Electronic supplementary information (ESI)

Synthesis of 2-amino and 2-arylazoazulenes via nucleophilic aromatic substitution of 2-chloroazulenes with amines and arylhydrazines

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General

Melting points were determined with a Yanagimoto MPS3 micromelting apparatus. The HRMS data were obtained with a JEOL JMS-700 instrument. The IR and UV/Vis spectra were recorded with JASCO FTIR-4100 and Shimadzu UV-2550 spectrophotometers. The 1H and 13C NMR spectra were recorded with a JEOL ECA500 spectrometer at 500 and 125 MHz, respectively. Column chromatography was carried out using spherical neutral silica gel 60N (40–50 μm) purchased from Kanto Chemical Co., Inc. or activated neutral alumina purchased from Sumitomo Chemical Co., Ltd. Voltammetry measurements were carried out with a BAS 100B/W electrochemical workstation using Pt working and auxiliary electrodes and an Ag/Ag+ reference electrode formed from AgNO3 (0.01 M) in acetonitrile containing tetrabutylammonium perchlorate (0.1 M).
1. Experimental details

1,3-Diethoxycarbonyl-2-morpholinoazulene (3)

A solution of 1 (307 mg, 1.00 mmol) in morpholine (10 mL, 115 mmol) was stirred at 80 °C for 1.5 h under the air atmosphere. After the reaction mixture was cooled, amine was removed under reduced pressure. The crude product was purified by silica gel column chromatography with hexane : AcOEt (4 : 1, \( R_f = 0.29 \)) as the eluent to afford 3 (342 mg, 96%) as orange crystals. M.p. 112−113 °C; IR (AT−IR): \( \nu_{\text{max}} = 2979 \text{ (w)}, 2901 \text{ (w)}, 2834 \text{ (w)}, 1692 \text{ (m)}, 1672 \text{ (s)}, 1521 \text{ (s)}, 1489 \text{ (w)}, 1453 \text{ (m)}, 1439 \text{ (s)}, 1420 \text{ (m)}, 1387 \text{ (m)}, 1373 \text{ (w)}, 1359 \text{ (m)}, 1331 \text{ (w)}, 1310 \text{ (m)}, 1289 \text{ (m)}, 1266 \text{ (m)}, 1226 \text{ (w)}, 1199 \text{ (m)}, 1151 \text{ (s)}, 1111 \text{ (s)}, 1068 \text{ (w)}, 1026 \text{ (m)}, 980 \text{ (w)}, 941 \text{ (m)}, 887 \text{ (m)}, 865 \text{ (w)}, 832 \text{ (w)}, 770 \text{ (m)}, 740 \text{ (w)}, 715 \text{ (w)}, 697 \text{ (w)}, 682 \text{ (w)} \text{ cm}^{-1}; ^1\text{H NMR (500 MHz, CDCl}_3): \delta_H = 8.78−8.76 \text{ (dd, 2H, } J = 1.5, 10.5 \text{ Hz, 4,8-H)}, 7.48-7.44 \text{ (m, 3H, 5,6,7-H)}, 4.45 \text{ (q, 4H, } J = 7.2 \text{ Hz, CO}_2\text{Et}), 3.89 \text{ (t, 4H, } J = 4.6 \text{ Hz, morpholine), 3.50 \text{ (t, 4H, } J = 4.6 \text{ Hz, morpholine), 1.45 \text{ (t, 6H, } J = 7.2 \text{ Hz, CO}_2\text{Et) ppm; } ^{13}\text{C NMR (125 MHz, CDCl}_3): } \delta_C = 166.27, 159.68, 143.05, 134.03, 131.54, 130.36, 108.11, 67.28, 60.51, 52.74, 14.73 \text{ ppm; HRMS (FAB-MS): calcd for } \text{C}_{29}\text{H}_{23}\text{NO}_5 + \text{H}^+ [M + H]^+ 358.1649; \text{found: 358.1646.}
1,3-Diethoxycarbonyl-2-piperidinoazulene (4)

A solution of 1 (305 mg, 0.994 mmol) in piperidine (10 mL, 102 mmol) was stirred at 80 °C for 1.5 h under the air atmosphere. After the reaction mixture was cooled, amine was removed under reduced pressure. The crude product was purified by silica gel column chromatography with hexane : AcOEt (4 : 1, \( R_f = 0.42 \)) as the eluent to afford 4 (348 mg, 98%) as orange crystals. M.p. 51−53 °C; IR (AT−IR): \( \nu_{\text{max}} = 2968 \) (w), 2948 (w), 2849 (w), 1686 (s), 1587 (w), 1517 (s), 1489 (m), 1465 (m), 1445 (s), 1429 (m), 1405 (w), 1376 (w), 1361 (w), 1309 (w), 1295 (w), 1255 (m), 1236 (w), 1191 (s), 1171 (m), 1145 (s), 1123 (m), 1098 (m), 1073 (w), 1038 (m), 1023 (m), 975 (w), 937 (w), 885 (m), 860 (w), 823 (w), 797 (w), 766 (w), 732 (w), 708 (w), 680 (w), 669 (w) cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta_H = 8.63 \) (dd, 2H, \( J = 1.5, 10.5 \) Hz, 4,8-H), 7.38−7.39 (m, 3H, 5,6,7-H), 4.45 (q, 4H, \( J = 7.2 \) Hz, CO\(_2\)Et), 3.43 (t, 4H, \( J = 5.3 \) Hz, piperidine), 1.76 (br.s, 4H, piperidine), 1.73−1.65 (br. s, 2H, piperidine), 1.44 (t, 6H, \( J = 7.2 \) Hz, CO\(_2\)Et) ppm; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta_C = 166.66, 160.24, 142.99, 132.84, 130.24, 130.03, 108.09, 60.41, 53.92, 26.26, 24.44, 14.73 \) ppm; HRMS (FAB-MS): calcd for C\(_{21}\)H\(_{25}\)NO\(_4\)\(^+\) [M\(^+\)] = 355.1779; found: 355.1783.
1,3-Diethoxycarbonyl-2-pyrrolidinoazulene (5)

A solution of 1 (310 mg, 1.01 mmol) in pyrrolidine (10 mL, 121 mmol) was stirred at 80 °C for 1.5 h under the air atmosphere. After the reaction mixture was cooled, amine was removed under reduced pressure. The crude product was purified by silica gel column chromatography with hexane : AcOEt (4 : 1, *R* = 0.35) as the eluent to afford 5 (345 mg, 99%). M.p. 98−99 °C; IR (AT−IR): ν_{max} = 2978 (w), 2931 (w), 2884 (w), 1702 (s), 1687 (s), 1514 (s), 1483 (s), 1470 (m), 1449 (m), 1403 (w), 1386 (w), 1364 (w), 1347 (m), 1326 (w), 1299 (w), 1256 (w), 1237 (w), 1207 (s), 1157 (w), 1124 (s), 1114 (s), 1051 (w), 1025 (w), 993 (w), 950 (w), 930 (w), 886 (w), 872 (w), 844 (w), 822 (w), 808 (w), 780 (w), 763 (w), 741 (w), 715 (w), 686 (w) cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ_H = 8.41 (d, 2H, J = 10.3 Hz, 4,8-H), 7.30−7.36 (m, 3H, 5,6,7-H), 4.44 (q, 4H, J = 7.2 Hz, CO₂Et), 3.57 (t, 4H, J = 6.6 Hz, pyrrolidine), 1.96 (t, 4H, J = 6.6 Hz, pyrrolidine), 1.43 (t, 6H, J = 7.2 Hz, CO₂Et) ppm; ¹³C NMR (125 MHz, CDCl₃): δ_C = 167.29, 154.84, 142.04, 131.24, 129.47, 128.21, 105.81, 60.63, 52.87, 26.00, 14.66 ppm; HRMS (FAB-MS): calcd for C_{20}H_{23}NO₄⁺ [M]⁺ 341.1622; found: 341.1633.
1,3-Diethoxycarbonyl-2-diethylaminoazulene (6)

A solution of 1 (307 mg, 1.00 mmol) in Et₂NH (10 mL, 96.7 mmol) was stirred at 80 °C for 1 h under the air atmosphere. After the reaction mixture was cooled, amine was removed under reduced pressure. The crude product was purified by silica gel column chromatography with hexane : AcOEt (4 : 1) as the eluent to afford 6 (338 mg, 98%, Rᵣ = 0.50) as orange crystals.

M.p. 44−45 °C; IR (AT-IR): ν<sub>max</sub> = 2981 (w), 2933 (w), 2898 (w), 1691 (m), 1672 (s), 1586 (w), 1516 (s), 1488 (w), 1451 (m), 1421 (m), 1406 (w), 1386 (w), 1356 (w), 1314 (w), 1296 (w), 1268 (w), 1206 (w), 1191 (m), 1149 (s), 1100 (w), 1070 (w), 1057 (w), 1035 (m), 1007 (w), 945 (w), 930 (w), 884 (w), 867 (w), 829 (w), 805 (w), 790 (w), 776 (w), 741 (w), 716 (w), 702 (w), 683 (w), 670 (w) cm<sup>−1</sup>; ¹H NMR (500 MHz, CDCl₃): δ<sub>H</sub> = 8.85 (dd, 2H, J = 1.5, 10.0 Hz, 4,8-H), 7.43−7.39 (m, 3H, 5,6,7-H), 4.41 (q, 4H, J = 7.2 Hz, CO₂Et), 3.50 (q, 4H, J = 7.1 Hz, Et₂N), 1.41 (t, 6H, J = 7.2 Hz, CO₂Et), 1.20 (t, 6H, J = 7.1 Hz, Et₂N) ppm; ¹³C NMR (125 MHz, CDCl₃): δ<sub>C</sub> = 166.24, 161.05, 143.62, 133.16, 130.54, 130.44, 108.91, 60.17, 47.27, 14.55, 13.44 ppm; HRMS (FAB-MS): calcd for C₂₀H₂₆NO₄<sup>+</sup> [M]<sup>+</sup> 344.1877; found: 344.1849.
1,3-Diethoxycarbonyl-2-dipropylazulene (7)

A solution of 1 (307 mg, 1.00 mmol) in n-Pr₂NH (10 mL, 73.3 mmol) was stirred at 80 °C for 1 h under the air atmosphere. After the reaction mixture was cooled, amine was removed under reduced pressure. The crude product was purified by silica gel column chromatography with hexane : AcOEt (4 : 1, Rf = 0.50) as the eluent to afford 7 (349 mg, 94%) as an orange oil. IR (AT-IR): νmax = 2975 (w), 2934 (w), 2873 (w), 1686 (m), 1587 (w), 1509 (s), 1486 (w), 1453 (m), 1434 (m), 1406 (w), 1383 (w), 1362 (w), 1341 (w), 1323 (w), 1297 (w), 1253 (w), 1226 (w), 1197 (m), 1136 (m), 1094 (m), 1030 (m), 986 (w), 957 (w), 884 (w), 832 (w), 771 (w), 732 (m), 683 (w), 665 (w) cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δH = 8.73–8.75 (dd, J = 2.0, 10.0 Hz, 2H, 4,8-H), 7.43–7.38 (m, 3H, 5,6,7-H), 4.43 (q, 4H, J = 7.2 Hz, CO₂Et), 3.38 (t, 4H, J = 7.1 Hz, n-Pr₂N), 1.64 (m, 4H, n-Pr₂N), 1.42 (t, 6H, J = 7.2 Hz, CO₂Et), 0.88 (t, 6H, J = 7.1 Hz, n-Pr₂N) ppm; ¹³C NMR (125 MHz, CDCl₃): δC = 166.41, 161.40, 143.63, 132.85, 130.40, 130.17, 108.46, 60.24, 55.22, 21.26, 14.64, 11.35 ppm; HRMS (FAB-MS): calcd for C₂₂H₂₉NO₄ + H⁺ [M + H⁺] = 372.2170; found: 342.1718.
1,3-Diethoxycarbonyl-2-n-butylaminoazulene (8)

A solution of 1 (294 mg, 0.96 mmol) in n-BuNH₂ (10 mL, 101 mmol) was stirred at 80 °C for 1 h under the air atmosphere. After the reaction mixture was cooled, amine was removed under reduced pressure. The crude product was purified by silica gel column chromatography with hexane : AcOEt (4 : 1, Rf = 0.50) as the eluent to afford 8 (320 mg, 97%) as an orange oil. IR (AT-IR): νmax = 3392 (w), 3297 (w), 2959 (w), 2932 (w), 2872 (w), 1689 (s), 1651 (s), 1591 (m), 1562 (s), 1523 (s), 1462 (m), 1430 (s), 1413 (m), 1384 (m), 1335 (w), 1281 (w), 1231 (w), 1207 (m), 1130 (s), 1059 (m), 1030 (m), 932 (w), 880 (w), 790 (s), 732 (m), 695 (w) cm⁻¹; 'H NMR (500 MHz, CDCl₃): δH = 8.77 (d, 2H, J = 10.5 Hz, 4,8-H), 8.36 (s, 1H, NH), 7.36 (t, 2H, J = 10.0 Hz, 5,7-H), 7.25 (t, 1H, J = 9.5 Hz, 6-H), 4.42 (q, 4H, J = 7.1 Hz, CO₂Et), 3.42 (q, 2H, J = 7.3 Hz, n-BuN), 1.66 (quint, 2H, J = 7.3 Hz, n-BuN), 1.46–1.40 (m, 8H, CO₂Et, n-BuN), 0.93 (t, 3H, J = 7.3 Hz, n-BuN) ppm; ¹³C NMR (125 MHz, CDCl₃): δC = 166.68, 160.13, 144.80, 131.68, 131.28, 129.71, 101.83, 59.91, 46.53, 32.39, 20.06, 14.50, 13.65 ppm; HRMS (FAB-MS): calcd for C₂₀H₂₅NO₄⁺ [M]+ 343.1779; found: 343.1779.
1,3-Diethoxycarbonyl-2-tert-butylaminolazulene (9)

A solution of 1 (308 mg, 1.00 mmol) in t-BuNH₂ (10 mL, 95.2 mmol) was stirred at 80 °C for 2 h under the air atmosphere. After the reaction mixture was cooled, amine was removed under reduced pressure. The crude product was purified by silica gel column chromatography with hexane : AcOEt (4 : 1, \( R_f = 0.50 \)) as the eluent to afford 9 (335 mg, 98%) as an orange oil. IR (AT-IR): \( \nu_{\text{max}} = 3380 \) (w), 2976 (w), 2929 (w), 2904 (w), 2869 (w), 1698 (m), 1654 (s), 1595 (m), 1572 (m), 1518 (s), 1458 (m), 1433 (s), 1413 (m), 1383 (m), 1366 (m), 1332 (w), 1285 (m), 1204 (s), 1137 (s), 1056 (m), 1028 (m), 989 (m), 958 (m), 929 (m), 885 (m), 790 (m), 727 (m), 669 (m) cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl₃): \( \delta_H = 8.76 \) (d, 2H, \( J = 10.0 \) Hz, 4,8-H), 8.34 (br. s, 1H, NH), 7.45–7.35 (m, 3H, 5,6,7-H), 4.45 (q, 4H, \( J = 7.1 \) Hz, CO₂Et), 1.43–1.47 (m, 15H, CO₂Et, t-BuN) ppm; \(^{13}\)C NMR (125 MHz, CDCl₃): \( \delta_C = 167.74, 158.26, 143.78, 132.56, 131.00, 130.43, 105.12, 60.39, 55.50, 30.54, 14.56 \) ppm; HRMS (FAB-MS): calcd for C\(_{20}\)H\(_{25}\)NO₄\(^+\) [M]\(^+\) 343.1779; found: 343.1779.
2-Morpholinoazulene (10)

**Synthesis by S<sub>N</sub>Ar reaction:** A solution of 2 (165 mg, 1.01 mmol) in morpholine (10 mL, 115 mmol) was stirred at 150 °C for 21 h in sealed-tube. After the reaction mixture was cooled, amine was removed under reduced pressure. The crude product was purified by alumina column chromatography with hexane : AcOEt (20 : 1) as the eluent to afford 10 (185 mg, 86%) as red crystals. M.p. 168–170 °C (lit. 170.0–170.5 °C); ¹H NMR (500 MHz, CDCl₃): δ<sub>H</sub> = 7.91 (d, 2H, J = 10.0 Hz, 4,8-H), 7.24 (t, 1H, J = 10.0 Hz, 6-H), 7.14 (t, 2H, J = 10.0 Hz, 5,7-H), 6.72 (s, 2H, 1,3-H), 3.89 (t, 4H, J = 5.0 Hz, morpholine), 3.50 (t, 4H, J = 5.0 Hz, morpholine) ppm. Data are in agreement with those previously reported in reference 11.

**Deesterification of 3:** A solution of 3 (178 mg, 0.498 mmol) in 100% H₃PO₄ (20 mL) was stirred at 150 °C for 2 h. After the reaction mixture was cooled, it was poured into water, neutralized by K₂CO₃, and extracted with CH₂Cl₂. The crude product was purified by alumina column chromatography with hexane : AcOEt (20 : 1) as the eluent to afford 10 (65 mg, 61%) as red crystals.
2-Piperidinoazulene (11)

![2-Piperidinoazulene (11)](image)

**Synthesis by S$_{\text{N}}$Ar reaction:** A solution of 2 (161 mg, 1.00 mmol) in piperidine (10 mL, 102 mmol) was stirred at 150 °C for 12 h in sealed-tube. After the reaction mixture was cooled, amine was removed under reduced pressure. The crude product was purified by alumina column chromatography with hexane : AcOEt (20 : 1, $R_f = 0.22$) as the eluent to afford 11 (192 mg, 91%) as red crystals. M.p. 104−105 °C (lit. 107.5−108.0 °C); $^1$H NMR (500 MHz, CDCl$_3$): δ$_H$ = 7.83 (d, 2H, $J = 10.0$ Hz, 4,8-H), 7.07−7.16 (m, 3H, 5,6,7-H), 6.71 (s, 2H, 1,3-H), 3.53 (t, 4H, $J = 5.5$ Hz, piperidine), 1.68−1.75 (m, 6H, piperidine) ppm. Data are in agreement with those previously reported in reference 11.

**Deesterification of 4:** A solution of 4 (180 mg, 0.506 mmol) in 100% H$_3$PO$_4$ (10 mL) was stirred at 150 °C for 2 h. After the reaction mixture was cooled, it was poured into water, neutralized by K$_2$CO$_3$ and extracted with CH$_2$Cl$_2$. The crude product was purified by alumina column chromatography with hexane : AcOEt (20 : 1) as the eluent to afford 11 (85 mg, 79%) as red crystals.
2-Pyrrolidinoazulene (12)

**Synthesis by S_NAr reaction:** A solution of 2 (162 mg, 1.00 mmol) in pyrrolidine (10 mL, 121 mmol) was stirred at 150 °C for 3 h in sealed-tube. After the reaction mixture was cooled, amine was removed under reduced pressure. The crude product was purified by alumina column chromatography with hexane ($R_f = 0.25$) as the eluent to afford 12 (141 mg, 72%) as red crystals. M.p. 116–117 °C (lit. 116.5–117.5 °C); $^1$H NMR (500 MHz, CDCl$_3$): $\delta_H = 7.84$ (dd, 2H, $J = 2.0, 10.0$ Hz, 4,8-H), 7.14–7.08 (m, 3H, 5,6,7-H), 6.55 (s, 2H, 1,3-H), 3.52 (t, 4H, $J = 6.6$ Hz, pyrrolidine), 2.09–2.06 (m, 4H, pyrrolidine) ppm. Data are in agreement with those previously reported in reference 11.

**Deesterification of 5:** A solution of 5 (347 mg, 1.02 mmol) in 100% H$_3$PO$_4$ (20 mL) was stirred at 150 °C for 2 h. After the reaction mixture was cooled, it was poured into water, neutralized by K$_2$CO$_3$, and extracted with CH$_2$Cl$_2$. The crude product was purified by alumina column chromatography with hexane as the eluent to afford 12 (187 mg, 87%) as red crystals.
2-Diethylaminoazulene (13)

A solution of 6 (236 mg, 0.687 mmol) in 100% H$_3$PO$_4$ (25 mL) was stirred at 150 °C for 2 h under the air atmosphere. After the reaction mixture was cooled, it was poured into water, neutralized by K$_2$CO$_3$, and extracted with CH$_2$Cl$_2$. The crude product was purified by alumina column chromatography with hexane : AcOEt (20 : 1, $R_f = 0.50$) as the eluent to afford 13 (87 mg, 64%) as a red oil. $^1$H NMR (500 MHz, CDCl$_3$): $\delta_H = 7.81$ (dd, 2H, $J = 1.5, 10.5$ Hz, 4,8-H), 7.08–7.12 (m, 3H, 5,6,7-H), 6.62 (s, 2H, 1,3-H), 3.54 (q, 4H, $J = 7.2$ Hz, Et$_2$N), 1.31 (t, 6H, $J = 7.2$ Hz, Et$_2$N) ppm. Data are in agreement with those previously reported in reference 11.

2-Dipropylazulene (14)

A solution of 7 (728 mg, 1.96 mmol) in 100% H$_3$PO$_4$ (25 mL) was stirred at 150 °C for 3 h under the air atmosphere. After the reaction mixture was cooled, it was poured into water, neutralized by K$_2$CO$_3$, and extracted with CH$_2$Cl$_2$. The crude product was purified by alumina column chromatography with hexane : AcOEt (20 : 1, $R_f = 0.55$) as the eluent to afford 14 (400 mg, 90%) as a red oil. IR (AT-IR): $\nu_{\text{max}} = 3013$ (w), 2960 (w), 2929 (w), 2871 (w), 1572 (s), 1539 (s), 1468 (m), 1455 (m), 1407 (w), 1366 (m), 1344 (w), 1290 (w), 1253 (w), 1221 (m), 1201 (w), 1140 (m), 1101 (w), 1038 (w), 1009 (w), 945 (m), 912 (w), 893 (w), 863 (w), 840 (w), 770 (s), 741 (w), 720 (s), 669 (w), 659 (w) cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$): $\delta_H = 7.82$ (dd, 2H, $J = 1.5, 10.5$ Hz, 4,8-H), 7.13–7.10 (m, 3H, 5,6,7-H), 6.62 (s, 2H, 1,3-H), 3.44 (t, 4H, $J = 7.5$ Hz, n-PrN), 1.78 (sext, 4H, $J = 7.5$ Hz, n-PrN), 1.03 (t, 6H, $J = 7.5$ Hz, n-PrN) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta_C = 159.01, 142.08, 127.30, 126.19, 124.60, 100.32, 53.51, 21.26, 11.58$ ppm; HRMS (FAB-MS): calcd for C$_{16}$H$_{21}$N$^+$ [M + H]$^+$ 228.1747; found: 228.1754.
To a solution of 1 (600 mg, 1.96 mmol) in EtOH (20 mL) was added phenylhydrazine (1.06 g, 9.80 mmol). The resulting mixture was refluxed for 12 h under an Ar atmosphere. The solvent was removed under reduced pressure and the residue was passed through an alumina column with CH₂Cl₂ to give a crude product. Pb(OAc)₄ (1.39 g, 3.14 mmol) and 80% N₂H₄ (5 drops) in CH₂Cl₂ (50 mL) was added to a solution of the crude product in CH₂Cl₂ (50 mL) at room temperature. The resulting mixture was stirred at the same temperature for 3 h under an Ar atmosphere. The reaction mixture was poured into water, extracted with CH₂Cl₂, and dried with Na₂SO₄. The solvent was removed under reduced pressure and the residue was purified by column chromatography on alumina with CH₂Cl₂ to give 15 (669 mg, 91%) as red crystals. M.p. 103−104 °C; IR (AT−IR): νₘₐₓ = 3066 (w), 2986 (w), 2957 (w), 2902 (w), 1688 (m), 1672 (s), 1591 (w), 1534 (w), 1496 (m), 1478 (w), 1452 (m), 1424 (s), 1411 (s), 1381 (m), 1354 (w), 1315 (m), 1297 (w), 1255 (m), 1221 (m), 1192 (s), 1168 (m), 1157 (m), 1115 (w), 1091 (s), 1074 (w), 1057 (m), 1024 (m), 974 (w), 938 (w), 913 (w), 884 (w), 849 (w), 814 (w), 803 (w), 791 (s), 777 (m), 746 (m), 725 (w), 703 (m), 690 (m), 676 (w), 661 (w) cm⁻¹; UV/Vis (CH₂Cl₂): λₘₐₓ (log ε) = 262 (4.32), 318 (4.69), 366 sh (4.04), 458 (3.14) nm; ¹H NMR (500 MHz, CDCl₃): δ_H = 9.78 (d, 2H, J = 10.0 Hz, 4,8-H), 8.01 (d, 2H, o-Ph), 7.96 (t, 1H, J = 10.0 Hz, 6-H), 7.79 (t, 2H, J = 10.0 Hz, 5,7-H), 7.60−7.55 (m, 3H, m,p-Ph), 4.22 (q, 4H, J = 7.2 Hz, CO₂Et), 1.06 (t, 6H, J = 7.2 Hz, CO₂Et) ppm; ¹³C NMR (125 MHz, CDCl₃): δ_C = 164.66, 164.58, 152.72, 143.20, 140.11, 139.12, 131.86, 131.54, 129.19, 123.24, 107.42, 60.32, 14.28 ppm; HRMS (FAB-MS): calcd for C₂₂H₂₀N₂O₄ + H⁺ [M +H]⁺ 377.1496; found: 377.1483.
1,3-Diethoxycarbonyl-2-(p-tolyazo)azulene (16)

To a solution of 1 (500 mg, 1.63 mmol) in EtOH (20 mL) was added p-tolyldrazine (994 mg, 8.15 mmol). The resulting mixture was refluxed for 12 h under an Ar atmosphere. The solvent was removed under reduced pressure and the residue was passed through an alumina column with CH₂Cl₂ to give a crude product. Pb(OAc)₄ (1.16 g, 2.61 mmol) and 80% N₂H₄ (5 drops) in CH₂Cl₂ (40 mL) was added to a solution of the crude product in CH₂Cl₂ (40 mL) at room temperature. The resulting mixture was stirred at the same temperature for 3 h under an Ar atmosphere. The reaction mixture was poured into water, extracted with CH₂Cl₂, and dried with Na₂SO₄. The solvent was removed under reduced pressure and the residue was purified by column chromatography on alumina with CH₂Cl₂ to give 16 (382 mg, 60%) as red crystals. M.p. 110–111 °C; IR (AT–IR): νₘₐₓ = 2980 (w), 2898 (w), 1672 (s), 1592 (w), 1558 (w), 1538 (w), 1518 (m), 1495 (m), 1457 (m), 1426 (s), 1412 (m), 1383 (m), 1353 (w), 1318 (w), 1295 (w), 1258 (m), 1220 (m), 1197 (s), 1181 (s), 1155 (m), 1113 (w), 1090 (m), 1061 (m), 1029 (m), 977 (w), 965 (w), 922 (w), 885 (w), 844 (w), 825 (w), 804 (w), 789 (m), 770 (w), 743 (m), 702 (w), 678 (w), 664 (w) cm⁻¹; UV/Vis (CH₂Cl₂): λₘₐₓ (log ε) = 262 (4.31), 324 (4.69), 367 sh (4.11), 462 sh (3.18) nm; ¹H NMR (500 MHz, CDCl₃): δ_H = 9.76 (d, 2H, J = 10.0 Hz, 4,8-H), 7.96–7.89 (m, 3H, 6-H and o-Ph), 7.77 (t, 2H, J = 10.0 Hz, 5,7-H), 7.36 (d, 2H, J = 8.0 Hz, m-Ph), 4.21 (q, 4H, J = 7.2 Hz, CO₂Et), 2.47 (s, 3H, Me), 1.06 (t, 6H, J = 7.2 Hz, CO₂Et) ppm; ¹³C NMR (125 MHz, CDCl₃): δ_C = 164.72, 164.67, 150.94, 143.20, 142.49, 139.98, 138.97, 131.45, 129.81, 123.25, 107.51, 60.26, 21.68, 14.31 ppm; HRMS (FAB-MS): calcd for C₂₃H₂₃N₂O₄ + H⁺ [M + H]⁺ 391.1653; found: 391.1665.
1,3-Diethoxycarbonyl-2-(p-chlorophenylazo)azulene (17)

To a solution of 1 (460 mg, 1.50 mmol) in EtOH (20 mL) was added p-chlorophenylhydrazine (1.07 g, 7.50 mmol). The resulting mixture was refluxed for 12 h under an Ar atmosphere. The solvent was removed under reduced pressure and the residue was passed through an alumina column with CH₂Cl₂ to give a crude product. Pb(OAc)₄ (1.06 g, 2.40 mmol) and 80% N₂H₄ (5 drops) in CH₂Cl₂ (40 mL) was added to a solution of the crude product in CH₂Cl₂ (40 mL) at room temperature. The resulting solution was stirred at the same temperature for 3 h under an Ar atmosphere. The reaction mixture was poured into water, extracted with CH₂Cl₂, and dried with Na₂SO₄. The solvent was removed under reduced pressure and the residue was purified by column chromatography on alumina with CH₂Cl₂ to give 17 (487 mg, 79%) as red crystals. M.p. 154–155 °C; IR (AT-IR): νₘₐₓ = 3093 (w), 2982 (w), 2901 (w), 1670 (s), 1584 (w), 1537 (w), 1497 (m), 1474 (m), 1457 (m), 1425 (s), 1380 (m), 1351 (m), 1319 (w), 1293 (w), 1261 (m), 1222 (s), 1198 (s), 1185 (s), 1156 (m), 1115 (m), 1091 (s), 1059 (m), 1026 (s), 977 (w), 922 (m), 885 (m), 849 (m), 793 (m), 749 (m), 722 (w), 699 (w), 670 (w) cm⁻¹; UV/Vis (CH₂Cl₂): λₘₐₓ (log ε) = 260 (4.33), 321 (4.73), 368 sh (4.08), 455 (3.17) nm; ¹H NMR (500 MHz, CDCl₃): δH = 9.77 (d, 2H, J = 10.0 Hz, 4,8-H), 7.99–7.94 (m, 3H, 6-H and o-Ph), 7.79 (t, 2H, J = 10.0 Hz, 5,7-H), 7.57–7.54 (m, 2H, m-Ph), 4.22 (q, 4H, J = 7.2 Hz, CO₂Et), 1.07 (t, 6H, J = 7.2 Hz, CO₂Et) ppm; ¹³C NMR (125 MHz, CDCl₃): δC = 164.56, 164.18, 151.05, 143.12, 140.28, 139.27, 137.94, 131.59, 129.53, 124.47, 107.39, 60.34, 14.37 ppm; HRMS (FAB-MS): calcd for C₂₂H₁₉ClN₂O₄ + H⁺ [M + H]⁺ 411.1107; found: 411.1095.
1,3-Diethoxycarbonyl-2-(1,3-diethoxycarbonylazulen-2-ylazo)azulene (18)

To a solution of 1 (306 mg, 0.998 mmol) in EtOH (50 mL) was added 1,3-diethoxycarbonylazulen-2-ylhydrazone (1.51 g, 4.99 mmol). The resulting mixture was refluxed for 24 h under an Ar atmosphere. The solvent was removed under reduced pressure and the residue was passed through an alumina column with CH$_2$Cl$_2$ to give a crude product. Pb(OAc)$_4$ (710 g, 1.60 mmol) and 80% N$_2$H$_4$ (5 drops) in CH$_2$Cl$_2$ (40 mL) was added to a solution of the crude product in CH$_2$Cl$_2$ (40 mL) at room temperature. The resulting solution was stirred at the same temperature for 3 h under an Ar atmosphere. The reaction mixture was poured into water, extracted with CH$_2$Cl$_2$, and dried with Na$_2$SO$_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography on alumina with CH$_2$Cl$_2$/AcOEt (10 : 1) to give 18 (82 mg, 20%) as dark green crystals. M.p. 168–169 °C; IR (AT-IR): $\nu_{\text{max}}$ = 2983 (w), 2900 (w), 1692 (s), 1578 (w), 1531 (w), 1496 (w), 1476 (w), 1454 (m), 1425 (s), 1387 (m), 1353 (w), 1316 (m), 1252 (w), 1241 (w), 1222 (m), 1190 (s), 1116 (w), 1093 (m), 1057 (m), 1031 (m), 977 (w), 948 (w), 921 (w), 878 (w), 864 (w), 828 (w), 788 (m), 761 (w), 736 (w), 720 (w), 669 (w), 661 (w) cm$^{-1}$; UV/Vis (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ (log $\varepsilon$) = 253 sh (4.45), 324 (4.86), 397 sh (4.28), 532 (3.63), 618 sh (3.37) nm; $^1$H NMR (500 MHz, CDCl$_3$): $\delta_H$ = 9.41 (d, 2H, $J = 10.0$ Hz, 4,8-H), 7.93 (t, 1H, $J = 10.0$ Hz, 6-H), 7.67 (t, 2H, $J = 10.0$ Hz, 5,7-H), 4.30 (q, 4H, $J = 7.2$ Hz, CO$_2$Et), 1.13 (t, 6H, $J = 7.2$ Hz, CO$_2$Et) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta_C$ = 165.59, 157.82, 141.13, 141.07, 140.41, 129.92, 111.19, 60.91, 14.19, ppm; HRMS (FAB-MS): calcd for C$_{32}$H$_{30}$N$_2$O$_8$ + H$^+$ [M + H]$^+$ 571.2075; found: 571.2090.
2. Copies of $^1$H NMR, $^{13}$C NMR, COSY and HRMS of compounds 3–18 (Figures S1–S56).

**Figure S1.** $^1$H NMR spectrum of 3 in CDCl$_3$ (500 MHz).

**Figure S2.** $^{13}$C NMR spectrum of 3 in CDCl$_3$ (125 MHz).
**Figure S3.** COSY spectrum of 3 in CDCl$_3$ (500 MHz).

**Figure S4.** HRMS (FAB-MS) of 3.

calcd for C$_{20}$H$_{23}$NO$_5$ + H$^+$ [M + H]$^+$ 358.1649.
found: 358.1646.
Figure S5. $^1$H NMR spectrum of 4 in CDCl$_3$ (500 MHz).

Figure S6. $^{13}$C NMR spectrum of 4 in CDCl$_3$ (125 MHz).
**Figure S7.** COSY spectrum of 4 in CDCl₃ (500 MHz).

**Figure S8.** HRMS (FAB-MS) of 4.

found: 355.1783.
Figure S9. $^1$H NMR spectrum of 5 in CDCl$_3$ (500 MHz).

Figure S10. $^{13}$C NMR spectrum of 5 in CDCl$_3$ (125 MHz).
Figure S11. COSY spectrum of 5 in CDCl₃ (500 MHz).

Figure S12. HRMS (FAB-MS) of 5.

found: 341.1633.
Figure S13. $^1$H NMR spectrum of 6 in CDCl$_3$ (500 MHz).

Figure S14. $^{13}$C NMR spectrum of 6 in CDCl$_3$ (125 MHz).
**Figure S15.** COSY spectrum of 6 in CDCl$_3$ (500 MHz).

**Figure S16.** HRMS (FAB-MS) of 6.

calcd for C$_{20}$H$_{26}$NO$_4^+$ [M]$^+$ 344.1877.
found: 344.1849.
Figure S17. $^1$H NMR spectrum of 7 in CDCl$_3$ (500 MHz).

Figure S18. $^{13}$C NMR spectrum of 7 in CDCl$_3$ (125 MHz).
**Figure S19.** COSY spectrum of 7 in CDCl$_3$ (500 MHz).

**Figure S20.** HRMS (FAB-MS) of 7.

calcd for C$_{22}$H$_{29}$NO$_4$ + H$^+$ [M + H]$^+$ 372.2170. found: 342.1718.
Figure S21. $^1$H NMR spectrum of 8 in CDCl$_3$ (500 MHz).

Figure S22. $^{13}$C NMR spectrum of 8 in CDCl$_3$ (125 MHz).
Figure S23. COSY spectrum of 8 in CDCl₃ (500 MHz).

Figure S24. HRMS (FAB-MS) of 8.

Figure S25. $^1$H NMR spectrum of 9 in CDCl$_3$ (500 MHz).

Figure S26. $^{13}$C NMR spectrum of 9 in CDCl$_3$ (125 MHz).
Figure S27. COSY spectrum of 9 in CDCl₃ (500 MHz).

Figure S28. HRMS (FAB-MS) of 9.
Figure S29. $^1$H NMR spectrum of 10 in CDCl$_3$ (500 MHz).

Figure S30. COSY spectrum of 10 in CDCl$_3$ (500 MHz).
Figure S31. $^1$H NMR spectrum of 11 in CDCl$_3$ (500 MHz).

Figure S32. COSY spectrum of 11 in CDCl$_3$ (500 MHz).
**Figure S33.** $^1$H NMR spectrum of 12 in CDCl$_3$ (500 MHz).

**Figure S34.** COSY spectrum of 12 in CDCl$_3$ (500 MHz).
Figure S35. $^1$H NMR spectrum of 13 in CDCl$_3$ (500 MHz).

Figure S36. COSY spectrum of 13 in CDCl$_3$ (500 MHz).
Figure S37. $^1$H NMR spectrum of 14 in CDCl$_3$ (500 MHz).

Figure S38. $^{13}$C NMR spectrum of 14 in CDCl$_3$ (125 MHz).
**Figure S39.** COSY spectrum of 14 in CDCl₃ (500 MHz).

**Figure S40.** HRMS (FAB-MS) of 14.

found: 228.1754.
Figure S41. $^1$H NMR spectrum of 15 in CDCl₃ (500 MHz).

Figure S42. $^{13}$C NMR spectrum of 15 in CDCl₃ (125 MHz).
**Figure S43.** COSY spectrum of 15 in CDCl$_3$ (500 MHz).

**Figure S44.** HRMS (FAB-MS) of 15.

calcd for $\text{C}_{22}\text{H}_{20}\text{N}_2\text{O}_4 + \text{H}^+$ [M +H]$^+$ 377.1496.
found: 377.1483.
Figure S45. $^1$H NMR spectrum of 16 in CDCl$_3$ (500 MHz).

Figure S46. $^{13}$C NMR spectrum of 16 in CDCl$_3$ (125 MHz).
**Figure S47.** COSY spectrum of **16** in CDCl₃ (500 MHz).

**Figure S48.** HRMS (FAB-MS) of **16**.

found: 391.1665.
Figure S49. $^1$H NMR spectrum of 17 in CDCl$_3$ (500 MHz).

Figure S50. $^{13}$C NMR spectrum of 17 in CDCl$_3$ (125 MHz).
**Figure S51.** COSY spectrum of 17 in CDCl₃ (500 MHz).

**Figure S52.** HRMS (FAB-MS) of 17.
Figure S53. $^1$H NMR spectrum of 18 in CDCl$_3$ (500 MHz).

Figure S54. $^{13}$C NMR spectrum of 18 in CDCl$_3$ (125 MHz).
Figure S55. COSY spectrum of 18 in CDCl₃ (500 MHz).

Figure S56. HRMS (FAB-MS) of 18.

found: 571.2090.
3. UV/Vis spectra of compounds 15–18 (Figures S57–S60).

**Figure S57.** UV/Vis spectrum of 15 in CH$_2$Cl$_2$.

**Figure S58.** UV/Vis spectrum of 16 in CH$_2$Cl$_2$. 

\[
\text{CO}_2\text{Et} \quad \text{CO}_2\text{Et} \\
\text{N} \quad \text{N} \\
\text{N} \quad \text{N} \\
\text{Me} \\
\]
**Figure S59.** UV/Vis spectrum of 17 in CH$_2$Cl$_2$.

**Figure S60.** UV/Vis spectrum of 18 in CH$_2$Cl$_2$. 
4. Cyclic and differential pulse voltammograms of compounds 15–18 (Figures S61–S64).

Figure S61. Cyclic voltammogram for oxidation (top, left) and reduction (top, right), and differential pulse voltammograms for oxidation (bottom, left) and reduction (bottom, right) of 15 (1 mM) in benzonitrile containing Et₄NClO₄ (0.1 M) as the supporting electrolyte; scan rate: CV = 100 mVs⁻¹, DPV = 20 mVs⁻¹.
Figure S62. Cyclic voltammogram for oxidation (top, left) and reduction (top, right), and differential pulse voltammograms for oxidation (bottom, left) and reduction (bottom, right) of 16 (1 mM) in benzonitrile containing Et₄NClO₄ (0.1 M) as the supporting electrolyte; scan rate: CV = 100 or 500 mVs⁻¹, DPV = 20 mVs⁻¹.
Figure S63. Cyclic voltammogram for oxidation (top, left) and reduction (top, right), and differential pulse voltammograms for oxidation (bottom, left) and reduction (bottom, right) of 17 (1 mM) in benzonitrile containing Et$_4$NClO$_4$ (0.1 M) as the supporting electrolyte; scan rate: CV = 100 or 500 mVs$^{-1}$, DPV = 20 mVs$^{-1}$.
Figure S64. Cyclic voltammogram for oxidation (top, left) and reduction (top, right), and differential pulse voltammograms for oxidation (bottom, left) and reduction (bottom, right) of 18 (1 mM) in benzonitrile containing Et$_4$NClO$_4$ (0.1 M) as the supporting electrolyte; scan rate: CV = 100 or 500 mVs$^{-1}$, DPV = 20 mVs$^{-1}$. 
5. Frontier Kohn–Sham orbitals of compounds 15–18 (Figures S65–S68)

HOMO (−5.79 eV)  LUMO (−2.37 eV)

HOMO−1 (−5.94 eV)  LUMO+1 (−1.80 eV)

HOMO−2 (−6.73 eV)  LUMO+2 (−1.75 eV)

HOMO−3 (−7.05 eV)  LUMO+3 (−0.38 eV)

Figure S65. Frontier Kohn–Sham orbitals of 15 at the B3LYP/6-31G** level.
HOMO (−5.75 eV)  

HOMO (−5.75 eV) 

HOMO−1 (−5.88 eV) 

HOMO−2 (−6.50 eV) 

HOMO−3 (−6.98 eV) 

LUMO (−2.34 eV)  

LUMO+1 (−1.74 eV) 

LUMO+2 (−1.68 eV) 

LUMO+3 (−0.33 eV) 

Figure S66. Frontier Kohn–Sham orbitals of 16 at the B3LYP/6-31G** level.
Figure S67. Frontier Kohn–Sham orbitals of 17 at the B3LYP/6-31G** level.
Figure S68. Frontier Kohn–Sham orbitals of 18 at the B3LYP/6-31G** level.
6. Crystal structure of 16 (Figures S69)

Figure S69. The ORTEP drawing of 16; Ellipsoids are drawn at 50% probability level.