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Redox-neutral functionalization of α-Csp^3–H bonds of secondary cyclic amines: a highly atom-economical strategy for *N*-arylation/formal cross-dehydrogenative couplings†

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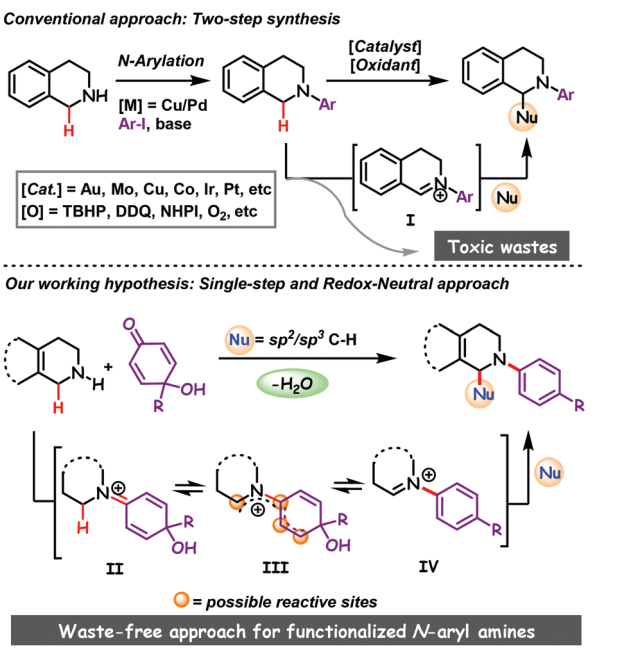
An efficient redox-neutral method has been developed for α-Csp^3–H functionalization of secondary cyclic amines *via* concurrent *N*-arylation/formal cross dehydrogenation coupling (CDC) with sp^2-C–H and sp^3-C–H bonds of arenes and ketones, respectively. The developed protocol is operationally simple, highly atom economical and environmentally benign (*E*-factor = *ca.* 0.5). The reaction mechanism has been explained based on the control experiments and examination of reactive intermediates by mass spectrometry.

Functional cyclic amines are key constituents of numerous natural products and drugs.[1] Amidst the development of several synthetic methods, functionalization of sp^3 C–H bonds in the α-position of the amine nitrogen atom and subsequent C–C bond formations has attracted much attention in recent years.[2,3] The majority of methods have largely relied on protected or tertiary amines, followed by the oxidative activation of C–H bonds. For instance, tetrahydroisoquinoline (THIQ) is a key prevalent structure in natural products and bioactive molecules.[4] Not surprisingly, numerous efforts have been devoted to the functionalization of THIQ with various coupling partners.[5,6] Conventionally, α-sp^3 C–H bond functionalization of THIQ required a two-step synthesis process; *viz* (i) protection on nitrogen[6q] or Cu/Pd-catalyzed *N*-arylation, where the aryl group acts as an activating group and then (ii) oxidative coupling in the presence of transition-metals (Ir,[6a–c] Ru,[6c,u] Au,[6d] Mo,[6e] V,[6f] Pt,[6g] Fe,[6h] Co,[6i] Cu,[6j–n] *etc.*) and oxidants (DDQ, TBHP, O_2, *etc.*)[6o–t] under thermal or photocatalytic conditions (Scheme 1). The oxidative coupling step involves the generation of a reactive intermediate, mostly iminium (**I**) followed by nucleophilic addition.[6u] Most of these protocols generate significant amounts of toxic metal-wastes in both steps (Scheme 1). With the emergence of the concepts of "green chemistry" and "atom economy", the long standing problem of how to avoid toxic waste needs to be addressed. In this context, the pioneering work of Seidel *et al.*[7] reported the redox-neutral functionalization of the amine α-C–H bond *via* an iminium intermediate, formed *in situ* by the condensation of amine with an aromatic aldehyde or ketones.[8] Herein, we envisioned *p*-quinol as a protective group and as an oxidant in one molecule that can be reduced to form an iminium intermediate (**IV**) with the concurrent elimination of water (Scheme 1). Such redox-neutral *N*-arylative functionalisations of amines using quinols are still underdeveloped,[9] which could be attributed to the difficulty in controlling the selecti-



Scheme 1 Functionalization of the α-Sp^3-C–H bond of secondary cyclic amines.

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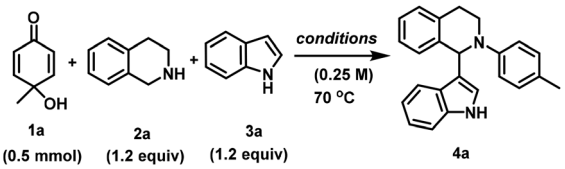
vity among multiple reactive sites of the quinone intermediate (**III**, Scheme 1).[10]

Recently, we reported that *p*-quinols can be activated by an amine and subsequent site-selective functionalisation at sp^2-C with different nucleophiles.[11] Here, we demonstrate the use of *p*-quinol as an "aromatic to be" electrophilic surrogate as well as for the selective functionalisation of amines at α-Csp^3 carbon with arenes and ketones.

We began our study with the evaluation of reaction conditions for a model reaction of *p*-quinol (**1a**) with THIQ (**2a**, 1.2 equiv.) and indole (**3a**, 1.2 equiv.) (Table 1).[12] The desired racemic CDC product **4a** was formed in 62% and 60% yields in acetonitrile and toluene, respectively (Table 1, entries 2 and 8). However, the reaction was reasonably fast in toluene. The reaction was equally effective with 1.0 equiv. of indole (Table 1, entry 9). Furthermore, the rate of the reaction and chemical yield were much improved in the presence of acetic acid (10–20 mol%) (Table 1, entries 11–13; 94–98% yield). It is worth mentioning that in an open air flask the desired product was obtained in a slightly inferior yield (Table 1, entry 14; 83%).[12] Under the optimum conditions (Table 1, entry 12), various indoles were employed to react with THIQs and *p*-quinols (Table 2). Irrespective of their electronic natures and positions of substituents, it always resulted in the formation of selective C3 position addition products (Table 2). 5-Methoxyindole gave the corresponding CDC product **4b** in 78% yield. Halogen containing indoles gave the corresponding products **4c–e** in good yields (70–76%). Electron withdrawing groups (nitrile, nitro and ester) on the indole at different positions (C5 and C6) were compatible to give the respective desired products in high chemical yields (**4f–h**; 62–72%). Notably, 5-nitroindole and 5-bromoindole required refluxing temperature (120 °C) to complete the reaction. 7-Azaindole also worked well to give the corresponding product **4i** in 62% yield. Differently substituted aryl surrogates i.e. *p*-quinol (4-methyl, 4-ethyl, 4-isopropyl, 4-cyclohexyl, and 3,4-dimethyl) were investigated to yield the corresponding *N*-aryl indonyl THIQs (**4a–m**). The reaction with 5-hydroxyindole gave the corresponding products **4n** and **4o** in 60% and 63% yields,

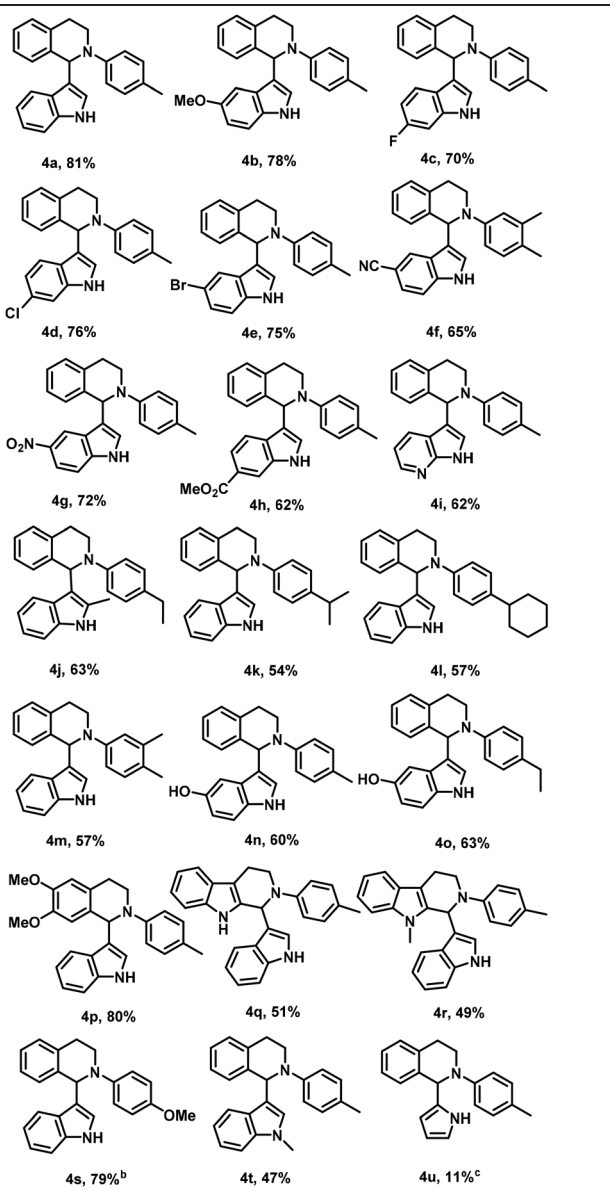
Table 1 Evaluation of redox-neutral conditions for α-Csp^3–H functionalization of THIQ with indoles[a]



Run	Solvent	Additive (mol%)	Time (h)	Yield[a] (**4a**, %)
1	Neat	—	24	39
2	CH_3CN	—	36	62
3	THF	—	48	36
4	HFIP	—	36	nd
5	DCE	—	36	nd
6	MeOH	—	18	49
7	Dioxane	—	48	nd
8	Toluene	—	12	60
9[b]	Toluene	—	12	59
10	Toluene	$PhCO_2H$ (20)	6	77
11	Toluene	AcOH (20)	6	98
12[b]	Toluene	AcOH (20)	6	98 (81)[c]
13[b]	Toluene	AcOH (10)	9	94 (78)[c]
14[b,d]	Toluene	AcOH (20)	10	83 (72)[c]

[a] NMR yields were calculated using 4-hydroxy-2,4,6-trimethylcyclohexa-2,5-dien-1-one as an internal standard. [b] 1.0 equiv. indole was used. [c] Isolated yields are mentioned in parentheses. [d] Open air reaction. nd = not determined; means a complex reaction mixture was observed.

Table 2 Substrate scope for α-Csp^3–H functionalization of secondary amines with indoles[a]



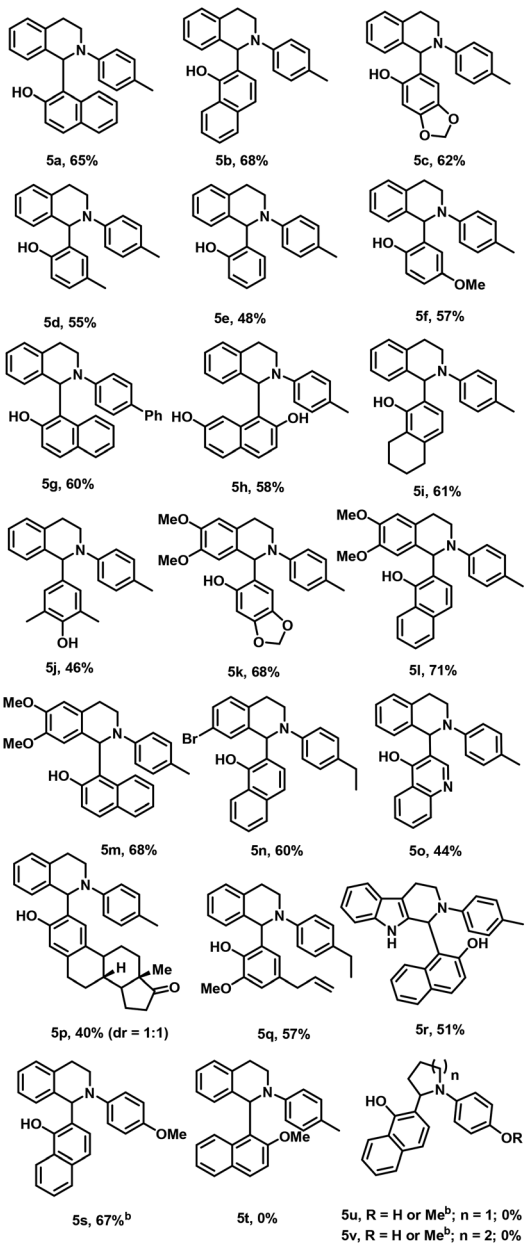
[a] Reaction was conducted on a 0.81 mmol scale (**1**), THIQ (1.2 equiv.), indole (1.0 equiv.) and acetic acid (20 mol%). [b] *p*-Quinone dimethyl monoketal was employed. [c] 1.2 equiv of pyrrole was used. Bis-addition product (at C2 and C5) was also obtained in 3% yield.

respectively. However, a minor regioisomer of addition at the C4 position (*ortho* to the phenolic group) was also observed (*ca.* 6%).[12] 6,7-Dimethoxy-THIQ gave the corresponding desired product **4p** in 80% yield. Tetrahydro-β-carboline or tryptoline, another privileged scaffold frequently encountered in bioactive molecules,[13] was also examined for its functionalization at α-Csp^3–H. Free indole (NH) and *N*-methyl substituted tryptoline gave the desired products (**4q** and **4r**, 51% and 49% yields, respectively). *p*-Quinone dimethyl monoketal was also compatible to give the corresponding *N*-*p*-methoxyphenyl (PMP) containing C1-indonyl THIQ (**4s**) in 79% yield. Reaction with *N*-methylindole gave the corresponding C3-alkylated product **4t** in a moderate yield (47%). However, it was noticed that there was no reaction in the absence of the acid (*cf* entry 9, Table 1). Other heterocycles (pyrrolidine and piperidine) were also tested with an indole (**3a**) under the present as well as slightly modified conditions, such as temperature, solvents and change of dienones. However, a complex reaction mixture was obtained in all of our attempts.[12]

Other arene nucleophiles, such as phenols, were employed for the CDC reaction to give amino-phenols, called Betti bases.[14] 2-Naphthol was first treated with THIQ and *p*-quinol under identical redox-conditions, giving **5a** in a moderate yield (48%), which was further increased to 65% after variation in the stoichiometry of reactants (Table S1,† entry 6).[12] The present reaction conditions were then examined with a range of phenols (Table 3). 1-Naphthol, sesamole, *p*-cresol, and other phenols underwent CDC reactions selectively at the *ortho*-position with THIQ and *p*-quinols (**5b–i**; 48–68% yields). Coupling took place at the *para*-position, when 2,6-disubstituted phenol was employed (**5j**). 6,7-Dimethoxy- and 7-bromo-substituted THIQs gave the corresponding products with 1- and 2-naphthols in good yields (**5k–5n**). Considering the privileged scaffolds in drug/drug-like molecules, quinolines are frequently found in anti-bacterials.[15] Under the present redox-neutral conditions, 4-hydroxyquinoline was compatible to give the corresponding *ortho*-substituted THIQ-quinolines **5o** in moderate yields (44%). Estrone gave the corresponding *ortho*-substituted estrone-THIQ hybrid product **5p** in 40% yield (1 : 1 dr). An essential oil extract, eugenol, underwent redox reaction with THIQ to form **5q** in a good yield (57%). Whereas, tryptoline gave the corresponding product **5r** with 2-naphthol in 51% yield. *p*-Quinone dimethyl monoketal gave the corresponding PMP group containing product (**5s**) with 1-naphthol and THIQ in 67% yield. 2-Methoxynaphthalene was examined in place of free-phenol, however, no reaction took place even at higher temperature (110 °C).

As a proof of concept, the present redox-neutral conditions were also investigated with ketones and esters as C(sp^3)–H enolizable coupling partners (Table 4). The alkylation product **6a** was obtained in 57% yield with acetone, whereas ethyl methyl ketone gave the alkylation product selectively on the methyl group (**6b**; 60% yield). The PMP-protected acetone addition product (**6c**) was synthesized from a *p*-quinone dimethyl monoketal in 73% yield. However, ethyl acetate failed to give any product, probably due to its lower nucleophilicity.

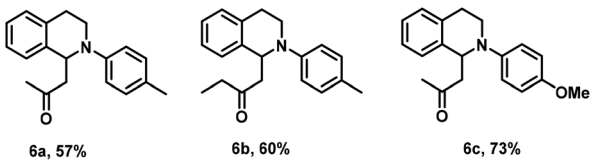
Table 3 Substrate scope for α-Csp^3–H functionalization of secondary amines with phenols[a]



[a] Reaction was conducted on a 0.81 mmol scale (**1**), THIQ (1.5 equiv.), phenol (1.2 equiv.) and acetic acid (20 mol%). [b] *p*-Quinone dimethyl monoketal was employed.

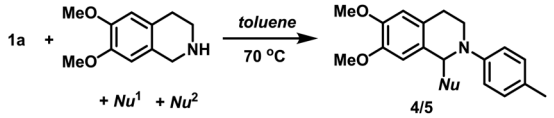
To see the reactivity pattern of arenes in the present reaction, we treated 6,7-dimethoxy-THIQ and **1a** with sets of equimolar mixtures of two nucleophiles (Table 5). For example, with 1- and 2-naphthols or 1-naphthols and indole, the reactivity of 2-naphthol and indole was completely suppressed and the product was selectively formed with 1-naphthol (**5l**; Table 5, entries 1 and 2). However, the selective formation of indolyl-THIQ occurred when a mixture of 2-naphthol and indole was employed (**4p**; Table 5, entry 3). These experiments

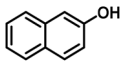
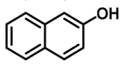
Table 4 Substrate scope of α-Csp^3–H functionalization of secondary amines with ketones[a]



[a] Reaction was conducted on a 0.81 mmol scale (**1a**). THIQ (1.2 equiv.), ketone/ester (10 equiv.) and acetic acid (20 mol%).

Table 5 CDC reaction towards different arenes[a]



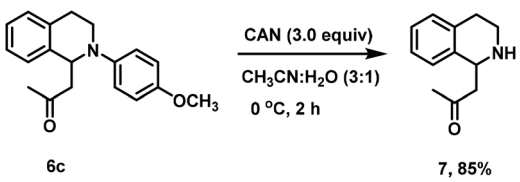
Entry	Nu^1 (1.0 equiv.)	Nu^2 (1.0 equiv.)	Selective product (% yield)
1			**5l** = 63%
2			**5l** = 61%[b]
3			**4p** = 68%

[a] Reaction was conducted at 0.5 mmol scale (**1a**), THIQ (1.2 equiv.) and AcOH (20 mol%), toluene (1.2 mL). [b] **4p** was also formed in *ca* < 5% yield.

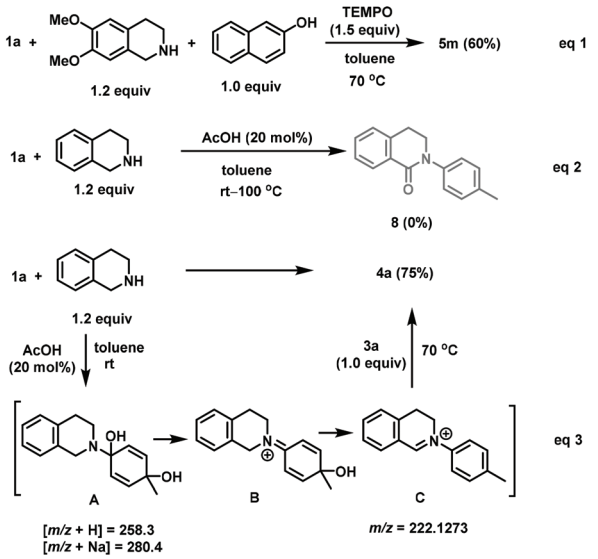
revealed the reactivity pattern of arenes under the present conditions as follows; 1-naphthol > indole > 2-naphthol.

As THIQ-addition products have cleavable PMP groups (**4s**, **5s** and **6c**), we attempted to deprotect it under oxidative conditions. A complex reaction mixture was obtained in all of our attempts with **4s** and **5s** (or with *N*-methylindole and *O*-methylnaphthol adducts).[12] This is probably due to oxidisable indole or naphthol units. However, PMP group was successfully cleaved from **6c** to afford free amine **7** in 85% yield under oxidation conditions using ceric ammonium nitrate (CAN) (Scheme 2). The greener aspect of the present reactions was evaluated with green chemistry metrics and they showed an excellent *E*-factor (0.5–1.1).[12]

To gain mechanistic insight into the present reaction, a control experiment was conducted with **1a**, 6,7-dimethoxy-THIQ, 2-naphthol and stable free radical TEMPO (1.5 equiv.)



Scheme 2 Cleavage of the PMP group.



Scheme 3 Mechanistic study. The reaction was conducted on a 0.5 mmol scale of **1a** and reaction aliquots were analysed at different intervals of time by mass spectrometry.

in the absence or presence of AcOH (Scheme 3, eqn (1)).[12] The desired product **5m** was obtained in 60% yield. Another control experiment was performed in the absence of any nucleophile and the progress of the reaction was monitored by HRMS analysis (eqn (2)).[12] A mass peak corresponding to *N*-arylimine (**C**) was distinctly observed and there was no molecular ion peak corresponding to the cyclic amide product (**8**; expected *via* radical pathway).[16] Another set of reactions was performed in the presence of indole and mass spectrometric analysis showed the formation of an hemiaminal (**A**) and *N*-aryliminium (**C**) intermediates along with indole addition product **4a** (*ca.* 20%) even at room temperature.[12] Furthermore, it was evident that the reaction proceeds faster and provides a high yield in the presence of acids (Table 1, entries 10–13). Here, we presume that acid might facilitate OH-elimination and in turn tautomerization to the iminium ion (**A** to **C**). These controlled experiments strongly support that the reaction proceeds *via* an iminium ion intermediate (**C**) which undergoes the Betti reaction or a Mannich-type reaction to give the C1-functionalized amines (**4–6**).

Conclusions

In conclusion, we developed a redox-neutral approach for the synthesis *N*-aryl-C1-functionalized THIQs and tryptolines in a single step. The developed method is highly compatible with a wide substrate scope. The reaction is highly atom economical, operationally simple and environmentally benign (*E*-factor = 0.5). The green features of the present method are the absence of any transition-metal and H_2O being the only by-product. Further exploration of this reaction and the development of asymmetric variants are in progress.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

1 E. Vitaku, D. T. Smith and J. T. Njardarson, *J. Med. Chem.*, 2014, **57**, 10257.

2 For review, see: (*a*) E. A. Mitchell, A. Peschiulli, N. Lefevre, L. Meerpoel and B. U. W. Maes, *Chem. – Eur. J.*, 2012, **18**, 10092; (*b*) K. R. Campos, *Chem. Soc. Rev.*, 2007, **36**, 1069.

3 For some recent examples, see: (*a*) W. Chen, L. Ma, A. Paul and D. Seidel, *Nat. Chem.*, 2018, **10**, 165; (*b*) Y. Liu and H. Ge, *Nat. Chem.*, 2017, **9**, 26; (*c*) G. He, B. Wang, W. A. Nack and G. Chen, *Acc. Chem. Res.*, 2016, **49**, 635 and references therein; (*d*) J. E. Spangler, Y. Kobayashi, P. Verma, D.-H. Wang and J.-Q. Yu, *J. Am. Chem. Soc.*, 2015, **137**, 11876; (*e*) S. A. Girard, T. Knauber and C.-J. Li, *Angew. Chem., Int. Ed.*, 2014, **53**, 74; (*f*) A. McNally, B. Haffemayer, B. S. L. Collins and M. J. Gaunt, *Nature*, 2014, **510**, 129; (*g*) L. Shi and W. Xia, *Chem. Soc. Rev.*, 2012, **41**, 7687.

4 For representative reviews, see: (*a*) M. Iranshahy, R. Quinn and M. Iranshahi, *RSC Adv.*, 2014, **4**, 15900; (*b*) K. W. Bentley, *Nat. Prod. Rep.*, 2005, **22**, 249; (*c*) K. W. Bentley, *Nat. Prod. Rep.*, 2004, **21**, 395.

5 For book chapter, see: M. C. Ortiz Villamizar, C. E. P. Galvis and V. V. Kouz-netsov, *Heterocycles via Cross Dehydrogenative Coupling*, 2019, pp. 77–105.

6 For representative examples of transition-metal catalysed reactions, see: (*a*) W.-J. Yoo and S. Kobayashi, *Green Chem.*, 2014, **16**, 2438; (*b*) J.-J. Zhong, Q.-Y. Meng, G.-X. Wang, Q. Liu, B. Chen, K. Feng, C.-H. Tung and L.-Z. Wu, *Chem. – Eur. J.*, 2013, **19**, 6443; (*c*) A. G. Condie, J. C. Gonzalez-Gomez and C. R. J. Stephenson, *J. Am. Chem. Soc.*, 2010, **132**, 1464; (*d*) J. Xie, H. Li, J. Zhou, Y. Cheng and C. Zhu, *Angew. Chem., Int. Ed.*, 2012, **51**, 1252; (*e*) K. Alagiri and K. R. Prabhu, *Org. Biomol. Chem.*, 2012, **10**, 835; (*f*) K. Alagiri, G. S. R. Kumara and K. R. Prabhu, *Chem. Commun.*, 2011, **47**, 11787; (*g*) X.-Z. Shu, Y.-F. Yang, X.-F. Xia, K.-G. Ji, X.-Y. Liu and Y. M. Liang, *Org. Biomol. Chem.*, 2010, **8**, 4077; (*h*) P. Liu, C.-Y. Zhou, S. Xiang and C.-M. Che, *Chem. Commun.*, 2010, **46**, 2739; (*i*) M. R. Patil, N. P. Dedhia, A. R. Kapdi and A. V. Kumar, *J. Org. Chem.*, 2018, **83**, 4477; (*j*) E. Boess, C. Schmitz and M. Klussmann, *J. Am. Chem. Soc.*, 2012, **134**, 5317; (*k*) Z. Li, D. S. Bohle and C.-J. Li, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, 8928; (*l*) Z. Li and C.-J. Li, *J. Am. Chem. Soc.*, 2005, **127**, 3672; (*m*) O. Baslé and C.-J. Li, *Green Chem.*, 2007, **9**, 1047; (*n*) Z. Li and C.-J. Li, *J. Am. Chem. Soc.*, 2005, **127**, 6968 For representative examples of transition-metal free conditions, see: (*o*) J. DineshKumar, M. Lamani, K. Alagiri and K. R. Prabhu, *Org. Lett.*, 2013, **15**, 1092; (*p*) D. P. Hari and B. Konig, *Org. Lett.*, 2011, **13**, 3852; (*q*) H. Yu, H. Kim, S.-H. Baek and D. Lee, *Front. Chem.*, 2020, **8**, 629; (*r*) A. S.-K. Tsang, K. Ingram, J. Keiser, D. B. Hibbertc and M. H. Todd, *Org. Biomol. Chem.*, 2013, **11**, 4921; (*s*) V. V. Kouznetsov, M. C. Ortiz-Villamizar, L. Y. Méndez-Vargas and G. C. E. Puerto, *Curr. Org. Chem.*, 2020, **24**, 809 and references therein; (*t*) J. Dhineshkumar, P. Samaddar and K. R. Prabhu, *ACS Omega*, 2017, **2**, 4885 See also for radical intermediate. (*u*) P. Kohls, D. Jadhav, G. Pandey and O. Reiser, *Org. Lett.*, 2012, **14**, 672.

7 (*a*) A. Paul, A. Adili and D. Seidel, *Org. Lett.*, 2019, **21**, 1845; (*b*) Z. Zhu, H. S. Chandak and D. Seidel, *Org. Lett.*, 2018, **20**, 4090; (*c*) D. Seidel, *Acc. Chem. Res.*, 2015, **48**, 317; (*d*) W. Chen, R. G. Wilde and D. Seidel, *Org. Lett.*, 2014, **16**, 730; (*e*) W. Chen, R. G. Wilde and D. Seidel, *Org. Lett.*, 2014, **16**, 3158; (*f*) C. Zhang, D. Dasa and D. Seidel, *Chem. Sci.*, 2011, **2**, 233.

8 (*a*) I. Rahman, B. Deka, R. Thakuria, M. L. Deb and P. K. Baruah, *Org. Biomol. Chem.*, 2020, **18**, 6514; (*b*) M. L. Deb, P. J. Borpatra and P. K. Baruah, *Green Chem.*, 2019, **21**, 69; (*c*) S. Haldar and C. K. Jana, *Org. Biomol. Chem.*, 2019, **17**, 1800; (*d*) J. Huang, L. Li, T. Xiao, Z.-W. Mao and L. Zhou, *Asian J. Org. Chem.*, 2016, **5**, 1204; (*e*) G. Shao, Y. He, Y. Xu, J. Chen, H. Yu and R. Cao, *Eur. J. Org. Chem.*, 2015, 4615; (*f*) F. Yi, J. Su, S. Zhang, W. Yi and L. Zhang, *Eur. J. Org. Chem.*, 2015, 7360; (*g*) Y. Chen and G. Feng, *Org. Biomol. Chem.*, 2015, **13**, 4260; (*h*) S. Haldar, S. K. Roy, B. Maity, D. Koley and C. K. Jana, *Chem. – Eur. J.*, 2015, **21**, 15290; (*i*) W. Lin, T. Cao, W. Fan, Y. Han, J. Kuang, H. Luo, B. Miao, X. Tang, Q. Yu, W. Yuan, J. Zhang, C. Zhu and S. Ma, *Angew. Chem., Int. Ed.*, 2014, **53**, 277; (*j*) S. Haldar, S. Mahato and C. K. Jana, *Asian J. Org. Chem.*, 2014, **3**, 44; (*k*) Q.-H. Zheng, W. Meng, G.-J. Jiang and Z.-X. Yu, *Org. Lett.*, 2013, **15**, 5928.

9 (*a*) L. Shi, M. Wang, L. Pan, Y. Li and Q. Liu, *Chem. Commun.*, 2018, **54**, 8721; (*b*) C.-B. Yi, Z.-Y. She, Y.-F. Cheng and J. Qu, *Org. Lett.*, 2018, **20**, 668; (*c*) X. Wang, G. Li, X. Li, D. Zhu and R. Shen, *Org. Chem. Front.*, 2021, **8**, 297.

10 For addition of arenes on sp^2–C of quinone, see; (*a*) J. Z. Wang, J. Zhou, C. Xu, H. B. Sun, L. Kürti and Q. L. Xu, *J. Am. Chem. Soc.*, 2016, **138**, 5202; (*b*) H. Gao, Q. L. Xu, C. Keene, M. Yousufuddin, D. H. Ess and L. Kürti, *Angew. Chem., Int. Ed.*, 2016, **55**, 566; (*c*) T. Kamitanaka, K. Morimoto, K. Tsuboshima, D. Koseki, H. Takamuro, T. Dohi and Y. Kita, *Angew. Chem., Int. Ed.*, 2016, **55**, 15535; (*d*) T. Dohi, N. Washimi, T. Kamitanaka, K. I. Fukushima and Y. Kita, *Angew. Chem., Int. Ed.*, 2011, **50**, 6142.

11 S. Husen, A. Chauhan and R. Kumar, *Green Chem.*, 2020, **22**, 1119.

12 See the ESI† for details.

13 For recent review, see: P. Maity, D. Adhikari and A. K. Jana, *Tetrahedron*, 2019, **75**, 965.
14 A. Olyaei and M. Sadeghpour, *RSC Adv.*, 2019, **9**, 18467.
15 For examples, see: (*a*) S. Heeb, M. P. Fletcher, S. R. Chhabra, S. P. Diggle, P. Williams and M. Cámara, *FEMS Microbiol. Rev.*, 2011, **35**, 247; (*b*) F. V. Bambeke, J. M. Michot, J. V. Eldere and P. M. Tulkens, *Clin. Microbiol. Infect.*, 2005, **11**, 256.
16 K. C. C. Aganda, B. Hong and A. Lee, *Adv. Synth. Catal.*, 2019, **361**, 1124.