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Electronic Supplementary Information (ESI)

Funnel shaped molecules containing benzo/pyrido[1,2,5]thiadiazole functionalities as peripheral acceptors for organic photovoltaic applications

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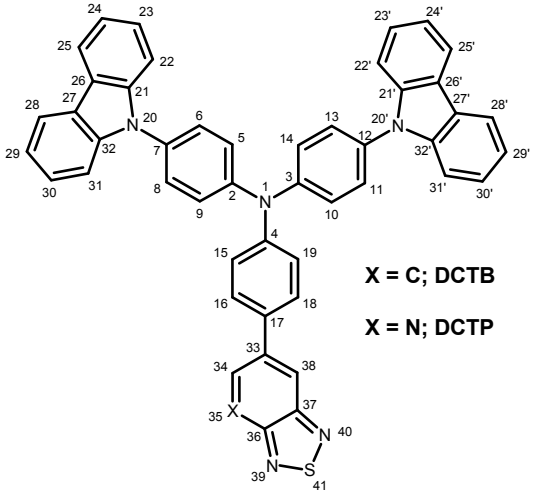
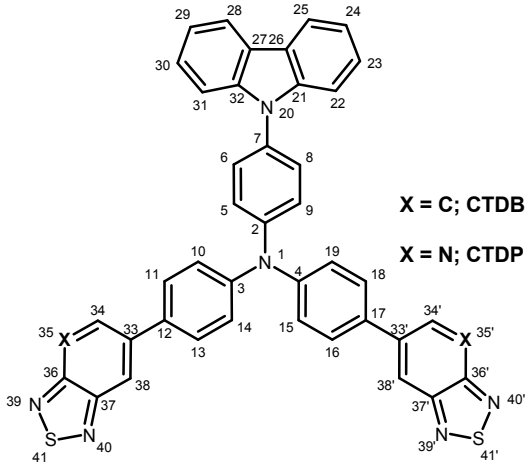




Bond Length	DCTB	DCTP
N_1-C_2 / N_1-C_3	1.421 / 1.421	1.423 / 1.422
N_1-C_4 / C_2-C_5	1.417 / 1.401	1.414 / 1.401
C_5-C_6 / C_6-C_7	1.389 / 1.398	1.389 / 1.398
C_7-C_8 / C_8-C_9	1.398 / 1.389	1.398 / 1.389
C_9-C_2 / C_3-C_{10}	1.401 / 1.401	1.401 / 1.401
C_3-C_{14} / C_{10}-C_{11}	1.401 / 1.389	1.401 / 1.389
C_{11}-C_{12} / C_{12}-C_{13}	1.398 / 1.398	1.398 / 1.398
C_{13}-C_{14} / C_4-C_{15}	1.389 / 1.402	1.389 / 1.403
C_4-C_{19} / C_{15}-C_{16}	1.403 / 1.388	1.404 / 1.387
C_{16}-C_{17} / C_{17}-C_{18}	1.403 / 1.404	1.404 / 1.404
C_{18}-C_{19} / C_7-N_{20}	1.387 / 1.419	1.386 / 1.418
C_{21}-N_{20} / C_{32}-N_{20}	1.399 / 1.399	1.399 / 1.400
C_{21}-C_{22} / C_{22}-C_{23}	1.396 / 1.389	1.396 / 1.389
C_{23}-C_{24} / C_{24}-C_{25}	1.410 / 1.392	1.410 / 1.392
C_{25}-C_{26} / C_{25}-C_{26}	1.399 / 1.447	1.399 / 1.447
C_{26}-C_{27} / C_{28}-C_{29}	1.399 / 1.392	1.399 / 1.392
C_{29}-C_{30} / C_{30}-C_{31}	1.410/ 1.389	1.410/ 1.389
C_{31}-C_{32} / C_{17}-C_{33}	1.396 / 1.481	1.396 / 1.478
C_{33}-C_{34} / C_{36}-C_{37}	1.443 / 1.448	1.448 / 1.448
C_{36}-X_{35} / C_{34}-X_{35}	**1.365 / 1.423**	**1.306 / 1.360**
C_{37}-C_{38}/C_{38}-C_{33}	1.420 / 1.377	1.417 / 1.376
C_{36}-N_{39} / C_{37}-N_{40}	1. 335 / 1.338	1. 335 / 1.335
N_{39}-S_{41} / N_{40}-S_{41}	1.642/ 1.641	1.635/ 1.647

Bond Length	CTDB	CTDP
N_1-C_2 / N_1-C_3	1.422 / 1.419	1.426 / 1.416
N_1-C_4 / C_2-C_5	1.417 / 1.401	1.416 / 1.400
C_5-C_6 / C_6-C_7	1.389 / 1.398	1.389 / 1.399
C_7-C_8 / C_8-C_9	1.398 / 1.389	1.399 / 1.389
C_9-C_2 / C_3-C_{10}	1.401 / 1.402	1.400 / 1.402
C_{10}-C_{11} / C_{11}-C_{12}	1.388 / 1.403	1.388 / 1.403
C_{12}-C_{13} / C_{13}-C_{14}	1.403 / 1.388	1.404 / 1.387
C_{14}-C_3 / C_4-C_{15}	1.402 / 1.402	1.403 / 1.403
C_{15}-C_{16} / C_{16}-C_{17}	1.387 / 1.404	1.387 / 1.404
C_{17}-C_{18} / C_{18}-C_{19}	1.403 / 1.388	1.403 / 1.388
C_7-N_{20} / C_{21}-N_{20}	1.419 / 1.399	1.417 / 1.400
C_{32}-N_{20} / C_{21}-C_{22}	1.399 / 1.396	1.400 / 1.396
C_{22}-C_{23} / C_{23}-C_{24}	1.389 / 1.410	1.389 / 1.410
C_{24}-C_{25} / C_{25}-C_{26}	1.392 / 1.399	1.392 / 1.399
C_{26}-C_{27} / C_{27}-C_{28}	1.447 / 1.399	1.447 / 1.399
C_{28}-C_{29} / C_{29}-C_{30}	1.392/ 1.410	1.392/ 1.410
C_{30}-C_{31} / C_{31}-C_{32}	1.389 / 1.396	1.389 / 1.396
C_{12}-C_{33} / C_{33}-C_{34}	1.482 / 1.443	1.478/ 1.447
C_{34}-X_{35} / X_{35}-C_{36}	**1.365 / 1.423**	**1.306 / 1.360**
C_{36}-C_{37} /C_{37}-C_{38}	1.448 / 1.420	1.448 / 1.417
C_{36}-N_{39} / C_{37}-N_{40}	1. 338 / 1.335	1. 335 / 1.335
N_{39}-S_{41} / N_{40}-S_{41}	1.641/ 1.642	1.646/ 1.635
C_{38}-C_{33} / C_{19}-C_4	1.377 / 1.402	1.377 / 1.402

Fig. S1. Geometrical Coordinates of target dyes.

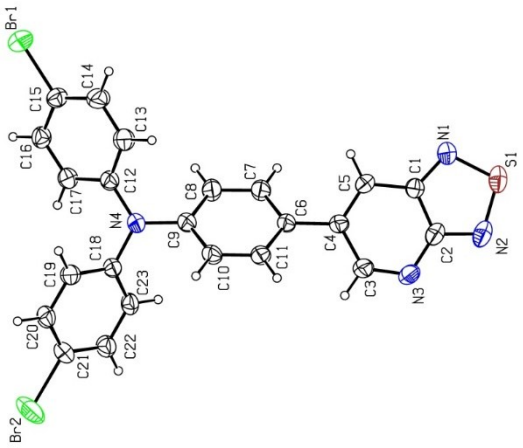


Fig. S2. The ORTEP diagram of intermediate **6b** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level for non-hydrogen atoms and H atoms are shown as small spheres of arbitrary radius.

Crystallographic data for DCTP: $C_{48}H_{40}N_8S_2$, M = 793.00, 0.43 x 0.21 x 0.12 mm^3, triclinic, space group $P\bar{1}$ (No. 2), a = 12.4586(9), b = 14.8169(10), c = 15.6249(11) Å, α = 110.3700(10), β = 99.7720(10), γ = 112.0440(10)°, V = 2351.8(3) Å^3, Z = 2, D_c = 1.120 g/cm^3, F_{000} = 832, CCD area detector, MoKα radiation, λ = 0.71073 Å, T = 293(2)K, $2\theta_{max}$ = 50.0º, 8274 reflections collected, 8274 unique (R_{int} = 0.0265), Final *GooF* = 0.998, *R1* = 0.0712, *wR2* = 0.1928, *R* indices based on 6084 reflections with I >2σ(I) (refinement on F^2), 529 parameters, 15 restraints and μ = 0.153 mm^{-1}.

Crystallographic data for Intermediate 6b: $C_{23}H_{14}Br_2N_4S$, M = 538.26, 0.32 x 0.19 x 0.12 mm^3, monoclinic, space group $P2_1/n$ (No. 14), a = 8.3446(12), b = 23.178(3), c = 10.9171(14) Å, β = 94.496(3)°, V = 2105.0(5) Å^3, Z = 4, D_c = 1.698 g/cm^3, F_{000} = 1064, CCD area detector, MoKα radiation, λ = 0.71073 Å, T = 293(2)K, $2\theta_{max}$ = 50.0º, 20022 reflections collected, 3696 unique (R_{int} = 0.0443), Final *GooF* = 1.024, *R1* = 0.0504, *wR2* = 0.1263, *R* indices based on 2718 reflections with I >2σ(I) (refinement on F^2), 271 parameters and μ = 3.968 mm^{-1}.

CCDC number of **DCTP**: 1038010

CCDC number of Intermediate **6b**: 1038011

Table S1: Photophysical properties of the dyes

Dye	λ_{flu}[a] (nm)	Stokes shift (cm^{-1})	Φ_f[c]	τ[d] (ns)	K_r[e] (10^9 s^{-1})	K_{nr}[f] (10^9 s^{-1})	K_{ET}[g] (x 10^8 s^{-1})
DCTB	542	6000	0.13	6.61	0.019	0.13	1.51
DCTP	576	5627	0.18	7.29	0.024	0.11	1.37
CTDB	507	4667	0.11	5.11	0.022	0.17	1.96
CTDP	581	5883	0.16	7.03	0.023	0.12	1.42

[a]Emission spectra in toluene (solution concentration = 10-5 M) at ambient temperature. [c]Fluorescence quantum yield measured in toluene; [d]Excited state lifetime in nanoseconds (ns); [e]Radiative decay constant (Kr= Φf/τ); [f]Non-radiative decay constant (Knr= (1-Φf)/τ)); [g]Electron transfer rate constants (error limit of τ and KET ~10%).

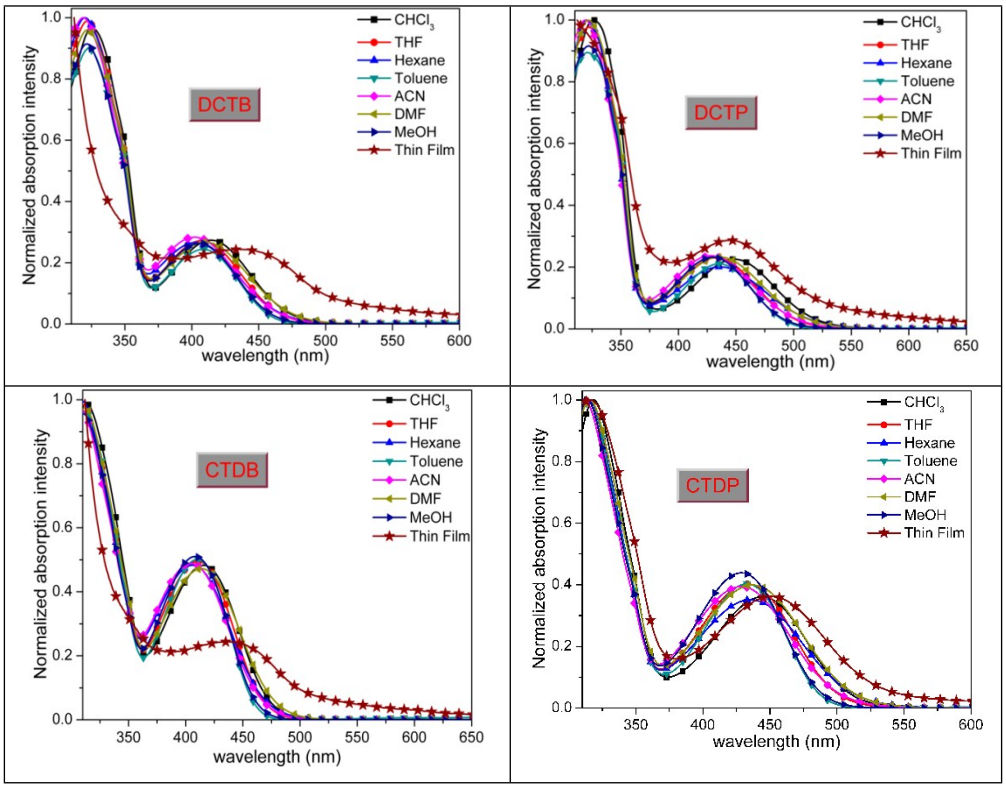


Fig. S3. UV-Vis absorption spectra of the dyes in different solvents and thin film state.

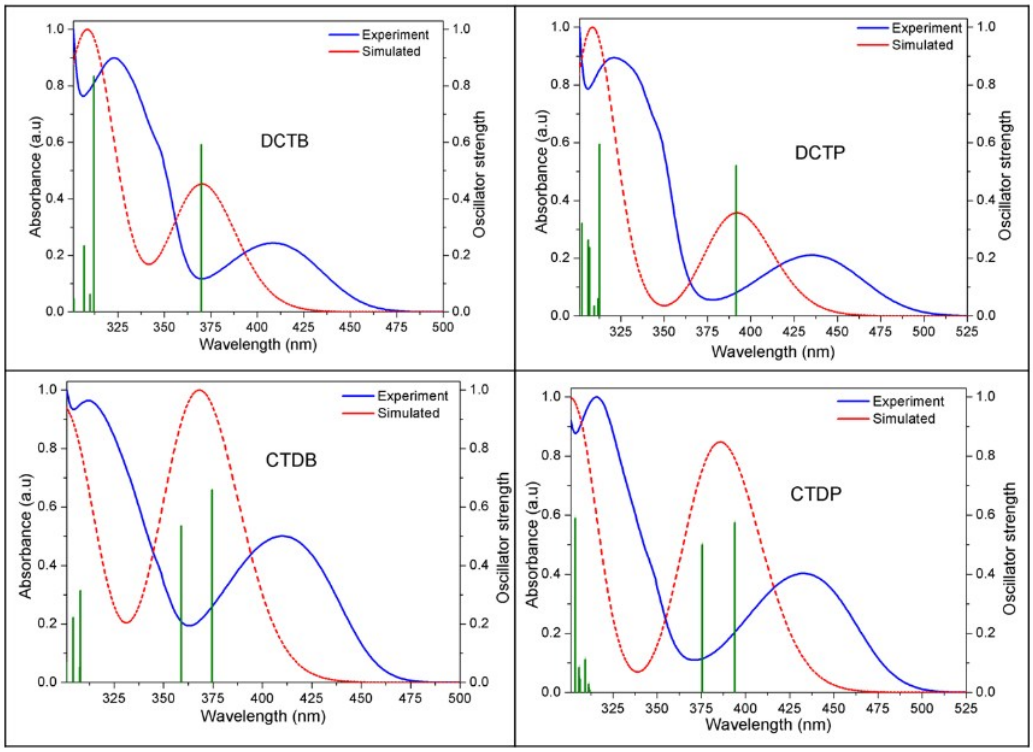


Fig. S4. Normalized plots of simulated and experimental UV-Vis spectra of the dyes. The green vertical bars correspond to the calculated singlet excited states in GaussSum 2.2.5.

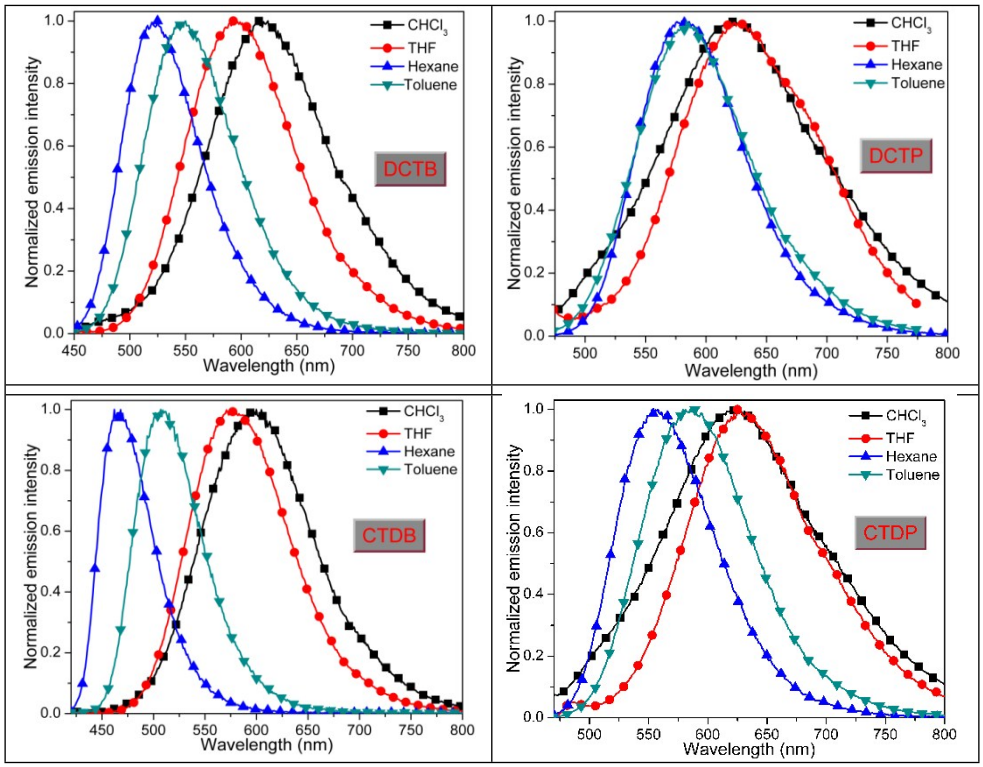


Fig. S5. Photoluminescence spectra of the dyes in different solvents.

Table S2. Absorption maxima of the dyes in different solvents (units in nm).

Compound	$CHCl_3$	THF	Hexane	Toluene	ACN	DMF	MeOH
DCTB	414	408	403	409	402	410	406
DCTP	449	433	436	435	428	436	430
CTDB	416	411	406	410	405	414	408
CTDP	444	434	436	433	428	437	429

Table S3. Emission maxima of the dyes in different solvents (units in nm).

Compound	$CHCl_3$	THF	Hexane	Toluene	ACN	DMF	MeOH
DCTB	616	602	560	616	-Q-	-Q-	-Q-
DCTP	649	656	608	648	-Q-	-Q-	-Q-
CTDB	573	574	531	573	-Q-	-Q-	-Q-
CTDP	598	593	550	596	-Q-	-Q-	-Q-

Table S4. Stokes shift of the dyes in different solvents (units in cm^{-1}).

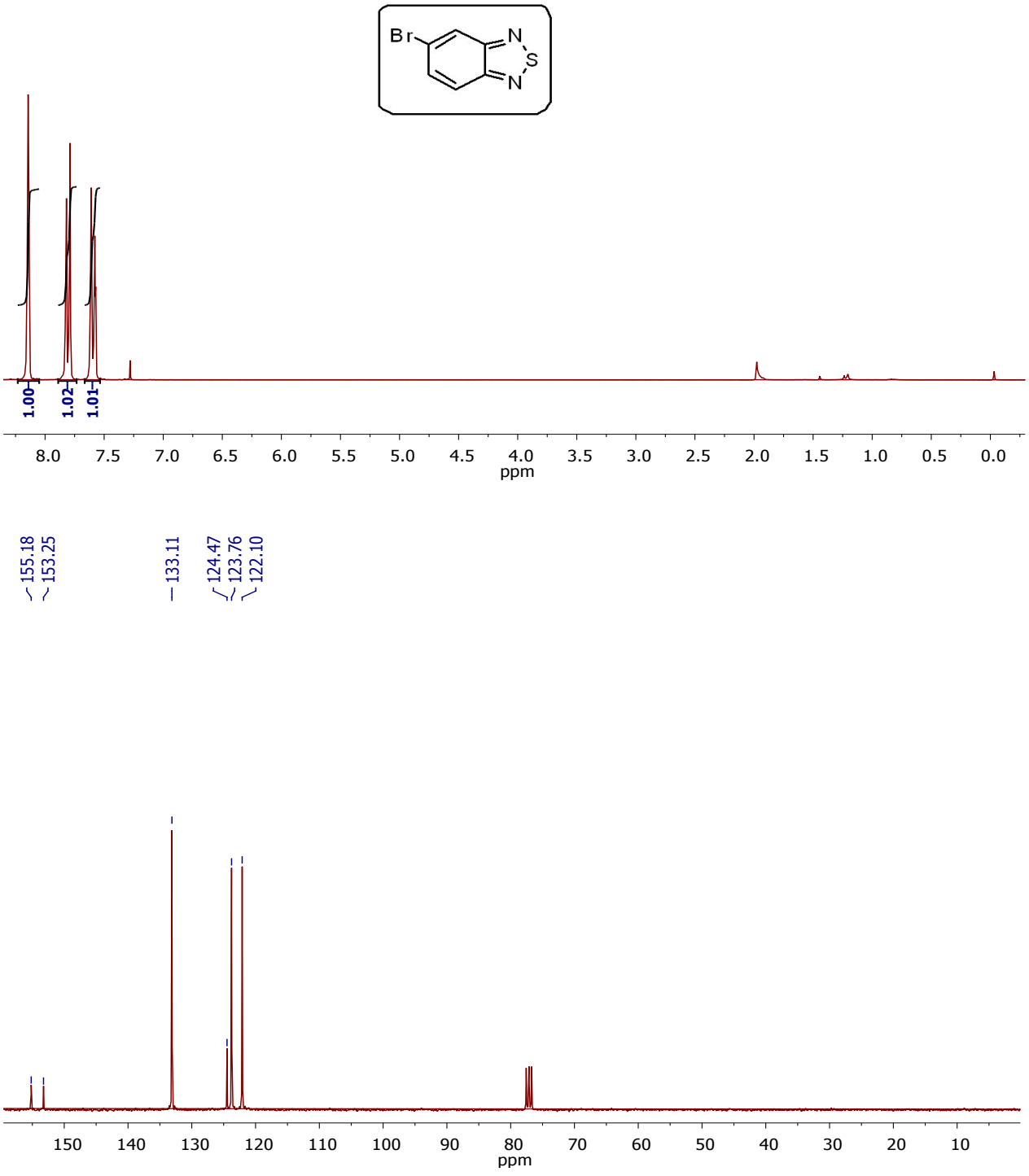
Compound	$CHCl_3$	THF	Hexane	Toluene	ACN	DMF	MeOH
DCTB	7921	7899	6957	8216	-	-	-
DCTP	6863	7851	6488	7556	-	-	-
CTDB	6587	6909	5798	6937	-	-	-
CTDP	5800	6178	4754	6316	-	-	-

Table S5. HOMO, LUMO energy values obtained from DFT studies

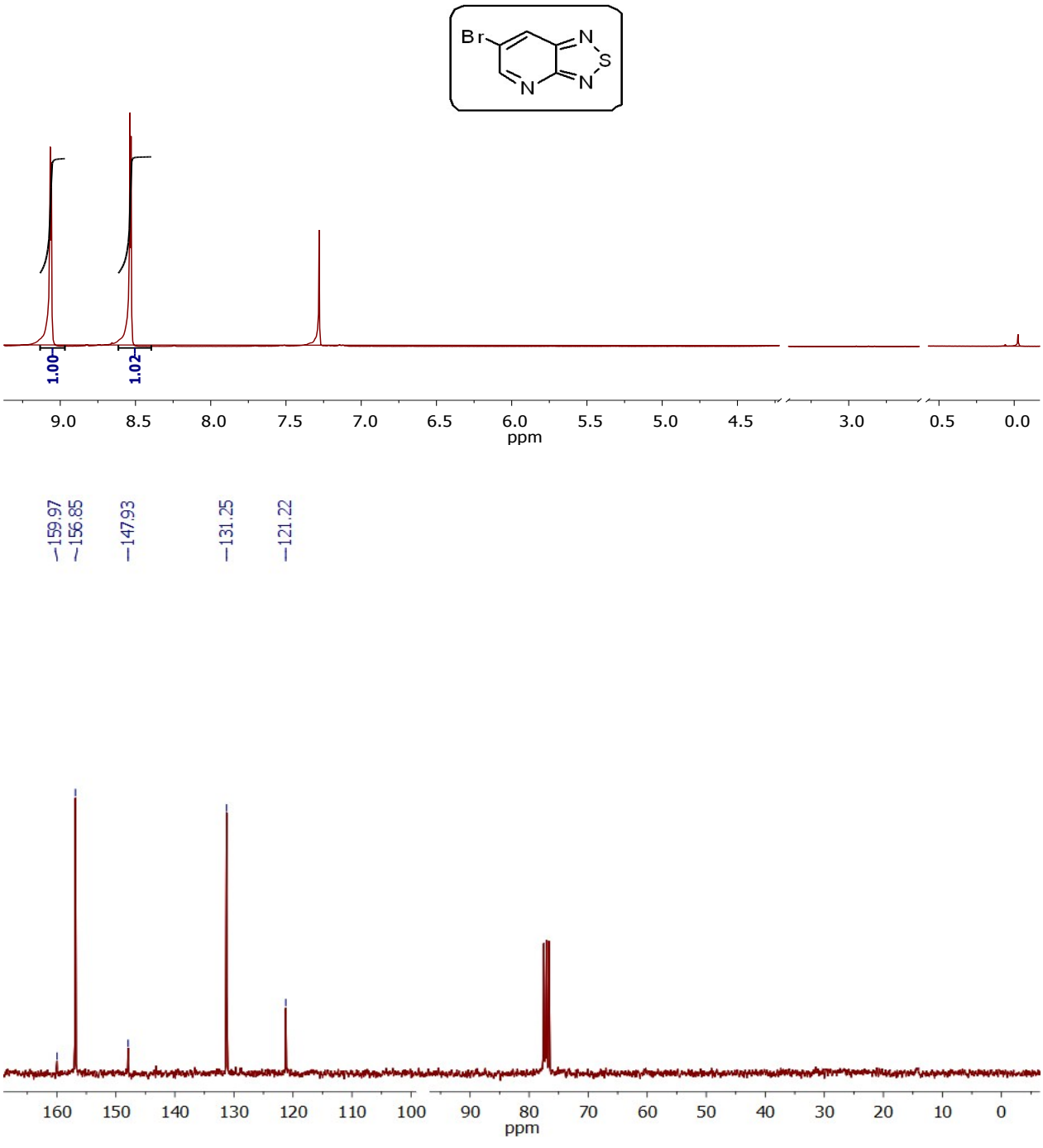
Dye	**HOMO(eV)**	**LUMO (eV)**	**$E_{g,HL}$ (eV)**
DCTB	-5.25	-2.60	2.65
DCTP	-5.32	-2.88	2.44
CTDB	-5.35	-2.84	2.51
CTDP	-5.47	-3.12	2.35

Table S6. Thermal data of the dyes

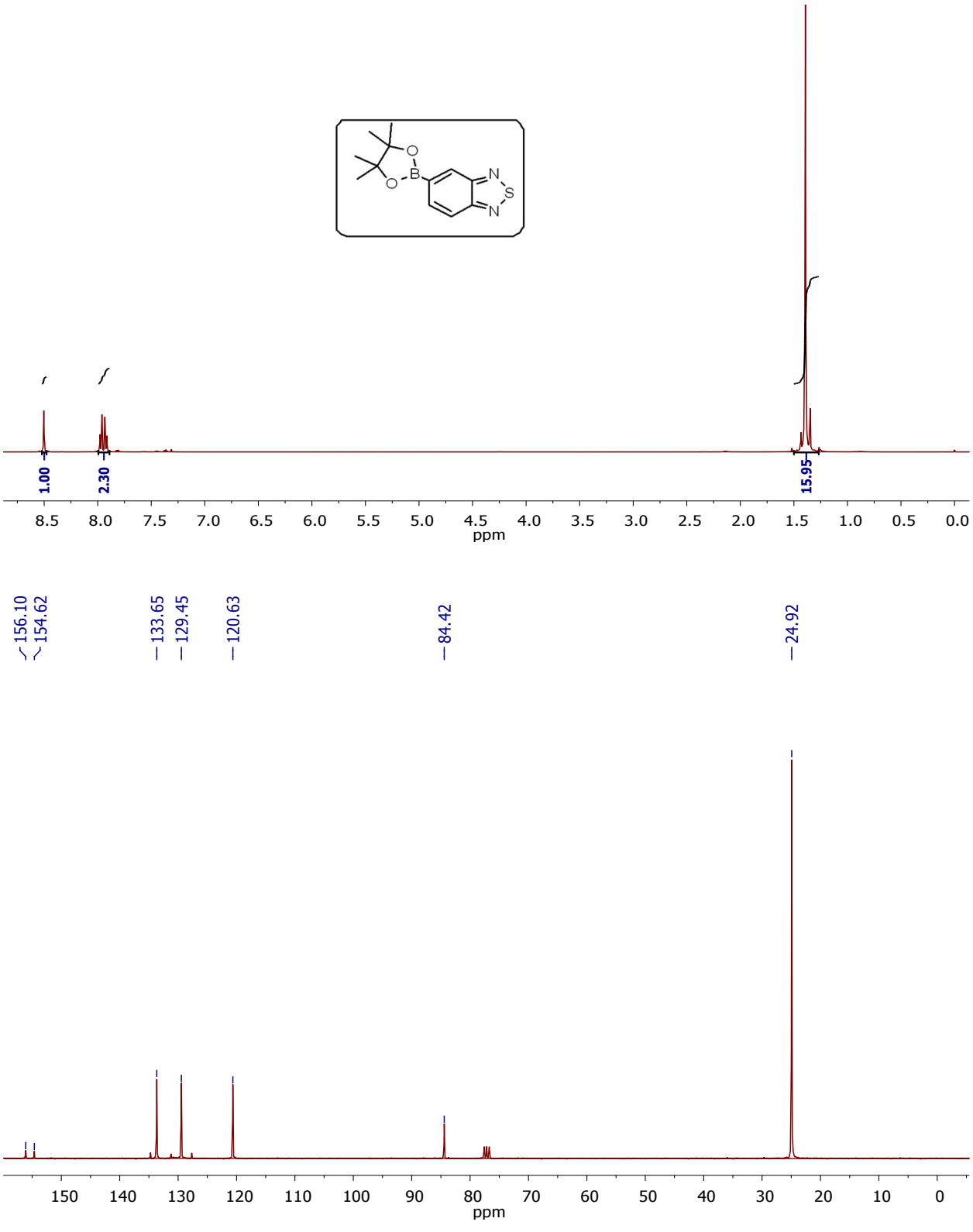
Dye	T_d (°C)	T_g (°C)	T_m (°C)
DCTB	434	148	313
DCTP	515	172	371
CTDB	389	189	316
CTDP	458	198	366



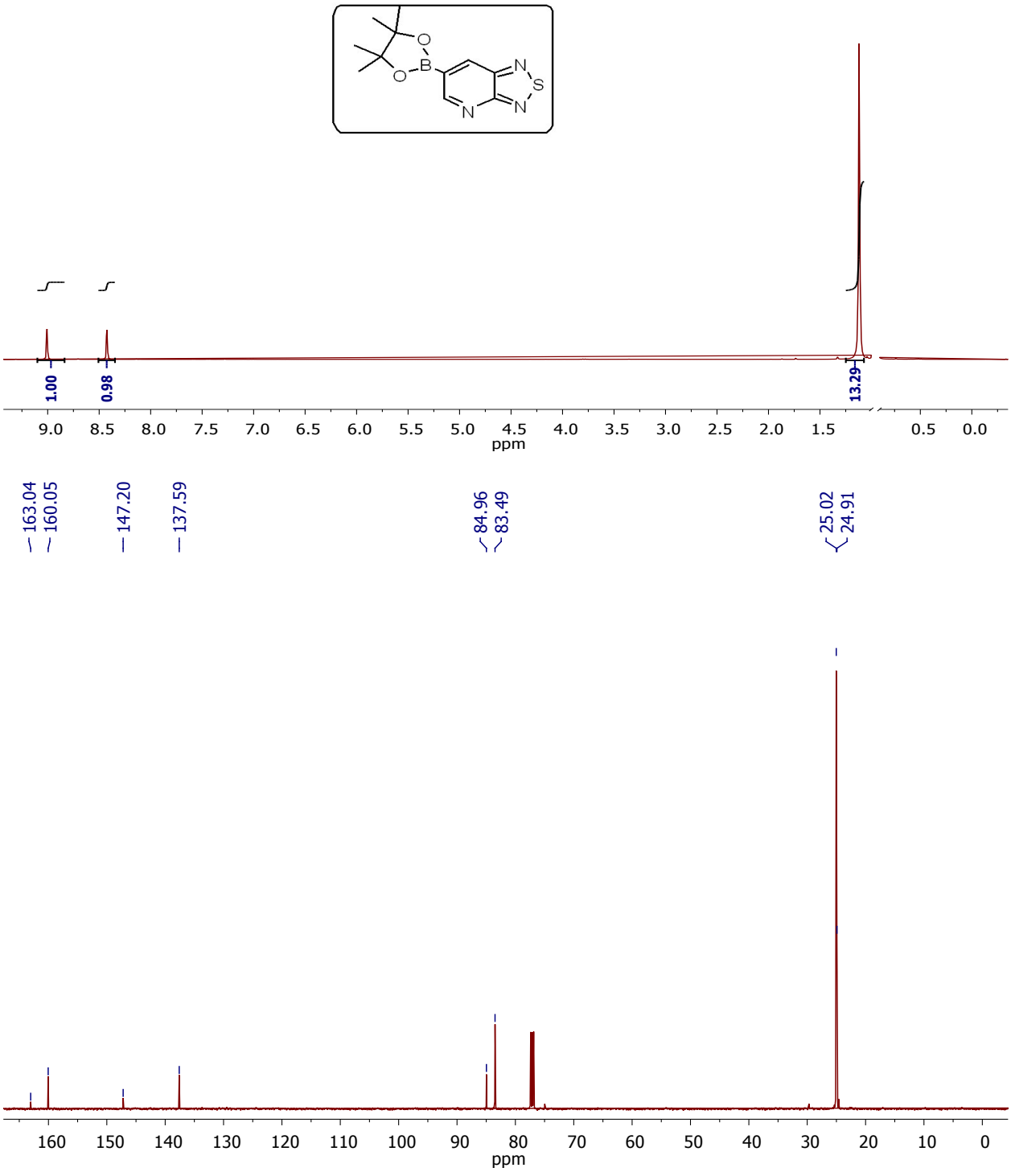
^{1}H and ^{13}C NMR spectra of molecule **1a**



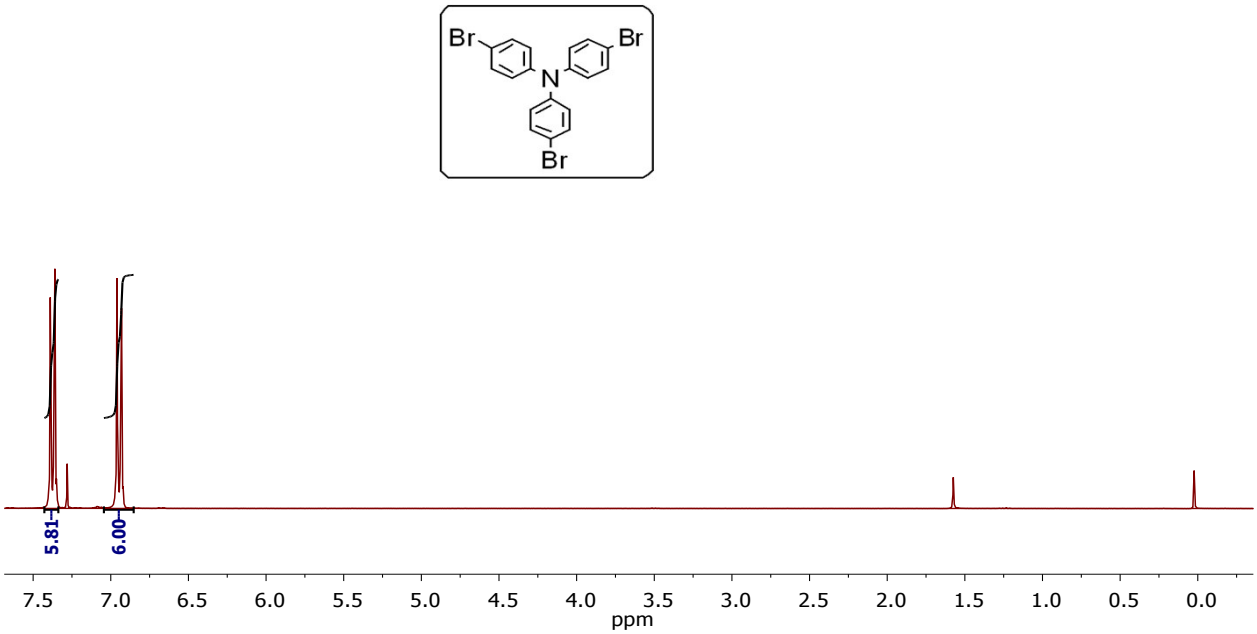
^{1}H and ^{13}C NMR spectra of molecule **1b**



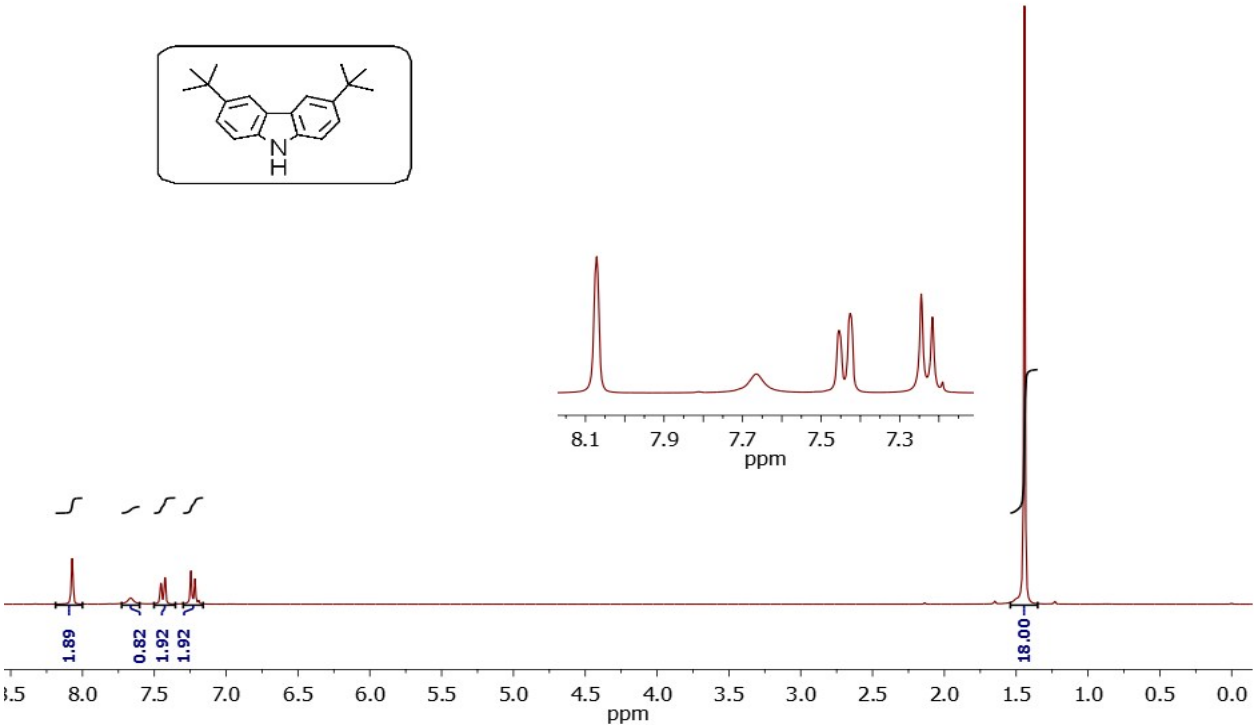
^{1}H and ^{13}C NMR spectra of molecule **2a**



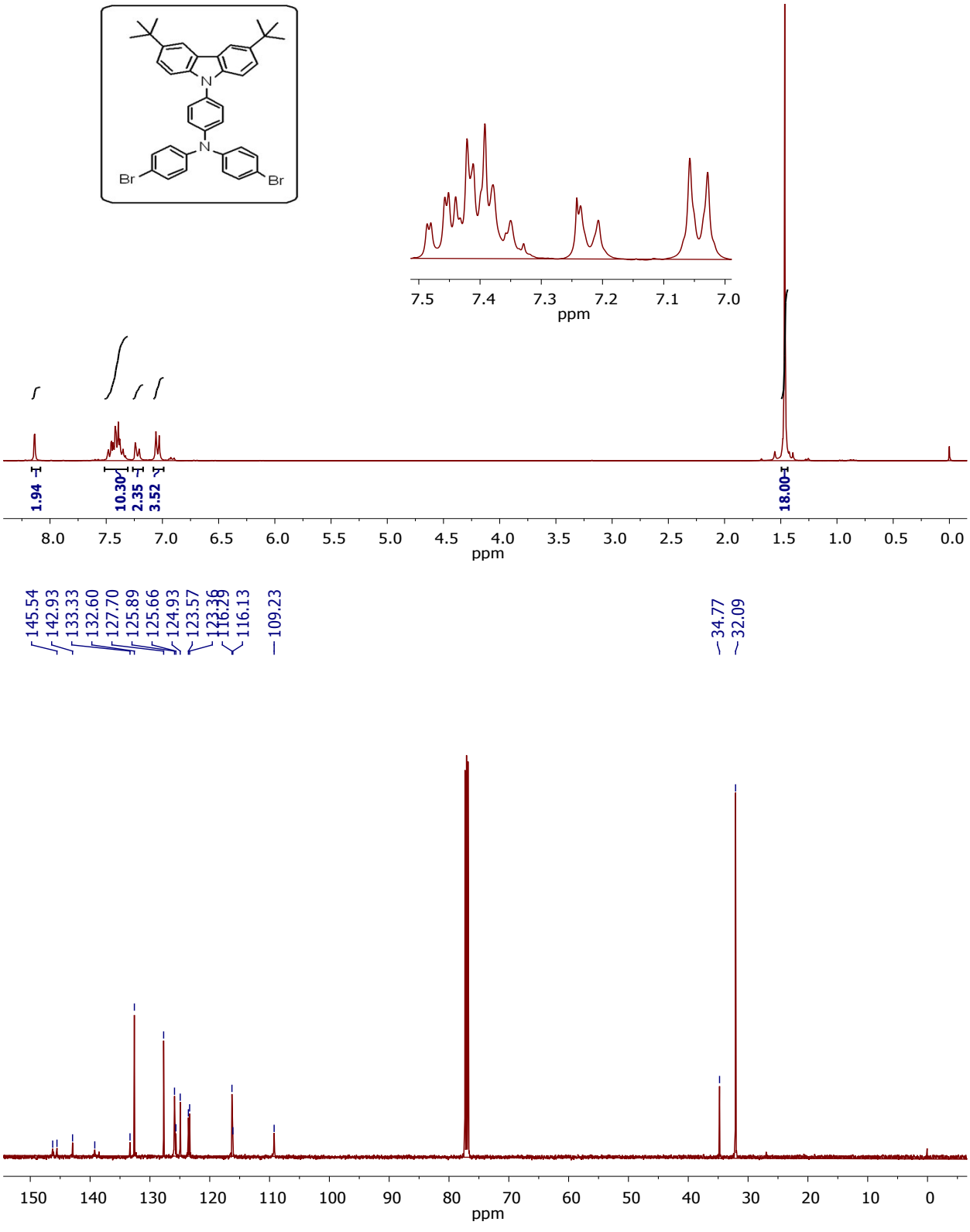
^{1}H and ^{13}C NMR spectra of molecule **2b**



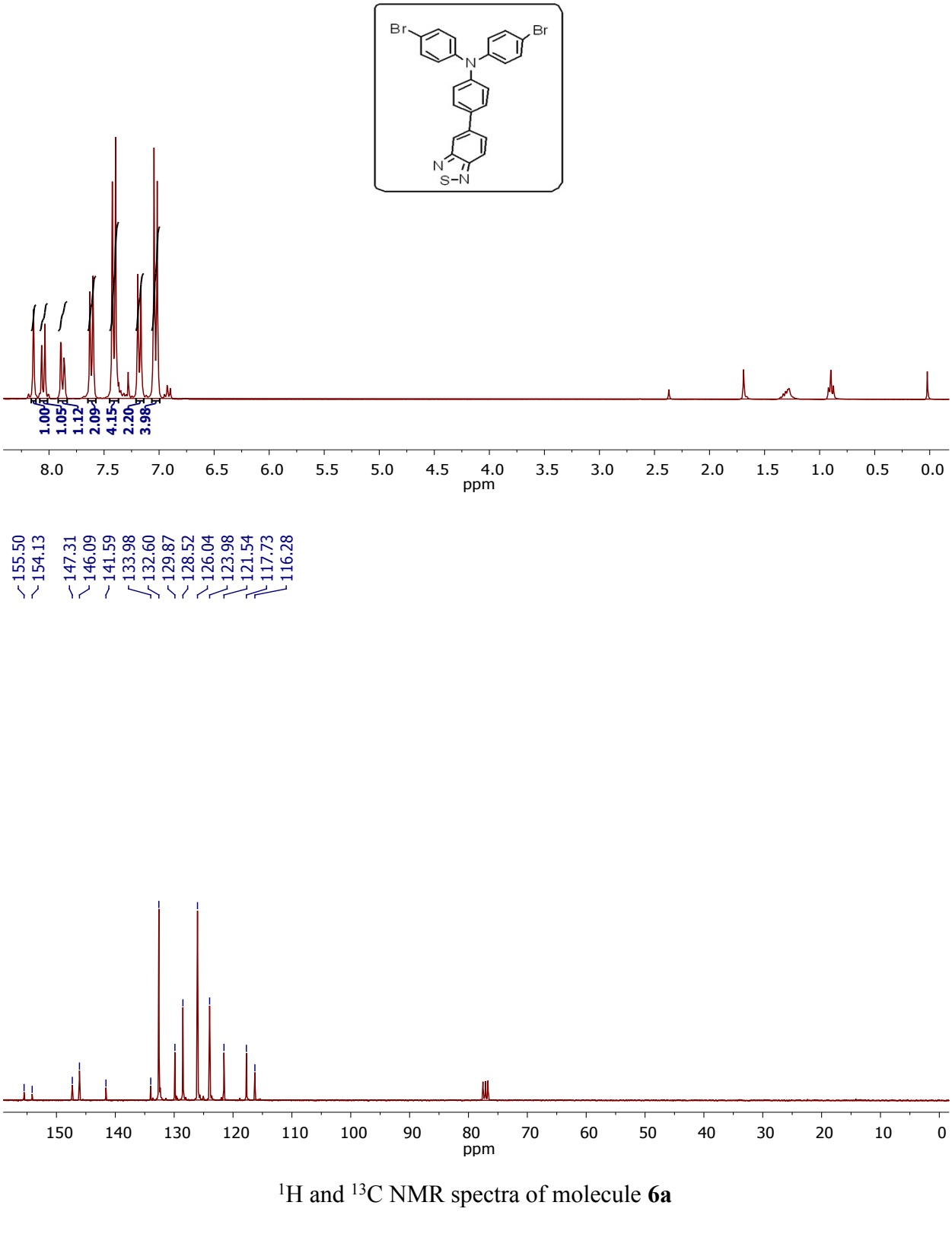
^{1}H NMR spectrum of molecule **3**



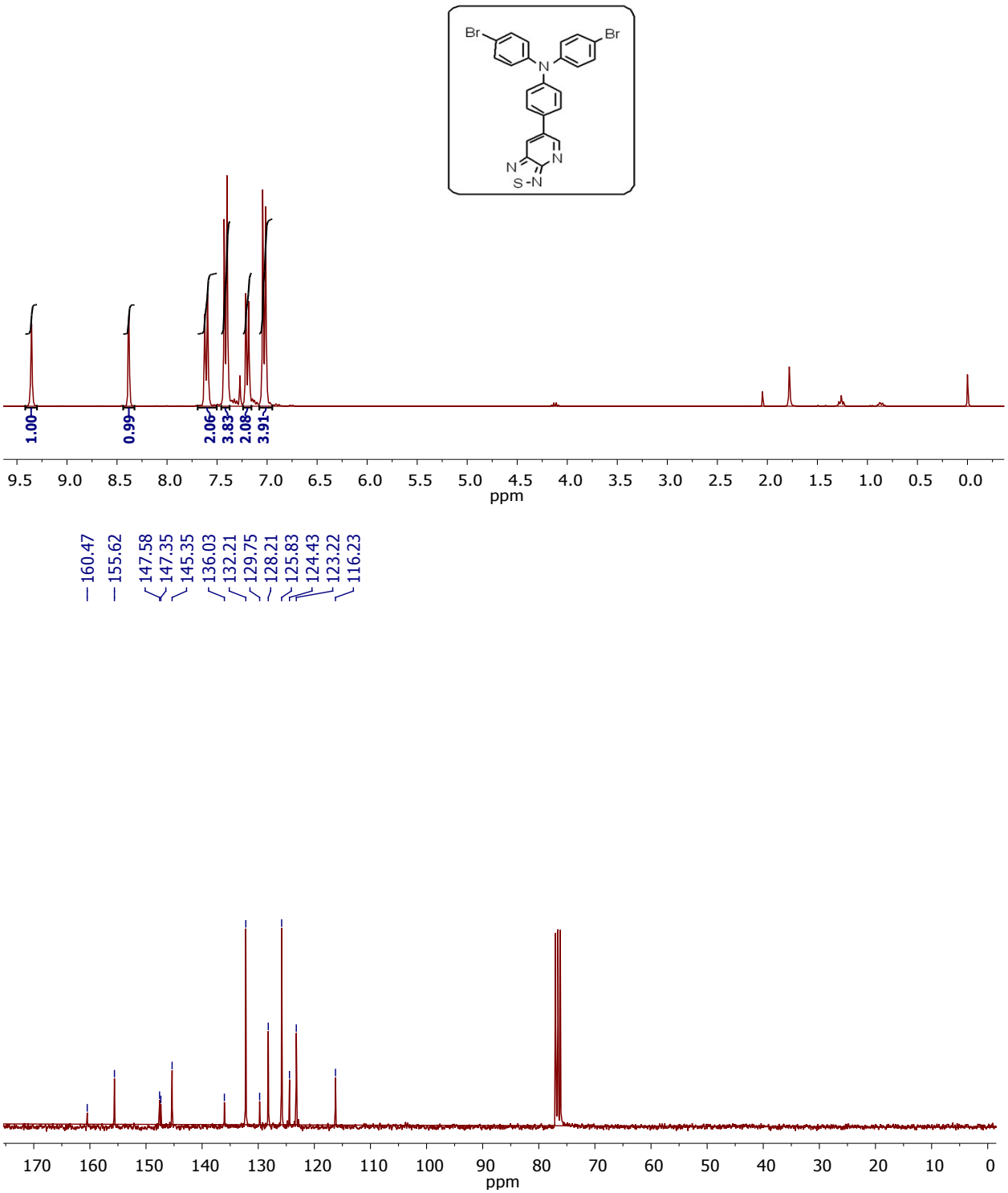
^{1}H NMR spectrum of molecule **4**



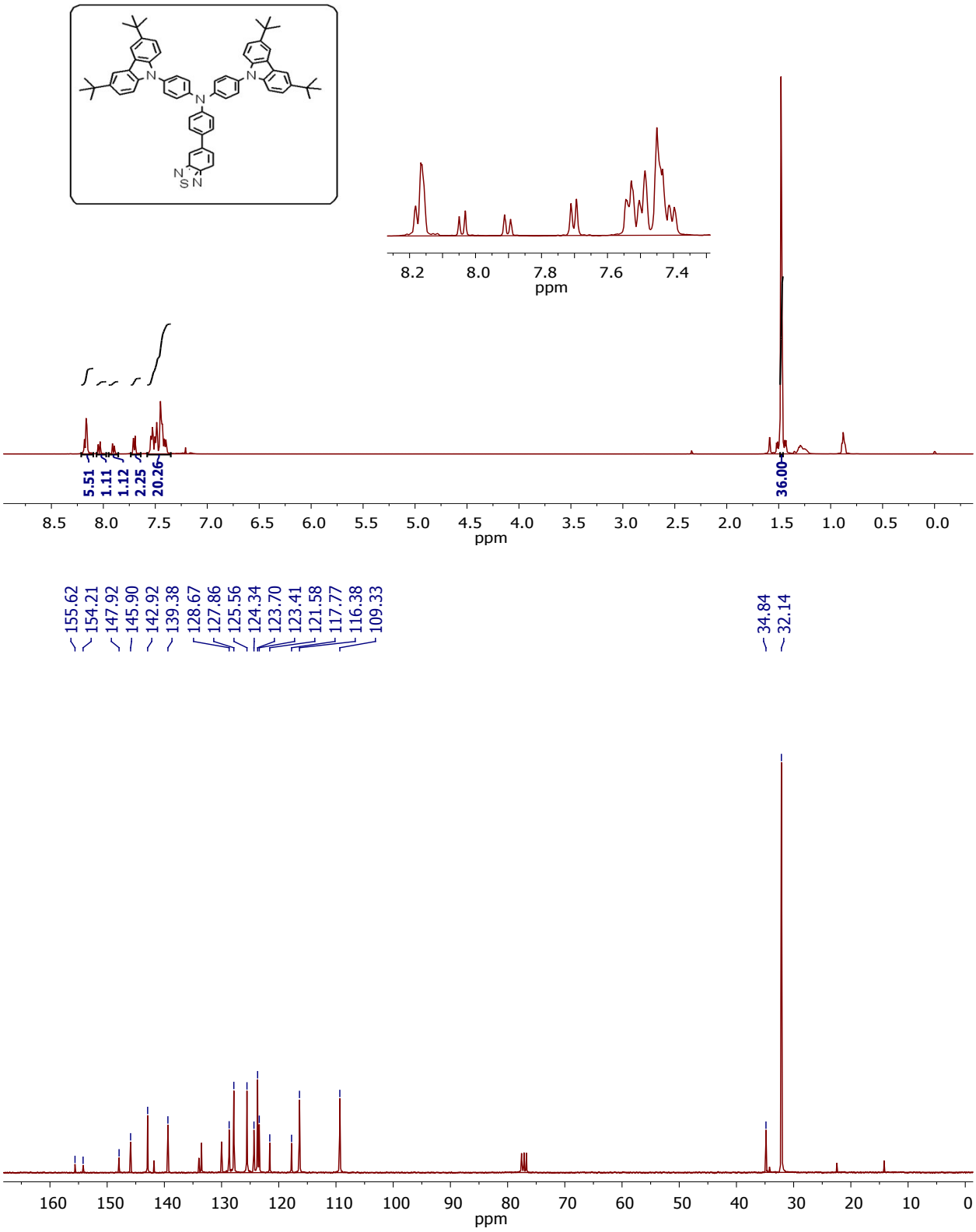
^{1}H and ^{13}C NMR spectra of molecule **5**



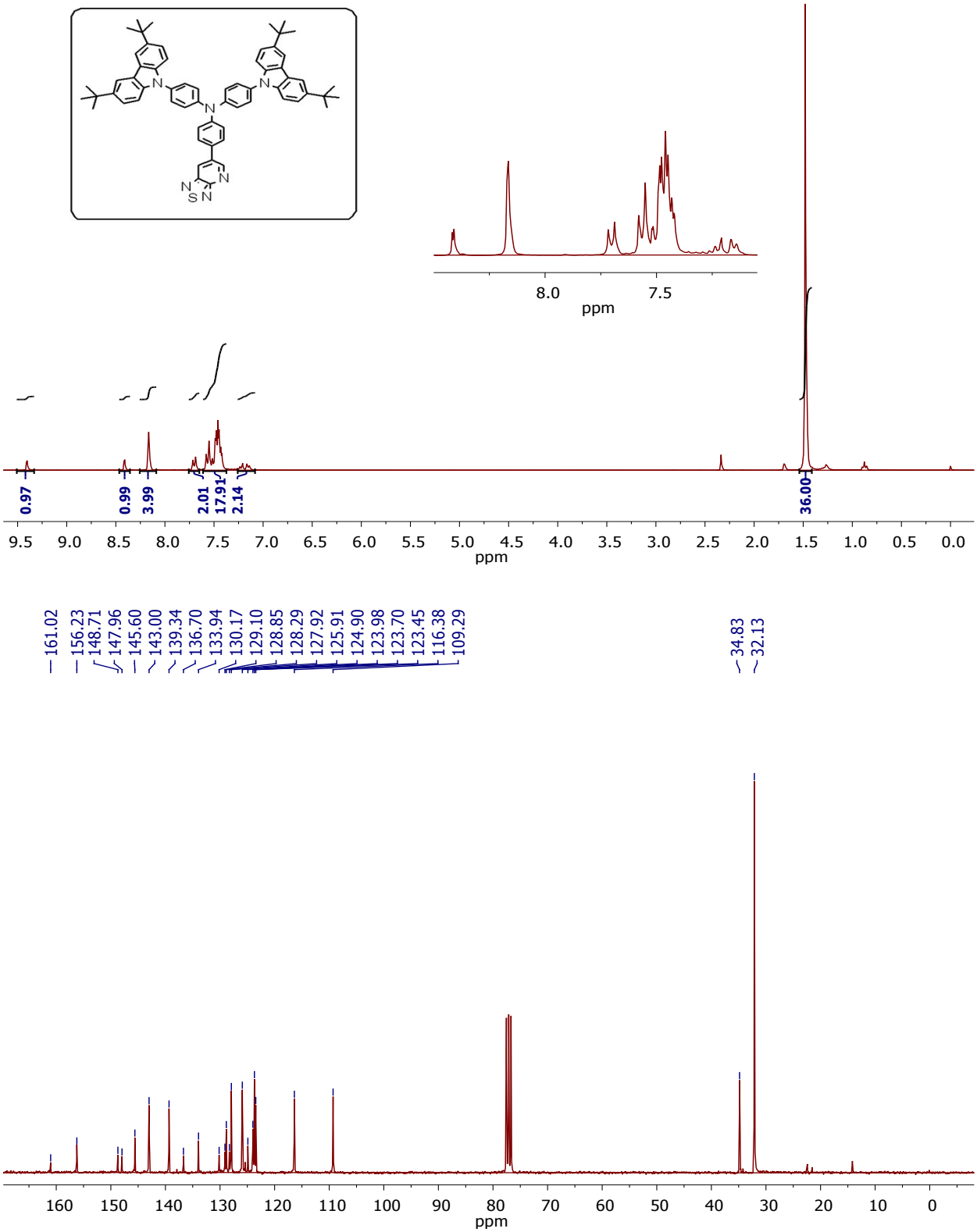
^{1}H and ^{13}C NMR spectra of molecule **6a**



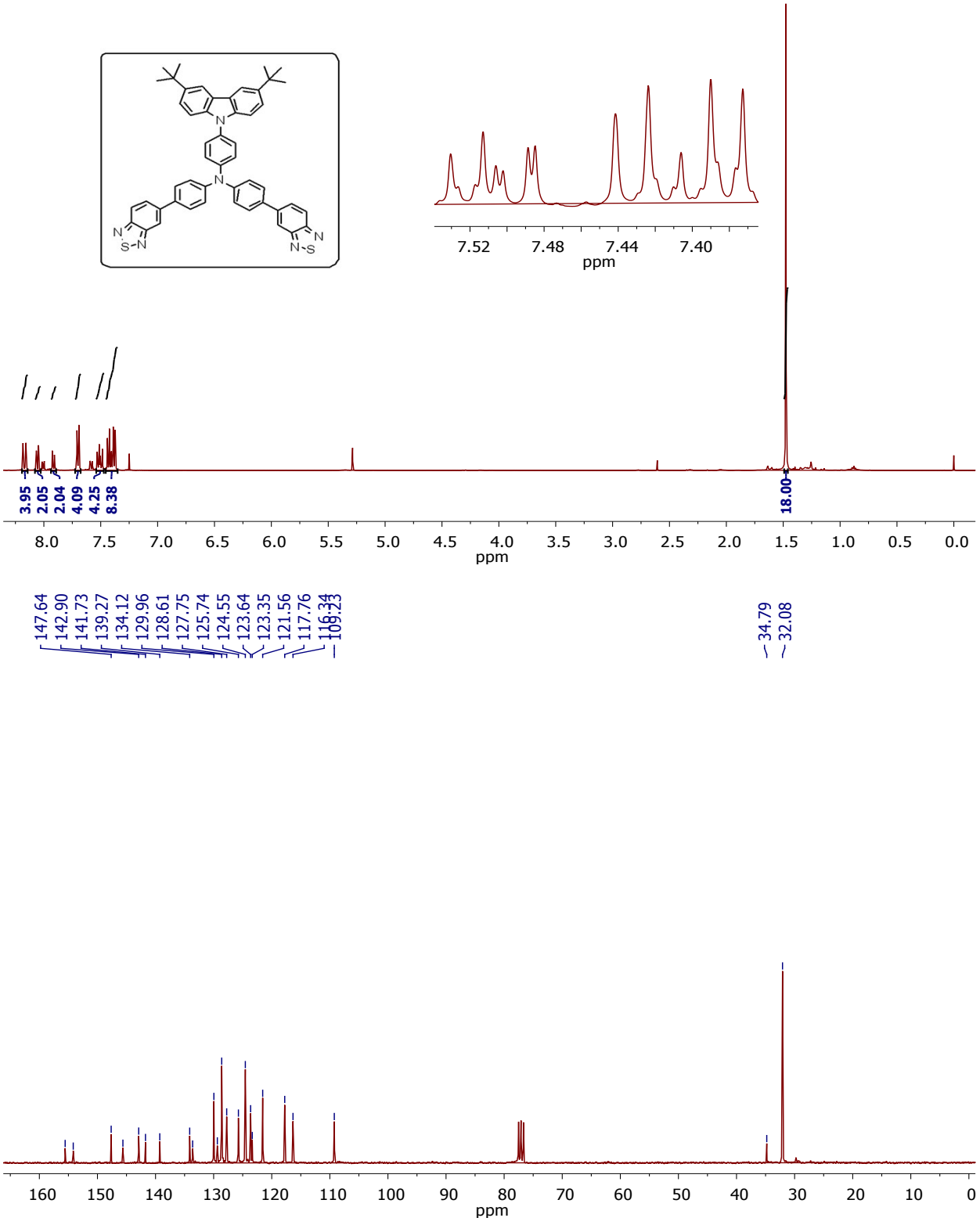
^{1}H and ^{13}C NMR spectra of molecule **6b**



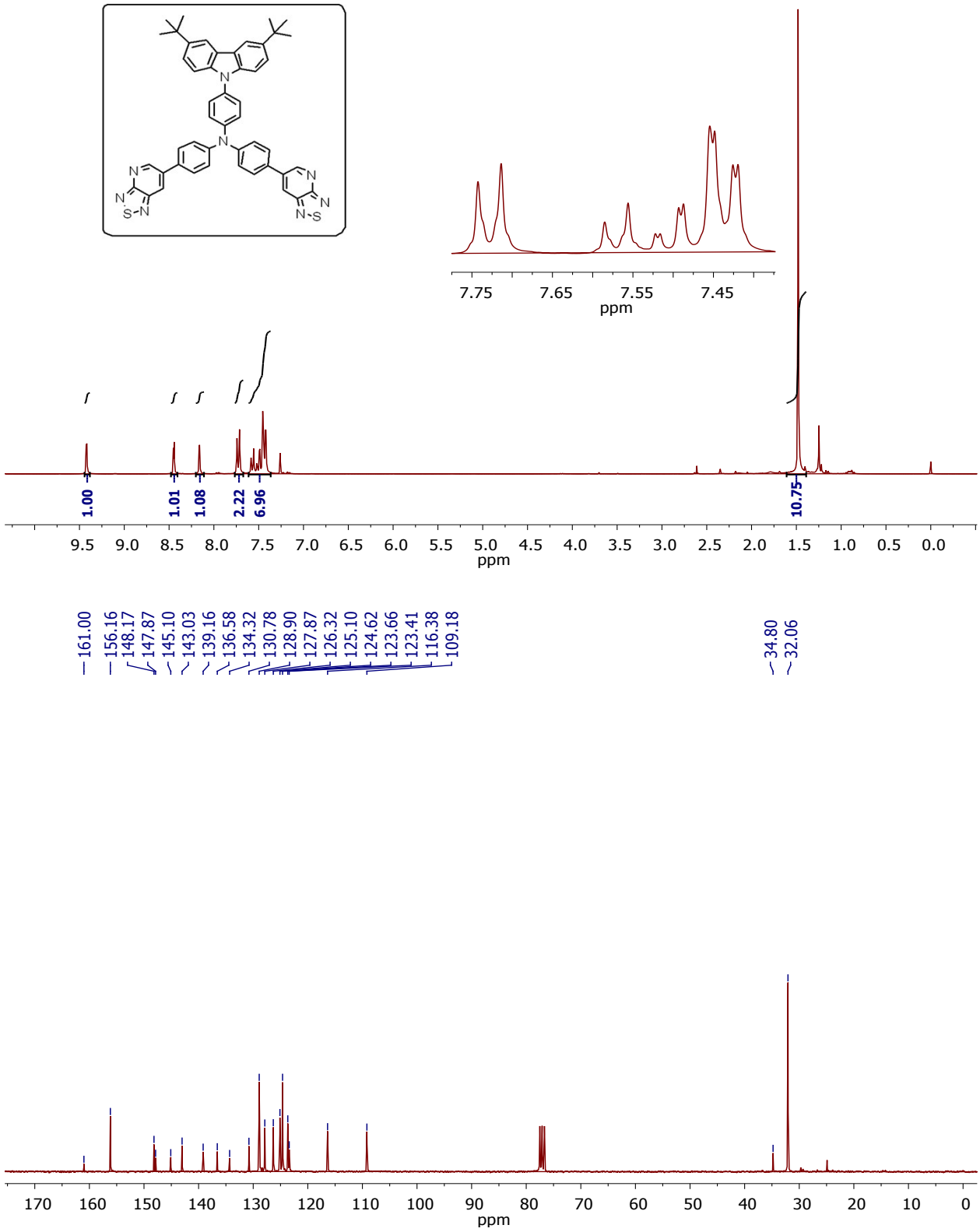
^{1}H and ^{13}C NMR spectra of **DCTB**



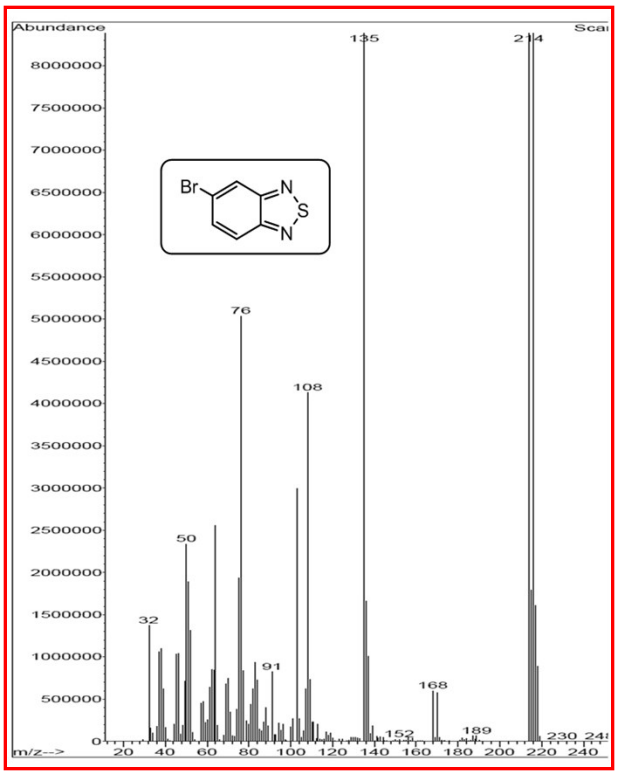
^{1}H and ^{13}C NMR spectra of **DCTP**



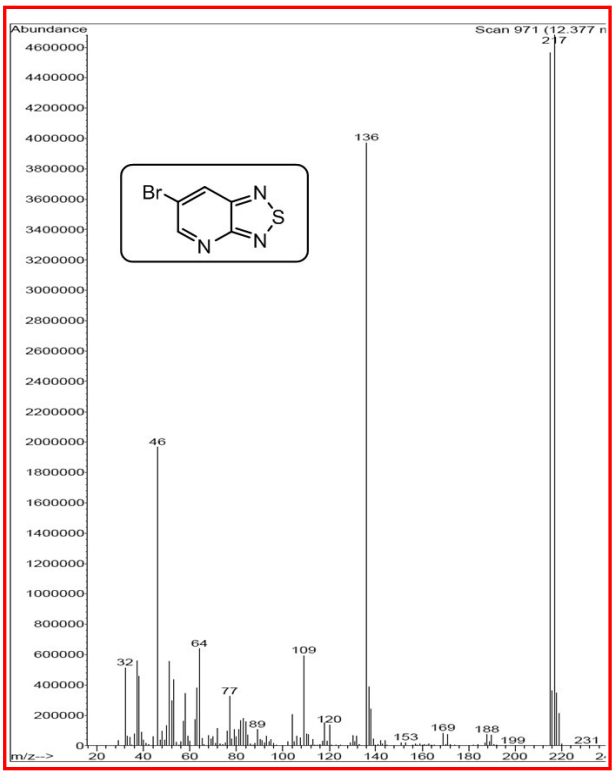
^{1}H and ^{13}C NMR spectra of **CTDB**



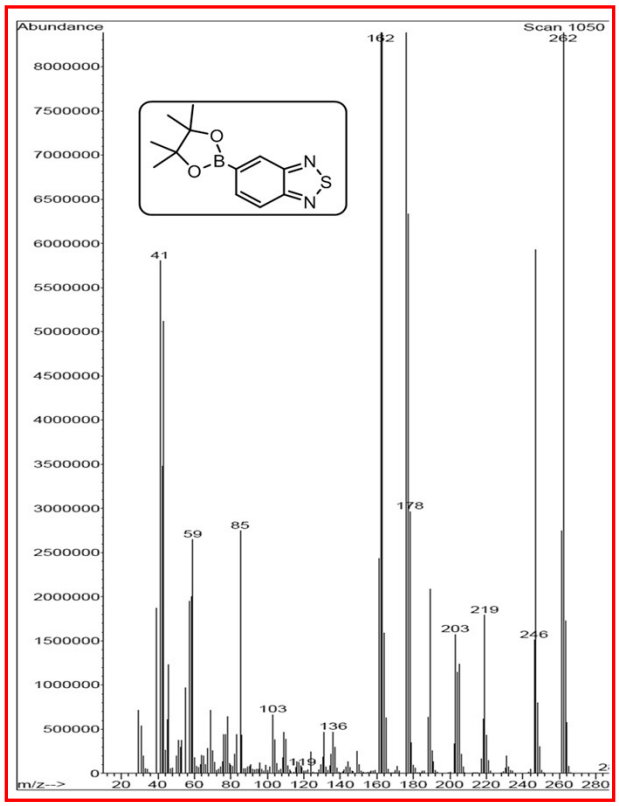
^{1}H and ^{13}C NMR spectra of molecule **CTDP**



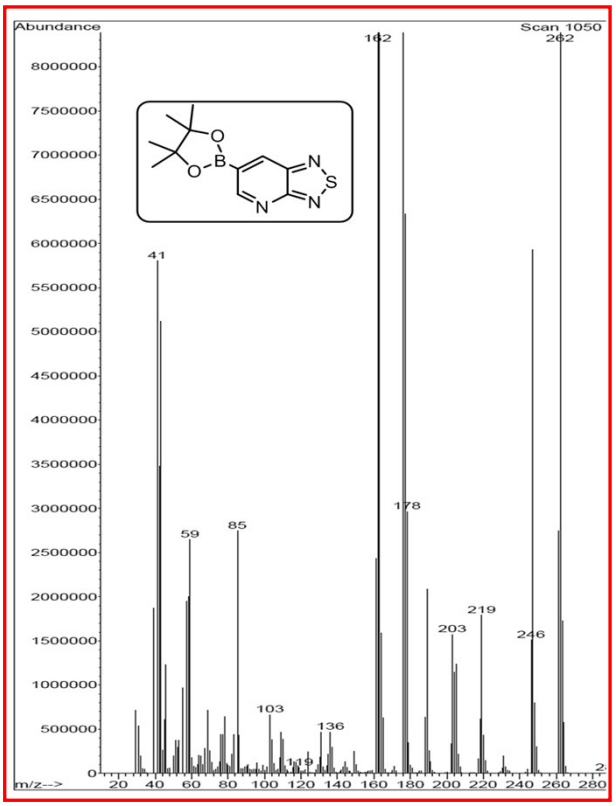
GC-Mass spectrum of molecule **1a**



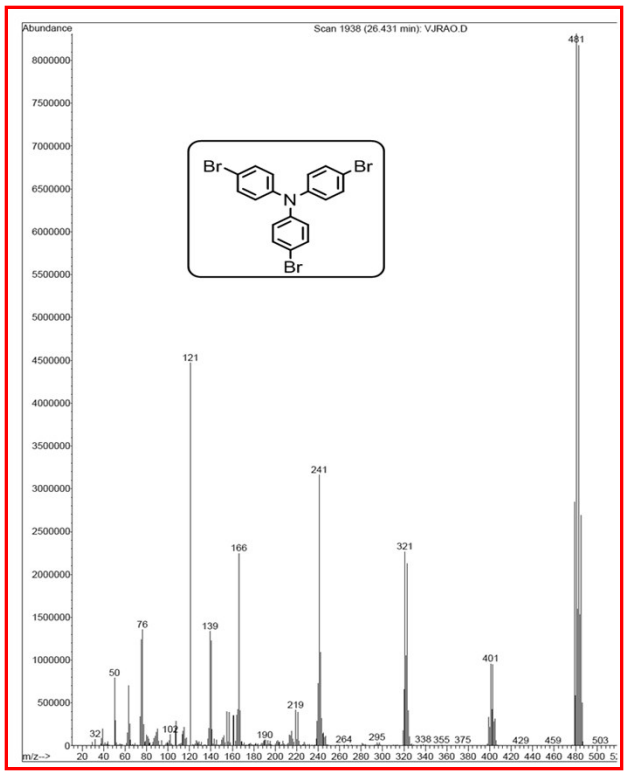
GC-Mass spectrum of molecule **1b**



GC-Mass spectrum of molecule **2a**



GC-Mass spectrum of molecule **2b**



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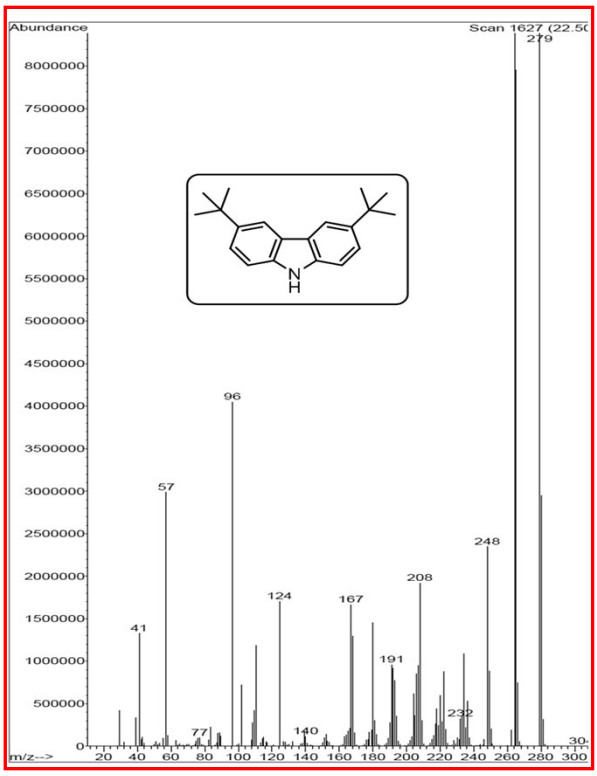
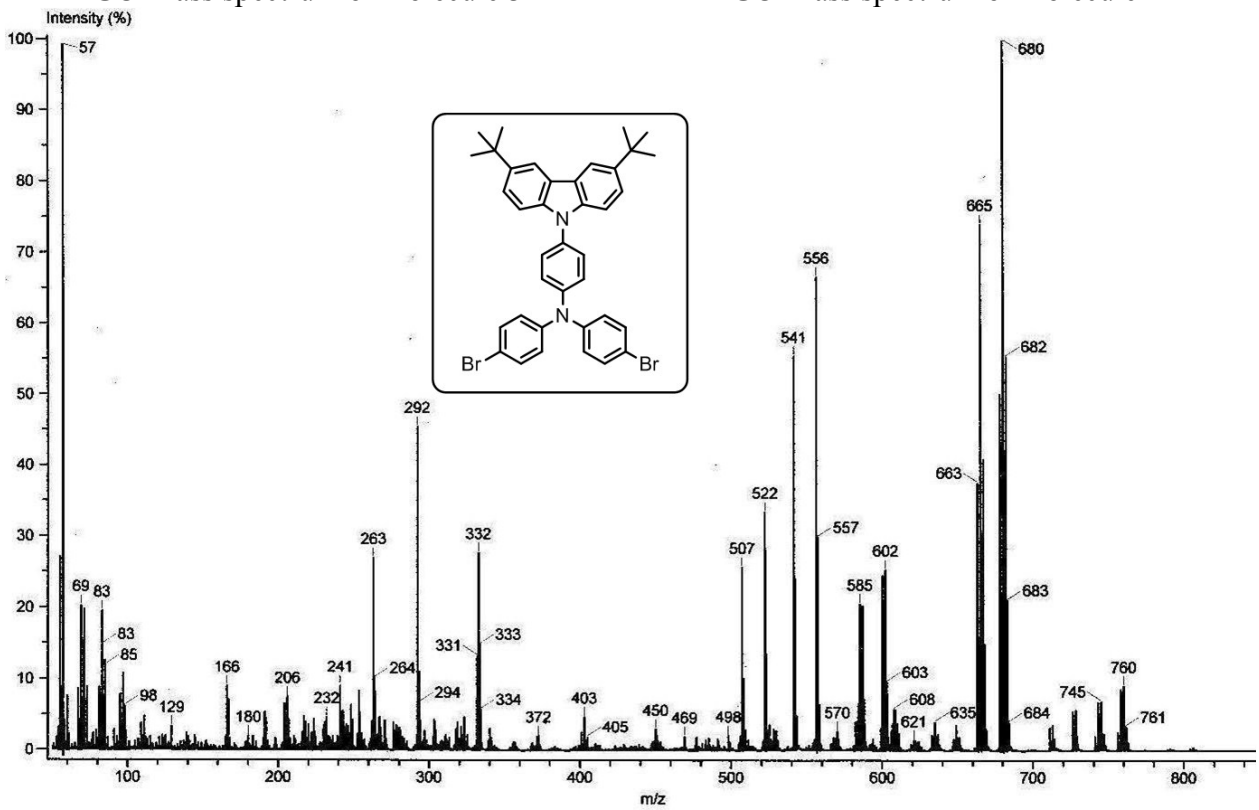
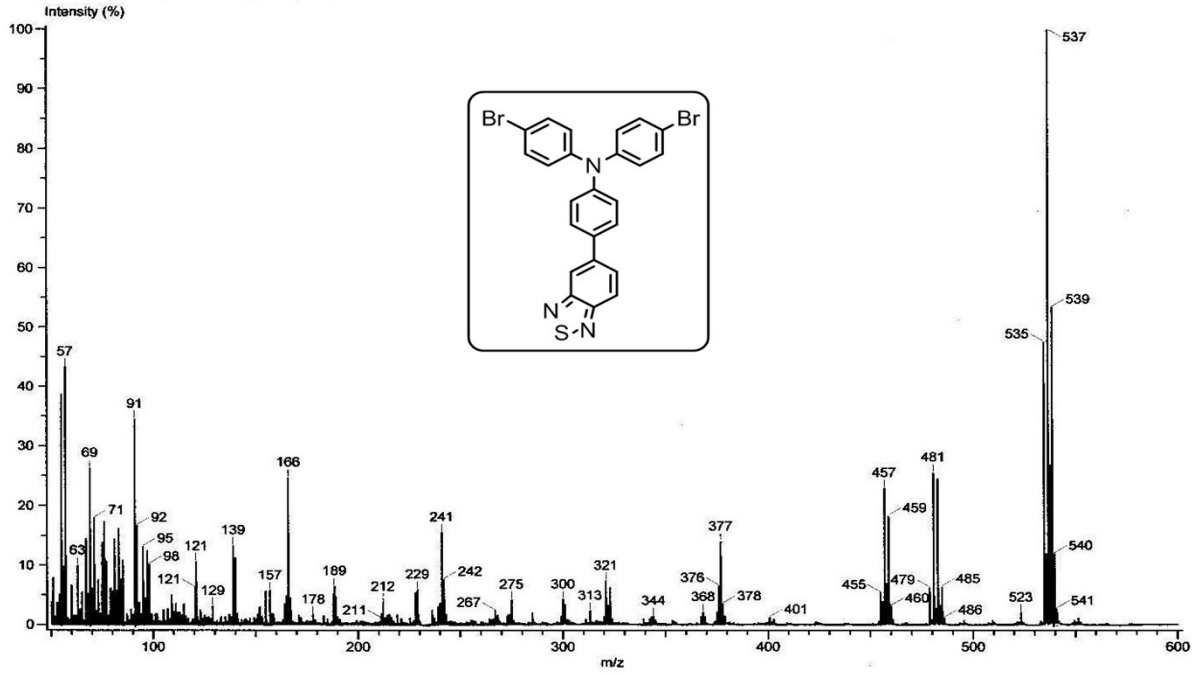


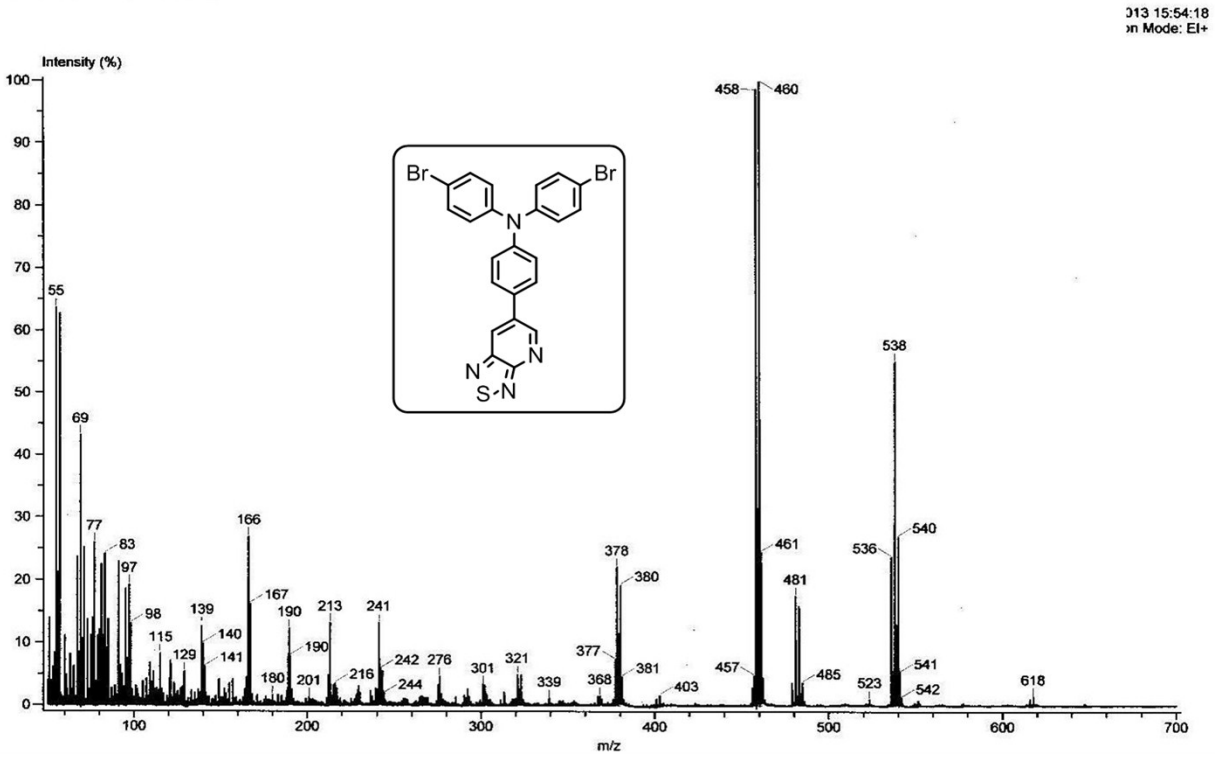
GC-Mass spectrum of molecule **4**



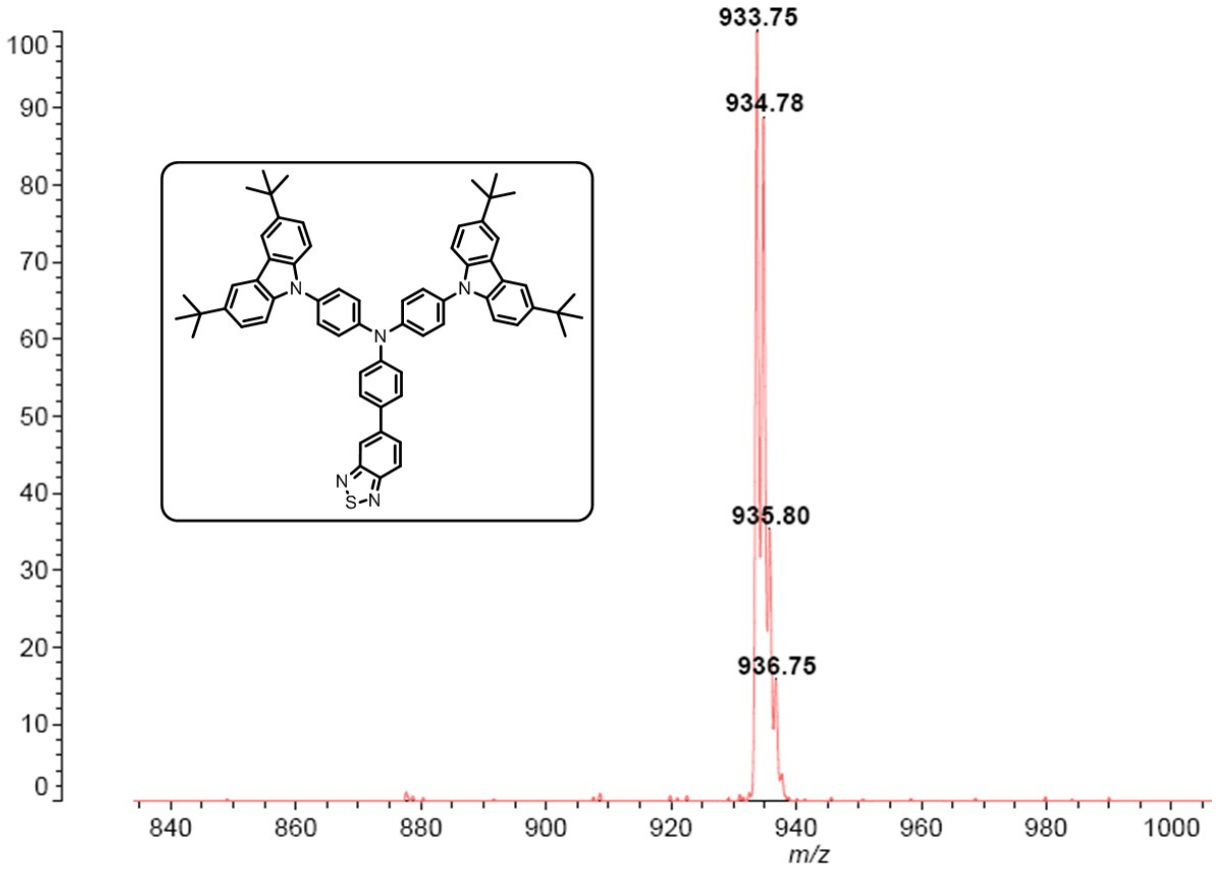
EI-Mass spectrum of molecule **5**



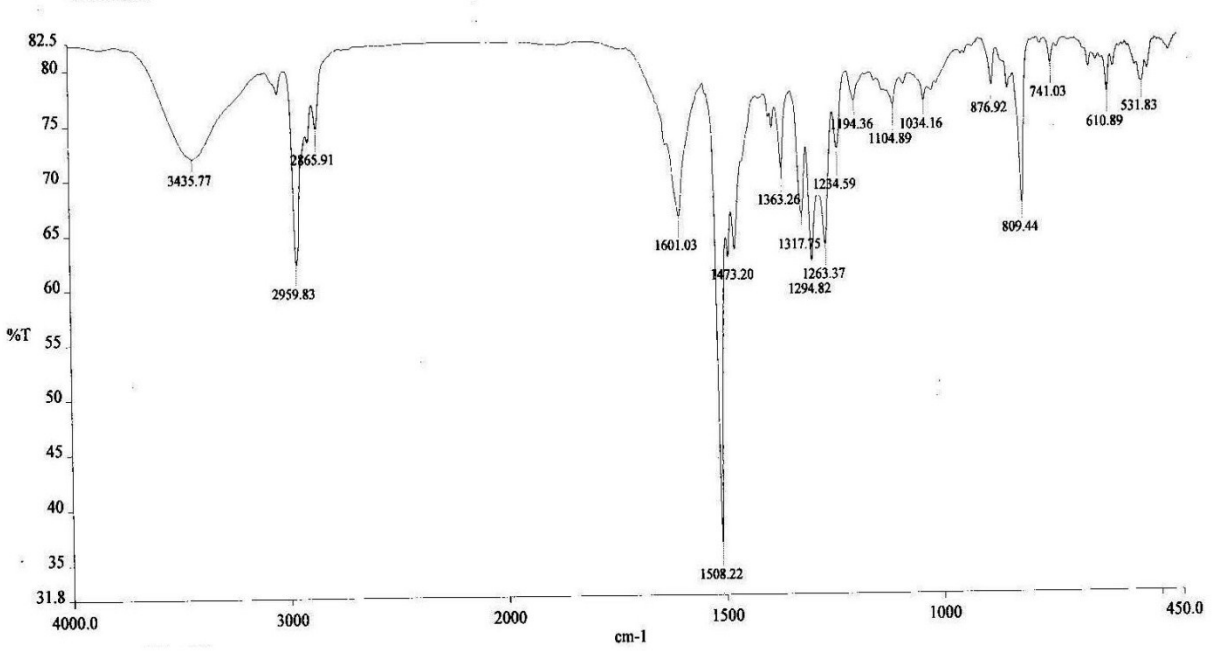
EI-Mass spectrum of molecule **6**



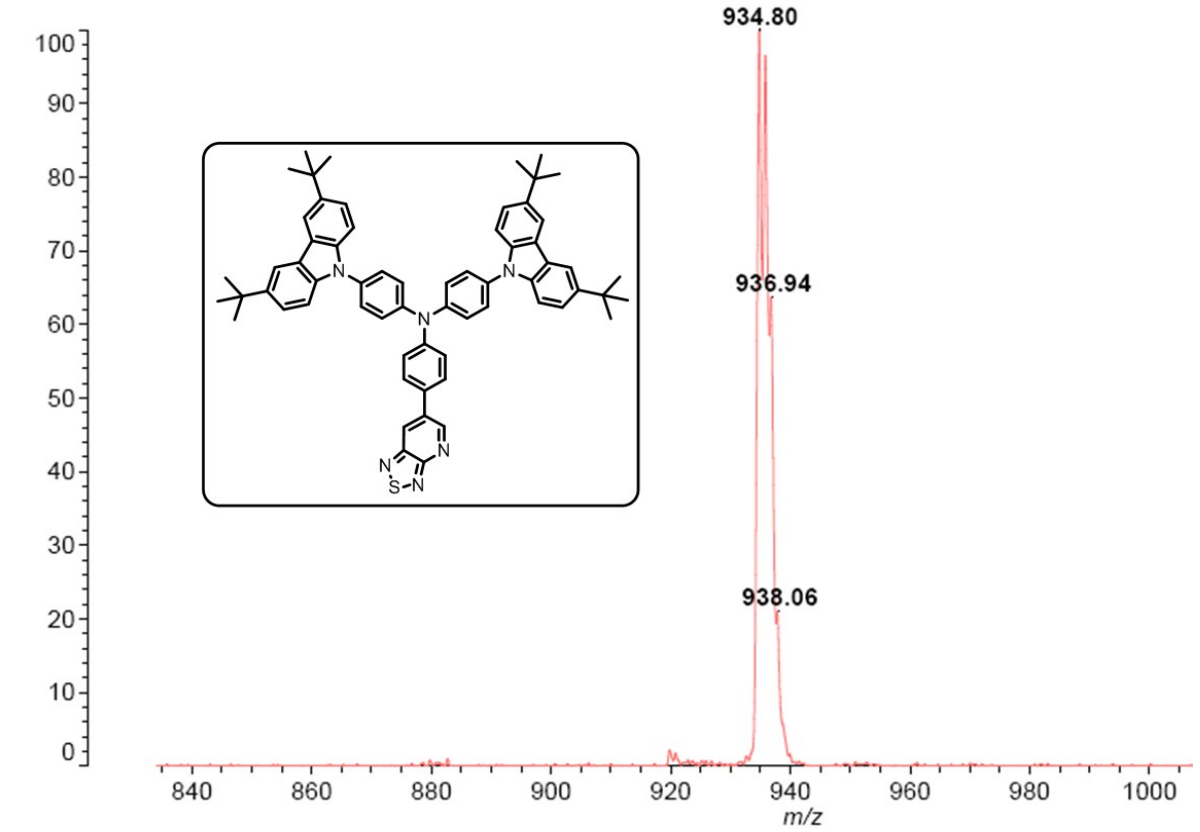
EI-Mass spectrum of molecule **7**



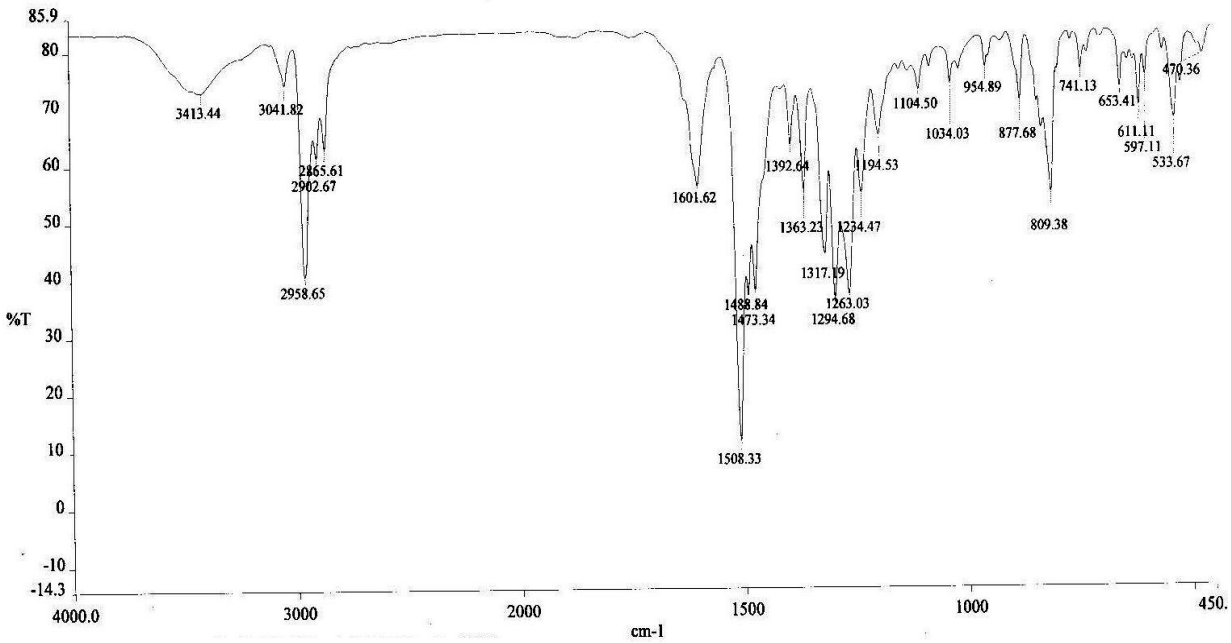
MALDI-TOF mass Spectrum of **DCTB**



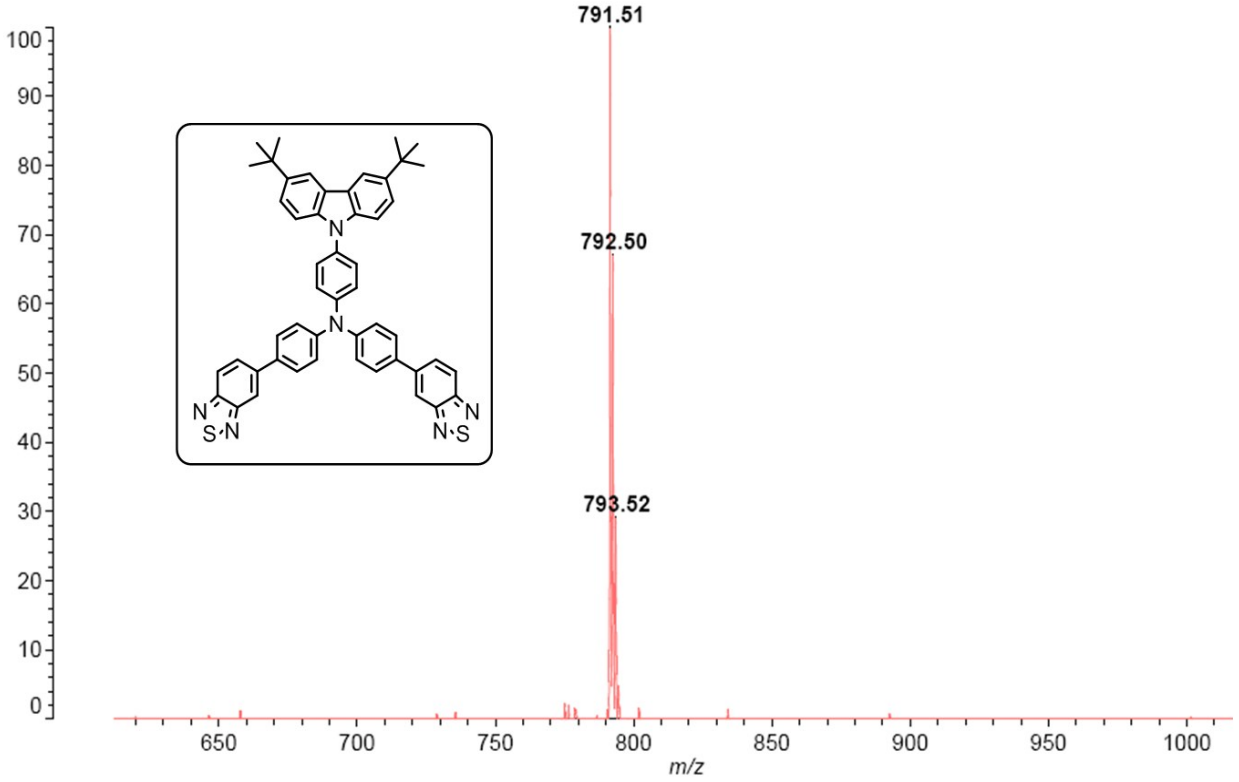
IR Spectrum of **DCTB**



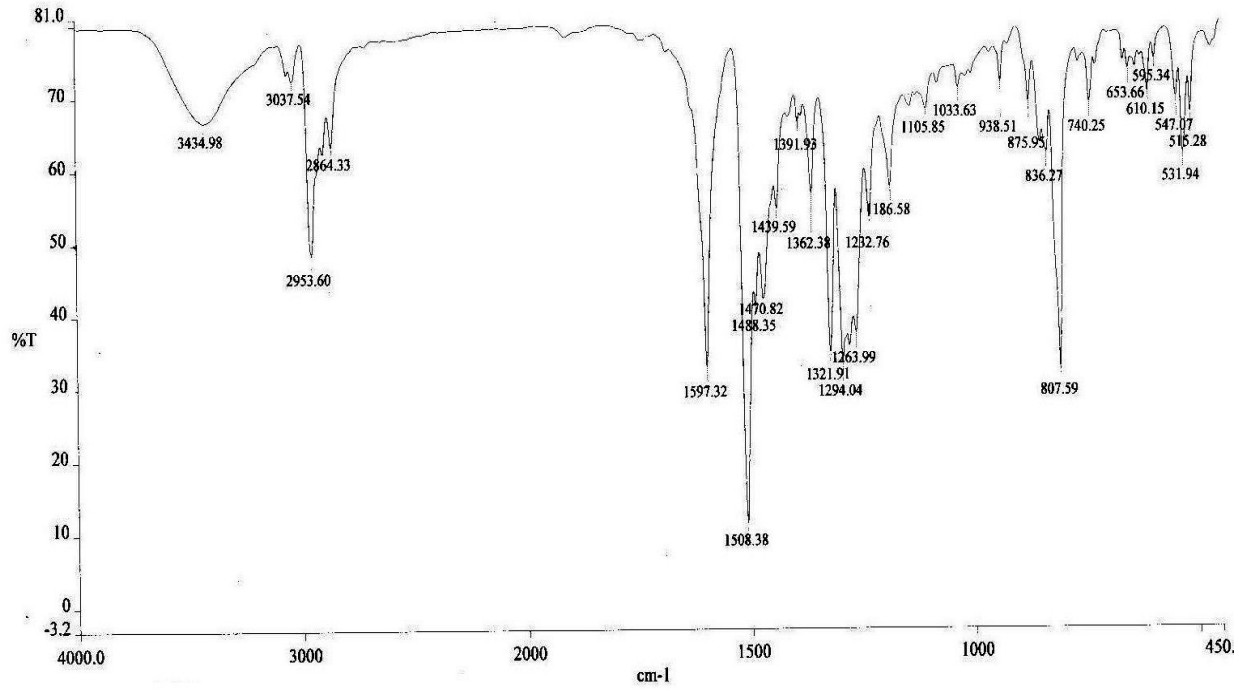
MALDI-TOF mass Spectrum of **DCTP**



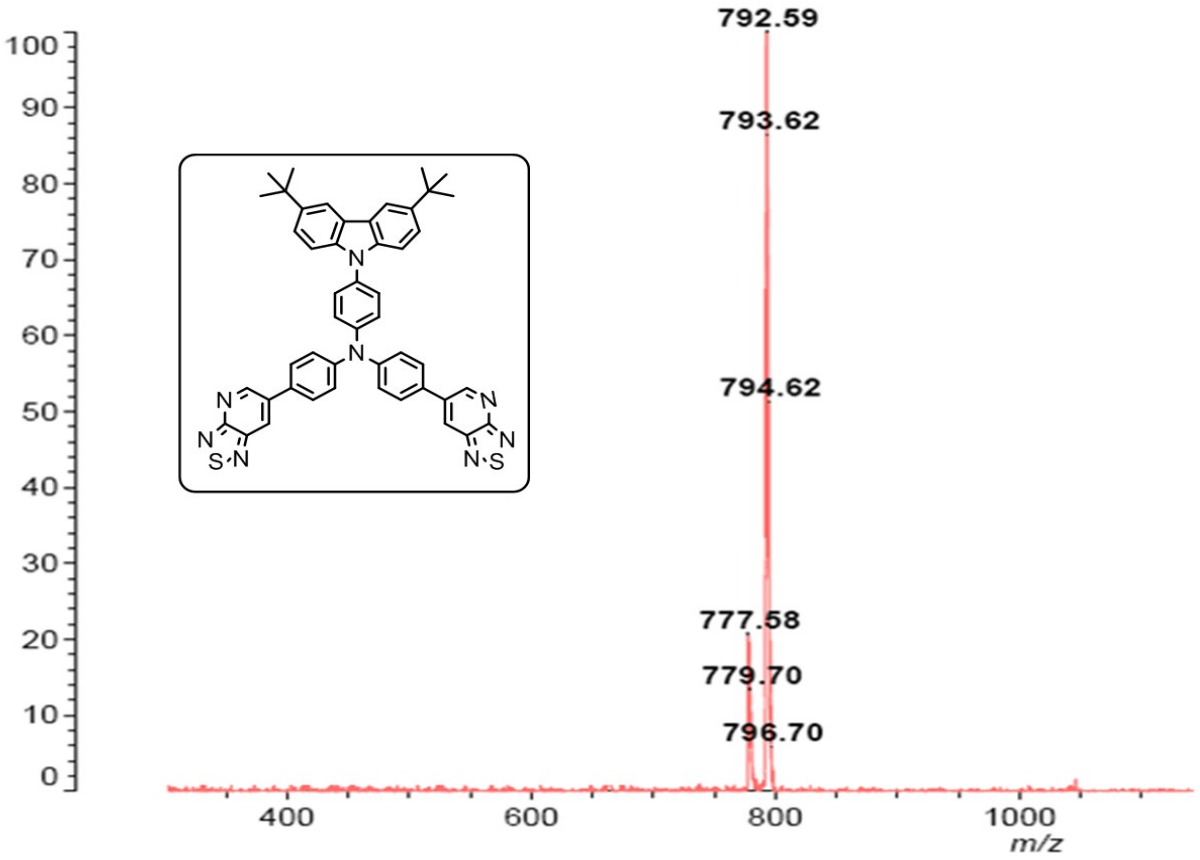
IR Spectrum of **DCTP**



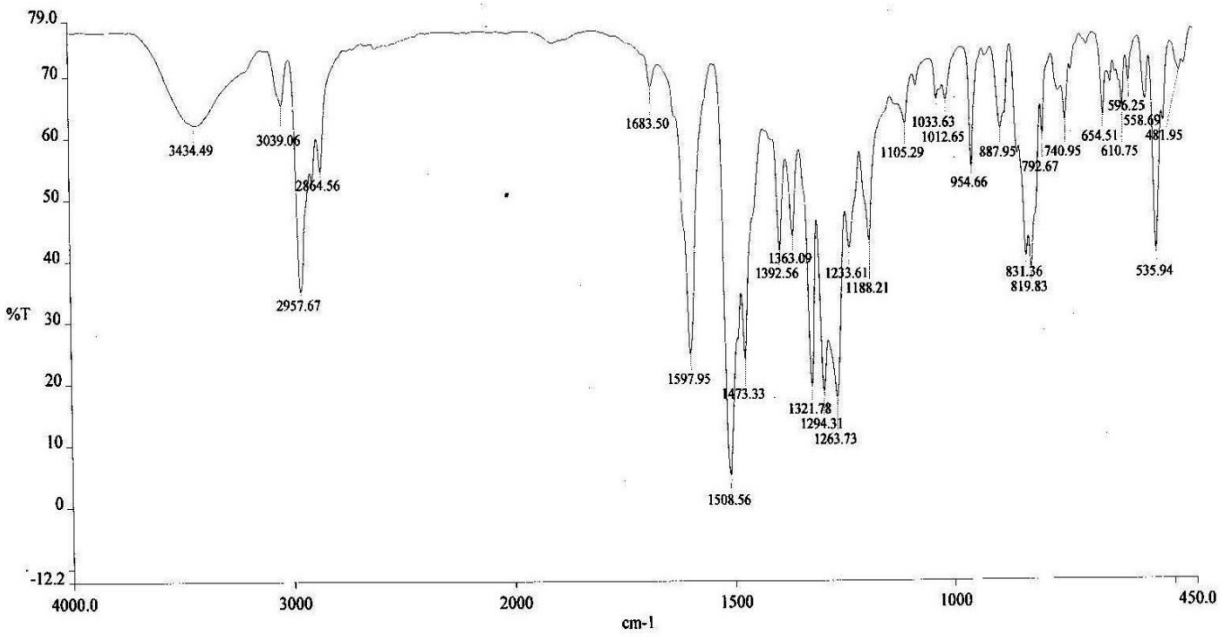
MALDI-TOF mass Spectrum of **CTDB**



IR Spectrum of **CTDB**



MALDI-TOF mass Spectrum of **CTDP**



IR Spectrum of **CTDP**