SynOpen R. Gujjarappa et al. THIEME OPEN ACCESS Paper

Efficient Syntheses of Diverse N-Heterocycles: The Molybdenum(VI)-Catalyzed Reductive Cyclization of Nitroarenes using Pinacol as a Deoxygenating Agent

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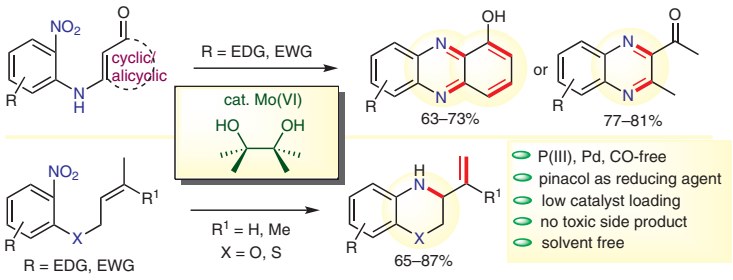


Received: 31.01.2018
Accepted after revision: 05.04.2018
Published online: 09.05.2018
DOI: 10.1055/s-0036-1591572; Art ID: so-2018-d0017-op

Abstract Molybdenum(VI)-catalyzed domino reductive cyclization of nitroarenes has been devised for the syntheses of 1,4-benzoxazines and 1,4-benzothiazines in the presence of pinacol as deoxygenating agent. The scope of the described method was further extended to the syntheses of the rarely explored scaffolds, 1-hydroxyphenazines and quinoxalines. The present method avoids the use of hazardous deoxygenating agents and operates under solvent-free conditions.

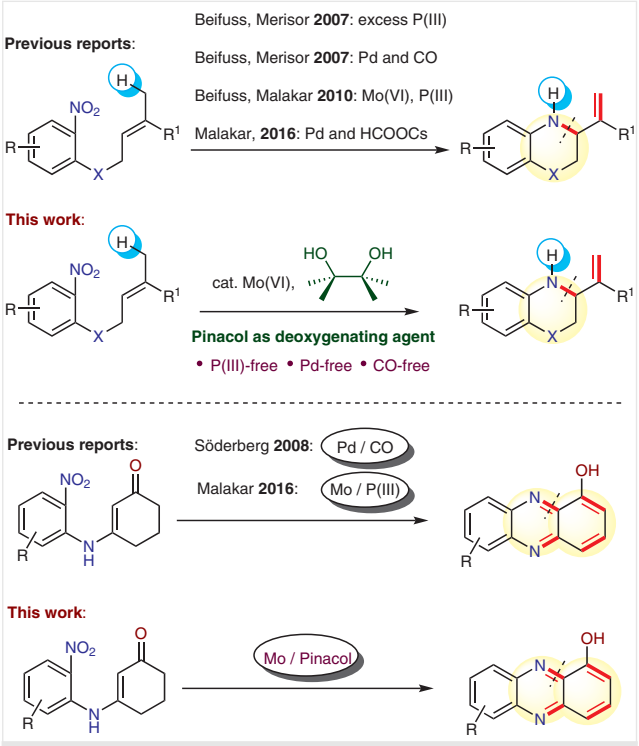
Key words N-heterocycles, domino reaction, reductive cyclization, nitroarenes, dioxo-Mo(VI) complex, pinacol

N-Heterocyclic compounds have received considerable attention in the field of medicinal chemistry and drug-discovery research because of their broad spectrum of pharmacological properties.[1] More than 70% of small molecule drugs contain N-heterocyclic moieties.[2] Moreover, among all the heterocycles, six-membered N-containing cyclic compounds are most commonly encountered.[2] Due to their immense impact in medicinal chemistry, several protocols have been devised during the past decades.[3] Among such approaches, one traditional approach relies on the reductive cyclization of nitroarenes.[4] Although, a number of useful methods have been reported in this area, the drive to develop efficient deoxygenation of nitroarenes continues.[5] However, major disadvantages of an approach based on the reduction of nitroarenes hinge on the use of P(III)-reagents,[6] carbon monoxide[7] and other hazardous deoxygenating agents.[8] In addition, the required use of molecular hydrogen as hydrogen source for the deoxygenation of nitroarenes restricts large-scale industrial applications.[5] Moreover, most of the developed processes are confined to the use of expensive metal catalysts[9] and the derived by-products are not easy to remove. Hence, the development of a more economical and environment-friendly process remains a challenge.

It is well-established that transition-metal complexes having multiple metal–oxygen bonds are efficient catalysts for deoxygenation reactions of organic compounds.[10] In this regard, $MoO_2Cl_2(DMF)_2$ was found to be an efficient catalyst due to its ease of preparation in aqueous medium and low cost.[11] Therefore, the redox properties of $MoO_2Cl_2(DMF)_2$ have been extensively studied for a broad spectrum of oxygen-transfer reactions, including our previous reports on reductive cyclization of nitroarenes.[12] However, to accomplish these processes, a number of deoxygenating agents such as P(III)-based reagents,[6] silanes,[8a] boranes,[8b] and molecular hydrogen[8c–d] have been used. Our attention was drawn towards a recent development from Sanz and coworkers,[13] wherein they describe a novel method for the chemoselective reduction of sulfoxides and nitroaromatics using catalytic amounts of Mo(VI) in the presence of pinacol as a deoxygenating agent. Inspired by this report, we herein describe a method for the preparation of 1,4-benzoxazines, 1,4-benzothiazines, 1-hydroxyphenazines, and quinoxalines using $MoO_2Cl_2(DMF)_2$ as catalyst and pinacol as deoxygenating agent in *o*-xylene as solvent.

Six-membered N-heterocycles such as 1,4-benzoxazines and 1,4-benzothiazines nucleus are well-known pharmacophoric scaffolds that have emerged as core structural units of a variety of antibacterial and antimicrobial agents.[14] Several approaches have been described for the syntheses of these scaffolds using ω-nitroalkenes as substrates (Scheme 1).[6] The reported protocols have been accomplished via the reductive cyclization of ω-nitroalkenes using P(III)-reagents and carbon monoxide as deoxygenating agents under both catalytic and non-catalytic conditions. The common drawbacks associated with these earlier approaches result from the use of excess of P(III)-reagents and the formation of

phosphine oxides in the reaction mixture. Moreover, when triethylphosphite was introduced as the deoxygenating agent, the corresponding N-alkylated side products were observed in considerable amounts.

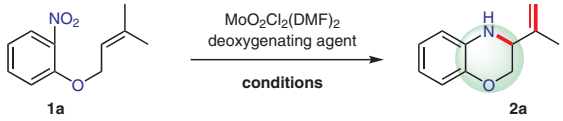


Scheme 1 Protocols for the synthesized scaffolds

The method reported herein has been extended towards the synthesis of 1-hydroxyphenazines and quinoxalines by the reductive cyclization of the appropriate β-(*N*-2-nitroaryl)-α,β-unsaturated ketones. Both 1-hydroxyphenazine and quinoxaline scaffolds have attracted considerable attention due to their unique biological activities such as antibacterial and DNA-cleaving properties.[15] Additionally, these molecules have also been used as intermediates for the syntheses of more complex molecules.[16]

Starting materials **1a–i** and **3a–f** were synthesized by using the previous reported methods.[9f,12d] In initial studies, 2-nitrophenyl ether **1a** was used as a model substrate in the presence of 10 mol% $MoO_2Cl_2(DMF)_2$ as catalyst and pinacol as reducing agent in toluene at 110 °C for 15 hours in a sealed vial. Under these conditions, the desired product 3-isopropenyl-3,4-dihydro-2*H*-1,4-benzoxazine (**2a**) was obtained in 64% yield (Table 1, entry 1). It could be demonstrated that, when alternative deoxygenating agents were employed with 10 mol% Mo(VI)-catalyst, the expected product **2a** was formed in lower yields (entries 3–6). We then investigated the optimum catalyst loading for the conversion of **1a** into **2a**. Similar yields of **2a** were obtained with 5 mol% and 2.5 mol% Mo(VI)-catalyst (entries 7 and 8). However, when the catalyst loading was decreased beyond 2.5 mol% the yield of the desired product **2a** decreased (entries 9–11). A number of aromatic and nonaromatic solvents were then screened for the conversion of **1a** into **2a**. Among the solvents examined, *o*-xylene was most effective (entries 12–18). It was further observed that replacing $MoO_2Cl_2(DMF)_2$ with MoO_2Cl_2 as Mo(VI)-source, resulted in the yield of **2a** dropping dramatically (entry 19). When the reaction was studied under solvent-free conditions for a shorter reaction time (entries 20–22), it was found that the reaction of **1a** in the presence of 2.5 mol% $MoO_2Cl_2(DMF)_2$ and 5.0 equiv of pinacol at 110 °C for 10 hours furnished the best yield (83%) of the desired product **2a** (entry 21). Therefore, these conditions were chosen as optimal conditions to establish the scope of the reaction.

Table 1 Screening of the Conditions for the $MoO_2Cl_2(DMF)_2$ Catalyzed Domino Reaction of **1a**[a]



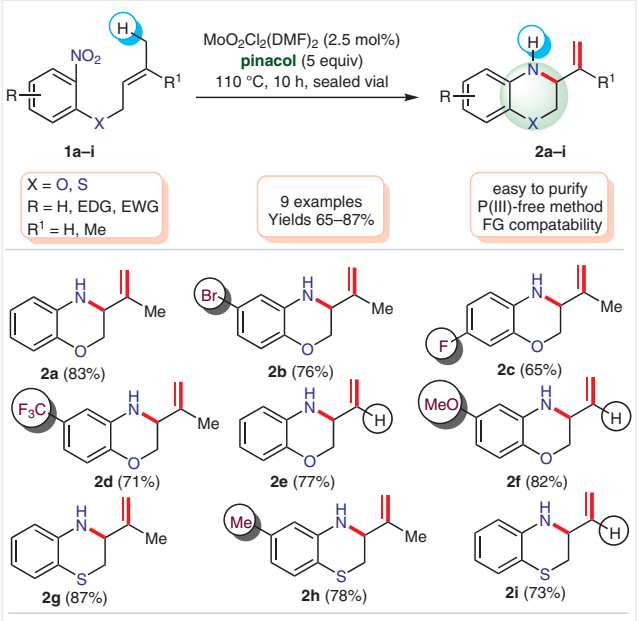
Entry	Catalyst (mol%)	Reagents (equiv)	Conditions	Yield **2a** (%)[b]
1	$MoO_2Cl_2(DMF)_2$ (10)	pinacol (2.5)	PhMe, 110 °C, 15 h	64
2	$MoO_2Cl_2(DMF)_2$ (10)	pinacol (2.0)	PhMe, 110 °C, 15 h	59
3	$MoO_2Cl_2(DMF)_2$ (10)	ascorbic acid (2.0)	PhMe, 110 °C, 12 h	7[c]
4	$MoO_2Cl_2(DMF)_2$ (10)	HFIP (5.0)	PhMe, 110 °C, 16 h	23
5	$MoO_2Cl_2(DMF)_2$ (10)	^{i}PrOH (5.0)	PhMe, 120 °C, 18 h	15
6	$MoO_2Cl_2(DMF)_2$ (10)	Et_3SiH (5.0)	PhMe, 90 °C, 15 h	36
7	$MoO_2Cl_2(DMF)_2$ (5)	pinacol (2.0)	PhMe, 110 °C, 16 h	61
8	$MoO_2Cl_2(DMF)_2$ (2.5)	pinacol (2.0)	PhMe, 110 °C, 12 h	57

Table 1 (continued)

Entry	Catalyst (mol%)	Reagents (equiv)	Conditions	Yield **2a** (%)[b]
9	$MoO_2Cl_2(DMF)_2$ (1.5)	pinacol (2.0)	PhMe, 110 °C, 15 h	29
10	$MoO_2Cl_2(DMF)_2$ (0.5)	pinacol (2.0)	PhMe, 110 °C, 15 h	12
11	–	pinacol (2.0)	PhMe, 110 °C, 20 h	0[c]
12	$MoO_2Cl_2(DMF)_2$ (2.5)	pinacol (2.0)	C_6H_6, 110 °C, 15 h	55
13	$MoO_2Cl_2(DMF)_2$ (2.5)	pinacol (2.0)	*o*-xylene, 130 °C, 15 h	73
14	$MoO_2Cl_2(DMF)_2$ (2.5)	–	PhMe, 110 °C, 16 h	9[c]
15	$MoO_2Cl_2(DMF)_2$ (2.5)	pinacol (2.0)	MeCN, 110 °C, 15 h	41
16	$MoO_2Cl_2(DMF)_2$ (2.5)	pinacol (2.0)	1,4-dioxane, 140 °C, 15 h	68
17	$MoO_2Cl_2(DMF)_2$ (2.5)	pinacol (2.0)	DCE, 110 °C, 15 h	17
18	$MoO_2Cl_2(DMF)_2$ (2.5)	pinacol (2.0)	DME, 110 °C, 15 h	45
19	MoO_2Cl_2 (2.5)	pinacol (2.0)	PhMe, 110 °C, 15 h	45
20	$MoO_2Cl_2(DMF)_2$ (2.5)	pinacol (5.0)	110 °C, 15 h	82[d]
21	$MoO_2Cl_2(DMF)_2$ (2.5)	pinacol (5.0)	110 °C, 10 h	83[d]
22	$MoO_2Cl_2(DMF)_2$ (2.5)	pinacol (5.0)	110 °C, 7 h	65[d]

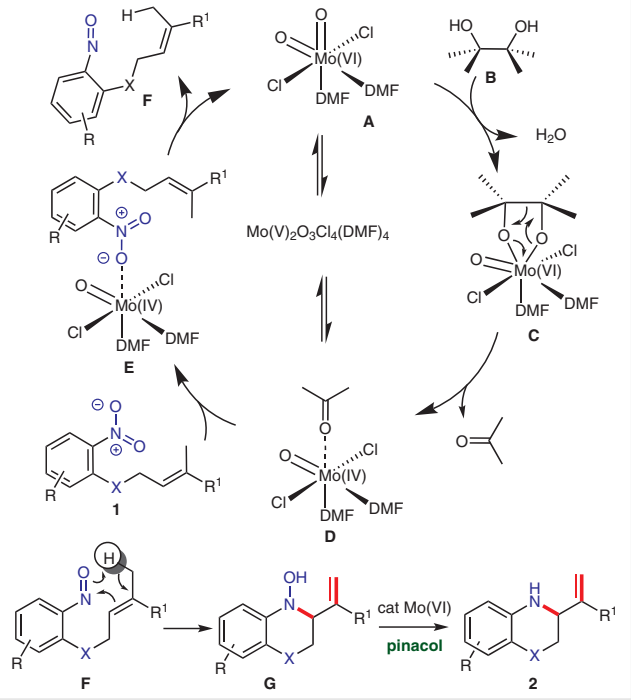
[a] Unless otherwise noted, all reactions were performed using **1a** (1.0 mmol) in solvent (2 mL) in a sealed vial.
[b] Isolated yield.
[c] Unreacted starting material **1a** was recovered.
[d] Reactions were performed in neat condition.

When the optimized conditions were employed on a variety of ω-nitroalkenes **1a–i** (Scheme 2), it was found that both 2-nitroaryl ethers **1a–f** and 2-nitroaryl thioethers **1g–i** containing electron-withdrawing groups such as bromo, fluoro, and trifluoromethyl and the electron-donating groups such as methoxy and methyl on the arene-moiety were well tolerated, furnishing the desired 1,4-benzoxazines **2a–f** and 1,4-benzothiazines **2g–i** in high yields ranging from 65 to 87%. It is noteworthy that slightly decreased yields of **2** were obtained with the substrates having electron-withdrawing groups on the aromatic ring compared with nonsubstituted or electron-rich arenes. The reaction also proceeded successfully when the alkene was functionalized with a methyl group. Moreover, the feasibility of this protocol has been demonstrated for the gram-scale synthesis of **2g**. Thus, 5.82 mmol (1.3 g) of 2-nitroaryl thioether **1g** reacted under the optimized conditions to afford the corresponding cyclized product **2g** in 67% yield (3.9 mmol 746 mg).

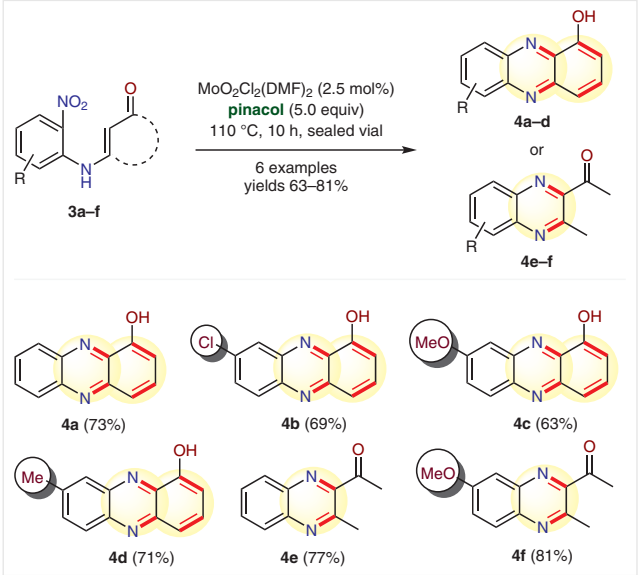


Scheme 2 Scope of the developed $MoO_2Cl_2(DMF)_2$-catalyzed domino approach for the synthesis of 1,4-benzoxazines **2a–f** and 1,4-benzothiazines **2g–i**. All reactions were performed using 1.0 mmol **1a–i** under solvent-free conditions in sealed vial. Isolated yields are given.

Based on previous reports,[13] a mechanistic proposal is shown in Scheme 3. In the first step, formation of the MoO(pinacolate)$Cl_2(DMF)_2$ complex **C** can be realized by the reaction between Mo(VI)-complex **A** and pinacol **B** on loss of a water molecule. Oxidative cleavage of the pinacolate ligands in complex **C** then delivers oxomolybdenum(IV) species **D**, having a weakly coordinated acetone molecule that could be replaced by the oxygen-atom from ω-nitroalkenes **1** to form the unstable Mo(IV)-species **E**. Next, cleavage of nitroso-aromatic **F** from the Mo(IV)-species **E** regenerates the active Mo(VI)-catalyst **A**. The derived intermediate nitroso-aromatic **F** may undergo the nitroso-ene reaction to obtain the N-hydroxy compounds **G** which, on further deoxygenation, would release the final product **2**.



Scheme 3 Plausible mechanism for the Mo(VI)-catalyzed reductive cyclization using pinacol as a deoxygenating agent



Scheme 4 Synthesis of 1-hydroxyphenazines and quinoxalines using $MoO_2Cl_2(DMF)_2$-catalyzed domino approach in the presence of pinacol as reducing agents. All reactions were performed using **3a–f** (1.0 mmol) under solvent-free conditions in sealed vial. Isolated yields are given.

To demonstrate further applications of this protocol, it was found that cyclic β-(*N*-2-nitroaryl)-α,β-unsaturated ketones **3a–d** can be employed under the optimized conditions to obtain 1-hydroxyphenazines **4a–d** (Scheme 4). Cyclic β-(*N*-2-nitroaryl)-α,β-unsaturated ketones having chloro, methoxy and methyl residues on the aromatic rings were well tolerated under the reaction conditions, delivering the desired 1-hydroxyphenazines **4a–d** in yields ranging from 63 to 73%. Furthermore, the protocol is not restricted to the synthesis of 1-hydroxyphenazines, but can be extended to the synthesis of quinoxaline derivatives. In this regard, acyclic β-(*N*-2-nitroaryl)-α,β-unsaturated ketones reacted under the optimized reaction conditions to obtain quinoxalines **4e–f** in yields ranging from 77 to 81% (Scheme 4). It is important to mention that only a limited number of methods are available for the synthesis of 1-hydroxyphenazines[7f,17] including our previous report (Scheme 1),[12d] in which the reaction was carried out using catalytic Mo(VI) and Ph_3P as deoxygenating agent. On the other hand, Söderberg and co-workers have described an approach towards the synthesis of the same scaffold using the Pd-catalyzed reductive cyclization of acyclic β-(*N*-2-nitroaryl)-α,β-unsaturated ketones in the presence of CO as deoxygenating agent (Scheme 1).[7f] Considering the advantages of the present method including low loading of inexpensive catalyst and the use of pinacol as deoxygenation reagent, this new protocol should find extensive application.

To summarize, we have demonstrated a domino reductive cyclization approach towards the synthesis of a broad spectrum of N-heterocycles in the presence of low loadings of Mo(VI) complex as catalyst and pinacol as a readily available and inexpensive deoxygenating agent. The reactions are executed under aerobic and solvent-free conditions to furnish high isolated yields of the desired compounds with the formation of acetone and water as side products allowing for easy purification.

All starting materials were purchased from commercial suppliers (Sigma–Aldrich, Alfa–Aesar, SD fine chemicals, Merck, HI Media) and were used without further purification unless otherwise indicated. All reactions were carried out in oven-dried glassware with magnetic stirring in a sealed vial. Solvents used in extraction and purification were distilled prior to use. Thin-layer chromatography (TLC) was performed on TLC plates purchased from Merck. Compounds were visualized with UV light (λ = 254 nm) and/or by immersion in $KMnO_4$ solution followed by heating. Products were purified by flash column chromatography on silica gel, 230–400 mesh. IR spectra were measured with a Perkin–Elmer Spectrum One FT-IR spectrometer. ^1H (^{13}C) NMR spectra were recorded at 300 (75.4) MHz with a Brucker spectrometer using $CDCl_3$ as a solvent. Chemical shifts were referenced to residual solvent signals at $\delta_{H/C}$ = 7.26 /77.28 ppm ($CDCl_3$) relative to TMS as internal standards. Coupling constants *J* [Hz] were directly taken from the spectra and are not averaged. Splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad).

Synthesis of Compounds 2a–i and 4a–f; General Procedure

A 10 mL vial was charged with a mixture of **1a–i** or **3a–f** (1.0 mmol), $MoO_2Cl_2(dmf)_2$ (0.025 mmol) and pinacol (5.0 mmol). The vial was then sealed and heated to 110 °C for 10 h. After completion of the reaction (progress was monitored by TLC; SiO_2, hexane/EtOAc = 20:1 for **2a–i** and hexane/EtOAc = 4:1 for **4a–f**), the mixture was diluted with hot EtOAc (15 mL) and water (25 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine (3 × 10 mL) and dried over anhydrous Na_2SO_4. After filtration, solvent was removed under reduced pressure and the remaining residue was purified by column chromatography over silica gel using hexane/EtOAc = 20:1 for **2a–i** and hexane/EtOAc = 4:1 for **4a–f** as an eluent to obtain the desired product **2a–i** and **4a–f** in high yields.

3-Isopropenyl-3,4-dihydro-2*H*-benzo[1,4]oxazine (2a)

Yield: 83%; pale-yellow oil; R_f = 0.56 (SiO_2, hexane/EtOAc = 20:1).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.85 (s, 3 H, 3′-H_3), 3.97 (overlapped, 1 H, 3-H), 3.95 (dd, ^3J = 7.6 Hz, ^2J = 16.8 Hz, 1 H, 2-H), 4.33 (dd, ^3J = 8.2 Hz, ^2J = 16.4 Hz, 1 H, 2-H), 5.06 (brs, 1 H, 2′-H), 5.17 (brs, 1 H, 2′-H), 6.71, 6.73, 6.81, 6.84 (overlapped, 4 H, 5-H, 6-H, 7-H, 8-H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.83 (C-3′), 55.38 (C-3), 68.75 (C-2), 113.61 (C-2′), 115.89 (C-5), 116.82 (C-8), 119.48 (C-7), 121.71 (C-6), 133.43 (C-10), 142.82 (C-1′), 143.95 (C-9).

6-Bromo-3-(prop-1-en-2-yl)-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazine (2b)[9f]

Yield: 76%; pale-yellow oil; R_f = 0.56 (SiO_2, hexane/EtOAc = 20:1); LCMS purity 99.3%.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.80 (s, 3 H, 3′-H_3), 3.89 (overlapped, 2 H, 2-H), 4.22 (m, 1 H, 3-H), 5.01 (s, 1 H, 2′-H), 5.1 (s, 1 H, 2′-H), 6.64 (d, ^3J = 8.1 Hz,1 H, 8-H), 6.71–6.74 (m, 2 H, 5-H and 7-H).

7-Fluoro-3-(prop-1-en-2-yl)-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazine (2c)[9f]

Yield: 65%; pale-yellow oil; R_f = 0.57 (SiO_2, hexane/EtOAc = 20:1).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.81 (s, 3 H, 3′-H_3), 3.83–3.93 (m, 2 H, 2-H), 4.22–4.26 (m, 1 H, 3-H), 5.01 (s, 1 H, 2′-H), 5.10 (s, 1 H, 2′-H), 6.47–6.56 (m, 3 H, 5-H, 6-H and 8-H).

3-(Prop-1-en-2-yl)-6-(trifluoromethyl)-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazine (2d)[9f]

Yield: 71%; pale-yellow oil; R_f = 0.58 (SiO_2, hexane/EtOAc = 20:1); LCMS purity 99.7%.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.82 (s, 3 H, 3′-H_3), 3.89–3.96 (m, 2 H, 2-H), 4.27–4.29 (m, 1 H, 3-H), 5.03 (s, 1 H, 2′-H), 5.09 (s, 1 H, 2′-H), 6.82–6.90 (m, 3 H, 5-H, 7-H and 8-H).

3-Vinyl-3,4-dihydro-2*H*-benzo[1,4]oxazine (2e)[9f]

Yield: 77%; pale-yellow oil; R_f = 0.45 (SiO_2, hexane/EtOAc = 20:1).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.8 (overlapped, 1 H, 2-H), 4.07 (overlapped, 1 H, 3-H), 4.28 (dd, ^3J = 9.8 Hz, 1 H, 2-H), 5.31 (brd, ^3J = 10.3 Hz, 1 H, 2′-H), 5.45 (brd, ^2J = 17.2 Hz, 1 H, 2′-H), 5.91 (m, 1 H, 1′-H), 6.67 (dd, ^3J = 7.7 Hz, 1 H, 8-H), 6.73 (dd, ^3J = 7.7 Hz, ^4J = 1.5 Hz, 1 H, 7-H), 6.76–6.85 (overlapped, 2 H, 5-H and 6-H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 52.22 (C-3), 69.14 (C-2), 115.75 (C-8), 116.86 (C-5), 118.23 (C-2′), 119.24 (C-7), 121.69 (C-6), 133.18 (C-10), 135.63 (C-1′), 143.79 (C-9).

6-Methoxy-3-vinyl-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazine (2f)[9f]

Yield: 82%; pale-yellow oil; R_f = 0.46 (SiO_2, hexane/EtOAc = 20:1); LCMS purity 98.7%.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.76 (s, 3 H, 11-H), 3.82–3.87 (m, 1 H, 2-H), 3.94–3.96 (m, 1 H, 3-H), 4.15–4.19 (m, 1 H, 2-H), 5.25 (d, ^3J = 16.1 Hz, 1 H, 2′-H), 5.37 (d, ^2J = 17.2 Hz, 1 H, 2′-H), 5.78–5.87 (m, 1 H, 1′-H), 6.20–6.23 (m, 2 H, 5-H and 7-H), 6.70 (d, ^3J = 8.2 Hz, 1 H, 8 H).

3-Isopropenyl-3,4-dihydro-2*H*-benzo[1,4]thiazine (2g)[9f,12a]

Yield: 87%; light-yellow oil; R_f = 0.56 (SiO_2, hexane/EtOAc = 20:1).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.85 (s, 3 H, 3′-H_3), 2.97 (dd, ^3J = 3.9 Hz, ^2J = 12.5 Hz, 1 H, 2-H), 3.00 (dd, ^3J = 7.3 Hz, ^2J = 12.5 Hz, 1 H, 2-H), 4.06 (brdd, ^3J = 3.9 Hz, ^3J = 7.2 Hz, 1 H, 3-H), 5.05 (brs, 1 H, 2′-H), 5.14 (brs, 1 H, 2′-H), 6.52 (dd, ^3J = 8.0 Hz, ^2J = 1.3 Hz, 1 H, 5-H), 6.65 (ddd, ^3J = 7.5 Hz, ^3J = 7.5 Hz, ^2J = 1.3 Hz, 1 H, 7-H), 6.91 (ddt, ^3J = 7.3 Hz, ^3J = 8.0 Hz, ^2J = 1.6 Hz, 1 H, 6-H), 7.03 (dd, ^3J = 7.8 Hz, ^2J = 1.5 Hz, 1 H, 8-H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.24 (C-3′), 30.17 (C-2), 57.18 (C-3), 112.93 (C-2′), 115.63 (C-5), 115.89 (C-9), 118.53 (C-7), 125.95 (C-6), 127.72 (C-8), 142.06 (C-10), 145.79 (C-1′).

MS (EI, 70 eV): *m*/*z* (%) = 191.1 (100) [M$^+$], 163.1 (18), 150.1 (46), 117.1 (21), 109.0 (11), 65 (5).

3-Isopropenyl-6-methyl-3,4-dihydro-2*H*-benzo[1,4]thiazine (2h)[9f,12a]

Yield: 78%; pale-yellow oil; R_f = 0.58 (SiO_2, hexane/EtOAc = 20:1).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.83 (s, 3 H, 3′-H_3), 2.23 (s, 3 H, 11-H_3), 2.97–2.99 (overlapped, 2 H, 2-H_2), 4.06 (brdd, ^3J = 3.9 Hz, ^3J = 7.2 Hz, 1 H, 3-H), 5.04 (brs, 1 H, 2′-H), 5.07 (brs, 1 H, 2′-H), 6.37 (s, 1 H, 5-H), 6.48 (ddd, ^3J = 7.5 Hz, ^3J = 7.6 Hz, ^4J = 1.2 Hz, 1 H, 7-H), 6.03 (dd, ^3J = 7.6 Hz, ^4J = 1.4 Hz, 1 H, 8-H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.93 (C-3′), 21.03 (C-11), 30.05 (C-2), 57.16 (C-3), 112.08 (C-2′), 112.53 (C-5), 115.84 (C-9), 119.14 (C-7), 127.43 (C-6), 135.57 (C-8), 141.75 (C-10), 145.83 (C-1′).

MS (EI, 70 eV): *m*/*z* (%) = 205.1 (100) [M$^+$], 206.1 (20), 190.1 (24), 177.1 (16), 164.1 (40), 158.1 (9), 131.1 (2), 44 (2).

3-Vinyl-3,4-dihydro-2*H*-benzo[1,4]thiazine (2i)[9f,12a]

Yield: 73%; pale-yellow oil; R_f = 0.44 (SiO_2, hexane/EtOAc = 20:1).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.97 (overlapped, ^3J = 11.2 Hz, 2 H, 2-H), 4.12 (overlapped, 1 H, 3-H), 5.21 (d, ^3J = 10.5 Hz, 1 H, 2′-H), 5.34 (d, ^2J = 17.1 Hz, 1 H, 2′-H), 5.88 (m, 1 H, 1′-H), 6.49 (d, ^3J = 8.1 Hz, 1 H, 5-H), 6.62 (td, ^3J = 6.3 Hz, ^4J = 1.3 Hz, 1 H, 7-H), 6.93 (td, ^3J = 11.7 Hz, ^4J = 1.2 Hz, 1 H, 6-H), 7.05 (dd, ^3J = 10.5 Hz, 1 H, 8-H).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 30.93 (C-2), 54.36 (C-3), 115.71 (C-5, C-2′ overlapped), 117.21 (C-9), 118.63 (C-7), 125.91 (C-6), 127.76 (C-8), 138.94 (C-1′), 141.83 (C-10).

MS (EI, 70 eV): *m*/*z* (%) = 177 (100) [M$^+$], 162.1 (82), 149.1 (66), 144.1 (31), 130.10 (17),117.1 (9), 109 (4).

1-Hydroxyphenazine (4a)[12d]

Yield: 73%; yellow solid; R_f = 0.30 (SiO_2, hexane/EtOAc = 4:1); mp 157–159 °C (Lit.[7f] 153–155 °C).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.77–7.88 (m, 4 H, 5-H, 6-H, 7-H and 8-H), 8.21–8.29 (m, 3 H, 2-H, 3-H and 4-H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 109.11 (C-2), 120.21 (C-3), 129.46 (C-6), 129.989 (C-7), 130.75 (C-8), 131.03 (C-5), 132.09 (C-4), 134.51 (C-1), 141.2 (C-11), 144.1 (C-13), 144.3 (C-14), 151.8 (C-12).

MS (GC-MS): *m*/*z* (%) = 197 (12) [M + 1]$^+$, 196 (100) [M$^+$], 168 (88), 140 (8), 114 (5), 102 (5), 77 (12) [C_6H_5]$^+$.

7-Chloro-1-hydroxyphenazine (4b)[12d]

Yield: 69%; yellow solid; R_f = 0.29 (SiO_2, hexane/EtOAc = 4:1); mp 181–183 °C.

IR (ATR): 2159 (m; O-H), 1511 (m; alkane C-H), 1480 (m), 1400 (m), 1174 (s), 1120 (m), 1095 (m), 830 (m; arom. C-H), 760 cm^{-1} (s).

UV/Vis (CH_3CN): λ_{max} (log ε) = 207 (3.51), 265 (3.76), 373 nm (2.69).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.25 (overlapped, 1 H, 2-H), 7.76–7.80 (m, 3 H, 3-H, 4-H and 5-H), 8.1 (s, 1 H, 6-H), 8.22 (overlapped, 2 H, 8-H and OH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 109.63 (C-2), 120.03 (C-3), 127.54 (C-6), 130.99 (C-8), 132.13 (C-5), 132.16 (C-4), 134.89 (C-1), 136.59 (C-7), 141.01 (C-11), 142.57 (C-13), 143.76 (C-14), 151.57 (C-12).

MS (EI, 70 eV): *m*/*z* (%) = 232 (14) [M+2]$^+$, 230 (39) [M$^+$], 202 (20) [$C_{11}H_7ClN_2$]$^+$, 167 (12) [$C_{11}H_7N_2$]$^+$, 149 (9), 114 (19), 97 (9).

HRMS (EI, M$^+$): *m*/*z* calcd for $C_{12}H_7OClN_2$: 230.0247; found: 230.0207.

7-Methoxy-1-hydroxyphenazine (4c)[12d]

Yield: 63%; yellow solid; R_f = 0.27 (SiO_2, hexane/EtOAc = 4:1); mp 179–182 °C.

IR (ATR): 2922 (w; CH_3), 1615 (m), 1485 (s; alkane C-H), 1212 (s), 1024 (m), 874 (m), 808 (s), 740 cm^{-1} (m)

UV/Vis (CH_3CN): λ_{max} (log ε) = 212 (3.68), 265 (4.0), 377 nm (3.17).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.03 (s, 3 H, 15-H_3), 7.17 (dd, ^3J (5-H, 6-H) = 5.1 Hz, ^4J (6-H, 8-H) = 1.5 Hz, 1 H, 6-H), 7.49 (overlapped, 2 H, 2-H and 3-H), 7.68–7.77 (m, 2 H, 4-H and 5-H), 8.10 (overlapped, 2 H, 8-H and OH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.98 (C-15), 104.58 (C-8), 108.02 (C-2), 119.09 (C-3), 126.36 (C-6), 130.0 (C-5), 130.18 (C-4), 131.03 (C-1), 132.91 (C-11), 138.39 (C-13), 146.3 (C-14), 151.92 (C-12), 161.6 (C-7).

MS (EI, 70 eV): *m*/*z* (%) = 227 (14) [M + 1]$^+$, 226 (100) [M$^+$], 198 (28) [M–CO]$^+$, 183 (19) [$C_{11}H_7N_2O$]$^+$, 155 (22), 114 (18), 72 (20), 59 (28).

HRMS (EI, M$^+$): *m*/*z* calcd for $C_{13}H_{10}N_2O_2$: 226.0743; found: 226.0736.

7-Methyl-1-hydroxyphenazine (4d)[12d]

Yield: 71%; yellow solid; R_f = 0.28 (SiO_2, hexane/EtOAc = 4:1); mp = 163–166 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.67 (s, 3 H, 15-H_3), 7.22 (overlapped, 1 H, 2-H), 7.66–7.76 (m, 3 H, 3-H, 4-H and 5-H), 7.99 (d, ^3J (5-H, 6-H) = 9.3 Hz, 1 H, 6-H), 8.15 (overlapped, 2 H, 8-H and OH).

1-(3-Methylquinoxalin-2-yl)ethanone (4e)[12d]

Yield: 77%; colorless solid; R_f = 0.46 (SiO_2, hexane/EtOAc = 4:1); mp 80–82 °C (Lit.[17a] 79–81 °C).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.83 (s, 3 H, 13-H_3), 2.96 (s, 3 H, 12-H_3), 7.72–7.85 (m, 2 H, 6-H and 7-H), 8.02 (d, ^3J (5-H, 6-H) = 8.1 Hz, 1 H, 5-H), 8.09 (dd, ^3J (7-H, 8-H) = 8.1 Hz, ^4J (6-H, 8-H) = 1.2 Hz, 1 H, 8-H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.69 (C-13), 28.05 (C-12), 128.68 (C-5), 129.82 (C-6), 130.09 (C-7), 132.24 (C-8), 140.03 (C-10), 143.1 (C-9), 147.8 (C-3), 153.72 (C-2), 201.9 (C-11).

1-(7-Methoxy-3-methylquinoxalin-2-yl)ethanone (4f)[12d]

Yield: 81%; colorless solid; R_f = 0.43 (SiO_2, hexane/EtOAc = 4:1); mp 87–90 °C.

IR (ATR): 3140 (w; CH_3), 1693 (s; C=O), 1616 (m; alkane C-H), 1491 (m), 1411 (m), 1362 (m; alkane C-H), 1316 (m; alkane C-H), 1216 (s), 1126 (m), 1059 (m), 1027 (m), 937 (m; arom. C-H), 845 cm^{-1} (s; arom. C-H).

UV/Vis (CH_3CN): λ_{max} (log ε) = 219 (3.64), 251 (3.75), 357 nm (2.82).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.83 (s, 3 H, 13-H_3), 2.92 (s, 3 H, 12-H_3), 3.99 (s, 3 H, 14-H_3), 7.36 (d, ^4J (6-H, 8-H) = 2.7 Hz, 1 H, 8-H), 7.48 (dd, ^3J (5-H, 6-H) = 6.6 Hz, ^4J (6-H, 8-H) = 2.4 Hz, 1 H, 6-H), 7.92 (d, ^3J (5-H, 6-H) = 9.3 Hz, 1 H, 5-H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.01 (C-13), 27.85 (C-12), 55.85 (C-14), 106.67 (C-8), 125.51 (C-5), 129.31 (C-6), 138.99 (C-10), 141.36 (C-9), 147.06 (C-3), 150.37 (C-2), 160.47 (C-7), 201.55 (C-11).

MS (EI, 70 eV): *m*/*z* (%) = 217 (12) [M + 1]$^+$, 216 (100) [M$^+$], 188 (44) [$C_{11}H_{12}N_2O$]$^+$, 173 (82), 159 (30), 130 (10), 117 (14), 89 (9), 77 (9) [C_6H_5]$^+$, 63 (14).

HRMS (EI, M$^+$): *m*/*z* calcd for $C_{12}H_{12}N_2O_2$: 216.0898; found: 216.0898.

Funding Information

C.C.M. acknowledges Science and Engineering Research Board (SERB), New Delhi and NIT Manipur for the financial support in the form of research grant (ECR/2016/000337). R.G., N.V., D.K. and A.K.K. are grateful to the Ministry of Human Resource and Development (MHRD), New Delhi for Fellowship support.

Acknowledgment

We acknowledge Mr. M. Wolf (Institut für Chemie, Universität Hohenheim) and the central instrumental facilities at the Indian Institute of Technology, Guwahati for recording NMR and Mass spectra. We sincerely thank Professors T. Punniyamurthy, V. Satheesh and R. Bag from Department of Chemistry, Indian Institute of Technology, Guwahati for sample analysis and research support.

Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0036-1591572.

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