Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

A convenient electro-catalyzed multicomponent synthesis of 4*H*-thiopyran derivatives

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Experimental

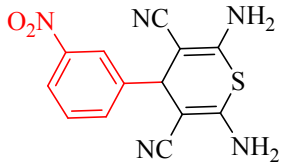
General Remarks

Reagents were obtained from commercial suppliers, all chemicals were reagent grade and purchased from Aldrich, Alfa Aesar, Merck, Spectrochem and Qualigens and were used without further purification. The reactions were monitored using pre-coated Aluminium TLC plates of silica gel G/UV-254 of 0.25 mm thickness (Merck 60 F-254). NMR spectra were recorded on a Bruker Avance-II 400FT spectrometer at 400 MHz (^{1}H) and 100 MHz (^{13}C) in DMSO or CDCl3 using TMS as an internal reference. Mass spectra (EIMS) were obtained on a Waters UPLC-TQD mass spectrometer. IR spectra were recorded on a Thermo Scientific Nicolet iS5 FT-IR spectrometer. Melting points were determined by open glass capillary method and were uncorrected.

Experimental Procedure

A solution of $LiClO_4$ (0.5 mmol) in ethanol (30mL) containing aromatic aldehyde (1 mmol) malononitrile (2 mmol), primary amine (1 mmol) and carbon disulfide (1 mmol), was stirred and electrolyzed in an undivided cell equipped with platinum electrode ($1cm^2$) working as well as the counter electrode at room temperature under constant potential (1.5 V). The progress of the reaction was monitored by TLC using hexane/ethyl acetate mixture. After completion of electrolysis (20-26 Min), the solid mixture was filtered and solvent was evaporated under vacuum. The residue was purified by recrystallization from EtOH to furnish the desired product. All the compounds are known and were characterized by comparison of their spectral data with those reported in the literature.

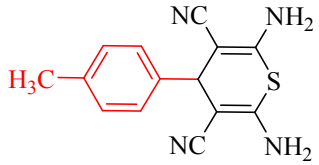
5a. 2,6-diamino-4-(3-nitrophenyl)-4*H*-thiopyran-3,5-dicarbonitrile



Solid cream; MP.: 212-215 ^{0}C

^{1}H NMR (400 MHz, DMSO): δ 8.14–8.09 (m, 2H), 7.73–7.64 (m, 2H), 7.047 (s, 4H), 4.52 (s, 1H); ^{13}C NMR (100 MHz, DMSO): δ 152.0, 147.9, 145.5, 133.3, 130.1, 122.06, 120.9, 118.5, 70.8, 42.58; Anal calcd for $C_{13}H_9N_5O_2S$ (299.30): C, 52.16; H, 3.03; N, 23.39; S, 10.71% found: C, 52.41; H, 3.09; N, 23.24; S, 10.91%.

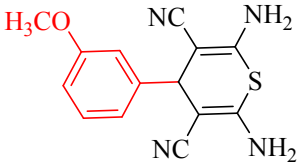
5b. 2,6-diamino-4-*p*-tolyl-4*H*-thiopyran-3,5-dicarbonitrile



Solid fade white powder; MP.: 183-186 ^{0}C

^{1}H NMR (400 MHz, DMSO): δ 7.41 (d, 2H, J = 8.2 Hz), 7.28 (d, 2H, J = 8.6 Hz), 6.93 (s, 4H), 4.2 (s, 1H), 2.54 (s, 3H); ^{13}C NMR (100 MHz, DMSO): δ 151.7, 141.1, 136.0, 130.1, 126.6, 119.1, 70.9, 42.8, 20.8; Anal calcd for $C_{14}H_{12}N_4S$ (268.33): C, 62.66; H, 4.50; N, 20.87; S, 11.94% found: C, 62.58; H, 4.6; N, 20.81; S, 11.84%.

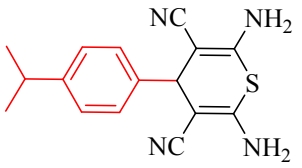
5c. 2,6-diamino-4-(3-methoxyphenyl)-4*H*-thiopyran-3,5-dicarbonitrile



Solid light yellow powder; MP.: 171-173 ^{0}C

^{1}H NMR (400 MHz, DMSO): δ 8.35 (d, 1H, J = 8.8 Hz), 7.82 (s, 1H), 7.79 (d, 1H, J = 8.7 Hz), 6.89 (m, 1H), 6.75 (s, 4H), 4.31 (s, 1H), 3.47 (s, 3H); ^{13}CNMR (100 MHz, DMSO): δ 158.2, 151.9, 145.5, 126.6, 122.0, 118.2, 112.2, 110.92, 70.9, 53.3, 43.12; Anal calcd for $C_{14}H_{12}ON_4S$ (284.33): C, 59.14; H, 4.25; O, 5.6; N, 19.70; S, 11.27% found: C, 58.92; H, 4.21; N, 19.61; S, 11.31%.

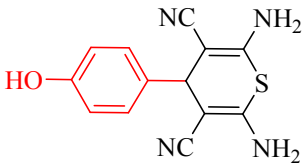
5d. 2,6-diamino-4-(4-isopropylphenyl)-4*H*-thiopyran-3,5-dicarbonitrile



Solid light yellowish; MP.: 230-232 ^{0}C

^{1}H NMR (400 MHz, DMSO): δ 7.34 (d, 2H, J = 8.4 Hz), 7.20 (d, 2H, J = 8 Hz), 6.6 (s, 4H), 4.10 (s, 1H), 2.81 (m, 1H), 1.34 (d, 6H); ^{13}C NMR (100 MHz, DMSO): δ 151.6, 145.9, 140.0, 127.1, 126.6, 119.3, 71.9, 42.8, 33.7, 23.6; Anal calcd for $C_{16}H_{16}N_4S$ (296.39): C, 64.83; H, 5.44; N, 18.90; S, 10.81% found: C, 64.78; H, 5.46; N, 18.81; S, 10.75%.

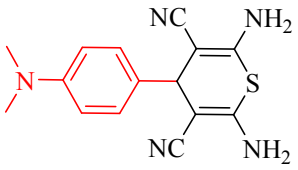
5e. 2,6-diamino-4-(4-hydroxyphenyl)-4*H*-thiopyran-3,5-dicarbonitrile



Solid white cream powder; MP.: 182-184 ^{0}C

^{1}H NMR (400 MHz, DMSO): δ 8.07 (s, 1H), 7.86 (d, 2H, J = 8.6 Hz), 7.27 (s, 4H), 6.93 (d, 2H, J = 8.6 Hz), 4.03 (s, 1H); ^{13}C NMR (100 MHz, DMSO): δ 156.1, 151.3, 135.0, 129.9, 118.9, 116.2, 71.9, 43.4; Anal calcd for $C_{13}H_{10}N_4OS$ (270.31): C, 57.76; H, 3.72; N, 20.72; S, 11.86% found: C, 57.71; H, 3.81; N, 20.81; S, 11.82%.

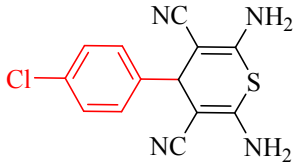
5f. 2,6-diamino-4-(4-(dimethylamino)phenyl)-4*H*-thiopyran-3,5-dicarbonitrile



Solid light yellow powder; MP.: 170-172 ^{0}C

^{1}H NMR (400 MHz, DMSO): δ 7.10 (d, 2H, J = 8.6 Hz), 6.8 (s, 4H), 6.72 (d, 2H, J = 8.6 Hz), 4.08 (s, 1H), 2.9 (s, 6H); ^{13}C NMR (100 MHz, DMSO): δ 150.8, 149.2, 131.4, 127.9, 118.7, 112.2, 72.6, 42.9, 41.8; Anal calcd for $C_{15}H_{15}N_5S$ (297.37): C, 60.58; H, 5.08; N, 23.55; S, 10.78% found: C, 60.54; H, 5.12; N, 23.58; S, 10.81%.

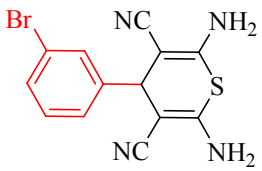
5g. 2,6-diamino-4-(4-chlorophenyl)-4*H*-thiopyran-3,5-dicarbonitrile



Solid white powder; MP.: 188-189 ^{0}C

^{1}H NMR (400 MHz, DMSO): δ 7.86 (d, 2H, J = 8.8 Hz), 7.53 (d, 2H, J = 8.6 Hz), 6.05 (s, 4H), 4.4 (s, 1H); ^{13}C NMR (100 MHz, DMSO): δ 151.4, 141.9, 131.5, 128.2, 127, 118.1, 71.3, 42.3; Anal calcd for $C_{13}H_9ClN_4S$ (288.75): C, 54.07; H, 3.14; N, 19.40; S, 11.10% found: C, 54.17; H, 3.09; N, 19.36; S, 11.08%.

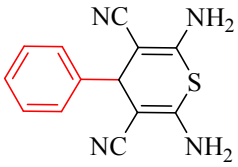
5h. 2,6-diamino-4-(3-bromophenyl)-4*H*-thiopyran-3,5-dicarbonitrile



Solid white powder; MP.: 181-183 ^{0}C

^{1}H NMR (400 MHz, DMSO): δ 8.71 (s, 1H), 8.28 (d, 1H, J = 7.3 Hz), 8.02 (t, 1H), 7.76 (d, 1H, J = 8.5 Hz), 7.37 (s, 4H), 4.48 (s, 1H); ^{13}C NMR (100 MHz, DMSO): δ 151.5, 142.2, 132.6, 130.4, 129.5, 122.0, 120.8, 118.5, 71.2, 42.5; Anal calcd for $C_{13}H_9BrN_4S$ (333.20): C, 46.86; H, 2.72; N, 16.81; S, 9.61% found: C, 46.91; H, 2.76; N, 16.91; S, 9.58%.

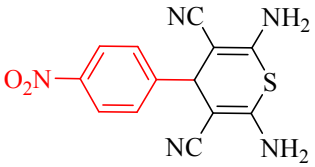
5i. 2,6-diamino-4-phenyl-4*H*-thiopyran-3,5-dicarbonitrile



Solid orange; MP.: 185-187 ^{0}C

^{1}H NMR (400 MHz, DMSO): δ 7.36-7.33 (m, 2H), 7.26-7.22 (m, 3H), 6.9 (s, 4H), 4.31 (s, 1H); ^{13}C NMR (100 MHz, DMSO): δ 151.2, 142.9, 128.5, 128, 126.1, 118.5, 71.8, 42.9; Anal calcd for $C_{13}H_{10}N_4S$ (254.31): C, 61.39; H, 3.96; N, 22.03; S, 12.60% found: C, 61.42; H, 4.01; N, 21.95; S, 12.61%.

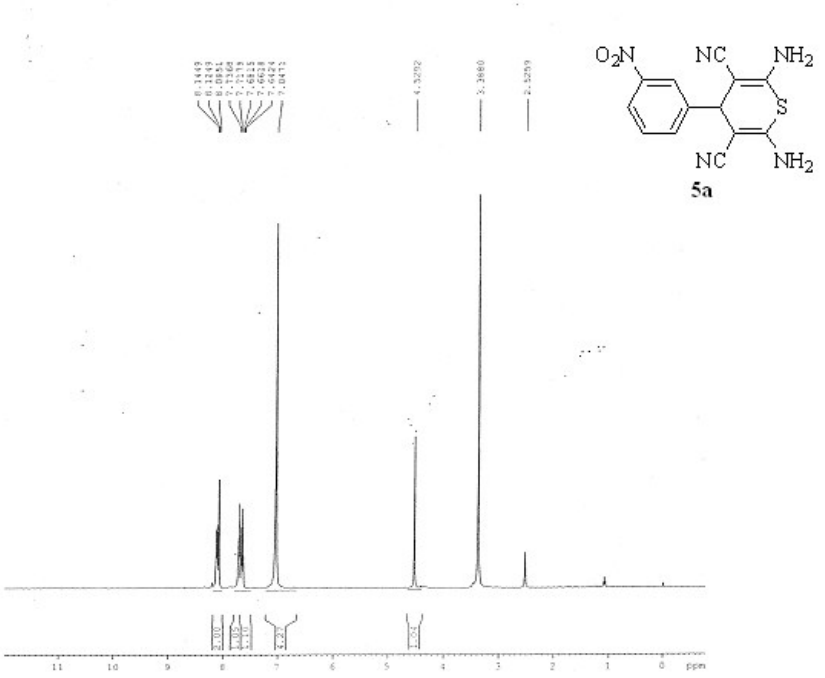
5j. 2,6-diamino-4-(4-nitrophenyl)-4*H*-thiopyran-3,5-dicarbonitrile



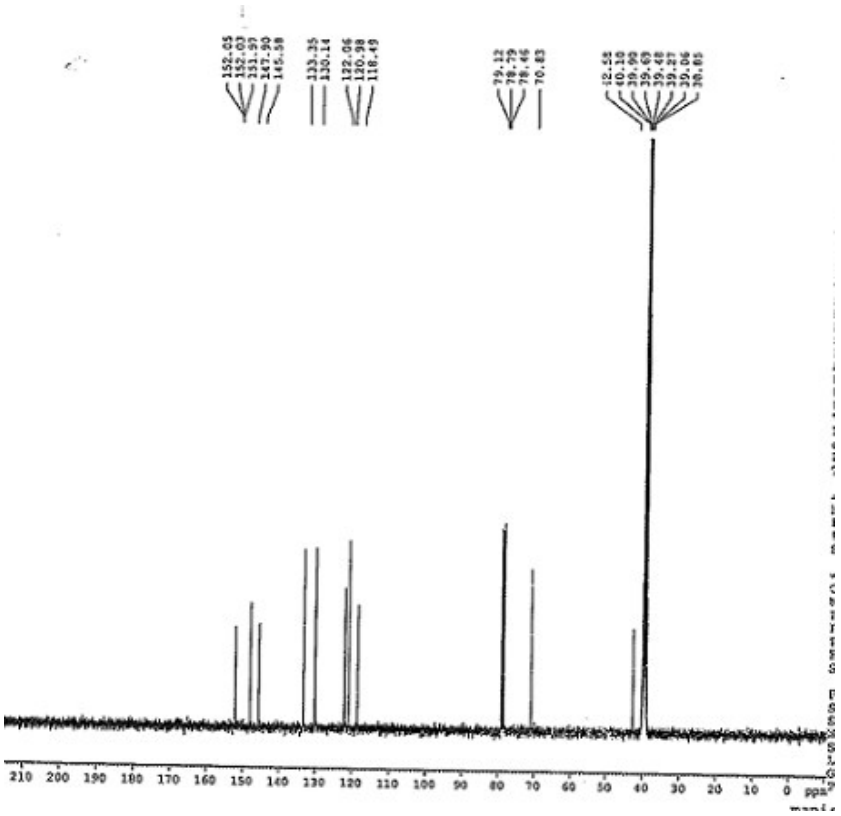
Solid fade brown; MP.: 198-200 ^{0}C

^{1}H NMR (400 MHz, DMSO): δ 8.35 (d, 2H, J = 8.8 Hz), 7.63 (d, 2H, J = 8.8 Hz), 6.75 (s, 4H), 4.45 (s, 1H); ^{13}C NMR (100 MHz, DMSO): δ 151.9, 148.0, 145.7, 125.9, 122.4, 120.0, 70.9, 42.5; Anal calcd for $C_{13}H_9N_5O_2S$ (299.30): C, 52.16; H, 3.03; N, 23.39; S, 10.71% found: C, 52.28; H, 3.12; N, 23.12; S, 10.66%.

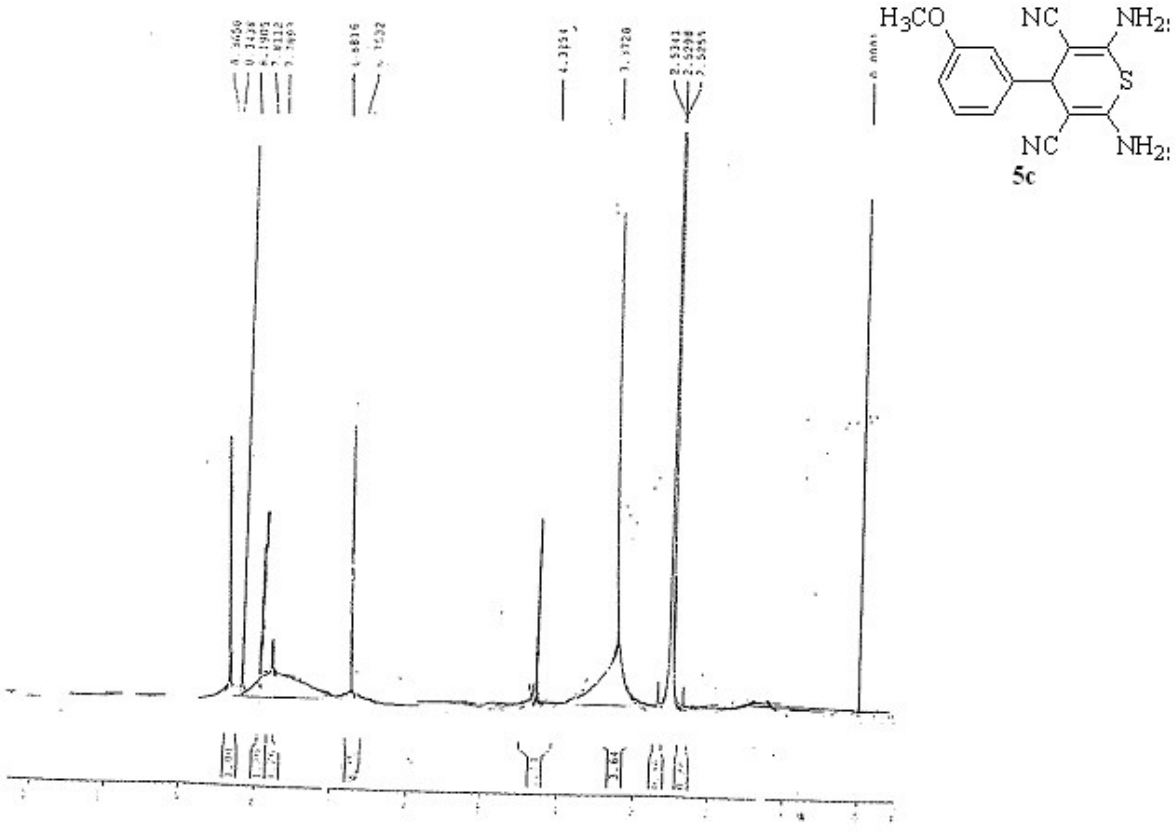
Spectral data of some representative of 4*H*-thiopyran derivatives….



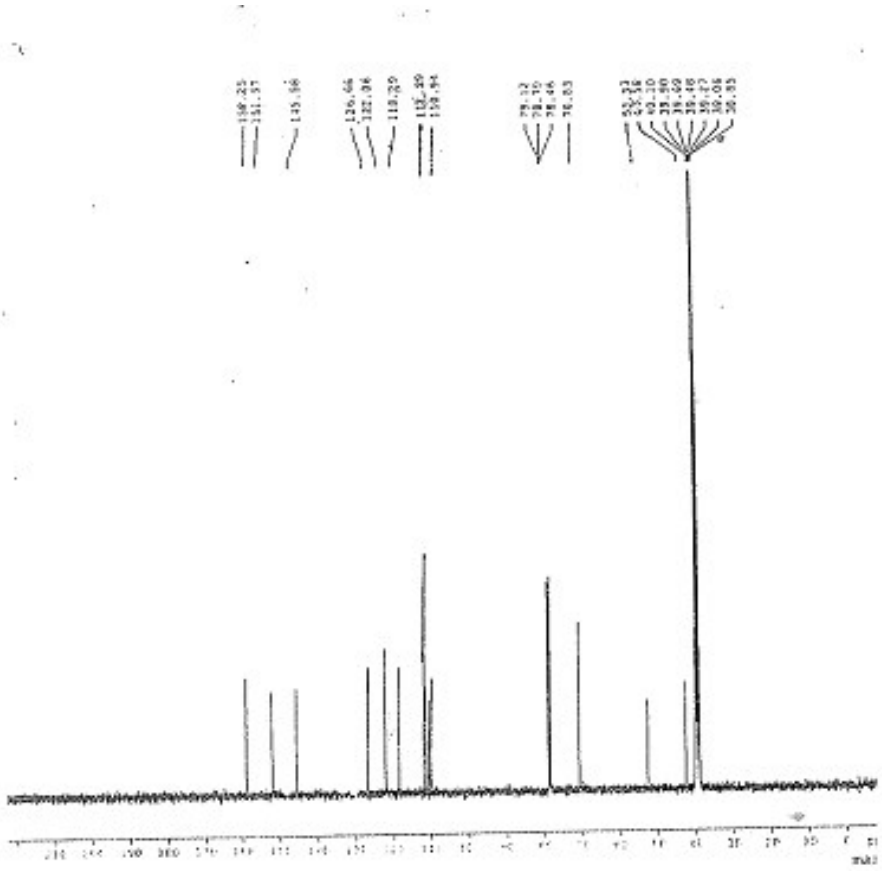
^{1}H NMR spectrum of compound **5a**



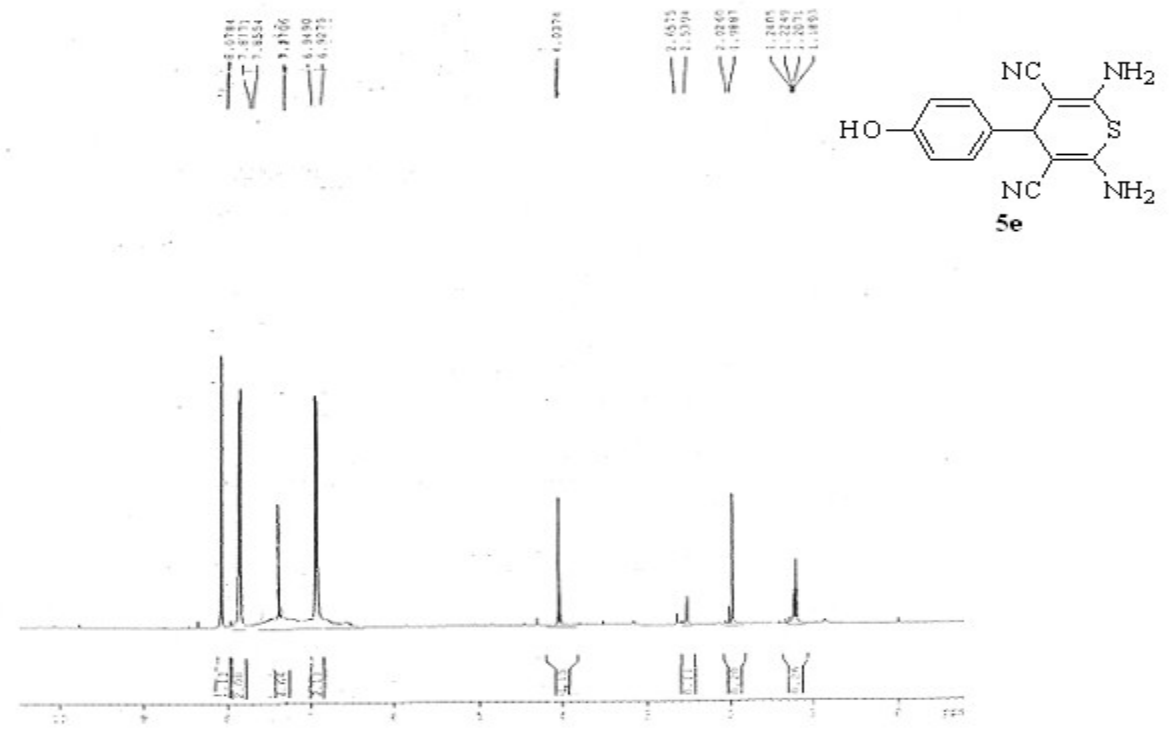
^{13}C NMR spectrum of compound **5a**



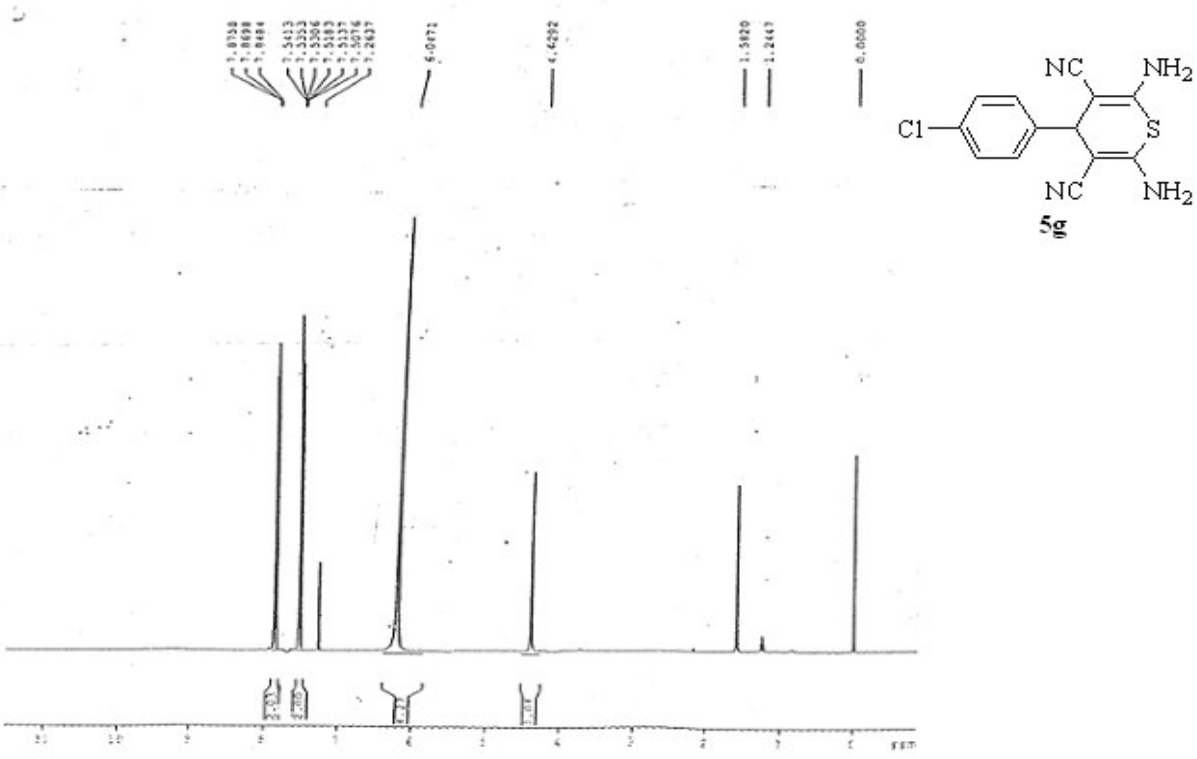
^{1}H NMR spectrum of compound **5c**



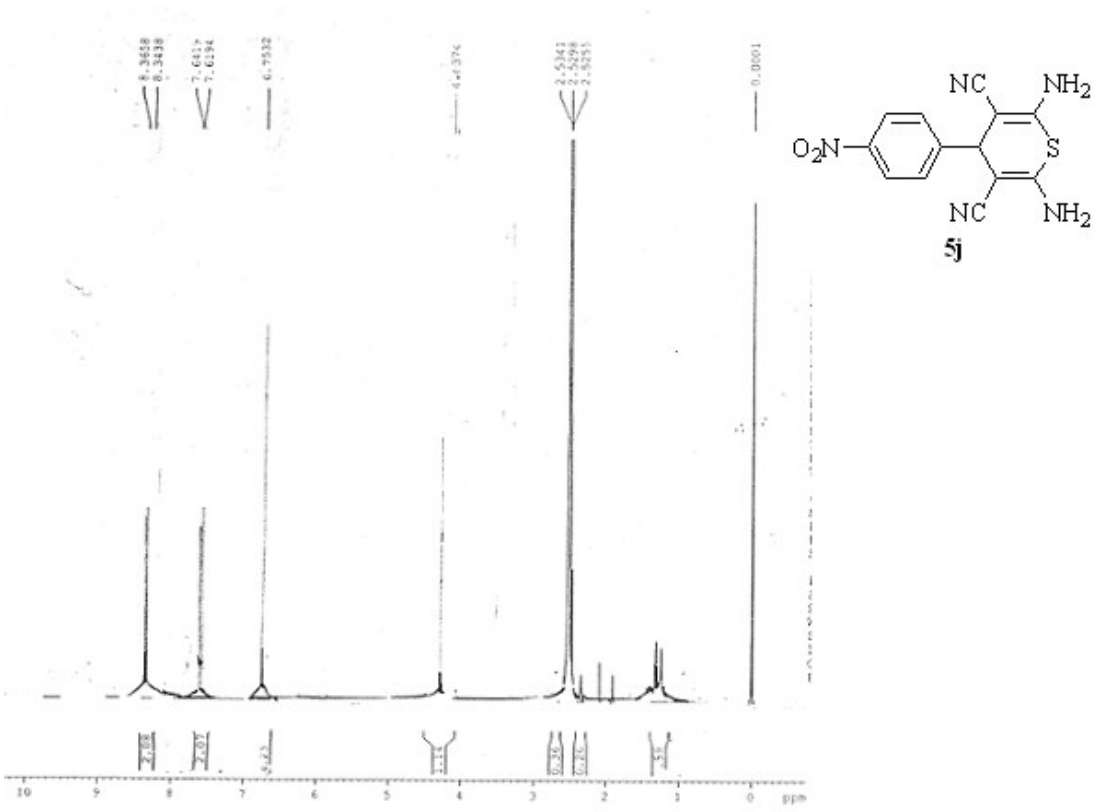
^{13}C NMR spectrum of compound **5c**



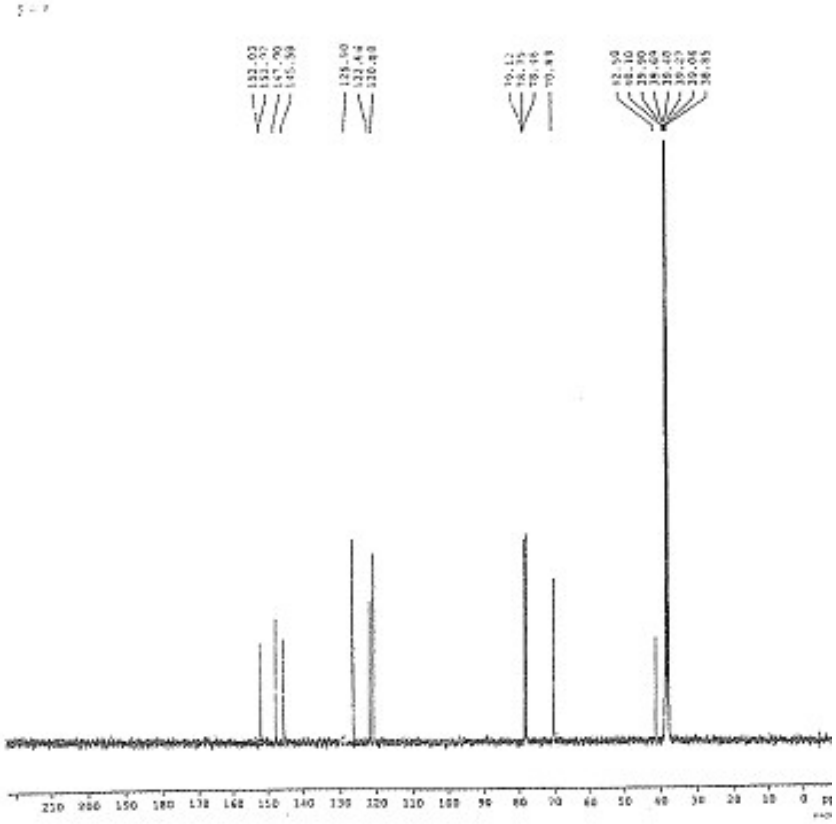
^{1}H NMR spectrum of compound **5e**



^{1}H NMR spectrum of compound **5g**



^{1}H NMR spectrum of compound **5j**



^{13}C NMR spectrum of compound **5j**

References

1. M. A. Bodaghifard, A. Mobinikhaledi, S. Asadbegi, *Appl. Organometal. Chem*. 2017, **31**, aoc.3557.
2. A. Mobinikhaledi, M. A. Bodaghifard, S. Asadbegi, *Mol Divers* 2016, **20,** 461-468.
3. V.D. Dyachenko, T.A. Ryl'skaya, I.V. Dyachenko, I.N. Kalashnik, A.V. Chernykh*, Russ. J. Gen. Chem.* 2015, **85**, 1069–1073.