Supporting Information

SYNTHESIS AND ELECTROCHEMICAL PROPERTIES OF AZULENE-SUBSTITUTED TETRACYANOBUTADIENE AND DICYANOQUINODIMETHANE CHROMOPHORES CONNECTED WITH NAPHTHALENE CORES

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1-[(5-Isopropyl-3-methoxycarbonyl-1-azulenyl)ethynyl]naphthalene (3): To a degassed solution of **1** (610 mg, 2.40 mmol), 1-iodonaphthalene (504 mg, 2.00 mmol), and CuI (38 mg, 0.20 mmol) in triethylamine (15 mL) and THF (15 mL) was added tetrakis(triphenylphosphine)palladium (116 mg, 0.10 mmol). The resulting mixture was stirred at room temperature for 24 h under an Ar atmosphere. The reaction mixture was poured into a 10% NH_4Cl solution and extracted with CH_2Cl_2. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with *n*-hexane/CH_2Cl_2 (3:1) to give **3** (638 mg, 84%) as green crystals. Mp 47–49 °C (*n*-hexane); IR (AT−IR): ν_{max} = 2956 (m), 2196 (m), 1693 (s), 1583 (m), 1502 (m), 1463 (m), 1445 (s), 1411 (m), 1381 (w), 1269 (w), 1237 (w), 1210 (s), 1167 (m), 1123 (m), 1071 (w), 1052 (w), 955 (w), 921 (w), 876 (m), 838 (w), 797 (s), 772 (s), 665 (w), 649 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 280 (4.22), 294 sh (4.44), 302 (4.47), 316 (4.49), 343 (4.36), 364 sh (4.29), 403 (4.21), 425 sh (4.07), 573 (2.86), 624 sh (2.75) nm; ^1H NMR (500 MHz, $CDCl_3$): δ_H = 9.76 (s, 1H, J = 1.5 Hz, H_4), 8.78 (d, 1H, J = 10.0 Hz, H_8), 8.57 (s, 1H, H_2), 8.55 (d, 1H, J = 8.0 Hz, H_2 or H_4 of Naph.), 7.88 (d, 1H, J = 8.0 Hz, H_5 or H_8 of Naph.), 7.85−7.83 (m, 3H, H_6, H_2 or H_4 of Naph., and H_5 or H_8 of Naph.), 7.62 (dd, 1H, J = 8.0, 8.0 Hz, H_3 of Naph.), 7.57−7.53 (m, 2H, H_7 and H_6 or H_7 of Naph.), 7.49 (dd, 1H, J = 8.0, 8.0 Hz, H_6 or H_7 of Naph.), 3.98 (s, 3H, CO_2Me), 3.25 (sept, 1H, J = 7.0 Hz, *i*-Pr), 1.45 (d, 6H, J = 7.0 Hz, *i*-Pr) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 165.48, 150.66, 144.82, 142.91, 141.38, 139.40, 138.38, 136.31, 133.33, 133.15, 130.05, 128.39, 128.33, 127.63, 126.76, 126.43, 126.38, 125.42, 121.64, 115.18, 109.33, 91.83, 89.85, 51.25, 39.30, 24.68 ppm; HRMS (FAB−MS): calcd for $C_{27}H_{22}O_2^+$ $[M]^+$ 378.1620; found: 378.1637.

2-[(5-Isopropyl-3-methoxycarbonyl-1-azulenyl)ethynyl]naphthalene (4): To a degassed solution of **1** (504 mg, 2.00 mmol), 2-naphtyl trifluoromethanesulfonate (663 mg, 2.40 mmol), and CuI (38 mg, 0.20 mmol) in triethylamine (15 mL) and THF (15 mL) was added tetrakis(triphenylphosphine)palladium (116 mg, 0.10 mmol). The resulting mixture was stirred at room temperature for 24 h under an Ar atmosphere. The reaction mixture was poured into a 10% NH_4Cl solution and extracted with CH_2Cl_2. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with *n*-hexane/CH_2Cl_2 (3:1) to give **4** (536 mg, 71%) as green crystals. Mp 107–108 °C (CH_2Cl_2/MeOH); IR (AT−IR): ν_{max} = 2960 (m), 2196 (m), 1691 (s), 1497 (w), 1469 (m), 1443 (s), 1421 (m), 1408 (m), 1372 (m), 1219 (m), 1208 (s), 1198 (m), 1168 (s), 1141 (s), 1107 (w), 1075 (s), 1039 (m), 954 (s), 916 (m), 899 (m), 879 (w), 862 (m), 822 (s), 807 (m), 778 (m), 744 (s), 696 (w), 647 (w), 606 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 248 (4.62), 281 (4.57), 317 (4.60), 327 sh (4.51), 354 sh (4.29), 402 (4.19), 420 sh (4.09), 572 (2.84), 620 sh (2.74), 699 sh (2.11) nm; ^1H NMR (500 MHz, $CDCl_3$): δ_H = 9.75 (s, 1H, H_4), 8.71 (d, 1H, J = 10.0 Hz, H_8), 8.52 (s, 1H, H_2), 8.12 (s, 1H, H_1 of Naph.), 7.84−7.82 (m, 3H, H_3 or H_4 of Naph. and $H_{5,8}$ of Naph.), 7.80 (d, 1H, J = 10.0 Hz, H_6), 7.66 (d, 1H, J = 8.5 Hz, H_3 or H_4 of Naph.), 7.53−7.47 (m, 3H, H_7 and $H_{6,7}$ of Naph.), 3.97 (s, 3H, CO_2Me), 3.23 (sept, 1H, J = 7.0 Hz, *i*-Pr), 1.44 (d, 6H, J = 7.0 Hz, *i*-Pr) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C =165.38, 150.51, 144.78, 142.69, 141.22, 139.29, 138.23, 136.20, 133.08, 132.53, 130.77, 128.36, 127.95, 127.72, 127.63, 127.45, 126.48, 126.38, 121.17, 115.02, 109.06, 94.10, 85.22, 51.15, 39.20, 24.58 ppm; HRMS (FAB−MS): calcd for $C_{27}H_{22}O_2^+$ $[M]^+$ 378.1620; found: 378.1637.

1,5-Bis[(5-isopropyl-3-methoxycarbonyl-1-azulenyl)ethynyl]naphthalene (5): To a degassed solution of 1,5-diethynylnaphtalene (176 mg, 1.00 mmol), **2** (850 mg, 2.40 mmol), and CuI (38 mg, 0.20 mmol) in triethylamine (15 mL) and THF (15 mL) was added tetrakis(triphenylphosphine)palladium (116 mg, 0.10 mmol). The resulting mixture was stirred at room temperature for 12 h under an Ar atmosphere. The reaction mixture was poured into a 10% NH_4Cl solution and extracted with CH_2Cl_2. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2 to give **5** (516 mg, 82%) as green crystals. Mp 111–112 °C (CH_2Cl_2/MeOH); IR (AT−IR): ν_{max} = 2959 (m), 2193 (m), 1692 (s), 1582 (w), 1499 (w), 1447 (s), 1414 (s), 1373 (w), 1306 (w), 1210 (s), 1166 (s), 1121 (m), 1074 (m), 1049 (m), 874 (m), 786 (s), 776 (s), 693 (w), 648 (w), 637 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 242 (4.82), 279 sh (4.73), 296 (4.75), 307 sh (4.73), 382 sh (4.57), 408 (4.60), 427 (4.54), 571 (3.16), 623 sh (3.03), 696 sh (2.41) nm; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 9.78 (s, 2H, H_4), 8.79 (d, 2H, J = 10.0 Hz, H_8), 8.59 (s, 2H, H_2), 8.57 (d, 2H, J = 8.0 Hz, $H_{2,6}$ of Naph.), 7.90 (d, 2H, J = 8.0 Hz, $H_{4,8}$ of Naph.), 7.85 (d, 2H, J = 10.0 Hz, H_6), 7.63 (dd, 2H, J = 8.0, 8.0 Hz, $H_{3,7}$ of Naph.), 7.58 (dd, 2H, J = 10.0, 10.0 Hz, H_7), 3.99 (s, 6H, CO_2Me), 3.26 (sept, 2H, J = 7.0 Hz, *i*-Pr), 1.43 (d, 12H, J = 7.0 Hz, *i*-Pr) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 165.46, 150.76, 144.84, 142.93, 141.39, 139.42, 138.44, 136.31, 133.07, 130.56, 127.65, 126.69, 126.19, 122.11, 115.20, 109.11, 91.65, 90.20, 51.24, 39.30, 24.65 ppm; HRMS (FAB−MS): calcd for $C_{44}H_{36}O_4^+$ $[M]^+$ 628.2614; found: 628.2587.

1,7-Bis[(5-isopropyl-3-methoxycarbonyl-1-azulenyl)ethynyl]naphthalene (6): To a degassed solution of 1,7-diethynylnaphtalene (176 mg, 1.00 mmol), **2** (850 mg, 2.40 mmol), and CuI (38 mg, 0.20 mmol) in triethylamine (15 mL) and THF (15 mL) was added tetrakis(triphenylphosphine)palladium (116 mg, 0.10 mmol). The resulting mixture was stirred at room temperature for 24 h under an Ar atmosphere. The reaction mixture was poured into a 10% NH_4Cl solution and extracted with CH_2Cl_2. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2/*n*-hexane (4:1) to give **6** (535 mg, 85%) as green crystals. Mp 109–110 °C (CH_2Cl_2/MeOH); IR (AT−IR): ν_{max} = 2957 (m), 2193 (m), 1693 (s), 1582 (w), 1449 (s), 1420 (s), 1373 (m), 1306 (w), 1210 (s), 1166 (s), 1121 (m), 1074 (w), 1050 (m), 884 (m), 831 (s), 804 (m), 775 (s), 667 (w), 656 (w), 647 (w), 606 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 245 (4.82), 278 sh (4.76), 295 sh (4.81), 311 (4.84), 338 sh (4.56), 381 (4.48), 404 (4.49), 428 sh (4.39), 572 (3.14), 618 sh (3.04), 694 sh (2.45) nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 9.78 (s, 1H, H_4 or $H_{4'}$), 9.74 (s, 1H, H_4 or $H_{4'}$), 8.86 (d, 1H, J = 10.0 Hz, H_8 or $H_{8'}$), 8.80 (s, 1H, H_8 of Naph.), 8.72 (d, 1H, J = 10.0 Hz, H_8 or $H_{8'}$), 8.62 (s, 1H, H_2 or $H_{2'}$), 8.53 (s, 1H, H_2 or $H_{2'}$), 7.88−7.78 (m, 5H, H_6, $H_{6'}$, and $H_{2,4,5}$ of Naph.), 7.72 (dd, 1H, J = 7.0, 1.5 Hz, H_6 of Naph.), 7.54 (dd, 1H, J = 10.0, 10.0 Hz, H_7 or $H_{7'}$), 7.50 (dd, 1H, J = 8.0, 8.0 Hz, H_3 of Naph.), 7.43 (dd, 1H, J = 10.0, 10.0 Hz, H_7 or $H_{7'}$), 3.97 (s, 3H, CO_2Me), 3.96 (s, 3H, CO_2Me), 3.25 (sept, 1H, J = 7.0 Hz, *i*-Pr), 3.24 (sept, 1H, J = 7.0 Hz, *i*-Pr), 1.44 (d, 6H, J = 7.0 Hz, *i*-Pr), 1.43 (d, 6H, J = 7.0 Hz, *i*-Pr) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 165.57, 165.55, 150.83, 150.76, 145.11, 145.04, 142.94, 141.54, 141.48, 139.50, 139.39, 138.54, 138.44, 136.46, 136.41, 133.06, 132.58, 130.65, 129.57, 129.01, 128.57, 128.13, 127.85, 127.68, 126.06, 122.26, 121.51, 115.33, 115.27, 109.30, 109.20, 94.55, 91.68, 90.59, 86.08, 51.33, 51.31, 39.39, 24.75 ppm, Three signals are overlapped with other signals; HRMS (FAB−MS): calcd for $C_{44}H_{36}O_4^+$ $[M]^+$ 628.2614; found: 628.2641.

2,6-Bis[(5-isopropyl-3-methoxycarbonyl-1-azulenyl)ethynyl]naphthalene (7): To a degassed solution of 2,6-diethynylnaphtalene (176 mg, 1.00 mmol), **2** (850 mg, 2.40 mmol), and CuI (38 mg, 0.20 mmol) in triethylamine (15 mL) and THF (15 mL) was added tetrakis(triphenylphosphine)palladium (116 mg, 0.10 mmol). The resulting mixture was stirred at room temperature for 24 h under an Ar atmosphere. The reaction mixture was poured into a 10% NH_4Cl solution and extracted with CH_2Cl_2. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2 to give **7** (593 mg, 94%) as green crystals. Mp 257–258 °C (CH_2Cl_2/MeOH); IR (AT−IR): ν_{max} = 2957 (m), 2192 (m), 1685 (s), 1590 (m), 1445 (s), 1374 (m), 1303 (w), 1210 (s), 1195 (m), 1167 (m), 1129 (m), 1049 (s), 892 (m), 876 (m), 813 (m), 776 (s), 732 (w), 691 (w), 657 (m) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 248 (4.87), 279 sh (4.82), 296 (4.87), 310 sh (4.77), 357 (4.74), 383 (4.74), 412 (4.78), 434 (4.76), 571 (3.27), 624 sh (3.13), 695 sh (2.51) nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 9.75 (s, 2H, H_4), 8.73 (d, 2H, J = 10.0 Hz, H_8), 8.51 (s, 2H, H_2), 8.09 (s, 2H, $H_{1,5}$ of Naph.), 7.83 (d, 2H, J = 10.0 Hz, H_6), 7.82 (d, 2H, J = 8.0 Hz, $H_{3,7}$ of Naph.), 7.68 (dd, 2H, J = 8.0 Hz, $H_{4,8}$ of Naph.), 7.55 (dd, 2H, J = 10.0, 10.0 Hz, H_7), 3.97 (s, 6H, CO_2Me), 3.25 (sept, 2H, J = 7.0 Hz, *i*-Pr), 1.43 (d, 12H, J = 7.0 Hz, *i*-Pr) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 165.44, 150.70, 144.90, 142.81, 141.34, 139.39, 138.38, 136.27, 132.30, 130.60, 129.14, 127.75, 127.55, 121.81, 115.17, 109.00, 94.12, 86.01, 51.22, 39.28, 24.64 ppm; HRMS (FAB−MS): calcd for $C_{44}H_{36}O_4^+$ $[M]^+$ 628.2614; found: 628.2587.

2,7-Bis[(5-isopropyl-3-methoxycarbonyl-1-azulenyl)ethynyl]naphthalene (8): To a degassed solution of 2,7-diethynylnaphtalene (176 mg, 1.00 mmol), **2** (850 mg, 2.40 mmol), and CuI (38 mg, 0.20 mmol) in triethylamine (15 mL) and THF (15 mL) was added tetrakis(triphenylphosphine)palladium (116 mg, 0.10 mmol). The resulting mixture was stirred at room temperature for 24 h under an Ar atmosphere. The reaction mixture was poured into a 10% NH_4Cl solution and extracted with CH_2Cl_2. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2 to give **8** (627 mg, 99%) as green crystals. Mp 258–259 °C (CH_2Cl_2/MeOH); IR (AT−IR): ν_{max} = 2958 (m), 2195 (m), 1691 (s), 1612 (w), 1499 (m), 1444 (m), 1413 (s), 1374 (m), 1310 (m), 1216 (w), 1166 (s), 1131 (m), 1073 (m), 1048 (w), 955 (m), 901 (w), 841 (m), 802 (w), 774 (s), 643 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 251 (4.85), 278 (4.79), 316 (4.93), 336 (4.82), 348 (4.81), 402 (4.60), 420 sh (4.09), 571 (3.19), 620 sh (3.08), 691 sh (2.50) nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 9.74 (s, 2H, H_4), 8.70 (d, 2H, J = 10.0 Hz, H_8), 8.51 (s, 2H, H_2), 8.06 (s, 2H, $H_{1,8}$ of Naph.), 7.80 (d, 2H, J = 10.0 Hz, H_6), 7.79 (d, 2H, J = 8.5 Hz, $H_{4,5}$ of Naph.), 7.64 (dd, 2H, J = 8.5, 1.5 Hz, $H_{3,6}$ of Naph.), 7.52 (dd, 2H, J = 10.0, 10.0 Hz, H_7), 3.97 (s, 6H, CO_2Me), 3.23 (sept, 2H, J = 7.0 Hz, *i*-Pr), 1.43 (d, 12H, J = 7.0 Hz, *i*-Pr) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 165.38, 150.60, 144.83, 142.75, 141.27, 139.33, 138.28, 136.20, 132.87, 131.62, 130.38, 128.94, 127.84, 127.52, 121.99, 115.08, 108.92, 93.93, 85.75, 51.17, 39.22, 24.60 ppm; HRMS (FAB−MS): calcd for $C_{44}H_{36}O_4^+$ $[M]^+$ 628.2614; found: 628.2641.

1-[1,1,4,4-Tetracyano-2-(5-isopropyl-3-methoxycarbonyl-1-azulenyl)butadien-3-yl]naphthalene (9): To a solution of **3** (189 mg, 0.50 mmol) in AcOEt (5 mL) was added tetracyanoethylene (77 mg, 0.60 mmol). The resulting mixture was refluxed for 4 h under an Ar atmosphere. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2/AcOEt (100:1) to give **9** (255 mg, 99%). Mp 140–142 °C (CH_2Cl_2/*n*-hexane); IR (AT−IR): ν_{max} = 2963 (m), 2221 (m), 1698 (s), 1506 (s), 1440 (s), 1419 (s), 1364 (s), 1214 (s), 1179 (s), 1131 (w), 1091 (w), 1057 (w), 1024 (w), 900 (m), 802 (m), 774 (s), 730 (m), 663 (w), 631 (w), 612 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 266 (4.44), 300 (4.47), 336 sh (4.25), 389 (4.07), 466 (3.95), 550 sh (3.85) nm; ^1H NMR (500 MHz, $CDCl_3$): δ_H = 10.00 (s, 1H, H_4), 8.41 (d, 1H, J = 9.5 Hz, H_8), 8.35 (s, 1H, H_2), 8.15−8.13 (m, 2H, H_6 and H_2 or H_4 of Naph.), 8.02 (d, 1H, J = 8.0 Hz, H_5 or H_8 of Naph.), 7.99 (d, 1H, J = 8.0 Hz, H_5 or H_8 of Naph.), 7.94 (d, 1H, J = 9.5 Hz, H_7), 7.74−7.70 (m, 2H, H_2 or H_4 of Naph. and H_6 or H_7 of Naph.), 7.65 (ddd, 1H, J = 8.0, 1.0, 1.0 Hz, H_6 or H_7 of Naph.), 7.60 (dd, 1H, J = 7.5 Hz, H_3 of Naph.), 3.95 (s, 3H, CO_2Me), 3.35 (sept, 1H, J = 7.0 Hz, *i*-Pr), 1.47 (d, 6H, J = 7.0 Hz, *i*-Pr) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 169.09, 164.53, 160.94, 156.67, 145.90, 142.53, 142.48, 142.06, 140.94, 137.35, 135.00, 133.98, 132.18, 130.77, 130.47, 129.95, 129.77, 128.90, 127.77, 125.15, 124.27, 119.98, 119.41, 113.97, 112.50, 111.89, 111.08, 93.03, 82.89, 51.81, 39.61, 24.62 ppm; HRMS (FAB−MS): calcd for $C_{33}H_{22}N_4O_2^+$ $[M]^+$ 506.1743; found: 506.1729.

2-[1,1,4,4-Tetracyano-2-(5-isopropyl-3-methoxycarbonyl-1-azulenyl)butadien-3-yl]naphthalene (10): To a solution of **4** (189 mg, 0.50 mmol) in AcOEt (5 mL) was added tetracyanoethylene (77 mg, 0.60 mmol). The resulting mixture was refluxed for 4 h under an Ar atmosphere. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2 to give **10** (227 mg, 90%) as red crystals. Mp 199–201 °C (CH_2Cl_2/*n*-hexane); IR (AT−IR): ν_{max} = 2964 (m), 2216 (s), 1699 (s), 1546 (m), 1487 (s), 1439 (m), 1417 (s), 1357 (s), 1307 (m), 1252 (m), 1214 (s), 1182 (s), 1133 (w), 1111 (m), 1021 (m), 903 (m), 819 (s), 808 (m), 778 (m), 759 (s), 736 (m), 689 (w), 677 (w), 650 (w), 638 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 265 (4.63), 274 sh (4.62), 301 (4.51), 337 (4.45), 398 (4.23), 459 (4.15), 530 sh (3.98) nm; ^1H NMR (500 MHz, $CDCl_3$): δ_H = 10.03 (d, 1H, J = 2.0 Hz, H_4), 8.52 (d, 1H, J = 10.0 Hz, H_8), 8.35 (d, 1H, J = 2.0 Hz, H_1 of Naph.), 8.34 (s, 1H, H_2), 8.17 (d, 1H, J = 10.0 Hz, H_6), 8.03 (d, 1H, J = 8.5 Hz, H_4 of Naph.), 7.99 (dd, 1H, J = 10.0, 10.0 Hz, H_7), 7.96 (d, 1H, J = 8.0 Hz, H_5 or H_8 of Naph.), 7.93 (d, 1H, J = 8.0 Hz, H_5 or H_8 of Naph.), 7.88 (dd, 1H, J = 8.0, 2.0 Hz, H_3 of Naph.), 7.71 (ddd, 1H, J = 8.0, 8.0, 1.0 Hz, H_6 or H_7 of Naph.), 7.63 (ddd, 1H, J = 8.0, 8.0, 1.0 Hz, H_6 or H_7 of Naph.), 3.93 (s, 3H, CO_2Me), 3.36 (sept, 1H, J = 7.0 Hz, *i*-Pr), 1.48 (d, 6H, J = 7.0 Hz, *i*-Pr) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 169.26, 164.51, 161.03, 157.16, 146.32, 142.70, 142.65, 142.13, 140.93, 137.71, 135.77, 132.72, 132.40, 132.37, 130.42, 130.27, 130.02, 129.61, 128.16, 124.46, 119.75, 119.63, 113.88, 112.64, 112.49, 111.60, 87.24, 80.86, 51.83, 39.64, 24.62 ppm, One signal is overlapped with other signals; HRMS (FAB−MS): calcd for $C_{33}H_{22}N_4O_2^+$ $[M]^+$ 506.1743; found: 506.1729.

1,5-Bis[1,1,4,4-tetracyano-2-(5-isopropyl-3-methoxycarbonyl-1-azulenyl)butadien-3-yl]naphthalene (11): To a solution of **5** (126 mg, 0.20 mmol) in AcOEt (10 mL) was added tetracyanoethylene (77 mg, 0.60 mmol). The resulting mixture was refluxed for 12 h under an Ar atmosphere. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2/AcOEt (50:1) to give **11** (161 mg, 91%) as red crystals. Mp 247–248 °C (CH_2Cl_2/*n*-hexane); IR (AT−IR): ν_{max} = 2965 (m), 2221 (m), 1703 (s), 1621 (w), 1506 (s), 1439 (s), 1420 (s), 1365 (m), 1293 (m), 1216 (s), 1180 (s), 1124 (w), 1089 (m), 1048 (w), 1008 (w), 898 (m), 817 (m), 799 (m), 781 (m), 740 (w), 657 (w), 648 (w), 620 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 266 sh (4.71), 299 (4.79), 340 sh (4.50), 394 (4.38), 460 (4.26), 557 sh (4.02) nm; ^1H NMR (500 MHz, $CDCl_3$): δ_H = 10.06 (d, 2H, J = 2.0 Hz, H_4), 8.42 (d, 2H, J = 10.0 Hz, H_8), 8.36 (d, 2H, J = 8.0 Hz, $H_{4,8}$ of Naph.), 8.30 (s, 2H, H_2), 8.18 (d, 2H, J = 10.0 Hz, H_6), 7.99 (dd, 2H, J = 10.0, 10.0 Hz, H_7), 7.85 (dd, 2H, J = 8.0, 7.5 Hz, $H_{3,7}$ of Naph.), 7.80 (d, 2H, J = 7.5 Hz, $H_{2,6}$ of Naph.), 3.97 (s, 6H, CO_2Me), 3.37 (sept, 2H, J = 7.0 Hz, *i*-Pr), 1.49 (d, 12H, J = 7.0 Hz, *i*-Pr) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 167.67, 164.44, 160.57, 157.15, 146.14, 142.88, 142.09, 142.04, 141.21, 137.53, 132.49, 132.00, 131.16, 130.49, 127.78, 119.76, 119.52, 113.63, 112.65, 111.31, 110.67, 94.42, 82.74, 51.88, 39.66, 24.62 ppm; HRMS (FAB−MS): calcd for $C_{56}H_{36}N_8O_4^+$ $[M]^+$ 884.2860; found: 884.2874.

1,7-Bis[1,1,4,4-tetracyano-2-(5-isopropyl-3-methoxycarbonyl-1-azulenyl)butadien-3-yl]naphthalene (12): To a solution of **6** (63 mg, 0.10 mmol) in AcOEt (5 mL) was added tetracyanoethylene (38 mg, 0.30 mmol). The resulting mixture was refluxed for 12 h under an Ar atmosphere. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2/AcOEt (100:1) to give **12** (80 mg, 90%) as red crystals. Mp 194–195 °C (CH_2Cl_2/*n*-hexane); IR (AT−IR): ν_{max} = 2963 (m), 2218 (m), 1702 (s), 1621 (w), 1495 (s), 1441 (s), 1419 (s), 1363 (s), 1299 (w), 1217 (s), 1181 (s), 1127 (m), 1055 (m), 898 (m), 811 (m), 779 (s), 749 (w), 670 (w), 647 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 265 (4.81), 297 (4.77), 344 sh (4.53), 396 (4.42), 457 sh (4.27), 548 sh (4.15) nm; ^1H NMR (500 MHz, $CDCl_3$): δ_H = 10.04 (s, 1H, H_4 or $H_{4'}$), 10.01 (s, 1H, H_4 or $H_{4'}$), 8.53 (d, 1H, *J* = 10.0 Hz, H_8 or $H_{8'}$), 8.48 (s, 1H, H_2 or $H_{2'}$), 8.42 (s, 1H, H_8 of Naph.), 8.37 (d, 1H, *J* = 10.0 Hz, H_8 or $H_{8'}$), 8.29 (s, 1H, H_2 or $H_{2'}$), 8.19–8.14 (m, 4H, H_6, $H_{6'}$, H_2 or H_4 of Naph., and H_5 of Naph.), 8.07 (d, 1H, *J* = 8.5 Hz, H_6 of Naph.), 8.00 (dd, 1H, *J* = 10.0, 10.0 Hz, H_7 or $H_{7'}$), 7.93 (d, 1H, *J* = 10.0, 10.0 Hz, H_7 or $H_{7'}$), 7.76 (t, 1H, *J* = 8.0 Hz, H_3 of Naph.), 7.69 (d, 1H, *J* = 8.0 Hz, H_2 or H_4 of Naph.), 3.92 (s, 3H, CO_2Me), 3.87 (s, 3H, CO_2Me), 3.36 (sept, 2H, *J* = 7.0 Hz, *i*-Pr), 1.48–1.46 (m, 12H, *i*-Pr) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 169.02, 167.87, 164.33, 164.30, 160.17, 159.61, 157.47, 157.12, 146.55, 146.00, 142.87, 142.83, 142.51, 142.18, 142.03, 141.89, 141.19, 141.15, 138.00, 137.76, 135.55, 134.10, 132.59, 132.52, 132.45, 132.34, 131.36, 131.06, 129.44, 128.72, 128.12, 126.76, 119.92, 119.75, 119.46, 119.28, 113.84, 113.46, 112.99, 112.86, 112.06, 111.35, 110.96, 110.07, 94.56, 90.17, 82.58, 80.95, 51.88, 51.70, 39.64, 24.58, 24.56 ppm, One signal is overlapped with other signals; HRMS (FAB−MS): calcd for $C_{56}H_{36}N_8O_4^+$ $[M]^+$ 884.2860; found: 884.2850.

2,6-Bis[1,1,4,4-tetracyano-2-(5-isopropyl-3-methoxycarbonyl-1-azulenyl)butadien-3-yl]naphthalene (13): To a solution of **7** (126 mg, 0.20 mmol) in AcOEt (10 mL) was added tetracyanoethylene (77 mg, 0.60 mmol). The resulting mixture was refluxed for 11 h under an Ar atmosphere. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2/AcOEt (50:1) to give **13** (166 mg, 94%) as red crystals. Mp 298–299 °C (CH_2Cl_2/*n*-hexane); IR (AT−IR): ν_{max} = 2963 (m), 2222 (m), 1708 (s), 1495 (s), 1430 (m), 1359 (m), 1290 (m), 1213 (s), 1181 (m), 1137 (w), 1098 (w), 1027 (w), 895 (m), 815 (m), 779 (m), 732 (w), 696 (w), 646 (w), 609 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 266 (4.87), 296 (4.79), 346 (4.66), 431 (4.59), 537 sh (4.24), 630 sh (3.51) nm; ^1H NMR (500 MHz, $CDCl_3$): δ_H = 10.05 (s, 2H, H_4), 8.48 (d, 2H, *J* = 10.0 Hz, H_8), 8.37 (s, 2H, $H_{1,5}$ of Naph.), 8.33 (s, 2H, H_2), 8.19 (d, 2H, *J* = 10.0 Hz, H_6), 8.14 (d, 2H, *J* = 8.0 Hz, $H_{3,7}$ of Naph.), 8.02 (dd, 2H, *J* = 10.0, 10.0 Hz, H_7), 7.82 (dd, 2H, *J* = 8.0, 1.5 Hz, $H_{4,8}$ of Naph.), 3.96 (s, 6H, CO_2Me), 3.37 (sept, 2H, *J* = 7.0 Hz, *i*-Pr), 1.48 (d, 12H, *J* = 7.0 Hz, *i*-Pr) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 168.42, 164.40, 159.95, 157.69, 146.54, 142.97, 142.47, 142.24, 141.20, 137.72, 134.57, 133.13, 132.67, 131.81, 131.31, 126.53, 119.98, 119.37, 113.66, 112.75, 111.91, 111.00, 89.94, 80.62, 51.91, 39.66, 24.58 ppm; HRMS (FAB−MS): calcd for $C_{56}H_{36}N_8O_4^+$ $[M]^+$ 884.2860; found: 884.2874.

2,7-Bis[1,1,4,4-tetracyano-2-(5-isopropyl-3-methoxycarbonyl-1-azulenyl)butadien-3-yl]naphthalene (14): To a solution of **8** (94 mg, 0.15 mmol) in AcOEt (5 mL) was added tetracyanoethylene (58 mg, 0.45 mmol). The resulting mixture was refluxed for 12 h under an Ar atmosphere. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2/AcOEt (50:1) to give **14** (119 mg, 89%) as red crystals. Mp 206–207 °C (CH_2Cl_2/*n*-hexane); IR (AT−IR): ν_{max} = 2962 (m), 2221 (m), 1704 (s), 1621 (w), 1499 (s), 1440 (s), 1418 (s), 1364 (s), 1287 (w), 1214 (s), 1179 (m), 1137 (w), 1094 (w), 1048 (w), 900 (m), 848 (w), 808 (w), 778 (s), 735 (w), 679 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 262 (4.76), 300 (4.79), 338 (4.67), 399 (4.44), 464 sh (4.26), 527 sh (4.19) nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 9.74 (s, 2H, H_4), 8.70 (d, 2H, J = 10.0 Hz, H_8), 8.51 (s, 2H, H_2), 8.06 (s, 2H, $H_{1,8}$ of Naph.), 7.80 (d, 2H, J = 10.0 Hz, H_6), 7.79 (d, 2H, J = 8.5 Hz, $H_{4,5}$ of Naph.), 7.64 (dd, 2H, J = 8.5, 1.5 Hz, $H_{3,6}$ of Naph.), 7.52 (dd, 2H, J = 10.0, 10.0 Hz, H_7), 3.97 (s, 6H, CO_2Me), 3.23 (sept, 2H, J = 7.0 Hz, *i*-Pr), 1.43 (d, 12H, J = 7.0 Hz, *i*-Pr) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 168.17, 164.34, 159.94, 157.57, 146.46, 142.90, 142.43, 142.19, 141.08, 137.64, 137.15, 132.71, 132.62, 132.18, 131.75, 130.29, 128.33, 119.94, 119.28, 113.64, 112.77, 111.87, 111.02, 89.62, 80.63, 51.86, 39.62, 24.55 ppm; HRMS (FAB−MS): calcd for $C_{56}H_{36}N_8O_4^+$ $[M]^+$ 884.2860; found: 884.2874.

{4-[3,3-Dicyano-1-(5-isopropyl-3-methoxycarbonylazulen-1-yl)-2-naphthalen-1-ylprop-2-en-1-ylidene]cyclohexa-2,5-dien-1-ylidene}malononitrile (15): To a solution of **3** (189 mg, 0.50 mmol) in AcOEt (5 mL) was added 7,7,8,8-tetracyanoquinodimethane (153 mg, 0.75 mmol). The resulting mixture was refluxed for 14 h under an Ar atmosphere. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2/AcOEt (50:1) to give **15** (248 mg, 85%) as deep greenish blue crystals. Mp 214−215 °C ($CHCl_3$/*n*-hexane); IR (AT−IR): ν_{max} = 2955 (w), 2215 (m), 1686 (m), 1601 (w), 1528 (w), 1505 (m), 1442 (s), 1417 (m), 1380 (m), 1340 (w), 1286 (w), 1253 (w), 1222 (s), 1196 (s), 1173 (m), 1134 (w), 1083 (m), 1053 (w), 1016 (w), 999 (w), 972 (w), 904 (w), 891 (w), 847 (m), 816 (w), 801 (m), 779 (m), 734 (w), 676 (w), 663 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 297 (4.56), 375 sh (4.29), 396 (4.31), 422 sh (4.29), 672 (4.30) nm; UV/Vis (90% *n*-hexane/CH_2Cl_2): λ_{max} (log ε) = 296 (4.56), 366 sh (4.30), 394 (4.34), 432 sh (4.25), 621 (4.26) nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 9.84 (s, 1H, H_4), 8.31 (s, 1H, H_2), 8.15 (d, 1H, *J* = 10.0 Hz, H_8), 8.04 (d, 1H, *J* = 10.0 Hz, H_6), 7.97−7.90 (m, 2H, $H_{2,5}$ of Naph.), 7.87 (d, 1H, *J* = 8.5 Hz, H_4 of Naph.), 7.69 (d, 1H, *J* = 8.0 Hz, H_8 of Naph.), 7.63 (t, 1H, *J* = 8.5 Hz, H_3 of Naph.), 7.59 (br s, 1H, H_7), 7.55 (t, 1H, *J* = 8.0 Hz, H_7 of Naph.), 7.50 (t, 1H, *J* = 8.0 Hz, H_6 of Naph.), 7.40 (s, 1H, H of DCNQ), 7.22 (s, 1H, H of DCNQ), 7.15 (br s, 1H, H of DCNQ), 6.95 (br s, 1H, H of DCNQ), 3.94 (s, 3H, CO_2Me), 3.27 (sept, 1H, *J* = 7.0 Hz, *i*-Pr), 1.42 (d, 6H, *J* = 7.0 Hz, *i*-Pr) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 172.00, 164.67, 154.48, 153.46, 146.52, 144.40, 143.67, 141.41, 140.07, 136.88, 136.05, 133.80, 133.74, 133.56, 130.73, 130.14, 129.70, 129.59, 128.45, 127.26, 126.16, 125.86, 124.98, 123.81, 118.50, 113.96, 91.67, 75.43, 51.56, 39.31, 24.46 ppm, Some signals were overlapped with other signals; HRMS (MALDI−TOF): calcd for $C_{39}H_{26}N_4O_2^+$ $[M]^+$ 582.2050; found: 582.2063.

{4-[3,3-Dicyano-1-(5-isopropyl-3-methoxycarbonylazulen-1-yl)-2-naphthalen-2-ylprop-2-en-1-ylidene]cyclohexa-2,5-dien-1-ylidene}malononitrile (16): To a solution of **4** (189 mg, 0.50 mmol) in AcOEt (5 mL) was added 7,7,8,8-tetracyanoquinodimethane (153 mg, 0.75 mmol). The resulting mixture was refluxed for 14 h under an Ar atmosphere. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2/AcOEt (50:1) to give **16** (239 mg, 82%) as deep greenish blue crystals. Mp 165−167 °C ($CHCl_3$/*n*-hexane); IR (AT−IR): ν_{max} = 2962 (w), 2208 (m), 1698 (m), 1601 (w), 1505 (m), 1441 (s), 1420 (s), 1399 (m), 1383 (m), 1357 (m), 1304 (w), 1281 (w), 1215 (s), 1192 (s), 1128 (m), 1085 (w), 1047 (w), 1004 (w), 963 (w), 899 (w), 841 (m), 817 (w), 776 (m), 753 (m), 729 (w), 677 (w), 667 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} ($\log \varepsilon$) = 240 (4.54), 281 (4.53), 297 (4.54), 327 sh (4.43), 355 sh (4.31), 397 (4.24), 642 (4.32) nm; UV/Vis (90% *n*-hexane/CH_2Cl_2): λ_{max} ($\log \varepsilon$) = 241 (4.54), 278 (4.52), 296 (4.54), 323 sh (4.44), 393 (4.25), 599 (4.30) nm; ^1H NMR (500 MHz, $CDCl_3$): δ_H = 9.90 (d, 1H, J = 1.5 Hz, H_4), 8.41 (d, 1H, J = 10.0 Hz, H_8), 8.31 (s, 1H, H_1 of Naph.), 8.28 (s, 1H, H_2), 8.01 (d, 1H, J = 10.0 Hz, H_6), 7.91−7.88 (m, 2H, $H_{4,5}$ of Naph.), 7.84 (d, 1H, J = 7.5 Hz, H_8 of Naph.), 7.77 (d, 1H, J = 8.5 Hz, H_3 of Naph.), 7.74 (dd, 1H, J = 10.0, 10.0 Hz, H_7), 7.61 (t, 1H, J = 7.5 Hz, H_7 of Naph.), 7.55 (t, 1H, J = 7.5 Hz, H_6 of Naph.), 7.25−7.14 (m, 4H, H of DCNQ), 3.95 (s, 3H, CO_2Me), 3.29 (sept, 1H, J = 7.0 Hz, *i*-Pr), 1.45 (s, 6H, J = 7.0 Hz, *i*-Pr) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 172.29, 164.59, 154.78, 153.75, 145.87, 144.79, 143.76, 143.53, 141.60, 140.12, 136.35, 136.26, 135.09, 134.02, 133.91, 132.46, 132.08, 131.57, 130.98, 129.71, 129.65, 129.50, 127.84, 127.69, 125.73, 125.33, 124.54, 124.25, 118.86, 114.14, 114.08, 113.29, 112.50, 87.08, 74.42, 51.52, 39.27, 24.40 ppm; HRMS (MALDI−TOF): calcd for $C_{39}H_{26}N_4O_2^+$ $[M]^+$ 582.2050; found: 582.2047.

2,2′-{2,6-Naphthalenebis{[1,1-dicyano-3-(5-isopropyl-3-methoxycarbonylazulen-1-yl)prop-1-en-2-yl-3-ylidene]cyclohexa-2,5-dien-1-ylidene}}dimalononitrile (17): To a solution of **7** (157 mg, 0.25 mmol) in AcOEt (5 mL) was added 7,7,8,8-tetracyanoquinodimethane (153 mg, 0.75 mmol). The resulting mixture was refluxed for 12 h under an Ar atmosphere. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2/AcOEt (50:1) to give **17** (192 mg, 74%) as deep greenish blue crystals. Mp 266−269 °C ($CHCl_3$/*n*-hexane); IR (AT−IR): ν_{max} = 2960 (w), 2208 (m), 1700 (m), 1599 (w), 1505 (m), 1441 (s), 1420 (s), 1399 (m), 1380 (m), 1353 (m), 1306 (w), 1286 (w), 1214 (s), 1191 (s), 1136 (w), 1087 (w), 1035 (w), 1006 (w), 973 (w), 897 (w), 843 (w), 813 (w), 777 (w), 741 (w), 730 (w), 682 (w), 665 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 243 (4.83), 283 sh (4.81), 294 (4.83), 360 (4.71), 435 sh (4.55), 650 (4.62) nm; UV/Vis (70% *n*-hexane/CH_2Cl_2): λ_{max} (log ε) = 243 (4.83), 281 sh (4.83), 294 (4.83), 353 (4.71), 428 sh (4.56), 615 (4.61) nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 9.87 (s, 2H, H_4), 8.28 (d, 2H, J = 10.0 Hz, H_8), 8.21 (s, 2H, $H_{1,5}$ of Naph.), 8.20 (s, 2H, H_2), 8.01 (d, 2H, J = 10.0 Hz, H_6), 7.94 (d, 2H, J =7.5 Hz, $H_{3,7}$ of Naph.), 7.74 (d, 2H, J = 7.5 Hz, $H_{4,8}$ of Naph.), 7.68 (dd, 2H, J = 10.0 Hz, H_7), 7.21 (d, 4H, J = 10.5 Hz, H of DCNQ), 7.10 (d, 4H, J = 10.5 Hz, H of DCNQ), 3.94 (s, 6H, CO_2Me), 3.29 (sept, 2H, J = 7.0 Hz, *i*-Pr), 1.44 (d, 12H, J = 7.0 Hz, *i*-Pr) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 171.53, 164.61, 155.22, 153.54, 144.83, 144.46, 143.85, 143.26, 141.89, 140.54, 136.19, 136.12, 135.43, 134.23, 134.13, 133.55, 131.23, 131.11, 130.57, 126.50, 126.27, 125.97, 123.99, 119.15, 113.98, 113.92, 112.90, 111.97, 89.13, 75.89, 51.75, 39.48, 24.57 ppm; HRMS (MALDI−TOF): calcd for $C_{68}H_{44}N_8O_4$ + H^+ $[M + H]^+$ 1037.3558; found: 1037.3563.

2,2′-{2,7-Naphthalenebis{[1,1-dicyano-3-(5-isopropyl-3-methoxycarbonylazulen-1-yl)prop-1-en-2-yl-3-ylidene]cyclohexa-2,5-diene-1-ylidene}}dimalononitrile (18): To a solution of **8** (157 mg, 0.25 mmol) in AcOEt (5 mL) was added 7,7,8,8-tetracyanoquinodimethane (153 mg, 0.75 mmol). The resulting mixture was refluxed for 12 h under an Ar atmosphere. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2/AcOEt (40:1) to give **18** (205 mg, 79%) as deep greenish blue crystals. Mp 251−253 °C ($CHCl_3$/*n*-hexane); IR (AT−IR): ν_{max} = 2961 (w), 2208 (m), 1699 (m), 1601 (w), 1523 (w), 1505 (m), 1441 (s), 1420 (s), 1398 (m), 1382 (m), 1304 (w), 1283 (w), 1214 (s), 1192 (s), 1138 (w), 1085 (w), 1046 (w), 973 (w), 902 (w), 840 (m), 806 (w), 777 (w), 743 (w), 731 (w), 678 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 242 (4.88), 296 (4.93), 315 sh (4.85), 336 sh (4.80), 363 sh (4.71), 420 sh (4.56), 644 (4.65) nm; UV/Vis (70% *n*-hexane/CH_2Cl_2): λ_{max} (log ε) = 242 (4.88), 297 (4.93), 315 sh (4.85), 336 sh (4.79), 363 sh (4.69), 420 sh (4.55), 618 (4.63) nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 9.87 (s, 2H, H_4), 8.29 (s, 2H, $H_{1,8}$ of Naph.), 8.26 (d, 2H, *J* = 10.0 Hz, H_8), 8.20 (s, 2H, H_2), 8.01 (d, 2H, *J* = 10.0 Hz, H_6), 7.88 (d, 2H, *J* = 8.5 Hz, $H_{3,6}$ of Naph.), 7.75 (d, 2H, *J* = 8.5 Hz, $H_{4,5}$ of Naph.), 7.67 (t, 2H, *J* = 10.0 Hz, H_7), 7.25−7.18 (d, 4H, *J* = 10.5 Hz, H of DCNQ), 7.11 (m, 4H, H of DCNQ), 3.94 (s, 6H, CO_2Me), 3.30 (sept, 2H, *J* = 7.0 Hz, *i*-Pr), 1.44 (d, 12H, *J* = 7.0 Hz, *i*-Pr) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 171.29, 164.64, 155.18, 153.56, 144.80, 144.48, 143.83, 143.21, 141.90, 140.49, 136.36, 136.20, 136.08, 134.24, 134.07, 133.54, 131.98, 131.79, 131.12, 129.88, 128.17, 126.29, 126.02, 123.88, 119.09, 113.97, 113.93, 112.91, 112.02, 88.79, 75.95, 51.77, 39.48, 24.58 ppm; HRMS (MALDI−TOF): calcd for $C_{68}H_{44}N_8O_4 + H^+$ $[M + H]^+$ 1037.3558; found: 1037.3549.

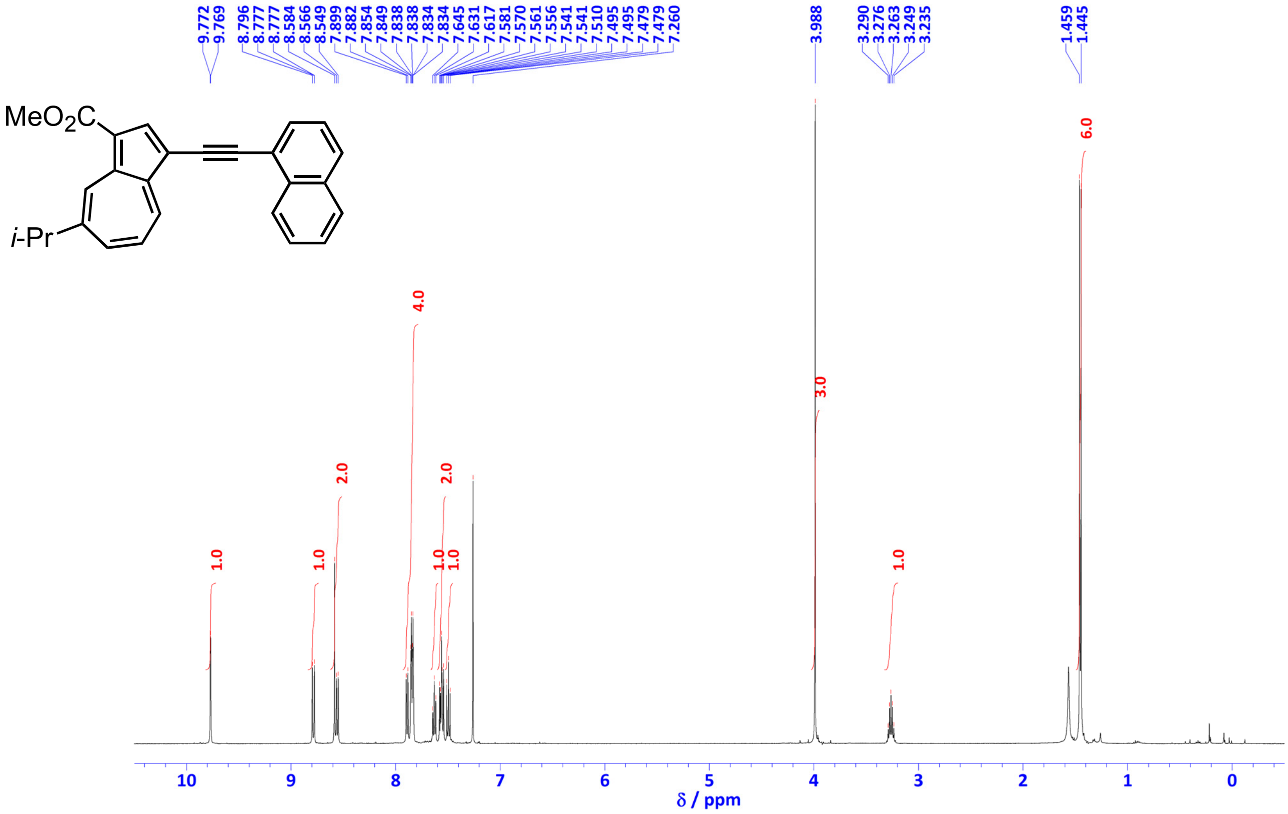


Figure S1. ^{1}H NMR spectrum of **3** in $CDCl_3$ (500 MHz).

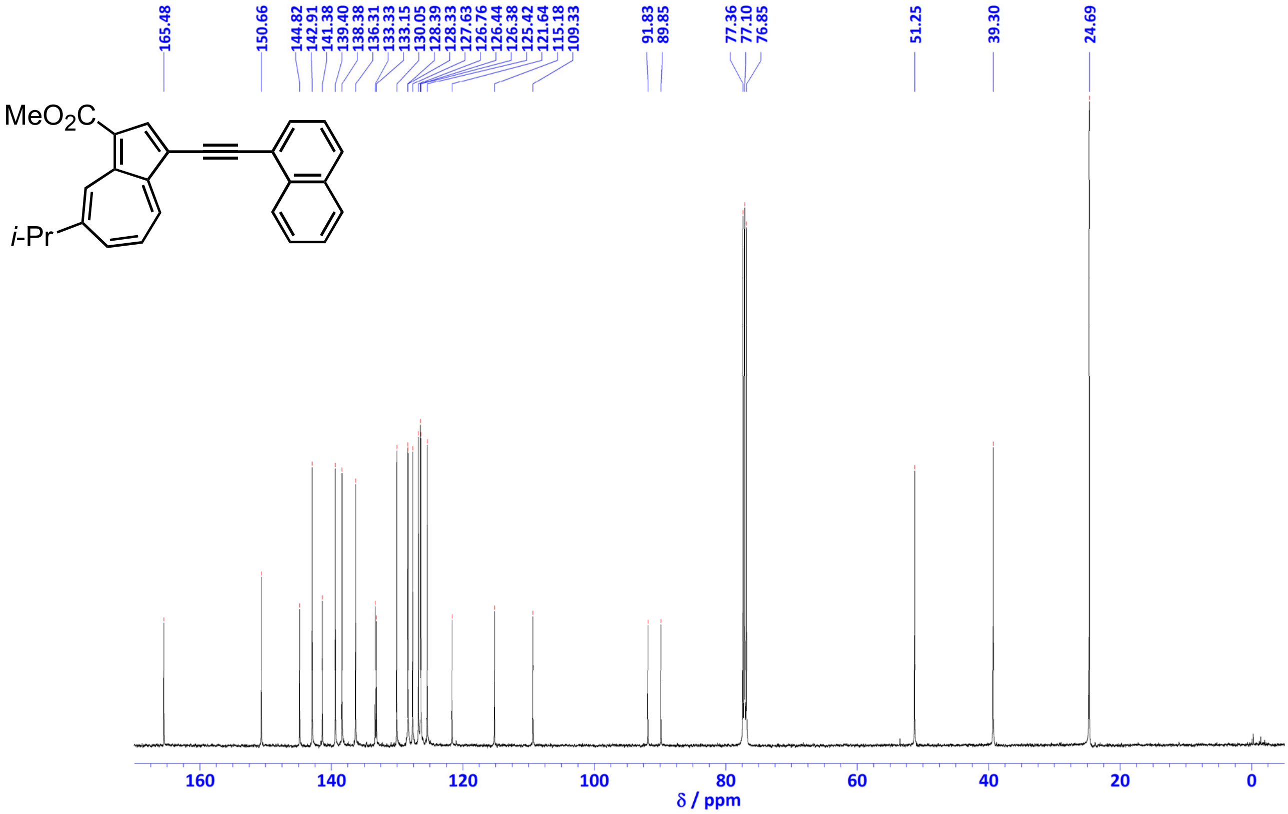


Figure S2. ^{13}C NMR spectrum of **3** in $CDCl_3$ (125 MHz).

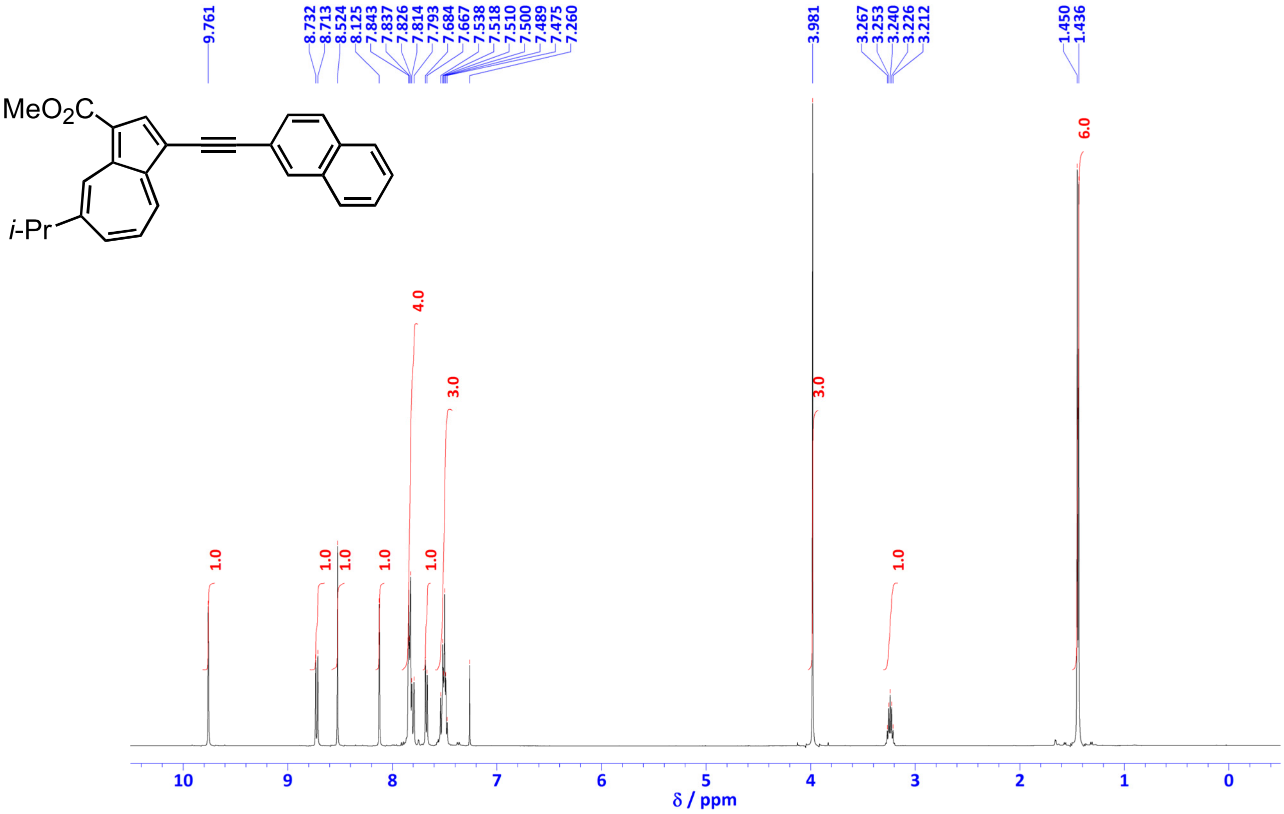


Figure S3. ^{1}H NMR spectrum of **4** in $CDCl_3$ (500 MHz).

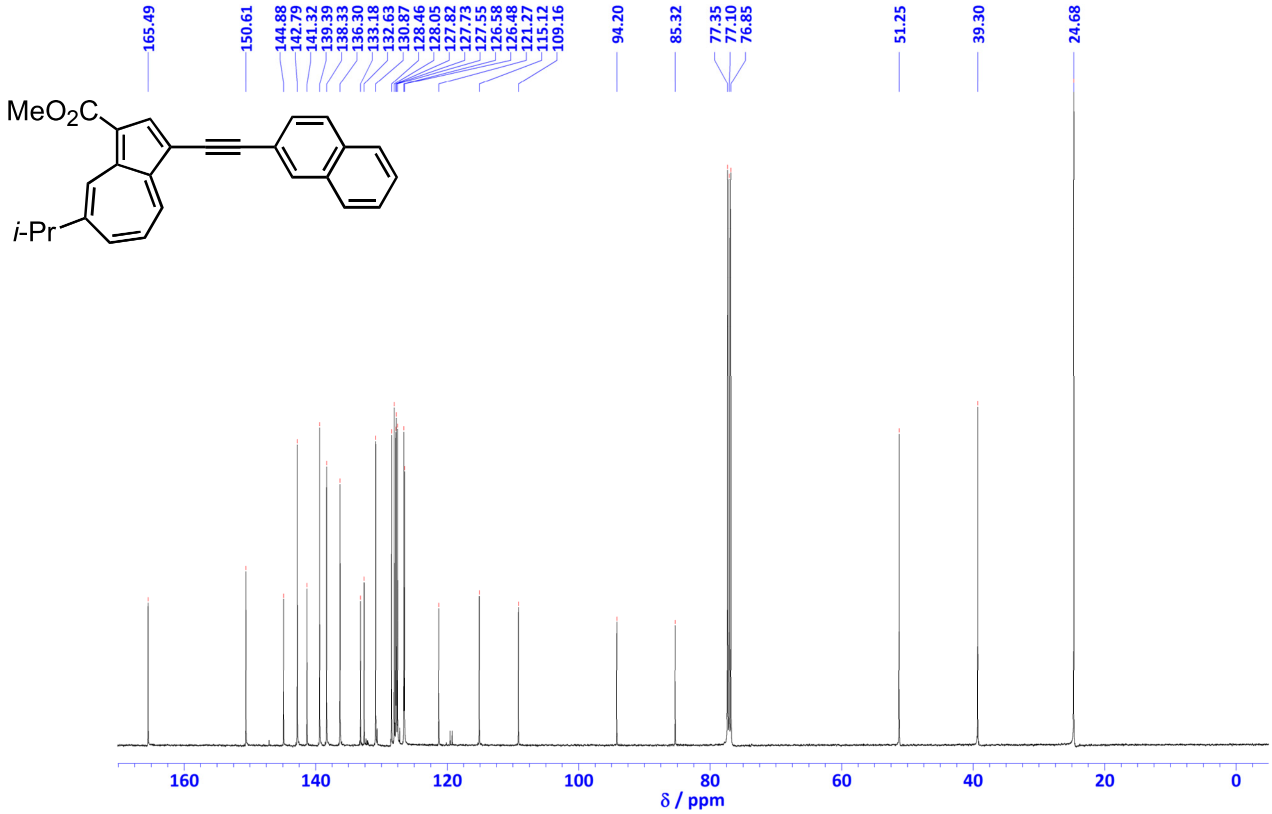


Figure S4. ^{13}C NMR spectrum of **4** in $CDCl_3$ (125 MHz).

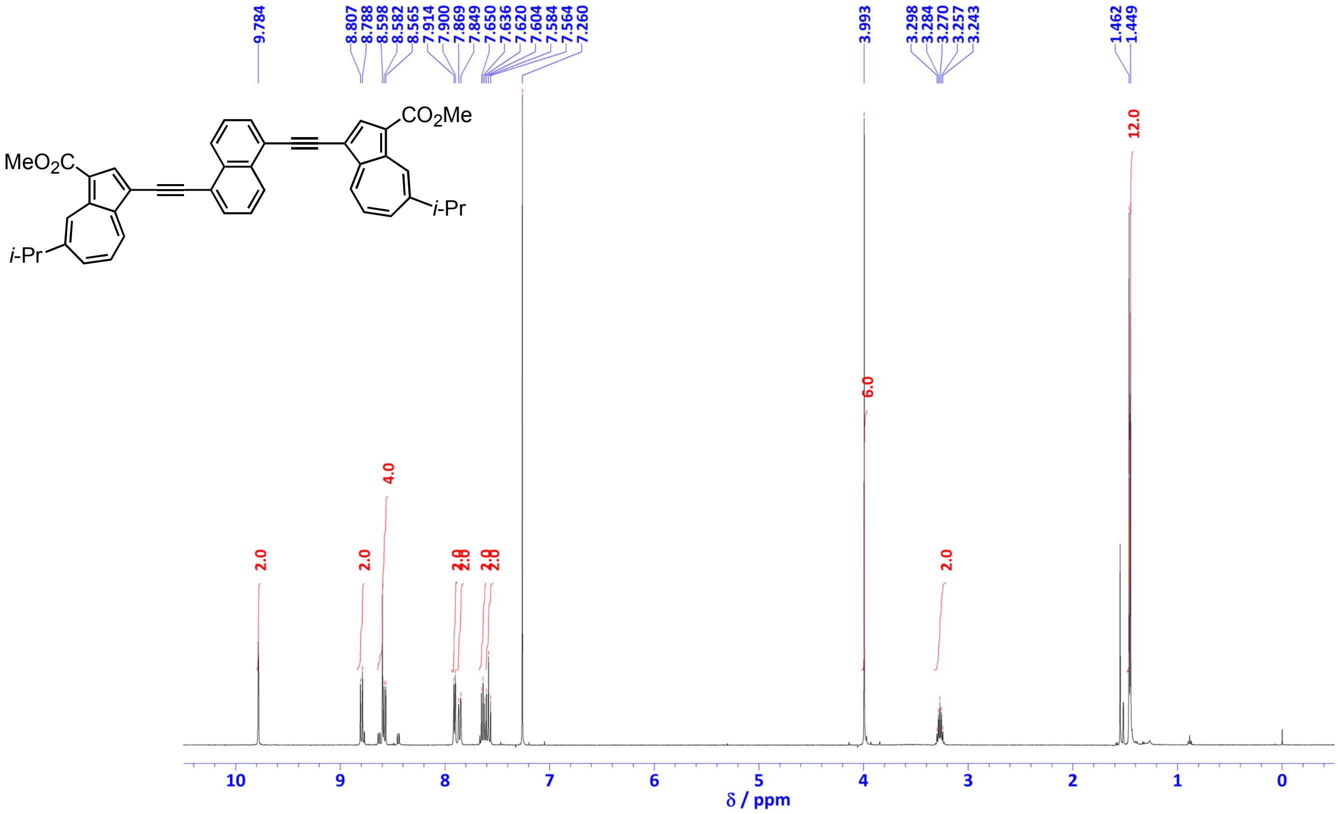


Figure S5. ^{1}H NMR spectrum of **5** in $CDCl_3$ (500 MHz).

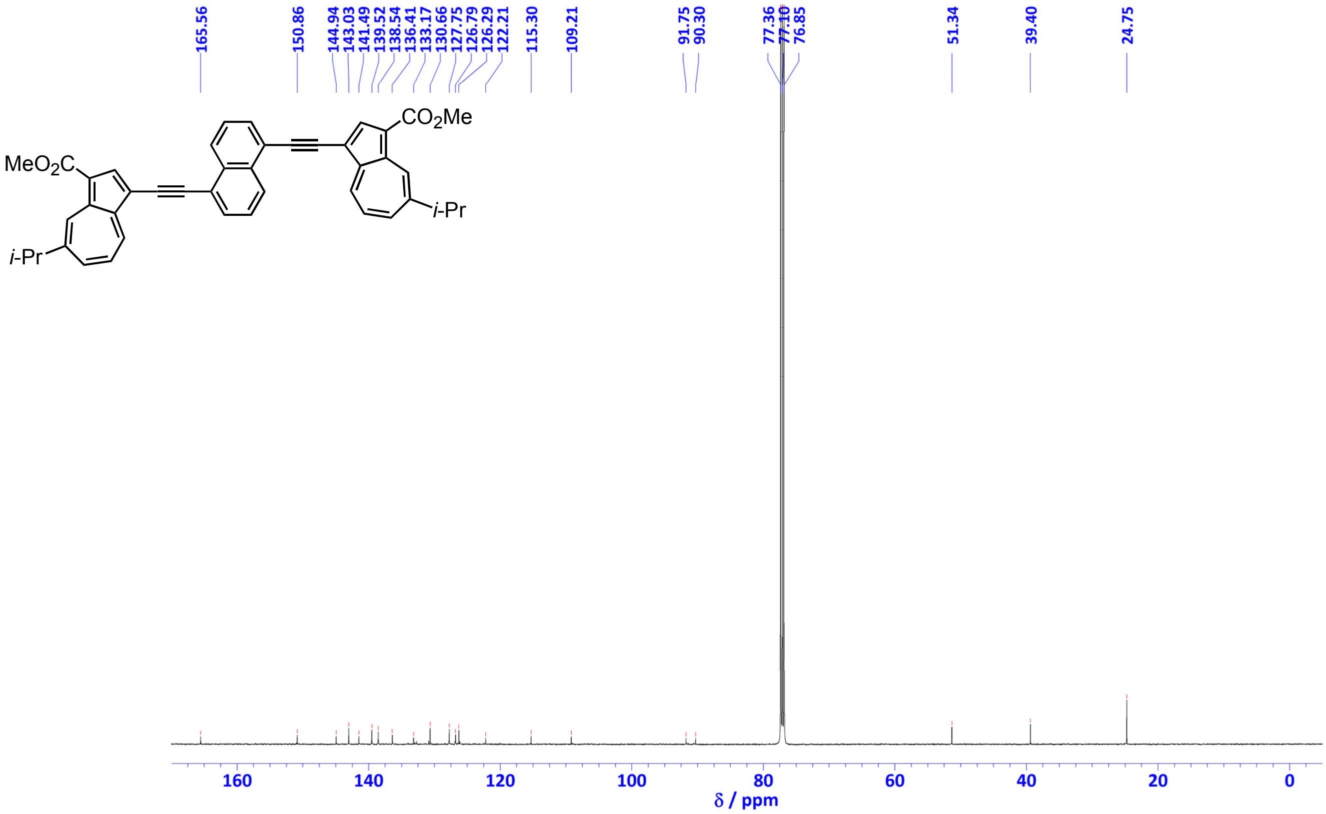


Figure S6. ^{13}C NMR spectrum of **5** in $CDCl_3$ (125 MHz).

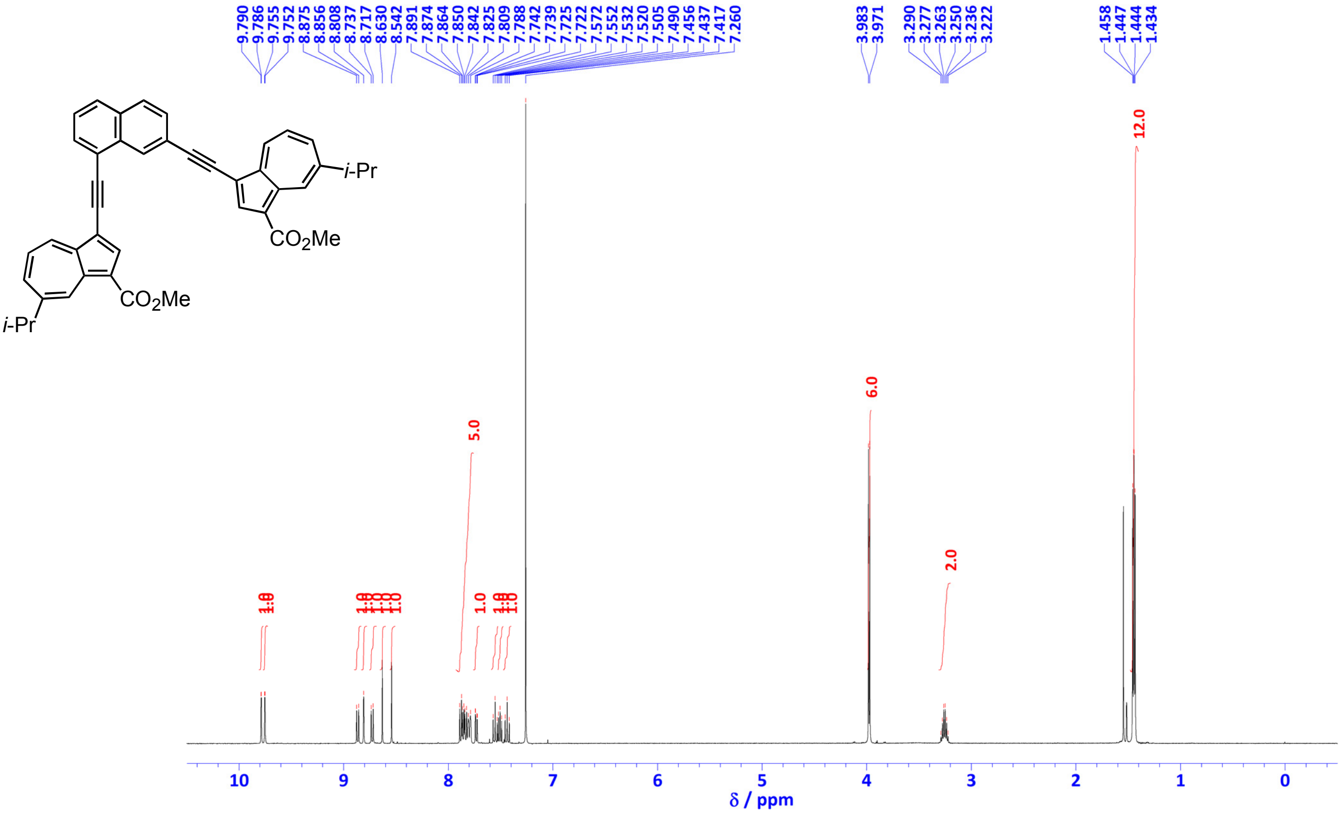


Figure S7. ^{1}H NMR spectrum of **6** in $CDCl_3$ (500 MHz).

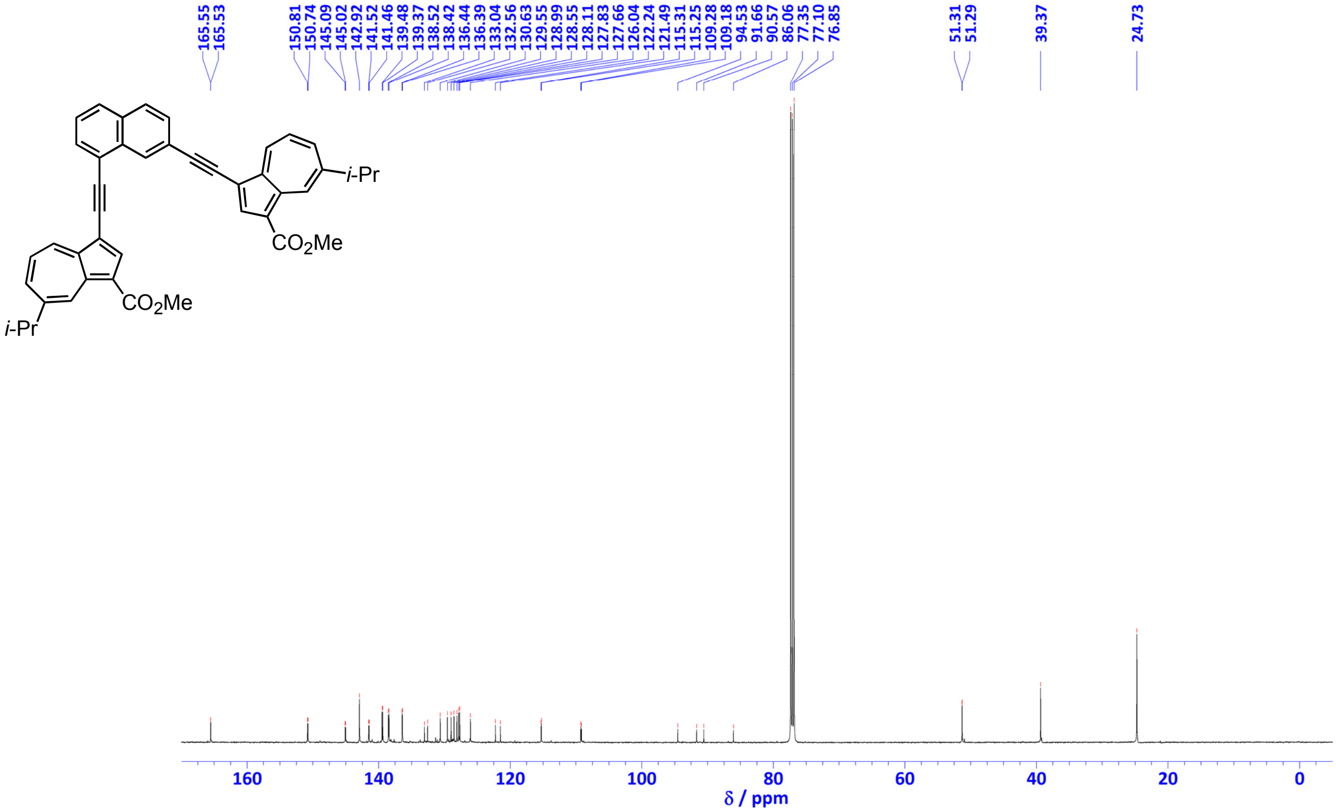


Figure S8. ^{13}C NMR spectrum of **6** in $CDCl_3$ (125 MHz).

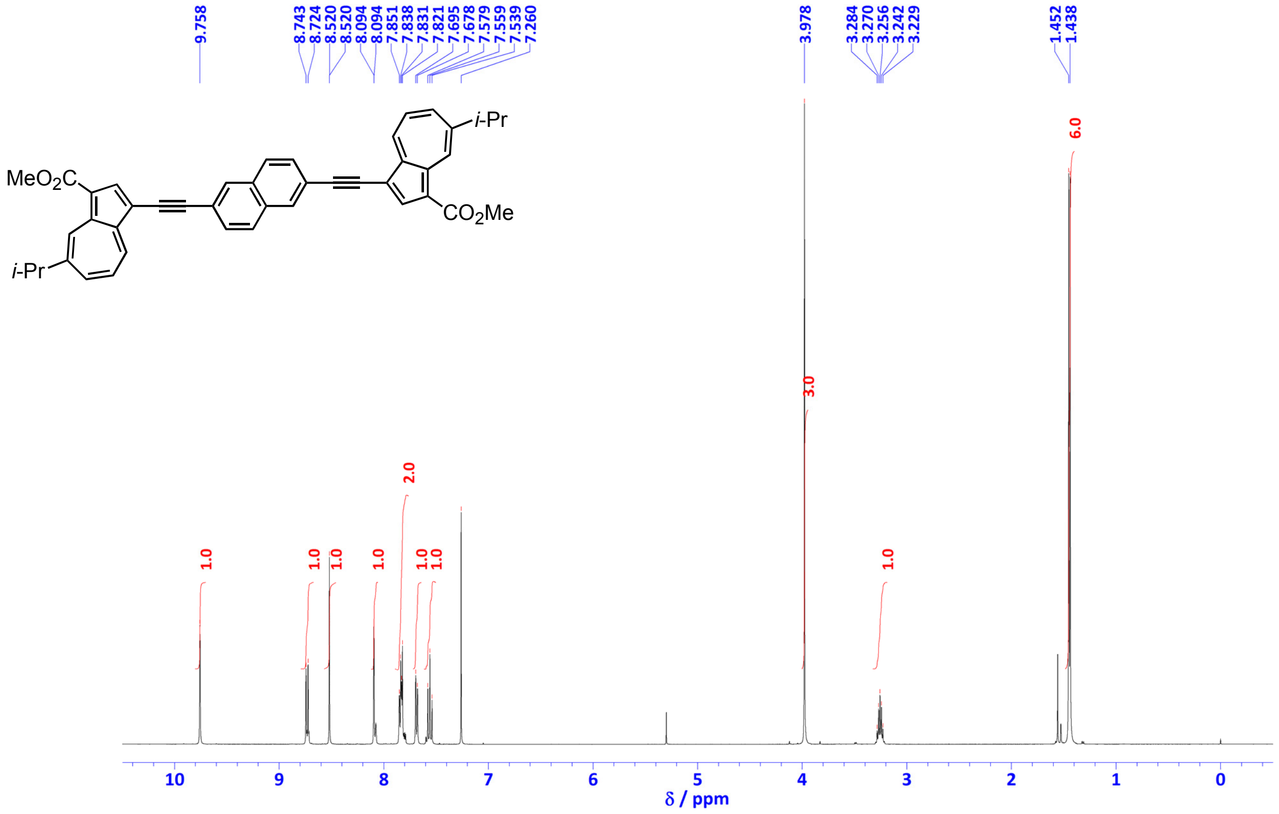


Figure S9. ^{1}H NMR spectrum of **7** in $CDCl_3$ (500 MHz).

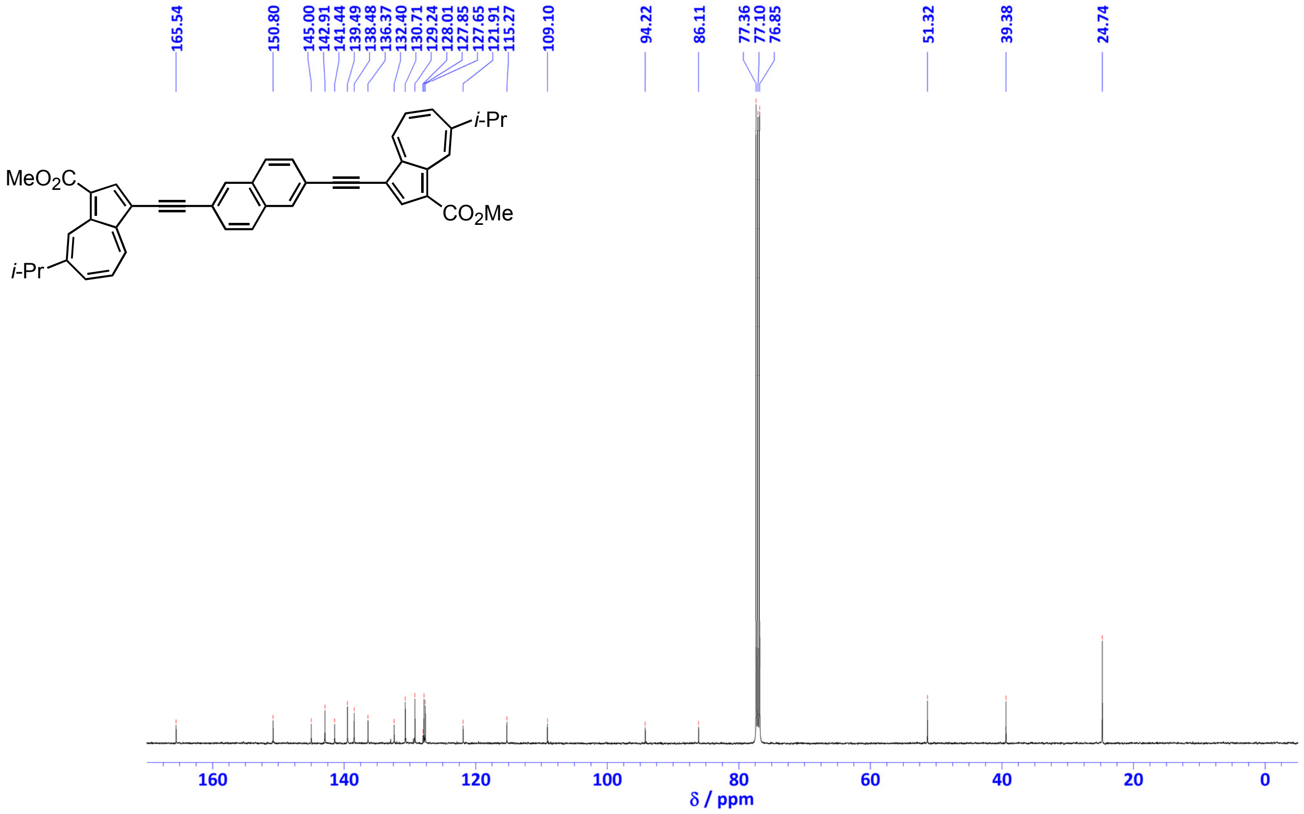


Figure S10. ^{13}C NMR spectrum of **7** in $CDCl_3$ (125 MHz).

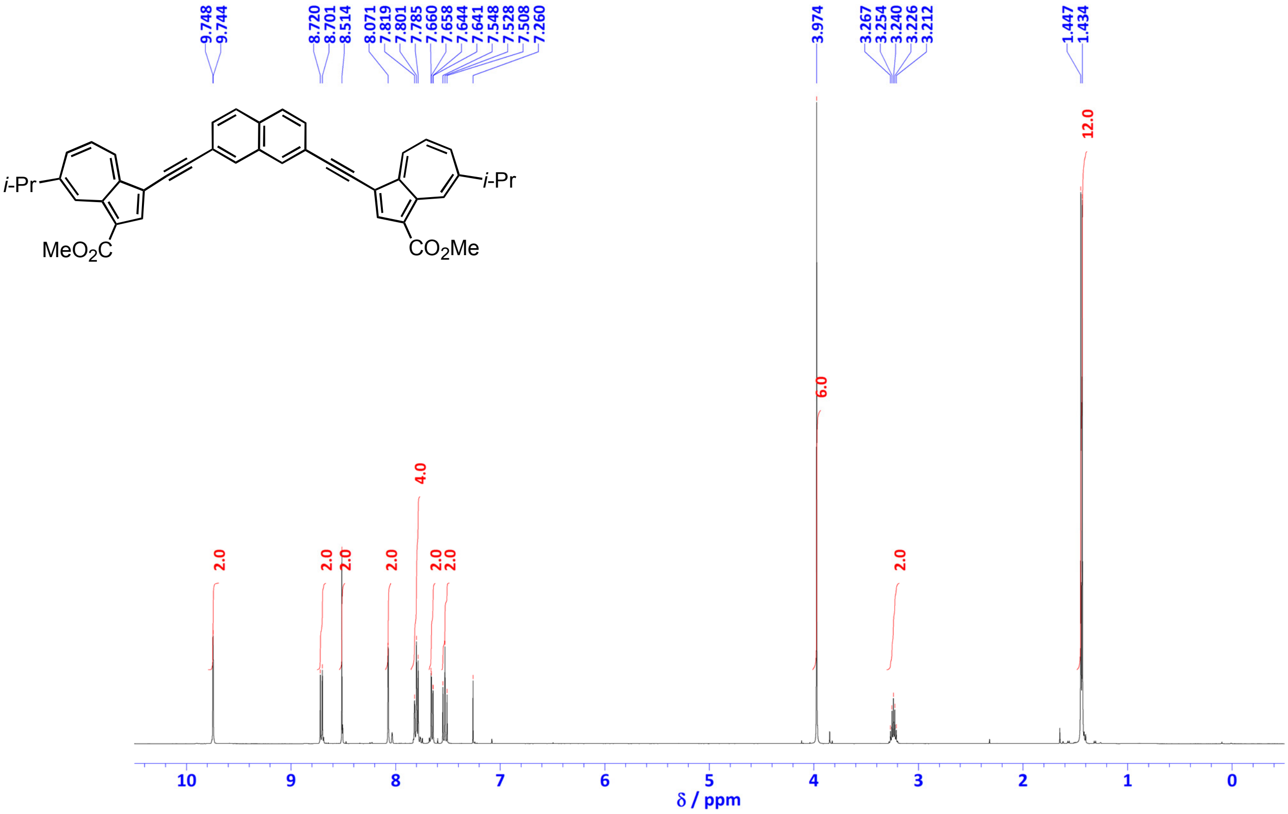


Figure S11. ^{1}H NMR spectrum of **8** in $CDCl_3$ (500 MHz).

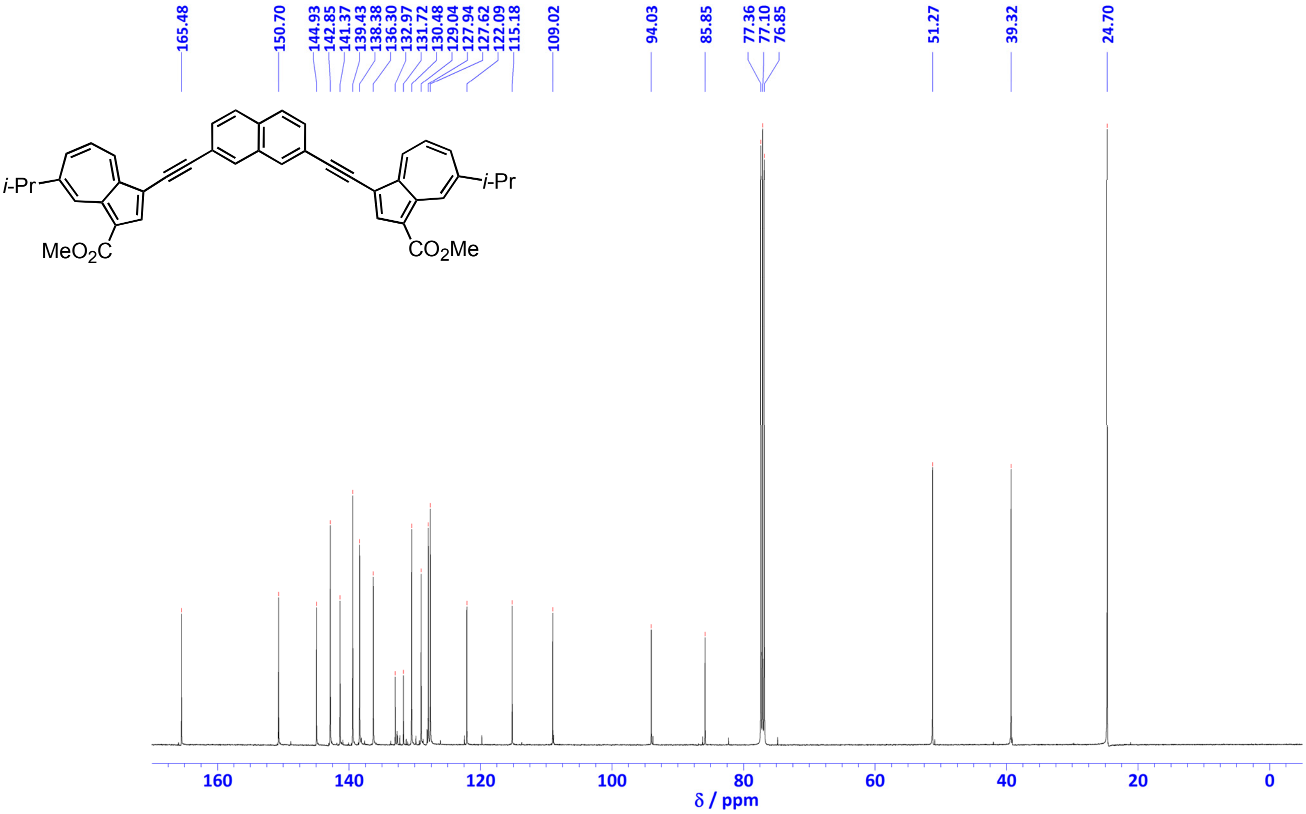


Figure S12. ^{13}C NMR spectrum of **8** in $CDCl_3$ (125 MHz).

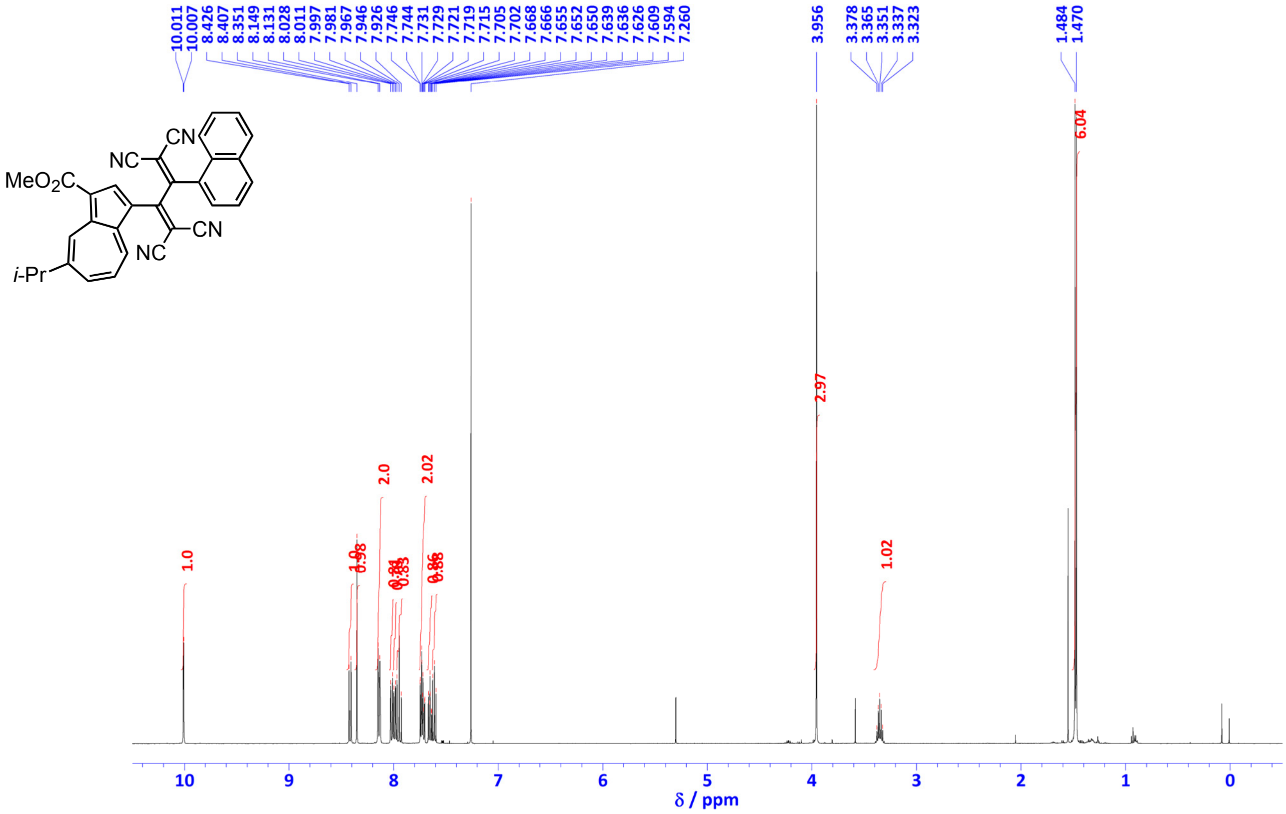


Figure S13. ^{1}H NMR spectrum of **9** in $CDCl_3$ (500 MHz).

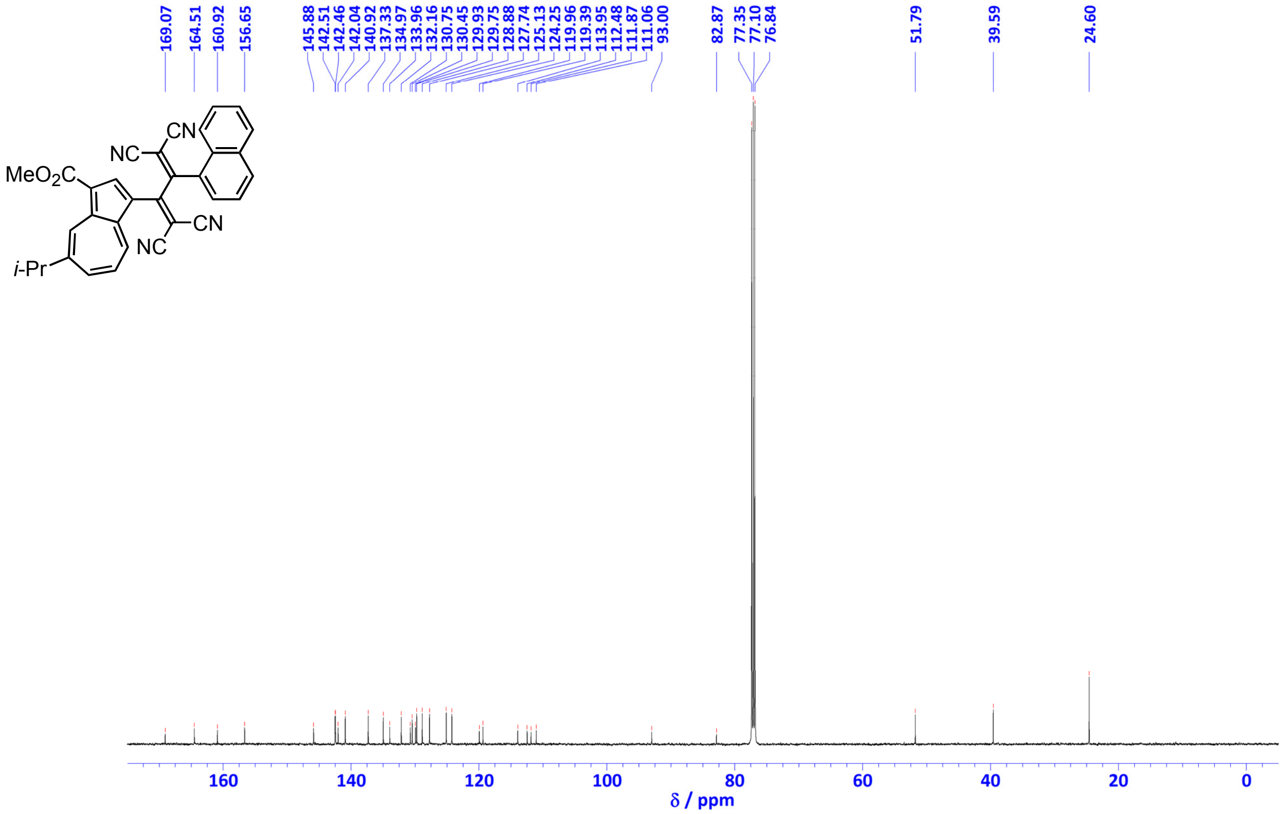


Figure S14. ^{13}C NMR spectrum of **9** in $CDCl_3$ (125 MHz).

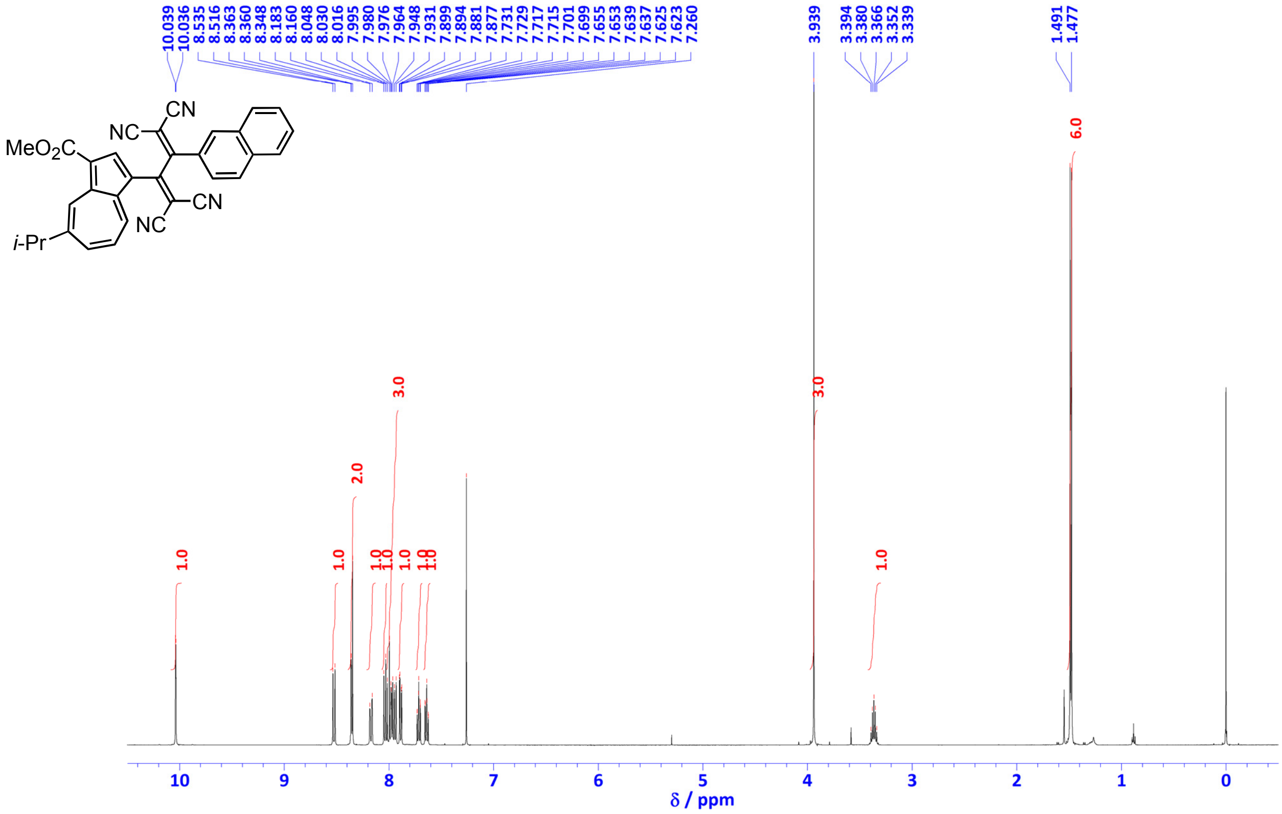


Figure S15. ^{1}H NMR spectrum of **10** in $CDCl_3$ (500 MHz).

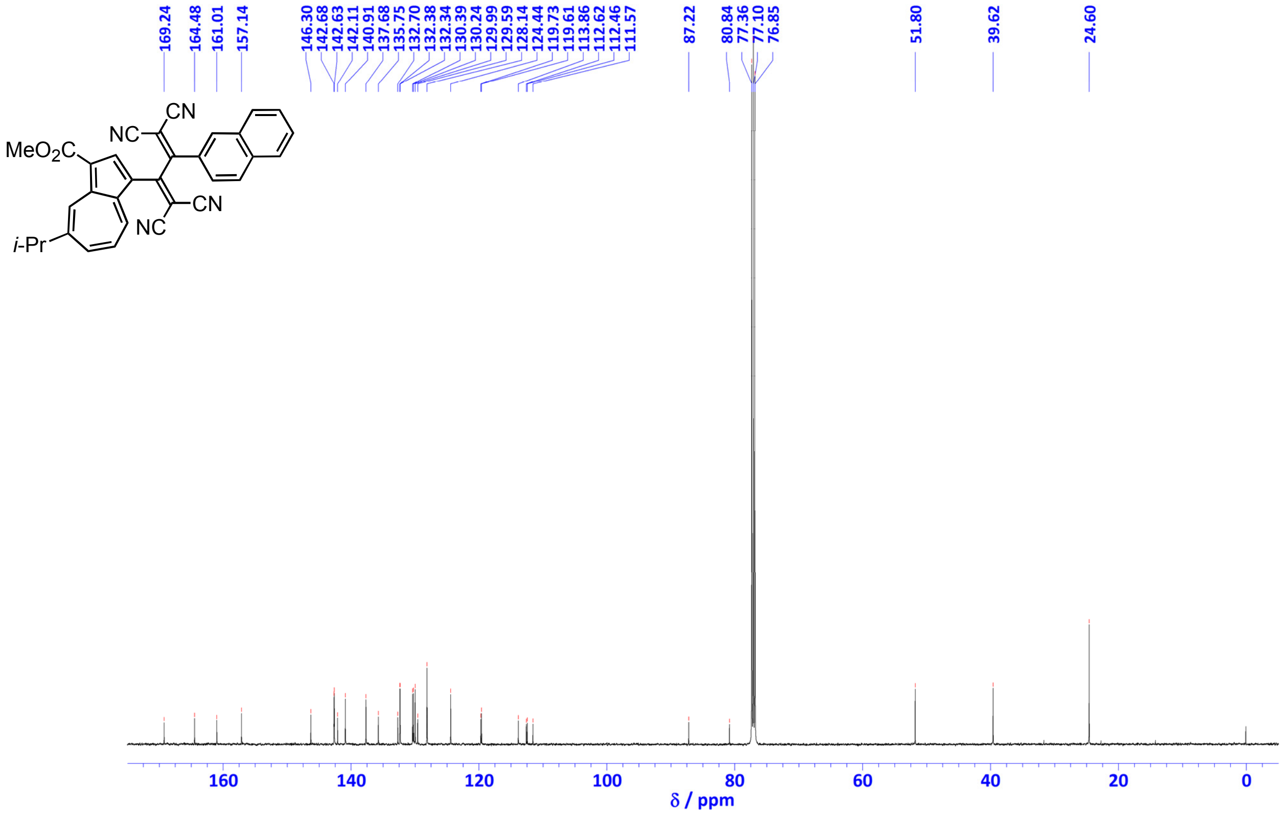


Figure S16. ^{13}C NMR spectrum of **10** in $CDCl_3$ (125 MHz).

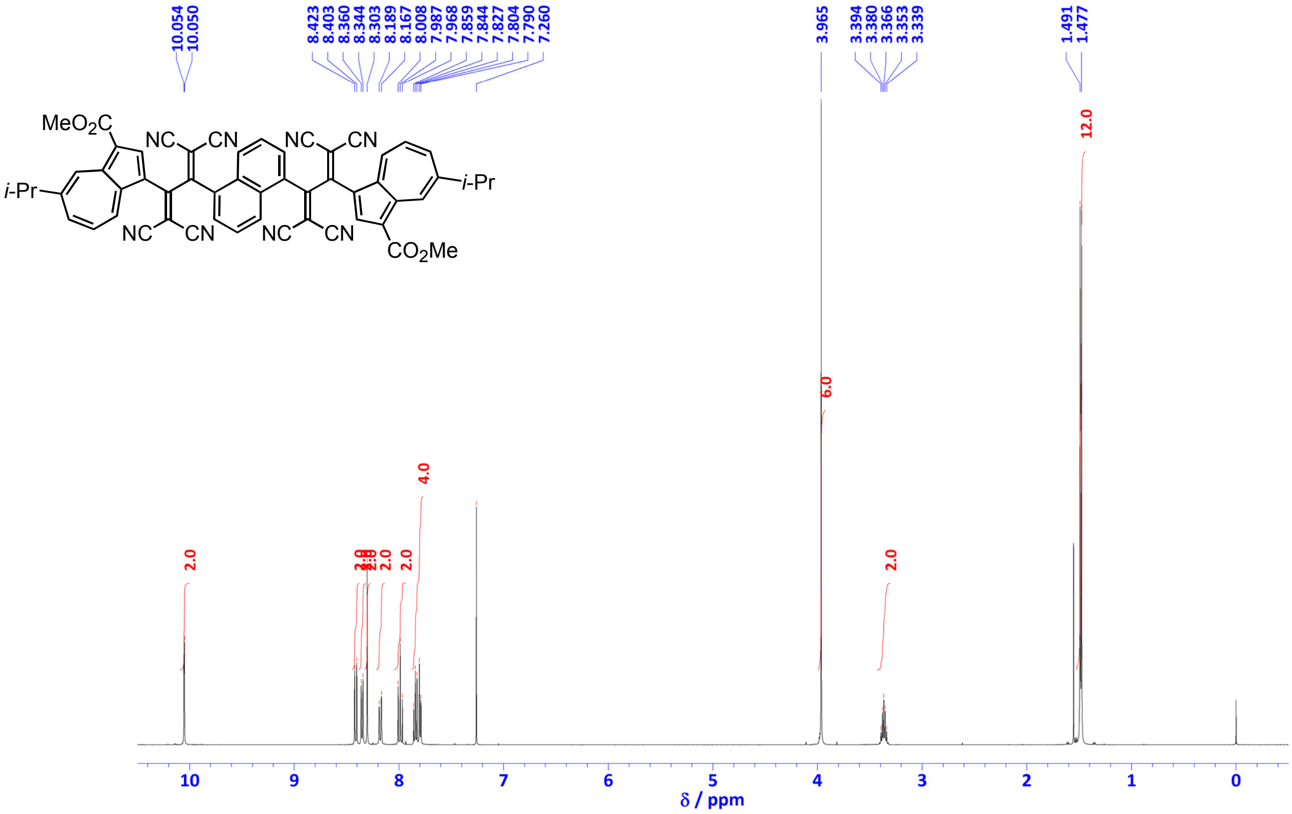


Figure S17. ^{1}H NMR spectrum of **11** in $CDCl_3$ (500 MHz).

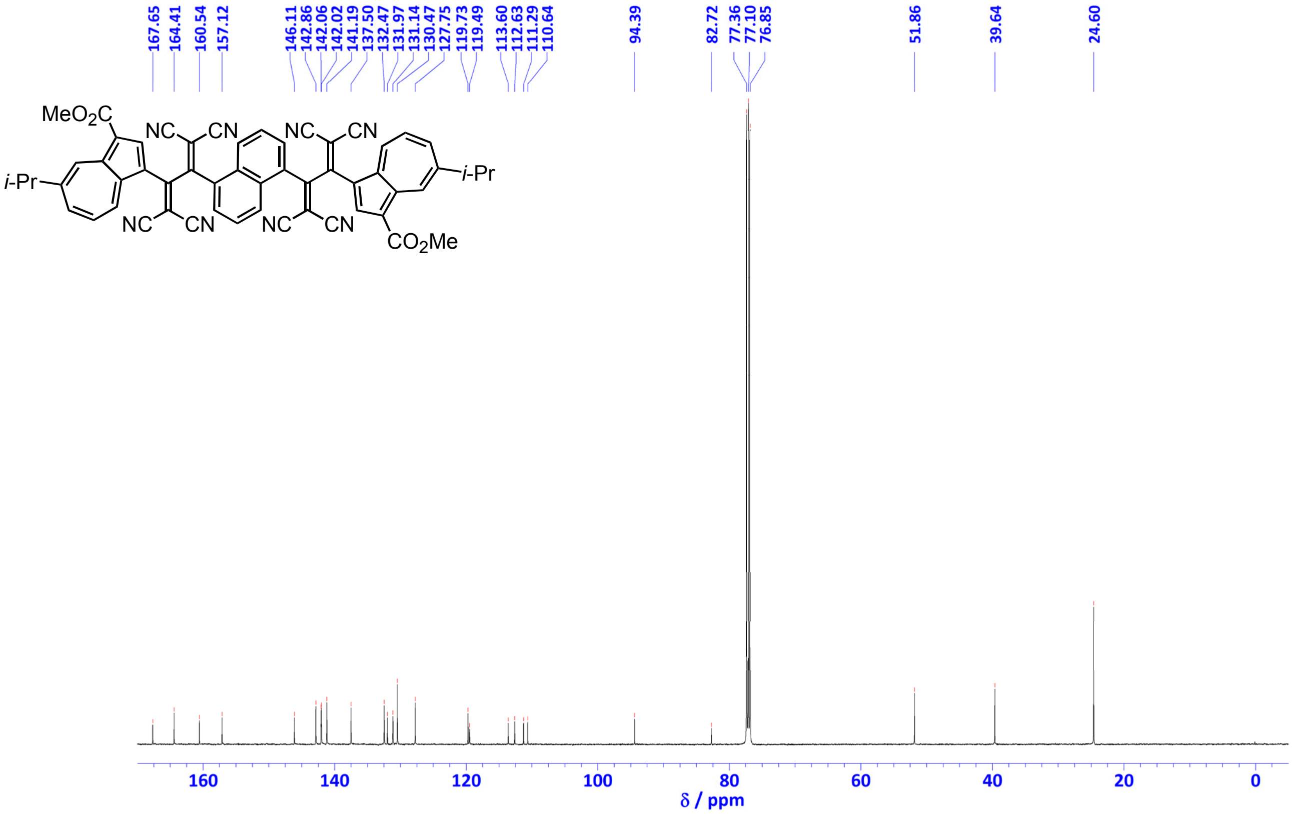


Figure S18. ^{13}C NMR spectrum of **11** in $CDCl_3$ (125 MHz).

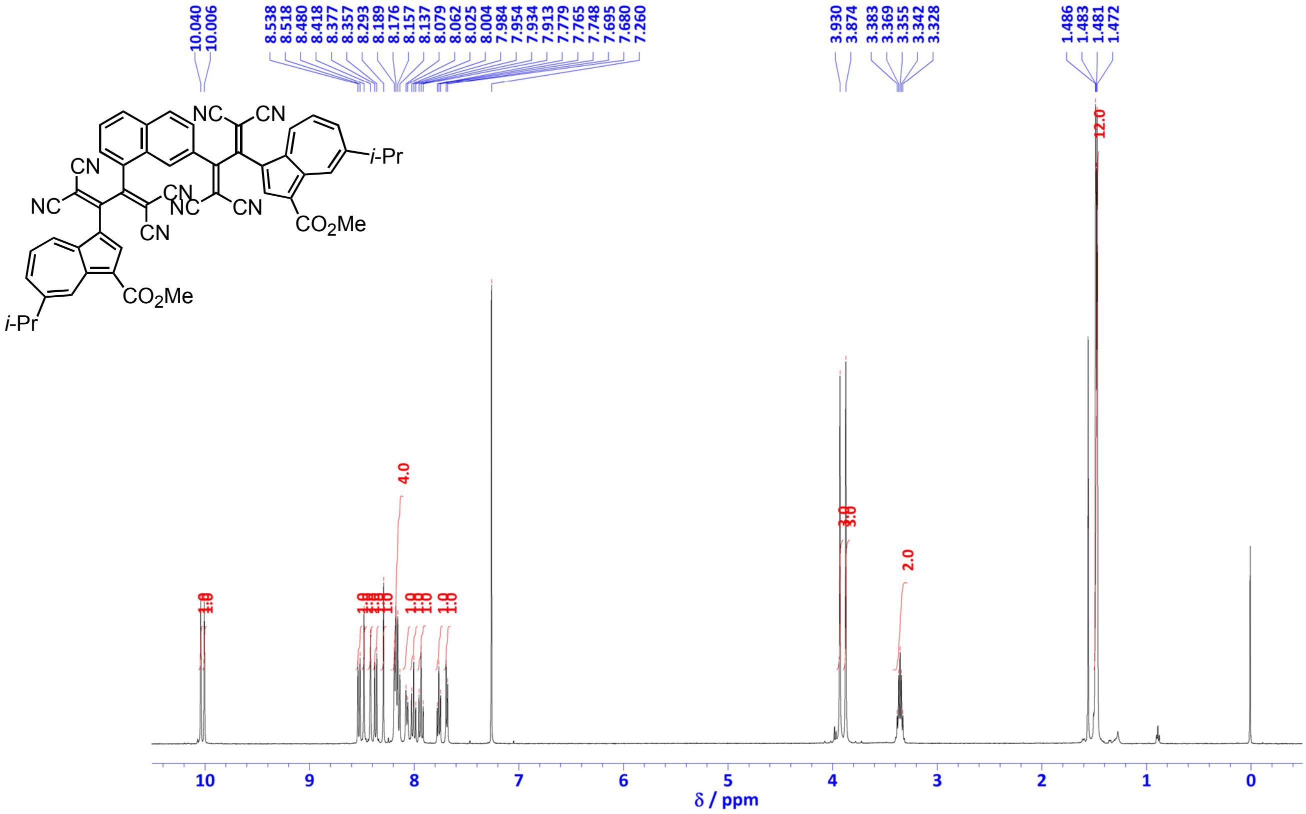


Figure S19. ^{1}H NMR spectrum of **12** in $CDCl_3$ (500 MHz).

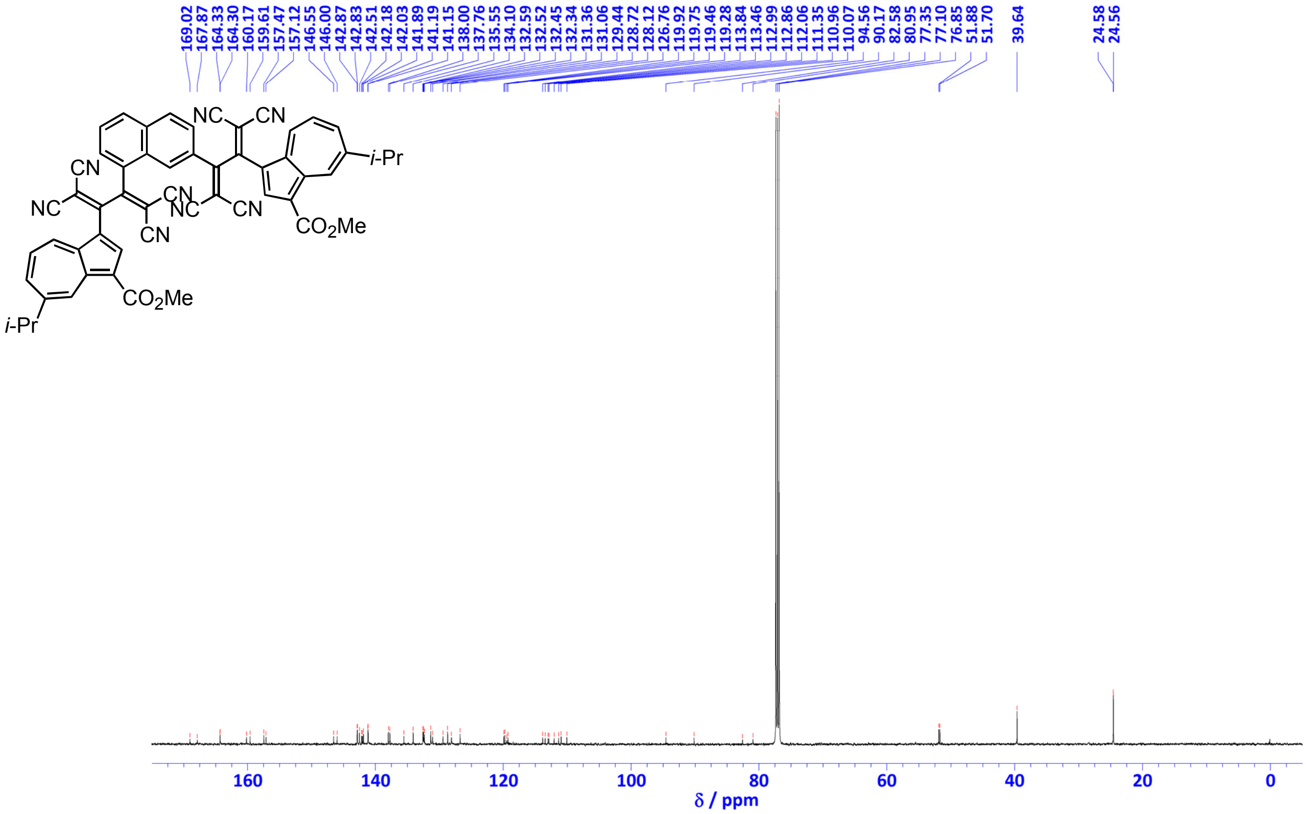


Figure S20. ^{13}C NMR spectrum of **12** in $CDCl_3$ (125 MHz).

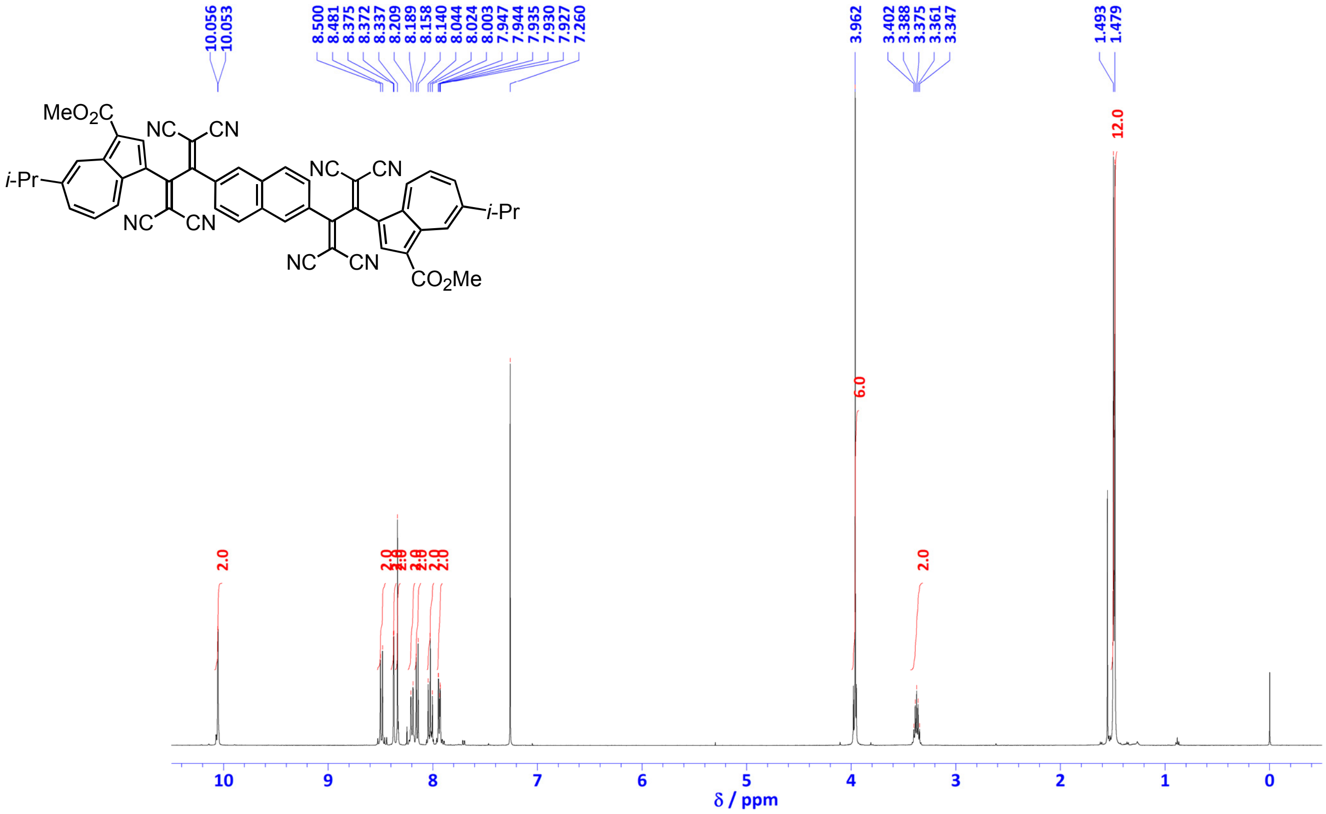


Figure S21. ^{1}H NMR spectrum of **13** in $CDCl_3$ (500 MHz).

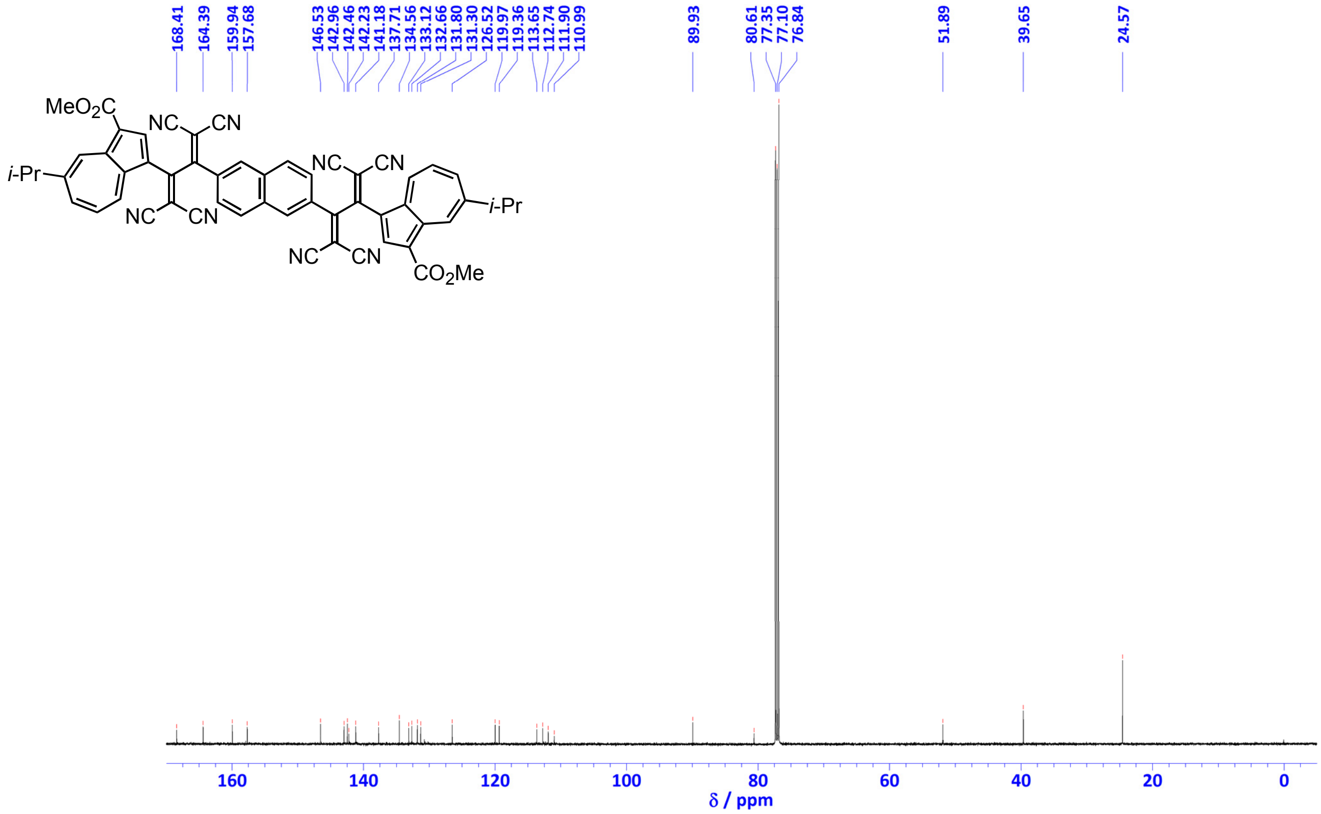


Figure S22. ^{13}C NMR spectrum of **13** in $CDCl_3$ (125 MHz).

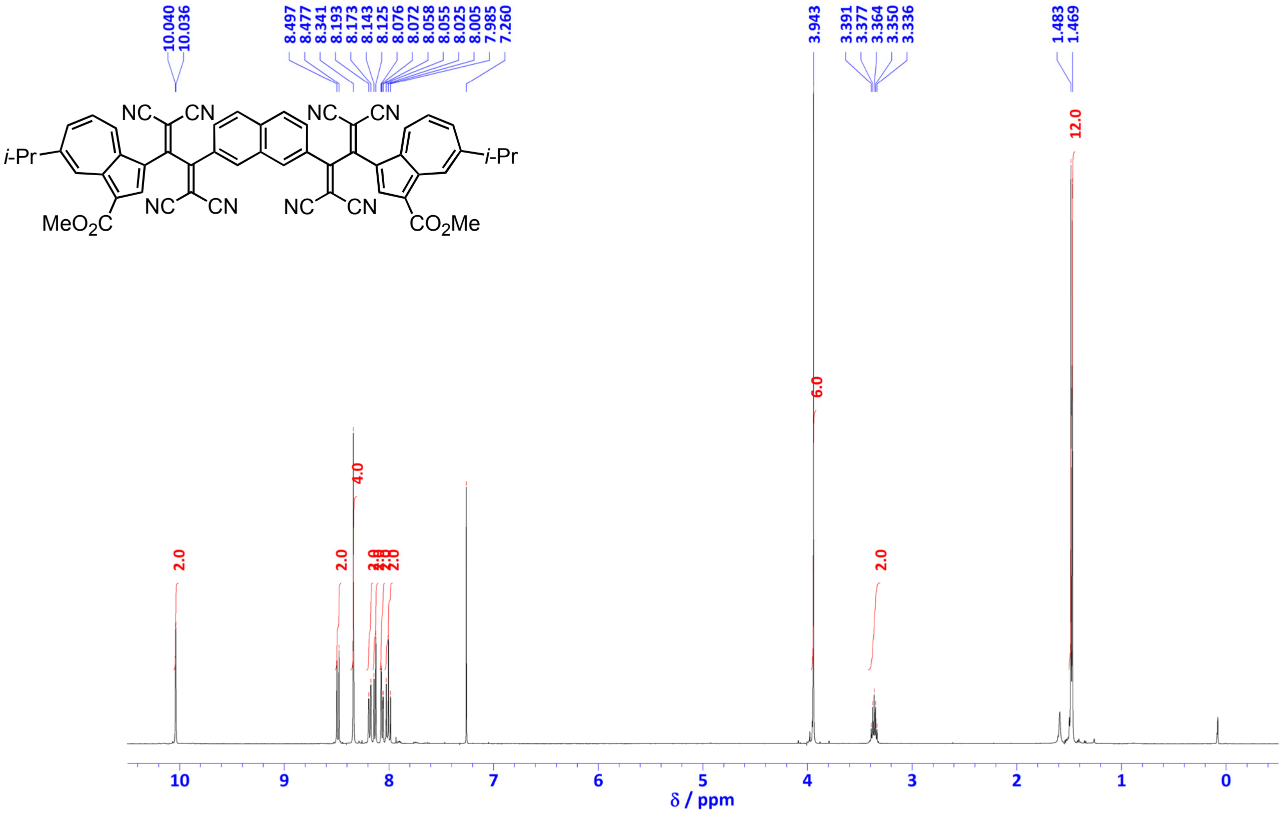


Figure S23. ^{1}H NMR spectrum of **14** in $CDCl_3$ (500 MHz).

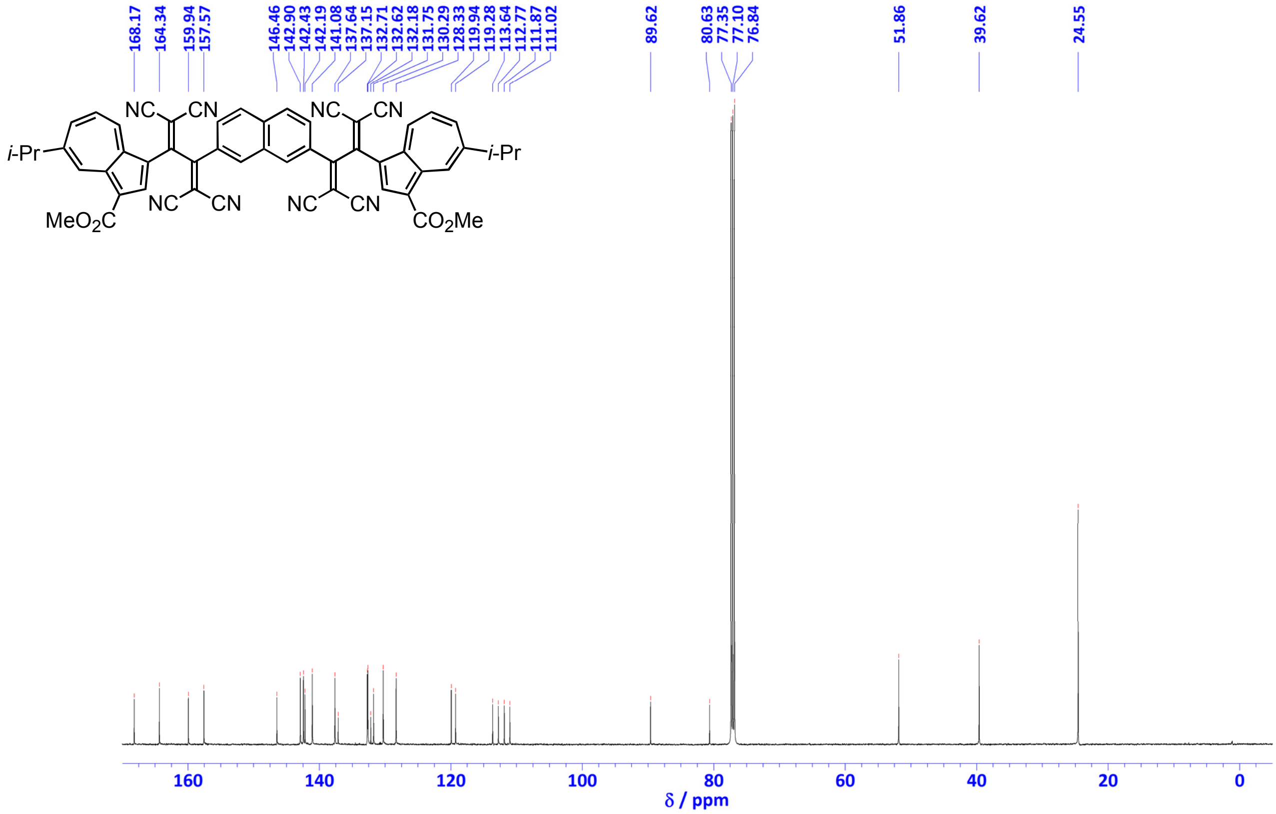


Figure S24. ^{13}C NMR spectrum of **14** in $CDCl_3$ (125 MHz).

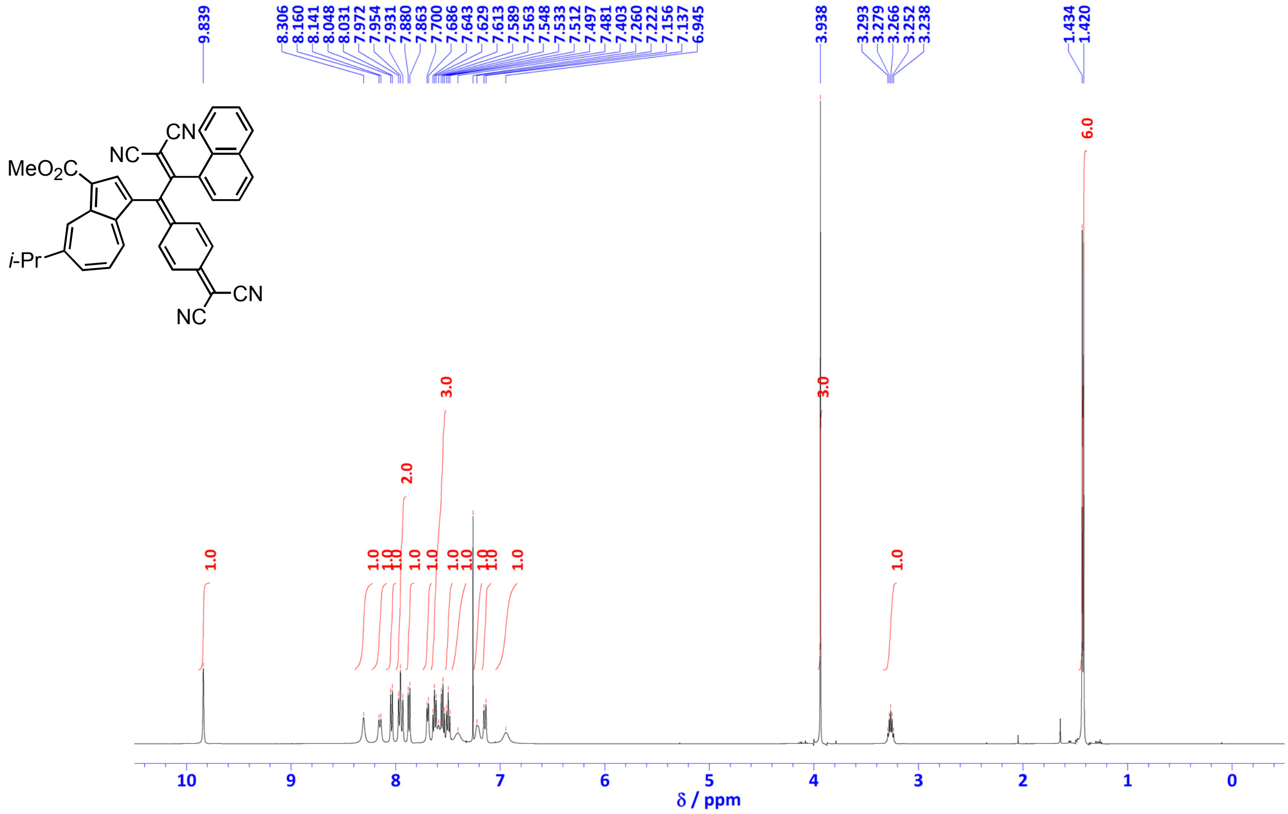


Figure S25. ^{1}H NMR spectrum of **15** in $CDCl_3$ (500 MHz).

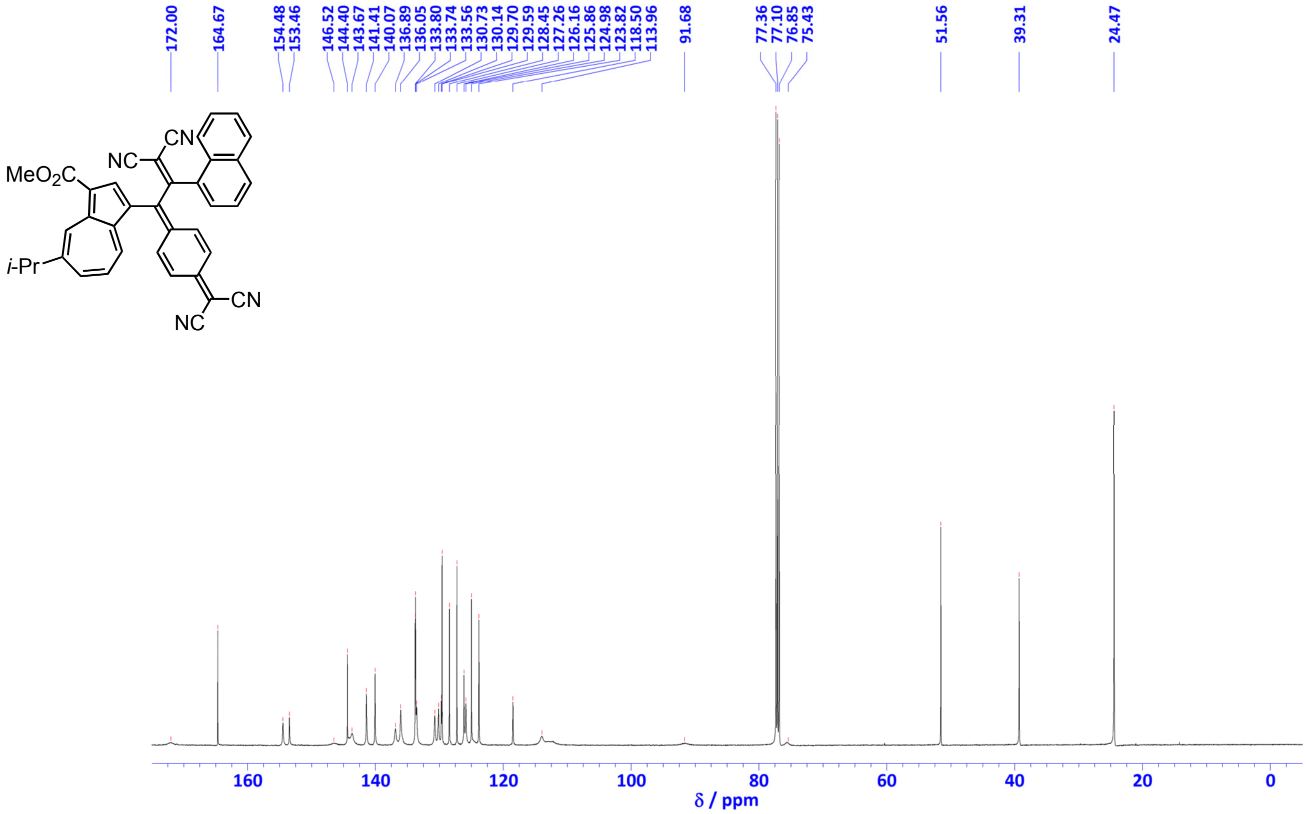


Figure S26. ^{13}C NMR spectrum of **15** in $CDCl_3$ (125 MHz).

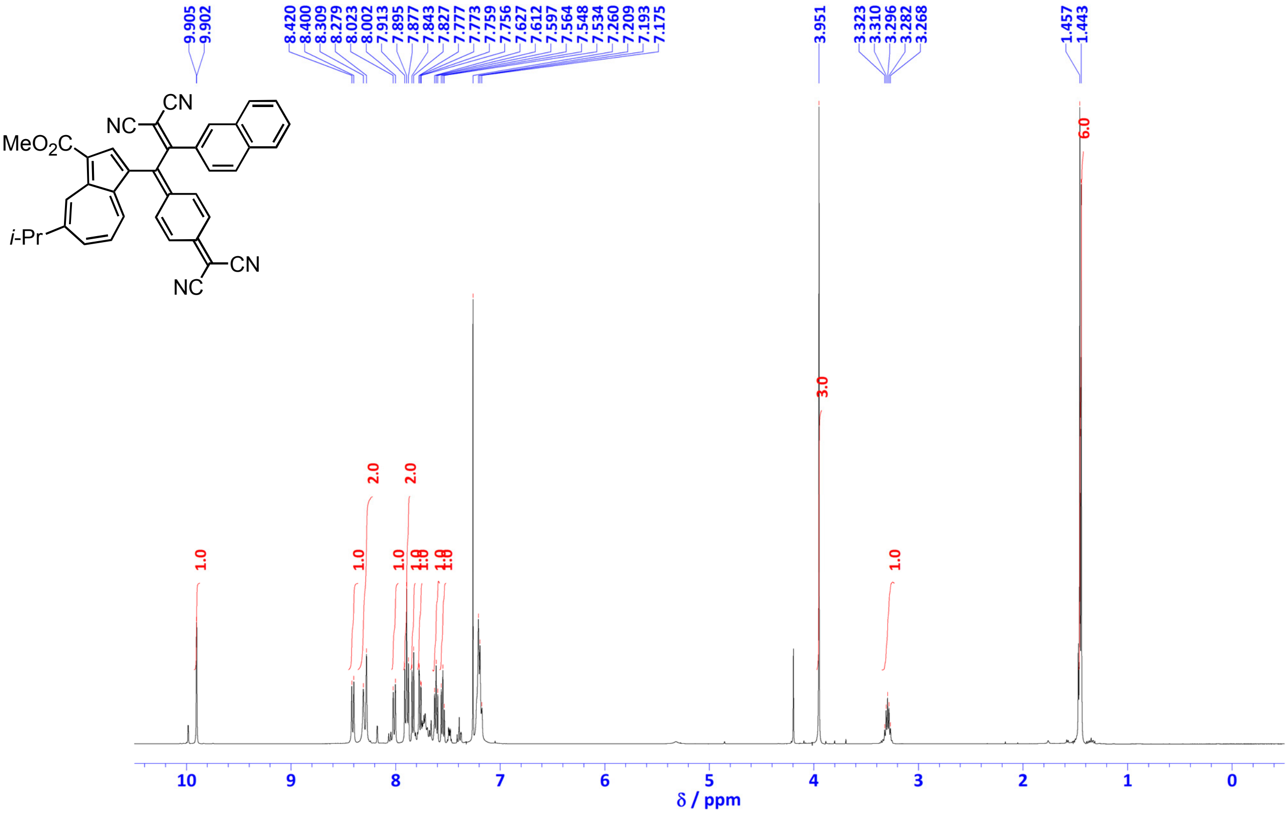


Figure S27. ^{1}H NMR spectrum of **16** in $CDCl_3$ (500 MHz).

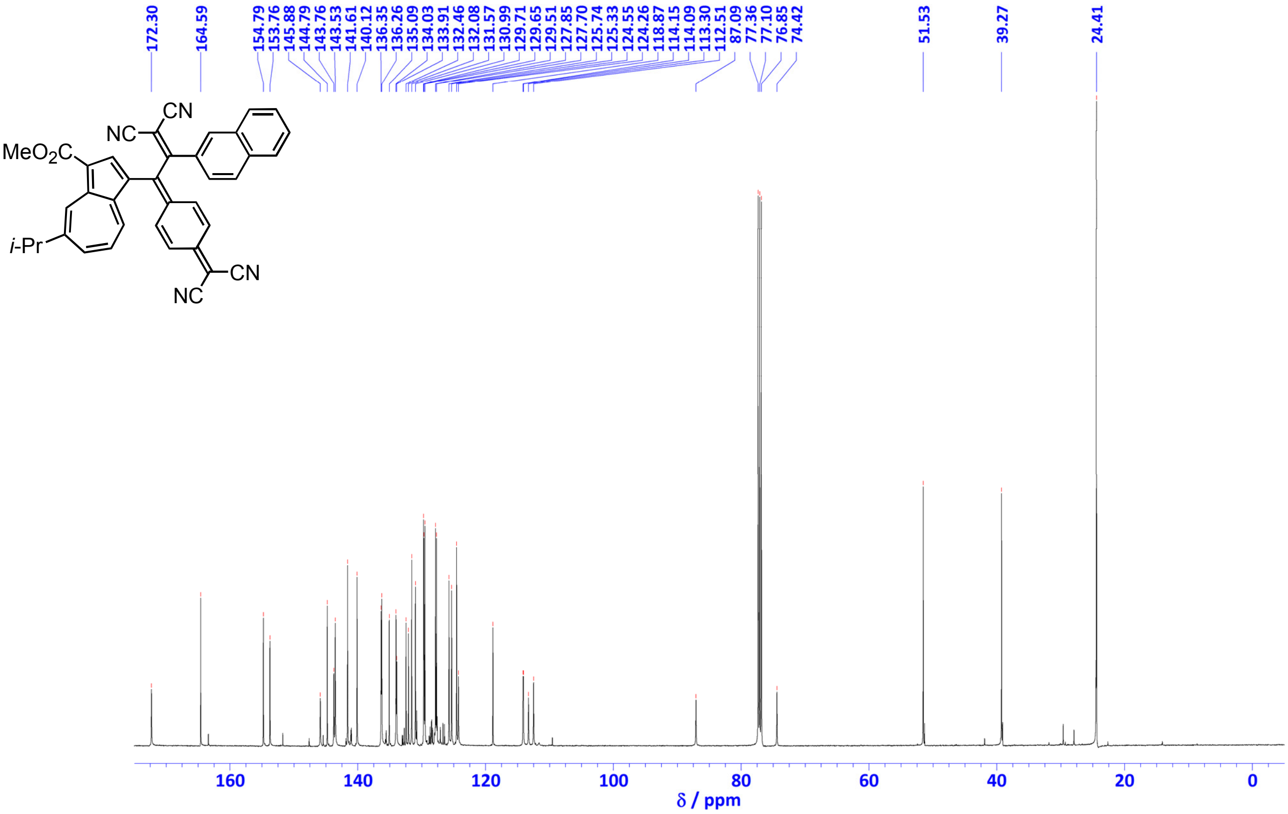


Figure S28. ^{13}C NMR spectrum of **16** in $CDCl_3$ (125 MHz).

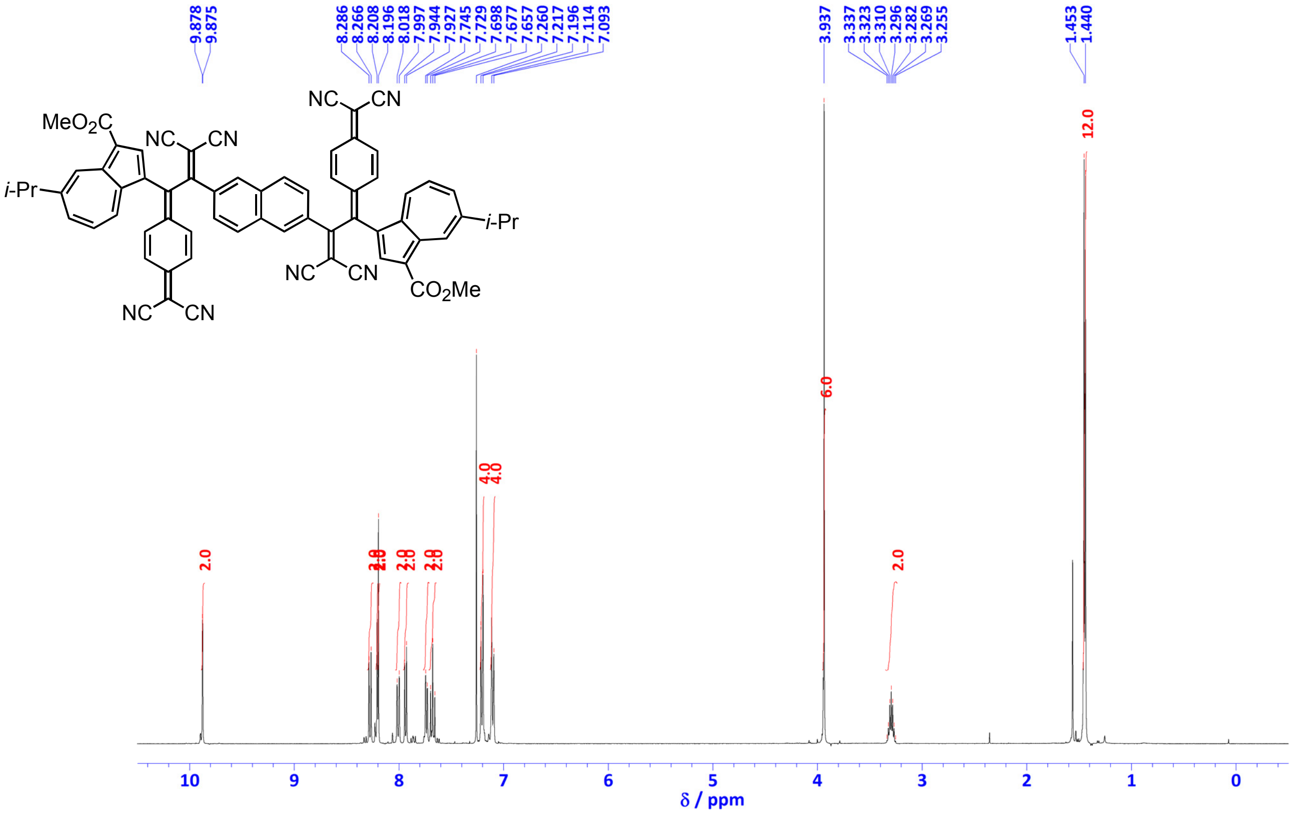


Figure S29. ^{1}H NMR spectrum of **17** in $CDCl_3$ (500 MHz).

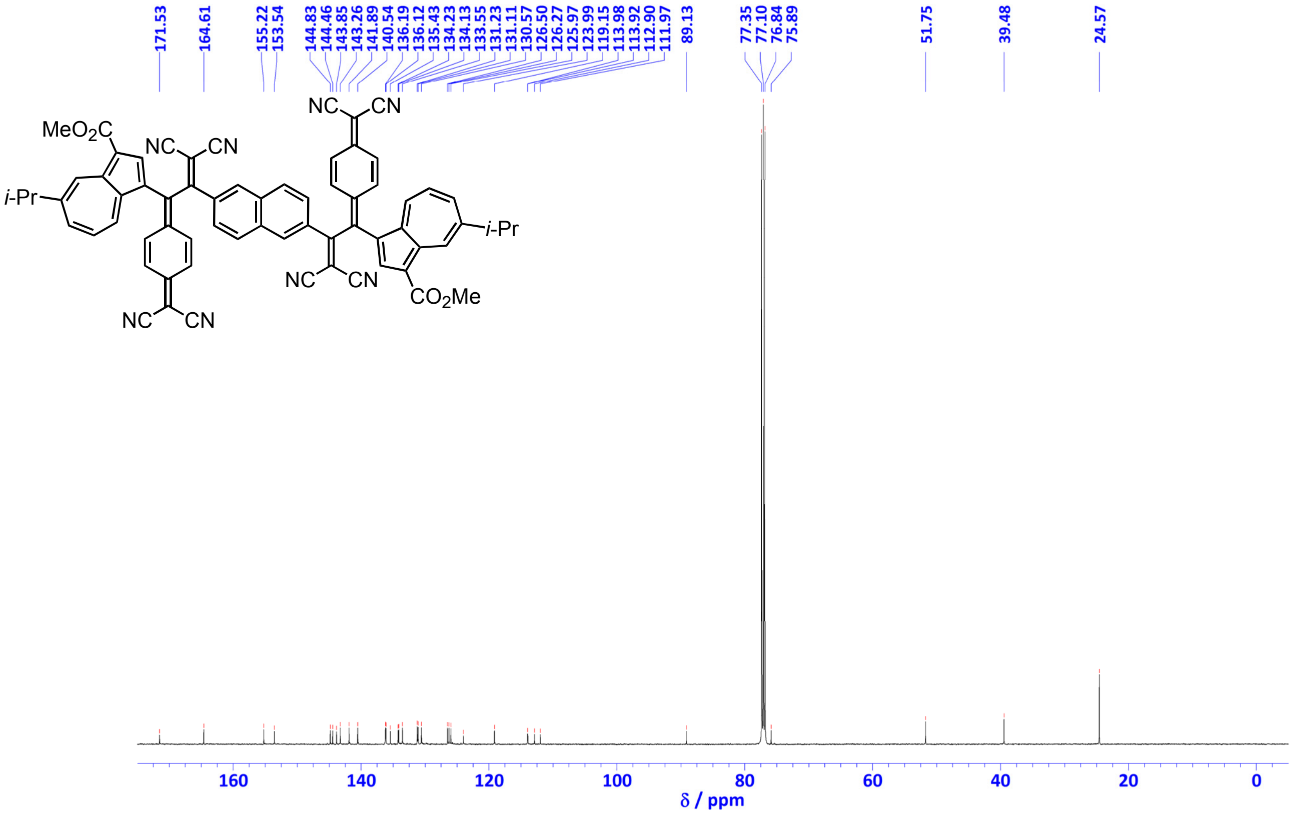


Figure S30. ^{13}C NMR spectrum of **17** in $CDCl_3$ (125 MHz).

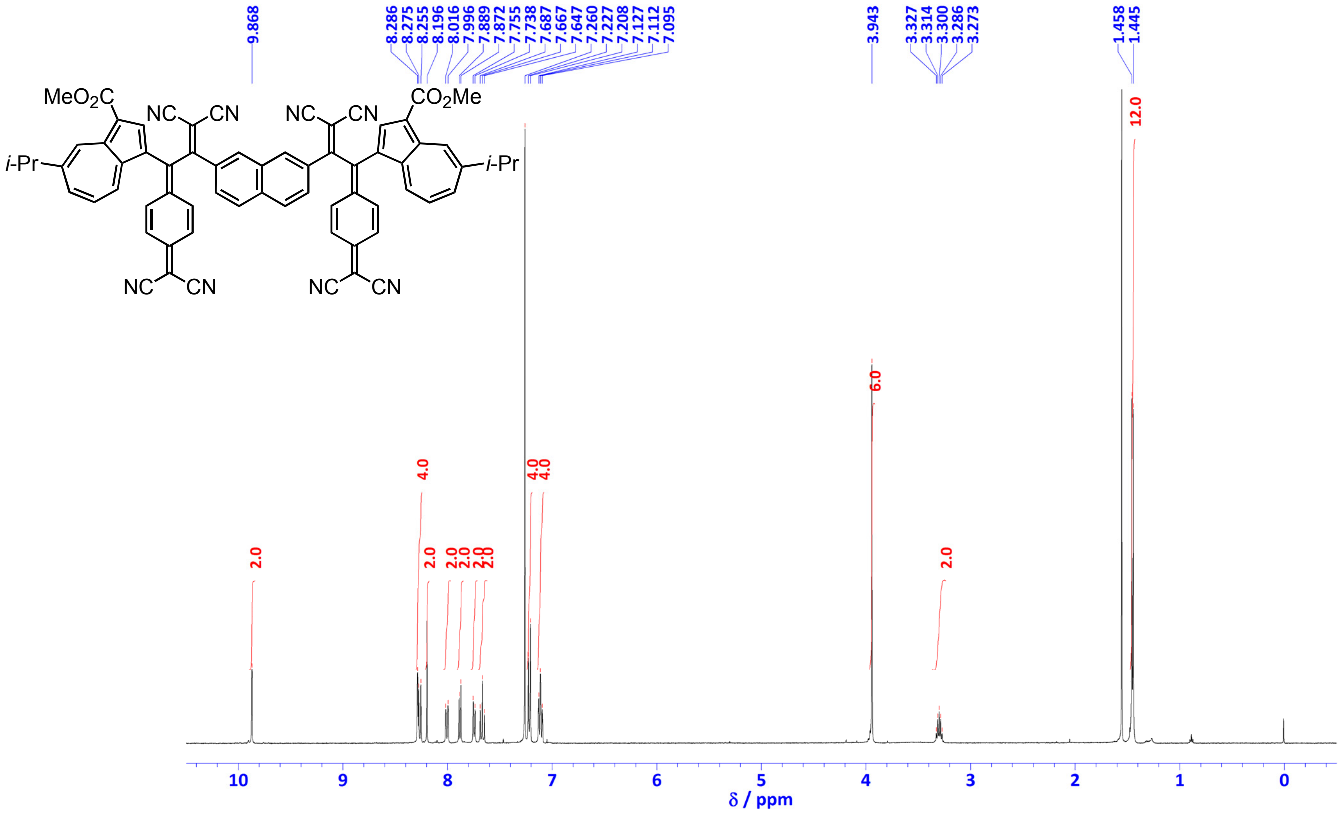


Figure S31. ^{1}H NMR spectrum of **18** in $CDCl_3$ (500 MHz).

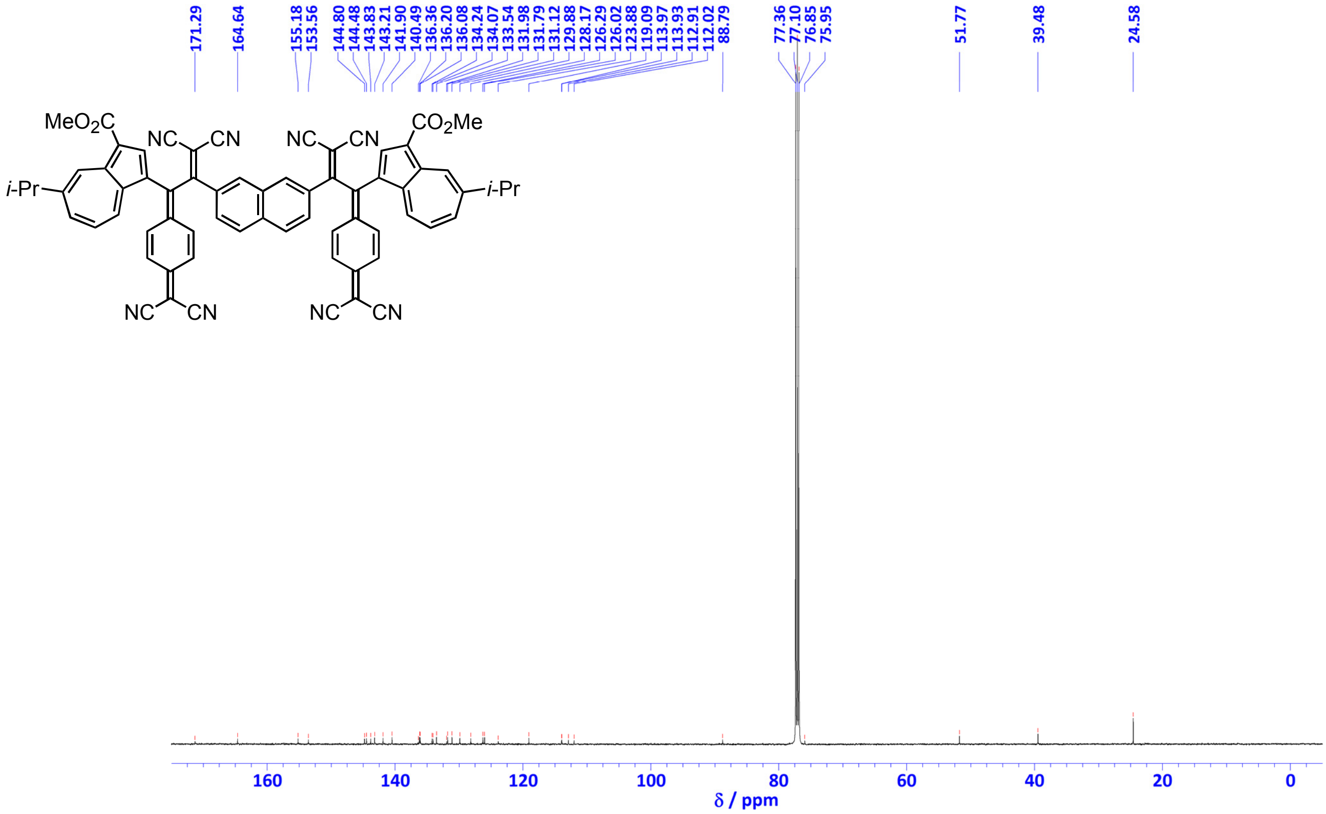


Figure S32. ^{13}C NMR spectrum of **18** in $CDCl_3$ (125 MHz).

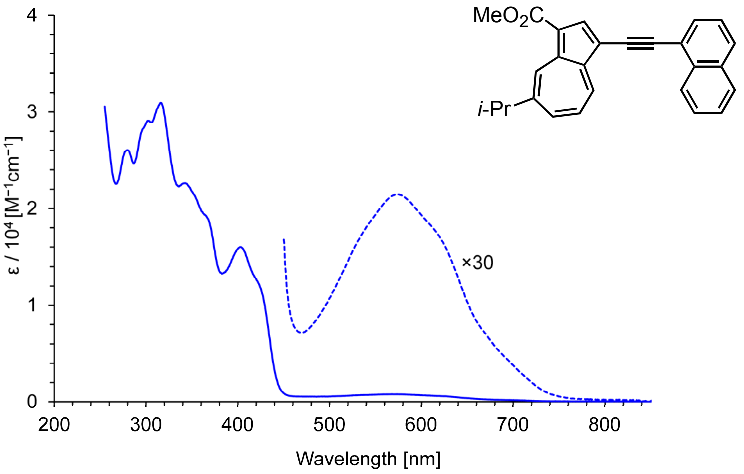


Figure S33. UV/Vis spectrum of **3** in dichloromethane.

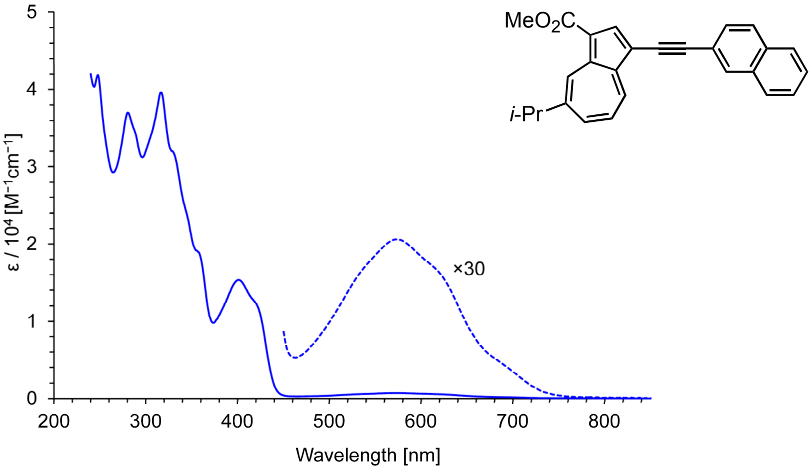


Figure S34. UV/Vis spectrum of **4** in dichloromethane.

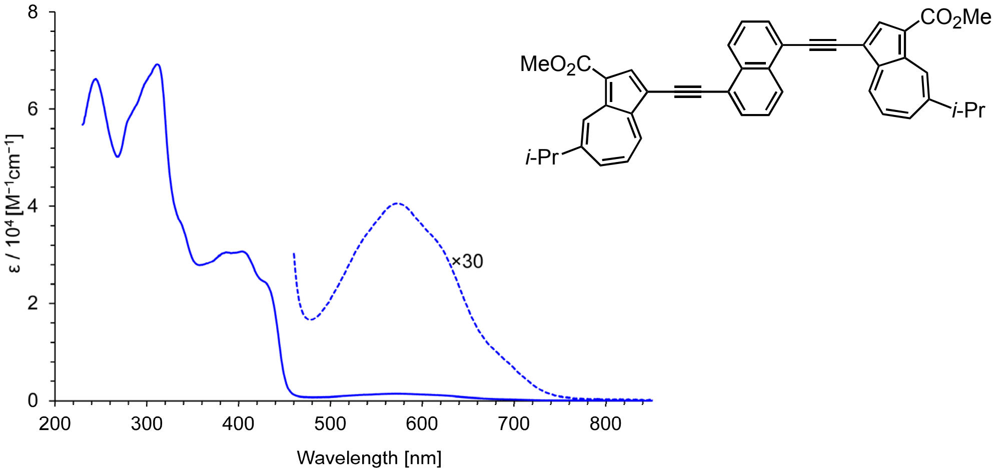


Figure S35. UV/Vis spectrum of **5** in dichloromethane.

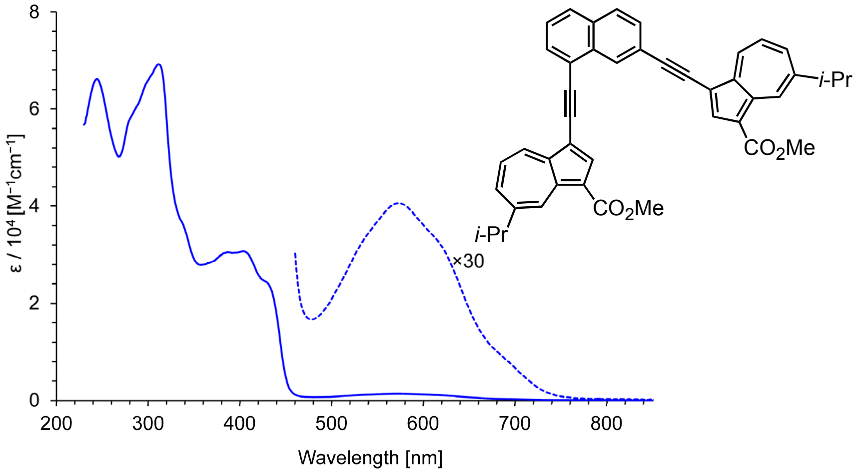


Figure S36. UV/Vis spectrum of **6** in dichloromethane.

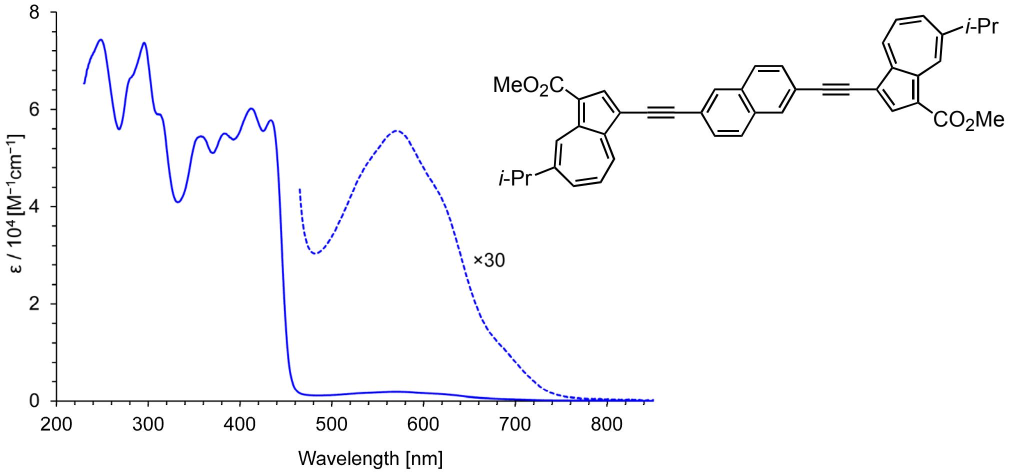


Figure S37. UV/Vis spectrum of **7** in dichloromethane.

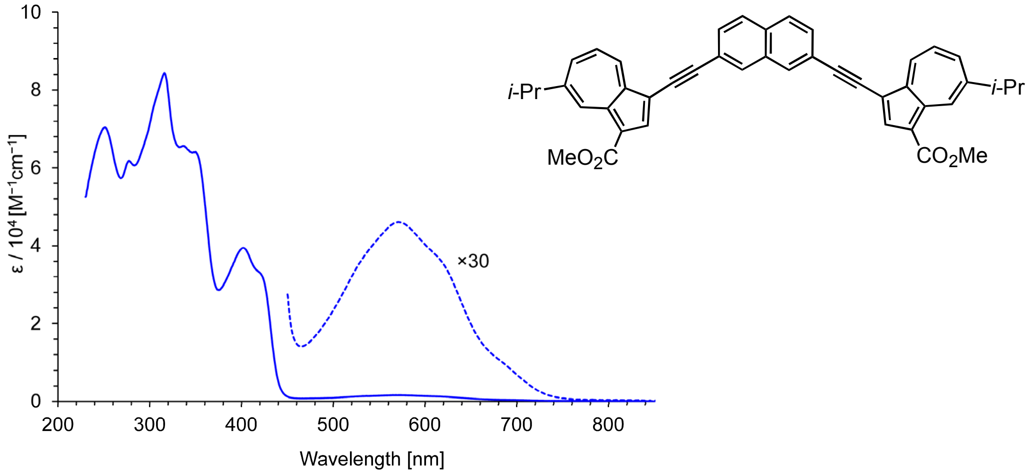


Figure S38. UV/Vis spectrum of **8** in dichloromethane.

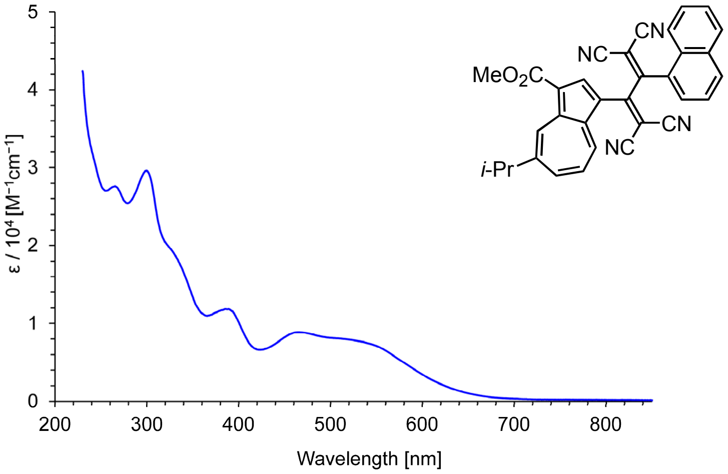


Figure S39. UV/Vis spectrum of **9** in dichloromethane.

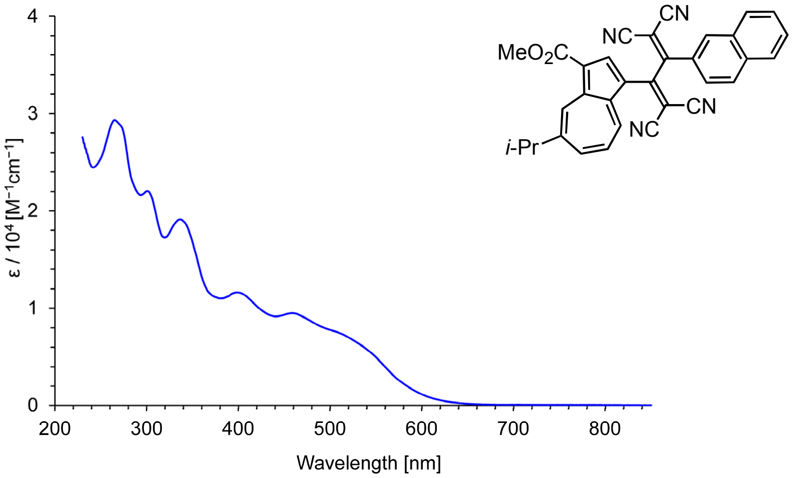


Figure S40. UV/Vis spectrum of **10** in dichloromethane.

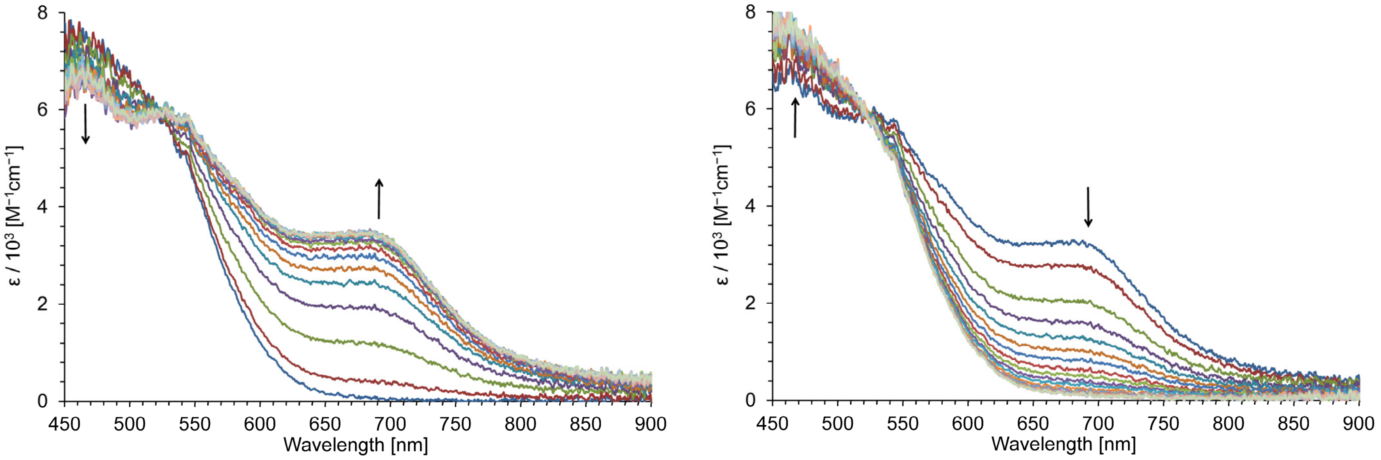


Figure S41. Continuous change in the UV/Vis spectrum of **10**: constant-voltage electrochemical reduction at −0.85 V (left) and reverse oxidation of the reduced species at −0.10 V (right) in benzonitrile containing Et_4NClO_4 (0.1 M) at 30 sec intervals.

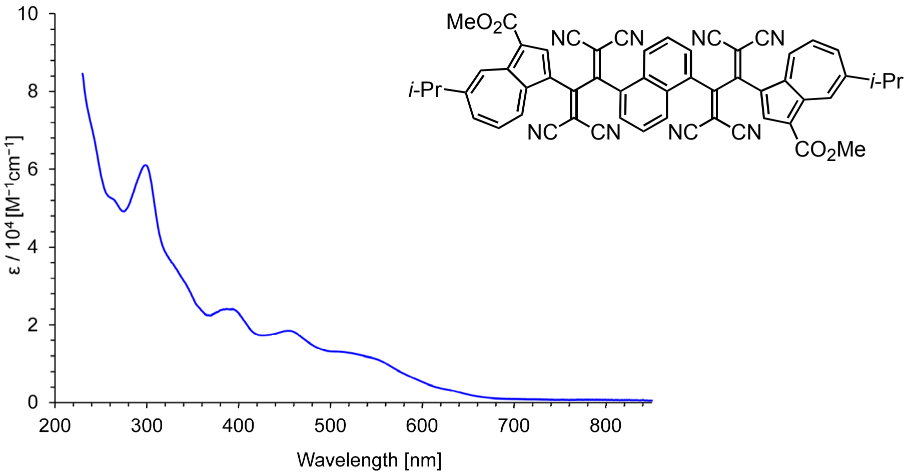


Figure S42. UV/Vis spectrum of **11** in dichloromethane.

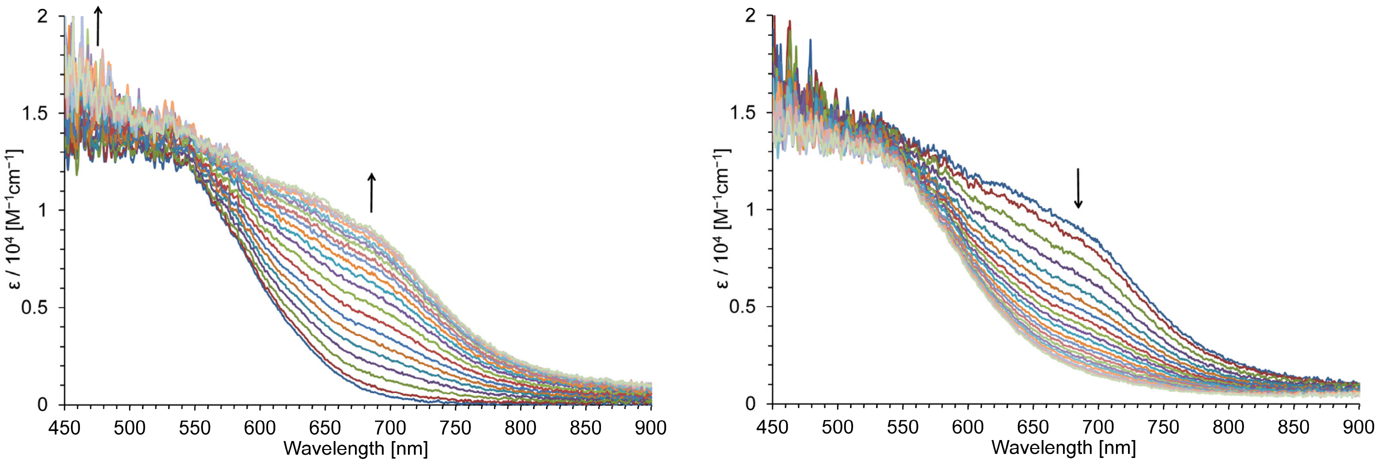


Figure S43. Continuous change in the UV/Vis spectrum of **11**: constant-voltage electrochemical reduction at −0.95 V (left) and reverse oxidation of the reduced species at −0.10 V (right) in benzonitrile containing Et_4NClO_4 (0.1 M) at 30 sec intervals.

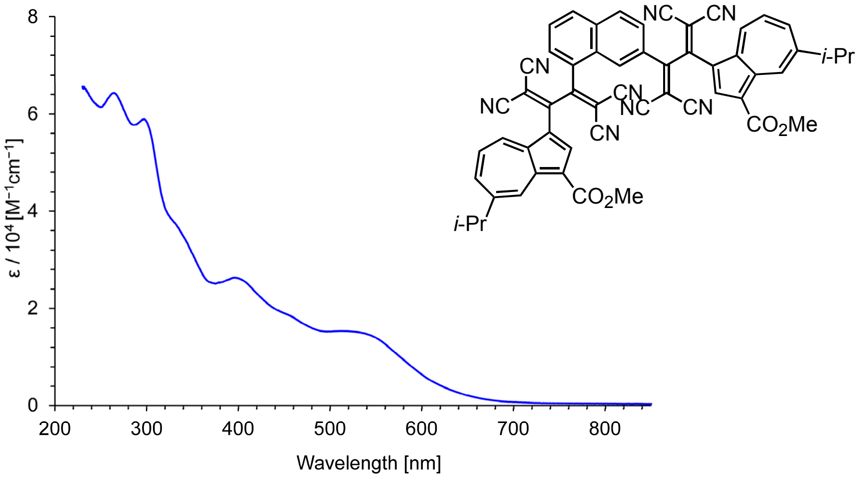


Figure S44. UV/Vis spectrum of **12** in dichloromethane.

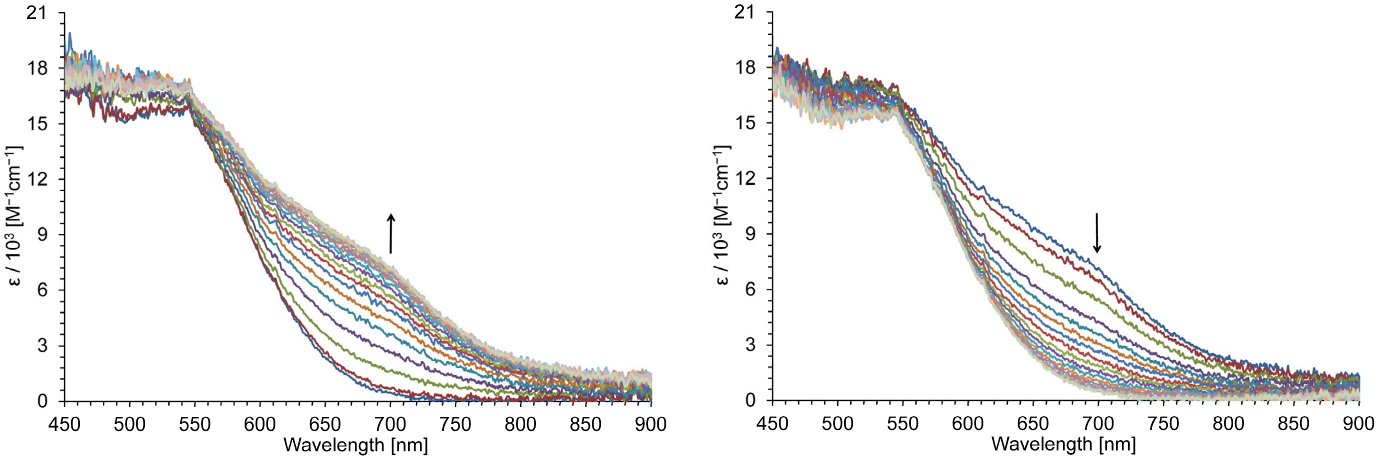


Figure S45. Continuous change in the UV/Vis spectrum of **12**: constant-voltage electrochemical reduction at −0.95 V (left) and reverse oxidation of the reduced species at −0.10 V (right) in benzonitrile containing Et_4NClO_4 (0.1 M) at 30 sec intervals.

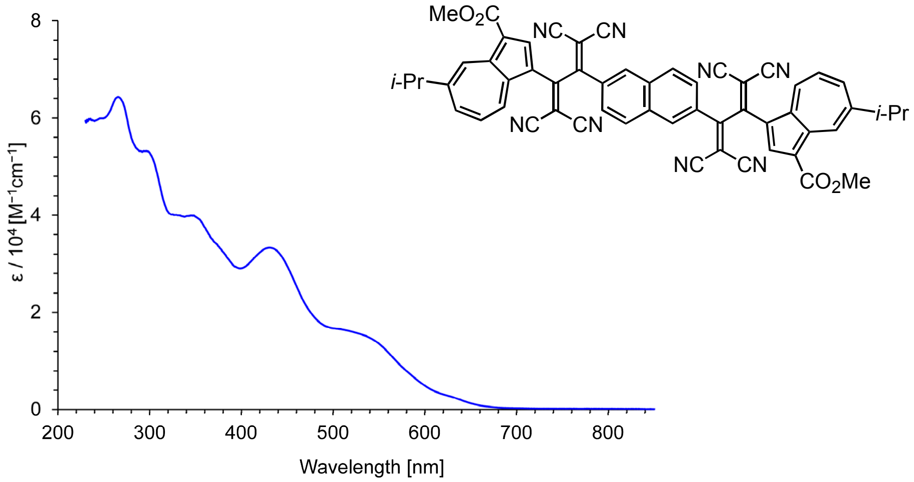


Figure S46. UV/Vis spectrum of **13** in dichloromethane.

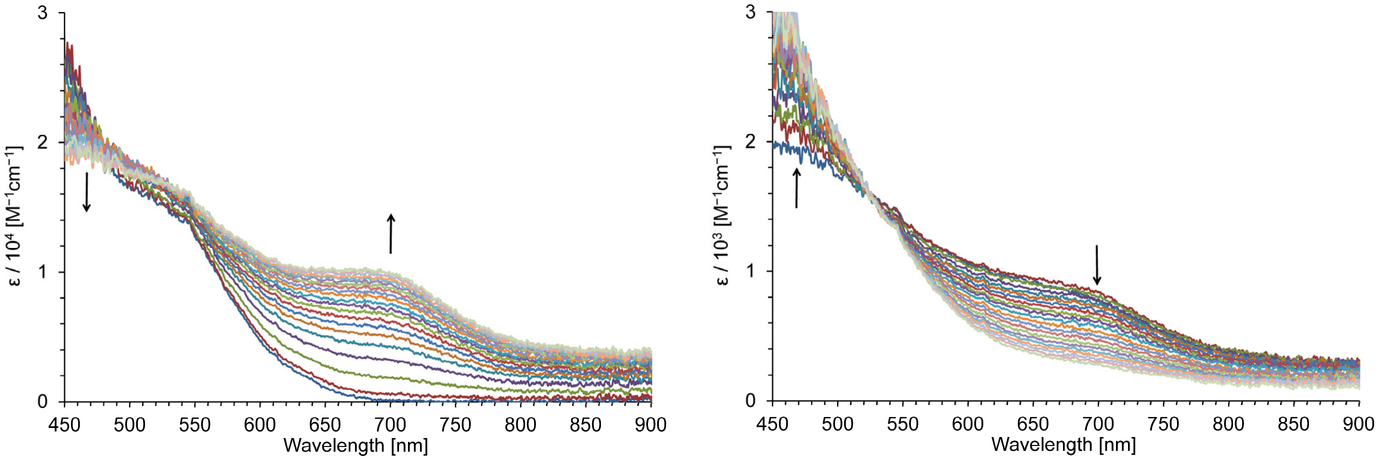


Figure S47. Continuous change in the UV/Vis spectrum of **13**: constant-voltage electrochemical reduction at −0.90 V (left) and reverse oxidation of the reduced species at −0.10 V (right) in benzonitrile containing Et_4NClO_4 (0.1 M) at 30 sec intervals.

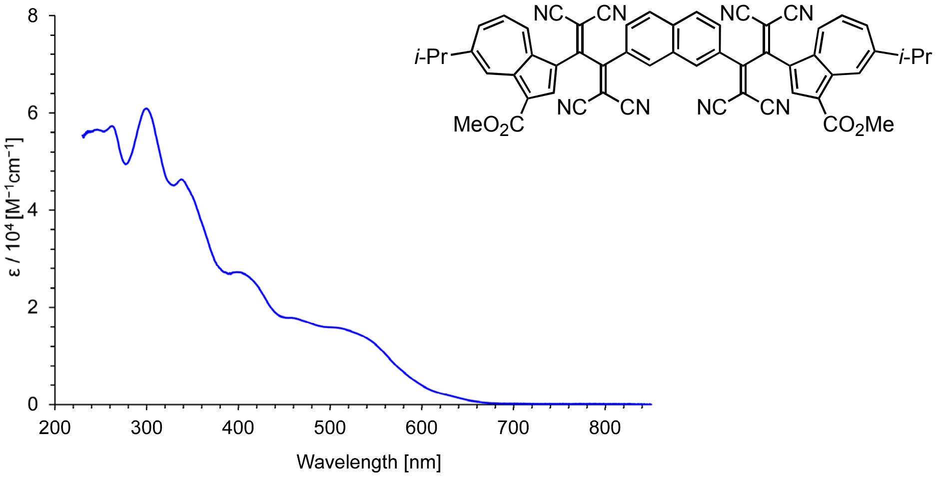


Figure S48. UV/Vis spectrum of **14** in dichloromethane.

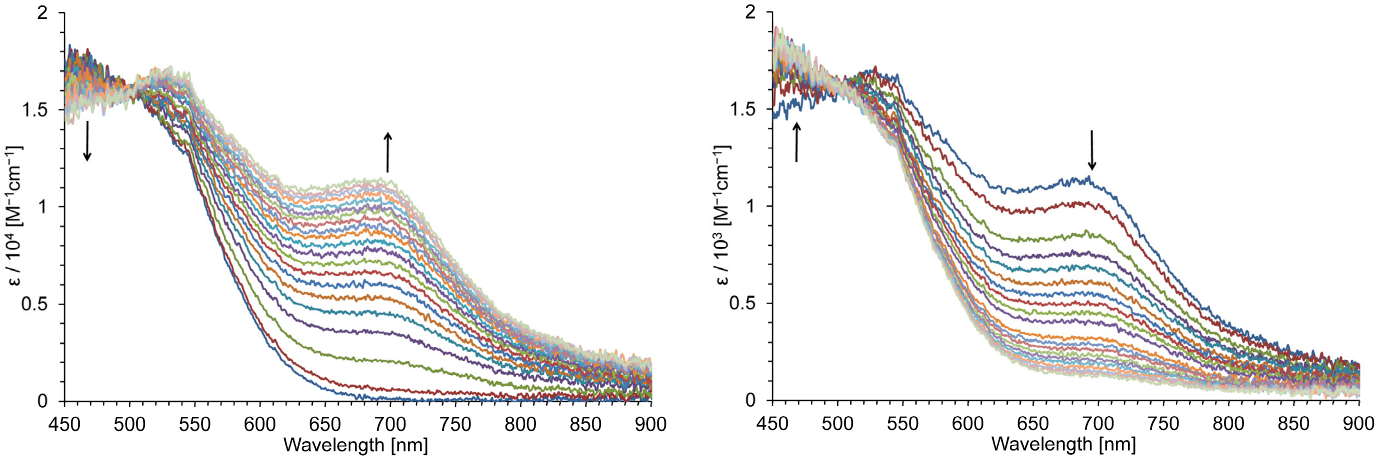


Figure S49. Continuous change in the UV/Vis spectrum of **14**: constant-voltage electrochemical reduction at −0.90 V (left) and reverse oxidation of the reduced species at −0.10 V (right) in benzonitrile containing Et_4NClO_4 (0.1 M) at 30 sec intervals.

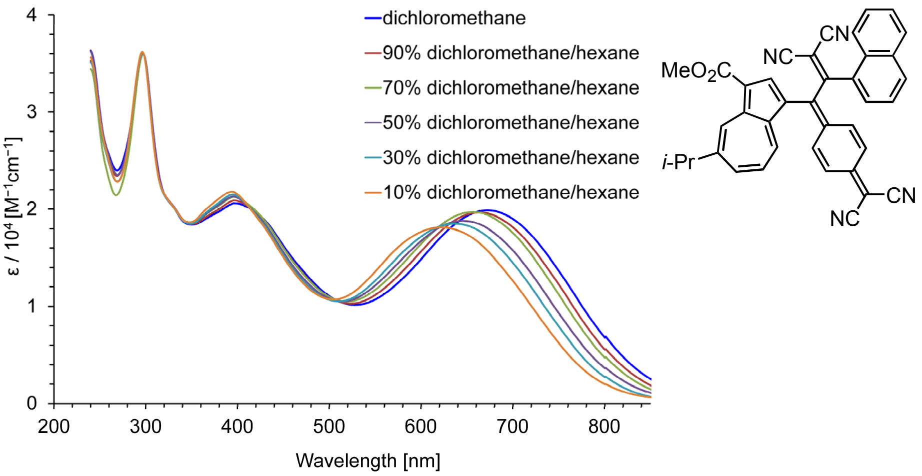


Figure S50. UV/Vis spectrum of **15** in dichloromethane and dichloromethane/hexane.

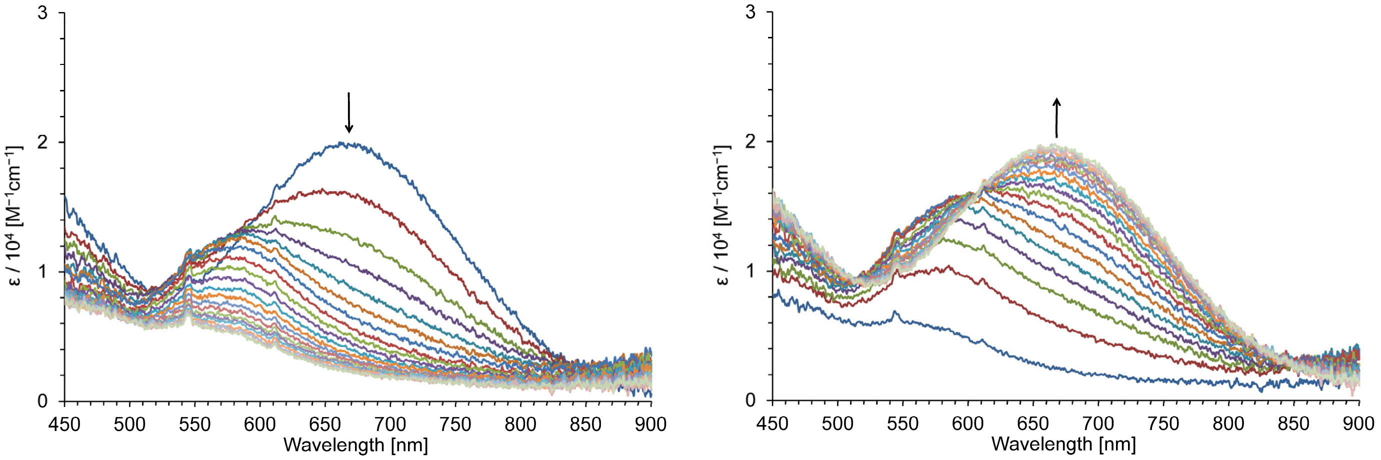


Figure S51. Continuous change in the UV/Vis spectrum of **15**: constant-voltage electrochemical reduction at −1.00 V (left) and reverse oxidation of the reduced species at −0.10 V (right) in benzonitrile containing Et_4NClO_4 (0.1 M) at 30 sec intervals.

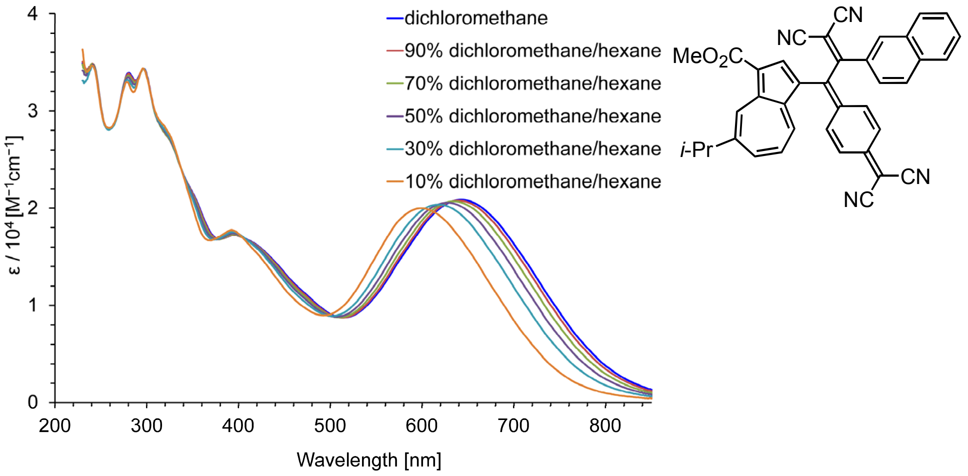


Figure S52. UV/Vis spectrum of **16** in dichloromethane.

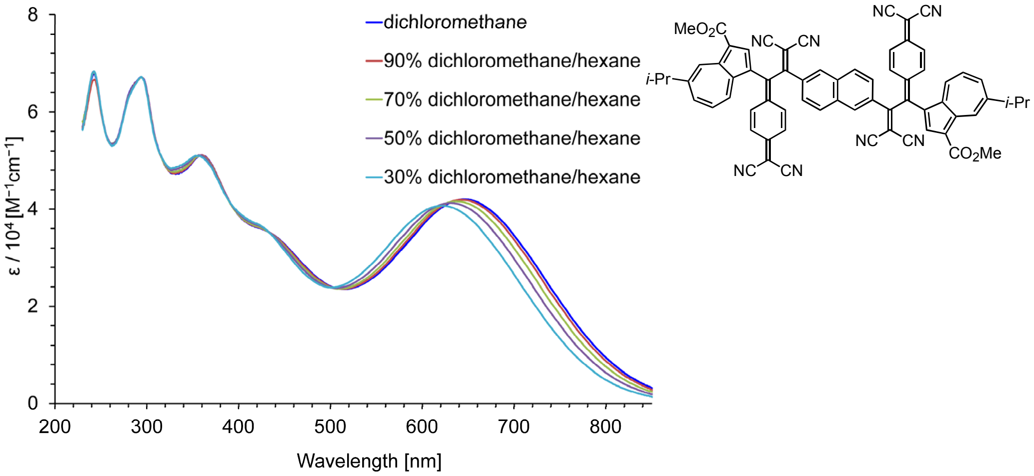


Figure S53. UV/Vis spectrum of **17** in dichloromethane.

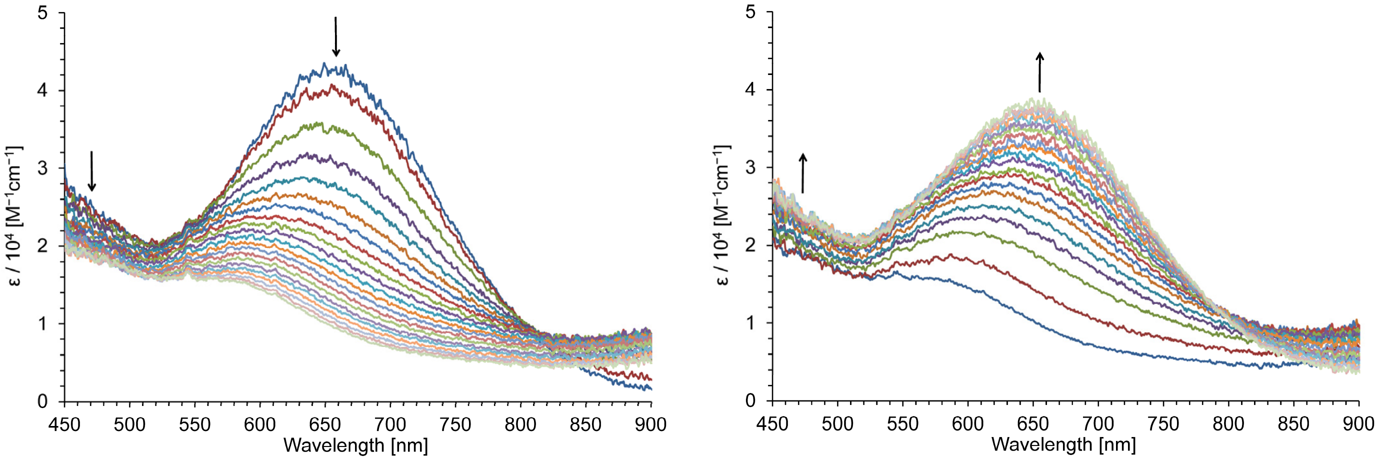


Figure S54. Continuous change in the UV/Vis spectrum of **17**: constant-voltage electrochemical reduction at −1.00 V (left) and reverse oxidation of the reduced species at −0.10 V (right) in benzonitrile containing Et_4NClO_4 (0.1 M) at 30 sec intervals.

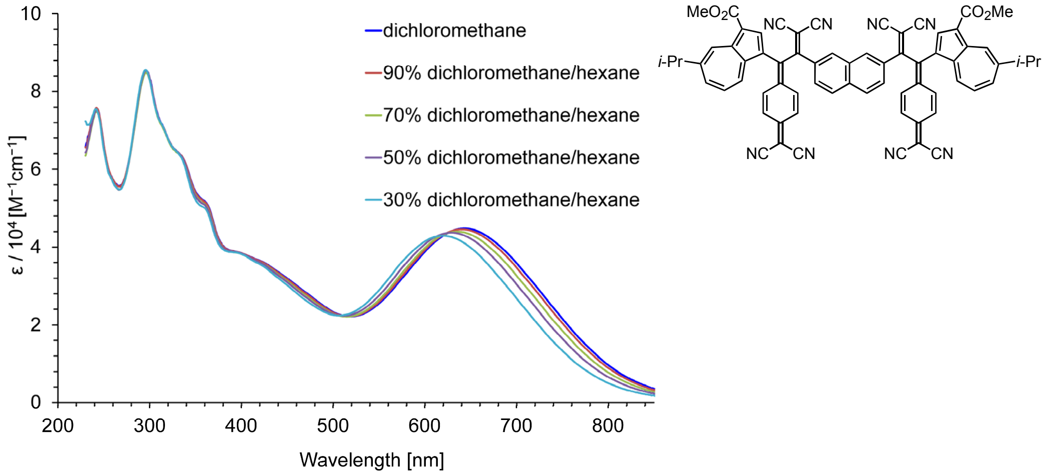


Figure S55. UV/Vis spectrum of **18** in dichloromethane.

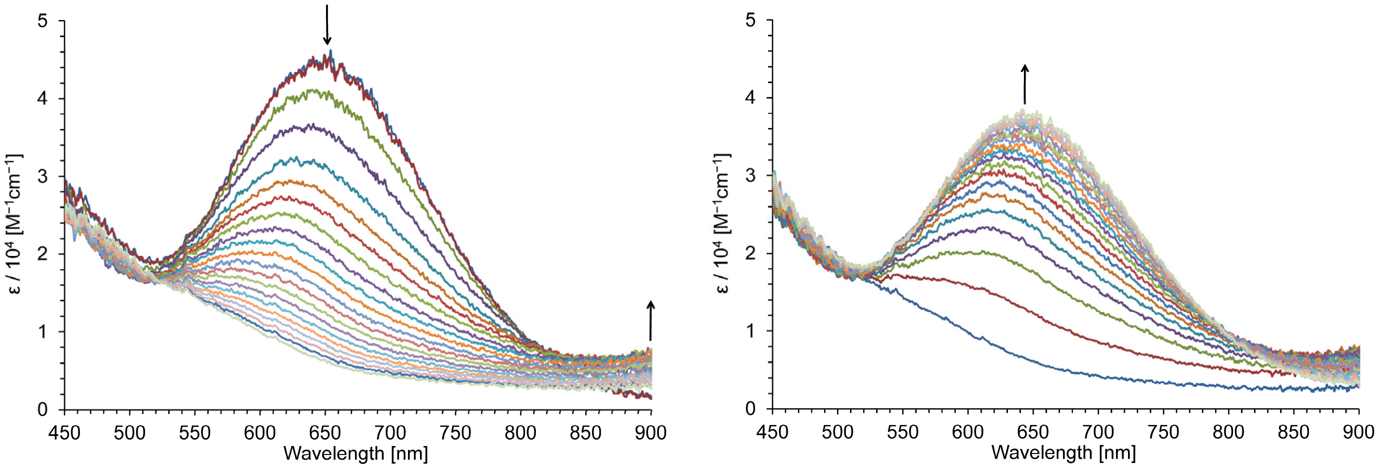


Figure S56. Continuous change in the UV/Vis spectrum of **18**: constant-voltage electrochemical reduction at −1.00 V (left) and reverse oxidation of the reduced species at −0.10 V (right) in benzonitrile containing Et_4NClO_4 (0.1 M) at 30 sec intervals.

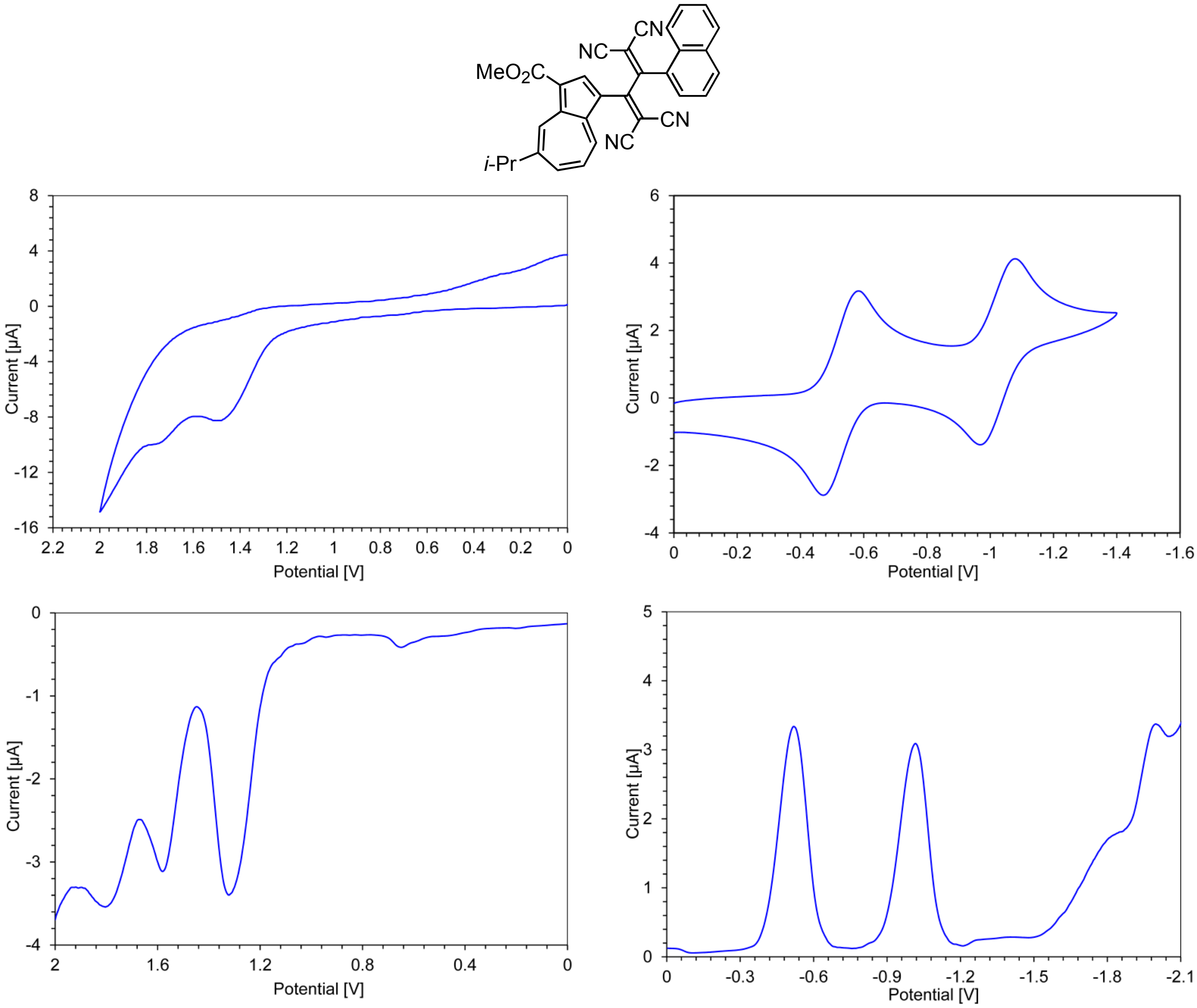


Figure S57. Cyclic voltammogram for oxidation (top, left) and reduction (top, right), and differential pulse voltammograms for oxidation (bottom, left) and reduction (bottom, right) of **9** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as the supporting electrolyte; scan rate: CV = 100 mVs^{-1}, DPV = 20 mVs^{-1}.

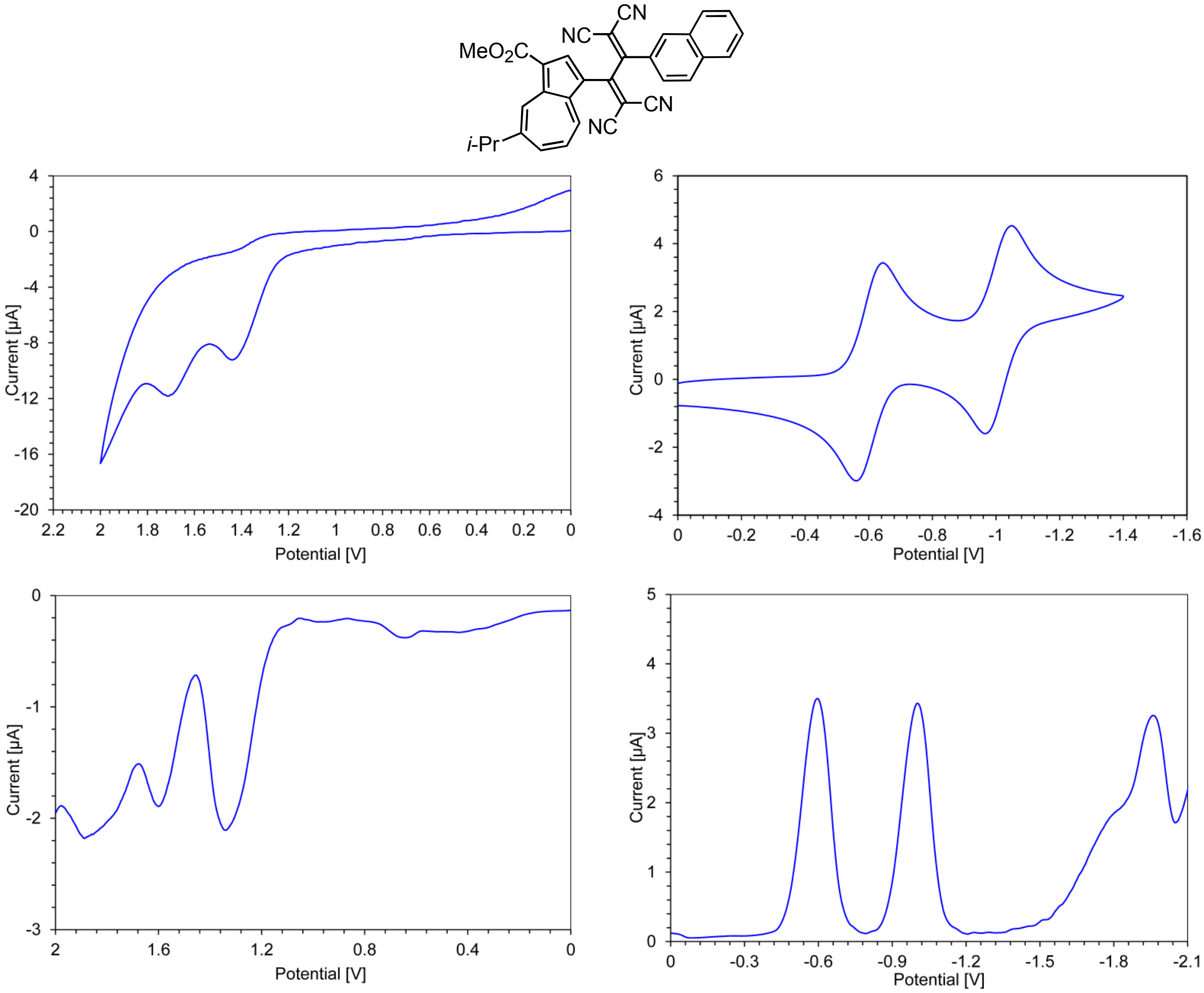
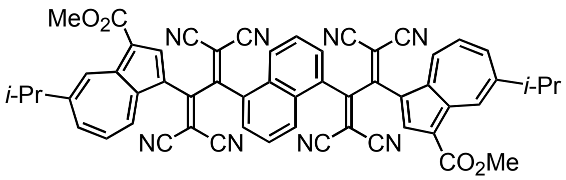


Figure S58. Cyclic voltammogram for oxidation (top, left) and reduction (top, right), and differential pulse voltammograms for oxidation (bottom, left) and reduction (bottom, right) of **10** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as the supporting electrolyte; scan rate: CV = 100 mVs^{-1}, DPV = 20 mVs^{-1}.



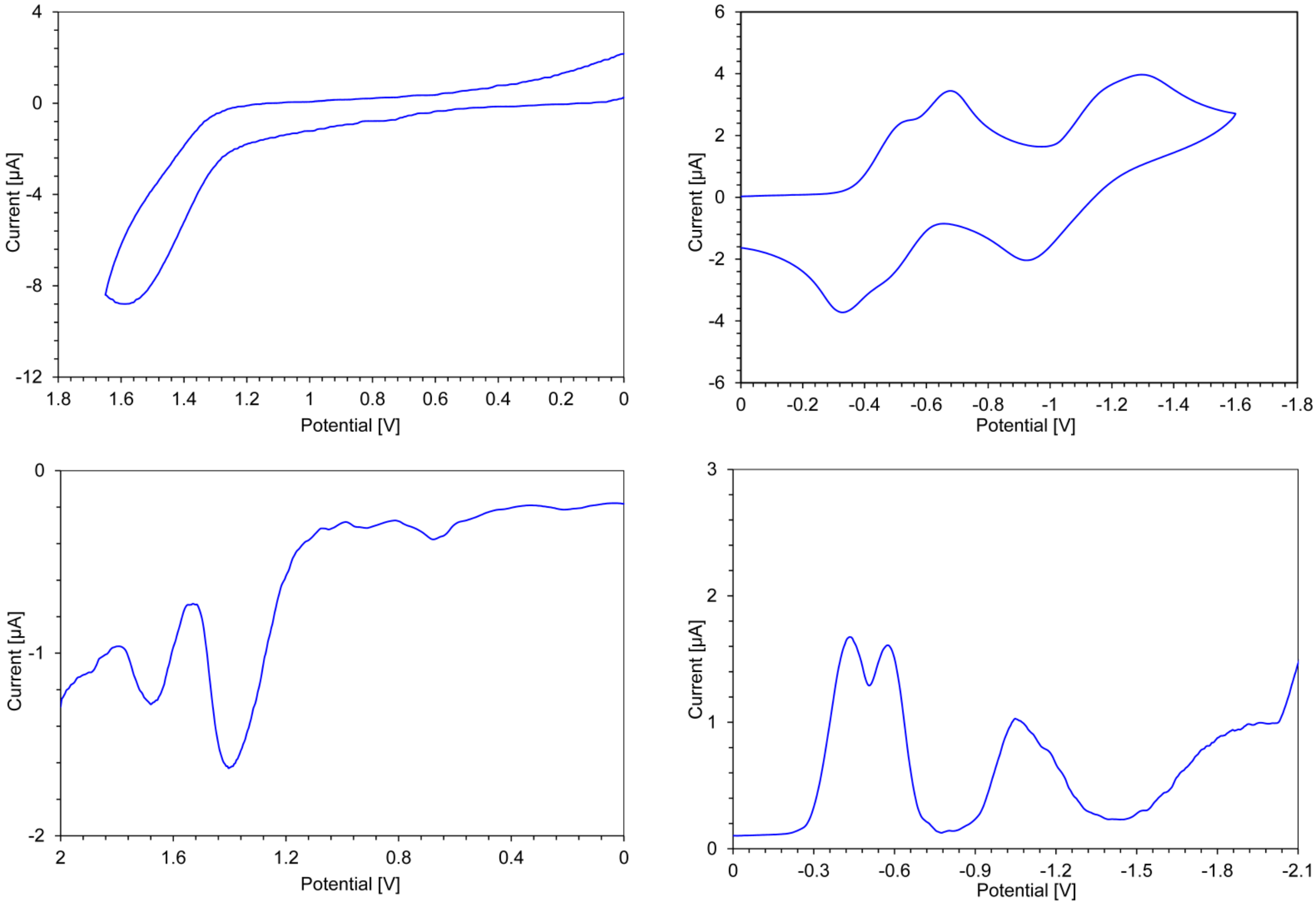
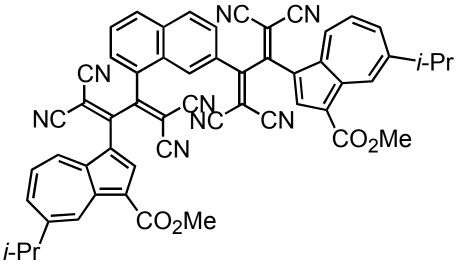


Figure S59. Cyclic voltammogram for oxidation (top, left) and reduction (top, right), and differential pulse voltammograms for oxidation (bottom, left) and reduction (bottom, right) of **11** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as the supporting electrolyte; scan rate: CV = 100 mVs^{-1}, DPV = 20 mVs^{-1}.



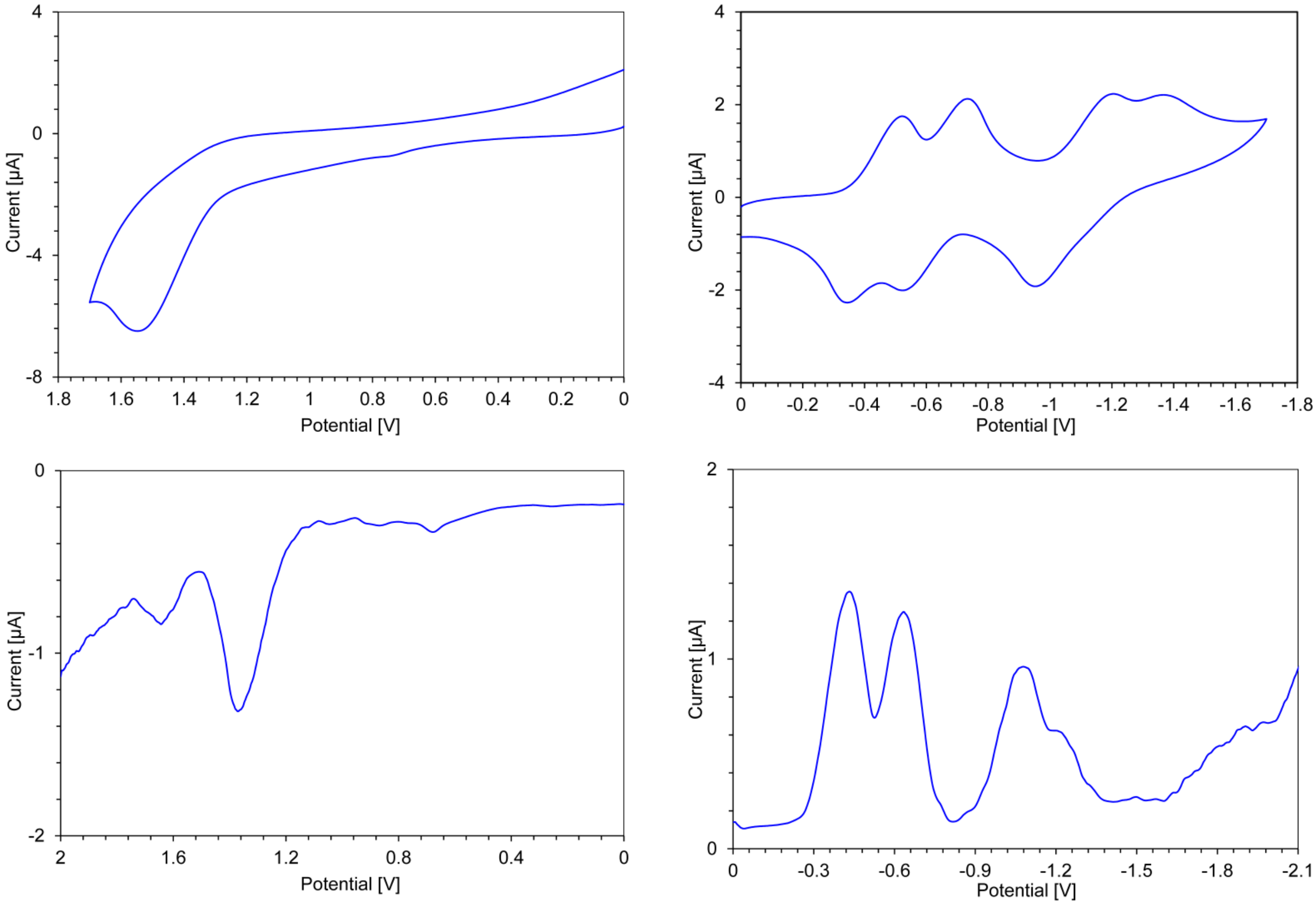


Figure S60. Cyclic voltammogram for oxidation (top, left) and reduction (top, right), and differential pulse voltammograms for oxidation (bottom, left) and reduction (bottom, right) of **12** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as the supporting electrolyte; scan rate: CV = 100 mVs^{-1}, DPV = 20 mVs^{-1}.

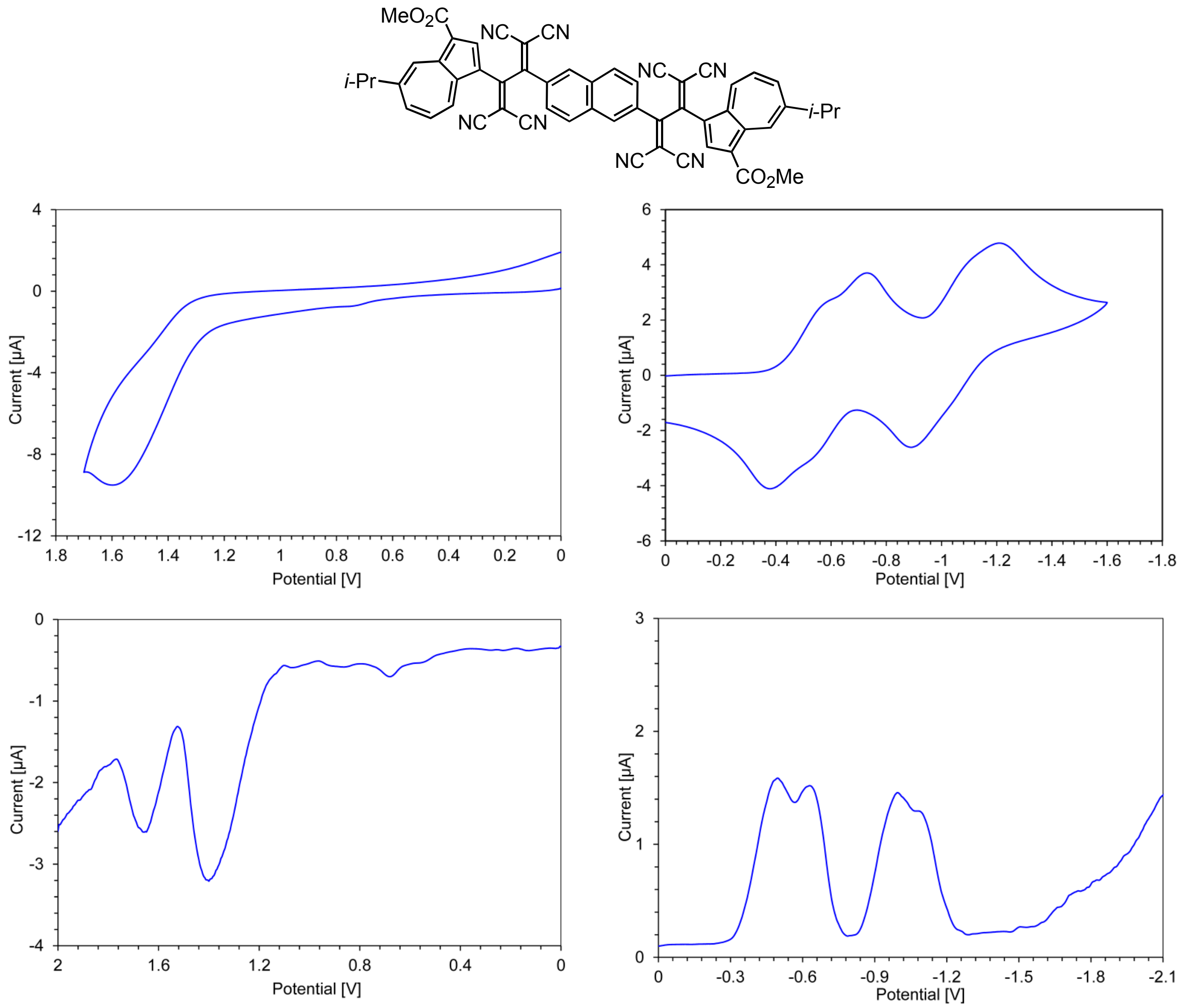


Figure S61. Cyclic voltammogram for oxidation (top, left) and reduction (top, right), and differential pulse voltammograms for oxidation (bottom, left) and reduction (bottom, right) of **13** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as the supporting electrolyte; scan rate: CV = 100 mVs^{-1}, DPV = 20 mVs^{-1}.

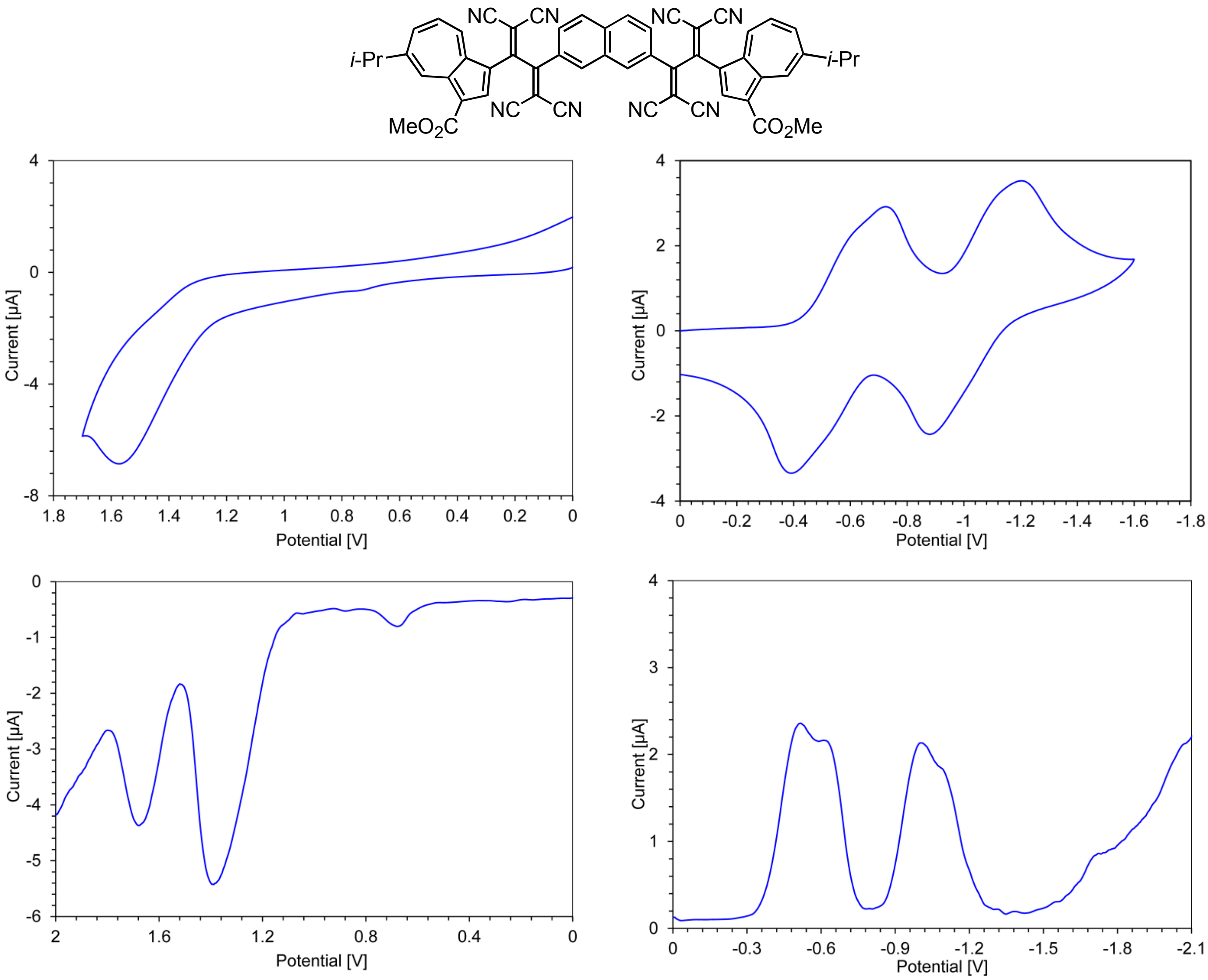


Figure S62. Cyclic voltammogram for oxidation (top, left) and reduction (top, right), and differential pulse voltammograms for oxidation (bottom, left) and reduction (bottom, right) of **14** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as the supporting electrolyte; scan rate: CV = 100 mVs^{-1}, DPV = 20 mVs^{-1}.

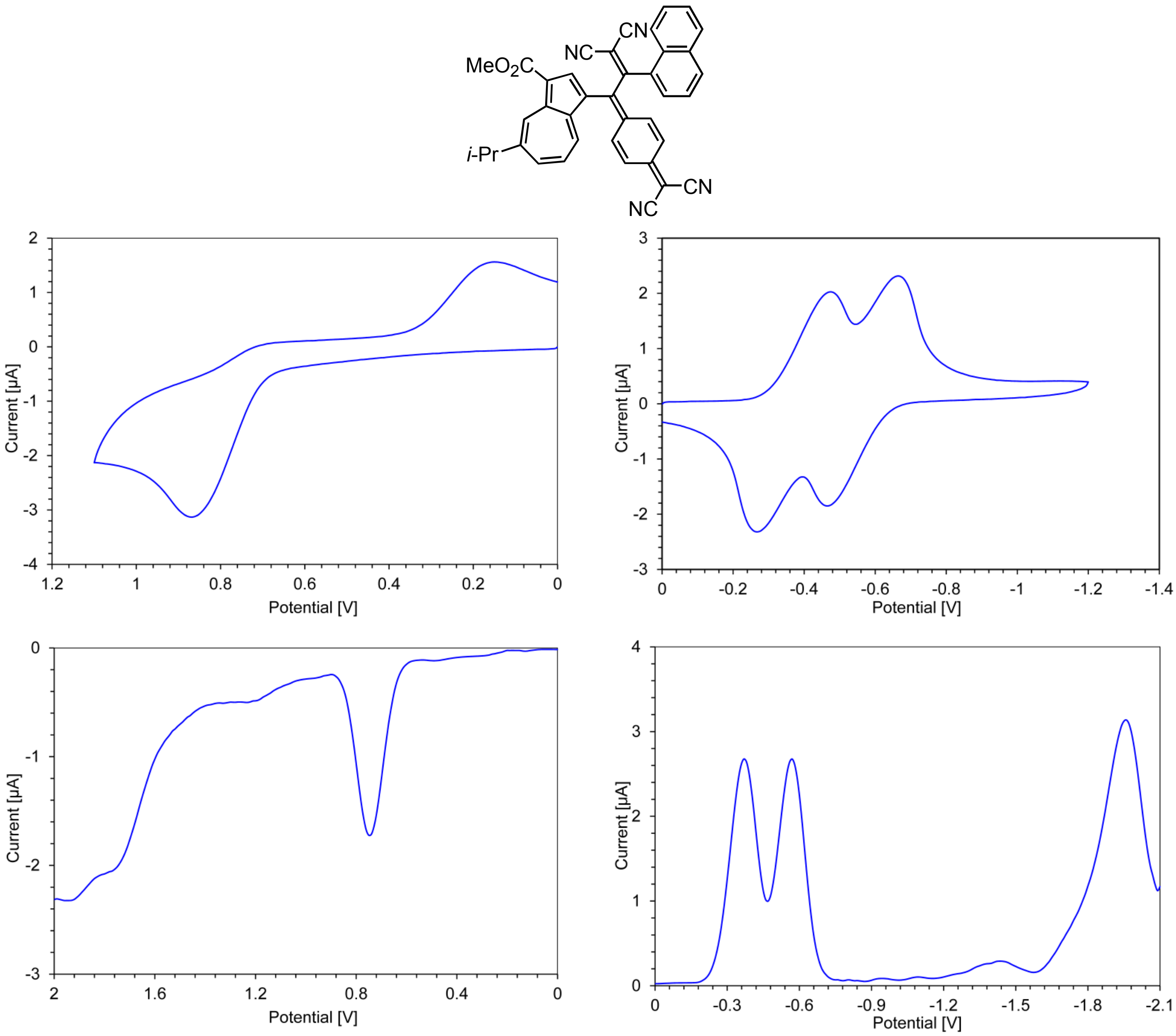
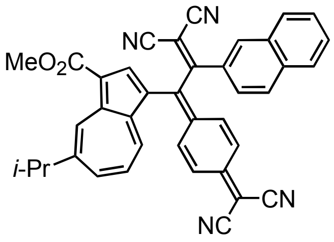


Figure S63. Cyclic voltammogram for oxidation (top, left) and reduction (top, right), and differential pulse voltammograms for oxidation (bottom, left) and reduction (bottom, right) of **15** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as the supporting electrolyte; scan rate: CV = 100 mVs^{-1}, DPV = 20 mVs^{-1}.



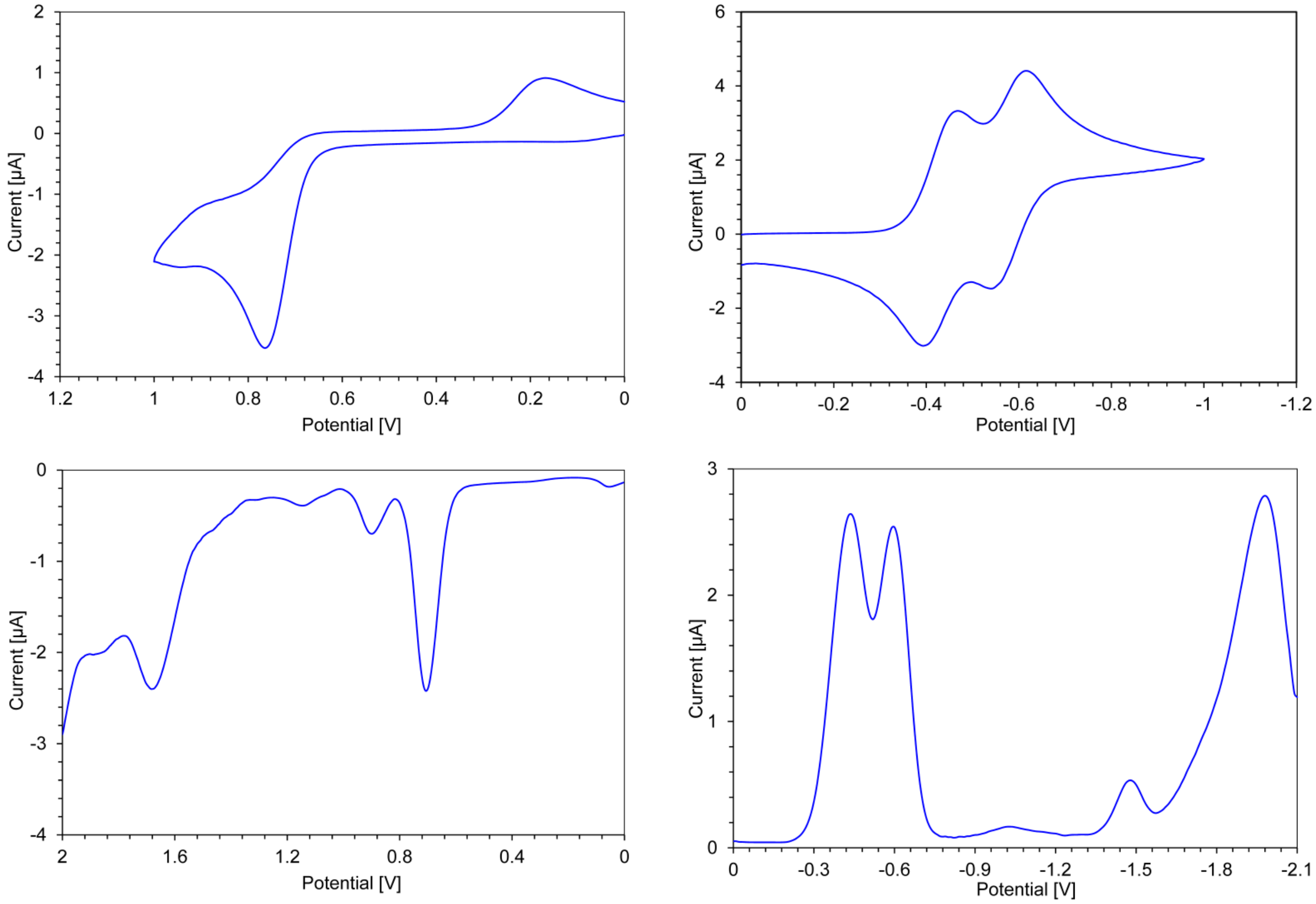


Figure S64. Cyclic voltammogram for oxidation (top, left) and reduction (top, right), and differential pulse voltammograms for oxidation (bottom, left) and reduction (bottom, right) of **16** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as the supporting electrolyte; scan rate: CV = 100 mVs^{-1}, DPV = 20 mVs^{-1}.

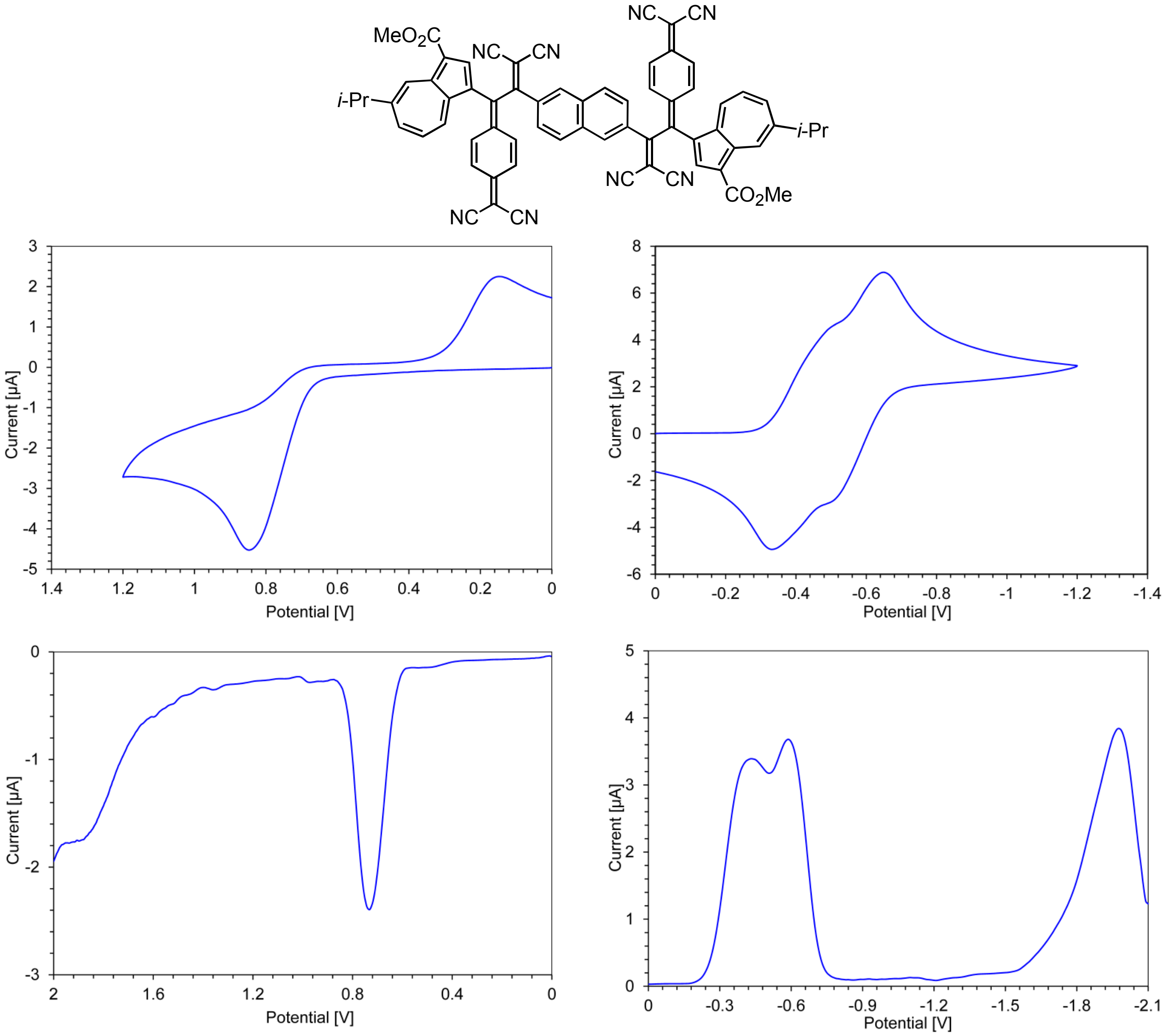


Figure S65. Cyclic voltammogram for oxidation (top, left) and reduction (top, right), and differential pulse voltammograms for oxidation (bottom, left) and reduction (bottom, right) of **17** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as the supporting electrolyte; scan rate: CV = 100 mVs^{-1}, DPV = 20 mVs^{-1}.

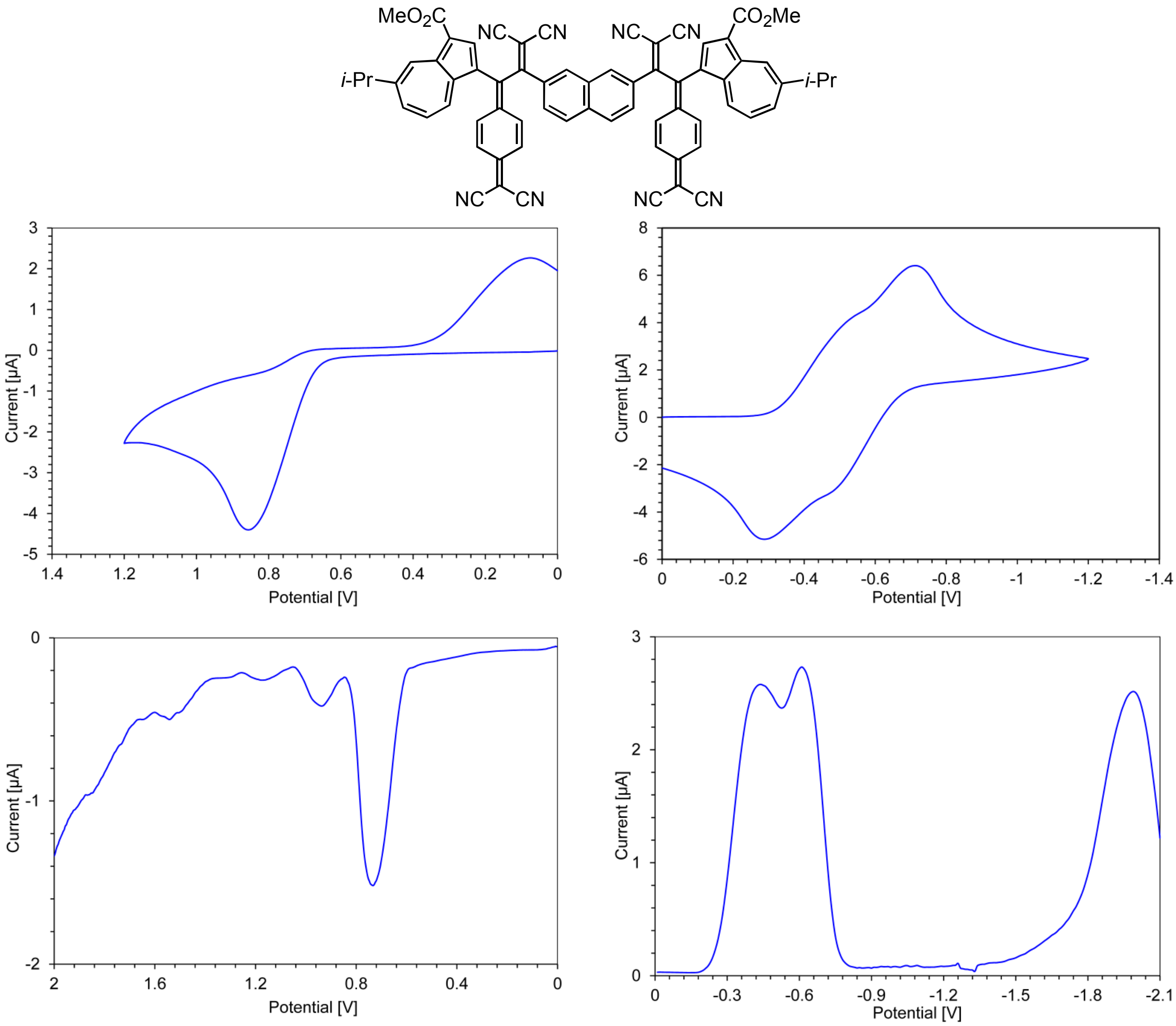
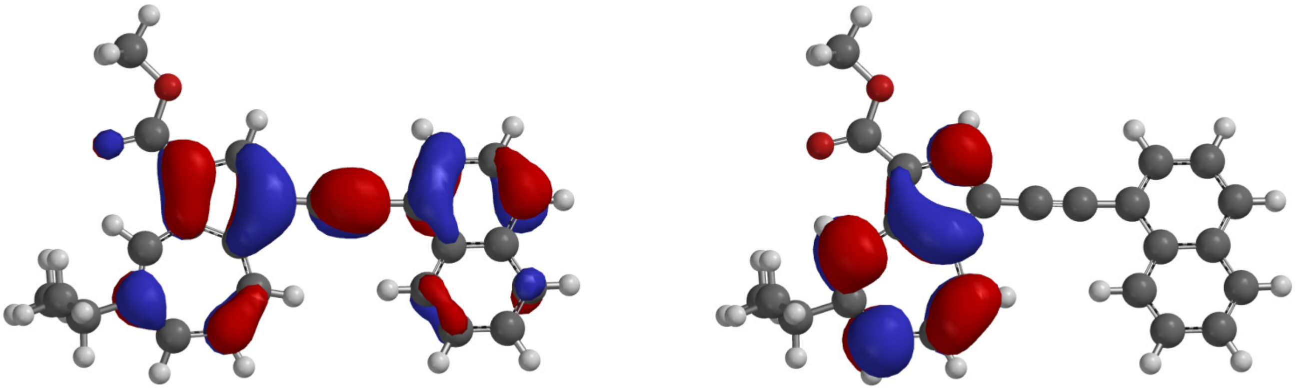
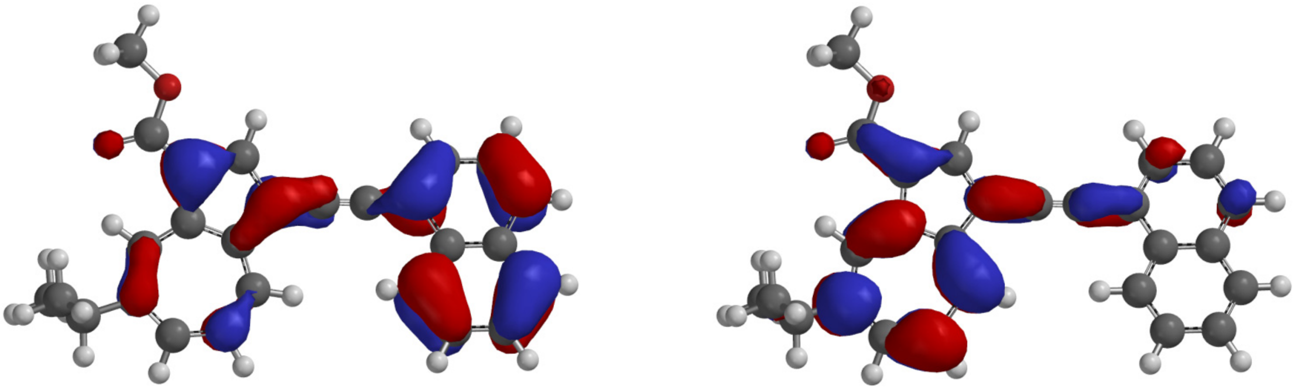


Figure S66. Cyclic voltammogram for oxidation (top, left) and reduction (top, right), and differential pulse voltammograms for oxidation (bottom, left) and reduction (bottom, right) of **18** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as the supporting electrolyte; scan rate: CV = 100 mVs^{-1}, DPV = 20 mVs^{-1}.



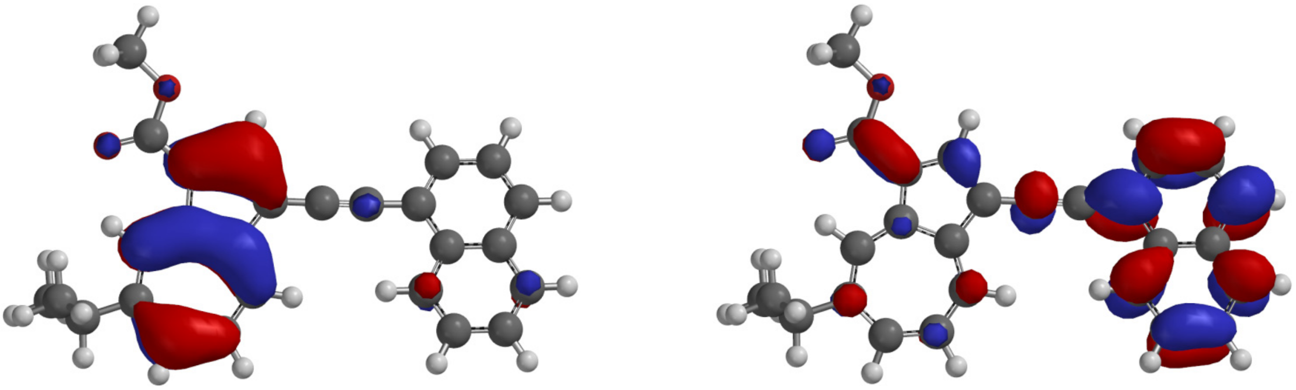
HOMO (−6.75 eV)

LUMO (+0.82 eV)



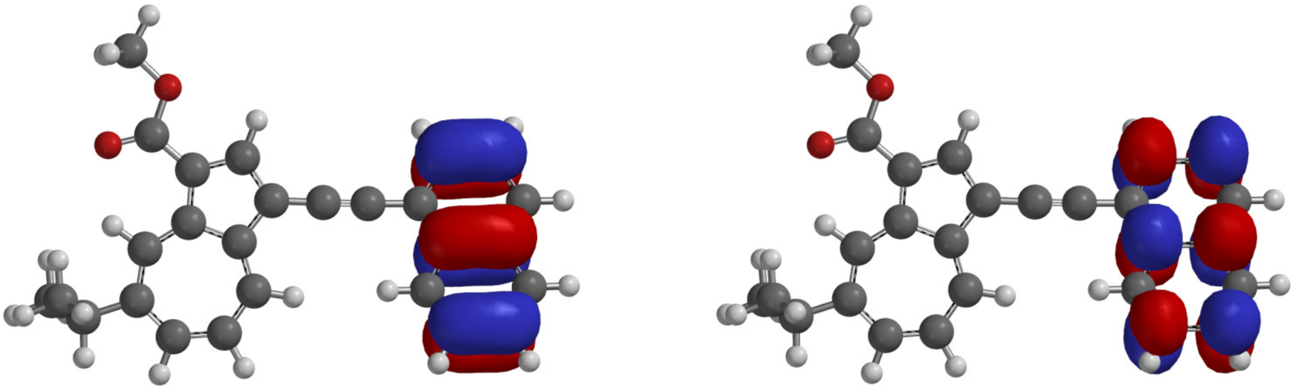
HOMO−1 (−8.10 eV)

LUMO+1 (+1.11 eV)



HOMO−2 (−8.78 eV)

LUMO+2 (+1.98 eV)

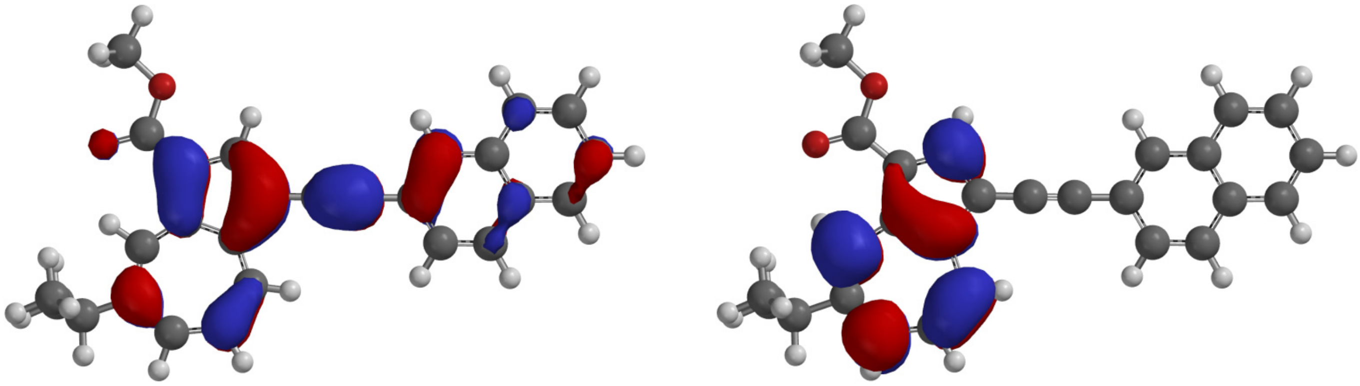


HOMO−3 (−8.87 eV)

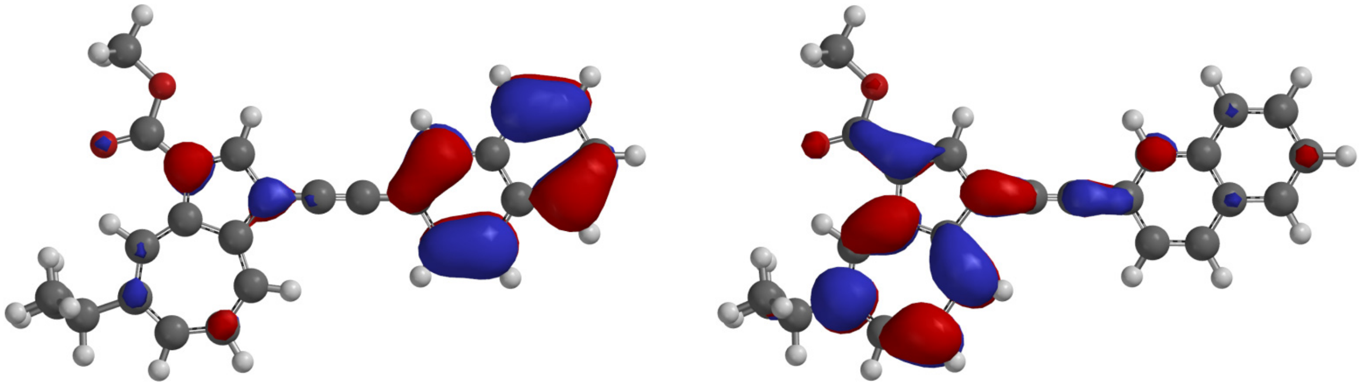
LUMO+3 (+3.23 eV)

Figure S-67. Frontier Kohn-Sham orbitals of **3** at the B3LYP/6-31G** level.

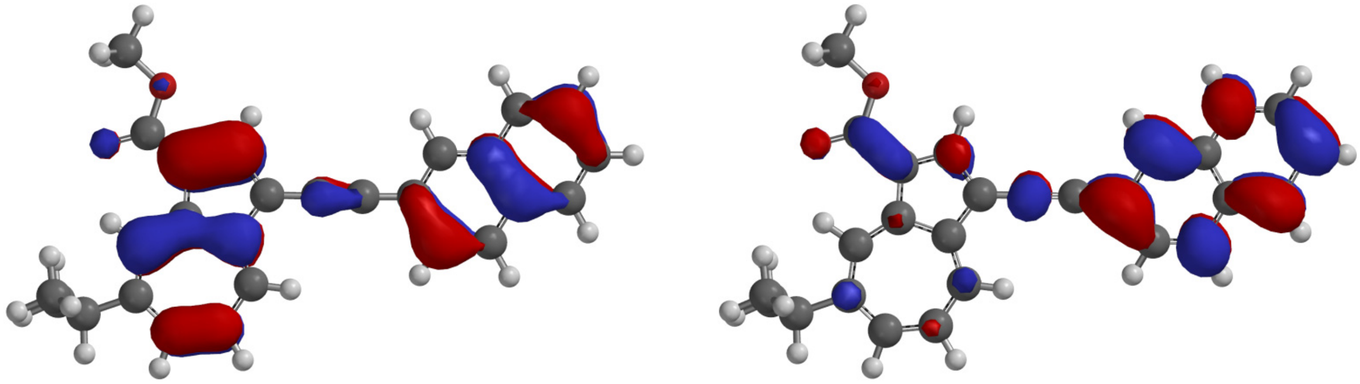
HOMO (−6.49 eV) LUMO (+1.13 eV)



HOMO−1 (−7.81 eV) LUMO+1 (+1.44 eV)



HOMO−2 (−8.33 eV) LUMO+2 (+2.38 eV)



HOMO−3 (−8.68 eV) LUMO+3 (+3.11 eV)

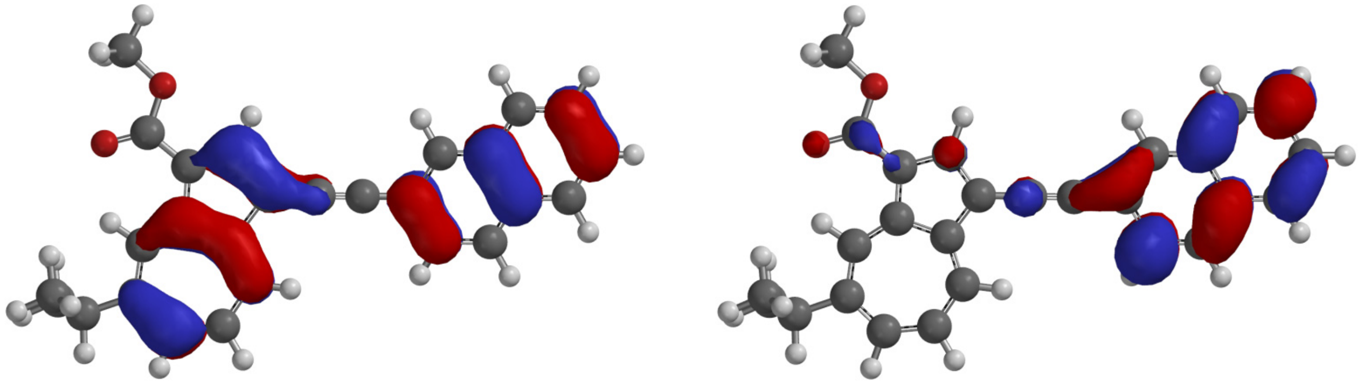
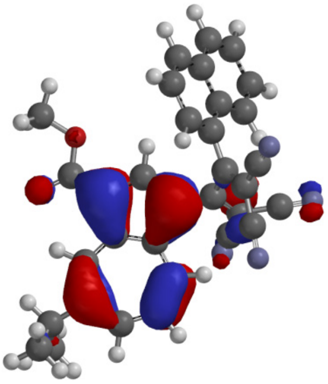
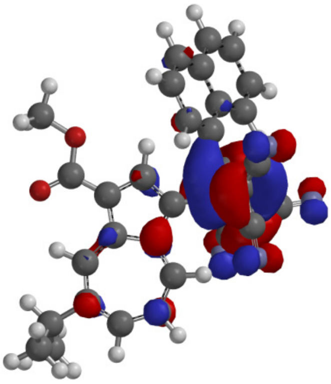


Figure S-68. Frontier Kohn-Sham orbitals of **4** at the B3LYP/6-31G** level.

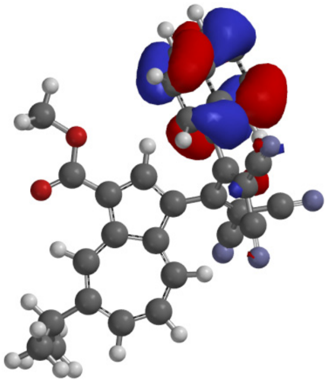
HOMO (−7.68 eV)



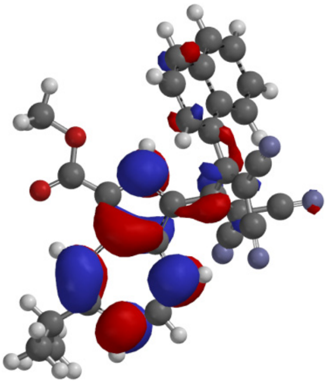
LUMO (−0.04 eV)



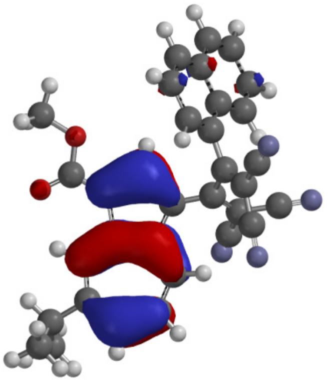
HOMO−1 (−8.43 eV)



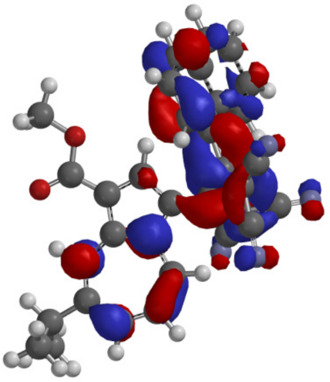
LUMO+1 (+0.75 eV)



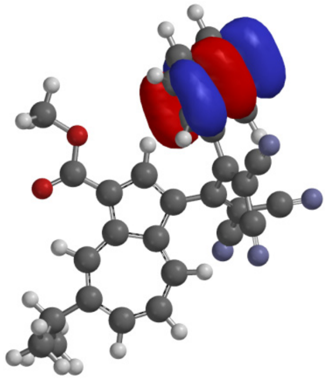
HOMO−2 (−8.96 eV)



LUMO+2 (+0.84 eV)



HOMO−3 (−9.35 eV)



LUMO+3 (+1.61 eV)

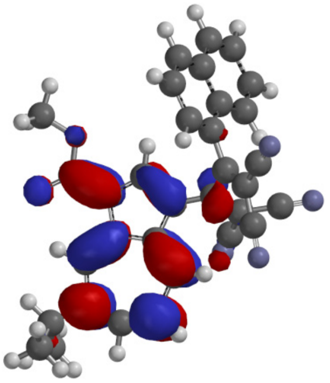
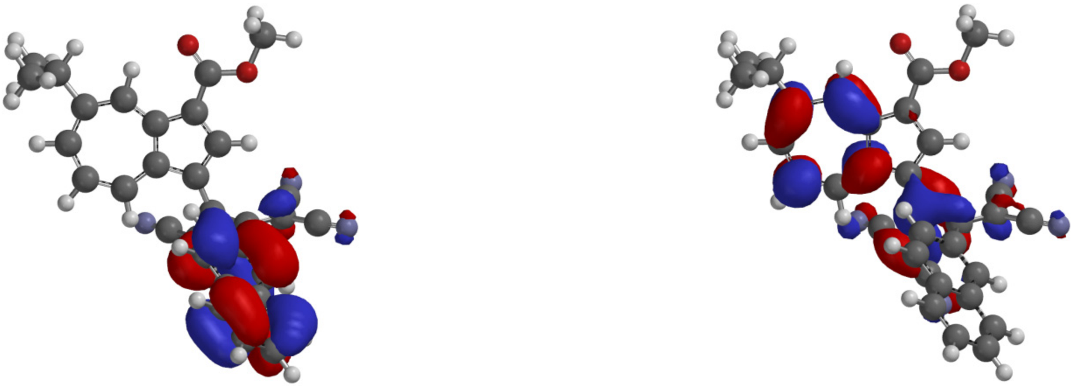


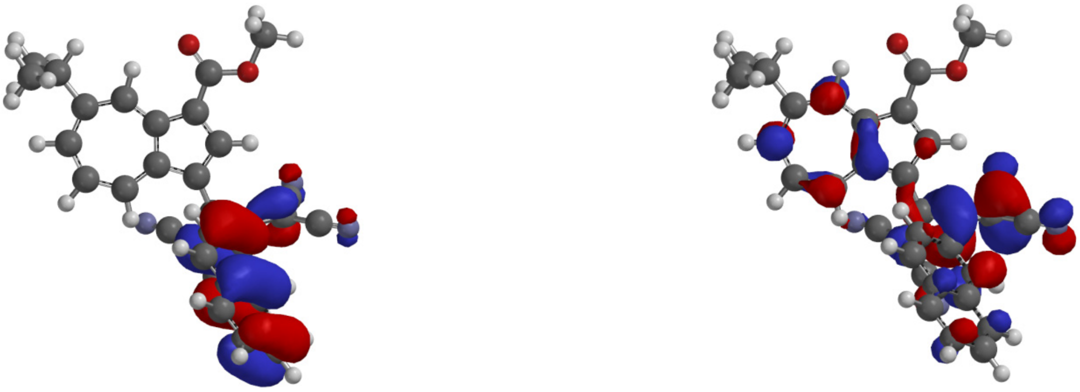
Figure S-69. Frontier Kohn-Sham orbitals of **9** at the B3LYP/6-31G** level.

HOMO (−7.76 eV) LUMO (+0.30 eV)

HOMO−1 (−8.11 eV) LUMO+1 (+0.31 eV)



HOMO−2 (−8.83 eV) LUMO+2 (+0.54 eV)



HOMO−3 (−9.28 eV) LUMO+3 (+1.71 eV)

Figure S-70. Frontier Kohn-Sham orbitals of **10** at the B3LYP/6-31G** level.