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PAPER

Cascade dearomatization of *N*-substituted tryptophols *via* Lewis acid-catalyzed Michael reactions†

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Lewis acid-catalyzed cascade dearomatization of *N*-substituted tryptophols *via* Michael addition reaction was developed. The generality of the method has been demonstrated by the synthesis of versatile furoindoline derivatives with a quaternary carbon center in good yields.

Introduction

Furoindolines with a quaternary carbon center at the C-3 position represents structural moieties widely existed in natural products (Fig. 1). However, current synthetic methods for this important type of fused indoline rings are rare. In many cases, the synthesis still relied on Fischer indole synthesis.[1] Recently, dearomatization strategy[2] has achieved significant progress for the synthesis of pyrrolidinoindolines with a quaternary carbon center at the C-3 position utilizing various cascade sequences. These reactions generally proceed *via* the generation of indolenine that can be further trapped by an intramolecular nucleophilic side chain.[3] To our surprise, this straightforward protocol has been mainly applied on dearomatization of tryptamines but much less explored for constructing furoindolines[4] *via* the corresponding cascade dearomatization of tryptophols.[3c,d,5] Lewis acid-catalyzed Michael reactions have been extensively studied[6] and shown compatible with Friedel–Crafts alkylation reaction with indoles.[7]

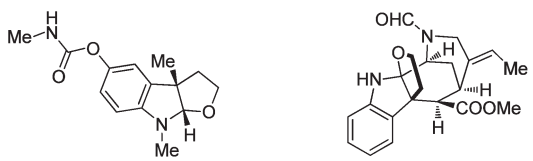

Fig. 1 Furoindoline core in selected natural products.

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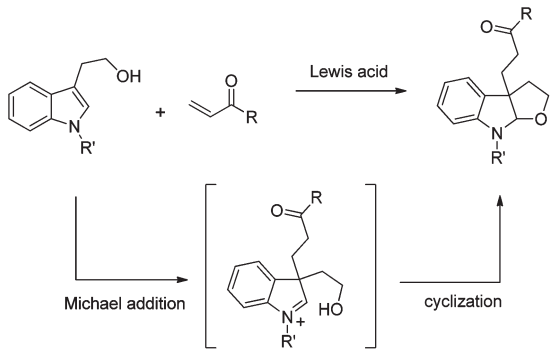


Scheme 1 Proposed cascade dearomatization of *N*-substituted tryptophols.

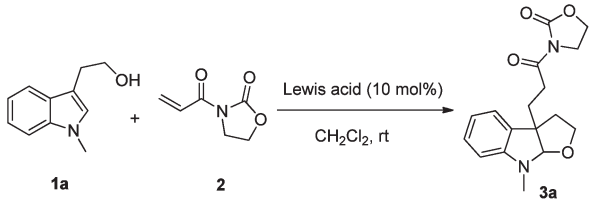
As part of our ongoing efforts to explore dearomatization reactions,[8] we envisioned that a Lewis acid-catalyzed cascade dearomatization of *N*-substituted tryptophols including Michael addition reaction and a subsequent iminium ion trapping would afford the furoindoline core (Scheme 1). Herein, we report a Lewis acid-catalyzed cascade dearomatization of *N*-substituted tryptophols for the synthesis of furoindoline derivatives with a quaternary carbon center.

Results and discussion

To test our proposed reaction sequence, *N*-methyl tryptophol **1a** was selected as the model substrate to react with 3-acryloyloxazolidin-2-one **2**[9] in CH_2Cl_2 in the presence of 10 mol% of Lewis acid. The results are summarized in Table 1.

To our great delight, all the tested Lewis acids could catalyze the cascade reaction smoothly to deliver the desired furoindoline **3a** (Table 1). $Sc(OTf)_3$ was found to be the optimal one, affording **3a** in 74% yield (entry 1, Table 1). Notably, with 20 mol% of $Cu(OTf)_2$, the reaction could proceed smoothly to afford the dearomatization product **3a** in 73% yield (entry 3, Table 1).

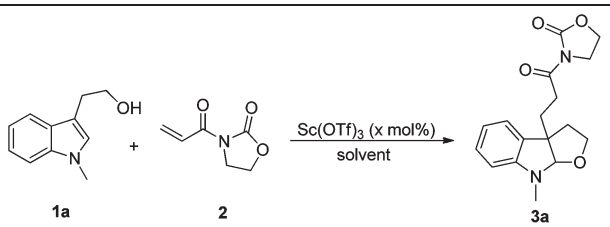
Table 1 Evaluation of Lewis acids



Entry[a]	Lewis acid	Time (d)	Yield[b] (%)
1	$Sc(OTf)_3$	3	74
2	$Cu(OTf)_2$	3	33
3[c]	$Cu(OTf)_2$	3	73
4	$Zn(OTf)_2$	3	12
5	$Yb(OTf)_3$	3	50
6	$SnCl_4$	3	55
7	$AlCl_3$	3	43
8	$TiCl_4$	3	39
9	$ZrCl_3$	3	18
10	$InBr_3$	3	22
11[d]	$BF_3{\cdot}Et_2O$	7	64

[a] *Reaction conditions*: **1a** (0.3 mmol), **2** (0.36 mmol), Lewis acid (0.03 mmol) in dichloromethane (3 mL) at rt. [b] Isolated yield. [c] With 20 mol% of Lewis acid. [d] With 100 mol% of Lewis acid.

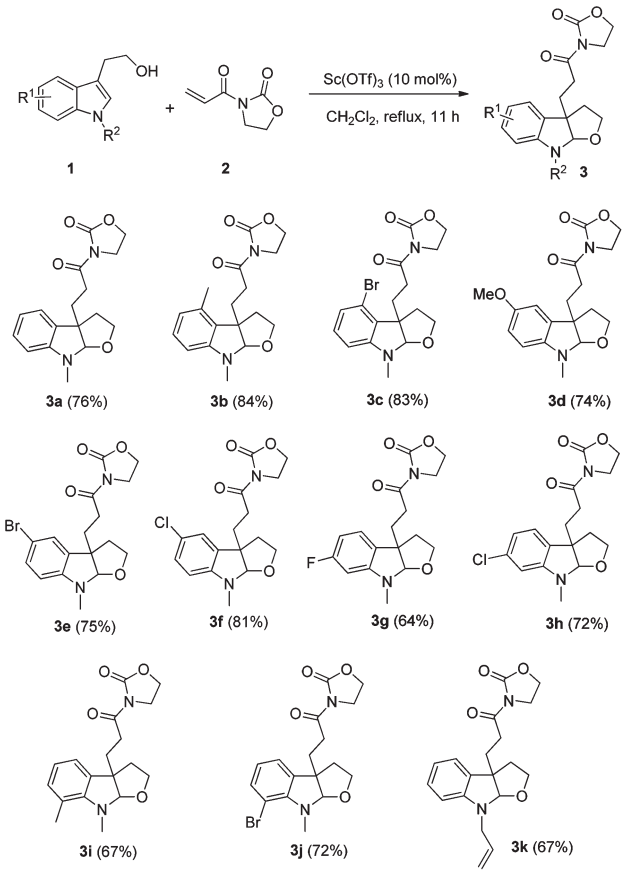
Table 2 Optimization of the reaction conditions



Entry[a]	*x* (mol%)	Solvent	Time	Yield[b] (%)
1	10	CH_2Cl_2	3 d	74
2	10	$CHCl_3$	3 d	73
3	10	DCE	3 d	54
4	10	Et_2O	3 d	55
5	10	THF	3 d	23
6	10	Toluene	3 d	68
7	10	Hexane	3 d	57
8	10	CH_2Cl_2	11 h	76
9[c]	10	Toluene	3 d	41
10[c]	2	CH_2Cl_2	20 h	61
11[c]	5	CH_2Cl_2	20 h	71
12[c]	20	CH_2Cl_2	11 h	76

[a] *Reaction conditions*: **1a** (0.3 mmol), **2** (0.36 mmol), $Sc(OTf)_3$ (0.03 mmol) in solvent unless otherwise noted. [b] Isolated yield. [c] Refluxed.

With $Sc(OTf)_3$ as the catalyst, further optimization of reaction conditions including solvents, temperature and catalyst loadings has been carried out. The results are summarized in Table 2. A variety of commonly used solvents such as $CHCl_3$, DCE, Et_2O, toluene, and hexane could be utilized in the cascade dearomatization reaction of **1a** (54–73% yields, entries 2–4, 6–7, Table 2). THF gave a relatively poor yield (23% yield, entry 5, Table 2). Increasing temperature significantly accelerated the reaction rate,



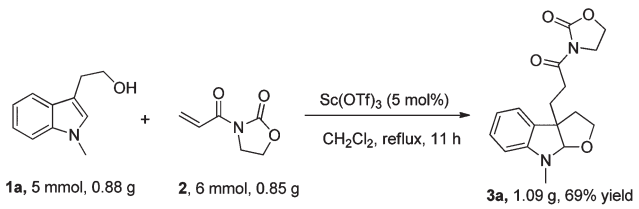
Scheme 2 Substrate scope.

and the reaction went to completion within 11 h in refluxed CH_2Cl_2 (entry 8, Table 2). However, when the reaction was carried out in refluxed toluene, the yield of **3a** was decreased likely due to the harsh reaction conditions (entry 9, Table 2). Notably, varying the catalyst loadings from 2 mol% to 20 mol% resulted in no obvious change of the yield of **3a** (entries 10–12, Table 2). Slightly higher yield was given upon the increase of catalyst loading (entry 12, Table 2).

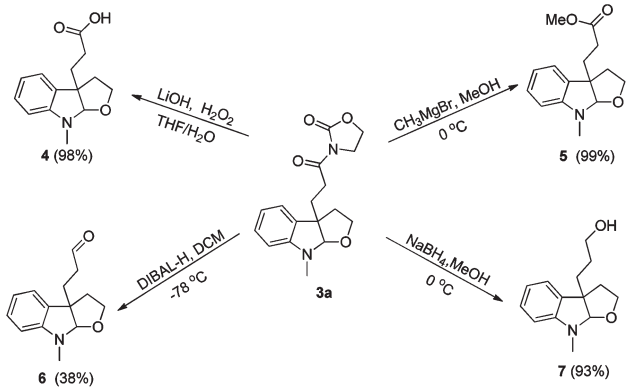
Under the standard conditions, various substituted tryptophols were examined to test the generality of this Lewis acid-catalyzed cascade dearomatization reaction (Scheme 2). On the indole core, substituents varying electronic properties and positions (4-Me, 4-Br, 5-OMe, 5-Br, 5-Cl, 6-F, 6-Cl, 7-Me, 7-Br) could all be tolerated. In all cases, the corresponding furoindolines were obtained in good yields (64–84%, **3a–3j**, Scheme 2). It should be noted that the *N*-allyl tryptaphol was also a suitable substrate, and the corresponding furoindoline was afforded in 67% yield under the optimized reaction conditions (**3k**, Scheme 2).

To demonstrate the synthetic value of the present catalytic reaction, we carried out the reaction of *N*-methyl tryptophol **1a** with 3-acryloyloxazolidin-2-one **2** on a gram scale with 5 mol% of catalyst (Scheme 3). To our great delight, the desired furoindoline **3a** could be obtained without notable loss of yield following the same reaction conditions and work-up procedure (69% yield).

Transformations of the oxazolidinone moiety of **3a** into some useful functionalities were also carried out to explore the



Scheme 3 Gram-scale preparation of **3a**.



Scheme 4 Transformations of product **3a**.

potential application of the current methodology. As shown in Scheme 4, conversions of oxazolidinone **3a** into the corresponding acid **4**, ester **5** and alcohol **7** could proceed smoothly in excellent yields (93–99%). In addition, aldehyde **6** could also be obtained under the reduction of DIBAL-H, albeit with a moderate yield (38%).

Conclusions

In conclusion, an unprecedented Lewis acid-catalyzed cascade dearomatization of *N*-substituted tryptophols was developed. In the presence of 10 mol% of $Sc(OTf)_3$, versatile furoindoline derivatives with a quaternary carbon center were obtained in good yields. Further development of an enantioselective reaction and application into the total synthesis of natural products are currently under way in our lab.

Experimental

General methods

Unless stated otherwise, all reactions were carried out in flame-dried glassware under a dry argon atmosphere. All solvents were purified and dried according to standard methods prior to use.

^{1}H and ^{13}C NMR spectra were recorded on Varian instruments (300 MHz and 75 MHz or 400 MHz and 100 MHz, respectively) and internally referenced to tetramethylsilane signal or residual protio solvent signals. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet or unresolved, coupling constant(s) in Hz, integration). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm).

The 3-acyloyl-1,3-oxazolidin-2-one[10a] and trytophol derivates[10b,c] were prepared according to the reported procedures. Scandium(III) trifluoromethanesulfonate was purchased from Alfa Aesar, dried under vacuum at 80 °C and stored under nitrogen before use.

General procedures for synthesis of the *N*-methyl tryptophol 1

tert-Butyldimethylsilylchloride (331.5 mg, 2.2 mmol, 1.1 equiv) was added to a solution of tryptophol (2.0 mmol, 1.0 equiv) and imidazole (272.3 mg, 4.0 mmol, 2.0 equiv) in DMF (30 mL) at 0 °C. The ice bath was then removed and the reaction mixture was stirred at room temperature for 3 h. The mixture was quenched with water (20 mL) and extracted with EtOAc (3 × 30 mL), then the combined organic layers were washed with water, brine, separated, and dried with Na_2SO_4, then filtered and concentrated under reduced pressure. The residue was used directly for the next step without further purification.

To a solution of the above TBS-tryptophol in THF (30 mL) was added NaH (80.0 mg, 2.0 mmol, 1.0 equiv, 60% dispersion in mineral oil) at 0 °C. After stirring at 0 °C for 15 min and then at rt for 1 h, the reaction mixture was cooled to 0 °C, treated with MeI (140 μl, 2.2 mmol, 1.1 equiv), and then allowed to stir at rt for 6–12 h. After the reaction was complete (monitored by TLC), 1 M HCl (5 mL) was added. After stirring for 30 min, aqueous saturated $NaHCO_3$ (30 mL) was added slowly. The organic layer was separated and the aqueous layer was extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine (30 mL), separated, dried with Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (2 : 1, PE–EtOAc) to afford the desired product **1**.

1a. Light yellow oil, 76% yield.[5d] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.0 Hz, 1H), 7.28 (d, J = 8.0 Hz, 1H), 7.22 (t, J = 7.6 Hz, 1H), 7.10 (t, J = 7.6 Hz, 1H), 6.89 (s, 1H), 3.85 (t, J = 6.4 Hz, 2H), 3.71 (s, 3H), 2.99 (t, J = 6.4 Hz, 2H), 1.76 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.0, 127.8, 127.2, 121.6, 118.8, 118.8, 110.6, 109.2, 62.6, 32.5, 28.5.

1b. Light yellow oil, 42% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (d, J = 3.6 Hz, 2H), 6.80 (t, J = 4.0 Hz, 1H), 6.76 (s, 1H), 3.78 (t, J = 6.4 Hz, 2H), 3.59 (s, 3H), 3.09 (t, J = 6.4 Hz, 2H), 2.65 (s, 3H), 2.25 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3, 130.6, 127.3, 126.0, 121.4, 120.5, 111.0, 107.0, 63.4, 32.4, 30.0, 20.2; IR (film): ν_{max} (cm^{-1}) = 3354, 2943, 1609, 1574, 1548, 1497, 1465, 1446, 1417, 1371, 1323, 1248, 1154, 1070, 1042, 912, 802, 774, 744, 669; MS (EI, m/z, rel. intensity) 189 ([M]$^+$, 17), 158 (100), 159 (13); HRMS (EI) calcd for $C_{12}H_{15}NO$ ([M]$^+$): 189.1154. Found: 189.1157.

1c. Light yellow oil, 54% yield.[10d] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (dd, J = 7.6, 0.8 Hz, 1H), 7.16 (dd, J = 8.4, 0.8 Hz, 1H), 6.98 (t, J = 8.0 Hz, 1H), 6.88 (s, 1H), 3.88 (t, J = 6.4 Hz, 2H), 3.63 (s, 3H), 3.20 (t, J = 6.8 Hz, 2H), 2.11 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2, 129.2, 125.5, 123.2, 122.1, 114.2, 111.2, 108.5, 63.5, 32.6, 29.1.

1d. Light yellow oil, 75% yield.[5d] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, J = 8.8 Hz, 1H), 7.01 (d, J = 2.4 Hz, 1H), 6.85 (dd, J = 8.8, 2.4 Hz, 1H), 6.79 (s, 1H), 3.81–3.78 (m, 5H),

3.58 (s, 3H), 2.91 (t, J = 6.8 Hz, 2H), 2.42 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 132.2, 127.9, 127.6, 111.5, 109.9, 109.8, 100.5, 62.4, 55.7, 32.4, 28.4.

1e. Yellow oil, 55% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 1.6 Hz, 1H), 7.23 (dd, J = 8.8, 2.0 Hz, 1H), 7.07 (d, J = 8.4 Hz, 1H), 6.84 (s, 1H), 3.78 (t, J = 6.4 Hz, 2H), 3.63 (s, 3H), 2.87 (t, J = 6.4 Hz, 2H), 2.16 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.5, 129.4, 128.3, 124.2, 121.2, 112.0, 110.6, 110.4, 62.4, 32.3, 28.0; IR (film): ν_{max} (cm^{-1}) = 3354, 2925, 1611, 1477, 1422, 1377, 1286, 1144, 1046, 865, 790, 746, 610; MS (EI, m/z, rel. intensity) 253 ([M]$^+$, 25), 144 (100), 222 (95); HRMS (EI) calcd for $C_{11}H_{12}BrNO$ ([M]$^+$): 253.0102. Found: 253.0106.

1f. Light yellow oil, 51% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (t, J = 0.8 Hz, 1H), 7.10 (d, J = 1.2 Hz, 2H), 6.84 (s, 1H), 3.76 (t, J = 6.4 Hz, 2H), 3.62 (s, 3H), 2.86 (t, J = 6.4 Hz, 2H), 2.29 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.2, 128.7, 128.4, 124.4, 121.6, 118.1, 110.4, 110.2, 62.4, 32.5, 28.2; IR (film): ν_{max} (cm^{-1}) = 3356, 2926, 1612, 1479, 1422, 1379, 1287, 1046, 864, 791, 623; MS (EI, m/z, rel. intensity) 209 ([M]$^+$), 178 (100); HRMS (EI) calcd for $C_{11}H_{12}$ ClNO ([M]$^+$): 209.0607. Found: 209.0609.

1g. Light yellow oil, 55% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, J = 8.8, 5.2 Hz, 1H), 6.87 (dd, J = 10.0, 2.0 Hz, 1H), 6.84–6.78 (m, 2H), 3.77 (t, J = 6.4 Hz, 2H), 3.54 (s, 3H), 2.89 (t, J = 6.4 Hz, 2H), 2.51 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7 (d, J = 235.8 Hz), 136.8 (d, J = 12.0 Hz), 127.2 (d, J = 3.6 Hz), 124.2, 119.4 (d, J = 10.1 Hz), 110.9, 107.2 (d, J = 24.4 Hz), 95.4 (d, J = 35.9 Hz), 62.4, 32.3, 28.3; IR (film): ν_{max} (cm^{-1}) = 3354, 2935, 1623, 1557,1479, 1422, 1382, 1335, 1242, 1106, 1045, 917, 828, 799; MS (EI, m/z, rel. intensity) 193 ([M] $^+$, 21), 162 (100); HRMS (EI) calcd for $C_{11}H_{12}FNO$ ([M]$^+$): 193.0903. Found: 193.0904.

1h. Yellow oil, 90% yield.[5d] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 8.4 Hz, 1H), 7.14 (d, J = 2.0 Hz, 1H), 6.97 (dd, J = 8.4, 2.0 Hz, 1H), 6.69 (s, 1H), 3.71 (t, J = 6.8 Hz, 2H), 3.45 (s, 3H), 2.97 (s, 1H), 2.83 (t, J = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.0, 127.5, 127.1, 126.2, 119.4, 119.0, 110.8, 108.9, 62.2, 32.1, 28.0.

1i. Light yellow solid, 51% yield. M.p. 65–68 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 8.4 Hz, 1H), 6.92 (t, J = 7.6 Hz, 1H), 6.85 (d, J = 7.2 Hz, 1H), 6.66 (s, 1H), 3.84 (s, 3H), 3.76 (t, J = 6.4 Hz, 2H), 2.88 (t, J = 6.4 Hz, 2H), 2.65 (s, 3H), 2.33 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.4, 128.6, 124.0, 121.0, 118.8, 116.6, 110.0, 62.3, 36.1, 28.1, 19.3; IR (film): ν_{max} (cm^{-1}) = 3346, 2927, 2875, 1605, 1584, 1494, 1460, 1407, 1319, 1252, 1212, 1135, 1105, 1045, 781, 743, 669, 580; MS (EI, m/z, rel. intensity) 189 ([M]$^+$, 20), 158 (100), 115 (15); HRMS (EI) calcd for $C_{12}H_{15}NO$ ([M]$^+$): 189.1154. Found: 189.1151.

1j. White solid, 81% yield. M.p. 68–70 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, J = 8.0, 0.8 Hz, 1H), 7.28 (dd, J = 7.6, 0.8 Hz, 1H), 6.83 (t, J = 7.6 Hz, 1H), 6.72 (s, 1H), 3.97 (s, 3H), 3.78–3.72 (m, 2H), 2.85 (t, J = 6.4 Hz, 2H), 2.45 (t, J = 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.1, 130.8, 130.0, 126.3, 119.8, 118.0, 110.6, 103.7, 62.2, 36.2, 28.1; IR (film): ν_{max} (cm^{-1}) = 3346, 2945, 1610, 1566, 1486, 1455, 1409, 1361, 1305, 1216, 1199, 1128, 1072, 1046, 1013, 809, 778, 733, 609; MS (EI, m/z, rel. intensity) 253 ([M]$^+$, 11), 144 (100), 222 (39); HRMS (EI) calcd for $C_{11}H_{12}BrNO$ ([M]$^+$): 253.0102. Found: 253.0097.

1k. Light yellow oil, 71% yield.[5d] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (t, J = 6.8 Hz, 1H), 7.19 (d, J = 7.6 Hz, 1H), 7.14–7.10 (m, 1H), 7.06–7.02 (m, 1H), 6.83 (s, 1H), 5.89–5.79 (m, 1H), 5.07 (d, J = 10.4 Hz, 1H), 4.97 (d, J = 17.2 Hz, 1H), 4.51 (s, 2H), 3.75 (t, J = 6.4 Hz, 2H), 2.89 (t, J = 6.4 Hz, 2H), 2.10 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.3, 133.4, 127.9, 126.0, 121.5, 118.8, 117.0, 111.0, 109.5, 62.5, 48.4, 28.5.

General procedure for cascade dearomatization of *N*-substituted tryptophols

To a flame-dried Schlenk tube under argon was added 3-acyloyl-1,3-oxazolidin-2-one (50.8 mg, 0.36 mmol, 120 mol%), scandium trifluoromethanesulfonate (14.8 mg, 0.03 mmol, 10 mol%) and DCM (1.0 mL). The reaction mixture was stirred at rt for 30 min then 2-(1-methyl-1*H*-indol-3-yl)ethanol (0.30 mmol, dissolved in 1.0 mL DCM) was added and another 1 mL DCM was added *via* syringe. The reaction mixture was then heated at 50 °C for 11 h. After the reaction was complete (monitored by TLC), the reaction mixture was loaded directly on silica gel and purified by column chromatography on silica gel (PE/EA = 2/5) to afford the desired product **3**.

3a. White solid, 76% yield, M.p. 143–145 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.09 (t, J = 7.5 Hz, 1H), 7.02 (d, J = 7.2 Hz, 1H), 6.64 (t, J = 7.2 Hz, 1H), 6.35 (d, J = 7.8 Hz, 1H), 5.18 (s, 1H), 4.34–4.22 (m, 2H), 3.96–3.83 (m, 3H), 3.44–3.39 (m, 1H), 2.92 (s, 3H), 2.85 (t, J = 7.8 Hz, 2H), 2.41–2.31 (m, 1H), 2.17–1.98 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.9, 153.1, 151.2, 131.0, 128.3, 123.3, 116.9, 104.8, 102.7, 66.9, 61.8, 55.7, 42.3, 40.2, 32.5, 31.0, 30.6; IR (thin film): ν_{max} (cm^{-1}) = 2924, 2870, 1779, 1698, 1607, 1494, 1388, 1362, 1304, 1224, 1122, 1039, 1019, 747, 666; MS (ESI) 317 ([M + H]$^+$); HRMS (MALDI) calcd for $C_{17}H_{21}N_2O_4$ ([M+H]$^+$): 317.1496. Found: 317.1504.

3b. Viscous colorless oil, 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (t, J = 7.6 Hz, 1H), 6.40 (d, J = 7.6 Hz, 1H), 6.19 (d, J = 7.6 Hz, 1H), 5.18 (s, 1H), 4.29–4.20 (m, 2H), 3.92–3.90 (m, 1H), 3.84–3.81 (m, 1H), 3.76–3.74 (m, 1H), 3.47–3.46 (m, 1H), 2.90 (s, 3H), 2.83–2.80 (m, 1H), 2.68–2.66 (m, 2H), 2.34–2.28 (m, 4H), 2.07–1.96 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8, 153.0, 151.7, 134.2, 128.3, 127.2, 119.6, 103.2, 102.5, 66.5, 61.7, 56.0, 42.4, 38.8, 32.0, 30.7, 30.7, 18.1; IR (thin film): ν_{max} (cm^{-1}) = 2923, 2868, 1780, 1697, 1596, 1479, 1448, 1388, 1362, 1298, 1223, 1153, 1117, 1037, 1014, 967, 772, 759; MS (ESI) 331 ([M + H]$^+$); HRMS (MALDI) calcd for $C_{18}H_{23}N_2O_4$ ([M + H]$^+$): 331.1652. Found: 331.1649.

3c. Viscous colorless oil, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 (t, J = 8.0 Hz, 1H), 6.74 (d, J = 8.8 Hz, 1H), 6.28 (d, J = 8.0 Hz, 1H), 5.21 (s, 1H), 4.37–4.26 (m, 2H), 3.94–3.86 (m, 3H), 3.45–3.44 (m, 1H), 2.91–2.80 (m, 5H), 2.65–2.61 (m, 2H), 2.05–1.94 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 153.2, 153.1, 130.1, 127.7, 121.0, 119.1, 103.8, 102.4, 66.7, 61.8, 57.5, 42.4, 38.1, 31.1, 30.6, 30.4; IR (thin film): ν_{max} (cm^{-1}) = 2924, 2867, 1778, 1697, 1597, 1478, 1387, 1362, 1328, 1298, 1224, 1106, 1016, 760, 736; MS (ESI) 397

([M + H]$^+$); HRMS (MALDI) calcd for $C_{17}H_{20}BrN_2O_4$ ([M + H]$^+$): 395.0610. Found: 395.0610.

3d. Viscous colorless oil, 74% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.68–6.65 (m, 2H), 6.28 (d, J = 8.4 Hz, 1H), 5.16 (s, 1H), 4.37–4.27 (m, 2H), 3.94–3.92 (m, 3H), 3.74 (s, 3H), 3.47–3.43 (m, 1H), 2.88–2.77 (m, 5H), 2.36–2.31 (m, 1H), 2.16–2.00 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 153.2, 152.4, 145.8, 132.5, 112.9, 110.7, 105.5, 103.4, 67.0, 61.8, 56.0, 55.9, 42.4, 40.1, 32.3, 31.4, 31.2; IR (thin film): ν_{max} (cm^{-1}) = 2926, 2872, 1780, 1698, 1596, 1498, 1448, 1388, 1362, 1325, 1280, 1226, 1156, 1120, 1035, 964, 802, 759, 697, 667; MS (ESI) 347 ([M + H]$^+$); HRMS (MALDI) calcd for $C_{18}H_{22}N_2O_5$ ([M]$^+$): 346.1523. Found: 346.1519.

3e. Viscous colorless oil, 75% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, J = 10.0 Hz, 1H), 7.08 (s, 1H), 6.22 (d, J = 8.4 Hz, 1H), 5.18 (s, 1H), 4.38–4.26 (m, 2H), 3.96–3.88 (m, 3H), 3.45–3.38 (m, 1H), 2.89 (s, 3H), 2.82 (t, J = 7.6 Hz, 2H), 2.41–2.34 (m, 1H), 2.11–2.00 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 153.1, 150.4, 133.4, 131.0, 126.2, 108.2, 106.2, 102.6, 66.8, 61.8, 55.9, 42.4, 40.3, 32.4, 30.9, 30.6; IR (thin film): ν_{max} (cm^{-1}) = 2925, 2872, 1780, 1698, 1600, 1494, 1388, 1362, 1325, 1272, 1224, 1108, 1039, 1016, 964, 804, 758, 667, 626, 523; MS (ESI) 395 ([M + H]$^+$); HRMS (MALDI) calcd for $C_{17}H_{20}BrN_2O_4$ ([M + H]$^+$): 395.0601. Found: 395.0607.

3f. Viscous colorless oil, 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (dd, J = 8.4, 2.0 Hz, 1H), 6.96 (d, J = 2.0 Hz, 1H), 6.26 (d, J = 8.0 Hz, 1H), 5.19 (s, 1H), 4.38–4.27 (m, 2H), 3.94–3.88 (m, 3H), 3.45–3.39 (m, 1H), 2.90 (s, 3H), 2.82 (t, J = 8.0 Hz, 2H), 2.41–2.33 (m, 1H), 2.12–2.00 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 153.2, 150.0, 132.9, 128.1, 123.5, 121.4, 105.6, 102.8, 66.9, 61.9, 55.9, 42.4, 40.3, 32.4, 30.9, 30.7; IR (thin film): ν_{max} (cm^{-1}) = 2924, 2872, 1779, 1698, 1604, 1495, 1387, 1362, 1325, 1271, 1223, 1108, 1086, 1039, 1016, 806, 758, 667, 525; MS (ESI) 351 ([M + H]$^+$); HRMS (MALDI) calcd for $C_{17}H_{20}ClN_2O_4$ ([M + H]$^+$): 351.1106. Found: 351.1114.

3g. White solid, 64% yield, M.p. 145–148 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.91 (dd, J = 8.0, 5.6 Hz, 1H), 6.30 (t, J = 10.0 Hz, 1H), 6.05 (dd, J = 10.0, 2.0 Hz, 1H), 5.21 (s, 1H), 4.38–4.28 (m, 2H), 3.97–3.86 (m, 3H), 3.46–3.40 (m, 1H), 2.90 (s, 3H), 2.87–2.82 (m, 2H), 2.39–2.32 (m, 1H), 2.10–1.98 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 164.1 (d, J = 240.3 Hz), 153.2, 152.9 (d, J = 11.8 Hz), 126.4 (d, J = 2.0 Hz), 123.9 (d, J = 10.7 Hz), 103.1, 102.6 (d, J = 22.7 Hz), 92.8 (d, J = 26.9 Hz), 67.0, 61.8, 55.4, 42.5, 40.4, 32.7, 31.0, 30.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ −114.3 (m); IR (thin film): ν_{max} (cm^{-1}) = 2925, 2868, 1780, 1698, 1618, 1602, 1500, 1388, 1362, 1324, 1224, 1177, 1118, 1097, 1039, 1016, 964, 824, 759, 705, 618, 540, 490; MS (ESI) 335 ([M + H]$^+$); HRMS (MALDI) calcd for $C_{17}H_{20}FN_2O_4$ ([M + H]$^+$): 335.1402. Found: 335.1405.

3h. Viscous colorless oil, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (d, J = 8.0 Hz, 1H), 6.59 (d, J = 9.2 Hz, 1H), 6.30 (s, 1H), 5.20 (s, 1H), 4.37–4.28 (m, 2H), 3.94–3.88 (m, 1H), 3.88–3.86 (m, 2H), 3.43–3.38 (m, 1H), 2.89 (s, 3H), 2.86–2.79 (m, 2H), 2.40–2.33 (m, 1H), 2.10–1.97 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8, 153.2, 152.4, 134.1, 129.5, 124.2, 116.5, 105.0, 102.8, 66.9, 61.8, 55.5, 42.4, 40.3, 32.5, 30.9, 30.4; IR (thin film): ν_{max} (cm^{-1}) = 2923, 2868, 1782, 1698, 1606, 1498, 1448, 1415, 1388, 1362, 1330, 1224, 1123, 1039, 1016, 964, 828, 758, 710, 607; MS (ESI) 351 ([M + H]$^+$); HRMS (MALDI) calcd for $C_{17}H_{20}ClN_2O_4$ ([M + H]$^+$): 351.1106. Found: 351.1113.

3i. White solid, 67% yield, M.p. 119–122 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 (dd, J = 10.0, 7.6 Hz, 2H), 6.64 (t, J = 7.6 Hz, 1H), 5.06 (s, 1H), 4.36–4.25 (m, 2H), 3.94–3.86 (m, 3H), 3. 50–3.44 (m, 1H), 3.18 (s, 3H), 2.88–2.75 (m, 2H), 2.39 (s, 3H), 2.37–2.34 (m, 1H), 2.15–1.96 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 153.2, 149.6, 132.2, 131.4, 121.3, 118.6, 118.3, 105.2, 66.5, 61.8, 55.2, 42.4, 40.4, 36.0, 33.0, 31.2, 19.1; IR (thin film): ν_{max} (cm^{-1}) = 2924, 2866, 1779, 1698, 1600, 1567, 1478, 1417, 1388, 1362, 1330, 1224, 1110, 1017, 965, 759, 686, 619; MS (ESI) 331 ([M + H]$^+$); HRMS (MALDI) calcd for $C_{18}H_{23}N_2O_4$ ([M + H]$^+$): 331.1652. Found: 331.1661.

3j. White solid, 72% yield, M.p. 102–105 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, J = 9.2 Hz, 1H), 6.95 (d, J = 7.2 Hz, 1H), 6.54 (t, J = 7.6 Hz, 1H), 5.11 (s, 1H), 4.40–4.30 (m, 2H), 3.96–3.91 (m, 3H), 3.50–3.44 (m, 1H), 3.31 (s, 3H), 2.89–2.74 (m, 2H), 2.37–2.29 (m, 1H), 2.12–1.98 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 153.2, 147.7, 134.9, 133.7, 122.6, 119.2, 104.4, 100.4, 66.5, 61.9, 55.0, 42.4, 40.5, 35.0, 32.7, 31.1; IR (thin film): ν_{max} (cm^{-1}) = 2922, 2866, 1780, 1698, 1592, 1474, 1451, 1388, 1362, 1323, 1271, 1225, 1072, 1038, 1002, 965, 750, 700; MS (ESI) 395 ([M + H]$^+$); HRMS (MALDI) calcd for $C_{17}H_{20}BrN_2O_4$ ([M + H]$^+$): 395.0601. Found: 395.0613.

3k. Viscous colorless oil, 67% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.09–7.02 (m, 2H), 6.65 (t, J = 7.2 Hz, 1H), 6.37 (d, J = 7.5 Hz, 1H), 5.96–5.83 (m, 1H), 5.28 (s, 1H), 5.27 (d, J = 17.1 Hz, 1H), 5.17 (d, J = 10.2 Hz, 1H), 4.33–4.26 (m, 2H), 3.96–3.84 (m, 5H), 3.50–3.41 (m, 1H), 2.95–2.71 (m, 2H), 2.42–2.32 (m, 1H), 2.19–1.98 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.9, 153.1, 150.4, 134.0, 130.9, 128.2, 123.3, 117.1, 116.5, 105.3, 101.3, 66.7, 61.8, 55.7, 47.2, 42.3, 40.5, 32.7, 31.2; IR (thin film): ν_{max} (cm^{-1}) = 3566, 2923, 2865, 1780, 1698, 1605, 1491, 1448, 1388, 1362, 1314, 1224, 1121, 1039, 1021, 955, 921, 747, 668, 615; MS (ESI) 343 ([M + H]$^+$); HRMS (MALDI) calcd for $C_{19}H_{23}N_2O_4$ ([M + H]$^+$): 343.1652. Found: 343.1649.

4. To a solution of **3a** (158.1 mg, 0.5 mmol) in THF–H_2O (35 mL, 4 : 1) was added H_2O_2 (30% solution in H_2O, 0.57 mL, 5.0 mmol) at 0 °C under argon over 2 min. Then a solution of LiOH·H_2O (126.0 mg, 3.0 mmol) in 2 mL water was added. The mixture was stirred at 0 °C for 3 h, aqueous solution (5 mL) of Na_2SO_3 (756.2 mg, 6.0 mmol) was added. The reaction mixture was then stirred for 30 min and acidified with 2 N aq. HCl (5 mL). The mixture was extracted with DCM (3 × 10 mL). The combined organic phases were dried with Na_2SO_4 and the solvent was evaporated under vacuum. The residue was purified by silica gel column chromatography using PE/EA = 5/2 as the eluent affording compound **4** as a white solid (127.1 mg 98% yield), M.p. 109–112 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.19 (brs, 1H), 7.03 (t, J = 7.5 Hz, 1H), 6.93 (d, J = 6.9 Hz, 1H), 6.60 (t, J = 7.5 Hz, 1H), 6.29 (d, J = 7.8 Hz, 1H), 5.05 (s, 1H), 3.87 (t, J = 7.2 Hz, 1H), 3.37–3.32 (m, 1H), 2.82 (s, 3H), 2.25–1.92 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.0, 151.1,

130.9, 128.6, 122.9, 117.5, 105.1, 102.4, 67.1, 55.7, 40.2, 32.5, 30.5, 30.2; IR (thin film): ν_{max} (cm^{-1}) = 2926, 1708, 1608, 1494, 1450, 1428, 1389, 1301, 1225, 1157, 1125, 996, 922, 872, 744, 666, 620, 604, 539, 455; MS (ESI) 248 ($[M + H]^+$); HRMS (MALDI) calcd for $C_{14}H_{17}NO_3$ ($[M]^+$): 247.1208. Found: 247.1214.

5. To a solution of **3a** (94.8 mg, 0.3 mmol) in CH_3OH (10 mL) at 0 °C was added CH_3MgBr (1 M in THF, 0.45 mL) with a syringe. After stirring at the same temperature for 1 h, the reaction was complete (monitored by TLC). Then the reaction mixture was loaded directly on silica gel and purified by silica gel column chromatography (PE/EA = 5/1) to afford the desired product **5** as a white solid (78.9 mg, 99% yield), M.p. 59–62 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.03 (t, J = 7.5 Hz, 1H), 6.94 (d, J = 7.2 Hz, 1H), 6.60 (t, J = 7.5 Hz, 1H), 6.29 (d, J = 7.8 Hz, 1H), 5.03 (s, 1H), 3.87 (t, J = 7.5 Hz, 1H), 3.53 (s, 3H), 3.38–3.29 m, 1H), 2.83 (s, 3H), 2.20–1.93 m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.7, 151.2, 131.1, 128.5, 122.9, 117.3, 105.0, 102.5, 67.1, 55.8, 51.5, 40.3, 32.8, 30.6, 30.3; IR (thin film): ν_{max} (cm^{-1}) = 3051, 2926, 2869, 1736, 1607, 1493, 1436, 1376, 1301, 1260, 1197, 1165, 1125, 1013, 923, 872, 799, 744, 666, 605, 456; MS (ESI) 262 ($[M + H]^+$); HRMS (MALDI) calcd for $C_{14}H_{17}NO_3$ ($[M]^+$): 261.1365. Found: 261.1371.

6. DIBAL-H (1.0 M, in THF, 1.2 mL, 1.2 mmol) was added dropwise to a stirring solution of **3a** (94.8 mg, 0.3 mmol) in dry CH_2Cl_2 (3 mL) at −78 °C under argon. The mixture was stirred at the same temperature for 2 h. Aqueous saturated potassium sodium tartrate (5 mL) was added, followed by DCM (5 mL). The mixture was stirred at ambient temperature until the phases were clear. Then the organic layer was separated. The aqueous layer was extracted with DCM (3 × 10 mL). The combined organic phases were washed with water, brine, separated and dried with Na_2SO_4. Removal of the solvent by rotary evaporation followed by column chromatography (PE/EA = 5/1) on silica gel gave compound **6** (26.2 mg, 38% yield) as a viscous colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.59 (s, 1H), 7.06 (t, J = 7.5 Hz, 1H), 6.93 (d, J = 7.2 Hz, 1H), 6.62 (t, J = 7.5 Hz, 1H), 6.31 (d, J = 7.8 Hz, 1H), 5.02 (s, 1H), 3.88 (t, J = 8.1 Hz, 1H), 3.36–3.32 (m, 1H), 2.84 (s, 3H), 2.40–1.91 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.6, 151.2, 131.1, 128.9, 123.0, 117.5, 105.0, 102.4, 67.2, 55.6, 40.4, 39.9, 30.6, 30.1; IR (thin film): ν_{max} (cm^{-1}) = 3420, 3051, 2924, 2869, 2723, 1756, 1722, 1607, 1493, 1448, 1389, 1362, 1302, 1260, 1223, 1125, 1020, 940, 913, 873, 801, 745, 661, 606, 539, 508, 456; MS (ESI) 232 ($[M + H]^+$); HRMS (MALDI) calcd for $C_{14}H_{17}NO_2$ ($[M]^+$): 231.1259. Found: 231.1267.

7. To a stirred solution of **3a** (94.8 mg, 0.3 mmol) in MeOH (10 mL) at 0 °C was added $NaBH_4$ portionwise (34.2 mg, 0.9 mmol). The reaction mixture was allowed to stir for 1 h at same temperature and then quenched with saturated aqueous NH_4Cl. The solvent was removed under reduced pressure and the resulting residue was diluted with water and extracted with EtOAc (3 × 10 mL). The combined organic layers were dried with Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (PE/EA = 5/3) to afford the product **7** (65.1 mg, 93%) as viscous colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.02 (t, J = 8.1 Hz, 1H), 6.93 (d, J = 7.2 Hz, 1H), 6.58 (t, J = 7.2 Hz, 1H), 6.28 (d, J = 7.8 Hz, 1H), 5.04 (s, 1H), 3.88–3.82 (m, 1H), 3.45 (t, J = 6.6 Hz, 2H), 3.37–3.31 (m, 1H), 2.82 (s, 3H), 2.06–1.88 (m, 2H), 1.80–1.64 (m, 3H), 1.51–1.343 (m, 1H), 1.32–1.24 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.1, 132.3, 128.1, 122.8, 117.1, 104.8, 102.9, 67.0, 62.8, 56.1, 40.4, 34.3, 30.6, 28.6; IR (thin film): ν_{max} (cm^{-1}) = 3405, 3051, 2938, 2871, 1607, 1494, 1449, 1428, 1388, 1357, 1300, 1222, 1156, 1125, 1058, 1020, 942, 911, 742, 675, 606, 539, 516, 456; MS (ESI) 234 ($[M + H]^+$); HRMS (MALDI) calcd for $C_{14}H_{19}NO_2$ ($[M]^+$): 233.1416. Found: 233.1424.

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References

1 (*a*) A. S. ElAzab, T. Taniguchi and K. Ogasawara, *Org. Lett.*, 2000, **2**, 2757; (*b*) A. W. Schammel, B. W. Boal, L. Zu, T. Mesganaw and N. K. Garg, *Tetrahedron*, 2010, **66**, 4687; (*c*) L. Zu, B. W. Boal and N. K. Garg, *J. Am. Chem. Soc.*, 2011, **133**, 8877.

2 For recent reviews, see: (*a*) S. P. Roche and J. A. Porco Jr, *Angew. Chem., Int. Ed.*, 2011, **50**, 4068; (*b*) L. Pouységu, D. Deffieux and S. Quideau, *Tetrahedron*, 2010, **66**, 2235; (*c*) D. Zhang, H. Song and Y. Qin, *Acc. Chem. Res.*, 2011, **44**, 447.

3 For selected dearomatization of indoles: (*a*) J. Lévy, J. Sapi, J.-Y. Laronze, D. Royer and L. Toupet, *Synlett*, 1992, 601; (*b*) J. M. Schkeryantz, J. C. G. Woo, P. Siliphaivanh, K. M. Depew and S. J. Danishefsky, *J. Am. Chem. Soc.*, 1999, **121**, 11964; (*c*) J. F. Austin, S.-G. Kim, C. J. Sinz, W.-J. Xiao and D. W. C. MacMillan, *Proc. Natl. Acad. Sci. U. S. A.*, 2004, **101**, 5482; (*d*) B. M. Trost and J. Quancard, *J. Am. Chem. Soc.*, 2006, **128**, 6314; (*e*) L. M. Repka, J. Ni and S. E. Reisman, *J. Am. Chem. Soc.*, 2010, **132**, 14418; (*f*) S. B. Jones, B. Simmons and D. W. C. MacMillan, *J. Am. Chem. Soc.*, 2009, **131**, 13606; (*g*) R. R. Knowles, J. Carpenter, S. B. Blakey, A. Kayano, I. K. Mangion, C. J. Sinz and D. W. C. MacMillan, *Chem. Sci.*, 2011, **2**, 308.

4 (*a*) Y. Liu, W. Xu and X. Wang, *Org. Lett.*, 2010, **12**, 1448; (*b*) G. Cera, P. Crispino, M. Monari and M. Bandini, *Chem. Commun.*, 2011, **47**, 7803; (*c*) E. L. Noey, X. Wang and K. N. Houk, *J. Org. Chem.*, 2011, **76**, 3477; (*d*) G. Cera, M. Chiarucci, A. Mazzanti, M. Mancinelli and M. Bandini, *Org. Lett.*, 2012, **14**, 1350; (*e*) F. Fan, W. Xie and D. Ma, *Org. Lett.*, 2012, **14**, 1405.

5 (*a*) T. Sunazuka, T. Hirose, T. Shirahata, Y. Harigaya, M. Hayashi, K. Komiyama, S. Ōmura and A. B. Smith III, *J. Am. Chem. Soc.*, 2000, **122**, 2122; (*b*) T. Sunazuka, K. Yoshida, N. Kojima, T. Shirahata, T. Hirose, M. Handa, D. Yamamoto, Y. Harigaya, I. Kuwajima and S. Ōmura, *Tetrahedron Lett.*, 2005, **46**, 1459; (*c*) S.-G. Kim, *Bull. Korean Chem. Soc.*, 2009, **30**, 2519; (*d*) O. Lozano, G. Blessley, T. Martinez del Campo, A. L. Thompson, G. T. Giuffredi, M. Bettati, M. Walker, R. Borman and V. Gouverneur, *Angew. Chem., Int. Ed.*, 2011, **50**, 8105.

6 For reviews on Lewis acid-catalyzed Michael reaction, see: (*a*) J. S. Johnson and D. A. Evans, *Acc. Chem. Res.*, 2000, **33**, 325; (*b*) G. Desimoni, G. Faita and K. A. Jørgensen, *Chem. Rev.*, 2006, **106**, 3561; (*c*) S. Kobayashi and Y. Yamashita, *Acc. Chem. Res.*, 2011, **44**, 58.

7 For reviews on Friedel–Crafts alkylation of indoles, see: (*a*) M. Bandini, A. Melloni and A. Umani-Ronchi, *Angew. Chem., Int. Ed.*, 2004, **43**, 550; (*b*) M. Bandini, A. Melloni, S. Tommasi and A. Umani-Ronchi, *Synlett*, 2005, 1199; (*c*) T. B. Poulsen and K. A. Jørgensen, *Chem. Rev.*, 2008, **108**, 2903; (*d*) S.-L. You, Q. Cai and M. Zeng, *Chem. Soc. Rev.*, 2009, **38**, 2190; (*e*) M. Zeng and S.-L. You, *Synlett*, 2010, 1289.

8 (*a*) Q.-F. Wu, H. He, W.-B. Liu and S.-L. You, *J. Am. Chem. Soc.*, 2010, **132**, 11418; (*b*) Q.-F. Wu, W.-B. Liu, C.-X. Zhuo, Z.-Q. Rong, K.-Y. Ye

and S.-L. You, *Angew. Chem., Int. Ed.*, 2011, **50**, 4455; (*c*) C.-X. Zhuo, W.-B. Liu, Q.-F. Wu and S.-L. You, *Chem. Sci.*, 2012, **3**, 205; (*d*) Q.-F. Wu, C. Zheng and S.-L. You, *Angew. Chem., Int. Ed.*, 2012, **51**, 1680; (*e*) Q. Cai, C. Zheng and S.-L. You, *Angew. Chem., Int. Ed.*, 2011, **50**, 8665.

9 For selected Lewis acid-catalyzed Michael reactions with oxazolidinone auxiliaries, see: (*a*) S. Murarka, I. Deb, C. Zhang and D. Seidel, *J. Am. Chem. Soc.*, 2009, **131**, 13226; (*b*) T. Poisson, Y. Yamashita and S. Kobayashi, *J. Am. Chem. Soc.*, 2010, **132**, 7890.

10 (*a*) K. Narasaka, H. Kusama and Y. Hayashi, *Bull. Chem. Soc. Jpn.*, 1991, **64**, 1471; (*b*) J. Yang, H. Wu, L. Shen and Y. Qin, *J. Am. Chem. Soc.*, 2007, **129**, 13794; (*c*) C. Menozzi, P. I. Dalko and J. Cossy, *Chem. Commun.*, 2006, 4638; (*d*) A. Palmieri and M. Petrini, *Org. Biomol. Chem.*, 2012, **10**, 3486.