Novel triphenylamine based rhodamine derivatives: Synthesis, characterization, photophysical properties and viscosity sensitivity

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Supporting information

Scheme S1. Synthesis of intermediate **A** and intermediate **B**

List of figures

List of Tables

List of Spectrum

Spectrum S1: ^{1}H NMR spectra of **Compound 3** in $CDCl_3$

Spectrum S2: ^{13}C NMR spectra of **Compound 3** in $CDCl_3$

Spectrum S3: ^{1}H NMR spectra of **Compound 4** in $CDCl_3$

Spectrum S4: ^{13}C NMR spectra of **Compound 4** in $CDCl_3$

Spectrum S5: ^{1}H NMR spectra of compound **6** in $CDCl_3$

Spectrum S6: ^{13}C NMR spectra of compound **6** in $CDCl_3$

Spectrum S7: ^{1}H NMR spectra of **Intermediate A** in $CDCl_3$

Spectrum S8: ^{1}H NMR spectra of **Intermediate B** in $CDCl_3$

Spectrum S9: ^{13}C NMR spectra of **Intermediate B** in $CDCl_3$

Spectrum S10: ^{1}H NMR spectra of **RH-1** in $CDCl_3$

Spectrum S11: ^{13}C NMR spectra of **RH-1** in $CDCl_3$

Spectrum S12: ^{1}H NMR spectra of **RH-2** in DMSO-d_6

Spectrum S13: ^{13}C NMR spectra of **RH-2** in DMSO-d_6

Spectrum S14: ^{1}H NMR spectra of **RH-3** in $CDCl_3$

Spectrum S15: ^{13}C NMR spectra of **RH-3** in $CDCl_3$

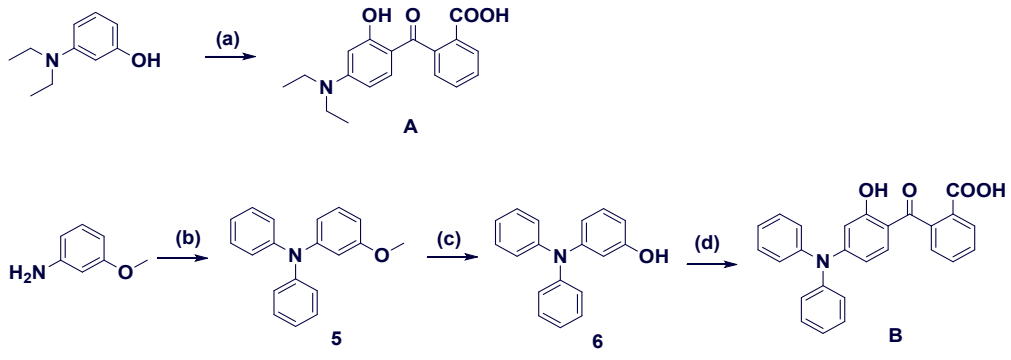
Spectrum S16: ^{1}H NMR spectra of **RH-4** in $CDCl_3$

Spectrum S17: ^{13}C NMR spectra of **RH-4** in $CDCl_3$

Spectrum S18: ^{1}H NMR spectra of **RH-5** in $CDCl_3$

Spectrum S19: ^{13}C NMR spectra of **RH-5** in $CDCl_3$

Scheme S1: Synthesis of intermediate **A** and intermediate **B**



Scheme 2: (a) Phthalic anhydride, toluene, reflux, overnight, N_2 atmosphere, (b) Iodobenzene, potassium-t-butoxide, 1, 10-phenanthroline/CuI, toluene, N_2 atmosphere (c) pyridine. HCl, 200 ^{o}C, overnight (d) Phthalic anhydride, anhydrous $AlCl_3$, 1, 2 dichloroethane, 50 ^{o}C, overnight, N_2 atmosphere.

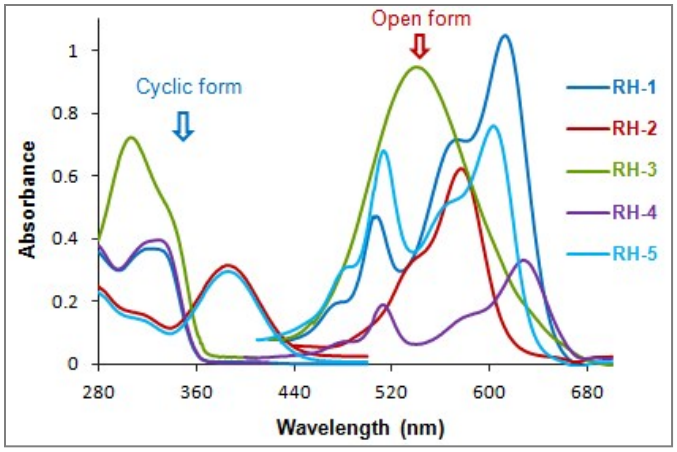


Figure S1. Absorption spectra of dyes **RH-1** to **RH-5** for their spirocyclic and open form in chloroform solvent (10^{-5} M concentrations) at room temperature.

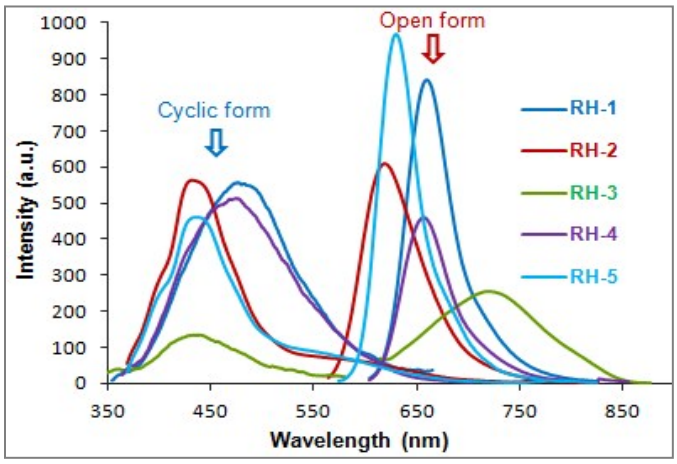


Figure S2. Emission spectra of dyes **RH-1** to **RH-5** for their spirocyclic and open form in chloroform solvent (10^{-5} M concentrations) at room temperature. (λ_{ex} : 322, 386, 307, 329 and 386 nm for **RH-1** to **RH-5** in cyclic form respectively and λ_{ex} : 613, 576, 540, 627 and 603 nm for **RH-1** to **RH-5** in open form respectively).

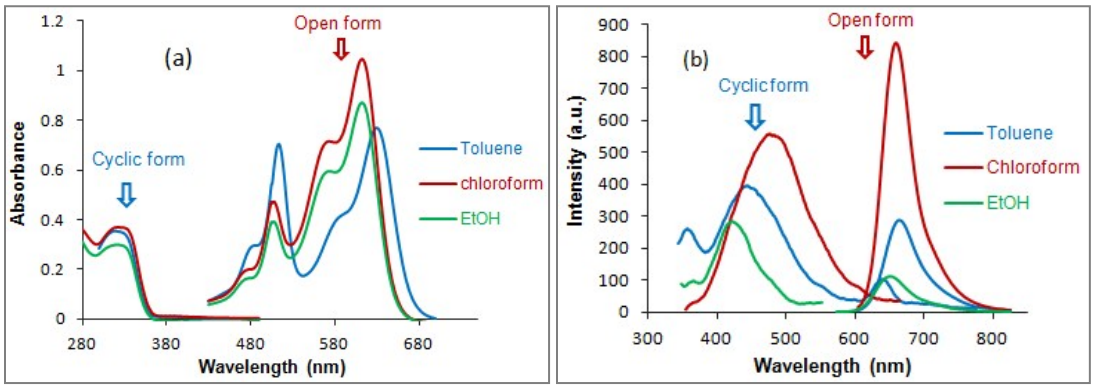


Figure S3. Absorption (a) and emission (b) spectra of **RH-1** in toluene, chloroform and ethanol solvent (10^{-5} M concentrations) at room temperature for their spirocyclic and open form. [λ_{ex} : 321 nm (cyclic form) and 613 nm (open form)].

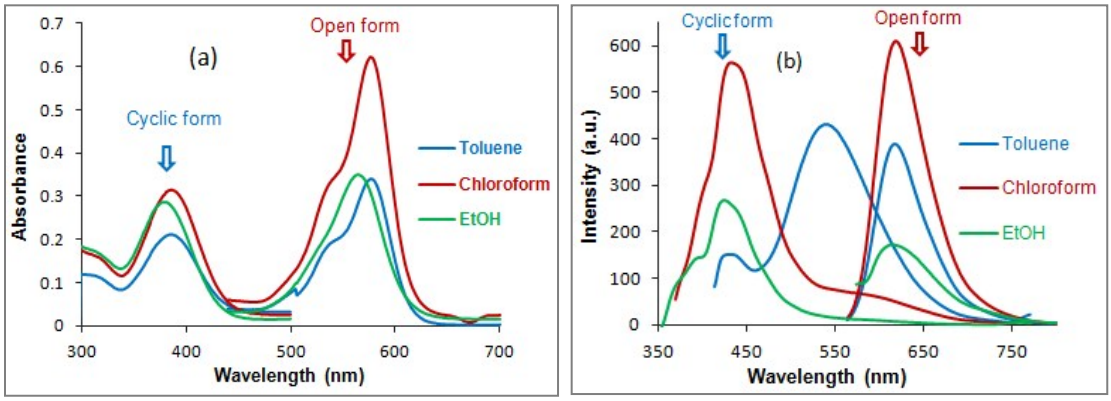


Figure S4. Absorption (a) and emission (b) spectra of **RH-2** in toluene, chloroform and ethanol solvent (10^{-5} M concentrations) at room temperature for their spirocyclic and open form. [λ_{ex} : 385 nm (cyclic form) and 579 nm (open form)].

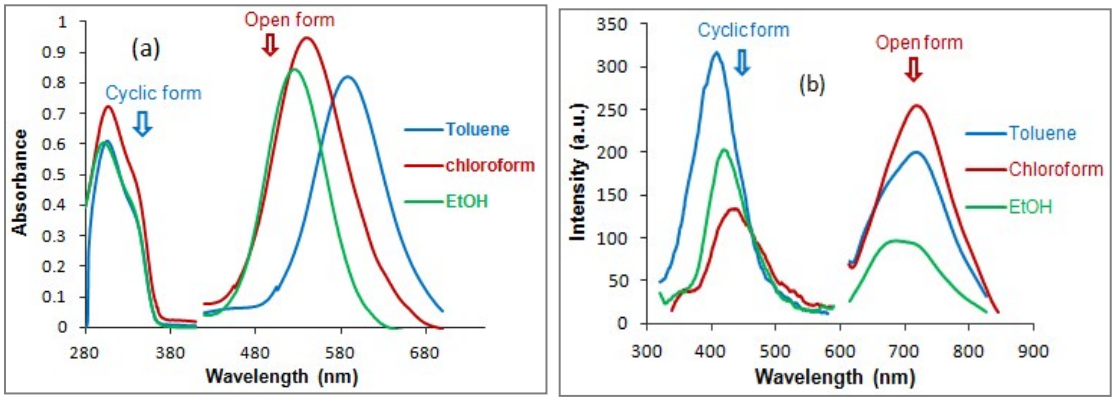


Figure S5. Absorption (a) and emission (b) spectra of **RH-3** in toluene, chloroform and ethanol solvent (10^{-5} M concentrations) at room temperature for their spirocyclic and open form. [λ_{ex} : 306 nm (cyclic form) and 540 nm (open form)].

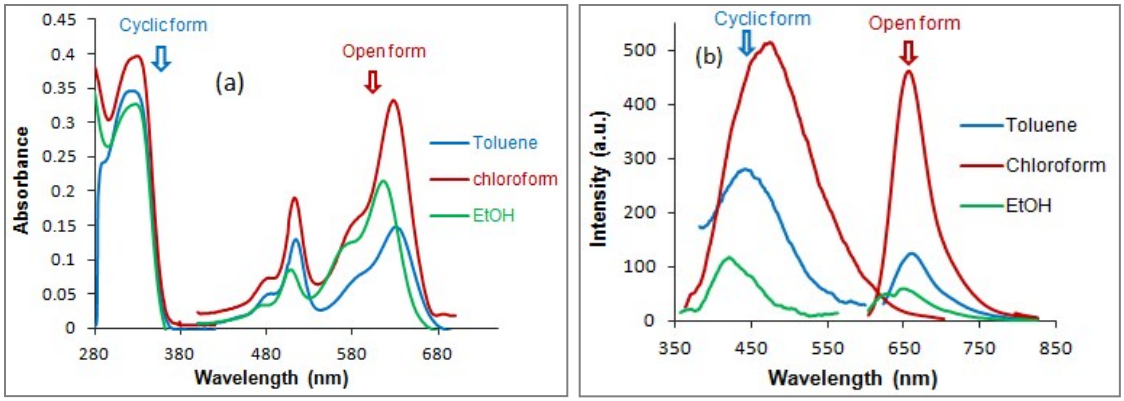


Figure S6. Absorption (a) and emission (b) spectra of **RH-4** in toluene, chloroform and ethanol solvent (10^{-5} M concentrations) at room temperature for their spirocyclic and open form. [λ_{ex} : 327 nm (cyclic form) and 615 nm (open form)].

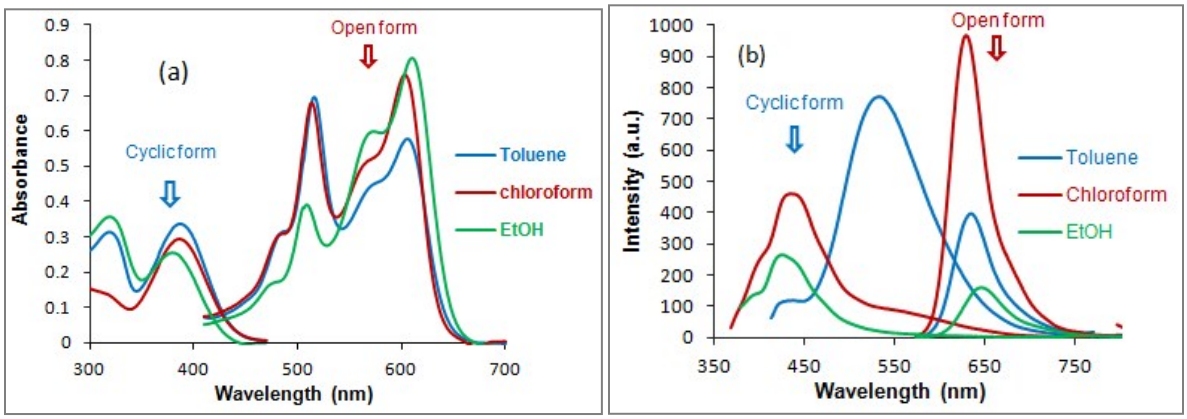


Figure S7. Absorption (a) and emission (b) spectra of **RH-5** in toluene, chloroform and ethanol solvent (10^{-5} M concentrations) at room temperature for their spirocyclic and open form. [λ_{ex} : 386 nm (cyclic form) and 605 nm (open form)].

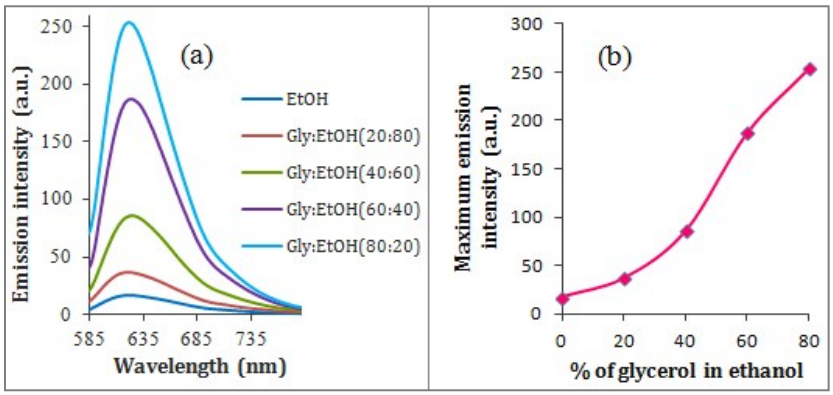


Figure S8. (A) Emission enhancement spectra of **RH-2** in different ratio of glycerol (0 to 80 %) in ethanol (0.5 x 10^{-5} M concentrations) at room temperature. (B) Plot of maximum emission intensity of **RH-2** versus percentage glycerol (0 to 80 %) in ethanol.

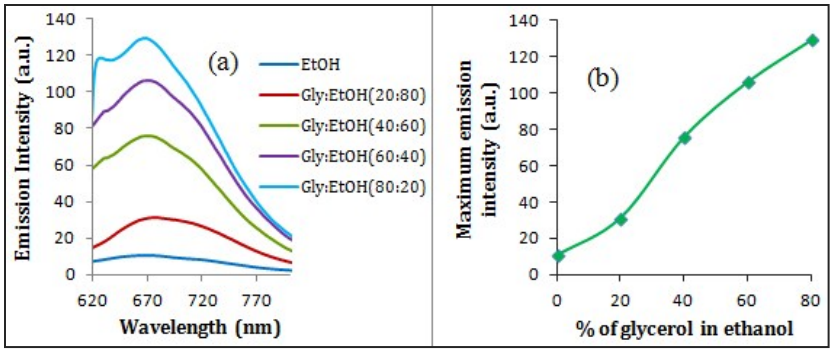


Figure S9. (A) Emission enhancement spectra of **RH-3** in different ratio of glycerol (0 to 80 %) in ethanol (0.5 x 10^{-5} M concentrations) at room temperature. (B) Plot of maximum emission intensity of **RH-3** versus percentage glycerol (0 to 80 %) in ethanol.

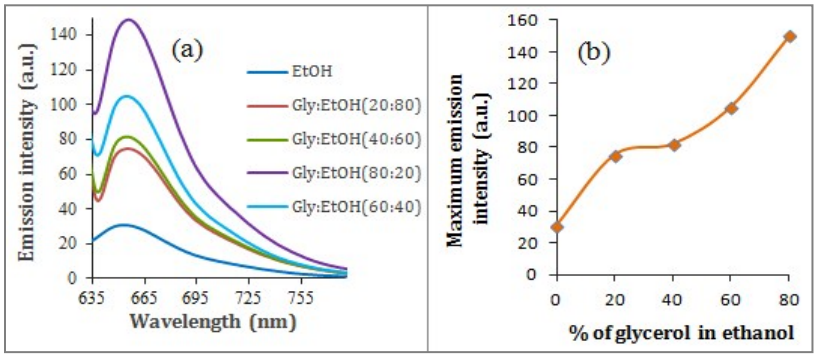


Figure S10. (A) Emission enhancement spectra of **RH-4** in different ratio of glycerol (0 to 80 %) in ethanol (0.5 x 10^{-5} M concentrations) at room temperature. (B) Plot of maximum emission intensity of **RH-4** versus percentage glycerol (0 to 80 %) in ethanol.

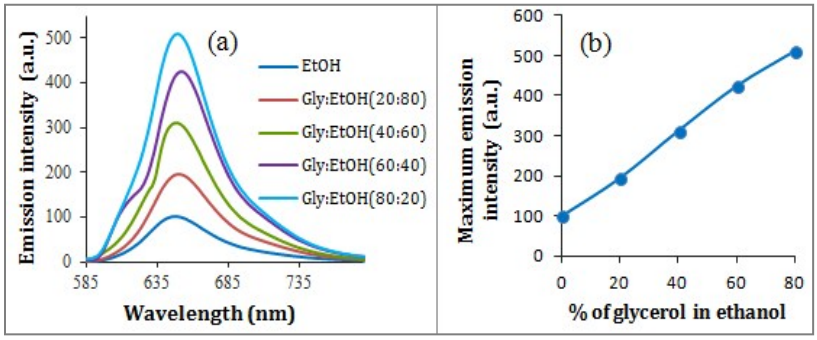


Figure S11. (A) Emission enhancement spectra of **RH-5** in different ratio of glycerol (0 to 80 %) in ethanol (0.5 x 10^{-5} M concentrations) at room temperature. (B) Plot of maximum emission intensity of **RH-5** versus percentage glycerol (0 to 80 %) in ethanol.

Table 1. Photophysical properties of **RH-1** in toluene, chloroform and ethanol solvent (spirocyclic and open form)

Solvent	λ_{abs} (nm)	$\varepsilon_{max} \times 10^4$ (M^{-1} cm^{-1})	fwhm (nm)	λ_{ems} (nm)	Stokes shift (nm)	Stokes shift (cm^{-1})	f	μ_{eg} (debye)	$K_r \times 10^8$ (cm^{-1})	Φ_F
Spirocyclic form										

Toluene	318	3.54	45	443	125	8873	0.68	6.79	3.54	---
$CHCl_3$	322	3.69	48	471	149	9824	0.73	7.08	2.99	---
EtOH	321	3	45	423	102	7512	0.56	6.17	2.71	---
Open form										
Toluene	630	7.68	72	656	26	629	1.21	12.72	1.89	0.61
$CHCl_3$	613	10.04	80	660	47	1162	1.38	13.43	2.52	0.82
EtOH	613	8.73	80	652	39	976	1.15	12.26	1.91	0.56

Table 2: Photophysical properties of **RH-2** in toluene, chloroform and ethanol solvent (spirocyclic and open form)

Solvent	**λ_{abs} (nm)**	**$\varepsilon_{max} \times 10^4$ (M^{-1} cm^{-1})**	**fwhm (nm)**	**λ_{ems} (nm)**	**Stokes shift (nm)**	**Stokes shift (cm^{-1})**	**f**	**μ_{eg} (debye)**	**$K_r \times 10^8$ (cm^{-1})**	**Φ_F**
Spirocyclic form										
Toluene	385	2.11	67	540	155	7456	0.45	6.05	1.57	---
$CHCl_3$	386	3.14	64	432	46	2759	0.63	7.18	3.62	---
EtOH	380	2.85	64	424	44	2731	0.55	6.68	3.30	---
Open form										
Toluene	577	3.39	66	618	41	1150	0.36	6.62	1.15	0.47
$CHCl_3$	576	6.21	64	619	43	1206	0.65	8.90	1.95	0.54
EtOH	564	3.49	65	614	50	1444	0.40	6.90	1.03	0.35

Table 3: Photophysical properties of **RH-3** in toluene, chloroform and ethanol solvent (spirocyclic and open form)

Solvent	**λ_{abs} (nm)**	**$\varepsilon_{max} \times 10^4$ (M^{-1} cm^{-1})**	**fwhm (nm)**	**λ_{ems} (nm)**	**Stokes shift (nm)**	**Stokes shift (cm^{-1})**	**f**	**μ_{eg} (debye)**	**$K_r \times 10^8$ (cm^{-1})**	**Φ_F**
Spirocyclic form										
Toluene	306	6.09	58	407	101	8110	1.39	9.53	9.66	---
$CHCl_3$	307	7.24	67	436	129	9638	1.87	11.06	9.52	---
EtOH	302	6.05	64	419	117	9246	1.54	9.96	7.64	---
Open form										
Toluene	588	8.18	95	717	129	3060	1.17	12.09	2.82	0.14
$CHCl_3$	540	9.48	100	719	179	4610	1.57	13.44	3.19	0.16
EtOH	525	8.45	81	696	171	4680	1.18	11.51	2.2	0.11

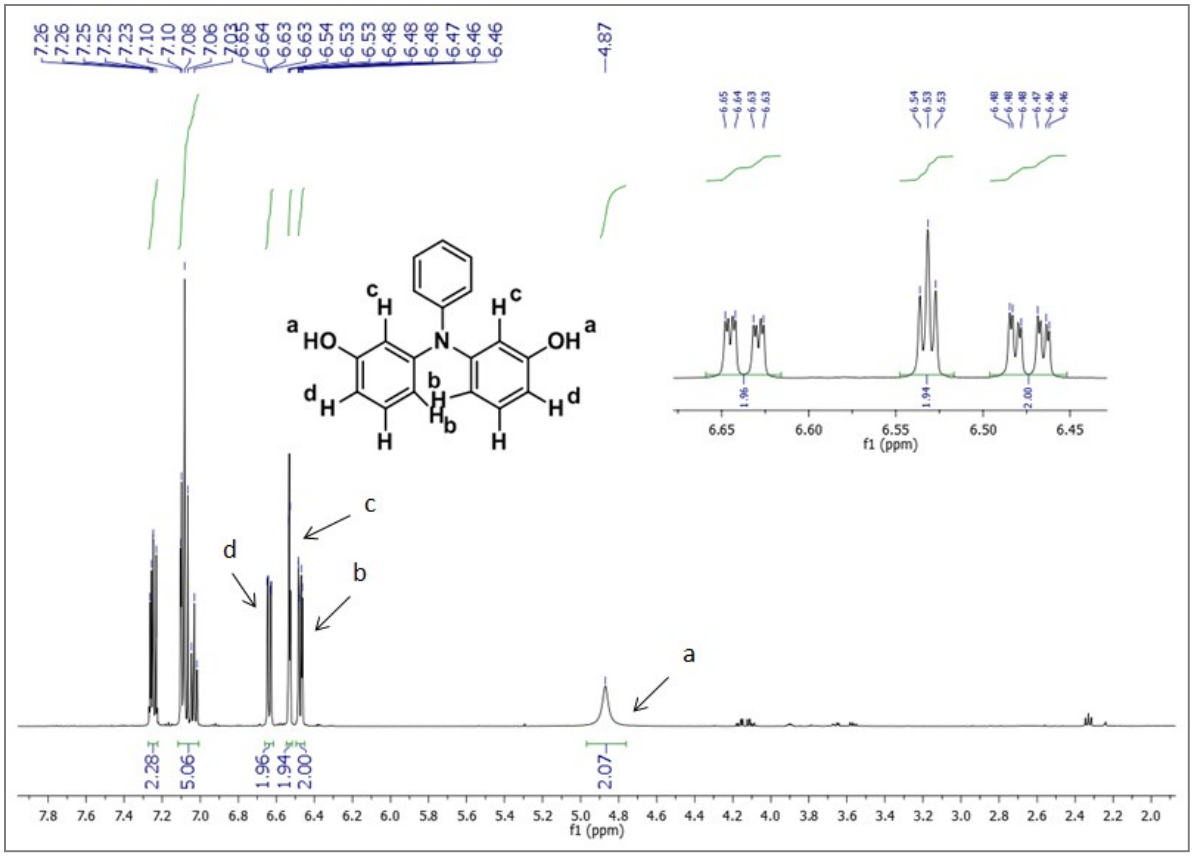
Table 4: Photophysical properties of **RH-4** in toluene, chloroform and ethanol solvent (spirocyclic and open form)

Solvent	λ_{abs} (nm)	$\varepsilon_{max} \times 10^4$ (M^{-1} cm^{-1})	fwhm (nm)	λ_{ems} (nm)	Stokes shift (nm)	Stokes shift (cm^{-1})	f	μ_{eg} (debye)	$K_r \times 10^8$ (cm^{-1})	Φ_F
Spirocyclic form										
Toluene	323	3.46	63	443	120	8386	0.78	7.32	4.30	---
$CHCl_3$	329	3.96	68	475	146	9343	0.92	8.02	4.41	---
EtOH	327	3.26	65	422	95	6884	0.74	7.18	4.19	---
Open form										
Toluene	629	1.48	70	661	32	770	0.22	5.48	0.37	0.31
$CHCl_3$	627	3.32	58	657	30	728	0.44	7.63	0.77	0.52
EtOH	615	2.14	74	650	35	876	0.26	5.82	0.46	0.23

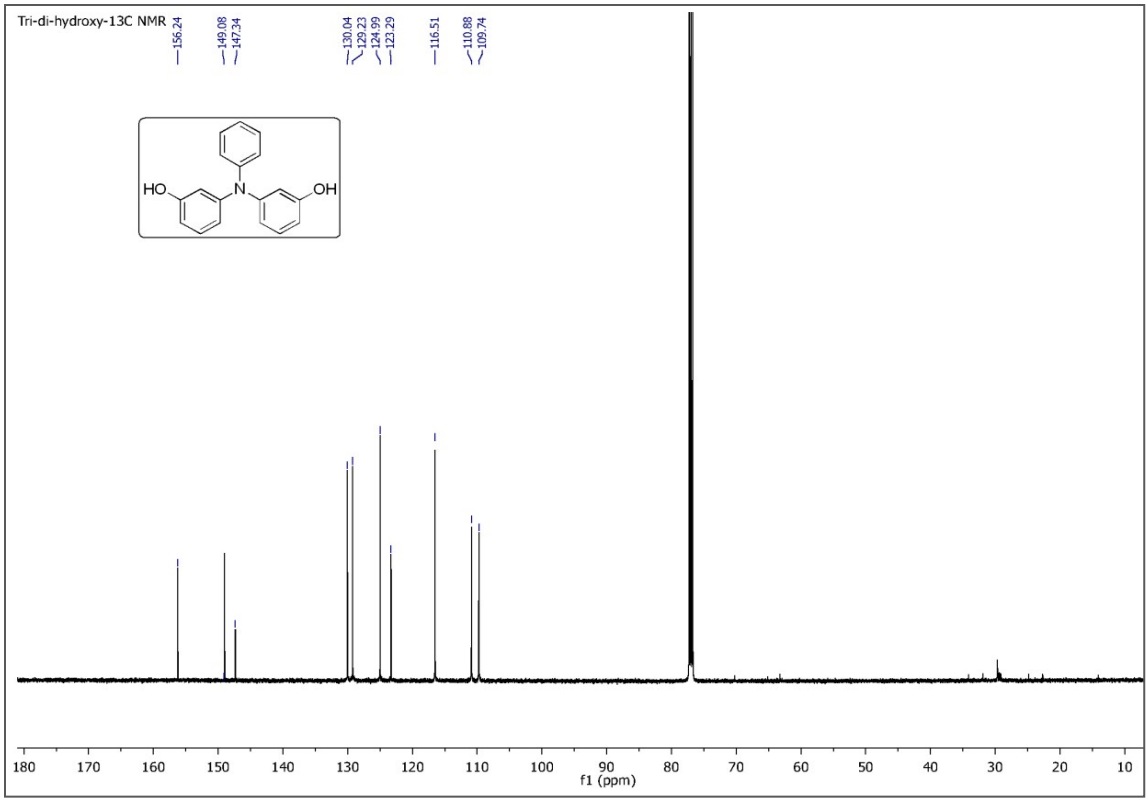
Table 5: Photophysical properties of **RH-5** in toluene, chloroform and ethanol solvent (spirocyclic and open form)

Solvent	λ_{abs} (nm)	$\varepsilon_{max} \times 10^4$ (M^{-1} cm^{-1})	fwhm (nm)	λ_{ems} (nm)	Stokes shift (nm)	Stokes shift (cm^{-1})	f	μ_{eg} (debye)	$K_r \times 10^8$ (cm^{-1})	Φ_F
Spirocyclic form										
Toluene	387	3.37	63	534	147	7113	0.63	7.23	2.31	---
$CHCl_3$	386	2.95	61	436	50	2971	0.55	6.73	2.98	---
EtOH	380	2.54	68	424	44	2731	0.49	6.27	2.61	---
Open form										
Toluene	605	5.78	96	635	30	781	1.17	12.28	1.85	0.71
$CHCl_3$	603	7.6	91	630	27	711	1.28	12.81	2.06	0.86
EtOH	610	8.05	82	646	36	914	1.16	12.25	1.94	0.59

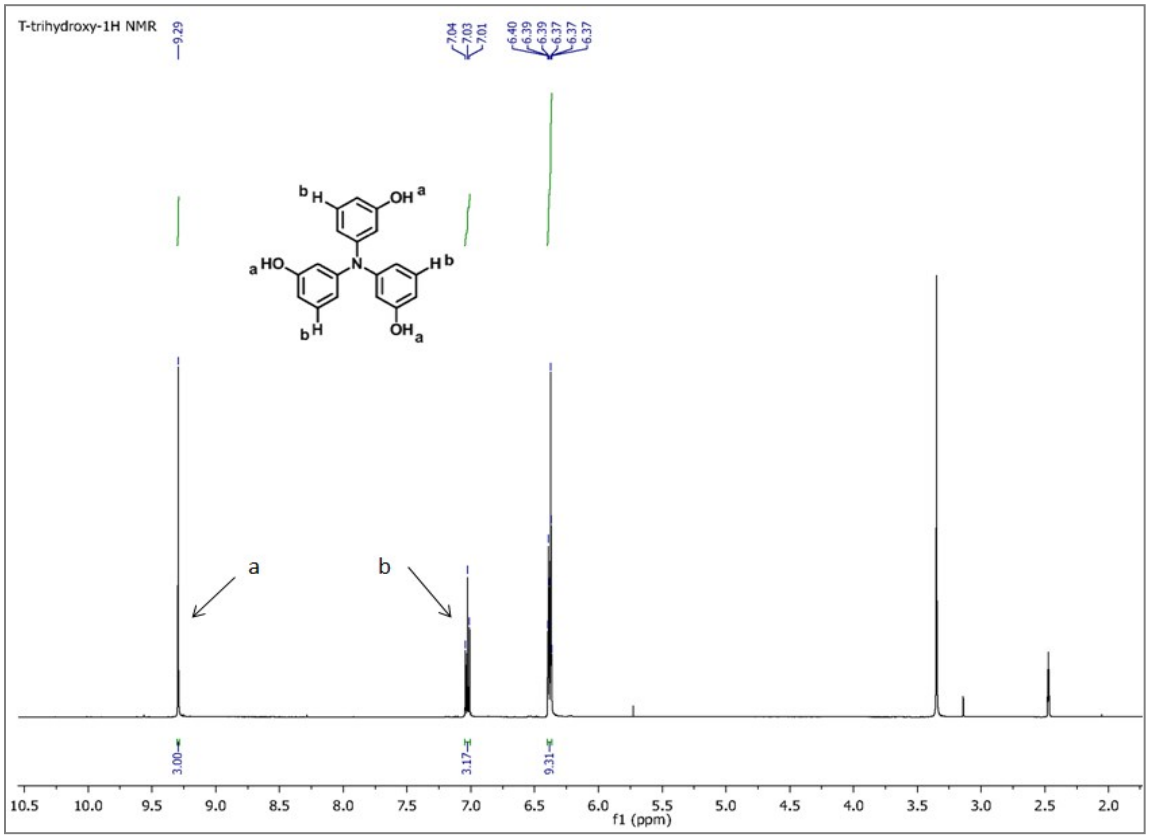
Spectrum S1: ^1H NMR spectra of **Compound 3** in $CDCl_3$



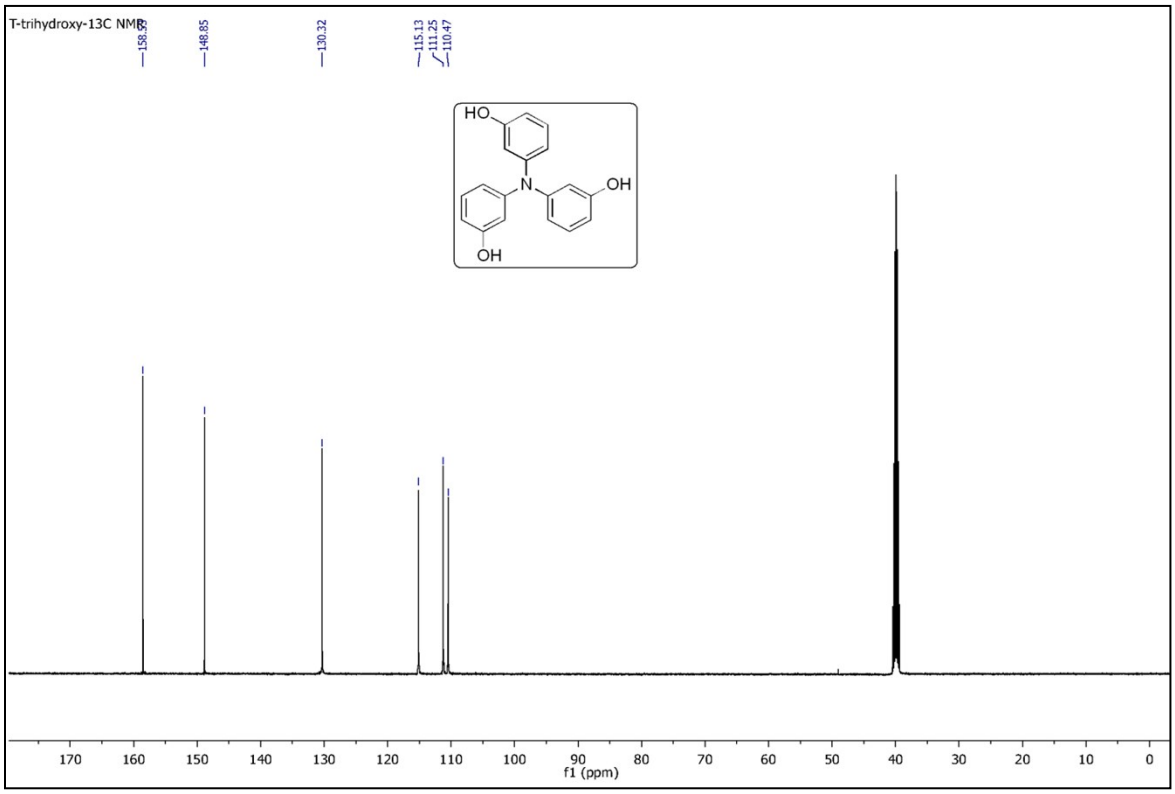
Spectrum S2: ^{13}C NMR spectra of **Compound 3** in $CDCl_3$



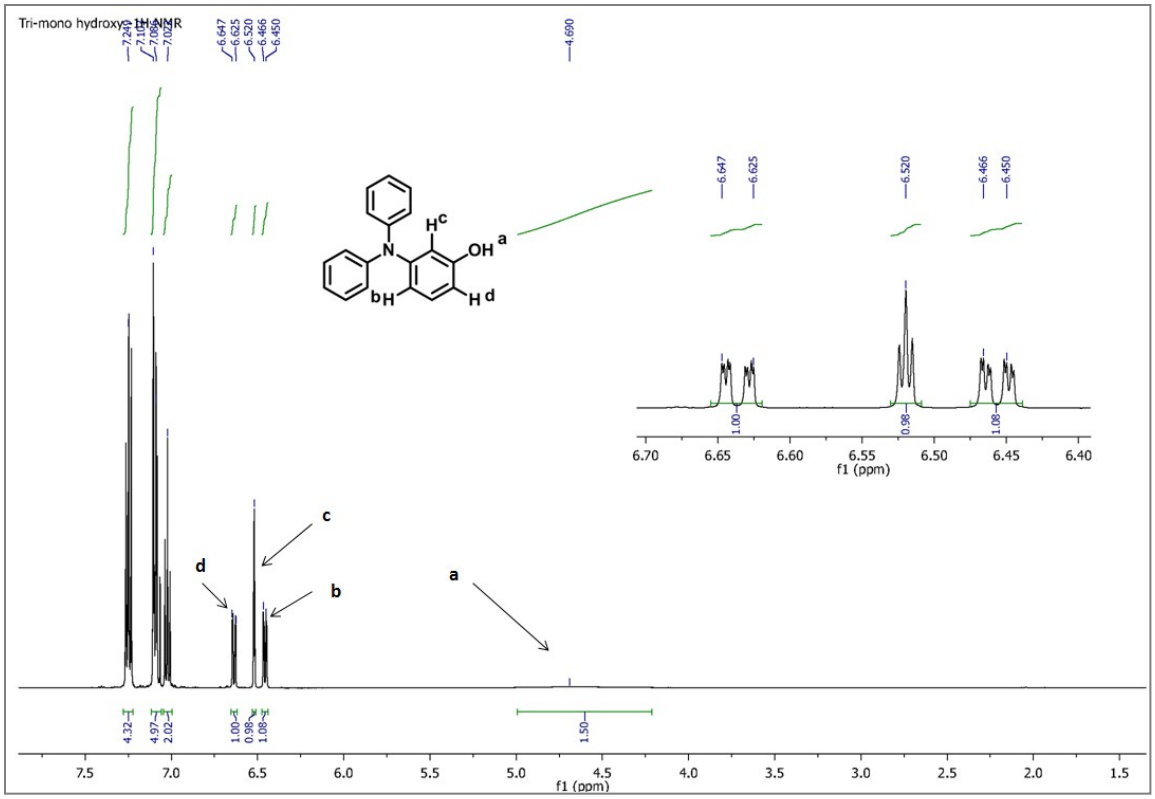
Spectrum S3: ^{1}H NMR spectra of **Compound 4** in $CDCl_3$



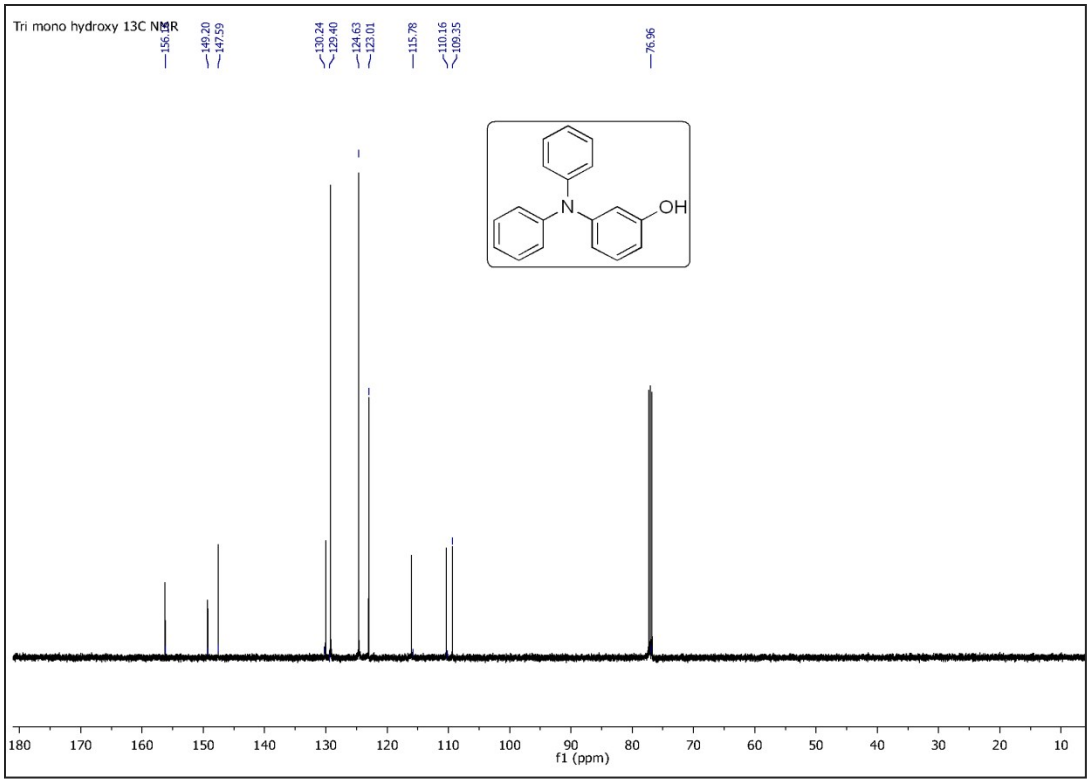
Spectrum S4: ^{13}C NMR spectra of **Compound 4** in $CDCl_3$



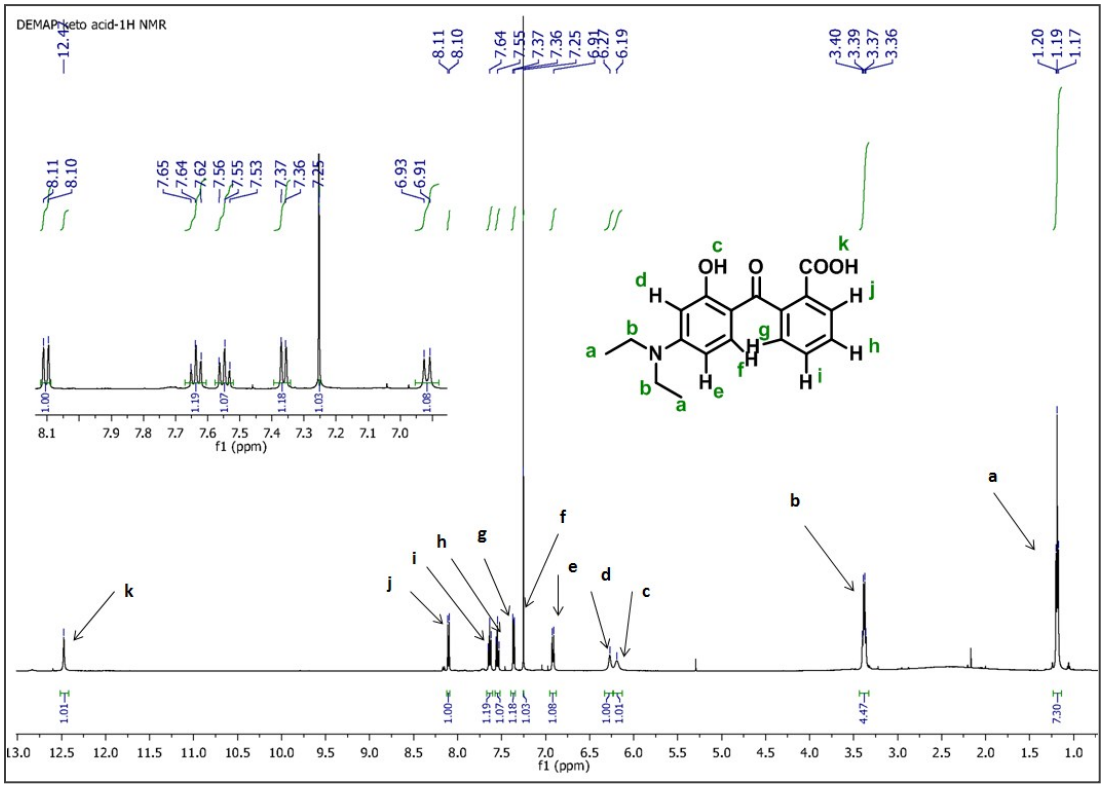
Spectrum S5: ^{1}H NMR spectra of compound **6** in $CDCl_3$



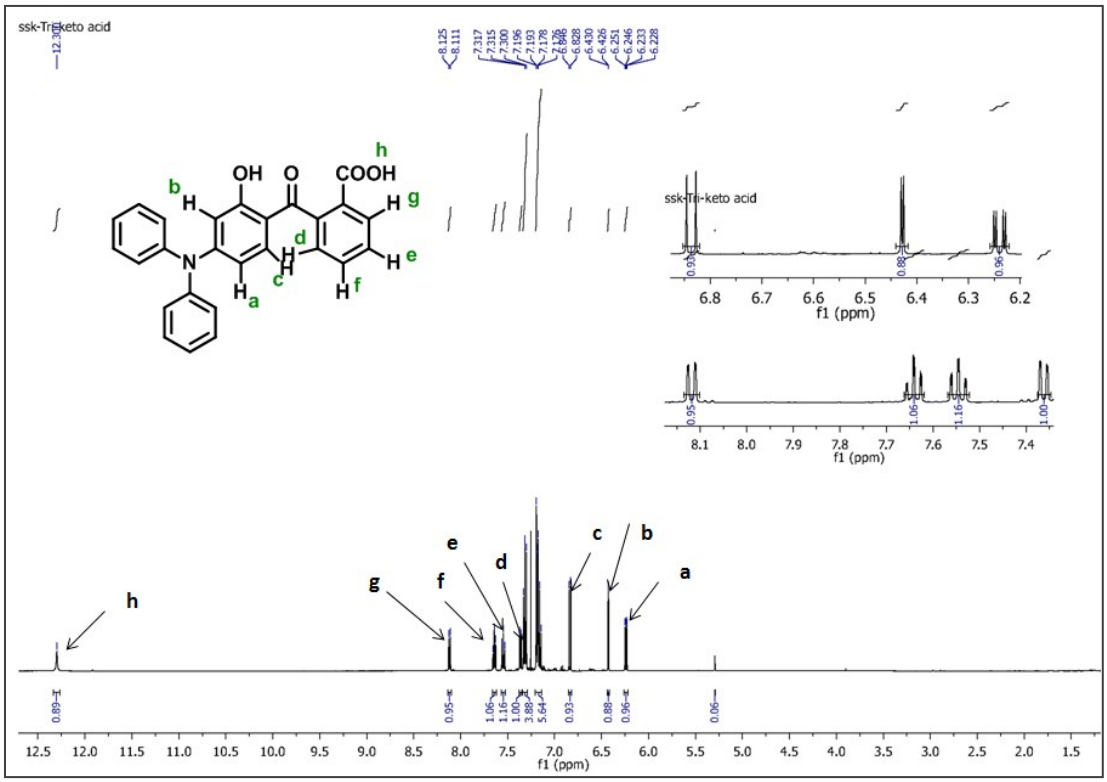
Spectrum S6: ^{13}C NMR spectra of compound **6** in $CDCl_3$



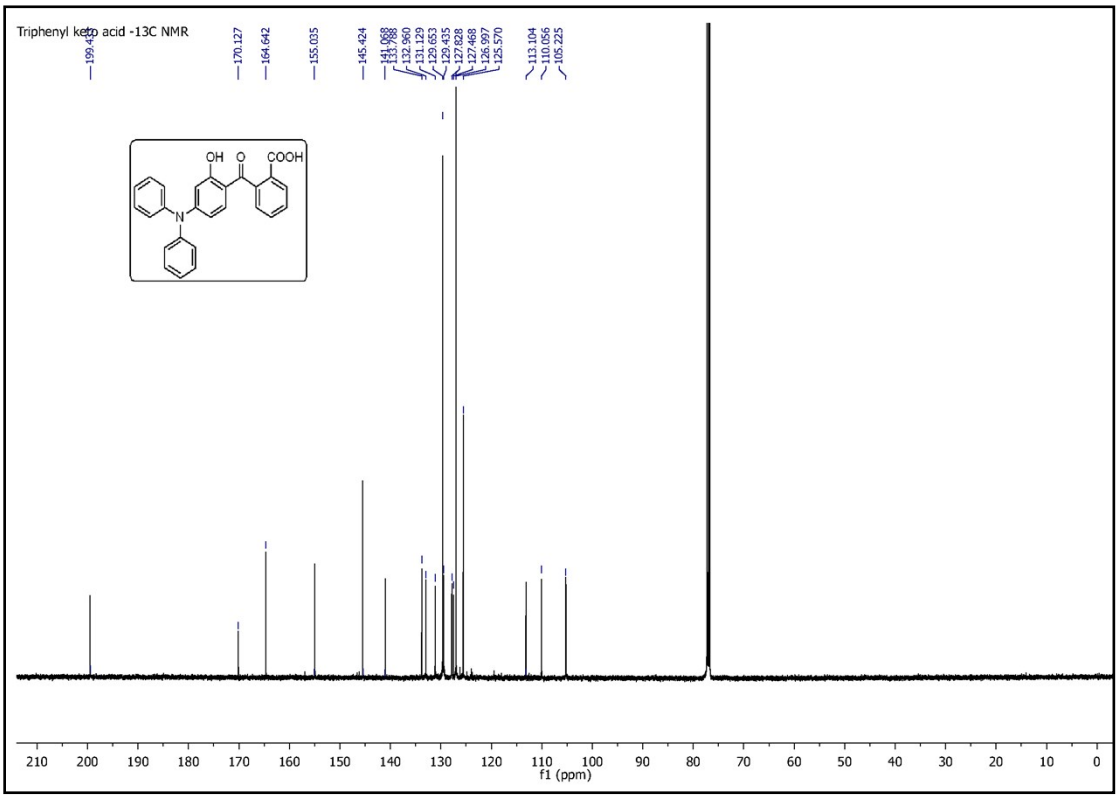
Spectrum S7: ^{1}H NMR spectra of **Intermediate A** in $CDCl_3$



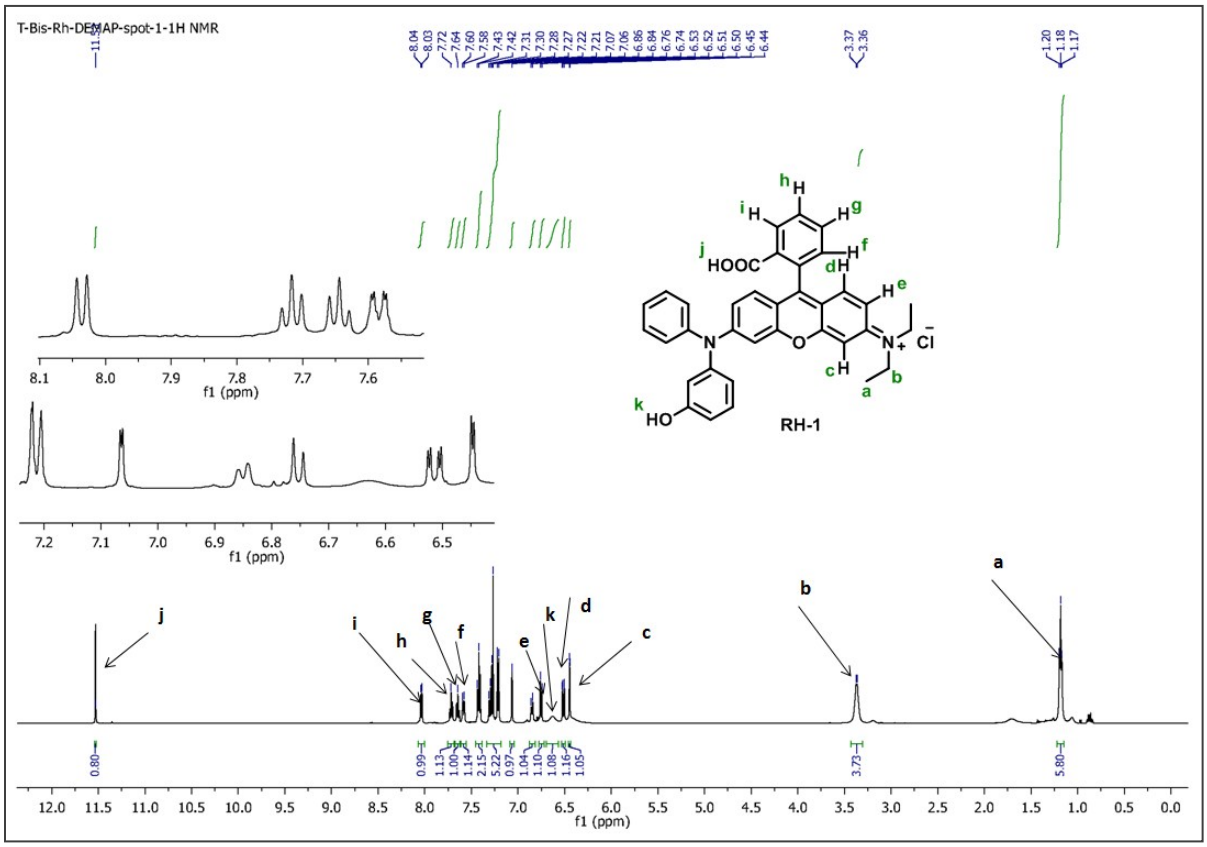
Spectrum S8: ^{1}H NMR spectra of **Intermediate B** in $CDCl_3$



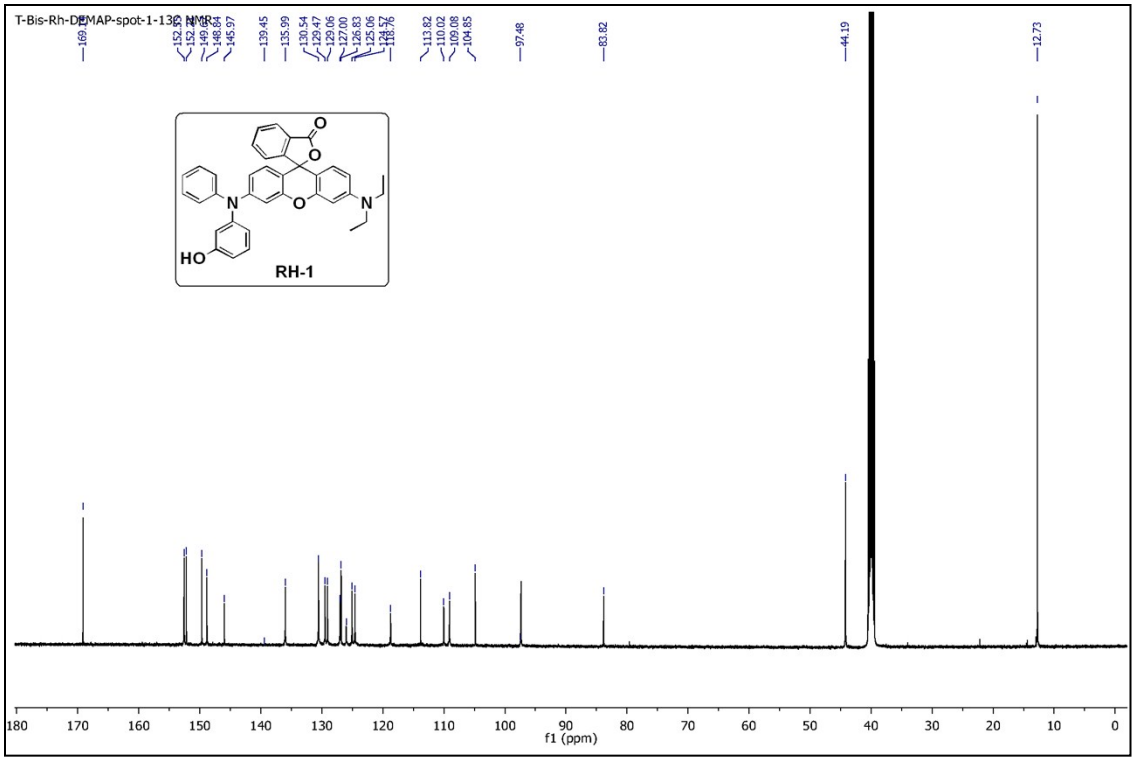
Spectrum S9: ^{13}C NMR spectra of **Intermediate B** in $CDCl_3$



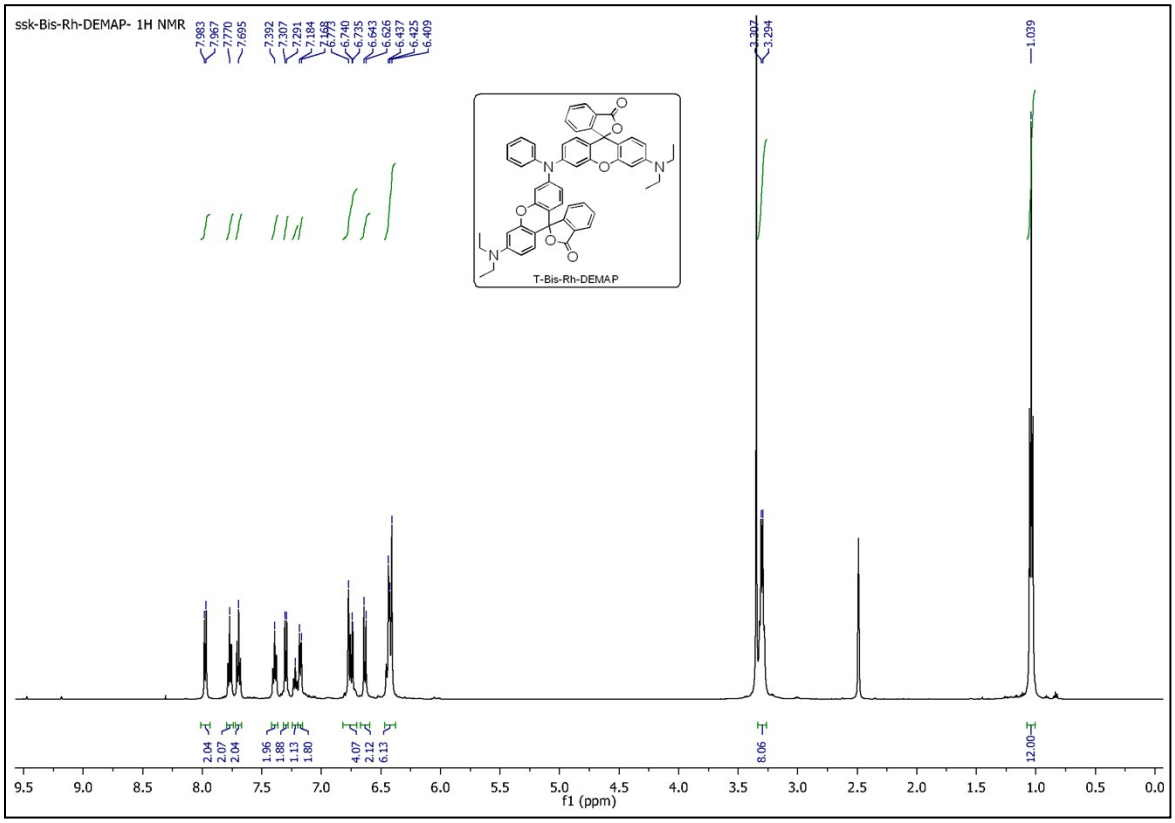
Spectrum S10: ^{1}H NMR spectra of **RH-1** in $CDCl_3$



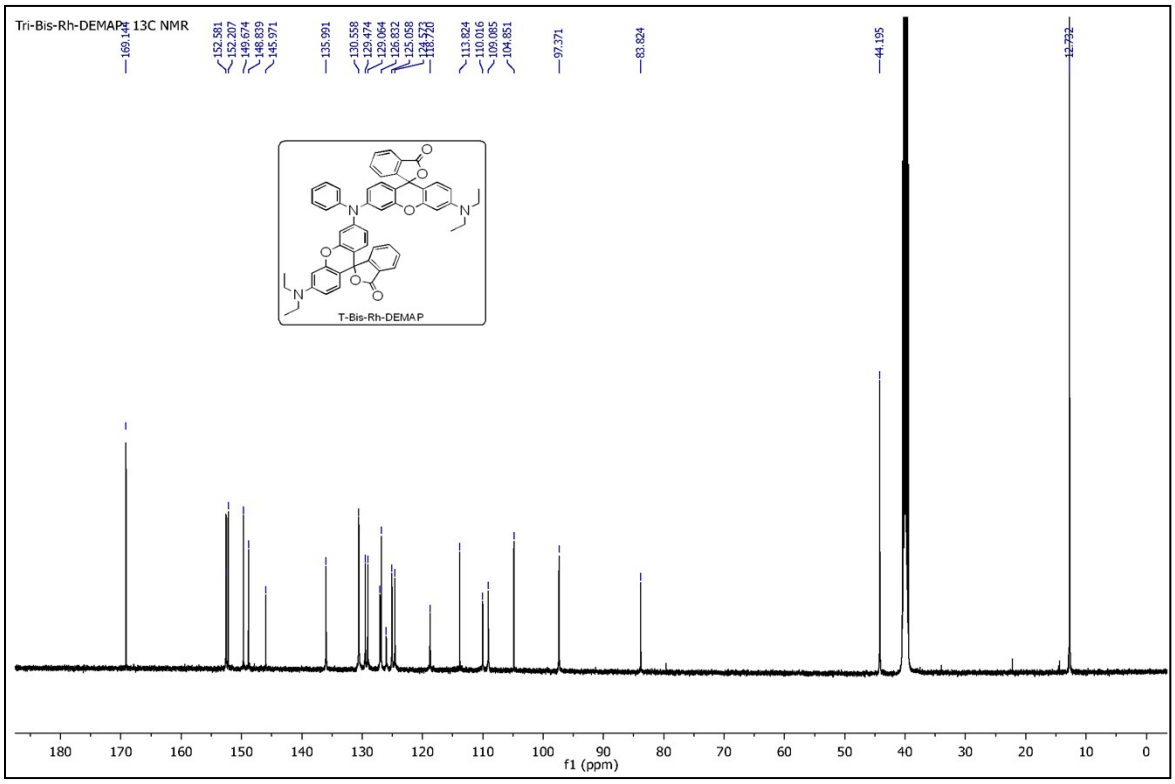
Spectrum S11: ^{13}C NMR spectra of **RH-1** in DMSO-d6



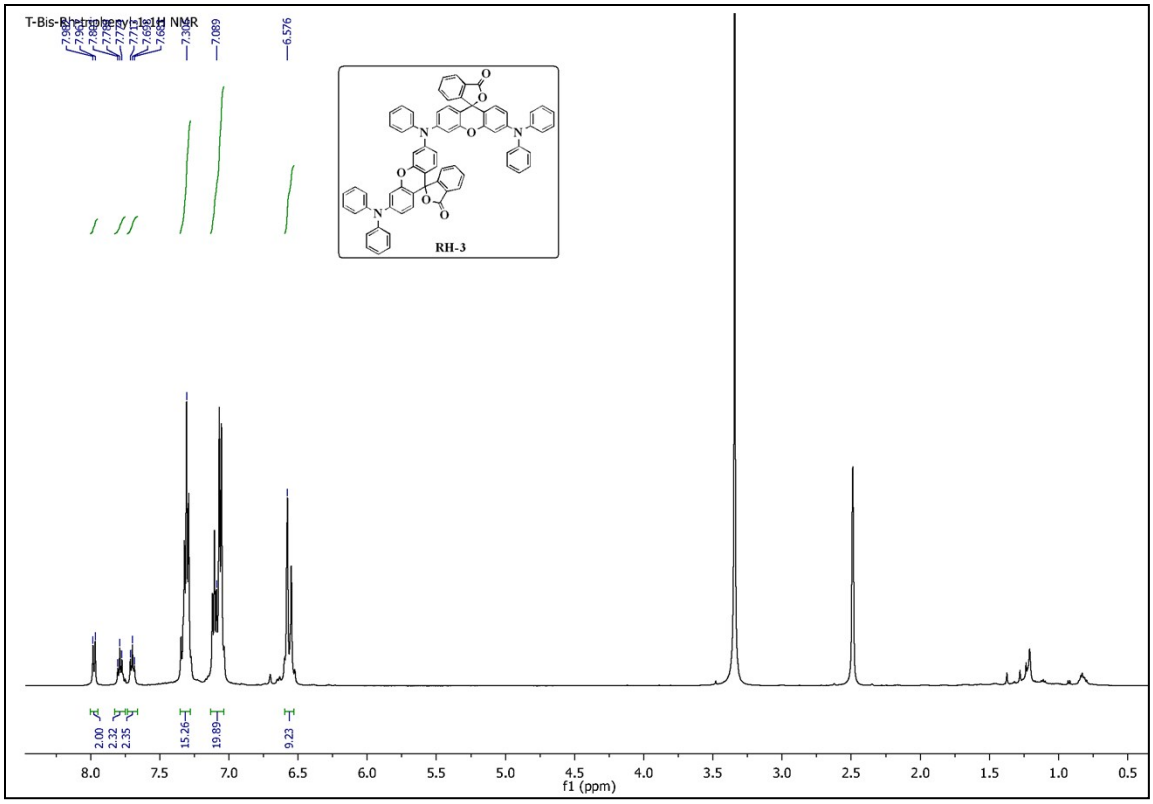
Spectrum S12: ^{1}H NMR spectra of **RH-2** in DMSO-d_6



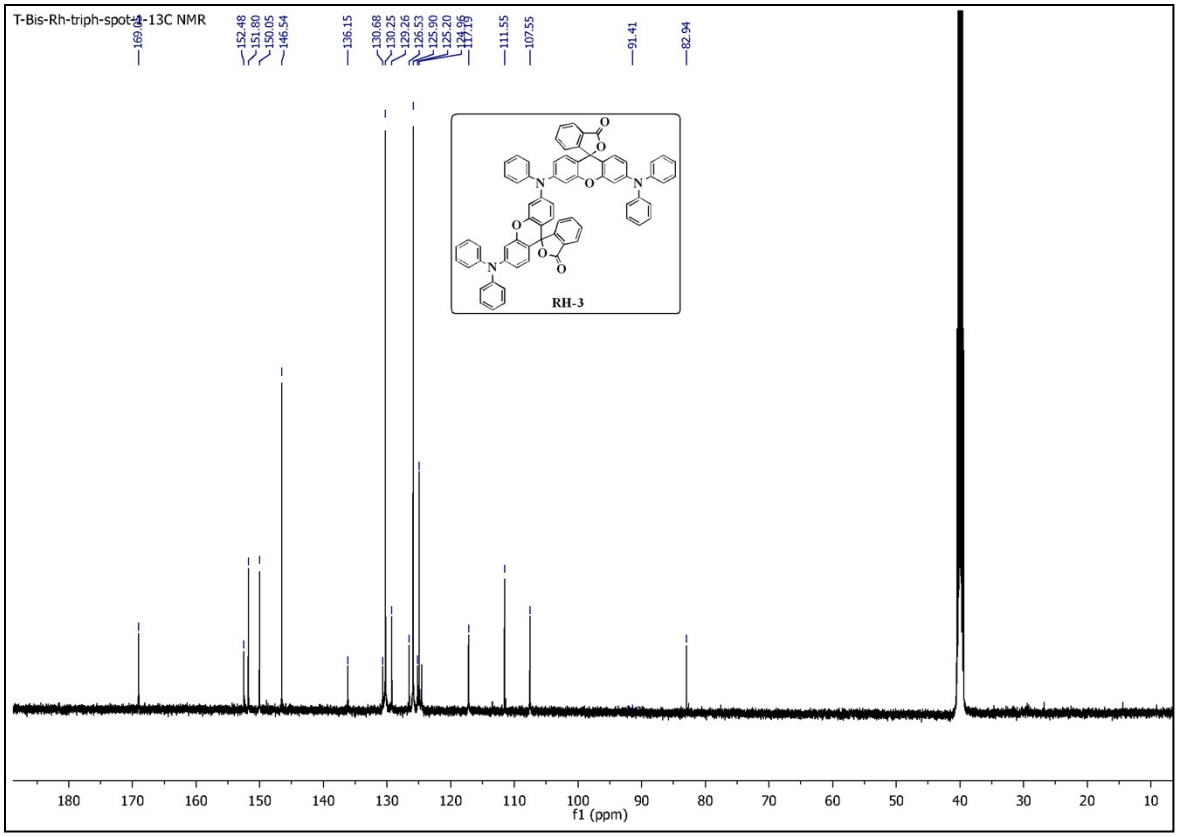
Spectrum S13: ^{13}C NMR spectra of **RH-2** in DMSO-d_6



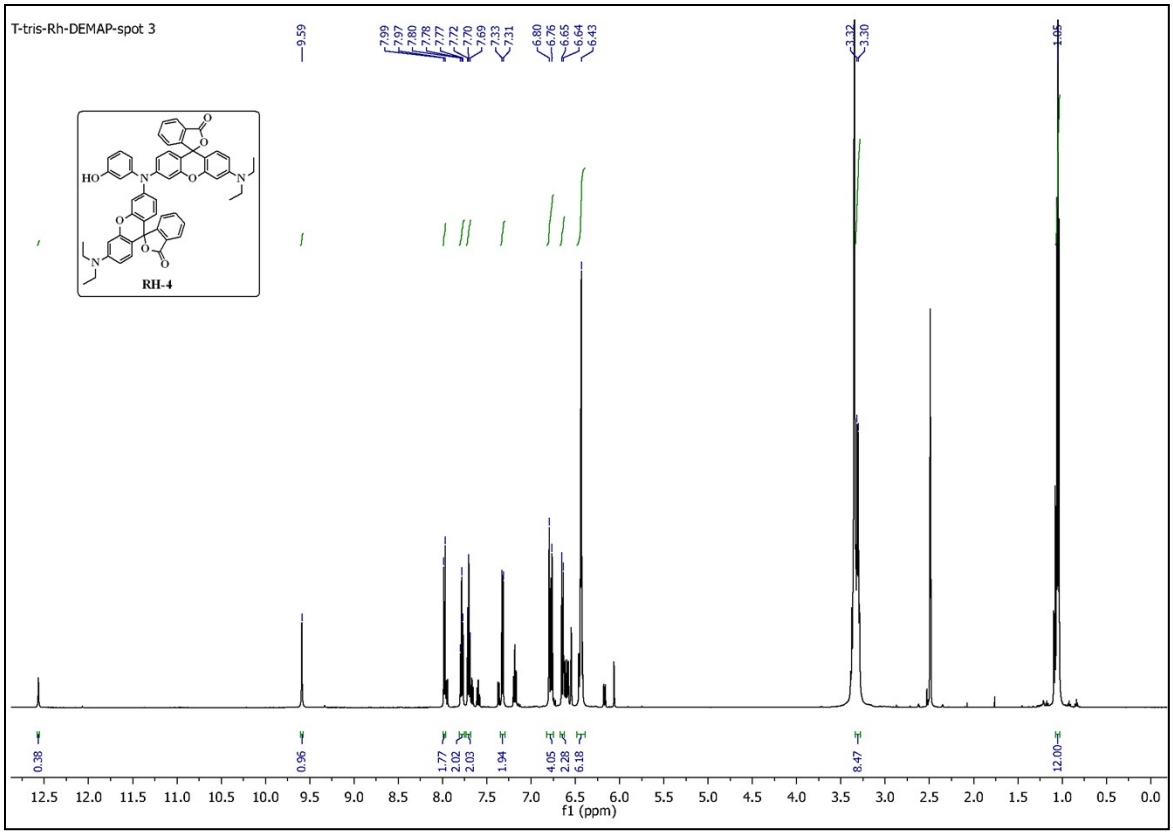
Spectrum S14: ^{1}H NMR spectra of **RH-3** in $CDCl_3$



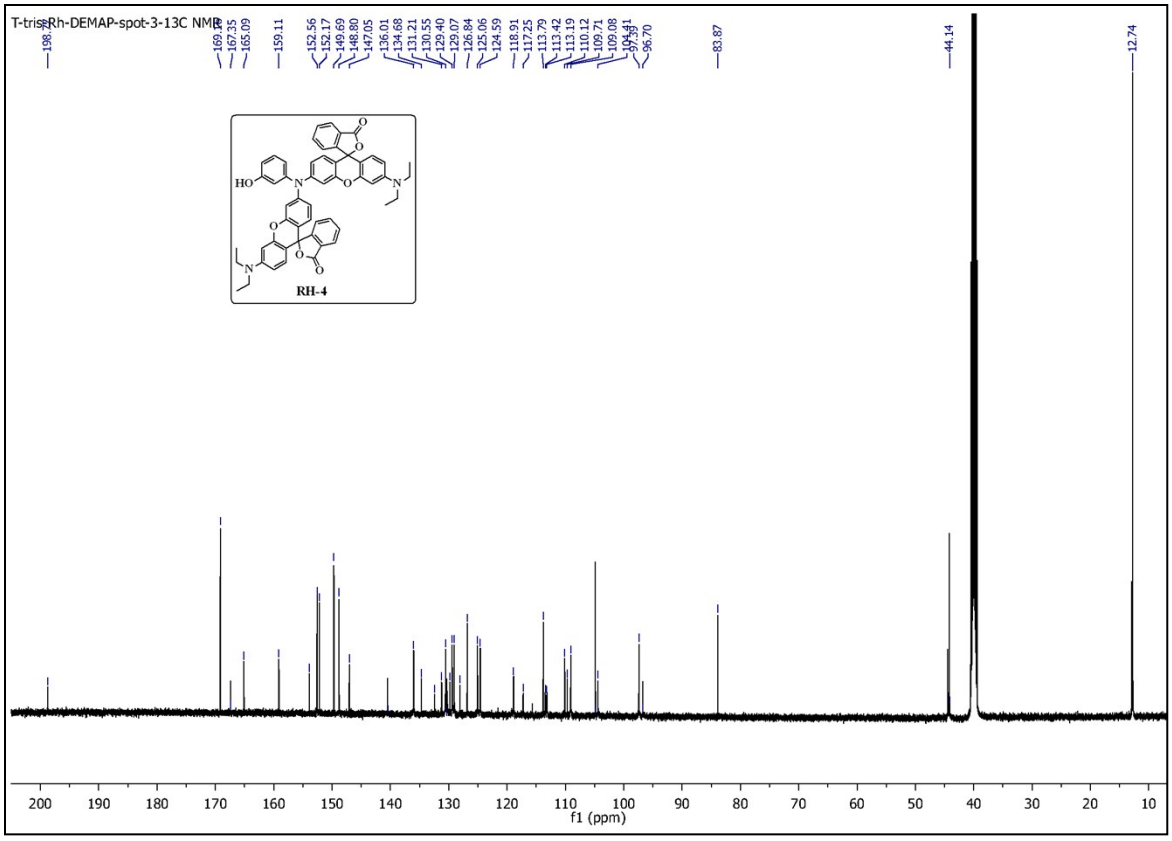
Spectrum S15: ^{13}C NMR spectra of **RH-3** in $CDCl_3$



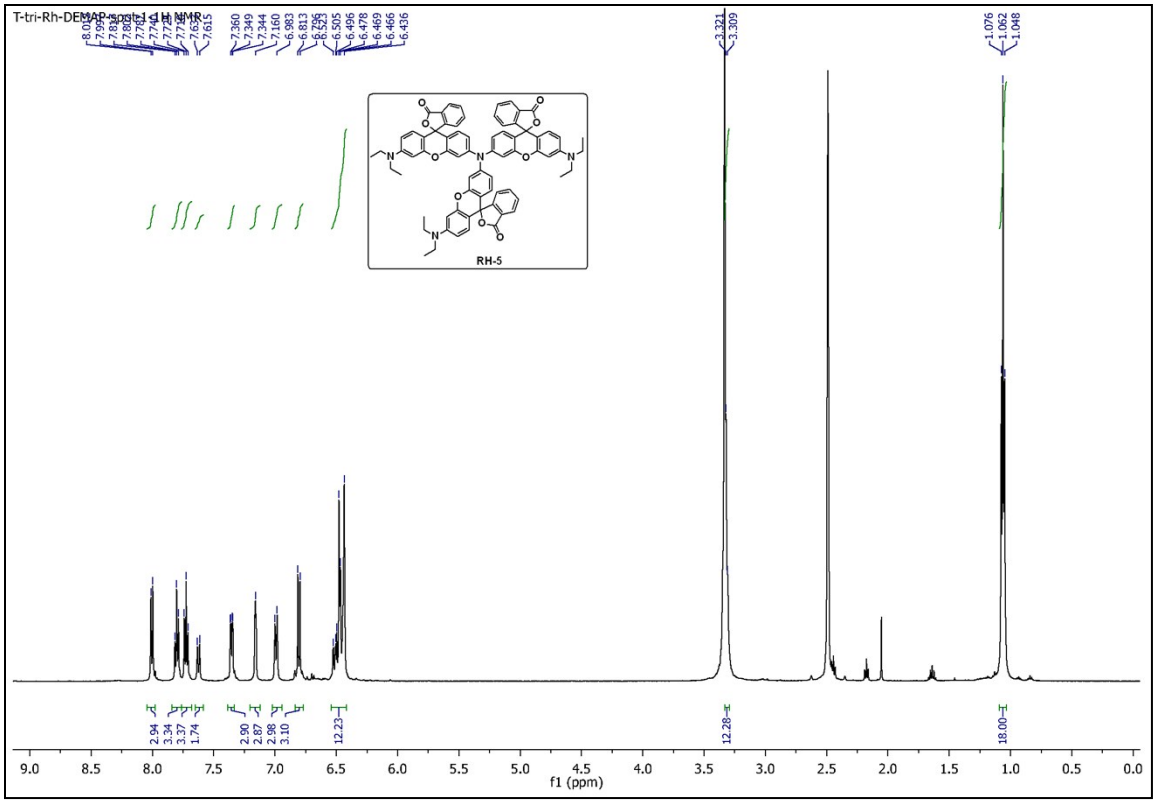
Spectrum S16: ^{1}H NMR spectra of **RH-4** in $CDCl_3$



Spectrum S17: ^{13}C NMR spectra of **RH-4** in $CDCl_3$



Spectrum S18: ^{1}H NMR spectra of **RH-5** in $CDCl_3$



Spectrum S19: ^{13}C NMR spectra of **RH-5** in $CDCl_3$