Organic dyes containing fluoren-9-ylidene chromophores for efficient dye-sensitized solar cells

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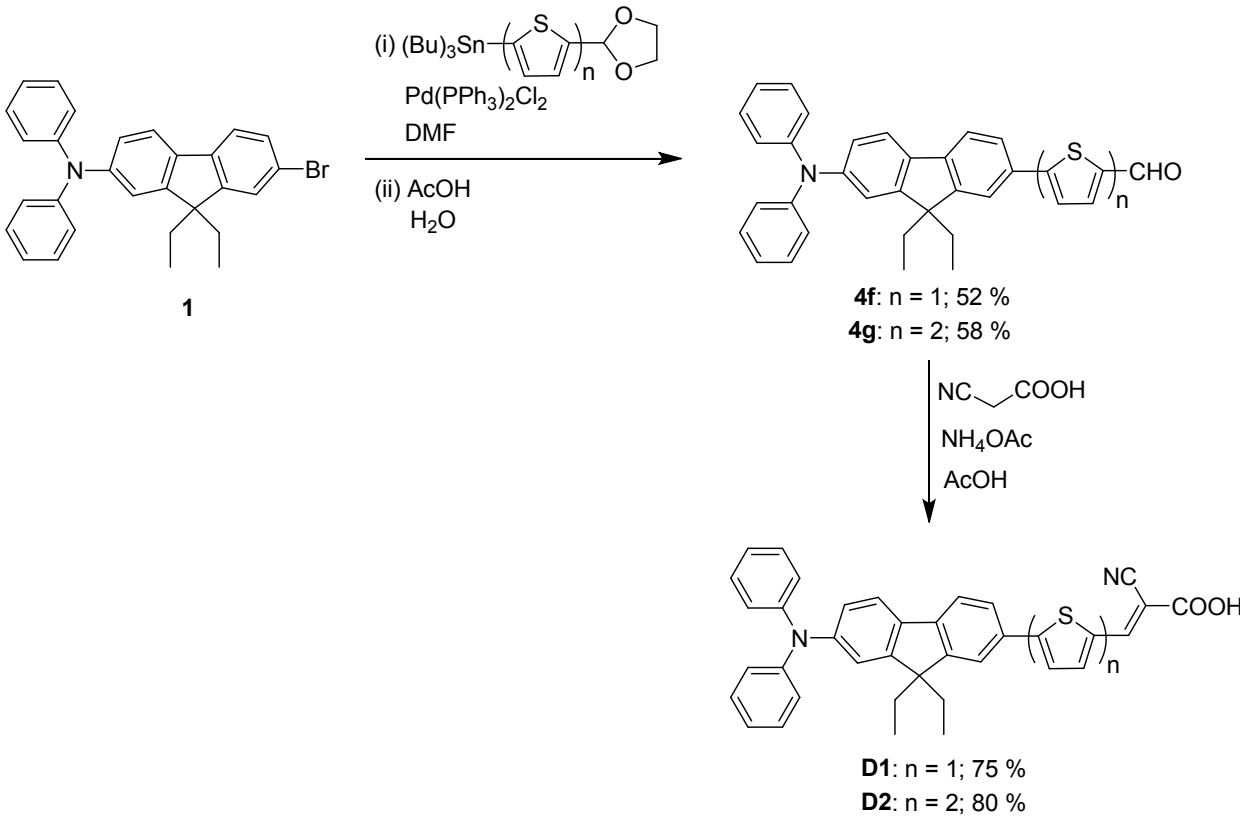
Electronic Supplementary Information

Synthesis of the reference dyes D1 and D2.



Scheme S1 Synthesis of the reference dyes **D1** and **D2**

Synthesis of 5-(7-(diphenylamino)-9,9-diethyl-9*H*-fluoren-2-yl)thiophene-2-carbaldehyde (4f). A mixture of (5-(1,3-dioxolan-2-yl)thiophen-2-yl)tributylstannane (0.77 mmol), **1** (0.30 g, 0.64 mmol), dry DMF (4 mL) was maintained at nitrogen atmosphere. After the addition of $Pd(PPh_3)_2Cl_2$ (4.5 mg, 1 mol%) it was heated at 80 °C for 24 h. On completion of the reaction, the mixture was poured into water and extracted with dichloromethane. The organic layer was washed with brine solution followed by water and dried over anhydrous Na_2SO_4. The volatiles were removed to obtain a solid residue. It was dissolved in glacial acetic acid (5 mL) and heated to 60 °C. After 30 min, it was treated with 10 mL water and the heating continued for further 6 h. The cooled solution was extracted with chloroform. The chloroform layer was washed liberally with water and dried over anhydrous Na_2SO_4. On removal of solvent a dark residue obtained was

purified by column chromatography on silica gel using hexane/chloroform (2:3) as eluant. yellow solid; yield 0.17 g (52 %); mp 158-160 °C; IR (KBr, cm^{-1}) 1660 ($\nu_{C=O}$); ^1H NMR (500 MHz, $CDCl_3$) δ 0.38 (t, J = 7.5 Hz, 6 H), 1.91-2.00 (m, 4 H), 7.02-7.06 (m, 3 H), 7.10-7.14 (m, 5 H), 7.25-7.26 (m, 1 H), 7.27-7.28 (m, 3 H), 7.45 (d, J = 4.0 Hz, 1 H), 7.57-7.59 (m, 2 H), 7.63 - 7.67 (m, 2 H), 7.75 (d, J = 4.0 Hz, 1 H), 9.89 (s, 1 H); ^{13}C NMR (125.77 MHz, $CDCl_3$) δ 182.7, 155.4, 151.8, 150.9, 148.0, 147.9, 143.1, 141.8, 137.6, 135.3, 130.9, 129.3, 125.7, 124.1, 123.6, 123.4, 122.8, 120.6, 120.6, 119.6, 118.3, 56.3, 32.7, 8.6.

Synthesis of 5'-(7-(diphenylamino)-9,9-diethyl-9H-fluoren-2-yl)-[2,2'-bithiophene]-5-carbaldehyde (4f). It was obtained from (5'-(1,3-dioxolan-2-yl)-2,2'-bithiophen-5-yl)tributylstannane (0.77 mmol) and **3a** (0.30 g, 0.64 mmol) by following a procedure described above for **4f**. Orange solid; yield 0.22 g (58%); mp 138-140 °C; IR (KBr, cm^{-1}) 1665 ($\nu_{C=O}$); ^1H NMR (500 MHz, $CDCl_3$) δ 0.37-0.40 (m, 6 H), 1.90-2.02 (m, 4 H), 7.00-7.05 (m, 3 H), 7.08-7.16 (m, 7 H), 7.24-7.26 (m, 1 H), 7.27-7.28 (m, 2 H), 7.32 (d, J = 3.5 Hz, 1 H), 7.36 (d, J = 4.0 Hz, 1 H), 7.49-7.51 (m, 1 H), 7.55 -7.59 (m, 2 H), 7.62-7.63 (m, 1 H), 7.69 (d, J = 4.0 Hz, 1 H), 9.87 (s, 1 H); ^{13}C NMR (125.77 MHz, $CDCl_3$) δ 182.5, 151.6, 151.5, 150.9, 148.0, 147.9, 147.6, 147.4, 147.4, 147.2, 141.9, 141.4, 137.5, 135.9, 135.8, 134.5, 131.4, 129.3, 129.2, 127.3, 127.1, 125.0, 124.9, 124.0, 123.9, 123.9, 123.8, 123.6, 123.5, 123.3, 122.9, 122.7, 122.6, 120.6, 120.4, 120.0, 119.8, 119.6, 119.5, 119.3, 119.1, 56.24, 56.20, 32.9, 8.6.

Synthesis of (E)-2-cyano-3-(5-(7-(diphenylamino)-9,9-diethyl-9H-fluoren-2-yl)thiophen-2-yl)acrylic acid (D1). A mixutre of 5-(7-(diphenylamino)-9,9-diethyl-9*H*-fluoren-2-yl)thiophene-2-carbaldehyde (0.10 g, 0.2 mmol) (**4f**), cyanoacetic acid (0.024 g, 0.28 mmol), acetic acid (5 ml) and ammonium acetate (4 mg) was heated at 120 °C for 12 h. The resulting red solution was poured into ice-cold water to produce a red precipitate. This was filtered and washed thoroughly with water and dried. The solid was further crystallized from hot chloroform. Red solid; yield 0.085 g (75%); mp 272-274 °C; IR (KBr, cm^{-1}) 2210 ($\nu_{C\equiv N}$); ^1H NMR (500 MHz, DMSO-d_6) δ 0.28 (t, J = 7.0 Hz, 1 H), 1.88-1.92 (m, 2 H), 2.01-2.05 (m, 2 H), 6.96 (d, J = 7.5 Hz, 1 H), 7.03-7.08 (m, 7 H), 7.31 (t, J = 7.0 Hz, 4 H), 7.75-7.79 (m, 2 H), 7.81-7.84 (m, 2 H), 8.02 (d, J = 4.0 Hz, 1 H), 8.49 (s, 1 H); ^{13}C NMR (125.77 MHz, DMSO-d_6) δ 164.3, 151.8, 151.2, 148.0, 147.6, 146.9, 146.8, 146.4, 141.7, 136.1, 134.4, 134.2, 131.6, 130.1, 129.0, 125.8, 125.4, 124.0, 124.0, 123.4, 121.8, 120.9, 120.3, 119.5, 117.2, 56.2, 32.3, 9.1.

Synthesis of (E)-2-cyano-3-(5'-(7-(diphenylamino)-9,9-diethyl-9H-fluoren-2-yl)-[2,2'-bithiophen]-5-yl)acrylic acid (D2). It was prepared in 80% yield from **4g** by following a procedure similar to that described above for **D1**. Red solid; mp 280-282 °C; IR (KBr, cm^{-1}) 2215 ($\nu_{C\equiv N}$); ^1H NMR (500 MHz, DMSO-d_6) δ 0.28 (t, J = 7.0 Hz, 1 H), 1.87-1.90 (m, 2 H), 2.02-2.06 (m, 2 H), 6.95-6.97 (m, 1 H), 7.02-7.05 (m, 6 H), 7.07 (d, J = 1.0 Hz, 1 H), 7.30 (t, J = 8.0 Hz, 4 H), 7.63 (d, J = 4.0 Hz, 1 H), 7.67-7.71 (m, 3 H), 7.75-7.78 (m, 3 H), 7.99 (d, J = 4.0 Hz, 1 H), 8.50 (s, 1 H); ^{13}C NMR (125.77 MHz, DMSO-d_6) δ 164.1, 151.7, 151.0, 147.6, 147.5,

146.8, 146.6, 146.2, 142.1, 141.6, 136.0, 134.3, 134.0, 131.5, 130.0, 128.9, 125.7, 125.3, 123.9, 123.8, 123.3, 121.7, 120.4, 120.2, 119.3, 117.1, 56.3, 32.1, 9.0.

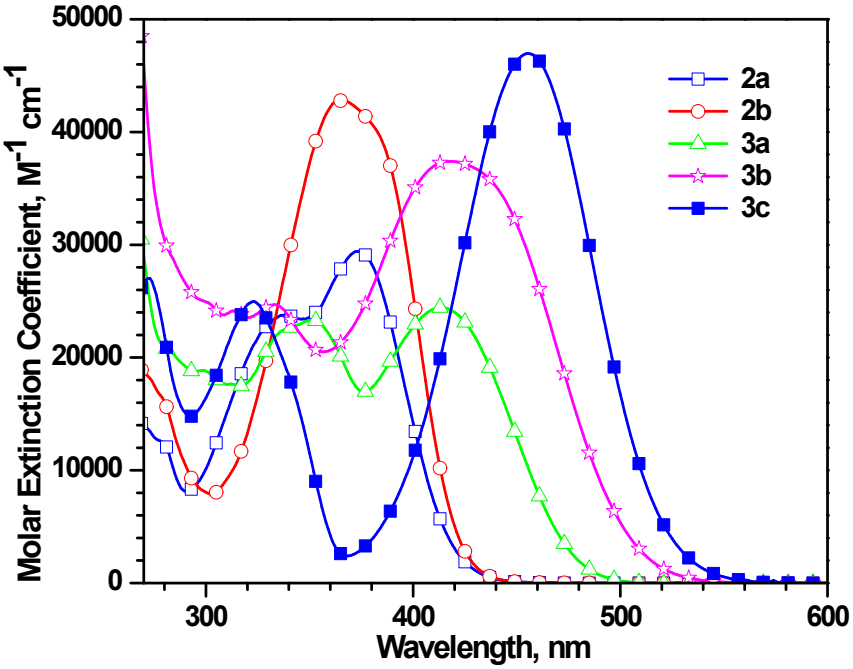


Fig. S1 Absorption spectra of the aryl bromides (**2a**, **2b** and **3a**-**3c**) recorded in dichloromethane

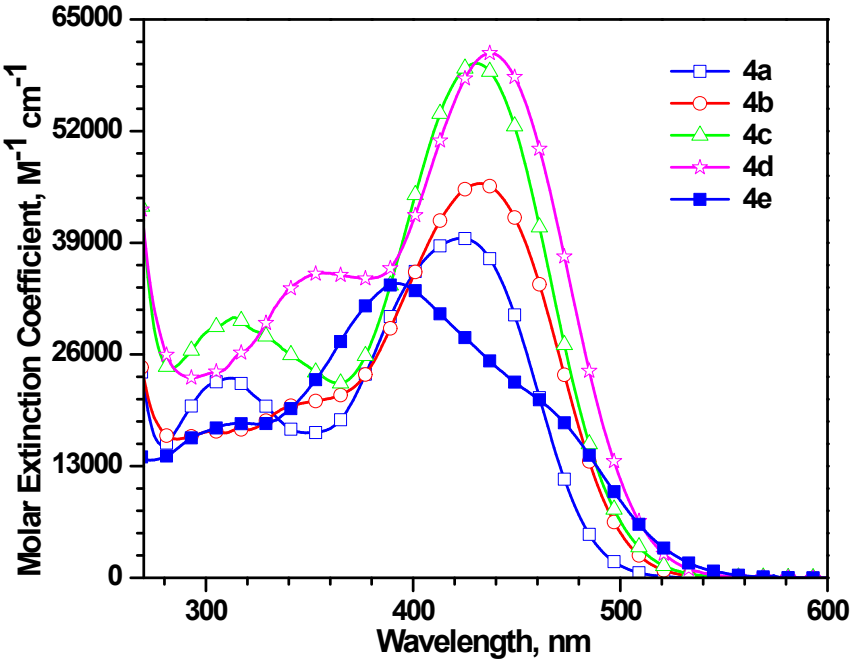


Fig. S2 Absorption spectra of the aldehydes (**4a**-**4e**) recorded in dichloromethane

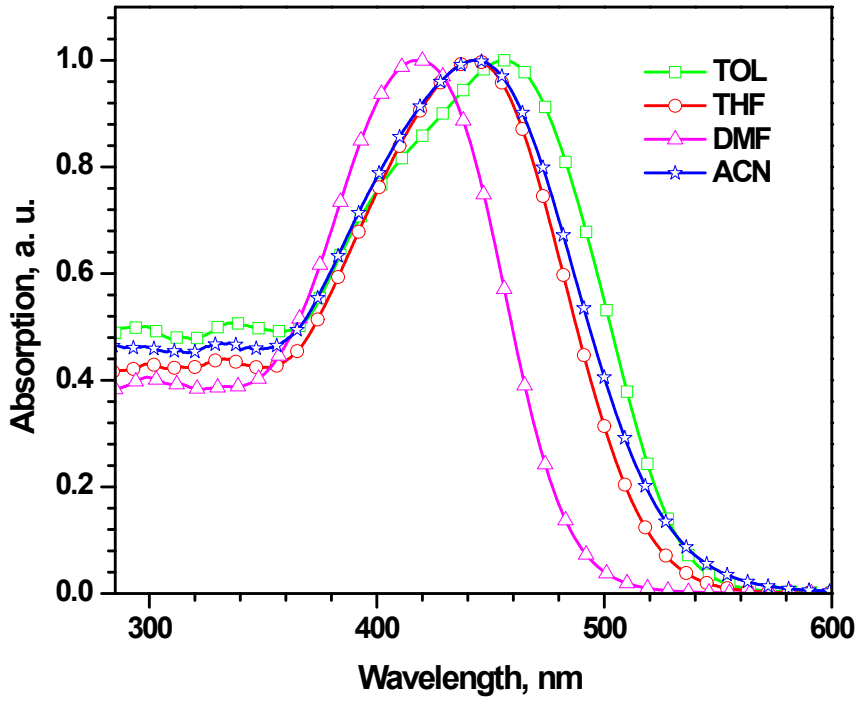


Fig. S3 Absorption spectra of the dye **5a** recorded in different solvents

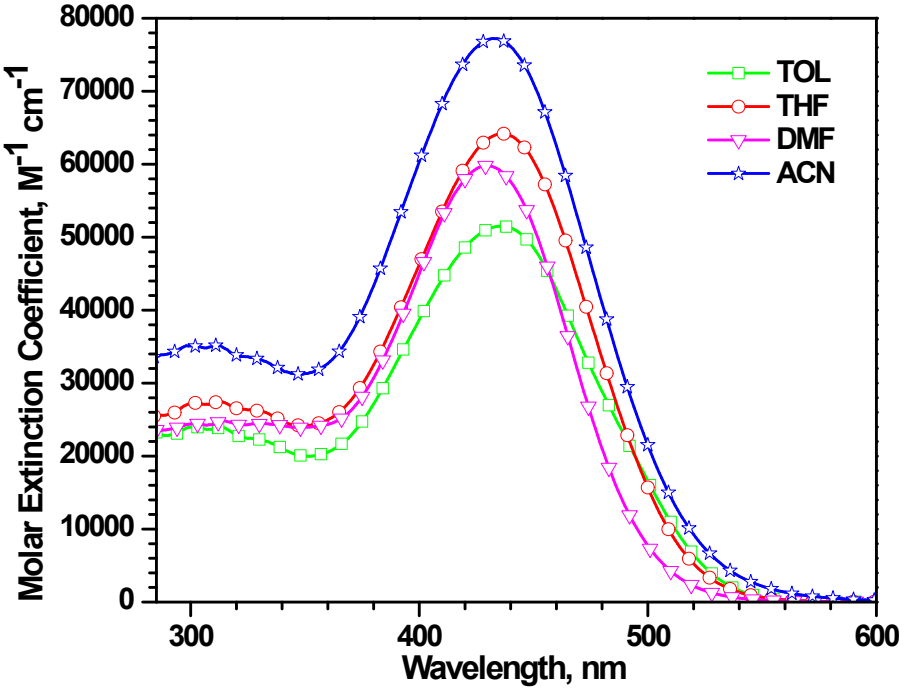


Fig. S4 Absorption spectra of the dye **5c** recorded in different solvents

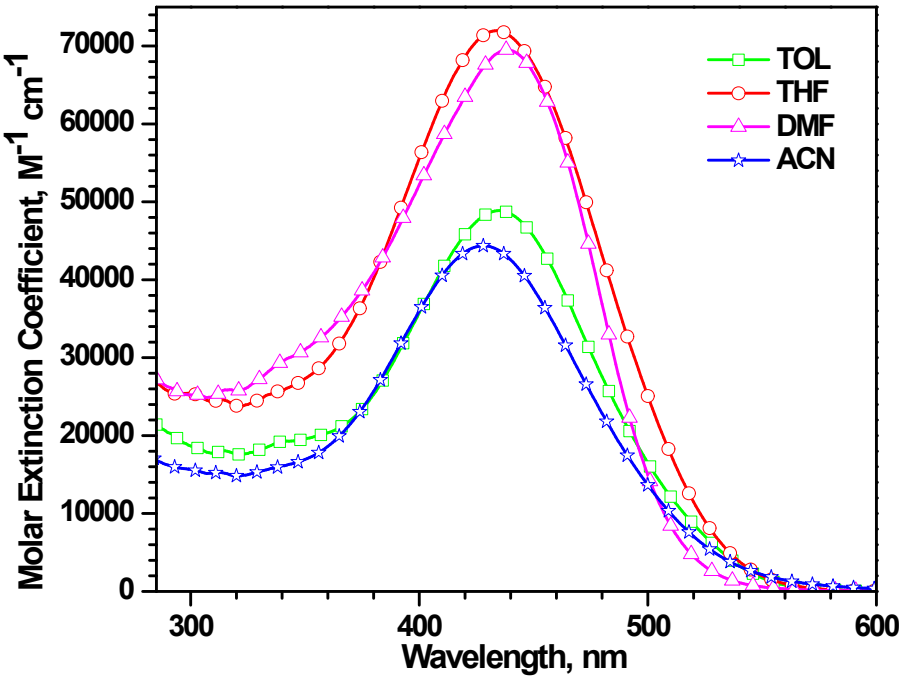


Fig. S5 Absorption spectra of the dye **5d** recorded in different solvents

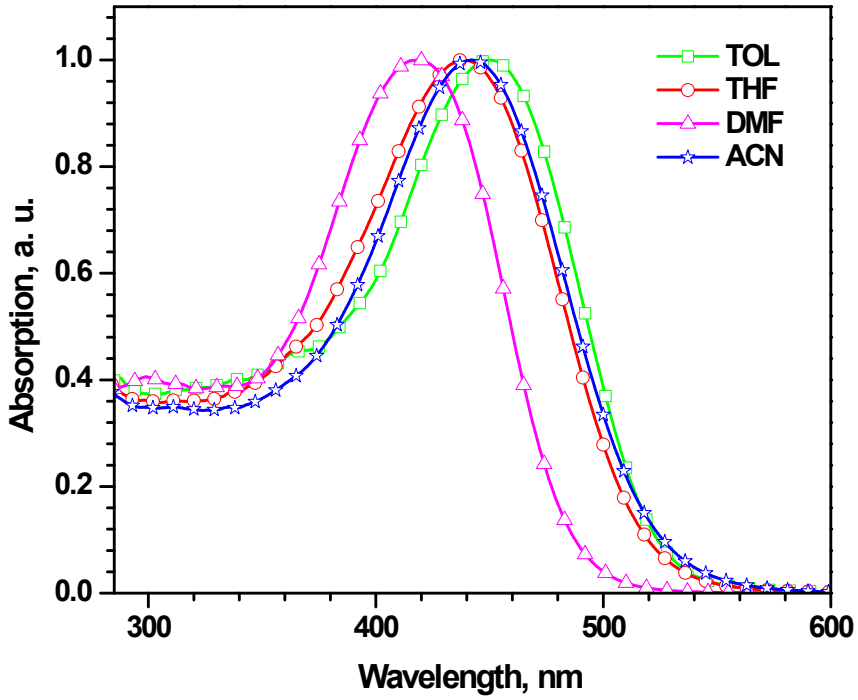


Fig. S6 Absorption spectra of the dye **5e** recorded in different solvents.

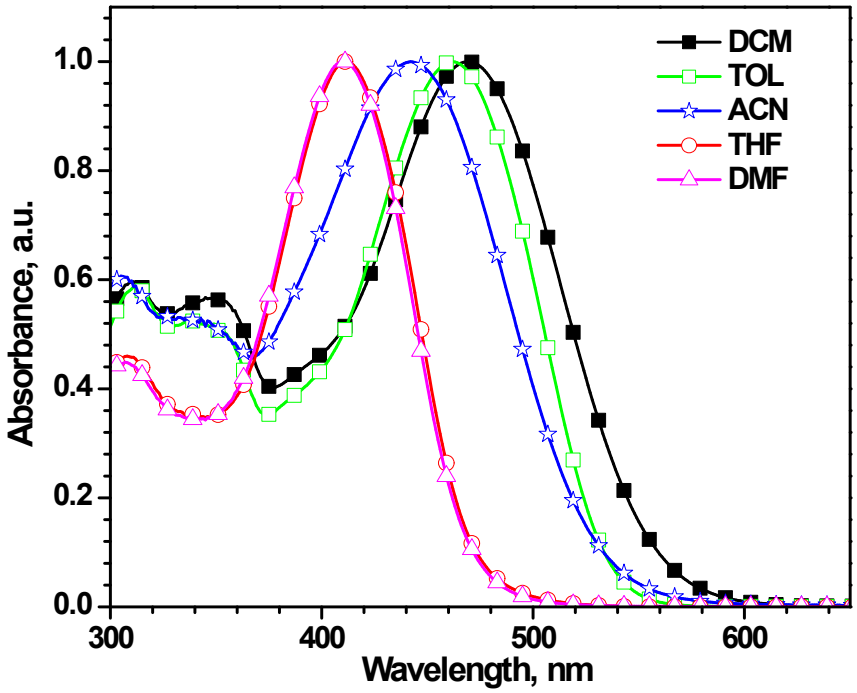


Fig. S7 Absorption spectra of the dye **D1** recorded in different solvents.

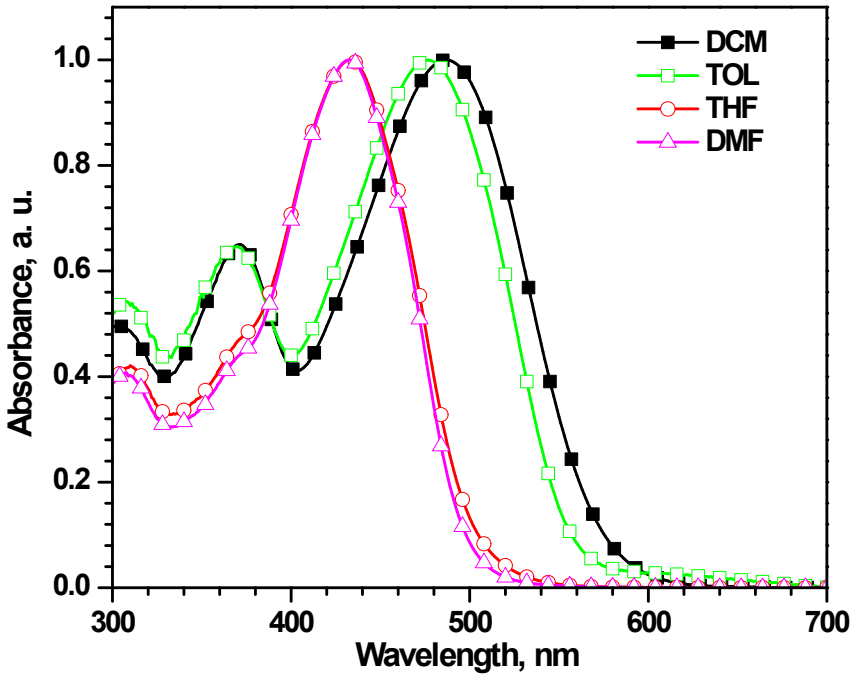


Fig. S8 Absorption spectra of the dye **D2** recorded in different solvents.

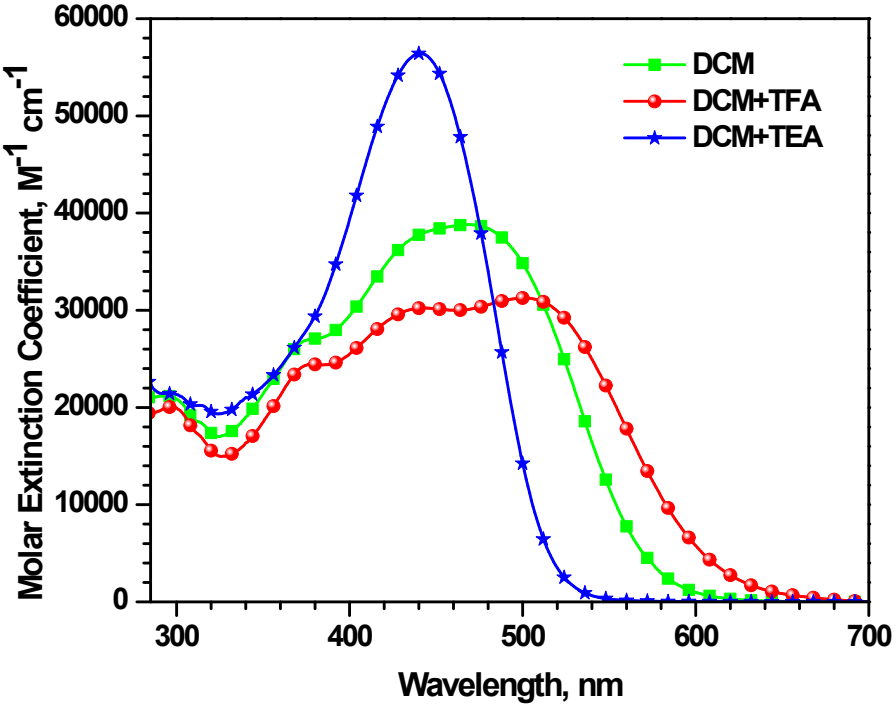


Fig. S9 Absorption spectra of the dye **5b** recorded in DCM before and after addition of TFA and TEA

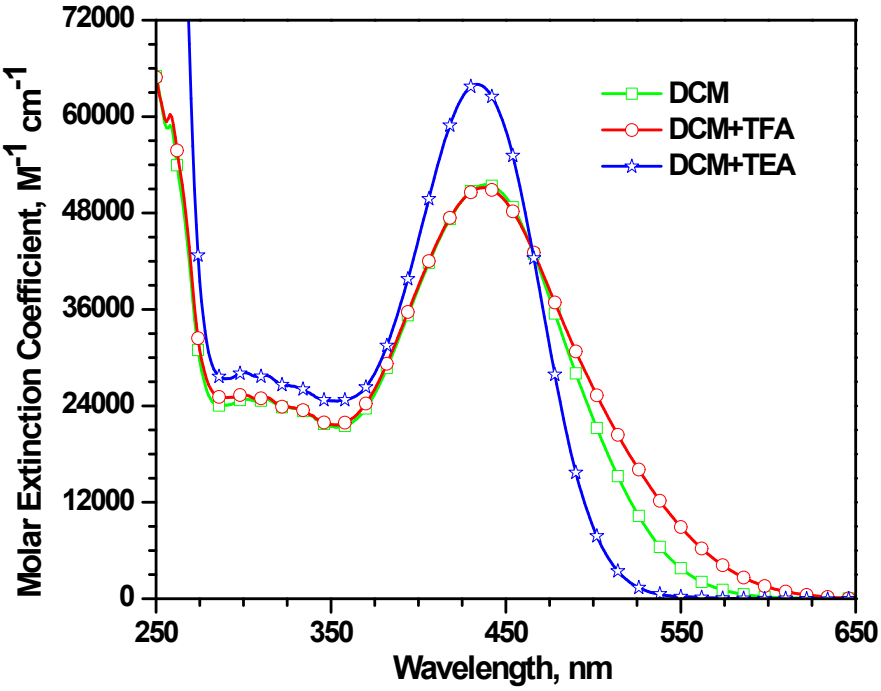


Fig. S10 Absorption spectra of the dye **5c** recorded in DCM before and after addition of TFA and TEA

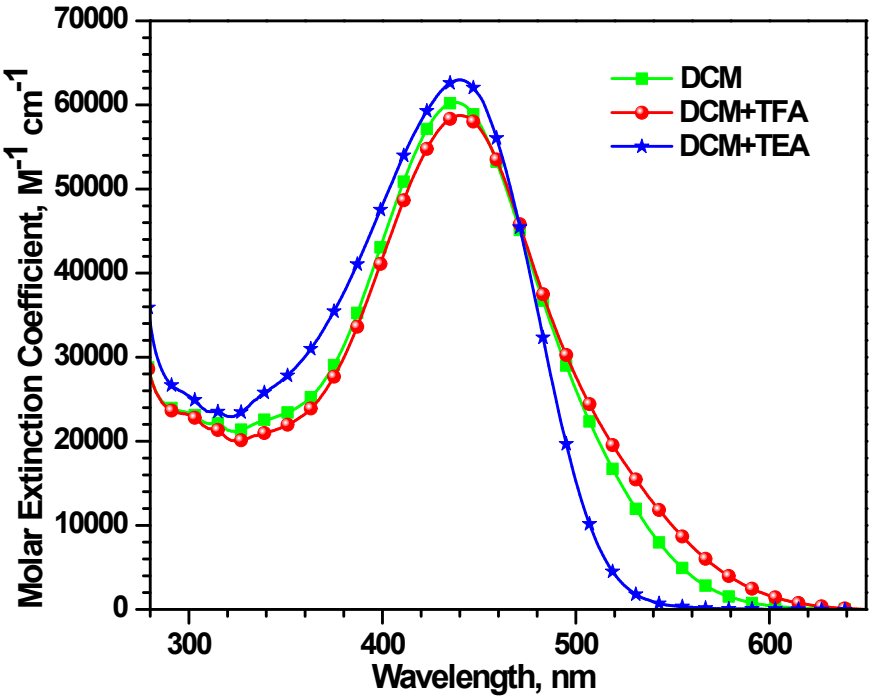


Fig. S11 Absorption spectra of the dye **5d** recorded in DCM before and after addition of TFA and TEA

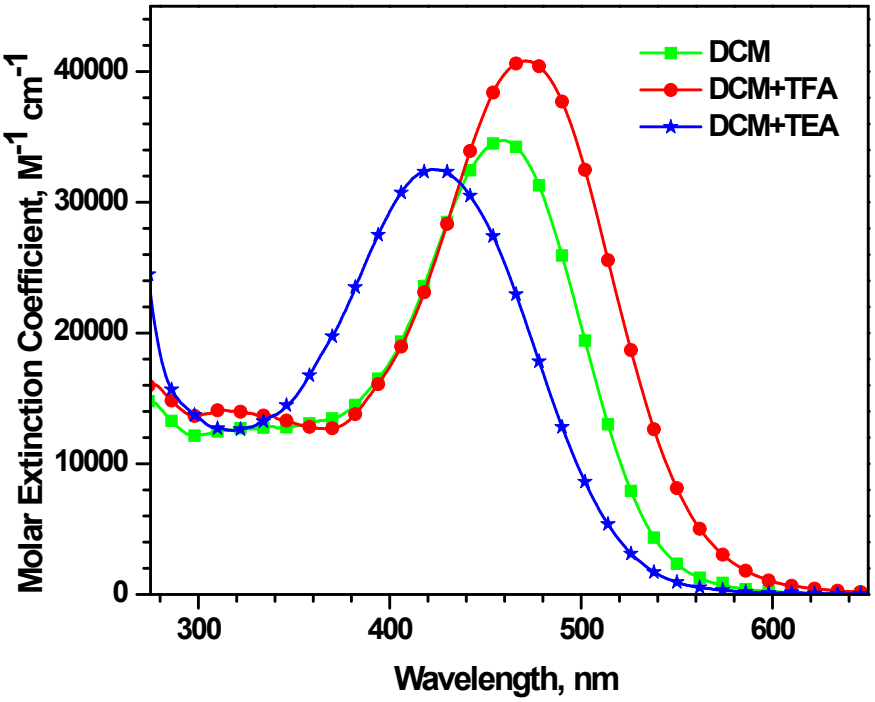


Fig. S12 Absorption spectra of the dye **5e** recorded in DCM before and after addition of TFA and TEA

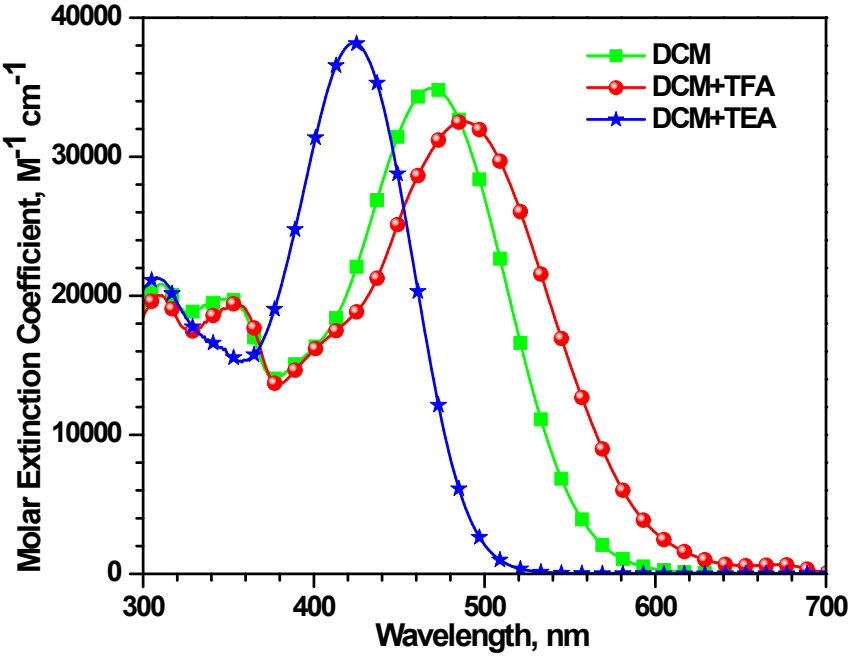


Fig. S13 Absorption spectra of the dye **D1** recorded in DCM before and after addition of TFA and TEA

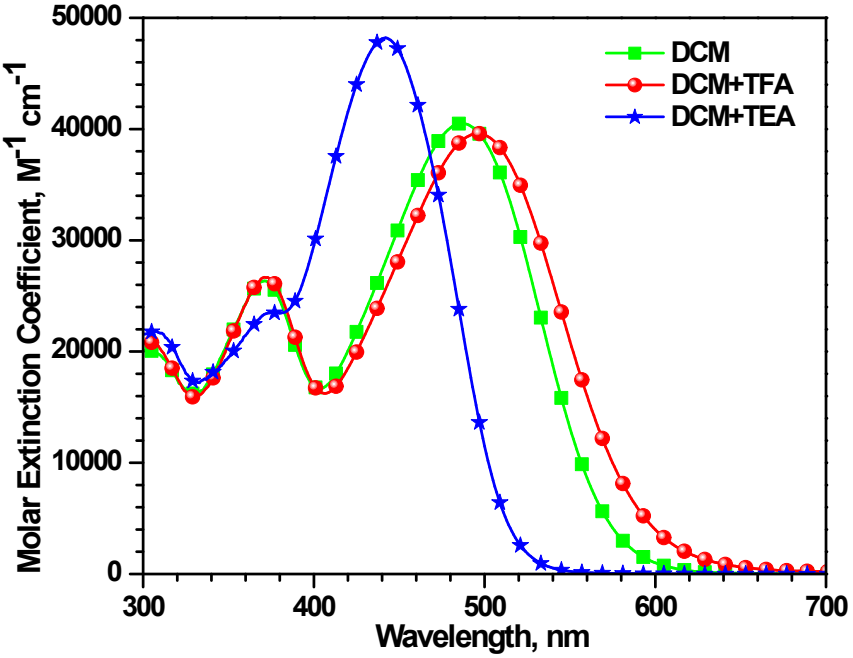


Fig. S14 Absorption spectra of the dye **D2** recorded in DCM before and after addition of TFA and TEA

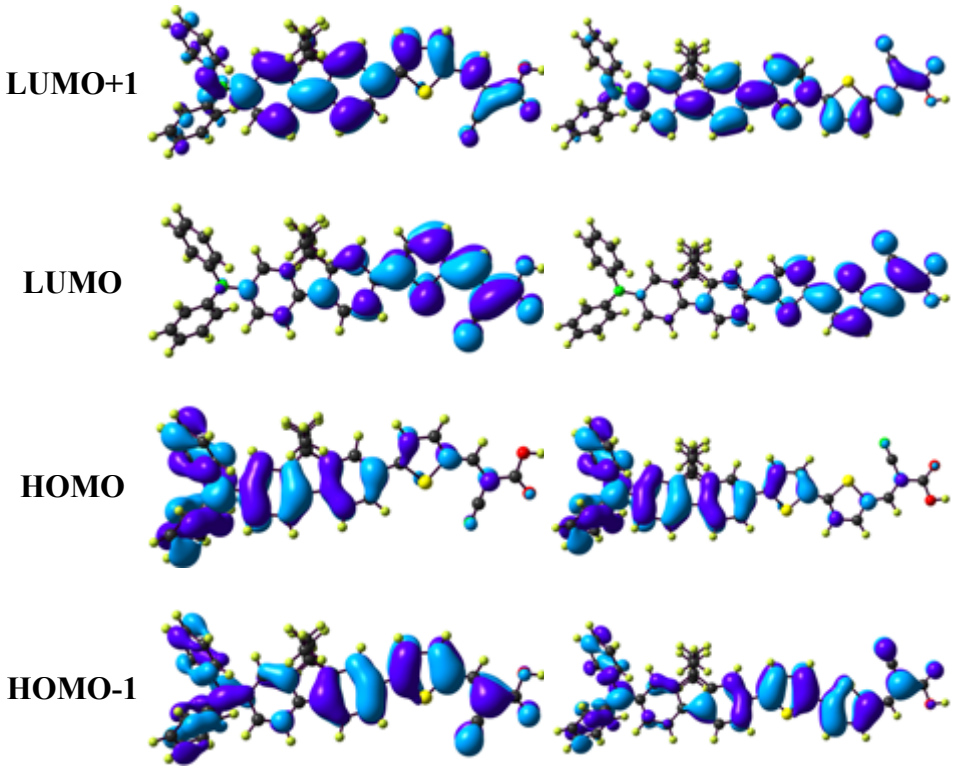


Fig. S15 Electronic distribution in the frontier molecular orbitals of the reference dyes **D1** and **D2**.

Table S1 Optical data of dyes recorded in different solvents

Dye	λ_{abs}, nm (ε, $M^{-1}cm^{-1} \times 10^3$)						
	TOL	DCM	DCM+TFA	DCM+TEA	THF	DMF	ACN
5a	456 (32.6) 335 (16.6)	464 (35.5)	486 (33.4) 422 (33.4)	430 (48.9)	443 (43.9)	419 (50.8)	444
5b	458 (35.9) 370 (22.6)	470 (38.8)	500 (31.3) 444 (30.2) 380 (24.4)	441 (56.4)	448 (54.0)	435 (60.6)	453
5c	436 (51.5)	439 (51.5)	437 (51.1)	434 (64.0)	437 (64.2)	430 (59.8)	432 (77.2)
5d	435 (48.9)	437 (60.3)	440 (58.7)	440 (62.9)	434 (71.9)	439 (69.5)	428 (44.4)
5e	450 (25.3)	460 (34.7)	471 (40.8)	422 (32.5)	438 (37.2)	410 (25.3)	442, 272
D1	462	469 (34.9) 353 (19.7) 310 (20.8)	488 (32.6) 354 (19.4) 309 (20.0)	423 (38.2) 308 (21.3)	411 (42.9)	410 (21.9)	442
D2	477	487 (40.5) 371 (26.3) 304 (20.1)	496 (39.6) 371 (26.7) 304 (20.9)	442 (48.2) 307 (21.8)	433 (44.3)	433 (50.3)	

Table S2 Computed vertical transition energies and their oscillator strengths and configurations for the dyes[a]

Dye	λ_{max}^{obs}, nm[b]	λ_{max}^{calc}, nm	f	Configuration	HOMO, eV	LUMO, eV	Band gap, eV
5a	464	575.7	0.58	HOMO→LUMO (99%)	-5.76	-2.65	2.39
		445.8	0.96	HOMO→LUMO+1 (83%), HOMO-1→LUMO (13%)			
5b	470	612.3	0.53	HOMO→LUMO (99%)	-4.99	-2.76	2.23
		476.5	1.38	HOMO-1→LUMO (86%), HOMO→LUMO +1(12%)			
		444.9	0.42	HOMO→LUMO+1 (85%), HOMO-1→LUMO (12%)			
5c	439	585.4	0.56	HOMO→LUMO (99%)	-5.04	-2.69	2.35
		473.0	0.55	HOMO→LUMO+1(99%)			
5d	437	615.1	0.54	HOMO→LUMO (99%)	-5.01	-2.79	2.22
		477.6	1.55	HOMO-1→LUMO (85%), HOMO→LUMO+1 (11%)			
		475.5	0.58	HOMO→LUMO+1 (96%)			
5e	460	502.4	0.95	HOMO→LUMO (98%)	-5.58	-2.84	2.74
		448.0	0.39	HOMO→LUMO +1(94%)			
D1	469	563.8	0.56	HOMO→LUMO (100%)	-5.04	-2.61	2.43
		401.3	0.94	HOMO-1→LUMO (92%)			
		361.2	0.19	HOMO→LUMO+1 (87%)			
D2	487	605.9	0.58	HOMO→LUMO (100%)	-4.98	-2.73	2.25
		459.0	1.17	HOMO-1→LUMO (95%)			
		398.5	0.32	HOMO→LUMO+1 (88%)			

[a] computed parameters for vacuum conditions. [b] measured in DCM.

Table S3. Cartesian coordinates for the optimized geometry of **5a**

Energy = - 2624.53480453 Ha

Atom	X	Y	Z
C	5.457274000	0.991950000	-1.007519000
C	5.519005000	-0.223163000	-0.295748000
C	4.333980000	-0.740580000	0.276265000
C	3.130457000	-0.071340000	0.115712000
C	3.095103000	1.155549000	-0.583360000
C	4.259628000	1.684416000	-1.146301000
H	6.357056000	1.389896000	-1.466906000
H	4.388203000	-1.647008000	0.868887000
H	4.238524000	2.624535000	-1.689459000
C	1.741436000	-0.428379000	0.663487000
C	0.920853000	0.771838000	0.169833000
C	-0.437409000	1.020595000	0.317512000
C	-1.000705000	2.184146000	-0.244123000
C	-0.180284000	3.080642000	-0.954274000
C	1.179215000	2.830211000	-1.106402000
C	1.731493000	1.672509000	-0.552523000
H	-1.081489000	0.333224000	0.852830000
H	-0.622287000	3.968631000	-1.392169000
H	1.793926000	3.525273000	-1.671181000
C	1.827466000	-0.512397000	2.218965000
H	2.589729000	-1.259032000	2.470505000
H	2.219232000	0.445008000	2.581418000
C	1.155159000	-1.722130000	0.018086000
H	0.100217000	-1.790300000	0.307539000
H	1.156996000	-1.580502000	-1.068969000
C	0.540397000	-0.851149000	2.978354000
H	0.755570000	-0.942030000	4.047934000
H	-0.218407000	-0.072441000	2.866603000
H	0.103123000	-1.800180000	2.652485000
C	1.845573000	-3.048425000	0.352115000
H	1.305241000	-3.876353000	-0.118174000
H	2.872356000	-3.078428000	-0.022514000
H	1.870101000	-3.245619000	1.428595000
N	-2.385197000	2.456329000	-0.091102000
C	-2.817054000	3.791252000	0.162941000
C	-3.909134000	4.328350000	-0.535479000
C	-2.154290000	4.583595000	1.112544000
C	-4.332719000	5.630816000	-0.278779000
H	-4.418847000	3.720686000	-1.275732000
C	-2.573960000	5.891061000	1.349375000
H	-1.313335000	4.169472000	1.658691000
C	-3.666595000	6.420915000	0.660193000
H	-5.179044000	6.033618000	-0.827530000

H	-2.051406000	6.492897000	2.087175000
H	-3.994751000	7.437670000	0.852248000
C	-3.341608000	1.415602000	-0.179511000
C	-4.456609000	1.393271000	0.677327000
C	-3.198150000	0.376875000	-1.116134000
C	-5.405825000	0.384335000	0.580091000
H	-4.565283000	2.166076000	1.430593000
C	-4.139913000	-0.640918000	-1.187433000
H	-2.344394000	0.373222000	-1.784943000
C	-5.285111000	-0.651252000	-0.366614000
H	-6.235446000	0.371328000	1.278428000
H	-4.005295000	-1.434797000	-1.917393000
C	6.778642000	-0.948851000	-0.140004000
C	6.957629000	-2.302512000	0.112064000
S	8.317854000	-0.130795000	-0.254550000
C	8.307200000	-2.678043000	0.200200000
H	6.133840000	-3.000666000	0.195130000
C	9.201550000	-1.626703000	0.018818000
H	8.643611000	-3.693890000	0.377904000
C	10.618058000	-1.779674000	0.059663000
C	11.625547000	-0.866649000	-0.106559000
H	10.943636000	-2.797313000	0.257012000
C	11.387858000	0.514866000	-0.374897000
C	13.052775000	-1.256892000	-0.020044000
N	11.166238000	1.636985000	-0.593737000
O	13.985874000	-0.494476000	-0.159788000
O	13.225371000	-2.581601000	0.236861000
H	14.186663000	-2.714503000	0.269999000
C	-6.225187000	-1.769702000	-0.457308000
H	-5.743489000	-2.721974000	-0.678930000
C	-7.573032000	-1.823702000	-0.300783000
C	-8.318294000	-3.105749000	-0.254861000
C	-8.607010000	-0.763472000	-0.189233000
C	-7.867189000	-4.423966000	-0.319897000
C	-9.695253000	-2.839078000	-0.079767000
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C	-9.876924000	-1.384583000	-0.052973000
C	-8.792872000	-5.465911000	-0.223783000
H	-6.811645000	-4.650796000	-0.441705000
C	-10.615859000	-3.880873000	0.024004000
C	-9.710607000	1.384343000	-0.204175000
H	-7.590105000	1.131995000	-0.434663000
C	-11.042355000	-0.625837000	0.037034000
C	-10.155994000	-5.197527000	-0.051616000
H	-8.450262000	-6.495011000	-0.279163000
H	-11.674111000	-3.677062000	0.161406000

C	-10.952743000	0.765659000	-0.030959000
H	-9.653636000	2.466478000	-0.277149000
H	-12.009556000	-1.108597000	0.145269000
H	-10.860721000	-6.020238000	0.026100000
H	-11.852787000	1.369641000	0.038053000

Table S4 Cartesian coordinates for the optimized geometry of **5b**

Energy = - 3176.35371675 Ha

Atom	X	Y	Z
C	3.673624000	2.097969000	-1.267711000
C	3.918443000	0.901925000	-0.564301000
C	2.832144000	0.240445000	0.052525000
C	1.548052000	0.752810000	-0.056795000
C	1.329394000	1.967114000	-0.743906000
C	2.393997000	2.636871000	-1.351533000
H	4.496624000	2.603488000	-1.764227000
H	3.023960000	-0.651138000	0.639048000
H	2.233065000	3.567491000	-1.887895000
C	0.239774000	0.224151000	0.547635000
C	-0.745600000	1.311372000	0.096722000
C	-2.117418000	1.384972000	0.300581000
C	-2.844936000	2.470971000	-0.225036000
C	-2.174890000	3.469902000	-0.954565000
C	-0.801790000	3.393692000	-1.165564000
C	-0.086041000	2.310431000	-0.649670000
H	-2.648435000	0.617750000	0.851564000
H	-2.743922000	4.298481000	-1.361738000
H	-0.303349000	4.164857000	-1.746033000
C	0.404588000	0.154329000	2.097514000
H	1.258148000	-0.499357000	2.311789000
H	0.699819000	1.151263000	2.444756000
C	-0.208012000	-1.134273000	-0.075675000
H	-1.234312000	-1.330294000	0.255611000
H	-0.266785000	-0.996628000	-1.161700000
C	-0.799513000	-0.326549000	2.914085000
H	-0.525970000	-0.390985000	3.972219000
H	-1.645372000	0.361849000	2.840367000
H	-1.142594000	-1.319354000	2.606145000
C	0.652069000	-2.364953000	0.228254000
H	0.203726000	-3.252529000	-0.229736000
H	1.662217000	-2.266790000	-0.178451000
H	0.734984000	-2.560017000	1.302117000
N	-4.247780000	2.560395000	-0.017370000
C	-4.829792000	3.817043000	0.317163000
C	-6.012821000	4.241856000	-0.307100000
C	-4.223557000	4.648076000	1.271714000
C	-6.580346000	5.469465000	0.028133000
H	-6.479425000	3.606770000	-1.052675000
C	-4.788902000	5.881958000	1.587043000
H	-3.311906000	4.320730000	1.760256000
C	-5.971457000	6.298440000	0.972480000
H	-7.495899000	5.784796000	-0.463863000

H	-4.308284000	6.514007000	2.328154000
H	-6.412755000	7.257277000	1.225939000
C	-5.065442000	1.410573000	-0.132594000
C	-6.142033000	1.203308000	0.748448000
C	-4.814350000	0.440972000	-1.119650000
C	-6.952178000	0.081897000	0.627650000
H	-6.328533000	1.921224000	1.539793000
C	-5.615364000	-0.688729000	-1.215322000
H	-3.986926000	0.579463000	-1.806934000
C	-6.724013000	-0.887249000	-0.368459000
H	-7.750604000	-0.072633000	1.344985000
H	-5.398739000	-1.425983000	-1.983903000
C	-7.506800000	-2.117861000	-0.491312000
H	-6.907546000	-2.981520000	-0.779380000
C	-8.827873000	-2.368157000	-0.299871000
C	-9.384829000	-3.743271000	-0.306124000
C	-9.994845000	-1.472024000	-0.098701000
C	-8.757297000	-4.979543000	-0.459146000
C	-10.778394000	-3.683390000	-0.077644000
C	-10.124260000	-0.080351000	-0.117145000
C	-11.159990000	-2.272720000	0.038060000
C	-9.524898000	-6.145191000	-0.397458000
H	-7.685467000	-5.048838000	-0.622949000
C	-11.540791000	-4.848580000	-0.008676000
C	-11.387164000	0.495912000	0.043370000
H	-9.262260000	0.558545000	-0.263735000
C	-12.415755000	-1.692273000	0.205661000
C	-10.905221000	-6.081354000	-0.172609000
H	-9.044387000	-7.111221000	-0.521530000
H	-12.611583000	-4.803506000	0.169382000
C	-12.523615000	-0.300482000	0.216572000
H	-11.484444000	1.577582000	0.031758000
H	-13.301503000	-2.312058000	0.313222000
H	-11.485267000	-6.998204000	-0.123031000
H	-13.495873000	0.165725000	0.347045000
C	5.265578000	0.341992000	-0.457753000
C	5.638259000	-0.969151000	-0.228203000
S	6.690020000	1.354269000	-0.599090000
C	7.035371000	-1.168745000	-0.177996000
H	4.919965000	-1.774473000	-0.133301000
C	7.769375000	-0.012186000	-0.368707000
H	7.495237000	-2.139356000	-0.028136000
C	9.199016000	0.157446000	-0.387913000
C	9.928040000	1.290531000	-0.733169000
S	10.260633000	-1.156200000	0.067802000
C	11.313951000	1.103290000	-0.640222000

H	9.463770000	2.215943000	-1.052915000
C	11.691158000	-0.171090000	-0.223387000
H	12.045040000	1.869600000	-0.873937000
C	13.045053000	-0.581494000	-0.063259000
C	13.579656000	-1.780491000	0.330988000
H	13.769054000	0.194935000	-0.294345000
C	12.781062000	-2.912258000	0.673659000
C	15.043588000	-1.986017000	0.429868000
N	12.104123000	-3.819672000	0.947266000
O	15.573159000	-3.021881000	0.773844000
O	15.758072000	-0.878942000	0.091004000
H	16.689797000	-1.132439000	0.193139000

Table S5 Cartesian coordinates for the optimized geometry of **5c**

Energy = - 3162.86720904 Ha

Atom	X	Y	Z
C	-6.709840000	-0.997143000	-1.126224000
C	-7.076676000	0.057304000	-0.265629000
C	-6.059236000	0.806589000	0.368608000
C	-4.724860000	0.518841000	0.125367000
C	-4.380066000	-0.557155000	-0.721966000
C	-5.374202000	-1.312491000	-1.349194000
H	-7.481857000	-1.567512000	-1.633761000
H	-6.337565000	1.583632000	1.071773000
H	-5.116049000	-2.137445000	-2.006482000
C	-3.468230000	1.174868000	0.714684000
C	-2.368909000	0.316173000	0.074237000
C	-0.989896000	0.435728000	0.188031000
C	-0.152033000	-0.454214000	-0.512007000
C	-0.718552000	-1.451892000	-1.326073000
C	-2.099433000	-1.568583000	-1.446391000
C	-2.926590000	-0.680399000	-0.754132000
H	-0.538207000	1.206587000	0.801181000
H	-0.065345000	-2.125106000	-1.870255000
H	-2.520575000	-2.333282000	-2.092686000
C	-3.521606000	1.040269000	2.267983000
H	-4.444183000	1.522499000	2.611770000
H	-3.636727000	-0.023689000	2.505051000
C	-3.279799000	2.649153000	0.239829000
H	-2.271713000	2.967441000	0.529948000
H	-3.287225000	2.647284000	-0.856395000
C	-2.343532000	1.608686000	3.066052000
H	-2.540998000	1.507246000	4.138088000
H	-1.412347000	1.075454000	2.857704000
H	-2.177870000	2.671910000	2.865346000
C	-4.288351000	3.684839000	0.746586000
H	-4.016736000	4.678498000	0.375936000
H	-5.301223000	3.473776000	0.392988000
H	-4.313618000	3.741108000	1.839422000
N	1.260717000	-0.342316000	-0.398893000
C	2.055910000	-1.508968000	-0.260100000
C	3.279868000	-1.626642000	-0.941171000
C	1.630496000	-2.579191000	0.544711000

C	4.063983000	-2.763850000	-0.797206000
H	3.602460000	-0.826519000	-1.598756000
C	2.409875000	-3.722454000	0.661430000
H	0.685627000	-2.509722000	1.072671000
C	3.660227000	-3.835870000	0.022085000
H	4.985218000	-2.846049000	-1.363402000
H	2.058714000	-4.540169000	1.285074000
C	1.876094000	0.935363000	-0.423983000
C	2.938184000	1.236621000	0.446247000
C	1.427315000	1.933726000	-1.305101000
C	3.548778000	2.483591000	0.413520000
H	3.270112000	0.490109000	1.159850000
C	2.028203000	3.185596000	-1.312259000
H	0.605293000	1.721267000	-1.980079000
C	3.123595000	3.486788000	-0.478965000
H	4.341048000	2.703221000	1.120663000
H	1.662837000	3.943707000	-1.999842000
C	-8.480962000	0.382243000	-0.019055000
C	-9.014587000	1.589010000	0.412826000
S	-9.740809000	-0.805542000	-0.249725000
C	-10.411765000	1.563178000	0.546203000
H	-8.410807000	2.469836000	0.593028000
C	-10.989828000	0.339394000	0.220845000
H	-11.006958000	2.414368000	0.859107000
C	-12.392185000	0.088906000	0.276421000
C	-13.115649000	-1.036206000	-0.017595000
H	-12.977260000	0.941669000	0.609587000
C	-12.517310000	-2.250078000	-0.471138000
C	-14.591756000	-1.070256000	0.114441000
N	-12.003480000	-3.227744000	-0.840280000
O	-15.283832000	-2.035168000	-0.133041000
O	-15.112063000	0.109005000	0.548987000
H	-16.071415000	-0.033763000	0.595140000
C	3.692411000	4.835925000	-0.499819000
H	2.950449000	5.614706000	-0.675218000
C	4.965362000	5.275001000	-0.326502000
C	5.300839000	6.715228000	-0.204047000
C	6.265882000	4.560865000	-0.257936000
C	4.481976000	7.844243000	-0.207446000
C	6.695527000	6.855454000	-0.023584000

C	6.608687000	3.216935000	-0.431279000
C	7.297045000	5.519158000	-0.070720000
C	5.060539000	9.105453000	-0.044707000
H	3.406162000	7.757506000	-0.332610000
C	7.269273000	8.114446000	0.147057000
C	7.952025000	2.836341000	-0.372906000
H	5.850444000	2.467374000	-0.621113000
C	8.634141000	5.132623000	-0.004511000
C	6.442542000	9.240143000	0.132949000
H	4.430521000	9.990010000	-0.052227000
H	8.340880000	8.223543000	0.288621000
C	8.957398000	3.782052000	-0.148180000
H	8.216115000	1.791431000	-0.507731000
H	9.416911000	5.871382000	0.142689000
H	6.874577000	10.228041000	0.262957000
H	9.995430000	3.466308000	-0.099264000
C	4.419511000	-5.081825000	0.146017000
C	5.755891000	-5.317367000	0.187119000
H	3.787612000	-5.967992000	0.202319000
C	6.924138000	-4.411049000	0.327548000
C	6.324774000	-6.686581000	0.132080000
C	7.022686000	-3.033798000	0.544817000
C	8.107340000	-5.196387000	0.318946000
C	5.700388000	-7.927684000	0.009497000
C	7.734888000	-6.608115000	0.184173000
C	8.282601000	-2.450667000	0.704281000
H	6.137224000	-2.412881000	0.602342000
C	9.361536000	-4.608092000	0.469354000
C	6.485410000	-9.082002000	-0.046435000
H	4.618320000	-8.009394000	-0.044302000
C	8.516151000	-7.760893000	0.119986000
C	9.444853000	-3.226743000	0.654111000
H	8.356807000	-1.380173000	0.872651000
H	10.262323000	-5.215231000	0.457421000
C	7.881869000	-9.000132000	0.006770000
H	6.006598000	-10.052623000	-0.136093000
H	9.600294000	-7.701583000	0.157238000
H	10.415731000	-2.754734000	0.773394000
H	8.476281000	-9.907711000	-0.042791000

Table S6 Cartesian coordinates for the optimized geometry of **5d**

Energy = - 3714.68616319 Ha

Atom	X	Y	Z
C	-5.148693000	-1.549267000	-1.505512000
C	-5.606886000	-0.518786000	-0.660854000
C	-4.657195000	0.284731000	0.010246000
C	-3.300278000	0.072960000	-0.183692000
C	-2.863310000	-0.980803000	-1.015950000
C	-3.789599000	-1.790127000	-1.677740000
H	-5.868855000	-2.159204000	-2.042802000
H	-5.005889000	1.043890000	0.701500000
H	-3.461103000	-2.598908000	-2.323993000
C	-2.105868000	0.797618000	0.452896000
C	-0.936107000	0.002930000	-0.143952000
C	0.428618000	0.201305000	0.021355000
C	1.342181000	-0.635189000	-0.649091000
C	0.864941000	-1.660995000	-1.484523000
C	-0.501872000	-1.857889000	-1.654821000
C	-1.404449000	-1.021469000	-0.993309000
H	0.811731000	0.995632000	0.651004000
H	1.575798000	-2.292789000	-2.005760000
H	-0.853396000	-2.644238000	-2.316699000
C	-2.211726000	0.659287000	2.002980000
H	-3.171086000	1.091530000	2.310188000
H	-2.279158000	-0.409570000	2.236685000
C	-1.980314000	2.280278000	-0.016614000
H	-1.003185000	2.652719000	0.312305000
H	-1.944402000	2.278429000	-1.112293000
C	-1.097240000	1.288955000	2.845100000
H	-1.330394000	1.176772000	3.908875000
H	-0.131642000	0.806049000	2.673579000
H	-0.980854000	2.359596000	2.649296000
C	-3.062701000	3.259962000	0.447741000
H	-2.828433000	4.267340000	0.088792000
H	-4.047804000	2.997510000	0.052533000
H	-3.136533000	3.312780000	1.538477000
N	2.741158000	-0.439391000	-0.485949000
C	3.601902000	-1.555197000	-0.324356000
C	4.855227000	-1.588507000	-0.960216000
C	3.218697000	-2.656082000	0.460173000

C	5.709298000	-2.669441000	-0.786079000
H	5.147991000	-0.766054000	-1.603988000
C	4.069402000	-3.744268000	0.606074000
H	2.251908000	-2.652370000	0.951771000
C	5.349079000	-3.768216000	0.017667000
H	6.656383000	-2.686168000	-1.314241000
H	3.751452000	-4.585857000	1.215643000
C	3.280144000	0.872714000	-0.481335000
C	4.294318000	1.225821000	0.425799000
C	2.805556000	1.851802000	-1.370529000
C	4.838326000	2.503385000	0.418130000
H	4.642472000	0.493804000	1.146567000
C	3.338766000	3.134149000	-1.352724000
H	2.018177000	1.600378000	-2.072873000
C	4.390612000	3.487250000	-0.484634000
H	5.595162000	2.760806000	1.150935000
H	2.955500000	3.875841000	-2.048428000
C	4.894416000	4.862353000	-0.483380000
H	4.121696000	5.607639000	-0.671296000
C	6.142282000	5.355805000	-0.276932000
C	6.412824000	6.807795000	-0.135897000
C	7.470583000	4.697241000	-0.184382000
C	5.546478000	7.900711000	-0.148794000
C	7.796012000	7.005952000	0.076498000
C	7.874283000	3.370738000	-0.360033000
C	8.455324000	5.697020000	0.032902000
C	6.066717000	9.184111000	0.036044000
H	4.478394000	7.768875000	-0.298086000
C	8.311322000	8.286907000	0.268936000
C	9.231042000	3.047065000	-0.274456000
H	7.152953000	2.591311000	-0.571841000
C	9.806036000	5.367170000	0.126165000
C	7.437493000	9.376289000	0.244937000
H	5.399560000	10.040902000	0.021405000
H	9.373935000	8.440711000	0.434758000
C	10.189854000	4.032878000	-0.020285000
H	9.542437000	2.015461000	-0.411201000
H	10.552924000	6.137439000	0.296392000
H	7.823761000	10.380654000	0.391709000
H	11.239136000	3.761280000	0.049418000

C	6.195129000	-4.953463000	0.175335000
C	7.542019000	-5.077282000	0.291114000
H	5.635451000	-5.888578000	0.190035000
C	8.617921000	-4.075990000	0.506187000
C	8.228855000	-6.391903000	0.260784000
C	8.584062000	-2.697849000	0.736354000
C	9.862555000	-4.757043000	0.564987000
C	7.721823000	-7.680096000	0.091765000
C	9.621488000	-6.193814000	0.398412000
C	9.776839000	-2.010644000	0.976947000
H	7.646378000	-2.156077000	0.740958000
C	11.049900000	-4.065150000	0.796288000
C	8.605007000	-8.762505000	0.074883000
H	6.655836000	-7.852783000	-0.028091000
C	10.501244000	-7.274927000	0.373029000
C	11.002475000	-2.683951000	0.994464000
H	9.748030000	-0.939618000	1.155726000
H	11.998696000	-4.592829000	0.836253000
C	9.983599000	-8.562299000	0.212789000
H	8.217632000	-9.769308000	-0.050482000
H	11.572175000	-7.123727000	0.475712000
H	11.920041000	-2.132095000	1.176483000
H	10.655799000	-9.415082000	0.192453000
C	-7.035396000	-0.270228000	-0.467330000
C	-7.661392000	0.901925000	-0.087136000
S	-8.224392000	-1.537297000	-0.699505000
C	-9.066653000	0.798231000	0.006089000
H	-7.121589000	1.825053000	0.085980000
C	-9.552986000	-0.459511000	-0.301196000
H	-9.710517000	1.629319000	0.272019000
C	-10.916832000	-0.921102000	-0.318209000
C	-11.404986000	-2.152884000	-0.741020000
S	-12.214908000	0.107816000	0.244618000
C	-12.796892000	-2.264921000	-0.619794000
H	-10.767993000	-2.937290000	-1.132329000
C	-13.418036000	-1.130018000	-0.104008000
H	-13.359703000	-3.147974000	-0.902279000
C	-14.822998000	-1.021643000	0.100477000
C	-15.582473000	0.010645000	0.586512000
H	-15.377270000	-1.913331000	-0.179037000

C	-15.025111000	1.256899000	1.001647000
C	-17.054562000	-0.097817000	0.715422000
N	-14.542451000	2.263681000	1.333191000
O	-17.776680000	0.781416000	1.136353000
O	-17.534421000	-1.303879000	0.308356000
H	-18.495536000	-1.256117000	0.438023000

Table S7 Cartesian coordinates for the optimized geometry of **5e**

Energy = - 2348.08622667 Ha

Atom	X	Y	Z
C	3.739901000	0.915191000	-1.115792000
C	3.933148000	-0.213925000	-0.294312000
C	2.814065000	-0.794966000	0.343674000
C	1.545745000	-0.269961000	0.143629000
C	1.378852000	0.875597000	-0.664032000
C	2.475994000	1.465868000	-1.295590000
H	4.589688000	1.358336000	-1.625906000
H	2.966948000	-1.630989000	1.016826000
H	2.353229000	2.344257000	-1.922175000
C	0.207092000	-0.711505000	0.751329000
C	-0.737125000	0.345323000	0.162814000
C	-2.113518000	0.468220000	0.308132000
C	-2.790031000	1.512062000	-0.349443000
C	-2.077413000	2.422712000	-1.145620000
C	-0.699842000	2.296657000	-1.300100000
C	-0.031535000	1.253609000	-0.654511000
H	-2.683590000	-0.226948000	0.913624000
H	-2.614450000	3.221345000	-1.645764000
H	-0.161263000	2.997084000	-1.931518000
C	0.318867000	-0.632267000	2.305723000
H	1.149749000	-1.278521000	2.611261000
H	0.625361000	0.387620000	2.565074000
C	-0.252871000	-2.115282000	0.247814000
H	-1.290328000	-2.260499000	0.570385000
H	-0.282369000	-2.081734000	-0.847557000
C	-0.921625000	-1.009509000	3.122202000
H	-0.684769000	-0.974956000	4.190348000
H	-1.750332000	-0.316728000	2.953556000
H	-1.274299000	-2.021590000	2.900118000
C	0.574893000	-3.325825000	0.690296000
H	0.115556000	-4.245766000	0.314863000
H	1.593481000	-3.288377000	0.294744000
H	0.634992000	-3.413283000	1.779681000
N	-4.201725000	1.665707000	-0.189554000
C	-4.702894000	2.966393000	0.138328000
C	-5.749236000	3.531618000	-0.603747000
C	-4.129139000	3.691860000	1.190732000

C	-6.223708000	4.802184000	-0.282262000
H	-6.184128000	2.973660000	-1.426533000
C	-4.599419000	4.968018000	1.494961000
H	-3.318640000	3.252062000	1.762364000
C	-5.649964000	5.526604000	0.764477000
H	-7.035614000	5.231196000	-0.861671000
H	-4.149258000	5.522253000	2.313001000
H	-6.017587000	6.518530000	1.007642000
C	-5.069357000	0.581703000	-0.346366000
C	-6.314550000	0.545598000	0.323537000
C	-4.729621000	-0.509208000	-1.176605000
C	-7.177991000	-0.522543000	0.171653000
H	-6.590985000	1.364053000	0.977288000
C	-5.599070000	-1.573571000	-1.321514000
H	-3.788601000	-0.503478000	-1.713275000
C	-6.848255000	-1.620908000	-0.658751000
H	-8.113571000	-0.510152000	0.716193000
H	-5.319290000	-2.393606000	-1.977645000
C	5.265450000	-0.783080000	-0.089142000
C	5.592347000	-2.077951000	0.287680000
S	6.704130000	0.184284000	-0.300107000
C	6.976064000	-2.292506000	0.396117000
H	4.851356000	-2.851552000	0.447228000
C	7.747344000	-1.171279000	0.105479000
H	7.422918000	-3.243105000	0.666772000
C	9.173431000	-1.161000000	0.145524000
C	10.070347000	-0.162068000	-0.121832000
H	9.611053000	-2.111272000	0.438693000
C	9.677096000	1.150062000	-0.523349000
C	11.533847000	-0.377565000	-0.013506000
N	9.328006000	2.211929000	-0.849779000
O	12.372293000	0.468763000	-0.240097000
O	11.855367000	-1.640954000	0.372375000
H	12.825570000	-1.662249000	0.407530000
C	-7.674130000	-2.779771000	-0.884573000
C	-8.912894000	-3.127122000	-0.405270000
H	-7.239811000	-3.515942000	-1.557290000
C	-9.496353000	-4.370199000	-0.813883000
N	-9.962755000	-5.382505000	-1.150327000
C	-9.698114000	-2.339104000	0.492901000

N	-10.346863000	-1.706508000	1.224635000

Table S8 Cartesian coordinates for the optimized geometry of **D1**

Energy = -2086.2068287 Ha

Atom	X	Y	Z
N	-5.521575000	0.390175000	-0.154539000
C	-4.115443000	0.483143000	-0.293809000
C	-3.539256000	1.560450000	-0.997113000
H	-4.187513000	2.310066000	-1.437011000
C	-2.159051000	1.668949000	-1.134054000
H	-1.738792000	2.507405000	-1.682351000
C	-1.333626000	0.686291000	-0.580281000
C	-1.903571000	-0.399514000	0.115824000
C	-3.277724000	-0.501911000	0.268404000
H	-3.720617000	-1.327652000	0.815820000
C	0.119982000	0.537830000	-0.566539000
C	1.135428000	1.335957000	-1.100665000
H	0.902361000	2.244440000	-1.648062000
C	2.461645000	0.950506000	-0.933808000
H	3.247631000	1.558918000	-1.371027000
C	2.803159000	-0.224891000	-0.232768000
C	1.765209000	-1.018806000	0.308390000
H	2.012515000	-1.909828000	0.877806000
C	0.444654000	-0.642343000	0.138587000
C	-0.819471000	-1.342862000	0.638673000
C	-0.962694000	-2.774144000	0.043598000
H	-0.151208000	-3.390694000	0.451840000
H	-1.894341000	-3.206344000	0.430524000
C	-0.954748000	-2.868225000	-1.484368000
H	-1.056668000	-3.910964000	-1.801474000
H	-0.022824000	-2.480271000	-1.906056000
H	-1.781928000	-2.303402000	-1.924239000
C	-0.845394000	-1.456443000	2.190921000
H	-1.776894000	-1.963329000	2.473976000
H	-0.032509000	-2.129547000	2.493036000
C	-0.729498000	-0.139042000	2.961972000
H	-0.757448000	-0.326613000	4.040013000
H	-1.552800000	0.539283000	2.719791000
H	0.208460000	0.377579000	2.737929000
C	-6.164112000	-0.879041000	-0.214925000
C	-5.807335000	-1.811445000	-1.201931000
C	-7.166825000	-1.212729000	0.708679000
H	-5.040998000	-1.553346000	-1.925203000
C	-6.433842000	-3.054909000	-1.252038000
C	-7.800711000	-2.451766000	0.638980000
H	-7.443588000	-0.496877000	1.475314000
H	-6.146989000	-3.765070000	-2.022281000
C	-7.435999000	-3.381970000	-0.336271000

C	-6.302917000	1.561283000	0.057429000
C	-5.872512000	2.554673000	0.951262000
C	-7.519801000	1.734429000	-0.620485000
H	-4.937261000	2.423213000	1.484969000
C	-6.640765000	3.699707000	1.150744000
C	-8.290016000	2.874409000	-0.399921000
H	-7.854805000	0.972409000	-1.316105000
H	-6.293495000	4.458847000	1.845698000
C	-7.855001000	3.865832000	0.481620000
C	4.197265000	-0.629392000	-0.062299000
C	4.690416000	-1.898501000	0.211917000
S	5.500613000	0.527628000	-0.185962000
C	6.089534000	-1.942458000	0.310491000
H	4.055153000	-2.770551000	0.305129000
C	6.711304000	-0.712125000	0.114907000
H	6.655356000	-2.847010000	0.506327000
C	8.123083000	-0.524604000	0.161657000
C	8.887220000	0.597683000	-0.021855000
H	8.679136000	-1.432138000	0.380118000
C	8.331548000	1.878034000	-0.319995000
C	10.365363000	0.557914000	0.075030000
N	7.853008000	2.911522000	-0.563134000
O	11.093188000	1.515884000	-0.080843000
O	10.844733000	-0.682662000	0.362074000
H	11.809942000	-0.583382000	0.398436000
H	-8.454318000	4.755988000	0.645358000
H	-9.229220000	2.992917000	-0.932543000
H	-8.574964000	-2.694825000	1.360979000
H	-7.927544000	-4.348737000	-0.383222000

Table S9 Cartesian coordinates for the optimized geometry of **D2**

Energy = -2638.025682 Ha

Atom	X	Y	Z
N	7.279379000	-0.166860000	-0.038375000
C	5.895428000	-0.400041000	-0.233938000
C	5.458475000	-1.546439000	-0.927283000
H	6.195728000	-2.239560000	-1.316716000
C	4.102308000	-1.794168000	-1.117019000
H	3.789516000	-2.684110000	-1.656047000
C	3.162092000	-0.883166000	-0.628143000
C	3.592868000	0.271706000	0.056701000
C	4.942683000	0.512556000	0.262832000
H	5.278945000	1.391527000	0.803431000
C	1.700850000	-0.877307000	-0.678555000
C	0.791202000	-1.783227000	-1.229946000
H	1.134885000	-2.677914000	-1.741009000
C	-0.572587000	-1.523350000	-1.130021000
H	-1.277767000	-2.213311000	-1.584043000
C	-1.056108000	-0.370737000	-0.477965000
C	-0.124090000	0.532610000	0.082683000
H	-0.482468000	1.408373000	0.615736000
C	1.233292000	0.283045000	-0.023554000
C	2.400581000	1.117465000	0.505208000
C	2.429610000	2.539406000	-0.127968000
H	1.544688000	3.083525000	0.226890000
H	3.296502000	3.072219000	0.283098000
C	2.479389000	2.590769000	-1.657443000
H	2.494043000	3.629519000	-2.002361000
H	1.608181000	2.102556000	-2.104098000
H	3.375453000	2.097382000	-2.045544000
C	2.347537000	1.275460000	2.052737000
H	3.213119000	1.877296000	2.358008000
H	1.461364000	1.874393000	2.299500000
C	2.323278000	-0.025798000	2.858948000
H	2.284118000	0.192509000	3.930832000
H	3.217577000	-0.627760000	2.673130000
H	1.449678000	-0.635754000	2.610689000
C	7.800487000	1.154919000	-0.127241000
C	7.403221000	2.008807000	-1.168397000
C	8.722817000	1.620898000	0.822612000

H	6.698722000	1.650269000	-1.911601000
C	7.911559000	3.303698000	-1.247092000
C	9.239777000	2.911242000	0.724871000
H	9.029953000	0.966629000	1.631624000
H	7.594721000	3.951501000	-2.059420000
C	8.834938000	3.762287000	-0.305357000
C	8.157011000	-1.248626000	0.252667000
C	7.778501000	-2.251967000	1.159085000
C	9.417919000	-1.324449000	-0.359864000
H	6.809101000	-2.195268000	1.642670000
C	8.640790000	-3.311084000	1.434621000
C	10.280414000	-2.377873000	-0.063572000
H	9.714459000	-0.555162000	-1.064793000
H	8.332142000	-4.078643000	2.138538000
C	9.897567000	-3.379921000	0.830073000
C	-2.488862000	-0.095466000	-0.377466000
C	-3.121325000	1.121687000	-0.204481000
S	-3.676960000	-1.382344000	-0.456042000
C	-4.529383000	1.034566000	-0.149022000
H	-2.582398000	2.060017000	-0.154332000
C	-5.012672000	-0.255063000	-0.277929000
H	-5.176908000	1.897419000	-0.038359000
C	-6.377608000	-0.712198000	-0.276234000
C	-6.858227000	-1.992234000	-0.532447000
S	-7.688777000	0.389038000	0.083342000
C	-8.253981000	-2.083965000	-0.447227000
H	-6.212354000	-2.825565000	-0.782554000
C	-8.886486000	-0.885319000	-0.125418000
H	-8.811956000	-2.998079000	-0.618771000
C	-10.296891000	-0.747527000	0.008737000
C	-11.068486000	0.344603000	0.310935000
H	-10.845704000	-1.670144000	-0.158525000
C	-10.520480000	1.638016000	0.561448000
C	-12.544547000	0.255240000	0.398987000
N	-10.045418000	2.682468000	0.761408000
O	-13.277918000	1.185425000	0.661449000
O	-13.015293000	-0.997331000	0.152373000
H	-13.980219000	-0.931065000	0.237925000
H	9.234557000	4.769248000	-0.374165000
H	9.952978000	3.256339000	1.467896000

H	11.252431000	-2.420979000	-0.546470000
H	10.569503000	-4.202863000	1.052842000

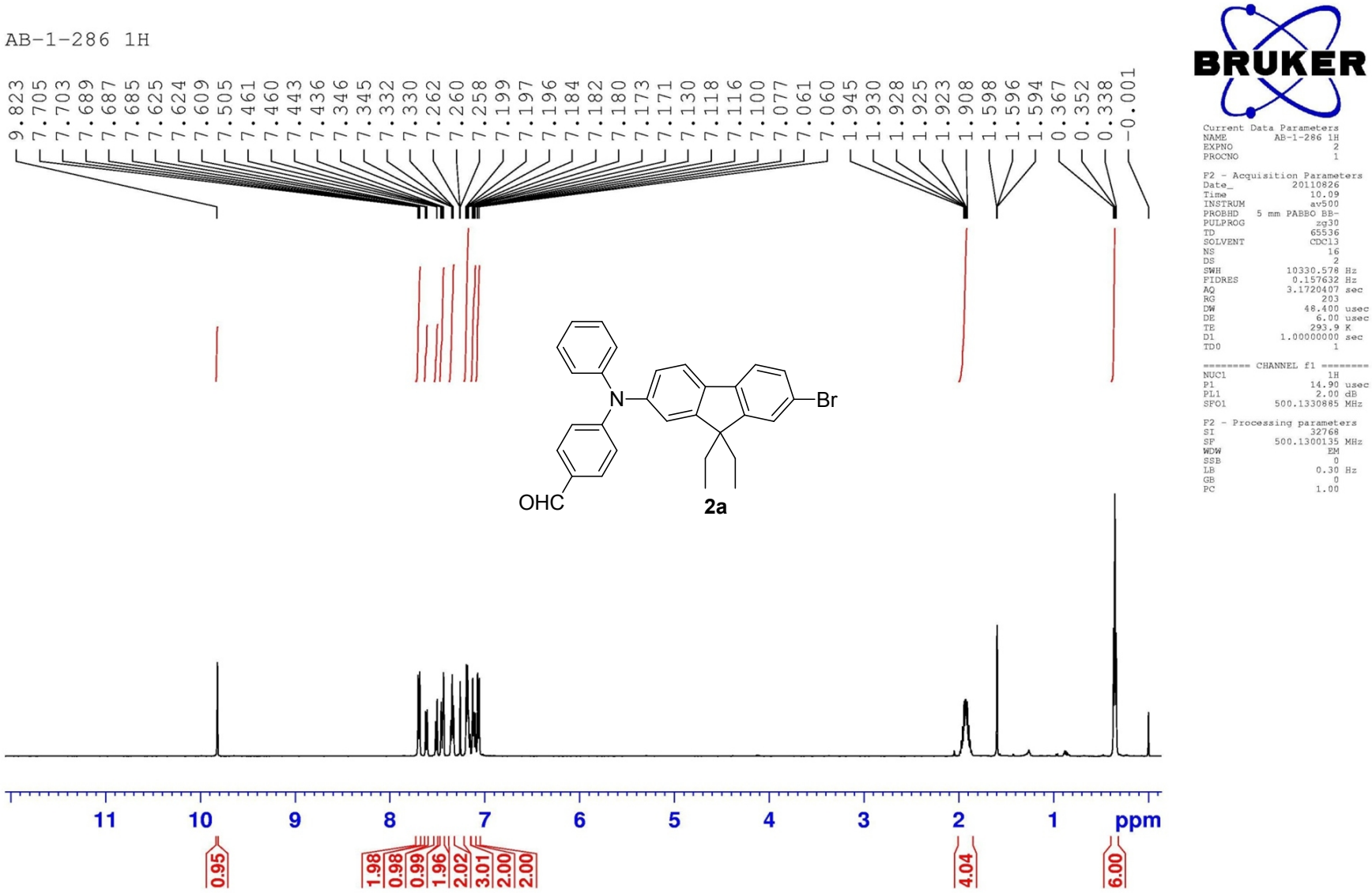

Fig. S16 ^{1}H NMR spectra of **2a** in $CDCl_3$

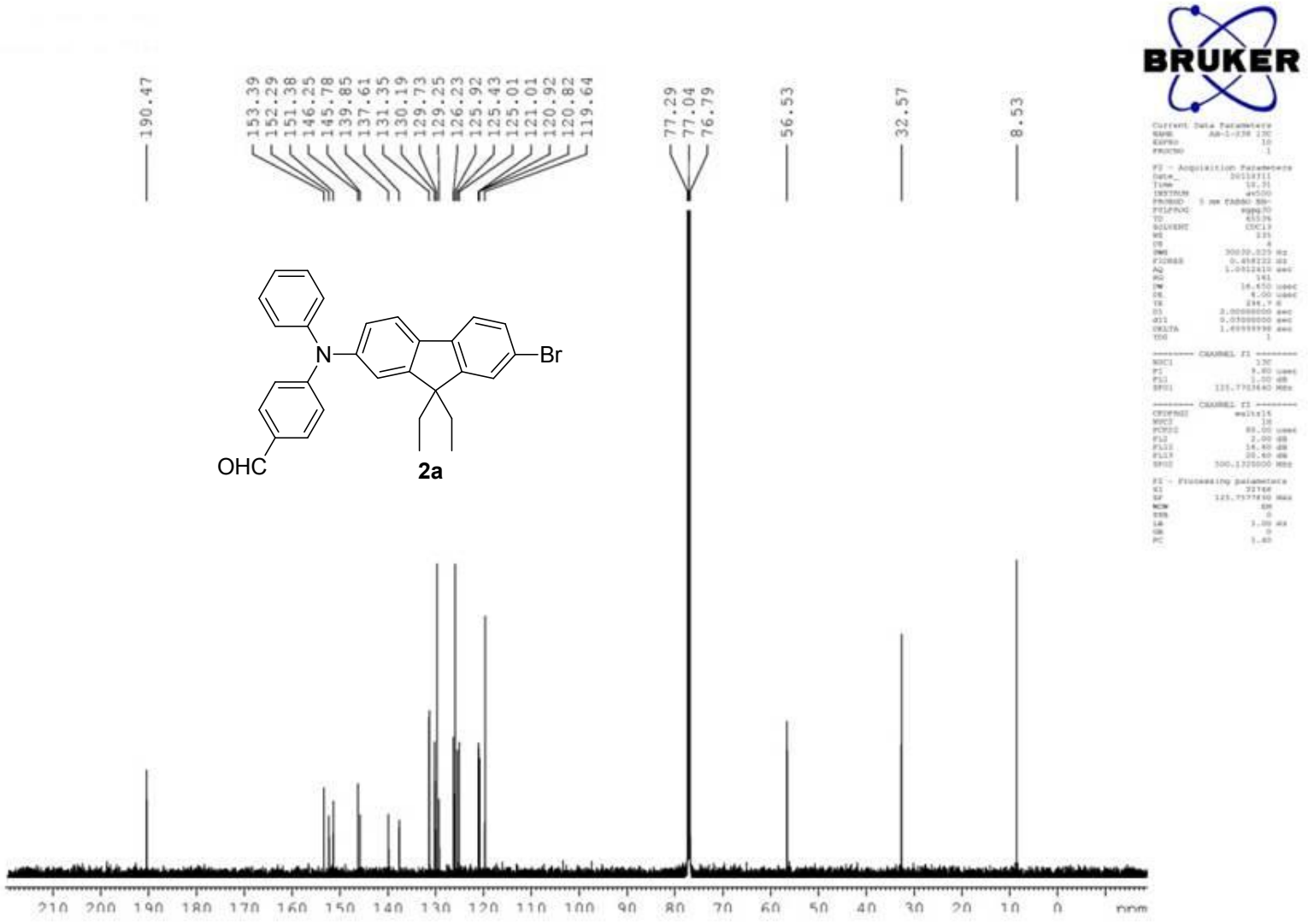

Fig. S17 ^{13}C NMR spectra of **2a** in $CDCl_3$

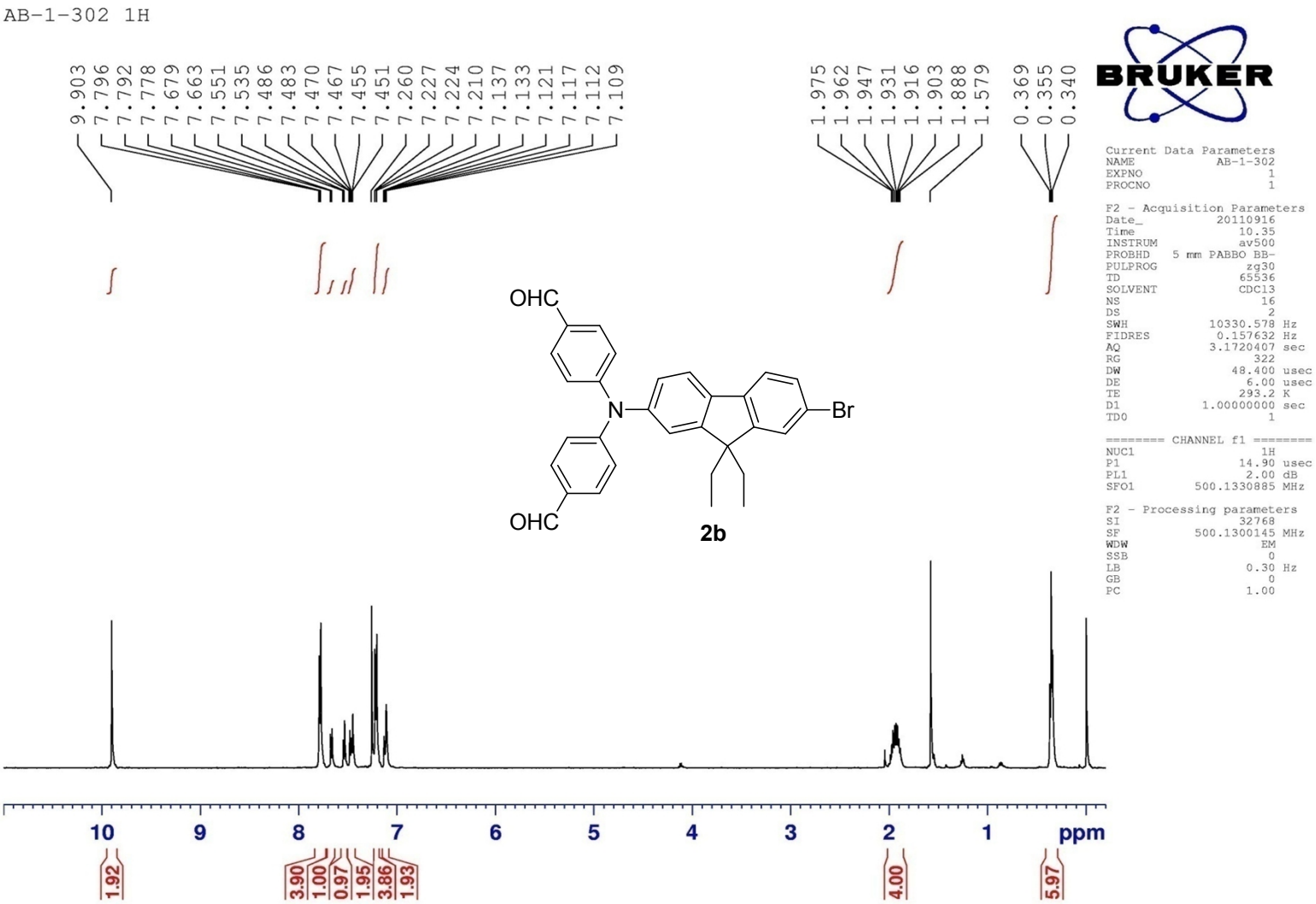

Fig. S18 ^{1}H NMR spectra of **2b** in $CDCl_3$

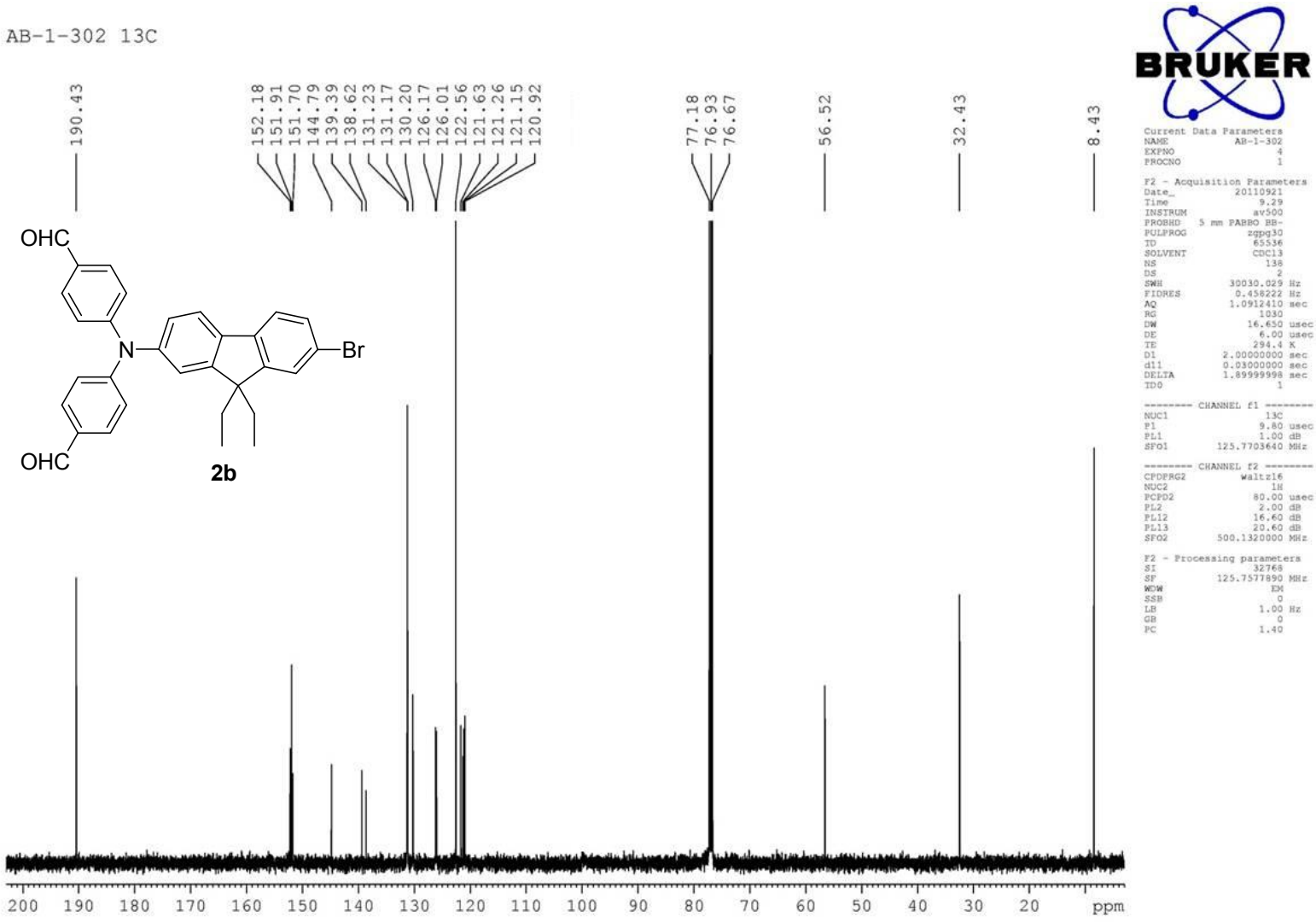

Fig. S19 ^{13}C NMR spectra of **2b** in $CDCl_3$

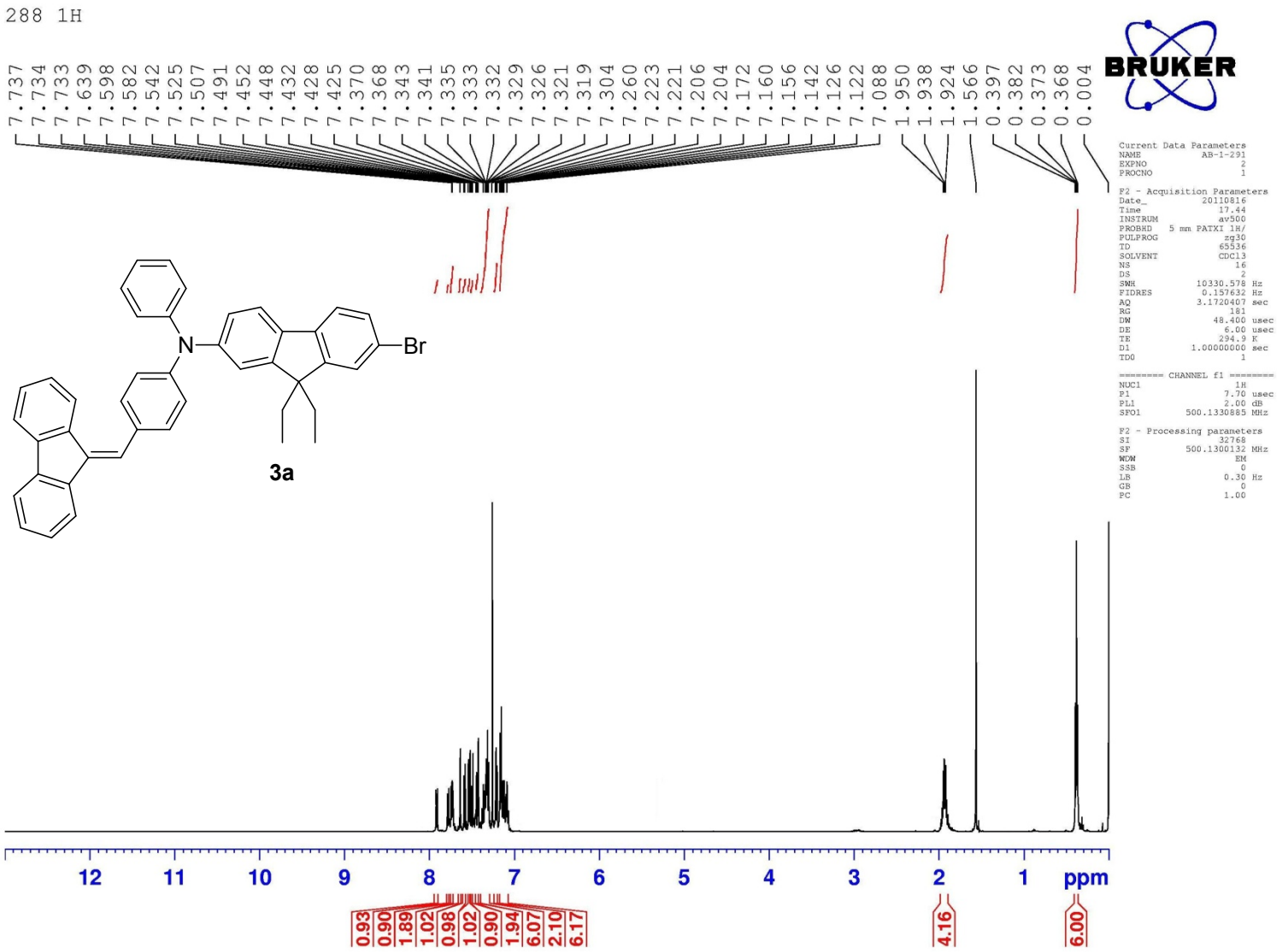

Fig. S20 ^{1}H NMR spectra of **3a** in $CDCl_3$

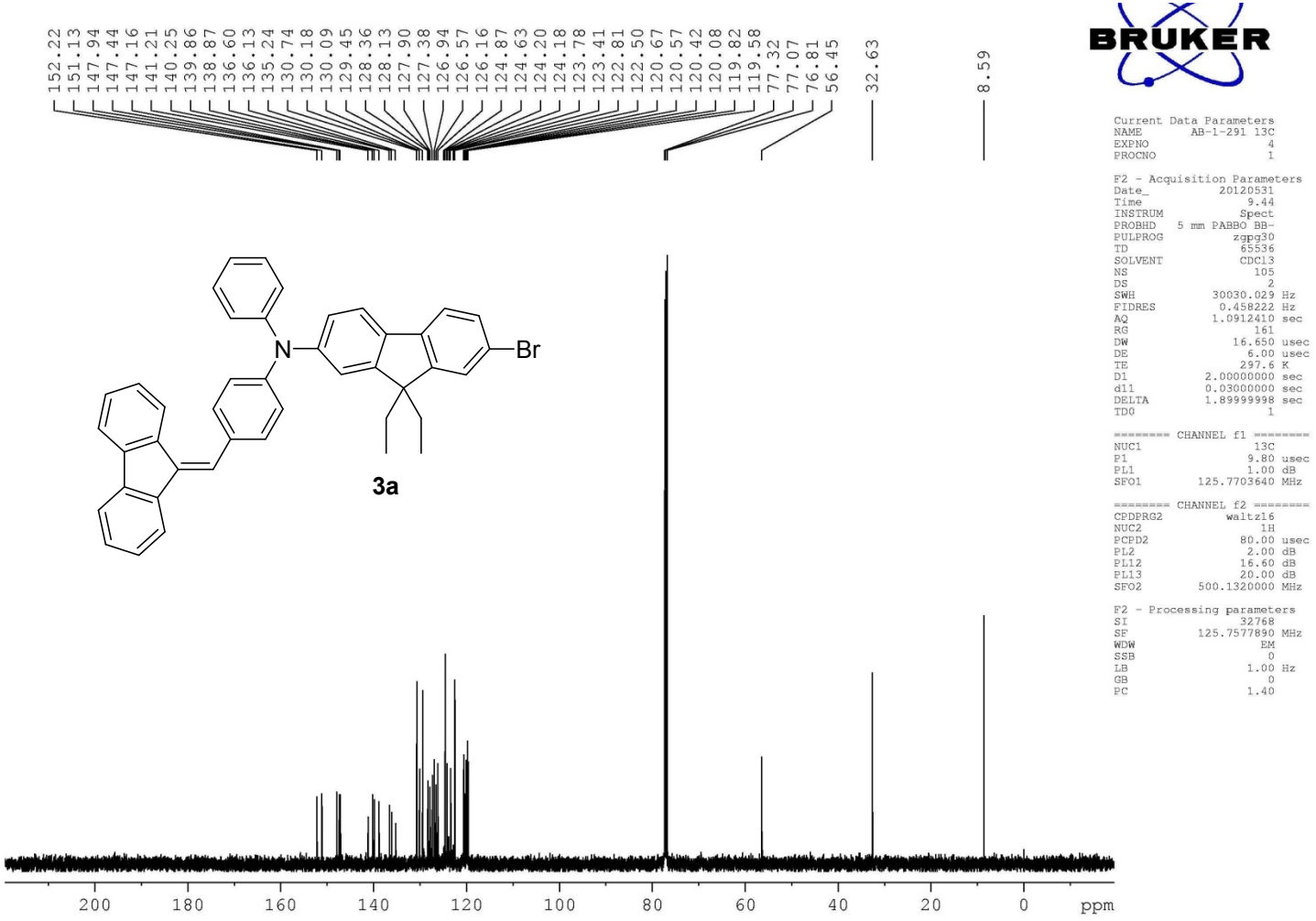

Fig. S21 ^{13}C NMR spectra of **3a** in $CDCl_3$

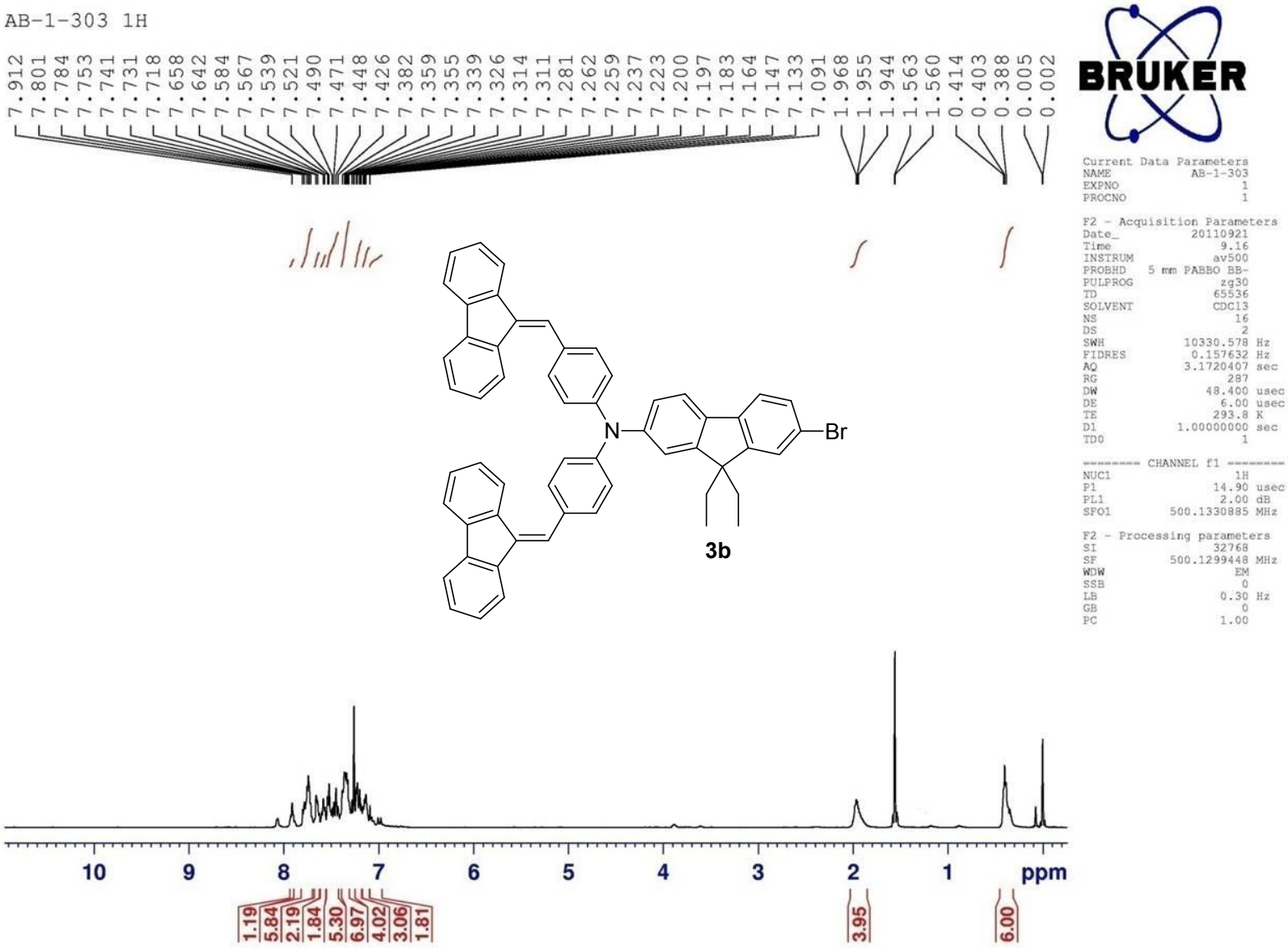

Fig. S22 ^{1}H NMR spectra of **3b** in $CDCl_3$

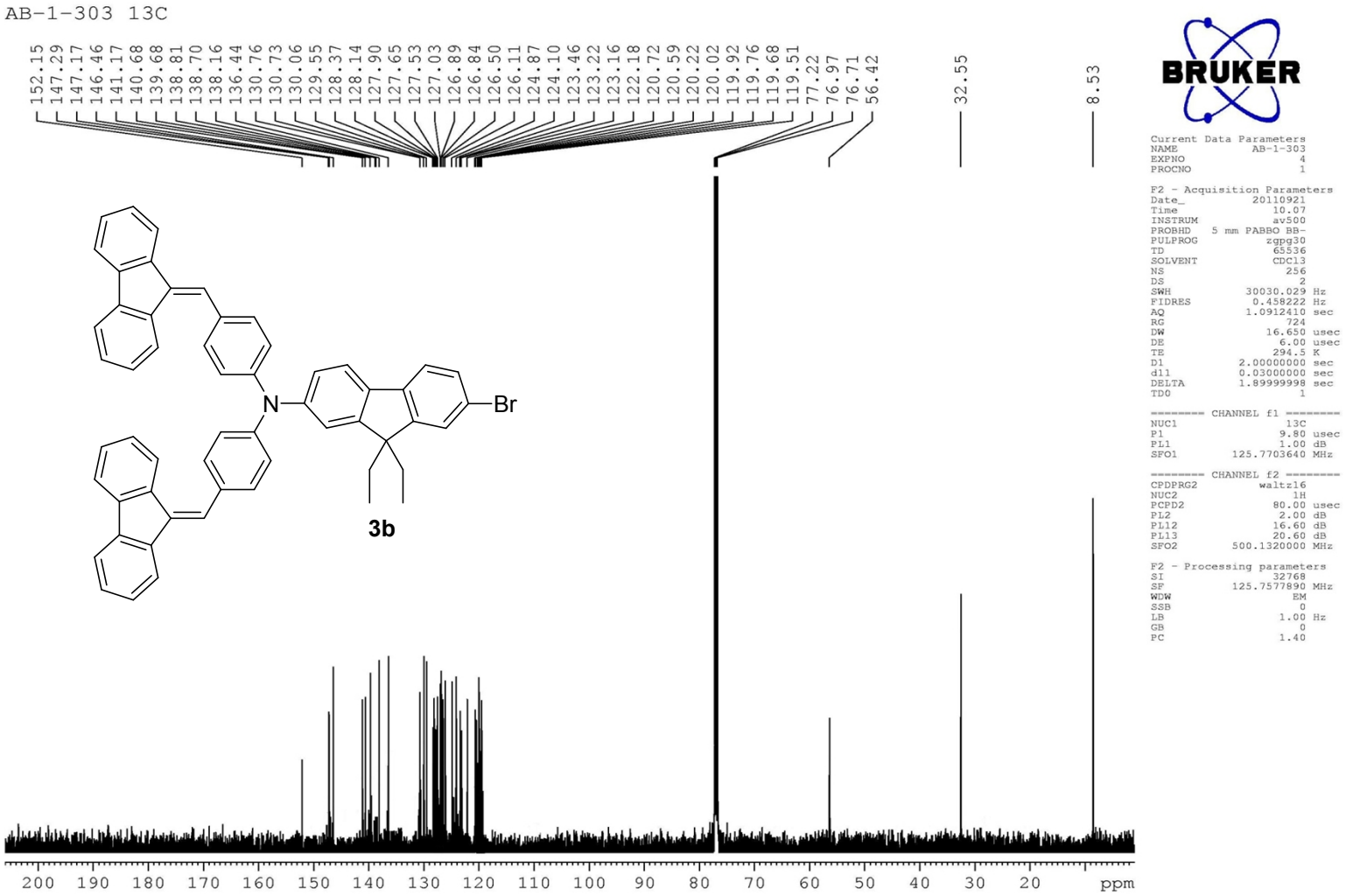

Fig. S23 ^{13}C NMR spectra of **3b** in $CDCl_3$

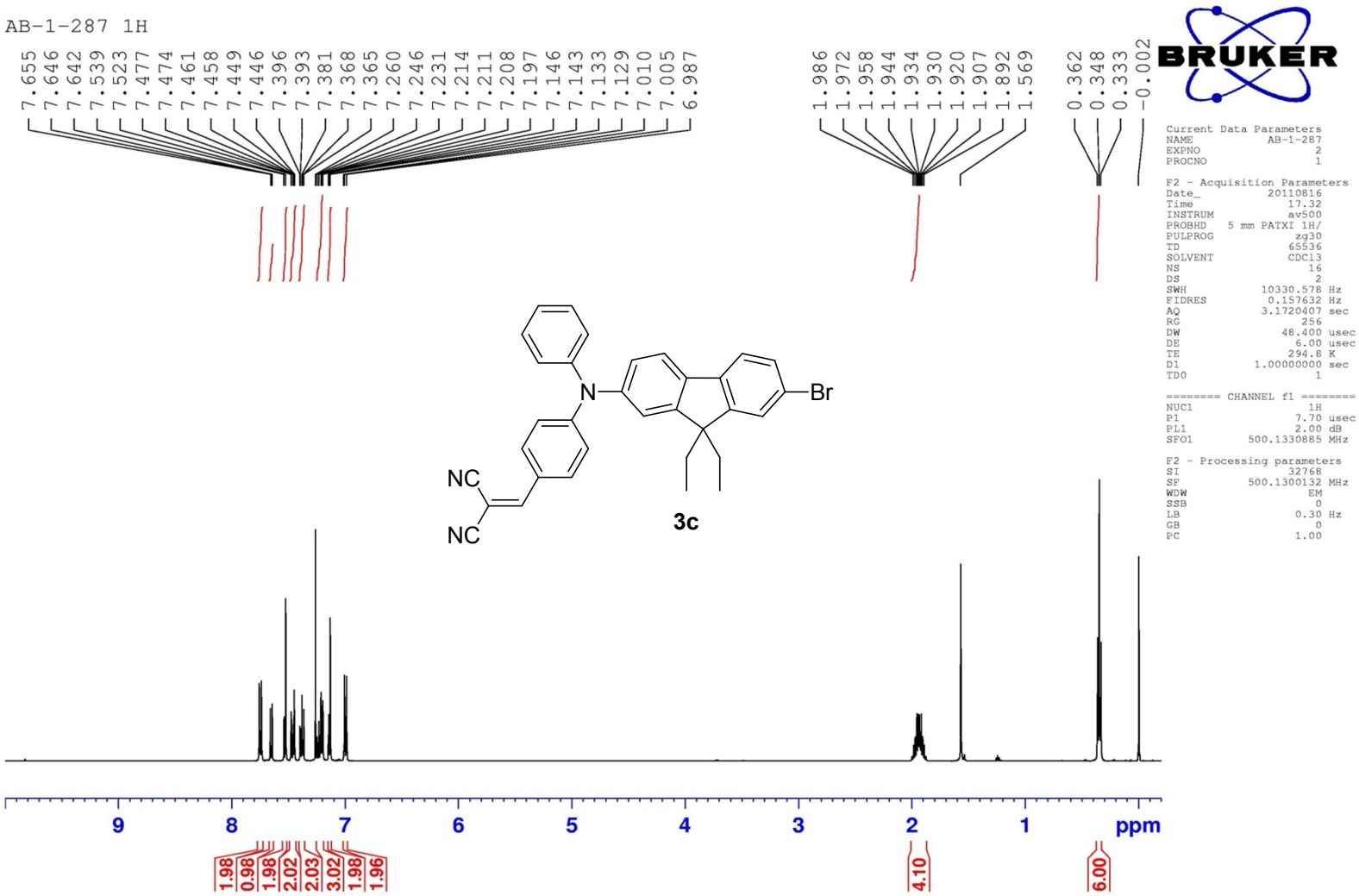

Fig. S24 ^{1}H NMR spectra of **3c** in $CDCl_3$

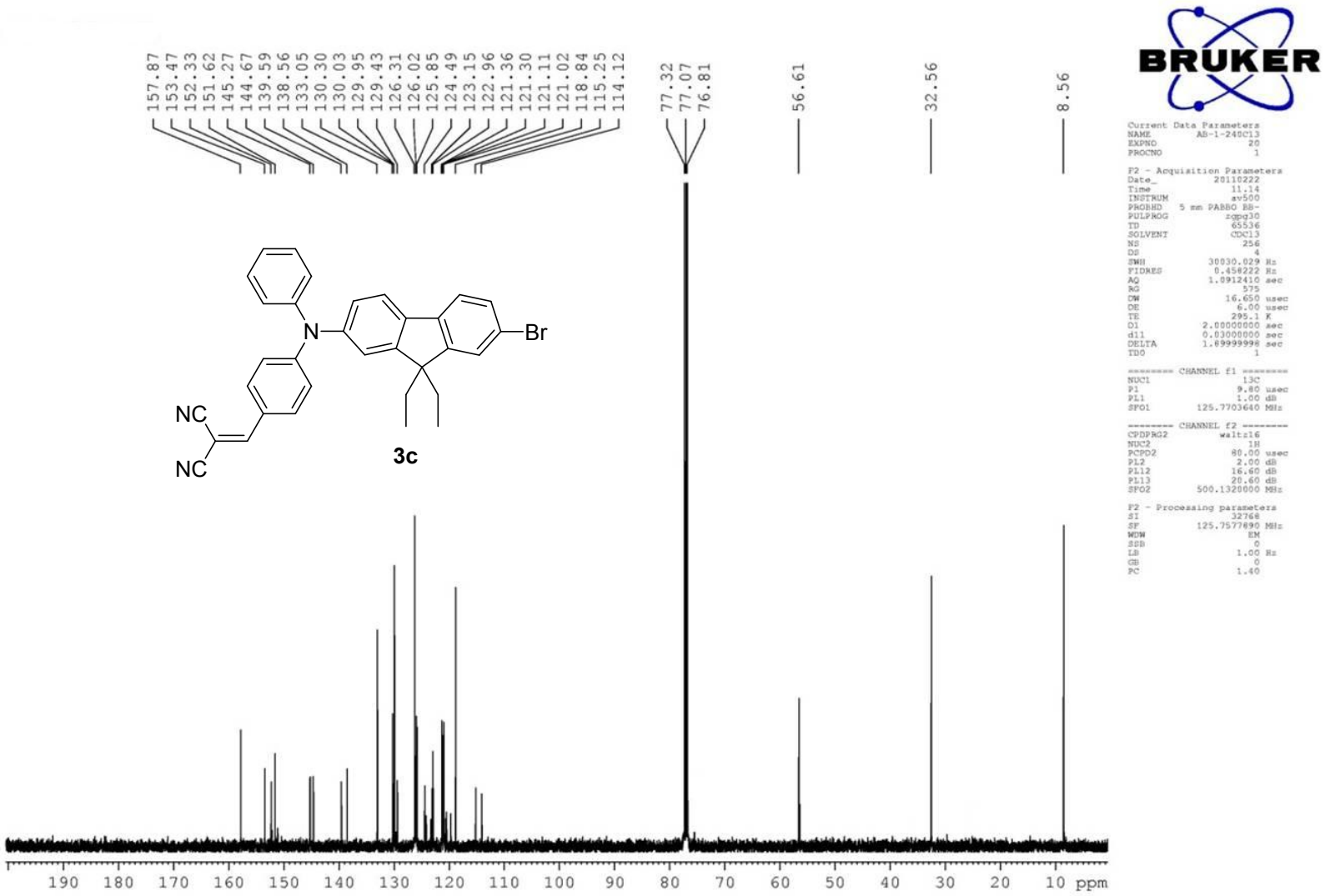

Fig. S25 ^{13}C NMR spectra of **3c** in $CDCl_3$

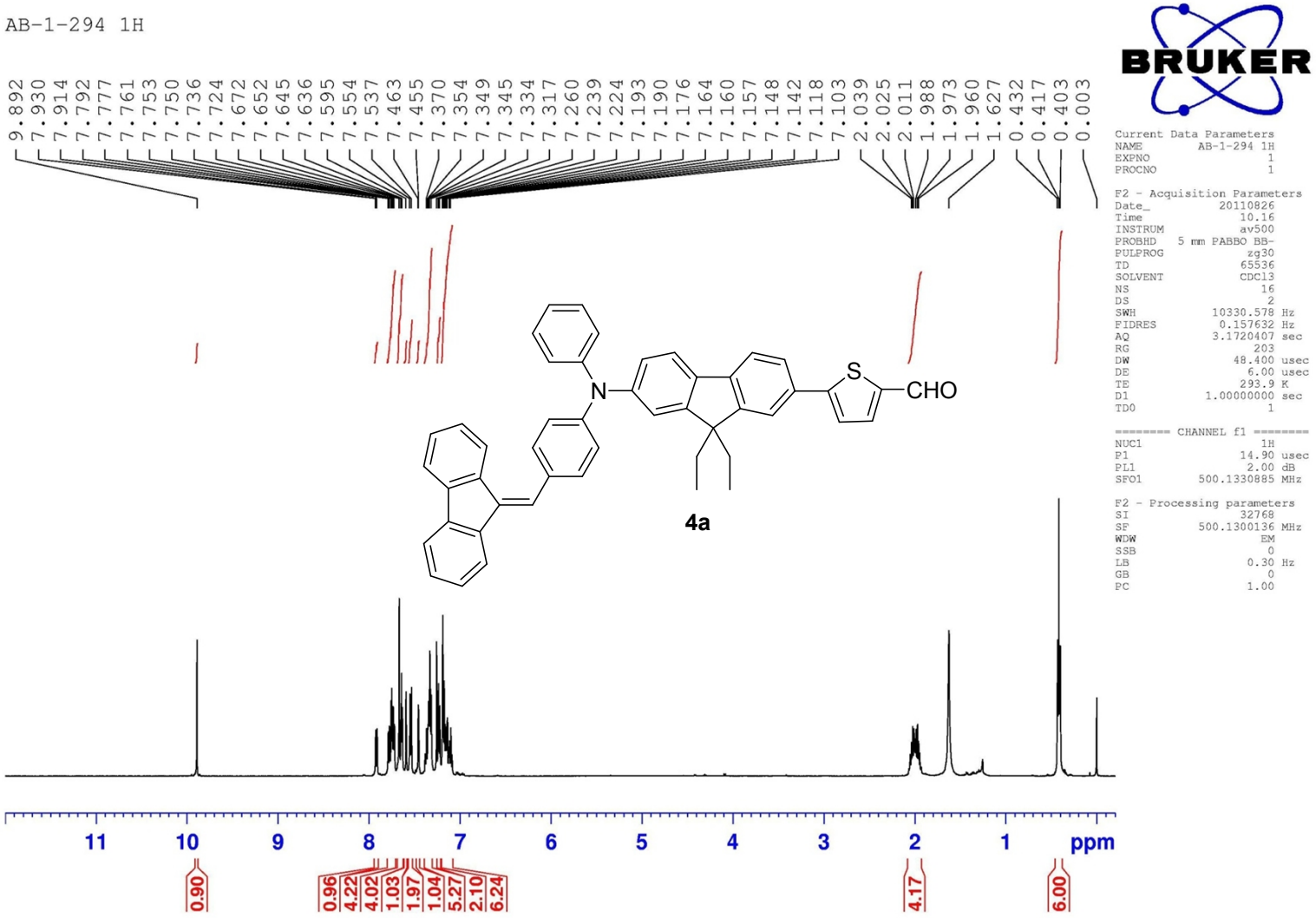

Fig. S26 ^{1}H NMR spectra of **4a** in $CDCl_3$

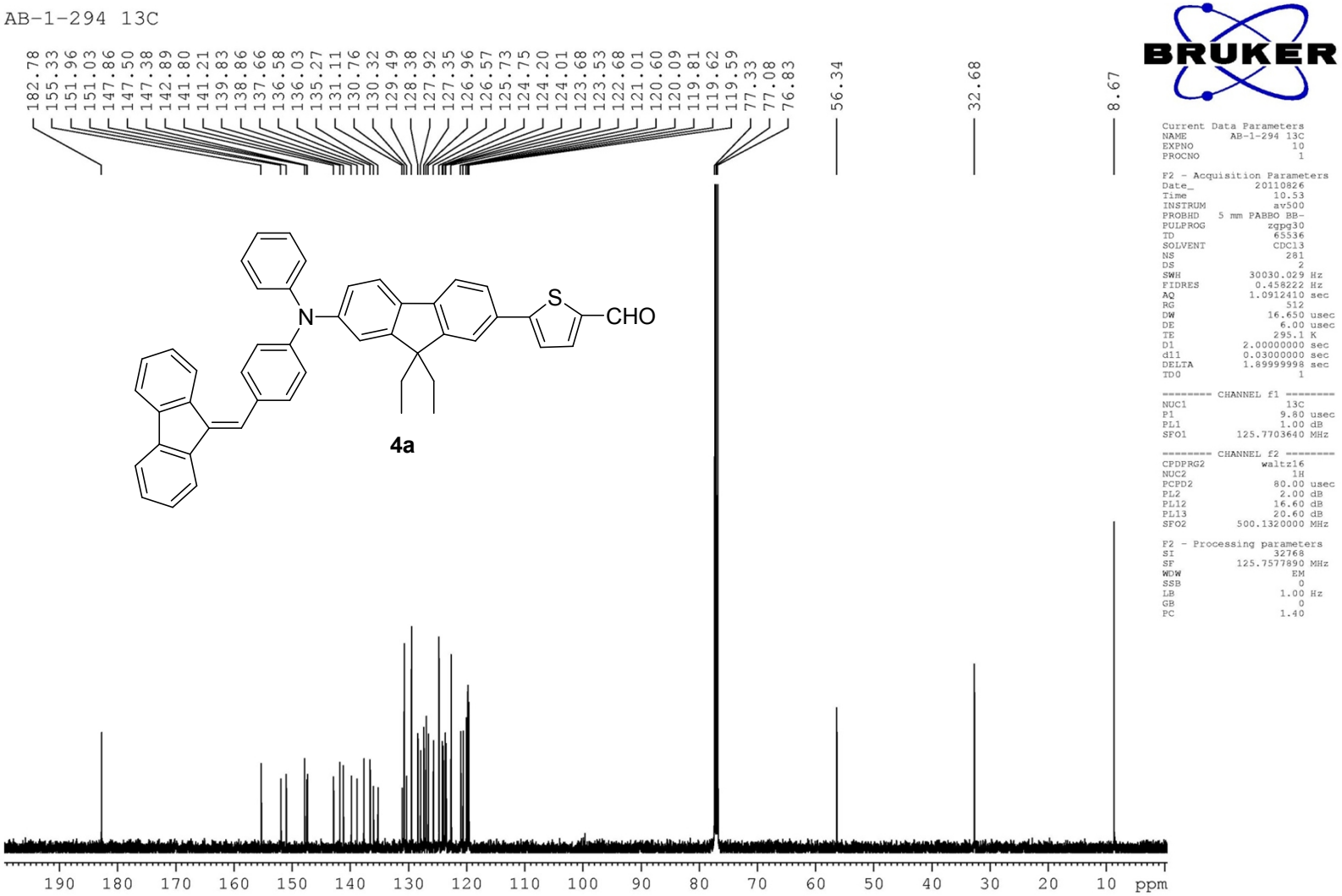

Fig. S27 ^{13}C NMR spectra of **4a** in $CDCl_3$

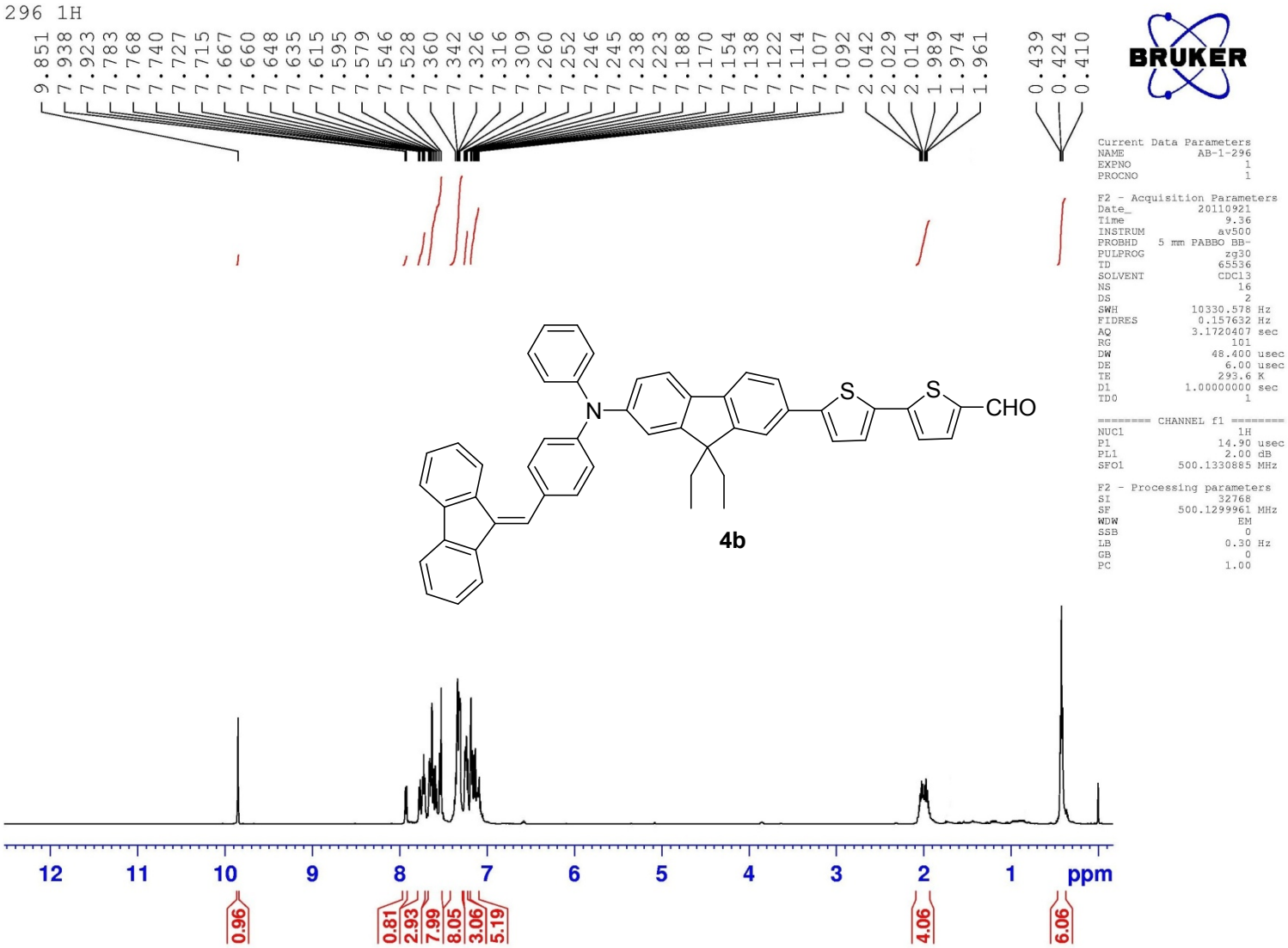

Fig. S28 ^{1}H NMR spectra of **4b** in $CDCl_3$

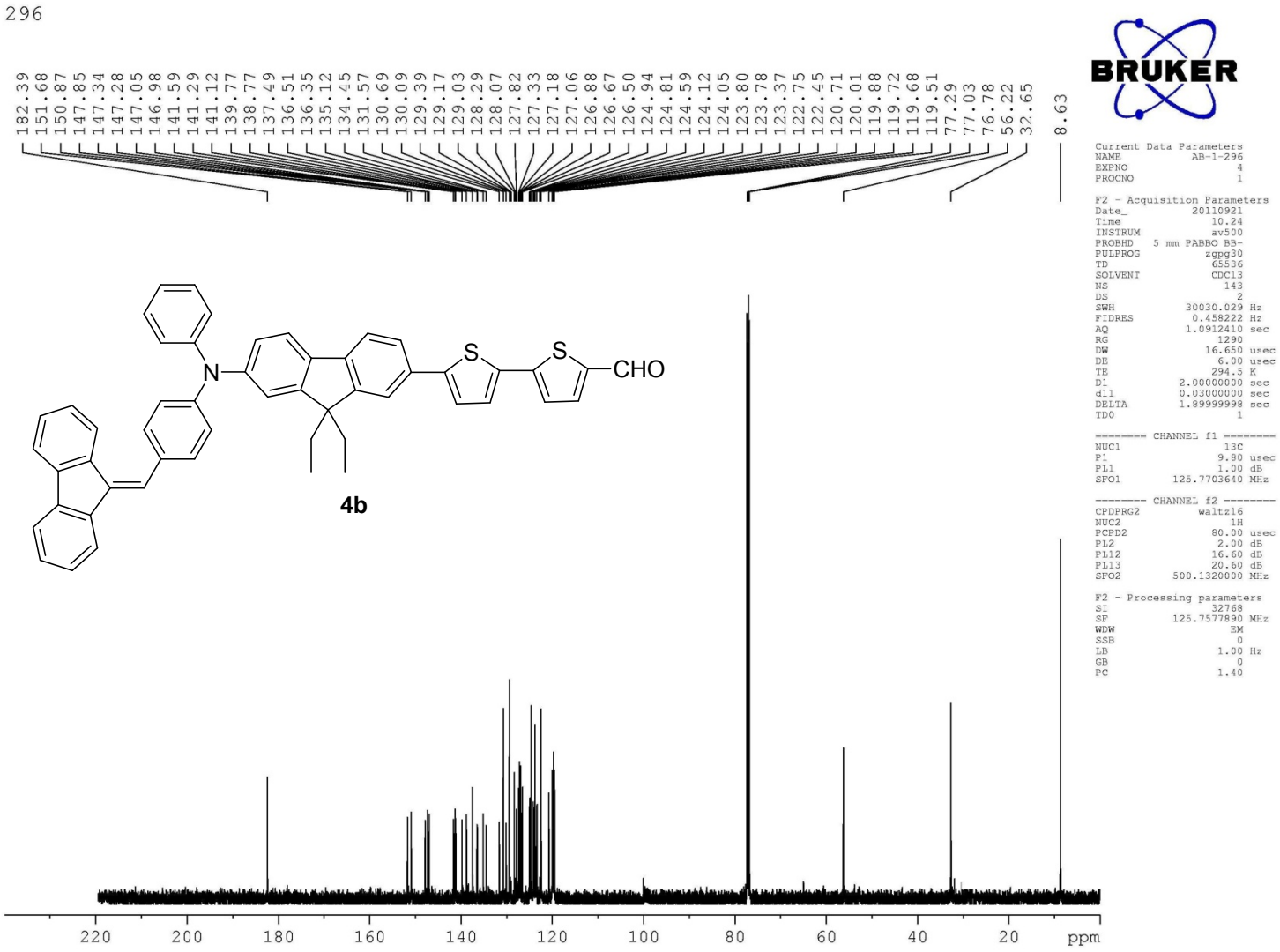

Fig. S29 ^{13}C NMR spectra of **4b** in $CDCl_3$

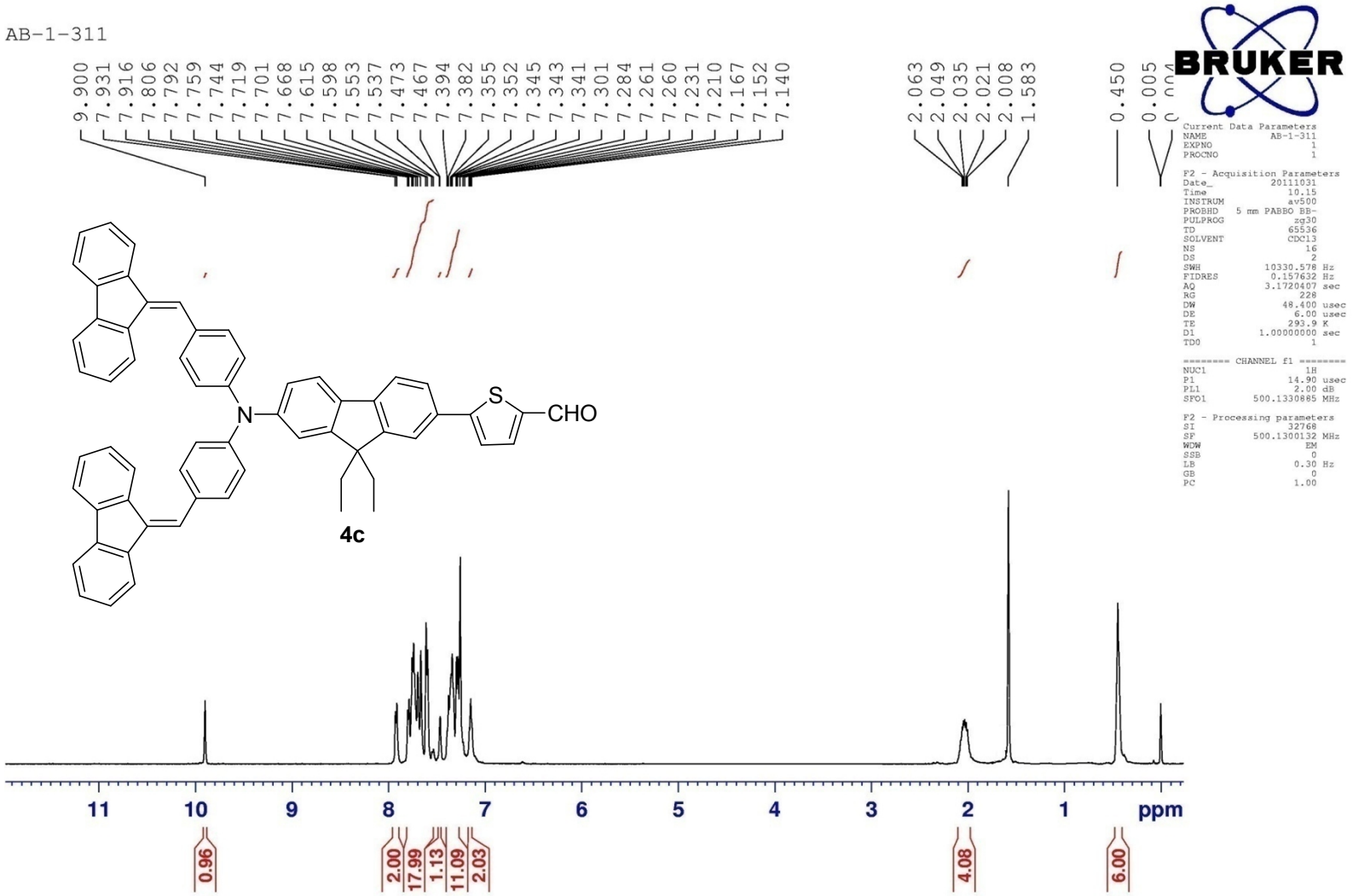

Fig. S30 ^{1}H NMR spectra of **4c** in $CDCl_3$

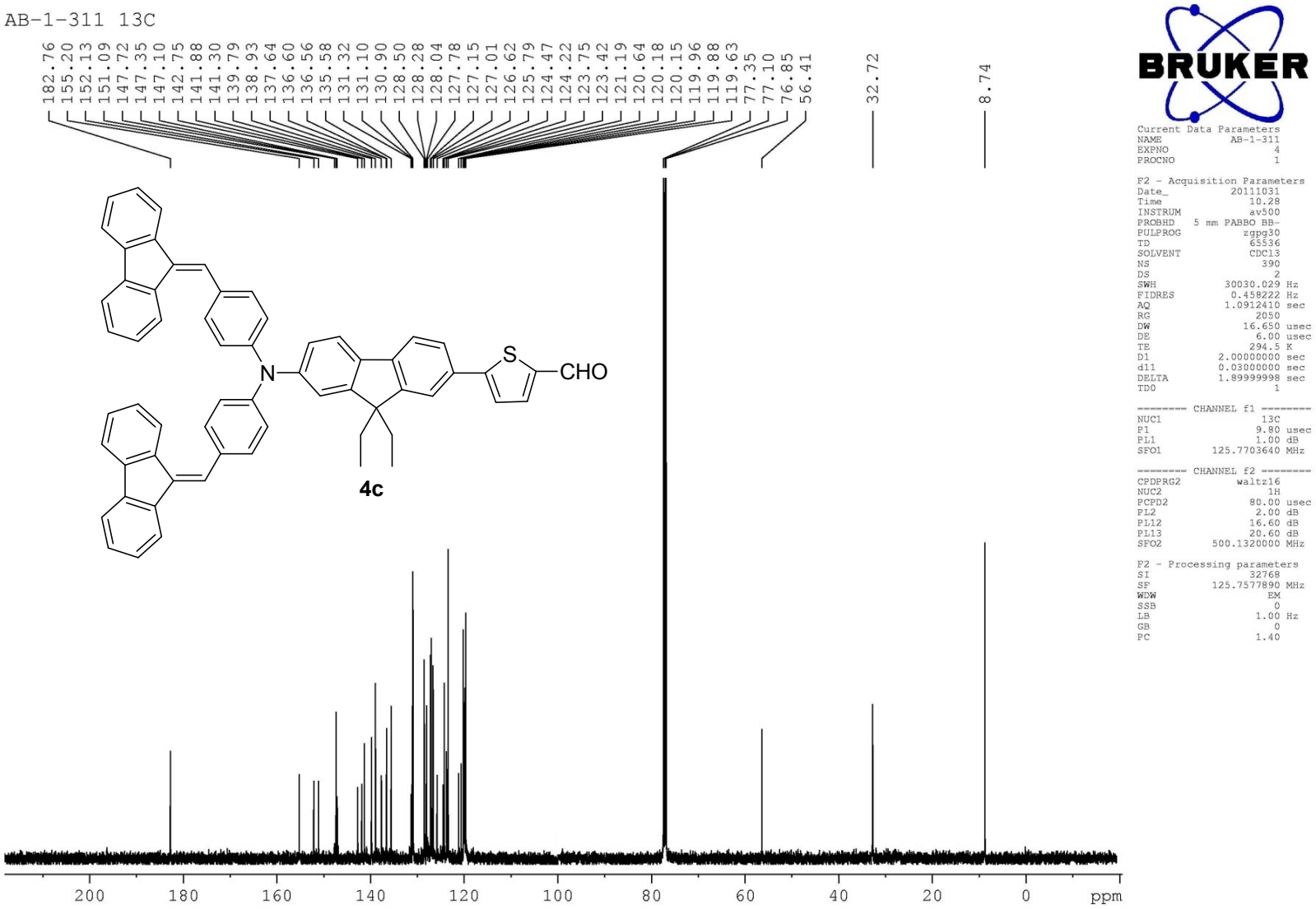

Fig. S31 ^{13}C NMR spectra of **4c** in $CDCl_3$

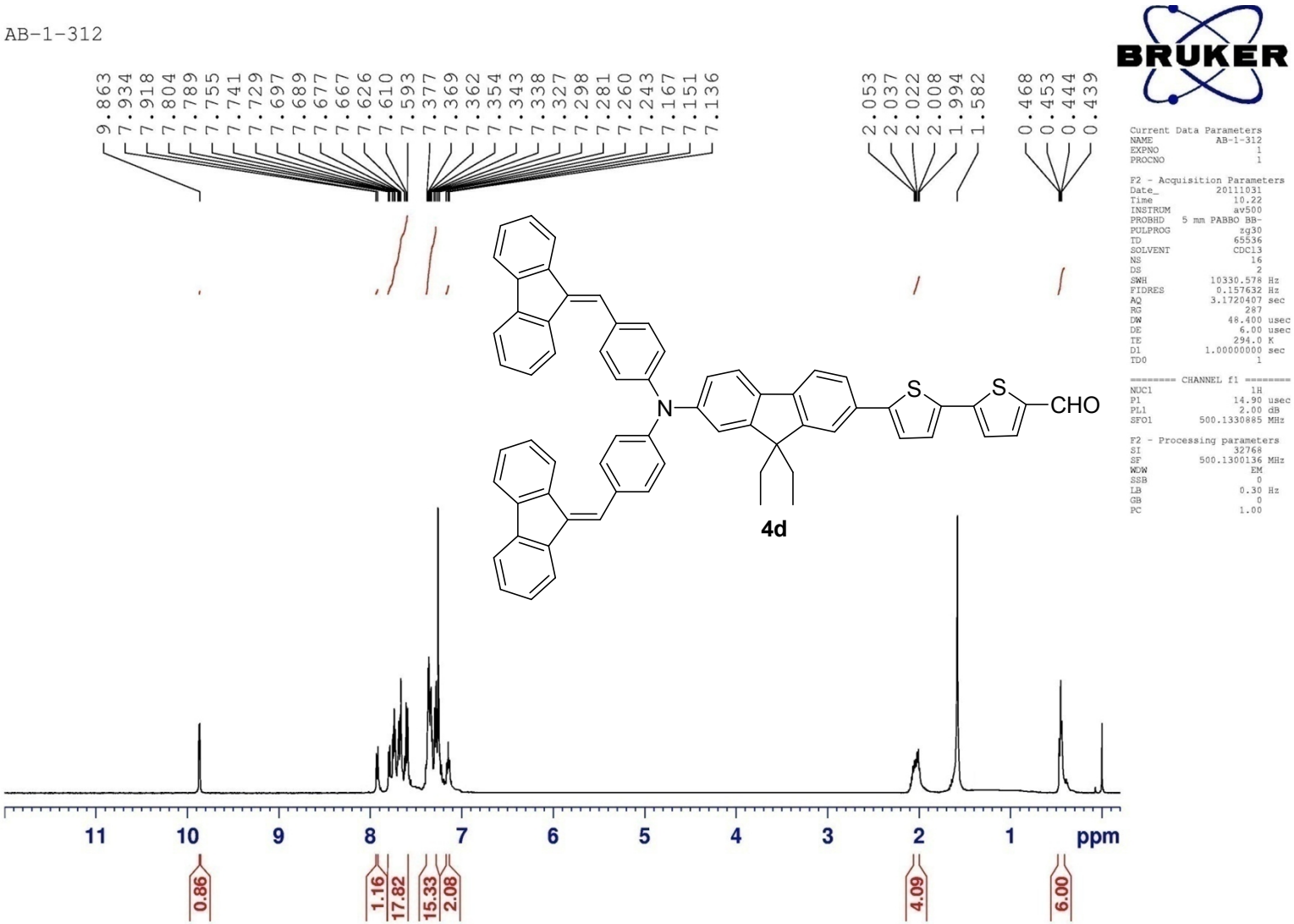

Fig. S32 ^{1}H NMR spectra of **4d** in $CDCl_3$

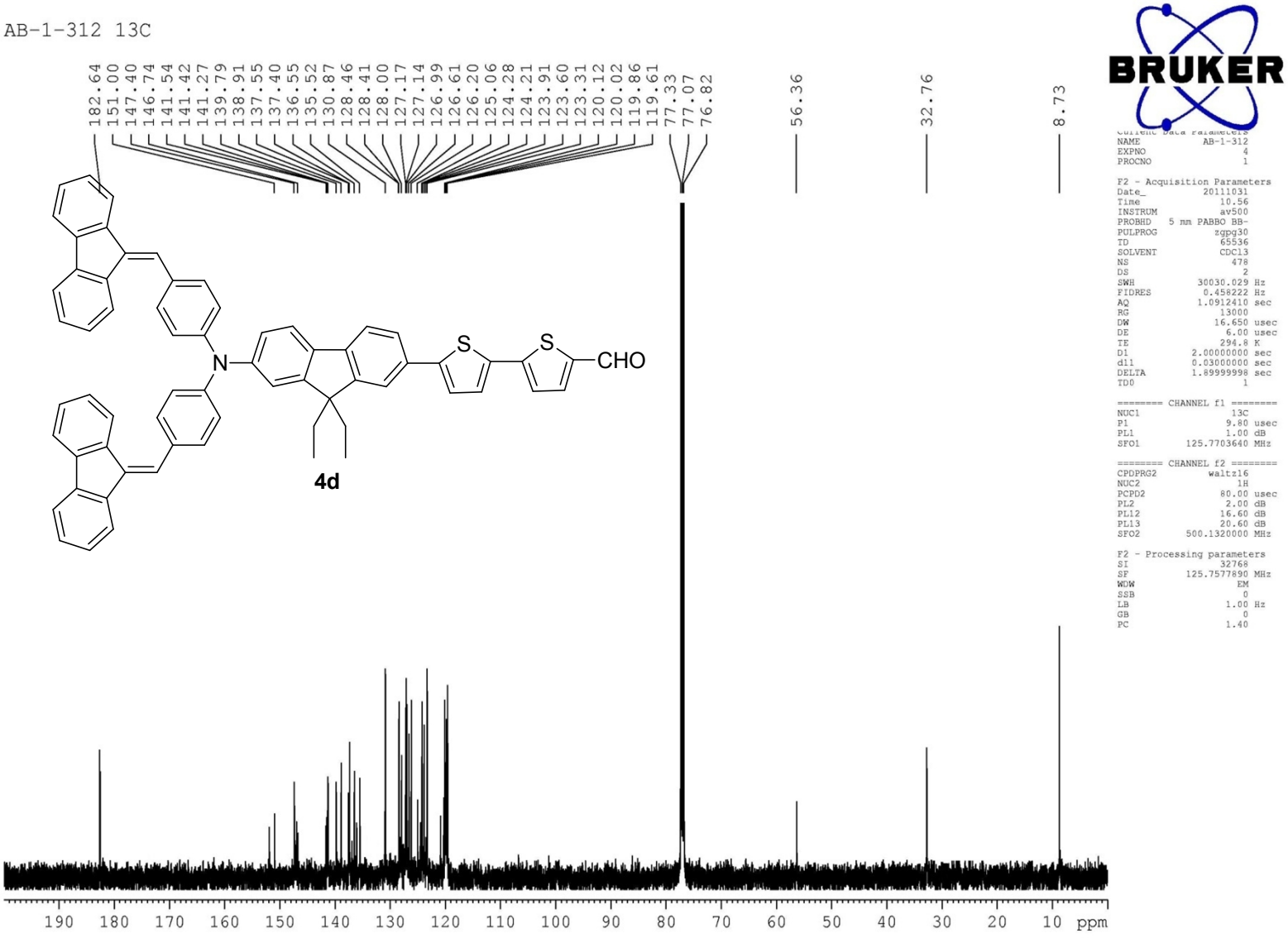

Fig. S33 ^{13}C NMR spectra of **4d** in $CDCl_3$

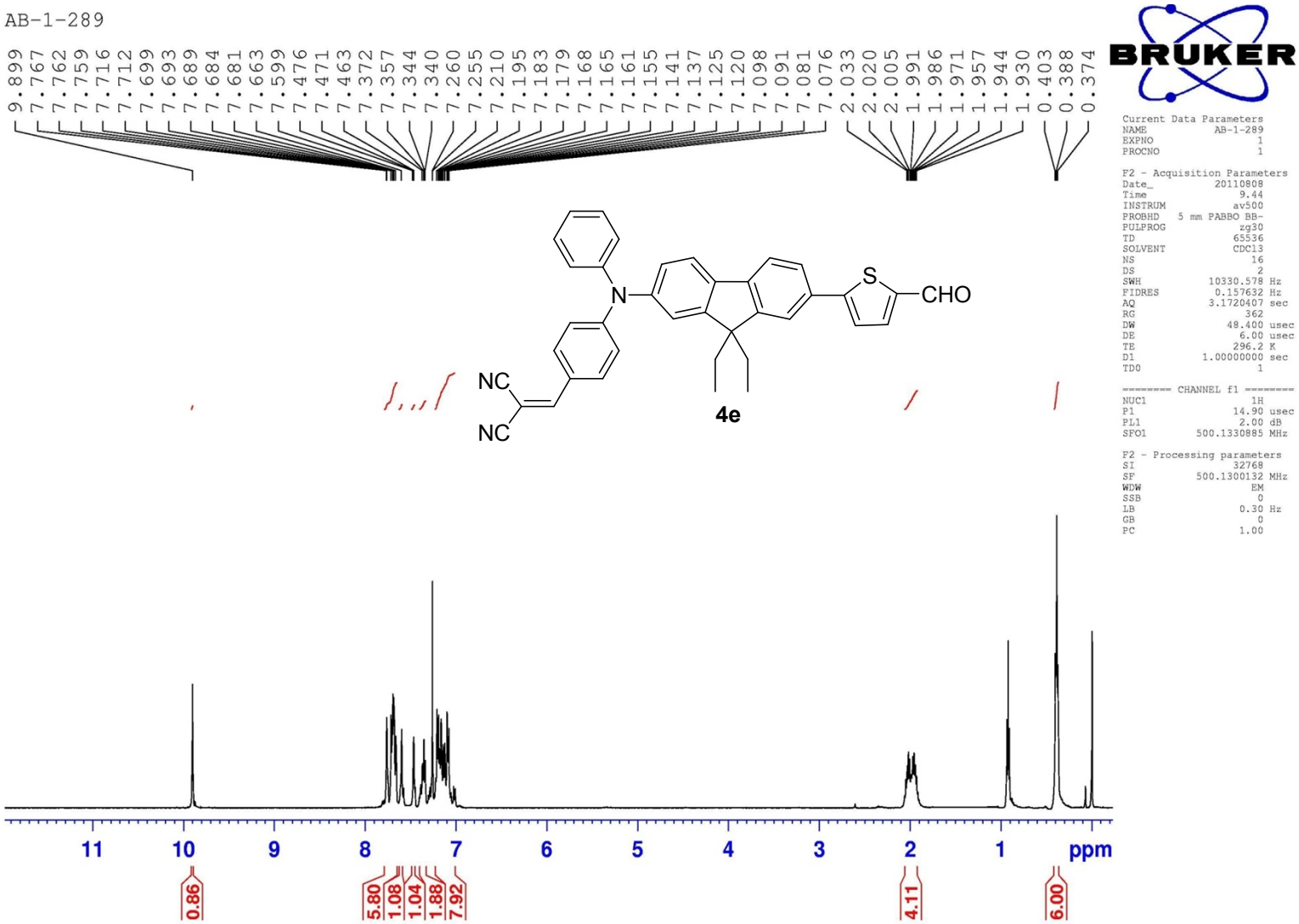

Fig. S34 ^{1}H NMR spectra of **4e** in $CDCl_3$

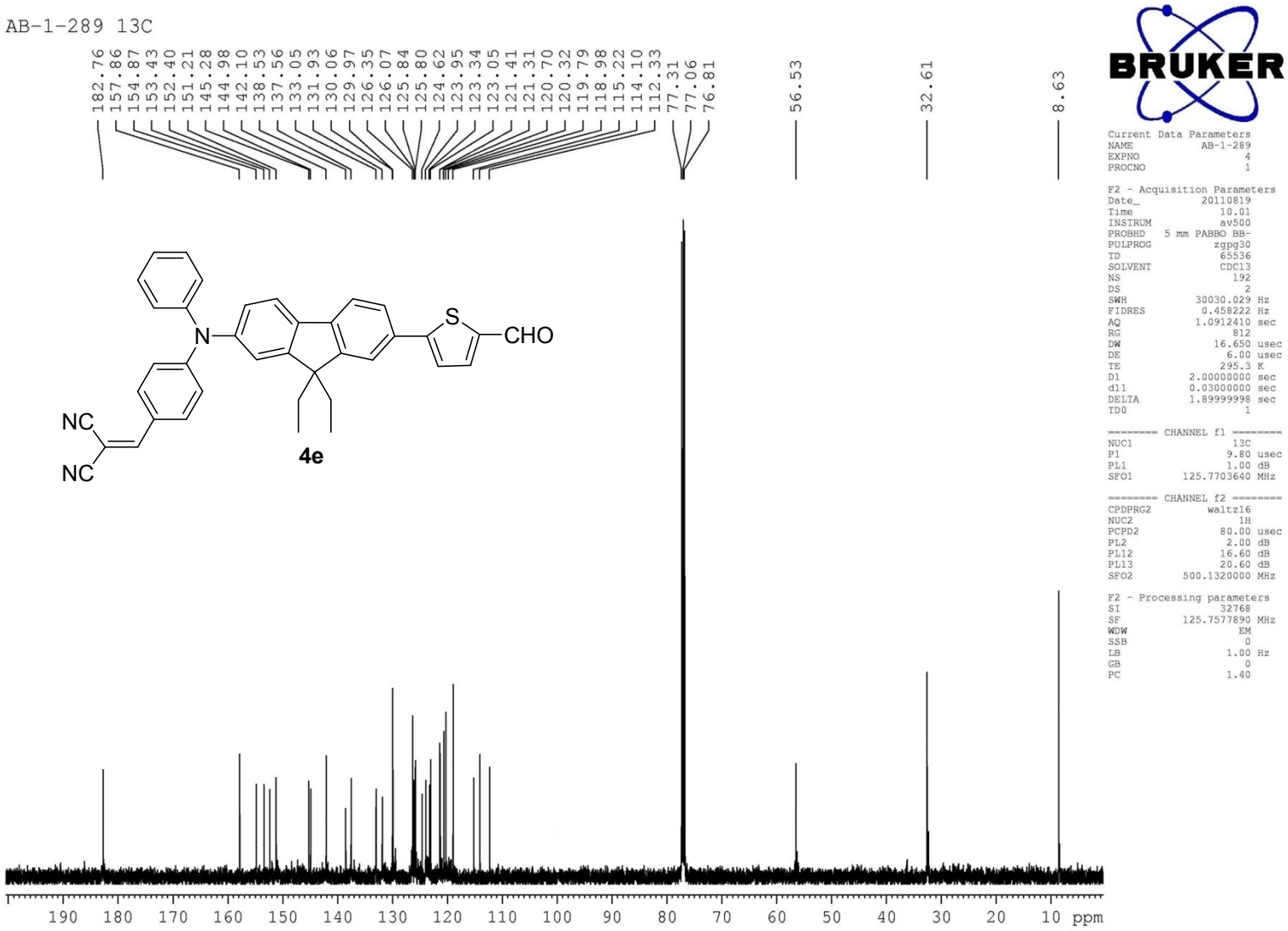

Fig. S35 ^{13}C NMR spectra of **4e** in $CDCl_3$

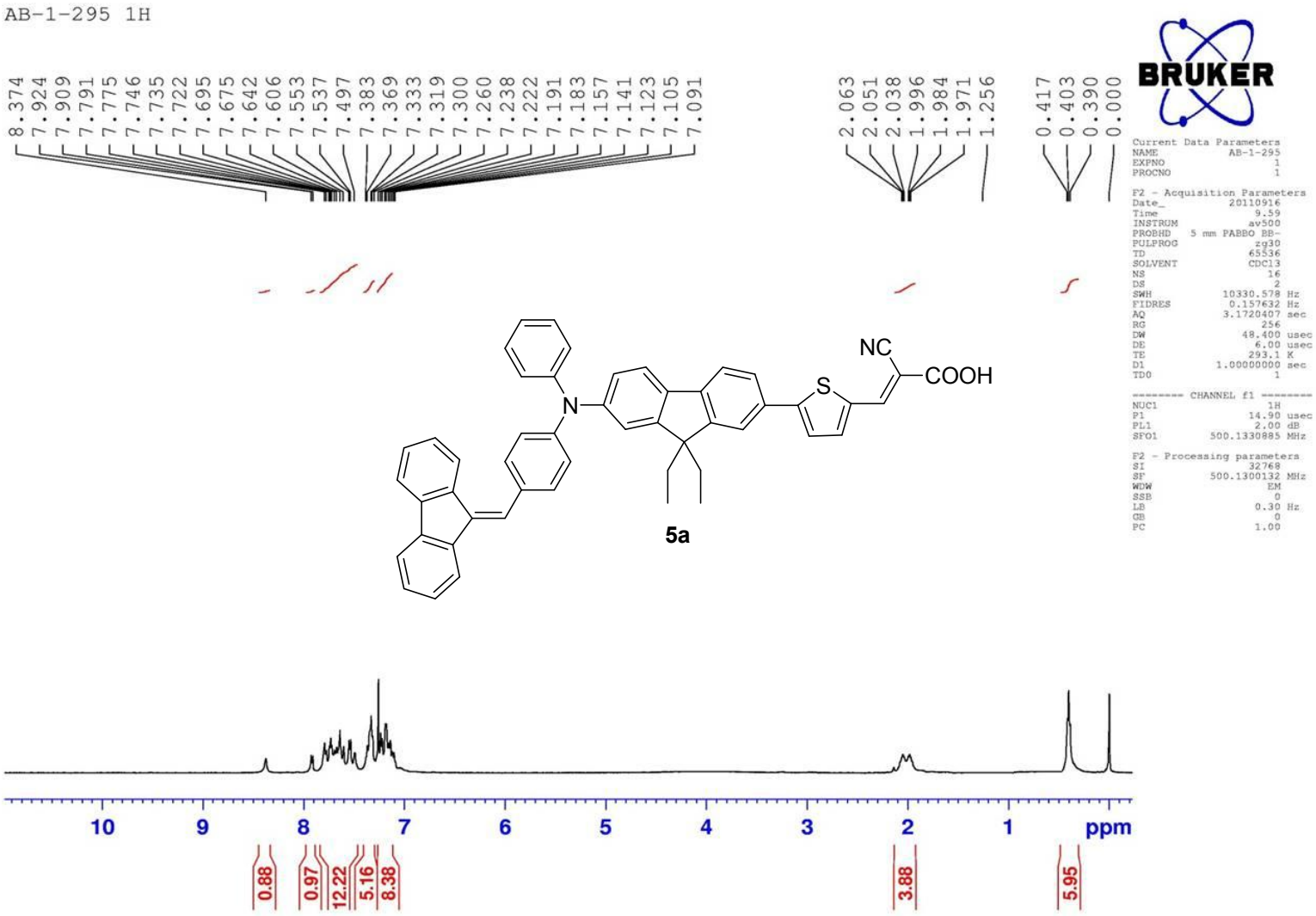

Fig. S36 ^{1}H NMR spectra of **5a** in $CDCl_3$

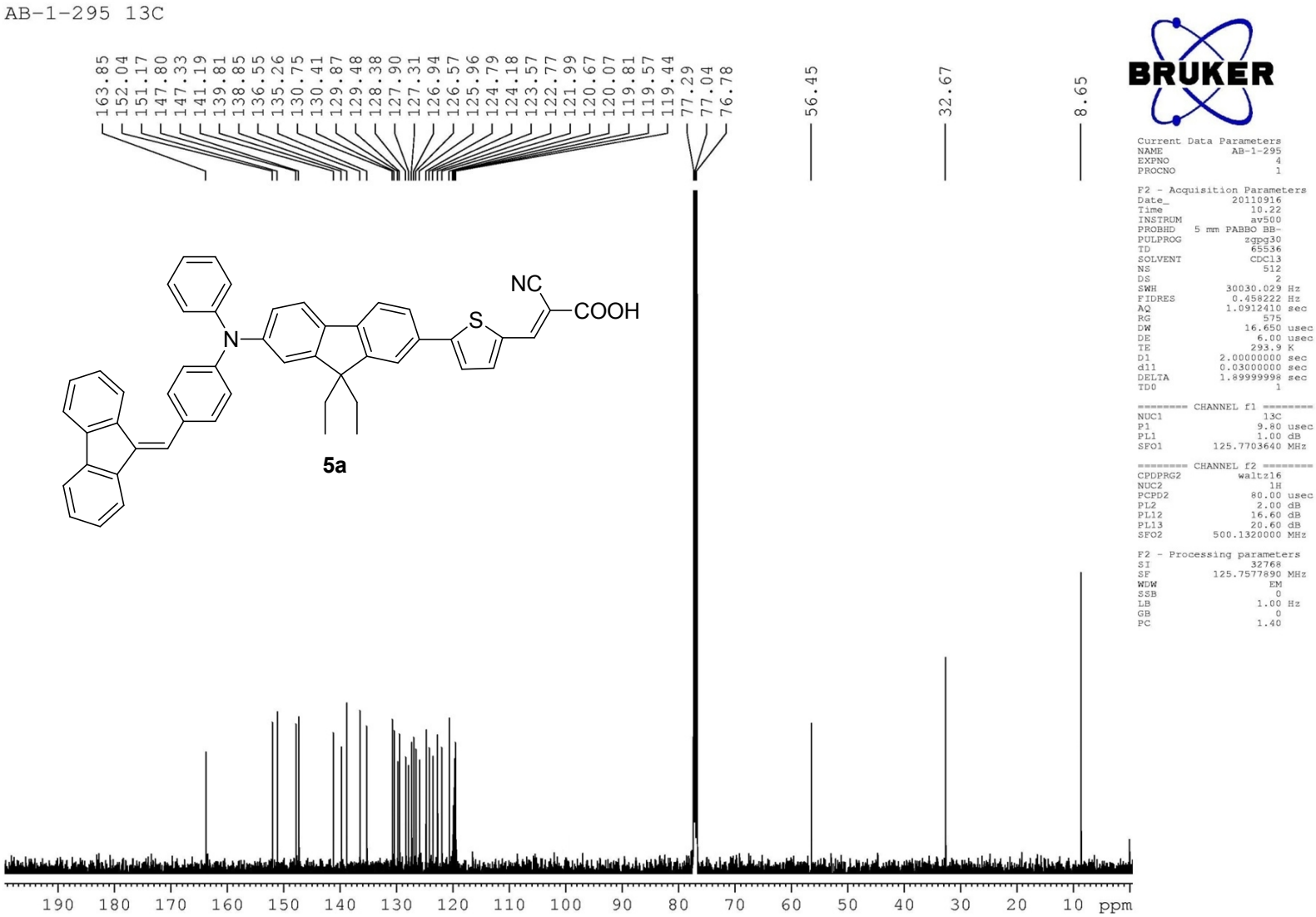

Fig. S37 ^{13}C NMR spectra of **5a** in $CDCl_3$

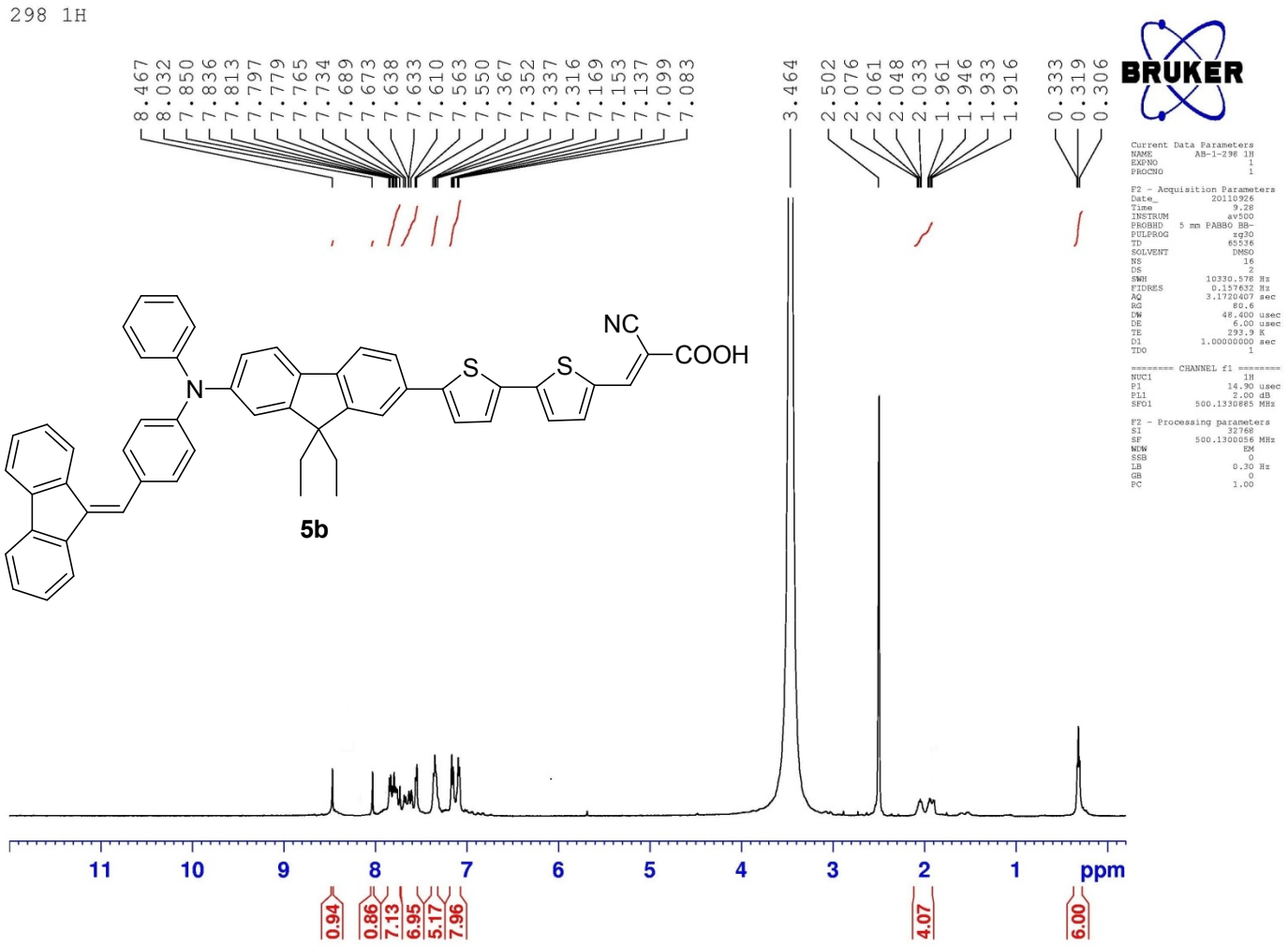

Fig. S38 ^{1}H NMR spectra of **5b** in DMSO-d_6

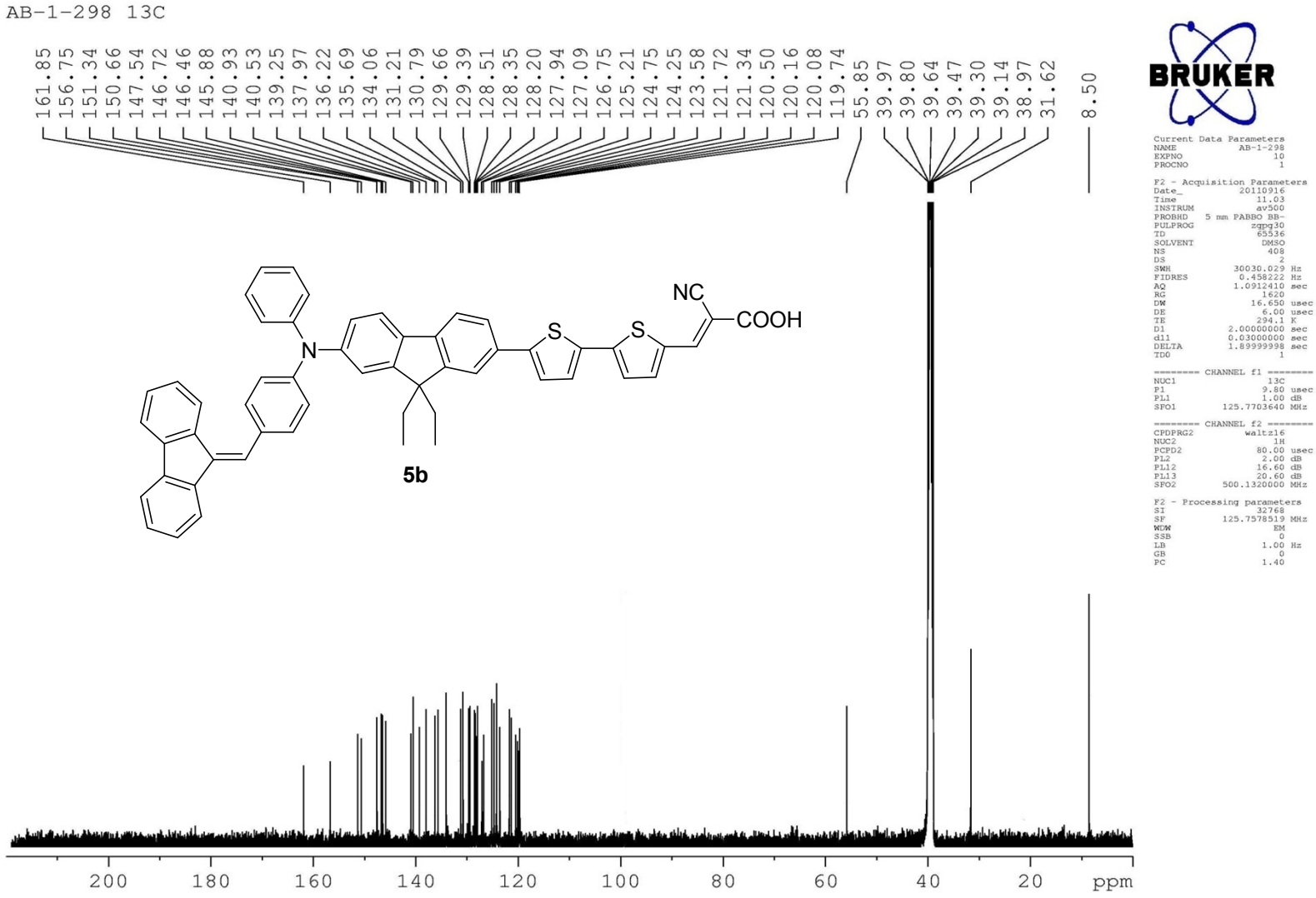

Fig. S39 ^{13}C NMR spectra of **5b** in DMSO-d_6

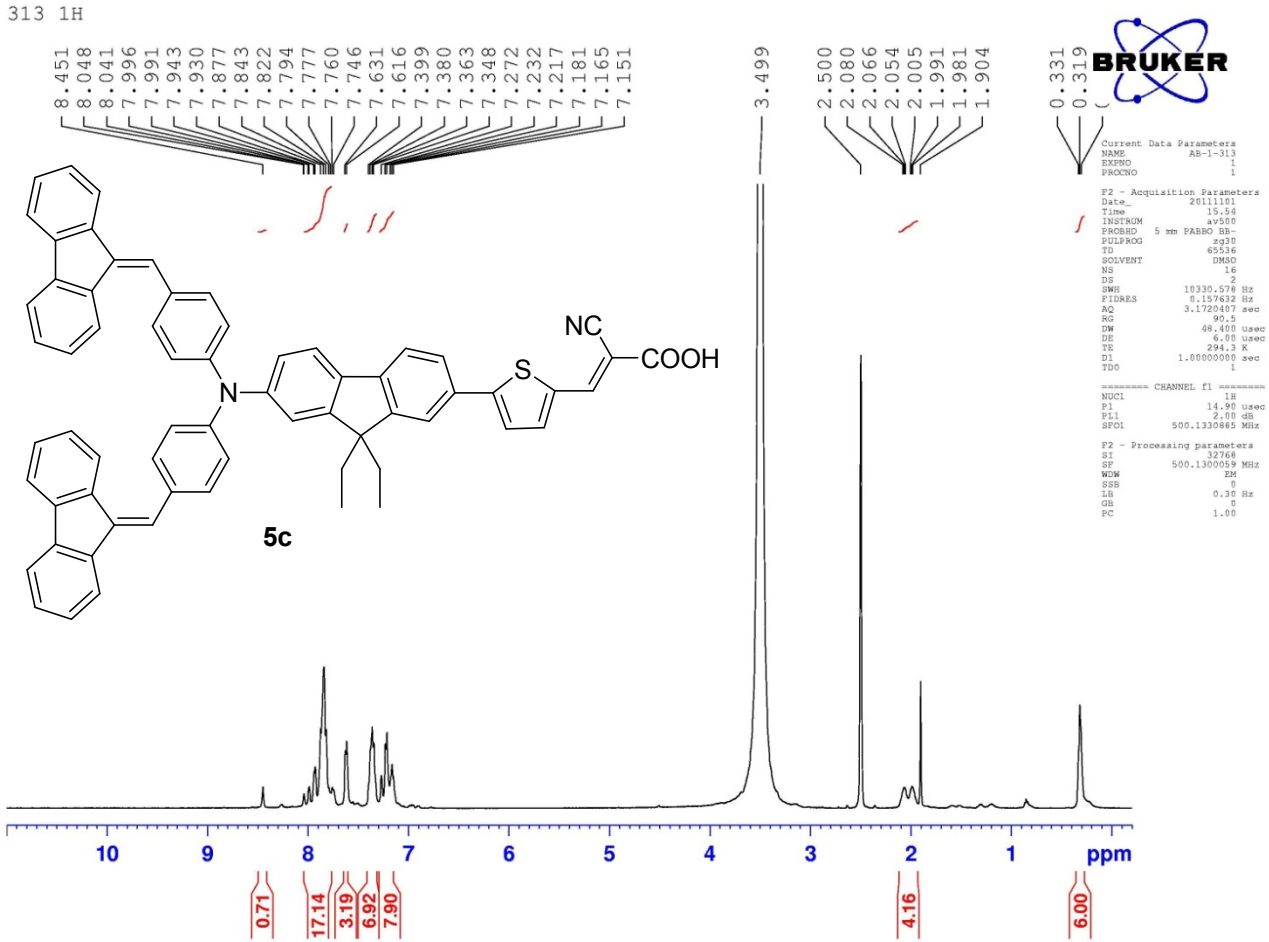

Fig. S40 ^{1}H NMR spectra of **5c** in DMSO-d_6

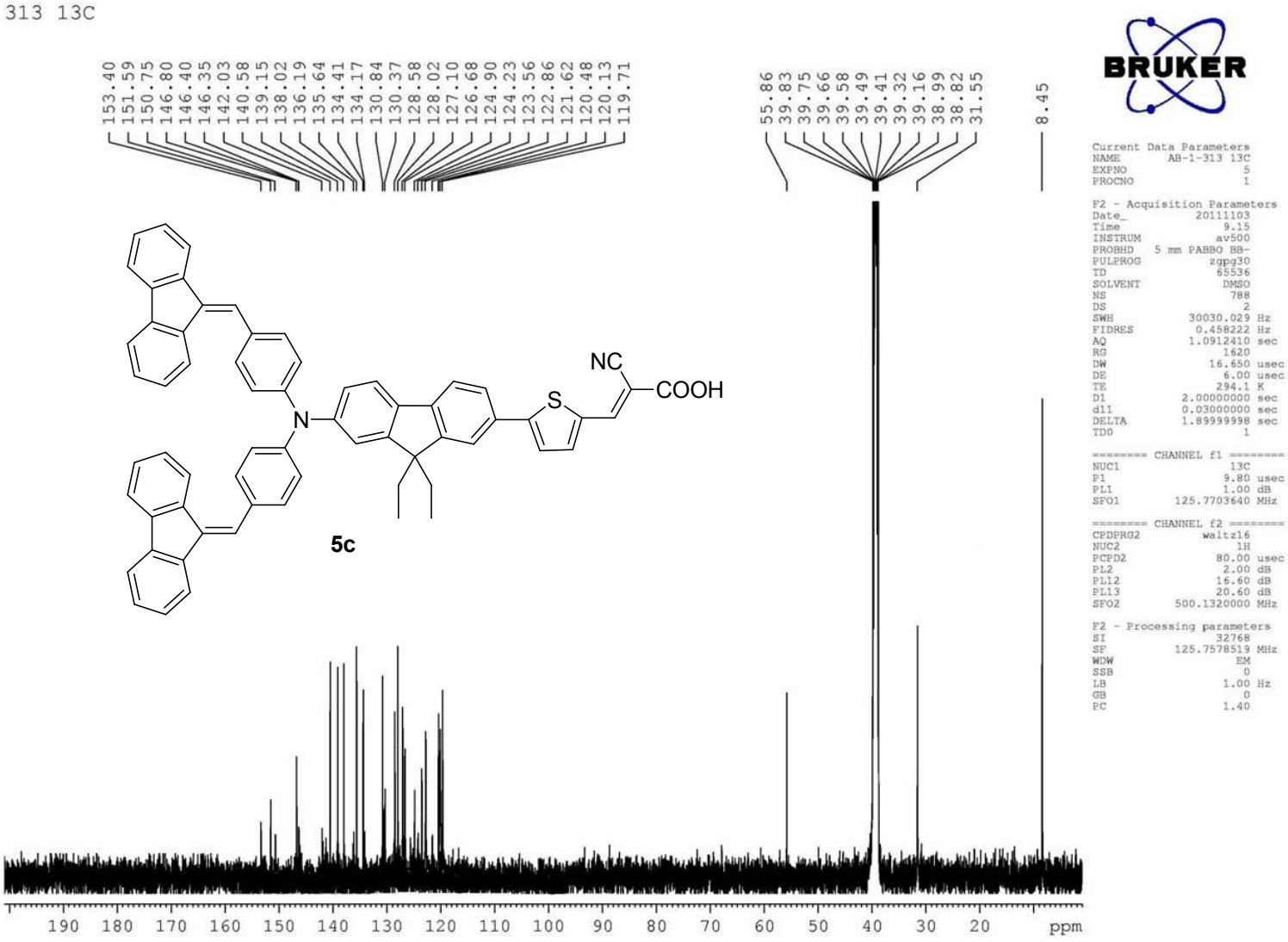

Fig. S41 ^{13}C NMR spectra of **5c** in DMSO-d_6

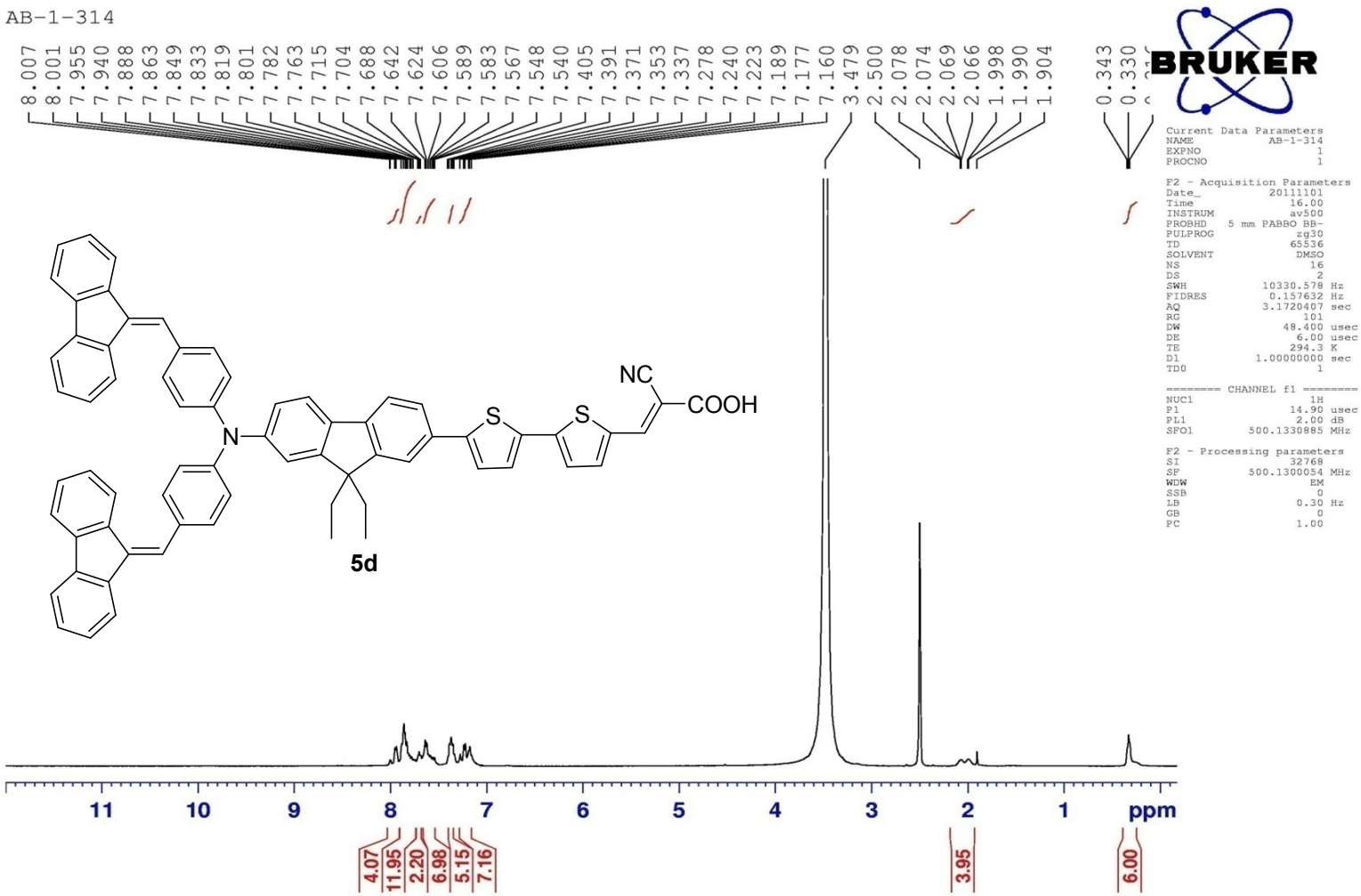

Fig. S42 ^{1}H NMR spectra of **5d** in DMSO-d_6

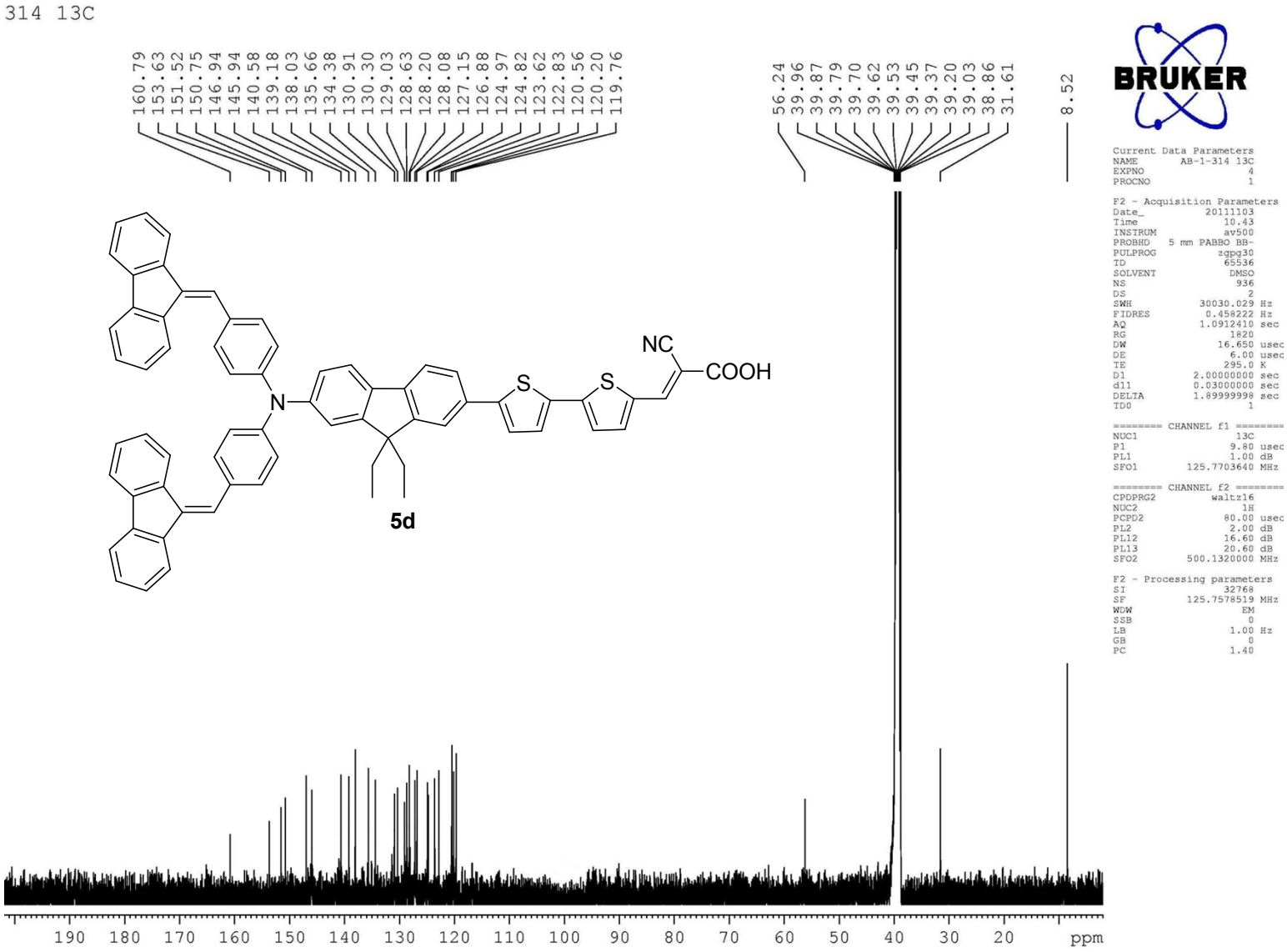

Fig. S43 ^{13}C NMR spectra of **5d** in DMSO-d_6

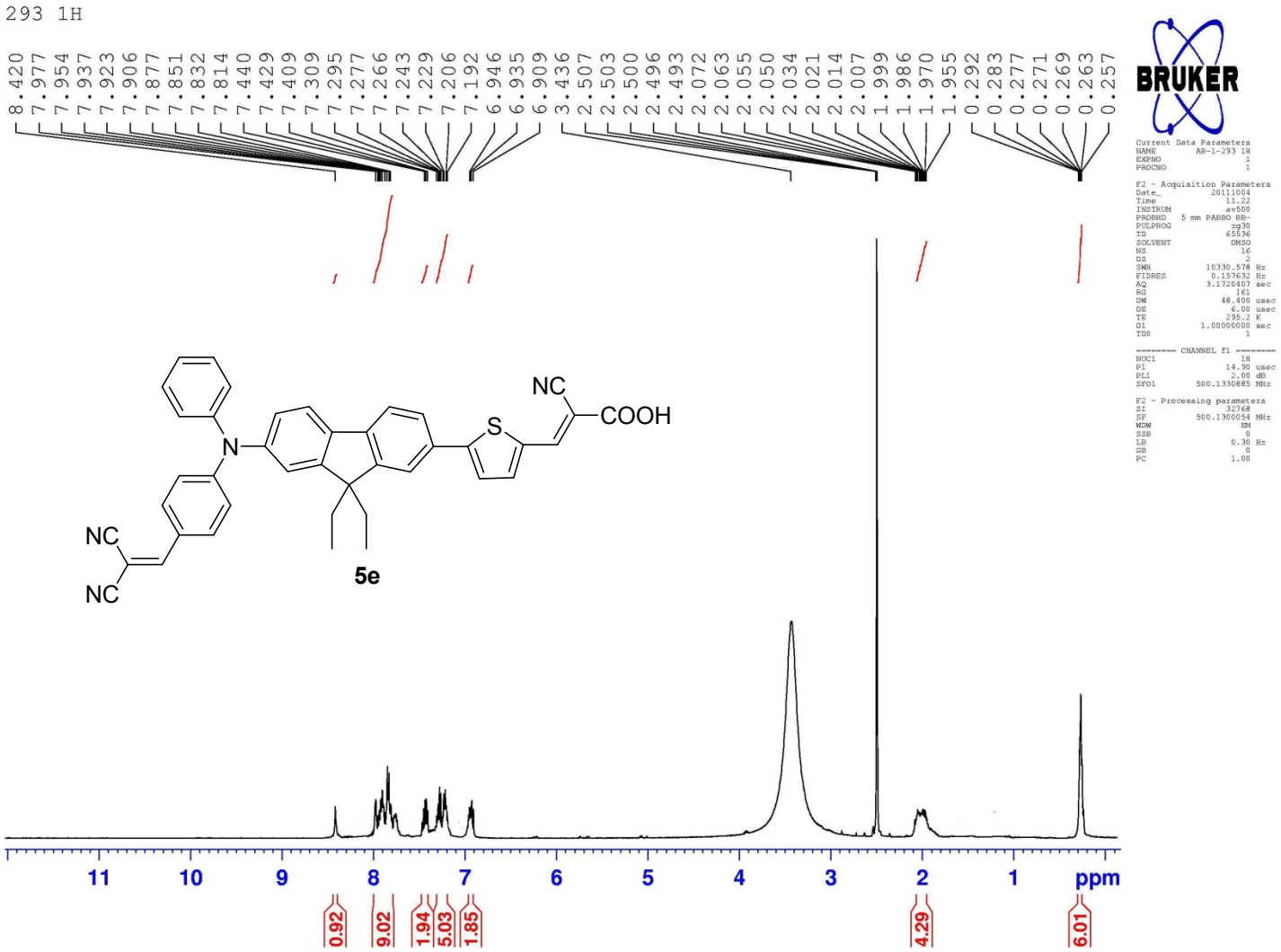

Fig. S44 ^{1}H NMR spectra of **5e** in DMSO-d_6

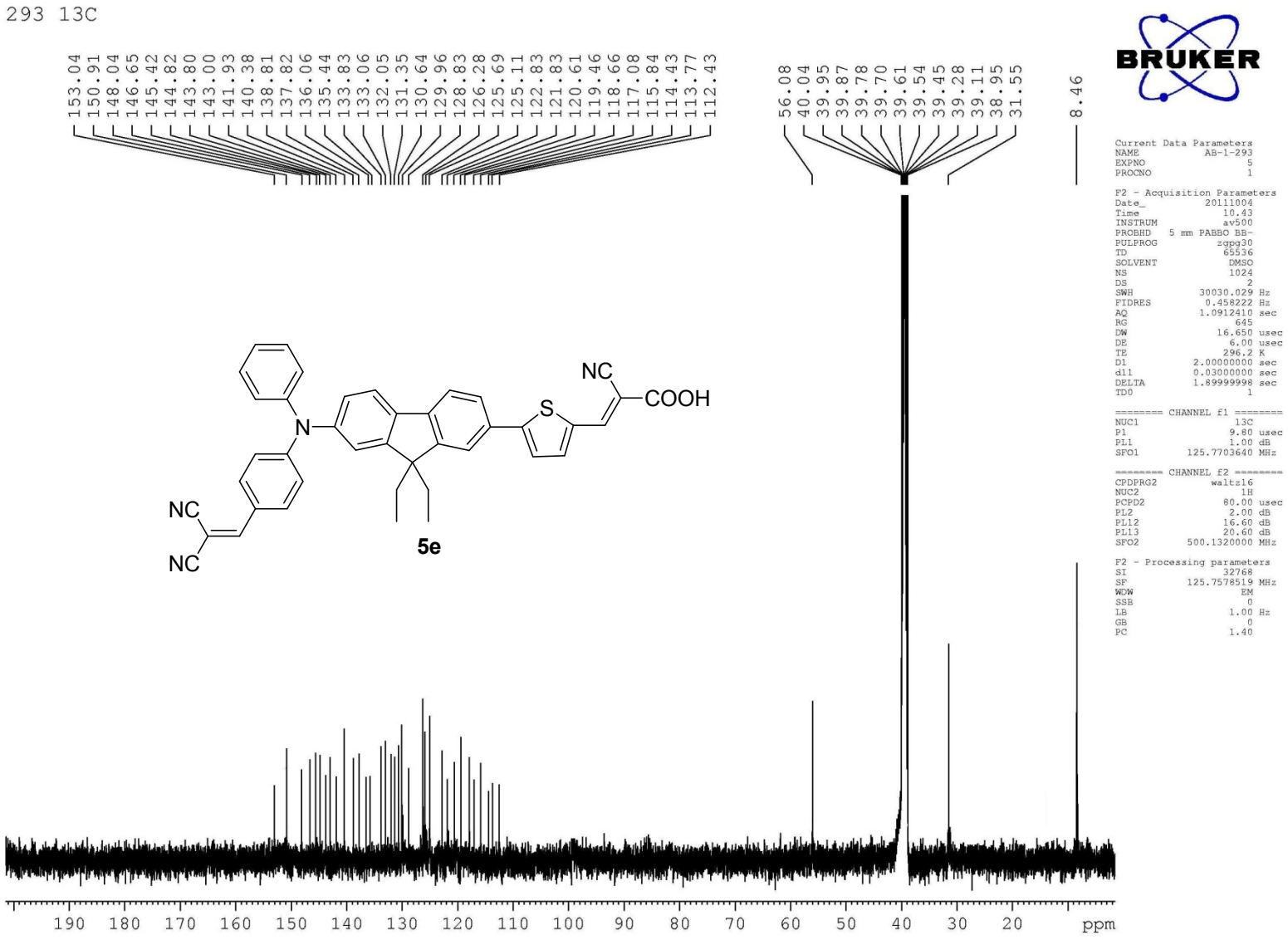

Fig. S45 ^{13}C NMR spectra of **5e** in DMSO-d_6

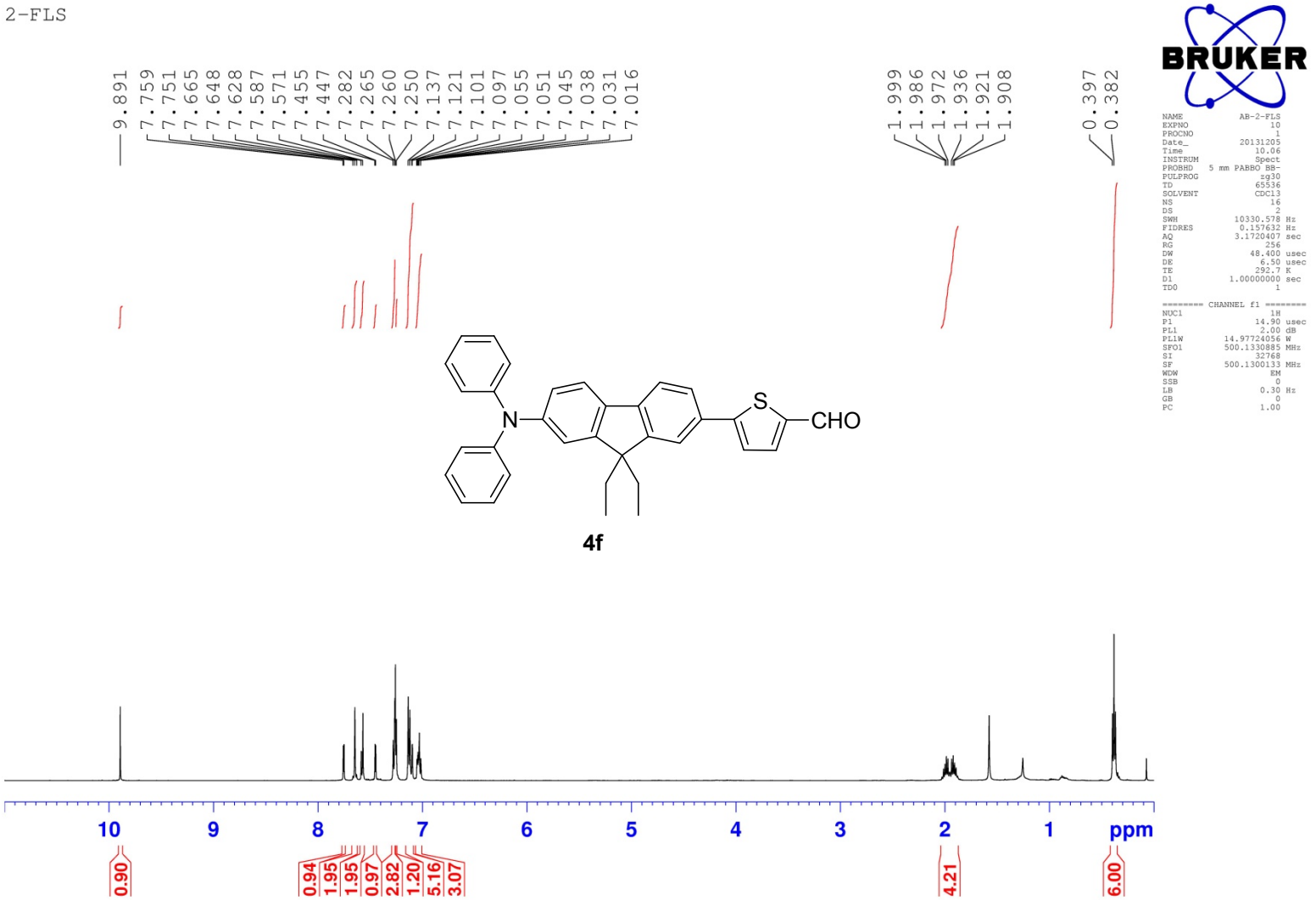

Fig. S46 ^{1}H NMR spectra of **4f** in $CDCl_3$

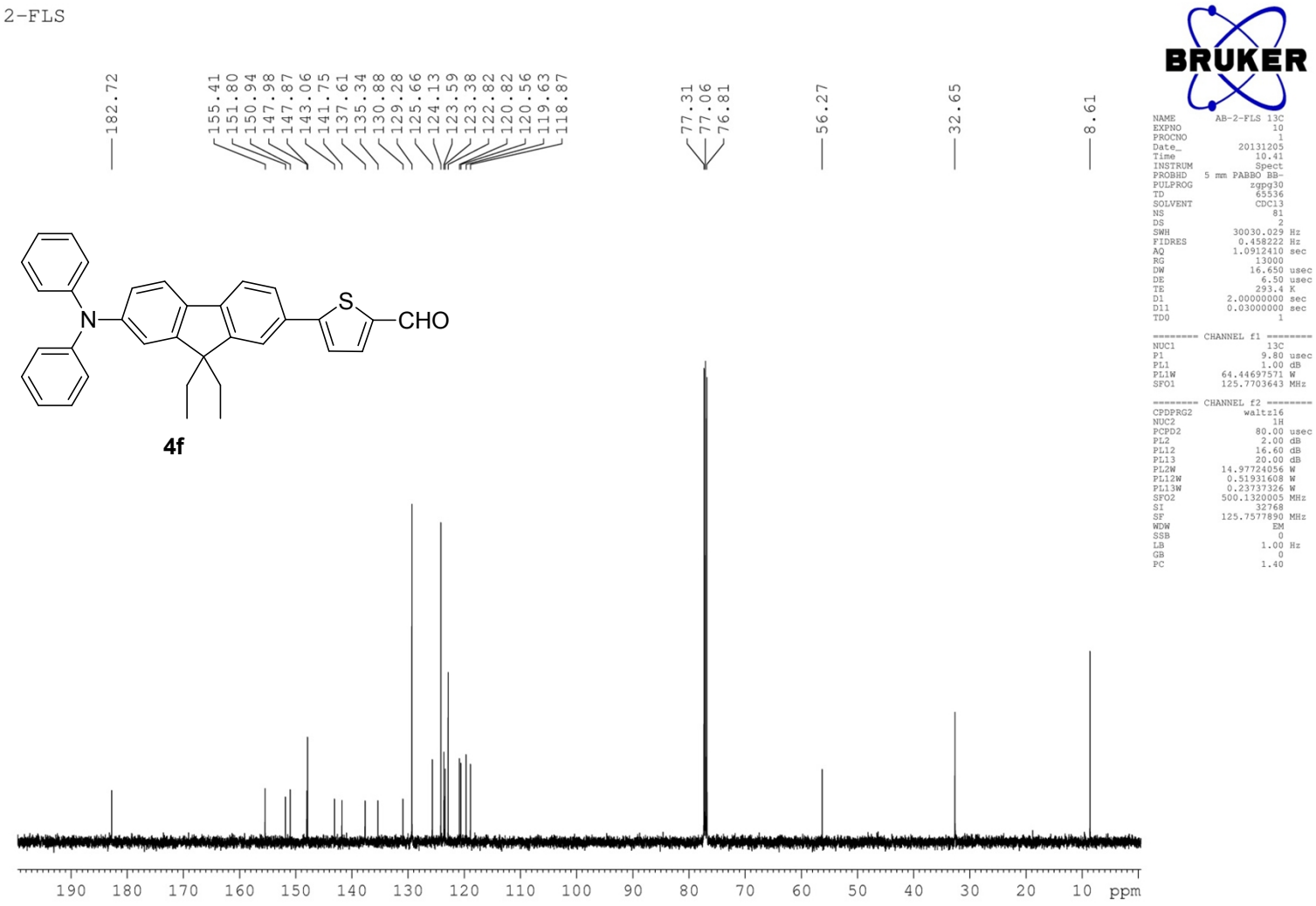

Fig. S47 ^{13}C NMR spectra of **4f** in $CDCl_3$

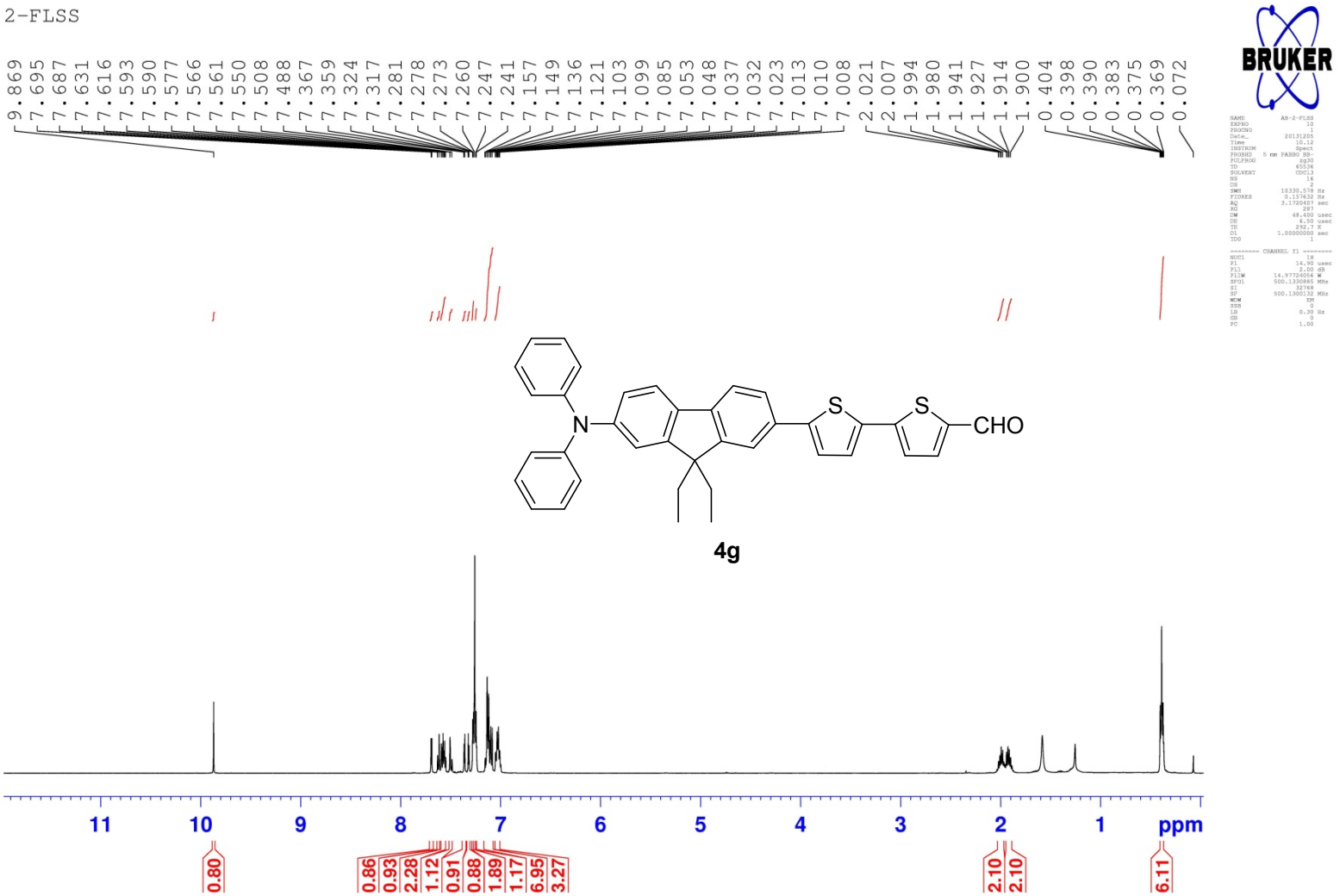

Fig. S48 ^{1}H NMR spectra of **4g** in $CDCl_3$

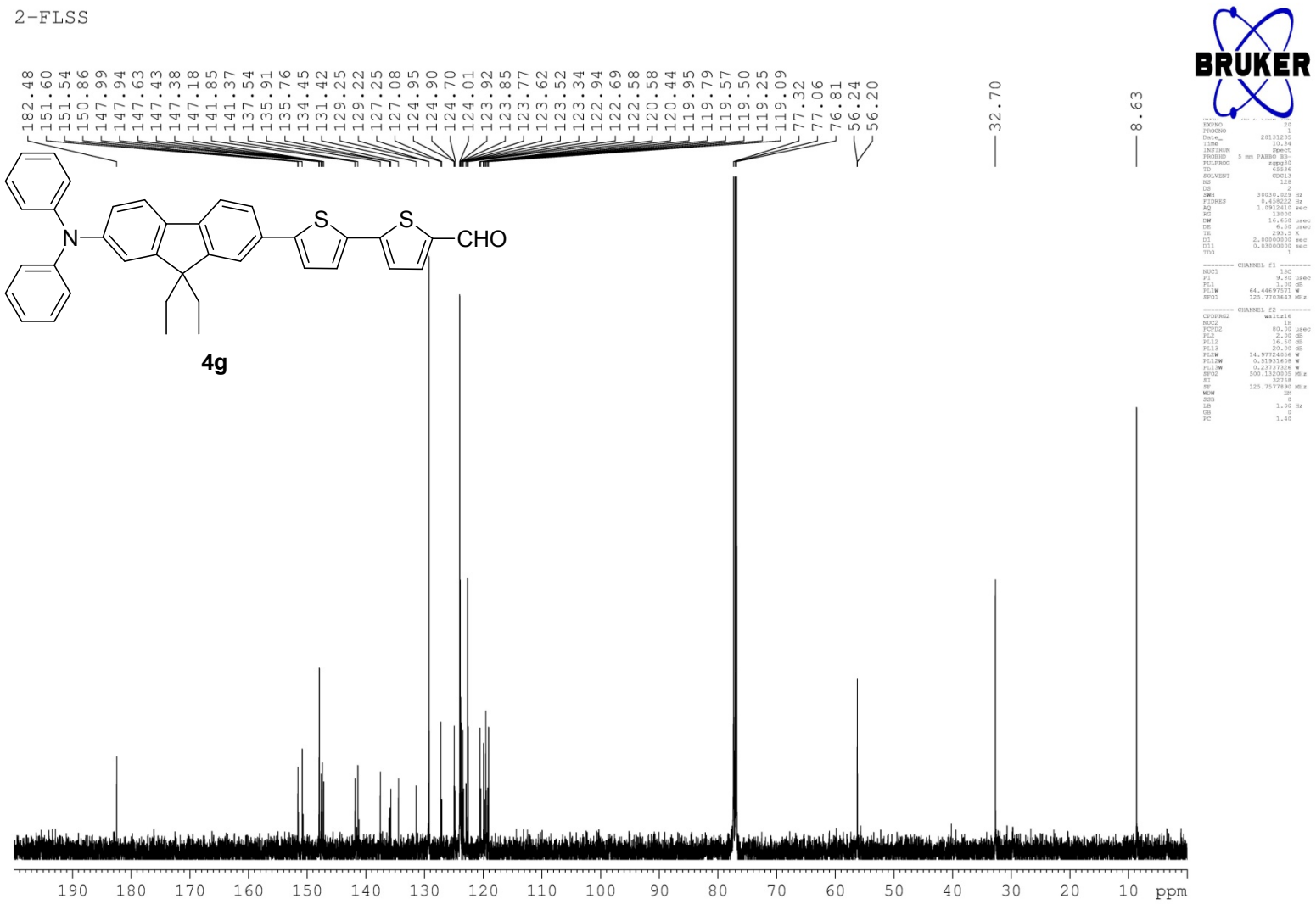

Fig. S49 ^{1}H NMR spectra of **4g** in $CDCl_3$

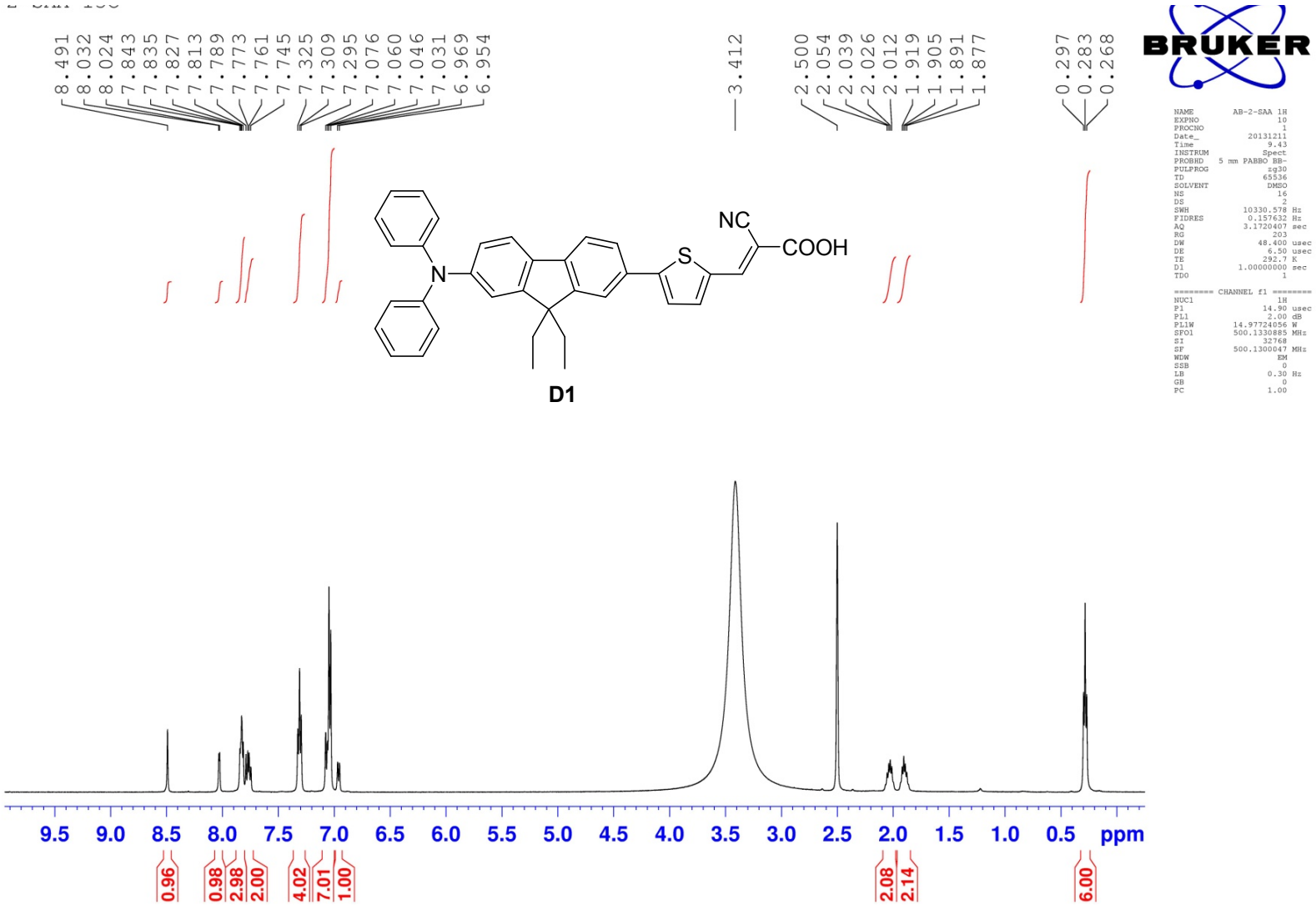

Fig. S50 ^{1}H NMR spectra of **D1** in DMSO-d_6

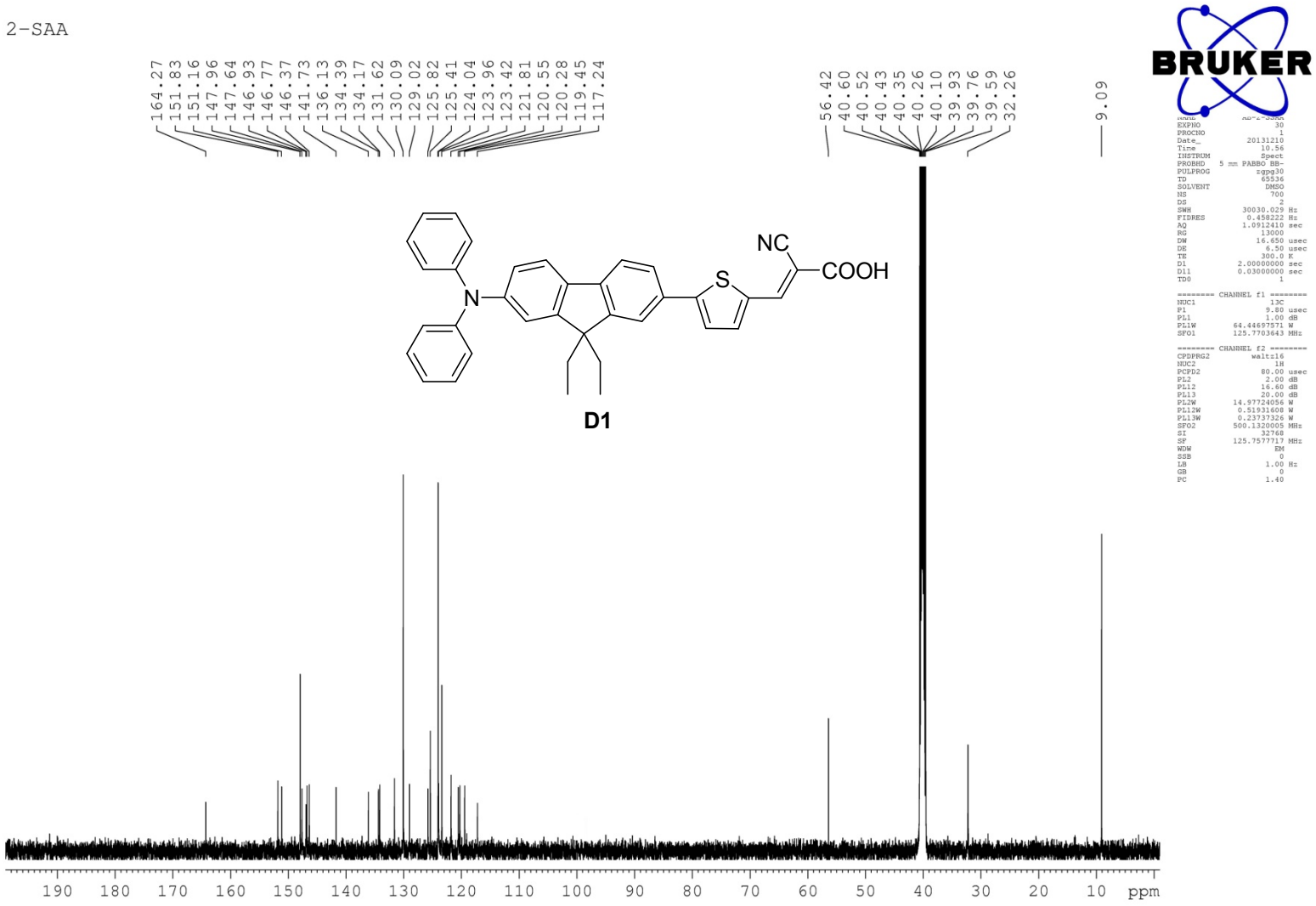

Fig. S51 ^{13}C NMR spectra of **D1** in DMSO-d_6

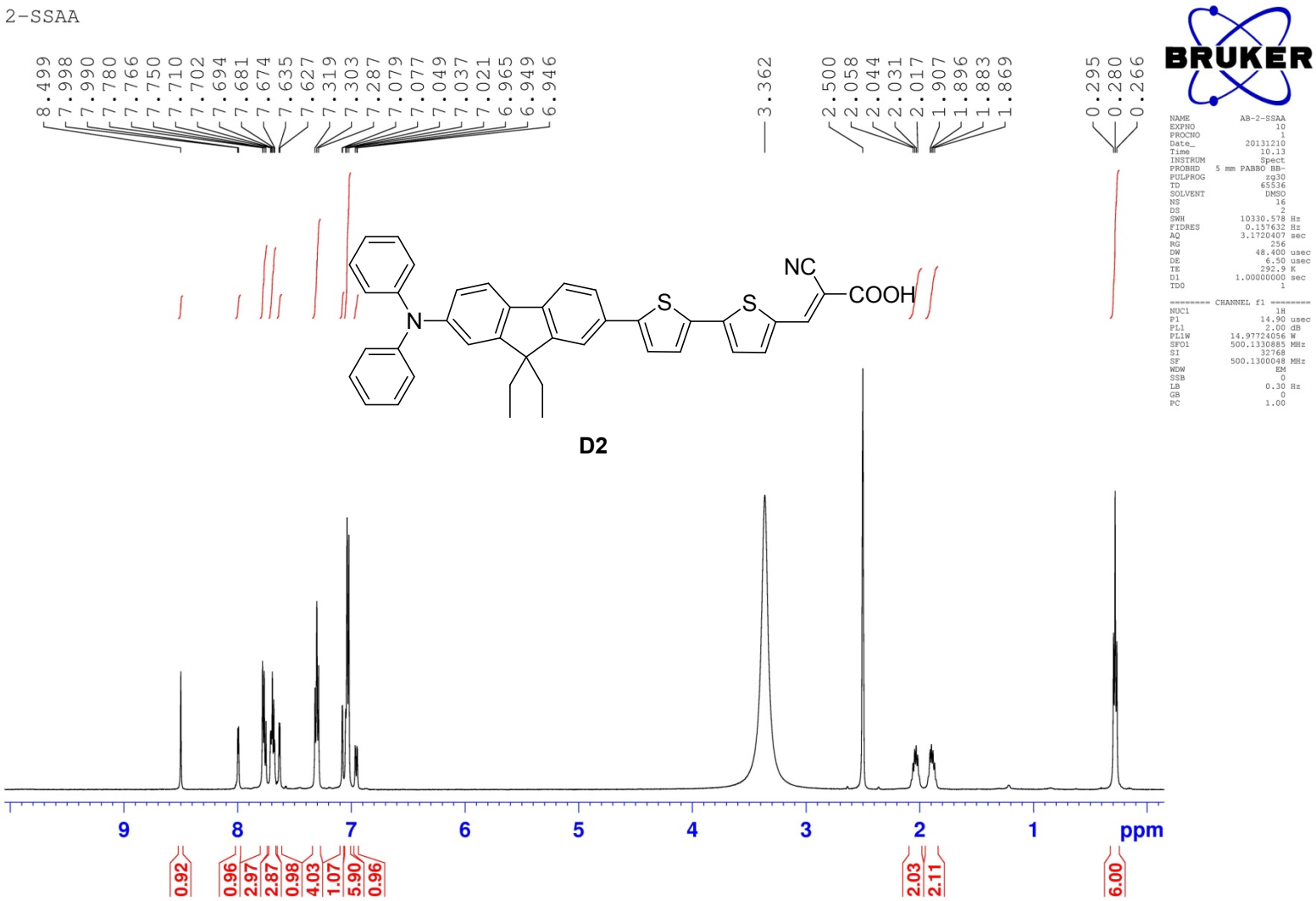

Fig. S52 ^{1}H NMR spectra of **D2** in DMSO-d_6

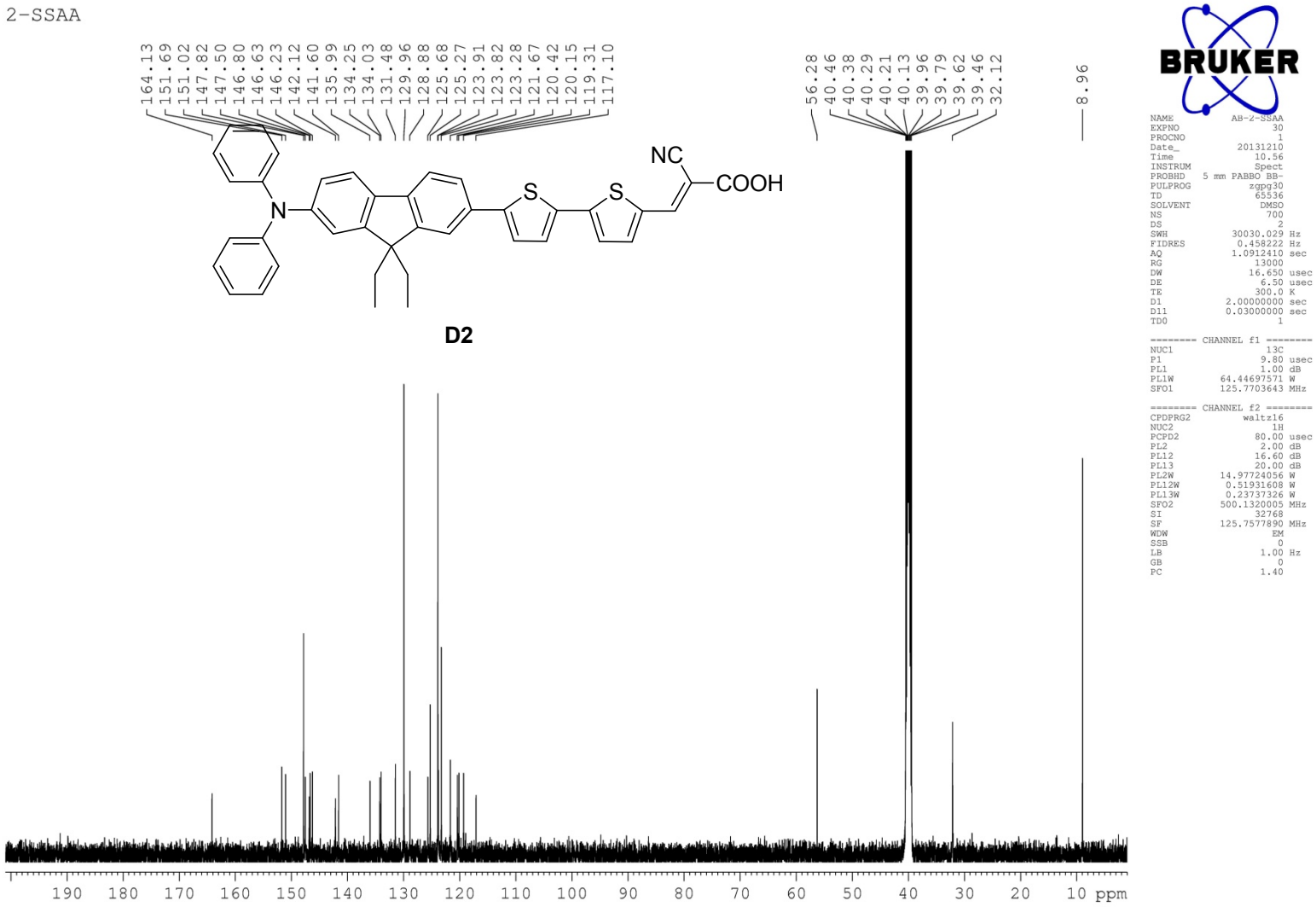

Fig. S53 ^{13}C NMR spectra of **D2** in DMSO-d_6