Direct synthesis of \(N\)-sulfinyl- and \(N\)-sulfonylimines via copper/L-proline-catalyzed aerobic oxidative cascade reaction of alcohols with sulfinamides or sulfonamides†

Guofu Zhang, Shengjun Xu, Xiaoqiang Xie, Chengrong Ding* and Shang Shan*

An efficient one-pot synthetic method of \(N\)-sulfinyl- and \(N\)-sulfonylimines by the condensation of alcohols with sulfinamides or sulfonamides under mild and green conditions has been developed using a combination of CuI, L-proline and TEMPO. This system shows excellent functional group compatibility for a wide range of substrates and affords the corresponding products in good to excellent yields.

\(N\)-Sulfinyl- and \(N\)-sulfonylimines are versatile intermediates in organic synthesis. As active substrates, they can undergo various nucleophilic addition reactions, \(^2\) radical reactions, \(^3\) and hetero-Diels–Alder reactions \(^4\) to afford the expected \(N\)-sulfinyl- and \(N\)-sulfonylamide derivatives which are a class of important structure motifs prevalent in drugs, such as potent thromboxane receptor antagonists (A), \(^5\) inhibitors of Mycobacterium tuberculosis (B), \(^6\) metalloprotease inhibitors (C) \(^7\) and potential antitrypanosomal agents (D) \(^8\) (Scheme 1).

Due to the wide range of synthetic utility of these \(N\)-sulfinyl- and \(N\)-sulfonylamides, numerous synthetic methods have been developed. The main methods for the preparation of \(N\)-sulfinyl- and \(N\)-sulfonylimines include: (1) reaction of nitriles with an organometallic reagent (DIBAL, MeLi) and menthylsulfinate; \(^9\) (2) asymmetric oxidation of sulf-enamines \(^10\) and (3) condensation of sulfinamides or sulfonamides with aldehydes (Scheme 2a). The last method seems to be the most common and useful because the pure starting materials are now commercially available. Therefore, in the past decades, much attention have been paid to the direct condensation of

---

Scheme 1  Biologically active sulfinamides scaffold.

---

College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310014, People’s Republic of China. E-mail: dingcr@zjut.edu.cn; shans2001@163.com; Fax: +86-571-88320147; Tel: +86-571-88320147

† Electronic supplementary information [ESI] available: Detailed experimental procedures, the optimization of copper-catalyzed oxidative cascade reaction and NMR data for products. See DOI: 10.1039/c6ra26490e

RSC Advances

PAPER

Cite this: RSC Adv., 2017, 7, 9431

Received 8th November 2016
Accepted 26th January 2017
DOI: 10.1039/c6ra26490e
rsc.li/rsc-advances

Scheme 2  Methods for the preparation of \(N\)-sulfinyl- and \(N\)-sulfonylimines.
sulfinamides or sulfonylamides with aldehydes for the synthesis of N-sulfonyl- and N-sulfonylimines [Scheme 2a, eqn (3)].

Even though these reported protocols could be easier to obtain N-sulfonyl- or N-sulfonylimines, excess Lewis acid or stoichiometric base had to be used, which generated a large amount of environmentally unfriendly metallic waste. On the other hand, aldehydes can be obtained from the oxidation of alcohols. Therefore, the method that utilizing alcohol as one of the staring materials to afford the N-sulfonyl- or N-sulfonylimine was attractive. To the best of our knowledge, there was only one report on the formation of sulfonylimine from alcohols, which involved saccharin-lithium bromide-catalyzed oxidation of alcohols to aldehydes/ketones with chloramine-T followed by their condensation to afford N-tosylimines (Scheme 2b).

Recently, Stahl et al. reported a copper/TEMPO-catalyzed oxidative cascade reaction between alcohol and 4-toluenesulfinamide to afford N-tosylimines from alcohols with sulfin- or sulfonylamides under air (Scheme 2c).

Initially, benzylic and 4-toluenesulfinamide were selected as the model substrates to determine the optimal conditions. First, the effect of solvent on this oxidative cascade transformation was examined (Table 1, entries 1–6). Good conversion of N-sulfinylamine was obtained, when the reaction was performed in CH₂Cl₂ or CH₃OH with 5 mol% CuI and 5 mol% 1-proline in the presence of 1.0 equiv. K₂CO₃ under air at 60 °C (Table 1, entries 1 and 4). The employment of THF, DMSO or DMF led to moderate conversions of the substrates (entries 2, 3, 6). To our delight, when switching the solvent to toluene, the conversion reached to 88% (entry 5). After then, the different copper salts were screened. As a result, the catalytic efficiency of Cu(i) salts were better than Cu(n) salts in this catalytic system with ambient air as the oxidant. Therefore, we sought to utilize the combination of copper salt, ligand and TEMPO as efficient catalysts for oxidation of aldehydes to aldehydes followed by condensation with sulfin- or sulfonylamides. Herein, we reported a copper-catalyzed one-pot multi-step reaction system for synthesis of N-sulfonyl- and N-sulfonylimines from alcohols with sulfin- or sulfonylamides under air (Scheme 2c).

| Entry | Solvent | Cu salt | Ligand | Conv. (%) |
|-------|---------|---------|--------|-----------|
| 1     | CH₂Cl₂  | CuI     | L-proline | 81        |
| 2     | THF     | CuI     | L-proline | 76        |
| 3     | DMSO    | CuI     | L-proline | 51        |
| 4     | CH₃OH   | CuI     | L-proline | 83        |
| 5     | Toluene | CuI     | L-proline | 88        |
| 6     | DMF     | CuI     | L-proline | 54        |
| 7     | Toluene | CuCl    | L-proline | 82        |
| 8     | Toluene | CuBr    | L-proline | 83        |
| 9     | Toluene | CuCl₂   | L-proline | 73        |
| 10    | Toluene | CuBr₂   | L-proline | 74        |
| 11    | Toluene | CuSO₄   | L-proline | 45        |
| 12    | Toluene | Cu(OAc)₂ | L-proline | 68        |
| 13    | Toluene | CuI     | L-proline | Trace     |
| 14    | Toluene | CuI     | L-proline | Trace     |
| 15    | Toluene | CuI     | L-proline | 74        |
| 16    | Toluene | CuI     | L-proline | 76        |
| 17    | Toluene | CuI     | L-proline | 8         |
| 18    | Toluene | CuI     | L-Valine  | 77        |
| 19    | Toluene | CuI     | β-Alanine | 40        |
| 20    | Toluene | CuI     | L-Histidine | 61        |
| 21    | Toluene | CuI     | Sarcosine | 57        |
| 22    | Toluene | CuI     | Glycine   | 68        |
| 23    | Toluene | CuI     | Phenylproamate | 46 |
| 24    | Toluene | CuI     | Pyrrolidine | 69 |
| 25    | Toluene | CuI     | L-proline | >99 (94%) |
| 26    | Toluene | CuI     | L-proline | 31        |
| 27    | Toluene | CuI     | L-proline | 11        |
| 28    | Toluene | CuI     | L-proline | 10        |
| 29    | Toluene | CuI     | —        | 20        |

Table 2 Scope of N- p-tolylsulfinyl aldmines formation

| Entry | Reaction conditions: substrates (1.0 mmol), CuI (5 mol%), L-proline (5 mol%), TEMPO (5 mol%), K₂CO₃ (0.5 equiv.), toluene (4.0 mL), 4 Å MS (700 mg), 60 °C, 12 h. a Isolated yields.

9432 | RSC Adv., 2017, 7, 9431–9435
(entries 5, 7–12), and CuI showed the better catalytic efficiency than other Cu(i) salts with the 88% conversion (entries 5, 7 and 8). Furthermore, the temperature also played a decisive role in this system. As shown in Table 1 entries 13 to 17, trace conversion of N-sulfinyllimine was obtained at 120 °C or 100 °C, and the conversions at 80 °C, 40 °C and 25 °C were only 74%, 76% and 8%, respectively. Further investigation revealed that the ligand played a critical role in this copper-catalyzed transformation. Among the examined ligands such as L-proline, i-valine, β-alanine, i-histidine, sarcosine, glycine, phenylpropanamide and pyrrolidine, L-proline was the best (Table 1, entries 5, 18–24). Finally, control experiments showed that when CuI, TEMPO, L-proline or K$_2$CO$_3$ was omitted most substrates were recovered (entries 26–29), and quantitative conversion was obtained when 0.5 equiv. K$_2$CO$_3$ was used under the reaction conditions (Table 1, entry 25). Thus, the optimized reaction conditions (entry 25): substrates (1.0 mmol), TEMPO (5 mol%), K$_2$CO$_3$ (0.5 equiv.) at 60 °C with CuI (5 mol%) as catalyst and L-proline (5 mol%) as ligand were found.

With the optimized conditions in hand, various aromatic alcohols were subjected to the standard reaction conditions. As shown in Table 2, various aromatic alcohols and 4-toluene-sulfonamide were efficiently oxidative condensed into the corresponding N-sulfinylimines. The reaction was not only highly efficient but also showed excellent functional groups compatibility. A wide range of aromatic alcohols bearing electron-donating groups such as methyl and methoxy, or electron-withdrawing groups including halogen, nitro and trifluoromethyl substituents were converted into their corresponding N-sulfinylimines with good to excellent isolated yields (entries 1–16, 18, 21). Surprisingly, the efficient transformation of p-methylthiobenzyl alcohol and 4-toluensulfonamide into the desired product was observed without transformation to sulfoxide or sulfone (entry 5). In addition, it was worth noting that the sterically hindered alcohols also provided the corresponding N-sulfinylimines in 85–90% yields (entries 11–15). Gratifyingly, heteroaryl alcohols such as 2-thiophen and 2-furyl methanol were also well tolerated to give the desired products in 88–90% yields (entries 19–20). Unsaturated alcohol (entries 17) also reacted to form the imine in 93% isolated yield. Unfortunately, less active aliphatic alcohols and secondary alcohols were not suitable in the reaction.

Next, the compatibility of a variety of other sulfanilamides on this oxidative cascade reaction was examined, including tert-butanesulfonamide, bezenesulfanilamide and 4-chloro-bezenesulfanilamide, shown in Table 3. Good to excellent isolated yields were obtained for aromatic alcohols with electron-withdrawing (products 2, 4–6, 8, 10, 12, 15) and electron-donating (products 1, 3, 11, 13, 14) substituents. For aromatic alcohols bearing either ortho- (products 2, 3, 12) or meta- (product 14) substituents, the reactions proceeded smoothly and afforded N-sulfinylimines in good yields. In addition, allyl alcohols could also well tolerated under the optimal conditions in good isolated yields (entries 7, 8). However less active aliphatic alcohols and secondary alcohols could not afford the target products. In general, aromatic alcohols bearing electron-withdrawing substituents condensed more effectively with sulfanilamides than those bearing electron-donating substituents (product 6 vs. 1, product 12 vs. 11, product 15 vs. 13).

Finally, we turned our efforts to expand the scope of sulfanilamides (Table 4). Although the strong electron-withdrawing character of the sulfonamide group leads to very low nucleophilicity of the RSO$_2$NH$_2$ nitrogen (much lower than of

### Table 3 Scope of N-sulfinyl imines formation $^a$

| Product | Yield (%) |
|---------|-----------|
| (1) R = 3,4,5-OMe | 86 |
| (2) R = o-I | 80 |
| (3) R = o-OMe | 78 |
| (4) R = p-Br | 96 |
| (5) R = p-Cl | 95 |
| (6) R = p-NO$_2$ | 97 |
| (7) R = H | 92 |
| (8) R = p-NO$_2$ | 95 |
| (9) R = H | 91 |
| (10) R = p-Cl | 92 |
| (11) R = 3,4,5-OMe | 89 |
| (12) R = o-NO$_2$ | 95 |
| (13) R = 3,4-Me | 89$^c$ |
| (14) R = m-OMe | 90$^d$ |
| (15) R = p-F | 91$^d$ |

$^a$ Reaction conditions: substrates (1.0 mmol), CuI (5 mol%), L-proline (5 mol%), TEMPO (5 mol%), K$_2$CO$_3$ (0.5 equiv.), toluene (4.0 mL), 4 Å MS (700 mg), 60 °C. $^b$ Isolated yields. $^c$ Reaction time 15 h. $^d$ Reaction time 14 h. $^e$ Reaction time 13 h.

### Table 4 Scope of N-sulfonamide imines formation $^a$

| Product | Yield (%) |
|---------|-----------|
| (1) R = H | 93 |
| (2) R = p-Br | 91 |
| (3) R = 3,4,5-OMe | 89$^c$ |
| (4) R = H | 76 |
| (5) R = o-Me | 78 |
| (6) R = m-OMe | 81 |
| (7) R = p-NO$_2$ | 80 |
| (8) R = H | 87 |
| (9) R = p-NO$_2$ | 90 |
| (10) R = p-F | 89$^d$ |

$^a$ Reaction conditions: substrates (1.0 mmol), CuI (5 mol%), L-proline (5 mol%), TEMPO (5 mol%), K$_2$CO$_3$ (0.5 equiv.), toluene (4.0 mL), 4 Å MS (700 mg), 60 °C. $^b$ Isolated yields. $^c$ 1.2 equiv. of alcohol was used.
isolated yields, such as that the chiral sulfonamide was also suitable in our system.

Based on the above promising results and related published research studies, a plausible catalytic cycle for the aerobic oxidative cascade condensation (Scheme 4) was proposed. The reaction of L-proline, K$_2$CO$_3$ and CuI gave the carbonyl product and TEMPOH, and regenerate A, followed by the insertion of a sulfonamide or sulfonylimine to afford species F. Liberation of water from the F gave the product G.

Conclusions

In summary, an efficient and mild copper-catalyzed aerobic oxidative cascade system for the synthesis of N-sulfinyl- and N-sulfonyl-imines directly from aryl or alkyl alcohols with sulfonamides or sulfonamides in one pot has been successfully developed. Under the optimized conditions, a wide range of arylalcohols and various sulfonamides (including chiral tert-sulfonylimine) or sulfonamides were smoothly condensed into corresponding N-sulfinyl- or N-sulfonylimines with good to excellent isolated yields. Less active aliphatic alcohols and secondary alcohols were not suitable in the oxidative condensation system, unfortunately. What's more, this is the first example of copper-catalyzed aerobic oxidative cascade condensation for the formation of N-sulfinyl- and N-sulfonyl-imines from sulfonamides or sulfonamides with alcohols.

Acknowledgements

We acknowledge financial support from the National Natural Science Foundation of China (no. 20702051), the Natural Science Foundation of Zhejiang Province (LY13B020017) and the Key Innovation Team of Science and Technology in Zhejiang Province (no. 2010R50018).

Notes and references

1 (a) J. P. Begue, D. Bonnet-Delpon, B. Crousse and J. Legros, Chem. Soc. Rev., 2005, 34, 562; (b) S. M. Weinreb and R. K. Orr, Synthesis, 2005, 1205; (c) C. H. Senanakande, D. Krishnamurthy, Z. H. Lu, Z. Han and I. Gallou, Aldrichimica Acta, 2005, 38, 93; (d) P. Zhou, B. C. Chen and F. A. Davis, Tetrahedron, 2004, 60, 8003; (e) M. Gohain, Synlett, 2003, 2097; (f) J. A. Ellman, T. D. Owens and T. P. Tang, Acc. Chem. Res., 2002, 35, 984; (g) J. A. Ellman, Pure Appl. Chem., 2003, 75, 39; (h) F. A. Davis and B. C. Chen, Chem. Soc. Rev., 1998, 27, 13; (i) R. Bloch, Chem. Rev., 1998, 98, 1407; (j) D. Enders and U. Reinhold, Tetrahedron: Asymmetry, 1997, 8, 1895.

2 (a) T. Ooi, Y. Uematsu and K. Maruoka, J. Am. Chem. Soc., 2006, 128, 2548; (b) H. F. Duan, Y. X. Jia, L. X. Wang and Q. L. Zhou, Org. Lett., 2006, 8, 2567; (c) H. Fujisawa, E. Takahashi and T. Mukaiyama, Chem.-Eur. J., 2006, 12, 5082; (d) M. Shi, L. H. Chen and C. Q. Li, J. Am. Chem. Soc., 2005, 127, 3790; (e) T. Soeta, M. Kuriyama and K. Tomioka, J. Org. Chem., 2005, 70, 297; (f) T. Hayashi, M. Kawai and N. Tokunaga, Angew. Chem., Int. Ed., 2004, 43, 6125; (g) H. K. Yim and H. N. C. Wong, J. Org. Chem., 2004, 69, 2892; (h) P. Wipf, C. Kendall and C. B. J. Stephenson, J. Am. Chem. Soc., 2003, 125, 761; (i) V. K. Aggarwal, E. Alonso, M. Ferrara and S. E. Spey, J. Org. Chem., 2002, 67, 2335; (j) K. I. Yamada, H. Fujihara, Y. Yamamoto, Y. Miwa, T. Taga and K. Tomioka, Org. Lett., 2002, 4, 3509;
D. K. Wang, Y. G. Zhou, Y. Tang, X. L. Hou and L. X. Dai, J. Org. Chem., 1999, 64, 4233.

3 (a) O. G. Mancheno, R. G. Arrayas and J. C. Carretero, J. Am. Chem. Soc., 2004, 126, 456; (b) P. E. Morgan, R. McCague and A. Whiting, J. Chem. Soc., Perkin Trans. 1, 2000, 515; (c) S. Yao, M. Johannsen, R. G. Hazell and K. A. Jorgensen, Angew. Chem., Int. Ed., 1998, 37, 3121; (d) T. Bauer, S. Szymanski, A. Jezewski, P. Gluzinski and J. Jurczak, Tetrahedron: Asymmetry, 1997, 8, 2619; (e) J. Sisko and S. M. Weinreb, Tetrahedron Lett., 1989, 30, 3037; (f) D. L. Boiger, W. L. Corbett, T. T. Curran and A. M. Kasper, J. Am. Chem. Soc., 1991, 113, 1713.

4 (a) C. Ballatore, J. H. Soper, F. Piscielliteli, M. James, L. C. Huang, O. Atasoyulu, D. M. Huryn, J. Q. Trojanowski, V. M. Y. Lee, K. R. Brunden and A. B. Smith, J. Med. Chem., 2011, 54, 6969; (b) S. R. Malwal, D. Srim, P. Yogoesswari, V. B. Konkimmalla and H. Chakrapani, J. Med. Chem., 2012, 55, 553; (c) C. F. Supuran, A. Scozzafava and B. W. Clare, Med. Res. Rev., 2002, 22, 329; (d) M. V. Papadopoulou, W. D. Bloomer, H. S. Rosenzweig, E. Chatelain, M. Kaiser, S. R. Wilkinson, C. McKenzie and J. R. Ioset, J. Med. Chem., 2012, 55, 5554.

5 (a) R. Annunziata, M. Cinquini and F. Cozzi, J. Chem. Soc., Perkin Trans. 1, 1982, 339; (b) D. H. Hua, S. W. Miao, J. S. Chen and S. Iguchi, J. Org. Chem., 1991, 56, 4; (c) P. Moreau, M. Essiz, J. Y. Merour and D. Bouzard, Tetrahedron: Asymmetry, 1997, 8, 591; (d) K. Yang, R. Y. Chen, D. S. Lee, W. S. Peng, Y. Z. Jiang, A. Q. Mi and T. T. Jong, J. Org. Chem., 1994, 59, 914; (e) G. C. Liu, D. A. Cogan and J. A. Ellman, J. Am. Chem. Soc., 1997, 119, 9913; (f) F. A. Davis, R. E. Reddy, J. M. Szewczyk and P. S. Portonovo, Tetrahedron Lett., 1993, 34, 6229.

6 F. A. Davis, R. E. Reddy and R. T. Reddy, J. Org. Chem., 1992, 57, 6387.

7 (a) D. A. Cogan and J. A. Ellman, J. Am. Chem. Soc., 1999, 121, 268; (b) G. C. Liu, D. A. Cogan, T. D. Owens, T. P. Tang and J. A. Ellman, J. Org. Chem., 1999, 64, 1278.

8 (a) F. A. Davis, R. E. Reddy, J. M. Szewczyk, G. V. Reddy, P. S. Portonovo, H. Zhang, D. Fanelli, R. T. Reddy, P. Zhou and P. J. Carroll, J. Org. Chem., 1997, 62, 2555; (b) F. A. Davis, Y. Zhang, Y. Andemichael, T. Fang, D. L. Fanelli and H. Zhang, J. Org. Chem., 1999, 64, 1403; (c) D. L. Fanelli, J. M. Szewczyk, Y. Zhang, G. V. Reddy, D. M. Burns and F. A. Davis, Org. Synth., 1999, 77, 50.

9 Z. Y. Jiang, W. H. Chan and A. W. M. Lee, J. Org. Chem., 2005, 70, 1081.

10 (a) W. A. White and H. Weingarten, J. Org. Chem., 1967, 32, 213; (b) H. Weingarten, J. P. Chupp and W. A. White, J. Org. Chem., 1967, 32, 3246; (c) I. Moretti and G. Torre, Synthesis, 1970, 141; (d) W. B. Jennigs and C. J. Lovely, Tetrahedron Lett., 1988, 29, 3725.

11 J. H. Billman and K. M. Tai, J. Org. Chem., 1958, 23, 535.

12 X. F. Wu, C. V. L. Bray, L. Bechki and C. Darcel, Tetrahedron, 2009, 65, 7380.

13 J. T. Reeves, M. D. Visco, M. A. Marsini, N. Grinberg, C. A. Busacca, A. E. Mattson and C. H. Senanayake, Org. Lett., 2015, 17, 2442.

14 S. Higashibayashi, H. Tohmiya, T. Mori, K. Hashimoto and M. Nakata, Synlett, 2004, 457.

15 M. Ardej-Jakubisiak, R. Kawecki and A. Swietlinska, Tetrahedron: Asymmetry, 2007, 18, 2507.

16 Z. Huang, M. Zhang, Y. Wang and Y. Qin, Synlett, 2005, 1334.

17 S. Morales, F. G. Guijarro, J. L. G. Ruano and M. B. Cid, J. Am. Chem. Soc., 2014, 136, 1082.

18 K. M. Wang, Z. G. Xing, Y. D. Ma and Q. L. Wang, Catal. Lett., 2008, 123, 129.

19 For examples, see: (a) J. M. Hoover and S. S. Stahl, J. Am. Chem. Soc., 2011, 133, 16901; (b) J. E. Steves and S. S. Stahl, J. Am. Chem. Soc., 2013, 135, 15742; (c) M. S. Sigman and D. R. Jensen, Acc. Chem. Res., 2006, 39, 221; (d) G. F. Zhang, Y. Wang, X. Wen, C. R. Ding and Y. Li, Chem. Commun., 2012, 48, 2979; (e) C. Liu, S. Tang and A. W. Li, Chem. Commun., 2013, 49, 1324; (f) B. T. Guan, D. Xing, G. X. Cai, X. B. Wan, N. Yu, Z. Fang, L. P. Yang and Z. J. Shi, J. Am. Chem. Soc., 2005, 127, 18004; (g) H. Miyamura, R. Matsubara, Y. Miyazaki and S. Kobayashi, Angew. Chem., Int. Ed., 2007, 46, 4151; (h) B. Karimi and F. K. Esfahani, Adv. Synth. Catal., 2012, 354, 1319; (i) N. W. Wang, R. H. Liu, J. P. Chen and X. M. Liang, Chem. Commun., 2005, 5322; (j) W. L. Yin, C. H. Chu, Q. Q. Lu, J. W. Tao, X. M. Liang and R. H. Liu, Adv. Synth. Catal., 2010, 352, 113; (k) N. Ji and A. J. Ragauskas, Org. Lett., 2005, 7, 3689; (l) G. Yang, W. Zhu, P. Zhang, H. Xue, W. Wang, J. Tian and M. Song, Adv. Synth. Catal., 2008, 350, 542; (m) N. Ji, D. Vinci, C. L. Liotta, C. A. Eckert and A. J. Ragauskas, Ind. Eng. Chem. Res., 2008, 47, 627; (n) N. Ji and A. J. Ragauskas, ChemSusChem, 2008, 1, 823; (o) P. J. Figiel, A. M. Kirillov, Y. Y. Karabach, M. N. Kopylovich and A. J. L. Pombeiro, J. Mol. Catal. A: Chem., 2009, 305, 178; (p) L. Liang, G. Rao, H. L. Sun and J. L. Zhang, Adv. Synth. Catal., 2010, 352, 2371; (q) N. Mase, T. Mizumori and Y. Tatemoto, Chem. Commun., 2011, 47, 2086; (r) G. F. Zhang, X. W. Han, Y. Luan, Y. Wang, X. Wen and C. R. Ding, Chem. Commun., 2013, 49, 7908.

20 R. Patel, V. P. Srivastava and L. D. S. Yadav, Adv. Synth. Catal., 2010, 352, 1610.

21 (a) J. M. Hoover, B. L. Ryland and S. S. Stahl, J. Am. Chem. Soc., 2013, 135, 2357; (b) N. J. Hill, J. M. Hoover and S. S. Stahl, J. Chem. Educ., 2013, 90, 102.