Supporting information

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Green route for synthesis of 1, 5-benzodiazepine over modified heteropolyacid as nano-catalyst: Kinetics and mechanism

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1. General experimental procedure

All experiments were carried out in 50 cm^3 glass reactor. The speed of agitation was maintained by using four bladed–pitched turbine impeller. The temperature was maintained at ±1°C of the desired value. Known quantities of reactants and catalyst were charged into glass reactor, the temperature increased to desired value and agitation started. Then, an initial sample was withdrawn. Further samples were withdrawn at periodic intervals up to 1.5 h. A standard experiment consists of 0.0066 mol of *o*-phenylenediamine, 0.1mol of acetophenone and a catalyst loading of 0.011 g/cm^3 with respect to total volume of the liquid. The temperature was maintained at 100 °C and the speed of agitation at 1100 rpm. The total volume of liquid phase was 15 cm^3. After completion of reaction catalyst was recovered by filtration. The reaction was diluted with water followed by extraction in ethyl acetate and concentrated to get product. The Product was further purified by column chromatography (ethyl acetate: n-hexane, 2:8 v/v). Obtained product was confirmed by GC-MS, melting point, FT-IR and ^{1}H-NMR.

2. Spectroscopic data of products

1. 2, 3- Dihydro-2- methyl- 2,4- diphenyl-1H-1,5- benzodiazepine

Yellow solid, M.P. 150-152 °C (Lit.151-152 °C).[1,4]

IR (KBr): 3374 cm^{-1} (N-H), 3061 cm^{-1} (Aromatic C-H), 2974 cm^{-1} (Aliphatic C-H), 1634 cm-1 (C=N). (Representative FT-IR is given)

^{1}H-NMR (CDCl3) δ: 1.74 (s, 3H, -CH3), 2.91 (d, 1H, -CH), 3.11 (d, 1H, -CH), 3.50 (s, 1H, -NH), 6.8-7.5 (m, 14H, ArH).

2. 2-methyl-2,4-bis(4-methylphenyl)-2,3-dihydro-1H-1,5-benzodiazepine

Yellow solid, M.P. 140-142 °C (Lit.141-142 °C).[2]

IR (KBr): 3380 cm^{-1} (N-H), 3070 cm-1 (Aromatic C-H), 2977 cm^{-1} (Aliphatic C-H), 1637 cm-1 (C=N).
^{1}H NMR (400 MHz, CDCl3) δ: = 2.40 (s, 3H), 2.43 (s, 3H), 1.73 (s, 3H), 2.98 (d, 1H), 3.05 (d, 1H), 3.52 (br, 1H), 6.73-7.15 (m, 4H), 7.25-7.55 (m, 8H).

3. 2-methyl-2,4-bis(4-methoxylphenyl)-2,3-dihydro-1H-1,5-benzodiazepine

Yellow solid, M. P. 121–123 °C (Lit. 120-121◦C).[3]

IR (KBr): 3366 cm-1 (N-H), 3065 cm^{-1} (Aromatic C-H), 2969 cm-1 (Aliphatic C-H), 1610 cm-1 (Aromatic C=N), 1470 (Aromatic C-H).

^{1}H NMR (400 MHz, CDCl3) δ: 1.83 (s, 3H, CH3), 2.91 (d, 1H, CH), 3.06 (d, 1H, CH), 3.45 (br, s, 1H, NH), 3.78 (s, 3H, OCH3), 3.81 (s, 3H, OCH3), 6.84–6.88 (m, 5H, Ar Hs), 7.19 (t, 2H, Ar Hs), 7.41 (m, 1H, Ar H), 7.49 (d, 2H, Ar Hs), 7.68 (d, 2H, Ar Hs).

4. 2-methyl-2,4-bis(4-chlorophenyl)-2,3-dihydro-1H-1,5-benzodiazepine

Yellow solid, M.P. 159–160 °C (Lit.162–163 °C).[4]
IR (KBr) ν: 3328 cm-1(NH), 1632cm-1(C=N), 1593(aromatic CH).

^{1}H NMR (400 MHz, CDCl3) δ: 1.76 (s, 3H, CH3), 2.96 (d, 1H, CH), 3.14 (d, 1H, CH), 3.50 (br, s, 1H, NH), 6.90 (d, 1H, Ar H), 7.11 (t, 1H, Ar H),
7.19 (t, 1H, Ar H), 7.31 (d, 1H, Ar H), 7.50 (d, 2H, Ar Hs), 7.55 (d, 2H, Ar Hs), 7.59 (d, 4H, Ar Hs).

5. 2-methyl-2,4-bis(4-nitrophenyl)-2,3-dihydro-1H-1,5-benzodiazepine

Yellow solid, M.P. 151–153◦C (Lit.154◦C).[3,4]

IR (KBr) *v*: 3312 cm^{-1}(NH), 3074cm-1 (Aromatic CH), 1597cm^{-1}(C=N), 1348, 855, 750, 694 cm−1(Aromatic CH).
^{1}H NMR (400 MHz, CDCl3) *δ*: 1.75 (s, 3H, CH3), 2.93 (d, 1H, CH), 3.14 (d, 1H, CH), 3.48 (br, s, 1H, NH), 6.90 (d, 1H, Ar H), 7.11 (t, 1H, Ar H), 7.18 (t, 1H, Ar H), 7.34 (d, 1H, Ar H), 7.68 (d, 2H, Ar Hs), 7.76 (d, 2H, Ar Hs), 8.06 (d, 4H, Ar Hs).

6. 2,2,4- Trimethyl- 2,3-dihydro -1H-1,5-benzodiazepine

Yellow solid, M. P.138-140°C (Lit.139°C).[3,4]
IR (KBr): 3291 cm^{-1} (NH), 2955 cm-1 (Aromatic CH), 1636 cm^{-1} (Alkene C=N), 1597 (Aromatic), 1474 cm^{-1} (Aromatic C=C).

^{1}H-NMR (400 MHz, CDCl3) *δ*: 1.36 (s, 6H, - (CH3)2), 2.15 (s, 2H, -CH2), 2.34 (s, 3H, -CH3), 6.7-7.4 (m, 4H, ArH).

7. 10 - Spirocyclohexan - 2,3,4,10,11,11a - hexahydro - 1*H*dibenzo[*b*,*e*][1,4]diazepine

Yellow solid, M.P. 135-139 (Lit.137-138).[1,4]
IR (KBr): 3376 cm^{-1} (N-H), 3070 cm-1 (Aromatic C-H), 2968 cm-1 (Aliphatic C-H), 1664 cm^{-1} (Aromatic C=N), 1599 (Aromatic C-H).
^{1}H NMR (400 MHz, CDCl3) *δ*: = 0.98-1.51 (m, 16H), 1.83-2.24 (m, 3H), 3.56 (br, 1H, N-H), 6.15-7.34 (m, 4H).

References:

(1) Curini, M.; Epifano, F.; Marcotullio, M. C.; Rosati, O. Ytterbium triflate promoted synthesis of 1,5-benzodiazepine derivatives. *Tetrahedron Lett.* **2001**, 3193-3195.

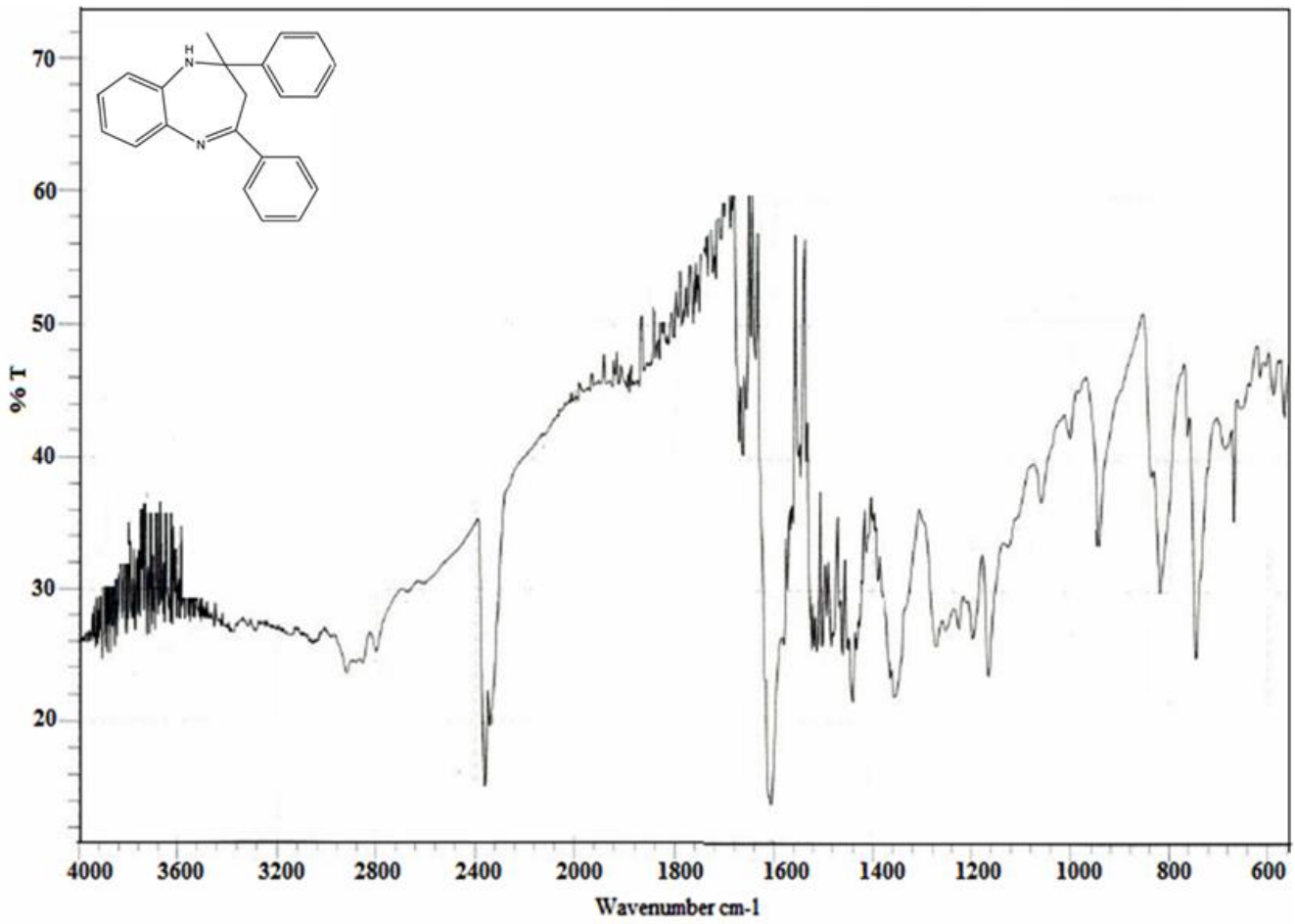
(2) Kuo, C. W.; More, S. V.; Yao, C. F. NBS as an efficient catalyst for the synthesis of 1,5-benzodiazepine derivatives under mild conditions. *Tetrahedron Lett*. **2006,** *47(48)*, 8523-8528.

(3) Reddy, K.S.; Reddy, C.V.; Mahesh, M.; Reddy, K. R.; Raju, P. V. K.; Reddy, V. V. N. Zirconium(IV) chloride catalyzed

synthesis of 1,5-benzodiazepine derivatives. *Can. J. Chem.* **2007,** *85(3)*, 184-188.

(4) Mahajan, D.; Naqvi, T.; Sharma, R. L., Kapoor, K.K. Alum-catalyzed one-pot solventless synthesis of 1,5-benzodiazepines. *Aust. J. Chem.* **2008,** *61(2)*, 159-162.

Representative FT-IR of model compound



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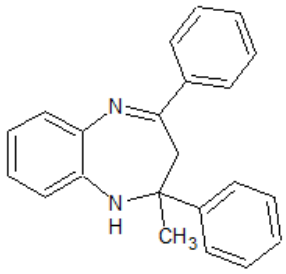
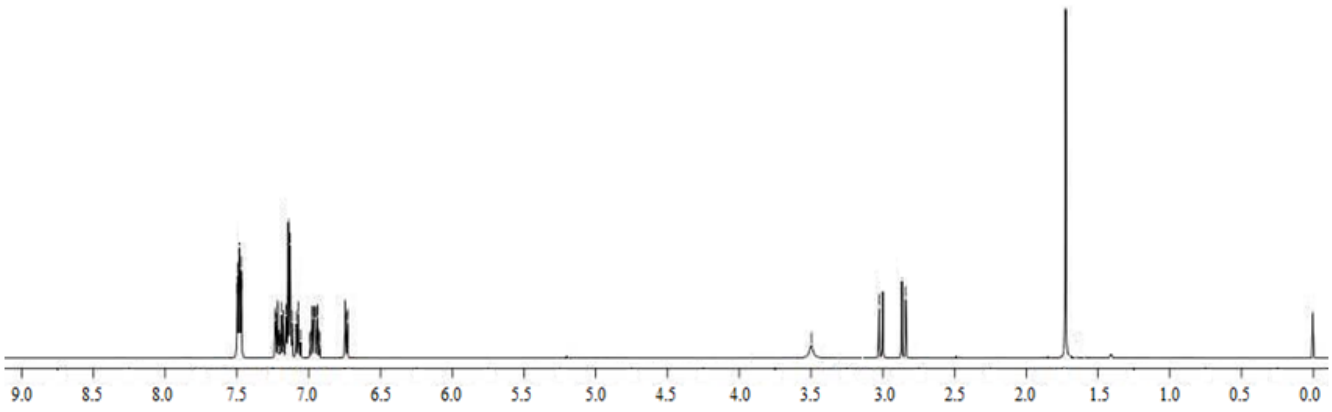


2-methyl-2,4-diphenyl-2,3-dihydro-1*H*-1,5-benzodiazepine



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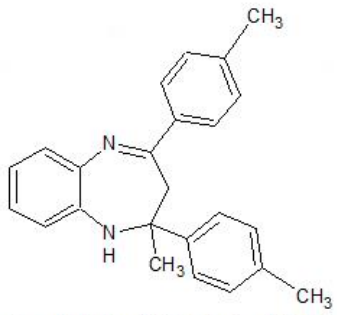

2-methyl-2,4-bis(4-methylphenyl)-2,3-dihydro-1*H*-1,5-benzodiazepine

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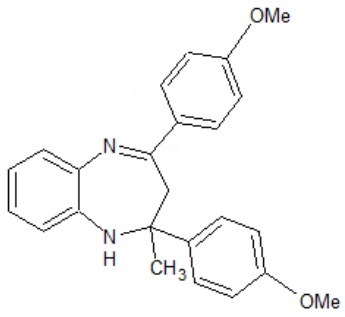

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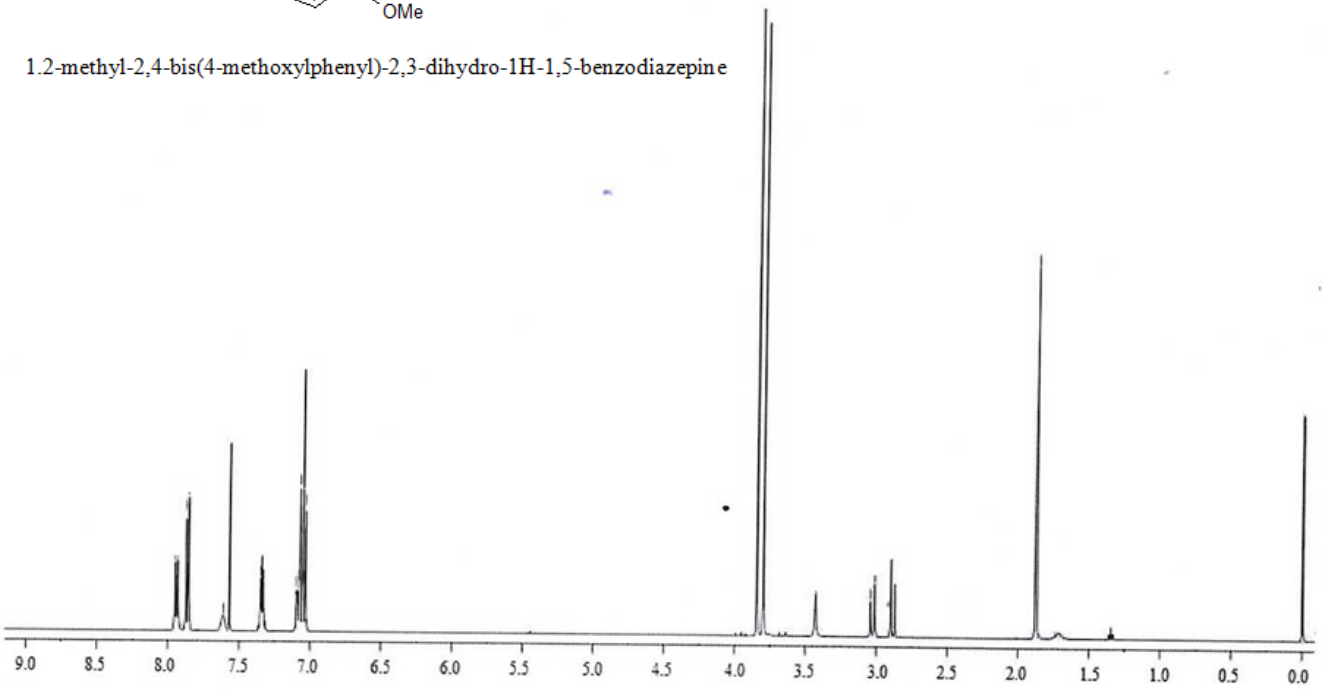

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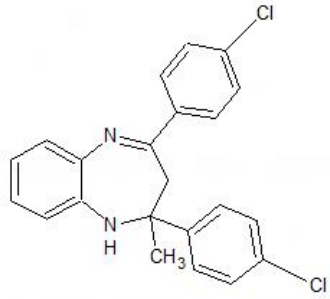

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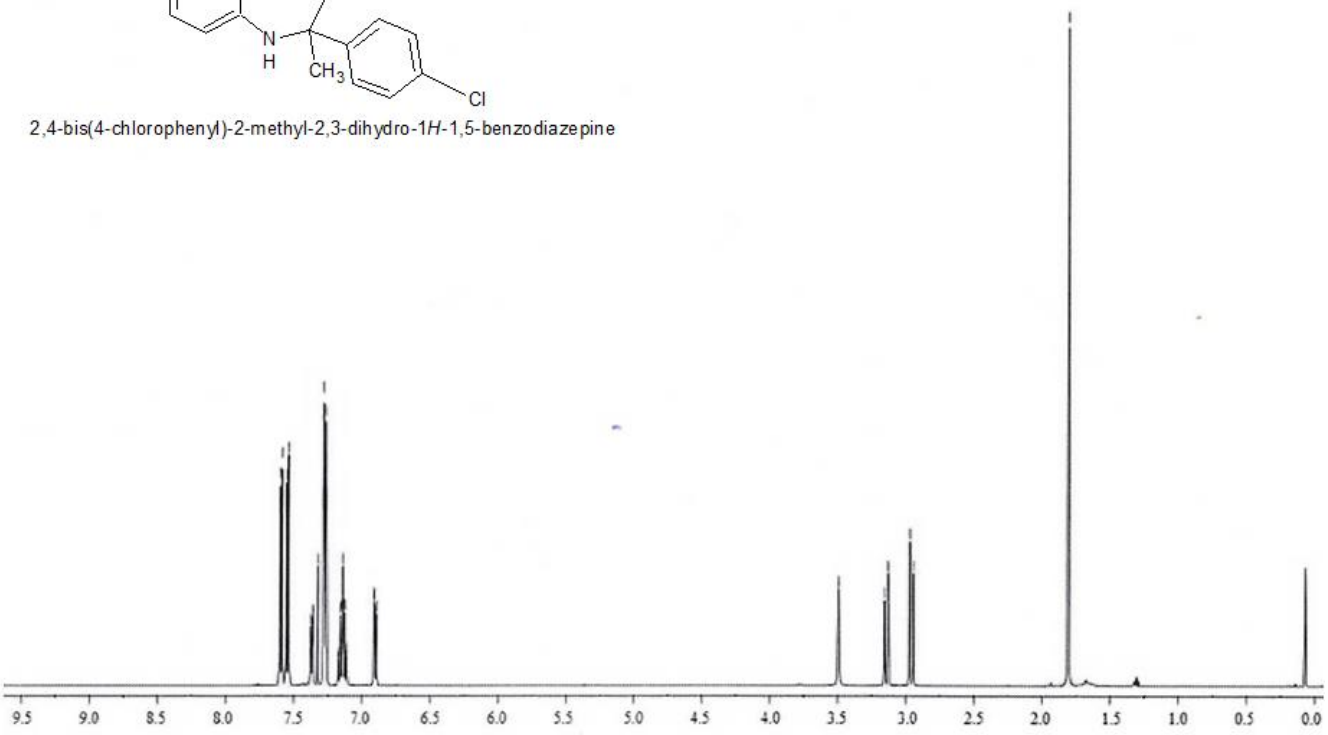

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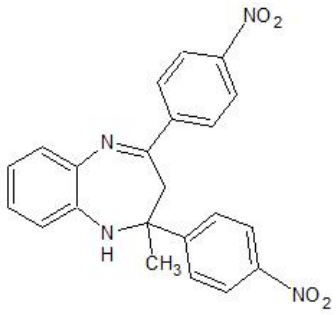

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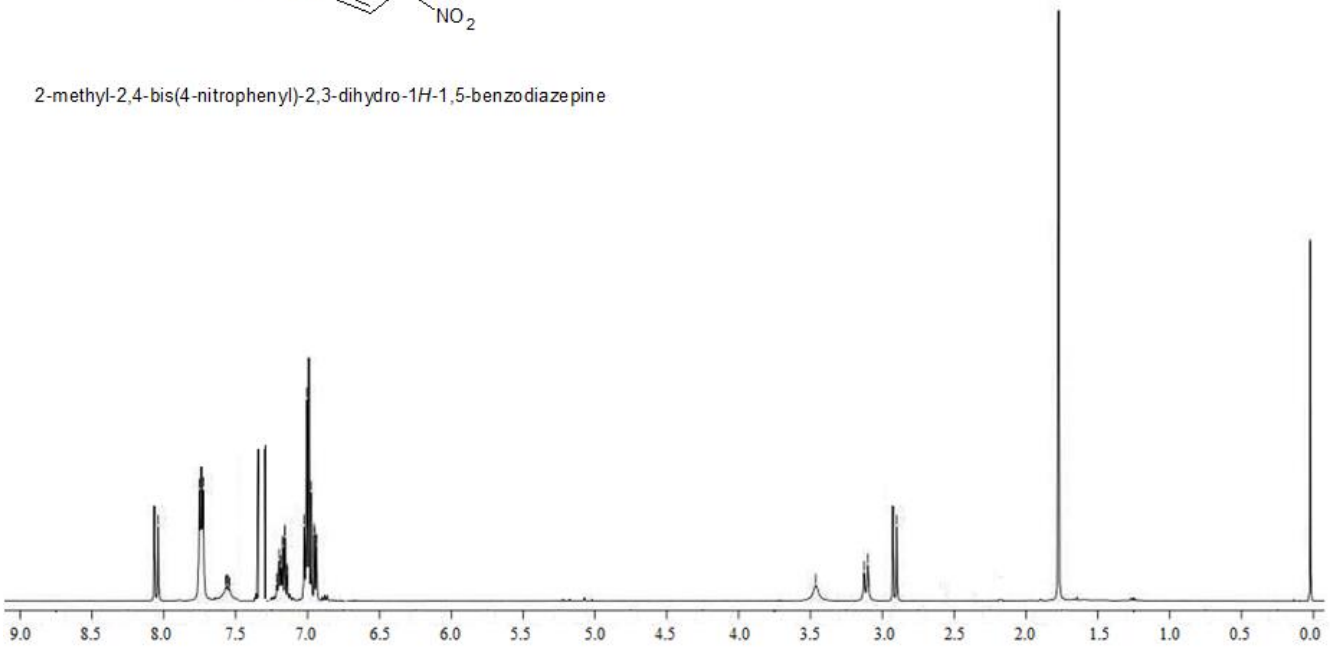

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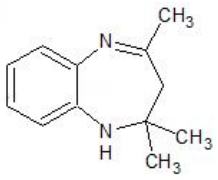
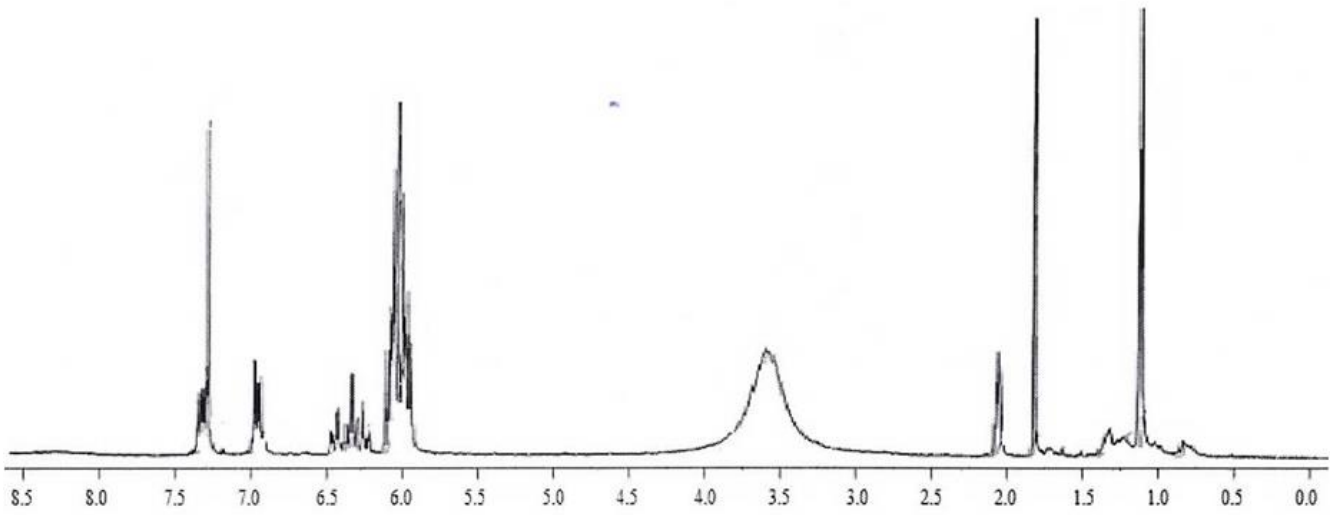


2,2,4-trimethyl-2,3-dihydro-1*H*-1,5-benzodiazepine



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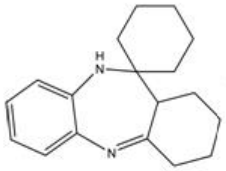

10 - Spirocyclohexan - 2,3,4,10,11,11a - hexahydro - 1*H*dibenzo[*b*,*e*][1,4]diazepine