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AN ARYLATIVE AZIRIDINATION PROCESS TOWARD ASPIDOSPERMA ALKALOIDS[1]

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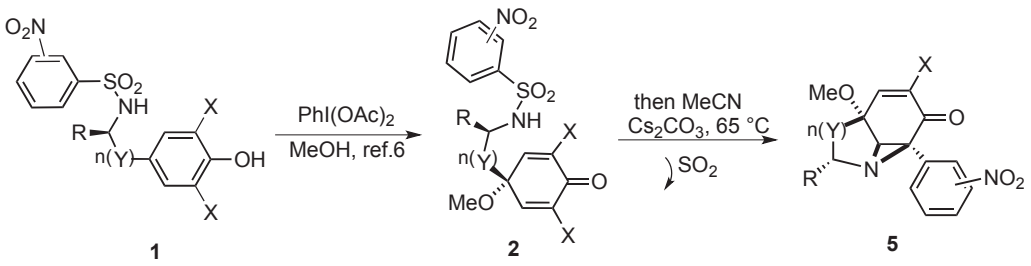
Abstract – An arylative aziridination process has been developed from dibrominated phenols containing a Fukuyama sulfonamide on the lateral chain. A two-step procedure involving the formation of a dienone by a phenol oxidation reaction mediated by a hypervalent iodine reagent (Kita reaction) followed by an intramolecular arylative aziridination process was used. This second step occurred under mild conditions via a Michael–Smiles ring-closure cascade, producing sulfur dioxide as the only byproduct. Additionally, a stereoselective approach was observed with tyrosine derivatives. This transformation respects the rules of green chemistry and atom economy. These new polyfunctionalized scaffolds could offer several synthetic possibilities for the total synthesis of natural products such as the main core of *Aspidosperma* alkaloids.

Aziridines[1a-f] are small heterocycles that can be used to produce a variety of more complex structures, including natural products. With epoxides[1g] and cyclopropanes,[1h] they represent the most important three-membered ring systems.[1] Therefore, they have attracted the attention of the synthetic community and several processes have been described in the literature. Currently, the consensus is that sustainable, environmentally benign routes to desirable synthetic targets should be atom economical and free of protecting groups[2] to respect the concept of "green chemistry." With this idea in mind, we were recently interested in the development of new processes enabling the rapid formation of functionalized heterocycles promoted by a Michael–Smiles tandem process[3] as well as their extension to halogen-dienone systems to yield cyclopropanes.[4] Encouraged by these results, we decided to extend this approach to a nitrogen nucleophile to yield aziridines. These heterocycles were produced from reactive dienones that were readily

[1] This paper is respectfully dedicated to Professor Yasuyaki Kita in honor of his 77th birthday.

obtained in one step from simple phenols in the presence of (diacetoxyiodo)benzene, an environmentally benign hypervalent iodine reagent,[5] using a process developed by Kita and coworkers in 1987.[6] This first approach has largely inspired the scientific community and led to the further development of innovative methodologies[7] and their applications in the total synthesis of natural products[8] based on hypervalent iodine chemistry. In this short paper, we present preliminary results describing the rapid formation of polyfunctionalized scaffolds containing an aziridine moiety from simple phenols in two steps. The first step involved an oxidative dearomatization process and a subsequent Michael–Smiles ring-closure cascade to produce polyfunctionalized arylated aziridines. One characteristic of the Truce–Smiles rearrangement[9] is its capacity to redesign a simple structure into a more elaborate one under mild conditions with only sulfur dioxide as the byproduct. Undeniably, this old reaction has a good potential to further develop current green chemistry methodologies. This transformation enabled us to produce the synthesis of complex structures **5** in one step from dienones **2** or in two steps from phenols **1**. Encouraging, preliminary results were obtained with tyramine and tyrosine precursors (Scheme 1). Different lateral chains and electron-poor sulfonamides were preliminarily investigated. A methoxy group was first introduced to dearomatize phenols **1**.[6] It should be noted that the nosyl group acts as a functional protecting group.[10] Indeed, as an activating group, it enabled the arylative-aziridination process and as a protecting group, it prevented the amino segment to be oxidized by the iodane during the formation of dienone **2**. By this method, scaffolds containing pyrrolidine **5a** or piperidine **5b** were rapidly obtained. Each nosylamide **5a**, **5d** or **5e** appeared to be a competent substrate for this transformation. Furthermore, a stereoselective approach was developed with the tyrosine derivative **1c** or **1f**, leading to **5c** or **5f**, respectively and only one diastereomer was observed by 300-MHz NMR. It should be noted that a dienone desymmetrization process mediated by a thiourea cinchonine catalyst could potentially lead to an enantioselective version of this process.[11] We investigated different halides as nucleofuges; however it appeared that bromine was the halide of choice for this transformation. Indeed, lower yields were observed with iodine **5h** and chlorine **5i**. These results demonstrated that the final S_N2 reaction was probably not the limiting step. Some examples are depicted in Table 1.



1 2 5

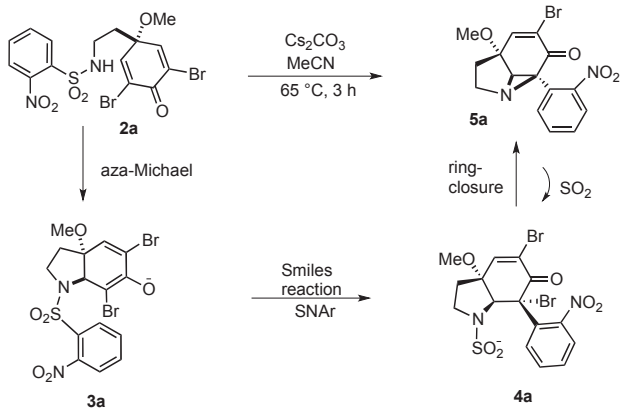
Scheme 1

Table 1. Arylative aziridination process

entry	n	X	Y	NO_2	R	yield[a] (%)	yield[b] (%)
5a	1	Br	CH_2	*ortho*	H	61	42
5b	2	Br	CH_2	*ortho*	H	54	37
5c	1	Br	CH_2	*ortho*	CO_2Me	41	30
5d	1	Br	CH_2	*ortho-para*	H	61	42
5e	1	Br	CH_2	*para*	H	57	40
5f	1	Br	CH_2	*ortho*	CH_2OTBS	N.D.	39
5g	1	Br	O-CH_2	*ortho*	H	N.D.	45
5h	1	I	CH_2	*ortho*	H	N.D.	24
5i	1	Cl	CH_2	*ortho*	H	N.D.	31

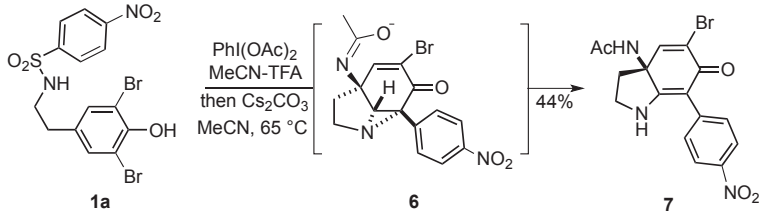
[a] Yields observed from dienone **2**; N.D., Not Determined.
[b] Yields obtained directly from phenol **1** (over 2 steps).

From a mechanistic point of view, this approach involves an aza-Michael process producing enolate **3**, which triggers the Truce–Smiles rearrangement and the loss of sulfur dioxide as the only byproduct. The aryl migration during the Smiles rearrangement occurred with retention of the configuration. Consequently, the released amine was ideally placed for an antiperiplanar attack on the tertiary alkyl halide by an S_N2-type process. Such intramolecular S_N2 reactions are possible due to neighboring allylic double bonds and similar examples are reported in the literature.[12] The formation of dienone **2** by oxidation of phenol **1** was accompanied by an amount of intermediate **3** that was also a competent substrate for the second step, leading to the formation of compound **5**. Therefore, we decided to use crude dienone **2** for the next step in order to have a higher overall yield and good reproducibility. Although the global yield obtained for this two-step procedure was moderate (24–45%), it should be noted that the highly functionalized core **5** was rapidly obtained from inexpensive phenols **1** under mild conditions. Multiple transformations occurring during this procedure could explain both the moderate yield observed as well as the structure complexity produced. Although a moderate yield was observed, the crude NMR described mainly the desired product. Most probably byproducts were very polar compounds or polymers removed during the work-up. A proposed mechanism for the Michael–Smiles ring-closure cascade is depicted in Scheme 2.



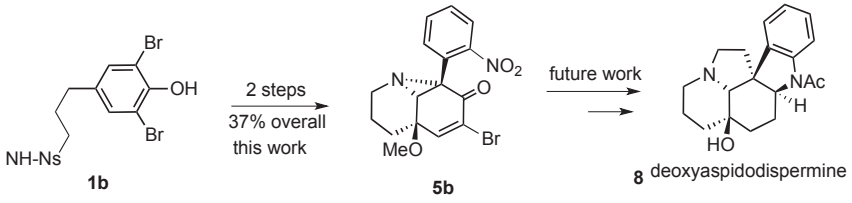
Scheme 2

This process was extended with the introduction of an acetamide as decribed by Ciufolini and coworkers[12] instead of a methoxy group at the former *para* position of phenol **1**. Interestingly, the conjugated enamine **7** was observed in 44% overall yield. We suppose that the expected aziridine was probably the intermediate **6**, which was further opened by the assistance of the neighboring basic acetamide, as presented in Scheme 3.



Scheme 3

It should be noted that compound **5b** is a quite functionalized heterocycle that could be used as a potential precursor for the synthesis of *Aspidosperma* alkaloids such as deoxyaspidodispermine **8**[14] (Scheme 4).



Scheme 4

In conclusion, a new stereoselective arylative aziridination method has been developed on dienone systems easily produced from phenols using a hypervalent iodine reagent and a one-pot multistep Michael–Smiles ring-closure cascade process. This approach occurs under mild conditions and releases only sulfur dioxide as the byproduct. The scaffolds obtained represent the main core of alkaloids belonging to some *Aspidosperma* family members and we are currently developing this process for their total synthesis.

EXPERIMENTAL

Unless otherwise indicated, ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, in $CDCl_3$ solutions. Chemical shifts are reported in ppm on the δ scale. Multiplicities are described as s (singlet), d (doublet), dd, ddd, etc. (doublet of doublets, doublet of doublets of doublets, etc.), t (triplet), q (quartet), p (pentuplet), m (multiplet) and further qualified as app (apparent) br (broad) c (complex).

Coupling constants, *J*, are reported in Hz. IR spectra (cm–1) were recorded from thin films. Mass spectra (m/e) were measured in the electrospray (ESI) mode.

General procedure for the formation of Phenol (1):

a) Nosylation: Sodium bicarbonate (2.0 mmol, 2 equiv.) was added to a solution of tyramine (1.0 mmol, 1 equiv.) in THF/H_2O (2:2 mL) at 0 °C and then nitrobenzenesulfonyl chloride (1.1 mmol, 1.1 equiv.) was added. The mixture was then stirred for 3 h and then a solution of sat. aq. NH_4Cl was added. The aqueous phase was extracted with EtOAc and the organic layer was dried with Na_2SO_4 and concentrated under vacuum. The residue was purified by silica gel chromatography with a mixture of EtOAc−hexane.

b) Dibromation: NBS (1.26 mmol, 2.1 equiv.) was added to a solution of the corresponding nosylamide-phenol (0.6 mmol, 1 equiv.) in DCM (5 mL) at 0 ºC. The mixture was then stirred for 3 h and then a solution of sat. aq. $Na_2S_2O_3$ was added and extracted with EtOAc. The organic layer was dried with Na_2SO_4 and concentrated under vacuum. The residue was purified by silica gel chromatography with a mixture of EtOAc−hexane.

General procedure for the formation of dienones (2).[6] To a stirred solution of phenols (0.1 mmol) in MeOH (1 mL) at 20 °C was added $PhI(OAc)_2$ ("DIB" 1.2 equiv.) dissolved in MeOH (0.5 mL), over 10 s. The reaction was stirred for 2-3 min and concentrated under vacuum. For the isolation of dienone **2**: the crude was purified by chromatography (hexane−EtOAc as required). For the two step-procedure enabling to transform intermediate **2** into **5**. The crude was rapidly filtrated on a small pad of silica gel with EtOAc then concentrated and the residue was used without further purification.

General procedure for the aziridine formation (5). To a solution of dienone (0.095 mmol, 1.0 equiv.) in MeCN (2.0 mL) was added cesium carbonate (3.0 equiv.). Then, the reaction was stirred overnight at 65 °C, the reaction was followed by TLC (2-3 h). After completion, the mixture was filtered through a pad of silica with EtOAc and concentrated under vacuum. The residue was purified by silica gel chromatography with a mixture of EtOAc–hexane to afford **5**.

Formation of enamine (7).[13] To a stirred solution of phenol **1a** (0.05 mmol) in MeCN (1 mL) at 0 °C was added TFA (0.065 mmol, 1.3 equiv.) and $PhI(OAc)_2$ (0.06 mmol, 1.2 equiv.). The reaction was stirred for 5 min and rapidly filtered on a small pad of silica gel with EtOAc then concentrated and the residue was used without further purification. The same procedure for the formation of aziridine (**5**) was further used.

5-Bromo-1,2,3,3a-tetrahydro-3a-methoxy-7-(2-nitrophenyl)indol-6-one (5a). This compound was obtained as yellow oil, 42% yield over two steps; ^1H NMR (300 MHz, $CDCl_3$) δ 8.09 (d, J = 8.1 Hz, 1H),

7.91 (d, *J* = 8.1 Hz, 1H), 7.68 (t, *J* = 8.1 Hz, 1H), 7.49 (t, *J* = 8.1 Hz, 1H), 7.37 (s, 1H), 3.59 (m+s, 4H), 3.19 (s, 1H), 2.86-2.64 (m, 2H), 2.2 (dd, *J* = 12.3 Hz, 4.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.7, 150.0, 146.5, 134.3, 133.9, 133.3, 129.1, 124.4, 123.9, 83.9, 59.7, 55.9, 53.8, 47.5, 46.7; HRMS (ESI): Calc. for $C_{15}H_{14}N_2O_4Br$ $(M+H)^+$: 365.0131; found: 365.0133.

6-Bromo-2,3,4,4a-tetrahydro-4a-methoxy-8-(2-nitrophenyl)quinolin-7(1*H*)-one (5b). This compound was obtained as an orange oil, 37% yield over two steps; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 8.1 Hz, 1.2 Hz, 1H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.68 (td, *J* = 8.1 Hz, 1.2 Hz, 1H), 7.50 (dd, *J* = 8.1 Hz, 1.2 Hz, 1H), 7.08 (d, *J* = 8.1 Hz, 1.2 Hz, 1H), 3.51 (s+m, 4H), 2.88 (m, 2H), 2.0-1.66 (c, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.7, 151.6, 147.3, 134.3, 133.9, 132.5, 129.1, 126.0, 124.6, 73.5, 53.2, 50.8, 47.4, 39.5, 19.2; HRMS (ESI): Calc. for $C_{16}H_{16}NO_4Br$ $(M+H)^+$: 379.0288; found: 379.0280.

(2*R*,31*S*,6a*S*)-Methyl 5-bromo-6a-methoxy-3a-(2-nitrophenyl)-4-oxo-1,2,31,3a,4,6a-hexahydro-azirino[2,3,1-*hi*]indole-2-carboxylate (5c). This compound was obtained as an yellow oil, 30% yield over two steps; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.3 Hz, 1H), 7.98 (d, *J* = 7.2 Hz, 1H), 7.71 (t, *J* = 7.3 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 1H), 7.40 (s, 1H), 3.85 (s, 3H), 3.55 (s+m, 4H), 3.31 (s, 1H), 3.05 (t, *J* = 12.4 Hz, 1H), 2.52 (dd, *J* = 12.6 Hz, 5.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ ^{13}C NMR (75 MHz, $CDCl_3$) δ 183.8, 171.0, 149.8, 134.5, 133.9, 133.8, 129.6, 124.7, 83.7, 60.0, 59.5, 56.1, 53.7, 53.0, 50.9, 31.0, 29.8; HRMS (ESI): Calc. for $C_{17}H_{16}BrN_2O_6$ $(M+H)^+$: 423.0186; found: 423.0174.

5-Bromo-1,2,3,3a-tetrahydro-3a-methoxy-7-(2,4-dinitrophenyl)indol-6-one (5d). This compound was obtained as an orange oil, 42% yield over two steps; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.92 (s, 1H), 8.48 (d, *J* = 8.5 Hz, 1H), 8.18 (d, *J* = 8.3 Hz, 1H), 7.41 (s, 1H), 3.77-3.41 (m+s, 4H), 3.25 (s, 1H), 2.90-2.51 (m, 2H), 2.21 (dd, *J* = 15.1 Hz, 6.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.2, 150.9, 147.8, 140.7, 135.4, 127.8, 123.6, 120.2, 84.3, 60.4, 55.0, 53.8, 47.4, 47.0, 29.4; HRMS (ESI): Calc. for $C_{15}H_{13}BrN_3O_6$ $(M+H)^+$: 409.9982; found: 409.9969.

5-Bromo-6a-methoxy-3a-(4-nitrophenyl)-1,3^1,3a, 6a-tetrahydroazirino-[2,3,1-*hi*]indol-4(2*H*)-one (5e). This compound was obtained as a pale yellow oil, 40% yield over two steps; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) : 8.20 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.48 (s, 1H), 3.69 – 3.61 (m, 1H), 3.59 (s, 3H), 3.28 (s, 1H), 2.83 (dd, *J* = 12.3, 8.0 Hz, 1H), 2.70 (td, *J* = 12.6, 4.4 Hz, 1H), 2.24 (dd, *J* = 12.1, 4.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) : 185.40, 151.6, 147.5, 144.6, 129.1, 124.3, 123.4, 84.1, 62.2, 55.4, 54.1, 47.0, 46.9. HRMS (ESI): Calc. for $C_{15}H_{14}BrN_2O_4$ $(M+H)^+$: 365.0131; found: 365.0128.

5-Bromo-2-(((*tert*-butyldimethylsilyl)oxy)methyl)-6a-methoxy-3a-(2-nitrophenyl)-1,31,3a,6a-tetrahydroazirino[2,3,1-*hi*]indol-4(2*H*)-one (5f). This compound was obtained as a colorless oil, 39% yield over two steps; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.2 Hz, 1H), 7.98 (d, *J* = 7.2 Hz, 1H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.39 (s, 1H), 3.96 (dd, *J* = 8.4, 4.6, 1H), 3.81 (dd, *J* =

10.1, 5.8, 1H), 3.57 (s, 3H), 3.24 (s, 1H), 3.16 – 3.00 (m, 1H), 2.56 (t, J = 11.9 Hz, 1H), 2.31 (dd, J = 8.0, 4.5, 1H), 0.93 (s, 9H), 0.11 (s, 3H), 0.10 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.6, 150.3, 146.5, 134.4, 129.1, 127.2, 124.3, 123.9, 133.8, 83.8, 66.1, 60.7, 59.5, 55.7, 52.9, 50.4, 25.8, 18.3, -5.1, -5.2.

5-Bromo-6a-methoxy-3b-(2-nitrophenyl)-2,3,3b,6a-tetrahydro-1-oxa-3a-azacyclopropa[*de*]naphthalen-4(3a1*H*)-one (5g). This compound was obtained as a yellow oil, 45% yield over two steps;^{1}H NMR (300 MHz, $CDCl_3$) δ ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 (d, J = 8.2 Hz, 1H), 7.95 (s, 1H), 7.73 (t, J = 7.5Hz, 1H), 7.56 (t, J = 7.1 Hz, 1H), 7.30 (d, J = 2.1 Hz, 1H), 4.14 (dd, J = 8.4, 2.9, 2H), 3.64 – 3.39 (m+s, 4H), 3.13 – 2.87 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.5, 147.6, 134.0, 133.4, 132.8, 132.2, 129.5, 129.4, 124.8, 91.5, 63.5, 49.6, 46.7, 45.0, 41.4.

5-Iodo-1,2,3,3a-tetrahydro-3a-methoxy-7-(2-nitrophenyl)indol-6-one (5h). This compound was obtained as a yellow solid, 24% yield over two steps; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 (d, J = 8.1 Hz, 1H), 7.93 (d, J = 7.5 Hz, 1H), 7.77 – 7.63 (s+t, J = 8.1 Hz, 2H), 7.51 (t, J = 8.1 Hz, 1H), 3.67 – 3.46 (m+s, 4H), 3.23 (s, 1H), 2.87 – 2.59 (m, 2H), 2.20 (dd, J = 11.6, 4.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.7, 158.4, 146.8, 134.7, 133.7, 133.4, 129.1, 124.6, 102.6, 84.9, 59.4, 56.1, 52.1, 47.3, 46.5.

5-Chloro-1,2,3,3a-tetrahydro-3a-methoxy-7-(2-nitrophenyl)indol-6-one (5i). This compound was obtained as a yellow oil, 31% yield over two steps; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (d, J = 8.2 Hz, 1H), 7.94 (d, J = 7.1 Hz, 1H), 7.71 (t, J = 7.6 Hz, 1H), 7.52 (t, J =7.1, 1H), 7.13 (s, 1H), 3.70 – 3.47 (m, 4H), 3.22 (s, 1H), 2.94 – 2.64 (m, 2H), 2.23 (dd, J = 11.8, 4.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.9, 148.6, 145.4, 134.4, 134.0, 133.4, 133.1, 129.3, 124.4, 83.2, 60.0, 55.9, 54.5, 47.8, 46.8.

***N*-(5-Bromo-7-(4-nitrophenyl)-6-oxo-2,3,3a,6-tetrahydro-1*H*-indol-3a-yl)acetamide (7).** This compound was obtained as a yellow solid, 42% yield over two steps; ^{1}H NMR (300 MHz, acetone-d_6) δ 8.17 (d, J = 7.0 Hz, 2H), 8.13 (br, 1H), 8.02 (br, 1H), 7.82 (s, 1H), 7.66 (d, J = 9.0 Hz, 2H), 3.76 (td, J = 10.5, 6.0 Hz, 1H), 3.65 (m, 1H), 3.00 (m, 1H), 2.06 (m, 2H), 1.92 (s, 3H); ^{13}C NMR (75 MHz, acetone-d_6) δ 174.2, 167.6, 165,4, 146.2, 142.7, 138.1, 130.4, 128.0, 123.4, 102.8, 61.9, 44.5, 32.8, 22.4.

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REFERENCES AND NOTES

1. For aziridine see: (a) U. M. Lindstrom and P. Somfai, *Synthesis*, 1998, 109; (b) P. Somfai and J. Ahman, *Targets Heterocycl. Syst.*, 1999, **3**, 341; (c) B. Zwanenburg and P. Ten Holte, *Top. Curr.*

Chem., 2001, **216**, 93; (d) J. B. Sweeney, *Chem. Soc. Rev.*, 2002, **31**, 247; (e) A. Padwa and S. S. Murphee, *Prog. Heterocycl. Chem.*, 2003, **15**, 75; (f) L. Degennaro, P. Trinchera, and R. Luisi, *Chem. Rev.*, 2014, **114**, 7881; (g) for epoxides see : A. Padwa and S. S. Murphree, *ARKIVOC*, 2006, **iii**, 6; (h) for cyclopropanes see: D. Y.-K. Chen, R. H. Pouwer, and J. A. Richard, *Chem. Soc. Rev.*, 2012, **41**, 4631.

2. (a) B. M. Trost, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 259; (b) P. S. Baran, T. J. Maimone, and J. M. Richter, *Nature*, 2007, **446**, 404.
3. S. Coulibali, T. Godou, and S. Canesi, *Org. Lett.*, 2016, **18**, 4348.
4. S. Coulibali, E. Deruer, E. Godin, and S. Canesi, *Org. Lett*., 2017, **19**, 1188.
5. (a) M. Ito, H. Kubo, I. Itani, K. Morimoto, T. Dohi, and Y. Kita, *J. Am. Chem. Soc*., 2013, **135**, 14078; (b) U. Farid, F. Malmedy, R. Claveau, L. Albers, and T. Wirth, *Angew. Chem. Int. Ed.*, 2013, **52**, 7018; (c) A. Yoshimura and V. V. Zhdankin, *Chem. Rev.*, 2016, **116**, 3328.
6. (a) Y. Tamura, T. Yakura, J. Haruta, and Y. Kita, *J. Org. Chem.*, 1987, **52**, 3927.
7. (a) T. Dohi and Y. Kita, *Chem. Commun.*, 2009, 2073; (b) S. Desjardins, G. Maertens, and S. Canesi, *Org. Lett.*, 2014, **16**, 4928; (c) F. Malmedy and T. Wirth, *Chem. Eur. J.*, 2016, **22**, 16072; (d) M. El Assal, P. A. Peixoto, R. Coffinier, T. Garnier, D. Deffieux, K. Miqueu, J. M. Sotiropoulos, L. Pouységu, and S. Quideau, *J. Org. Chem.*, 2017, **82**, 11816.
8. (a) L. Pouységu, D. Deffieux, and S. Quideau, *Tetrahedron*, 2010, **66**, 2235; (b) G. Jacquemot, G. Maertens, and S. Canesi, S. *Chem. Eur. J*., 2015, **21**, 7713; (c) A. A. Levy, H. C. Rains, and S. Smiles, *J. Chem. Soc.*, 1931, 3264; (d) W. E. Truce, E. M. Kreider, and W. W. Brand, *Org. React.*, 1970, **18**, 99.
9. T. Kan and T. Fukuyama, *Chem. Commun.*, 2004, 353.
10. (a) Q. Gu and S. L. You, *Chem. Sci.*, 2011, **2**, 1519; (b) G. Maertens, M. A. Menard, and S. Canesi, *Synthesis*, 2014, **46**, 1573.
11. G. Jiménez-Osés, A. Avenoza, J. H. Busto, F. Rodríguez, and J. M. Peregrina, *Chem. Eur. J.*, 2009, **15**, 9810.
12. (a) H. Liang and M. A. Ciufolini, *Tetrahedron*, 2010, **66**, 5884; (b) J. Chau and M. A. Ciufolini, *Org. Synth.*, 2013, **90**, 190; (c) J. Chau, S. Xu, and M. A. Ciufolini, *J. Org. Chem.*, 2013, **78**, 11901; (d) S. Canesi, D. Bouchu, and M. A. Ciufolini, *Org. Lett.*, 2005, **7**, 175; (e) H. Liang and M. A. Ciufolini, *J. Org. Chem.*, 2008, **73**, 4299.
13. (a) M. Ikeda and C. Djerassi, *Tetrahedron Lett.*, 1968, **56**, 5837; (b) N. C. Ling and C. Djerassi, *Tetrahedron Lett.*, 1970, **34**, 3015; (c) Y. Honma and Y. Ban, *Heterocycles*, 1977, **6**, 129; (d) K. Yoshida, Y. Sakuma, and Y. Ban, *Heterocycles*, 1987, **25**, 47.