CHEMISTRY
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Supporting Information

N-Heterocyclic Carbene Formation Induced Fluorescent and Colorimetric Sensing of Fluoride Using Perimidinium Derivatives

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chem_201404806_sm_miscellaneous_information.pdf

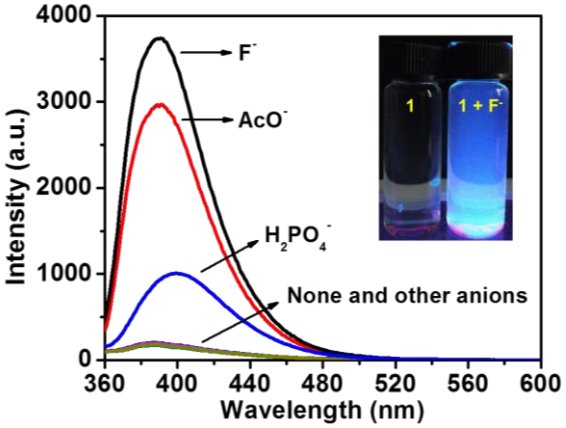


Figure S1 Fluorescence spectra of 5 μM chemodosisensor **1** excited at 353 nm upon addition of 3 equiv. of different anions (TBA salts) in DMSO. Inset: fluorescent color of chemodosisensor **1** (5 μM) in the absence and presence of TBAF under UV lamp excited at 365 nm.

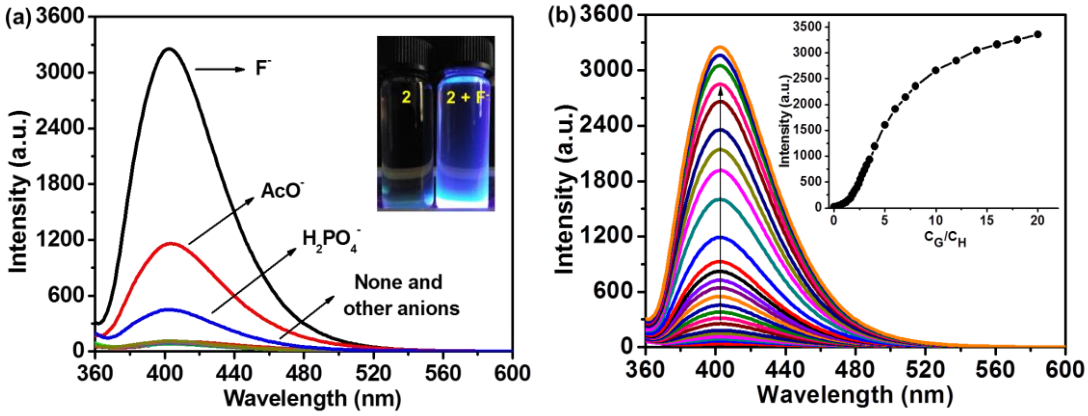


Figure S2 (a) Fluorescence spectra of 5 μM chemodosisensor **2** excited at 357 nm upon addition of 20 equiv. of different anions (TBA salts) in DMSO. Inset: fluorescent color of chemodosisensor **2** (5 μM) in the absence and presence of TBAF under UV lamp excited at 365 nm. (b) Fluorescence titrations of 5 μM chemodosisensor **2** with TBAF in DMSO. Inset: the fluorescence intensity at 402 nm as a function of the added TBAF.

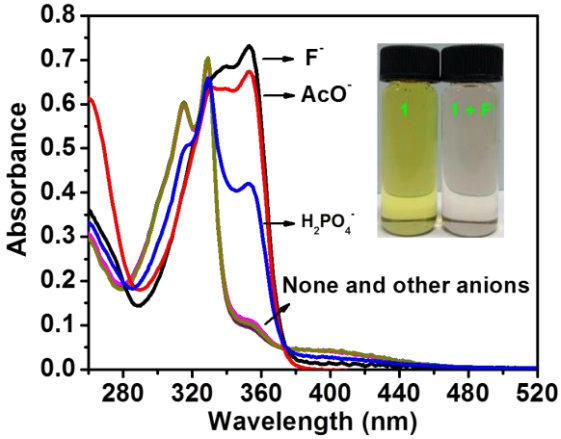


Figure S3 (a) Absorption spectra of 50 μM chemodosisensor **1** upon addition of 3 equiv. of different anions (TBA salts) in DMSO. Inset: solution color of the chemodosisensor **1** in the absence and presence of TBAF.

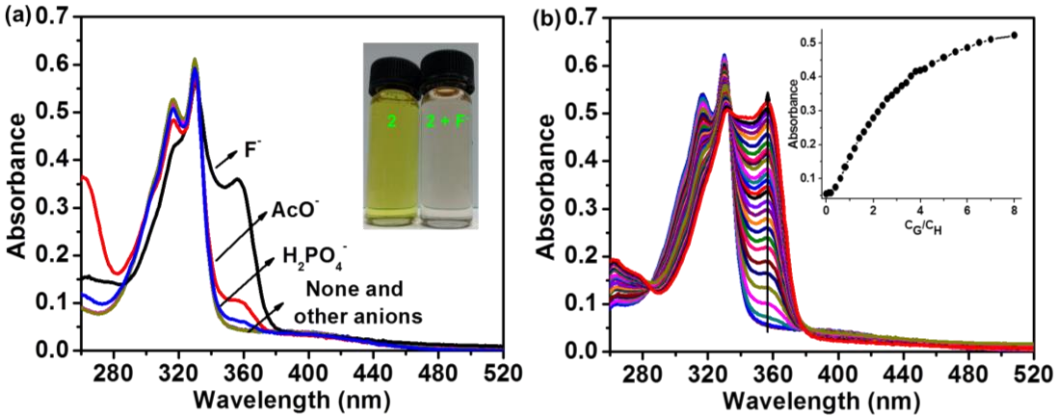


Figure S4 (a) Absorption spectra of 50 μM chemodosisensor **2** upon addition of 3 equiv. of different TBA anions in DMSO. Inset: solution color of the chemodosisensor **2** in the absence and presence of TBAF. (b) Absorption titrations of 50 μM chemodosisensor **2** with TBAF in DMSO. Inset: the absorbance at 357 nm as a function of added TBAF.

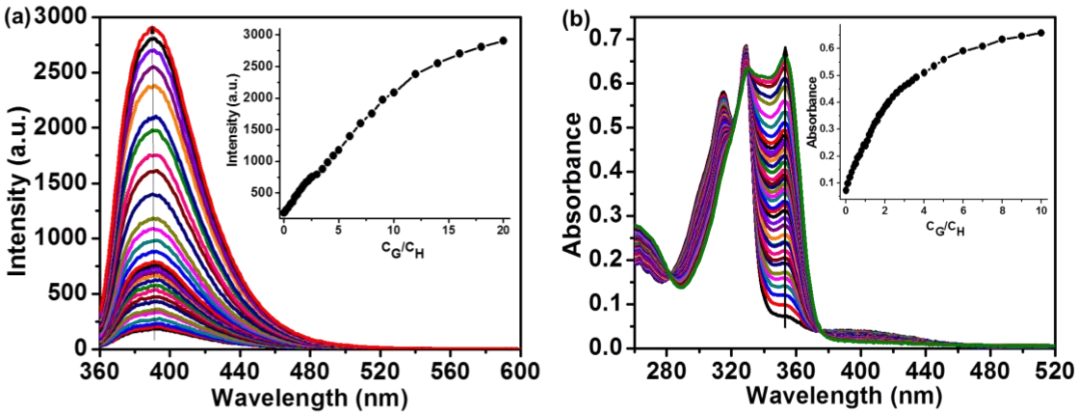


Figure S5 (a) Fluorescence titrations of 5 μM chemodosisensor **1** with TBAF excited at 353 nm in DMSO containing 10% water. Inset: the fluorescence intensity at 400 nm as a function of added TBAF. (b) Absorption titrations of 50 μM **1** with TBAF in DMSO containing 10% water. Inset: the absorbance at 353 nm as a function of added TBAF.

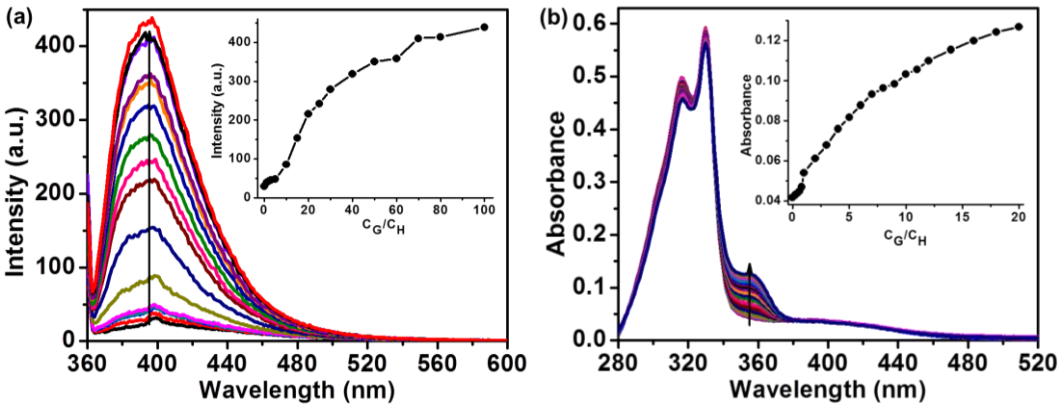


Figure S6 (a) Fluorescence titrations of 5 μM chemodosisensor **2** with TBAF excited at 357 nm in DMSO containing 10% water. Inset: the fluorescence intensity at 402 nm as a function of added TBAF. (b) Absorption titrations of 50 μM **2** with TBAF in DMSO containing 10% water. Inset: the absorbance at 357 nm as a function of added TBAF.

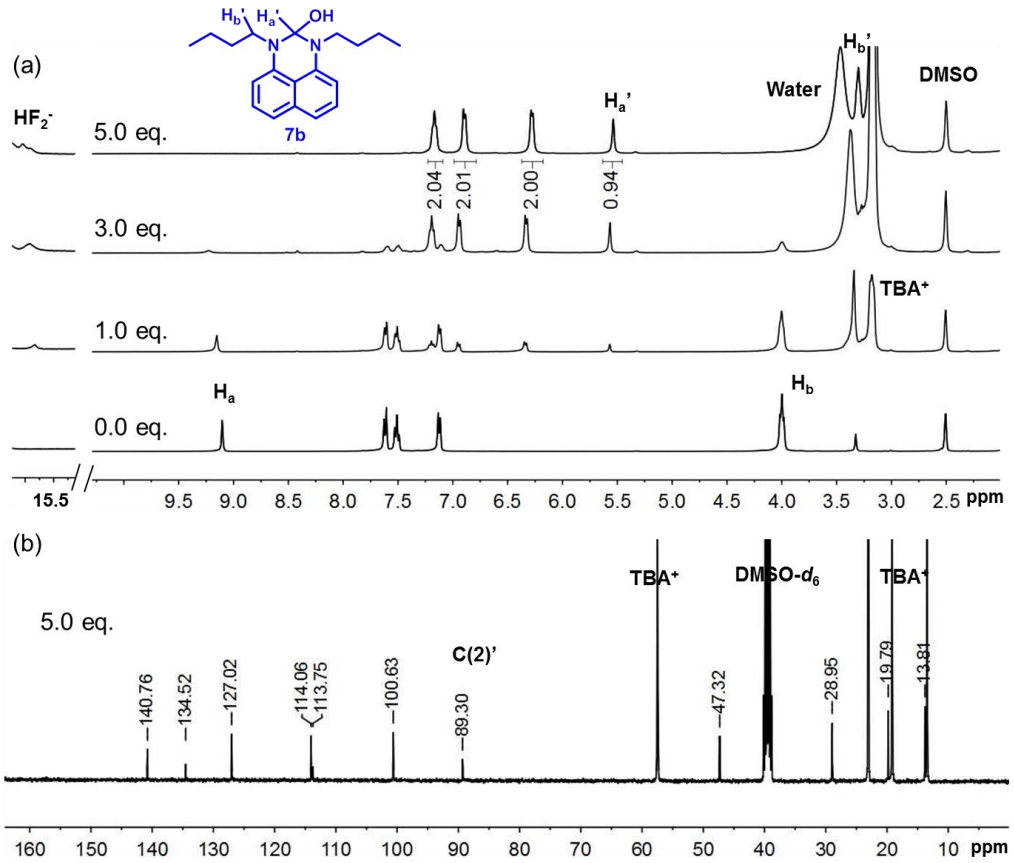


Figure S7 (a) ^{1}H NMR titrations of chemodosisensor **2** (5 mM) with TBAF in DMSO-d_6. (b) ^{13}C NMR spectra of chemodosisensor **2** (5 mM) when in presence of 5.0 equiv. of TBAF in DMSO-d_6.

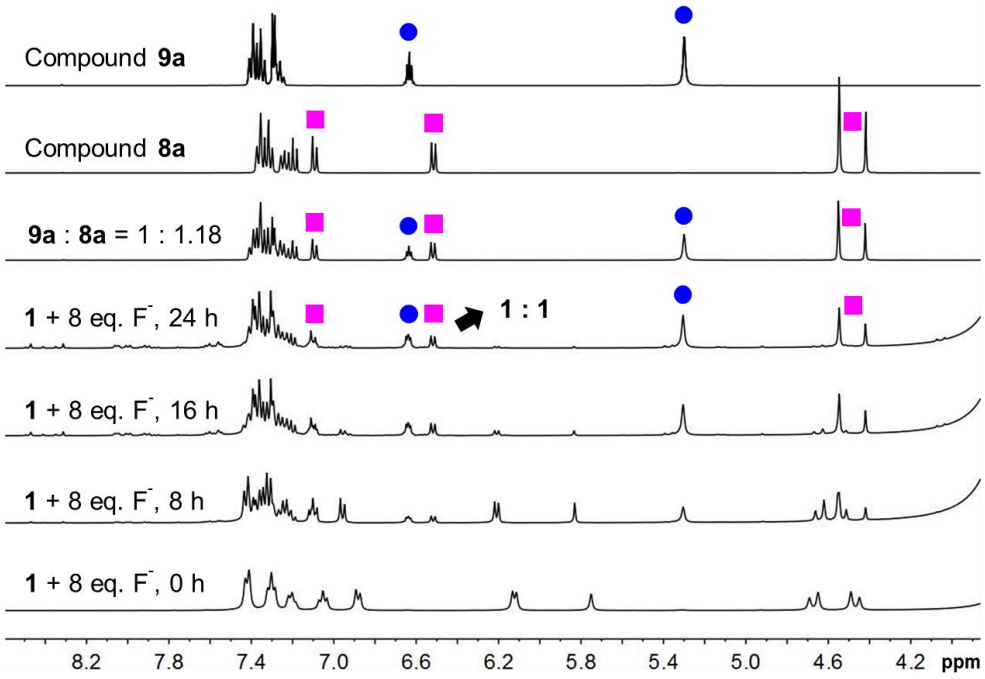
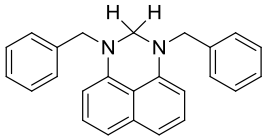


Figure S8 ^{1}H NMR spectra of chemodosisensor **1** unpon addition of 8.0 equiv. of TBAF in DMSO-d_6 after different time, and the spectra of compound **8a**, **9a** and the 1 : 1.18 mixture of **9a** and **8a**.



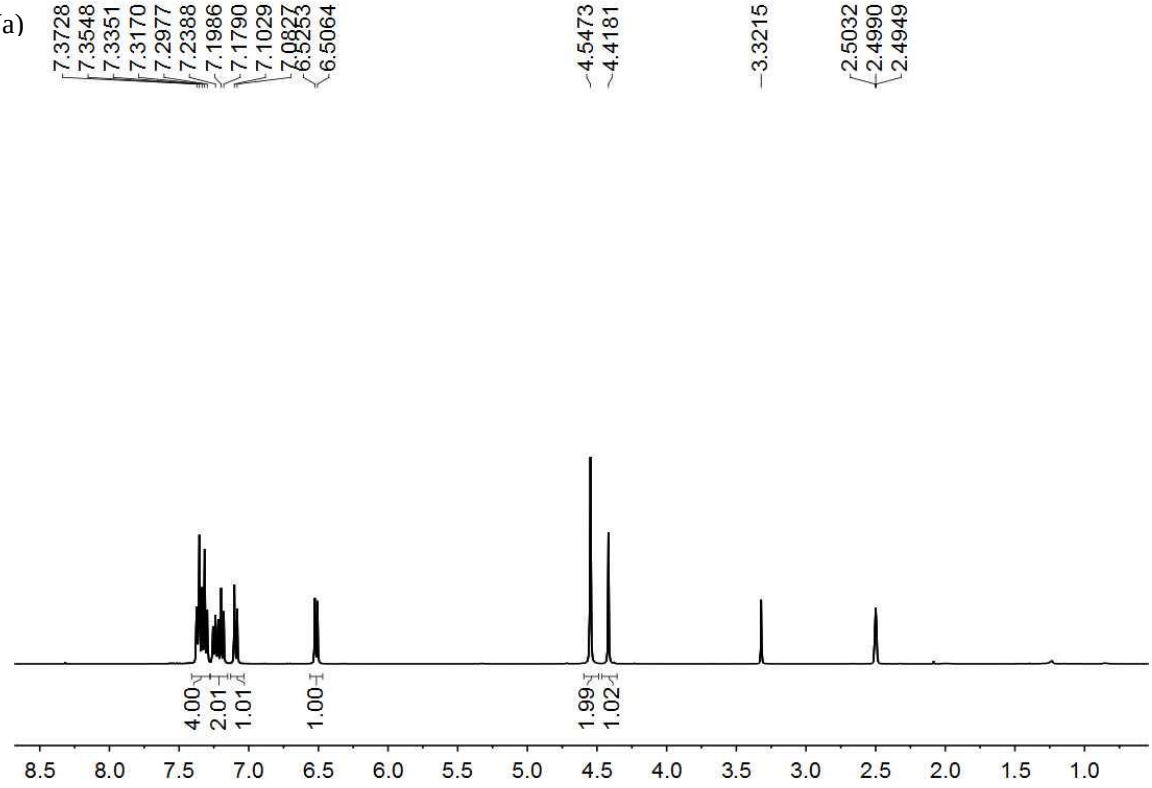
8a

^{1}H NMR (400 MHz, DMSO-d_6) δ 4.42 (s, 2H), 4.55 (s, 4H), 6.51 (d, J = 7.6 Hz, 2H), 7.09 (d, J = 8.1 Hz, 2H), 7.18-7.26 (m, 4H), 7.30-7.37 (m, 8H).

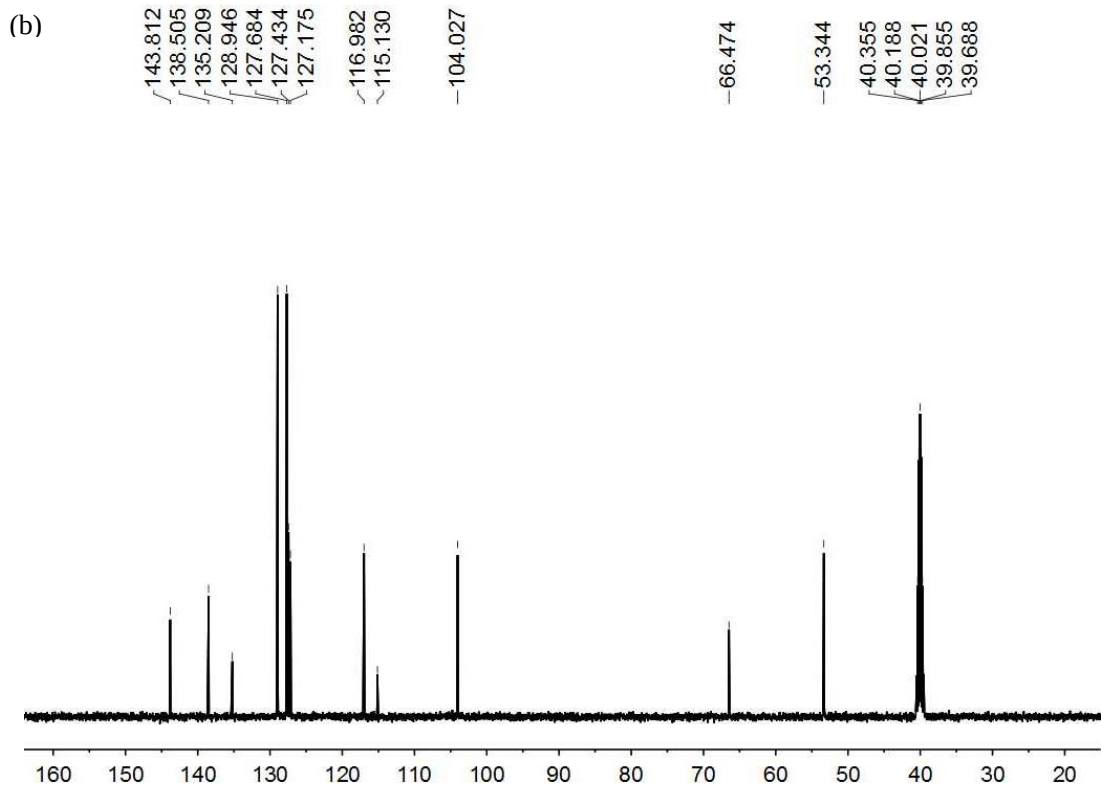
^{13}C NMR (100 MHz, DMSO-d_6) δ 53.34, 66.47, 104.03, 115.13, 116.98, 127.18, 127.43, 127.68, 128.95, 135.21, 138.50, 143.81.

HR MS: $C_{25}H_{22}N_2$, requires 350.1783, found $[C_{25}H_{22}N_2Na]^+$ 373.1686.

(a)



(b)



(c)

Mass Spectrum SmartFormula Report

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Comment			

Acquisition Parameter

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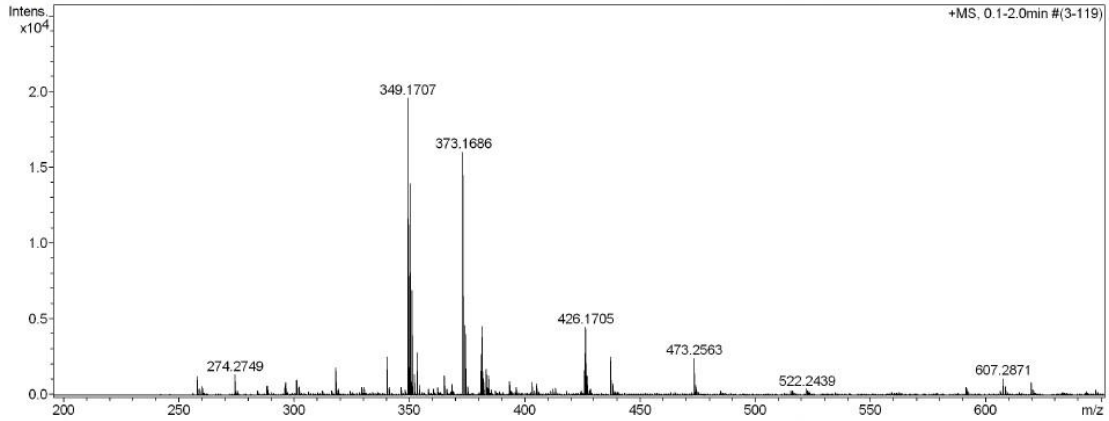

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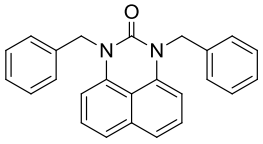
Figure S9 ^{1}H NMR (a), ^{13}C NMR (b) and HR MS (c) spectra of compound **8a**.



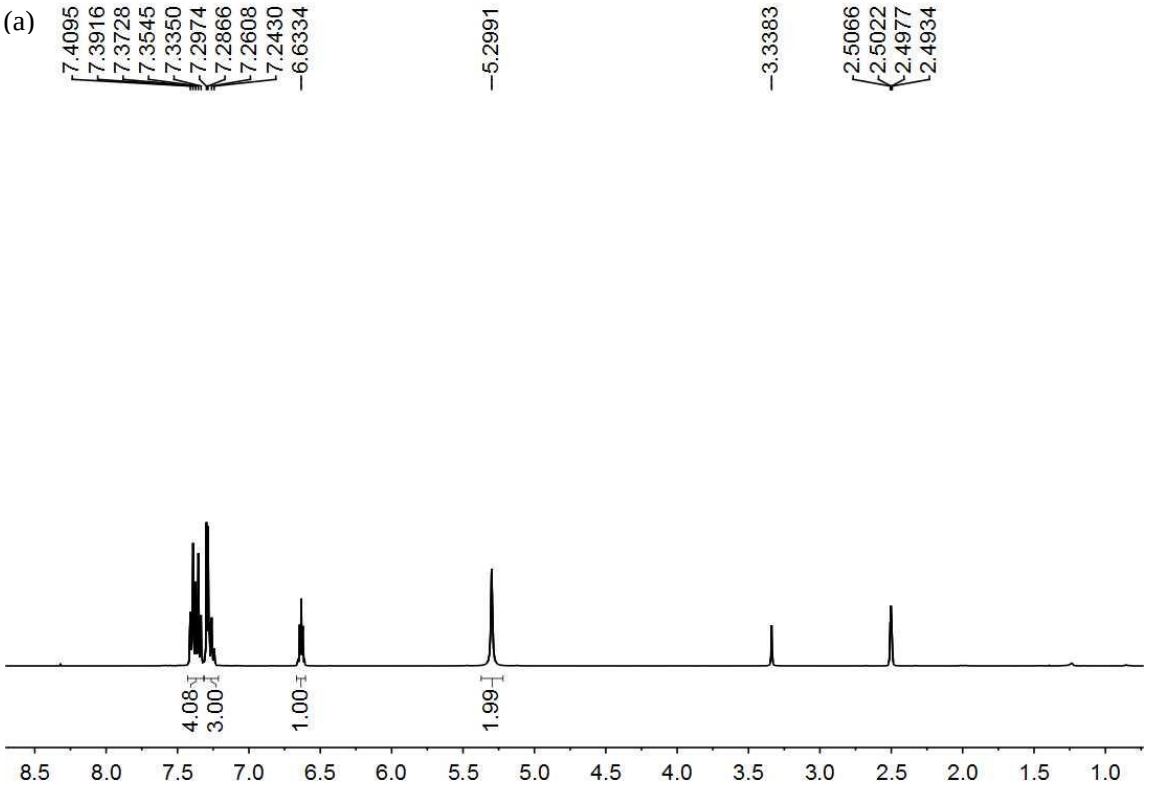
9a

^{1}H NMR (400 MHz, DMSO-d_6) δ 5.30 (s, 4H), 6.61-6.66 (m, 2H), 7.24-7.41 (m, 14H).

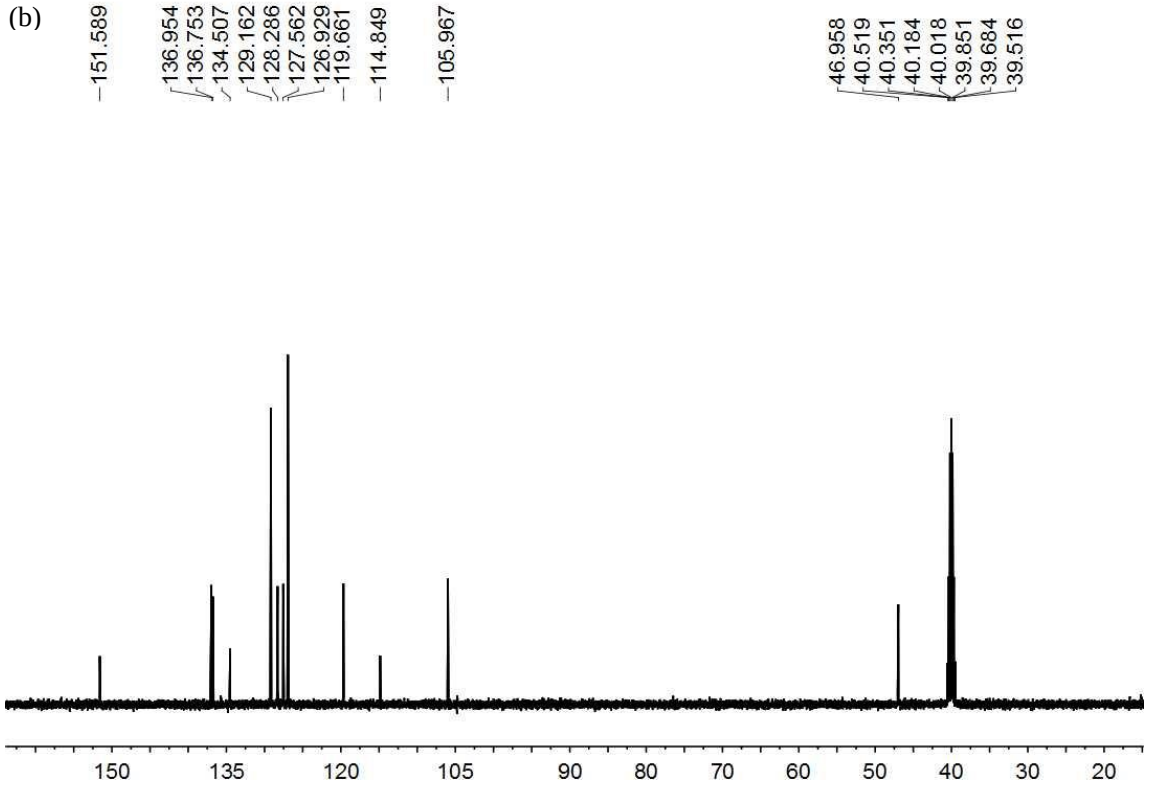
^{13}C NMR (100 MHz, DMSO-d_6) δ 46.96, 105.97, 114.85, 119.66, 126.93, 127.56, 128.28, 129.16, 134.51, 136.75, 136.95, 151.59.

HR MS: $C_{25}H_{20}N_2O$, requires 364.1576, found $[C_{25}H_{20}N_2ONa]^+$ 387.1495.

(a)



(b)



(c)

Mass Spectrum SmartFormula Report

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Comment			

Acquisition Parameter

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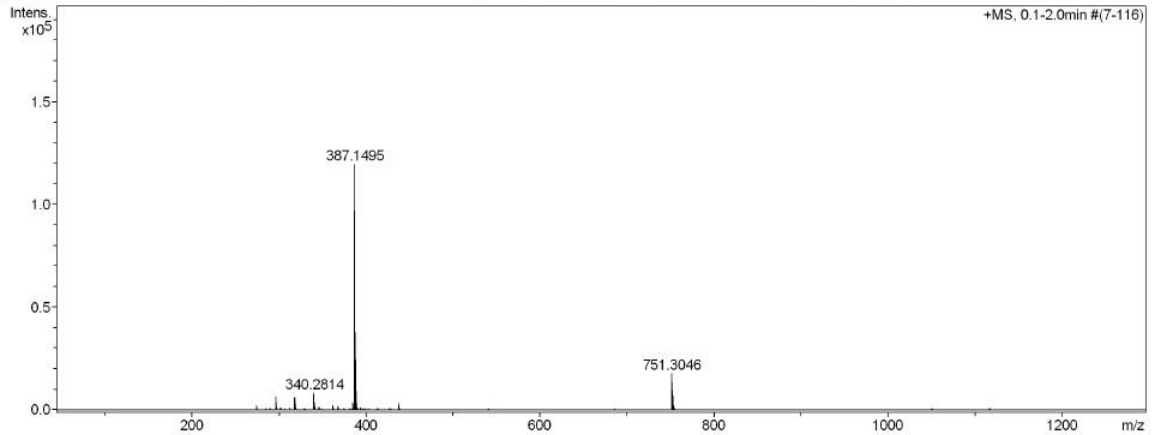

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Figure S10 ^{1}H NMR (a), ^{13}C NMR (b) and HR MS (c) spectra of compound **9a**.

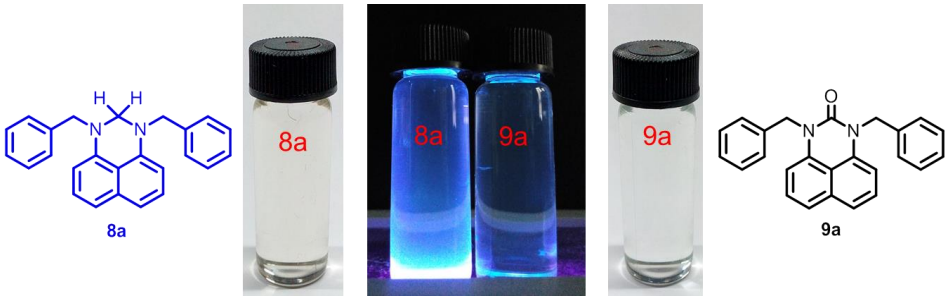
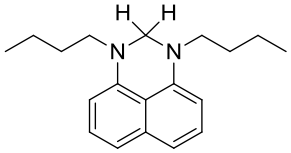


Figure S11 Solution colors and fluorescent colors of compounds **8a** and **9a** (5 μM).

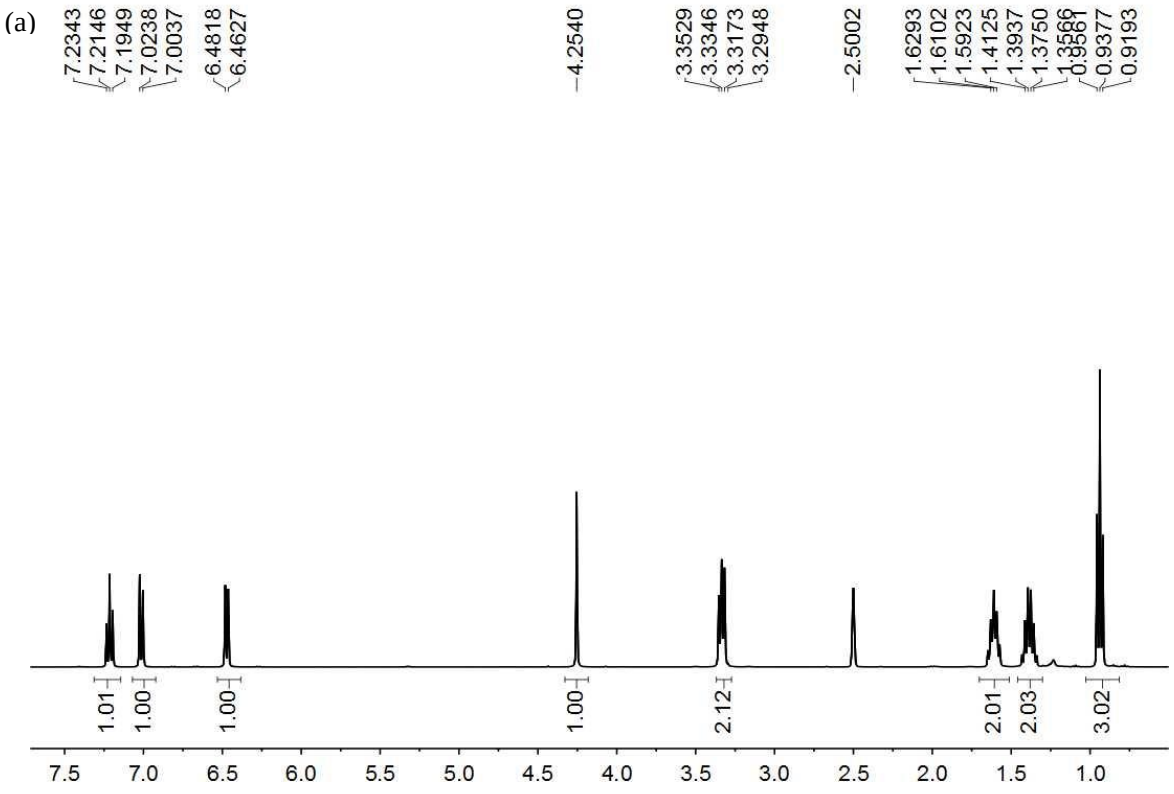


8b

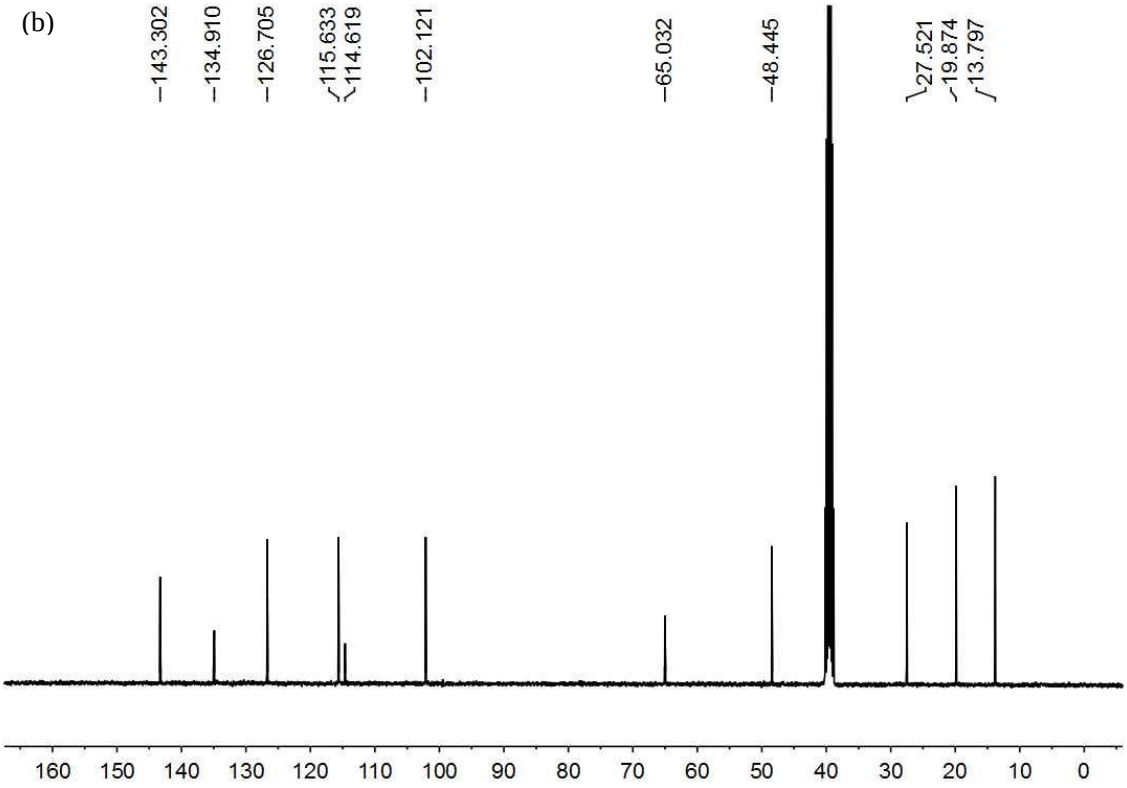
^{1}H NMR (400 MHz, DMSO-d_6) δ 0.94 (t, J = 7.4 Hz, 6H), 1.35-1.41 (m, 4H), 1.57-1.63 (m, 4H), 3.33 (t, J = 7.4 Hz, 4H), 4.25 (s, 2H), 6.47 (d, J = 7.6 Hz, 2H), 7.01 (d, J = 8.0 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 13.80, 19.87, 27.52, 48.45, 65.03, 102.12, 114.62, 115.63, 126.71, 134.91, 143.30.

HR MS: $C_{19}H_{26}N_2$, requires 282.2096, found $[C_{19}H_{27}N_2]^+$ 283.2179.



(b)



(c)

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Sample Name	YHQ-5201	Instrument / Ser#	micrOTOF 10293
Comment			

Acquisition Parameter

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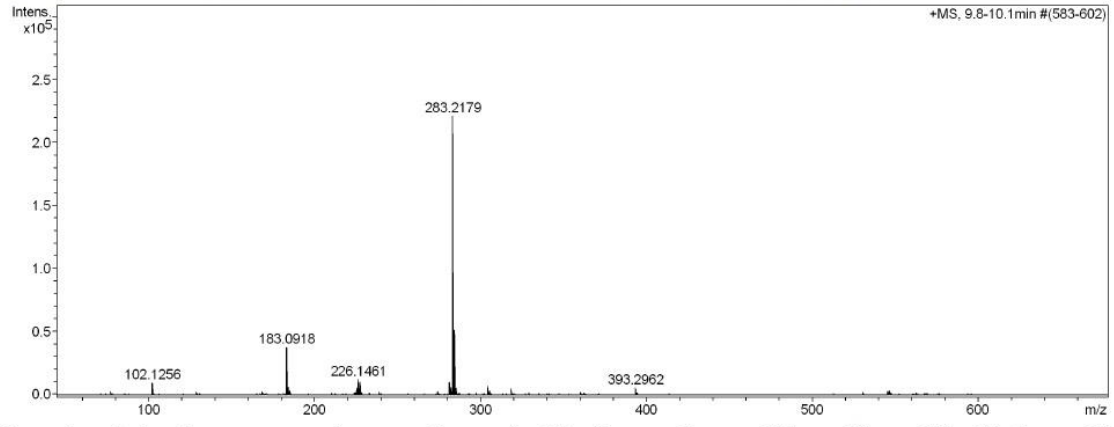
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



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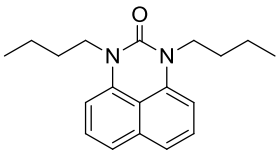
	1	C 19 H 27 N 2	283.2169	-3.8	-2.5	7.5	ok	even	10.23	0.0172	0.0010	0.0068	0.0018	0.4781

Figure S12 ^{1}H NMR (a), ^{13}C NMR (b) and HR MS spectra of compound **8b**.



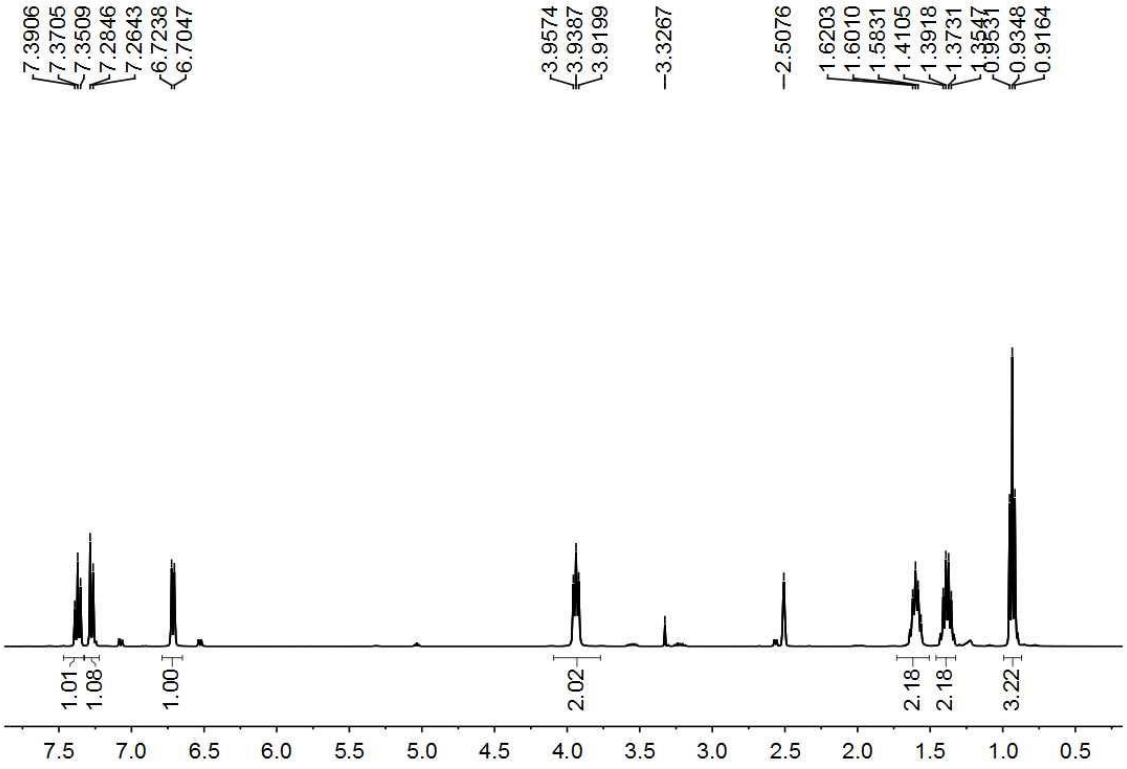
9b

^{1}H NMR (400 MHz, DMSO-d_6): δ 0.90-0.95 (m, 6H), 1.35-1.41 (m, 4H), 1.56-1.64 (m, 4H), 3.94 (t, J = 7.4 Hz, 4H), 6.72 (d, J = 7.6 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 7.37 (t, J = 8.0 Hz, 2H).

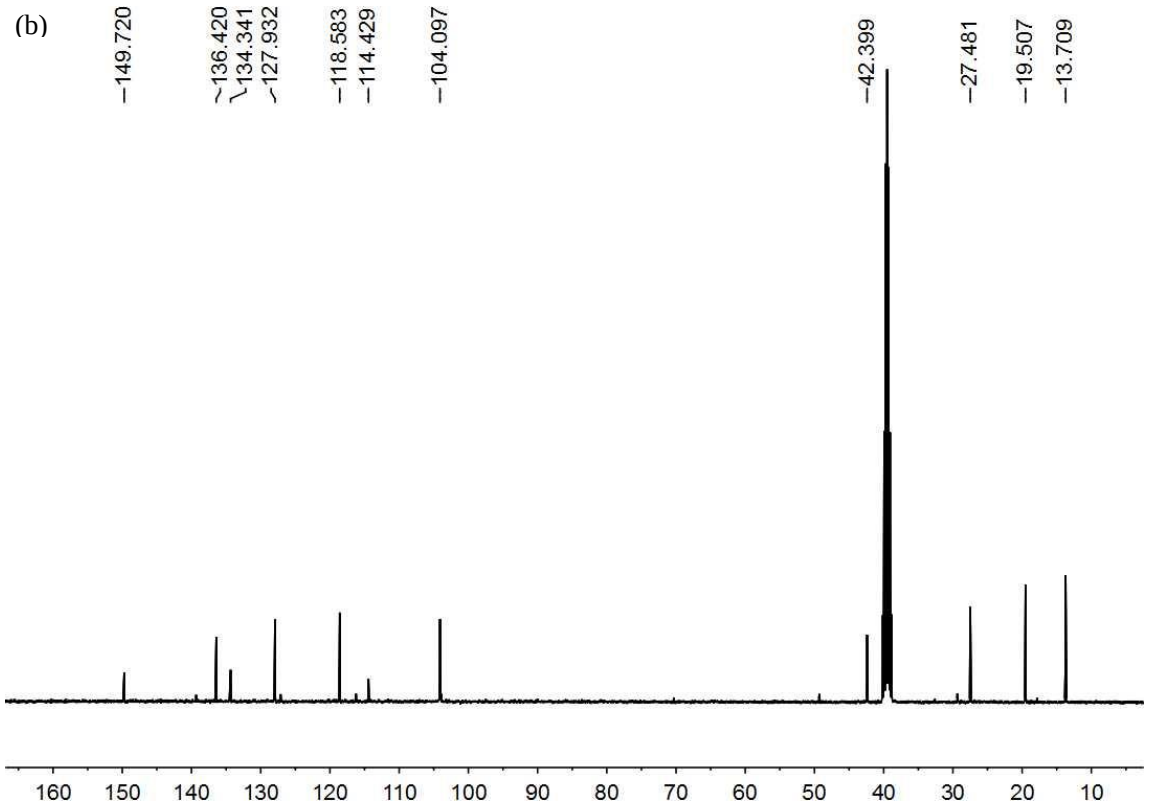
^{13}C NMR (100 MHz, DMSO-d_6) δ 13.71, 19.51, 27.48, 42.40, 104.10, 114.43, 118.58, 127.93, 134.34, 136.42, 149.72.

HR MS: $C_{19}H_{24}N_2O$, requires 296.1889, found $[C_{19}H_{24}N_2ONa]^+$ 319.1792.

(a)



(b)



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Comment			

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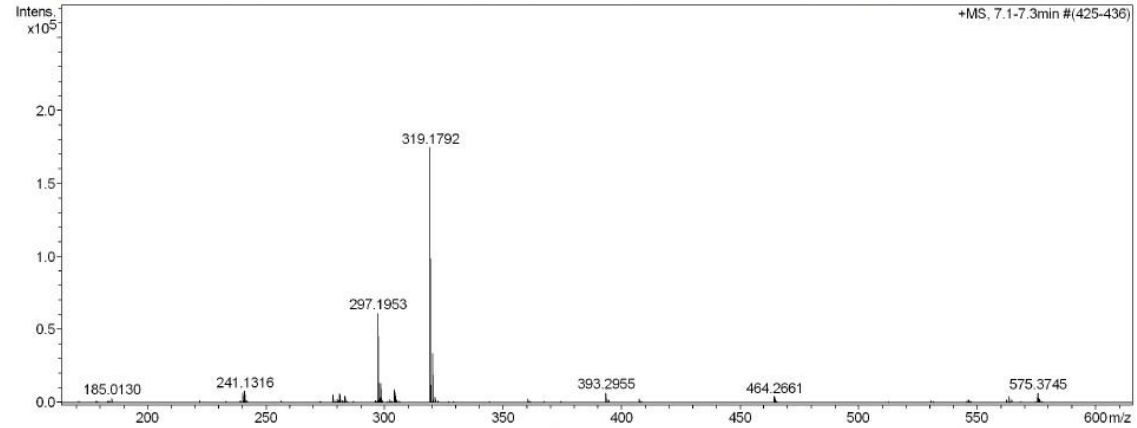

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Figure S13 ^{1}H NMR (a), ^{13}C NMR (b) and HR MS spectra of compound **9b**.

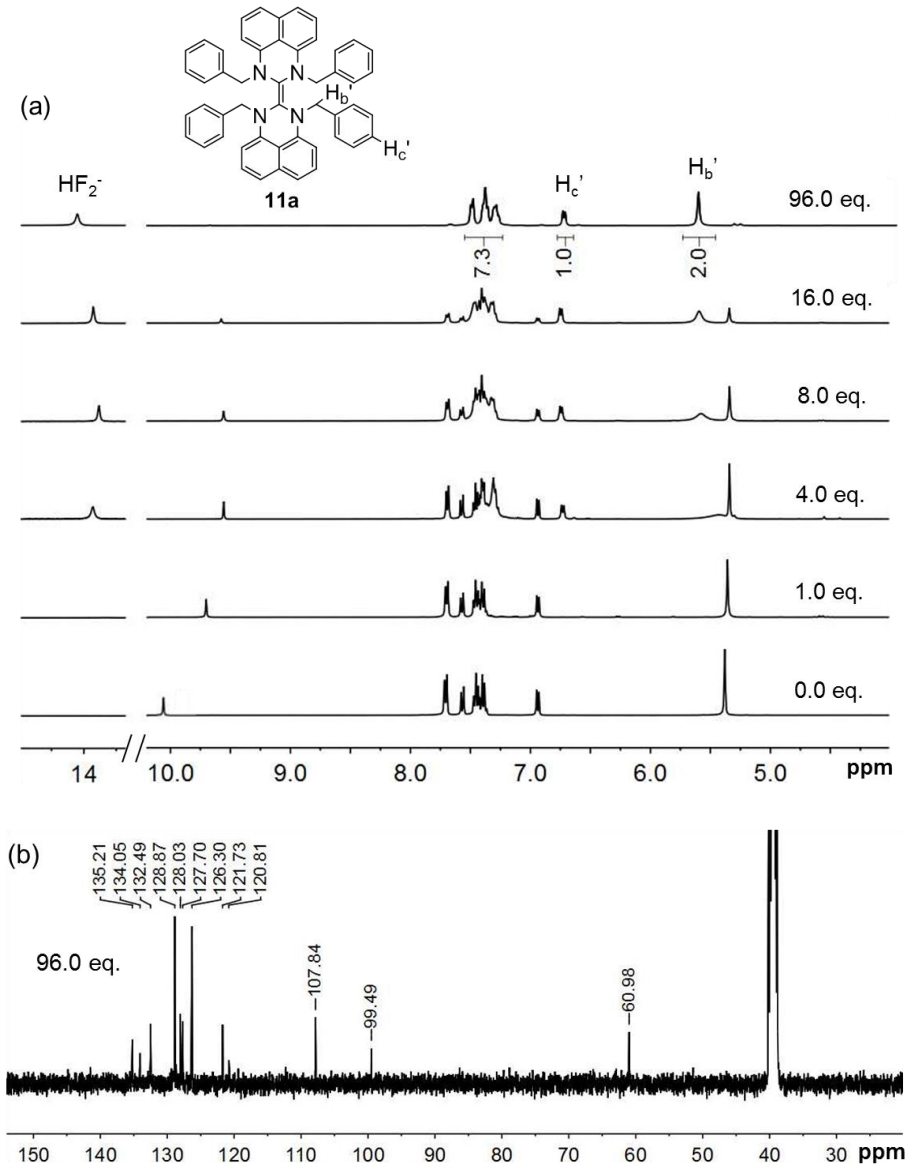
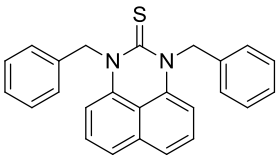


Figure S14 (a) ^{1}H NMR titrations of chemodosisensor **1** (5 mM) with AgF in DMSO-d_6. (b) ^{13}C NMR spectra of chemodosisensor **1** (5 mM) when in presence of 96.0 equiv. of AgF in DMSO-d_6.



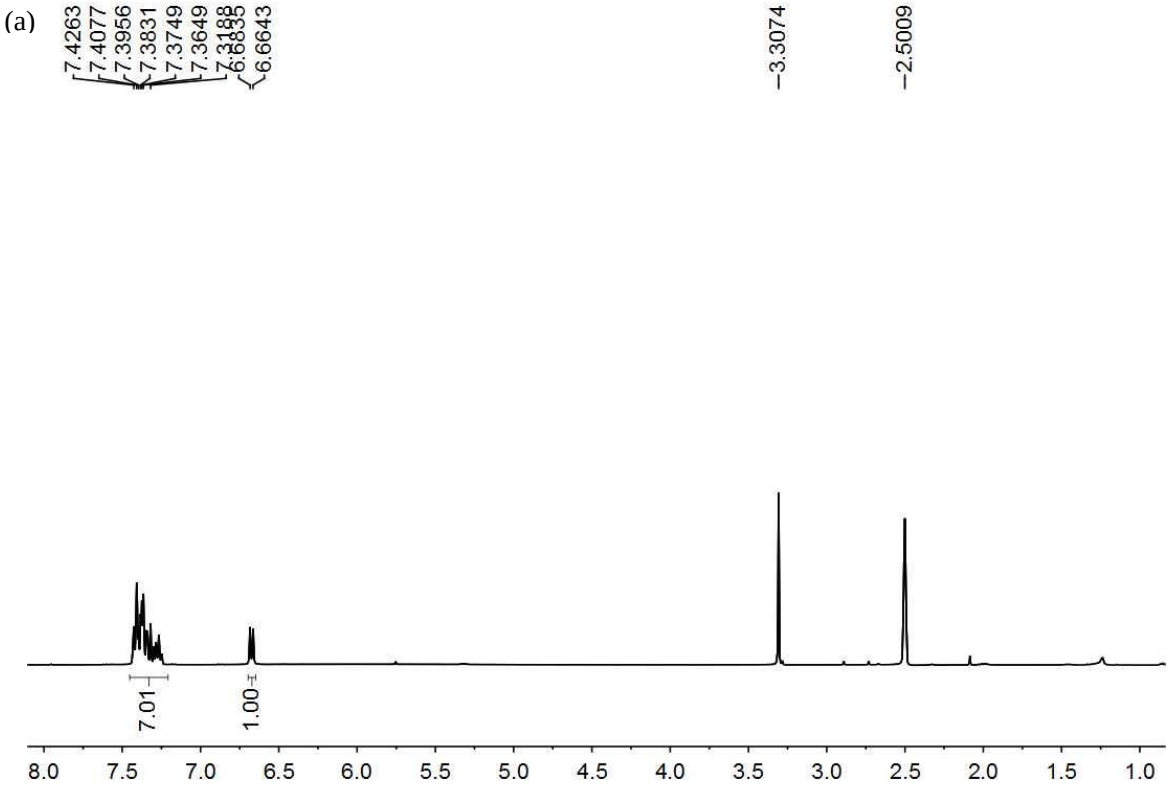
11a

^{1}H NMR (400 MHz, DMSO-d_6) δ 6.67 (d, J = 8.0 Hz, 2H), 7.27-7.42 (m,14H).

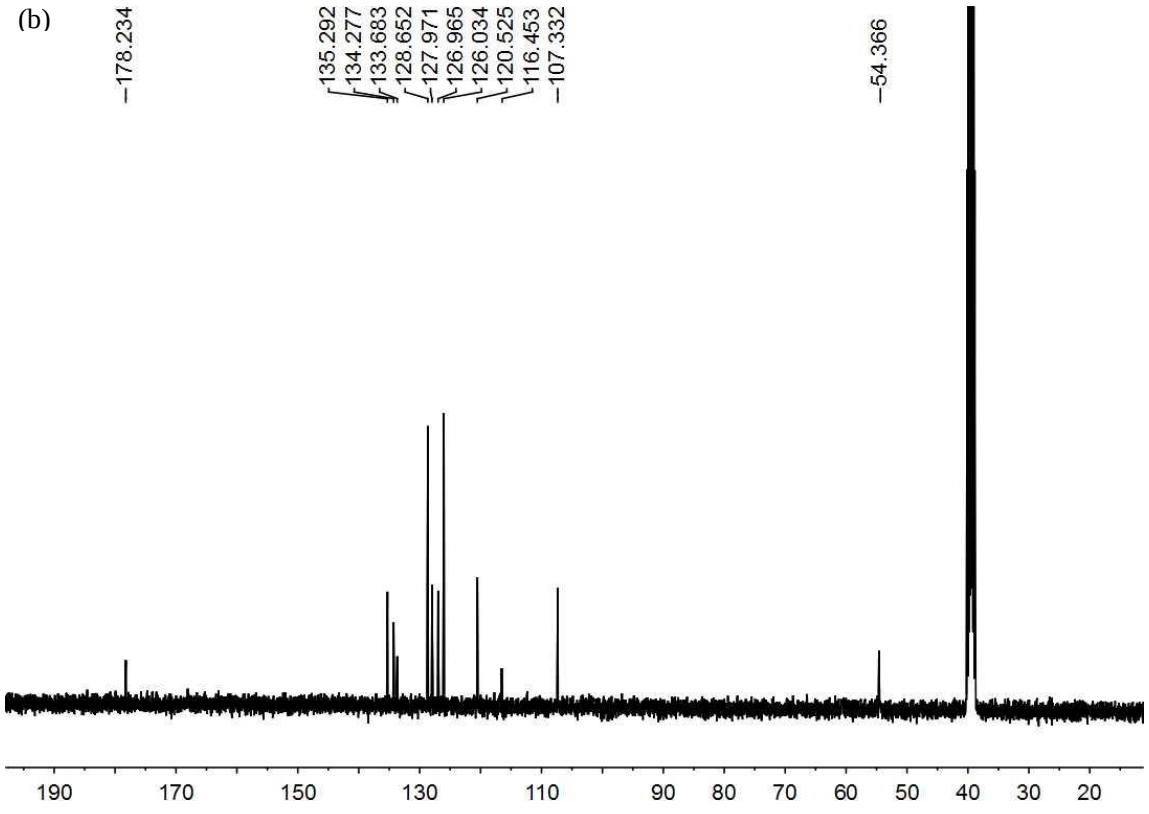
^{13}C NMR (100 MHz, DMSO-d_6) δ 54.37, 107.33, 116.45, 120.52, 126.03, 126.96, 127.97, 128.65, 133.68, 134.28, 135.29, 178.23.

HRMS: $C_{25}H_{20}N_2S$, requires 380.1347, found $[C_{25}H_{20}N_2SNa]^+$ 403.1253.

(a)



(b)



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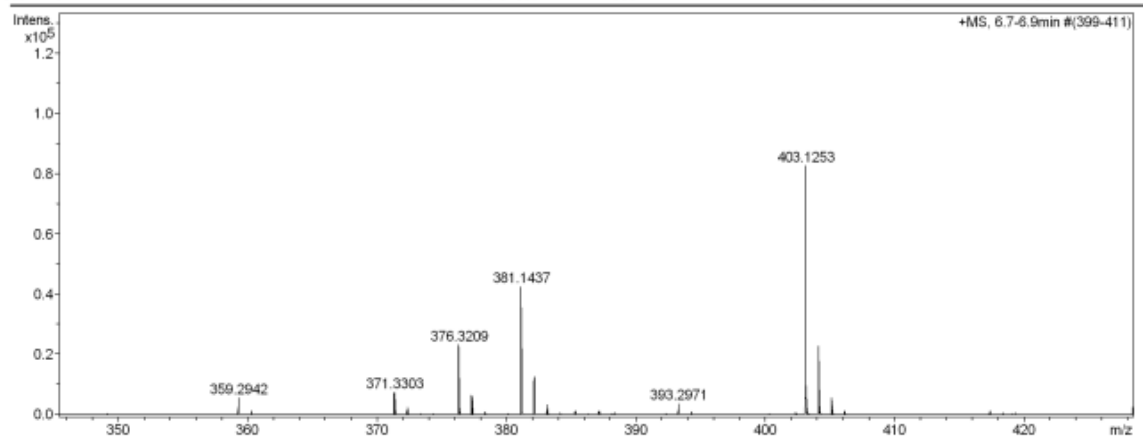

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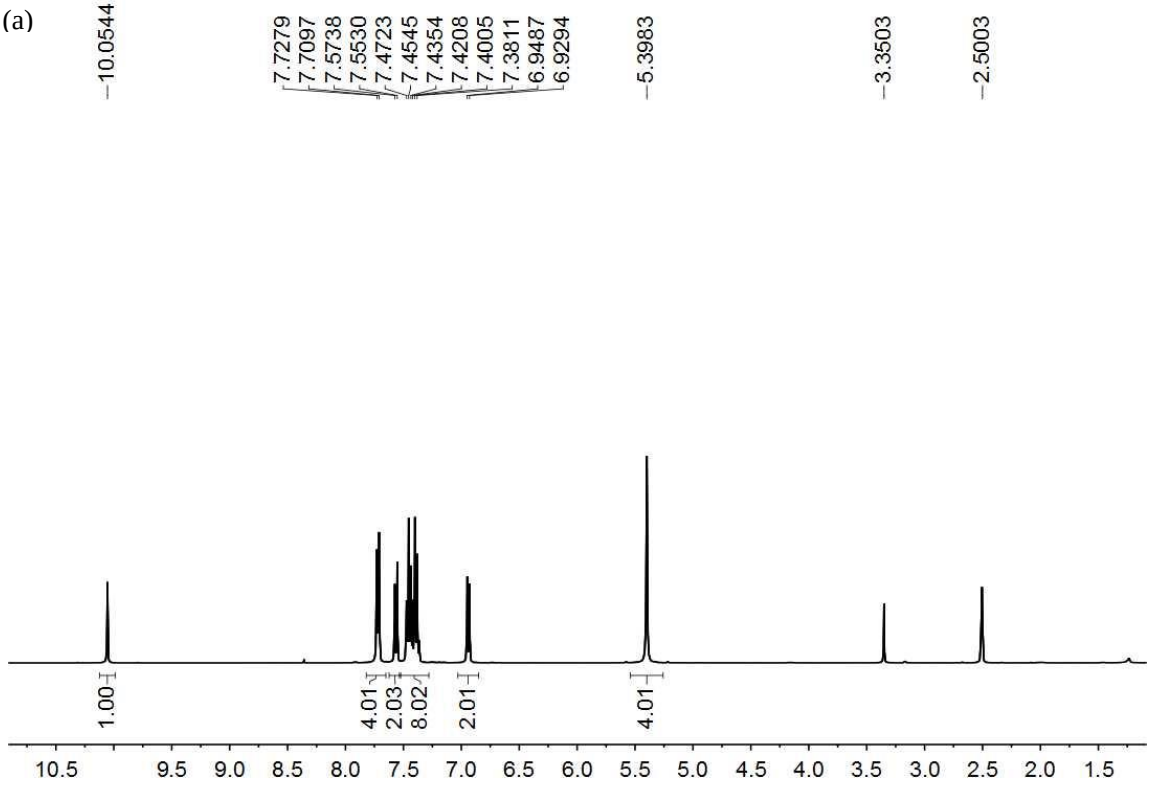
Figure S15 ^{1}H NMR (a), ^{13}C NMR (b) and HR MS (c) spectra of compound **11a**.

(a)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5.3983
3.3503
2.5003
1.00
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2.03
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10.5
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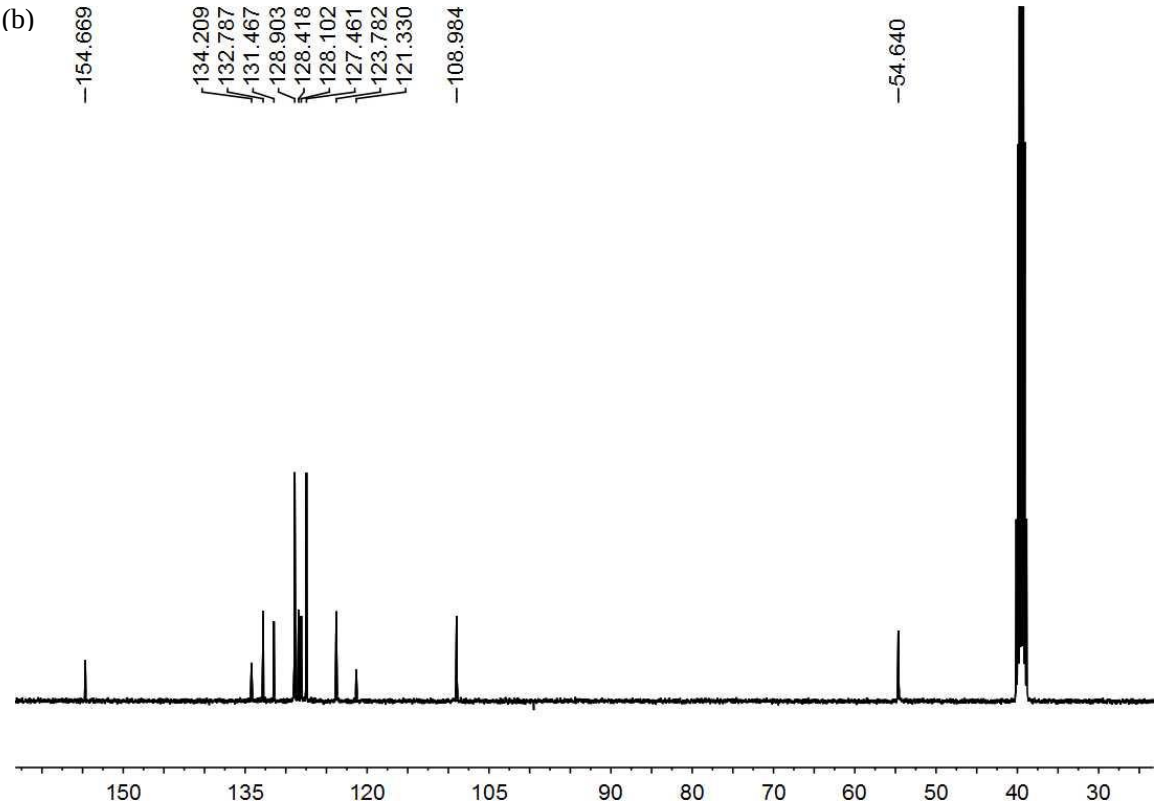
2.5
2.0
1.5

(b)


154.669
134.209
132.787
131.467
128.903
128.418
128.102
127.461
123.782
121.330
108.984
54.640
150
135
120
105
90
80
70
60
50
40
30

(c)

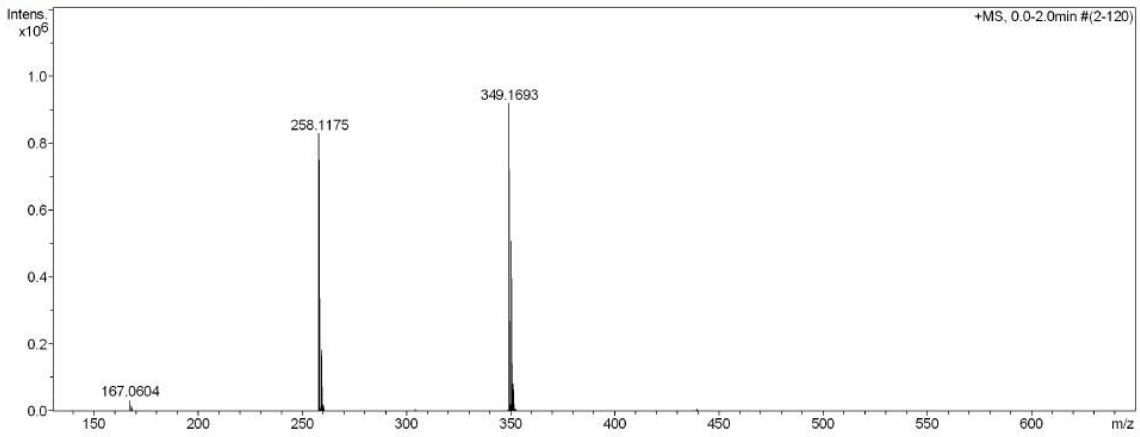
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\tj&yf-20140515\YHQ-5131.d	Acquisition Date	5/15/2014 1:35:28 PM
Method	tune_low.m	Operator and analyzer	ECNU.CHEM. G.D.Yang
Sample Name	YHQ-5131	Instrument / Ser#	micrOTOF 10293
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste

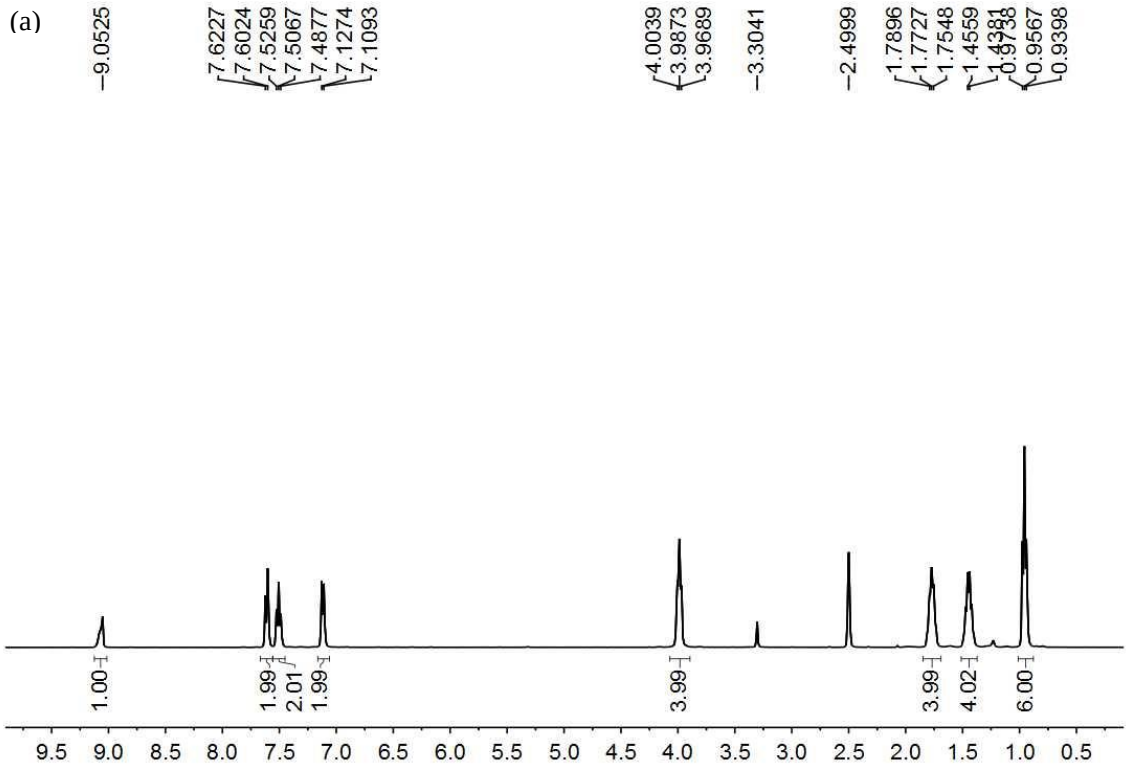


Meas. m/z	#	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev

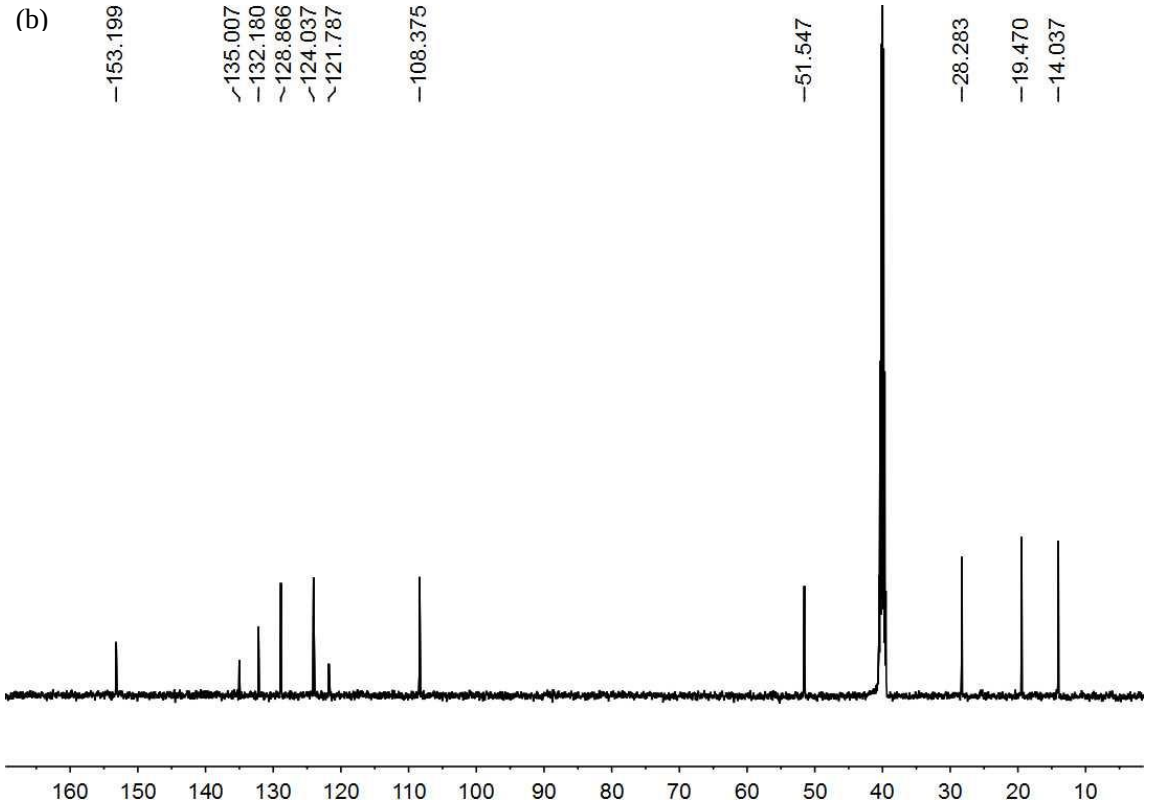
Figure S16 ^{1}H NMR (a), ^{13}C NMR (b) and HR MS (c) spectra of chemodosisensor **1**.

.

(a)



(b)



(c)

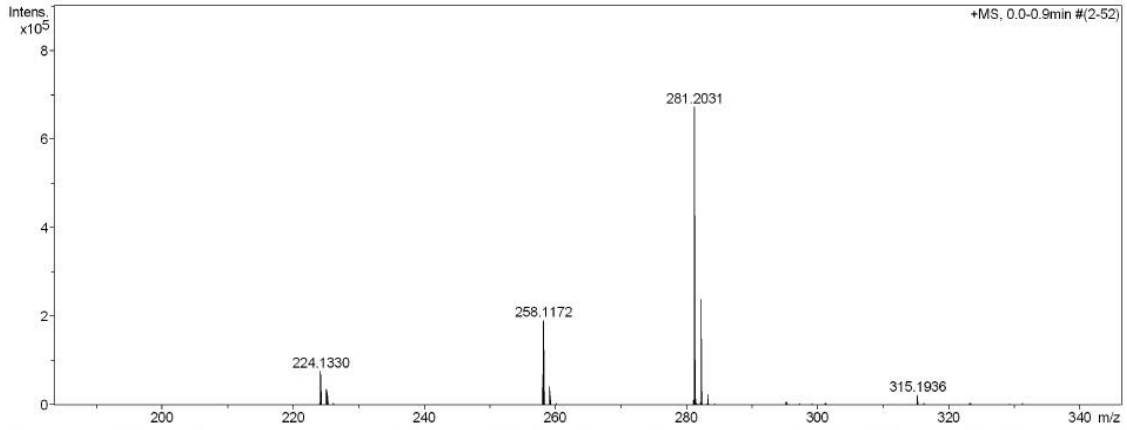
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\tj&yf-20140515\YHQ-5132.d	Acquisition Date	5/15/2014 1:44:30 PM
Method	tune_low.m	Operator and analyzer	ECNU.CHEM. G.D.Yang
Sample Name	YHQ-5132	Instrument / Ser#	micrOTOF 10293
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Meas. m/z	#	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev

Figure S17 ^{1}H NMR (a), ^{13}C NMR (b) and HR MS (c) spectra of chemodosisensor **2**.

Table S1. Crystal data and refinement of compounds **1**, **2** and **9a**.

Compound	**1**	**2**	**9a**
CCDC	1005672	1005673	1005674
Empirical formula	C25H21ClN2	C19H25BrN2O	C25H20N2O
M_r	384.90	377.32	364.43
Temperature (K)	296(2)	296(2)	296(2)
Crystal system	Orthorhombic	Triclinic	Monoclinic
Space group	$P2_12_12_1$	P-1	C2/c
a/Å	7.2746(10)	10.4898(12)	30.3297(13)
b/Å	14.2457(19)	11.5739(13)	8.7540(4)
c/Å	18.631(3)	16.4456(19)	14.8727(6)
α/°	90.00	93.603(4)	90.00
β/°	90.00	98.485(3)	105.795(2)
γ/°	90.00)	106.291(4)	90.00
V/Å^3	1930.8(5)	1884.0(4)	3799.7(3)
Z	4	4	8
Crystal size (mm^3)	0.32×0.21×0.12	0.48×0.36×0.22	0.33×0.28×0.14
D_c/g cm^{-3}	1.324	1.330	1.274
μ/mm^{-1}	0.21	2.188	0.078
F(000)	808.0	784	1536
θ range (°)	1.80-25.01	1.26-25.01	2.43-25.00
Reflections collected	22626	22167	21508
Unique reflections	3397	6613	3349
GOF on F^2	1.029	1.036	1.028
$R_{(int)}$	0.0795	0.0240	0.0531
R_1 [I >2σ(I)]	0.0418	0.0518	0.0420
wR_2 (all data)	0.0973	0.1536	0.1124