Supporting information

MOF as a syringe pump for the controlled release of iodine catalyst in the synthesis of *meso*-thienyl dipyrromethanes

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Experimental section:

Materials: All the reagents and solvents for synthesis were purchased from commercial sources and used as supplied without further purification. Pyrrole and substituted thiophene-2-carboxaldehydes, $Cd(NO_3)_2 \cdot 4H_2O$, 1,4-benzenedicarboxyic acid and 2-aminobenzenedicarboxylic acid were obtained from the Sigma-Aldrich Chemical Co. India. 4-bpmh has been synthesized by the literature procedure.[1]

Physical Measurements: Thermo gravimetric analysis was recorded on a Perkin-Elmer TGA 4000 instrument. IR spectrum of the compounds **NH_2-MOF** and **H-MOF** were recorded on a Perkin-Elmer FT-IR Spectrum BX using the KBr pellets in the region 4000-400 cm^{-1}. Elemental analysis was carried out on an Elementar vario Micro Cube Elemental Analyzer.

Preparation of iodine encapsulated NH_2-MOF and H-MOH:

Preparations of iodine encapsulation of both MOFs have already been discussed in our previous report.[2] In brief, fresh samples of **H-MOF** and **NH_2-MOF** (100 mg) were immersed in hexane (3.5 mL) solution of I_2 (0.1 mol L^{-1}) at room temperature and were monitored in real time with optical digital camera. For the amino functionalized **NH_2-MOF**, the color of the crystals intensified from yellow to dark brown and the dark brown solution of I_2 faded quickly to pale red in 4 hours whereas in case of the non-functionalized H-MOF, the process is much slower and took around 24 hours (Figure S3 and S4). The targeted I_2 encapsulated MOFs obtained by filtration and followed by hexane wash (5 times) to remove any traces of free iodine on the surface of sample. This was followed by air-drying at room temperature to allow sublimation of free iodine (if present) on the surface to finally obtain a dark brown phase. All the physical measurements of iodine encapsulated MOFs (**H-MOF(I_2)** and **NH_2-MOF(I_2)**) prepared for catalytic study were performed and are well matched with our previous report.

General procedure for the synthesis of *meso*-thienyl dipyrromethanes using H-MOF(I_2) or NH_2-MOF(I_2) as catalyst.

NH_2-MOF(I_2) catalysed reactions:

A mixture of 2-thienylcarboxaldehyde (0.1 mL, 1 mmol), 0.35 mL (5 mmol) of pyrrole and 0.1 mmol of **NH_2-MOF(I_2)** was stirred at room temperature and the progress of the reaction was monitored by TLC and LC-MS (during the course of the reaction it become light green in color). At the end of the period (4 hours), 5 ml of dichloromethane was added to reaction mixture and filtered. The filtrate was treated with water (5mL, 3 times) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to obtain viscous red compound and the product was purified by column chromatography (1:1 ratio of hexane and dichloromethane mixture). All the reactions of substituted 2-thienylcarboxaldehyde with **NH_2-MOF(I_2)** were performed under same condition.

H-MOF(I_2) catalysed reactions:

A mixture of 2-thienylcarboxaldehyde (0.1 mL, 1 mmol), 0.70 mL (10 mmol) of pyrrole and 0.1 mmol of **H-MOF(I_2)** was stirred at room temperature and the progress of the reaction was monitored by TLC and LC-MS (during the course of the reaction it become light green in color). At the end of the period (1 hours), 5 ml of dichloromethane was added to reaction mixture and filtered. The filtrate was treated with water (5mL, 3 times) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to obtain viscous red compound and the product was purified by column chromatography (1:1 ratio of hexane and dichloromethane mixture). All the reactions of substituted 2-thienylcarboxaldehyde with **H-MOF(I_2)** were performed under same condition.

Iodometric titration

20 mg of each of iodine loaded samples I_2@NH_2-MOF and I_2@H-MOF were dispersed in 20 ml aqueous 0.1 N potassium iodide (KI) solution and vigorously stirred in a closed vial for 24 h in dark. The pale yellow solution was obtained after the filtration and filtrate was stored in dark until the titration was carried out. Separately, 0.0005 N sodium thiosulfate ($Na_2S_2O_3$) solution was prepared and standardized with $K_2Cr_2O_7$ solution as primary standard.

10 ml aliquots from each of the iodine-KI solutions were taken in various 50 ml conical flasks and 1 ml of starch solution was added as indicator. The light blue colored solution thus obtained was titrated with 0.0005 N sodium thiosulfate solution taken in burette. Disappearance of blue color was assumed as end point and the burette readings at end point were used for determination of iodine present in each sample. The overall reaction can be written as:

$$I_2 + 2\ Na_2S_2O_3 \rightarrow 2\ NaI + Na_2S_4O_6$$

Iodine determination was carried out according to calculations reported in literature. The results are summarized below.[3]

Table S1. The adsorbed I_2 amount in I_2@NH_2-MOF and I_2@H-MOF by using TG analysis and Iodometric titrations.

Sample	**Amount of Iodine adsorbed (wt%)**	
	Identified by TG analysis	**Identified by iodometric titration**
I_2@NH_2-MOF	28	27.67
I_2@H-MOF	14	13.82

Table S2. The amount of I_2 release in I_2@NH_2-MOF and I_2@H-MOF by using TG analysis and Iodometric titrations

Sample	Cycles	Amount of I_2 left in MOF's after consecutive cycles (wt%)*		Amount of I_2 released (wt%) = Iodine content in MOF's of previous cycles*- Amount of I_2 left in MOF's after consecutive reaction cycles	
		TGA	Iodometric	TGA	Iodometric
I_2@NH_2-MOF	1st	**24**	**23.56**	28-24 = **4**	27.67- 23.56 = **4.11**
	2nd	**19**	**18.64**	24-19 = **5**	23.56 - 18.64 = **4.92**
	3rd	**14.5**	**13.93**	19-14.5 = **4.5**	18.64 - 13.93 = **4.71**
I_2@H-MOF	1st	**1.7**	**2.3**	14-1.7 = **12.3**	13.82 - 2.3 =**11.52**

NMR measurements

^{1}H and ^{13}C NMR spectra were recorded on 400 MHz spectrometer with ^{13}C operating frequencies of 100 MHz respectively. Chemical shifts (δ) are reported in ppm relative to the residual solvent ($CDCl_3$) signal (δ = 7.26 for ^{1}H NMR and δ = 77.0 for ^{13}C NMR). Abbreviations are as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). ESI-Mass Spectra were recorded on MicrOTOF-Q-II mass spectrometer.

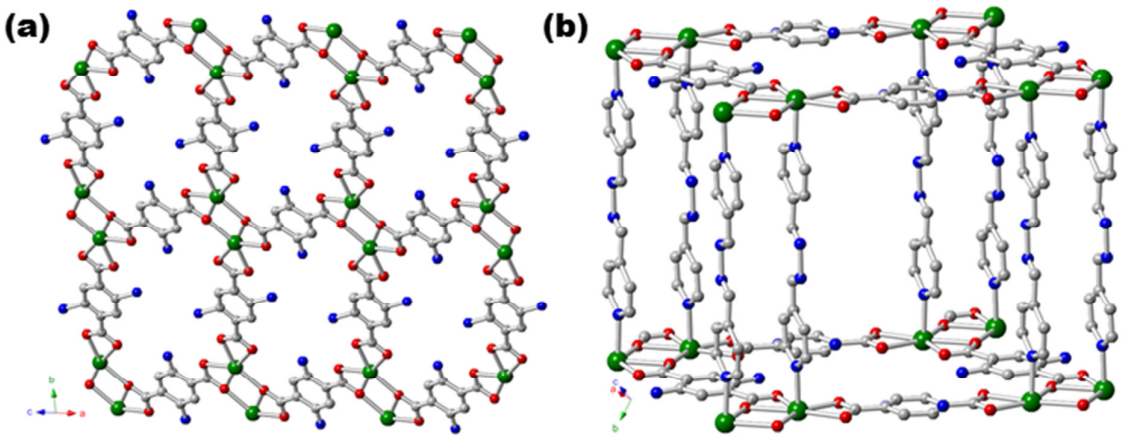


Figure S1. (a) Illustration of 2D square grid arrangement found in NH_2-MOF along the *a*-axis (b) 3D bi-pillared layer framework in 2- NH_2bdc. (The amino group in 2- NH_2bdc ligand is disordered and disposed in 2- and 5-position).

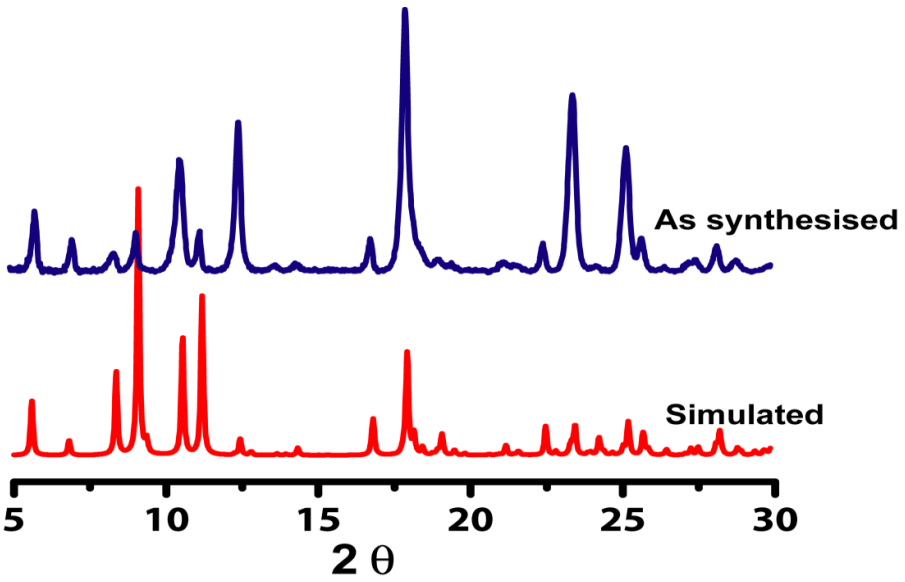


Figure S2. PXRD patterns of H-MOF.

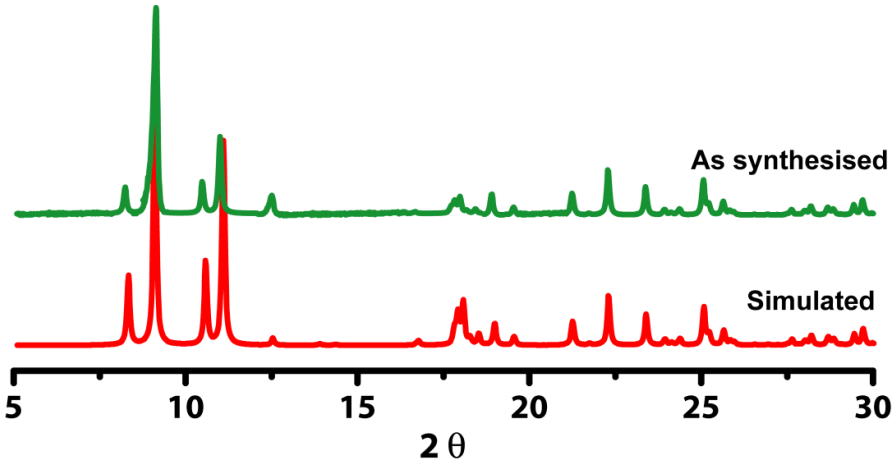


Figure S3. PXRD patterns of NH_2-MOF.

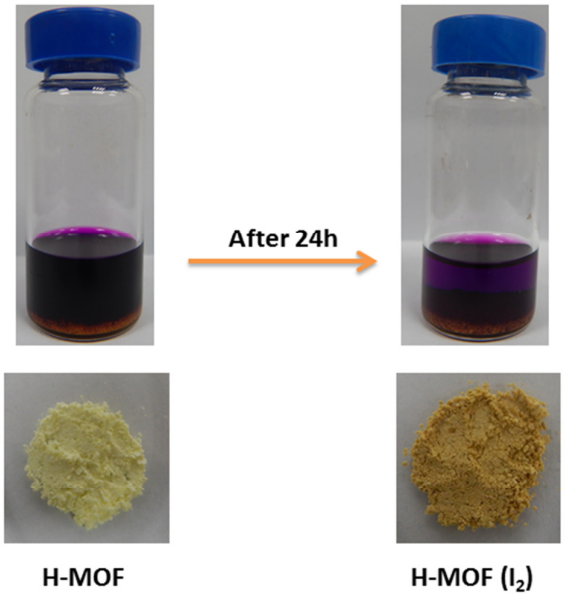


Figure S4. Photographs of fresh H-MOF and after I_2 adsorption H-MOF(I_2)

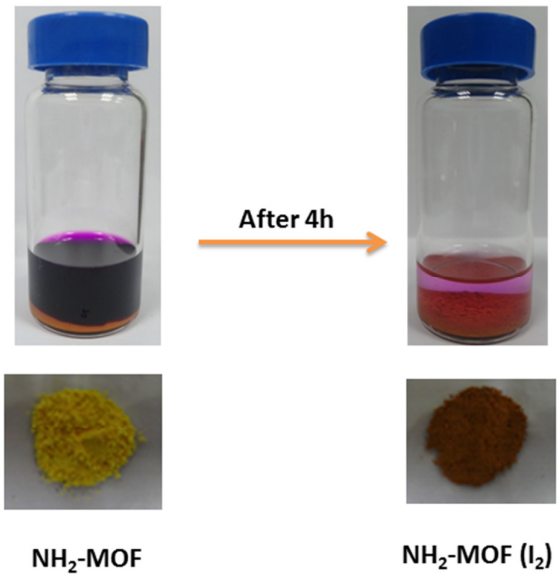


Figure S5. Photographs of fresh NH_2-MOF and after I_2 adsorption NH_2-MOF(I_2)

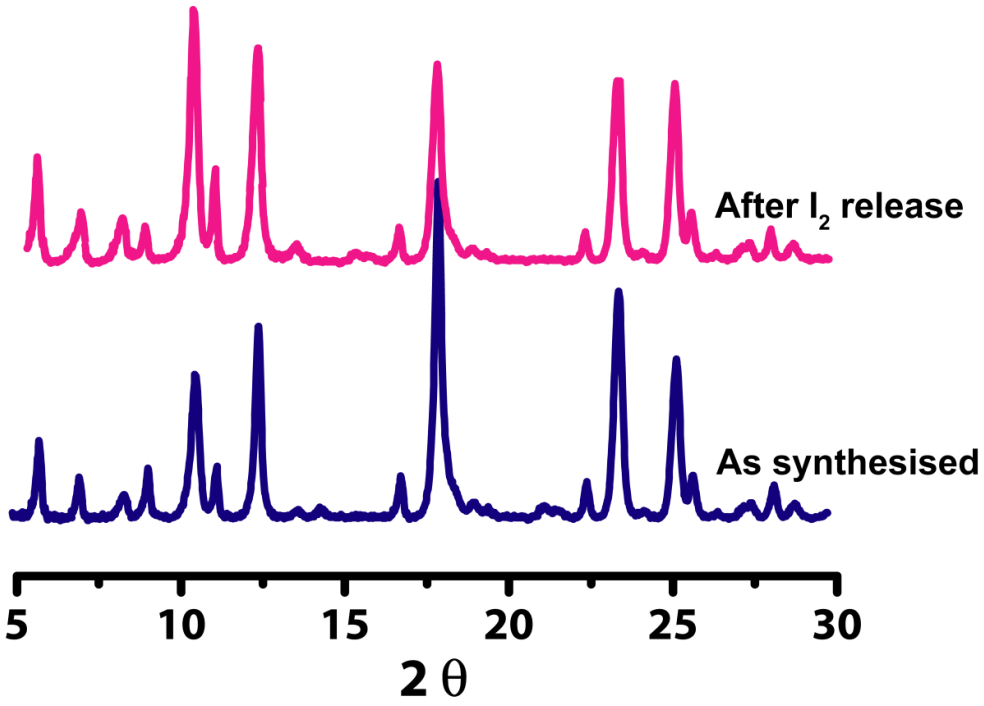


Figure S6. PXRD patterns of H-MOF and After I_2 release from H-MOF.

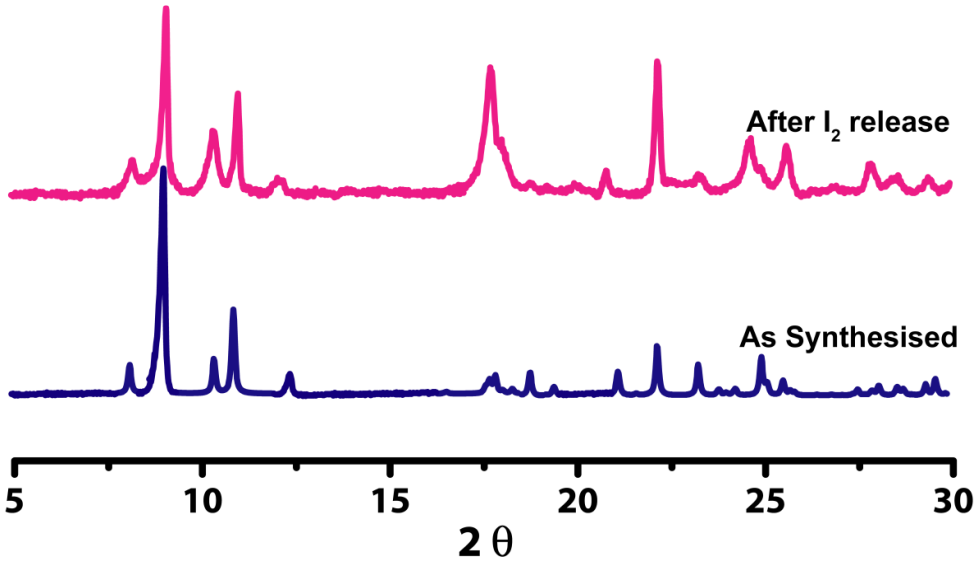


Figure S7. PXRD patterns of NH_2-MOF and After I_2 release from NH_2-MOF.

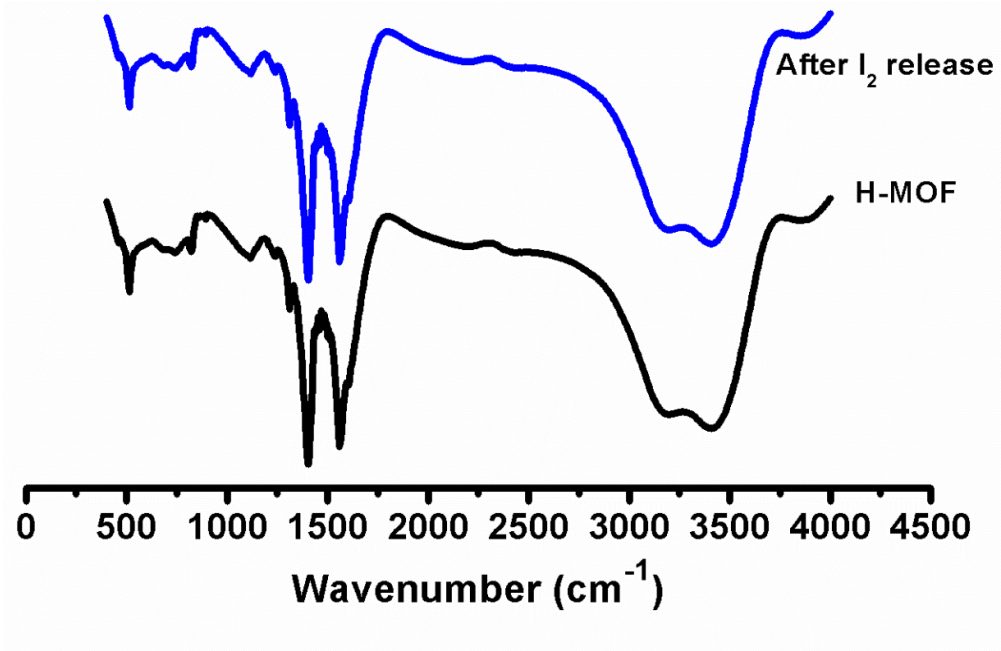


Figure S8. FTIR spectra of H-MOF and after I_2 release from the H-MOF.

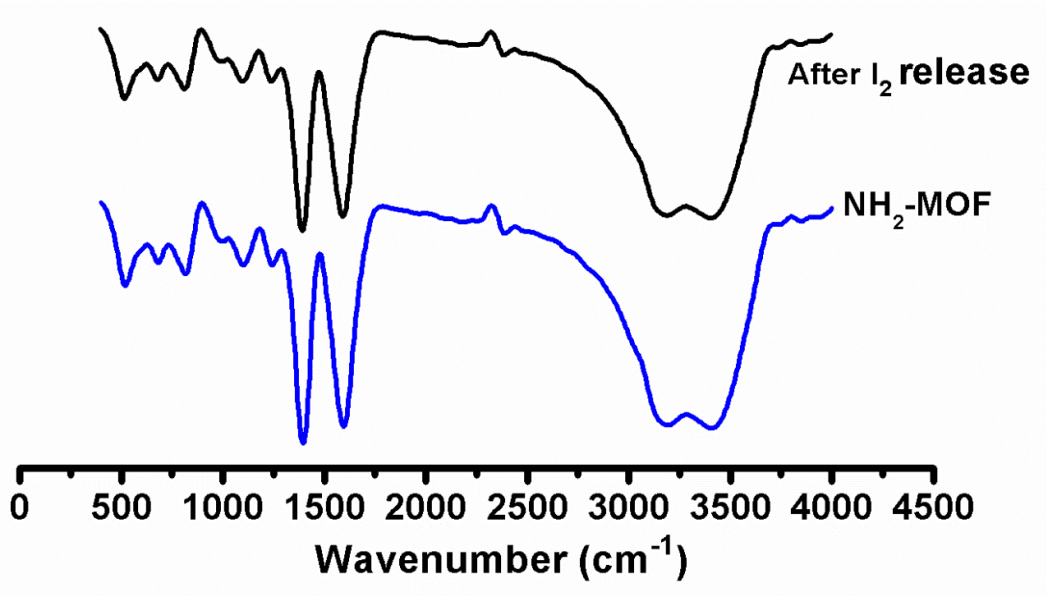


Figure S9. FTIR spectra of NH_2-MOF and after I_2 release from the NH_2-MOF.

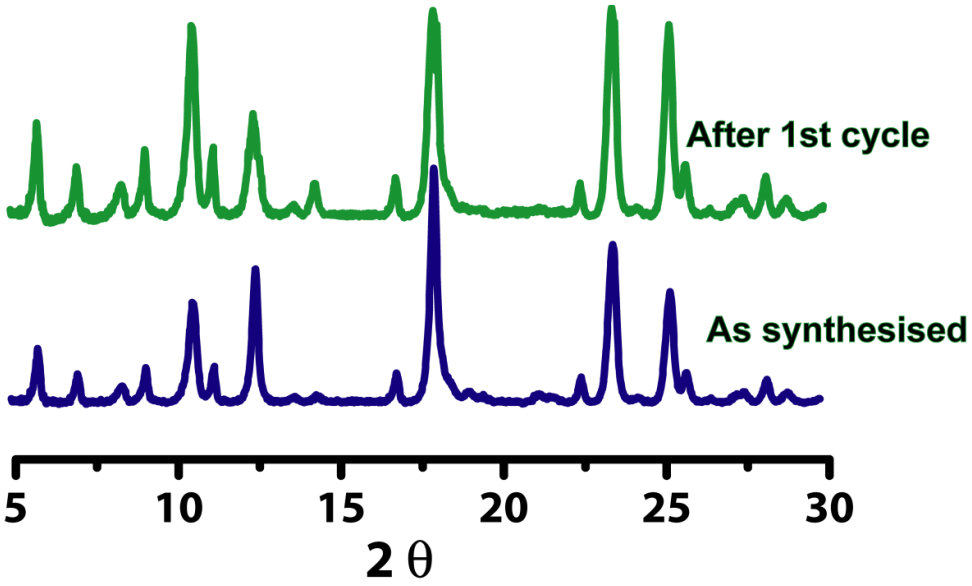


Figure S10. PXRD patterns of H-MOF and after first reaction cycle of H-MOF

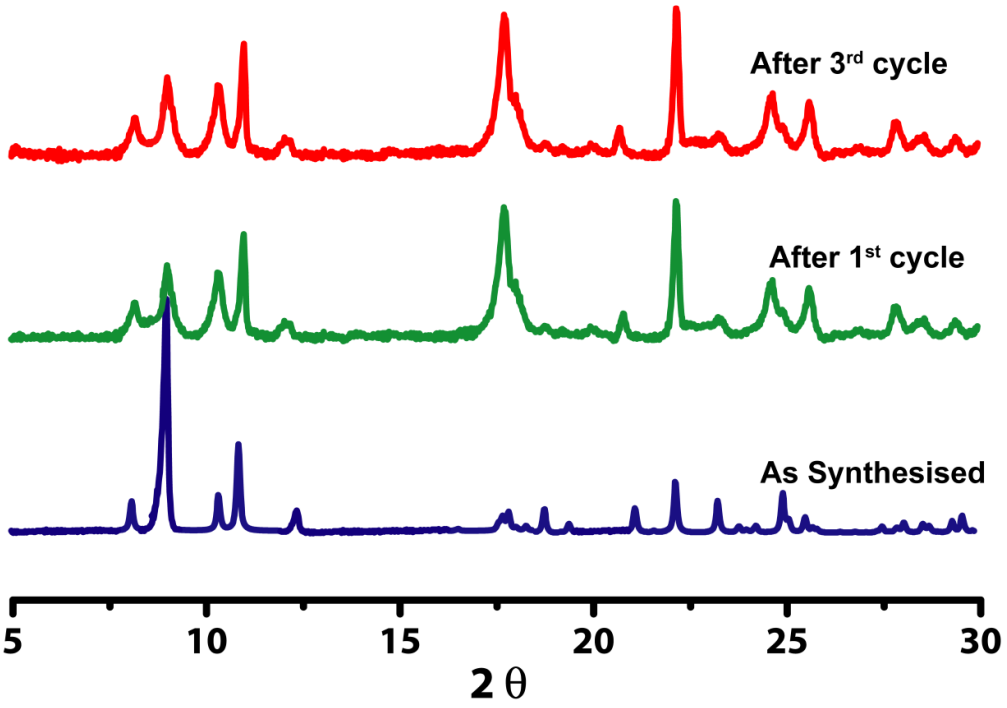
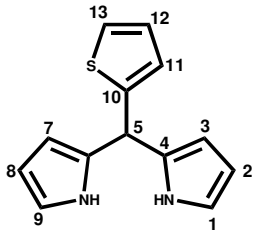


Figure S11. PXRD patterns of NH_2-MOF and after first and third reaction cycle of NH_2-MOF.

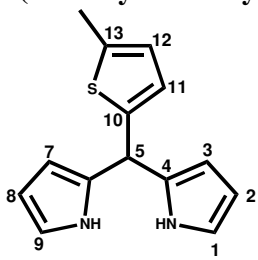
Spectral and analytical details of the synthesized compounds are given below.

5(2-thienyl)dipyrromethane (1)



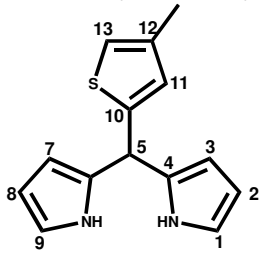
Dirty white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.55-5.74 (br, 1H, H^{5}), 5.89-6.04 (m, 2H, $H^{3,7}$), 6.13-6.25 (m, 2H, $H^{2,8}$)6.69 (d, 2H, $H^{1,9}$), 6.81 (d, 1H, H^{11}), 6.89-6.95 (m, 1H, H^{12}), 7.18-7.21 (m, 1H, H^{13}), 7.80-8.25 (b, 2H, NH); ^{13}C NMR (100 MHz): 39.20, 106.95, 107.02, 107.25, 108.19, 108.50, 117.41, 117.69, 124.64, 125.47, 126.74, 131.96, 145.79. ESI-MS[M+1]: 229.1. Anal. found for $C_{13}H_{12}N_2S$: C 67.96, H 5.24 and N 12.06.

5(5-methyl-2-thienyl)dipyrromethane (2)



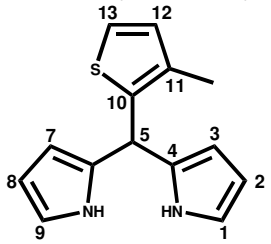
Dirty white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.43 (s, 3H, $-CH_3$), 5.44-5.64 (br, 1H, H^{5}), 5.89-6.06 (m, 2H, $H^{3,7}$), 6.27 (d, 2H, $H^{1,9}$), 6.60-6.62 (m, 2H, $H^{2,8}$), 6.66 (d, 1H, H^{11}), 6.81 (d, 1H, H^{12}), 7.79-8.22 (b, 2H, NH); ^{13}C NMR (100 MHz): 15.39, 39.28, 106.82, 106.94, 107.12, 108.20, 108.44, 117.34, 117.74, 124.70, 125.24, 126.74, 131.93, 143.26. ESI-MS[M-1]: 241.30. Anal. found for $C_{14}H_{14}N_2S$: C 69.30, H 5.74 and N 11.48.

5(4-methyl-2-thienyl)dipyrromethane (3)



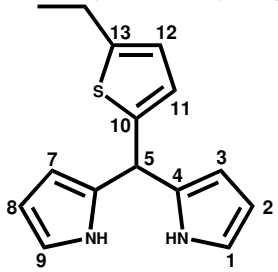
Dirty white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.26 (s, 3H, $-CH_3$), 5.65 (s, 1H, H^{5}), 6.09 (s, 2H, $H^{3,7}$), 6.21-6.23 (q, 2H, $H^{2,8}$), 6.67 (d, 2H, $H^{1,9}$), 6.71 (s, 1H, H^{11}), 6.82 (s, 1H, H^{13}), 7.88 (bs, 2H, NH); ^{13}C NMR (100 MHz): 15.93, 39.18, 107.13, 108.46, 117.46, 119.83, 128.03, 132.16, 137.37, 145.46. ESI-MS[M-1]: 241.10. Anal. found for $C_{14}H_{14}N_2S$: C 69.29, H 5.69 and N 11.50.

5(3-methyl-2-thienyl)dipyrromethane (4)



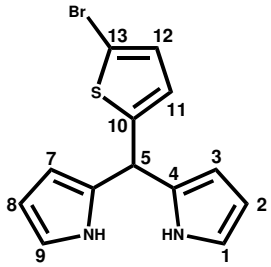
Dirty white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.15 (m, 3H, -CH_3), 5.53-5.71 (m, 1H, H^5), 5.84-6.01 (m, 2H, $H^{3,7}$), 6.13-6.26 (m, 2H, $H^{2,8}$), 6.68 (bs, 1H, H^{12}), 6.80-6.84 (m, 2H, $H^{1,9}$), 7.05-7.10 (m, 1H, H^{13}), 7.77-8.24 (b, 2H, NH); ^{13}C NMR (100 MHz): 13.78, 37.53, 107.12, 108.19, 108.40, 117.33, 117.71, 122.64, 130.32, 131.61, 131.73, 133.94, 139.00. ESI-MS[M-1]: 241.2. Anal. found for $C_{14}H_{14}N_2S$: C 69.30, H 5.64 and N 11.49.

5(5-ethyl-2-thienyl)dipyrromethane (5)



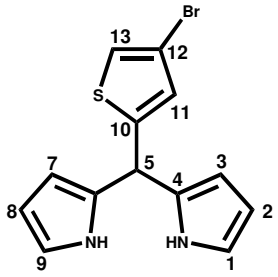
Dirty white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.33 (t, 3H, -CH_3), 2.84 (q, 2H, -CH_2-), 5.45-5.65 (br, 1H, H^5), 5.93-6.30 (m, 4H, $H^{2,3,7,8}$), 6.67-6.80 (m, 4H, $H^{1,9,11,12}$), 7.85-8.92 (b, 2H, NH); ^{13}C NMR (100 MHz): 15.88, 23.74, 39.34, 107.00, 107.12, 108.21, 108.43, 117.44, 117.80, 122.80, 125.08, 125.15, 132.08, 132.25, 142.94, 146.80. ESI-MS[M+1]: 257.2. Anal. found for $C_{15}H_{16}N_2S$: C 70.20, H 6.22 and N 10.88.

5(5-bromo-2-thienyl)dipyrromethane (6)



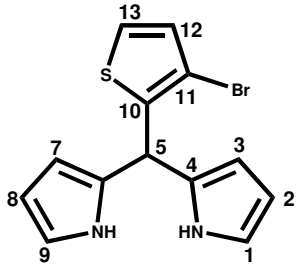
Dirty white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.44-5.63 (br, 1H, H^5), 5.86-5.99 (m, 2H, $H^{3,7}$), 6.05-6.25 (m, 2H, $H^{2,8}$), 6.58-6.62 (m, 1H, H^1), 6.69 (d, 1H, H^{11}), 6.81 (d, 1H, H^{12}), 6.86-6.88 (m, 1H, H^9), 7.79-8.24 (b, 2H, NH); ^{13}C NMR (100 MHz): 39.47, 107.30, 108.20, 108.63, 111.17, 117.72, 121.81, 129.48, 131.13, 147.49. ESI-MS[M+1]: 307.01. Anal. found for $C_{13}H_{11}BrN_2S$: C 50.76, H 3.56 and N 8.88.

5(4-bromo-2-thienyl)dipyrromethane (7)



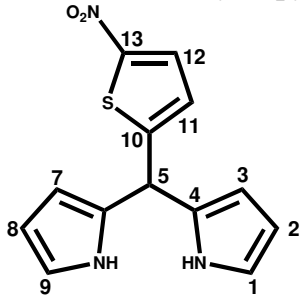
Dirty white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.65 (s, 1H, H^{5}), 6.05 (s, 2H, $H^{3,7}$), 6.16-6.18 (q, 2H, $H^{2,8}$), 6.68 (s, 2H, $H^{1,9}$), 6.79 (s, 1H, H^{11}), 7.10 (s, 1H, H^{13}), 7.80 (bs, 2H, NH); ^{13}C NMR (100 MHz): 39.12, 107.12, 108.22, 108.67, 109.13, 117.65, 121.98, 131.02, 147.29. ESI-MS [M+1]: 307.10. Anal. found for $C_{13}H_{11}BrN_2S$: C 50.74, H 3.52 and N 9.00.

5(3-bromo-2-thienyl)dipyrromethane (8)



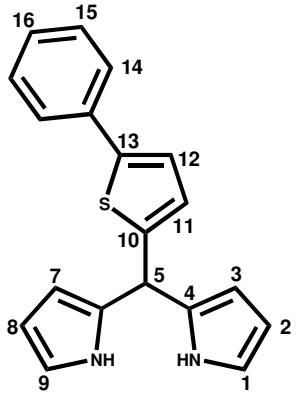
Dirty white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.65-5.83 (m, 1H, H^{5}), 5.83-6.03 (m, 2H, $H^{3,7}$), 6.13-6.17 (m, 1H, H^{8}), 6.24 (d, 1H, H^{12}), 6.69-6.71 (m, 1H, H^{2}), 6.81 (d, 1H, H^{13}), 6.91-6.95 (m, 1H, H^{9}), 7.18-7.20 (m, 1H, H^{1}), 7.77-8.24 (b, 2H, NH); ^{13}C NMR (100 MHz): 38.64, 107.45, 107.80, 108.20, 108.60, 117.62, 117.69, 124.68, 124.72, 129.97, 140.72. ESI-MS[M-1]: 307.00. Anal. found for $C_{13}H_{11}BrN_2S$: C 50.64, H 3.42 and N 9.02.

5(5-nitro-2-thienyl)dipyrromethane (9)



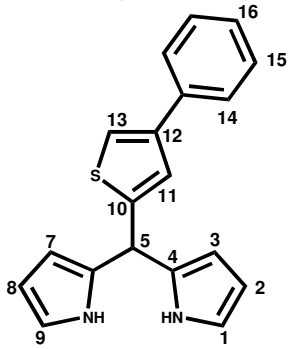
Dark solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.15 (s, 2H, $H^{3,7}$), 6.13-6.25 (q, 2H, $H^{2,8}$), 6.72 (d, 2H, $H^{1,9}$), 6.91 (d, 1H, H^{11}), 7.75 (d, 1H, H^{12}), 8.08 (bs, 2H, NH); ^{13}C NMR (100 MHz): 48.97, 108.59, 109.14, 118.21, 125.62, 128.22, 132.26, 150.51, 159.97. ESI-MS[M-1]: 272.10. Anal. found for $C_{13}H_{11}N_3O_2S$: C 57.06, H 3.96 and N 15.28.

5(5-Phenyl-2-thienyl)dipyrromethane (10)



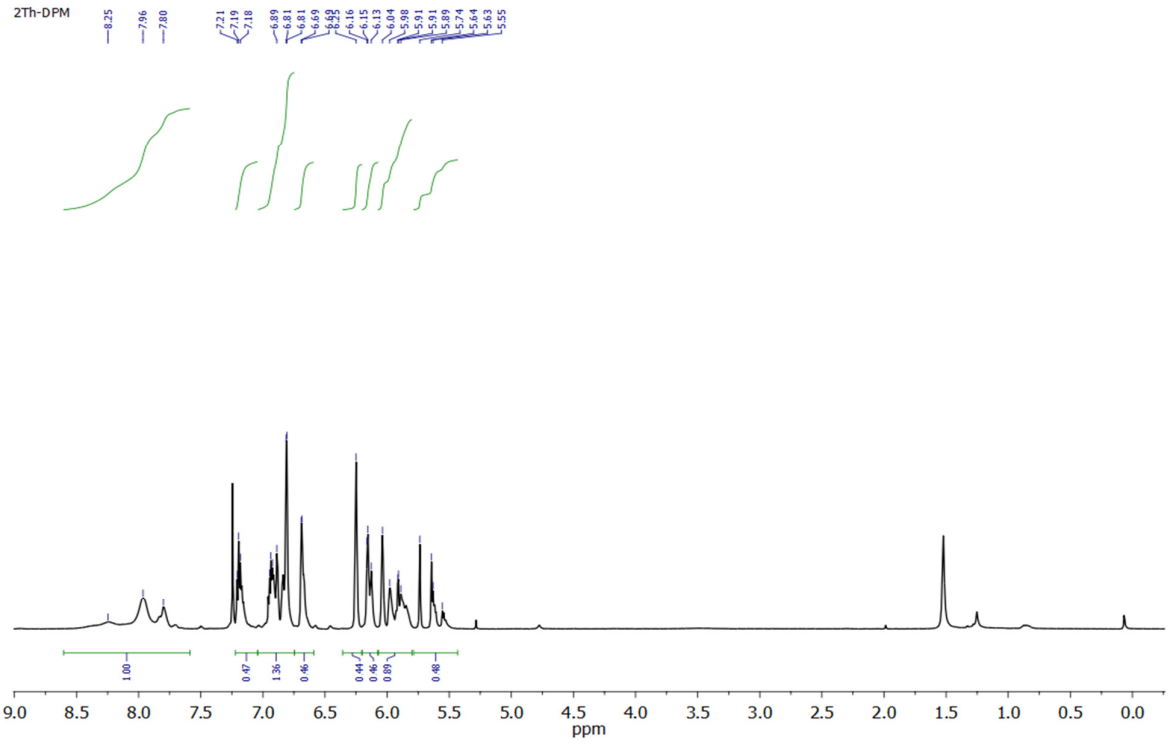
Dirty white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.71 (s, 1H, H^{5}), 6.10 (s, 2H, $H^{3,7}$), 6.18-6.20 (q, 2H, $H^{2,8}$), 6.70 (d, 2H, $H^{1,9}$), 6.84(d, 1H, H^{11}), 7.15 (d, 1H, H^{12}), 7.25 (m, 1H, H^{16}), 7.36 (t, 2H, H^{15}), 7.54 (d, 2H, H^{14}), 8.00 (bs, 2H, NH); ^{13}C NMR (100 MHz): 39.42, 107.18, 108.55, 117.56, 122.61, 125.61, 126.49, 126.54, 127.44, 128.88, 131.76, 131.83, 134.34, 143.53, 145.29. ESI-MS[M+1]: 229.1. Anal. found for $C_{19}H_{16}N_2S$: C 74.92, H 5.20 and N 9.14.

5(4-Phenyl-2-thienyl)dipyrromethane (11)

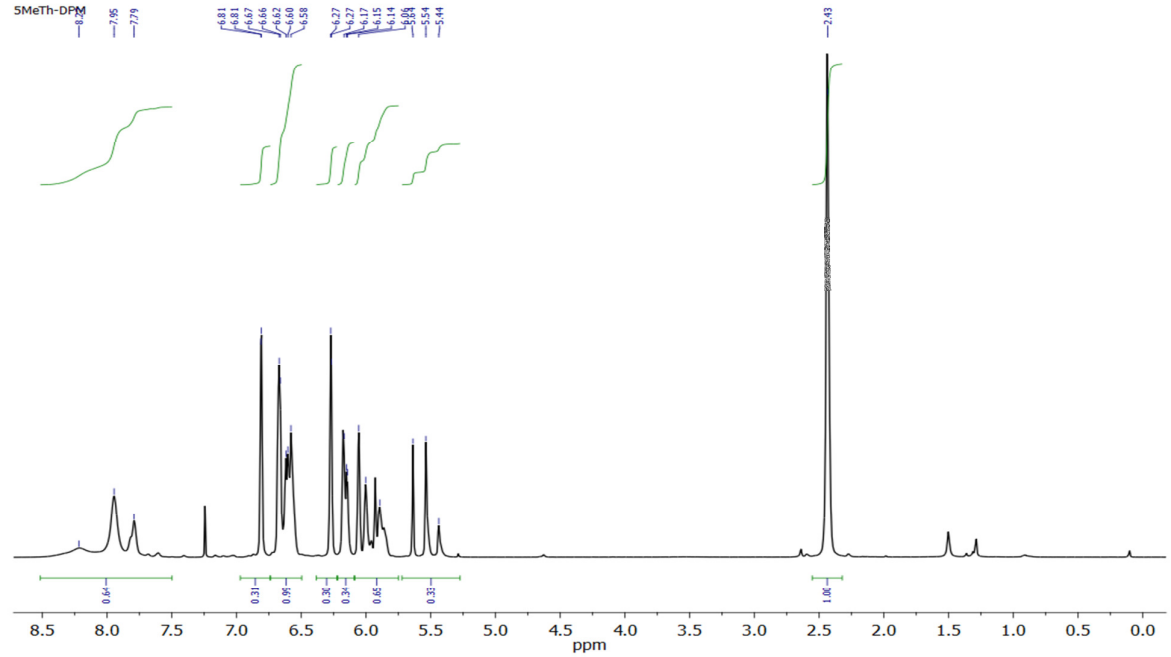


Dirty white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.65-5.74 (m, 1H, H^{5}), 5.95-6.18 (m, 1H, $H^{3,7,8}$), 6.25 (s, 1H, H^{11}), 6.71 (s, 1H, H^{3}), 6.81 (s, 1H, H^{13}), 7.19-7.36 (m, 5H, $H^{1,9,14,14',16}$), 7.49-7.52 (m, 2H, H^{15}), 7.91-8.22 (b, 2H, NH); ^{13}C NMR (100 MHz): 39.49, 107.14, 107.19, 107.44, 108.20, 108.57, 117.55, 117.70, 119.40, 124.83, 126.26, 127.19, 128.80, 131.70, 135.78, 141.88, 146.68. ESI-MS[M-1]: 303.20. Anal. found for $C_{19}H_{16}N_2S$: C 74.90, H 5.24 and N 9.12.

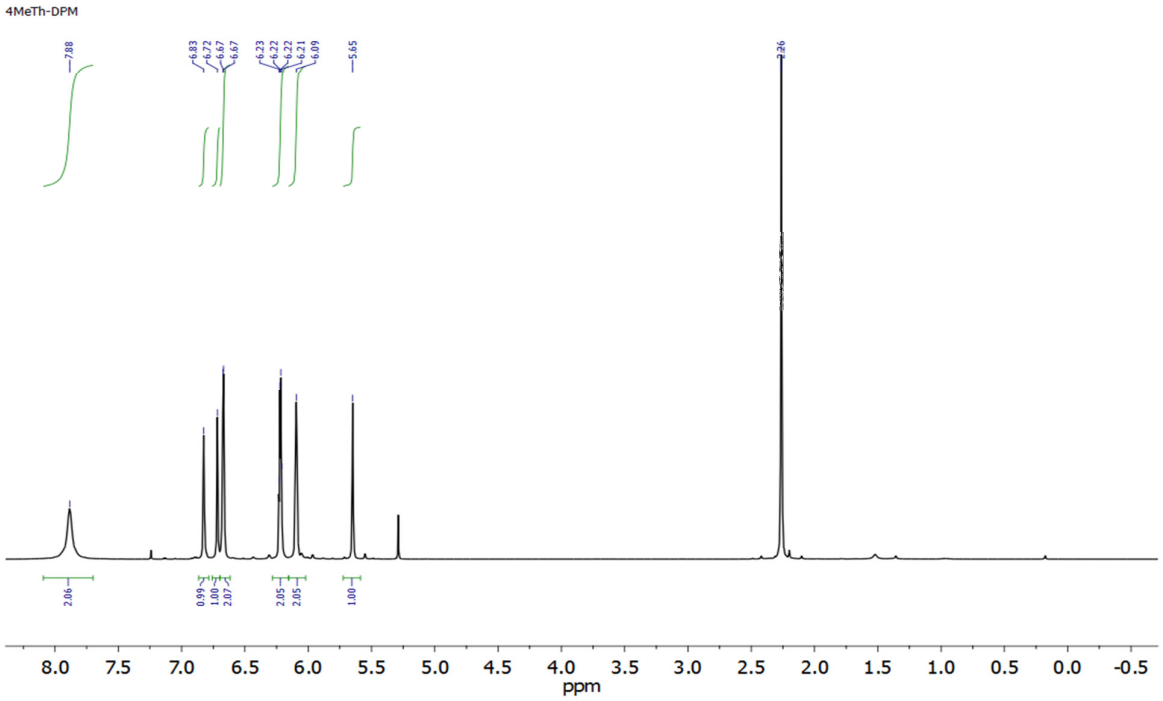
^{1}H NMR of 5(2-thienyl)dipyrromethane (1)



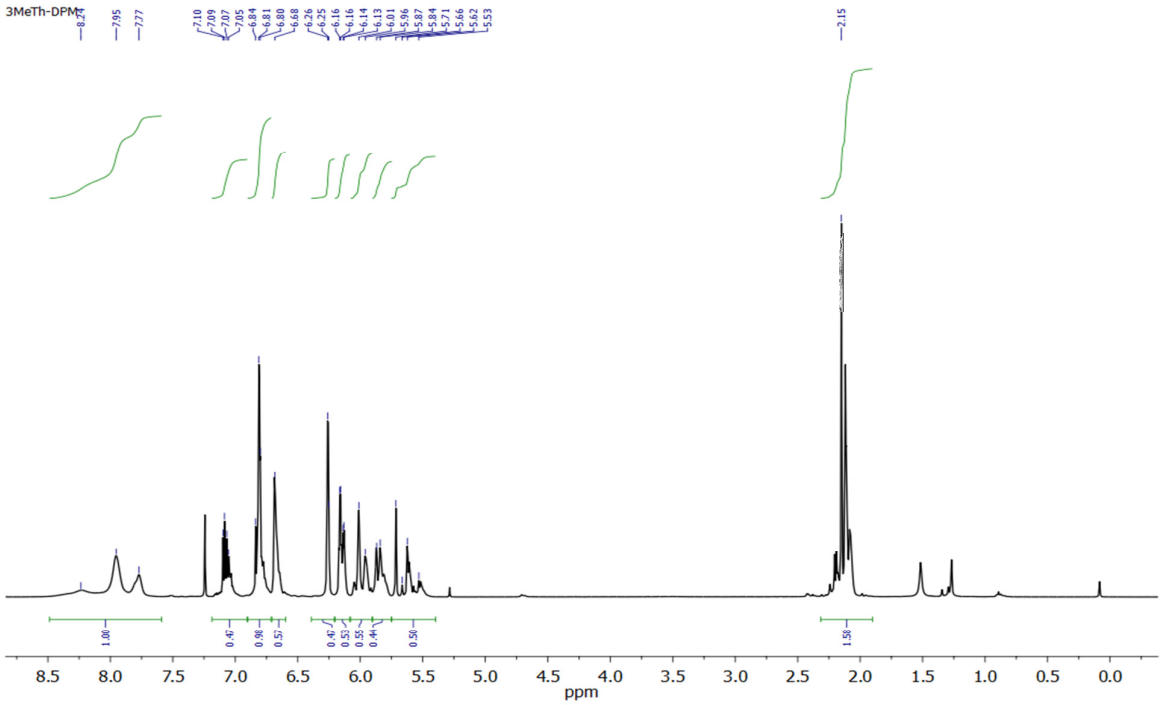
^{1}H NMR of 5(5-methyl-2-thienyl)dipyrromethane (2)



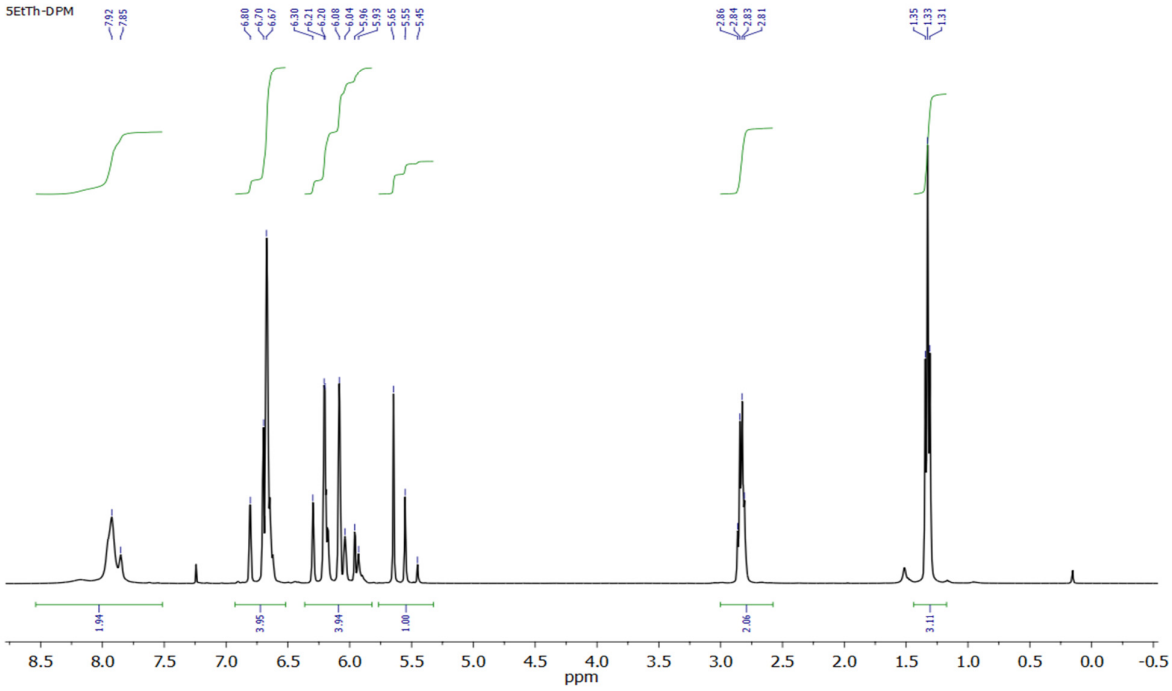
^{1}H NMR of 5(4-methyl-2-thienyl)dipyrromethane (3)



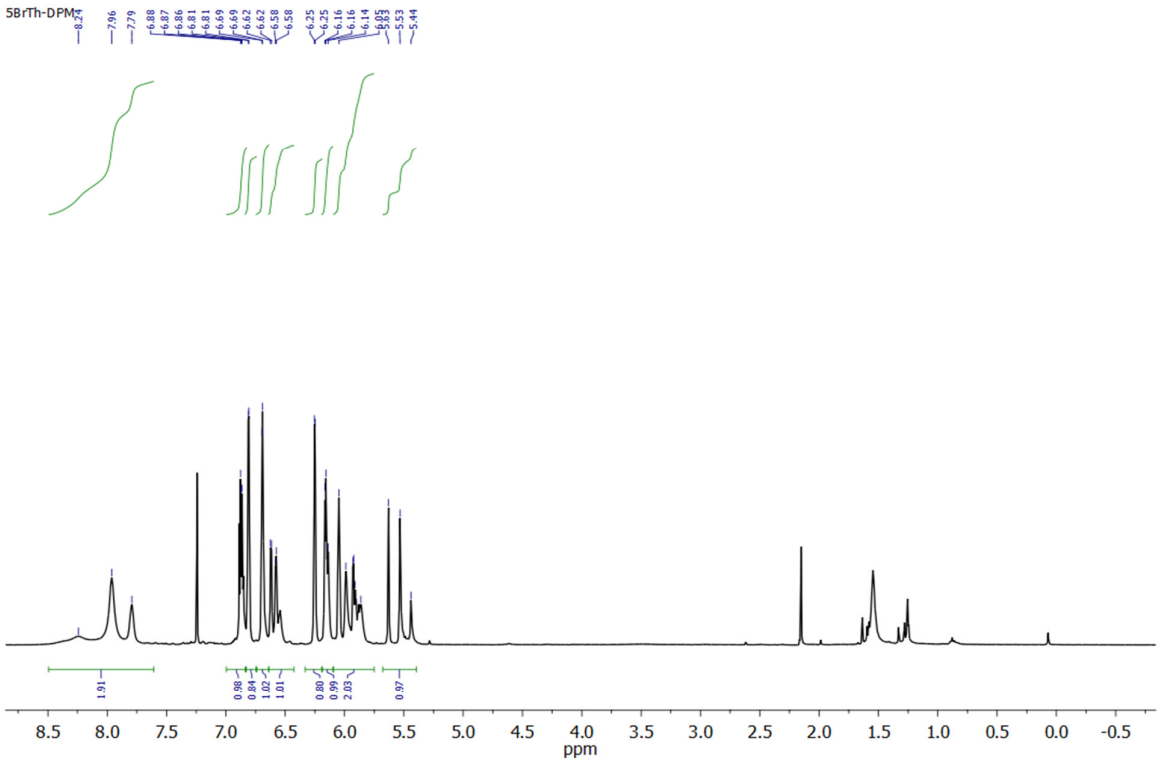
^{1}H NMR of 5(3-methyl-2-thienyl)dipyrromethane (4)



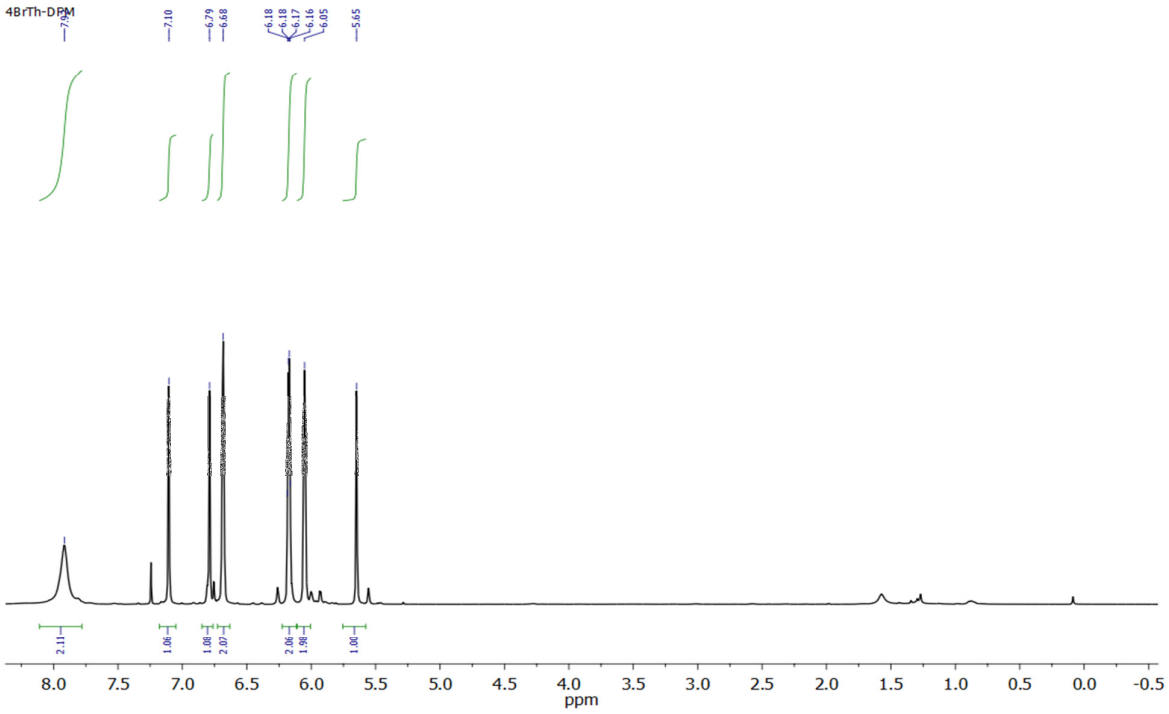
^{1}H NMR of 5(5-ethyl-2-thienyl)dipyrromethane (5)



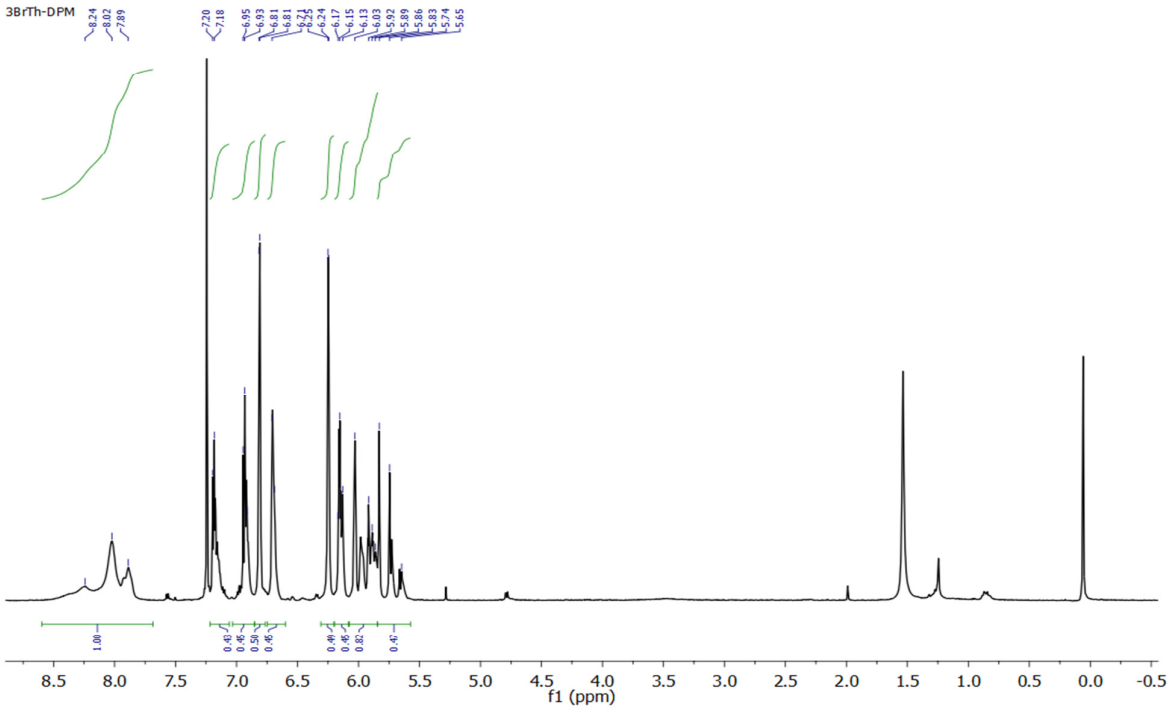
^{1}H NMR of 5(5-bromo-2-thienyl)dipyrromethane (6)



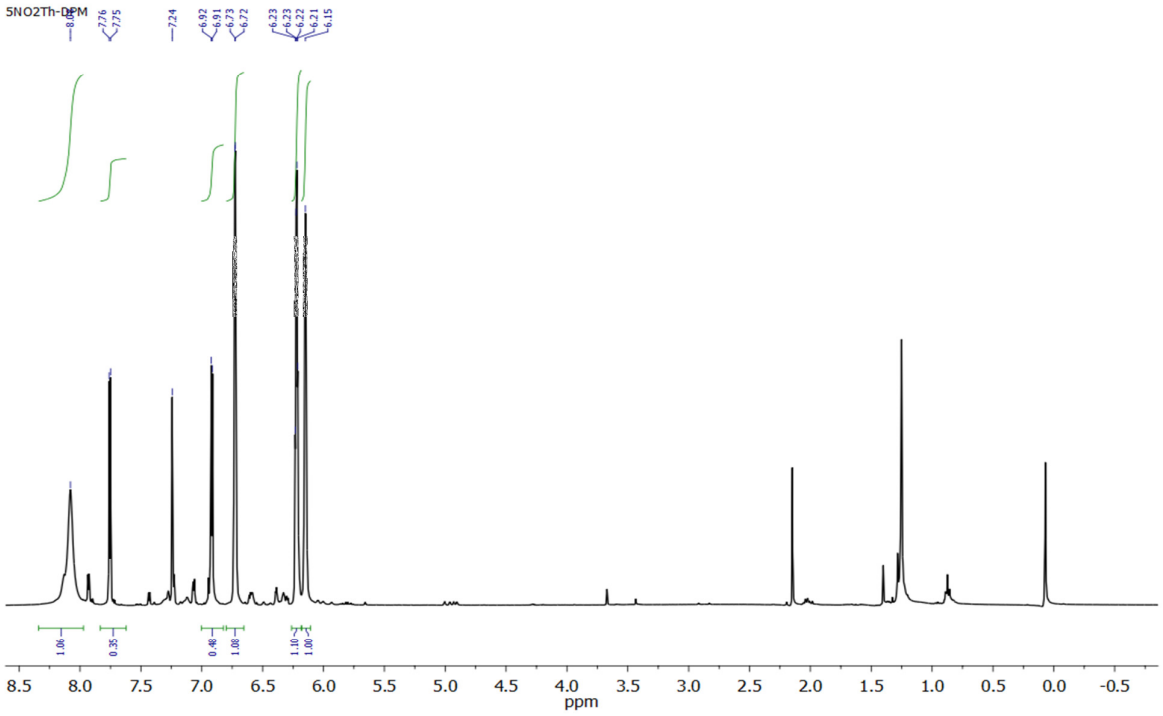
^{1}H NMR of 5(4-bromo-2-thienyl)dipyrromethane (7)



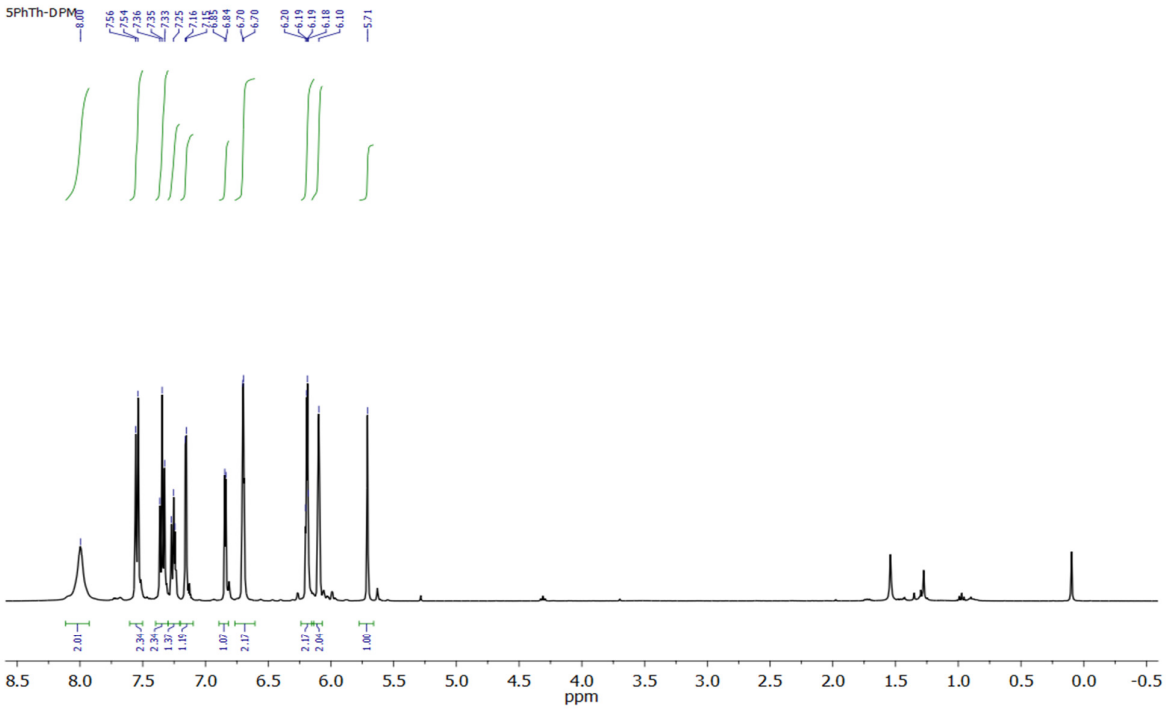
^{1}H NMR of 5(3-bromo-2-thienyl)dipyrromethane (8)



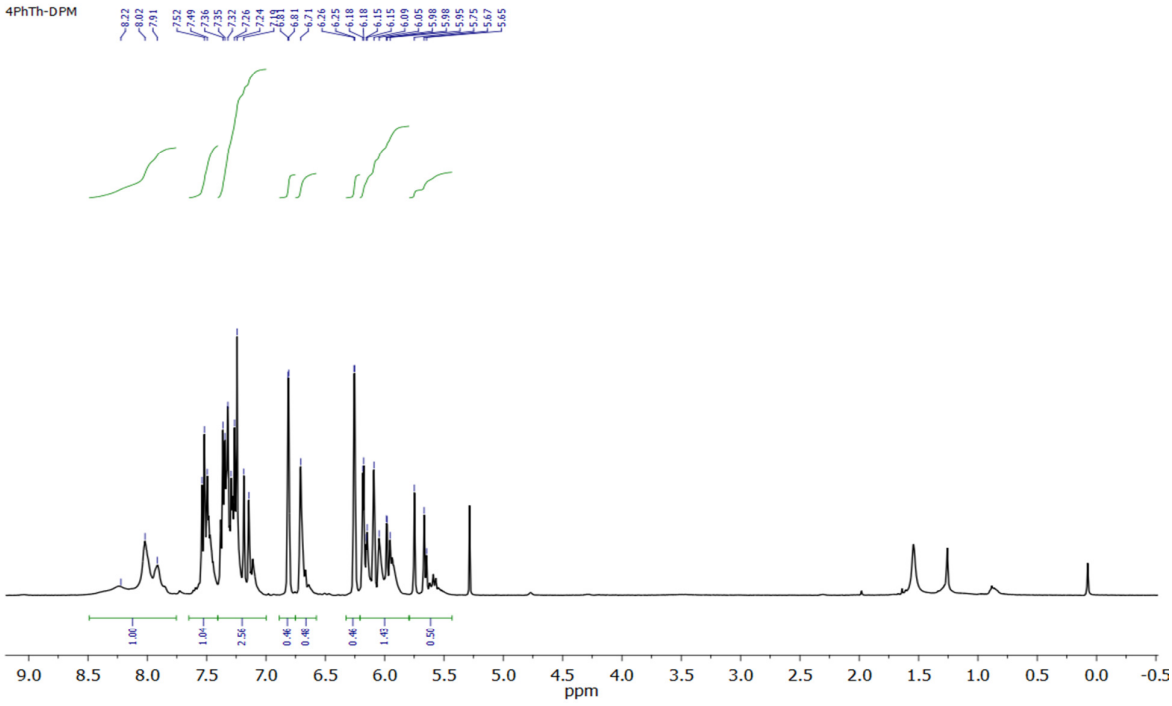
^{1}H NMR of 5(5-nitro-2-thienyl)dipyrromethane (9)



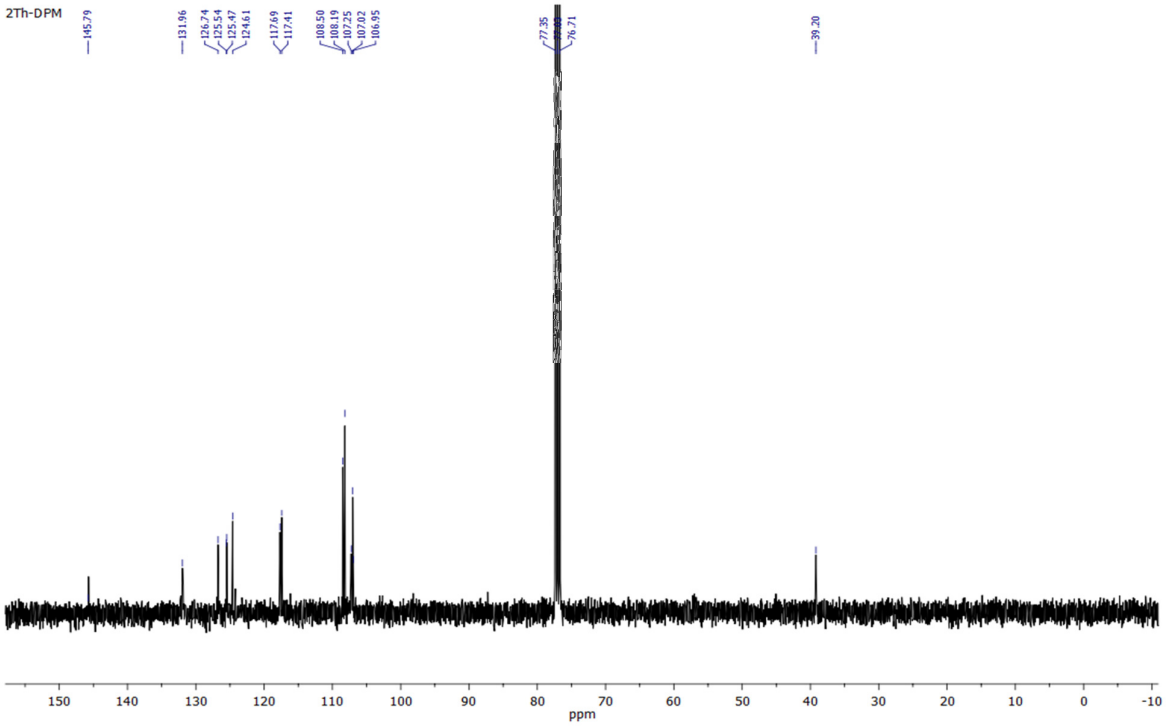
^{1}H NMR of 5(5-Phenyl-2-thienyl)dipyrromethane (10)



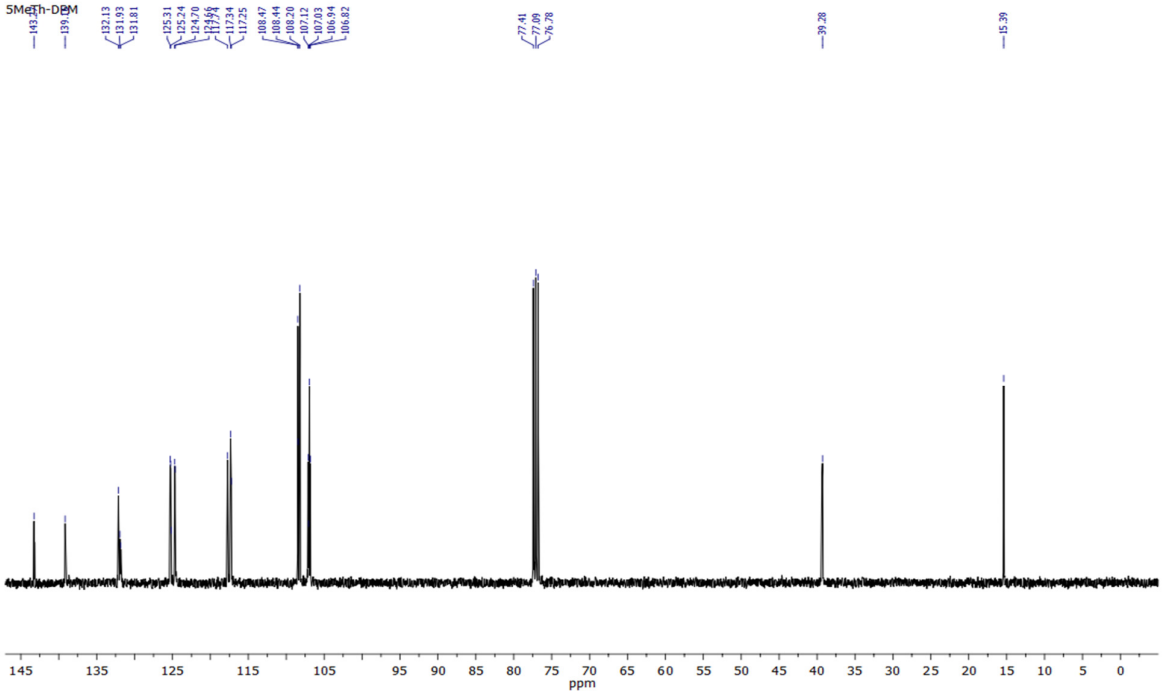
^{1}H NMR of 5(4-Phenyl-2-thienyl)dipyrromethane (11)



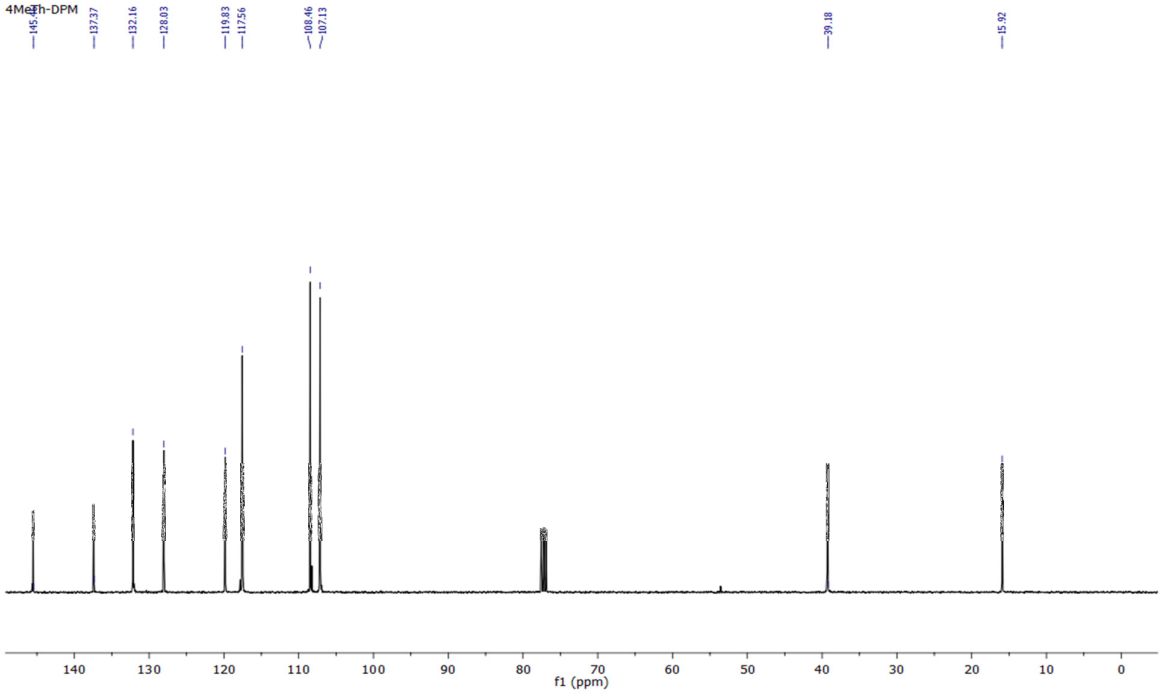
^{13}C NMR of 5(2-thienyl)dipyrromethane (1)



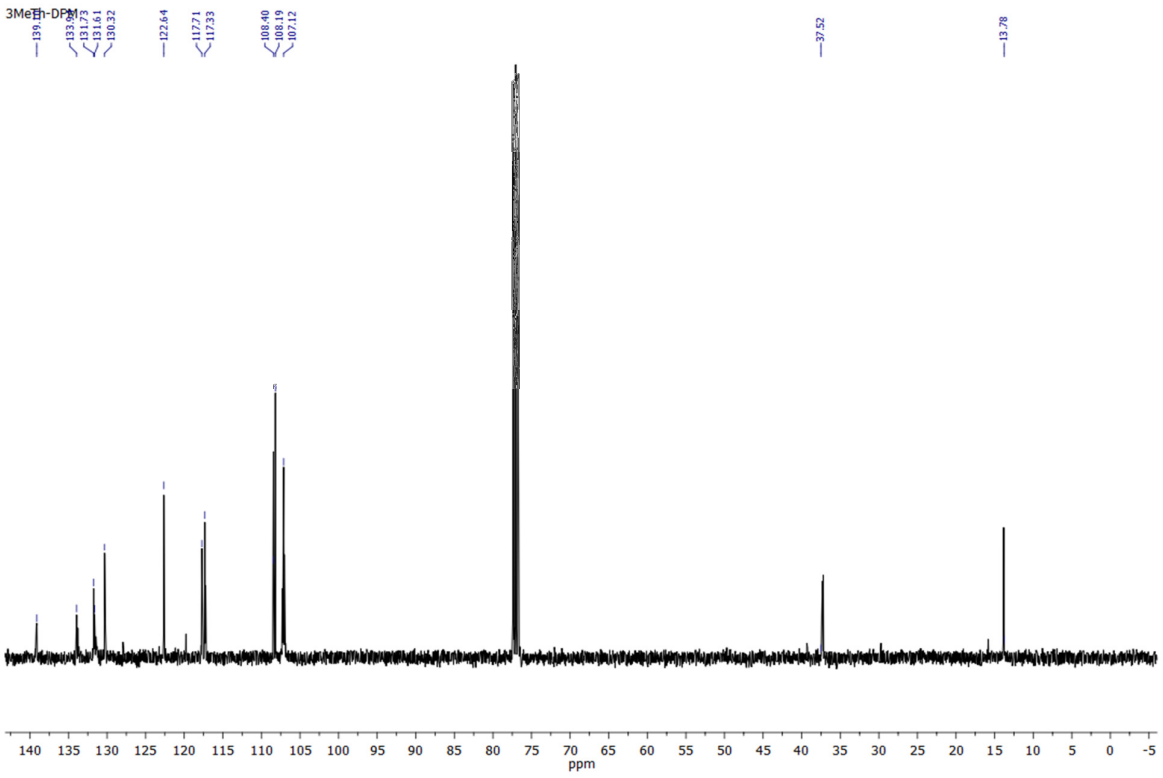
^{13}C NMR of 5(5-methyl-2-thienyl)dipyrromethane (2)



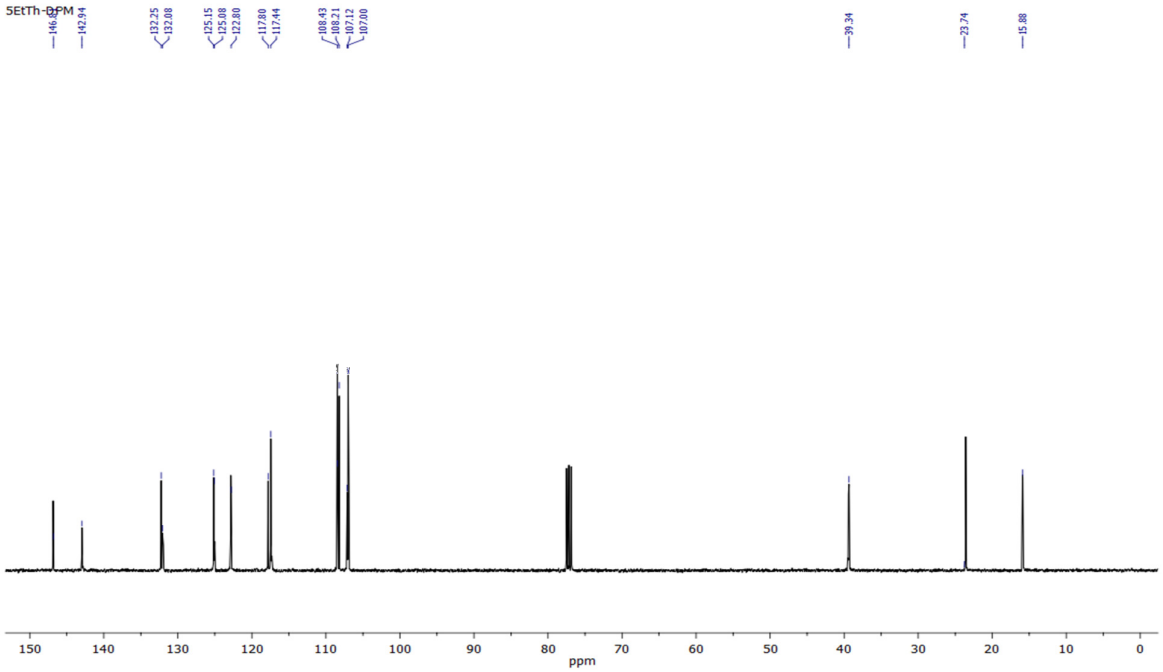
^{13}C NMR of 5(4-methyl-2-thienyl)dipyrromethane (3)



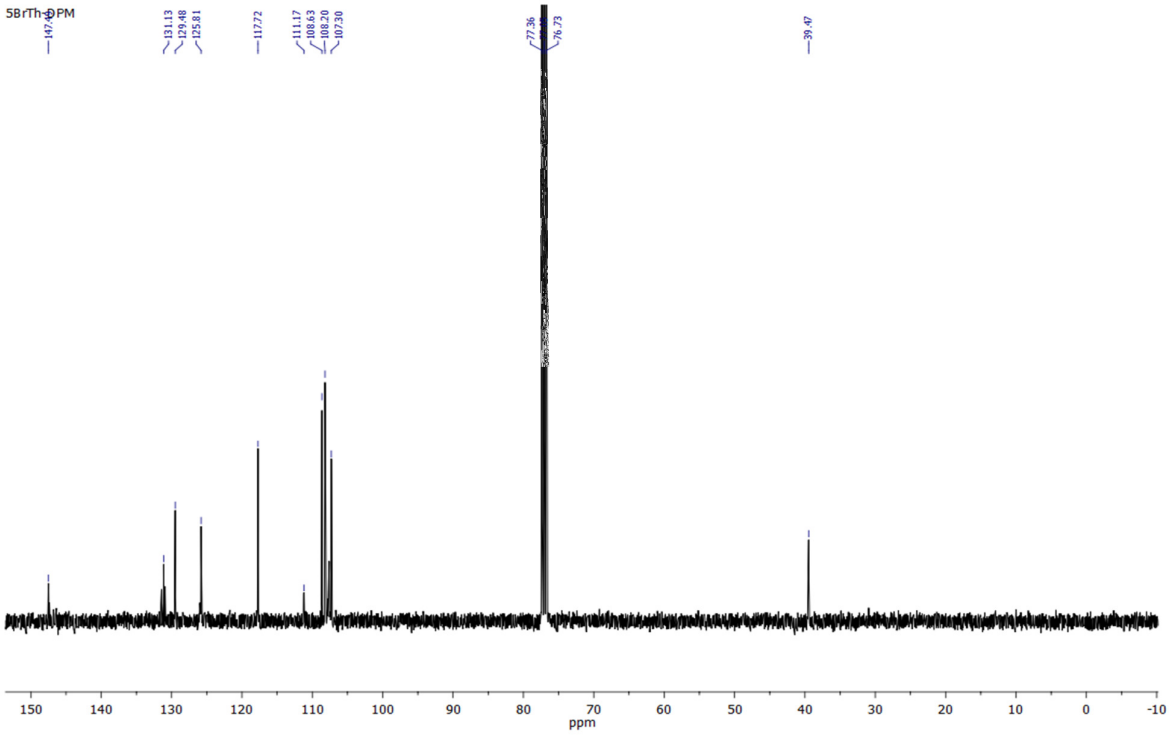
^{13}C NMR of 5(3-methyl-2-thienyl)dipyrromethane (4)



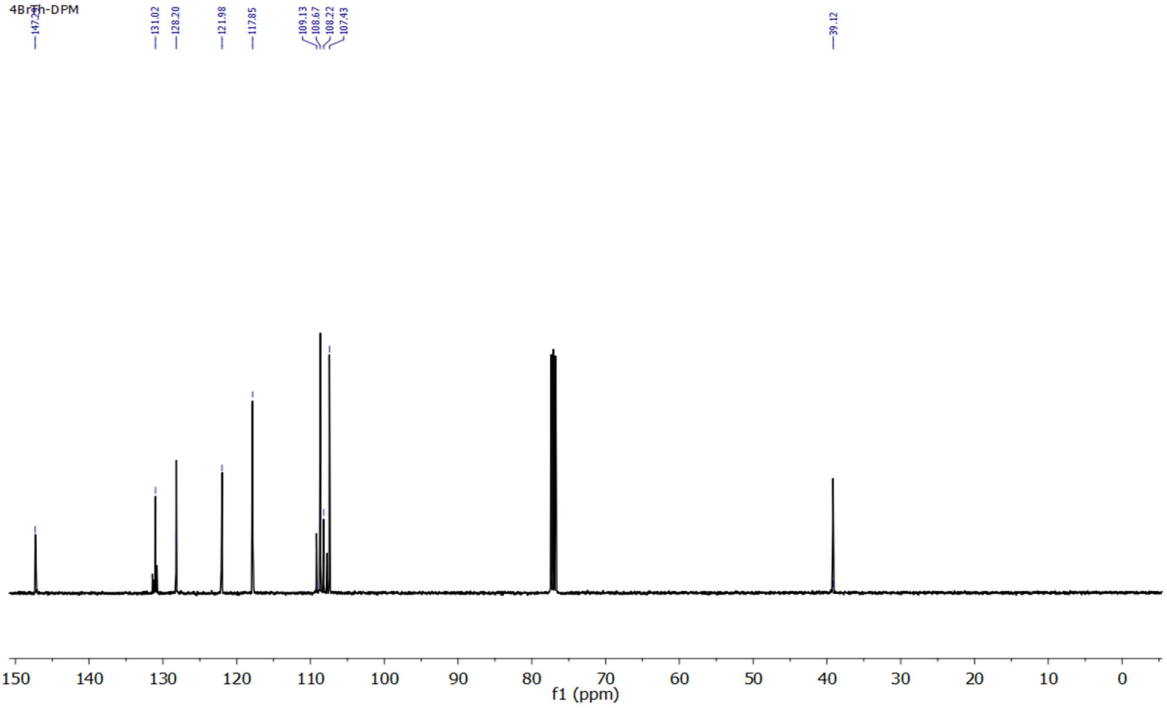
^{13}C NMR of 5(5-ethyl-2-thienyl)dipyrromethane (5)



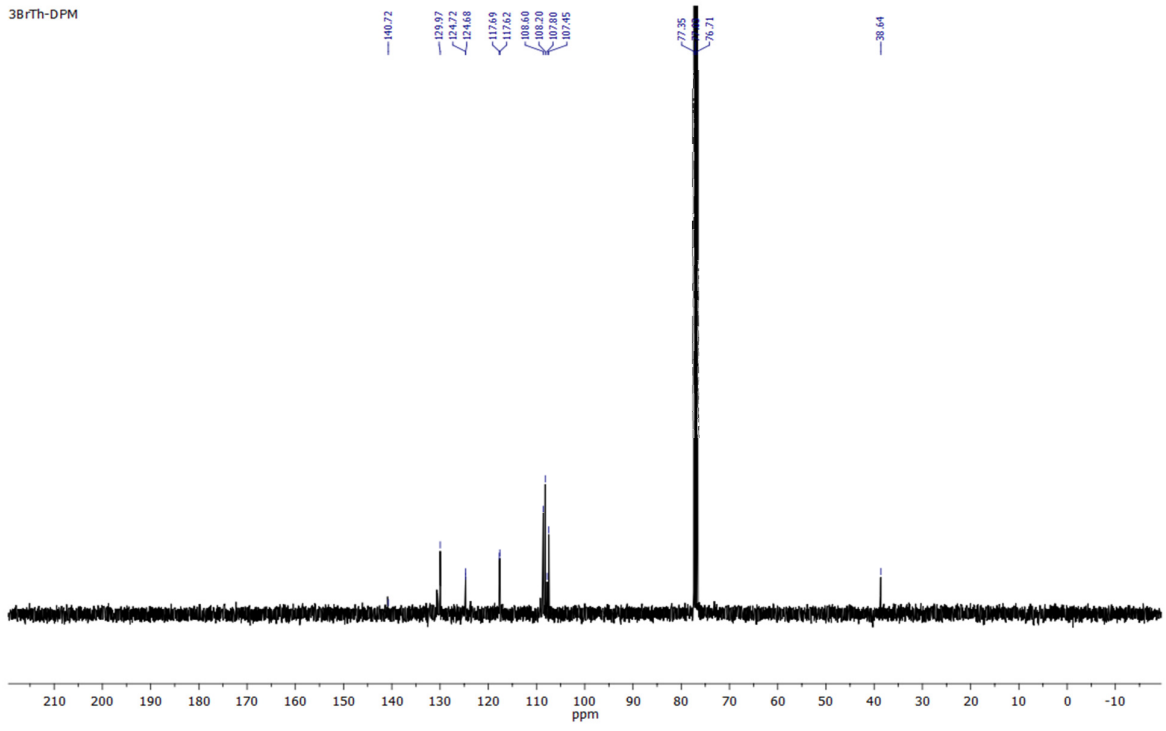
^{13}C NMR of 5(5-bromo-2-thienyl)dipyrromethane (6)



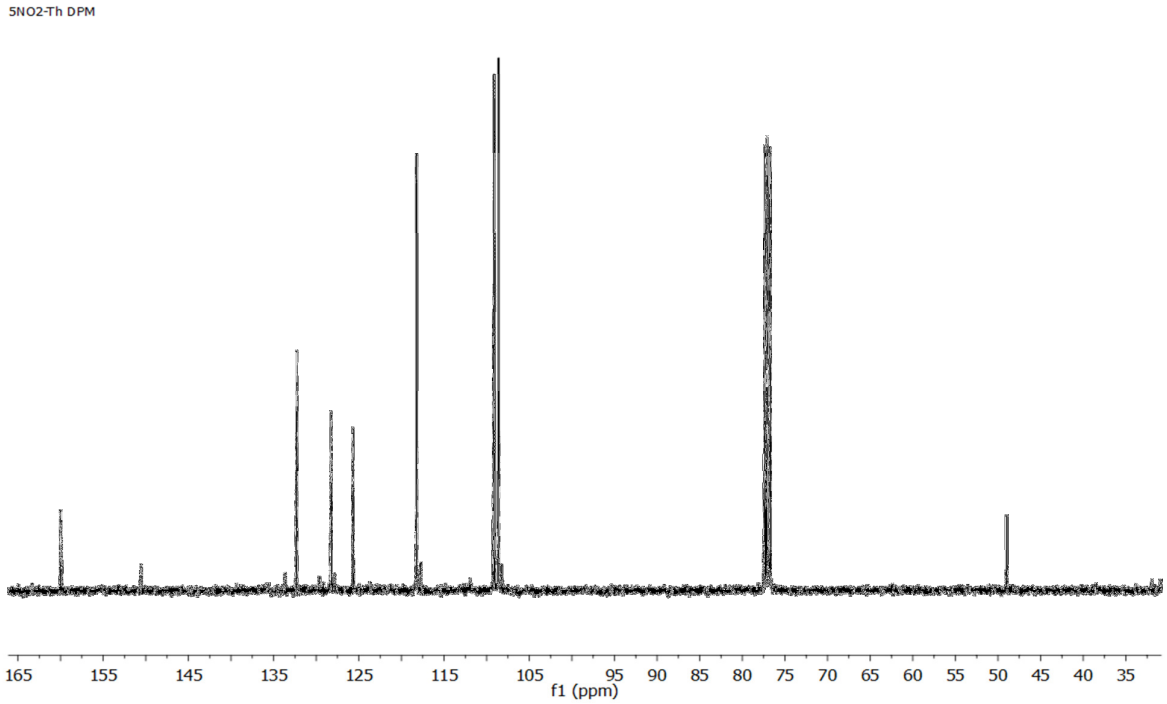
^{13}C NMR of 5(4-bromo-2-thienyl)dipyrromethane (7)



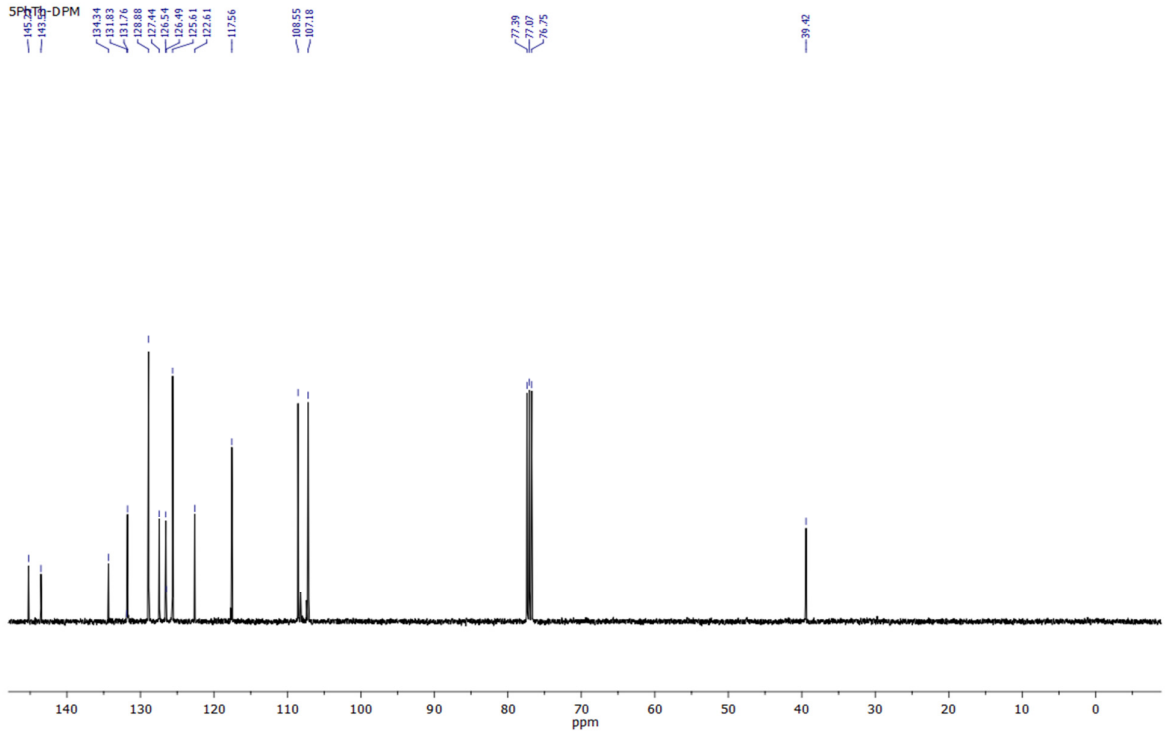
^{13}C NMR of 5(3-bromo-2-thienyl)dipyrromethane (8)



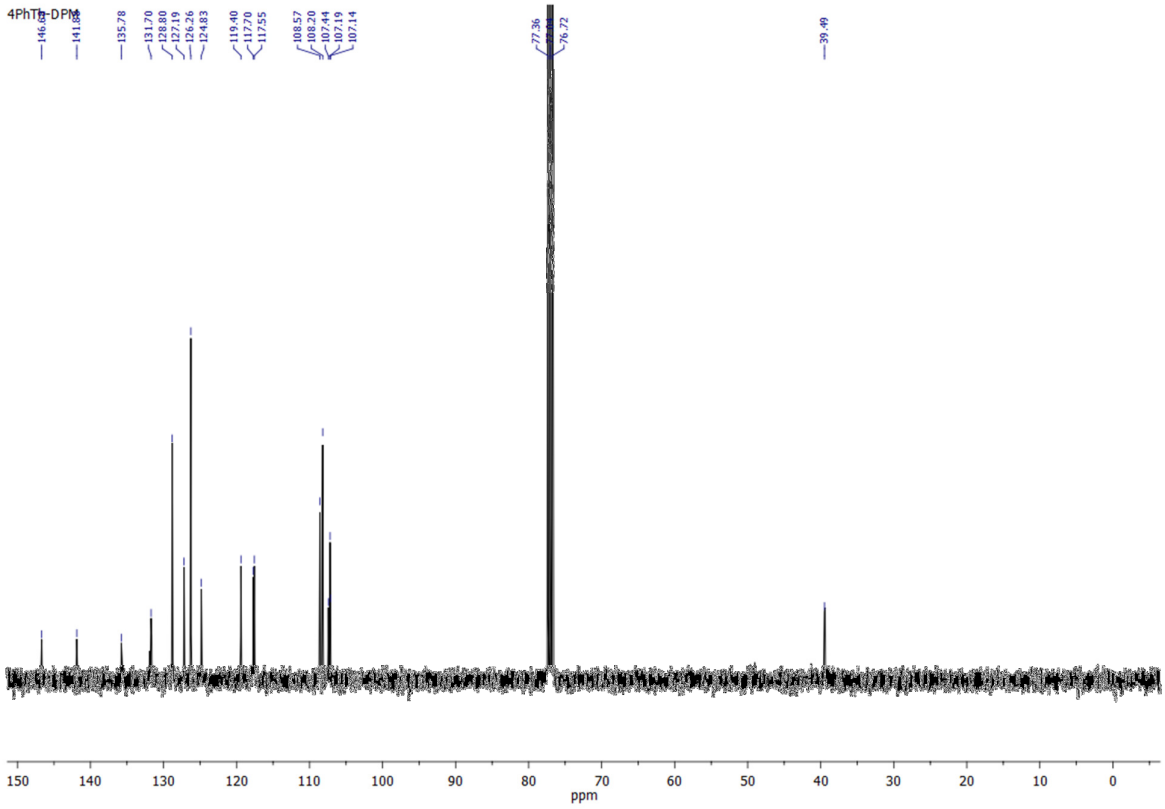
^{13}C NMR of 5(5-nitro-2-thienyl)dipyrromethane (9)



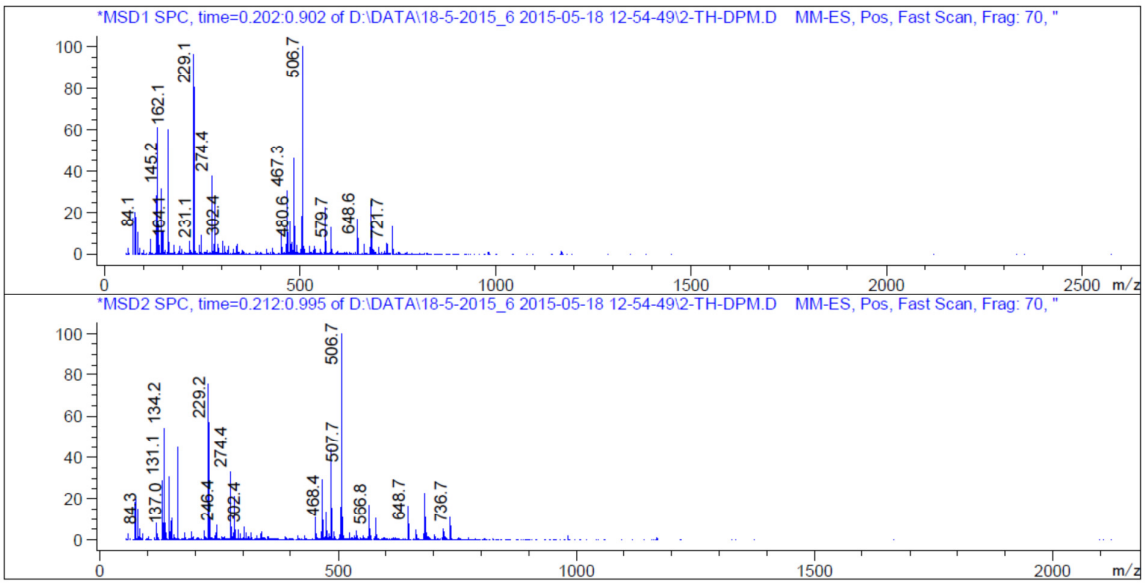
^{13}C NMR of 5(5-Phenyl-2-thienyl)dipyrromethane (10)



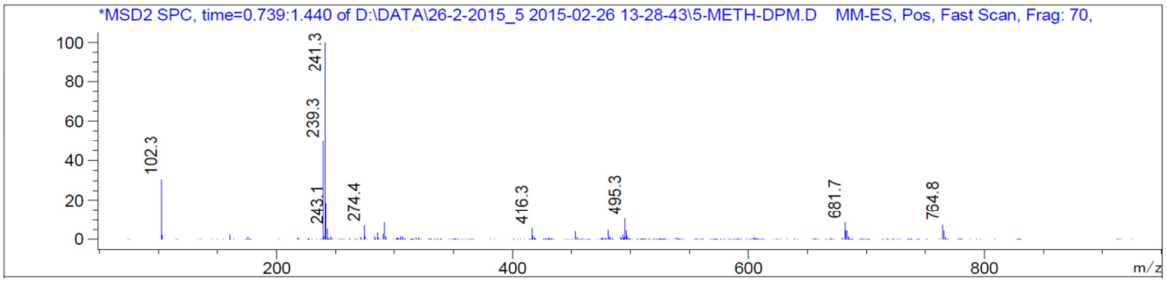
^{13}C NMR of 5(4-Phenyl-2-thienyl)dipyrromethane (11)



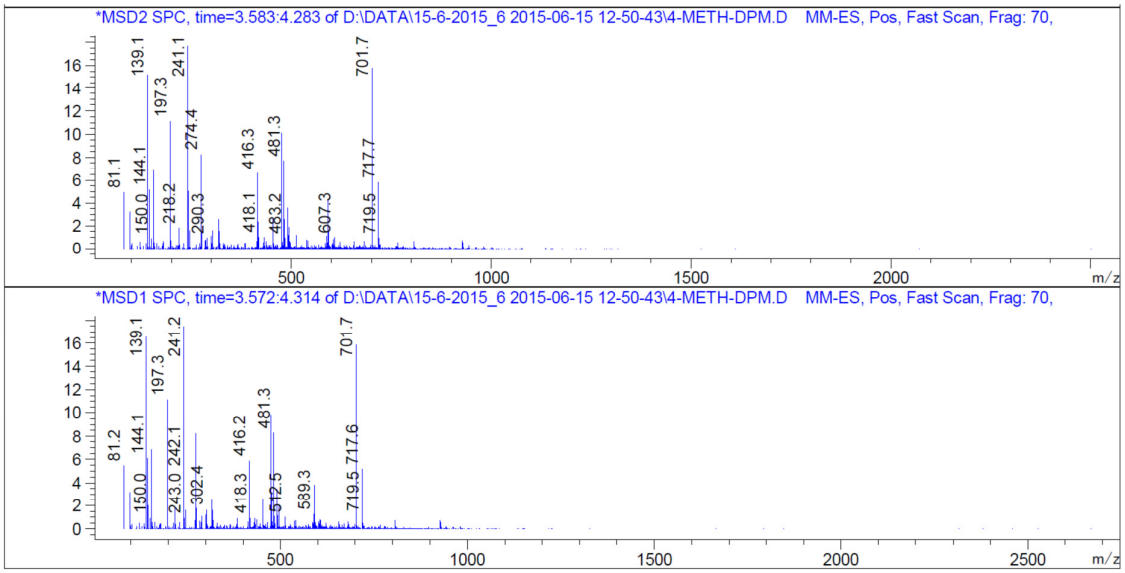
ESI-MS of 5(2-thienyl)dipyrromethane (1)



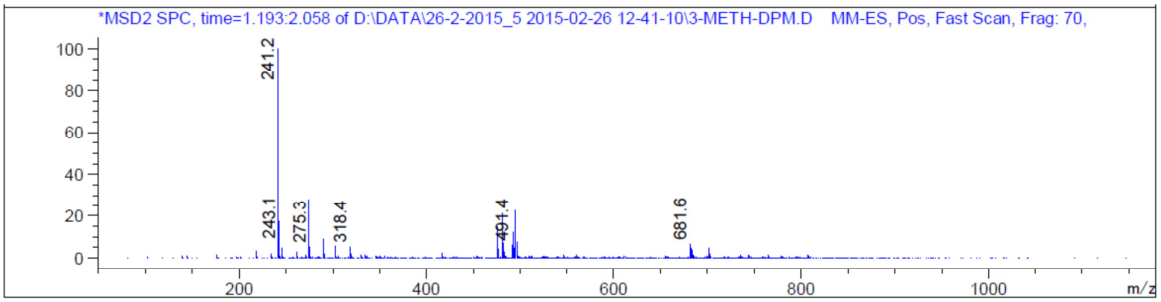
ESI-MS of 5(5-methyl-2-thienyl)dipyrromethane (2)



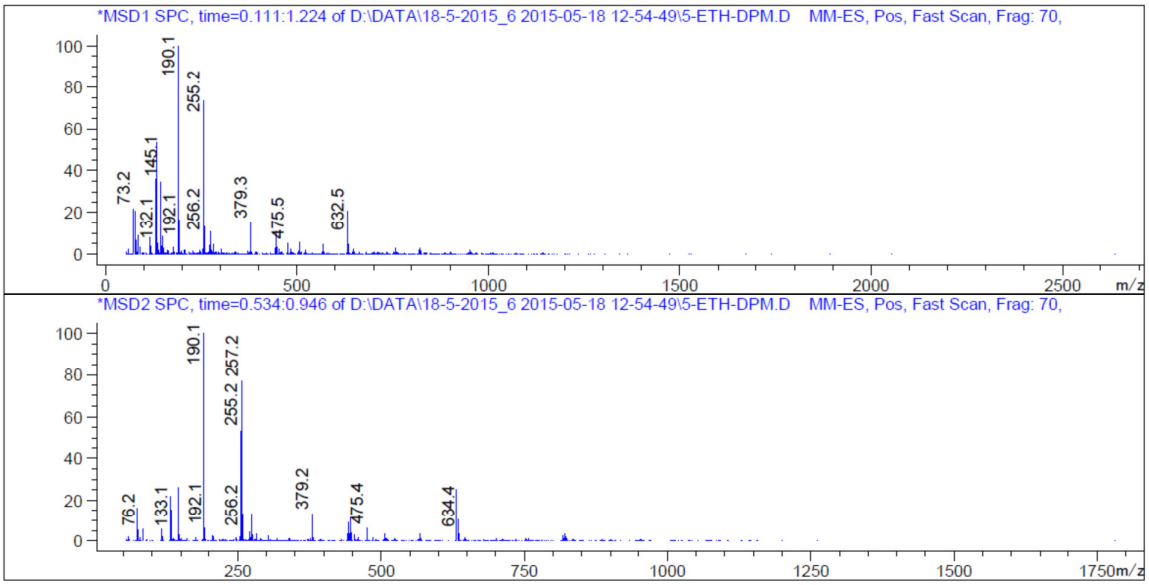
ESI-MS of 5(4-methyl-2-thienyl)dipyrromethane (3)



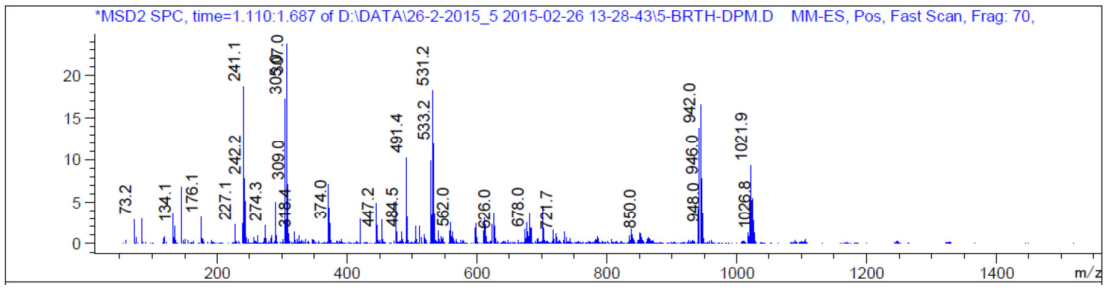
ESI-MS of 5(3-methyl-2-thienyl)dipyrromethane (4)



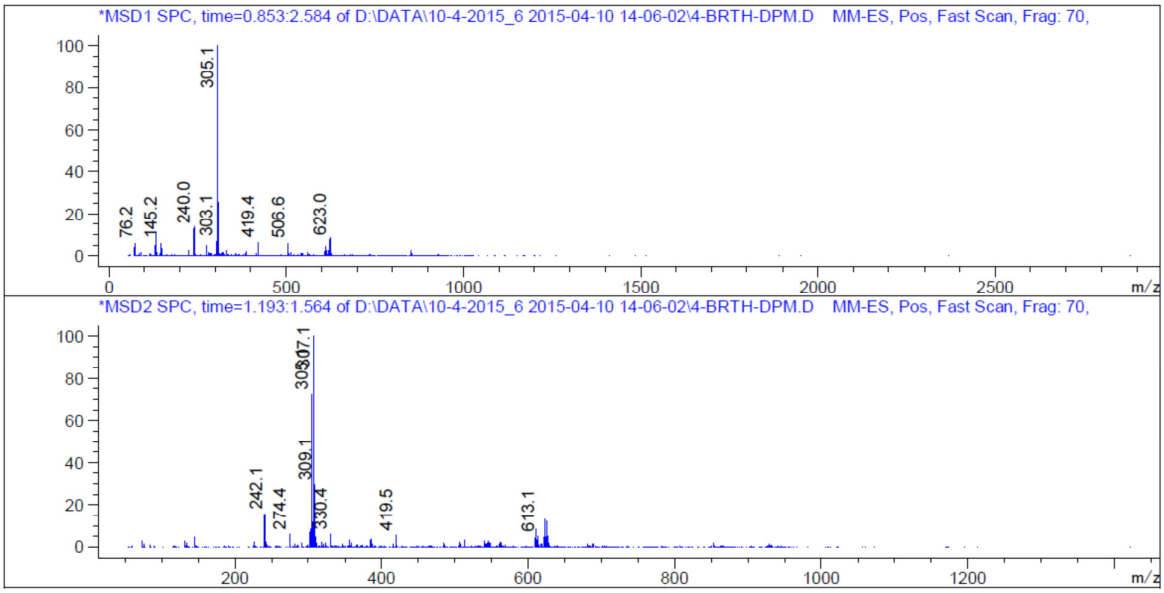
ESI-MS of 5(5-ethyl-2-thienyl)dipyrromethane (5)



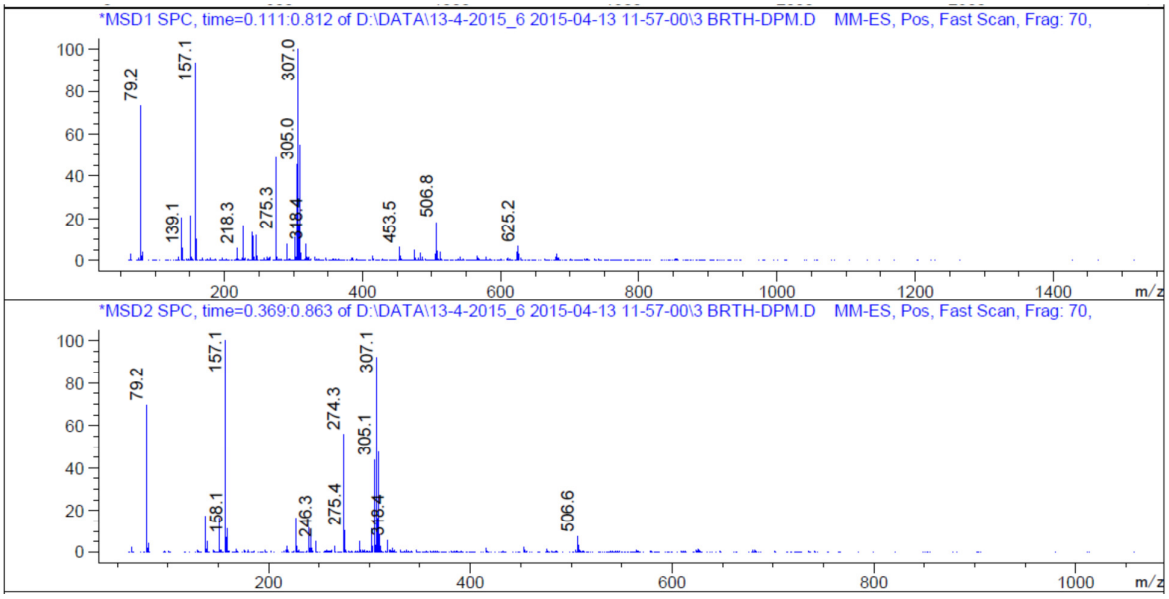
ESI-MS of 5(5-bromo-2-thienyl)dipyrromethane (6)



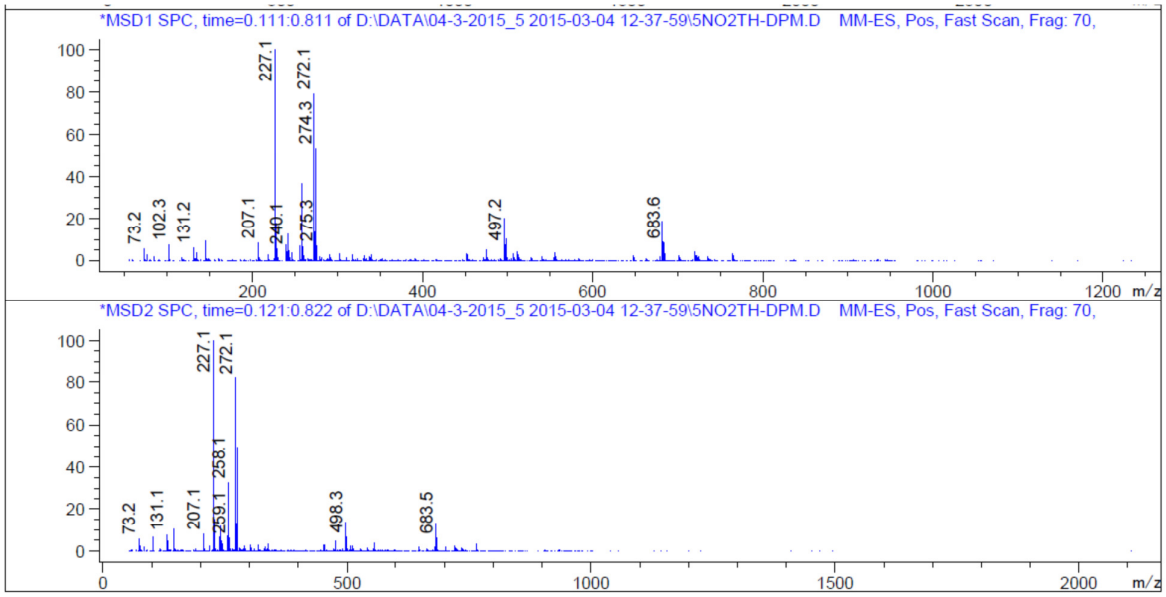
ESI-MS of 5(4-bromo-2-thienyl)dipyrromethane (7)



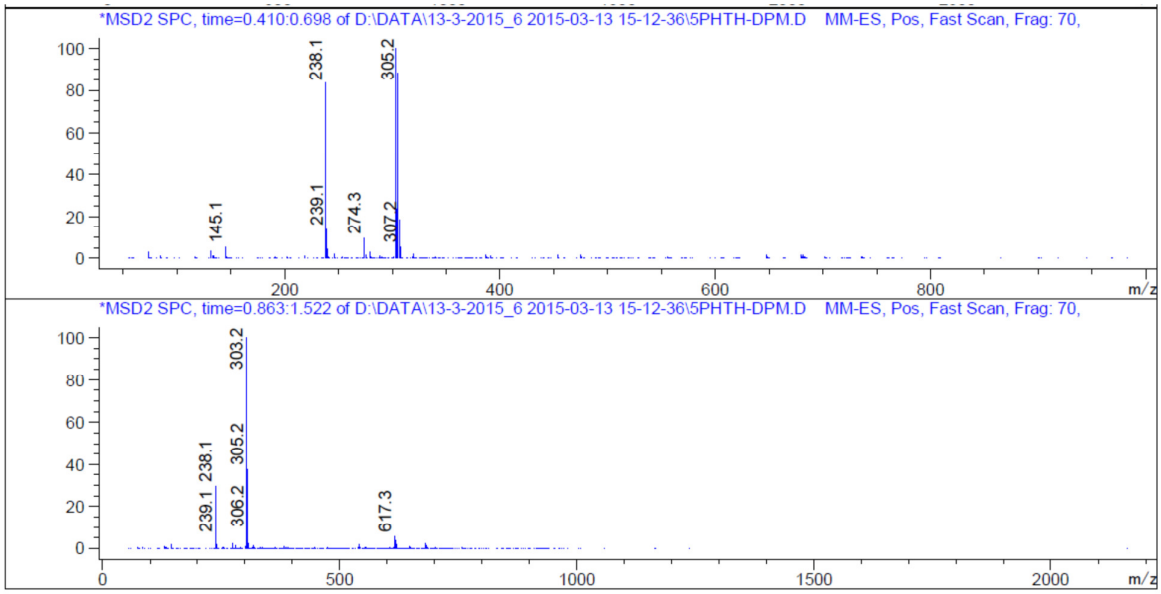
ESI-MS of 5(3-bromo-2-thienyl)dipyrromethane (8)



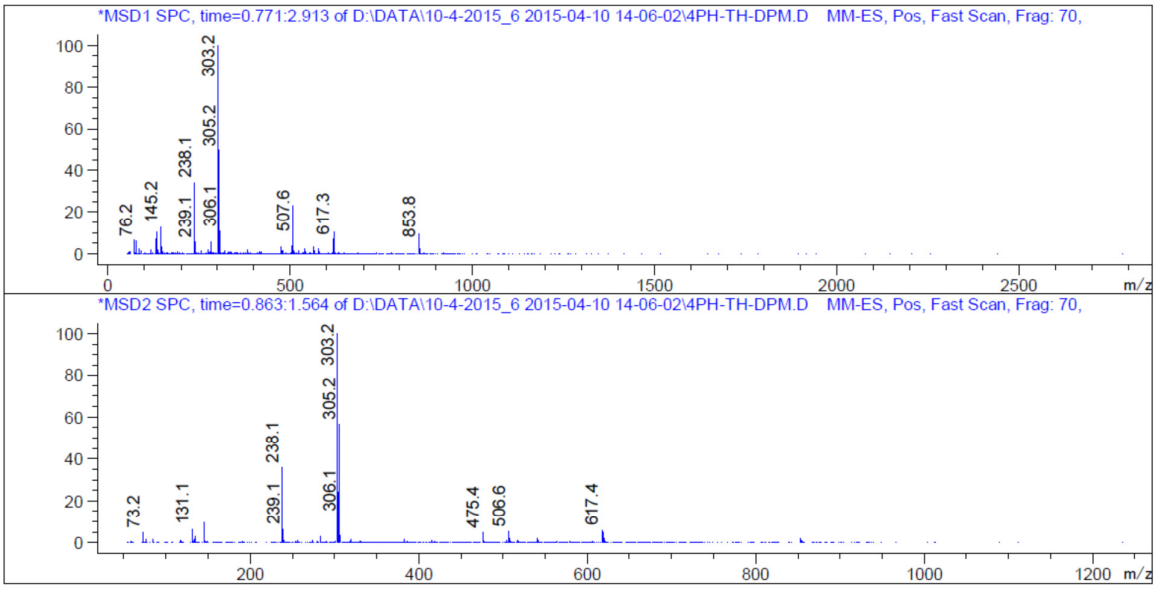
ESI-MS of 5(5-nitro-2-thienyl)dipyrromethane (9)



ESI-MS of 5(5-Phenyl-2-thienyl)dipyrromethane (10)



ESI-MS of 5(4-Phenyl-2-thienyl)dipyrromethane (11)



References

1. A. R. Kennedy, K. G. Brown, D. Graham, J. B. Kirkhouse, M. Kittner, C. Major, C. J. McHugh, P. Murdoch, W. E. Smith, *New J. Chem*. 2005, **26**, 826.
2. S. Parshamoni, S. Sanda, H. S. Jena and S. Konar, *Chem. Asian J*., 2015, **10**, 653.
3. Y. Rachuri, K. K. Bisht and E. Suresh, *Cryst. Growth Des.* 2014, **14**, 3300; (b) http://www.meduniv.lviv.ua/files/kafedry/tokshim/English/Analytical/Manuals_Analytchem/Iodomet ry.pdf (c) Vogel's TEXTBOOK OF QUANTITATIVE CHEMICAL ANALYSIS, Fifth edition, John Wiley & Sons, Inc., New York.