Supplementary Material (ESI) for Chemical Communications

Supplementry Information for

Cyclopropenium ion catalysed Beckmann rearrangement

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General Information: Reagents were obtained from commercial supplier, and used without further purification unless otherwise specified by a reference. The pre-catalyst 3,3-dichloro-1,2-diphenylcyclopropene and ketoximes were prepared from 1,3-diphenylacetone and ketones, respectively following reported procedures.[1,2] Solvents were purified by the usual methods and stored over molecular sieves. All reactions were performed using oven-dried glassware under a nitrogen atmosphere. Organic solutions were concentrated using a Buchi rotary evaporator. Column chromatography was carried out over silica gel (Merck 100–200 mesh) and TLC was performed using silica gel GF254 (Merck) plates. Melting points were determined by open glass capillary method and are uncorrected. IR spectra in KBr were recorded on a Perkin-Elmer 993 IR spectrophotometer, ^{1}H NMR spectra were recorded on a Bruker AVII 400 spectrometer in $CDCl_3$/DMSO-d_6 using TMS as internal reference with chemical shift value being reported in ppm. All coupling constants (*J*) are reported in Hertz (Hz). GC-MS were obtained on a Hewlett-Packard model GCD-HP1800A.

General Procedure for Cyclopropenium Ion Catalysed Beckmann Rearrangement (Table 2)

To a solution of ketoxime **1** (1 mmol) in dry acetonitrile (3 mL), 3,3-dichloro-1,2-diphenylcyclopropene **2** (3 mol%) and $ZnCl_2$ (3 mol%) were added at rt and the reaction mixture was heated at reflux under a nitrogen atomosphere. After completion of the

reaction as indicated by TLC, it was quenched with saturated aqueous sodium hydrogen carbonate (10 mL) and extracted with ethyl acetate (3 × 10 mL). The organic phase was dried over anhydrous magnesium sulfate and concentrated in vacuo to yield the crude product, which was purified by silica gel column chromatography (EtOAc-Hexane) to give the corresponding amide in high yield. The structure of the products was confirmed by comparison of their mp, TLC, IR and ^{1}H NMR data with authentic samples obtained commercially or prepared by literature methods.[2-4]

***N*-phenylacetamide (Table 2, Entry 1):** Mp 114-115 °C, (Lit.[4] Mp 114-116 °C), IR (KBr): ν_{max} = 3304, 3148, 3035, 2935, 2850, 1668, 1597, 1555, 1502, 1435, 1369, 1325, 1265, 755, 695 cm^1; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (br, 1H), 7.51 (d, *J* = 8.5 Hz, 2H), 7.25 (t, *J* = 7.8 Hz, 2H), 7.03 (t, *J* = 7.2 Hz, 1H), 2.09 (s, 3H).

***N*-(2-methoxyphenyl)acetamide (Table 2, Entry 2):** Mp 85-87 °C, (Lit.[4] Mp 85-86 °C), IR (KBr): ν_{max} = 3252, 2980, 2865, 1657, 1541, 1495, 1457, 1252, 1025, 750 cm^1; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.36 (dd, *J* = 1.8, 7.8 Hz, 1H), 7.77 (br, 1H), 7.08-6.91 (m, 2H), 6.87 (dd, *J* = 1.8, 8.1 Hz, 1H), 3.88 (s, 3H), 2.21 (s, 3H).

***N*-(3-methoxyphenyl)acetamide (Table 2, Entry 3):** Mp 86-88 °C, (Lit.[4] Mp 87-88 °C), IR (KBr): ν_{max} = 3257, 2973, 2867, 2853, 1664, 1606, 1560, 1494, 1415, 1268, 1051, 860, 765, 689 cm^1; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77 (br, 1H), 7.29-7.17 (m, 2H), 6.94 (d, *J* = 8.0 Hz, 1H), 6.63 (dd, *J* = 2.1, 8.1 Hz, 1H), 3.80 (s, 3H), 2.17 (s, 3H).

***N*-(4-methoxyphenyl)acetamide (Table 2, Entry 4):** Mp 129-131 °C, (Lit.[4] Mp 129-130 °C), IR (KBr): ν_{max} = 3255, 2976, 2859, 1655, 1604, 1549, 1513,1245, 1030, 835 cm^1; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (d, *J* = 9.0 Hz, 2H), 7.06 (br, 1H), 6.84 (d, *J* = 9.0 Hz, 2H), 3.80 (s, 3H), 2.15 (s, 3H).

***N*-(2-chlorophenyl)acetamide (Table 2, Entry 5):** Mp 90-91 °C, (Lit.[4] Mp 90-91 °C), IR (KBr): ν_{max} = 3302, 2974, 2820, 1656, 1600, 1547, 1510, 1415, 1249, 1045, 765 cm^1;

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.34 (d, *J* = 8.0 Hz, 1H), 7.65 (bs, 1H), 7.35 (dd, *J* = 8.0 Hz; 1.5 Hz, 1H), 7.28-7.24 (m, 1H), 7.03 (t, *J* = 7.2 Hz, 1H), 2.23 (s, 3H).

***N*-phenylpropionamide (Table 2, Entry 6):** Mp 102-103 °C, (Lit.[4] Mp 103-104 °C), IR (KBr): ν_{max} = 3304, 3148, 3035, 2945, 2865, 1667, 1595, 1554,1455, 1369, 1327, 1263, 735, 695 cm^1; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (br, 1H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.28 (t, *J* = 7.5, 8.5 Hz, 2H), 7.10 (t, *J* = 7.5, 7.0 Hz, 1H), 2.35 (q, *J* = 7.5 Hz, 2H), 1.22 (t, *J* = 7.5 Hz, 3H).

***N*-(2-naphthyl)acetamide (Table 2, Entry 7):** Mp 132-134 °C, (Lit.[8] Mp 133-135 °C), IR (KBr): ν_{max} = 3287, 1669, 1590, 1562, 1470, 1395, 1350, 1279, 856, 745 cm^1; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 (br, 1H), 7.76–7.80 (m, 4H), 7.40–7.46 (m, 3H), 2.24 (s, 3H).

***N*-phenylbenzamide (Table 2, Entry 8)** Mp 162-163 °C, (Lit.[3] Mp 164-165 °C), IR (KBr): ν_{max} = 3298, 3075, 3029, 1674, 1556, 1446, 735 cm^1; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (bs, 1H), 7.85-7.83 (m, 2H), 7.62 (d, *J* = 7.9 Hz, 2H), 7.54-7.49 (m, 1H), 7.46-7.43 (m, 2H), 7.37-7.31 (m, 2H), 7.14-711 (m, 1H).

***N*-(4-fluorophenyl)benzamide and 4-fluoro-*N*-phenylbenzamide (Table 2, entry 9):** Mp 168-180 °C, (Lit.[4] Mp 167-178 °C), IR (KBr): ν_{max} = 3290, 3071, 3032, 1680, 1617, 1558, 1506, 1235, 837 cm^1; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.32 (bs, 1H), 10.27 (bs, 1H), 8.07-8.02 (m, 2H), 7.96 (d, *J* = 7.0 Hz, 2H), 7.83-7.81 (m, 1H), 7.79-7.76 (m, 3H), 7.61-7.58 (m, 1H), 7.56-7.51 (m, 2H), 7.39-7.34 (m, 4H), 7.20 (t, *J* = 9.0 Hz, 2H), 7.13-7.09 (m, 1H).

***N*-(4-methoxyphenyl)benzamide and 4-methoxy-*N*-phenylbenzamide (Table 2, entry 10):** Mp 147-158 °C, (Lit.[4] Mp 148-161 °C), IR (KBr): ν_{max} = 3292, 3024, 1669, 1605, 1558, 1502, 1415, 1270, 1057, 854, 752 cm^1; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.15 (bs, 1H), 10.10 (br, 1H), 7.99-7.95 (m, 3H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 9.0 Hz,

2H), 7.59-7.50 (m, 2H), 7.54-7.50 (m, 3H), 7.34 (t, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 9.0 Hz, 2H), 6.94 (d, *J* = 9.0 Hz, 2H), 3.84 (s, 3H), 3.75 (s, 3H).

***N*-benzyl-2-phenylacetamide (Table 2, Entry 11):** Mp 68 °C, (Lit.[5] Mp 68 °C), IR (KBr): ν_{max} = 3292, 3024, 1669, 1605, 1558, 1502, 1415, 1270, 1057, 854, 752 cm^{1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31-7.34 (m, 2H), 7.21-7.29 (m, 6H), 7.14-7.17 (m, 2H), 5.80 (s, 1H), 4.38 (d, *J* = 5.9 Hz, 2H), 3.59 (s, 2H).

***N*-isopropylisobutyramide (Table 2, entry 12):** Mp 101-102 °C, (Lit.[7] Mp 103-104 °C), IR (KBr): ν_{max} = 3297, 2970, 2933, 2874, 1645, 1551, 1366, 1243, 1095, 699 cm^{1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.23 (br, 1H). 4.01-4.11 (m, 1H), 2.28 (septet, *J* = 6.9 Hz, 1H), 1.15 (d, *J* = 6.9 Hz, 12H).

***N*-octylacetamide (Table 2, entry 13)[2]:** IR (film): ν_{max} = 3272, 2970, 2925, 2869, 1641, 1554, 1229, 1141, 1045, 723 cm^{1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.97 (br, 1H). 3.21-3.26 (m, 2H), 1.96 (s, 3H), 1.45-1.52 (m, 2H), 1.29 (br, 10H), 0.93 (t, *J* = 6.9 Hz, 3H).

Azacyclotridecan-2-one (Table 2, entry 14): Mp 149-153 °C, (Lit.[5] Mp 151.5 °C), IR (KBr): ν_{max} = 3301, 2932, 2855, 1640, 1547, 1449, 1060 cm^{1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.02 (br, 1H), 3.29 (dd, *J* = 6.1, 10.6 Hz, 2H), 2.16-2.18 (m, 2H), 1.63-167 (m, 2H), 1.45-1.47 (m, 2H), 1.33 (br, 14H).

Azacycloundecan-2-one (Table 2, entry 15): Mp 161-162 °C, (Lit.[6] Mp 163-164 °C), IR (KBr): ν_{max} = 3309, 2932, 2859, 1638, 1552, 1462, 689 cm^{1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.01 (br, 1H), 3.34 (dd, *J* = 5.6, 10.9 Hz, 2H), 2.18-2.22 (m, 2H), 1.33-1.78 (m, 14H).

Azacyclononan-2-one (Table 2, entry 16): Mp 75-76 °C, (Lit.[5] Mp 74-76 °C), IR (KBr): ν_{max} = 3315, 2930, 2864, 1646, 1541, 1445, 1035, 796, 732 cm^{1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.99 (br, 1H), 3.35 (m, 2H), 2.45 (t, *J* = 6.4 Hz, 2H), 1.80-1.87 (m, 2H), 1.57-1.62 (m, 8H).

ε-Caprolactam (Table 2, entry 17): Mp 69-71 °C, (Lit.[4] Mp 70-71 °C), IR (KBr): ν_{max} = 3295, 3078, 2930, 2856, 1675, 1486, 1435, 1365, 1198, 1125, 823 cm^{1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.10 (br, 1H), 3.21 (t, *J* = 6.3 Hz, 2H), 2.48 (t, *J* = 5.8 Hz, 2H), 1.60-1.80 (m, 6H).

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