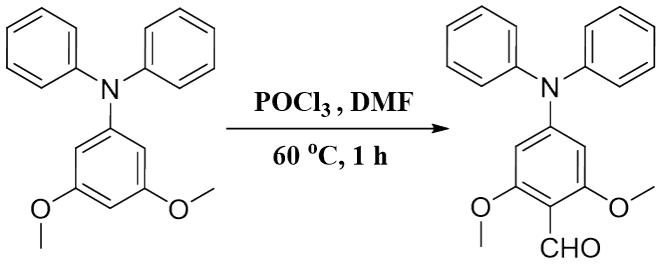
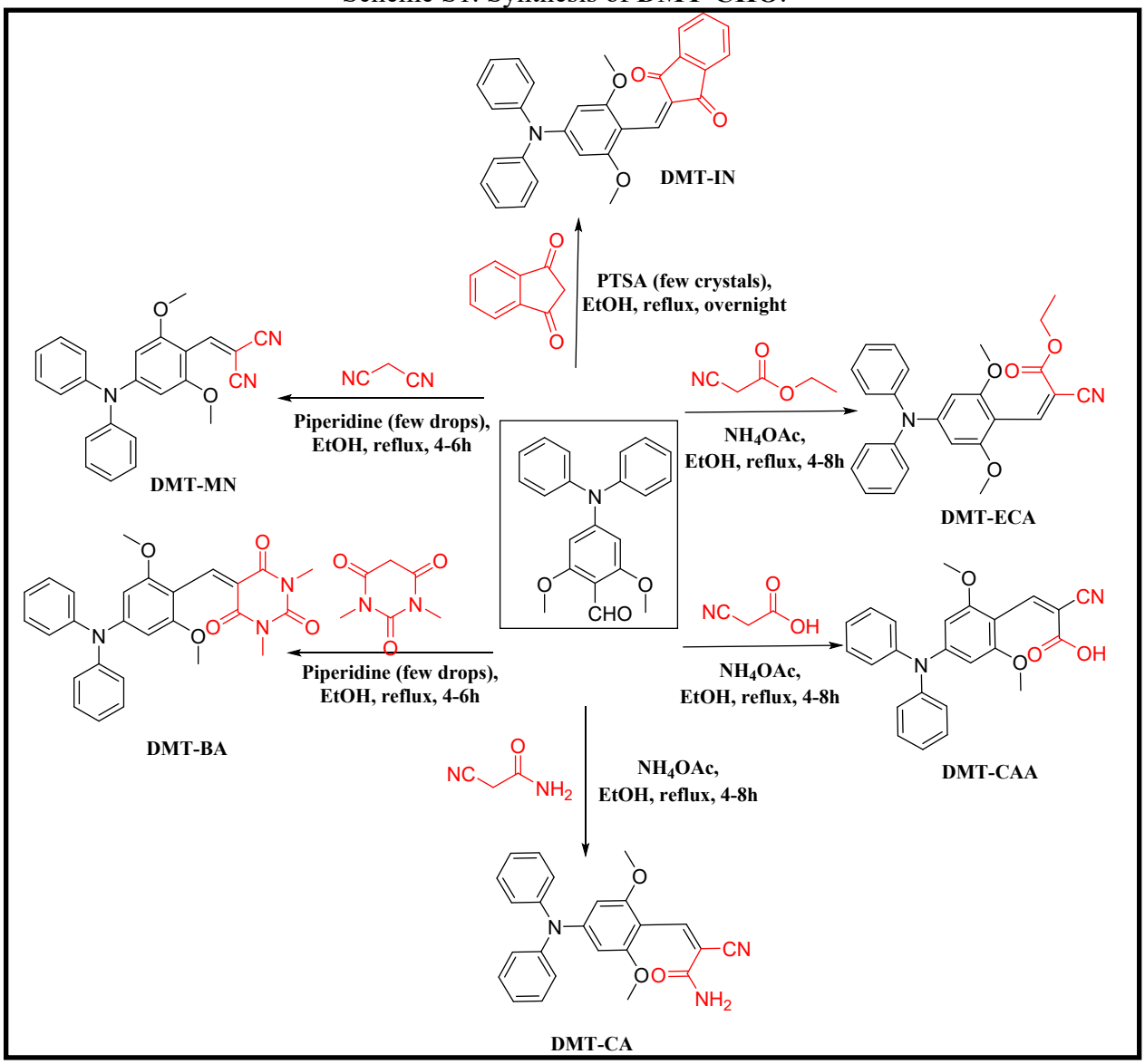
Electronic Supplementary Information (ESI)

Dimethoxy substituted triphenylamine based donor-acceptor fluorophores: tunable solid-state emission and reversible thermofluorochromism

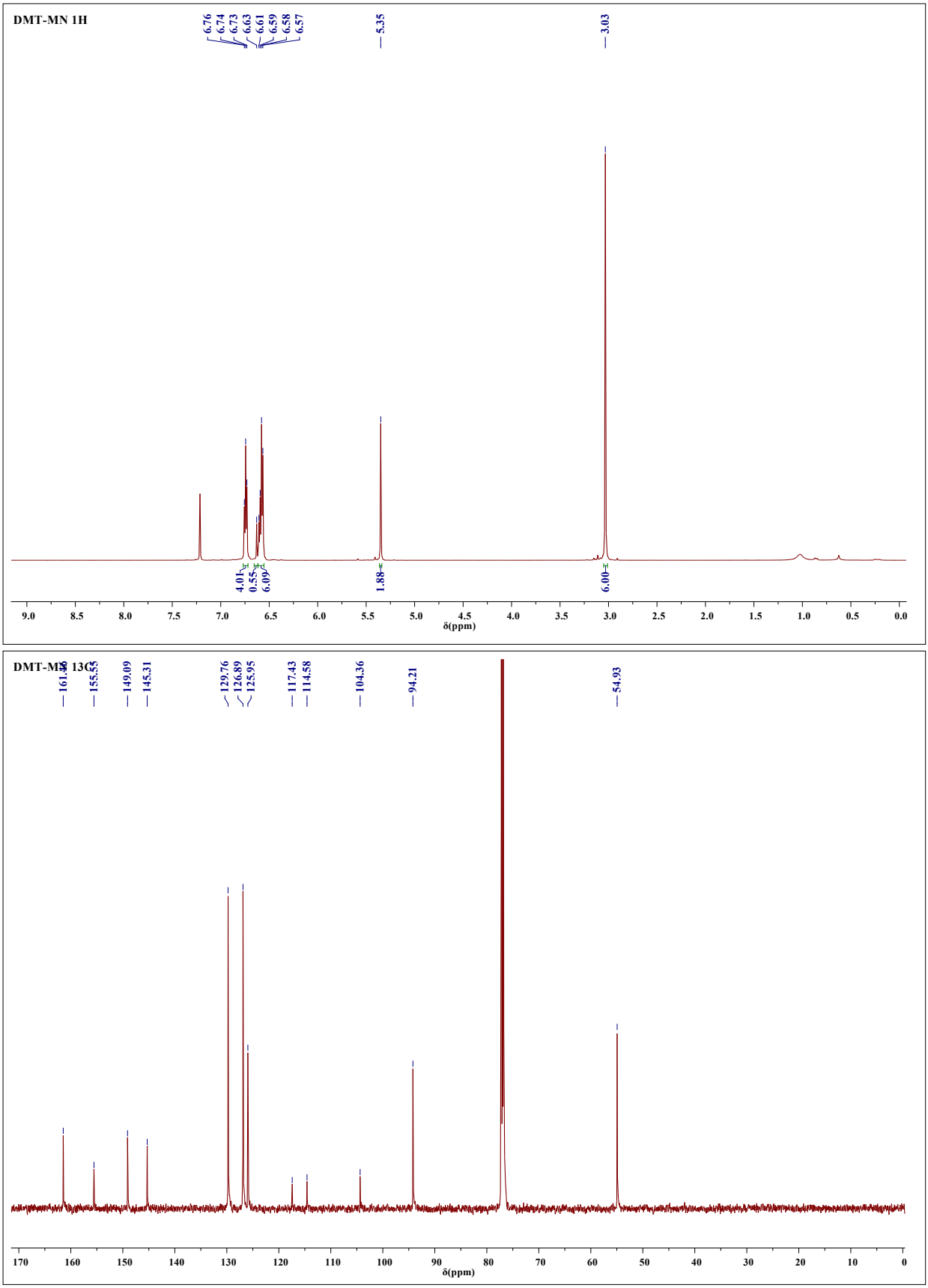


1

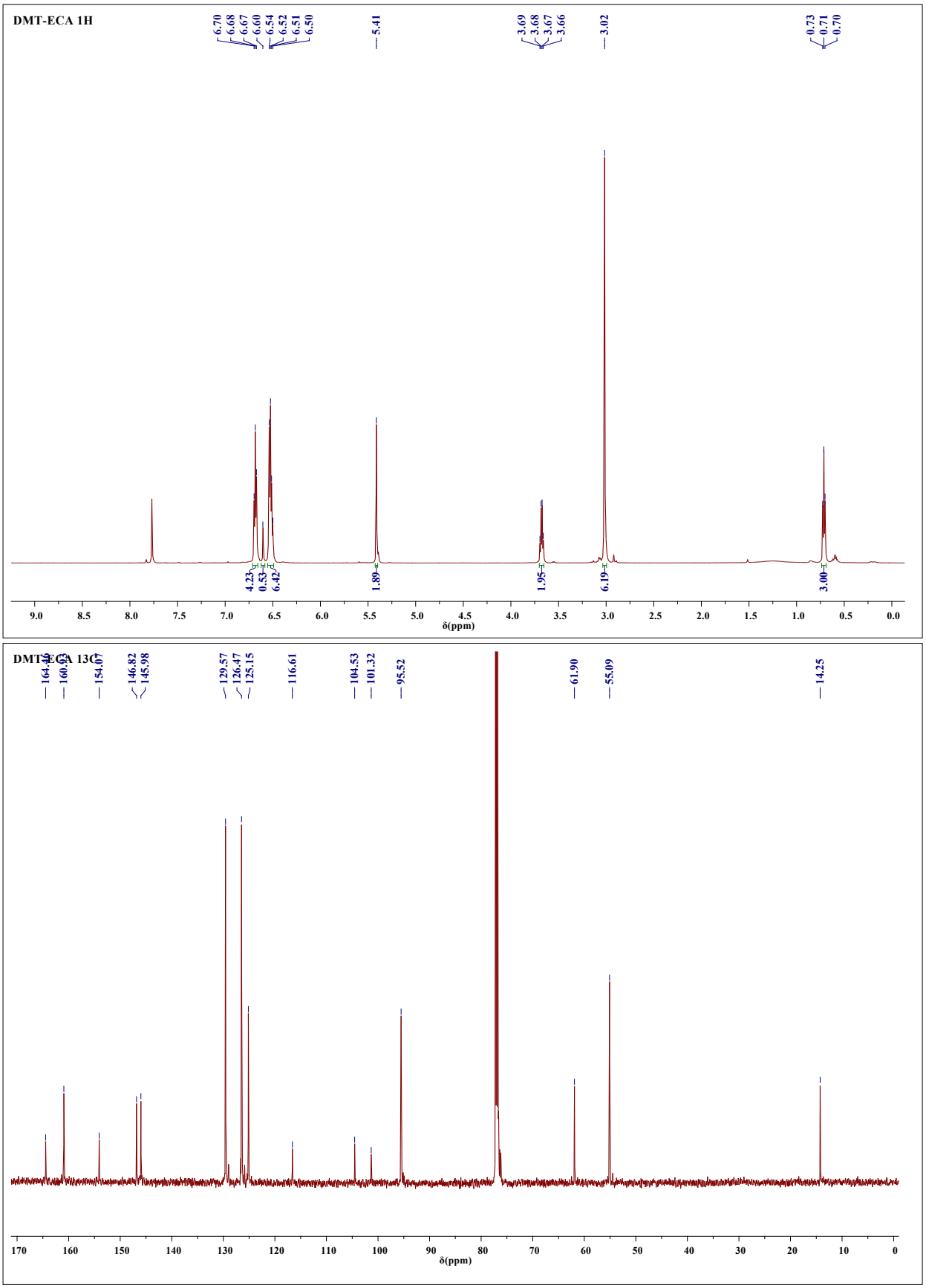
Scheme S1. Synthesis of **DMT-CHO**.



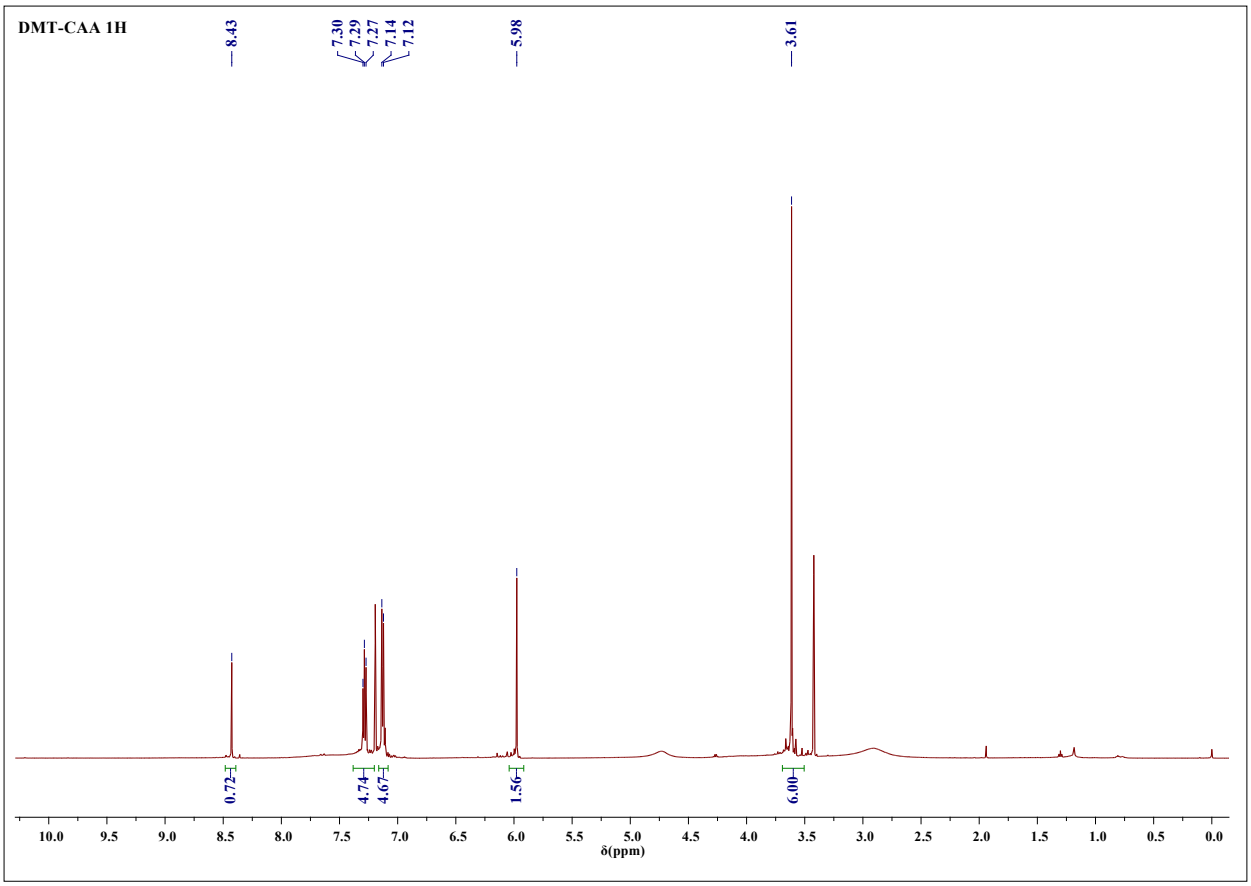
Scheme S2. Synthesis of **DMT-acceptor derivatives**.

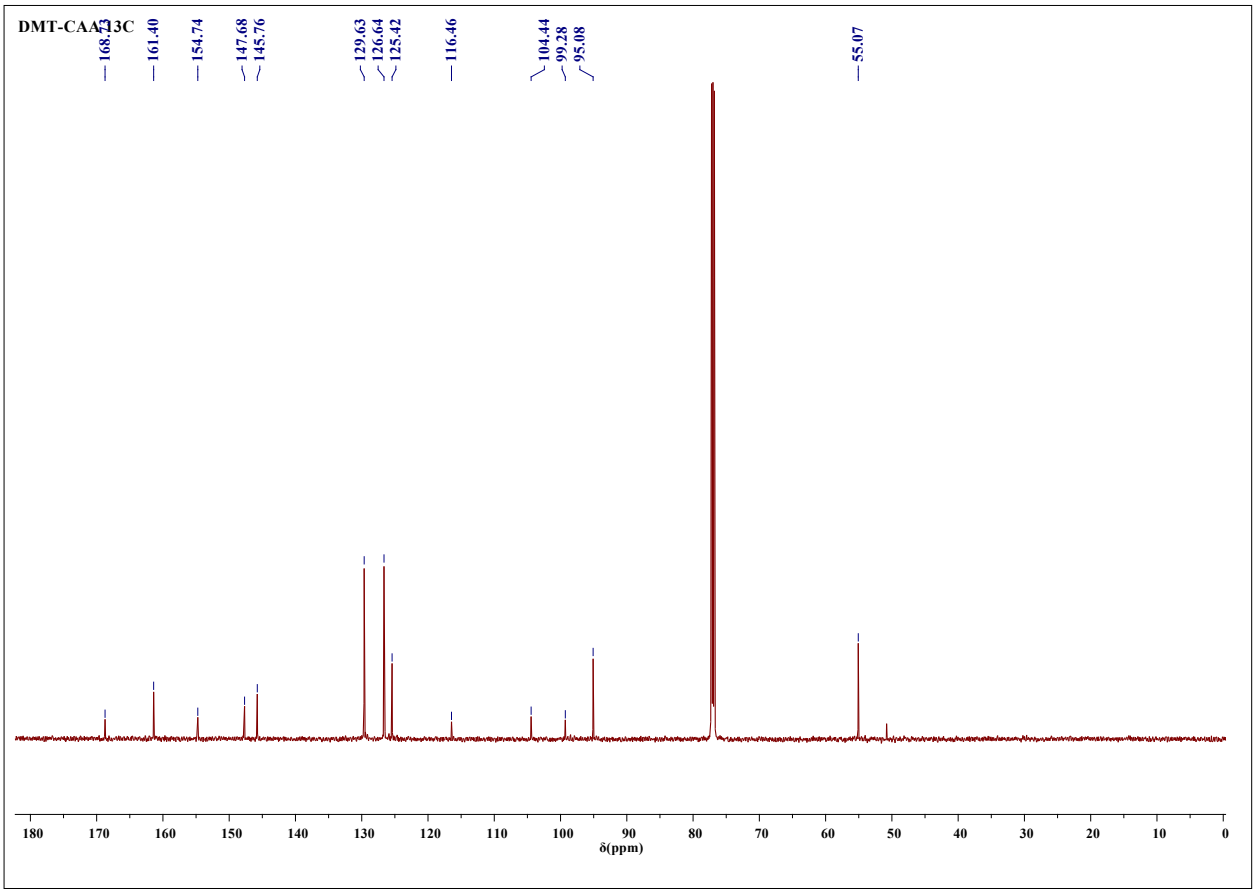


^{1}H & ^{13}C NMR spectra of DMT-MN in $CDCl_3$

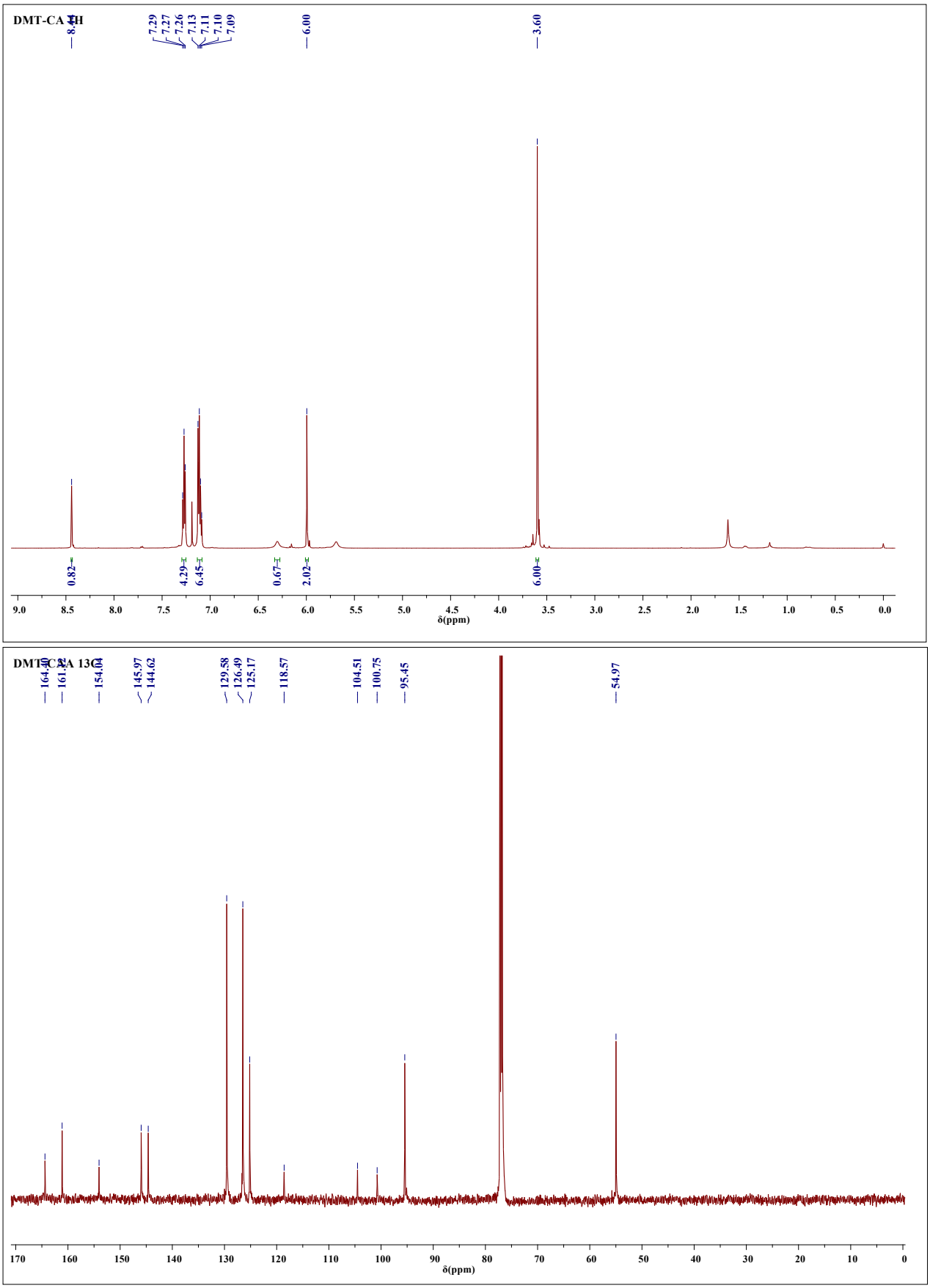


^{1}H & ^{13}C NMR spectra of DMT-ECA in $CDCl_3$

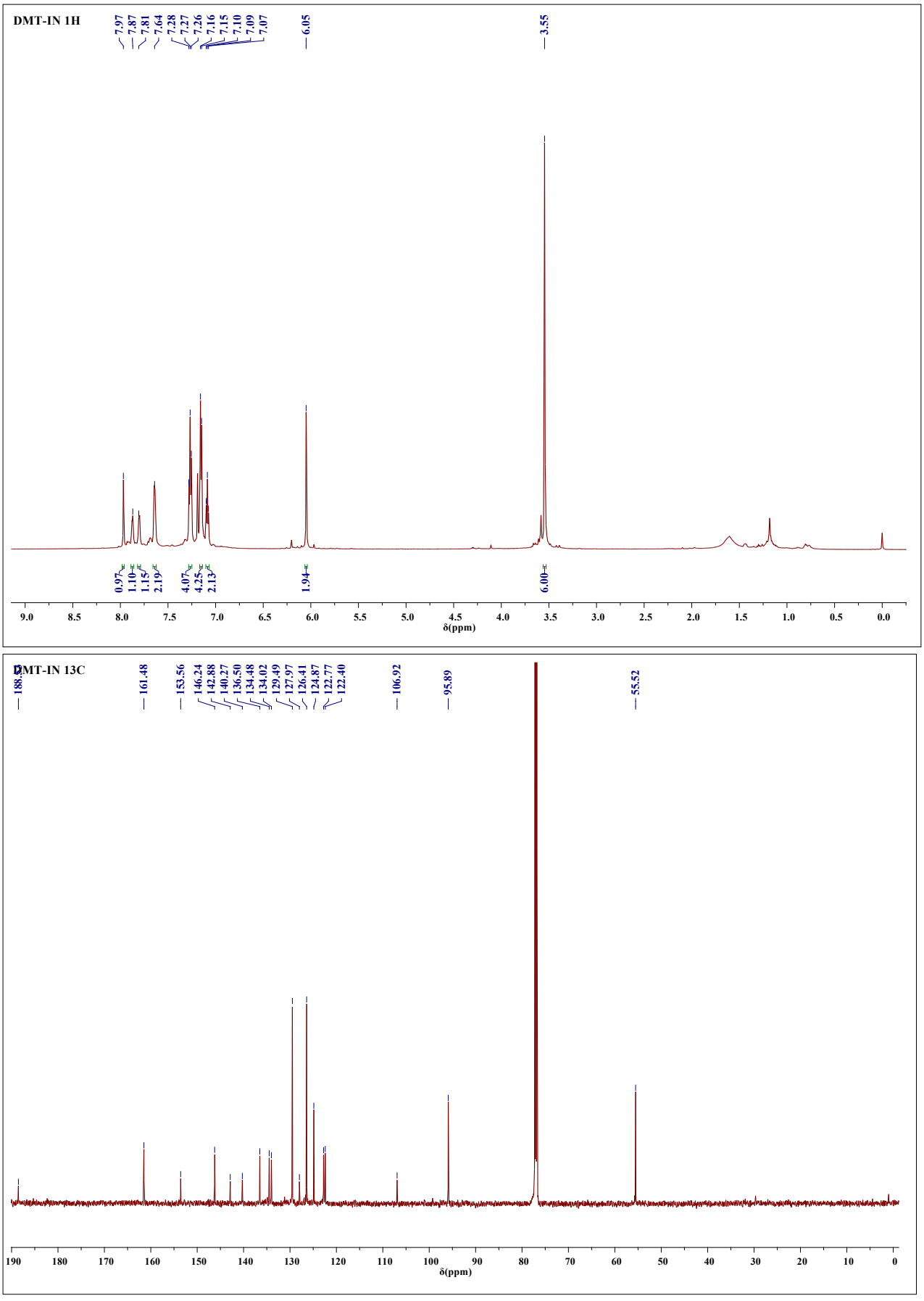




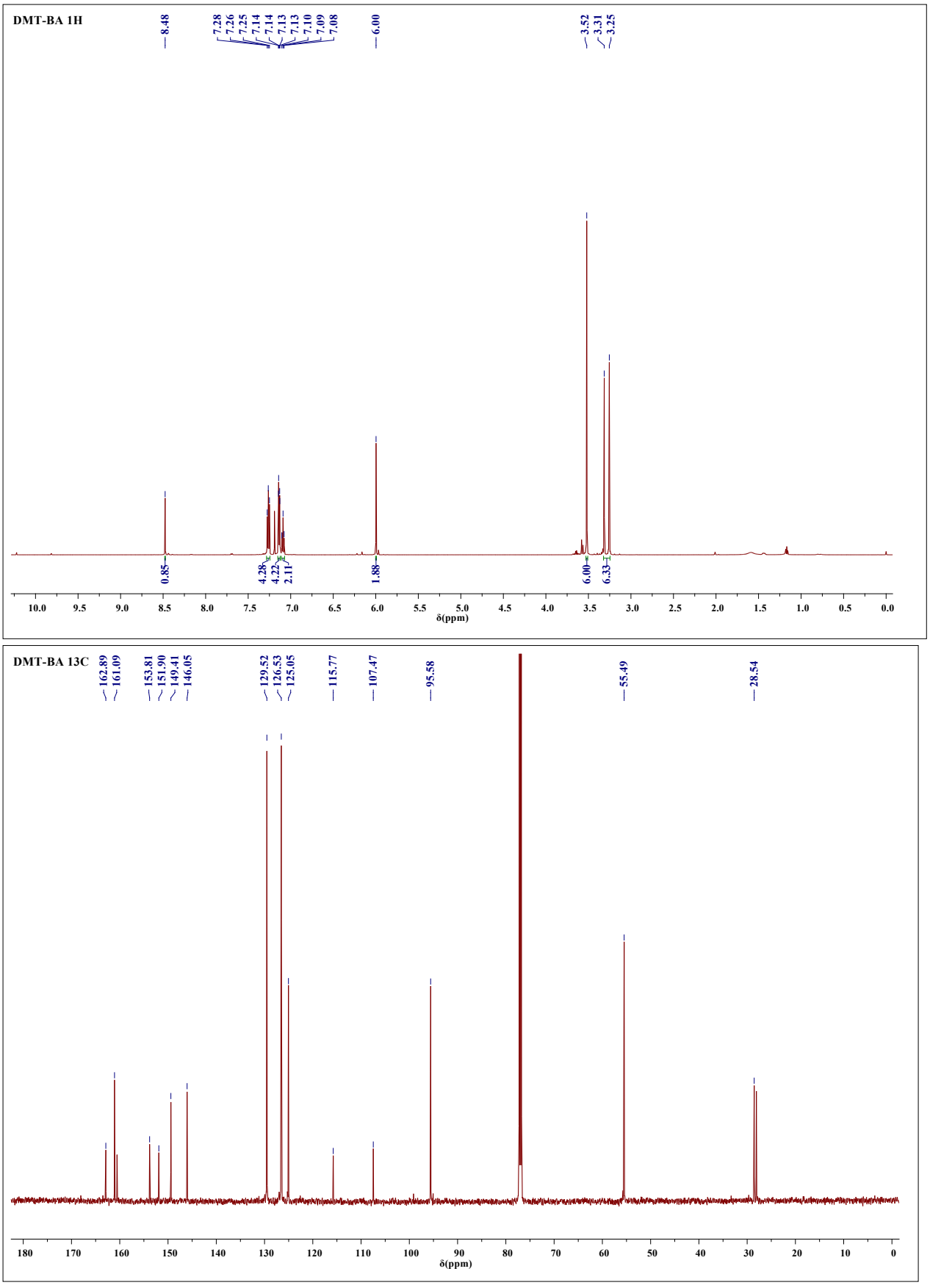
^{1}H & ^{13}C NMR spectra of DMT-CAA in $CDCl_3$



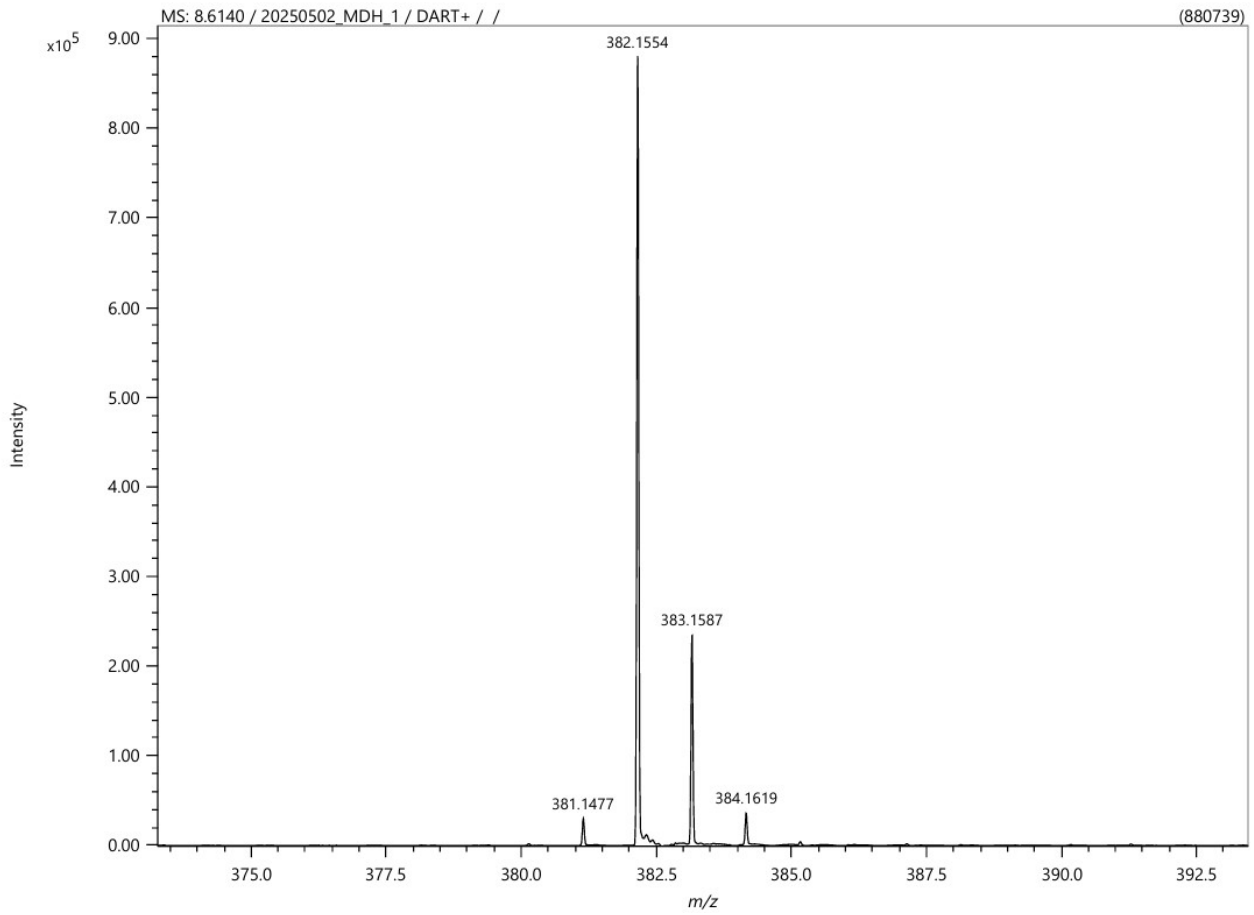
^{1}H & ^{13}C NMR spectra of DMT-CA in $CDCl_3$



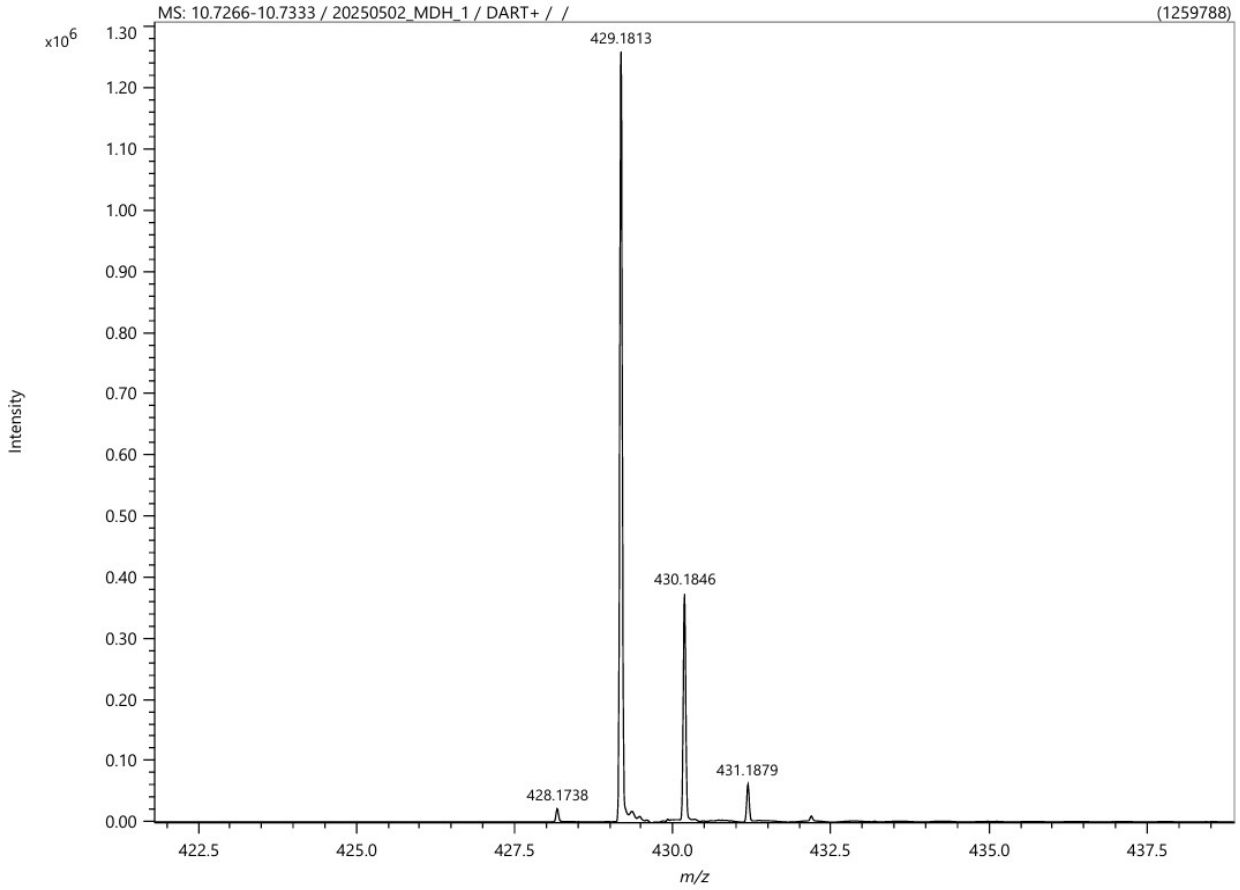
^{1}H & ^{13}C NMR spectra of DMT-ID in $CDCl_3$



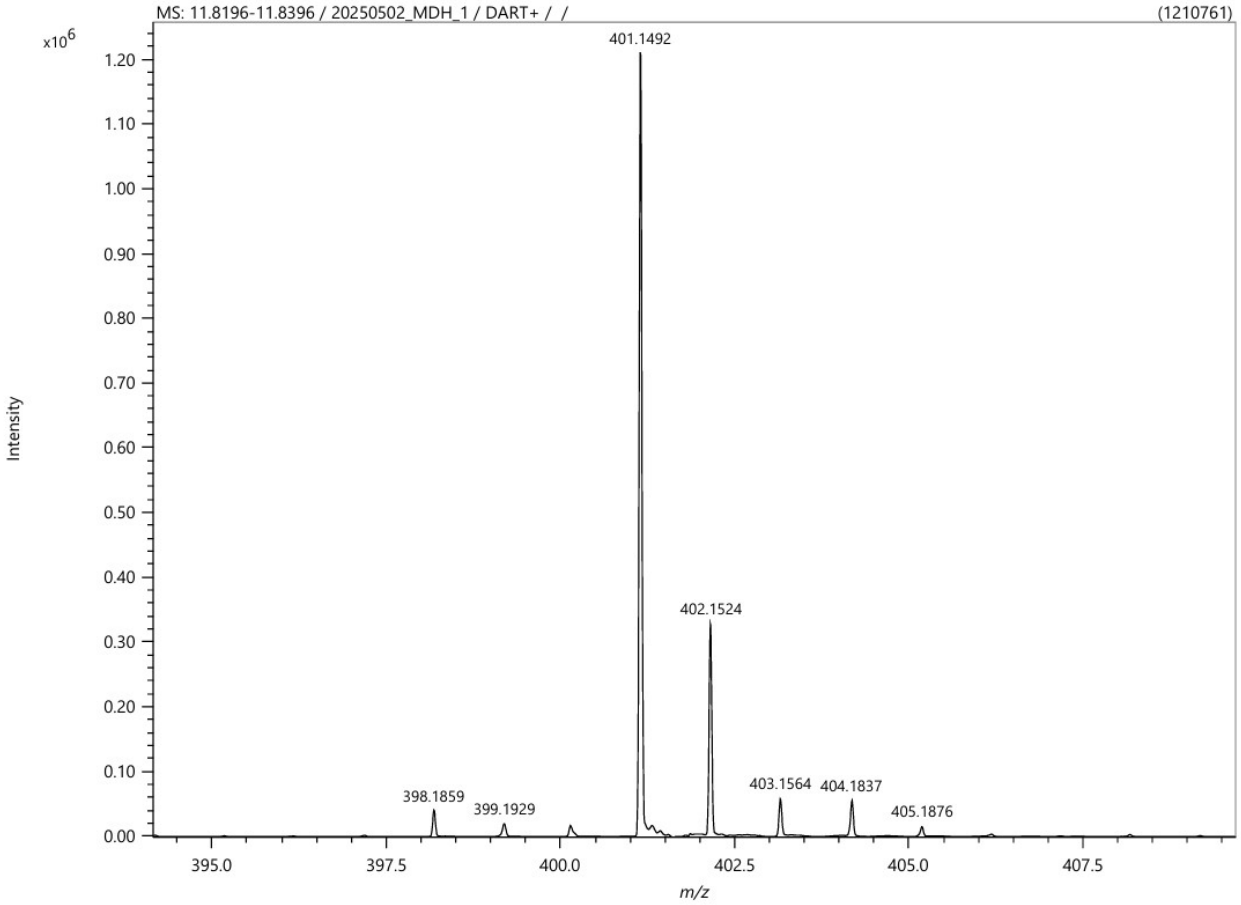
^{1}H & ^{13}C NMR spectra of DMT-BA in $CDCl_3$



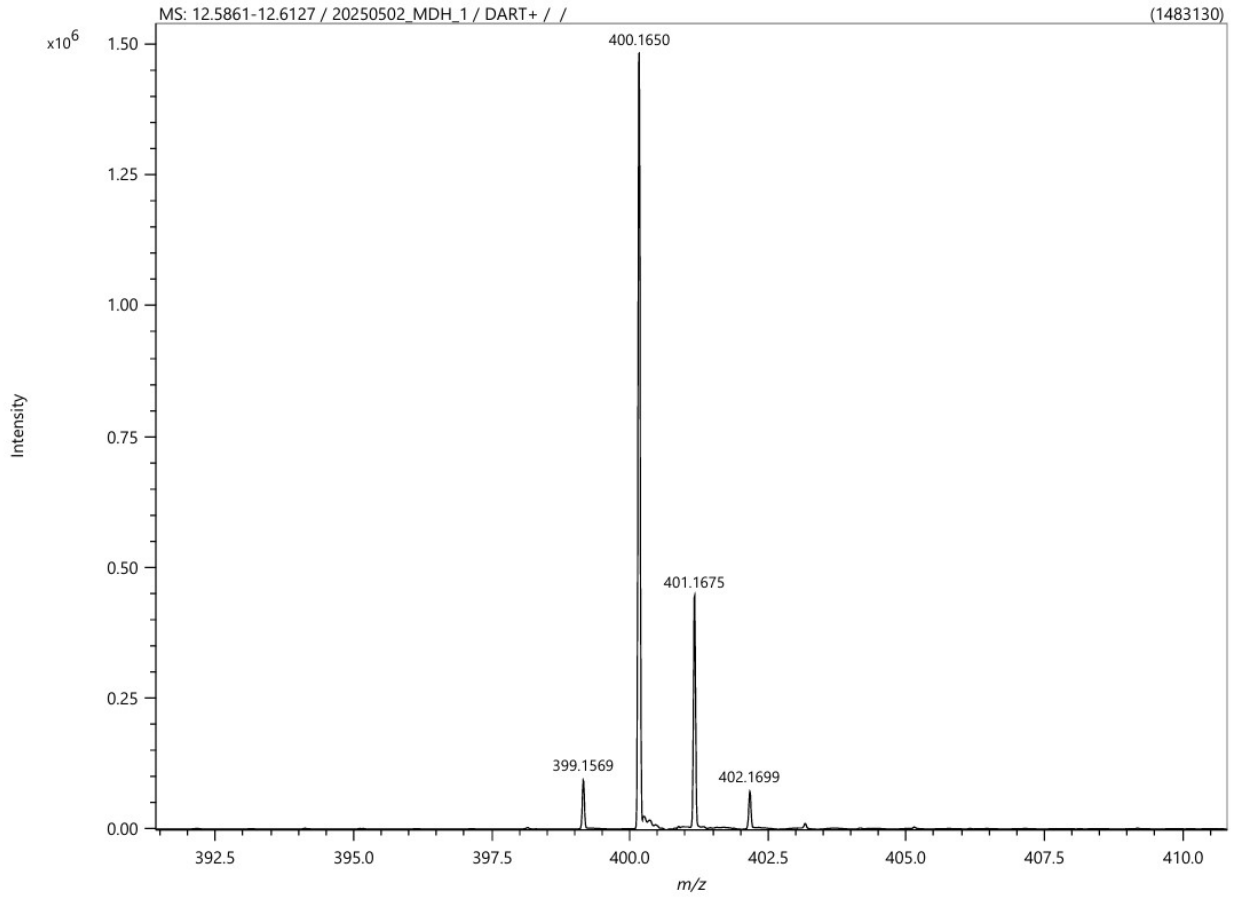
*HRMS spectra of **DMT-MN**.* Calculated [M+H]: 382.1557; found: 382.1554.



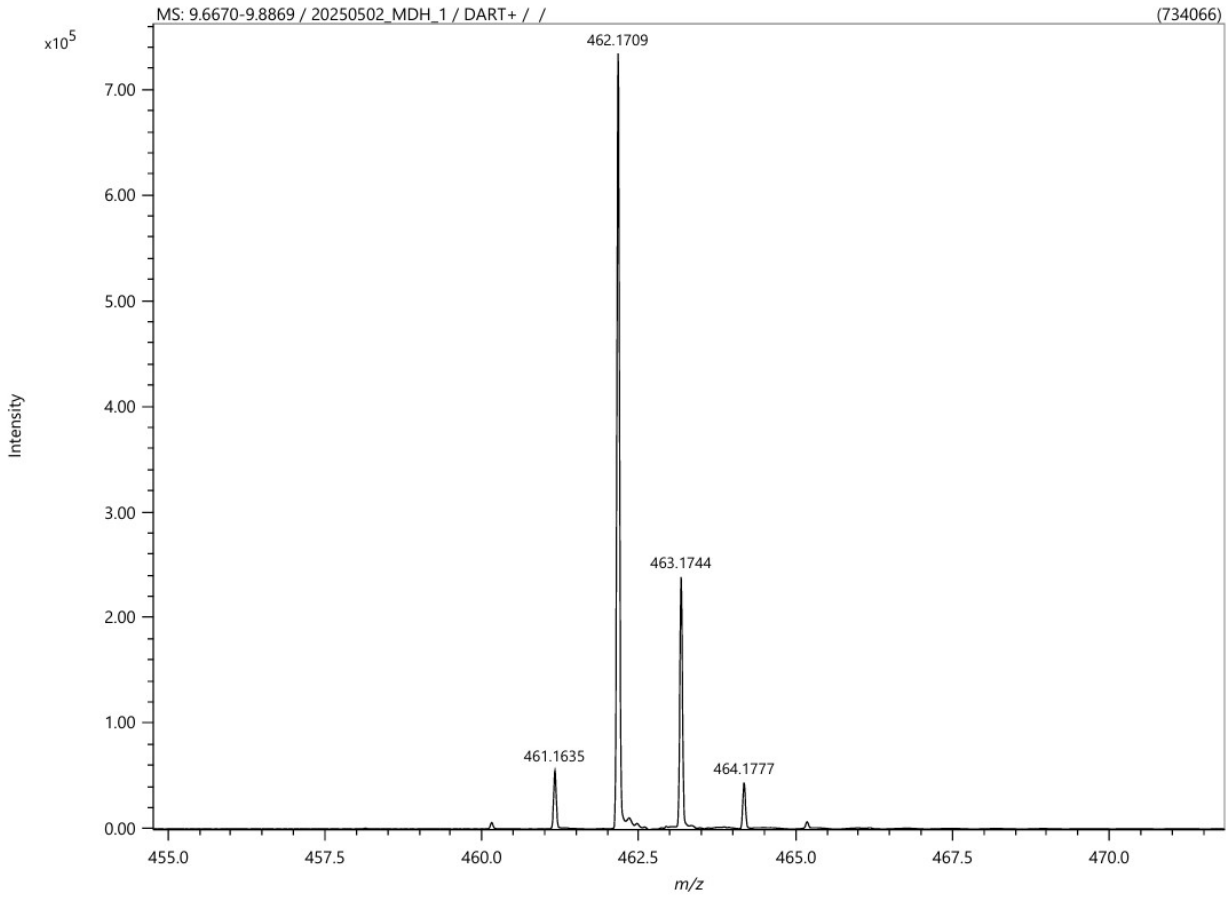
*HRMS spectra of **DMT-ECA**.* Calculated: 429.1816; found: 429.1813.



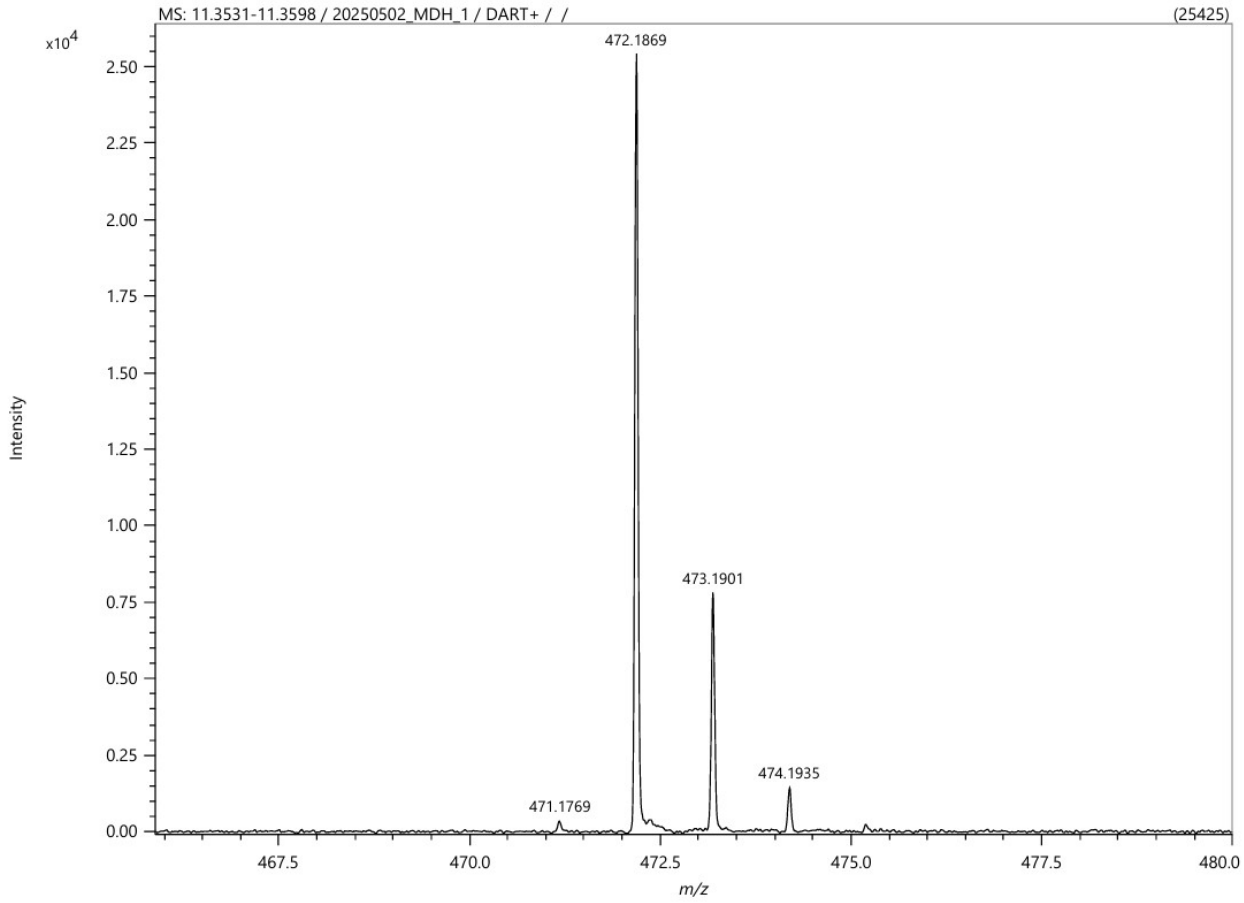
*HRMS spectra of **DMT-CAA**.* Calculated: 401.1503; found: 401.1492.



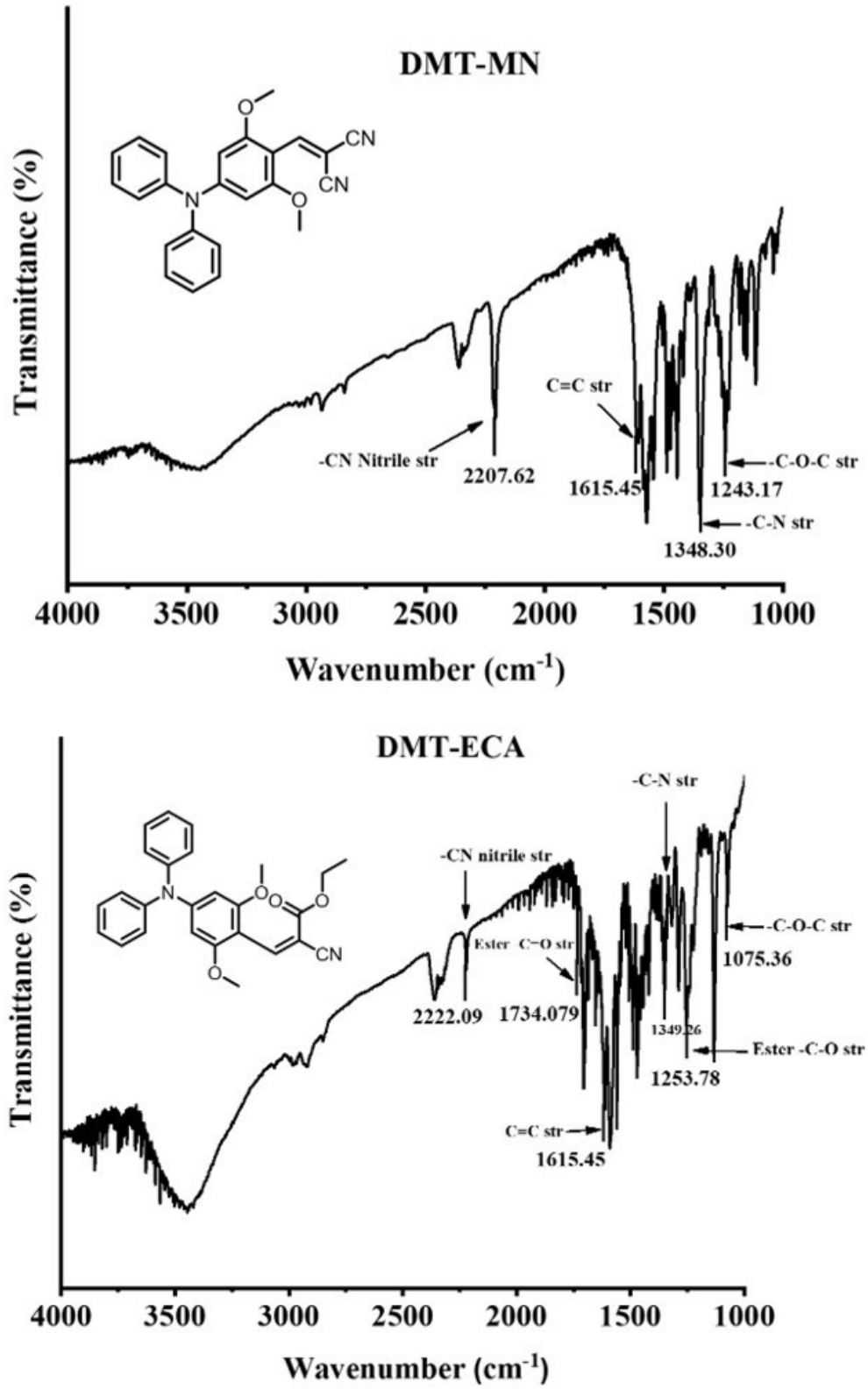
*HRMS spectra of **DMT-CA**.* Calculated: 400.1662; found: 400.1650.



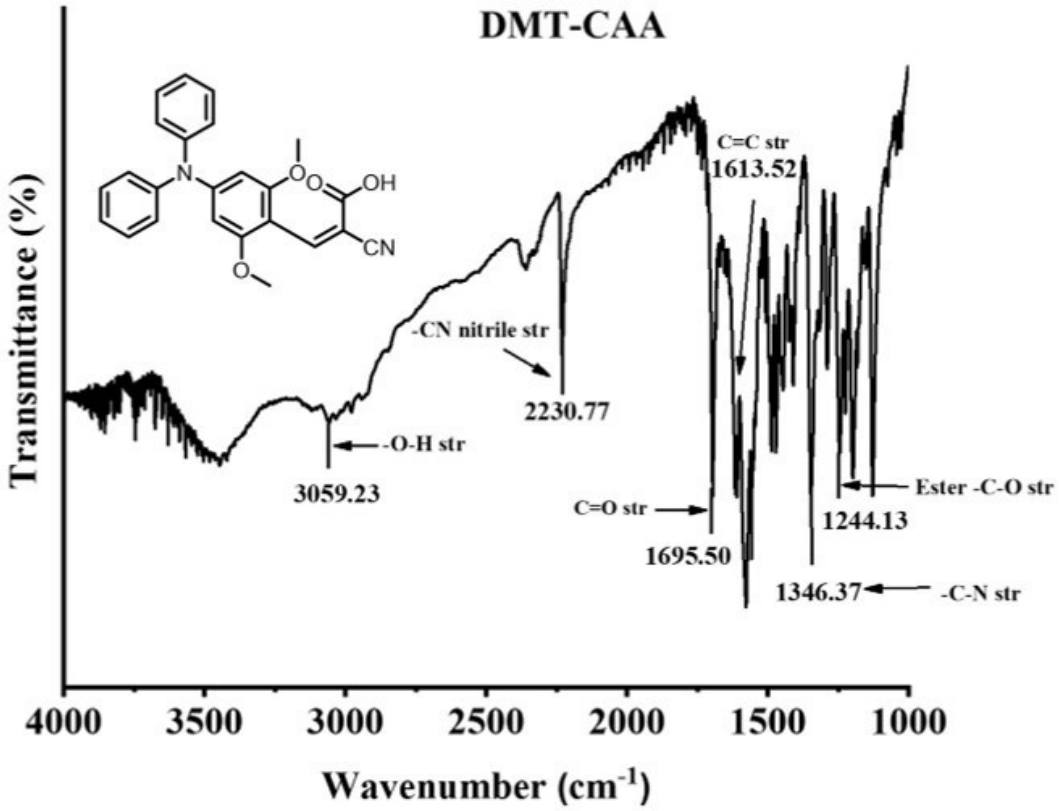
*HRMS spectra of **DMT-IN**.* Calculated: 462.1707; found: 462.1709.

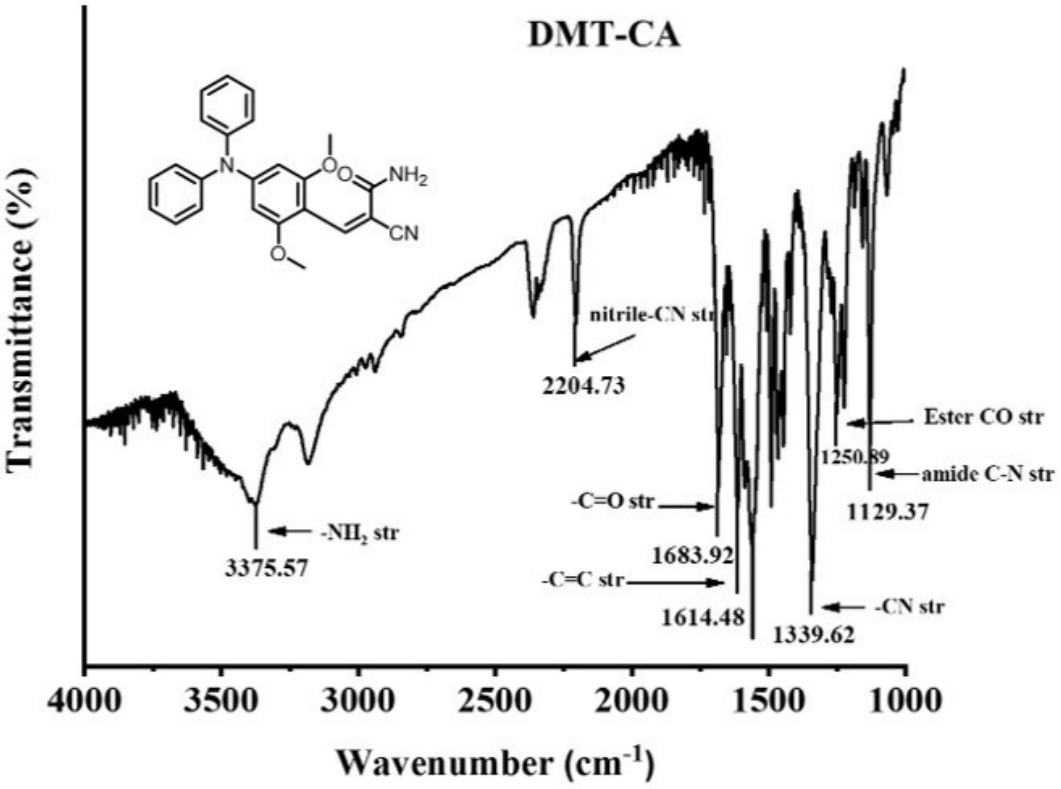


*HRMS spectra of **DMT-BA***. Calculated: 472.1874; found: 472.1869.

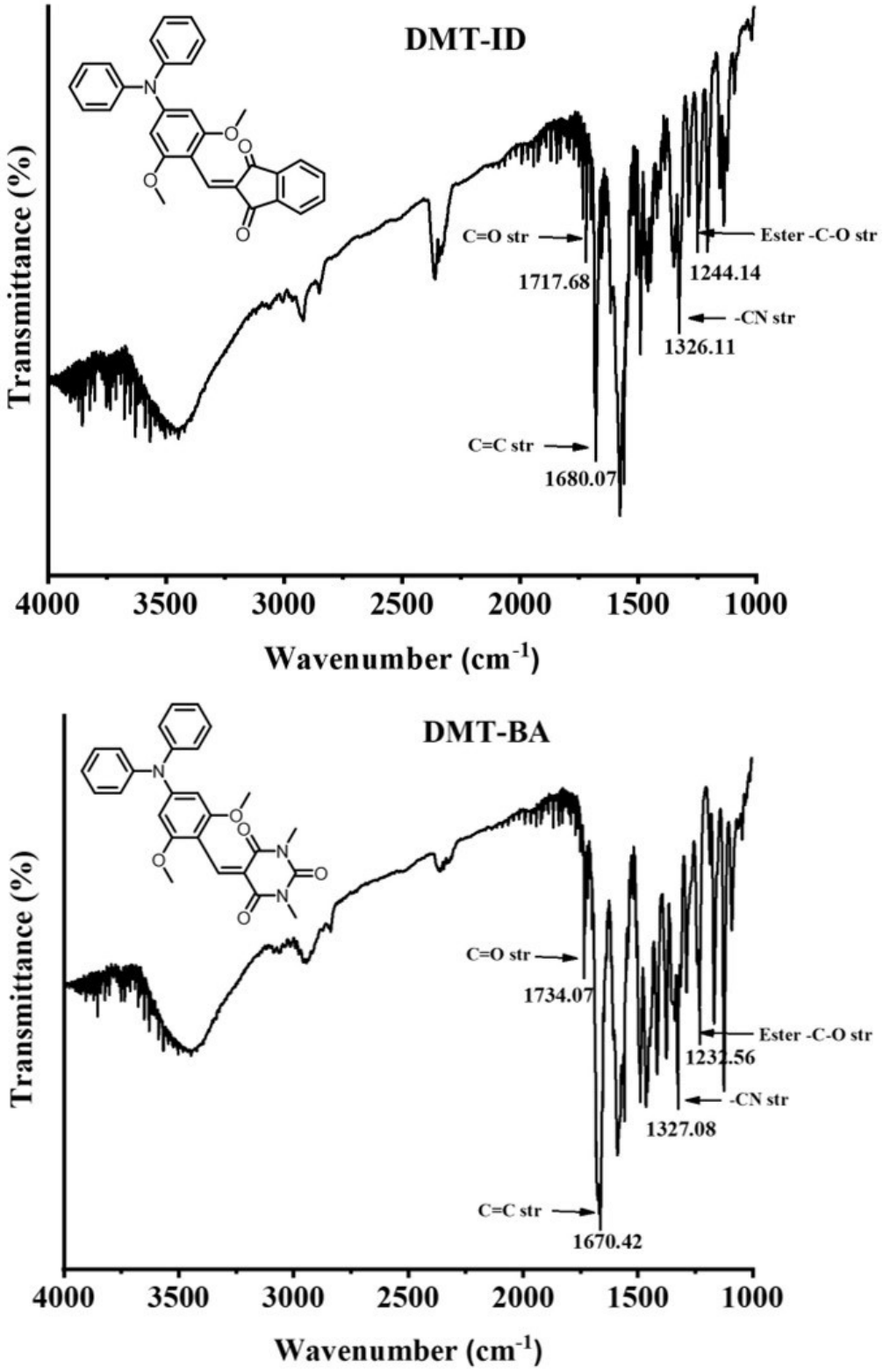


FT-IR of **DMT-MN** and **DMT-ECA**.





FT-IR of **DMT-CAA** and **DMT-CA**.



FT-IR of **DMT-ID** and **DMT-BA**.

Table S1. Crystallographic details of DMT-MN (CCDC No. 2496511).

Empirical formula	C24 H19 N3 O2	
Formula weight	381.42	
Temperature	220(2) K	
Wavelength	0.630 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.5830(19) Å	α = 111.09(3)°
	b = 10.432(2) Å	β = 106.87(3)°
	c = 11.513(2) Å	γ = 94.31(3)°
Volume	1006.6(4) $Å^3$	
Z	2	
Density (calculated)	1.258 Mg/m^3	
Absorption coefficient	0.064 mm^{-1}	
F(000)	400	
Crystal size	0.054 x 0.027 x 0.011 mm^3	
Theta range for data collection	1.788 to 24.999°.	
Index ranges	-12<=h<=12, -13<=k<=13, -15<=l<=15	
Reflections collected	9552	
Independent reflections	4810 [R(int) = 0.0302]	
Completeness to theta = 22.210°	95.3 %	
Absorption correction	Empirical	
Max. and min. transmission	1.000 and 0.974	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4810 / 0 / 265	
Goodness-of-fit on F^2	1.039	
Final R indices [I>2sigma(I)]	R1 = 0.0458, wR2 = 0.1222	
R indices (all data)	R1 = 0.0577, wR2 = 0.1308	
Extinction coefficient	0.237(18)	
Largest diff. peak and hole	0.309 and -0.209 $e \cdot Å^{-3}$	

Table S2. Crystallographic details of DMT-ECA (CCDC No. 2496512).

Empirical formula	C26 H24 N2 O4	
Formula weight	428.47	
Temperature	220(2) K	
Wavelength	0.630 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 8.5990(17) Å	α = 90°
	b = 15.820(3) Å	β = 98.30(3)°
	c = 16.419(3) Å	γ = 90°
Volume	2210.2(8) $Å^3$	
Z	4	
Density (calculated)	1.288 Mg/m^3	
Absorption coefficient	0.068 mm^{-1}	
F(000)	904	
Crystal size	0.097 x 0.008 x 0.007 mm^3	
Theta range for data collection	1.593 to 24.999°.	
Index ranges	-11<=h<=11, -21<=k<=21, -22<=l<=22	
Reflections collected	20707	
Independent reflections	5317 [R(int) = 0.0611]	
Completeness to theta = 22.210°	96.1 %	
Absorption correction	Empirical	
Max. and min. transmission	1.000 and 0.953	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5317 / 0 / 293	
Goodness-of-fit on F^2	1.043	
Final R indices [I>2sigma(I)]	R1 = 0.0552, wR2 = 0.1393	
R indices (all data)	R1 = 0.0877, wR2 = 0.1571	
Extinction coefficient	0.028(3)	
Largest diff. peak and hole	0.381 and -0.283 $e \cdot Å^{-3}$	

Table S3. Crystallographic details of DMT-CAA (CCDC No. 2496513).

Empirical formula	C25 H24 N2 O5	
Formula weight	432.46	
Temperature	220(2) K	
Wavelength	0.630 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 8.3310(17) Å	α = 90°
	b = 15.739(3) Å	β = 100.30(3)°
	c = 16.743(3) Å	γ = 90°
Volume	2160.0(8) $Å^3$	
Z	4	
Density (calculated)	1.330 Mg/m^3	
Absorption coefficient	0.072 mm^{-1}	
F(000)	912	
Crystal size	0.049 x 0.028 x 0.011 mm^3	
Theta range for data collection	2.202 to 24.999°.	
Index ranges	-11<=h<=11, -21<=k<=21, -22<=l<=22	
Reflections collected	20110	
Independent reflections	5452 [R(int) = 0.1219]	
Completeness to theta = 22.210°	99.8 %	
Absorption correction	Empirical	
Max. and min. transmission	1.000 and 0.899	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5452 / 0 / 295	
Goodness-of-fit on F^2	0.980	
Final R indices [I>2sigma(I)]	R1 = 0.0715, wR2 = 0.1680	
R indices (all data)	R1 = 0.1645, wR2 = 0.2163	
Extinction coefficient	0.031(4)	
Largest diff. peak and hole	0.293 and -0.249 $e \cdot Å^{-3}$	

Table S4. Crystallographic details of DMT-CA (CCDC No. 2496514).

Empirical formula	C24 H21 N3 O3	
Formula weight	399.44	
Temperature	220(2) K	
Wavelength	0.630 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.1920(18) Å	α = 92.24(3)°
	b = 10.190(2) Å	β = 95.24(3)°
	c = 23.366(5) Å	γ = 110.23(3)°
Volume	2039.2(8) $Å^3$	
Z	4	
Density (calculated)	1.301 Mg/m^3	
Absorption coefficient	0.068 mm^{-1}	
F(000)	840	
Crystal size	0.069 x 0.054 x 0.027 mm^3	
Theta range for data collection	1.556 to 25.000°.	
Index ranges	-12<=h<=12, -13<=k<=13, -31<=l<=31	
Reflections collected	20301	
Independent reflections	10235 [R(int) = 0.0298]	
Completeness to theta = 22.210°	99.6 %	
Absorption correction	Empirical	
Max. and min. transmission	1.000 and 0.780	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10235 / 0 / 546	
Goodness-of-fit on F^2	1.034	
Final R indices [I>2sigma(I)]	R1 = 0.0525, wR2 = 0.1351	
R indices (all data)	R1 = 0.0770, wR2 = 0.1498	
Extinction coefficient	0.120(5)	
Largest diff. peak and hole	0.369 and -0.267 $e \cdot Å^{-3}$	

Table S5. Crystallographic details of DMT-ID (CCDC No. 2496515)

Empirical formula	C30 H23 N O4	
Formula weight	461.49	
Temperature	220(2) K	
Wavelength	0.630 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 16.077(3) Å	α = 90°
	b = 8.4550(17) Å	β = 112.88(3)°
	c = 18.890(4) Å	γ = 90°
Volume	2365.8(10) $Å^3$	
Z	4	
Density (calculated)	1.296 Mg/m^3	
Absorption coefficient	0.067 mm^{-1}	
F(000)	968	
Crystal size	0.079 x 0.064 x 0.049 mm^3	
Theta range for data collection	1.882 to 24.997°.	
Index ranges	-21<=h<=21, -11<=k<=11, -25<=l<=25	
Reflections collected	21713	
Independent reflections	5989 [R(int) = 0.0725]	
Completeness to theta = 22.210°	100.0 %	
Absorption correction	Empirical	
Max. and min. transmission	1.000 and 0.982	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5989 / 0 / 319	
Goodness-of-fit on F^2	1.070	
Final R indices [I>2sigma(I)]	R1 = 0.0505, wR2 = 0.1307	
R indices (all data)	R1 = 0.0684, wR2 = 0.1411	
Extinction coefficient	0.042(3)	
Largest diff. peak and hole	0.245 and -0.243 $e \cdot Å^{-3}$	

Table S6. Crystallographic details of DMT-BA (CCDC No. 2496516)

Empirical formula	C27 H25 N3 O5	
Formula weight	471.50	
Temperature	220(2) K	
Wavelength	0.630 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.187(2) Å	α = 81.72(3)°
	b = 14.173(3) Å	β = 82.40(3)°
	c = 14.888(3) Å	γ = 89.71(3)°
Volume	2315.1(8) $Å^3$	
Z	4	
Density (calculated)	1.353 Mg/m^3	
Absorption coefficient	0.073 mm^{-1}	
F(000)	992	
Crystal size	0.059 x 0.048 x 0.011 mm^3	
Theta range for data collection	1.287 to 25.000°.	
Index ranges	-15<=h<=15, -19<=k<=19, -19<=l<=19	
Reflections collected	23392	
Independent reflections	11698 [R(int) = 0.0502]	
Completeness to theta = 22.210°	100.0 %	
Absorption correction	Empirical	
Max. and min. transmission	1.000 and 0.815	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11698 / 0 / 640	
Goodness-of-fit on F^2	0.979	
Final R indices [I>2sigma(I)]	R1 = 0.0837, wR2 = 0.2202	
R indices (all data)	R1 = 0.1647, wR2 = 0.2743	
Extinction coefficient	0.049(4)	
Largest diff. peak and hole	0.444 and -0.213 $e·Å^{-3}$	

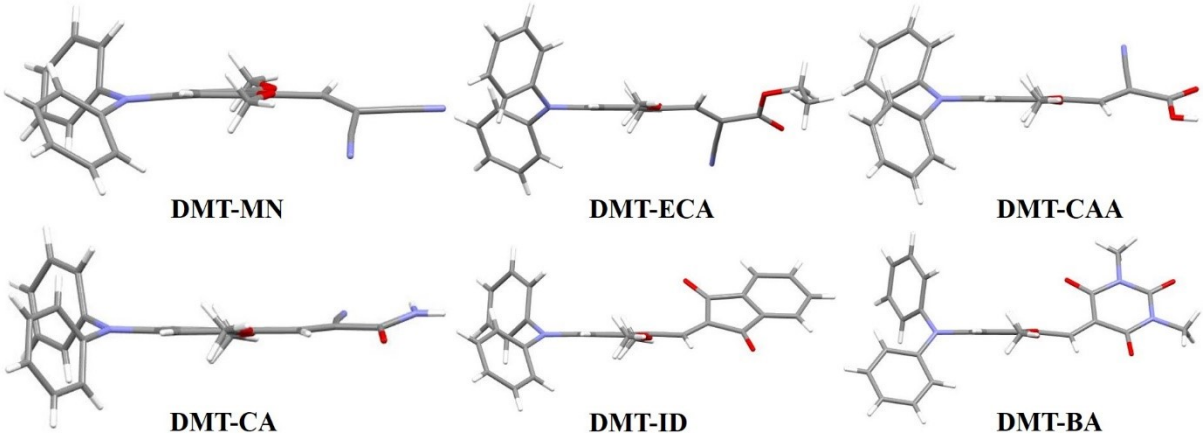
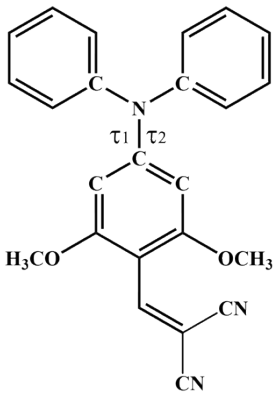


Figure S1. Molecular conformation in the crystal lattice of DMT-acceptor fluorophores**.** C (grey), H (white), N (blue) and O (red).

Table S7. Torsion angle of DMT-acceptor fluorophores in the crystal lattice.



	Torsion angle (τ)	
	τ1	τ2
DMT-MN	17.32	14.86
DMT-ECA	40.63	32.68
DMT-CAA	31.23	34.98
DMT-CA-I	15.51	15.45
DMT-CA-II	19.07	28.59
DMT-ID	24.69	29.79
DMT-BA-I	49.53	50.58
DMT-BA-II	52.17	49.07

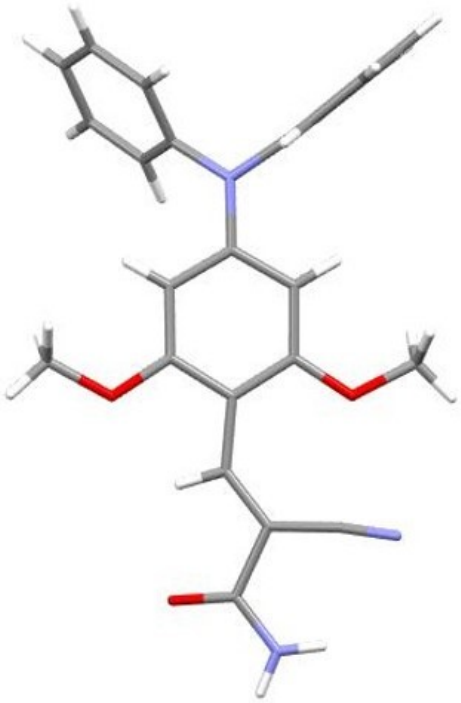


Figure S2. Molecular conformation of DMT-CA in the crystal lattice. It is noted that DMT-CA has two molecules in the unit cell, and both showed different conformation.

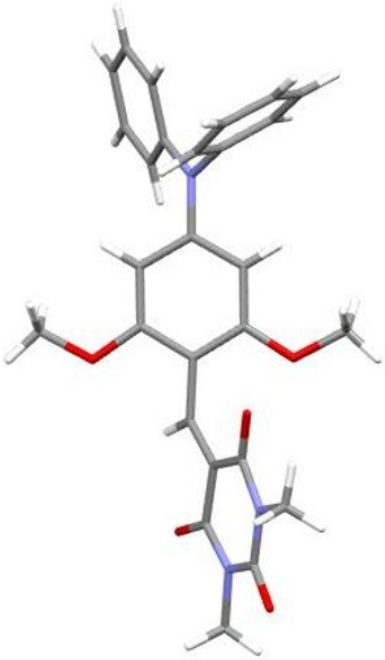


Figure S3. Molecular conformation of DMT-BA in the crystal lattice. It is noted that DMT-BA has two molecules in the unit cell and both showed different conformation.

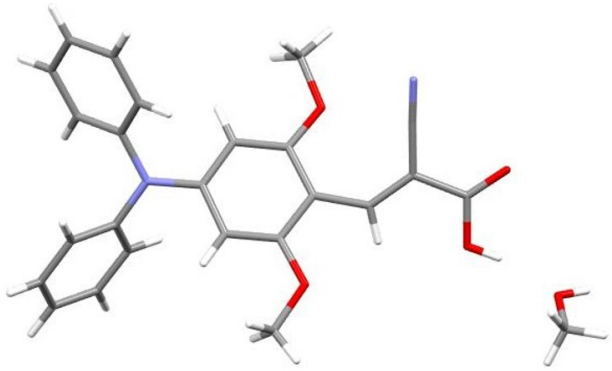


Figure S4. Asymmetric unit in the crystal lattice of DMT-CAA**.**

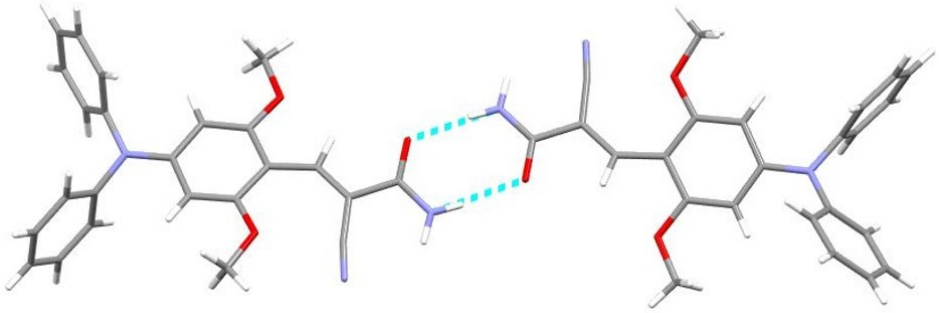


Figure S5. Complimentary amide H-bonding in the crystal lattice of DMT-CA**.**

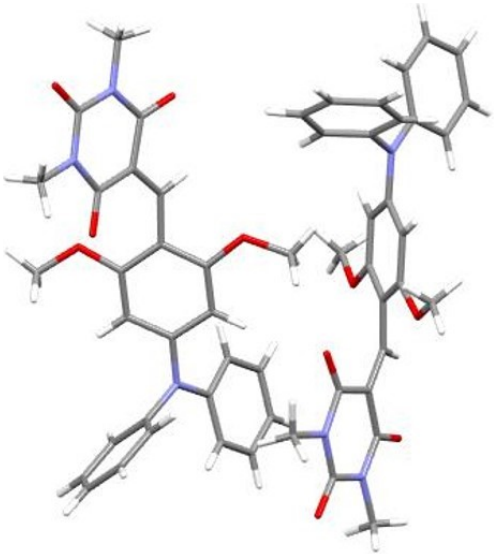


Figure S6. Unit cell of DMT-BA.

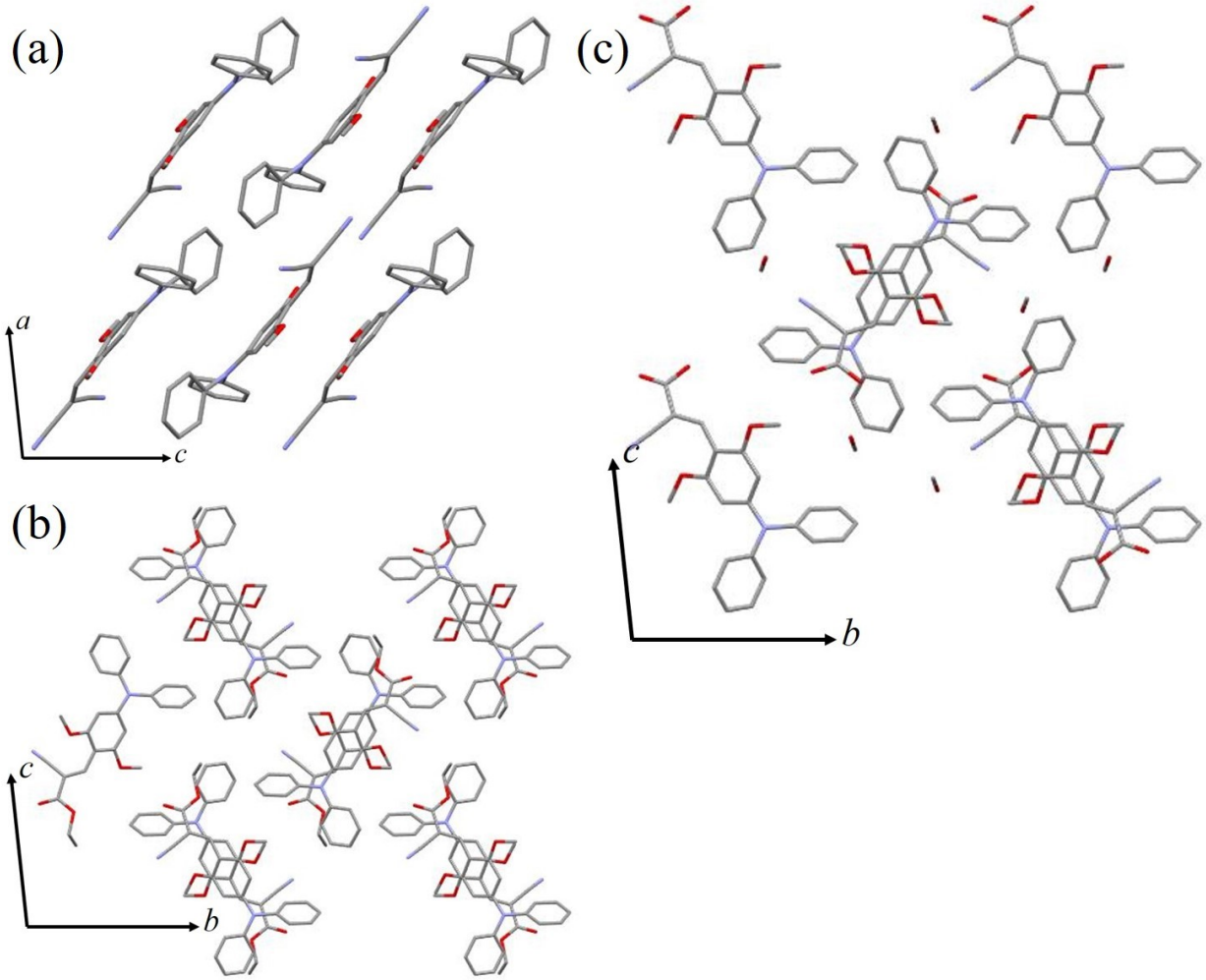


Figure S7. Molecular packing in the crystal lattice of (a) DMT-MN, (b) DMT-ECA and (c) DMT-CAA**.** C (grey), H (white), N (blue) and O (red). H-atoms are omitted for clarity.

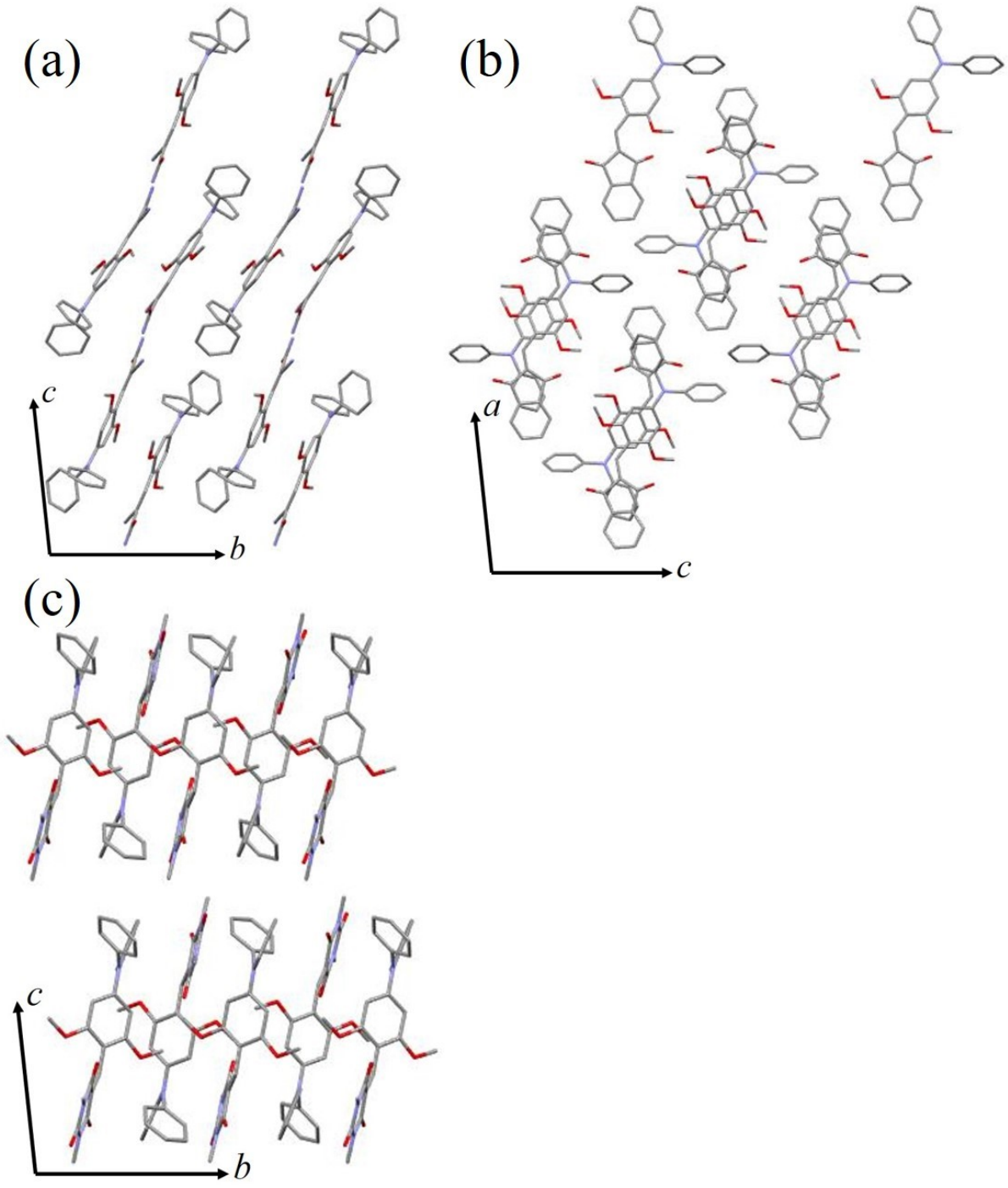


Figure S8. Molecular packing in the crystal lattice of (a) DMT-CA, (b) DMT-ID and (c) DMT-BA**.** C (grey), H (white), N (blue) and O (red). H-atoms are omitted for clarity.

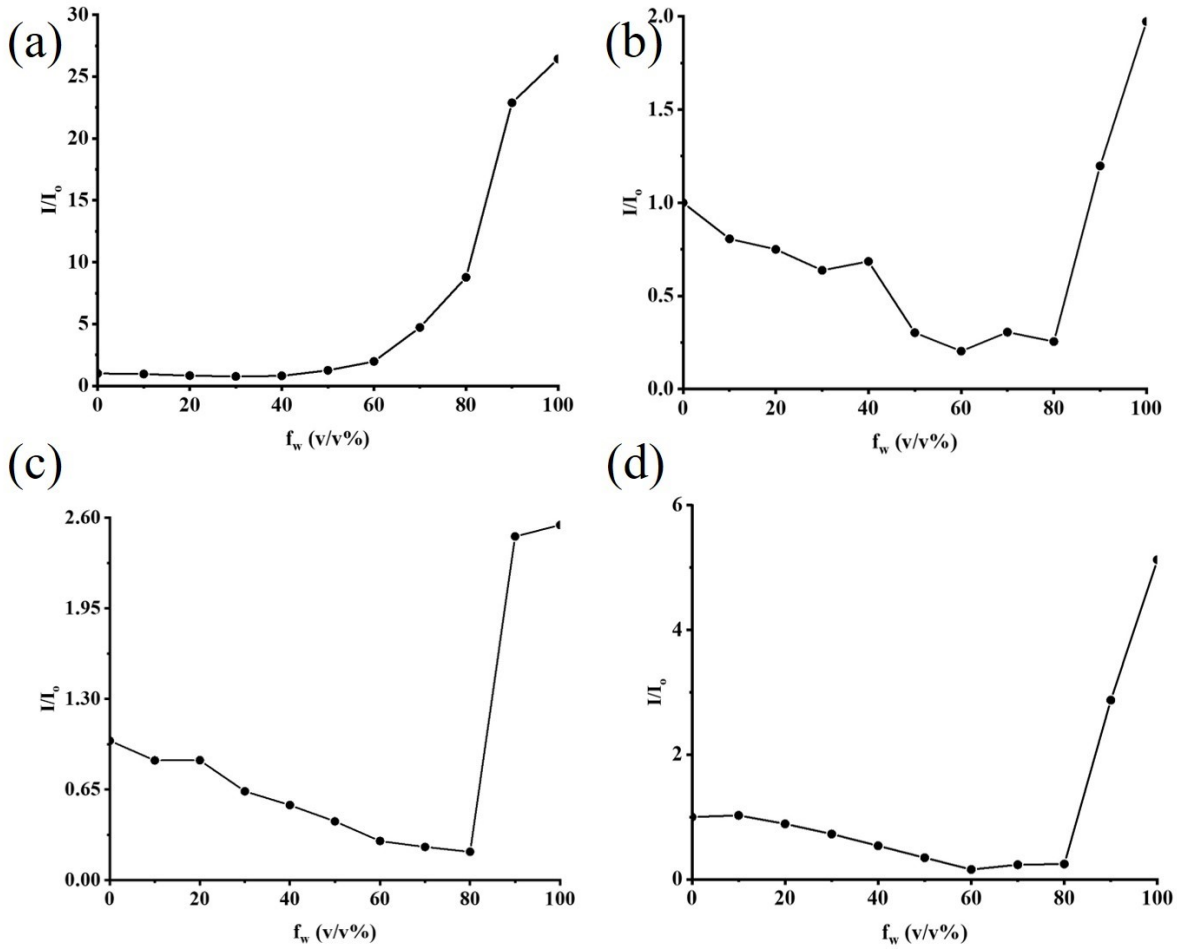


Figure S9. Change of fluorescence intensity of (DMT-MN, (b) DMT-ECA, (c) DMT-CA and (d) DMT-ID with water fractions.

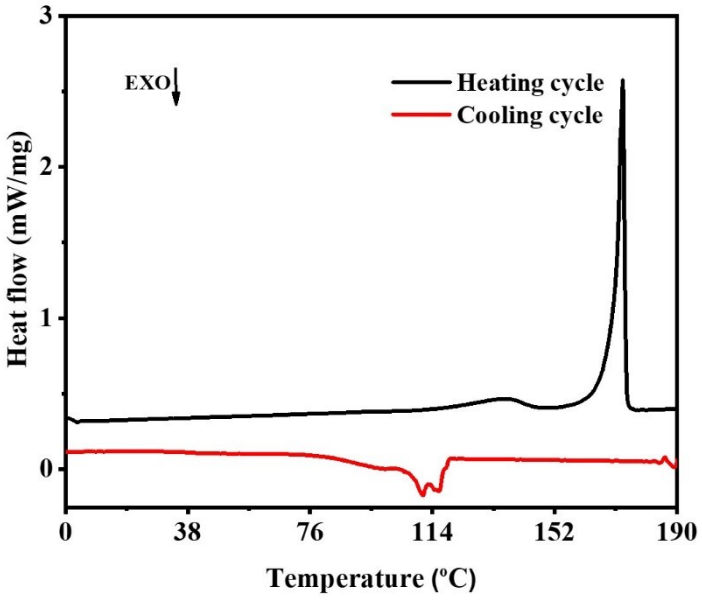
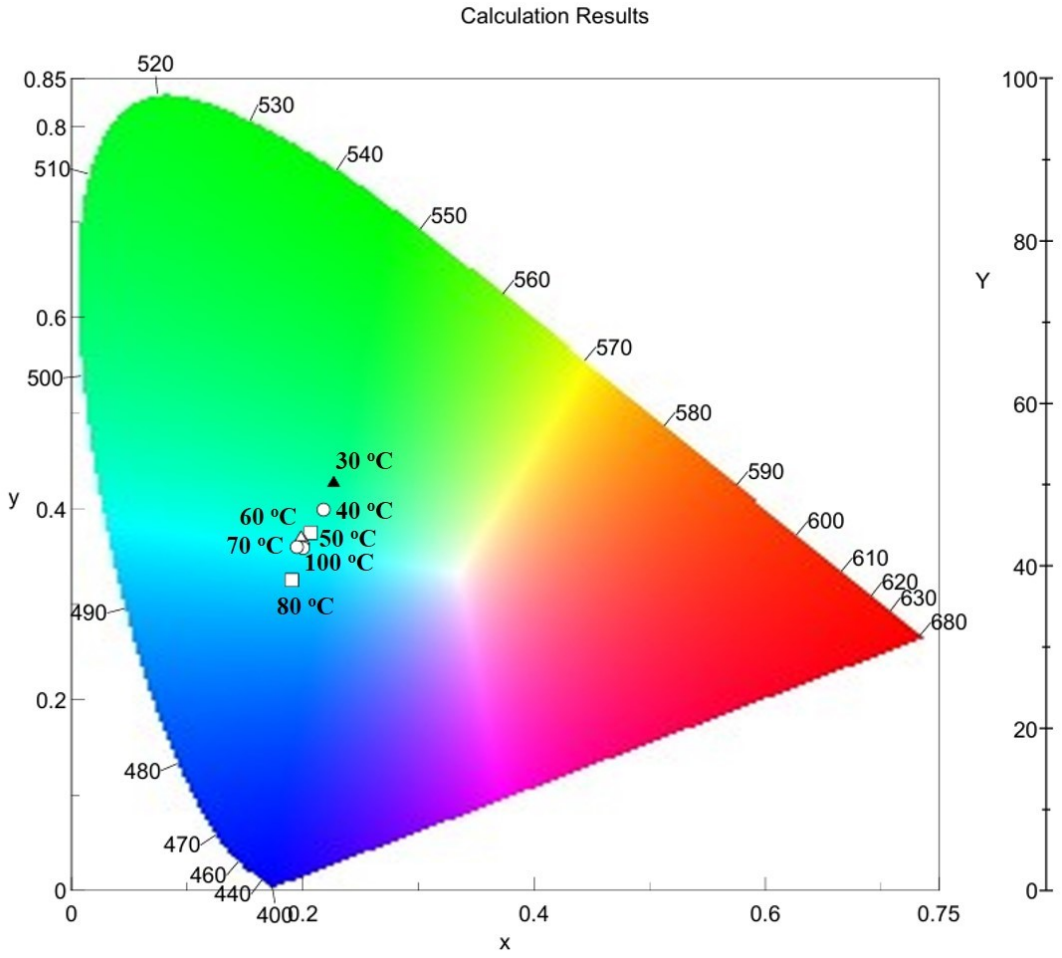
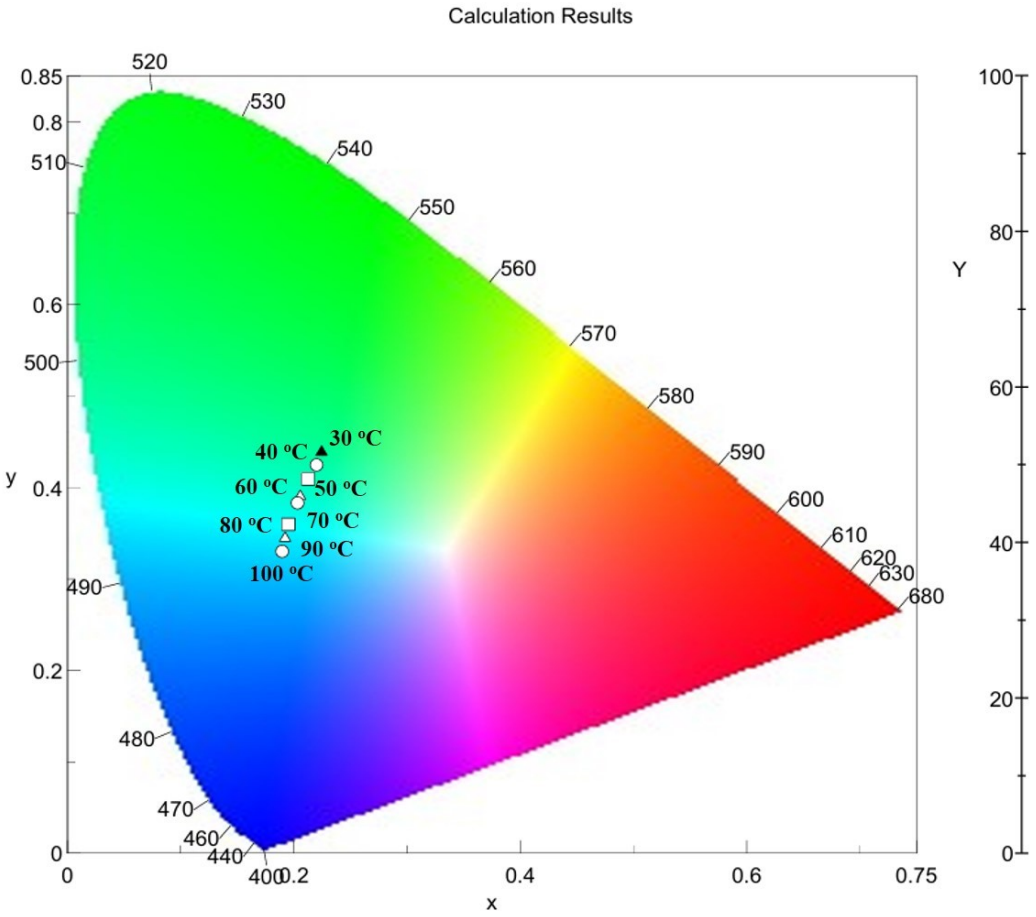


Figure S10. DSC of DMT-ECA.



No.	Legend	File Name	x	y	u	v	Tcp (K)	duv	Lambda
1	▲	30 °C	0.2268	0.4262	0.1184	0.3338	9196	0.082	503.46
2	○	40 °C	0.218	0.3985	0.1187	0.3255	10338	0.079	499.1
3	□	50 °C	0.2071	0.3741	0.1171	0.3173	12080	0.077	495.87
4	△	60 °C	0.2013	0.3654	0.1153	0.314	13123	0.077	494.83
5	○	70 °C	0.2004	0.3581	0.1162	0.3116	13762	0.075	494.11
6	□	80 °C	0.1906	0.3248	0.117	0.2991	19975	0.07	490.95
7	△	90 °C	0.1985	0.3694	0.1129	0.315	13117	0.08	495.15
8	○	100 °C	0.1949	0.3592	0.1127	0.3114	14254	0.079	494.11

Figure S11. CIE coordinate of DMT-ECA in toluene while heating from 30 to 100°C.



No.	Legend	File Name	x	y	u	v	Tcp (K)	duv	Lambda
1	▲	30 °C	0.2246	0.4382	0.115	0.3367	9068	0.087	504.83
2	○	40 °C	0.2201	0.4243	0.1151	0.3327	9543	0.085	502.45
3	□	50 °C	0.2129	0.4088	0.1138	0.3279	10309	0.084	499.95
4	△	60 °C	0.2057	0.3901	0.1132	0.322	11416	0.082	497.49
5	○	70 °C	0.2033	0.3829	0.1131	0.3196	11927	0.081	496.63
6	□	80 °C	0.1953	0.3594	0.1128	0.3115	14208	0.078	494.13
7	△	90 °C	0.1923	0.3442	0.114	0.3061	16227	0.075	492.7
8	○	100 °C	0.1897	0.3299	0.1153	0.3008	19059	0.073	491.41

Figure S12. CIE coordinate of DMT-ECA in toluene while cooling from 100 to 30°C.

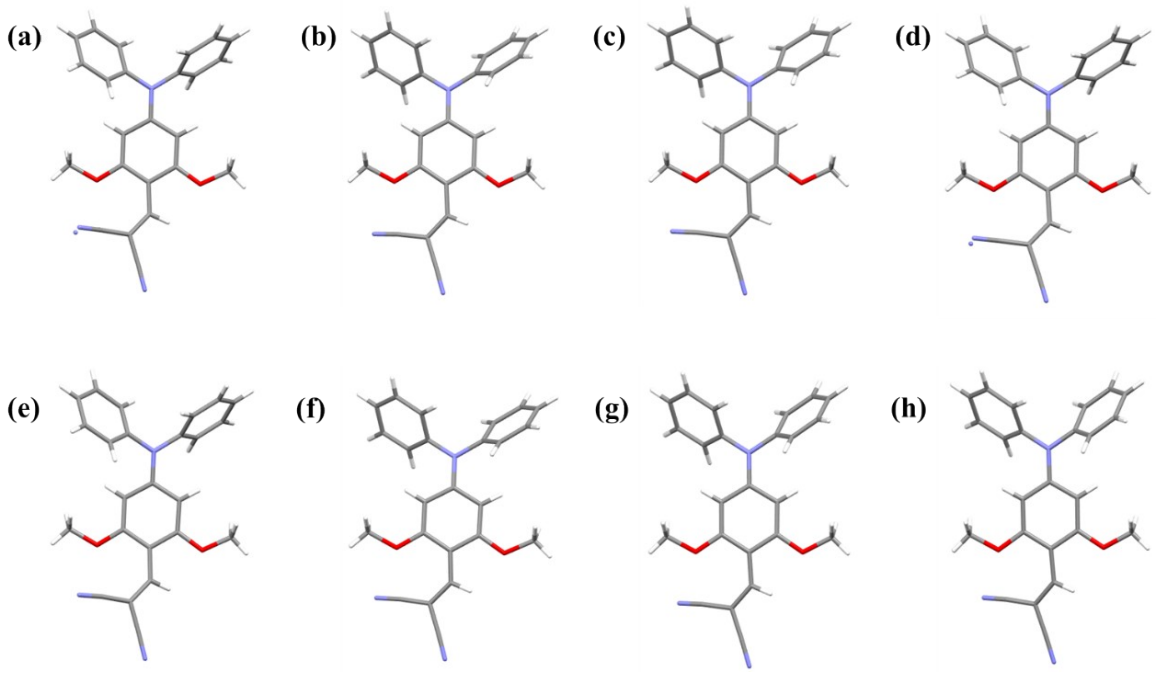
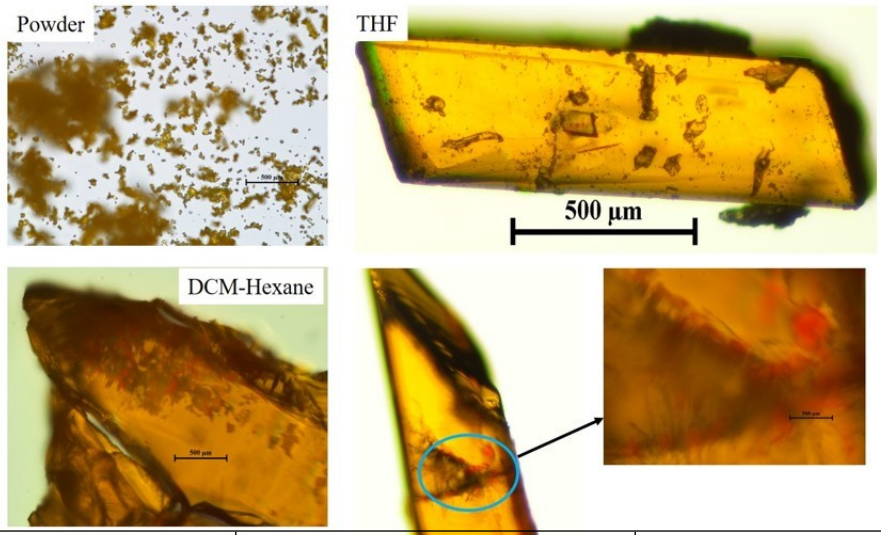


Figure S13. DMT-MN molecular conformation in the crystal lattice of DMT-MN crystallized from different solvents **(a)** $CHCl_3$: MeOH **(b)** EtOAc **(c)** acetonitrile **(d)** toluene **(e)** $CHCl_3$: EtOH **(f)** THF **(g)** DCM: EtOH **(h)** DCM: Hexane**.** C (grey), H (white), N (blue) and O (red).

Table S8. Twist angle between acceptor and TPA phenyl unit of DMT-MN.

(a)



(b)

S.No	DMT-MN crystals	Twist angle (° deg)
1	$CHCl_3$:MeOH	23.30
2	EtOAc	23.21
3	CH_3CN	23.47
4	Toluene	23.54
5	$CHCl_3$:EtOH	23.44
6	THF	23.09
7	DCM:EtOH	23.36
8	DCM:Hexane	23.42

Figure S14. Optical images of DMT-MN crystals grown from different solvents.