

Supporting information

Synthesis and characterization of triphenylamine-based polymers and their application towards solid-state electrochromic cells

Jaemyeng Jeong[‡], Rangaraju Satish Kumar[‡], Mergu Naveen and Young-A Son *

Department of Advanced Organic Materials Engineering, Chungnam National University, 220 Gung-dong, Yuseong-gu, Daejeon 305-764, South Korea.

*Corresponding author. Tel.: +82 42 821 6620; fax: +82 42 821 8870.

E-mail address: yason@cnu.ac.kr (Y.-A. Son).

Materials and Characterization

All solvents and reagents (analytical and spectroscopic grades) were commercially obtained and used as received unless otherwise noted. Fourier 300, 7.05 Tesla, 300 MHz, an AVANCE III 600 spectrometer (Akishima, Japan) was operated at 600 MHz and 150 MHz for ^1H and ^{13}C NMR spectroscopy, respectively. CDCl_3 was used as the solvent, and Alice 4.0 software was used for analysis. The chemical shifts (δ values) are reported in ppm downfield from an internal standard (Me_4Si). Mass spectra were recorded on a 4000 Q TRAP mass spectrometer. HRMS spectra were obtained using a micrOTOF-QII mass spectrometer. FT-IR spectra were recorded on an ALPHA-P spectrometer. UV-visible absorption spectra were recorded using an Agilent 8453 spectrophotometer. The electrochemical measurements, i.e., cyclic voltammetry (CV) experiments, were conducted using a Versa STAT 3 instrument using polymer films sprayed on platinum button, the electrolyte used was 0.1 M TBABF₄ in propylene carbonate, Ag/Ag^+ electrode as the reference electrode and platinum wire as the counter electrode.

Thermogravimetric analyses (TGA) were performed on a Mettler Toledo instrument using a heating rate of 20 °C/min and nitrogen flow rate of 50 mL/min. Number-average (M_n) and weight-average (M_w) molecular weights were determined by gel permeation chromatography (GPC) using a Waters model 2690 instrument with THF (HPLC grade, Aldrich) as the eluting solvent. Spectroelectrochemical data of the polymers films were recorded by using an Instek model GPS-3303 instrument as a DC power source.

1. 4-bromo-N-(4-bromophenyl)-N-(4-butylphenyl)aniline (2): Compound 2 was prepared by adopting a reported procedure.¹ N-bromosuccinimide (NBS) (5.69 g, 32

mmol) was added to a solution of 4-butyl-N,N-diphenylaniline (1) (5.032 g, 16 mmol) in DMF (70 mL). The mixture was stirred for 12 h at room temperature. 200 mL of water was added, and the mixture was extracted with ethyl acetate (2×150 mL). The combined organic layers were dried over sodium sulfate, concentrated, and purified by silica gel column chromatography (10% ethyl acetate in hexane) to yield (6.85 g, 93%) as a yellow, sticky oil. ¹H NMR (300 MHz, CDCl₃): δ 7.27-7.21 (m, 4H), 7.00 (d, *J* = 8.3 Hz, 2H), 6.93-6.80 (m, 6H), 2.49 (t, *J* = 7.7 Hz, 2H), 1.58-1.46 (m, 2H), 1.37-1.22 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 3H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 146.7, 144.4, 138.8, 132.3, 129.6, 125.0, 115.0, 35.1, 33.7, 22.5, 14.1 ppm; IR ν_{\max} in cm⁻¹(in CHCl₃): 3014, 2957, 2929, 2858, 1578, 1508, 1483, 1310, 1280, 1214, 1176, 1102, 1071, 1006, 908, 820, 748, 667; ESI-MS: 460 [M+H]⁺.

2. 4-butyl-N,N-bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (3):

Compound 3 was prepared by adopting a reported procedure.² A solution of 4-bromo-N-(4-bromophenyl)-N-(4-butylphenyl)aniline (1.97 g, 4.3 mmol) in anhydrous THF (45 mL) was cooled to -78 °C under a nitrogen atmosphere. *n*BuLi (2.5 M in hexane, 4.3 mL, 10.7 mmol) was added drop wise, and the mixture was stirred for 1 h at the same temperature. Subsequently, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.7 mL, 12.8 mmol) was added, and the mixture was stirred for 2 h at -78 °C. The reaction was quenched with water, extracted with ethyl acetate, and the organic layer was dried over sodium sulfate. The solvent was removed, and the crude product was purified by recrystallization from methanol to afford a white solid (1.26 g, 53%). ¹H NMR (300 MHz, CDCl₃): δ 7.59 (d, *J* = 8.3 Hz, 4H), 7.04-6.90 (m, 8H), 2.51 (t, *J* = 7.6 Hz, 2H),

1.60-1.46 (m, 2H), 1.35-1.22 (m, 24H), 0.87 (t, $J = 7.3$ Hz, 3H) ppm; ^{13}C NMR (150 MHz, CDCl_3): δ 150.3, 144.4, 138.9, 135.9, 129.9, 125.8, 122.4, 83.5, 35.0, 33.5, 24.8, 22.4, 13.9 ppm; IR ν_{max} in cm^{-1} (KBr): 3028, 2975, 1592, 1271, 1213, 1139, 857, 826, 738, 673; HR-MS (ESI-MS) m/z calcd. For $\text{C}_{34}\text{H}_{46}\text{B}_2\text{NO}_4$ $[\text{M}+\text{H}]^+$: 554.3619, found 554.3620.

3. 2,5-dibromothiophene (4): Compound 4 was prepared by adopting a reported procedure.³ *N*-bromosuccinimide (60 g, 0.33 mol) was added to a solution of thiophene (14.0 g, 0.16 mol) in 250 mL of a 50:50 (v/v) mixture of acetic acid and chloroform. The mixture was refluxed for 15 min. After cooling to room temperature, water was added, and the mixture was extracted with chloroform. The organic phase was dried over sodium sulfate and concentrated by evaporation. The crude product was purified by column chromatography with hexane to yield the desired compound (31.5 g, 84%) as a liquid. ^1H NMR (600 MHz, CDCl_3): δ 6.75 (s, 2H) ppm; ^{13}C NMR (75 MHz, CDCl_3): δ 130.2, 111.5 ppm; IR ν_{max} in cm^{-1} (in CHCl_3): 3095, 2953, 1567, 1516, 1202, 1032, 779, 710, 689; ESI-MS: 241 $[\text{M}+\text{H}]^+$.

4. 2,5-dibromo-3,4-dinitrothiophene (5): Compound 5 was prepared by adopting a reported procedure.^{4,5} Fuming H_2SO_4 (110 mL), fuming HNO_3 (60 mL), and concentrated H_2SO_4 (73 mL) were mixed in a flask and cooled in an ice bath. 2,5-dibromothiophene 4 (21.54 g, 89 mmol) was added drop wise so that the temperature was maintained at 20-30 $^\circ\text{C}$. The reaction was stirred for 4 h and then poured over ice. The solid residue was recovered by filtration, washed with water and purified by column chromatography (20%

ethyl acetate in hexane) to afford a light yellow powder (25.94 g, 88%). ^{13}C NMR (150 MHz, $\text{DMSO-}d_6$): δ 139.7, 116.5 ppm; IR ν_{max} in cm^{-1} (KBr): 2850, 2627, 1536, 1496, 1452, 1079, 800, 748, 733; ESI-MS: 332 $[\text{M}+\text{H}]^+$.

5. Thiophene-3,4-diamine (6): Compound 6 was prepared by adopting a reported procedure.⁶ Compound 5 (3.53 g, 11 mmol) and a mixture of HCl/ethanol (48 mL/69 mL) were stirred in a flask and cooled in an ice bath. Tin(II) chloride dihydrate (81 g, 360 mmol) was added in small portions to maintain the temperature at 25 °C. The reaction was stirred overnight, and 4 M KOH was added until the solution reached pH 10. The solution was extracted with ethyl acetate, and the organic layer was dried with sodium sulfate and then purified by column chromatography (70% ethyl acetate in hexane) to afford a brown solid (0.5 g, 40%). ^1H NMR (300 MHz, CDCl_3): δ 6.17 (s, 2H), 3.35 (s, 4H) ppm; ^{13}C NMR (150 MHz, CDCl_3): δ 136.9, 101.4 ppm; IR ν_{max} in cm^{-1} (KBr): 3355, 3279, 1605, 1475, 1442, 1259, 1090, 772, 702, 645.

6. 3-octylthiophene (9): Compound 9 was prepared by adopting a reported procedure.⁷⁻⁹ 1-bromooctane (28.7 mL) was added drop wise to a solution of magnesium (4.63 g, 193 mmol) in anhydrous diethyl ether (130 mL). The mixture was stirred under nitrogen for 2 h. The resulting Grignard reagent was added dropwise to a flask containing 3-bromothiophene (19 g, 116.6 mmol) and $\text{Ni}(\text{dppp})\text{Cl}_2$ (0.31 g, 0.571 mmol). After heating and stirring for 24 h, the reaction mixture was put into an ice bath, HCl (2N) was added and extracted with diethyl ether. The organic layer was dried over sodium sulfate, concentrated by evaporation and purified by column chromatography using hexane to

afford a colorless oil (15.54 g, 68%). ¹H NMR (300 MHz, CDCl₃): δ 7.20 (m, 1H), 6.90 (m, 2H), 2.61 (t, *J* = 7.68, 2H), 1.67-1.55 (m, 2H), 1.38-1.19 (m, 10H), 0.88 (t, *J* = 6.52 Hz, 3H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 143.2, 128.2, 124.9, 119.6, 31.8, 30.6, 30.3, 29.4, 29.3, 29.2, 22.6, 14.1 ppm; IR ν_{\max} in cm⁻¹(in CHCl₃): 2926, 2855, 1462, 1379, 1082, 904, 725, 649; ESI-MS: 197 [M+H]⁺.

7. 2-bromo-3-octylthiophene (10): Compound 10 was prepared by adopting a reported procedure.¹⁰ Compound 9 (5.49 g, 28 mmol) was added dropwise in the dark to a solution of N-bromosuccinimide (NBS) (5.76 g, 28 mmol) in DMF (30 mL). The mixture was stirred for 12 h at room temperature. Water (150 mL) was added, and the resultant mixture was extracted with ethyl acetate (2×150 mL). The organic layer was dried over sodium sulfate and concentrated. The crude product was purified by column chromatography using hexane to yield the desired compound as a colorless oil (6.95 g, 90%). ¹H NMR (600 MHz, CDCl₃): δ 7.18 (d, *J* = 5.5 Hz, 1H), 6.80 (d, *J* = 5.6 Hz, 1H), 2.57 (t, *J* = 7.7 Hz, 2H), 1.62-1.55 (m, 2H), 1.38-1.24(m, 10H), 0.89 (t, *J* = 6.9 Hz, 3H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 141.8, 128.3, 125.0, 108.9, 31.9, 29.7, 29.4, 29.2, 29.2, 22.7, 14.1 ppm; IR ν_{\max} in cm⁻¹(in CHCl₃): 2953, 2922, 2853, 1539, 1462, 1408, 991, 757, 713, 683; ESI-MS: 276 [M+H]⁺.

8. Tributyl(3-octylthiophene-2-yl)stannane (11): Compound 11 was prepared by adopting a reported procedure.^{11,12} A solution of 10 (2.1 g, 7.6 mmol) was added dropwise to a refluxing suspension of magnesium (0.17 g, 7 mmol) in anhydrous THF (10 mL). After the mixture was refluxed for 2 h, a solution of tributyltin chloride (1.90 mL,

6.5 mmol) in anhydrous THF (10 mL) was added drop wise at 0 °C. The reaction mixture was warmed to room temperature and stirred overnight and mixture was poured into water and extracted with hexane. The organic layer was dried over sodium sulfate and evaporated to afford a colorless oil (3.4 g, 92%). ¹H NMR (300 MHz, CDCl₃): δ 7.53 (d, *J*=4.6 Hz, 1H), 7.10 (d, *J*=4.6 Hz, 1H), 2.59 (t, *J*= 7.9 Hz, 2H), 1.77-1.49 (m, 8H), 1.42-1.18 (m, 16H), 1.16-1.07 (m, 6H), 0.97-0.79 (m, 12H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 150.7, 130.8, 130.6, 129.1, 32.9, 32.2, 31.8, 29.8, 29.6, 29.3, 29.0, 27.3, 22.6, 14.1, 13.6, 10.8 ppm; IR ν_{max} in cm⁻¹(in CHCl₃): 3097, 1568, 1517, 1033, 980, 947, 783, 727, 649; ESI-MS: 486 [M+H]⁺.

9. 3',4'-dinitro-3,3''-dioctyl-2,2':5',2''-terthiophene (12): Compound 12 was prepared by adopting a reported procedure.¹³ Compounds 5 (2.2 g, 6.6 mmol) and 11 (6.77 g, 13.8 mmol) were added to a solution of PdCl₂(PPh₃)₂ (98 mg) in toluene (30 mL). The reaction mixture was refluxed under nitrogen for 12 h. The reaction mixture was allowed to cool to room temperature. The solvent was removed, and the crude product was purified by silica gel column chromatography (10% ethyl acetate in hexane) to afford the desired compound as an orange oil (3.3 g, 89%). ¹H NMR (300 MHz, CDCl₃): δ 7.49 (d, *J*=5.1 Hz, 2H), 7.03 (d, *J*=5.0 Hz, 2H), 2.58 (t, *J*=7.6 Hz, 4H), 1.64-1.53 (m, 4H), 1.33-1.18 (m, 20H), 0.86 (t, *J*=6.1 Hz, 6H) ppm; ¹³C NMR (150 MHz, CDCl₃): δ 146.2, 134.7, 129.5, 129.2, 128.9, 120.3, 31.8, 30.4, 29.3, 29.2, 29.2, 29.1, 22.6, 14.1 ppm; IR ν_{max} in cm⁻¹(in CHCl₃): 2926, 2856, 1543, 1512, 1461, 1093, 723, 675, 668; ESI-MS: 563 [M+H]⁺.

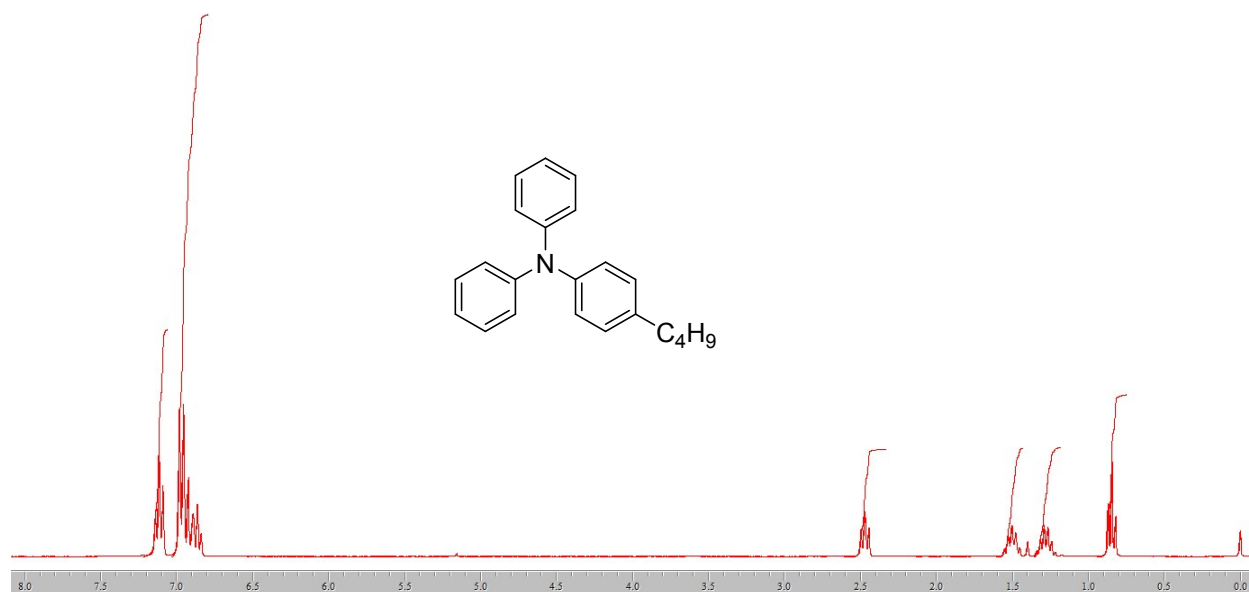


Figure 1. ¹H-NMR spectrum of 4-butyl-N,N-diphenylaniline (**1**) in CDCl₃

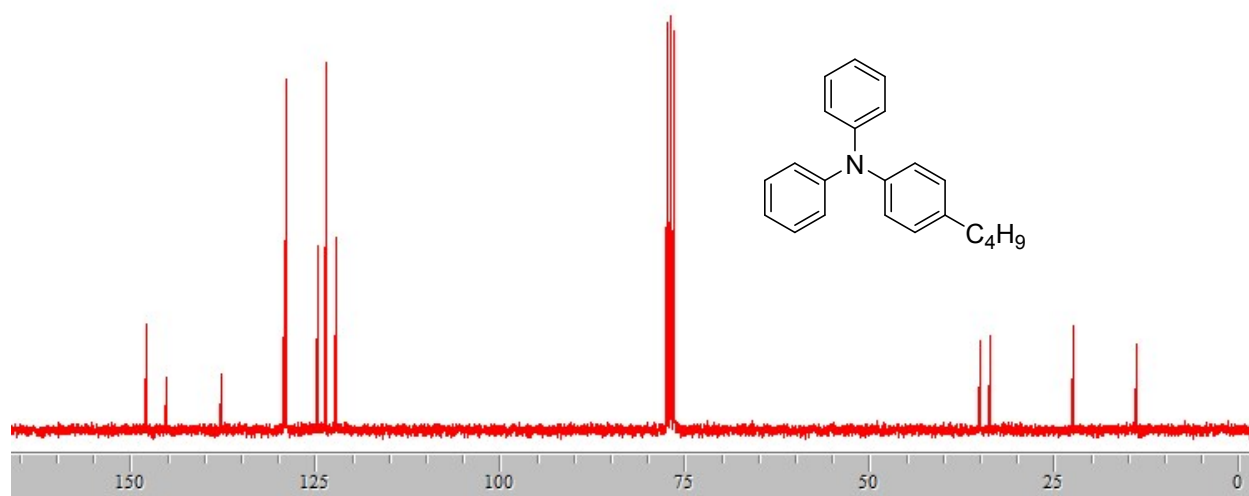


Figure 2. ¹³C-NMR spectrum of 4-butyl-N,N-diphenylaniline (**1**) in CDCl₃

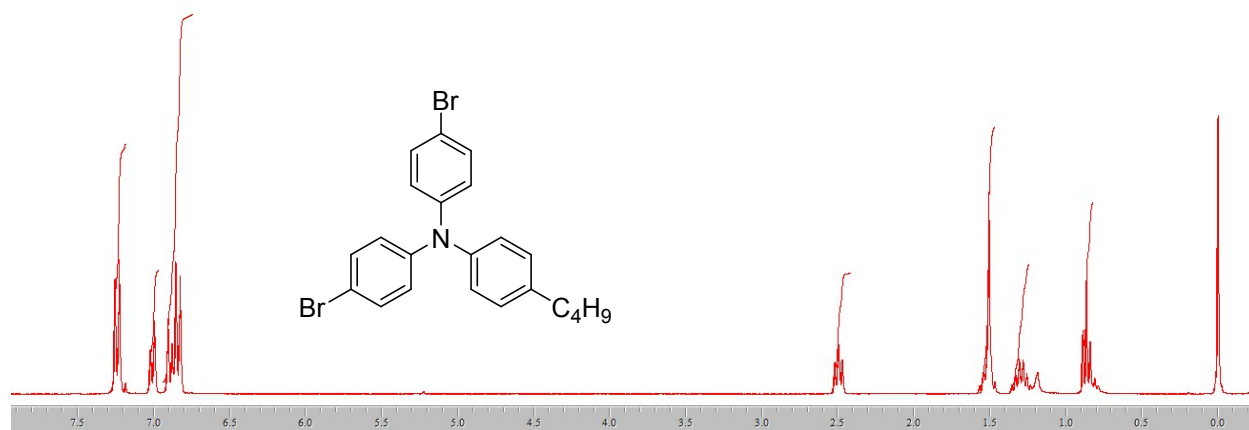


Figure 3. ¹H-NMR spectrum of 4-bromo-N-(4-bromophenyl)-N-(4-butylphenyl)aniline (**2**) in CDCl₃

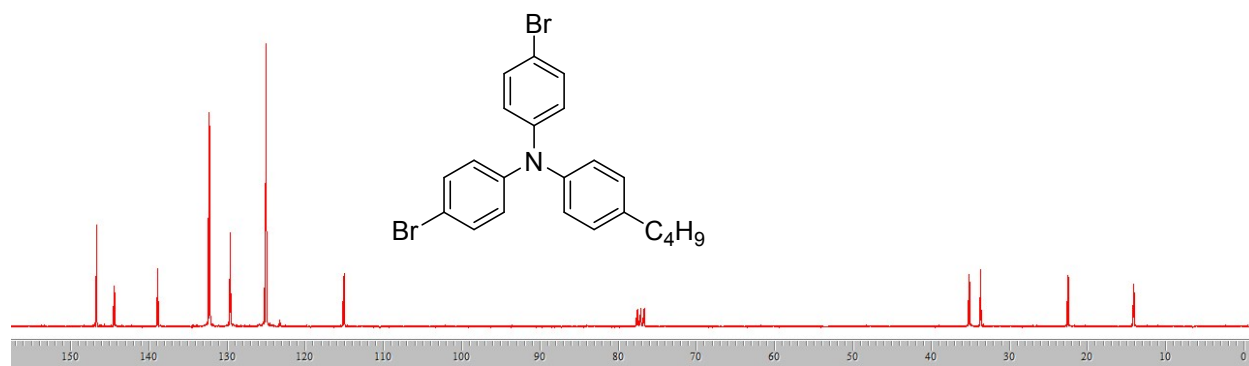


Figure 4. ¹³C-NMR spectrum of 4-bromo-N-(4-bromophenyl)-N-(4-butylphenyl)aniline (**2**) in CDCl₃

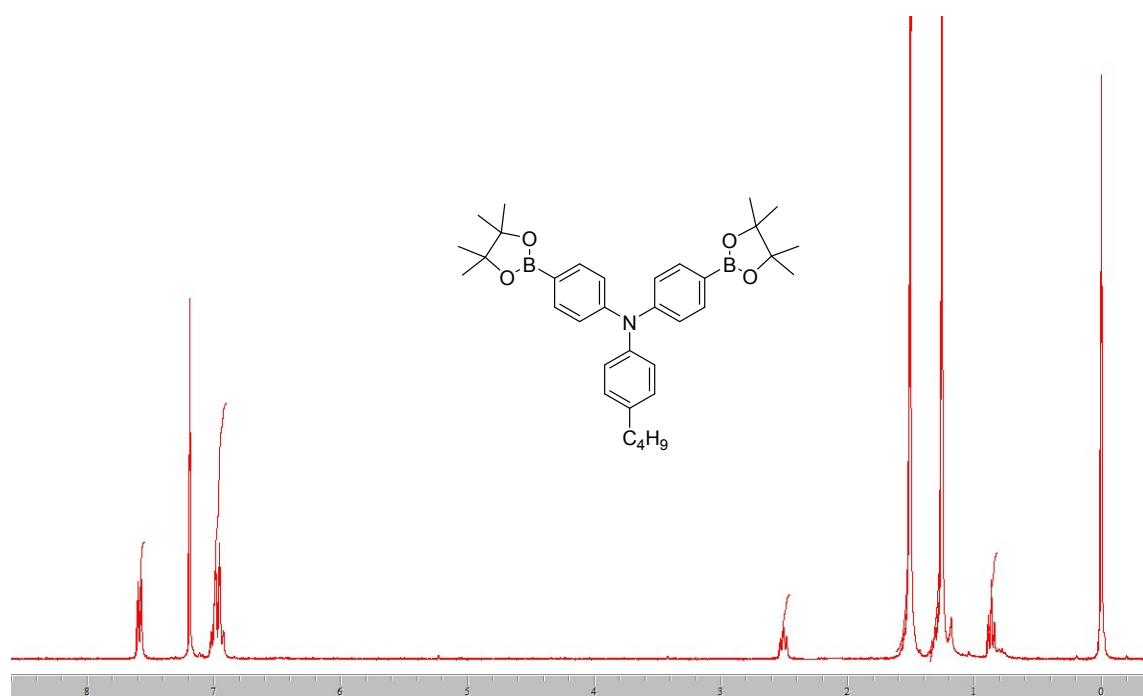


Figure 5. ¹H-NMR spectrum of 4-butyl-N,N-bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (**3**) in CDCl₃

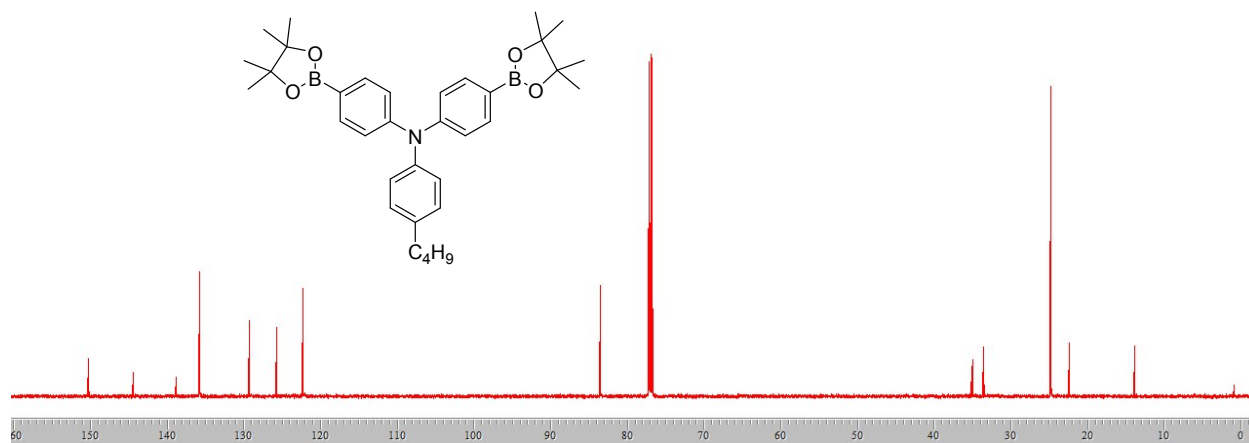


Figure 6. ¹³C-NMR spectrum of 4-butyl-N,N-bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (**3**) in CDCl₃

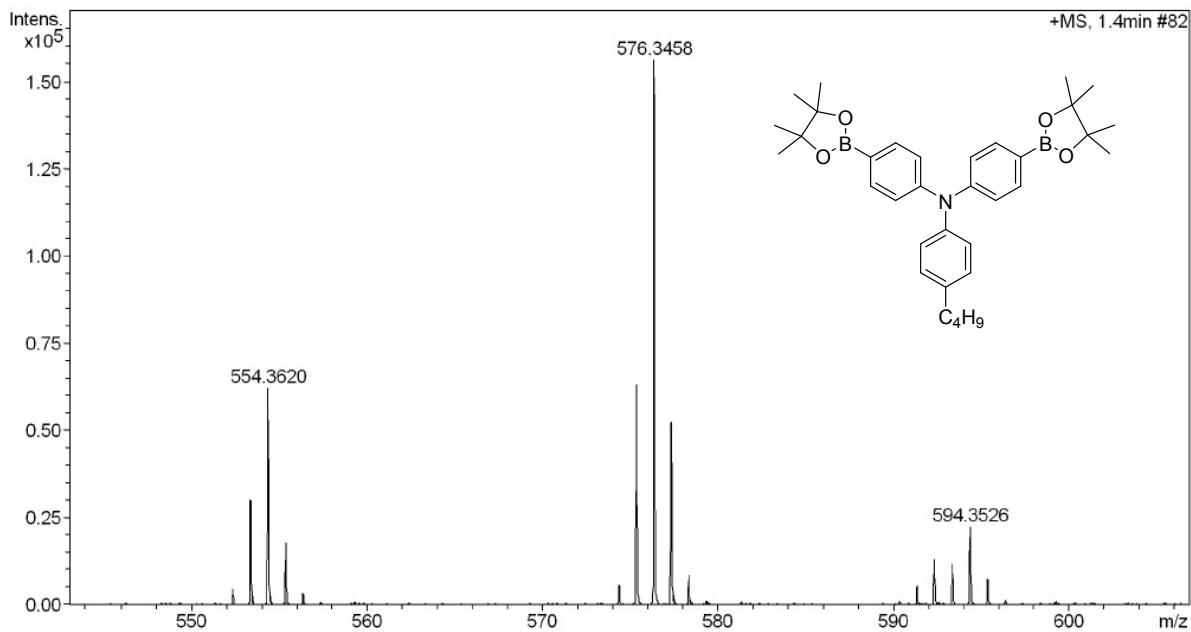


Figure 7. high-resolution ESI-MS of Compound **3**

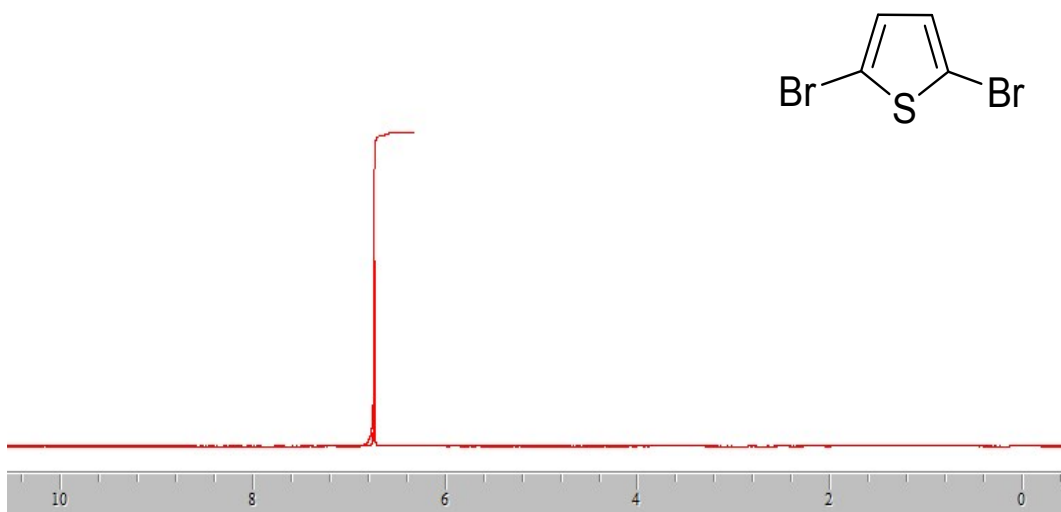


Figure 8. ¹H-NMR spectrum of 2,5-dibromothiophene (**4**) in CDCl₃

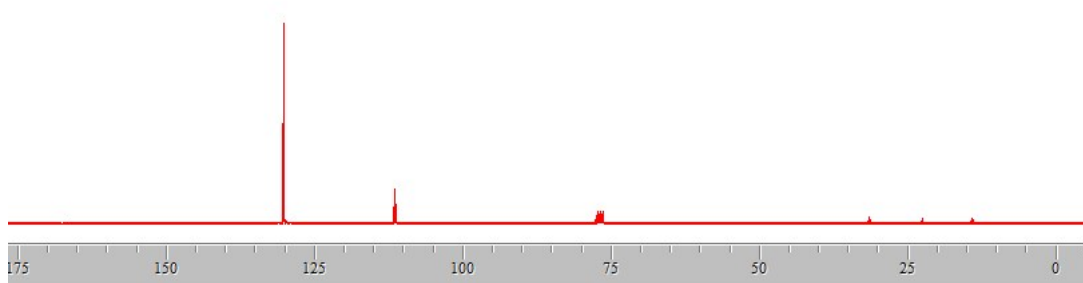
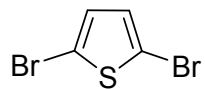


Figure 9. ¹³C-NMR spectrum of 2,5-dibromothiophene (**4**) in CDCl₃

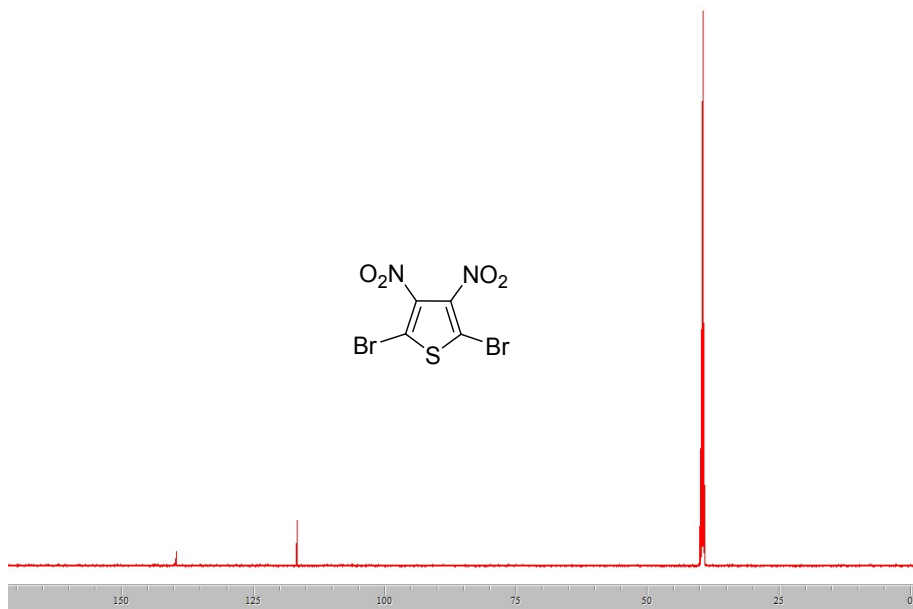
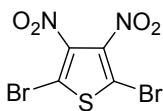


Figure 10. ¹³C-NMR spectrum of 2,5-dibromo-3,4-dinitrothiophene (**5**) in CDCl₃

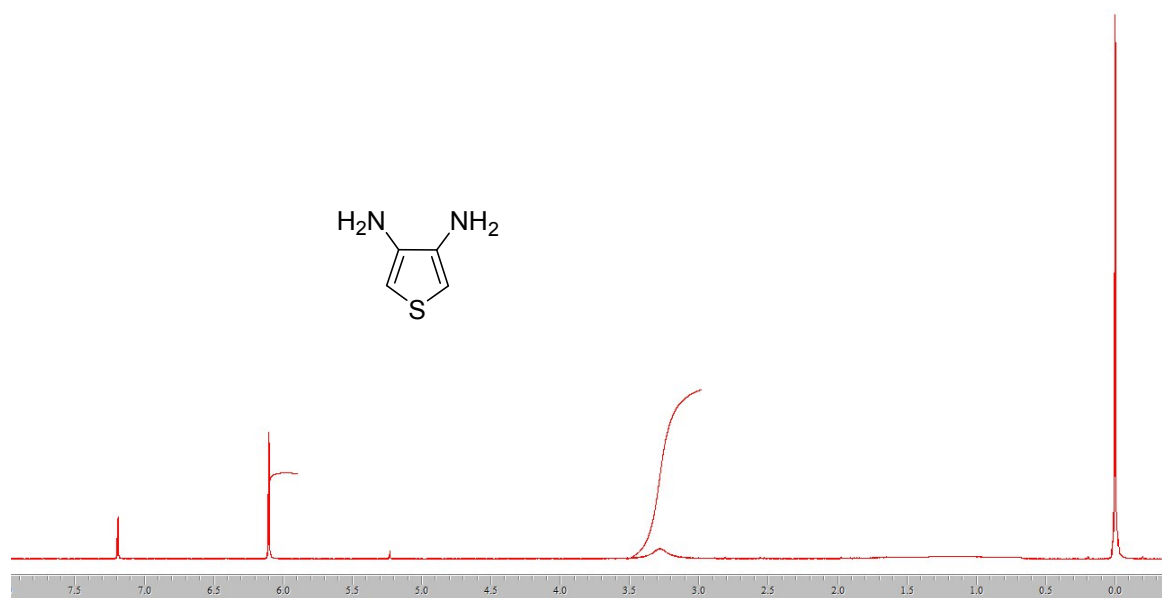


Figure 11. $^1\text{H-NMR}$ spectrum of thiophene-3,4-diamine (**6**) in CDCl_3

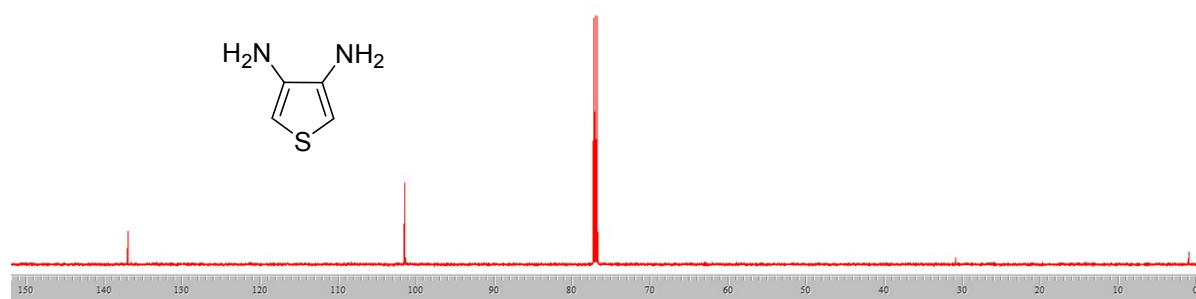


Figure 12. $^{13}\text{C-NMR}$ spectrum of thiophene-3,4-diamine (**6**) in CDCl_3

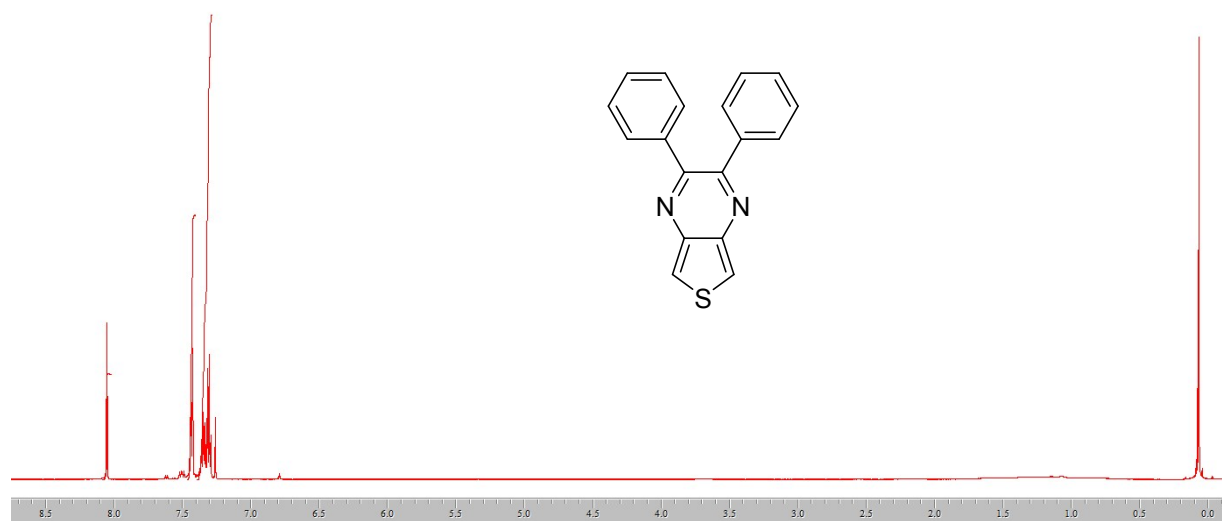


Figure 13. ¹H-NMR spectrum of 2,3-diphenylthieno[3,4-b]pyrazine (**7**) in CDCl₃

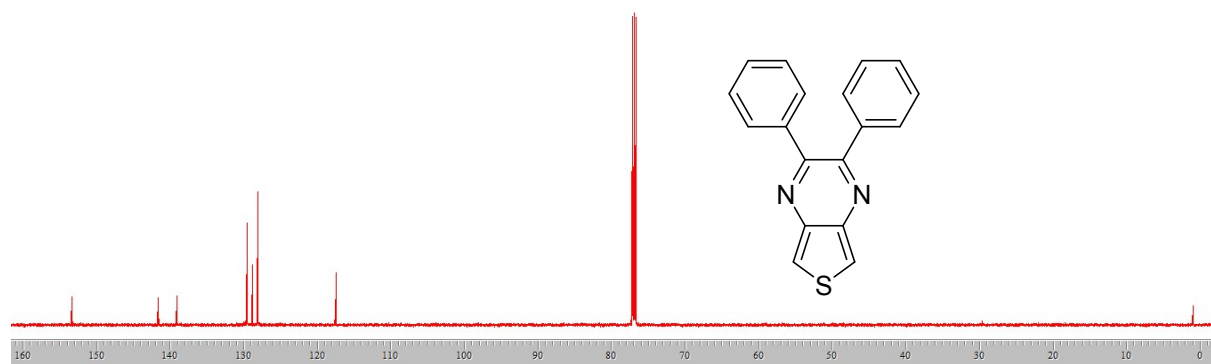


Figure 14. ¹³C-NMR spectrum of 2,3-diphenylthieno[3,4-b]pyrazine (**7**) in CDCl₃

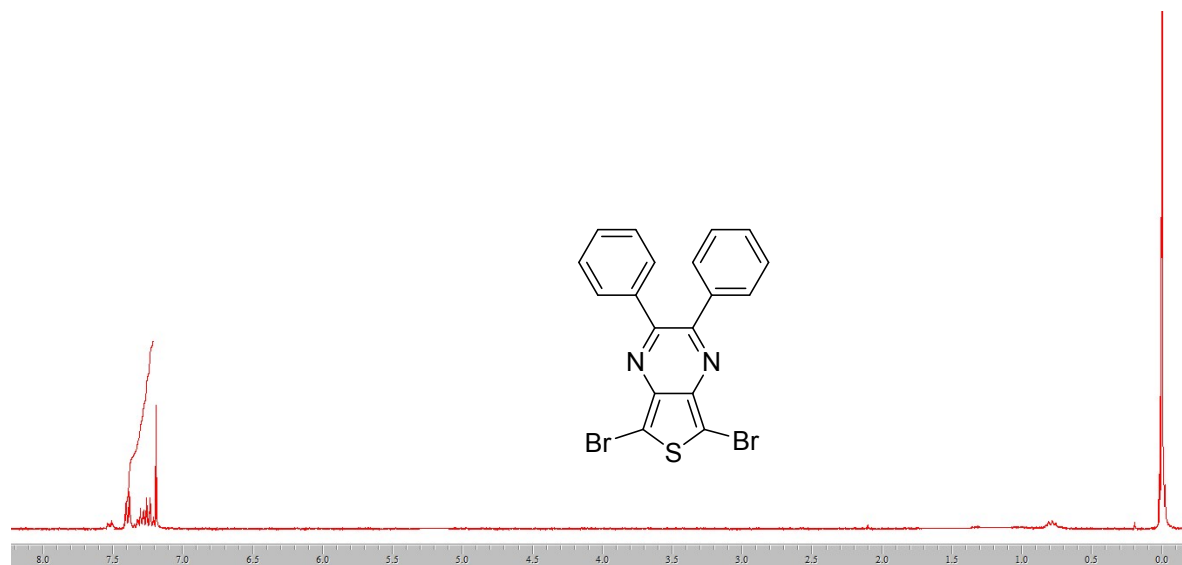


Figure 15. ¹H-NMR spectrum of 5,7-dibromo-2,3-diphenylthieno[3,4-b]pyrazine (**8**) in CDCl₃

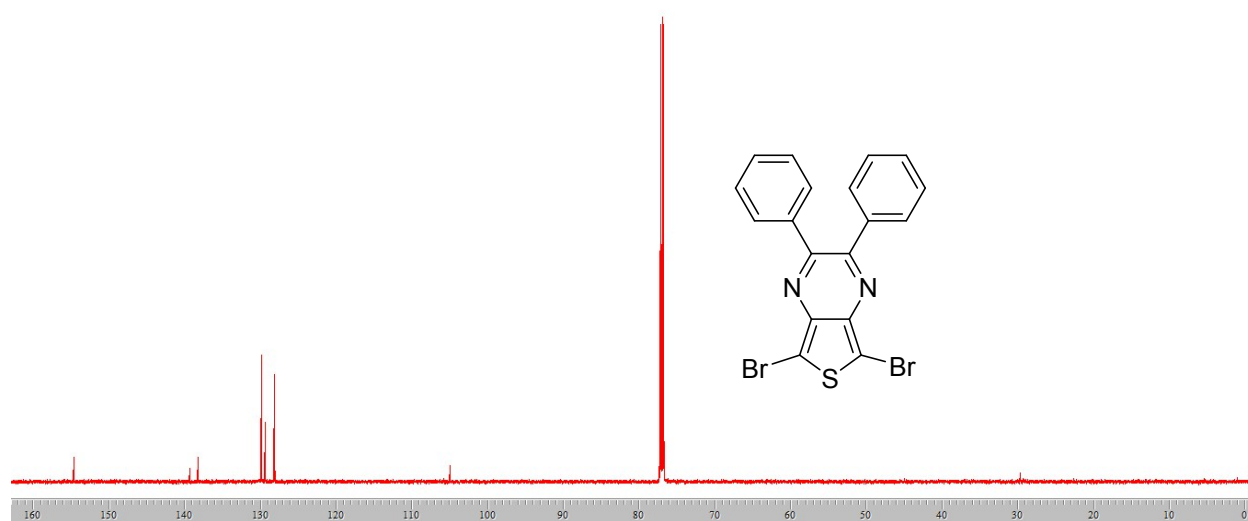


Figure 16. ¹³C-NMR spectrum of 5,7-dibromo-2,3-diphenylthieno[3,4-b]pyrazine (**8**) in CDCl₃

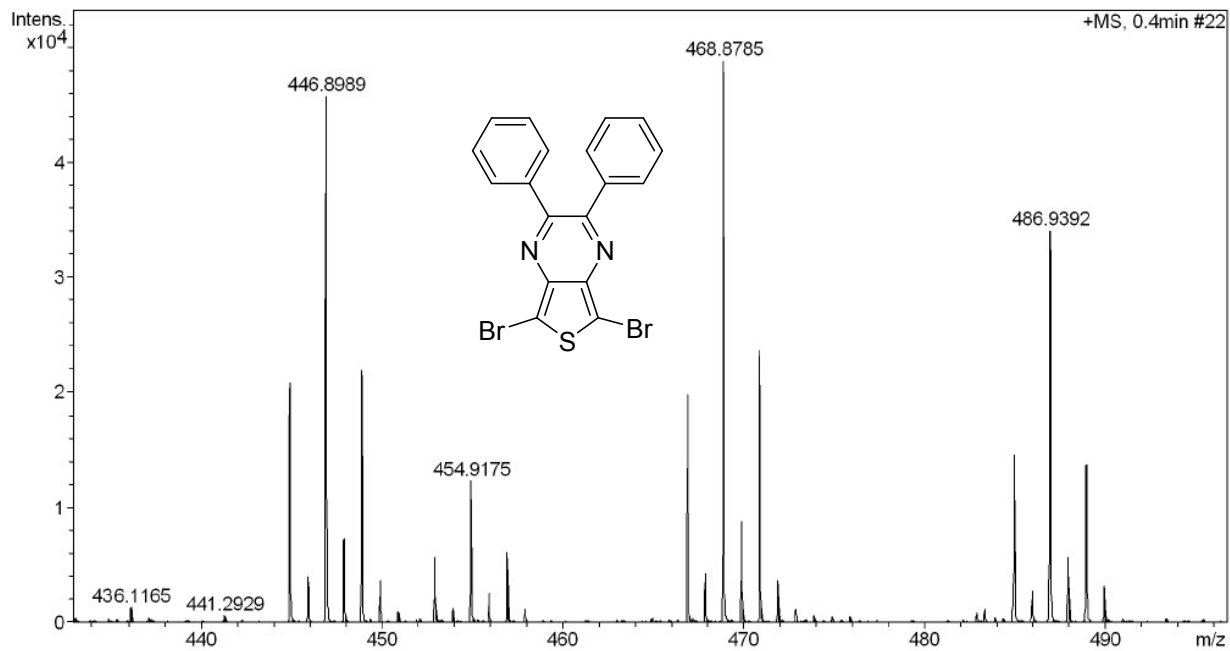


Figure 17. high-resolution ESI-MS of Compound **8**

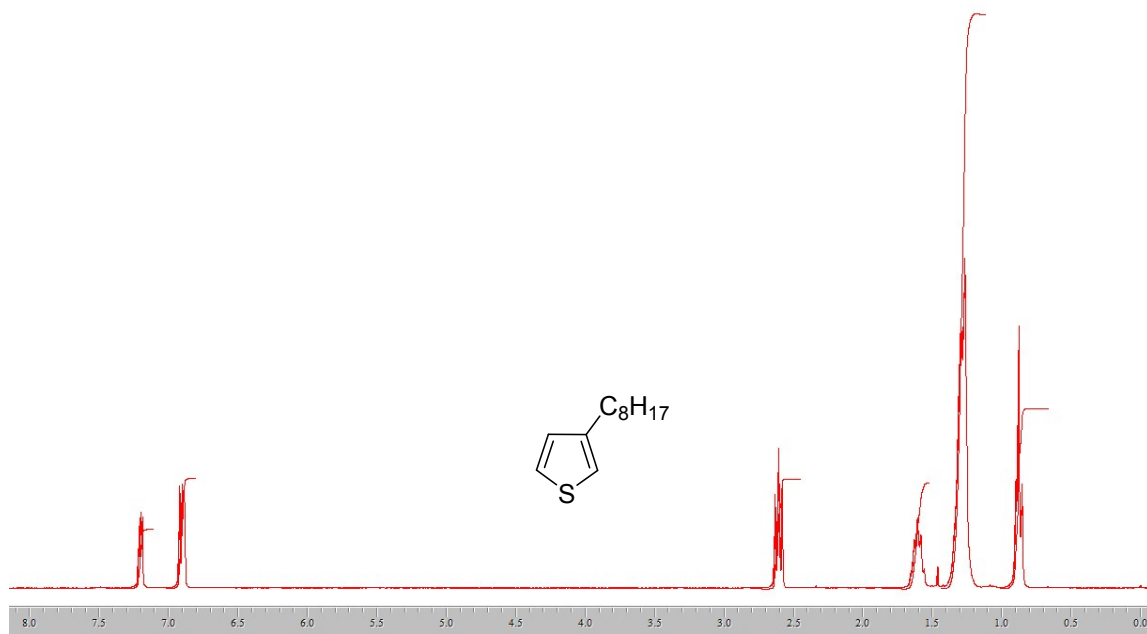


Figure 18. $^1\text{H-NMR}$ spectrum of 3-octylthiophene (**9**) in CDCl_3

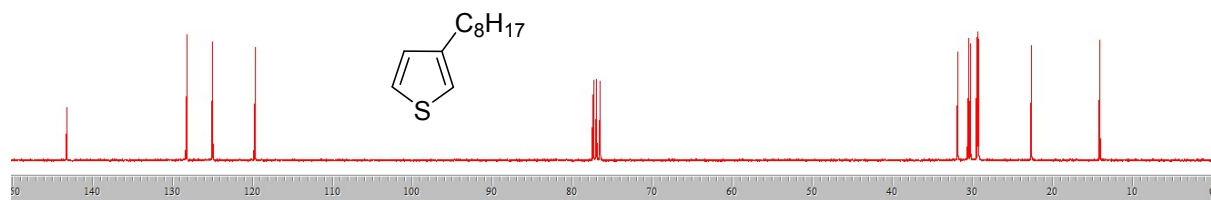


Figure 19. ^{13}C -NMR spectrum of 3-octylthiophene (**9**) in CDCl_3

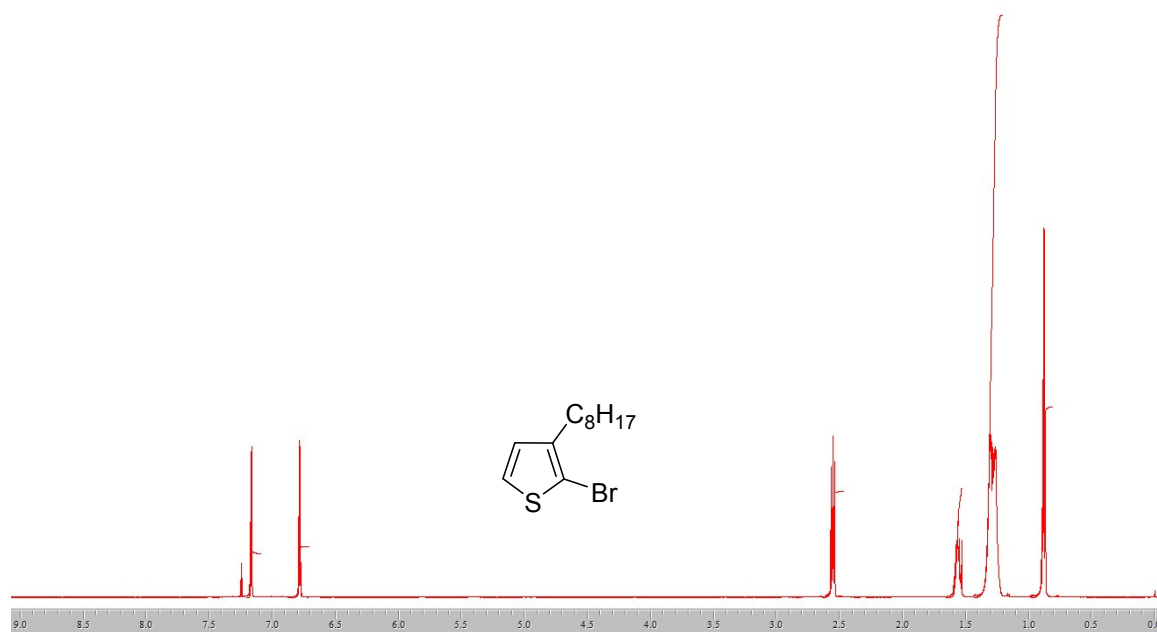


Figure 20. ^1H -NMR spectrum of 2-bromo-3-octylthiophene (**10**) in CDCl_3

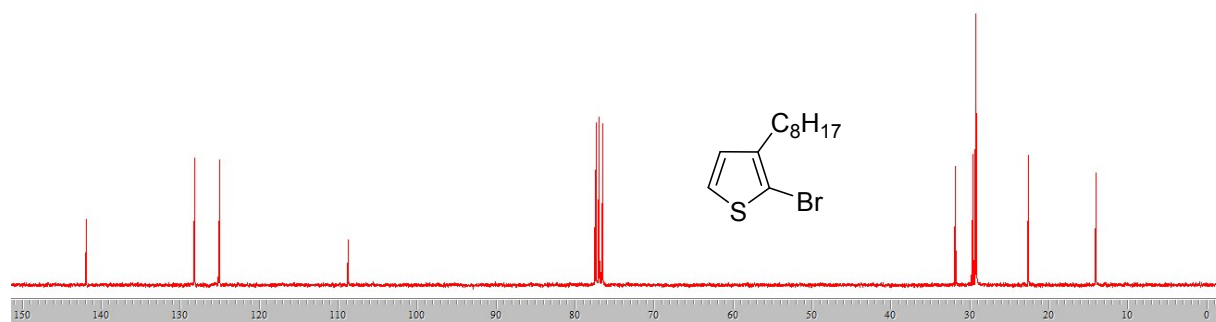


Figure 21. ^{13}C -NMR spectrum of 2-bromo-3-octylthiophene (**10**) in CDCl_3

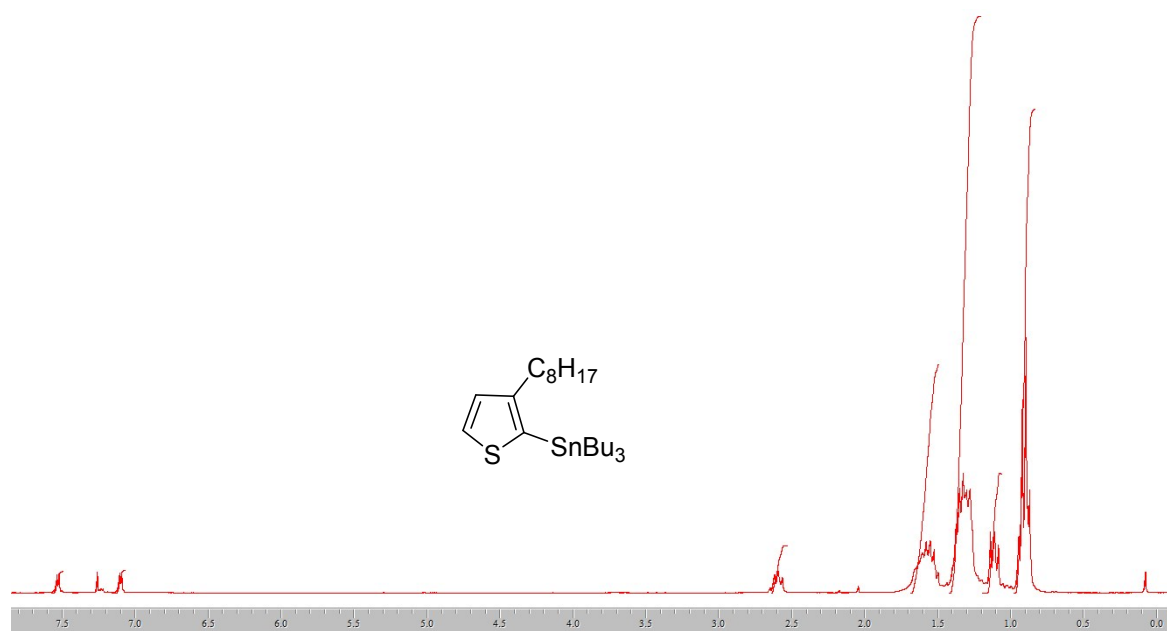


Figure 22. ^1H -NMR spectrum of tributyl(3-octylthiophen-2-yl)stannane (**11**) in CDCl_3

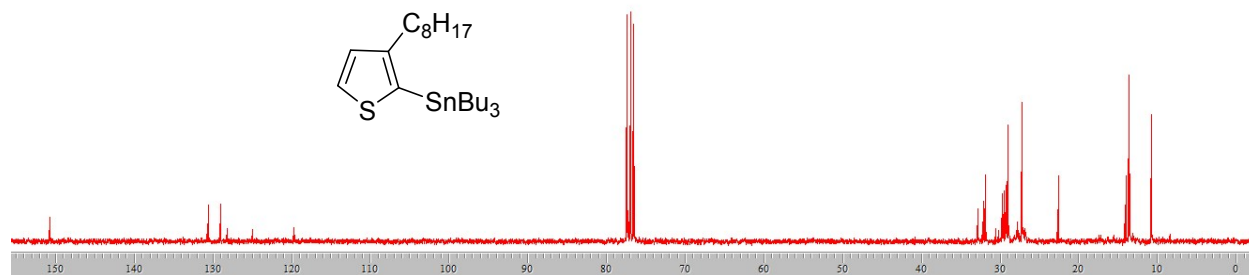


Figure 23. ^{13}C -NMR spectrum of tributyl(3-octylthiophen-2-yl)stannane (**11**) in CDCl_3

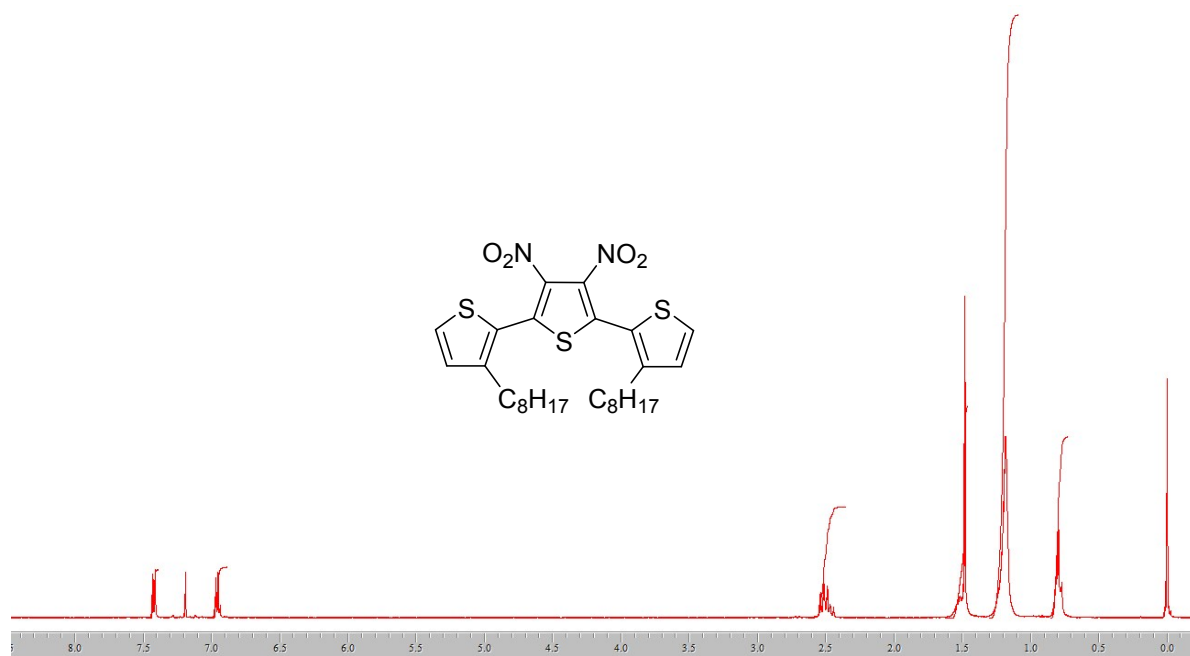


Figure 24. ^1H -NMR spectrum of 3',4'-dinitro-3,3''-dioctyl-2,2':5,2''-terthiophene (**12**) in CDCl_3

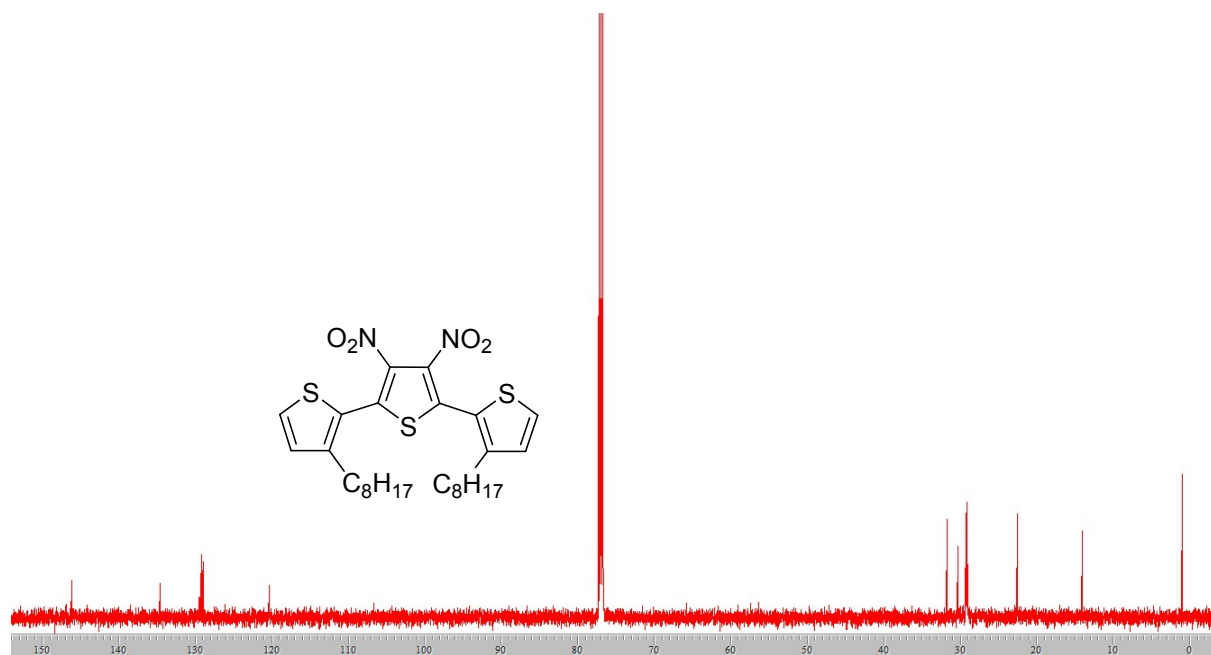


Figure 25. ^{13}C -NMR spectrum of 3',4'-dinitro-3,3''-dioctyl-2,2':5',2''-terthiophene (**12**) in CDCl_3

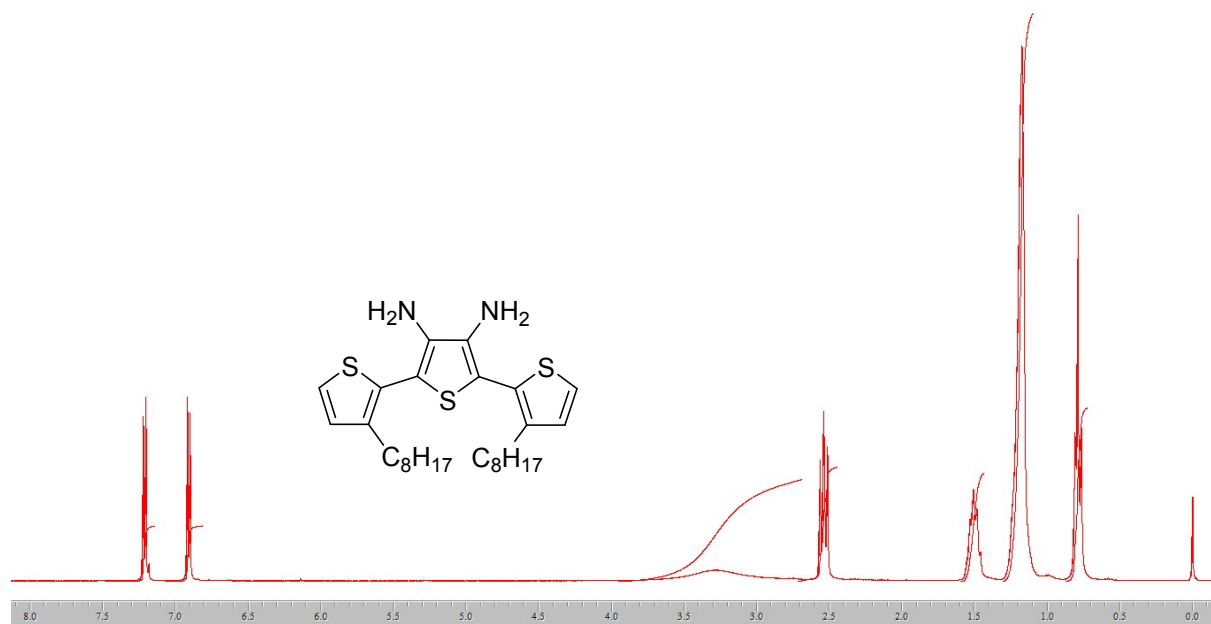


Figure 26. ^1H -NMR spectrum of 3,3''-dioctyl-[2,2':5',2''-terthiophene]-3',4'-diamine (**13**) in CDCl_3

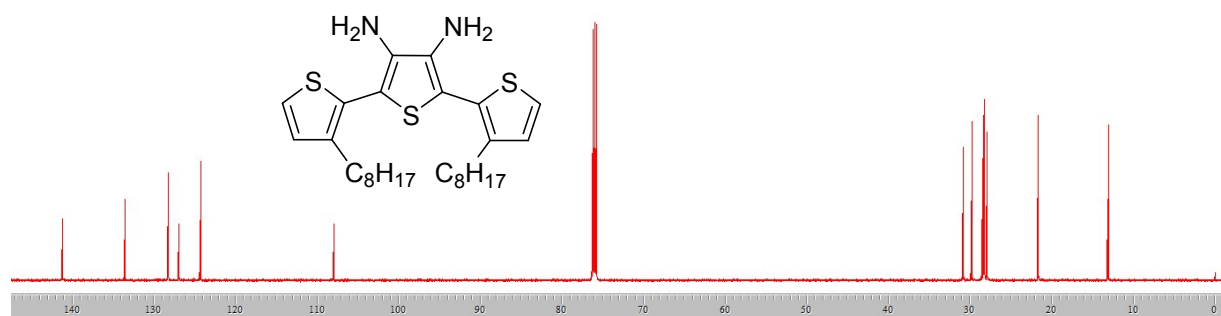


Figure 27. ^{13}C -NMR spectrum of 3,3''-dioctyl-[2,2':5',2''-terthiophene]-3,4'-diamine (**13**) in CDCl_3

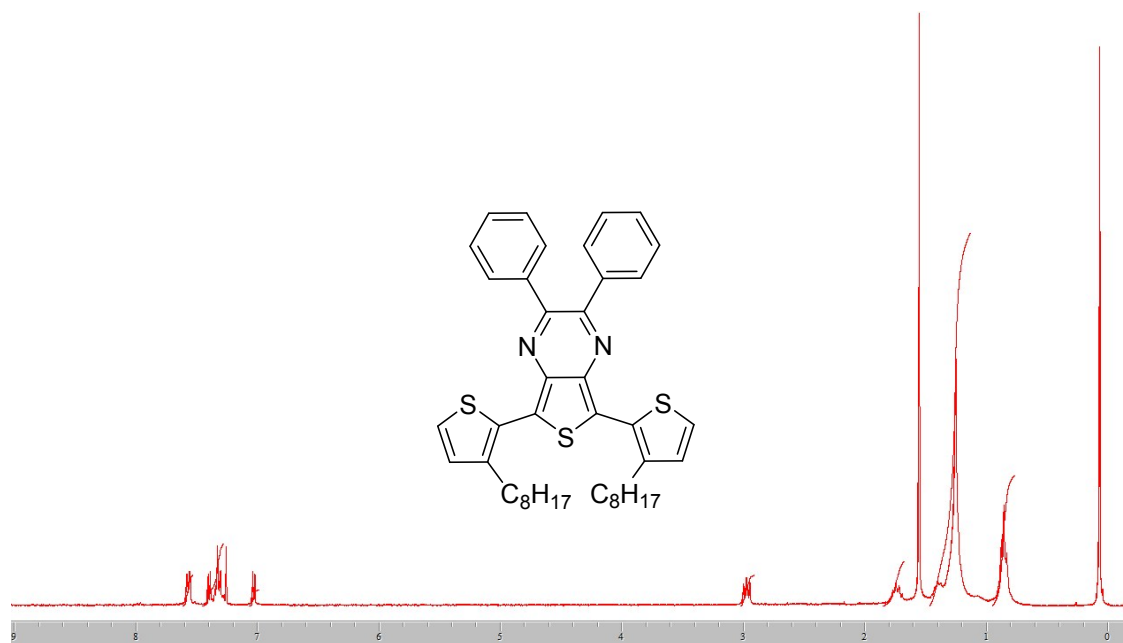


Figure 28. ^1H -NMR spectrum of 5,7-bis(3-octylthiophen-2-yl)-2,3-diphenylthieno[3,4-b]pyrazine (**14**) CDCl_3

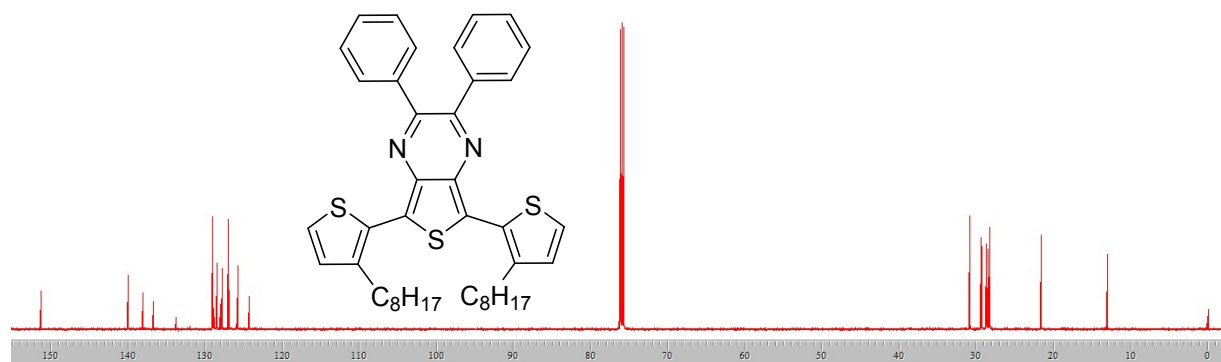


Figure 29. ¹³C-NMR spectrum of 5,7-bis(3-octylthiophen-2-yl)-2,3-diphenylthieno[3,4-b]pyrazine (**14**) in CDCl₃

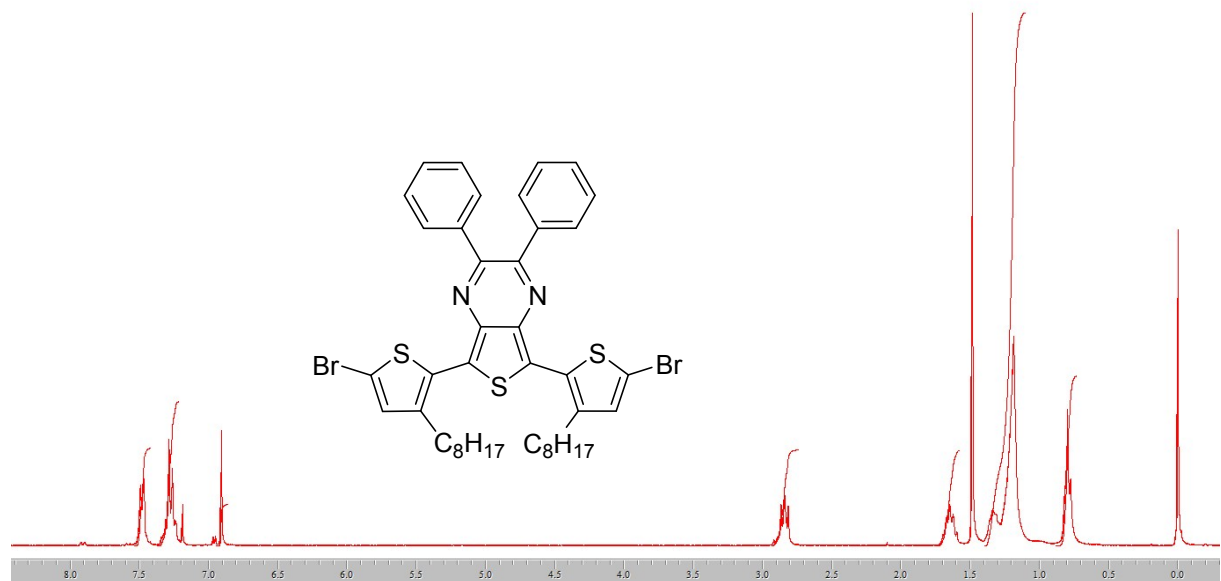


Figure 30. ¹H-NMR spectrum of 5,7-bis(5-bromo-3-octylthiophen-2-yl)-2,3-diphenylthieno[3,4-b]pyrazine (**15**) in CDCl₃

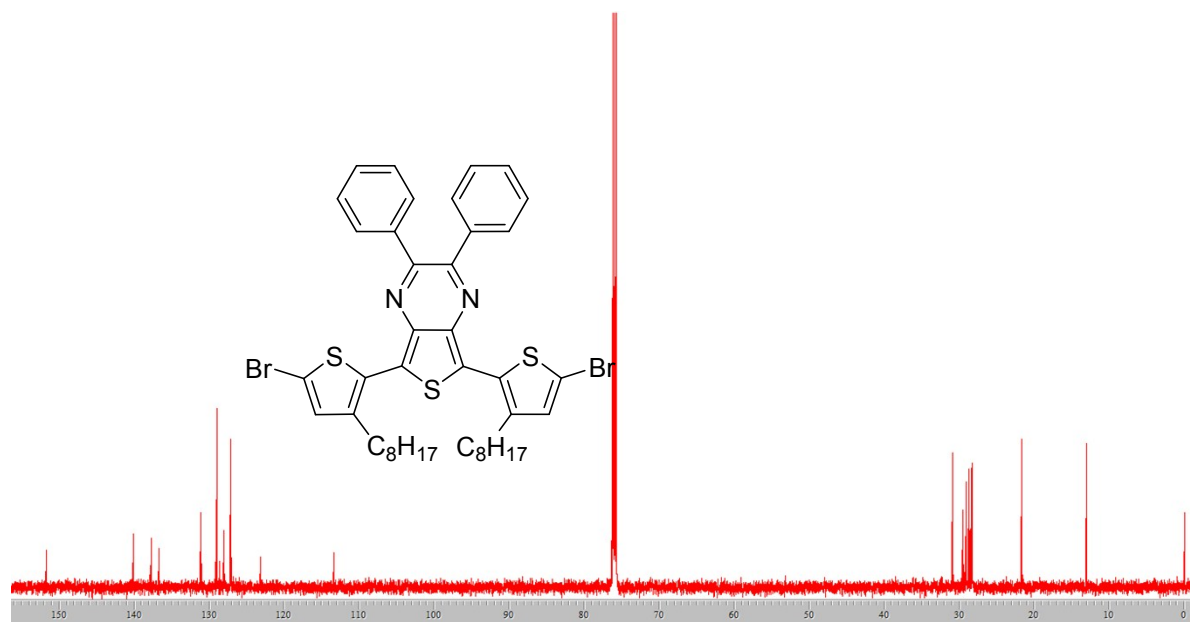


Figure 31. ¹³C-NMR spectrum of 5,7-bis(5-bromo-3-octylthiophen-2-yl)-2,3-diphenylthieno[3,4-b]pyrazine (**15**) in CDCl₃

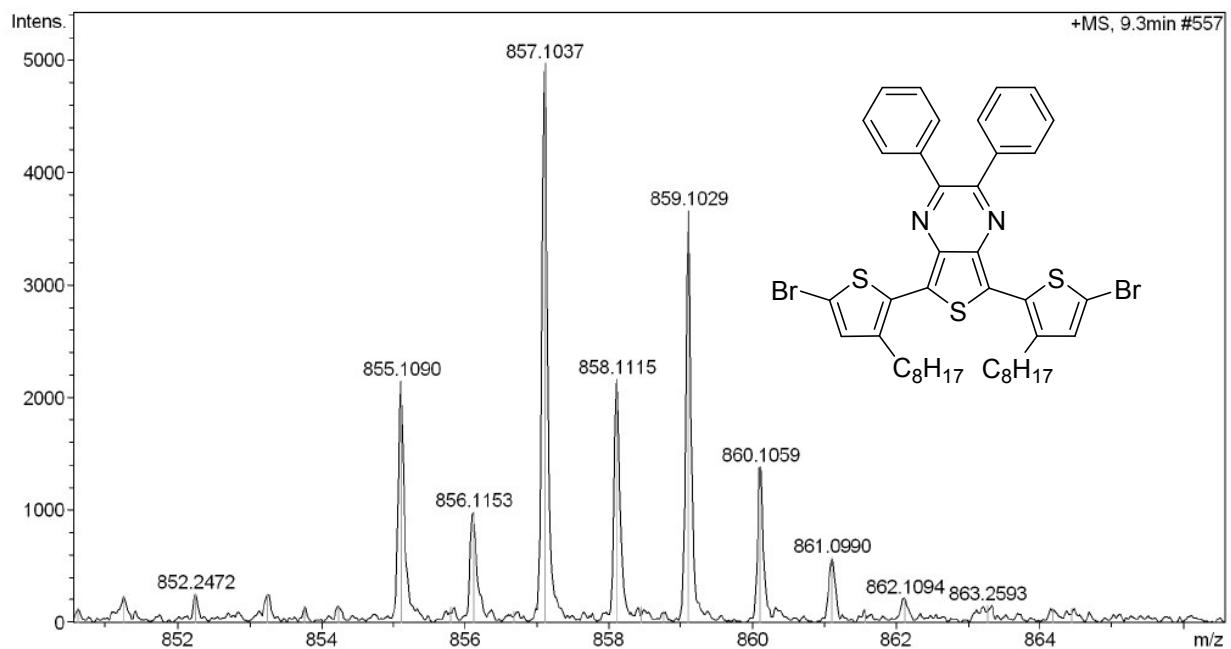


Figure 32. high-resolution ESI-MS of Compound **15**

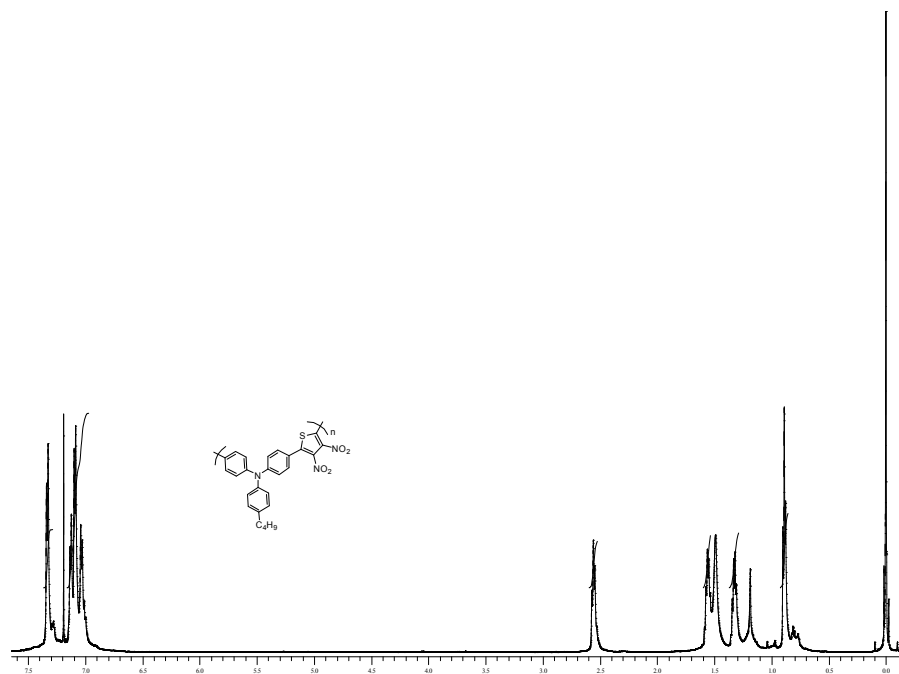


Figure 33. ¹H-NMR spectrum of **PJK1** in CDCl₃

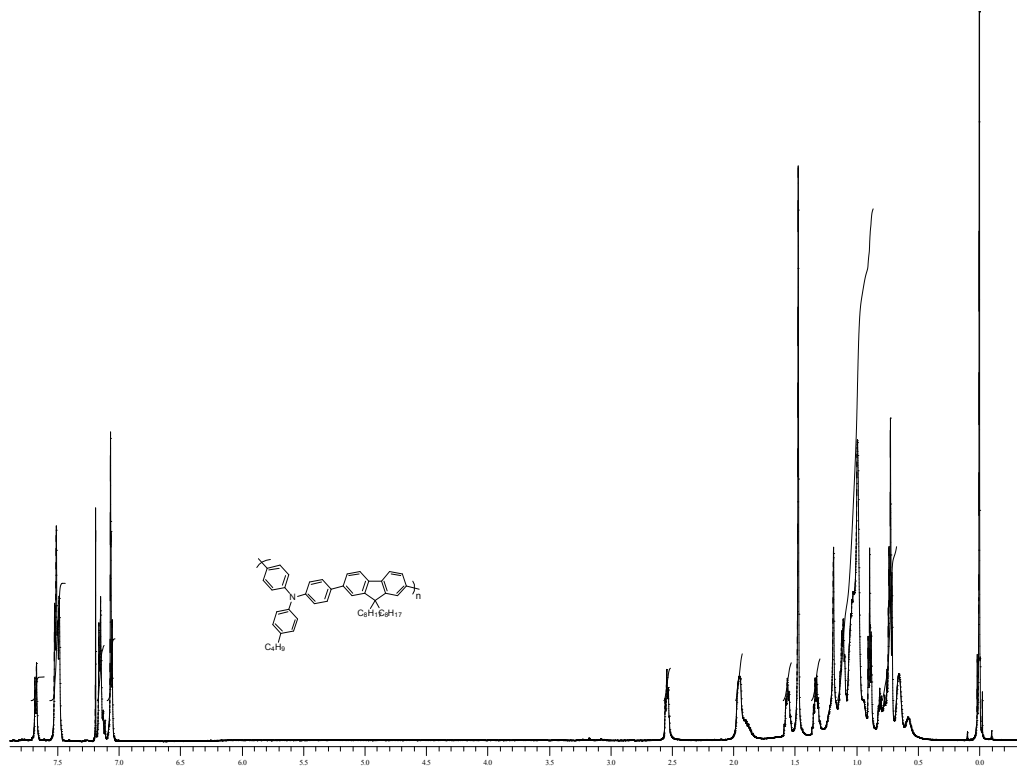


Figure 34. ¹H-NMR spectrum of **PJK2** in CDCl₃

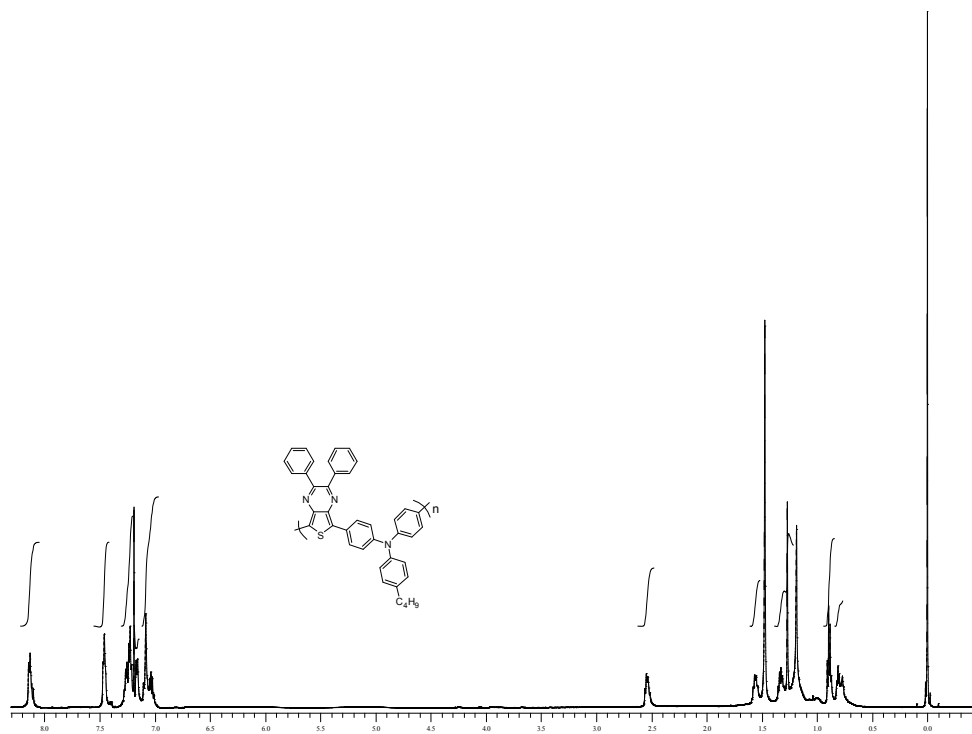


Figure 35. $^1\text{H-NMR}$ spectrum of **PJK3** in CDCl_3

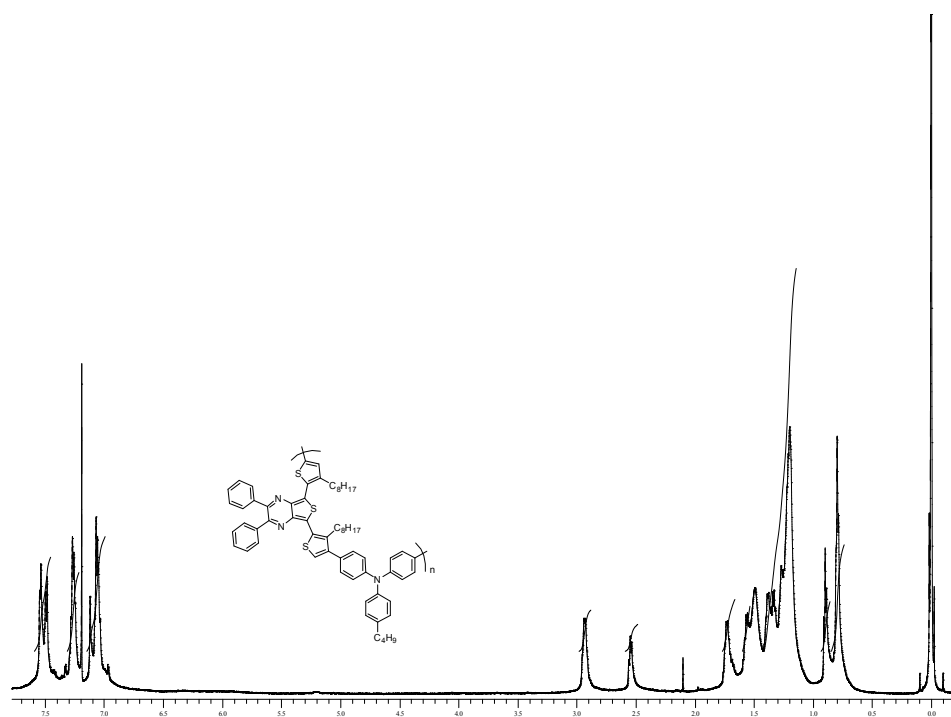
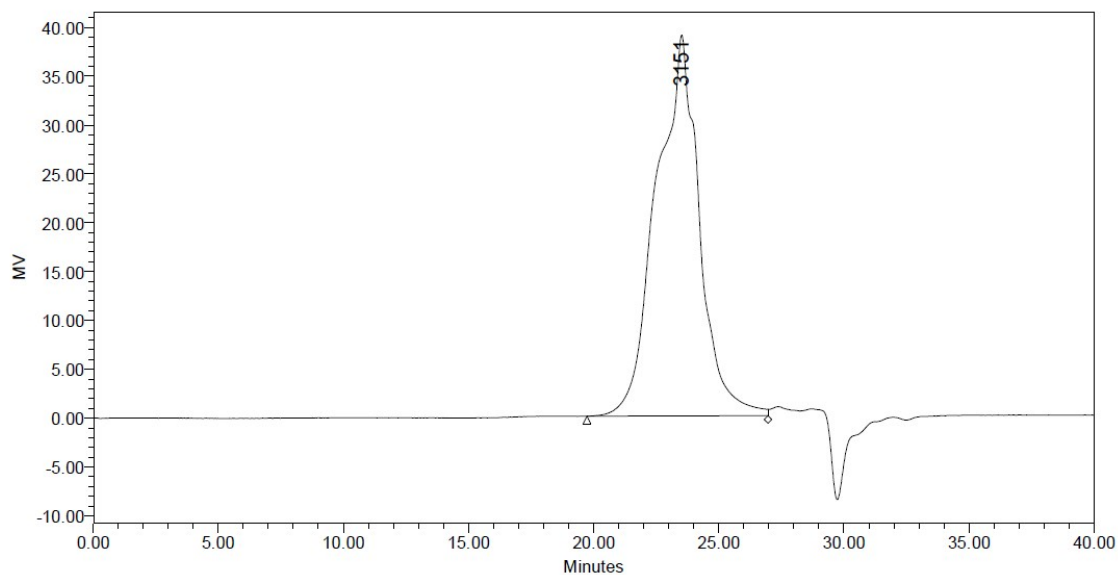


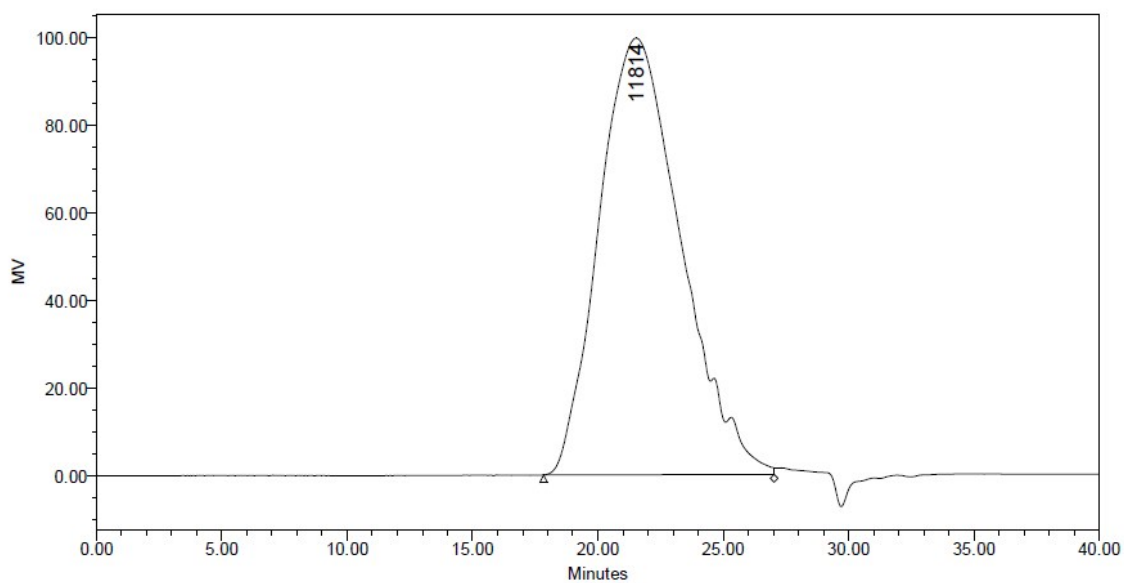
Figure 36. $^1\text{H-NMR}$ spectrum of **PJK4** in CDCl_3



GPC Results

Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1	2618	4210	3151	5988	8311		1.607988		

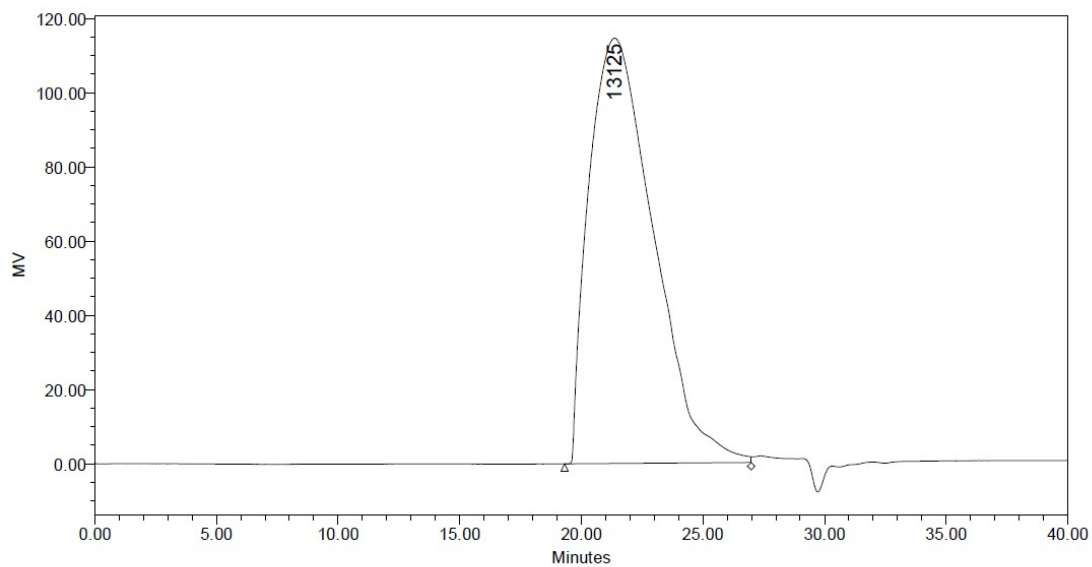
Figure 37. GPC spectrum of **PJK1**



GPC Results

Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1	4743	15021	11814	30341	48264		3.166781		

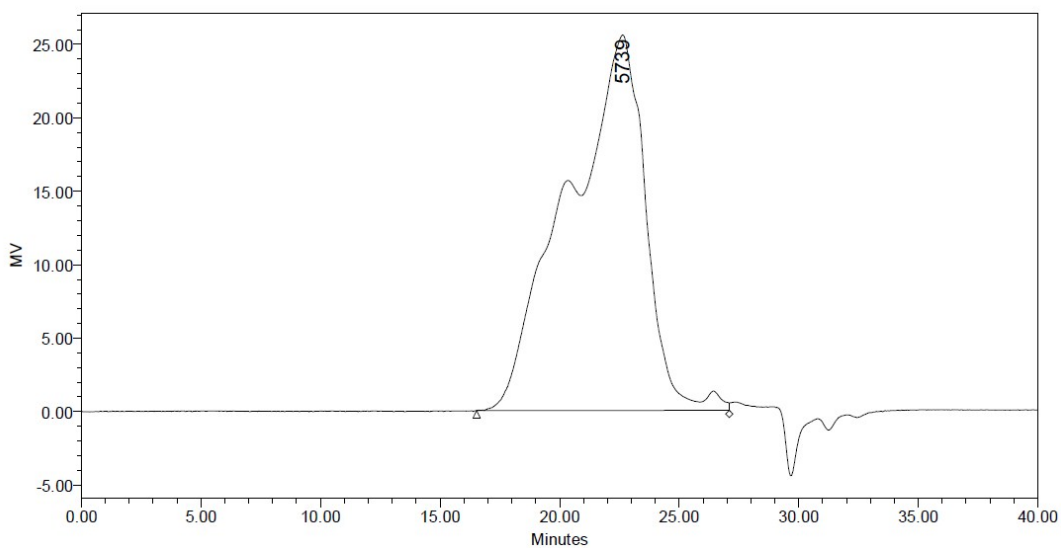
Figure 38. GPC spectrum of **PJK2**



GPC Results

Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1	5419	12398	13125	18387	23005		2.287958		

Figure 39. GPC spectrum of PJK3



GPC Results

Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1	5312	21590	5739	65720	129217		4.064033		

Figure 40. GPC spectrum of PJK4

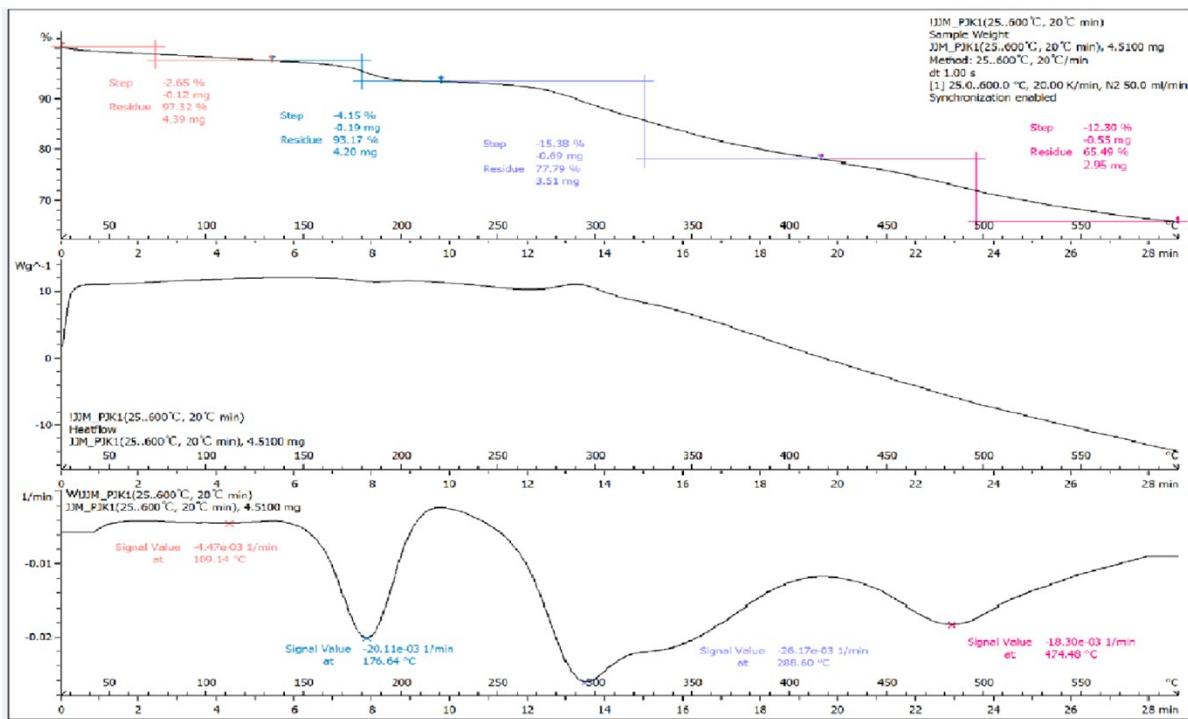


Figure 41. TGA spectrum of PJK1

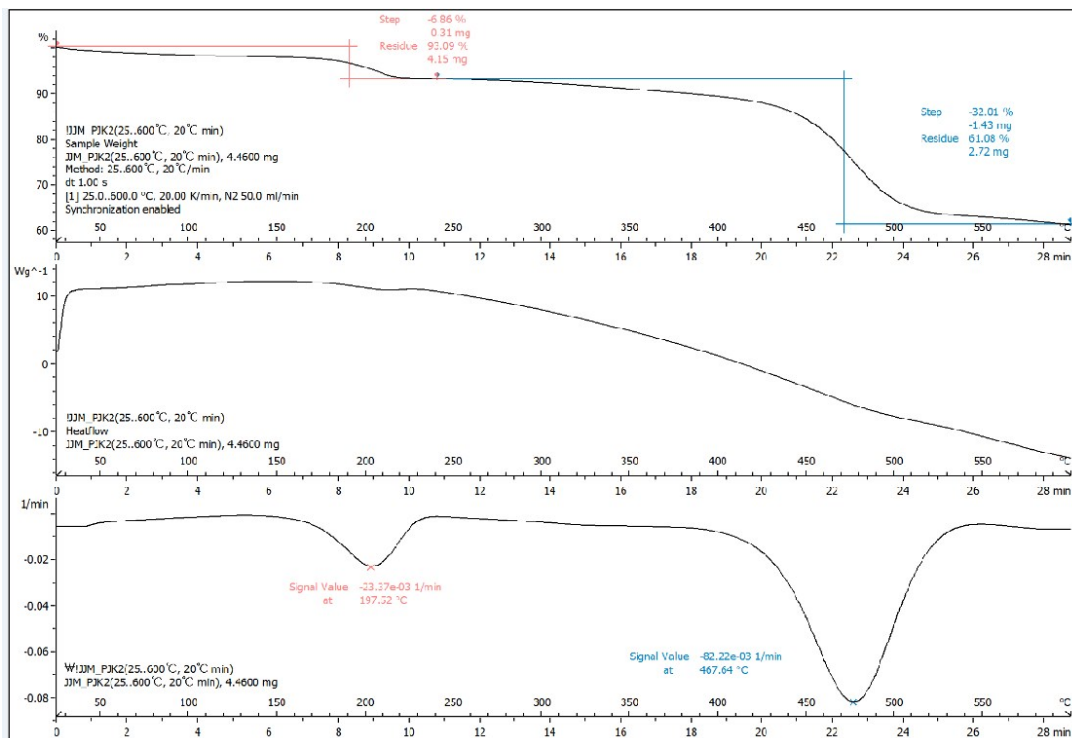


Figure 42. TGA spectrum of PJK2

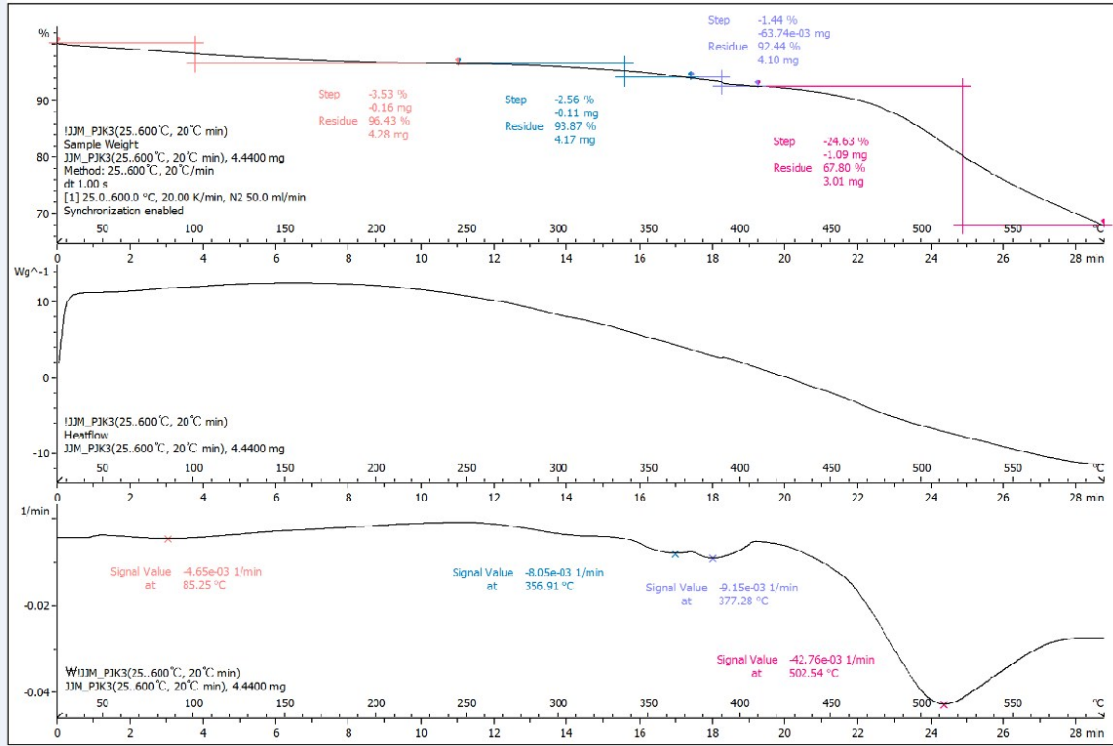


Figure 43. TGA spectrum of PJK3

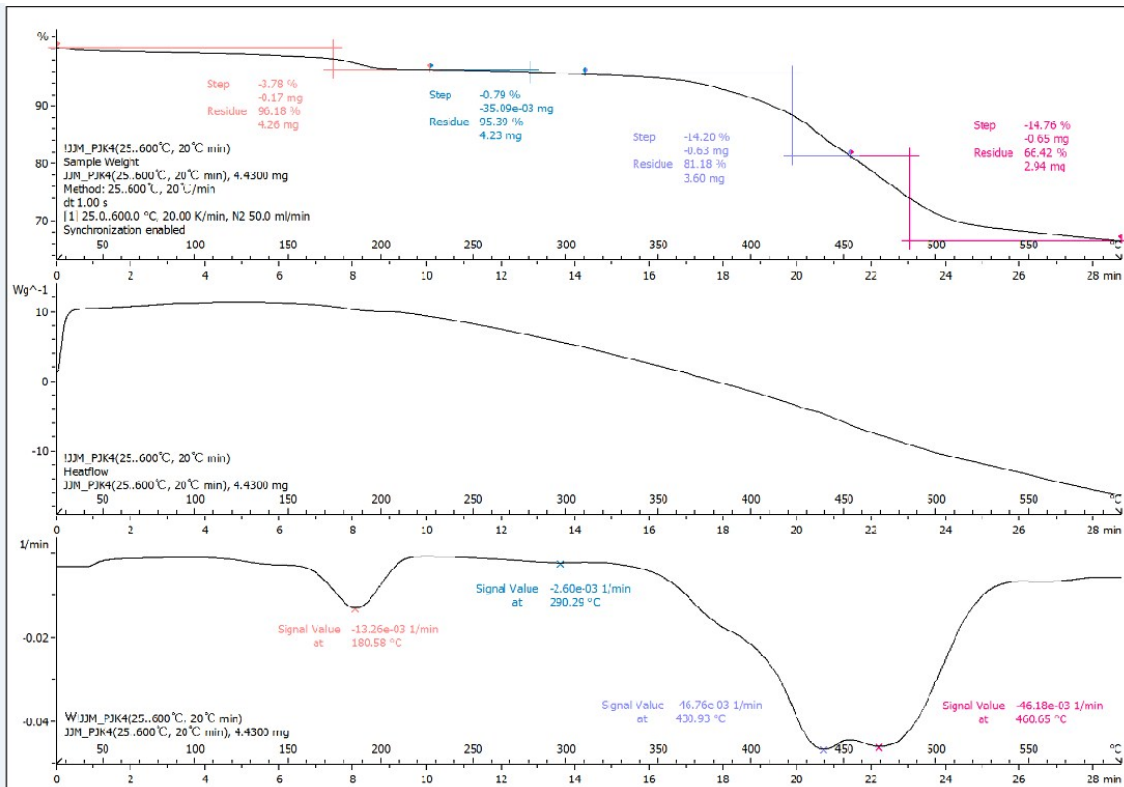


Figure 44. TGA spectrum of PJK4

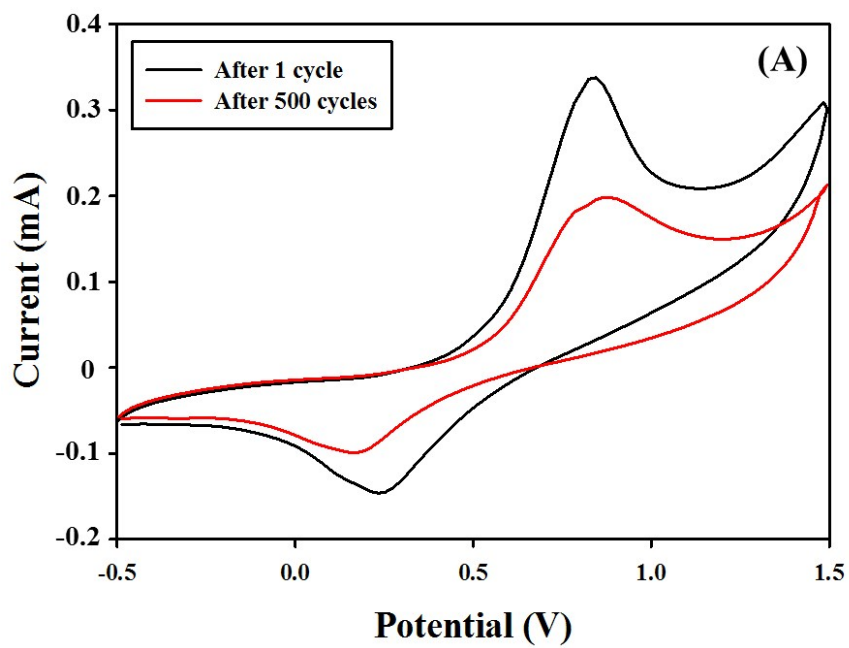


Figure 45. Cyclic voltammograms of **PJK1** on platinum button with 0.1M tetrabutylammonium tetrafluoroborate in propylene carbonate as a function of repeated scans at 50 mV/S: after 1 cycle (black), after 500 cycles (red).

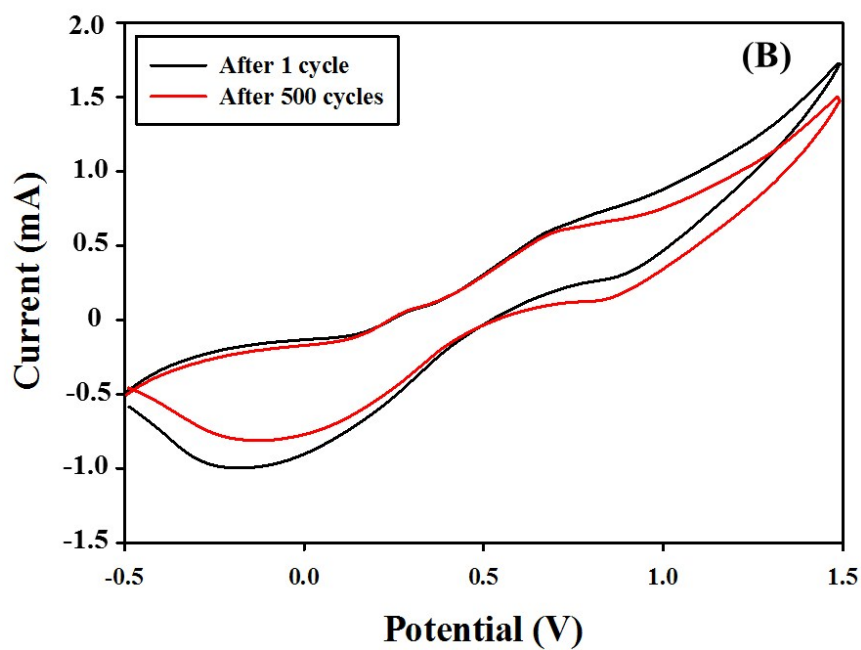


Figure 46. Cyclic voltammograms of **PJK2** on platinum button with 0.1M tetrabutylammonium tetrafluoroborate in propylene carbonate as a function of repeated scans at 50 mV/S: after 1 cycle (black), after 500 cycles (red).

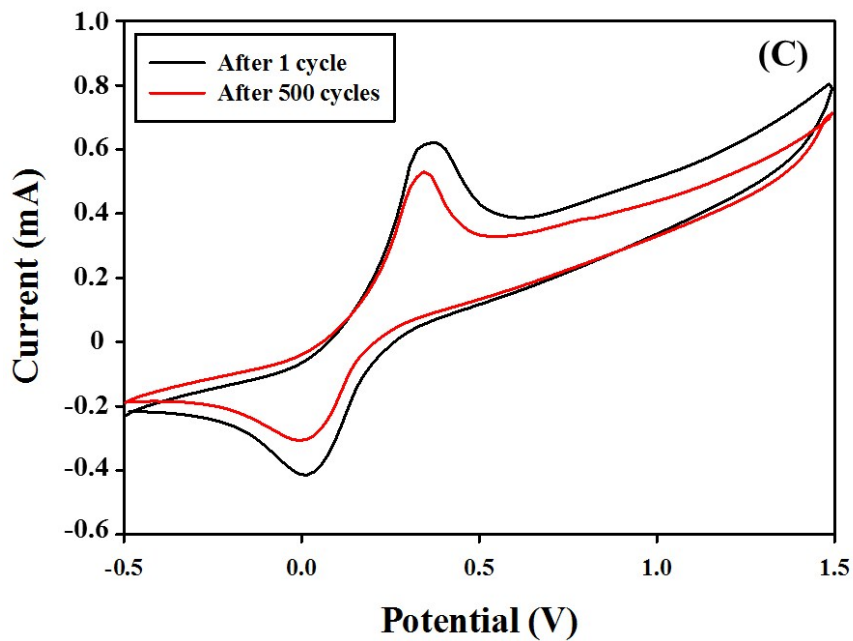


Figure 47. Cyclic voltammograms of **PJK3** on platinum button with 0.1M tetrabutylammonium tetrafluoroborate in propylene carbonate as a function of repeated scans at 50 mV/S: after 1 cycle (black), after 500 cycles (red).

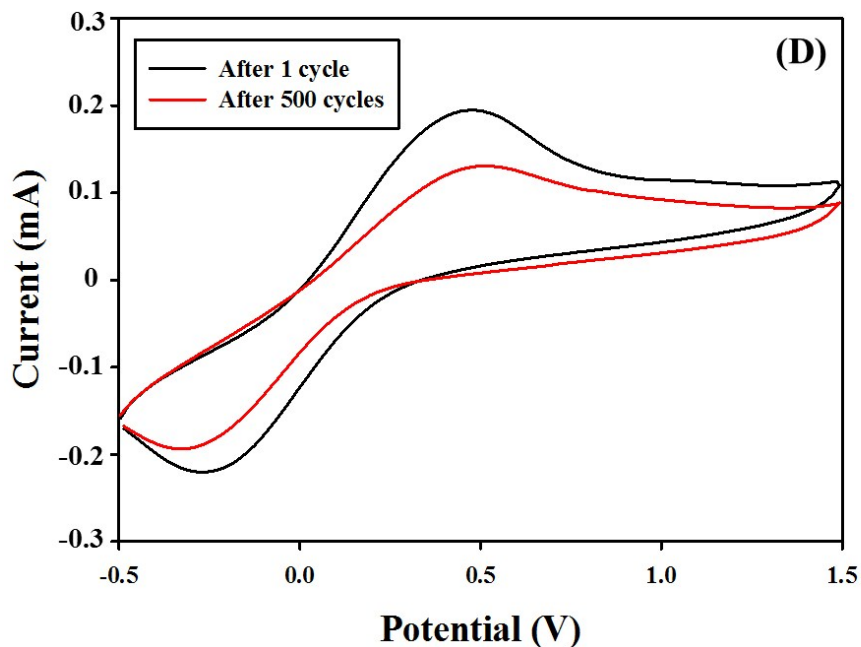


Figure 48. Cyclic voltammograms of **PJK4** on platinum button with 0.1M tetrabutylammonium tetrafluoroborate in propylene carbonate as a function of repeated scans at 50 mV/S: after 1 cycle (black), after 500 cycles (red).

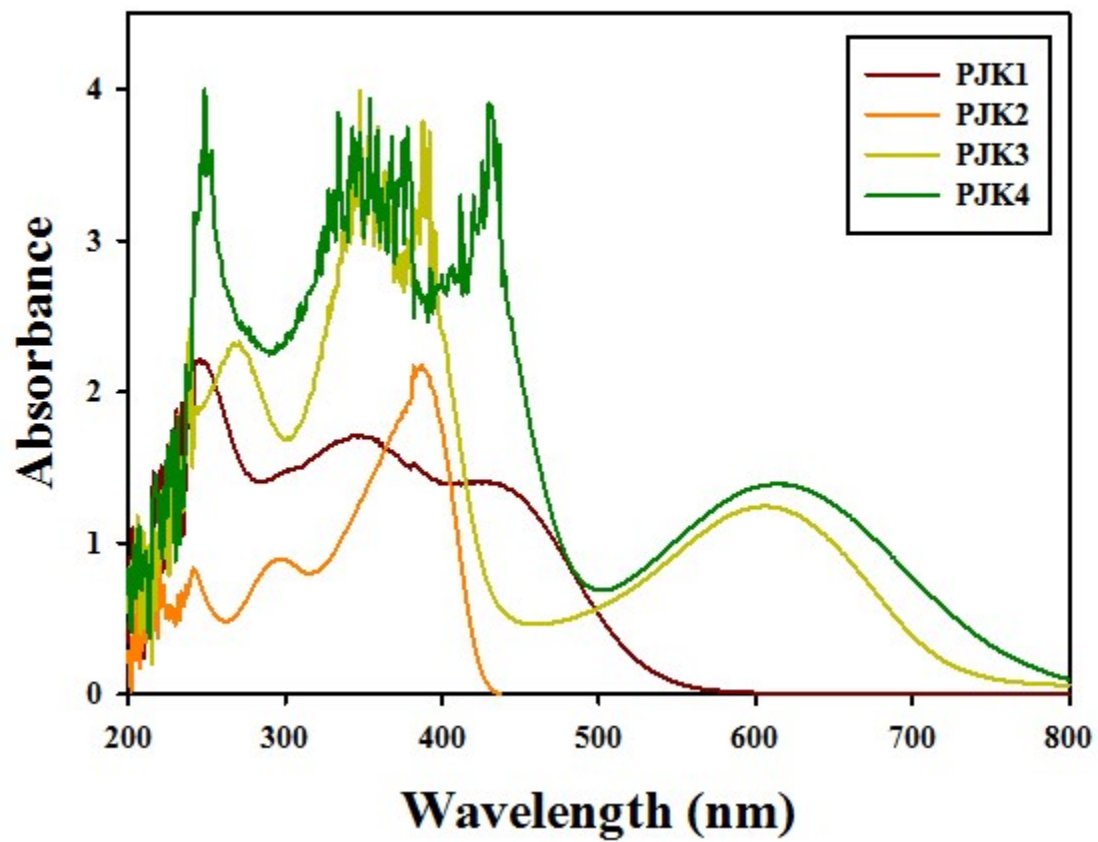


Figure 49. Absorption spectra of PJK1, PJK2, PJK3 and PJK4 in CHCl_3 ($1 \times 10^{-5} \text{ M}$)

References:

- 1 H. Hong, M. Y. Jo, Y. E. Ha and J. H. Kim, *Macromol. Res.*, 2013, **21**, 321-326.
- 2 Y-L. Chu, C-C. Cheng, Y-C. Yen and F-C. Chang, *Adv. Mater.*, 2012, **24**, 1894-1898.
- 3 R. M. Kellogg, A. P. Schaap, E. T. Harper and N. D. H. Wynberg, *J. Org. Chem.*, 1968, **33**, 2902-2909.
- 4 R. Mozingo, S. A. Harris, D. E. Wolf, C. E. Hoffhine, N. R. Easton and K. Folkers, *J. Am. Chem. Soc.*, 1945, **67**, 2092-2095.
- 5 H. Hailu, B. Atsbeha, S. Admassie, W. Mammo, V. J. T. Raju and Y. Chebude, *Bull. Chem. Soc. Ethiop.*, 2011, **25**, 221-231.
- 6 X. Liu, L. Li, J. Sun, Y. Yan, X. Shu, B. Liu, W. Sha, H. Feng, S. Sun and J. Zhu, *Inorg. Chem.*, 2012, **51**, 188-192.
- 7 C. L. Chochos, S. P. Economopoulos, V. Deimede, V. G. Gregoriou, M. T. Lloyd, G. G. Malliaras and J. K. Kallitsis, *J. Phys. Chem. C*, 2007, **111**, 10732-10740.
- 8 C. V. Pharn, H. B. Mark and H. Zirnmer, *Synth. Commun.*, 1986, **16**, 689-696.
- 9 R. Gong, Z. Guo, F. Li, Y. Song, Y. Mu, M. Li and X. Wan, *Macromol. Chem. Phys.*, 2014, **215**, 906-914.
- 10 M. He, T. M. Leslie and J. A. Sinicropi, *Chem. Mater.* 2002, **14**, 4662-4668.
- 11 H. Usta, C. Risko, Z. Wang, H. Huang, M. K. Deliomeroğlu, A. Zhukhovitskiy, A. Facchetti and T. J. Marks, *J. Am. Chem. Soc.*, 2009, **131**, 5586-5608.
- 12 J. Bras, S. Guillerez and B. P. Donat, *Chem. Mater.*, 2000, **12**, 2372-2384.
- 13 S. Beaupre', A-C. Breton, J. Dumas and M. Leclerc, *Chem. Mater.*, 2009, **21**, 1504-1513.