

Supporting Information

For

**MoO₂Cl₂(dmf)₂ catalyzed microwave assisted reductive cyclisation of
nitroaromatics into dibenzodiazepines**

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Experimental

Materials

All chemical were reagent grade purchased from Aldrich and Alfa Aesar and were used without purification. NMR spectra were recorded on a BRUKER AVANCE II-400FT Spectrometer (400 for ¹H NMR, 100MHz for ¹³C) using CDCl₃ as solvent and TMS as an internal reference. Mass spectra were recorded on a JEOL SX-102 (FAB) mass spectra at 70ev. Elemental analyses were carried out in a Coleman automatic carbon, hydrogen, oxygen, chlorine and nitrogen analyzer. All the reactions were monitored by TLC using 40 precoated sheets of silica gel G/UV-254 of 0.25mm thickness (Merck 60F254). Melting points were determined by open glass capillary method and were uncorrected.

Method

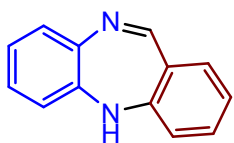
Typical procedure for the formation of 5'-amino-6'-isocyanospiro[thiazolidine-2,7'-thiazolo[3,2-a]pyrimidin]-4-one (5a)

Herein, Microwave assisted synthesis of diabenzodiazepines **3(a-j)** procedure by a mixture of 2-nitroaniline **1** (1mmol), various aromatic aldehydes **2(a-j)** (1mmol), Ph₃P (2.4 equivalents), 10% mol of MoO₂Cl₂ (dmf)₂ and toluene (3ml) was irradiated with microwaves at 200°C for 30-35

minutes. After completion of reaction (indicated by TLC), reaction mass was filtered and stand for 1.5 hours to remove the solvent. The mixture was poured into H₂O (100ml) and extracted with EtOAc (3 x 50ml) and washed with brine (3 x 20ml) dried over MgSO₄, and the solvent was removed under the reduced pressure. The remaining residue was purified by flash column chromatography to give analytically pure 3(a-j). All products were characterized by comparison of their mp, ¹H NMR spectra with those of authentic samples. [4]

Spectral data for 3(a-j)

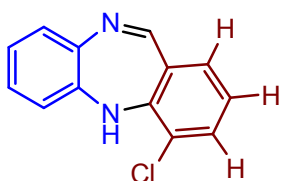
Compound 3a: 5H-dibenzo[b,e][1,4]diazepine.



White solid, mp 138°C; yield 75% (MW), 42% (Thermal). ¹H NMR (CDCl₃): δ 4.0 (s, 1H, NH), 6.6-6.9 (m, 4H, ArH), 7.0-7.4 (m, 4H, Ar'H), 8.39 (s, 1H, CH). ¹³C NMR (CDCl₃): δ 114.1, 118.7, 118.9, 119.6, 120.4,

123.2, 128.2, 130.0, 139.5, 141.6, 142.1, 144.4, 160.9. MS (EI): m/z: 194. Anal. Calcd for C₁₃H₁₀N₂: H,5.19, N,14.42, C,80.39. Found H,5.22, N,14.45, C,80.41.

Compound 3b: 4-chloro-5H-dibenzo[b,e][1,4]diazepine.

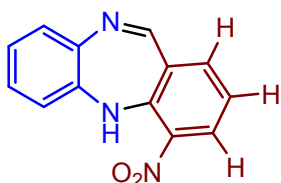


White solid, mp 144°C; yield 74% (MW), 44% (Thermal). ¹H NMR (CDCl₃): δ 4.0 (s, 1H, NH), 6.6-7.0 (m, 4H, ArH), 7.2-7.6 (m, 3H, Ar'H), 8.39 (s, 1H, CH). ¹³C NMR (CDCl₃): δ 115.5, 119.6, 120.1,

120.4, 123.2, 128.1, 128.2, 133.4, 139.2, 139.5, 144.0, 144.4, 160.9. MS (EI): m/z: 228. Anal.

Calcd for $C_{13}H_9ClN_2$: H,3.96, N,12.25, Cl,15.50, C,68.28. Found H,3.98, N,12.31, Cl,15.57, C, 68.31.

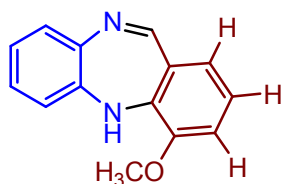
Compound 3c: 4-nitro-5H-dibenzo[b,e][1,4]diazepine.



Pale white solid, mp 152°C; yield 73% (MW), 40% (Thermal). 1H NMR ($CDCl_3$): δ 4.0 (s, 1H, NH), 6.5-7.0 (m, 4H, ArH), 7.2-7.6 (m, 3H, Ar'H), 8.39 (s, 1H, CH). ^{13}C NMR ($CDCl_3$): δ 115.0, 119.6, 119.8, 120.4, 123.2, 128.2, 136.1, 138.6, 138.7, 139.5, 139.8, 144.4, 160.9.

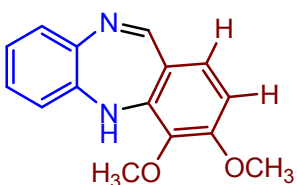
MS (EI): m/z: 239. Anal. Calcd for $C_{13}H_9N_3O_2$; H,3.79, O,13.38, N,17.56, C,65.27. Found H,3.81, O,13.46, N,17.58, C,65.29.

Compound 3d: 4-methoxy-5H-dibenzo[b,e][1,4]diazepine



Whitish solid, mp 128°C; yield 75% (MW), 42% (Thermal). 1H NMR ($CDCl_3$): δ 3.73 (s, 3H, OCH_3), 4.0 (s, 1H, NH), 6.5-7.0 (m, 4H, ArH), 7.1-7.6 (m, 3H, Ar'H), 8.39 (s, 1H, CH). ^{13}C NMR ($CDCl_3$): δ 55.9, 114.4, 117.5, 118.1, 119.4, 119.6, 120.4, 122.4, 123.2, 128.2, 130.3, 139.5, 150.4, 160.9. MS (EI): m/z: 224. Anal. Calcd for $C_{14}H_{12}N_2O$: H,5.39, O,7.13, N,12.49, C,74.98. Found H,5.42, O,7.19, N,12.52, C,74.96.

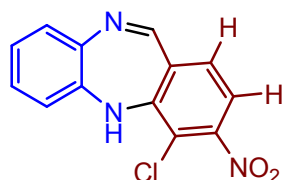
Compound 3e: 3,4-dimethoxy-5H-dibenzo[b,e][1,4]diazepine.



White solid, mp 120°C; yield 78% (MW), 45% (Thermal). 1H NMR ($CDCl_3$): δ 3.73 (s, 6H, 2 x OCH_3), 4.0 (s, 1H, NH), 6.9-6.7 (m, 4H, ArH), 7.4-7.0 (m, 2H, Ar'H), 8.39 (s, 1H, CH). ^{13}C NMR ($CDCl_3$): δ

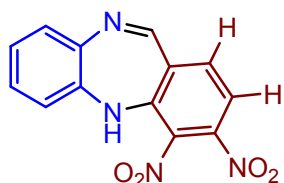
49.8, 56.2, 115.1, 119.6, 119.7, 120.4, 122.3, 123.2, 127.7, 128.2, 130.2, 139.5, 144.4, 160.6, 160.9. MS (EI): m/z:254. Anal. Calcd for C₁₅H₁₄N₂O₂: H,5.55, N,11.02, O,12.58, C,70.85. Found H,5.58, O,12.61, N,11.09, C,70.89.

Compound 3f: 4-chloro-3-nitro-5H-dibenzo[b,e][1,4]diazepine



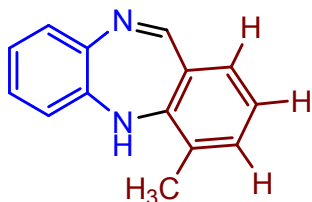
Dirty white solid. mp 158°C; yield 80% (MW), 43% (Thermal). ¹H NMR (CDCl₃): δ 4.0 (s, 1H, NH), 7.0-6.5 (m, 4H, ArH), 7.3-7.5 (m, 2H, Ar'H), 8.39 (s, 1H, CH). ¹³C NMR (CDCl₃): δ 112.1, 118.4, 119.6, 120.4, 123.2, 124.6, 128.2, 129.1, 139.5, 144.4, 145.0, 152.0, 160.9. MS (EI): m/z: 273. Anal. Calcd for C₁₃H₈ClN₃O₂: H,2.95, O,11.68, Cl,12.95, N,15.35, C,57.05. Found H,2.98, O,11.72, Cl,12.98, N,15.39, C,57.12.

Compound 3g: 3,4-dinitro-5H-dibenzo[b,e][1,4]diazepine



Pale white solid. mp 148°C; yield 76% (MW), 44% (Thermal). ¹H NMR (CDCl₃): δ 4.0 (s, 1H, NH), 7.1-6.7 (m, 4H, ArH), 7.5-7.3 (m, 2H, Ar'H), 8.39 (s, 1H, CH). ¹³C NMR (CDCl₃): δ 111.6, 119.6, 120.4, 123.2, 124.1, 128.2, 133.1, 137.1, 139.5, 139.7, 144.4, 146.7, 160.9. MS (EI): m/z: 284. Anal. Calcd for C₁₃H₈N₄O₄: H,2.84, N,19.72, O,22.52, C,54.93. Found H,2.86, N,19.75, O,22.55, C,54.99.

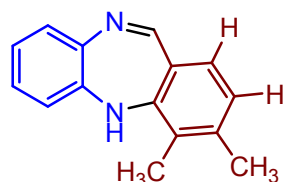
Compound 3h: 4-methyl-5H-dibenzo[b,e][1,4]diazepine



Dirty yellow solid, mp 136°C; yield 75% (MW), 42% (Thermal). ¹H NMR (CDCl₃): δ 2.35 (s, 3H, CH₃), 4.0 (s, 1H, NH), 7.0-6.5 (m, 4H, ArH), 7.7-7.2 (m, 3H, Ar'H), 8.39 (s, 1H, CH). ¹³C NMR (CDCl₃): δ 15.5, 117.0, 118.3, 119.6, 120.4, 123.2, 127.1, 128.2, 131.9, 132.3,

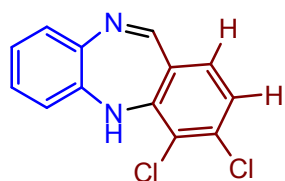
138.3, 139.5, 144.4, 160.9. MS (EI): m/z: 208. Anal. Calcd for C₁₄H₁₂N₂:; H,5.81, N,13.45, C,80.74. Found H,5.87, N,13.54, C,80.79.

Compound 3i: 3,4-dimethyl-5H-dibenzo[b,e][1,4]diazepine



White solid, mp 132°C; yield 77% (MW), 41% (Thermal). ¹H NMR (CDCl₃): δ 2.35 (s, 6H, 2 x CH₃), 4.0 (s, 1H, NH), 6.9-6.5 (m, 4H, ArH), 7.3-7.0 (m, 2H, Ar'H), 8.39 (s, 1H, CH). ¹³C NMR (CDCl₃): δ 9.0, 17.8, 114.0, 118.6, 119.6, 120.4, 123.2, 125.7, 127.0, 128.2, 138.2, 139.5, 140.1, 144.4, 160.9. MS (EI): m/z: 222. Anal. Calcd for C₁₅H₁₄N₂: H,6.35, N,12.60, C,81.05. Found H,6.38, N,12.72, C,81.11.

Compound 3j: 3,4-dichloro-5H-dibenzo[b,e][1,4]diazepine



Dirty white solid mp.146°C; yield 78% (MW), 40% (Thermal). ¹H NMR (CDCl₃): δ 4.0 (s, 1H, NH), 7.0-6.5 (m, 4H, ArH), 7.4-7.1 (m, 2H, Ar'H), 8.39 (s, 1H, CH). ¹³C NMR (CDCl₃): δ 116.6, 119.6, 119.9, 120.4, 123.2, 128.2, 128.7, 129.6, 136.6, 139.5, 144.4, 145.5, 160.9 MS (EI): m/z: 262. Anal. Calcd for C₁₃H₈Cl₂N₂: H,3.06, N,10.65, Cl,26.95, C,59.34. Found H,3.07, N,10.71, Cl,26.98, C,59.43.