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Construction of seven- and eight-membered carbocycles by Lewis acid catalyzed C(sp<sup>3</sup>)–H bond functionalization<sup>†</sup>

Yuna Otawa and Keiji Mori 🕩 \*

We achieved a concise construction of seven- and eight-membered carbocycles *via* Lewis acid catalyzed  $C(sp^3)$ -H bond functionalization. In these reactions, a quite rare [1,6 (or 7)]-hydride shift/cyclization process proceeded smoothly to afford seven- and eight-membered carbocycles with good chemical yields starting from substrates with high conformational freedom.

The construction of seven-membered or larger carbocycles is a major research topic in modern synthetic organic chemistry. Because of their utility in pharmaceuticals and agrochemicals as well as the difficulty of the construction due to ring strain and entropic reasons, many organic chemists have devoted much time and effort to the development of an effective method for the synthesis of this class of skeleton.<sup>1</sup> Such strategies as ring-closing metathesis (RCM),<sup>2</sup> intramolecular cyclization reaction,<sup>3</sup> [5+2]- and [4+3]-cycloaddition reactions,<sup>4</sup> and ring expansion reaction<sup>5</sup> have been developed. Among them, the intramolecular cyclization reaction is the simplest strategy for the construction of the target structure. Most of the reported methods require relatively dilute conditions (lower than 0.05 M) and special precautions (e.g., dropwise addition of substrate) to suppress unwanted intermolecular reactions, thereby decreasing the practicality of the synthesis. Thus, the achievement of a cyclization reaction for the construction of a carbocyclic skeleton using a simple operation and non-high dilution conditions is not a trivial issue, and there is a strong demand for the development of a novel and effective method.

Recently, our group has been focusing on the development of novel  $C(sp^3)$ –H bond functionalization methods that involve hydride shift-triggered  $C(sp^3)$ –H bond functionalization, namely, the "internal redox process".<sup>6–12</sup> A notable feature of this method is its high synthetic utility: various complex cyclic structures could be constructed using this method. Not only six-membered

ring heterocycles,<sup>7–12</sup> but also five- and seven-membered ring heterocycles<sup>13,14</sup> could be synthesized by the [1,n (n = 4, 5, or 6)]-hydride shift/cyclization process. These reactions have two important characteristics: the reactions can be performed under normal reaction concentrations (higher than 0.1 M is acceptable) and occur intramolecularly. We envisioned that these characteristics would lead to a novel synthetic method for the construction of seven-membered or larger carbocycles without special precautions.

We describe herein a positive answer to this assumption, achieving the concise construction of seven- and eight-membered carbocycles *via* [1,n]-hydride shift triggered C(sp<sup>3</sup>)–H bond functionalization (n = 6 or 7). When a solution of benzylidene malonates having an alkylpropyl ether moiety at the *ortho*-position in ClCH<sub>2</sub>CH<sub>2</sub>Cl was treated with a catalytic amount of Sc(OTf)<sub>3</sub>, the desired [1,6]-hydride shift/cyclization process proceeded smoothly to afford seven-membered carbocycles in good chemical yields. Interestingly, a synthetically difficult, eight-membered ring formation was also attainable by the [1,7]-hydride shift/cyclization process starting from benzylidene malonates having an alkylbutyl ether moiety (Scheme 1).

The results of screening for the reaction conditions are illustrated in Table 1. At first, a solution of benzylidene malonate 3a having an *O*-benzylpropyl ether moiety in ClCH<sub>2</sub>CH<sub>2</sub>Cl was treated with 5 mol% of Sc(OTf)<sub>3</sub>, which has shown excellent catalytic performance



**Scheme 1** Formation of seven- and eight-membered carbocycles by [1,n (n = 6, or 7)]-hydride shift triggered C(sp<sup>3</sup>)-H functionalization.

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Department of Applied Chemistry, Graduate School of Engineering, Tokyo University of Agriculture and Technology, 2-24-16 Nakacho, Koganei, Tokyo 184-8588, Japan. E-mail: k\_mori@cc.tuat.ac.jp; Fax: +81-42-388-7034; Tel: +81-42-388-7034

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<sup>a</sup> Unless otherwise noted, all reactions were conducted with 0.10 mmol of 3a in the presence of an acid catalyst (30 mol%) in ClCH<sub>2</sub>CH<sub>2</sub>Cl (1.0 mL) at refluxing temperature. <sup>b</sup> Isolated yield. <sup>c</sup> In CH<sub>3</sub>CN. <sup>d</sup> In toluene. <sup>e</sup> In *o*-xylene at 120 °C.  $^{f}$  In MeOH.  $^{g}$  The reaction was conducted under 0.50 M.  $^{h}$  0.89 mmol scale.

in most of the internal redox reactions we have reported.8 Gratifyingly, the desired reaction proceeded smoothly to give desired seven-membered carbocycle 4a in good chemical yield (75%, entry 1). Whereas Yb(OTf)<sub>3</sub> and Hf(OTf)<sub>4</sub> exhibited good catalytic performance (50% and 49% yields, respectively, entries 2 and 3), only the recovery of 3a was observed with  $Gd(OTf)_3$  (87%, entry 4). Both  $Mg(OTf)_2$  and  $Zn(OTf)_2$  were ineffective (entries 5 and 6). Versatile strong Lewis acids, such as TiCl<sub>4</sub> and SnCl<sub>4</sub>, promoted the reaction effectively, but the chemical yields remained moderate (40% and 55%, respectively, entries 7 and 8). The chemical yield of 4a when TfOH (strong Brønsted acid) was used was only 30%, which clearly indicated that Lewis acids were the effective acid catalysts in this reaction (entry 9).

Solvent screening was conducted with Sc(OTf)<sub>3</sub> as the optimal catalyst, and the results suggested that ClCH<sub>2</sub>CH<sub>2</sub>Cl was the solvent of choice (entries 10-13). In the case of CH<sub>3</sub>CN, the reaction did not reach completion even with a long reaction time (4a: 38%, 3a: 17%, and 51 h, entry 10). Complete consumption of 3a was observed in some aromatic solvents, such as toluene and o-xylene; however, the chemical yields of 4a remained moderate (56% and 41%, respectively, entries 11 and 12). Desired compound 4a was not obtained at all when MeOH was employed as the reaction medium (entry 13).

It should be noted that a high reaction concentration (0.50 M) was acceptable, affording 4a in good chemical yield (60%, entry 14). A scale-up reaction (0.89 mmol) resulted in the formation of 4a without sacrificing the chemical yield (66%, entry 15), which clearly indicates the high practicability of the present reaction.

With the optimized reaction conditions determined, the substrate scope of this reaction was examined (Fig. 1). At first,



the substituent effect on the aromatic ring was investigated, which suggested that various substituents were acceptable in this reaction. Seven-membered ring adducts 4b-h with electron-donating groups (Me and OMe) and an electron-withdrawing group (F) were obtained in good chemical yields (53-72%).15 This reaction was applicable to the formation of seven-membered carbocycle 4i with a naphthalene core (65% yield). The substituent on the oxygen atom was not limited to a benzyl group: both allyl and ethyl ether derivatives also promoted the reaction effectively.

Further examination revealed that the formation of eightmembered carbocycle 6a by way of the [1,7]-hydride shift process was also possible by employing benzylidene malonate 5a having an O-benzylbutyl ether moiety. The desired [1,7]-hydride/cyclization process proceeded smoothly even with a low catalytic amount of Sc(OTf)<sub>3</sub> (5 mol%), and corresponding eight-membered ring adduct 6a was obtained in good chemical yield (56%). Actually, there was a report on C(sp<sup>3</sup>)-H bond functionalization involving a [1,7]-hydride shift.<sup>16</sup> However, this process was only observed in relatively reactive substrates with an adjacent nitrogen atom and in conformationally constrained substrates with a biphenyl linkage. To the best of our knowledge, the present reaction is the first example of [1,7]-hydride shift involved C(sp<sup>3</sup>)-H bond functionalization starting from a less reactive substrate without a nitrogen atom, and a substrate with high conformational freedom. The substrate scope for this process was sufficiently wide, as shown in Fig. 2. Eight-membered carbocycles 6b-e with various substituents on the aromatic ring and ethyl-ether type product 6f were obtained in moderate to good chemical yields (45-82%).

Deuterium labeling experiments were conducted to clarify the mechanism of both reactions (Scheme 2). Observation of the primary kinetic isotope effect in both cases  $(k_{\rm H}/k_{\rm D} = 2.0 \text{ for } [1,6])$ hydride shift and  $k_{\rm H}/k_{\rm D}$  = 2.3 for [1,7]-hydride shift) suggested that the hydride shift process was the rate-determining step, like most of the internal redox reactions reported so far.8-14

The products thus obtained could be transformed into various related molecules, as shown in Scheme 3. Removal of







Scheme 2 Kinetic studies.



Scheme 3 Transformation from adduct 4a.

the pendant benzyl group was attainable under hydrogenation conditions (H<sub>2</sub>, Pd/C, AcOH, and MeOH) to give alcohol 7 in 68% yield. Reduction of the two ester moieties followed by acetonide formation afforded synthetically interesting spiro compound **8** (32%, 2 steps). The synthesis of seven-membered carbocycle containing  $\alpha$ , $\beta$ -unsaturated ester moiety **9** was also achieved in 73% chemical yield by the treatment with LiCl in DMSO.

In summary, we have developed a concise synthetic route to seven- and eight-membered carbocycles *via*  $Sc(OTf)_3$ -catalyzed  $C(sp^3)$ -H bond functionalization. This reaction could be performed by following a simple procedure (only mixing the substrate and the acid catalyst) and using a high reaction concentration (0.50 M), and is applicable to the synthesis of several kinds of seven- and eight-membered carbocycles with various substituents on the aromatic ring. Deuterium labeling experiments revealed that the hydride shift process is the ratedetermining step. Further investigation of the synthesis of more complex, medium-sized carbocycles by the hydride shift/ cyclization is under way.

## Conflicts of interest

There are no conflicts of interest.

## Notes and references

- Selected reviews on the synthesis of medium sized rings, see:
   (a) G. A. Molander, Acc. Chem. Res., 1998, 31, 603; (b) A. Deiters and R. Martin, Chem. Rev., 2005, 104, 2199; (c) I. Shiina, Chem. Rev., 2007, 107, 239; (d) T. V. Nguyen, J. M. Hartmann and D. Enders, Synthesis, 2013, 845; (e) Y. Wang and Z.-W. Yu, Acc. Chem. Res., 2015, 48, 2288; (f) K. T. Mortensen, T. J. Osberger, T. A. King, H. F. Sore and D. R. Spring, Chem. Rev., 2019, 119, 10288.
- Selected examples, see: (a) I. Hanna and L. Ricard, Org. Lett., 2000, 2, 2651; (b) K. Nakashima, K. Inoue, M. Sono and M. Tori, J. Org. Chem., 2002, 67, 6034; (c) B. Shi, N. A. Hawryluk and B. B. Snider, J. Org. Chem., 2003, 68, 1030; (d) D. J. Kerr, A. C. Willis and B. L. Flynn, Org. Lett., 2004, 6, 457; (e) S. F. Oliver, K. Högenauer, O. Simic, A. Antonello, M. D. Smith and S. V. Ley, Angew. Chem., Int. Ed., 2003, 42, 5996; (f) F. D. Boyer and I. Hanna, Eur. J. Org. Chem., 2008, 4938; (g) T. Ohyoshi, S. Funakubo, Y. Miyazawa, K. Niida, I. Hayakawa and H. Kigoshi, Angew. Chem., Int. Ed., 2012, 51, 4972.
- Selected examples, see: (a) M. Mandal, H. Yun, G. B. Dudley, S. Lin, D. S. Tan and S. J. Danishefsky, J. Org. Chem., 2005, 70, 10619; (b) M. Reiter, S. Torssell, S. Lee and D. W. C. MacMillan, Chem. Sci., 2010, 1, 37; (c) R. A. Taj and J. R. Green, J. Org. Chem., 2010, 75, 825; (d) K. C. Nicolaou, H. Ding, J.-A. Richard and D. Y. K. Chen, J. Am. Chem. Soc., 2010, 132, 3815; (e) N. Kanoh, K. Sakanishi, E. Iimori, K. Nishimura and Y. Iwabuchi, Org. Lett., 2011, 13, 2864; (f) F. J. Pulido, A. Barbero and P. Castreno, J. Org. Chem., 2011, 76, 5850; (g) F. J. Pulido, A. Barbero, P. Val, A. Diez and A. González-Ortega, Eur. J. Org. Chem., 2012, 5350.
- 4 Selected examples, see: (a) J. C. Lee and J. K. Cha, J. Am. Chem. Soc., 2001, 123, 3243; (b) K. Lee and J. K. Cha, J. Am. Chem. Soc., 2001, 123, 5590; (c) N. Iwasawa, M. Shido and H. Kusama, J. Am. Chem. Soc., 2001, 123, 5814; (d) J. Huang and R. P. Hsung, J. Am. Chem. Soc., 2005, 127, 50; (e) K. Ishida, H. Kusama and N. Iwasawa, J. Am. Chem. Soc., 2010, 132, 8842; (f) D. Garayalde, K. Kruger and C. Nevado, Angew. Chem., Int. Ed., 2011, 50, 911; (g) N. Z. Burns, M. R. Witten and E. N. Jacobsen, J. Am. Chem. Soc., 2011, 133, 14578; (h) M. G. Nilson and R. L. Funk, J. Am. Chem. Soc., 2011, 133, 12451; (i) X. Xum, P. Liu, Z.-Z. Shu, W. Tang and K. N. Houk, J. Am. Chem. Soc., 2012, 135, 9271; (j) H. Faustino, I. Alonso, J. L. Mascareñas and F. López, Angew. Chem., Int. Ed., 2013, 52, 6526; (k) M. R. Witten and E. N. Jacobsen, Angew. Chem., Int. Ed., 2014, 53, 5912; (l) P. A. Wender, F. Inagaki, M. Pfaffenbach and M. C. Stevens, Org. Lett., 2014, 16, 2923; (m) Y. Li and M. Dai, Angew. Chem., Int. Ed., 2017, 56, 11624; (n) X. Di, Y. Wang, L. Wu, Z.-M. Zhang, Q. Dai, W. Li and J. Zhang, Org. Lett., 2019, 21, 3018.
- 5 (a) Y.-S. Do, R. Sun, H. J. Kim, J. E. Yeo, S.-H. Bae and S. Koo, J. Org. Chem., 2009, 74, 917; (b) E. Alvarez-Manzaneda, R. Chahboun, E. Alvarez, M. J. Cano, A. Haidour and R. Alvarez-Manzaneda, Org. Lett., 2010, 12, 4450; (c) E. Elamparuthi, C. Fellay, M. Neuburger and K. Gademann, Angew. Chem., Int. Ed., 2012, 51, 4071; (d) J. Zhao, J. Liu, X. Xie, S. Li and Y. Liu, Org. Lett., 2015, 17, 5926. Synthesis of polycycles containing middle sized rings, see: (e) J. E. Hall, J. V. Matlock, J. W. Ward, K. V. Gray and J. Clayden, Angew. Chem., Int. Ed., 2016, 55, 11153; (f) T. C. Stephen, M. Lodi, A. M. Steer, Y. Lin, M. T. Gill and W. P. Unsworth, Chem. Eur. J., 2017, 23, 13314; (g) R. Mendoza-Sanchez, V. B. Corless, Q. N. N. Ngyuyen, M. Bergeron-Brlek, J. Frost, S. Adchi, D. J. Tantillo and A. K. Yudin, Chem. Eur. J., 2017, 23, 13319; (h) J. E. Hill, J. V. Matlock, Q. Lefebvre, K. G. Cooper and J. Clayden, Angew. Chem., Int. Ed., 2018, 57, 5788.
- 6 For recent reviews on C-H activation, see: (a) K. Godula and D. Sames, *Science*, 2006, 312, 67; (b) D. Alberico, M. E. Scott and M. Lautens, *Chem. Rev.*, 2007, 107, 174; (c) H. M. L. Davies and J. R. Manning, *Nature*, 2008, 451, 417; (d) X. Chen, K. M. Engle, D.-H. Wang and J.-Q. Yu, *Angew. Chem., Int. Ed.*, 2009, 48, 5094;

(e) T. W. Lyons and M. S. Sanford, Chem. Rev., 2010, 110, 1147;
(f) H. M. L. Davies, J. Du Bois and J.-Q. Yu, Chem. Soc. Rev., 2011, 40, 1855;
(g) T. Brückl, R. D. Baxter, Y. Ishihara and P. S. Baran, Acc. Chem. Res., 2012, 45, 826;
(h) H. M. L. Davies and D. Morton, J. Org. Chem., 2016, 81, 343. See also, highlight on visible-light photocatalysis: X.-Q. Hu, J.-R. Chen and W.-J. Xiao, Angew. Chem., Int. Ed., 2017, 56, 1960.

- 7 For recent reviews on internal redox processes, see: (a) M. Tobisu and N. Chatani, Angew. Chem., Int. Ed., 2006, 45, 1683; (b) M. Wang, ChemCatChem, 2013, 5, 1291; (c) B. Peng and N. Maulide, Chem. Eur. J., 2013, 19, 13274; (d) L. Wang and J. Xiao, Adv. Synth. Catal., 2014, 356, 1137; (e) M. C. Haibach and D. Seidel, Angew. Chem., Int. Ed., 2014, 53, 5010; (f) S. J. Kwon and D. Y. Kim, Chem. Rec., 2016, 16, 1191; (g) M. Xiao, S. Zhu, Y. Shen, L. Wang and J. Xiao, Chin. J. Org. Chem., 2018, 38, 328.
- 8 For the internal redox reaction developed by our group, see: (a) K. Mori, Y. Ohshima, K. Ehara and T. Akiyama, Chem. Lett., 2009, 38, 524; (b) K. Mori, T. Kawasaki, S. Sueoka and T. Akiyama, Org. Lett., 2010, 12, 1732; (c) K. Mori, S. Sueoka and T. Akiyama, J. Am. Chem. Soc., 2011, 133, 2424; (d) K. Mori, S. Sueoka and T. Akiyama, Chem. Lett., 2011, 40, 1386; (e) K. Mori, K. Ehara, K. Kurihara and T. Akiyama, J. Am. Chem. Soc., 2011, 133, 6166; (f) K. Mori, T. Kawasaki and T. Akiyama, Org. Lett., 2012, 14, 1436; (g) K. Mori, K. Kurihara and T. Akiyama, Chem. Commun., 2014, 50, 3729; (h) K. Mori, N. Umehara and T. Akiyama, Adv. Synth. Catal., 2015, 357, 901; (i) T. Yoshida and K. Mori, Chem. Commun., 2017, 53, 4319; (j) M. Machida and K. Mori, Chem. Lett., 2018, 47, 868; (k) K. Yokoo and K. Mori, Chem. Commun., 2018, 54, 6927; (1) N. Hisano, Y. Kamei, Y. Kansaku, M. Yamanaka and K. Mori, Org. Lett., 2018, 20, 4223; (m) T. Yoshida and K. Mori, Chem. Commun., 2018, 54, 12686; (n) R. Tamura, E. Kitamura, R. Tustsumi, M. Yamanaka, T. Akiyama and K. Mori, Org. Lett., 2019, 21, 2383.
- 9 For the double C(sp<sup>3</sup>)-H bond functionalization by sequential utilization of the internal redox reaction developed by our group, see: (a) K. Mori, K. Kurihara, S. Yabe, M. Yamanaka and T. Akiyama, *J. Am. Chem. Soc.*, 2014, **136**, 3744; (b) K. Mori, N. Umehara and T. Akiyama, *Chem. Sci.*, 2018, **9**, 7327; (c) K. Mori, R. Isogai, Y. Kamei, M. Yamanaka and T. Akiyama, *J. Am. Chem. Soc.*, 2018, **140**, 6203.
- 10 These types of reactions are classified as "tert-amino effect." For reviews, see: (a) O. Meth-Cohn and H. Suschitzky, Adv. Heterocycl. Chem., 1972, 14, 211; (b) W. Verboom and D. N. Reinhoudt, Recl. Trav. Chim. Pays-Bas, 1990, 109, 311; (c) O. Meth-Cohn, Adv. Heterocycl. Chem., 1996, 65, 1; (d) P. Mátyus, O. Éliás, P. Tapolcsányi, Á. Polonka-Bálint and B. Halász-Dajka, Synthesis, 2006, 2025.
- 11 For selected examples of the internal redox reactions, see: (a) S. J. Pastine, K. M. McQuaid and D. Sames, J. Am. Chem. Soc., 2005, 127, 12180; (b) S. J. Pastine and D. Sames, Org. Lett., 2005, 7, 5429; (c) C. Zhang, C. Kanta De, R. Mal and D. Seidel, J. Am. Chem. Soc., 2008, 130, 416; (d) C. Zhang, S. Murarka and D. Seidel, J. Org. Chem., 2009, 74, 419; (e) K. M. McQuaid and D. Sames, J. Am. Chem. Soc., 2009, 131, 402; (f) J. C. Ruble, A. R. Hurd, T. A. Johnson, D. A. Sherry, M. Barbachyn, R. P. L. Toogood, G. L. Bundy, D. R. Graber and G. M. Kamilar, J. Am. Chem. Soc., 2009, 131, 3991; (g) K. M. McQuaid,

- J. Z. Long and D. Sames, Org. Lett., 2009, 11, 2972; (h) I. D. Jurberg,
  B. Peng, E. Wöstefeld, M. Wasserloos and N. Maulide, Angew. Chem., Int. Ed., 2012, 51, 1950; (i) Y.-Y. Han, W.-Y. Han, X.-M. Zheng and W.-C. Yuan, Org. Lett., 2012, 14, 4054; (j) P. A. Vadpla, I. Carrea and D. Sames, J. Org. Chem., 2012, 77, 6689; (k) X. Gao, V. Gaddam, E. Altenhofer, R. R. Tata,
  Z. Cai, N. A. Yongpruksa, K. Garimallaprabhakaran and M. Harmata, Angew. Chem., Int. Ed., 2012, 51, 7016; (l) D.-F. Chen, Z.-Y. Han, Y.-P. He,
  J. Yu and L.-Z. Gong, Angew. Chem., Int. Ed., 2012, 51, 12307; (m) K. Eamakumar, T. Maji, J. J. Partridge and J. A. Tunge, Org. Lett., 2017, 19, 4014; (n) S. Wang, X. D. An, S. S. Li, X. Liu, Q. Liu and J. Xiao, Chem. Commun., 2018, 54, 13833; (o) S.-S. Li, S. Zhu, C. Chen, K. Duan,
  Q. Liu and J. Xiao, Org. Lett., 2019, 21, 1058; (p) S. Zhao, X. Wang,
  P. Wang, G. Wang, W. Xhao, X. Tang and M. Guo, Org. Lett., 2019, 21, 3990; (q) A. Paul and D. Seidel, J. Am. Chem. Soc., 2019, 141, 8778.
- 12 For examples of the enantioselective internal redox reactions, see: (a) S. Murarka, I. Deb, C. Zhang and D. Seidel, J. Am. Chem. Soc., 2009, 131, 13226; (b) Y. K. Kang, S. M. Kim and D. Y. Kim, J. Am. Chem. Soc., 2010, 132, 11847; (c) W. Cao, X. Liu, W. Wang, L. Lin and X. Feng, Org. Lett., 2011, 13, 600; (d) G. Zhou, F. Liu and J. Zhang, Chem. – Eur. J., 2011, 17, 3101; (e) Y.-P. He, Y.-L. Du, S.-W. Luo and L. Z. Gong, Tetrahedron Lett., 2011, 52, 7064; (f) L. Chen, L. Zhang, Z. Lv, J.-P. Cheng and S. Luo, Chem. – Eur. J., 2012, 18, 8891; (g) Z.-W. Jiao, S.-Y. Zhang, C. He, Y.-Q. Tu, S.-H. Wang, F.-M. Zhang, Y.-Q. Zhang and H. Li, Angew. Chem., Int. Ed., 2012, 51, 8811; (h) Y. K. Kang and D. Y. Kim, Adv. Synth. Catal., 2013, 355, 3131; (i) Y. K. Kang and D. Y. Kim, Chem. Commun., 2014, 50, 222; (j) C. W. Suh and D. Y. Kim, Org. Lett., 2014, 16, 5374; (k) W. Cao, X. Liu, J. Guo, L. Lin and X. Feng, Chem. – Eur. J., 2015, 21, 1632. See also, ref. 8e and 9c.
- 13 For examples of the internal redox reactions for the formation of five-membered heterocycles, see: (a) D. N. Reinhoudt, G. W. Visser, W. Verboom, P. H. Benders and M. L. M. Pennings, J. Am. Chem. Soc., 1983, 105, 4775; (b) W. Verboom, D. N. Reinhoudt, R. Visser and S. Harkema, J. Org. Chem., 1984, 49, 269; (c) B. De Boeck, S. Jiang, Z. Janousek and H. G. Viehe, Tetrahedron, 1994, 50, 7075; (d) B. De Boeck, Z. Janousek and H. G. Viehe, Tetrahedron, 1995, 51, 13239; (e) X. Che, L. Sheng, Q. Dang and X. Bai, Synlett, 2008, 2373; (f) S. Yang, Z. Li, X. Jian and C. He, Angew. Chem., Int. Ed., 2009, 48, 3999; (g) P. A. Vadola and D. Sames, J. Am. Chem. Soc., 2009, 131, 16525; (h) M. Alajarin, M. Martin-Luna and A. Vidal, Adv. Synth. Catal., 2011, 353, 557; (i) A. P. Gorulya, A. V. Tverdokhlebov, A. A. Tolmachev, O. V. Shishkin and S. V. Shinshikina, Tetrahedron, 2011, 67, 1030. See also, ref. 8l and 9a.
- 14 For examples of the internal redox reactions for the formation of seven-membered heterocycles, see: (a) A. A. Földi, K. Ludányi, A. C. Bényei and P. Mátyus, *Synlett*, 2010, 2109; (b) G. Zhou and J. Zhang, *Chem. Commun.*, 2010, 46, 6593; (c) Y.-Z. Li, M.-L. Zhao, W.-F. Chang, X. Wen, H. Sun and Q.-L. Xu, *J. Org. Chem.*, 2015, 80, 9620; (d) C. W. Suh, S. J. Kwon and D. Y. Kim, *Org. Lett.*, 2017, 19, 1334; (e) S.-S. Li, L. Zhou, L. Wang, H. Zhao, L. Yu and J. Xiao, *Org. Lett.*, 2018, 20, 138. See also, ref. 9a.
- 15 CCDC 1953402 contains the supplementary crystallographic data of **4c**†.
- 16 A. Polonka-Bálint, C. Saraceno, K. Ludányi, A. Bényei and P. Mátyus, *Synlett*, 2008, 2846.