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Supporting Information

Water-SDS-[BMIm]Br composite system for one-pot multicomponent synthesis of pyrano[2,3-c]pyrazole derivatives and their structural assessment by NMR, X-ray, and DFT studies

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Contents

Experimental section

General

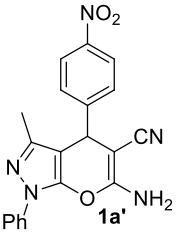
The starting aldehydes (aromatic, aliphatic, heterocyclic etc.), malonitrile, Ethyl acetoacetate, hydrazine, phenyl hydrazine, SDS were purchased from either from Sigma Aldrich chemical Co., USA or Across Organics or SRL India and were used as received. Ionic liquid butyl methyl imidazolium bromide ([BMIm]Br) was prepared in the laboratory using standard protocol. ^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature using Bruker Ascend 400 MHz spectrometers (400 MHz for ^{1}H and 100 MHz for ^{13}C). Chemical shifts were reported in parts per million from the tetramethyl silane internal reference, and coupling constants were reported in Hertz. Proton multiplicities were represented as s (singlet), d (doublet), dd (double doublet), t (triplet), q (quartet), and m (multiplet). FTIR spectra were recorded on Bruker Alpha FTIR spectrometer on Neat or KBr pellets. Mass spectra (HRMS) were obtained from XEVO G2-XS QTOF (Waters) using 70 ev in positive ion mode. The single-crystal X-ray diffraction (XRD) data were collected on a Bruker D8 Venture system with a microfocus optics using Cu Kα radiation. The data were analysed and processed with Bruker Apex III software suite 61 incorporated with multiple tools such as cell_now and RLATT for the determination of the unit cell, SAINT-plus for data reduction, and SADABS for absorption correction. The structure solutions were performed with SHELXT and the full-matrix least-squares refinements were performed with SHELXL suite of programs incorporated in Olex 2.6.For the optimization of geometry of represented compounds the structures were drawn in Gauss view with Gaussian-09W-Gaussview-6 program to obtain the energy minimized structure. The density functional theory (DFT) with the B3LYP correlation function as basis set of calculations have been employed imposing 6-311G(d,p) as additional constraints. Frequency calculations were carried out with the DFT optimized structures using the same basis set to confirm the correctness of optimization and found no imaginary frequency.

Experimental procedure for the synthesis of 1a'-e' and 1f-o:

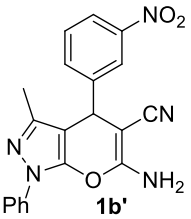
To a mixture of SDS (10 mg, 3.5 mol%), ionic liquid [BMIm]Br (20 mg, 10 mol%), aromatic aldehydes (**2**, 1 mmol), malononitrile (73 mg, 1.1 mmol) in H_2O (4 mL) were stirred at 80^{o}C until the disappearance of aldehydes (TLC, usually 20-40 min.). Then pyrazolones (**6**, 1 mmol) was added in the reaction mixture and continued heating at the same temperature till the complete consumption of pyrazolones (Table 2). After the completion of reaction as

indicated by TLC, the reaction mixture is cooled to 40°C, the solid obtained was filtered, washed with water and recrystallized from recrystallized from ethanol-water (~1:1) mixture.

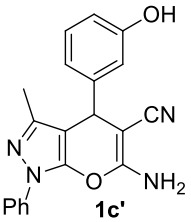
Physical and spectral data 1a'-e' and 1f-o



6-amino-3-methyl-4-(4-nitrophenyl)-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (**1a'**):[1] Yield: 96% (40 min), white solid, m. p. 198-200 °C (lit. m. p. 197-199 °C); IR (KBr) ν_{max} 3320, 3085, 2200, 1675, 1595, 1455, 1335, 1125 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 8.24 (d, *J* = 8.0 Hz, 2H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.51 (t, *J* = 8.0 Hz, 2H), 7.39 (s, 2H), 7.34 (t, *J* = 8.0 Hz, 1H), 4.93 (s, 1H), 1.80 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 160.2, 151.7, 147.1, 145.6, 144.5, 137.9, 129.8, 129.7, 126.8, 124.4, 120.6, 120.2, 98.1, 57.4, 36.8, 13.0.

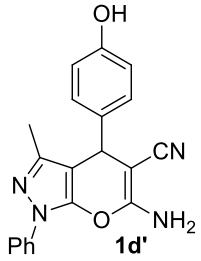


6-amino-3-methyl-4-(3-nitrophenyl)-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (**1b'**):[1] Yield: 95% (50 min), white solid, m. p. 192-194 °C (lit. m. p. 191-193 °C); IR (KBr) ν_{max} 3320, 3095, 2205, 1675, 1590, 1475, 1335, 1250, 1020 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 8.16 (s, 2H), 7.80 (d, *J* = 8.0 Hz, 3H), 7.68 (t, *J* = 8.0 Hz, 1H), 7.50 (t, *J* = 8.0 Hz, 2H), 7.39-7.32 (m, 3H), 4.98 (s, 1H), 1.80 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 160.2, 148.4, 146.4, 145.6, 144.5, 137.9, 135.2, 130.8, 129.8, 126.8, 122.8, 122.7, 120.6, 120.2, 98.1, 57.6, 36.7, 13.1.



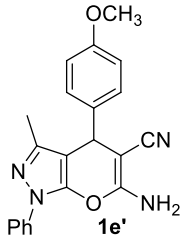
6-amino-4-(3-hydroxyphenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (**1c'**):[2] Yield: 94% (50 min), white solid, m. p. 294-296 °C (lit. m. p. 295-297 °C); IR (KBr) ν_{max} 3380, 3310, 2210, 1660, 1410, 1350 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6)

δ 9.37 (s, 1H), 7.78 (s, 2H), 7.50 (s, 2H), 7.33 (s, 1H), 7.20-7.14 (m, 3H), 6.69-6.62 (m, 3H), 4.59 (s, 1H), 1.83 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 159.9, 158.0, 145.8, 145.6, 144.3, 138.0, 129.9, 129.8, 126.6, 120.5, 120.4, 118.9, 114.9, 114.6, 99.2, 58.8, 37.1, 13.1.



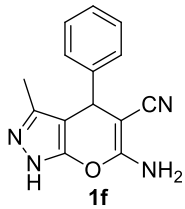
1d'

6-amino-4-(4-hydroxyphenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (**1d'**):[1] Yield: 94% (70 min), white solid, m. p. 206-208 °C (lit. m. p. 208-210 °C); IR (KBr) ν_{max} 3390, 3310, 2210, 1650, 1405, 1300 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.35 (s, 1H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.49 (s, 2H), 7.32 (s, 1H), 7.14 (s, 2H), 7.04 (d, *J* = 8.0 Hz, 2H),6.72 (d, *J* = 8.0 Hz, 2H), 4.56 (s, 1H), 1.79 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 159.7, 156.7, 145.8, 144.2, 138.1, 134.4, 129.8, 129.2, 126.5, 120.6, 120.3, 115.7, 99.5, 59.3, 36.5, 13.1.



1e'

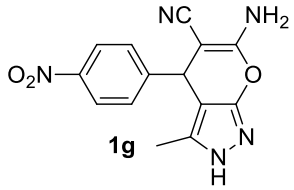
6-amino-4-(4-methoxyphenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (**1e'**):[1] Yield: 95% (70 min), white solid, m. p. 168-170 °C (lit. m. p. 172-174 °C); IR (KBr) ν_{max} 3380, 3310, 2990, 2205, 1670, 1445, 1225, 1105, 1015 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.79 (d, *J* = 8.0 Hz, 2H), 7.49 (t, *J* = 8.0 Hz, 2H), 7.32 (t, *J* = 8.0 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 4H), 6.90 (d, *J* = 8.0 Hz, 2H), 4.63 (s, 1H), 3.75 (s, 3H), 1.79 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 159.7, 158.6, 145.8, 144.3, 138.0, 136.1, 129.8, 129.3, 126.6, 120.5, 120.4, 114.3, 99.3, 59.0, 55.5, 36.4, 13.1.



1f

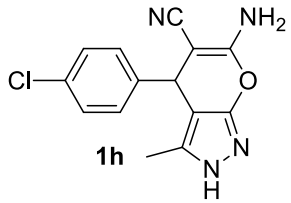
6-amino-3-methyl-4-phenyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile **(1f)**:[3] Yield: 78%, white solid, m. p. 262-264 °C; lit. m. p. 258-259 °C; IR (KBr) ν_{max} 3374, 3311,

3172, 2193, 1045 cm^{-1}; ^1H NMR (400 MHz, DMSO-d6) δ 12.10 (s, 1H), 7.32 (t, *J* = 8.0 Hz, 2H), 7.23 (t, *J* = 8.0 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.88 (s, 2H), 4.60 (s, 1H), 1.79 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d6) δ 161.3, 155.2, 144.9, 136.0, 128.9, 127.9, 127.2, 121.2, 98.1, 57.7, 36.7, 10.2.



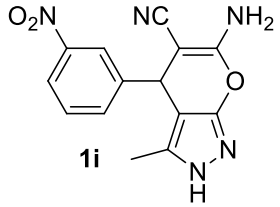
1g

6-amino-3-methyl-4-(4-nitrophenyl)-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (1g):[3] Yield: 96% (40 min), white solid, m. p. 250-252 °C (lit. m. p. 251-253 °C); IR (KBr) ν_{max} 3425, 3231, 2925, 2192, 1644, 1403 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 12.21 (s, 1H), 8.21 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.07 (s, 2H), 4.84 (s, 1H), 1.81 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 161.6, 155.1, 152.6, 146.8, 136.3, 129.3, 124.4, 121.0, 97.0, 56.3, 36.3, 10.2.



1h

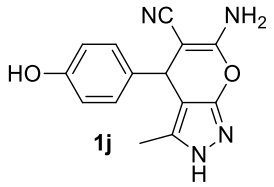
6-amino-4-(4-chlorophenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (1h):[3] Yield: 94% (50 min), white solid, m. p. 232-234 °C (lit. m. p. 234-236 °C); IR (KBr) ν_{max} 3408, 3369, 3307, 2188, 1643 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 12.15 (s, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.94 (s, 2H), 4.64 (s, 1H), 1.80 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 161.4, 155.2, 144.0, 136.1, 131.7, 129.8, 128.9, 121.1, 97.7, 57.2, 36.0, 10.2.



1i

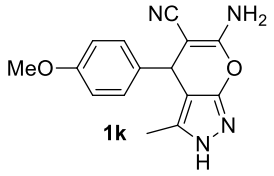
6-amino-3-methyl-4-(3-nitrophenyl)-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (1i):[4] Yield: 94% (50 min), white solid, m. p. 210-212 °C (lit. m. p. 214-216 °C); IR (KBr) ν_{max} 3445, 3230, 2930, 2194, 1602, 1408 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 12.22 (s, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 8.03 (s, 1H), 7.69-7.63 (m, 2H), 7.07 (s, 2H), 4.89 (s, 1H), 1.81

(s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 161.6, 155.2, 148.3, 147.3, 136.4, 134.9, 130.7, 122.5, 122.3, 121.0, 97.1, 56.6, 36.1, 10.2.



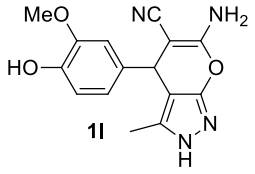
1j

6-amino-4-(4-hydroxyphenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (**1j**):[3] Yield: 94%, white solid, m. p. 224-226 °C (lit. m. p. 222-224 °C); IR (KBr) ν_{max} 3425, 3231, 2925, 2192, 1644, 1403 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.05 (s, 1H), 9.29 (s, 1H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.80 (s, 2H), 6.69 (d, *J* = 8.0 Hz, 2H), 4.47 (s, 1H), 1.79 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 161.1, 156.5, 155.2, 136.0, 135.2, 129.0, 121.4, 115.6, 98.5, 58.2, 36.0, 10.2.



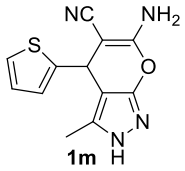
1k

6-amino-4-(4-methoxyphenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (1k):[3] Yield: 94% (70 min), white solid, m. p. 206-208 °C (lit. m. p. 210-212 °C); IR (KBr) ν_{max} 3420, 3249, 2899, 2201, 1644 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.09 (s, 1H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.88-6.84 (m, 4H), 4.54 (s, 1H), 3.73 (s, 3H), 1.79 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 161.1, 158.4, 155.2, 136.9, 136.0, 129.0, 121.3, 114.2, 98.3, 58.0, 55.4, 35.9, 10.2.



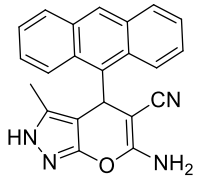
1l

6-amino-4-(4-hydroxy-3-methoxyphenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (1l):[3] Yield: 93% (60 min), white solid, m. p. 230-232 °C (lit. m. p. 234-236 °C); IR (KBr) ν_{max} 3435, 3257, 2887, 2201, 1621, 1407 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.06 (s, 1H), 8.86 (s, 1H), 6.81 (s, 2H), 6.73-6.70 (m. 2H), 6.55 (d, *J* = 8.0 Hz, 1H), 4.50 (s, 1H), 3.71 (s, 3H) 1.82 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 161.1, 155.2, 147.8, 145.7, 136.0, 135.8, 121.4, 120.2, 115.9, 112.1, 98.4, 58.1, 56.1, 36.3, 10.3.



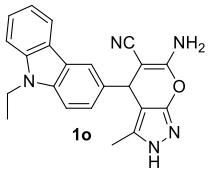
1m

6-amino-3-methyl-4-(thiophen-2-yl)-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (**1m**)[4]: Yield: 92% (120 min), yellowish white solid, m. p. 220-222 °C (lit. m. p. 222-22 °C); IR (KBr) ν_{max} 3365, 3102, 2881, 2282, 1560, 1370, 1220, 1135, 1106, 783 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.18 (s, 1H), 7.38 (d, *J* = 4.0 Hz, 1H), 7.01 (d, *J* = 4.0 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 3H), 5.00 (s, 1H), 1.92 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 161.1, 154.8, 150.2, 136.5, 127.0, 125.4, 124.8, 121.1, 98.0, 58.1, 31.9, 10.2.



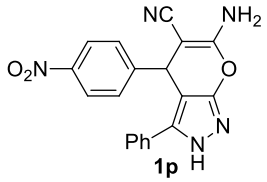
1n

6-amino-4-(anthracen-9-yl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (**1n**): Yield: 87% (720 min), yellowish solid, m. p. 190-192 °C; IR (KBr) ν_{max} 3394, 3297, 3171, 2888, 2188, 1719, 1636, 1541, 1391, 1155, 1046, 1012, 878, 832, 775, 716 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.02 (s, 1H), 8.71 (d, *J* = 8.0 Hz, 1H), 8.70 (s, 1H), 8.15-8.05 (m, 3H), 7.61-7.54 (m, 2H), 7.44 (t, *J* = 8.0 Hz, 1H), 7.34 (t, *J* = 8.0 Hz, 1H), 6.96 (s, 2H), 6.40 (s, 1H), 1.19 (d, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 161.1, 155.1, 135.7, 133.4, 132.1, 131.2, 131.1, 130.1, 129.8, 129.5, 128.4, 127.1, 125.5, 125.1, 124.5, 124.0, 120.8, 99.1, 58.1, 29.8, 9.8; HRMS calcd. for ($C_{22}H_{16}N_4O$ +H+) 353.1402 found 353.1402.

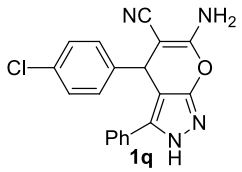


1o

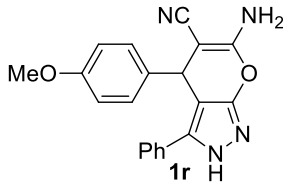
6-amino-4-(9-ethyl-9H-carbazol-3-yl)-3-methyl-2,4-dihydro- pyrano[2,3-c]pyrazole-5-carbonitrile (**1o**): Yield: 85% (720 min), yellowish white solid, m. p. 200-202 °C; IR (KBr) ν_{max} 3352, 3177, 2970, 2192, 1652, 1600, 1482, 1392, 1332, 1223, 1150, 1103, 1039, 752 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.08 (s, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 7.98 (s, 1H), 7.59-7.53 (m, 2H), 7.44 (t, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.17 (t, *J* = 8.0 Hz, 1H), 6.86 (s, 2H), 4.77 (s, 1H), 4.41 (d, *J* = 8.0 Hz, 2H), 1.76 (s, 3H), 1.32 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 161.1, 155.2, 140.3, 139.0, 136.1, 135.6, 126.1, 126.0, 122.5, 122.3, 121.5, 120.8, 119.5, 119.1, 109.6, 109.5, 98.9, 58.7, 37.5, 36.9, 14.3, 10.3. HRMS calcd ($C_{22}H_{19}N_5O$+H+) 370.1668 found 370.1668.



6-amino-4-(4-nitrophenyl)-3-phenyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (1p):[5] Yield: 95% (60 min), yellowish white solid, m. p. 222-224 °C (lit. m. p. 224-226 °C); IR (KBr) ν_{max} 3438, 3286, 3122, 2871, 2186, 1646, 1597, 1515, 1419, 1351, 1066, 977, 768 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 13.01 (s, 1H), 8.08 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.33-7.26 (m, 3H), 7.12 (s, 2H), 5.28 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 160.8, 156.3, 152.5, 146.7, 138.7, 129.2, 129.1, 129.0, 128.8, 126.7, 124.1, 120.7, 96.8, 57.4, 36.7.

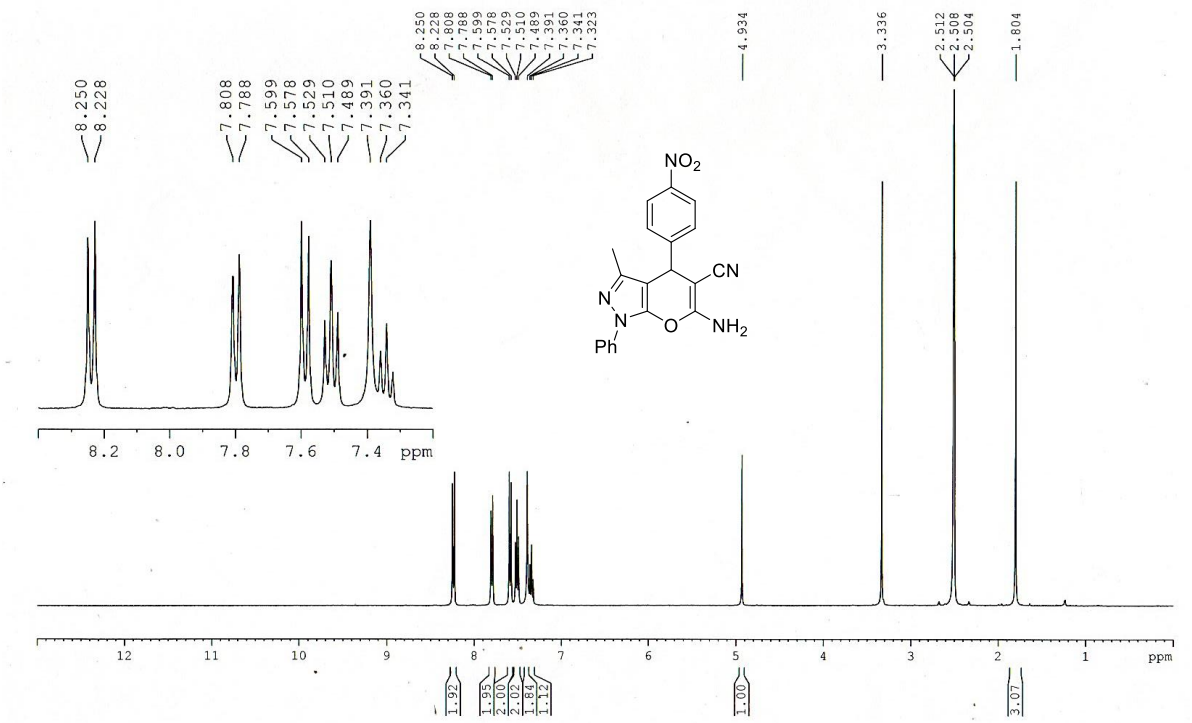


6-amino-4-(4-chlorophenyl)-3-phenyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (1q):[6] Yield: 94% (60 min), white solid, m. p. 252-254 °C (lit. m. p. 254-256 °C); IR (KBr) ν_{max} 3435, 3290, 3139, 3065, 2189, 1643, 1597, 1493, 1409, 1218, 1093, 978, 767 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 12.94 (s, 1H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.34-7.25 (m, 5H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.01 (s, 2H); 5.07 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 160.6, 156.4, 144.0, 138.5, 131.6, 129.7, 129.1, 128.9, 128.8, 128.7, 126.7, 121.0, 97.4, 58.2, 36.5.

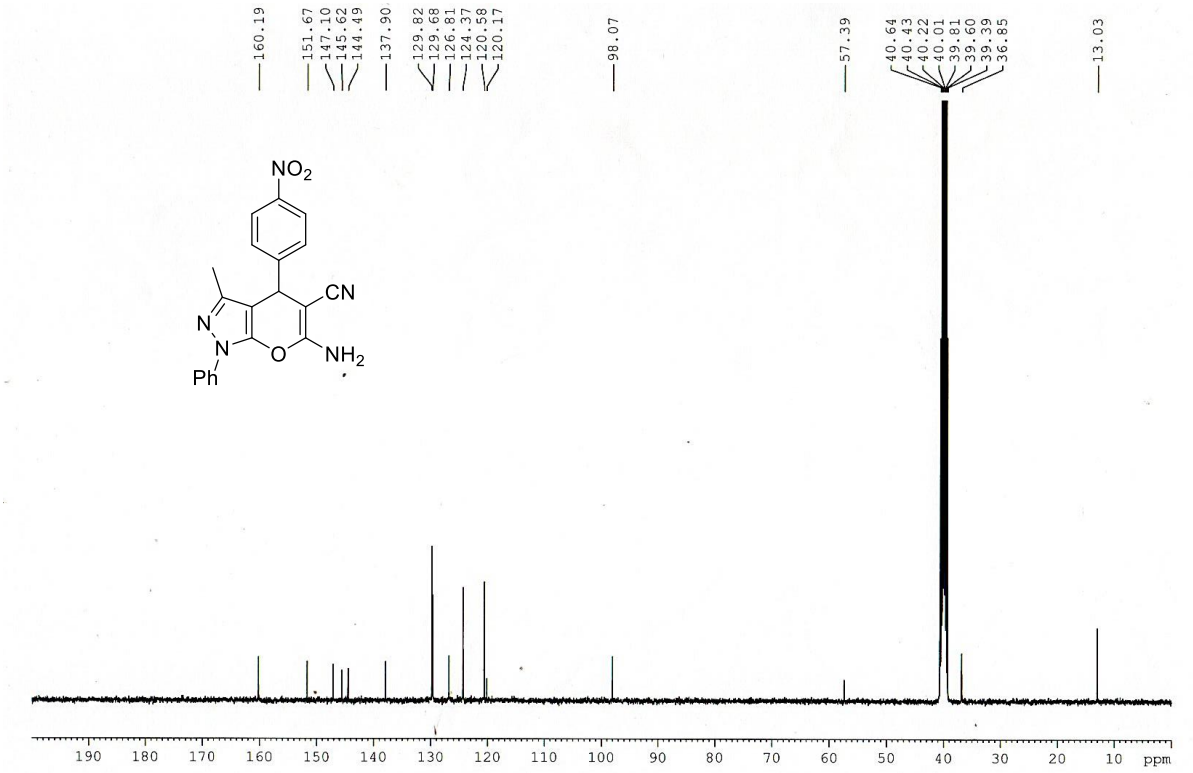


6-amino-4-(4-methoxyphenyl)-3-phenyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (1r):[5] Yield: 93% (80 min), yellowish white solid, m. p. 220-222 °C (lit. m. p. 225-227 °C); IR (KBr) ν_{max} 3411, 3302, 3282, 2192, 1639, 1509, 1449, 1408, 1259, 1170, 1063, 1031 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 12.89 (s, 1H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.31-7.26 (m, 3H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.90 (s, 1H), 6.76 (d, *J* = 8.0 Hz, 2H), 4.94 (s, 1H), 3.66 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 160.3, 158.3, 156.5, 138.2, 137.3, 129.1, 129.0, 128.8, 128.7, 126.6, 121.1, 114.1, 98.1, 59.2, 55.4, 36.5.

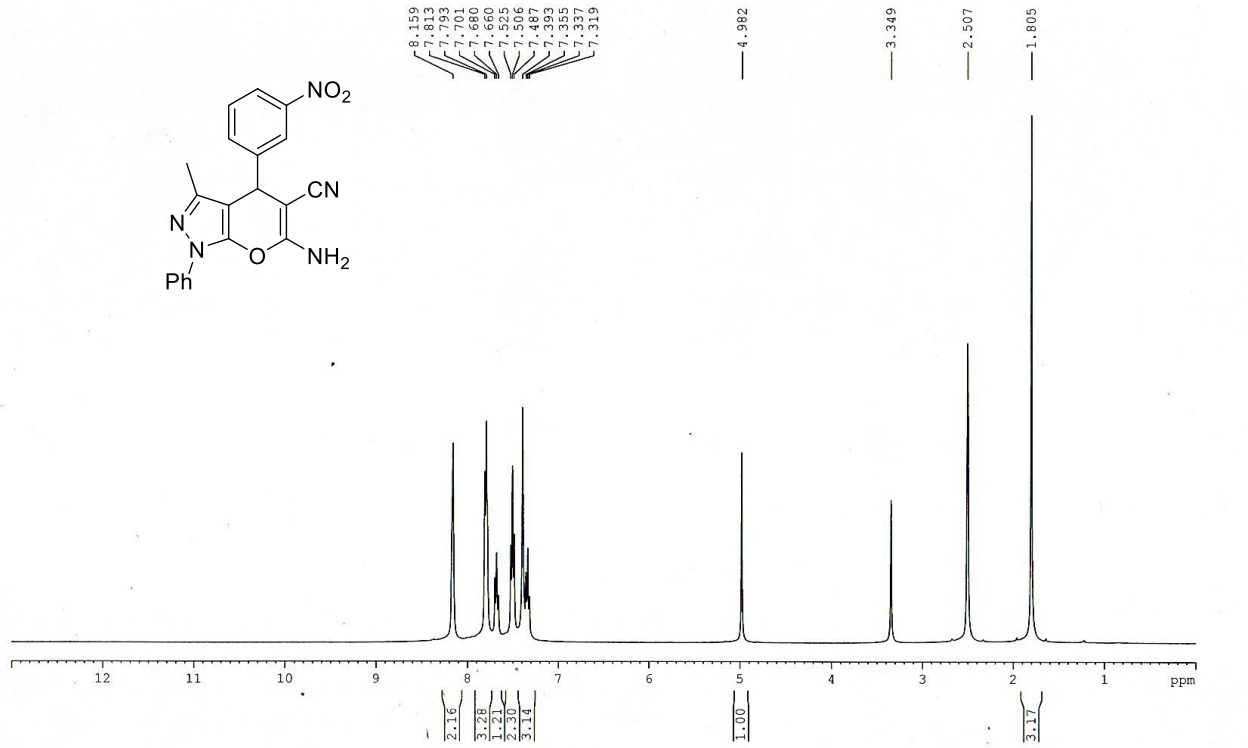
^{1}H NMR of **1a'** (400 MHz, DMSO-d_6)



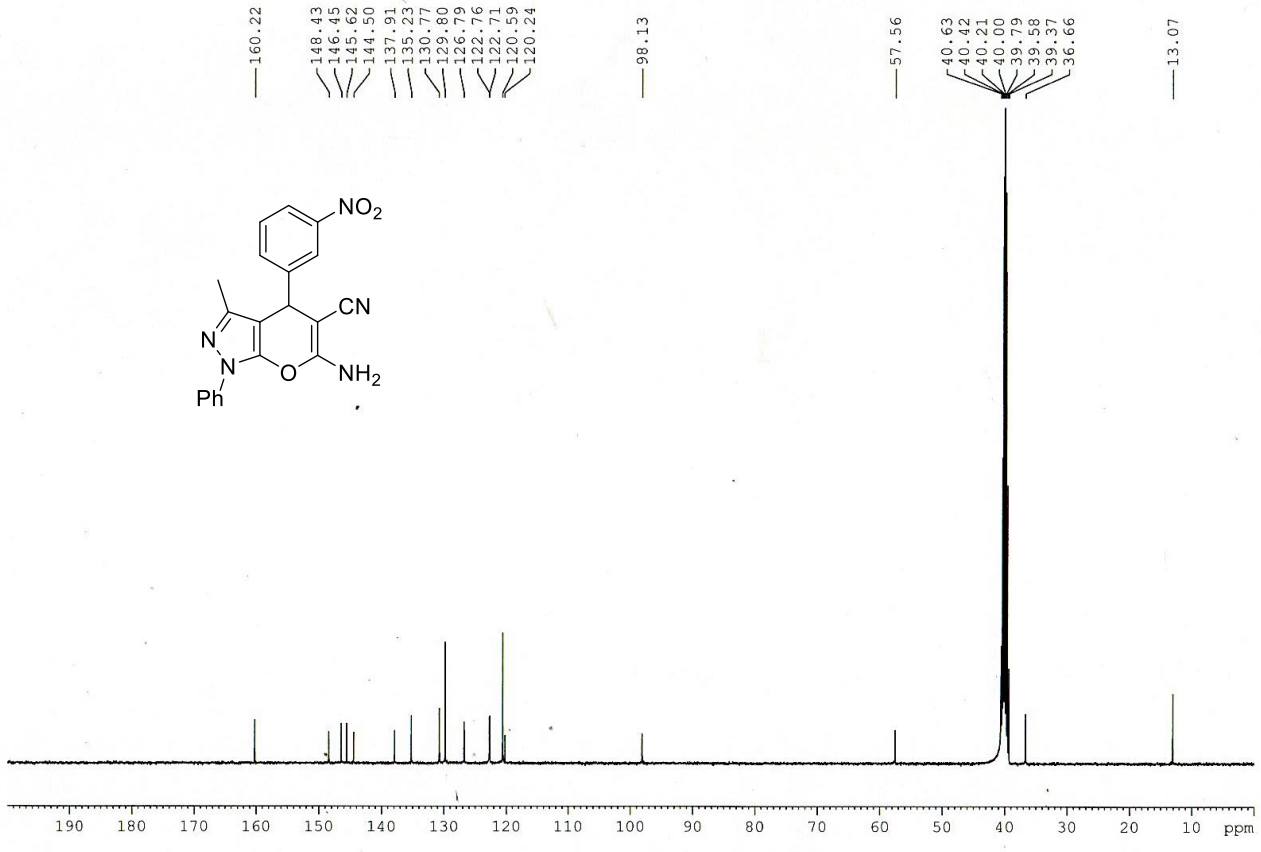
^{13}C NMR of **1a'** (100 MHz, DMSO-d_6)



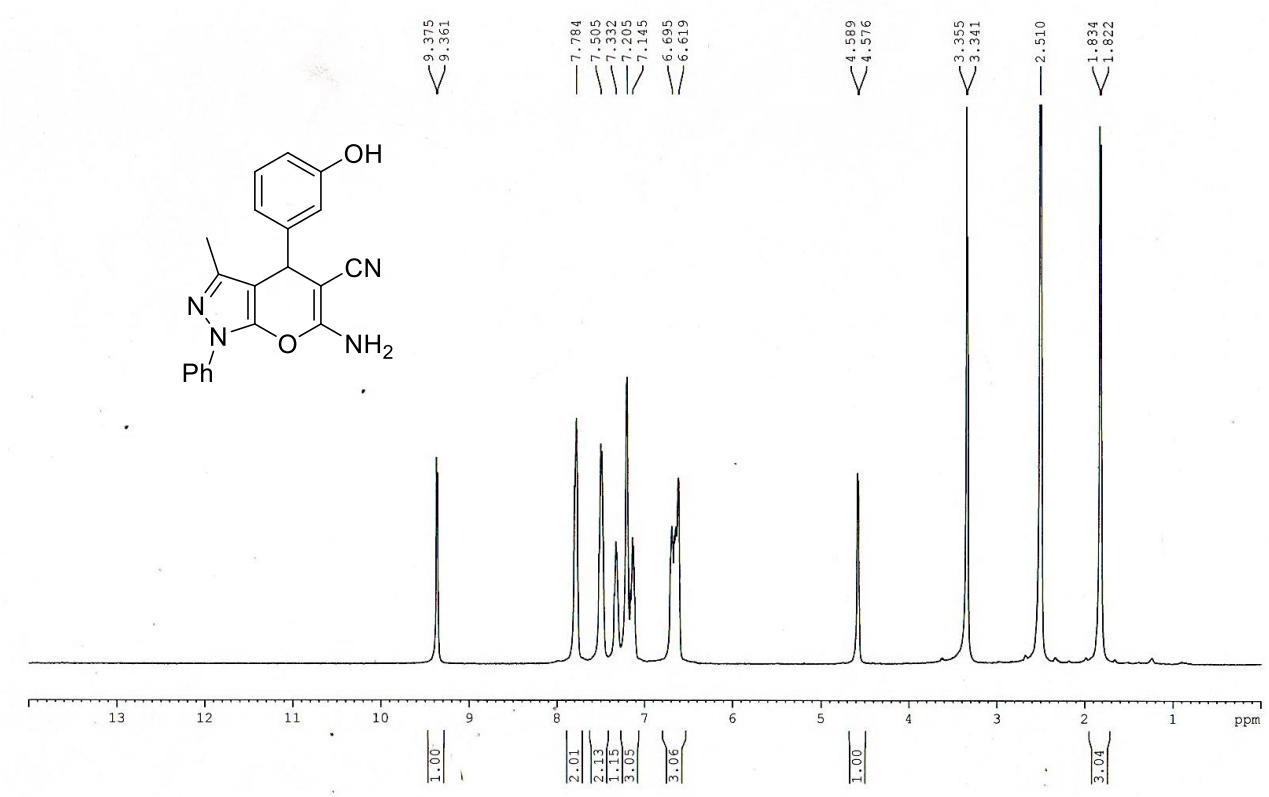
^{1}H NMR of **1b'** (400 MHz, DMSO-d_6)



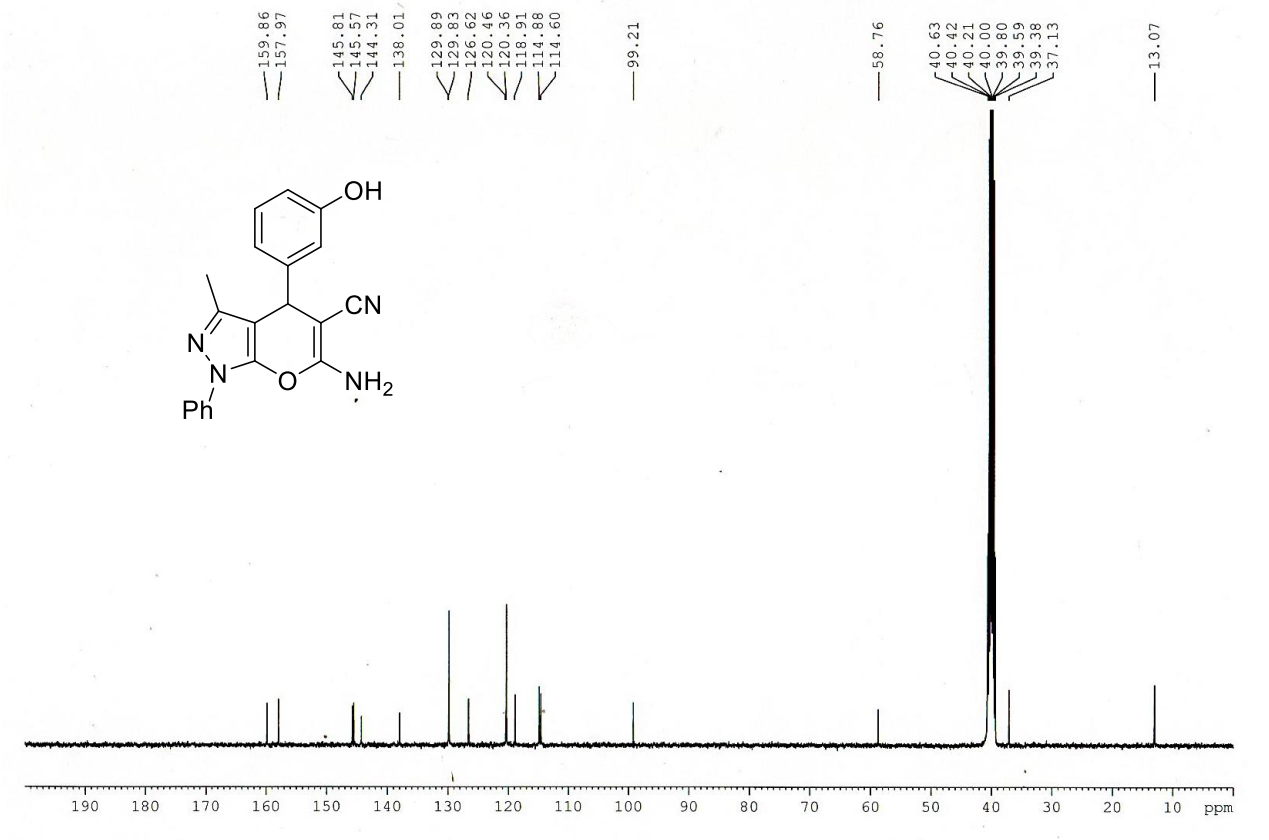
^{13}C NMR of **1b'** (100 MHz, DMSO-d_6)



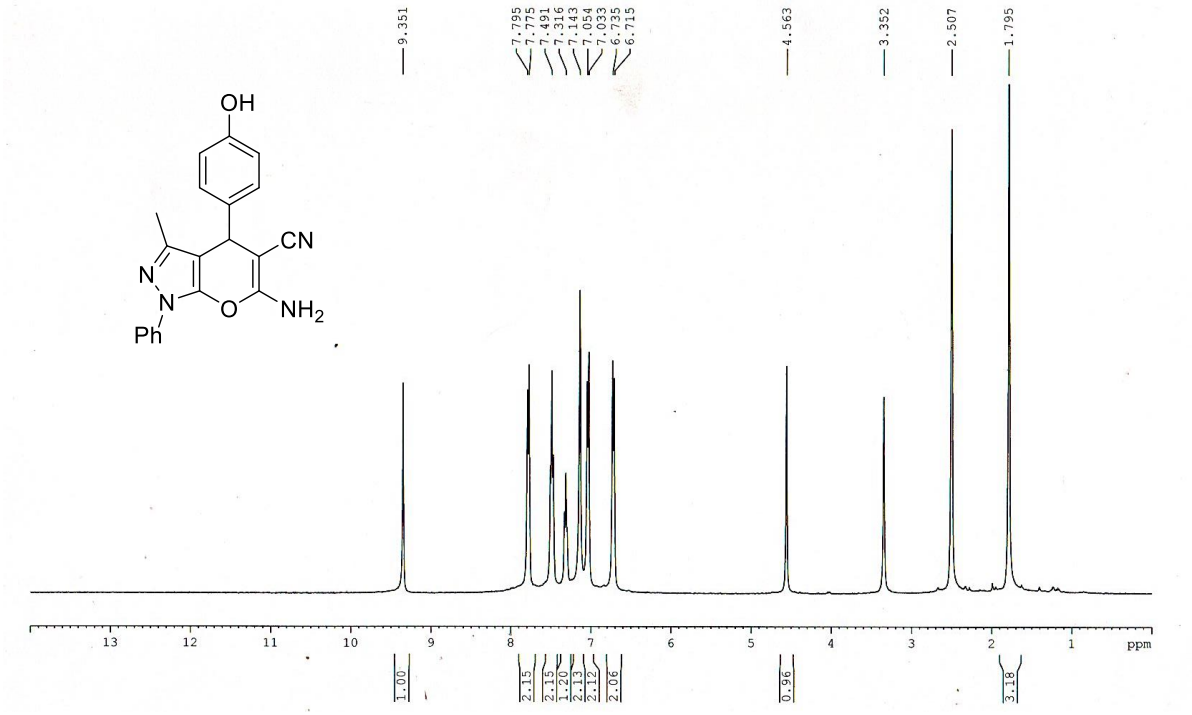
^{1}H NMR of **1c'** (400 MHz, DMSO-d_6)



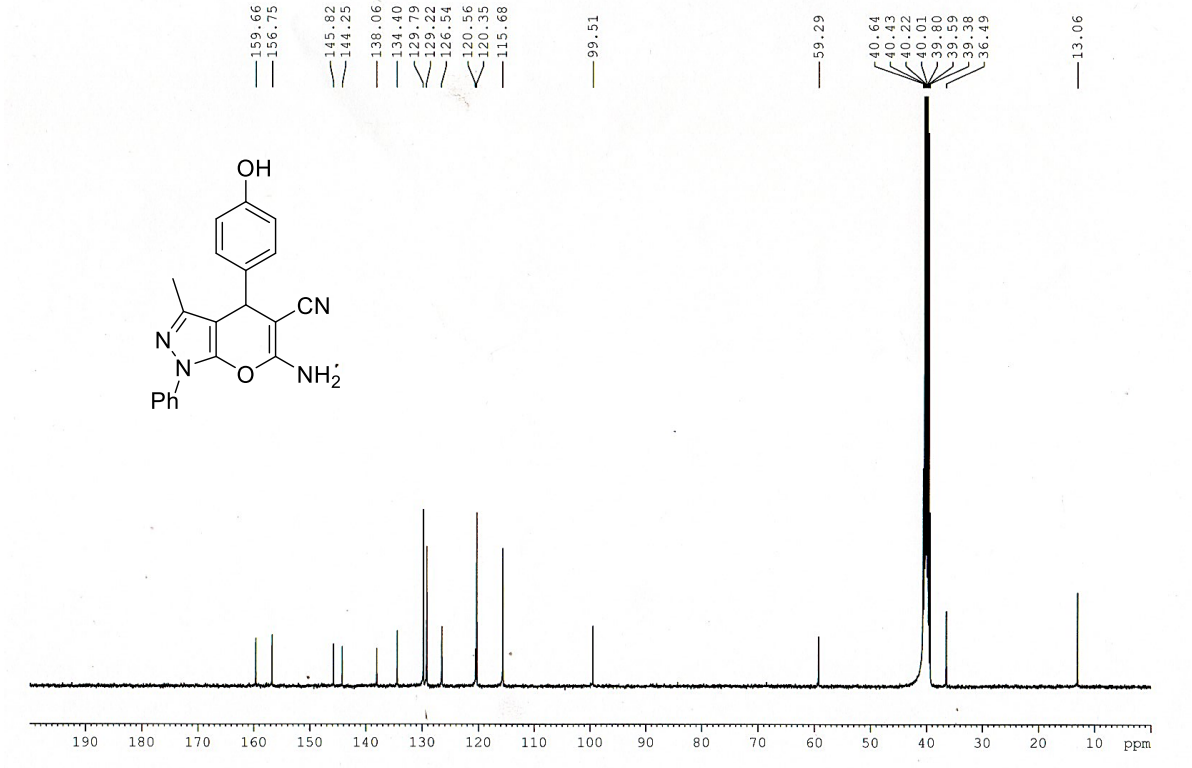
^{13}C NMR of **1c'** (100 MHz, DMSO-d_6)



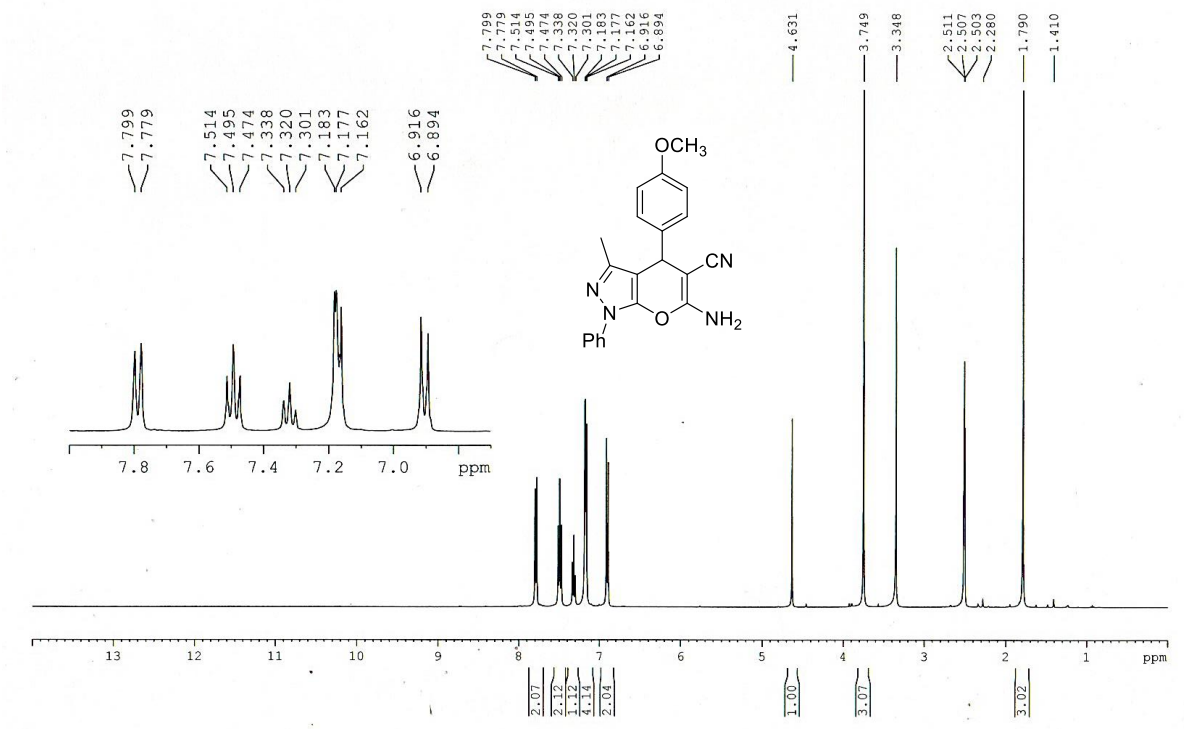
^{1}H NMR of **1d'** (400 MHz, DMSO-d_6)



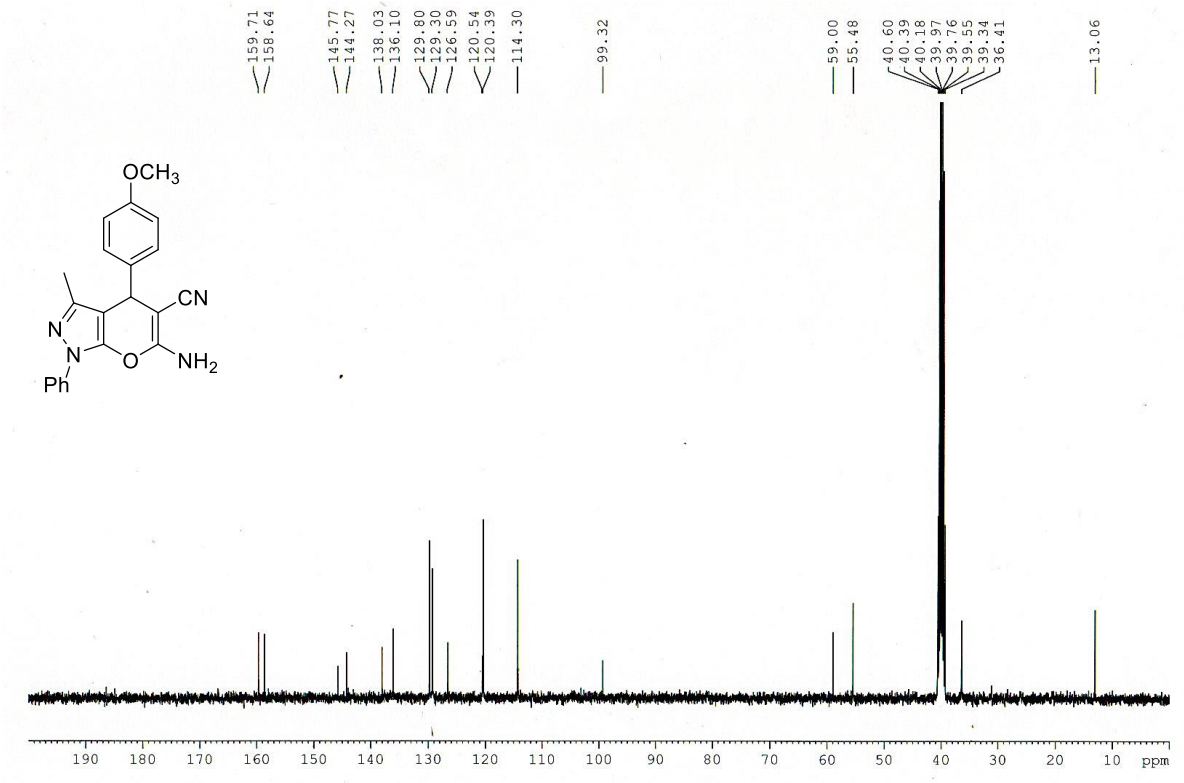
^{13}C NMR of **1d'** (100 MHz, DMSO-d_6)



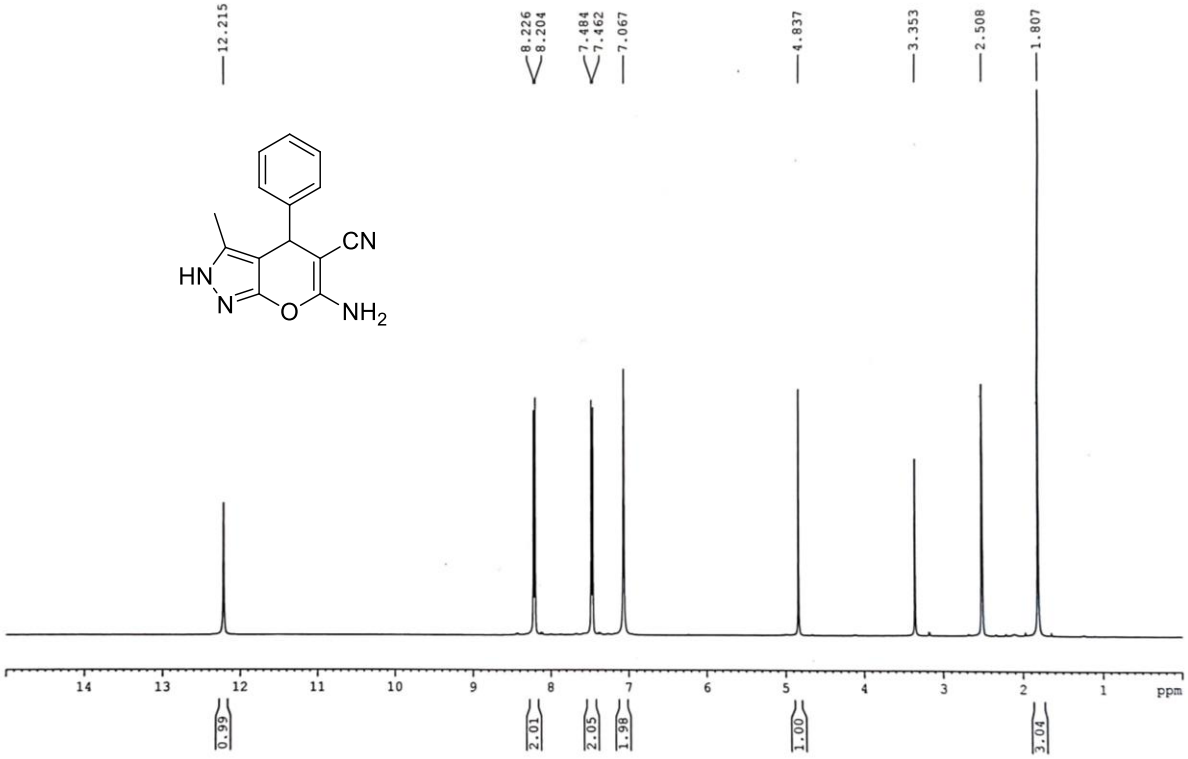
^{1}H NMR of **1e'** (400 MHz, DMSO-d_6)



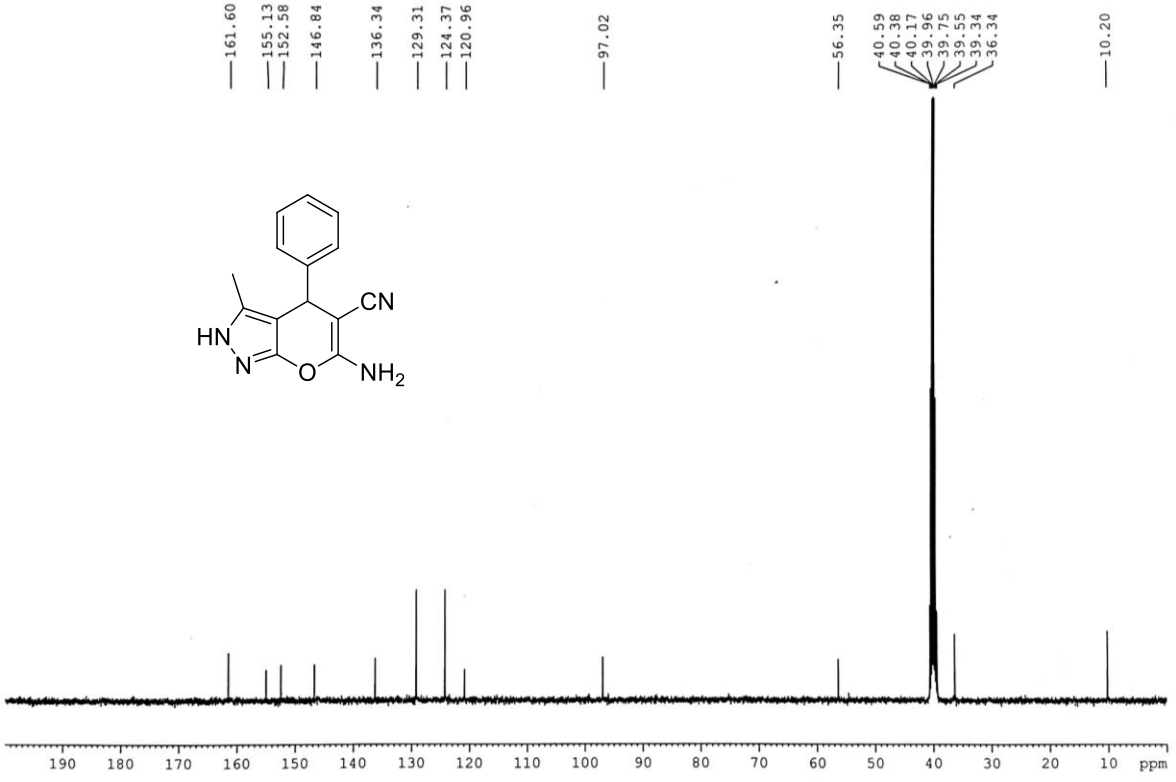
^{13}C NMR of **1e'** (100 MHz, DMSO-d_6)



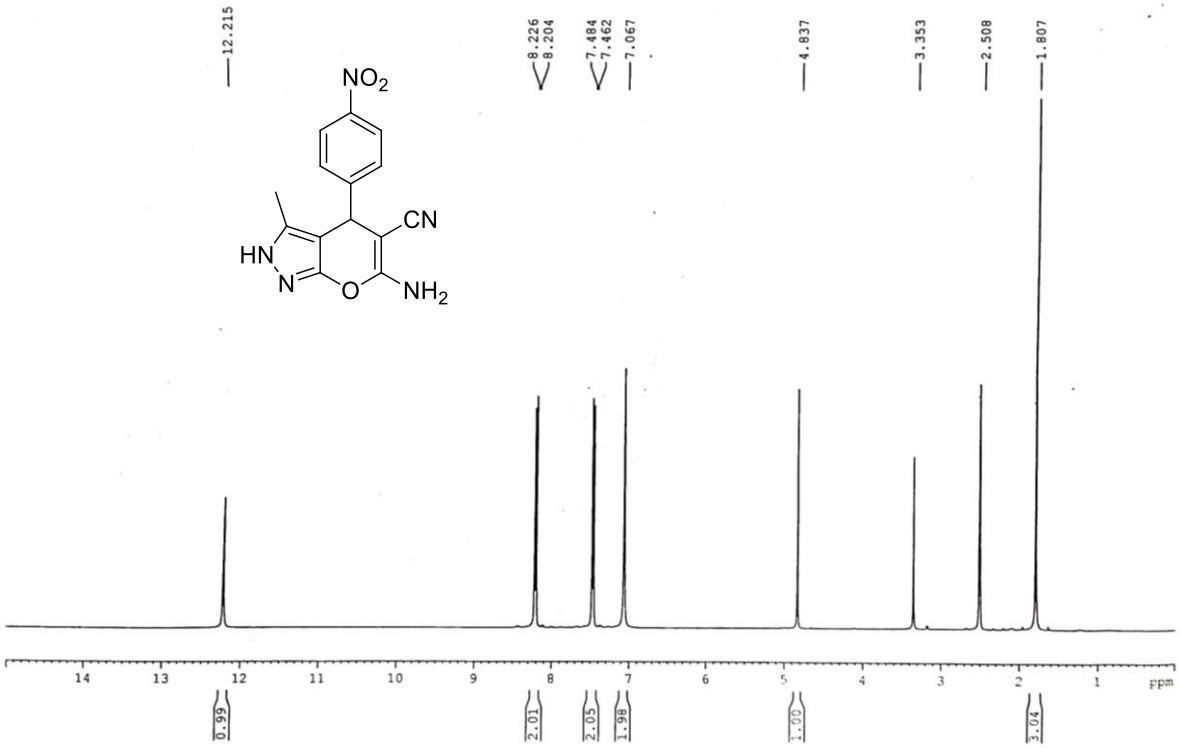
^{1}H NMR of **1f** (400 MHz, DMSO-d_6)



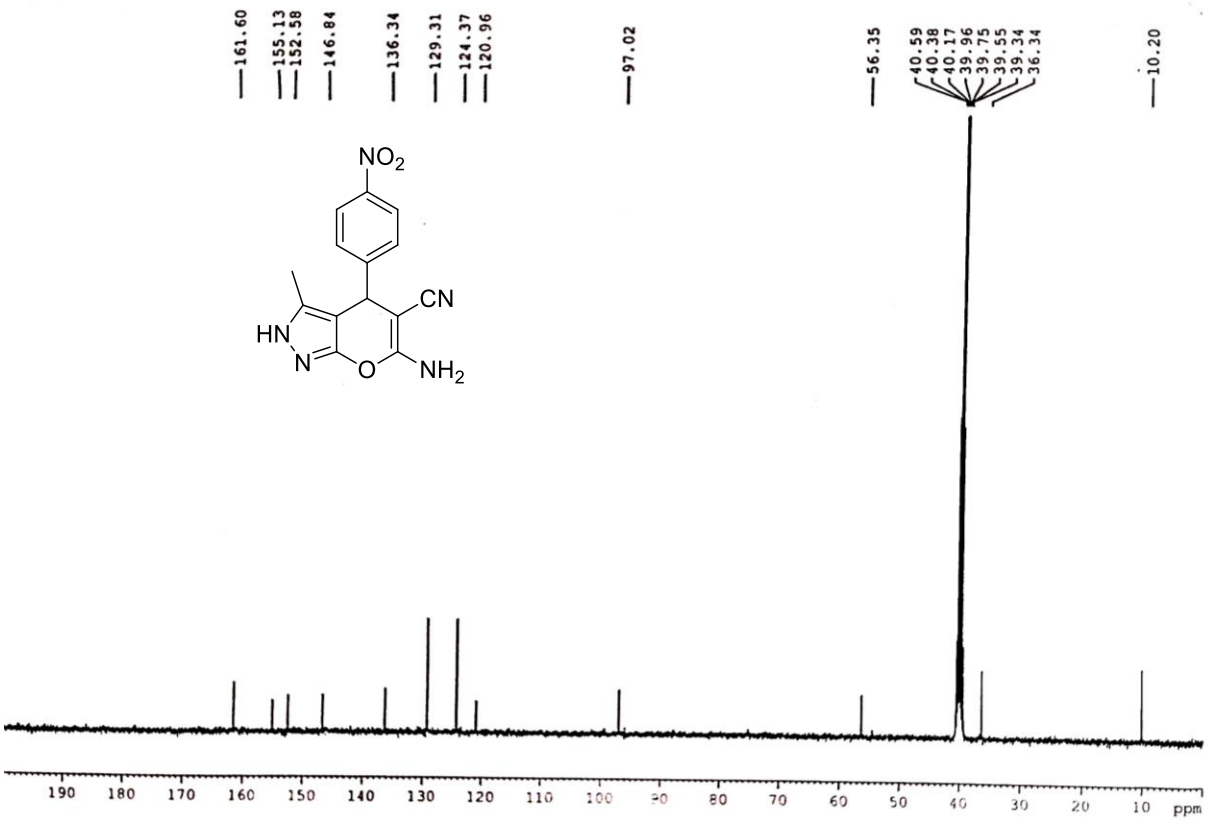
^{13}C NMR of **1f** (100 MHz, DMSO-d_6)



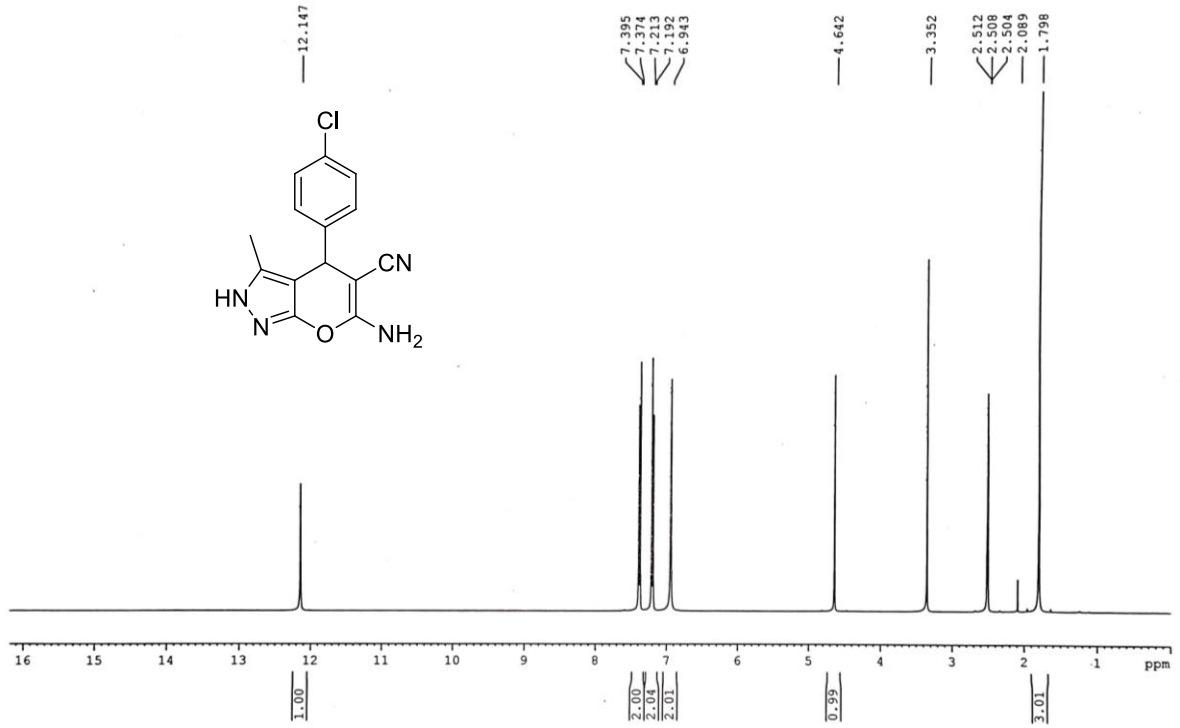
^{1}H NMR of **1g** (400 MHz, DMSO-d_6)



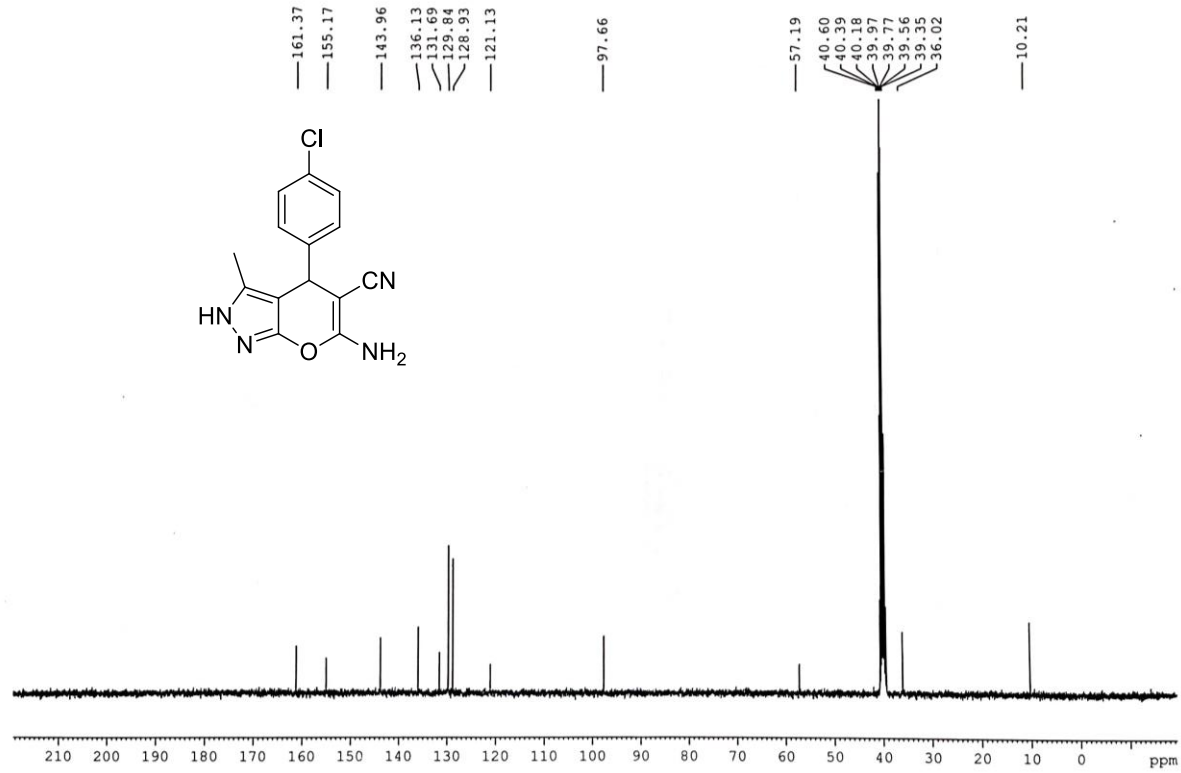
^{13}C NMR of **1g** (100 MHz, DMSO-d_6)



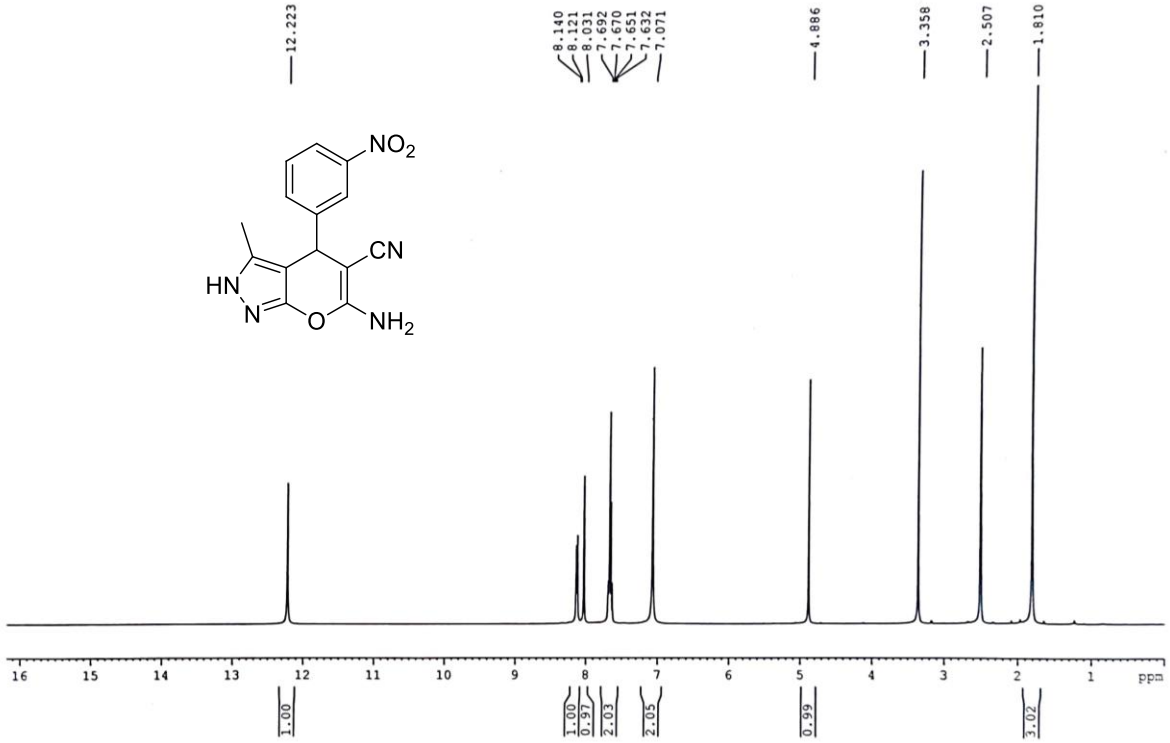
^{1}H NMR of **1h** (400 MHz, DMSO-d_6)



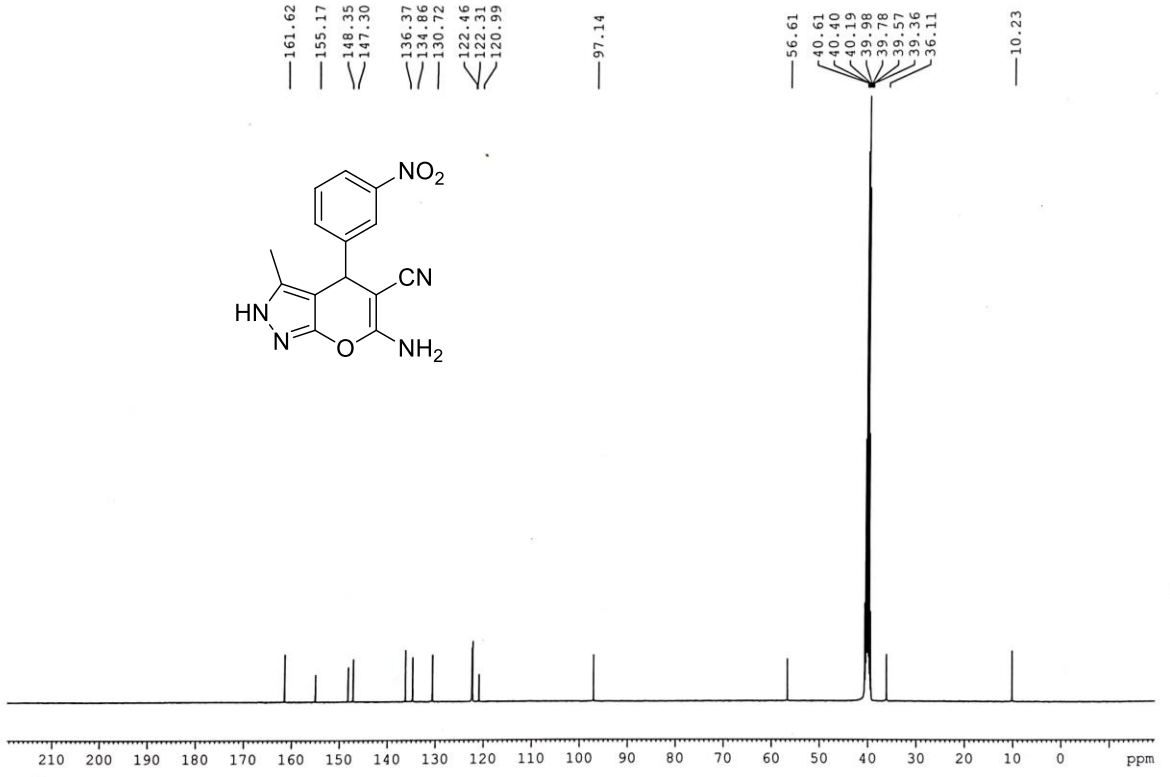
^{13}C NMR of **1h** (100 MHz, DMSO-d_6)



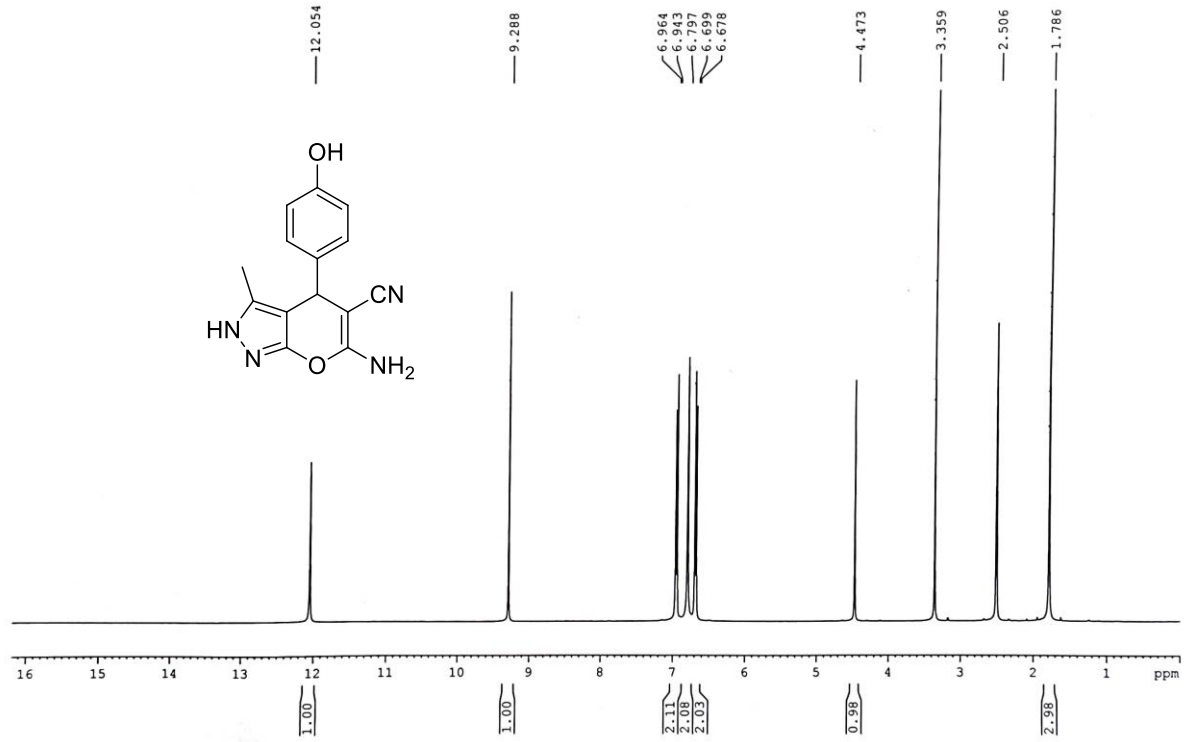
^{1}H NMR of **1i** (400 MHz, DMSO-d_6)



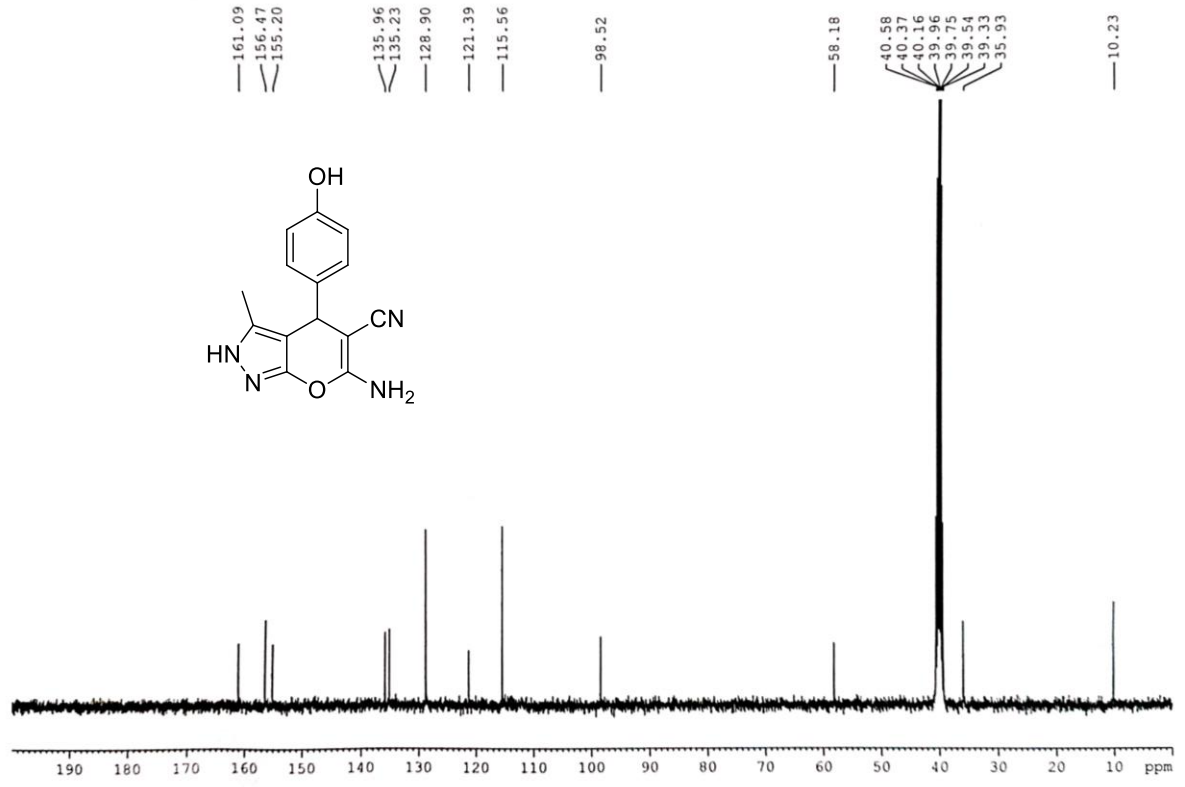
^{13}C NMR of **1i** (100 MHz, DMSO-d_6)



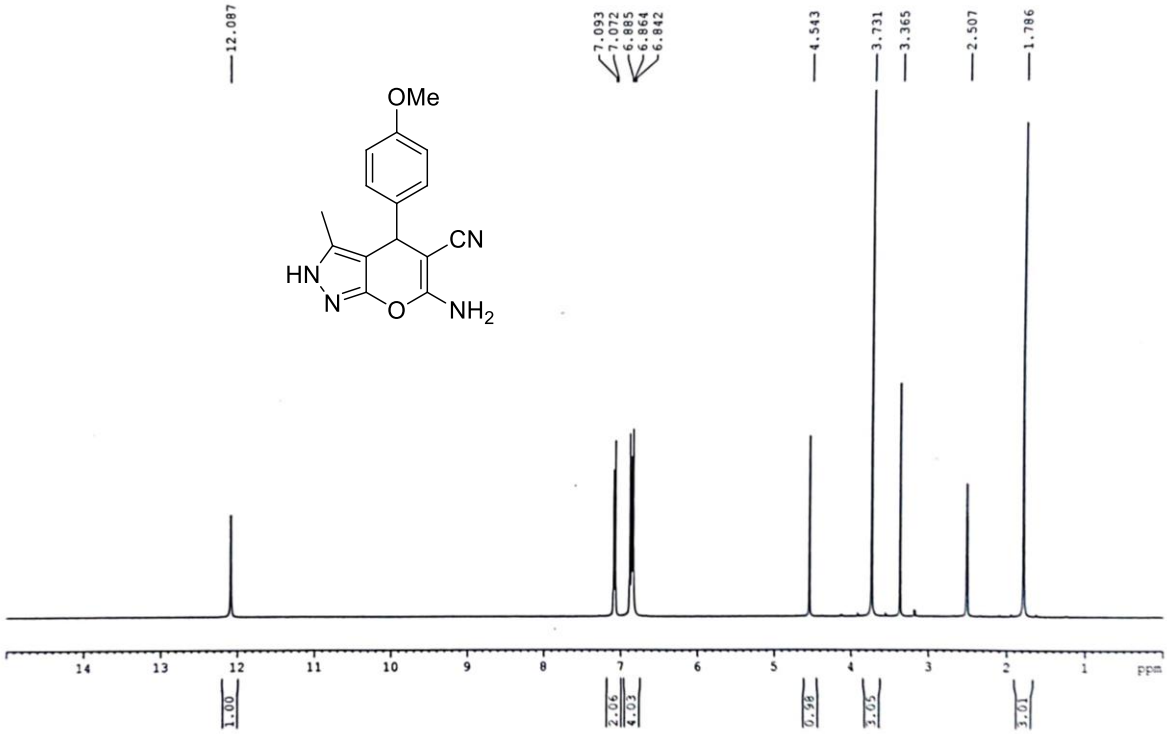
^{1}H NMR of **1j** (400 MHz, DMSO-d_6)



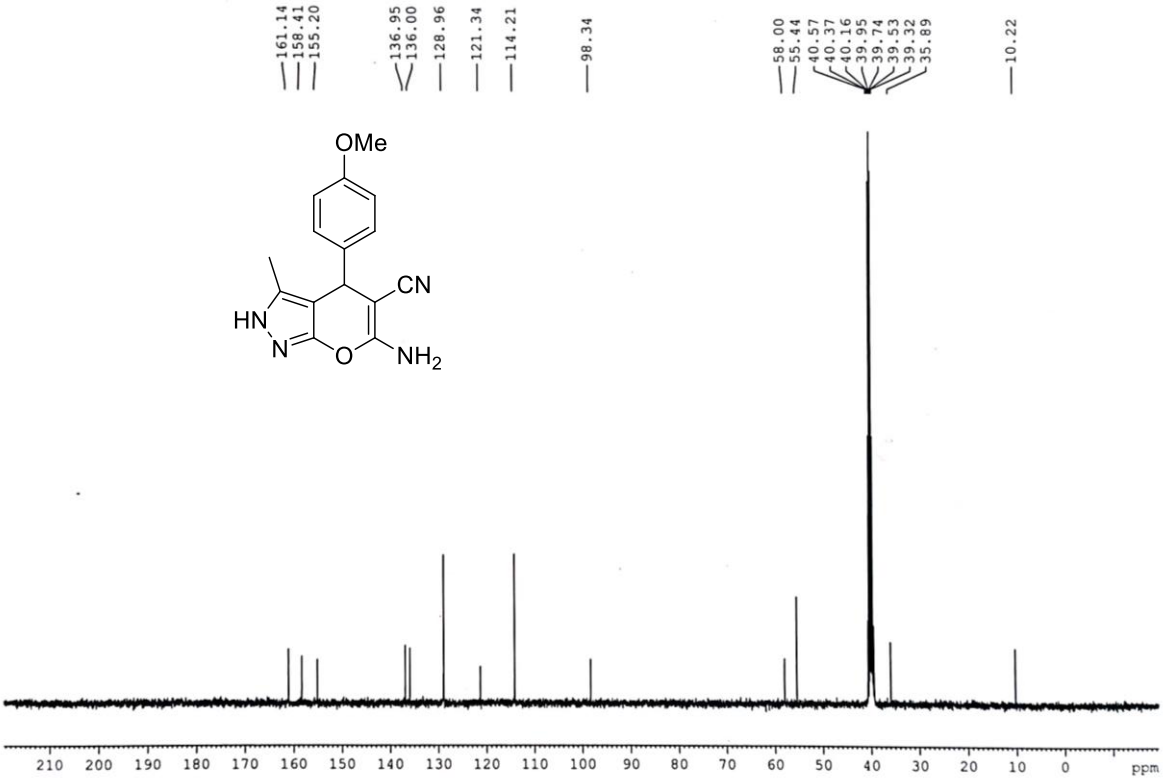
^{13}C NMR of **1j** (100 MHz, DMSO-d_6)



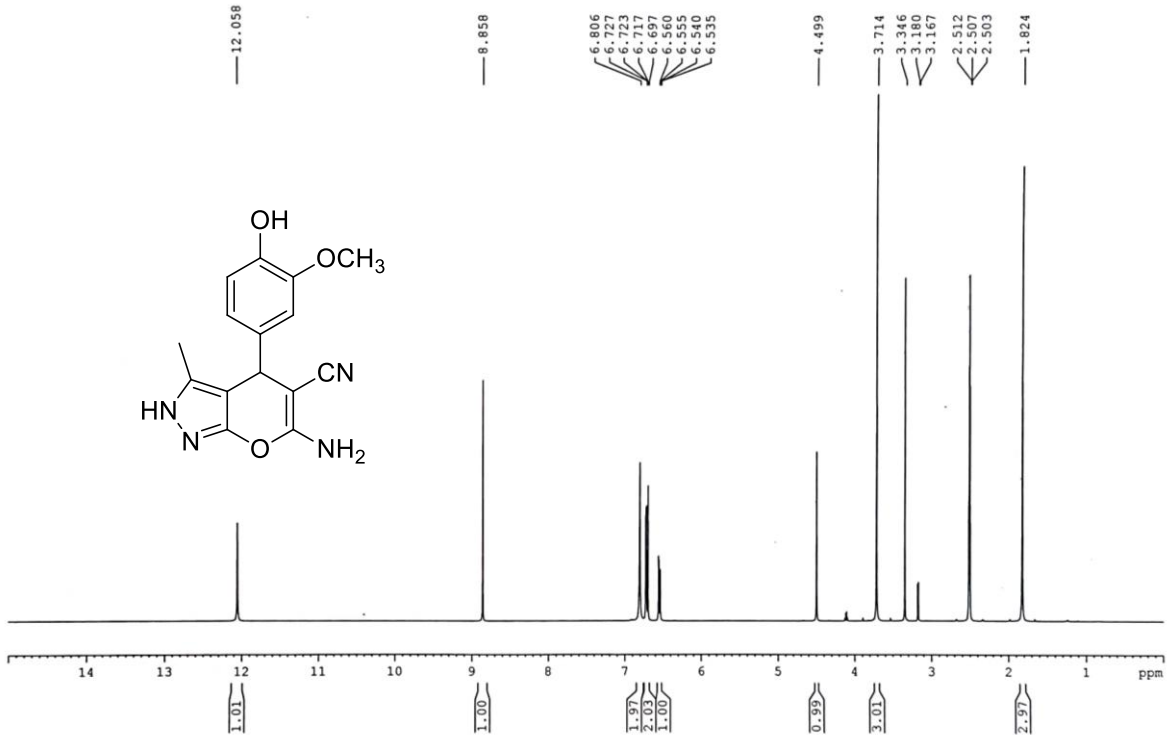
^{1}H NMR of **1k** (400 MHz, DMSO-d_6)



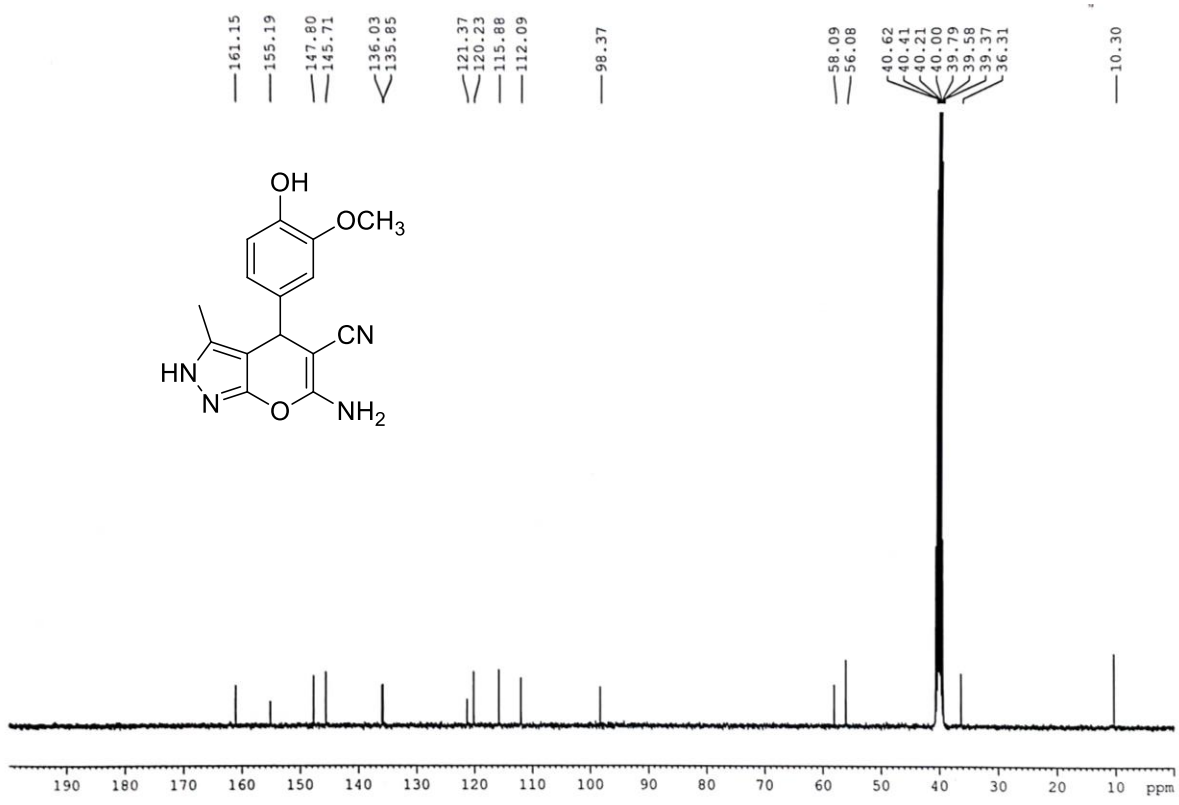
^{13}C NMR of **1k** (100 MHz, DMSO-d6)



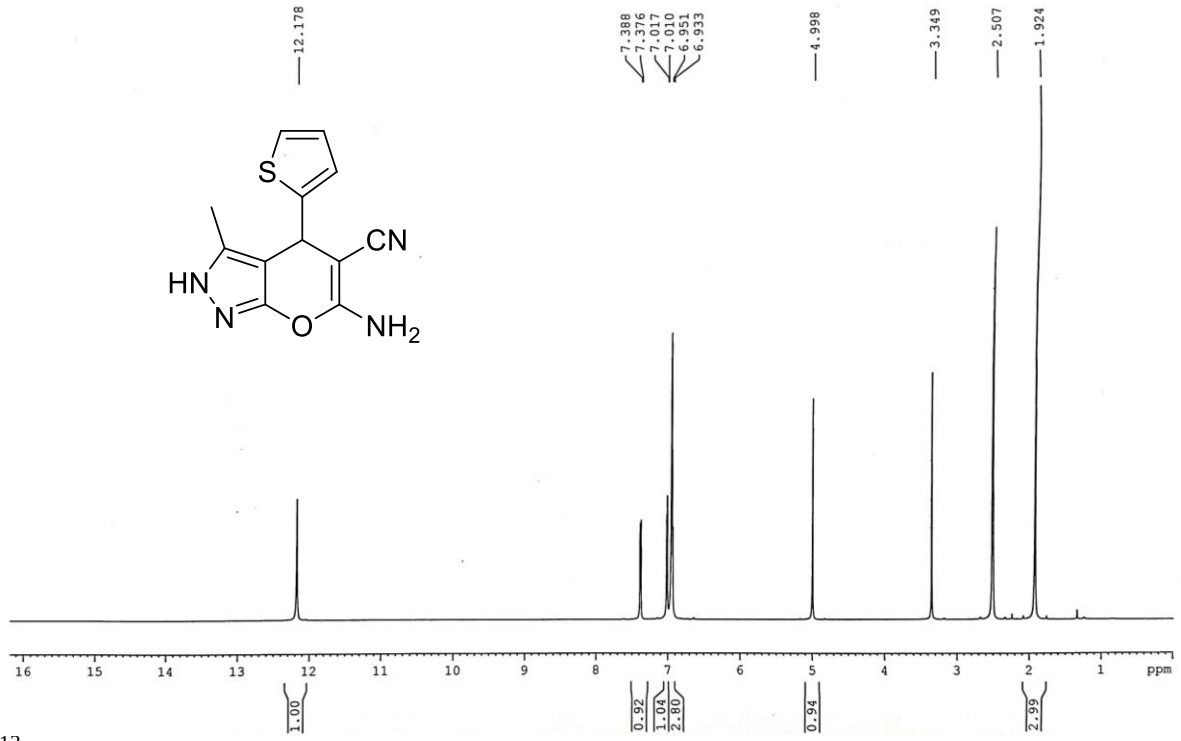
^{1}H NMR of **1l** (400 MHz, DMSO-d6)



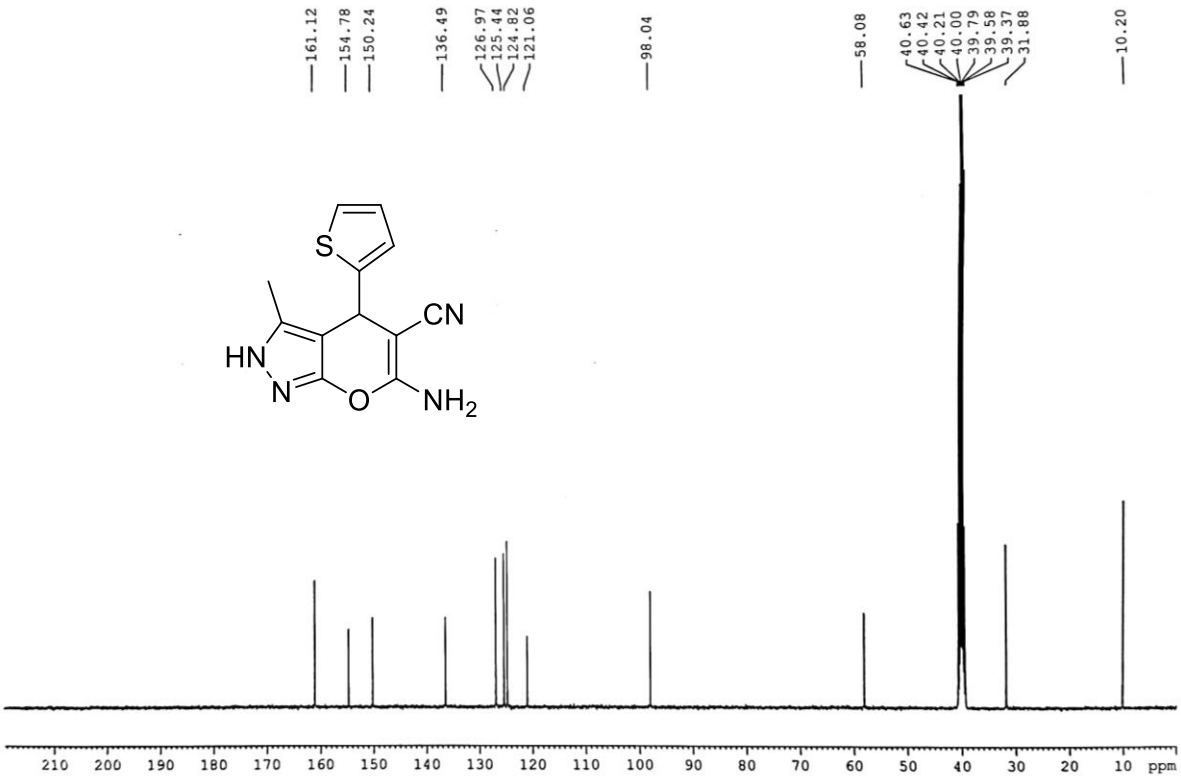
^{13}C NMR of **1l** (100 MHz, DMSO-d6)



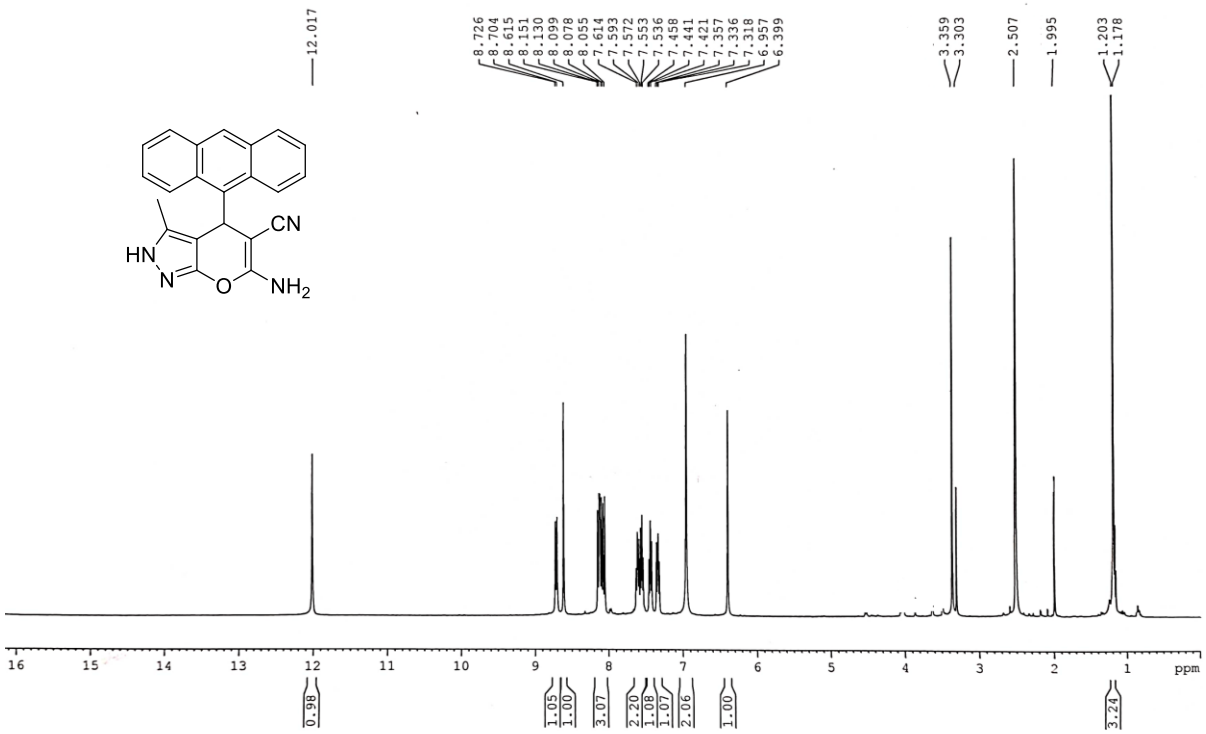
^{1}H NMR of **1m** (400 MHz, DMSO-d_6)



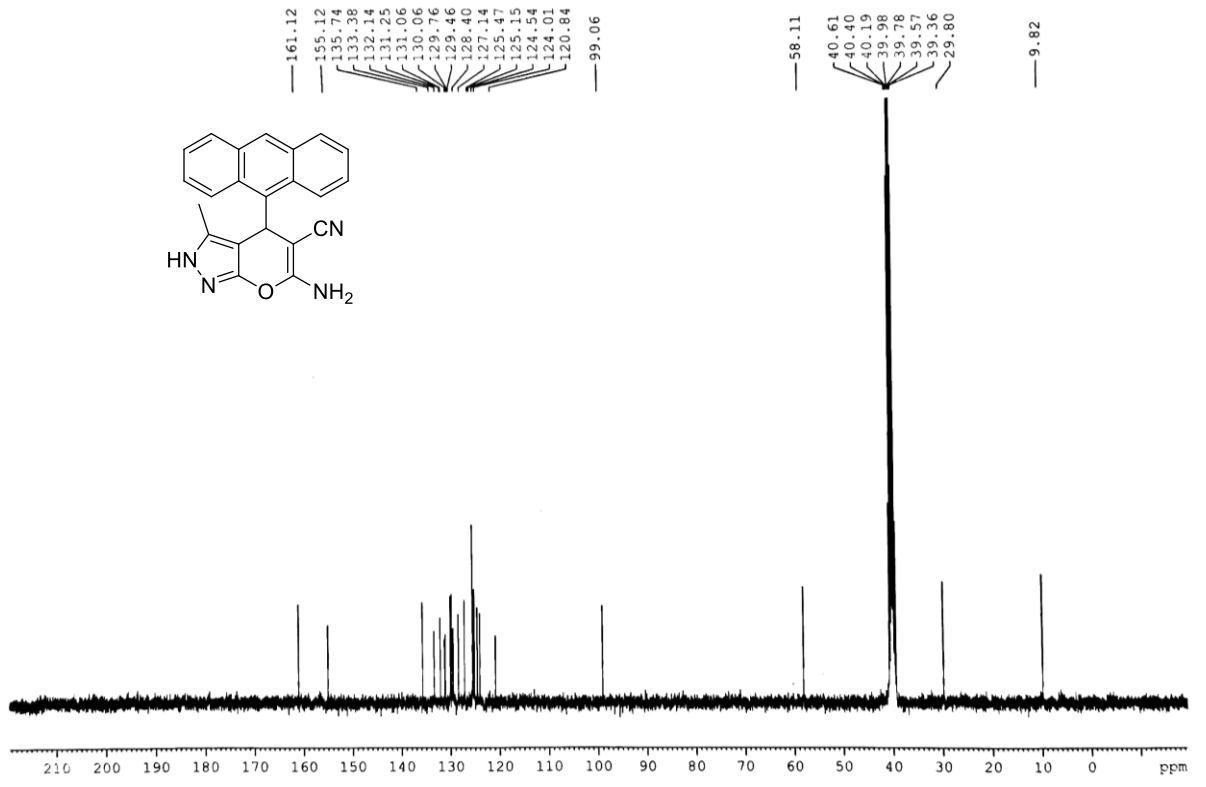
^{13}C NMR of **1m**(100 MHz, DMSO-d_6)



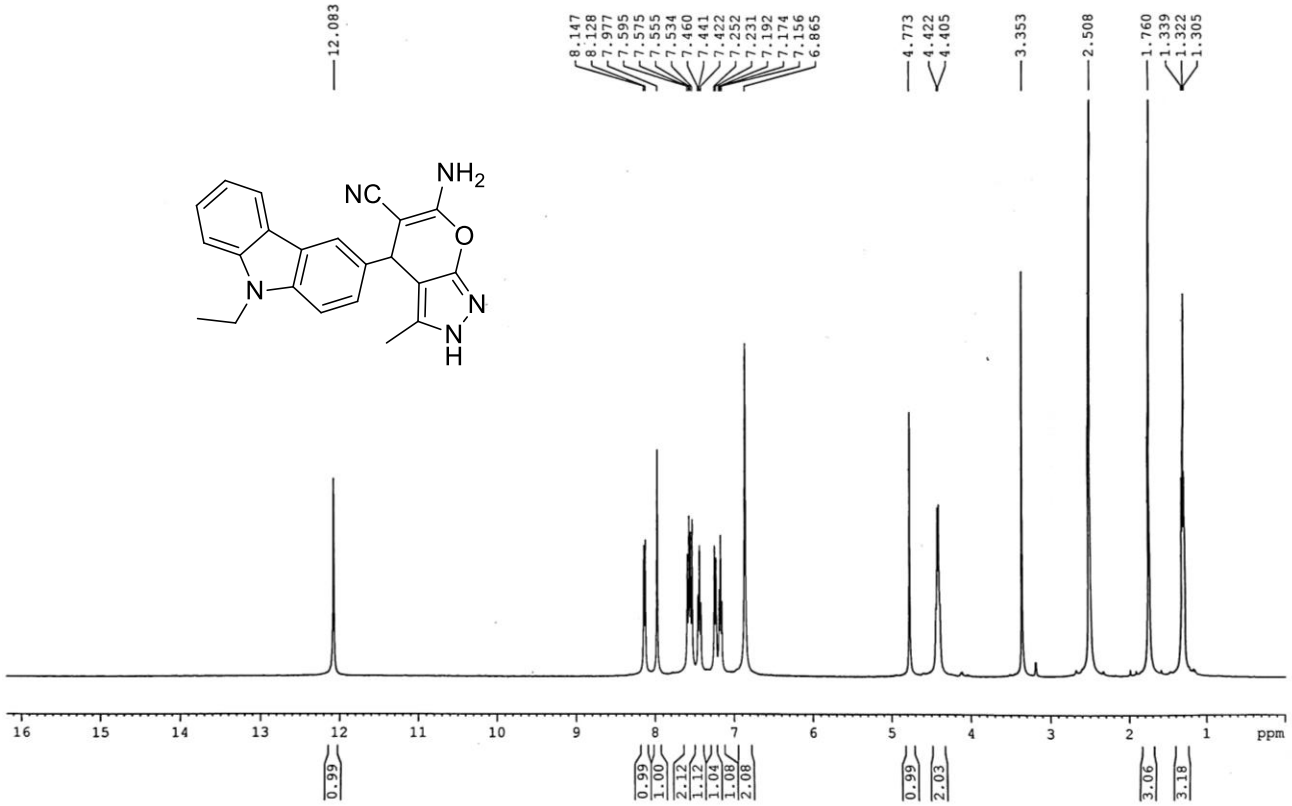
^{1}H NMR of **1n** (400 MHz, DMSO-d_6)



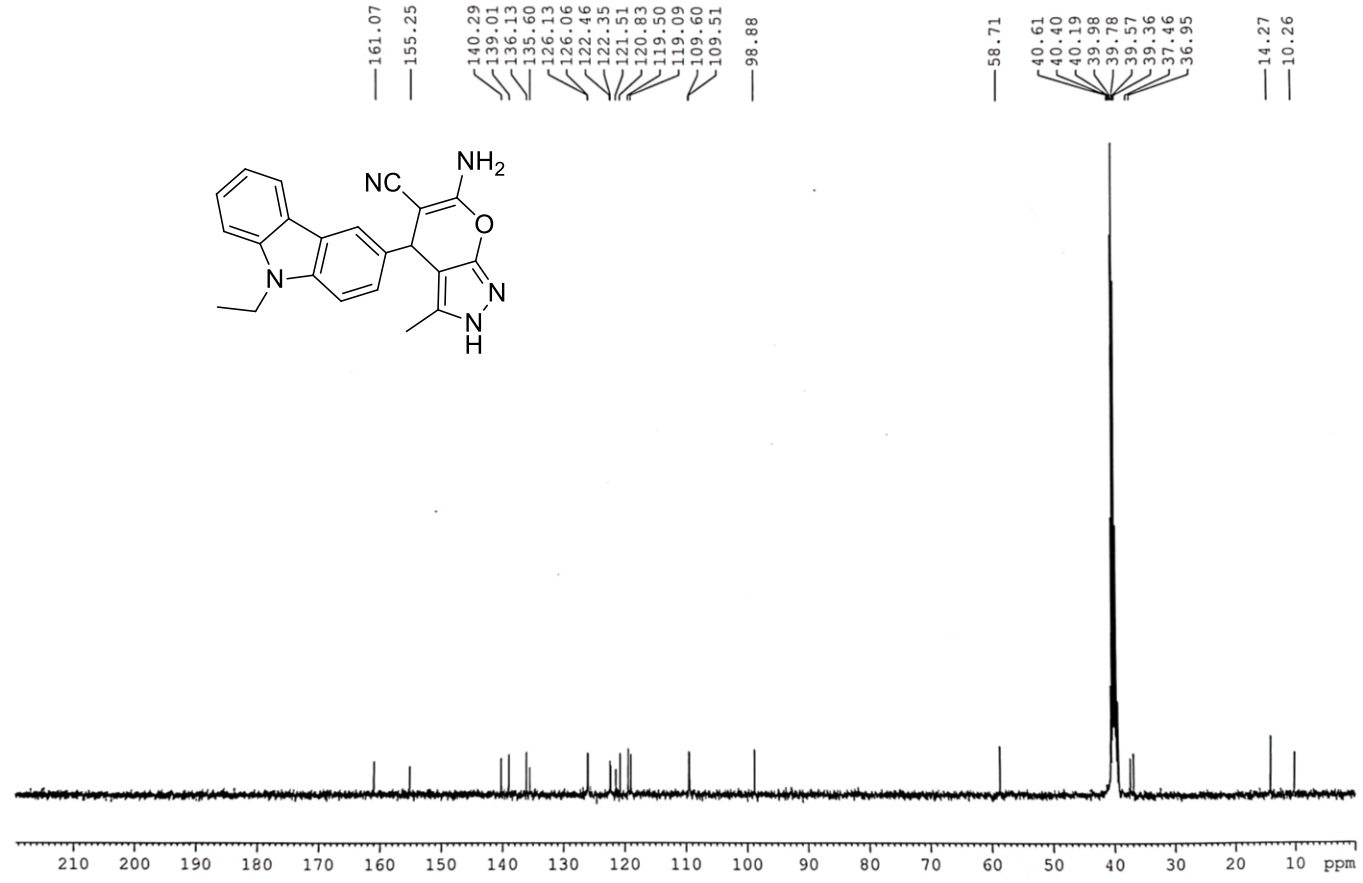
^{13}C NMR of **1n** (100 MHz, DMSO-d_6)



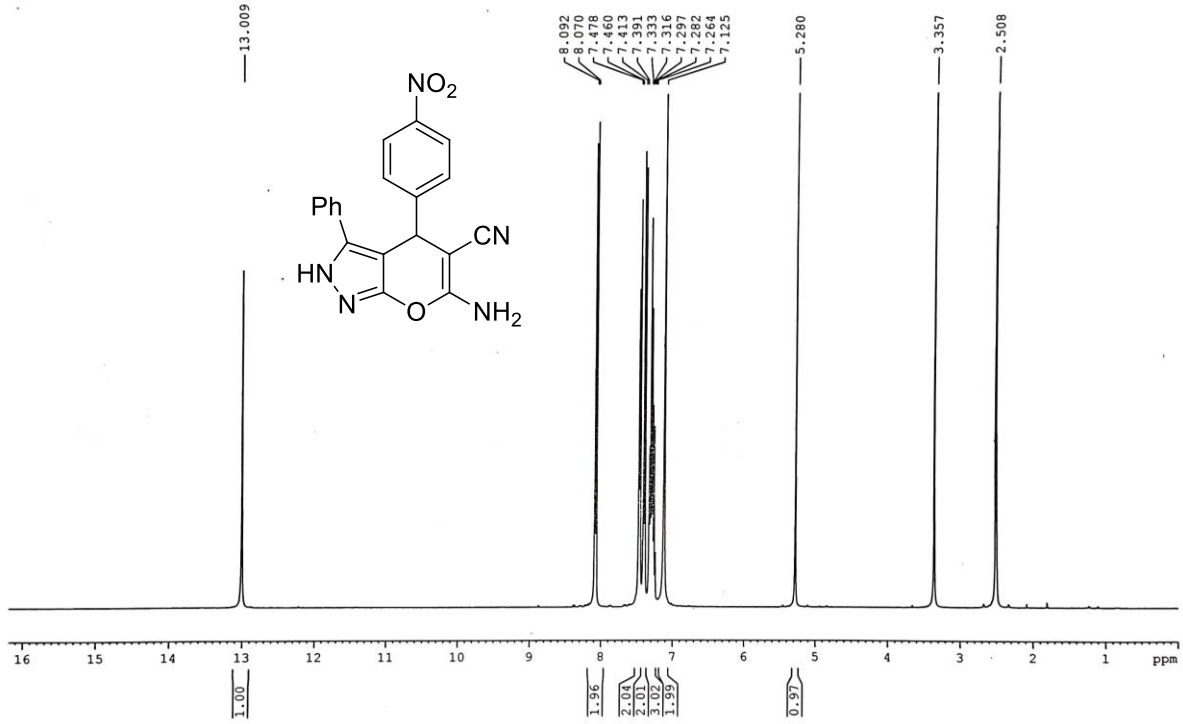
^{1}H NMR of **1o**(400 MHz, DMSO-d_6)



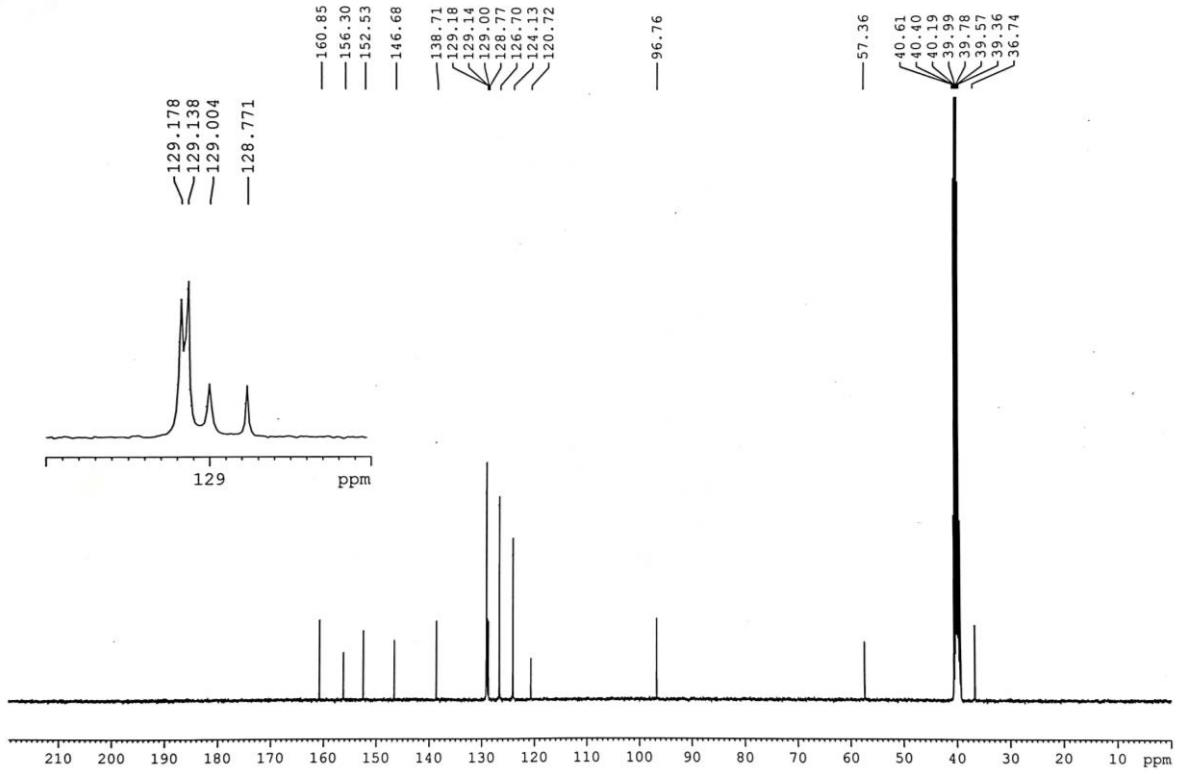
^{13}C NMR of **1o** (100 MHz, DMSO-d_6)



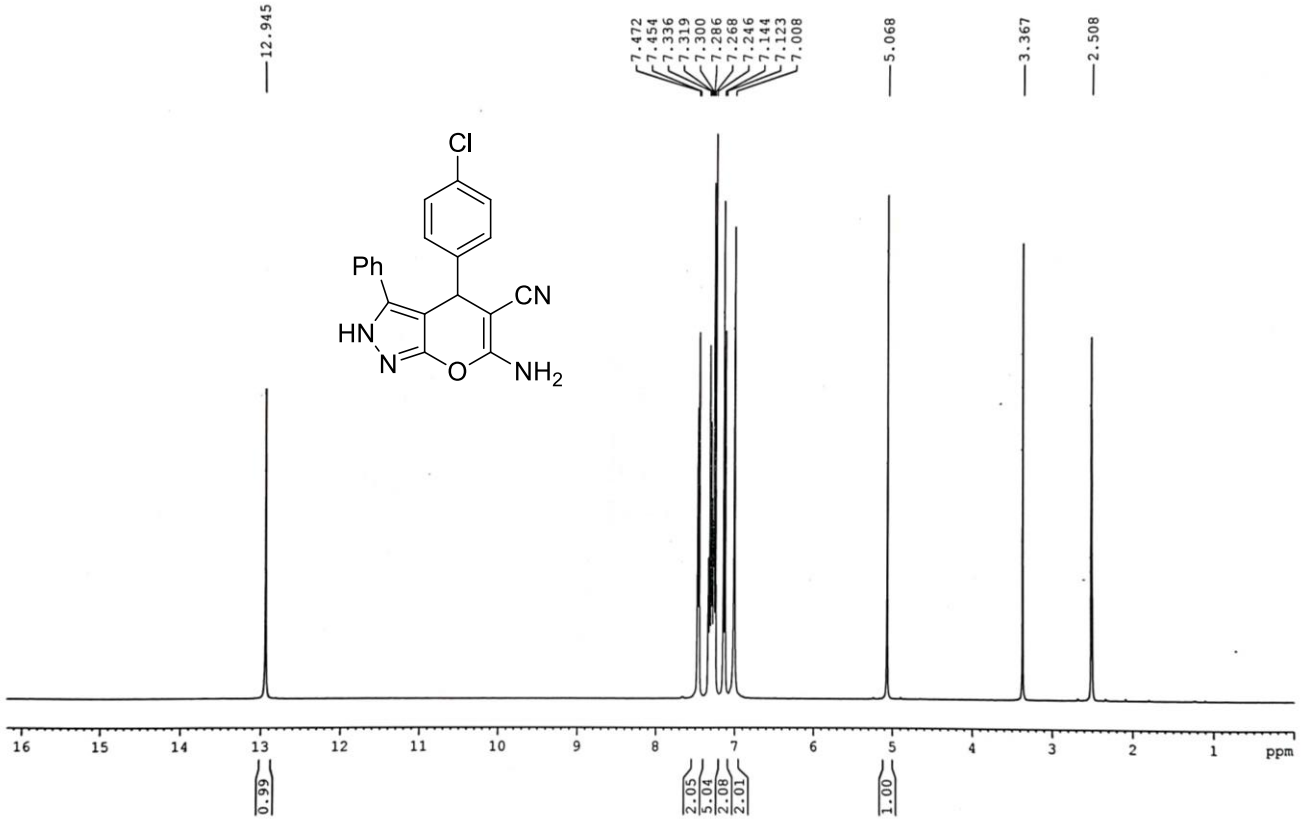
^{1}H NMR of **1p** (400 MHz, DMSO-d_6)



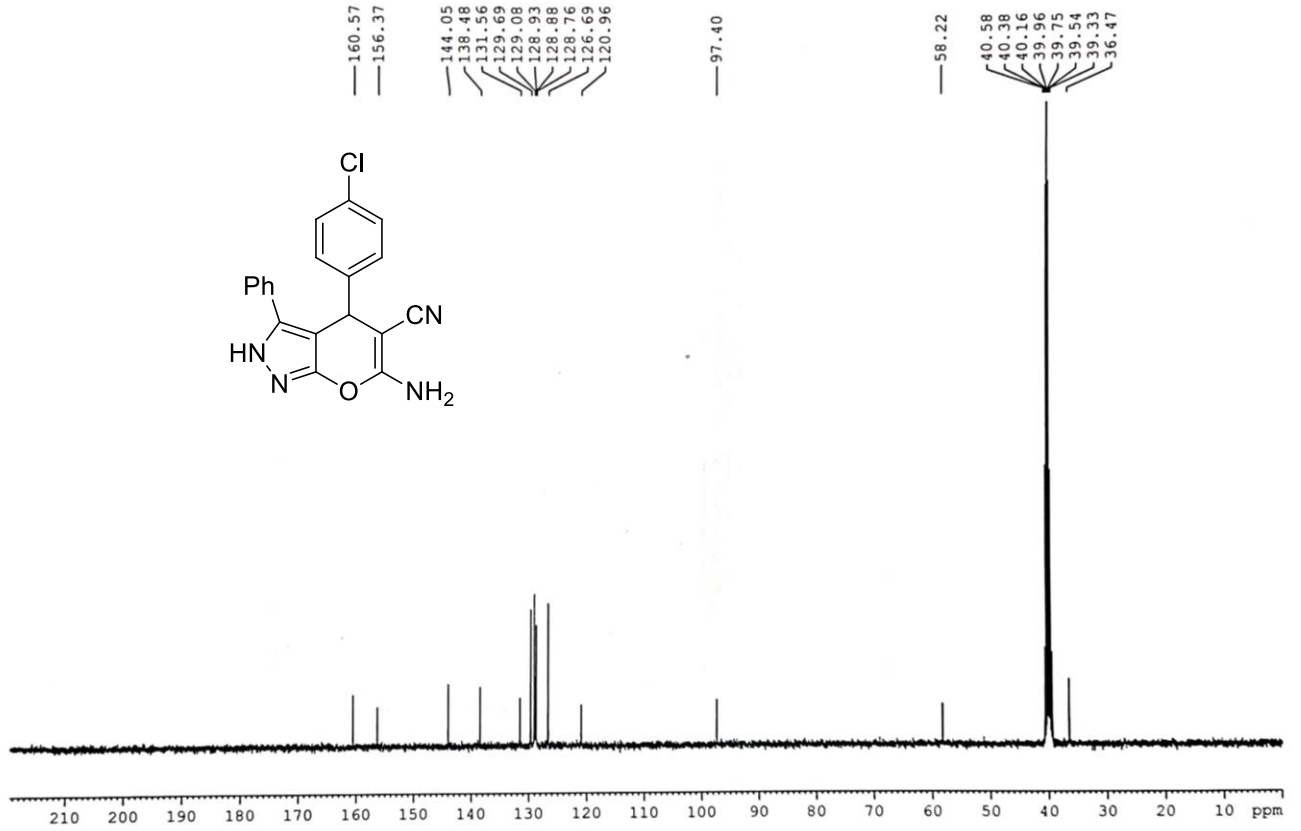
^{13}C NMR of **1p** (100 MHz, DMSO-d_6)



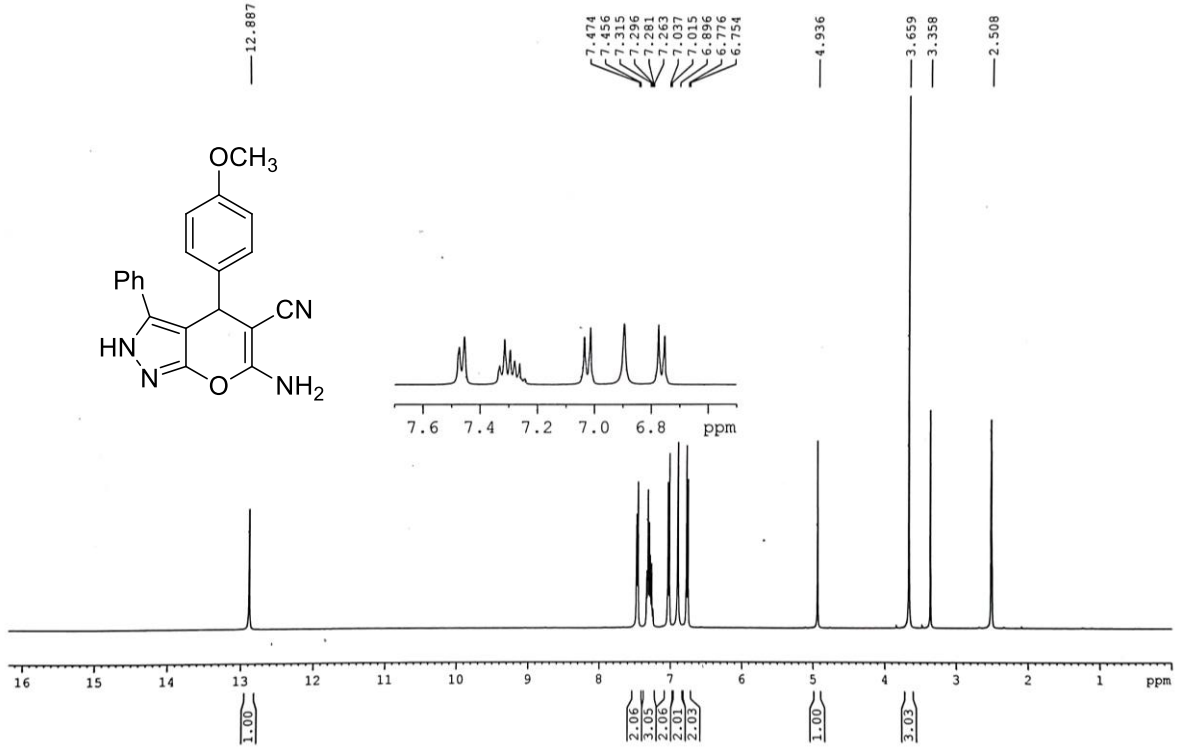
^{1}H NMR of **1q** (400 MHz, DMSO-d_6)



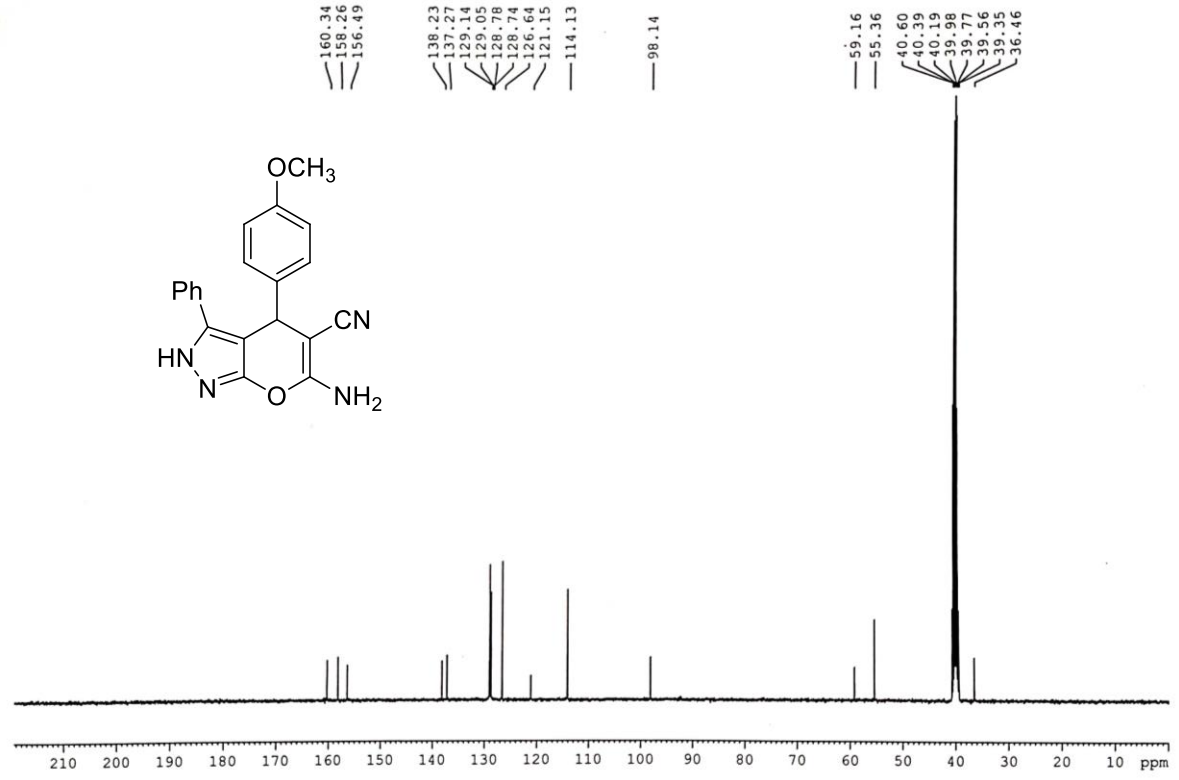
^{13}C NMR of **1q** (100 MHz, DMSO-d_6)



^{1}H NMR of **1r** (400 MHz, DMSO-d_6)

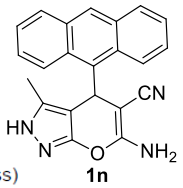


^{13}C NMR of **1r** (100 MHz, DMSO-d6)



HRMS of 1n

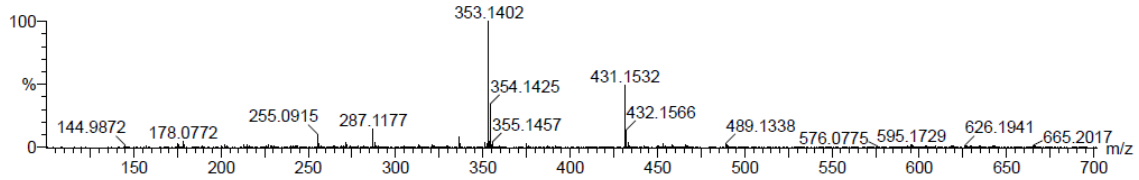
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 5



1n

Monoisotopic Mass, Even Electron Ions
354 formula(e) evaluated with 1 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C: 1-50 H: 1-100 N: 1-10 O: 1-10

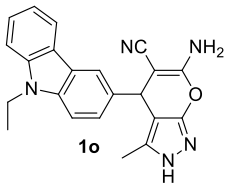
Sample Name : SC_182 IITRPR XEVO G2-XS QTOF
Test Name :
280622_SC_182 19 (0.214) 1: TOF MS ES+
1.26e+007



Minimum:				-1.5				
Maximum:		2.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
353.1402	353.1402	0.0	0.0	16.5	909.4	n/a	n/a	C22 H17 N4 O

HRMS of 1o

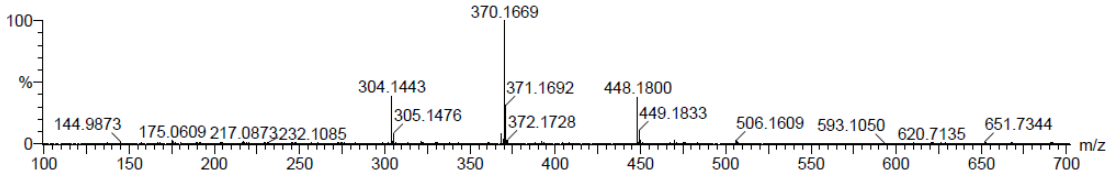
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 5



1o

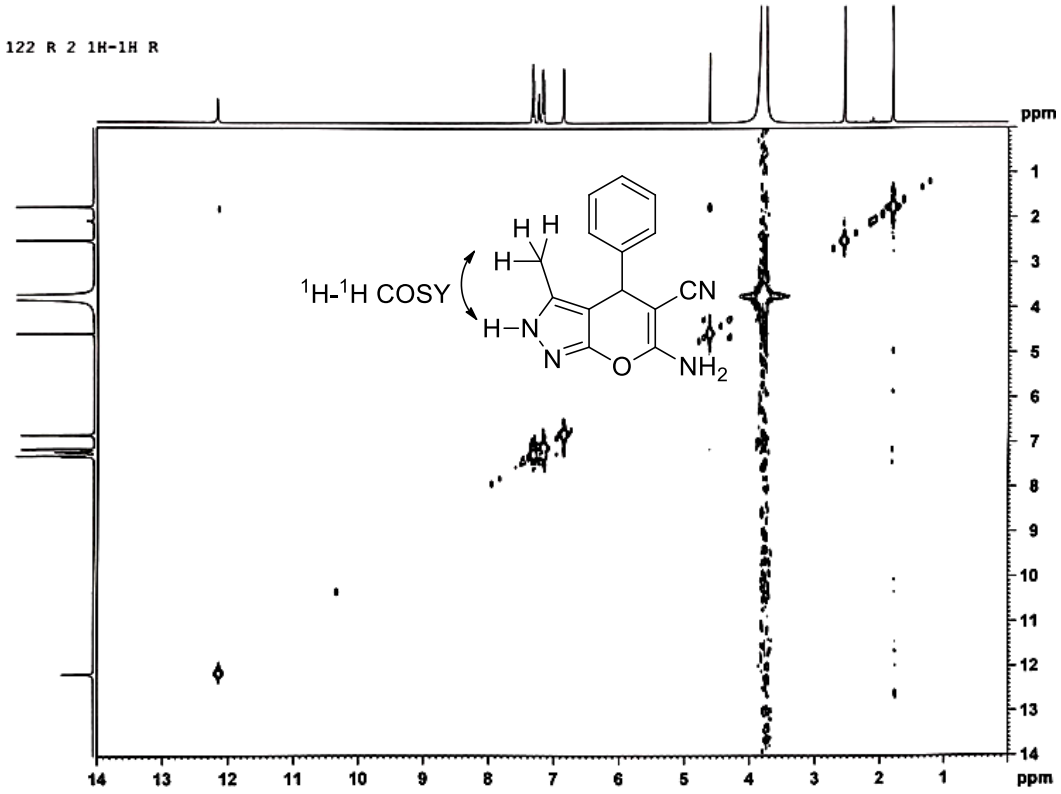
Monoisotopic Mass, Even Electron Ions
366 formula(e) evaluated with 3 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C: 1-50 H: 1-100 N: 1-10 O: 1-10

Sample Name : SC_185 IITRPR XEVO G2-XS QTOF
Test Name :
280622_SC_185 16 (0.177) 1: TOF MS ES+
4.34e+007

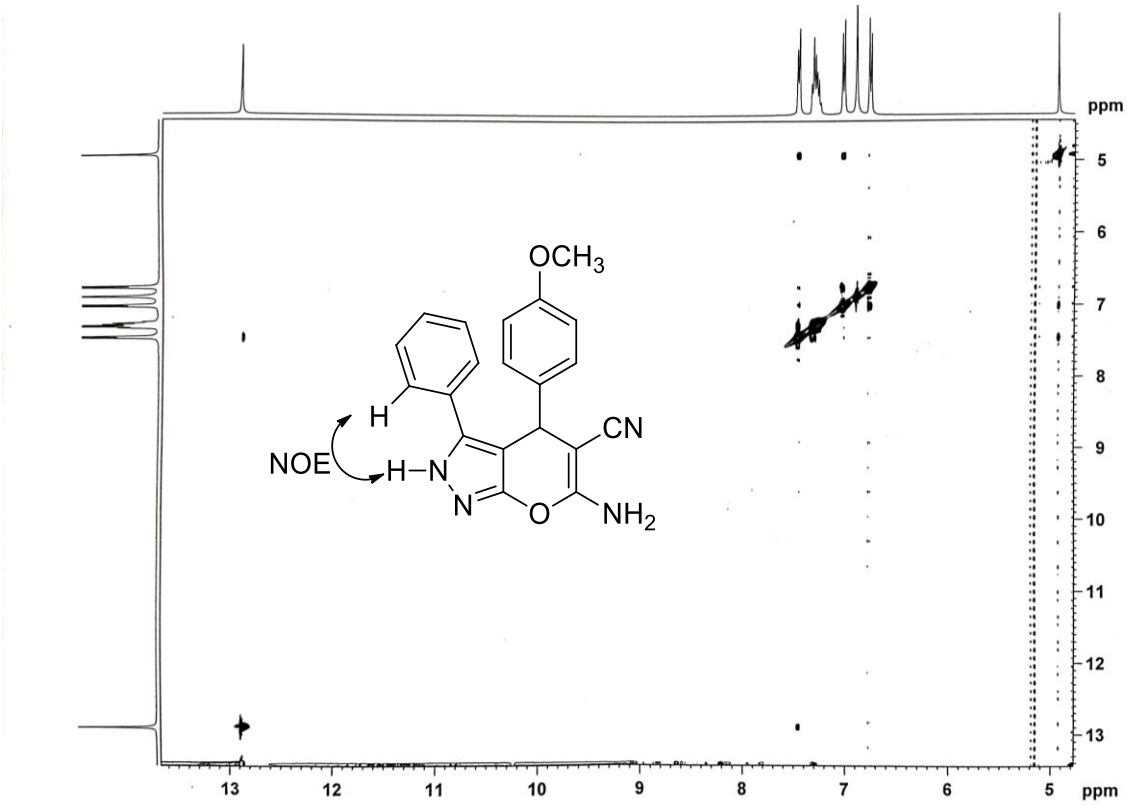


Minimum:				-1.5				
Maximum:		2.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
370.1669	370.1668	0.1	0.3	15.5	1274.8	n/a	n/a	C22 H20 N5 O

^{1}H-1H COSY of 1f



NOESY Spectrum of **1r**



References:

1. J. Albadi and A. Mansournezhad, *Curr. Chem. Lett.*, 2014, **3**, 221-227.
2. V. N. Bhosale, J. A. Angulwar, G. S. Khansole and G. S. Waghmare, *J. Chem. Pharm. Res*., 2014, **6**, 733-737.
3. U. D. Nimbalkar, J. A. Seijas, M. P. Vazquez-Tato, M. G. Damale, J. N. Sangshetti and A. P. Nikalje, *Molecules*, 2017, 22, 1628.
4. G. S. Kumar, C. Kurumurthy, B. Veeraswamy, P. S. Rao, P. S. Rao, B. Narsaiah, *Org. Prep. Proced. Int*., 2013, **45**, 429-436.
5. M. G. Dehbalaei, N. Foroughifar, H. Pasdar, A. Khajeh-Amiri, N. Foroughifar and M. Alikarami, *Res. Chem. Intermed*., 2017, **43**, 3035–3051
6. Y. Zou, Y. Hu, H. Liu, D. Q. Shi, *J. Heterocycl. Chem.*, 2013, **50**, 1174-1179.

X-ray crystallographic data of 1n

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) rn_bp_sc182_2_0m_a

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: rn_bp_sc182_2_0m_a

```
Bond precision:   C-C = 0.0029 A          Wavelength=1.54178

Cell:              a=28.496(2)      b=28.496(2)      c=10.1953(12)
                   alpha=90         beta=90          gamma=90
Temperature:       100 K
```

	Calculated	Reported
Volume	8278.8(15)	8279.0(17)
Space group	I 41/a	I 41/a
Hall group	-I 4ad	-I 4ad
Moiety formula	C22 H16 N4 O [+ solvent]	C22 H16 N4 O
Sum formula	C22 H16 N4 O [+ solvent]	C22 H16 N4 O
Mr	352.39	352.39
Dx,g cm-3	1.131	1.131
Z	16	16
Mu (mm-1)	0.577	0.577
F000	2944.0	2944.0
F000'	2952.50	
h,k,lmax	34,34,12	34,34,12
Nref	3804	3782
Tmin,Tmax	0.785,0.891	0.630,0.753
Tmin'	0.771	

```
Correction method= # Reported T Limits: Tmin=0.630 Tmax=0.753
AbsCorr = MULTI-SCAN

Data completeness= 0.994           Theta(max)= 68.321

R(reflections)= 0.0639( 3615)                    wR2(reflections)=
                                                 0.1999( 3782)
S = 1.075                 Npar= 245
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT410_ALERT_2_B Short Intra H...H Contact	H3	..H15	.	1.88 Ang.
		x,y,z =		1_555 Check

Alert level C

PLAT420_ALERT_2_C D-H Bond Without Acceptor	N2	--H2A	. Please Check
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance			2.223 Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=		0.600	17 Report
PLAT913_ALERT_3_C Missing # of Very Strong Reflections in FCF			6 Note
PLAT918_ALERT_3_C Reflection(s) with I(obs) much Smaller I(calc) .			10 Check

Alert level G

PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms			3 Report
PLAT072_ALERT_2_G SHELXL First Parameter in WGHT Unusually Large			0.14 Report
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large			7.58 Why ?
PLAT152_ALERT_1_G The Supplied and Calc. Volume s.u. Differ by ...			-2 Units
PLAT605_ALERT_4_G Largest Solvent Accessible VOID in the Structure			450 A**3
PLAT767_ALERT_4_G INS Embedded LIST 6 Instruction Should be LIST 4			Please Check
PLAT793_ALERT_4_G Model has Chirality at C15		(Centro SPGR)	R Verify
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).			2 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=		0.600	5 Note
PLAT933_ALERT_2_G Number of HKL-OMIT Records in Embedded .res File			4 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.			1 Info

0 **ALERT level A** = Most likely a serious problem - resolve or explain
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11 **ALERT level G** = General information/check it is not something unexpected

1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
6 ALERT type 2 Indicator that the structure model may be wrong or deficient
5 ALERT type 3 Indicator that the structure quality may be low
4 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

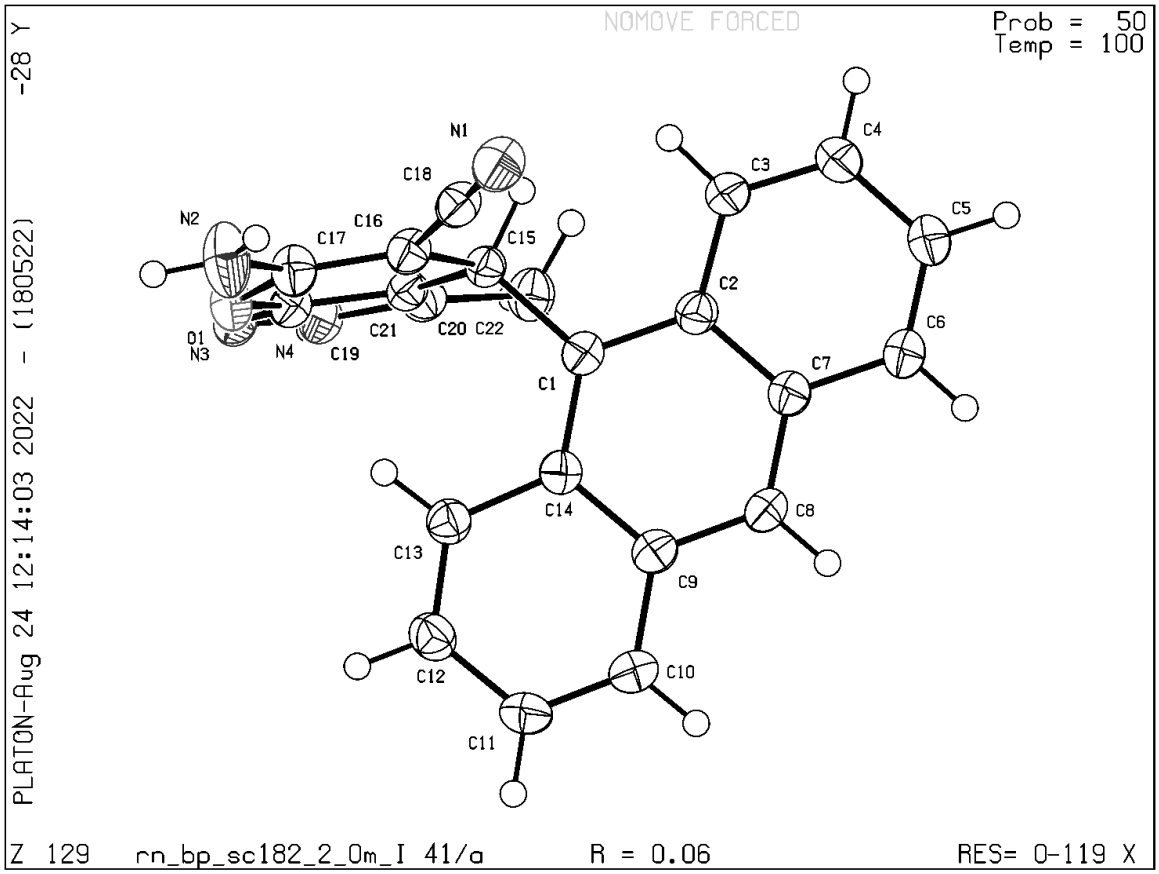
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 18/05/2022; check.def file version of 17/05/2022

Datablock rn_bp_sc182_2_0m_a - ellipsoid plot



X-ray crystallographic data of 1o

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) rn_bp_sc185_0m_a

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: rn_bp_sc185_0m_a

```
Bond precision:   C-C = 0.0024 A          Wavelength=1.54178

Cell:               a=22.861(2)      b=22.861(2)      c=14.185(2)
                    alpha=90         beta=90          gamma=90
Temperature:        101 K

                Calculated                Reported
Volume          7413.4(17)                7413.4(17)
Space group     I 41/a                    I 41/a
Hall group      -I 4ad                    -I 4ad
Moiety formula  C22 H19 N5 O              C22 H19 N5 O
Sum formula     C22 H19 N5 O              C22 H19 N5 O
Mr              369.42                    369.42
Dx,g cm-3       1.324                     1.324
Z               16                        16
Mu (mm-1)       0.682                     0.682
F000            3104.0                    3104.0
F000'           3112.91
h,k,lmax        27,27,17                  27,27,17
Nref            3404                      3383
Tmin,Tmax       0.906,0.921               0.607,0.753
Tmin'           0.884

Correction method= # Reported T Limits: Tmin=0.607 Tmax=0.753
AbsCorr = MULTI-SCAN

Data completeness= 0.994           Theta(max)= 68.340

R(reflections)= 0.0466( 3059)                wR2(reflections)=
                                             0.1229( 3383)
S = 1.084                  Npar= 256
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The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT420_ALERT_2_C D-H Bond Without Acceptor N5 --H5 . Please Check
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ..... 3.945 Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L= 0.600 13 Report
PLAT913_ALERT_3_C Missing # of Very Strong Reflections in FCF .... 4 Note

Alert level G

PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..... 3 Report
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large 6.40 Why ?
PLAT767_ALERT_4_G INS Embedded LIST 6 Instruction Should be LIST 4 Please Check
PLAT793_ALERT_4_G Model has Chirality at C1 (Centro SPGR) S Verify
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600 9 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density. 11 Info

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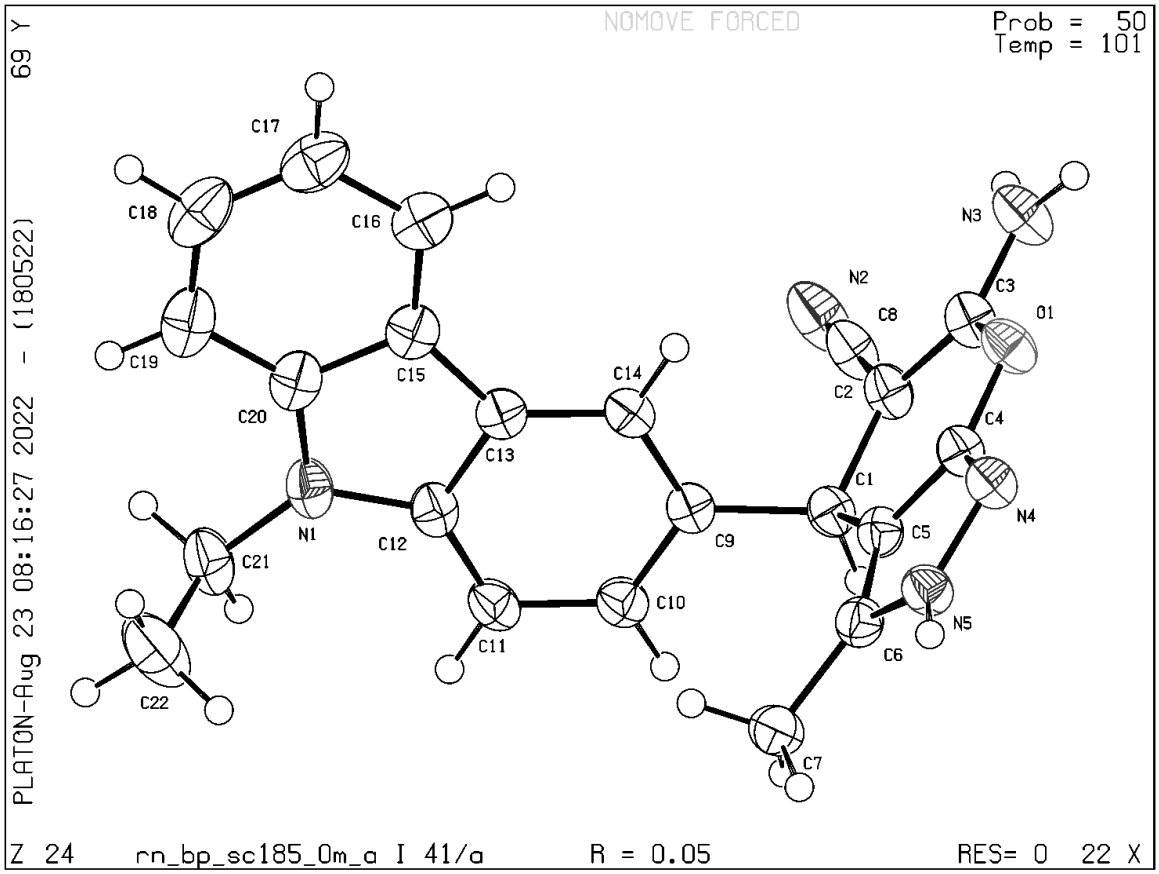
PLATON version of 18/05/2022; check.def file version of 17/05/2022

Datablock rn_bp_sc185_0m_a - ellipsoid plot



RN_BP_SC182_2_0m_a

Compund 1n

Table 1 Crystal data and structure refinement for RN_BP_SC182_2_0m_a.

Identification code	RN_BP_SC182_2_0m_a
Empirical formula	$C_{22}H_{16}N_4O$
Formula weight	352.39
Temperature/K	100.00
Crystal system	tetragonal
Space group	$I4_1/a$
a/Å	28.496(2)
b/Å	28.496(2)
c/Å	10.1953(12)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	8279.0(17)
Z	16
ρ_{calc}g/cm^3	1.131
μ/mm^{-1}	0.577
F(000)	2944.0
Crystal size/mm^3	0.45 × 0.35 × 0.2
Radiation	Cu Kα (λ = 1.54178)
2Θ range for data collection/°	9.212 to 136.642
Index ranges	$-32 \le h \le 34$, $-30 \le k \le 34$, $-11 \le l \le 12$
Reflections collected	126607
Independent reflections	3782 [R_{int} = 0.0660, R_{sigma} = 0.0196]
Data/restraints/parameters	3782/0/245
Goodness-of-fit on F^2	1.075
Final R indexes [I>=2σ (I)]	R_1 = 0.0639, wR_2 = 0.1982
Final R indexes [all data]	R_1 = 0.0653, wR_2 = 0.1999
Largest diff. peak/hole / e Å^{-3}	0.30/-0.32

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for RN_BP_SC182_2_0m_a. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	3755.2(5)	3437.7(5)	7307.6(14)	30.9(3)
N1	2230.0(6)	3583.2(7)	5502.2(18)	39.9(5)
N2	3285.5(7)	4031.7(6)	6783(2)	49.1(5)
N3	4179.0(6)	2802.2(6)	8114.4(15)	28.7(4)
N4	4125.7(6)	2328.3(6)	8015.3(15)	29.0(4)
C1	3091.0(6)	2507.2(6)	4767.0(17)	25.0(4)
C2	2714.0(6)	2211.7(7)	4407.9(17)	26.6(4)
C3	2300.6(7)	2140.6(8)	5186.8(19)	34.0(5)
C4	1946.3(8)	1852.2(9)	4789(2)	41.0(5)
C5	1975.7(8)	1600.4(9)	3594(2)	40.7(5)
C6	2357.9(7)	1659.2(8)	2813(2)	35.7(5)
C7	2731.0(7)	1964.9(7)	3176.0(18)	29.1(4)
C8	3114.5(7)	2027.1(7)	2348.7(18)	29.9(4)
C9	3477.2(7)	2333.4(7)	2659.5(18)	29.0(4)
C10	3858.8(7)	2400.2(7)	1772.4(19)	33.1(5)
C11	4213.2(7)	2699.4(7)	2053(2)	34.4(5)
C12	4201.0(7)	2961.3(7)	3233(2)	33.1(5)
C13	3845.9(7)	2906.4(7)	4111.8(19)	29.0(4)
C14	3466.0(6)	2585.0(6)	3883.7(18)	26.0(4)
C15	3095.3(6)	2720.1(6)	6149.3(17)	25.0(4)
C16	3027.7(7)	3251.3(7)	6220.8(18)	28.3(4)
C17	3338.5(7)	3565.6(7)	6741(2)	32.0(5)
C18	2590.3(7)	3436.2(7)	5813.2(19)	30.5(4)
C19	3818.3(7)	2961.7(7)	7438.1(18)	27.0(4)
C20	3532.4(6)	2615.3(6)	6915.3(17)	24.8(4)
C21	3743.2(7)	2203.6(7)	7308.8(18)	27.5(4)
C22	3615.9(8)	1704.0(7)	7055(2)	34.2(5)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for RN_BP_SC182_2_0m_a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	28.6(7)	25.8(7)	38.5(8)	-2.8(5)	-6.9(6)	0.7(5)
N1	34.0(10)	45.0(10)	40.8(10)	-7.3(8)	-5.6(8)	10.2(8)
N2	43.8(11)	27.8(9)	75.7(14)	-7.6(9)	-22.2(10)	5.2(8)
N3	29.2(8)	29.4(8)	27.5(8)	-2.5(6)	-2.5(6)	1.5(6)
N4	31.1(8)	28.9(8)	27.0(8)	-0.1(6)	-3.8(6)	1.7(6)
C1	26.0(9)	24.7(9)	24.4(9)	-0.2(7)	-2.1(7)	2.7(7)
C2	26.6(9)	29.3(9)	24.0(9)	-0.1(7)	-1.2(7)	0.2(7)
C3	30.1(10)	44.8(12)	27.0(9)	-5.2(8)	2.1(8)	-6.0(8)
C4	31.0(11)	57.4(14)	34.6(11)	-6.3(10)	3.5(8)	-12.8(9)
C5	34.3(11)	51.5(13)	36.4(11)	-7.3(9)	-1.4(9)	-13.9(9)
C6	36.5(11)	41.3(12)	29.3(10)	-6.4(8)	-2.1(8)	-8.2(9)
C7	29.3(10)	31.8(10)	26.1(9)	-1.3(7)	-1.4(7)	-2.5(8)
C8	34.1(10)	31.7(10)	23.9(9)	-4.8(7)	0.8(7)	-1.4(8)
C9	31.3(10)	30.3(10)	25.4(9)	0.0(7)	0.2(7)	0.8(8)
C10	35.4(11)	37.3(11)	26.5(10)	-1.6(8)	4.6(8)	-0.4(8)
C11	33.0(10)	37.9(11)	32.2(10)	3.5(8)	7.9(8)	-1.9(8)
C12	32.6(10)	33.1(10)	33.7(10)	3.3(8)	0.5(8)	-5.7(8)
C13	30.1(10)	29.3(9)	27.7(9)	0.7(7)	-0.8(7)	-1.2(7)
C14	26.5(9)	25.6(9)	25.8(9)	1.1(7)	-1.7(7)	0.8(7)
C15	24.0(9)	27.6(9)	23.5(9)	-1.8(7)	-0.6(7)	0.0(7)
C16	27.6(9)	29.3(10)	28.0(9)	-2.9(7)	-2.4(7)	4.2(7)
C17	30.6(10)	28.0(10)	37.4(11)	-2.6(8)	-3.9(8)	2.8(8)
C18	32.2(11)	32.0(10)	27.1(9)	-4.4(7)	-0.3(8)	2.7(8)
C19	28.7(9)	26.2(9)	26.2(9)	-2.6(7)	0.5(7)	0.4(7)
C20	24.7(9)	28.3(9)	21.3(8)	-1.6(7)	0.1(7)	-0.1(7)
C21	29.1(9)	29.9(10)	23.3(9)	-0.6(7)	0.5(7)	0.7(7)
C22	38.7(11)	27.7(10)	36.0(10)	-0.1(8)	-3.3(8)	-0.3(8)

Table 4 Bond Lengths for RN_BP_SC182_2_0m_a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C17	1.370(2)	C7	C8	1.392(3)
O1	C19	1.375(2)	C8	C9	1.389(3)
N1	C18	1.154(3)	C9	C10	1.427(3)
N2	C17	1.338(3)	C9	C14	1.440(3)
N3	N4	1.363(2)	C10	C11	1.352(3)
N3	C19	1.319(2)	C11	C12	1.417(3)
N4	C21	1.354(2)	C12	C13	1.360(3)
C1	C2	1.413(3)	C13	C14	1.437(3)
C1	C14	1.415(3)	C15	C16	1.528(3)
C1	C15	1.534(2)	C15	C20	1.500(2)
C2	C3	1.435(3)	C16	C17	1.366(3)
C2	C7	1.440(3)	C16	C18	1.416(3)
C3	C4	1.363(3)	C19	C20	1.386(3)
C4	C5	1.417(3)	C20	C21	1.378(3)
C5	C6	1.359(3)	C21	C22	1.492(3)
C6	C7	1.424(3)			

Table 5 Bond Angles for RN_BP_SC182_2_0m_a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C17	O1	C19	114.62(15)	C12	C13	C14	121.81(18)
C19	N3	N4	102.46(15)	C1	C14	C9	119.37(17)
C21	N4	N3	112.92(15)	C1	C14	C13	124.46(17)
C2	C1	C14	120.17(16)	C13	C14	C9	116.17(17)
C2	C1	C15	118.66(16)	C16	C15	C1	115.76(15)
C14	C1	C15	121.10(16)	C20	C15	C1	113.95(15)
C1	C2	C3	124.38(17)	C20	C15	C16	106.08(15)
C1	C2	C7	119.43(17)	C17	C16	C15	125.89(17)
C3	C2	C7	116.19(17)	C17	C16	C18	116.14(17)
C4	C3	C2	121.89(19)	C18	C16	C15	117.76(16)
C3	C4	C5	121.2(2)	N2	C17	O1	110.38(17)
C6	C5	C4	119.25(19)	N2	C17	C16	126.18(19)
C5	C6	C7	121.44(19)	C16	C17	O1	123.44(17)
C6	C7	C2	120.02(18)	N1	C18	C16	178.7(2)
C8	C7	C2	119.53(17)	O1	C19	C20	126.05(17)
C8	C7	C6	120.46(18)	N3	C19	O1	119.51(16)
C9	C8	C7	121.73(18)	N3	C19	C20	114.44(17)
C8	C9	C10	120.40(18)	C19	C20	C15	123.11(16)
C8	C9	C14	119.61(17)	C21	C20	C15	133.08(17)
C10	C9	C14	119.99(18)	C21	C20	C19	103.78(16)
C11	C10	C9	121.29(19)	N4	C21	C20	106.40(16)
C10	C11	C12	119.56(18)	N4	C21	C22	122.58(17)
C13	C12	C11	121.13(19)	C20	C21	C22	131.02(17)

Table 6 Torsion Angles for RN_BP_SC182_2_0m_a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	C19	C20	C15	-2.0(3)	C9	C10	C11	C12	-1.6(3)
O1	C19	C20	C21	179.63(17)	C10	C9	C14	C1	-178.56(17)
N3	N4	C21	C20	0.2(2)	C10	C9	C14	C13	1.9(3)
N3	N4	C21	C22	179.31(17)	C10	C11	C12	C13	2.1(3)
N3	C19	C20	C15	178.02(16)	C11	C12	C13	C14	-0.5(3)
N3	C19	C20	C21	-0.4(2)	C12	C13	C14	C1	179.00(18)
N4	N3	C19	O1	-179.54(16)	C12	C13	C14	C9	-1.4(3)
N4	N3	C19	C20	0.5(2)	C14	C1	C2	C3	-174.72(18)
C1	C2	C3	C4	179.7(2)	C14	C1	C2	C7	4.4(3)
C1	C2	C7	C6	178.82(18)	C14	C1	C15	C16	70.8(2)
C1	C2	C7	C8	-1.1(3)	C14	C1	C15	C20	-52.7(2)
C1	C15	C16	C17	-120.1(2)	C14	C9	C10	C11	-0.4(3)
C1	C15	C16	C18	65.4(2)	C15	C1	C2	C3	8.2(3)
C1	C15	C20	C19	123.06(19)	C15	C1	C2	C7	-172.71(16)
C1	C15	C20	C21	-59.1(3)	C15	C1	C14	C9	172.37(16)
C2	C1	C14	C9	-4.6(3)	C15	C1	C14	C13	-8.1(3)
C2	C1	C14	C13	174.92(17)	C15	C16	C17	O1	-1.8(3)
C2	C1	C15	C16	-112.21(19)	C15	C16	C17	N2	178.6(2)
C2	C1	C15	C20	124.36(18)	C15	C20	C21	N4	-178.06(18)
C2	C3	C4	C5	1.4(4)	C15	C20	C21	C22	2.9(3)
C2	C7	C8	C9	-2.0(3)	C16	C15	C20	C19	-5.5(2)
C3	C2	C7	C6	-2.0(3)	C16	C15	C20	C21	172.39(19)
C3	C2	C7	C8	178.11(18)	C17	O1	C19	N3	-171.67(17)
C3	C4	C5	C6	-2.0(4)	C17	O1	C19	C20	8.3(3)
C4	C5	C6	C7	0.6(4)	C18	C16	C17	O1	172.82(18)
C5	C6	C7	C2	1.5(3)	C18	C16	C17	N2	-6.8(3)
C5	C6	C7	C8	-178.7(2)	C19	O1	C17	N2	173.30(18)
C6	C7	C8	C9	178.10(19)	C19	O1	C17	C16	-6.3(3)
C7	C2	C3	C4	0.6(3)	C19	N3	N4	C21	-0.4(2)
C7	C8	C9	C10	-178.10(19)	C19	C20	C21	N4	0.1(2)
C7	C8	C9	C14	1.8(3)	C19	C20	C21	C22	-178.9(2)
C8	C9	C10	C11	179.5(2)	C20	C15	C16	C17	7.4(3)
C8	C9	C14	C1	1.6(3)	C20	C15	C16	C18	-167.15(16)
C8	C9	C14	C13	-178.00(17)					

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for RN_BP_SC182_2_0m_a.

Atom	*x*	*y*	*z*	U(eq)
H2A	3031.26	4162.13	6456.25	59
H2B	3504.92	4207.95	7138.85	59
H4	4319.53	2124.74	8372.79	35
H3	2272.99	2299.02	6003.05	41
H4A	1675.04	1819.55	5322.83	49
H5	1731.1	1392.71	3341.1	49
H6	2376.33	1492.64	2007.5	43
H8	3128.62	1855.6	1550.58	36
H10	3863.89	2231.13	969.37	40
H11	4468.64	2733.71	1461.59	41
H12	4445.06	3178.98	3414.77	40
H13	3849.18	3085.49	4897.76	35
H15	2828.13	2575.09	6639.58	30
H22A	3648.02	1636.7	6116.85	51
H22B	3290.72	1649.06	7327.37	51
H22C	3825.47	1498.05	7554.8	51

Table 8 Solvent masks information for RN_BP_SC182_2_0m_a.

Number	X	Y	Z	Volume	Electron count	Content
1	0.250	0.000	-0.518	461.5	128.5	?
2	0.250	0.500	-0.959	461.5	128.5	?
3	0.750	0.000	-0.459	461.5	128.5	?
4	0.750	0.500	-0.018	461.5	128.5	?

RN_BP_SC182_2_0m_a

Table 1 Crystal data and structure refinement for RN_BP_SC182_2_0m_a.

Identification code	RN_BP_SC182_2_0m_a
Empirical formula	$C_{22}H_{16}N_4O$
Formula weight	352.39
Temperature/K	100.00
Crystal system	tetragonal
Space group	$I4_1/a$
a/Å	28.496(2)
b/Å	28.496(2)
c/Å	10.1953(12)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	8279.0(17)
Z	16
ρ_{calc}g/cm^3	1.131
μ/mm^{-1}	0.577
F(000)	2944.0
Crystal size/mm^3	0.45 × 0.35 × 0.2
Radiation	Cu Kα (λ = 1.54178)
2Θ range for data collection/°	9.212 to 136.642
Index ranges	$-32 \le h \le 34$, $-30 \le k \le 34$, $-11 \le l \le 12$
Reflections collected	126607
Independent reflections	3782 [R_{int} = 0.0660, R_{sigma} = 0.0196]
Data/restraints/parameters	3782/0/245
Goodness-of-fit on F^2	1.075
Final R indexes [I>=2σ (I)]	R_1 = 0.0639, wR_2 = 0.1982
Final R indexes [all data]	R_1 = 0.0653, wR_2 = 0.1999
Largest diff. peak/hole / e Å^{-3}	0.30/-0.32

RN_BP_SC185_0m_a

Compound 1o

Table 1 Crystal data and structure refinement for RN_BP_SC185_0m_a.

Identification code	RN_BP_SC185_0m_a
Empirical formula	$C_{22}H_{19}N_5O$
Formula weight	369.42
Temperature/K	101.0
Crystal system	tetragonal
Space group	$I4_1/a$
a/Å	22.861(2)
b/Å	22.861(2)
c/Å	14.185(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	7413.4(17)
Z	16
ρ_{calc}g/cm^3	1.324
μ/mm^{-1}	0.682
F(000)	3104.0
Crystal size/mm^3	0.18 × 0.12 × 0.12
Radiation	Cu Kα (λ = 1.54178)
2Θ range for data collection/°	7.334 to 136.68
Index ranges	$-25 \le h \le 27$, $-27 \le k \le 25$, $-17 \le l \le 16$
Reflections collected	76619
Independent reflections	3383 [R_{int} = 0.0823, R_{sigma} = 0.0235]
Data/restraints/parameters	3383/0/256
Goodness-of-fit on F^2	1.084
Final R indexes [I>=2σ (I)]	R_1 = 0.0466, wR_2 = 0.1192
Final R indexes [all data]	R_1 = 0.0518, wR_2 = 0.1229
Largest diff. peak/hole / e Å^{-3}	0.21/-0.19

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for RN_BP_SC185_0m_a. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	7001.8(5)	7061.6(5)	2381.9(9)	34.6(3)
N1	5500.2(6)	4352.2(6)	4782.1(11)	35.2(4)
N2	4935.7(7)	6791.5(7)	2451.8(15)	50.6(5)
N3	6245.5(7)	7648.9(6)	2607.2(12)	40.4(4)
N4	7793.3(6)	6436.9(6)	2169.3(10)	32.3(3)
N5	7832.0(6)	5854.8(6)	1955.8(10)	31.9(3)
C1	6234.0(7)	6006.9(7)	2033.1(12)	29.1(4)
C2	6040.4(7)	6630.5(7)	2267.2(12)	31.7(4)
C3	6403.5(7)	7099.1(7)	2410.3(12)	32.1(4)
C4	7220.2(7)	6516.0(7)	2196.8(12)	29.9(4)
C5	6890.6(7)	6017.5(7)	2012.6(11)	28.9(4)
C6	7304.6(7)	5588.8(7)	1863.6(12)	30.5(4)
C7	7240.9(8)	4950.3(7)	1695.2(13)	36.3(4)
C8	5431.5(8)	6727.5(7)	2359.9(14)	37.8(4)
C9	6005.5(7)	5556.8(7)	2739.9(12)	28.1(4)
C10	5715.3(7)	5051.0(7)	2433.9(13)	32.3(4)
C11	5527.1(7)	4618.9(7)	3057.2(13)	33.7(4)
C12	5637.8(7)	4702.1(7)	4011.5(12)	30.9(4)
C13	5929.6(7)	5208.3(7)	4335.2(12)	29.4(4)
C14	6106.2(7)	5636.4(7)	3695.6(12)	28.5(4)
C15	5973.2(7)	5156.9(8)	5347.0(12)	33.1(4)
C16	6204.2(8)	5517.2(9)	6052.5(13)	39.8(4)
C17	6154.1(9)	5339.2(10)	6985.5(14)	48.2(5)
C18	5880.4(9)	4813.2(10)	7208.5(14)	50.0(5)
C19	5654.2(8)	4443.4(9)	6527.0(14)	43.9(5)
C20	5701.3(7)	4624.6(8)	5591.1(13)	34.9(4)
C21	5175.2(9)	3805.7(8)	4763.8(15)	44.1(5)
C22	5567.0(11)	3273.4(10)	4798(2)	69.2(8)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for RN_BP_SC185_0m_a.
The Anisotropic displacement factor exponent takes the form:
$-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	26.7(6)	26.5(6)	50.7(8)	-1.4(5)	-2.8(5)	-0.7(5)
N1	29.4(8)	32.3(8)	43.9(9)	8.3(6)	3.7(6)	-1.1(6)
N2	31.1(9)	30.4(9)	90.3(14)	3.8(8)	1.5(8)	-0.3(7)
N3	28.9(8)	26.8(8)	65.6(11)	-1.3(7)	-1.9(7)	-0.5(6)
N4	30.4(7)	28.3(7)	38.2(8)	-0.1(6)	-0.5(6)	-0.5(6)
N5	28.1(7)	28.8(7)	38.9(8)	-0.9(6)	2.5(6)	1.2(6)
C1	27.4(8)	27.8(8)	32.1(9)	1.3(6)	-2.5(6)	-1.5(7)
C2	27.3(8)	28.3(9)	39.6(10)	4.0(7)	-1.1(7)	-0.7(7)
C3	26.5(8)	30.6(9)	39.3(10)	3.4(7)	-2.4(7)	0.6(7)
C4	29.5(9)	27.2(8)	33.1(9)	2.0(7)	-0.8(7)	0.0(7)
C5	28.2(8)	29.6(8)	28.8(8)	2.1(6)	-0.1(6)	-2.6(7)
C6	30.4(9)	31.3(9)	29.9(9)	0.9(7)	1.4(7)	-1.8(7)
C7	36.8(9)	31.4(9)	40.7(10)	-4.1(7)	2.5(8)	-0.8(7)
C8	33.5(10)	24.5(8)	55.3(12)	4.2(8)	-1.2(8)	-2.1(7)
C9	23.8(8)	27.8(8)	32.8(9)	1.7(6)	-0.4(6)	1.3(6)
C10	31.3(9)	30.7(9)	35.0(9)	-1.8(7)	-0.4(7)	-1.1(7)
C11	31.4(9)	27.2(9)	42.4(10)	-2.2(7)	0.2(7)	-4.4(7)
C12	24.4(8)	29.6(8)	38.5(10)	4.2(7)	2.6(7)	1.0(7)
C13	23.2(8)	30.8(9)	34.1(9)	0.6(7)	0.3(6)	3.5(6)
C14	23.3(8)	26.2(8)	35.9(9)	-1.3(7)	-1.3(6)	0.1(6)
C15	25.5(8)	37.4(9)	36.3(9)	2.4(7)	0.6(7)	6.0(7)
C16	35.6(10)	46.5(11)	37.3(10)	-0.4(8)	-3.2(8)	6.1(8)
C17	47.3(12)	62.9(14)	34.4(10)	-1.3(9)	-5.0(8)	13.5(10)
C18	42.4(11)	71.9(15)	35.8(10)	10.9(10)	2.1(8)	19.0(10)
C19	31.1(9)	53.1(12)	47.5(11)	16.1(9)	7.4(8)	11.5(8)
C20	26.2(8)	41.1(10)	37.2(10)	7.3(8)	2.4(7)	7.6(7)
C21	38.2(10)	35.4(10)	58.6(13)	10.1(9)	5.9(9)	-5.3(8)
C22	59.6(15)	34.2(11)	114(2)	0.8(12)	24.5(14)	-2.4(10)

Table 4 Bond Lengths for RN_BP_SC185_0m_a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C3	1.371(2)	C5	C6	1.379(2)
O1	C4	1.369(2)	C6	C7	1.486(2)
N1	C12	1.390(2)	C9	C10	1.402(2)
N1	C20	1.384(2)	C9	C14	1.387(2)
N1	C21	1.454(2)	C10	C11	1.394(2)
N2	C8	1.150(2)	C11	C12	1.390(3)
N3	C3	1.337(2)	C12	C13	1.413(2)
N4	N5	1.368(2)	C13	C14	1.394(2)
N4	C4	1.323(2)	C13	C15	1.443(2)
N5	C6	1.357(2)	C15	C16	1.400(3)
C1	C2	1.529(2)	C15	C20	1.410(3)
C1	C5	1.502(2)	C16	C17	1.389(3)
C1	C9	1.529(2)	C17	C18	1.392(3)
C2	C3	1.370(2)	C18	C19	1.384(3)
C2	C8	1.416(2)	C19	C20	1.395(3)
C4	C5	1.391(2)	C21	C22	1.512(3)

Table 5 Bond Angles for RN_BP_SC185_0m_a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C4	O1	C3	115.25(13)	N2	C8	C2	177.9(2)
C12	N1	C21	126.58(16)	C10	C9	C1	120.91(15)
C20	N1	C12	108.53(14)	C14	C9	C1	119.75(14)
C20	N1	C21	124.82(15)	C14	C9	C10	119.29(15)
C4	N4	N5	101.75(13)	C11	C10	C9	122.29(16)
C6	N5	N4	113.56(14)	C12	C11	C10	117.68(16)
C5	C1	C2	106.16(13)	N1	C12	C13	108.82(15)
C5	C1	C9	111.41(13)	C11	C12	N1	130.21(16)
C9	C1	C2	112.71(14)	C11	C12	C13	120.97(15)
C3	C2	C1	125.84(15)	C12	C13	C15	106.79(15)
C3	C2	C8	117.35(15)	C14	C13	C12	120.02(16)
C8	C2	C1	116.80(14)	C14	C13	C15	133.18(16)
N3	C3	O1	109.54(14)	C9	C14	C13	119.74(15)
N3	C3	C2	127.02(16)	C16	C15	C13	133.55(17)
C2	C3	O1	123.44(15)	C16	C15	C20	119.92(17)
O1	C4	C5	125.79(15)	C20	C15	C13	106.51(15)
N4	C4	O1	119.42(14)	C17	C16	C15	118.53(19)
N4	C4	C5	114.78(15)	C16	C17	C18	120.4(2)
C4	C5	C1	123.46(15)	C19	C18	C17	122.46(19)
C6	C5	C1	132.66(15)	C18	C19	C20	117.04(19)
C6	C5	C4	103.85(15)	N1	C20	C15	109.33(15)
N5	C6	C5	106.06(14)	N1	C20	C19	129.05(18)
N5	C6	C7	122.86(15)	C19	C20	C15	121.61(18)
C5	C6	C7	130.96(16)	N1	C21	C22	112.86(17)

Table 6 Torsion Angles for RN_BP_SC185_0m_a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	C4	C5	C1	-2.7(3)	C9	C1	C5	C6	55.2(2)
O1	C4	C5	C6	179.38(16)	C9	C10	C11	C12	-0.2(3)
N1	C12	C13	C14	-178.92(14)	C10	C9	C14	C13	1.4(2)
N1	C12	C13	C15	0.48(18)	C10	C11	C12	N1	179.61(16)
N4	N5	C6	C5	0.72(19)	C10	C11	C12	C13	0.2(2)
N4	N5	C6	C7	-175.89(15)	C11	C12	C13	C14	0.6(2)
N4	C4	C5	C1	178.34(15)	C11	C12	C13	C15	-179.95(15)
N4	C4	C5	C6	0.4(2)	C12	N1	C20	C15	-0.05(18)
N5	N4	C4	O1	-179.04(14)	C12	N1	C20	C19	178.76(17)
N5	N4	C4	C5	-0.02(19)	C12	N1	C21	C22	99.6(2)
C1	C2	C3	O1	-1.6(3)	C12	C13	C14	C9	-1.4(2)
C1	C2	C3	N3	179.35(17)	C12	C13	C15	C16	-178.86(18)
C1	C5	C6	N5	-178.28(17)	C12	C13	C15	C20	-0.50(18)
C1	C5	C6	C7	-2.1(3)	C13	C15	C16	C17	177.71(18)
C1	C9	C10	C11	176.81(15)	C13	C15	C20	N1	0.35(18)
C1	C9	C14	C13	-176.05(14)	C13	C15	C20	C19	-178.57(15)
C2	C1	C5	C4	1.0(2)	C14	C9	C10	C11	-0.6(2)
C2	C1	C5	C6	178.25(17)	C14	C13	C15	C16	0.4(3)
C2	C1	C9	C10	129.26(16)	C14	C13	C15	C20	178.79(17)
C2	C1	C9	C14	-53.3(2)	C15	C13	C14	C9	179.37(17)
C3	O1	C4	N4	-179.04(15)	C15	C16	C17	C18	0.1(3)
C3	O1	C4	C5	2.1(2)	C16	C15	C20	N1	178.97(15)
C4	O1	C3	N3	179.24(15)	C16	C15	C20	C19	0.1(3)
C4	O1	C3	C2	0.1(2)	C16	C17	C18	C19	0.8(3)
C4	N4	N5	C6	-0.44(18)	C17	C18	C19	C20	-1.2(3)
C4	C5	C6	N5	-0.66(18)	C18	C19	C20	N1	-177.94(17)
C4	C5	C6	C7	175.57(17)	C18	C19	C20	C15	0.7(3)
C5	C1	C2	C3	1.0(2)	C20	N1	C12	C11	-179.78(17)
C5	C1	C2	C8	-177.81(15)	C20	N1	C12	C13	-0.27(18)
C5	C1	C9	C10	-111.51(17)	C20	N1	C21	C22	-83.7(2)
C5	C1	C9	C14	65.88(19)	C20	C15	C16	C17	-0.5(3)
C8	C2	C3	O1	177.17(16)	C21	N1	C12	C11	-2.6(3)
C8	C2	C3	N3	-1.8(3)	C21	N1	C12	C13	176.92(16)
C9	C1	C2	C3	123.24(18)	C21	N1	C20	C15	-177.31(15)
C9	C1	C2	C8	-55.6(2)	C21	N1	C20	C19	1.5(3)
C9	C1	C5	C4	-122.04(17)					

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for RN_BP_SC185_0m_a.

Atom	*x*	*y*	*z*	U(eq)
H3A	5872.7	7739.7	2657	48
H3B	6514.33	7919.96	2687.02	48
H5	8167.05	5670.35	1884.94	38
H1	6086.85	5902.74	1390.73	35
H7A	7610.19	4792.52	1453.59	54
H7B	6929.67	4882.83	1232.7	54
H7C	7140.78	4754.58	2288.31	54
H10	5644.45	5001	1778.96	39
H11	5330.11	4279.31	2837.6	40
H14	6294.65	5981.19	3913.47	34
H16	6391.05	5875.62	5896.8	48
H17	6307.73	5578.08	7474.5	58
H18	5847.64	4703.8	7852.44	60
H19	5474.86	4082.4	6689.54	53
H21A	4936.63	3790.83	4181.88	53
H21B	4904.62	3795.38	5308.45	53
H22A	5811.25	3261.51	4230.93	104
H22B	5326.03	2919.32	4828.56	104
H22C	5817.56	3294.27	5357.83	104

RN_BP_SC185_0m_a

Table 1 Crystal data and structure refinement for RN_BP_SC185_0m_a.

Identification code	RN_BP_SC185_0m_a
Empirical formula	$C_{22}H_{19}N_5O$
Formula weight	369.42
Temperature/K	101.0
Crystal system	tetragonal
Space group	$I4_1/a$
a/Å	22.861(2)
b/Å	22.861(2)
c/Å	14.185(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	7413.4(17)
Z	16
ρ_{calc}g/cm^3	1.324
μ/mm^{-1}	0.682
F(000)	3104.0
Crystal size/mm^3	0.18 × 0.12 × 0.12

Radiation	Cu Kα (λ = 1.54178)
2Θ range for data collection/°	7.334 to 136.68
Index ranges	$-25 \leq h \leq 27$, $-27 \leq k \leq 25$, $-17 \leq l \leq 16$
Reflections collected	76619
Independent reflections	3383 [R_{int} = 0.0823, R_{sigma} = 0.0235]
Data/restraints/parameters	3383/0/256
Goodness-of-fit on F^2	1.084
Final R indexes [I>=2σ (I)]	R_1 = 0.0466, wR_2 = 0.1192
Final R indexes [all data]	R_1 = 0.0518, wR_2 = 0.1229
Largest diff. peak/hole / e $Å^{-3}$	0.21/-0.19