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ARTICLE

Unravelling 2-aminoquinazolin-4(*3H*)-one as an organocatalyst for the chemoselective reduction of nitroarenes

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A novel, mild and transition metal free, 2-aminoquinazolin-4(*3H*)-one assisted reduction of nitroarenes employing hydrazine hydrate as reducing agent and potassium carbonate as a base is reported. Activation of hydrazine hydrate with organocatalyst was first time explored for the reduction reactions. 2-Aminoquinazolin-4(*3H*)-one and its derivatives were first time investigated as hydrogen bonding organocatalyst for the reduction of nitroarenes to anilines. Sensitive functional groups such as sulphonamide, carboxyl, amide and aryl halides were well tolerated in this green methodology with scalability and high chemoselectivity.

Introduction

Hydrogen bond donor and acceptor molecules have emerged as powerful tool in sustainable organic synthesis, which led to selective organocatalysis enabling new approaches.[1] Distinct hydrogen bond donor motifs associated with complementary functional or structural frameworks offer promising interfaces with other molecules.[2] Therefore, these are known to catalyze an array of various cross-coupling reactions with high chemoselectivity and broad substrate scope.[3] Thioureas,[4a,4b] squaramides,[4c,4d,4e] 2-aminobenzimidazoles,[4f,4g] 2-aminopyridinium salts[4h] and silanediols[4i,4j] type motifs have been introduced to date as hydrogen bond (H-B) catalyst. So, numerous endeavors were ongoing towards the design and synthesis of new H-B organocatalyst. In this frame, inspired from selective hydrogen bond mechanism of guanine with cytosine in DNA (Fig. 1a),[5a] Suez *et al.* in 2011 disclosed the H-bond interaction properties of 2-aminoquinazolin-4(*3H*)-ones with various organic molecules (Fig. 1b and 1c) and used as H-bond organocatalyst in Michael addition reactions.[5a] Similarly, Kobayashi *et al.* described benzothiadiazine catalyzed epoxidation of *α,β*-unsaturated amides for the synthesis of chiral 2-oxiranecarboxamides through H-B interactions.[5b] Moreover, Takemoto group also reported the enantioselective hydrazination of *β*-keto esters facilitated by H-B donor sites of 2-aminoquinazolin-4-one.[5c]

Above reports splashed that 2-aminoquinazolin-4(*3H*)-one have hydrogen bond donor (D) as well as acceptor (A) sites along with Lewis basic site those are capable of interacting with the diverse class of molecules (Fig 2). These ADDA or DADA hydrogen bonding sites enforce us to explore its potential as an organocatalyst in transfer hydrogenation reactions (Fig. 2).

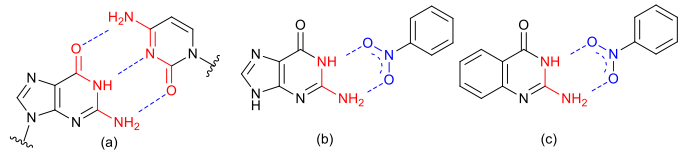

Fig. 1 (a) H-Bond interactions between guanine and cytosine in DNA.[5a] (b) Hypothetical interactions of guanine with nitrobenzene.[5a] (c) Hypothetical interactions of 2-aminoquinazolin-4(*3H*)-one with nitrobenzene.

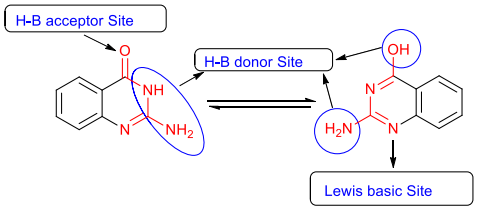

Fig. 2 Various catalytic sites on 2-aminoquinazolin-4(*3H*)-one

Moreover, we have been working for the development of approaches for the reduction of nitroarenes and recently reported a reduction reaction of nitroarenes using vasicine, a quinazoline alkaloid, as an organocatalyst.[6a] However, this reaction required prolonged reaction time, high catalyst loading and elevated temperature. Therefore to overcome these limitations, we continue our studies further and envisioned to investigate the application of selected quinazolin-4(*3H*)-one molecules, synthesized earlier,[6b] as an organocatalyst in the reduction of nitroarenes to anilines (Fig.

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3). Anilines are present in a broad range of natural products, pharmaceuticals, dyes, agrochemicals and photographic materials.[7] Owing to their immense importance, numerous metal catalyzed methodologies have been reported for the reduction of nitroarenes using variety of reducing agents such as sodium borohydride,[8] hydrosilane,[9] hydrazine derivatives[10] and formates.[11] However, most of these methods demands harsh reaction conditions, non-ecofriendly solvents, utilized relatively expensive and toxic metal catalyst.[12]

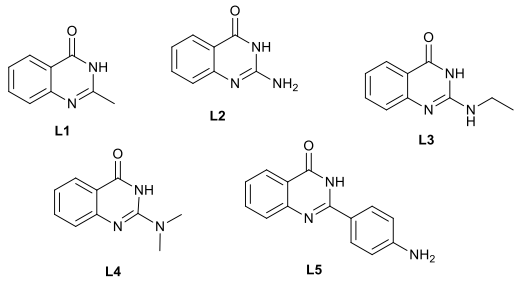


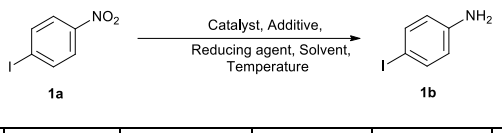
Fig. 3 Variety of quinazolin-4(*3H*)-one derivative synthesized[6b].

Therefore, development of sustainable and greener method for the reduction of nitroarenes to anilines is highly desirable. Accordingly, few transition metal free reports are demonstrated to date using 9,10-dihydroanthracene,[13a] (2-pyridyl)phenylmethanol,[13b] graphene oxide,[13e] fullerenes,[13d] 1,4-dihydropyridines,[13c] mesoporous carbon[13f] and glucose[13g] as catalyst. Herein, we report pristine 2-aminoquinazolin-4(*3H*)-one catalyzed reduction of aromatic nitro compounds utilizing hydrazine hydrate as reducing agent in methanol. Notably, hydrazine hydrate is stable, safe and convenient to handle as compared to its anhydrous form.[10a] Moreover, the by-product of hydrazine hydrate is non-toxic N_2 gas which makes it a suitable and safe reducing agent.[10a] Also, this protocol employed methanol as a non-toxic and easily available solvent.[12a]

Results and discussion

For the optimization of reaction conditions, 4-iodonitrobenzene (**1a**) was chosen as model substrate. Initially, various quinazolin-4(*3H*)-one derivatives (Fig. **3**) were screened for the reduction of **1a** in the presence of 4 equivalents of hydrazine hydrate in methanol. It was observed that **L2** afforded relatively higher yield than **L1**, **L3**, **L4** and **L5** (Table 1, entries **1-5**). It might be due to less steric hindrance and effective H-bond interactions in case of **L2**. To enhance the yield, various additives such as K_2CO_3, Na_2CO_3, NaCl, KCl were tested (Table 1, entries **6-9**). Among them, K_2CO_3 showed a significant increase in the yield of the desired product (Table 1, entries **6**). In addition, investigations were extended for the activity of different reducing agents and only hydrazine hydrate afforded the optimum yield of desired product (Table 1, entries **6** and **10-12**). Moreover, significant variations in the yield of desired product were monitored with changing the quantity of hydrazine hydrate. Decrease in yield was observed when quantity of reducing agent was decreased from 6 to 4 equivalents while slight increase in yield was observed on increasing the quantity from 6 to 8 equivalents (Table 1, entries **6, 13** and **14**). 6 Equivalents of hydrazine hydrate was found optimum for this reaction (Table 1, entries **14**).

Table 1 Optimization of reaction conditions



Entry	Catalyst	Reducing source	Additive	Solvent	Yield[b]
1	**L1**	$N_2H_4.H_2O$	-	CH_3OH	16
2	**L2**	$N_2H_4.H_2O$	-	CH_3OH	34
3	**L3**	$N_2H_4.H_2O$	-	CH_3OH	27
4	**L4**	$N_2H_4.H_2O$	-	CH_3OH	19
5	**L5**	$N_2H_4.H_2O$	-	CH_3OH	13
6	**L2**	**$N_2H_4.H_2O$**	**K_2CO_3**	**CH_3OH**	**78**
7	**L2**	$N_2H_4.H_2O$	Na_2CO_3	CH_3OH	21
8	**L2**	$N_2H_4.H_2O$	KCl	CH_3OH	22
9	**L2**	$N_2H_4.H_2O$	NaCl	CH_3OH	24
10	**L2**	HCOOH	K_2CO_3	CH_3OH	N.R.
11	**L2**	$PhSiH_3$	K_2CO_3	CH_3OH	N.R.
12	**L2**	PMHS	K_2CO_3	CH_3OH	N.R.
13	**L2**	$N_2H_4.H_2O$	K_2CO_3	CH_3OH	80[c]
14	**L2**	$N_2H_4.H_2O$	K_2CO_3	CH_3OH	60[d]
15	-	$N_2H_4.H_2O$	K_2CO_3	CH_3OH	51

[a]Reaction conditions: 4-Iodonitrobenzene (0.1mmol), catalyst (10 mol%), reducing agent (6 equiv.), additive (1 equiv.), solvent (2 mL) at 100 °C for 5h. [b]Isolated yield. [c]8 equiv. hydrazine hydrate. [d]4 equiv. hydrazine hydrate.

In the absence of catalyst, 51% of the desired product was observed (Table 1, entry **15**). Comparative observation in the yield are shown by NMR titration in figure 4 and figure 5.

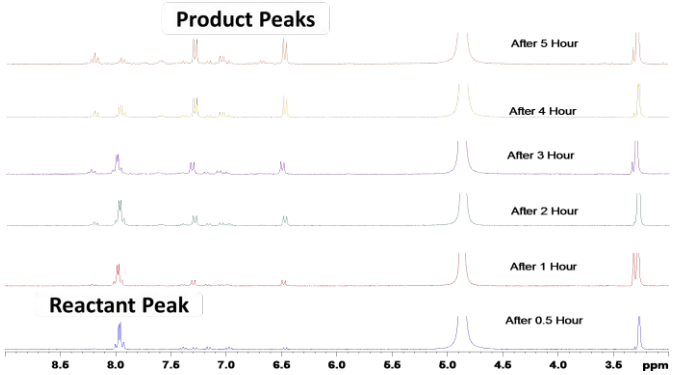


Fig. 4 Reaction observation by NMR in the presence of catalyst

Subsequently, the effect of solvent was checked and it was observed that reaction proceeded efficiently in protic solvents and highest yield was found in methanol (SI Table 1, entries **8** and **20-25**). However, no reaction was observed in polar aprotic solvents and non-polar solvents (SI Table 1, entries **22-25**). Also, variation in yield was observed with temperature and at 100 °C highest yield of desired product was observed (SI Table 1, entries **8, 26** and **27**).

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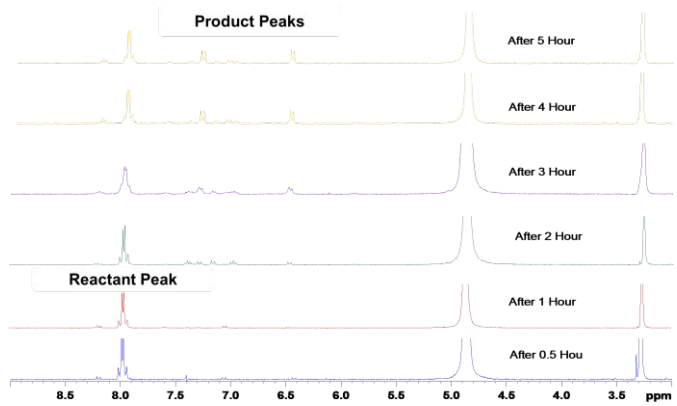
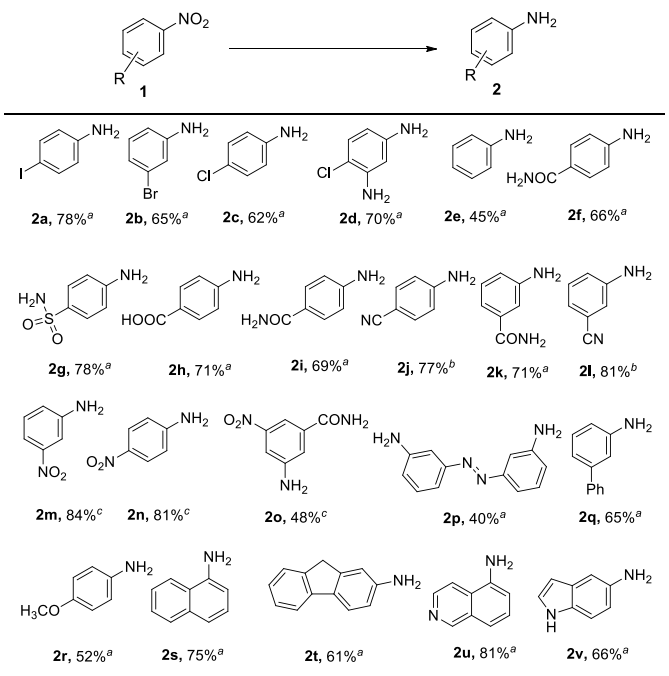


Fig.5 Reaction observation by NMR in the absence of catalyst

After the optimization of reaction conditions, the feasibility of the developed method (Table 1, entry **6**) was assessed for the reduction of nitroarenes and hetero-nitroarenes. First, halogen substituted nitroarenes were reduced to corresponding haloanilines in good yield (Table 2, **2a-2d**). Previously, dehalogenated products of halonitroarenes were reported using different approaches such as catalytic hydrogenation, $Pd(OAc)_2$/PMHS and S_8/mild.[14]

Table 2 Substrate scope

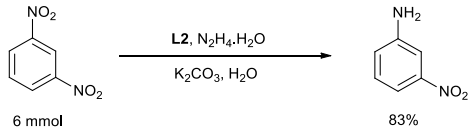


[a]Reaction conditions: nitroarene (0.5 mmol), 2-aminoquinazolin-4(*3H*)-one (**L2,** 10 mol%), $N_2H_4.2H_2O$ (6 equiv.), K_2CO_3 (1 equiv.), CH_3OH (3 mL) at 100 °C. [b]Reaction carried out in the absence of base. [c]Reaction carried out in water.

Next, the reductions of nitroarenes having electron withdrawing functional groups were investigated (Table 2, **2f-2o**). Electron withdrawing functional groups such as amides, sulphonamide, carboxyl and nitro were well tolerated and quite high yield was observed with optimized conditions (Table 2, **2f-2h** and **2m-2o**). However, in the reduction of *m*- and *p*-nitrobenzonitrile, hydration of nitrile group along with the reduction of nitro group was observed (Table 2, entries **2i** and **2k**). To overcome this hydration, reduction of nitrile substituted nitroarenes was conducted in the absence of base and good yield was obtained (Table 2, entries **2j** and **2l**).

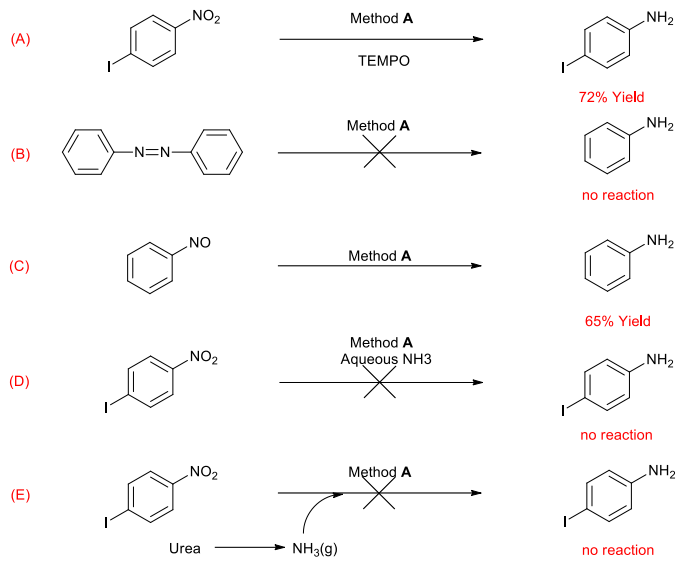
Reduction of 1,3-dinitrobenzene in methanol afforded mixture of 3,3'-diaminoazobenzene, 3-nitroaniline and 1,3-diaminobenzene while reduction in water gave regioselectively 3-nitroaniline (Table 2, **2m**). Hence, reductions of dinitroarenes were carried out in water (Table 2, **2m-2o**). 1,4-Dinitrobenzene was selectively reduced to 4-nitroaniline (**2n**) in good yield while 3,5-dinitrobenzamide afforded a regioselectively reduced product, 3-amino-5-nitrobenzamide (**2o**) in a moderate yield (Table 2, **2n** and **2o**). Electron rich nitroarenes such as 3-phenylnitrobenzene and 4-methoxynitrobenzene were reduced successfully to afford corresponding anilines in moderate yield (Table 2, **2q** and **2r**). However, reduction of 3-nitroaniline afforded 3,3'-diaminoazobenzene (**2p**) instead of desired 1,3-diaminobenzene (Table 2, **2p**). Developed method was further explored for the reduction of polycyclic nitroarenes. Reduction of 1-nitronaphthalene and 2-nitrofluorene afforded corresponding amines in moderate yield (Table 2, **2s** and **2t**), while heterocyclic nitroarenes such as 5-nitroisoquinoline and 5-nitroindole were converted to their corresponding amines in a good yield without affecting the heterocyclic ring (Table 2, **2u** and **2v**).

Encouraged by these results, we subsequently carried out the reduction of 1,3-dinitrobenzene in gram scale to demonstrate the utility of this method. The reaction of 1 gram of 1,3-dinitrobenzene in water afforded 83% of regioselectively reduced product *i.e.* 3-nitroaniline (Scheme **1**).



Scheme 1 Gram scale reaction of 1,3-dinitrobenzene

To understand the reaction mechanism, numbers of control experiments were conducted (Scheme **2**). First, the reduction pathway was investigated. It was well established that nitro reduction follows radical pathway, direct pathway or condensation pathway.[8] Therefore, to rule out the involvement of radical pathway, model reaction was carried out in the presence of TEMPO (Scheme **2A**). As expected, no appreciable change in the yield of the product (**1b**) was observed, indicating the absence of radical pathway. No product was observed when the reaction was carried out with azobenzene under method A (Scheme **2B**). Even its partially reduced product *i.e.* hydrazobenzene was not found in GC-MS analysis. However, 65% of desired product was obtained with nitrosobenzene (Scheme **2C**). These experiments revealed that reaction followed the direct pathway rather than the condensation pathway.



Scheme 2 Control experiments performed for the mechanism of reaction.

After the successful finding of reaction pathway, the role of hydrazine hydrate for the reduction of nitro group was investigated. In literature, hydrazine hydrate was outlined to dissociates into hydrogen ions, nitrogen gas and ammonia in the presence of metal salts.[15a] Therefore, to ascertain the role of ammonia in reaction,[15b] reduction of **1a** was attempted with aqueous ammonia (Scheme **2D**) and gaseous ammonia *i.e.* by means of heating urea (Scheme **2E**), but the reduced product was not observed in both cases. These experiments indicated that hydrogen ions and electrons from hydrazine actually participated in the reduction process. [15]

Table 3. Data comparing yield of reaction with catalyst L2, Thiourea and Guanidine

Catalyst	L2	Thiourea	Guanidine
Yield	34%[a]	8%[b]	12%[b]

[a]Reaction conditions: 4-iodonitrobenzene (0.1 mmol), $N_2H_4.H_2O$ (6 equiv.), catalyst (10 mol%), methanol (2 mL), isolated yield. [b]NMR yield

Next, we sought to investigate the facet of organocatalyst in the reduction of nitroarenes. Since **L2** have proton acceptor as well as proton donor sites and hydrazine is proton rich molecule, therefore the possibility of hydrogen bond interaction between **L2** and hydrazine could not be ignored. To compare the extent of H-B interaction, parallel reactions were performed with other catalyst (Table 3). However 34%, 8% and 12% yield was observed using catalyst **L2**, thiourea and guanidine respectively. Further, infrared spectroscopy was performed to find hydrogen bond interactions between **L2** and hydrazine.

The infrared spectra of hot aqueous solution of **L2** (SI Figure **1**) and hydrazine hydrate (SI Figure **2**) were compared with IR spectra of the reaction of $N_2H_4.H_2O$ with **L2** (SI Figure **3**) in water. Blue shift was observed for N-N stretching frequency from 1080 to 1089 cm^{-1} indicating the decrease in N-N bond length of hydrazine while red shift is observed for N-H bending frequency from 1612 to 1606 cm^{-1} signifying N-H bond elongation of N_2H_4 (SI Figure **3**).[16] Also new peaks at 2017, 2032, 2158 and 2181 cm^{-1} might be due to polarization of C=O, C=N and C-N bonds of **L2** because of hydrogen bond interactions (SI Figure **3**).[17]

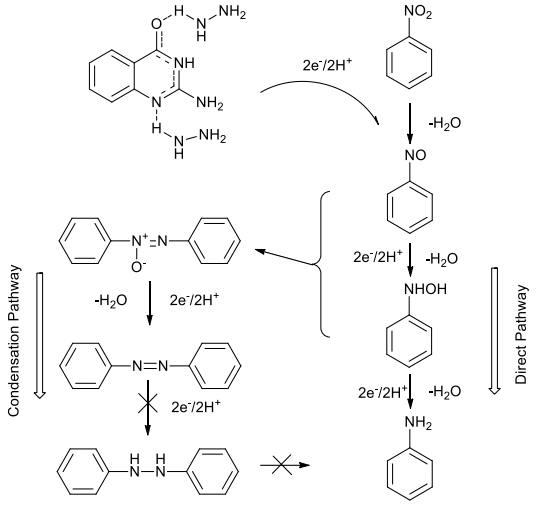


Fig. 6 Plausible mechanism of the reaction.

Moreover, to support the IR observation, we performed UV-Vis and Fluorescence spectroscopy experiment of the reaction of **L2** with hydrazine hydrate. In the UV-Vis spectroscopy, 2-aminoquinazolin-4(*3H*)-one (**L2**) showed absorption at 260 nm and 315 nm in methanol. However, addition of hydrazine hydrate resulted in the very low intensity band at 260 nm and decrease in the intensity of band at 315 nm was observed (SI, Figure **4**). Moreover, in fluorescence experiment, excitation at 315 nm, it exhibited a blue emission at 400 nm. Further, the addition of hydrazine hydrate resulted in quenching of emission spectrum (SI, Figure **5**). Thus, absorption and emission results suggested that the hydrazine hydrate attack at the nucleophilic carbonyl center and distorts the conjugation in molecules.

On the basis of results of above experiments, it was discovered that reduction reaction followed the direct pathway and the catalytic role of **L2** catalyst could be attributed to the transfer of hydrogen ions and electrons from hydrazine hydrate for this pathway. Taking into account the above discussion, the plausible mechanism was depicted in figure **6**.

Conclusions

Herein, guanine type bicyclic moiety *i.e.* 2-aminoquinazolin-4(*3H*)-one is first time reported as hydrogen bond donor/accepter organocatalyst which facilitates the reduction of nitroarenes by interacting with hydrazine. This transition metal free methodology avoids the implementation of hazardous reagents, high pressure, flammable hydrogen gas and harsh reaction conditions. Additionally, moderate reaction time, relatively less expensive reagents, good to high yields and broad functional group tolerance are other noticeable features of this important organic transformation. Further

investigations of the mechanism and synthetic applications of this method are ongoing and will be disclosed in due course.

Experimental

Hydrazine hydrate (3 mmol) was added to the mixture of nitroarene (0.5 mmol), K_2CO_3 (0.5 mmol) and 2-aminoquinazolin-4(*3H*)-one (10 mol%) in solvent (H_2O/CH_3OH according to reactant) 3 mL at 100 °C for 2-12 h. However, in case of methanol as a solvent, it was also added to the vessel during the progress of reaction before it become dry. After completion of the reaction (as monitored by TLC and GC-MS), reaction vessel was kept at room temeperature and product was extracted with ethyl acetate (3 x 5 mL). Combined organic layer was washed with brine and distilled water (3 x 5 mL), dried on anhydrous sodium sulphate and solvent was evaporated under vaccum. Crude product was analyzed directly using GC-MS and product was isolated from crude by column chromatography.

Conflicts of interest

Authors declare no conflict of interest.

Acknowledgements

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Unravelling 2-aminoquinazolin-4(*3H*)-one as an organocatalyst for the chemoselective reduction of nitroarenes

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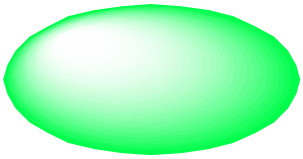

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