Electronic Supplementary Material (ESI) for RSC Advances.

A new type of triphenylamine based coumarin-rhodamine hybrid compounds: Synthesis, Photophysical properties, viscosity sensitivity and energy transfer

Shantaram Kothavale, Nagaiyan Sekar*

Department of Dyestuff Technology, Institute of Chemical Technology, Matunga,

Mumbai - 400 019, India.

E-mail: n.sekar@ictmumbai.edu.in, nethi.sekar@gmail.com

Tel: +91 22 3361 2707; Fax: +91 22 3361 1020.

Supporting information contents

List of Figures:

List of Tables:

List of Spectrum:

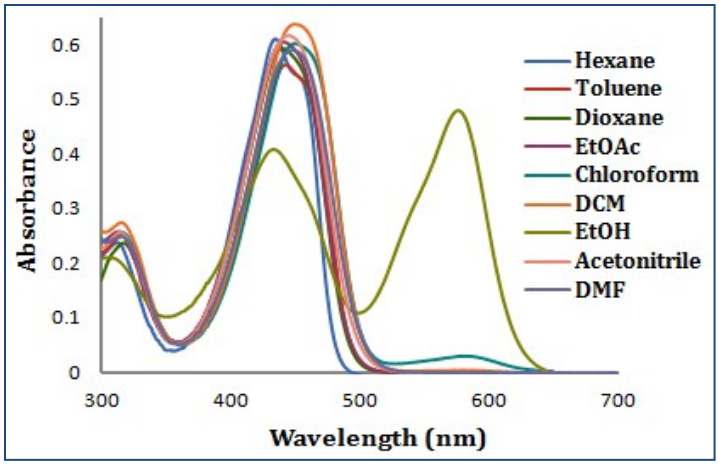


Figure S1: Absorption spectra of **MCMR** in all solvents (spirocyclic form)

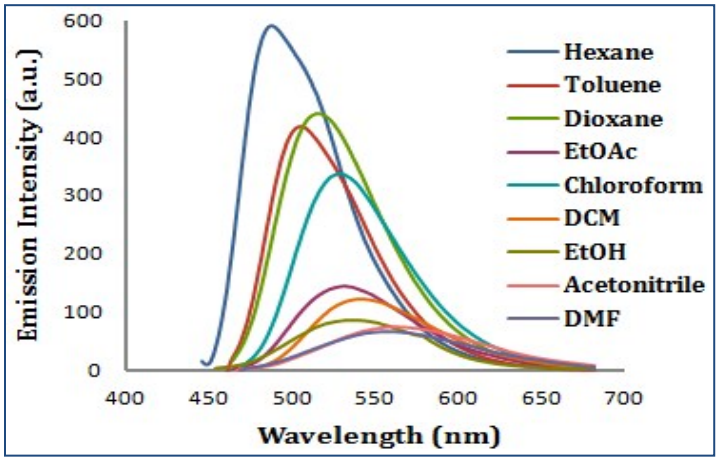


Figure S2: Emission spectra of **MCMR** in all solvents (spirocyclic form)

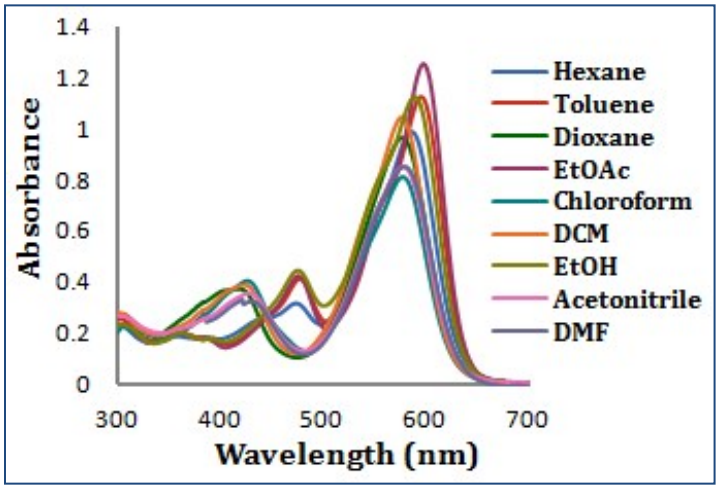


Figure S3: Absorption spectra of **MCMR** in all solvents (open form)

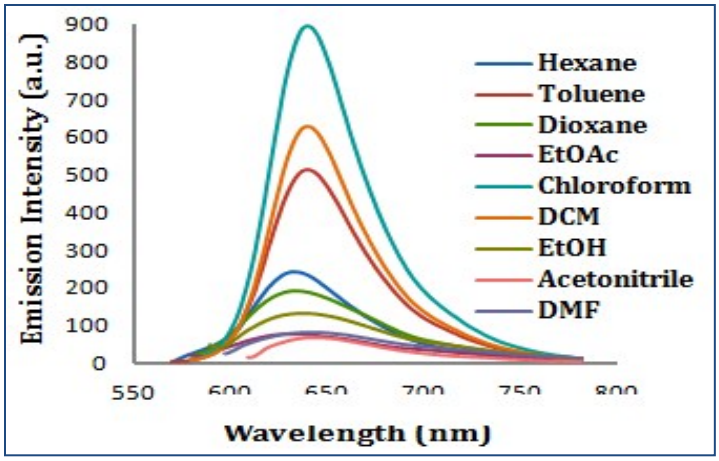


Figure S4: Emission spectra of **MCMR** in all solvents (open form)

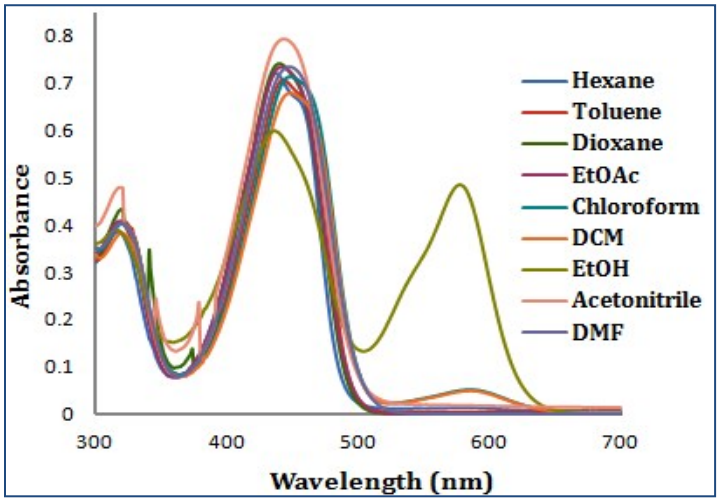


Figure S5: Absorption spectra of **MCDR** in all solvents (spirocyclic form)

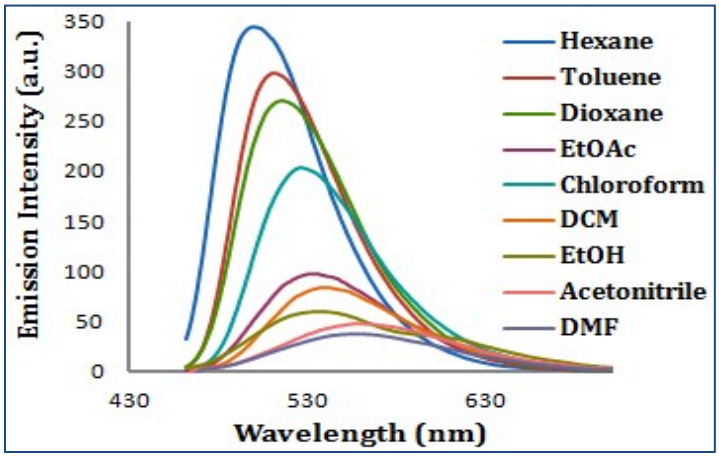


Figure S6: Emission spectra of **MCDR** in all solvents (spirocyclic form)

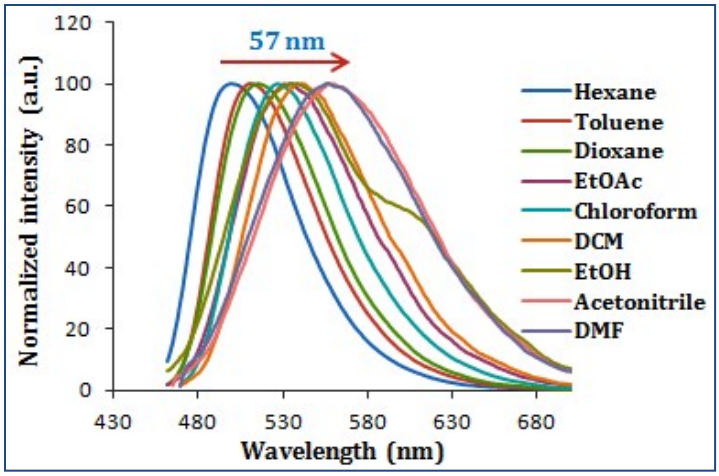


Figure S7: Normalized spectra of **MCDR** in all solvents (spirocyclic form)

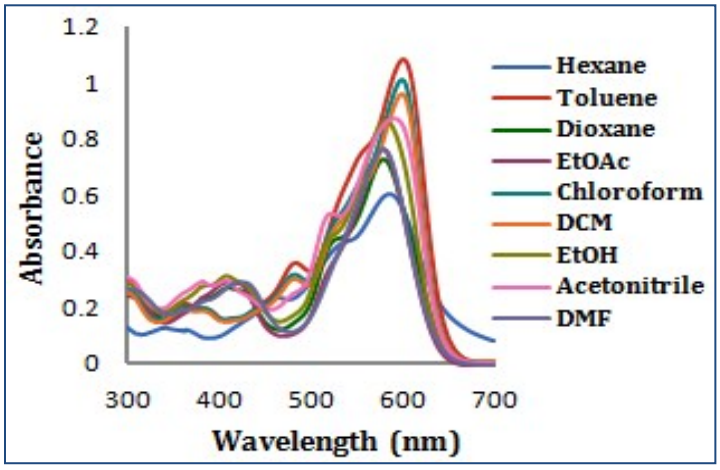


Figure S8: Absorption spectra of **MCDR** in all solvents (open form)

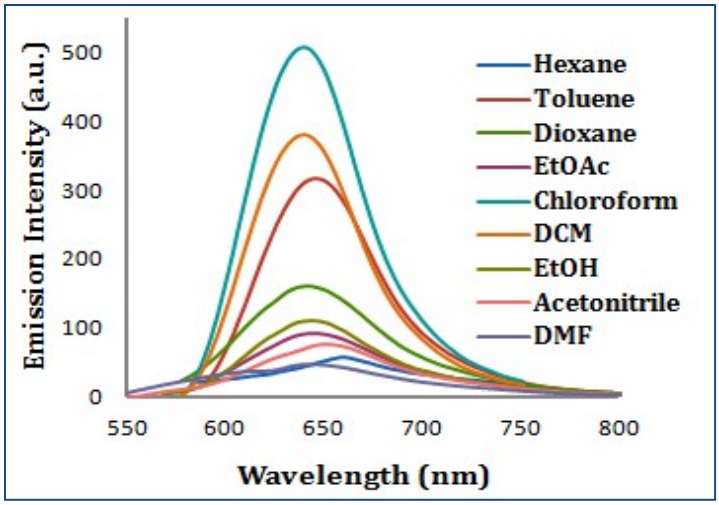


Figure S9: Emission spectra of **MCDR** in all solvents (open form)

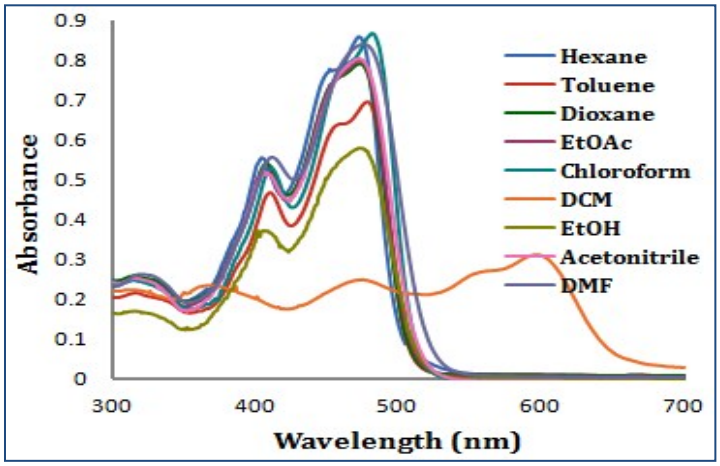


Figure S10: Absorption spectra of **DCDR** in all solvents (spirocyclic form)

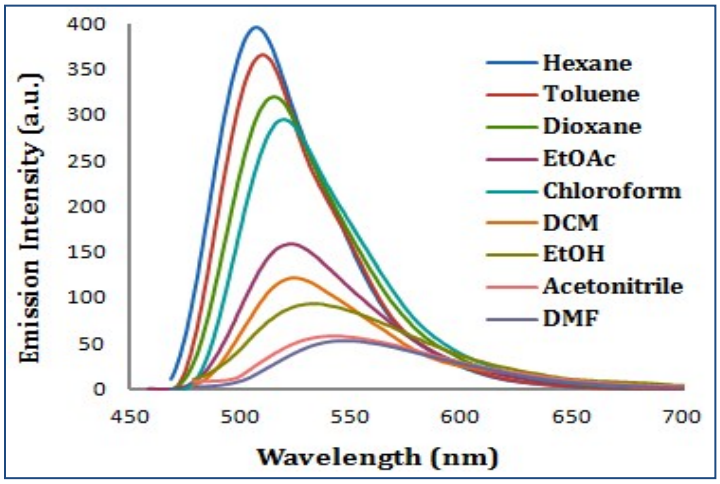


Figure S11: Emission spectra of **DCDR** in all solvents (spirocyclic form)

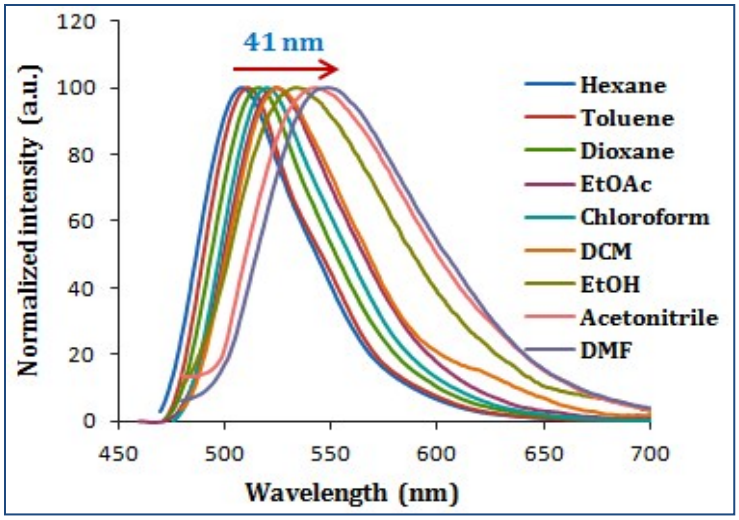


Figure S12: Normalized spectra of **DCDR** in all solvents (spirocyclic form)

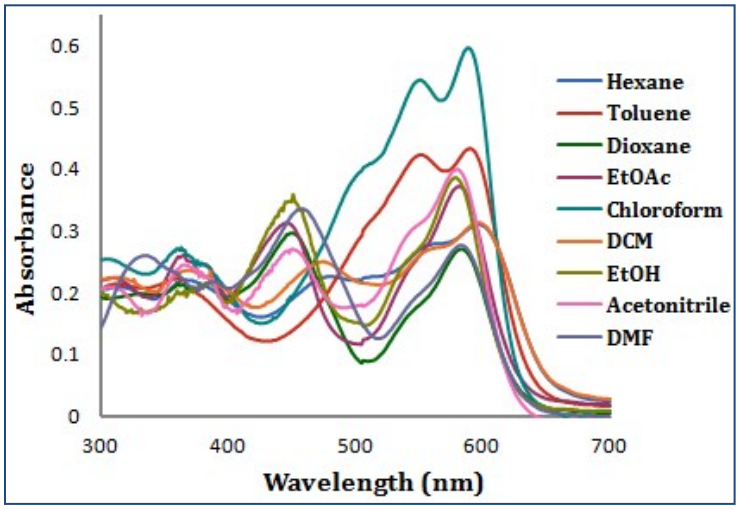


Figure S13: Absorption spectra of **DCDR** in all solvents (open form)

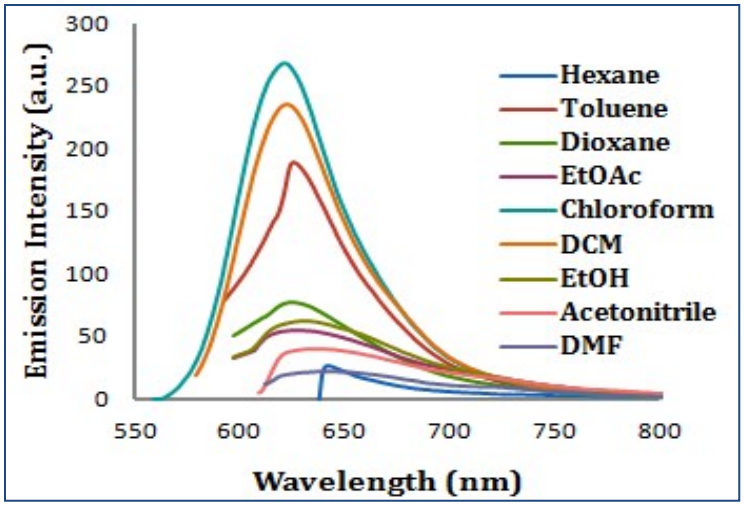


Figure S14: Emission spectra of **DCDR** in all solvents (open form)

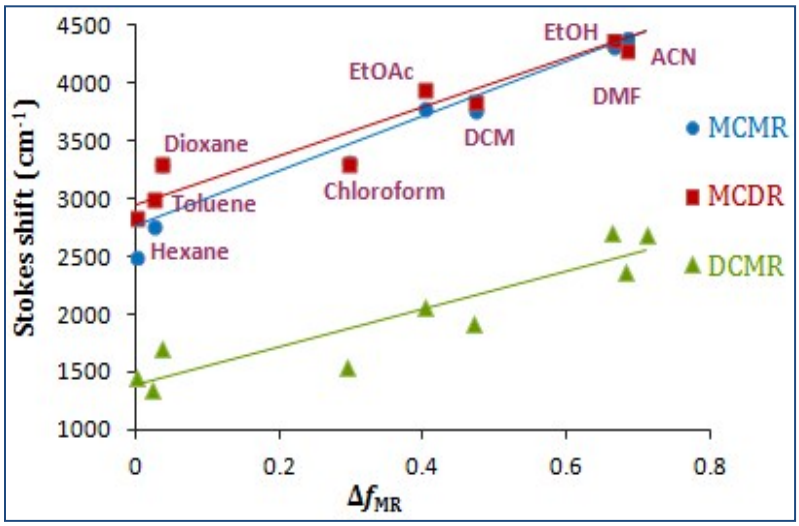


Figure S15: Mac-Rae solvent polarity plots of **MCMR, MCDR** and **DCMR** in all solvents

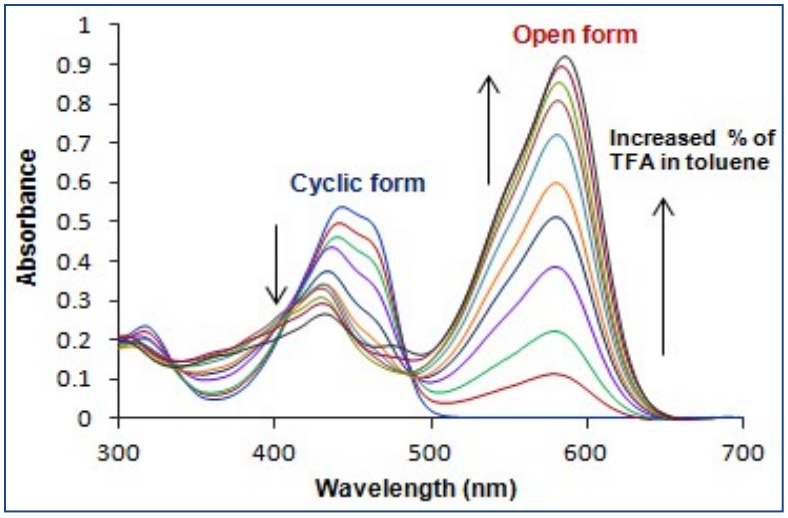


Figure S16: Absorption spectra of **MCMR** with the increased percentage of TFA (5 to 90 µl) in toluene

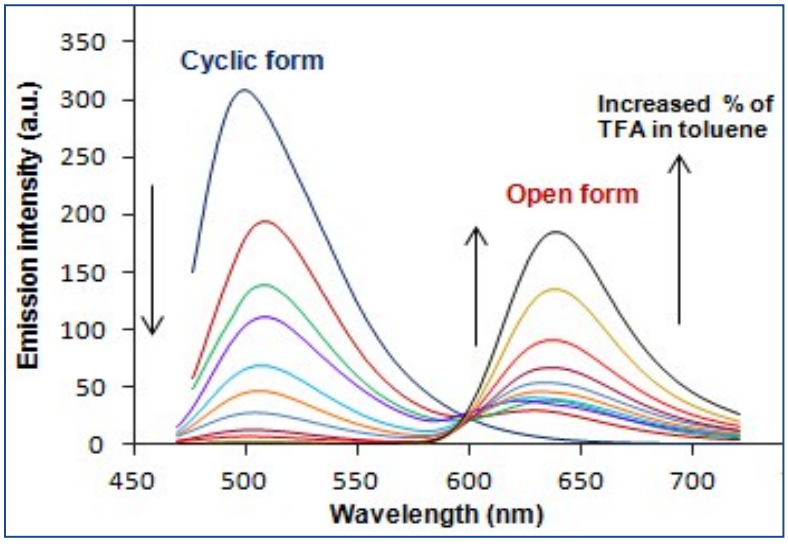


Figure S17: Emission spectra of **MCMR** with the increased percentage of TFA (5 to 90 µl) in toluene

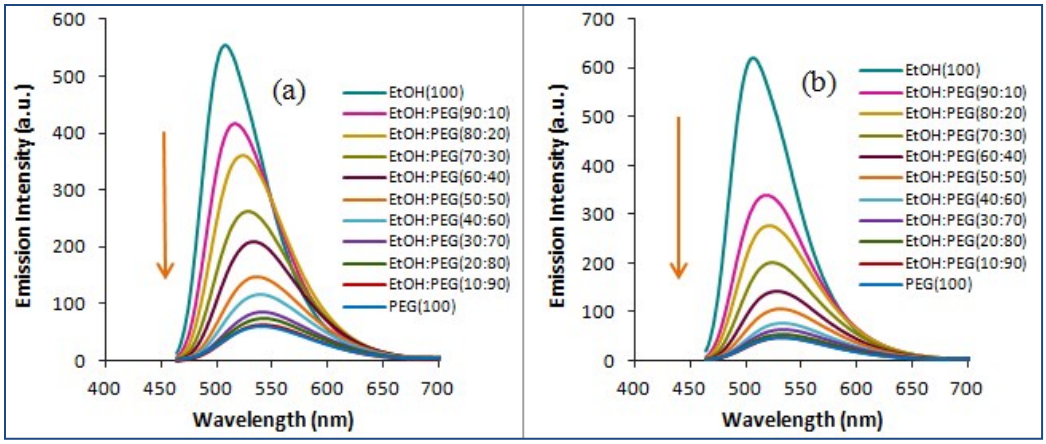


Figure S18: Emission spectra of **MCMR** (a) and **MCDR** (b) with the increased percentage of PEG in ethanol for their spirocyclic form.

Table S1: Photophysical parameters of **MCMR** in all solvents (spirocyclic form)

Compound	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_{ge} (debye)
Hexane	435	6.11	64	488	53	2497	0.98	9.55
Toluene	443	5.62	68	505	62	2771	0.98	9.61
Dioxane	440	5.94	68	515	75	3310	1.05	9.90
EtOAc	442	6.04	68	531	89	3792	1.06	10.01
$CHCl_3$	450	6.00	70	529	79	3319	1.07	10.11
DCM	450	6.37	70	542	92	3772	1.12	10.38
EtOH	434	4.09	83	536	102	4385	0.95	9.38
ACN	446	6.16	70	560	114	4564	1.11	10.25
DMF	449	5.90	72	557	108	4318	1.07	10.12

Table S2: Photophysical parameters of **MCMR** in all solvents (open form)

Compound	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_{ge} (debye)
Hexane	586	9.85	77	632	46	1242	1.26	12.54
Toluene	596	11.21	74	639	43	1129	1.40	13.33
Dioxane	577	9.60	73	633	56	1533	1.09	11.59
EtOAc	598	12.50	68	630	32	849	1.44	13.55
$CHCl_3$	577	8.09	74	639	62	1682	0.95	10.83

DCM	577	10.42	71	639	62	1682	1.15	11.90
EtOH	589	11.24	79	637	48	1279	1.52	13.83
ACN	578	8.53	75	643	65	1749	1.03	11.24
DMF	579	8.49	76	642	63	1695	1.02	11.19

Table S3: Photophysical parameters of **MCDR** in all solvents (spirocyclic form)

Compound	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_{ge} (debye)
Hexane	438	7.22	67	500	62	2831	1.22	10.66
Toluene	443	7.08	69	511	68	3004	1.21	10.70
Dioxane	441	7.41	68	516	75	3296	1.28	10.95
EtOAc	441	7.35	69	534	93	3949	1.28	10.95
$CHCl_3$	448	7.16	71	526	78	3310	1.27	10.99
DCM	448	6.80	71	541	93	3837	1.20	10.71
EtOH	436	5.99	81	536	100	4279	1.27	10.88
ACN	443	7.94	72	558	115	4652	1.47	11.79
DMF	448	7.36	71	557	109	4368	1.31	11.20

Table S4: Photophysical parameters of **MCDR** in all solvents (open form)

Compound	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_{ge} (debye)
Hexane	586	6.05	124	660	74	1913	1.05	11.45
Toluene	601	10.83	100	646	45	1159	1.52	13.95
Dioxane	580	7.24	101	642	62	1665	0.97	10.94
EtOAc	579	7.60	81	644	65	1743	0.91	10.57
$CHCl_3$	600	10.10	96	640	40	1042	1.35	13.14
DCM	600	9.60	96	640	40	1042	1.28	12.81
EtOH	582	8.63	98	644	62	1654	1.14	11.89
ACN	591	8.70	114	652	61	1583	1.30	12.80
DMF	580	7.60	82	642	62	1665	0.92	10.67

Table S5: Photophysical parameters of **DCMR** in all solvents (spirocyclic form)

Compound	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_{ge} (debye)
Hexane	472	8.58	94	507	35	1463	1.79	13.42

Toluene	478	6.95	96	511	33	1351	1.48	12.26
Dioxane	474	7.91	99	516	42	1717	1.73	13.23
EtOAc	472	8.02	99	523	51	2066	1.74	13.22
$CHCl_3$	481	8.68	97	520	39	1559	1.76	13.43
DCM	476	2.5	163	524	48	1924	0.85	9.27
EtOH	473	5.79	102	533	60	2380	1.27	11.30
ACN	473	8.05	102	542	69	2691	1.75	13.29
DMF	477	8.41	106	548	71	2716	1.92	13.97

Table S6: Photophysical parameters of **DCMR** in all solvents (open form)

Compound	λ_{abs} (nm)	$\varepsilon_{max} \times 10^4$ (M^{-1} cm^{-1})	**fwhm** (nm)	λ_{ems} (nm)	**Stokes shift** (nm)	(cm^{-1})	**f**	μ_{ge} (debye)
Hexane	595	3.11	129	642	47	1230	0.49	7.92
Toluene	590	4.33	116	626	36	975	0.65	9.04
Dioxane	582	5.94	77	625	43	1182	0.29	6.02
EtOAc	581	3.73	78	628	47	1288	0.41	7.16
$CHCl_3$	588	5.96	109	621	33	904	0.80	9.99
DCM	595	3.12	129	622	27	730	0.48	7.83
EtOH	578	3.87	77	631	53	1453	0.42	7.15
ACN	580	4.01	86	636	56	1518	0.45	7.47
DMF	582	3.36	108	643	61	1630	0.32	6.27

Table S7: Estimated coefficients (y_0, a, b, c, d), their standard errors and correlation coefficients (r) for the multi-linear analyis of ($\bar{\upsilon}_{abs}$), ($\bar{\upsilon}_{emi}$) and ($\Delta\bar{\upsilon}$) of **MCDR** as a function of Kamlet-Taft (2) and Catalan (3) solvent scales. Where, α or SA for solvent acidity, β or SB for solvent basicity, π* for collective parameter of solvent dipolarity and polarizability in the case of Kamlet-Taft equation, SdP and SP for solvent dipolarity and polarizability respectively in the case of Catalan equation.

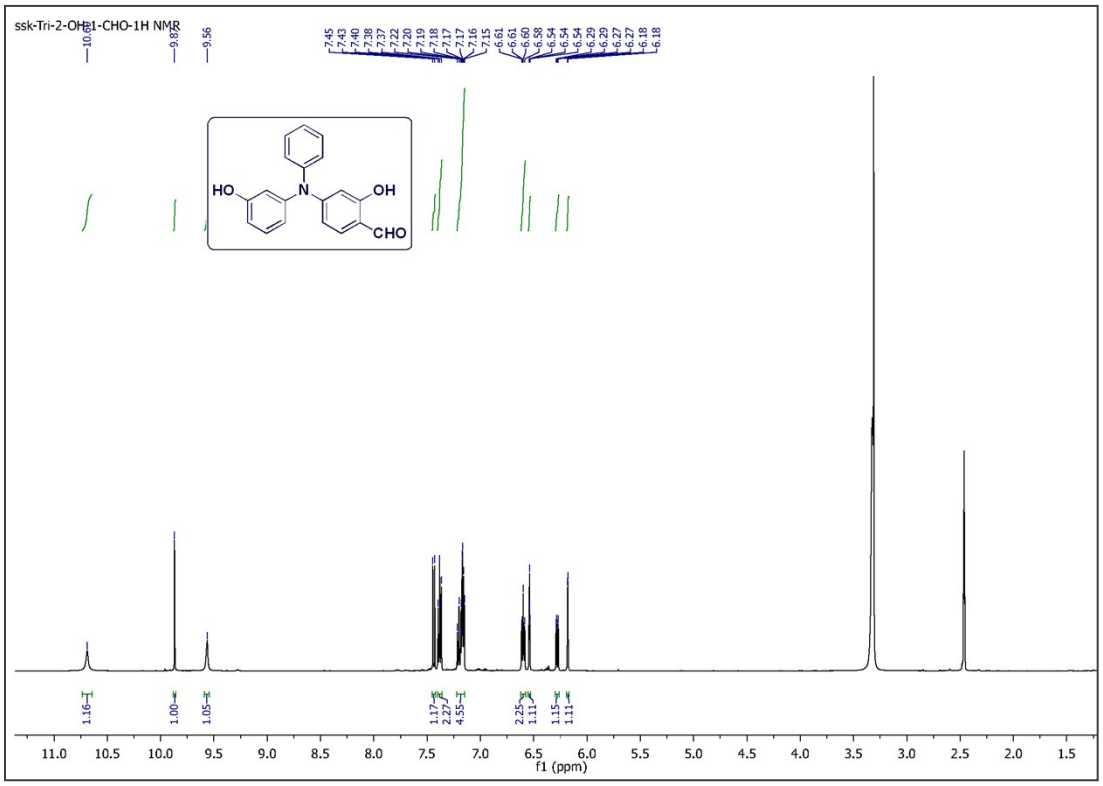
Kamlet-Taft	$y_0 \times 10^3$	a_α	b_β	c_{π^*}		**r**
$\bar{\upsilon}_{abs}$	22.84 ± 0.10	0.15 ± 0.19	0.48 ± 0.21	-0.76 ± 0.19		0.69
$\bar{\upsilon}_{emi}$	20.14 ± 0.34	-0.34 ± 0.62	-0.44 ± 0.71	-1.86 ± 0.63		0.65
$\Delta\bar{\upsilon}$	2.70 ± 0.34	0.49 ± 0.62	0.92 ± 0.71	1.10 ± 0.63		0.58
Catalan	$y_0 \times 10^3$	a_{SA}	b_{SB}	c_{SdP}	d_{SP}	**r**
$\bar{\upsilon}_{abs}$	23.96 ± 0.20	0.41 ± 0.20	0.40 ± 0.12	-0.41 ± 0.08	-1.81 ± 0.29	0.93

$\bar{\upsilon}_{emi}$	20.04 ± 0.70	0.36 ± 0.70	0.04 ± 0.40	-2.08 ± 0.26	0.08 ± 0.99	0.92
$\Delta\bar{\upsilon}$	3.92 ± 0.71	0.05 ± 0.71	0.36 ± 0.40	1.67 ± 0.26	-1.88 ± 1.00	0.89

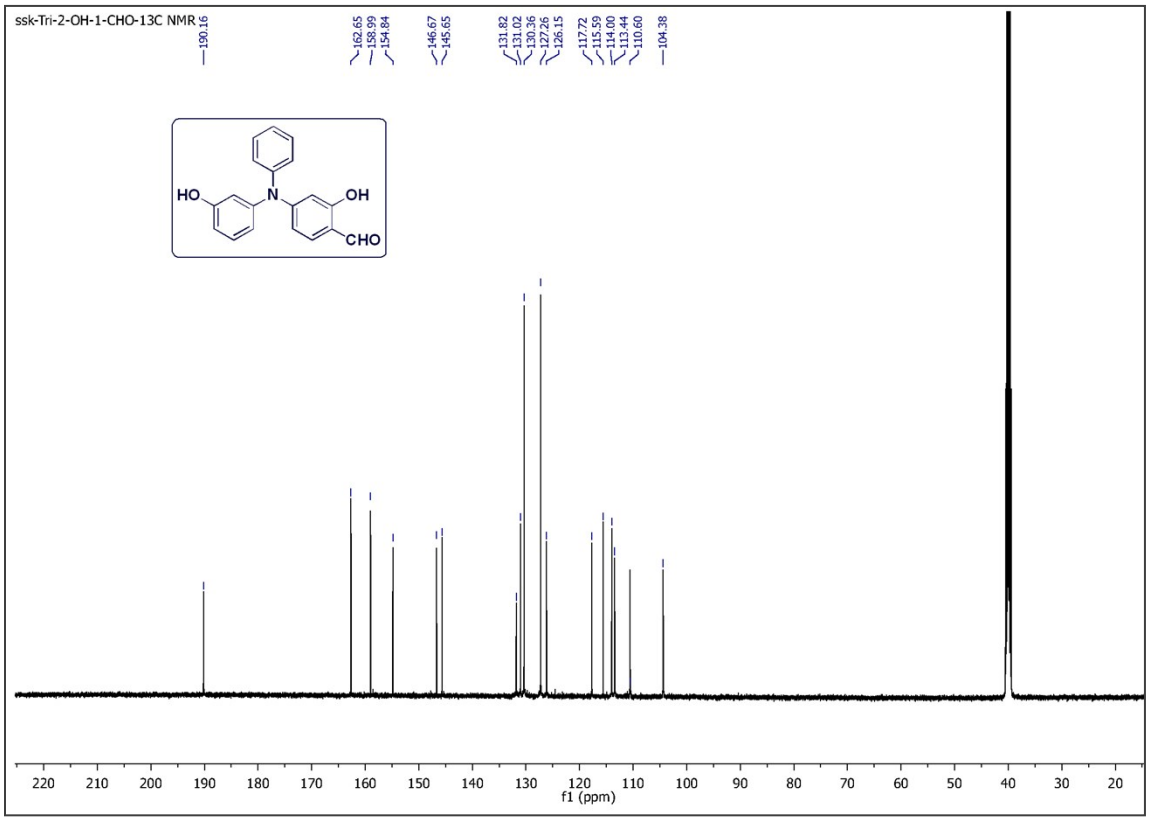
Table S8: Estimated coefficients (y_0, a, b, c, d), their standard errors and correlation coefficients (r) for the multi-linear analyis of ($\bar{\upsilon}_{abs}$), ($\bar{\upsilon}_{emi}$) and ($\Delta\bar{\upsilon}$) of **DCMR** as a function of Kamlet-Taft (2) and Catalan (3) solvent scales. Where, α or SA for solvent acidity, β or SB for solvent basicity, π* for collective parameter of solvent dipolarity and polarizability in the case of Kamlet-Taft equation, SdP and SP for solvent dipolarity and polarizability respectively in the case of Catalan equation.

Kamlet-Taft	$y_0 \times 10^3$	a_α	b_β	c_{π^*}		r
$\bar{\upsilon}_{abs}$	21.14 ± 0.11	-0.08 ± 0.20	0.34 ± 0.23	-0.33 ± 0.20		0.03
$\bar{\upsilon}_{emi}$	19.89 ± 0.23	-0.15 ± 0.42	-0.80 ± 0.48	-0.92 ± 0.42		0.67
$\Delta\bar{\upsilon}$	1.25 ± 0.27	0.07 ± 0.50	1.13 ± 0.57	0.59 ± 0.51		0.57
Catalan	$y_0 \times 10^3$	a_{SA}	b_{SB}	c_{SdP}	d_{SP}	r
$\bar{\upsilon}_{abs}$	22.11 ± 0.20	-0.39 ± 0.20	0.32 ± 0.12	-0.05 ± 0.08	-1.55 ± 0.29	0.81
$\bar{\upsilon}_{emi}$	20.03 ± 0.91	-0.18 ± 0.90	-0.32 ± 0.51	-1.16 ± 0.34	-0.19 ± 1.28	0.72
$\Delta\bar{\upsilon}$	2.08 ± 0.98	-0.20 ± 0.97	0.64 ± 0.55	1.11 ± 0.37	-1.36 ± 1.38	0.70

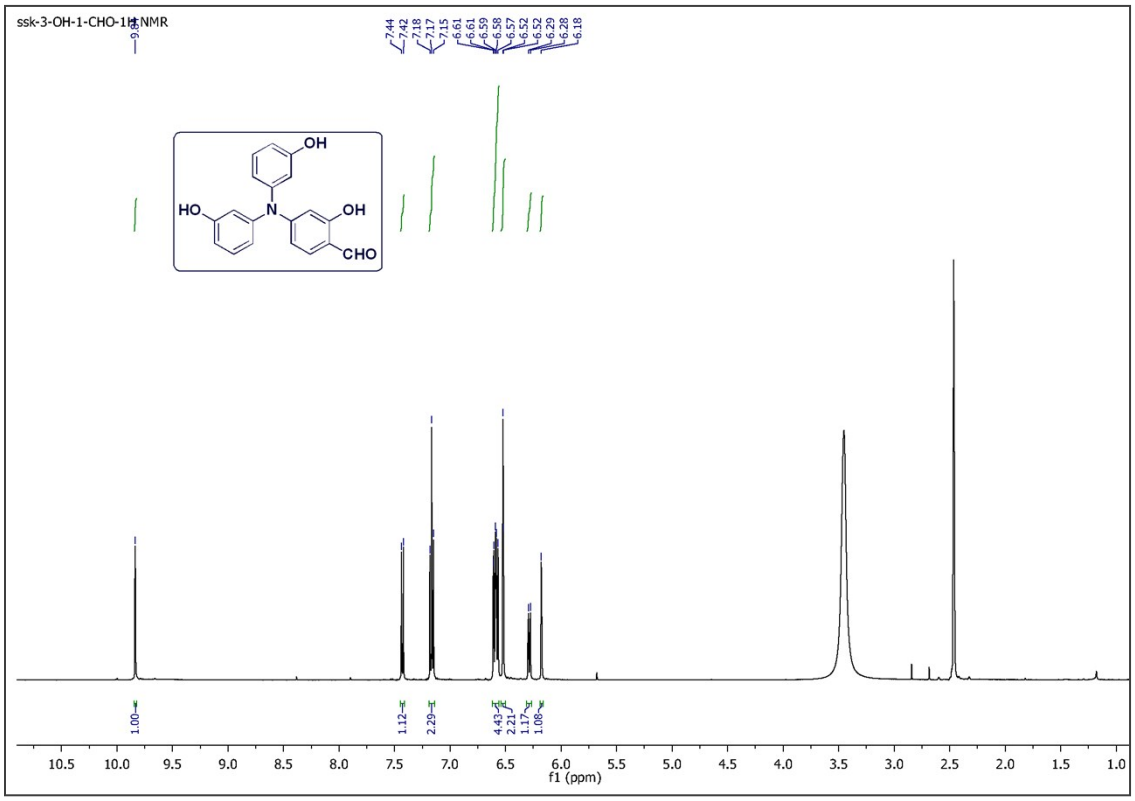
Spectrum S1: ^{1}H NMR spectra of **compound 2** in DMSO-d_6



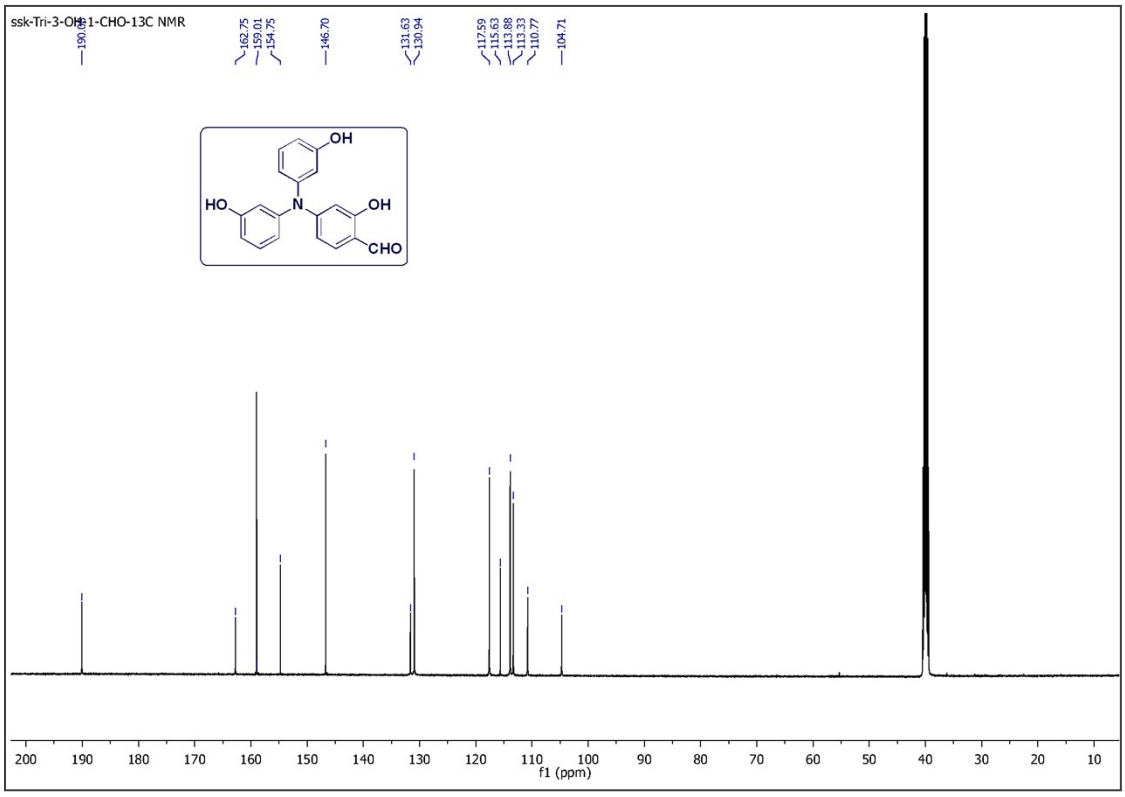
Spectrum S2: ^{13}C NMR spectra of **compound 2** in DMSO-d_6



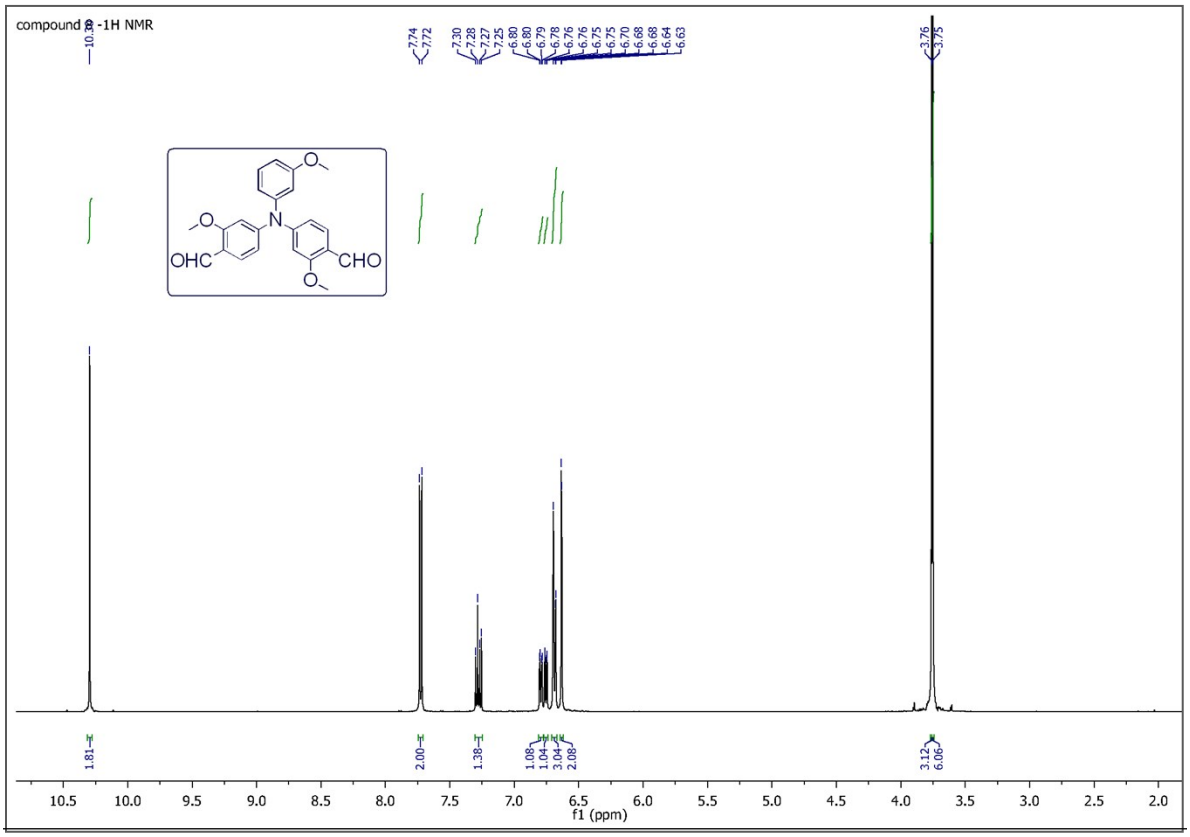
Spectrum S3: ^{1}H NMR spectra of **compound 5** in DMSO-d_6



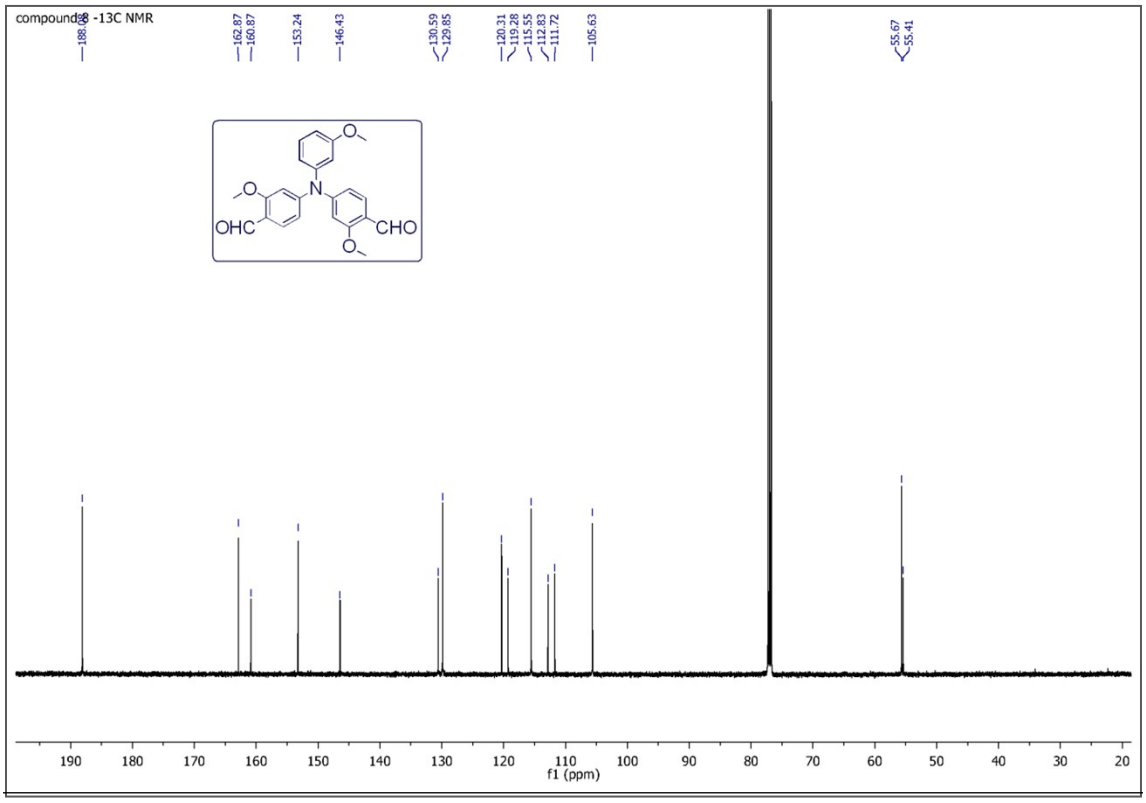
Spectrum S4: ^{13}C NMR spectra of **compound 5** in DMSO-d_6



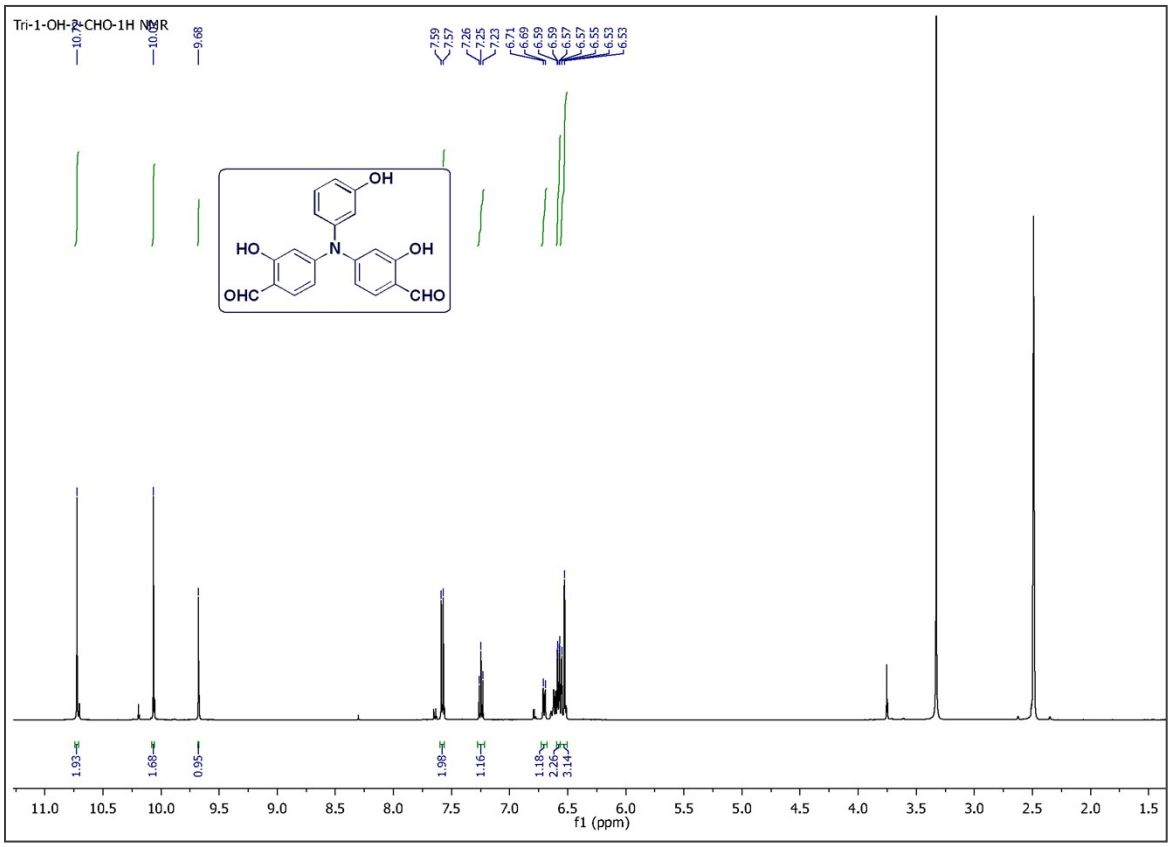
Spectrum S5: ^{1}H NMR spectra of **compound 8** in $CDCl_3$



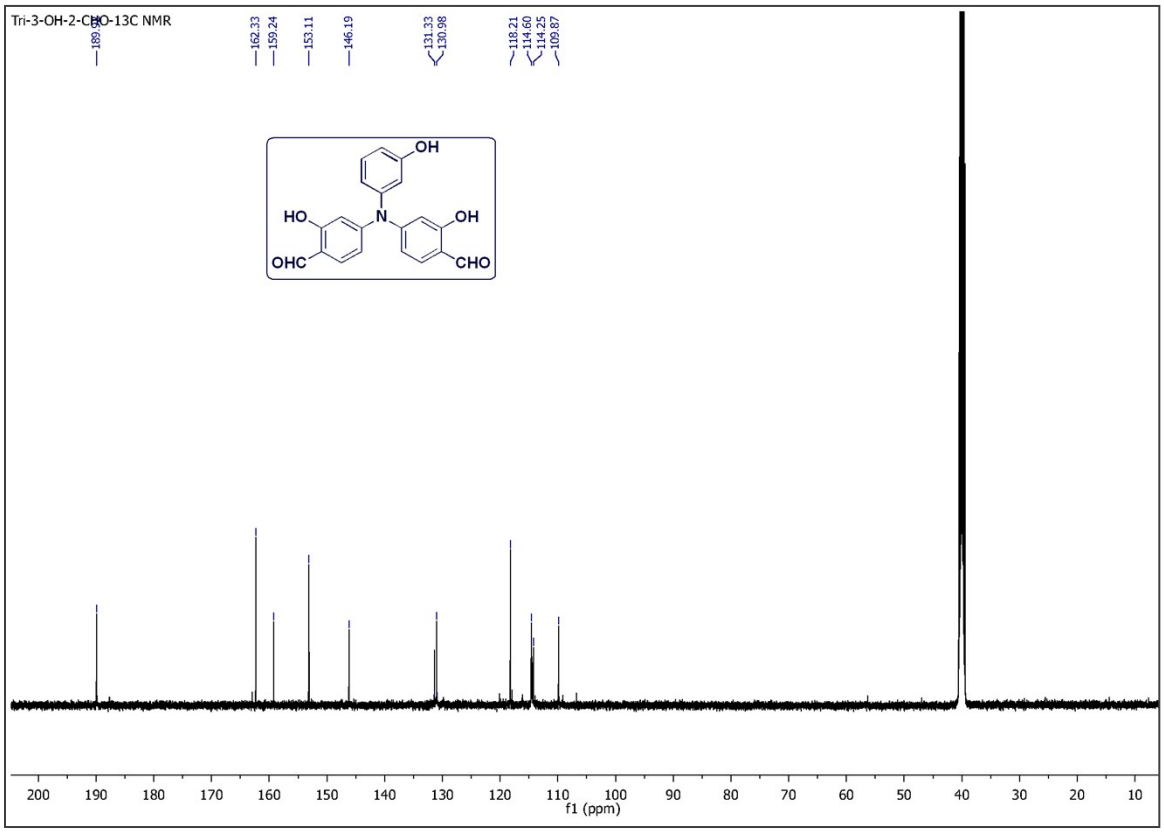
Spectrum S6: ^{13}C NMR spectra of **compound 8** in $CDCl_3$



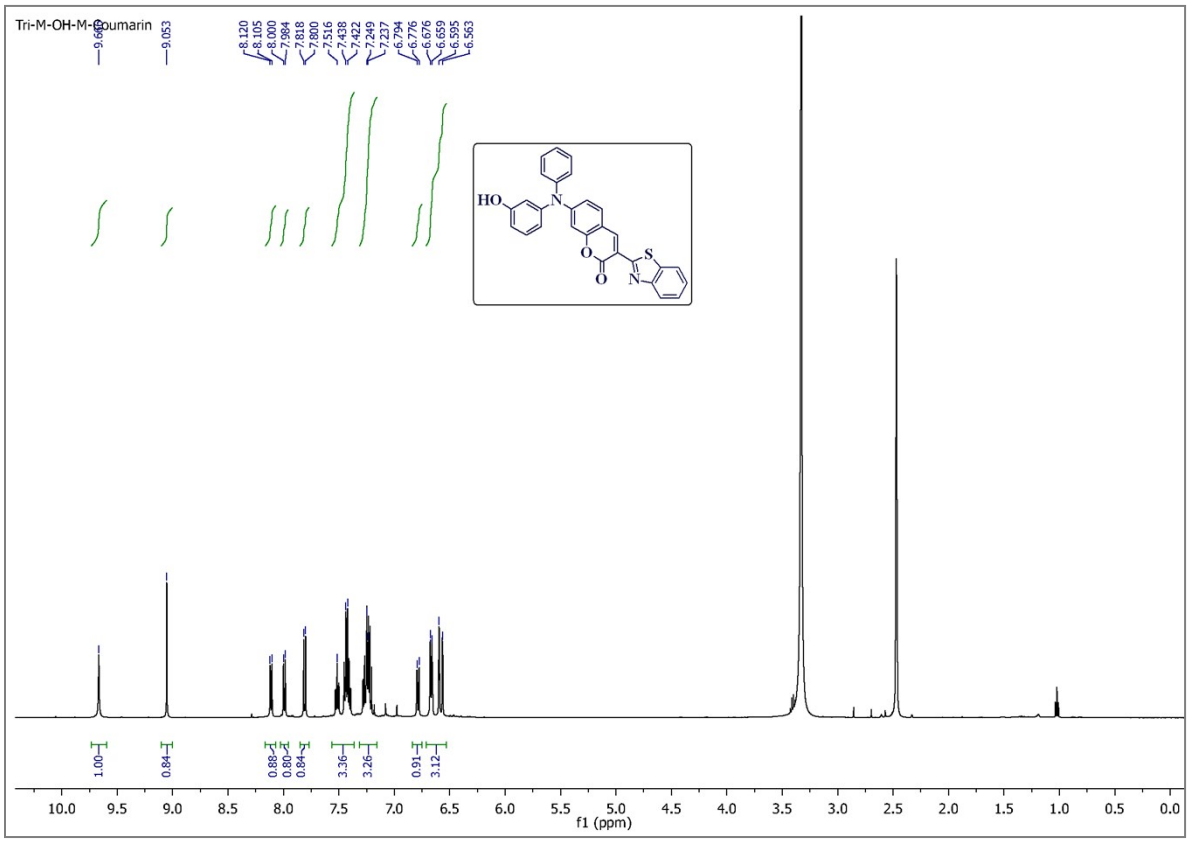
Spectrum S7: ^{1}H NMR spectra of **compound 9** in DMSO-d_6



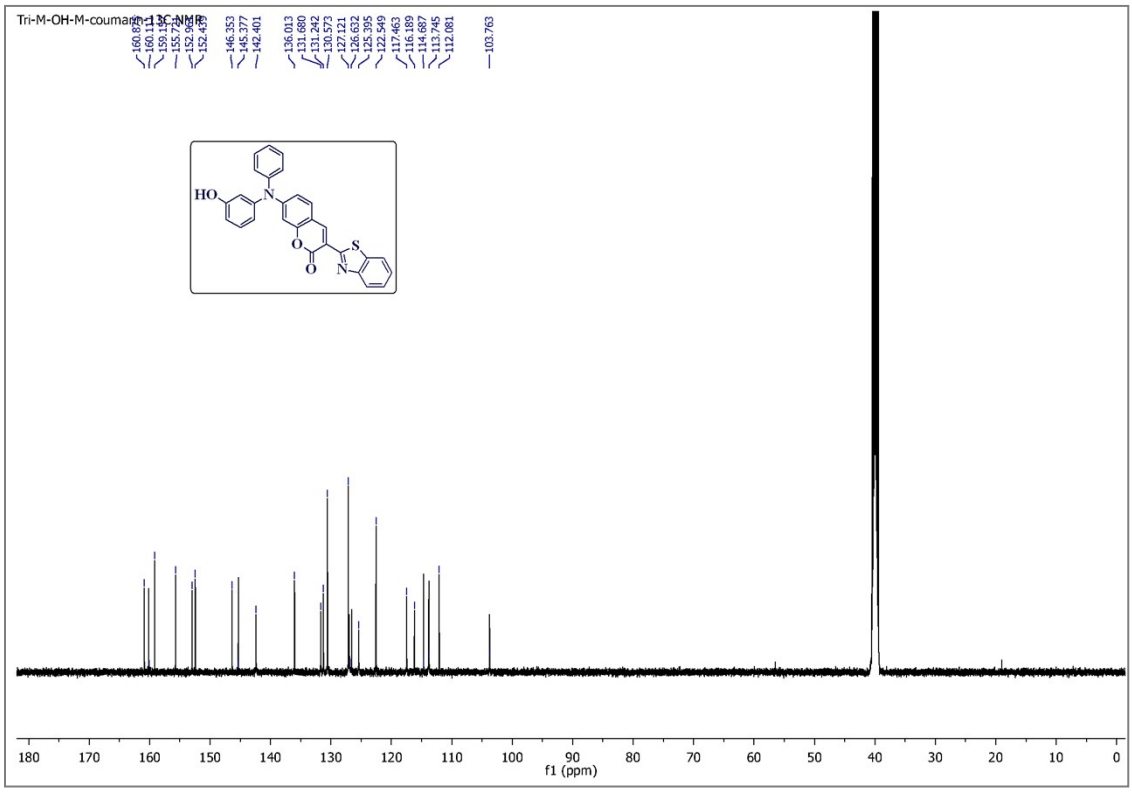
Spectrum S8: ^{13}C NMR spectra of **compound 9** in DMSO-d_6



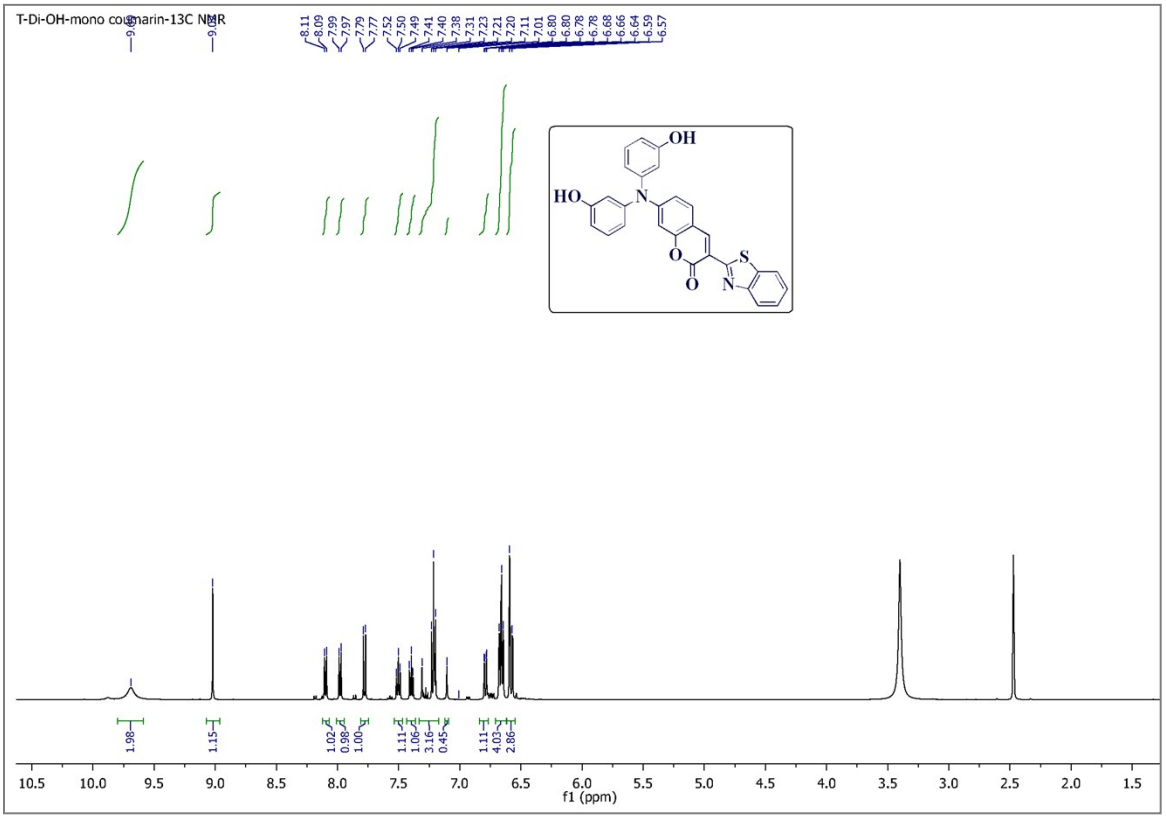
Spectrum S9: ^{1}H NMR spectra of **compound 3** in DMSO-d_6



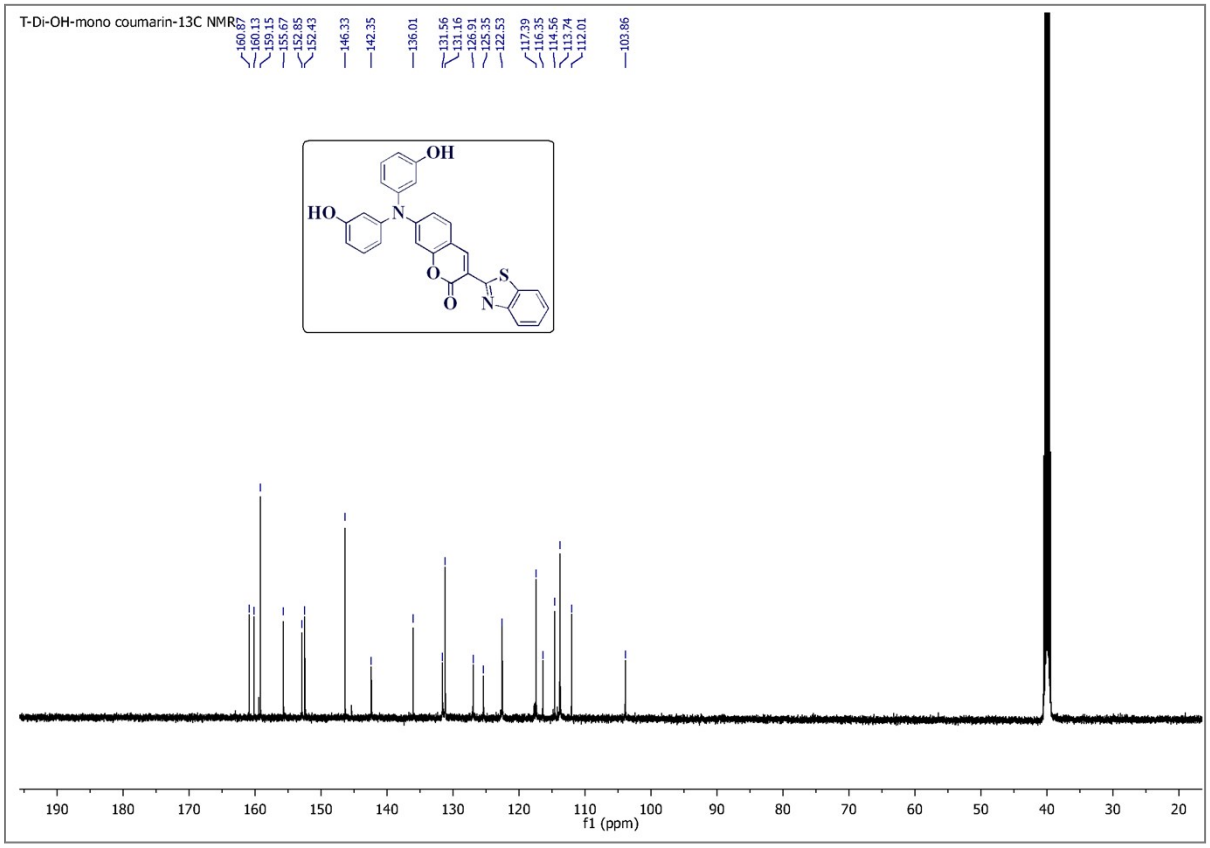
Spectrum S10: ^{13}C NMR spectra of **compound 3** in DMSO-d_6



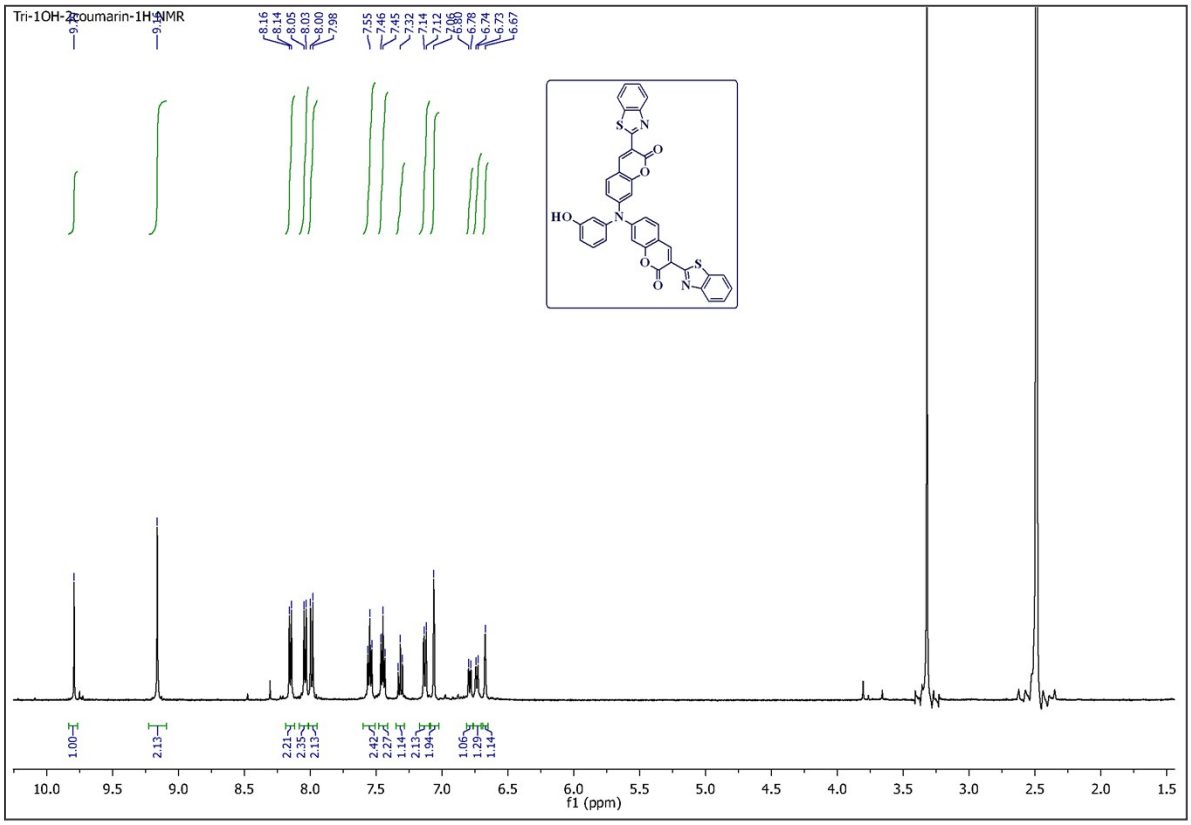
Spectrum S11: ^{1}H NMR spectra of **compound 6** in DMSO-d_6



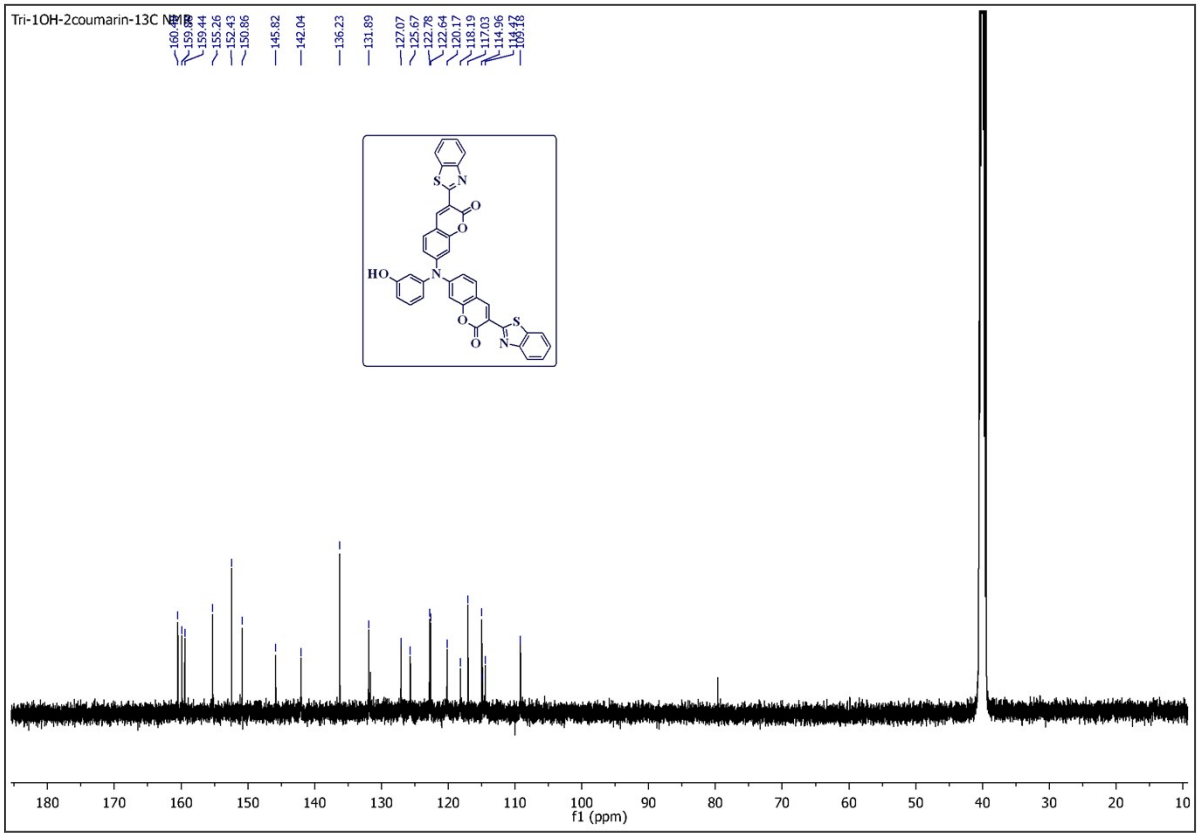
Spectrum S12: ^{13}C NMR spectra of **compound 6** in DMSO-d_6



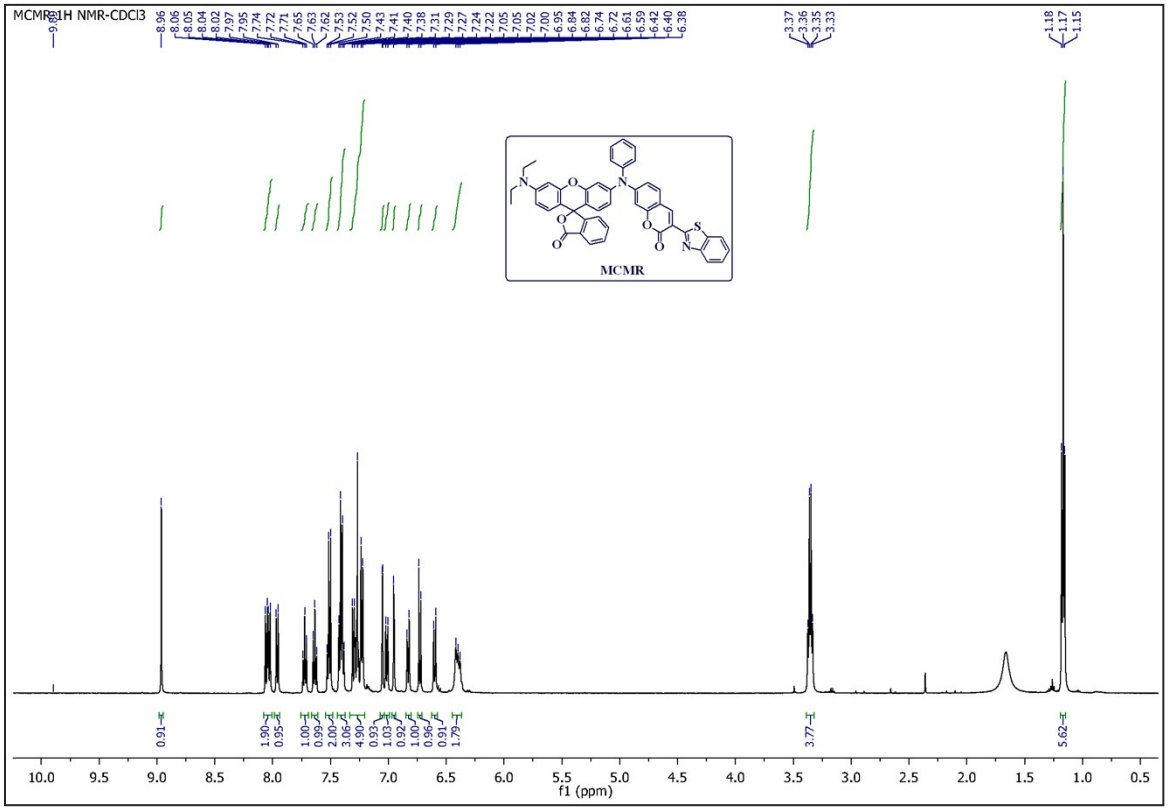
Spectrum S13: ^{1}H NMR spectra of **compound 10** in DMSO-d_6



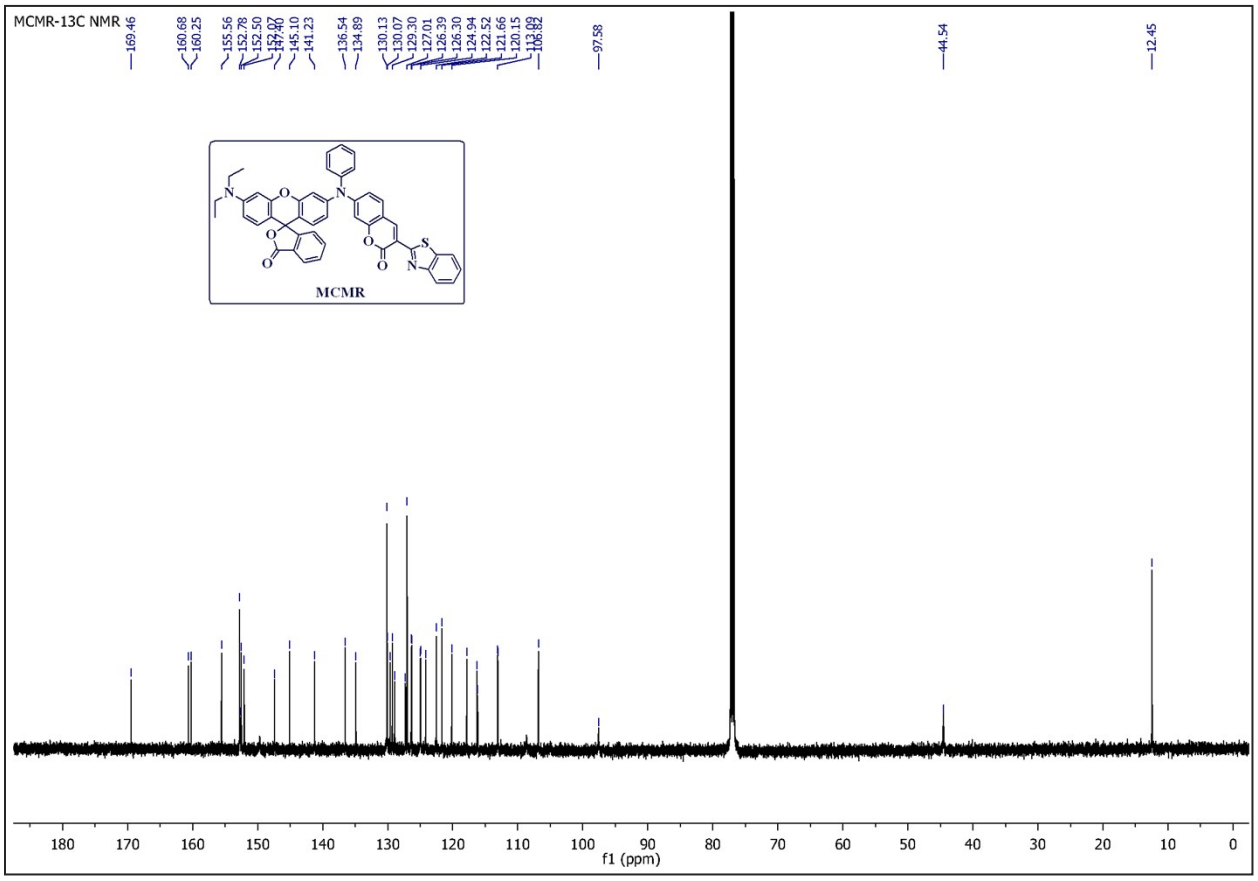
Spectrum S14: ^{13}C NMR spectra of **compound 10** in DMSO-d_6



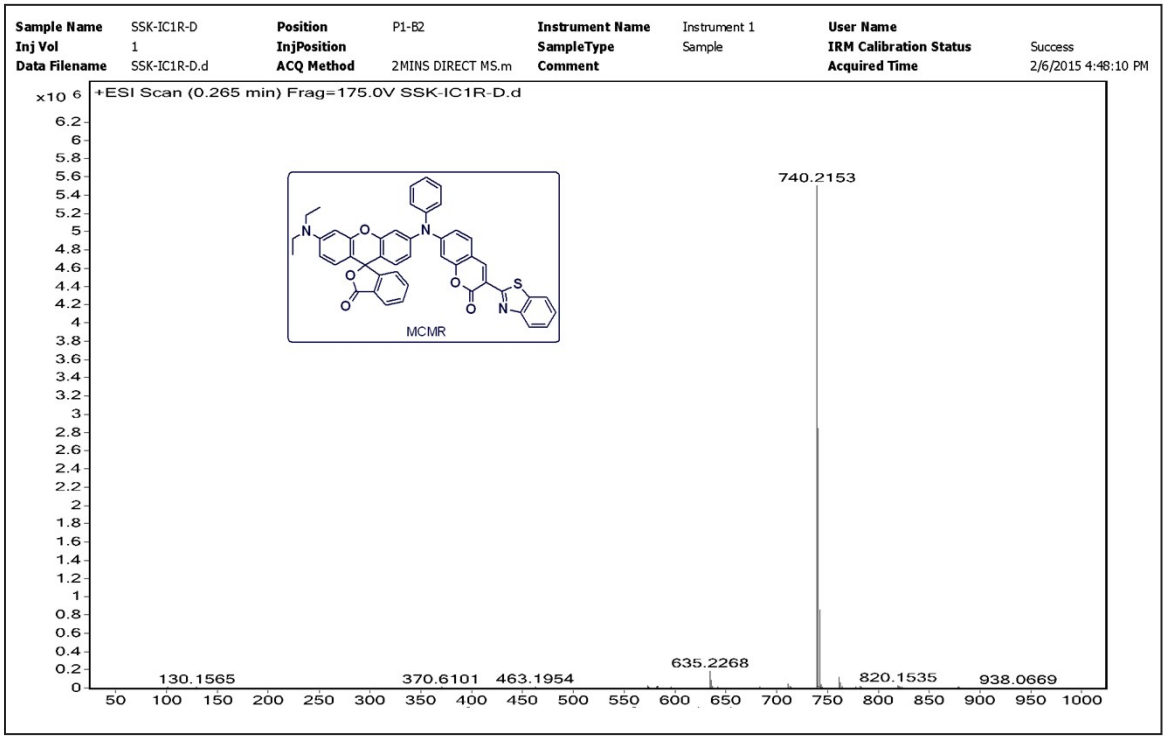
Spectrum S15: ^{1}H NMR spectra of **MCMR** in $CDCl_3$



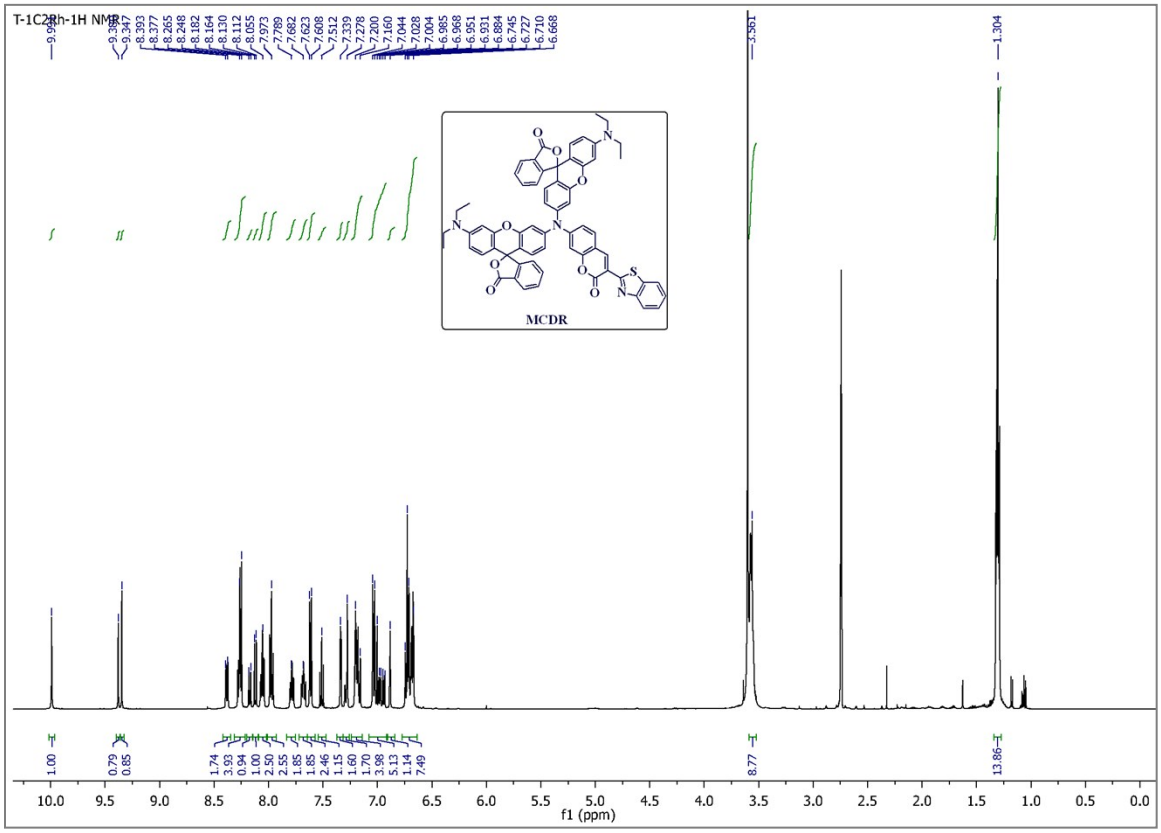
Spectrum S16: ^{13}C NMR spectra of **MCMR** in $CDCl_3$



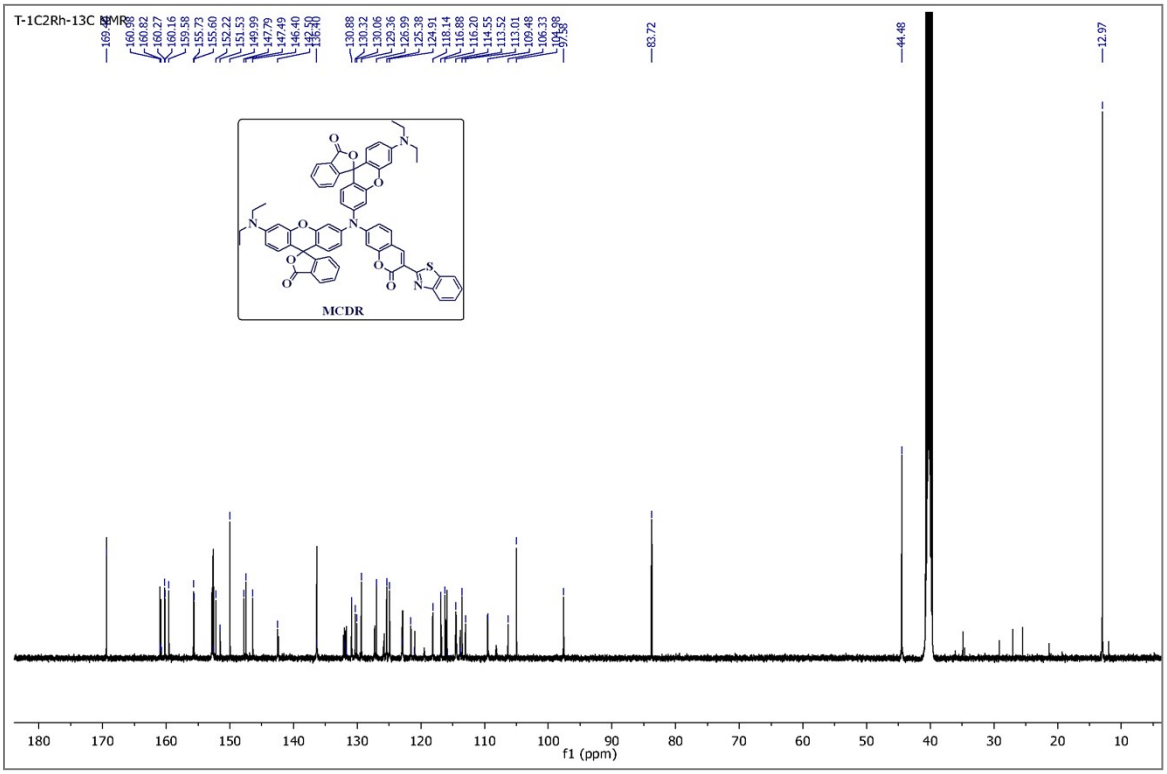
Spectrum S17: HR-MS spectra of **MCMR**



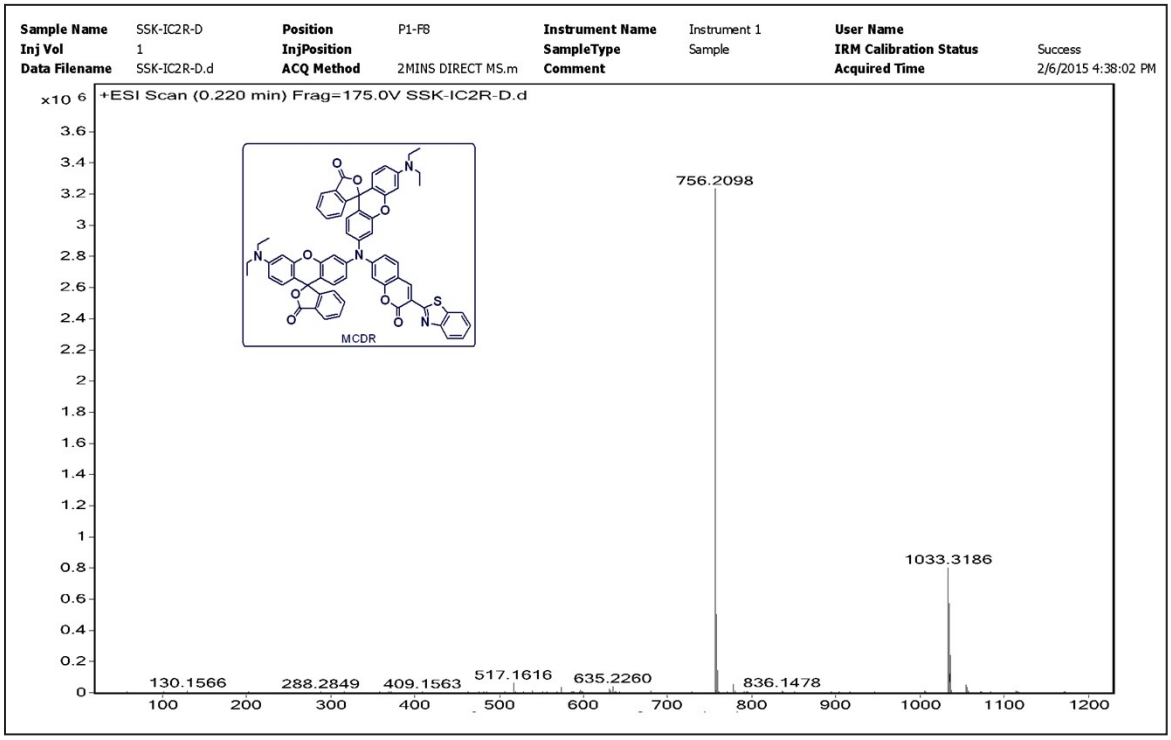
Spectrum S18: ^{1}H NMR spectra of **MCDR** in DMSO-d_6



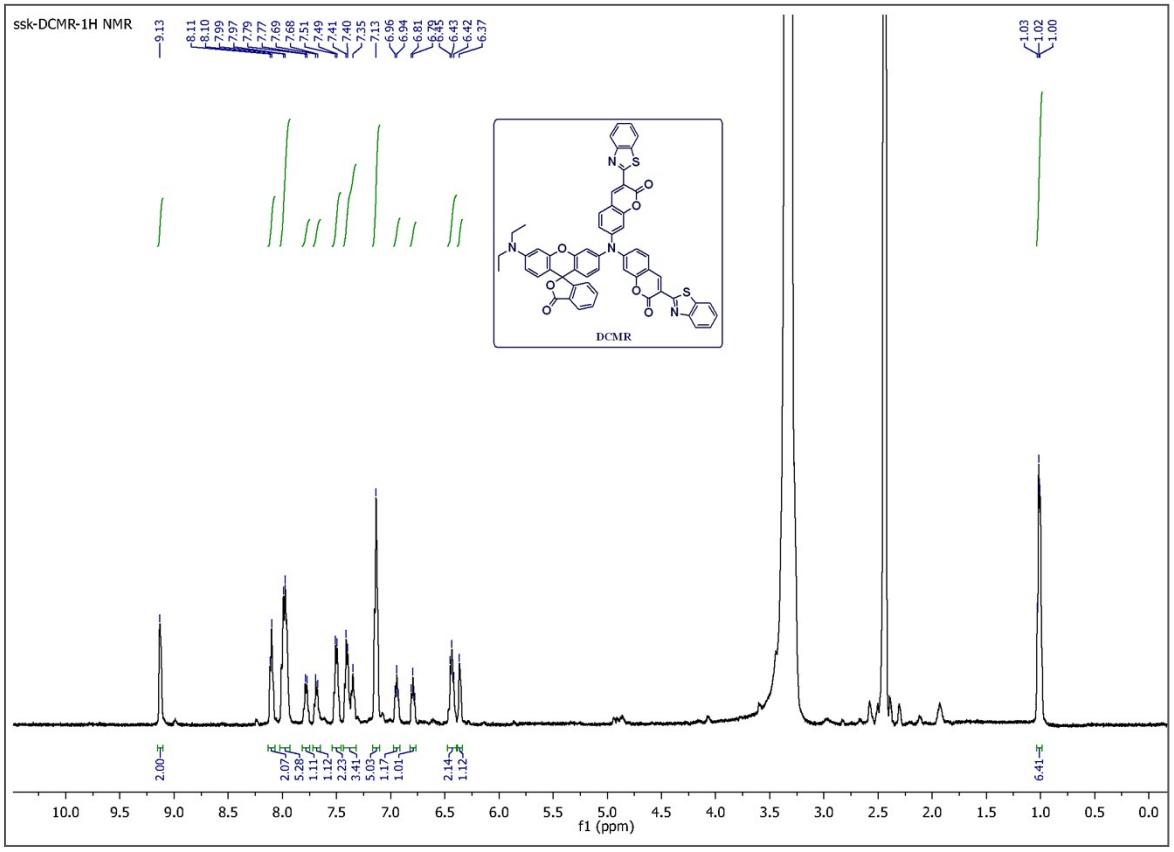
Spectrum S19: ^{13}C NMR spectra of **MCDR** in DMSO-d_6



Spectrum S20: HR-MS spectra of **MCDR**



Spectrum S21: ^{1}H NMR spectra of **DCMR** in DMSO-d_6



Spectrum S22: ^{13}C NMR spectra of **DCMR** in DMSO-d_6