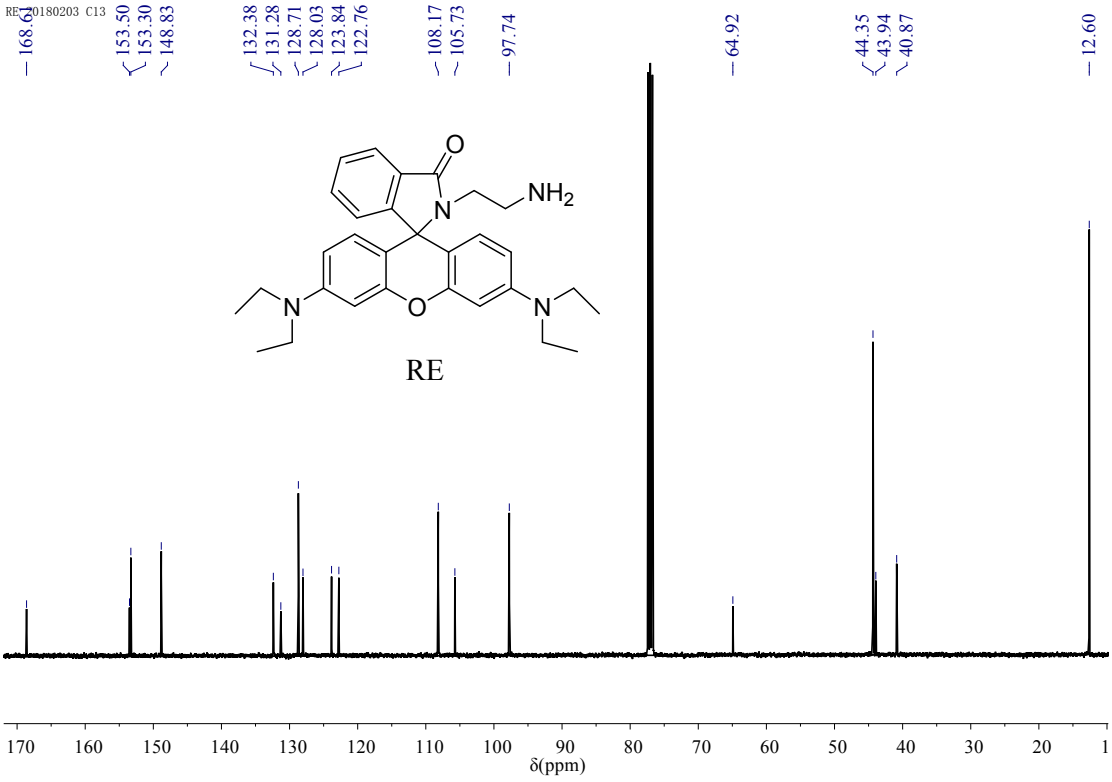
RDFB		CH_3CN-HEPES buffer (8/2, v/v, pH = 7.2)	1.13×10^5	6600	*Sens. Actuators, B*, 2017, **245**, 395-405
RL		DMSO-H_2O (1/1, v/v)	4.67×10^8	280	*Dyes Pigm*, 2017, **142**, 429-436
1		CH_3CN-Tris-HCl (1/1, v/v, 10 mM, pH = 7.4)	2.98×10^4	44.1	*Sens. Actuators, B,* 2016, **237**, 605-612
L		MeOH-H_2O (1/1, v/v)	0.67×10^4	57	*Sens. Actuators, B,* 2016, **237**, 501-508
RE2		H_2O	2.87×10^5 M^{-1}	18.6	Present work

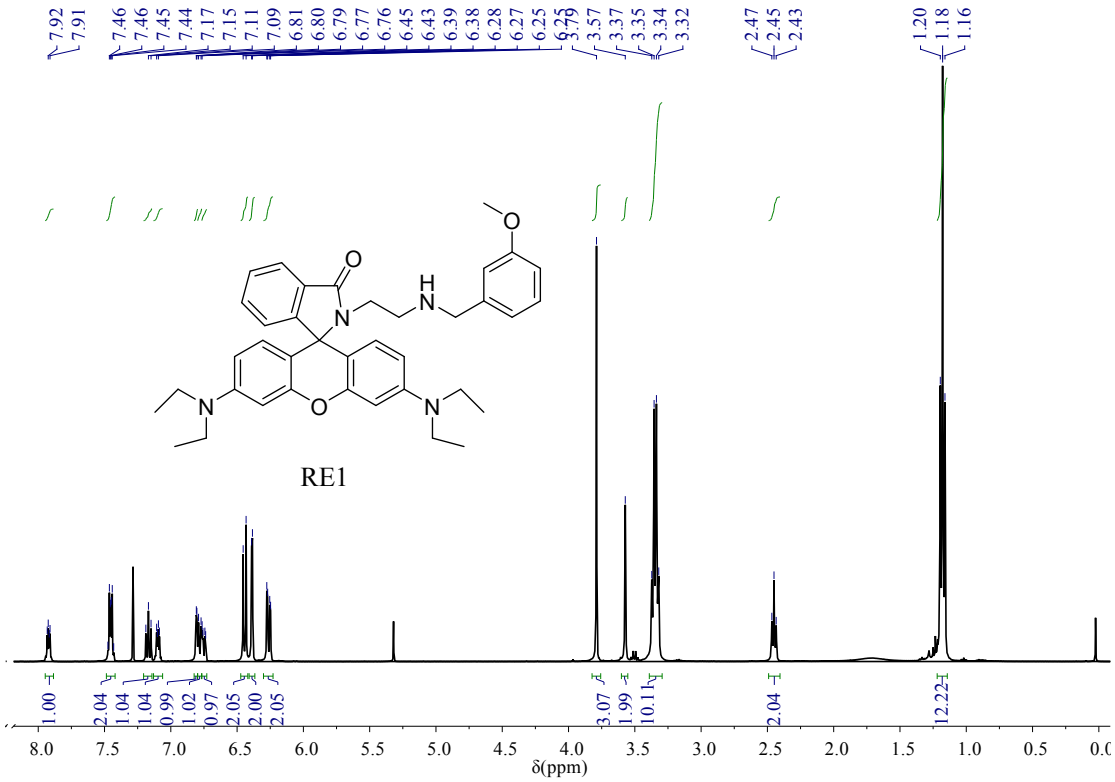
Table S3 Detection of Fe^{3+} by **RE2** in water samples (n=3)

Sample	The concentration of Fe^{3+}		Recovery
	Added (μM)	Found (μM)	
Drinking Water	10.0	9.89 ± 0.01	98.9%
Tap Water	10.0	10.09 ± 0.01	100.9%
River Water	10.0	10.22 ± 0.02	102.2%

(III) Supporting NMR spectra



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7.46
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7.44
7.17
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7.11
7.09
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6.80
6.79
6.77
6.76
6.45
6.43
6.39
6.38
6.28
6.27
6.25
3.57
3.37
3.35
3.34
3.32
2.47
2.45
2.43
1.20
1.18
1.16
O
O
N
H
N
N
O
N
RE1
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2.04
1.04
1.04
0.99
1.02
0.97
2.05
2.00
2.05
3.07
1.99
10.11
2.04
12.22
8.0
7.5
7.0
6.5
6.0
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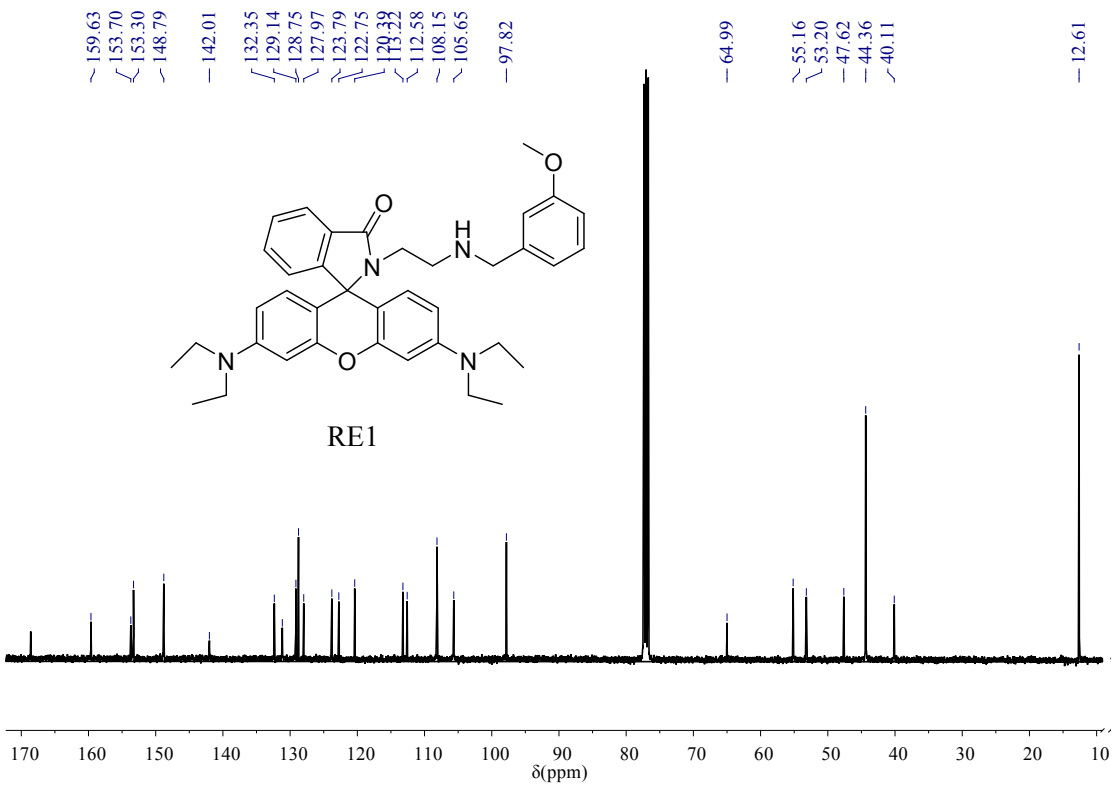
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113.22
112.58
108.15
105.65
97.82
64.99
55.16
53.20
47.62
44.36
40.11
12.61
O
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N
H
N
N
O
N
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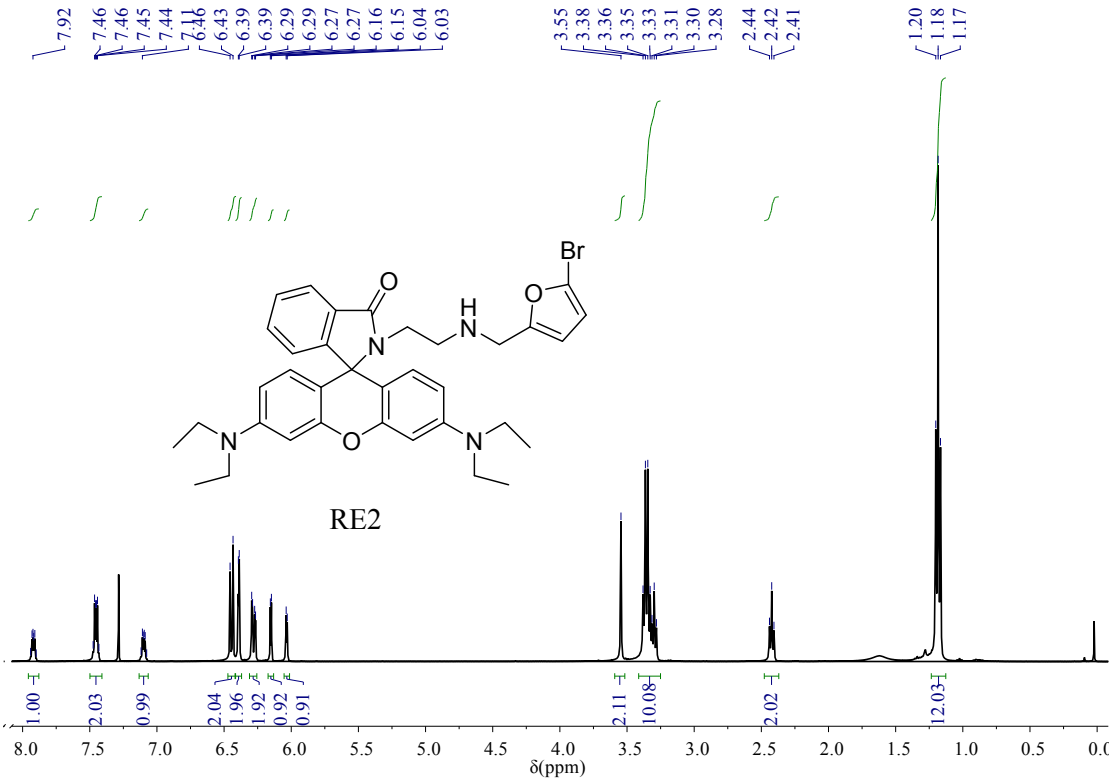
δ(ppm)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6.04
6.03
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2.41
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1.17
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0.92
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10.08
2.02
12.03
8.0
7.5
7.0
6.5
6.0
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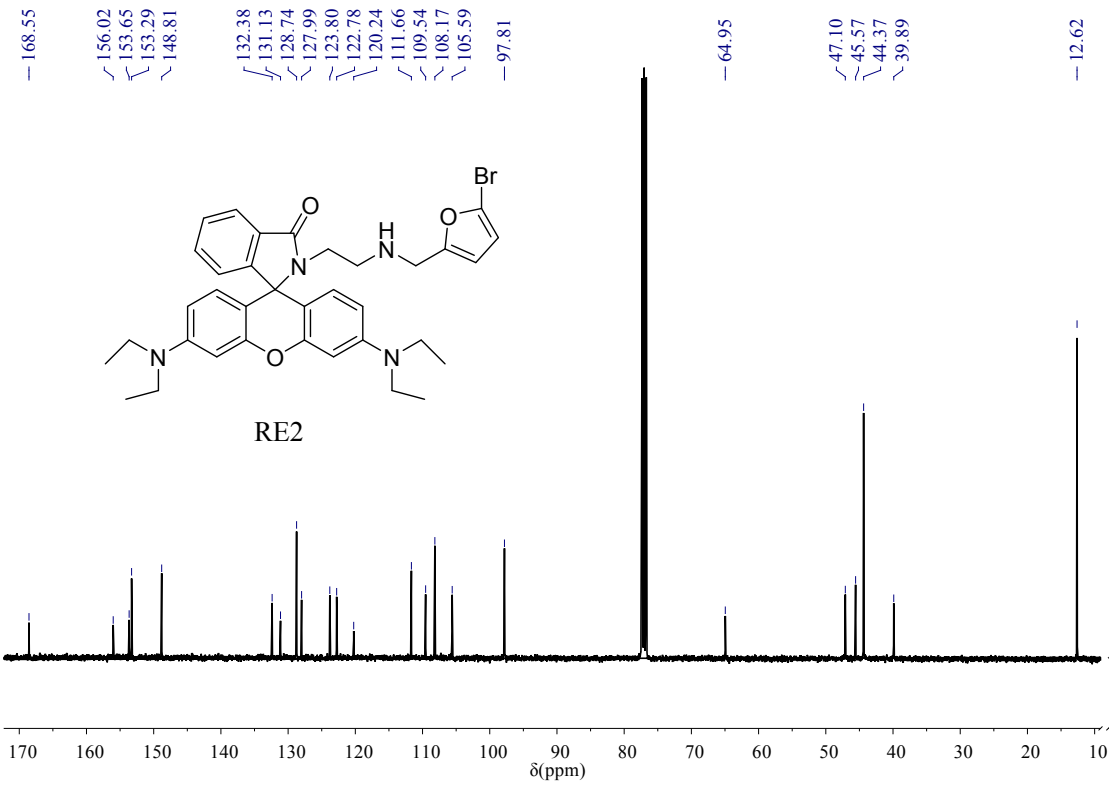
δ(ppm)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97.81
64.95
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39.89
12.62
Br
O
H
N
O
N
O
N
N
RE2
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110
100
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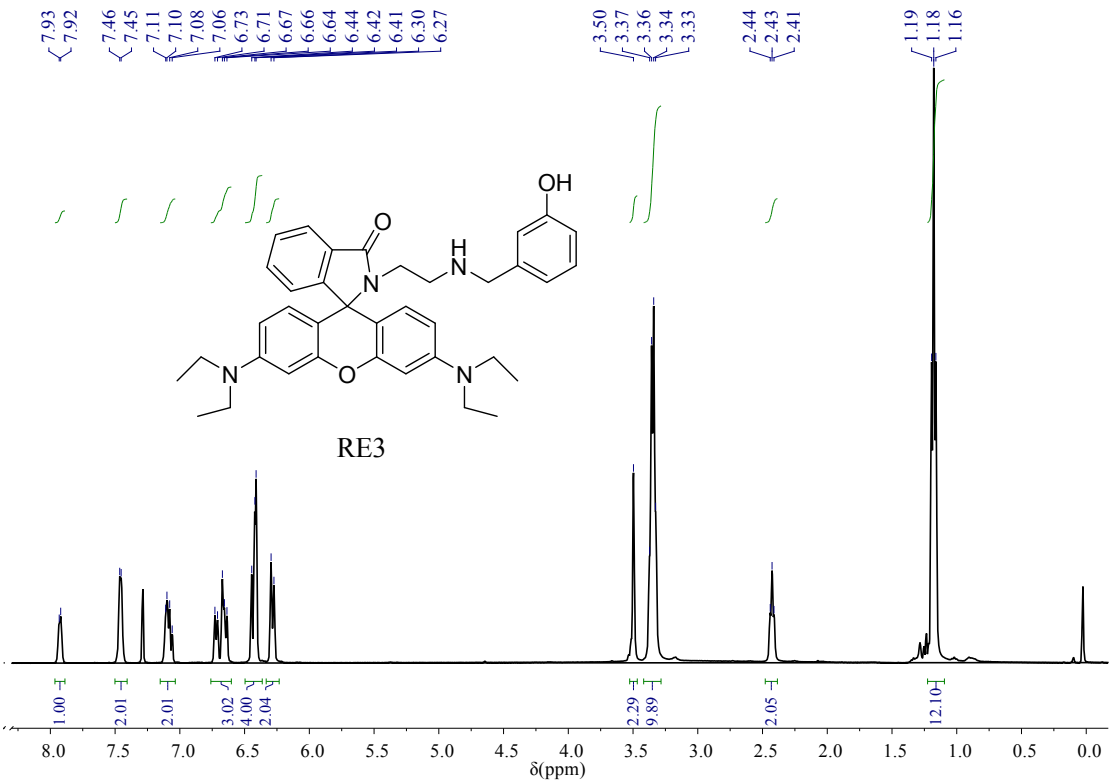
70
60
50
40
30
20
10
δ(ppm)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3.34
3.33
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2.43
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1.16
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H
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N
O
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3.02
4.00
2.04
2.29
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12.10
8.0
7.5
7.0
6.5
6.0
5.5
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3.5
3.0
2.5
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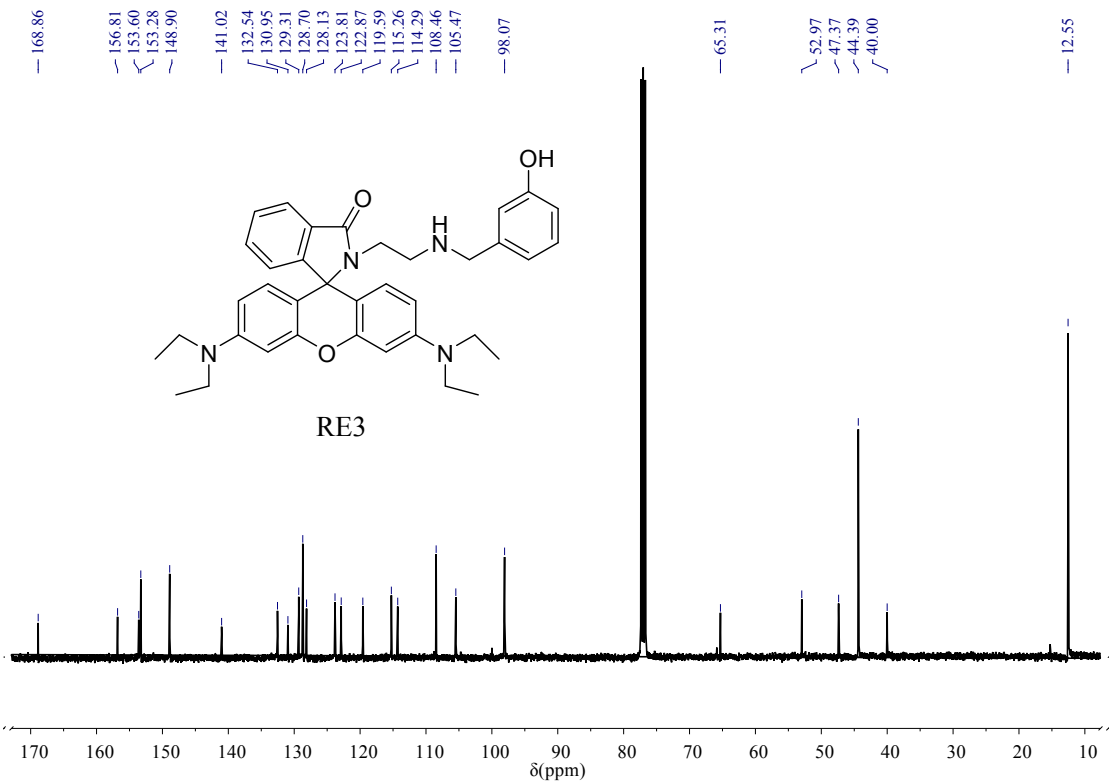
0.0
δ(ppm)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47.37
44.39
40.00
12.55
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H
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N
N
O
N
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130
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80
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60
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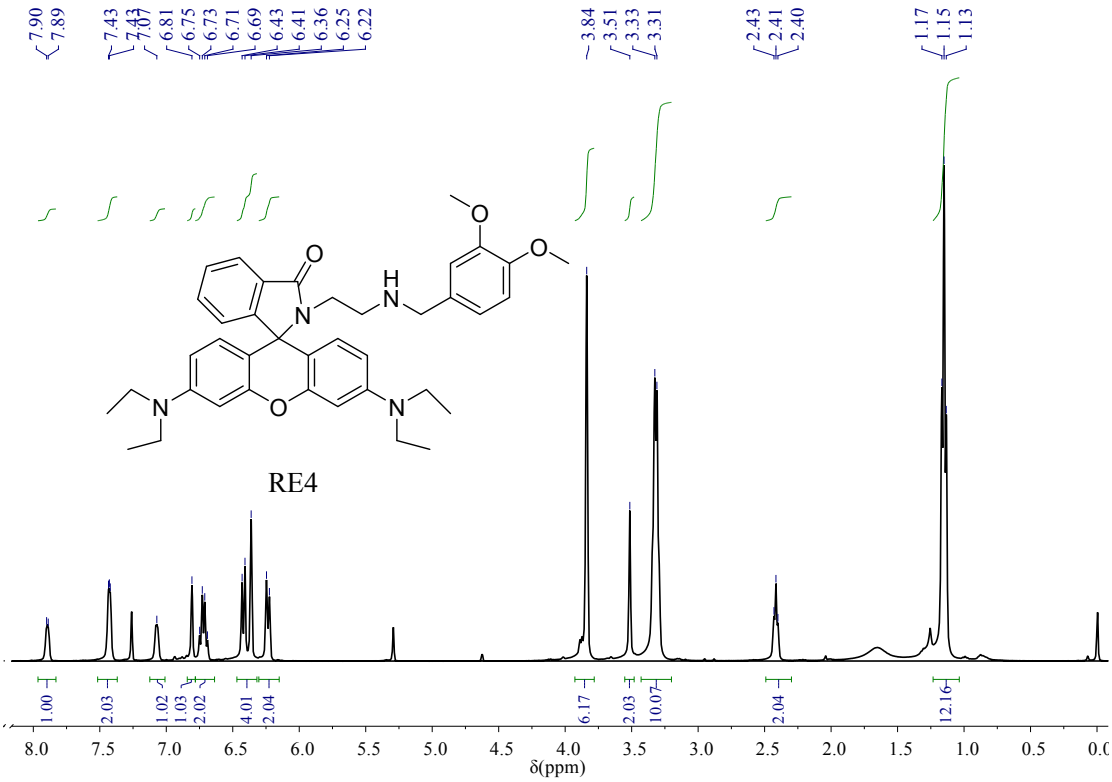
40
30
20
10
δ(ppm)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6.25
6.22
3.84
3.51
3.33
3.31
2.43
2.41
2.40
1.17
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1.13
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O
O
H
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N
O
N
RE4
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2.03
1.02
1.03
2.02
4.01
2.04
6.17
2.03
10.07
2.04
12.16
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7.5
7.0
6.5
6.0
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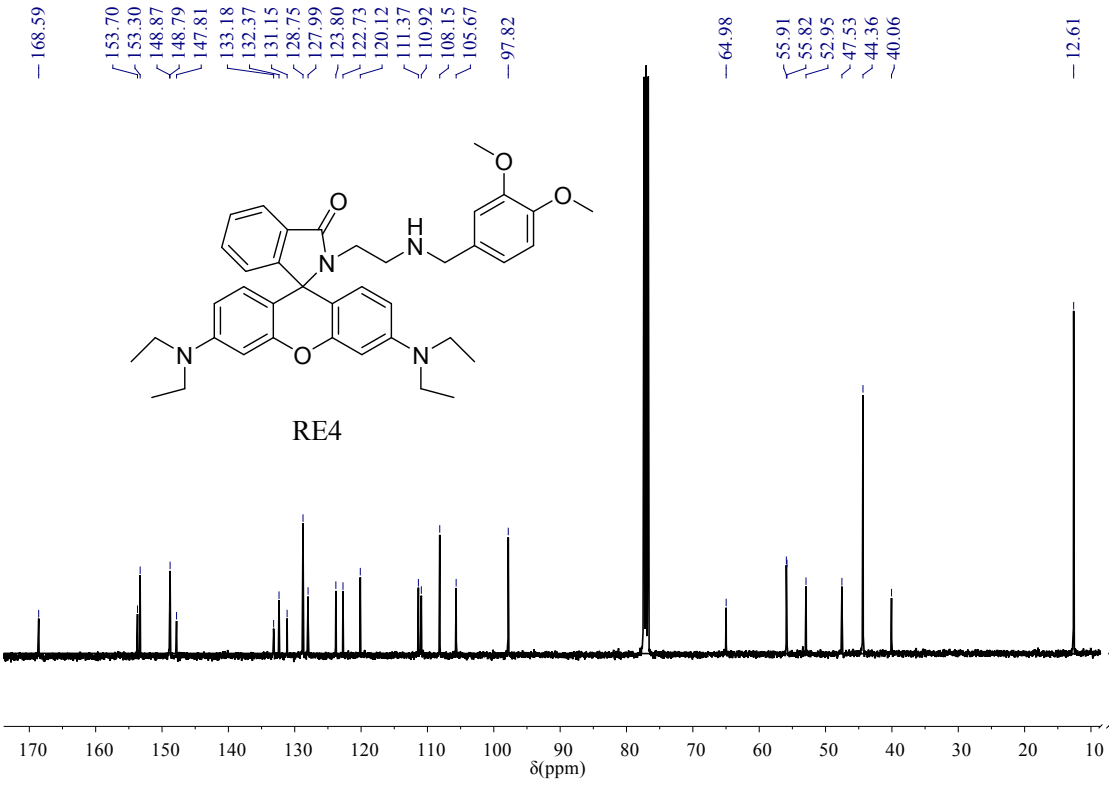
0.5
δ(ppm)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RE4
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40
30
20
10
δ(ppm)