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Synthetic Methods

Synthesis of Oxazolidin-2-ones by Oxidative Coupling of Isonitriles, Phenyl Vinyl Selenone, and Water

Thomas Buyck, Delphine Pasche, Qian Wang, and Jieping Zhu*[a]

Abstract: Reaction of alkyl isocyanides, phenyl vinyl selenone, and water in the presence of a catalytic amount of Cs_2CO_3 afforded oxazolidin-2-ones in good yields. This unprecedented heteroannulation process created four chemical bonds in a single operation with the isocyano group acting formally as a polarized double bond and phenyl vinyl selenone as a latent 1,3-dipole. The phenylselenonyl group played a triple role as an electron-withdrawing group to activate the 1,4-addition, a leaving group, and a latent oxidant in this transformation.

Oxazolidinones are of great importance as chiral auxiliaries in organic chemistry[1] and as pharmacophores in medicinal chemistry.[2] This 5-membered heterocycle, as illustrated by the marketed antibiotic linezolid (**1**; Figure 1), is a key structural

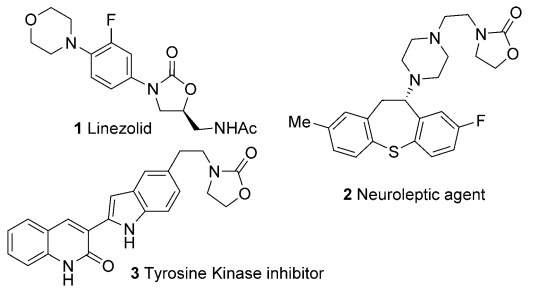
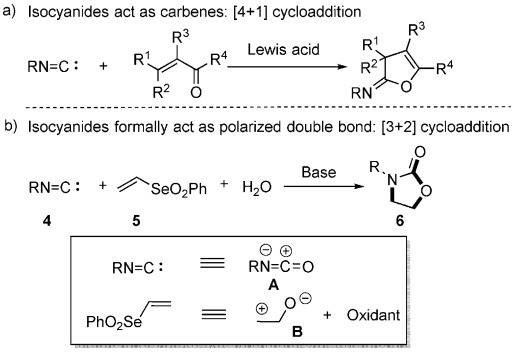


Figure 1. Bioactive molecules containing oxazolidin-2-one.

unit of a new class of antibacterial agents active against vancomycin-resistant *enterococci* (VRE).[2] In addition, converting a primary amine to N-substituted oxazolidin-2-one is a common practice in drug development endeavors in order to improve the activity profile of drug candidates; indeed, this structural motif is found in many bioactive compounds, such as neuroleptic agent **2**[3] and tyrosine kinase inhibitor **3** (Figure 1).[4] Among many known synthetic methods,[5] the 5-*exo*-trig cyclization of allylic carbamate and carbonylation of β-aminoalcohols are the most popular ones.

Numerous isonitrile-based organic transformations have been developed in the past decades, most of them being triggered by an α-addition of the divalent carbon to both nucleophiles and electrophiles.[6] As a consequence, the isocyano group acts generally as a one-carbon synthon in cycloaddition processes (Scheme 1 a).[7,8] In connection with our ongoing research program aimed at exploiting unconventional reactivity of the isocyano group,[9] we uncovered serendipitously a base-catalyzed heteroannulation reaction between isonitriles **4** and phenyl vinyl selenone (**5**)[10] leading to N-alkylated oxazolidinones **6** (Scheme 1 b). One C–N, two C–O, and one C=O bonds were created in this unprecedented transformation with the isocyano group acting formally as a polarized double bond (**A**) and phenyl vinyl selenone as a latent 1,3-dipole (**B**).[11] The phenylselenonyl group served as an electron-withdrawing group to activate the 1,4-addition, a leaving group, and a latent oxidant in this transformation.[12]



Scheme 1. Synthesis of oxazolidinones.

The reaction between benzyl isonitrile (**4a**) and phenyl vinyl selenone (**5**) was initially investigated. In the presence of a catalytic amount of cesium hydroxide monohydrate, the reaction between **4a** and **5** in *tert*-butanol at room temperature afforded unexpectedly oxazolidinone **6a** in about 20% yield (Table 1, entry 1). Realizing the synthetic potential of this transformation, the reaction conditions were systematically surveyed. This allowed us to conclude the following optimum conditions: Cs_2CO_3 (0.1 equiv), CH_2Cl_2 (ca. 0.5 M), H_2O (1.0 equiv), 40 °C. Under these conditions, the reaction of **4a** (1.1 equiv) with **5** (1.0 equiv) and water furnished oxazolidinone **6a** in 73% isolated yield (entry 6). The yield is excellent considering that four

[a] *Dr. T. Buyck, D. Pasche, Dr. Q. Wang, Prof. Dr. J. Zhu*
Laboratory of Synthesis and Natural Products
école Polytechnique Fédérale de Lausanne
EPFL-SB-ISIC-LSPN, BCH 5304, 1015 Lausanne (Switzerland)
E-mail: Jieping.zhu@epfl.ch
Homepage: http://lspn.epfl.ch

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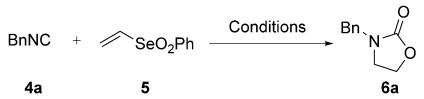
Table 1. Optimization of the reaction conditions.

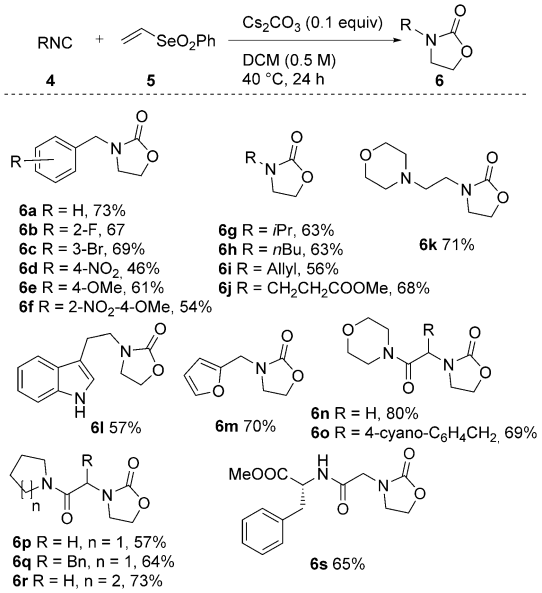


Entry	Conditions	Yield [%][a]
1	*t*BuOH (0.1 M), CsOH (0.2 equiv), RT	20
2	*t*BuOH (0.1 M), Cs_2CO_3 (0.2 equiv), RT	22
3	acetonitrile (0.1 M), Cs_2CO_3 (0.2 equiv), 40 °C	51
4	CH_2Cl_2 (0.1 M), Cs_2CO_3 (0.2 equiv), 40 °C	61
5	CH_2Cl_2 (0.1 M), $PhSeO_2H$ (0.2 equiv), 40 °C	43
6[b]	CH_2Cl_2 (0.5 M), Cs_2CO_3 (0.1 equiv), 40 °C	78 (73)[c]
7	CH_2Cl_2 (0.5 M), Cs_2CO_3 (0.1 equiv), 40 °C, CuOAc (0.1 equiv)	49

[a] NMR yield using trimethoxybenzene as an internal standard. [b] Anhydrous conditions with H_2O (1.0 equiv) added. [c] Isolated yield.

chemical bonds are created in this domino process. The average yield per chemical bond formation is therefore over 92%. We noted that addition of $Cu(OAc)_2$ to the reaction mixture is detrimental to the synthetic efficiency of the reaction (entry 7).

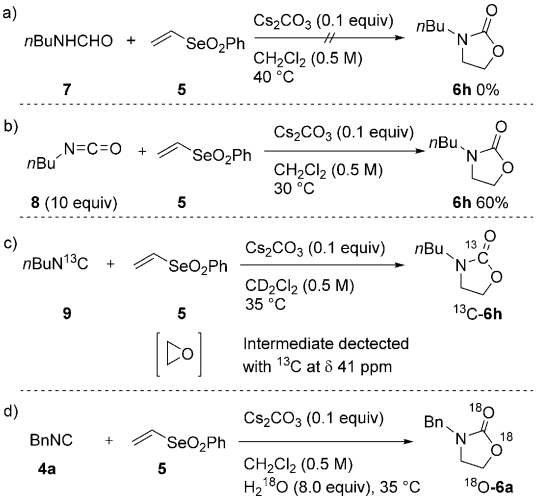
The scope of this novel transformation was next examined. Derivatives of benzyl isocyanide, regardless of the electronic properties and the position of the substituents, participated in this reaction (Scheme 2, **6a**–**6f**). Even the 4-nitrobenzyl isocyanide containing acidic benzylic protons reacted with **5** to furnish **6d** in 46% yield. Alkyl isonitriles, including isopropyl and functionalized ones (allyl and $MeOOCCH_2CH_2$), were converted to the corresponding oxazolidinones (**6g**–**6j**) in good yields. The presence of heterocycles, such as indole and furan, were well tolerated. The reaction was successfully extended to α-isocyanoacetamides leading to the corresponding oxazolidinones in good yields (**6n**–**6r**). Dipeptide-derived oxazolidinone **6s** was also accessible without erosion of the enantiopurity. The



Scheme 2. Scope of the oxazolidinone synthesis.

successful synthesis of **6n**–**6r** indicated that the nitrilium intermediate, generally associated with isocyanide chemistry, is not involved in this transformation. Had this been the case, oxazoles would be inevitably produced from the isocyanoacetamide.[13] Attempts to use α- or β-substituted phenyl vinyl selenones were nevertheless unsuccessful.

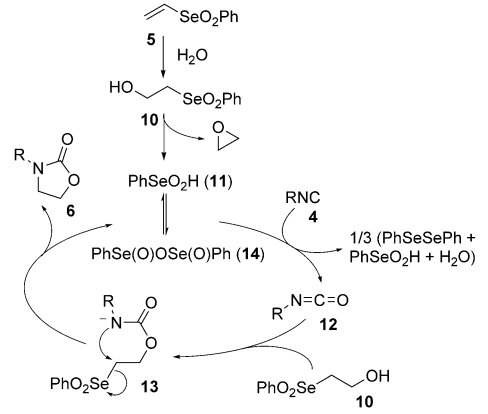
Next, control experiments were carried out to gain mechanistic insights (Scheme 3). The heteroannulation worked equally well under strictly inert atmosphere, indicating that oxygen



Scheme 3. Mechanistic studies: results of the control experiments.

is not responsible for the oxidation. The reaction of *N*-butylformamide **7** with **5** under our standard conditions failed to produce even a trace amount of oxazolidinone **6h**, indicating a significant mechanistic deviation from our previous oxazinanone synthesis (Scheme 3a).[12] Heating a solution of isocyanate **8** and **5** under standard conditions afforded only a trace amount of oxazolidinone. However, slow addition (5 h) of an excess of isocyanate **8** (10.0 equiv) to a CH_2Cl_2 solution of **5** in the presence of Cs_2CO_3 (0.1 equiv) afforded **6h** in 60% yield, indicating that isocyanate could be an intermediate in the reaction between isocyanide **4** and phenyl vinyl selenone (**5**; Scheme 3b). We next synthesized ^{13}C-labeled *n*-butylisocyanide (**9**). Under standard conditions, **9** was converted to ^{13}C-labeled oxazolidinone ^{13}C-**6h**, indicating that the carbonyl carbon in **6h** was derived from the divalent isocyano carbon rather than from carbonate (Scheme 3c).[14] While monitoring the reaction between **9** and **5**, we observed an induction period during which isocyanate and oxazolidinone were not formed. Instead, we observed a slow formation of a product at $\delta = 41$ ppm in the ^{13}C NMR spectra, which was tentatively attributed to an oxirane. Finally, the reaction of benzylisocyanide (**4a**) with **5** in dry CH_2Cl_2 with added $H_2{}^{18}O$ afforded the double and mono labeled ^{18}O-oxazolidinone (Scheme 3d). Diphenyl diselenide was isolated as a by-product in all these transformations, indicating that the phenyl vinyl selenone **5** acted as an oxidant.[15,16]

Based on the results of the aforementioned control experiments, a possible reaction pathway was proposed to account for the formation of oxazolidinone **6** (Scheme 4). Under basic



Scheme 4. Mechanistic proposal.

conditions, water could add to phenyl vinyl selenone **5** to generate the 2-(phenylselenonyl)ethan-1-ol (**10**). A small amount of **10** would undergo a cyclization to afford the oxirane[17] and benzene seleninic acid **11**.[18] The latter, in equilibrium with its anhydride form (BSA, **14**),[19] would act as an oxidant to transform the isocyanide into the corresponding isocyanate **12**.[20] The generation of benzene seleninic acid **11**, a species needed for initiating the desired catalytic cycle, could correspond to the incubation time observed in our NMR experiment. A nucleophilic addition of the Michael adduct **10** to isocyanate **12** would generate carbamate **13**, which could further cyclize to afford oxazolidinone **6** with the concomitant regeneration of benzene seleninic acid **11**. In this catalytic process, two starting materials **4** and **5** have to be converted to two reactive intermediates **10** and **12**, respectively, which would undergo subsequently a formal [2+3] heteroannulation to afford oxazolidinone **6**. While the formation of mono ^{18}O-labeled oxazolidinone is easily understandable, the formation of double ^{18}O-labeled product could be accounted for by the equilibrium between benzene seleninic acid **11** and its anhydride **14** leading to ^{18}O-labeled BSA, hence ^{18}O-labeled isocyanate.

In summary, we developed a novel synthesis of *N*-alkyl-oxazolidin-2-one **6** from isonitriles **4** and phenyl vinyl selenone **5**. Four chemical bonds were created in this unprecedented heteroannulation process with the isocyano group acting formally as a polarized double bond and phenyl vinyl selenone as a latent 1,3-dipole. The oxidative coupling took place in the absence of external oxidant thanks to the triple role of phenylselenonyl group. Indeed, it acted in this transformation as an electron-withdrawing group to activate the 1,4-addition, a leaving group, and a latent oxidant.

Experimental Section

Typical procedure: To phenyl vinyl selenone (**5**; 21.5 mg, 0.1 mmol) and cesium carbonate (3.3 mg, 0.01 mmol, 0.1 equiv) was added a solution of benzyl isocyanide **4a** (12.9 mg, 0.11 mmol, 1.1 equiv) in CH_2Cl_2 (0.2 mL, ca. 0.5 m) and water (1.8 μL, 1.0 equiv). The resulting mixture was heated in a sealed tube at 40 °C for 24 h. Volatiles were removed under vacuo and the residue was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate, gradient from 7:3 to 1:1) to afford **6a** as colourless oil (12.8 mg, 72%). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.40–7.27$ (m, 5H), 4.43 (s, 2H), 4.35–4.26 (m, 2H), 3.46–3.36 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 158.7$, 135.9, 129.0, 128.3, 128.1, 61.9, 48.6, 44.1 ppm; IR (ATR): $\tilde{\nu} = 2919$ (w), 1744 (s), 1485 (w), 1427 (w), 1360 (w), 1260 (w), 1203 (w), 1064 (w), 1035 (w), 763 (w), 703 cm^{-1} (m); HRMS (ESI): *m/z* calcd for $C_{10}H_{12}NO_2^+$: 178.0863 $[M+H]^+$; found 178.0862.

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Keywords: annulation · domino reactions · isocyanide · oxazolidinone · selenium

[1] a) D. A. Evans, J. Bartroli, T. L. Shih, *J. Am. Chem. Soc.* **1981**, *103*, 2127–2129; b) M. M. Heravi, V. Zadsirjan, *Tetrahedron: Asymmetry* **2013**, *24*, 1149–1188.

[2] a) M. R. Barbachyn, C. W. Ford, *Angew. Chem. Int. Ed.* **2003**, *42*, 2010–2023; *Angew. Chem.* **2003**, *115*, 2056–2070; b) T. A. Mukhtar, G. D. Wright, *Chem. Rev.* **2005**, *105*, 529–542; c) K. Michalska, I. Karpiuk, M. Król, S. Tyski, *Bioorg. Med. Chem.* **2013**, *21*, 577–591.

[3] a) W. Aschwanden, E. Kyburz, P. Schönholzer, *Helv. Chim. Acta* **1976**, *59*, 1245–1252; b) J. K. Seydel, K.-J. Schaper, E. A. Coats, H. P. Cordes, P. Emig, J. Engel, B. Kutscher, E. E. Polymeropoulos, *J. Med. Chem.* **1994**, *37*, 3016–3022.

[4] J. P. Peckham, W. F. Hoffman, K. L. Arrington, M. E. Fraley, G. D. Hartman, Y. Kim, B. Hanney, K. L. Spencer, WO2003020699A2 20030313.

[5] a) M. E. Dyen, D. Swern, *Chem. Rev.* **1967**, *67*, 197–246; b) G. Zappia, E. Gacs-Baitz, G. Delle Monache, D. Misiti, L. Nevola, B. Botta, *Curr. Org. Synth.* **2007**, *4*, 81–135.

[6] For reviews on the isocyanide-based multicomponent reactions, see: a) C. Hulme, V. Gore, *Curr. Med. Chem.* **2003**, *10*, 51–80; b) J. Zhu, *Eur. J. Org. Chem.* **2003**, 1133–1144; c) A. Dömling, *Chem. Rev.* **2006**, *106*, 17–89; d) N. Isambert, R. Lavilla, *Chem. Eur. J.* **2008**, *14*, 8444–8454; e) L. El Kaim, L. Grimaud, *Tetrahedron* **2009**, *65*, 2153–2171; f) L. Banfi, R. Riva, A. Basso, *Synlett* **2010**, 23–41; g) A. V. Gulevich, A. G. Zhdanko, R. V. A. Orru, V. G. Nenajdenko, *Chem. Rev.* **2010**, *110*, 5235–5331; h) G. C. Tron, *Eur. J. Org. Chem.* **2013**, 1849–1859.

[7] For [4+1] cycloaddition reaction, see: a) Y. Ito, H. Kato, T. Saegusa, *J. Org. Chem.* **1982**, *47*, 741–743; b) A. Shaabani, S. Ajabi, F. Farrokhzad, H. R. Bijanzadeh, *J. Chem. Res. Synop.* **1999**, 582–583; c) N. Chatani, M. Oshita, M. Tobisu, Y. Ishii, S. Murai, *J. Am. Chem. Soc.* **2003**, *125*, 7812–7813; d) M. Oshita, K. Yamashita, M. Tobisu, N. Chatani, *J. Am. Chem. Soc.* **2005**, *127*, 761–766; e) P. Fontaine, G. Masson, J. Zhu, *Org. Lett.* **2009**, *11*, 1555–1558; f) T. Soeta, K. Tamura, Y. Ukaji, *Tetrahedron* **2014**, *70*, 3005–3010. For [5+1] cycloaddition reactions, see: g) T. Soeta, K. Tamura, Y. Ukaji, *Org. Lett.* **2012**, *14*, 1226–1229; h) C.-L. Lei, D.-X. Wang, L. Zhao, J. Zhu, M.-X. Wang, *J. Am. Chem. Soc.* **2013**, *135*, 4708–4711. For [2+2+1] cycloaddition reactions, see: i) J. Li, Y. Liu, C. Li, X. Jia, *Adv. Synth. Catal.* **2011**, *353*, 913–917; j) J. Li, N. Wang, C. Li, X. Jia, *Chem. Eur. J.* **2012**, *18*, 9645–9650.

[8] For reviews, see: a) A. V. Lygin, A. de Meijere, *Angew. Chem. Int. Ed.* **2010**, *49*, 9094–9124; *Angew. Chem.* **2010**, *122*, 9280–9311; b) G. Qiu, Q. Ding, J. Wu, *Chem. Soc. Rev.* **2013**, *42*, 5257–5269.

[9] a) Y. Odabachian, S. Tong, Q. Wang, M.-X. Wang, J. Zhu, *Angew. Chem. Int. Ed.* **2013**, *52*, 10878–10882; *Angew. Chem.* **2013**, *125*, 11078–11082; b) T. Buyck, Q. Wang, J. Zhu, *Angew. Chem. Int. Ed.* **2013**, *52*, 12714–12718; *Angew. Chem.* **2013**, *125*, 12946–12950; c) S. Tong, Q. Wang, M.-X. Wang, J. Zhu, *Angew. Chem. Int. Ed.* **2015**, *54*, 1293–1297; *Angew. Chem.* **2015**, *127*, 1309–1313.

[10] a) M. Tiecco, D. Chianelli, L. Testaferri, M. Tingoli, D. Bartoli, *Tetrahedron* **1986**, *42*, 4889–4896; b) F. Marini, S. Sternativo, F. Del Verme, L. Testaferri, M. Tiecco, *Adv. Synth. Catal.* **2009**, *351*, 103–106; c) F. Marini, S. Sternativo, F. Del Verme, L. Testaferri, M. Tiecco, *Adv. Synth. Catal.* **2009**,

351, 1801 – 1806; d) T. Zhang, L. Cheng, S. Hameed, L. Liu, D. Wang, Y.-J. Chen, *Chem. Commun.* **2011**, *47*, 6644 – 6646; e) S. Sternativo, O. Walczak, B. Battistelli, L. Testaferri, F. Marini, *Tetrahedron* **2012**, *68*, 10536 – 10541.

[11] Phenyl vinyl selenone as ethane dication equivalent, see: a) M. Shimizu, I. Kuwajima, *J. Org. Chem.* **1980**, *45*, 4063 – 4065; b) M. Shimizu, R. Ando, I. Kuwajima, *J. Org. Chem.* **1981**, *46*, 5246 – 5248; c) I. Kuwajima, R. Ando, T. Sugawara, *Tetrahedron Lett.* **1983**, *24*, 4429 – 4432; d) R. Ando, T. Sugawara, I. Kuwajima, *J. Chem. Soc. Chem. Commun.* **1983**, 1514 – 1515; e) M. Shimizu, R. Ando, I. Kuwajima, *J. Org. Chem.* **1984**, *49*, 1230 – 1238; f) R. Ando, T. Sugawara, M. Shimizu, I. Kuwajima, *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2897 – 2904; g) T. Sugawara, I. Kuwajima, *Tetrahedron Lett.* **1985**, *26*, 5571 – 5574; h) J. C. Wu, J. Chattopadhyaya, *Tetrahedron* **1989**, *45*, 4507 – 4522; i) W. Jin-Chang, J. Chattopadhyaya, *Tetrahedron* **1990**, *46*, 2587 – 2592; j) W. Tong, J. C. Wu, A. Sandström, J. Chattopadhyaya, *Tetrahedron* **1990**, *46*, 3037 – 3060; k) W. Tong, Z. Xi, C. Gioeli, J. Chattopadhyaya, *Tetrahedron* **1991**, *47*, 3431 – 3450; l) L. Bagnoli, C. Scarponi, L. Testaferri, M. Tiecco, *Tetrahedron: Asymmetry* **2009**, *20*, 1506 – 1514; m) S. Sternativo, F. Marini, F. Del Verme, A. Calandriello, L. Testaferri, M. Tiecco, *Tetrahedron* **2010**, *66*, 6851 – 6857; n) L. Bagnoli, C. Scarponi, M. G. Rossi, L. Testaferri, M. Tiecco, *Chem. Eur. J.* **2011**, *17*, 993 – 999; o) S. Sternativo, A. Calandriello, F. Costantino, L. Testaferri, M. Tiecco, F. Marini, *Angew. Chem. Int. Ed.* **2011**, *50*, 9382 – 9385; *Angew. Chem.* **2011**, *123*, 9554 – 9557; p) L. Bagnoli, S. Casini, F. Marini, C. Santi, L. Testaferri, *Tetrahedron* **2013**, *69*, 481 – 486; q) S. Sternativo, B. Battistelli, L. Bagnoli, C. Santi, L. Testaferri, F. Marini, *Tetrahedron Lett.* **2013**, *54*, 6755 – 6757.

[12] T. Buyck, Q. Wang, J. Zhu, *J. Am. Chem. Soc.* **2014**, *136*, 11524 – 11528.

[13] a) G. Zhao, X. Sun, H. Bienaymé, J. Zhu, *J. Am. Chem. Soc.* **2001**, *123*, 6700 – 6701; b) P. Janvier, X. Sun, H. Bienaymé, J. Zhu, *J. Am. Chem. Soc.* **2002**, *124*, 2560 – 2567; c) A. Fayol, J. Zhu, *Angew. Chem. Int. Ed.* **2002**, *41*, 3633 – 3635; *Angew. Chem.* **2002**, *114*, 3785 – 3787; d) P. Janvier, H. Bienaymé, J. Zhu, *Angew. Chem. Int. Ed.* **2002**, *41*, 4291 – 4294; *Angew. Chem.* **2002**, *114*, 4467 – 4470; e) P. Janvier, M. Bois-Choussy, H. Bienaymé, J. Zhu, *Angew. Chem. Int. Ed.* **2003**, *42*, 811 – 814; *Angew. Chem.* **2003**, *115*, 835 – 838; f) A. Fayol, J. Zhu, *Org. Lett.* **2004**, *6*, 115 – 118; g) A. Fayol, J. Zhu, *Org. Lett.* **2005**, *7*, 239 – 242; h) S.-X. Wang, M.-X. Wang, D.-X. Wang, J. Zhu, *Org. Lett.* **2007**, *9*, 3615 – 3618; i) T. Yue, M.-X. Wang, D.-X. Wang, G. Masson, J. Zhu, *J. Org. Chem.* **2009**, *74*, 8396 – 8399.

[14] Carbonates can react with amines to afford carbamoic acids as in the classic Bucherer – Bergs reaction, see: E. Ware, *Chem. Rev.* **1950**, *46*, 403 – 470.

[15] For a review on selenium-based oxidations, see: J. Młochowski, M. Brząszcz, M. Giurg, J. Palus, H. Wójtowicz, *Eur. J. Org. Chem.* **2003**, 4329 – 4339.

[16] For the disproportionation of benzene selenenic acid, see: H. J. Reich, S. Wollowitz, J. E. Trend, F. Chow, D. F. Wendelborn, *J. Org. Chem.* **1978**, *43*, 1697 – 1705.

[17] Selenonyl as leaving group, see: a) A. Krief, W. Dumont, J.-N. Denis, *J. Chem. Soc. Chem. Commun.* **1985**, 571 – 572; b) A. Krief, W. Dumont, A. F. De Mahieu, *Tetrahedron Lett.* **1988**, *29*, 3269 – 3272; c) A. Krief, W. Dumont, J. L. Laboureur, *Tetrahedron Lett.* **1988**, *29*, 3265 – 3268; d) S. I. Kang, C. P. Spears, *J. Med. Chem.* **1990**, *33*, 1544 – 1547; e) S. Uemura, K. Ohe, N. Sugita, *J. Chem. Soc. Perkin Trans. 1* **1990**, 1697 – 1703; f) A. Toshimitsu, H. Fuji, *Chem. Lett.* **1992**, *21*, 2017 – 2018; g) A. Toshimitsu, C. Hirosawa, S. Tanimoto, S. Uemura, *Tetrahedron Lett.* **1992**, *33*, 4017 – 4020; h) P. Ceccherelli, M. Curini, F. Epifano, M. C. Marcotullio, O. Rosati, *J. Org. Chem.* **1995**, *60*, 8412 – 8413; i) M. A. Cooper, A. D. Ward, *Aust. J. Chem.* **1997**, *50*, 181 – 188; j) V. R. Ward, M. A. Cooper, A. D. Ward, *J. Chem. Soc. Perkin Trans. 1* **2001**, 944 – 945; k) M. Tiecco, L. Testaferri, A. Temperini, L. Bagnoli, F. Marini, C. Santi, *Chem. Eur. J.* **2004**, *10*, 1752 – 1764; l) M. Tiecco, A. Carlone, S. Sternativo, F. Marini, G. Bartoli, P. Melchiorre, *Angew. Chem. Int. Ed.* **2007**, *46*, 6882 – 6885; *Angew. Chem.* **2007**, *119*, 7006 – 7009; m) M. Tiecco, L. Testaferri, L. Bagnoli, C. Scarponi, A. Temperini, F. Marini, C. Santi, *Tetrahedron: Asymmetry* **2007**, *18*, 2758 – 2767; n) M. Tiecco, L. Testaferri, A. Temperini, R. Terlizzi, L. Bagnoli, F. Marini, C. Santi, *Org. Biomol. Chem.* **2007**, *5*, 3510 – 3519; o) A. Temperini, R. Terlizzi, L. Testaferri, M. Tiecco, *Chem. Eur. J.* **2009**, *15*, 7883 – 7895.

[18] Epoxide formation from vinyl selenone, see: M. Tiecco, D. Chianelli, M. Tingoli, L. Testaferri, D. Bartoli, *Tetrahedron* **1986**, *42*, 4897 – 4906.

[19] Oxidation of alcohols, see: a) D. H. R. Barton, A. G. Brewster, R. A. H. F. Hui, D. J. Lester, S. V. Ley, T. G. Back, *J. Chem. Soc. Chem. Commun.* **1978**, 952 – 954; b) M. Shimizu, I. Kuwajima, *Tetrahedron Lett.* **1979**, *20*, 2801 – 2804. Oxidation of amines, see: c) D. H. R. Barton, A. Billion, J. Boivin, *Tetrahedron Lett.* **1985**, *26*, 1229 – 1232; d) D. H. R. Barton, X. Lusinchi, P. Milliet, *Tetrahedron* **1985**, *41*, 4727 – 4738.

[20] For the oxidation of isonitrile into isocyanate, see: a) H. Feuer, H. Rubinstein, A. T. Nielsen, *J. Org. Chem.* **1958**, *23*, 1107 – 1109; b) D. G. Martin, *Ann. N. Y. Acad. Sci.* **1967**, *145*, 161 – 168; c) T. Tsuda, S.-i. Sanada, T. Saegusa, *J. Organomet. Chem.* **1976**, *116*, C10 – C12; d) J. Hiebl, E. Zbiral, *Liebigs Ann. Chem.* **1988**, *1988*, 765 – 774; e) Y. Ichikawa, F. Ohara, H. Kotsuki, K. Nakano, *Org. Lett.* **2006**, *8*, 5009 – 5012; f) J. M. Richter, Y. Ishihara, T. Masuda, B. W. Whitefield, T. Llamas, A. Pohjakallio, P. S. Baran, *J. Am. Chem. Soc.* **2008**, *130*, 17938 – 17954; g) H. V. Le, B. Ganem, *Org. Lett.* **2011**, *13*, 2584 – 2585; h) E. R. Klobukowski, R. J. Angelici, L. K. Woo, *Organometallics* **2012**, *31*, 2785 – 2792; i) H. V. Le, B. Ganem, *Tetrahedron Lett.* **2014**, *55*, 2003 – 2005.

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