

## Supporting Information

### Crystal structures of 9,9-disubstituted fluorene derivatives bearing methyl, hydroxymethyl or pyridinylmethyl groups

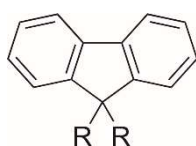
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## 1. Examples of reported crystal structures of 9,9-disubstituted fluorenes



**Table S1:** 1. Examples of reported crystal structures of 9,9-disubstituted fluorenes

R	Literature*
Benzoylmethyl	Mori et al.
3-Bromopropyl	Wang et al.
4-( <i>N-tert</i> -Butylaminoxyl)phenyl	Shultz et al.
2-Carboxyethyl	Feng et al.
4-(2-Chloroethoxy)phenyl	Shah et al. (2010a)
2-Cyanoethyl	Liu et al.
4-(Di- <i>p</i> -tolylamino)phenyl	Jiao et al.
Ethoxycarbonyl	Hu et al. (2006)
2-Hydroxyethyl	Alder et al.
4-Hydroxy-3-methylphenyl	Toda et al.
2-(Methoxycarbonyl)ethyl	Hu et al. (2005)
4-(Prop-2-yn-1-yloxy)phenyl	Shah et al. (2010b)

\* References [17–28] in the article.

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## 2. Crystallographic and structure refinement data of the crystal structures 1-3 and 2a

**Table S2:** Crystallographic and structure refinement data of the crystal structures examined.

Compound	1	2	2a
Empirical formula	C <sub>15</sub> H <sub>14</sub>	C <sub>15</sub> H <sub>14</sub> O <sub>2</sub>	4 C <sub>15</sub> H <sub>14</sub> O <sub>2</sub> · 2 C <sub>7</sub> H <sub>8</sub>
Formula weight	194.26	226.26	1089.31
Crystal system	Orthorhombic	Orthorhombic	Triclinic
Space group	<i>Iba</i> 2	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> -1
<i>a</i> (Å)	15.193(2)	6.0106(3)	11.503(4)
<i>b</i> (Å)	21.892(4)	12.0412(6)	14.280(4)
<i>c</i> (Å)	6.8654(13)	16.2062(9)	19.347(7)
$\alpha$ (°)	90.0	90.0	108.93(2)
$\beta$ (°)	90.0	90.0	104.87(2)
$\gamma$ (°)	90.0	90.0	91.12(2)
<i>V</i> (Å <sup>3</sup> )	2283.4(7)	1172.92(11)	2887.2(16)
<i>Z</i>	8	4	2
<i>F</i> (000)	832	480	1160
<i>D</i> <sub>c</sub> (Mg m <sup>-3</sup> )	1.130	1.281	1.253
$\mu$ (mm <sup>-1</sup> )	0.063	0.084	0.080
Data collection			
Temperature (K)	153(2)	123(2)	123(2)
No. of collected reflections	8949	14990	30484
Within the $\theta$ -limit (°)	3.1 - 26.5	3.0 - 26.0	2.6 - 27.0
Index ranges $\pm h, \pm k, \pm l$	-19/19, -27/26, -8/8	-7/7, -14/14, -19/19	-12/14, -18/18, -24/24
No. of unique reflections	2242	2304	12395
<i>R</i> <sub>int</sub>	0.0516	0.0380	0.0743
Refinement calculations: full-matrix least-squares on all <i>F</i> <sup>2</sup> values			
Weighting expression <i>w</i> <sup>a</sup>	$[\sigma^2(F_o^2) + (0.0684P)^2 + 0.8266P]^{-1}$	$[\sigma^2(F_o^2) + (0.0227P)^2 + 0.3170P]^{-1}$	$[\sigma^2(F_o^2) + (0.0411P)^2 + 1.9745P]^{-1}$
No. of refined parameters	139	162	773
No. of F values used [ <i>I</i> > 2σ( <i>I</i> )]	1871	2106	6800
Final <i>R</i> -Indices			
<i>R</i> (=Σ Δ <i>F</i>   / Σ  <i>F</i> <sub>o</sub>  )	0.0495	0.0301	0.0576
<i>wR</i> on <i>F</i> <sup>2</sup>	0.1462	0.0695	0.1524
<i>S</i> (=Goodness of fit on <i>F</i> <sup>2</sup> )	1.188	1.150	1.064
Final Δρ <sub>max</sub> /Δρ <sub>min</sub> (e Å <sup>-3</sup> )	0.16/-0.15	0.15/-0.14	0.25/-0.34

<sup>a</sup>  $P = (F_o^2 + 2F_c^2)/3$

**Table S2:** Continued

Compound	<b>3</b>
Empirical formula	C <sub>25</sub> H <sub>20</sub> N <sub>2</sub>
Formula weight	348.43
Crystal system	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> (Å)	11.0151(3)
<i>b</i> (Å)	12.9054(4)
<i>c</i> (Å)	13.0023(3)
$\alpha$ (°)	90.0
$\beta$ (°)	100.0760(6)
$\gamma$ (°)	90.0
<i>V</i> (Å <sup>3</sup> )	1819.82(8)
<i>Z</i>	4
<i>F</i> (000)	736
<i>D</i> <sub>c</sub> (Mg m <sup>-3</sup> )	1.272
$\mu$ (mm <sup>-1</sup> )	0.075
Data collection	
Temperature (K)	100(2)
No. of collected reflections	24934
Within the $\theta$ -limit (°)	2.2 - 29.4
Index ranges $\pm h, \pm k, \pm l$	-15/15, -17/17, -17/17
No. of unique reflections	5000
<i>R</i> <sub>int</sub>	0.0220
Refinement calculations: full-matrix least-squares on all <i>F</i> <sup>2</sup> values	
Weighting expression <i>w</i> <sup>a</sup>	$[\sigma^2(F_o^2) + (0.0633P)^2 + 0.6077P]^{-1}$
No. of refined parameters	244
No. of F values used [ <i>I</i> > 2σ( <i>I</i> )]	4547
Final <i>R</i> -Indices	
<i>R</i> (=Σ Δ <i>F</i>   / Σ  <i>F</i> <sub>o</sub>  )	0.0416
<i>wR</i> on <i>F</i> <sup>2</sup>	0.1146
<i>S</i> (=Goodness of fit on <i>F</i> <sup>2</sup> )	1.045
Final Δρ <sub>max</sub> /Δρ <sub>min</sub> (e Å <sup>-3</sup> )	0.39/-0.23

<sup>a</sup>  $P = (F_o^2 + 2F_c^2)/3$

### 3. Geometric parameters for non-covalent interactions in the crystal structures 1-3 and 2a

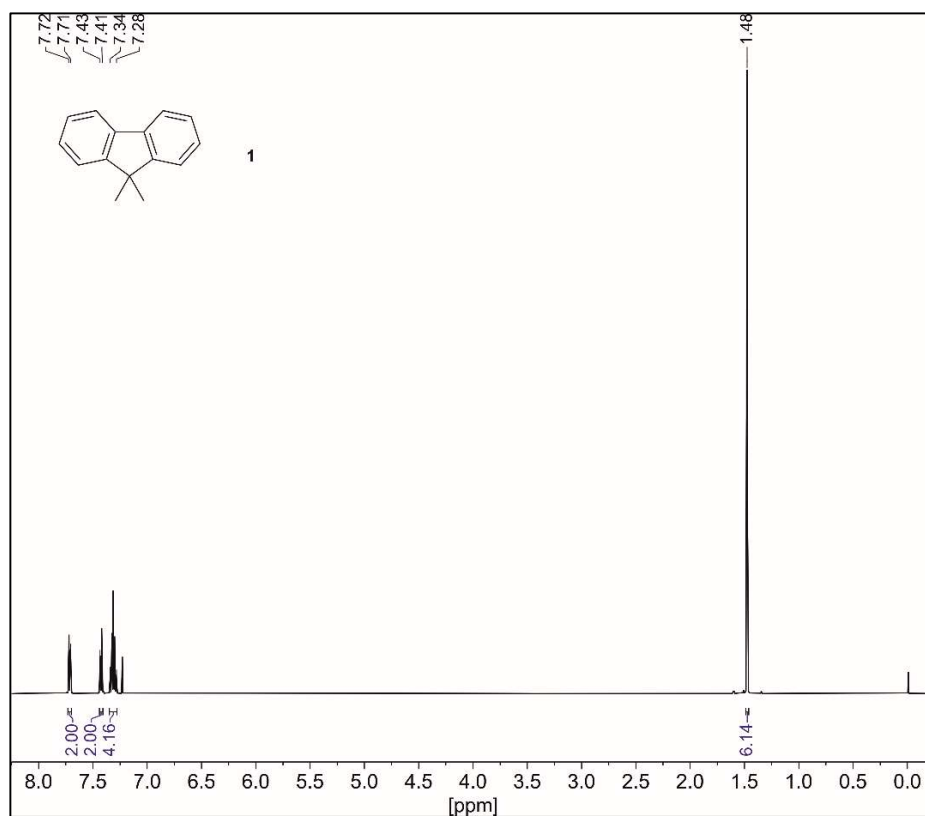
**Table S3:** Geometric parameters for non-covalent interactions in the crystal structures examined.

Atoms		Distance (Å)		Angle (°)	Slippage (Å)
D-H...A		D...A	H...A	D-H...A	
C-H... $\pi$		C...Cg	H...Cg	C-H...Cg	
$\pi$ ... $\pi$		Cg...Cg			
<b>1</b>					
C(3)-H(3)...Cg(A)	$x, 1-y, 0.5+z$	3.812(2)	2.95	151	
C(9)-H(9)...Cg(B)	$0.5-x, 1.5-y, -0.5+z$	3.786(2)	2.84	176	
C(12)-H(12)...Cg(B)	$1-x, y, 0.5+z$	3.889(2)	3.01	155	
<b>2</b>					
O(1)-H(1)...O(2)	$1+x, y, z$	2.672(2)	1.86(2)	160(3)	
O(2)-H(2)...O(1)	$-0.5+x, 0.5-y, 1-z$	2.702(2)	1.87(2)	165(3)	
C(4)-H(4)...Cg(A)	$0.5+x, 1.5-y, 1-z$	3.556(2)	2.67	157	
Cg(A)...Cg(B)	$1+x, y, z$	4.121(2)			1.026
Cg(B)...Cg(A)	$-1+x, y, z$	4.121(2)			0.991
<b>2a</b>					
O(1A)-H(1A)...O(1D)	$x, y, z$	2.736(3)	1.93(2)	160(5)	
O(2A)-H(2A)...O(2C)	$1+x, y, z$	2.695(3)	1.91(2)	154(3)	
O(1B)-H(1B)...O(2D)	$-1+x, y, z$	2.671(3)	1.83(1)	174(4)	
O(2B)-H(2B)...O(1C)	$x, y, z$	2.663(3)	1.86(2)	161(4)	
O(1C)-H(1C)...O(1B)	$x, y, z$	2.677(3)	1.90(2)	152(3)	
O(2C)-H(2C)...O(1A)	$x, y, z$	2.705(3)	1.91(2)	157(6)	
O(1C)-H(1C)...O(1B)	$x, y, z$	2.677(3)	1.90(2)	152(3)	
O(2C)-H(2C)...O(1A)	$x, y, z$	2.705(3)	1.91(2)	157(6)	
C(15A)-H(15A)...O(1D)	$x, y, z$	3.386(4)	2.58	139	
C(14C)-H(14F)...O(1B)	$x, y, z$	3.385(3)	2.59	137	
C(3A)-H(3A)...Cg(E)	$1+x, y, z$	3.564(3)	2.77	142	
C(3B)-H(3B)...Cg(G) <sup>a</sup>	$x, y, z$	3.646(3)	2.83	145	
C(12C)-H(12C)...Cg(B) <sup>a</sup>	$x, y, z$	3.598(3)	2.81	141	
C(12D)-H(12D)...Cg(D) <sup>a</sup>	$1+x, y, z$	3.860(3)	2.90	149	
C(15A)-H(15B)...Cg(D) <sup>a</sup>	$1-x, 1-y, 1-z$	3.860(3)	2.88	169	
C(15B)-H(15C)...Cg(B) <sup>a</sup>	$1-x, 1-y, 1-z$	3.913(3)	2.97	160	
C(15D)-H(15H)...Cg(E) <sup>a</sup>	$1-x, -y, 1-z$	3.690(3)	2.73	164	
C(17A)-H(17A)...C(10C) <sup>b</sup>	$x, y, z$	3.675(3)	2.82	150	
C(6B)-H(6B)...Cg(J) <sup>a</sup>	$-x, 1-y, -z$	3.665(3)	2.85	144	
C(6D)-H(6D)...Cg(J) <sup>a</sup>	$x, -1+y, z$	3.728(3)	2.91	144	
<b>3</b>					
C20-H(20A)...N(1)	$x, y, z$ (intra)	3.190(1)	2.66	113	
C(17)-H(17)...N(2)	$0.5-x, 0.5+y, 0.5-z$	3.472(1)	2.60	154	
C(22)-H(22)...Cg(A)	$1.5-x, -0.5+y, 0.5-z$	3.456(1)	2.71	136	

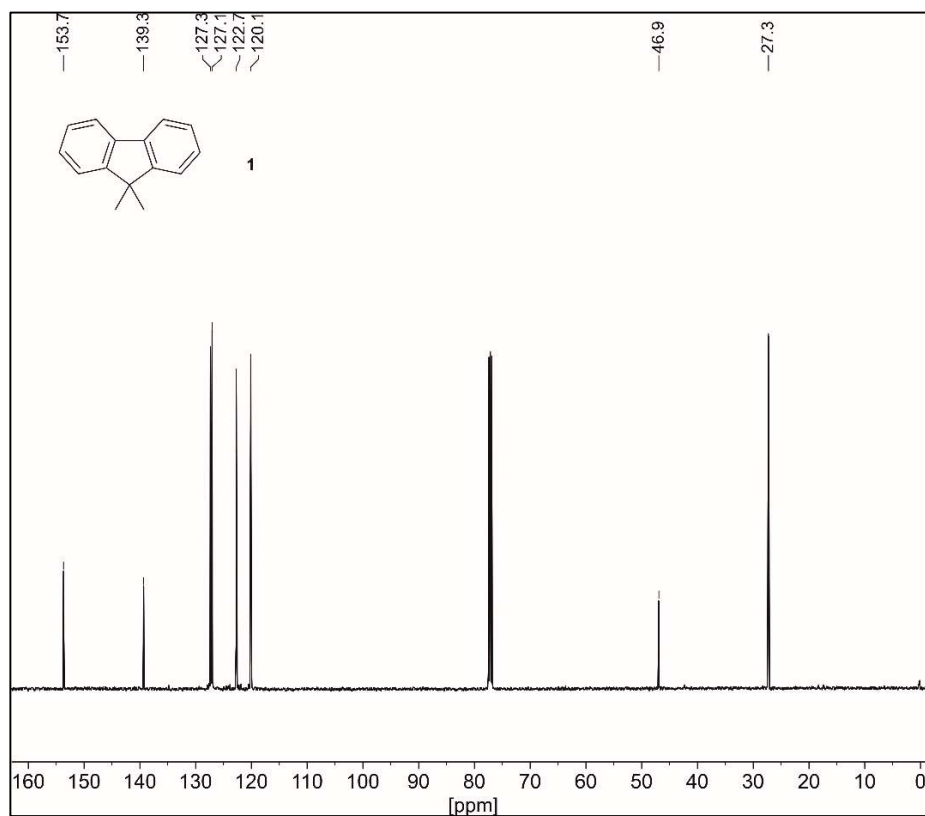
<sup>a</sup> Cg means the centroid (centre of gravity) of the aromatic ring. <sup>b</sup> An individual ring atom instead of the ring centre was chosen as the acceptor site.

**1, 2:** Ring A: C(2)...C(7); ring B: C(8)...C(13). **2a:** Ring B: C(8A)...C(13A); ring D: C(8B)...C(13B); ring E: C(2C)...C(7C); ring G: C(2D)...C(7D); ring J: C(16B)...C(21B). **3:** Ring A: C(2)...C(7). **4:** Ring A: C(2A)...C(7A); ring C: C(2B)...C(7B).

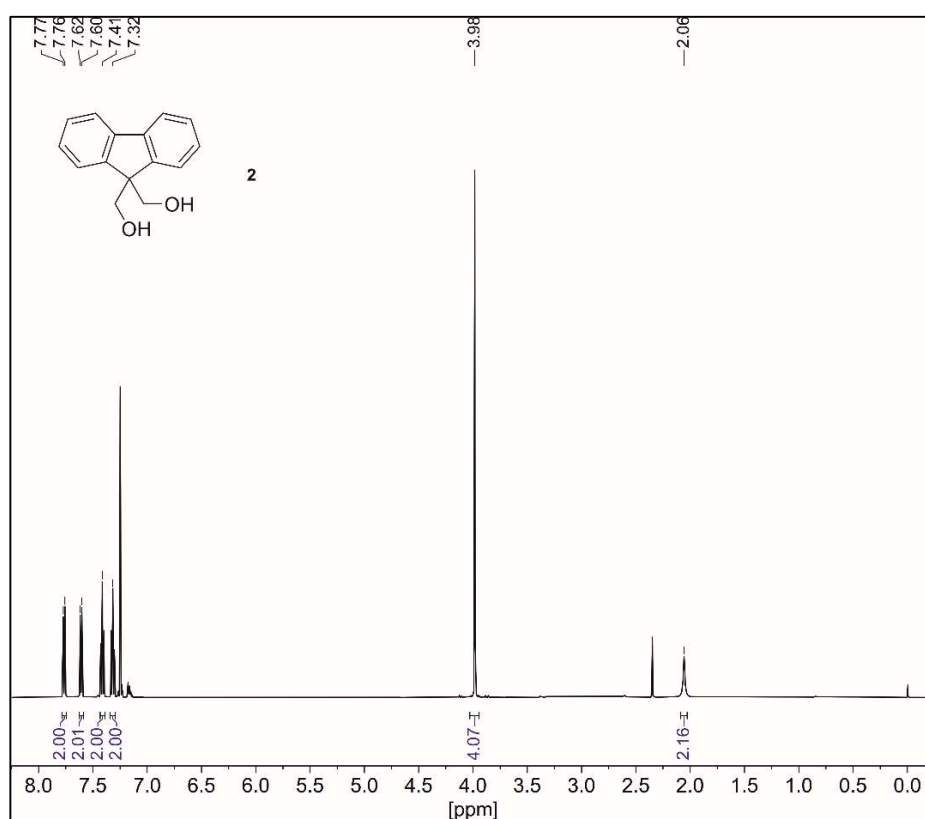
#### 4. $^1\text{H}$ - and $^{13}\text{C}$ -NMR spectra of compounds 1-4 (Figures S1-S6)



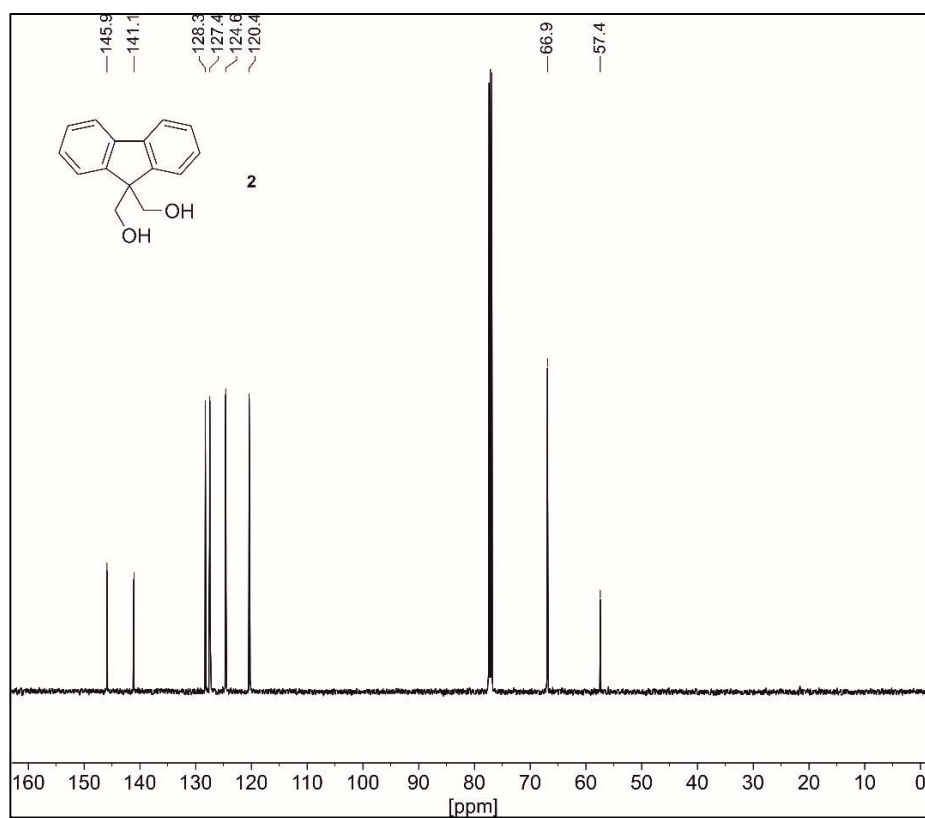
**Figure S1.**  $^1\text{H}$  NMR (500 MHz) spectrum of **1** in  $\text{CDCl}_3$ .



**Figure S2.**  $^{13}\text{C}$  NMR (125 MHz) spectrum of **1** in  $\text{CDCl}_3$ .

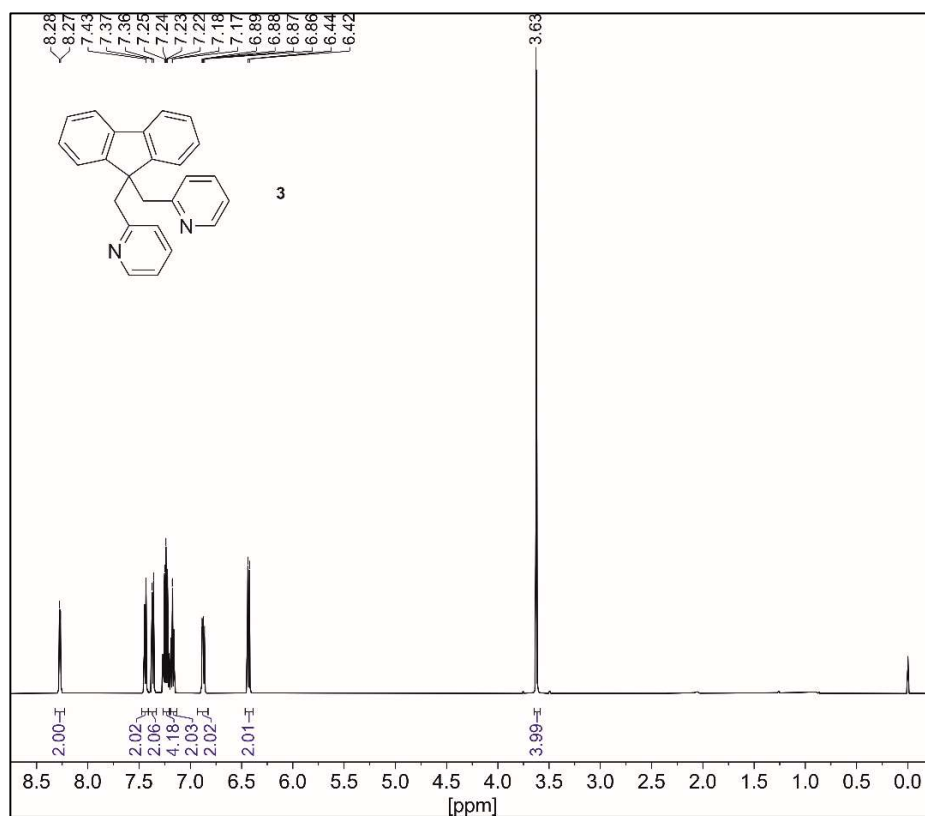


**Figure S3.**  $^1\text{H}$  NMR (500 MHz) spectrum of **2** in  $\text{CDCl}_3$ .

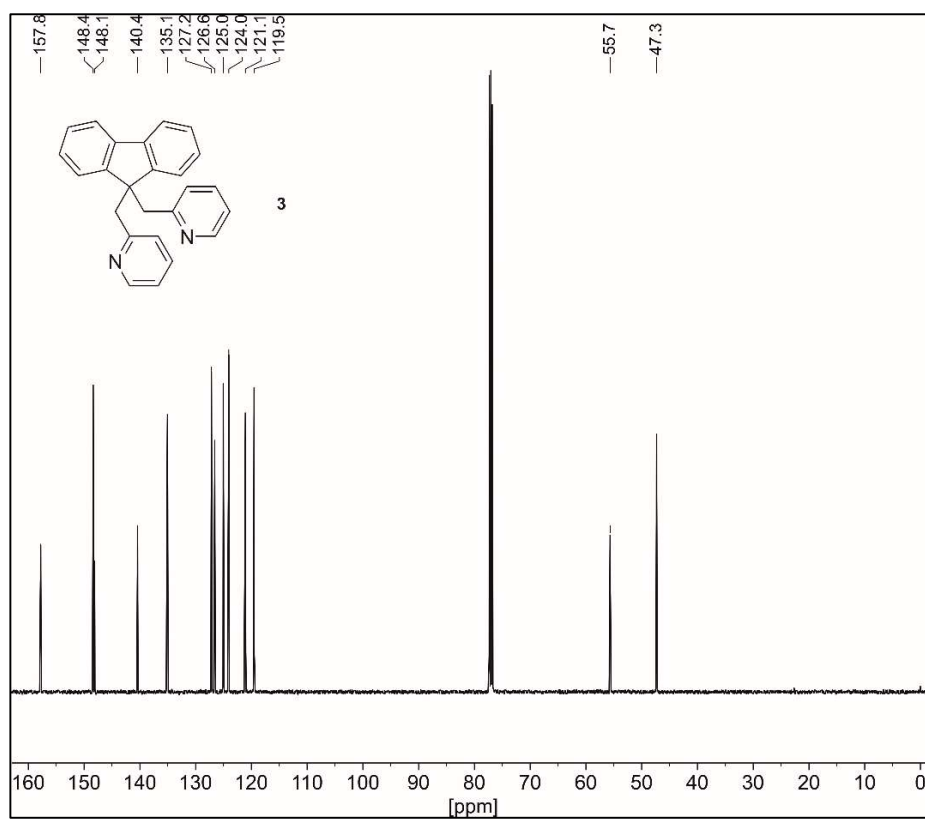


**Figure S4.**  $^{13}\text{C}$  NMR (125 MHz) spectrum of **2** in  $\text{CDCl}_3$ .





**Figure S5.**  $^1\text{H}$  NMR (500 MHz) spectrum of **3** in  $\text{CDCl}_3$ .



**Figure S6.**  $^{13}\text{C}$  NMR (125 MHz) spectrum of **3** in  $\text{CDCl}_3$ .

## 5. Synthetic procedures of compounds 1-3

**9,9-Dimethyl-9H-fluorene (1)** [Shaya *et al.*]. Fluorene (22.4 g, 135 mmol) and potassium hydroxide powder (39.4 g, 702 mmol) were suspended in dimethyl sulfoxide (230 mL) and cooled to room temperature using a water bath. Then, methyl iodide (28 mL, 450 mmol) was added over 60 minutes to the red colored reaction mixture. After stirring for about 20 hours, the mixture was poured on water (150 mL) and extracted three times with hexanes (3 x 75 mL). The combined organic phases were washed once with distilled water (100 mL). The mixture was then dried over sodium sulfate, filtered, and the solvent was removed under vacuum. After recrystallization from methanol, colorless plates are obtained as crystals. Yield 93 % (24.3 g, 125 mmol); m. p. 366 K. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm): δ = 1.48 (s, 6H), 7.28–7.34 (m, 4H), 7.41–7.43 (m, 2H), 7.71–7.72 (m, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm): δ = 27.3, 46.9, 120.1, 122.7, 127.1, 127.3, 139.3, 153.7.

**9,9-Bis(hydroxymethyl)-9H-fluorene (2)** [Nakazano *et al.*]. Fluorene (10.0 g, 60.3 mmol) and paraformaldehyde (14.5 g, 481 mmol) were suspended in dimethyl sulfoxide (60 mL) under a nitrogen atmosphere, degassed in an ultrasonic bath, and cooled to 0 °C. Then, a 5 M sodium methanolate solution (5.88 g, 256 mmol sodium, and 50 mL methanol) was added to the reaction mixture. While stirring at 0 °C for 60 minutes, a discoloration is observed from orange to yellow. After acidifying with conc. hydrochloric acid and adding water (120 mL), the aqueous phase was extracted four times with ethyl acetate (40 mL). The organic phase was dried over sodium sulfate, filtered, and the solvent was removed by distillation. Finally, recrystallization is performed using toluene/hexanes (colorless plates) or toluene/ethanol (colorless blocks). Yield 55 % (7.45 g, 32.9 mmol); m. p. 408–410 K. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm): δ = 2.06 (s, 2H), 3.98 (s, 4H), 7.32 (dt, 2H), 7.41 (dt, 2H), 7.61 (ddd, 2H), 7.77 (ddd, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm): δ = 57.4, 66.9, 120.4, 124.6, 127.4, 128.3, 141.1, 145.9.

**9,9-Bis(pyridin-2-ylmethyl)-9H-fluorene (3)** [Earl *et al.*]. Fluorene (1.0 g, 6.01 mmol) and 2-bromomethylpyridine (3.2 g, 12.7 mmol) were dissolved in toluene (20 mL). Furthermore, a spatula tip of Aliquat 336 and a 50% potassium hydroxide solution (10 mL) were added. The mixture was stirred for 10 h at 60 °C and the organic phase was separated. The aqueous phase was extracted with toluene (3 x 10 mL), and the organic phases were combined and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under vacuum and the residue was recrystallized from *n*-hexane/toluene. Yield 43 % (906 mg, 2.60 mmol); m. p. 396–397 K. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm): δ = 3.63 (s, 4H), 6.42–6.45 (m, 2H), 6.85–6.90 (m, 2H), 7.15–7.20 (m, 2H), 7.20–7.28 (m, 4H), 7.35–7.38 (m, 2H), 7.42–7.45 (m, 2H), 8.26–8.29 (m, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm): δ = 47.3, 55.7, 119.5, 121.1, 124.0, 125.0, 126.6, 127.2, 135.1, 140.4, 148.1, 148.4, 157.8.

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Notice: References [31–33] in the article.