Supporting Information

Novel Annulation Reactions of Aryl Methyl Ketenes with Zwitterions Derived from Dimethyl Acetylenedicarboxylate and *N*-Alkylimidazoles

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General

α -Methylaryl acetic acid were prepared according to literatures,^[1-5] α -ethylphenyl acetic acid, *N*-methylimidazole, *N*-ethylimidazole, DMAD and *i*-Pr₂NEt were commercially available.

All reactions were carried out under a nitrogen atmosphere with dry, freshly distilled solvents under anhydrous conditions. Dichloromethane was distilled from calcium hydride immediately prior to use. THF and toluene were distilled from sodium-benzophenone. All chemicals were distilled or recrystallized before use, when necessary.

All reactions were monitored by thin-layer chromatography (TLC) carried out on Merck silica gel plates (60F-254) using UV-light (254 and 365 nm). Flash chromatography was performed on Merck silica gel Kieselgel 60 (300-400 mesh). NMR spectra were recorded on AM400 or AM500 (Bruker) instruments in *d*₆-DMSO or CDCl₃. High resolution mass spectral (HRMS) analyses were measured on an APEX (Bruker) mass spectrometer using ESI (electrospray ionisation) techniques. Infrared spectra were recorded on a Nicolet 470 FT-IR Spectrometer. Melting points are uncorrected.

General procedure for the synthesis of compound 3a-m, 3o and 3p (Table 2 and Scheme 2)

Table 2, entry 1. A mixture of DMAD (1 mmol) and α -methyl 4-methylphenylacetyl chloride (1 mmol) in DCM (3 ml) was added dropwise to the solution of *N*-methylimidazole (1 mmol) and *i*-Pr₂NEt (1.5 mmol) in dry DCM (10 ml) under a nitrogen atmosphere at -20 °C. Afterward, the reaction solution was allowed to warm to r.t. for additional 3 hours. The solvent was then removed under vacuum, and the residue was chromatographed on a silica gel column with a hexane-ether mixture (1:1) to afford 1,3a-diazapentalene derivative **3a** in 58% yield.

Compound **3a**: Pale yellow solid; m.p. 114-116 °C; **IR** (KBr) ν_{max} : 3154, 2993, 2948, 1724, 1682, 1502, 1382, 1217, 1112, 830, 697 cm^{-1} ; **¹H NMR** (500 MHz, *d*₆-DMSO, TMS) δ 7.63 (d, *J* = 1.5 Hz, 1H), 7.26 (d, *J* = 2.0 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 7.5 Hz, 2H), 5.59 (s, 1H), 5.18 (s, 1H), 3.75 (s, 3H), 3.59 (s, 3H), 3.12 (s, 3H), 2.30 (s, 3H); **¹³C NMR** (125 MHz, *d*₆-DMSO, TMS) δ 166.3, 160.3, 139.9, 139.2, 138.2, 136.6, 129.6, 127.5, 127.4, 125.3, 115.2, 108.6, 103.0, 99.5, 52.4, 51.5, 34.1, 21.3; **HRMS (ESI)**: calculated for C₂₀H₂₀N₂O₄Na [M+Na]⁺ 375.1315, found 375.1297.

Table 2, entry 2. A mixture of DMAD (1 mmol) and α -methyl 4-methoxyphenylacetyl chloride (1 mmol) in DCM (3 ml) was added dropwise to the solution of *N*-methylimidazole (1 mmol) and *i*-Pr₂NEt (1.5 mmol) in dry DCM (10 ml) under a nitrogen atmosphere at -20 °C. Afterward, the reaction solution was allowed to warm to r.t. for additional 3 hours. The solvent was then removed under vacuum, and the residue was chromatographed on a silica gel column with a hexane-ether mixture (1:1) to afford 1,3a-diazapentalene derivative **3b** in 60% yield.

Compound **3b**: Pale yellow oil; **IR** (film) ν_{max} : 3150, 2952, 1729, 1674, 1510, 1493, 1380, 1247, 1117, 824, 761 cm^{-1} ; **¹H NMR** (400 MHz, *d*₆-DMSO, TMS) δ 7.62 (d, *J* = 1.6 Hz, 1H), 7.26-7.24 (m, 3H), 6.90 (d, *J* = 8.8 Hz, 2H), 5.51 (d, *J* = 1.2 Hz, 1H), 5.12 (d, *J* = 1.2 Hz, 1H), 3.75 (s, 6H), 3.59 (s, 3H), 3.13 (s, 3H); **¹³C NMR** (100 MHz, *d*₆-DMSO, TMS) δ 165.7, 159.6, 138.8, 135.9, 133.8, 129.3, 128.1,

126.8, 125.7, 124.6, 113.7, 108.0, 102.3, 98.9, 55.1, 51.8, 50.8, 33.4; **HRMS (ESI)**: calculated for $C_{20}H_{20}N_2O_5Na$ $[M+Na]^+$ 391.1264, found 391.1253.

Table 2, entry 3. A mixture of DMAD (1 mmol) and α -methyl phenylacetyl chloride (1 mmol) in DCM (3 ml) was added dropwise to the solution of N-methylimidazole (1 mmol) and *i*-Pr₂NEt (1.5 mmol) in dry DCM (10 ml) under a nitrogen atmosphere at -20 °C. Afterward, the reaction solution was allowed to warm to r.t. for additional 3 hours. The solvent was then removed under vacuum, and the residue was chromatographed on a silica gel column with a hexane-ether mixture (1:1) to afford 1,3a-diazapentalene derivative **3c** in 55% yield.

Compound **3c**: Pale yellow viscos oil; **IR** (film) ν_{max} : 3136, 2993, 2949, 1731, 1683, 1494, 1380, 1214, 1115, 762, 692 cm^{-1} ; **¹H NMR** (500 MHz, *d*₆-DMSO, TMS) δ 7.63 (d, *J* = 1.5 Hz, 1H), 7.33 (s, 5H), 7.27 (d, *J* = 2.0 Hz, 1H), 5.63 (s, 1H), 5.24 (s, 1H), 3.75 (s, 3H), 3.55 (s, 3H), 3.13 (s, 3H); **¹³C NMR** (125 MHz, *d*₆-DMSO, TMS) δ 168.0, 160.1, 141.8, 139.9, 136.4, 128.9, 128.6, 126.5, 125.2, 115.9, 108.5, 108.0, 102.9, 99.1, 52.2, 51.3, 34.0; **HRMS (ESI)**: calculated for $C_{19}H_{18}N_2O_4Na$ $[M+Na]^+$ 361.1159, found 361.1144.

Table 2, entry 4. A mixture of DMAD (1 mmol) and α -methyl 4-chlorophenylacetyl chloride (1 mmol) in DCM (3 ml) was added dropwise to the solution of N-methylimidazole (1 mmol) and *i*-Pr₂NEt (1.5 mmol) in dry DCM (10 ml) under a nitrogen atmosphere at -20 °C. Afterward, the reaction solution was allowed to warm to r.t. for additional 3 hours. The solvent was then removed under vacuum, and the residue was chromatographed on a silica gel column with a hexane-ether mixture (1:1) to afford 1,3a-diazapentalene derivative **3d** in 50% yield.

Compound **3d**: Pale yellow solid; m.p. 141-143 °C; **IR** (KBr) ν_{max} : 2949, 1721, 1675, 1499, 1216, 1120, 837, 760, 677 cm^{-1} ; **¹H NMR** (400 MHz, *d*₆-DMSO, TMS) δ 7.63 (d, *J* = 2.4 Hz, 1H), 7.40 (d, *J* = 8.8 Hz, 2H), 7.35 (d, *J* = 9.2 Hz, 2H), 7.30 (d, *J* = 2.4 Hz, 1H), 5.68 (s, 1H), 5.27 (s, 1H), 3.74 (s, 3H), 3.54 (s, 3H), 3.21 (s, 3H); **¹³C NMR** (100 MHz, *d*₆-DMSO, TMS) δ 169.9, 164.1, 144.6, 142.6, 140.3, 137.1, 133.1, 132.9, 131.0, 129.3, 120.8, 112.5, 107.1, 102.6, 56.2, 55.4, 38.1; **HRMS (ESI)**: calculated for $C_{19}H_{17}N_2O_4ClNa$ $[M+Na]^+$ 395.0769, found 395.0750.

Table 2, entry 5. A mixture of DMAD (1 mmol) and α -methyl 3-chlorophenylacetyl chloride (1 mmol) in DCM (3 ml) was added dropwise to the solution of N-methylimidazole (1 mmol) and *i*-Pr₂NEt (1.5 mmol) in dry DCM (10 ml) under a nitrogen atmosphere at -20 °C. Afterward, the reaction solution was allowed to warm to r.t. for additional 3 hours. The solvent was then removed under vacuum, and the residue was chromatographed on a silica gel column with a hexane-ether mixture (1:1) to afford 1,3a-diazapentalene derivative **3e** in 52% yield.

Compound **3e**: White solid; m.p. 139-140 °C; **IR** (film) ν_{max} : 2952, 1726, 1674, 1495, 1380, 1217, 1119, 824, 762 cm^{-1} ; **¹H NMR** (400 MHz, *d*₆-DMSO, TMS) δ 7.67 (d, *J* = 2.4 Hz, 1H), 7.39-7.37 (m, 3H), 7.33 (d, *J* = 2.4 Hz, 2H), 5.75 (s, 1H), 5.34 (s, 1H), 3.77 (s, 3H), 3.54 (s, 3H), 3.29 (s, 3H); **¹³C NMR** (100 MHz, *d*₆-DMSO, TMS) δ 169.9, 164.2, 147.9, 142.5, 140.4, 137.7, 134.7, 132.4, 131.1, 130.9, 130.1, 129.3, 121.5, 112.5, 107.2, 102.5, 56.2, 55.4, 38.2; **HRMS (ESI)**: calculated for C₁₉H₁₇N₂O₄ClNa [M+Na]⁺ 395.0769, found 395.0751.

Table 2, entry 6. A mixture of DMAD (1 mmol) and α -methyl 2-chlorophenylacetyl chloride (1 mmol) in DCM (3 ml) was added dropwise to the solution of N-methylimidazole (1 mmol) and *i*-Pr₂NEt (1.5 mmol) in dry DCM (10 ml) under a nitrogen atmosphere at -20 °C. Afterward, the reaction solution was allowed to warm to r.t. for additional 3 hours. The solvent was then removed under vacuum, and the residue was chromatographed on a silica gel column with a hexane-ether mixture (1:1) to afford 1,3a-diazapentalene derivative **3f** in 47% yield.

Compound **3f**: White solid; m.p. 136-137 °C; **IR** (film) ν_{max} : 2952, 1726, 1674, 1495, 1380, 1217, 1119, 824, 762 cm^{-1} ; **¹H NMR** (400 MHz, *d*₆-DMSO, TMS) δ 7.62 (d, *J* = 2.4 Hz, 1H), 7.41-7.38 (m, 1H), 7.35-7.31 (m, 4H), 5.54 (s, 1H), 5.43 (s, 1H), 3.70 (s, 3H), 3.50 (s, 3H), 3.39 (s, 3H); **¹³C NMR** (100 MHz, *d*₆-DMSO, TMS) δ 169.9, 164.1, 144.4, 142.4, 140.2, 136.5, 136.2, 134.2, 133.9, 131.4, 130.3, 129.4, 123.6, 112.3, 106.8, 103.7, 56.1, 55.3, 38.5; **HRMS (ESI)**: calculated for C₁₉H₁₇N₂O₄ClNa [M+Na]⁺ 395.0769, found 395.0751.

Table 2, entry 7. A mixture of DMAD (1 mmol) and α -methyl naphthalen-1-yl-acetyl chloride (1 mmol) in DCM (3 ml) was added dropwise to the solution of N-methylimidazole (1 mmol) and *i*-Pr₂NEt (1.5 mmol) in dry DCM (10 ml) under a nitrogen atmosphere at -20 °C. Afterward, the

reaction solution was allowed to warm to r.t. for additional 5 hours. The solvent was then removed under vacuum, and the residue was chromatographed on a silica gel column with a hexane-ether mixture (1:1) to afford 1,3a-diazapentalene derivative **3g** in 53% yield.

Compound **3g**: White solid; m.p.146-147 °C; **IR** (film) ν_{max} : 2952, 1727, 1672, 1496, 1381, 1222, 1120, 825, 762 cm^{-1} ; **^1H NMR** (400 MHz, d_6 - DMSO, TMS) δ 8.06 (d, J = 8.4 Hz, 1H), 7.90 (t, J = 6.6 Hz, 2H), 7.58 (d, J = 2.0 Hz, 1H), 7.50-7.37 (m, 4H), 7.17 (s, 1H), 5.58 (s, 1H), 5.43 (s, 1H), 3.72 (s, 3H), 3.47 (s, 3H), 3.02 (s, 3H) ; **^{13}C NMR** (100 MHz, d_6 - DMSO, TMS) δ 170.4, 164.1, 144.0, 143.4, 140.0, 138.0, 135.4, 132.9, 132.8, 132.1, 130.8, 130.6, 130.2, 129.9, 129.8, 129.4, 122.2, 112.3, 107.0, 105.2, 56.3, 55.4, 38.6; **HRMS (ESI)**: calculated for $\text{C}_{23}\text{H}_{20}\text{N}_2\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$ 411.1315, found 411.1296.

Table 2, entry 8. A mixture of DMAD (1 mmol) and α -methyl 2,4-dichlorophenylacetyl chloride (1 mmol) in DCM (3 ml) was added dropwise to the solution of N-methylimidazole (1 mmol) and *i*-Pr₂NEt (1.5 mmol) in dry DCM (10 ml) under a nitrogen atmosphere at -20 °C. Afterward, the reaction solution was allowed to warm to r.t. for additional 5 hours. The solvent was then removed under vacuum, and the residue was chromatographed on a silica gel column with a hexane-ether mixture (1:1) to afford 1,3a-diazapentalene derivative **3h** in 51% yield.

Compound **3h**: White solid; m.p.138-140 °C; **IR** (film) ν_{max} : 2953, 1724, 1673, 1495, 1380, 1217, 1119, 825, 762 cm^{-1} ; **^1H NMR** (400 MHz, d_6 - DMSO, TMS) δ 7.63 (d, J = 2.4 Hz, 1H), 7.56 (d, J = 2.0 Hz, 1H), 7.44 (dd, J_1 = 8.4 Hz, J_2 = 2.2 Hz, 1H), 7.36 (d, J = 2.4 Hz, 1H), 7.33 (d, J = 8.4 Hz, 1H), 5.57 (s, 1H), 5.46 (s, 1H), 3.71 (s, 3H), 3.56 (s, 3H), 3.42 (s, 3H) ; **^{13}C NMR** (100 MHz, d_6 - DMSO, TMS) δ 169.9, 164.1, 143.4, 141.3, 140.2, 137.6, 137.4, 133.5, 131.5, 130.1, 129.4, 124.2, 112.3, 106.9, 103.2, 56.1, 55.4, 38.6; **HRMS (ESI)**: calculated for $\text{C}_{19}\text{H}_{16}\text{N}_2\text{O}_4\text{Cl}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 429.0379, found 429.0359.

Table 2, entry 9. A mixture of DMAD (1 mmol) and α -methyl 2-bromophenylacetyl chloride (1 mmol) in DCM (3 ml) was added dropwise to the solution of N-methylimidazole (1 mmol) and *i*-Pr₂NEt (1.5 mmol) in dry DCM (10 ml) under a nitrogen atmosphere at -20 °C. Afterward, the

reaction solution was allowed to warm to r.t. for additional 5 hours. The solvent was then removed under vacuum, and the residue was chromatographed on a silica gel column with a hexane-ether mixture (1:1) to afford 1,3a-diazapentalene derivative **3i** in 46% yield.

Compound **3i**: White solid; m.p. 141-142 °C; **IR** (film) ν_{max} : 2956, 1727, 1673, 1495, 1380, 1217, 1119, 824, 762 cm^{-1} ; **¹H NMR** (400 MHz, *d*₆-DMSO, TMS) δ 7.62 (d, *J* = 2.0 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.41-7.31 (m, 3H), 7.27-7.23 (m, 1H), 5.52 (s, 1H), 5.39 (s, 1H), 3.71 (s, 3H), 3.56 (s, 3H), 3.37 (s, 3H); **¹³C NMR** (100 MHz, *d*₆-DMSO, TMS) δ 169.9, 164.1, 146.2, 144.1, 140.4, 137.3, 136.5, 134.1, 131.8, 130.3, 129.3, 126.8, 123.2, 112.3, 106.8, 103.6, 56.1, 55.3, 38.6; **HRMS (ESI)**: calculated for C₁₉H₁₇N₂O₄BrNa [M+Na]⁺ 439.0264, found 439.0245.

Table 2, entry 10. A mixture of DMAD (1 mmol) and α -methyl 4-bromophenylacetyl chloride (1 mmol) in DCM (3 ml) was added dropwise to the solution of N-methylimidazole (1 mmol) and *i*-Pr₂NEt (1.5 mmol) in dry DCM (10 ml) under a nitrogen atmosphere at -20 °C. Afterward, the reaction solution was allowed to warm to r.t. for additional 5 hours. The solvent was then removed under vacuum, and the residue was chromatographed on a silica gel column with a hexane-ether mixture (1:1) to afford 1,3a-diazapentalene derivative **3j** in 43% yield.

Compound **3j**: White solid; m.p. 155-156 °C; **IR** (film) ν_{max} : 2957, 1720, 1668, 1217, 1118, 825, 763 cm^{-1} ; **¹H NMR** (400 MHz, *d*₆-DMSO, TMS) δ 7.64 (s, 1H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.27 (s, 1H), 5.69 (s, 1H), 5.29 (s, 1H), 3.75 (s, 3H), 3.55 (s, 3H), 3.22 (s, 3H); **¹³C NMR** (100 MHz, *d*₆-DMSO, TMS) δ 170.0, 164.2, 145.0, 142.7, 140.3, 135.8, 133.4, 131.0, 129.3, 125.8, 120.9, 112.5, 107.1, 102.6, 56.3, 55.4, 38.1; **HRMS (ESI)**: calculated for C₁₉H₁₇N₂O₄BrNa [M+Na]⁺ 439.0264, found 439.0244.

Table 2, entry 11. A mixture of DMAD (1 mmol) and α -methyl 2-chlorophenylacetyl chloride (1 mmol) in DCM (3 ml) was added dropwise to the solution of N-ethylimidazole (1 mmol) and *i*-Pr₂NEt (1.5 mmol) in dry DCM (10 ml) under a nitrogen atmosphere at -20 °C. Afterward, the reaction solution was allowed to warm to r.t. for additional 10 hours. The solvent was then removed under vacuum, and the residue was chromatographed on a silica gel column with a hexane-ether mixture (1:1) to afford 1,3a-diazapentalene derivative **3k** in 38% yield.

Compound **3k**: colorless viscous oil; **IR** (film) ν_{max} : 2958, 1728, 1676, 1495, 1381, 1213, 1119, 824, 762 cm^{-1} ; **^1H NMR** (400 MHz, d_6 -DMSO, TMS) δ 7.64 (d, J = 2.0 Hz, 1H), 7.40-7.37 (m, 2H), 7.32-7.30 (m, 3H), 5.50 (s, 1H), 5.48 (s, 1H), 3.85 (q, J = 7.2 Hz, 2H), 3.71 (s, 3H), 3.42 (s, 3H), 1.10 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, d_6 -DMSO, TMS) δ 170.0, 164.1, 144.1, 142.4, 139.4, 136.4, 136.3, 134.4, 133.9, 131.4, 130.8, 127.5, 123.7, 112.8, 106.9, 103.5, 56.1, 55.3, 46.0, 20.0; **HRMS (ESI)**: calculated for $\text{C}_{20}\text{H}_{19}\text{N}_2\text{O}_4\text{ClNa}$ $[\text{M}+\text{Na}]^+$ 409.0926, found 409.0908.

Table 2, entry 12. A mixture of DMAD (1 mmol) and α -methyl 2,4-dichlorophenylacetyl chloride (1 mmol) in DCM (3 ml) was added dropwise to the solution of N-ethylimidazole (1 mmol) and *i*-Pr₂NEt (1.5 mmol) in dry DCM (10 ml) under a nitrogen atmosphere at -20 °C. Afterward, the reaction solution was allowed to warm to r.t. for additional 12 hours. The solvent was then removed under vacuum, and the residue was chromatographed on a silica gel column with a hexane-ether mixture (1:1) to afford 1,3a-diazapentalene derivative **3l** in 42% yield.

Compound **3l**: colorless viscous oil; **IR** (film) ν_{max} : 3133, 3080, 1731, 1668, 1495, 1378, 1214, 1119, 824, 761 cm^{-1} ; **^1H NMR** (400 MHz, d_6 -DMSO, TMS) δ 7.64 (d, J = 2.0 Hz, 1H), 7.55 (d, J = 1.6 Hz, 1H), 7.42-7.40 (m, 2H), 7.31 (d, J = 8.4 Hz, 1H), 5.52 (s, 1H), 5.50 (s, 1H), 3.91 (q, J = 7.2 Hz, 2H), 3.70 (s, 3H), 3.42 (s, 3H), 1.15 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, d_6 -DMSO, TMS) δ 169.9, 164.1, 143.1, 141.3, 139.4, 137.6, 137.5, 137.4, 133.7, 131.6, 130.5, 127.7, 124.2, 112.8, 107.0, 103.0, 56.1, 55.4, 46.0, 20.1; **HRMS (ESI)**: calculated for $\text{C}_{20}\text{H}_{18}\text{N}_2\text{O}_4\text{Cl}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 443.0536, found 443.0518.

Table 2, entry 13. A mixture of DMAD (1 mmol) and α -methyl 4-methylphenylacetyl chloride (1 mmol) in DCM (3 ml) was added dropwise to the solution of 1-butylimidazole (1 mmol) and *i*-Pr₂NEt (1.5 mmol) in dry DCM (10 ml) under a nitrogen atmosphere at -20 °C. Afterward, the reaction solution was allowed to warm to r.t. for additional 3 hours. The solvent was then removed under vacuum, and the residue was chromatographed on a silica gel column with a hexane-ether mixture (1:1) to afford 1,3a-diazapentalene derivative **3m** in 49% yield.

Compound **3m**: Pale yellow solid; m.p. 99-100 °C; **IR** (film) ν_{max} : 2955, 1729, 1672, 1494, 1378, 1216, 1115, 824, 761 cm^{-1} ; **^1H NMR** (400 MHz, d_6 -DMSO, TMS) δ 7.63 (d, J = 1.2 Hz, 1H), 7.32 (d, J = 2.4 Hz, 1H), 7.20 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 5.60 (s, 1H), 5.14 (s, 1H), 3.74 (s, 3H), 3.58 (s, 3H), 3.40 (t, J = 7.2 Hz, 2H), 2.28 (s, 3H), 1.33-1.26 (m, 2H), 0.97-0.88 (m, 2H), 0.66 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, d_6 -DMSO, TMS) δ 170.1, 164.1, 144.2, 142.8, 142.1, 139.7, 133.5, 131.5, 131.1, 128.2, 119.2, 112.5, 106.8, 103.1, 56.3, 55.3, 50.7, 36.4, 25.2, 23.4, 17.8; **HRMS (ESI)**: calculated for $\text{C}_{23}\text{H}_{26}\text{N}_2\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$ 417.1785, found 417.1767.

Scheme 2, entry 1. A mixture of DMAD (1 mmol) and α -methyl 4-methylphenylacetyl chloride (1 mmol) in DCM (3 ml) was added dropwise to the solution of 1,4-dimethylimidazole (1 mmol) and i -Pr₂NEt (1.5 mmol) in dry DCM (10 ml) under a nitrogen atmosphere at -20 °C. Afterward, the reaction solution was allowed to warm to r.t. for additional 11 hours. The solvent was then removed under vacuum, and the residue was chromatographed on a silica gel column with a hexane-ether mixture (1:1) to afford 1,3a-diazapentalene derivative **3o** in 57% yield.

Compound **3o**: Pale yellow solid; m.p. 163-165 °C; **IR** (film) ν_{max} : 2950, 1728, 1676, 1492, 1377, 1219, 822, 760, 666 cm^{-1} ; **^1H NMR** (400 MHz, d_6 -DMSO, TMS) δ 7.47 (d, J = 0.4 Hz, 1H), 7.22 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 5.61 (d, J = 0.8 Hz, 1H), 5.16 (d, J = 0.4 Hz, 1H), 3.73 (s, 3H), 3.56 (s, 3H), 3.03 (s, 3H), 2.29 (s, 3H), 2.20 (s, 3H); **^{13}C NMR** (100 MHz, d_6 -DMSO, TMS) δ 165.7, 159.6, 139.2, 138.5, 137.4, 135.9, 131.6, 129.0, 126.6, 125.8, 114.8, 105.6, 102.2, 98.7, 51.7, 50.8, 30.0, 20.7, 9.5; **HRMS (ESI)**: calculated for $\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_4$ $[\text{M}+\text{Na}]^+$ 389.1472, found 389.1455.

Scheme 2, entry 2. A mixture of DMAD (1 mmol) and α -methyl 4-methylphenylacetyl chloride (1 mmol) in DCM (3 ml) was added dropwise to the solution of 1,5-dimethylimidazole (1 mmol) and i -Pr₂NEt (1.5 mmol) in dry DCM (10 ml) under a nitrogen atmosphere at -20 °C. Afterward, the reaction solution was allowed to warm to r.t. for additional 11 hours. The solvent was then removed under vacuum, and the residue was chromatographed on a silica gel column with a hexane-ether mixture (1:1) to afford 1,3a-diazapentalene derivative **3p** in 61% yield.

Compound **3p**: Pale brown solid; m.p. 123-126 °C; **IR** (film) ν_{max} : 2949, 1729, 1689, 1490, 1370, 1200, 822, 759, 666 cm^{-1} ; **^1H NMR** (400 MHz, d_6 -DMSO, TMS) δ 7.20 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 6.87 (s, 1H), 5.57 (d, J = 1.6 Hz, 1H), 5.15 (d, J = 1.2 Hz, 1H), 3.67 (s, 3H), 3.59 (s, 3H), 2.99 (s, 3H), 2.48 (s, 3H), 2.28 (s, 3H); **^{13}C NMR** (100 MHz, d_6 -DMSO, TMS) δ 166.1, 159.3, 139.1, 138.5, 137.6, 137.5, 129.2, 129.0, 126.6, 121.9, 118.2, 114.6, 103.5, 97.5, 51.8, 50.7, 33.1, 20.7, 12.3; **HRMS (ESI)**: calculated for $\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_4$ $[\text{M}+\text{Na}]^+$ 389.1472, found 389.1456.

General procedure for the synthesis of compound **5** (Scheme 3)

A mixture of DMAD (1 mmol) and α -ethyl phenylacetyl chloride (1 mmol) in DCM (3 ml) was added dropwise to the solution of N-methylimidazole (1 mmol) and *i*-Pr₂NEt (1.5 mmol) in dry DCM (10 ml) under a nitrogen atmosphere at -20 °C. Afterward, the reaction solution was allowed to warm to r.t. for additional 3 hours. The solvent was then removed under vacuum, and the residue was chromatographed on a silica gel column with a hexane-ether mixture (1:1) to afford the unstable compound **3q** as a crude. To a solution of the crude **3q** in ethyl acetate (5 mL) was added 10% Pd/C (10 wt % of the substrate). The mixture was stirred overnight under H₂ atmosphere. Then the reaction mixture was filtered and concentrated. The residue was purified by chromatography (hexane:ether = 1:1) to give 1,3a-diazapentalene derivative **5** in 51% overall yield.

Compound **5**: colorless viscous oil; **IR** (film) ν_{max} : 2963, 1757, 1682, 1468, 1379, 1213, 1147, 921, 846, 780 cm^{-1} ; **^1H NMR** (400 MHz, d_6 -DMSO, TMS) δ 7.53 (d, J = 1.6 Hz, 1H), 7.33 (d, J = 6.8 Hz, 2H), 7.26 (t, J = 7.4 Hz, 2H), 7.19-7.13 (m, 2H), 4.14-4.10 (m, 1H), 3.73 (s, 3H), 3.71 (s, 3H), 3.49 (s, 3H), 2.07 (q, J = 6.8 Hz, 1H), 1.93-1.85 (m, 1H), 0.86 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, d_6 -DMSO, TMS) δ 171.7, 164.0, 149.7, 140.6, 132.7, 132.1, 130.7, 130.5, 129.1, 112.0, 105.8, 105.0, 56.5, 55.1, 46.5, 38.8, 32.1, 17.3; **HRMS (ESI)**: calculated for $\text{C}_{20}\text{H}_{22}\text{N}_2\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$ 377.1472, found 377.1481.

Single crystal X-ray structure

Crystal structure of compound **3a** has been deposited at the Cambridge Crystallographic Data Center and allocated the reference no. CCDC **605460**.

Single crystal X-ray structure of **3a**

Packing diagram of **3a**

References

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compound 3a

compound 3a

166.271

160.313

139.854

139.190

138.152

136.569

129.636

127.455

127.372

125.297

115.172

108.625

103.033

99.459

52.430

51.478

40.519

40.353

40.183

40.021

39.852

34.148

21.348

compound 3b

compound 3b

compound 3c

compound 3c

compound 3d

compound 3d

compound 3e

compound 3e

compound 3f

7.619
7.613
7.405
7.399
7.392
7.382
7.349
7.335
7.324
7.311

5.535
5.426

3.703
3.500
3.390

2.510

-0.000

compound 3f

compound 3g

compound 3g

170.409
164.070

144.008
143.385
139.959
137.951
135.379
132.902
132.753
132.088
130.759
130.637
130.165
129.858
129.756
129.376
122.244
112.251
107.030
105.232

56.287
55.365
44.607
44.404
44.196
43.989
43.783
43.569
43.356
38.569

compound 3h

compound 3h

compound 3i

compound 3i

compound 3j

compound 3j

compound 3k

compound 3l

compound 3I

compound 3m

compound 3m

compound 3o

compound 3p

compound 3p

compound 5

compound 5