Supporting Information

Direct synthesis of novel quinoxaline derivatives via palladium-catalyzed reductive annulation of catechols and nitroarylamines

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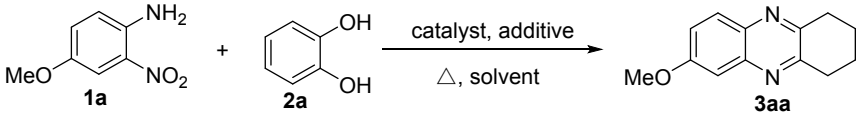
1. General Information

All the obtained products were characterized by melting points (m.p.), ^{1}H-NMR, ^{13}C-NMR, infrared spectra (IR), and mass spectra (MS), the NMR spectra of the known compounds were found to be identical with the ones reported in the literatures. Additionally, all the new compounds were further characterized by high resolution mass spectra (HRMS). Melting points were measured on an Electrothemal SGW-X4 microscopy digital melting point apparatus and are uncorrected; IR spectra were recorded on a FTLA2000 spectrometer; ^{1}H-NMR, ^{13}C-NMR spectra were obtained on Bruker-400; Mass spectra were recorded on Trace DSQ GC/MS, High-resolution mass spectra (HRMS) were recorded on a JEOL JMS-600 spectrometer. Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane. Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), multiplet (m); TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF254), and visualization was effected at 254 nm; All the reagents were purchased from commercial sources (J&KChemic, TCI, Fluka, Acros, SCRC), and used without further purification. Especially for commercially available Pd/C (10 wt %, wetted with 55% H_2O) purchased from Energy Chemical.

2.1 Table S1. Optimization of reaction conditions.[a]



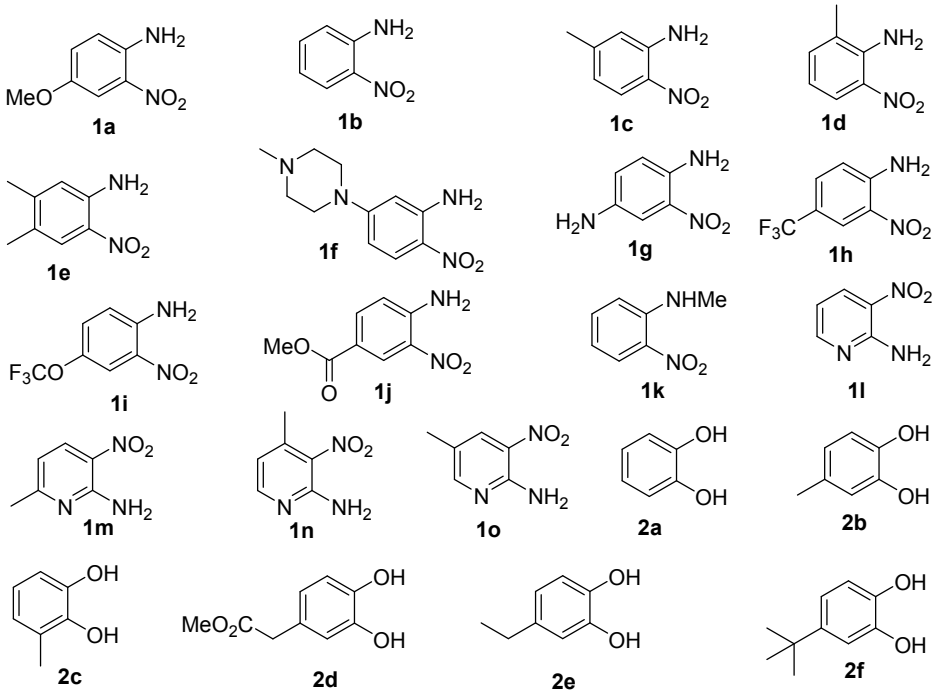
Entry	Catalyst	Additive	Yield(%)[b]
1	Pd/C	-	42
2	Pd/C	*t*-BuOK	75
3	-	*t*-BuOK	0
4	Pd/C	*t*-BuOK	0[c]
5	$Pd(OAc)_2$	*t*-BuOK	0
6	$Pd(TFA)_2$	*t*-BuOK	5
7	$Pd(OH)_2/C$	*t*-BuOK	62
8	Pd/C	K_2CO_3	80
9	Pd/C	NaOH	53
10	Pd/C	Cs_2CO_3	68
11	Pd/C	DABCO	45
12	Pd/C	pyrrolidine	69
13	Pd/C	CF_3COOH	5
14	Pd/C	K_2CO_3	28[d]
15	Pd/C	K_2CO_3	[76,48,36,0][e]
16	Pd/C	K_2CO_3	[85,84][f]
17	Pd/C	K_2CO_3	[91,90][g]
18	Pd/C	K_2CO_3	[78,89][h]
19	Pd/C	K_2CO_3	[80,87][i]

20	Pd/C	K_2CO_3	87[j]

[a] Unless otherwise stated, all reactions charged with a H_2 balloon were performed with **1a** (0.25 mmol), **2a** (0.25 mmol), catalyst (2 mol%), *p*-xylene (1.5 mL), K_2CO_3 (20 mol%) at 120 °C for 12 h. [b] GC Yield. [c] without H_2. [d] HCOONa as the hydrogen sources. [e] Yields are respect to toluene, 1,4-dioxane, *t*-AmOH and DMF used as the reaction solvents, respectively. [f] The yields are with respect to 0.35 mmol and 0.375mmol of **2a**. [g] The yields (**2a**: 0.35 mmol) are with respect to 3 mol% and 4 mol% of catalyst, respectively. [h] Yields [**2a** (0.35 mmol), catalyst (3 mol%)] are with respect to 10 mol% and 30 mol% of K_2CO_3, respectively. [i] Yields [**2a** (0.35 mmol), K_2CO_3 (20 mol%), catalyst (3 mol%)] of the temperature at 110 °C and 130 °C, respectively. [j] Yields [**2a** (0.35 mmol), K_2CO_3 (20 mol%), pyrrolidine (20 mol%), catalyst (3 mol%)] of the temperature at 120 °C.

We initiated our investigations by chosing the reductive annulation of 4-methoxy-2-nitroaniline **(1a)** and catechol **(2a)** as a benchmark system to evaluate different reaction parameters. First, the reaction was performed at 120 ℃ for 12 h under H_2 atmosphere in the presence of 2 mol% Pd/C. To our delight, a 1,2,3,4-tetrahydrophenazine **3aa** was obtained in 42% yield (Table S1, entry 1). Interestingly, the addition of *t*-BuOK significantly improved the product yield 75% (entry 2), and the blank experiments showed that both the catalyst and H_2 are essential for the reaction (entries 3-4). Then, the use of other Pd catalysts exhibited either low or no activity (entries 5-7). The screening of base and acid additives showed that K_2CO_3 was the best choice (entries 8–13). The use of HCOONa as an reductant only resulted in a 28% yield (entry 14). The test of polar and less-polar solvents indicated that they were inferior to *p*-xylene (entry 15). Further, the use of a slight excess of catechol increased the yield to 85% (entry 16), 3 mol% of catalyst and 20 mol% of K_2CO_3 appeared to be sufficient for this reaction (entries 17-18). Finally, the increase or decrease of reaction temperature resulted in diminished yield (entry 19). The extra addition of pyrrolidine rarely accelerated the reaction (entry 20). Hence, the optimal conditions are as described in (entry 17): 3 mol% of catalyst, 20 mol% of K_2CO_3, the temperature at 120 °C.

Scheme S1. Substrates employed for synthesizing novel quinoxaline derivatives



2.2 Time-concentration profile of 4-methoxy-2-nitroaniline coupled with catechol

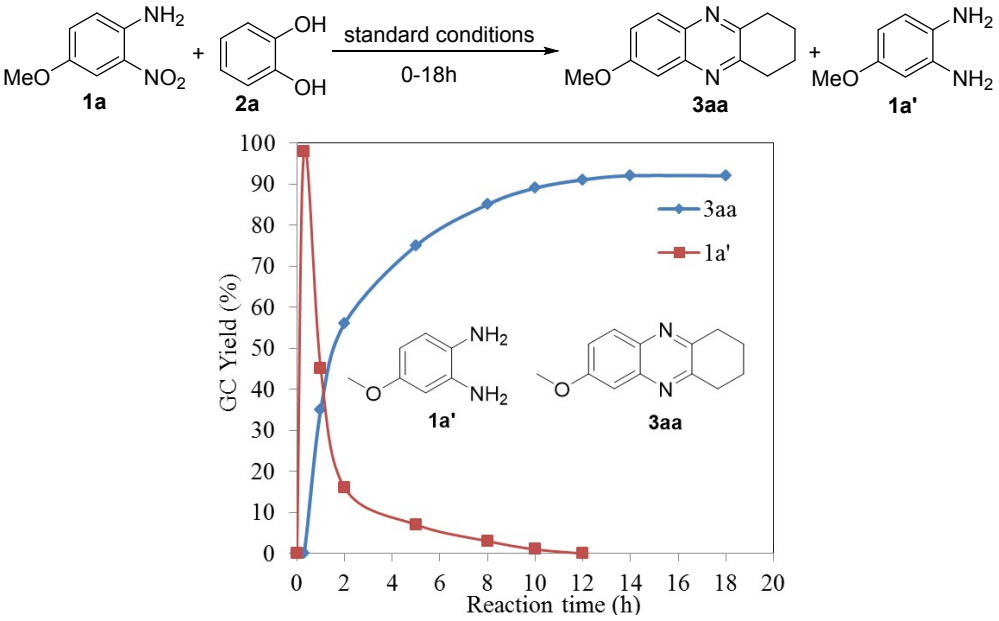


Figure S1. Time-concentration profile of **1a** coupled with **2a** under standard conditions.

To gain mechanistic insights into the reaction, a time-concentration profile of the model reaction under standard condition is depicted in Figure S1. **1a** was totally hydrogenated to diamine **1a'** within 0.5 h, which was fully converted into **3aa** in a maximum yield (91%) within 12 h. The product generating rate (**3aa**) and the consuming rate of **1a'** are very fast within the first 2 h and then gradually becom slow. During the whole reaction process, the intermediates from the hydrogenation of catechol **2a** were not observed, which indicates that the annulation is much faster than the hydrogenation of catechol, and diamine **1a'** is a reaction intermediate. Furthermore, byproduct 2-methoxyphenazine was detected in 5% yield, a compound arising from the dehydroaromatization of product **3aa.**

2.3. Typical experimental procedure for the synthesis of 3aa

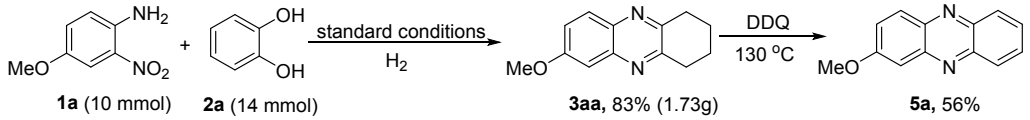
The mixture of 4-methoxy-2-nitroaniline **1a** (42mg, 0.25 mmol), catechol **2a** (38 mg, 0.35 mmol), K_2CO_3 (7 mg, 20 mol%), Pd/C (10 wt %, wetted with 55% H_2O, 18 mg, 3 mol % based on Pd content), and *p*-xylene (1.5 mL) were added successively to a Schlenk tube (50 mL) equipped with a magnetic stirrer bar, the Schlenk tube was then closed and the resulting reaction mixture was heated at 120 °C for 12 h under 1 atm of H_2 atmosphere (using H_2 balloon). After cooling to room temperature, the reaction mixture was filtrated and then concentrated under vacuum. The residue was directly purified by preparative TLC on silica, eluting with petroleum ether (60-90°C): ethyl acetate (8:1) to give 7-methoxy-1,2,3,4-tetrahydrophenazine (**3aa**) as a light yellow solid (45 mg, 85%).

2.4. Typical procedure for the synthesis of 4la

The mixture of 3-nitropyridin-2-amine 1l (35mg, 0.25 mmol), catechol 2a (38 mg, 0.35 mmol), *t*-BuOK (14 mg, 50 mol%), Pd/C (10 wt %, wetted with 55% H_2O, 30 mg, 5 mol % based on Pd content), and *p*-xylene (1.5 mL) were added successively to a Schlenk tube (50 mL) equipped with a magnetic stirrer bar, the Schlenk tube was then closed and the resulting

reaction mixture was heated at 120 °C for 18 h under 1 atm of H_2 atmosphere (using H_2 balloon). After cooling to room temperature, the reaction mixture was filtrated and then concentrated under vacuum. The residue was directly purified by preparative TLC on silica, eluting with petroleum ether (60-90°C): ethyl acetate (3:1) to give 1,2,3,4,6,7,8,9-octahydropyrido[2,3-b]quinoxaline (**4la**) as a white solid (29 mg, 63%).

2.5. Gram synthesis and the synthetic utility



1a (10 mmol) **2a** (14 mmol) **3aa,** 83% (1.73g) **5a,** 56%

Scheme S2. Gram scale synthesis and the utility of the new synthetic protocol.

In 250 mL autoclave, 4-methoxy-2-nitroaniline **1a** (1.68g, 10 mmol)，catechol **2a** (1.54 g, 14 mmol)，K_2CO_3 (276mg, 2 mmol), Pd/C (10 wt %, wetted with 55% H_2O, 706 mg, 3 mol % based on Pd content) was mixed with 30 mL *p*-xylene. The autoclave was evacuated with with hydrogen gas thrice and pressurized to 2 MPa hydrogen. Then, reaction mixture was heated at 120 °C for 12 h. After cooling to room temperature, the hydrogen was slowly released, the reaction mixture was filtrated and then concentrated under vacuum. The crude reaction mixture was purified by column chromatography, eluting with petroleum ether (60-90°C): ethyl acetate (8:1) to give the desired product **3aa** (1.73g, 83%). Then, **3aa** (107 mg, 0.5 mmol), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ; 227 mg, 1 mmol) and chlorobenzene (1.5 mL) were added successively to a Schlenk tube (50 mL) equipped with a magnetic stirrer bar, the Schlenk tube was then closed and the resulting reaction mixture was heated at 130 °C for 16 h. After cooling to room temperature, the reaction mixture was filtrated and then concentrated under vacuum. The residue was directly purified by preparative TLC on silica, eluting with petroleum ether (60-90°C): ethyl acetate (6 : 1) to give 2-methoxyphenazine (**5a**) as a yellow solid (58 mg, 56%).

2-methoxyphenazine (**5a**); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (dd, *J* = 15.7, 8.5 Hz, 2H), 8.03 (d, *J* = 9.5 Hz, 1H), 7.72 (dd, *J* = 13.7, 7.4 Hz, 2H), 7.44 (dd, *J* = 9.4, 2.5 Hz, 1H), 7.35 (d, *J* = 2.3 Hz, 1H), 3.95 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.35, 145.05, 143.28, 141.94, 140.81, 130.71, 130.49, 129.66, 129.06, 128.84, 126.45, 104.47, 55.94.

2.6. Procedure for catalyst recycling

The mixture of 4-methoxy-2-nitroaniline **1a** (126 mg, 0.75 mmol), catechol **2a** (115 mg, 1.05 mmol), K_2CO_3 (21 mg, 20 mol%), Pd/C (10 wt %, wetted with 55% H_2O, 53 mg, 3 mol % based on Pd content), and *p*-xylene (2 mL) were added successively to a Schlenk tube (50 mL) equipped with a magnetic stirrer bar, the Schlenk tube was then closed and the resulting reaction mixture was heated at 120 °C for 12 h under 1 atm of H_2 atmosphere (using H_2 balloon). After cooling to room temperature, 35 mg *n*-hexadecane was added to the solution and the yield was determined by GC-MS analysis. The catalyst was isolated by centrifugation, washed with ethyl acetate for three times, then dried under vacuum at 50 °C for 2 h. After that, the catalyst was reused for the next circular reaction.

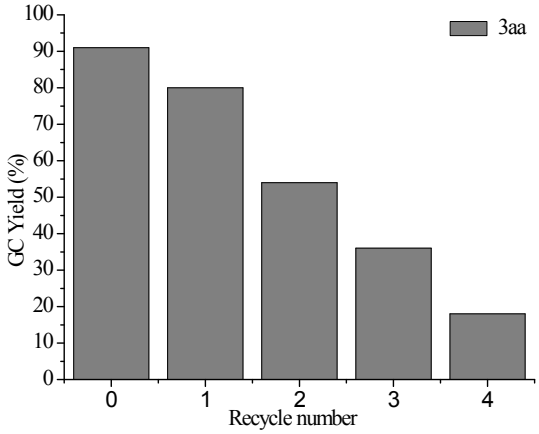
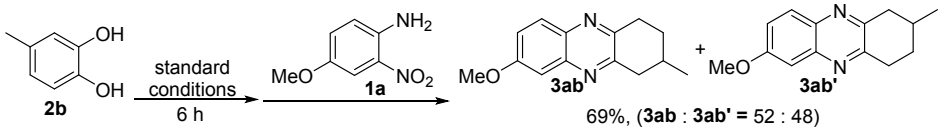


Figure S2. Reuse of the Pd/C catalysts.

2.7. Regioselective Control experiment

To examine the regioselectivity of reaction, we conducted the control experiment. As shown in scheme **S2**, the reaction was conducted by reducing first the methyl-catechol **2b** under the standard conditions for 6 h. After that, the 4-methoxy-2-nitroaniline (1a) was added to the above mixture, the whole reaction mixture was stirred at 120 °C for another 10 h. After cooling to room temperature, the reaction mixture was filtrated and then concentrated under vacuum. The residue was directly purified by preparative TLC on silica, eluting with petroleum ether (60-90°C): ethyl acetate (10:1) to give two regioisomers **3ab** and **3ab'** with the ratios of 52 : 48.

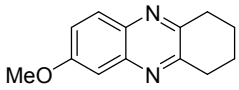
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82 (d, J = 9.0 Hz, 1H), 7.30-7.28 (m,1.16H), 7.25 (d, J = 2.5 Hz, 0.84 H), 3.92 (s, 3H), 3.24 – 3.13 (m, 2H), 3.12-3.03 (m, 1H), 2.74-2.67 (m, 1H), 2.17 – 2.04 (m, 2H), 1.69 – 1.58 (m, 1H), 1.16 (d, J = 6.5 Hz, 3H).



Scheme S3. Regioselective control experiment

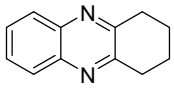
5. Analytical data of the obtained compounds

7-methoxy-1,2,3,4-tetrahydrophenazine (3aa)



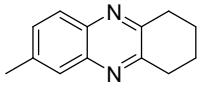
Light yellow solid, m.p.: 115-116°C (Lit[1], 115°C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 9.1 Hz, 1H), 7.19 (dd, J = 9.1, 2.7 Hz, 1H), 7.14 (d, J = 2.7 Hz, 1H), 3.81 (s, 3H), 3.00 (d, J = 4.2 Hz, 4H), 1.90 (dd, J = 6.5, 3.0 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.92, 153.79, 151.14, 142.51, 137.17, 129.20, 121.93, 105.83, 55.56, 33.04, 32.73, 22.84, 22.77; IR (KBr): 2928, 2859, 1618, 1450, 1213, 1020, 821; MS (EI, m/z): 214.01 $[M]^+$.

1,2,3,4-tetrahydrophenazine (3ba)



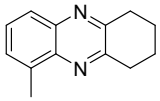
White solid, m.p.: 87-88°C (Lit[2], 91-92°C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (dd, *J* = 6.4, 3.2 Hz, 2H), 7.66 (dd, *J* = 6.0, 3.2 Hz, 2H), 3.17 (s, 4H), 2.09-2.01 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.14, 141.21, 128.91, 128.34, 33.21, 22.80; IR (KBr): 3058, 2934, 1598, 1509, 1289, 1126, 760; MS (EI, m/z): 184.15 $[M]^+$

7-methyl-1,2,3,4-tetrahydrophenazine (3ca)



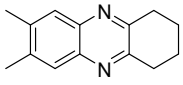
Yellow solid, m.p.: 78-79°C (Lit[1], 81°C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.5 Hz, 1H), 7.65 (s, 1H), 7.40 (dd, *J* = 8.5, 1.5 Hz, 1H), 3.06 (s, 4H), 2.47 (s, 3H), 1.95 (dd, *J* = 6.6, 3.4 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.59, 152.53, 140.16, 140.13, 139.18, 139.16, 127.45, 127.42, 41.48, 32.27, 30.96, 29.26, 21.60, 20.26; IR (KBr): 2938, 2863, 1493, 1399, 1243, 1124, 816; MS (EI, m/z): 198.03 $[M]^+$.

6-methyl-1,2,3,4-tetrahydrophenazine (3da)



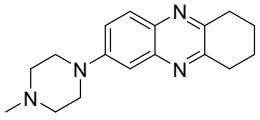
Yellow solid, m.p.: 72-74°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 8.3 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 1H), 7.37 (d, *J* = 7.0 Hz, 1H), 3.05 (d, *J* = 5.5 Hz, 4H), 2.66 (s, 3H), 1.93 (t, *J* = 3.3 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.38, 152.86, 141.19, 140.51, 136.63, 128.76, 128.51, 126.16, 33.37, 33.08, 22.91, 17.17; IR (KBr): 2941, 1474, 1335, 1136, 806, 767; MS (EI, m/z): 198.03 $[M]^+$.

7,8-dimethyl-1,2,3,4-tetrahydrophenazine (3ea)



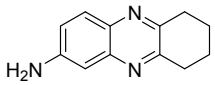
Light yellow solid, m.p.:142-144°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (s, 2H), 3.03 (s, 4H), 2.36 (s, 6H), 1.93 (dd, *J* = 6.3, 3.3 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.91, 140.14, 139.14, 127.42, 33.07, 22.88, 20.25; IR (KBr): 2938, 1482, 1338, 1210, 1149, 1027, 878, 736; MS (EI, m/z): 212.03$[M]^+$.

7-(4-methylpiperazin-1-yl)-1,2,3,4-tetrahydrophenazine (3fa)



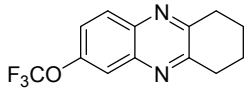
Yellow solid, m.p.:83-85°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 9.3 Hz, 1H), 7.35 (dd, *J* = 9.3, 2.4 Hz, 1H), 7.12 (d, *J* = 2.4 Hz, 1H), 3.35-3.27 (m, 4H), 3.01 (d, *J* = 2.0 Hz, 4H), 2.57-2.49 (m, 4H), 2.28 (s, 3H), 1.98-1.88 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.88, 151.35, 150.58, 142.67, 136.52, 128.61, 121.54, 109.32, 54.85, 48.68, 46.10, 33.13, 32.77, 22.95, 22.87; IR (KBr): 2935, 1615, 1498, 1347, 1217, 1143, 817; HRMS (ESI): Calcd. for $C_{17}H_{23}N_4$ $[M+1]^+$: 283.1917; found: 283.1921.

6,7,8,9-tetrahydrophenazin-2-amine (**3ga**)



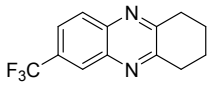
Yellow solid, m.p.:151-153°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, *J* = 8.8 Hz, 1H), 7.04 (dd, *J* = 12.0, 3.2 Hz, 2H), 4.11 (s, 2H), 3.04 (d, *J* = 1.9 Hz, 4H), 2.01-1.90 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.89, 149.73, 147.24, 142.92, 136.15, 129.21, 121.00, 107.54, 33.09, 32.67, 22.95, 22.85; IR (KBr): 3330, 3214, 2934, 1620, 1499, 1237, 1158, 825; MS (EI, m/z): 199.03 $[M]^+$.

7-(trifluoromethoxy)-1,2,3,4-tetrahydrophenazine (**3ha**)



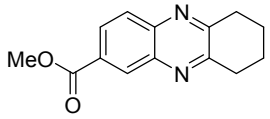
Brown solid, m.p.:88-89°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 9.1 Hz, 1H), 7.72 (d, *J* = 1.0 Hz, 1H), 7.41 (dd, *J* = 9.1, 2.4 Hz, 1H), 3.07 (s, 4H), 1.97-1.94 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 155.47, 154.67, 148.80 (q, *J* = 2 Hz), 141.26, 139.45, 130.13, 122.75, 121.77, 119.20, 118.24, 33.17, 33.10, 22.64, 22.61; IR (KBr): 2944, 1490, 1424, 1212, 1154, 842; HRMS (ESI): Calcd. for $C_{13}H_{12}F_3N_2O$ $[M+1]^+$: 269.0896; found: 269.0899.

7-(trifluoromethyl)-1,2,3,4-tetrahydrophenazine (**3ia**)



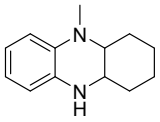
Brown oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (s, 1H), 8.08 (d, *J* = 8.7 Hz, 1H), 7.84 (dd, *J* = 8.7, 1.5 Hz, 1H), 3.20 (d, *J* = 1.8 Hz, 4H), 2.09-2.05 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.60, 155.91, 142.30, 140.19, 130.58 (d, *J* = 33 Hz), 129.58, 126.46 (q, *J* = 4Hz), 124.55 (q, *J* = 3.0 Hz),123.8 (d, *J* = 270 Hz), 33.35, 33.23, 22.59; IR (KBr): 2931, 1446, 1330, 1194, 1126, 1056, 839; HRMS (ESI): Calcd. for $C_{13}H_{12}F_3N_2$ $[M+1]^+$: 253.0947; found: 253.0949.

methyl 6,7,8,9-tetrahydrophenazine-2-carboxylate (**3ja**)



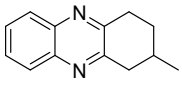
Brown solid, m.p.:75-77°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (s, 1H), 8.16 (d, *J* = 8.7 Hz, 1H), 7.90 (d, *J* = 8.7 Hz, 1H), 3.91 (s, 3H), 3.09 (s, 4H), 2.01-1.93 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$)：δ 166.43, 156.36, 155.39, 143.24, 140.39, 131.14, 130.25, 128.56, 128.46, 52.47, 33.39, 33.21, 22.63; IR (KBr): 2944, 1723, 1441, 1266, 1186, 1091, 850, 759; HRMS (ESI): Calcd. for $C_{14}H_{15}N_2O_2$ $[M+1]^+$: 243.1128; found: 243.1131.

5-methyl-1,2,3,4,4a,5,10,10a-octahydrophenazine (**3ka**)



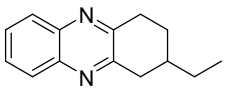
Yellow oil，^{1}H NMR (400 MHz, $CDCl_3$): δ 6.57 (t, *J* = 7.5 Hz, 1H), 6.48 (t, *J* = 7.4 Hz, 1H), 6.39 (d, *J* = 7.8 Hz, 2H), 3.63 (s, 1H), 3.01 (d, *J* = 3.1 Hz, 1H), 2.78 (s, 3H), 1.72-1.61 (m, 3H), 1.58-1.52 (m, 2H), 1.38-1.31(m, 2H), 1.28-1.12 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 134.05, 133.64, 118.52, 117.26, 112.75, 110.90, 59.59, 48.52, 36.98, 31.68, 24.86, 23.75, 19.55. IR (KBr): 2928, 1653, 1588, 1509, 1291, 737; MS (EI, m/z): 202.08$[M]^+$.

2-methyl-1,2,3,4-tetrahydrophenazine (**3bb**)



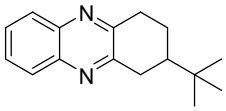
Brown oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (dd, *J* = 6.3, 3.5 Hz, 2H), 7.55 (dd, *J* = 6.4, 3.4 Hz, 2H), 3.22-3.11 (m, 2H), 3.10-2.97 (m, 1H), 2.65 (dd, *J* = 16, 8 Hz, 1H), 2.06-1.99 (m, 2H), 1.62-1.51 (m, 1H), 1.08 (d, *J* = 8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.74, 153.68, 141.20, 141.17, 128.87, 128.84, 128.36, 128.32, 41.55, 32.35, 30.83, 29.17, 21.56; IR (KBr): 3061, 2928, 1485, 1394, 1125, 760; MS (EI, m/z): 198.03$[M]^+$.

2-ethyl-1,2,3,4-tetrahydrophenazine (3be)



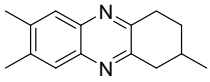
Yellow oil, ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00 – 7.93 (m, 2H), 7.68 – 7.62 (m, 2H), 3.33 – 3.21 (m, 2H), 3.14-3.07 (m, 1H), 2.75 (dd, *J* = 17.6, 10.9 Hz, 1H), 2.18-2.13 (m, 1H), 1.94 – 1.86 (m, 1H), 1.68-1.59 (m, 1H), 1.55 – 1.48 (m, 2H), 1.04 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 154.03, 153.90, 141.18, 141.16, 128.91, 128.90, 128.32, 128.31, 39.40, 35.81, 32.37, 28.85, 28.57, 11.46; IR (KBr): 2925, 1456, 1364, 1155, 750; MS (EI, m/z): 212.21$[M]^+$.

2-(tert-butyl)-1,2,3,4-tetrahydrophenazine (**3bf**)



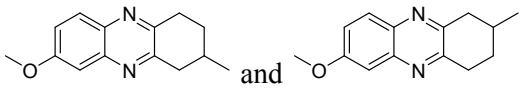
Brown oil, ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.02 – 7.94 (m, 2H), 7.73 – 7.62 (m, 2H), 3.34 – 3.26 (m, 2H), 3.12 – 3.03 (m, 1H), 2.89 (dd, *J* = 17.5, 12.5 Hz, 1H), 2.25-2.21 (m, 1H), 1.74 (tdd, *J* = 12.4, 4.7, 2.4 Hz, 1H), 1.60 (ddd, *J* = 25.1, 12.8, 5.0 Hz, 1H), 1.03 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 154.58, 154.03, 141.15, 141.10, 128.96, 128.31, 128.26, 44.61, 35.01, 33.42, 32.57, 27.19, 24.15; IR (KBr): 2946, 1657, 1474, 1362, 1166, 750; MS (EI, m/z): 240.20$[M]^+$.

2,7,8-trimethyl-1,2,3,4-tetrahydrophenazine (3eb)



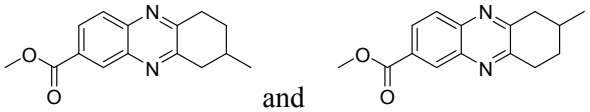
Yellow solid, m.p.:115-116°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (s, 2H), 3.13 (dq, *J* = 16 Hz, 4H), 3.06-2.94 (m, 1H), 2.64 (dd, *J* = 16 Hz, 8 Hz, 1H), 2.37 (s, 6H), 2.06-1.98 (m, 2H), 1.61-1.51 (m, 1H), 1.09 (d, *J* = 8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.59, 152.53, 140.16, 140.13, 139.18, 139.16, 127.45, 127.42, 41.48, 32.27, 30.96, 29.26, 21.60, 20.26; IR (KBr): 2923, 1624, 1483, 1454, 1337, 1204, 1155, 868, 735; HRMS (ESI): Calcd. for $C_{15}H_{19}N_2$ $[M+1]^+$: 227.1543; found: 227.1547.

8-methoxy-2-methyl-1,2,3,4-tetrahydrophenazine (3ab) and 7-methoxy-2-methyl-1,2,3,4-tetrahydrophenazine (3ab'')



Yellow oil，^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.0 Hz, 1H), 7.20 (dd, *J* = 8, 4 Hz, 1H), 7.16 (d, *J* = 4 Hz, 1H), 3.83 (s, 3H), 3.13-3.06 (m, 2H), 3.05-2.93 (m, 1H), 2.67-2.54 (m, 1H), 2.02-1.98 (m, 2H), 1.59-1.49 (m, 1H), 1.07 (d, *J* =8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.97 (159.95), 153.49 (153.44), 150.85 (150.78), 142.55 (142.53), 137.22 (137.18), 129.26 (129.23), 121.99 (121.96), 105.89 (105.86), 55.59, 41.44 (41.15), 32.27 (31.95), 30.92 (30.84), 29.22 (29.14), 21.54. IR (KBr): 2928, 1619, 1493, 1342, 1215, 1028, 831; HRMS (ESI): Calcd. for $C_{14}H_{17}N_2O$ $[M+1]^+$: 229.1335; found: 229.1340.

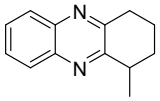
methyl 8-methyl-6,7,8,9-tetrahydrophenazine-2-carboxylate (3jb) and methyl 7-methyl-6,7,8,9-tetrahydrophenazine-2-carboxylate (3jb'')



Light yellow solid, m.p.: 86-88°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (d, *J* = 2 Hz, 1H), 8.16 (dd, *J* = 8, 2 Hz, 1H), 7.90 (d, *J* = 8 Hz, 1H), 3.91 (s, 3H), 3.23 -3.14 (m, 2H), 3.10-3.01 (m, 1H), 2.68 (dd, *J* = 16, 8 Hz, 1H), 2.07-2.03 (m, 2H), 1.65-1.54 (m, 1H), 1.11 (d, *J* = 8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.42, 156.00 (155.96), 155.04 (154.99), 143.22, 140.41, 131.18 (131.14), 130.27 (130.25), 128.59 (128.56), 128.47 (128.44), 52.45, 41.72 (41.54), 32.58 (32.38), 30.69, 29.10 (29.08), 21.53; IR (KBr): 2952, 1720, 1441, 1245, 1179, 1091,

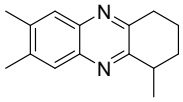
987, 759; HRMS (ESI): Calcd. for $C_{15}H_{17}N_2O_2$ $[M+1]^+$: 257.1285; found: 257.1287.

1-methyl-1,2,3,4-tetrahydrophenazine (3bc)



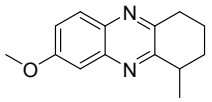
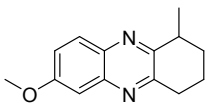
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (ddd, *J* = 13.4, 6.3, 3.7 Hz, 2H), 7.58 (dt, *J* = 12, 4Hz, 2H), 3.23-3.03 (m, 3H), 2.15-1.99 (m, 2H), 1.93-1.83 (m, 1H), 1.72-1.64 (m, 1H), 1.42 (d, *J* = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.98, 153.83, 141.45, 141.02, 128.91, 128.71, 128.61, 128.24, 36.71, 33.65, 31.05, 20.75, 20.31; IR (KBr): 2936, 1667, 1484, 1352, 1196, 762; MS (EI, m/z): 198.03$[M]^+$.

1,7,8-trimethyl-1,2,3,4-tetrahydrophenazine (3ec)



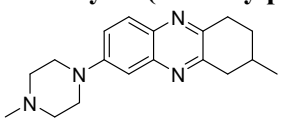
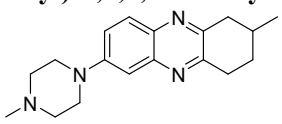
Brown red solid, m.p.:72-74°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 16Hz, 2H), 3.22-3.15 (m, 1H), 3.11 (t, *J* = 8Hz, 2H), 2.44 (s, 6H), 2.18-2.05 (m, 2H), 1.97-1.88 (m, 1H), 1.76-1.69 (m, 1H), 1.47 (d, *J* = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.79, 152.59, 140.35, 139.94, 139.13, 138.92, 127.67, 127.31, 36.51, 33.51, 31.13, 20.79, 20.35, 20.24, 20.17; IR (KBr): 2934, 1483, 1453, 1300, 1151, 1001, 871; HRMS (ESI): Calcd. for $C_{15}H_{19}N_2$ $[M+1]^+$: 227.1543; found: 227.1547.

8-methoxy-1-methyl-1,2,3,4-tetrahydrophenazine (3ac) and
7-methoxy-1-methyl-1,2,3,4-tetrahydrophenazine (3ac'')

 and 

Red oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81-7.72 (m, 1H), 7.25 -7.16 (m, 2H), [3.85 (s, 2.33H), 3.84 (s, 0.68H)], 3.10 (dd, *J* = 12.8, 7.0 Hz, 1H), 3.03 (dd, *J* = 11.9, 5.7 Hz, 2H), 2.11-1.97 (m, 2H), 1.89-1.80 (m, 1H), 1.70-1.59 (m, 1H), [1.40 (d, *J* = 8.0 Hz, 2.72H), 1.38 (s, 0.34H)]; ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.06 (159.90), 157.76, 150.92, 142.78 (142.34), 137.49 (137.06), 129.53 (129.16), 122.10 (121.86), 106.08 (105.75), 55.65, 36.55 (36.29), 33.53 (33.24), 31.14 (31.04) , 20.84 (20.79), 20.30; IR (KBr): 2936, 1619, 1492, 1304, 1219, 1026, 831; HRMS (ESI): Calcd. for $C_{14}H_{17}N_2O$ $[M+1]^+$: 229.1335; found: 229.1339.

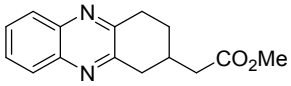
2-methyl-8-(4-methylpiperazin-1-yl)-1,2,3,4-tetrahydrophenazine (3gb) and
2-methyl-7-(4-methylpiperazin-1-yl)-1,2,3,4-tetrahydrophenazine (3gb'')

 and 

Yellow solid, m.p.:72-74°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 9.2 Hz, 1H), 7.37 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.15 (d, *J* = 2.4 Hz, 1H), 3.32 (t, *J* = 4.0 Hz, 4H), 3.15-3.07 (m, 2H),

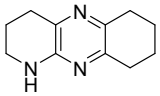
3.06-3.01 (m, 1H), 2.68-2.60 (m, 1H), 2.55 (t, *J* = 5.2 Hz, 4H), 2.30 (s, 3H), 2.02 (d, *J* = 15.6 Hz, 2H), 1.62-1.52 (m, 1H), 1.10 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.44 (153.41), 151.33 (151.31), 150.17 (150.10), 142.65 (142.62), 136.49 (136.45), 128.61(128.58), 121.49, 109.31(109.28), 54.82, 48.65, 46.08, 41.47 (41.14), 32.28 (31.90), 30.97 (30.89), 29.25 (29.16), 21.55; IR (KBr): 2931, 2796, 1616, 1499, 1345, 1217, 1144, 823; HRMS (ESI): Calcd. for $C_{18}H_{25}N_4$ $[M+1]^+$: 297.2074; found: 297.2078.

methyl 2-(1,2,3,4-tetrahydrophenazin-2-yl)acetate (3bd)



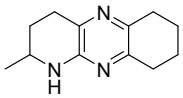
Brown solid, m.p.:78-79°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94-7.84 (m, 2H), 7.64 -7.55 (m, 2H), 3.65 (s, 3H), 3.30-3.05(m, 3H), 2.77 (dd, *J* = 17.6, 10.4 Hz, 1H), 2.55-2.39 (m, 3H), 2.17-2.12 (m, 1H), 1.72-1.61 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.51, 153.16, 152.67, 141.32, 141.24, 129.13, 129.07, 128.42, 128.39, 51.70, 40.41, 39.20, 32.10, 31.28, 28.68; IR (KBr): 2944, 1728, 1485, 1352, 1162, 763; HRMS (ESI): Calcd. for $C_{15}H_{17}N_2O_2$ $[M+1]^+$: 257.1285; found: 257.1284.

1,2,3,4,6,7,8,9-octahydropyrido[2,3-b]quinoxaline (4la)



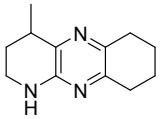
White solid, m.p.:151-152°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.09 (brs, 1H), 3.40 (t, *J* = 5.2 Hz, 2H), 2.88 (t, *J* = 6.4 Hz, 2H), 2.75 (t, *J* = 5.2 Hz, 2H), 2.69 (d, *J* = 5.6 Hz, 2H), 2.08-1.93 (m, 2H), 1.89-1.73 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.13, 146.99, 139.08, 136.21, 41.29, 31.31, 30.64, 29.94, 23.18, 22.86, 21.47; IR (KBr): 3247, 2940, 1581, 1440, 1345, 1165; MS (EI, m/z): 189.18 $[M]^+$.

2-methyl-1,2,3,4,6,7,8,9-octahydropyrido[2,3-b]quinoxaline (4ma)



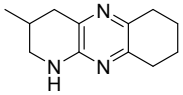
Yellow solid, m.p.:120-122°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.57 (brs, 1H), 3.55-3.43 (m, 1H), 2.80 (dd, *J* = 8.4, 5.2 Hz, 2H), 2.68 (q, *J* = 4.0 Hz, 2H), 2.61 (d, *J* = 5.6 Hz, 2H), 1.99-1.89 (m, 1H), 1.82-1.69 (m, 4H), 1.64-1.54 (m, 1H), 1.17 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.79, 147.08, 139.23, 135.88, 47.00, 31.36, 30.70, 29.32, 28.90, 23.20, 22.87, 22.19; IR (KBr): 3255, 2929, 1560, 1495, 1417, 1328, 1190; MS (EI, m/z): 203.17 $[M]^+$.

4-methyl-1,2,3,4,6,7,8,9-octahydropyrido[2,3-b]quinoxaline (4na)



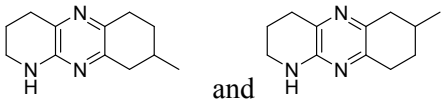
Yellow solid, m.p.:124-126°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.93 (brs, 1H), 3.43-3.26 (m, 2H), 2.97-2.89 (m, 1H), 2.69 (q, *J* = 4.0 Hz, 2H), 2.62 (t, *J* = 5.0 Hz, 2H), 2.02-1.94 (m, 1H), 1.79-1.65 (m, 5H), 1.25 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.41, 146.81, 140.21, 139.23, 38.27, 33.36, 31.30, 30.73, 28.85, 23.23, 22.88, 20.04; IR (KBr): 3242, 2926, 1583, 1437, 1346, 1185; MS (EI, m/z): 203.22 $[M]^+$.

3-methyl-1,2,3,4,6,7,8,9-octahydropyrido[2,3-b]quinoxaline (**4oa**)



Brown red solid, m.p.:140-146°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.83 (s, 1H), 3.40-3.24 (m, 1H), 2.96 (t, *J* = 9.6 Hz,1H), 2.86 (dd, *J* = 16.5, 4.0 Hz, 1H), 2.68 (t, *J* = 4.8 Hz, 2H), 2.62 (d, *J* = 5.6 Hz, 2H), 2.46 (dd, *J* = 16.8, 10.2 Hz, 1H), 2.15-2.06 (m, 1H), 1.76 (t, *J* = 3.2 Hz, 4H), 1.02 (d, *J* = 6.8Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.63, 146.90, 139.11, 135.94, 120.31, 114.98, 47.97, 37.99, 31.23, 30.58, 26.86 23.15, 22.83, 18.54; IR (KBr): 3245, 2932, 1576, 1443, 1348, 1190; HRMS (ESI): Calcd. for $C_{12}H_{18}N_3$ $[M+1]^+$: 204.1495; found: 204.1498.

8-methyl-1,2,3,4,6,7,8,9-octahydropyrido[2,3-b]quinoxaline (4lb) and
7-methyl-1,2,3,4,6,7,8,9-octahydropyrido[2,3-b]quinoxaline (4lb'')



Brown green solid, m.p.:111-112°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.87 (brs, 1H), 3.44-3.27 (m, 2H), 2.81 (t, *J* = 6.4 Hz, 2H), 2.78-2.61 (m, 3H), 2.37-2.20 (m, 1H), 1.99-1.90 (m, 2H), 1.84 (t, *J* = 10.4 Hz, 2H), 1.44-1.35 (m, 1H), 1.00 (dd, *J* = 6.4, 3.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.09, 146.60, 138.77, 136.21, 41.33, 39.71, 39.12, 31.25, 30.90, 30.68, 30.01,29.96, 29.35, 29.02, 21.49; IR (KBr): 3243, 2921, 1579, 1438, 1344, 1174; HRMS (ESI): Calcd. for $C_{12}H_{18}N_3$ $[M+1]^+$: 204.1495; found: 204.1499.

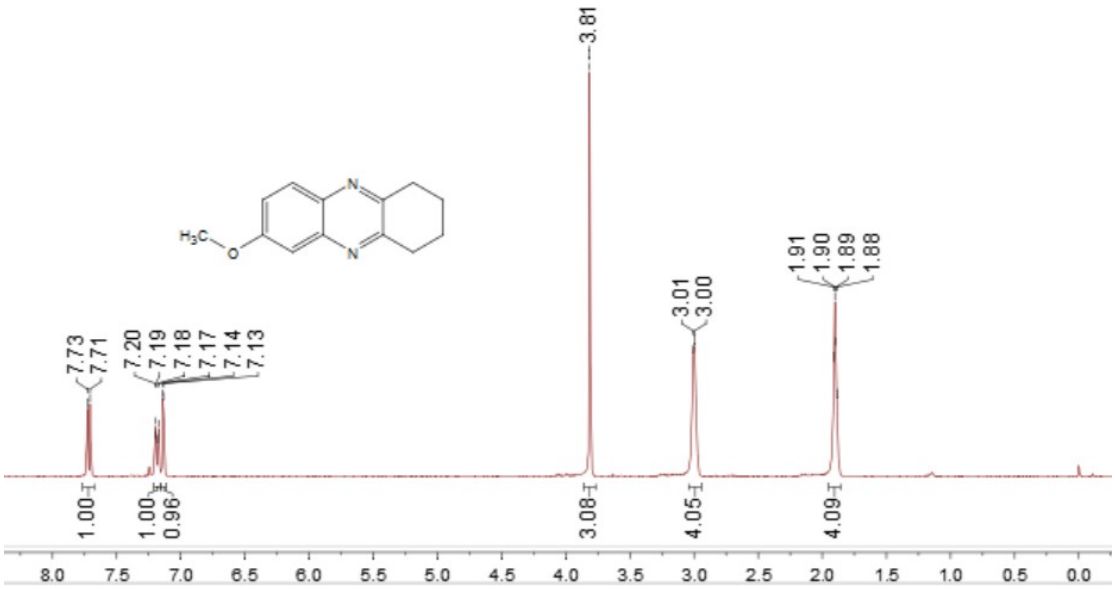
References

[1] J. K. Landquist, *J. Chem. Soc.* **1956**, 2551-2553.

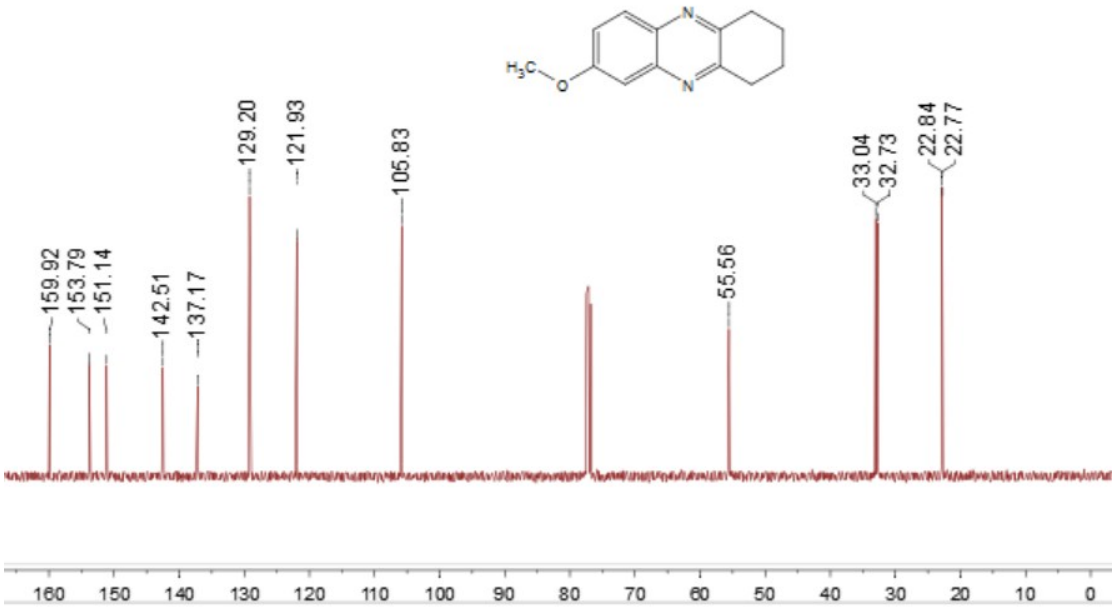
[2] T. M. Potewar, S. A. Ingale, K. V. Srinivasan, *Synth. Commun.* **2008**, *38*, 3601-3612;

6. NMR Spectra of the Obtained Compounds

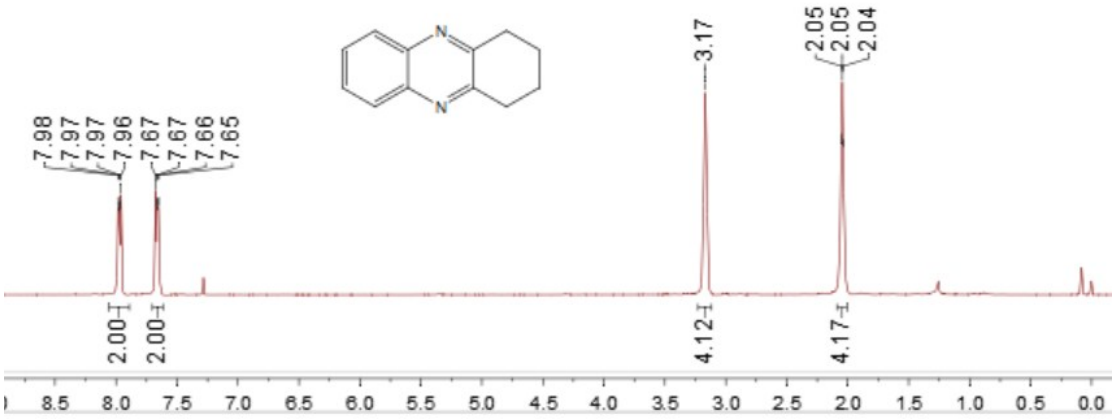
^{1}H- NMR spectrum of 7-methoxy-1,2,3,4-tetrahydrophenazine (3aa)



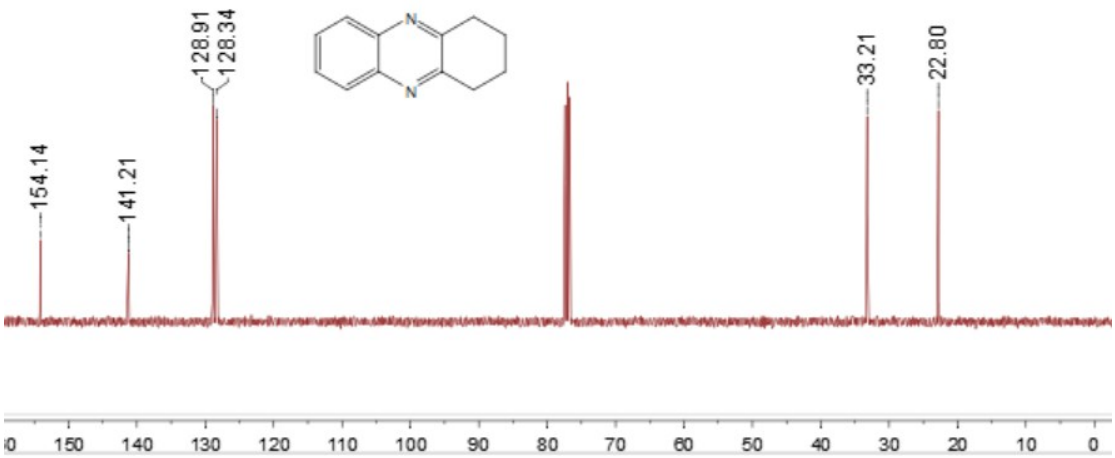
^{13}C-NMR spectrum of 7-methoxy-1,2,3,4-tetrahydrophenazine (3aa)



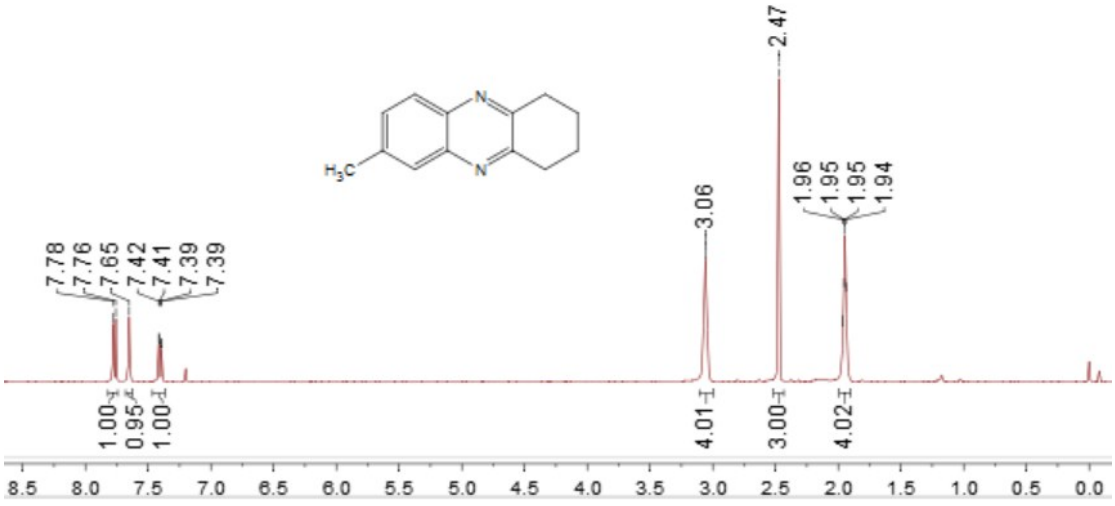
^{1}H- NMR spectrum of 1,2,3,4-tetrahydrophenazine (3ba)



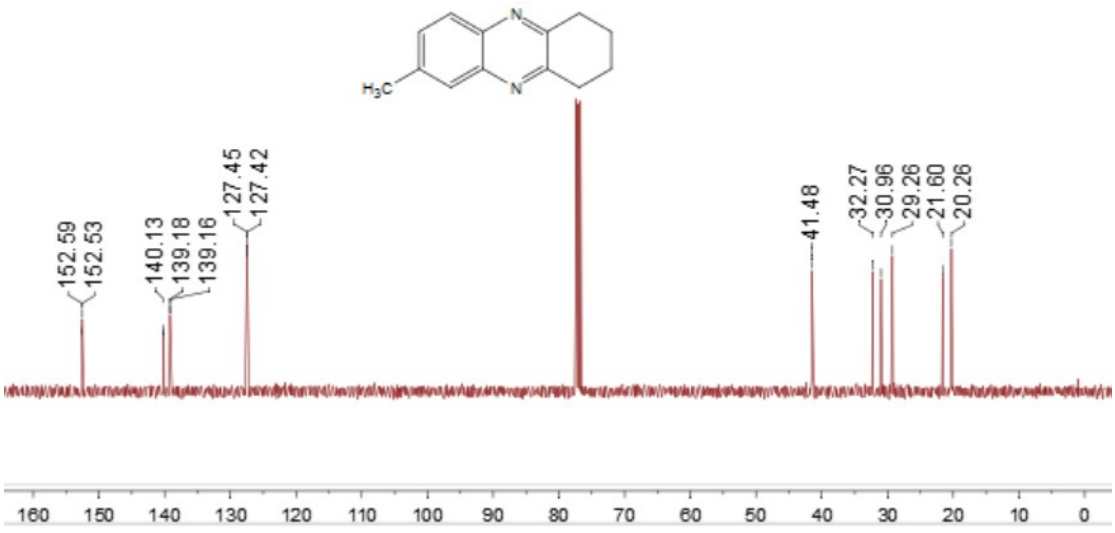
^{13}C-NMR spectrum of 1,2,3,4-tetrahydrophenazine (3ba)



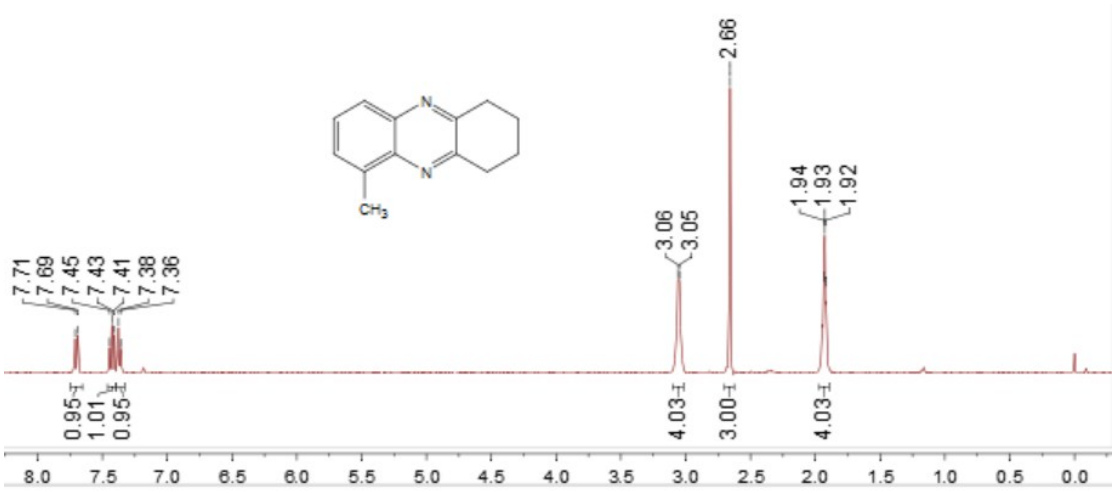
^{1}H- NMR spectrum of 7-methyl-1,2,3,4-tetrahydrophenazine (3ca)



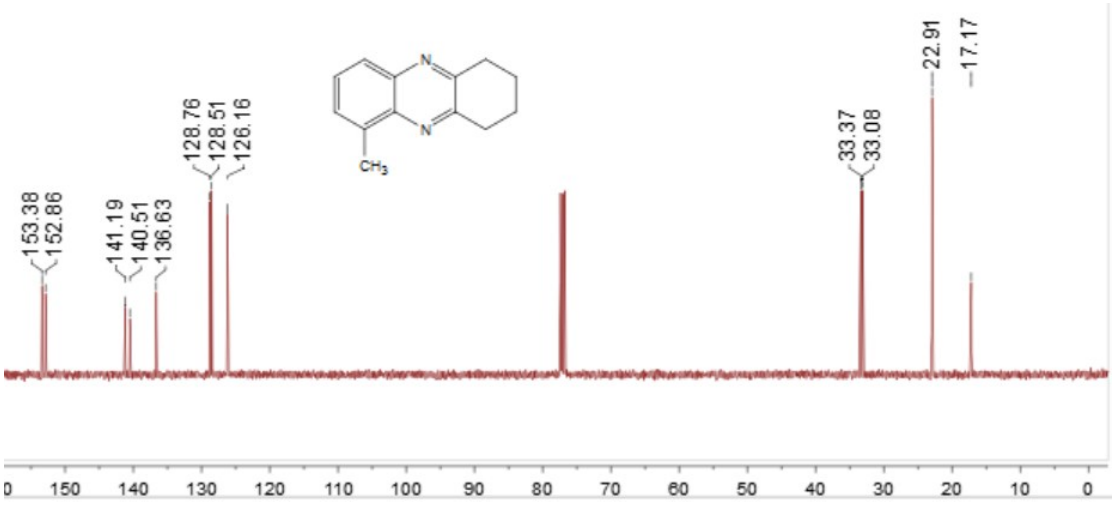
^{13}C-NMR spectrum of 7-methyl-1,2,3,4-tetrahydrophenazine (3ca)



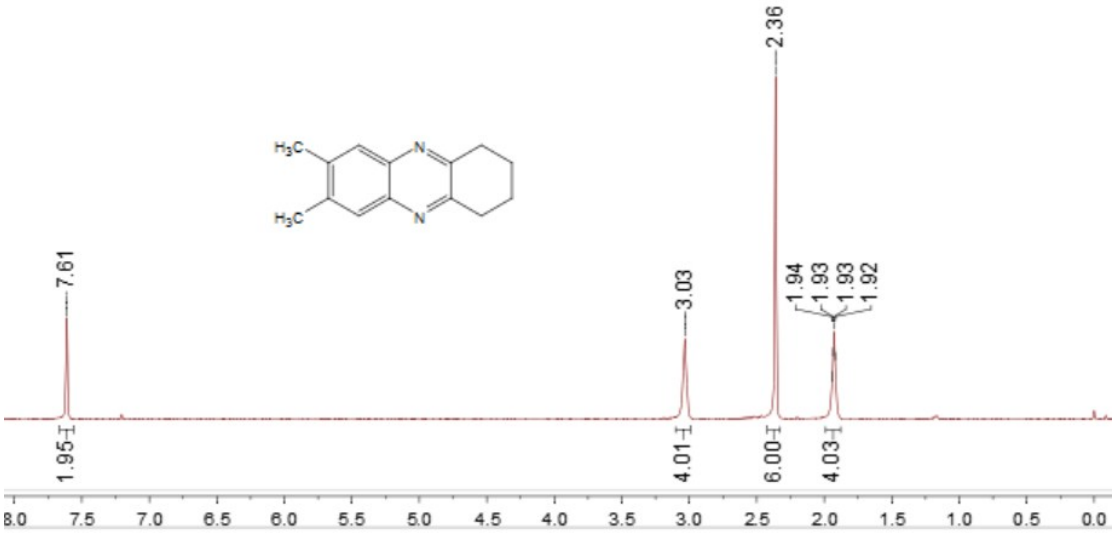
^{1}H- NMR spectrum of 6-methyl-1,2,3,4-tetrahydrophenazine (3da)



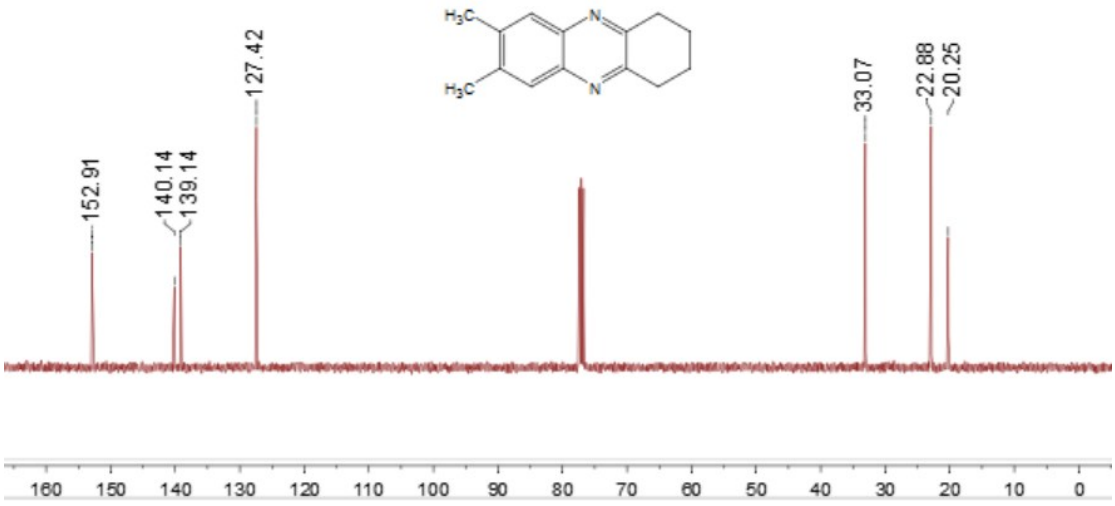
^{13}C-NMR spectrum of 6-methyl-1,2,3,4-tetrahydrophenazine (3da)



^{1}H- NMR spectrum of 7,8-dimethyl-1,2,3,4-tetrahydrophenazine (3ea)

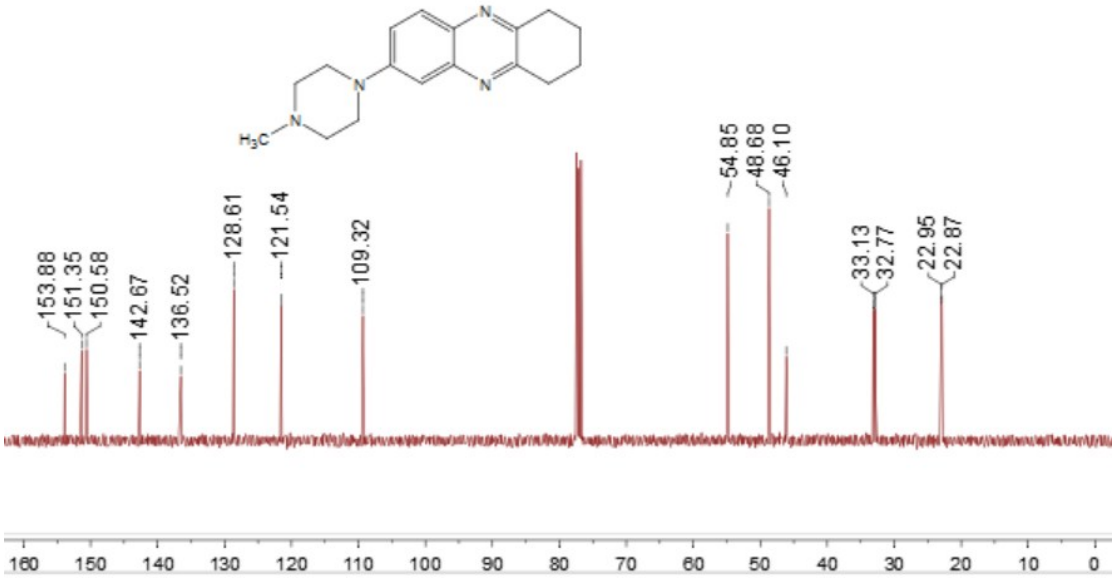


^{13}C-NMR spectrum of 7,8-dimethyl-1,2,3,4-tetrahydrophenazine (3ea)

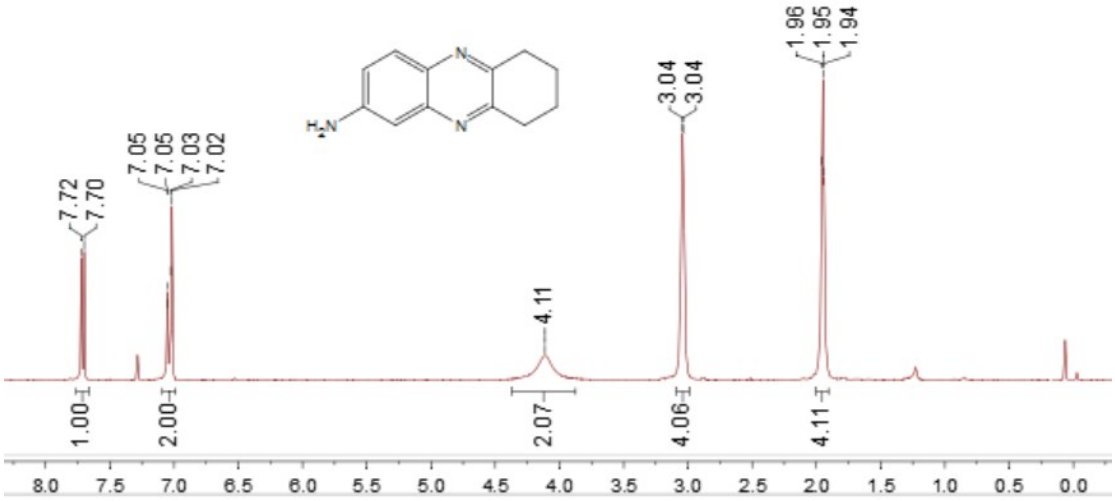


[1]H- NMR spectrum of 7-(4-methylpiperazin-1-yl)-1,2,3,4-tetrahydrophenazine (3fa)

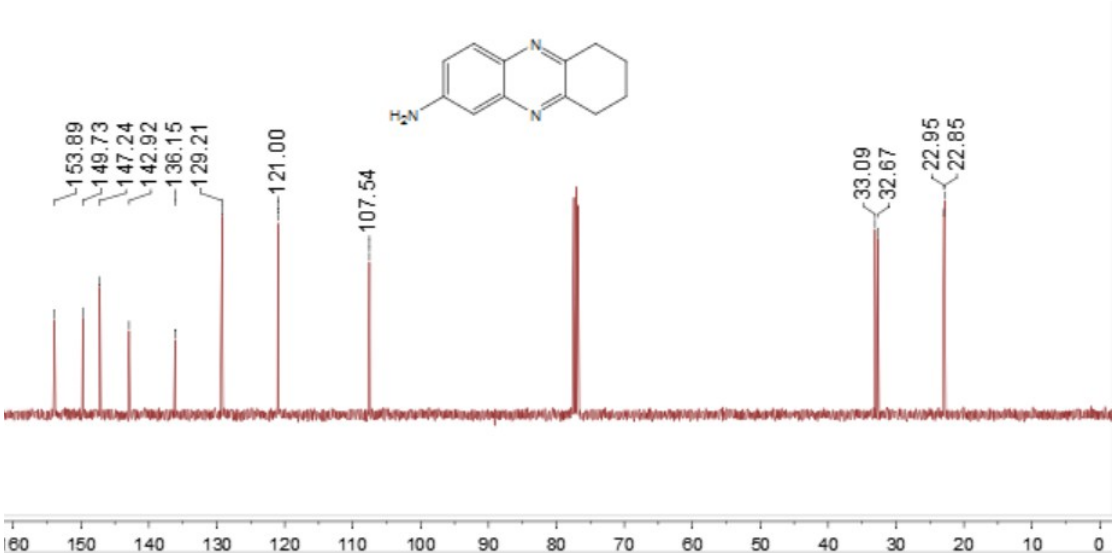
[13]C-NMR spectrum of 7-(4-methylpiperazin-1-yl)-1,2,3,4-tetrahydrophenazine (3fa)



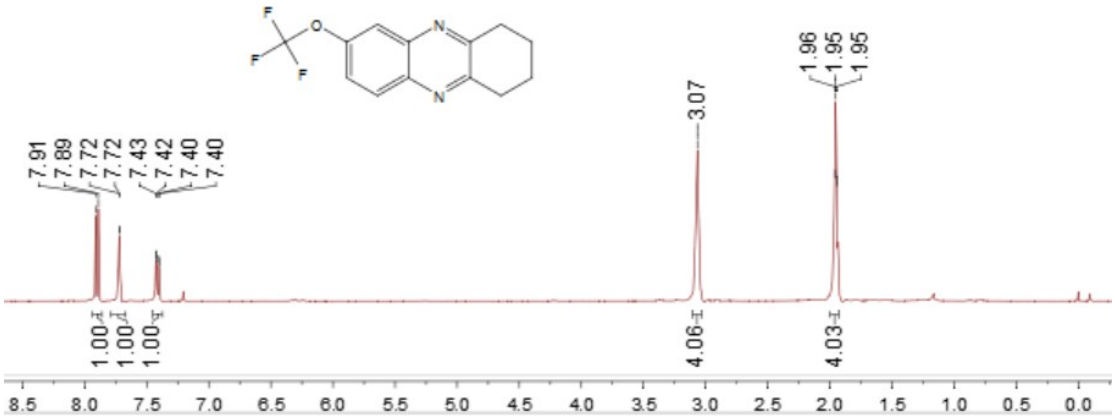
^{1}H- NMR spectrum of 6,7,8,9-tetrahydrophenazin-2-amine (3ga)



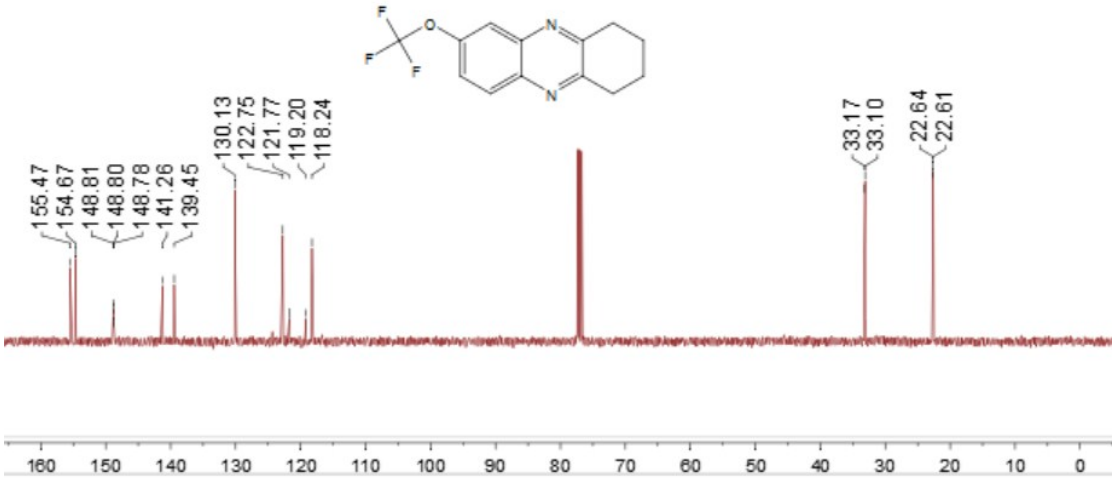
^{13}C-NMR spectrum of 6,7,8,9-tetrahydrophenazin-2-amine (3ga)



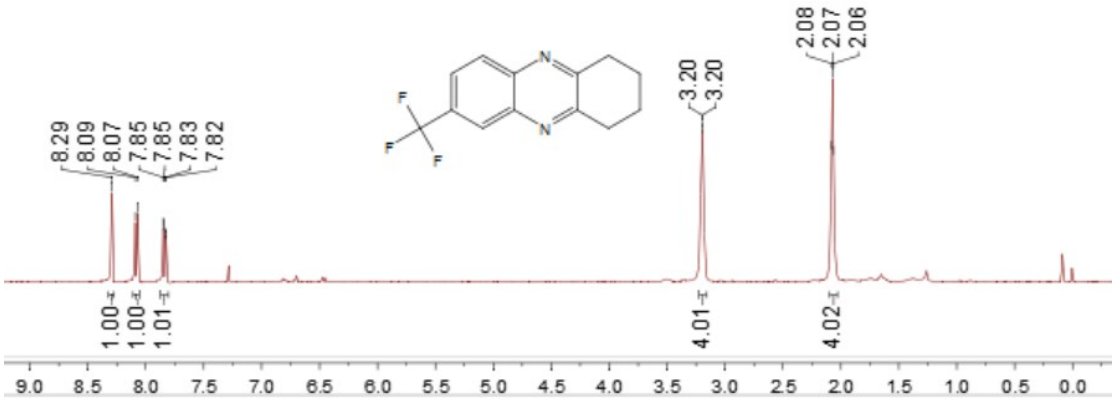
^{1}H- NMR spectrum of 7-(trifluoromethoxy)-1,2,3,4-tetrahydrophenazine (3ha)



^{13}C-NMR spectrum of 7-(trifluoromethoxy)-1,2,3,4-tetrahydrophenazine (3ha)

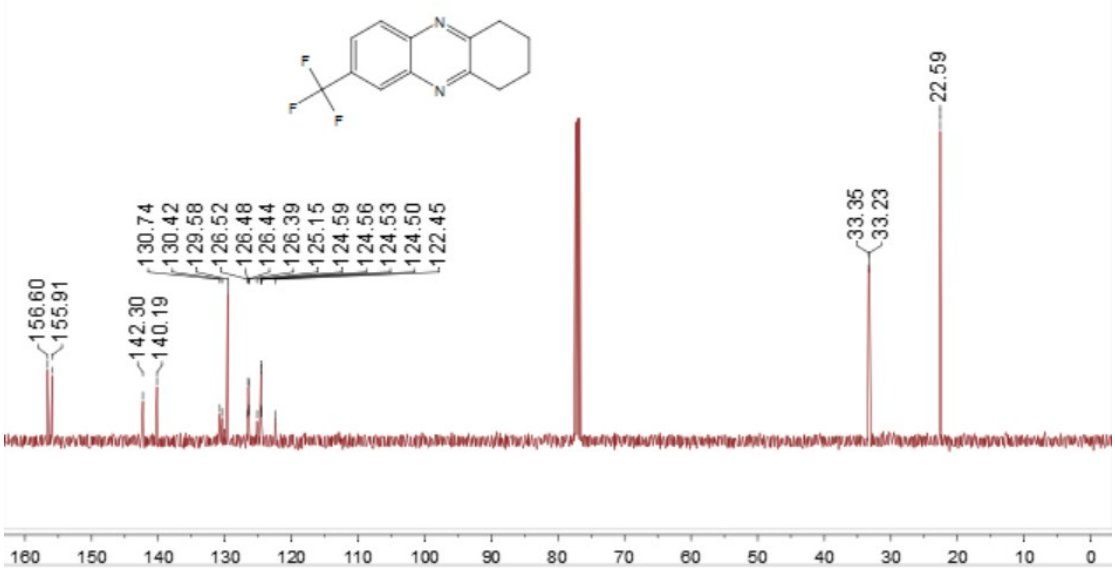


^{1}H- NMR spectrum of 7-(trifluoromethyl)-1,2,3,4-tetrahydrophenazine (3ia)

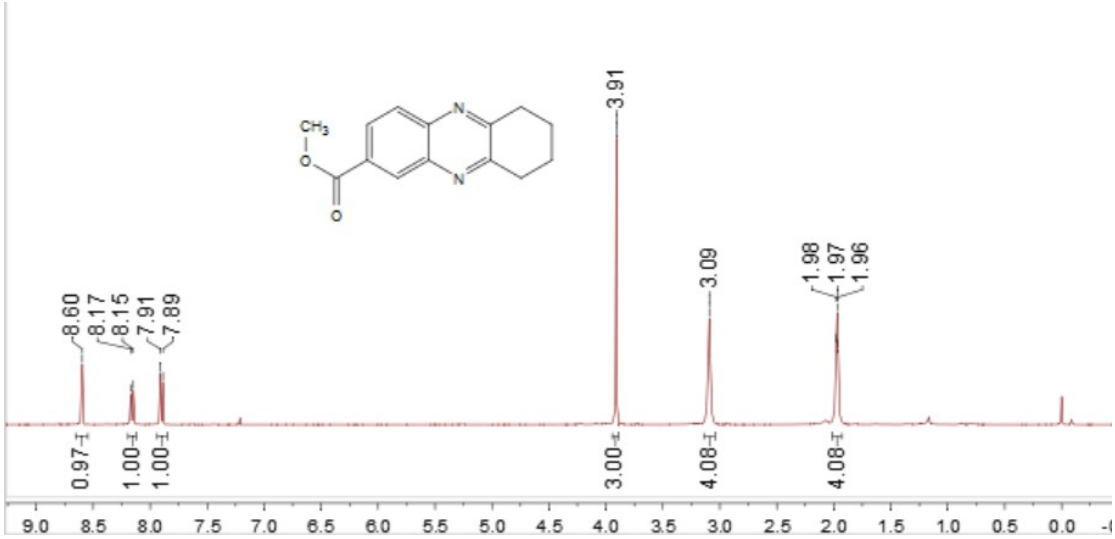


^{13}C-NMR spectrum of

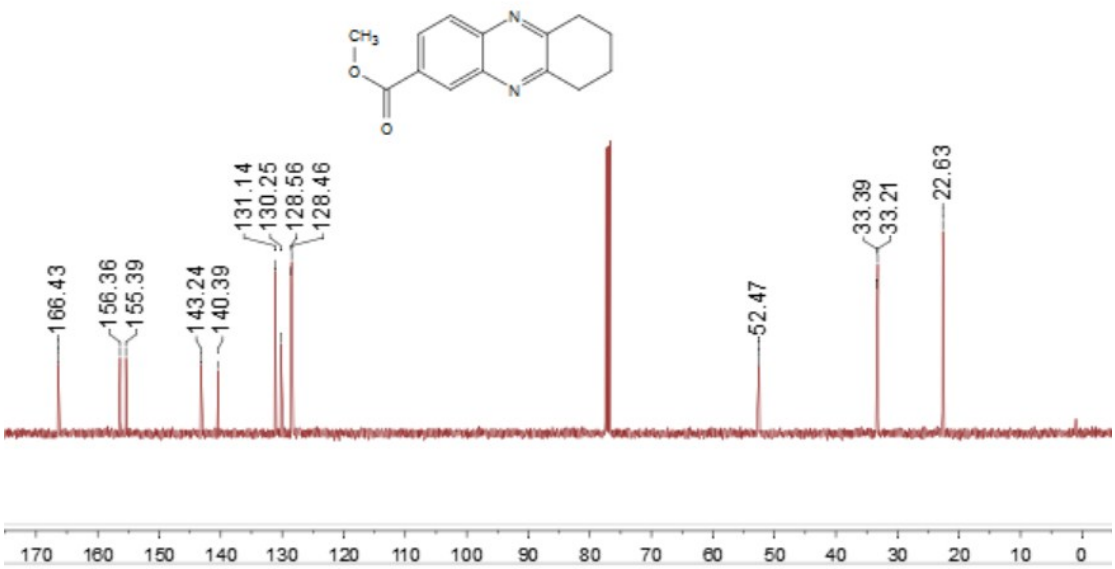
7-(trifluoromethyl)-1,2,3,4-tetrahydrophenazine (3ia)



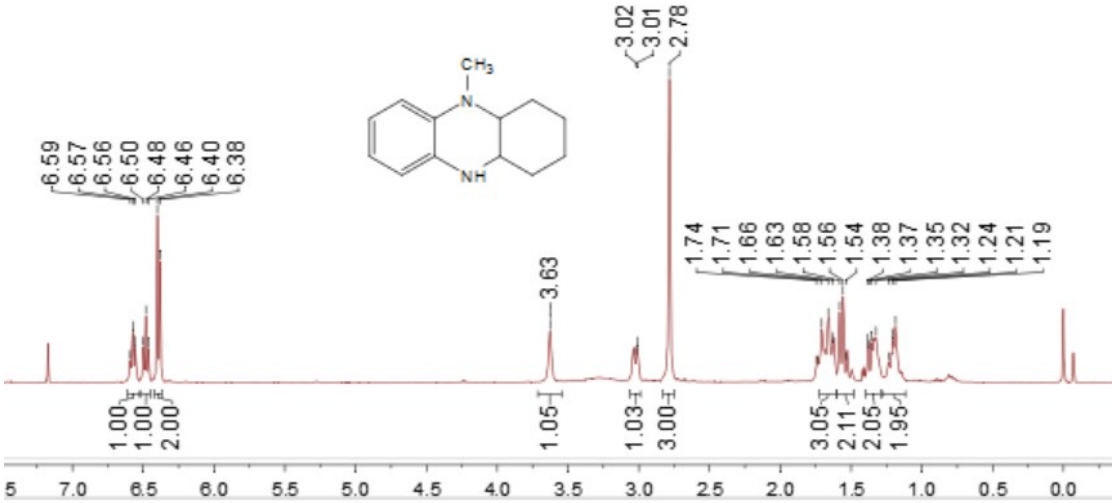
^{1}H- NMR spectrum of methyl 6,7,8,9-tetrahydrophenazine-2-carboxylate(3ja)



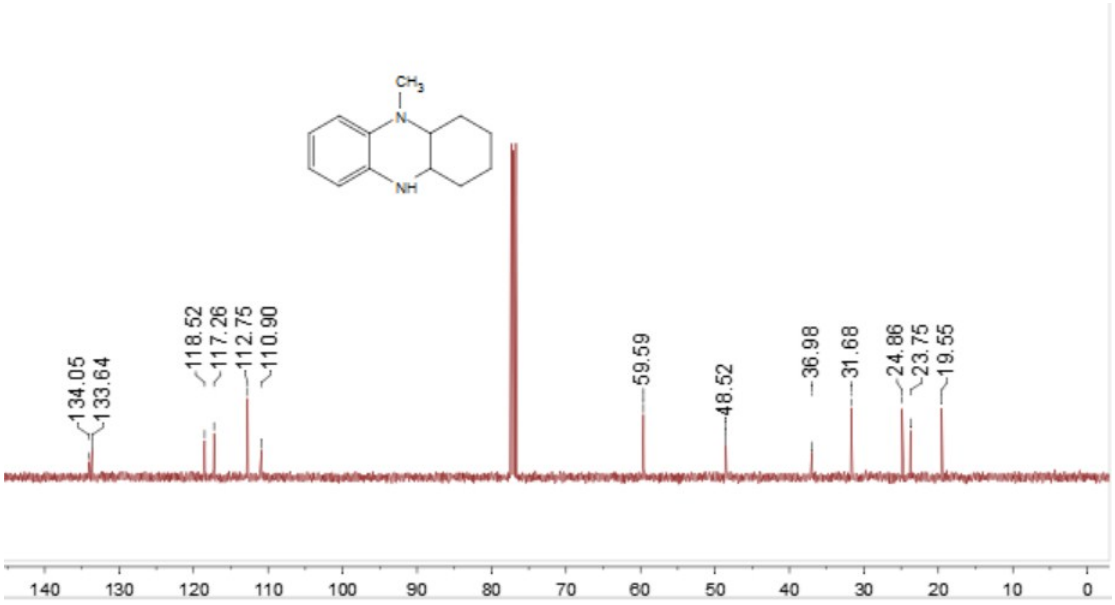
^{13}C-NMR spectrum of methyl 6,7,8,9-tetrahydrophenazine-2-carboxylate (3ja)



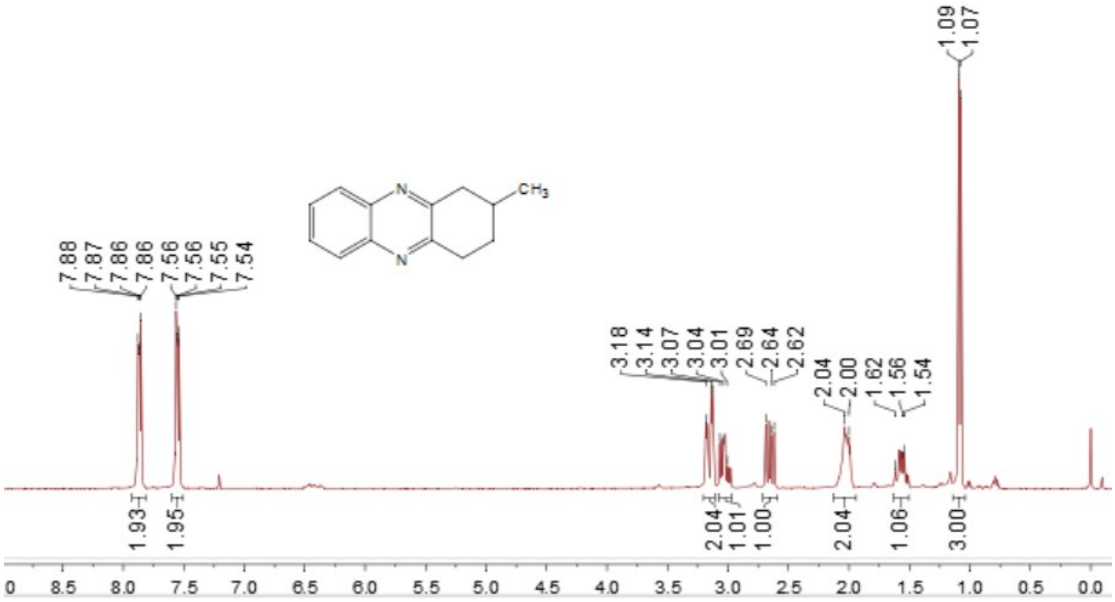
^{1}H- NMR spectrum of 5-methyl-1,2,3,4,4a,5,10,10a-octahydrophenazine (3ka)



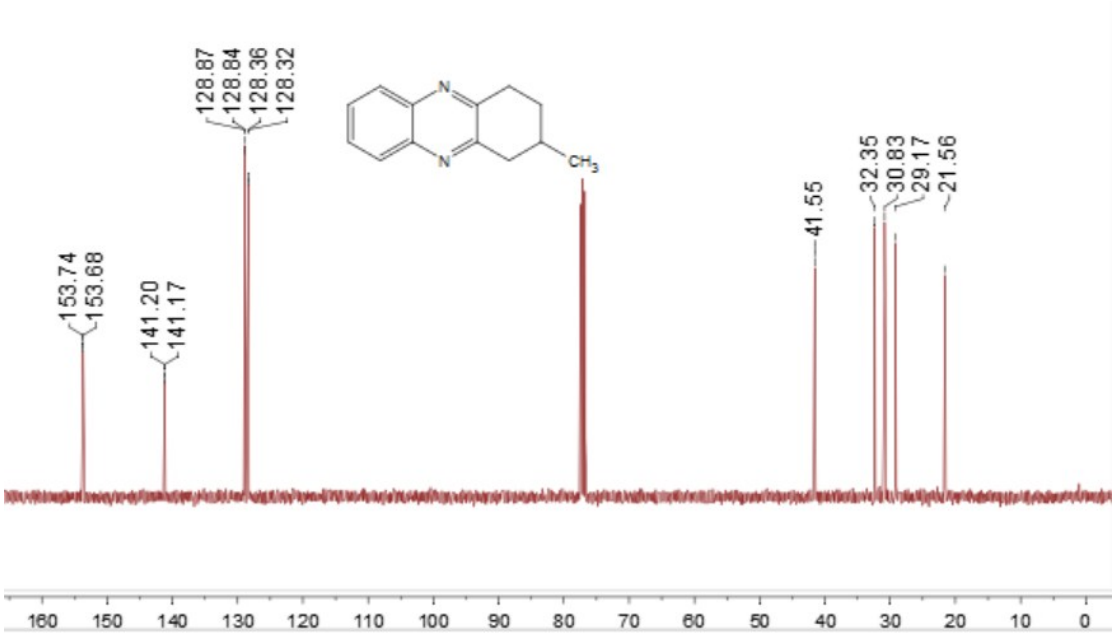
^{13}C-NMR spectrum of 5-methyl-1,2,3,4,4a,5,10,10a-octahydrophenazine (3ka)



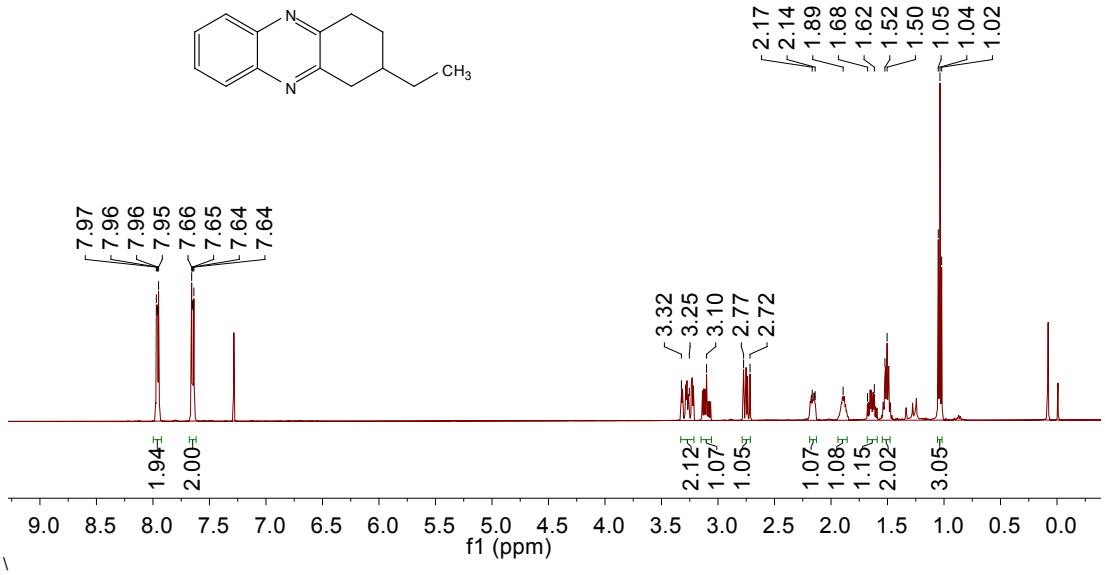
^{1}H- NMR spectrum of 2-methyl-1,2,3,4-tetrahydrophenazine (3bb)



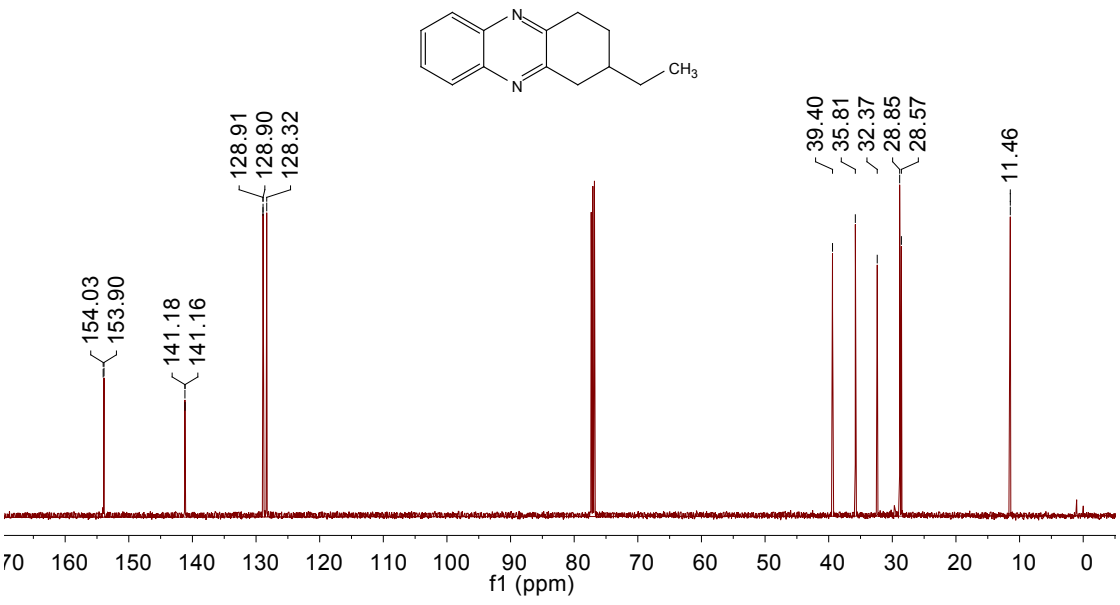
^{13}C-NMR spectrum of 2-methyl-1,2,3,4-tetrahydrophenazine (3bb)



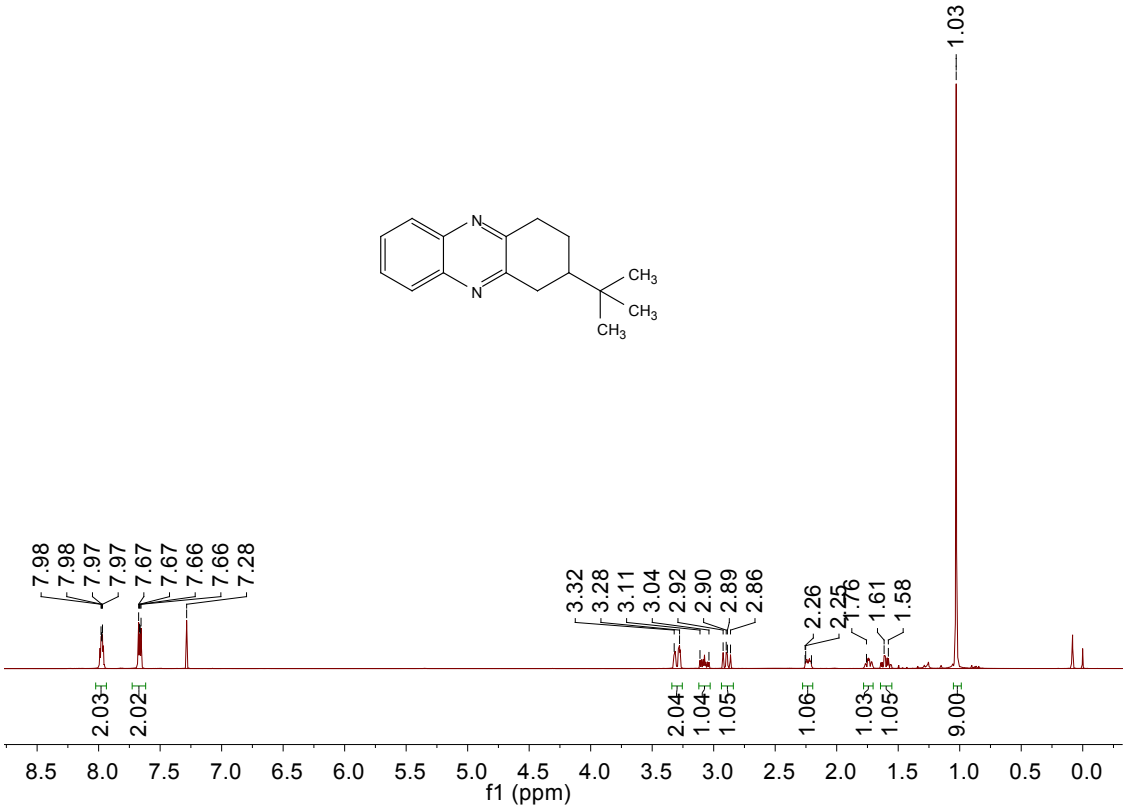
^{1}H- NMR spectrum of 2-ethyl-1,2,3,4-tetrahydrophenazine (3be)



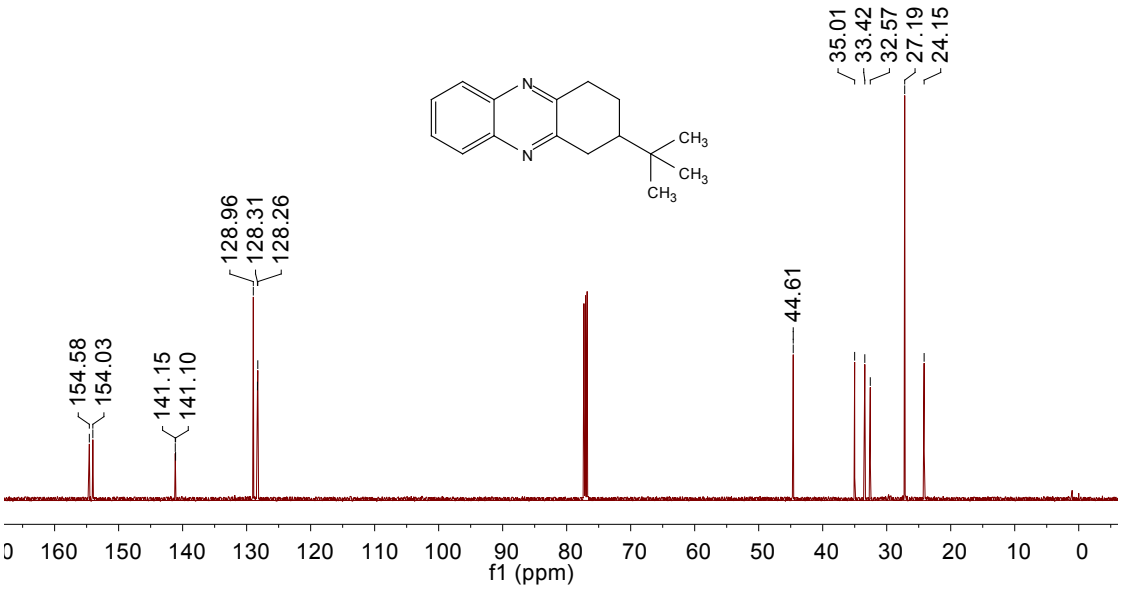
^{13}C-NMR spectrum of 2-ethyl-1,2,3,4-tetrahydrophenazine (3be)



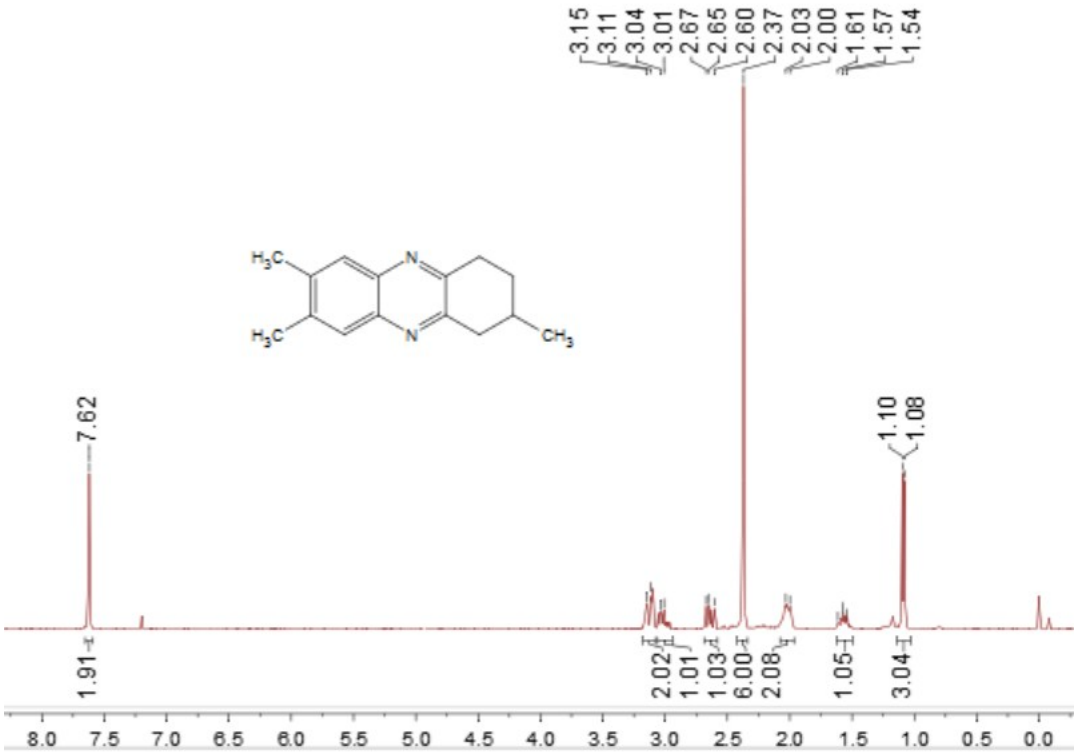
^{1}H- NMR spectrum of 2-(tert-butyl)-1,2,3,4-tetrahydrophenazine (3bf)



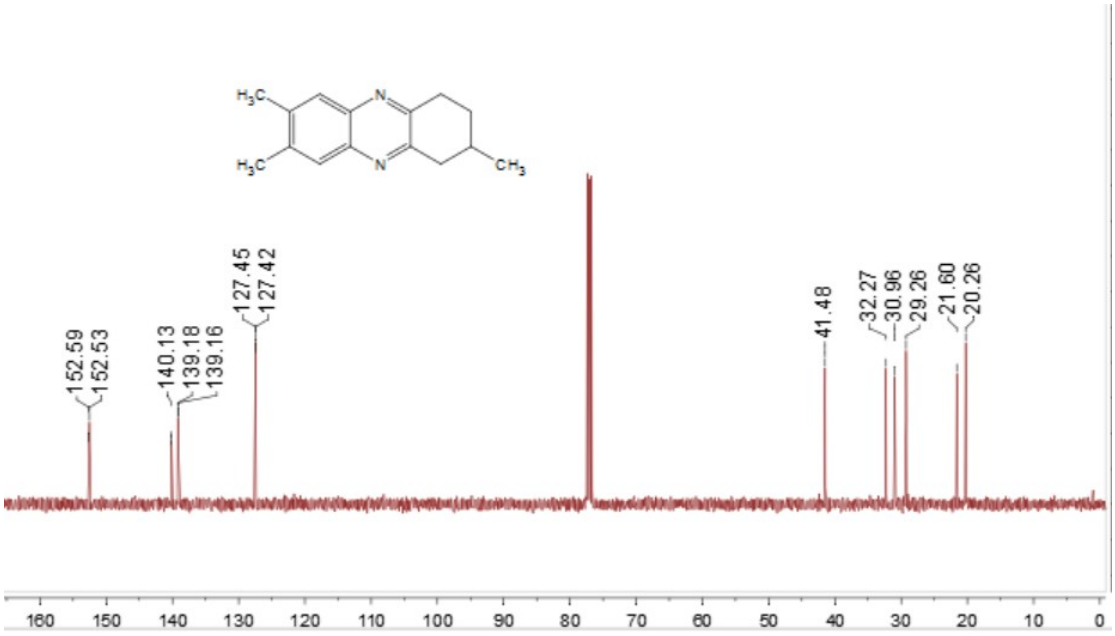
^{13}C-NMR spectrum of 2-(tert-butyl)-1,2,3,4-tetrahydrophenazine (3bf)



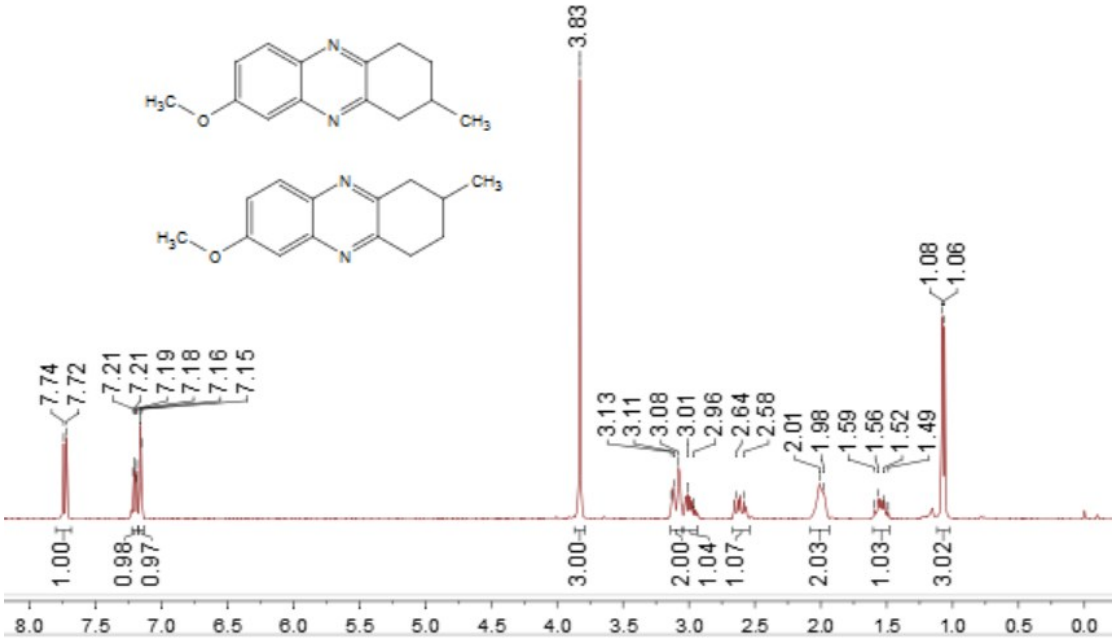
^{1}H- NMR spectrum of 2,7,8-trimethyl-1,2,3,4-tetrahydrophenazine (3eb)



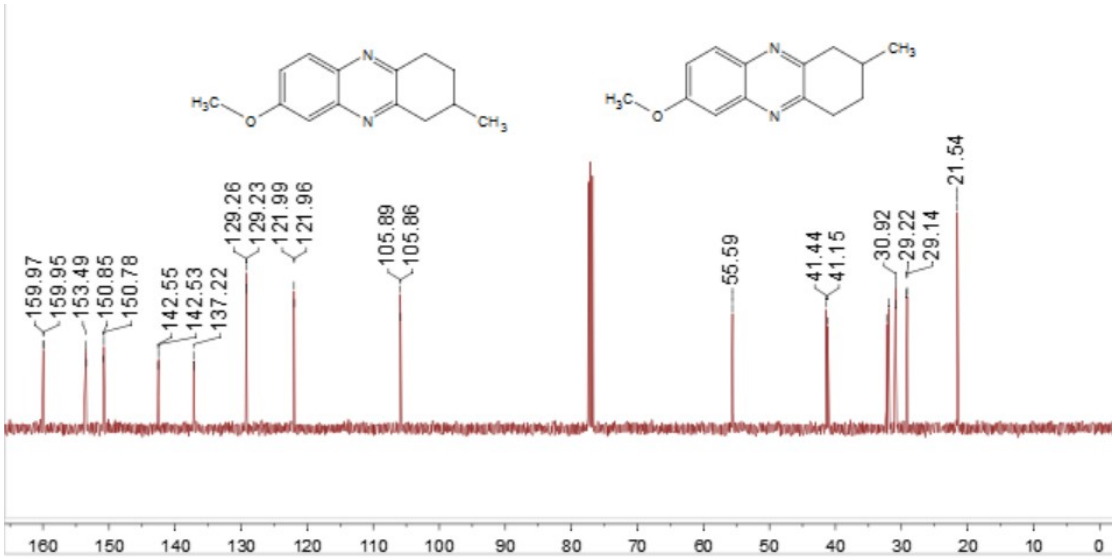
^{13}C-NMR spectrum of 2,7,8-trimethyl-1,2,3,4-tetrahydrophenazine (3eb)



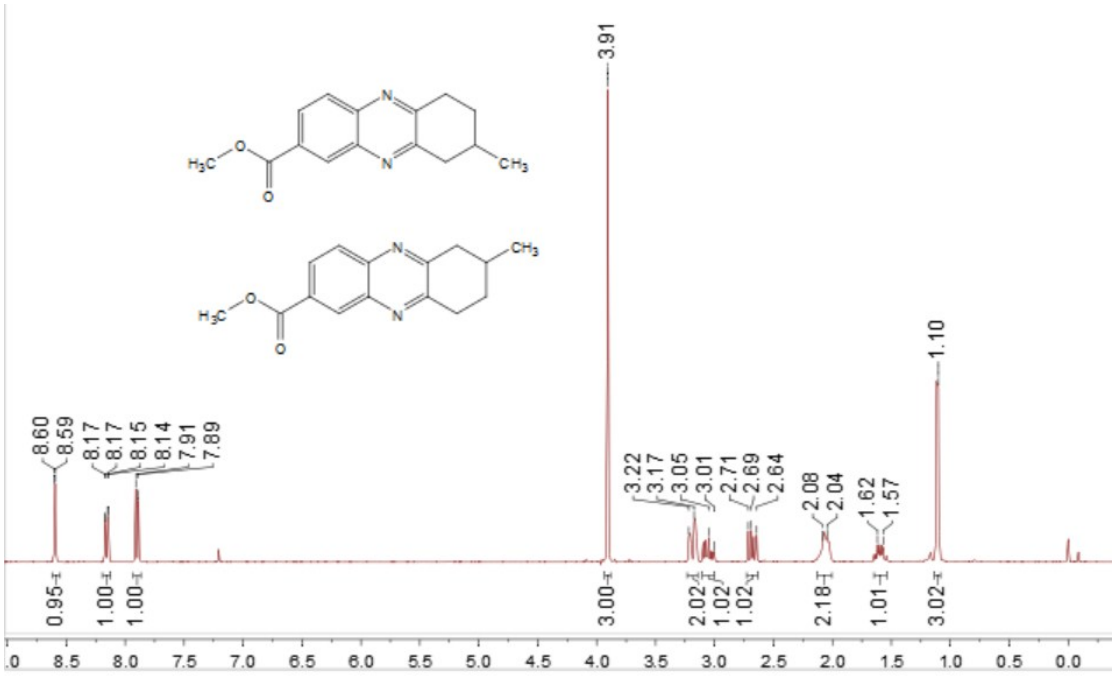
^{1}H- NMR spectrum of 8-methoxy-2-methyl-1,2,3,4-tetrahydrophenazine (3ab) and 7-methoxy-2-methyl-1,2,3,4-tetrahydrophenazine (3ab'')



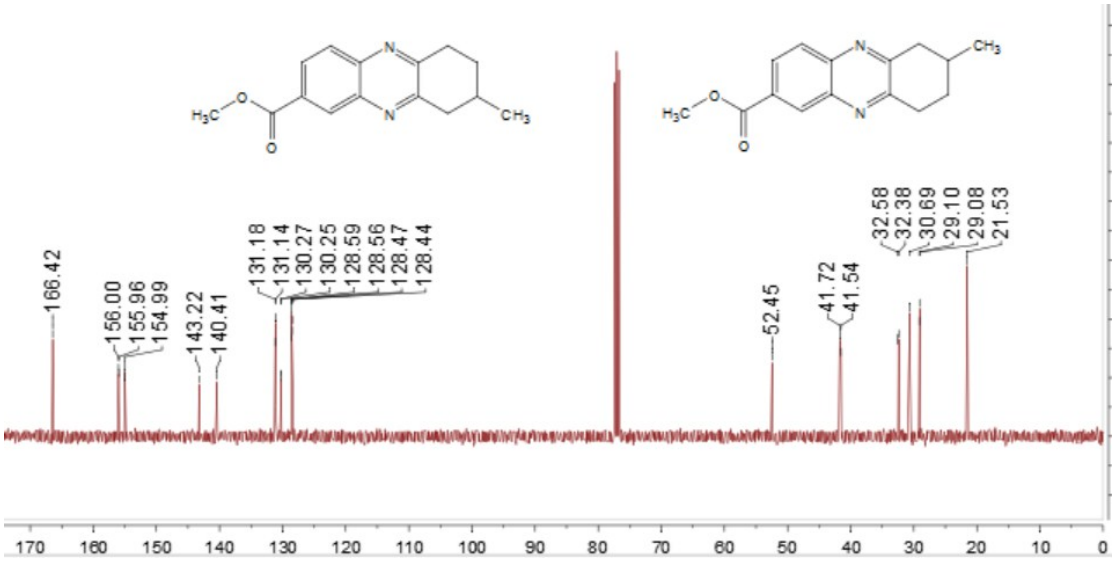
^{13}C-NMR spectrum of 8-methoxy-2-methyl-1,2,3,4-tetrahydrophenazine (3ab) and 7-methoxy-2-methyl-1,2,3,4-tetrahydrophenazine (3ab'')



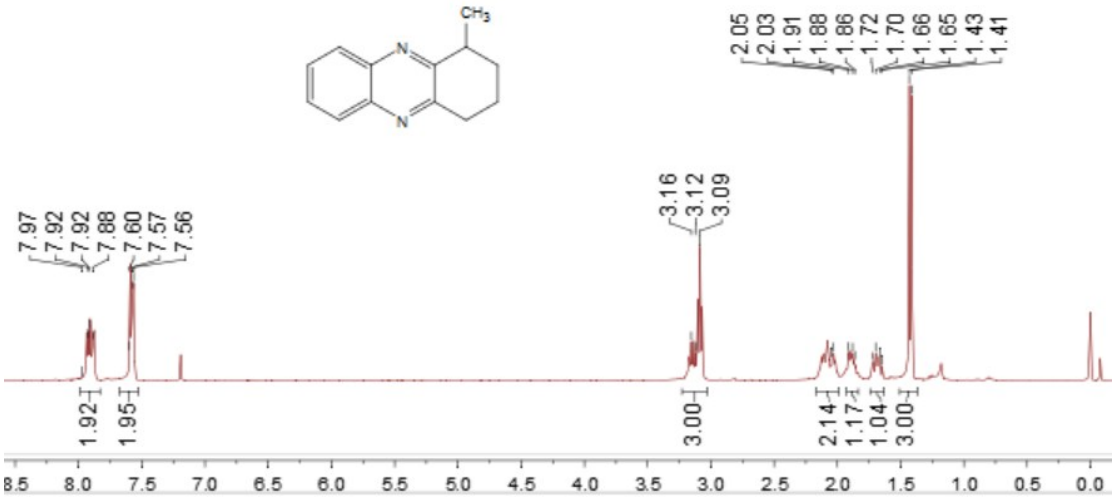
^{1}H- NMR spectrum of methyl 8-methyl-6,7,8,9-tetrahydrophenazine-2-carboxylate (3jb) and methyl 7-methyl-6,7,8,9-tetrahydrophenazine-2-carboxylate (3jb'')



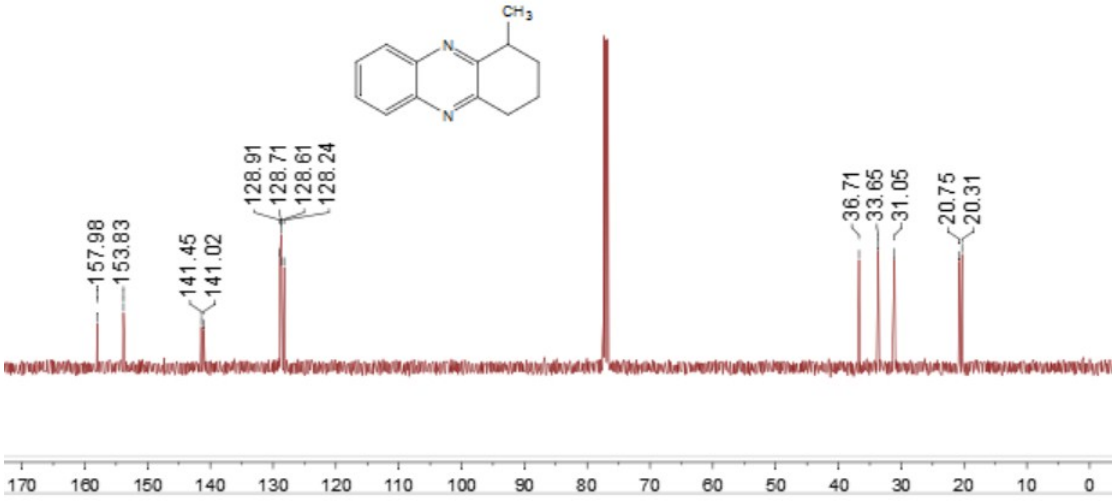
^{13}C-NMR spectrum of methyl 8-methyl-6,7,8,9-tetrahydrophenazine-2-carboxylate (3jb) and methyl 7-methyl-6,7,8,9-tetrahydrophenazine-2-carboxylate (3jb'')



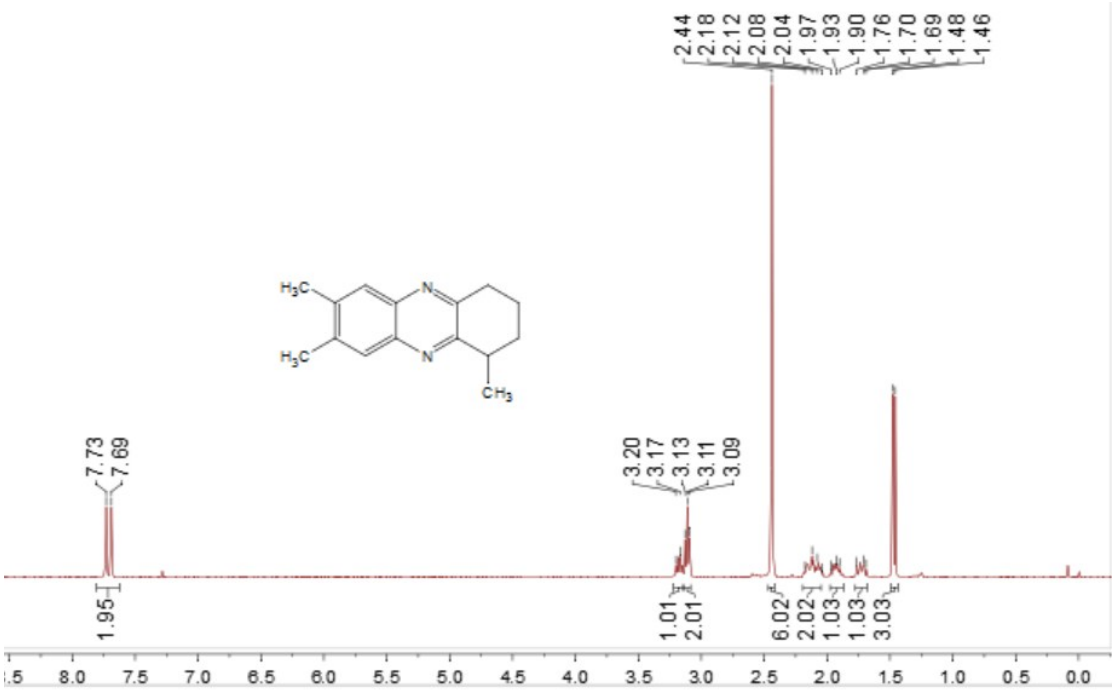
^{1}H- NMR spectrum of 1-methyl-1,2,3,4-tetrahydrophenazine (3bc)



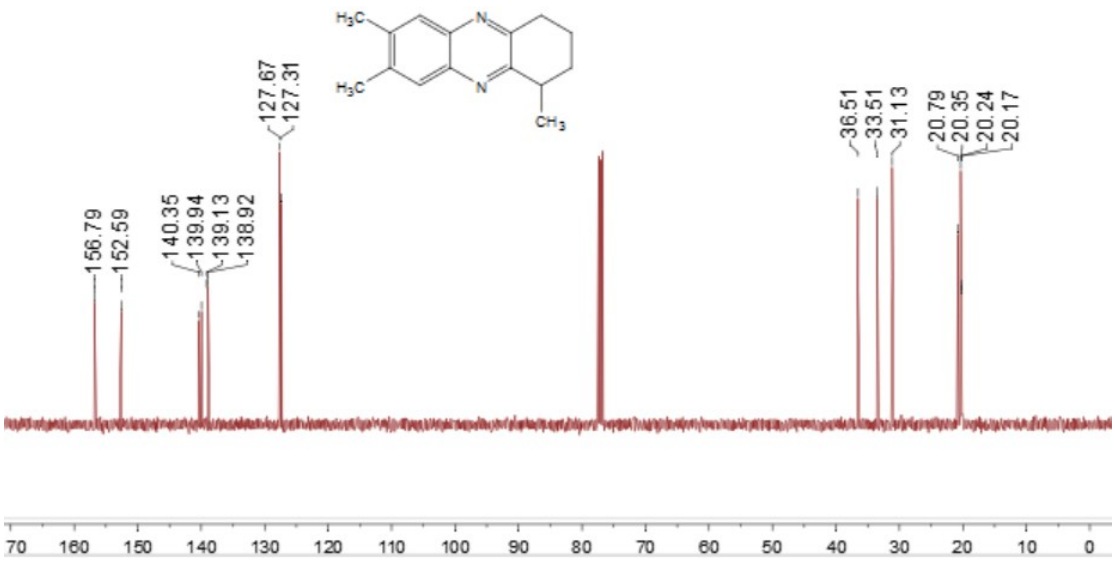
^{13}C-NMR spectrum of 1-methyl-1,2,3,4-tetrahydrophenazine (3bc)



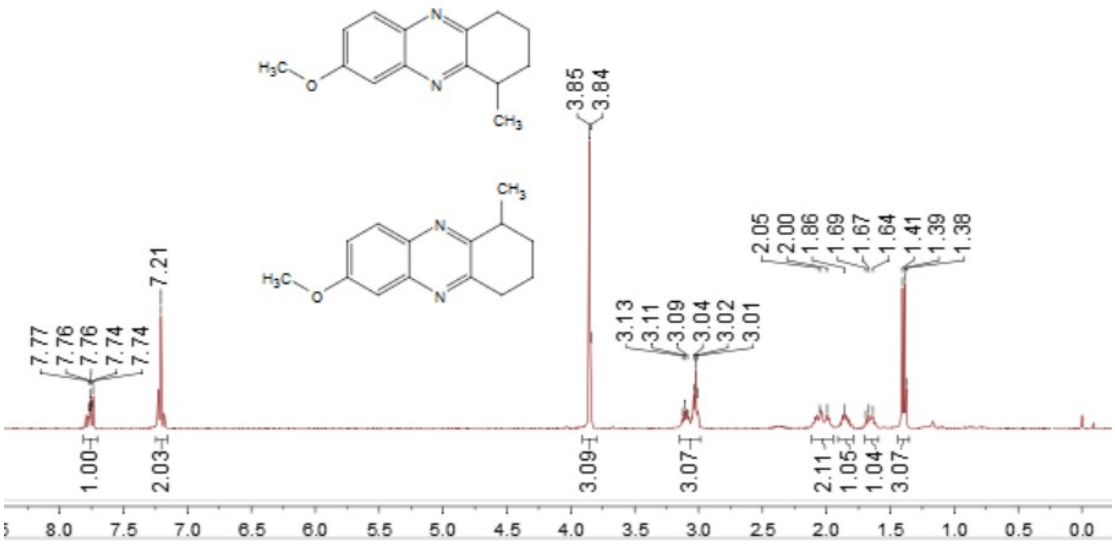
^{1}H- NMR spectrum of 1,7,8-trimethyl-1,2,3,4-tetrahydrophenazine (3ec)



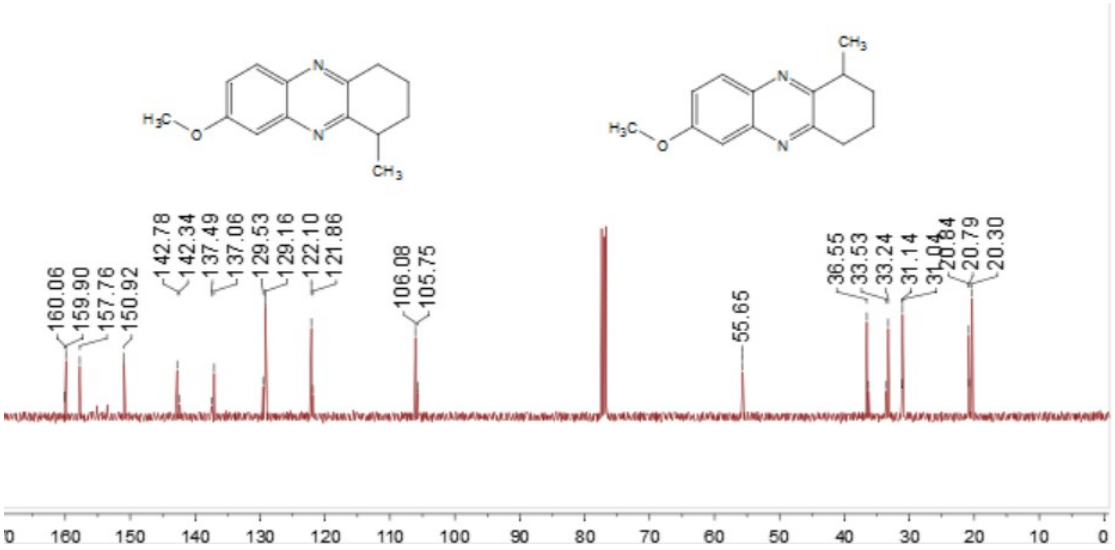
^{13}C-NMR spectrum of 1,7,8-trimethyl-1,2,3,4-tetrahydrophenazine (3ec)



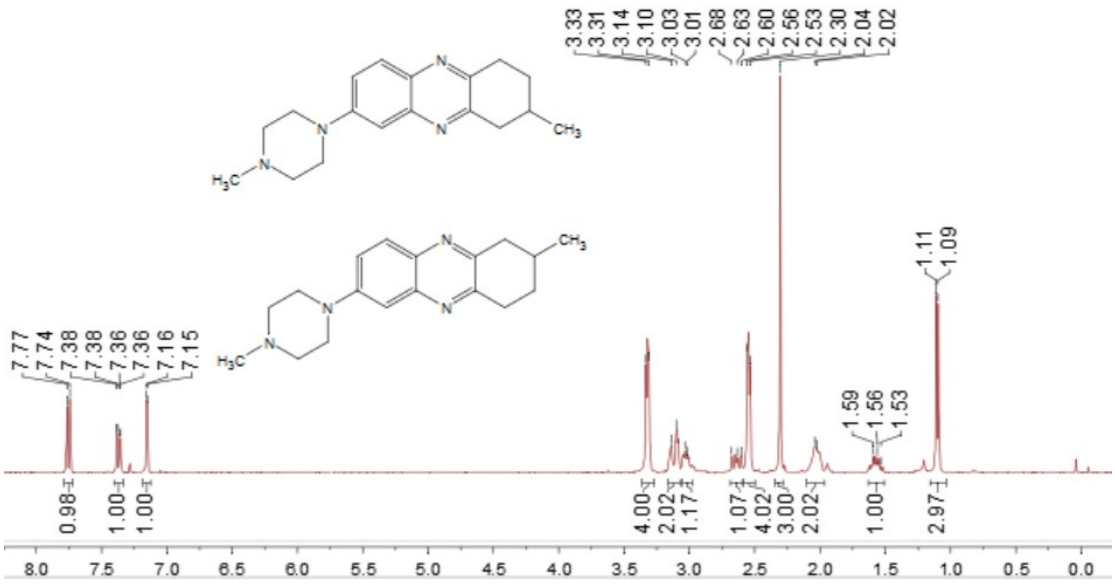
[1]H- NMR spectrum of 8-methoxy-1-methyl-1,2,3,4-tetrahydrophenazine (3ac) and 7-methoxy-1-methyl-1,2,3,4-tetrahydrophenazine (3ac'')



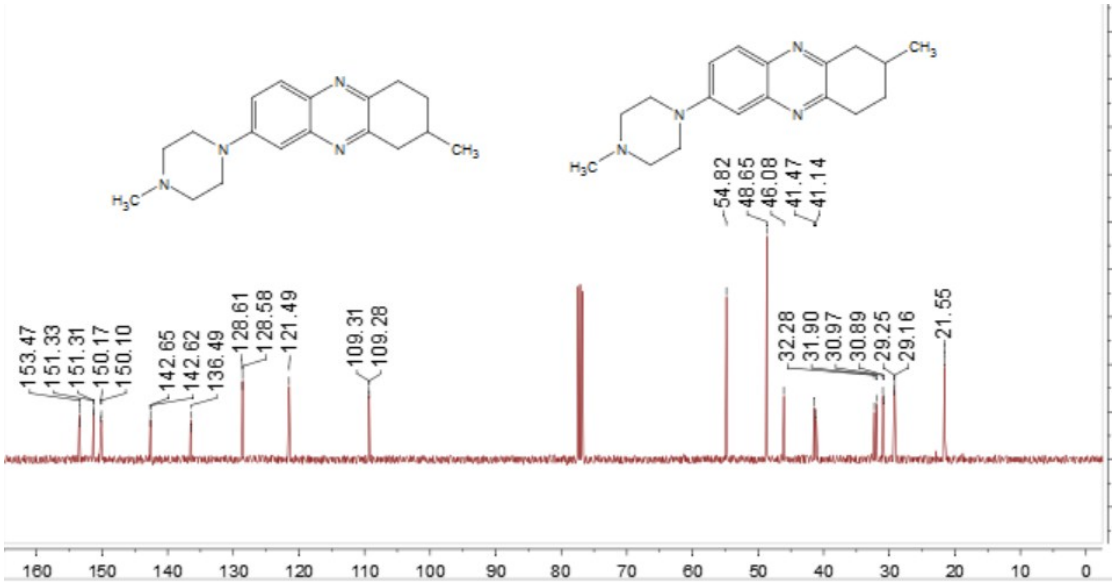
[13]C-NMR spectrum of 8-methoxy-1-methyl-1,2,3,4-tetrahydrophenazine (3ac) and 7-methoxy-1-methyl-1,2,3,4-tetrahydrophenazine (3ac'')



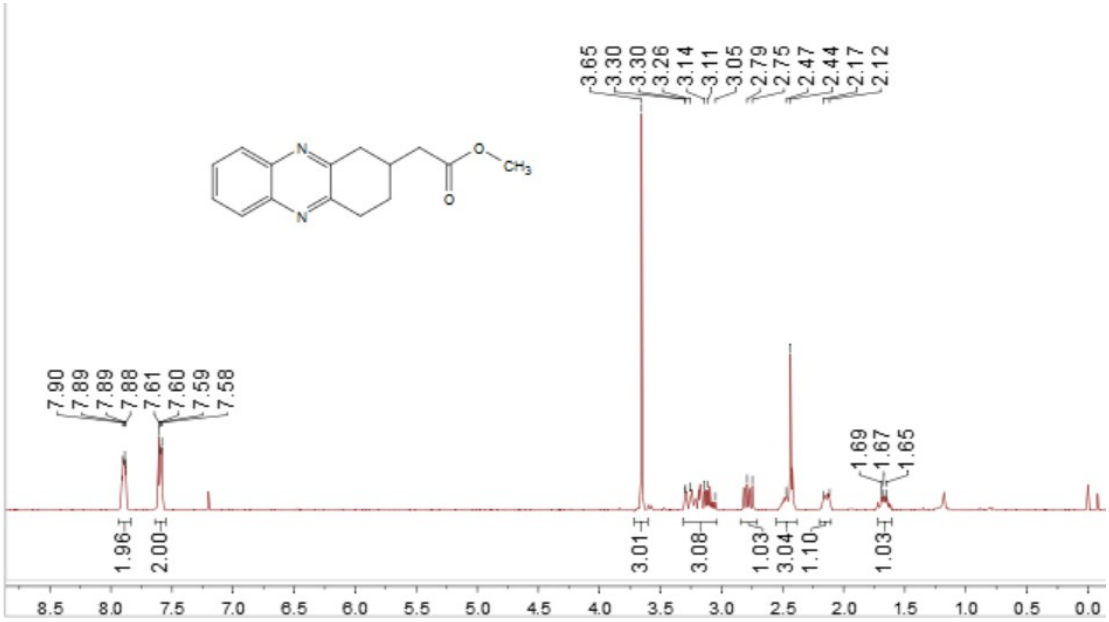
^{1}H-NMR spectrum of 2-methyl-8-(4-methylpiperazin-1-yl)-1,2,3,4-tetrahydrophenazine (3gb) and 2-methyl-7-(4-methylpiperazin-1-yl)-1,2,3,4-tetrahydrophenazine (3gb'')



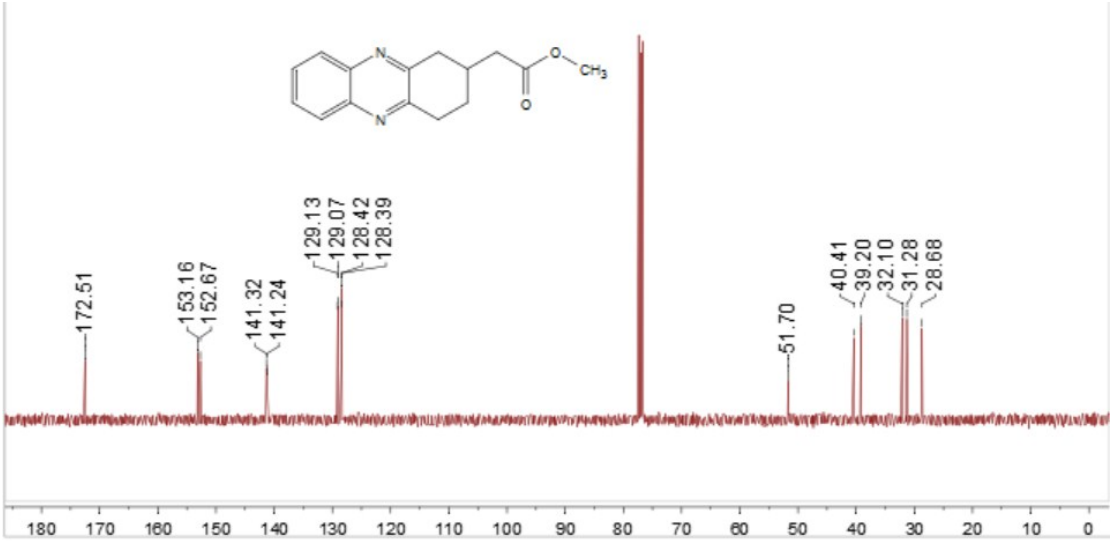
^{13}C-NMR spectrum of 2-methyl-8-(4-methylpiperazin-1-yl)-1,2,3,4-tetrahydrophenazine (3gb) and 2-methyl-7-(4-methylpiperazin-1-yl)-1,2,3,4-tetrahydrophenazine (3gb'')



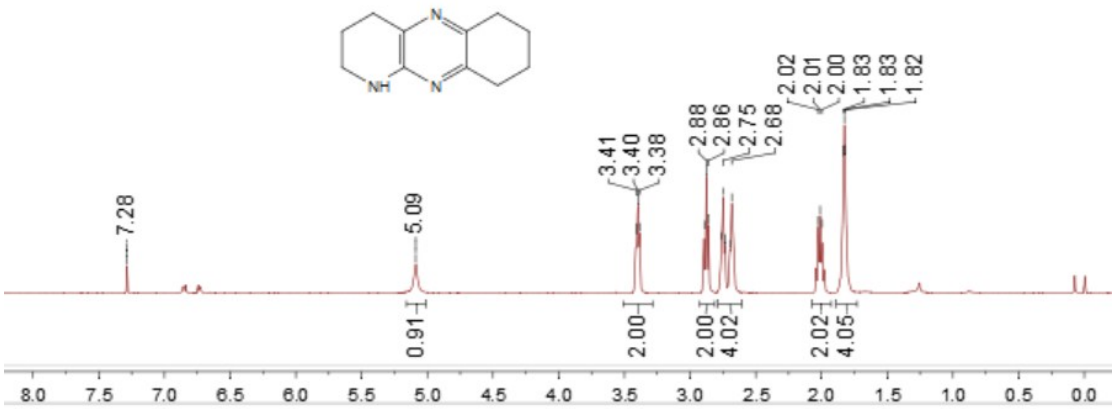
^{1}H-NMR spectrum of methyl 2-(1,2,3,4-tetrahydrophenazin-2-yl)acetate (3bd)



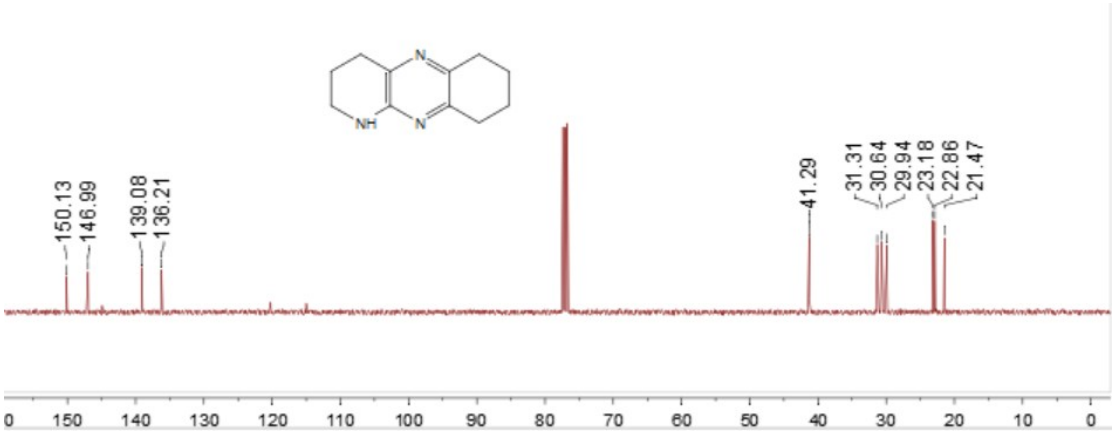
^{13}C-NMR spectrum of methyl 2-(1,2,3,4-tetrahydrophenazin-2-yl)acetate (3bd)



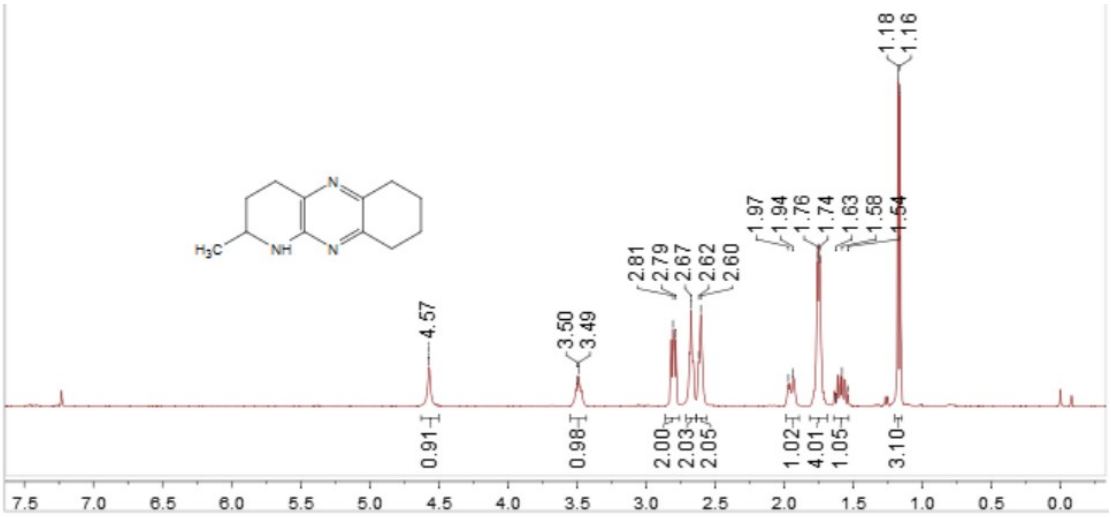
^{1}H-NMR spectrum of 1,2,3,4,6,7,8,9-octahydropyrido[2,3-b]quinoxaline (4la)



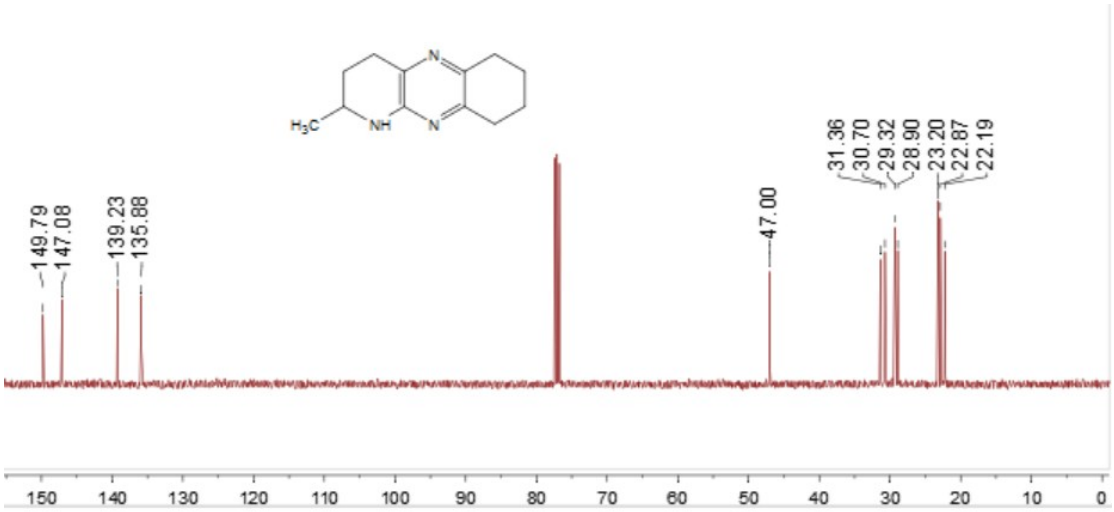
^{13}C-NMR spectrum of 1,2,3,4,6,7,8,9-octahydropyrido[2,3-b]quinoxaline (4la)



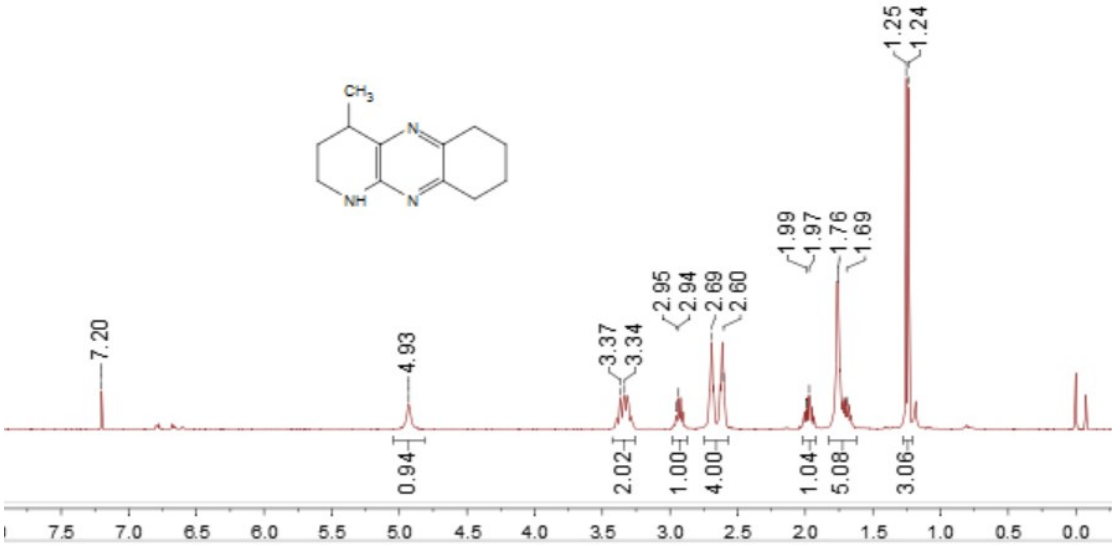
^{1}H-NMR spectrum of 2-methyl-1,2,3,4,6,7,8,9-octahydropyrido[2,3-b]quinoxaline (4ma)



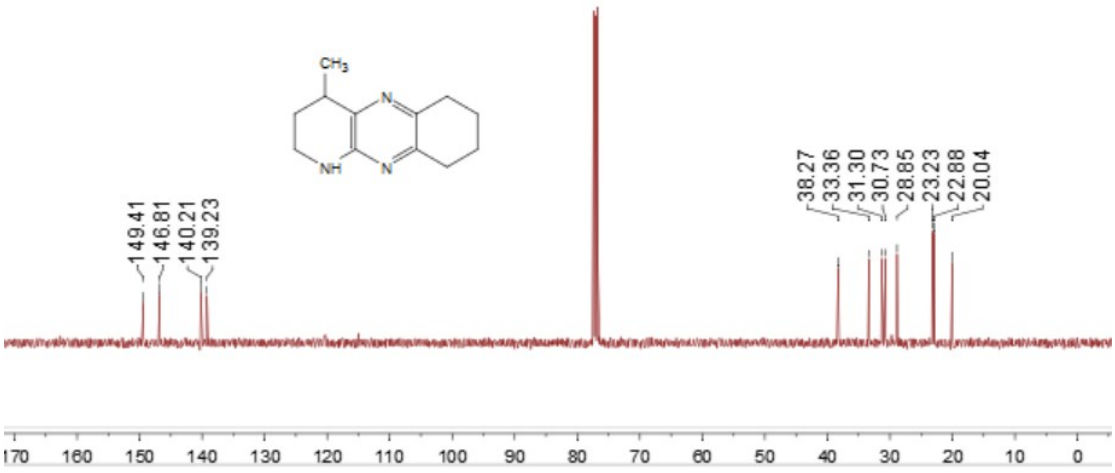
^{13}C-NMR spectrum of 2-methyl-1,2,3,4,6,7,8,9-octahydropyrido[2,3-b]quinoxaline (4ma)



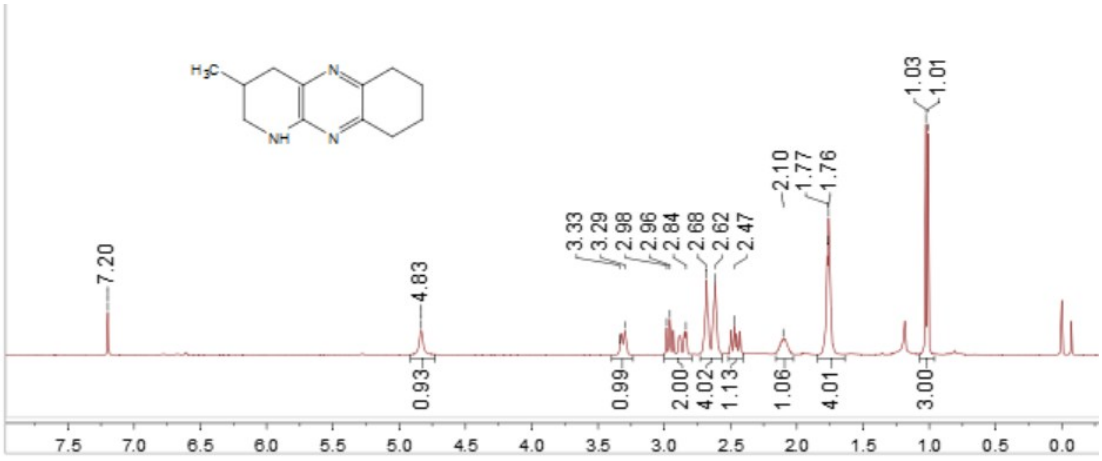
[1]H-NMR spectrum of 4-methyl-1,2,3,4,6,7,8,9-octahydropyrido[2,3-b]quinoxaline (4na)



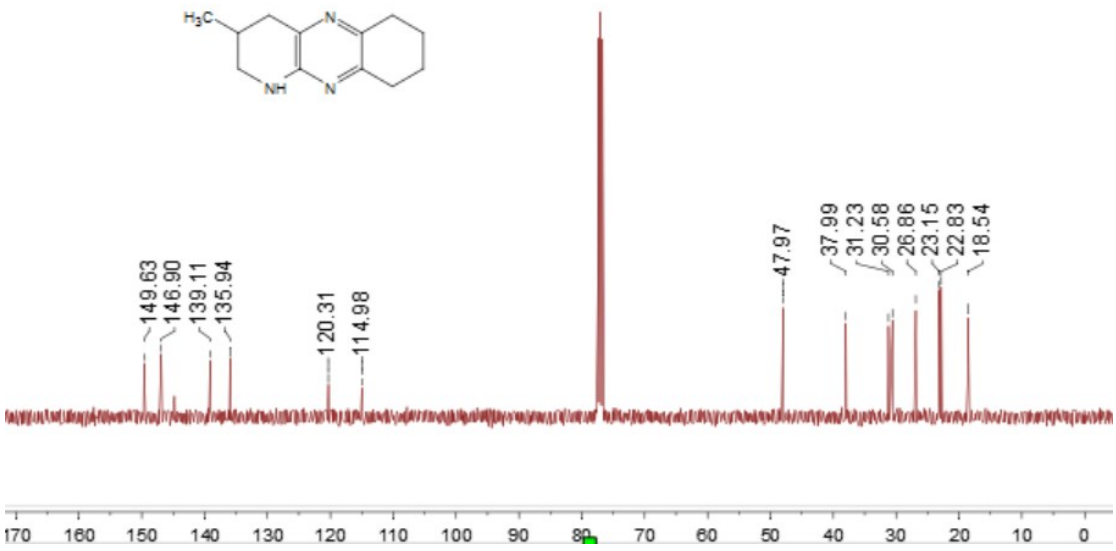
[13]C-NMR spectrum of 4-methyl-1,2,3,4,6,7,8,9-octahydropyrido[2,3-b]quinoxaline (4na)



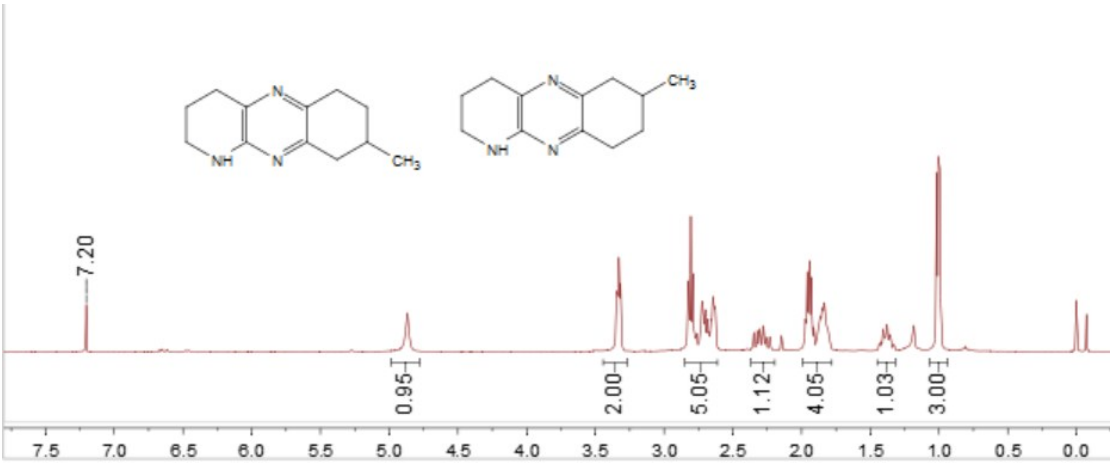
^{1}H-NMR spectrum of 3-methyl-1,2,3,4,6,7,8,9-octahydropyrido[2,3-b]quinoxaline (4oa)



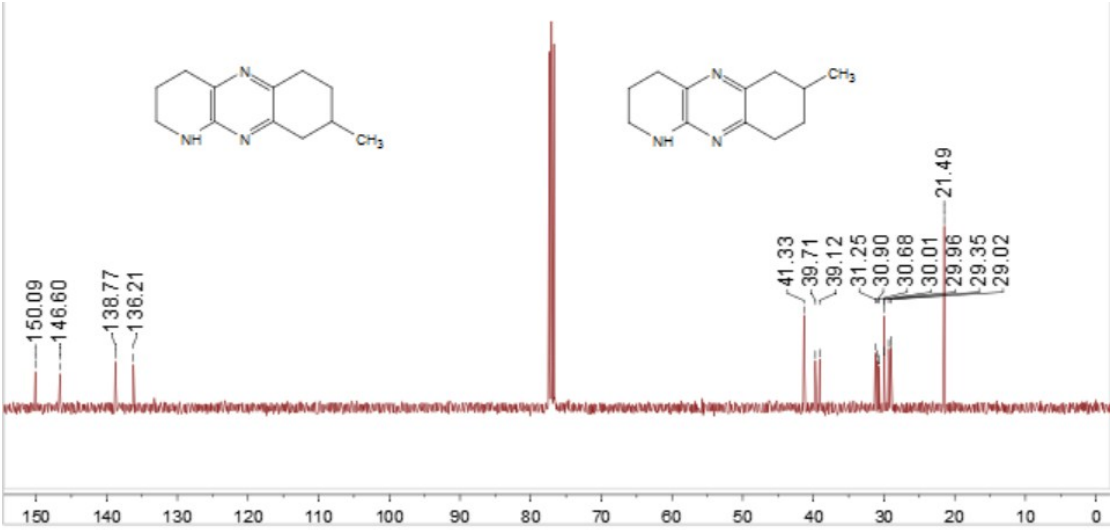
^{13}C-NMR spectrum of 3-methyl-1,2,3,4,6,7,8,9-octahydropyrido[2,3-b]quinoxaline (4oa)



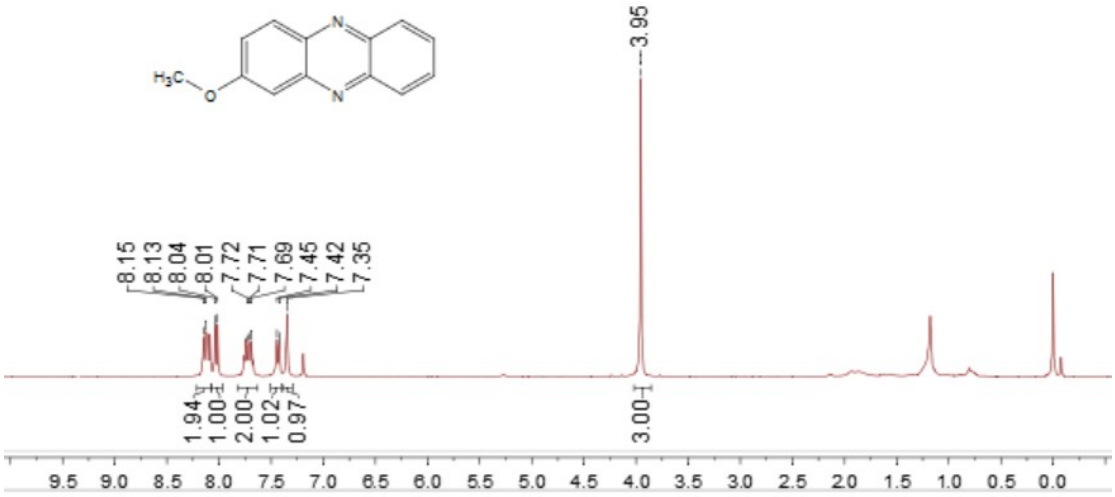
[1]H-NMR spectrum of 8-methyl-1,2,3,4,6,7,8,9-octahydropyrido[2,3-b]quinoxaline (4lb) and 7-methyl-1,2,3,4,6,7,8,9-octahydropyrido[2,3-b]quinoxaline (4lb'')



[13]C-NMR spectrum of 8-methyl-1,2,3,4,6,7,8,9-octahydropyrido[2,3-b]quinoxaline (4lb) and 7-methyl-1,2,3,4,6,7,8,9-octahydropyrido[2,3-b]quinoxaline (4lb'')



^{1}H-NMR spectrum of 2-methoxyphenazine (5a)



^{13}C-NMR spectrum of 2-methoxyphenazine (5a)