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Electroreductive heterocyclization of *ortho*-piperidino substituted nitro(het)arenes

Roman S. Begunov, Valeria O. Sakulina, Mikhail A. Syroeshkin, Evgeniya A. Saverina, Alexandr A. Sokolov and Mikhail E. Minyaev

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1. Experimental

The melting points were determined with a Poly Therm A instrument with a heating rate of 3 °C and were not corrected. ^{1}H NMR spectra were recorded on a Bruker DRX400 instrument at a frequency of 400 MHz. ^{13}C NMR spectra were recorded at a frequency of 100 MHz using DMSO-d_6 as the solvent and internal standard. High-resolution mass spectra were recorded on a Bruker micrOTOF II instrument (Bruker Daltonics) with the electrospray ionization method (ESI) and MeCN as the solvent. Electrolysis was performed using a QJ5003C power source. Voltammetric curves were recorded with an IPC-Pro MF potentiostat (Econix). A disk glassy carbon working electrode (d = 1.7 mm) was used. It was thoroughly polished before each recording. The recording was carried out in a standard five-necked conical electrochemical cell equipped with a water jacket for temperature control. A platinum spiral was used as the counter electrode, and a silver chloride electrode was used as the reference electrode. The solution was purged with high purity argon before recording in order to remove dissolved oxygen. The polarograms were obtained using a PU-1 polarograph.

Electrochemical investigation of 1-[2-nitro(het)aryl]piperidine reduction by cyclic voltammetry

Cyclic voltammetry was carried out using a PC-piloted digital potentiostat IPC-Pro-MF (Econix). A standard thermostated (T = 25 ± 0.5 °C) 10 ml electrochemical cell was used in a three-electrode configuration. As a working electrode, a GC (1.7 mm) disk was used, polished before each run; a Pt wire was used as an auxiliary electrode. The potentials are referred to the AgCl/KCl sat. electrode separated from the analyte by an electrolytic bridge filled with the same solution. All measurements were carried out under high purity argon. Each CV curve was reproduced at least three times. The one-electron current was determined from the peak current of the fully reversible reduction of nitrobenzene in acetonitrile and DMF at the same potential scan rates. A correction was used with the known viscosity values of these solvents and water according to the Stokes-Einstein and Randles-Sevcik equations. It was determined that in the range of scan rates 0.1-5.0 V s^{-1}, the reduction of **1a** in 8% HCl remains completely irreversible and has a two-electron level.

Synthesis and Characterization of the Products. The electrolysis was carried out in a cylindrical undivided electrolyzer in the galvanostatic mode with intense magnetic stirring. A lead plate with an area of 20 cm^2 was used as a cathode, the current was 0.5 A. A graphite plate was used as an anode.

General method for the synthesis of 1,2,3,4-tetrahydropyrido[1,2-*a*]benzimidazoles and 6,7,8,9-tetrahydropyrido[3',2':4,5]imidazo[1,2-*a*]pyridine

Substrate **1** (0.5 g, 1.8–3 mmol) was used; a solution of 8% hydrochloric acid (50 ml) served as the electrolyte. The solution was preheated to 40 °C. Electrolysis was conducted until the initial compound completely disappeared in the electrolyte: as a rule, this occurred after passing 2.2-2.3 F•mol^{-1} of electricity. The completion of the process was monitored polarographically. After electrolysis was completed, the electrolyte was treated with aqueous ammonia until neutral and extracted three times with hot chloroform (3×25 ml). The extract was evaporated under reduced pressure to give the corresponding products **2**.

7-Trifluoromethyl-1,2,3,4-tetrahydropyrido[1,2-*a*]benzimidazole (2a). White solid. Yield 0.42 g (97%). mp = 129-132 °C. ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 1.94 (m, 2H, piperidine), 2.04 (m, 2H, piperidine), 2.99 (m, 2H, piperidine), 4.14 (m, 2H, piperidine), 7.48 (m, 1H, H^9), 7.64 (dd, *J* 8.5 Hz, 2.3 Hz, 1H, H^8), 7.86 (s, 1H, H^6). ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 20.6, 22.5, 25.6, 43.1, 111.1, 115.8, 118.4, 123.1 (q, *J* 31 Hz), 125.9 (q, *J* 270 Hz), 137.5, 142.7, 154.9. HRMS: *m/z* calcd for $C_{12}H_{12}F_3N_2^+$ 241.0953 [M+H]$^+$, found: 241.0947.

1,2,3,4-Tetrahydropyrido[1,2-*a*]benzimidazole (2b). White solid. Yield 0.38 g (91%). mp = 90-93 °C (lit. [S1] mp = 93-94 °C). ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 1.91 (m, 2H, piperidine), 2.04 (m, 2H, piperidine), 2.94 (t, *J* 6.4 Hz, 2H, piperidine), 4.06 (t, *J* 6.1 Hz, 2H, piperidine), 7.16 (m, 2H), 7.40 (m, 1H), 7.52 (m, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 20.9, 22.7, 25.6, 42.7, 110.0, 118.7, 121.7, 122.1, 135.2, 143.2, 152.1. HRMS: *m/z* calcd for $C_{11}H_{13}N_2^+$ 173.1079 [M+H]$^+$, found: 173.1068.

1,2,3,4-Tetrahydropyrido[1,2-*a*]benzimidazole-7-carbonitrile (2c). Light yellow solid. Yield 0.39 g (92%). mp = 169-172 °C. ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 1.93 (m, 2H, piperidine), 2.04 (m, 2H, piperidine), 2.99 (t, *J* 6.1 Hz, 2H, piperidine), 4.14 (t, *J* 6.1 Hz, 2H, piperidine), 7.57 (dd, *J* 8.3 Hz, 1.6 Hz, 1H, H^8), 7.63 (d, *J* 8.3 Hz, 1H, H^9), 8.02 (s, 1H, H^6). ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 20.5, 22.4, 25.6, 43.2, 104.3, 111.7, 120.8, 123.4, 125.4, 138.2, 142.7, 155.4. HRMS: *m/z* calcd for $C_{12}H_{12}N_3^+$ 198.1032 [M+H]$^+$, found: 198.1021.

7-Chloro-1,2,3,4-tetrahydropyrido[1,2-*a*]benzimidazole (2d). White solid. Yield 0.40 g (93%). mp = 147-149 °C (lit. mp = 152 °C)[2]. ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 1.92 (m, 2H, piperidine), 2.03 (m, 2H, piperidine), 2.95 (t, *J* 6.3 Hz, 2H, piperidine), 4.08 (t, *J* 6.0 Hz, 2H, piperidine), 7.19 (dd, *J* 8.5 Hz, 2.0 Hz, 1H, H^8), 7.47 (d, *J* 8.5 Hz, 1H, H^9), 7.56 (d, *J* 2.0 Hz, 1H, H^6). ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 20.6, 22.5, 25.6, 42.9, 111.4, 118.1, 121.7, 126.6, 134.0, 144.1, 154.0. HRMS: *m/z* calcd for $C_{11}H_{12}N_2Cl^+$ 207.0689 [M+H]$^+$, found: 207.0684.

7-Nitro-1,2,3,4-tetrahydropyrido[1,2-*a*]benzimidazole (2e). Brown solid. Yield 0.41 g (95%). mp = 213-216 °C (lit. [S1] mp = 216-218 °C]). ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 1.97 (m, 2H, piperidine), 2.07 (m, 2H, piperidine), 3.03 (t, *J* 6.4 Hz, 2H, piperidine), 4.18 (t, *J* 6.1 Hz, 2H, piperidine), 7.63 (d, *J* 8.9 Hz, 1H, H^9), 8.09 (dd, *J* 8.8 Hz, 2.2 Hz, 1H, H^8), 8.36 (d, *J* 2.2 Hz,

1H, H^6). ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 20.4, 22.4, 25.7, 43.4, 110.7, 114.7, 117.6, 139.7, 142.4, 143.3, 156.8. HRMS: *m/z* calcd for $C_{11}H_{12}N_3O_2^+$ 218.0930 $[M+H]^+$, found: 218.0921.

6,7,8,9-Tetrahydropyrido[3',2':4,5]imidazo[1,2-*a*]pyridine (2f). White solid. Yield 0.38 g (91%). mp = 95-98 °C (lit. [S3] mp = 93 °C). ^1H NMR (DMSO-d_6, 400 MHz) δ: 1.95 (m, 2H, piperidine), 2.04 (m, 2H, piperidine), 2.98 (t, *J* 6.5 Hz, 2H, piperidine), 4.14 (t, *J* 6.1 Hz, 2H, piperidine), 7.20 (ddd, *J* 8.2 Hz, 4.3 Hz, 2.2 Hz, 1H, H^3), 7.90 (d, *J* 7.8 Hz, 1H, H^4), 8.23 (dt, *J* 3.5 Hz, 1.8 Hz, 1H, H^2). ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 20.6, 22.4, 25.8, 41.8, 118.5, 126.0, 135.2, 142.7, 148.2, 154.0. HRMS: *m/z* calcd for $C_{10}H_{12}N_3^+$ 174.1032 $[M+H]^+$, found: 174.1023.

2-(Piperidine-1-yl)-5-(trifluoromethyl)aniline. Substrate **1a** (0.5 g, 1.8 mmol) was used; a solution of 36% hydrochloric acid (50 ml) served as the electrolyte. The solution was preheated to 80 °C. Electrolysis was conducted until the initial compound **1a** completely disappeared in the electrolyte: this occurred after passing 6-6.1 F•mol^{-1} of electricity. The completion of the process was monitored polarographically. After electrolysis was completed, the electrolyte was teated with aqueous ammonia until neutral and extracted with hot chloroform (3×25 ml). The extract was evaporated under reduced pressure to give the corresponding product as the white solid. Yield 0.42 g (94%). mp = 50-51 °C. ^1H NMR (DMSO-d_6, 400 MHz) δ: 1.52 (m, 2H, piperidine), 1.66 (m, 4H, piperidine), 2.77 (t, *J* 5.2 Hz, 4H, piperidine), 5.07 (s, 2H, NH_2), 6.83 (dd, *J* 8.1 Hz, 2.2 Hz, 1H, H^4), 6.92-7.02 (m, 2H, $H^{3,6}$). ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 24.5, 26.6, 52.0, 110.6, 113.6, 119.8, 125.0 (q, *J* 31.0 Hz), 125.5 (q, *J* 270.0 Hz), 143.2, 143.4. HRMS: *m/z* calcd for $C_{12}H_{16}F_3N_2^+$ 245.1266 $[M+H]^+$, found: 245.1182.

2. Table S1. The effect of current, temperature and concentration of hydrochloric acid on the process of electroreduction of N-[2-nitro-4-(trifluoromethyl)phenyl]piperidine (**1a**)

Current strength, A	Electric charge, *F*•mol^{-1}	*T*, ºC	ω HCl, %	Ratio of **2a** : **1a** : **3a***
0.5	2	80	36	1 : 12.43 : 6.56
0.5	2	80	24	1 : 2.21 : 0.92
0.5	2	80	18	1 : 1.23 : 0.63
0.5	2	80	12	1 : 0.55 : 0.27
0.5	2	80	8	1 : 0.08 : 0.03
0.5	2	80	4	1 : 0.12 : 0.06
0.5	2	60	8	1 : 0.03 : 0.02
0.5	2	40	8	1 : 0.03 : 0.02
0.5	2	20	8	1 : 0.16 : 0.09
0.5	2.2	40	8	**2a** + traces of impurities
1	6.1	80	36	**3a** + traces of impurities

* - according to ^1H NMR spectroscopy

3. X-ray diffraction studies of 2a and 2c.

3.1. X-ray crystallographic data and refinement details.

X-ray diffraction data were collected at 100K on a Bruker Quest D8 diffractometer equipped with a Photon-III area-detector (graphite monochromator, shutterless φ- and ω-scan technique), using Mo K_α-radiation (0.71073 Å). The intensity data were integrated by the SAINT program [S4] and corrected for absorption and decay using SADABS (semi-empirical from equivalents) [S5]. The structure was solved by direct methods using SHELXT [S6] and refined on F^2 using full-matrix least-squares with SHELXL-2018 [S7]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were found from the electron density-difference map, but placed geomitrically (C-H distance = 0.950 Å for aromatic, 0.990 Å for methylene hydrogen atoms) and refined as riding atoms with relative isotropic displacement parameters $U_{iso}(H)=1.2U_{eq}(C)$. The SHELXTL program suite[4] was used for molecular graphics. Crystal data and structure refinement are summarized in Table S2.

Table S2. Crystal data and structure refinement for **2a** and **2c**.

Identification code	**2a**	**2c**
Empirical formula	$C_{12}H_{11}F_3N_2$	$C_{12}H_{11}N_3$
Formula weight	240.23	197.24
Crystal system	triclinic	orthorhombic
Space group	$P\bar{1}$,	*Pbca*
Unit cell dimensions		
a, Å	6.2608(2)	7.1674(2)
b, Å	8.2336(3)	11.8345(4)
c, Å	10.2971(4)	22.7718(8)
α, °	85.4144(10)	90
β, °	89.7475(10)	90
γ, °	79.8077(10)	90
Volume, $Å^3$	520.73(3)	1931.56(11)
Z	2	8
Calcd. density, g/cm^3	1.532	1.356
Absorption coefficient, mm^{-1}	0.130	0.084
F(000)	248	832
Crystal size, mm^3	0.57 x 0.14 x 0.08	0.58 x 0.10 x 0.08
Theta range for data collection	1.984 to 32.033	3.359 to 31.250
Index ranges	-9<=h<=9 -12<=k<=12 -15<=l<=15	-10<=h<=10 -17<=k<=17 -33<=l<=33
Reflections collected	22692	49378
Independent reflections [R(int)]	3618 [0.0392]	3144 [0.0672]
Observed reflections	2939	2504
Max. / min. transmission	0.8254 / 0.7857	0.8880 / 0.8490
Data / restraints / parameters	3618 / 84 / 181	3144 / 3 / 155
Goodness-of-fit on F2	1.040	1.033
R1 / wR2 indices [I>2sigma(I)]	0.0467 / 0.1071	0.0467 / 0.1096
R1 / wR2 indices (all data)	0.0618 / 0.1183	0.0640 / 0.1234
Largest diff. peak / hole, $e \cdot Å^{-3}$	0.431 / -0.353	0.336 / -0.242
CCDC	1991687	1991688

3.2. 7-Trifluoromethyl-1,2,3,4-tetrahydropyrido[1,2-*a*]benzimidazole (2a)

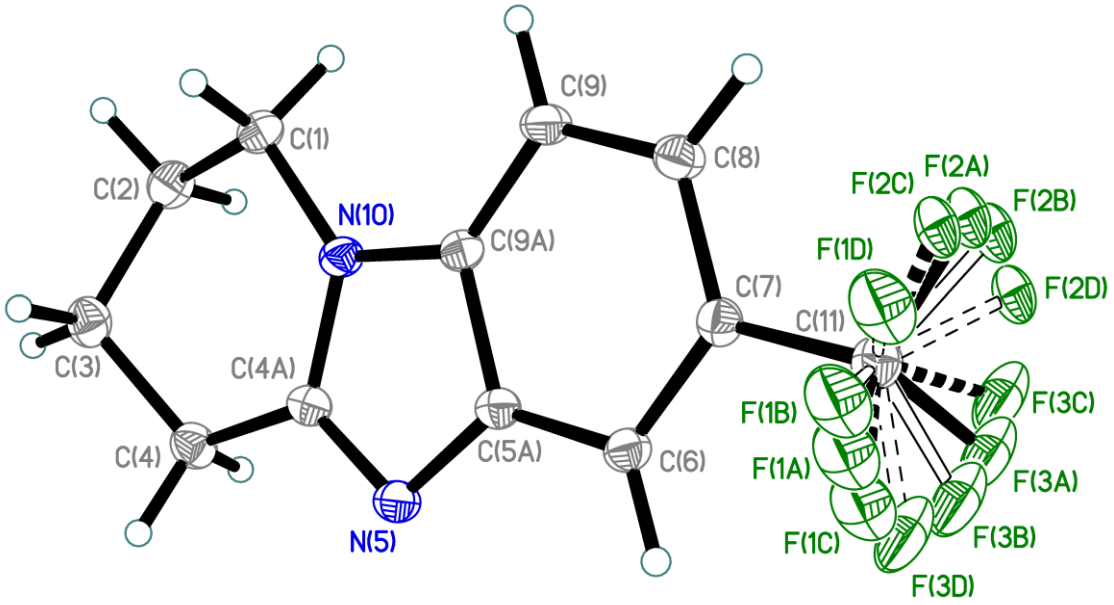

Figure S1. The crystal structure of **2a**. The thermal ellipsoids are set to 50%.

The fluorine atoms F1, F2 and F3 were disordered over four positions A/B/C/D (Fig. S1) with the occupancy ratio of 0.557(6):0.244(6):0.167(5):0.032(1). The thermal ellipsoids for equal atoms (A/B/C/D sets) were restrained to be the same. Bond distances in each of three sets (C(12)-F(1A/B/C/D), C(12)-F(2A/B/C/D) and C(12)-F(3A/B/C/D)) were refined as equal with the ESD of 0.002Å. Interatomic distances between F1, F2 and F3 atoms were set to be equal within 0.004Å. Carbon and nitrogen atoms, with the exception of C(2) and C(3), are located in one plane with largest deviations from the plane of 0.0522(8)Å for C(1), 0.0246(9)Å for N(10) and 0.0224(9)Å for C(4). Upon exclusion of atoms C(1) and C(4), the largest devaition from the plane fromed by atoms C(4A)..N(10), C(11) is much smaller — 0.0066(8)Å for N(10).

Table S3. Bond lengths (Å) in **2a**.

F(1A)-C(11)	1.3475(15)	F(2D)-C(11)	1.351(2)	C(5A)-C(6)	1.3949(15)
F(2A)-C(11)	1.3583(14)	F(3D)-C(11)	1.348(2)	C(5A)-C(9A)	1.4117(14)
F(3A)-C(11)	1.3497(15)	C(1)-N(10)	1.4628(14)	C(6)-C(7)	1.3915(15)
F(1B)-C(11)	1.346(2)	C(1)-C(2)	1.5236(16)	C(7)-C(8)	1.4059(15)
F(2B)-C(11)	1.348(2)	C(2)-C(3)	1.5253(17)	C(7)-C(11)	1.4947(15)
F(3B)-C(11)	1.347(2)	C(3)-C(4)	1.5311(17)	C(8)-C(9)	1.3904(15)
F(1C)-C(11)	1.344(2)	C(4)-C(4A)	1.4923(16)	C(9)-C(9A)	1.3874(15)
F(2C)-C(11)	1.348(2)	C(4A)-N(5)	1.3185(14)	C(9A)-N(10)	1.3758(14)
F(3C)-C(11)	1.348(2)	C(4A)-N(10)	1.3743(14)		
F(1D)-C(11)	1.346(2)	N(5)-C(5A)	1.3892(14)		

Table S4. Bond angles (Å) in **2a**.

F(1A)-C(11)-F(2A)	104.66(12)	N(10)-C(4A)-C(4)	120.55(10)
F(1A)-C(11)-F(3A)	107.33(13)	C(4A)-N(5)-C(5A)	104.47(9)
F(3A)-C(11)-F(2A)	104.95(12)	N(5)-C(5A)-C(6)	129.79(10)
F(1B)-C(11)-F(2B)	106.4(2)	N(5)-C(5A)-C(9A)	110.19(9)
F(1B)-C(11)-F(3B)	106.3(2)	C(6)-C(5A)-C(9A)	120.01(10)
F(3B)-C(11)-F(2B)	107.0(2)	C(7)-C(6)-C(5A)	117.23(10)
F(1C)-C(11)-F(3C)	106.3(2)	C(6)-C(7)-C(8)	122.37(10)
F(1C)-C(11)-F(2C)	106.8(2)	C(6)-C(7)-C(11)	118.33(10)
F(3C)-C(11)-F(2C)	106.3(2)	C(8)-C(7)-C(11)	119.30(10)
F(1D)-C(11)-F(2D)	106.3(3)	C(9)-C(8)-C(7)	120.61(10)
F(1D)-C(11)-F(3D)	106.5(3)	C(9A)-C(9)-C(8)	117.07(10)
F(3D)-C(11)-F(2D)	106.2(3)	N(10)-C(9A)-C(9)	132.13(10)
N(10)-C(1)-C(2)	110.26(9)	N(10)-C(9A)-C(5A)	105.17(9)
C(1)-C(2)-C(3)	111.46(9)	C(9)-C(9A)-C(5A)	122.69(10)
C(2)-C(3)-C(4)	110.52(10)	C(4A)-N(10)-C(9A)	106.71(9)
C(4A)-C(4)-C(3)	111.35(9)	C(4A)-N(10)-C(1)	126.49(9)
N(5)-C(4A)-N(10)	113.44(10)	C(9A)-N(10)-C(1)	126.55(9)
N(5)-C(4A)-C(4)	125.99(10)		

3.3. 1,2,3,4-Tetrahydropyrido[1,2-*a*]benzimidazole-7-carbonitrile (2c)

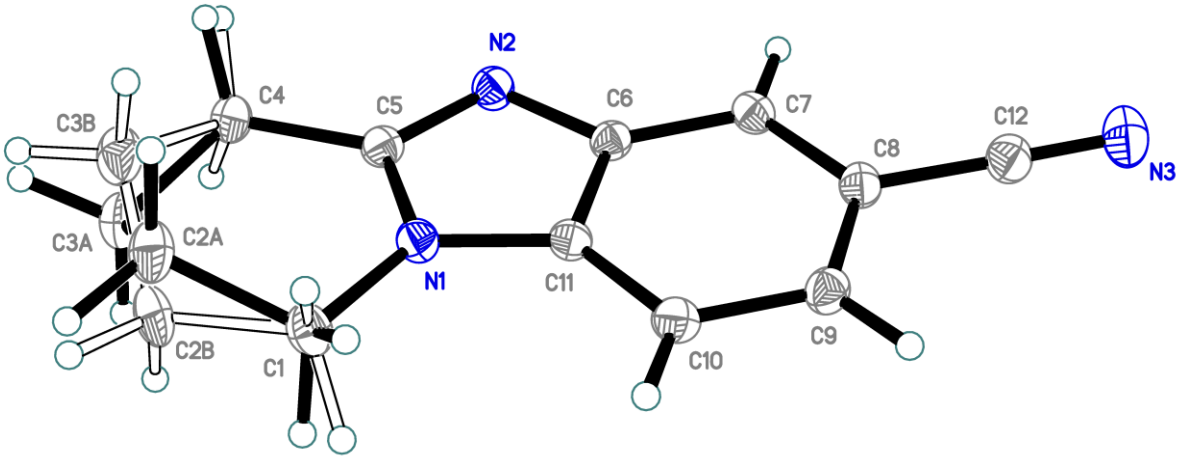

Figure S2. The crystal structure of **2c**. The thermal ellipsoids are set to 50%. A minor component of the disorder is drawn with open solid lines.

All hydrogen atoms and atoms C(2), C(3) of the –$(CH_2)_4$– fragment are disordered over two positions (Fig. S2) with the occupancy ratio of 0.733(4):0.267(4). Bond distances for equivalent C-C bonds in the disordered fragment were set as equal within 0.001Å. Carbon and nitrogen atoms, with the exception of C(2) and C(3), are located in one plane with largest deviations from the plane of 0.0335(9)Å for C(1), 0.0295(9)Å for C(4) and 0.0295(9)Å for N(5). For the plane defined by atoms C(4A)..N(10), C(11) and N(12), the largest deviations are 0.0194(9) for C(6), 0.0186(8) for N(5) and 0.0142(8) for N(10).

Table S5. Bond lengths (Å) in **2c**.

C(1)-N(10)	1.4648(14)	C(4)-C(4A)	1.4938(15)	C(7)-C(8)	1.4128(16)
C(1)-C(2A)	1.5232(18)	C(4A)-N(5)	1.3216(15)	C(7)-C(11)	1.4382(16)
C(1)-C(2B)	1.524(2)	C(4A)-N(10)	1.3739(14)	C(8)-C(9)	1.3838(16)
C(2A)-C(3A)	1.524(2)	N(5)-C(5A)	1.3875(14)	C(9)-C(9A)	1.3925(15)
C(3A)-C(4)	1.5327(19)	C(5A)-C(6)	1.3899(15)	C(9A)-N(10)	1.3758(14)
C(2B)-C(3B)	1.524(2)	C(5A)-C(9A)	1.4092(15)	C(11)-N(12)	1.1526(16)
C(3B)-C(4)	1.531(2)	C(6)-C(7)	1.3927(15)		

Table S6. Bond angles (Å) in **2c**.

N(10)-C(1)-C(2A)	109.40(11)	C(6)-C(5A)-C(9A)	119.67(10)
N(10)-C(1)-C(2B)	109.37(18)	C(5A)-C(6)-C(7)	117.60(10)
C(1)-C(2A)-C(3A)	109.82(13)	C(6)-C(7)-C(8)	122.22(10)
C(2A)-C(3A)-C(4)	112.20(13)	C(6)-C(7)-C(11)	118.34(11)
C(1)-C(2B)-C(3B)	112.3(3)	C(8)-C(7)-C(11)	119.44(10)
C(2B)-C(3B)-C(4)	107.6(3)	C(9)-C(8)-C(7)	120.42(10)
C(4A)-C(4)-C(3B)	111.0(2)	C(8)-C(9)-C(9A)	117.06(11)
C(4A)-C(4)-C(3A)	112.37(11)	N(10)-C(9A)-C(9)	131.86(10)
N(5)-C(4A)-N(10)	113.23(10)	N(10)-C(9A)-C(5A)	105.13(9)
N(5)-C(4A)-C(4)	125.91(10)	C(9)-C(9A)-C(5A)	123.00(10)
N(10)-C(4A)-C(4)	120.83(10)	C(4A)-N(10)-C(9A)	106.83(9)
C(4A)-N(5)-C(5A)	104.47(9)	C(4A)-N(10)-C(1)	126.26(9)
N(5)-C(5A)-C(6)	129.99(10)	C(9A)-N(10)-C(1)	126.90(9)
N(5)-C(5A)-C(9A)	110.33(9)	N(12)-C(11)-C(7)	178.81(14)

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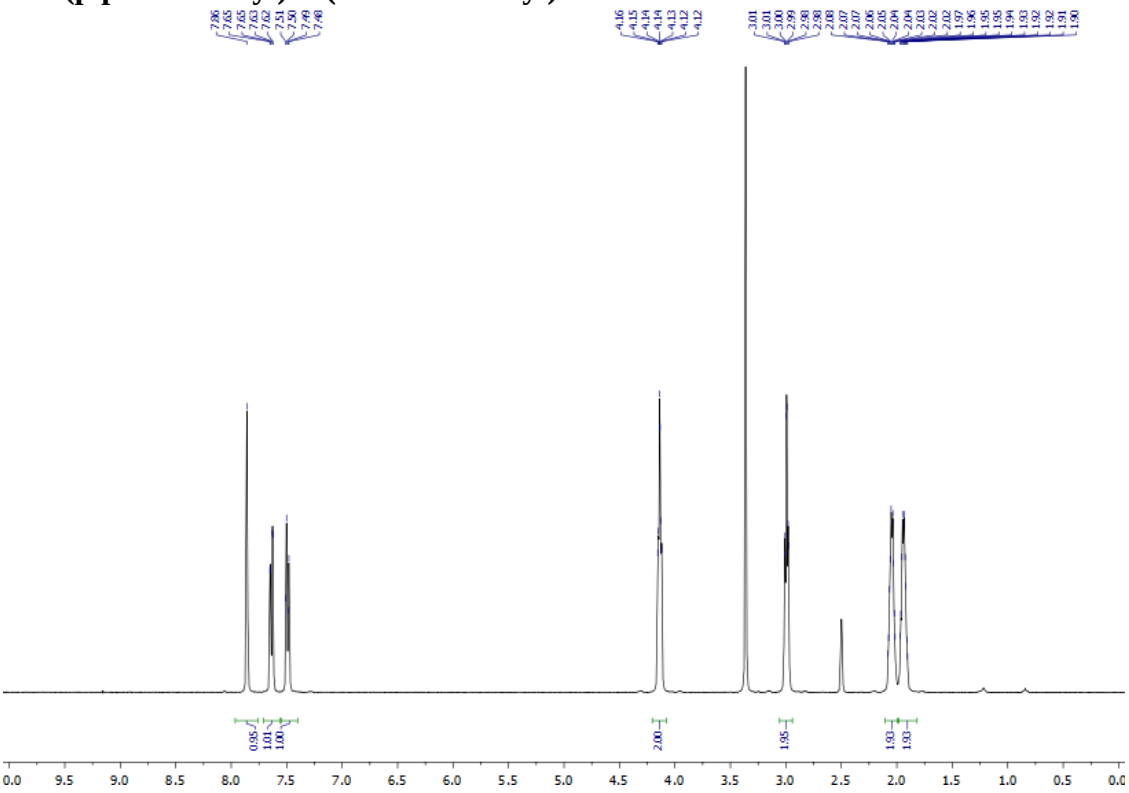
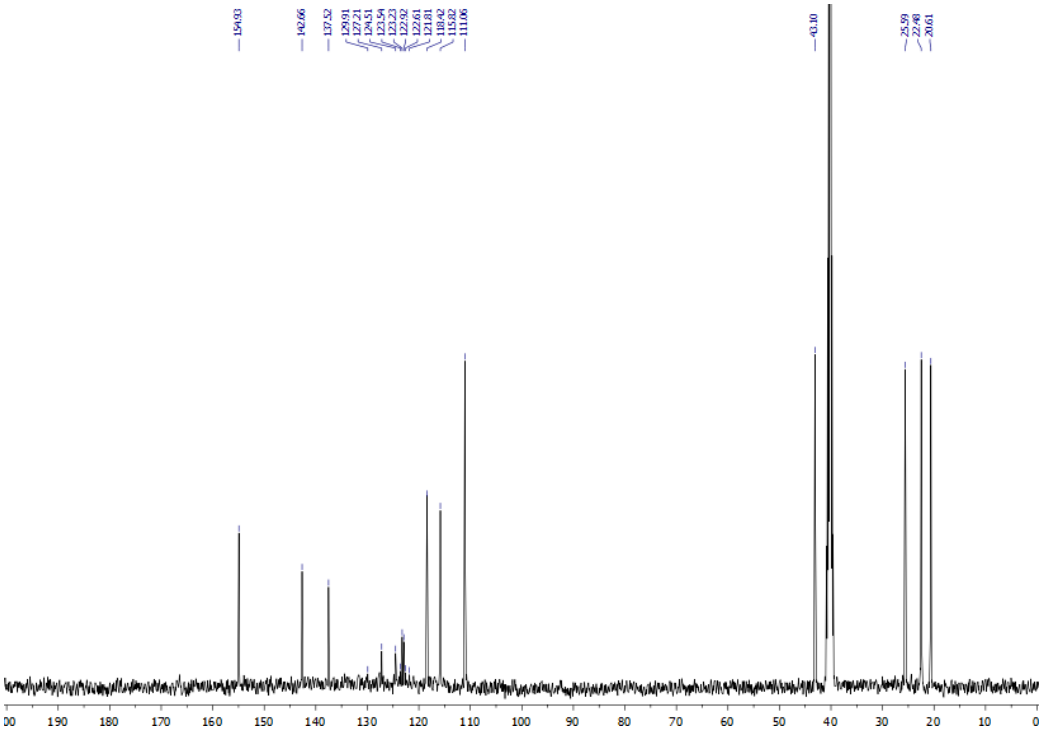
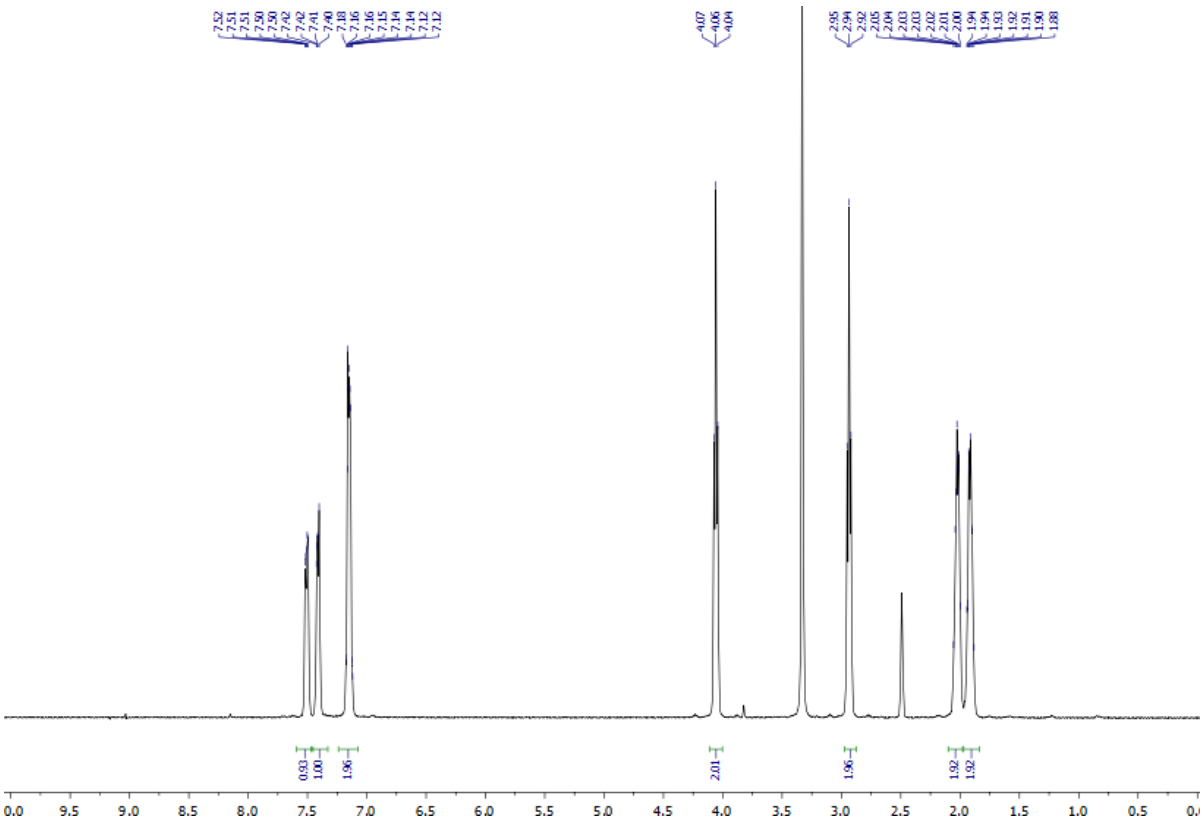
5. ^{1}H and ^{13}C NMR spectra of 1,2,3,4-tetrahydropyrido[1,2-*a*]benzimidazoles, 6,7,8,9-tetrahydropyrido[3',2':4,5]imidazo[1,2-*a*]pyridine and 2-(piperidine-1-yl)-5-(trifluoromethyl)aniline



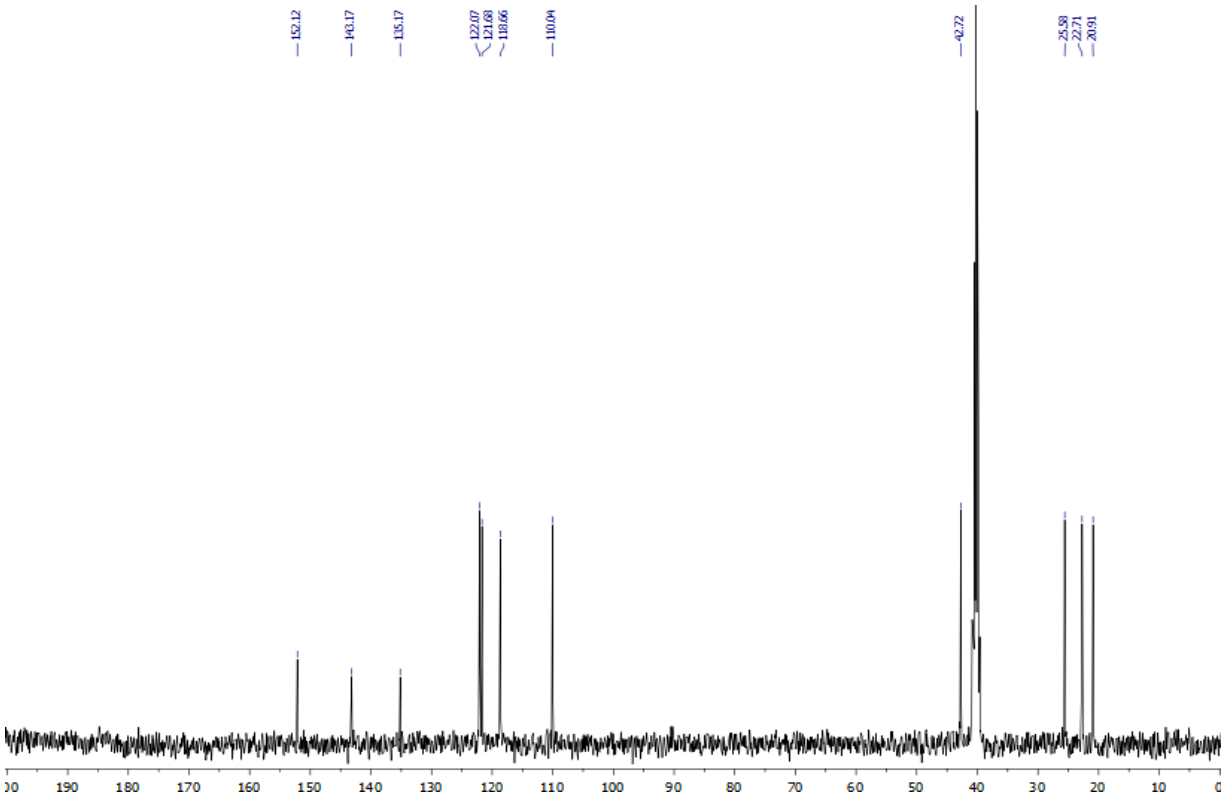
^{1}H NMR spectrum of 7-trifluoromethyl-1,2,3,4-tetrahydropyrido[1,2-*a*]benzimidazole (Bruker DRX400, SF=400 MHz, DMSO-d_6)



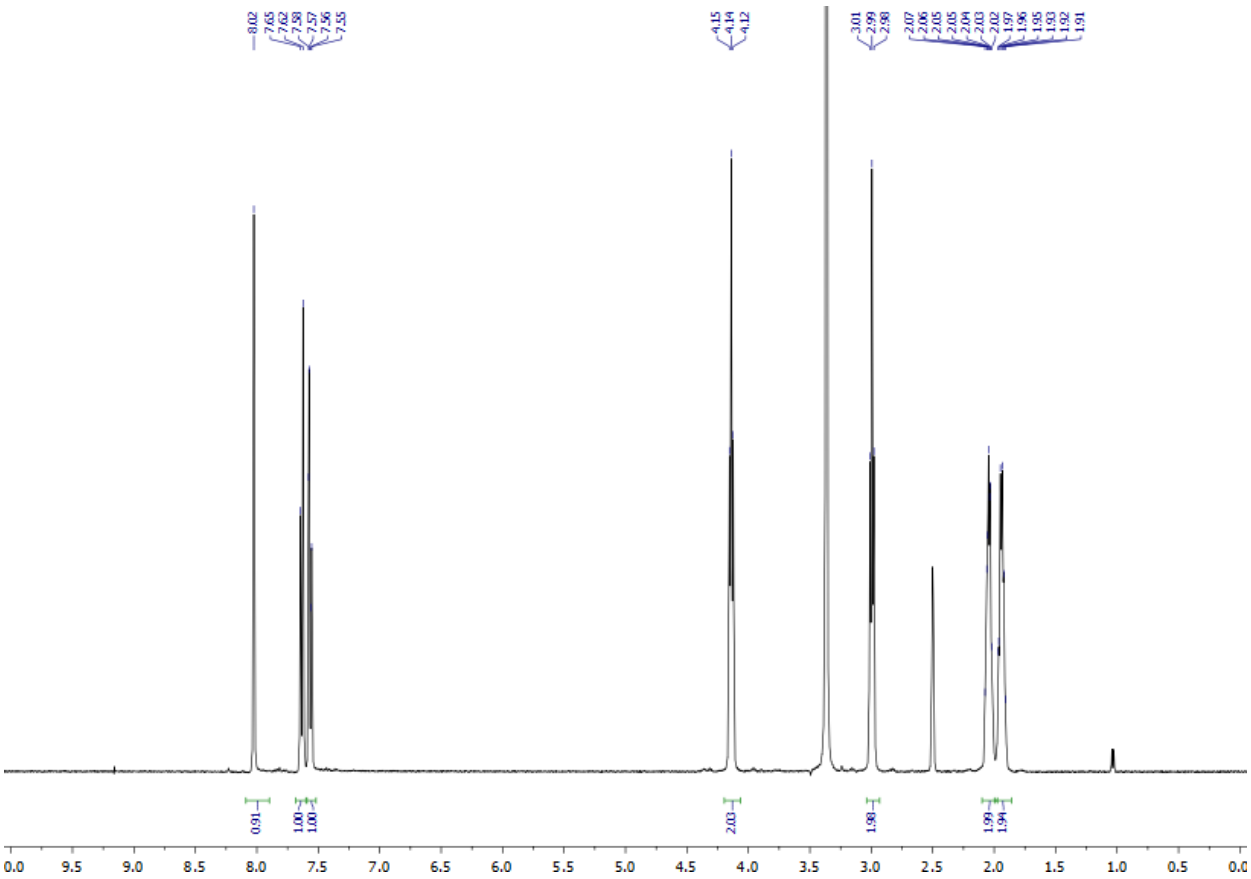
^{13}C NMR spectrum of 7-trifluoromethyl-1,2,3,4-tetrahydropyrido[1,2-*a*]benzimidazole (Bruker DRX400, SF=100 MHz, DMSO-d_6)



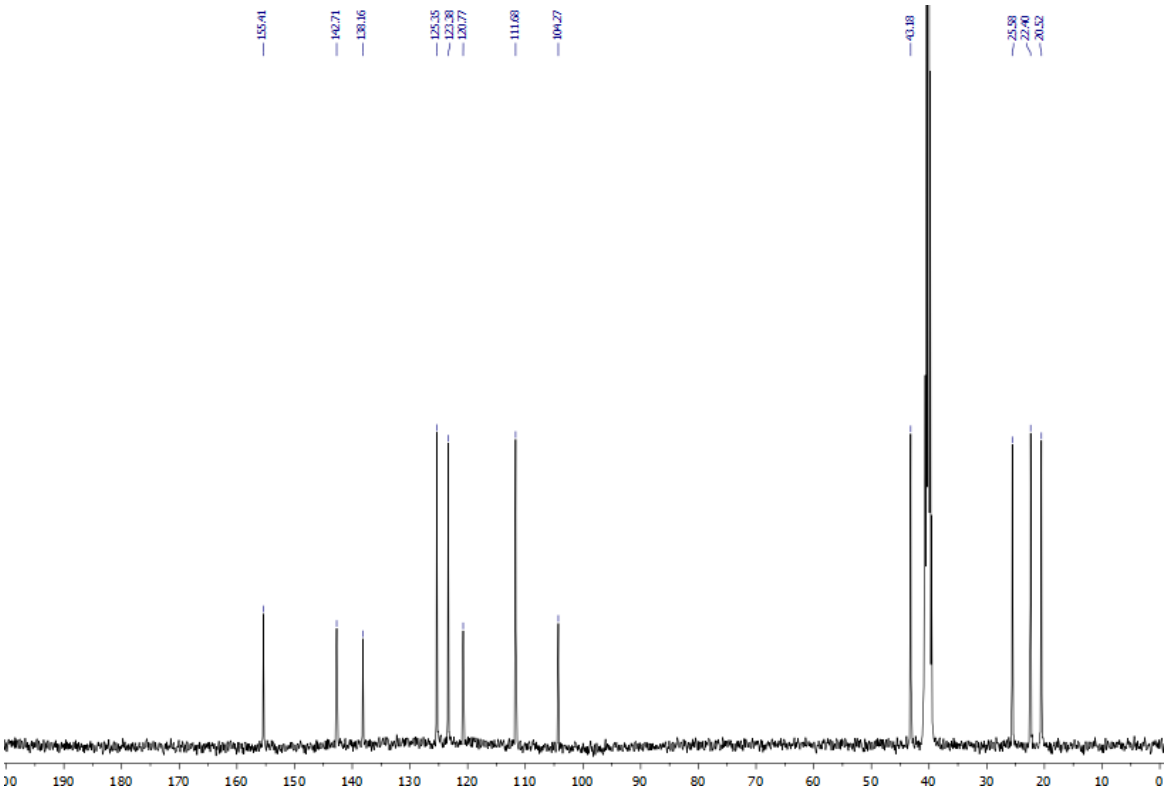
^{1}H NMR spectrum of 1,2,3,4-tetrahydropyrido[1,2-*a*]benzimidazole (Bruker DRX400, SF=400 MHz, DMSO-d_6)



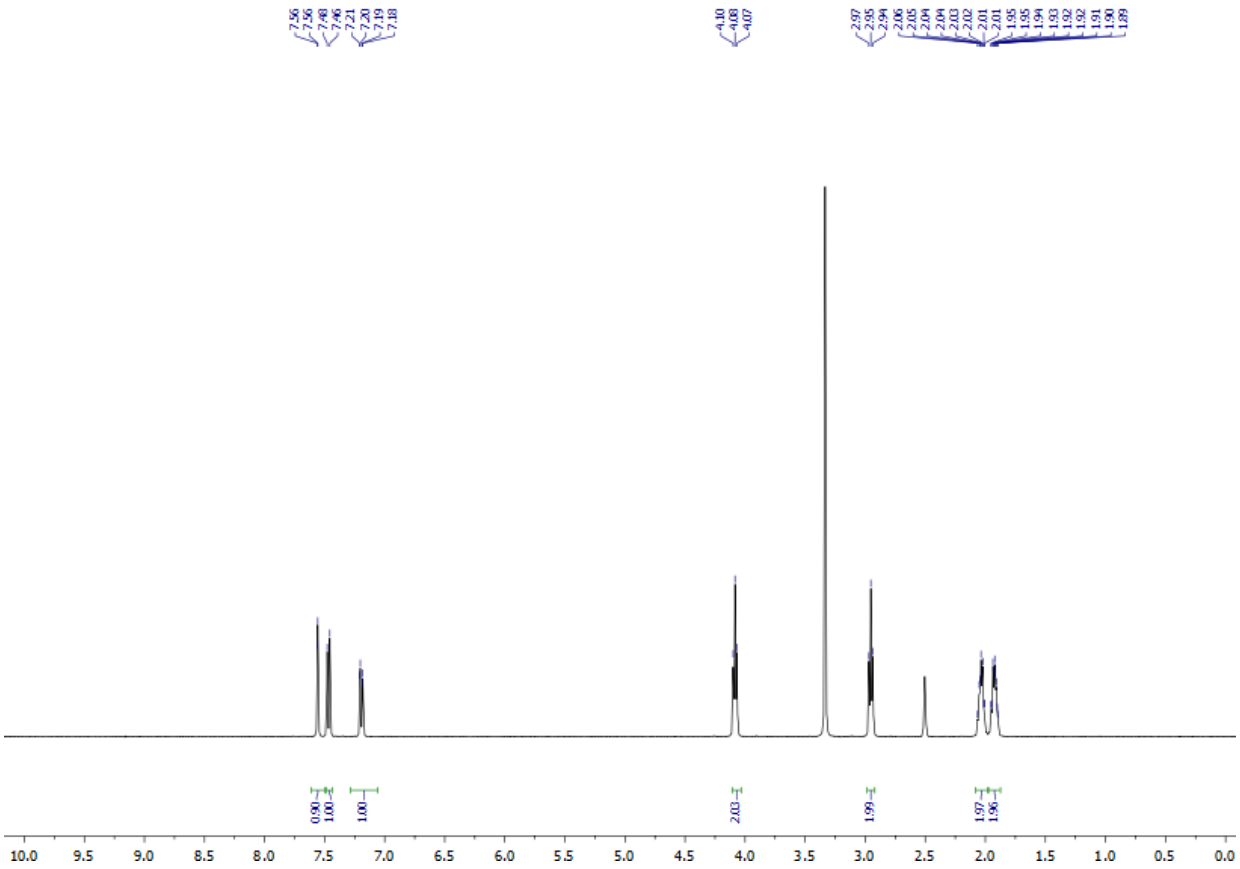
^{13}C NMR spectrum of 1,2,3,4-tetrahydropyrido[1,2-*a*]benzimidazole (Bruker DRX400, SF=100 MHz, DMSO-d_6)



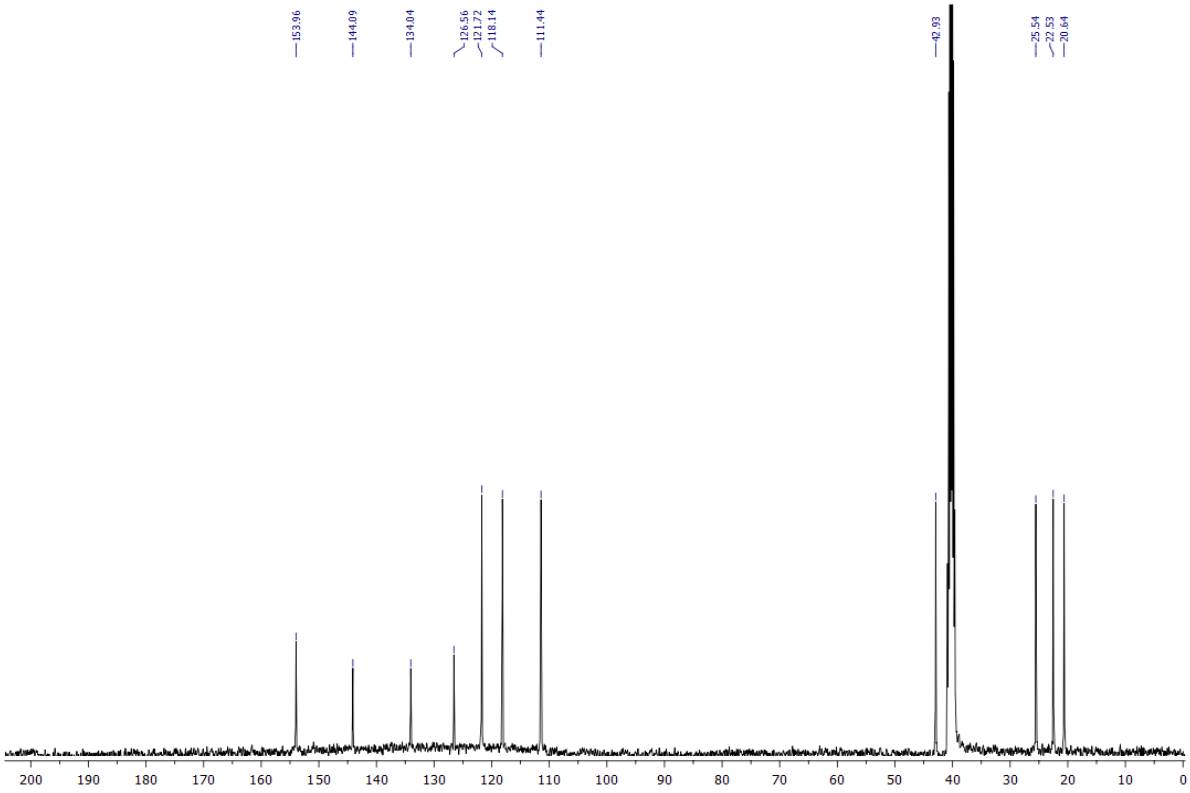
^{1}H NMR spectrum of 1,2,3,4-tetrahydropyrido[1,2-*a*]benzimidazole-7-carbonitrile (Bruker DRX400, SF=400 MHz, DMSO-d_6)



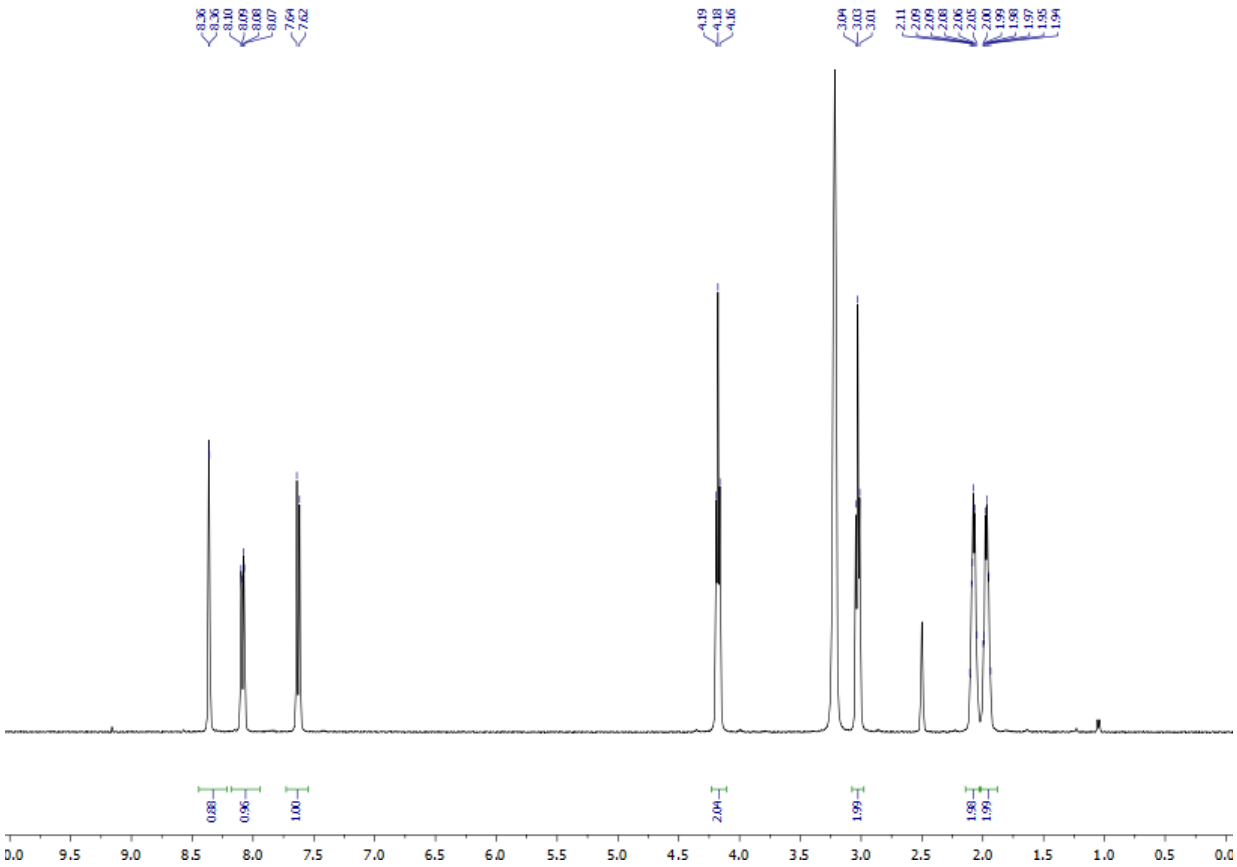
^{13}C NMR spectrum of 1,2,3,4-tetrahydropyrido[1,2-*a*]benzimidazole-7-carbonitrile (Bruker DRX400, SF=100 MHz, DMSO-d_6)



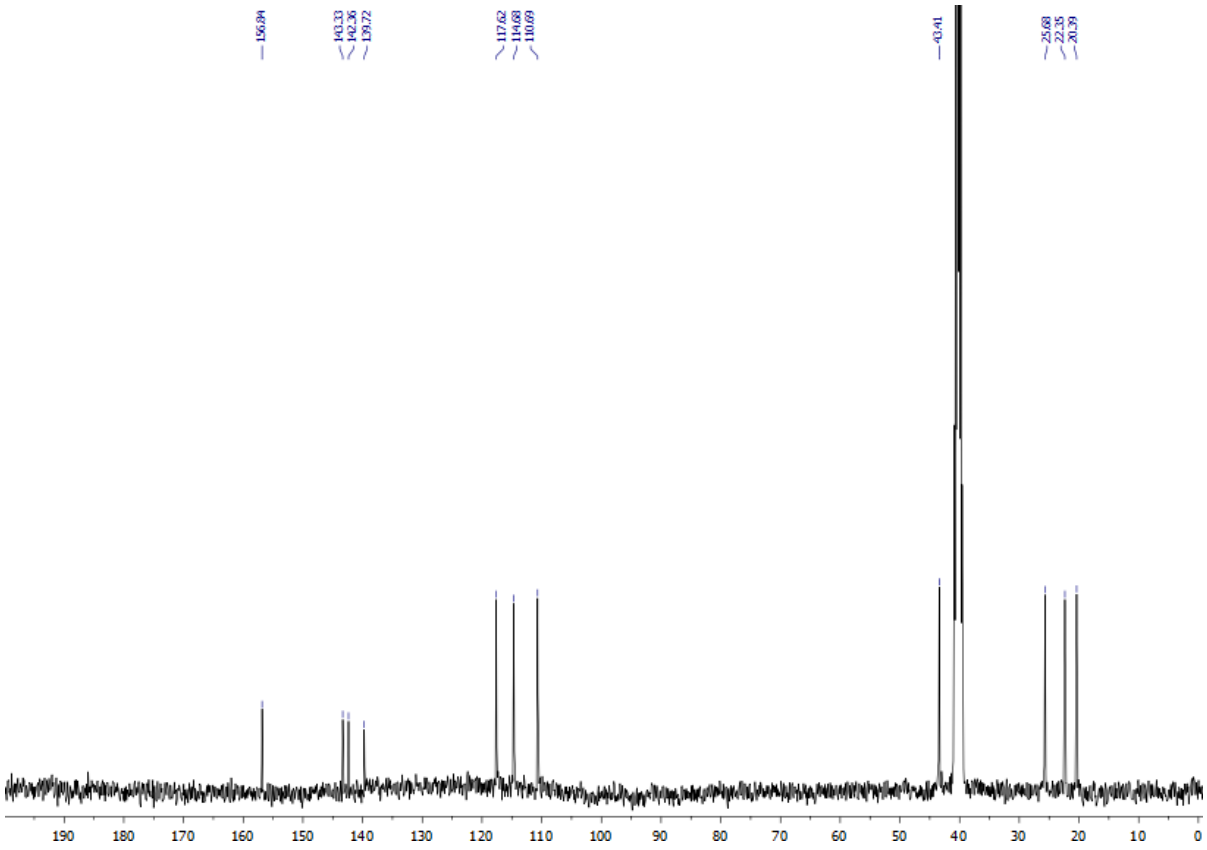
^{1}H NMR spectrum of 7-chloro-1,2,3,4-tetrahydropyrido[1,2-*a*]benzimidazole (Bruker DRX400, SF=400 MHz, DMSO-d_6)



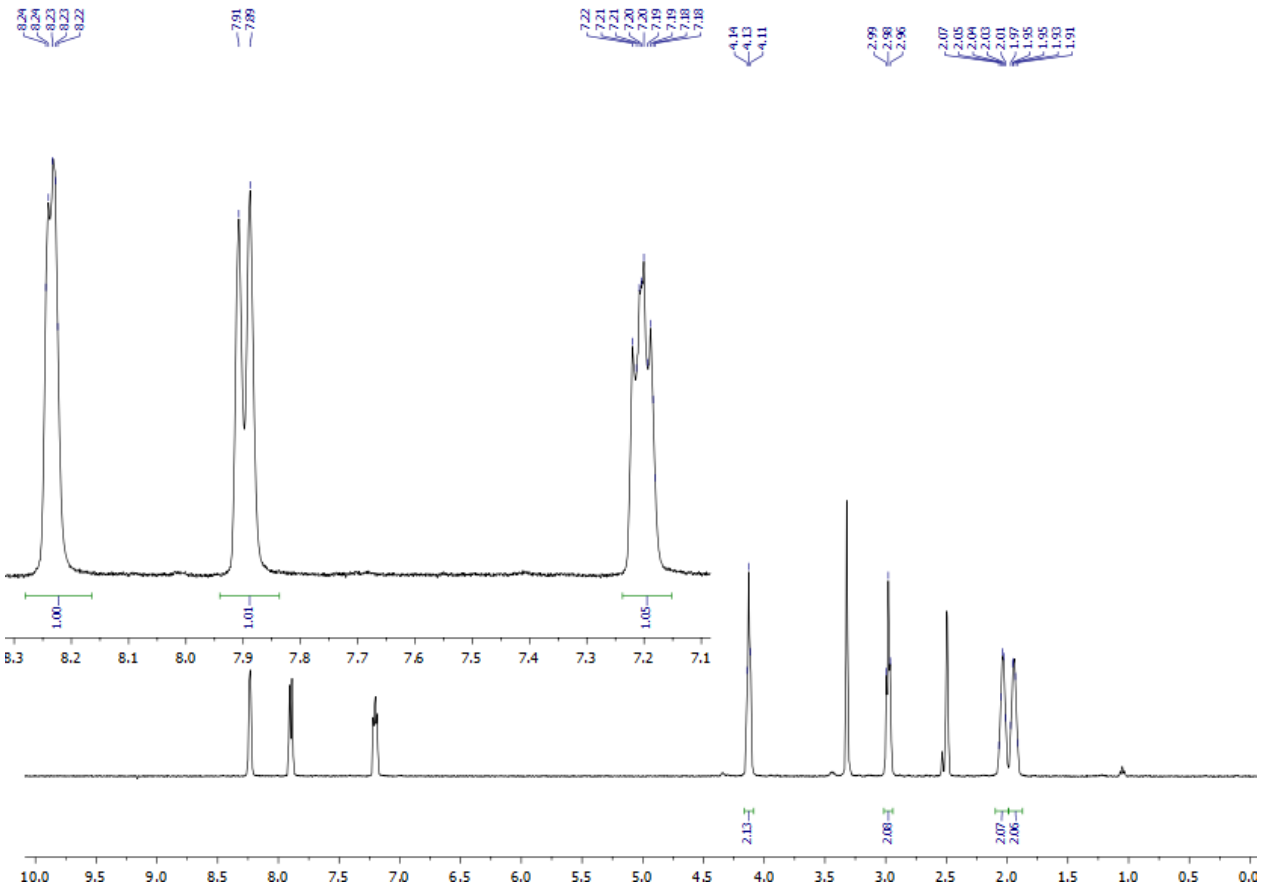
^{13}C NMR spectrum of 7-chloro-1,2,3,4-tetrahydropyrido[1,2-*a*]benzimidazole (Bruker DRX400, SF=100 MHz, DMSO-d_6)



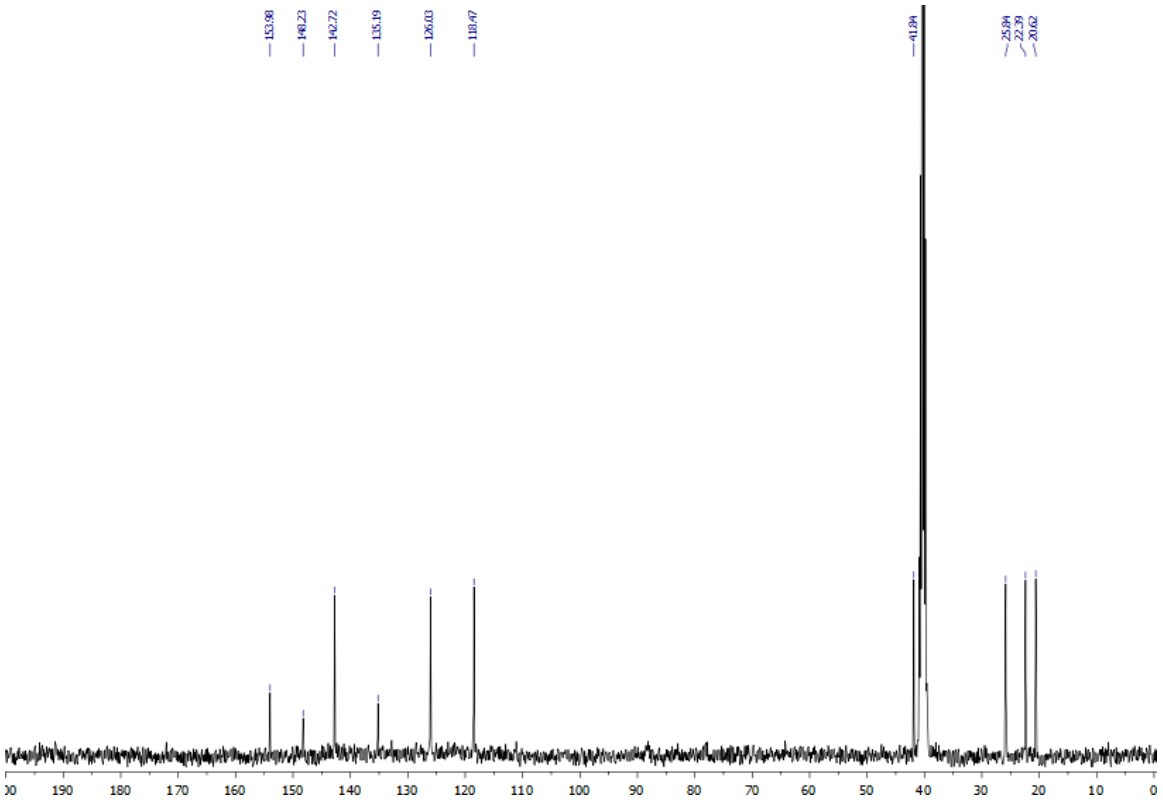
^{1}H NMR spectrum of 7-nitro-1,2,3,4-tetrahydropyrido[1,2-*a*]benzimidazole (Bruker DRX400, SF=400 MHz, DMSO-d_6)



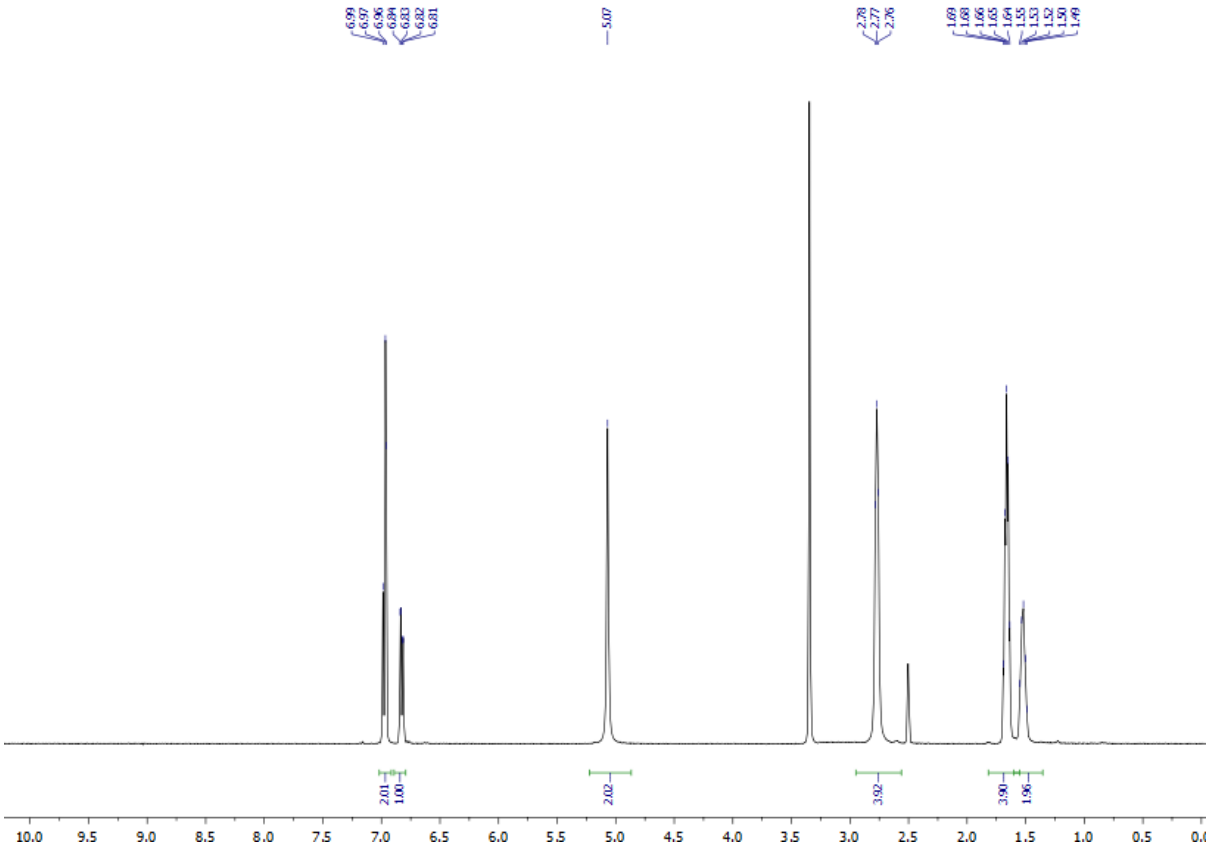
^{13}C NMR spectrum of 7-nitro-1,2,3,4-tetrahydropyrido[1,2-*a*]benzimidazole (Bruker DRX400, SF=100 MHz, DMSO-d_6)



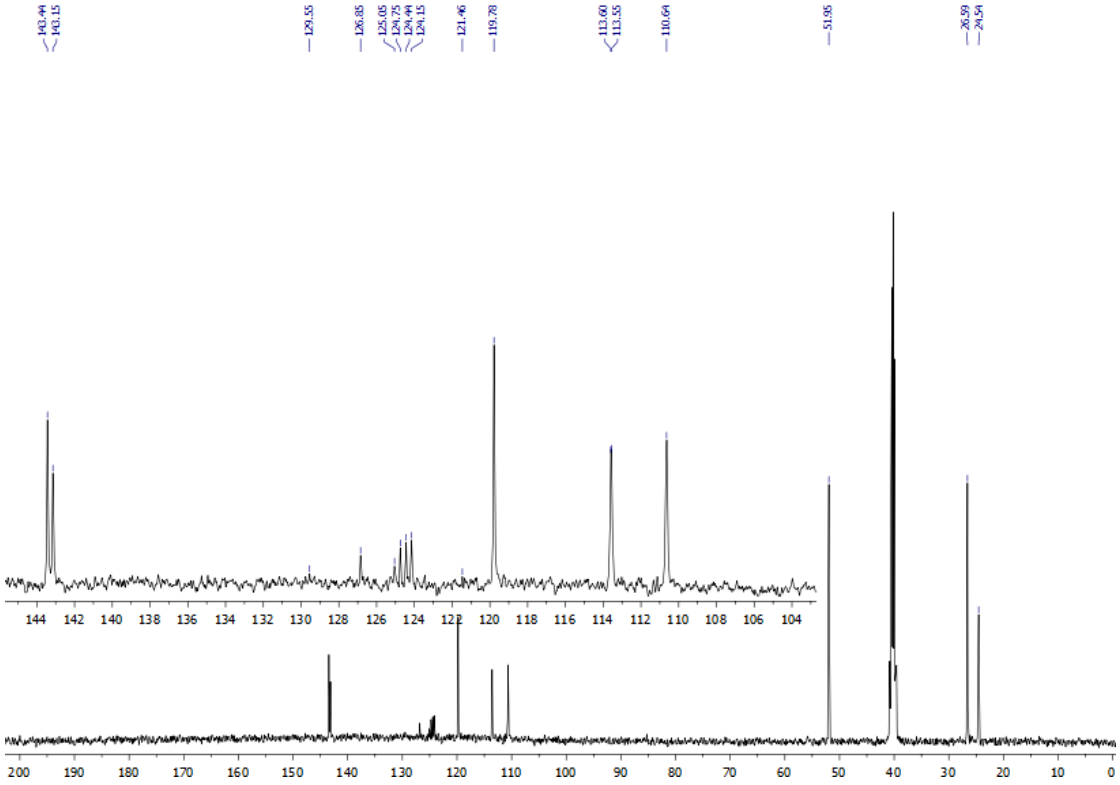
^{1}H NMR spectrum of 6,7,8,9-tetrahydropyrido[3',2':4,5]imidazo[1,2-*a*]pyridine (Bruker DRX400, SF=400 MHz, DMSO-d_6)



^{13}C NMR spectrum of 6,7,8,9-tetrahydropyrido[3',2':4,5]imidazo[1,2-*a*]pyridine (Bruker DRX400, SF=100 MHz, DMSO-d_6)



^{1}H NMR spectrum of 2-(piperidin-1-yl)-5-(trifluoromethyl)aniline (Bruker DRX400, SF=400 MHz, DMSO-d_6)



^{13}C NMR spectrum of 2-(piperidin-1-yl)-5-(trifluoromethyl)aniline (Bruker DRX400, SF=100 MHz, DMSO-d_6)