Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

Unprecedented Carbon-Carbon Bond Cleavage in Nucleophilic Aziridine Ring Opening Reaction, Efficient Ring Transformation of Aziridines to Imidazolidin-4-ones

*Jin-Yuan Wang, Yuan Hu, De-Xian Wang, Jie Pan, Zhi-Tang Huang, and Mei-Xiang Wang**

Beijing National Laboratory for Molecular Sciences, Laboratory of Chemical Biology, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

mxwang@iccas.ac.cn

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1. General experimental methods and spectroscopic data of compounds prepared.

Both melting points and boiling points are uncorrected. Starting materials **1**,[1-3] **2**,[4] **5**,[4] and **7**[1-3] were prepared according to the literature methods.

1.1 General procedure for the cross-coupling reaction of trans- and cis-3-aryl-1-methylaziridine-2-carboxamides 1 and 7 with 1-aryl-2-bromoethenes 2 and 5.

Under argon protection, a mixture of trans- or cis-3-aryl-1-methylaziridine-2-carboxamides **1** or **7** (1 mmol), *N,N*-dimethylglycine (112 mg, 0.8 mmol), Cs_2CO_3 (652 mg, 2 mmol), CuI (76 mg, 0.4 mmol) and 1-aryl-2-bromoethenes **2** or **5** (3 mmol) in dry 1,4-dioxane (40 mL) was refluxed for a period of time (Table 1 and Scheme2 3-5). After completion of the reaction, which was

monitored by TLC, the mixture was filtrated through a pad silica gel (100-200 mesh). The filtrate was concentrated under vacuum, the resulting residue was chromatographed on a silica gel column using a mixture of petroleum ether and ethyl acetate (1:5) to give pure products **3**, **4**, **6, 8** and **9** (Table 1 and Schemes 3-5).

1.2 Conversion of *N*-styryl-3-phenyl-1-methylaziridine-2-carboxamides 3 and 9 into the corresponding imidazolidin-4-one products 4a and 6a.

Under argon protection, a mixture of *N*-styryl-3-phenyl-1-methylaziridine-2-carboxamide **3** (0.5 mmol) and Cs_2CO_3 (2 mmol) in dry 1,4-dioxane (10 mL) was refluxed 12 h, while in the case of **9**, a mixture of **9** (0.5 mmol) and NaH (2 mmol) in dry DMF was stirred at 70 ^oC. After completion of the reaction, which was monitored by TLC, water was added and resulting mixture was extracted with ethyl acetate (20 mL×3). The organic layer was dried over with anhydrous Na_2SO_4, concentrated under vacuum to give a residue. Column chromatography on a silica gel column using a mixture of petroleum ether and ethyl acetate (1:5) to give pure products **4a** or **6a**.

1.3 Characterization of the products prepared.

***N*-(*Z*-Phenylvinyl)-*trans*-1-methyl-3-phenylaziridine-2-carboxamide 3:** oil; ^1H NMR (300 MHz, $CDCl_3$ TMS) δ 9.07 (d, 1H, J = 10.8 Hz), 6.88-7.44 (m, 11H), 5.75 (d, 1H, J = 9.6 Hz), 3.29 (s, 1H), 2.69 (s, 1H), 2.15 (s, 3H); IR (KBr) ν 3335 (N-H), 1687 (C=O), 1654 cm^{-1}; ^{13}C NMR (75 MHz, $CDCl_3$ TMS) δ 168.1, 135.8, 131.5, 130.0, 129.0, 127.9, 126.8, 121.0, 110.5, 48.0, 44.0, 37.9; MS (EI) *m/z* (%) 278 (15) $[M]^+$, 233 (22), 208 (19), 160 (28), 132 (100). HRMS Calcd for $C_{18}H_{18}N_2O$ (M+1) 278.1419, Found 278.1423.

1-Methyl-2-phenyl-3-(*Z*-phenylvinyl)imidazolidin-4-one 4a: oil; ^1H NMR (300 MHz, $CDCl_3$ TMS) δ 6.79-.739 (m, 10H), 6.29 (d, 2H, J = 9.5 Hz), 5.96 (d, 1H, J = 9.5 Hz), 4.89 (s, 1H), 3.70 (d, 1H, J = 15.0 Hz), 3.28 (d, 1H, J = 14.9 Hz) 2.24 (s, 3H); IR (KBr) ν 1719 (C=O), 1650 cm^{-1}; ^{13}C NMR (75 MHz, $CDCl_3$ TMS) δ 170.1, 139.3, 136.1, 133.8, 129.6, 128.5, 127.4, 126.7, 125.6, 121.3, 114.6, 82.8, 56.6, 39.1; MS (EI) *m/z* (%) 278 (20) $[M]^+$, 184 (15), 184 (15), 132 (100). HRMS Calcd for $C_{18}H_{18}N_2O$ (M+1) 278.1419,

Found 278.1422.

3-(*Z*-4-Chlorophenylvinyl)-1-methyl-2-phenylimidazolidin-4-one 4b: mp 102-103 °C; ^{1}H NMR (300 MHz, $CDCl_3$ TMS) δ 7.12-7.20 (m, 5H), 6.88 (d, 2H, J = 9.6 Hz), 6.80 (d, 2H, J = 9.0 Hz), 6.17 (d, 1H, J = 9.5 Hz), 5.82 (d, 1H, J = 9.7 Hz), 4.78 (s, 1H), 3.61 (d, 1H, J = 14.9 Hz), 3.20 (d, 1H, J = 14.9 Hz), 2.18 (s, 3H); IR (KBr) ν 1720 (C=O), 1650 cm^{-1}; ^{13}C NMR (75 MHz, $CDCl_3$ TMS) δ 171.0, 136.1, 134.3, 133.1, 130.2, 129.1, 128.3, 128.2, 127.8, 121.7, 119.7, 83.6, 56.5, 38.9; MS (EI) *m/z* (%) 312 (15) $[M]^+$, 314 (5) $[M+2]^+$, 132 (100). HRMS Calcd for $C_{18}H_{17}ClN_2O$ (M +1) 312.1029, Found 312.1034.

1-Methyl-2-phenyl-3-(*Z*)-(4-tolylvinyl)imidazolidin-4-one 4c: oil; ^{1}H NMR (300 MHz, $CDCl_3$ TMS) δ 6.77-7.20 (m, 9H), 6.11 (d, 1H, J = 9.4 Hz), 5.89 (d, 1H, J = 9.4 Hz), 4.85 (s, 1H), 3.62 (d, 1H, J = 14.9 Hz), 3.22 (d, 1H, J = 14.8 Hz), 2.30 (s, 3H), 2.19 (s, 3H); IR (KBr) ν 1718 (C=O), 1650 cm^{-1}; ^{13}C NMR (75 MHz, $CDCl_3$ TMS) δ 170.2, 139.3, 136.2, 133.8, 129.6, 128.5, 127.5, 126.7, 125.6, 121.3, 114.6, 82.8, 56.6, 39.1, 21.3; MS (EI) *m/z* (%) 292 (28) $[M]^+$, 194 (3), 132 (100). HRMS Calcd for $C_{19}H_{20}N_2O$ (M+1) 292.1576, Found 292.1580.

2-(4-Fluorophenyl)-1-methyl-3-(*Z*-phenylvinyl)imidazolidin-4-one 4d: mp 131-132 °C; ^{1}H NMR (300 MHz, $CDCl_3$ TMS) δ 6.73-7.29 (m, 9H), 6.30 (d, 1H, J = 9.4 Hz), 5.97 (d, 1H, J = 9.4 Hz), 4.86 (s, 1H), 3.68 (d, 1H, J = 14.9 Hz), 3.32 (d, 1H, J = 14.9 Hz), 2.23 (s, 3H); IR (KBr) ν 1720 (C=O), 1650 cm^{-1}; ^{13}C NMR (75 MHz, $CDCl_3$ TMS) δ 171.0, 165.0, 162.5, 135.8, 132.3, 129.7, 129.6, 129.0, 128.0, 127.4, 121.2, 120.8, 115.1, 114.8, 82.7, 56.4, 39.0; MS (EI) *m/z* (%) 296 (19) $[M]^+$, 224 (3), 151 (20), 150 (100). HRMS Calcd for $C_{18}H_{17}FN_2O$ (M+1) 296.1325, Found 296.1324. Anal. Calcd for $C_{18}H_{17}FN_2O$: C, 72.95; H, 5.78; N, 9.45. Found: C, 77.99; H, 5.79; N, 9.43.

2-(4-Chlorophenyl)-1-methyl-3-(*Z*-phenylvinyl)imidazolidin-4-one 4e: mp 104-105 °C; ^{1}H NMR (300 MHz, $CDCl_3$ TMS) δ 7.21-7.29 (m, 3H), 7.13 (d, 2H, J = 8.3 Hz), 6.99-7.02 (m, 2H), 6.70 (d, 2H, J = 8.4 Hz), 6.31 (d, 1H, J = 9.5 Hz), 5.97 (d, 1H, J = 9.5 Hz), 4.86 (s, 1H), 3.67 (d, 1H, J = 14.9 Hz), 3.26 (d, 1H, J = 14.9 Hz), 2.23 (s, 3H); IR (KBr) ν 1720 (C=O), 1649 cm^{-1}; ^{13}C NMR (75 MHz, $CDCl_3$ TMS) δ171.1, 135.7, 135.1, 134.8, 129.2, 129.0, 128.3, 128.0, 127.5, 121.1, 120.8, 82.7, 56.4, 39.0; MS (EI) *m/z* (%):

312 (18) $[M]^+$, 314 (6) $[M+2]^+$, 166 (100). HRMS Calcd for $C_{18}H_{17}ClN_2O$ (M+1) 312.1029, Found 312.1032.

1-Methyl-2-phenyl-3-(*E*-phenylvinyl)imidazolidin-4-one 6a: oil; ^{1}H NMR (300 MHz, $CDCl_3$ TMS) δ 7.11-7.40 (m, 11H), 5.71 (d, 1H, J = 15.1 Hz), 5.13 (s, 1H), 3.75 (d, 1H J = 15.2 Hz), 3.32 (d, 1H, J = 15.2 Hz), 2.38 (s, 3H); IR (KBr) ν 1718 (C=O), 1649 cm^{-1}; ^{13}C NMR (75 MHz, $CDCl_3$ TMS) δ 170.2, 136.8, 136.1, 129.4, 128.9, 128.5, 127.5, 126.8, 125.6, 121.2, 114.7, 83.0, 56.5, 39.2; MS (EI) *m/z* (%) 278 (20) $[M]^+$, 132 (100). HRMS Calcd. for $C_{18}H_{18}N_2O$ (M+1) 278.1419, Found 278.1421.

3-(*E*-3-Chlorophenylvinyl)-1-methyl-2-phenylimidazolidin-4-one 6b: oil; ^{1}H NMR (300 MHz, $CDCl_3$ TMS) δ 7.12-7.38 (m, 10H), 5.71 (d, 1H, J = 15.2 Hz), 5.07 (s, 1H), 3.72 (d, 1H J = 15.3 Hz), 3.29 (d, 1H, J = 15.2 Hz), 2.35 (s, 3H); IR (KBr) ν 1720 (C=O), 1650 cm^{-1}; ^{13}C NMR (75 MHz, $CDCl_3$ TMS) δ 170.0, 135.8, 135.0, 130.2, 129.7, 129.0, 128.6, 127.7, 127.0, 125.7, 121.1, 114.7, 82.2, 56.4, 39.2; MS (EI) *m/z* (%) 312 (18) $[M]^+$, 314 (6) $[M+2]^+$, 166 (100). HRMS Calcd for $C_{18}H_{17}ClN_2O$ (M+1) 312.1029, Found 312.1033.

1-Methyl-3-(*E*-phenylvinyl)-2-tolylimidazolidin-4-one 6c: oil; ^{1}H NMR (300 MHz, $CDCl_3$ TMS) δ 7.10-7.33 (m, 10H), 5.75 (d, 1H, J = 15.1 Hz), 5.08 (s, 1H), 3.72 (d, 1H, J = 15.1 Hz), 3.29 (d, 1H, J = 15.1 Hz), 2.35 (s, 3H), 2.34 (s, 3H); IR (KBr) ν 1719 (C=O), 1649 cm^{-1}; ^{13}C NMR (75 MHz, $CDCl_3$ TMS) δ 170.2, 139.3, 136.2, 133.8, 129.6, 128.5, 127.5, 126.7, 125.6, 121.3, 114.6, 82.8, 56.6, 39.1, 21.3; MS (EI) *m/z* (%) 292 (24) $[M]^+$, 171 (18), 146 (100). HRMS Calcd for $C_{19}H_{20}N_2O$ (M+1) 292.1576, Found 292.1579.

***N*-(*Z*-Phenylvinyl)-*cis*-1-methyl-3-phenylaziridine-2-carboxamide 8:** mp 67-68 °C; ^{1}H NMR (300 MHz, $CDCl_3$ TMS) δ 8.43 (d, 1H, J = 11.0 Hz), 6.60-7.41 (m, 11H), 5.57 (d, 1H, J = 9.6 Hz), 3.00 (d, 1H, J = 7.0 Hz), 2.61 (s, 3H), 2.47 (d, 1H, J = 7.0 Hz); IR (KBr) ν 3364 (N-H), 1689 (C=O), 1654 cm^{-1}; ^{13}C NMR (75 MHz, $CDCl_3$ TMS) δ 166.1, 135.6, 134.8, 128.8, 128.3, 127.8, 127.7, 126.7, 120.5, 110.2, 49.2, 47.3, 46.4; MS (EI) *m/z* (%) 278 (27) $[M]^+$, 160 (80), 132 (100). HRMS Calcd for $C_{18}H_{18}N_2O$ (M +1) 278.1419, Found 278.1421. Anal. Calcd for $C_{18}H_{18}N_2O$: C, 77.67; H, 6.52; N, 10.06. Found: C,

77.32; H, 6.51; N, 10.10.

***N*-(*E*-Phenylvinyl)-*cis*-1-methyl-3-phenylaziridine-2-carboxamide 9:** mp 175-176 °C; ^{1}H NMR (300 MHz, $CDCl_3$ TMS) δ 7.96 (d, 1H J = 11.1 Hz), 7.09-7.33 (m, 11H), 5.90 (d, 1H, J = 14.6 Hz), 3.00 (d, 1H, J = 7.0 Hz), 2.64 (s, 3H), 2.48 (d, 1H, J = 7.1 Hz); IR (KBr) ν 3312 (N-H), 1671 (C=O), 1649 cm^{-1}; ^{13}C NMR (75 MHz, $CDCl_3$ TMS) δ 165.6, 135.5, 133.8, 131.4, 129.3, 128.8, 127.8, 126.9, 121.7, 120.5, 110.6, 48.4, 47.4, 46.2; MS (EI) *m/z* (%) 278 (28) $[M]^+$, 233 (26) 208 (11), 178 (50), 160 (40), 132 (100). Anal. Calcd for $C_{18}H_{18}N_2O$: C, 77.67; H, 6.52; N, 10.06. Found: C, 77.28; H, 6.51; N, 9.90.

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