Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


# Electronic Supplementary Information

**Model dyads for 2PA uncaging of a protecting group *via* photoinduced electron transfer**

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# 1. Synthesis

## 1.1 General methods

All solvents and reagents were purchased from commercial suppliers (Fisher or Sigma-Aldrich). Anhydrous THF, DCM and MeCN were obtained by passing solvents through a column of activated alumina. Diisopropylamine (DIPA) and triethylamine were distilled from $CaH_2$. All other reagents were used as supplied by commercial agents. Analytical thin layer chromatography *TLC* was carried out on Merck silica gel 60 $F_{254}$aluminium supported plates and visualized by absorption of UV light. Flash column chromatography was performed with VWR silica gel 60 applying pressure of $N_2$. Size exclusion chromatography was carried out with use of Bio-rad Bio-beads S-X1. HPLC separation was conducted on an Agilent 1100 system equipped with a G1315B diode array detector, a G1311A quaternary pump and a G1316A fraction collector. Analytical HPLC was performed with C18 5 µm, 4.6 × 150 mm Eclipse XDB-C18 column (Agilent) using 1 mL $min^{-1}$ flow and stepwise gradient at 40 °C. The chromatographic separations were monitored in the range 190 –900 nm.

***HPLC method 1***:

| Time [min] | $H_2O$ (0.1% TFA) [v/v, %] | MeCN [v/v, %] |
|---|---|---|
| 0.00 | 95 | 5 |
| 9.00 | 0 | 100 |
| 11.00 | 0 | 100 |

***HPLC method 2:***

| Time [min] | $H_2O$ (0.1% TFA) [v/v, %] | MeCN [v/v, %] |
|---|---|---|
| 0.00 | 50 | 50 |
| 3.00 | 20 | 80 |
| 5.00 | 0 | 100 |
| 10.00 | 0 | 100 |
| 10.01 | 50 | 50 |
| 12.00 | 50 | 50 |

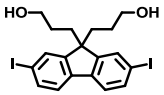
ESI-MS measurements were performed operating in positive or negative mode on a Waters LCT Premier (LRMS) or Bruker µTOF (HRMS) from acetonitrile solutions. MALDI-ToF mass spectrometry was carried out using a Micromass MALDI micro MX spectrometer and following matrices: dithranol (1,8,9-anthracenetriol), DTCB (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile), CHCA (α-cyano-4-hydroxycinnamic acid).

NMR spectra were acquired at ambient temperature with Bruker instruments DPX200 (200 MHz), DPX250 (250 MHz), DPX400 (400 MHz), AV400 (400 MHz), DRX500 (500 MHz).

Chemical shifts for the $^{1}$H-NMR and $^{13}$C spectra are reported with $CDCl_3$ or DMSO-$d_6$ as reference. Data are displayed as follows: chemical shift δ (ppm), multiplicity, integration and coupling constants *J* (Hz).

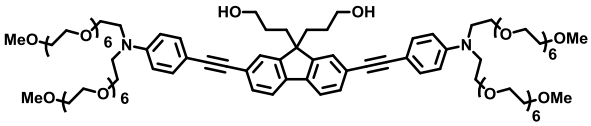
## 1.2 Synthetic procedures

### 3,3'-(2,7-diiodo-9H-fluorene-9,9-diyl)bis(propan-1-ol) (2)




This compound was prepared using modified reaction conditions reported in the literature.[1] A solution of borane-THF complex (1.0 M, 56 mL, 56 mmol) was added slowly to a cooled (0 °C) solution of 3,3'-(2,7-diiodo-9H-fluorene-9,9-diyl)dipropionic acid (7.20 g, 12.8 mmol) in anhydrous THF (10 mL). After 2 h of stirring at 20 °C the reaction mixture was poured into ice (500 mL) and precipitated solid was removed by filtration. The precipitate was redissolved in THF and crystalized by addition of $Et_2O$ to give **2** (6.00 g, 11.2 mmol, 87% yield) as a white powder.
$^{1}$H NMR (400 MHz, DMSO-$d_6$) *δ:* 0.59-0.65 (m, 4H), 1.96-2.00 (m, 4H), 3.10-3.14 (m, 4H), 7.66 (d, *J*=7.8 Hz, 2H), 7.71 (dd, *J*=1.3 Hz, *J*=7.8 Hz, 2H), 7.83 (d, *J*=1.3 Hz, 2H); $^{13}$C NMR (50 MHz, DMSO-$d_6$) *δ:* 27.7, 35.7, 55.2, 61.2, 94.4, 122.6, 132.1, 136.3, 139.7, 152.4; *m/z* ESI+ 557.0, $[M+Na]^+$, $C_{19}H_{20}I_2O_2Na^+$ requires 556.9 (100%).

### BEF-OH

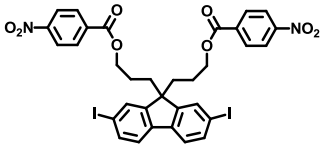



This compound was prepared using modified reaction conditions reported in the literature.[2] The following solids were dried under vacuum: CuI (1 mg, 0.005 mmol), $Pd(OAc)_2$ (1 mg, 0.004 mmol) $PPh_3$ (2 mg, 0.008 mmol) and 3,3'-(2,7-diiodo-9H-fluorene-9,9-diyl)bis(propan-1-ol) (**2**) (50 mg, 0.10 mmol). Distilled DIPA (0.5 mL) was added and two freeze-thaw cycles were carried out. A solution of acetylene **1** (157 mg, 0.21 mmol) in anhydrous MeCN (0.5 mL) was added and additional freeze-thaw cycle was run. The progress of the reaction was monitored by HPLC (*method 1*). After 2 h of stirring at 20 °C the reaction mixture was diluted with DCM (50 mL) and the crude mixture was washed with $H_2O$ (20 mL) and saturated aqueous solution of $NH_4Cl$ (20 mL). The organic layer was dried over $MgSO_4$ and evaporated to dryness. The final compound was isolated from the mixture with use of reverse phase column chromatography (in gradient from 100% of $H_2O$ (0.1% TFA v/v) to 100% MeCN). **BEF-OH** was obtained in 33% yield (55 mg, 0.03 mmol).

$^{1}$H NMR (400 MHz, $CDCl_3$)*δ:* 0.87-0.94 (m, 4H), 2.09-2.13 (m, 4H), 3.38 (m, 16H), 3.53-3.55 (m, 8H), 3.60-3.67 (m, 104H), 6.70 (d, *J*=8.5 Hz, 4H), 7.39 (d, *J*=8.5 Hz, 4H), 7.47-7.49

(m, 4H), 7.63 (d, *J*=8.2 Hz, 2H); *m/z* MALDI-TOF$^+$ 1825.08, $[M+Na]^+$, $C_{95}H_{152}N_2O_{30}Na^+$ requires 1825.04 (100%).

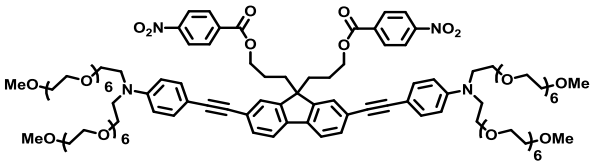
**(2,7-diiodo-9H-fluorene-9,9-diyl)bis(propane-3,1-diyl) bis(4-nitrobenzoate) (3)**



This compound was prepared using reaction conditions reported in the literature.[3] 3,3'-(2,7-Diiodo-9H-fluorene-9,9-diyl)bis(propan-1-ol) (**2**) (178 mg, 0.33 mmol), *p*-nitrobenzoic acid (93 mg, 0.55 mmol), EDC (114 mg, 0.59 mmol) and DMAP (8 mg, 0.07 mmol) were dissolved in anhydrous MeCN and THF (1:1 v/v, 6 mL) and stirred overnight at 20 °C. The mixture was diluted with $H_2O$ and extracted with $CHCl_3$ (50 mL). The organic extracts were combined, dried over $MgSO_4$ and evaporated to dryness. The product was isolated by column chromatography on silica with PE/$CHCl_3$ 4:1 v/v as eluent to give compound **3** as a white solid (21%, 60 mg, 0.072 mmol).

$^1$H NMR ($CDCl_3$, 400 MHz) $\delta$: 1.04-1.11 (m, 4H), 2.14-2.18 (m, 4H), 4.07-4.10 (m, 4H), 7.49 (d, *J*=8.5 Hz, 2H), 7.72-7.64 (m, 4H), 8.13 (d, *J*=8.2 Hz, 4H), 8.30 (d, *J*=8.2 Hz, 4H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$: 23.1, 36.2, 54.6, 65.4, 93.7, 122.0, 123.6, 130.7, 131.8, 131.5, 136.9, 139.9, 150.5, 150.6, 164.5; *m/z* EI$^+$ 831.9778, $[M]^+$, $C_{33}H_{26}I_2N_2O_8$ requires 831.9778 (100%).

**BEF-NB**

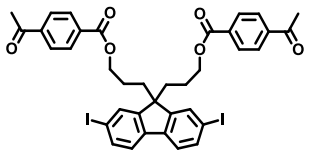


This compound was prepared using modified reaction conditions reported in the literature.[2] The following solids were dried under vacuum: CuI (3.0 mg, 0.016 mmol), $Pd(OAc)_2$ (4.7 mg, 0.021 mmol), $PPh_3$ (11 mg, 0.042 mmol) and (2,7-diiodo-9H-fluorene-9,9-diyl)bis(propane-3,1-diyl) bis(4-nitrobenzoate) (**3**) (88 mg, 0.10 mmol). Distilled DIPA (1 mL) was added and two freeze-thaw cycles were carried out. A solution of acetylene **1** (160 mg, 0.21 mmol) in anhydrous MeCN (2 mL) was added and additional freeze-thaw cycle was run. The progress of the reaction was monitored by TLC. After 1 h of stirring at 20 °C additional portion of CuI (3.0 mg, 0.016 mmol), $Pd(OAc)_2$ (4.7 mg, 0.021 mmol), $PPh_3$ (11 mg, 0.042 mmol) was added. After 18 h of stirring the reaction mixture was diluted with EtOAc (50 mL) and the crude mixture was washed with $H_2O$ (20 mL) and saturated aqueous solution of $NH_4Cl$ (20 mL). The organic layer was dried over $MgSO_4$ and evaporated to dryness. The residue was redissolved in $CHCl_3$ and passed through the silica column eluting

with $CHCl_3$/MeOH (95:5 v/v). The product was purified with use of size exclusion chromatography with $CHCl_3$ as eluent to yield **BEF-NB** (33 mg, 0.016 mmol, 15% yield).

$^1$H NMR ($CDCl_3$, 400 MHz) *δ*: 1.04-1.07 (m, 4H), 2.12-16 (m, 4H), 3.30 (s, 12H), 3.46-3.48 (m, 8H), 3.51-3.62 (m, 104H), 3.97-4.00 (m, 4H), 6.61 (d, *J*=8.8 Hz, 4H), 7.27 (d, *J*=8.8 Hz, 4H), 7.42 (s, 2H), 7.45 (d, *J*=7.8 Hz, 2H), 7.61 (d, *J*=7.8 Hz, 2H), 8.04 (d, *J*=8.0 Hz, 4H), 8.13 (d, *J*=8.0 Hz, 4H); $^{13}$C NMR ($CDCl_3$, 100 MHz) *δ*: 23.2, 36.4, 50.8, 54.2, 59.0, 65.5, 68.4, 70.5-70.7, 72.0, 87.9, 91.6, 109.3, 111.5, 120.2, 123.4, 123.5, 125.3, 130.6, 131.0, 132.8, 133.8, 135.5, 140.0, 147.9. 149.0, 150.5, 164.5; *m/z* MALDI-TOF$^+$ 2123.47, $[M+Na]^+$, $C_{109}H_{158}N_4O_{36}Na^+$ requires 2123.06 (100%).

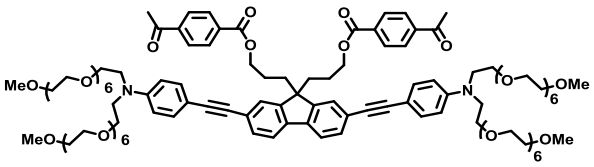
**2,7-diiodo-9H-fluorene-9,9-diyl)bis(propane-3,1-diyl) bis(4-acetylbenzoate) (4)**



This compound was prepared using reaction conditions reported in the literature.[3] 3,3'-(2,7-Diiodo-9H-fluorene-9,9-diyl)bis(propan-1-ol) (**2**) (300 mg, 0.56 mmol), 4-acetoxybenzoic acid (200 mg, 1.22 mmol), EDC (234 mg, 1.23 mmol) and DMAP (25 mg, 0.20 mmol) were dissolved in anhydrous DCM (5 mL) and stirred for 2 h at 20 °C. The mixture was diluted with $H_2O$ and extracted with DCM (50 mL). The organic extracts were combined and dried over $MgSO_4$ and evaporated to dryness. The residue was dissolved in $CHCl_3$ and passed through a silica plug with $CHCl_3$ as eluent. Product containing fractions were combined and evaporated in *vacuo*. The product was purified further by redissolving in MeOH and precipitating with $Et_2O$/hexane (1:1 v/v ) to yield **4** as a white solid (54%, 250 mg, 0.3 mmol).

$^1$H NMR ($CDCl_3$, 400 MHz) *δ*: 1.04-1.16 (m, 4H), 2.13-2.17 (m, 4H), 2.65 (s, 6H), 4.07 (t, *J*=6.2 Hz, 4H), 7.47 (d, *J*=8.4 Hz, 2H), 7.72-7.73 (m, 4H), 8.02 (d, *J*=8.7 Hz, 4H), 8.06 (d, *J*=8.7 Hz, 4H); $^{13}$C NMR ($CDCl_3$, 1200 MHz) *δ*: 22.1, 25.9, 30.6, 35.3, 53.6, 63.9, 92.5, 120.9, 127.3, 128.8, 130.8, 132.9, 135.9, 138.9, 139.2, 149.7, 164.5, 196.5; *m/z* EI$^+$ 826.0248, [M], $C_{37}H_{32}I_2O_6^+$ requires 826.0289 (100%).

**BEF-Phen**

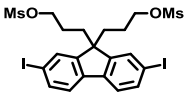



This compound was prepared using reaction conditions reported in the literature.[2] The following solids were dried under vacuum: CuI (0.9 mg, 0.005 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) $PPh_3$ (2.6 mg, 0.01 mmol) and 2,7-diiodo-9H-fluorene-9,9-diyl)bis(propane-3,1-diyl) bis(4-acetylbenzoate) (**4**) (74 mg, 0.09 mmol). Distilled DIPA (1 mL) was added and

two freeze-thaw cycles were carried out. A solution of acetylene **1** (150 mg, 0.20 mmol) in anhydrous MeCN (2 mL) was added and additional freeze-thaw cycle was run. The progress of the reaction was monitored by TLC. After 1 h of stirring at 20 °C, additional portion of CuI (0.9 mg, 0.005 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) $PPh_3$ (2.6 mg, 0.01 mmol) and acetylene **1** (50 mg, 0.07 mmol) in anhydrous MeCN (1 mL) were added. Once the reaction was completed the mixture was diluted with DCM (50 mL) followed by washing with $H_2O$ (20 mL) and saturated aqueous solution of $NH_4Cl$ (20 mL). The organic layer was dried over $MgSO_4$ and evaporated to dryness. The residue was redissolved in $CHCl_3$ and passed through the silica column eluting with $CHCl_3$/MeOH (95:5 v/v). The product was purified with use of size exclusion chromatography with $CHCl_3$ as eluent to yield **BEF-Phen** (31 mg, 0.015 mmol, 16 %).

$^1$H NMR ($CDCl_3$, 500 MHz) *δ:* 1.09-1.15 (m, 4H), 2.21-2.24 (m, 4H), 2.44 (s, 6H), 3.38 (s, 12H), 3.54-3.56 (m, 8H), 3.58-3.69 (m, 104H), 4.05-4.07 (m, 4H), 6.68 (d, *J*=8.9 Hz, 4H), 7.37 (d, *J*=8.9 Hz, 4H), 7.54 (m, 4H), 7.69 (d, *J*=8.1 Hz, 2H), 7.94 (d, *J*=8.5 Hz, 4H), 8.04 (d, *J*=8.5 Hz, 4H); $^{13}$C NMR ($CDCl_3$, 125 MHz) *δ:* 22.2, 25.7, 35.4, 49.8, 53.3, 58.0, 64.1, 67.3, 69.6-69.7, 70.9, 87.1, 90.4, 108.6, 110.5, 119.2, 122.3, 124.4, 127.2, 128.8, 130.0 132.0, 133.0, 139.2, 146.8 148.2, 164.6, 196.5; *m/z* MALDI-TOF$^+$ 2093.23, [M], $C_{113}H_{164}N_4O_{34}^+$ requires 2094.12 (100%).

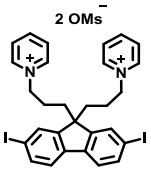
**2,7-diiodo-9H-fluorene-9,9-diyl)bis(propane-3,1-diyldimethanesulfonate (5)**




This compound was prepared using reaction conditions reported in the literature.[4] To a cooled (0 °C) solution of compound (**2**) (1.00 g, 1.87 mmol) in anhydrous DCM (10 mL), $Et_3N$ (1.6 mL, 11.48 mmol) and methanesulfonyl chloride (580 µL, 7.50 mmol) were added dropwise. After 1 h of stirring at 20 °C the mixture was diluted with $H_2O$ and extracted with $CHCl_3$ (50 mL). The organic extracts were combined, dried over $MgSO_4$ and evaporated to dryness. The product was isolated with use of column chromatography on silica with $CHCl_3$ as eluent to give **5** as a white solid (900 mg, 1.3 mmol, 70% yield).

$^1$H NMR ($CDCl_3$, 400 MHz) *δ:* 0.94-1.00 (m, 4H), 2.04-2.09 (m, 4H), 2.89 (s, 6H), 3.89-3.93 (m, 4H), 7.42 (d, *J*=8.5 Hz, 2H), 7.64-7.67 (m, 4H); $^{13}$C NMR ($CDCl_3$, 100 MHz) *δ:* 23.6, 35.5, 37.4, 54.3, 69.8, 93.8, 122.0, 131.9, 137.0, 139.7, 150.2.

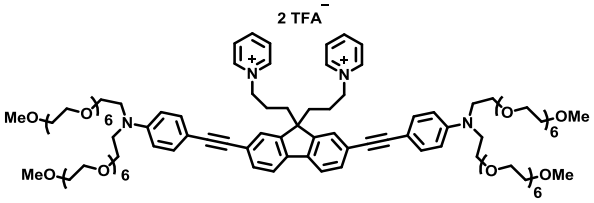
**1,1'-((2,7-diiodo-9H-fluorene-9,9-diyl)bis(propane-3,1-diyl))bis(pyridin-1-ium) methanesulfonate (6)**




This compound was prepared using reaction conditions reported in the literature.[5] 2,7-Diiodo-9H-fluorene-9,9-diyl)bis(propane-3,1-diyl dimethanesulfonate (**5**) (200 mg, 0.28 mmol) was dissolved in anhydrous pyridine (5 mL) and heated for 15 h at 115 °C. The reaction was allowed to cool to 20 °C and solvent was evaporated to dryness. The residue was dissolved in MeCN and precipitated with THF. Solvent was decanted and precipitation procedure was repeated several times, to yield the product **6** as a fine red powder (120 mg, 0.14 mmol, 50%).

$^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$: 1.02-1.10 (m, 4H), 1.96-2.02 (m, 4H), 2.32 (s, 6H), 4.35-4.39 (m, 4H), 7.65-7.67 (m, 4H), 7.71 (d, $J$=8.0 Hz, 2H), 8.07-8.10 (m, 4H), 8.56-8.60 (m, 2H), 8.89 (d, $J$=6.0 Hz, 4H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$: 26.4, 35.1, 40.7, 54.9, 61.2, 95.4, 123.3, 128.9, 132.5, 137.4, 140.1, 145.5, 146.4, 151.0; *m/z* ESI-MS+ 329.1, $[M]^{2+}$ $C_{29}H_{28}I_2N_2^{2+}$ requires 329.0 (100%).

**BEF-Pyr**




This compound was prepared using reaction conditions reported in the literature.[2] The following solids were dried under vacuum: CuI (1.3 mg, 0.007 mmol), $Pd(OAc)_2$ (1.5 mg, 0.007 mmol), $PPh_3$ (4 mg, 0.015 mmol) and 1,1'-((2,7-diiodo-9H-fluorene-9,9-diyl)bis(propane-3,1-diyl))bis(pyridin-1-ium) methanesulfonate (**6**) (60 mg, 0.071 mmol). Distilled DIPA (2 mL) was added and two freeze-thaw cycles were carried out. A solution of acetylene **1** (120 mg, 0.160 mmol) in anhydrous MeCN (3 mL) was added and additional freeze-thaw cycle was run. The progress of the reaction was monitored by HPLC (method 1). After 2 h of stirring at 20 °C the reaction mixture was diluted with $CHCl_3$ (50 mL) and the crude mixture was washed with $H_2O$ (20 mL) and saturated aqueous solution of $NH_4Cl$ (20 mL). The organic layer was dried over $MgSO_4$ and evaporated to dryness. The final compound was isolated from the crude mixture with use of reverse phase column chromatography (in gradient from 100% of $H_2O$ (0.1% TFA v/v) to 100% MeCN). Product containing fractions were extracted with $CHCl_3$, organic washings were combined, dried over $MgSO_4$ and evaporated to dryness. Further purification required use of size exclusion chromatography with $CHCl_3$ as eluent to give **BEF-Pyr** (22 mg, 0.01 mmol, 14 %). The methanesulfonate counterion was replaced by the TFA anion during column chromatography with TFA-buffer.

$^{1}$H NMR ($CDCl_3$, 500 MHz) *δ*: 1.35-1.47 (m, 4H), 1.98-2.12 (m, 4H), 3.34 (s, 12H), 3.49-3.53 (m, 8H), 3.55-3.69 (m, 104H), 4.46-4.61 (m, 4H), 6.65 (d, *J*=8.5 Hz, 4H), 7.16 (s, 2H), 7.35 (d, *J*=8.5 Hz, 4H), 7.42 (d, *J*=7.8 Hz, 2H), 7.59 (d, *J*=7.8 Hz, 2H), 7.92-8.04 (m, 4H), 8.31-8.39 (m, 2H), 8.97-9.14 (m, 4H); $^{13}$C NMR ($CDCl_3$, 125 MHz) *δ*: 26.7, 35.0, 51.2, 53.9, 59.4, 62.1, 68.8, 70.9-71.0, 71.1, 72.3, 88.5, 92.6, 109.8, 120.0, 120.8, 123.9, 125.7, 128.8, 131.6, 133.4, 139.9, 145.4, 145.5, 148.3, 148.8; $^{19}$F NMR ($CDCl_3$, 376 MHz) *δ*: -75.4; *m/z* MALDI-TOF$^{+}$ 1926.49, $[M]^{+}$, $C_{105}H_{160}N_4O_{28}$ requires 1926.13 (100%).

## 2. NMR and MS spectra, HPLC chromatograms

In this section we present $^{1}$H and $^{13}$C NMR spectra of all synthesized compounds. 2D NMR experiments aided assignment of $^{1}$H NMR peaks to the corresponding protons in each molecule, however as splitting patterns and chemical shifts are very similar within each series (intermediate fluorene cores **2-6** and **BEF** derivatives) therefore we present 2D NMR spectra only for two representative compounds from each series, namely compound **4** and **BEF-NB**.

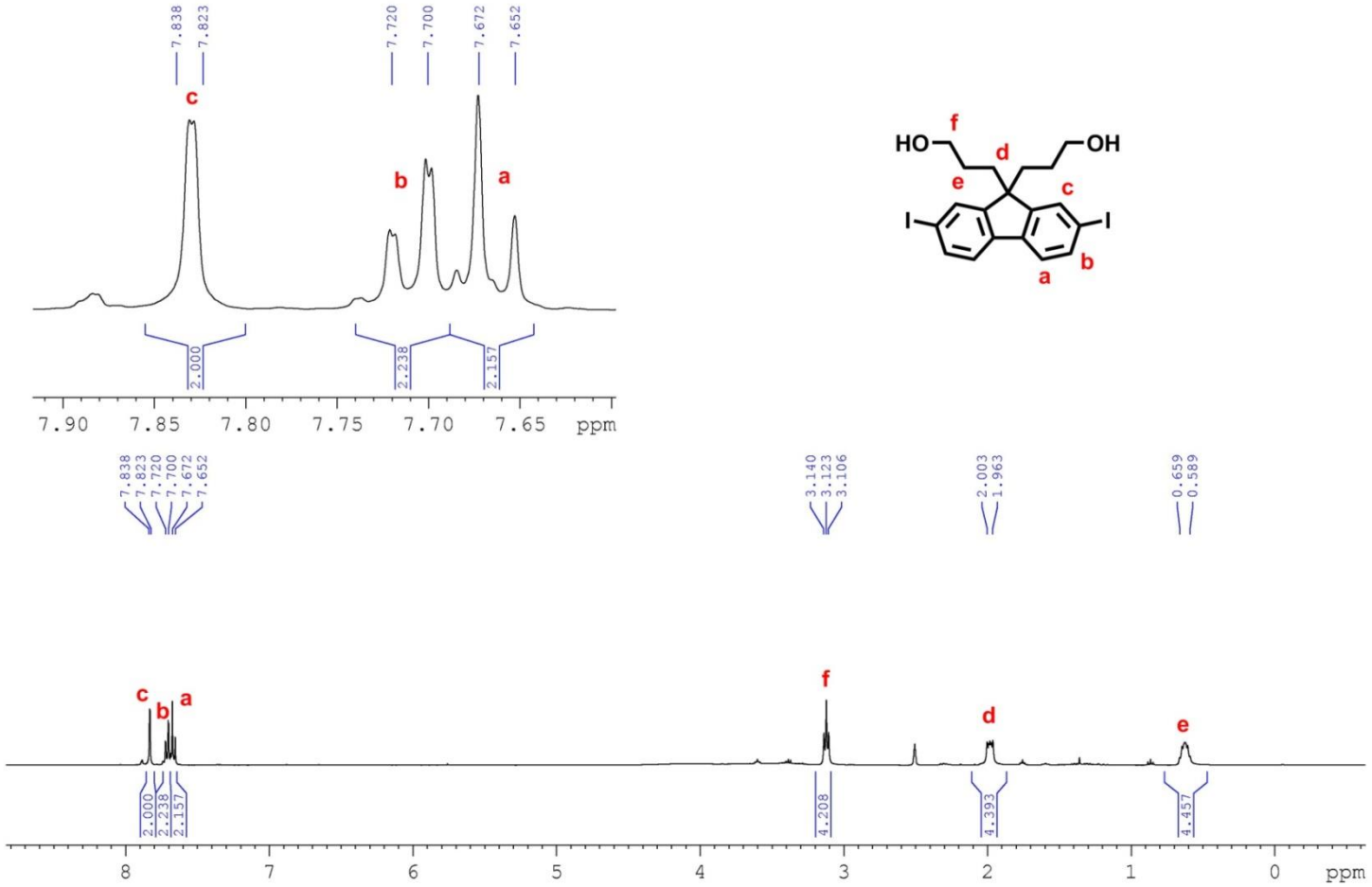



**Figure S1**. $^{1}$H NMR spectrum of compound **2** with zoom on the aromatic region (400 MHz, DMSO-$d_6$, 298 K).

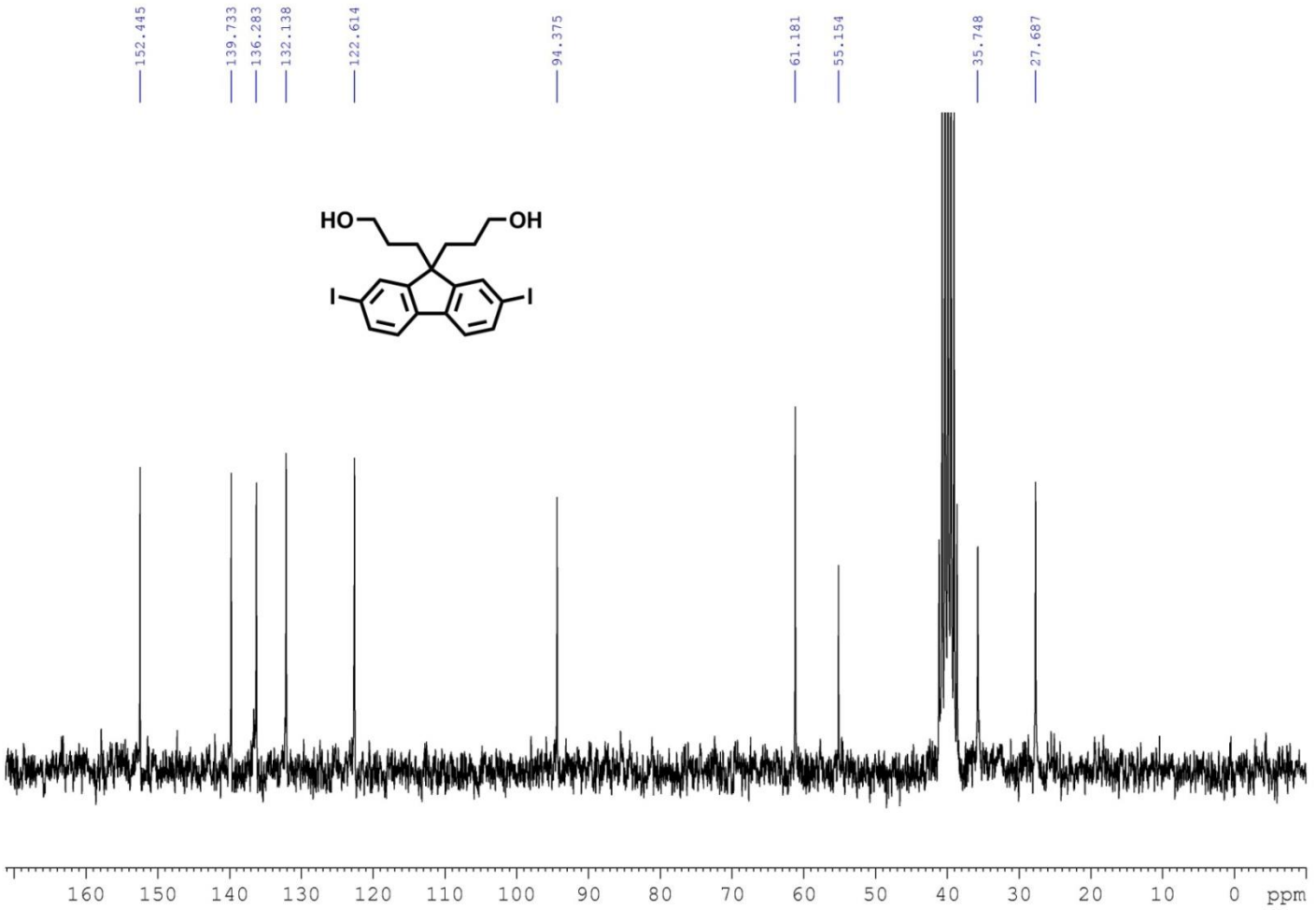



**Figure S2**. $^{13}$C NMR spectrum of compound **2** (200 MHz, DMSO-$d_6$, 298 K).

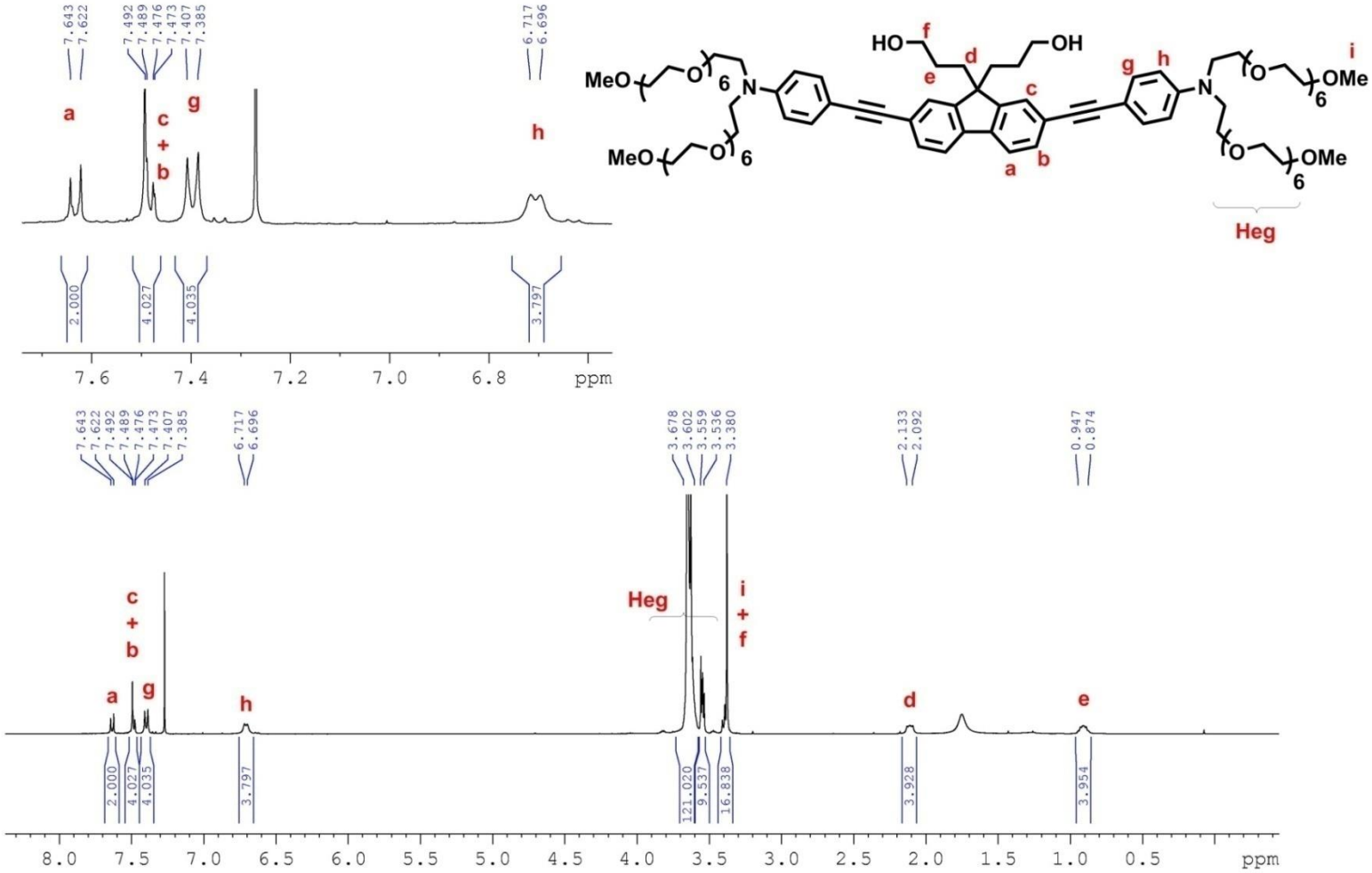



**Figure S3**. $^{1}$H NMR spectrum of **BEF-OH** with zoom on the aromatic region (400 MHz, $CDCl_3$, 298 K).

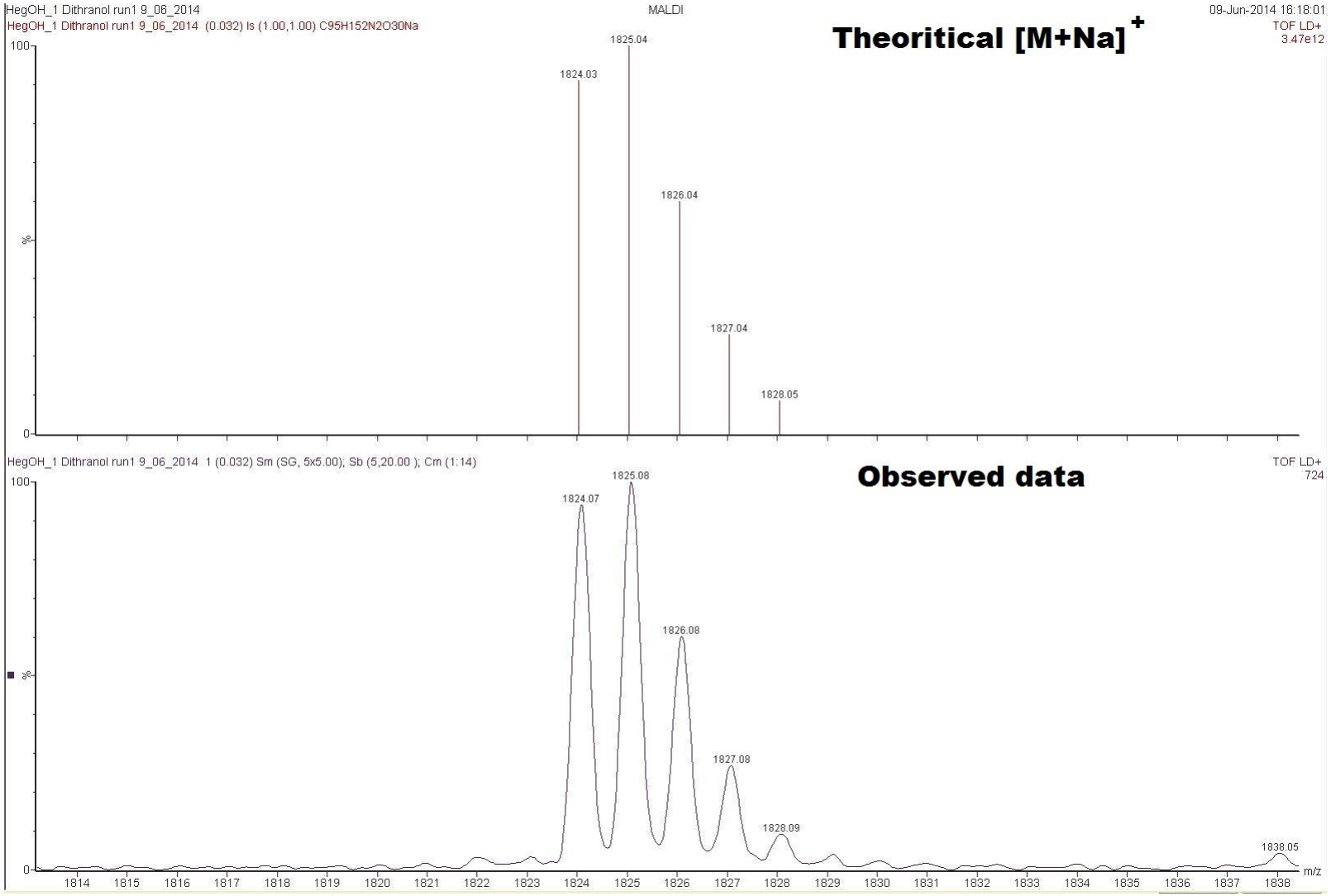



**Figure S4**. MALDI-TOF isotope patterning of [**BEF-OH**+Na]$^+$ *(bottom)* and theoretical pattern calculated for $C_{95}H_{152}N_2O_{30}Na$ *(top).*

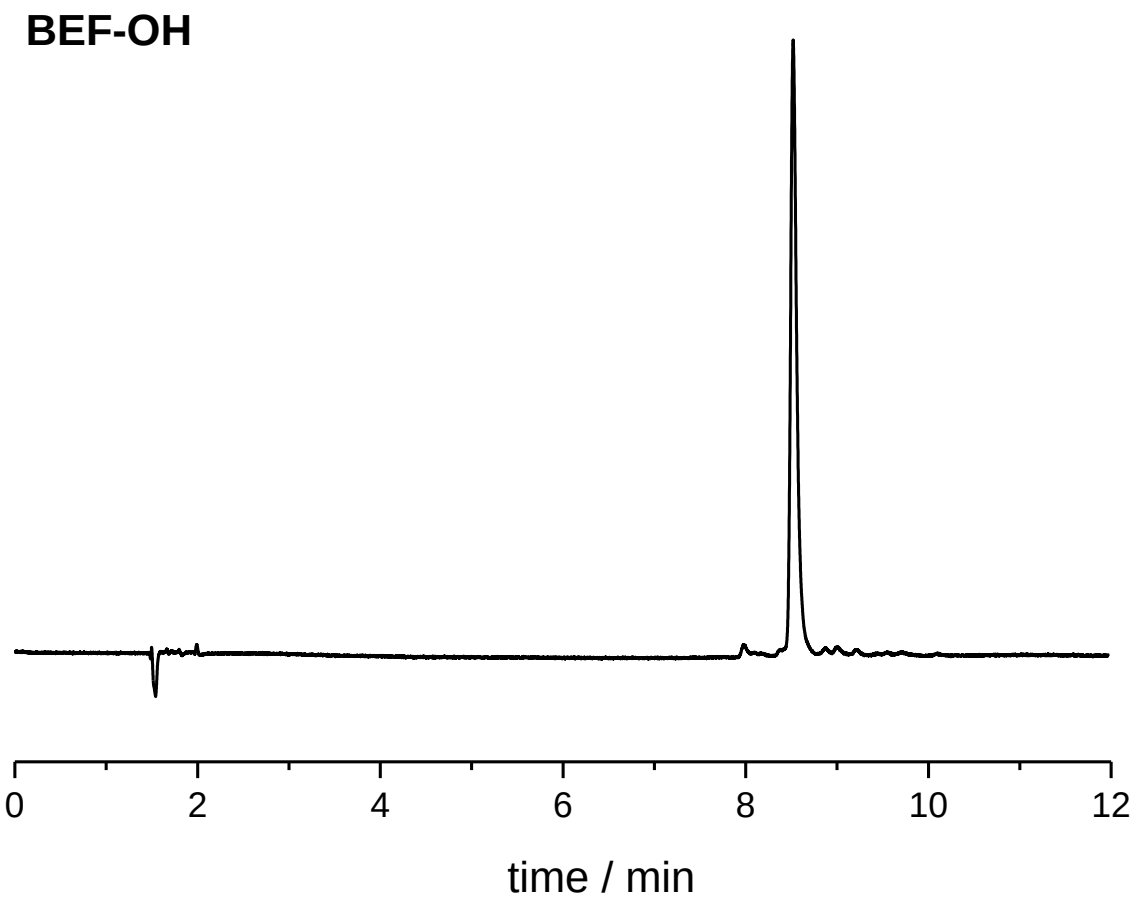



**Figure S5**. HPLC chromatogram of **BEF-OH**, absorption recorded at 375 nm, *HPLC method 1*.

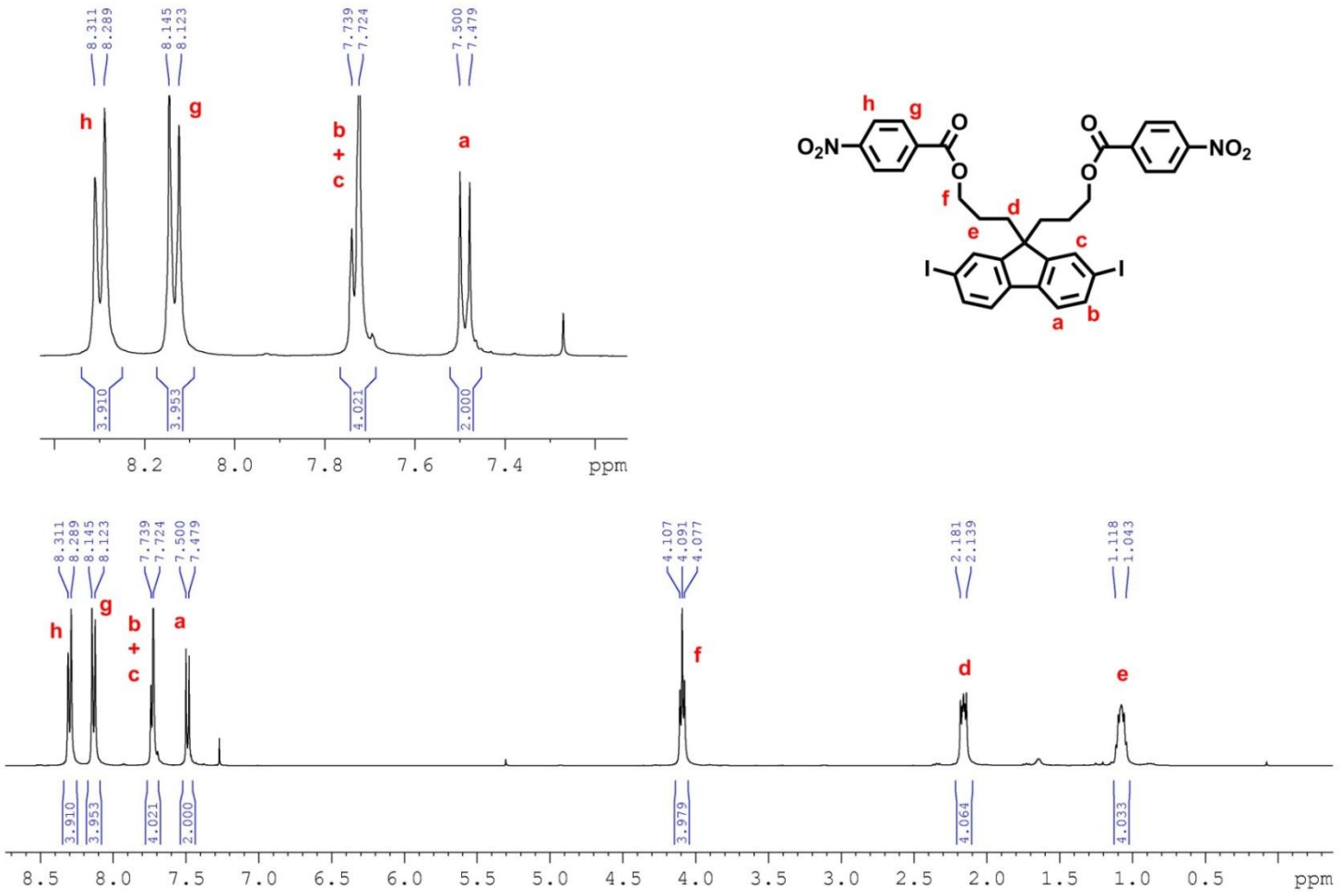



**Figure S6**. $^{1}$H NMR spectrum of compound **3** with zoom on the aromatic region (400 MHz, $CDCl_3$, 298 K).

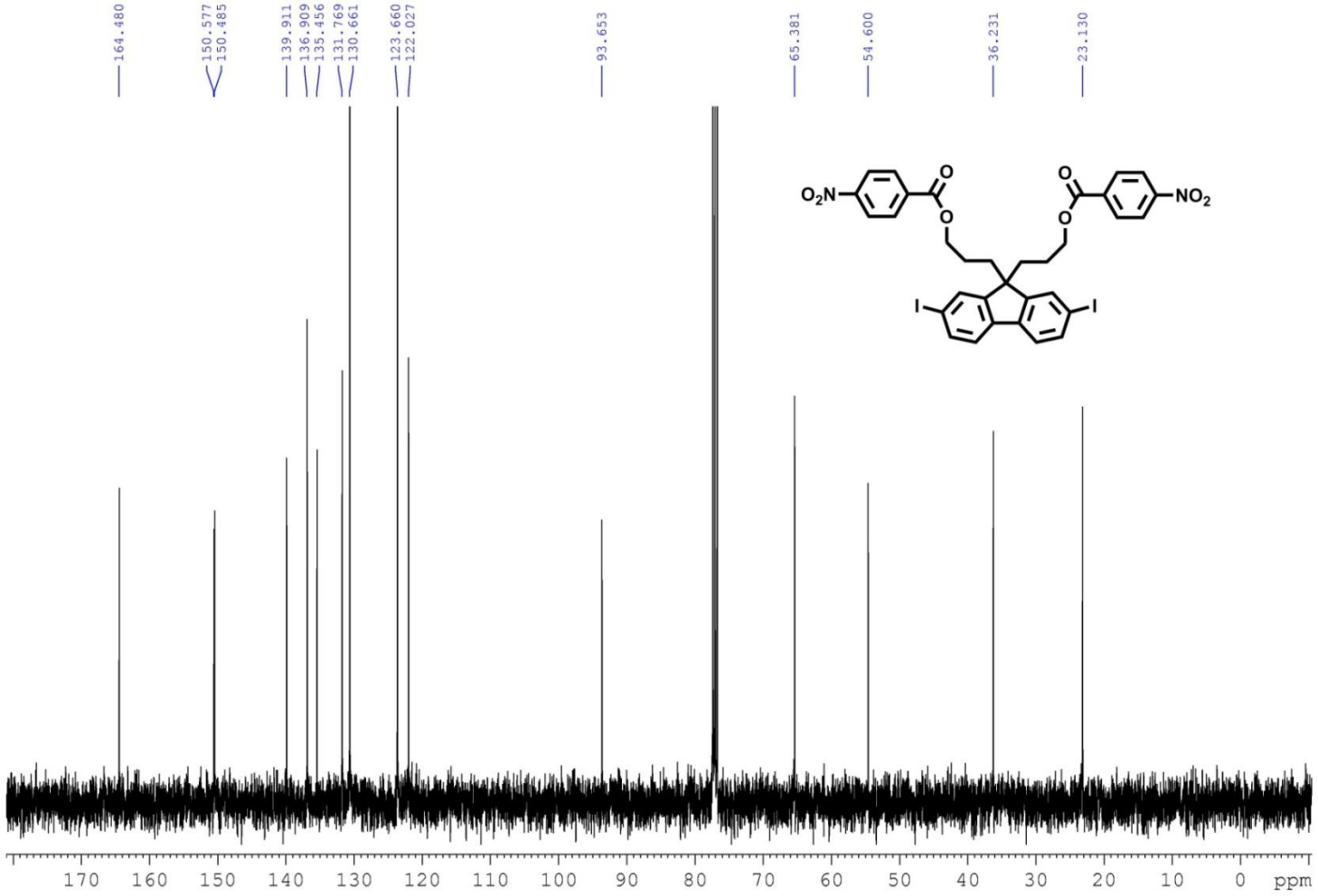



**Figure S7**. $^{13}C$ NMR spectrum of compound **3** (200 MHz, $CDCl_3$, 298 K).

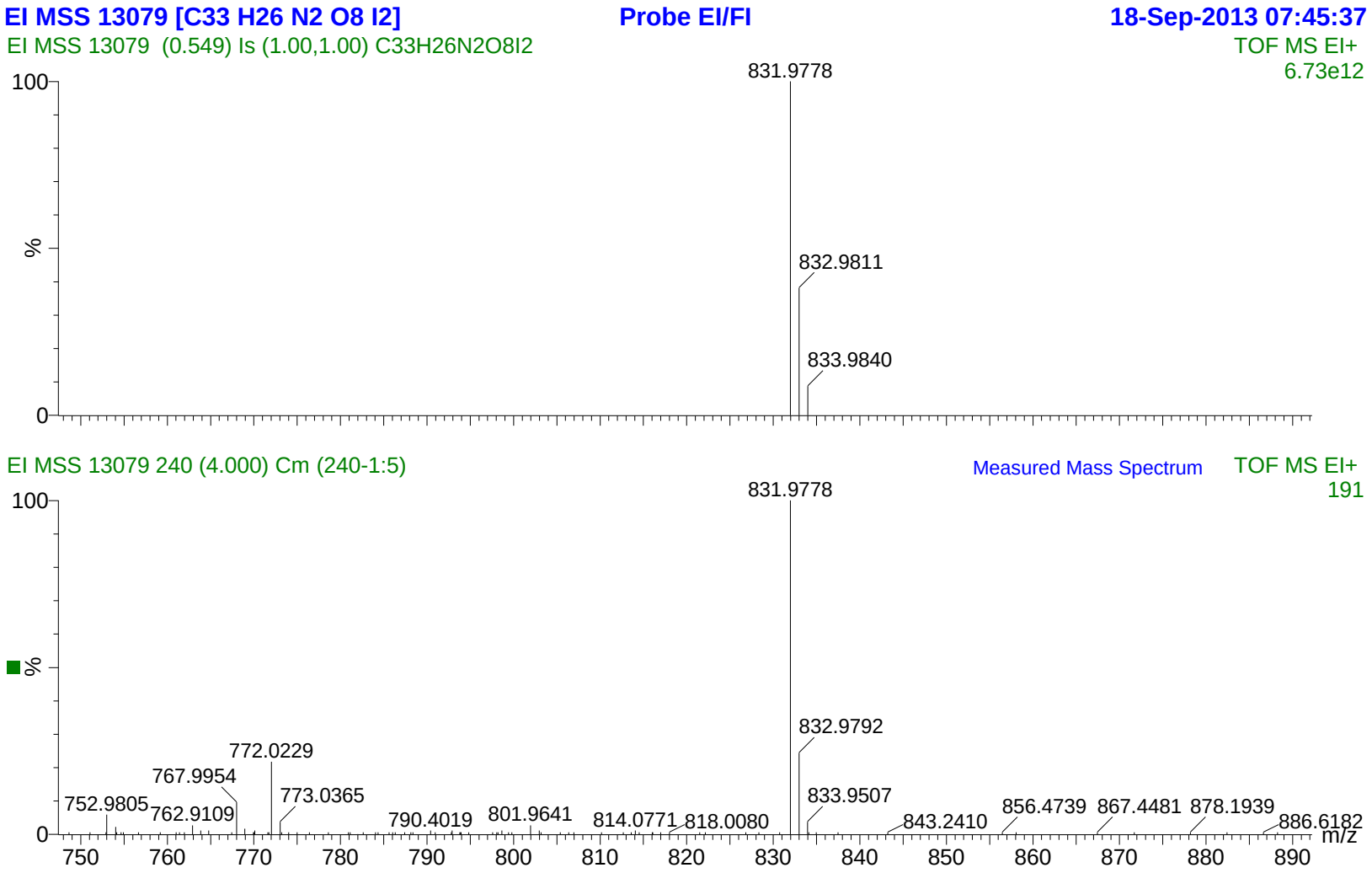



**Figure S8**. EI+ mass spectrum of compound **3** *(bottom)* and theoretical isotopic pattern calculated for $C_{33}H_{26}I_2N_2O_8$ is 831.97 *(top)*.

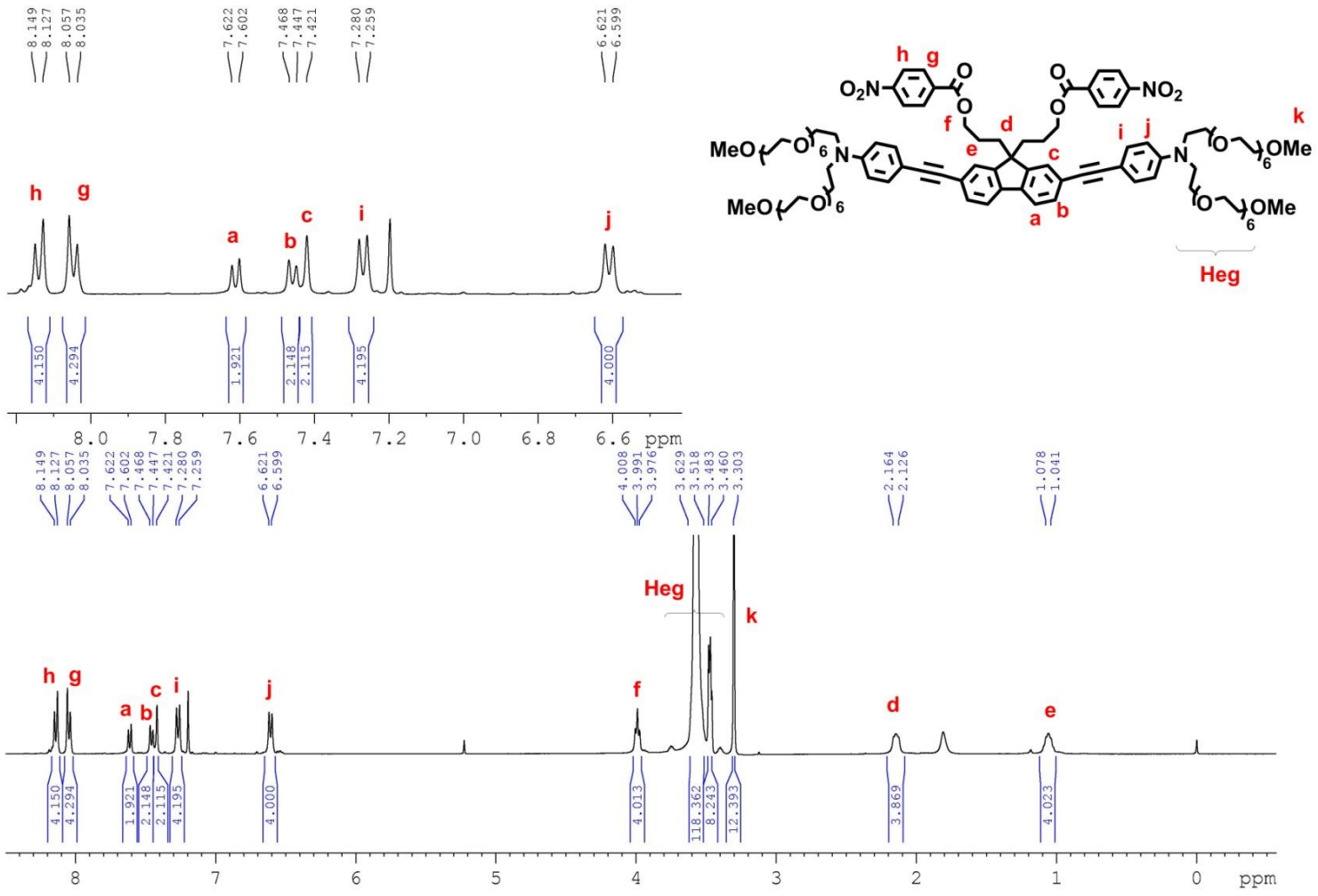



**Figure S9**. $^{1}$H NMR spectrum of **BEF-NB** with zoom on the aromatic region (400 MHz, $CDCl_3$, 298 K).

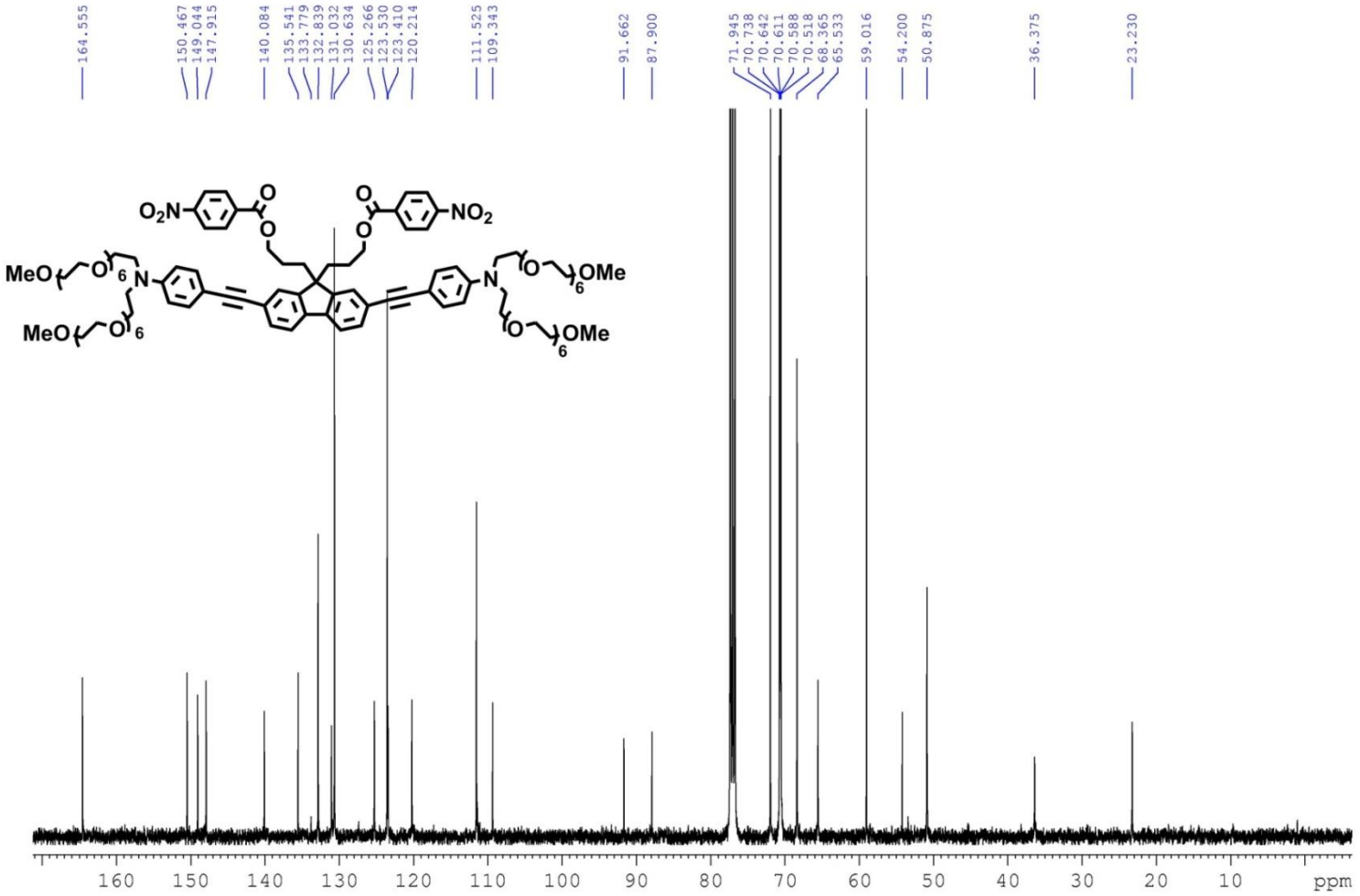



**Figure S10**. $^{13}C$ NMR spectrum of compound **BEF-NB** (200 MHz, $CDCl_3$, 298 K).

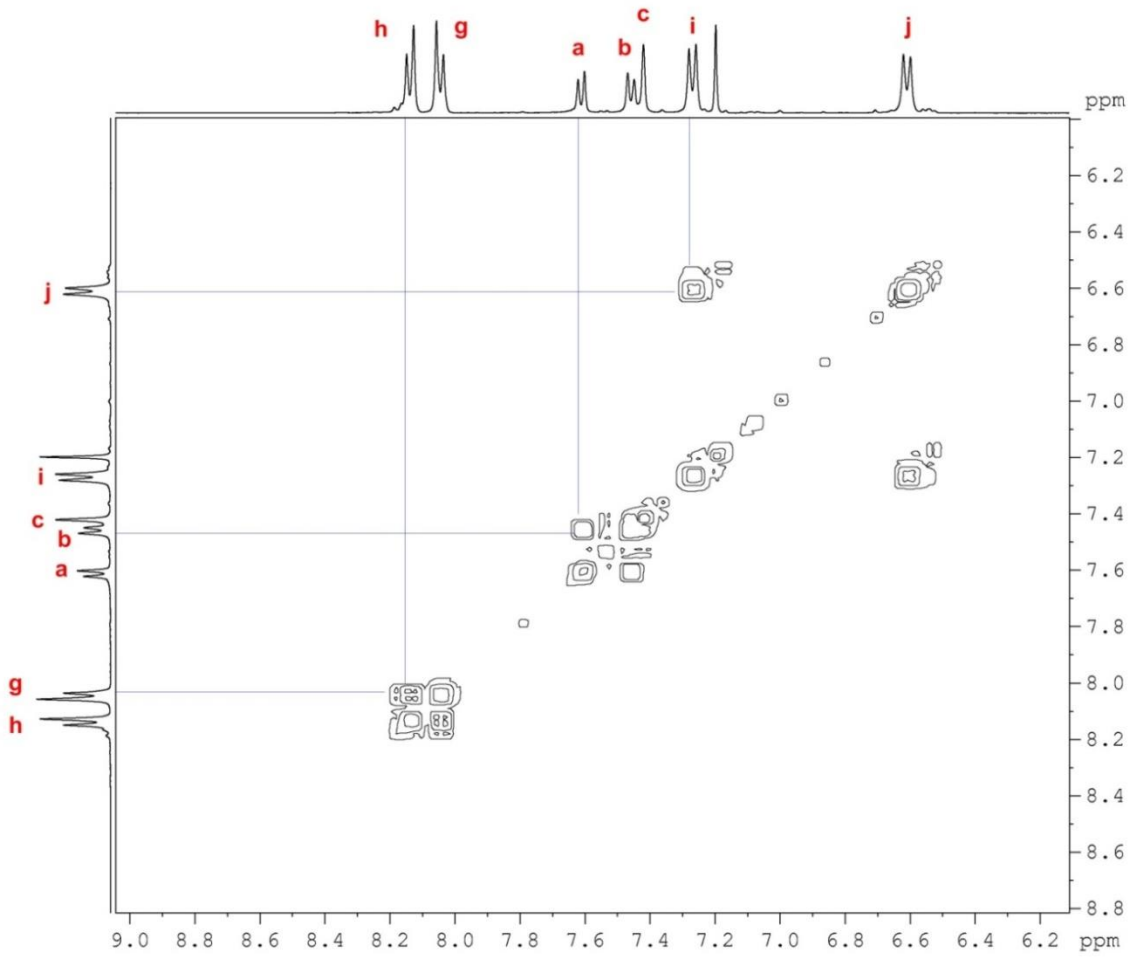



**Figure S11**. Part of the $^{1}$H-$^{1}$H COSY spectrum showing coupling between the fluorene core protons (**a**, **b**), *p*-nitrobenzoate protons (**g**, **h**) and aniline unit protons (**i**, **j**) in **BEF-NB** (400 MHz, $CDCl_3$, 298 K).

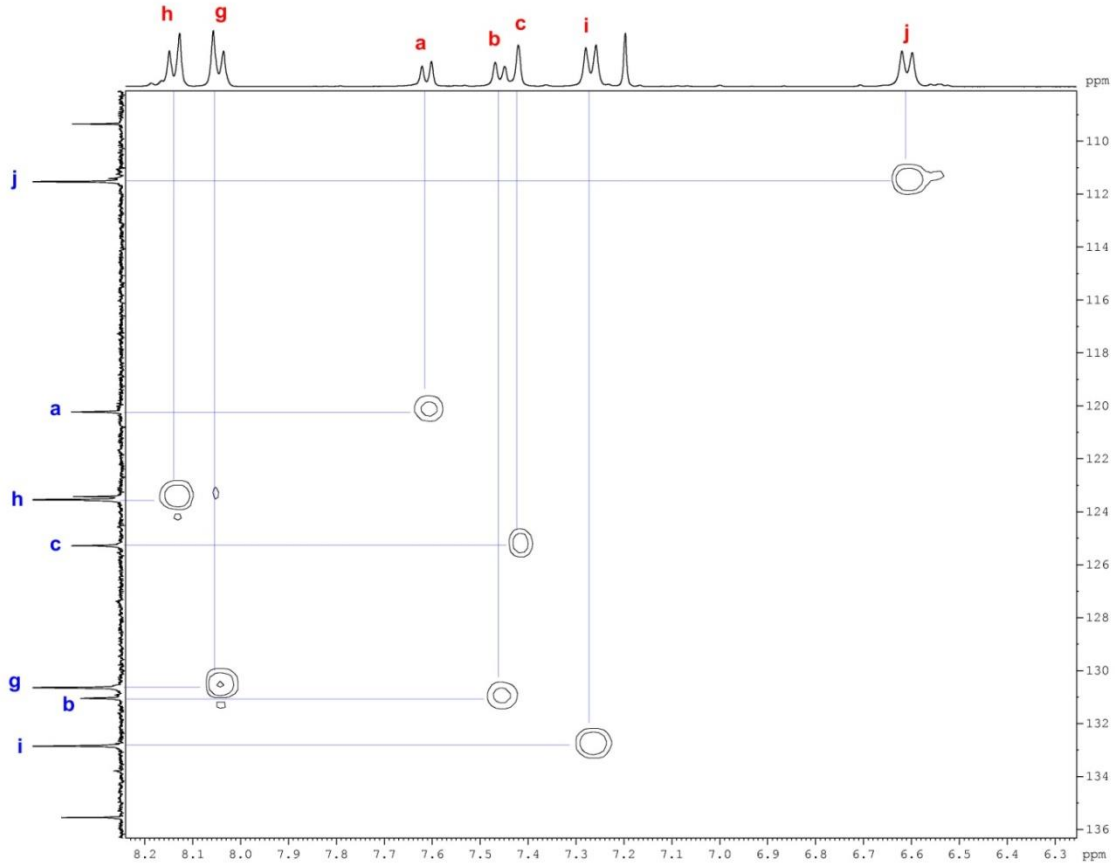



**Figure S12**. Part of the $^{1}H$-$^{13}C$ HSQC spectrum showing one bond H-C correlations between $sp^2$ carbons atoms and fluorene core aromatic protons (**a**, **b, c**), *p*-nitrobenzoate protons (**g**, **h**) and aniline unit protons (**i**, **j**) in **BEF-NB** (400 MHz, $CDCl_3$, 298 K).

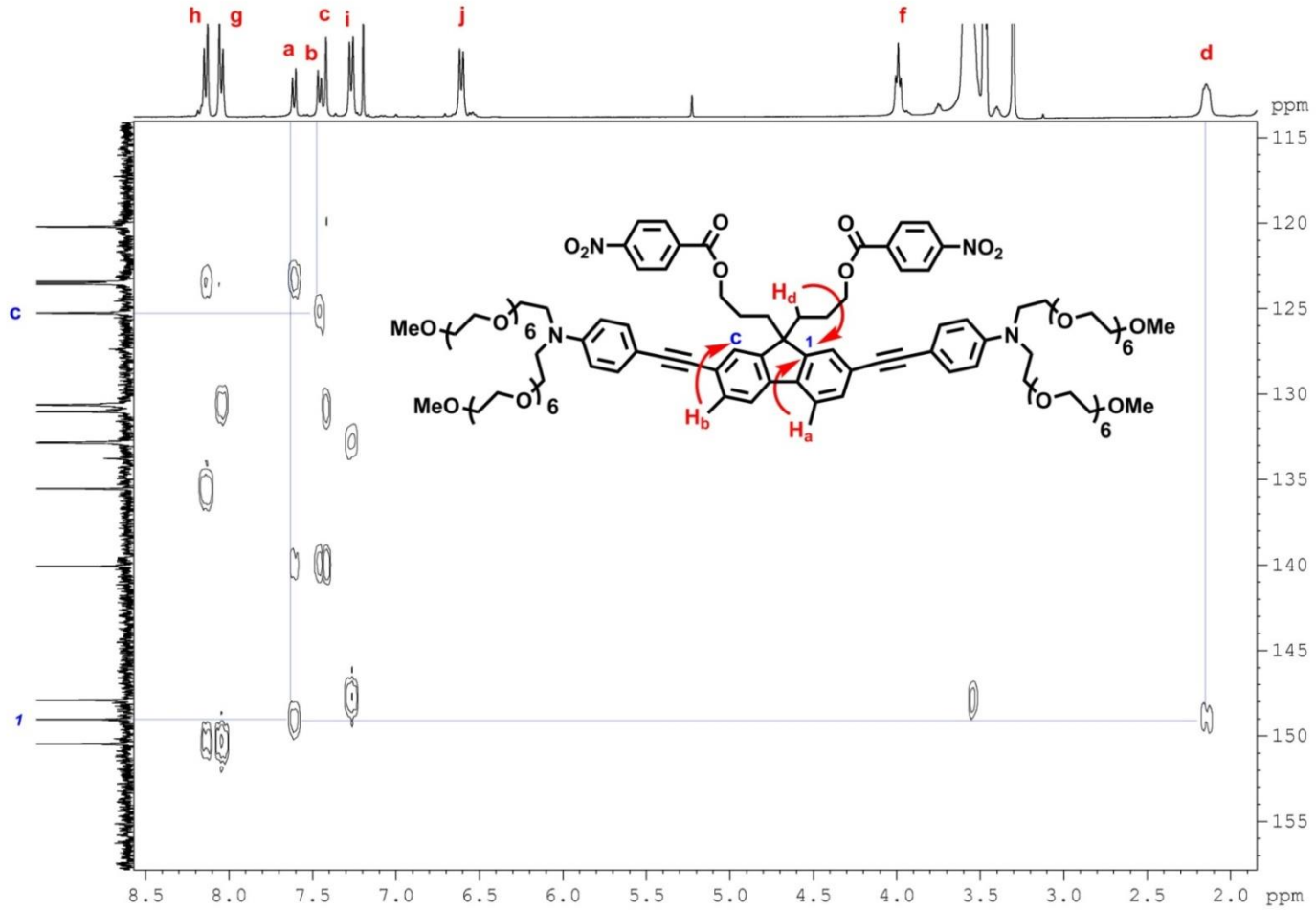



**Figure S13**. Part of the $^{1}$H-$^{13}$C HMBC spectrum showing coupling over three bonds between sp$^{2}$ carbon atom **c** (previously assigned with HSQC spectrum) and fluorene core aromatic proton **b** and coupling over three bonds between aliphatic proton **d** and aromatic proton **a** with sp carbon atom **1** in **BEF-NB** (400 MHz, $CDCl_3$, 298 K).

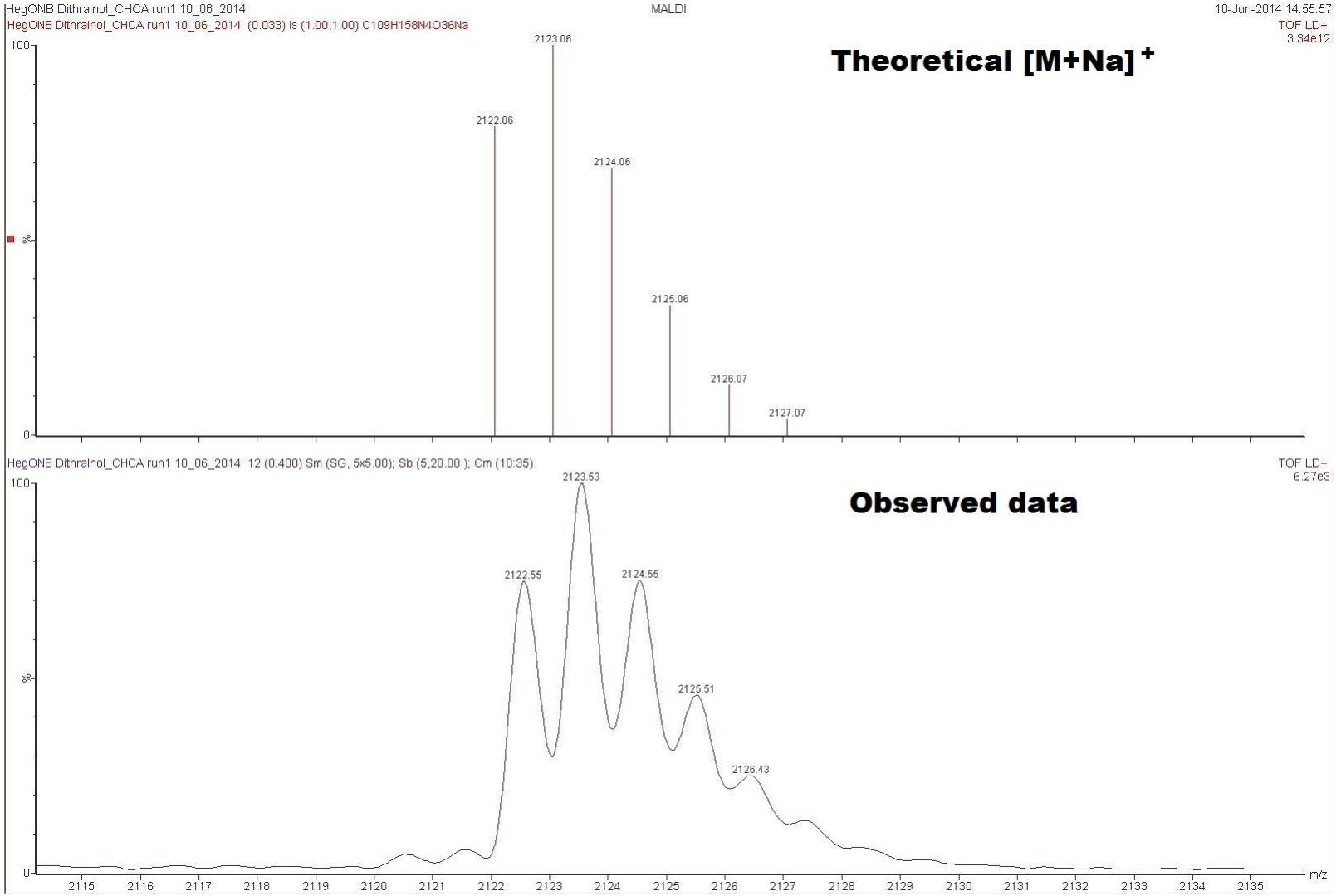



**Figure S14**. MALDI-TOF isotope patterning of [**BEF-NB**+Na]$^+$ *(bottom)* and theoretical pattern calculated for $C_{109}H_{158}N_4O_{36}Na$ *(top)*.

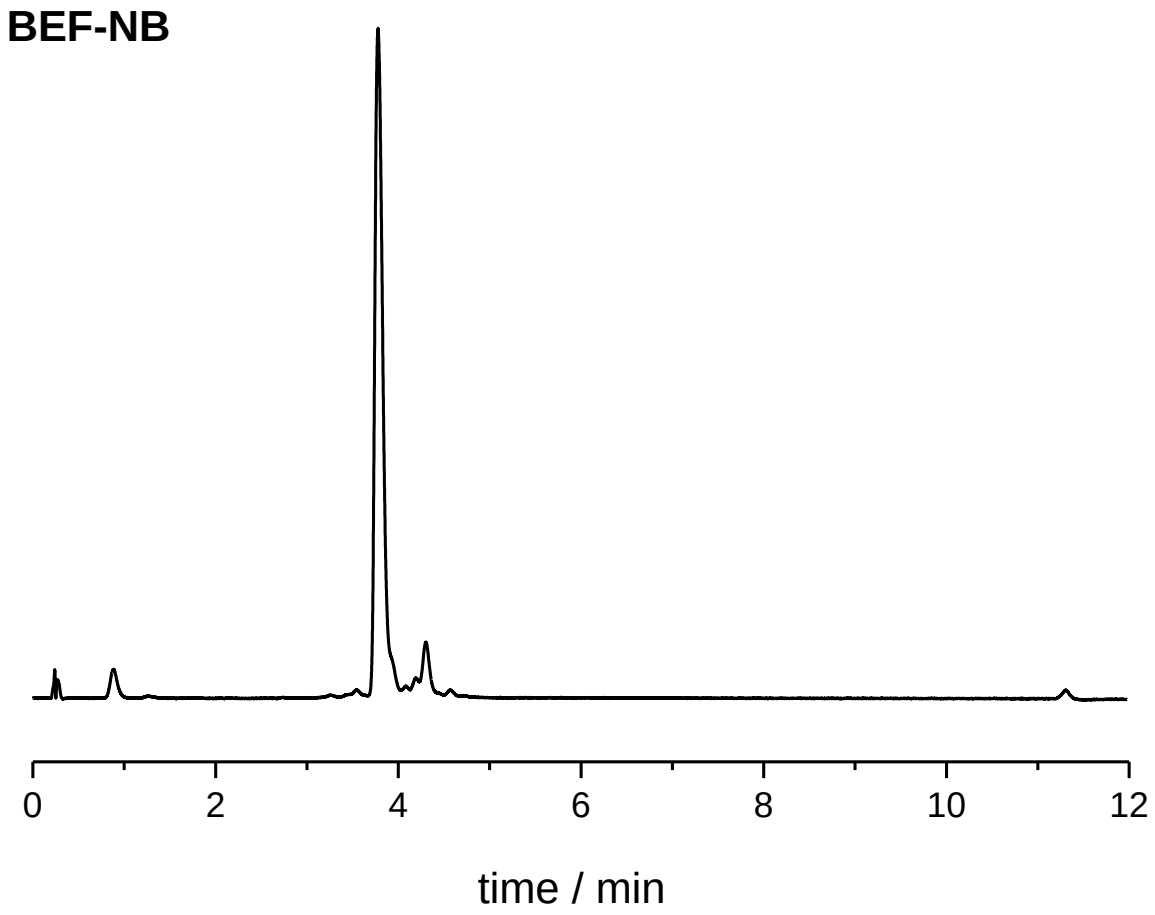



**Figure S15**. HPLC chromatogram of **BEF-NB**, absorption recorded at 375 nm, *HPLC method 2*.

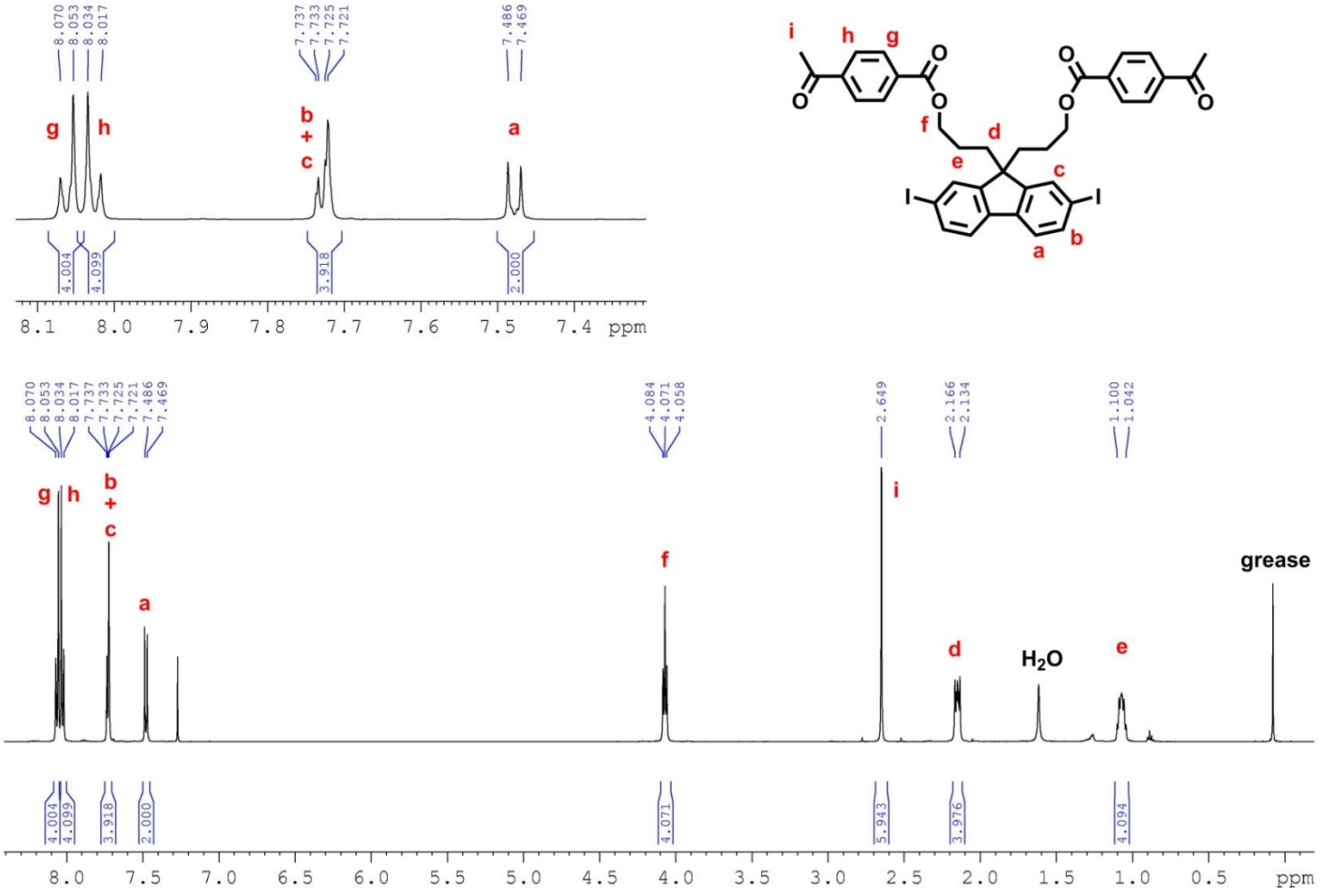



**Figure S16**. $^{1}$H NMR spectrum of compound **4** with zoom on the aromatic region (400 MHz, $CDCl_3$, 298 K).

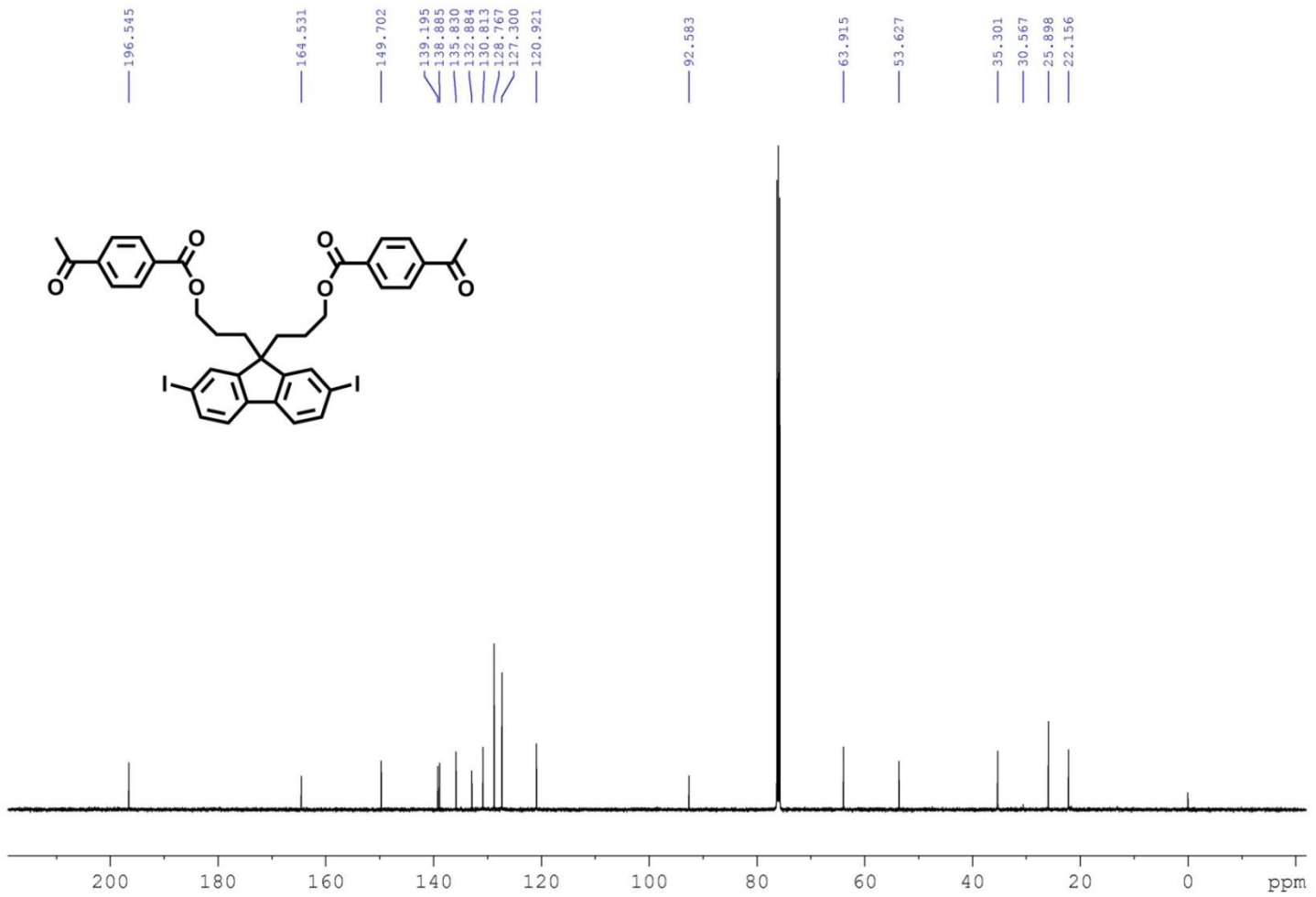



**Figure S17**. $^{13}C$ NMR spectrum of compound **4** (200 MHz, $CDCl_3$, 298 K).

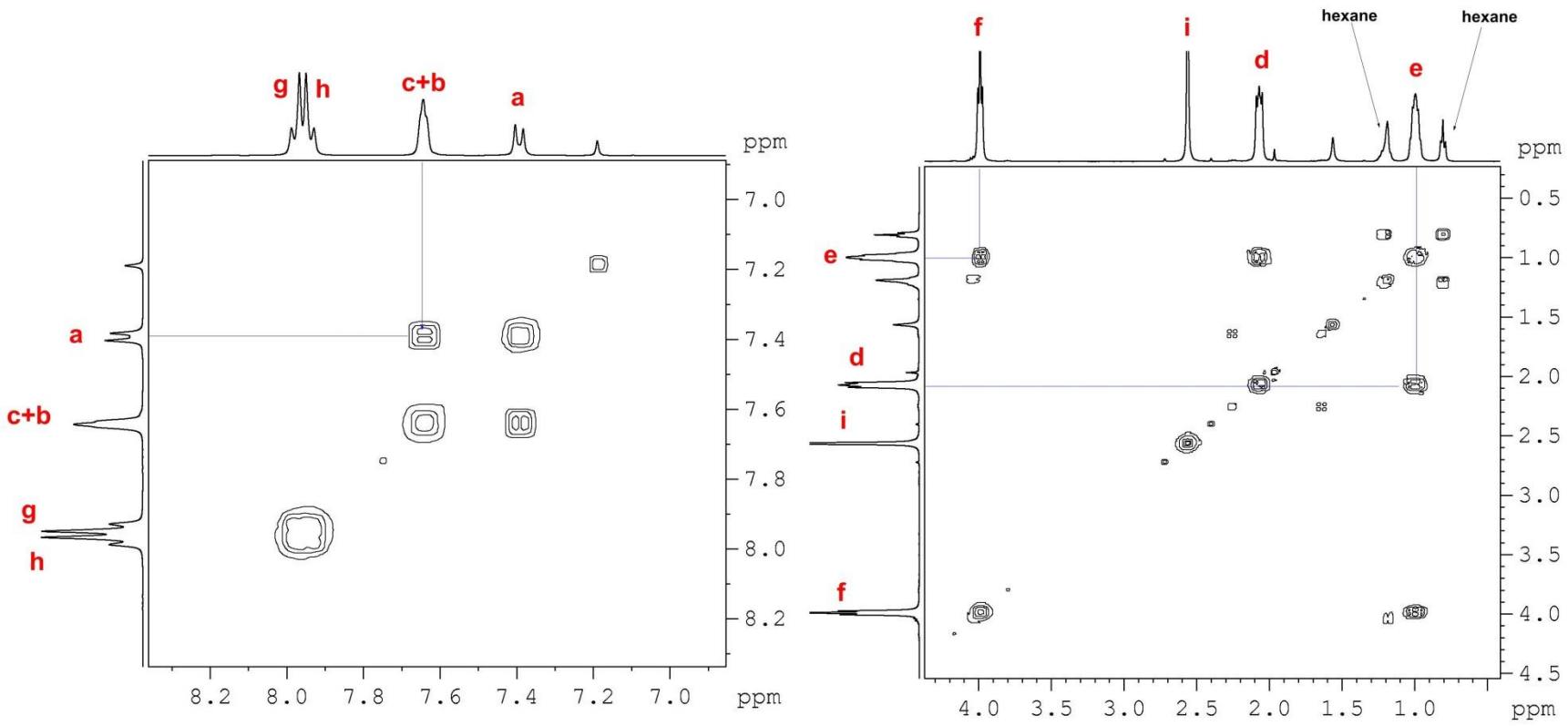



**Figure S18**. Part of the $^{1}$H-$^{1}$H COSY spectrum showing coupling between the fluorene core protons (**a**, **b**), phenacyl protons (**g**, **h**) and aliphatic protons (**d**, **e**, **f**) in compound **4** (400 MHz, $CDCl_3$, 298 K).

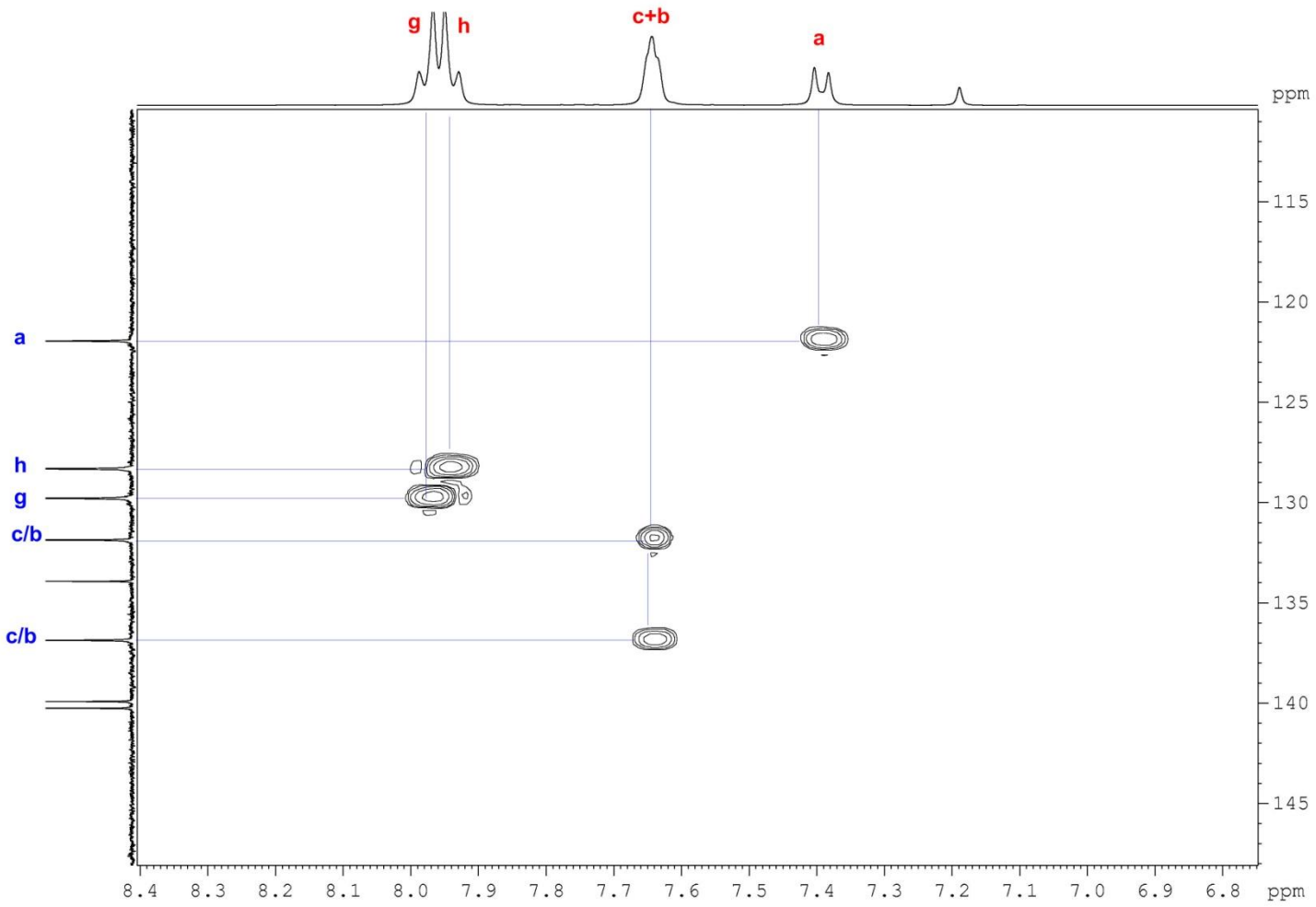



**Figure S19**. Part of the $^{1}$H-$^{13}$C HSQC spectrum showing one bond H-C correlations between sp$^{2}$ carbons atoms and the fluorene core aromatic protons (**a**, **b, c**) and phenacyl protons (**g**, **h**) in compound **4** (400 MHz, $CDCl_3$, 298 K).

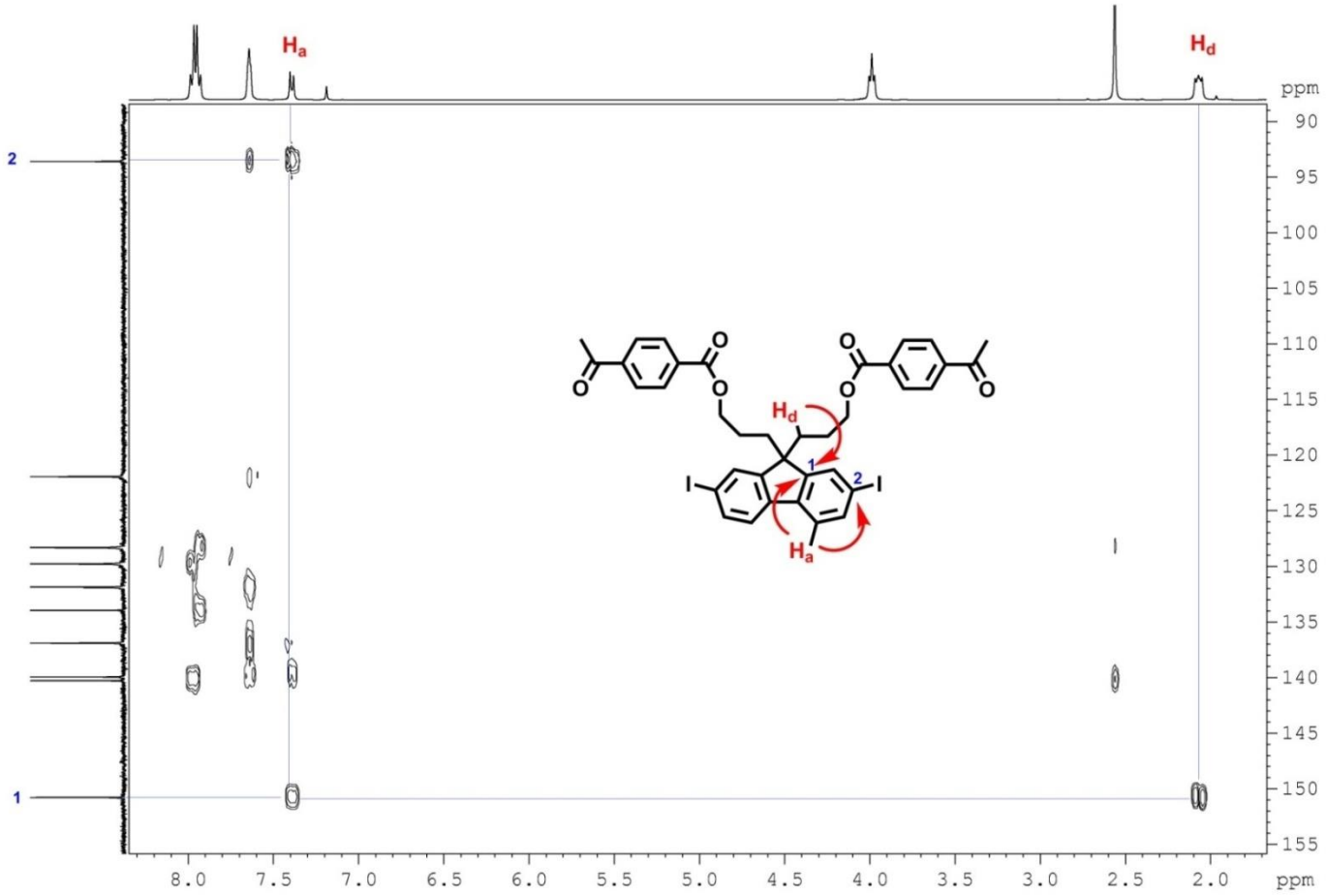



**Figure S20**. Part of the $^{1}H$-$^{13}C$ HMBC spectrum showing coupling over three bonds between sp carbon atom **2** and fluorene core aromatic proton **a** and coupling over three bonds between aliphatic proton **d** and aromatic proton **a** with sp carbon atom **1** in compound **4** (400 MHz, $CDCl_3$, 298 K).

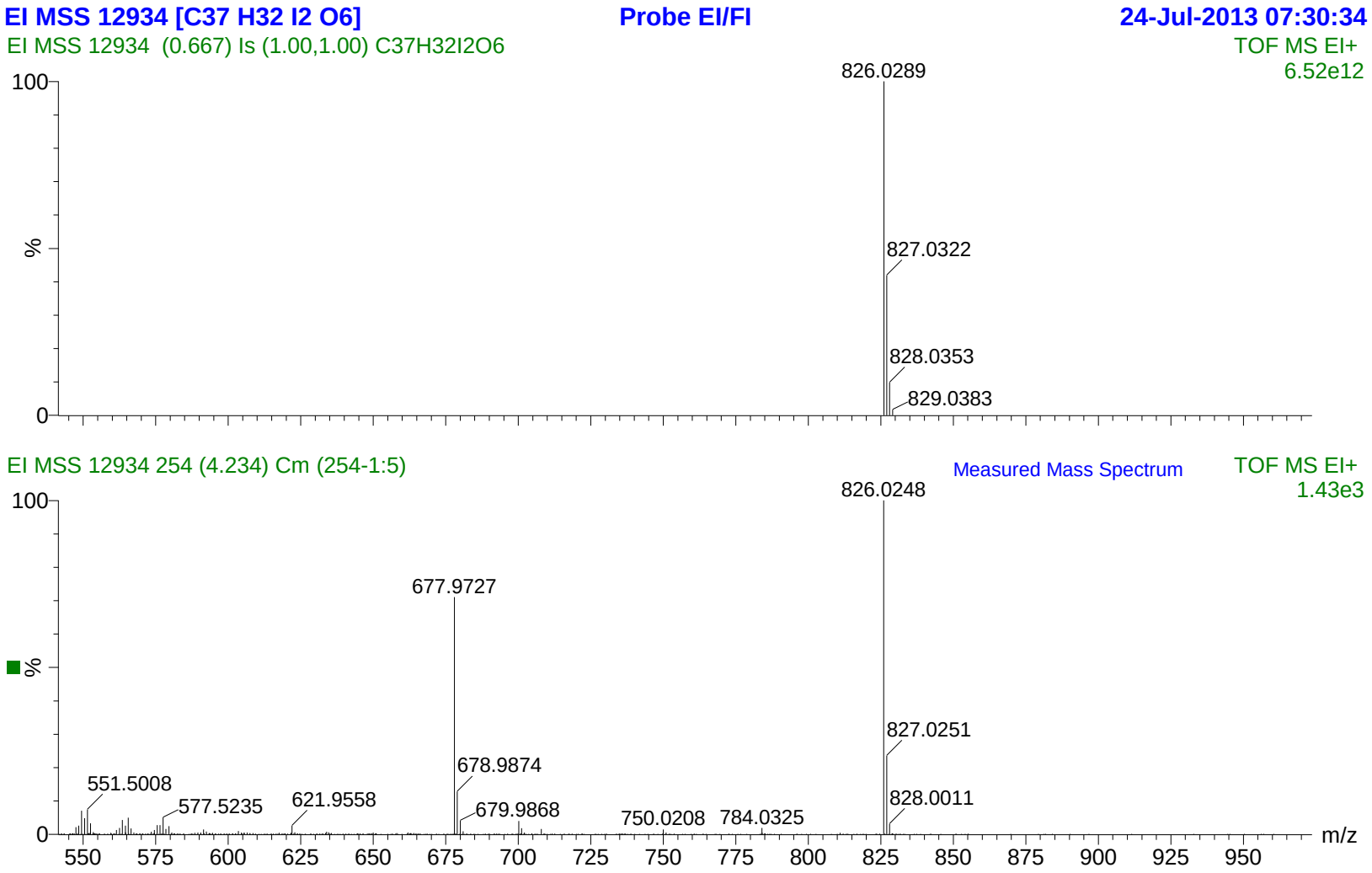



**Figure S21**. EI+ mass spectrum of compound **4** (bottom) and theoretical isotopic pattern calculated for $C_{37}H_{32}I_2O_6$ is 826.02

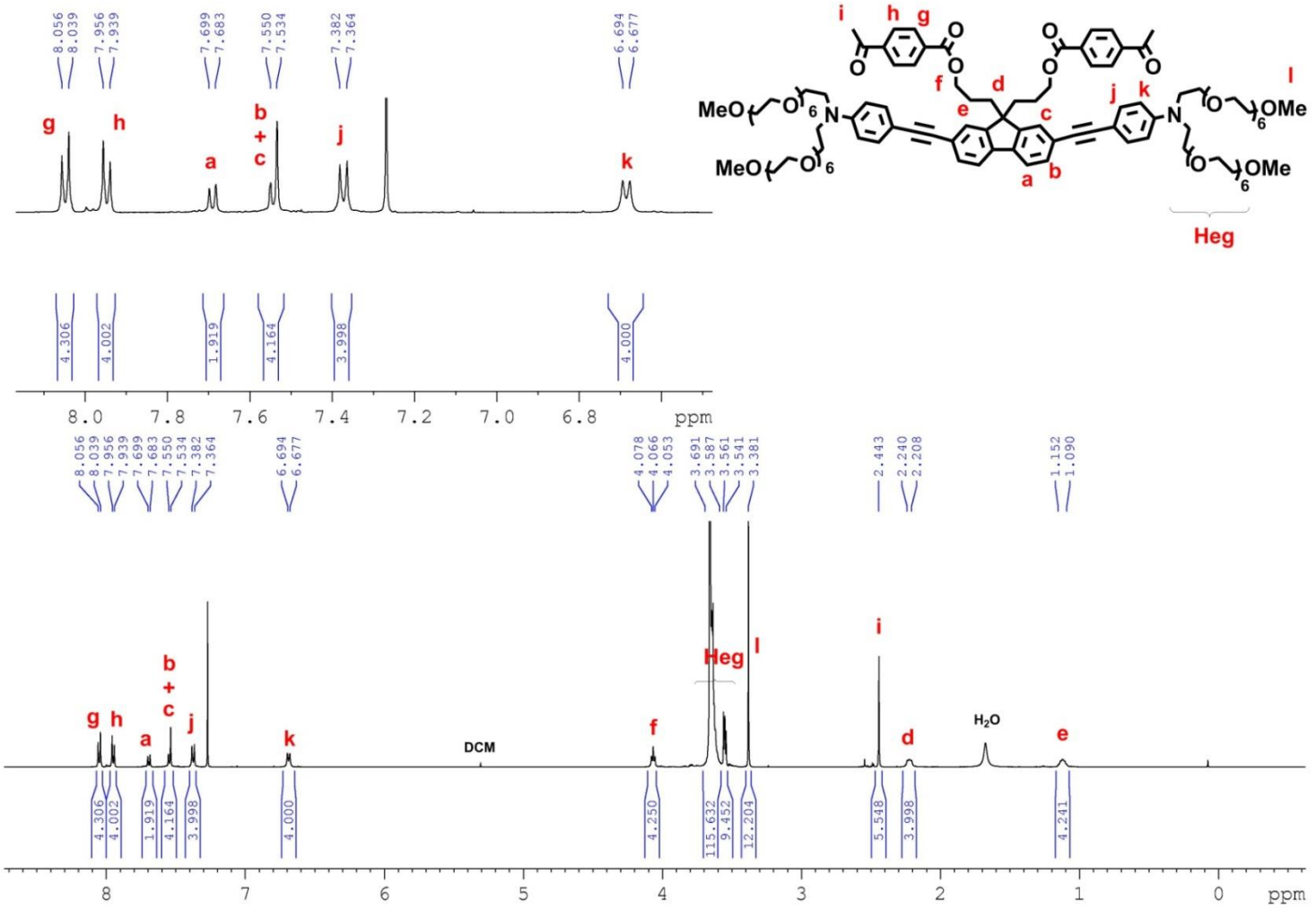



**Figure S22**. $^{1}$H NMR spectrum of **BEF-Phen** with zoom on the aromatic region (500 MHz, $CDCl_3$, 298 K).

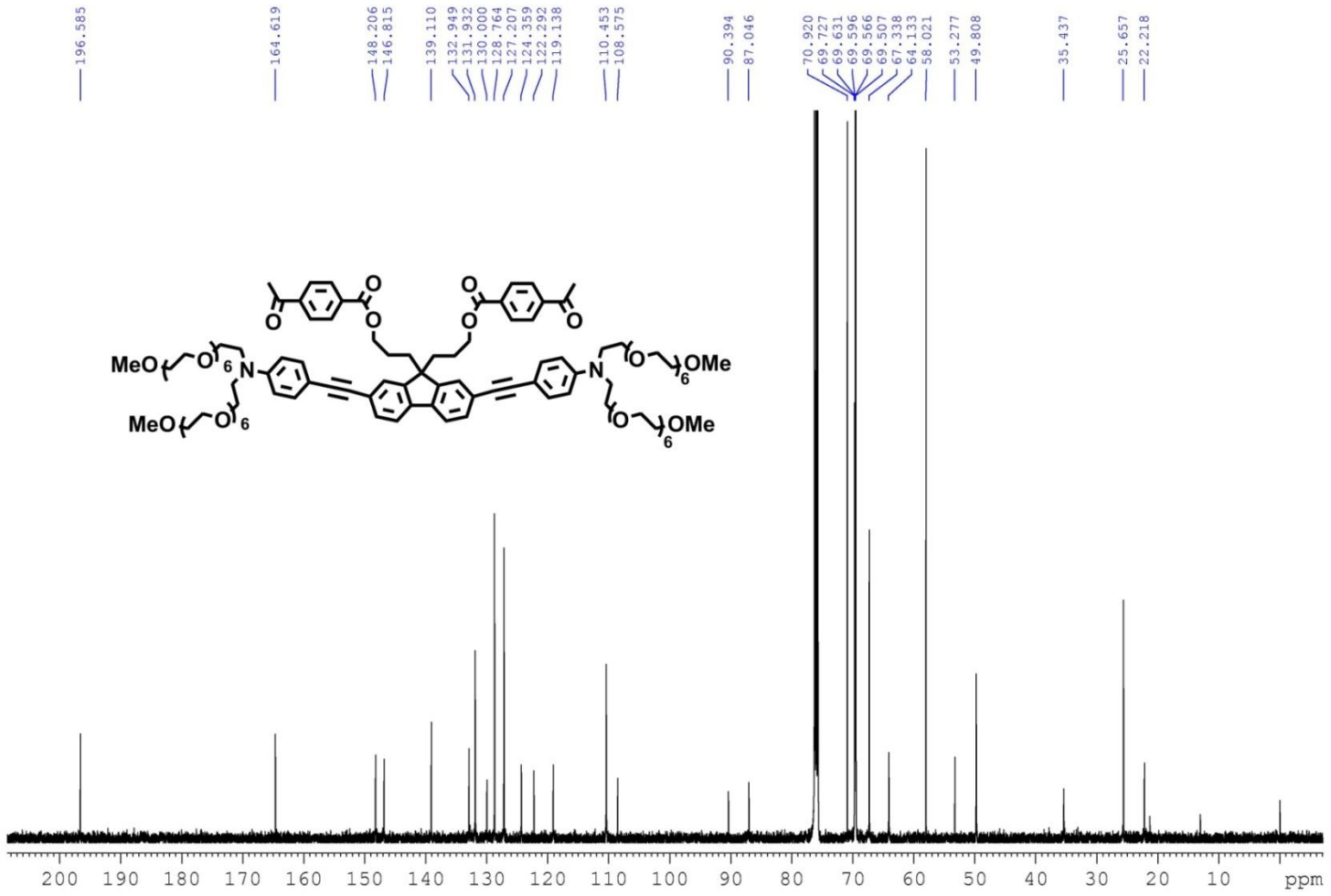



**Figure S23**. $^{13}C$ NMR spectrum of **BEF-Phen** (250 MHz, $CDCl_3$, 298 K).

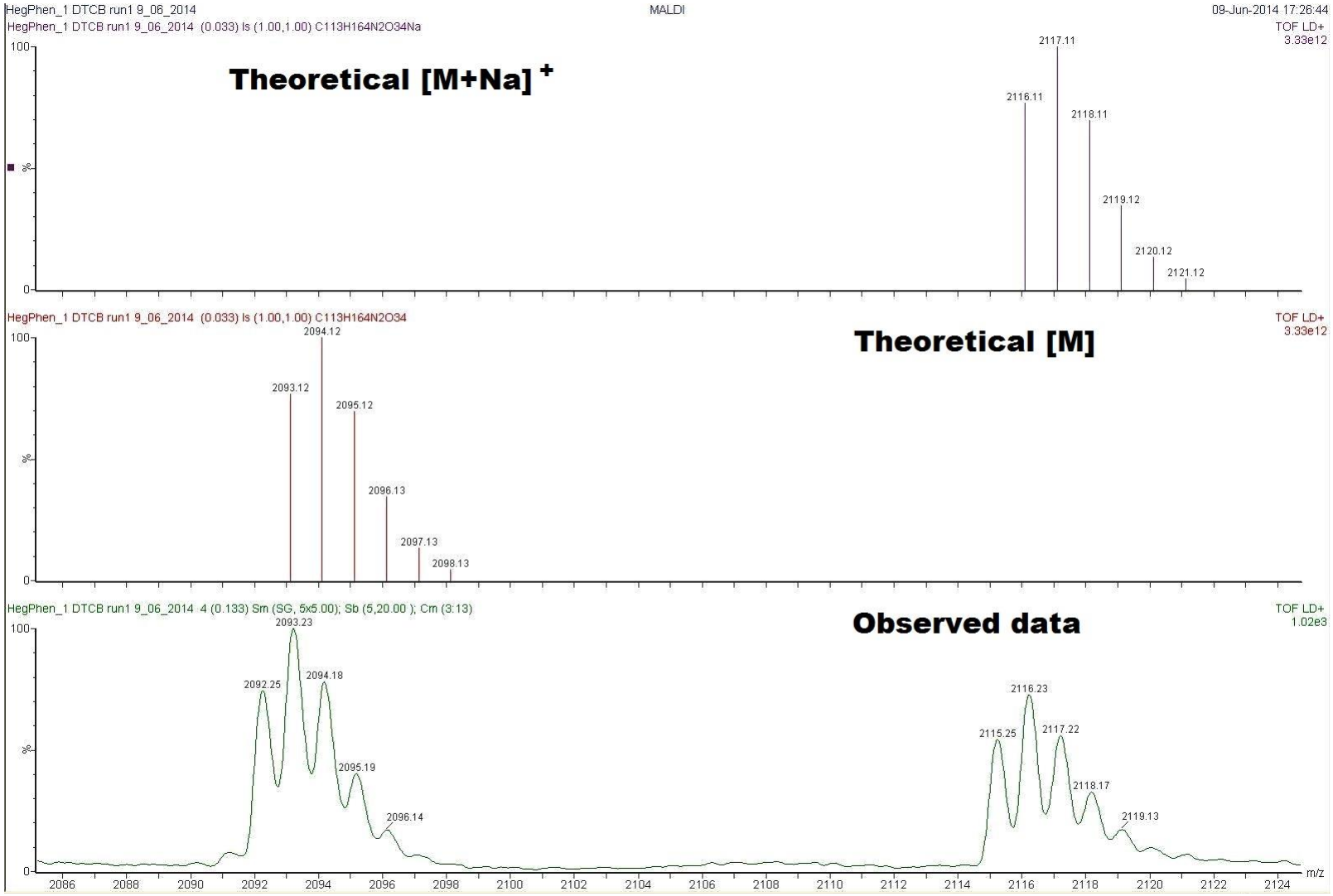



**Figure S24**. MALDI-TOF isotope patterning of [**BEF-NB**] and [**BEF-NB**+Na]$^+$ *(bottom)* and theoretical pattern calculated for $C_{113}H_{164}N_4O_{34}$ *(middle)* and $C_{113}H_{164}N_4O_{34}Na$ *(top).*

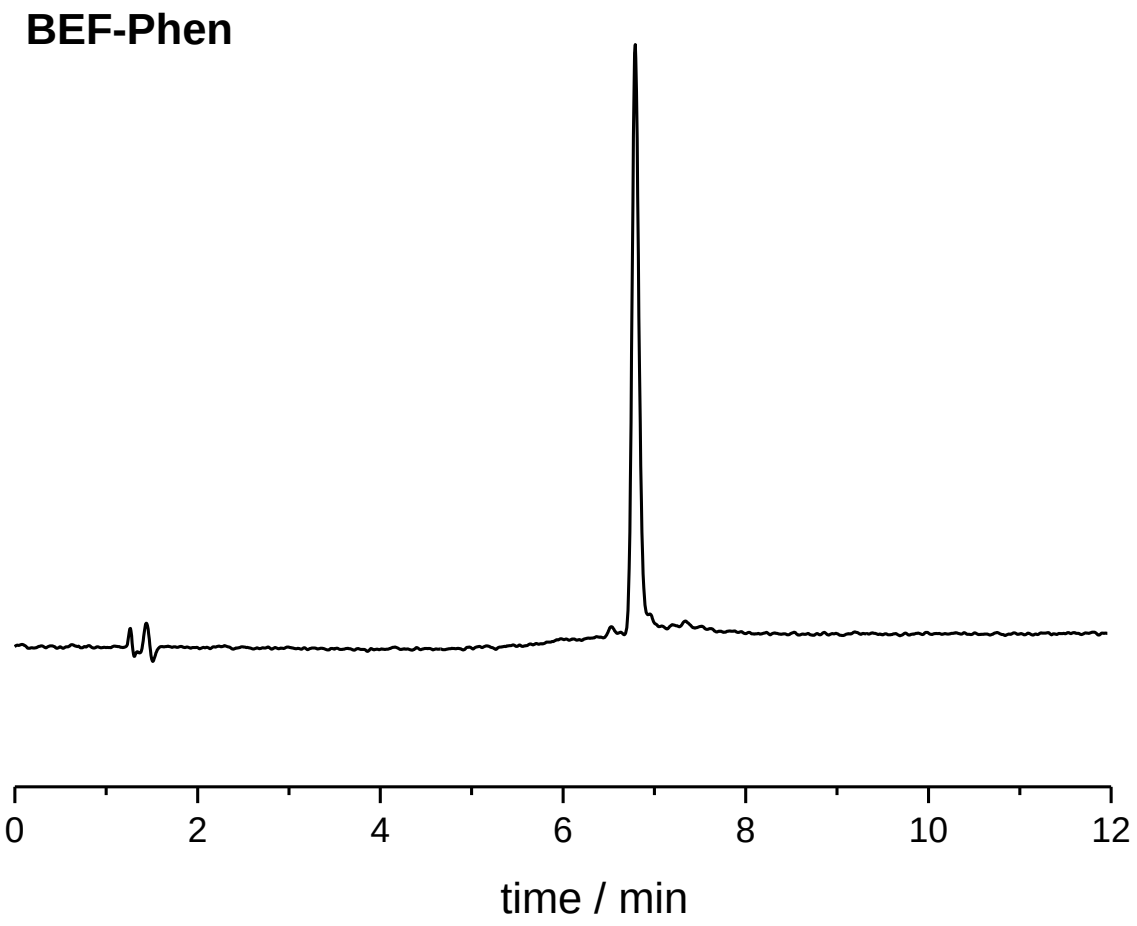



**Figure S25**. HPLC chromatogram of **BEF-Phen**, absorption recorded at 375 nm, *HPLC method 2*.

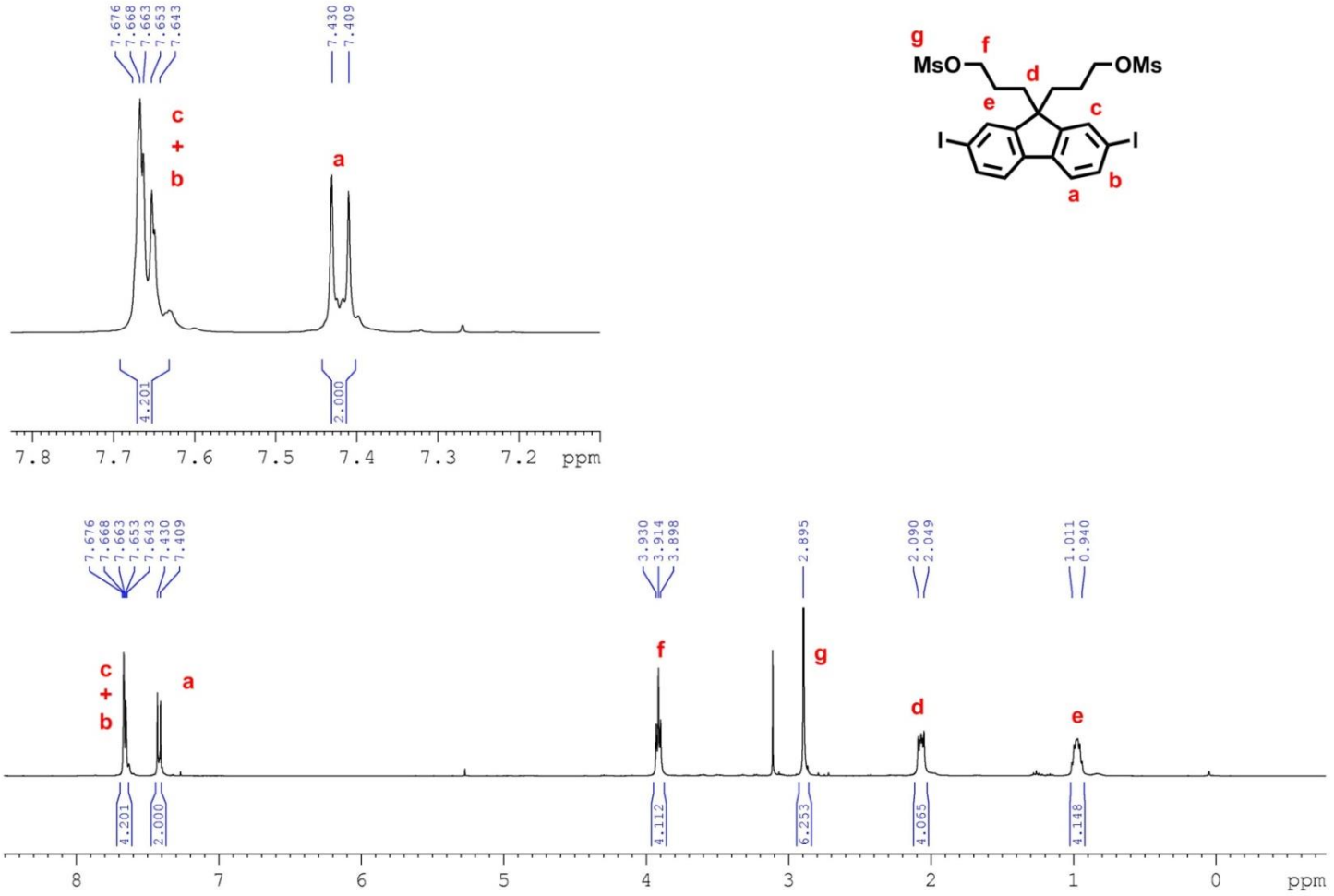



**Figure S26**. $^{1}$H NMR spectrum of compound **5** with zoom on the aromatic region (400 MHz, $CDCl_3$, 298 K).

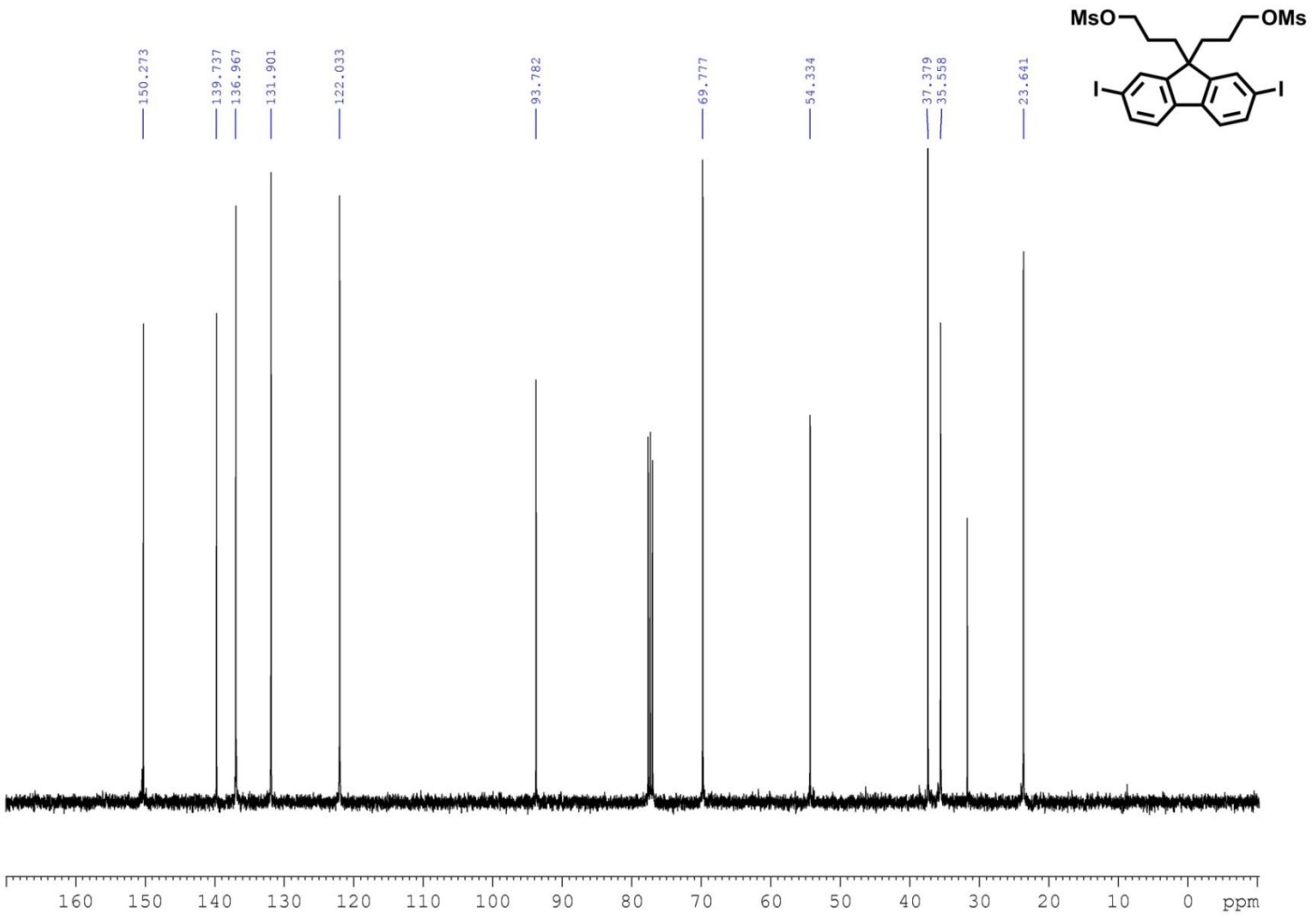



**Figure S27**. $^{13}C$ NMR spectrum of compound **5** (200 MHz, $CDCl_3$, 298 K).

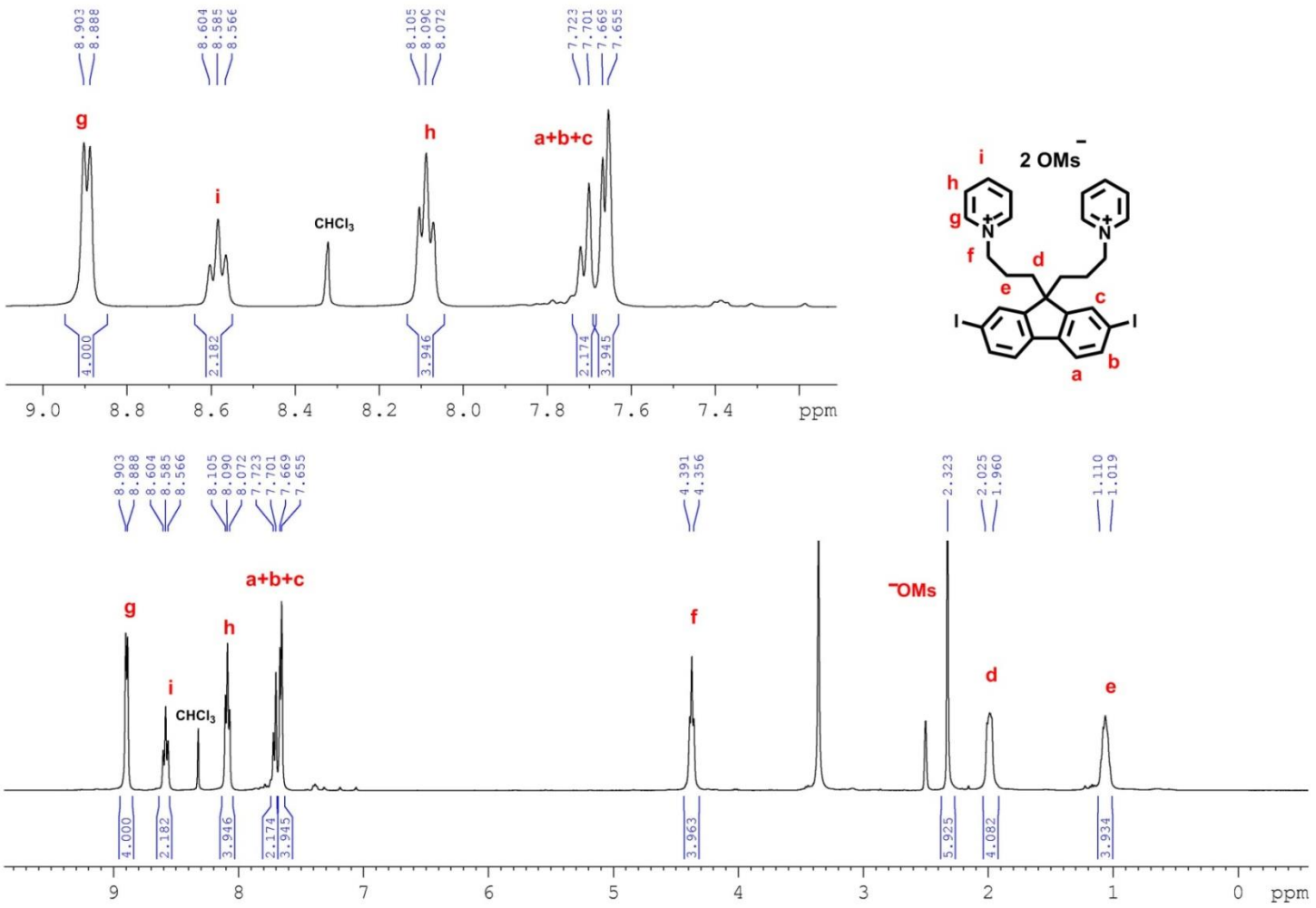



**Figure S28**. [1]H NMR spectrum of compound **6** with zoom on the aromatic region (400 MHz, DMSO-$d_6$, 298 K).

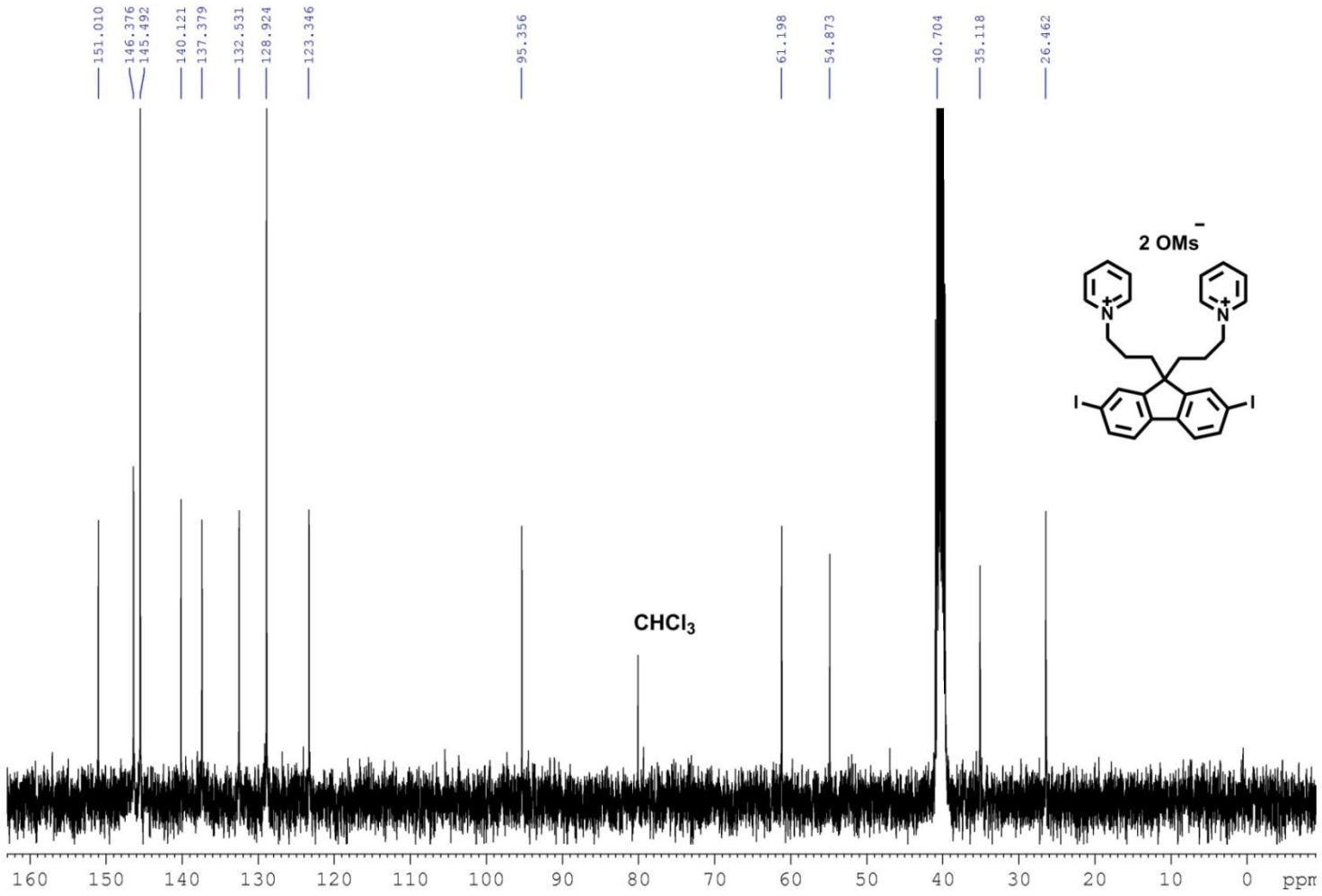



**Figure S29**. $^{13}$C NMR spectrum of compound **6** (200 MHz, DMSO-$d_6$, 298 K).

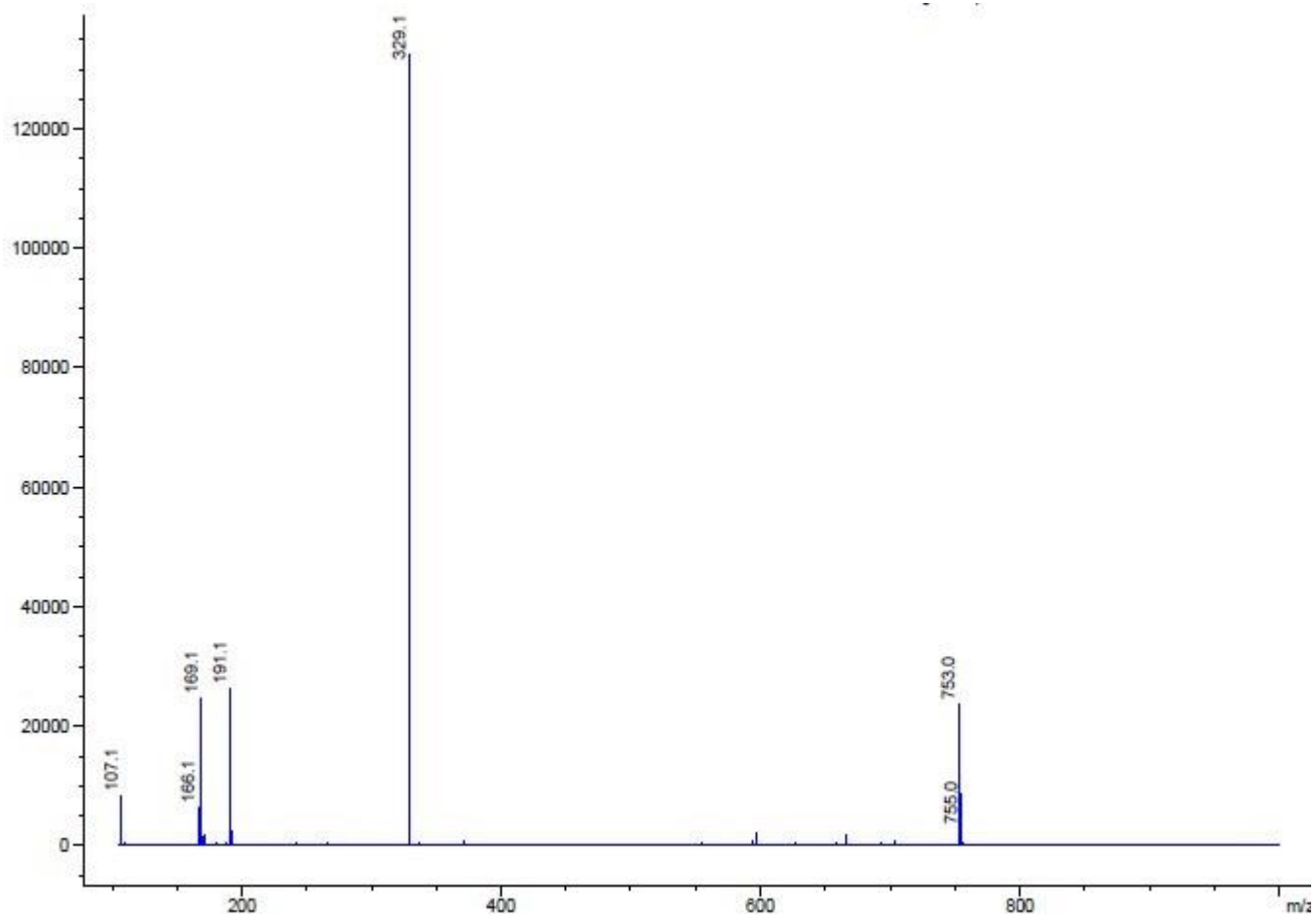



**Figure S30**. ESI+ mass spectrum of compound **6**. Theoretical mass calculated for $[M]^{2+}$ $C_{29}H_{28}I_2N_2$ is 329.0

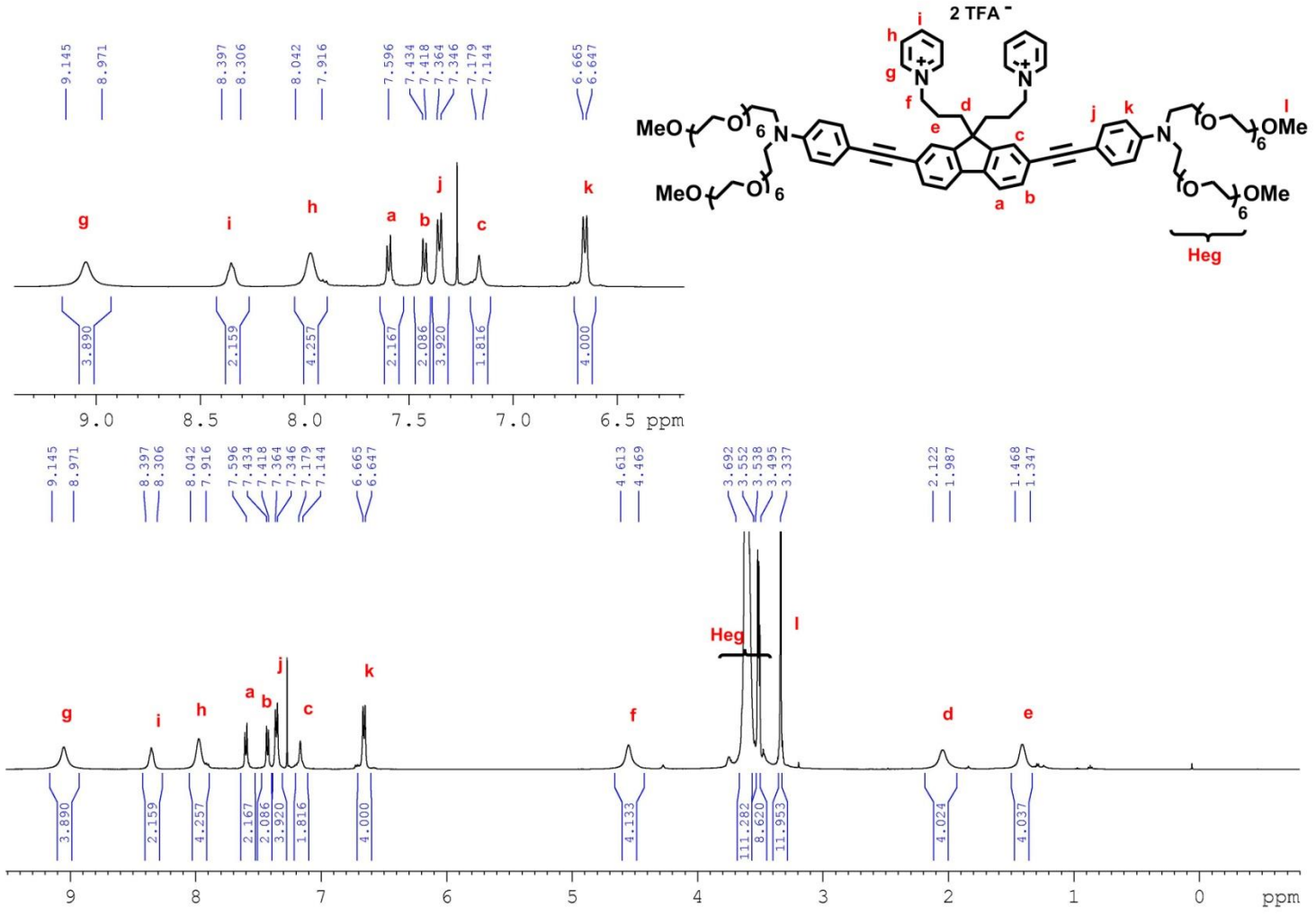



**Figure S31**. $^{1}$H NMR spectrum of **BEF-Pyr** with zoom on the aromatic region (500 MHz, $CDCl_3$, 298 K).

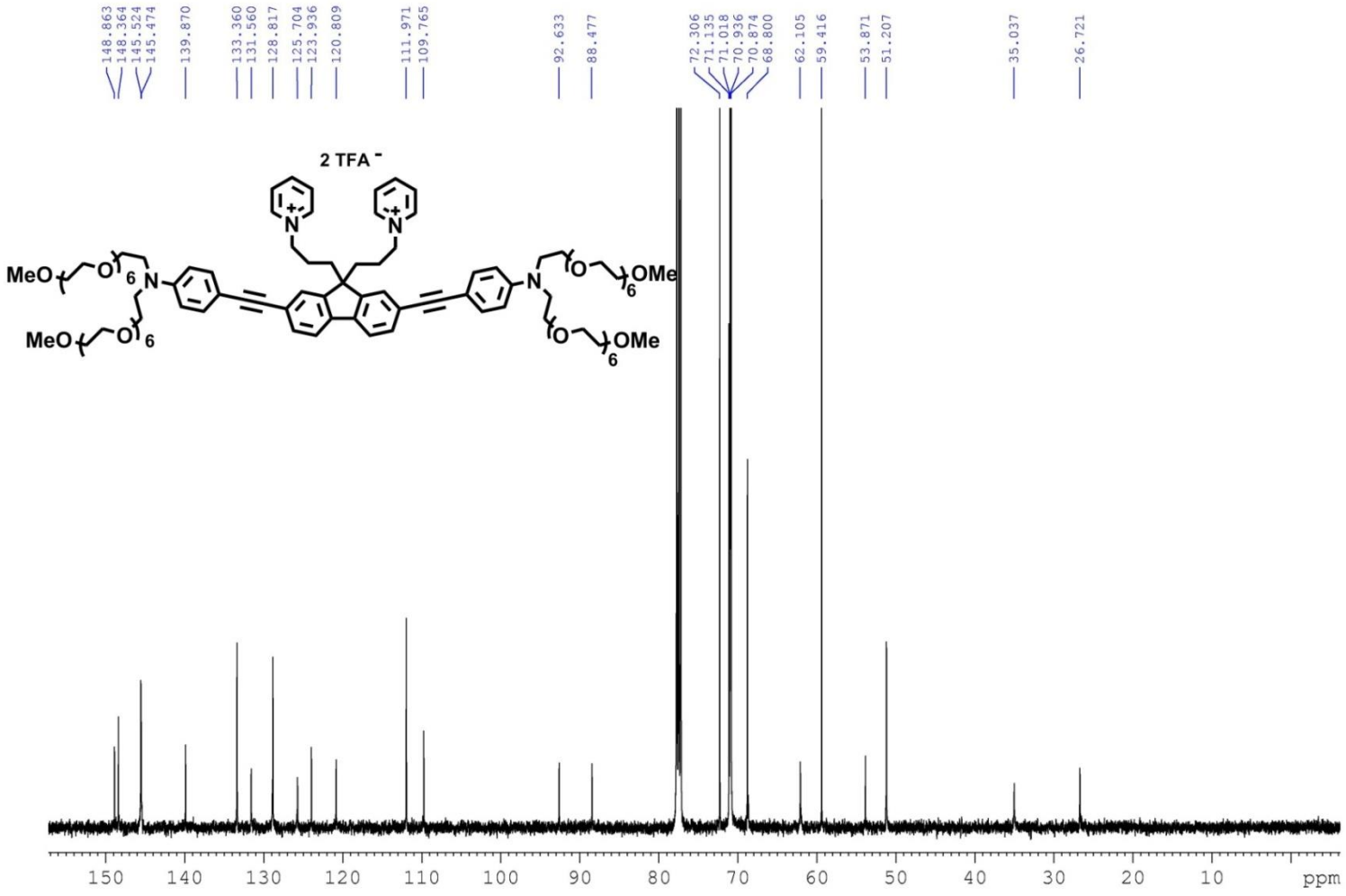



**Figure S32**. $^{13}C$ NMR spectrum of **BEF-Pyr** (250 MHz, $CDCl_3$, 298 K).

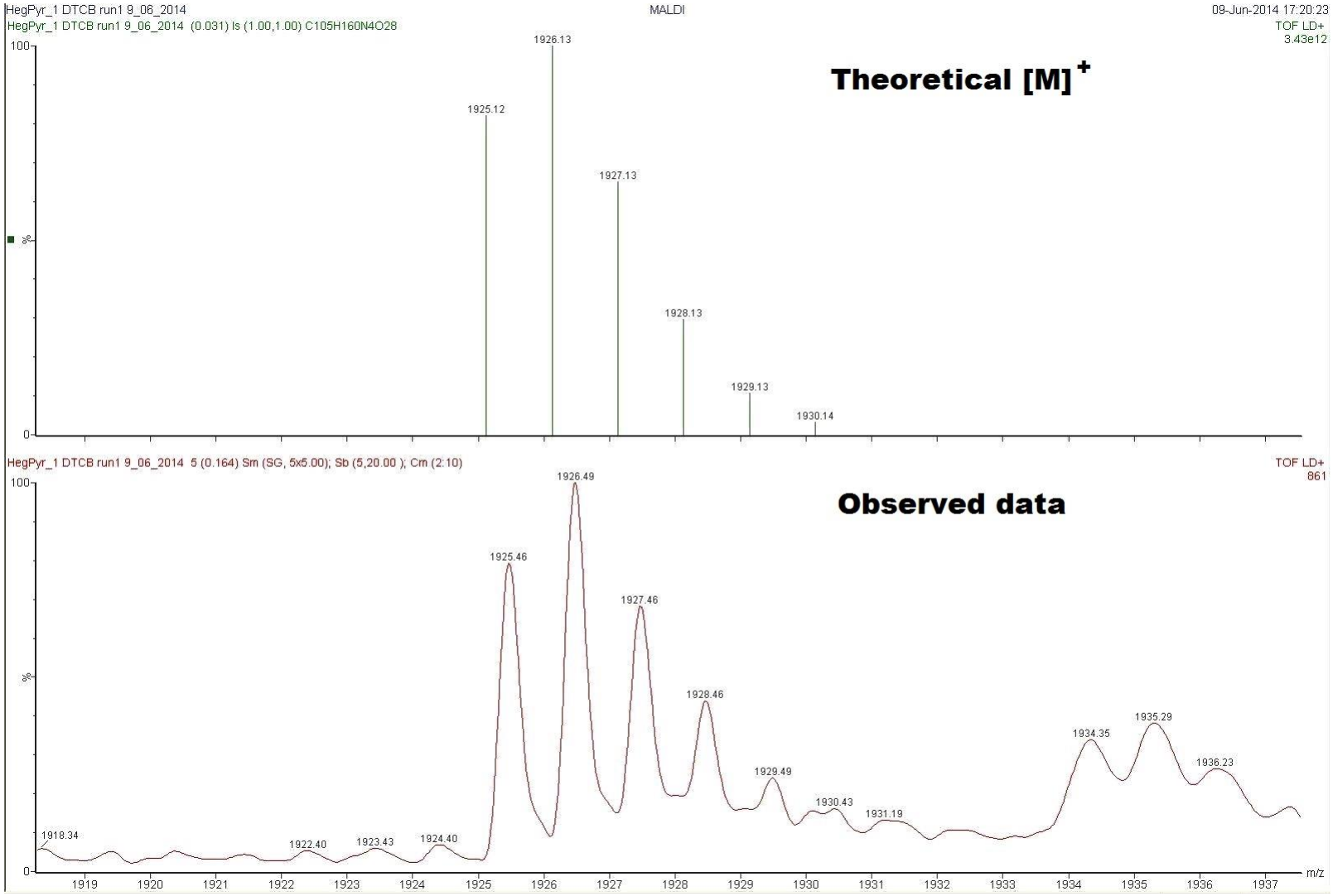



**Figure S33**. MALDI-TOF isotope patterning of [**BEF-Pyr**]$^{+}$ *(bottom)* and theoretical pattern calculated for $C_{105}H_{160}N_4O_{28}$ *(top).*

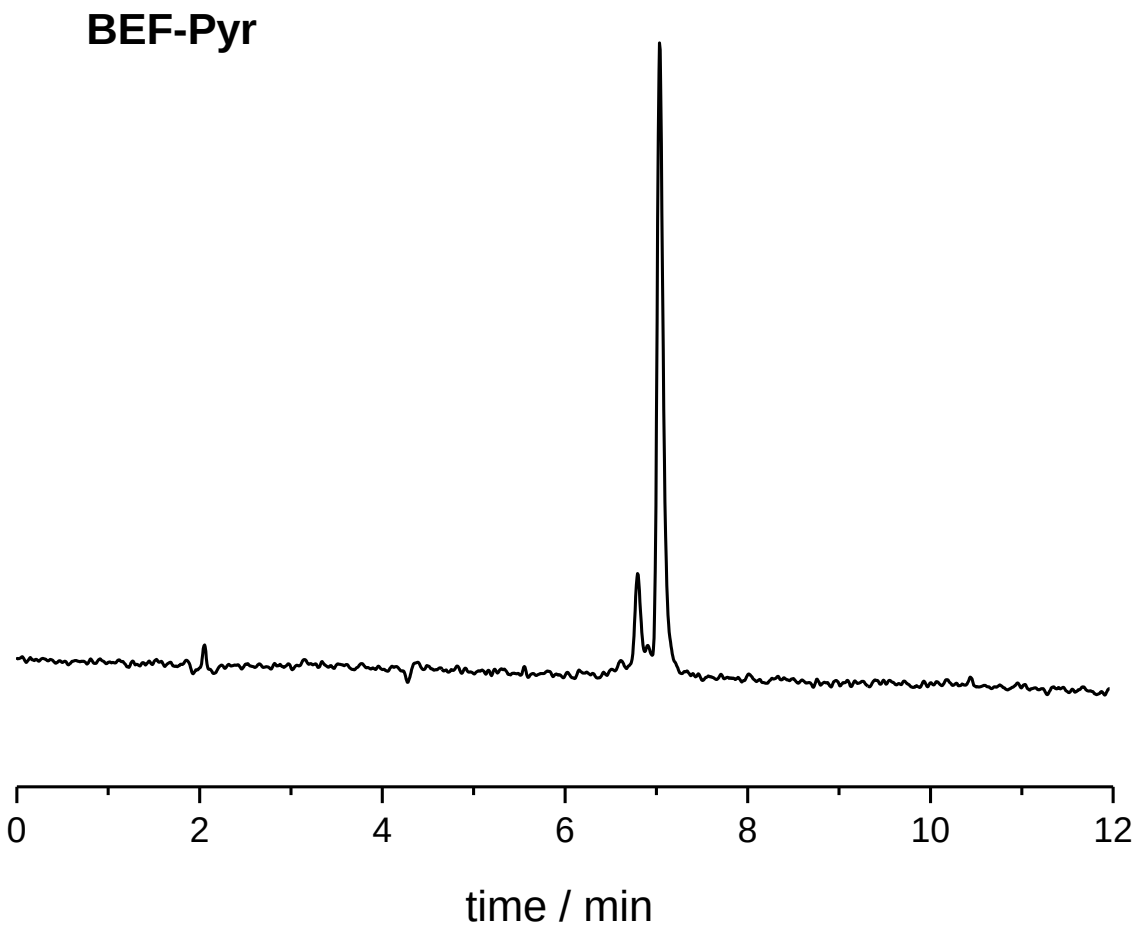



**Figure S34**. HPLC chromatogram of **BEF-Pyr**, absorption recorded at 375 nm, *HPLC method 1*.

## 3. Spectroscopy and photophysics

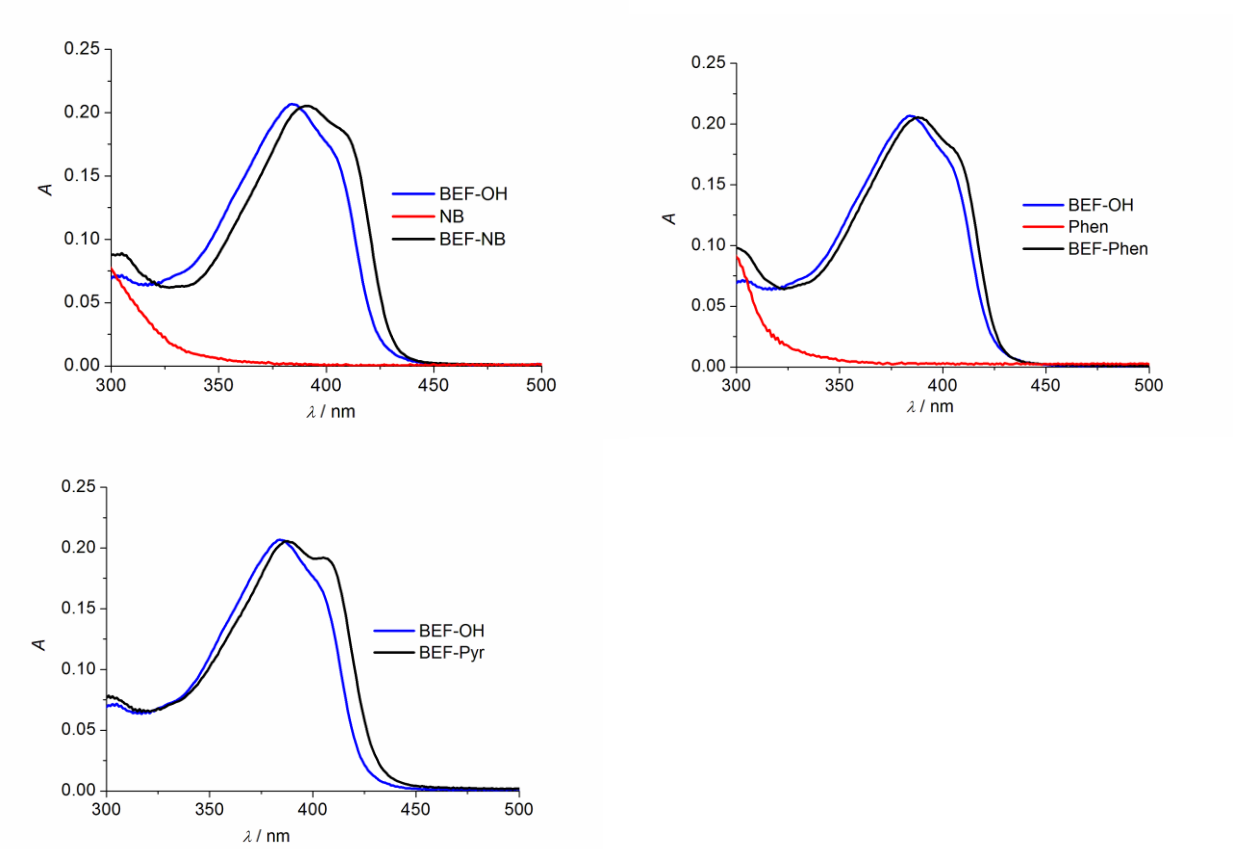



**Figure S35**. Arbitrary scaled absorption spectra of the dyads and models in toluene (TOL) solutions. **Pyr** is not soluble in TOL.

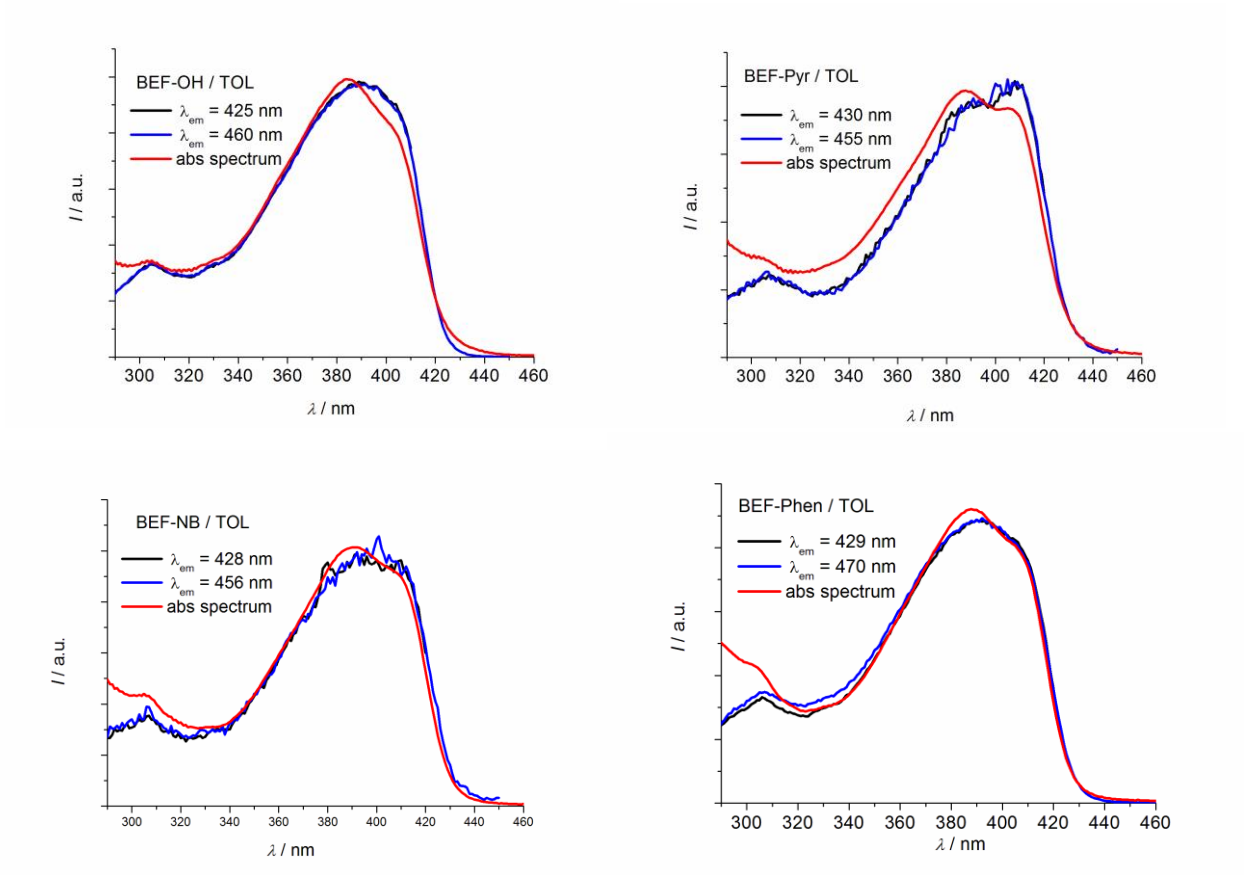



**Figure S36**. Corrected excitation spectra of the fluorene model and dyads in toluene (TOL) overlaying the corresponding absorption spectra.

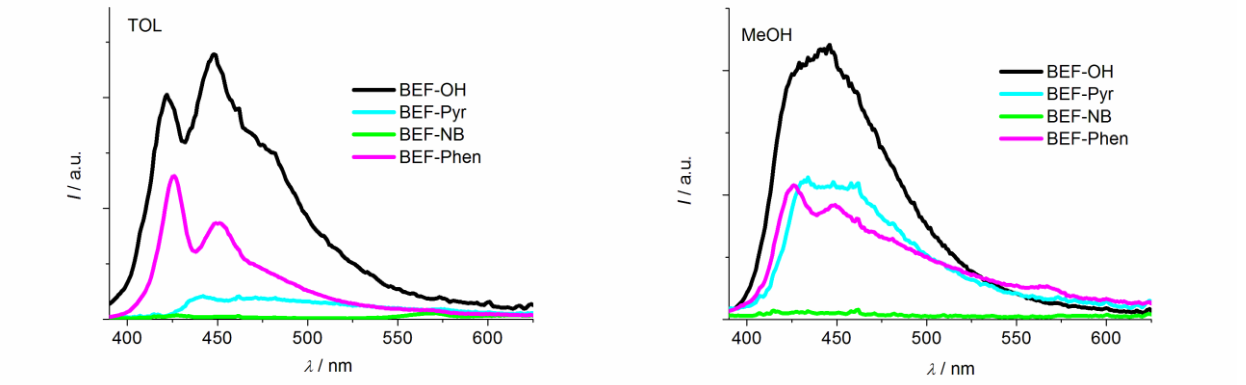



**Figure S37**. Luminescence spectra of the fluorene model and dyads in TOL and MeOH glasses at 77 K, excitation is at 370 nm.

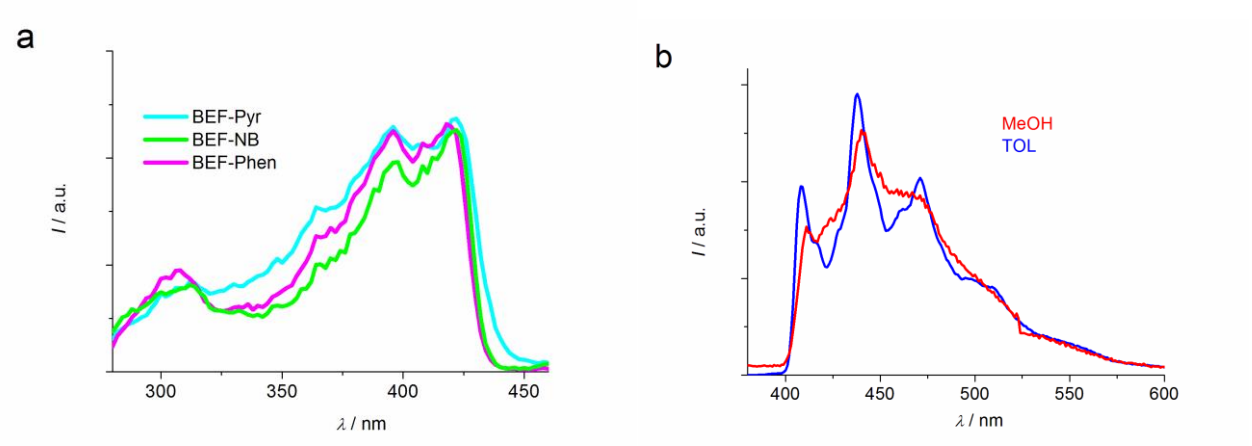



**Figure S38**. a) Arbitrarily scaled corrected excitation spectra measured on the maxima of the phosphorescence of the dyads in TOL at 77 K, (1 ms delay, 4 ms gate), see Figure 5 main text. b) Arbitrarily scaled delayed luminescence (1 ms delay, 4 ms gate) spectra of **Phen** in TOL and MeOH glasses at 77 K. Excitation is at 300 nm in TOL and 270 nm in MeOH.

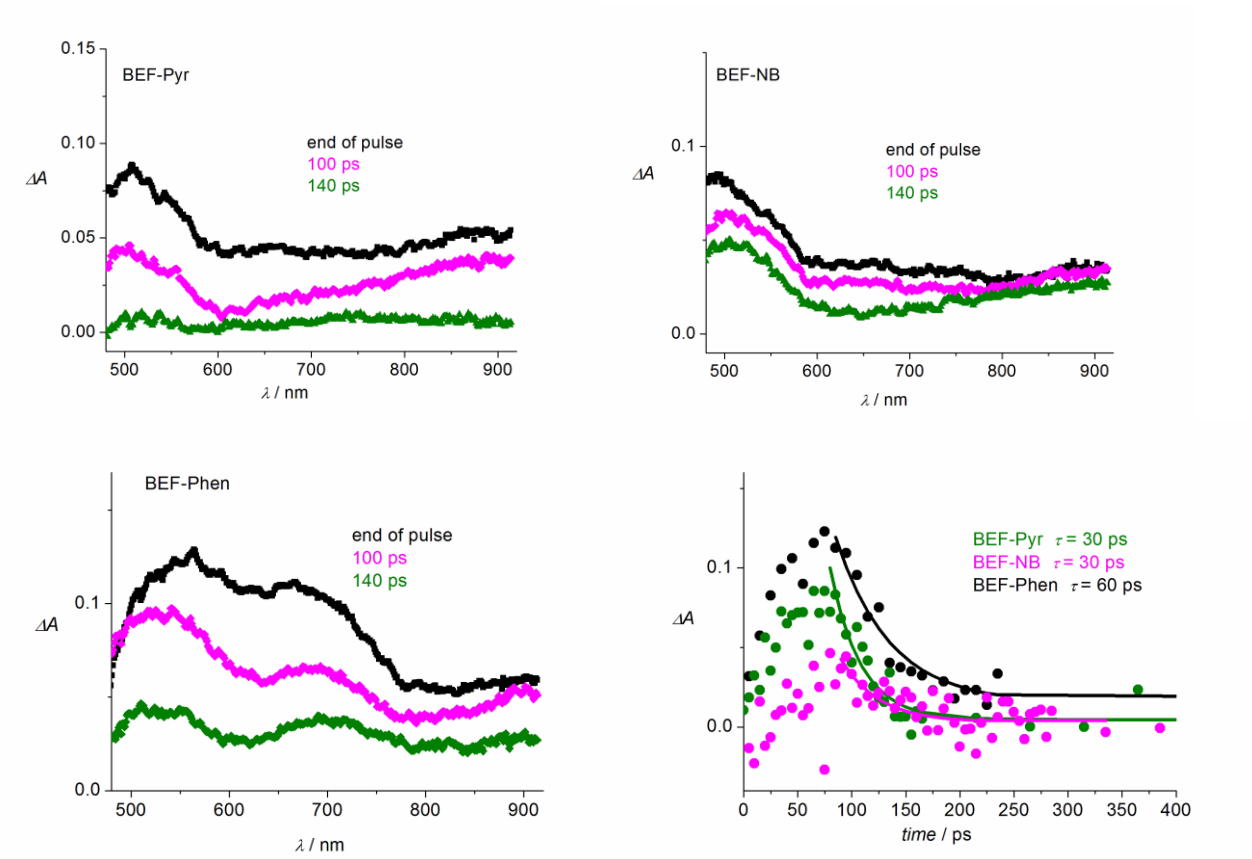



**Figure S39**. Transient absorption spectra of dyads in MeOH at various delays, after laser excitation (355 nm, 35 ps FWMH, 3 mJ/pulse) and time profiles with fittings at 510 nm for **BEF-Pyr** and **BEF-NB**, and 540 nm for **BEF-Phen**.

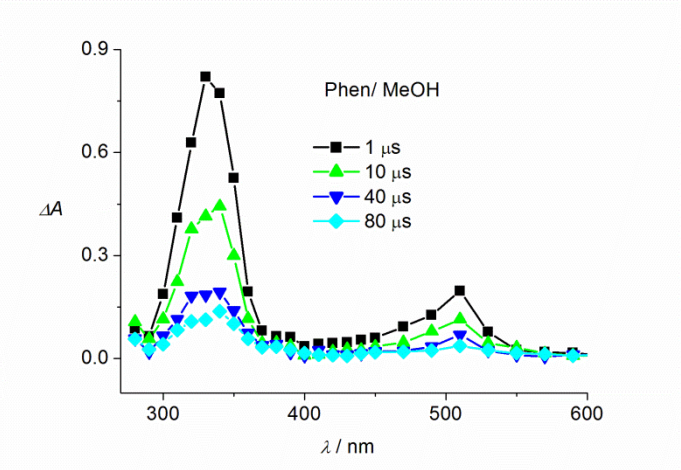



**Figure S40**. Transient absorption spectra of **Phen** in MeOH solutions at various delays after laser excitation (18 ns pulse, 266 nm, 3 mJ/pulse).

## 4. Electrochemistry

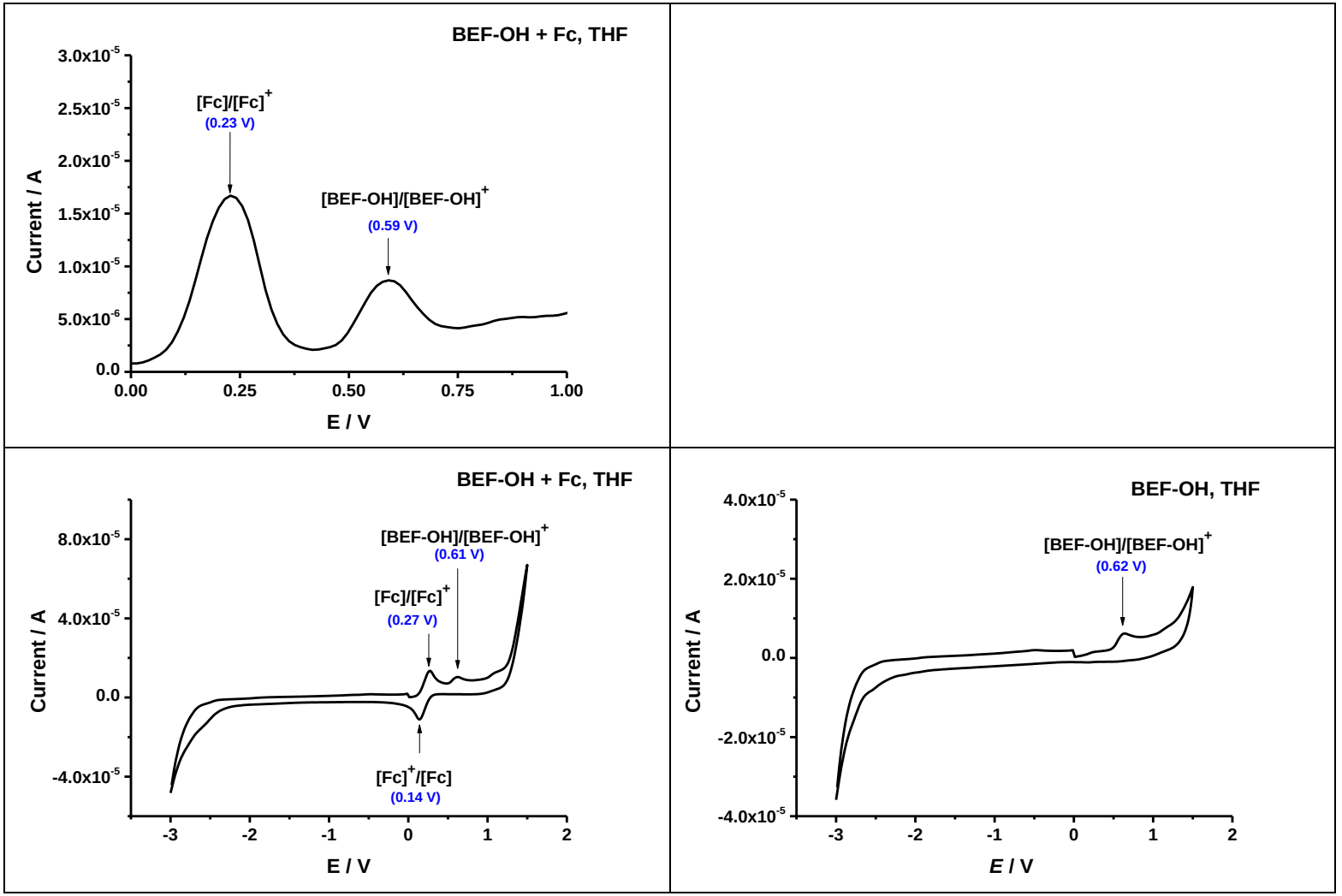



**Figure S341**. Determination of electrochemical properties of the model electron donor **BEF-OH**.Top left – square wave with ferrocene as internal standard; bottom left – cyclic voltammetry with ferrocene as internal standard; bottom right – cyclic voltammetry without standard.The results show that the first oxidation potential of **BEF-OH** is 0.36 V vs $Fc/Fc^+$ (in THF, with 0.1 M $Bu_4PF6$).

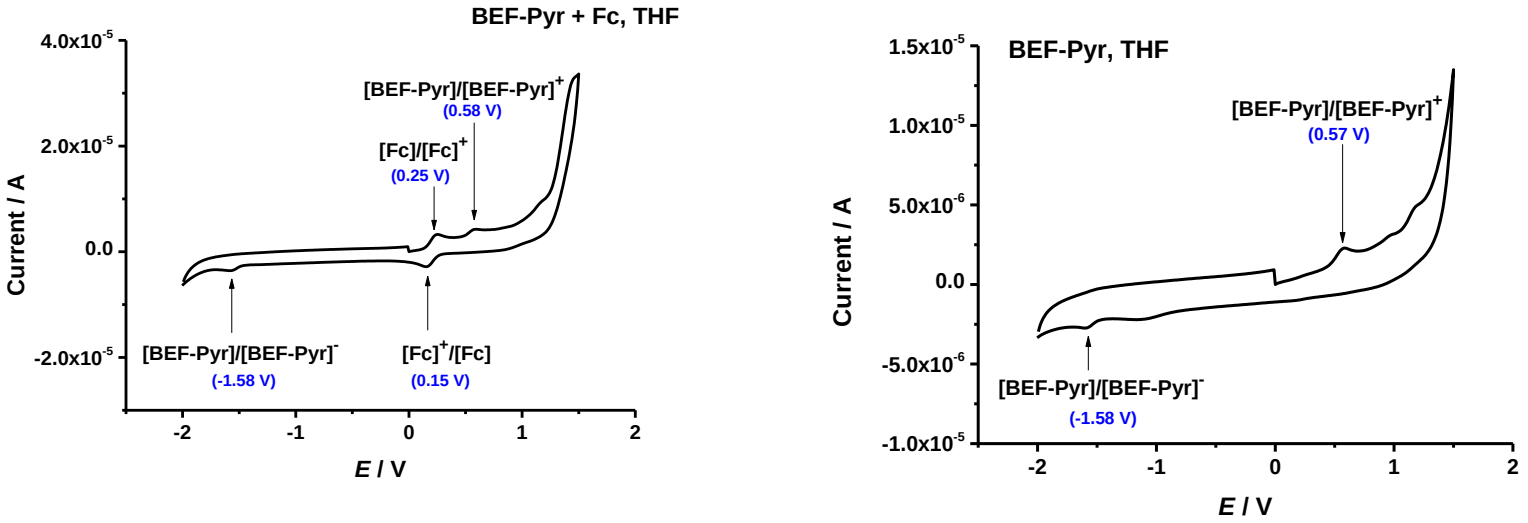



**Figure S42**. Determination of electrochemical properties ofthe model dyad **BEF-Pyr**. Left – cyclic voltammetry with ferrocene as internal standard; right – cyclic voltammetry without standard. Due to the insufficient amount of **BEF-Pyr**, square wave analysis peaks were ill-defined and did not allow for the accurate determination of red-ox values. In this case oxidation potentialwas determined by measuring the distance between the half-wave potential of ferrocene and the oxidation peak of the analyzed compound. The same method was used to determine reduction potential.The results show that the first oxidation potential of **BEF-Py**r is 0.38 V vs $Fc/Fc^+$ and the first reduction potential is -1.78 V vs $Fc/Fc^+$ (in THF, with 0.1 M $Bu_4PF_6$).

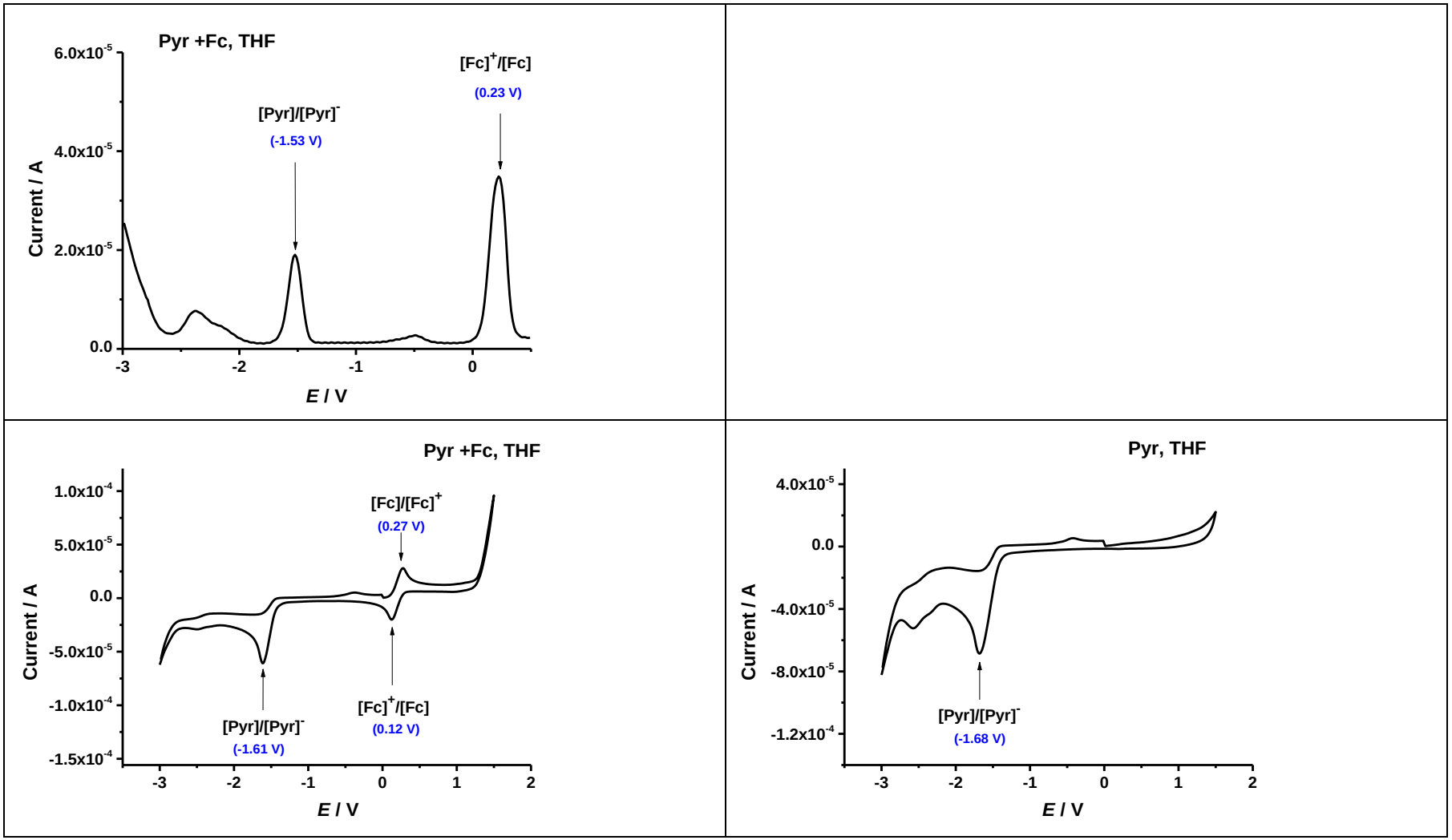



**Figure S43**. Determination of electrochemical properties of the model electron acceptor **Pyr**.Top left – square wave-reductionwith ferrocene as standard; bottom left – cyclic voltammetry with ferrocene as internal standard; bottom right – cyclic voltammetry without standard. The results show that the first reduction potential of **Pyr** is -1.76 V vs $Fc/Fc^+$ (in THF, with 0.1 M $Bu_4PF_6$).

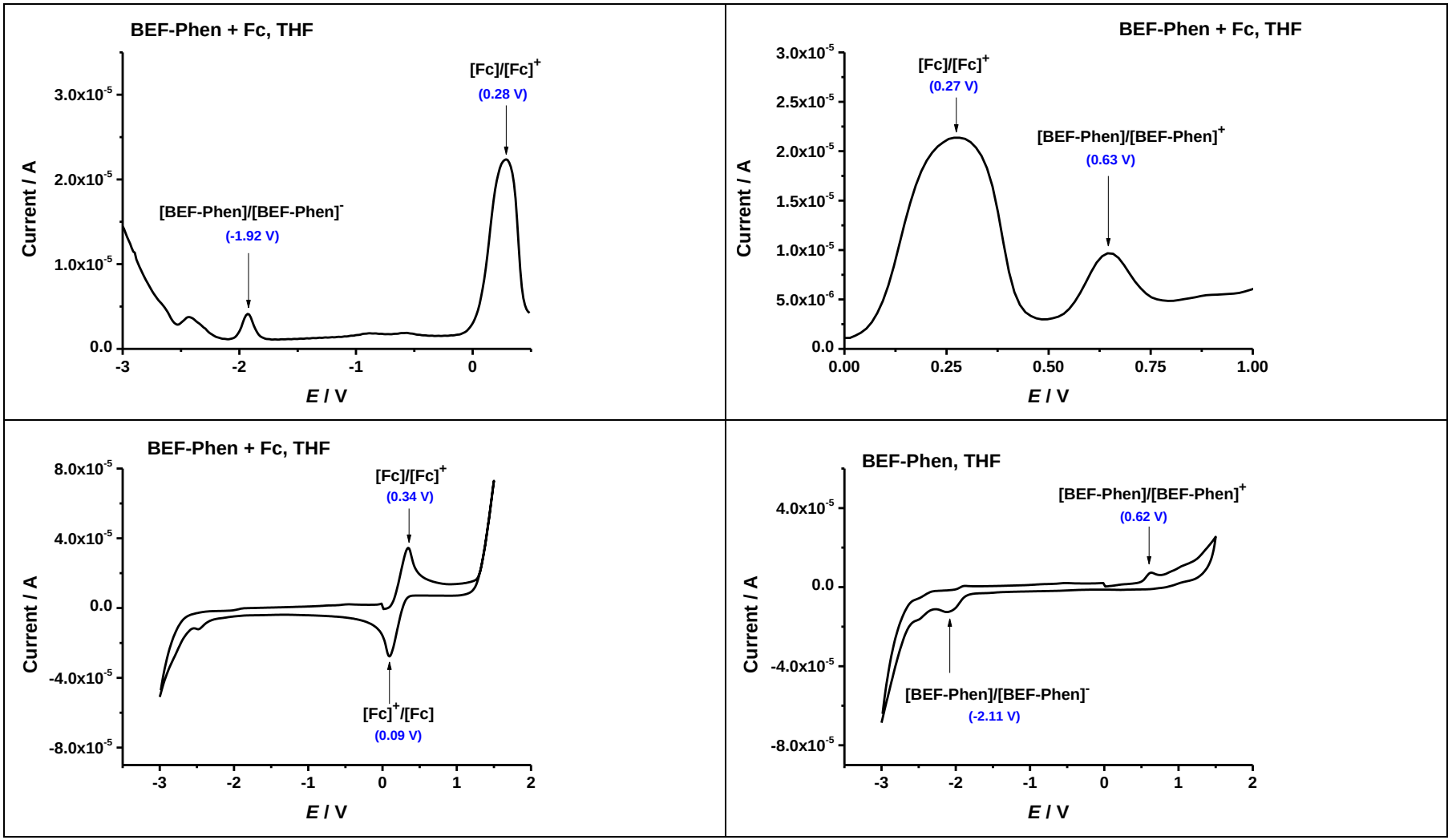



**Figure S44**. Determination of electrochemical properties of the model dyad **HegPhenBEF-Phen**. Top left – square wave-reduction with ferrocene as internal standard; top right – square wave oxidation with ferrocene as internal standard; bottom left – cyclic voltammetry with ferrocene as internal standard; bottom right – cyclic voltammetry without standard. The results show that the first oxidation potential of **HegPhen BEF-Phen** is 0.36 V vs $Fc/Fc^+$ and the first reduction potential is -2.20 V vs $Fc/Fc^+$ (in THF, with 0.1 M $Bu_4PF_6$).

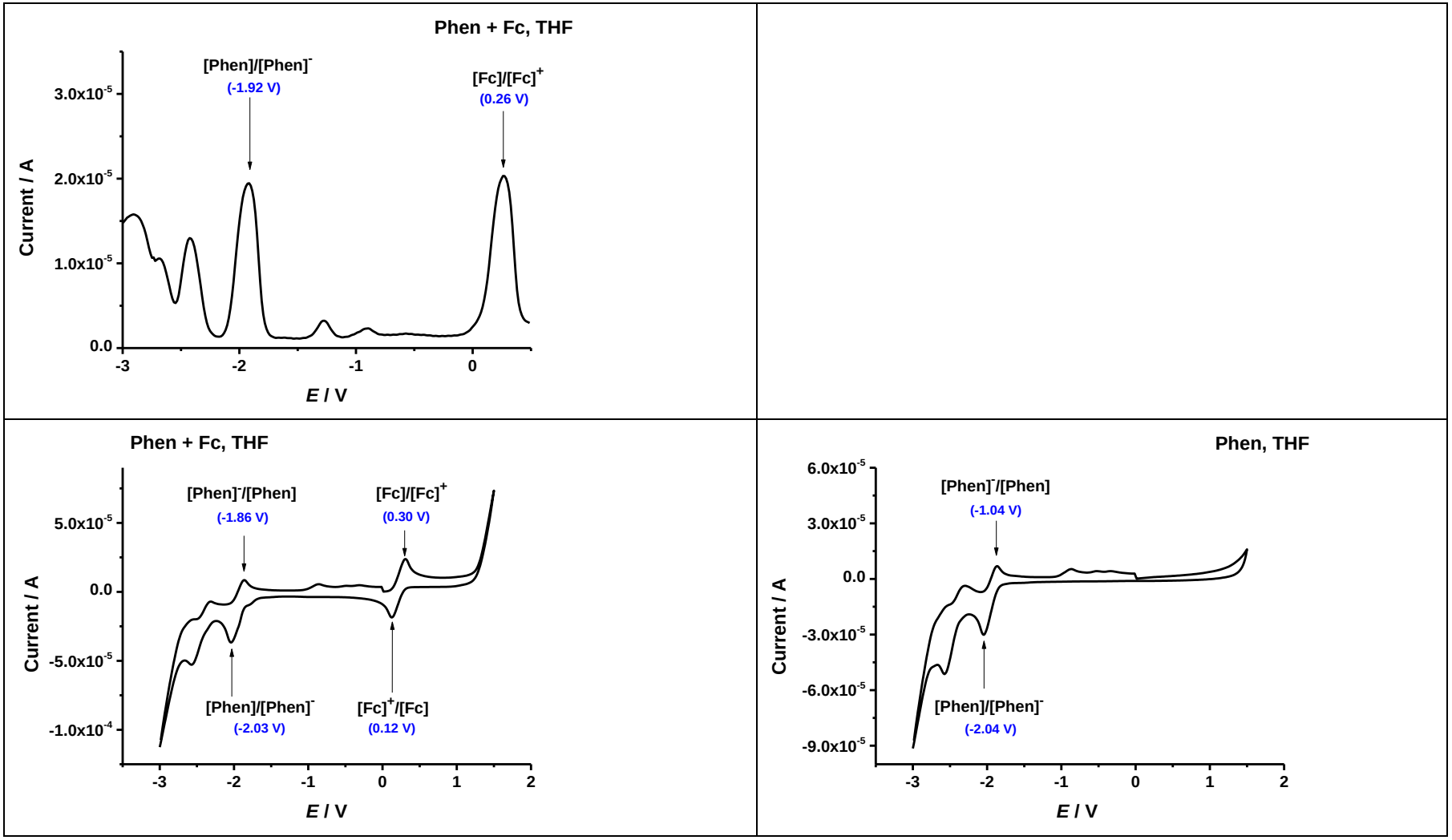



**Figure S45**. Determination of electrochemical properties of the model electron acceptor **Phen**. Top left – square wave-reduction with ferrocene as internal standard; bottom left – cyclic voltammetry with ferrocene as internal standard; bottom right – cyclic voltammetry without standard. The results show the first reduction potential of **Phen** is -2.18 V vs $Fc/Fc^{+}$ (in THF, with 0.1 M $Bu_4PF_6$).

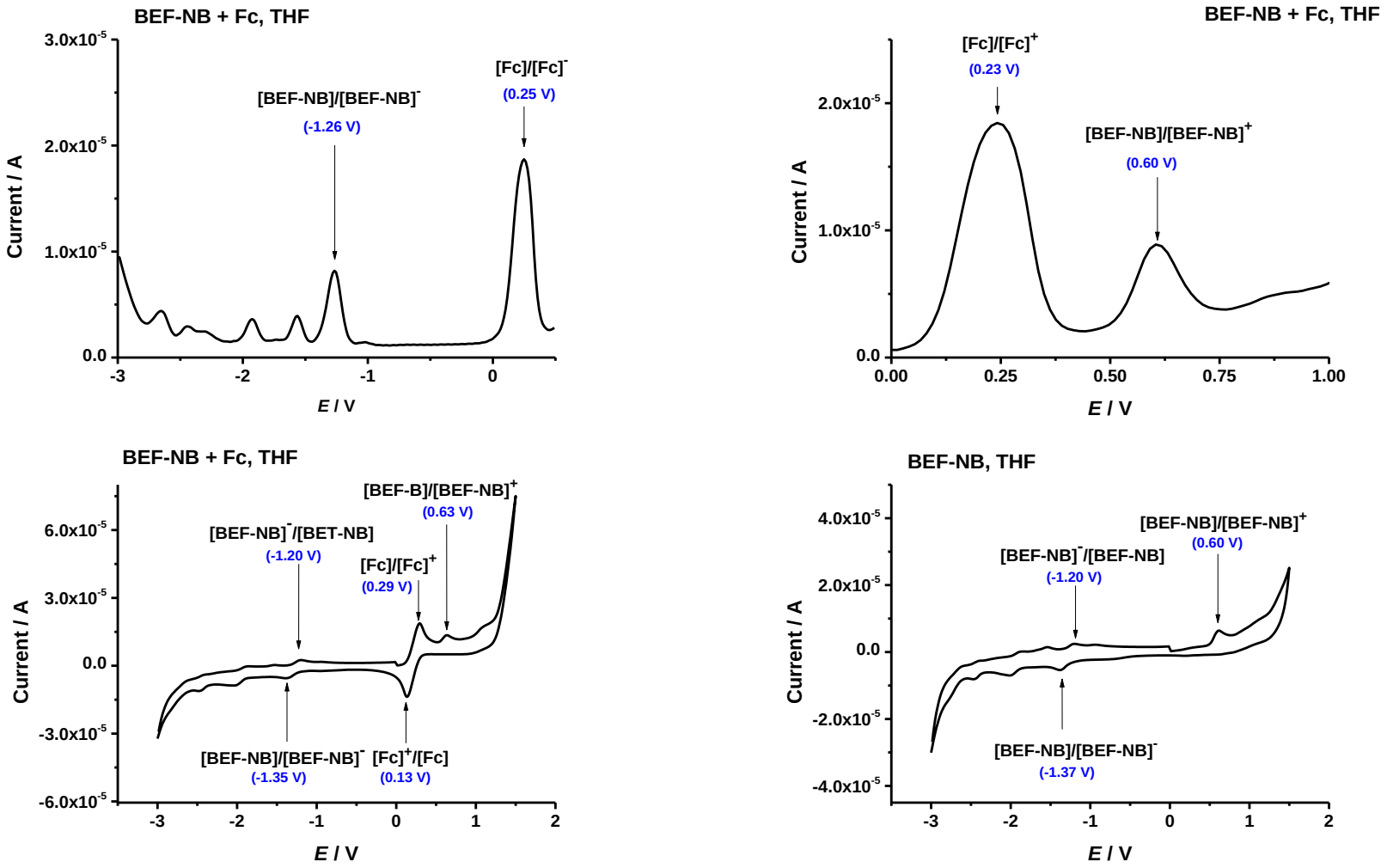



**Figure S46**. Determination of electrochemical properties of the model dyad **BEF-NB**. Top left – square wave-reduction with ferrocene as internal standard; top right – square wave oxidation with ferrocene as internal standard; bottom left – cyclic voltammetry with ferrocene as internal standard; bottom right – cyclic voltammetry without standard. The results show that the first oxidation potential of **BEF-NB** is 0.37 V vs $Fc/Fc^+$ and the first reduction potential is -1.51 V vs $Fc/Fc^+$ (in THF, with 0.1 M $Bu_4PF_6$).

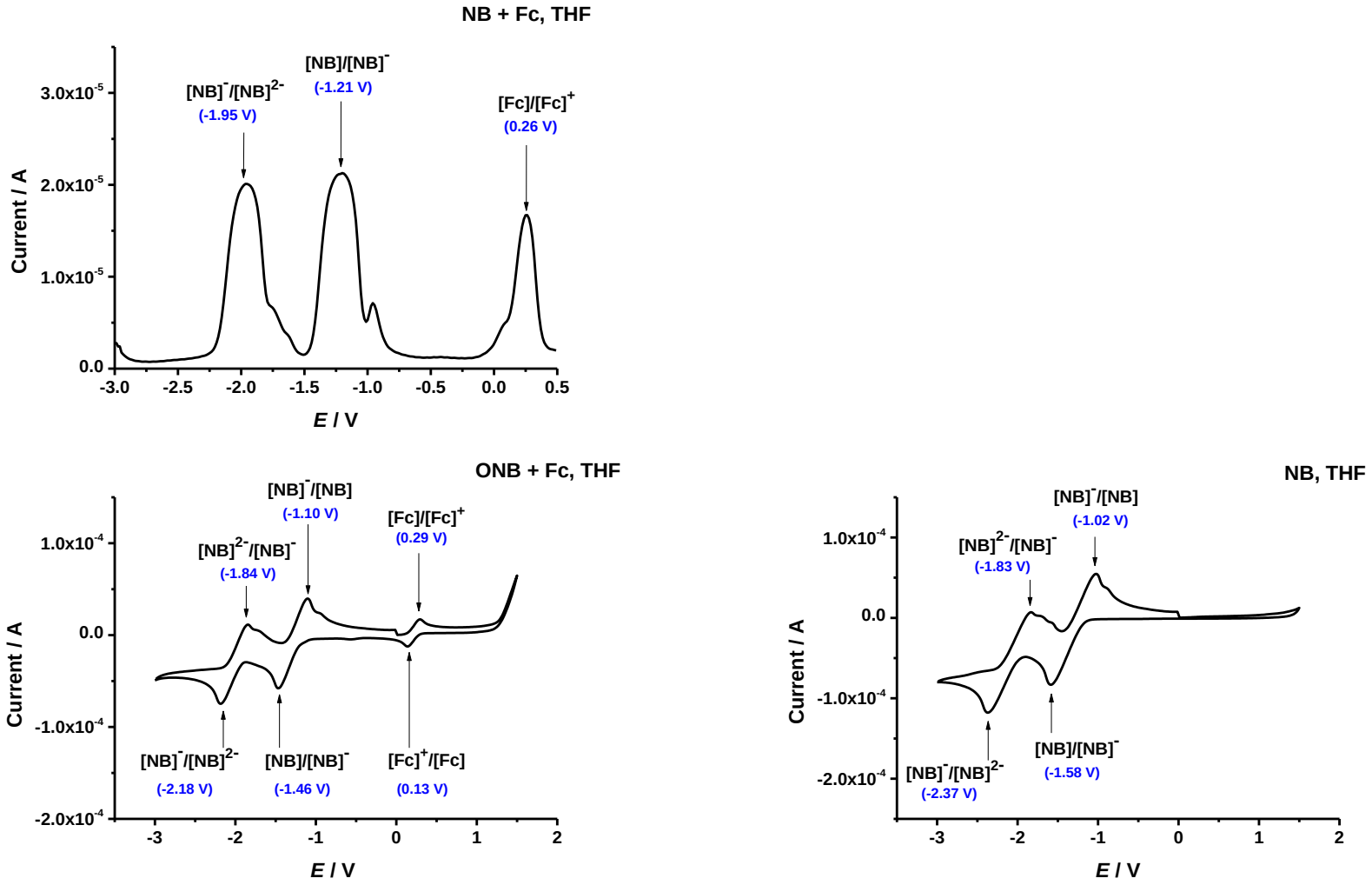



**Figure S47**. Determination of electrochemical properties of the model electron acceptor **NB**. Top left – square wave-reduction with ferrocene as internal standard; bottom left – cyclic voltammetry with ferrocene as internal standard; bottom right – cyclic voltammetry without standard. The results show that the first reduction potential of **NB** is -1.47 V vs $Fc/Fc^+$ (in THF, with 0.1 M $Bu_4PF_6$).

## 5. Literature references


1. N. M. Yoon, H. C. S. Pak, C. Brown, S. Krishnamurthy, T. P. Stocky, *J. Org. Chem*., 1973, **38**, 2786-2792.
2. O. Mongin, L. Porres, M. Charlot, C. Katan, M. Blanchard-Desce, *Chem. Eur. J*., 2007, **13**, 1481-1498.
3. K. Lee, D. E. Falvey, *J. Am. Chem. Soc*., 2000, **122**, 9361-9366.
4. T. Terasaka, T. Kinoshita, M. Kuno, N. Seki, K. Tanaka, I. Nakanishi, *J. Med. Chem*., 2004, **47**, 3730-3743.
5. A. Boccia, V. Lanzilotto, V. Di Castro, R. Zanoni, L. Pescatori, A. Arduinib, A. Secchi, Phys. Chem. Chem. Phys., 2011, **13**, 4452–4462.