

**Unparalleled fluorescence of a polyazomethine prepared from the self-condensation of an
automer and its potential use as a fluorimetric sensor for explosive detection**

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Experimental Methods

Absorption measurements were done on a Varian Cary 500 spectrometer and fluorescence measurements were performed on an Edinburgh Instrument FLSP-920 spectrometer after deaerating the samples for 20 minutes with dry nitrogen. Absolute fluorescence quantum yield measurements were using an integrating sphere.

Synthesis

2,7-Dibromo-9,9-dihexylfluorene (7). A suspension of **6** (5.00 g, 15 mmol), NaOH (3.7 g, 66 mmol) and potassium iodide (0.37 g, 2.2 mmol) in DMSO was stirred for 15 min at 60°C. To the purple suspension, 1-hexylbromide (6.2 g, 37.5 mmol) was added, and the mixture was kept under stirring overnight at room temperature. The product was extracted with dichloromethane (40 mL) and the organic layer was washed with water and dried over Na₂SO₄. After removing the solvent under vacuum, the crude product was purified by a flash chromatography on silica gel (hexane/dichloromethane (3:1)) to afford **4** (6 g, 82%) as a white solid. ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.52 (dd, 2H, *J* = 6.8 Hz, *J* = 2.0 Hz), 7.46 (d, 2H, *J* = 1.6 Hz), 7.44 (d, 2H, *J* = 2 Hz), 1.94-1.89 (m, 4H), 1.14-1.10 (m, 12H), 0.78 (t, 6H, *J* = 6.8 Hz), 0.61-0.57 (s, 4H). ¹³C NMR (CDCl₃, 101 MHz): δ (ppm) 150.2, 138.8, 136.1, 130.4, 130.2, 128.0, 127.4, 126.3, 121.2, 120.6, 57.2, 45.2. HRMS: *m/z*_{cal} = 490.0865 [M+•], *m/z*_{mes} = 490.0842.

7-Bromo-9,9-dihexylfluorene-2-carboxaldehyde (8). To the solution containing **7** (2.0 g, 4.10 mmol) and tetramethylethylene diamine (732 μL, 4.88 mmol) in anhydrous THF (60 mL) purged with N₂ at -78°C was added 1.6 M *n*-butyl lithium in hexane (3.50 mL, 4.88 mmol) and the reaction was allowed to stir for 1 h. Afterwards, anhydrous DMF (360 μL, 4.88 mmol) was added

dropwise to the reaction mixture at -78°C , after which the temperature was allowed to warm to room temperature and stirred overnight. The reaction mixture was cooled to 0°C and 10% HCl was added until the solution was acidic. The solution was stirred for 2 h then the product was extracted in ether. The organic layer was isolated while the aqueous layer was washed with ether once more and the combined organic extracts were dried over Na_2SO_4 . The crude product was purified by flash chromatography on silica gel (hexane/dichloromethane (1:1)) to afford **8** (1.15 g, 65%) as a yellow solid. ^1H NMR (CDCl_3 , 400 MHz): δ (ppm) 10.05 (s, 1H), 7.88 (s, 1H), 7.84 (dd, 1H, $J = 7.9\text{ Hz}$, $J = 1.7\text{ Hz}$), 7.78 (d, 1H, $J = 7.9\text{ Hz}$), 7.61 (d, 1H, $J = 7.9\text{ Hz}$), 7.52 (d, 1H, $J = 1.5\text{ Hz}$), 7.48 (dd, 1H, $J = 7.9\text{ Hz}$, $J = 1.5\text{ Hz}$), 2.07-1.92 (s, 4H), 1.10-0.97 (s, 12H), 0.73 (t, 6H, $J = 6.4\text{ Hz}$), 0.63-0.53 (s, 4H). ^{13}C NMR (CDCl_3 , 100.6 MHz): δ (ppm) 192.3, 154.4, 151.3, 146.4, 138.7, 135.8, 130.7, 130.6, 126.6, 123.2, 122.4, 120.2, 55.7, 40.2, 31.6, 29.7, 23.8, 22.7, 14.1. HRMS: $m/z_{\text{cal}} = 441.1788$ $[\text{M}+\text{H}]^+$, $m/z_{\text{mes}} = 441.1803$.

2-(7-Bromo-9,9-dihexyl-9H-fluoren-2-yl)-1,3-dioxolane (9). To a solution of **8** (0.59 g, 1.3 mmol) in toluene (5 mL), ethylene glycol (298 μL , 5 mmol) and *para*-toluenesulphonic acid (3 mg, 1% molar) were added. The reaction was heated under reflux for 4 h using Dean-Stark apparatus. Subsequently, the reaction mixture was washed once with aqueous saturated NaHCO_3 (10 mL) and twice with brine (2 x 10 mL). Drying over Na_2SO_4 and evaporation of the solvent in vacuo gave **6** (0.59 g, 92%), which was sufficiently pure to be used in the next step without further purification. ^1H NMR ($(\text{CD}_3)_2\text{CO}$, 400 MHz): δ (ppm) 7.81-7.49 (m, 5H), 5.84 (s, 1H), 4.15-3.99 (d, 4H), 2.10-2.06 (m, 4H), 1.16-1.03 (m, 16H), 0.78 (t, 6H). ^{13}C NMR ($(\text{CD}_3)_2\text{CO}$, 100.6 MHz): δ (ppm) 154.2, 150.9, 141.6, 140.8, 139.0, 130.8, 126.9, 126.6, 122.3, 121.9, 121.7, 120.4, 104.5, 65.8, 56.2, 40.6, 31.1, 30.4, 30.2, 30.0, 29.8, 29.6, 29.5, 29.3, 24.4, 23.1, 14.3.

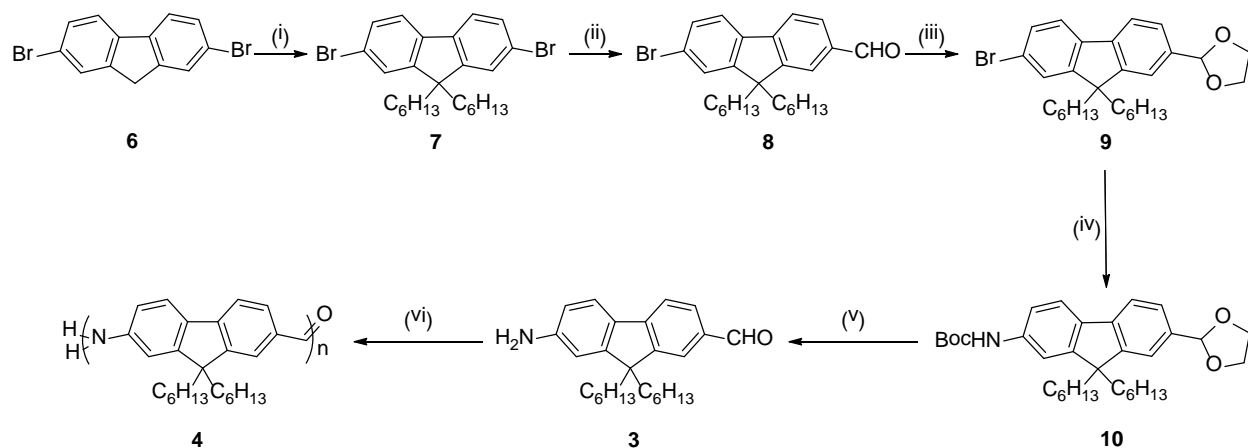
***tert*-Butyl 7-(1,3-dioxolan-2-yl)-9,9-dihexyl-9H-fluoren-2-ylcarbamate (10).** An air-dried glass reaction vessel equipped with a magnetic stir bar was charged with Pd₂(dba)₃•CHCl₃ (11 mg, 0.012 mmol), 2-di-*tert*-butylphosphino-2',4',6'-triisopropylbiphenyl (5.4 mg, 0.036 mmol), NaO-*t*-Bu (63 mg, 0.56 mmol), *tert*-butyl carbamate (58 mg, 0.5 mmol), and **9** (200 mg, 0.4 mmol). Anhydrous toluene (15 mL) was added, and the resultant solution was degassed using one cycle vacuum and nitrogen purge. The reaction mixture was stirred at room temperature under nitrogen. Once the reaction was judged complete by TLC (48 h), the reaction mixture was diluted with 20 mL of diethyl ether and filtered through a pad of Celite. The filtrate was concentrated in vacuo. The residue was purified by flash chromatography on alumina gel (hexane/Ethyl acetate (0.95:0.05)) to afford of **10** (160 mg, 74 %) as a colorless oil. ¹H NMR ((CD₃)₂CO, 400 MHz): δ (ppm) 8.47 (s, 1H), 7.91 (s, 1H), 7.70 (m, 3H), 7.51(d, 1H, *J* = 7.9 Hz), 7.50 (s, 1H), 7.41 (d, 1H, *J* = 1.5 Hz), 5.80 (s, 1H), 4.12 (m, 2H), 4.07 (m, 2H), 2.86 (s, 4H), 1.53 (s, 10H), 1.06 (m, 6H), 0.89 (t, 9H), 0.63-0.53 (s, 4H).

7-Amino-9,9-dihexyl-9H-fluorene-2-carbaldehyde (3). In dichloromethane (40 mL) was dissolved **10** (500 mg, 0.96 mmol). Silica (1 g) was added and the mixture was stirred for 48 h at room temperature. After complete transformation of **10** as determined by TLC, **3** was desorbed by filtering the silica and washing it with dichloromethane. The residue was purified by flash chromatography on silica gel (hexane/dichloromethane (1:1)) to afford pure **3** as a white solid (390 mg, 66%). ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 10.03 (s, 1H), 7.82 (d, 1H, *J* = 8 Hz), 7.73 (d, 1H, *J* = 8.4 Hz), 7.67 (d, 1H, *J* = 8 Hz), 7.44 (s, 1H), 7.361 (d, 1H, *J* = 8 Hz), 6.71 (s, 1H), 2.05-1.90 (m, 4H), 1.10-0.99 (m, 12H), 0.75 (t, 6H, *J* = 7.24 Hz), 0.70-0.49 (m, 4H). ¹³C NMR (CDCl₃, 100.6 MHz): δ (ppm) 192.8, 154.0, 152.9, 151.6, 147.9, 139.9, 135.1, 131.1, 123.3,

121.9, 119.7, 117.8, 113.2, 55.8, 40.7, 31.9, 30.0, 28.8, 24.1, 23.0, 14.4. HRMS: $m/z_{\text{cal}} = 378.2791$

$[\text{M}+\text{H}]^+$, $m/z_{\text{mes}} = 378.2775$.

Polyfluorenylazomethine (4). The polymerization was performed via the self-condensation of **3** (8.5 mg, 0.02 mmol) in toluene (2 mL) in a pressure tube. Both DABCO (excess) and neat TiCl_4 (500 μL , 0.45 mmol) were added and the tube was sealed and heated at 120°C . Periodically, the reaction vessel was cooled and aliquots were removed to follow the polymerization progress. Neat TiCl_4 (500 μL) was also added after the aliquot removal and prior to continuing heating. After 7 days of heating, the reaction mixture was cooled to room temperature and it washed with NaHCO_3 . The organic layer was extracted and the solvent was removed under vacuo. The resulting **4** was quantitatively isolated as a yellow powder after drying under vacuum overnight. $^1\text{H-NMR}$ (CDCl_3 , 400 MHz): δ (ppm) 10.1 (s, CHO-), 8.52 (m, N=CH-), 8.1-7.0 (m, FI-H), 2.0-0.7 (m, H-alkyl). $\text{DP}_n = 8$; $\text{M}_n = 2.1$ kg/mol.



Scheme S1. Synthetic route for the preparation of fluorene automer (**3**) and its polymerization: (i) DMSO, 50% NaOH, 1-bromohexane, room temperature, overnight; (ii) THF, *n*-BuLi/TMEDA, -78°C, DMF, room temperature, overnight; (iii) toluene, ethylene glycol, p-TSA, reflux, 4h, Dean-Stark; (iv) toluene, Pd₂(dba)₃•CHCl₃, ligand, NaO-*t*Bu, *tert*-butyl-aminocarbamate, room temperature, 2 days; (v) dichloromethane, silica gel, room temperature, 2 days, (vi) toluene, DABCO, TiCl₄, 110°C, 7 days.

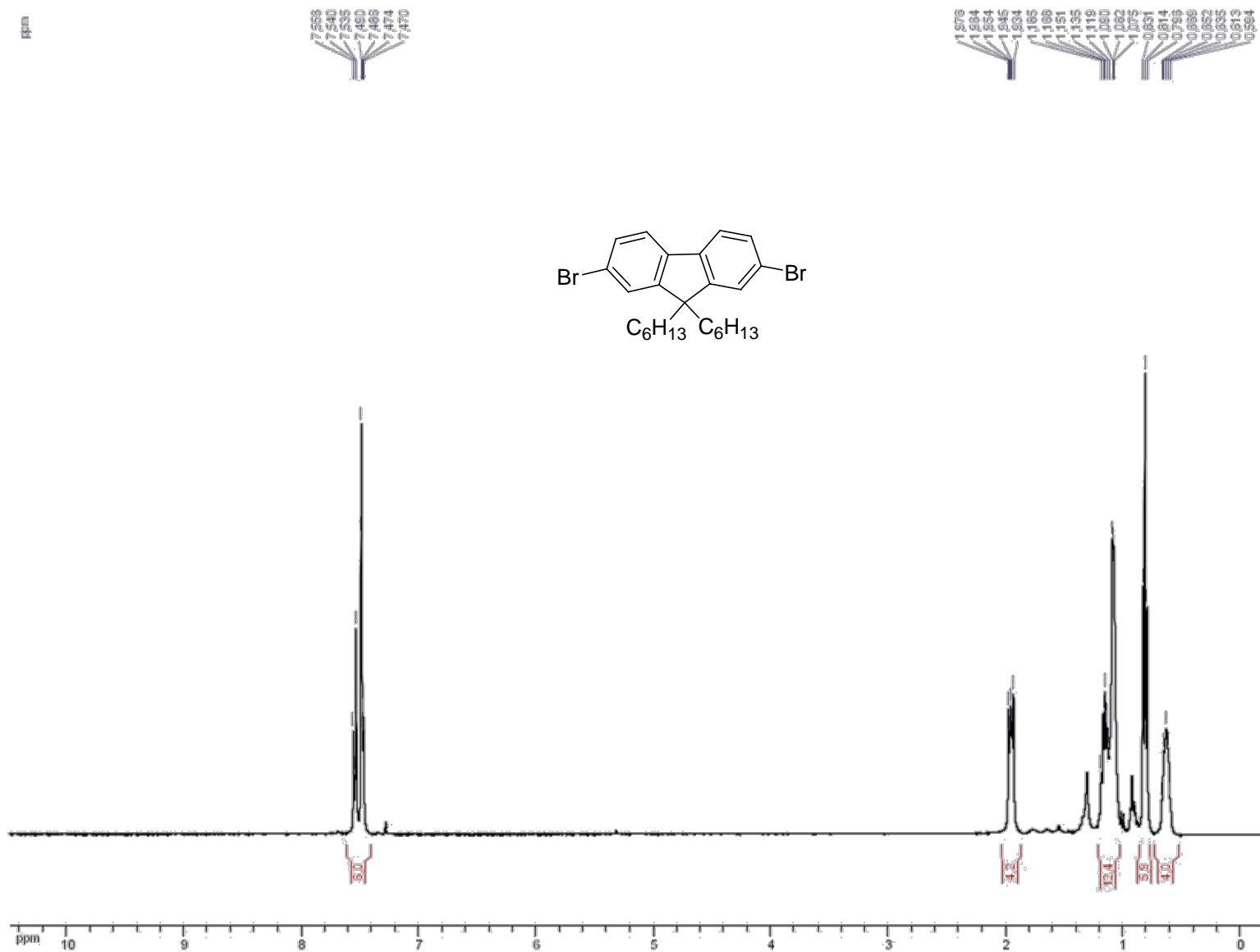


Figure S1. ¹H NMR spectrum of **7** in CDCl₃.

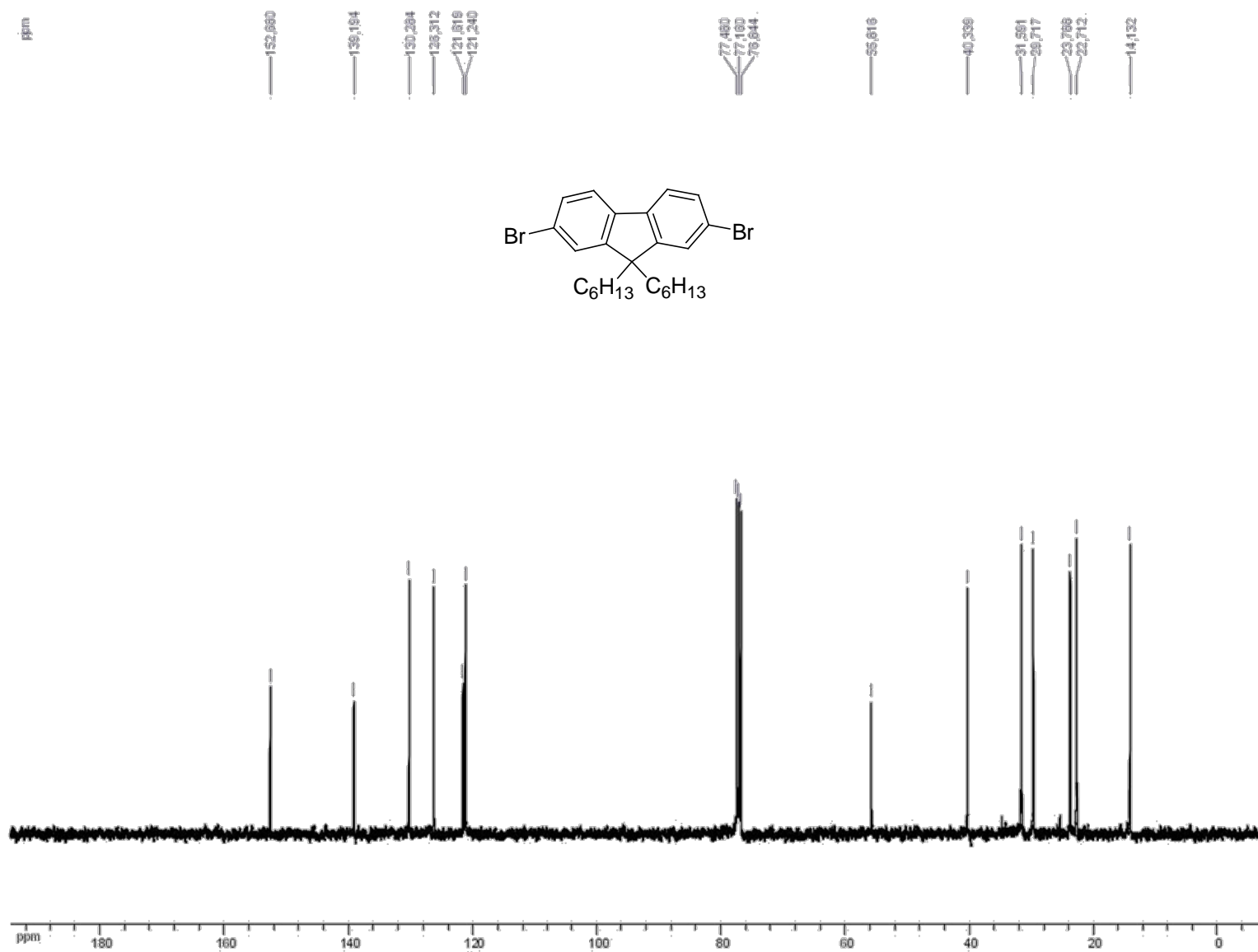


Figure S2. ^{13}C NMR of **7** in CDCl_3 .

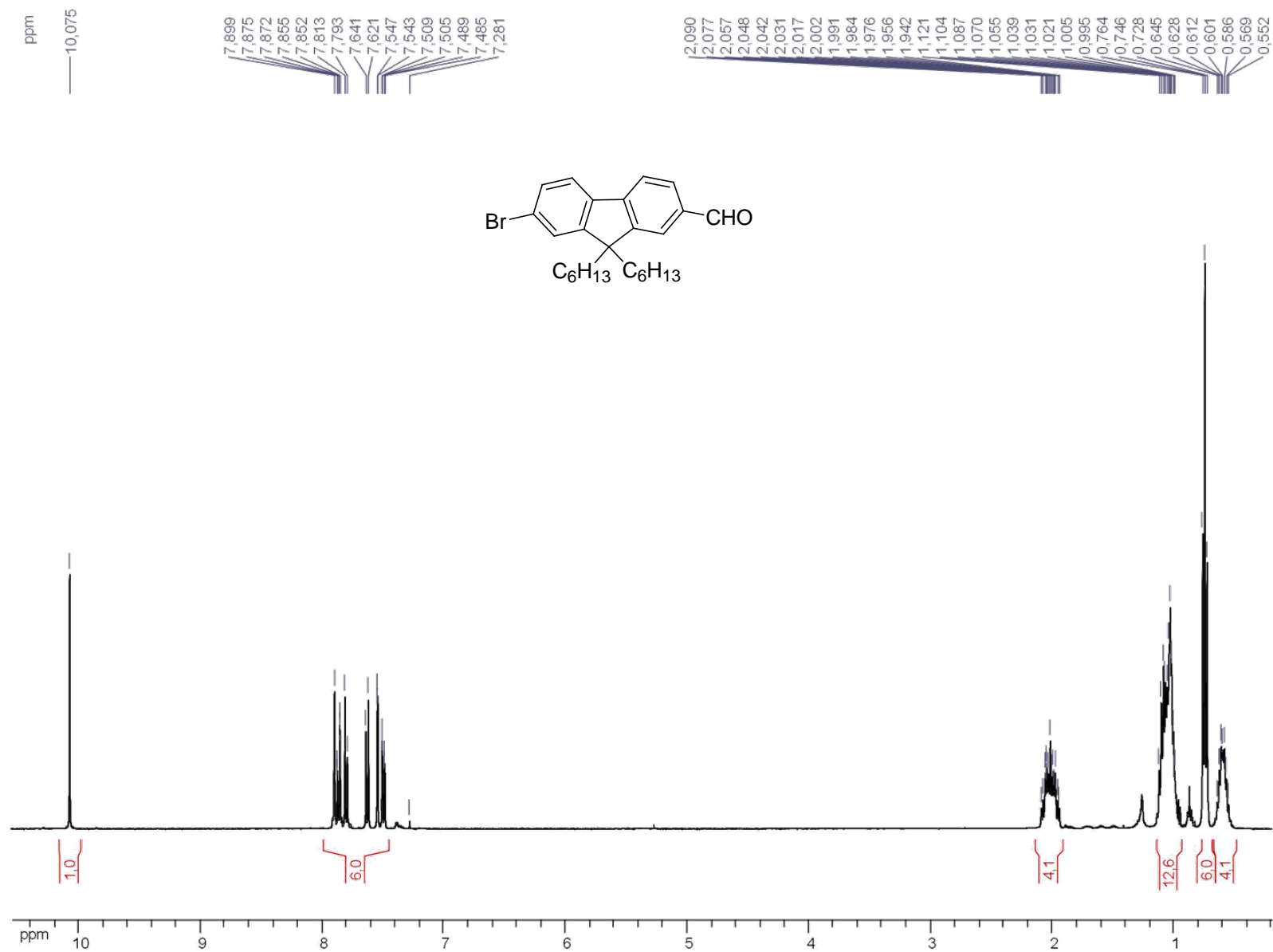


Figure S3. ^1H NMR spectrum of **8** in CDCl_3 .

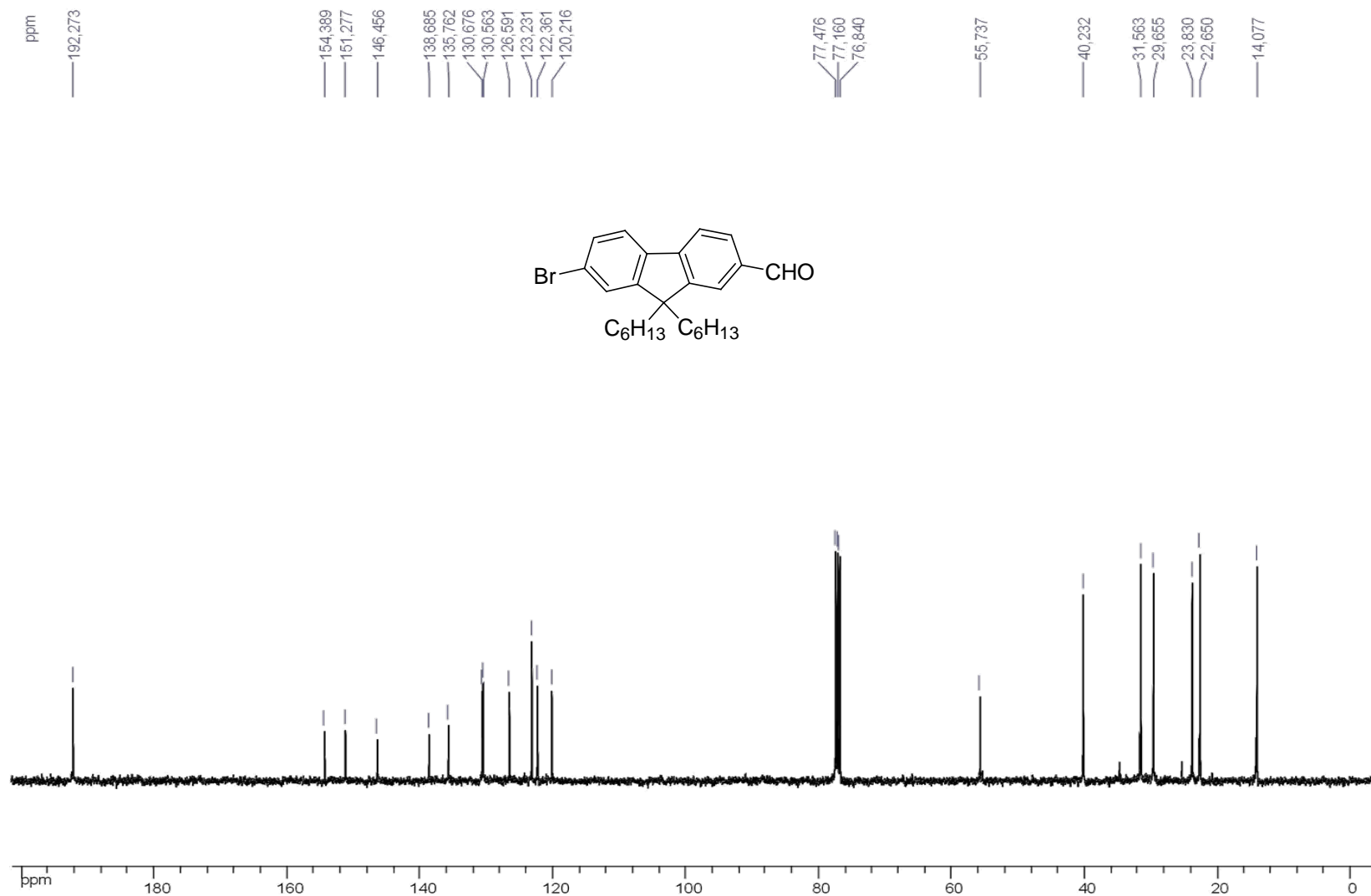


Figure S4. ^{13}C NMR spectrum of **8** in CDCl_3 .

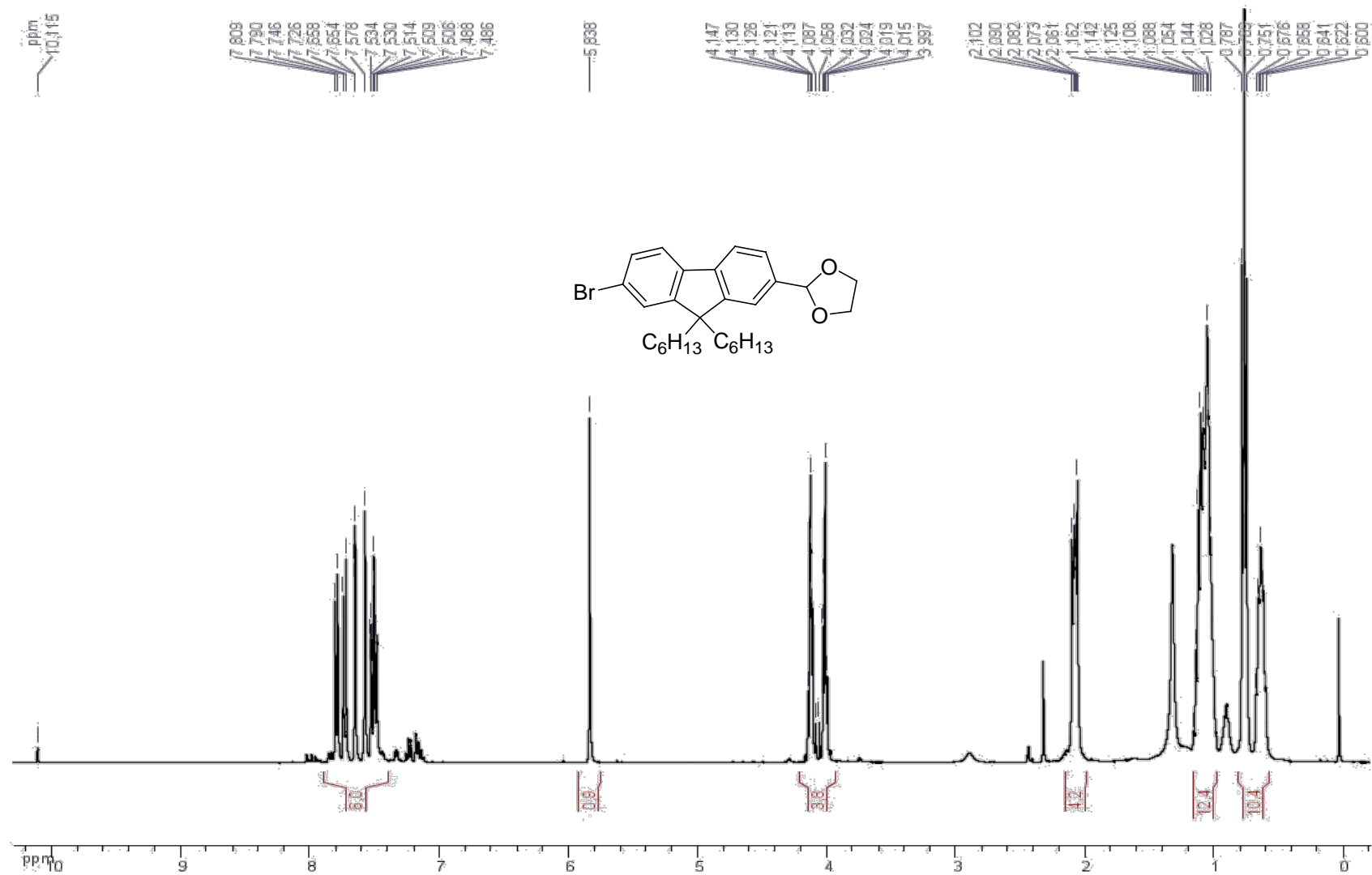


Figure S5. ¹H NMR spectrum of **9** in (CD₃)₂CO.

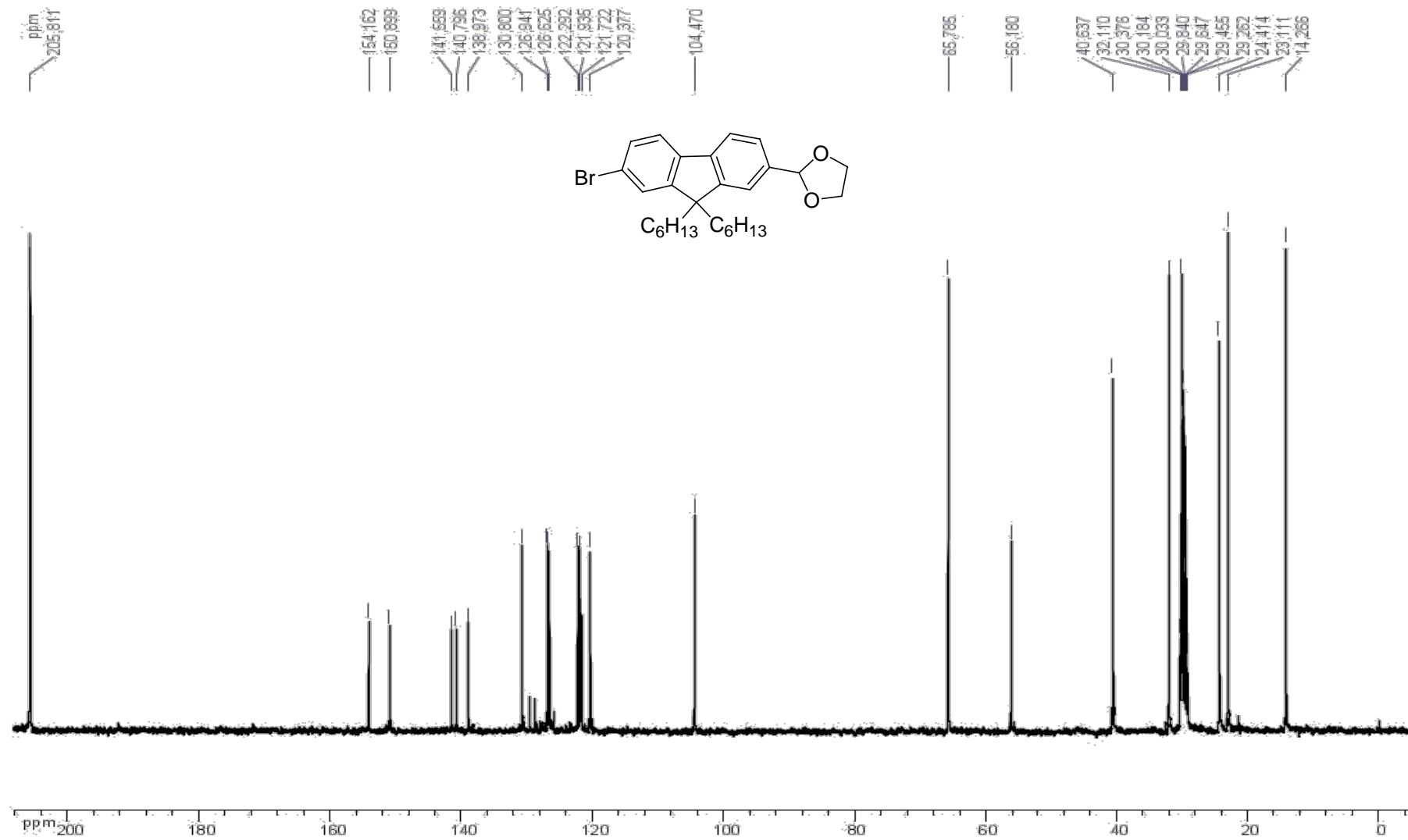


Figure S6. ^{13}C NMR spectrum of **9** in $(CD_3)_2CO$.

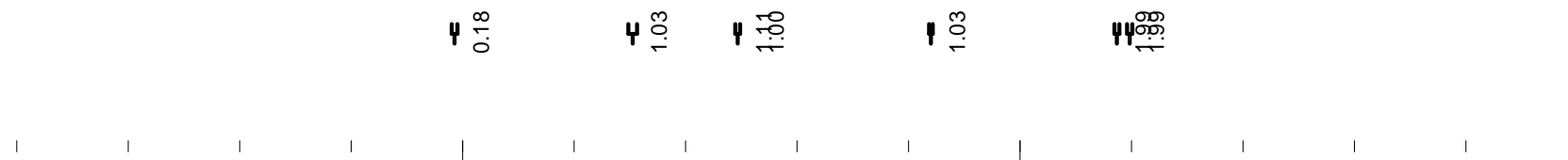
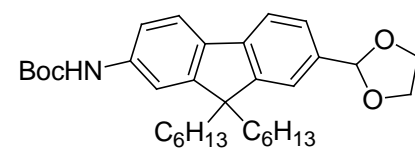


Figure S7: ¹H NMR spectrum of **10** in (CD₃)₂CO.

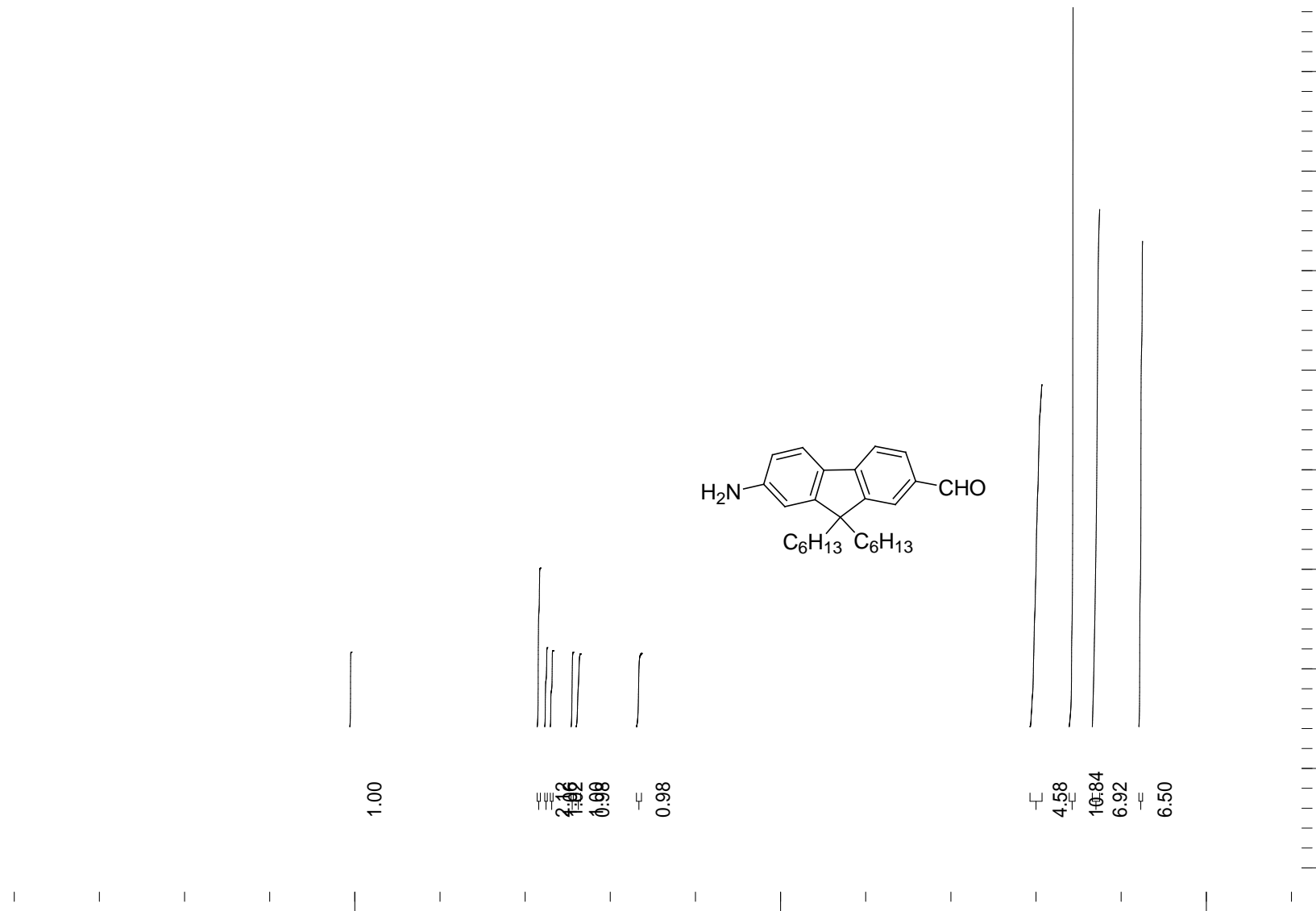


Figure S8. ¹H NMR spectrum of **3** in CDCl₃.

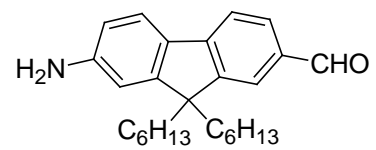


Figure S9. ^{13}C NMR spectrum of **3** in CDCl_3 .

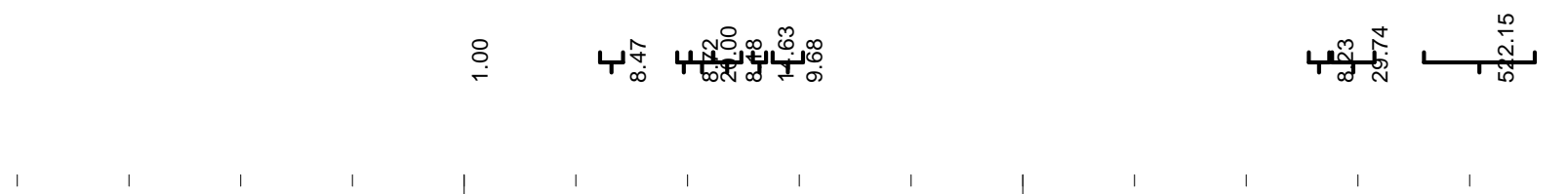
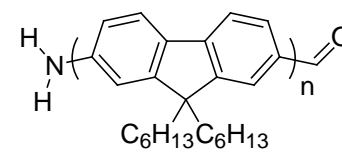


Figure S10. ¹H NMR spectrum of **4** in CDCl₃.

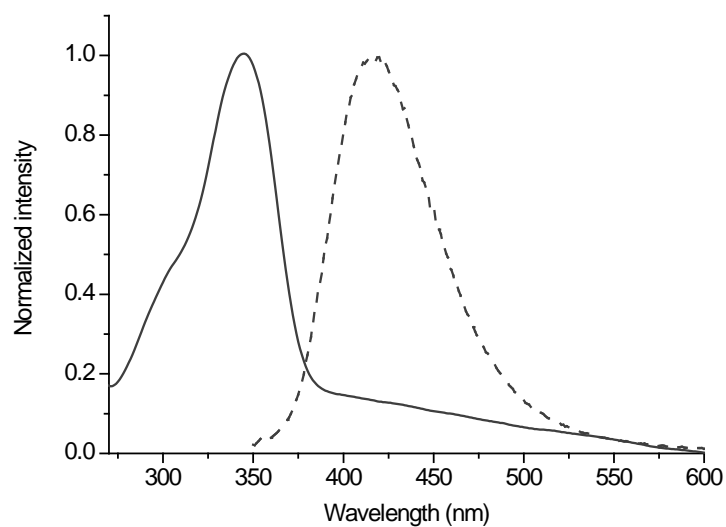


Figure S11. Absorbance and emission spectra of **3** in dichloromethane solution.

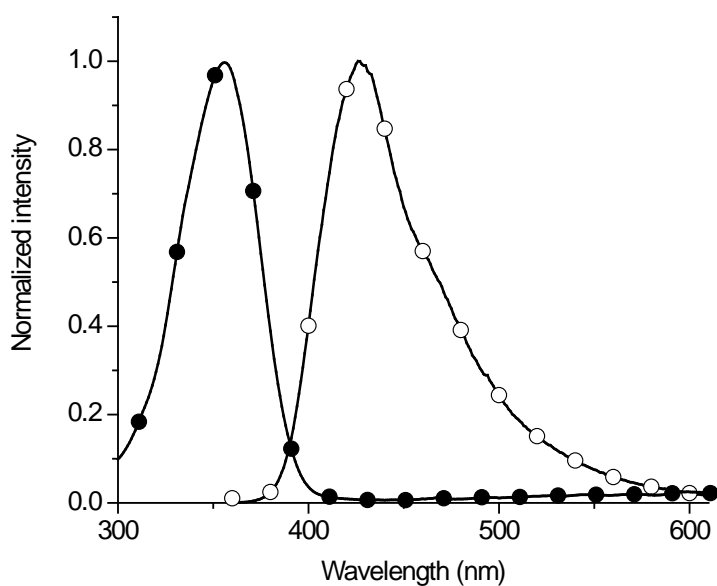


Figure S12. Absorbance (●) and emission (○) spectra of **3** in thin film.

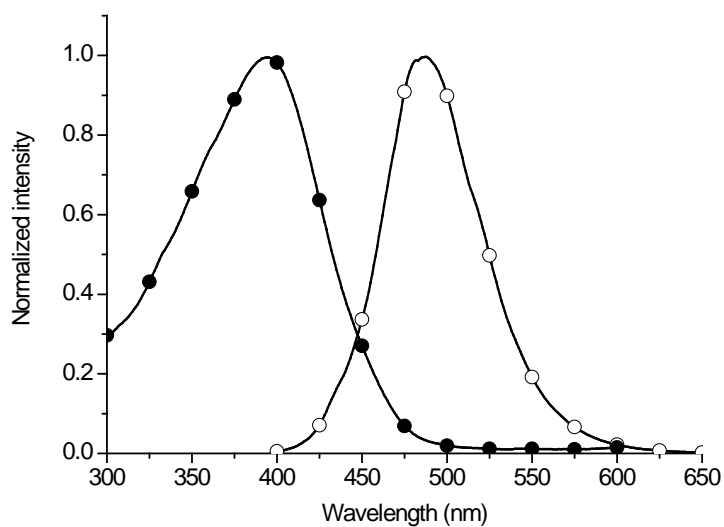


Figure S13. Absorbance (●) and emission (○) spectra of **4** in dichloromethane solution.

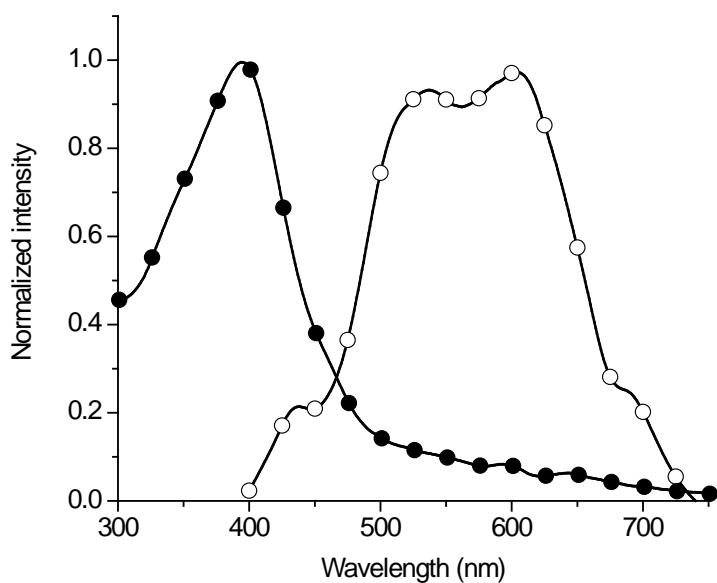


Figure S14. Absorbance (●) and emission (○) spectra of **4** in thin film.

Table S1. Molecular weight determination of **4** by GPC.

Sample	Polymerization time (h)	M_n (g/mol)	M_w (g/mol)	PDI
4	168	2 180	4 433	1.78

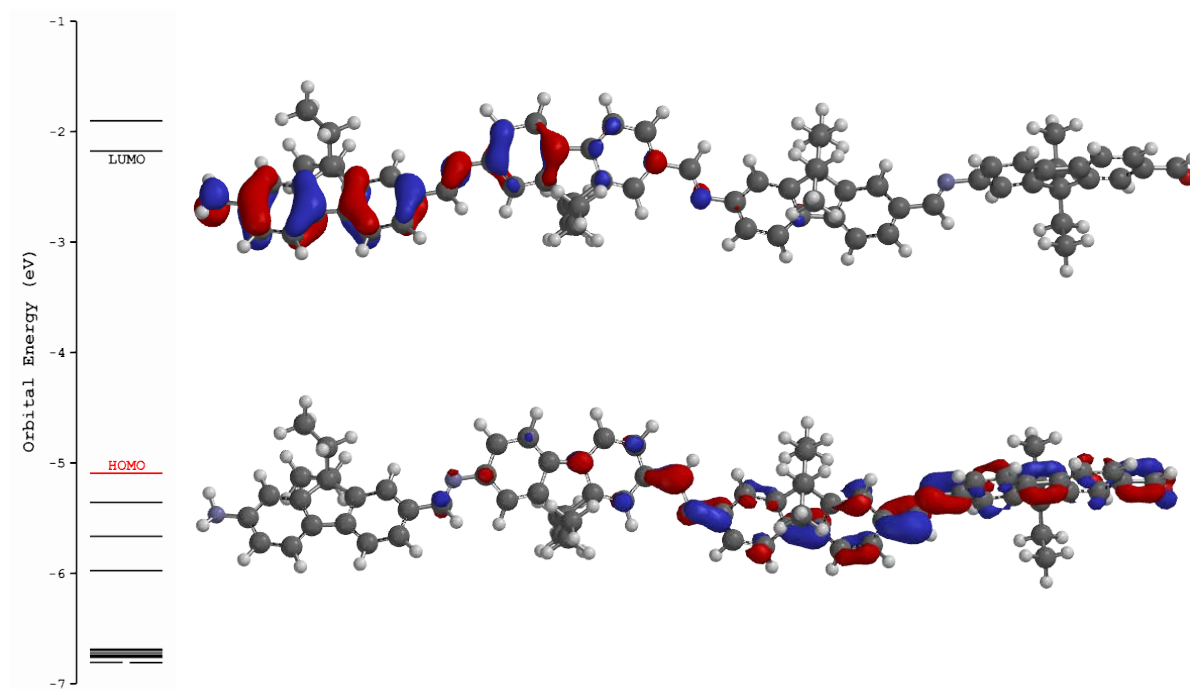


Figure S15. DFT molecular orbitals calculations of **4**: HOMO (top) -5.09 eV; LUMO (bottom) -2.18 eV; E_g 2.90 eV; Δ 53 nm.

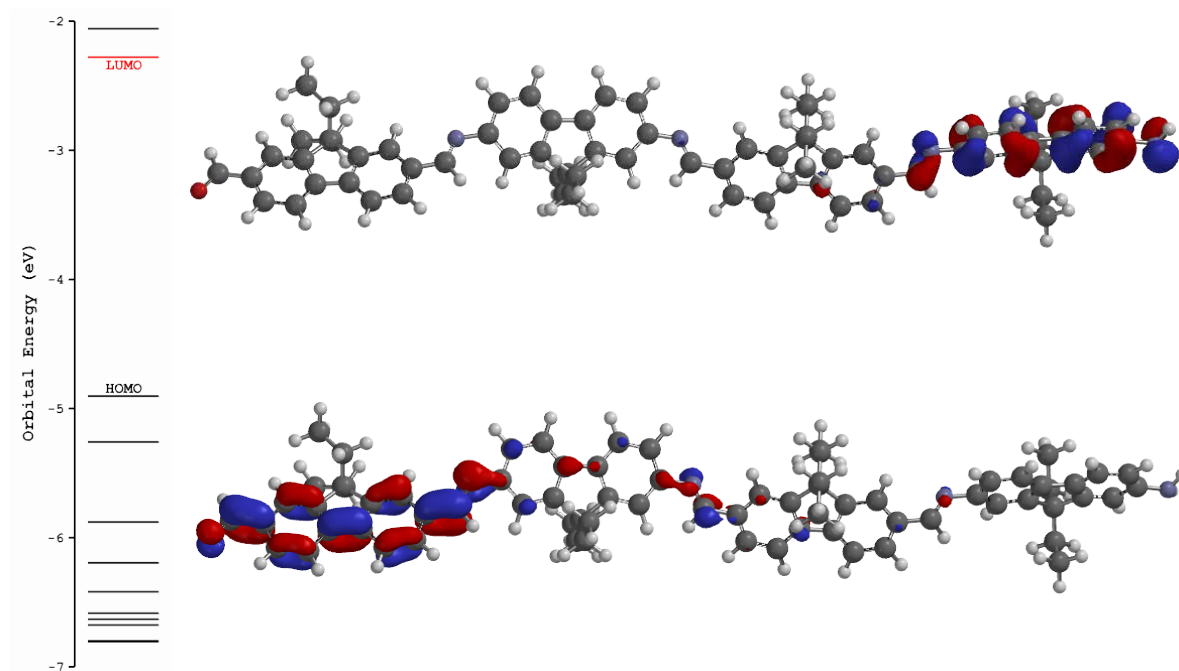


Figure S16. DFT molecular orbitals calculations of **5**: HOMO (top) -4.90 eV; LUMO (bottom) -2.28 eV; E_g 2.62 eV; Δ 53 nm.