Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Fluorous molecules for dye-senzitized solar cells: synthesis and properties of di-branched, di-anchoring organic sensitizers containing fluorene subunits

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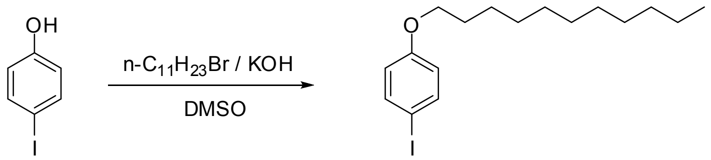
NEW JOURNAL OF CHEMISTRY

Electronic Supplementary Information

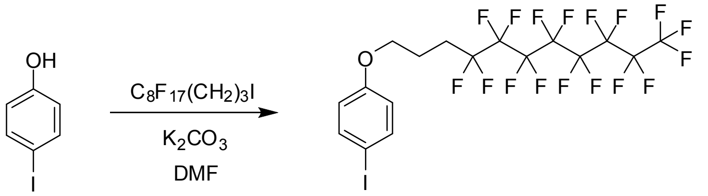
Synthesis of aryl halides

All commercially available chemicals were used as received without further purification. 2-(4-Bromophenyl)-2-(hydroxymethyl)propane-1,3-diol[1] and *n*-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoro)undecyliodide[2] were prepared as described in the literature. Solvents were purified by standard methods and dried if necessary. Reactions were monitored by thin layer chromatography (TLC) that was conducted on plates precoated with silica gel Si 60-F254 (Merck, Germany). Column chromatography was carried out on silica gel SI 60 (Merck, Germany), mesh size 0.063 – 0.200 mm (normal) or 0.040 – 0.063 mm (flash). ^{1}H NMR and ^{13}C NMR were recorded on a Bruker Avance 400 spectrometer (400 and 100.6 MHz, respectively); ^{19}F NMR spectra were recorded on a Bruker AC 300 spectrometer (282 MHz).



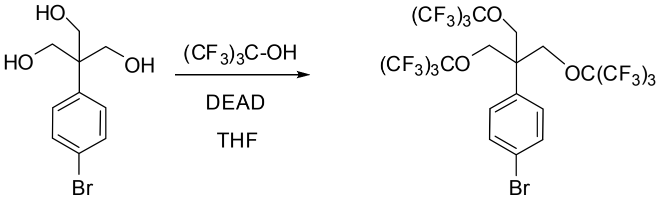
1-Iodo-4-(undecyloxy)benzene. To a solution of 4-iodophenol (2.20 g, 10 mmol) in DMSO (30 ml) pelleted KOH (2.20 g, 40 mmol) was added. The mixture was stirred 10 minutes at RT, then *n*-undecylbromide (2.24 mL, 10 mmol) was added dropwise by a syringe. The mixture was stirred overnight at RT. After addition of H_2O (150 mL). the resulting suspension was extracted with CH_2Cl_2 (3 x 30 mL). The combined organic layers were washed with H_2O (3 x 30 mL) and dried over $MgSO_4$. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography (silica gel, hexane/CH_2Cl_2 8/1) affording the title compound as a white solid. Yield: 3.40 g (91%).

^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm] = 7.54 (d, *J* = 8.9 Hz, 2H) 6.67 (d, *J* = 8.9 Hz, 2H), 3.91 (t, *J* = 6.6 Hz, 2H), 1.81 – 1.71 (m, 2H), 1.49 – 1.39 (m, 2H), 1.37 – 1.21 (m, 14H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100.6 MHz, CDCl3) δ [ppm] = 159.2, 138.3, 117.1, 82.5, 68.3, 32.1, 29.8, 29.8, 29.7, 29.5, 29.5, 29.28, 26.1, 22.8, 14.3.



1-iodo-4-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyloxy)benzene. A flame-dried Schlenk tube was charged with 4-iodophenol (0.44 g, 2.0 mmol), anhydrous K_2CO_3 (1.12 g, 3.4 mmol) and dry DMF (8 mL), evacuated, and backfilled with nitrogen. Neat *n*-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoro)undecyliodide (1.17 g, 2.0 mmol) was added under nitrogen. The Schlenk tube was sealed and the reaction mixture was stirred overnight at 60 °C. The resulting suspension was allowed to reach room temperature and partitioned between H_2O (40 mL) and Et_2O (40 ml). The organic layer was recovered, washed with H_2O (3 x 20 mL) and dried over $MgSO_4$. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography (silica gel, hexane/Et_2O 9/1) affording the title compound as an off-white solid.

Yield: 1.20 g (88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm] = 7.56 (d, *J* = 8.9 Hz, 2H) 6.67 (d, *J* = 8.9 Hz, 2H), 4.00 (t, *J* = 5.9 Hz, 2H), 2.44 – 2.19 (m, 2H), 2.17 – 2.01 (m, 2H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ [ppm] = 158.4, 138.3, 116.8, 83.1, 66.4, 27.9 (t, J_{CF} = 22.5 Hz, $\underline{CH_2}CF_2$), 20.5 (t, J_{CF} = 3.9 Hz, $\underline{CH_2}CH_2CF_2$). ^{19}F NMR (282 MHz, $CDCl_3$): δ [ppm] = -81.7 (t, *J* = 10.1 Hz, 3F), -114.91 – -115.70 (m, 2F), -122.5 – -123.0 (m, 6F), -123.6 (br s, 2F), -124.3 (br s, 2F), -127.01 (br s, 2F).

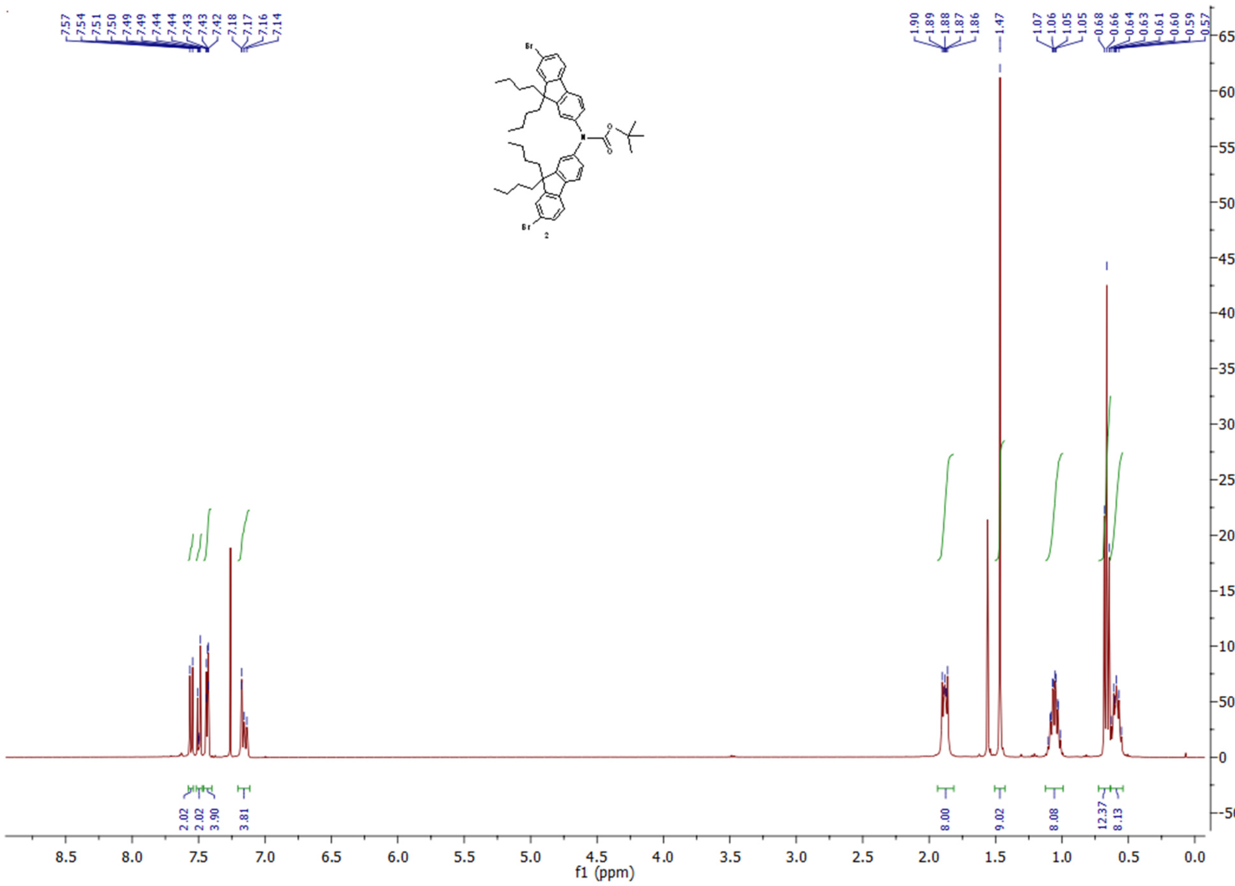


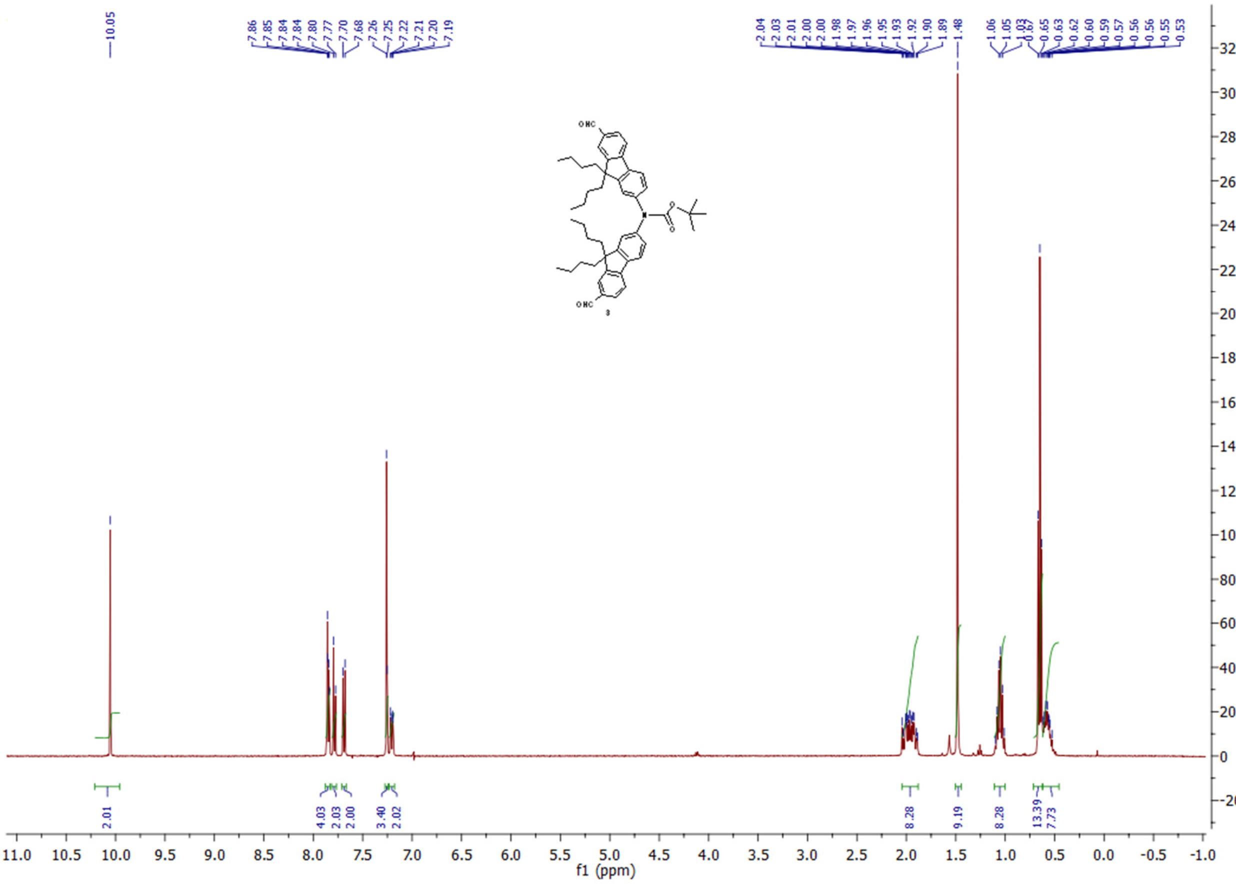
1-(1,3-Bis(1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yloxy)-2-((1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yloxy)methyl)propan-2-yl)-4-bromobenzene. 2-(4-Bromophenyl)-2-(hydroxymethyl)propane-1,3-diol (1.57 g, 6.0 mmol) and PPh_3 (6.02 g, 23.0 mmol) were dissolved under nitrogen in dry THF (20 mL). To the stirred solution cooled at 0 °C, a 40% solution of diisopropyl azodicarboxilate in toluene (10.8 mL, 23.0 mmol) was added dropwise by a syringe. After 10 minutes the reactor was brought to RT and perfluoro-*tert*-butanol (3.3 mL, 23 mmol) was added dropwise by a syringe. The reaction mixture was warmed at 45 °C for 48h. The solvent was the removed under reduced pressure and the residue was partitioned between AcOEt (10 mL) and perfluorodimethylcyclohexane (PFDMC, 20 mL). The organic layer was extracted twice with PFDMC (10 mL). The combined perfluorocarbon layers were washed with AcOEt (5mL) and evaporated to dryness affording the title compound as a white solid. Yield: 2.53 g (46%). ^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm] **=** 7.52 (d, *J* = 8.7 Hz, 2H), 7.12 (d, *J* = 8.7 Hz, 2H), 4.36 (s, 6H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ [ppm] = 134.8, 131.9, 127.6, 122.4, 120.0 (q, J_{CF} = 293 Hz), 79.4 (m), 67.9, 48.1. ^{19}F NMR (282 MHz, $CDCl_3$): δ [ppm] = -71.1

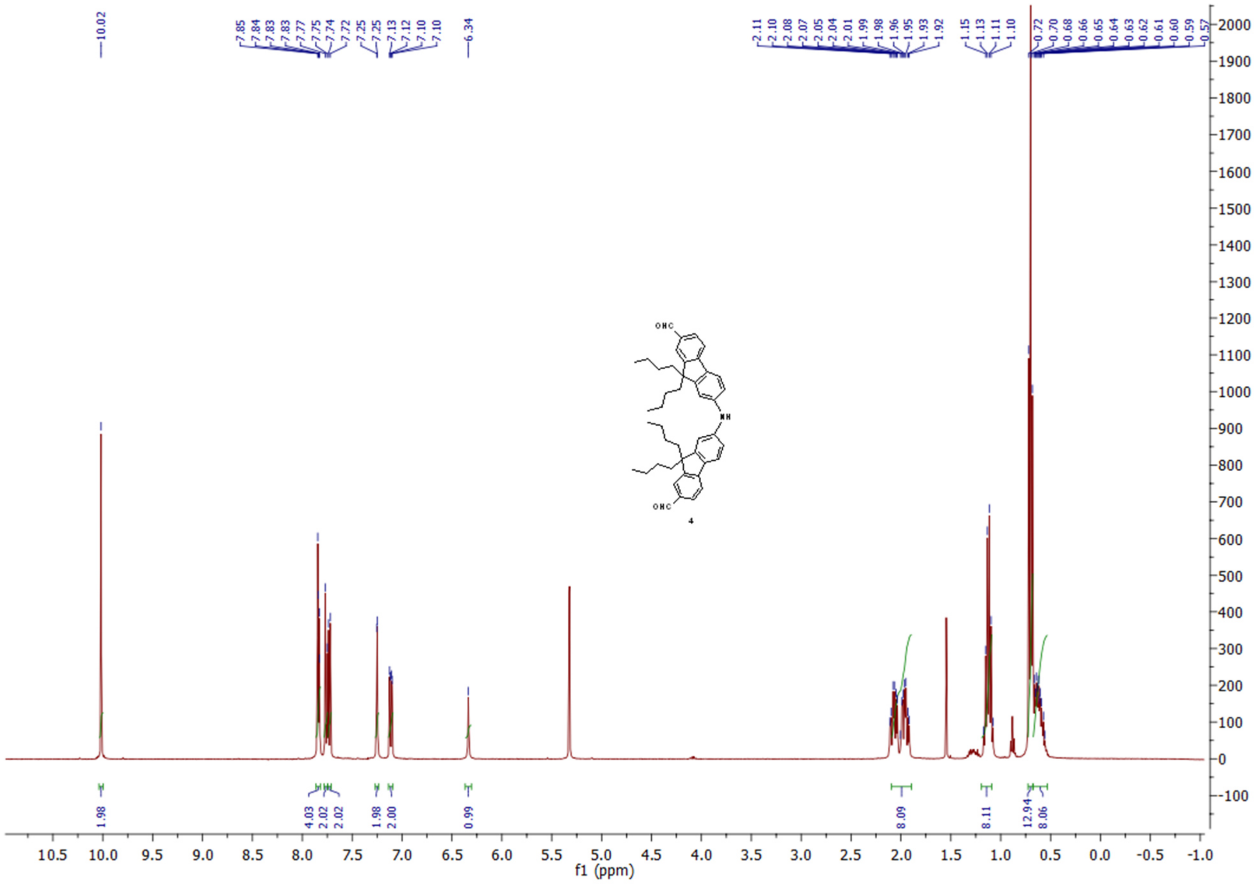
1. J. S. Lindsay, D. F. Bocian, R. Loewe, I. Sanchez, W. G. Kuhr, K. Padmaja and L.Wei, *WO 2007/053192*

2. J.-M. Vincent, A. Rabion, V. K. Yachandra and R. H. Fish, *Can. J. Chem.* 2001, **79**, 888.

1H NMR spectra of fluorene derivatives



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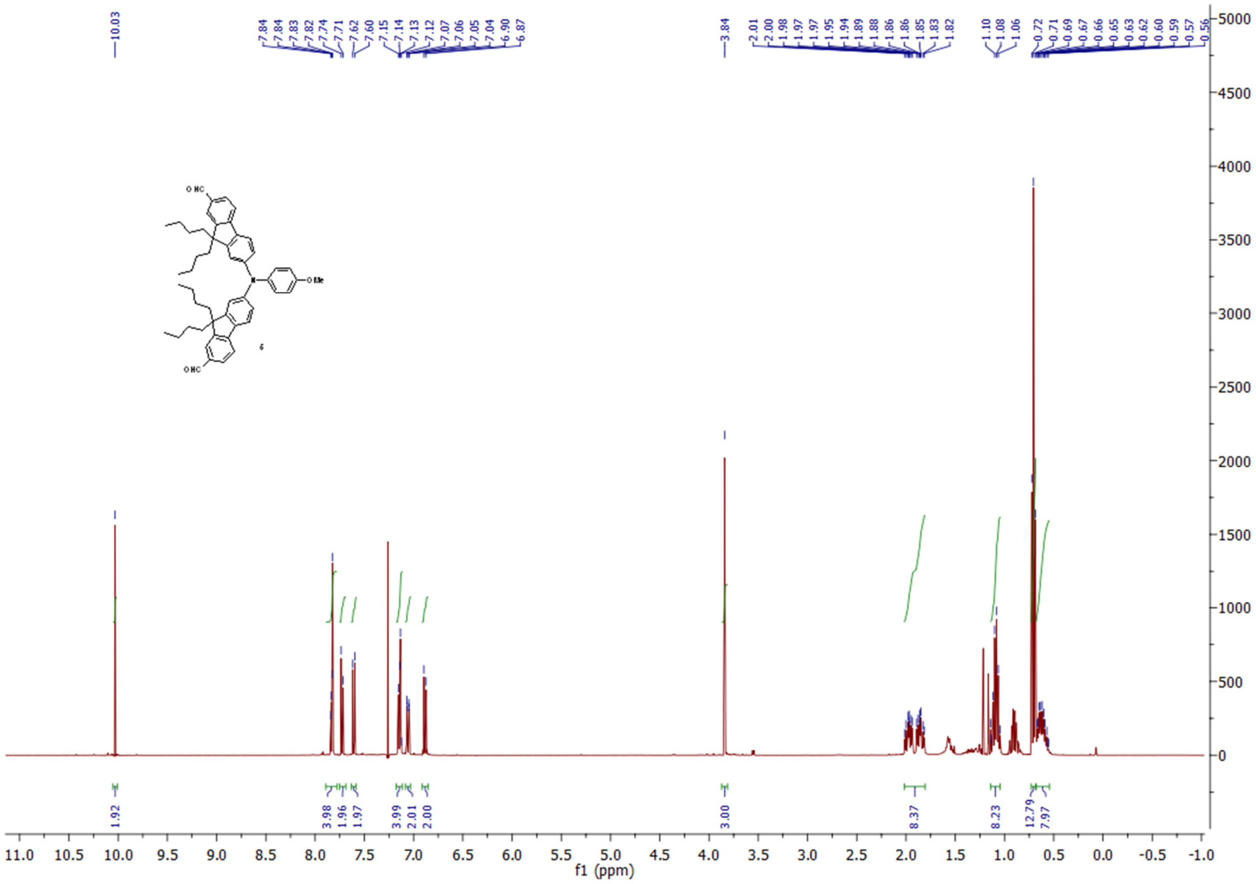
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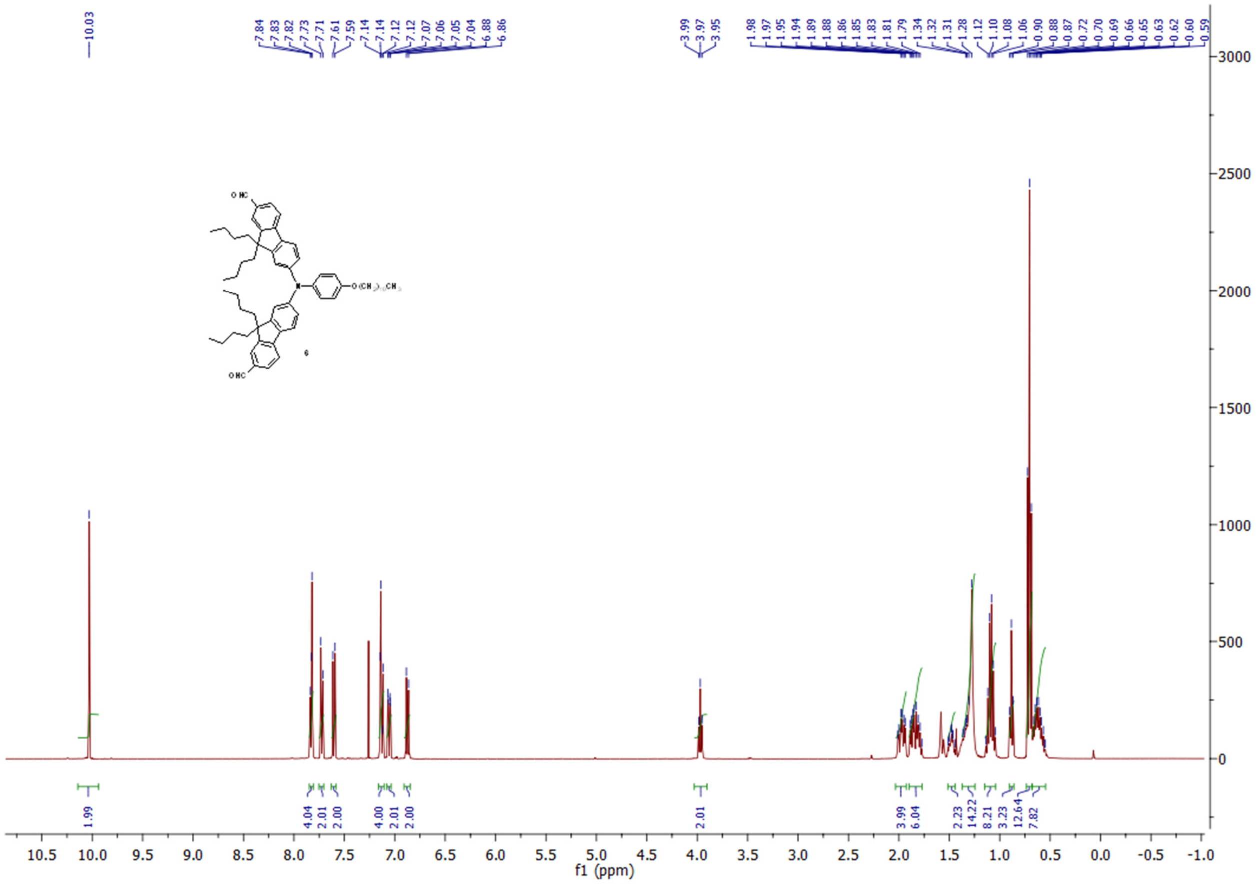
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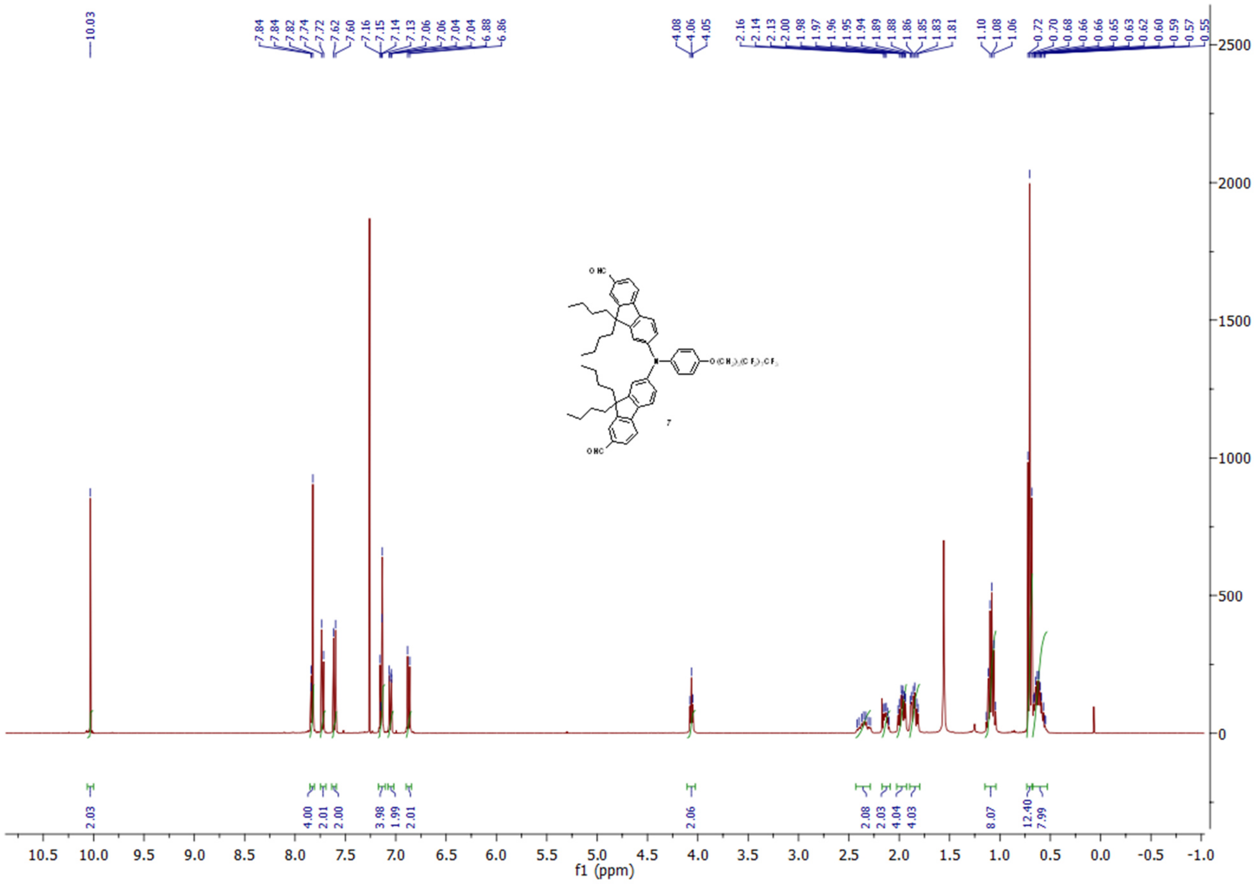
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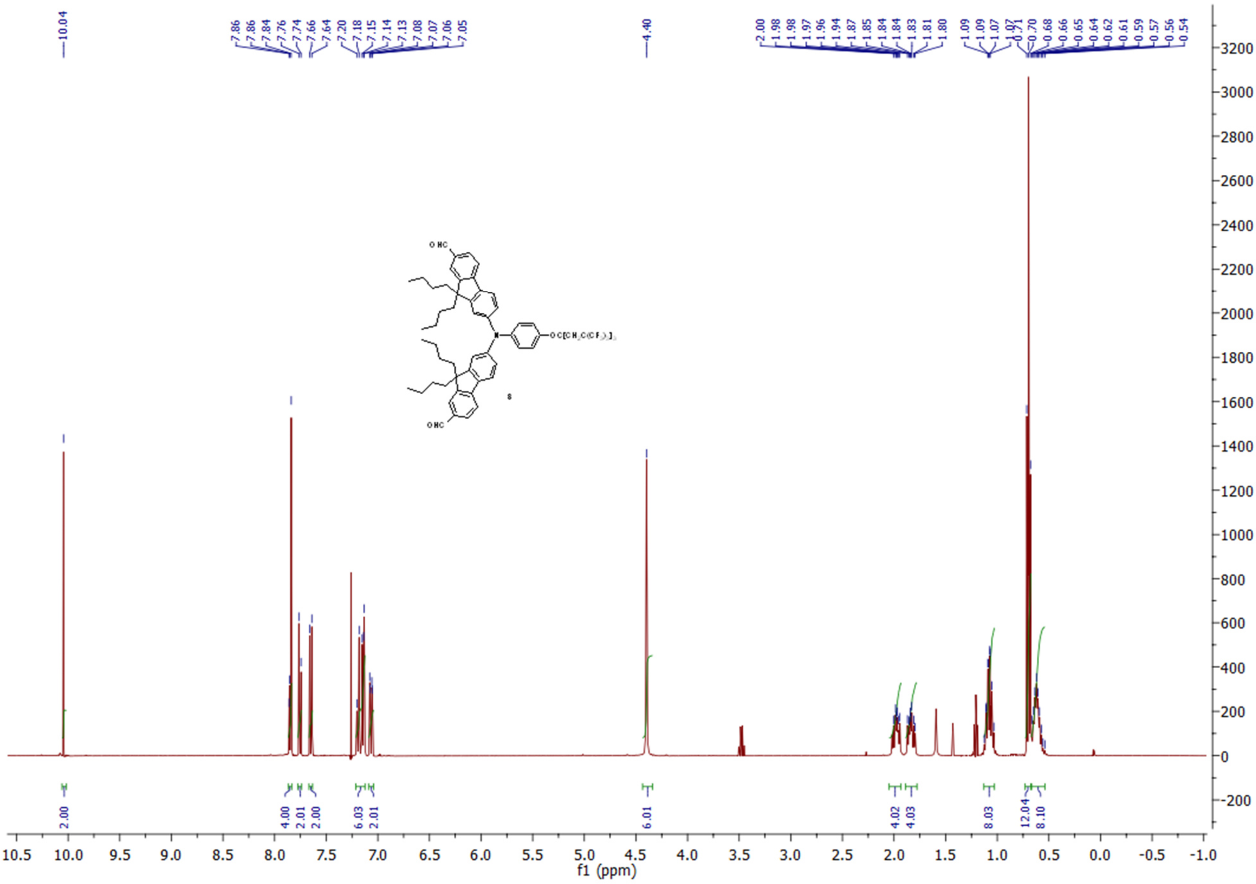
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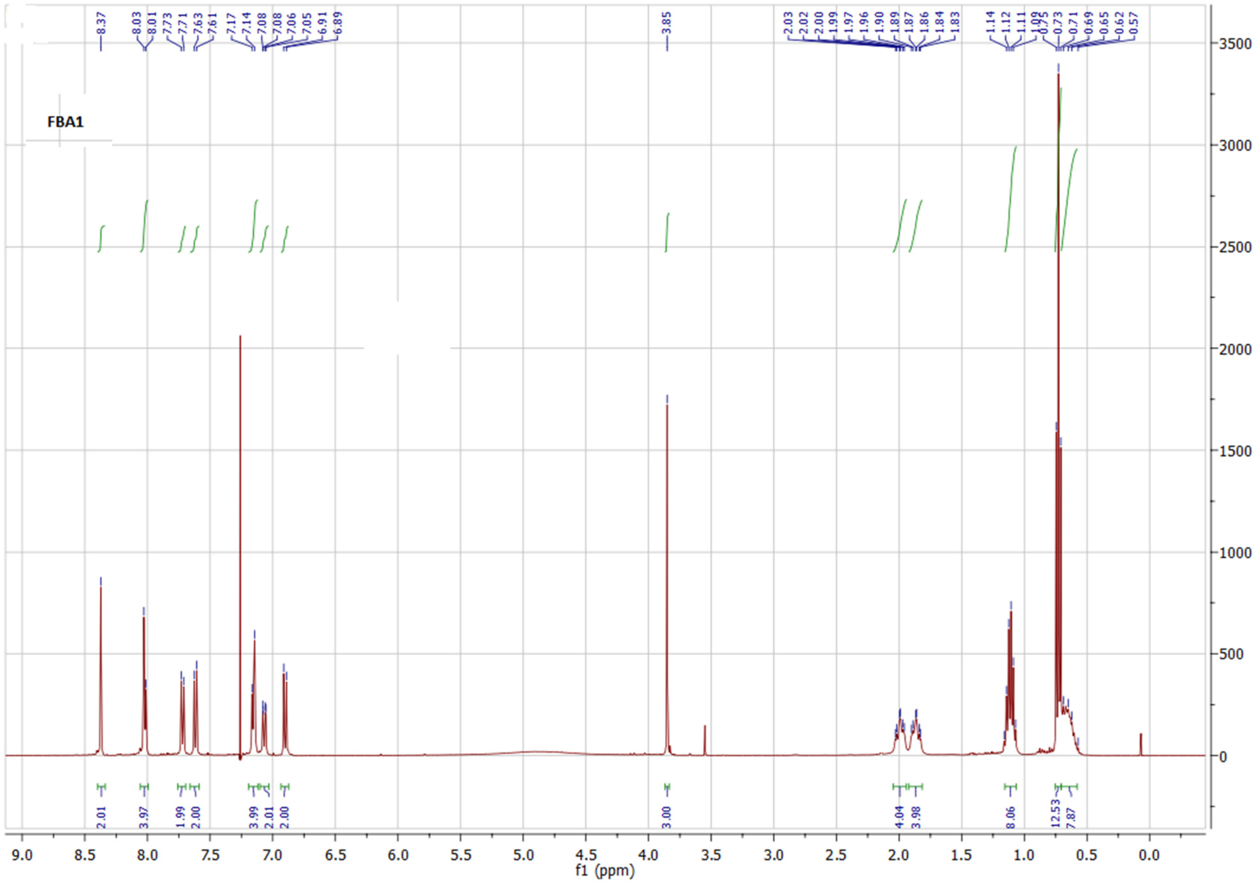
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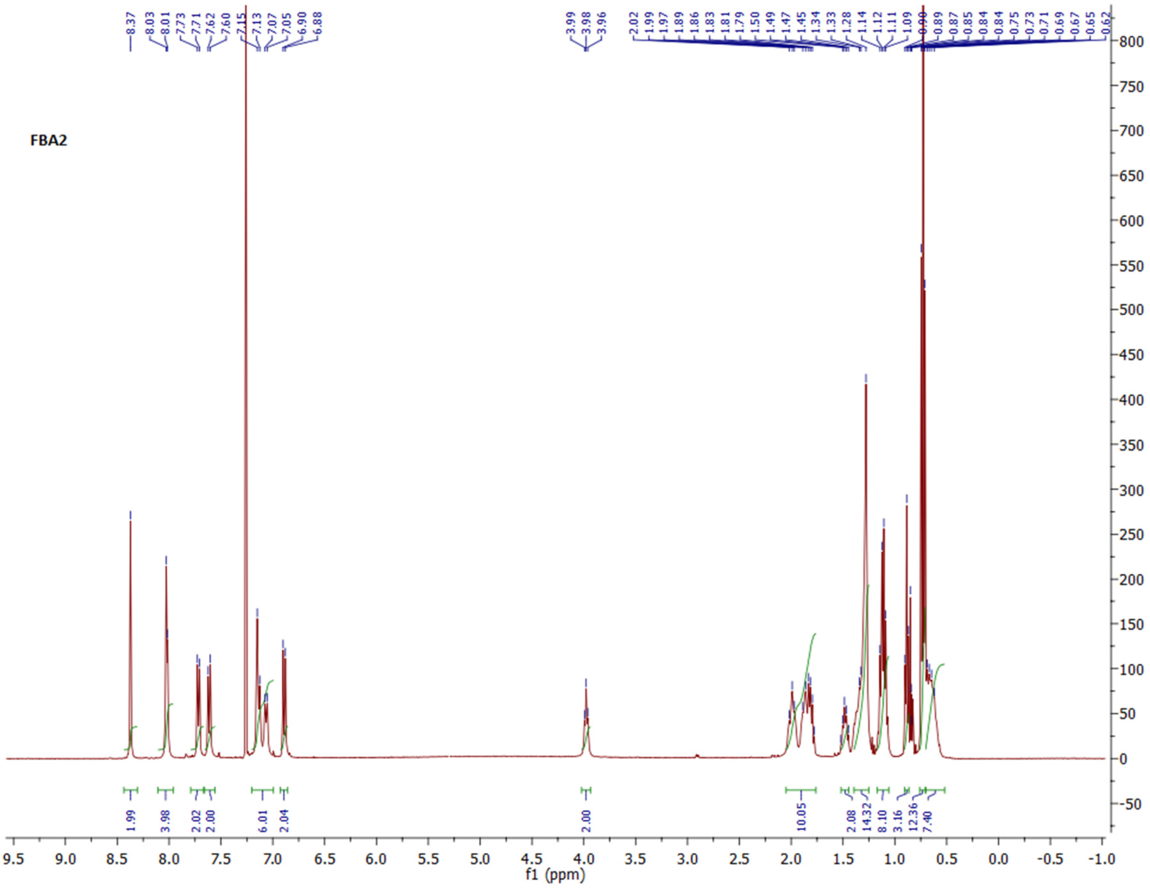

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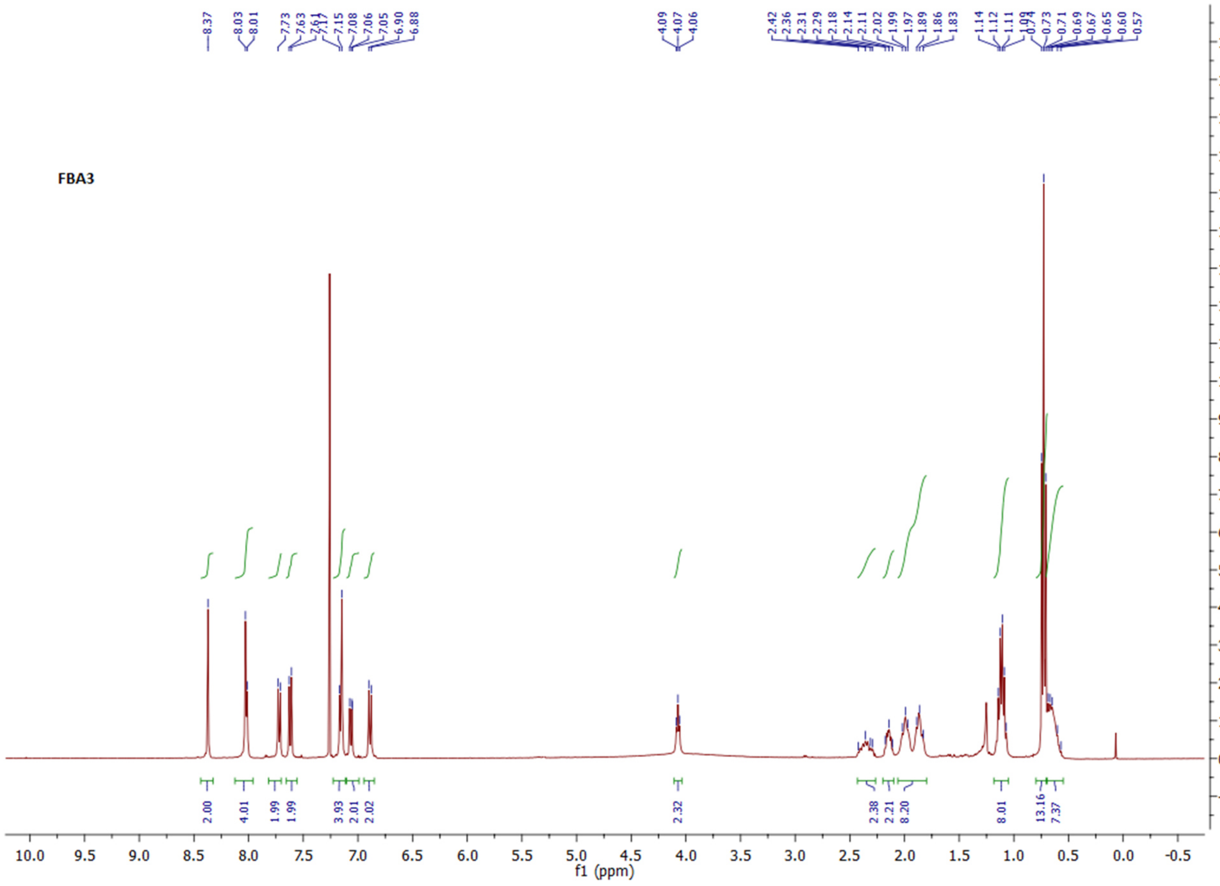

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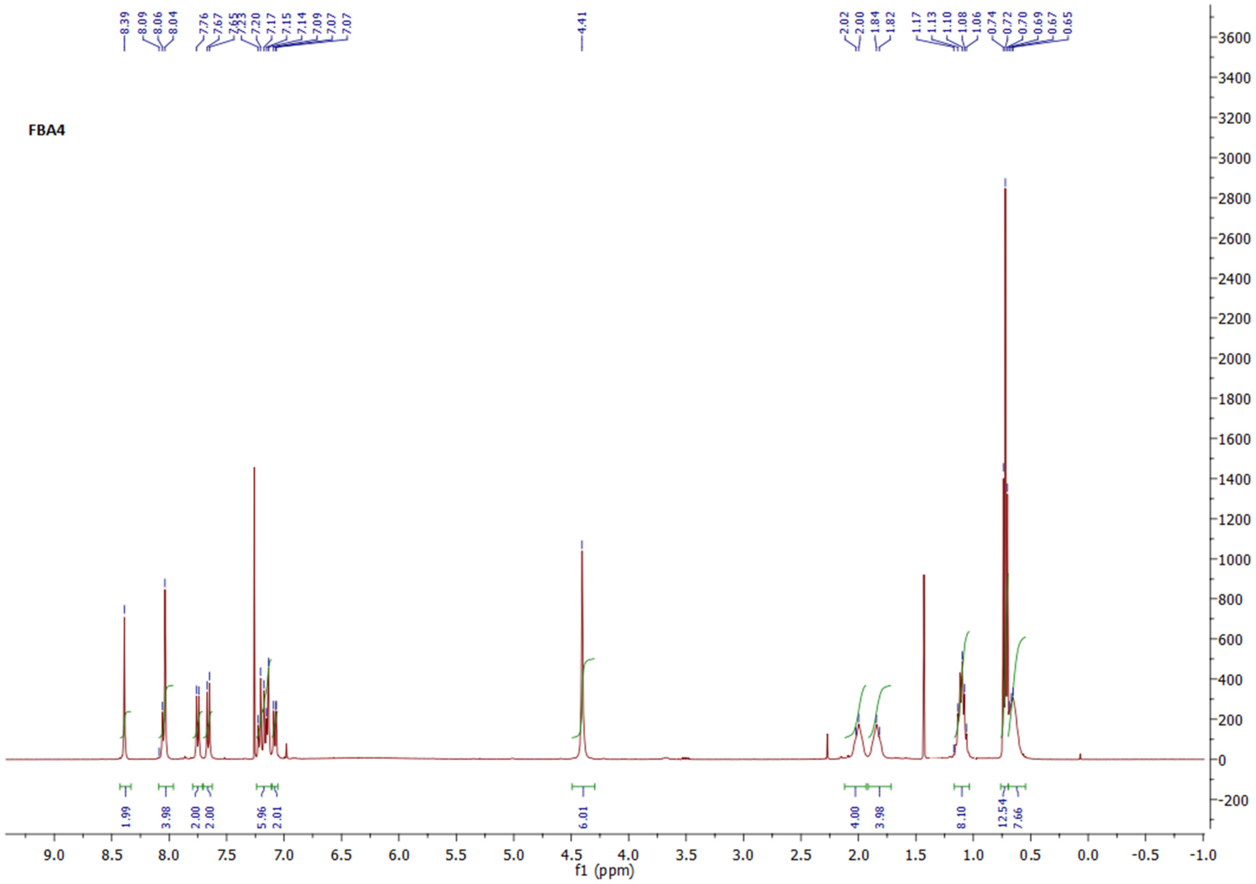
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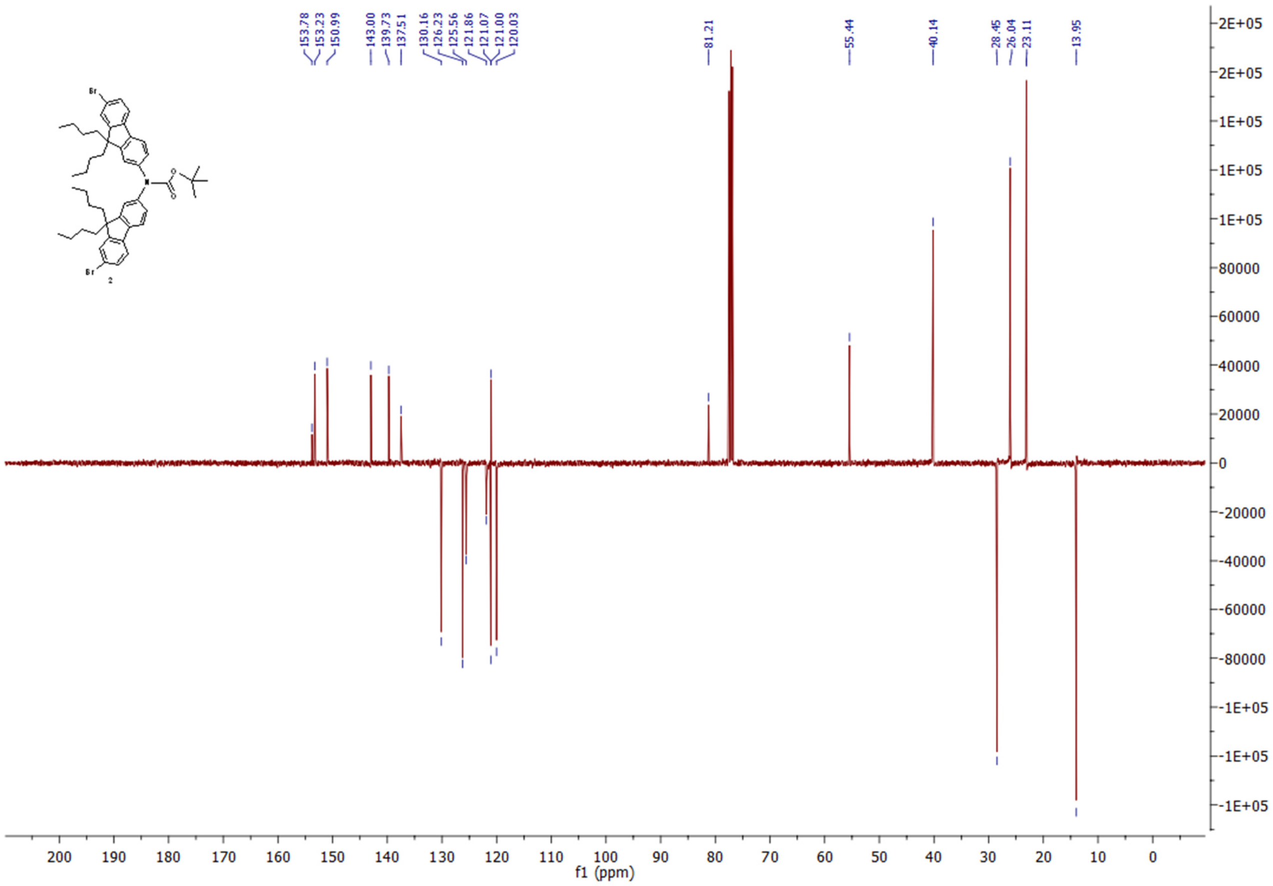
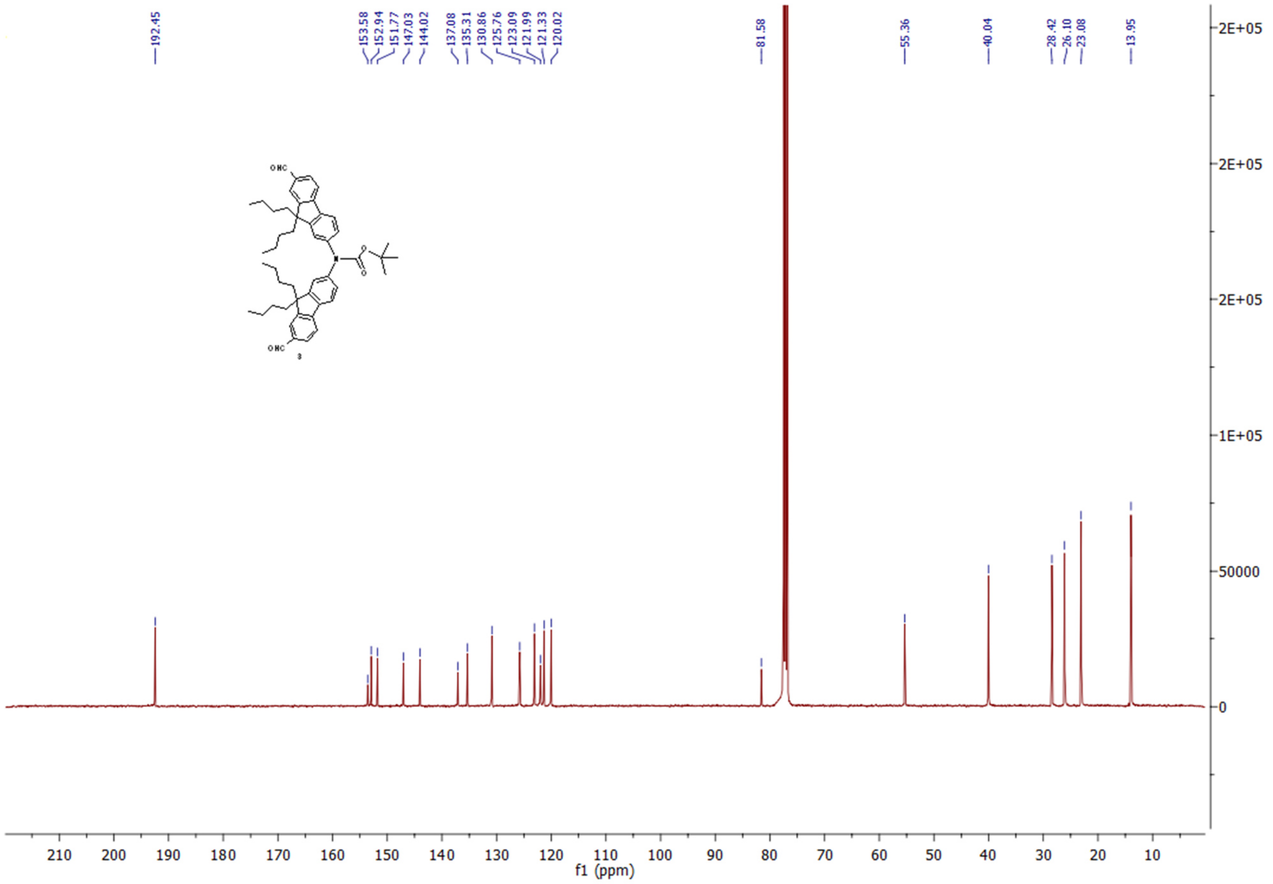
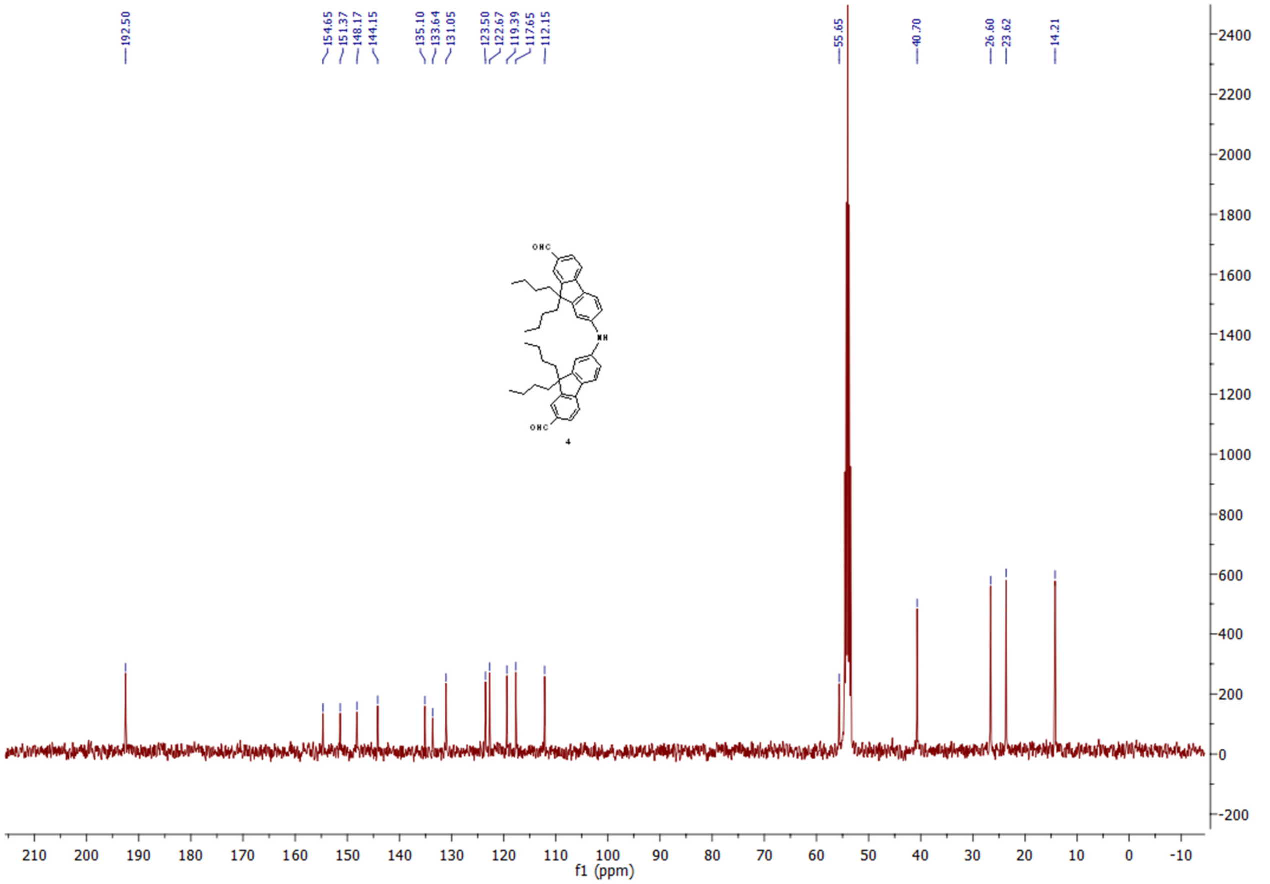
13C NMR spectra of fluorene derivatives



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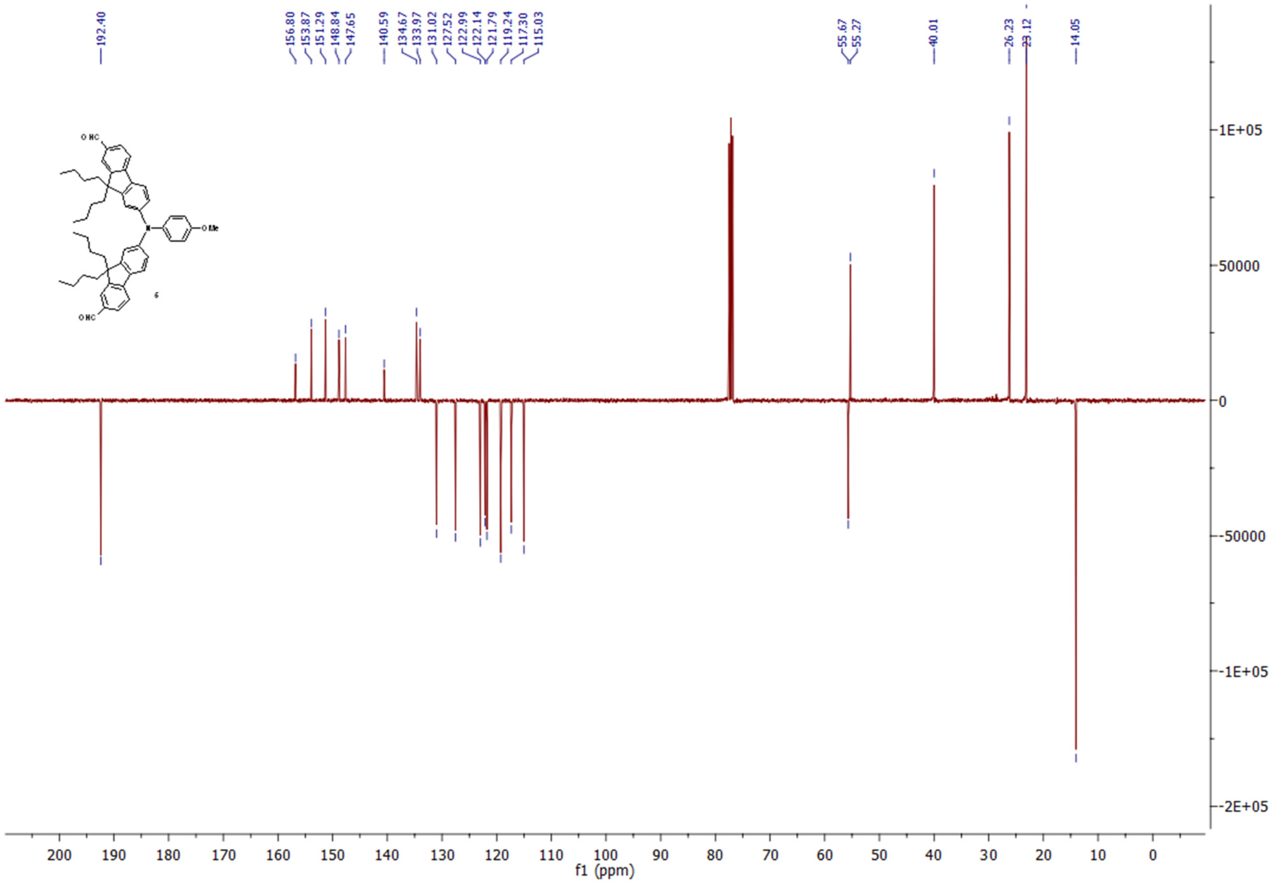
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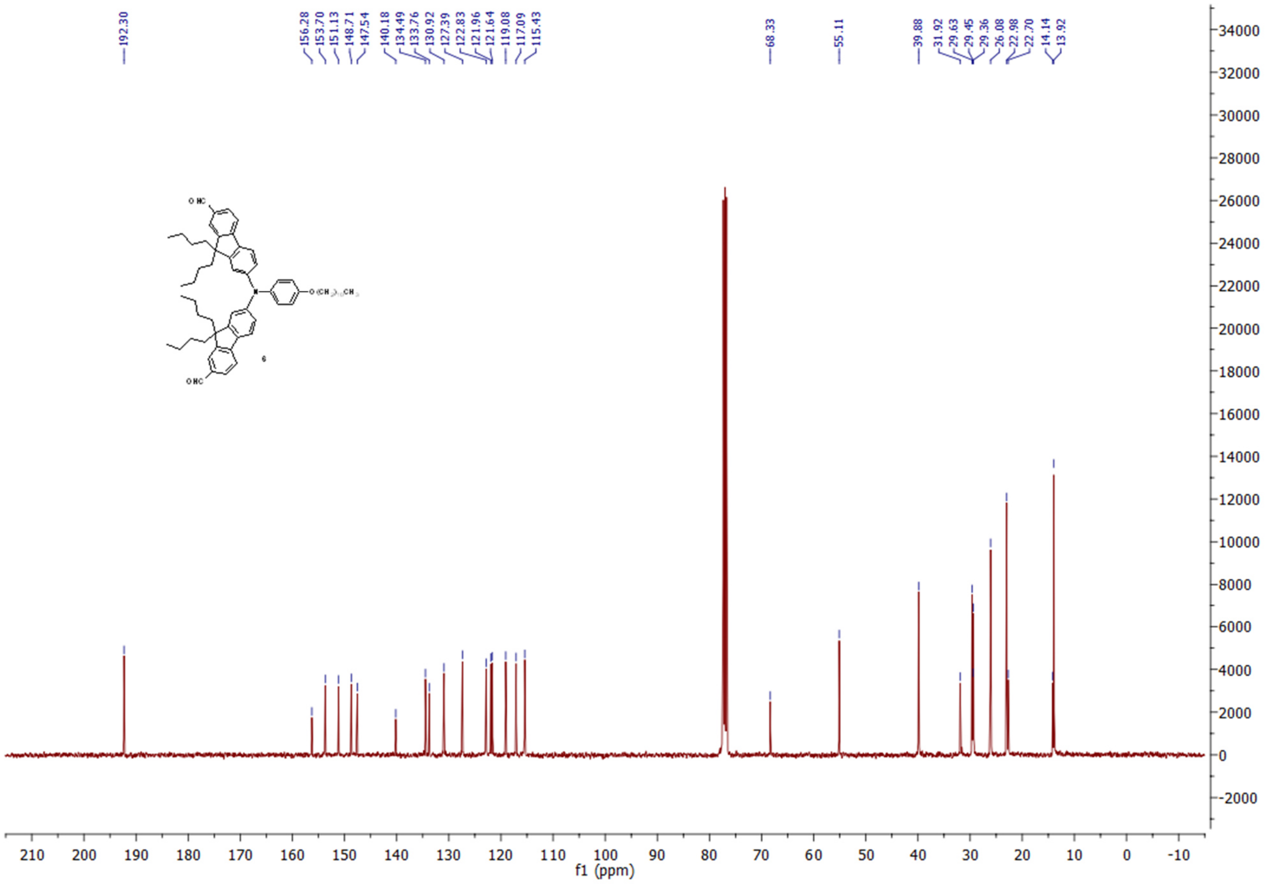

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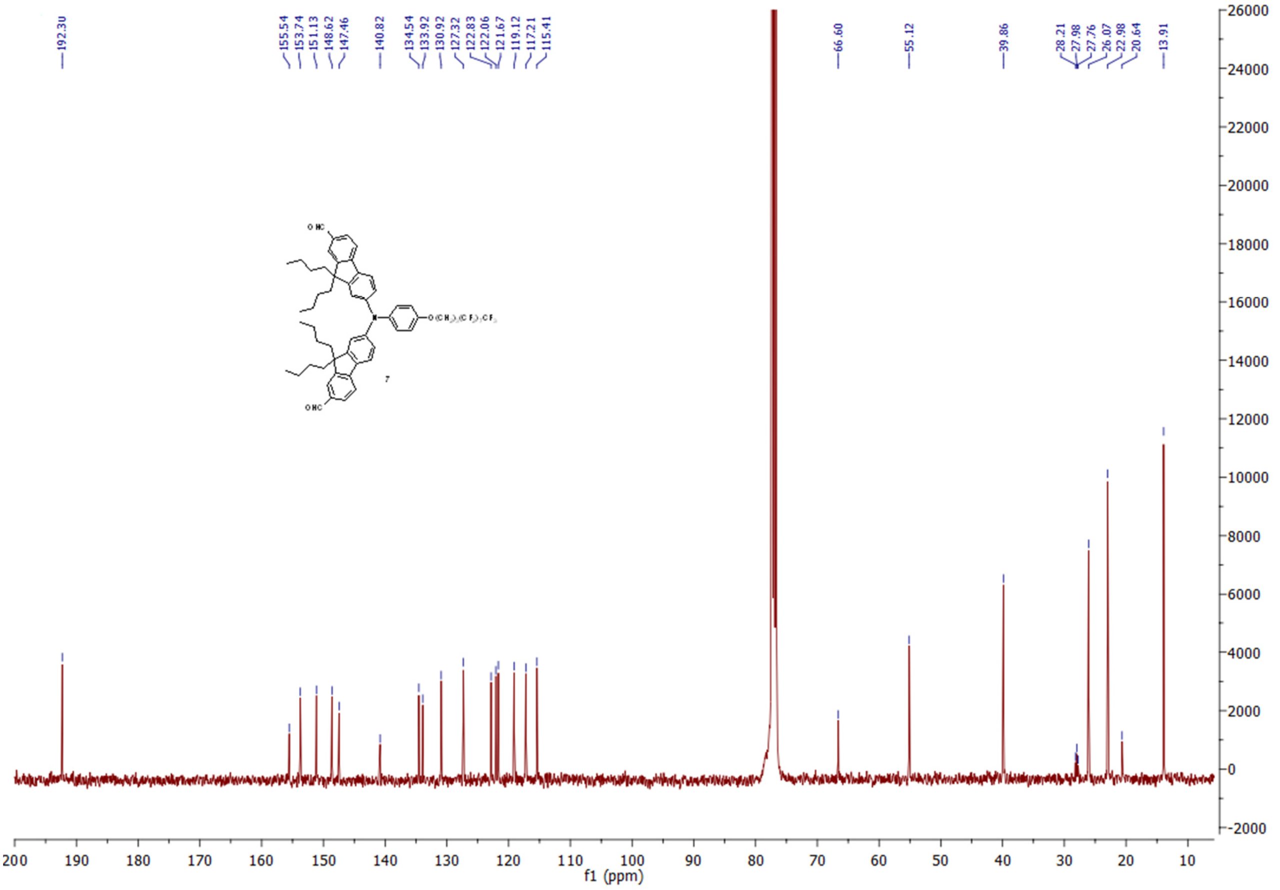
f1 (ppm)



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151.13
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147.46
140.82
134.54
133.92
130.92
127.32
122.83
122.06
121.67
119.12
117.21
115.41
66.60
55.12
39.86
28.21
27.98
27.76
26.07
22.98
20.64
13.91
OHC
N
O(CH2)(CF2)CF3
OHC
7
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
200
190
180
170
160
150
140
130
120
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100
90
80
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60
50
40
30
20
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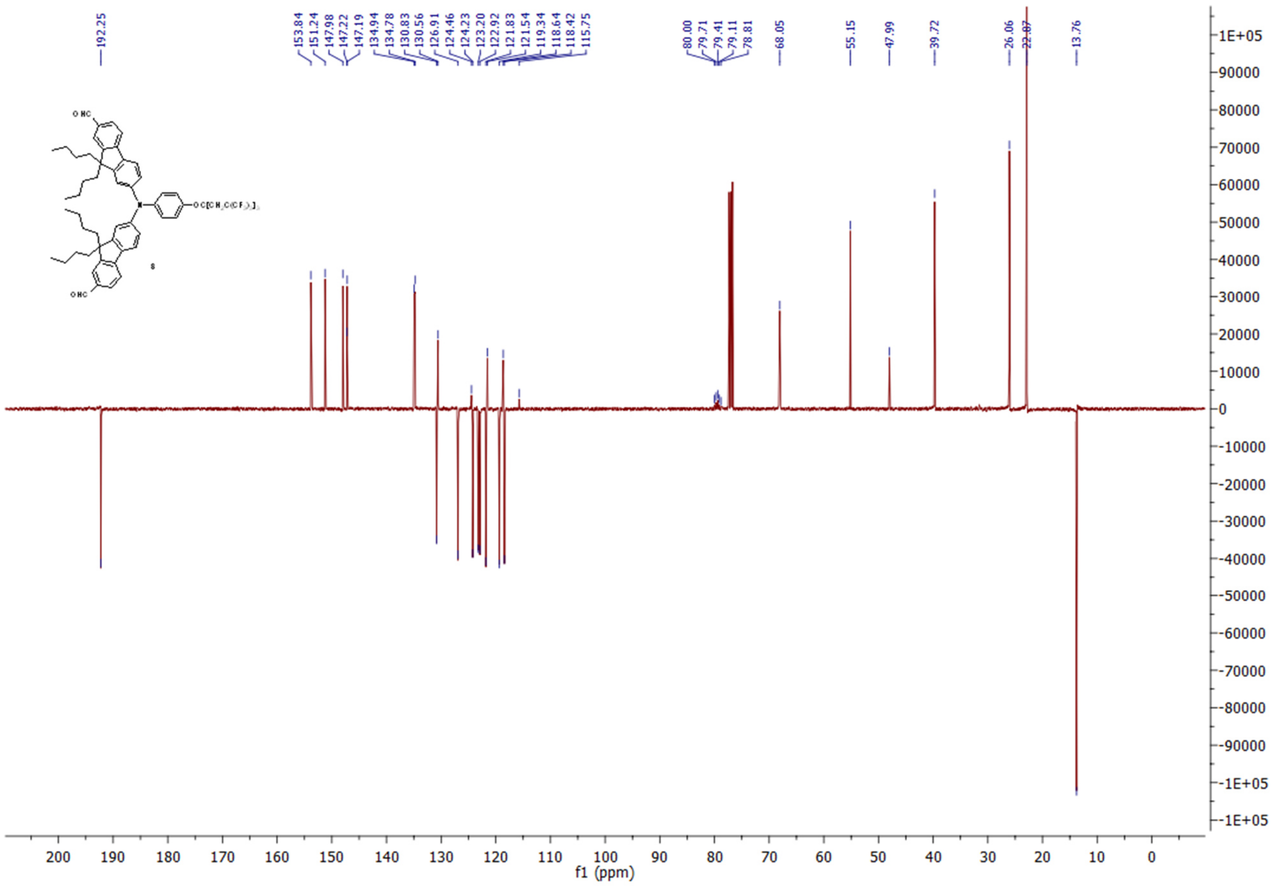
f1 (ppm)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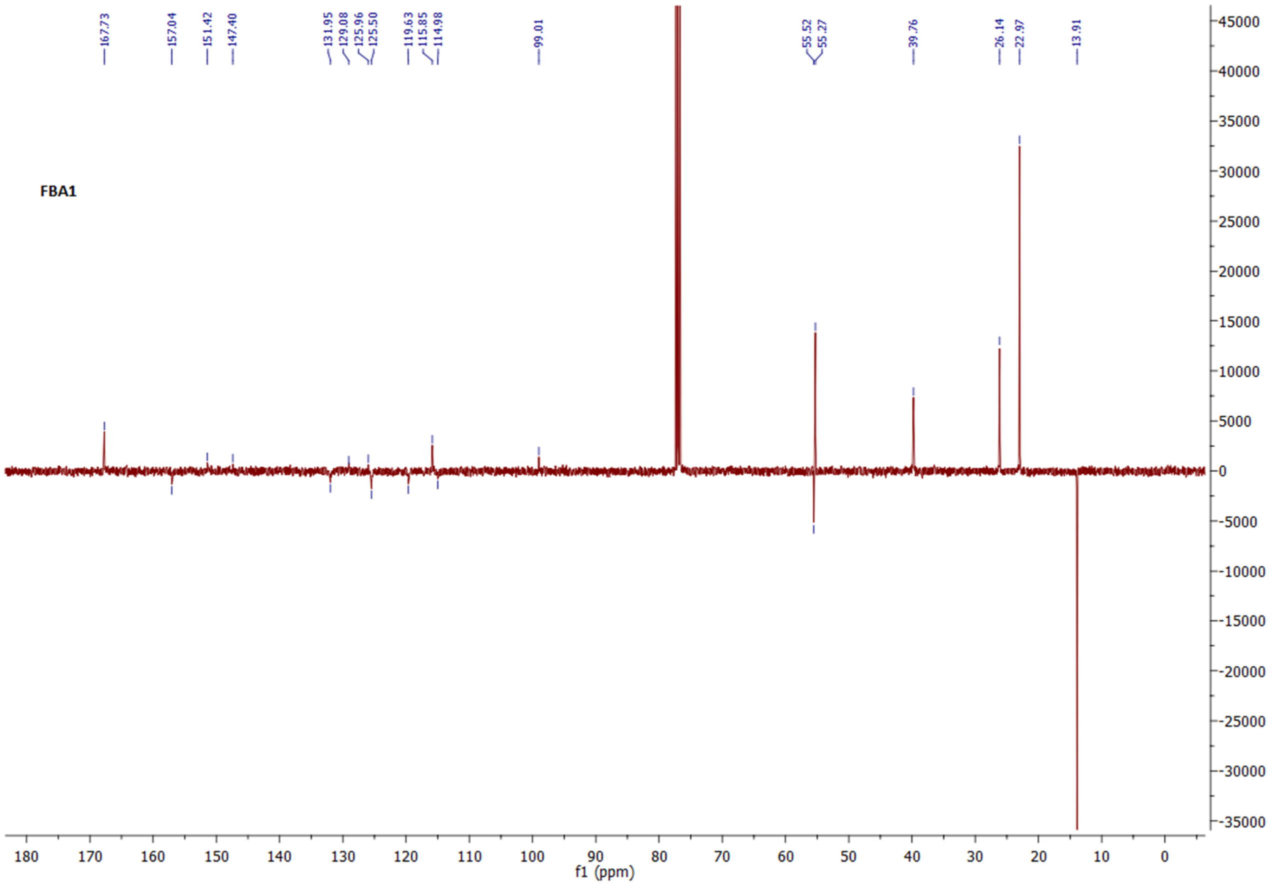
151.24
147.98
147.22
147.19
134.94
134.78
130.83
130.56
126.91
124.46
124.23
123.20
122.92
121.83
121.54
119.34
118.64
118.42
115.75
80.00
79.71
79.41
79.11
78.81
68.05
55.15
47.99
39.72
26.06
22.87
13.76
OHC
OHC
N
OC[CH$_2$C(CF$_3$)$_3$]$_3$
8
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
-20000
-30000
-40000
-50000
-60000
-70000
-80000
-90000
-1E+05
-1E+05
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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157.04
151.42
147.40
131.95
129.08
125.96
125.50
119.63
115.85
114.98
99.01
55.52
55.27
39.76
26.14
22.97
13.91
FBA1
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
-10000
-15000
-20000
-25000
-30000
-35000
180
170
160
150
140
130
120
110
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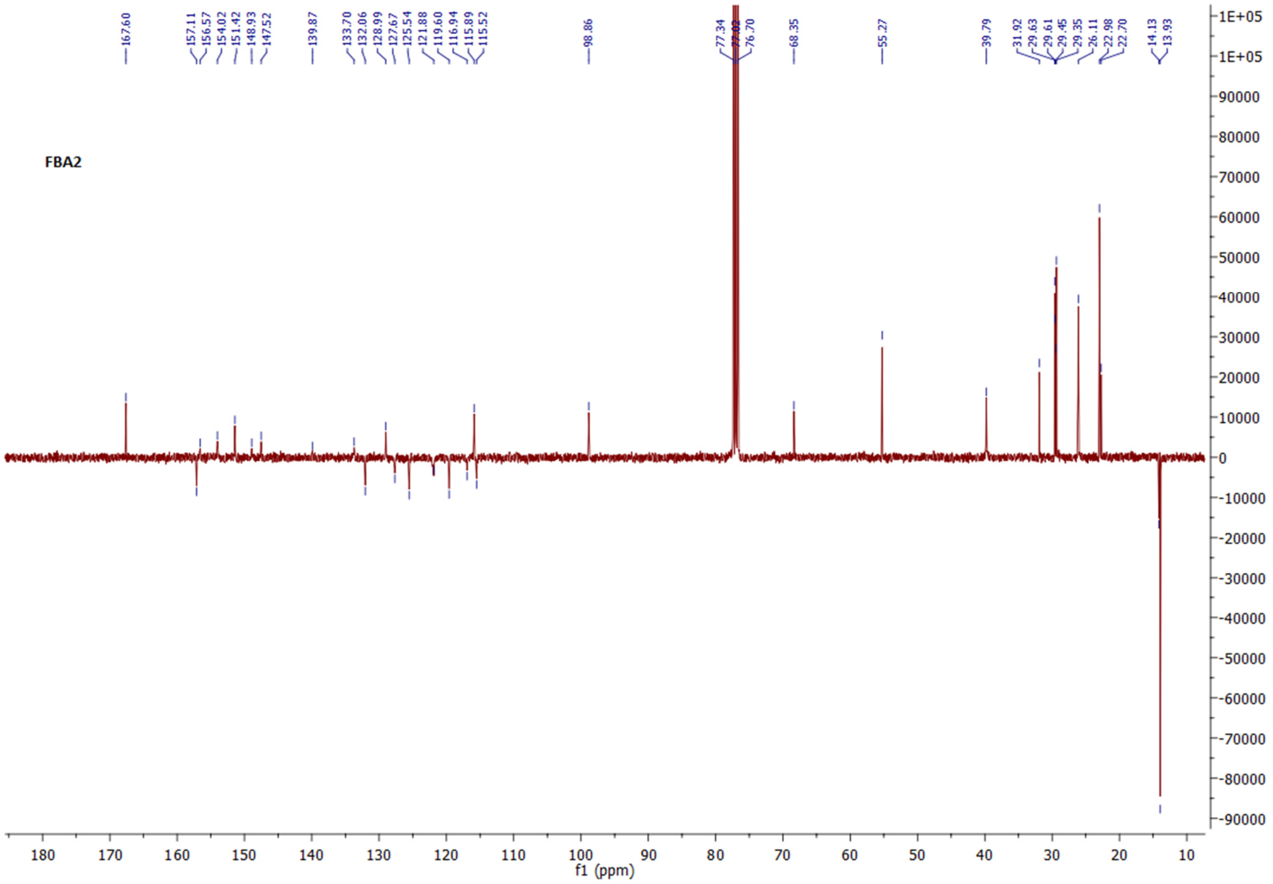
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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156.57
154.02
151.42
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147.52
139.87
133.70
132.06
128.99
127.67
125.54
121.88
119.60
116.94
115.89
115.52
98.86
77.34
77.02
76.70
68.35
55.27
39.79
31.92
29.63
29.61
29.45
29.35
26.11
22.98
22.70
14.13
13.93
1E+05
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
-20000
-30000
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-60000
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-80000
-90000
180
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120
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100
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80
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60
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40
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20
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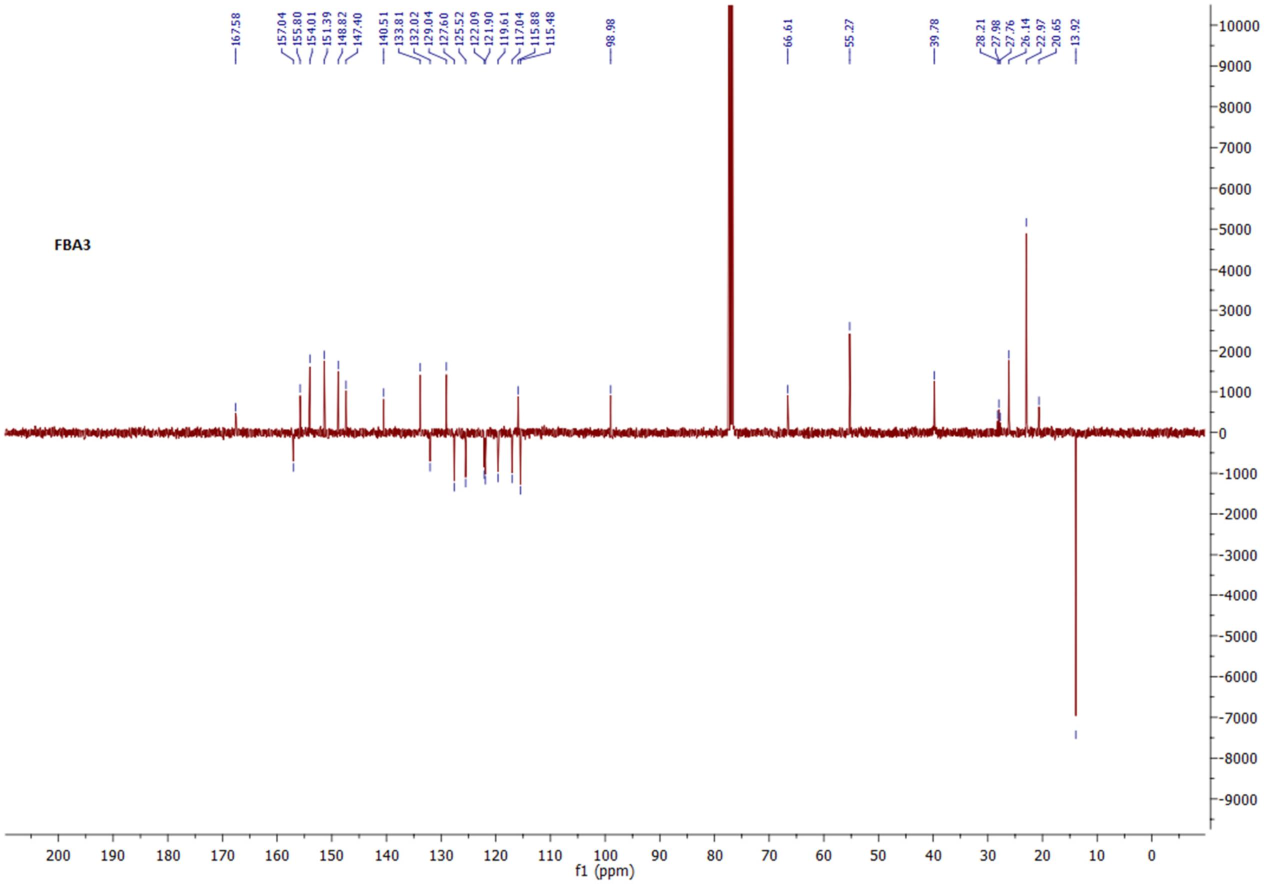
f1 (ppm)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151.39
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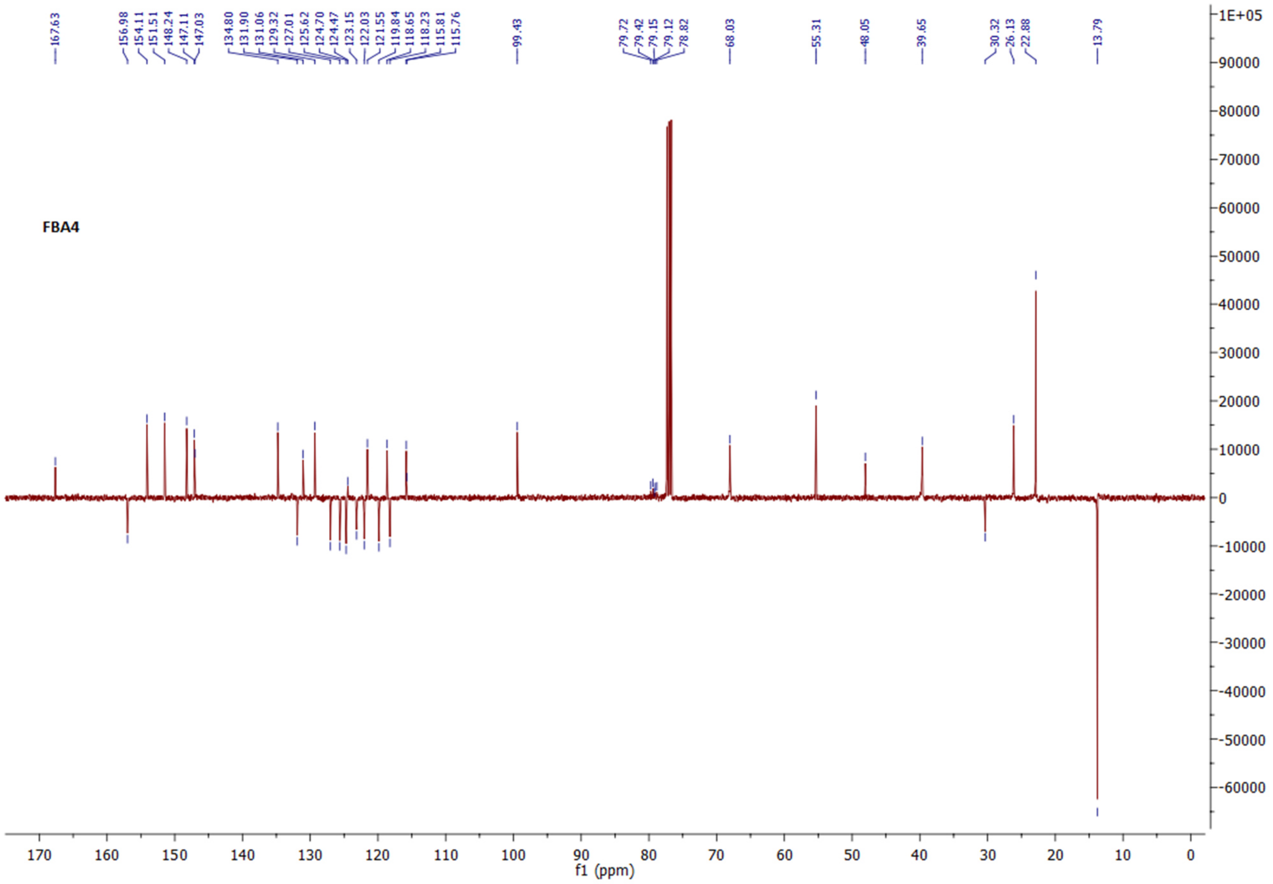
127.60
125.52
122.09
121.90
119.61
117.04
115.88
115.48
98.98
66.61
55.27
39.78
28.21
27.98
27.76
26.14
22.97
20.65
13.92
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
-3000
-4000
-5000
-6000
-7000
-8000
-9000
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


FBA4
167.63
156.98
154.11
151.51
148.24
147.11
147.03
134.80
131.90
131.06
129.32
127.01
125.62
124.70
124.47
123.15
122.03
121.55
119.84
118.65
118.23
115.81
115.76
99.43
79.72
79.42
79.15
79.12
78.82
68.03
55.31
48.05
39.65
30.32
26.13
22.88
13.79
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
-20000
-30000
-40000
-50000
-60000
170
160
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120
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100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

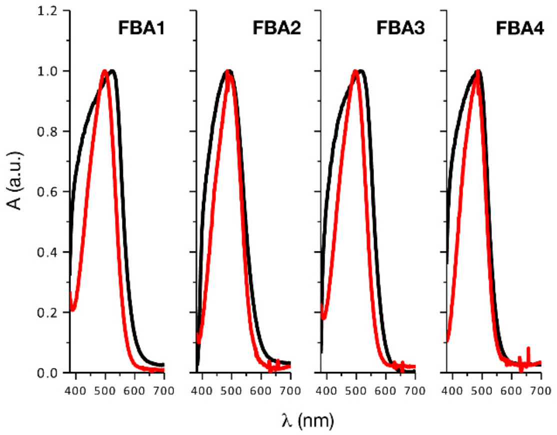

Figure S1: UV-Vis diffuse reflectance spectra of the **FBA** dyes adsorbed on TiO2 porous films (black line) compared to spectra in DCE solution (red line).

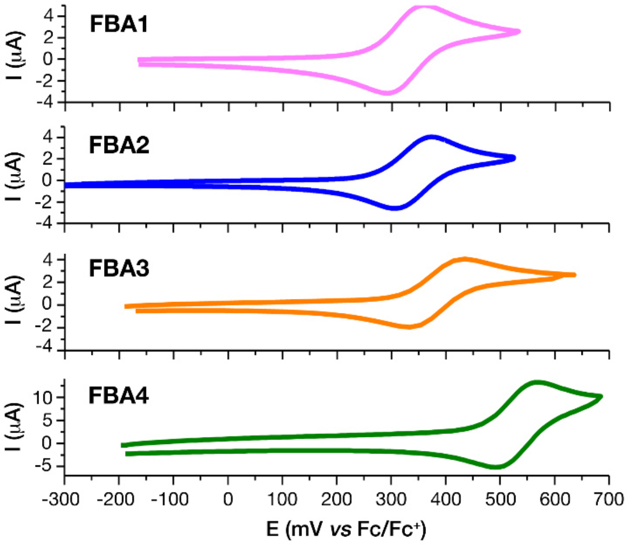

Figure S2: Cyclic voltamperometry profiles for the **FBA** dyes solutions onto Pt electrodes. Electrolyte: TBAPF6 0.1M, scan rate: 75 mV/s.

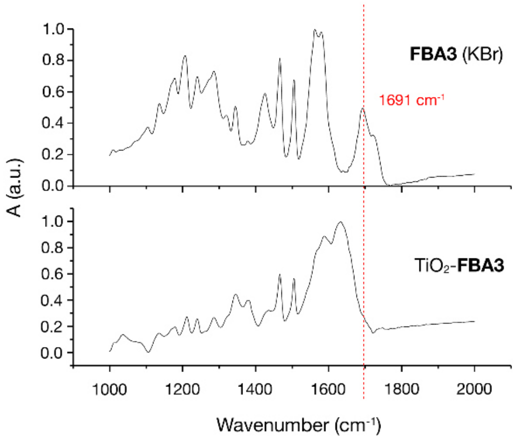

Figure S3: FT-IR spectra of **FBA3** in KBr pellets (up) and adsorbed onto TiO$_2$ nanoparticles.

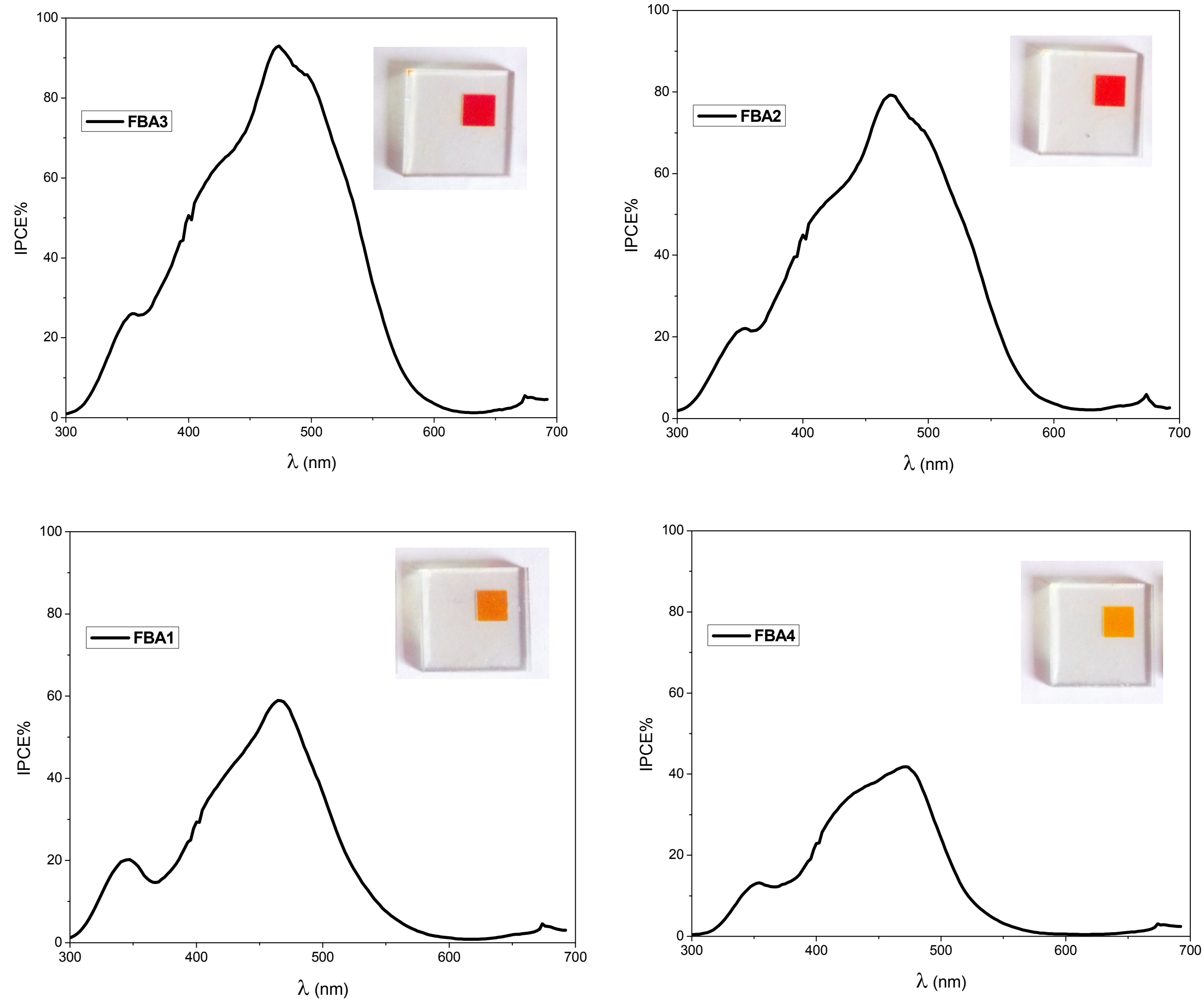

Figure S4: IPCE spectra of the DSSCs fabricated with the **FBA1-4** dyes.