

Electronic Supporting Information (ESI)

Tuning the Photovoltaic Performance of Benzocarbazole Based Sensitizers for Dye-Sensitized Solar Cells — A Joint Experimental and Theoretical Study of the Influence of π -spacers

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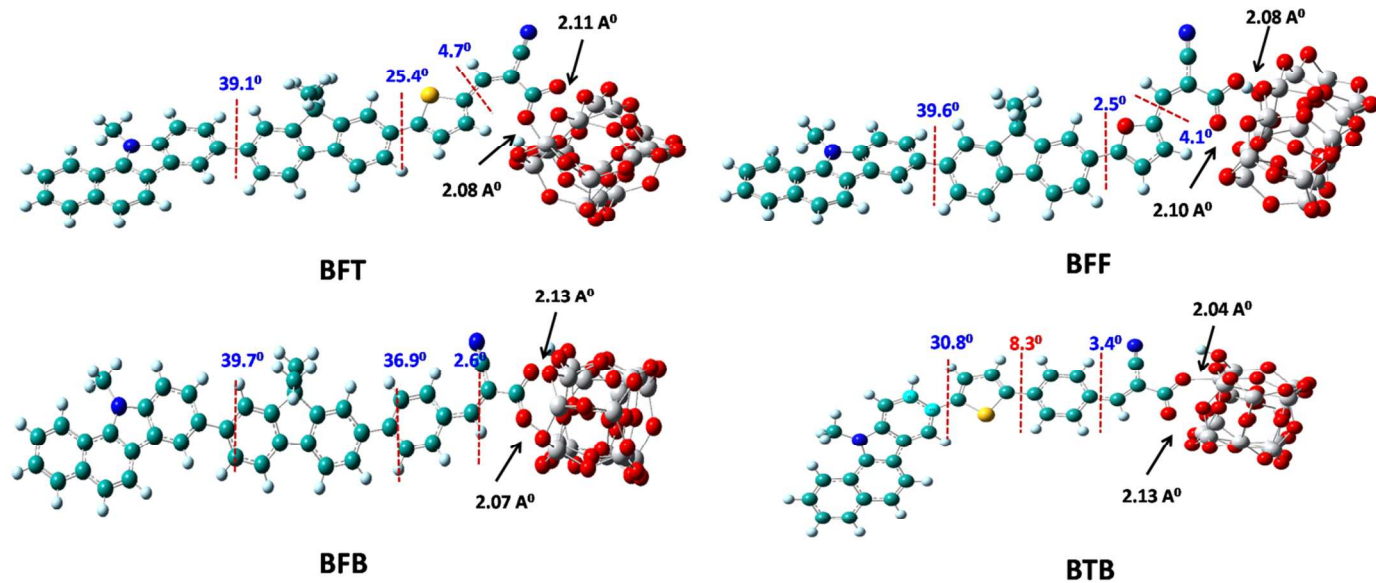


Figure S1 Geometry optimized structures and the dihedral angles between neighboring segments of dyes on TiO_2 assembly.

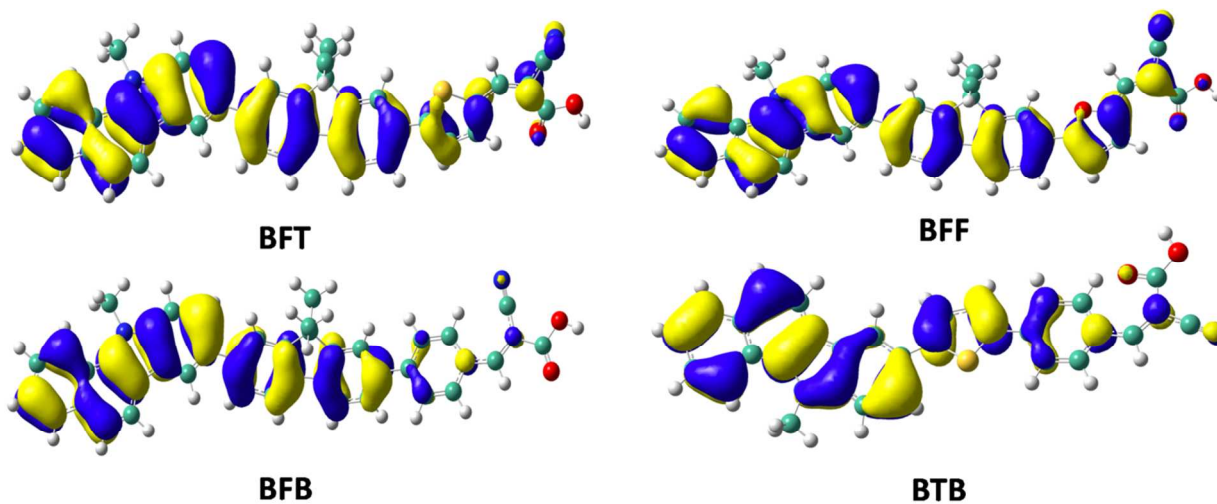


Figure S2 Electron density distribution of the isolated dyes in HOMO-1 level.

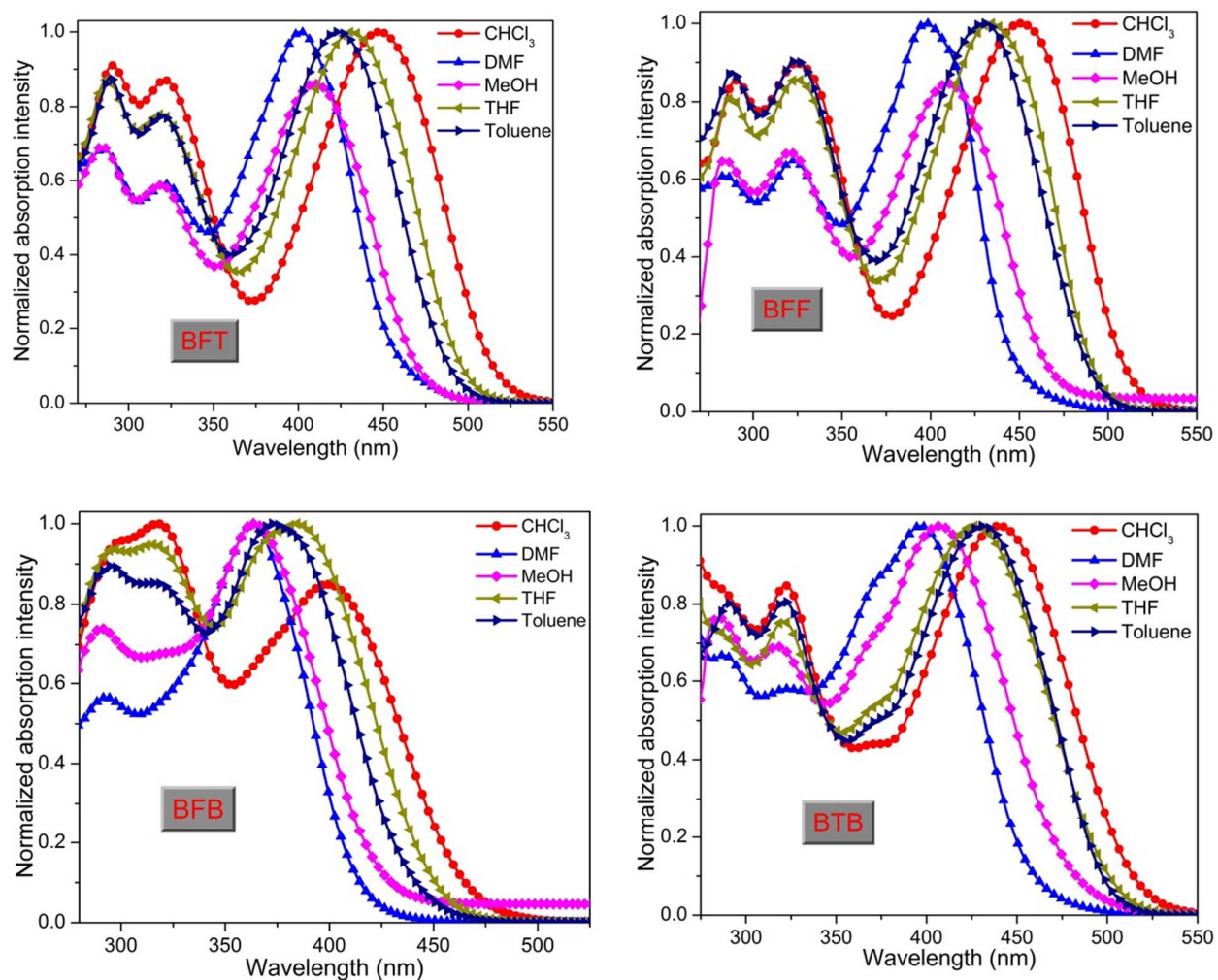


Figure S3 Absorption of the dyes recorded in different solvents

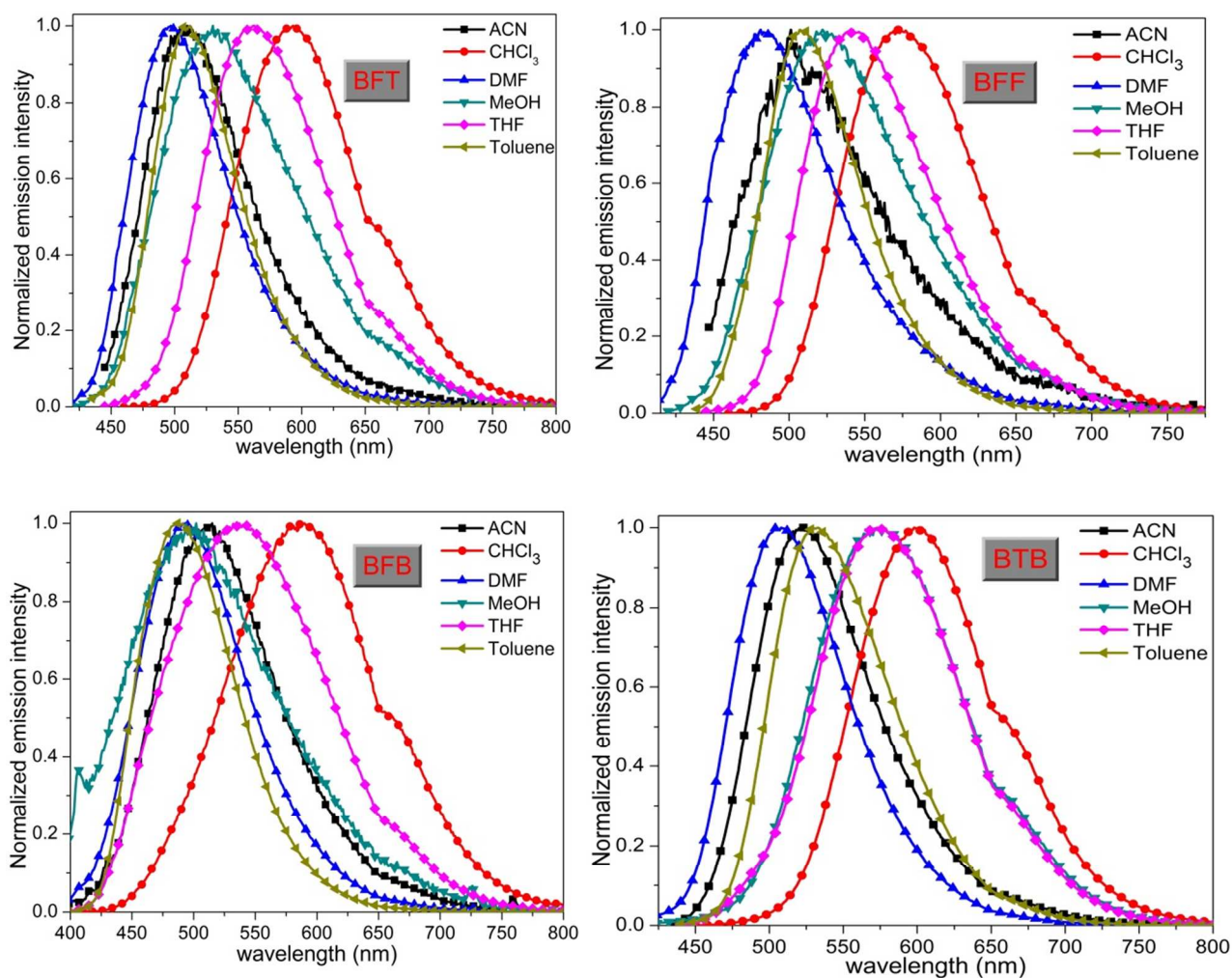


Figure S4 Fluorescence spectra of the dyes recorded in different solvents.

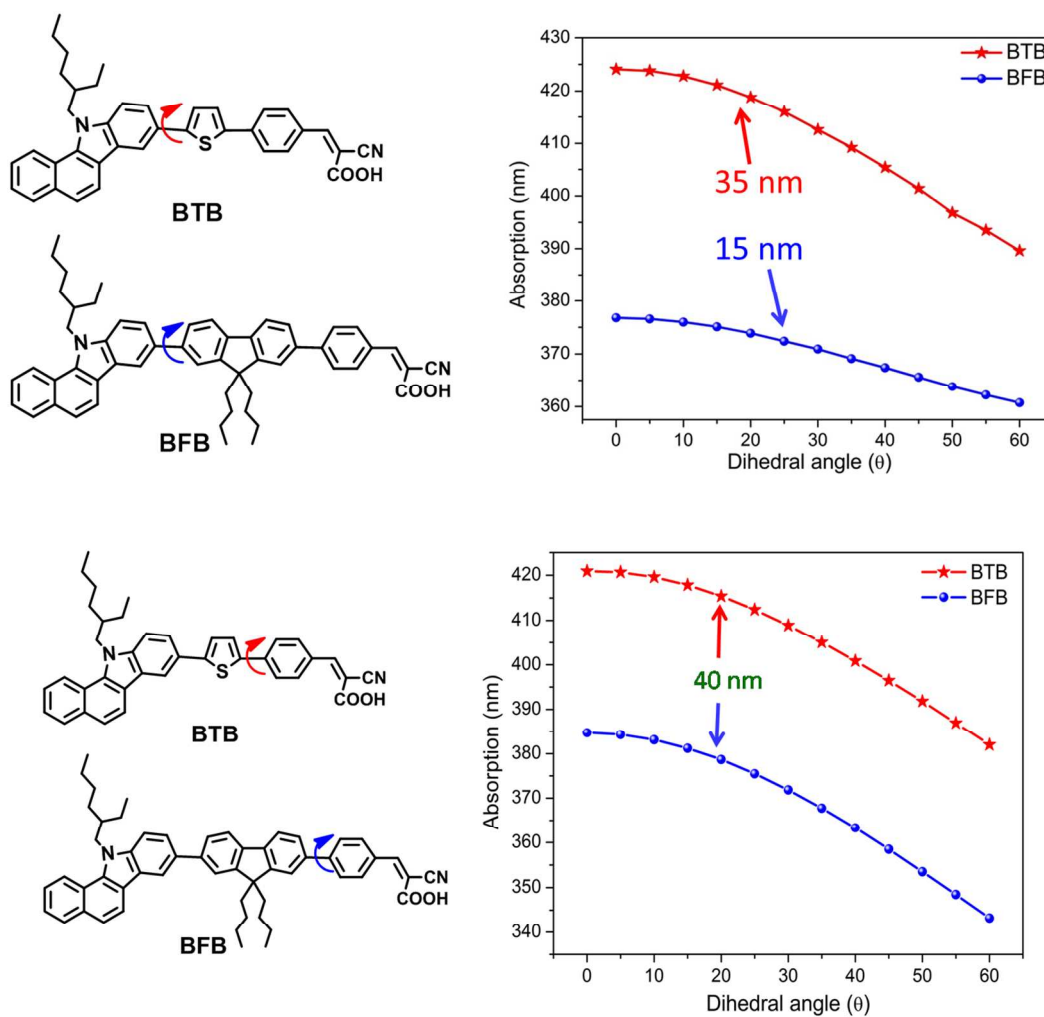


Figure S5 Computed absorption vs. variation of dihedral angle θ (in $^{\circ}$)

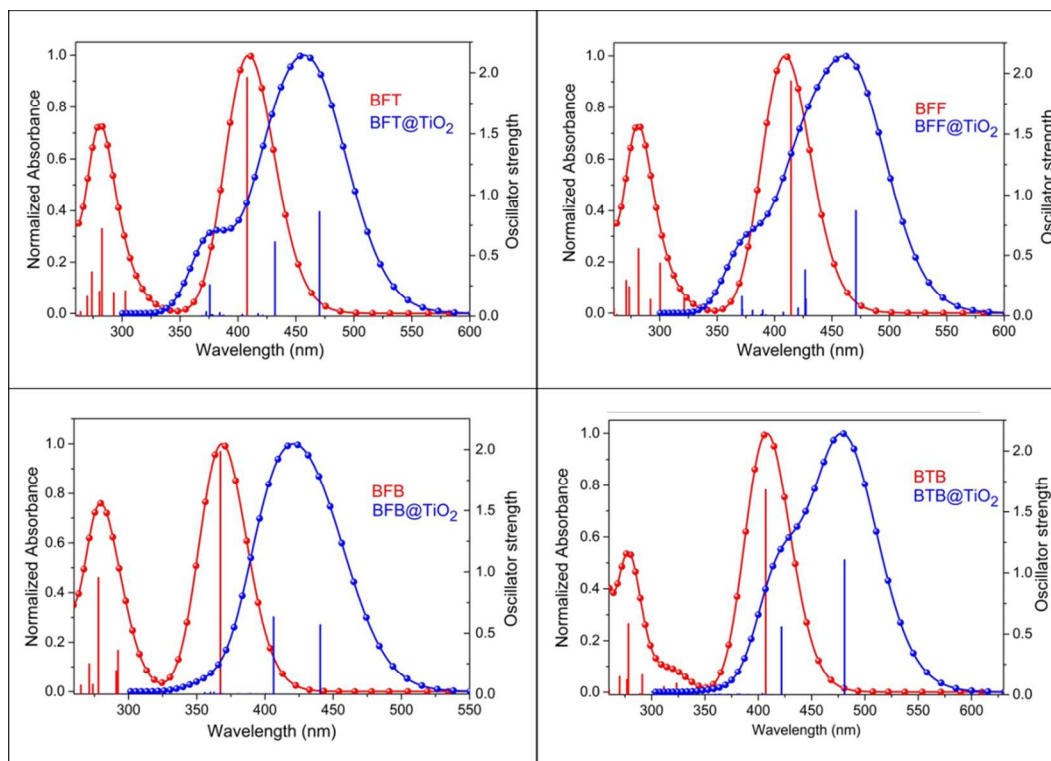


Figure S6 Comparison of simulated absorption spectra of dyes and dyes on $(\text{TiO}_2)_{16}$ obtained from M06-2X/6-311g (d, p) and PBE0/3-21g (d) level of theory respectively.

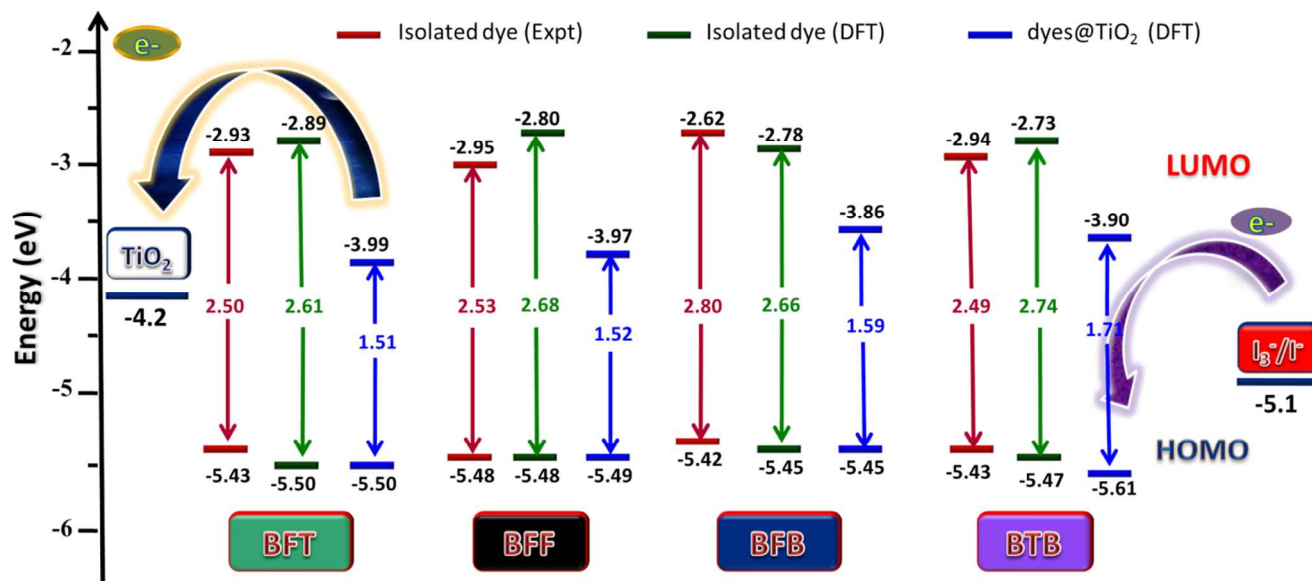


Figure S7 Schematic HOMO and LUMO energy levels estimated from experimental and DFT Studies.

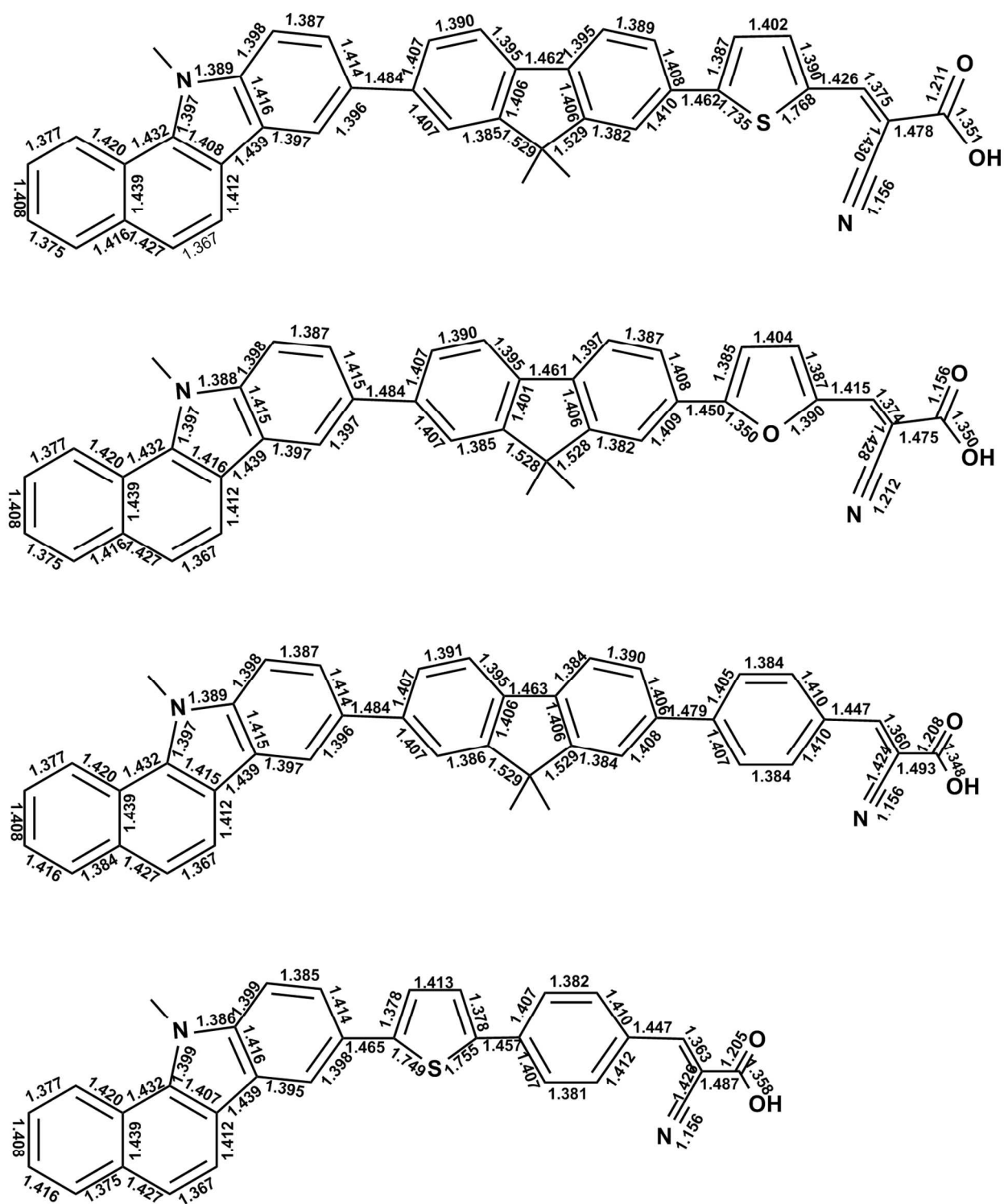


Figure S8 Geometry of the dyes

Table S1 Absorption maximum (in nm) for the dyes recorded in different solvents.

Dye	CHCl ₃	THF	ACN	Toluene	MeOH	DMF
BFT	448	432	431	423	410	401
BFF	451	434	435	430	409	397
BFB	399	385	381	373	364	363
BFB	440	427	422	431	405	397

Table S2 Emission maximum (in nm)) for the dyes recorded in different solvents.

Dye	CHCl ₃	THF	ACN	Toluene	MeOH	DMF
BFT	593	562	510	512	534	497
BFF	572	542	501	507	522	481
BFB	590	532	515	487	494	493
BTB	598	573	523	533	572	508

Table S3 Stokes shift (in cm⁻¹) of the compounds in different solvents

Dye	CHCl ₃	THF	ACN	Toluene	MeOH	DMF
BFT	5458	5355	4594	4109	5564	4449
BFF	5690	4691	3028	3532	5293	4399
BFB	8114	7177	6829	6276	7230	7264
BTB	6005	5967	4576	4440	7209	5503

Table S4 Comparison of absorption, emission, properties of the dyes/dyes@(TiO₂)₁₆ with computed excitation energy, oscillator strength, composition in terms of molecular orbitals, and dipole moments.

Dye	$\lambda_{\max}^a$ (nm)	$\lambda_{\max}^b$ (nm)	λ_{flu}^a (nm)	Stokes shift (cm ⁻¹)	CAM-B3LYP ^c (THF)			PBE0 ^d			μ^e (Debye)
					$\lambda_{\max}$	f	Composition	λ_{TiO_2}	f	Composition	
BFT	433 319	469	562	5301	413 (3.00 eV)	1.9	H->L (24%) H-1->L (34%) H-2->L (29%)	470 (2.64eV)	0.86	H->L (87%) H-1->L (11%)	11.0
BFF	436 325	470	542	4486	418 (2.97 eV)	1.9	H->L (30%) H-1->L (36%) H-2->L (24%)	471 (2.63eV)	0.87	H->L (83%) H-1->L (13%)	10.9
BFB	389 315	434	532	6910	367 (3.37 eV)	2.0	H->L (24%) H-1->L 29%) H-2->L (25%)	440 (2.81eV)	0.57	H->L (78%) H-1->L (6%)	8.1
BTB	427 321	483	573	5077	409 (3.03 eV)	1.7	H->L (55%) H-1->L (23%) H-2->L (11%)	481 (2.58eV)	1.11	H->L (96%) H-1->L (3%)	11.8

^a absorption and emission spectra were measured in THF in the concentration of 1x10⁻⁵ M at ambient temperature.

^b absorption maxima on TiO₂ film.

^c obtained with 6-31G+(d) basis set.

^dTD-DFT values of dyes on (TiO₂)₁₆ obtained using PBE0/3-21g (d) level.

^edipole moment of the dyes on TiO₂ obtained using B3LYP functional.

Table S5 Computed S0- S1 excitation energies (E) with electron volt in parenthesis, oscillator strength (f), configuration compositions obtained from B3LYP, PBE functionals using THF as solvent with experimental absorption values.

Dye	$\lambda_{\max}^a$ (nm)	B3LYP ^b (THF)		PBE0 ^b (THF)		$\lambda_{\text{TIO}_2}^a$ (nm)	B3LYP ^c (THF)		CAM-B3LYP ^c (THF)		M06-2X ^c (THF)	
		$\lambda_{\max}$	f	$\lambda_{\max}$	f		$\lambda_{\max}$	f	$\lambda_{\max}$	f	$\lambda_{\max}$	f
BFT	433	454 (2.73 eV)	0.39	448 (2.77 eV)	0.7	469	529 (2.34 eV)	0.44	392 (3.16 eV)	2.03	392 (3.16 eV)	1.99
BFF	436	453 (2.74 eV)	0.48	444 (2.79 eV)	0.8	470	522 (2.38 eV)	0.45	394 (3.14 eV)	2.08	395 (3.14 eV)	2.04
BFB	389	331 (3.75 eV)	0.29	319 (3.89 eV)	0.5	434	555 (2.23 eV)	0.03	345 (3.59 eV)	2.36	349 (3.55 eV)	2.08
BTB	427	473 (2.62 eV)	0.60	454 (2.73 eV)	0.8	483	520 (2.38 eV)	0.83	390 (2.73 eV)	2.15	393 (3.15 eV)	2.02

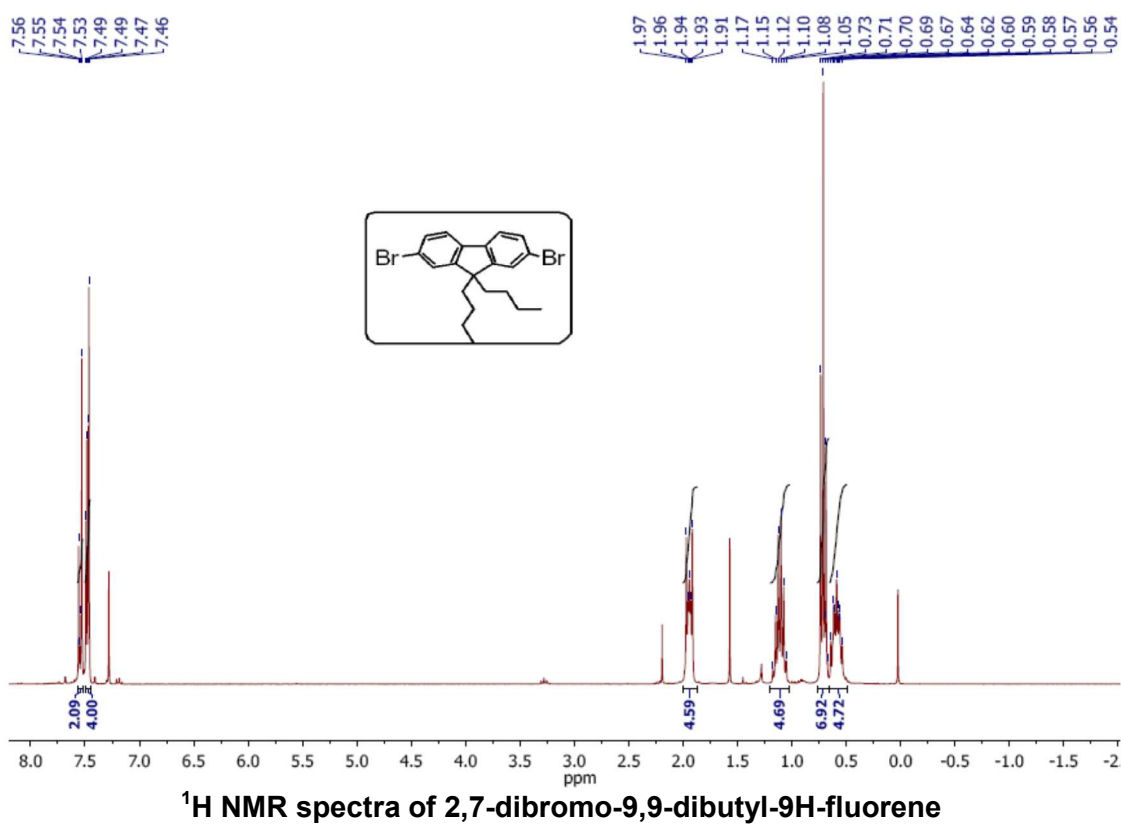
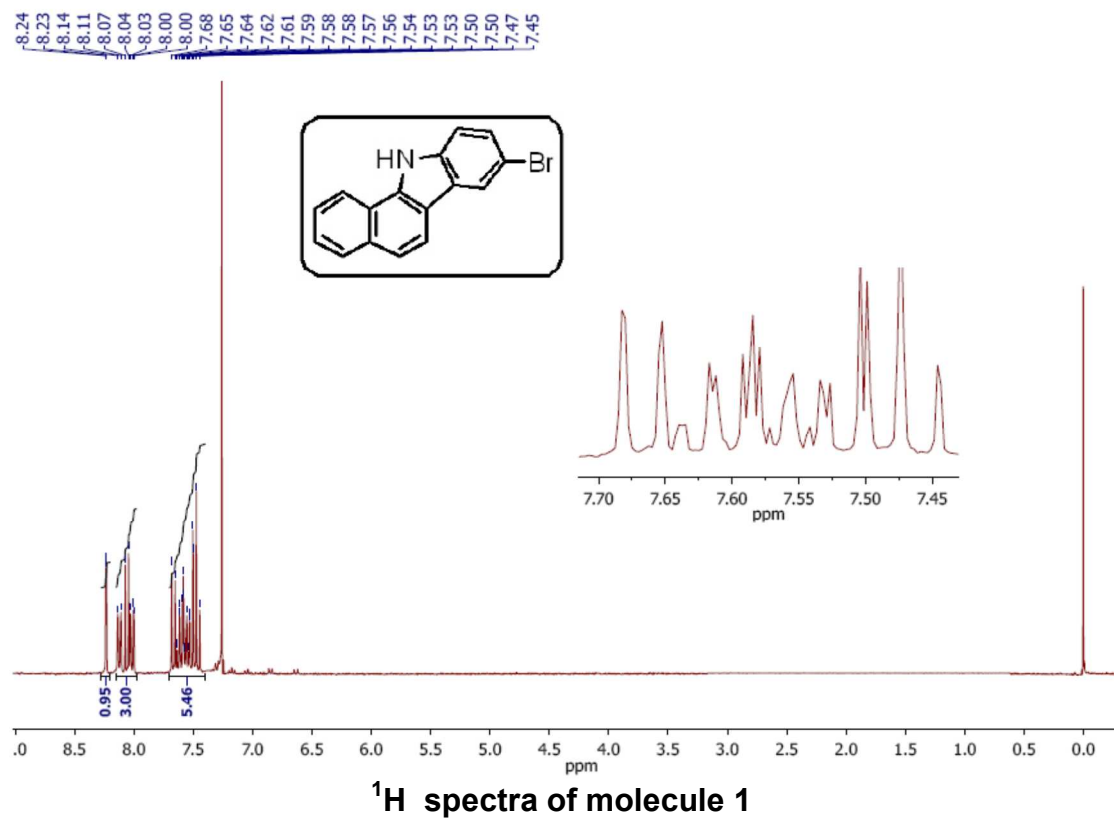
^a absorption values obtained from experimental data.

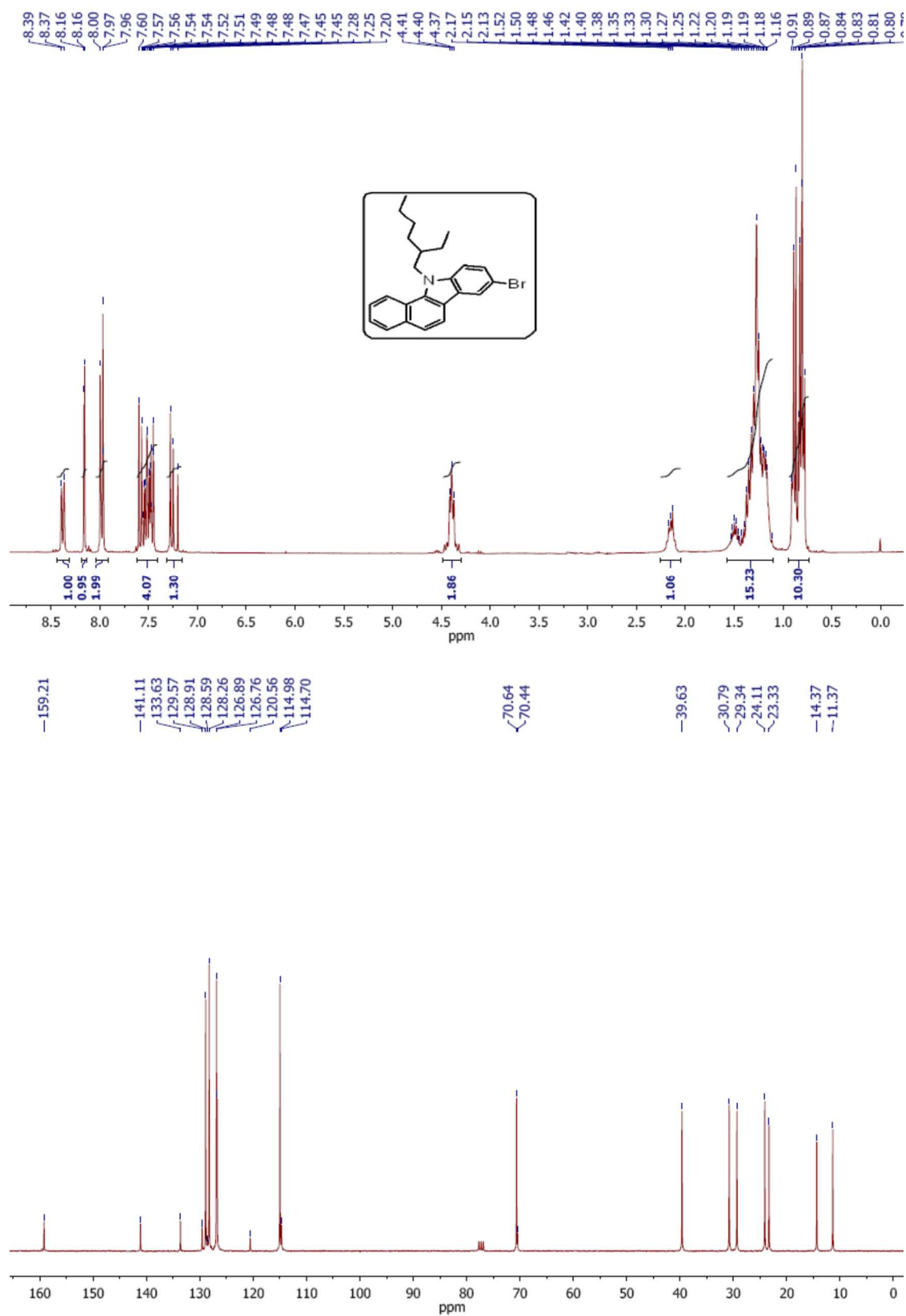
^b obtained with 6-311G(d, p) basis set.

^c obtained with 3-21G(d) basis set.

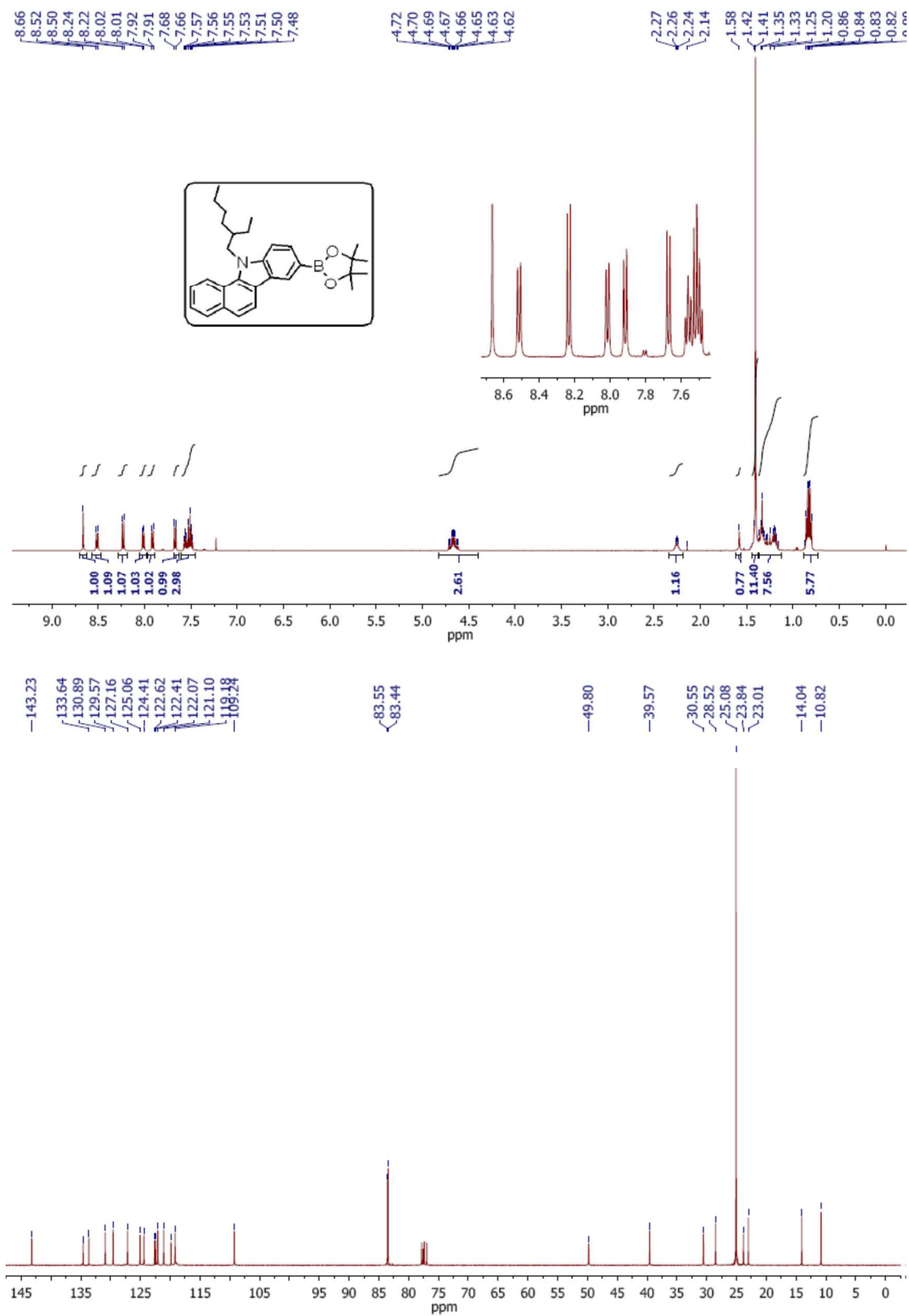
References

1. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; et al., *Gaussian 03*, revision D.01; Gaussian, Inc.: Wallingford, CT, **2004**.

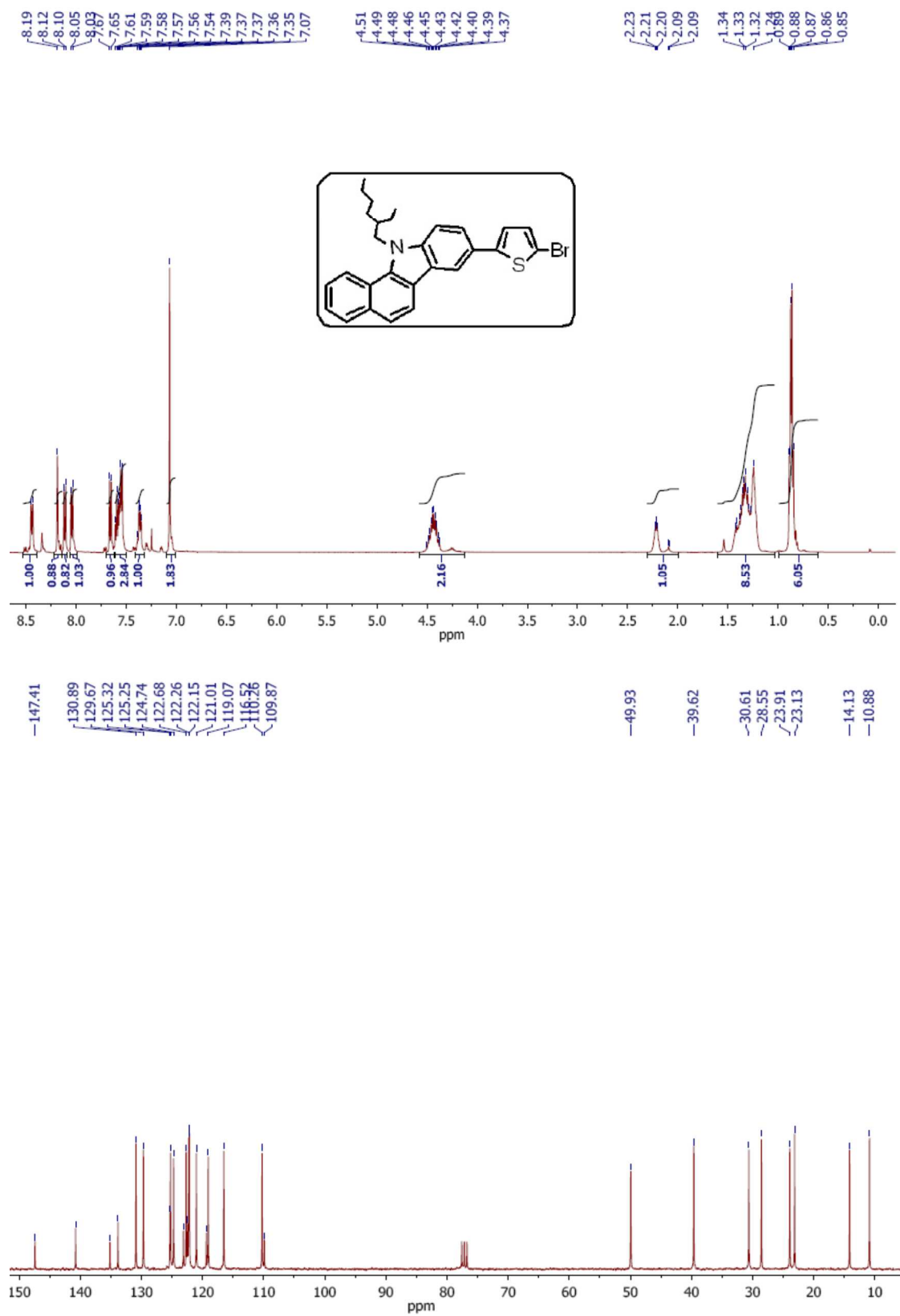




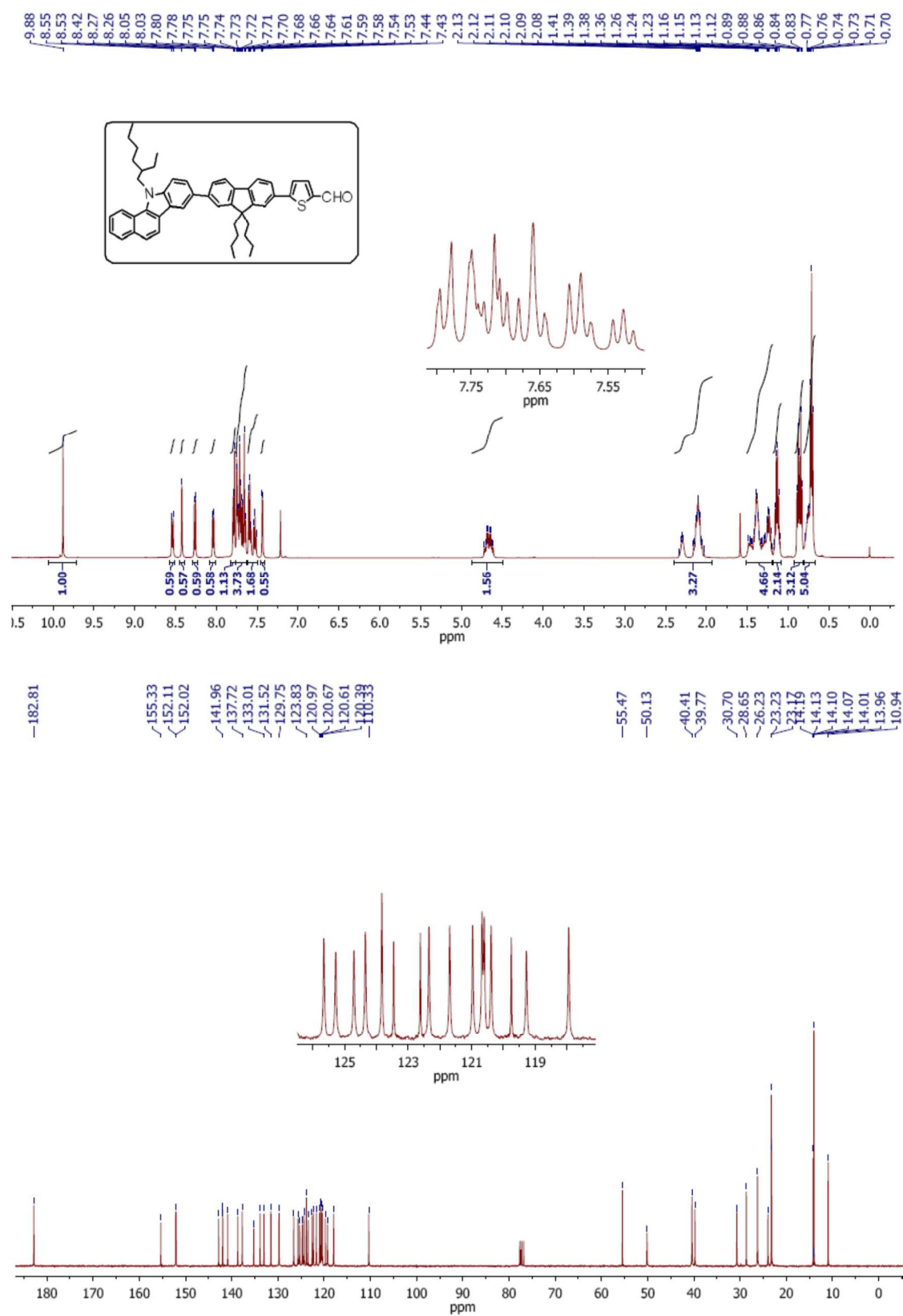
¹H and ¹³C spectra of molecule 2



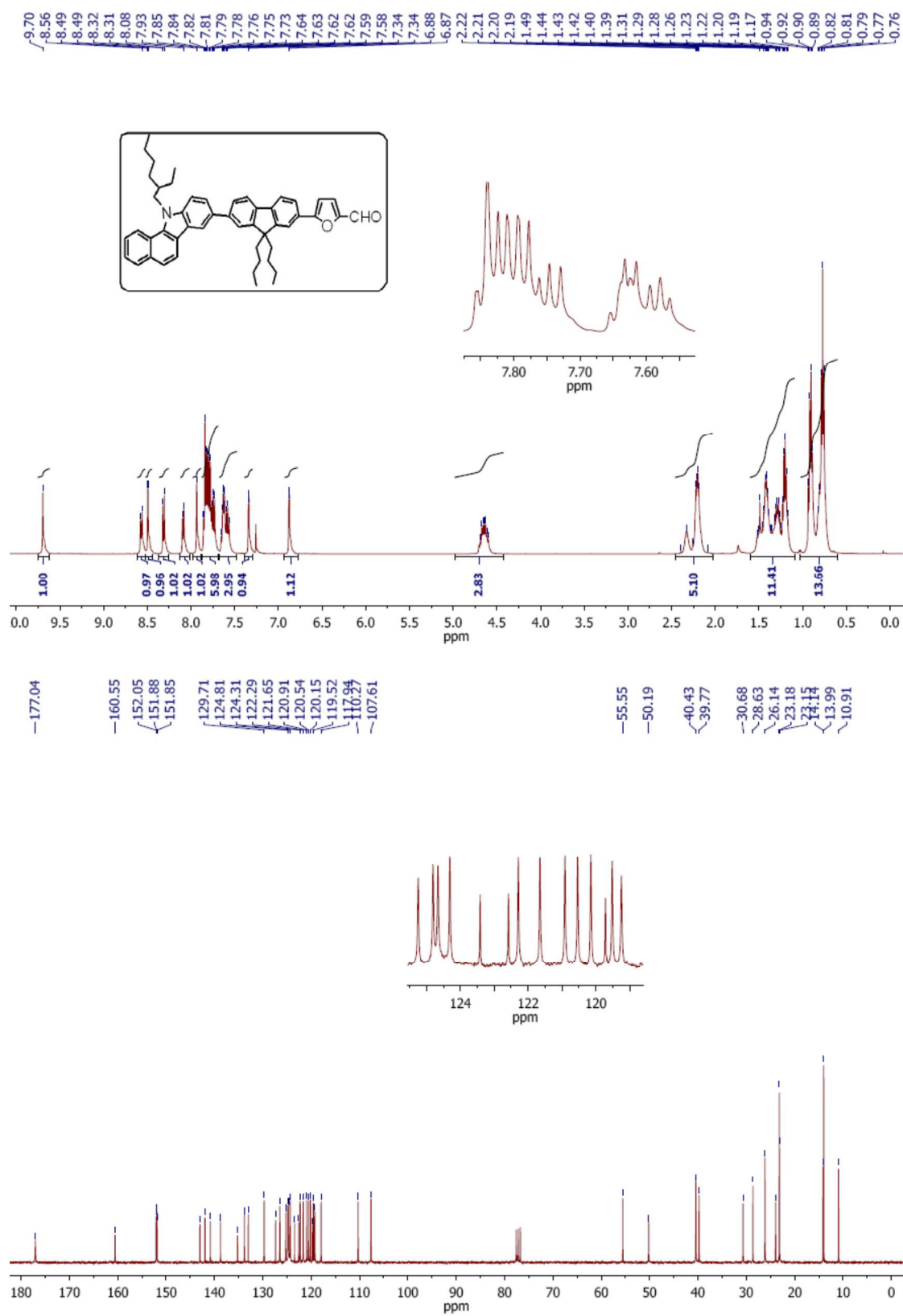
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¹H and ¹³C spectra of molecule 5

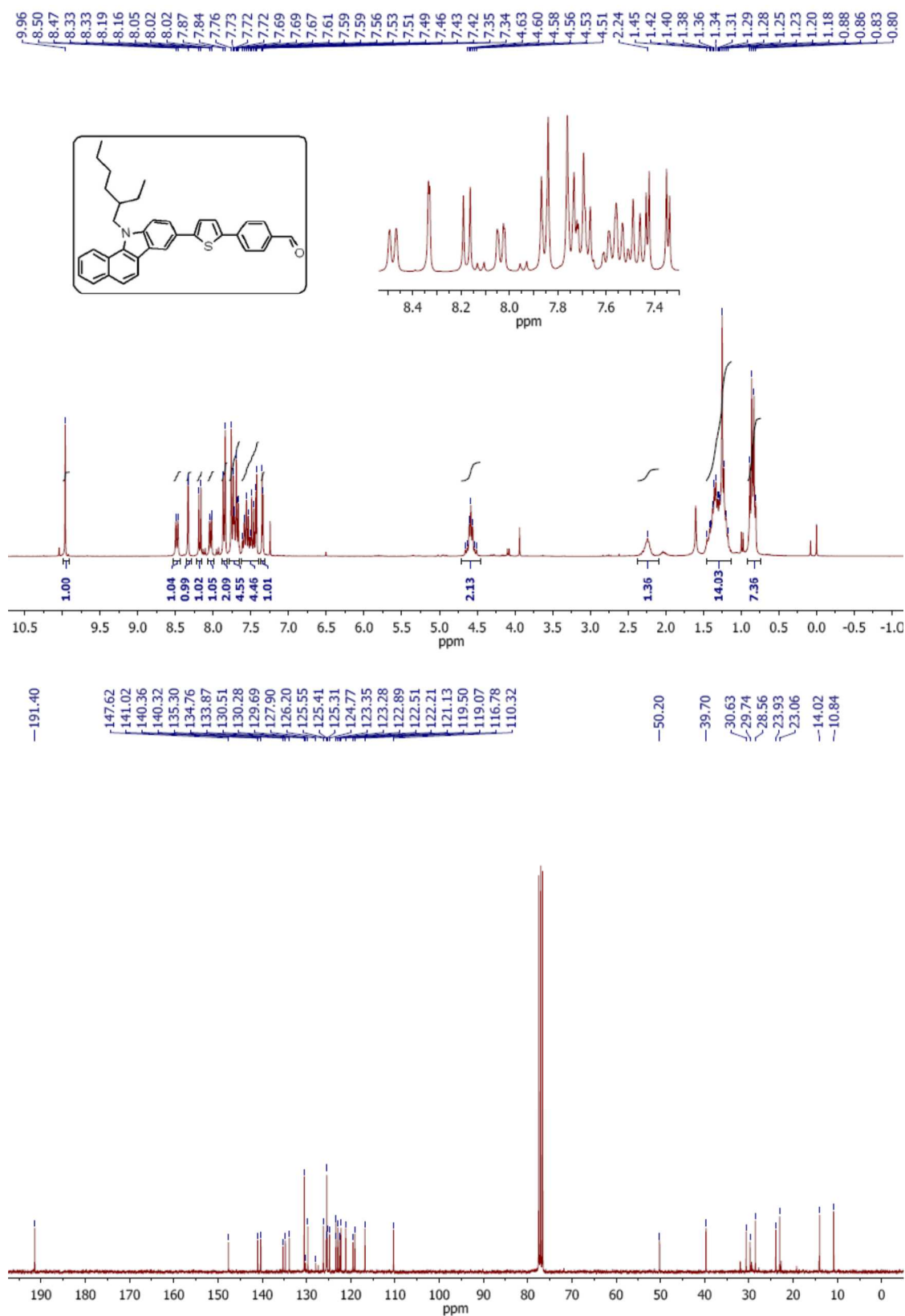


¹H and ¹³C spectra of molecule 6

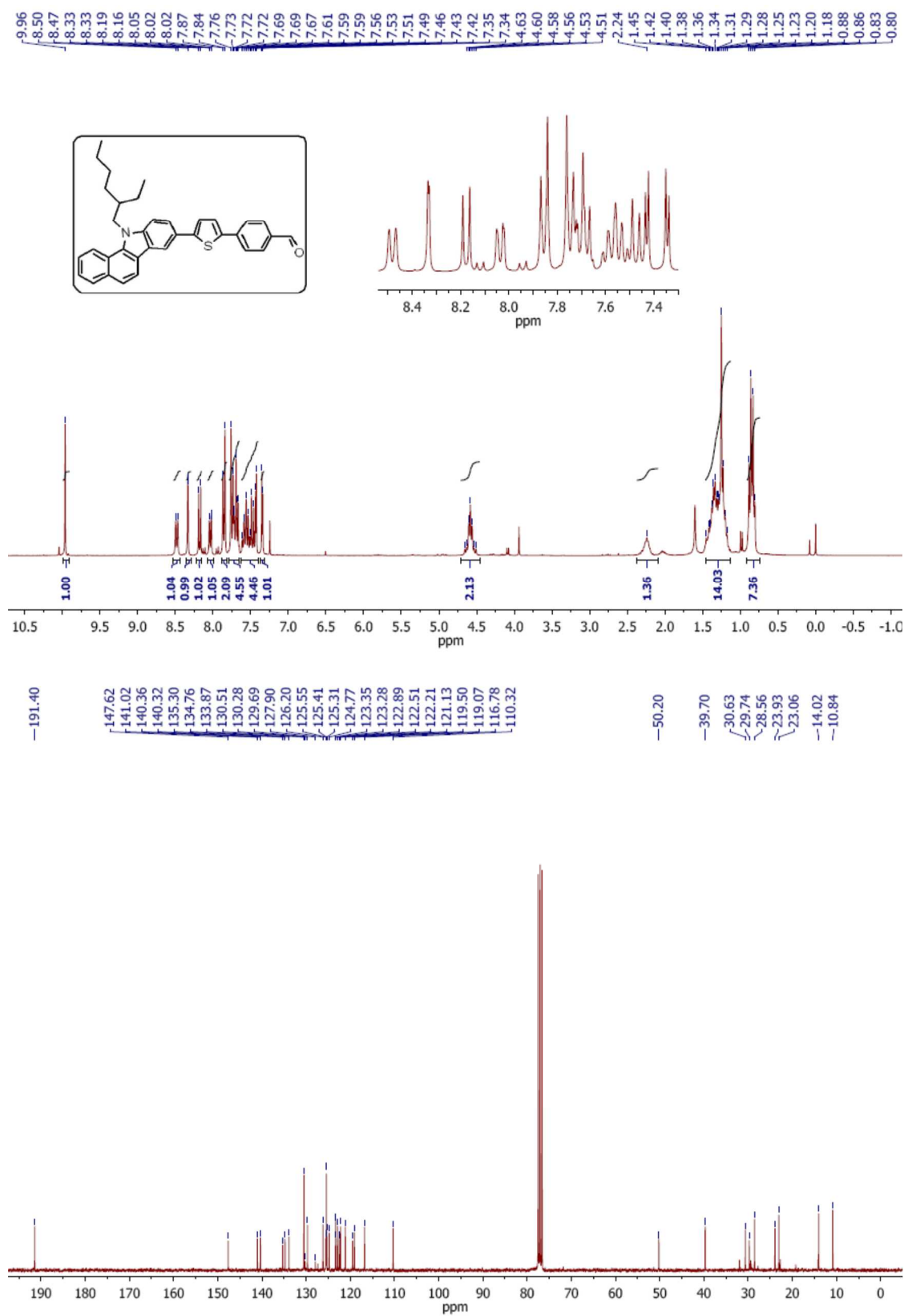


¹H and ¹³C spectra of molecule 7

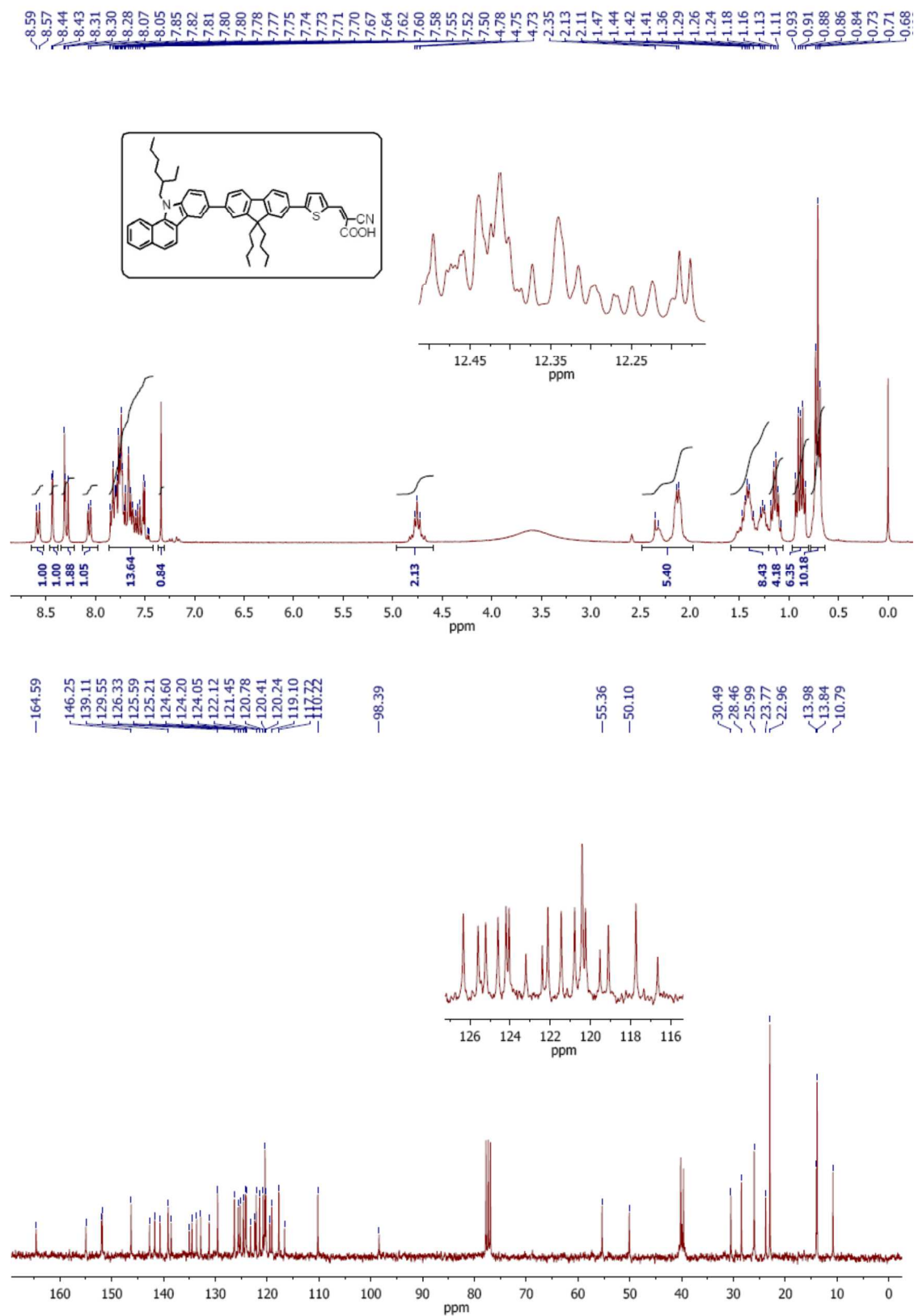




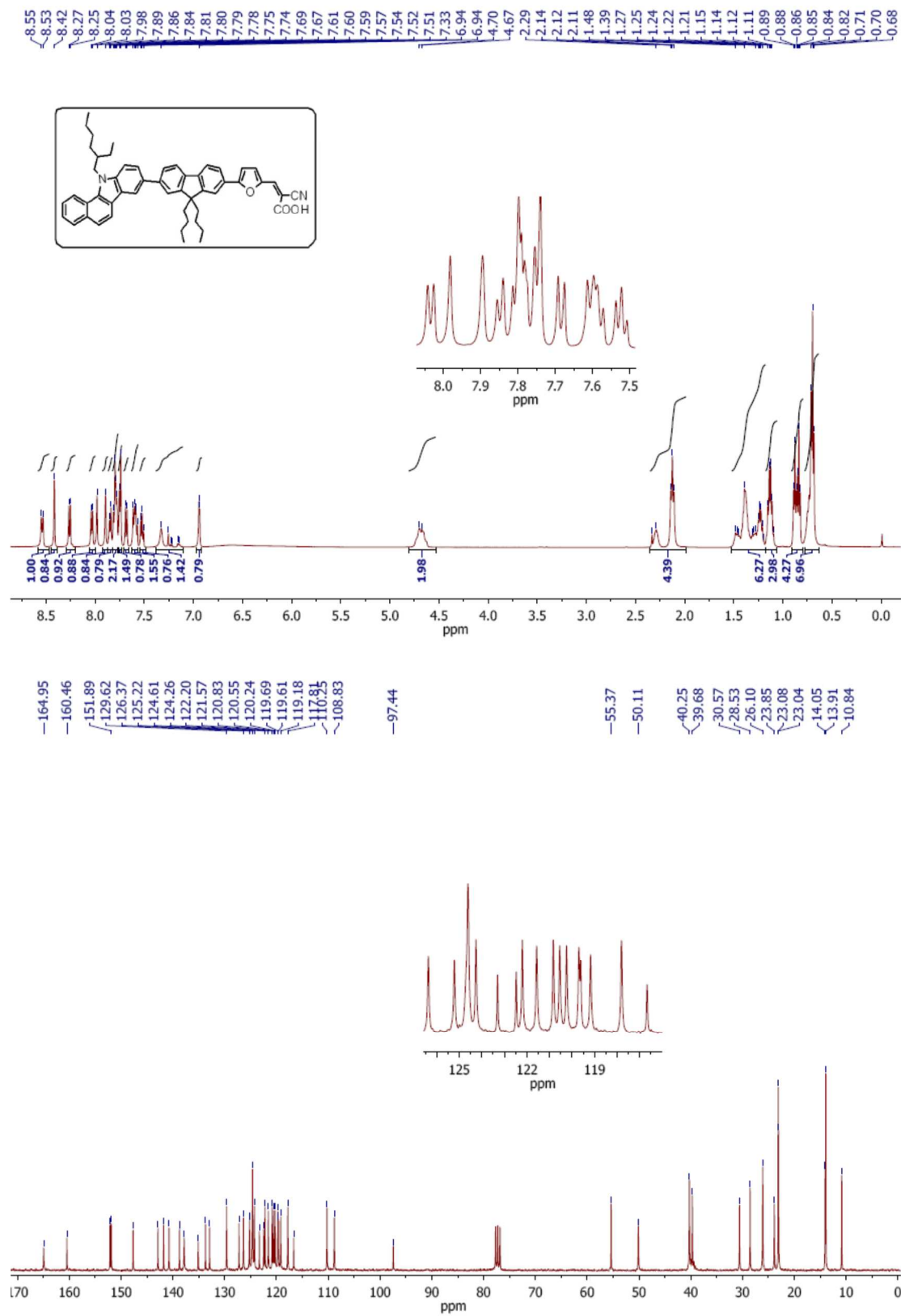
¹H and ¹³C spectra of molecule 9



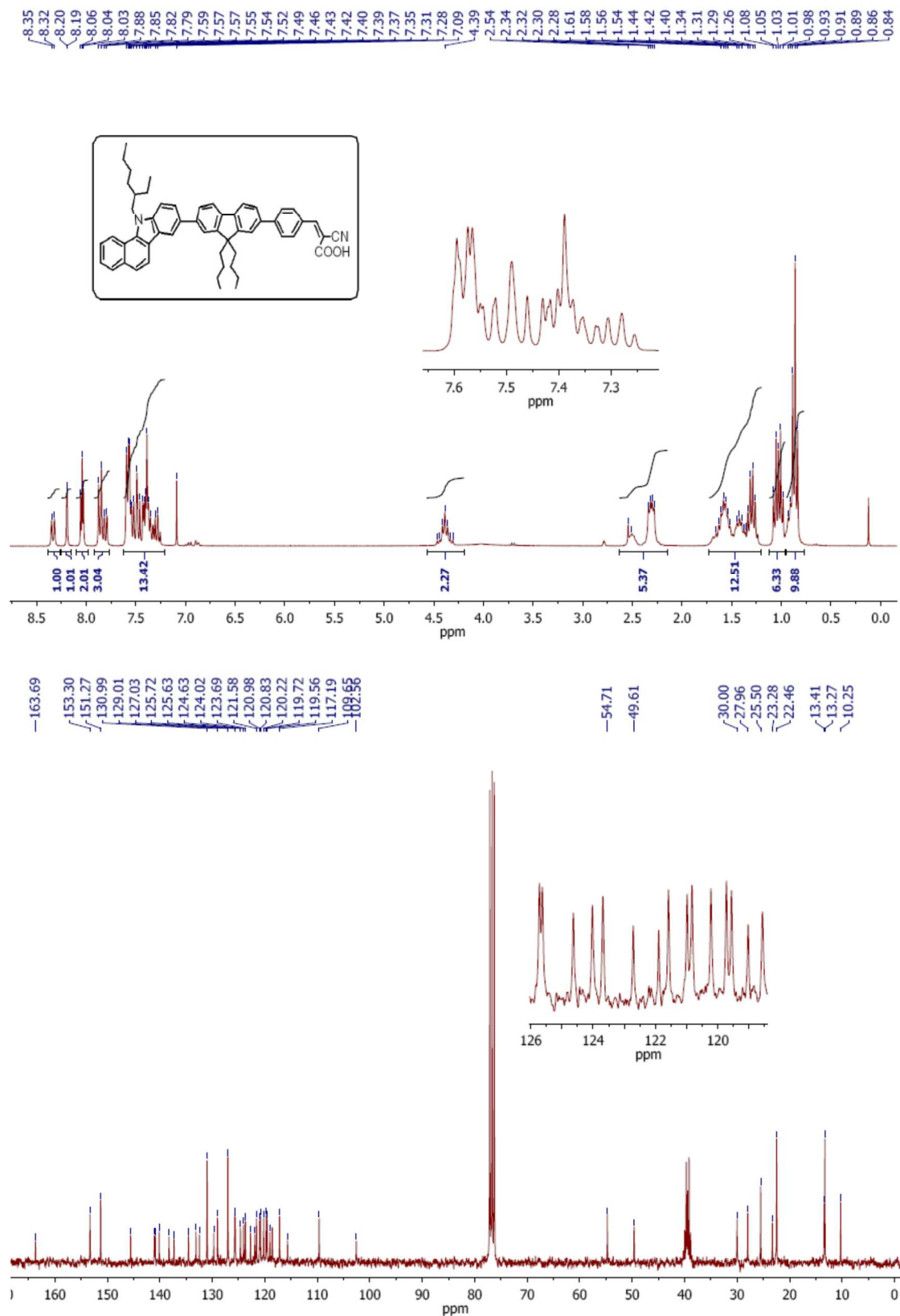
¹H and ¹³C spectra of molecule 10

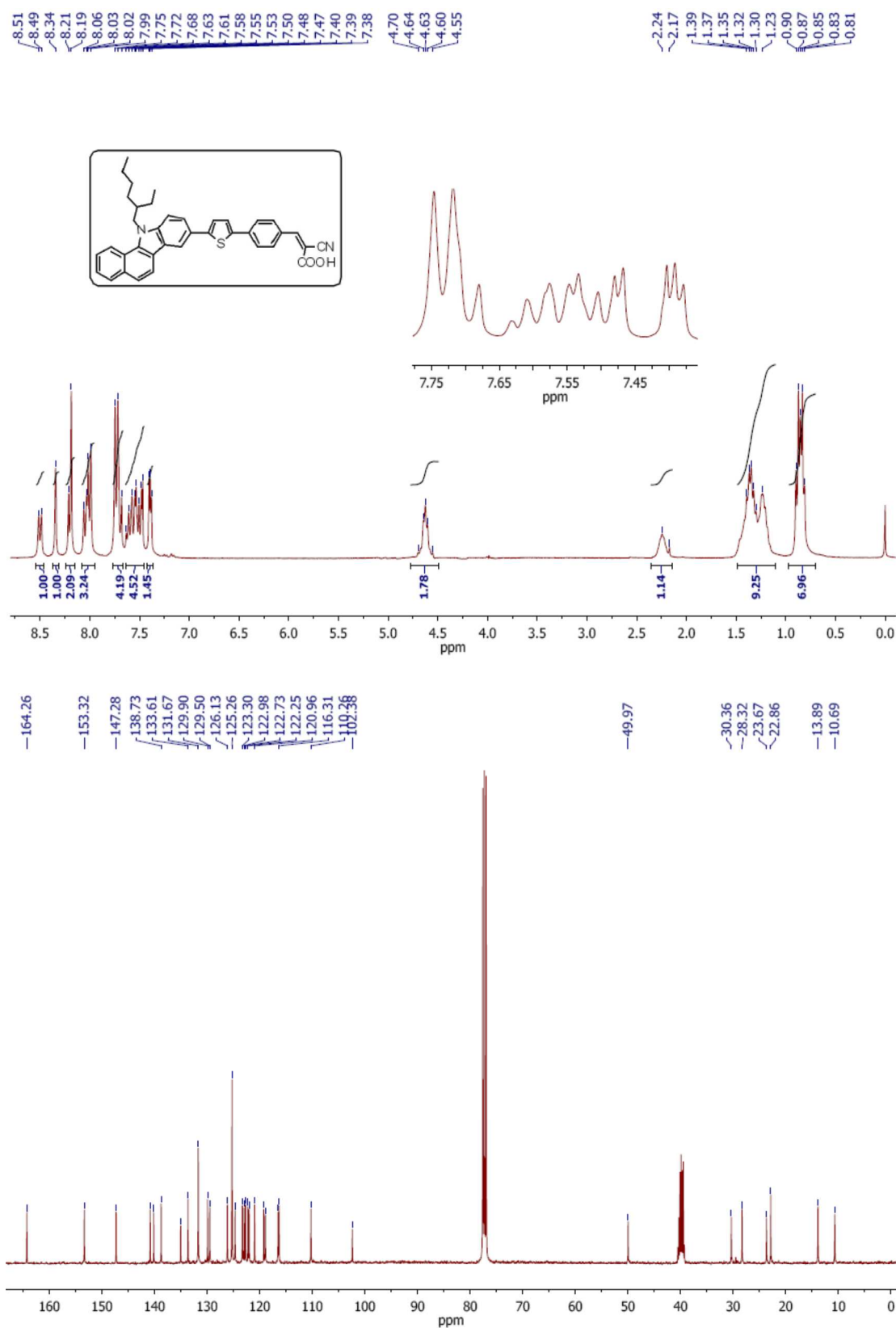


¹H and ¹³C spectra of molecule 11

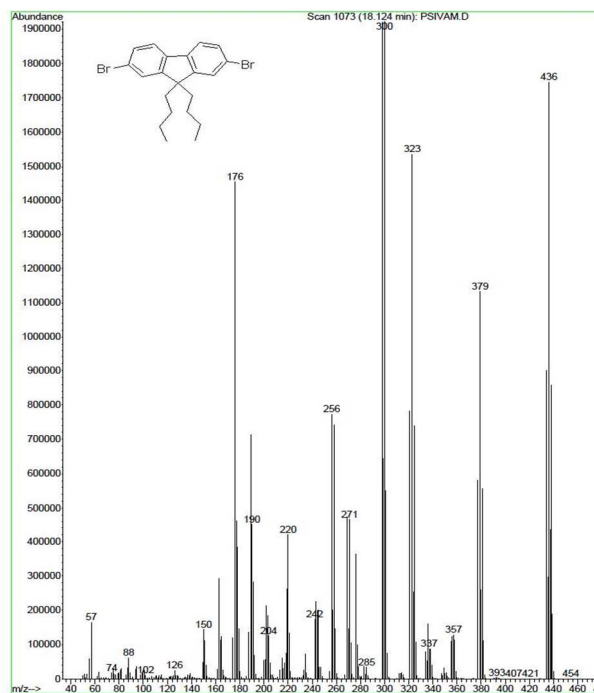


¹H and ¹³C spectra of molecule 12

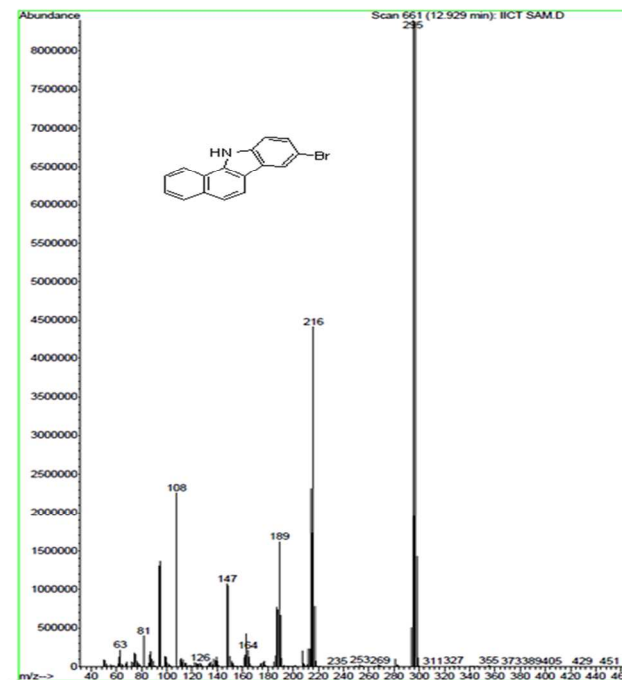




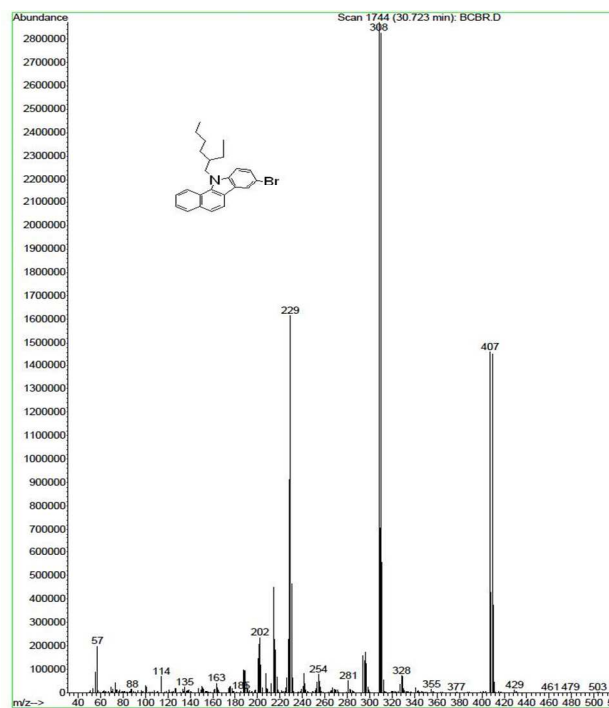
¹H and ¹³C spectra of molecule 14



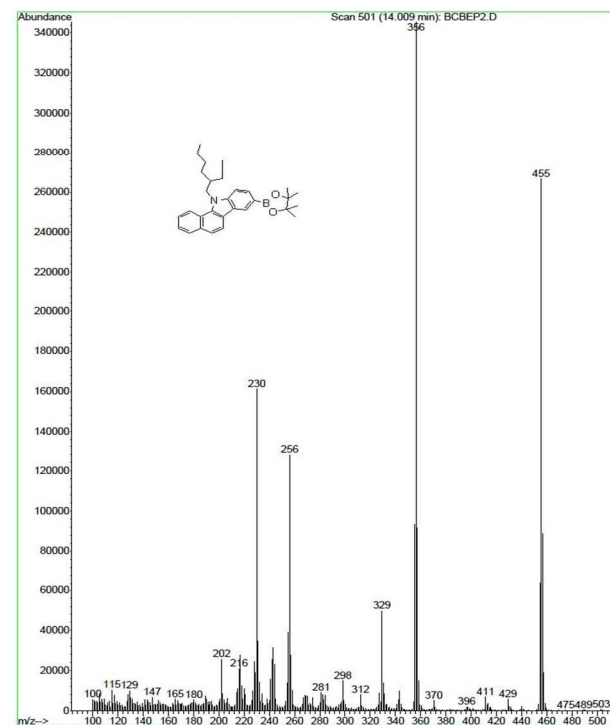
**GC-Mass spectrum of
2,7-dibromo-9,9-dibutyl-9H-fluorene**



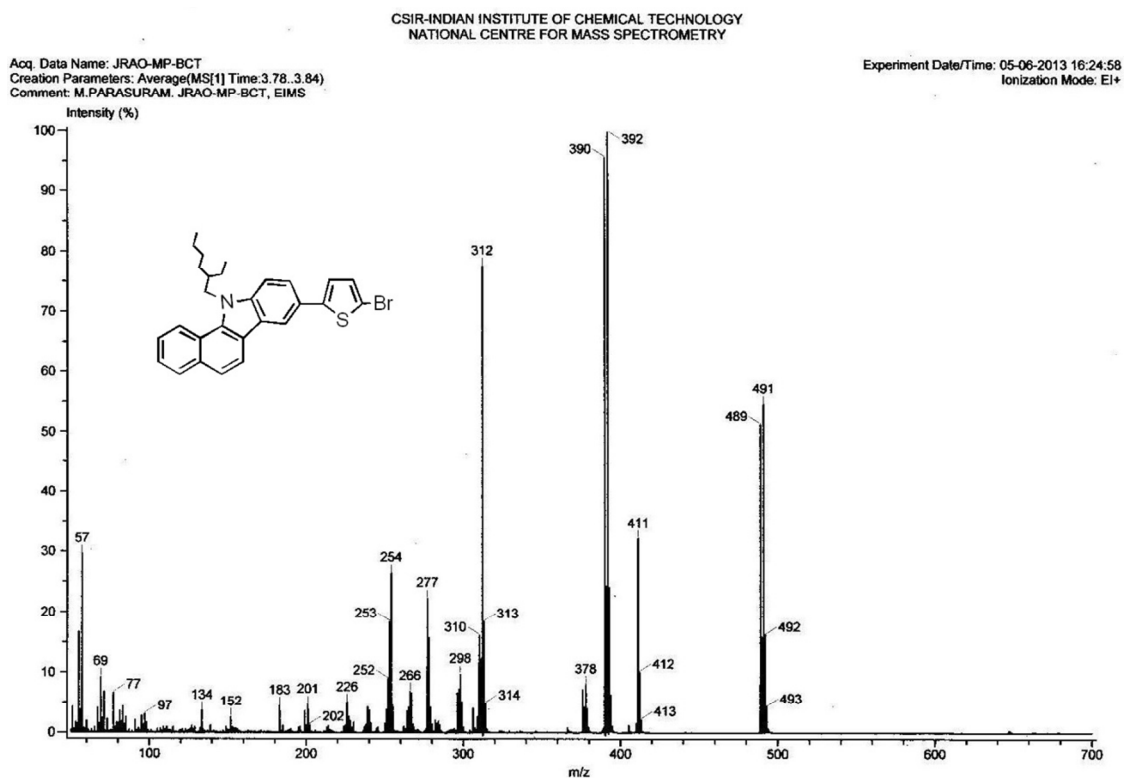
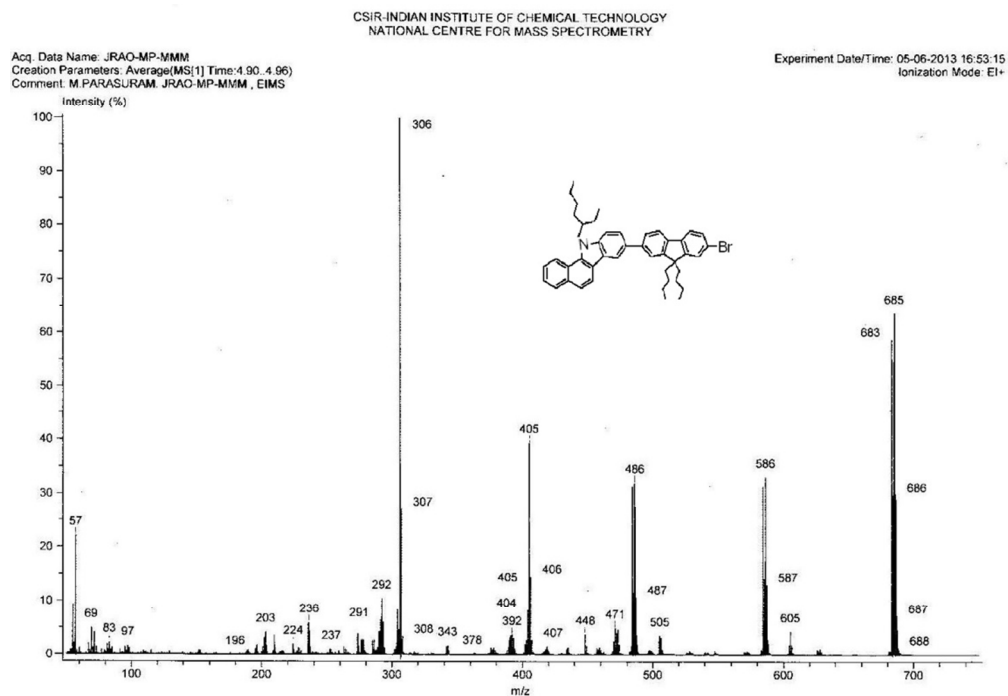
GC-Mass spectrum of molecule 1



GC-Mass spectrum of molecule 2



GC-Mass spectrum of molecule 3



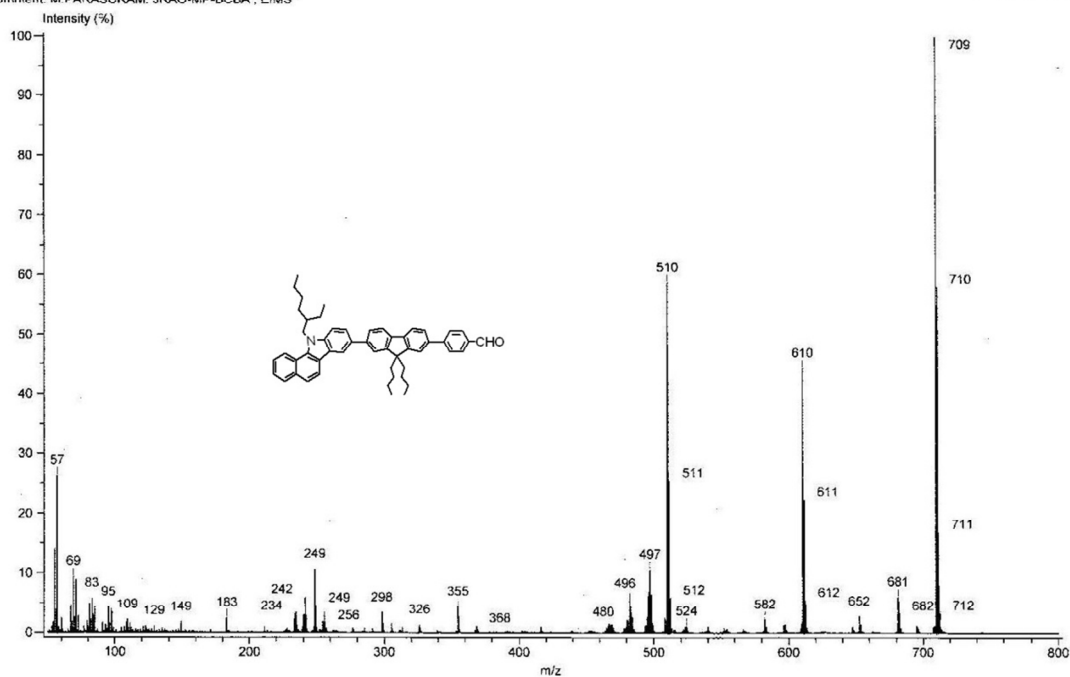


Mass spectrum of compound 10. The x-axis represents the mass-to-charge ratio (m/z) from 0 to 1400, and the y-axis represents the relative abundance from 0 to 100. The base peak is at m/z 700.5. Other labeled peaks include 180.7, 279.0, 394.6, 502.9, 593.9, 825.1, 963.1, 1208.0, and 1401.0. The chemical structure of compound 10 is shown as an inset, featuring a complex polycyclic aromatic system with a central fluorene core, a naphthalene ring, and a furan ring substituted with an aldehyde group.

ESI-Mass spectrum of molecule 7

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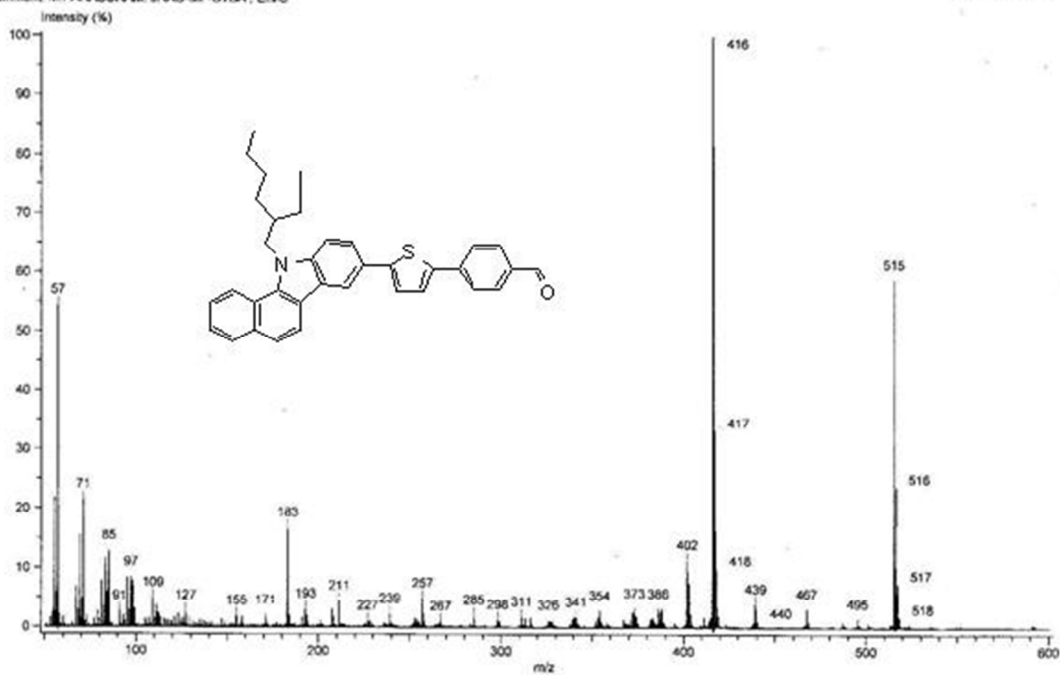
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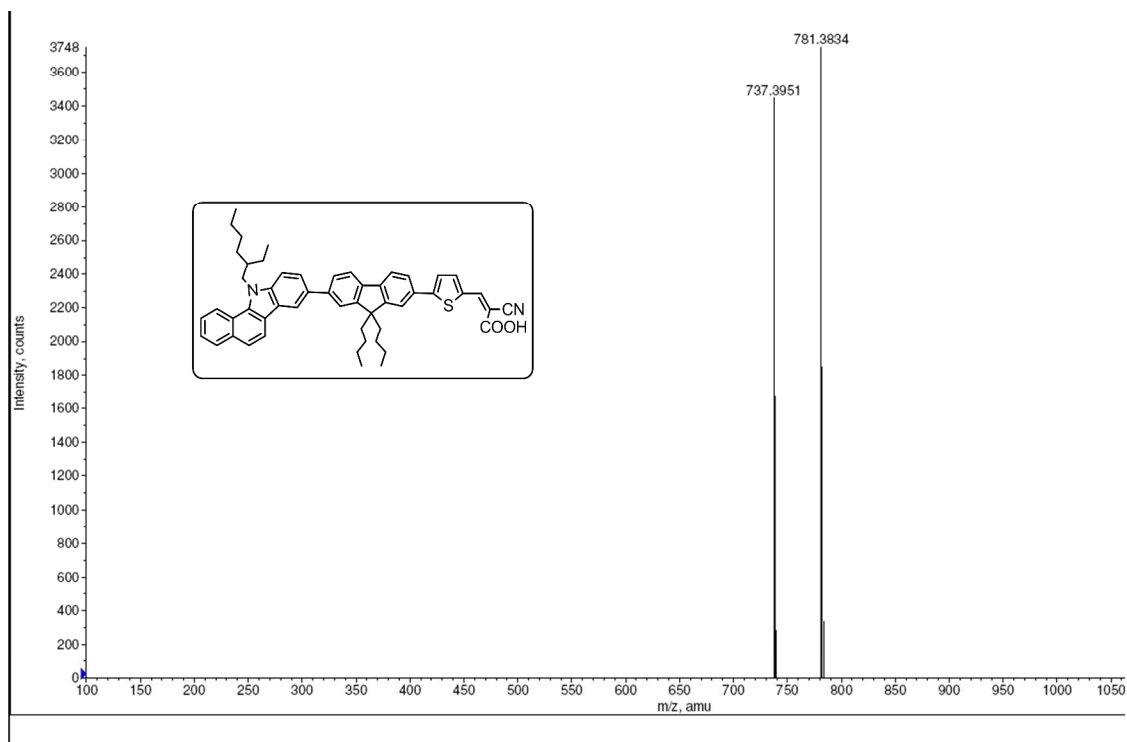
EI-Mass spectrum of molecule 8

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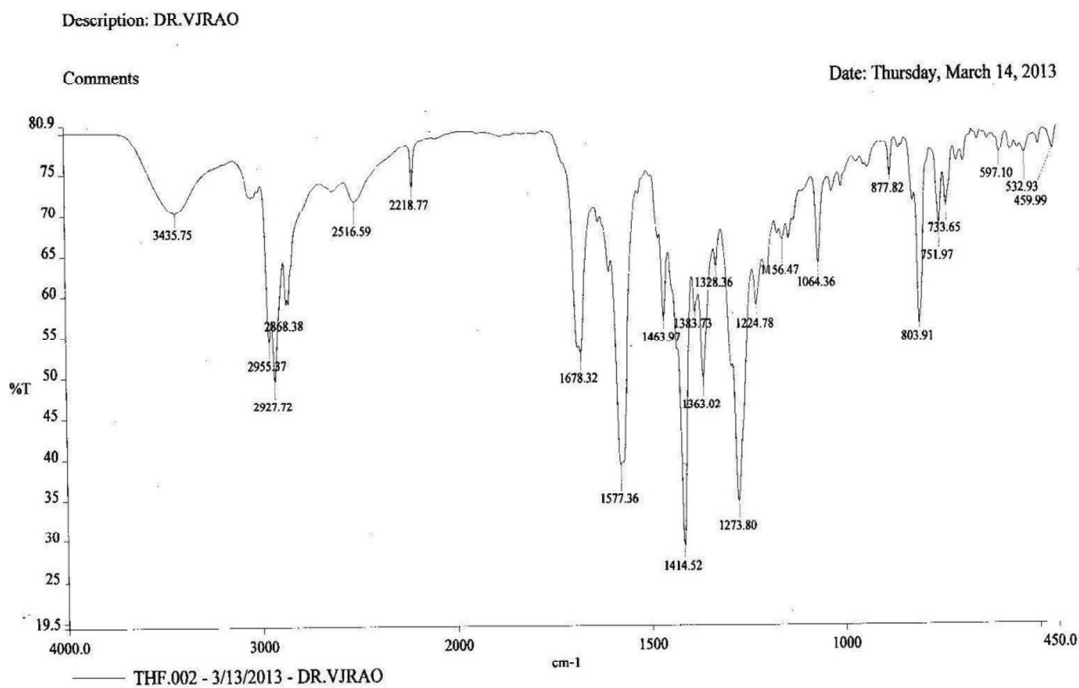


EI-Mass spectrum of molecule 9

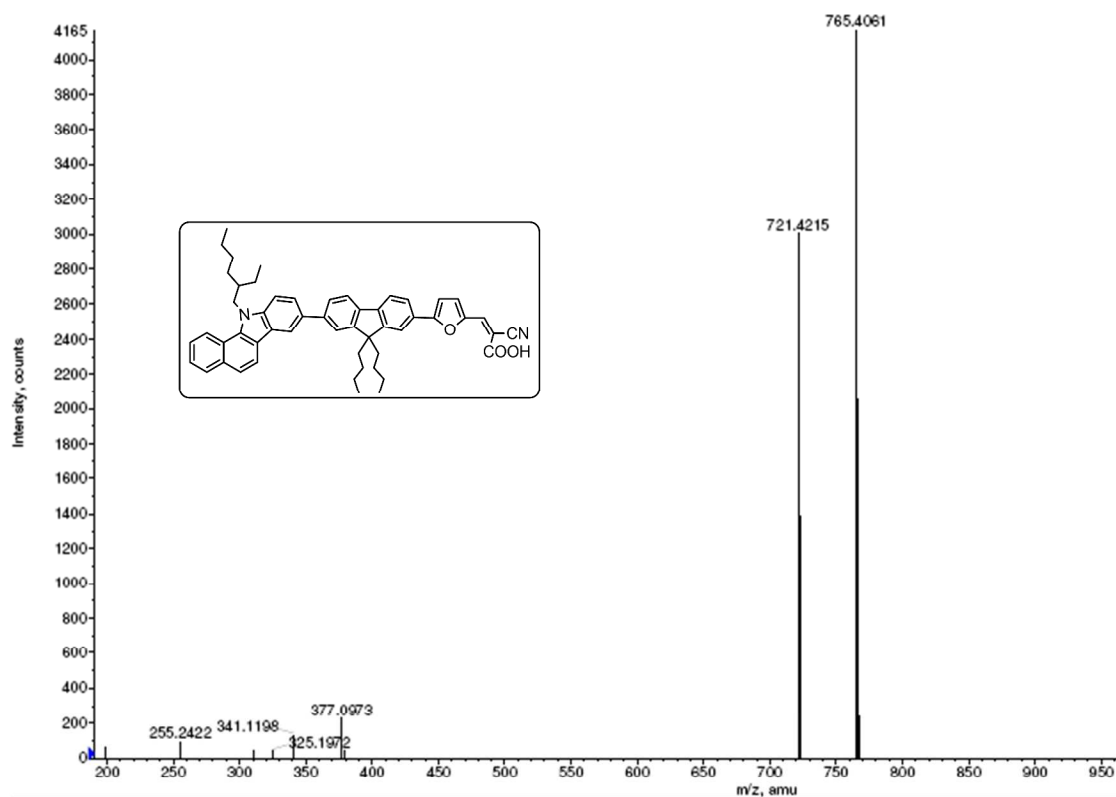


ESI-HRMS of molecule BFT

ORGANIC - II, IICT



IR Spectrum of molecule BFT



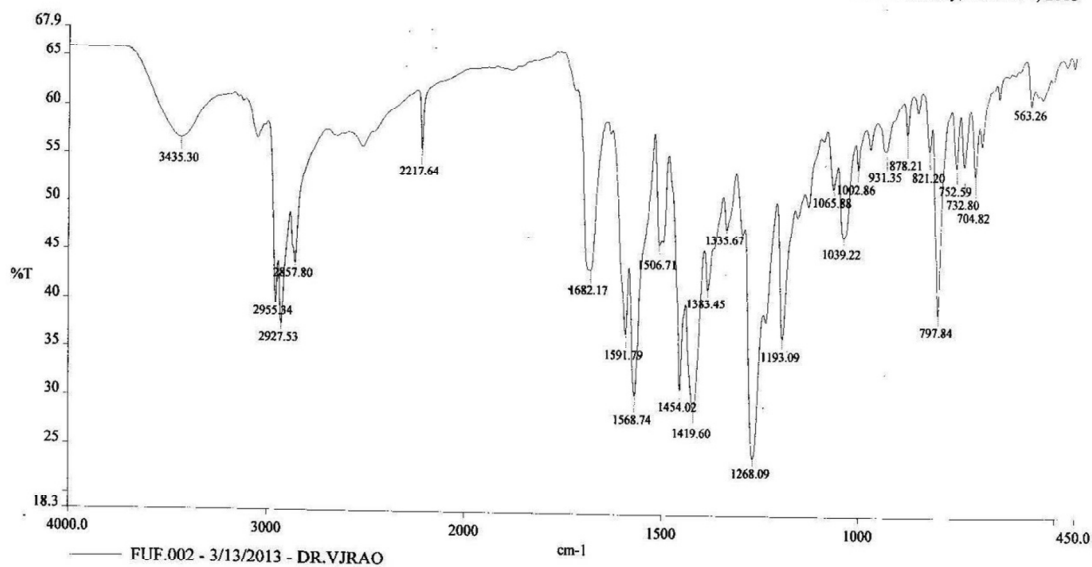
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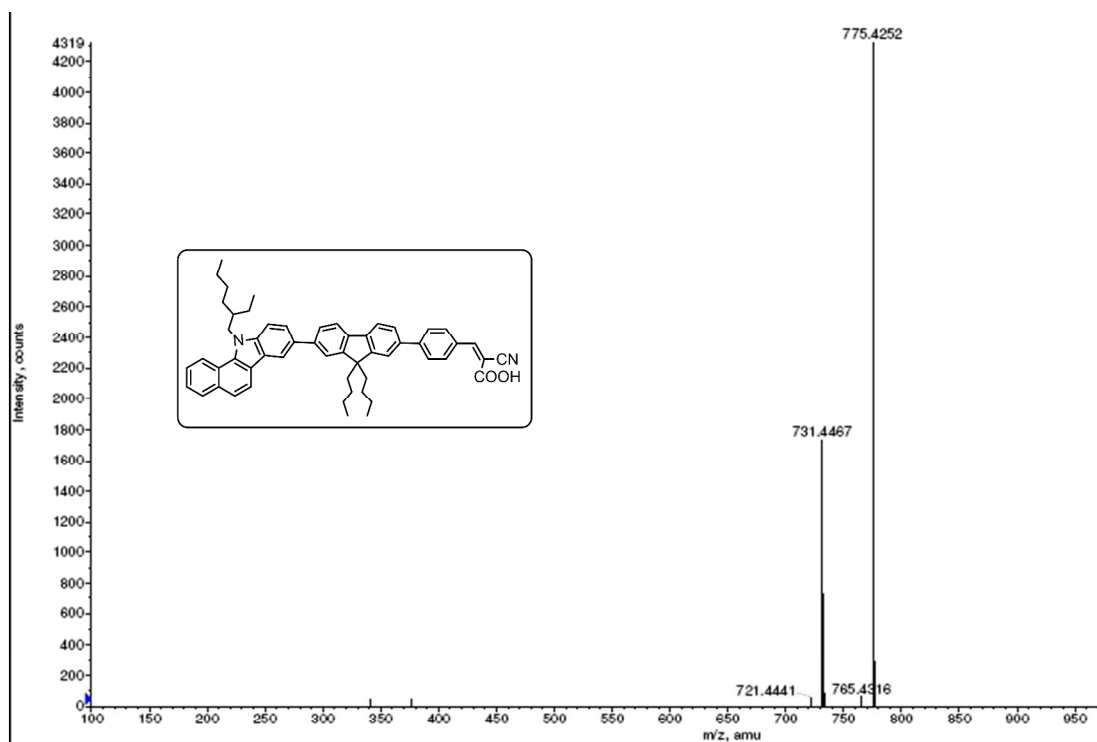
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Comments

Date: Thursday, March 14, 2013



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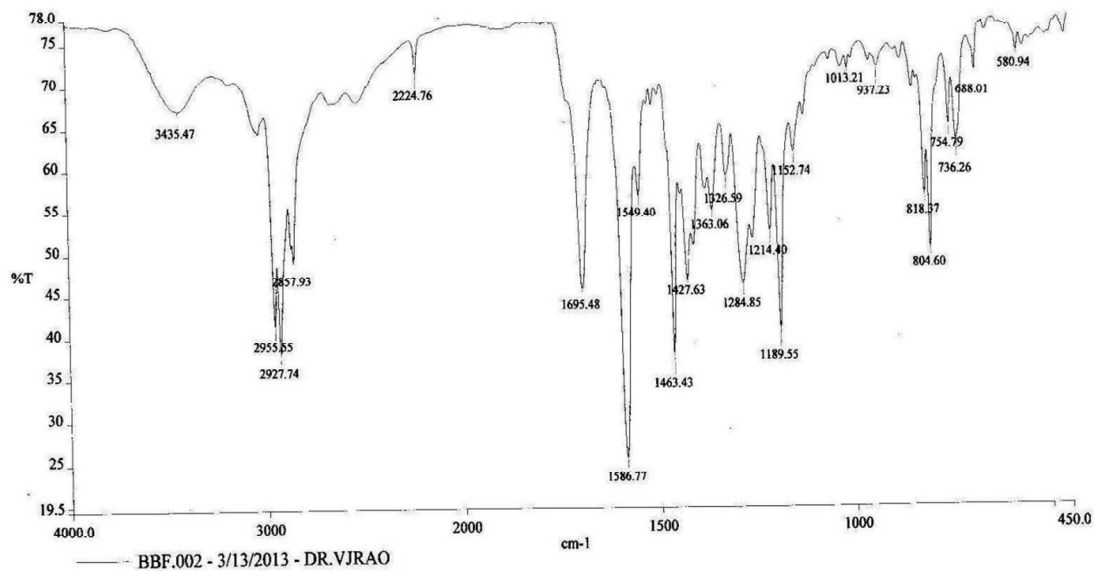
ESI-HRMS of molecule BFB

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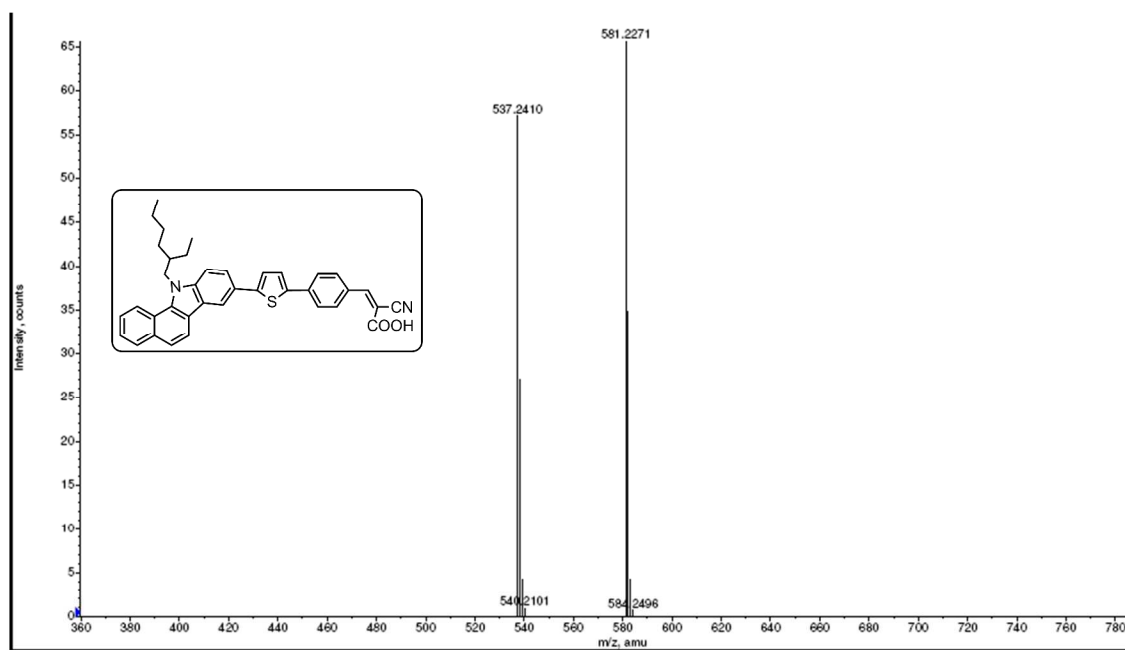
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IR Spectrum of molecule BFB



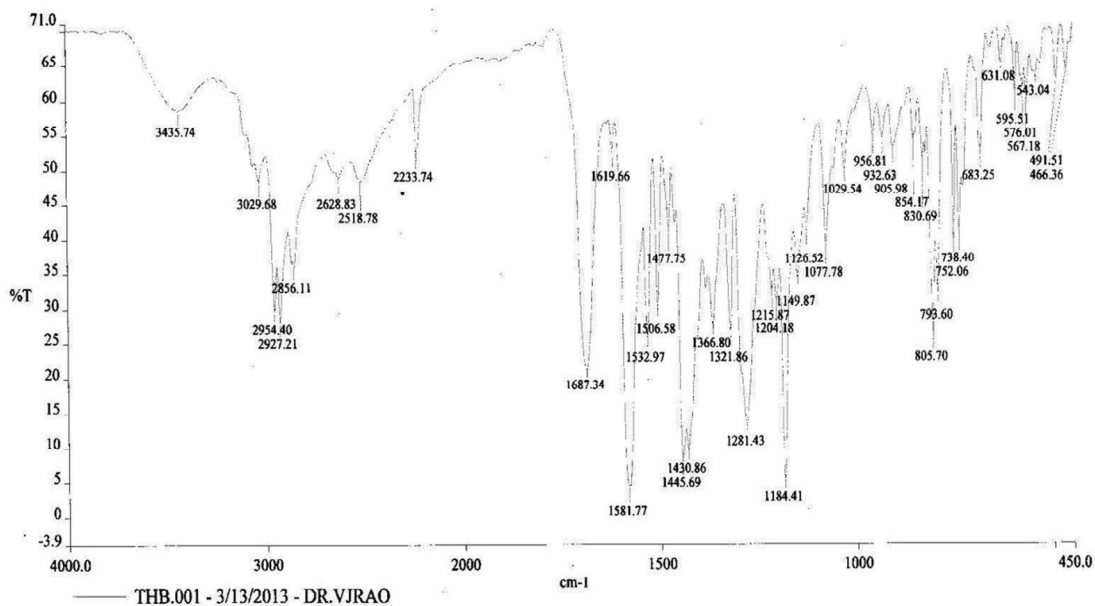
ESI-HRMS of molecule BTB

ORGANIC - II, IICT

Description: DR.VJRAO

Comments

Date: Thursday, March 14, 2013



IR Spectrum of molecule BTB