

# - Supporting Information -

## Photochemical Degradation of Various Bridge-Substituted Fluorene-Based Materials

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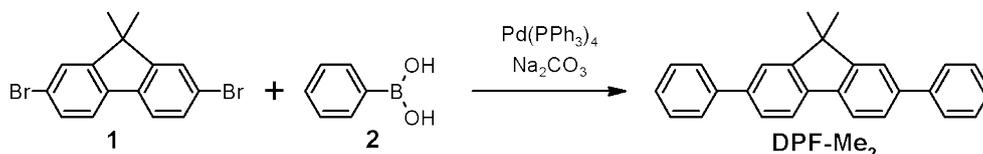
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## 1 Organic Synthesis

$^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra are referenced to 7.26 ppm and 77.16 ppm, respectively, for  $\text{CDCl}_3$  and 5.32 ppm and 53.8 ppm, respectively, for  $\text{CD}_2\text{Cl}_2$ .

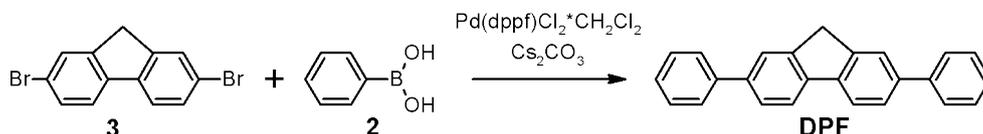


### 9,9-Dimethyl-2,7-diphenyl-9*H*-fluorene (DPF-Me<sub>2</sub>)

Under an argon atmosphere  $\text{Pd}(\text{PPh}_3)_4$  (0.116 g, 0.10 mmol) was added to a stirred solution of **1** (1.76 g, 5.0 mmol) in THF (100 mL). After stirring for 10 min, phenylboronic acid **2** (1.46 g, 12.0 mmol), as well as aqueous  $\text{Na}_2\text{CO}_3$  (40 mL, 2.0 mol  $\text{L}^{-1}$ ) were added and the reaction was stirred for 4 h at 65 °C. After cooling to room temperature, water was added and the mixture was extracted with ethyl acetate. The organic phase was dried ( $\text{MgSO}_4$ ) and the solvent was removed. Purification by column chromatography (petroleum ether/ethyl acetate), recrystallization ( $\text{CH}_2\text{Cl}_2$ /cyclohexane), and sublimation yielded 0.9 g (2.6 mmol, 52% yield) of **DPF-Me<sub>2</sub>**.

$^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ , Fig. S5.2)  $\delta$  [ppm] = 7.81 (d,  $J$  = 7.8 Hz, 2H), 7.72 - 7.65 (m, 6H), 7.60 (dd,  $J$  = 7.9, 1.6 Hz, 2H), 7.48 (t,  $J$  = 7.5 Hz, 4H), 7.37 (t,  $J$  = 7.3 Hz, 2H), 1.59 (s, 6H).

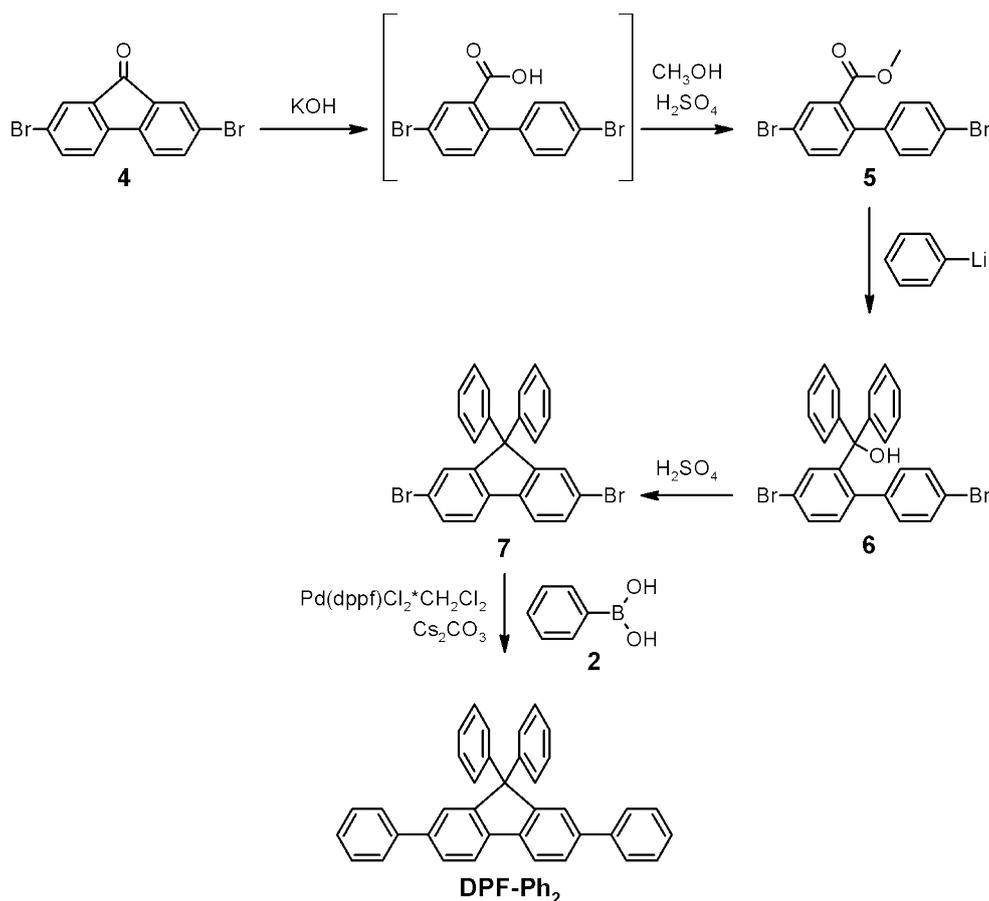
$^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ , Fig. S5.2)  $\delta$  [ppm] = 154.7, 141.7, 140.6, 138.3, 128.9, 127.4, 127.3, 126.4, 121.6, 120.5, 47.2, 27.5.



### 2,7-Diphenyl-9*H*-fluorene (DPF)

Under argon, a mixture of 2,7-dibromo-9*H*-fluorene **3** (1.62 g, 5.0 mmol), phenylboronic acid **2** (1.53 g, 12.5 mmol),  $\text{Pd}(\text{dppf})\text{Cl}_2 \cdot \text{CH}_2\text{Cl}_2$  (0.83 g, 0.10 mmol), and  $\text{Cs}_2\text{CO}_3$  (4.88 g, 15.0 mmol) in THF/ethanol/DMF (40/40/10 mL) was stirred at 65 °C for 2 h. After cooling to room temperature, water was added and the mixture was extracted with  $\text{CH}_2\text{Cl}_2$  (>400 mL, low solubility). The organic phase was dried ( $\text{MgSO}_4$ ) and the major amount of solvent was removed. The precipitate was filtered off and purified by gradient sublimation. **DPF** (1.3 g, 4.1 mmol, 82% yield) was obtained as a nearly colorless solid.

$^1\text{H-NMR}$  (300 MHz,  $\text{CD}_2\text{Cl}_2$ , Fig. S5.1)  $\delta$  [ppm] = 7.89 (d,  $J$  = 8.0 Hz, 2H), 7.84 - 7.81 (m, 2H), 7.72 - 7.63 (m, 6H), 7.51 - 7.43 (m, 4H), 7.40 - 7.32 (m, 2H), 4.05 (s, 2H).



### Methyl-4,4'-dibromo-[1,1'biphenyl]-2-carboxylate (**5**)

The literature procedure<sup>1</sup> was modified: A stirred suspension of 2,7-dibromofluoren-9-one **4** (10.4 g, 30.8 mmol) in anisole (100 mL) was heated to 100 °C. KOH (12.0 g, 214 mmol) was added and the solution was heated to 160 °C. The mixture was stirred at that temperature, until a white precipitate had formed and the yellow color of the solution had vanished. The precipitate was filtered from the hot solution, washed with petroleum ether and dissolved in water. Upon adding conc. hydrochloric acid, the product precipitated. It was filtered off and dried in air.

The crude carboxylic acid was dissolved in methanol (200 mL) at 65 °C. After adding conc. sulfuric acid (8 mL), the mixture was stirred over night at that temperature. Then, methanol was removed and the residue was dissolved in ethyl acetate. The solution was washed with aqueous NaHCO<sub>3</sub> and water (3x). The organic phase was dried (MgSO<sub>4</sub>) and the solvent was removed. The crude product was purified by column chromatography (petroleum ether/ethyl acetate) to give 11.0 g (29.6 mmol, 95% yield) of methyl ester **5**.

<sup>1</sup>H-NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ [ppm] = 7.98 (d, *J* = 2.2 Hz, 1H), 7.68 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.58 - 7.49 (m, 2H), 7.23 (d, *J* = 8.2 Hz, 1H), 7.20 - 7.12 (m, 2H), 3.67 (s, 3H).

<sup>13</sup>C-NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ [ppm] = 167.4, 140.1, 139.6, 134.8, 133.2, 132.6, 131.6, 130.4, 122.1, 121.8, 52.6.

<sup>1</sup>Bradsher, C. K.; Beavers, L.E.; Tokura, N. Aromatic Cyclodehydration. XXXIII. 2,7-Disubstituted Phenanthrenes. *J. Am. Chem. Soc.* **1956**, *78*, 3196 - 3198.

**(4,4'-Dibromo-1,1'-biphenyl-2-yl)diphenylmethanol (6)<sup>2</sup>**

Under an argon atmosphere *n*BuLi (3.2 mL, 7.0 mmol, 2.2 mol L<sup>-1</sup> in cyclohexane) was added to a solution of bromobenzene (1.1 g, 7 mmol) in THF (10 mL) at -78 °C. After stirring the mixture at that temperature for 30 min, it was added to a solution of **5** (1.1 g, 3.0 mmol) in THF (20 mL). The reaction was stirred at 60 °C for one hour. After cooling to room temperature, the reaction was quenched with diluted aqueous NH<sub>4</sub>Cl and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic phase was dried (MgSO<sub>4</sub>), the solvent was removed and the product was crystallized from CH<sub>2</sub>Cl<sub>2</sub>/ethanol. **6** (1.02 g, 2.06 mmol, 69% yield) was obtained as colorless crystals.

<sup>1</sup>H-NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ [ppm] = 7.46 (dd, *J* = 8.1, 2.1 Hz, 1H), 7.33 - 7.22 (m, 8H), 7.15 - 7.08 (m, 4H), 6.97 (dd, *J* = 5.1, 2.9 Hz, 2H), 6.68 - 6.60 (m, 2H), 2.75 (s, 1H).

<sup>13</sup>C-NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ [ppm] = 146.9, 140.6, 134.3, 133.0, 131.5, 131.1, 130.5, 129.4, 128.3, 128.2, 127.9, 121.8, 121.3, 110.4, 83.2.

**2,7-Dibromo-9,9-diphenyl-9H-fluorene (7)<sup>3</sup>**

Concentrated sulfuric acid (0.5 mL) was added to a stirred solution of **6** (0.5 g, 1.0 mmol) in acetic acid (15 mL) at 100 °C. The mixture was stirred at that temperature for one hour and finally poured into water. The precipitate was filtered off and crystallized from chloroform/ethanol to give **7** (0.4 g, 0.84 mmol, 83% yield) as white powder.

<sup>1</sup>H-NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ [ppm] = 7.69 - 7.62 (m, 2H), 7.52 (m, 4H), 7.30 - 7.23 (m, 6H), 7.19 - 7.10 (m, 4H).

<sup>13</sup>C-NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ = 153.4, 144.8, 138.5, 131.4, 129.6, 128.9, 128.3, 127.6, 122.2, 110.4, 66.0.

**2,7,9,9-Tetraphenyl-9H-fluorene (DPF-Ph<sub>2</sub>)**

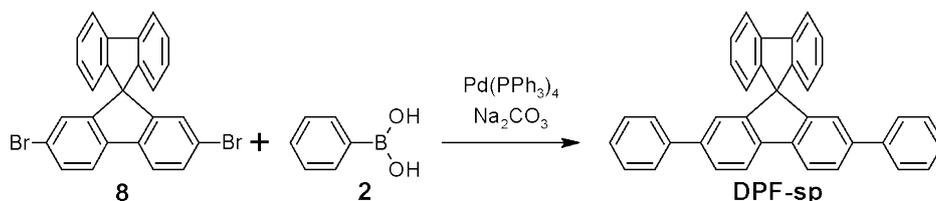
A mixture of **7** (0.4 g, 0.84 mmol), phenylboronic acid **2** (0.26 g, 2.1 mmol), Cs<sub>2</sub>CO<sub>3</sub> (1.26 g, 3.8 mmol), and Pd(dppf)Cl<sub>2</sub> · CH<sub>2</sub>Cl<sub>2</sub> (0.014 g, 0.017 mmol) in THF/ethanol/DMF (10/10/2.5 mL) was stirred under an argon atmosphere for 30 min at 70 °C. Afterwards, it was poured into water and extracted with ethyl acetate. The organic phase was dried (MgSO<sub>4</sub>) and the solvent was removed. The crude product was purified by column chromatography (petroleum ether/ethyl acetate) to give **DPF-Ph<sub>2</sub>** (0.24 g, 0.51 mmol, 61% yield) as white powder.

<sup>1</sup>H-NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>, Fig. S5.3) δ [ppm] = 7.95 - 7.88 (m, 2H), 7.72 - 7.64 (m, 4H), 7.64 - 7.56 (m, 4H), 7.48 - 7.39 (m, 4H), 7.38 - 7.22 (m, 12H).

<sup>13</sup>C-NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>, Fig. S5.3) δ [ppm] = 152.5, 146.2, 141.4, 141.2, 139.4, 129.1, 128.7, 128.5, 127.7, 127.4, 127.2, 127.2, 125.2, 121.0, 66.1.

<sup>2</sup>According to Setayesh, S.; Grimsdale, A. C.; Weil, T.; Enkelmann, V.; Müllen, K.; Meghdadi, F.; List, E. J. W.; Leising, G. Polyfluorenes with Polyphenylene Dendron Side Chains: Toward Non-Aggregating, Light-Emitting Polymers. *J. Am. Chem. Soc.* **2001**, *123*, 946 - 953.

<sup>3</sup>The synthesis was carried out according to a slightly modified literature procedure from Setayesh, S.; Grimsdale, A. C.; Weil, T.; Enkelmann, V.; Müllen, K.; Meghdadi, F.; List, E. J. W.; Leising, G. Polyfluorenes with Polyphenylene Dendron Side Chains: Toward Non-Aggregating, Light-Emitting Polymers. *J. Am. Chem. Soc.* **2001**, *123*, 946 - 953.

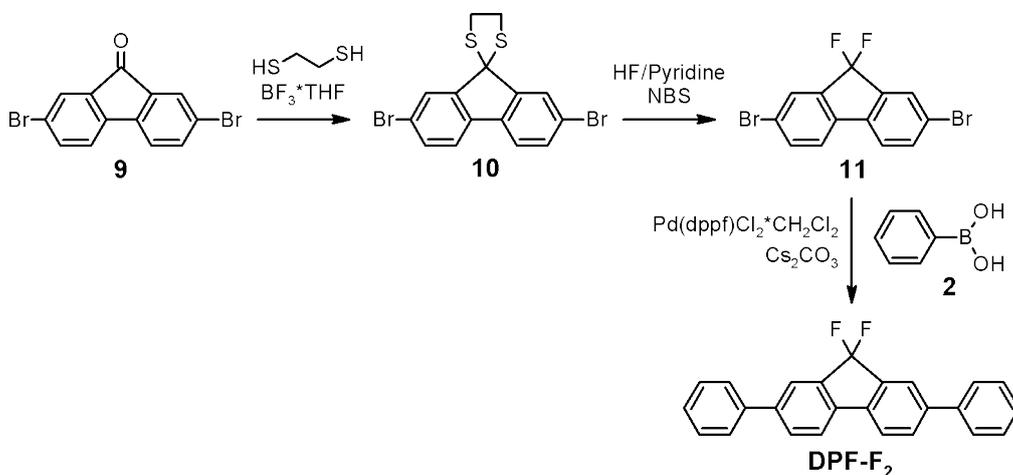


### 2,7-Diphenyl-9,9'-spirobi[fluorene] (DPF-sp)

Under an argon atmosphere Pd(PPh<sub>3</sub>)<sub>4</sub> (0.18 g, 0.16 mmol) was added to a solution of 2,7-dibromospiro[fluorene] **8** (0.75 g, 1.6 mmol) in THF (40 mL). After stirring for 10 min, aqueous Na<sub>2</sub>CO<sub>3</sub> (12.6 mL, 2.0 mol L<sup>-1</sup>) and phenylboronic acid **2** (0.46 g, 3.8 mmol) were added. The reaction was stirred for 24 h at 65 °C. After cooling to room temperature, water was added and the mixture was extracted with ethyl acetate. The organic phase was dried (MgSO<sub>4</sub>) and the solvent was removed. The crude product was purified by column chromatography (petroleum ether/ethyl acetate) and subsequent crystallization (ethyl acetate) to give **DPF-sp** (0.50 g, 1.1 mmol, 68% yield) as colorless solid.

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, Fig. S5.4) δ [ppm] = 7.93 (d, *J* = 7.9 Hz, 2H), 7.87 (d, *J* = 7.6 Hz, 2H), 7.63 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.46 - 7.21 (m, 12H), 7.12 (td, *J* = 7.5, 1.1 Hz, 2H), 6.94 (d, *J* = 1.6 Hz, 2H), 6.83 (d, *J* = 7.6 Hz, 2H).

<sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>, Fig. S5.4) δ [ppm] = 150.1, 148.9, 142.1, 141.2, 140.9, 128.8, 128.1, 128.0, 127.4, 127.3, 127.2, 124.5, 123.0, 120.6, 120.3, 66.3.



### 2,7-Dibromospiro[fluorene-9,2'-[1,3]dithiolane] (10)

Ethane dithiol (3.4 mL, 45 mmol,  $\rho = 1.23$  g/cm<sup>3</sup>), and subsequently BF<sub>3</sub>·THF (50%, 6.6 mL, 30 mmol,  $\rho = 1.27$  g/cm<sup>3</sup>) were added to a suspension of 2,7-dibromofluorenone **9** (10.1 g, 30 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 mL). After stirring the mixture for 3 days at room temperature, the yellow color disappeared and 150 mL of 10% aqueous NaOH were added. Stirring was continued for 1 h. Subsequently, the phases were separated and the crude product was filtered from the organic phase. After drying in vacuum, **10** (11.5 g, 27.7 mmol, 92% yield) was obtained as a colorless crystalline solid.

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) δ [ppm] = 7.78 (dd, *J* = 1.6, 0.5 Hz, 2H), 7.47

(dd,  $J = 8.1, 1.7$  Hz, 2H), 7.43 (dd,  $J = 8.1, 0.6$  Hz, 2H), 3.78 (s, 4H).

$^{13}\text{C}$ -NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  [ppm] = 152.4, 136.5, 132.1, 128.8, 122.4, 121.3, 110.2, 42.6.

#### 2,7-Dibromo-9,9-difluoro-9H-fluorene (**11**)<sup>4</sup>

In a polypropylene screw-cap beaker, dithiolane **10** (11.4 g, 27.5 mmol) was slowly added to a mixture of *N*-bromosuccinimide (NBS, 12.2g, 68.8 mmol) and HF/pyridine (70%, 4.2 ml, 165 mmol HF,  $\rho = 1.1$  g/cm<sup>3</sup>) in  $\text{CH}_2\text{Cl}_2$  (50 mL) at 0 °C. The mixture was stirred for 30 min. Then, excess basic alumina was added and stirring was continued for 15 min. After filtering off the solid components, the organic phase was washed with aqueous sodium hydro-sulfite and dried ( $\text{MgSO}_4$ ). The solvent was removed and the crude product was purified by column chromatography (petroleum ether/ $\text{CH}_2\text{Cl}_2$ ) to give **11** (9.2 g, 25.6 mmol, 93% yield) as colorless solid.

$^1\text{H}$ -NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  [ppm] = 7.69 - 7.66 (m, 2H), 7.56 - 7.52 (m, 2H), 7.35 (d,  $J = 8.1$  Hz, 2H).

$^{13}\text{C}$ -NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  [ppm] = 139.5 (t,  $J = 25.4$  Hz), 137.6 (t,  $J = 5.0$  Hz), 135.5 (s), 127.6 (s), 123.0 (s), 122.0 (s), 121.9 (t,  $J = 245.4$  Hz).

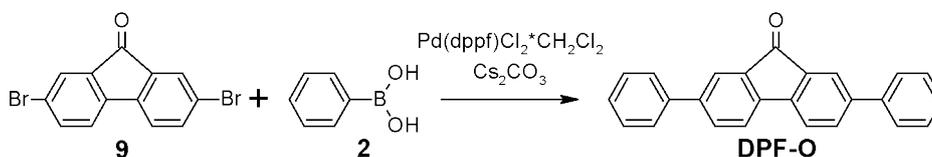
#### 9,9-Difluoro-2,7-diphenyl-9H-fluorene (DPF-F<sub>2</sub>)

Under an argon atmosphere, phenylboronic acid **2** (0.36 g, 3.0 mmol) was added to a mixture of **11** (0.40 g, 1.1 mmol),  $\text{Pd}(\text{dppf})\text{Cl}_2 \cdot \text{CH}_2\text{Cl}_2$  (0.06 g, 0.09 mmol) and  $\text{Cs}_2\text{CO}_3$  (0.89 g, 2.75 mmol) in THF/ethanol/DMF (8/8/2 mL). After stirring the mixture for 2 h at 65 °C, water was added and the (cooled) mixture was extracted with  $\text{CH}_2\text{Cl}_2$ . The organic phase was dried ( $\text{MgSO}_4$ ) and all volatiles were removed. Column chromatography (petroleum ether/ethyl acetate) gave 0,20 g (0.56 mmol, 51% yield) of **DPF-F<sub>2</sub>**.

$^1\text{H}$ -NMR (300 MHz,  $\text{CDCl}_3$ , Fig. S5.5)  $\delta$  [ppm] = 7.88 (d,  $J = 1.1$  Hz, 2H), 7.72 (dd,  $J = 7.9, 1.6$  Hz, 2H), 7.68 - 7.62 (m, 6H), 7.53 - 7.44 (m, 4H), 7.44 - 7.36 (m, 2H).

$^{13}\text{C}$ -NMR<sup>5</sup> (75 MHz,  $\text{CDCl}_3$ , Fig. 5.5)  $\delta$  [ppm] = 142.2, 140.3, 139.0, 138.3, 131.1, 129.1, 128.0, 127.2, 122.8, 120.92.

For further purification **DPF-F<sub>2</sub>** was crystallized from THF.



#### 2,7-Diphenyl-9H-fluoren-9-one (DPF-O)<sup>6</sup>

<sup>4</sup>Although several methods for the preparation of **11** are known, we favor this very facile and low-cost procedure, adapted and simplified from Sondej, S. C.; Katzenellenbogen, J. A. Gem-Difluoro Compounds: a Convenient Preparation from Ketones and Aldehydes by Halogen Fluoride Treatment of 1,3-Dithiolanes. *J. Org. Chem.* **1986**, *51*, 3508 - 3513.

<sup>5</sup>spectrum incomplete/multiplets not assigned

<sup>6</sup>The synthesis of **DPF-O** has previously been published by us in: Kobin, B.; Bianchi, F.; Halm, S.; Leistner, J.; Blumstengel, S.; Henneberger, F.; Hecht, S. Green Emission in Ladder-Type Quarterphenyl: Beyond the Fluorenone-Defect. *Adv. Func. Mater.* **2014**, *24*, 7717 - 7727. For the purpose of completeness it is shown here, again.

A mixture of 2,7-dibromofluorenone **9** (1.01 g, 3.0 mmol), phenylboronic acid **2** (0.88 g, 7.2 mmol), Pd(dppf)Cl<sub>2</sub> · CH<sub>2</sub>Cl<sub>2</sub> (0.13g, 0.15 mmol), and Cs<sub>2</sub>CO<sub>3</sub> (2.44 g, 7.5 mmol) in ethanol (30 mL), THF (30 mL) and DMF (10 mL) was stirred over night under an argon atmosphere at 60 °C. After cooling to room temperature, the mixture was poured into water and the precipitate was filtered off. The crude product was dissolved in warm THF and filtered through a pad of celite. The solvent was removed and crude **DPF-O** was recrystallized in THF to give 0.83g (2.50 mmol, 83% yield) of the final compound.

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, Fig. 5.6) δ [ppm] = 7.94 (d, *J* = 1.3 Hz, 2H), 7.75 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.67 - 7.59 (m, 6H), 7.52 - 7.44 (m, 4H), 7.43 - 7.35 (m, 2H).

<sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>, Fig. 5.6) δ [ppm] = 143.2, 142.4, 140.0, 135.4, 133.5, 129.1, 128.1, 127.0, 123.2, 120.9.

## 2 Crystal Structure Analysis

The diffraction data were collected on a STOE IPDS 2 $\theta$  diffractometer at 100 K. Crystallographic data are depicted in the crystallographic table. The structures were solved by direct methods (SHELXS-97)<sup>7</sup> and were refined with the full-matrix least-squares method on  $F^2$  (SHELX-97 and SHELXL-2013)<sup>8</sup>. The hydrogen atoms were placed at the calculated positions and were refined by using a riding model. The data, which contain the supplementary crystallographic information, can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Crystallographic Table**

compound	DPF-Me <sub>2</sub>	DPF-sp	DPF-F <sub>2</sub>	DPF-O
Formular	C <sub>27</sub> H <sub>22</sub>	C <sub>37</sub> H <sub>24</sub>	C <sub>25</sub> H <sub>16</sub> F <sub>2</sub>	C <sub>25</sub> H <sub>16</sub> O
Formular weight / g·mol <sup>-1</sup>	346.45	468.56	354.38	332.38
$\lambda$ / Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Orthorhombic
Space group	<i>Pna</i> 2 <sub>1</sub>	<i>Pna</i> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> / <i>m</i>	<i>Cmc</i> 2 <sub>1</sub>
<i>a</i> / Å	12.1659(5)	13.7193(3)	9.6134(4)	34.7372(18)
<i>b</i> / Å	21.9295(12)	16.2571(4)	19.636(1)	6.7517(3)
<i>c</i> / Å	7.1708(3)	11.2574(4)	9.8168(4)	7.1631(3)
$\alpha$ / °	90	90	90	90
$\beta$ / °	90	90	110.275(3)	90
$\gamma$ / °	90	90	90	90
<i>V</i> / Å <sup>3</sup>	1913.11(15)	2510.81(12)	1738.29(14)	1680.00(13)
<i>Z</i>	4	4	4	4
Density / g·cm <sup>-3</sup>	1.203	1.240	1.354	1.314
$\mu$ / mm <sup>-1</sup>	0.068	0.070	0.092	0.079
<i>F</i> (000)	736.0	984.0	736.0	696.0
$\Theta$ range / °	2.50 - 27.50	4.68 - 27.50	4.70 - 27.50	3.49 - 27.49
Reflections collected	17895	35448	27855	11906
Independent reflections	2372	5731	4091	1953
Completeness to $\Theta$	1.00	0.99	0.99	1.00
<i>R</i> <sub>int</sub>	0.0744	0.0393	0.0736	0.0337
<i>GoF</i> on <i>F</i> <sup>2</sup>	1.080	0.999	0.992	1.088
<i>R</i> <sub>1</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0442	0.0389	0.0383	0.0299
<i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0837	0.1109	0.0682	0.0769
<i>R</i> <sub>1</sub> (all data)	0.0590	0.0411	0.0714	0.0301
<i>wR</i> <sub>2</sub> (all data)	0.0873	0.1127	0.0731	0.0771
$\Delta\rho_{max}/\Delta\rho_{min}$ / e·Å <sup>-3</sup>	0.366 / -0.251	0.283 / -0.256	0.229 / -0.242	0.333 / -0.272
CCDC	1036983	1036985	1036984	1036986

<sup>7</sup>Sheldrick, G. M. A Short History of SHELX. *Acta Cryst.* **2008**, *A64*, 112 - 122.

<sup>8</sup>Sheldrick, G. M. A Short History of SHELX. *Acta Cryst.* **2008**, *A64*, 112 - 122.; Sheldrick, G. M., *SHELXL, Crystal Structure Refinement*, **2013** University of Göttingen, Germany.

### 3 UV-Vis Spectroscopy

Absorption spectra were recorded on a Varian Cary 50 Bio UV-Visible spectrometer and fluorescence spectra on a Varian Cary Eclipse Fluorescence spectrometer using 10.0 x 10.0 mm quartz cuvettes.

#### 3.1 Fluorescence Quantum Yield

The fluorescence quantum yield was determined according to

$$\Phi_S = \Phi_R \cdot \frac{\int I_S(\lambda_S) d\lambda_S}{\int I_R(\lambda_R) d\lambda_R} \cdot \frac{(1 - 10^{-E_R(\lambda_{Ex})})}{(1 - 10^{-E_S(\lambda_{Ex})})} \cdot \frac{n_S^2}{n_R^2}. \quad (1)$$

In the equation  $\Phi$  depicts the fluorescence quantum yield,  $\int I(\lambda) d\lambda$  the area under the fluorescence spectrum,  $E(\lambda_{Ex})$  the extinction (absorbance) at the excitation wavelength (which was kept the same for sample and reference), and  $n$  the refractive index of the solvents used. Index  $R$  denotes properties of the reference, and  $S$  of the unknown sample. *p*-quarterphenyl in cyclohexane, assuming  $\Phi = 0.89^9$ , was used as reference.<sup>10,11</sup>

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<sup>9</sup>Berlman, I. B. *Handbook of Fluorescence Spectra of Aromatic Molecules*, Academic Press: New York **1971**

<sup>10</sup>Valeur, B. *Molecular Fluorescence - Principles and Applications*, WILEY-VCH: Weinheim, **2002**.

<sup>11</sup>Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*, 3rd Ed., Springer, **2006**.

### 3.2 Absorption and PL Spectra

#### Absorption Data

compound	solvent	$\lambda_{max}$ / nm	$\epsilon_{max}$ / $10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$ ( $\lambda$ / nm)
<b>DPF-Me<sub>2</sub></b>	ethyl acetate	325	48 (325)
	CH <sub>2</sub> Cl <sub>2</sub>	326	46 (326)
<b>DPF</b>	ethyl acetate	322	45 (322)
	CH <sub>2</sub> Cl <sub>2</sub>	325	47 (325)
<b>DPF-Ph<sub>2</sub></b>	ethyl acetate	313, 330	39 (330)
	CH <sub>2</sub> Cl <sub>2</sub>	314, 331	38 (331)
<b>DPF-sp</b>	ethyl acetate	309, 332	42 (309)
	CH <sub>2</sub> Cl <sub>2</sub>	310, 333	44 (310)
<b>DPF-F<sub>2</sub></b>	ethyl acetate	317	45 (317)
	CH <sub>2</sub> Cl <sub>2</sub>	320	43 (320)
<b>DPF-O</b>	ethyl acetate	286, 322, 335, 431	19 (322)
	CH <sub>2</sub> Cl <sub>2</sub>	289, 324, 337, 437	19 (324)

$\lambda_{max}$ : Absorption maxima;  $\epsilon_{max}$  ( $\lambda$ ): Absorption coefficient and corresponding wavelength.

#### Emission Data

compound	solvent	$\lambda_{Em}$ / nm	$\lambda_{Ex}$ / nm	$\Phi_{PL}$
<b>DPF-Me<sub>2</sub></b>	ethyl acetate	356, 372	325	
	CH <sub>2</sub> Cl <sub>2</sub>	355, 372	303	0.8
<b>DPF</b>	ethyl acetate	352, 369	322	
	CH <sub>2</sub> Cl <sub>2</sub>	356, 372	303	0.5
<b>DPF-Ph<sub>2</sub></b>	ethyl acetate	357, 374	330	
	CH <sub>2</sub> Cl <sub>2</sub>	361, 376	303	<0.01
<b>DPF-sp</b>	ethyl acetate	357, 374	320	
	CH <sub>2</sub> Cl <sub>2</sub>	360, 376	310	1.0
<b>DPF-F<sub>2</sub></b>	ethyl acetate	396	318	
	CH <sub>2</sub> Cl <sub>2</sub>	395	310	<0.01
<b>DPF-O</b>	ethyl acetate	538	322	
	CH <sub>2</sub> Cl <sub>2</sub>	≈550	310	0.04

$\lambda_{Em}$ : Emission maxima;  $\lambda_{Ex}$ : Excitation wavelength;  $\Phi_{PL}$ : Photoluminescence quantum yield.

## 4 Photodegradation Experiments

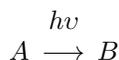
Absorption spectra were recorded on a Varian Cary 50 Bio UV-Visible spectrometer and fluorescence spectra on a Varian Cary Eclipse Fluorescence spectrometer using 10.0 x 10.0 mm quartz cuvettes. For the studies on degradation a 1000 W Oriel Xe high pressure arc lamp was used equipped with a water-filter and an UG11-filter, providing an intensity of 15 - 20 mW/cm<sup>2</sup> at the position of the cuvette.

For the degradation experiments ethyl acetate was used as purchased (99.5% for analysis from ACROS Organics<sup>TM</sup>). The maximum water content was specified by the supplier to be 0.05%, agreeing well with our measurement of 0.025% by Fischer titration. The solutions were handled under air and also stirred under air during irradiation. Assuming oxygen saturation at an oxygen partial pressure of 0.21 atm, the oxygen concentration in the solutions is estimated to be around  $1 - 2 * 10^{-3}$  mol/L according to the literature<sup>12,13</sup>

Analytical LC was performed on a Waters Acquity UPLC equipped with a Waters LCT Premier XE Mass detector for high-resolution MS (HR-MS, ESI<sup>+</sup>-ionization) and with Waters Alliance systems (consisting of a Waters Separations Module 2695, a Waters Diode Array Detector 996 and a Waters LCT Premier XE Mass Detector).

### 4.1 Quantum Yield of Simple Photoreactions

Regarding a simple photoreaction



the change in concentration  $a$  of  $A$  can be expressed in the following way:

$$\frac{da}{dt} = -\varphi_A I_A. \quad (2)$$

In this equation  $\varphi_A$  denotes the quantum yield of the above mentioned reaction and  $I_A$  the number of absorbed (only by  $A$ ) photons per unit time and unit volume.<sup>14</sup> In a cuvette with coplanar windows, the intensity of the absorbed light  $I_A$  at a position  $z$  is given by

$$I_A(z) = \varepsilon_A^* a I(z) \quad (3)$$

with  $\varepsilon^*$  being the natural absorption coefficient and  $I(z)$  the intensity of light.<sup>15</sup> Under the constraints that monochromatic light is used, which propagates perpendicular to the windows with constant intensity in time and over the whole area of the cuvette window. Furthermore scattering and reflection are

<sup>12</sup>Clever, H. L.; Battino, R.; Miyamoto, H.; Yampolski, Y.; Young, C. L. IUPAC-NIST Solubility Data Series. 103. Oxygen and Ozone in Water, Aqueous Solutions, and Organic Liquids (Supplement to Solubility Data Series Volume 7). *J. Phys. Chem. Ref. Data*, **2014**, *43*, 033102-157.

<sup>13</sup>Fischer, F.; Pfeleiderer, G. Über die Löslichkeit von Sauerstoff in verschiedenen organischen Lösungsmitteln. *Z. Anorg. Allg. Chem.*, **1922**, *124*, 61 - 69.

<sup>14</sup>Mausser, H. *Formale Kinetik*, Bertelsmann Universitätsverlag: Düsseldorf, **1974**, p.135.

<sup>15</sup>Mausser, H. *Formale Kinetik*, Bertelsmann Universitätsverlag: Düsseldorf, **1974**, pp.167.

not taken into consideration.

Assuming that the absorption of  $B$  can be neglected,<sup>16</sup> the Lambert-Beer-Law ( $I(z) = I_0 e^{-z\varepsilon_A^* a}$ ) can be substituted into (2). This gives a measure for the intensity of absorbed light after a path length  $z$  in the absorbing medium:

$$I_A(z) = \varepsilon_A^* a I_0 e^{-z\varepsilon_A^* a} \quad (4)$$

To obtain the mean intensity of absorbed light  $I_A$  in the cuvette,  $I_A(z)$  needs to be integrated over the length  $l$  of the cuvette and divided by  $l$ :

$$I_A = \frac{1}{l} \int_0^l I_A(z) dz = \frac{I_0}{l} (1 - e^{-\varepsilon_A^* a l}) \quad (5)$$

For practical reasons, the natural extinction coefficient  $\varepsilon^*$  is substituted by the decadic extinction coefficient  $\varepsilon$ :

$$I_A = \frac{I_0}{l} (1 - 10^{-\varepsilon_A a l}) \quad (6)$$

Now,  $I_A$  in equation (1) can be substituted with equation (5) and  $\varepsilon_A a l$  by the extinction  $E_A$ :

$$\frac{da}{dt} = \frac{-\varphi_A I_0}{l} (1 - 10^{-E_A}) \quad (7)$$

Equation (6) only accounts for monochromatic light. In our setup, a broader range of wavelengths was used. Assuming, that  $\varphi_A$  is independent of the wavelength of irradiation, the term for the absorbed light (denoted by the index  $ir$ ) can be summed up over the range of irradiation wavelengths as follows:<sup>17</sup>

$$\boxed{\frac{da}{dt} = \frac{-\varphi_A}{l} \sum_{\lambda_{ir}} I_0(\lambda_{ir}) (1 - 10^{-E_A(\lambda_{ir})})} \quad (8)$$

The change of concentration of  $\frac{da}{dt}$  was determined by means of UV/Vis absorption spectroscopy. Regarding the reaction  $A \xrightarrow{h\nu} B$ , the absorbance (normalized over the length) for the sample is given by

$$\frac{1}{l} E = a\varepsilon_A + b\varepsilon_B \quad (9)$$

with  $a = a_0 - \alpha a_0 = a_0(1 - \alpha)$  and  $b = a_0\alpha$ , with  $a_0$  being the initial concentration of A and  $\alpha$  being the degree of reaction. This leads to the following expression for the absorbance during the reaction:

$$\frac{1}{l} E = a_0(1 - \alpha)\varepsilon_A + a_0\alpha\varepsilon_B = a_0(\varepsilon_A + \alpha(\varepsilon_B - \varepsilon_A)). \quad (10)$$

The time derivative of equation (9) is given by:

$$\frac{1}{l} \frac{dE}{dt} = (\varepsilon_B - \varepsilon_A) a_0 \frac{d\alpha}{dt} \quad (11)$$

<sup>16</sup>This assumption is valid at the very beginning of the photoreaction and if  $\varepsilon_B$  is considerably smaller than  $\varepsilon_A$ . Here, we only used the first few per cent of conversion for the analysis of the kinetics.

<sup>17</sup>Integration would be the formally correct operation at this point, the summation accounts for the numeric processing of the recorded spectral data.

The time derivative of the concentration  $\frac{da}{dt} = -a_0 \frac{d\alpha}{dt}$  allows for further simplification:

$$\frac{1}{l} \frac{dE}{dt} = (\varepsilon_A - \varepsilon_B) \frac{da}{dt} = \varepsilon_A \beta \frac{da}{dt} \quad (12)$$

with  $\beta = \frac{\varepsilon_A - \varepsilon_B}{\varepsilon_A}$  being a factor that describes to which extent a change in concentration of A leads to a change in absorbance. In case  $\varepsilon_B$  is not known,  $\beta$  was determined by UPLC-UV/Vis-spectroscopy. In equation (7),  $\frac{da}{dt}$  was substituted according to equation (11), leading to the following expression for the reaction quantum yield ( $\lambda_{obs}$  is the wavelength at which the change of absorbance is detected):

$$\varphi_A = -\frac{dE(\lambda_{obs})}{dt} \cdot \frac{1}{\varepsilon_A(\lambda_{obs})\beta} \cdot \frac{1}{\sum_{\lambda_{ir}} I_0(\lambda_{ir})(1 - 10^{-E_A(\lambda_{ir})})} \quad (13)$$

Unfortunately we were not able to determine the actual intensity  $I_0$  at the cuvette. However, for the determination of the proportion of the quantum yield of the different compounds, the relative intensity of the irradiation wavelengths is suited, as well. The relative intensity will be referred to as  $I_0^*$ . The output power (power per area and wavelength interval) of the Xenon arc lamp is more or less constant over the range of irradiation wavelengths ( $\approx 300 - 400$  nm) we used.<sup>18</sup> This was converted to photons per area and time and multiplied by the transmittance of the UG11 filter to give the relative light intensity  $I_0^*$ , as depicted in figure S4.1.

Now, a number  $\varphi^*$  can be determined, that is in linear relationship to the actual quantum yield:

$$\varphi_A^* = -\frac{dE(\lambda_{obs})}{dt} \cdot \frac{1}{\varepsilon_A(\lambda_{obs})\beta} \cdot \frac{1}{\sum_{\lambda_{ir}} I_0^*(\lambda_{ir})(1 - 10^{-E_A(\lambda_{ir})})} \quad (14)$$

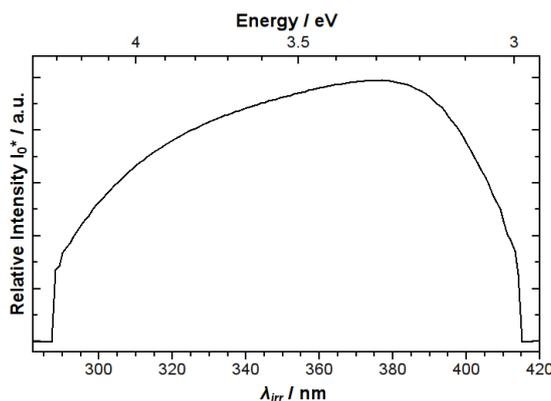


Figure S4.1: Estimated relative light intensity for the degradation experiments.

<sup>18</sup>ORIEL PRODUCT TRAINING: Spectral Irradiance, p. 26, downloaded June 12, 2014 at [http://assets.newport.com/webDocuments-EN/images/Light\\_Sources.pdf](http://assets.newport.com/webDocuments-EN/images/Light_Sources.pdf)

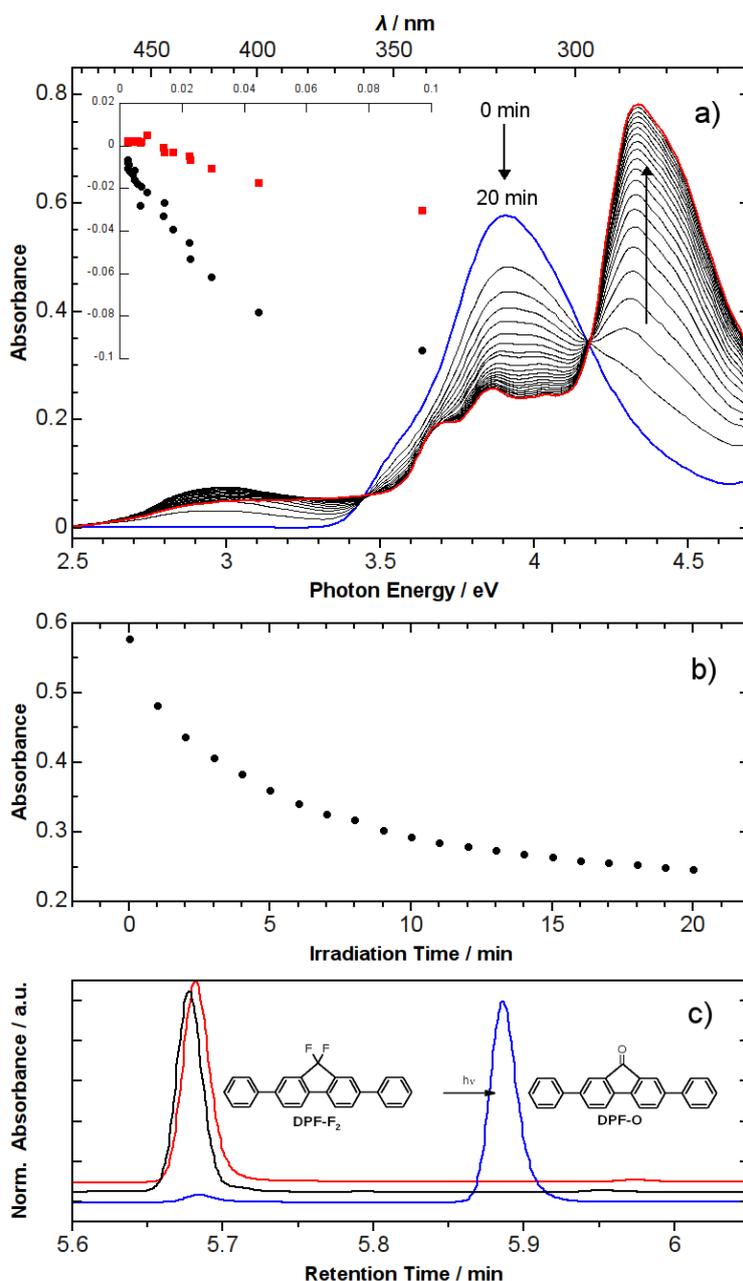
4.2 Photodegradation of DPF-F<sub>2</sub>, DPF-Ph<sub>2</sub>, and DPF-sp

Figure S4.2: Photochemical degradation of **DPF-F<sub>2</sub>** in ethyl acetate with light of 290 - 410 nm. a) Changes in the absorption (initial concentration:  $1.30 \cdot 10^{-5}$  mol L<sup>-1</sup>), time interval: 1 min. Inset: Extinction difference (ED) plot, ED at 285 nm vs ED at 320 nm (black circles), ED at 420 nm vs. ED at 320 nm (red squares). b) Absorbance at 317 nm vs. irradiation time. c) Absorption trace ( $280 \pm 5$  nm) of liquid chromatography runs of pristine **DPF-F<sub>2</sub>** (blue), degraded **DPF-F<sub>2</sub>** (black), as well as **DPF-O** (red).

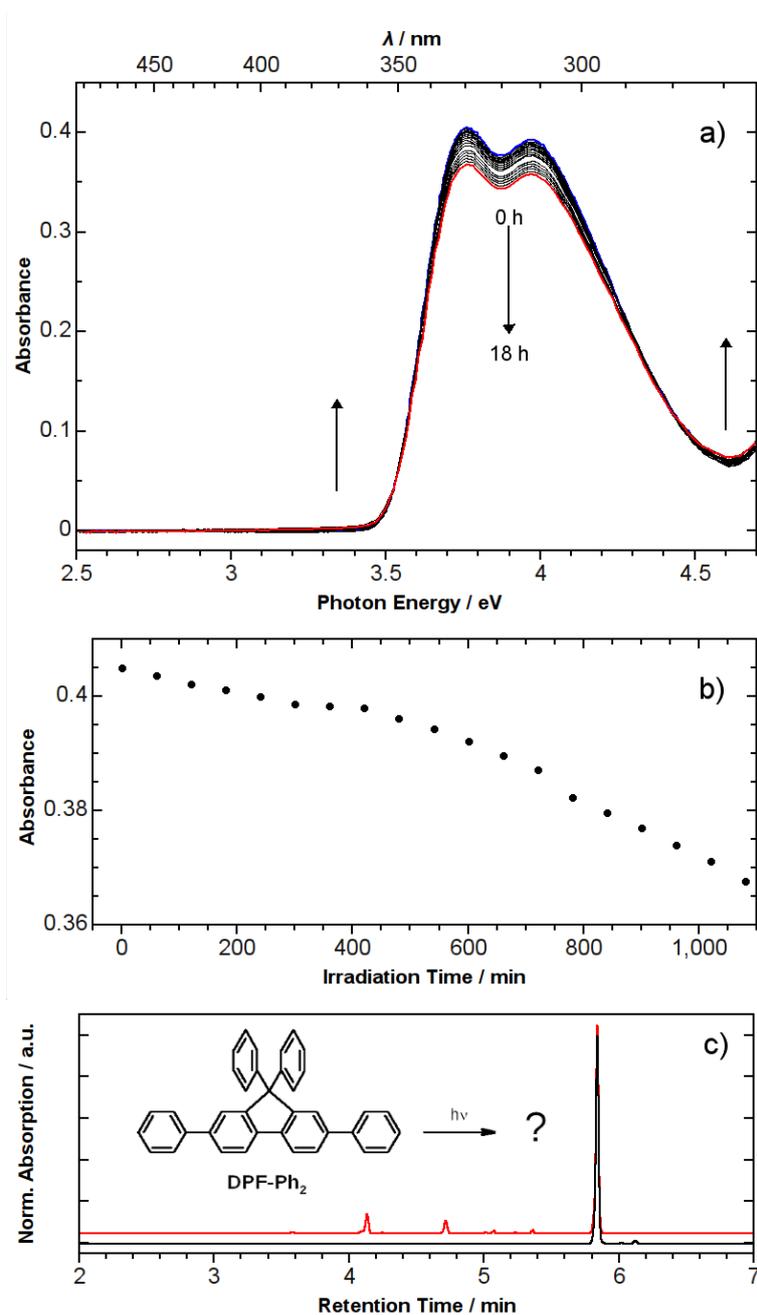


Figure S4.3: Photochemical degradation of **DPF-Ph<sub>2</sub>** in ethyl acetate with light of 290 - 410 nm. a) Changes in the absorption (initial concentration:  $1.04 \cdot 10^{-5} \text{ mol L}^{-1}$ ), time interval: 1 h. b) Absorbance at 330 nm vs. irradiation time. c) Absorption trace ( $330 \pm 5 \text{ nm}$ ) of liquid chromatography runs of pristine **DPF-Ph<sub>2</sub>** (black), and degraded **DPF-Ph<sub>2</sub>** (red).

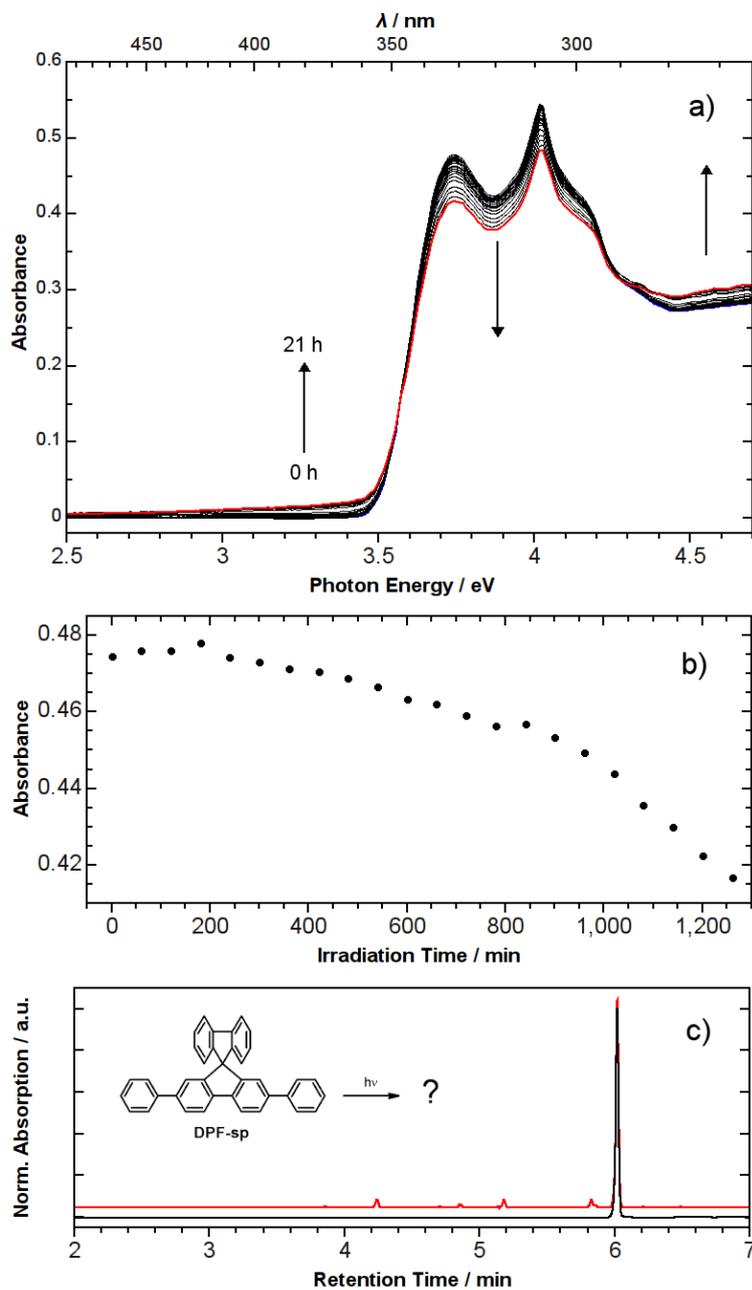


Figure S4.4: Photochemical degradation of **DPF-sp** in ethyl acetate with light of 290 - 410 nm. a) Changes in the absorption (initial concentration:  $1.24 \cdot 10^{-5}$  mol L<sup>-1</sup>), time interval: 1 h. b) Absorbance at 332 nm vs. irradiation time. c) Absorption trace (330  $\pm$  5 nm) of liquid chromatography runs of pristine **DPF-sp** (black), and degraded **DPF-sp**(red).

## 5 NMR-Spectra

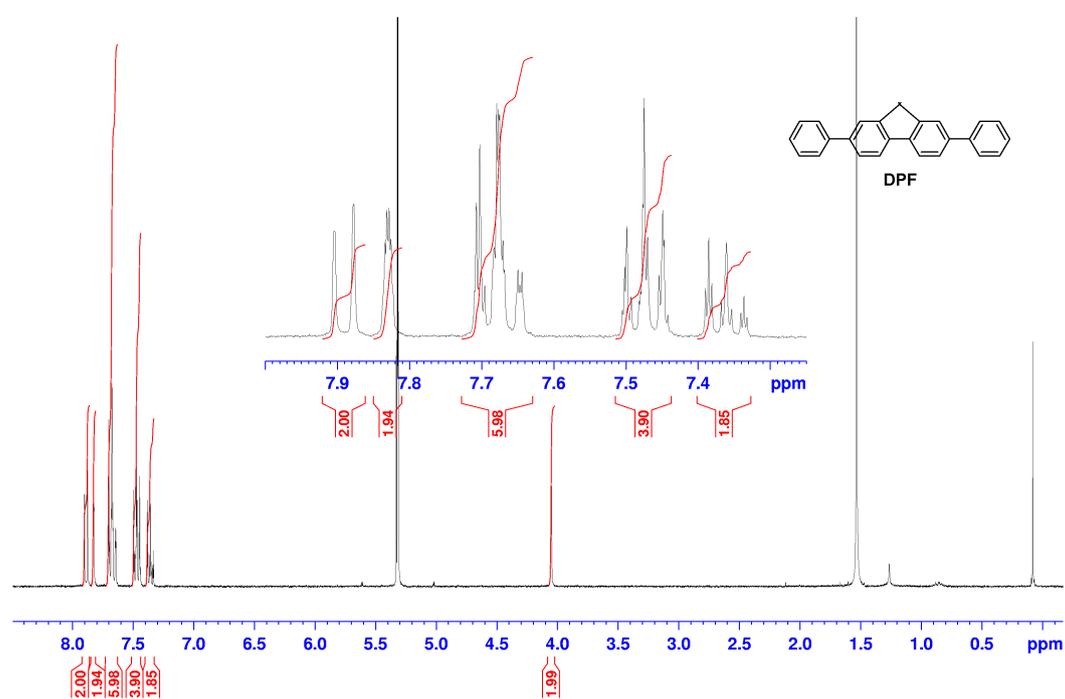


Figure S5.1:  $^1\text{H-NMR}$  spectrum of **DPF**.

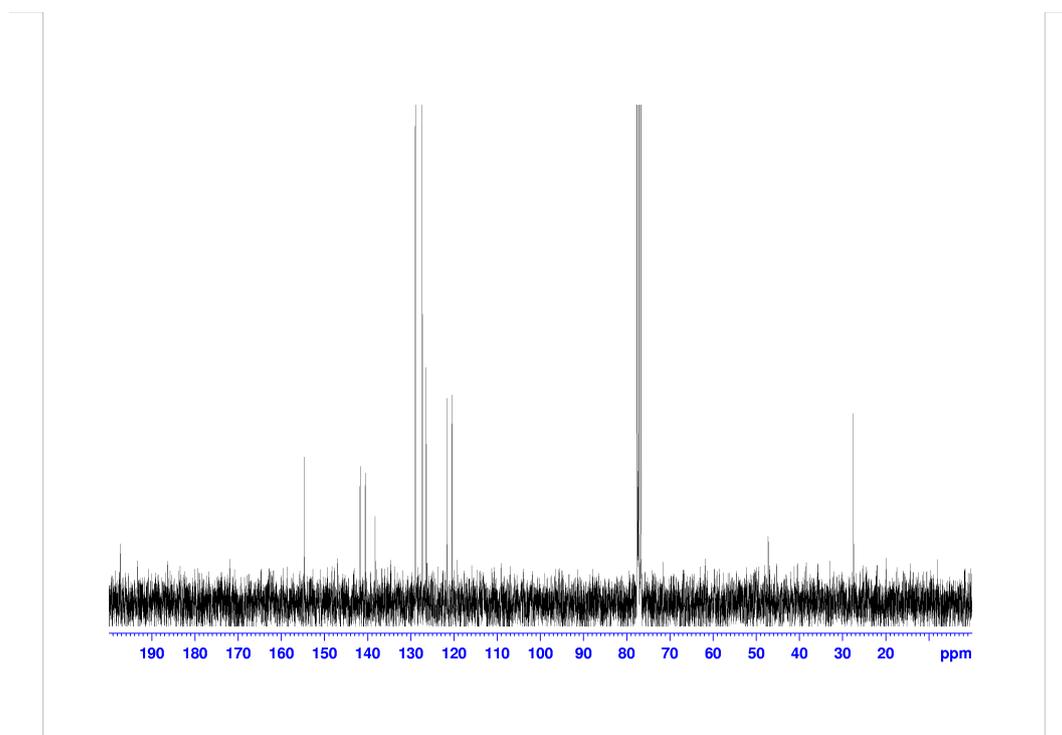
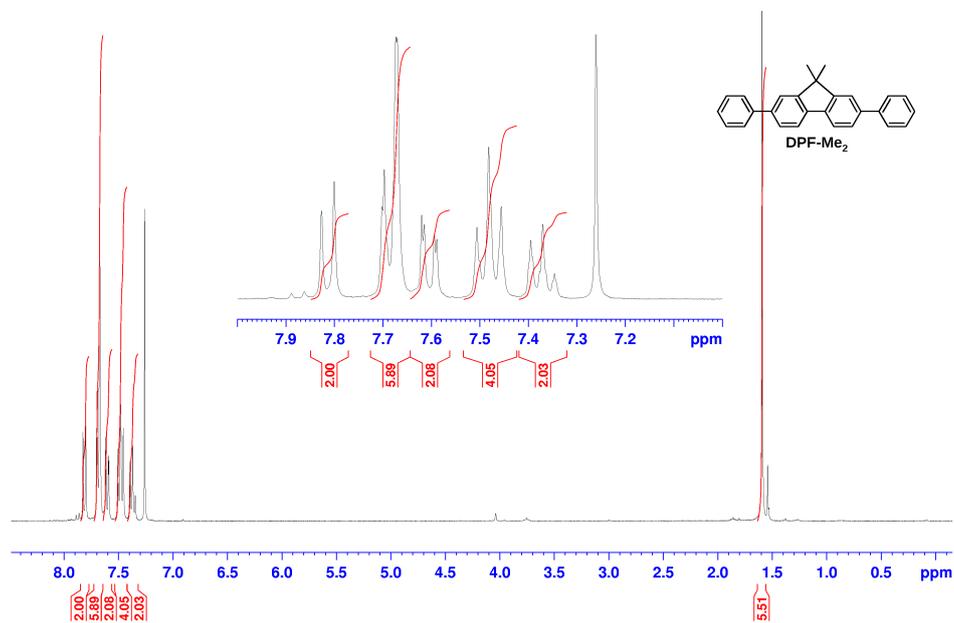
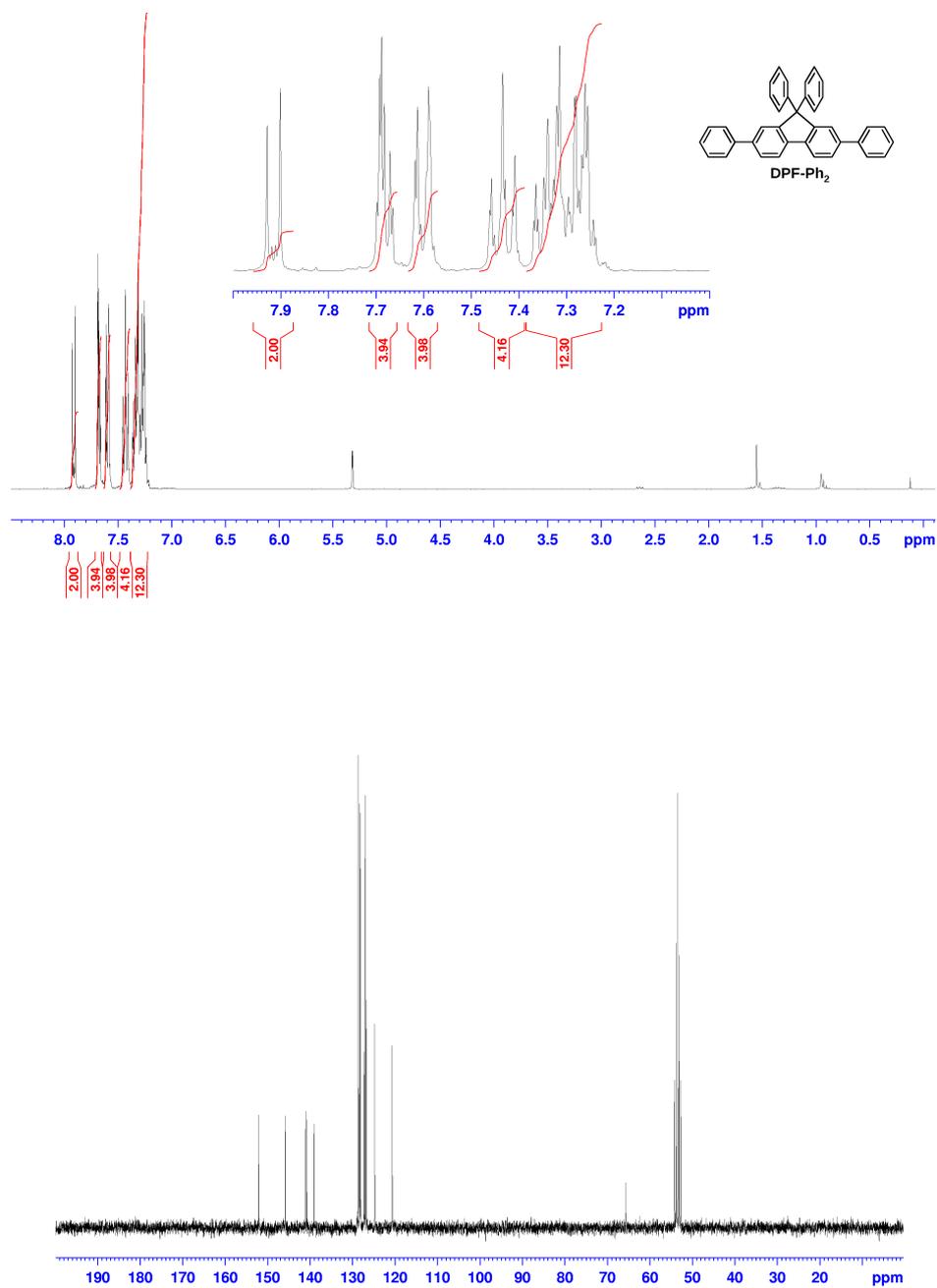
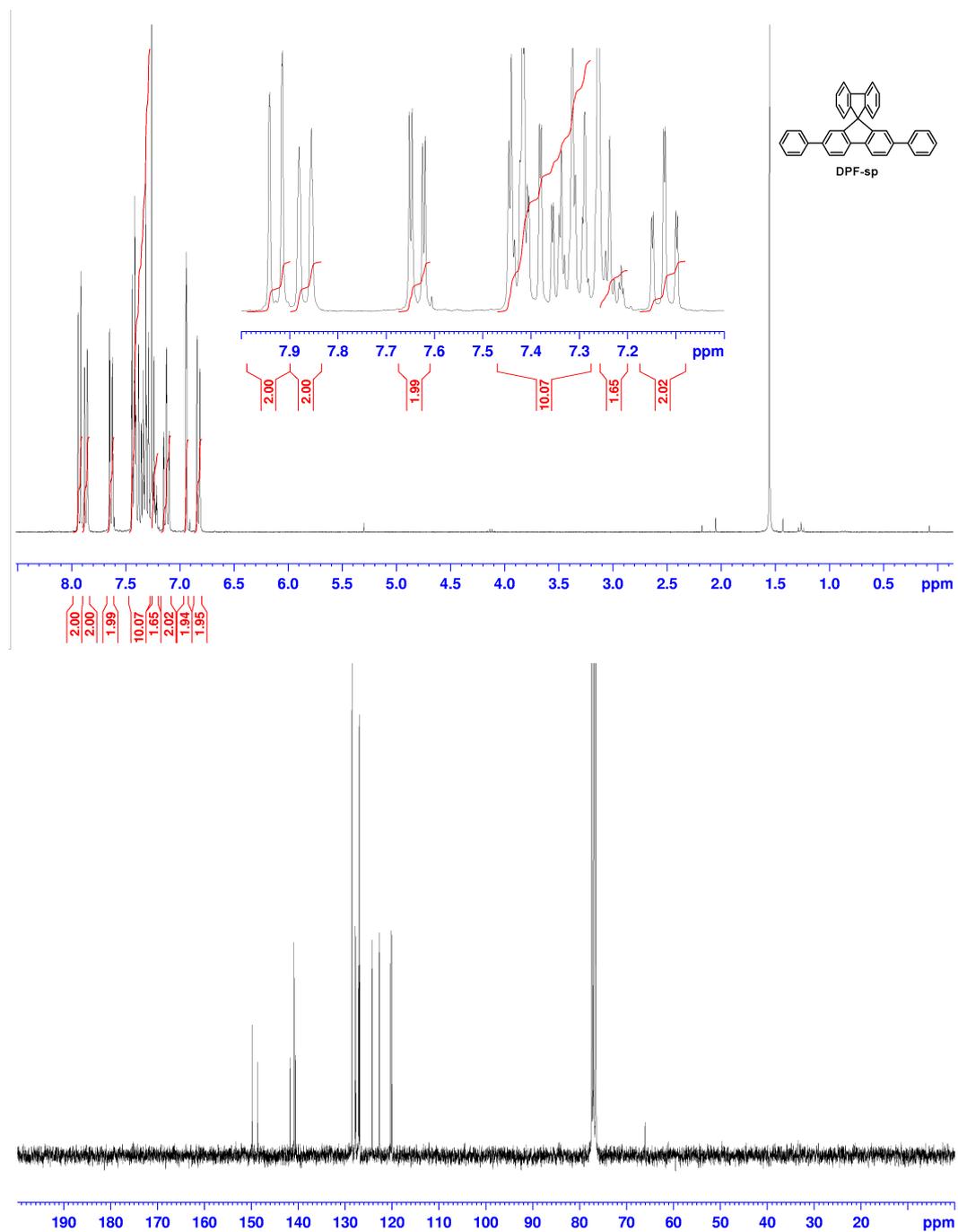
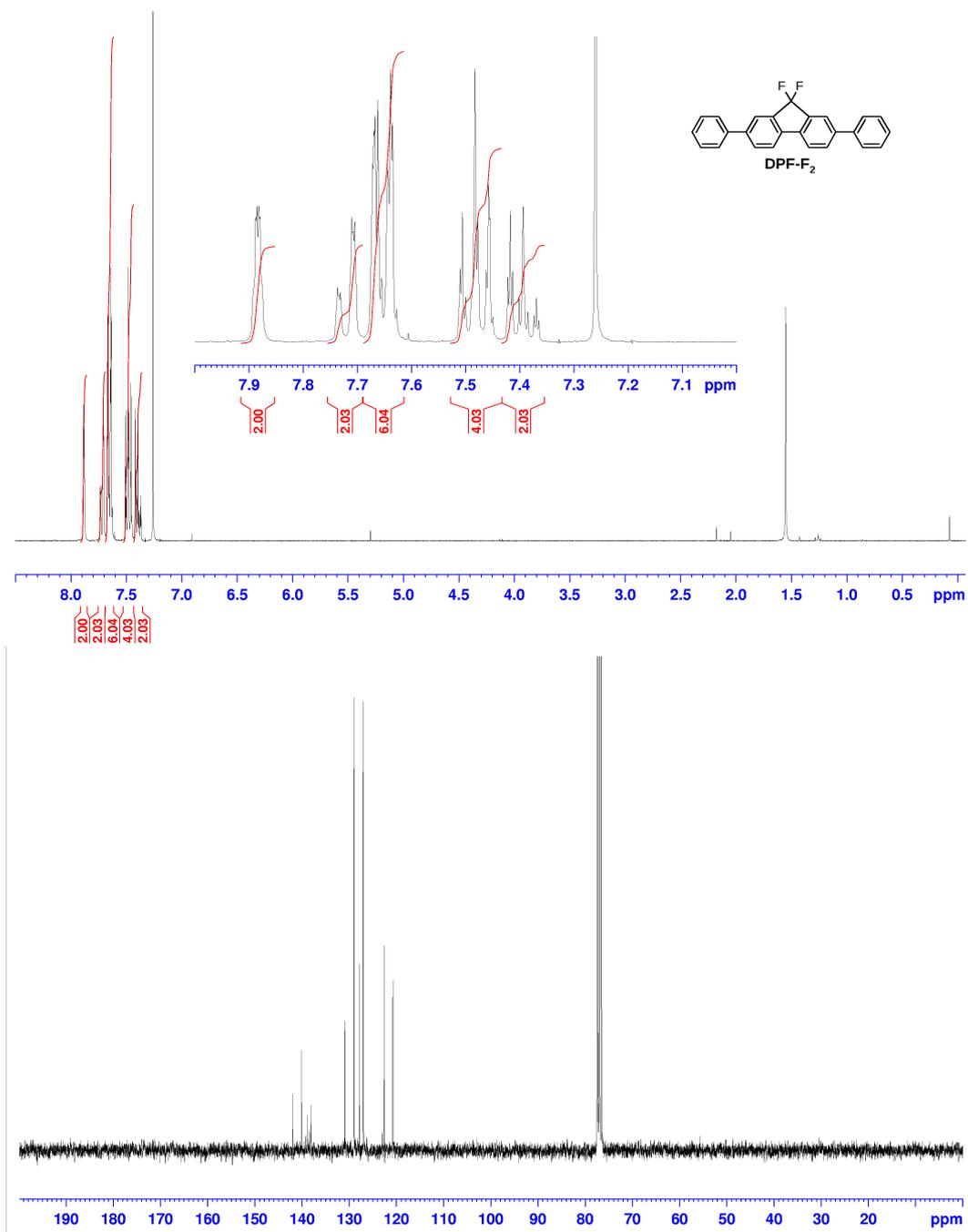
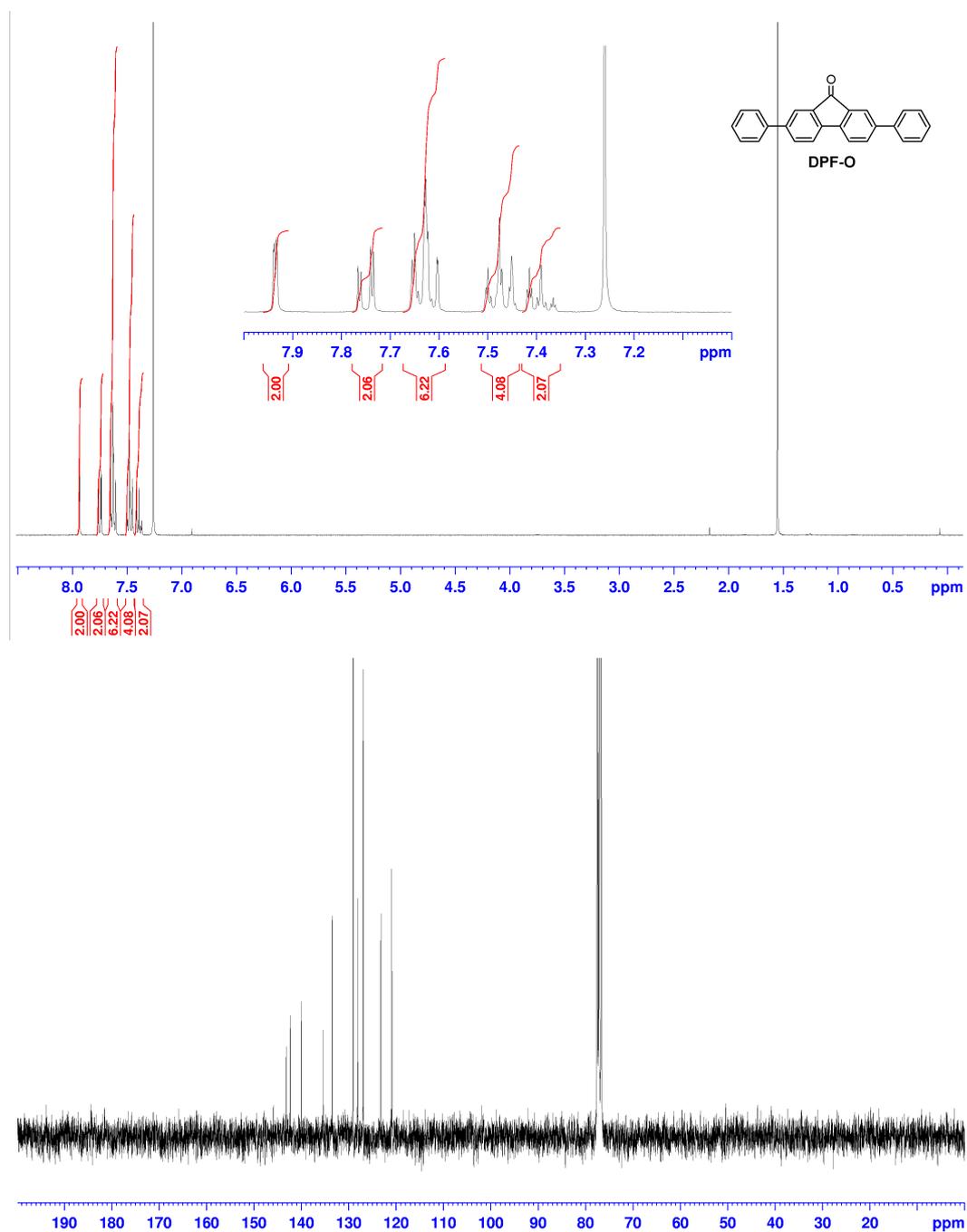


Figure S5.2:  $^1\text{H-NMR}$  (top) and  $^{13}\text{C-NMR}$  spectrum (bottom) of **DPF-Me<sub>2</sub>**.

Figure S5.3: <sup>1</sup>H-NMR (top) and <sup>13</sup>C-NMR spectrum (bottom) of DPF-Ph<sub>2</sub>.

Figure S5.4:  $^1\text{H-NMR}$  (top) and  $^{13}\text{C-NMR}$  spectrum (bottom) of **DPF-sp**.

Figure S5.5: <sup>1</sup>H-NMR (top) and <sup>13</sup>C-NMR spectrum (bottom) of **DPF-F<sub>2</sub>**.

Figure S5.6:  $^1\text{H-NMR}$  (top) and  $^{13}\text{C-NMR}$  spectrum (bottom) of **DPF-O**.