Supporting Information

For

An AIEgen-based Fluorescence Probe for Ratiometric Detection of Phosgene in Solution and Gas

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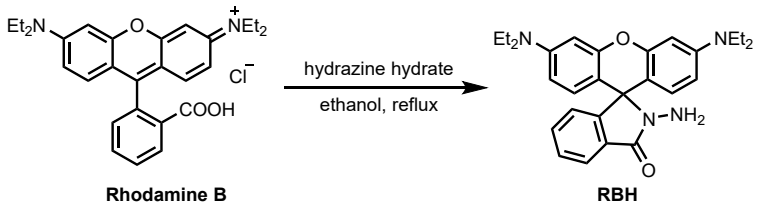
General Information

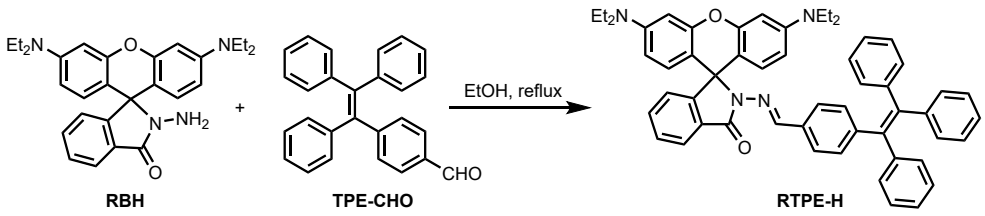
NMR was recorded on Bruker-400 MHz Spectrometer (^{1}H NMR: 400MHz; ^{13}C NMR: 100 MHz) and Bruker-500 MHz Spectrometer (^{1}H NMR: 500MHz; ^{13}C NMR: 125 MHz) using TMS as internal reference. The chemical shifts (δ) and coupling constants (*J*) were expressed in ppm and Hz respectively. The Photoluminescence (PL) spectra were obtained on Hitachi F-4600 Fluorescence Spectrometer. High resolution mass spectra were recorded on P-SIMS-Gly of Bruker Daltonics Inc. using ESI-TOF (electrospray ionization-time of flight). Commercially available compounds were used without further purification. All solvents were purified according to the standard procedures unless otherwise noted.

Synthesis of RTPE-H molecule



Rhodamine B **RBH**

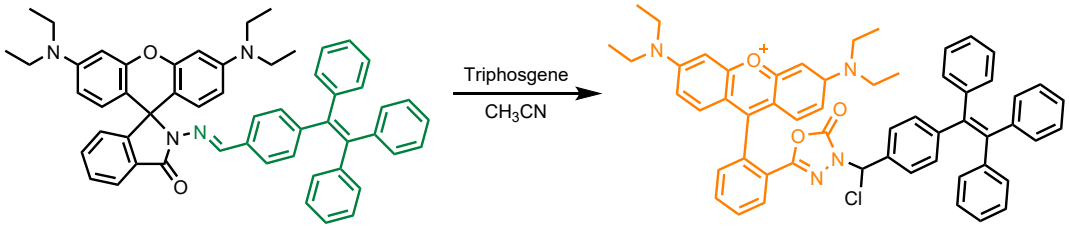
Hydrazine hydrate (1.0 mL, 20.6 mmol) was added to the solution of Rhodamine B hydrochloride (1.0 g, 2.09 mmol) in 50 mL of EtOH. The solution mixture was stirred at 90°C for 4 h. After the completion, the organic solvent of the reaction was removed under reduced pressure. The crude was purified by silica gel column chromatography using MeOH:CH_2Cl_2 (5 : 95) as an eluent to provide Rhodamine B hydrazide (680 mg, 72%) as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.84 – 7.70 (m, 1H), 7.56 – 7.41 (m, 2H), 7.11 – 6.92 (m, 1H), 6.43 – 6.37 (m, 2H), 6.35 – 6.28 (m, 4H), 3.31 (q, *J* = 7.9 Hz, 8H), 1.08 (t, *J* = 7.0 Hz, 12H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.8, 153.5, 152.4, 148.6, 132.9, 130.1, 128.6, 128.2, 124.0, 122.6, 108.3, 105.9, 97.9, 65.2, 44.2, 12.9.



RBH **TPE-CHO** **RTPE-H**

Rhodamine B hydrazide RBH (0.46 g, 1.0 mmol) and triphenylvinyl-benzaldehyde (0.40 g, 1.1 mmol) were dissolved in EtOH (20 mL). Add a drop of acetic acid to the reaction system. After being stirred and refluxed for 12 h, it was purified with silica gel column chromatography (PE: EA =6:1) to obtain a yellow solid (0.61 g, 76.3 %). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.75 (s, 1H), 7.93 – 7.85 (m, 1H), 7.60

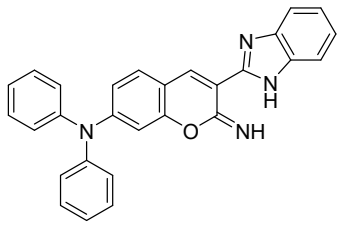
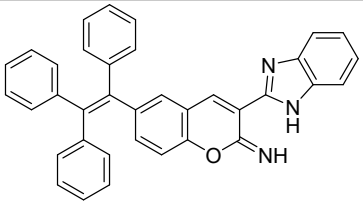
– 7.51 (m, 2H), 7.17 (d, J = 8.4 Hz, 2H), 7.14 – 7.04 (m, 10H), 6.99 – 6.88 (m, 8H), 6.44 – 6.35 (m, 4H), 6.33 – 6.28 (m, 2H), 3.28 (q, J = 7.3 Hz, 8H), 1.05 (t, J = 7.0 Hz, 12H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 164.1, 153.2, 151.5, 148.9, 147.8, 145.8, 143.5, 143.4, 143.2, 141.7, 140.3, 134.3, 133.1, 131.7, 131.2, 131.1, 131.1, 129.3, 129.3, 128.5, 128.3, 128.3, 128.0, 127.2, 127.1, 126.7, 124.3, 123.5, 108.4, 105.9, 97.7, 65.9, 44.1, 12.9. HRMS (ESI) m/z calcd. $[M+Na]^+$ for $C_{55}H_{50}N_4O_2Na^+$ 821.3826, found 821.3826.

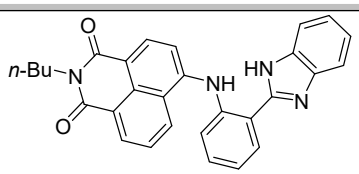
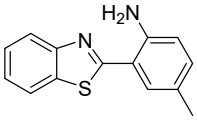
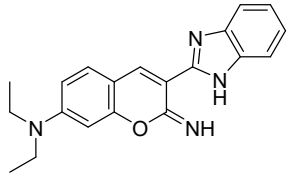
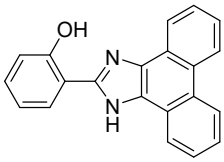
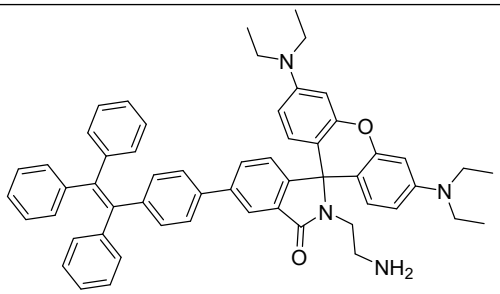
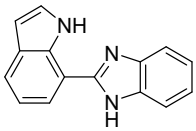
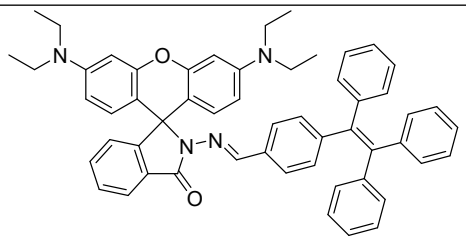


RTPE-HO

RTPE-HO. ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.22 (s, 1H), 8.03 – 7.93 (m, 2H), 7.77 – 7.61 (m, 2H), 7.30 (d, J = 6.6 Hz, 1H), 7.20 – 7.05 (m, 13H), 6.92 (dd, J = 15.7, 7.8 Hz, 11H), 3.57 – 3.47 (m, 8H), 1.02 (t, J = 7.1 Hz, 12H). HRMS (ESI) m/z calcd. $[M]^+$ for $C_{56}H_{50}ClN_4O_3^+$ 861.3566, found 861.3569.

Table S1 The enhanced Stokes shift of fluorescence probe reported for ratiometric detection of phosgene.

Structure	Enhanced stokes shift (Red shift in emissions)	LOD in solution	Ref.
	76 nm	0.27 μM	Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2021, 253, 119589
	75 nm	0.36 μM	Dyes and Pigments, 2020, 176, 108229

	52 nm	6.7 nM	Talanta, 2022, 236, 122826
	50 nm	0.14 ppm	Anal. Chem. 2017, 89, 22, 12596–12601
	68 nm	27 nM	Anal. Chim. Acta, 2018, 1029, 97-103.
	76 nm	0.14 ppm	Talanta, 2019, 200, 78-83.
	124 nm	0.54 ppm	New J. Chem., 2022, 46, 12062-12068
	57 nm	23.8 nM	Talanta, 2025, 283, 127172
	103 nm	0.1 μM	This work

Photoluminescence spectra

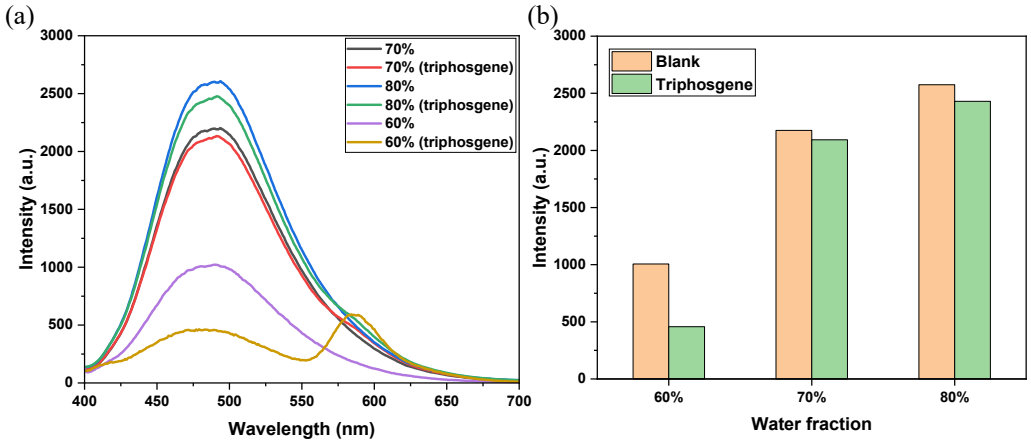


Fig. S1 (a) Photoluminescence (PL) spectra of 10^{-5} M RTPE-H and 2×10^{-5} M triphosgene in CH_3CN/H_2O mixture with with different water fraction excited with 365 nm light. (b) Changes of the PL intensity at 482 nm before and after adding triphosgene under different water content.

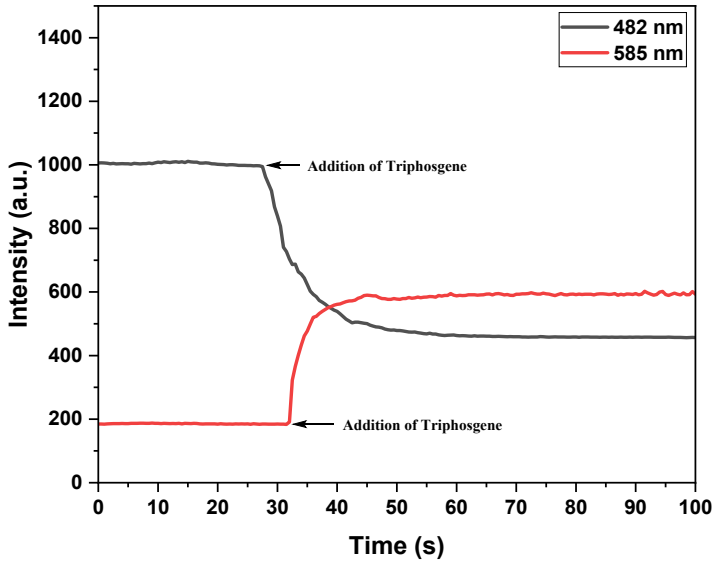


Fig. S2 The detection of response time.

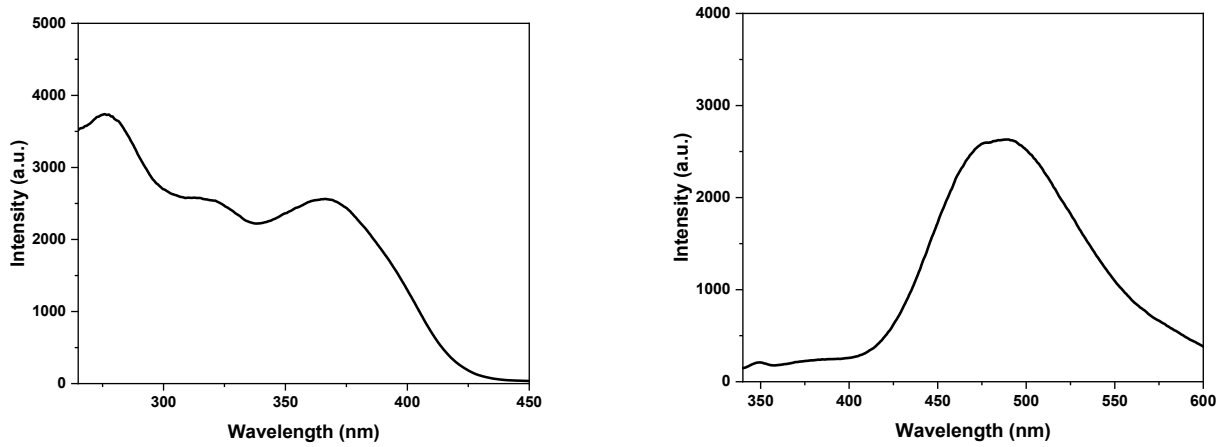


Fig S3. The excitation and emission spectrum (excited with 310 nm) of RTPE-H in CH_3CN/H_2O (20/80) mixture.

Fig S4. Stability testing of fluorescent test strips

Mechanism study

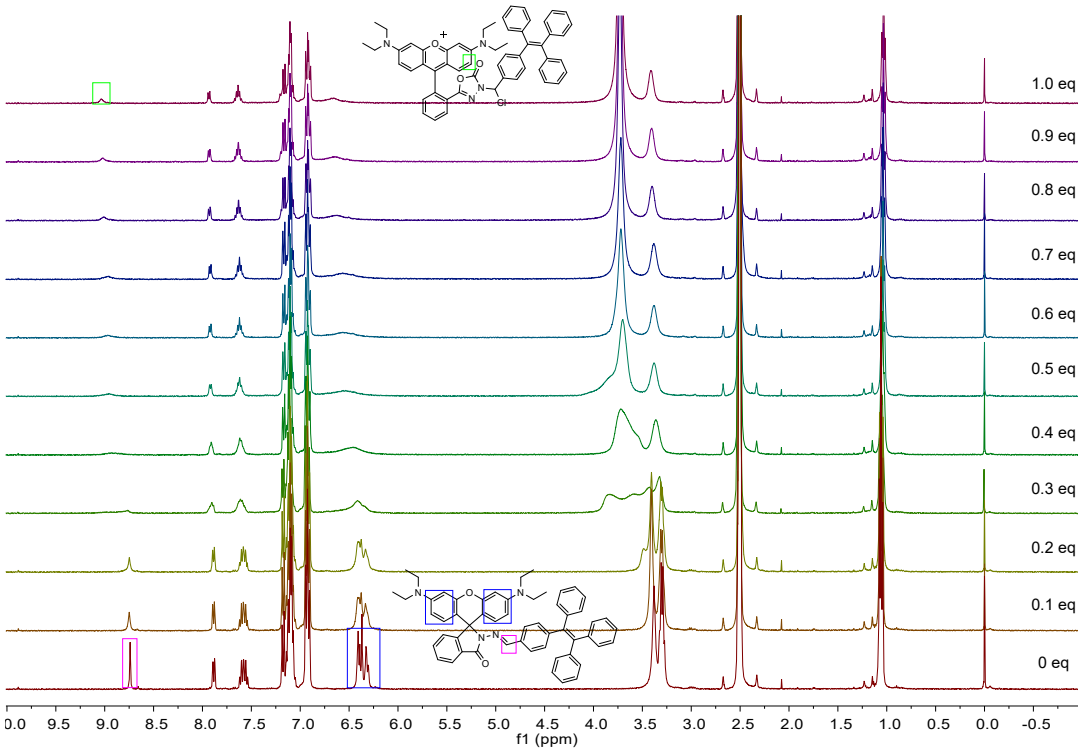


Fig. S5 The stacked ^{1}H NMR titration spectra of RTPE-H with different equivalents of triphosgene

TD-DFT calculation

All the calculations were performed using Gaussian 16[1] software packages. The geometries of all reactants were optimized using the B3LYP[2]-D3(Becke-Johnson damping function). In these geometry optimizations, basis set of 6-31G(d) was used.

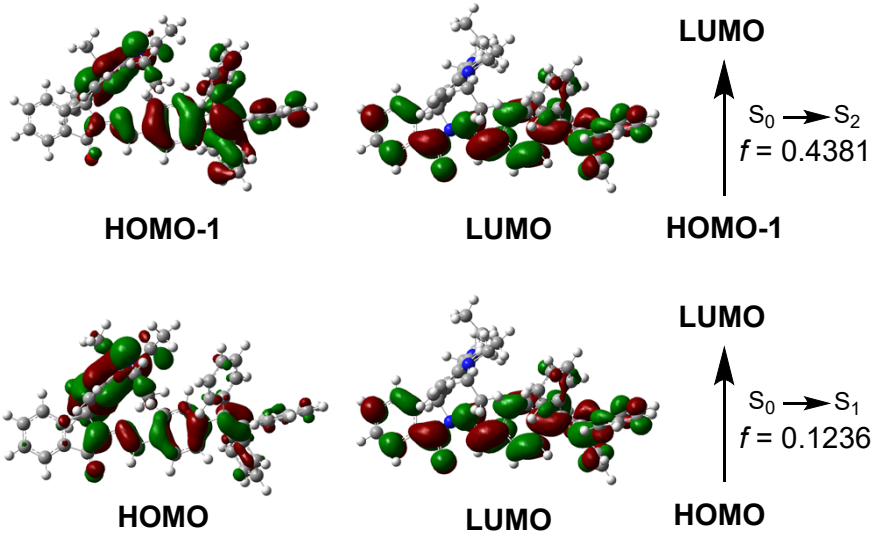


Fig.S6 TD-DFT calculated frontier molecular orbitals, selected electronic transitions and oscillator strengths of RTPE-H.

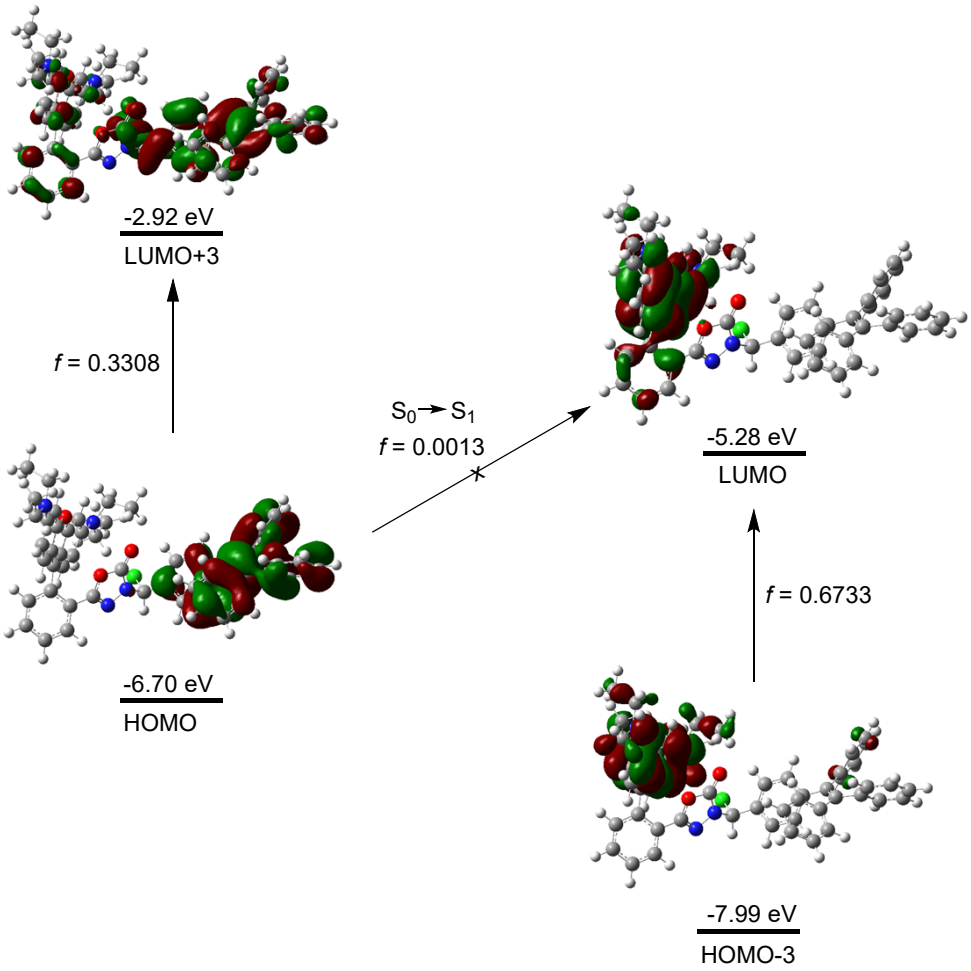


Fig.S7 TD-DFT calculated frontier molecular orbitals, selected electronic transitions and oscillator strengths of RTPE-HO.

RTPE-H

N	-1.88152000	0.22243000	1.54084300
N	-3.14391600	0.52398300	1.91695500
C	-3.60619100	0.96041000	3.15403300
C	-4.93511300	1.56222300	2.88405300
C	-5.19760200	1.54540700	1.51512000
C	-4.05487800	0.89896000	0.76126700
O	-3.01707600	0.87009900	4.22312700
C	-5.83519600	2.10873800	3.79531900
C	-7.02342200	2.64378900	3.29815500
C	-7.29173000	2.62561800	1.92147200
C	-6.38154600	2.07327800	1.01567000
C	-3.27848500	1.83845400	-0.13224500
C	-2.59925600	1.33810300	-1.24128500
O	-2.83536800	0.08847000	-1.75476400

C	-3.80617600	-0.69382200	-1.18344600
C	-4.45955300	-0.33923700	-0.00169500
C	-2.93861000	3.13371100	0.27776100
C	-1.93802200	3.86304300	-0.33898300
C	-1.18860300	3.31136700	-1.41031400
C	-1.58187300	2.04691600	-1.87837700
C	-4.10187400	-1.86450600	-1.87532100
C	-5.06995700	-2.76512800	-1.39314300
C	-5.74802500	-2.40142800	-0.20224300
C	-5.43238100	-1.22777000	0.46493000
N	-0.10073500	3.99525700	-1.96239600
N	-5.33824300	-3.96613800	-2.05079600
C	0.70356800	3.25455500	-2.94121000
C	0.63534900	4.89612600	-1.06694600
C	-6.47453700	-4.75841800	-1.57353600
C	-4.96092100	-4.09158100	-3.45713500
C	-5.84224300	-3.28064500	-4.41359900
C	-6.61065900	-6.13433300	-2.22041200
C	1.36699300	4.17163400	0.06807300
C	1.81238900	4.06839700	-3.60216600
C	-0.91442000	0.07726000	2.37855500
C	0.43968900	-0.05921300	1.83395700
C	1.52442700	-0.31434900	2.68593500
C	2.82022300	-0.39473000	2.18571900
C	3.07470700	-0.21310400	0.81783600
C	1.98568100	0.06988200	-0.02868100
C	0.69259700	0.13414200	0.46258600
C	4.45029600	-0.27051000	0.26048900
C	5.33149600	-1.26612700	0.56303400
C	4.78968500	0.83791200	-0.67491100
C	6.76847800	-1.19896300	0.18333200
C	4.92214300	-2.49922500	1.28838500
C	5.33346500	0.58136400	-1.94266100
C	5.61674300	1.62488500	-2.82097000
C	5.36558500	2.94666300	-2.44737200
C	4.81792500	3.21473400	-1.19109000
C	4.52160900	2.16873100	-0.31895900
C	3.77291100	-3.21482800	0.91680100
C	3.40502000	-4.37327600	1.59568200

C	4.18005300	-4.84133200	2.65882600
C	5.33356600	-4.14774800	3.02864000
C	5.70641400	-2.99367200	2.34268200
C	7.40317500	-2.31669400	-0.38233100
C	8.74781400	-2.26728100	-0.74328900
C	9.49029600	-1.10528400	-0.52558000
C	8.87709700	0.00477100	0.05857000
C	7.53056000	-0.04201100	0.41011700
H	-5.60143600	2.11167800	4.85538800
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H	-3.44601300	3.55961200	1.13885300
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H	-1.07995100	1.54705100	-2.69421800
H	-3.54796300	-2.04240100	-2.78645300
H	-6.52824200	-3.02782500	0.20671300
H	-5.96488900	-0.98619400	1.38001700
H	1.13981500	2.34709600	-2.48849800
H	0.02113100	2.91671400	-3.72724500
H	1.34300900	5.46290100	-1.67362600
H	-0.05855400	5.63865100	-0.66573300
H	-6.33682200	-4.91204300	-0.49869400
H	-7.42183900	-4.20457300	-1.69201800
H	-3.91271200	-3.80146500	-3.56403300
H	-4.99341900	-5.14901000	-3.72333600
H	-5.50398200	-3.40103600	-5.44912500
H	-6.88569000	-3.61119200	-4.35703900
H	-5.81130700	-2.21587800	-4.16266400
H	-7.39686300	-6.68951800	-1.69834500
H	-6.89426600	-6.08155000	-3.27603100
H	-5.68089700	-6.70688600	-2.13681600
H	1.91926800	4.88648600	0.68965600
H	0.66266300	3.63065700	0.70698500
H	2.07946700	3.44403500	-0.33075600
H	2.23118200	3.48332100	-4.42753600
H	1.42542700	5.00806100	-4.01093800
H	2.63638200	4.28868400	-2.91844600
H	-1.04980100	0.10664000	3.45756100

H	1.34804600	-0.44372300	3.75096000
H	3.64800100	-0.60021600	2.85614300
H	2.16876500	0.23672700	-1.08649600
H	-0.13904400	0.35226100	-0.19671900
H	5.53522900	-0.44476800	-2.23186100
H	6.03363600	1.40544900	-3.79999700
H	5.59087100	3.76062000	-3.13066400
H	4.61833400	4.23938000	-0.88933900
H	4.08367300	2.37687300	0.65253700
H	3.16604100	-2.85087400	0.09460100
H	2.51192800	-4.91272100	1.29286200
H	3.89061400	-5.74349100	3.19040300
H	5.94579600	-4.50697900	3.85130500
H	6.60905500	-2.46023300	2.62524600
H	6.82964000	-3.22470100	-0.54236600
H	9.21745600	-3.13838100	-1.19196000
H	10.54046400	-1.06775800	-0.80132100
H	9.45013900	0.90885700	0.24509000
H	7.05681500	0.82250500	0.86272500

RTPE-HO

N	-0.45149600	-1.28662200	1.83169900
N	-1.39259900	-1.38288100	2.84567600
C	-2.36070800	-0.62034000	2.45953800
C	-3.63889600	-0.43017200	3.14732400
C	-4.85028100	-0.27678300	2.43034600
C	-4.85311800	-0.29722500	0.94527700
O	-2.13348100	-0.02593700	1.24851600
C	-3.65816300	-0.45412300	4.54735200
C	-4.85929700	-0.32313000	5.23893300
C	-6.05413000	-0.16094600	4.53680600
C	-6.04596000	-0.13561600	3.14245300
C	-4.41660400	-1.44502300	0.25907000
C	-4.14756700	-1.35511300	-1.13619400
O	-4.49691200	-0.24103800	-1.83507300
C	-5.02808800	0.84284300	-1.20841000
C	-5.18960700	0.85548600	0.20730600
C	-4.08184500	-2.68090100	0.88174600
C	-3.47100900	-3.69211400	0.19462200

C	-3.10634400	-3.54263200	-1.18924600
C	-3.49594900	-2.34287400	-1.83760600
C	-5.35402200	1.91286000	-2.01299300
C	-5.84889100	3.11281600	-1.44269800
C	-5.98615400	3.15152600	-0.01164200
C	-5.65669800	2.07655100	0.76789400
N	-2.41296000	-4.51136800	-1.83978000
N	-6.16345500	4.19346500	-2.20388100
C	-1.71731800	-4.18587200	-3.09415300
C	-2.07018700	-5.75929100	-1.12277800
C	-6.11145200	4.10526600	-3.66856300
C	-6.76595800	5.37978000	-1.55651000
C	-7.03224100	6.56592400	-2.47593900
C	-7.34141600	3.42380200	-4.27330700
C	-1.46466800	-6.85839100	-1.98746500
C	-0.44677700	-3.36395600	-2.85690200
C	0.66481200	-2.18954100	1.83792700
C	1.93428800	-1.61385600	1.27378800
C	2.83858000	-1.04765900	2.18003000
C	4.00669900	-0.44672000	1.72661500
C	4.30543400	-0.40259400	0.35619500
C	3.41108200	-1.01378400	-0.53831800
C	2.23388900	-1.60018700	-0.09115900
C	5.55360500	0.23214100	-0.14300700
C	5.95953400	1.46193400	0.28665000
C	6.31010000	-0.56392600	-1.14674700
C	7.31322500	2.00375700	-0.00373400
C	5.07121100	2.35752300	1.07609400
C	6.77892100	0.02214000	-2.33309300
C	7.47322500	-0.73386800	-3.27365800
C	7.71101700	-2.09136800	-3.04805700
C	7.23831100	-2.68945100	-1.87882300
C	6.53568500	-1.93446600	-0.94185100
C	3.74661100	2.60045900	0.67955300
C	2.92483700	3.44453900	1.42206000
C	3.41197900	4.06388700	2.57474500
C	4.73265100	3.84354500	2.97076400
C	5.55774200	3.00756800	2.22161000
C	8.46332700	1.21868300	0.17524000

C	9.72748000	1.74100800	-0.08325700
C	9.86650700	3.05786000	-0.52684900
C	8.73178500	3.85283300	-0.69668800
C	7.46744400	3.33380700	-0.42643200
C	-0.92500900	-0.54081000	0.76736900
O	-0.49502200	-0.33467100	-0.33400000
Cl	0.17359800	-3.76980500	0.99314600
H	-2.72097400	-0.57098300	5.08068200
H	-4.86080200	-0.34200800	6.32390800
H	-6.99314200	-0.05918700	5.07145100
H	-6.97680900	-0.03313900	2.59344800
H	-4.30133000	-2.81135700	1.93495500
H	-3.21192200	-4.59432900	0.72828700
H	-3.28395900	-2.15597300	-2.87979000
H	-5.20060700	1.79855900	-3.07592700
H	-6.34919200	4.04566700	0.47379100
H	-5.76088200	2.14962700	1.84386100
H	-1.48053800	-5.11998600	-3.59915300
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H	-1.38515100	-5.52769500	-0.29851000
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H	-7.70661400	5.07867200	-1.07650600
H	-6.08911400	5.70969700	-0.76097700
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H	-8.25196700	3.98431700	-4.03831800
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H	-2.11549200	-7.12771100	-2.82511900
H	-0.47627000	-6.59420800	-2.37399800
H	0.03093200	-3.12687000	-3.81328200
H	-0.66708900	-2.42655400	-2.33638100
H	0.26666100	-3.92582300	-2.24565500
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H	2.62836800	-1.07558800	3.24632700

H	4.69736000	-0.00512800	2.43596000
H	3.64287200	-1.01386800	-1.59837300
H	1.54580400	-2.04347100	-0.80007200
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H	6.16502200	-2.40352700	-0.03502700
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H	10.85306900	3.46377200	-0.73089700
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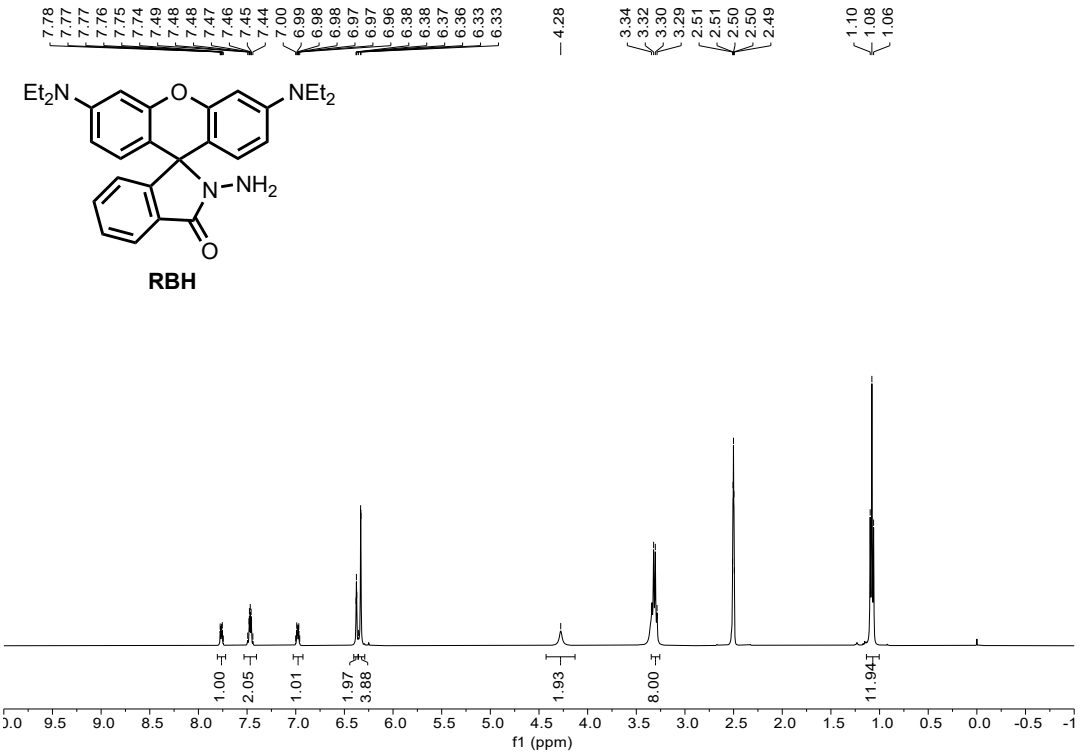
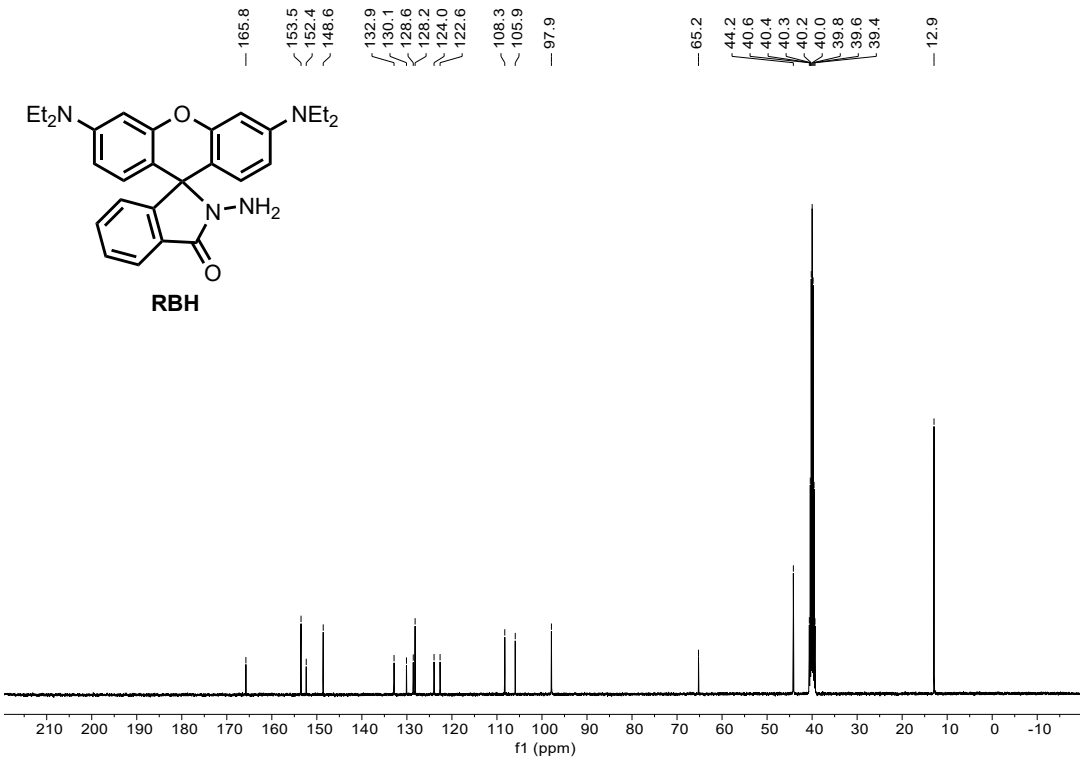
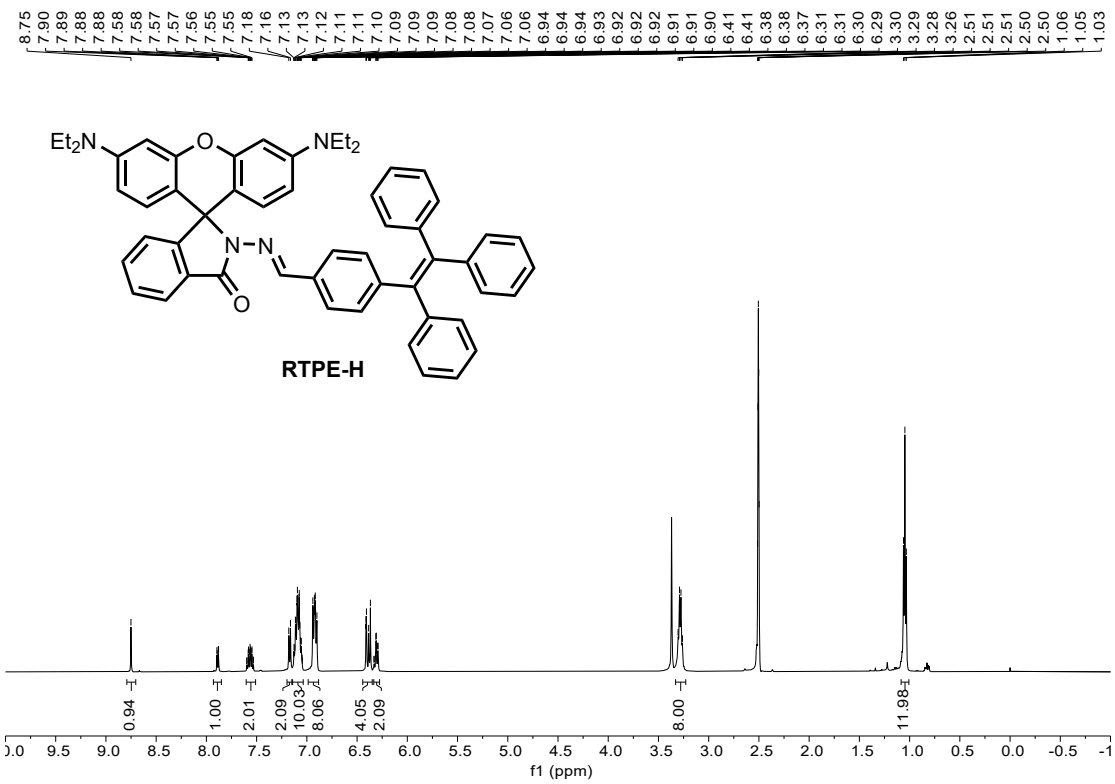
NMR Spectra and HRMS



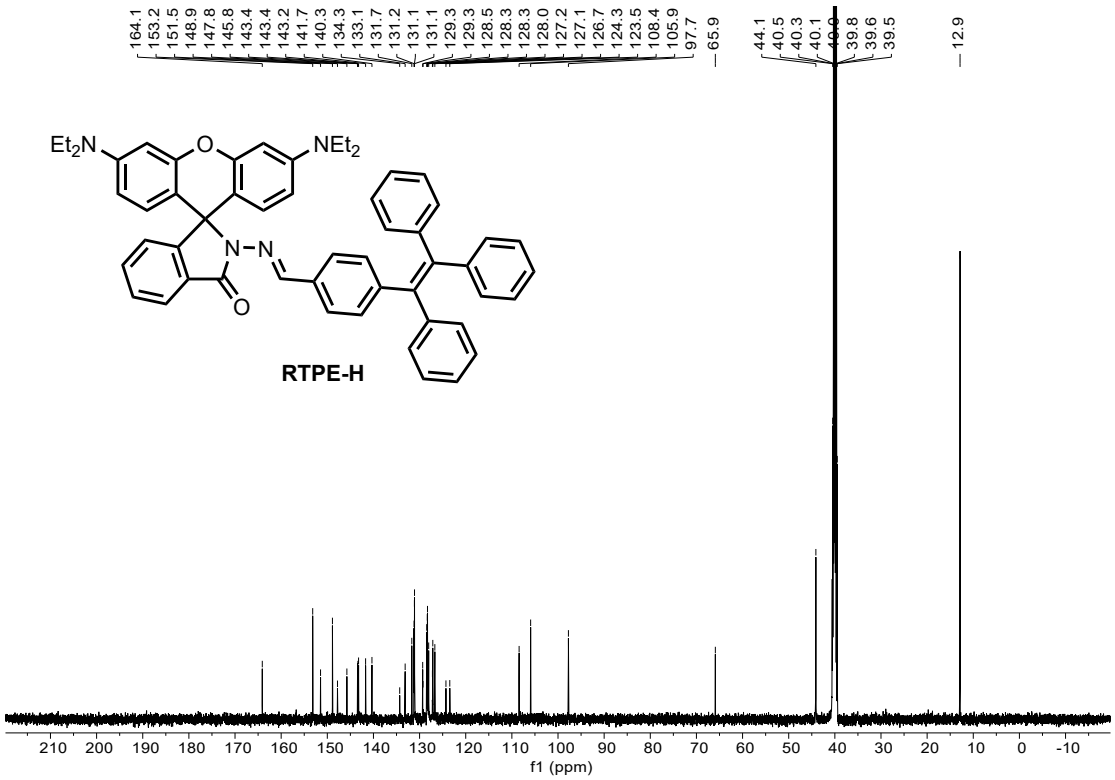
^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of RBH



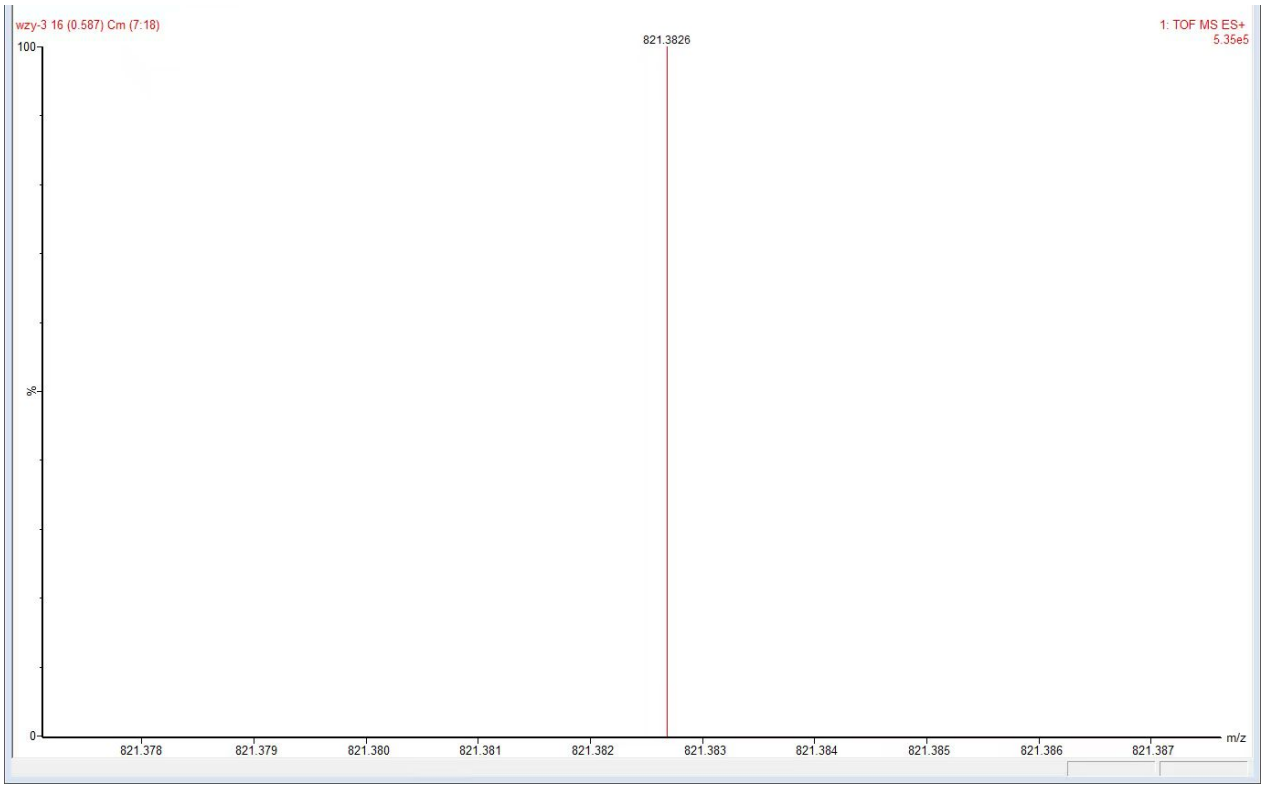
^{13}C NMR (125 MHz, DMSO-d_6) Spectrum of RBH



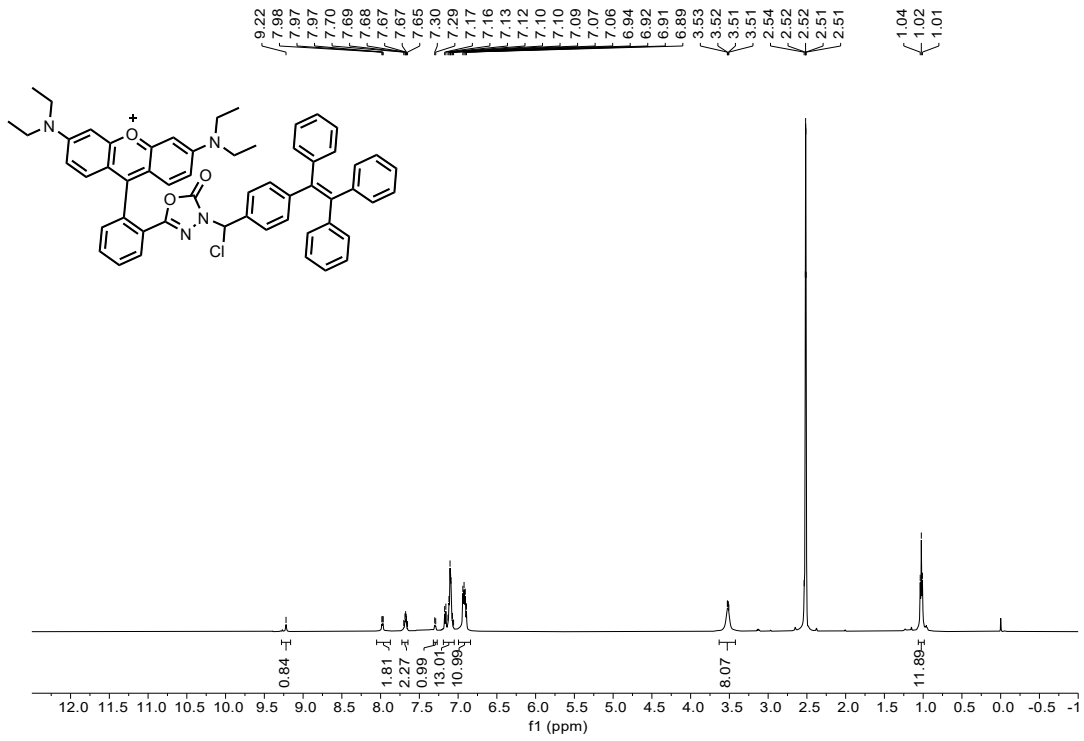
^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of RTPE-H



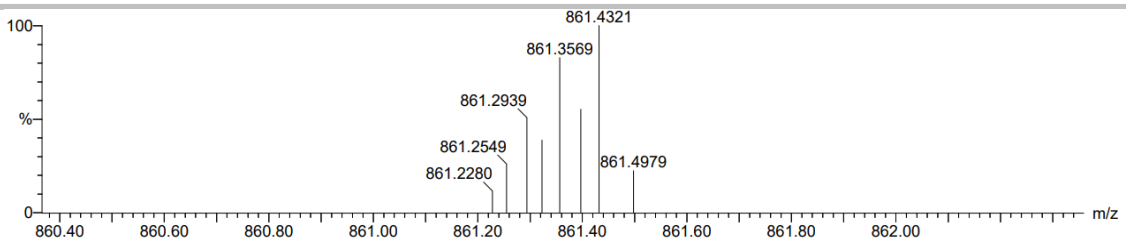
^{13}C NMR (125 MHz, DMSO-d_6) Spectrum of RTPE-H



HRMS Spectrum of RTPE-H



^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of RTPE-HO



HRMS Spectrum of RTPE-HO

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