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Electronic Supplementary Information (ESI)

Synthesis of Azulene-substituted Benzofurans and Isocoumarins *via* Intramolecular Cyclization of 1-Ethynylazulenes, and their Structural and Optical Properties

Taku Shoji, Miwa Tanaka, Sho Takagaki, Kota Miura, Akira Ohta, Ryuta Sekiguchi, Shunji Ito, Shigeki Mori, and Tetsuo Okujima

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1. Experimental details



Methyl 1-trimethylsilylethynylazulene-3-carboxylate: To a degassed solution of 1a (628 mg, 2.01 mmol), trimethylsilylacetylene (417 mg, 4.25 mmol), and Cul (41 mg, 0.22 mmol) in THF (10 mL) and triethylamine (10 mL) was added tetrakis(triphenylphosphine)palladium(0) (73 mg, 0.063 mmol). The resulting mixture was stirred at 50 °C for 2 h under an Ar atmosphere. The reaction mixture was poured into a 10% NH₄Cl solution and extracted with hexane. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified column chromatography on CH₂Cl₂ by silica gel with to give methyl 1-trimethylsilylethynylazulene-3-carboxylate (556 mg, 98%). mp 97-100 °C; IR (AT-IR): v_{max} = 2973 (w), 2945 (w), 2137 (m), 1698 (s), 1577 (w), 1536 (w), 1510 (w), 1455 (s), 1442 (m), 1424 (m), 1411 (m), 1384 (w), 1368 (w), 1310 (w), 1296 (w), 1242 (m), 1223 (s), 1205 (s), 1140 (w), 1047 (s), 997 (m), 959 (w), 892 (m), 874 (s), 844 (s), 774 (s), 735 (s), 702 (m) cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ_H = 9.60 (d, 1H, J = 9.7 Hz, H₄), 8.68 (d, 1H, J = 9.7 Hz, H₈), 8.44 (s, 1H, H₂), 7.84 (t, 1H, J = 9.7 Hz, H₆), 7.60-7.52 (m, 2H, H_{5.7}), 3.95 (s, 3H, CO₂Me), 0.32 (s, 9H, TMS) ppm; ¹³C NMR (125) MHz, CDCl₃): δ_{C} = 165.3, 145.4, 143.1, 141.1, 140.3, 138.5, 138.0, 129.2, 127.8, 116.1, 110.4, 100.1, 99.0, 51.4, 0.4 ppm; HRMS (EI-MS, positive): calcd for $C_{17}H_{18}O_2Si^+$ [M]⁺ 282.1071; found: 282.1078.



Methyl 1-ethynylazulene-3-carboxylate То (2a): solution of methyl а 1-trimethylsilylethynylazulene-3-carboxylate (556 mg, 1.97 mmol) in MeOH (30 mL) was added K₂CO₃ (1.39 g, 10.1 mmol). The resulting mixture was stirred at room temperature for 1 h. The reaction mixture was poured into water and extracted with AcOEt. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with toluene to give 2a (353 mg, 85%). mp 110-113 °C; IR (AT-IR): $v_{max} = 3239$ (m), 2950 (w), 2851 (w), 2091 (w), 1692 (m), 1595 (w), 1582 (w), 1538 (w), 1516 (w), 1458 (w), 1437 (m), 1421 (w), 1413 (w), 1392 (w), 1314 (w), 1299 (w), 1261 (w), 1226 (w), 1205 (s), 1183 (w), 1167 (w), 1127 (w), 1045 (m), 985 (w), 962 (w), 948 (w), 887 (w), 870 (w), 777 (w), 741 (m), 712 (w), 661 (w) cm⁻¹; ¹H NMR (500 MHz, CDCl₃): $\delta_{\rm H}$ = 9.63 (d, 1H, J = 10.0 Hz, H₄), 8.73 (d, 1H, J = 10.0 Hz, H₈), 8.46 (s, 1H, H₂), 7.87 (t, 1H, J = 10.0 Hz, H₆), 7.61 (t, 1H, J = 10.0 Hz, H₅), 7.55 (t, 1H, J = 10.0 Hz, H₇), 3.95 (s, 3H, CO₂Me), 3.45 (s, 1H, C≡CH) ppm; ¹³C NMR (125 MHz, CDCl₃): δ_{C} = 165.3, 145.6, 143.2, 141.1, 140.4, 138.7, 137.9, 129.3, 127.9, 116.1, 109.2, 81.7, 79.0, 51.4 ppm; HRMS (EI-MS, positive): calcd for $C_{14}H_{10}O_2^+$ [M]⁺ 210.0676; found: 210.0684.



Methyl 6-isopropyl-1-trimethylsilylethynylazulene-3-carboxylate: To a degassed solution of 1c (357 mg, 1.01 mmol), trimethylsilylacetylene (196 mg, 1.99 mmol), and Cul (20 mg, 0.11 mmol) in THF (5 mL) and triethylamine (5 mL) was added tetrakis(triphenylphosphine)palladium(0) (44 mg, 0.038 mmol). The resulting mixture was stirred at 50 °C for 21 h under an Ar atmosphere. The reaction mixture was poured into a 10% NH₄Cl solution and extracted with hexane. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/AcOEt (5 : 1) to give methyl 6-isopropyl-1-trimethylsilylethynylazulene-3-carboxylate (324 mg, 99%) as purple solid. mp 106-107 °C; IR (AT-IR): v_{max} = 2961 (w), 2148 (m), 1695 (s), 1579 (m), 1550 (w), 1508 (w), 1442 (s), 1422 (s), 1403 (m), 1391 (m), 1379 (m), 1365 (m), 1330 (w), 1302 (w), 1250 (s), 1199 (s), 1138 (w), 1125 (w), 1103 (w), 1073 (m), 1055 (s), 1036 (m), 999 (m), 910 (w), 874 (s), 843 (s), 774 (s), 760 (s), 735 (m), 701 (m), 678 (w), 661 (w), 652 (w) cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ_{H} = 9.50 (d, 1H, J = 10.3 Hz, H₄), 8.61 (d, 1H, J = 10.0 Hz, H₈), 8.34 (s, 1H, H₂), 7.53-7.48 (m, 2H, H_{5.7}), 3.93 (s, 3H, CO₂Me), 3.15 (sept, 1H, J = 6.9 Hz, *i*-Pr), 1.38 (d, 6H, J = 6.9 Hz, *i*-Pr), 0.32 (s, 9H, TMS) ppm; ¹³C NMR (125 MHz, CDCl₃): $δ_{C}$ = 165.4, 163.2, 144.2, 141.9, 139.8, 138.2, 137.6, 128.6, 127.1, 115.7, 109.9, 100.4, 98.5, 51.3, 39.9, 24.4, 0.4 ppm; HRMS (EI-MS, positive) calcd for C₂₀H₂₄O₂Si⁺ [M]⁺ 324.1541; found: 324.1558.



1-ethynyl-6-isopropylazulene-3-carboxylate (2c): Methvl То а solution of methyl 6-isopropyl-1-trimethylsilylethynylazulene-3-carboxylate (148 mg, 0.46 mmol) in MeOH (20 mL) was added K₂CO₃ (323 mg, 2.34 mmol). The resulting mixture was stirred at room temperature for 1 h. The reaction mixture was poured into water and extracted with hexane. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/AcOEt (15 : 1) to give 2c (105 mg, 90%) as purple oil. IR (AT-IR): v_{max} = 3296 (w), 2962 (w), 2097 (w), 1692 (m), 1583 (w), 1508 (w), 1445 (s), 1424 (m), 1390 (w), 1327 (w), 1307 (w), 1242 (w), 1205 (s), 1129 (w), 1069 (w), 1050 (m), 1030 (w), 980 (w), 847 (m), 773 (w), 726 (w), 681 (w), 665 (w) cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ_H = 9.53 (d, 1H, J = 10.3 Hz, H₄), 8.64 (d, 1H, J = 10.3 Hz, H₈), 8.35 (s, 1H, H₂), 7.54 (dd, 1H, J = 10.3, 1.3 Hz, H₅), 7.48 (d, 1H, J = 10.3 Hz, H₇), 3.94 (s, 3H, CO₂Me), 3.43 (s, 1H, C≡CH), 3.15 (sept, 1H, J = 6.9 Hz, *i*-Pr), 1.38 (d, 6H, J = 6.9 Hz, *i*-Pr) ppm; ¹³C NMR (125 MHz, CDCl₃): $\delta_{C} = 165.4$, 163.3, 144.3, 142.0, 139.8, 138.3, 137.4, 128.6, 127.2, 115.7, 108.7, 81.2, 79.2, 51.3, 39.9, 24.3 ppm; HRMS (EI–MS, positive) calcd for $C_{17}H_{16}O_2^+$ [M]⁺ 252.1145; found: 252.1153.



Methyl 5-isopropyl-2-methyl-1-trimethylsilylethynylazulene-3-carboxylate: To a degassed solution of 1d (1.41 g, 3.83 mmol), trimethylsilylacetylene (563 mg, 5.73 mmol), and Cul (73 mg, 0.38 mmol) in THF (10 mL) triethylamine (10 mL) added and was tetrakis(triphenylphosphine)palladium(0) (133 mg, 115 mmol). The resulting mixture was stirred at 50 °C for 12 h under an Ar atmosphere. The reaction mixture was poured into a 10% NH₄Cl solution and extracted with toluene. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica with hexane/AcOEt (10 1) methyl gel to give 2 5-isopropyl-2-methyl-1-trimethylsilylethynylazulene-3-carboxylate (1.28 g, 99%) as purple solid. mp 125-126°C; IR (AT-IR): v_{max} = 2959 (w), 2134 (w), 1686 (s), 1493 (w), 1439 (s), 1422 (m), 1381 (m), 1305 (w), 1249 (m), 1220 (s), 1196 (w), 1173 (w), 1117 (m), 1071 (w), 1033 (w), 1006 (w), 960 (w), 895 (m), 842 (s), 805 (m), 778 (m), 759 (m), 747 (w), 700 (w), 677 (w), 666 (w) cm⁻¹; ¹H NMR $(500 \text{ MHz}, \text{ CDCI}_3)$: $\delta_H = 9.59 \text{ (d, 1H, } J = 1.1 \text{ Hz}, \text{ H}_4)$, 8.46 (d, 1H, $J = 10.0 \text{ Hz}, \text{ H}_8)$, 7.69 (d, 1H, $J = 1.1 \text{ Hz}, \text{ H}_4$) 10.0 Hz, H₆), 7.46 (t, 1H, J = 10.0 Hz, H₇), 3.97 (s, 3H, CO₂Me), 3.19 (sept, 1H, J = 6.9 Hz, *i*-Pr), 2.87 (s, 3H, Me), 1.41 (d, 6H, J = 6.9 Hz, *i*-Pr), 0.33 (s, 9H, TMS) ppm; ¹³C NMR (125 MHz, CDCl₃): $\delta_{\rm C}$ = 166.5, 156.4, 150.6, 144.2, 142.1, 137.4, 136.7, 134.3, 127.9, 113.8, 111.3, 101.3, 100.0, 51.0, 39.5, 24.7, 17.0, 0.5 ppm; HRMS (EI-MS, positive): calcd for C₂₁H₂₆O₂Si⁺ [M]⁺ 338.1697; found: 338.1704.



Methyl 1-ethynyl-5-isopropyl-2-methylazulene-3-carboxylate (2d): To a solution of methyl 7-isopropyl-2-methyl-3-trimethylsilylethynylazulene-1-carboxylate (849 mg, 2.51 mmol) in MeOH (30 mL) was added K₂CO₃ (1.75 g, 12.7 mmol). The resulting mixture was stirred at room temperature for 1 h. The reaction mixture was poured into water and extracted with hexane. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/AcOEt (10 : 1) to give **2d** (668 mg, 99%) as purple oil. IR (AT–IR): v_{max} = 2959 (w), 2092 (w), 1682 (s), 1578 (w), 1496 (w), 1442 (s), 1420 (s), 1389 (m), 1380 (m),1305 (w), 1221 (s), 1194 (m), 1167 (w), 1135 (m), 1107 (s), 1066 (w), 1029 (w), 1005 (w), 957 (w), 930 (w), 843 (w), 795 (m), 780 (s), 734 (m), 665 (w) cm⁻¹; ¹H NMR (500 MHz, CDCI₃): δ_{H} = 9.62 (d, 1H, *J* = 1.4 Hz, H₄), 8.49 (d, 1H, *J* = 10.3 Hz, H₈), 7.71 (d, 1H, *J* = 10.3 Hz, H₆), 7.47 (t, 1H, *J* = 10.0 Hz, H₇), 3.98 (s, 3H, CO₂Me), 3.58 (s, 1H, C≡CH), 3.21 (sept, 1H, *J* = 6.9 Hz, *i*-Pr), 2.89 (s, 3H, Me), 1.41 (d, 6H, *J* = 6.9 Hz, *i*-Pr) ppm; ¹³C NMR (125 MHz, CDCI₃): δ_{C} = 166.4, 156.5, 150.7, 144.4, 142.0, 137.5, 136.8, 134.1, 127.9, 113.7, 110.0, 83.9, 78.8, 51.0, 39.5, 24.7, 16.9 ppm; HRMS (EI–MS, positive): calcd for C₁₈H₁₈O₂⁺ [M]⁺ 266.1302; found: 266.1314.



2-(3-Methoxycarbonylazulen-1-yl)benzofuran (3a): To a degassed solution of 2a (211 mg, 1.00 mmol), 2-iodophenol (335 mg, 1.52 mmol), and Cul (18 mg, 0.095 mmol) in triethylamine (5 mL) and THF (5 mL) was added tetrakis(triphenylphosphine)palladium(0) (34 mg, 0.029 mmol). The resulting mixture was stirred at 50 °C for 21 h under an Ar atmosphere. The reaction mixture was poured into a 10% NH₄Cl solution and extracted with toluene. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2CI_2 to give **3a** (196 mg, 65%) as green crystals. mp 110-111°C; IR (AT-IR): v_{max} = 3109 (w), 2959 (w), 1693 (s), 1573 (m), 1524 (w), 1447 (m), 1386 (m), 1303 (w), 1259 (m), 1241 (m), 1237 (m), 1208 (s), 1169 (m), 1125 (m), 1091 (m), 1085 (m), 1047 (w), 1012 (m), 964 (w), 929 (w), 898 (m), 888 (m), 881 (m), 850 (w), 800 (m), 776 (m), 761 (w), 749 (s), 738 (m), 727 (w) cm⁻¹; UV/Vis (CH₂Cl₂): λ_{max} (log ε) = 277 (4.47), 314 (4.59), 340 sh (4.30), 408 (3.99), 432 sh (3.82), 579 (2.72), 640 sh (2.53) nm; ¹H NMR (500 MHz, CDCl₃): δ_{H} = 9.66 (d, 1H, J = 10.0 Hz, H₄), 9.22 (d, 1H, J = 10.0 Hz, H₈), 8.74 (s, 1H, H₂), 7.83 (t, 1H, J = 10.0 Hz, H₆), 7.61 (d, 1H, J = 7.4 Hz, $H_{4'}$ or $H_{7'}$ of benzofuran), 7.58-7.51 (m, 3H, $H_{5.7}$ and $H_{4'}$ or $H_{7'}$ of benzofuran), 7.32 -7.25 (m, 2H, $H_{5'}$ and $H_{6'}$ of benzofuran), 7.03 (s, 1H, $H_{3'}$ of benzofuran), 3.99 (s, 3H, CO₂Me) ppm; ¹³C NMR (125 MHz, CDCl₃): δ_{C} = 165.5, 154.7, 153.6, 142.6, 140.4, 139.5, 139.2, 138.6, 138.0, 129.3, 128.8, 128.0, 123.9, 123.0, 120.6, 118.6, 116.7, 111.0, 102.5, 51.4 ppm; HRMS (FAB-MS, positive): calcd for $C_{20}H_{14}O_3^+$ [M]⁺ 302.0938; found: 302.0943.



2-(6-IsopropyI-3-methoxycarbonylazulen-1-yl)benzofuran (3c): To a degassed solution of 2c (146 mg, 0.579 mmol), 2-iodophenol (192 mg, 0.873 mmol), and Cul (11 mg, 0.058 mmol) in triethylamine (3 mL) and THF (3 mL) was added tetrakis(triphenylphosphine)palladium(0) (23 mg, 0.020 mmol). The resulting mixture was stirred at 50 °C for 18.5 h under an Ar atmosphere. The reaction mixture was poured into a 10% NH₄Cl solution and extracted with toluene. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with CH₂Cl₂ to give **3c** (144 mg, 72%) as green crystals. mp 115–116 °C; IR (AT–IR): v_{max} = 2963 (w), 1692 (s), 1580 (m), 1505 (w), 1443 (m), 1430 (w), 1417 (m), 1353 (w), 1308 (w), 1257 (w), 1230 (w), 1204 (s), 1174 (w), 1133 (w), 1102 (w), 1074 (w), 1046 (m), 1023 (w), 953 (m), 910 (w), 881 (w), 863 (w), 844 (w), 772 (m), 757 (w), 744 (s), 729 (w), 669 (w), 664 (w) cm⁻¹; UV/Vis (CH₂Cl₂): λ_{max} (log ϵ) = 281 (4.47), 319 (4.62), 347 sh (4.36), 408 (4.02), 434 sh (3.82), 564 (2.80), 621 sh (2.61) nm; ¹H NMR (500 MHz, CDCl₃): $\delta_{\rm H}$ = 9.58 (d, 1H, J = 10.6 Hz, H₄), 9.15 (d, 1H, J = 10.6 Hz, H₈), 8.64 (s, 1H, H₂), 7.61 (d, 1H, J = 10.5 Hz, H₅), 7.58 (d, 1H, J = 8.0 Hz, H₄, of benzofuran), 7.57 (d, 1H, J = 10.5 Hz, H₇), 7.48 (1H, J = 7.7 Hz, $H_{7'}$ of benzofuran), 7.31-7.25 (m, 2H, $H_{5',6'}$ of benzofuran), 7.00 (s, 1H, $H_{3'}$ of benzofuran), 3.99 (s, 3H, CO₂Me), 3.14 (sept, 1H, J = 6.9 Hz, *i*-Pr), 1.40 (d, 6H, J = 6.9 Hz, *i*-Pr) ppm; ¹³C NMR (125) MHz, CDCl₃): δ_{C} = 165.6, 163.1, 154.6, 154.0, 141.2, 138.3, 138.2, 138.0, 137.6, 129.4, 128.0, 127.4, 123.7, 122.9, 120.5, 118.2, 116.4, 110.9, 102.1, 51.3, 39.7, 24.3 ppm; HRMS (FAB-MS, positive): calcd for $C_{23}H_{20}O_3^+$ [M]⁺ 344.1407; found: 344.1399.



2-(5-IsopropyI-3-methoxycarbonyI-2-methylazulen-1-yl)benzofuran (3d): To a degassed solution of 2d (268 mg, 1.01 mmol), 2-iodophenol (335 mg, 1.52 mmol), and Cul (18 mg, 0.095 mmol) in triethylamine (5 mL) and THF (5 mL) was added tetrakis(triphenylphosphine)palladium(0) (16 mg, 0.014 mmol). The resulting mixture was stirred at 50 °C for 16 h under an Ar atmosphere. The reaction mixture was poured into a 10% NH₄Cl solution and extracted with toluene. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with CH₂Cl₂ to give 3d (111 mg, 31%) as green crystals. mp 124–125 °C; IR (AT–IR): v_{max} = 2956 (w), 1675 (s), 1589 (w), 1518 (w), 1492 (w), 1455 (s), 1441 (s), 1419 (m), 1379 (m), 1367 (w), 1340 (w), 1307 (w), 1257 (w), 1221 (s), 1205 (w), 1173 (m), 1135 (m), 1106 (w), 1072 (m), 1035 (w), 1011 (w), 955 (w), 924 (w), 886 (w), 841 (w), 810 (m), 780 (m), 755 (s), 710 (w), 685 (w), 661 (w) cm⁻¹; UV/Vis (CH₂Cl₂): λ_{max} $(\log \epsilon) = 236 (4.37), 287 (4.56), 309 (4.62), 318 sh (4.60), 344 sh (4.22), 392 (3.90), 546 (2.72) nm;$ ¹H NMR (500 MHz, CDCl₃): δ_{H} = 9.69 (s, 1H, H₄), 8.68 (d, 1H, J = 10.0 Hz, H₈), 7.72 (d, 1H, J = 10.0 Hz, H₆), 7.66 (d, 1H, J = 7.7 Hz, H₄ of benzofuran), 7.58 (d, 1H, J = 7.7 Hz, H₇ of benzofuran), 7.45 (t, 1H, J = 10.0 Hz, H₅), 7.34-7.27 (m, 2H, H_{5',6'} of benzofuran), 6.86 (s, 1H, H_{3'} of benzofuran), 4.02 (s, 3H, CO₂Me), 3.23 (sept, 1H, J = 6.9 Hz, *i*-Pr), 2.94 (s, 3H, Me), 1.43 (d, 6H, J = 6.9 Hz, *i*-Pr) ppm; ¹³C NMR (125 MHz, CDCl₃): $\delta_{\rm C}$ = 166.9, 155.0, 152.9, 152.6, 150.0, 142.4, 141.0, 137.5, 136.8, 134.2, 129.2, 128.0, 123.8, 122.8, 120.6, 118.5, 114.8, 111.2, 106.2, 51.1, 39.4, 24.8, 16.7 ppm; HRMS (FAB-MS, positive): calcd for C₂₄H₂₂O₃⁺ [M]⁺ 358.1564; found: 358.1579.



2,3-Bis(3-methoxycarbonylazulen-1-yl)benzofuran (4a): To a degassed solution of **1a** (557 mg, 1.78 mmol), 2-ethynylphenol (106 mg, 0.897 mmol), and Cul (26 mg, 0.14 mmol) in THF (5 mL) and triethylamine (5 mL) was added tetrakis(triphenylphosphine)palladium(0) (36 mg, 0.031 mmol). The resulting mixture was stirred at 50 °C for 8.5 h under an Ar atmosphere. The reaction mixture was poured into a 10% NH₄Cl solution and extracted with toluene. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with toluene/AcOEt (20 : 1) to give **4a** (82 mg, 19%, purple oil) and **3a** (54 mg, 10%, green crystals).

4a: mp 158–159 °C; IR (AT–IR): v_{max} = 2952 (w), 1686 (s), 1577 (w), 1529 (w), 1507 (w), 1451 (s), 1420 (s), 1383 (m), 1347 (w), 1291 (w), 1266 (m), 1236 (w), 1200 (s), 1162 (m), 1135 (w), 1091 (w), 1065 (m), 1042 (m), 1028 (m), 968 (w), 917 (w), 877 (m), 862 (w), 822 (w), 806 (w), 779 (s), 744 (s), 712 (w), 687 (w), 679 (w), 667 (m), 659 (m) cm⁻¹; UV/Vis (CH₂Cl₂): λ_{max} (log ε) = 236 (4.77), 292 (4.91), 304 sh (4.86), 342 sh (4.44), 385 (4.27), 415 sh (4.19), 566 (3.11), 597 sh (3.07) nm; ¹H NMR (500 MHz, CDCl₃): δ_{H} = 9.70 (d, 1H, *J* = 10.0 Hz, H₄ or H₄'), 9.59 (d, 1H, *J* = 10.0 Hz, H₄ or H₄'), 8.86 (d, 1H, *J* = 10.0 Hz, H₈ or H₆'), 8.49 (s, 1H, H₂ or H₂'), 8.20 (m, 2H, H₂ or H₂' and H₄ or H₄'), 7.75 -7.67 (m, 3H, H_{6.6}' and H₄' of benzofuran), 7.56-7.49 (m, 2H, H_{5.5}'), 7.45 (d, 1H, *J* = 7.7 Hz, H₇' of benzofuran), 7.39 (t, 1H, *J* = 7.7 Hz, H₇ or H₆' of benzofuran), 7.29-7.24 (m, 2H, H₇ or H₇' and H₅' or H₆' of benzofuran), 7.29-7.24 (m, 2H, H₇ or H₇' and H₅' or H₆' of benzofuran), 7.13 (t, 1H, *J* = 9.7 Hz, H₇ or H₇'), 3.95 (s, 3H, CO₂Me), 3.80 (s, 3H, CO₂Me) ppm; ¹³C NMR (125 MHz, CDCl₃): δ_{C} = 165.8, 165.4, 154.7, 149.9, 142.2, 141.8, 141.2, 140.7, 140.5, 140.2, 140.1, 139.7, 138.41, 138.37, 138.1, 137.3, 130.7, 128.8, 128.1, 127.8, 126.8, 124.5, 123.1, 120.7, 120.4, 118.5, 116.8, 116.7, 112.3, 111.2, 51.3, 51.2 ppm; HRMS (FAB–MS, positive): calcd for C₃₂H₂₂O₅⁺ [M]* 486.1462; found: 486.1470.



2,3-Bis(5-isopropyl-3-methoxycarbonylazulen-1-yl)benzofuran (4b): To a degassed solution of **1b** (265 mg, 0.748 mmol), 2-ethynylphenol (57 mg, 0.48 mmol), and Cul (13 mg, 0.068 mmol) in THF (5 mL) and triethylamine (5 mL) was added tetrakis(triphenylphosphine)palladium(0) (26 mg, 0.022 mmol). The resulting mixture was stirred at 50 °C for 8 h under an Ar atmosphere. The reaction mixture was poured into a 10% NH₄Cl solution and extracted with toluene. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2 to give **4b** (65 mg, 30 %, purple oil) and **3c** (39 mg, 30 %, green crystals).

4b: mp 110 °C; IR (AT–IR): v_{max} = 2959 (w), 1693 (m), 1573 (w), 1524 (w), 1447 (m), 1386 (w), 1303 (w), 1259 (w), 1237 (w), 1208 (s), 1169 (w), 1125 (w), 1091 (w), 1012 (w), 964 (w), 929 (w), 898 (m), 800 (m), 776 (m), 749 (m), 738 (m) cm⁻¹; UV/Vis (CH₂Cl₂): λ_{max} (log ε) = 241 (4.79), 280 sh (4.87), 296 (4.92), 344 sh (4.50), 391 (4.36), 572 (3.23), 591 sh (3.22) nm; ¹H NMR (500 MHz, CDCl₃): δ_{H} = 9.81 (s, 1H, H₄ or H₄), 9.70 (d, 1H, *J* = 1.1 Hz, H₄ or H₄), 8.82 (d, 1H, *J* = 10.0 Hz, H₈ or H₈), 8.44 (s, 1H, H₂ or H₂), 8.16 (s, 1H, H₂ or H₂), 8.11 (d, 1H, *J* = 10.0 Hz, H₈ or H₈), 7.70-7.65 (m, 3H, H_{6,6} and H₄ of benzofuran), 7.43 (d, 1H, *J* = 7.4 Hz, H₇ of benzofuran), 7.37 (t, 1H, *J* = 7.6 Hz, H₆ of benzofuran), 7.29-7.24 (m, 2H, H₇ or H₇, H₅ of benzofuran), 7.12 (t, 1H, *J* = 10.0 Hz, H₇ or H₇), 3.94 (s, 3H, CO₂Me), 3.79 (s, 3H, CO₂Me), 3.26-3.16 (m, 2H, *i*-Pr), 1.43 (d, 6H, *J* = 6.9 Hz, *i*-Pr), 1.39 (d, 6H, *J* = 6.9 Hz, *i*-Pr) ppm; ¹³C NMR (125 MHz, CDCl₃): δ_{C} = 166.0, 165.7, 154.6, 150.1, 149.3, 142.2, 141.9, 141.3, 140.7, 140.6, 140.1, 139.1, 138.5, 138.2, 137.8, 136.8, 135.7, 130.8, 127.6, 126.6, 124.2, 123.0, 120.4, 119.6, 117.4, 115.6, 115.3, 111.9, 111.1, 51.13, 51.08, 39.2, 39.1, 24.8, 24.6 ppm, one signal is overlapped with the other; HRMS (FAB–MS, positive): calcd for C₃₈H₃₄O₅ ⁺ [M]⁺ 570.2406; found: 570.2391.



2,3-Bis(6-isopropyl-3-methoxycarbonylazulen-1-yl)benzofuran (4c): To a degassed solution of **1c** (510 mg, 1.44 mmol), 2-ethynylphenol (85 mg, 0.72 mmol), and Cul (14 mg, 0.074 mmol) in THF (5 mL) and triethylamine (5 mL) was added tetrakis(triphenylphosphine)palladium(0) (25 mg, 0.022 mmol). The resulting mixture was stirred at 50 °C for 1 h under an Ar atmosphere. The reaction mixture was poured into a 10% NH₄Cl solution and extracted with toluene. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with toluene/AcOEt (20 : 1) to give **4c** (108 mg, 27%, purple oil) and **3c** (31 mg, 13%, green crystals).

4c: mp 119–121 °C; IR (AT–IR): $v_{max} = 2962$ (w), 1694 (s), 1581 (m), 1505 (w), 1445 (s), 1420 (m), 1388 (w), 1362 (w), 1329 (w), 1310 (w), 1295 (w), 1267 (w), 1235 (w), 1204 (s), 1168 (w), 1131 (w), 1098 (w), 1071 (m), 1046 (m), 1020 (w), 959 (w), 920 (w), 879 (w), 846 (m), 790 (w), 773 (w), 747 (m), 731 (w), 714 (w), 694 (w), 676 (w), 664 (w), 652 (w) cm⁻¹; UV/Vis (CH₂Cl₂): λ_{max} (log ϵ) = 236 (4.71), 297 (4.92), 346 sh (4.51), 384 (4.25), 414 sh (4.20), 553 (3.18), 579 sh (3.15) nm; ¹H NMR (500 MHz, CDCl₃): $\delta_{H} = 9.62$ (d, 1H, J = 10.6 Hz, H₄ or H₄), 9.50 (d, 1H, J = 10.3 Hz, H₄ or H₄), 8.84 (d, 1H, J = 10.6 Hz, H₈ or H₈), 8.41 (s, 1H, H₂ or H₂), 8.10 (m, 2H, H₈ or H₈ and H₂ or H₂), 7.67 (d, 1H, J = 7.6 Hz, H₄° of benzofuran), 7.49-7.43 (m, 3H, H_{7,7}° and H₆° of benzofuran), 7.37 (t, 1H, J = 7.6 Hz, H₅° of benzofuran), 7.27 (d, 1H, J = 7.6 Hz, H₇° of benzofuran), 7.21 (d, 1H, J = 10.6 Hz, H₅ or H₅), 3.95 (s, 3H, CO₂Me), 3.79 (s, 3H, CO₂Me), 3.08-3.02 (m, 2H, *i*-Pr), 1.32 (d, 6H, J = 6.9 Hz, *i*-Pr), 1.29 (d, 6H, J = 6.9 Hz, *i*-Pr) ppm; ¹³C NMR (125 MHz, CDCl₃): $\delta_{C} = 165.9$, 165.5, 162.9, 162.2, 154.5, 150.2, 140.9, 140.5, 140.0, 139.5, 139.3, 138.8, 138.1, 137.9, 137.6, 137.0, 130.8, 127.9, 127.2, 126.1, 124.2, 123.0, 120.5, 120.4, 118.2, 116.4, 116.3, 112.0, 111.1, 51.13, 51.08, 39.72, 39.66, 24.3, 24.2 ppm, one signal is overlapped with the other; HRMS (FAB–MS, positive): calcd for C₃₈H₃₄O₅⁺ [M]⁺ 570.2406; found: 570.2411.



2,3-Bis(5-isopropyl-3-methoxycarbonyl-2-methylazulen-1-yl)benzofuran (4d): To a degassed solution of 1d (825 mg, 2.24 mmol), 2-ethynylphenol (132 mg, 1.12 mmol), and Cul (21 mg, 0.11 mmol) THF (10)mL) triethylamine (10)mL) added in and was tetrakis(triphenylphosphine)palladium(0) (38 mg, 0.034 mmol). The resulting mixture was stirred at 50 °C for 12 h under an Ar atmosphere. The reaction mixture was poured into a 10% NH₄Cl solution and extracted with toluene. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with CH₂Cl₂ to give **4d** (221 mg, 33%, purple oil) and **3d** (185 mg, 23%, green crystals). **4d:** mp 158–159 °C; IR (AT–IR): v_{max} = 2959 (w), 1685 (m), 1586 (w), 1520 (w), 1442 (m), 1419 (m), 1379 (w), 1335 (w), 1262 (w), 1219 (s), 1193 (w), 1173 (w), 1119 (w), 1104 (w), 1076 (m), 1035 (w), 1010 (w), 977 (w), 957 (w), 909 (w), 842 (w), 803 (w), 781 (w), 748 (m), 733 (w), 680 (w), 668 (w) cm^{-1} ; UV/Vis (CH₂Cl₂): λ_{max} (log ϵ) = 242 (4.76), 296 (4.91), 310 sh (4.84), 385 (4.21), 544 (3.14), 578 sh (3.09) nm; ¹H NMR (500 MHz, CDCl₃): δ_{H} = 9.61 (m, 2H, H_{4.4}), 8.28 (d, 1H, J = 10.0 Hz, H₈) or $H_{8'}$), 8.09 (d, 1H, J = 10.0 Hz, H_8 or $H_{8'}$), 7.67 (d, 1H, J = 8.3 Hz, $H_{4''}$ of benzofuran), 7.60-7.57 (m, 2H, H_{6.6}), 7.39 (td, 1H, J = 8.3, 1.5 Hz, H₅" of benzofuran), 7.29-7.14 (m, 4H, H_{7.7}" and H_{6".7}" of benzofuran), 3.90 (s, 3H, CO₂Me), 3.89 (s, 3H, CO₂Me), 3.17 (m, 2H, *i*-Pr), 2.45 (s, 3H, Me), 2.38 (s, 3H, Me), 1.40 (d, 6H, J = 6.9 Hz, *i*-Pr), 1.38 (d, 6H, J = 6.9 Hz, *i*-Pr) ppm; ¹³C NMR (125 MHz, CDCl₃): δ_{C} = 166.9, 166.7, 155.3, 153.9, 153.1, 150.3, 150.1, 149.1, 142.6, 142.3, 141.3, 140.6, 137.3, 136.7, 136.6, 136.0, 133.8, 133.4, 130.7, 127.8, 126.7, 124.2, 122.8, 120.8, 120.2, 118.8, 114.5, 114.3, 114.0, 111.4, 50.9, 50.8, 39.4, 24.80, 24.76, 24.7, 16.6 ppm, one signal is overlapped with the other; HRMS (FAB-MS, positive): calcd for $C_{40}H_{38}O_5^+$ [M]⁺ 598.2714; found: 598.2742.



(3-Methoxycarbonylazulen-1-yl)(2-methoxycarbonylphenyl)acetylene (5a): To a degassed solution of 1a (174 mg, 0.558 mmol), methyl 2-ethynylbenzoate (139 mg, 0.868 mmol), and Cul (15 0.079 mg, mmol) in THF (5 mL) and triethylamine (5 mL) was added tetrakis(triphenylphosphine)palladium(0) (21 mg, 0.018 mmol). The resulting mixture was stirred at 50 °C for 15.5 h under an Ar atmosphere. The reaction mixture was poured into a 10% NH₄CI solution and extracted with AcOEt. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/AcOEt (10 :1) to give 5a (192 mg, 99%) as green crystals. mp 123-124 °C; IR (AT-IR): v_{max} = 2954 (w), 2184 (w), 1716 (m), 1687 (s), 1578 (w), 1481 (m), 1450 (m), 1439 (m), 1426 (w), 1382 (m), 1302 (w), 1271 (m), 1249 (s), 1196 (s), 1186 (s), 1165 (w), 1141 (w), 1116 (w), 1081 (s), 1036 (m), 977 (w), 883 (w), 828 (w), 805 (w), 785 (w), 770 (s), 746 (m), 698 (w) cm^{-1} ; UV/Vis (CH₂Cl₂): λ_{max} (log ϵ) = 237 (4.45), 255 sh (4.41), 308 (4.51), 349 sh (4.24), 398 (4.11), 415 sh (4.07), 525 sh (2.61), 567 (2.72), 613 sh (2.61), 687 sh (1.99) nm; ¹H NMR (500 MHz, CDCl₃): δ_H = 9.63 (d, 1H, J = 9.7 Hz, H₄), 9.04 (d, 1H, J = 9.7 Hz, H₈), 8.53 (s, 1H, H₂), 8.01 (d, 1H, J = 7.7 Hz, $H_{3'}$ of Ph), 7.87 (t, 1H, J = 9.7 Hz, H_6), 7.73 (d, 1H, J = 7.7 Hz, $H_{6'}$ of Ph), 7.61 (t, 2H, J = 9.7 Hz, $H_{6'}$) H_{5.7}), 7.52 (t, 1H, J = 7.7 Hz, H₅, of Ph), 7.37 (t, 1H, J = 7.7 Hz, H₄, of Ph), 4.01 (s, 3H, CO₂Me), 3.97 (s, 3H, CO₂Me) ppm; ¹³C NMR (125 MHz, CDCl₃): $\delta_{\rm C}$ = 166.7, 165.4, 145.6, 142.8, 141.4, 140.4, 138.7, 138.6, 133.9, 131.8, 131.2, 130.6, 129.3, 128.1, 127.5, 124.5, 116.6, 110.6, 93.2, 90.2, 52.3, 51.4 ppm; HRMS (FAB-MS, positive): calcd for $C_{22}H_{16}O_4^+$ [M]⁺ 344.1044; found: 344.1056.



(5-lsopropyl-3-methoxycarbonylazulen-1-yl)(2-methoxycarbonylphenyl)acetylene (5b): To a degassed solution of **1b** (360 mg, 1.02 mmol), methyl 2-ethynylbenzoate (238 mg, 1.49 mmol), and Cul (18 mg, 0.095 mmol) in THF (5 mL) and triethylamine (5 mL) was added tetrakis(triphenylphosphine)palladium(0) (34 mg, 0.029 mmol). The resulting mixture was stirred at 50 °C for 18 h under an Ar atmosphere. The reaction mixture was poured into a 10% NH₄Cl solution and extracted with toluene. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/AcOEt (10 :1) to give **5b** (380 mg, 96%) as green crystals. mp 107-108 °C; IR (AT-IR): v_{max} = 2964 (w), 2195 (w), 1724 (s), 1683 (s), 1595 (w), 1564 (w), 1524 (w), 1482 (s), 1454 (s), 1425 (s), 1373 (m), 1301 (w), 1272 (s), 1249 (s), 1227 (m), 1212 (s), 1169 (s), 1135 (m), 1126 (m), 1117 (m), 1082 (s), 1048 (s), 967 (w), 919 (w), 876 (m), 820 (w), 811 (m), 780 (m), 757 (s), 743 (w), 732 (w), 694 (m), 681 (w), 654 (w) cm⁻¹; UV/Vis (CH₂Cl₂): λ_{max} (log ϵ) = 242 (4.43), 261 (4.43), 310 (4.50), 343 (4.28), 359 sh (4.23), 401 (4.21), 420 sh (4.16), 528 sh (2.72), 569 (2.83), 618 sh (2.72), 689 sh (2.11) nm; ¹H NMR (500 MHz, CDCl₃): $\delta_{\rm H}$ = 9.74 (d, 1H, J = 1.4 Hz, H₄), 8.92 (d, 1H, J = 9.9 Hz, H₈), 8.50 (s, 1H, H₂), 8.01 (d, 1H, J = 7.7 Hz, H₃ of Ph), 7.83 (d, 1H, J = 9.9 Hz, H_6), 7.72 (d, 1H, J = 7.7 Hz, $H_{6'}$ of Ph), 7.58 (t, 1H, J = 9.9 Hz, H_7), 7.52 (t, 1H, J = 7.7 Hz, $H_{5'}$ of Ph), 7.36 (t, 1H, J = 7.7 Hz, H₄, of Ph), 4.00 (s, 3H, CO₂Me), 3.96 (s, 3H, CO₂Me), 3.25 (sept, 1H, J = 6.9 Hz, *i*-Pr), 1.44 (d, 6H, J = 6.9 Hz, *i*-Pr) ppm; ¹³C NMR (125 MHz, CDCl₃): $\delta_{\rm C}$ = 166.8, 165.6, 150.8, 145.6, 143.0, 141.5, 139.5, 138.4, 136.9, 133.8, 131.8, 131.1, 130.6, 128.0, 127.3, 124.7, 115.3, 109.3, 92.9, 90.5, 52.3, 51.3, 39.4, 24.7 ppm; HRMS (FAB-MS, positive): calcd for C₂₅H₂₂O₄⁺ [M]⁺ 386.1513; found: 386.1504.



(6-lsopropyl-3-methoxycarbonylazulen-1-yl)(2-methoxycarbonylphenyl)acetylene (5c): To a degassed solution of 1c (291 mg, 0.822 mmol), methyl 2-ethynylbenzoate (196 mg, 1.22 mmol), and Cul (16 mg, 0.084 mmol) in THF (5 mL) and triethylamine (5 mL) was added tetrakis(triphenylphosphine)palladium(0) (29 mg, 0.025 mmol). The resulting mixture was stirred at 50 °C for 19 h under an Ar atmosphere. The reaction mixture was poured into a 10% NH₄Cl solution and extracted with toluene. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with CH₂Cl₂ to give **5c** (316 mg, 99%) as purple oil. IR (AT-IR): v_{max} = 2959 (w), 2196 (w), 1727 (m), 1696 (s), 1579 (m), 1483 (m), 1443 (s), 1402 (w), 1377 (w), 1295 (m), 1272 (m), 1251 (s), 1200 (s), 1129 (m), 1081 (s), 1051 (s), 1027 (w), 963 (w), 910 (w), 879 (w), 848 (m), 756 (s), 728 (m), 698 (m), 674 (w) cm⁻¹; UV/Vis (CH₂Cl₂): λ_{max} (log ϵ) = 236 (4.44), 265 (4.36), 315 (4.55), 351 sh (4.29), 399 (4.11), 415 sh (4.08), 510 sh (2.67), 550 (2.79), 595 sh (2.68), 662 sh (2.05) nm; ¹H NMR (500 MHz, CDCl₃): δ_{H} = 9.53 (d, 1H, J = 10.3 Hz, H₄), 8.95 (d, 1H, J = 10.3 Hz, H₈), 8.43 (s, 1H, H₂), 8.00 (d, 1H, J = 8.0 Hz, H₃, of Ph), 7.71 (d, 1H, J = 8.0 Hz, H₆ of Ph), 7.55-7.49 (m, 3H, H_{5.7} and H_{5'} of Ph), 7.35 (t, 1H, J = 8.0 Hz, H_{4'} of Ph), 4.01 (s, 3H, CO₂Me), 3.95 (s, 3H, CO₂Me), 3.16 (sept, 1H, J = 6.9 Hz, *i*-Pr), 1.39 (d, 6H, J = 6.9 Hz, *i*-Pr) ppm; ¹³C NMR (125 MHz, CDCl₃): $\delta_{\rm C}$ = 166.8, 165.4, 163.3, 144.3, 141.7, 140.2, 138.22, 138.16, 133.8, 131.8, 131.1, 130.6, 128.6, 127.5, 127.3, 124.7, 116.2, 110.1, 92.8, 90.5, 52.2, 51.3, 39.9, 24.3 ppm; HRMS (FAB-MS, positive): calcd for C₂₅H₂₂O₄⁺ [M]⁺ 386.1518; found: 386.1522.



Reaction of 1-iodoazulene with methyl 2-ethynylbenzoate: To a degassed solution of **1d** (513 mg, 1.39 mmol), methyl 2-ethynylbenzoate (340 mg, 2.12 mmol), and Cul (30 mg, 0.16 mmol) in THF (8 mL) and triethylamine (8 mL) was added tetrakis(triphenylphosphine)palladium(0) (48 mg, 0.042 mmol). The resulting mixture was stirred at 50 °C for 18.5 h under an Ar atmosphere. The reaction mixture was poured into a 10% NH₄Cl solution and extracted with toluene. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/AcOEt (8 : 1) to give **5d** (323 mg, 58%, green crystals) and **6** (57 mg, 17%, purple crystals).

(5-IsopropyI-3-methoxycarbonyI-2-methylazulen-1-yI)(2-methoxycarbonyIphenyI)acetylene (5d): mp 135–136 °C; IR (AT–IR): v_{max} = 3081 (w), 3034 (w), 2959 (w), 2869 (w), 2185 (w), 1723 (s), 1683 (s), 1593 (w), 1562 (w), 1479 (m), 1440 (s), 1425 (m), 1420 (m), 1384 (w), 1380 (w), 1304 (w), 1288 (w), 1277 (m), 1249 (s), 1226 (m), 1216 (s), 1194 (m), 1175 (w), 1168 (m), 1138 (m), 1103 (w), 1079 (s), 1028 (w), 1002 (w), 968 (w), 882 (w), 833 (w), 827 (w), 799 (m), 782 (m), 761 (s), 709 (w), 698 (w) cm⁻¹; UV/Vis (CH₂Cl₂): λ_{max} (log ε) = 241 (4.44), 258 (4.43), 318 (4.57), 359 sh (4.30), 404 (4.18), 421 (4.16), 515 sh (2.67), 555 (2.77), 600 sh (2.66), 670 sh (2.03) nm; ¹H NMR (500 MHz, CDCl₃): $\delta_{\rm H}$ = 9.63 (s, 1H, H₄), 8.76 (d, 1H, *J* = 9.7 Hz, H₈), 8.01 (d, 1H, *J* = 7.7 Hz, H₃^o of Ph), 7.75-7.71 (m, 2H, H₆ and H_{5'} of Ph), 7.54-7.50 (m, 2H, H₇ and H_{6'} of Ph), 7.36 (t, 1H, *J* = 7.7 Hz, H_{4'} of Ph), 4.00 (s, 6H, CO₂Me), 3.22 (sept, 1H, *J* = 6.9 Hz, *i*-Pr), 3.00 (s, 3H, Me), 1.42 (d, 6H, *J* = 6.9 Hz, *i*-Pr) ppm; ¹³C NMR (125 MHz, CDCl₃): $\delta_{\rm C}$ = 166.9, 166.5, 156.3, 150.8, 144.4, 142.5, 137.6, 136.7, 134.7, 133.9, 131.8, 130.9, 130.6, 128.2, 127.2, 124.8, 114.2, 111.4, 95.8, 90.1, 52.3, 51.0, 39.5, 24.7, 17.1 ppm; HRMS (FAB–MS, positive): calcd for C₂₆H₂₄O₄⁺ [M]⁺ 400.1670; found: 400.1679.



5,5'-Diisopropyl-3,3'-dimethoxycarbonyl-2,2'-dimethyl-1,1'-biazulene (6): mp 179–180°C; IR (AT–IR): $v_{max} = 2962$ (w), 1670 (m), 1519 (w), 1506 (w), 1488 (w), 1446 (s), 1417 (m), 1388 (m), 1362 (w), 1335 (w), 1300 (w), 1220 (s), 1190 (m), 1122 (w), 1077 (m), 1033 (w), 1011 (w), 980 (w), 934 (w), 842 (w), 813 (w), 797 (w), 780 (w), 737 (w), 709 (w), 672 (w), 661 (w) cm⁻¹; ¹H NMR (500 MHz, CDCl₃): $\delta_{H} = 9.75$ (s, 2H, H₄), 7.63 (d, 2H, J = 10.0 Hz, H₈), 7.60 (d, 2H, J = 10.0 Hz, H₆), 7.18 (t, 2H, J = 9.9 Hz, H₇), 4.03 (s, 6H, CO₂Me), 3.24 (sept, 2H J = 6.9 Hz, *i*-Pr), 2.50 (s, 6H, Me), 1.45 (d, 12H, J = 6.9 Hz, *i*-Pr) ppm; ¹³C NMR (125 MHz, CDCl₃): $\delta_{C} = 167.1$, 154.2, 149.0, 142.2, 136.5, 136.1, 133.8, 126.7, 124.1, 113.7, 51.0, 39.5, 24.9, 16.7 ppm, one signal is overlapped with the other; HRMS (FAB–MS, positive): calcd for C₃₂H₃₄O₄⁺ [M]⁺ 482.2452; found: 482.2443.

Reaction of 1-ethynylazulene with methyl 2-iodobenzoate: To a degassed solution of **2d** (32 mg, 0.12 mmol), methyl 2-iodobenzoate (63 mg, 0.24 mmol), and Cul (3 mg, 0.02 mmol) in THF (2 mL) and triethylamine (2 mL) was added tetrakis(triphenylphosphine)palladium(0) (6 mg, 0.005 mmol). The resulting mixture was stirred at 50 °C for 19.5 h under an Ar atmosphere. The reaction mixture was poured into a 10% NH₄Cl solution and extracted with toluene. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with toluene to give **5d** (37 mg, 77%) as green crystals.



3-(3-Methoxycarbonylazulen-1-yl)isocoumarin (7a): To a solution of 5a (283 mg, 0.822 mmol) in THF (5 mL) was added CF₃CO₂H (1 mL). The resulting mixture was stirred at 50 °C for 23 h. The reaction mixture was poured into K₂CO₃ aq. and extracted with AcOEt. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with toluene/AcOEt (5 : 1) to give 7a (216 mg, 80%) as purple crystals. mp 206–207 °C; IR (AT–IR): v_{max} = 2958 (w), 1733 (s), 1703 (s), 1621 (s), 1562 (m), 1523 (w), 1483 (m), 1458 (s), 1440 (s), 1415 (m), 1333 (w), 1281 (w), 1219 (s), 1200 (s), 1159 (m), 1095 (m), 1056 (m), 1042 (m), 1015 (s), 975 (w), 915 (m), 874 (m), 827 (m), 775 (s), 746 (s), 685 (s) cm⁻¹; UV/Vis (CH₂Cl₂): λ_{max} (log ϵ) = 236 (4.45), 271 sh (4.38), 314 (4.52), 341 sh (4.29), 398 (4.12), 440 sh (3.65), 556 (2.76), 617 sh (2.53) nm; ¹H NMR (500 MHz, CDCl₃): δ_{H} = 9.73 (d, 1H, J = 10.0 Hz, H₄), 9.33 (d, 1H, J = 10.0 Hz, H₈), 8.72 (s, 1H, H₂), 8.33 (d, 1H, J = 8.0 Hz, H₈, of isocoumarin), 7.91 (t, 1H, J = 10.0 Hz, H₆), 7.73 (dd, 1H, J = 8.0, 1.0 Hz, H₆ of isocoumarin), 7.64 (t, 2H, J = 10.0 Hz, H_{5,7}), 7.51-7.47 (m, 2H, H_{5',7'} of isocoumarin), 6.93 (s, 1H, H_{4'} of isocoumarin), 3.98 (s, 3H, CO₂Me) ppm; ¹³C NMR (125 MHz, CDCl₃): δ_{C} = 165.4, 162.6, 152.7, 143.2, 140.8, 140.2, 139.7, 139.0, 138.5, 138.2, 135.0, 129.8, 129.5, 129.0, 127.7, 125.7, 119.9, 119.8, 116.7, 103.6, 51.5 ppm; HRMS (FAB-MS, positive): calcd for $C_{21}H_{14}O_4^+$ [M]⁺ 330.0892; found: 330.0899.



3-(5-IsopropyI-3-methoxycarbonylazulen-1-yl)isocoumarin (7b): To a solution of 5b (190 mg, 0.492 mmol) in THF (3 mL) was added CF₃CO₂H (0.5 mL). The resulting mixture was stirred at 50 °C for 22 h. The reaction mixture was poured into K₂CO₃ ag. and extracted with AcOEt. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/AcOEt (5 : 1) to give **7b** (125 mg, 68%) as purple crystals. mp 135–136 °C; IR (AT–IR): v_{max} = 2955 (w), 1733 (s), 1694 (s), 1614 (s), 1560 (m), 1523 (m), 1480 (m), 1439 (s), 1417 (m), 1400 (m), 1334 (m), 1283 (w), 1219 (s), 1167 (m), 1111 (m), 1077 (m), 1037 (m), 1011 (m), 980 (m), 957 (w), 903 (m), 877 (m), 812 (s), 778 (m), 749 (s), 722 (m), 702 (w), 682 (s) cm⁻¹; UV/Vis (CH₂Cl₂): λ_{max} (log ε) = 235 (4.43), 273 sh (4.37), 283 (4.43), 316 (4.52), 343 (4.32), 403 (4.22), 442 sh (3.80), 560 (2.88), 618 sh (2.67) nm; ¹H NMR (500 MHz, CDCl₃): $\delta_{\rm H}$ = 9.83 (d, 1H, J = 1.7 Hz, H₄), 9.22 (d, 1H, J = 10.2 Hz, H₈), 8.69 (s, 1H, H₂), 8.31 (d, 1H, J = 7.7 Hz, H₈ of isocoumarin), 7.85 (d, 1H, J = 10.2 Hz, H₆), 7.71 (ddd, 1H, J = 7.7, 7.7, 1.1 Hz, H₆ of isocoumarin), 7.59 (t, 1H, J = 10.2 Hz, H₇), 7.49-7.45 (m, 2H, $H_{5'7'}$ of isocoumarin), 6.90 (s, 1H, $H_{4'}$ of isocoumarin), 3.98 (s, 3H, CO₂Me), 3.25 (sept, 1H, J = 6.9 Hz, *i*-Pr), 1.44 (d, 6H, J = 6.9 Hz, *i*-Pr) ppm; ¹³C NMR (125 MHz, CDCl₃): $\delta_{\rm C}$ = 165.5, 162.7, 153.0, 151.0, 143.3, 140.1, 139.8, 139.7, 138.8, 138.4, 136.8, 134.9, 129.7, 128.8, 127.5, 125.6, 119.8, 118.6, 115.5, 102.9, 51.3, 39.1, 24.7 ppm; HRMS (FAB-MS, positive): calcd for C₂₄H₂₀O₄⁺ [M]⁺ 372.1357; found: 372.1360.



3-(6-IsopropyI-3-methoxycarbonylazulen-1-yl)isocoumarin (7c): To a solution of 5c (174 mg, 0.450 mmol) in THF (3 mL) was added CF₃CO₂H (0.5 mL). The resulting mixture was stirred at 50 °C for 20 h. The reaction mixture was poured into K₂CO₃ aq. and extracted with AcOEt. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with toluene/AcOEt (20 : 1) to give **7c** (133 mg, 79%) as purple crystals. mp 187–189 °C; IR (AT–IR): v_{max} = 3043 (w), 2958 (w), 1733 (m), 1702 (s), 1622 (m), 1564 (w), 1525 (w), 1482 (w), 1458 (m), 1443 (m), 1420 (m), 1335 (w), 1313 (w), 1281 (w), 1219 (s), 1208 (m), 1165 (w), 1099 (w), 1048 (m), 1018 (m), 977 (w), 916 (w), 877 (w), 825 (w), 772 (w), 746 (m), 742 (m), 681 (w), 659 (w) cm⁻¹; UV/Vis (CH₂Cl₂): λ_{max} (log ϵ) = 234 (4.42), 274 sh (4.33), 285 (4.44), 318 (4.56), 342 sh (4.36), 402 (4.15), 440 sh (3.73), 539 (2.87), 595 sh (2.66) nm; ¹H NMR (500 MHz, CDCl₃): $\delta_{\rm H}$ = 9.62 (d, 1H, J = 10.6 Hz, H₄), 9.28 (d, 1H, J = 10.6 Hz, H₈), 8.61 (s, 1H, H₂), 8.32 (d, 1H, J = 7.6 Hz, H₈ of isocoumarin), 7.71 (t, 1H, J = 7.6 Hz, H_{6'} of isocoumarin), 7.57 (t, 2H, J = 10.6 Hz, H_{5.7}), 7.49-7.45 (m, 2H, H_{5',7'} of isocoumarin), 6.91 (s, 1H, H₄, of isocoumarin), 3.97 (s, 3H, CO₂Me), 3.18 (sept, 1H, J = 6.9 Hz, *i*-Pr), 1.40 (d, 6H, J = 6.9 Hz, *i*-Pr) ppm; ¹³C NMR (125 MHz, CDCl₃): $\delta_{\rm C} = 165.5$, 163.8, 162.7, 153.0, 141.9, 138.9, 138.7, 138.4, 138.2, 134.9, 129.7, 128.8, 128.4, 127.5, 125.6, 119.8, 119.4, 116.4, 103.0, 51.4, 39.8, 24.3 ppm, one signal is overlapped with the other; HRMS (FAB-MS, positive): calcd for C₂₄H₂₀O₄⁺ [M]⁺ 372.1357; found: 372.1360.



3-(5-IsopropyI-3-methoxycarbonyI-2-methylazulen-1-yl)isocoumarin (7d): To a solution of 5d (183 mg, 0.458 mmol) in THF (3 mL) was added CF₃CO₂H (0.5 mL). The resulting mixture was stirred at 50 °C for 19 h. The reaction mixture was poured into K₂CO₃ ag. and extracted with toluene. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with toluene/AcOEt (5 : 1) to give 7d (168 mg, 95%) as purple crystals. mp 119-120 °C; IR (AT-IR): v_{max} = 3078 (w), 2963 (w), 1734 (m), 1702 (s), 1621 (m), 1565 (m), 1526 (m), 1484 (m), 1460 (m), 1444 (m), 1421 (m), 1389 (w), 1335 (w), 1313 (w), 1283 (w), 1220 (s), 1209 (m), 1167 (m), 1101 (m), 1052 (m), 1019 (m), 978 (w), 918 (m), 877 (m), 812 (m), 771 (m), 747 (m), 685 (m) cm⁻¹; UV/Vis (CH_2CI_2) : λ_{max} (log ϵ) = 291 sh (4.53), 310 (4.59), 386 sh (4.03), 530 (2.72), 563 sh (2.66) nm; ¹H NMR (500 MHz, CDCl₃): δ_{H} = 9.70 (d, 1H, J = 1.1 Hz, H₄), 8.52 (d, 1H, J = 10.0 Hz, H₈), 8.36 (d, 1H, J = 7.7 Hz, H₈, of isocoumarin), 7.76-7.73 (m, 2H, H₆ and H₅, of isocoumarin), 7.54 (t, 1H, J = 7.7 Hz, $H_{7'}$ of isocoumarin), 7.51-7.45 (m, 2H, H_5 and $H_{6'}$ of isocoumarin), 6.61 (s, 1H, $H_{4'}$ of isocoumarin), 4.00 (s, 3H, CO₂Me), 3.23 (t, 1H, J = 6.9 Hz, *i*-Pr), 2.90 (s, 3H, Me), 1.42 (d, 6H, J = 6.9 Hz, *i*-Pr) ppm; ¹³C NMR (125 MHz, CDCl₃): δ_{C} = 166.7, 163.2, 152.9, 151.3, 150.6, 142.4, 141.1, 137.7, 137.1, 134.9, 133.6, 129.7, 128.4, 128.2, 125.7, 120.7, 120.4, 114.6, 108.3, 51.2, 39.4, 24.8, 16.7 ppm, one signal is overlapped with the other; HRMS (FAB-MS, positive): calcd for C₂₅H₂₂O₄⁺ [M]⁺ 386.1513; found: 386.1522.



3-(3-Methoxycarbonylazulen-1-yl)-4-iodoisocoumarin (8a): To a solution of 5a (327 mg, 0.950 mmol) in CH₂Cl₂ (20 mL) was added NIS (327 mg, 1.45 mmol). The resulting mixture was stirred at room temperature for 1.5 h. The reaction mixture was poured into Na₂SO₃ ag. and extracted with CH₂Cl₂. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with CH₂Cl₂ to give 8a (156 mg, 36%) as purple crystals. mp 202-203 °C; IR (AT-IR): v_{max} = 2946 (w), 1730 (s), 1694 (s), 1601 (m), 1536 (w), 1514 (w), 1456 (m), 1437 (w), 1415 (w), 1318 (w), 1267 (w), 1224 (w), 1206 (s), 1167 (m), 1093 (w), 1060 (m), 1045 (w), 1036 (m), 989 (w), 934 (w), 874 (w), 786 (w), 768 (m), 739 (w), 687 (m), 654 (w) cm⁻¹; UV/Vis (CH₂Cl₂): λ_{max} (log ϵ) = 236 (4.54), 292 (4.46), 305 (4.45), 376 (4.09), 497 sh (2.68), 533 (2.81), 571 sh (2.74), 631 sh (2.19) nm; ¹H NMR (500 MHz, CDCl₃): δ_{H} = 9.80 (d, 1H, J = 10.0 Hz, H₄), 8.72 (s, 1H, H₂), 8.59 (d, 1H, J = 10.0 Hz, H₈), 8.34 (d, 1H, J = 8.0 Hz, H₈, of isocoumarin), 7.99-7.90 (m, 2H, H₆ and H₅, of isocoumarin), 7.85 (ddd, 1H, J =8.0, 8.0, 1.0 Hz, H_{6'} of isocoumarin), 7.72 (t, 1H, J = 10.0 Hz, H₅), 7.63-7.59 (m, 2H, H₇ and H_{7'} of isocoumarin), 3.98 (s, 3H, CO₂Me) ppm; ¹³C NMR (125 MHz, CDCl₃): δ_{C} = 165.4, 162.0, 152.0, 142.9, 142.1, 141.3, 140.5, 139.2, 138.5, 138.0, 135.8, 131.5, 129.9, 129.8, 129.3, 128.6, 122.4, 120.4, 115.8, 79.6, 51.5 ppm; HRMS (FAB-MS, positive): calcd for C₂₁H₁₃IO₄⁺ [M]⁺ 455.9854; found: 455.9883.



3-(5-IsopropyI-3-methoxycarbonylazulen-1-yl)-4-iodoisocoumarin (8b): To a solution of 5b (238 mg, 0.616 mmol) in CH₂Cl₂ (10 mL) was added NIS (280 mg, 1.25 mmol). The resulting mixture was stirred at room temperature for 1.5 h. The reaction mixture was poured into Na₂SO₃ ag. and extracted with AcOEt. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with CH₂Cl₂ to give **8b** (141 mg, 46%) as purple crystals. mp 205-206 °C; IR (AT-IR): v_{max} = 2943 (w), 1727 (s), 1687 (s), 1599 (m), 1557 (w), 1527 (w), 1457 (m), 1439 (m), 1430 (m), 1375 (m), 1322 (w), 1288 (w), 1213 (s), 1183 (s), 1127 (w), 1097 (m), 1061 (m), 1021 (m), 992 (w), 939 (w), 916 (w), 874 (w), 807 (m), 787 (w), 777 (m), 759 (s), 687 (m), 683 (m), 661 (w) cm⁻¹; UV/Vis (CH_2CI_2) : λ_{max} (log ϵ) = 293 (4.51), 300 (4.51), 374 sh (4.05), 529 (2.79), 567 sh (2.71), 628 sh (2.13) nm; ¹H NMR (500 MHz, CDCl₃): δ_{H} = 9.90 (s, 1H, H₄), 8.70 (s, 1H, H₂), 8.50 (d, 1H, J = 10.0 Hz, H₈), 8.34 (d, 1H, J = 7.7 Hz, H₈, of isocoumarin), 7.91-7.83 (m, 3H, H₆, and H_{5'.6'} of isocoumarin), 7.61-7.55 (m, 2H, H₇ and H₇ of isocoumarin), 3.98 (s, 3H, CO₂Me), 3.29 (sept, 1H, J = 6.9 Hz, *i*-Pr), 1.46 (d, 6H, J = 6.9 Hz, *i*-Pr) ppm; ¹³C NMR (125 MHz, CDCl₃): $\delta_{\rm C} = 165.6$, 162.0, 152.3, 151.4, 143.1, 142.2, 141.2, 139.5, 139.0, 138.7, 136.4, 135.8, 131.5, 129.9, 129.2, 128.5, 121.2, 120.3, 114.6, 79.1, 51.3, 39.3, 24.8 ppm; HRMS (FAB-MS, positive): calcd for C₂₄H₁₉IO₄⁺ [M]⁺ 498.0323; found: 498.0324.



3-(6-IsopropyI-3-methoxycarbonylazulen-1-yl)-4-iodoisocoumarin (8c): To a solution of 5c (137 mg, 0.355 mmol) in CH₂Cl₂ (15 mL) was added NIS (126 mg, 0.560 mmol). The resulting mixture was stirred at room temperature for 1 h. The reaction mixture was poured into Na₂SO₃ aq. and extracted with CH₂Cl₂. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with CH₂Cl₂ to give 8c (100 mg, 57%) as purple crystals. mp 201-202 °C; IR (AT-IR): v_{max} = 2956 (w), 1718 (s), 1709 (s), 1688 (s), 1599 (s), 1588 (m), 1582 (m), 1557 (m), 1514 (w), 1470 (m), 1445 (m), 1419 (m), 1313 (w), 1285 (w), 1262 (w), 1203 (s), 1168 (m), 1150 (w), 1106 (w), 1079 (s), 1066 (m), 1050 (m), 1036 (m), 1020 (w), 988 (w), 930 (w), 874 (w), 866 (w), 855 (m), 771 (w), 760 (s), 727 (w), 687 (m), 661 (w) cm⁻¹; UV/Vis (CH₂Cl₂): λ_{max} (log ϵ) = 295 sh (4.54), 309 (4.58), 344 sh (4.25), 389 sh (3.99), 516 (2.82), 554 sh (2.71), 611 sh (2.08) nm; ¹H NMR (500 MHz, CDCl₃): δ_{H} = 9.69 (d, 1H, J = 10.6 Hz, H₄), 8.64 (s, 1H, H₂), 8.54 (d, 1H, J = 10.6 Hz, H₈), 8.33 (d, 1H, J = 8.0 Hz, H_{8'} of isocoumarin), 7.91 (d, 1H, J = 8.0 Hz, H_{6'} of isocoumarin), 7.84 (ddd, 1H, J =8.0, 8.0, 1.5 Hz, H_{5'} of isocoumarin), 7.65 (dd, 1H, J = 10.6, 1.4 Hz, H₅), 7.60 (t, 1H, J = 8.0 Hz, H_{7'} of isocoumarin), 7.54 (dd, 1H, J = 10.6, 1.4 Hz, H₇), 3.97 (s, 3H, CO₂Me), 3.20 (sept, 1H, J = 6.9 Hz, *i*-Pr), 1.40 (d, 6H, J = 6.9 Hz, *i*-Pr) ppm; ¹³C NMR (125 MHz, CDCl₃): $\delta_{\rm C}$ = 165.6, 163.5, 162.0, 152.3, 141.8, 140.8, 140.1, 138.9, 138.7, 137.7, 135.8, 131.5, 129.9, 129.2, 129.1, 128.1, 122.0, 120.3, 115.5, 79.1, 51.4, 40.0, 24.4 ppm; HRMS (FAB-MS, positive): calcd for C₂₄H₁₉IO₄⁺ [M]⁺ 498.0323; found: 498.0323.



3-(5-IsopropyI-3-methoxycarbonyI-2-methylazulen-1-yl)-4-iodoisocoumarin (8d): To a solution of 5d (26 mg, 0.065 mmol) in CH₂Cl₂ (10 mL) was added NIS (25 mg, 0.11 mmol). The resulting mixture was stirred at room temperature for 2.5 h. The reaction mixture was poured into Na₂SO₃ ag. and extracted with CH₂Cl₂. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with CH₂Cl₂ to give 8d (14 mg, 42 %) as purple crystals. mp 181-183 °C; IR (AT-IR): v_{max} = 2962 (w), 2920 (w), 2874 (w), 2849 (w), 1732 (s), 1683 (s), 1617 (m), 1563 (w), 1499 (w), 1438 (s), 1381 (m), 1321 (w), 1292 (w), 1271 (w), 1226 (m), 1176 (m), 1146 (s), 1115 (w), 1080 (m), 1058 (s), 1029 (m), 964 (m), 940 (w), 893 (w), 839 (w), 806 (m), 782 (m), 756 (s), 712 (w), 686 (m), 668 (m) cm⁻¹; UV/Vis (CH₂Cl₂): λ_{max} (log ϵ) = 239 (4.62), 298 sh (4.62), 307 (4.66), 344 sh (4.12), 378 (3.97), 521 (2.80), 555 sh (2.73), 613 sh (2.19) nm; ¹H NMR (500 MHz, CDCl₃): $\delta_{\rm H}$ = 9.78 (d, 1H, J = 1.1 Hz, H₄), 8.36 (d, 1H, J = 7.7 Hz, H₈, of isocoumarin), 8.10 (d, 1H, J = 10.0 Hz, H₈), 7.89-7.84 (m, 2H, $H_{5',6'}$ of isocoumarin), 7.77 (d, 1H, J = 10.0 Hz, H_6), 7.64 (dt, 1H, J = 7.7, 1.5 Hz, $H_{7'}$ of isocoumarin), 7.47 (t, 1H, J = 10.0 Hz, H₇), 4.01 (s, 3H, CO₂Me), 3.26 (sept, 1H, J = 6.9 Hz, *i*-Pr), 2.78 (s, 3H, Me), 1.44 (d, 6H, J = 6.9 Hz, *i*-Pr) ppm; ¹³C NMR (125 MHz, CDCl₃): $\delta_{\rm C} = 166.7$, 162.3, 153.4, 152.4, 150.9, 142.3, 140.4, 138.1, 137.6, 137.4, 135.8, 133.5, 131.2, 129.9, 129.5, 128.3, 123.7, 120.6, 113.9, 83.1, 51.1, 39.5, 24.8, 17.0 ppm; HRMS (FAB-MS, positive): calcd for $C_{25}H_{21}IO_4^+$ [M]⁺ 512.0480; found: 512.0483.

2. Copies of ¹H NMR, ¹³C NMR, COSY and HRMS of new compounds (Figures S1–S102).



Figure S1. ¹H NMR spectrum of methyl 1-trimethylsilylethynylazulene-3-carboxylate in CDCl₃ (500 MHz).



Figure S2. ¹³C NMR spectrum of methyl 1-trimethylsilylethynylazulene-3-carboxylate in $CDCI_3$ (125 MHz).



Figure S3. COSY spectrum of methyl 1-trimethylsilylethynylazulene-3-carboxylate in $CDCI_3$ (500 MHz).





Figure S5. ¹H NMR spectrum of methyl 6-isopropyl-1-trimethylsilylethynylazulene-3-carboxylate in CDCl₃ (500 MHz).



Figure S6. ¹³C NMR spectrum of methyl 6-isopropyl-1-trimethylsilylethynylazulene-3-carboxylate in CDCl₃ (125 MHz).



Figure S7. COSY spectrum of methyl 6-isopropyl-1-trimethylsilylethynylazulene-3-carboxylate in $CDCI_3$ (500 MHz).





Figure S10. ¹³C NMR spectrum of meth 5-isopropyl-2-methyl-1-trimethylsilylethynylazulene-3-carboxylate in CDCl₃ (125 MHz).



FigureS11.COSYspectrumofmethyl5-isopropyl-2-methyl-1-trimethylsilylethynylazulene-3-carboxylate in CDCl3 (500 MHz).methyl





Figure S14. ¹³C NMR spectrum of **2a** in CDCI₃ (125 MHz).



Figure S15. COSY spectrum of 2a in CDCl₃ (500 MHz).







Figure S18. ¹³C NMR spectrum of **2c** in CDCl₃ (125 MHz).








Figure S22. ¹³C NMR spectrum of 2d in CDCl₃ (125 MHz).



Figure S23. COSY spectrum of 2d in CDCl₃ (500 MHz).





Figure S26. ¹³C NMR spectrum of **3a** in CDCI₃ (125 MHz).



Figure S27. COSY spectrum of 3a in CDCl₃ (500 MHz).





Figure S30. ¹³C NMR spectrum of 3c in CDCI₃ (125 MHz).









Figure S34. ¹³C NMR spectrum of 3d in CDCl₃ (125 MHz).









Figure S38. ¹³C NMR spectrum of **4a** in CDCI₃ (125 MHz).



Figure S39. COSY spectrum of 4a in CDCl₃ (500 MHz).





Figure S42. ¹³C NMR spectrum of 4b in CDCl₃ (125 MHz).







Figure S44. HRMS (FAB-MS, positive) of 4b.



Figure S46. ¹³C NMR spectrum of 4c in CDCl₃ (125 MHz).



Figure S47. COSY spectrum of 4c in CDCl₃ (500 MHz).





Figure S50. ¹³C NMR spectrum of 4d in CDCl₃ (125 MHz).



Figure S51. COSY spectrum of 4d in CDCl₃ (500 MHz).





Figure S52. ¹³C NMR spectrum of 5a in CDCl₃ (125 MHz).









Figure S56. ¹³C NMR spectrum of **5b** in CDCl₃ (125 MHz).



Figure S57. COSY spectrum of 5b in CDCl₃ (500 MHz).





Figure S60. ¹³C NMR spectrum of 5c in CDCI₃ (125 MHz).









Figure S64. ¹³C NMR spectrum of 5d in CDCl₃ (125 MHz).



Figure S65. COSY spectrum of 5d in CDCl₃ (500 MHz).





Figure S68. ¹³C NMR spectrum of **6** in CDCI₃ (125 MHz).



Figure S69. COSY spectrum of 6 in CDCl₃ (500 MHz).





Figure S72. ¹³C NMR spectrum of **7a** in CDCI₃ (125 MHz).







gure 374. TRIVIS (FAB-IVIS, positive) of 7



Figure S76. ¹³C NMR spectrum of **7b** in CDCl₃ (125 MHz).



Figure S77. COSY spectrum of 7b in CDCl₃ (500 MHz).



Figure S78. HRMS (FAB-MS, positive) of 7b.



Figure S80. ¹³C NMR spectrum of **7c** in CDCl₃ (125 MHz).



Figure S81. COSY spectrum of 7c in CDCl₃ (500 MHz).





Figure S84. ¹³C NMR spectrum of 7d in CDCl₃ (125 MHz).



Figure S85. COSY spectrum of 7d in CDCI₃ (500 MHz).





Figure S88. ¹³C NMR spectrum of 8a in CDCI₃ (125 MHz).


Figure S89. COSY spectrum of 8a in CDCl₃ (500 MHz).





Figure S92. ¹³C NMR spectrum of **8b** in CDCl₃ (125 MHz).









Figure S96. ¹³C NMR spectrum of 8c in CDCI₃ (125 MHz).



Figure S97. COSY spectrum of 8c in CDCl₃ (500 MHz).





Figure S100. ¹³C NMR spectrum of 8d in CDCI₃ (125 MHz).



Figure S101. COSY spectrum of 8d in CDCI₃ (500 MHz).



3. ORTEP drawing of 3d, 8a and 8d (Figures S103-S105).



Figure S103. ORTEP drawing of 3d; ellipsoids are drawn at the 50% probability level.



Figure S104. ORTEP drawing of 8a; ellipsoids are drawn at the 50% probability level.



Figure S105. ORTEP drawing of 8d; ellipsoids are drawn at the 50% probability level.

4. Frontier Kohn–Sham orbitals of compounds 3a–3d (Figures S106–S109).

HOMO (-5.07 eV)

HOMO-1 (-6.27 eV)

HOMO-2 (-6.49 eV)

HOMO-3 (-6.92 eV)



LUMO (-2.22 eV)

LUMO+1 (-1.78 eV)



LUMO+2 (-0.74 eV)



LUMO+3 (+0.34 eV)



Figure S106. Frontier Kohn–Sham orbitals of 3a at the B3LYP/6-31G** level.

	Table S1. Cartesian coordinates of 3a; absolute energy is −996.236338 au.										
		Atom	Х	Y	Z			Atom	Х	Y	Z
1	0	O1	4.655879	1.069752	0.011796	20	С	C12	4.367384	3.685606	0.010456
2	0	O2	3.225193	2.818874	0.005525	21	Н	H12A	4.978535	3.517608	0.901004
3	0	O3	-2.23971	-0.71779	0.020559	22	Н	H12B	3.966654	4.699411	0.008438
4	С	C1	2.286439	0.679678	0.001596	23	Н	H12C	4.986215	3.517016	-0.87462
5	С	C2	0.979702	1.184637	-0.00065	24	С	C16	-1.38725	0.374373	-0.00762
6	Н	H2	0.739154	2.239329	0.002897	25	С	C17	-2.10631	1.541069	-0.03156
7	С	C3	0.039003	0.13778	-0.00499	26	Н	H17	-1.69244	2.538514	-0.05607
8	С	C4	0.765506	-1.09194	-0.00611	27	С	C18	-3.4954	1.180893	-0.01758
9	С	C5	0.2218	-2.37924	-0.0138	28	С	C19	-4.71755	1.872708	-0.02811
10	Н	H5	-0.86131	-2.42377	-0.01864	29	Н	H19	-4.74127	2.957974	-0.05195
11	С	C6	0.872005	-3.61392	-0.01582	30	С	C20	-5.89813	1.135494	-0.00629
12	Н	H6	0.217273	-4.48181	-0.02304	31	Н	H20	-6.85201	1.65435	-0.01415
13	С	C7	2.242656	-3.89218	-0.00975	32	С	C21	-5.88412	-0.27086	0.026113
14	Н	H7	2.504563	-4.94853	-0.01208	33	Н	H21	-6.8233	-0.81505	0.042176
15	С	C8	3.318104	-3.00638	-0.00149	34	С	C22	-4.68269	-0.98131	0.037164
16	С	C9	3.301216	-1.60697	0.001717	35	Н	H22	-4.65368	-2.06534	0.061218
17	Н	H9	4.266674	-1.10954	0.006862	36	С	C23	-3.51879	-0.22661	0.014645
18	С	C10	2.20945	-0.74267	-0.00112	37	Н	H3	4.306011	-3.46015	0.00238
19	С	C11	3.508302	1.488731	0.006959						



Figure S107. Frontier Kohn–Sham orbitals of 3b at the B3LYP/6-31G** level.

	Table S2 . Cartesian coordinates of 3b ; absolute energy is −1114.1873373 au.											
		Atom	Х	Y	Z			Atom	Х	Y	Z	
1	0	O1	3.322418	2.740044	-0.06736	24	С	C13	4.817149	-1.72025	-0.05227	
2	0	02	1.440361	3.989523	-0.0538	25	Н	H13	5.258969	-0.71865	0.000186	
3	0	O3	-2.73185	-1.00913	0.007668	26	С	C14	5.320799	-2.37643	-1.3518	
4	С	C1	1.172888	1.668318	-0.04836	27	Н	H14A	6.413439	-2.44969	-1.34337	
5	С	C2	-0.22584	1.768033	-0.03593	28	Н	H14B	5.025384	-1.79526	-2.23057	
6	Н	H2	-0.76414	2.706475	-0.0266	29	Н	H14C	4.922372	-3.3903	-1.47	
7	С	C3	-0.81747	0.492172	-0.03449	30	С	C15	5.301079	-2.49634	1.186885	
8	С	C4	0.240222	-0.46892	-0.0492	31	Н	H15A	6.394408	-2.55743	1.194229	
9	С	C5	0.109175	-1.85734	-0.06607	32	Н	H15B	4.914802	-3.52165	1.20036	
10	Н	H5	-0.90814	-2.23126	-0.0671	33	Н	H15C	4.981144	-2.00706	2.111886	
11	С	C6	1.110837	-2.82949	-0.08347	34	С	C16	-2.24874	0.290044	-0.0196	
12	Н	H6	0.753855	-3.85659	-0.09961	35	С	C17	-3.28676	1.18505	-0.02438	
13	С	C7	2.499876	-2.68571	-0.0793	36	Н	H17	-3.19352	2.260762	-0.04591	
14	Н	H7	3.047389	-3.62628	-0.09164	37	С	C18	-4.5021	0.422368	0.002392	
15	С	C8	3.29556	-1.53304	-0.05989	38	С	C19	-5.87592	0.71323	0.012837	
16	С	C9	2.8188	-0.21159	-0.0546	39	Н	H19	-6.22622	1.740961	-0.00024	
17	Н	H9	3.577033	0.566718	-0.05008	40	С	C20	-6.77884	-0.34595	0.040652	
18	С	C10	1.517047	0.284994	-0.05382	41	Н	H20	-7.84483	-0.13869	0.048606	
19	С	C11	2.101489	2.800163	-0.05699	42	С	C21	-6.34122	-1.68266	0.058818	
20	С	C12	2.279245	5.151633	-0.06809	43	Н	H21	-7.07257	-2.48463	0.081501	
21	Н	H12A	2.928268	5.173994	0.811207	44	С	C22	-4.98121	-1.99735	0.048658	
22	Н	H12B	1.599861	6.004204	-0.06188	45	Н	H22	-4.62569	-3.02205	0.062171	
23	Н	H12C	2.905181	5.167786	-0.96416	46	С	C23	-4.09956	-0.92669	0.020875	



Figure S108. Frontier Kohn–Sham orbitals of 3c at the B3LYP/6-31G** level.

	Table S3 . Cartesian coordinates of 3c ; absolute energy is −1114.188295 au.											
		Atom	Х	Y	Z			Atom	Х	Y	Z	
1	0	01	3.14223	-3.38114	0.00277	24	С	C17	-3.25516	-1.09226	-0.05982	
2	0	02	1.135103	-4.41993	0.006055	25	Н	H17	-3.28834	-2.17016	-0.11929	
3	0	O3	-2.44951	1.019302	0.057756	26	С	C18	-4.37395	-0.1935	-0.03024	
4	С	C1	1.12278	-2.08316	-0.00033	27	С	C19	-5.7723	-0.32048	-0.05891	
5	С	C2	-0.27897	-2.02402	0.000968	28	Н	H19	-6.23962	-1.29886	-0.11535	
6	Н	H2	-0.9204	-2.89507	0.005826	29	С	C20	-6.54521	0.836494	-0.01435	
7	С	C3	-0.72111	-0.68936	-0.00099	30	Н	H20	-7.62801	0.756446	-0.03589	
8	С	C4	0.440711	0.14487	-0.00336	31	С	C21	-5.95441	2.111053	0.058396	
9	С	C5	0.470226	1.540344	-0.01107	32	Н	H21	-6.58719	2.992415	0.092667	
10	Н	H5	-0.50129	2.02149	-0.01299	33	С	C22	-4.56725	2.263484	0.087994	
11	С	C6	1.558262	2.414717	-0.01545	34	Н	H22	-4.09524	3.23837	0.144322	
12	Н	H6	1.282668	3.467174	-0.02144	35	С	C23	-3.81703	1.097684	0.041863	
13	С	C7	2.939569	2.161928	-0.01243	36	Н	H3	4.624846	0.887879	-0.00573	
14	С	C8	3.537706	0.893492	-0.00674	37	С	C13	3.86765	3.379893	-0.01672	
15	С	C9	2.962558	-0.3783	-0.00335	38	Н	H7	3.226544	4.270161	-0.01746	
16	Н	H9	3.654438	-1.21561	-0.00154	39	С	C14	4.731763	3.439799	-1.2902	
17	С	C10	1.618605	-0.74898	-0.00246	40	Н	H1	5.327268	4.358876	-1.30165	
18	С	C11	1.922352	-3.31024	0.002919	41	Н	H8	4.111362	3.424817	-2.19151	
19	С	C12	1.841296	-5.66735	0.008624	42	Н	H10	5.425809	2.59506	-1.34768	
20	Н	H12A	2.475919	-5.75655	-0.87729	43	С	C15	4.735041	3.446467	1.253957	
21	Н	H12B	1.072576	-6.44081	0.006636	44	Н	H4	5.327478	4.367401	1.259985	
22	Н	H12C	2.470361	-5.75542	0.898569	45	Н	H11	5.432454	2.604461	1.313145	
23	С	C16	-2.12005	-0.32582	-0.005	46	Н	H12	4.11697	3.432731	2.156797	



Figure S109. Frontier Kohn–Sham orbitals of 3d at the B3LYP/6-31G** level.

Table S4. Cartesian coordinates of 3d; absolute energy is -1153.233945 au.											
		Atom	Х	Y	Z			Atom	Х	Y	Z
1	0	04	3.578747	2.141427	0.299824	26	Н	H37C	-1.823	2.841509	0.539006
2	0	O5	1.940842	3.672895	0.115151	27	С	C38	-2.22053	0.248392	-0.10251
3	0	O6	-2.76221	-0.87995	0.50589	28	С	C39	-3.21168	0.997351	-0.67776
4	С	C25	1.301524	1.401961	0.115184	29	Н	H39	-3.0653	1.901449	-1.24925
5	С	C26	-0.09799	1.645749	0.102255	30	С	C40	-4.45677	0.325333	-0.42243
6	С	C27	-0.7796	0.409581	-0.02403	31	С	C41	-5.80784	0.553223	-0.72829
7	С	C28	0.184481	-0.63547	-0.07955	32	Н	H41	-6.10976	1.431324	-1.2912
8	С	C29	-0.08278	-1.99627	-0.24104	33	С	C42	-6.75195	-0.37246	-0.29282
9	Н	H29	-1.13194	-2.26235	-0.31428	34	Н	H42	-7.80179	-0.21148	-0.51921
10	С	C30	0.813979	-3.0599	-0.30825	35	С	C43	-6.37623	-1.5151	0.43715
11	Н	H30	0.359667	-4.03918	-0.44032	36	Н	H43	-7.13902	-2.21563	0.762875
12	С	C31	2.209733	-3.05982	-0.22352	37	С	C44	-5.03985	-1.76459	0.750969
13	Н	H31	2.666839	-4.0454	-0.29216	38	Н	H44	-4.73217	-2.63916	1.313857
14	С	C32	3.105246	-1.9964	-0.07016	39	С	C45	-4.11536	-0.82875	0.307344
15	С	C33	2.758887	-0.63656	0.022062	40	С	C46	4.598869	-2.33281	-0.00094
16	Н	H33	3.583802	0.060343	0.12134	41	Н	H46	4.686713	-3.42265	-0.09188
17	С	C34	1.516213	-0.00763	0.018457	42	С	C47	5.385936	-1.70971	-1.16912
18	С	C35	2.383872	2.387755	0.19362	43	Н	H47A	5.358175	-0.61591	-1.13301
19	С	C36	2.96727	4.672943	0.169589	44	Н	H47B	4.978599	-2.02489	-2.13492
20	Н	H36A	3.666595	4.55534	-0.66195	45	Н	H47C	6.436316	-2.01656	-1.12632
21	Н	H36B	3.526245	4.607419	1.106406	46	С	C48	5.207884	-1.93342	1.356337
22	Н	H36C	2.447784	5.628948	0.099787	47	Н	H48A	4.676822	-2.41242	2.184934
23	С	C37	-0.77754	2.973295	0.256166	48	Н	H48B	5.162675	-0.85039	1.510368
24	Н	H37A	-0.74452	3.545914	-0.6786	49	Н	H48C	6.260053	-2.23355	1.407112
25	Н	H37B	-0.27431	3.585145	1.005858						