Electronic Supplementary Material (ESI) for RSC Advances.

Functional tuning of organic dyes containing 2,7-carbazole and other electron-rich segments in the conjugation pathway

A. Venkateswararao,[a] K. R. Justin Thomas,*[a] Chun-Ting Li[b] and Kuo-Chuan Ho[b]

[a] *Organic Materials Laboratory, Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee-247 667, India. E-mail: krjt8fcy@iitr.ernet.in. Phone: +91-1332-285376*

[b] *Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan*

Supporting Information

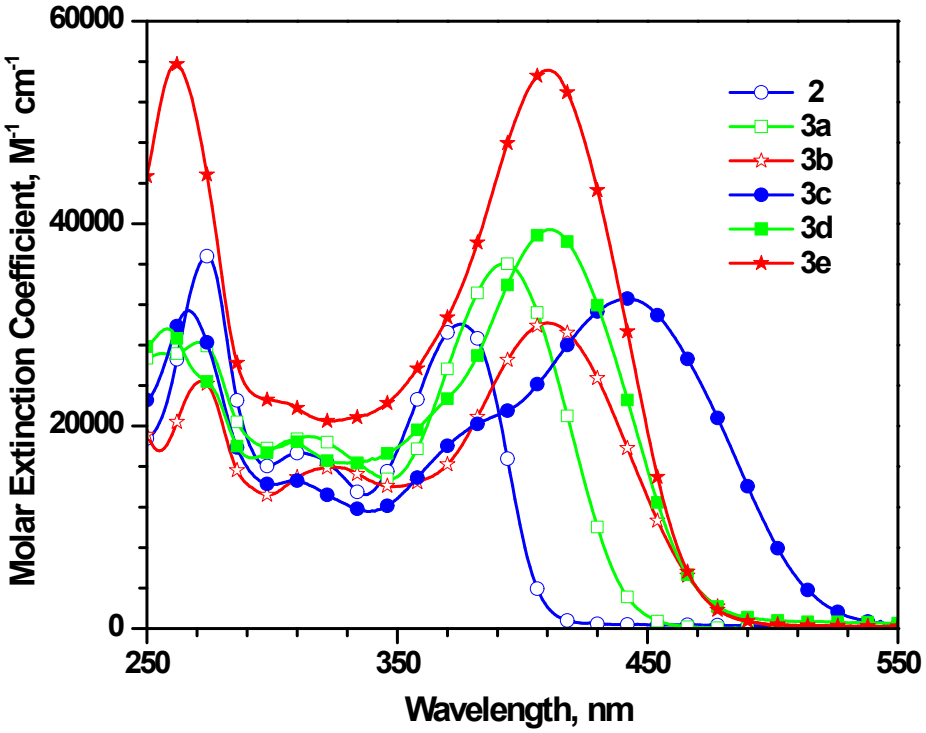

Fig. S1 Absorption spectra of precursor derivatives **2** and **3a-3e** recorded in dichloromethane solutions.

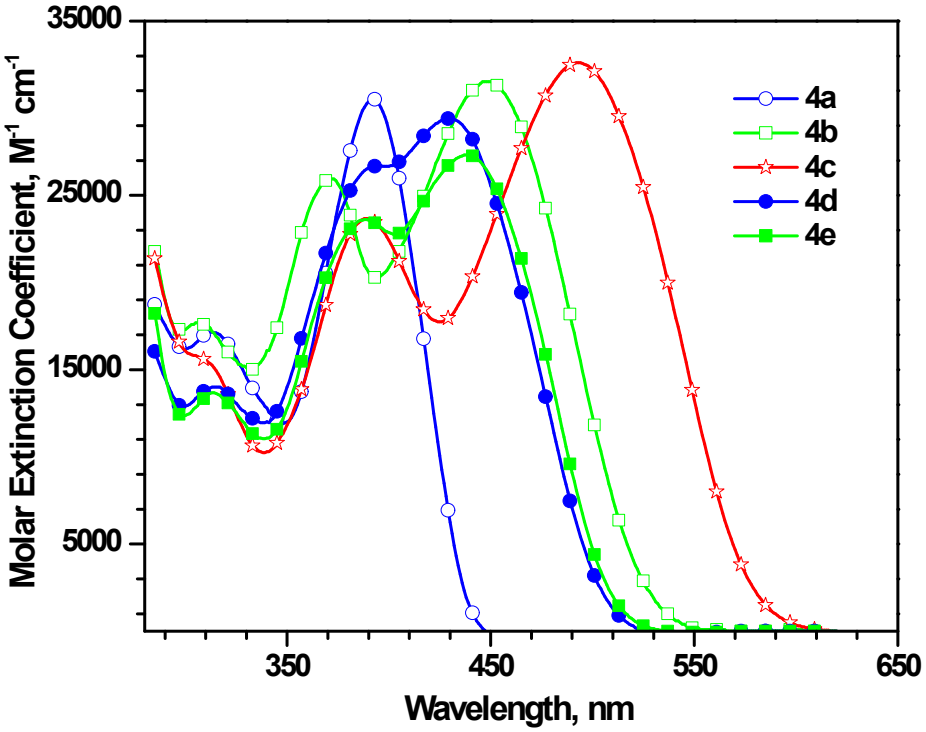

Fig. S2 Absorption spectra of the dyes (**4a-4e**) recorded in toluene solutions.

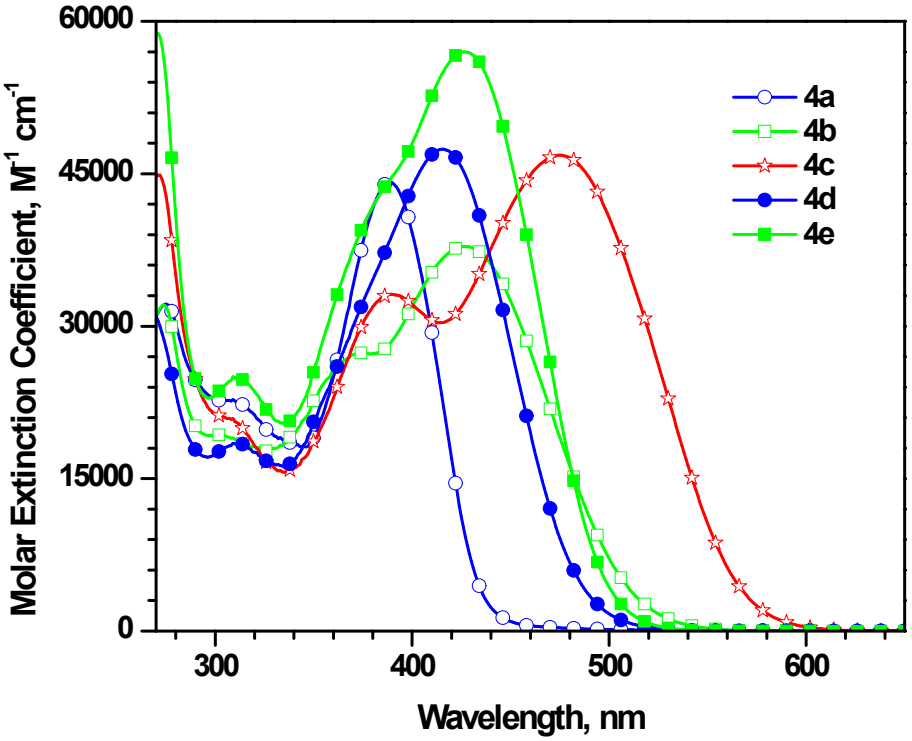

Fig. S3 Absorption spectra of the dyes (**4a**-**4e**) recorded in tetrahydrofuran solutions.

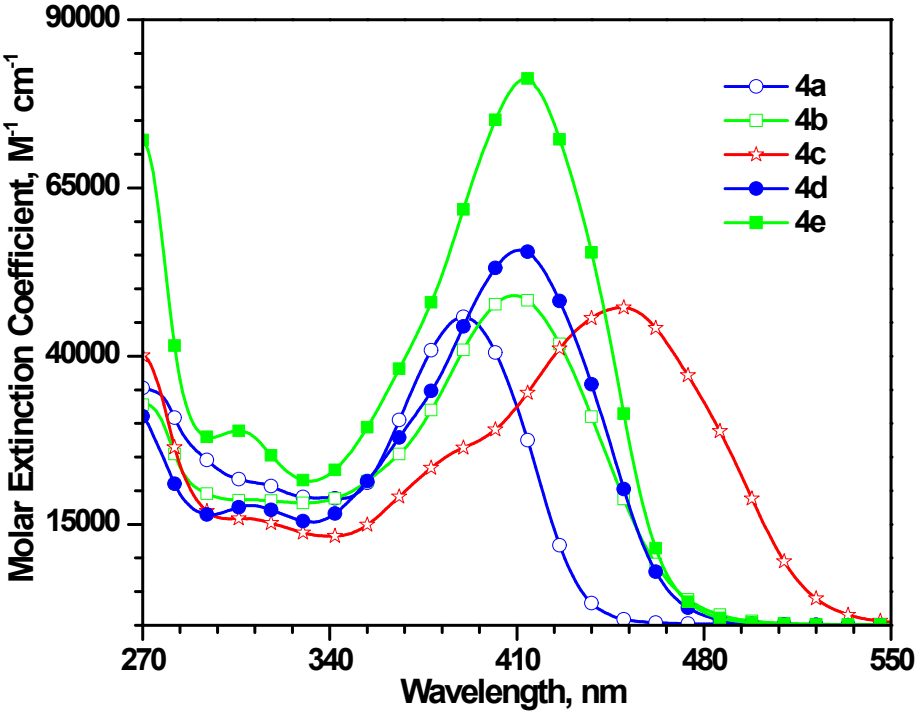

Fig. S4 Absorption spectra of the dyes (**4a**-**4e**) recorded in *N,N*-dimethyl formamide solutions.

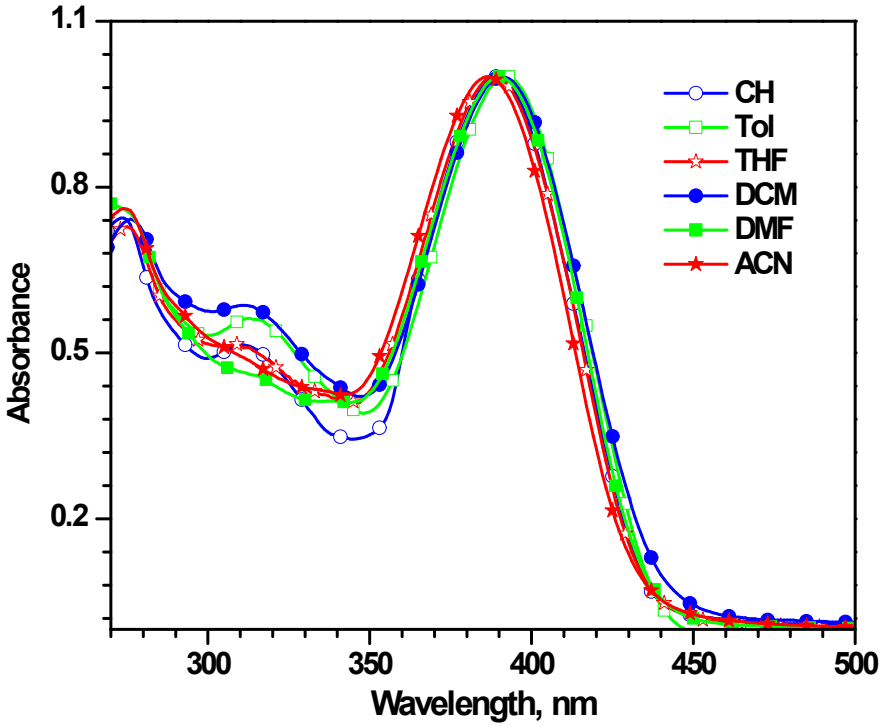

Fig. S5 Absorption spectra of the dye **4a** recorded in different solvents.

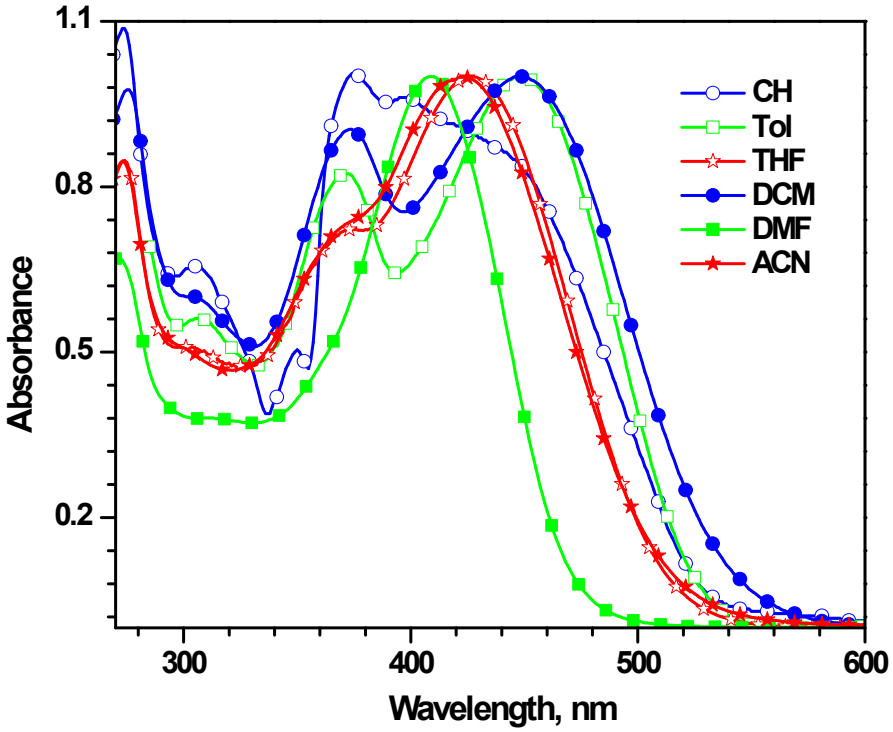

Fig. S6 Absorption spectra of the dye **4b** recorded in different solvents.

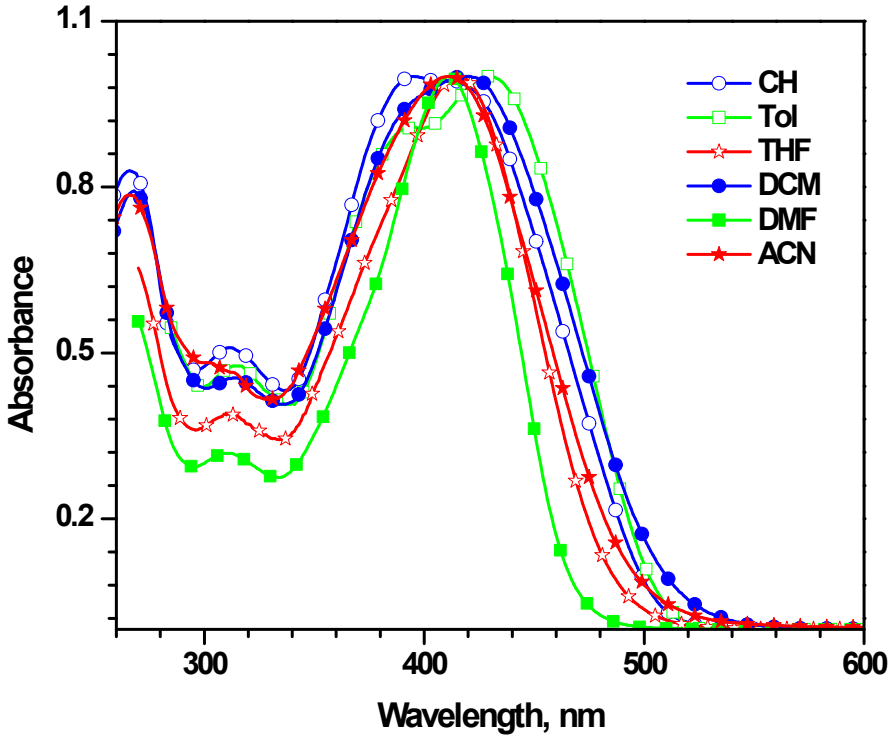

Fig. S7 Absorption spectra of the dye **4d** recorded in different solvents.

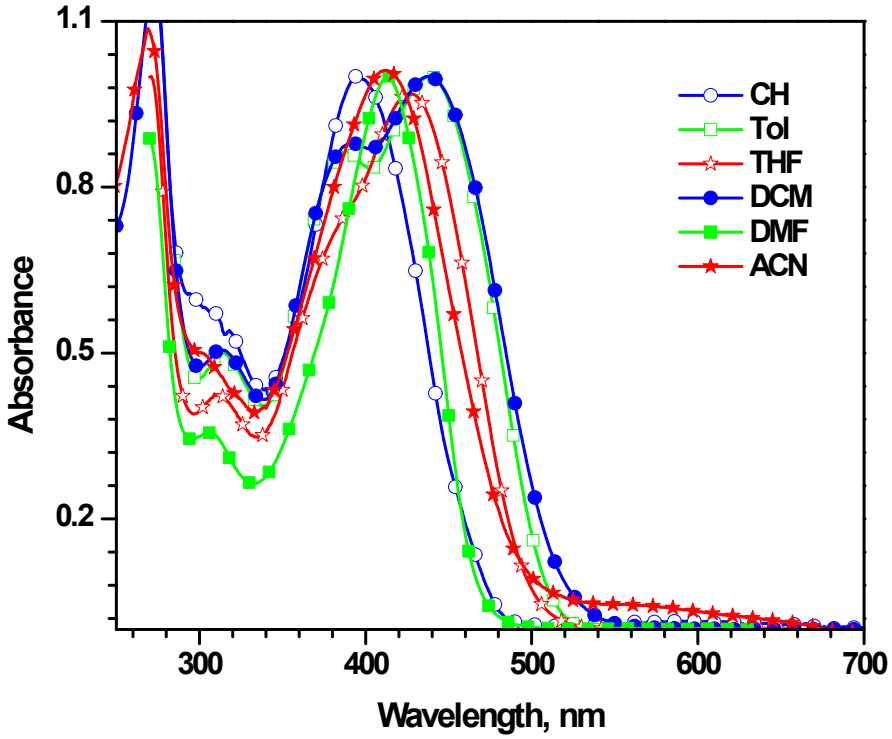

Fig. S8 Absorption spectra of the dye **4e** recorded in different solvents.

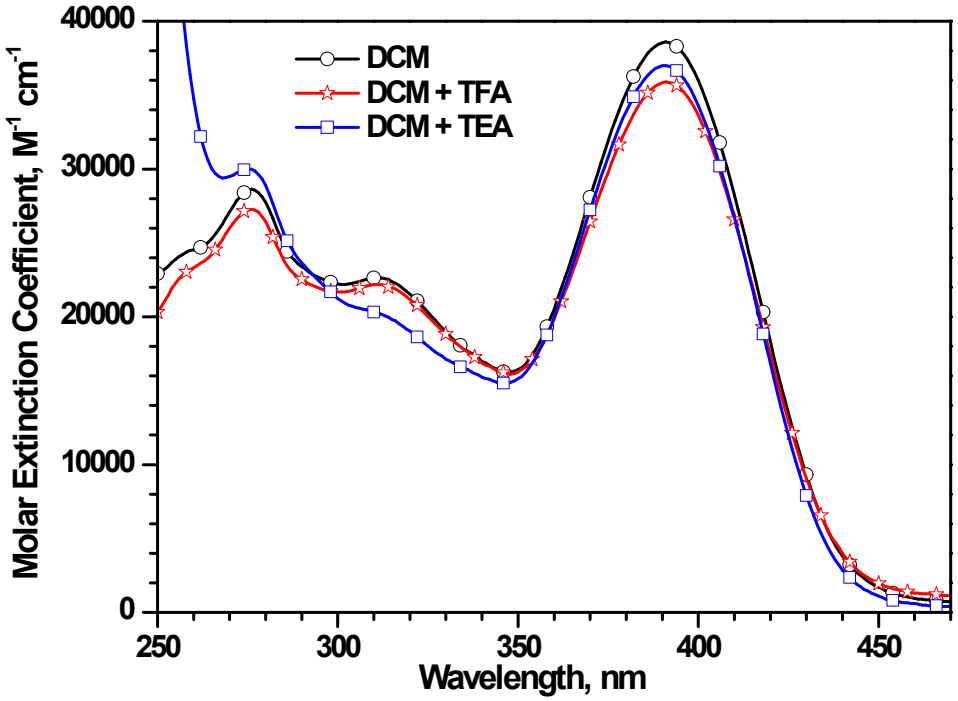

Fig. S9 Absorption spectra of the dye **4a** recorded in dichloromethane, after the addition of TFA and TEA.

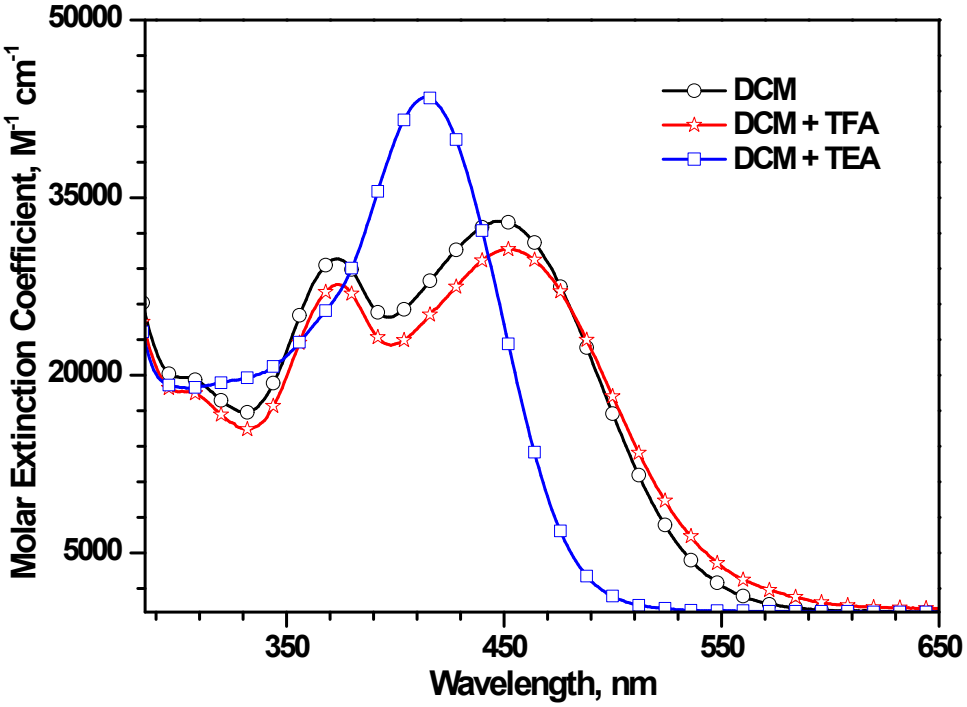

Fig. S10 Absorption spectra of the dye **4b** recorded in dichloromethane, after the addition of TFA and TEA.

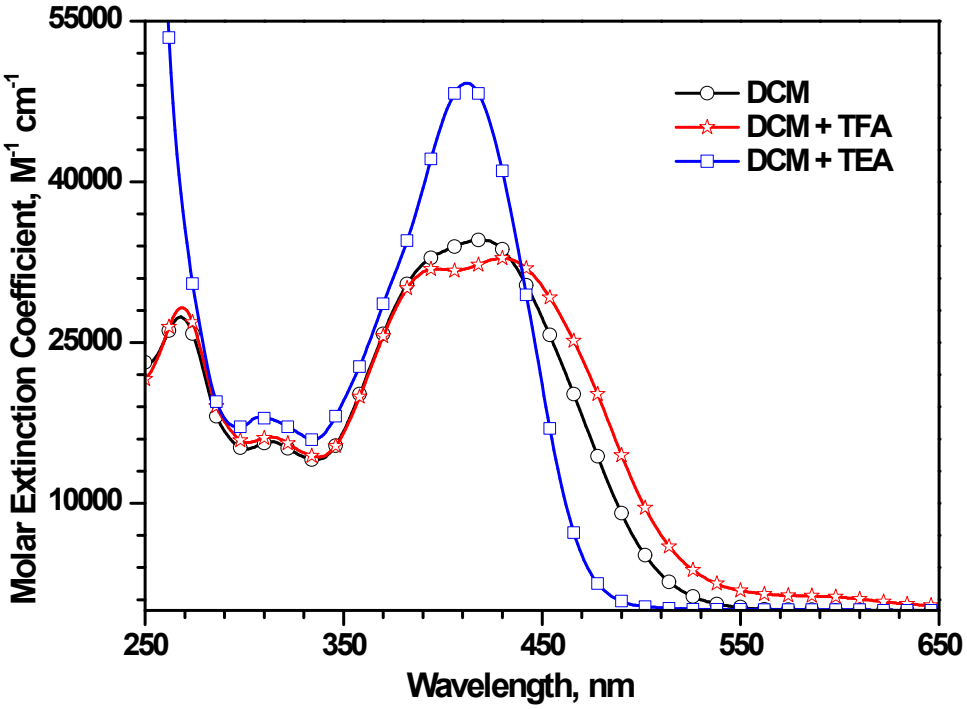

Fig. S11 Absorption spectra of the dye **4d** recorded in dichloromethane, after the addition of TFA and TEA.

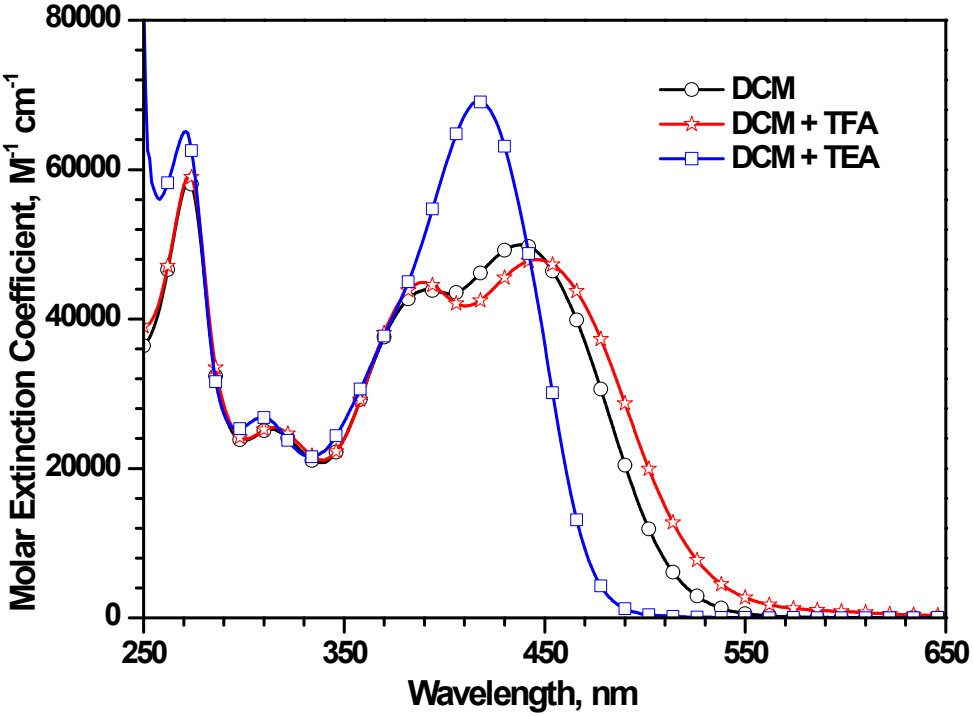

Fig. S12 Absorption spectra of the dye **4e** recorded in dichloromethane, after the addition of TFA and TEA.

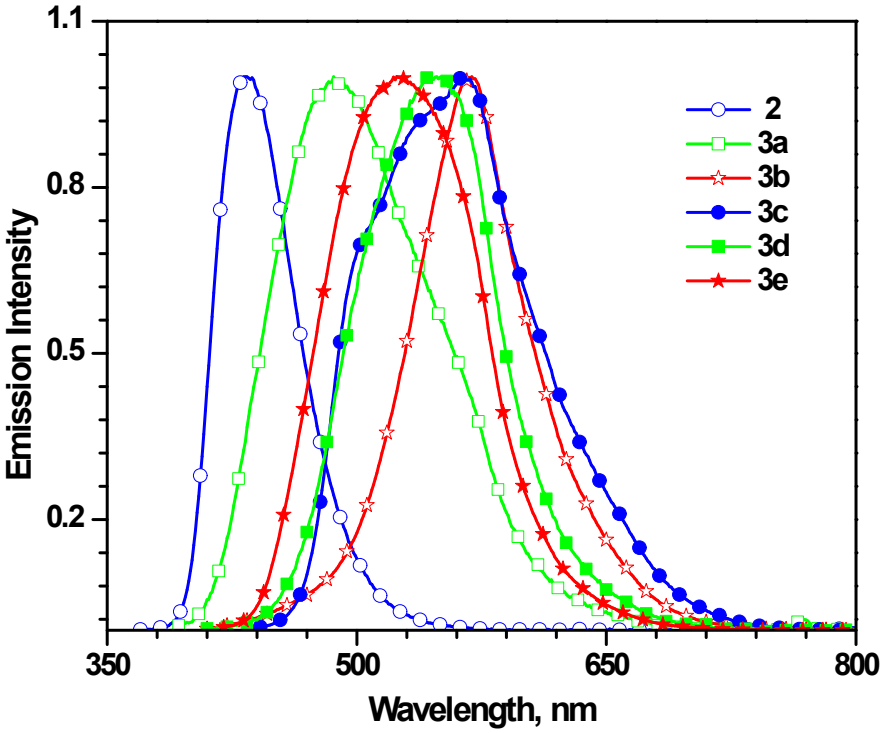

Fig. S13 Emission spectra of the carbazole precursor and aldehyde derivatives (**2** and **3a-3e**) recorded in dichloromethane solutions.

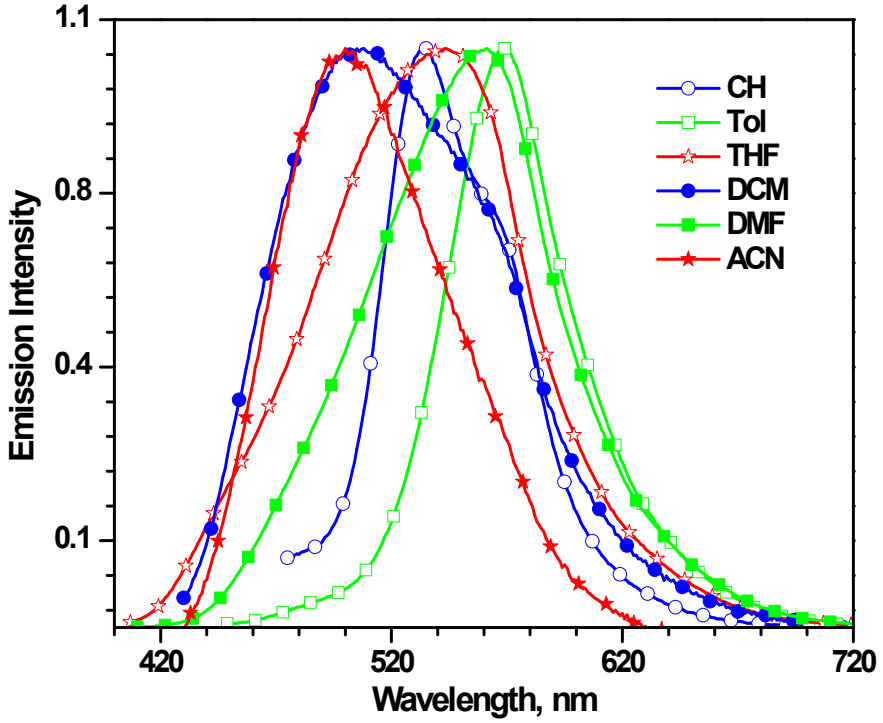

Fig. S14 Emission spectra of the dye (**4b**) recorded in different solvents.

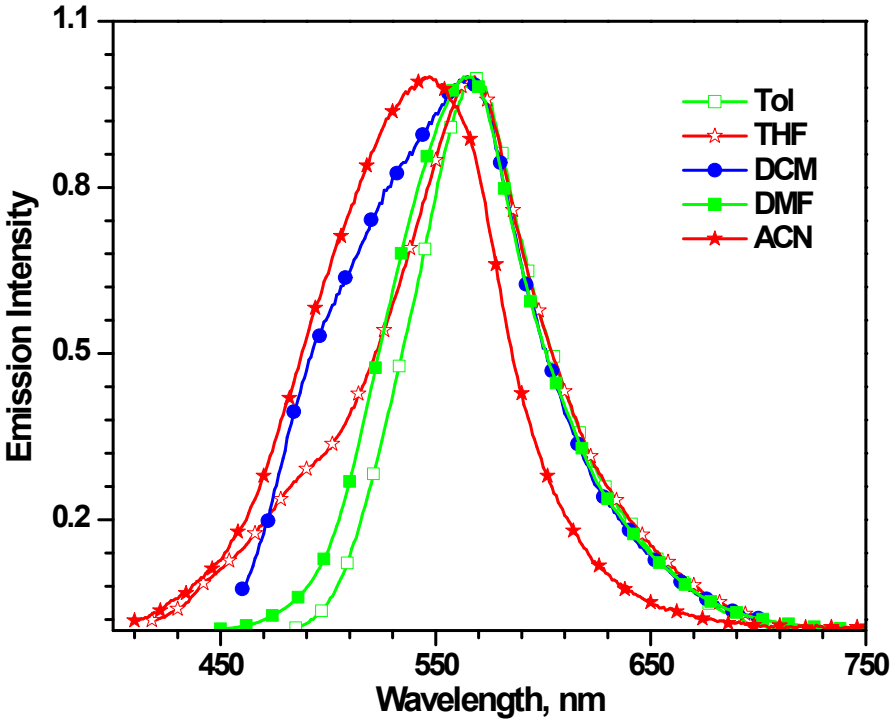

Fig. S15 Emission spectra of the dye (**4c**) recorded in different solvents.

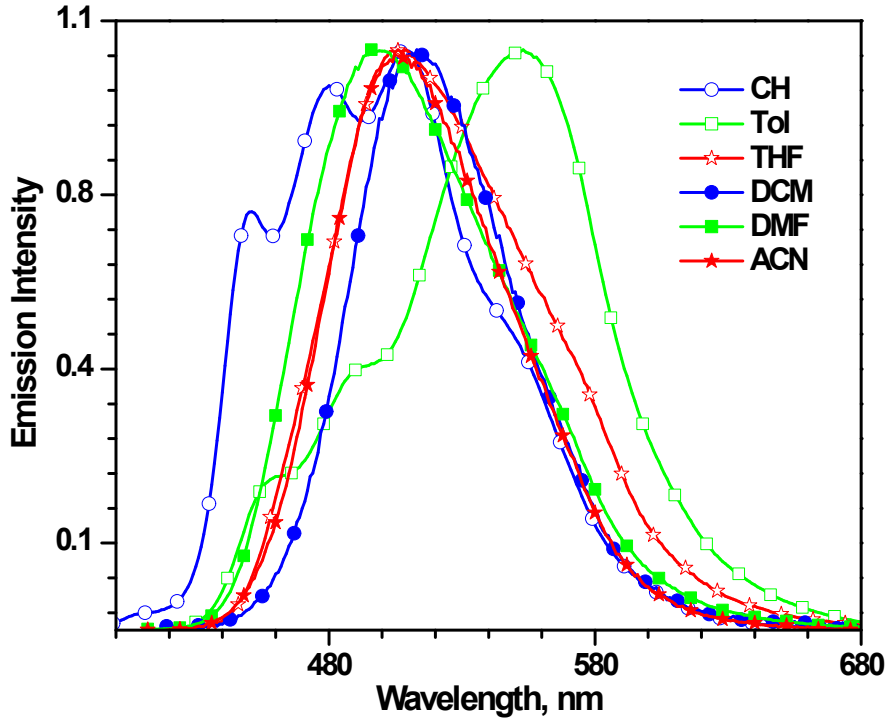

Fig. S16 Emission spectra of the dye (**4d**) recorded in different solvents.

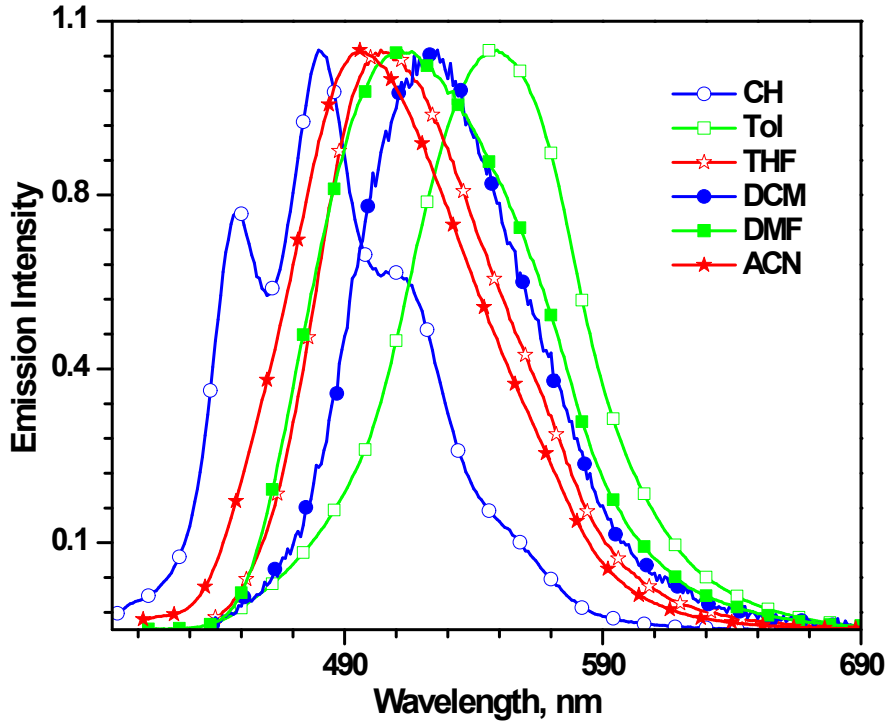

Fig. S17 Emission spectra of the dyes (**4e**) recorded in different solvents.

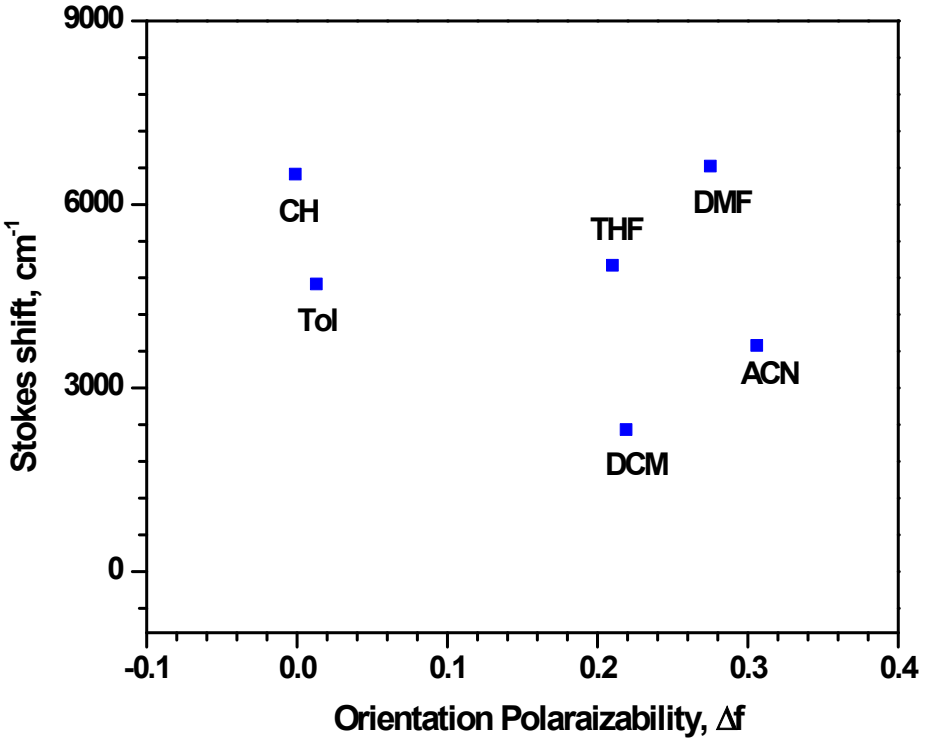

Fig. S18 Lippert-Mataga plot of the dye **4b**.

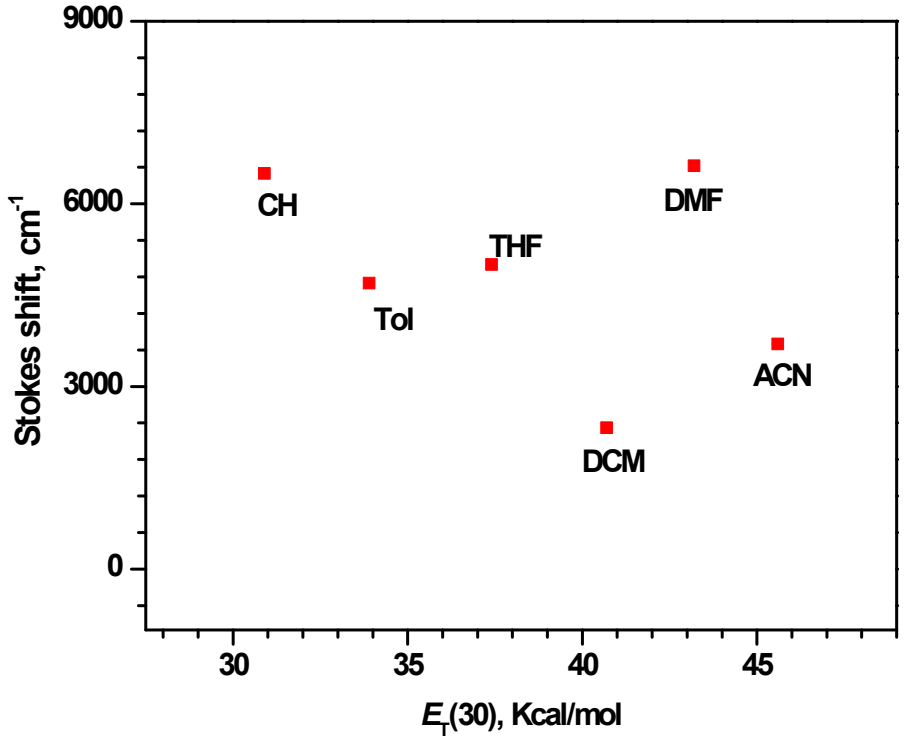

Fig. S19 $E_T(30)$ plot of the dye **4b**.

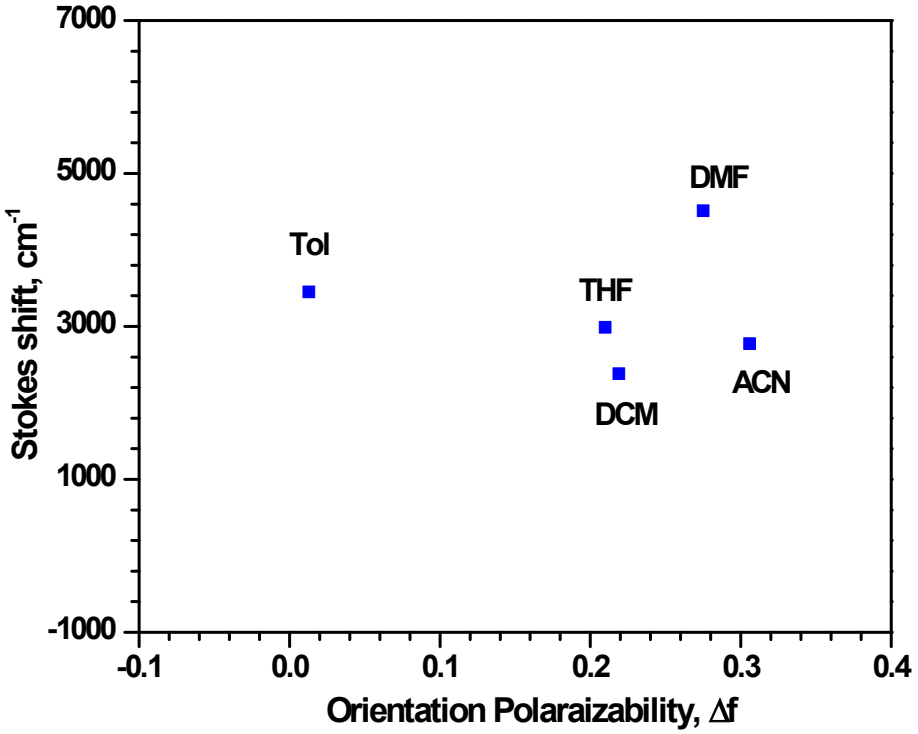

Fig. S20 Lippert-Mataga plot of the dye **4c**.

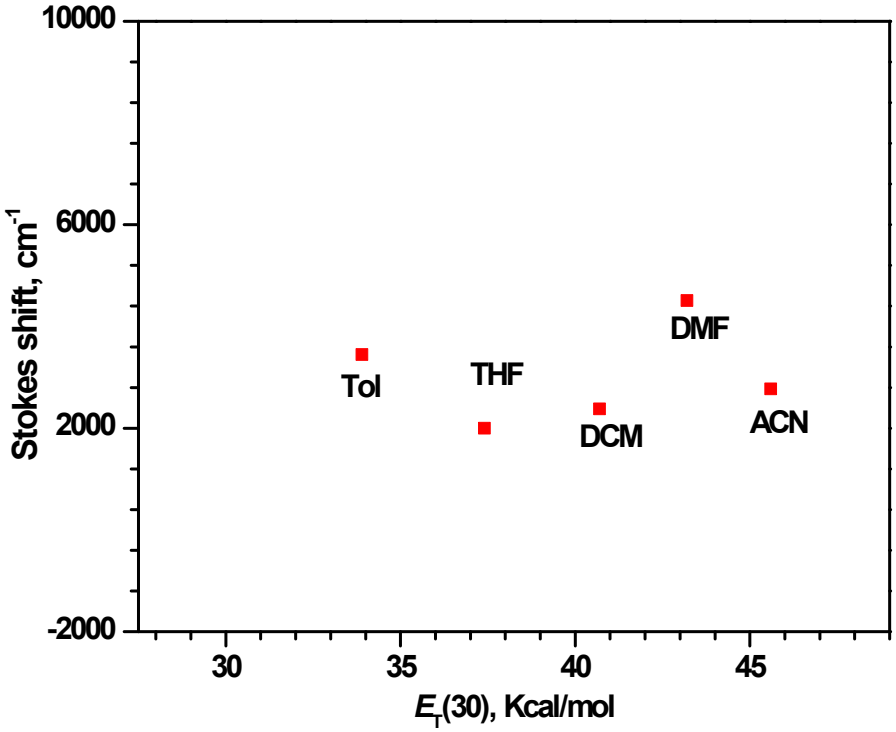

Fig. S21 $E_T(30)$ plot of the dye **4c**.

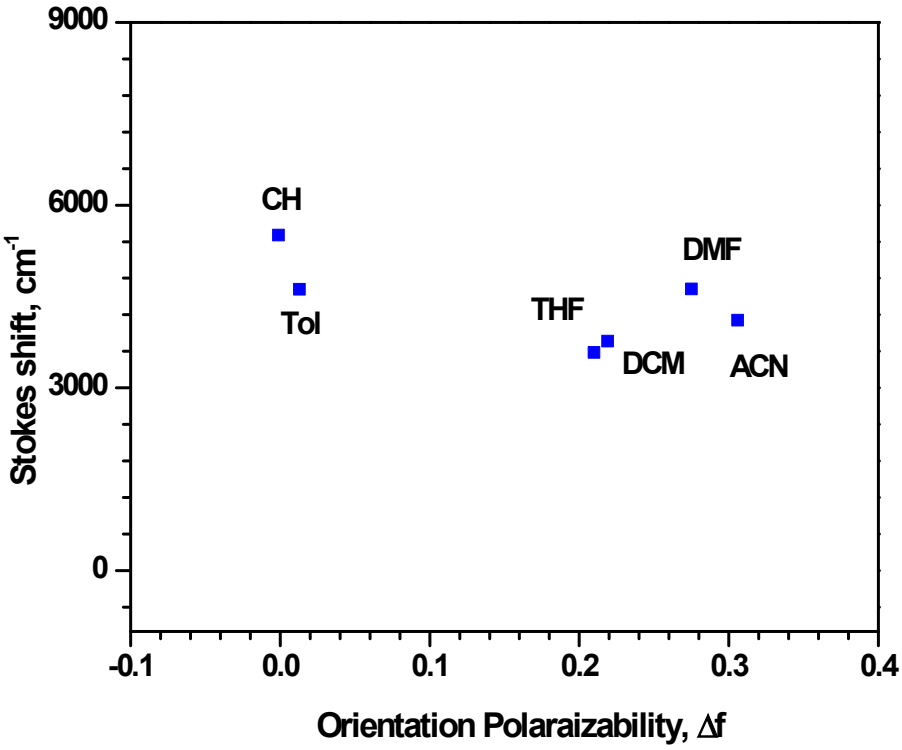

Fig. S22 Lippert-Mataga plot of the dye **4e**.

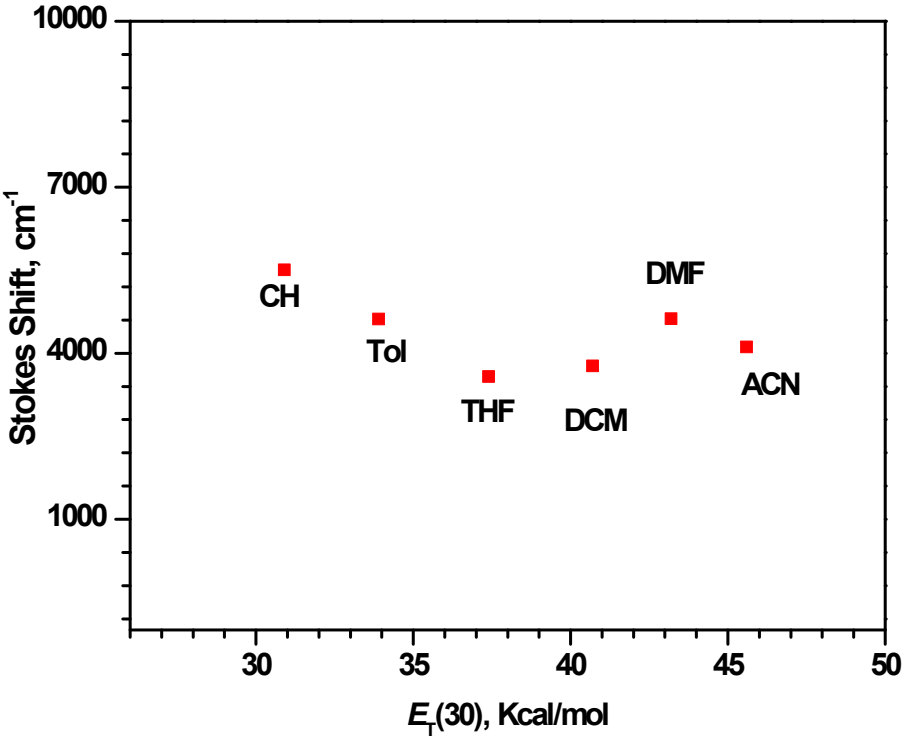

Fig. S23 $E_T(30)$ plot of the dye **4e**.

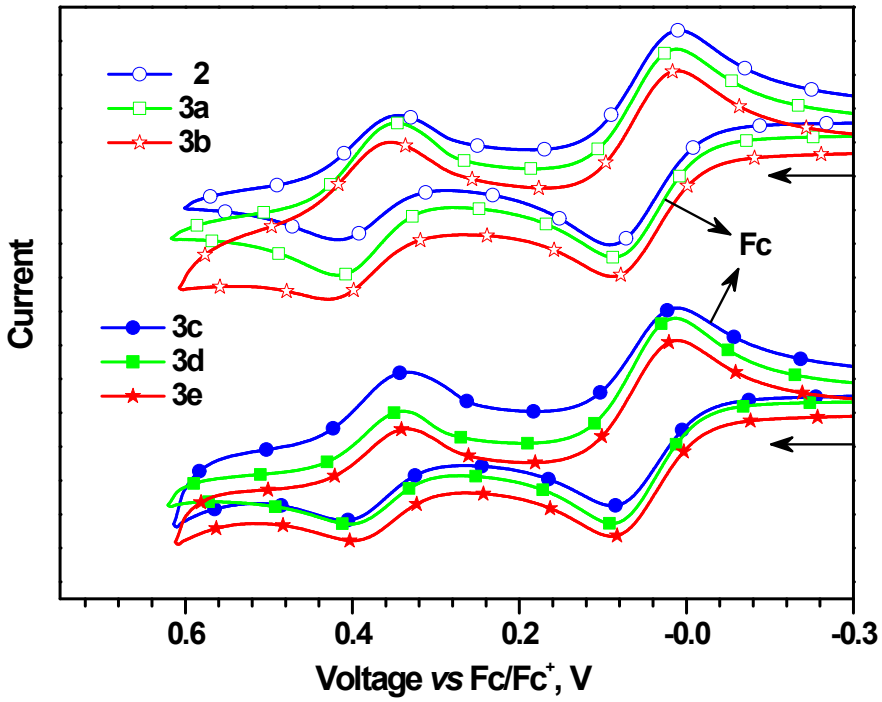

Fig. S24 Cyclic voltammograms of the carbazole aldehyde derivatives (**2** and **3a-3e**) recorded in dichloromethane solutions.

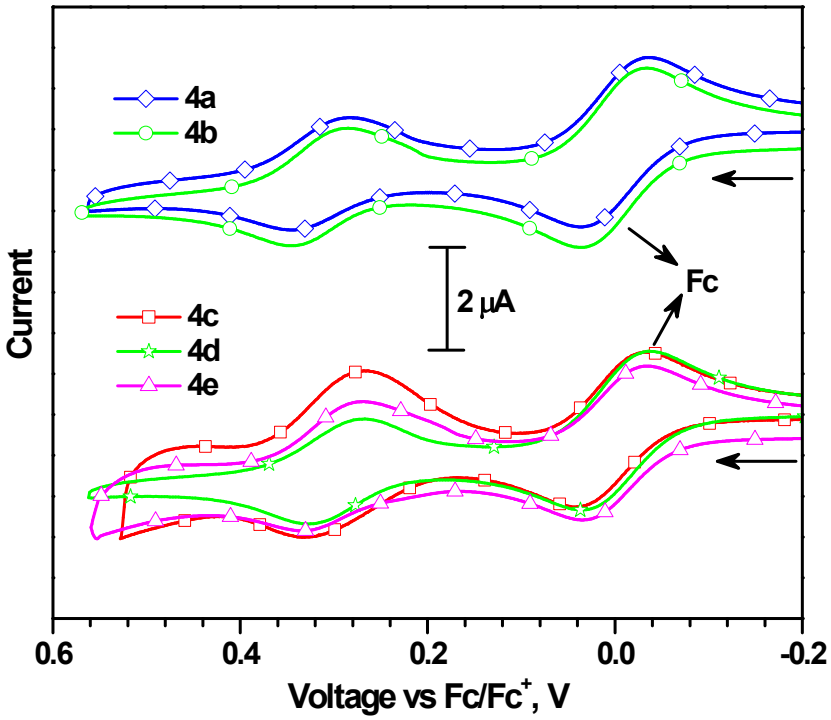

Fig. S25 Cyclic voltammograms of the dyes (**4a-4e**) recorded in dichloromethane solutions.

Table S1 Absorption properties of the dyes recorded in different solvents

Dye	$\lambda_{abs,}$ nm ($\varepsilon_{max} \times 10^3$ M^{-1} cm^{-1})							
	TiO_2 film	CH	Tol	THF	DCM + TFA	DCM + TEA	DMF	ACN
4a	na	390, 311, 274	393 (30.5), 313 (17.1)	389 (44.2), 309 (22.8), 275 (32.2)	391 (35.9), 313 (22.1), 276 (27.2)	391 (37.0), 276 (30.0)	390 (45.8)	387, 274
4b	483	397, 375, 350, 305	448 (31.5), 372 (26.0), 307 (17.8)	427 (37.8), 368 (27.0)	452 (30.6), 374 (27.7), 276 (30.1)	414 (43.5), 275 (31.1)	409 (49.0)	422, 368, 273
4c	525	ns	493 (32.6), 389 (23.7), 312 (15.3)	475 (46.8), 389 (33.1), 309 (20.9)	505 (31.1), 391 (25.1)	456 (35.8), 387 (21.1), 271 (30.9)	449 (47.2), 386 (25.6), 310 (15.9)	475, 389, 270
4d	464	397, 351, 304, 267	430 (29.4), 396 (26.7), 315 (14.0)	416 (47.4), 312 (18.5)	430 (32.9), 397 (31.9), 313 (16,2)	412 (49.2), 307 (18.0)	412 (55.7), 311 (17.7)	411, 303, 266
4e	470	416, 402, 348, 305	438 (27.3), 388 (23.6), 314 (13.7)	427 (57.0), 312 (25.0)	446 (47.9), 389 (44.9), 316 (25.5), 273 (59.3)	417 (69.0), 309 (26.8), 271 (65.1)	414 (81.2), 305 (28.9)	412, 303, 269

na = not soluble

Table S2 Emission properties of the dyes recorded in different solvents

Dye	λ_{em}, nm					Stoke shift, cm^{-1}				
	CH	Tol	THF	DMF	ACN	CH	Tol	THF	DMF	ACN
4a	462, 438	448	469	485	491	2810	3123	4385	5022	5473
4b	535	569	543	561	500	6497	4697	5003	6625	3697
4c	na	594	568	563	547	na	3449	2986	4510	2771
4d	508, 480	553	509	496	506	5504	5172	4625	4111	4568
4e	509, 480	549	504	512	496	5229	4616	3578	4623	4111

na = not applicable

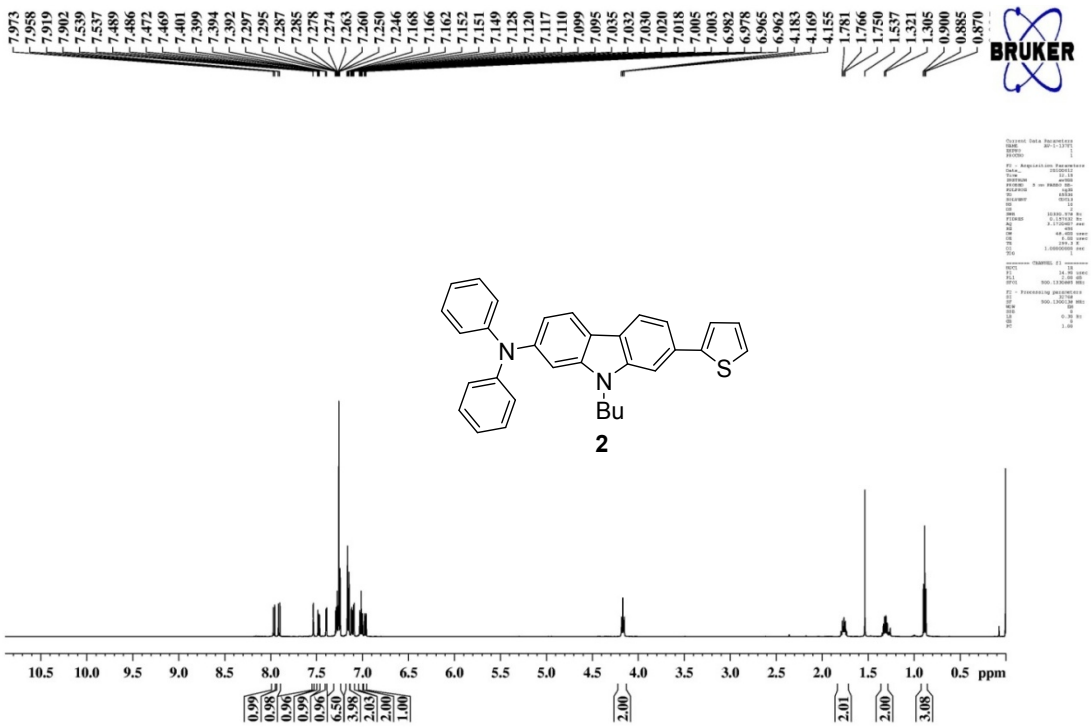

Fig. S26 ^{1}H NMR spectrum of **2** recorded in $CDCl_3$.

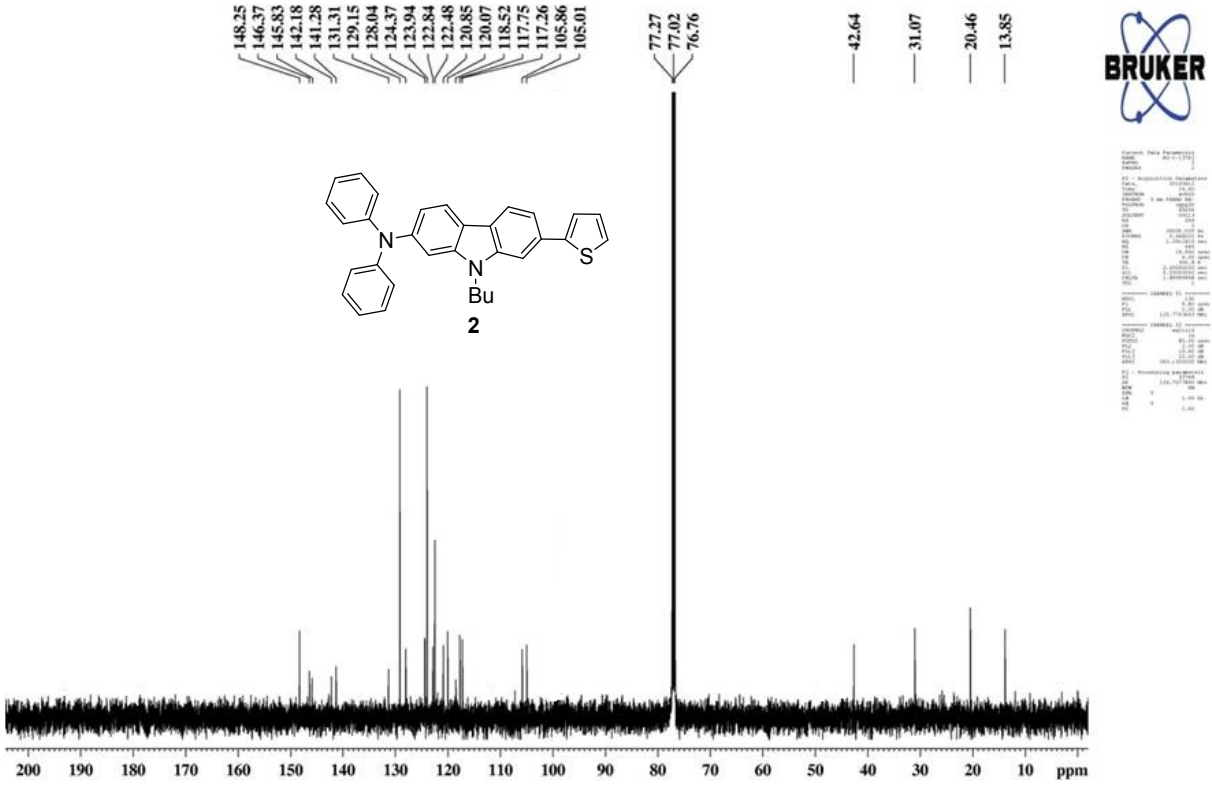

Fig. S27 ^{13}C NMR spectrum of **2** recorded in $CDCl_3$.

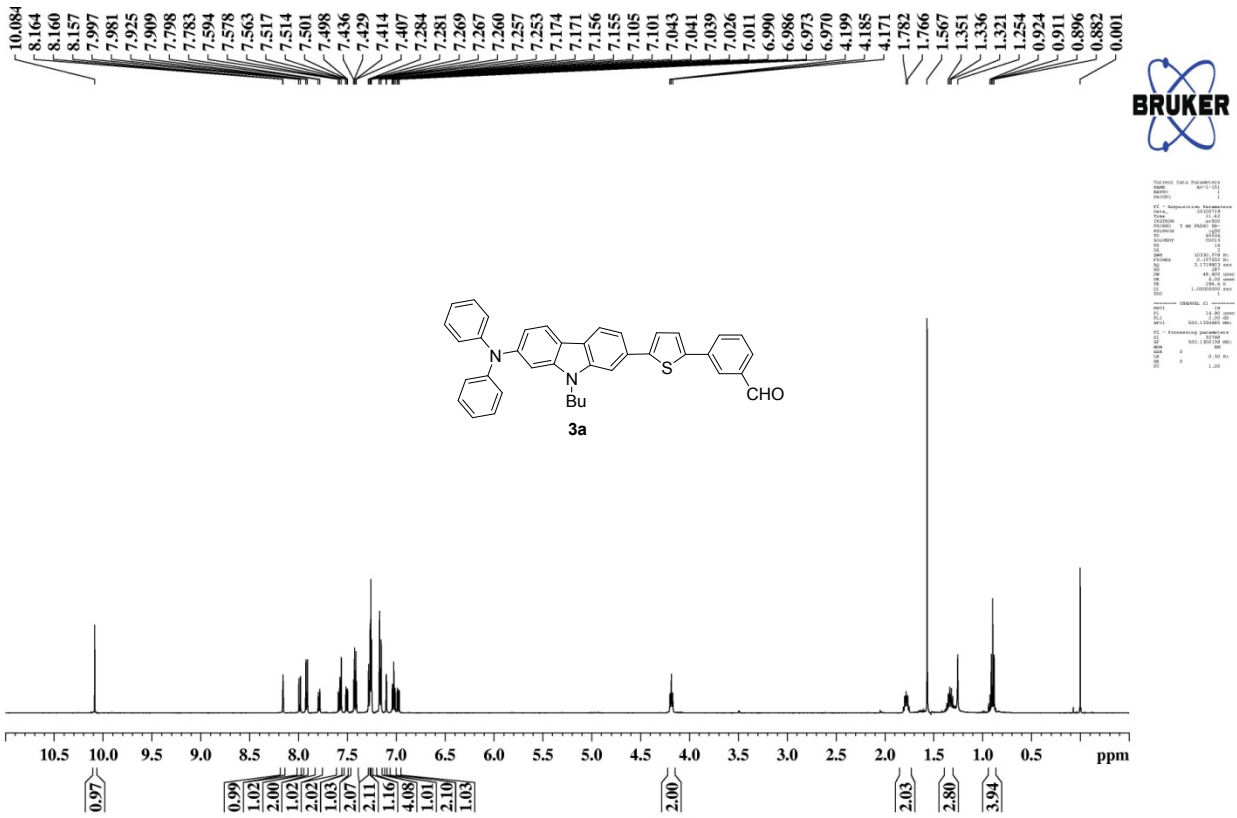

Fig. S28 ^{1}H NMR spectrum of **3a** recorded in $CDCl_3$.

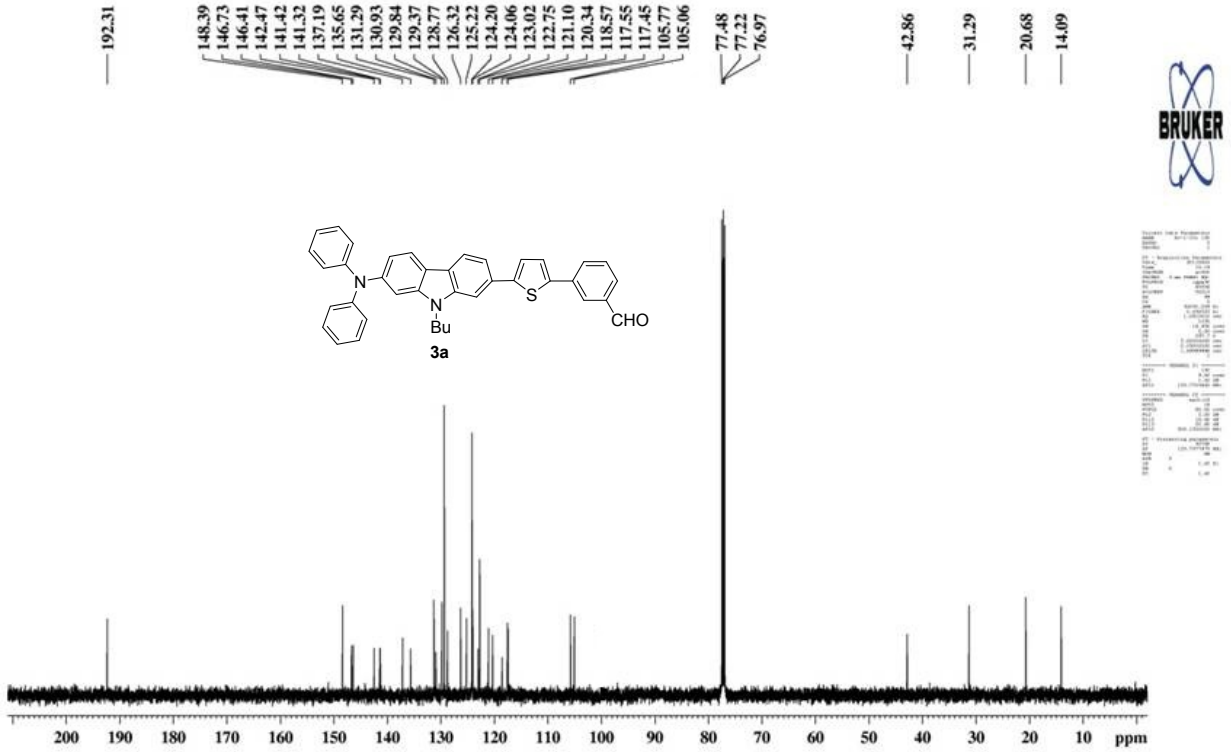

Fig. S29 ^{13}C NMR spectrum of **3a** recorded in $CDCl_3$.

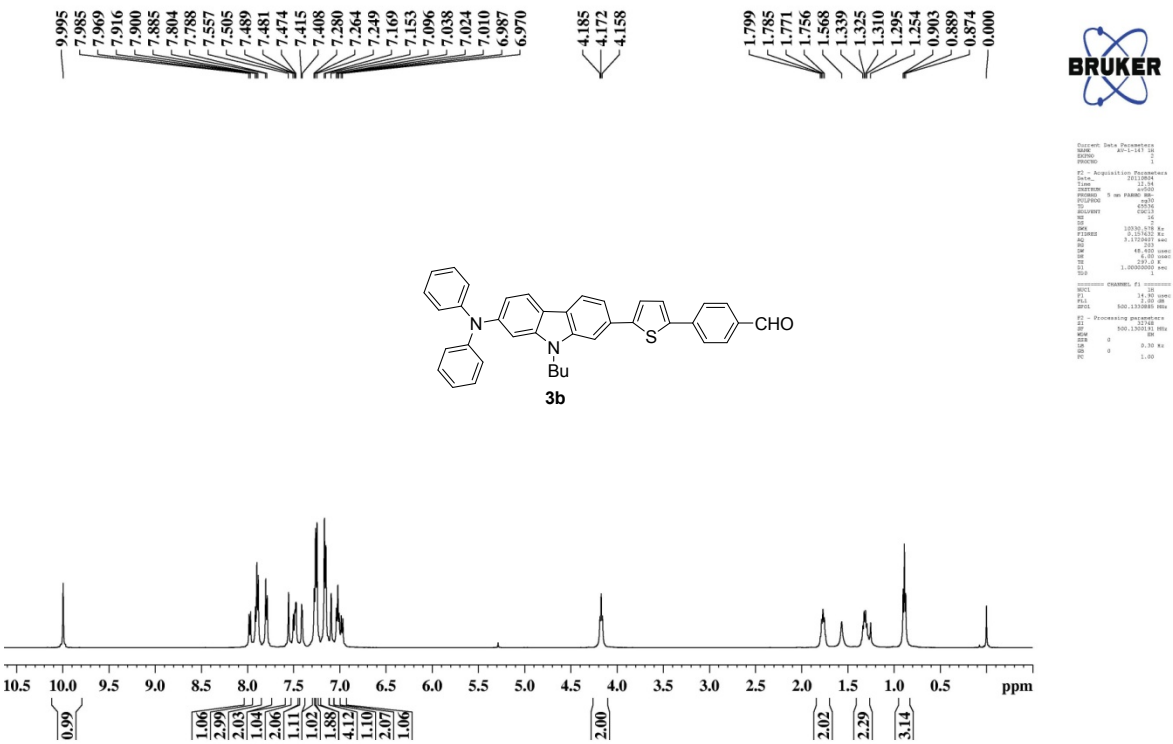

Fig. S30 ^{1}H NMR spectrum of **3b** recorded in $CDCl_3$.

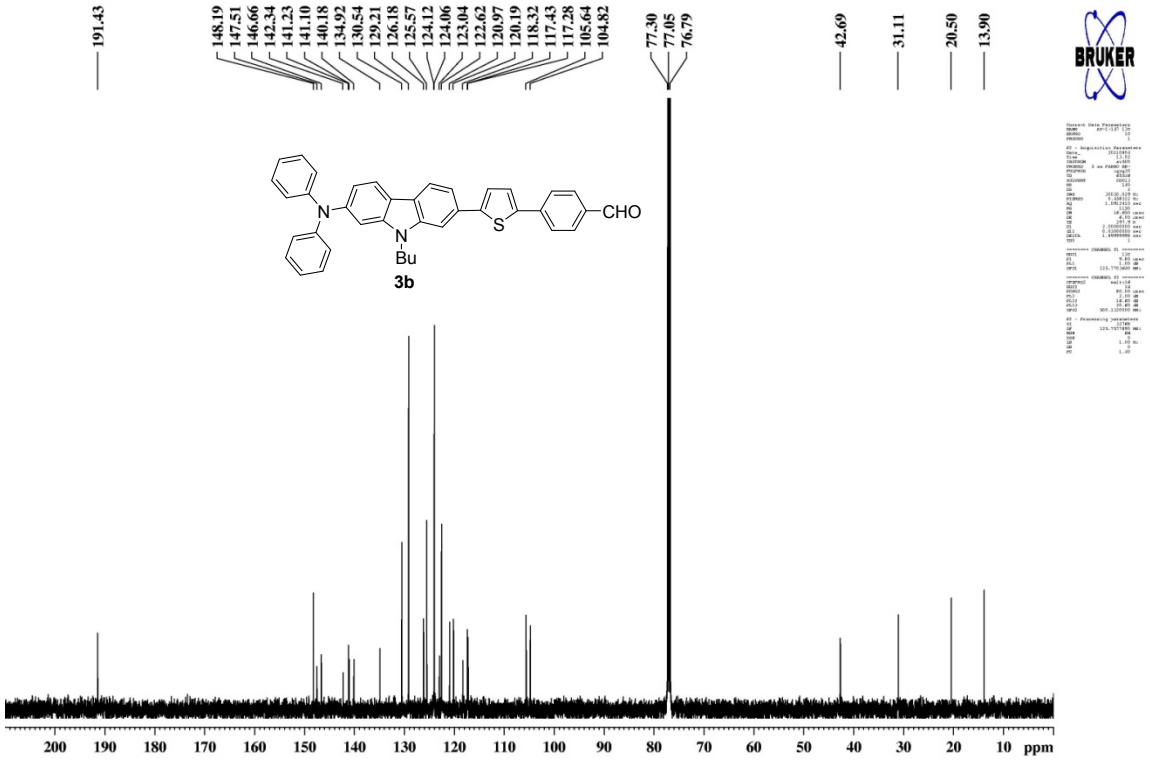

Fig. S31 ^{13}C NMR spectrum of **3b** recorded in $CDCl_3$.

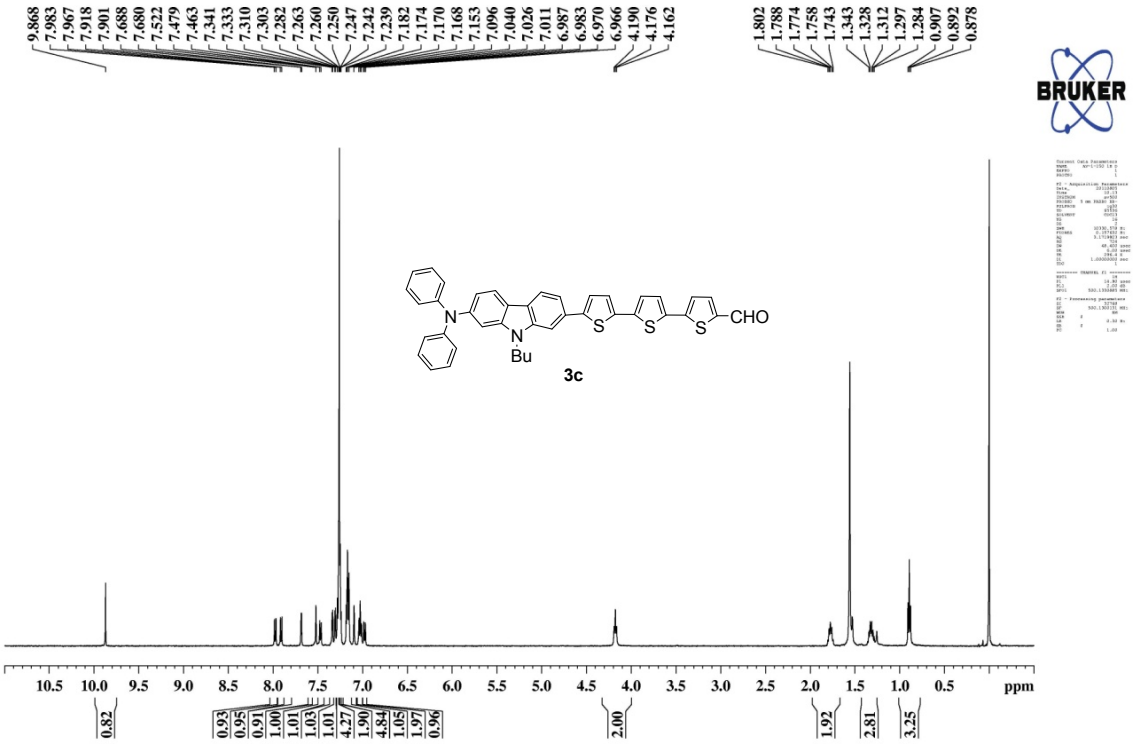

Fig. S32 ^{1}H NMR spectrum of **3c** recorded in $CDCl_3$.

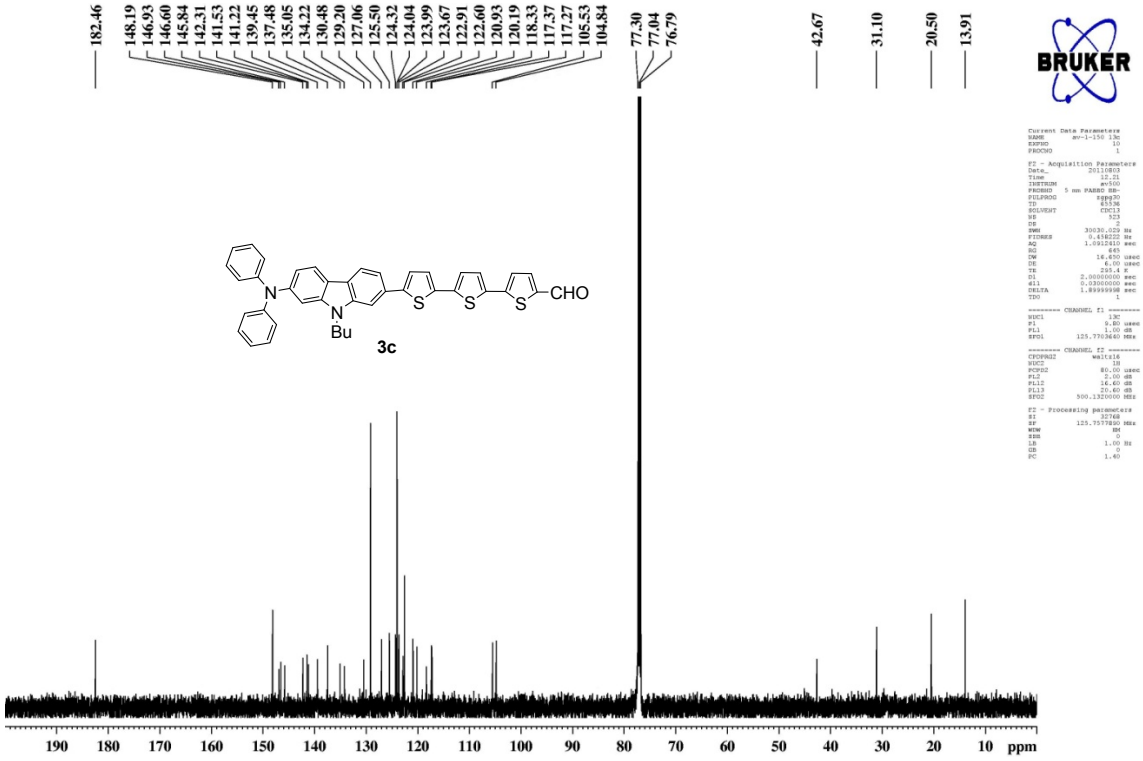

Fig. S33 ^{13}C NMR spectrum of **3c** recorded in $CDCl_3$.

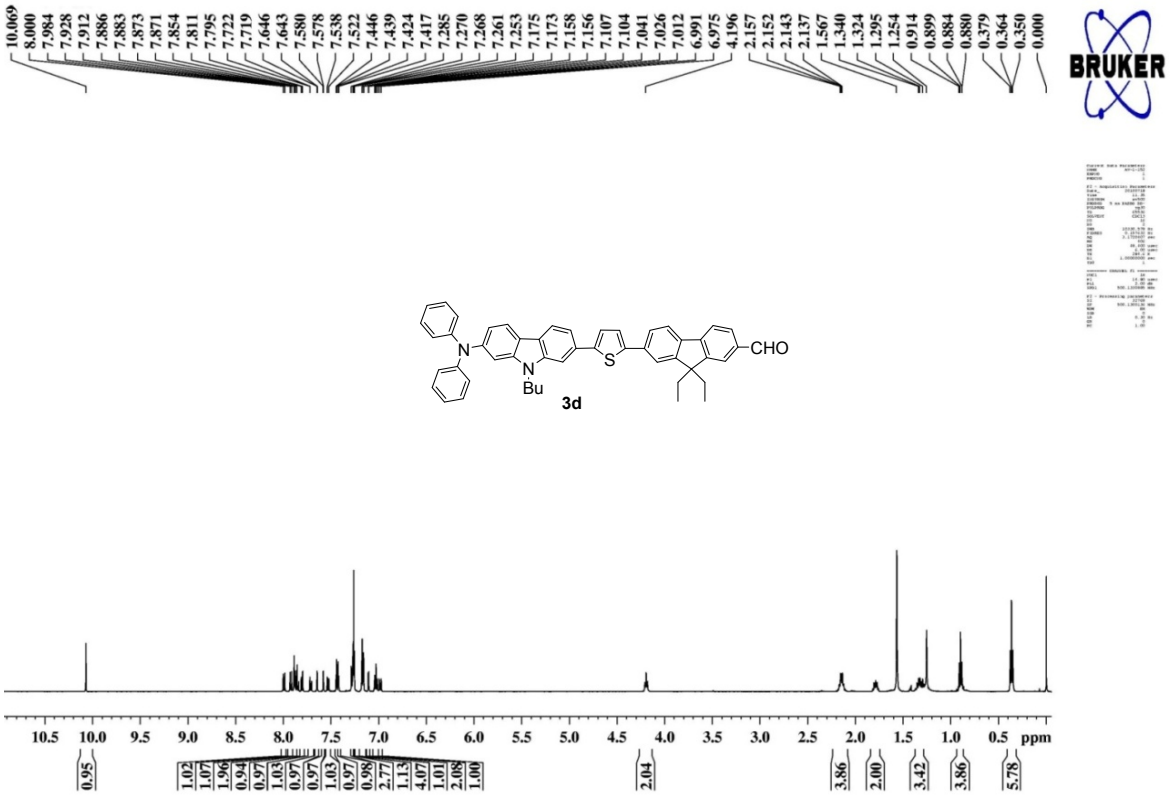

Fig. S34 ^{1}H NMR spectrum of **3d** recorded in $CDCl_3$.

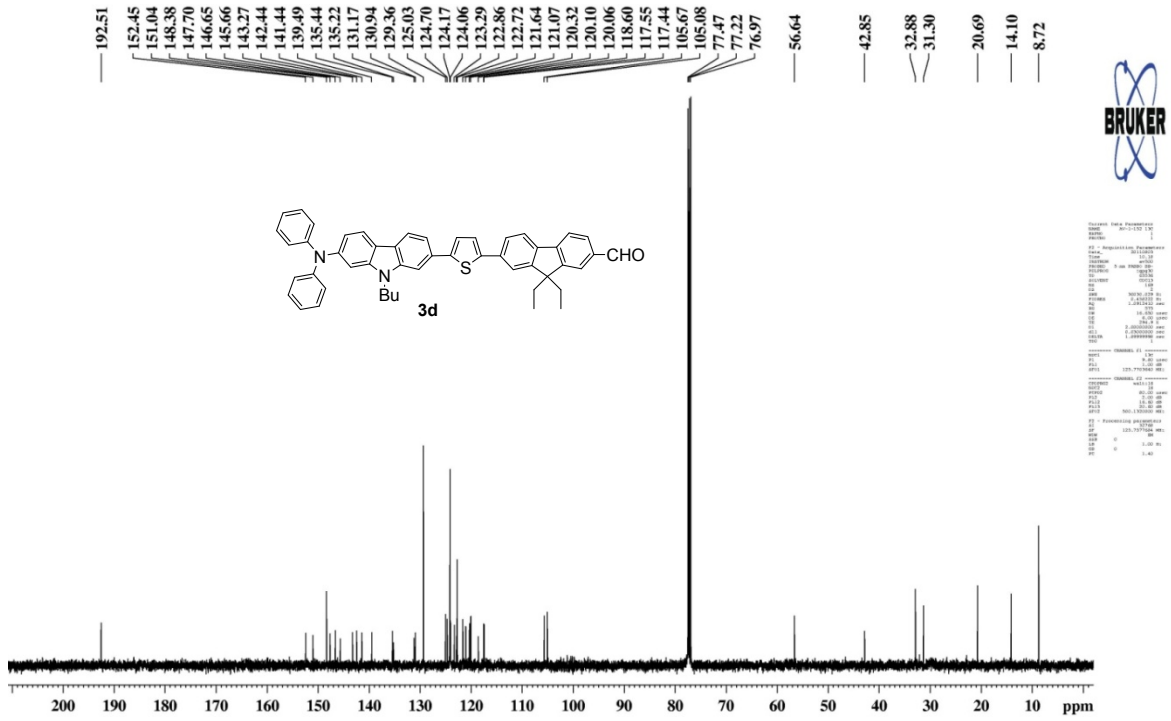

Fig. S35 ^{13}C NMR spectrum of **3d** recorded in $CDCl_3$.

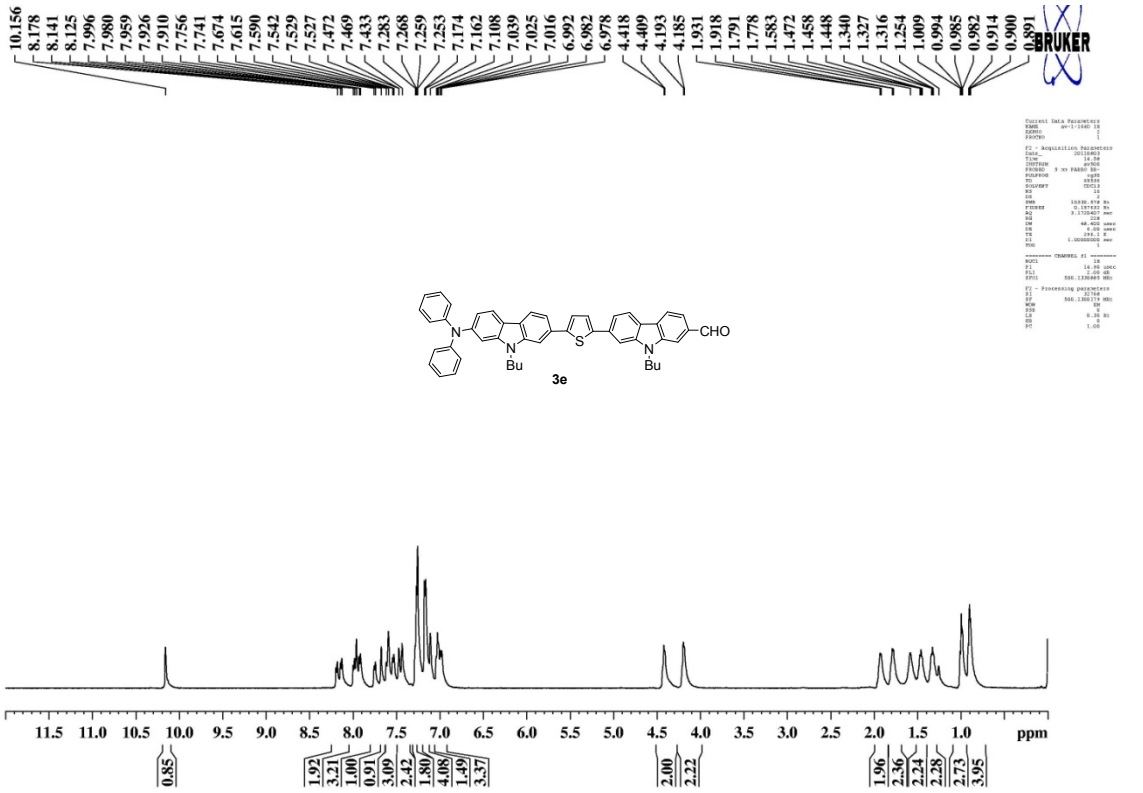

Fig. S36 ^{1}H NMR spectrum of **3e** recorded in $CDCl_3$.

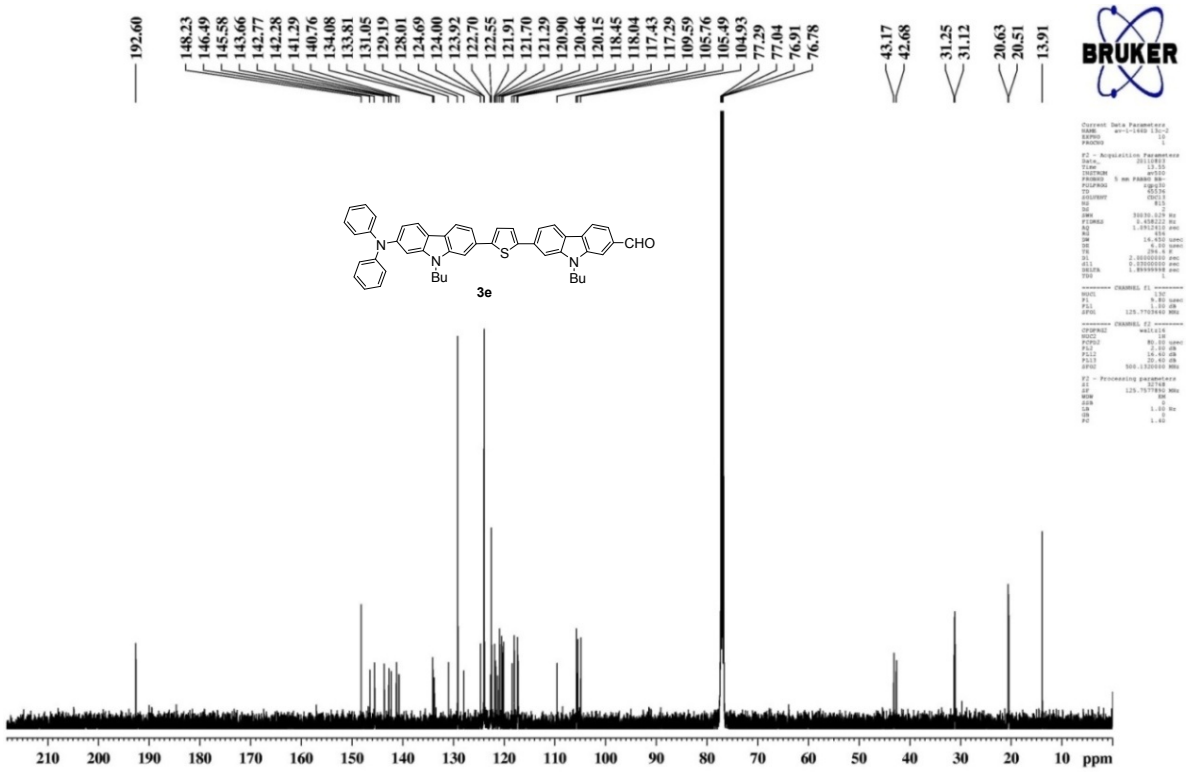

Fig. S37 ^{13}C NMR spectrum of **3e** recorded in $CDCl_3$.

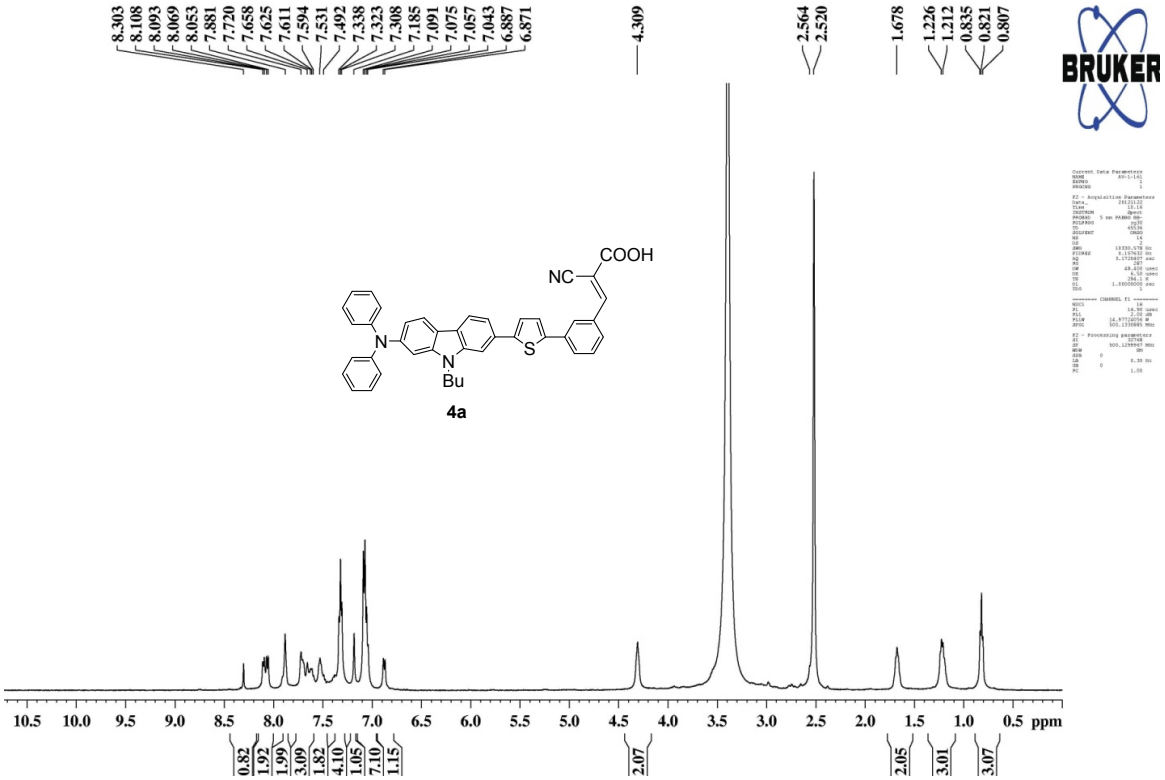

Fig. S38 ^{1}H NMR spectrum of **4a** recorded in DMSO-d_6.

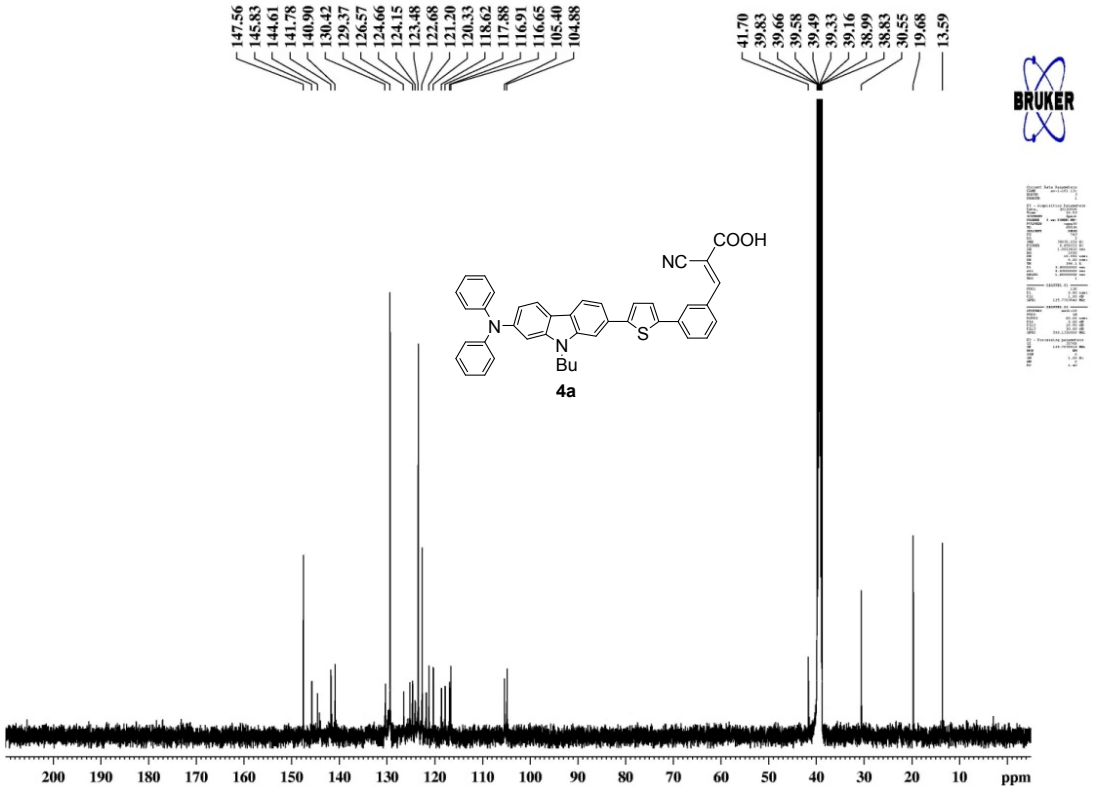

Fig. S39 ^{13}C NMR spectrum of **4a** recorded in DMSO-d_6.

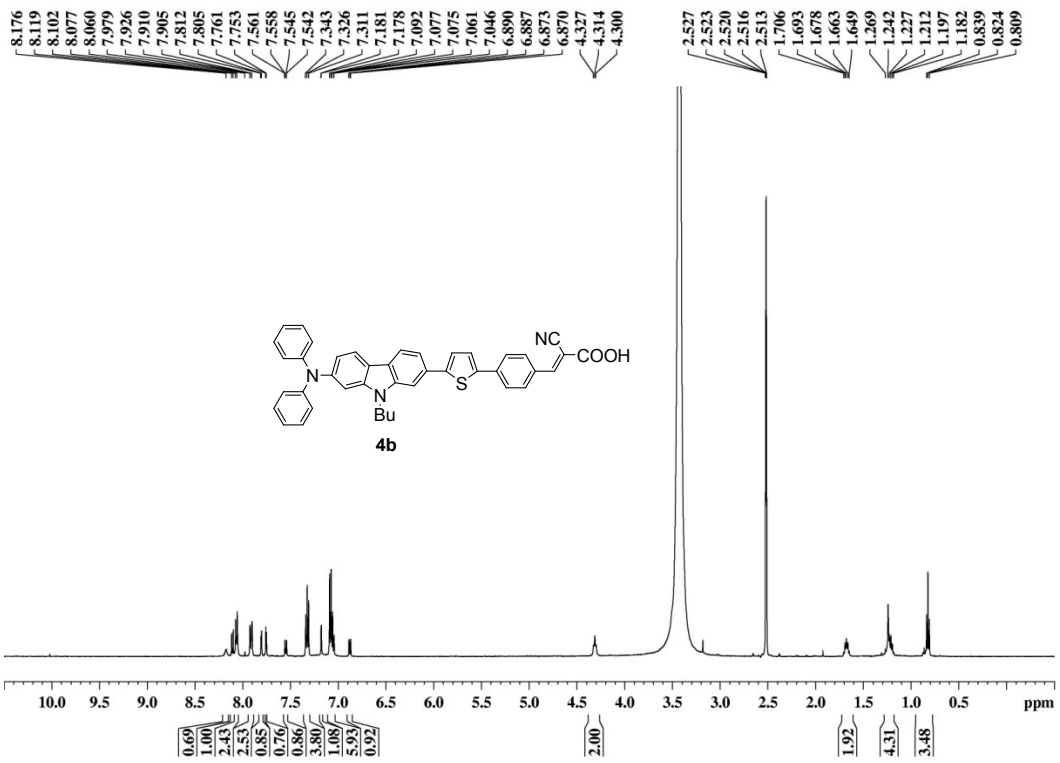

Fig. S40 ^{1}H NMR spectrum of **4b** recorded in DMSO-d_6.

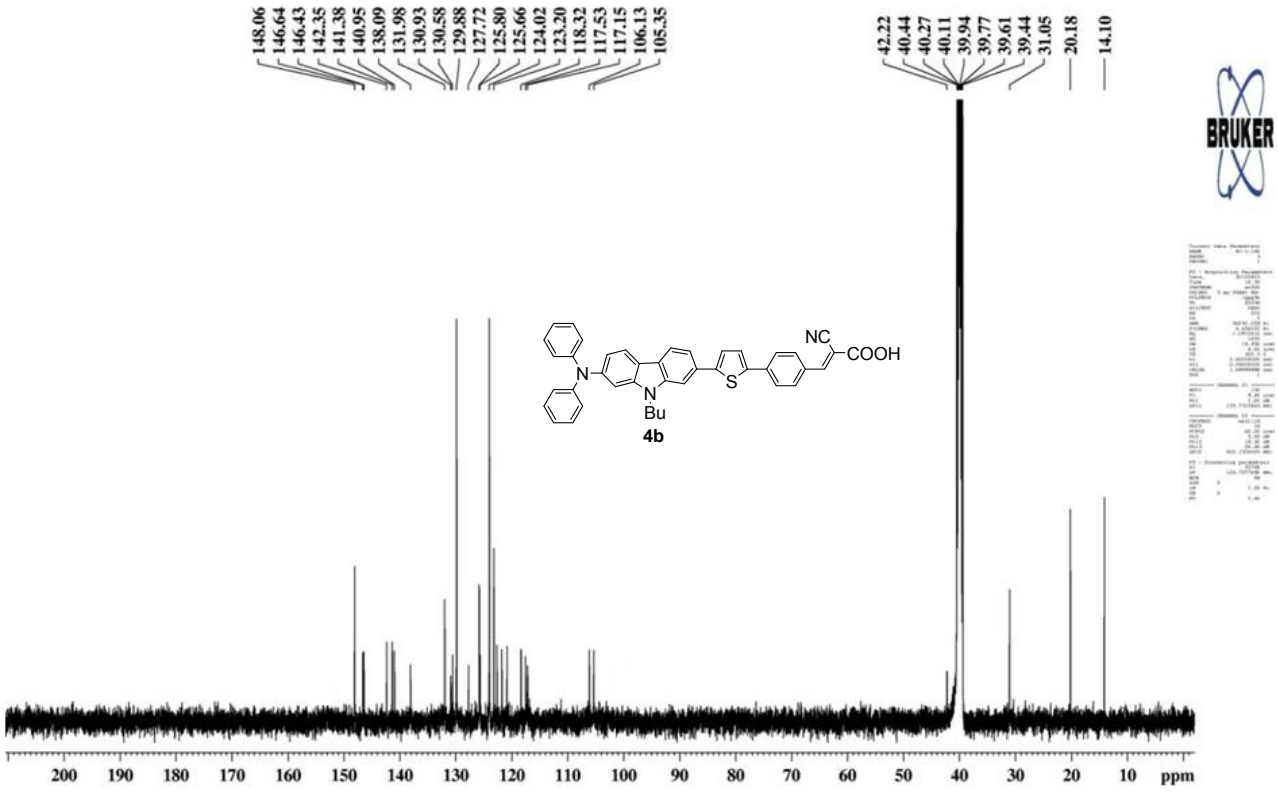

Fig. S41 ^{13}C NMR spectrum of **4b** recorded in DMSO-d_6.

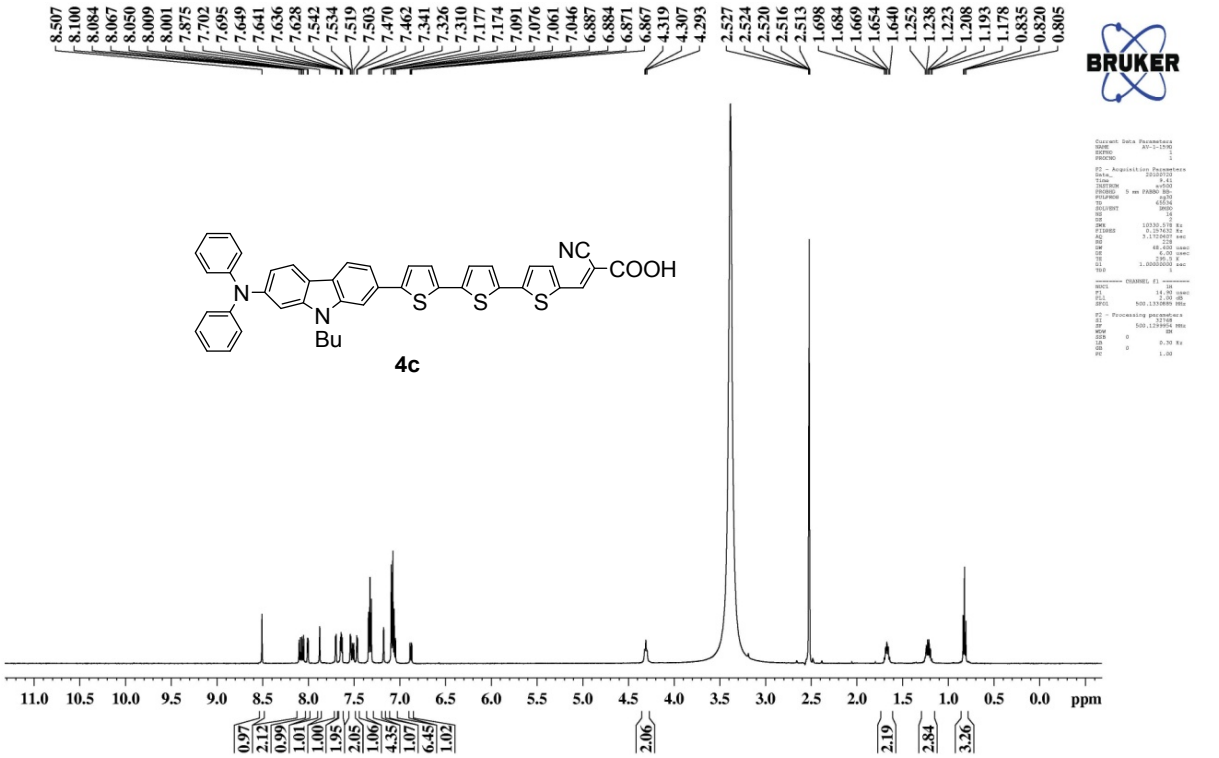

Fig. S42 ^{1}H NMR spectrum of **4c** recorded in DMSO-d_6.

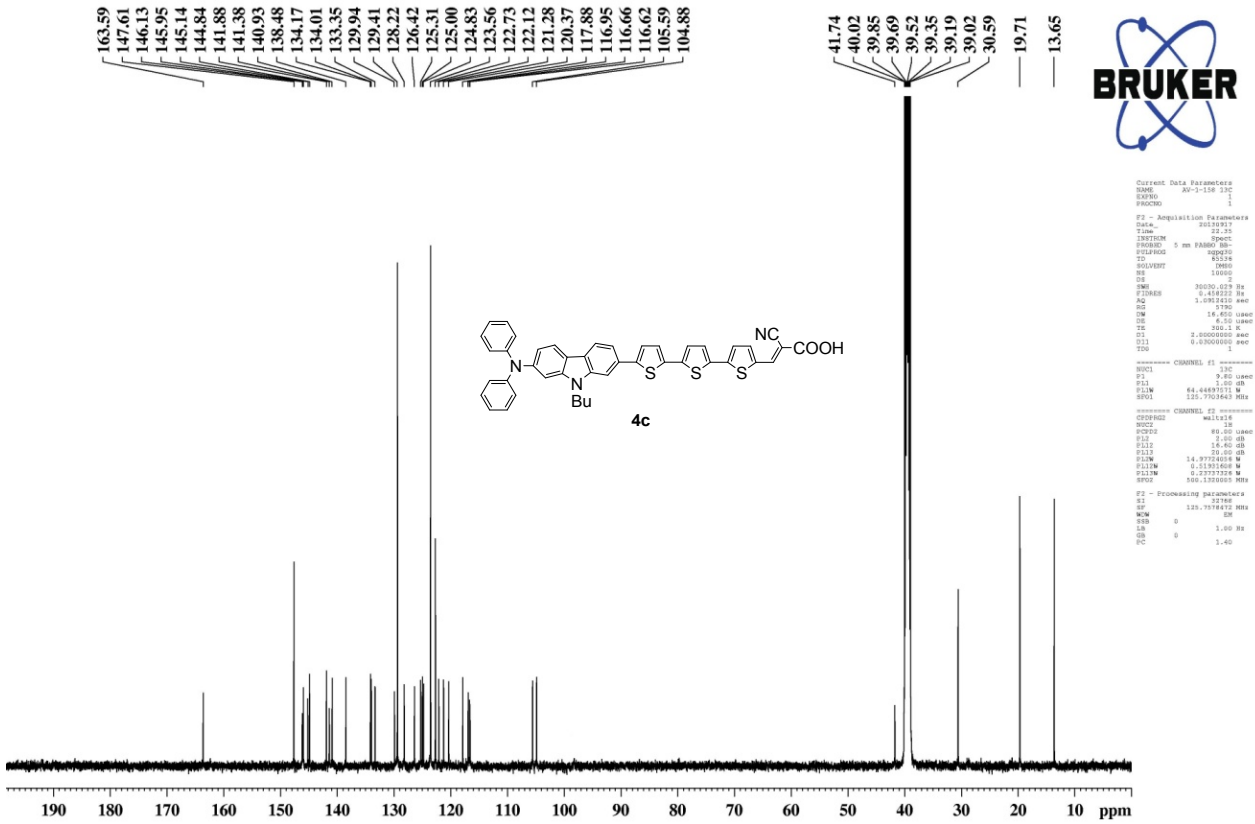

Fig. S43 ^{13}C NMR spectrum of **4c** recorded in DMSO-d_6.

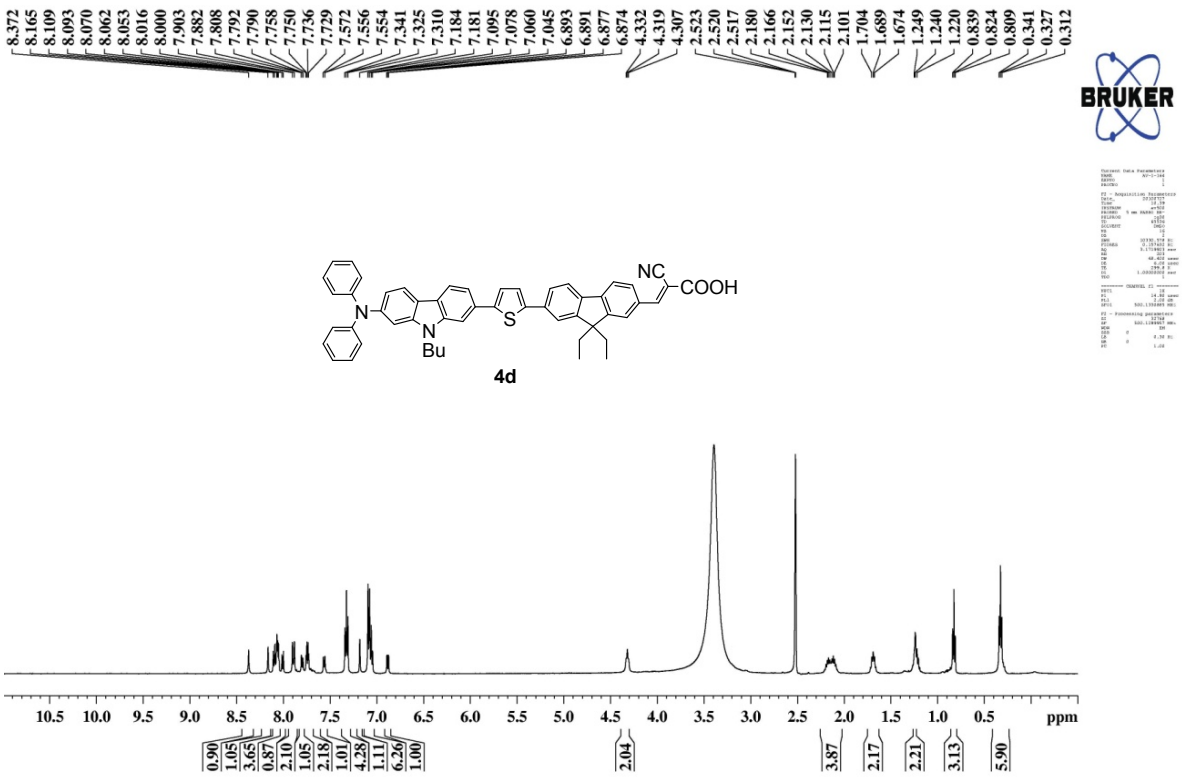

Fig. S44 ^{1}H NMR spectrum of **4d** recorded in DMSO-d_6.

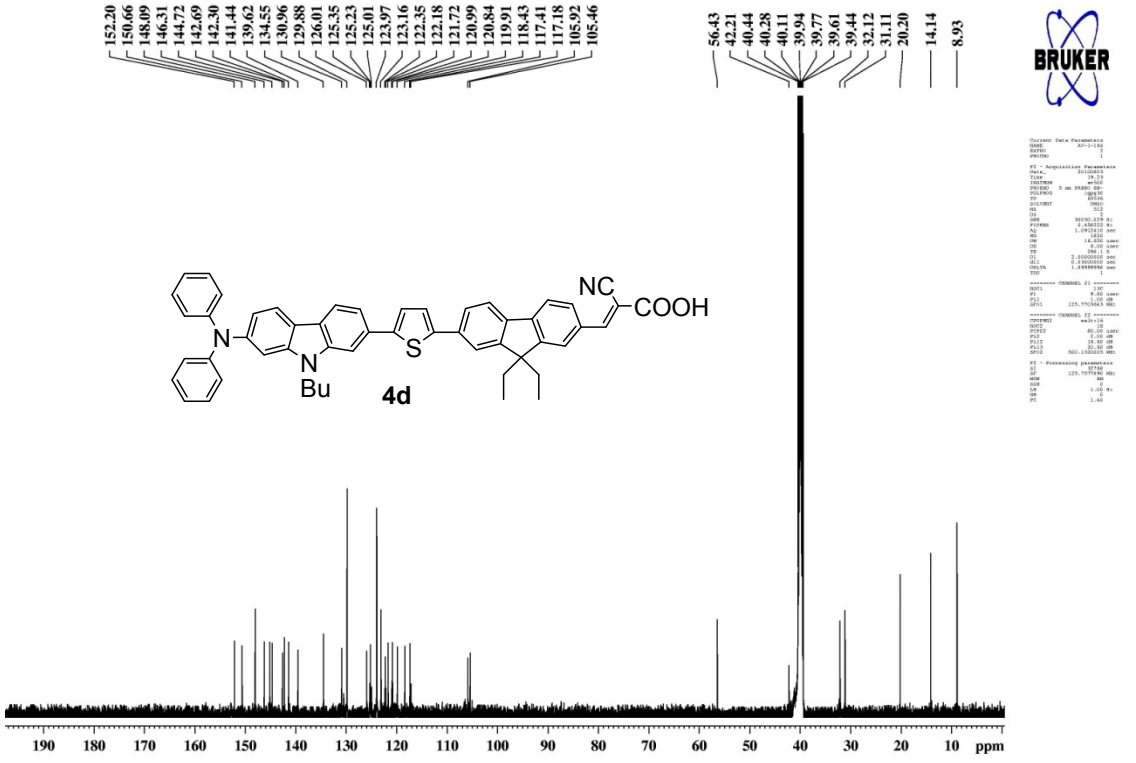

Fig. S45 ^{13}C NMR spectrum of **4d** recorded in DMSO-d_6.

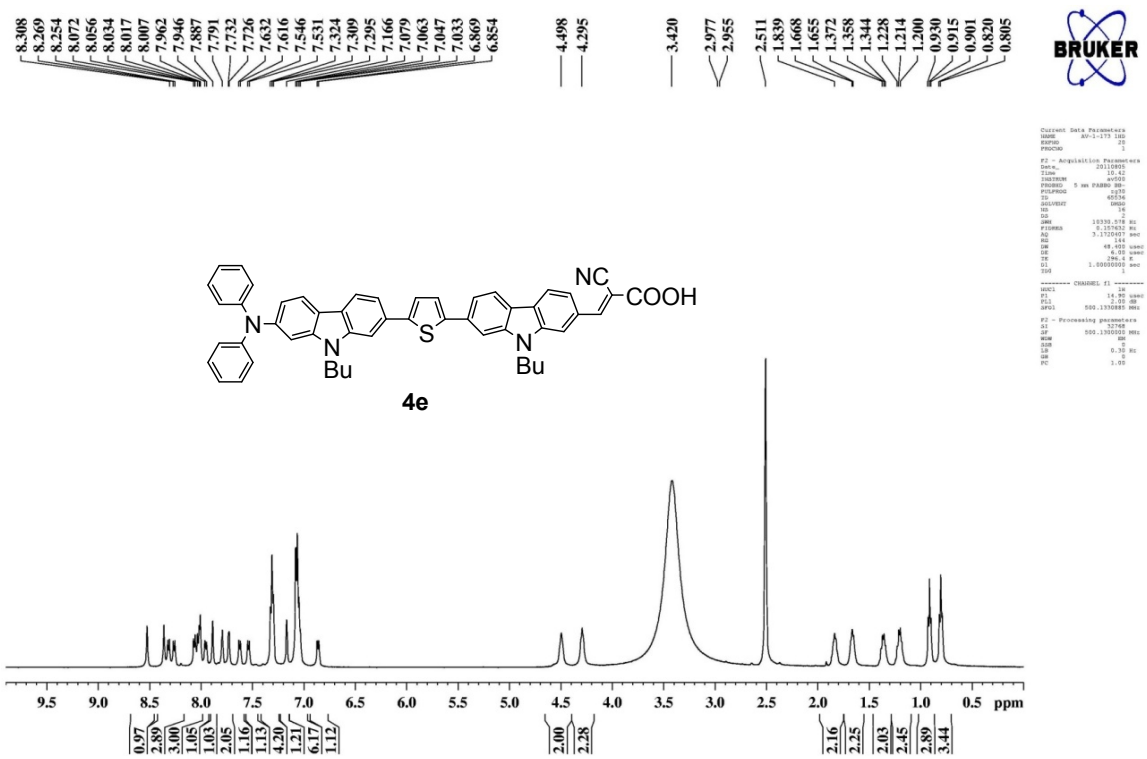

Fig. S46 ^{1}H NMR spectrum of **4e** recorded in DMSO-d_6.

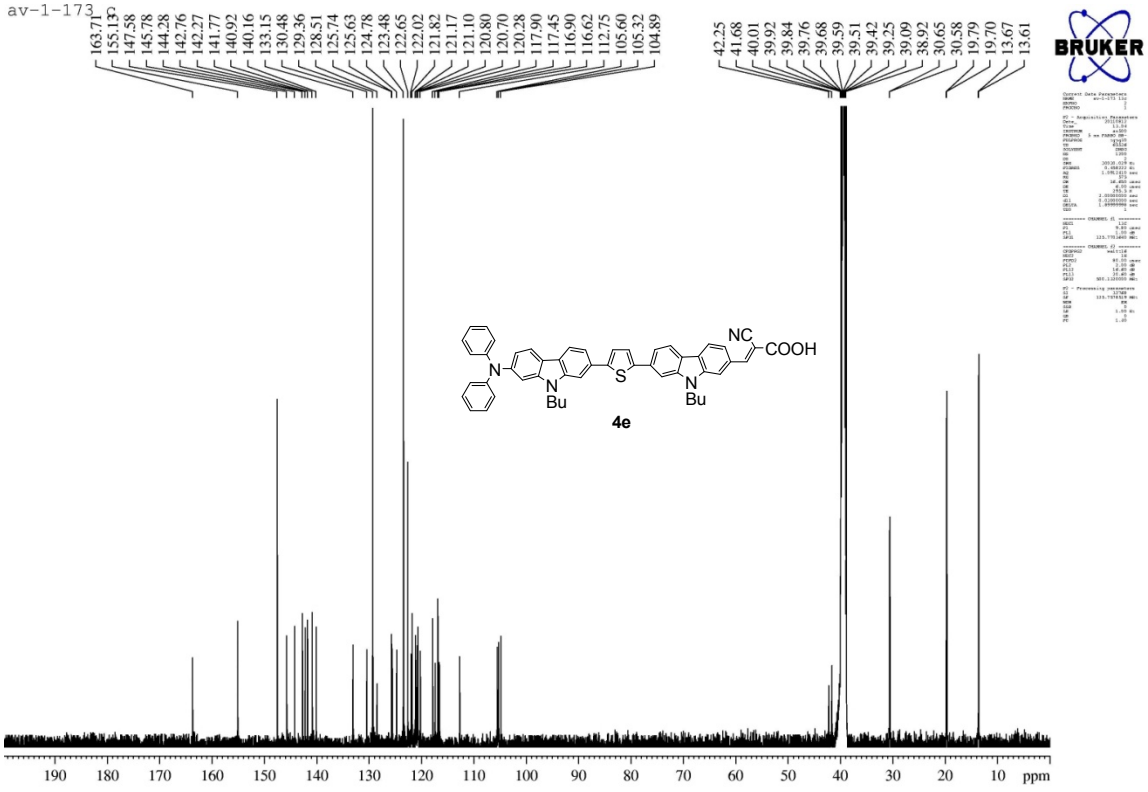

Fig. S47 ^{13}C NMR spectrum of **4e** recorded in DMSO-d_6.

Table S3 Cartesian coordinates for the optimized geometry of **4a**

Energy = -2333.31661463 H_a

Atom	X	Y	Z
6	-4.900722000	-2.215371000	0.525514000
6	-5.521139000	-0.986813000	0.197717000
6	-4.751563000	0.100549000	-0.236590000
6	-3.368542000	-0.062942000	-0.319904000
6	-2.735484000	-1.293439000	0.001074000
6	-3.525638000	-2.370924000	0.419938000
7	-2.403934000	0.854053000	-0.723804000
6	-1.155270000	0.244828000	-0.647034000
6	-1.320349000	-1.097185000	-0.204678000
6	0.102162000	0.777613000	-0.922311000
6	1.230182000	-0.048505000	-0.778003000
6	1.066607000	-1.386121000	-0.344603000
6	-0.188547000	-1.906266000	-0.057209000
7	-6.930348000	-0.851590000	0.322008000
6	-7.484045000	0.340568000	0.863826000
6	-7.787466000	-1.894528000	-0.122722000
6	-8.606218000	0.941681000	0.271371000
6	-9.150329000	2.104000000	0.814802000
6	-8.578674000	2.697107000	1.941859000
6	-7.456801000	2.106666000	2.527895000
6	-6.916122000	0.935059000	2.002828000
6	-7.512512000	-2.586411000	-1.313432000
6	-8.350576000	-3.615391000	-1.738012000
6	-9.483287000	-3.960871000	-0.998647000
6	-9.764260000	-3.268299000	0.180802000
6	-8.922698000	-2.250384000	0.623862000
6	5.043638000	0.979947000	-1.155315000
6	4.296050000	1.764310000	-2.005895000
6	2.905513000	1.488668000	-1.965286000
6	2.560019000	0.488723000	-1.081356000
16	3.994167000	-0.110227000	-0.270167000
6	-2.912315000	5.619458000	0.896894000
6	-2.906946000	4.655135000	-0.293018000
6	-2.649849000	3.200561000	0.117741000
6	-2.652374000	2.241121000	-1.081587000
1	-5.516957000	-3.037883000	0.869952000
1	-5.233966000	1.037521000	-0.488912000
1	-3.068108000	-3.320929000	0.680705000
1	0.224506000	1.815864000	-1.210219000
1	1.940277000	-2.024149000	-0.257782000
1	-0.286780000	-2.936660000	0.271652000

1	-9.047404000	0.491716000	-0.611641000
1	-10.019368000	2.554611000	0.343831000
1	-9.002182000	3.605526000	2.358922000
1	-7.006826000	2.550608000	3.411450000
1	-6.054254000	0.471354000	2.470903000
1	-6.641296000	-2.313691000	-1.899289000
1	-8.121886000	-4.140012000	-2.661335000
1	-10.137546000	-4.758579000	-1.336349000
1	-10.637510000	-3.530398000	0.771402000
1	-9.138368000	-1.726557000	1.548993000
1	4.738966000	2.491629000	-2.676966000
1	2.180438000	1.982718000	-2.601543000
1	-3.097301000	6.648860000	0.574392000
1	-1.952259000	5.602541000	1.424442000
1	-3.691369000	5.351259000	1.618860000
1	-3.868491000	4.719984000	-0.820237000
1	-2.142196000	4.970408000	-1.016144000
1	-1.684942000	3.121929000	0.634435000
1	-3.413852000	2.875180000	0.834786000
1	-3.614462000	2.289562000	-1.603533000
1	-1.892462000	2.541758000	-1.811050000
6	9.297245000	1.019908000	-0.576727000
6	8.632600000	2.148625000	-1.045925000
6	8.569058000	-0.146051000	-0.279127000
6	7.249499000	2.146035000	-1.211824000
6	7.180748000	-0.152378000	-0.503177000
1	6.745237000	3.048190000	-1.542411000
1	6.626510000	-1.070419000	-0.328803000
6	6.494761000	0.987152000	-0.948439000
1	10.372419000	1.035651000	-0.458815000
1	9.197776000	3.046177000	-1.277987000
6	9.170953000	-1.405631000	0.159894000
1	8.617809000	-2.283345000	-0.170770000
6	10.289621000	-1.696817000	0.880664000
6	10.640213000	-3.083600000	1.017136000
7	10.888024000	-4.216037000	1.111763000
6	11.228297000	-0.780406000	1.598585000
8	12.350969000	-1.099100000	1.923747000
8	10.690065000	0.420406000	1.907487000
1	11.382079000	0.901505000	2.392590000

Table S4 Cartesian coordinates for the optimized geometry of **4b**

Energy = - 2332.02095392 H_a

Atom	X	Y	Z
7	7.350352000	-0.467690000	-0.160954000
7	2.585775000	0.642303000	0.655839000
6	9.954351000	-3.637153000	0.940016000
6	10.348159000	-2.693874000	-0.018451000
1	11.323132000	-2.774522000	-0.494000000
6	9.491282000	-1.653801000	-0.388962000
1	9.803618000	-0.939296000	-1.145378000
6	8.222586000	-1.528400000	0.209980000
6	7.832908000	-2.473219000	1.178506000
1	6.861057000	-2.386674000	1.655880000
6	8.689777000	-3.520197000	1.530927000
6	7.861437000	0.849555000	-0.342418000
6	8.813536000	1.381284000	0.547324000
1	9.158188000	0.785617000	1.387847000
6	9.316506000	2.671776000	0.355748000
1	10.051658000	3.065506000	1.054108000
6	8.869077000	3.460408000	-0.711847000
1	9.257778000	4.465667000	-0.854405000
6	7.913800000	2.936995000	-1.593536000
1	7.561647000	3.533470000	-2.432212000
6	7.418223000	1.641896000	-1.418511000
1	6.688625000	1.241503000	-2.117044000
6	5.949693000	-0.707081000	-0.270817000
6	5.488601000	-1.848147000	-0.977012000
1	6.213285000	-2.517621000	-1.430650000
6	4.128195000	-2.115413000	-1.094693000
1	3.795008000	-2.997311000	-1.636842000
6	3.197304000	-1.231887000	-0.523412000
6	3.669278000	-0.078502000	0.164988000
6	5.036905000	0.186187000	0.309128000
1	5.392233000	1.054085000	0.854573000
6	1.755946000	-1.203259000	-0.432367000
6	0.728953000	-2.042156000	-0.891897000
1	0.960541000	-2.940801000	-1.458732000
6	-0.595557000	-1.724332000	-0.605464000
1	-1.380517000	-2.395749000	-0.943647000
6	-0.932671000	-0.565768000	0.144356000
6	0.089927000	0.291597000	0.597502000
1	-0.158318000	1.196572000	1.141921000
6	1.418027000	-0.033689000	0.311355000

6	2.684757000	1.881839000	1.429453000
1	1.750568000	2.006260000	1.982915000
6	2.976250000	3.135201000	0.588184000
1	3.915570000	2.991110000	0.040456000
6	1.863937000	3.529952000	-0.392574000
1	0.936178000	3.715871000	0.164935000
1	1.656928000	2.694005000	-1.071739000
6	2.219207000	4.773454000	-1.217334000
1	1.407838000	5.037264000	-1.905762000
1	3.476090000	1.749393000	2.174910000
1	3.152529000	3.959076000	1.292790000
1	3.122696000	4.607186000	-1.816593000
6	-2.330364000	-0.249589000	0.464217000
6	-2.820946000	0.534257000	1.495409000
16	-3.657405000	-0.864088000	-0.497161000
6	-4.232617000	0.633408000	1.518215000
1	-2.181313000	1.004853000	2.235087000
6	-4.863364000	-0.070333000	0.504402000
1	-4.768010000	1.198961000	2.273493000
1	8.369448000	-4.239049000	2.281803000
1	10.620608000	-4.449206000	1.220426000
6	-6.292481000	-0.192904000	0.235964000
6	-6.790939000	-0.986386000	-0.823171000
6	-7.239519000	0.491695000	1.040206000
6	-8.153834000	-1.086440000	-1.061919000
1	-6.110363000	-1.534700000	-1.469120000
6	-8.600551000	0.391250000	0.803258000
1	-6.903838000	1.113356000	1.863985000
6	-9.100859000	-0.403313000	-0.259750000
1	-8.503079000	-1.704992000	-1.885458000
1	-9.275240000	0.937661000	1.451329000
6	-10.494719000	-0.576450000	-0.603296000
6	-11.647519000	-0.070014000	-0.056724000
1	-10.659728000	-1.227442000	-1.457880000
6	-11.698600000	0.807218000	1.073707000
6	-12.984090000	-0.398612000	-0.614634000
7	-11.756152000	1.518815000	1.996888000
8	-14.035252000	0.040488000	-0.170275000
8	-12.936969000	-1.238160000	-1.675885000
1	-13.862022000	-1.380718000	-1.967951000
1	2.403660000	5.641125000	-0.571929000

Table S5 Cartesian coordinates for the optimized geometry of **4c**

Energy = - 3204.25230372 H_a

Atom	X	Y	Z
7	-9.039067000	-0.499878000	0.154921000
7	-4.274065000	0.655225000	-0.598556000
6	-11.611271000	-3.650673000	-1.067833000
6	-12.013792000	-2.750379000	-0.072357000
1	-12.987019000	-2.860325000	0.400930000
6	-11.167366000	-1.716609000	0.337668000
1	-11.485872000	-1.035697000	1.121921000
6	-9.900986000	-1.554244000	-0.257032000
6	-9.502345000	-2.456115000	-1.262132000
1	-8.531883000	-2.341198000	-1.736542000
6	-10.348835000	-3.497208000	-1.654857000
6	-9.561675000	0.804773000	0.384295000
6	-10.529223000	1.354382000	-0.477920000
1	-10.877160000	0.782201000	-1.333203000
6	-11.043732000	2.632445000	-0.240097000
1	-11.790533000	3.039690000	-0.918034000
6	-10.593470000	3.391859000	0.847302000
1	-10.991443000	4.387661000	1.026016000
6	-9.623368000	2.850969000	1.701828000
1	-9.268662000	3.424086000	2.555554000
6	-9.115578000	1.567773000	1.480472000
1	-8.373933000	1.153991000	2.158141000
6	-7.637683000	-0.735242000	0.267101000
6	-7.175895000	-1.896974000	0.937964000
1	-7.900384000	-2.584240000	1.364434000
6	-5.814997000	-2.161785000	1.056185000
1	-5.481026000	-3.059412000	1.571362000
6	-4.884561000	-1.256012000	0.520261000
6	-5.357459000	-0.083671000	-0.134807000
6	-6.725312000	0.180195000	-0.277895000
1	-7.081101000	1.063313000	-0.798070000
6	-3.442751000	-1.218083000	0.439961000
6	-2.414886000	-2.064178000	0.883786000
1	-2.645679000	-2.978986000	1.424522000
6	-1.089998000	-1.732406000	0.615489000
1	-0.304627000	-2.409764000	0.940745000
6	-0.753211000	-0.552359000	-0.100305000
6	-1.776962000	0.313284000	-0.535197000
1	-1.529362000	1.234723000	-1.051709000
6	-3.105399000	-0.025884000	-0.267153000
6	-4.372116000	1.921211000	-1.328081000

1	-3.435246000	2.067023000	-1.871712000
6	-4.668706000	3.143326000	-0.443573000
1	-5.617293000	2.985470000	0.084082000
6	-3.568536000	3.490195000	0.568182000
1	-2.629814000	3.684332000	0.032339000
1	-3.382282000	2.627570000	1.219452000
6	-3.922552000	4.708036000	1.430961000
1	-3.118792000	4.938806000	2.139886000
1	-4.087807000	5.599672000	0.813604000
1	-5.159432000	1.814999000	-2.082007000
1	-4.828323000	3.994951000	-1.118557000
1	-4.836625000	4.531743000	2.011081000
6	0.644748000	-0.223402000	-0.404515000
6	1.138676000	0.595568000	-1.405336000
16	1.970653000	-0.876850000	0.539658000
6	2.551341000	0.693436000	-1.424333000
1	0.500970000	1.092762000	-2.128989000
6	3.174638000	-0.049507000	-0.434715000
1	3.092684000	1.285165000	-2.157156000
1	-10.022259000	-4.182520000	-2.433872000
1	-12.269413000	-4.457900000	-1.379645000
6	4.585911000	-0.197365000	-0.164063000
6	5.211168000	-0.948416000	0.823283000
16	5.781113000	0.629059000	-1.144490000
6	6.619959000	-0.864943000	0.793647000
1	4.669724000	-1.545523000	1.550658000
6	7.111897000	-0.049630000	-0.216074000
1	7.256114000	-1.394068000	1.497244000
6	8.477850000	0.260567000	-0.546307000
6	8.951913000	1.069501000	-1.581798000
16	9.803397000	-0.396920000	0.387122000
6	10.349757000	1.156365000	-1.619653000
1	8.302333000	1.577419000	-2.287756000
6	10.995921000	0.420621000	-0.621471000
1	10.902606000	1.735965000	-2.353218000
6	12.408109000	0.369959000	-0.483214000
6	13.213201000	-0.297974000	0.415557000
1	12.932686000	0.968033000	-1.224518000
6	12.700302000	-1.129239000	1.458131000
6	14.687453000	-0.204353000	0.367679000
7	12.270798000	-1.805509000	2.308005000
8	15.438140000	-0.785455000	1.140209000
8	15.145329000	0.596696000	-0.626391000
1	16.123756000	0.589744000	-0.568968000

Table S6 Cartesian coordinates for the optimized geometry of **4d**

Energy = -2759.76270650 H_a

Atom	X	Y	Z
7	9.855038000	-0.271814000	-0.139719000
7	5.024768000	0.558449000	0.625237000
6	12.663973000	-3.242071000	1.011707000
6	12.989852000	-2.298040000	0.028715000
1	13.965048000	-2.326570000	-0.452320000
6	12.065165000	-1.324565000	-0.358946000
1	12.325741000	-0.609353000	-1.134129000
6	10.795150000	-1.266924000	0.247509000
6	10.473034000	-2.212681000	1.239507000
1	9.500280000	-2.178121000	1.721553000
6	11.397942000	-3.193796000	1.609178000
6	10.279978000	1.072631000	-0.340213000
6	11.203134000	1.673519000	0.536223000
1	11.591555000	1.109720000	1.379688000
6	11.621301000	2.991344000	0.327561000
1	12.334883000	3.438427000	1.016079000
6	11.116481000	3.738554000	-0.744204000
1	11.438300000	4.765284000	-0.899913000
6	10.190507000	3.145578000	-1.613140000
1	9.794422000	3.709254000	-2.454856000
6	9.779841000	1.823563000	-1.421151000
1	9.071719000	1.370057000	-2.109080000
6	8.472793000	-0.603404000	-0.247450000
6	8.087706000	-1.785684000	-0.930236000
1	8.854486000	-2.419323000	-1.365694000
6	6.746545000	-2.137495000	-1.051861000
1	6.472428000	-3.048869000	-1.578240000
6	5.758883000	-1.299778000	-0.508588000
6	6.154465000	-0.106872000	0.159956000
6	7.502175000	0.243644000	0.307914000
1	7.799090000	1.144031000	0.835308000
6	4.316700000	-1.352947000	-0.434331000
6	3.345904000	-2.256855000	-0.891402000
1	3.635951000	-3.151526000	-1.437298000
6	2.001232000	-2.008474000	-0.630538000
1	1.261021000	-2.729970000	-0.966344000
6	1.585814000	-0.854981000	0.087300000
6	2.552181000	0.066829000	0.536896000
1	2.244788000	0.969004000	1.054861000
6	3.901731000	-0.190358000	0.280125000
6	5.044036000	1.817596000	1.372843000

1	4.099302000	1.898639000	1.916528000
6	5.268290000	3.067686000	0.505798000
1	6.220859000	2.968718000	-0.029050000
6	4.145202000	3.369463000	-0.495031000
1	3.201816000	3.512477000	0.048725000
1	3.997212000	2.505191000	-1.153604000
6	4.433693000	4.610847000	-1.348684000
1	3.613993000	4.810496000	-2.048736000
1	5.835394000	1.747979000	2.126909000
1	5.385732000	3.916827000	1.192411000
1	5.350167000	4.482554000	-1.937477000
6	0.164257000	-0.612420000	0.371605000
6	-0.399797000	0.171882000	1.361153000
16	-1.102982000	-1.342035000	-0.595865000
6	-1.819536000	0.182374000	1.349023000
1	0.190257000	0.703620000	2.101273000
6	-2.378384000	-0.596020000	0.351871000
1	-2.412404000	0.724315000	2.079454000
1	11.129608000	-3.914400000	2.378540000
1	13.383424000	-4.002201000	1.305857000
6	-3.796539000	-0.823568000	0.052274000
6	-4.214225000	-1.931437000	-0.724995000
6	-4.779231000	0.069947000	0.543606000
1	-3.477783000	-2.638888000	-1.097727000
6	-5.559794000	-2.155398000	-1.009178000
6	-6.121337000	-0.153710000	0.269572000
1	-4.477180000	0.939089000	1.121474000
1	-5.851670000	-3.016331000	-1.605777000
6	-6.518059000	-1.264102000	-0.508002000
6	-7.330617000	0.678408000	0.696594000
6	-7.971857000	-1.243486000	-0.640420000
6	-8.470540000	-0.115233000	0.056800000
6	-7.259780000	2.135840000	0.150071000
6	-7.470030000	0.752044000	2.246750000
6	-8.846313000	-2.114104000	-1.306810000
6	-9.827730000	0.150166000	0.091099000
1	-8.167250000	2.657670000	0.476764000
1	-6.420745000	2.636390000	0.648761000
6	-7.107364000	2.287783000	-1.367798000
1	-6.621866000	1.334616000	2.627371000
1	-8.370586000	1.335845000	2.473469000
6	-7.534824000	-0.588227000	2.988827000
1	-8.473976000	-2.982615000	-1.844035000
6	-10.210328000	-1.844989000	-1.270741000
6	-10.731853000	-0.717716000	-0.580544000
1	-10.192216000	1.018046000	0.628666000

1	-7.074563000	3.350649000	-1.634156000
1	-7.946471000	1.839967000	-1.910935000
1	-6.183369000	1.828014000	-1.734152000
1	-7.622444000	-0.412897000	4.067296000
1	-6.634352000	-1.189812000	2.825449000
1	-8.400292000	-1.185806000	2.682665000
1	-10.900304000	-2.511402000	-1.782748000
6	-12.167950000	-0.550009000	-0.631684000
6	-13.007388000	0.400095000	-0.104911000
1	-12.680116000	-1.322465000	-1.199015000
6	-12.584097000	1.519258000	0.681067000
7	-12.250762000	2.435242000	1.322848000
6	-14.475805000	0.346052000	-0.318381000
8	-15.260535000	1.173897000	0.122465000
8	-14.877477000	-0.715127000	-1.057637000
1	-15.851493000	-0.649210000	-1.146725000
1	4.562562000	5.503579000	-0.724274000

Table S7 Cartesian coordinates for the optimized geometry of **4e**

Energy = -2775.81289855 H_a

Atom	X	Y	Z
7	9.805048000	-0.446238000	-0.095775000
7	4.994324000	0.496333000	0.668306000
6	12.254962000	-3.912303000	0.076062000
6	12.753466000	-2.714665000	-0.453896000
1	13.771636000	-2.668620000	-0.833820000
6	11.948306000	-1.574289000	-0.518486000
1	12.344101000	-0.657786000	-0.946796000
6	10.625627000	-1.606171000	-0.034526000
6	10.130488000	-2.809070000	0.505216000
1	9.115740000	-2.850520000	0.890141000
6	10.937540000	-3.949840000	0.549948000
6	10.346039000	0.832871000	0.218684000
6	11.231481000	0.994991000	1.301065000
1	11.500912000	0.137324000	1.910993000
6	11.763910000	2.253747000	1.595827000
1	12.446529000	2.359153000	2.436132000
6	11.412529000	3.374106000	0.831867000
1	11.824126000	4.352454000	1.067300000
6	10.522429000	3.217562000	-0.238945000
1	10.244565000	4.075618000	-0.847012000
6	9.998741000	1.959843000	-0.550502000
1	9.321659000	1.848594000	-1.392761000
6	8.416875000	-0.574736000	-0.398880000
6	8.011174000	-1.377703000	-1.495247000
1	8.766984000	-1.876145000	-2.094799000
6	6.664056000	-1.531929000	-1.809918000
1	6.373456000	-2.154811000	-2.652731000
6	5.693515000	-0.866890000	-1.043113000
6	6.111620000	-0.047387000	0.042846000
6	7.463145000	0.096753000	0.380324000
1	7.773604000	0.705886000	1.222623000
6	4.249636000	-0.813288000	-1.065830000
6	3.262016000	-1.395361000	-1.874541000
1	3.536602000	-2.044502000	-2.702650000
6	1.919254000	-1.149904000	-1.600289000
1	1.162308000	-1.629628000	-2.215288000
6	1.524287000	-0.318964000	-0.518037000
6	2.508873000	0.284308000	0.289181000
1	2.219036000	0.946908000	1.097838000
6	3.855734000	0.031038000	0.013775000
6	5.036529000	1.388699000	1.828510000

1	4.062638000	1.341781000	2.322474000
6	5.394172000	2.846775000	1.495742000
1	6.367298000	2.872582000	0.989878000
6	4.352513000	3.588904000	0.647711000
1	3.389586000	3.590404000	1.175734000
1	4.190543000	3.049553000	-0.293327000
6	4.763805000	5.033410000	0.336546000
1	4.000583000	5.541786000	-0.264230000
1	5.767961000	0.984345000	2.536335000
1	5.527843000	3.370721000	2.451735000
1	5.705193000	5.066621000	-0.225492000
6	0.103554000	-0.088314000	-0.217937000
6	-0.474281000	0.283212000	0.981774000
16	-1.139453000	-0.259857000	-1.442587000
6	-1.886189000	0.421692000	0.922817000
1	0.098466000	0.435963000	1.891266000
6	-2.424119000	0.163824000	-0.324181000
1	-2.487561000	0.715038000	1.777629000
1	10.535556000	-4.868748000	0.971021000
1	12.881513000	-4.799775000	0.117985000
6	-3.832491000	0.195238000	-0.740080000
6	-4.185523000	0.324022000	-2.114274000
6	-4.845850000	0.095174000	0.231012000
1	-3.404159000	0.413946000	-2.864111000
6	-5.512146000	0.362356000	-2.521683000
6	-6.181707000	0.144252000	-0.180896000
1	-4.591340000	-0.039642000	1.276329000
1	-5.755338000	0.466171000	-3.576273000
6	-6.531184000	0.276191000	-1.557464000
7	-7.340276000	0.079733000	0.584282000
6	-7.968148000	0.300993000	-1.618103000
6	-8.432653000	0.179903000	-0.270274000
6	-7.422702000	-0.020809000	2.044974000
6	-8.899812000	0.427445000	-2.662481000
6	-9.789006000	0.189243000	0.042402000
1	-8.198727000	0.673569000	2.382590000
1	-6.477318000	0.341878000	2.456516000
6	-7.728777000	-1.431546000	2.572036000
1	-8.568843000	0.520486000	-3.693643000
6	-10.253101000	0.436168000	-2.357102000
6	-10.722015000	0.320022000	-1.013342000
1	-10.114436000	0.103972000	1.070976000
1	-7.896063000	-1.335964000	3.653093000
1	-8.676348000	-1.780476000	2.143249000
6	-6.629055000	-2.470354000	2.314334000
1	-10.983405000	0.533757000	-3.156095000

1	-5.690184000	-2.124108000	2.766934000
1	-6.442821000	-2.552350000	1.236448000
6	-6.981716000	-3.854734000	2.872827000
1	-7.145363000	-3.818350000	3.956979000
1	-6.177454000	-4.574741000	2.681782000
1	-7.896360000	-4.248183000	2.412548000
6	-12.159115000	0.350707000	-0.844597000
6	-12.966983000	0.247678000	0.260841000
1	-12.703640000	0.482655000	-1.775712000
6	-12.498872000	0.059967000	1.600879000
7	-12.125900000	-0.094953000	2.695949000
6	-14.445886000	0.323438000	0.156031000
8	-15.201418000	0.245503000	1.114649000
8	-14.893980000	0.489620000	-1.111282000
1	-15.872196000	0.532814000	-1.063985000
1	4.905501000	5.615310000	1.255685000