SUPPORTING INFORMATION to the paper

"Non-classical Heteroacenes: Synthesis and Properties of Anthra[2,3-c;6,7-c']dithiophene Derivatives"

*by Brandon Djukic and Dmitrii F. Perepichka**

Diagrams of molecules discussed in the text

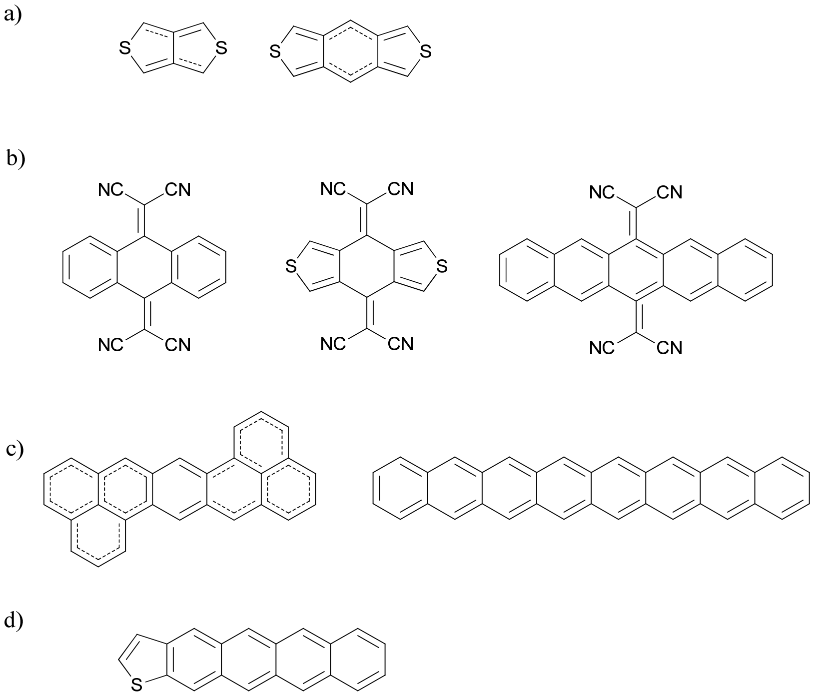


Fig. 1 Related molecules a) non-classical thiophenes: thieno[3,4-c]thiophene (left), benzo[1,2-c,4,5-c]dithiohene (right); b) TCAQ [tetracyanoanthraquinodimethane] (left), tetracyano-benzo[1,2-c, 4,5-c]dithio-phene (centre),TCPQ [tetracyanopentaquinodimethane] (right); c) large acenes: heptazethrene (left), octacene (right); d) tetraceno[2,3-b]thiophenes

Experimental

Materials and Methods

Thiophene-3,4-dicarbaldehyde was prepared from thiophene following established literature procedures.[1] The reagents 1,4-cyclohexanedione, $TiCl_4$ (1.0 M in DCM), malononitrile and *n*-hexyllithium (2.3 M solution in hexane) were obtained commercially from Sigma-Aldrich and used as received. All solvents were of at least reagent grade and dried if necessary. FTIR spectra were collected using a Thermo Scientific Nicolet 6700 FT-IR spectrometer.^{1}H NMR and ^{13}C NMR spectra were run on either Varian Mercury 300, 400, 500 MHz NMR spectrometers. APCI and EI Mass spectra were run on Finnigan LCQ/DUO and Kratos 7525 RFA mass spectrometers respectively. UV-Vis-NIR spectra were measured with a JASCO V-670 or Varian Cary 5000 spectrophotometer using either quartz cuvettes or a BASi spectroelectrochemical cell.

X-ray Measurements

X-ray crystallographic data were collected on a yellow plate of **4** at 100 K, which was mounted on a loop fiber. Data were collected using a Bruker SMART diffractometer equipped with an APEX II CCD detector, a graphite monochromator and Cu Kα (λ = 1.54178 Å) radiation source. The crystal-to-detector distance was 5.0 cm, and the data collection was carried out in 512 x 512 pixel mode. The data were scanned using Bruker's SMART program and integrated using Bruker's SAINT software. The initial unit cell parameters were determined by a least-squares fit of the angular setting of strong reflections, collected by a 10.0 degree scan in 33 frames over four different parts of the reciprocal space (132 frames total). The structure was solved by direct methods using SHELXS-97 and refined by a least-squares methods using SHELXL-97 incorporated in the SHELXTL suite of programs.[2]

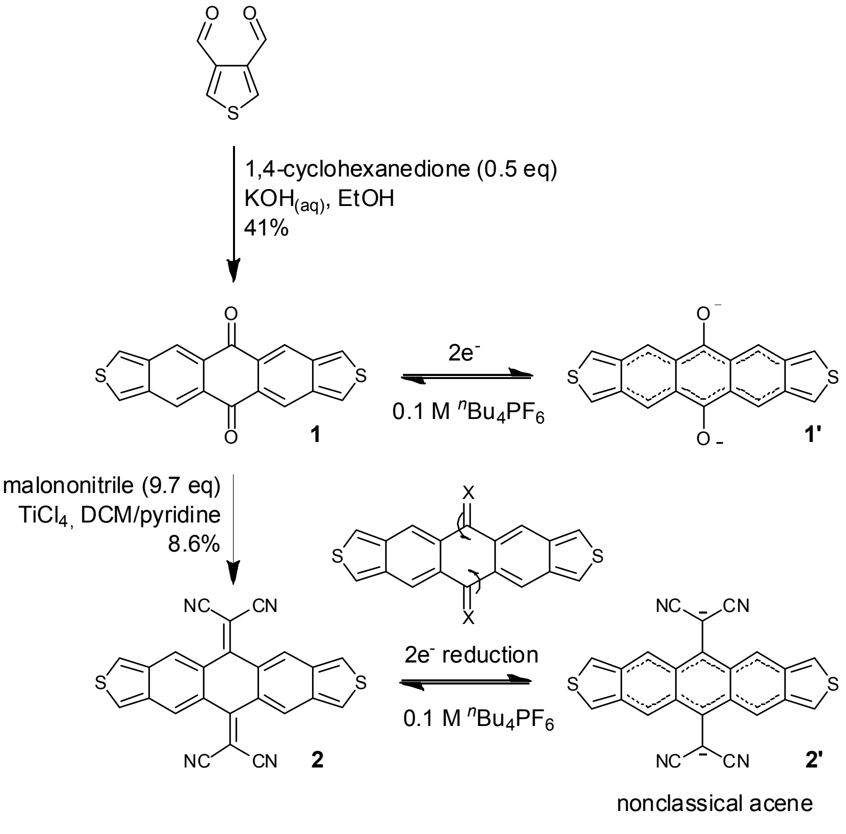
Electrochemical Measurements

All electrochemical measurements were performed at room temperature with a CHI-760C or BASi Epsilon electrochemical workstation. Saturated solutions of the analyte in anhydrous solvent (DCM: **4**, DMA: **5** and MeCN: spectroelectrochemistry) containing 0.1 M supporting electrolyte (Bu_4NPF_6) were prepared and deareated by sparging with N_2 gas for 15 min. A typical three-electrode setup was used including a platinum working electrode, Ag/AgCl reference electrode(or Ag wire), and a platinum wire auxiliary electrode. Potentials quoted are versus the Ag/AgCl reference electrode and ferrocene was used in all cases as an internal standard (Fc vs. Ag/AgCl = 0.56 V in DMA, Fc vs Ag = 0.40 V in DCM).

DFT Calculations

GAUSSIAN 03W was used for Density Functional Theory Calculations (DFT) calculations on molecules with density functional theory at the B3LYP/6-31G(d,p) level of theory. GAUSSIAN 09W was used for DFT calculations on molecules with density functional theory at the M062X/6-311G(d,p) level and for TD-DFT calculations at the B3LYP/6-311G(d,p) level.[3]

Synthesis and characterization



Scheme 1: Synthesis and electrochemical reduction of **4** and **5**

4: Thiophene-3,4-dicarbaldehyde (4.62 g, 0.0330 mol) and 1,4-cyclohexanedione (1.85 g, 0.0165 mol) were dissolved in EtOH (60 mL). An aqueous solution of 30% KOH (9 mL) was added and the mixture was stirred overnight. The resulting precipitate was filtered, washed with water, EtOH, and hot chloroform to afford a yellow powder (2.13 g, 41%). IR (neat): 3090 (m), 1663 (s), 1566 (s), 1500 (w), 1454 (s), 1384 (m), 1342 (w), 1264 (s), 1163 (m), 980 (w), 919 (w), 761 (m), 507 (w), 488 (w) cm^{-1}. ^1H-NMR (400 MHz, DMSO-d6): 8.76 (s, 4H), 8.64 (s, 4H) ppm. ^{13}C-NMR: insolubility precluded analysis. APCI-MS (*m/z*): 321.1 ($[M + H]^+$, 100%). APCI-HRMS (*m/z*) for $C_{18}H_9O_2S_2$ $[M + H]^+$: calculated 321.00385, found 321.00449. mp: >240°C (decomposition). Crystals suitable for X-ray crystallographic analysis were obtained by slow evaporation of a saturated solution of **3** in dichloroethane. Structure determination is based on data obtained from a twinned crystal.[4]

5: Anthra[2,3-c:6,7-c']dithiophene-5,11-dione **4** (879 mg, 2.74 mmol) and malononitrile (1.76 g, 26.6 mmol) were added to a three neck round bottom flask, containing a magnetic stirring bar and fitted with a septum, that was flushed with nitrogen gas for 10 minutes. Anhydrous pyridine (13 mL) was added and the mixture was sparged, while stirring, for an additional 30 minutes. The flask was covered with aluminum foil and then a 1.0 M solution of $TiCl_4$ (8.6 mL) in anhydrous DCM was added through the septum via syringe and then refluxed, while stirring, for 15 hours. The crude material was combined with chloroform (250 mL) and filtered. The filtrate was washed with water (to remove the pyridine) containing 5% hydrochloric acid and then dried with $MgSO_4$. A Soxhlet extraction of the crude solid followed, using the chloroform filtrate as the extraction solvent. After the extraction, the chloroform solution was precipitated with hexanes (750 mL), filtered and the precipitate was washed with hexanes (25 mL) affording a vibrant orange solid (98.3 mg, 8.6 %). FT-IR (neat): 3100.3 (m), 2221.5 (s), 1558.8 (m), 1538.8 (s), 1496.7 (m), 1459.7 (s), 1393.9 (s), 1289.5 (s), 1170.4 (s), 953.7 (w), 908.4 (w), 869.2 (w), 848.6 (w), 790.4 (m), 764.2 (s), 695.7 (w), 569.7 (w), 518.5 (w) cm^{-1}. ^{1}H-NMR (300 MHz, DMSO-d6): δ 8.60 (s, 4H), 8.57 (s, 4H) ppm. ^{13}C-NMR (125 MHz, DMSO-d6) δ 164.11, 135.88, 125.33, 125.08, 123.85, 115.12, 80.34 ppm. EI-MS (*m/z*): 416 ([M]$^+$, 100%). APCI-HRMS (*m/z*) for $C_{24}H_9N_4S_2$ [M+H]$^+$: calculated 417.02686, found 417.2599. mp: >240°C.[5]

X-ray crystallographic analysis

Table 1: Bond lengths, angles and tortion angles of **4**

	Å		°		°
S(1)-C(1)	1.664(8)	C(1)-S(1)-C(9)#1	98.6(4)	C(9)#1-S(1)-C(1)-C(2) S(1)-	-0.1(5)
S(1)-C(9)#1	1.673(7)	C(2)-C(1)-S(1)	108.2(5)	C(1)-C(2)-C(3)	178.9(6)
O(1)-C(5)	1.216(9)	C(3)-C(2)-C(8)#1	118.8(6)	S(1)-C(1)-C(2)-C(8)#1	0.5(7)
C(1)-C(2)	1.452(10)	C(3)-C(2)-C(1)	129.0(7)	C(8)#1-C(2)-C(3)-C(4)	-2.2(10)
C(2)-C(3)	1.419(10)	c(8)#1-C(2)-C(1)	112.2(6)	C(1)-C(2)-C(3)-C(4)	179.5(7)
C(2)-C(8)#1	1.447(10)	C(4)-C(3)-C(2)	119.4(7)	C(2)-C(3)-C(4)-C(6)#1	0.9(11)
C(3)-C(4)	1.358(9)	C(3)-C(4)-C(6)#1	122.2(7)	C(2)-C(3)-C(4)-C(5)	179.7(6)
C(4)-C(6)#1	1.432(10)	C(3)-C(4)-C(5)	117.1(7)	C(3)-C(4)-C(5)-O(1)	-2.1(11)
C(4)-C(5)	1.499(10)	C(6)#1-C(4)-C(5)	120.7(6)	C(6)#1-C(4)-C(5)-O(1)	176.6(6)
C(5)-C(6)	1.489(9)	O(1)-C(5)-C(6)	122.0(6)	C(3)-C(4)-C(5)-C(6)	178.4(6)
C(6)-C(7)	1.367(11)	O(1)-C(5)-C(4)	121.2(7)	C(6)#1-C(4)-C(5)-C(6)	-2.8(10)
C(6)-C(4)#1	1.432(10)	C(6)-C(5)-C(4)	116.8(6)	O(1)-C(5)-C(6)-C(7)	1.7(10)
C(7)-C(8)	1.414(10)	C(7)-C(6)-C(4)#1	119.9(7)	C(4)-C(5)-C(6)-C(7) O(1)-	-178.9(7)
C(8)-C(9)	1.429(10)	C(7)-C(6)-C(5)	117.7(7)	C(5)-C(6)-C(4)#1 C(4)-	-176.6(7)
C(8)-C(2)#1	1.447(10)	C(4)#1-C(6)-C(5)	122.4(6)	C(5)-C(6)-C(4)#1 C(4)#1-	2.9(11)
C(9)-S(1)#1	1.673(7)	C(6)-C(7)-C(8)	119.7(7)	C(6)-C(7)-C(8) C(5)-C(6)-	-0.6(11)
		C(7)-C(8)-C(9)	128.0(7)	C(7)-C(8) C(6)-C(7)-C(8)-	-178.9(6)
		C(7)-C(8)-C(2)#1	120.0(7)	C(9) C(6)-C(7)-C(8)-	179.4(7)
		C(9)-C(8)-C(2)#1	111.9(6)	C(2)#1 C(7)-C(8)-C(9)-	1.9(11)
		C(8)-C(9)-S(1)#1	109.1(5)	S(1)#1 C(2)#1-C(8)-C(9)-	-178.5(6)
				S(1)#1	-0.8(7)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z

DFT Calculations

DFT Optimized Structures

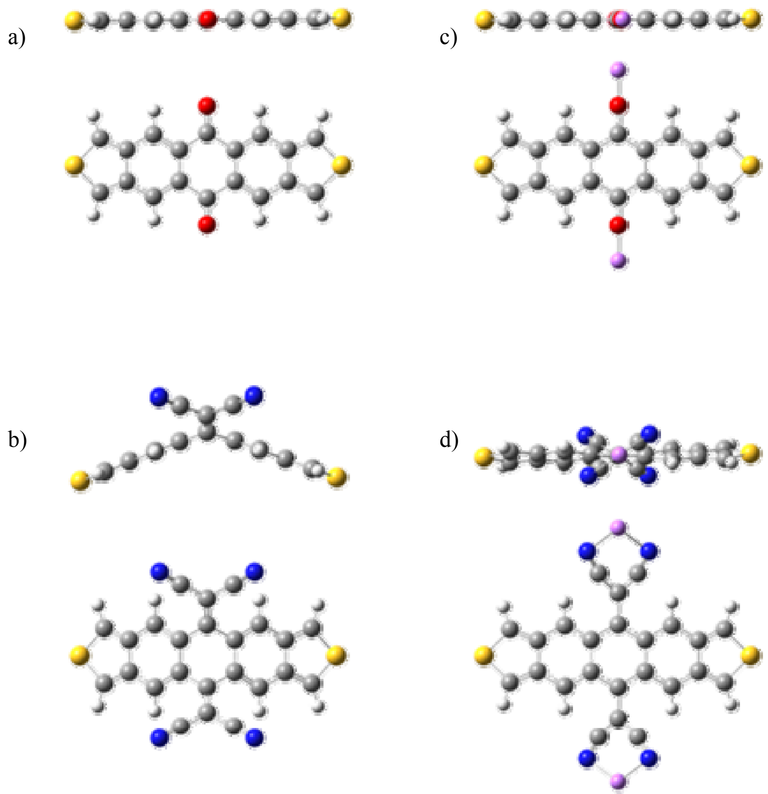


Fig. 2: Top and side view of the optimized molecular structure for a) **4** b) **5** c) **4’** d) **5’**

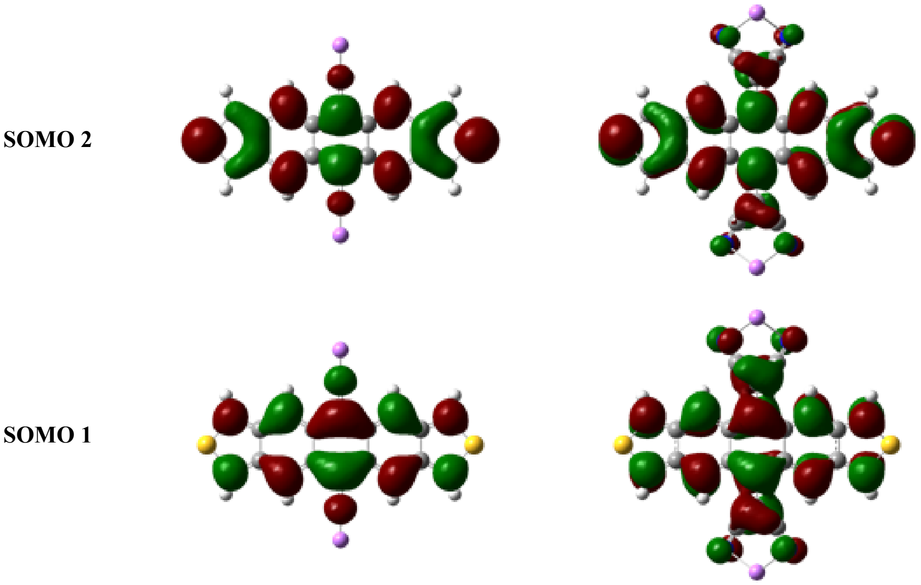


Fig. 3: SOMO diagrams of **4’** (left) and **5’** (right)

Table 2: Closed shell, and triplet energy comparison for optimized molecular structures (all values are in eV)

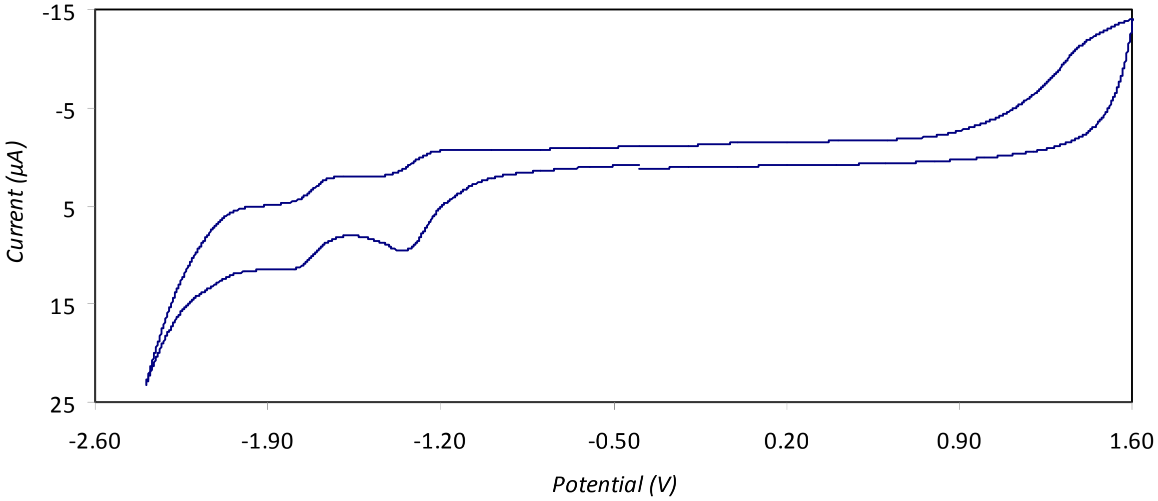
Compound		UB3LYP TRIPLET	UB3LYP SINGLET	B3LYP SINGLET	M062X TRIPLET	M062X SINGLET
4'	Total Energy	-44971.465	-44971.152	-44971.152	-44960.105	-44959.741
	$\Delta E_{T\text{-}S}$		-0.313	-0.313		-0.364
	Spin cont.	2.029	0.000			
5’	Total Energy	-53056.145	-53056.026	-53056.025	-53042.213	-53042.148
	$\Delta E_{T\text{-}S}$		-0.119	-0.120		-0.065
	Spin cont.	2.037	0.000			
2	Total Energy	-40497.883	-	-40497.854		
	$\Delta E_{T\text{-}S}$			-0.029		

Table 3: UB3LYP 6-31G(d,p) calculated energy gaps (all values are in eV)

Compound	SINGLET		TRIPLET	
4'	LUMO	-1.639	LUMO (α)	-1.608
	HOMO	-2.496	SOMO 2 (β)	-1.619
			SOMO 1 (α)	-2.788
			HOMO (β)	-4.223
	$\Delta E_{L\text{-}H}$	0.857	$\Delta E_{L\text{-}S1}$	1.180
			$\Delta E_{S2\text{-}H}$	2.609
5'	LUMO	-2.684	LUMO(α)	-1.767
	HOMO	-3.849	SOMO 2 (β)	-2.537
			SOMO 1 (α)	-3.824
			HOMO (β)	-4.985
	$\Delta E_{L\text{-}H}$	1.166	$\Delta E_{L\text{-}S2}$	2.057
			$\Delta E_{S1\text{-}H}$	2.467

Supplementary Figures

Electrochemistry



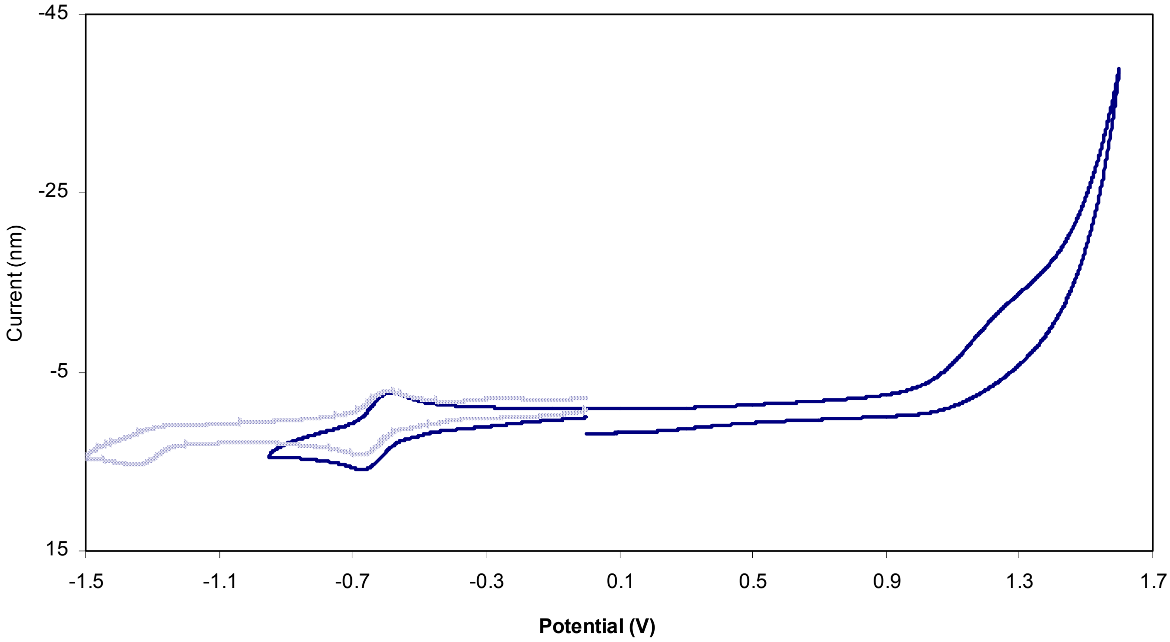


Fig. 4: Cyclic voltammograms of **4** (top) and **5** (bottom). Potentials are vs. Ag/AgCl.

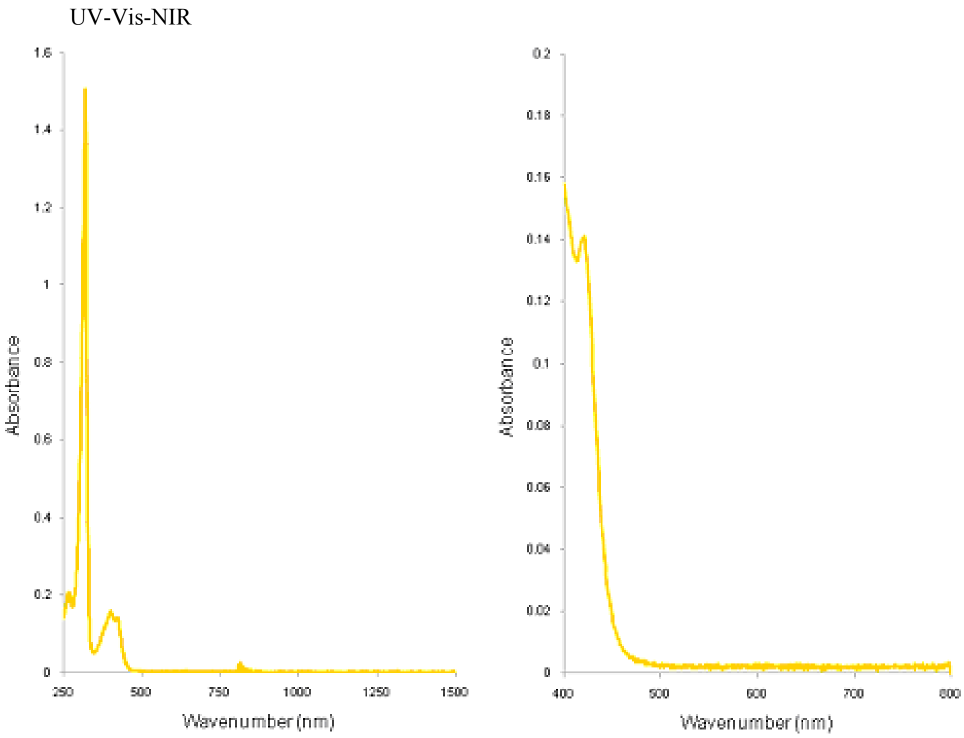


Fig. 05: UV-Vis-NIR (left) and visible region (right) of **4**

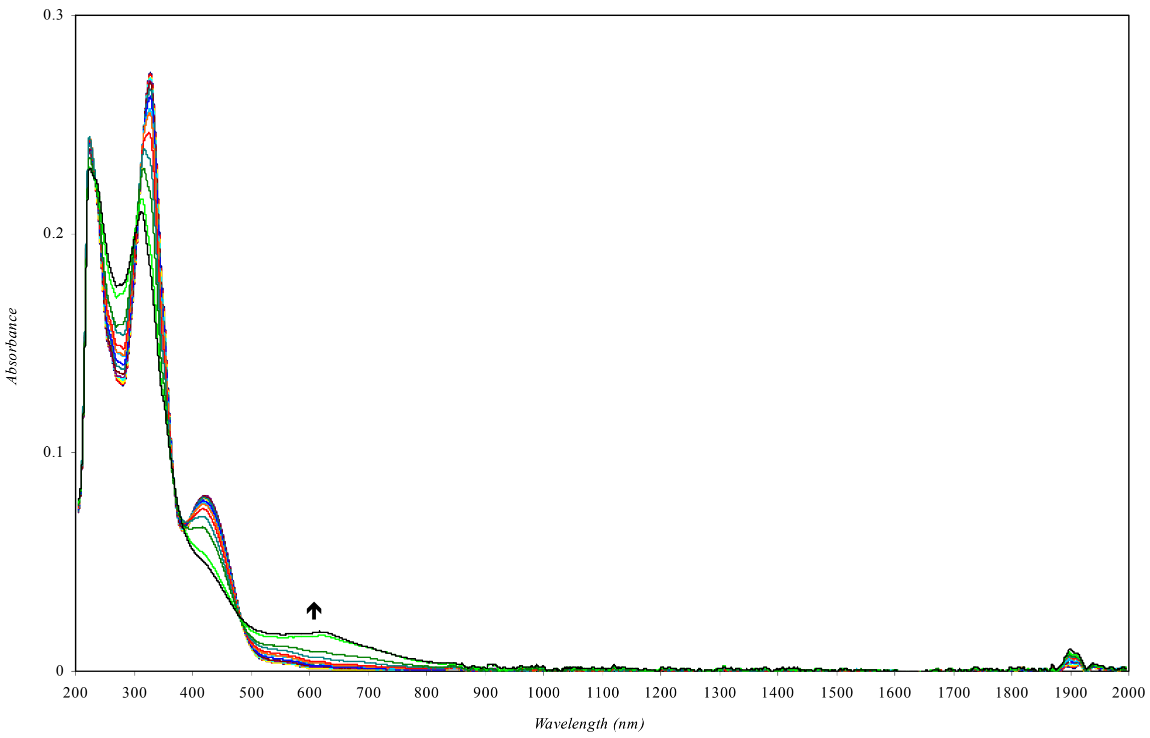
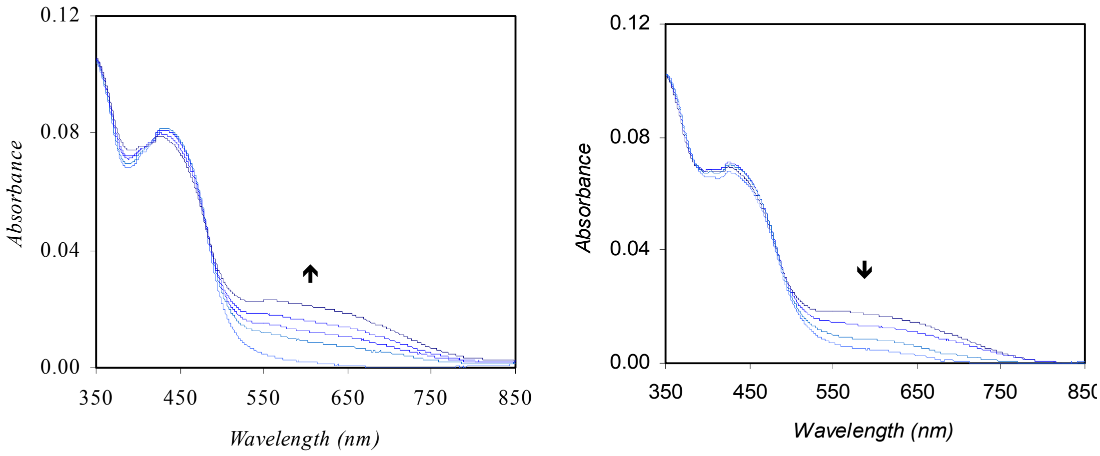


Fig. 6: UV-Vis-NIR spectroelectrochemistry of **5** between 200-2000 nm.



Reduction **Re-oxidation**

Fig. 7: Spectroelectrochemistry of **5** (reversibility)

Supplementary Spectra of 4

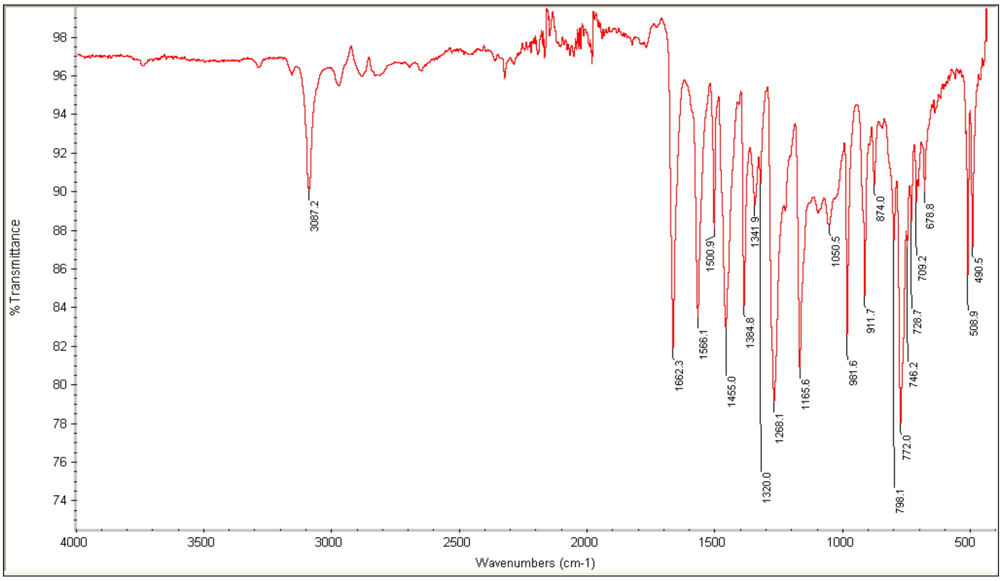


Fig. 8: FT-IR

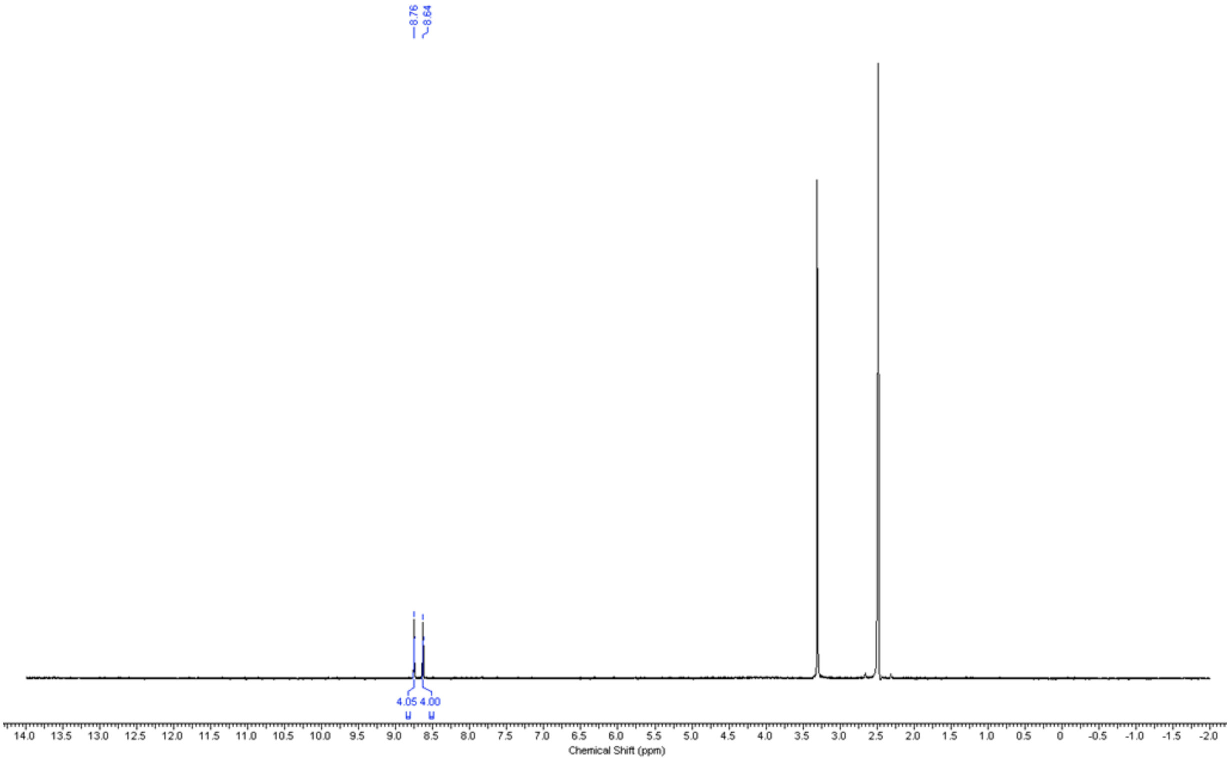


Fig. 9: ^{1}H-NMR (400 MHz, DMSO-d6)

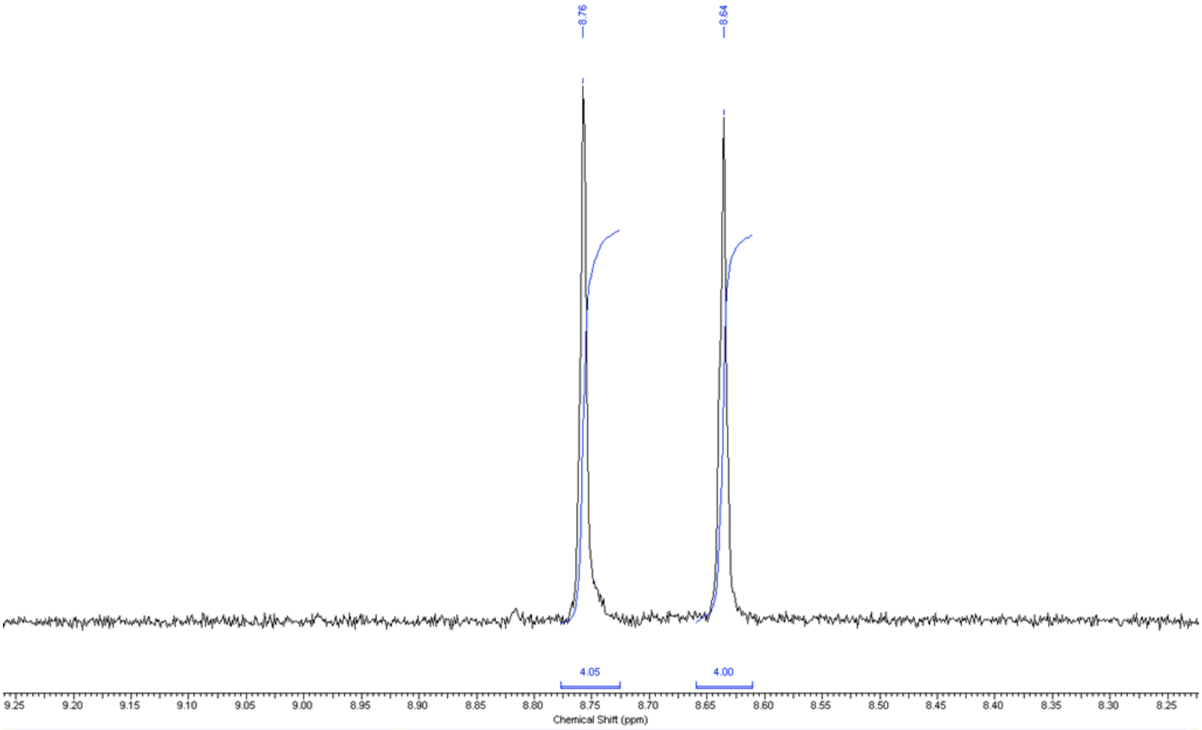


Fig. 10: ^{1}H-NMR (400 MHz, DMSO-d6) aromatic region

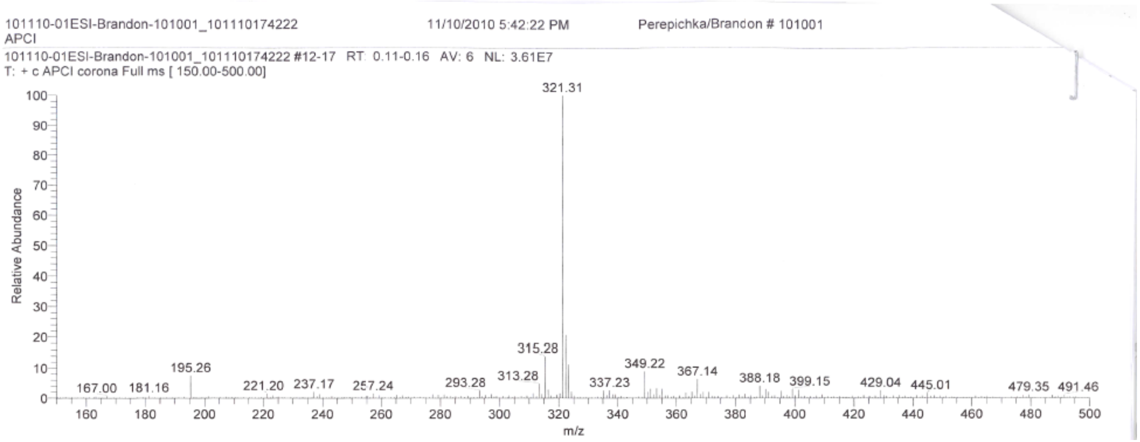


Fig. 11: APCI-MS

Supplementary Spectra of 5

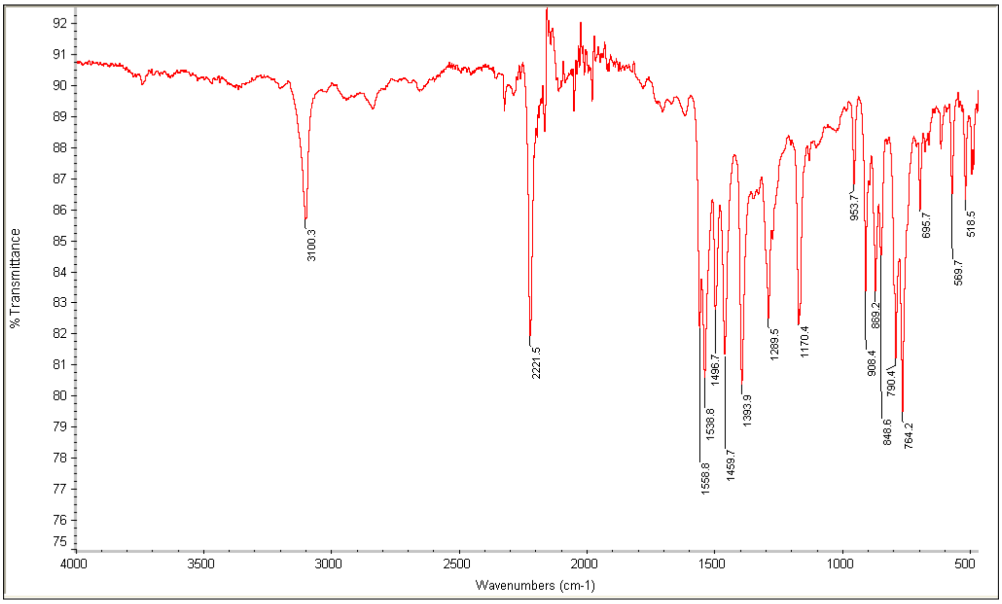


Fig. 12: FT-IR

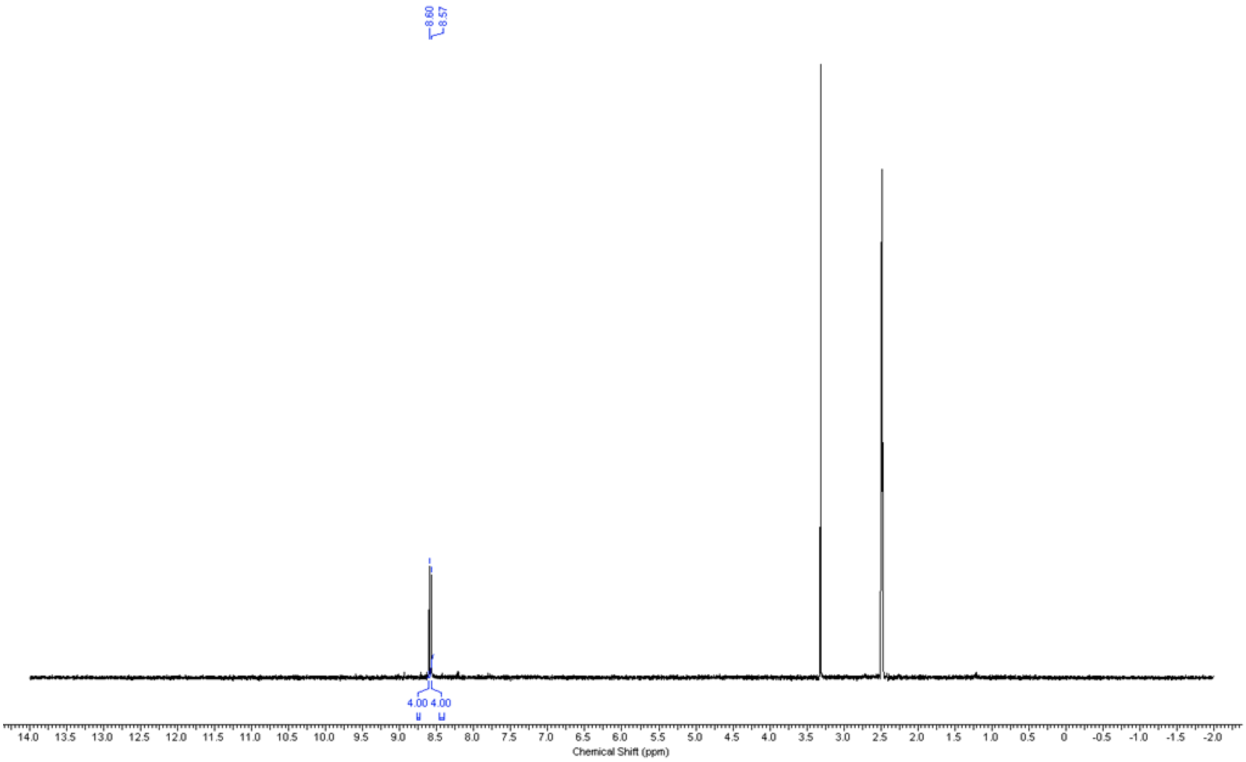


Fig. 13: ^{1}H-NMR (300 MHz, DMSO-d6)

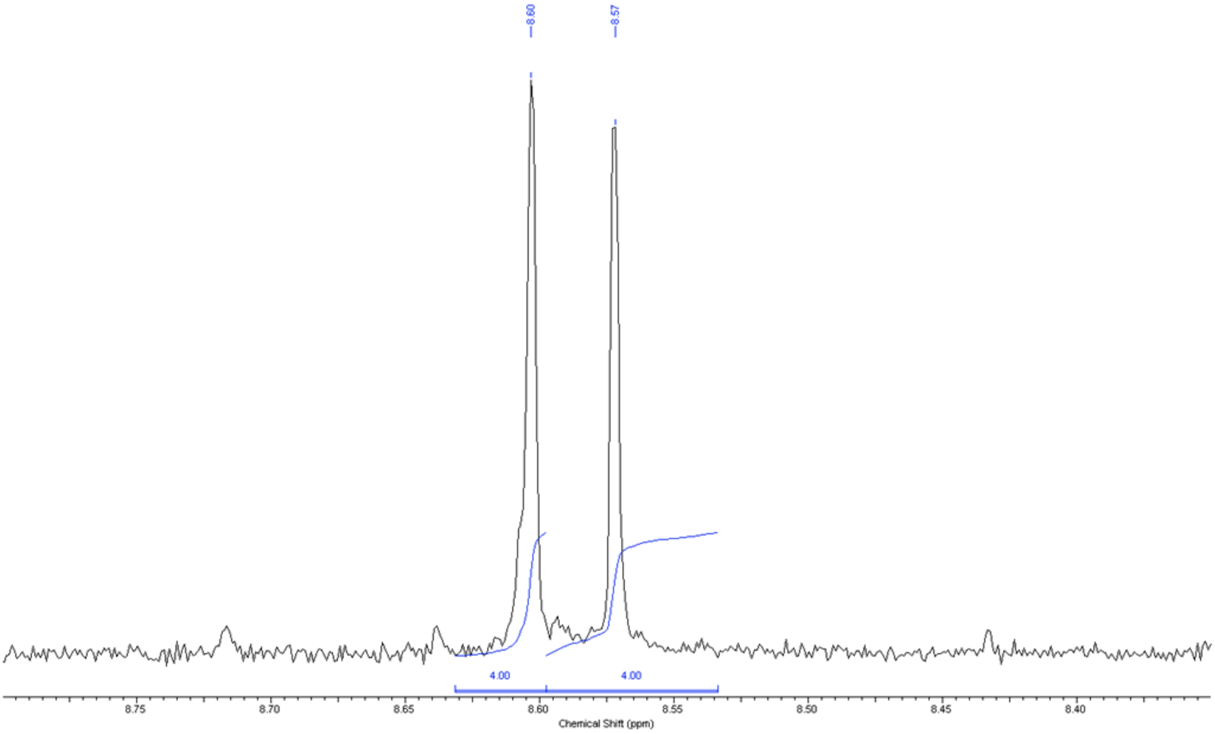


Fig. 14: ^{1}H-NMR (300 MHz, DMSO-d6) aromatic region

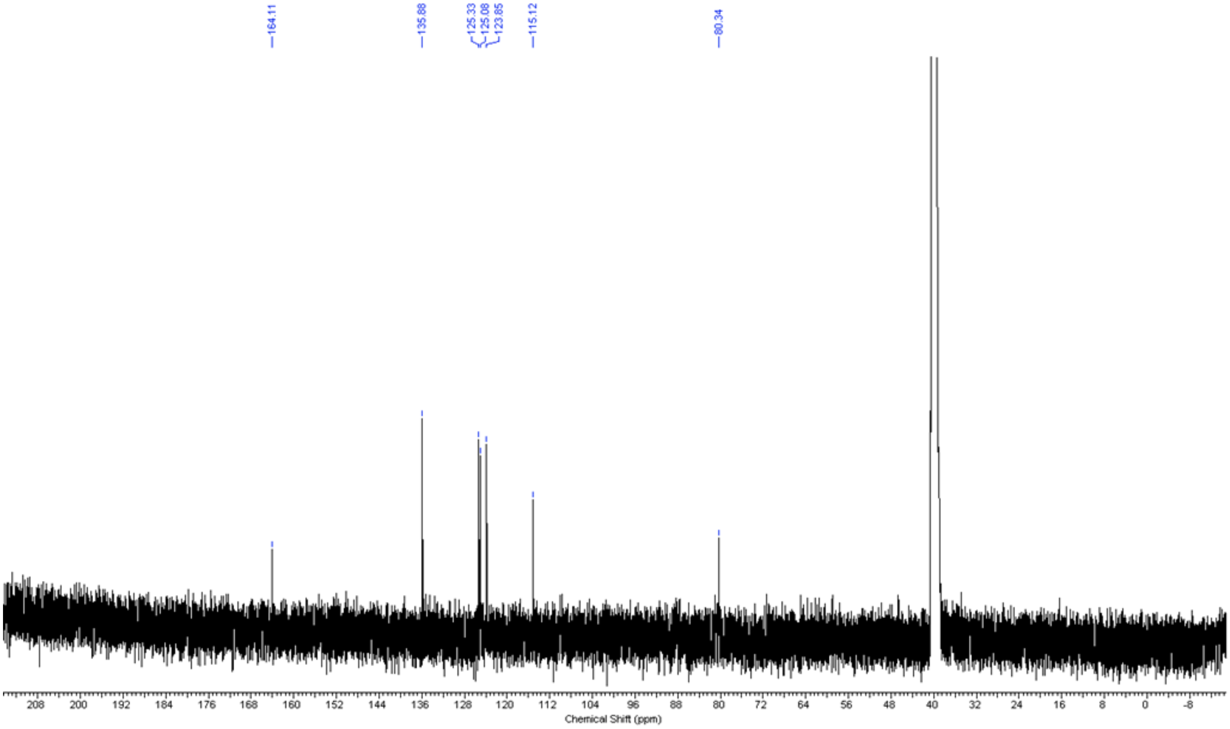


Fig. 15: ^{13}C-NMR (125 MHz, DMSO-d6)

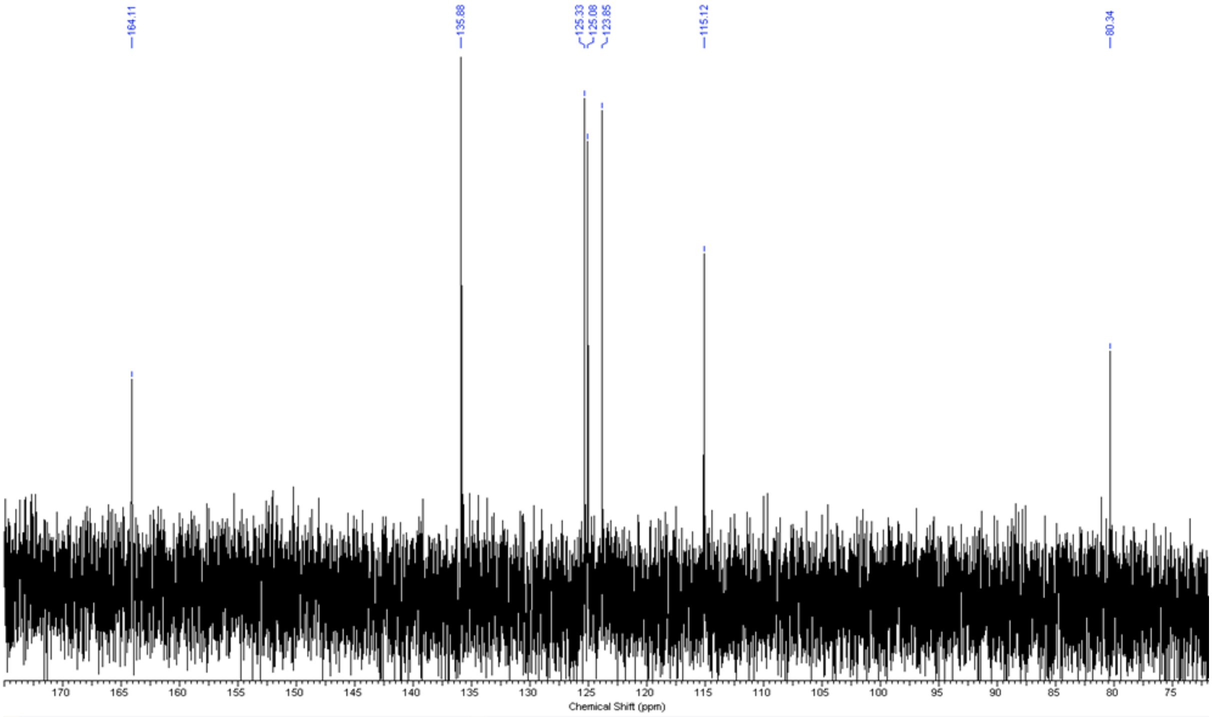
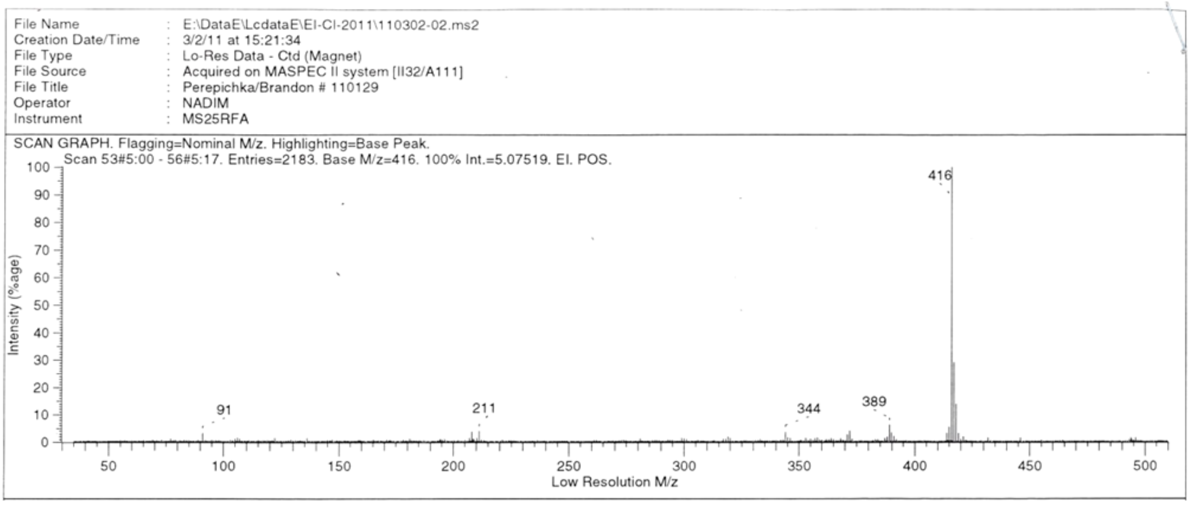


Fig. 16: ^{13}C-NMR (125 MHz, DMSO-d6) aromatic region



File Name : E:\DataE\LcdataE\EI-CI-2011\110302-02.ms2
Creation Date/Time : 3/2/11 at 15:21:34
File Type : Lo-Res Data - Ctd (Magnet)
File Source : Acquired on MASPEC II system [II32/A111]
File Title : Perepichka/Brandon # 110129
Operator : NADIM
Instrument : MS25RFA

SCAN GRAPH. Flagging=Nominal M/z. Highlighting=Base Peak.
Scan 53#5:00 - 56#5:17. Entries=2183. Base M/z=416. 100% Int.=5.07519. EI. POS.

Fig. 17: EI-MS

References

1 K. Araki, H. Endo, G. Masuda and T. Ogawa, *Chem. Eur. J.* 2004, **10**, 3331; B. Wex, B. R. Kaafarani, K. Kirschbaum and D. C. Neckers, *J. Org. Chem.* 2005, **70**, 4502.

2 SAINT (2006) Release 7.34A; Integration Software for Single Crystal Data. Bruker AXS Inc., Madison, WI 53719-1173; Sheldrick, G.M. (2008). SADABS, Bruker Area Detector Absorption Corrections. Bruker AXS Inc., Madison, WI 53719-1173; Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122; SHELXTL (2001) version 6.12; Bruker Analytical X-ray Systems Inc., Madison, WI 53719-1173; APEX2 (2009) ; Bruker Molecular Analysis Research Tool. Bruker AXS Inc., Madison, WI 53719-1173; Spek, A.L. (2008). PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands; Maris, T. (2004). UdMX, University of Montréal, Montréal, QC, Canada; XPREP (2008) Version 2008/2; X-ray data Preparation and Reciprocal space Exploration Program. Bruker AXS Inc., Madison, WI 53719-1173.M. M. Payne,

3 Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004; Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.S. A.

4 Odom, S. R. Parkin and J. E. Anthony *Org. Lett.*, 2004, **6**, 3325.

5 N. Martin, R. Behnisch and M. Hanack, *J. Org. Chem.* 1989, **54**, 2563.