

Pyrene-based organic dyes with thiophene containing π -linkers for dye-sensitized solar cells: optical, electrochemical and theoretical investigations

Abhishek Baheti,^a Chuan-Pei Lee,^b K. R. Justin Thomas,^{*a} and Kuo-Chuan Ho^b

^a Organic Materials Lab, Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee – 247 667, India.

^b Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan.

Electronic Supplementary Information

Content	Page
Fig. S1 Absorption spectra of dye 4a recorded in THF before and after the addition of TEA or TFA.	S3
Fig. S2 Absorption spectra of dye 4b recorded in THF before and after the addition of TEA or TFA.	S3
Fig. S3 Absorption spectra of dye 4c recorded in THF before and after the addition of TEA or TFA.	S4
Fig. S4 Absorption spectra of dye 4d recorded in THF before and after the addition of TEA or TFA.	S4
Fig. S5 Absorption spectra of the dye 4a recorded in different solvents.	S5
Fig. S6 Absorption spectra of the dye 4b recorded in different solvents.	S5
Fig. S7 Absorption spectra of the dye 4d recorded in different solvents.	S6
Fig. S8 Absorption spectra of the dye 4e recorded in different solvents.	S6
Fig. S9 Emission spectra of the dye 4a recorded in different solvents.	S7
Fig. S10 Emission spectra of the dye 4b recorded in different solvents.	S7
Fig. S11 Emission spectra of the dye 4d recorded in different solvents.	S8
Fig. S12 Emission spectra of the dye 4e recorded in different solvents.	S8
Fig. S13 Potential energy surface scan as a function of dihedral angle defining the rotation between the key units in 4a .	S9
Fig. S14 Potential energy surface scan as a function of dihedral angle defining the rotation between the key units in 4c .	S10
Fig. S15 Potential energy surface scan as a function of dihedral angle defining the rotation between the key units in 4e .	S11
Fig. S16 Electronic distributions in the frontier molecular orbitals of the dyes 4a-4b .	S12
Fig. S17 ¹ H NMR spectra of 3a recorded in CDCl ₃ .	S13
Fig. S18 ¹³ C NMR spectra of 3a recorded in CDCl ₃ .	S14
Fig. S19 ¹ H NMR spectra of 3b recorded in CDCl ₃ .	S15
Fig. S20 ¹³ C NMR spectra of 3b recorded in CDCl ₃ .	S16
Fig. S21 ¹ H NMR spectra of 3c recorded in CDCl ₃ .	S17
Fig. S22 ¹³ C NMR spectra of 3c recorded in CDCl ₃ .	S18
Fig. S23 ¹ H NMR spectra of 3d recorded in CDCl ₃ .	S19
Fig. S24 ¹³ C NMR spectra of 3d recorded in CDCl ₃ .	S20

Fig. S25 ^1H NMR spectra of 3e recorded in CDCl_3 .	S21
Fig. S26 ^{13}C NMR spectra of 3e recorded in CDCl_3 .	S22
Fig. S27 ^1H NMR spectra of 4a recorded in DMSO-d_6 .	S23
Fig. S28 ^{13}C NMR spectra of 4a recorded in DMSO-d_6 .	S24
Fig. S29 ^1H NMR spectra of 4b recorded in DMSO-d_6 .	S25
Fig. S30 ^{13}C NMR spectra of 4b recorded in DMSO-d_6 .	S26
Fig. S31 ^1H NMR spectra of 4c recorded in DMSO-d_6 .	S27
Fig. S32 ^{13}C NMR spectra of 4c recorded in DMSO-d_6 .	S28
Fig. S33 ^1H NMR spectra of 4d recorded in DMSO-d_6 .	S29
Fig. S34 ^{13}C NMR spectra of 4d recorded in DMSO-d_6 .	S30
Fig. S35 ^1H NMR spectra of 4e recorded in DMSO-d_6 .	S31
Fig. S36 ^{13}C NMR spectra of 4e recorded in DMSO-d_6 .	S32
Table S1 XYZ coordinates for the optimized geometry of 4a .	S33
Table S2 XYZ coordinates for the optimized geometry of 4b .	S34
Table S3 XYZ coordinates for the optimized geometry of 4c .	S36
Table S4 XYZ coordinates for the optimized geometry of 4d .	S38
Table S5 XYZ coordinates for the optimized geometry of 4e .	S40
Table S6 Photophysical data for the dyes measured in different solvents.	S42

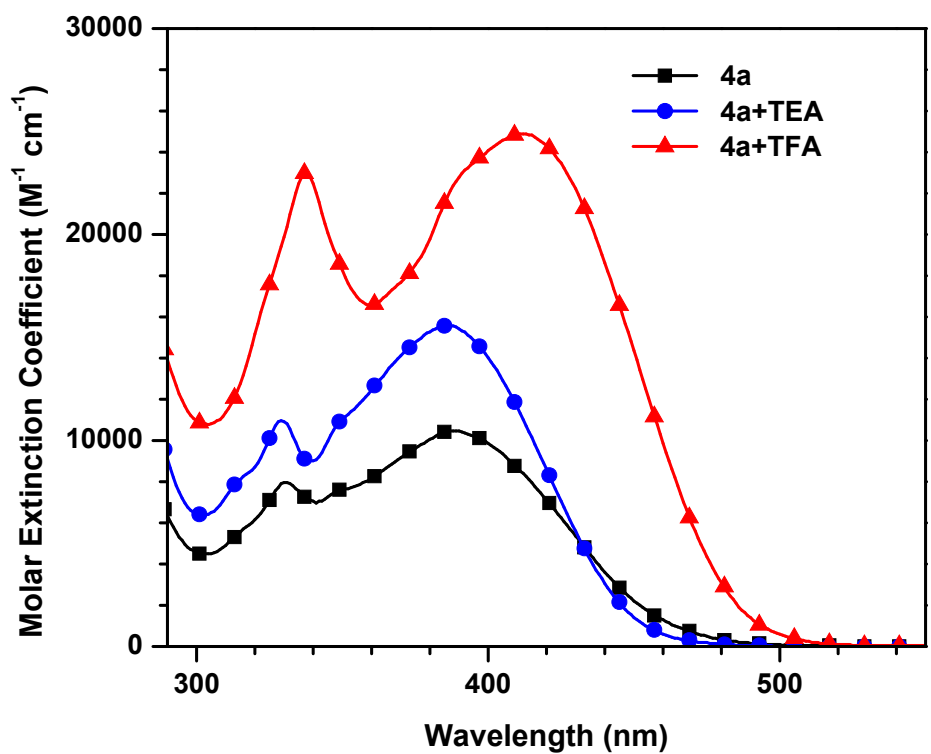


Fig. S1. Absorption spectra of the dye **4a** recorded in THF solutions before and after the addition of TEA or TFA.

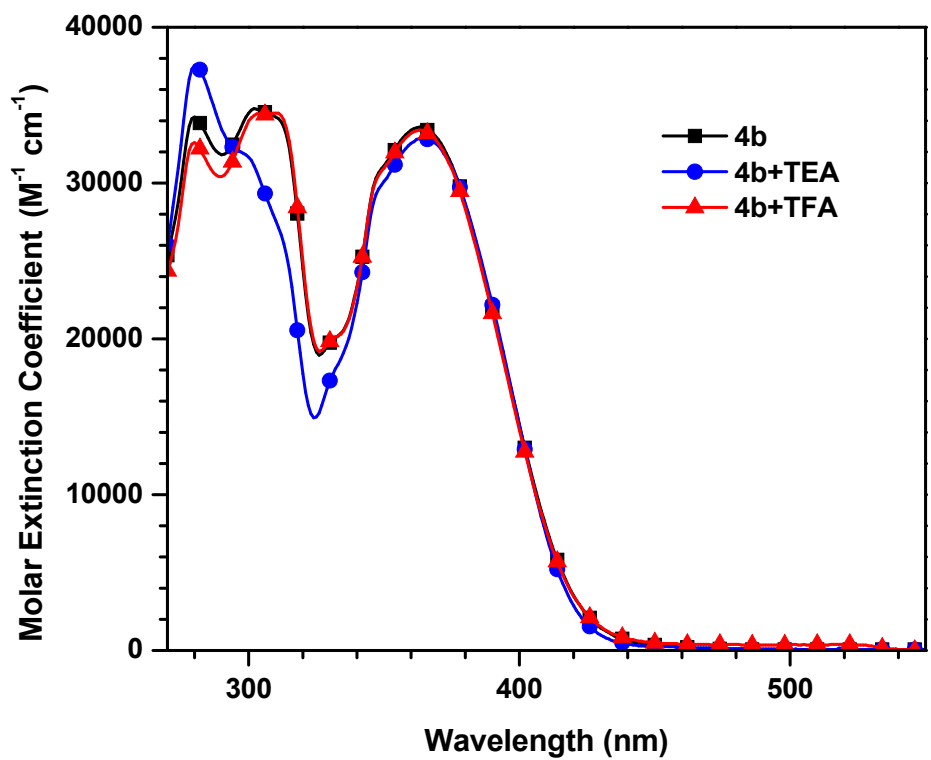


Fig. S2. Absorption spectra of the dye **4b** recorded in THF solutions before and after the addition of TEA or TFA.

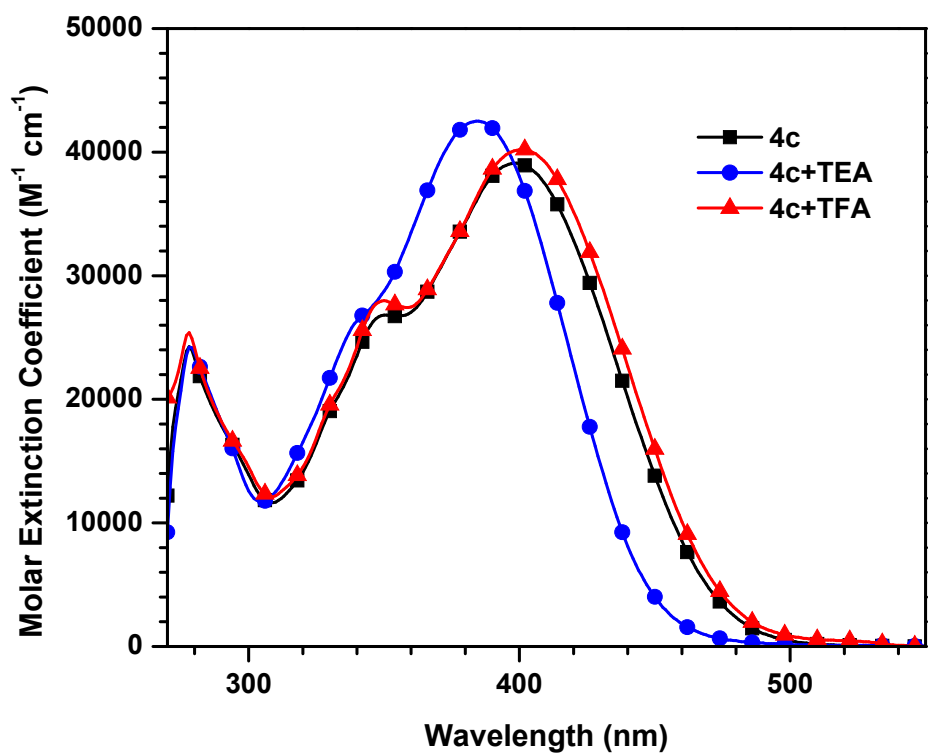


Fig. S3. Absorption spectra of the dye **4c** recorded in THF solutions before and after the addition of TEA or TFA.

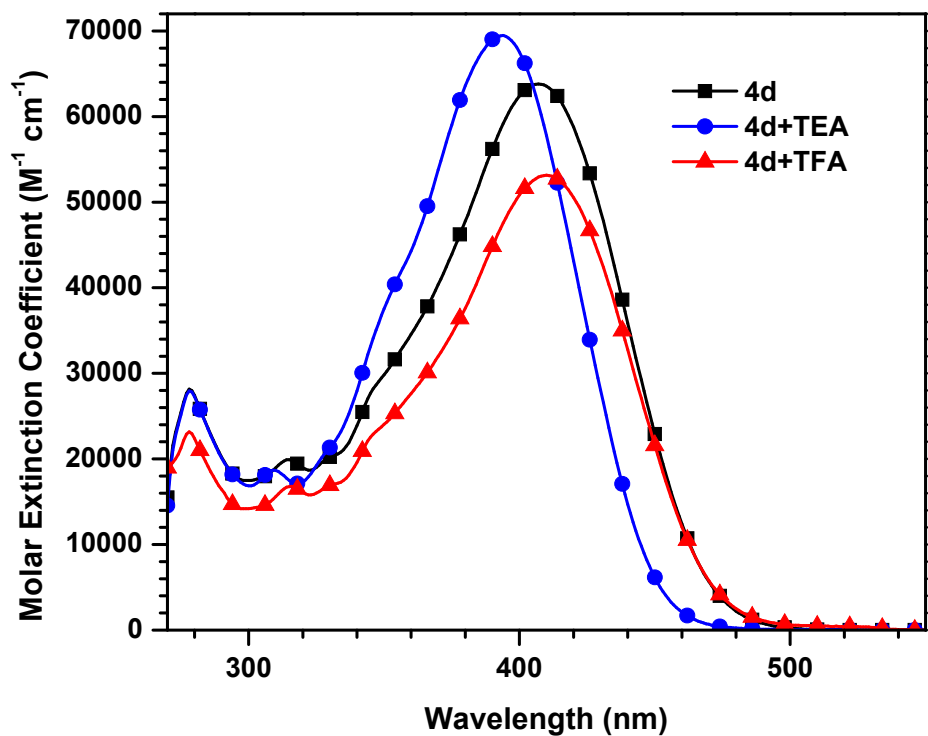


Fig. S4. Absorption spectra of the dye **4d** recorded in THF solutions before and after the addition of TEA or TFA.

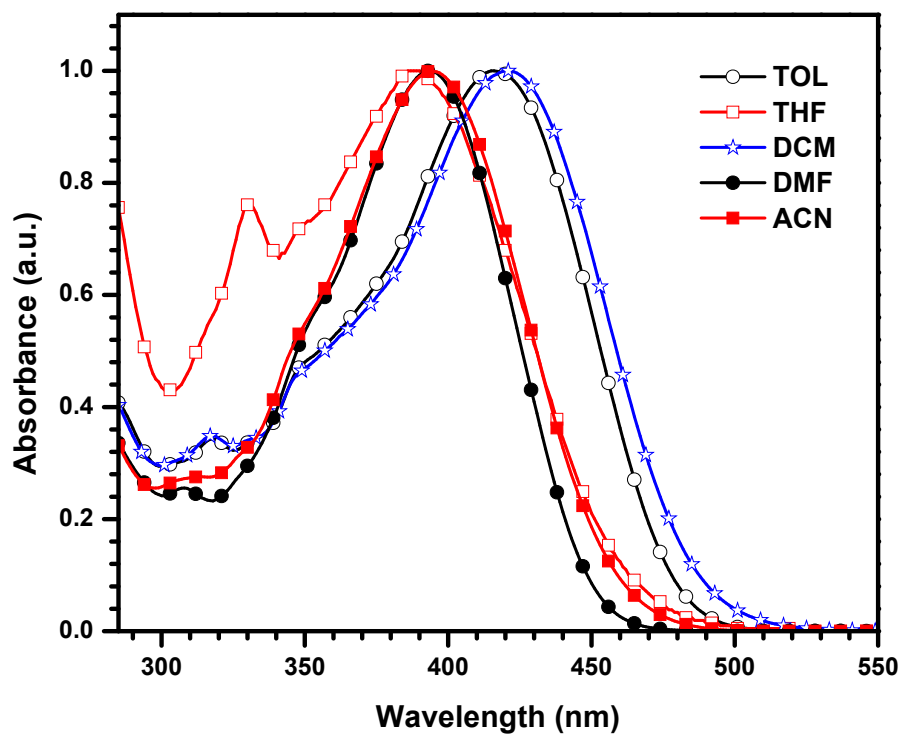


Fig. S5 Absorption spectra of the dye **4a** recorded in different solvents.

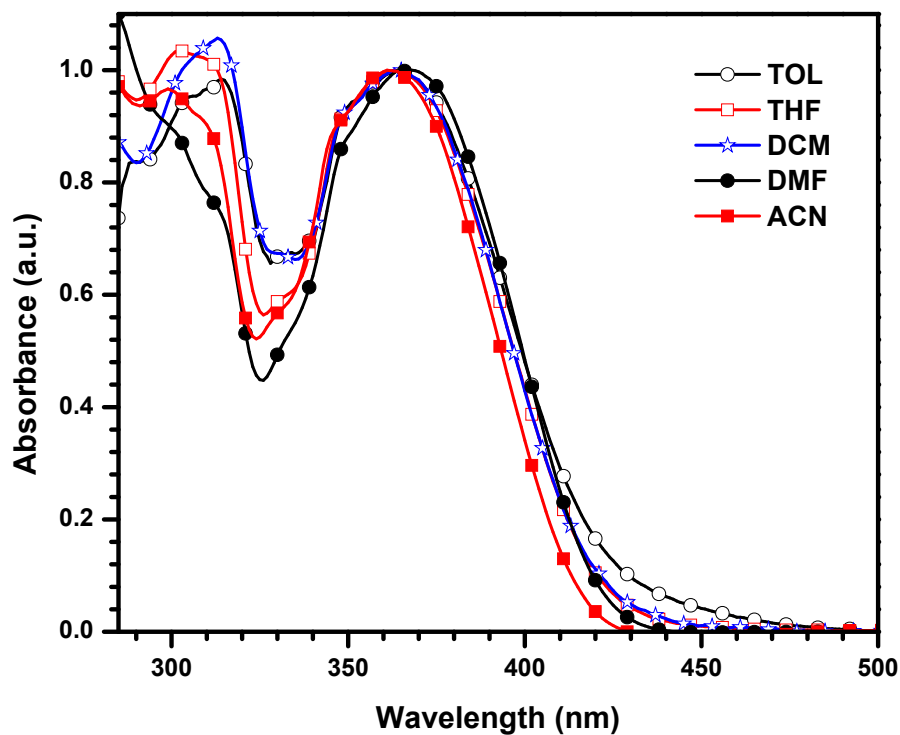


Fig. S6 Absorption spectra of the dye **4b** recorded in different solvents.

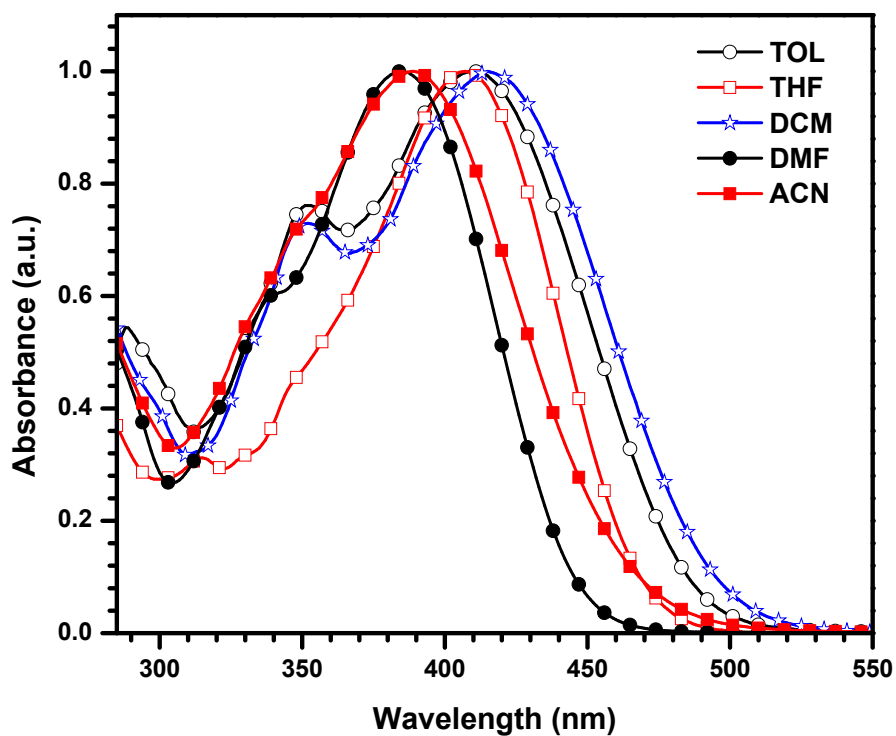


Fig. S7 Absorption spectra of the dye **4d** recorded in different solvents.

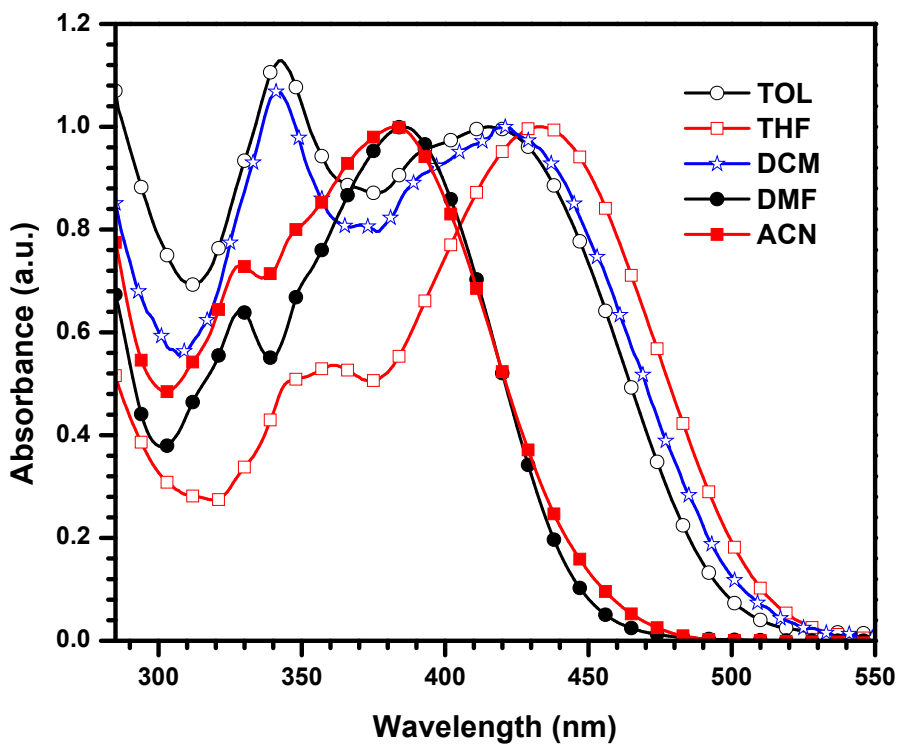


Fig. S8 Absorption spectra of the dye **4e** recorded in different solvents.

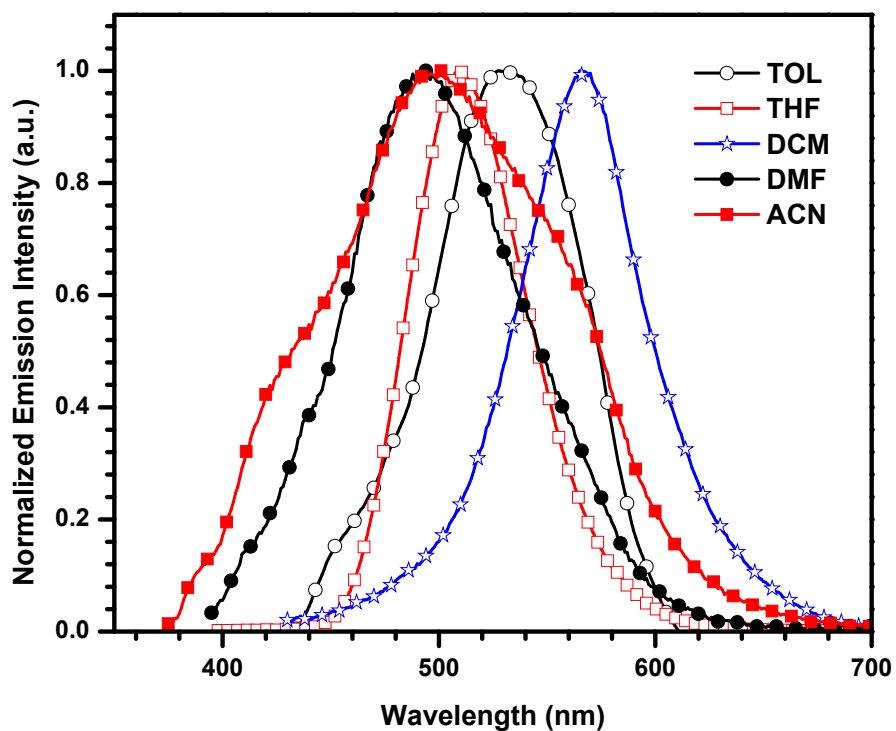


Fig. S9 Emission spectra of **4a** recorded in different solvents.

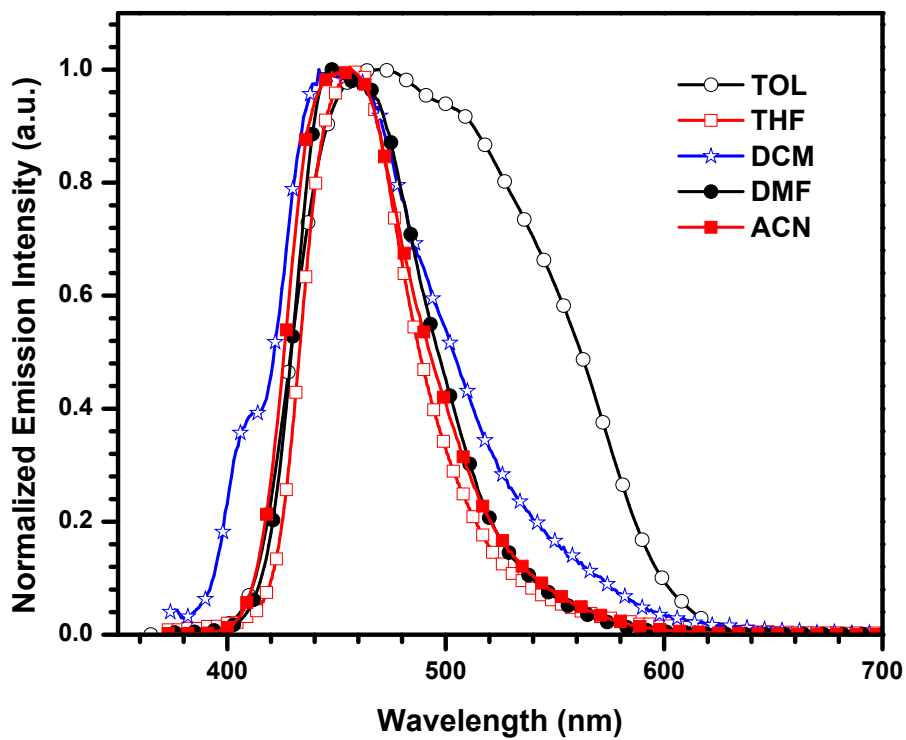


Fig. S10 Emission spectra of **4b** recorded in different solvents.

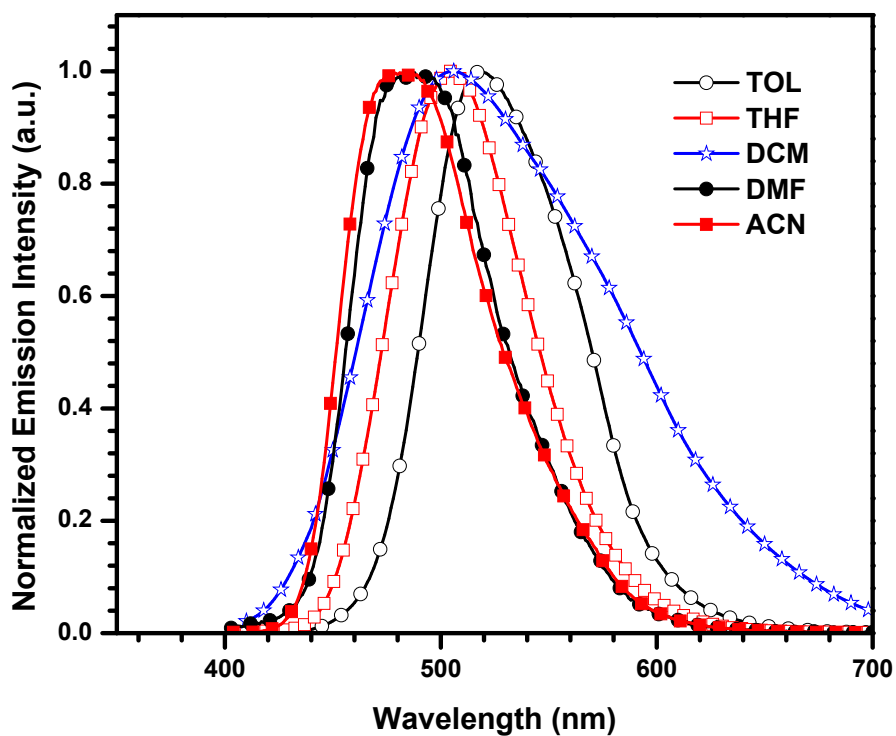


Fig. S11 Emission spectra of 4d recorded in different solvents.

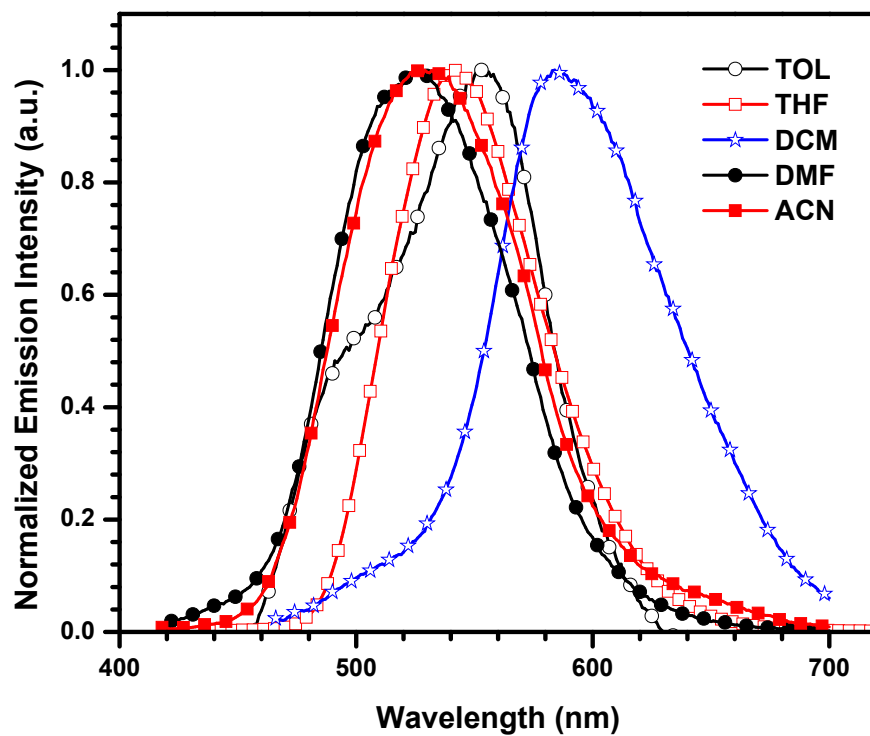


Fig. S12 Emission spectra of 4e recorded in different solvents.

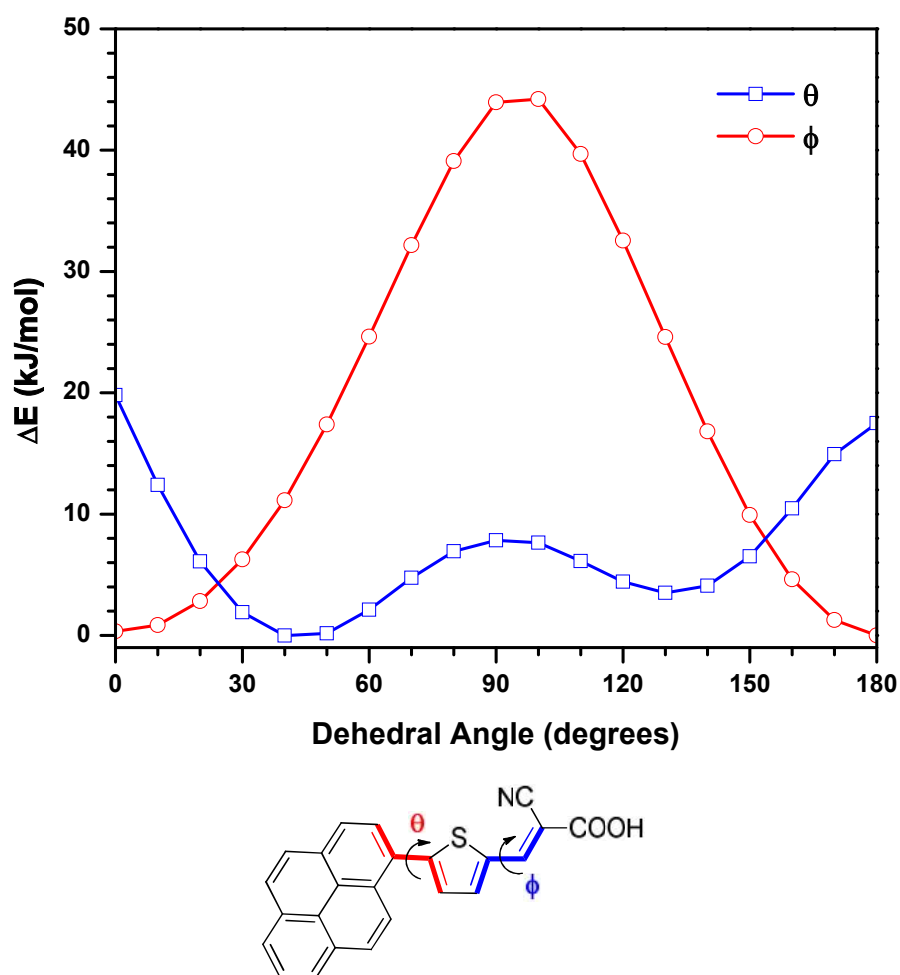


Fig. S13 Potential energy surface scan as a function of dihedral angle defining the rotation between the key units in **4a**.

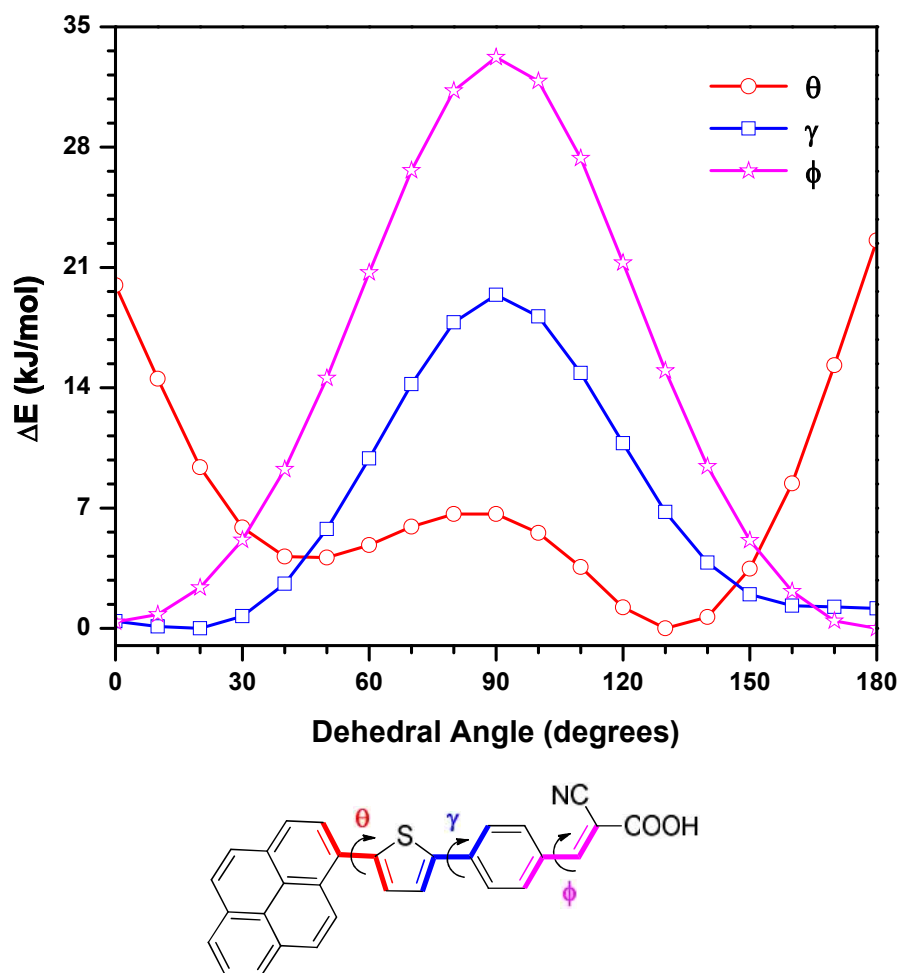


Fig. S14 Potential energy surface scan as a function of dihedral angle defining the rotation between the key units in **4c**.

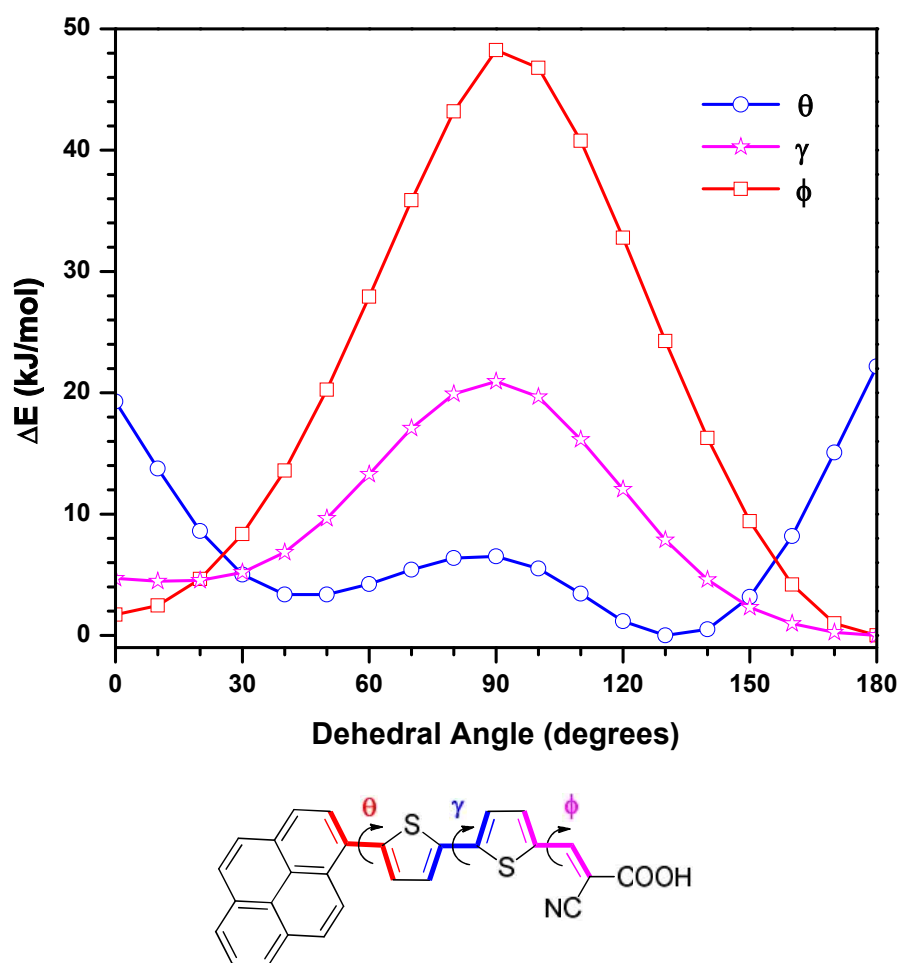


Fig. S15 Potential energy surface scan as a function of dihedral angle defining the rotation between the key units in **4e**.

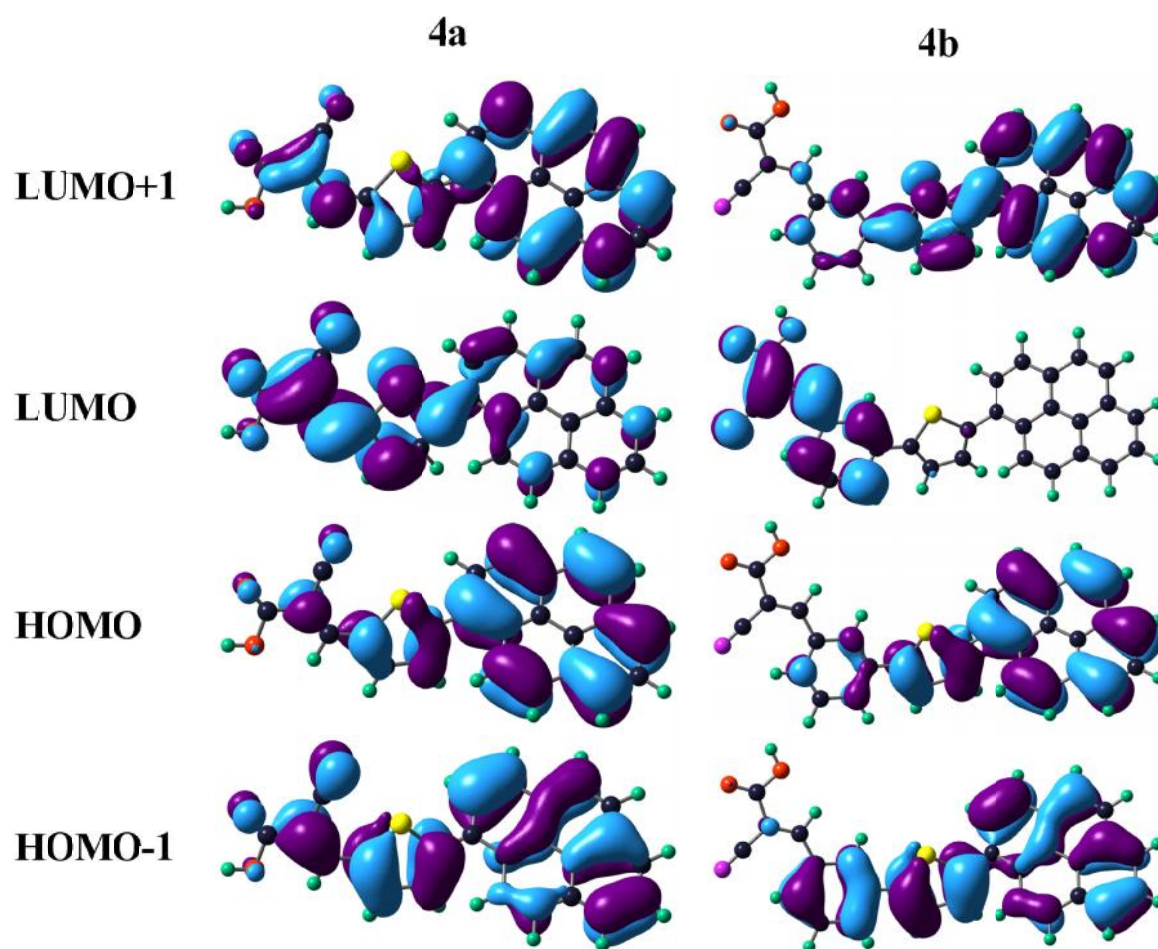


Fig. S16 Electronic distributions in the frontier molecular orbitals of the dyes **4a** and **4b**.

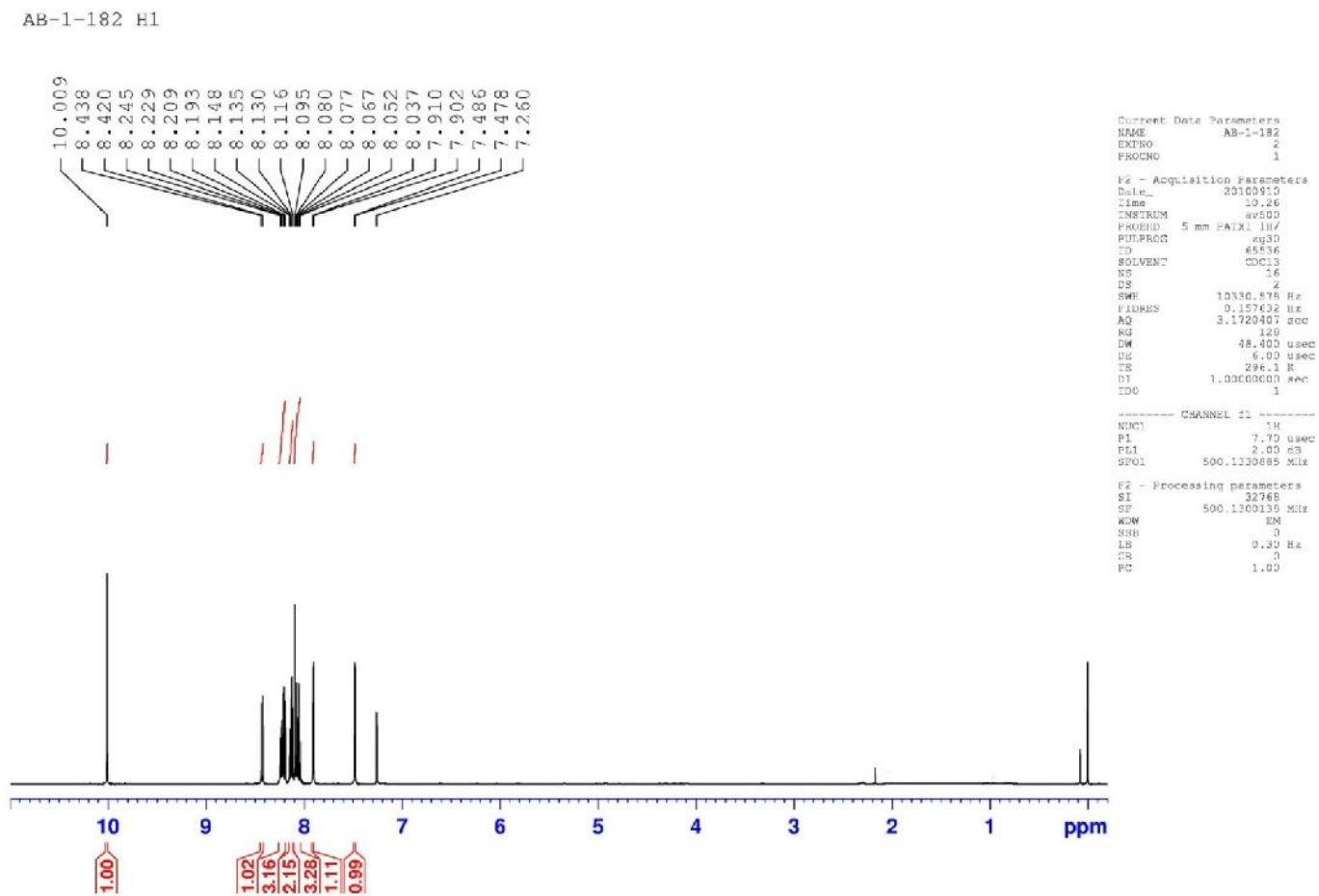


Fig. S17 ^1H NMR spectra of **3a** recorded in CDCl_3 .

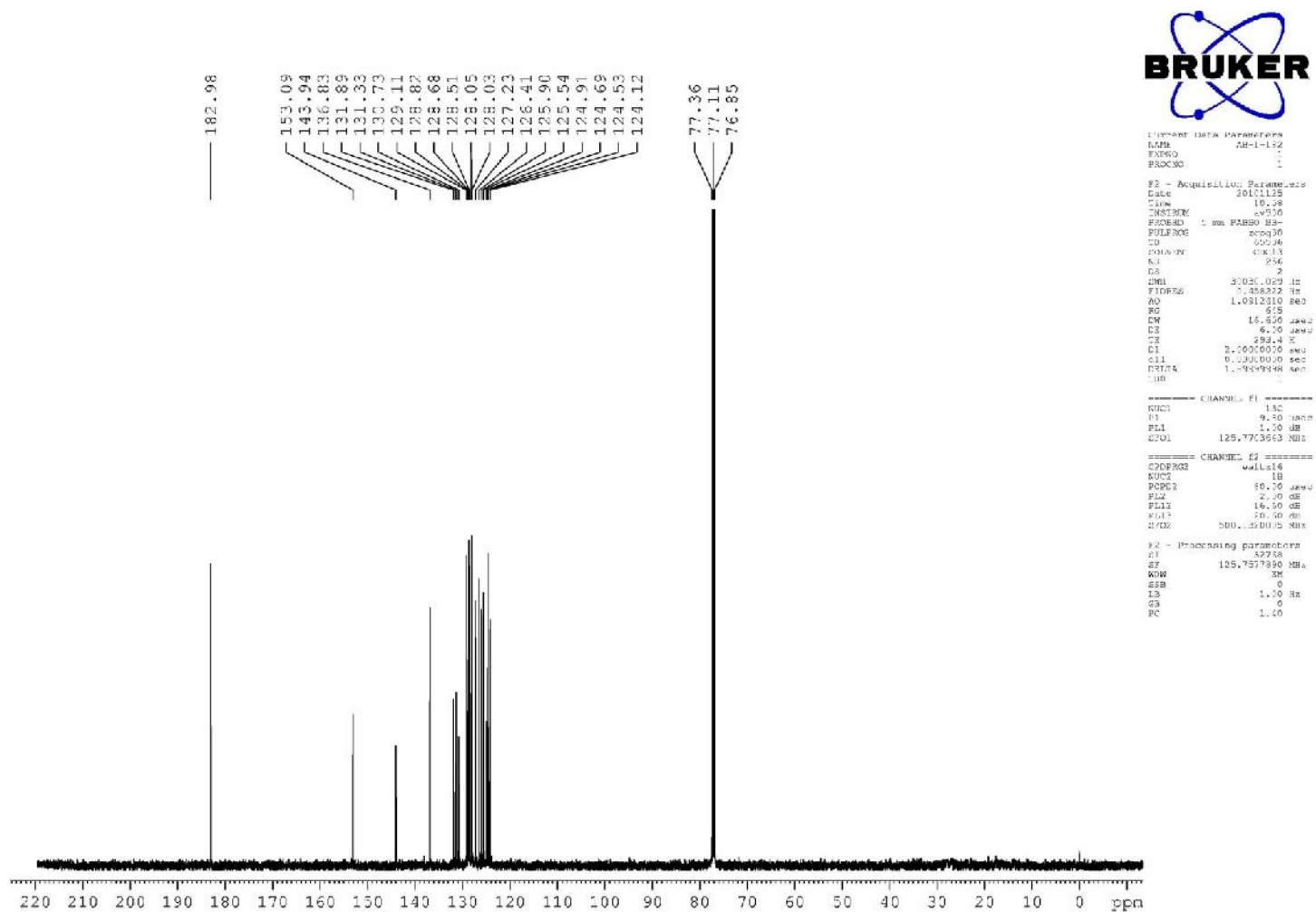


Fig. S18 ^{13}C NMR spectra of 3a recorded in CDCl_3 .

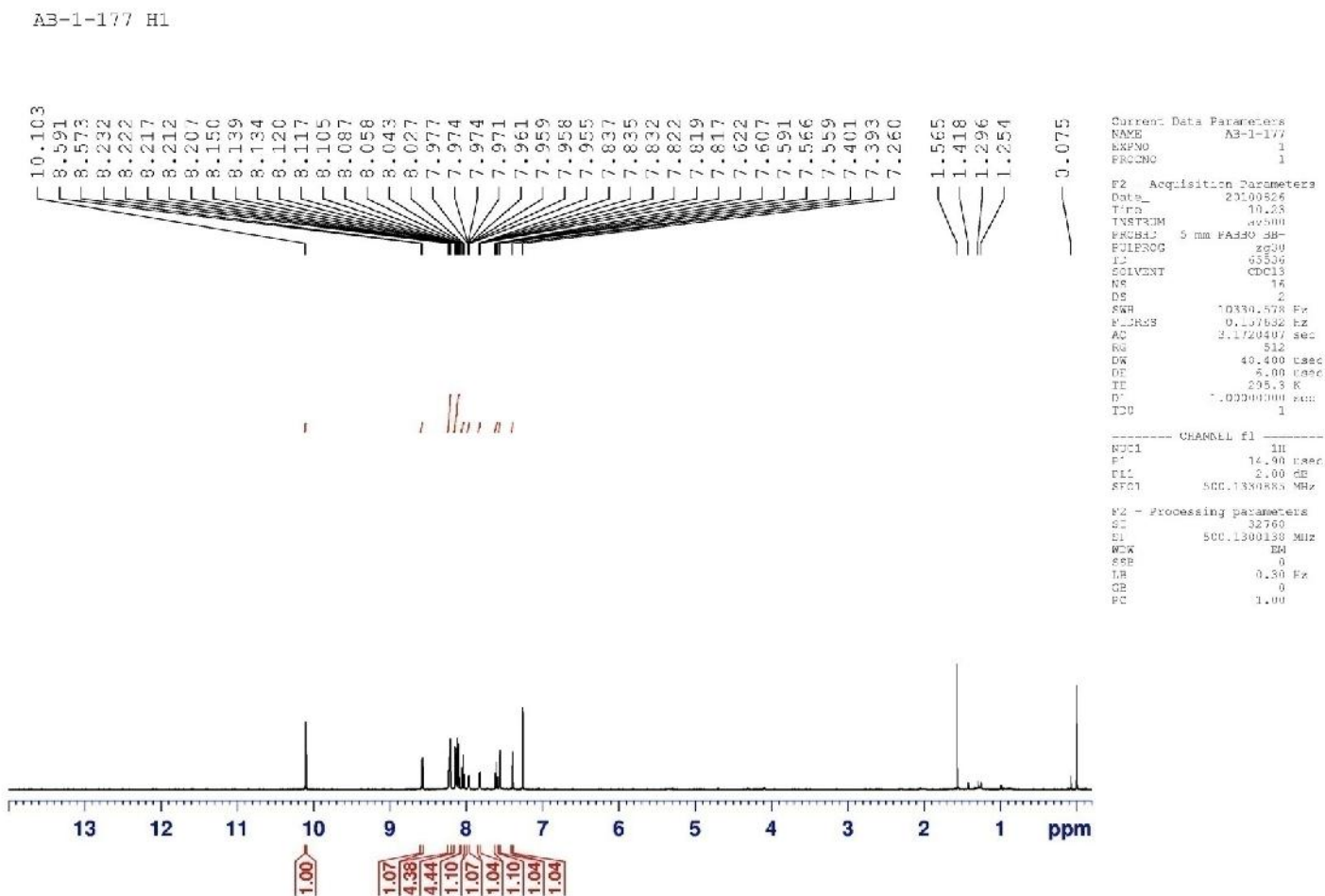


Fig. S19 ^1H NMR spectra of **3b** recorded in CDCl_3 .

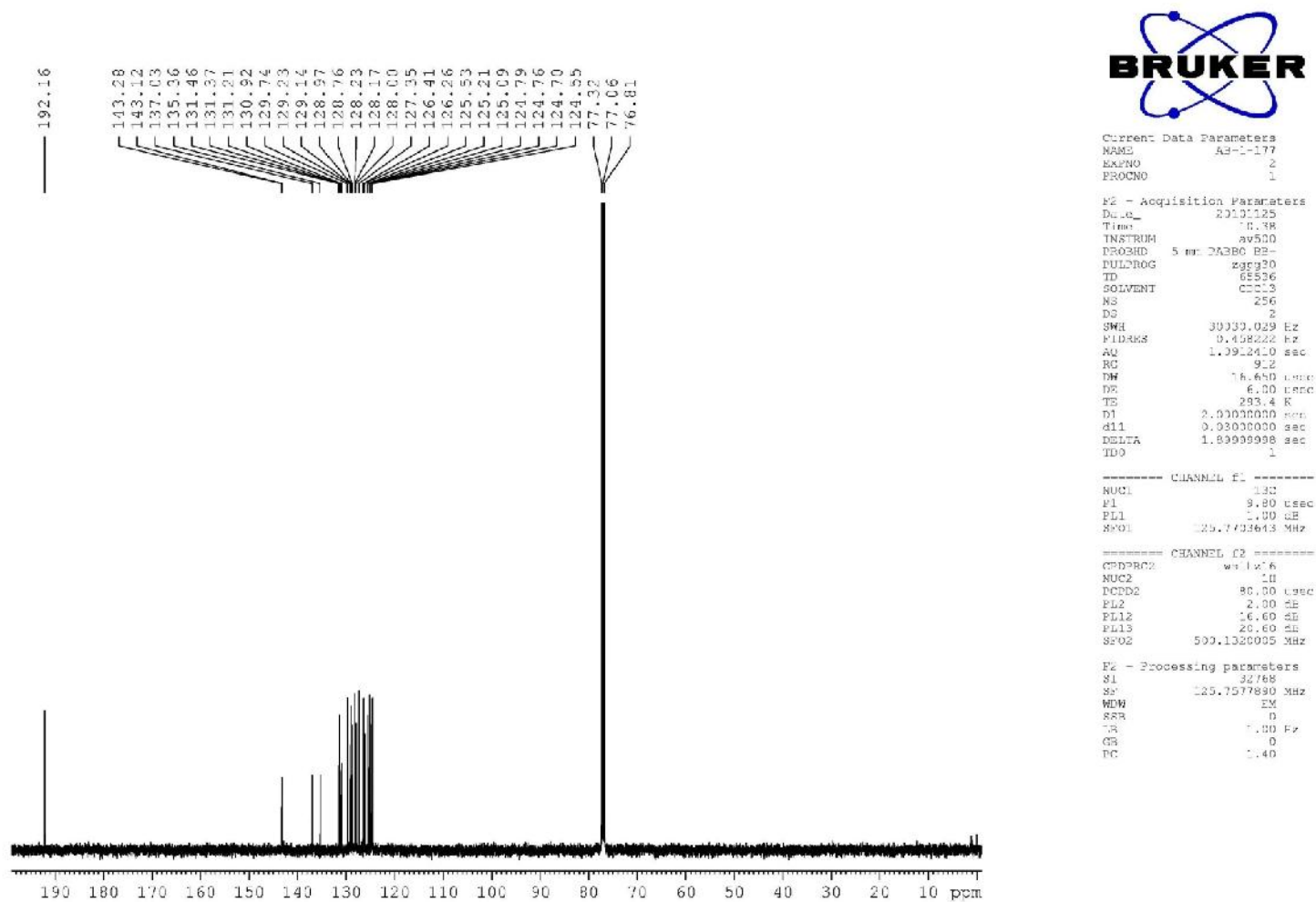


Fig. S20 ^{13}C NMR spectra of **3b** recorded in CDCl_3 .

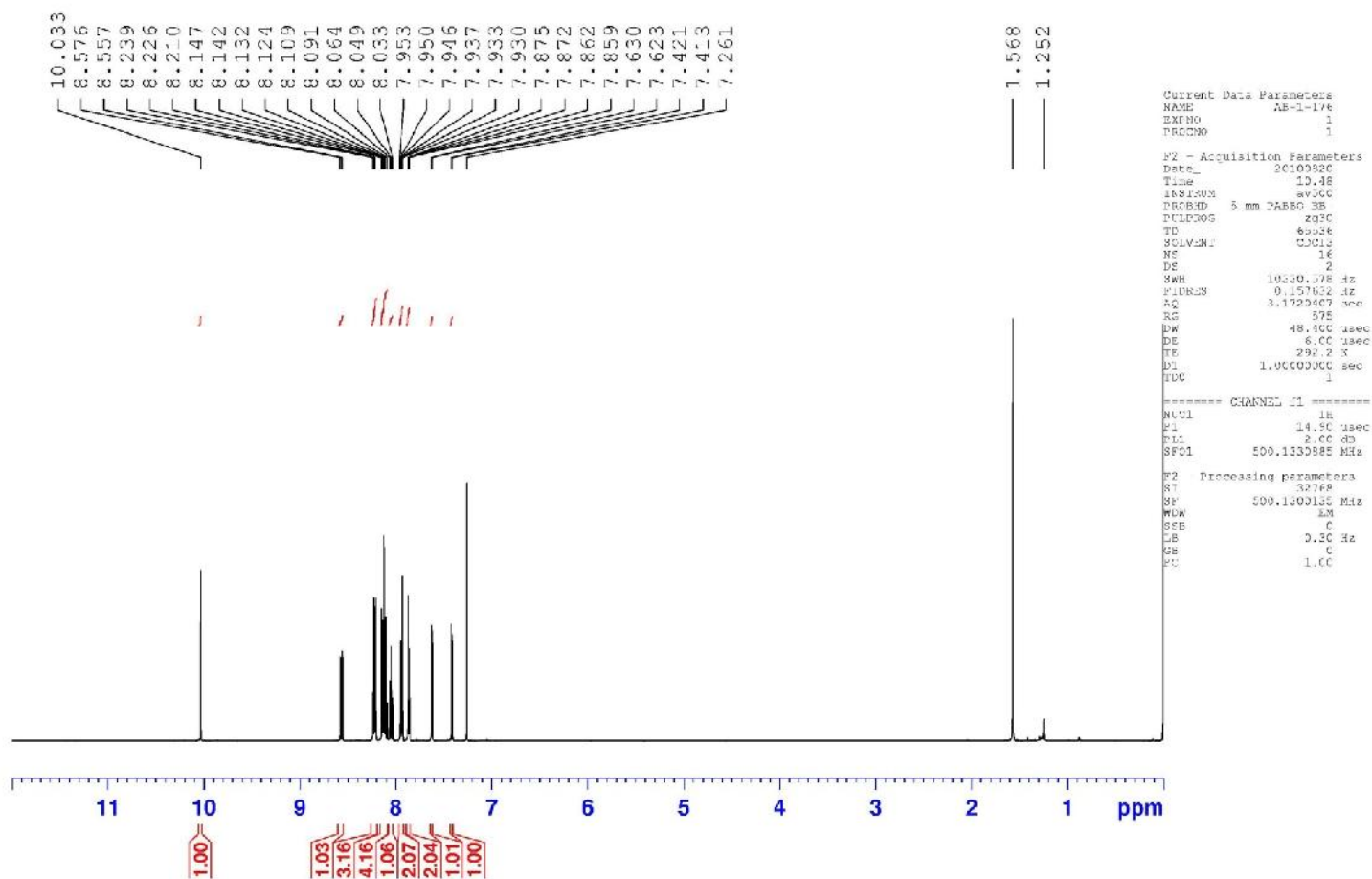


Fig. S21 ^1H NMR spectra of **3c** recorded in CDCl_3 .

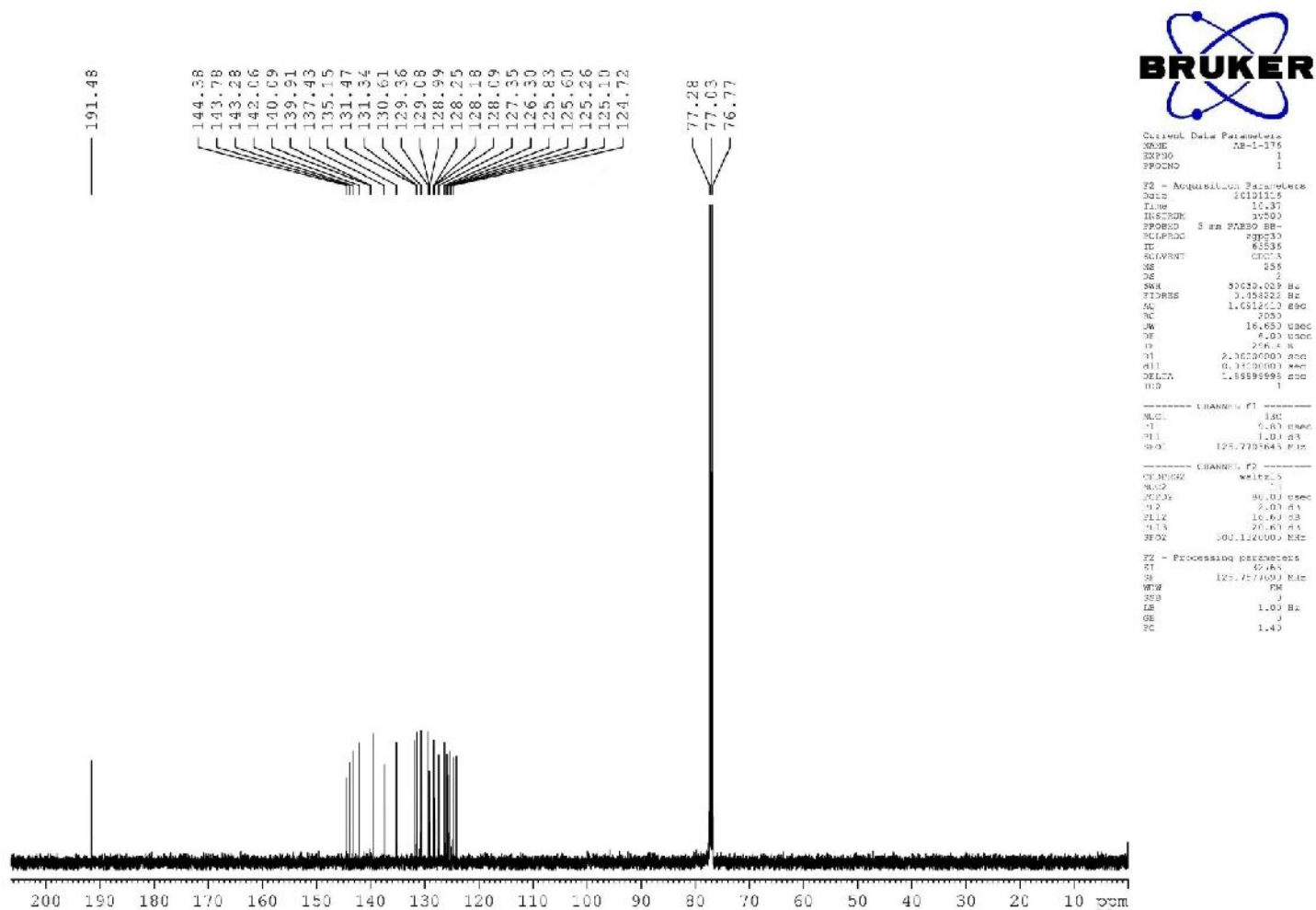


Fig. S22 ^{13}C NMR spectra of **3c** recorded in CDCl_3 .

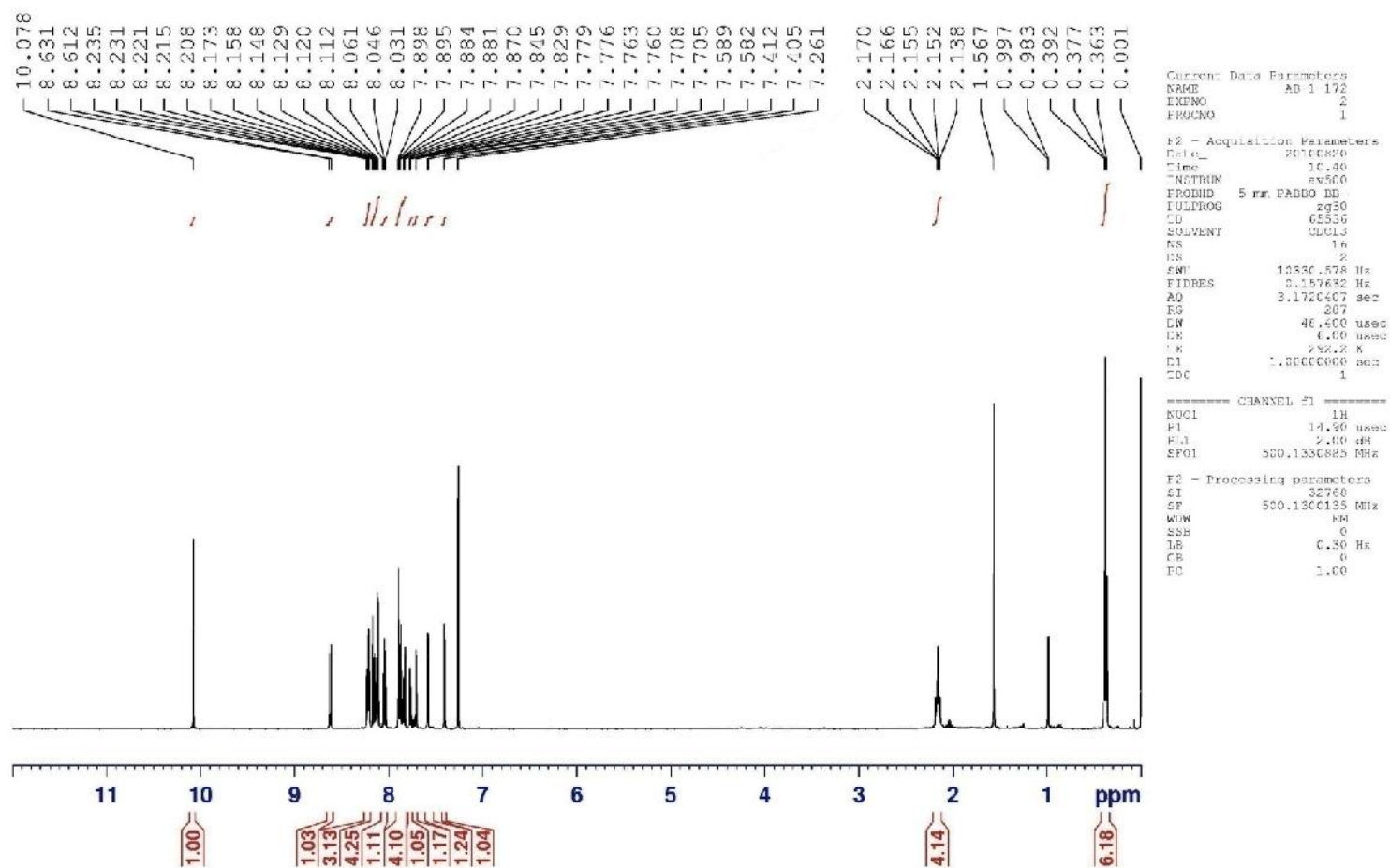


Fig. S23 ^1H NMR spectra of **3d** recorded in CDCl_3 .

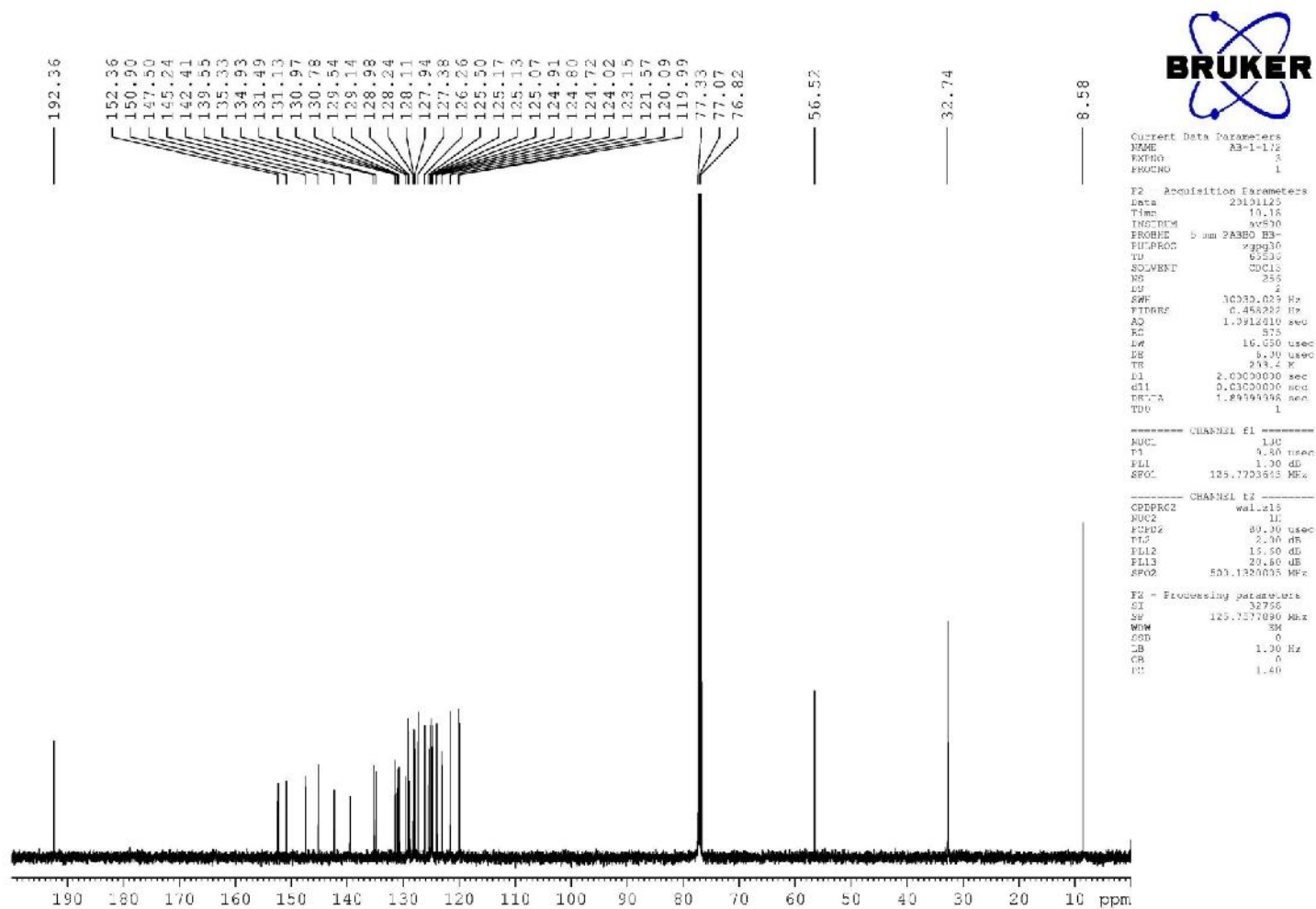


Fig. S24 ^{13}C NMR spectra of **3d** recorded in CDCl_3 .

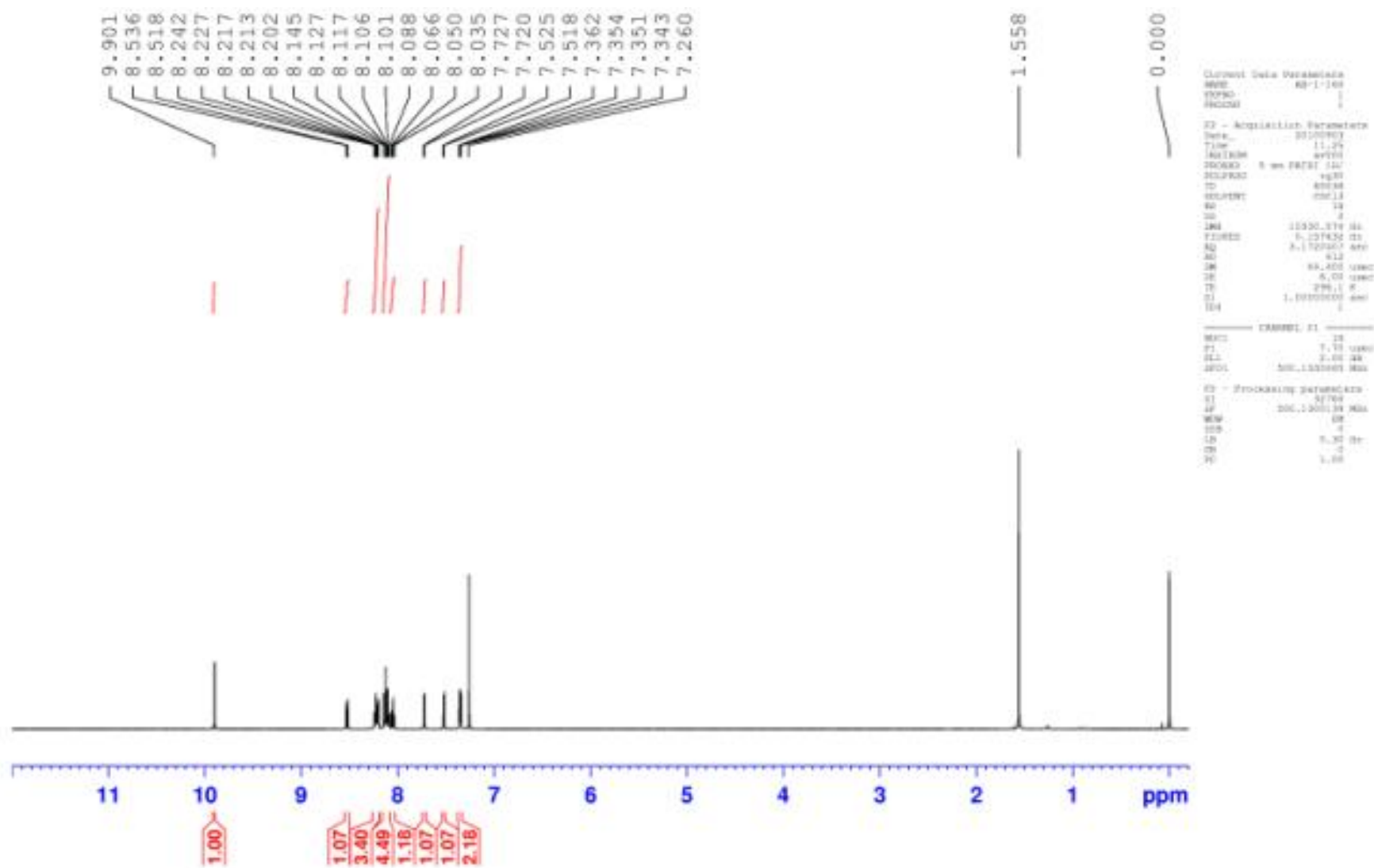


Fig. S25 ¹H NMR spectra of **3e** recorded in CDCl₃.

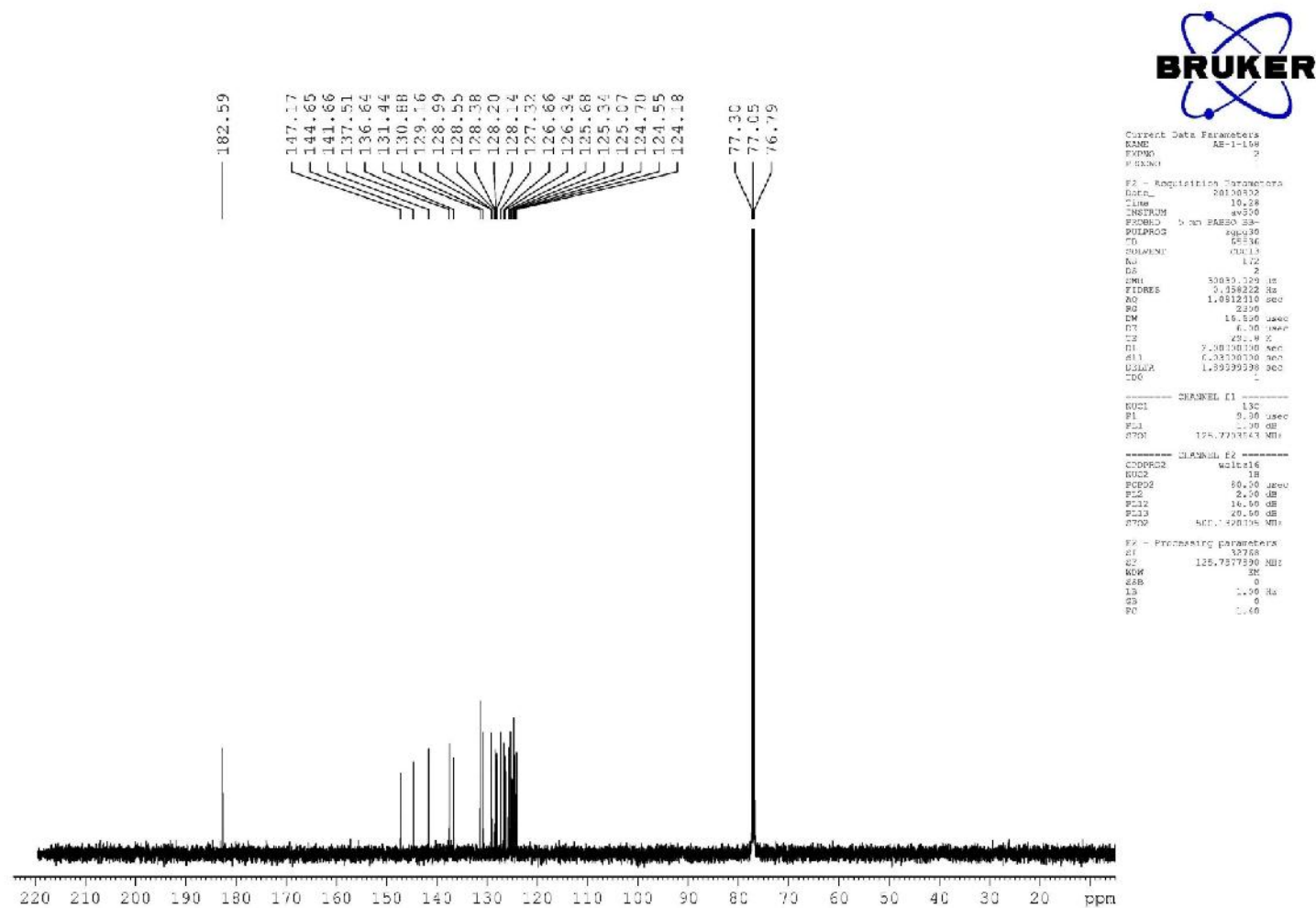


Fig. S26 ^{13}C NMR spectra of **3e** recorded in CDCl_3 .

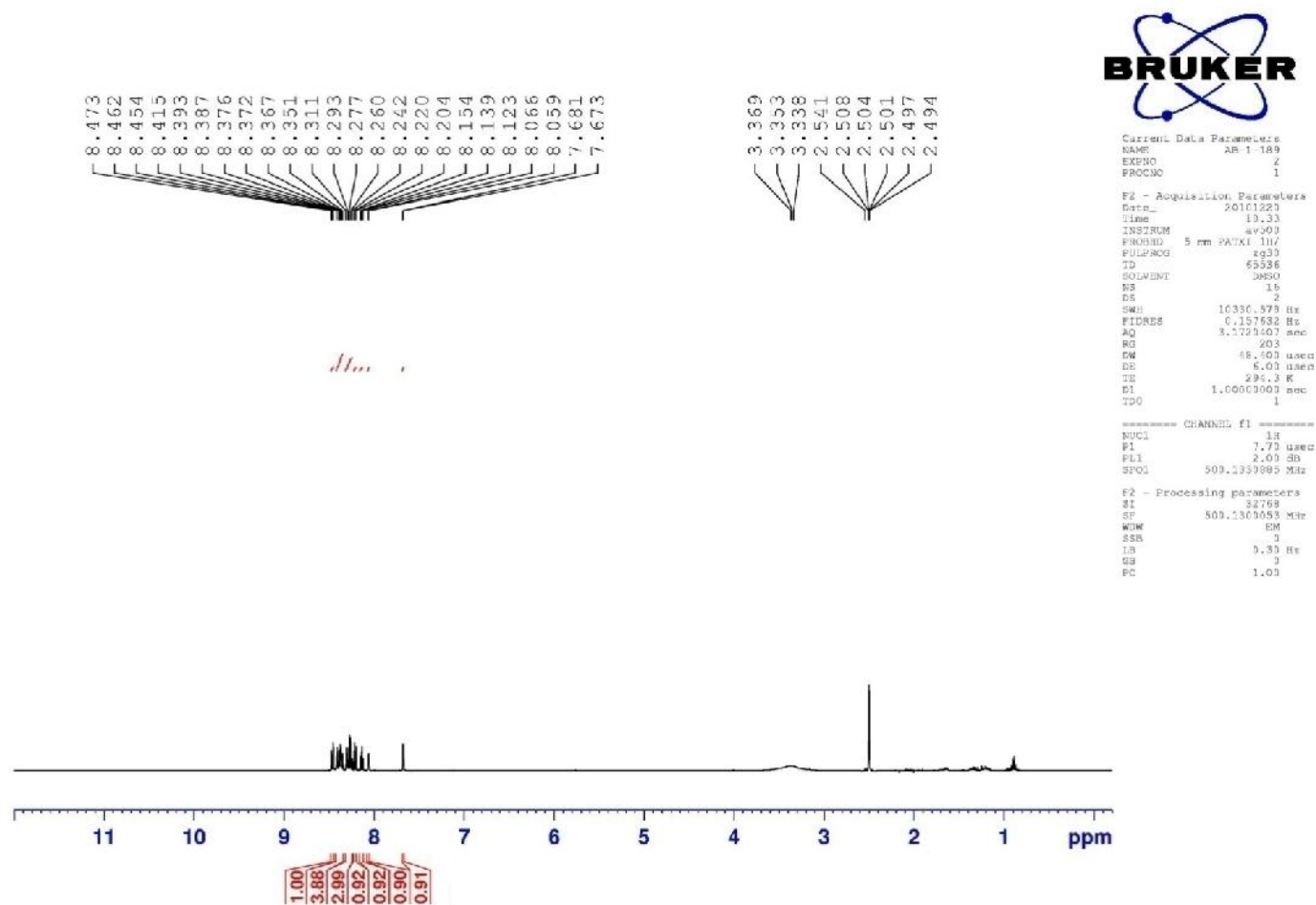


Fig. S27 ^1H NMR spectra of **4a** recorded in DMSO- d_6 .

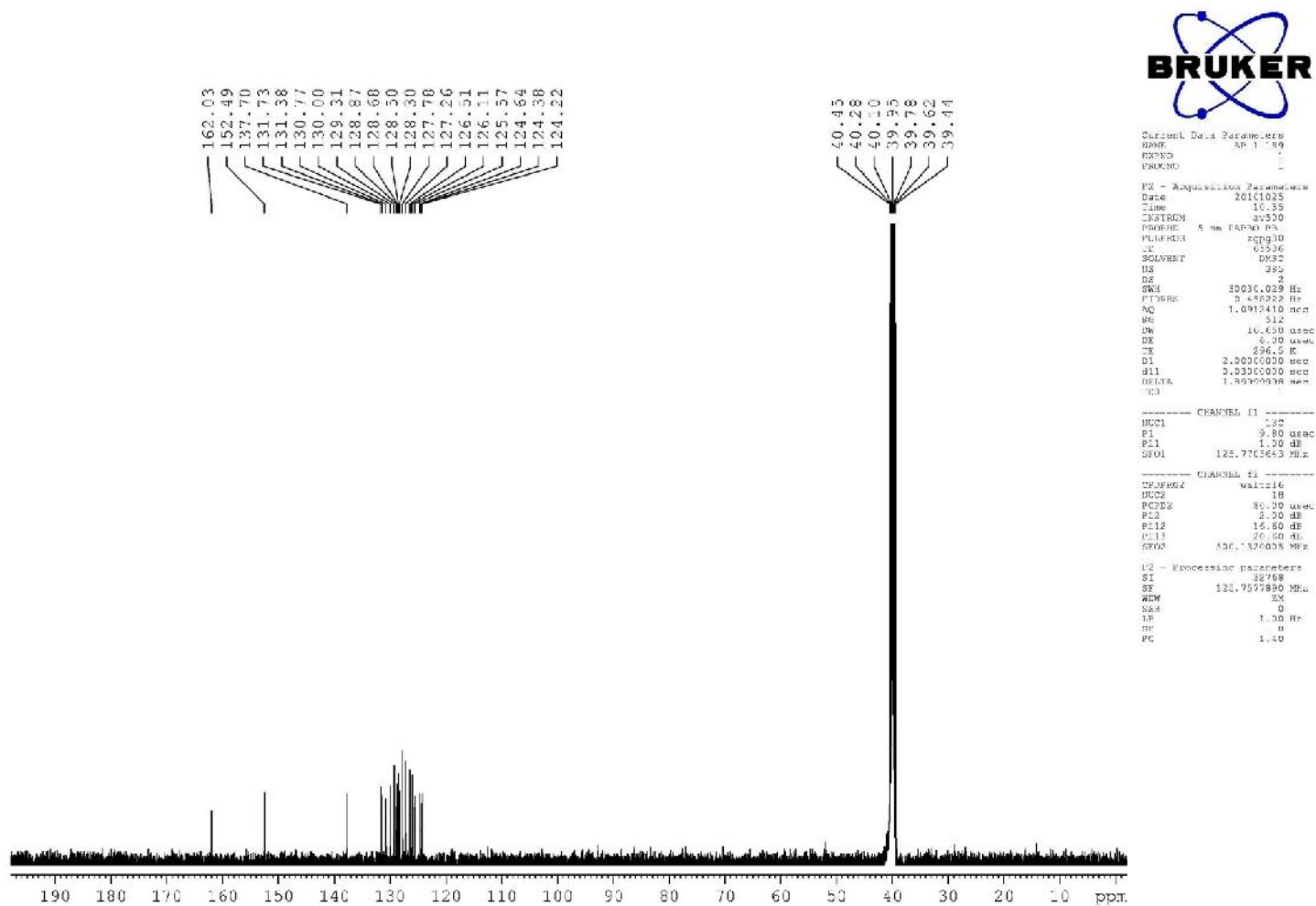


Fig. S28 ^{13}C NMR spectra of **4a** recorded in DMSO- d_6 .

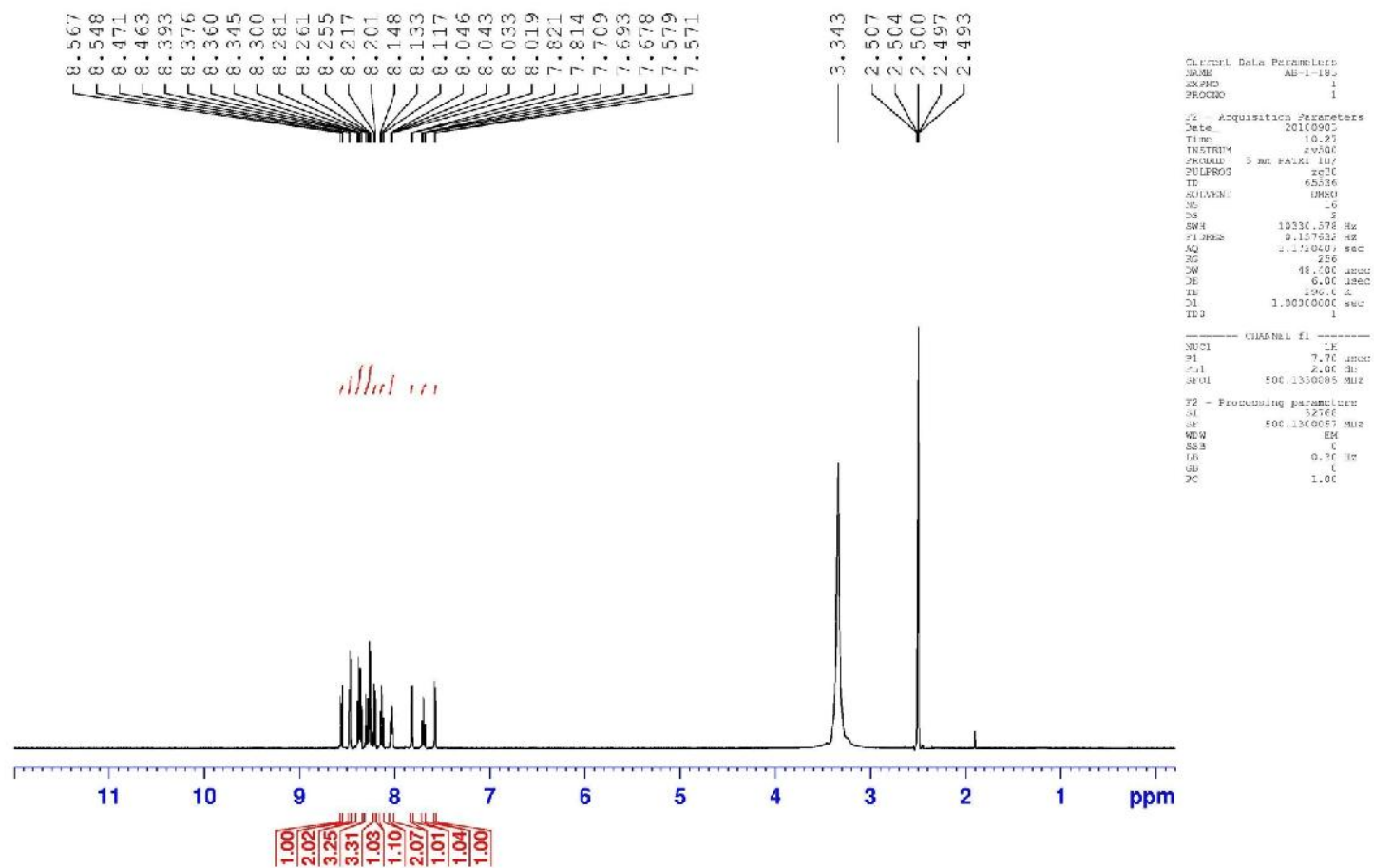


Fig. S29 ¹H NMR spectra of **4b** recorded in DMSO-d₆.

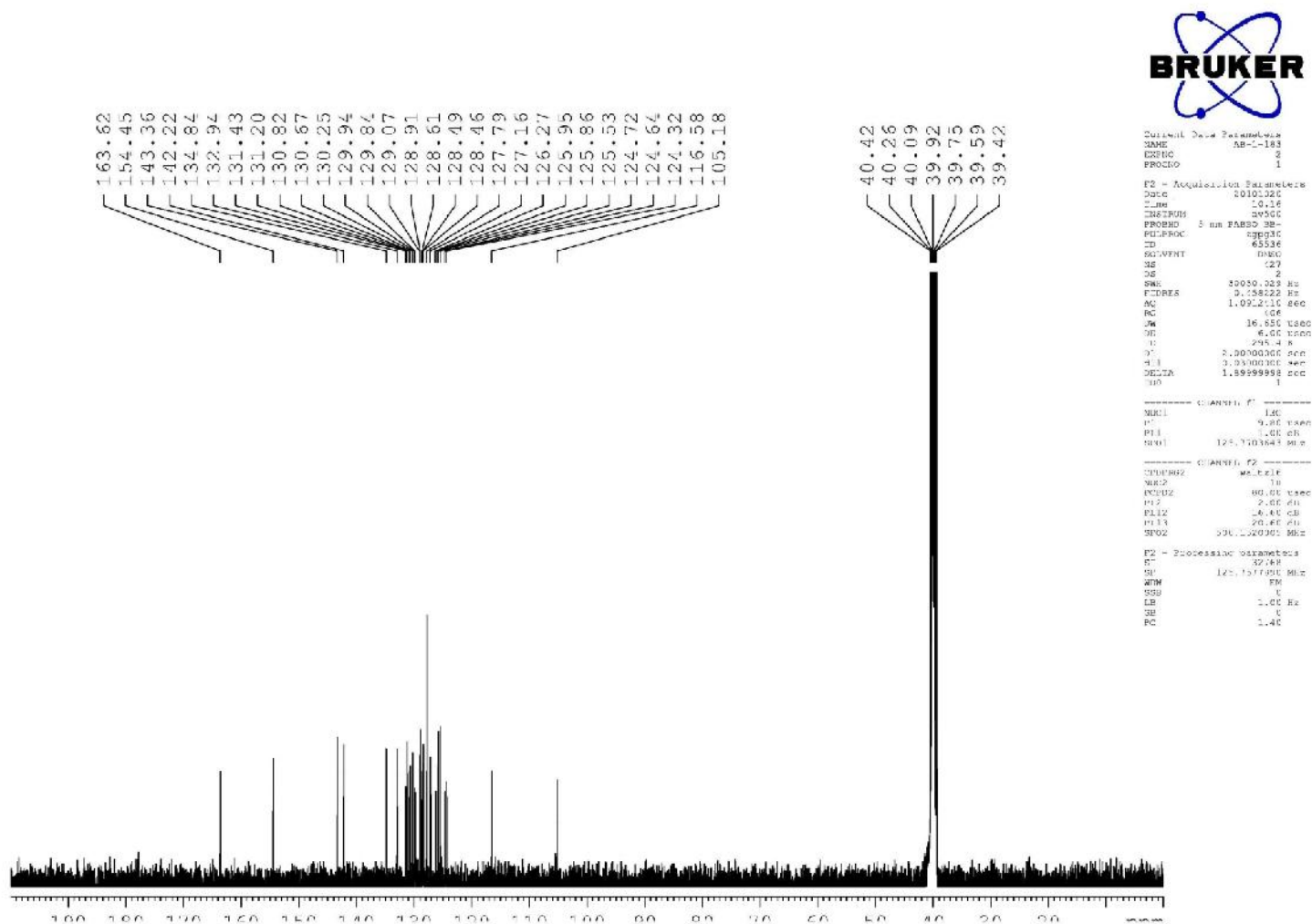


Fig. S30 ^{13}C NMR spectra of **4b** recorded in DMSO- d_6 .

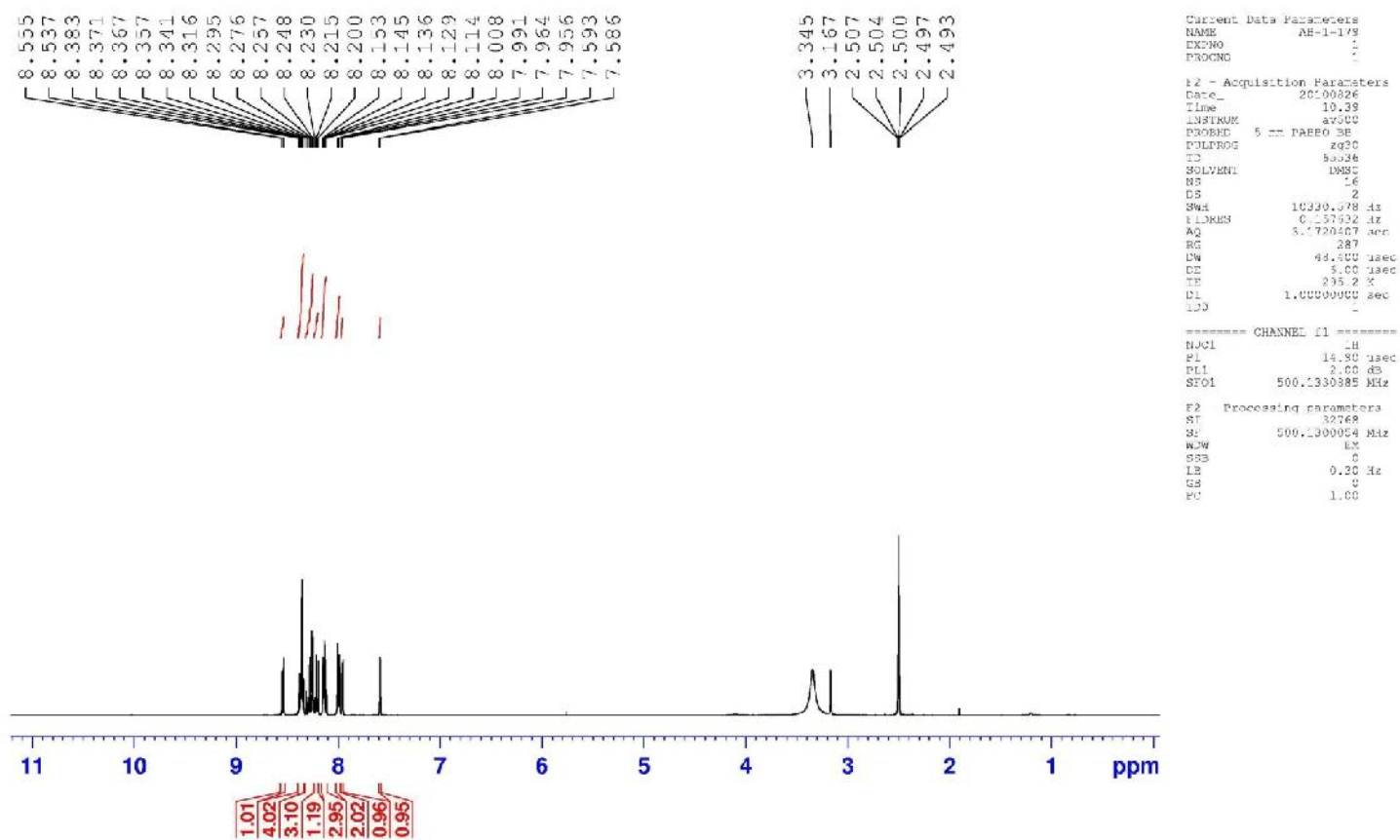


Fig. S31 ^1H NMR spectra of **4c** recorded in DMSO-d_6 .

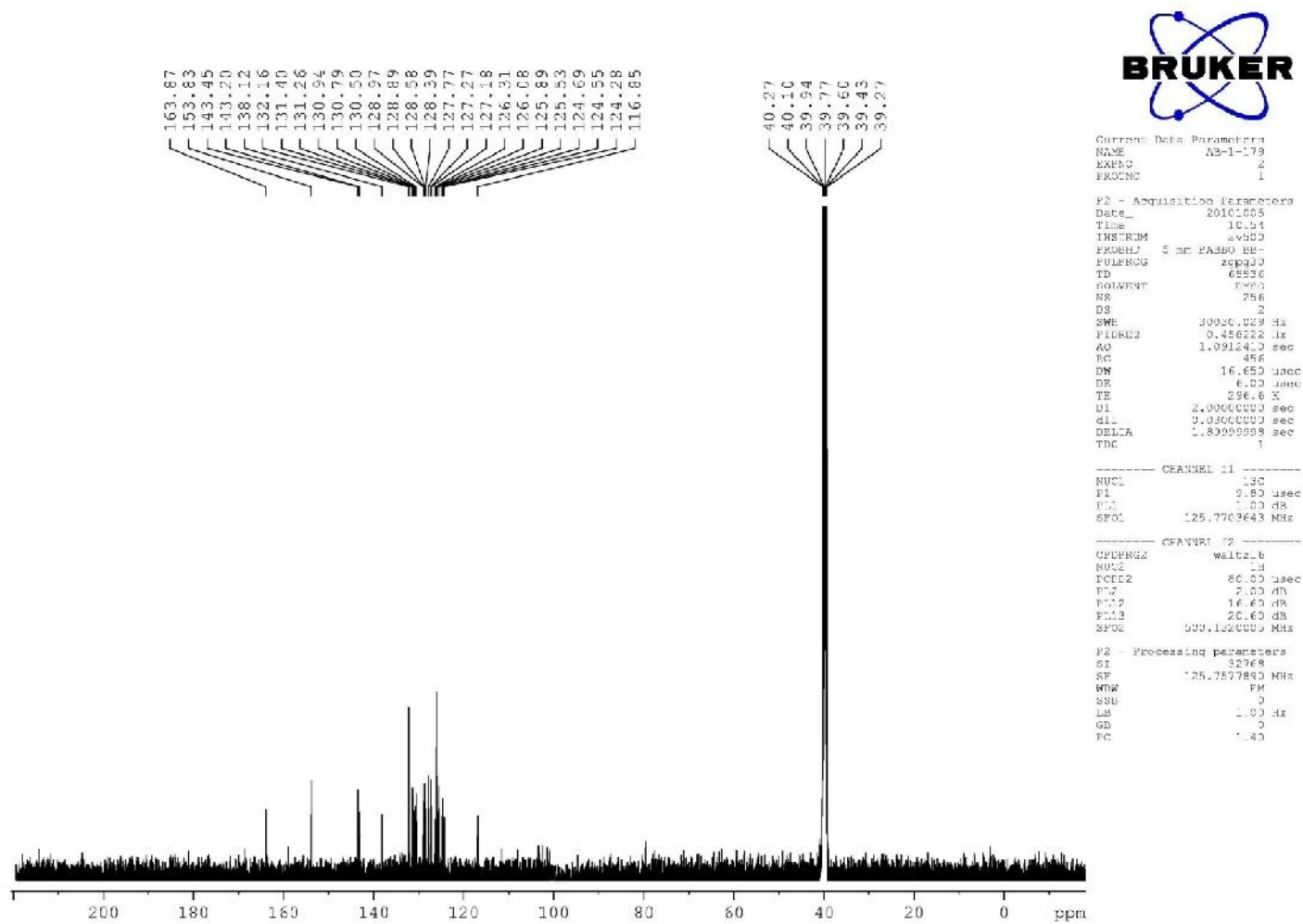


Fig. S32 ¹³C NMR spectra of 4c recorded in DMSO-d₆.

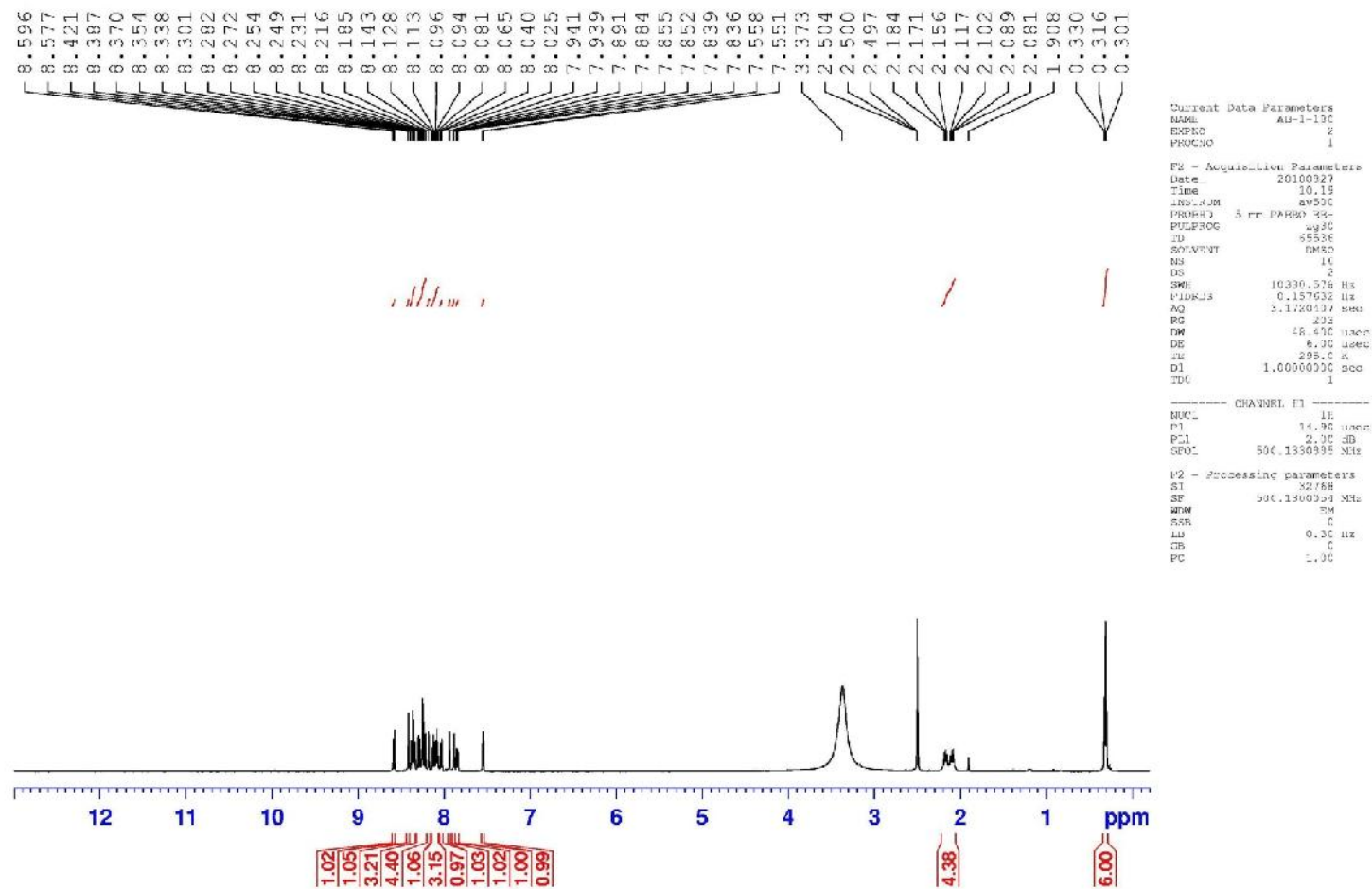


Fig. S33 ^1H NMR spectra of **4d** recorded in DMSO- d_6 .

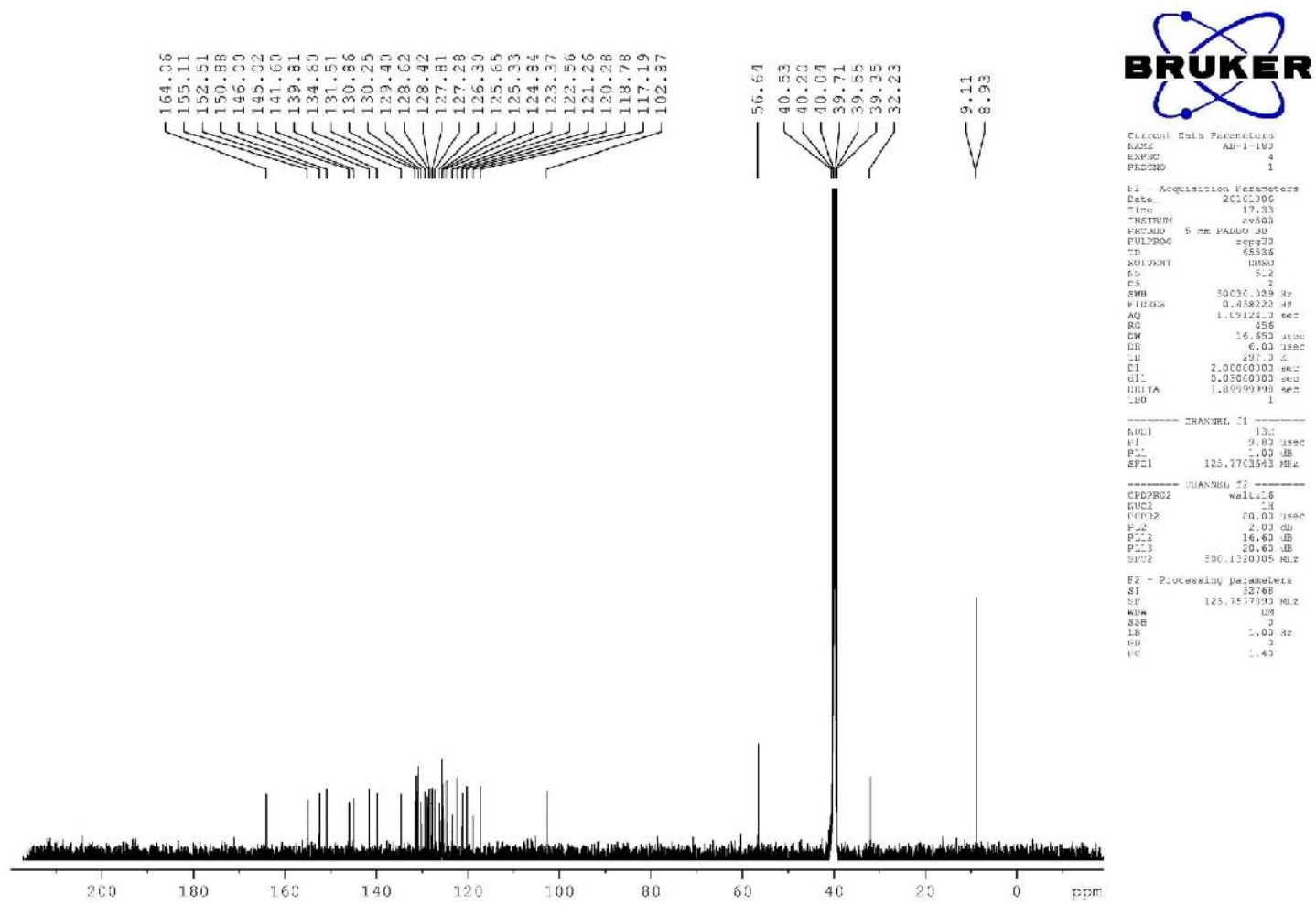


Fig. S34 ¹³C NMR spectra of **4d** recorded in DMSO-d₆.

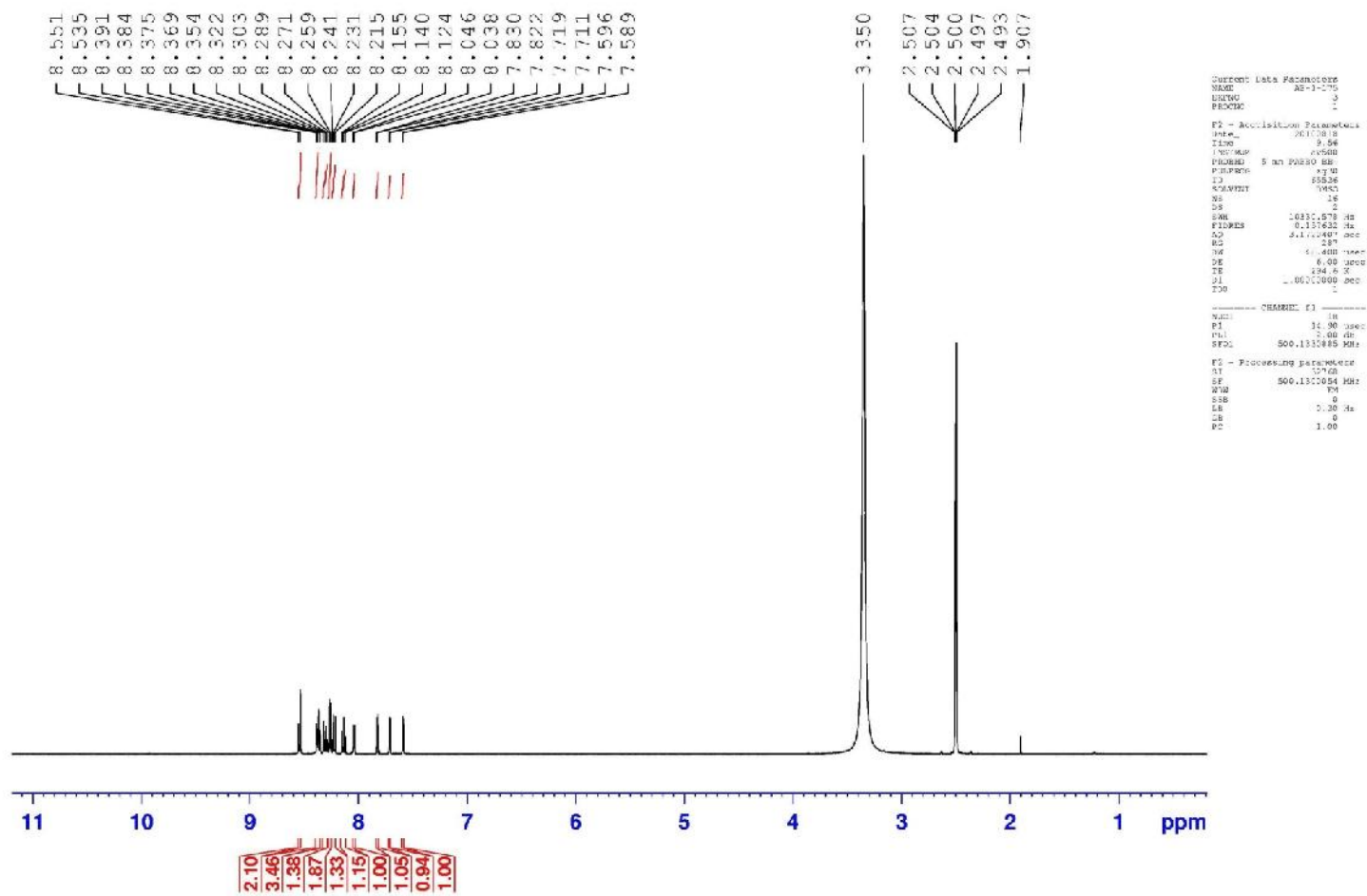


Fig. S35 ^1H NMR spectra of **4e** recorded in DMSO-d_6 .

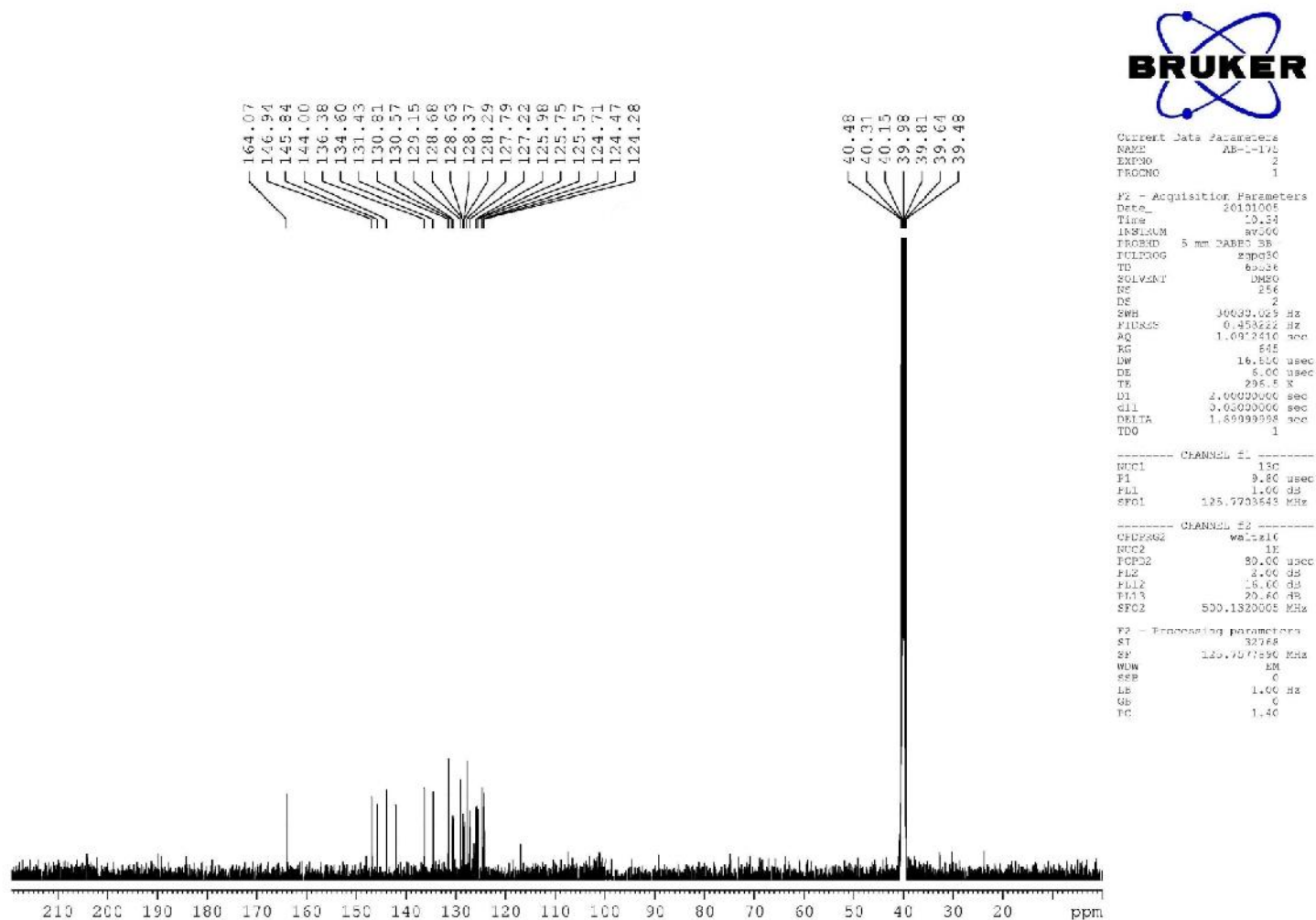


Fig. S36 ^{13}C NMR spectra of **4e** recorded in DMSO- d_6 .

Table S1 XYZ coordinates for the optimized geometry of **4a**.

At. No.	X	Y	Z
6	3.206347000	-0.694936000	0.533784000
6	2.447371000	-1.618228000	1.246260000
6	1.073570000	-1.322708000	1.283678000
6	0.743636000	-0.162381000	0.598992000
16	2.164604000	0.565756000	-0.109732000
1	2.896431000	-2.475134000	1.736967000
1	0.343725000	-1.910057000	1.826637000
6	-0.563674000	0.494831000	0.467096000
6	-0.640928000	1.884983000	0.671098000
6	-1.751032000	-0.227867000	0.157965000
6	-1.848586000	2.563130000	0.624155000
1	0.266667000	2.430984000	0.907950000
6	-2.999903000	0.472670000	0.125282000
6	-1.758754000	-1.628564000	-0.167794000
6	-3.047328000	1.879628000	0.368845000
1	-1.874147000	3.633940000	0.804454000
6	-4.212128000	-0.229427000	-0.157694000
6	-2.915042000	-2.293419000	-0.444053000
1	-0.815429000	-2.158003000	-0.216924000
6	-4.314547000	2.553027000	0.344137000
6	-5.460632000	0.466100000	-0.172403000
6	-4.185037000	-1.629174000	-0.432734000
1	-2.886882000	-3.350482000	-0.694761000
6	-5.468594000	1.877857000	0.089767000
1	-4.331875000	3.622464000	0.535017000
6	-6.638365000	-0.247982000	-0.445385000
6	-5.388129000	-2.301486000	-0.703587000
1	-6.420922000	2.400926000	0.076224000
1	-7.586752000	0.282232000	-0.453060000
6	-6.600615000	-1.616368000	-0.706517000
1	-5.362058000	-3.367049000	-0.914542000
1	-7.522180000	-2.150700000	-0.916890000
6	4.620358000	-0.798227000	0.368872000
6	5.510265000	0.018640000	-0.274292000
1	5.053485000	-1.677812000	0.837196000
6	5.122931000	1.219162000	-0.942601000
7	4.780355000	2.194042000	-1.479362000
6	6.960172000	-0.290376000	-0.319602000
8	7.793455000	0.396363000	-0.871608000
8	7.276282000	-1.442221000	0.330306000
1	8.237745000	-1.538147000	0.233780000

Table S2 XYZ coordinates for the optimized geometry of **4b**.

At. No.	X	Y	Z
6	1.400876000	-1.355312000	0.602404000
6	0.524823000	-2.213182000	1.229685000
6	-0.812158000	-1.738123000	1.272024000
6	-0.985487000	-0.506978000	0.678220000
16	0.545038000	0.066684000	0.041280000
1	0.838570000	-3.145148000	1.686055000
1	-1.619918000	-2.265834000	1.765125000
6	-2.193237000	0.326866000	0.570018000
6	-2.108700000	1.686892000	0.916866000
6	-3.442342000	-0.198437000	0.135501000
6	-3.215828000	2.521168000	0.883058000
1	-1.154219000	2.081300000	1.251251000
6	-4.589258000	0.659684000	0.117356000
6	-3.608382000	-1.551116000	-0.324544000
6	-4.473411000	2.030809000	0.500808000
1	-3.117145000	3.563505000	1.173102000
6	-5.861391000	0.152961000	-0.292454000
6	-4.820469000	-2.029286000	-0.720449000
1	-2.737279000	-2.192852000	-0.372581000
6	-5.641858000	2.864627000	0.483493000
6	-7.008931000	1.005369000	-0.296901000
6	-5.994729000	-1.206539000	-0.705300000
1	-4.912266000	-3.054015000	-1.070766000
6	-6.854246000	2.375101000	0.106193000
1	-5.535713000	3.904134000	0.781740000
6	-8.248536000	0.481699000	-0.697799000
6	-7.254472000	-1.685685000	-1.100175000
1	-7.730391000	3.017884000	0.099566000
1	-9.119900000	1.130874000	-0.698532000
6	-8.368037000	-0.849123000	-1.093202000
1	-7.350796000	-2.721206000	-1.414987000
1	-9.335222000	-1.235407000	-1.400774000
6	2.840479000	-1.526788000	0.379123000
6	3.697195000	-0.429693000	0.218613000
6	3.407051000	-2.814156000	0.320716000
6	5.080837000	-0.583005000	0.003070000
1	3.288223000	0.575155000	0.276725000
6	4.776218000	-2.982513000	0.123809000
1	2.765534000	-3.684726000	0.410460000
6	5.617612000	-1.886698000	-0.038620000
1	5.191442000	-3.984673000	0.082565000
1	6.675635000	-2.044530000	-0.198894000
6	5.849422000	0.644603000	-0.153379000
6	7.175571000	0.863756000	-0.374377000

1	5.256613000	1.551960000	-0.083336000
6	8.160878000	-0.165401000	-0.505663000
7	8.954068000	-1.010287000	-0.610416000
6	7.722732000	2.244822000	-0.502718000
8	8.891005000	2.498510000	-0.700344000
8	6.774225000	3.206433000	-0.375780000
1	7.242589000	4.051159000	-0.477551000

Table S3 XYZ coordinates for the optimized geometry of **4c**.

At. No.	X	Y	Z
6	1.266663000	-0.575916000	0.666594000
6	0.503864000	-1.493534000	1.361461000
6	-0.882731000	-1.207161000	1.359175000
6	-1.214803000	-0.063729000	0.661190000
16	0.229154000	0.663704000	-0.013571000
1	0.933108000	-2.332743000	1.896339000
1	-1.617058000	-1.797772000	1.893624000
6	-2.524435000	0.581074000	0.483554000
6	-2.629521000	1.967012000	0.698911000
6	-3.688558000	-0.151481000	0.117454000
6	-3.842411000	2.631958000	0.604319000
1	-1.739565000	2.520449000	0.981716000
6	-4.944229000	0.533247000	0.037823000
6	-3.664651000	-1.550526000	-0.215291000
6	-5.020337000	1.937116000	0.290759000
1	-3.889442000	3.700624000	0.793896000
6	-6.134284000	-0.181941000	-0.301536000
6	-4.799157000	-2.227822000	-0.545429000
1	-2.712681000	-2.066759000	-0.221891000
6	-6.294242000	2.594569000	0.216950000
6	-7.390175000	0.497814000	-0.364191000
6	-6.077178000	-1.579339000	-0.585063000
1	-4.747241000	-3.283091000	-0.800127000
6	-7.427625000	1.907304000	-0.091698000
1	-6.333802000	3.662072000	0.415839000
6	-8.545813000	-0.228954000	-0.692649000
6	-7.258880000	-2.264456000	-0.911812000
1	-8.385312000	2.418331000	-0.141554000
1	-9.499836000	0.289236000	-0.737180000
6	-8.478943000	-1.594573000	-0.961879000
1	-7.210272000	-3.328113000	-1.128532000
1	-9.383658000	-2.139039000	-1.215377000
6	2.712728000	-0.562627000	0.470470000
6	3.400888000	0.608451000	0.088015000
6	3.473583000	-1.734931000	0.661082000
6	4.774010000	0.619868000	-0.093070000
1	2.848134000	1.532151000	-0.053041000
6	4.846544000	-1.723478000	0.488923000
1	2.977512000	-2.662543000	0.925235000
6	5.538448000	-0.551408000	0.107380000
1	5.254843000	1.544797000	-0.383719000
1	5.408407000	-2.641359000	0.639713000
6	6.975712000	-0.657194000	-0.047570000
6	7.926335000	0.261819000	-0.388467000

1	7.371137000	-1.650637000	0.143862000
6	7.657091000	1.634396000	-0.684938000
7	7.422153000	2.749186000	-0.923271000
6	9.365023000	-0.107676000	-0.479095000
8	10.251770000	0.664019000	-0.775949000
8	9.599210000	-1.414576000	-0.193094000
1	10.558864000	-1.532001000	-0.284656000

Table S4 XYZ coordinates for the optimized geometry of **4d**.

At. No.	X	Y	Z
6	1.207480000	-1.307574000	-0.737551000
6	2.110460000	-2.187337000	-1.296705000
6	3.450286000	-1.722185000	-1.285549000
6	3.603578000	-0.475257000	-0.718311000
16	2.047666000	0.125619000	-0.175583000
1	1.814157000	-3.129489000	-1.743202000
1	4.277031000	-2.268064000	-1.724528000
6	4.810396000	0.354256000	-0.578698000
6	4.749872000	1.706060000	-0.961859000
6	6.037571000	-0.166645000	-0.080380000
6	5.860694000	2.533972000	-0.904592000
1	3.812498000	2.097764000	-1.344272000
6	7.189102000	0.684355000	-0.038116000
6	6.174924000	-1.507477000	0.421678000
6	7.098850000	2.045728000	-0.460922000
1	5.780933000	3.569269000	-1.224293000
6	8.440238000	0.180367000	0.435034000
6	7.366605000	-1.982925000	0.878316000
1	5.297500000	-2.141634000	0.451805000
6	8.271905000	2.872013000	-0.419137000
6	9.593147000	1.025161000	0.462804000
6	8.546762000	-1.168578000	0.888451000
1	7.436552000	-2.998485000	1.259121000
6	9.464952000	2.384681000	0.018115000
1	8.185295000	3.904089000	-0.748042000
6	10.811982000	0.504213000	0.926215000
6	9.786270000	-1.645163000	1.345683000
1	10.345094000	3.021564000	0.042465000
1	11.687524000	1.147517000	0.944516000
6	10.905508000	-0.816313000	1.361090000
1	9.862316000	-2.672611000	1.691107000
1	11.856806000	-1.200596000	1.717058000
6	-0.240370000	-1.460004000	-0.581783000
6	-1.084200000	-0.339197000	-0.432319000
6	-0.818223000	-2.749430000	-0.579347000
6	-2.452604000	-0.511128000	-0.287013000
1	-0.654610000	0.658419000	-0.448176000
6	-2.189555000	-2.926547000	-0.446354000
1	-0.174174000	-3.618481000	-0.661444000
6	-3.532587000	0.562619000	-0.102470000
6	-3.010455000	-1.803764000	-0.297054000
1	-2.608567000	-3.928752000	-0.445823000
6	-4.789395000	-0.313135000	-0.015138000
6	-4.453150000	-1.685116000	-0.133688000

6	-6.114616000	0.061579000	0.131623000
6	-5.443202000	-2.671905000	-0.091604000
6	-7.133533000	-0.924014000	0.169482000
1	-6.379232000	1.103578000	0.227949000
6	-6.767048000	-2.286134000	0.061889000
1	-5.186301000	-3.723325000	-0.178261000
1	-7.546053000	-3.042798000	0.096358000
6	-3.523082000	1.467176000	-1.378206000
6	-4.451201000	2.685255000	-1.432733000
1	-3.731012000	0.818595000	-2.237821000
1	-2.491886000	1.817824000	-1.510524000
1	-4.356176000	3.165363000	-2.412385000
1	-5.505294000	2.428653000	-1.301992000
1	-4.190934000	3.435418000	-0.681547000
6	-3.216225000	1.351751000	1.214183000
6	-4.352470000	2.102107000	1.921677000
1	-2.405650000	2.053204000	0.977657000
1	-2.792778000	0.639287000	1.931130000
1	-3.943191000	2.652706000	2.775239000
1	-4.865674000	2.823126000	1.282417000
1	-5.103336000	1.410500000	2.312703000
6	-8.547316000	-0.641576000	0.315494000
6	-9.241951000	0.533455000	0.387991000
1	-9.174632000	-1.526512000	0.373335000
6	-8.647784000	1.831965000	0.314449000
7	-8.148368000	2.881643000	0.249157000
6	-10.720667000	0.552532000	0.542678000
8	-11.389466000	1.562269000	0.606644000
8	-11.267189000	-0.689514000	0.607766000
1	-12.222734000	-0.546606000	0.705465000

Table S5 XYZ coordinates for the optimized geometry of **4e**.

At. No.	X	Y	Z
6	-1.446570000	-0.453867000	0.157048000
6	-0.941616000	0.604902000	0.889165000
6	0.467348000	0.593178000	1.008480000
6	1.074819000	-0.472912000	0.374371000
16	-0.134880000	-1.477438000	-0.401923000
1	-1.572592000	1.358632000	1.347272000
1	1.024095000	1.323782000	1.582460000
6	2.492464000	-0.857840000	0.331181000
6	2.834541000	-2.199038000	0.583039000
6	3.527953000	0.080647000	0.059403000
6	4.153462000	-2.624055000	0.614094000
1	2.041523000	-2.909195000	0.795396000
6	4.891310000	-0.356380000	0.110078000
6	3.274503000	1.449053000	-0.303238000
6	5.204594000	-1.720378000	0.396621000
1	4.381893000	-3.664063000	0.829483000
6	5.953323000	0.568959000	-0.132077000
6	4.288739000	2.326753000	-0.540027000
1	2.248073000	1.777318000	-0.409929000
6	6.579843000	-2.127078000	0.453805000
6	7.314282000	0.137020000	-0.064679000
6	5.663238000	1.929953000	-0.447534000
1	4.064650000	3.352774000	-0.819468000
6	7.588754000	-1.239618000	0.237809000
1	6.799049000	-3.167695000	0.676732000
6	8.339543000	1.067329000	-0.298959000
6	6.721613000	2.824363000	-0.676809000
1	8.625521000	-1.561318000	0.286675000
1	9.373459000	0.737588000	-0.244585000
6	8.044508000	2.395510000	-0.600165000
1	6.495729000	3.859483000	-0.917906000
1	8.851394000	3.099795000	-0.779234000
6	-2.818802000	-0.759755000	-0.159756000
6	-3.324759000	-1.887796000	-0.795806000
16	-4.101883000	0.352956000	0.258386000
6	-4.719118000	-1.860655000	-0.939055000
1	-2.699095000	-2.704930000	-1.134999000
6	-5.323436000	-0.718442000	-0.420109000
1	-5.294937000	-2.652669000	-1.405371000
6	-6.727998000	-0.484086000	-0.450793000
6	-7.472895000	0.566926000	0.016410000
1	-7.295271000	-1.279314000	-0.926420000
6	-6.897225000	1.698036000	0.668724000
7	-6.399554000	2.608662000	1.197395000

6	-8.947772000	0.601076000	-0.124585000
8	-9.657250000	1.502345000	0.270168000
8	-9.445246000	-0.498118000	-0.752608000
1	-10.406345000	-0.363741000	-0.785571000

Table S6 Photophysical data for the dyes measured in different solvents.

Dye	λ_{abs} , nm				λ_{em} , nm				Stokes shift, cm^{-1}			
	TOL	ACN	DCM	DMF	TOL	ACN	DCM	DMF	TOL	ACN	DCM	DMF
4a	416	394	420	394	528	501	565	494	5099	5420	6110	5137
4b	364	361	363	368	469	457	442	448	6151	5819	4924	4852
4c	445	408	457	411	533	502	575	501	3710	4589	4491	4371
4d	410	389	415	385	518	483	505	485	5085	5003	4294	5355
4e	415	383	420	385	553	529	584	521	6013	7206	6686	6999