Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary information

The unexpected and facile molybdenum mediated formation of tri- and tetracyclic pentathiepins from pyrazine-alkynes and sulfur

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General Experimental

Materials and Methods:

All commercially available chemicals were used as supplied by Sigma Aldrich and Acros Organics. 2-chloro-7-methyl-quinoxaline and 2-chloro-6,7-dimethyl-quinoxaline and the molybdenum precursors $(Et_4N)_2[MoO(S_4)_2]$ were synthesised as reported in the literature.[1] Melting point values were recorded on a Stuart scientific SMP3 melting point apparatus and are uncorrected. All infrared spectra were recorded (4000–650 cm^{-1}) on a Perkin-Elmer Fourier-Transform Infrared (FTIR) spectrophotometer. All ^{1}H-NMR spectra were recorded on a Bruker AV400 operating at 400.13 MHz as well as ^{13}C-NMR spectra recorded at 100.65 MHz. All samples were dissolved in deuterated solvents and chemical shift values are reported in parts per million (ppm). Elemental analyses (C, H, and N) were carried out with an Exeter Analytical CE 440 microanalyser by the Microanalysis Laboratory, Chemistry Department, University College Dublin, Belfield, Dublin 4. High resolution mass spectrometry (HRMS) analyses were carried out on a Water-Micromass Q-TOF hybrid mass spectrometer equipped with an orthogonal electrospray source (z–spray). This was operated in an electrospray positive ion mode (ESI^+) or electrospray negative ion mode (ESI^-). Sodium formate was used for mass calibration checks and optimal parameter tuning was performed using flow injection of standard solutions. All TOF measurements were performed at high resolution settings (5000FWHM at mass 1500). Data were always taken in continuum mode.

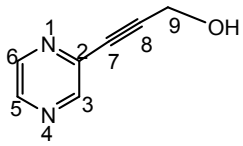
X-ray crystallography:

X-ray crystallographic studies were performed for a single crystal of **3b**, which was coated in Paratone N heavy oil, then mounted on a glass fiber. The respective data were collected on a Rigaku Saturn-724 diffractometer (graphite-monochromated Mo Kα radiation, λ = 0.71073 Å) at 108(2) K. The structures were solved by direct methods (SHELXS-97) and refined against all data by full matrix least-squares methods on F^2 (SHELXL-97).[2] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were located and then refined isotropically on calculated positions using a riding model with their U_{iso} values constrained to 1.5 U_{eq} of their pivotal atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. For further details see table S1.

Table S1: Crystal data and structure refinement for **3b**

Empirical formula	$C_{13}H_{10}N_2OS_5$
Formula weight	370.53
Temperature	108(2) K
Wavelength	0.71073 A
Crystal system	Monoclinic
Space group	P21/n
Unit cell dimensions	a = 8.1317(16) Å α = 90° b = 20.856(4) Å β = 101.63(3)° c = 8.7162(17) Å γ = 9°
Volume	1447.9(5) $Å^3$
Z	4
Density (calculated)	1.700 Mg/m^3
Absorption coefficient	0.798 mm^{-1}
F(000)	760
Crystal size	0.45 x 0.30 x 0.20 mm^3
Theta range for data collection	2.74 to 41.39°
Index ranges	-10<=h<=11, -30<=k<=30,-11<=l<=12
Independent reflections	15450 / 4250 [R(int) = 0.0326]
Completeness to theta = 25.00°	98.3 %
Absorption correction	Numerical
Max. and min. transmission	0.9545 and 0.8010
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4250 / 0 / 191
Goodness-of-fit on F^2	1.152
Final R indices [I>2sigma(I)]	R1 = 0.0444, wR2 = 0.1434
R indices (all data)	R1 = 0.0504, wR2 = 0.1775
Largest diff. peak and hole	0.694 and -0.781 e.A^-3

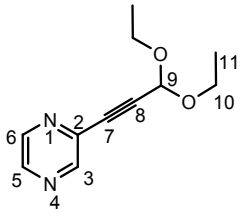
Synthesis of the 3-(pyrazin-2-yl)prop-2-yn-1-ol (1a)



A solution of 2-chloropyrazine (5.00 ml, 56.0 mmol) and propargyl alcohol (3.48 ml, 60.0 mmol) in acetonitrile (60 ml) and triethylamine (30 ml) was degassed under vacuum. Then were added palladium(II) acetate (0.11 g, 0.50 mmol), triphenylphosphine (0.78 g, 3.00 mmol) and copper(I) iodide (0.57 g, 3.00 mmol). The reaction mixture was heated under reflux for 6 hrs. After evaporation of organic solvents, the obtained solid residue was diluted with water (1 x 100 ml) and extracted with dichloromethane (3 x 50 ml). The combined organic extracts were washed with brine (50 ml), dried over $MgSO_4$ and then concentrated in vacuum. The purification of the concentrated mixture was achieved by column chromatography over silica gel, eluting with petroleum ether – diethyl ether (60 : 40) to give 3-(pyrazin-2-yl)prop-2-yn-1-ol as a brown solid.

Yield: 40 %, 3.00 g. Molecular Formula: $C_7H_6N_2O$ (134.13 g/mol). M.P.: 112-113 °C. IR (KBr, ν_{max}/cm^{-1}): (O-H) 3248, (C≡C) 2213, (C=N) 1514, (C-O) 1026. ^{1}H-NMR ($CDCl_3$) δ_H/ppm: 8.70 (s, 1H, Ar-H_3), 8.57 (s, 1H, Ar-H_6), 8.53 (s, 1H, Ar-H_5), 4.58 (s, 2H, H_9), 2.19 (s, 1H, OH); ^{13}C-NMR ($CDCl_3$) δ_C/ppm: C_2 – 147.2, C_3 – 143.2, C_6 – 142.8, C_5 – 139.1, C_8 – 91.4, C_7 – 81.5, C_9 – 50.8. HRMS (ESI): *m/z* Calculated for $C_7H_6N_2O$ $[M + H]^+$: 135.0550; Found: 135.0480.

Synthesis of the 2-(3,3-diethoxyprop-1-ynyl)pyrazine (1b)

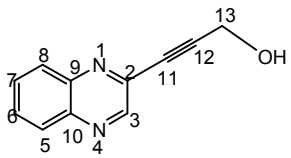


The solution of 2-chloropyrazine (2.30 ml, 27.5 mmol) and 3,3-diethoxypropyne (5.00 ml, 35.0 mmol) in acetonitrile (60 ml) and triethylamine (30 ml) was degassed under vacuum. Then were added palladium(II) acetate (0.11 g. 0.50 mmol), triphenylphosphine (0.78 g, 3.00 mmol) and copper(I) iodide (0.57 g, 3.00 mmol). The reaction mixture was heated under reflux for 6 hrs. After evaporation of organic solvents, the obtained solid residue was diluted with water (100 ml) and extracted with dichloromethane (3 x 50 ml). The combined organic extracts were washed with brine (50 ml), dried over $MgSO_4$ and then concentrated in vacuum. The purification of the concentrated

mixture was achieved by column chromatography over silica gel, eluting with petroleum ether – diethyl ether (60 : 40) to give 2-(3,3-diethoxyprop-1-ynyl)quinoxaline as a brown oil.

Yield: 70 %, 3.80 ml. Molecular Formula: $C_{11}H_{14}N_2O_2$ (206.24 g/mol). IR (KBr, ν_{max}/cm^{-1}): (C≡C) 2198, (C=N) 1555, (C-O) 1010. ^{1}H-NMR ($CDCl_3$) δ_H/ppm: 8.66 (s, 1H, Ar-H_3) 8.52 (s, 1H, Ar-H_6), 8.47 (s, 1H, Ar-H_5), 5.48 (s, 1H, H_9), 3.82-3.60 (m, 4H, H_{10}), 1.22 (t, 6H, H_{11}, J = 7.01 Hz); ^{13}C-NMR ($CDCl_3$) δ_C/ppm: C_2 – 150.7, C_3 – 148.0, C_6 – 144.6, C_5 – 144.4, C_9 – 91.8, C_8 – 83.0, C_7 – 76.4, C_{10} – 55.9, C_{11} – 14.1. HRMS (ESI): *m/z* calculated for $C_{11}H_{14}N_2O_2$ $[M + H]^+$: 207.1134; Found: 207.1136.

Synthesis of the 3-(quinoxalin-2-yl)prop-2-yn-1-ol (2a)



The experimental procedure used for the synthesis of this compound was the same as that employed to prepare compound **1a** except 2-chloroquinoxaline (5.0 g, 30.3 mmol) and propargyl alcohol (1.90 ml, 33.0 mmol) were used instead of 2-chloropyrazine. **2a** was isolated as light brown solid.

Yield: 44 %, 2.50 g. Molecular Formula: $C_{11}H_8N_2O$ (184.19 g/mol).[3] M.P.: 140-141 °C. IR (KBr, ν_{max}/cm^{-1}): (O-H) 3275, (C≡C) 2229, (C=N) 1544, (C-O) 1041. ^{1}H-NMR ($CDCl_3$) δ_H/ppm: 8.91 (s, 1H, Ar-H_3), 8.10 (m, 2H, Ar-$H_{8,5}$), 7.82 (m, 2H, Ar-$H_{7,6}$), 4.66 (d, 2H, H_{13}, J = 6.2 Hz), 2.28 (s, 1H, OH); ^{13}C-NMR ($CDCl_3$) δ_C/ppm: C_2 – 146.4, C_3 – 141.5, C_9 – 140.6, C_{10} – 138.3, C_8 – 130.4, C_5 – 130.3, C_7 – 128.7, C_6 – 128.7, C_{12} – 91.6, C_{11} – 82.5, C_{13} – 50.9. HRMS (ESI): *m/z* calculated for $C_{11}H_8N_2O$ $[M + H]^+$: 185.0715; Found: 185.0735.

Attempted synthesis of pyrazine and quinoxaline-derived molybdenum complexes

Method A

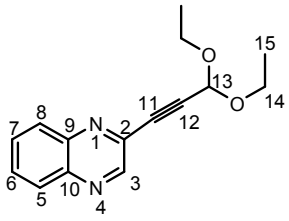
$(Et_4N)_2[MoO(S_4)_2]$ (0.31 g, 0.50 mmol) was dissolved in dry DMF (5 ml) by warming in an oil bath at 50 °C for 10 mins. Then 3-(pyrazin-2-yl)prop-2-yn-1-ol (**1a**) (0.134 g, 1.00 mmol) or 3-(quinoxalin-2-yl)prop-2-yn-1-ol (**2a**) (0.184 g, 1.00 mmol) was added to the reaction mixture and heated for another 40 mins. After cooling the reaction mixture, iso-propanol (50 ml) was added which

resulted in the formation of red crystals that were collected by filtration and dried under vacuum.

Method B

$(Et_4N)_2[MoO(S_4)_2]$ (0.314 g, 0.5 mmol) was dissolved in dry acetonitrile (40 ml) by warming on an oil bath at 50 °C for 10 mins. Then 3-(pyrazin-2-yl)prop-2-yn-1-ol (**1a**) (0.134 g, 1.00 mmol) or 3-(quinoxalin-2-yl)prop-2-yn-1-ol (**2a**) (0.184 g, 1.00 mmol) was added to the reaction mixture and heated for another 3-4 hrs. The reaction mixture was left for 3-4 days at 5 °C allowing crystallisation. The resulting crystals of both methods (A and B) were analysed by X-ray crystallography. The obtained data corresponded to the molybdenum precursor.

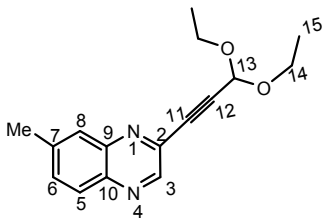
Synthesis of the 2-(3,3-diethoxyprop-1-ynyl)quinoxaline (2b)



The experimental procedure used for the synthesis of this compound was the same as that employed to prepare compound **1b** except 2-chloroquinoxaline (5.0 g, 30.3 mmol) and 3,3-diethoxypropyne (5.00 ml, 35.0 mmol) were used instead of 2-chloropyrazine. **2b** was isolated as a yellow oil.

Yield: 65 %, 5.00 ml. Molecular Formula: $C_{15}H_{16}N_2O_2$ (256.29 g/mol).[3] IR (KBr, ν_{max}/cm^{-1}): (C≡C) 2192, (C=N) 1542, (C-O) 1059. ^{1}H-NMR ($CDCl_3$) δ_H/ppm: 8.78 (s, 1H, Ar-H_3) 7.93 (d, 2H, Ar-$H_{8,5}$, J = 7.59 Hz), 7.63 (d, 2H, Ar-$H_{7,6}$, J = 7.52 Hz) 5.47 (s, 1H, H_{13}), 3.78-3.55 (m, 4H, H_{14}) 1.17 (t, 6H, H_{15}, J = 7.01 Hz); ^{13}C-NMR ($CDCl_3$) δ_C/ppm: C_2 – 148.6, C_3 – 145.7, C_9 – 143.5, C_{10} – 143.1, C_8 – 140.2, C_5 – 138.4, C_7 – 129.4, C_6 – 128.2, C_{13} – 93.1, C_{12} – 87.8, C_{11} – 83.2, C_{14} – 60.8, C_{15} – 14.6. HRMS (ESI): *m/z* calculated for $C_{15}H_{16}N_2O_2$ $[M + H]^+$: 257.1290; Found: 257.1285.

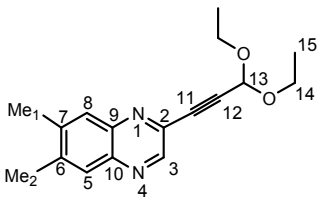
Synthesis of the 2-(3,3-diethoxyprop-1-ynyl)-7-methylquinoxaline (2c)



The experimental procedure used for the synthesis of this compound was the same as that employed to prepare compound **1b** except 2-chloro-7-quinoxaline (5.0 g, 27.9 mmol) and 3,3-diethoxypropyne (5.00 ml, 35.0 mmol) were used instead of 2-chloropyrazine. 2c was isolated as a dark brown oil.

Yield: 60 %, 4.90 ml. Molecular Formula: $C_{16}H_{18}N_2O_2$ (270.31 g/mol). IR (KBr, ν_{max}/cm^{-1}): (C≡C) 2180, (C=N) 1534, (CH_3) 1336, (C-O) 1049. ^{1}H-NMR ($CDCl_3$) δ_H/ppm: 8.61 (s, 1H, Ar-H_3) 7.71-7.68 (m, 1H, Ar-H_8), 7.56 (s, 1H, Ar-H_5), 7.33 (d, 1H, Ar-H_6, J = 7.40 Hz), 5.40 (s, 1H, H_{13}), 3.72-3.49 (m, 4H, H_{14}) 2.33 (s, 3H, H_{Me}), 1.10 (t, 6H, H_{15}, J = 7.04 Hz); ^{13}C-NMR ($CDCl_3$) δ_C/ppm: C_2 – 145.8, C_3 – 141.4, C_9 – 139.8, C_{10} – 138.9, C_8 – 137.5, C_5 – 132.3, C_6 – 128.1, C_7 – 127.3, C_{13} – 91.1, C_{12} – 87.4, C_{11} – 81.9, C_{14} – 60.7, C_{Me} – 21.2, C_{15} – 14.4. HRMS (ESI): *m/z* calculated for $C_{16}H_{18}N_2O_2$ $[M + Na]^+$: 293.1266; Found: 293.1254.

Synthesis of the 2-(3,3-diethoxyprop-1-ynyl)-6,7-methylquinoxaline (2d)

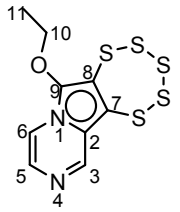


The experimental procedure used for the synthesis of this compound was the same as that employed to prepare compound **1b** except 2-chloro-6,7-quinoxaline (5.28 g, 27.5 mmol) and 3,3-diethoxypropyne (5.00 ml, 35.0 mmol) were used instead of 2-chloropyrazine. **2d** was isolated as a brown solid.

Yield: 73 %, 5.70 g. Molecular Formula: $C_{17}H_{20}N_2O_2$ (284.35 g/mol). M.P.: 50-51°C. IR (KBr, ν_{max}/cm^{-1}): (C≡C) 2172, (C=N) 1531, (CH_3) 1360, (C-O) 1052. ^{1}H-NMR ($CDCl_3$) δ_H/ppm: 8.69 (s, 1H, Ar-H_3) 7.63 (s, 2H, Ar-$H_{8,5}$), 5.49 (s, 1H, H_{13}), 3.79-3.60 (m, 4H, H_{14}) 2.33 (s, 6H, $H_{Me1,Me2}$), 1.20 (t, 6H, H_{15}, J = 7.23 Hz); ^{13}C-NMR ($CDCl_3$) δ_C/ppm: C_2 – 145.7, C_3 – 141.0, C_9 – 140.7, C_{10} – 140.1, C_8 – 139.6, C_5 – 136.7, C_7 – 127.6, C_6 – 127.6, C_{13} – 91.0, C_{12} – 87.0, C_{11} – 82.1, C_{14} – 60.7, C_{Me1} – 19.8, C_{Me2} – 19.7 C_{15} – 14.5. HRMS (ESI): *m/z* calculated for $C_{17}H_{20}N_2O_2$ $[M + Na]^+$: 307.1422; Found: 307.1423.

Synthesis of pentathiepino-pyrrolo[1,2-a]pyrazine drivatives

Synthesis of the 10-ethoxy-pentathiepino-pyrrolo[1,2-*a*]pyrazine (3a)



Method A

$(Et_4N)_2[MoO(S_4)_2]$ (0.25 g, 0.40 mmol) and elemental sulfur (0.20 g, 0.80 mmol) were added to DMF (5 ml) and dissolved by heating (40 ° C) in an oil bath for 20 mins. 2-(3,3-Diethoxyprop-1-ynyl)pyrazine (**1b**) (0.16 ml, 0.8 mmol) was added to the reaction mixture and stirred for 3 hrs. After filtering to remove excess sulfur, the product was precipitated out by the addition of iso-propanol which resulted in the formation of a brick red powder. The obtained solid residue was filtered and washed with diethyl ether (2 x 20 ml). The product was recrystallised with acetone (5 ml) to give a red solid.

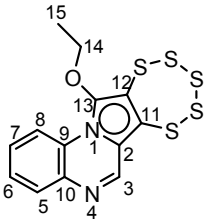
Method B

$(Et_4N)_2[MoO(S_4)_2]$ (0.25 g, 0.40 mmol) and elemental sulfur (0.20 g, 0.80 mmol) were added to acetonitrile (40 ml) and dissolved by heating (40° C) in an oil bath for 20 mins. 2-(3,3-Diethoxyprop-1-ynyl)pyrazine (**1b**) (0.16 ml, 0.8 mmol) was added to the reaction mixture and stirred for 5 hrs. After filtering to remove excess sulfur, the solvent was removed under reduced pressure and the residue was purified by chromatography. Residual sulfur was removed by elution with DCM followed by subsequent elution with Methanol-hexane(97:3) to give **3a** as a red solid.

Yield A (relative to **1b**): 27 %, 0.07 g. Yield B (relative to **1b**): 57 %, 0.14 g. Molecular Formula: $C_9H_9N_2OS_5$ (321.50 g/mol). Actual %, C: 30.23, H: 3.66, N: 7.84; Found %, C: 30.79, H: 3.82, N: 8.25. M.P.: 150-151 °C. IR (KBr, ν_{max}/cm^{-1}): (Sym, Ar-CH) 1642, (C=N) 1538, (C-O) 997, (C-S) 784. ^{1}H-NMR ($CDCl_3$) δ_H/ppm: 8.39 (s, 1H, Ar-H_3) 7.56 (d, 1H, Ar-H_5, J = 7.00 Hz), 7.00 (d, 1H, Ar-H_6, J = 6.08 Hz), 4.91-4.87 (m, 2H, H_{10}), 1.42 (t, 3H, H_{11}, J = 6.90 Hz); ^{13}C-NMR ($CDCl_3$) δ_C/ppm: C_2 – 143.2, C_3 – 137.4, C_5 – 135.0, C_6 – 129.8, C_8 – 124.4, C_9 – 122.0, C_7 – 116.2, C_{10} –

52.2, C_{11} – 15.0 HRMS (ESI): *m/z* calculated for $C_9H_9N_2OS_5$ $[M]^+$: 320.9318; Found: 320.9310.

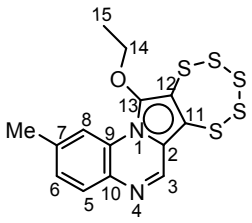
Synthesis of the 10-ethoxy-pentathiepino-pyrrolo[1,2-*a*]quinoxaline (3b)



The experimental procedures used for the synthesis of this compound were the same as those employed to prepare compound **3a** except diethoxyprop-1-ynyl)quinoxaline (**2b**) (0.20 ml, 0.8 mmol) was used instead of 2-(3,3-diethoxyprop-1-ynyl)pyrazine (**1b**). **3b** was isolated as a red powder.

Yield A (relative to **2b**): 37 %, 0.11 g. Yield B (relative to **2b**): 68 %, 0.20 g. Molecular Formula: $C_{13}H_{10}N_2OS_5$ (370.55 g/mol). Actual %, C: 38.40, H: 3.47, N: 6.89; Found %, C: 38.60, H: 3.58, N: 6.67. M.P.: 205-206 °C. IR (KBr, ν_{max}/cm^{-1}): (Sym, Ar-CH) 1625, (C=N) 1521, (C-O) 1012, (C-S) 752. ^{1}H-NMR ($CDCl_3$) δ_H/ppm: 8.88 (br s, 1H, Ar-H_3), 8.56 (d, 1H, Ar-H_8, J = 7.13 Hz), 7.94 (br. s, 1H, Ar-H_5, J = 7.93 Hz), 7.52-7.51 (m, 2H, Ar-$H_{7,6}$), 4.60-4.62 (m, 2H, H_{14}), 1.60 (t, 3H, H_{15}, J = 8.10 Hz); ^{13}C-NMR ($CDCl_3$) δ_C/ppm: C_2 – 146.3, C_3 – 144.0, C_8 – 138.6, C_9 – 136.3, C_{10} – 133.9, C_5 – 129.6, C_7 – 127.8, C_6 – 126.1, C_{12} – 118.5, C_{13} – 116.2, C_{11} – 114.2, C_{14} – 51.6, C_{15} – 15.1. HRMS (ESI): *m/z* calculated for $C_{13}H_{10}N_2OS_5$ $[M+H]^+$: 370.9475; Found: 370.9526.

Synthesis of the 7-methyl 10-ethoxy-pentathiepino-pyrrolo[1,2-*a*]quinoxaline (3c)

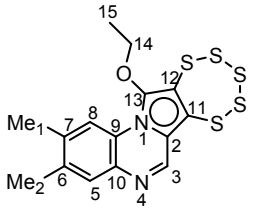


The experimental procedures used for the synthesis of this compound were the same as those employed to prepare compound **3a** except 2-(3,3-diethoxyprop-1-ynyl)-7-methylquinoxaline (**2c**) (0.21 ml, 0.8 mmol) was used instead of 2-(3,3-diethoxyprop-1-ynyl)pyrazine (**1b**). **3c** was isolated as a red solid.

Yield A (relative to **2c**): 33 %, 0.10 g. Yield B (relative to **2c**): 67 %, 0.20 g. Molecular Formula:

$C_{14}H_{12}N_2OS_5$ (384.58 g/mol). Actual %, C: 47.13, H: 4.83, N: 6.11; Found %, C: 47.96, H: 4.55, N: 7.71. M.P.: 245-247 °C. IR (KBr, ν_{max}/cm^{-1}): (Sym, Ar-CH) 1618, (C=N) 1548, (Ar-CH_3) 1378, (C-O) 1017, (C-S) 783. ^{1}H-NMR (d_6-DMSO) δ_H/ppm: 8.87 (s, 1H, Ar-H_3), 8.44 (d, 1H, Ar-H_8, J = 7.68 Hz) 7.80 (d, 1H, Ar-H_5, J = 7.93 Hz), 7.47 (d, 1H, Ar-H_6, J = 7.80 Hz) 4.62-4.56 (m, 2H, H_{14}), 2.46 (s, 3H, H_{Me}, J = 7.30 Hz), 1.50 (t, 3H, H_{15} J = 7.12 Hz); ^{13}C-NMR (d_6-DMSO) δ_C/ppm: C_2 – 144.1, C_3 – 143.1, C_8 – 138.8, C_9 – 136.2, C_{10} – 134.3, C_5 – 129.8, C_7 – 129.4, C_6 – 125.9, C_{12} – 117.3, C_{13} – 116.4, C_{11} – 114.3, C_{14} – 51.4, C_{Me} – 20.5, C_{15} – 15.4. HRMS (ESI): *m/z* calculated for $C_{14}H_{12}N_2OS_5$ $[M+H]^+$: 384.9631; Found: 384.9632.

Synthesis of the 6,7-dimethyl 10-ethoxy-pentathiepino-pyrrolo[1,2-*a*]quinoxaline (3d)



The experimental procedures used for the synthesis of this compound were the same as those employed to prepare compound **3a** except 2-(3,3-diethoxyprop-1-ynyl)-6,7-methylquinoxaline (**2d**) (0.22 ml, 0.80 mmol) was used instead of 2-(3,3-diethoxyprop-1-ynyl)pyrazine (**1b**). 3d was isolated as a reddish brown solid.

Yield A (relative to **2d**): 32 %, 0.10 g. Yield B (relative to **2d**): 63 %, 0.20 g. Molecular Formula: $C_{15}H_{14}N_2OS_5$ (398.60 g/mol). Actual %, C: 47.23, H: 4.83, N: 6.11; Found %, C: 47.89, H: 5.22, N: 7.23. M.P.: 266-267 °C. IR (KBr, ν_{max}/cm^{-1}): (Sym, Ar-CH) 1619, (C=N) 1537, (Ar-CH_3) 1329, (C-O) 1016, (C-S) 742. ^{1}H-NMR (d_6-DMSO) δ_H/ppm: 8.84 (s, 1H, Ar-H_3), 8.39 (s, 1H, Ar-H_8) 7.71 (s, 1H, Ar-H_5), 4.67-4.59 (m, 2H, H_{14}), 2.46 (s, 3H, H_{Me1}), 2.41 (s, 3H, H_{Me2}), 1.34 (t, 3H, H_{15} J = 7.10 Hz); ^{13}C-NMR (d_6-DMSO) δ_C/ppm: C_2 – 145.7, C_3 – 143.9, C_8 – 137.7, C_9 – 135.2, C_{10} – 134.3, C_5 – 129.7, C_7 – 124.2, C_6 – 122.0, C_{12} – 117.8, C_{13} – 116.6, C_{11} – 114.5, C_{14} – 52.5, C_{Me1} – 20.5, C_{Me2} – 19.4 C_{15} – 15.0. HRMS (ESI): *m/z* calculated for $C_{15}H_{15}N_2OS_5$ $[M+H]^+$: 398.9788; Found: 398.9786.

Figure S1: Mass spectrum of **3a**

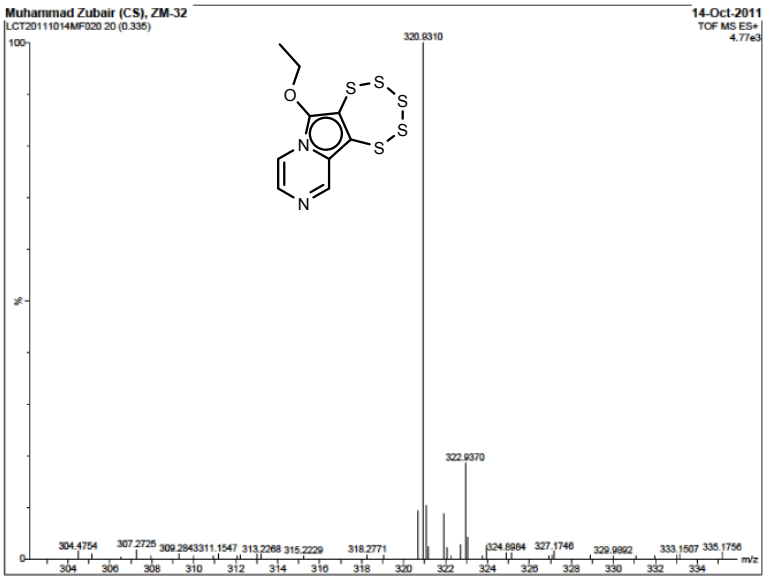


Figure S2: Mass spectrum of **3b**

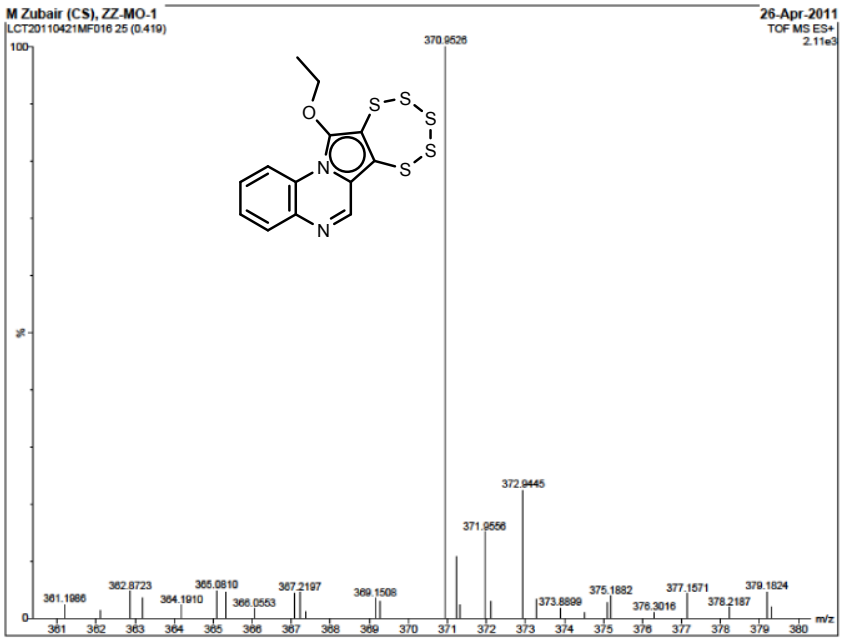


Figure S3: Mass spectrum of **3c**

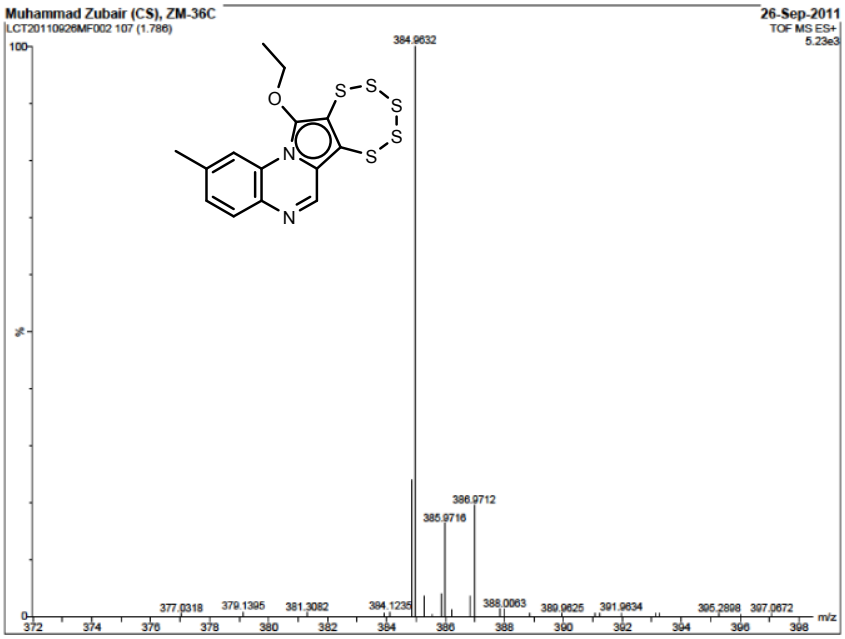


Figure S4: Mass spectrum of **3d**

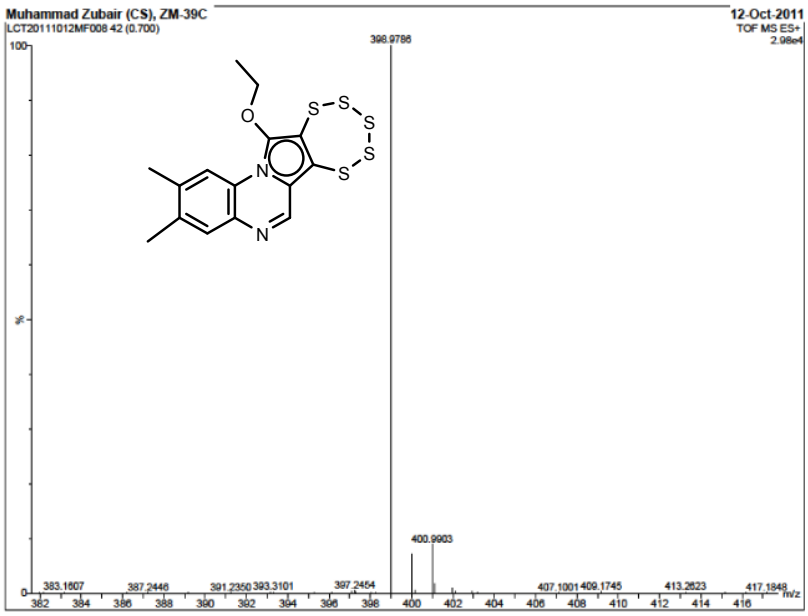


Figure S5: ^{1}H-NMR spectrum of **3a**

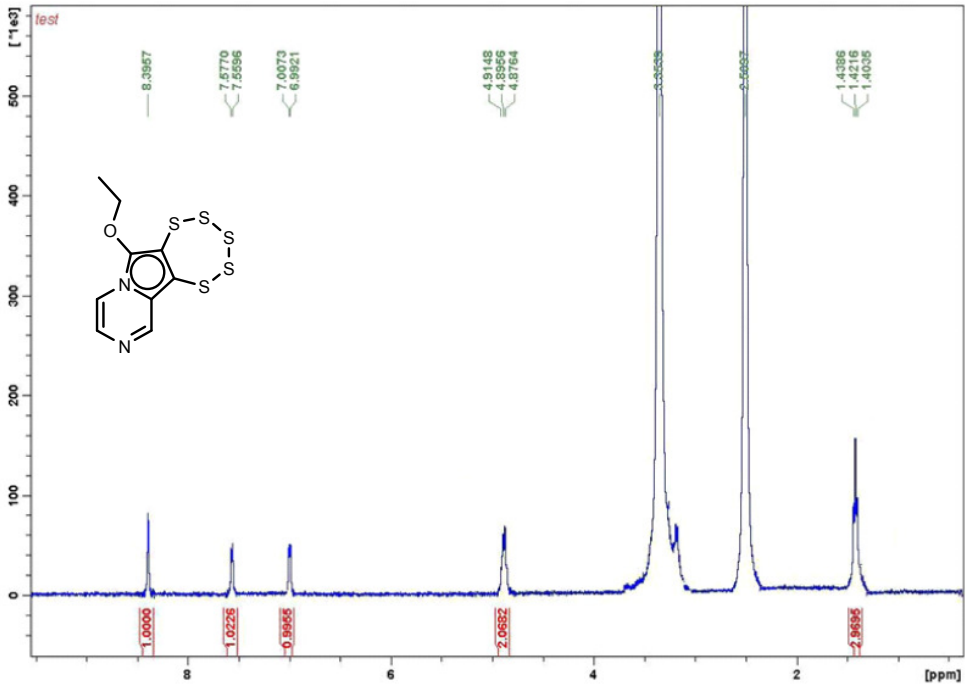


Figure S6: ^{13}C-NMR spectrum of **3a**

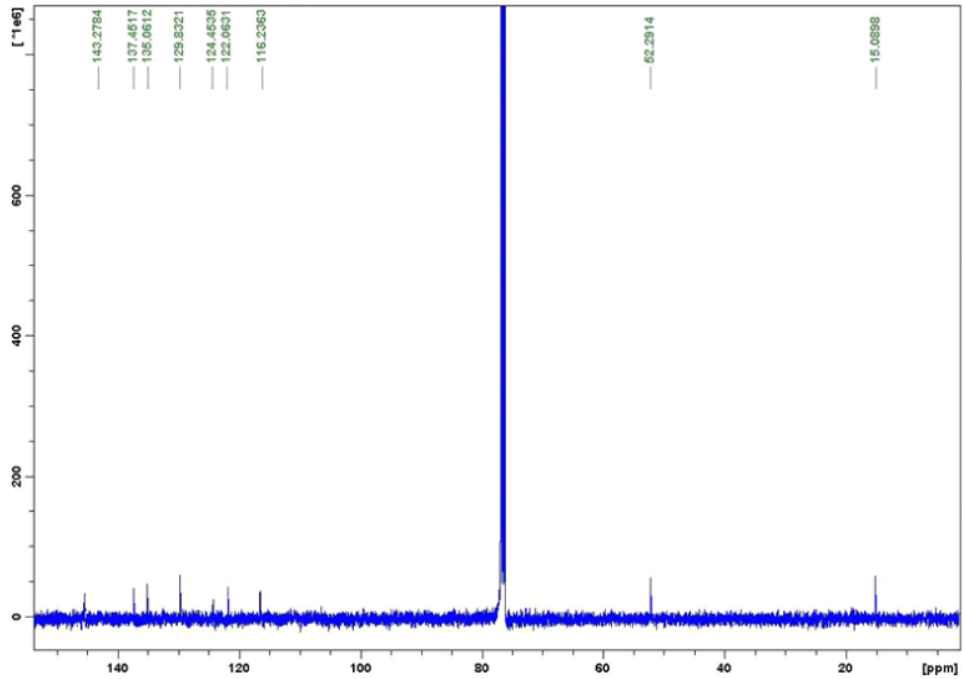


Figure S7: ^{1}H-NMR spectrum of **3b**

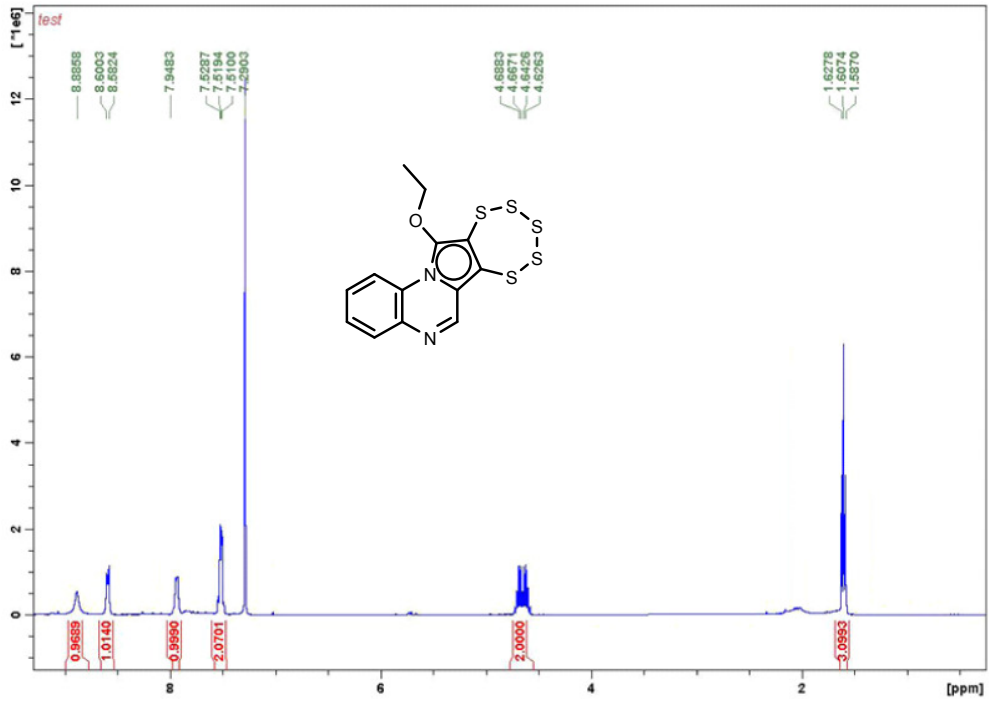


Figure S8: ^{13}C-NMR spectrum of **3b**

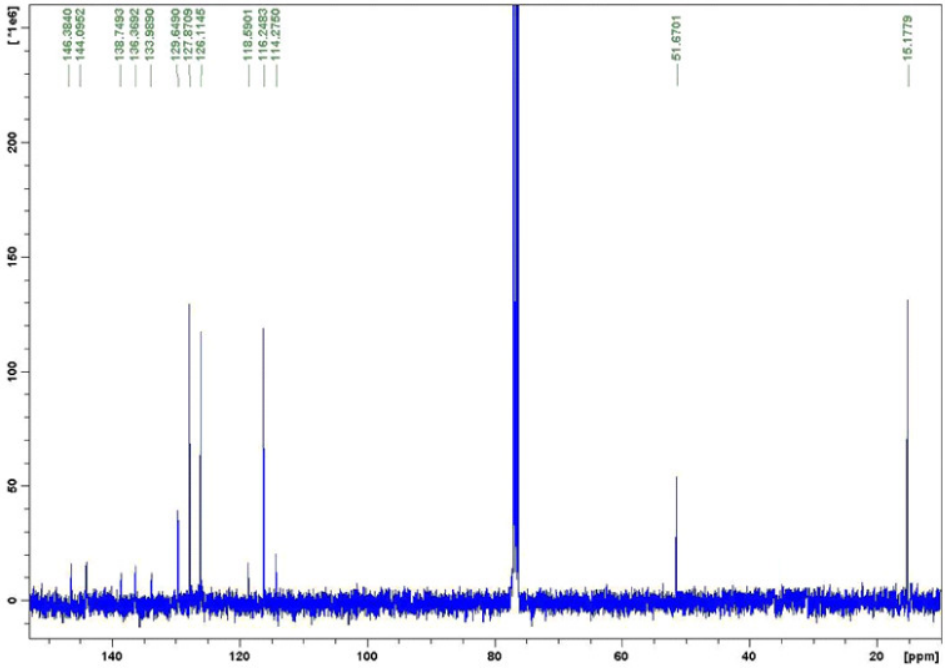


Figure S9: ^{1}H-NMR spectrum of **3c**

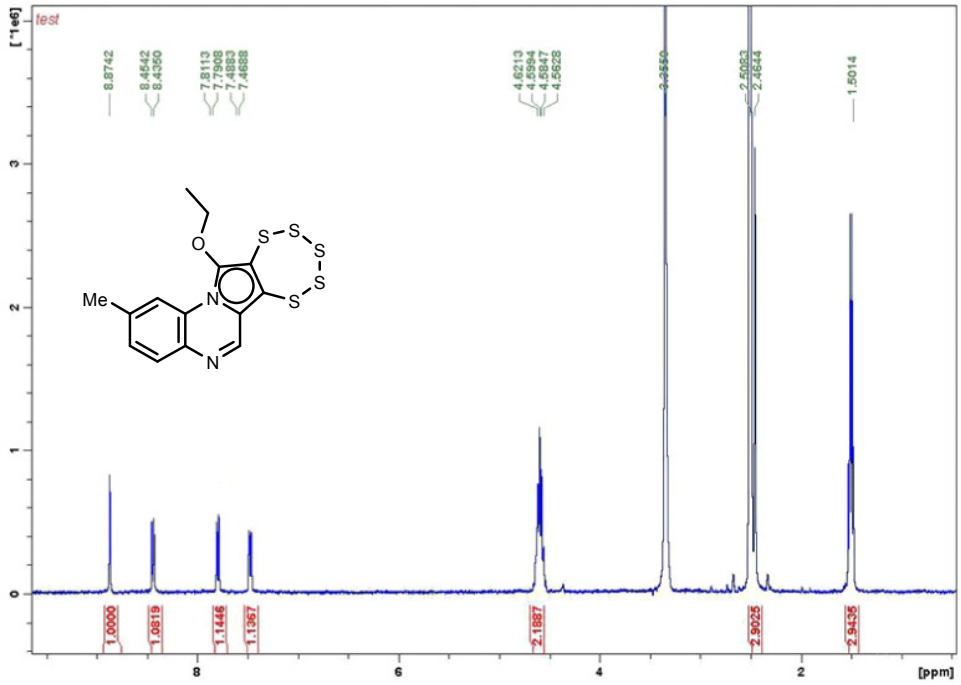


Figure S10: ^{13}C-NMR spectrum of **3c**

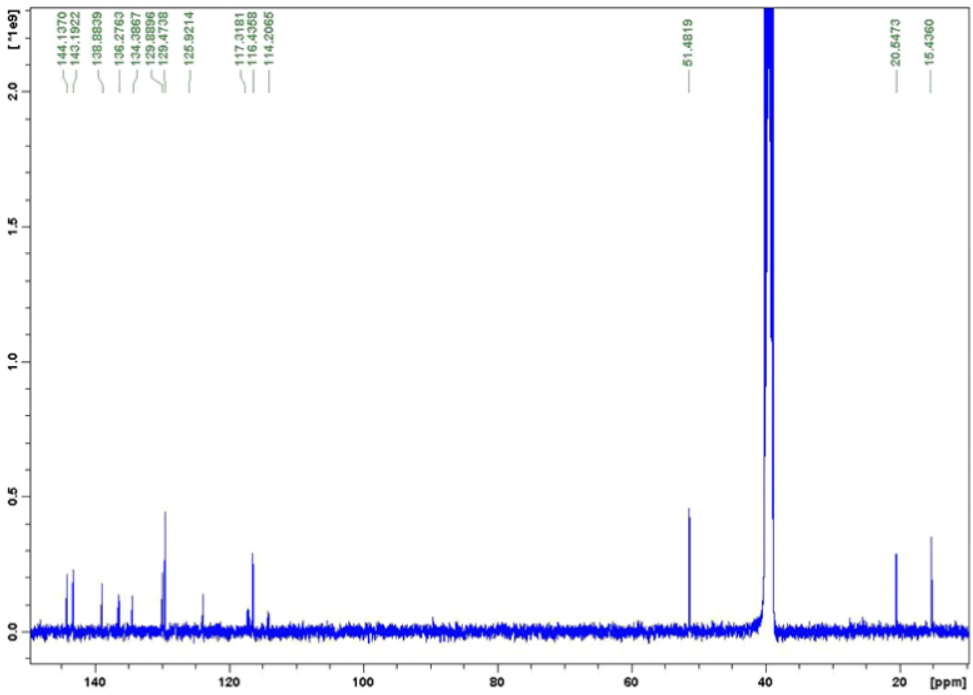


Figure S11: ^{1}H-NMR spectrum of **3d**

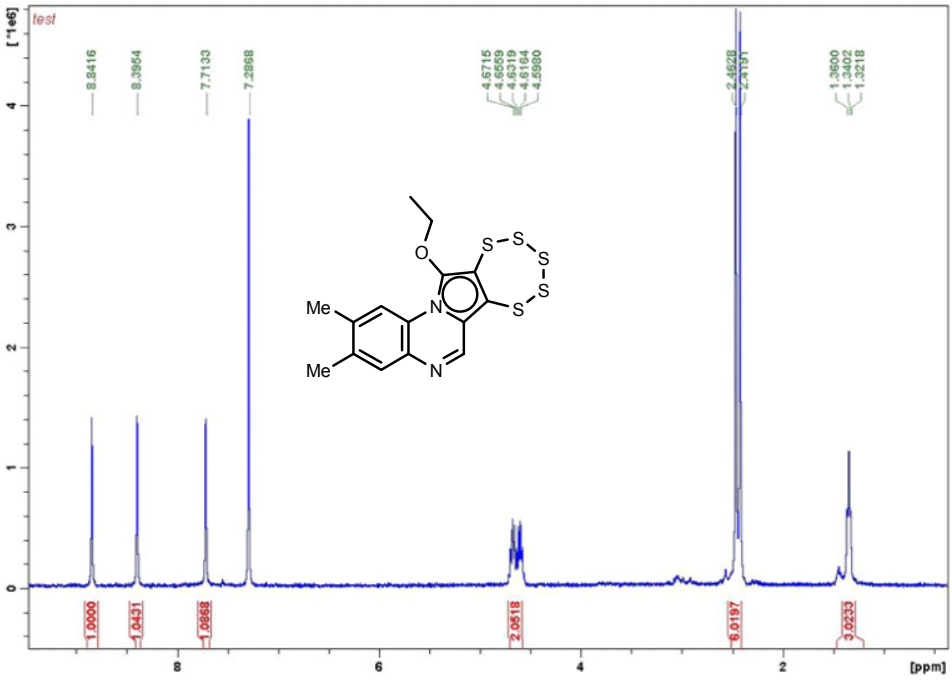
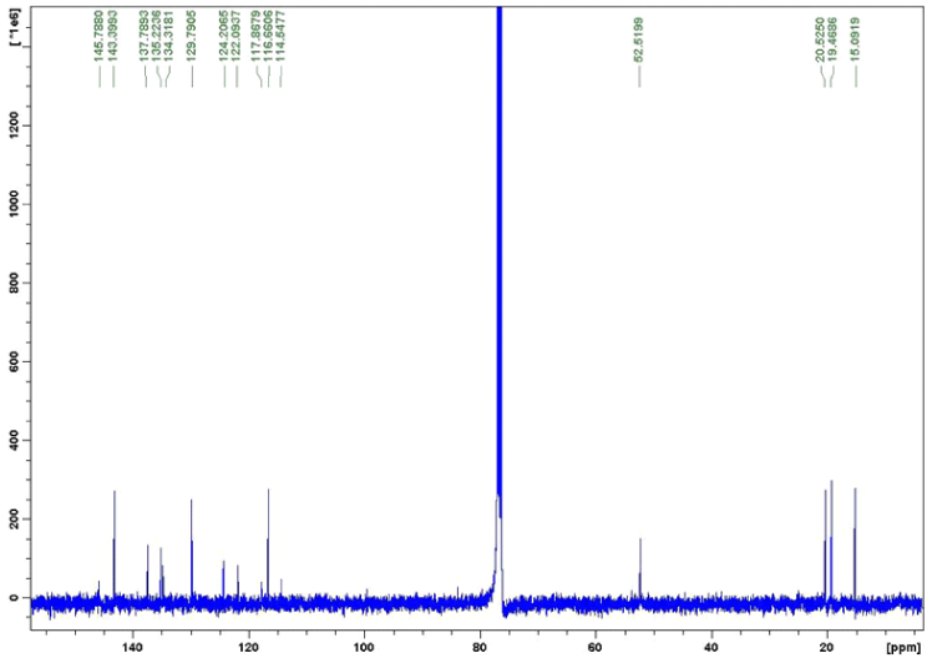


Figure S12: ^{13}C-NMR spectrum of **3d**



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