

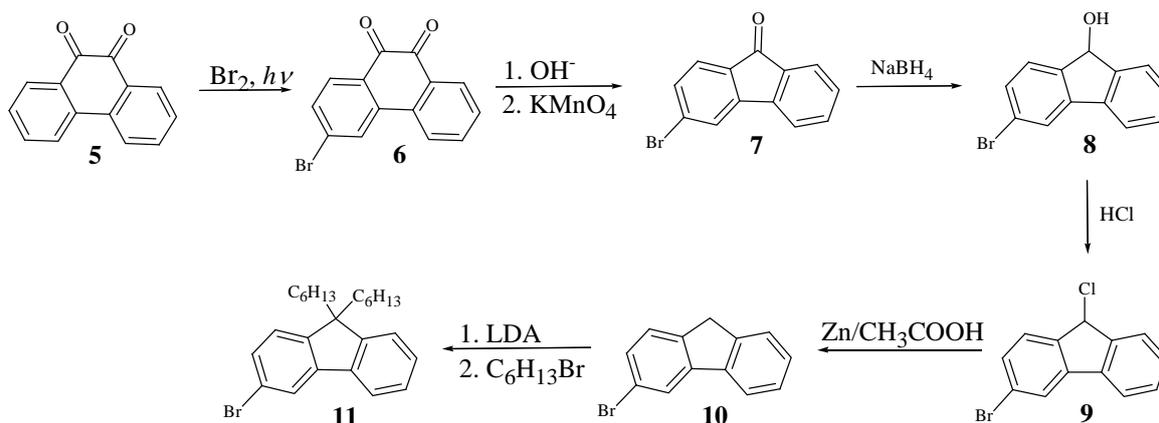
Supporting information

Synthesis and Spectroscopy of Poly(9,9-dihexylfluorene-2,7-diyl-co-9,9-dihexylfluorene-3,6-diyl)s and Their Model Oligomers

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Scheme S1. Synthesis of 3-bromo-9,9-dihexylfluorene.

3-bromophenanthrenequinone (6): phenanthrenequinone (2.1 g, 7.3 mmol) and 5 wt.% of benzoyl peroxide (0.1 g, 0.41 moles) were dissolved in 10 ml of nitrobenzene and Br₂ (6 ml, 12.1 mmol) was added to the mixture dropwise. The reaction mixture was exposed to the light of Hg (100W) lamp for 3h, than cooled to room temperature. Brown precipitate was filtered off and recrystallized twice from nitrobenzene, than washed with methanol to give product as golden needles. Yield: 52 %. ¹H NMR (400 MHz, DMSO): δ= 8.52 (d, J= 1.6 Hz, 1H), 8.37 (d, J= 8 Hz, 1H), 8.04 (dd, J₁= 7.6 Hz, J₂= 1.6 Hz, 1H), 7.91 (d, J= 8 Hz, 1H), 7.79-7.71 (m, 2H), 7.57 (t, J= 7.6 Hz, 1H) ppm. ¹³C NMR (100 MHz, DMSO): δ = 178.27, 178.06, 137.11, 135.23, 133.96, 132.10, 131.58, 130.81, 130.32, 129.88, 129.07, 127.14, 124.90 ppm. HRMS: m/z: 285.9589 [M⁺] (calc.: 285.9600).

3-bromofluorenone (7): 3-bromophenanthrenequinone (1g, 3.48 mmol) was stirred with KOH (1.52 g) in 11.5 ml H₂O for 18 hours under reflux. After that KMnO₄ (1.6 g) was added to the refluxing reaction mixture in 3 portions within 24 h. At the end of 24 hrs reaction mixture was cooled to room temperature and filtered. Solid material was transferred to Soxhlett extractor and extracted with toluene for 3 days. Yellow crystals of pure product were isolated with 55% yield. ¹H

NMR (400 MHz, DMSO): δ = 8.13 (d, J = 1.2 Hz, 1H), 7.88 (d, J = 8 Hz, 1H), 7.66-7.62 (m, 2H), 7.58 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 2H), 7.53 (d, J = 8 Hz, 1H), 7.42 (t, J = 7.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, DMSO): δ = 192.07, 145.92, 142.66, 135.52, 133.31, 132.18, 130.22, 129.37, 125.58, 124.54, 124.14, 121.88 ppm. HRMS: m/z : 257.9670 [M^+] (calc.: 257.9680).

3-bromofluorenol (8): to suspension of 3-bromofluorenone (2.5g, 9.61 mmol) in 60 ml THF NaBH_4 (2 g, 52.6 mmol) was added and the reaction mixture was refluxed for 2 hrs. At the reaction was completed 60 ml of water were added to the reaction mixture; the product (white solid) was filtered out and air-dried. Yield: 72%. ^1H NMR (400 MHz, DMSO): δ = 8.07 (d, J = 1.6 Hz, 1H), 7.87 (d, J = 7.2 Hz, 1H), 7.61 (d, J = 6 Hz, 1H), 7.55-7.49 (m, 2H), 7.44-7.34 (m, 2H), 5.94 (d, J = 7.2 Hz, 1H), 5.48 (d, J = 7.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, DMSO): δ = 147.65, 146.51, 142.41, 138.59, 130.42, 129.03, 128.70, 127.46, 125.60, 123.50, 122.18, 121.07, 73.66 ppm. HRMS: m/z : 258.9761 [M-H] (calc.: 258.9764).

3-bromo-9-chlorofluorene (9): 3-bromofluorenol (1g, 3.83 mmol) was refluxed with 60 ml of conc. HCl for 2 h. The mixture was cooled to RT, diluted with 30 ml of water, solid product was filtered off, washed with water and dried. Yield: 83.5%. ^1H NMR (400 MHz, CDCl_3): δ = 7.8 (d, J = 1.6 Hz, 1H), 7.66-7.63 (m, 2H), 7.52-7.36 (m, 4H), 5.74 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 144.03, 142.55, 142.05, 138.73, 130.81, 129.53, 128.73, 127.21, 125.93, 123.57, 123.44, 120.36, 56.85 ppm. HRMS: m/z : 277.9496 [M^+] (calc.: 277.9498).

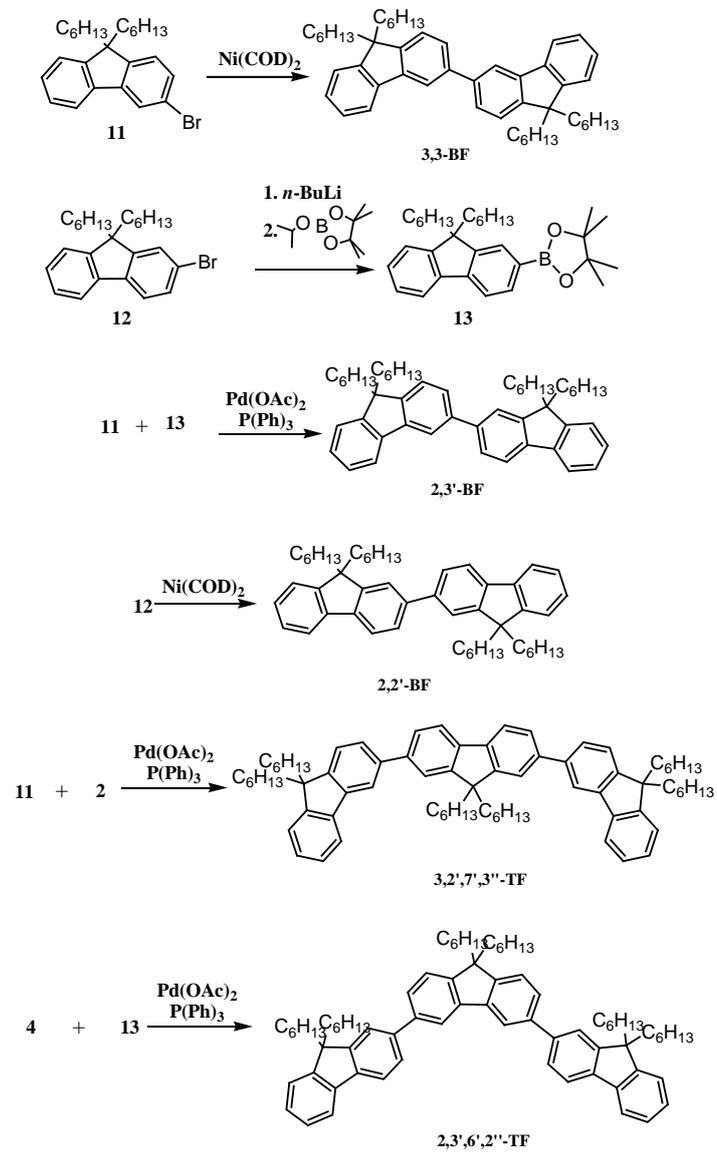
3-bromofluorene (10): 3-bromo-9-chlorofluorene (0.15g, 0.54 mmol) and zinc powder (0.1g, 1.55 mmol) in 5ml of glacial acetic acid were stirred at 60°C for 5h. After mixture was cooled to RT, hot solution was filtered and organic product was precipitated with 7 ml of 4M HCl. Precipitate was filtered off, washed with water, and dried air-dried. Yield: 86%. ^1H NMR (400 MHz, CDCl_3): δ = 7.9 (s, 1H), 7.75 (d, J = 7.2 Hz, 1H), 7.55 (d, J = 19.6 Hz, 1H), 7.44-7.31 (m, 4H), 3.85 (s, 2H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 143.81, 143.47, 141.82, 140.40, 129.37,

127.36, 126.89, 126.37, 125.06, 123.03, 120.73, 120.07, 36.51 ppm. HRMS: m/z : 243.9878 [M^+] (calc.: 243.9888).

3-bromo-9,9-dihexylfluorene (11): to diisopropylamine (0.42 ml, 1.5 mmol) in 2 ml THF *n*-BuLi (1.88 ml (1.6M solution in hexane), 1.5 mmol) was added dropwise at 0°C under nitrogen and stirred for 30 min, than cooled to -78°C and 3-bromofluorene (0.36 g, 1.47 mmol) in 3 ml of THF was added in one portion. The reaction mixture was kept at -78°C for another hour, than quenched with C₆H₁₃Br (0.62 ml, 4.4 mmol) and the reaction was let warm up overnight. The reaction mixture was partitioned between H₂O/Et₂O and organic layer was dried over Na₂SO₃. The solvent was removed under vacuum and the residue was purified by column chromatography (hexane as eluent). Yield: 69%. ¹H NMR (400 MHz, CDCl₃): δ = 7.81 (d, *J* = 1.6 Hz, 1H), 7.67-7.64 (m, 1H), 7.41 (dd, *J*₁ = 8 Hz, *J*₂ = 2 Hz, 1H), 7.34-7.32 (m, 3H), 7.2 (d, *J* = 8 Hz, 1H), 1.95-1.91 (m, 4H), 1.13-1.00 (m, 12H), 0.76 (t, *J* = 7.2 Hz, 6H), 0.62-0.54 (m, 4H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 150.84, 149.45, 143.72, 139.72, 129.67, 127.73, 124.29, 122.88, 120.56, 119.90, 54.93, 40.20, 31.45, 29.63, 23.64, 22.54, 13.98 ppm. HRMS: m/z : 412.1760 [M^+] (calc.: 412.1766).

2-bromo-9,9-dihexylfluorene (12): 2-bromofluorene (0.899g, 3.7 mmol) and benzyltriethylammonium chloride (0.277g, 1.3 mmol) in 5 ml DMSO were purged with argon for 50 min, than 50% NaOH (1ml, 18 mmol) was added dropwise and the reaction mixture was stirred for 30 min, than quenched with iodohexane (2.2 ml, 14.8 mmol) and allowed to react for 18 h. After the reaction was completed the mixture was partitioned between Et₂O and water and dried over MgSO₄. The residue was purified on silica gel column with hexane as eluent yielding colorless liquid product (90.1%). ¹H NMR (400 MHz, CDCl₃): δ = 7.67-1.65 (m, 1H), 7.52 (d, *J* = 16 Hz, 1H), 7.46-7.43 (m, 2H), 7.34-7.31 (m, 2H), 2.0-1.87 (m, 4H), 1.14-1.02 (m, 12H), 0.77 (t, *J* = 7 Hz, 6H), 0.64-0.56 (m, 4H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 152.93, 150.28, 140.11, 140.0, 129.83, 127.42, 126.88, 126.09, 122.84, 120.98, 119.70, 55.34, 40.27, 31.45, 29.62, 23.65, 22.56, 13.98 ppm.

(4,4,5,5-tetramethyl[1.3.2]dioxaborolan-2-yl)-9,9-bis(hexyl)fluorene (13): to a solution of **12** (0.52g, 1.26 mmol) in dry THF (8.5 ml) at -78°C 1.6M solution of *n*-BuLi in hexane (2.35 ml, 3.78 mmol) was added dropwise and the reaction mixture was stirred for 1 h at -78°C under protection of N_2 . After that 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.756 ml, 3.78 mmol) was added in one portion and the reaction mixture was allowed to warm to room temperature overnight. Saturated solution of NaHCO_3 (15 ml) was added to the reaction mixture, organic phase was extracted with diethyl ether and dried over MgSO_4 . The solvent was evaporated under vacuum and the residue was purified by column chromatography with diethyl ether/DCM (3/1) as the eluent to yield the product as colorless oil (85%). ^1H NMR (400 MHz, CDCl_3): δ = 7.8 (d, $J=8$ Hz, 1H), 7.76-7.69 (m, 3H), 7.35-7.30 (m, 3H), 2.04-1.91 (m, 4H), 1.39 (s, 12H), 1.12-1.01 (m, 12H), 0.75 (t, $J=7$ Hz, 6H), 0.61-0.55 (m, 4H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 151.27, 149.84, 144.09, 140.89, 133.66, 128.80, 127.44, 126.62, 122.90, 120.05, 118.92, 83.67, 55.05, 40.22, 31.46, 29.66, 24.93, 24.81, 23.63, 22.56, 13.99 ppm.



Scheme S2. Synthesis of the model oligomers.

Figure S1. ^1H NMR of **1** (CDCl_3):

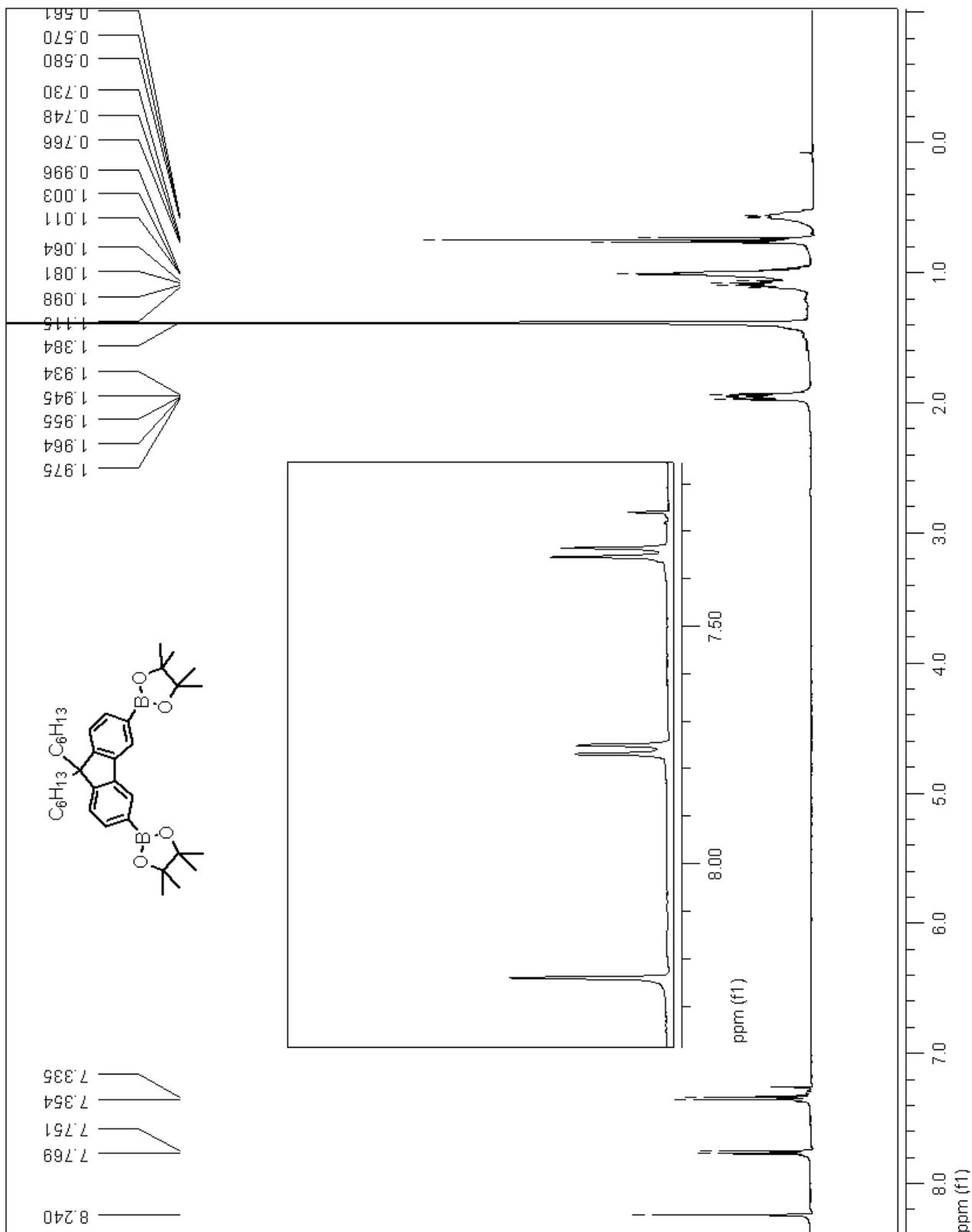


Figure S2. ^{13}C NMR of **1** (CDCl_3):

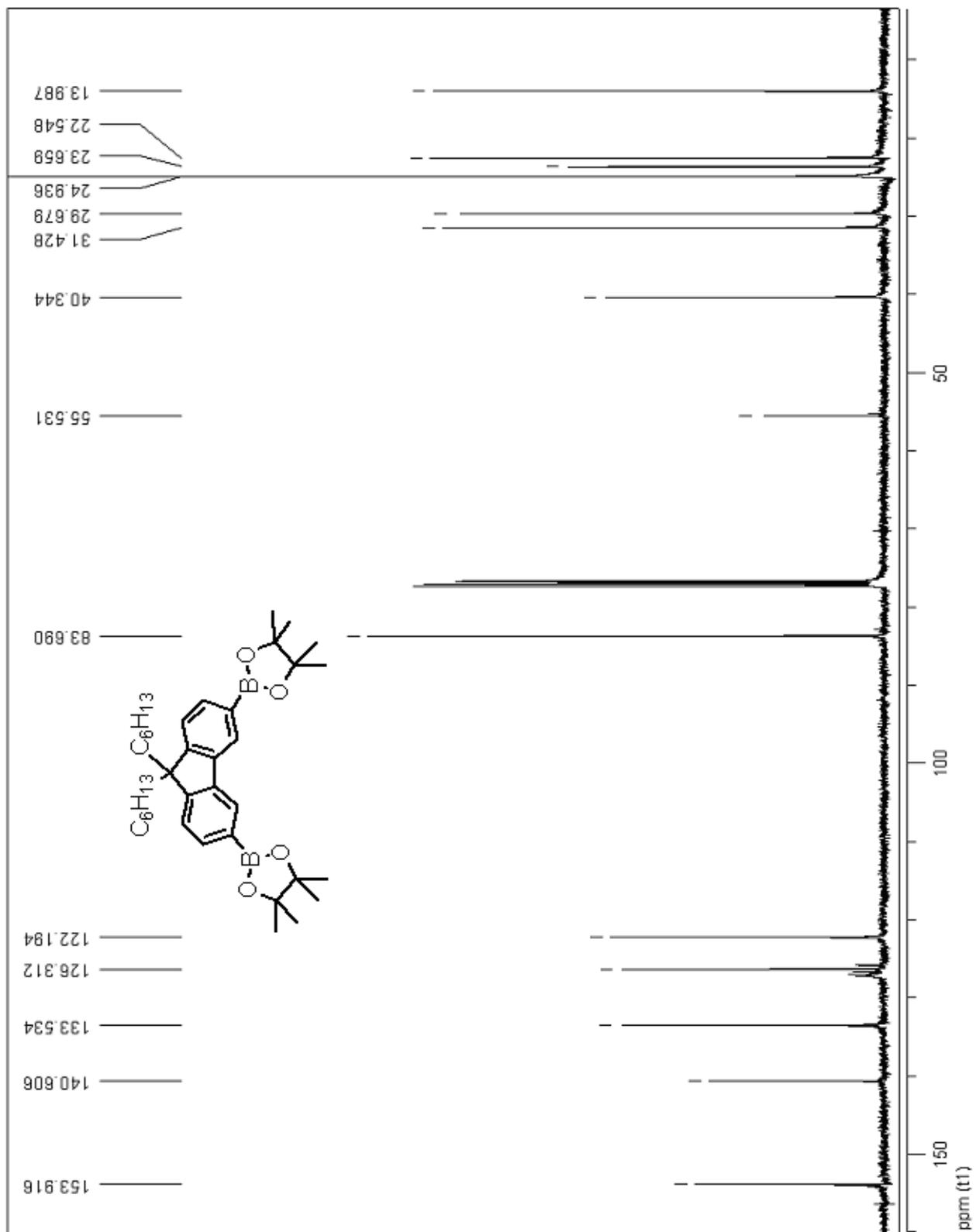


Figure S3. ^1H NMR of 2,2'-BF (CDCl_3):

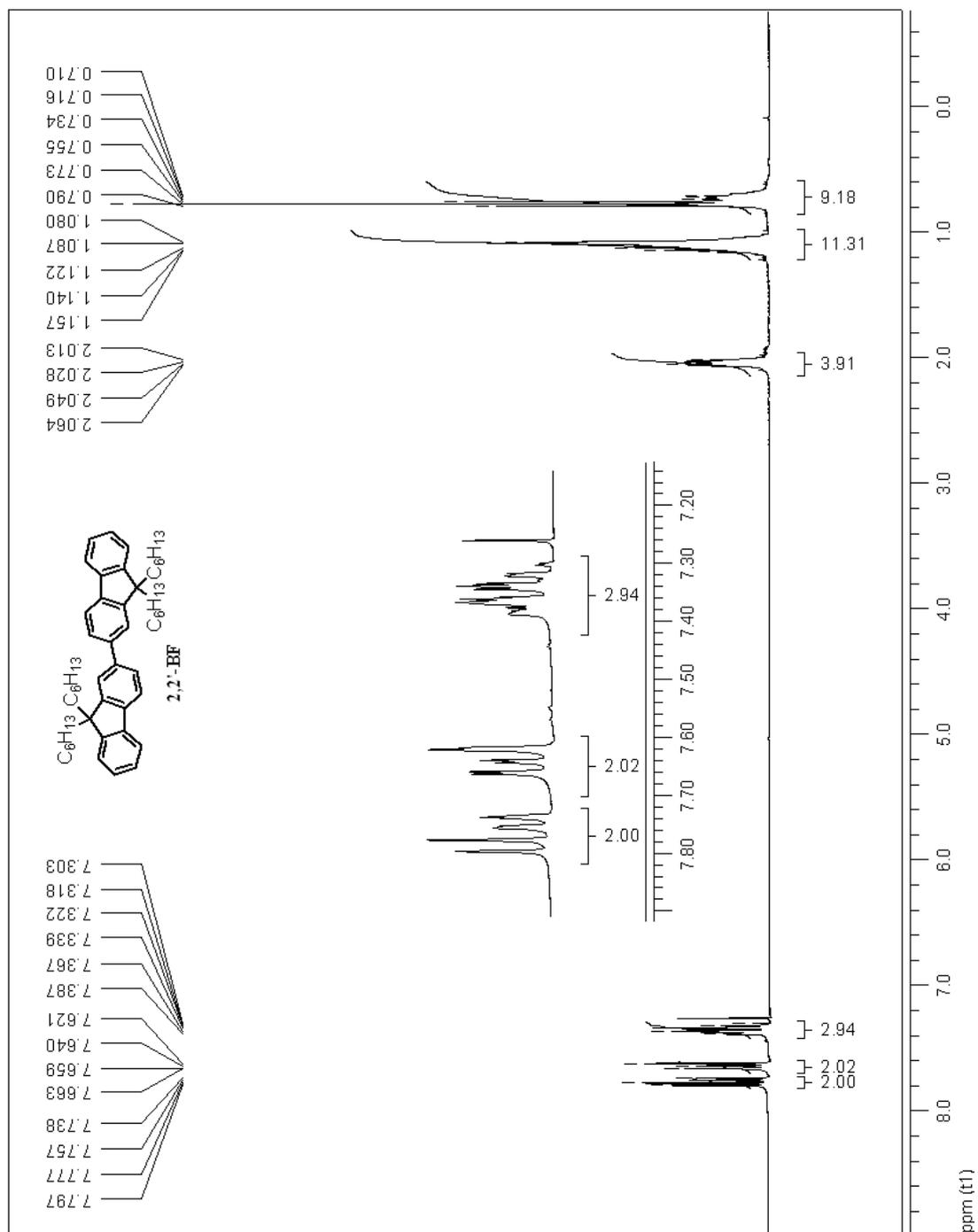


Figure S4. ^{13}C NMR of 2,2'-BF (CDCl_3):

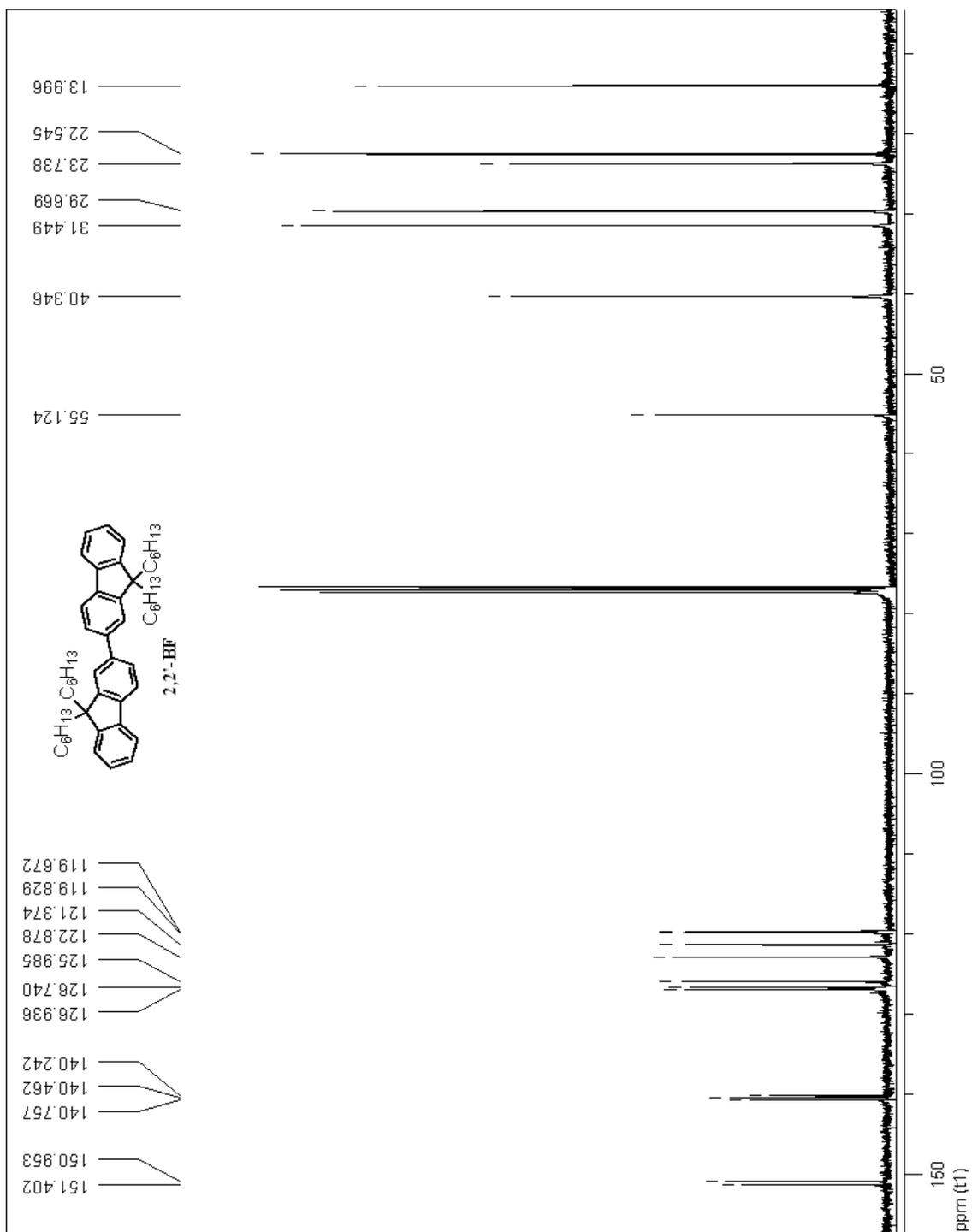


Figure S5. ^1H NMR of **2,3'-BF** (CDCl_3):

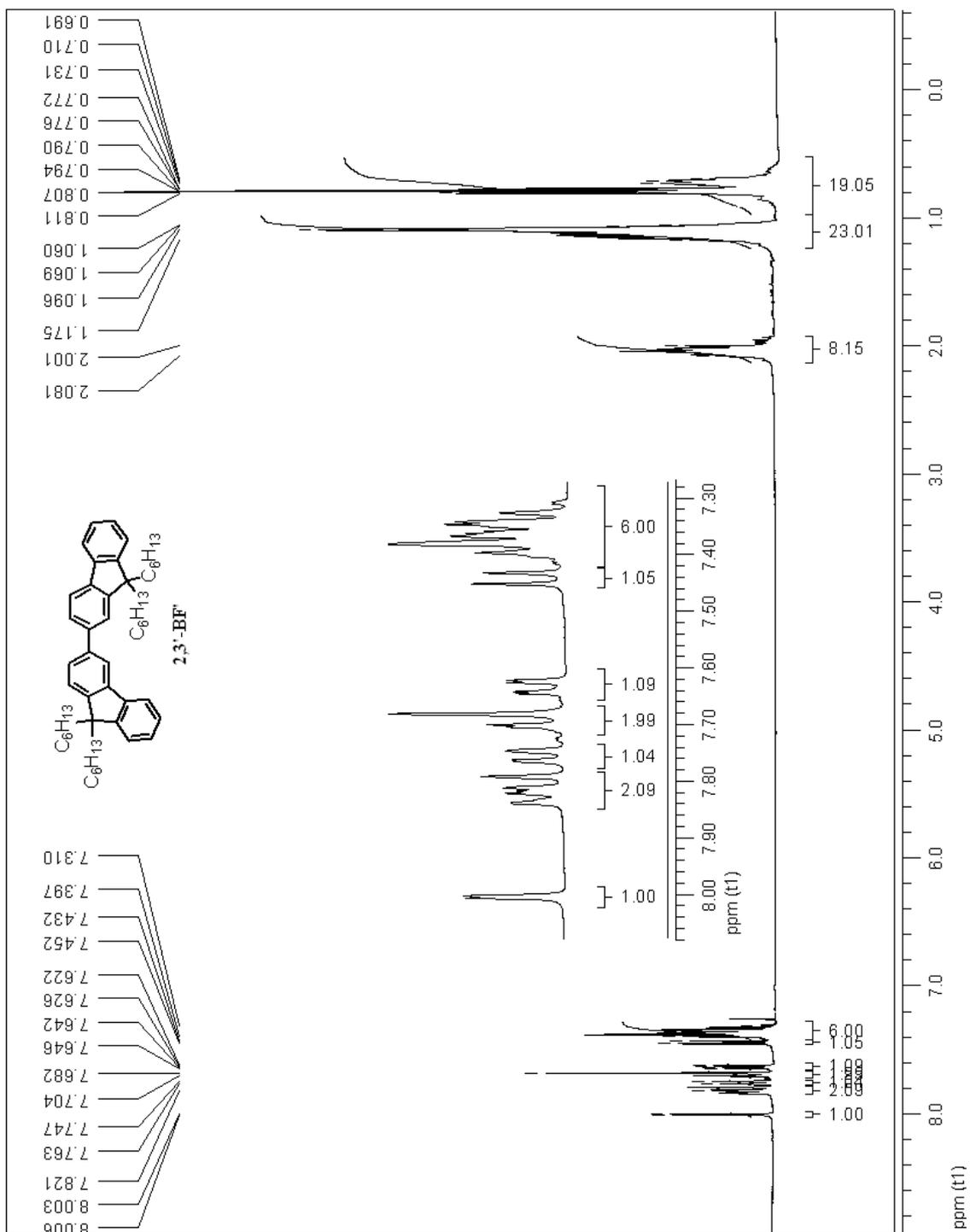


Figure S6. ^{13}C NMR of 2,3'-BF (CDCl_3):

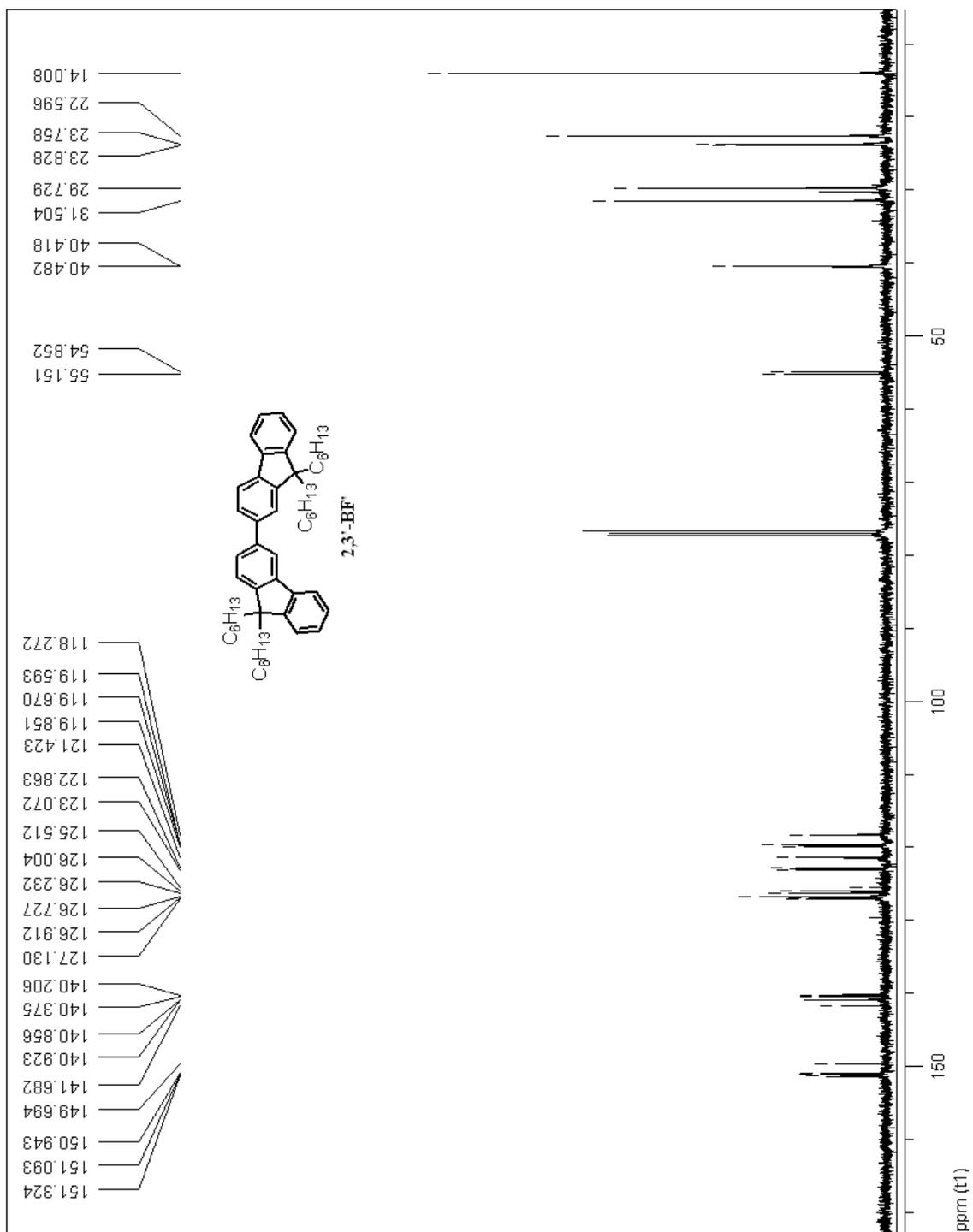


Figure S7. ^1H NMR of **3,3'-BF** (CDCl_3).

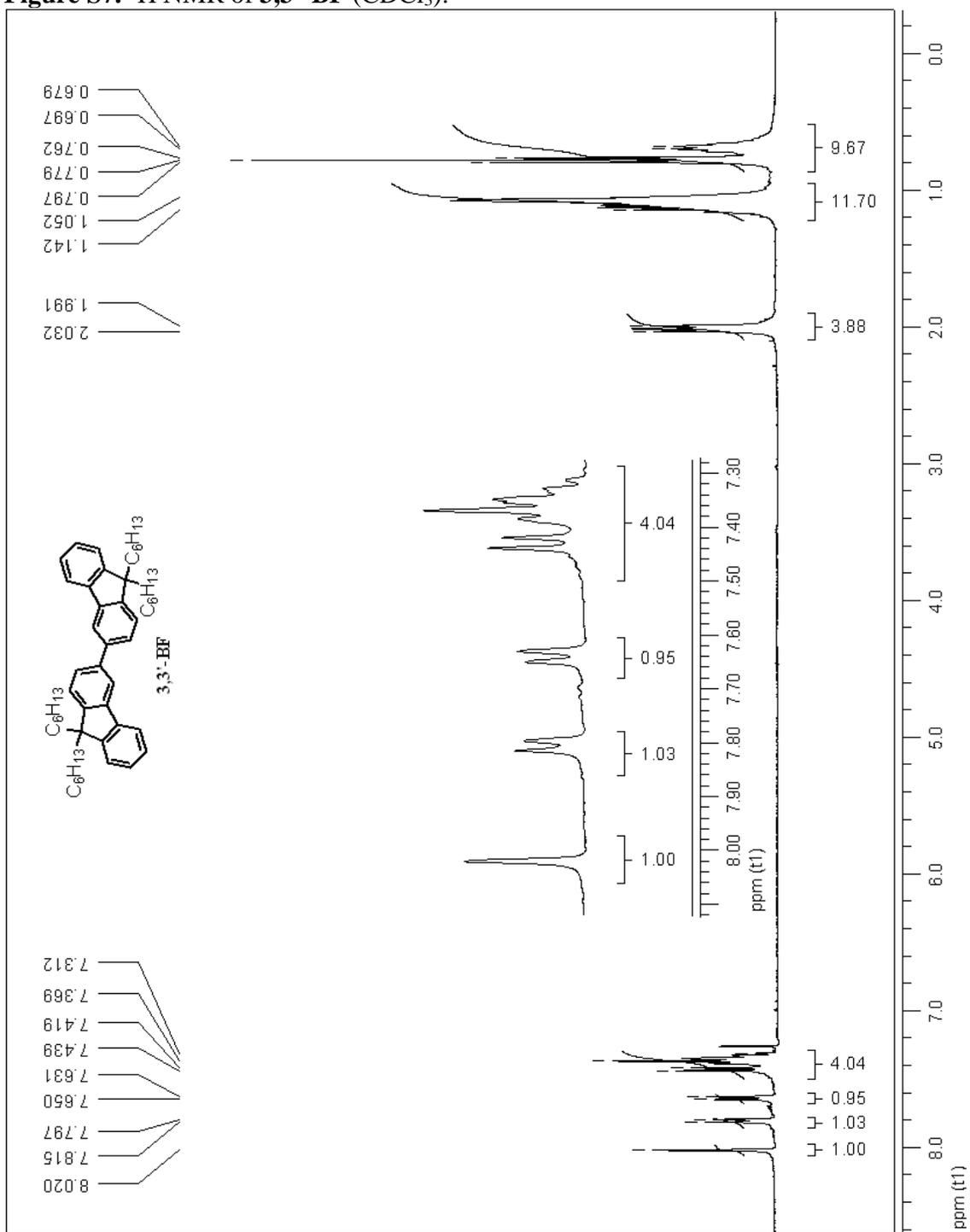


Figure S8. ^{13}C NMR of **3,3'-BF** (CDCl_3).

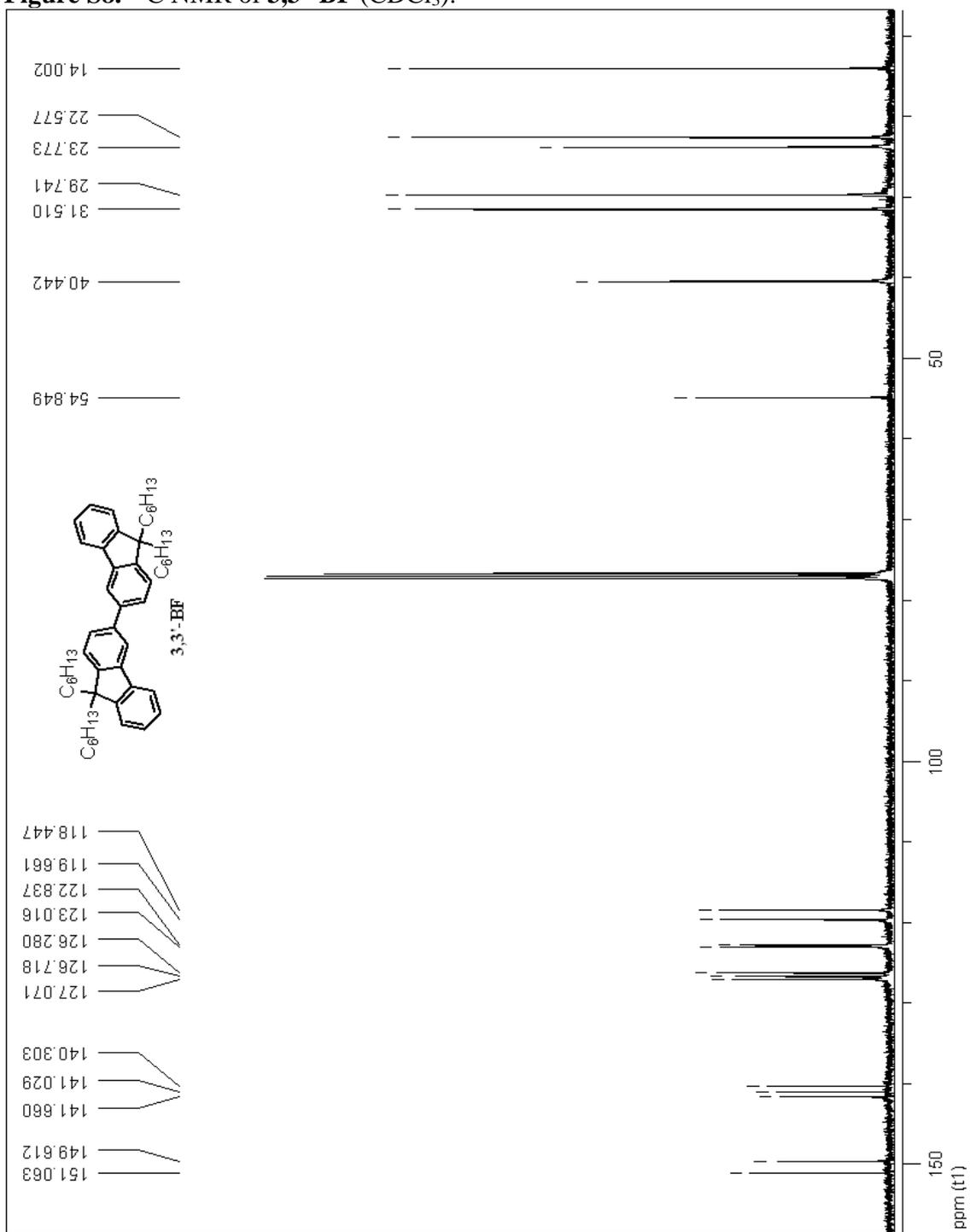


Figure S9. ^1H NMR of 2,3',6',2''-TF (CDCl_3):

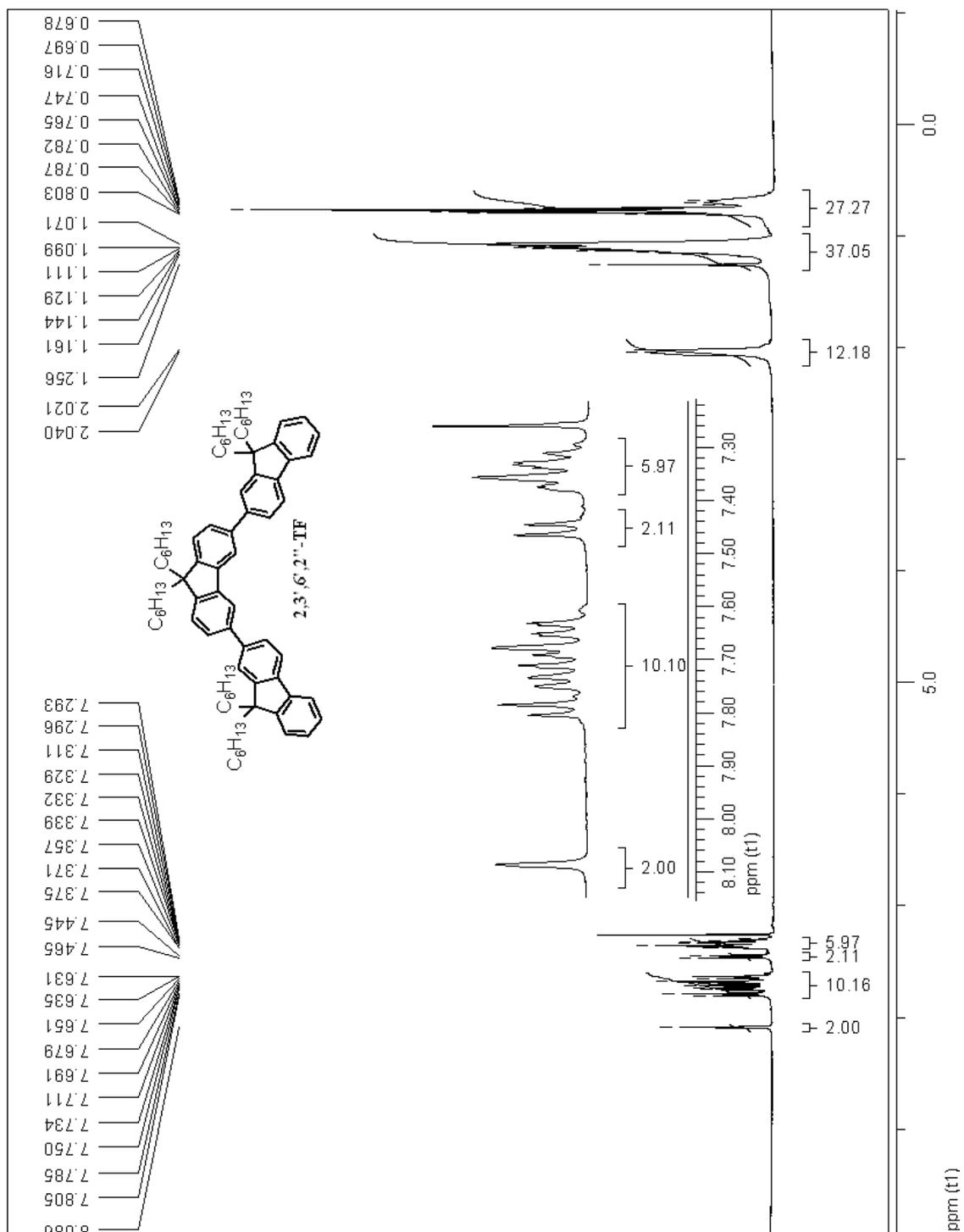


Figure S10. ^{13}C NMR of 2,3',6',2''-TF (CDCl_3):

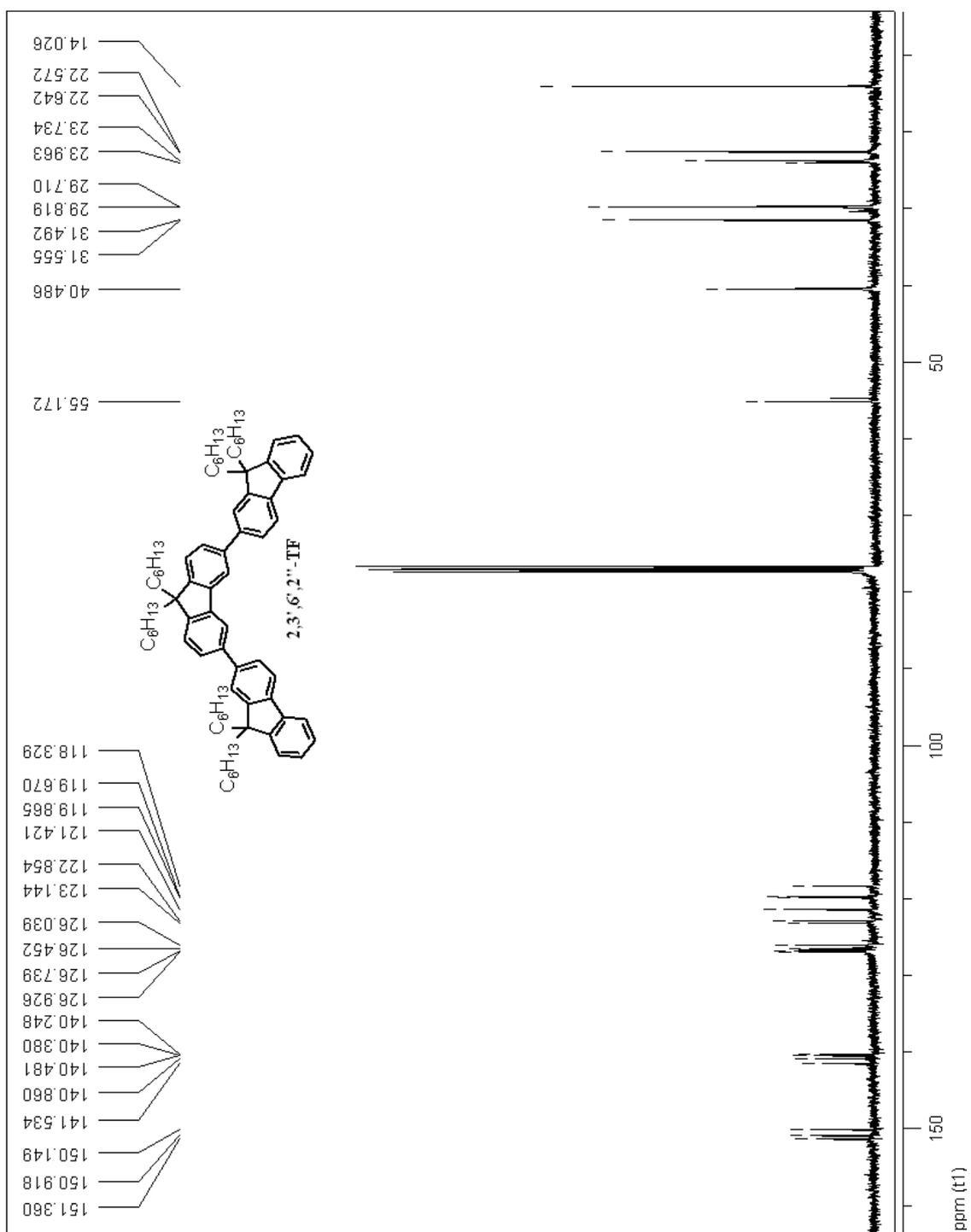


Figure S11. ^1H NMR of 3,2',7',3''-TF (CDCl_3):

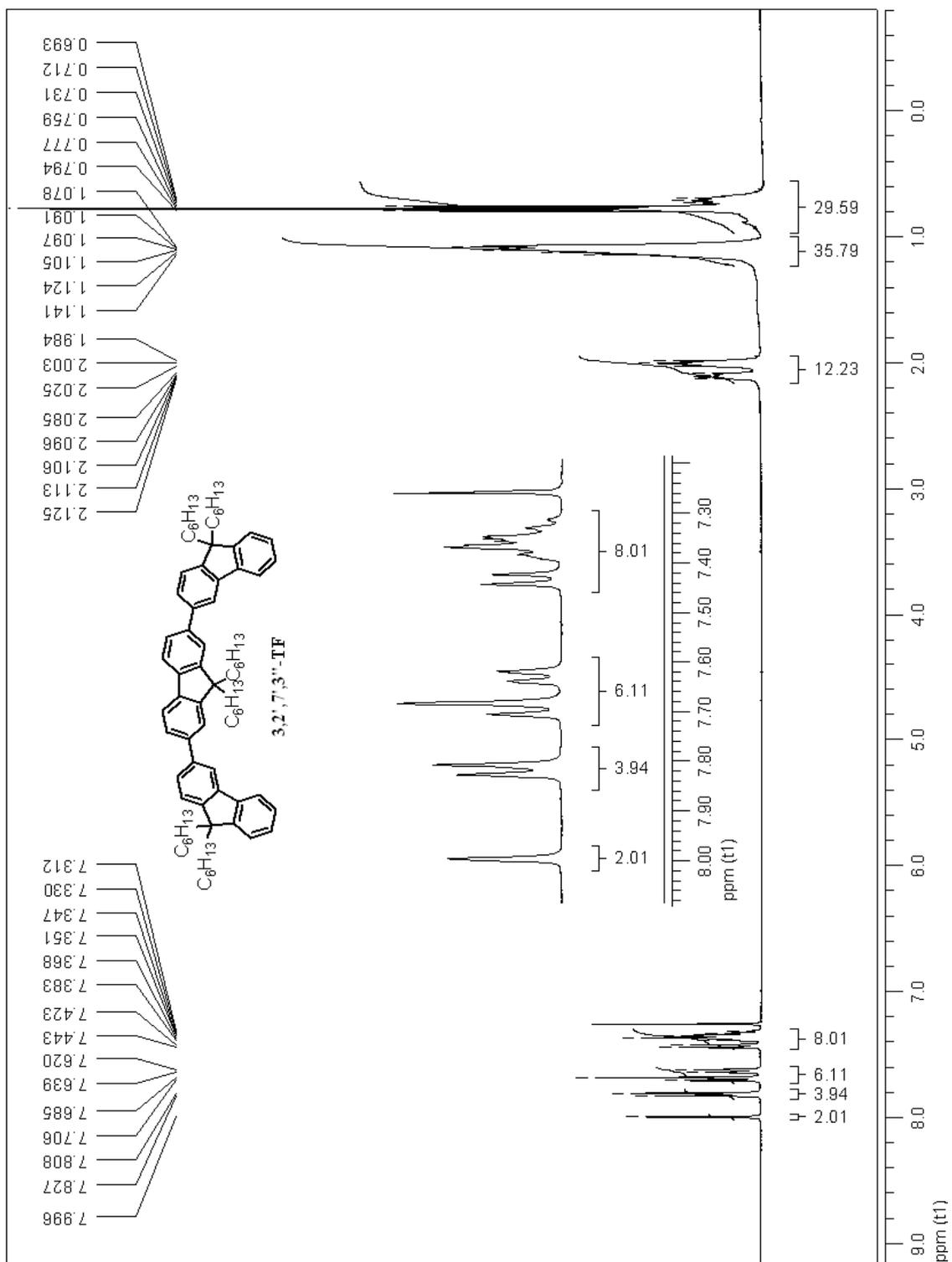


Figure S12. ^{13}C NMR of 3,2',7',3''-TF (CDCl_3):

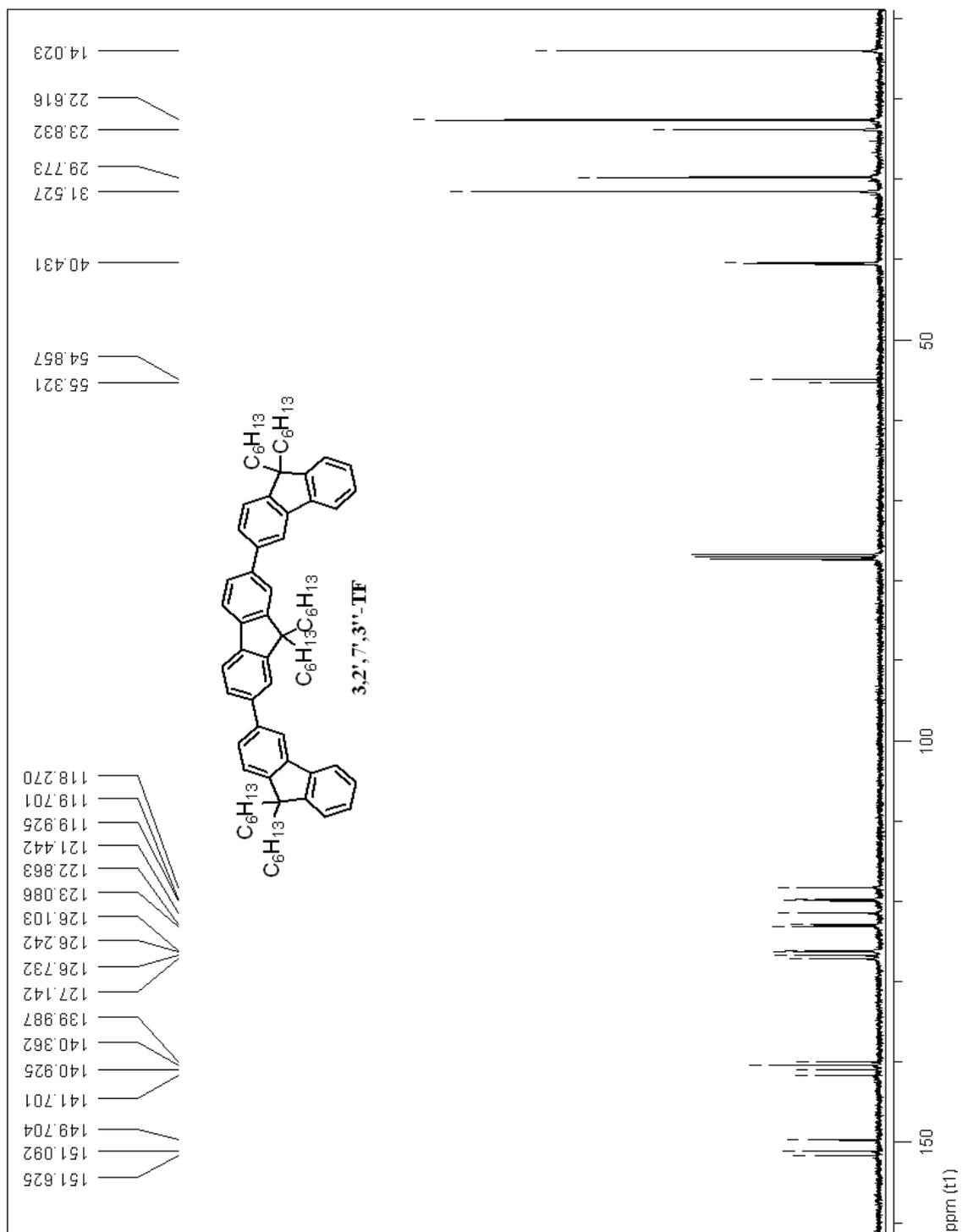


Figure S13. ^1H NMR of **4** (CDCl_3).

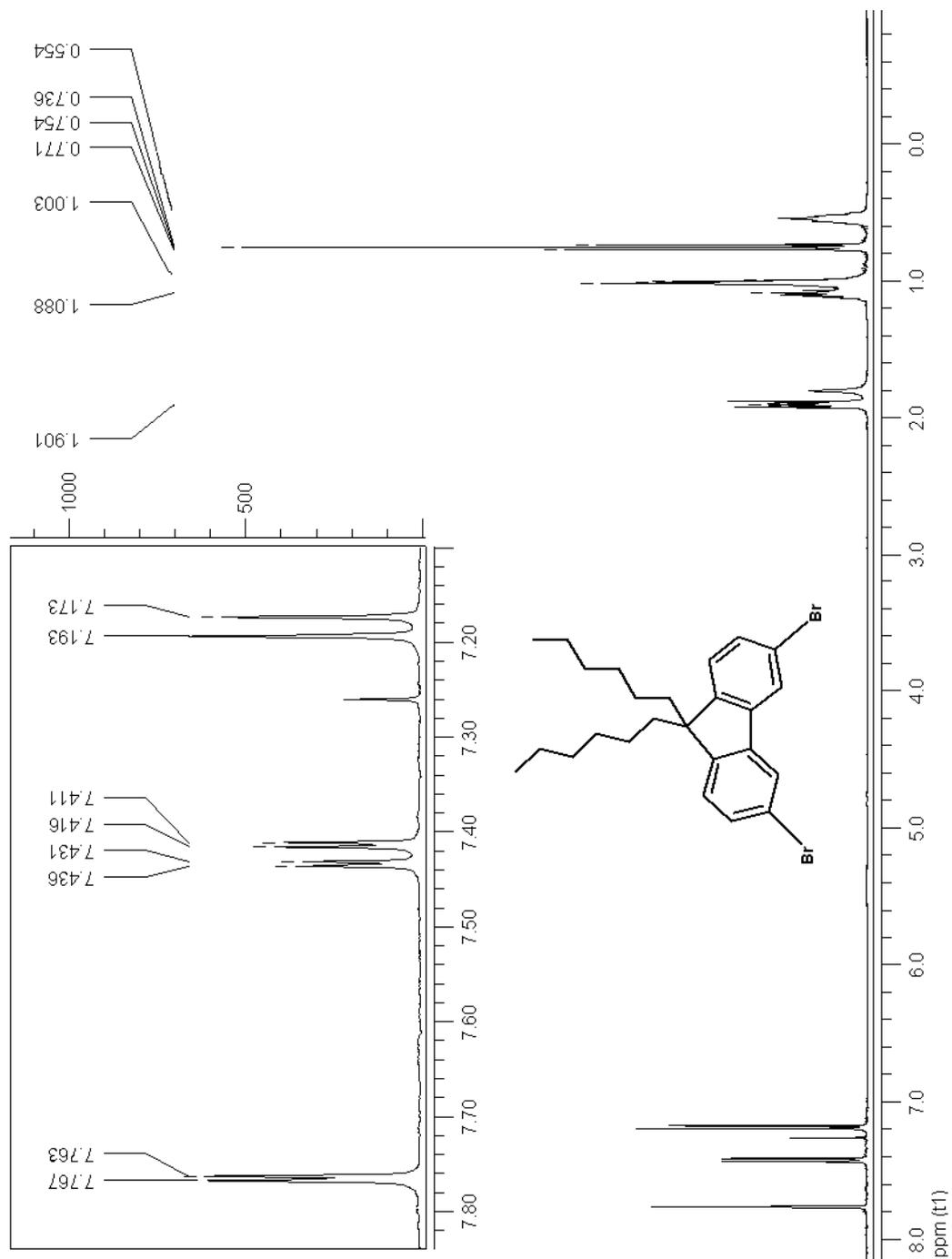


Figure S14. ^{13}C NMR of **4** (CDCl_3).

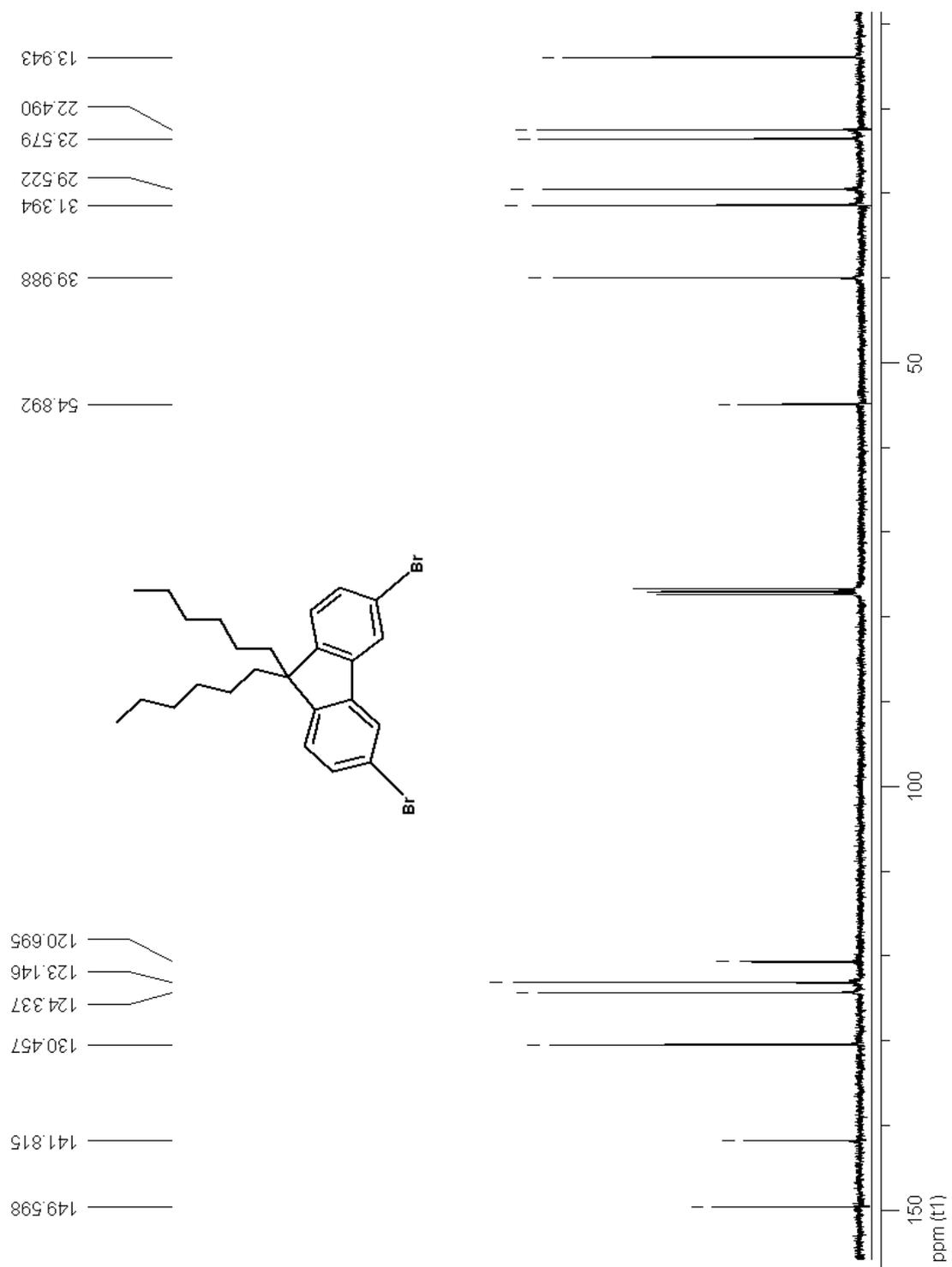


Figure S15. ^1H NMR of **36PDHF** (CDCl_3).

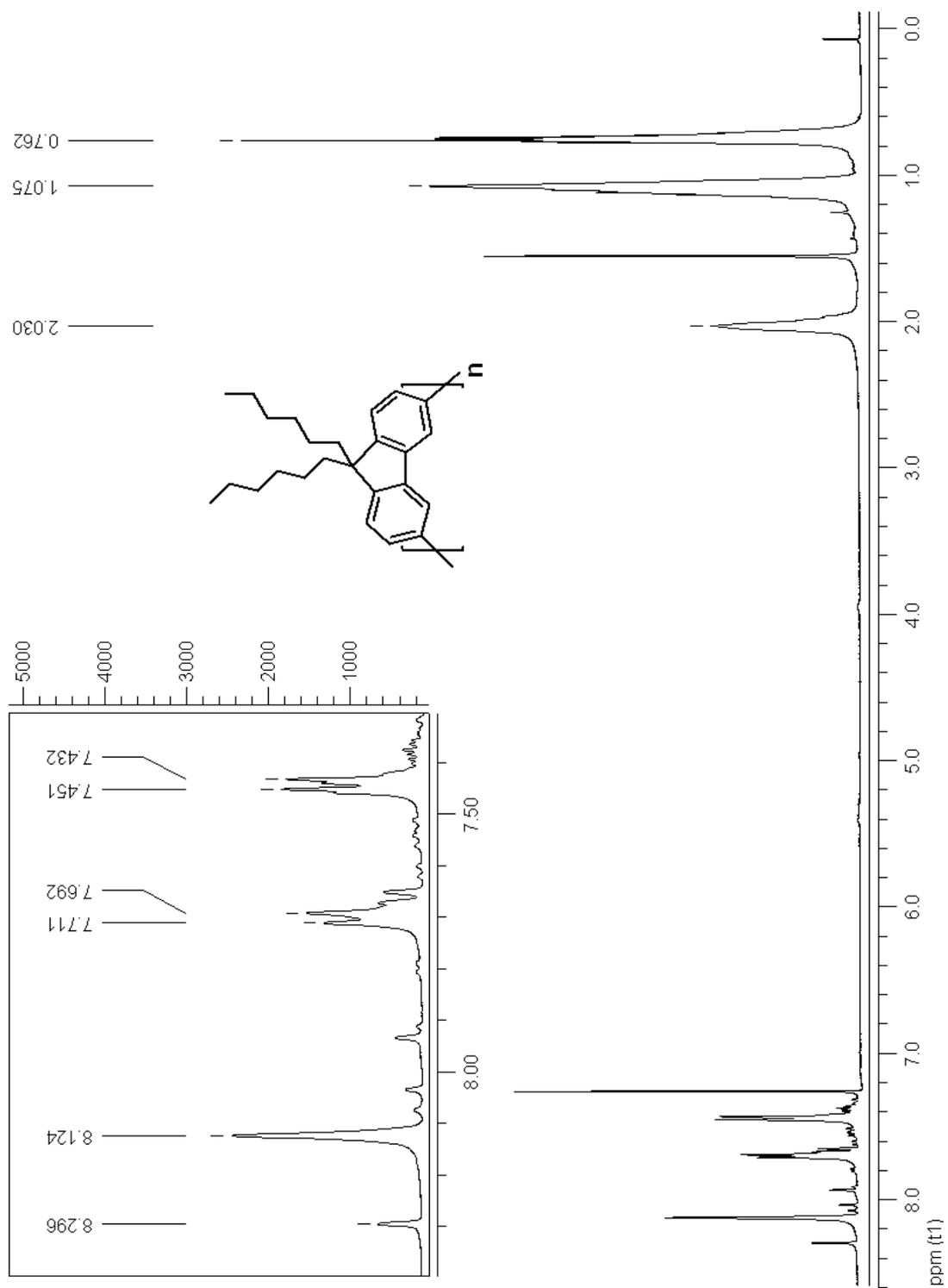


Figure S16. ^{13}C NMR of **36PDHF** (CDCl_3).

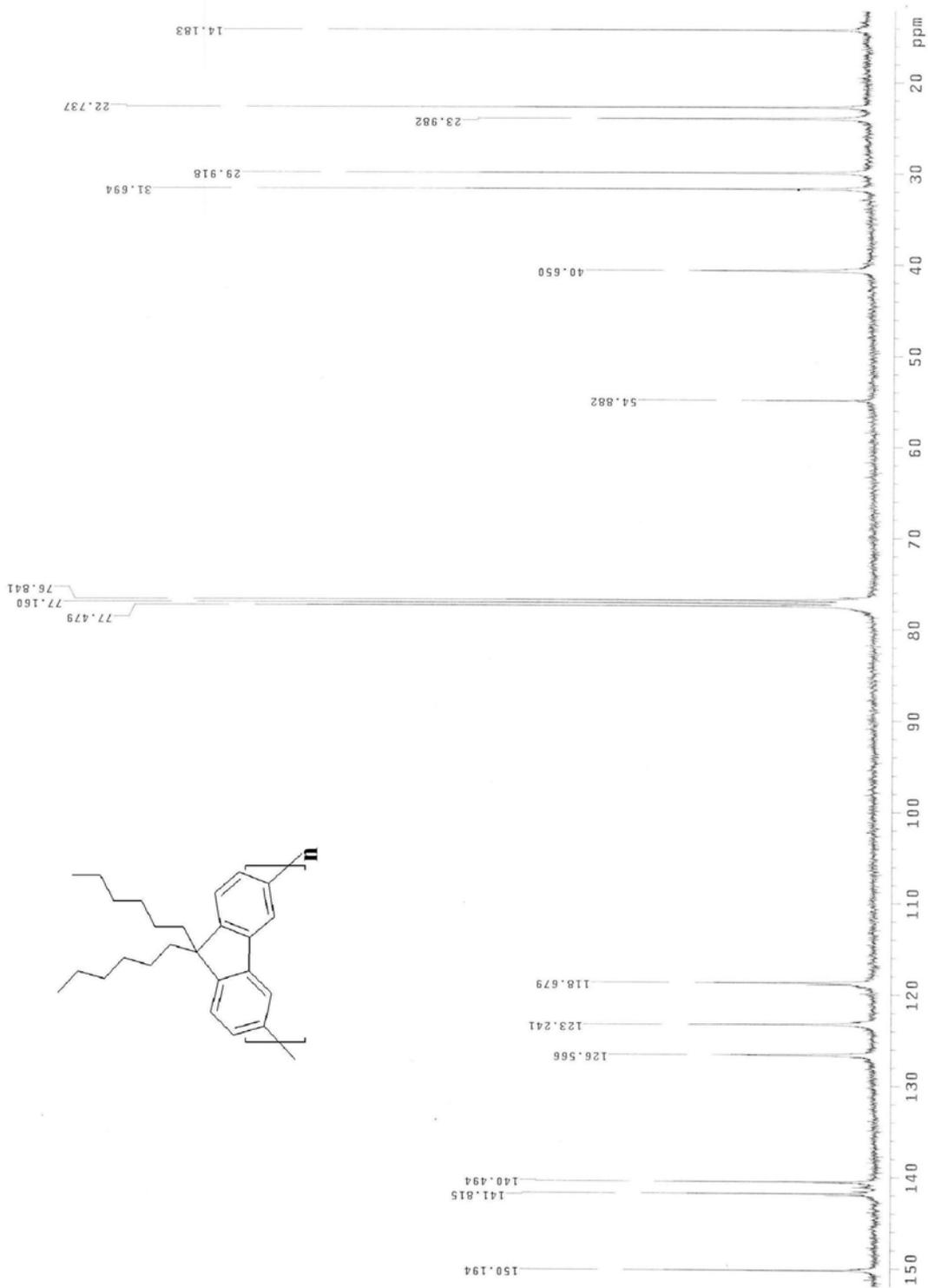
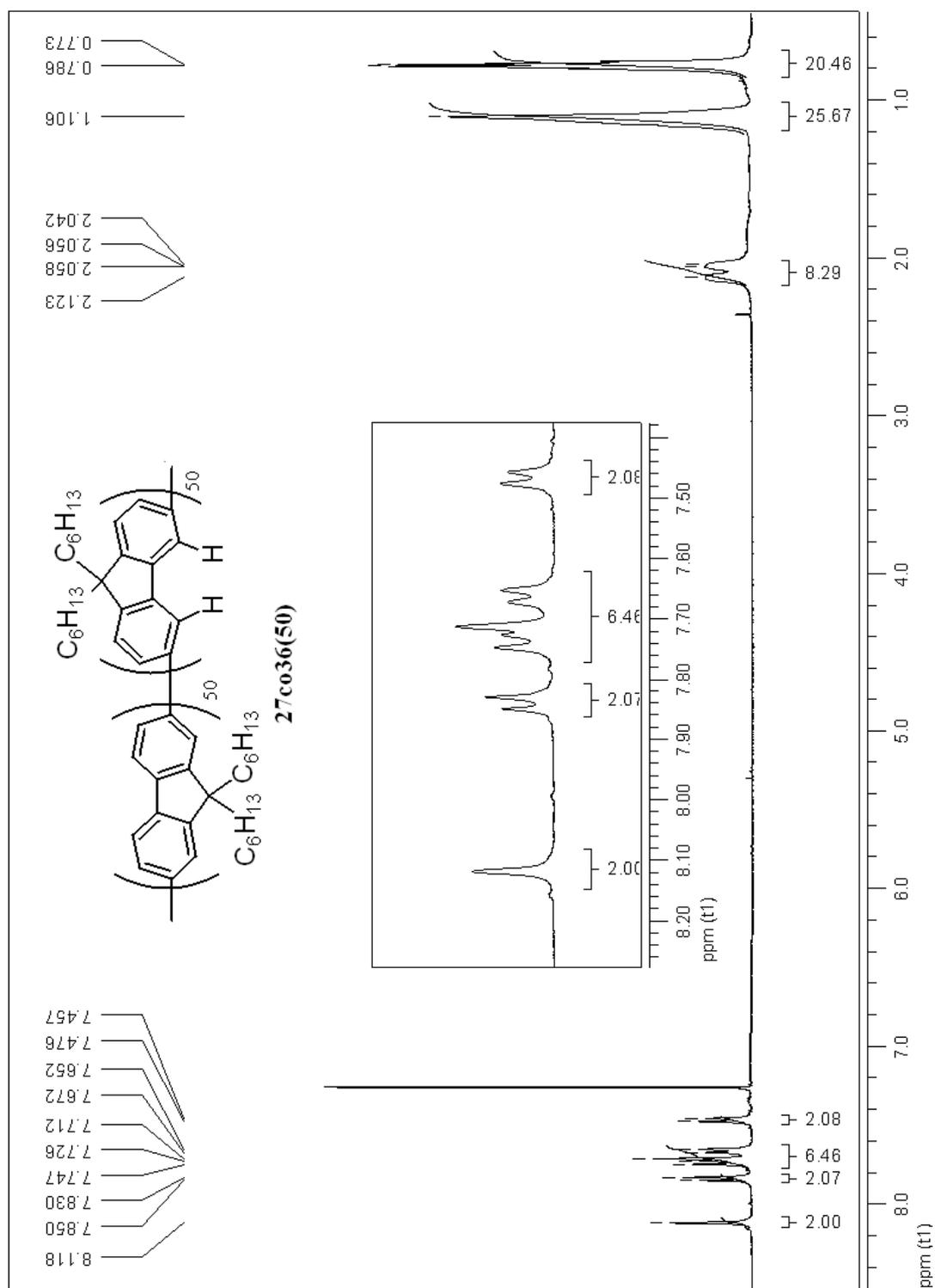


Figure S17. ^1H NMR of **27co36(50)** (CDCl_3):



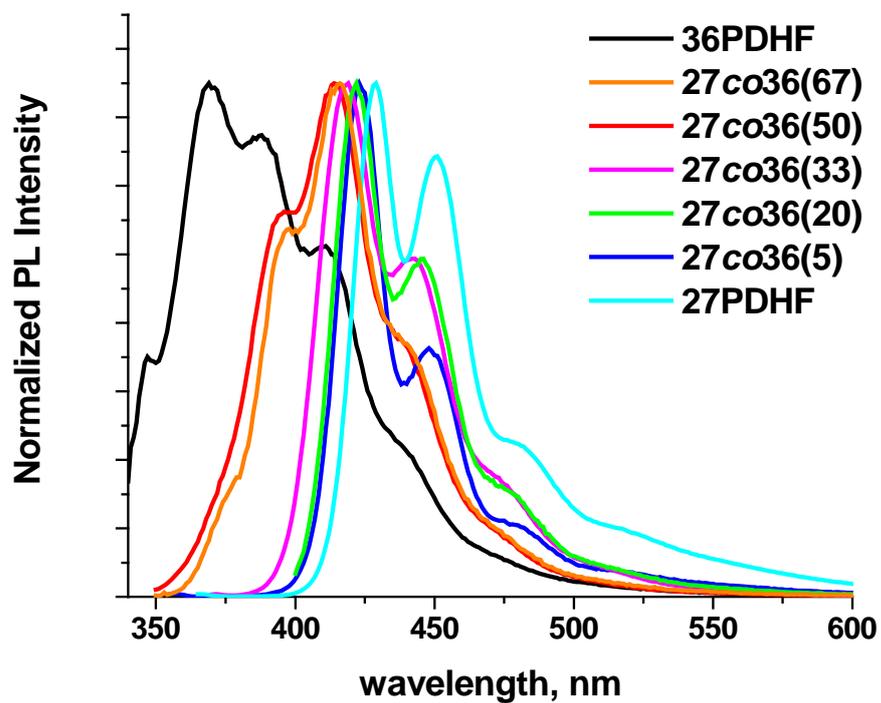


Figure S18. Emissions of 27,36 copolymers in thin films annealed at 150⁰C in vacuum. (The λ_{exc} were chosen at the lower energy absorption bands maxima).

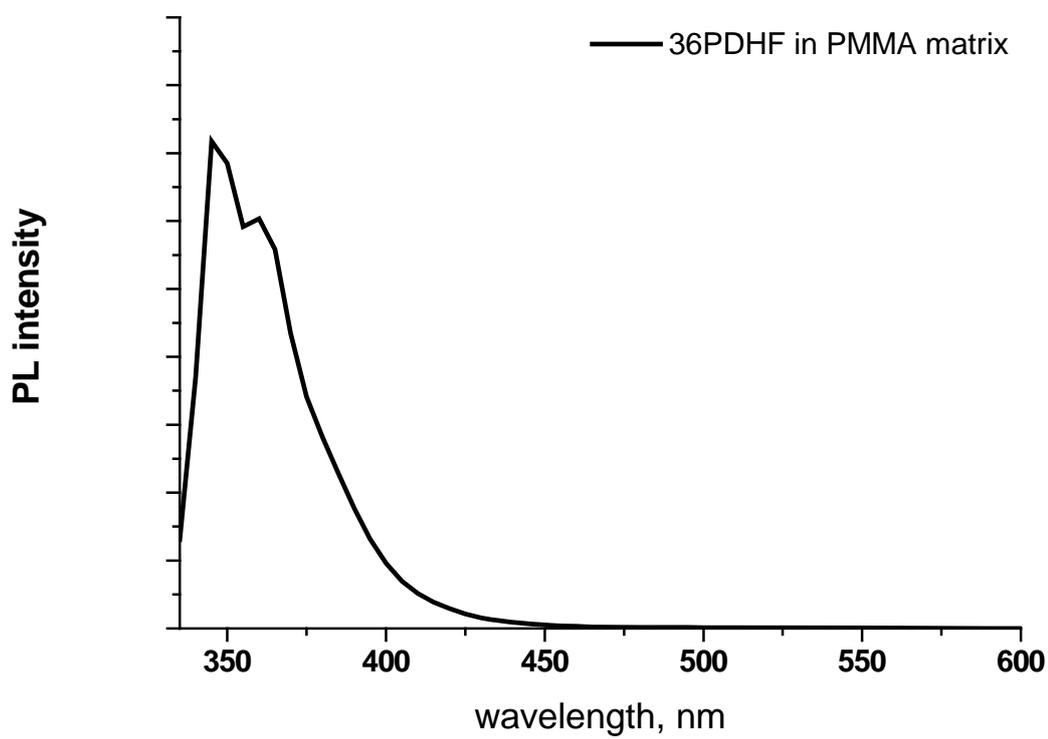


Figure S19. Emission spectrum of 36PDHF in PMMA matrix.