

Conjugated Fluorene-Thiophenes Prepared From Azomethines
Connections-I: The Effect of Electronic and Aryl Groups on the
Spectroscopic and Electrochemical Properties

**Stéphane Dufresne, Sergio Andrés Pérez Guarín, Andréanne Bolduc, Alex N. Bourque,
and W. G. Skene***

*Centre for Self-Assembled Chemical Structures, Department of Chemistry, Department of
Chemistry University of Montreal, Pavillon J.A. Bombardier, C.P. 6128,
succ. Centre-ville, Montreal, QC, H3C 3J7, Canada Fax (514) 340-5290; Tel (514) 340-
5174; E-mail: w.skene@umontreal.ca*

Table of contents

Figure 1. ^1H spectrum of 1 (400 MHz, Acetone- d_6).....	4
Figure 2. ^{13}C spectrum of 1 (80 MHz, DMSO- d_6).....	5
Figure 3. ^1H spectrum of 2 (400 MHz, DMSO- d_6).....	6
Figure 4. ^{13}C spectrum of 2 (80 MHz, Acetone- d_6).....	7
Figure 5. ^1H spectrum of 3 (400 MHz, Acetone- d_6).....	8
Figure 6. ^{13}C spectrum of 3 (80 MHz, DMSO- d_6).....	9
Figure 7. ^1H spectrum of 4 (400 MHz, Acetone- d_6).....	10
Figure 8. ^1H spectrum of 5 (400 MHz, Acetone- d_6).....	11
Figure 9. ^{13}C spectrum of 5 (80 MHz, Acetone- d_6).....	12
Figure 10. ^1H spectrum of 7 (400 MHz, DMSO- d_6).....	13
Figure 11. ^1H spectrum of 9 (400 MHz, DMSO- d_6).....	14
Figure 12. ^1H spectrum of 10 (400 MHz, DMSO- d_6).....	15
Figure 13. Absorbance (black) and fluorescence (red) spectra of 1 measured in anhydrous and deaerated dichloromethane.....	16
Figure 14. Absorbance (black) and fluorescence (red) spectra of 2 measured in anhydrous and deaerated dichloromethane.....	16
Figure 15. Absorbance (black) and fluorescence (red) spectra of 3 measured in anhydrous and deaerated dichloromethane.....	17
Figure 16. Absorbance (black) and fluorescence (red) spectra of 4 measured in anhydrous and deaerated dichloromethane.....	17
Figure 17. Absorbance (black) and fluorescence (red) spectra of 5 measured in anhydrous and deaerated dichloromethane.....	18
Figure 18. Absorbance (black) and fluorescence (red) spectra of 6 measured in anhydrous and deaerated dichloromethane.....	18
Figure 19. Absorbance (black) and fluorescence (red) spectra of 7 measured in anhydrous and deaerated dichloromethane.....	19
Figure 20. Absorbance (black) and fluorescence (red) spectra of 8 measured in anhydrous and deaerated dichloromethane.....	19
Figure 21. Absorbance (black) and fluorescence (red) spectra of 9 measured in anhydrous and deaerated dichloromethane.....	20
Figure 22. Oxidation cyclic voltamogram of 1 measured in 0.1 M TBA•PF ₆ in anhydrous DCM at a scan rate of 100 mV/sec.....	21
Figure 23. Reduction cyclic voltamogram of 1 measured in 0.1 M TBA•PF ₆ in anhydrous DCM at a scan rate of 100 mV/sec.....	21
Figure 24. Oxidation cyclic voltamogram of 2 measured in 0.1 M TBA•PF ₆ in anhydrous DCM at a scan rate of 100 mV/sec.....	22
Figure 25. Reduction cyclic voltamogram of 2 measured in 0.1 M TBA•PF ₆ in anhydrous DCM at a scan rate of 100 mV/sec.....	22
Figure 26. Oxidation cyclic voltamogram of 3 measured in 0.1 M TBA•PF ₆ in anhydrous DCM at a scan rate of 100 mV/sec.....	23
Figure 27. Reduction cyclic voltamogram of 3 measured in 0.1 M TBA•PF ₆ in anhydrous DCM at a scan rate of 100 mV/sec.....	23
Figure 28. Oxidation cyclic voltamogram of 4 measured in 0.1 M TBA•PF ₆ in anhydrous DCM at a scan rate of 100 mV/sec.....	24

Figure 29. Reduction cyclic voltamogram of 4 measured in 0.1 M TBA•PF ₆ in anhydrous DCM at a scan rate of 100 mV/sec.....	24
Figure 30. Oxydation cyclic voltamogram of 5 measured in 0.1 M TBA•PF ₆ in anhydrous DCM at a scan rate of 100 mV/sec.....	25
Figure 31. Reduction cyclic voltamogram of 5 measured in 0.1 M TBA•PF ₆ in anhydrous DCM at a scan rate of 100 mV/sec.....	25
Figure 32. Oxydation cyclic voltamogram of 6 measured in 0.1 M TBA•PF ₆ in anhydrous DCM at a scan rate of 100 mV/sec.....	26
Figure 33. Reduction cyclic voltamogram of 6 measured in 0.1 M TBA•PF ₆ in anhydrous DCM at a scan rate of 100 mV/sec.....	26
Figure 34. Oxydation cyclic voltamogram of 7 measured in 0.1 M TBA•PF ₆ in anhydrous DCM at a scan rate of 100 mV/sec.....	27
Figure 35. Reduction cyclic voltamogram of 7 measured in 0.1 M TBA•PF ₆ in anhydrous DCM at a scan rate of 100 mV/sec.....	27
Figure 36. Oxydation cyclic voltamogram of 8 measured in 0.1 M TBA•PF ₆ in anhydrous DCM at a scan rate of 100 mV/sec.....	28
Figure 37. Reduction cyclic voltamogram of 8 measured in 0.1 M TBA•PF ₆ in anhydrous DCM at a scan rate of 100 mV/sec.....	28
Figure 38. Oxydation cyclic voltamogram of 9 measured in 0.1 M TBA•PF ₆ in anhydrous DCM at a scan rate of 100 mV/sec.....	29
Figure 39. Reduction cyclic voltamogram of 9 measured in 0.1 M TBA•PF ₆ in anhydrous DCM at a scan rate of 100 mV/sec.....	29
Table 1. Details of Crystal Structure Determination for 6.....	30

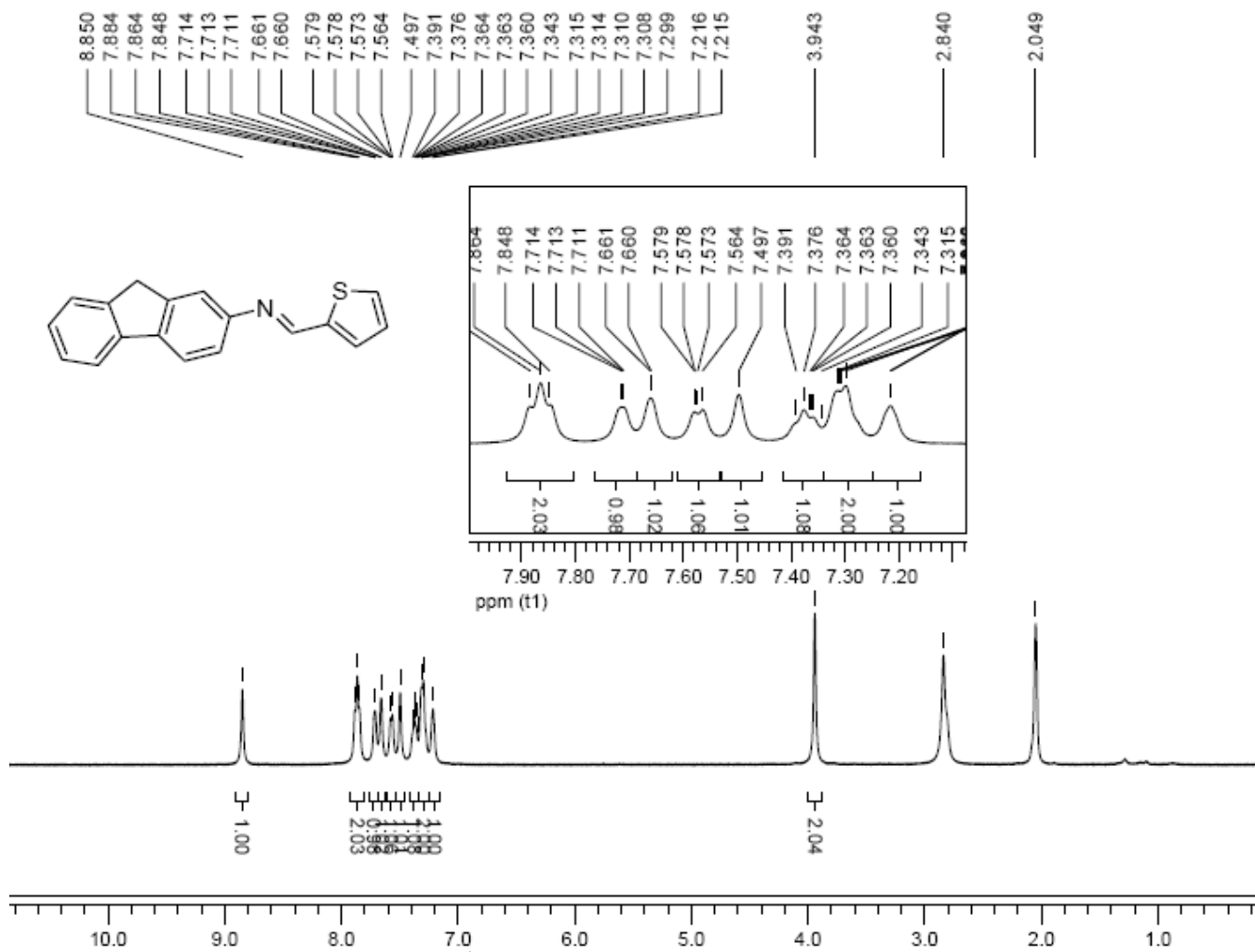


Figure 1. ¹H spectrum of **1** (400 MHz, Acetone-d₆).

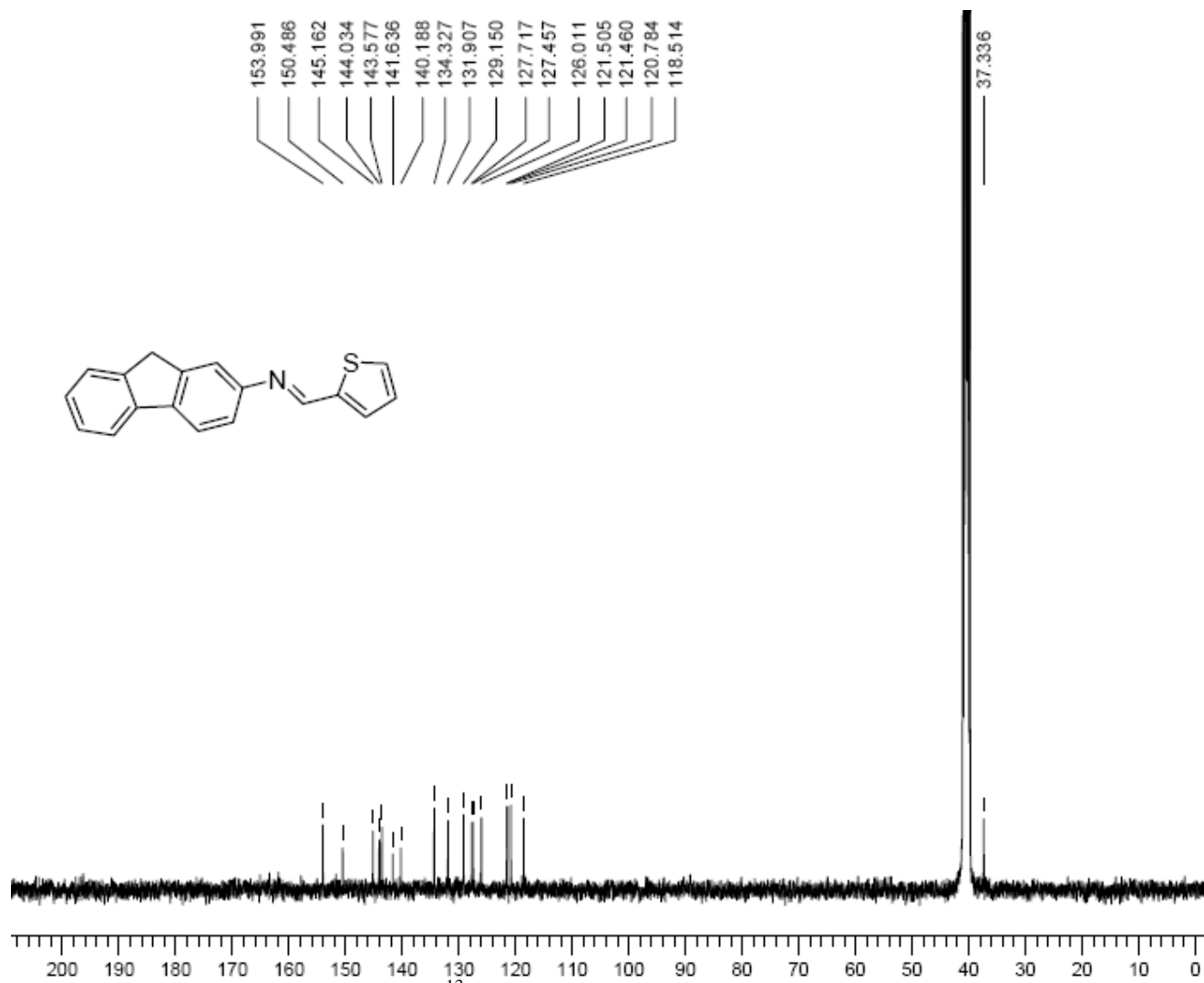
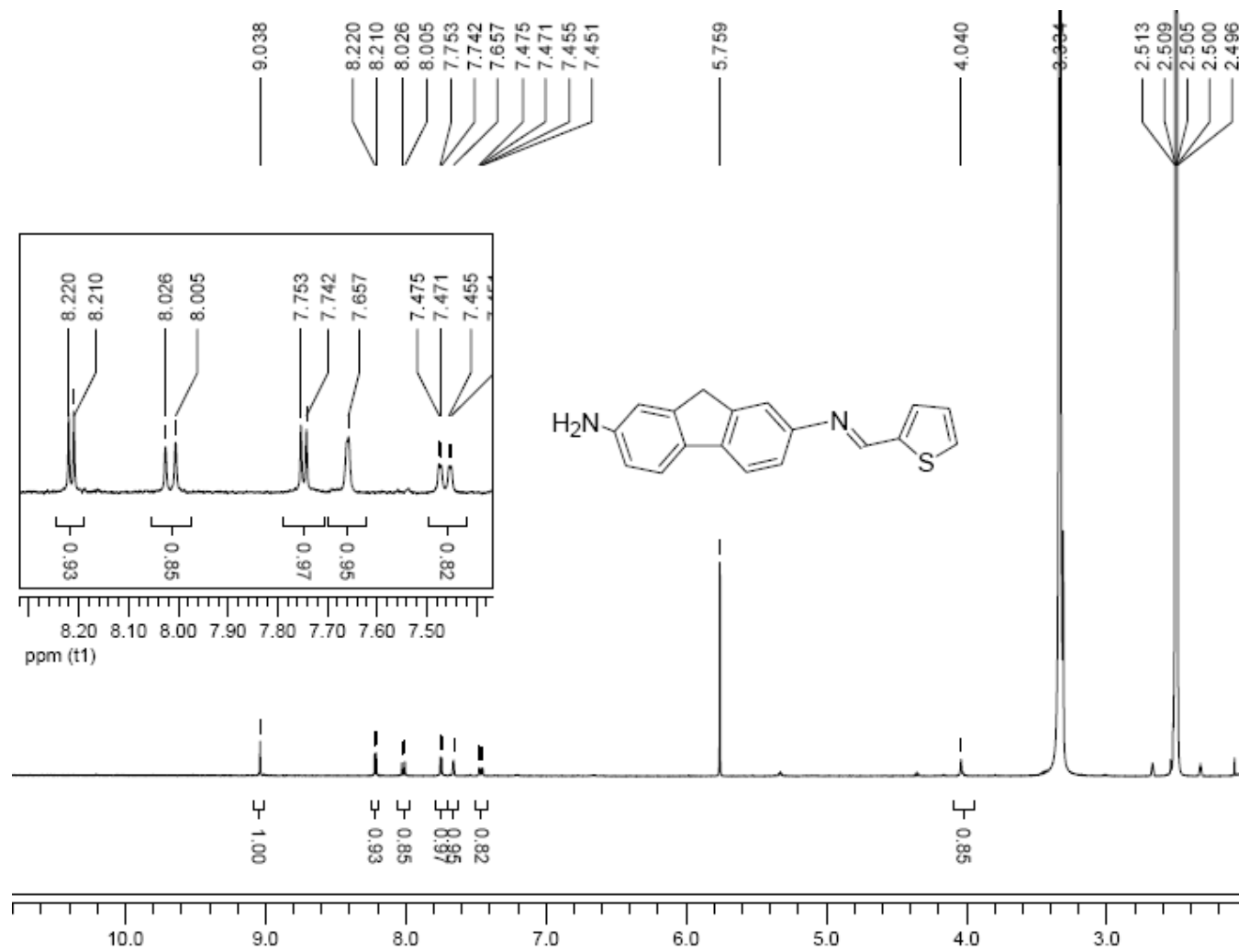


Figure 2. ¹³C spectrum of 1 (80 MHz, DMSO-d₆).



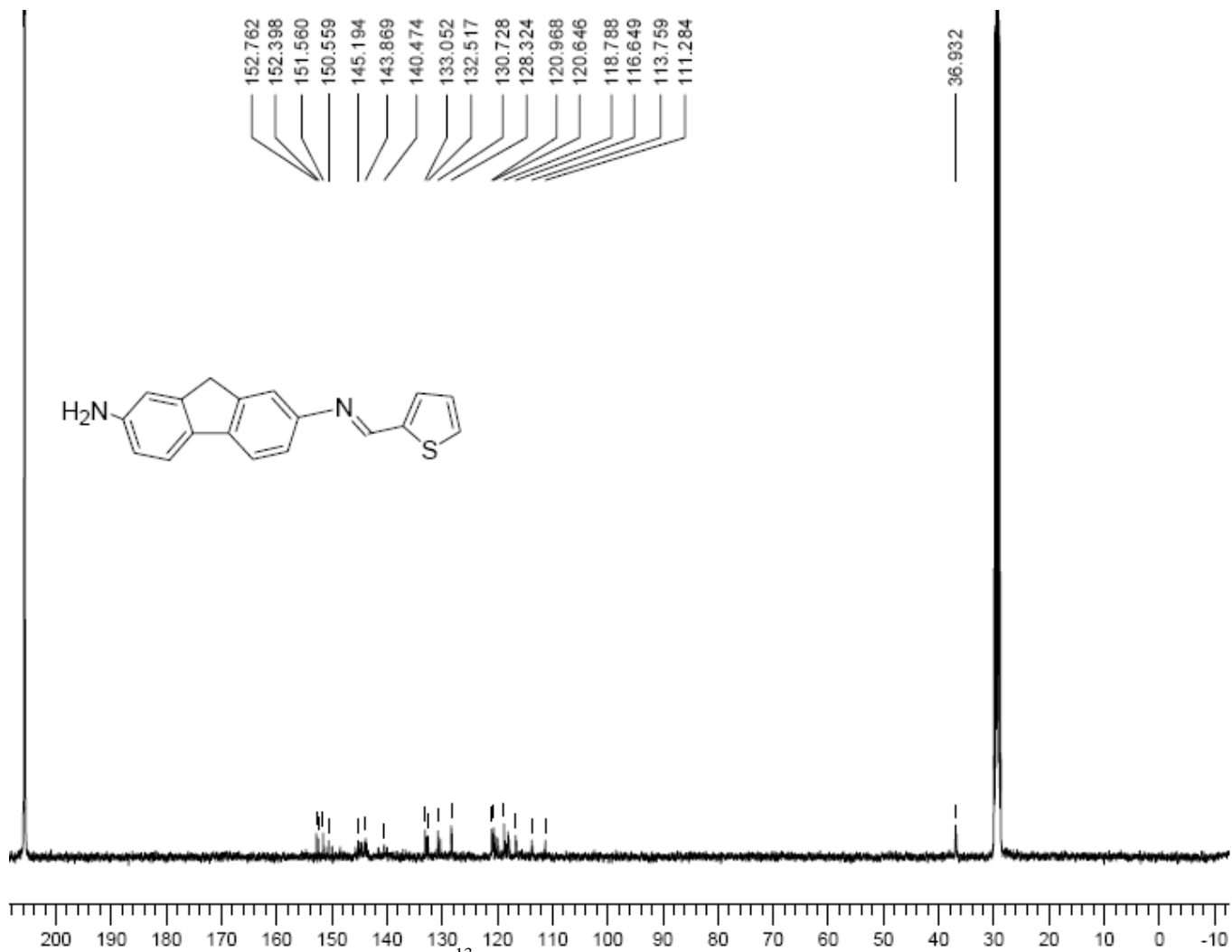


Figure 4. ¹³C spectrum of 2 (80 MHz, Acetone-d₆).

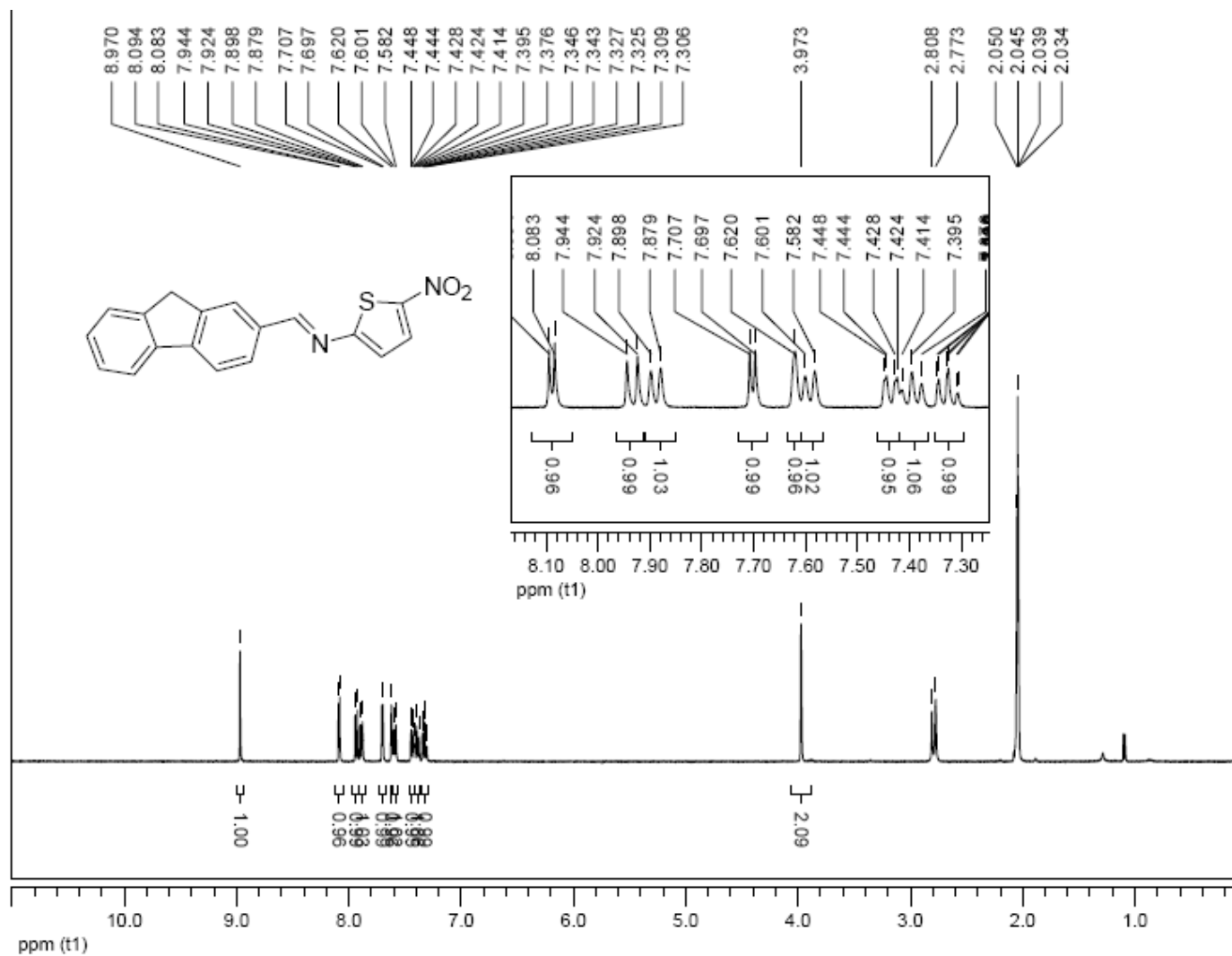
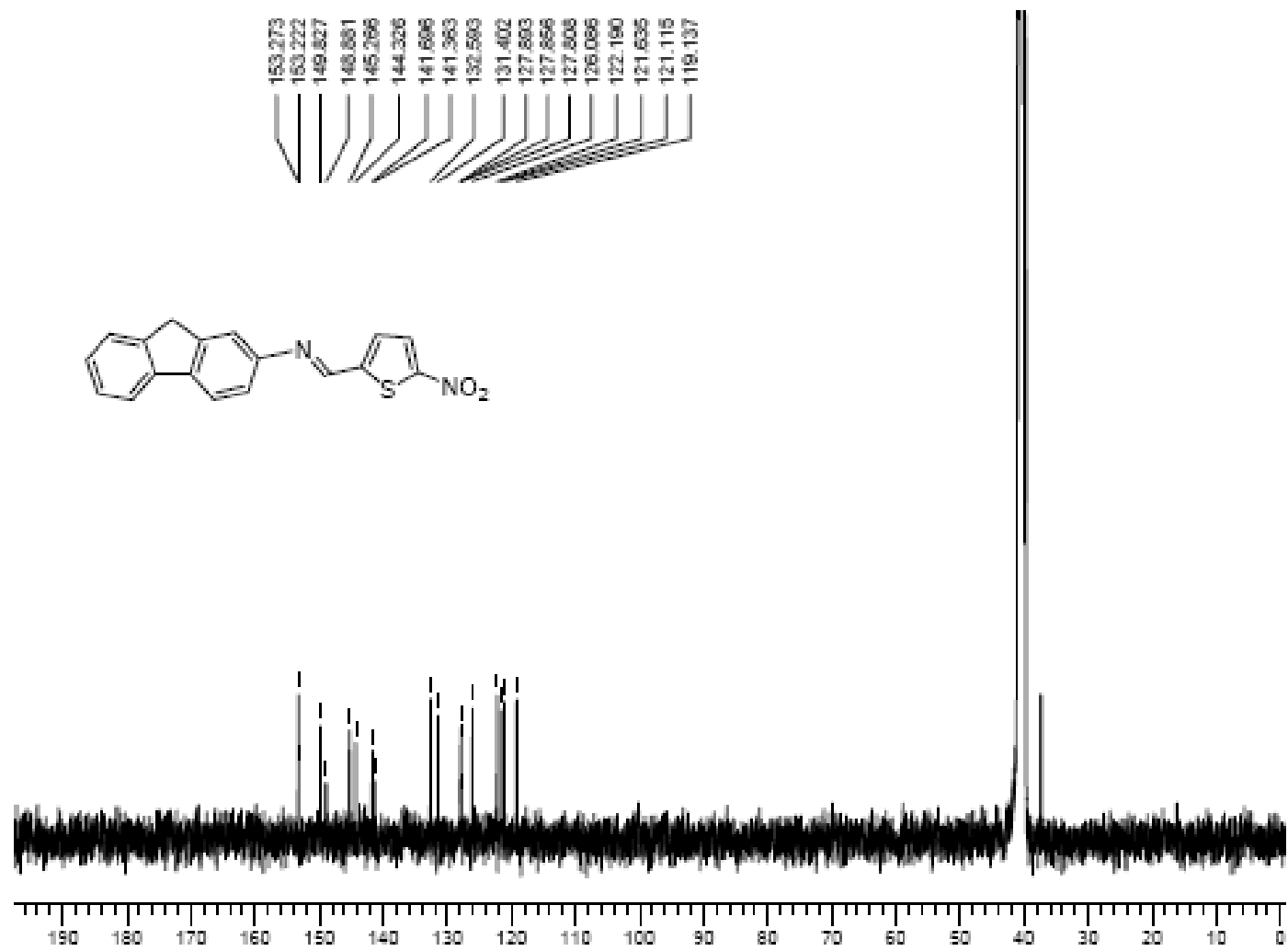


Figure 5. ^1H spectrum of **3** (400 MHz, Acetone- d_6).



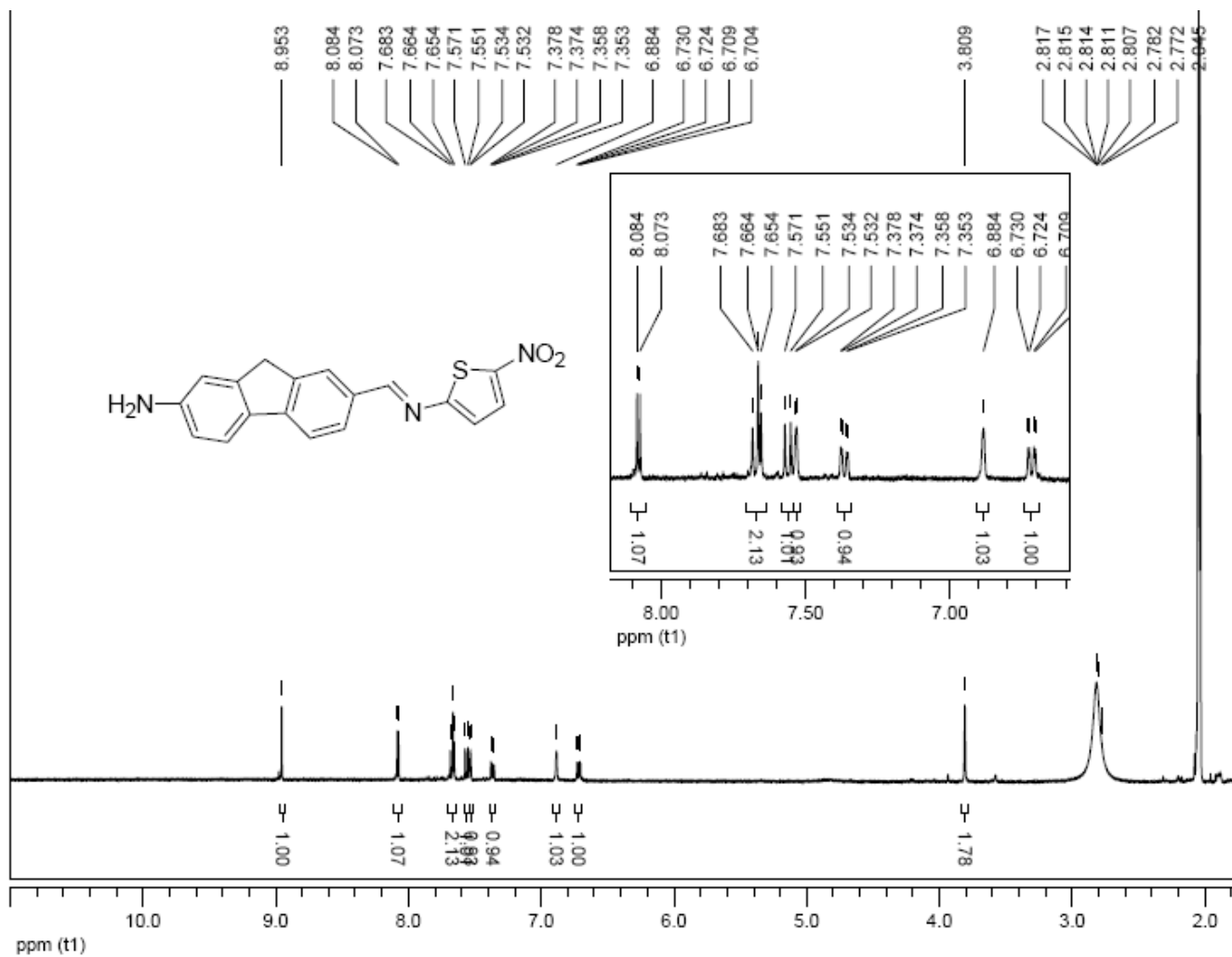
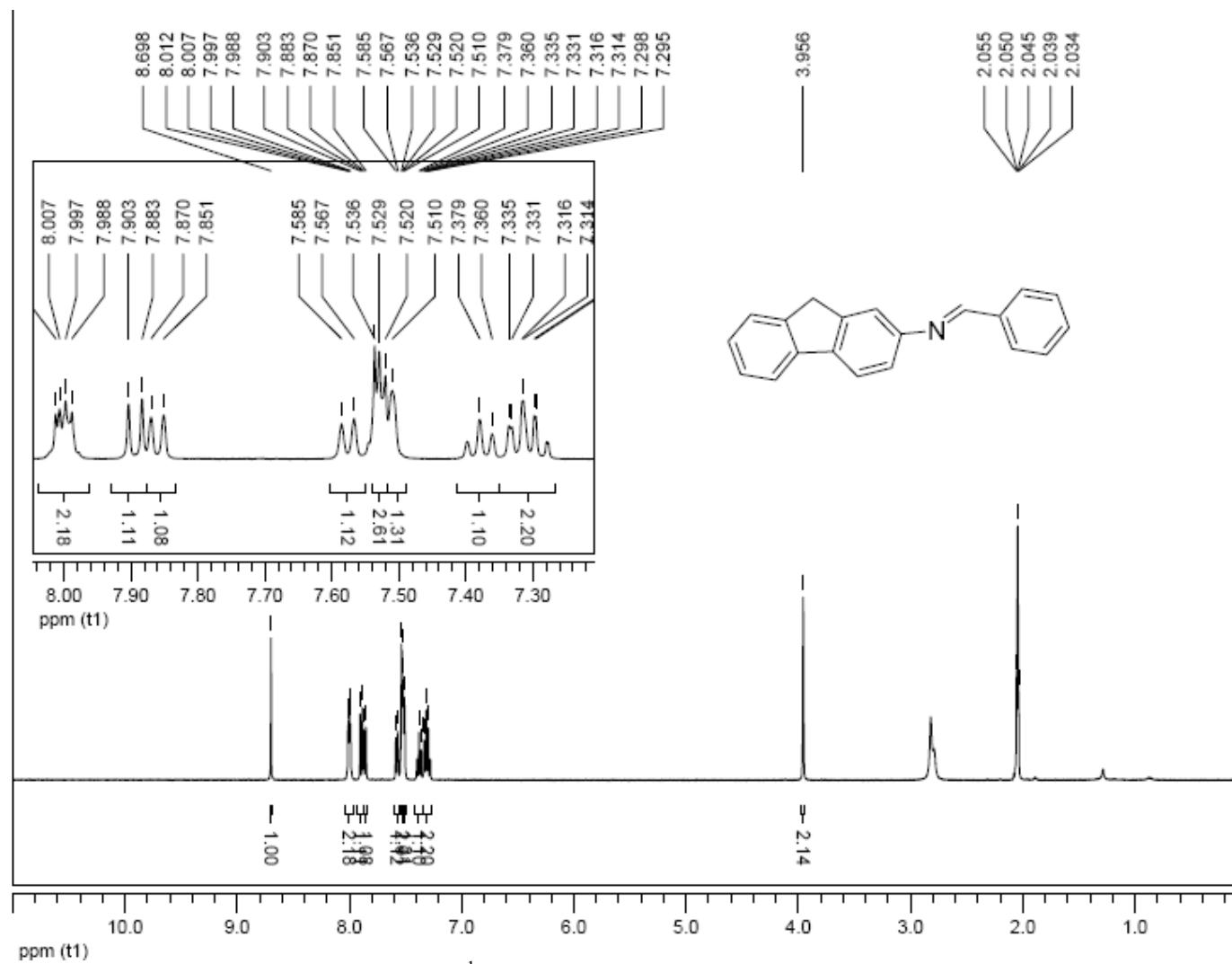


Figure 7. ^1H spectrum of **4** (400 MHz, Acetone- d_6).



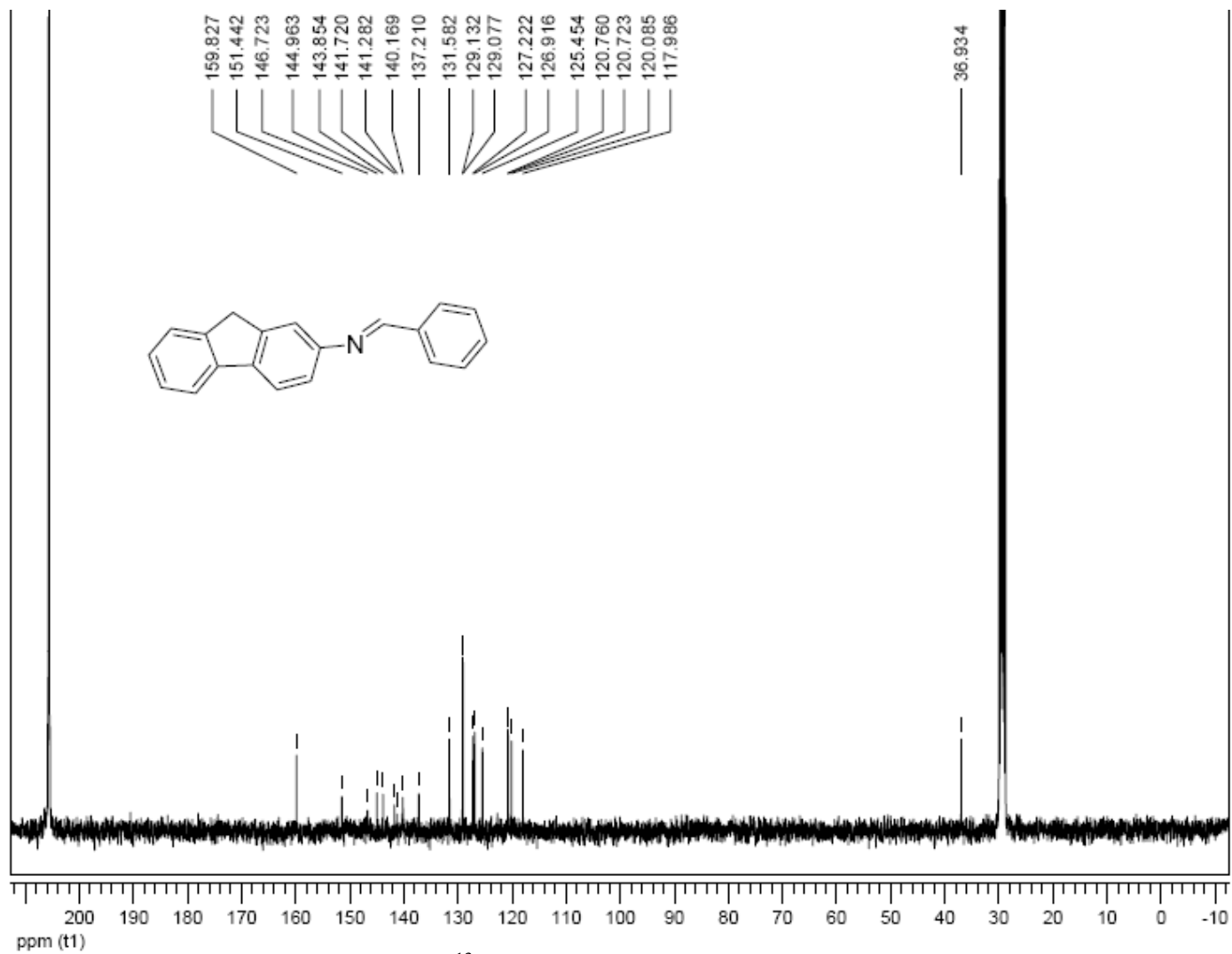


Figure 9. ^{13}C spectrum of **5** (80 MHz, Acetone- d_6).

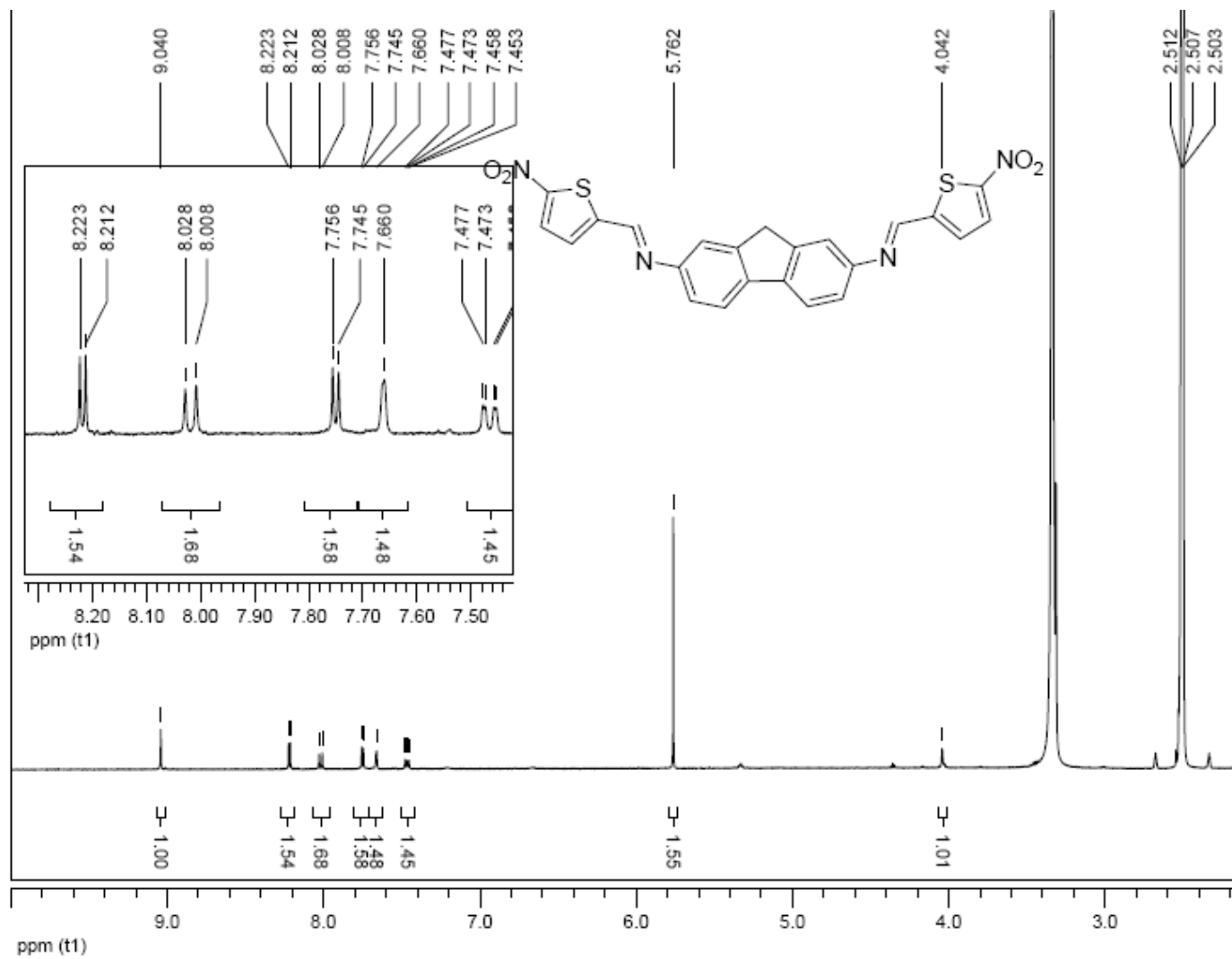


Figure 10. ¹H spectrum of 7 (400 MHz, DMSO-d₆).

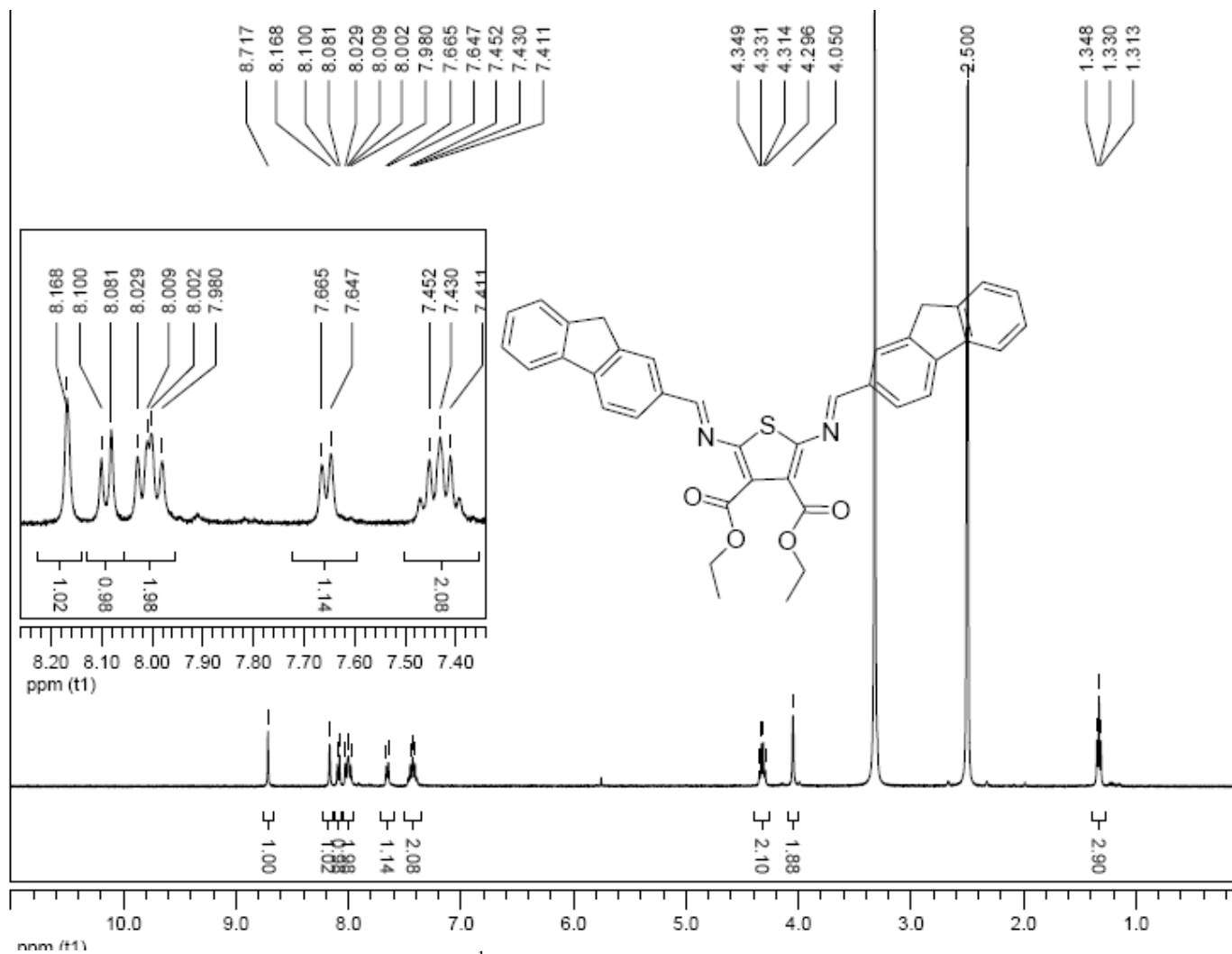


Figure 11. ¹H spectrum of **9** (400 MHz, DMSO-d₆).

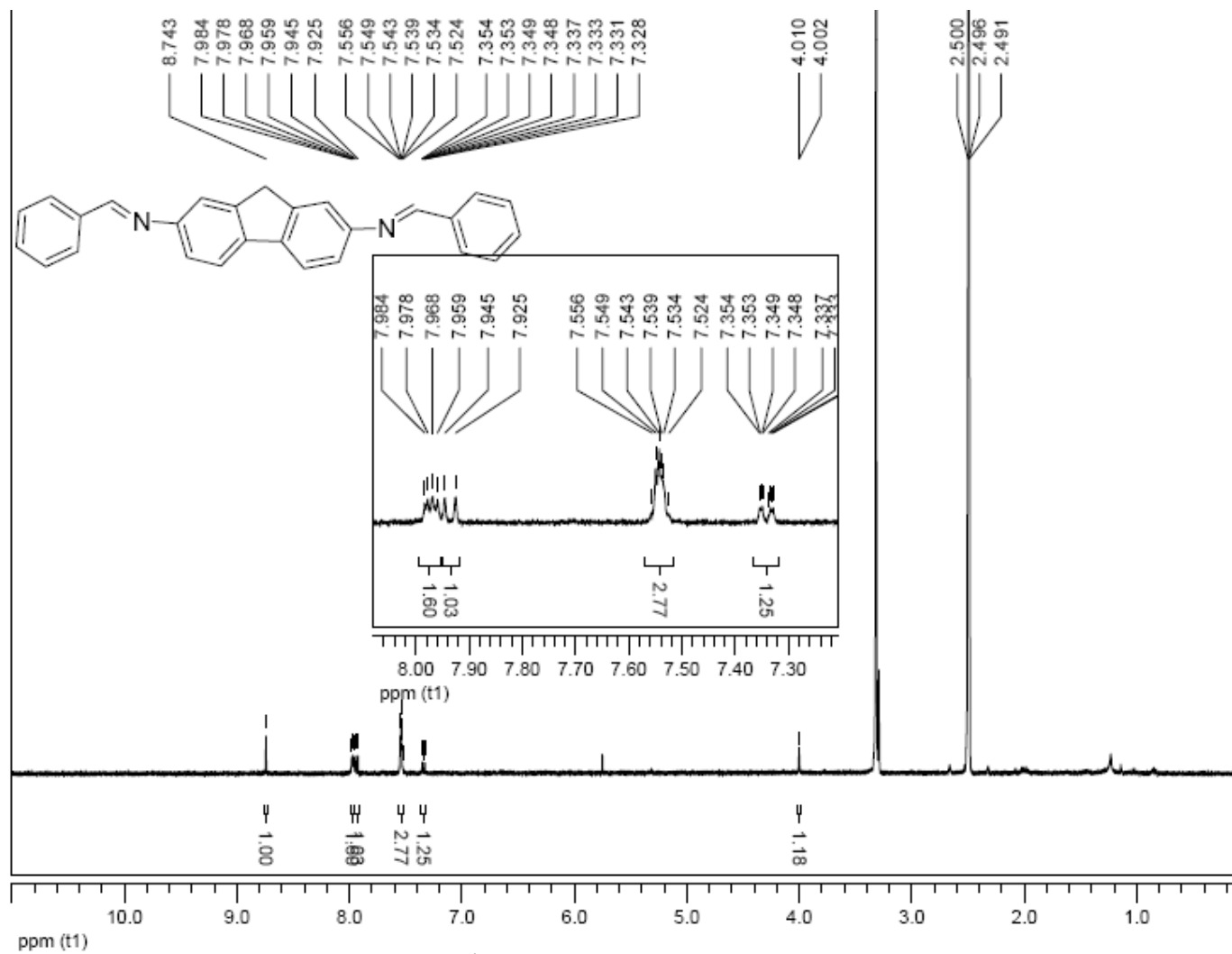


Figure 12. ¹H spectrum of **10** (400 MHz, DMSO-d₆).

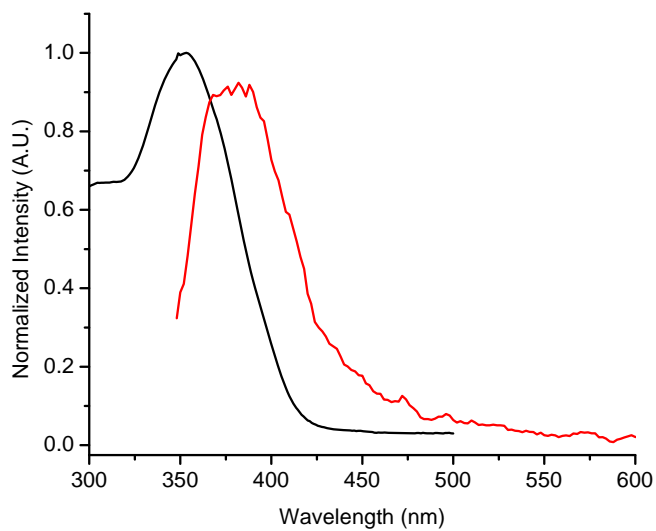


Figure 13. Absorbance (black) and fluorescence (red) spectra of **1** measured in anhydrous and deaerated dichloromethane. Excitation wavelength: 357 nm.

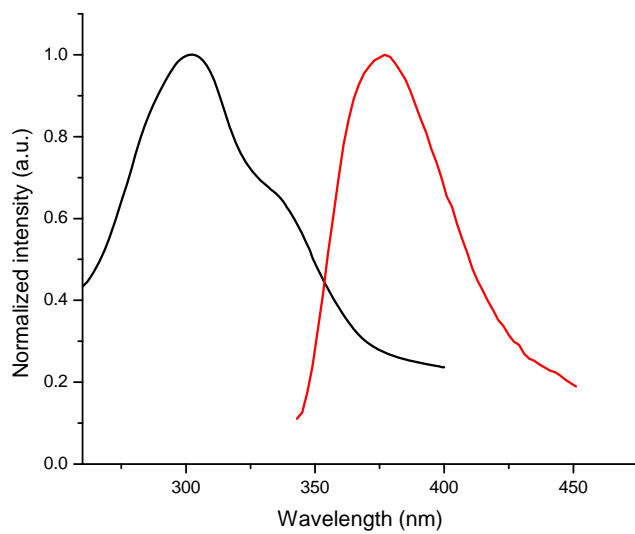


Figure 14. Absorbance (black) and fluorescence (red) spectra of **2** measured in anhydrous and deaerated dichloromethane. Excitation wavelength: 338 nm.

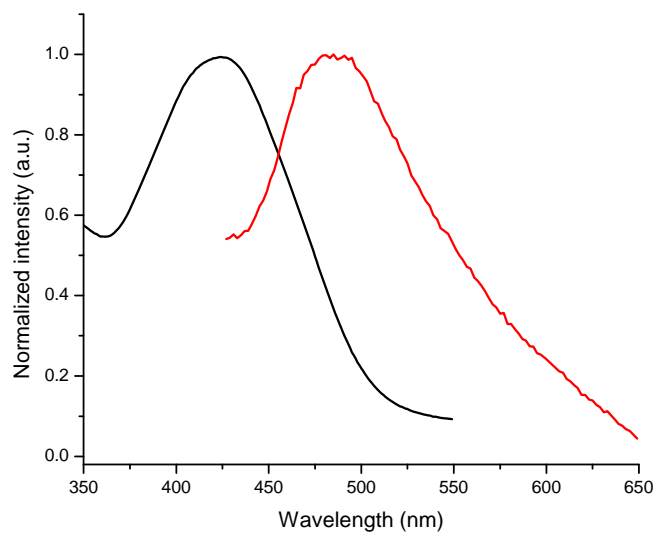


Figure 15. Absorbance (black) and fluorescence (red) spectra of **3** measured in anhydrous and deaerated dichloromethane. Excitation wavelength: 424 nm.

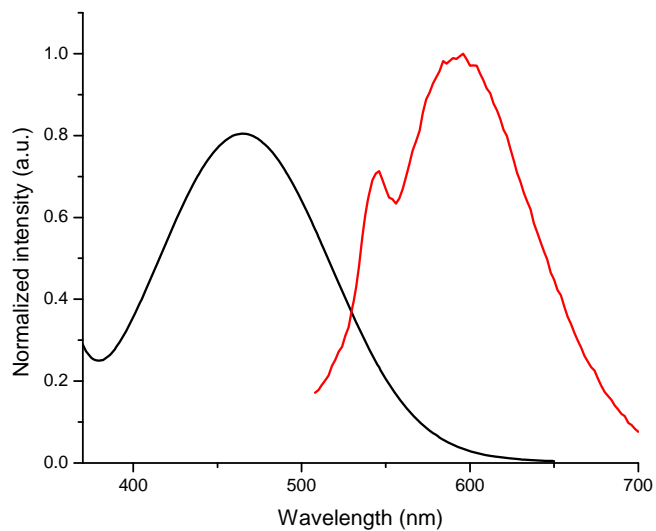


Figure 16. Absorbance (black) and fluorescence (red) spectra of **4** measured in anhydrous and deaerated dichloromethane. Excitation wavelength: 466 nm.

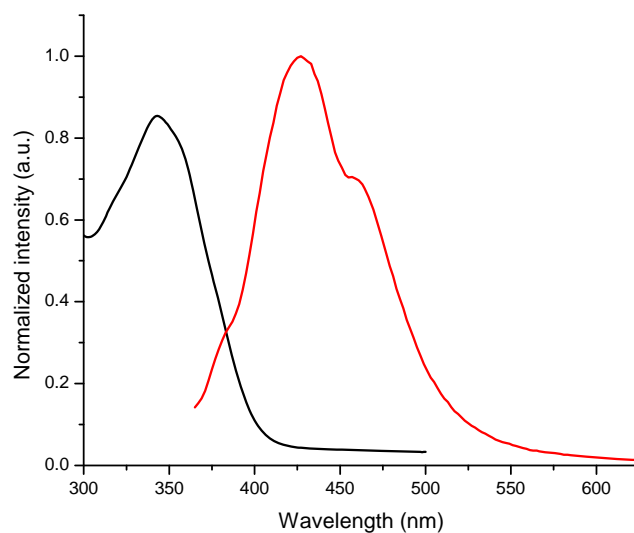


Figure 17. Absorbance (black) and fluorescence (red) spectra of **5** measured in anhydrous and deaerated dichloromethane. Excitation wavelength: 343 nm.

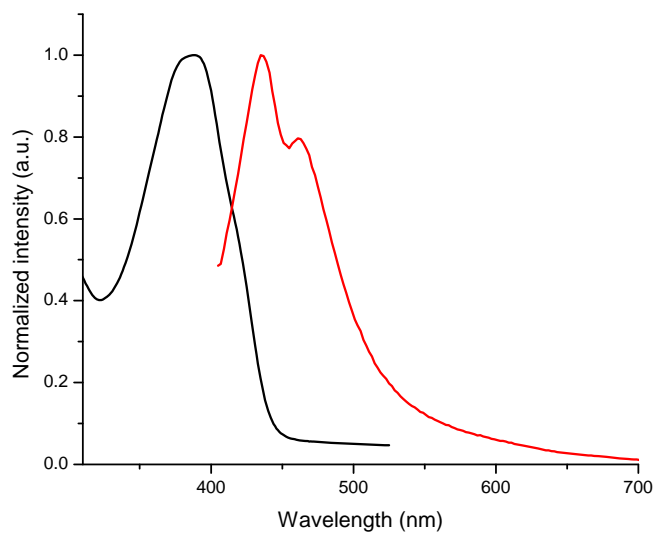


Figure 18. Absorbance (black) and fluorescence (red) spectra of **6** measured in anhydrous and deaerated dichloromethane. Excitation wavelength: 387 nm.

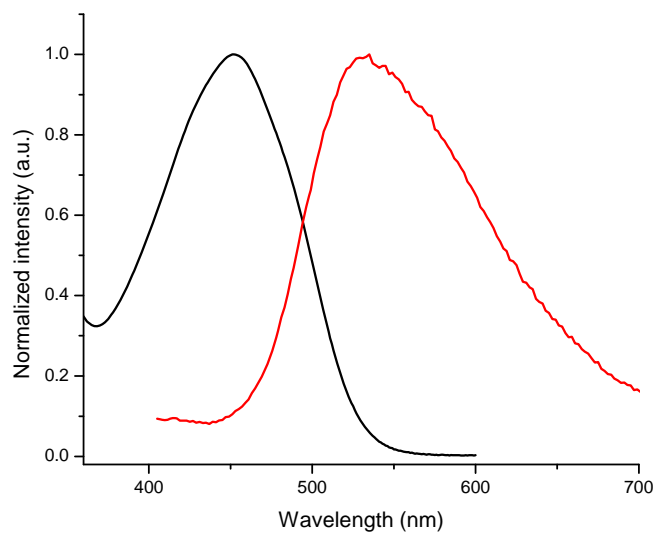


Figure 19. Absorbance (black) and fluorescence (red) spectra of **7** measured in anhydrous and deaerated dichloromethane. Excitation wavelength: 452 nm.

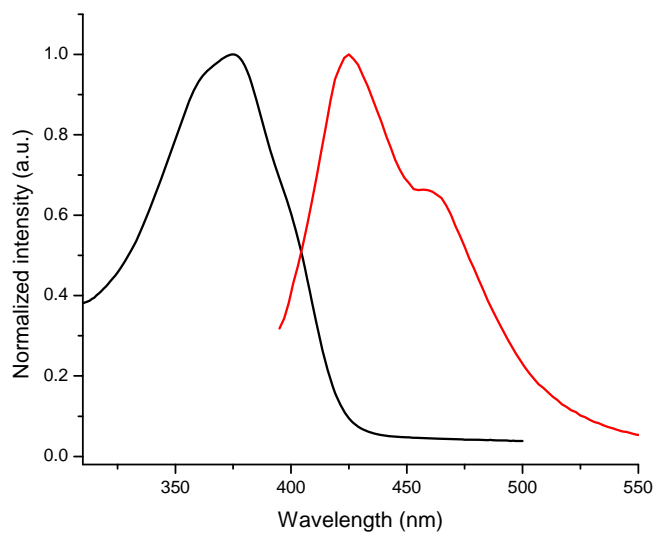


Figure 20. Absorbance (black) and fluorescence (red) spectra of **8** measured in anhydrous and deaerated dichloromethane. Excitation wavelength: 375 nm.

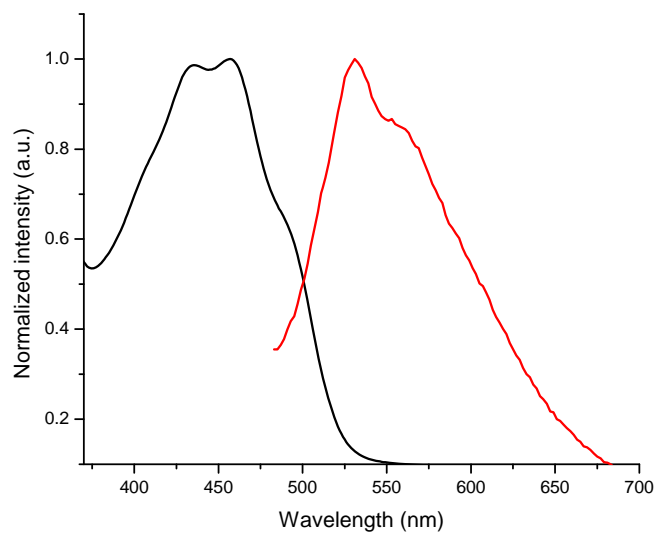


Figure 21. Absorbance (black) and fluorescence (red) spectra of **9** measured in anhydrous and deaerated dichloromethane. Excitation wavelength: 457 nm.

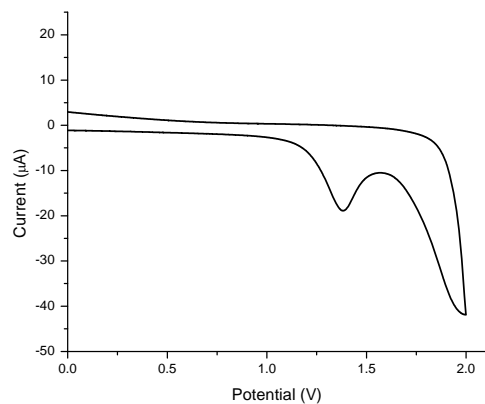


Figure 22. Oxidation cyclic voltammogram of **1** measured in 0.1 M TBA•PF₆ in anhydrous DCM at a scan rate of 100 mV/sec.

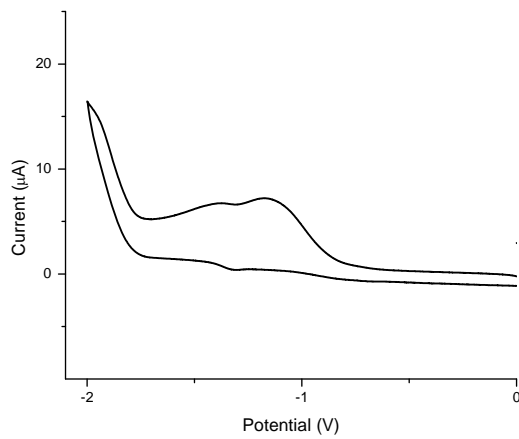


Figure 23. Reduction cyclic voltammogram of **1** measured in 0.1 M TBA•PF₆ in anhydrous DCM at a scan rate of 100 mV/sec.

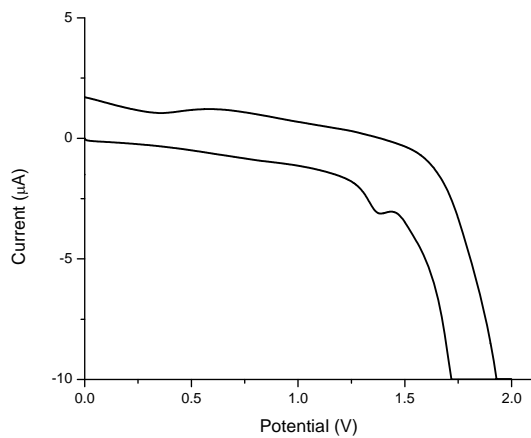


Figure 24. Oxidation cyclic voltammogram of **2** measured in 0.1 M TBA•PF₆ in anhydrous DCM at a scan rate of 100 mV/sec.

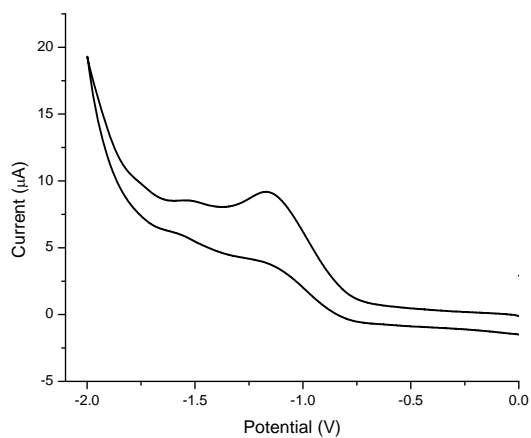


Figure 25. Reduction cyclic voltammogram of **2** measured in 0.1 M TBA•PF₆ in anhydrous DCM at a scan rate of 100 mV/sec.

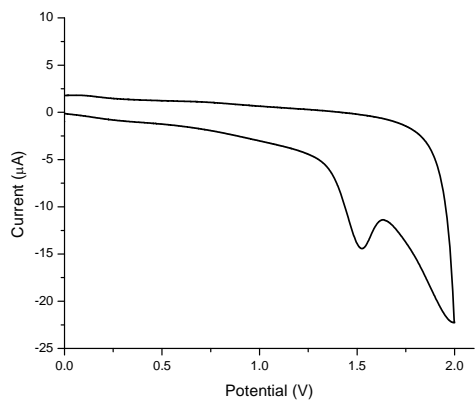


Figure 26. Oxidation cyclic voltammogram of **3** measured in 0.1 M TBA•PF₆ in anhydrous DCM at a scan rate of 100 mV/sec.

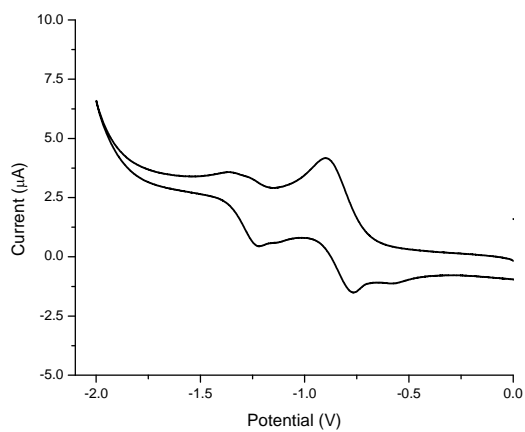


Figure 27. Reduction cyclic voltammogram of **3** measured in 0.1 M TBA•PF₆ in anhydrous DCM at a scan rate of 100 mV/sec.

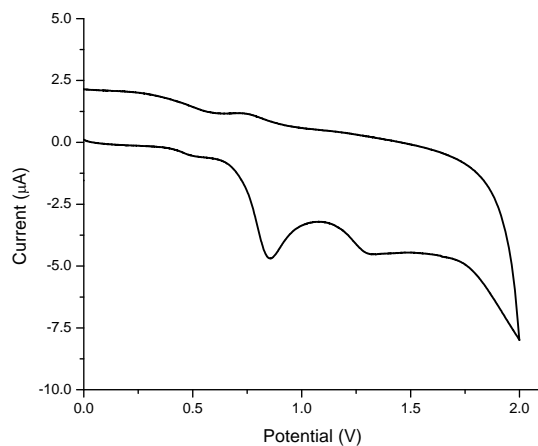


Figure 28. Oxidation cyclic voltammogram of **4** measured in 0.1 M TBA•PF₆ in anhydrous DCM at a scan rate of 100 mV/sec.

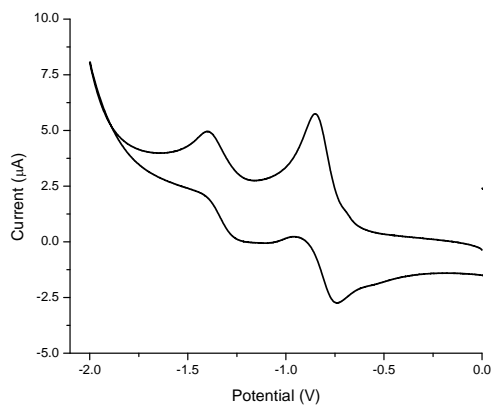


Figure 29. Reduction cyclic voltammogram of **4** measured in 0.1 M TBA•PF₆ in anhydrous DCM at a scan rate of 100 mV/sec.

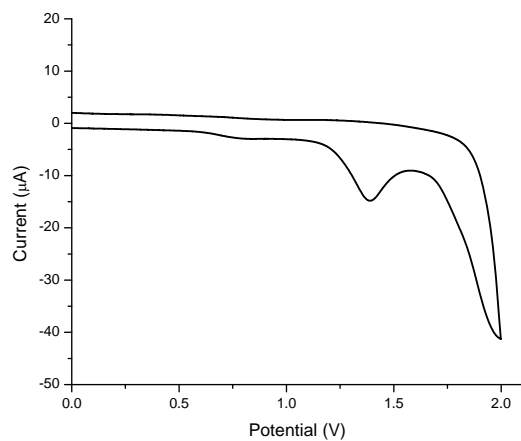


Figure 30. Oxidation cyclic voltammogram of **5** measured in 0.1 M TBA•PF₆ in anhydrous DCM at a scan rate of 100 mV/sec.

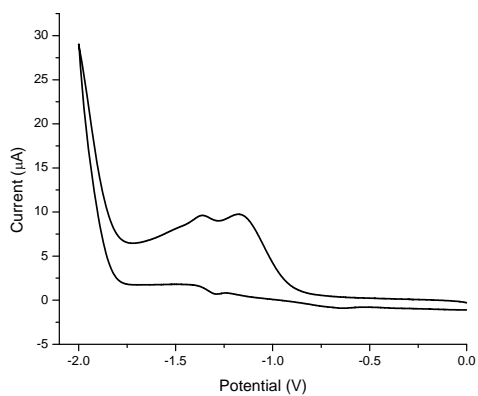


Figure 31. Reduction cyclic voltammogram of **5** measured in 0.1 M TBA•PF₆ in anhydrous DCM at a scan rate of 100 mV/sec.

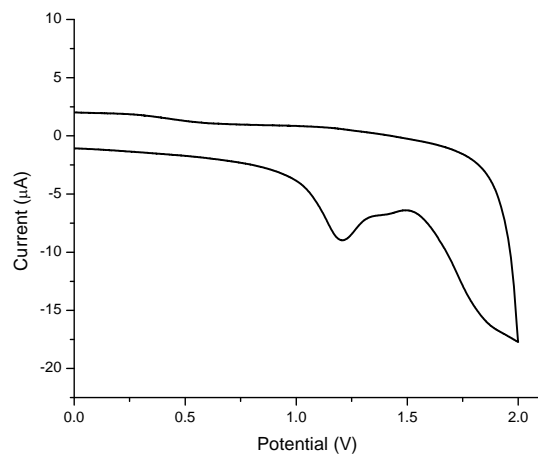


Figure 32. Oxidation cyclic voltammogram of **6** measured in 0.1 M TBA•PF₆ in anhydrous DCM at a scan rate of 100 mV/sec.

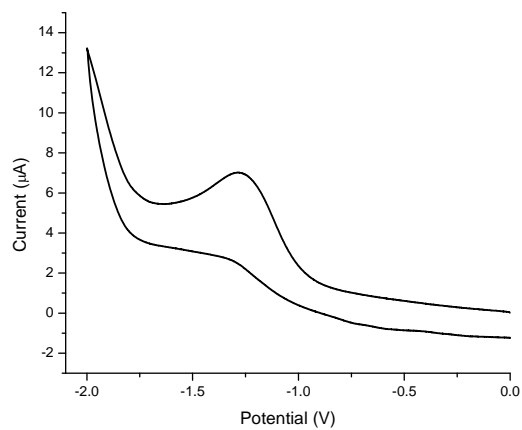


Figure 33. Reduction cyclic voltammogram of **6** measured in 0.1 M TBA•PF₆ in anhydrous DCM at a scan rate of 100 mV/sec.

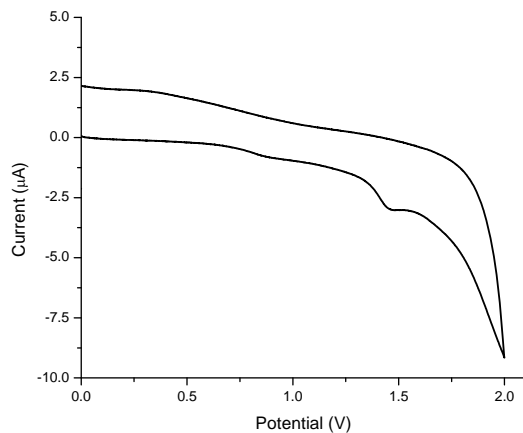


Figure 34. Oxidation cyclic voltammogram of **7** measured in 0.1 M TBA•PF₆ in anhydrous DCM at a scan rate of 100 mV/sec.

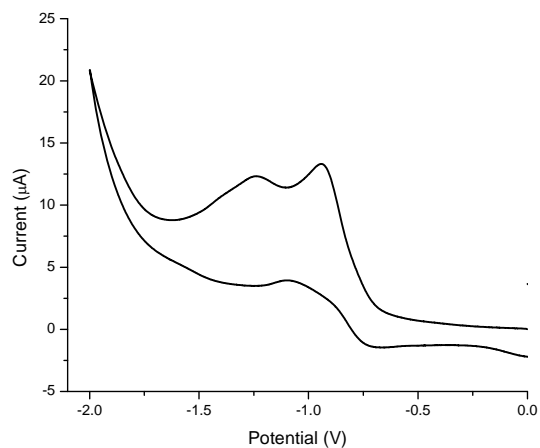


Figure 35. Reduction cyclic voltammogram of **7** measured in 0.1 M TBA•PF₆ in anhydrous DCM at a scan rate of 100 mV/sec.

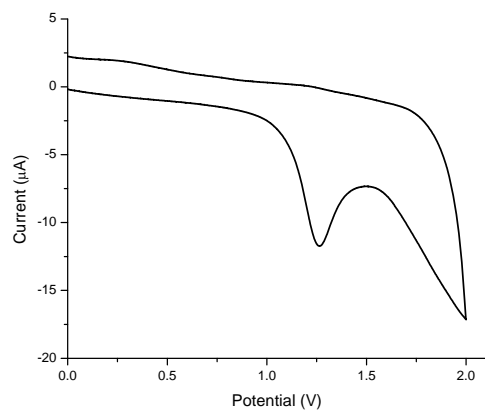


Figure 36. Oxidation cyclic voltammogram of **8** measured in 0.1 M TBA•PF₆ in anhydrous DCM at a scan rate of 100 mV/sec.

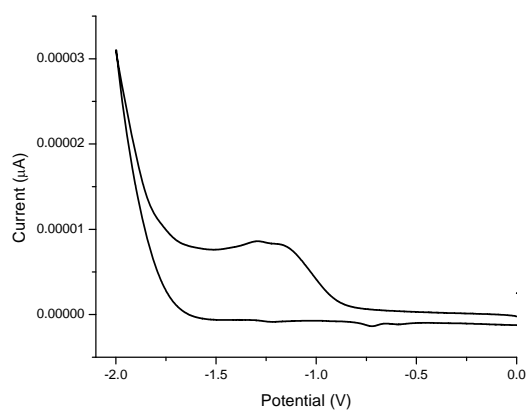


Figure 37. Reduction cyclic voltammogram of **8** measured in 0.1 M TBA•PF₆ in anhydrous DCM at a scan rate of 100 mV/sec.

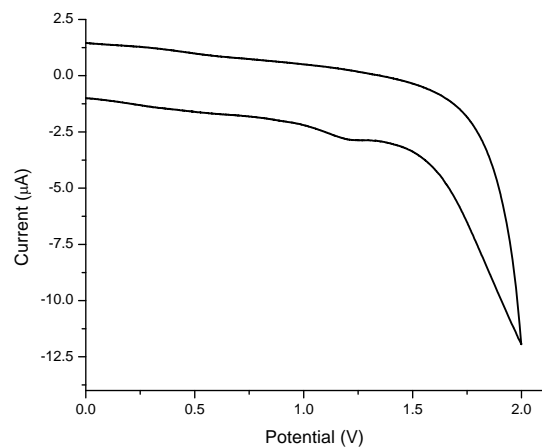


Figure 38. Oxidation cyclic voltammogram of **9** measured in 0.1 M TBA•PF₆ in anhydrous DCM at a scan rate of 100 mV/sec.

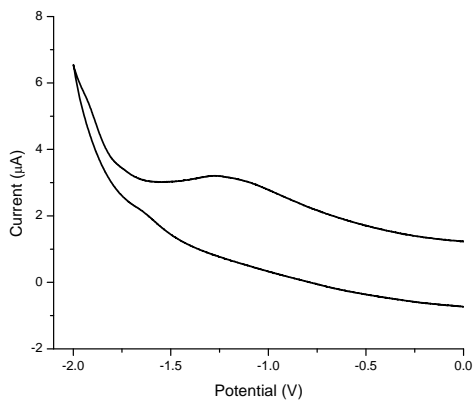


Figure 39. Reduction cyclic voltammogram of **9** measured in 0.1 M TBA•PF₆ in anhydrous DCM at a scan rate of 100 mV/sec.

Table 1. Details of Crystal Structure Determination for **6**.

Formula	C ₂₃ H ₁₆ N ₂ S ₂
CCSD no.	see remark 1
<i>M_w</i> (g/mol); F(000)	384.50 g/mol ; 800
Crystal color and form	Yellow plate
Crystal size (mm)	0.48 x 0.46 x 0.08
<i>T</i> (K); <i>d</i> _{calcd.} (g/cm ³)	293 (2) ; 1.363
Crystal System	Orthorhombic
Space Group	P2 ₁ 2 ₁ 2 ₁
Unit Cell: <i>a</i> (Å)	6.0019 (16)
<i>b</i> (Å)	9.123 (3)
<i>c</i> (Å)	34.230 (9)
<i>α</i> (°)	90.000
<i>β</i> (°)	90.000
<i>γ</i> (°)	90.000
<i>V</i> (Å ³); <i>Z</i>	1874.3 (9) ; 4
<i>θ</i> range (°); completeness	2.58 – 70.03 ; 1.000
Reflections: collected / independent; <i>R</i> _{int}	20210 / 3569 ; 0.034
<i>μ</i> (mm ⁻¹)	2.639
Abs. Corr.	Semi-empirical
<i>R</i> 1(F); <i>wR</i> (F ²) [<i>I</i> > 2σ(<i>I</i>)]	0.0327; 0.0767
<i>R</i> 1(F); <i>wR</i> (F ²) (all data)	0.0390; 0.0790
GoF(F ²)	0.928
Max. residual e ⁻ density	0.146 e ⁻ · Å ⁻³