# *Electronic Supplementary Information (ESI)*

## Synthesis of 2- and 6-thienylazulenes by palladium-catalyzed direct arylation of 2- and 6-haloazulenes with thiophene derivatives

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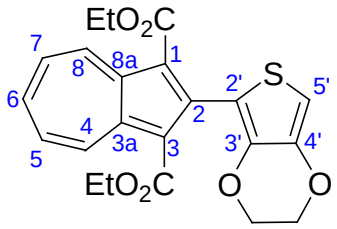
## ➢ *General*

Melting points were determined with a Yanagimoto MPS3 micromelting apparatus, and the solvent in the parenthesis shows the solvent used for recrystallization. The HRMS data were obtained with a JEOL JMS-700 instrument using 3-nitrobenzylalcohol as a matrix of FAB–MS. The IR and UV/Vis spectra were recorded with JASCO FTIR-4100 and Shimadzu UV-2550 spectrophotometers, respectively. The $^{1}$H and $^{13}$C NMR spectra were recorded with a JEOL ECA500 spectrometer at 500 and 125 MHz, respectively. The voltammetry measurements were performed with a BAS 100B/W electrochemical workstation equipped and with a standard three-electrode configuration and all measurements were carried out under an argon atmosphere. Tetraethylammonium perchlorate (0.10 M) in benzonitrile was used as a supporting electrolyte, with a platinum wire auxiliary and disk working electrodes. Reference electrode was formed from Ag/$AgNO_3$ (0.01 M) in acetonitrile containing tetrabutylammonium perchlorate (0.10 M). The half-wave potential of the ferrocene/ferrocenium ion couple ($Fc/Fc^{+}$) under these conditions using this reference electrode was observed at +0.15 V on CV. Accuracy of the reference electrode was confirmed by CV measurements of the couple in each sample as an internal ferrocene standard.

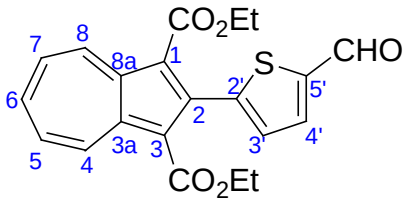
**1,3-Bis(ethoxycarbonyl)-2-(3,4-ethylenedioxythiophen-2-yl)azulene (9)**




To a solution of **2** (307 mg, 1.00 mmol), EDOT (**4**) (284 mg, 2.00 mmol), $PCy_3 \cdot HBF_4$ (37 mg, 0.10 mmol), PivOH (31 mg, 0.30 mmol) and $K_2CO_3$ (207 mg, 1.50 mmol) in toluene (3 mL) was added $Pd(OAc)_2$ (11 mg, 0.05 mmol). The resulting mixture was stirred at 100 °C for 12 h under an Ar atmosphere. The reaction mixture was poured into water and extracted with toluene. The organic layer was washed with brine, dried with $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography with $CH_2Cl_2$ to give **9** (334 mg, 81%, red crystals) and **19** (46 mg, 7%, red crystals).

M.p. 110.0–111.0 °C (EtOH); IR (KBr disk): $\nu_{max}$ = 2979 (w), 2941 (w), 1693 (m), 1678 (s), 1579 (w), 1514 (m), 1479 (w), 1432 (m), 1418 (m), 1386 (w), 1371 (m), 1354 (w), 1314 (w), 1302 (w), 1272 (w), 1256 (w), 1244 (w), 1185 (s), 1153 (m), 1114 (w), 1065 (s), 1030 (m), 992 (w), 977 (w), 934 (w), 909 (m), 885 (w), 859 (w), 800 (w), 789 (m), 740 (w), 713 (w), 699 (w), 670 (w), 661 (w) $cm^{-1}$; UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ (log ε) = 236 (4.44), 274 sh (4.44), 291 (4.57), 342 (4.29), 419 (3.81), 528 (2.79) nm; $^1H$ NMR (500 MHz, $CDCl_3$): $\delta_H$ = 9.46 (d, 2H, *J* = 10.0 Hz, 4,8-H), 7.86 (t, 1H, *J* = 10.0 Hz, 6-H), 7.64 (t, 2H, *J* = 10.0 Hz, 5,7-H), 6.50 (s, 1H, 5'-H of Th), 4.26 (q, 4H, *J* = 7.0 Hz, $CO_2Et$), 4.19–4.16 (m, 4H, $OCH_2CH_2O$), 1.19 (t, 6H, *J* = 7.0 Hz, $CO_2Et$) ppm; $^{13}C$ NMR (125 MHz, $CDCl_3$): $\delta_C$ = 165.64 ($CO_2Et$), 143.66 (C-2), 142.34 (C-3a,8a), 140.89 (C-3' or C-4' of Th), 140.39 (C-6), 138.88 (C-3' or C-4' of Th), 138.61 (C-4,8), 130.12 (C-5,7), 118.33 (C-1,3), 113.16 (C-2' of Th), 99.98 (C-5' of Th), 64.88 ($OCH_2$), 64.74 ($OCH_2$), 60.31 ($CO_2Et$), 14.18 ($CO_2Et$) ppm; HR-EI-MS: calcd for $C_{22}H_{20}O_6S^+$ $[M]^+$ 412.0981; found: 412.0985.

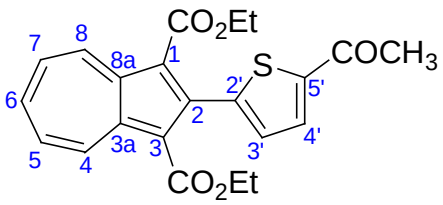
**1,3-Bis(ethoxycarbonyl)-2-(5'-formylthiophen-2'-yl)azulene (10)**




To a solution of **2** (307 mg, 1.00 mmol), 2-formylthiophene (**5**) (224 mg, 2.00 mmol), $PCy_3 \cdot HBF_4$ (37 mg, 0.10 mmol), PivOH (31 mg, 0.30 mmol) and $K_2CO_3$ (207 mg, 1.50 mmol) in toluene (3 mL) was added $Pd(OAc)_2$ (11 mg, 0.05 mmol). The resulting mixture was stirred at 100 °C for 12 h under an Ar atmosphere. The reaction mixture was poured into water and extracted with toluene. The organic layer was washed with brine, dried with $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography with $CH_2Cl_2$ to give **10** (345 mg, 90%) as red crystals.

M.p. 108.0–109.0 °C (EtOH); IR (KBr disk): $\nu_{max}$ = 2980 (w), 2802 (w), 1674 (s), 1659 (s), 1532 (w), 1486 (w), 1460 (w), 1427 (s), 1408 (s), 1380 (w), 1354 (w), 1315 (w), 1294 (w), 1254 (m), 1234 (m), 1222 (m), 1197 (m), 1182 (m), 1132 (w), 1091 (w), 1055 (m), 1031 (w), 982 (w), 947 (w), 908 (w), 886 (w), 868 (w), 823 (w), 796 (w), 755 (w), 745 (w), 705 (w), 687 (w), 666 (w), 658 (w) $cm^{-1}$; UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ (log ε) = 236 (4.45), 272 (4.38), 296 sh (4.55), 307 (4.65), 328 (4.45), 364 sh (4.05), 525 (2.86) nm; $^1H$ NMR (500 MHz, $CDCl_3$): $\delta_H$ = 9.96 (s, 1H, CHO), 9.69 (d, 2H, *J* = 10.0 Hz, 4,8-H), 8.01 (t, 1H, *J* = 10.0 Hz, 6-H), 7.79–7.75 (m, 3H, 5,7-H and 4'-H of Th), 7.10 (d, 1H, *J* = 3.5 Hz, 3'-H of Th), 4.17 (q, 4H, *J* = 7.0 Hz, $CO_2Et$), 1.04 (t, 6H, *J* = 7.0 Hz, $CO_2Et$) ppm; $^{13}C$ NMR (125 MHz, $CDCl_3$): $\delta_C$ = 182.98 (CHO), 164.92 ($CO_2Et$), 150.55 (C-5' of Th), 145.33 (C-2), 143.77 (C-2' of Th), 142.57 (C-3a,8a), 141.73 (C-6), 140.17 (C-4,8), 135.65 (C-4' of Th), 131.05 (C-5,7), 128.56 (C-3' of Th), 117.86 (C-1,3), 60.39 ($CO_2Et$), 13.84 ($CO_2Et$) ppm; HR-EI-MS: calcd for $C_{21}H_{18}O_5S^+$ $[M]^+$ 382.0875; found: 382.0869.

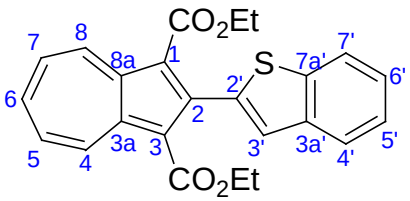
**1,3-Bis(ethoxycarbonyl)-2-(5'-acetylthiophen-2'-yl)azulene (11)**




To a solution of **2** (307 mg, 1.00 mmol), 2-acetylthiophene (**6**) (252 mg, 2.00 mmol), $PCy_3 \cdot HBF_4$ (37 mg, 0.10 mmol), PivOH (31 mg, 0.30 mmol) and $K_2CO_3$ (207 mg, 1.50 mmol) in toluene (3 mL) was added $Pd(OAc)_2$ (11 mg, 0.05 mmol). The resulting mixture was stirred at 100 °C for 12 h under an Ar atmosphere. The reaction mixture was poured into water and extracted with toluene. The organic layer was washed with brine, dried with $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography with $CH_2Cl_2$ to give **11** (351 mg, 89%) as red crystals.

M.p. 102.0–104.0 °C (MeOH); IR (KBr disk): $\nu_{max}$ = 2983 (w), 2898 (w), 1692 (s), 1671 (m), 1655 (s), 1581 (w), 1530 (w), 1478 (w), 1453 (w), 1432 (s), 1406 (s), 1368 (w), 1354 (w), 1317 (w), 1275 (m), 1250 (m), 1214 (m), 1190 (s), 1122 (w), 1072 (w), 1060 (m), 1028 (m), 973 (w), 929 (w), 883 (w), 815 (w), 795 (m), 760 (w), 747 (w), 732 (w), 722 (w), 701 (w), 684 (w), 663 (w) $cm^{-1}$; UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ (log ε) = 236 (4.44), 274 (4.35), 296 sh (4.57), 306 (4.64), 333 (4.40), 363 sh (4.03), 514 (2.85) nm; $^1H$ NMR (500 MHz, $CDCl_3$): $\delta_H$ = 9.64 (d, 2H, *J* = 10.0 Hz, 4,8-H), 7.99 (t, 1H, *J* = 10.0 Hz, 6-H), 7.76 (t, 2H, *J* = 10.0 Hz, 5,7-H), 7.69 (d, 1H, *J* = 3.5 Hz, 4'-H of Th), 7.03 (d, 1H, *J* = 3.5 Hz, 3'-H of Th), 4.18 (q, 4H, *J* = 7.0 Hz, $CO_2Et$), 2.59 (s, 3H, $COCH_3$), 1.06 (t, 6H, *J* = 7.0 Hz, $CO_2Et$) ppm; $^{13}C$ NMR (125 MHz, $CDCl_3$): $\delta_C$ = 190.76 ($COCH_3$), 165.05 ($CO_2Et$), 148.57 (C-5' of Th), 145.75 (C-2), 144.28 (C-2' of Th), 142.46 (C-3a,8a), 141.49 (C-6), 139.93 (C-4,8), 131.70 (C-4' of Th), 130.87 (C-5,7), 128.38 (C-3' of Th), 118.01 (C-1,3), 60.39 ($CO_2Et$), 26.95 ($CO_2Et$), 13.90 ($COCH_3$) ppm; HR-EI-MS: calcd for $C_{22}H_{20}O_5S^+$ $[M]^+$ 396.1031; found: 396.1036.

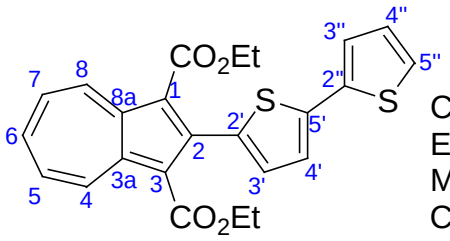
**1,3-Bis(ethoxycarbonyl)-2-(benzothiopen-2'-yl)azulene (12)**




To a solution of **2** (307 mg, 1.00 mmol), benzothiophene (**7**) (268 mg, 2.00 mmol), $PCy_3 \cdot HBF_4$ (37 mg, 0.10 mmol), PivOH (31 mg, 0.30 mmol) and $K_2CO_3$ (207 mg, 1.50 mmol) in toluene (3 mL) was added $Pd(OAc)_2$ (11 mg, 0.05 mmol). The resulting mixture was stirred at 100 °C for 12 h under an Ar atmosphere. The reaction mixture was poured into water and extracted with toluene. The organic layer was washed with brine, dried with $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography with $CH_2Cl_2$ to give **12** (353 mg, 87%) as red crystals.

M.p. 110.0–111.0 °C ($CHCl_3$/EtOH); IR (KBr disk): $\nu_{max}$ = 2984 (w), 2898 (w), 1672 (s), 1656 (w), 1536 (w), 1454 (m), 1427 (s), 1411 (m), 1380 (w), 1348 (w), 1312 (w), 1293 (w), 1256 (m), 1217 (m), 1197 (m), 1178 (m), 1158 (w), 1134 (w), 1113 (m), 1069 (w), 1057 (m), 1031 (m), 969 (w), 934 (w), 886 (w), 834 (w), 790 (w), 744 (s), 726 (w), 705 (w), 689 (w), 666 (w), 652 (w) $cm^{-1}$; UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ (log ε) = 235 (4.67), 274 sh (4.47), 298 (4.68), 330 (4.28), 364 sh (4.00), 392 (3.61), 522 (2.82) nm; $^1H$ NMR (500 MHz, $CDCl_3$): $\delta_H$ = 9.62 (d, 2H, *J* = 10.0 Hz, 4,8-H), 7.98 (t, 1H, *J* = 10.0 Hz, 6-H), 7.84 (d, 1H, *J* = 7.5 Hz, 7'-H of BzTh), 7.77 (d, 1H, *J* = 7.5 Hz, 4'-H of BzTh), 7.75 (t, 2H, *J* = 10.0 Hz, 5,7-H), 7.69 (dd, 1H, *J* = 7.5, 7.5 Hz, 5'-H of BzTh), 7.32 (dd, 1H, *J* = 7.5, 7.5 Hz, 6'-H of BzTh), 7.23 (s, 1H, 3'-H of BzTh), 4.15 (q, 4H, *J* = 7.5 Hz, $CO_2Et$), 0.88 (t, 6H, *J* = 7.5 Hz, $CO_2Et$) ppm; $^{13}C$ NMR (125 MHz, $CDCl_3$): $\delta_C$ = 165.47 ($CO_2Et$), 146.90 (C-2'), 142.43 (C-3a',7a' of BzTh), 141.01 (C-3a,8a), 140.95 (C-2 or C-6), 139.83 (C-2 or C-6), 139.46 (C-4,8), 130.55 (C-5,7), 124.10 (C-3' of BzTh), 123.89 (C-5' and C-6' of BzTh), 123.44 (C-4' of BzTh), 121.83 (C-7' of BzTh), 118.42 (C-1,3), 60.34 ($CO_2Et$), 13.71 ($CO_2Et$) ppm; HR-EI-MS: calcd for $C_{24}H_{20}O_4S^+$ $[M]^+$ 404.1082; found: 404.1089.

**1,3-Bis(ethoxycarbonyl)-2-(5',2"-bithiophen-2'-yl)azulene (13)**

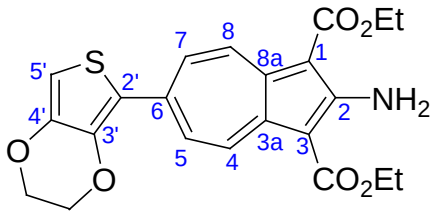



$C_{24}H_{20}O_4S_2$
Exact Mass: 436.0803
Mol. Wt.: 436.5452
C, 66.03; H, 4.62; O, 14.66; S, 14.69

To a solution of **1** (307 mg, 1.00 mmol), 2,2'-bithiophene (**8**) (333 mg, 2.00 mmol), $PCy_3 \cdot HBF_4$ (37 mg, 0.10 mmol), PivOH (31 mg, 0.30 mmol) and $K_2CO_3$ (207 mg, 1.50 mmol) in toluene (3 mL) was added $Pd(OAc)_2$ (11 mg, 0.05 mmol). The resulting mixture was stirred at 100 °C for 24 h under an Ar atmosphere. The reaction mixture was poured into water and extracted with toluene. The organic layer was washed with brine, dried with $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography with $CH_2Cl_2$ to give **13** (371 mg, 85%, red crystals) and **20** (39 mg, 11%, red crystals).

M.p. 108.0–109.0 °C (EtOH); IR (KBr disk): $\nu_{max}$ = 2979 (w), 1686 (s), 1586 (w), 1557 (w), 1532 (w), 1507 (w), 1480 (w), 1455 (w), 1420 (m), 1382 (w), 1354 (w), 1316 (w), 1302 (w), 1256 (w), 1190 (s), 1125 (w), 1057 (w), 1029 (w), 991 (w), 934 (w), 883 (w), 867 (w), 839 (w), 808 (w), 788 (w), 779 (w), 756 (w), 742 (w), 693 (m), 659 (w) $cm^{-1}$; UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ (log ε) = 238 (4.48), 274 sh (4.35), 304 (4.63), 344 sh (4.37), 426 (3.92), 541 sh (2.82) nm; $^1H$ NMR (500 MHz, $CDCl_3$): $\delta_H$ = 9.53 (d, 2H, *J* = 10.0 Hz, 4,8-H), 7.93 (t, 1H, *J* = 10.0 Hz, 6-H), 7.71 (t, 2H, *J* = 10.0 Hz, 5,7-H), 7.22 (dd, 1H, *J* = 4.0, 1.0 Hz, 3"-H of Th), 7.19 (dd, 1H, *J* = 4.0, 1.0 Hz, 5"-H of Th), 7.18 (d, 1H, *J* = 4.0 Hz, 4'-H of Th), 7.03 (dd, 1H, *J* = 4.0, 4.0 Hz, 4"-H of Th), 6.96 (d, 1H, *J* = 4.0 Hz, 3'-H of Th), 4.24 (q, 4H, *J* = 7.0 Hz, $CO_2Et$), 1.13 (t, 6H, *J* = 7.0 Hz, $CO_2Et$) ppm; $^{13}C$ NMR (125 MHz, $CDCl_3$): $\delta_C$ = 165.53 ($CO_2Et$), 145.99 (C-2' or C-5' of Th), 142.22 (C-3a,8a), 140.56 (C-6), 138.93 (C-4,8), 138.24 (C-2 or C-2' of Th), 137.58 (C-2 or C-2' of Th), 137.53 (C-2" of Th), 130.29 (C-5,7), 128.42 (C-3' of Th), 127.82 (C-4" of Th), 124.23 (C-3"of Th), 123.48 (C-4' or C-5" of Th), 123.12 (C-4' or C-5" of Th), 118.27 (C-1,3), 60.38 ($CO_2Et$), 13.84 ($CO_2Et$) ppm; HR-EI-MS: calcd for $C_{24}H_{20}O_4S_2^+$ $[M]^+$ 436.0803; found: 436.0812.

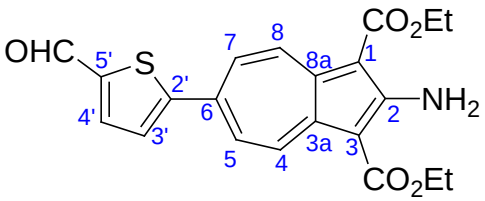
**2-Amino-1,3-bis(ethoxycarbonyl)-6-(3',4'-ethylenedioxythiophen-2'-yl)azulene (14)**




To a solution of **3** (366 mg, 1.00 mmol), EDOT (**4**) (284 mg, 2.00 mmol), $PCy_3 \cdot HBF_4$ (37 mg, 0.10 mmol), PivOH (31 mg, 0.30 mmol) and $K_2CO_3$ (207 mg, 1.50 mmol) in toluene (3 mL) was added $Pd(OAc)_2$ (11 mg, 0.05 mmol). The resulting mixture was stirred at 100 °C for 24 h under an Ar atmosphere. The reaction mixture was poured into water and extracted with toluene. The organic layer was washed with brine, dried with $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography with $CH_2Cl_2$ to give **14** (342 mg, 80%) as orange crystals.

M.p. 210.0–211.0 °C (EtOH); IR (KBr disk): $\nu_{max}$ = 3492 (w), 3364 (w), 2980 (w), 2929 (w), 2873 (w), 1681 (m), 1656 (s), 1568 (s), 1540 (m), 1479 (s), 1428 (s), 1384 (w), 1373 (m), 1360 (m), 1324 (w), 1286 (w), 1258 (w), 1248 (w), 1176 (s), 1122 (s), 1110 (s), 1067 (s), 1037 (m), 1023 (w), 953 (m), 914 (w), 882 (w), 854 (s), 806 (w), 787 (w), 714 (w), 694 (w), 658 (w) $cm^{-1}$; UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ (log ε) = 249 (4.60), 272 sh (4.19), 329 sh (4.51), 353 (4.65), 361 sh (4.61), 433 sh (4.42), 451 (4.51) nm; UV/Vis (50% $CF_3CO_2H/CH_2Cl_2$): $\lambda_{max}$ (log ε) = 272 (4.31), 292 (4.30), 345 (4.43), 357 (4.42), 440 (4.57), 463 sh (4.51), 512 sh (4.12), 590 (3.35), 722 sh (2.75), 776 sh (2.77) nm; $^1$H NMR (500 MHz, $CDCl_3$): $\delta_H$ = 9.06 (d, 2H, *J* = 11.5 Hz, 4,8-H), 7.99 (d, 2H, *J* = 11.5 Hz, 5,7-H), 7.75 (br. s, 2H, $NH_2$), 6.43 (s, 1H, 5'-H of Th), 4.46 (q, 4H, *J* = 7.5 Hz, $CO_2Et$), 4.38–4.36 (m, 2H, $OCH_2$), 4.29–4.27 (m, 2H, $OCH_2$), 1.49 (t, 6H, *J* = 7.5 Hz, $CO_2Et$) ppm; $^1$H NMR (500 MHz, acetone-$d_6$): $\delta_H$ = 9.11 (d, 2H, *J* = 11.5 Hz, 4,8-H), 8.06 (d, 2H, *J* = 11.5 Hz, 5,7-H), 7.86 (br. s, 2H, $NH_2$), 6.63 (s, 1H, 5'-H of Th), 4.46 (m, 6H, $CO_2Et$ and $OCH_2$), 4.32–4.30 (m, 2H, $OCH_2$), 1.43 (t, 6H, *J* = 7.5 Hz, $CO_2Et$) ppm; $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta_C$ = 166.57 ($CO_2Et$), 162.23 (C-2), 144.42 (C-3a,8a), 142.45 (C-3' of Th), 139.34 (C-4' of Th), 138.39 (C-6), 130.95 (C-5,7), 130.66 (C-4,8), 119.84 (C-2' of Th), 100.22 (C-5' of Th), 100.03 (C-1,3), 64.93 ($OCH_2$), 64.28 ($OCH_2$), 59.79 ($CO_2Et$), 14.74 ($CO_2Et$) ppm; HR-EI-MS: calcd for $C_{22}H_{21}NO_6S^+$ $[M]^+$ 427.1090; found: 427.1100.

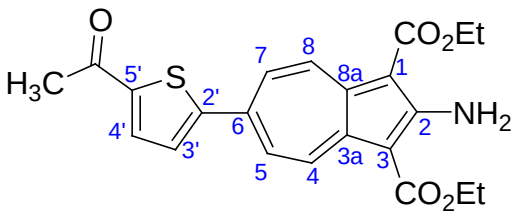
**2-Amino-1,3-bis(ethoxycarbonyl)-6-(5'-formylthiophen-2'-yl)azulene (15)**




To a solution of **3** (366 mg, 1.00 mmol), 2-formylthiophene (**5**) (224 mg, 2.00 mmol), $PCy_3 \cdot HBF_4$ (37 mg, 0.10 mmol), PivOH (31 mg, 0.30 mmol) and $K_2CO_3$ (207 mg, 1.50 mmol) in toluene (3 mL) was added $Pd(OAc)_2$ (11 mg, 0.05 mmol). The resulting mixture was stirred at 100 °C for 24 h under an Ar atmosphere. The reaction mixture was poured into water and extracted with toluene. The organic layer was washed with brine, dried with $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography with $CH_2Cl_2$ to give **15** (346 mg, 87%) as orange crystals.

M.p. 189.0–190.0 °C (EtOH); IR (KBr disk): $\nu_{max}$ = 3484 (w), 3357 (w), 3096 (w), 2987 (w), 2806 (w), 1666 (s), 1594 (s), 1573 (s), 1542 (m), 1508 (w), 1493 (m), 1444 (m), 1433 (s), 1389 (w), 1361 (w), 1329 (w), 1288 (w), 1213 (m), 1155 (m), 1133 (m), 1119 (m), 1070 (w), 1027 (m), 971 (w), 931 (w), 914 (w), 891 (w), 853 (w), 841 (w), 818 (m), 786 (w), 754 (w), 691 (w), 672 (w) $cm^{-1}$; UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ (log ε) = 249 (4.61), 275 sh (4.12), 310 sh (4.10), 354 (4.72), 457 (4.48) nm; $^1H$ NMR (500 MHz, $CDCl_3$): $\delta_H$ = 9.91 (s, 1H, CHO), 9.09 (d, 2H, *J* = 11.0 Hz, 4,8-H), 7.91 (br. s, 2H, $NH_2$), 7.89 (d, 2H, *J* = 11.0 Hz, 5,7-H), 7.77 (d, 1H, *J* = 4.0 Hz, 4'-H of Th), 7.52 (d, 1H, *J* = 4.0 Hz, 3'-H of Th), 4.48 (q, 4H, *J* = 7.5 Hz, $CO_2Et$), 1.50 (t, 6H, *J* = 7.5 Hz, $CO_2Et$) ppm; $^{13}C$ NMR (125 MHz, $CDCl_3$): $\delta_C$ = 182.75 (CHO), 166.43 ($CO_2Et$), 163.07 (C-2), 156.39 (C-5' of Th), 145.34 (C-3a,8a), 144.59 (C-2' of Th), 137.37 (C-4' of Th), 136.58 (C-6), 130.73 (C-5,7), 130.20 (C-4,8), 125.99 (C-3' of Th), 101.11 (C-1,3), 60.23 ($CO_2Et$), 14.80 ($CO_2Et$) ppm; HR-EI-MS: calcd for $C_{21}H_{19}NO_5S^+$ $[M]^+$ 397.0984; found: 397.0981.

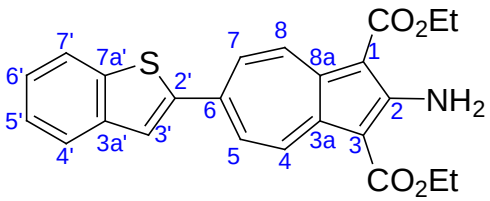
**2-Amino-1,3-bis(ethoxycarbonyl)-6-(5'-acetylthiophen-2'-yl)azulene (16)**




To a solution of **3** (366 mg, 1.00 mmol), 2-acetylthiophene (**6**) (252 mg, 2.00 mmol), $PCy_3 \cdot HBF_4$ (37 mg, 0.10 mmol), PivOH (31 mg, 0.30 mmol) and $K_2CO_3$ (207 mg, 1.50 mmol) in toluene (3 mL) was added $Pd(OAc)_2$ (11 mg, 0.05 mmol). The resulting mixture was stirred at 100 °C for 24 h under an Ar atmosphere. The reaction mixture was poured into water and extracted with toluene. The organic layer was washed with brine, dried with $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography with $CH_2Cl_2$ to give **16** (342 mg, 83%) as orange crystals.

M.p. 202.0–203.0 °C (EtOH); IR (KBr disk): $\nu_{max}$ = 3566 (w), 3484 (w), 3355 (m), 2983 (w), 1665 (s), 1592 (s), 1574 (s), 1542 (m), 1507 (m), 1496 (m), 1433 (s), 1387 (m), 1362 (w), 1339 (w), 1322 (w), 1274 (s), 1250 (m), 1210 (m), 1159 (s), 1132 (s), 1070 (m), 1029 (s), 970 (m), 932 (w), 915 (w), 889 (w), 855 (w), 840 (m), 812 (w), 792 (s), 749 (w), 691 (w), 672 (w) $cm^{-1}$; UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ (log ε) = 250 (4.60), 271 sh (4.15), 353 (4.72), 455 (4.48) nm; $^1H$ NMR (500 MHz, $CDCl_3$): $\delta_H$ = 9.08 (d, 2H, *J* = 11.5 Hz, 4,8-H), 7.89 (d, 2H, *J* = 11.5 Hz, 5,7-H), 7.88 (br. s, 2H, $NH_2$), 7.68 (d, 1H, *J* = 4.0 Hz, 4'-H of Th), 7.44 (d, 1H, *J* = 4.0 Hz, 3'-H of Th), 4.48 (q, 4H, *J* = 7.5 Hz, $CO_2Et$), 2.59 (s, 3H, $COCH_3$), 1.49 (t, 6H, *J* = 7.5 Hz, $CO_2Et$) ppm; $^{13}C$ NMR (125 MHz, $CDCl_3$): $\delta_C$ = 190.50 ($COCH_3$), 166.46 ($CO_2Et$), 162.93 (C-2), 154.82 (C-5' of Th), 145.21 (C-3a,8a), 144.59 (C-2' of Th), 137.04 (C-6), 133.54 (C-4' of Th), 130.66 (C-5,7), 130.30 (C-4,8), 125.88 (C-3' of Th), 100.96 (C-1,3), 60.18 ($CO_2Et$), 26.76 ($COCH_3$), 14.80 ($CO_2Et$) ppm; HR-EI-MS: calcd for $C_{22}H_{21}NO_5S^+$ $[M]^+$ 411.1140; found: 411.1134.

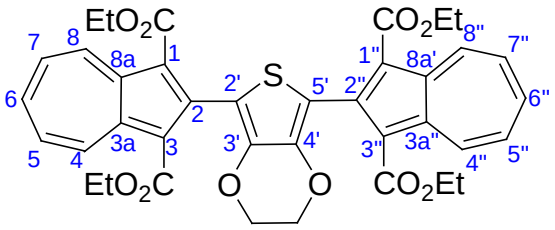
**2-Amino-1,3-bis(ethoxycarbonyl)-6-(benzothiophen-2'-yl)azulene (17)**




To a solution of **3** (366 mg, 1.00 mmol), benzothiophene (**7**) (268 mg, 2.00 mmol), $PCy_3 \cdot HBF_4$ (37 mg, 0.10 mmol), PivOH (31 mg, 0.30 mmol) and $K_2CO_3$ (207 mg, 1.50 mmol) in toluene (3 mL) was added $Pd(OAc)_2$ (11 mg, 0.05 mmol). The resulting mixture was stirred at 100 °C for 24 h under an Ar atmosphere. The reaction mixture was poured into water and extracted with toluene. The organic layer was washed with brine, dried with $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography with $CH_2Cl_2$ to give **17** (343 mg, 82%) as orange crystals.

M.p. 169.0 – 170.0 °C (EtOH); IR (KBr disk): $\nu_{max}$ = 3485 (w), 3321 (w), 2979 (w), 2910 (w), 1691 (s), 1657 (s), 1589 (s), 1542 (m), 1515 (m), 1480 (m), 1431 (s), 1400 (w), 1384 (m), 1355 (w), 1312 (w), 1281 (w), 1247 (m), 1195 (m), 1133 (m), 1119 (s), 1105 (s), 1074 (m), 1036 (m), 1023 (m), 962 (m), 930 (w), 893 (w), 857 (m), 831 (w), 821 (m), 787 (m), 739 (m), 720 (m), 688 (w), 675 (w), 663 (w) $cm^{-1}$; UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ (log ε) = 249 (4.61), 274 sh (4.15), 348 (4.73), 366 sh (4.58), 430 sh (4.41), 451 (4.51) nm; $^1H$ NMR (500 MHz, $CDCl_3$): $\delta_H$ = 9.11 (d, 2H, *J* = 11.5 Hz, 4,8-H), 7.98 (d, 2H, *J* = 11.5 Hz, 5,7-H), 7.84 (d, 1H, *J* = 8.0 Hz, 4'-H or 7'-H of BzTh), 7.83 (br. s, 2H, $NH_2$), 7.80 (d, 1H, *J* = 8.0 Hz, 4'-H or 7'-H of BzTh), 7.69 (s, 1H, 3'-H of BzTh), 7.40–7.34 (m, 2H, 5',6'-H of BzTh), 4.48 (q, 4H, *J* = 7.5 Hz, $CO_2Et$), 1.50 (t, 6H, *J* = 7.5 Hz, $CO_2Et$) ppm; $^{13}C$ NMR (125 MHz, $CDCl_3$): $\delta_C$ = 166.57 ($CO_2Et$), 162.70 (C-2), 146.46 (C-3a' or C-7a' of BTh), 144.98 (C-3a,8a), 140.78 (C-3a' or C-7a' of BzTh), 140.34 (C-2' of BzTh) , 138.50 (C-6), 131.13 (C-5,7), 130.48 (C-4,8), 125.17 (C-5' or C-6' of BzTh), 124.98 (C-5' or C-6' of BzTh), 124.09 (C-4' or C-7' of BzTh), 122.37 (C-4' or C-7' of BzTh), 122.07 (C-3' of BzTh), 100.64 (C-1,3), 60.09 ($CO_2Et$), 14.82 ($CO_2Et$) ppm; HR-EI-MS: calcd for $C_{24}H_{21}NO_4S^+$ $[M]^+$ 419.1191; found: 419.1188.

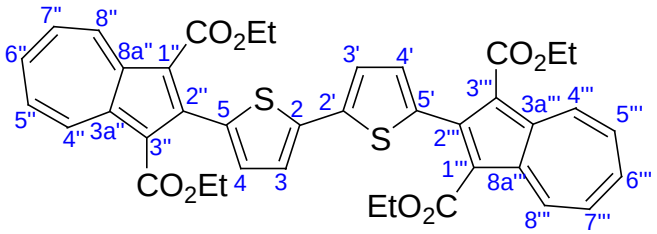
**2,5-Bis[1,3-bis(ethoxycarbonyl)azulen-2-yl]-3',4'-ethylenedioxythiophene (19)**




To a solution of **2** (218 mg, 0.50 mmol), **9** (206 mg, 0.50 mmol), $PCy_3 \cdot HBF_4$ (19 mg, 0.05 mmol), PivOH (16 mg, 0.15 mmol) and $K_2CO_3$ (104 mg, 0.75 mmol) in toluene (3 mL) was added $Pd(OAc)_2$ (6 mg, 0.025 mmol). The resulting mixture was stirred at 100 °C for 24 h under an Ar atmosphere. The reaction mixture was poured into water and extracted with $CH_2Cl_2$. The organic layer was washed with brine, dried with $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography with $CH_2Cl_2$/AcOEt (10 : 1) to give **19** (300 mg, 88%) as red crystals.

M.p. 203.0–205.0 °C ($CHCl_3$/EtOH); IR (KBr disk): $\nu_{max}$ = 2976 (w), 1697 (s), 1590 (w), 1510 (w), 1457 (m), 1430 (s), 1381 (w), 1361 (w), 1312 (w), 1268 (w), 1248 (w), 1222 (w), 1193 (s), 1165 (m), 1151 (m), 1114 (w), 1087 (m), 1049 (w), 1027 (m), 969 (w), 924 (w), 875 (w), 855 (w), 782 (w), 767 (w), 744 (w), 733 (w), 712 (w), 688 (w), 674 (w) $cm^{-1}$; UV/Vis ($CH_2Cl_2$) $\lambda_{max}$ (log ε) = 236 (4.64), 274 sh (4.61), 294 (4.80), 348 (4.61), 463 (4.38) nm; $^1H$ NMR (500 MHz, $CDCl_3$): $\delta_H$ = 9.33 (d, 4H, *J* = 10.0 Hz, 4,8,4",8"-H), 7.85 (t, 2H, *J* = 10.0 Hz, 6,6"-H), 7.63 (t, 4H, *J* = 10.0 Hz, 5,7,5",7"-H), 4.35 (q, 8H, *J* = 7.0 Hz, $CO_2Et$), 4.23 (s, 4H, $OCH_2CH_2O$), 1.29 (t, 12H, *J* = 7.0 Hz, $CO_2Et$) ppm; $^{13}C$ NMR (125 MHz, $CDCl_3$): $\delta_C$ = 166.01 ($CO_2Et$), 141.97 (C-4,8,4",8"), 141.85 (C-2',5' of Th), 139.84 (C-6,6"), 138.84 (C-2,2"), 137.93 (C-4,8,4",8"), 129.72 (C-5,7,5",7"), 118.21 (C-1,3,1",3"), 114.62 (C-3',4' of Th), 64.77 ($OCH_2CH_2O$), 60.66 ($CO_2Et$), 14.44 ($CO_2Et$) ppm; HR-FAB-MS: calcd for $C_{38}H_{34}O_{10}S^+$ $[M]^+$ 682.1873; found: 682.1883.

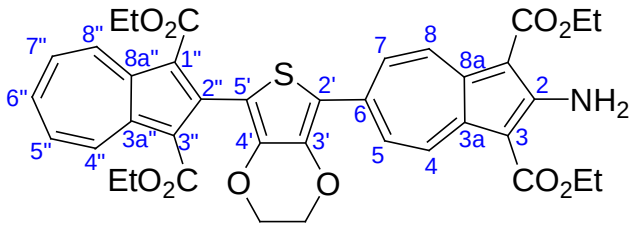
**5,5'-Bis[1,3-bis(ethoxycarbonyl)azulen-2-yl]-2,2'-bithiophene (20)**




To a solution of **2** (218 mg, 0.50 mmol), **13** (230 mg, 0.75 mmol), $PCy_3 \cdot HBF_4$ (19 mg, 0.05 mmol), PivOH (16 mg, 0.15 mmol) and $K_2CO_3$ (104 mg, 0.75 mmol) in toluene (3 mL) was added $Pd(OAc)_2$ (6 mg, 0.025 mmol). The resulting mixture was stirred at 100 °C for 24 h under an Ar atmosphere. The reaction mixture was poured into water and extracted with $CH_2Cl_2$. The organic layer was washed with brine, dried with $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography with $CH_2Cl_2$/AcOEt (10 : 1) to give **20** (325 mg, 92%) as brown crystals.

M.p. 230.0–231.0 °C ($CHCl_3$/EtOH); IR (KBr disk): $\nu_{max}$ = 2977 (w), 2927 (w), 1682 (s), 1585 (w), 1534 (w), 1485 (w), 1460 (w), 1427 (s), 1416 (s), 1377 (m), 1354 (w), 1311 (w), 1296 (w), 1243 (m), 1216 (m), 1183 (s), 1138 (m), 1111 (w), 1093 (w), 1055 (m), 1035 (m), 982 (w), 948 (w), 882 (w), 865 (w), 823 (w), 797 (w), 778 (w), 747 (w), 710 (w), 676 (w) $cm^{-1}$; UV/Vis ($CH_2Cl_2$) $\lambda_{max}$ (log ε) = 238 (4.71), 276 (4.61), 304 (4.84), 341 (4.59), 356 (4.60), 446 (4.26) nm; $^1H$ NMR (500 MHz, $CDCl_3$): $\delta_H$ = 9.54 (d, 4H, *J* = 10.0 Hz, 4",8",4"',8"'-H), 7.95 (t, 2H, *J* = 10.0 Hz, 6",6"'-H), 7.73 (t, 4H, *J* = 10.0 Hz, 5",7",5"',7"'-H), 7.20 (d, 2H, *J* = 4.0 Hz, 3,3'-H or 4,4'-H of Th), 6.97 (d, 2H, *J* = 4.0 Hz, 3,3'-H or 4,4'-H of Th), 4.25 (q, 8H, *J* = 7.0 Hz, $CO_2Et$), 1.14 (t, 12H, *J* = 7.0 Hz, $CO_2Et$) ppm; $^{13}C$ NMR (125 MHz, $CDCl_3$): $\delta_C$ = 165.56 ($CO_2Et$), 146.09 (C-2,2' or C-5,5' of Th), 142.31 (C-3"a,8"a,3a"',8a"'), 140.59 (C-6",6"'), 138.95 (C-4",8",4"',8"'), 138.39 (C-2",2"'), 137.54 (C-2,2' or C-5,5' of Th), 130.35 (C-5",7",5"',7"'), 128.45 (C-3,3' or C-4,4' of Th), 122.83 (C-3,3' or C-4,4' of Th), 118.24 (C-1",3",1"',3"'), 60.35 ($CO_2Et$), 13.73 ($CO_2Et$) ppm; HR-FAB-MS: calcd for $C_{40}H_{34}O_8S_2^+$ $[M]^+$ 706.1695; found: 706.1698.

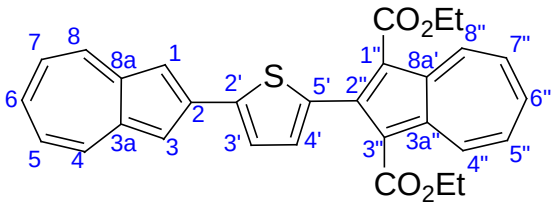
**2'-[2-Amino-1,3-bis(ethoxycarbonyl)azulen-6-yl]-5'-[1",3"-bis(ethoxycarbonyl)azulen-2"-yl]-3',4'-ethylenedioxythiophene (21)**




To a solution of **2** (59 mg, 0.19 mmol), **14** (55 mg, 0.13 mmol), $PCy_3 \cdot HBF_4$ (5 mg, 0.013 mmol), PivOH (4 mg, 0.038 mmol) and $K_2CO_3$ (27 mg, 0.19 mmol) in toluene (2 mL) was added $Pd(OAc)_2$ (1.4 mg, 0.006 mmol). The resulting mixture was stirred at 100 °C for 24 h under an Ar atmosphere. The reaction mixture was poured into water and extracted with $CH_2Cl_2$. The organic layer was washed with brine, dried with $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography with $CH_2Cl_2$ to give **21** (73 mg, 82%) as brown crystals.

M.p. 216.0–218.0 °C decomp. ($CHCl_3$/EtOH); IR (KBr disk): $\nu_{max}$ = 3445 (w), 3315 (w), 2981 (w), 1706 (w), 1675 (s), 1635 (w), 1591 (m), 1539 (w), 1500 (w), 1450 (m), 1424 (s), 1382 (w), 1365 (m), 1336 (w), 1316 (w), 1298 (w), 1271 (w), 1244 (w), 1211 (m), 1188 (s), 1149 (m), 1106 (m), 1083 (m), 1026 (m), 970 (w), 951 (w), 925 (w), 879 (w), 857 (w), 840 (w), 811 (w), 792 (m), 763 (w), 737 (w), 706 (w), 685 (w), 670 (w), 658 (w) $cm^{-1}$; UV/Vis ($CH_2Cl_2$) $\lambda_{max}$ (log ε) = 238 sh (4.61), 250 (4.65), 275 sh (4.52), 295 (4.54), 300 sh (4.54), 334 (4.51), 359 (4.61), 479 (4.58) nm; $^1$H NMR (500 MHz, $CDCl_3$): $\delta_H$ = 9.54 (d, 2H, *J* = 10.5 Hz, 4",8"-H), 9.07 (d, 2H, *J* = 11.5 Hz, 4,8-H), 8.07 (d, 2H, *J* = 11.5 Hz, 5,7-H), 7.94 (t, 1H, *J* = 10.5 Hz, 6"-H), 7.75 (s, 2H, $NH_2$), 7.71 (dd, 2H, *J* = 10.5, 10.5 Hz, 5",7"-H), 4.47 (q, 4H, *J* = 7.0 Hz, $CO_2Et$), 4.40–4.39 (m, 2H, $OCH_2$), 4.32 (q, 4H, *J* = 7.0 Hz, $CO_2Et$), 4.28–4.26 (m, 2H, $OCH_2$), 1.49 (t, 6H, *J* = 7.0 Hz, $CO_2Et$), 1.23 (t, 6H, *J* = 7.0 Hz, $CO_2Et$) ppm; $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta_C$ = 166.59 ($CO_2Et$), 165.36 ($CO_2Et$), 162.18 (C-6), 144.30 (C-3a,8a), 142.58 (C-3"a,8"a), 142.36 (Th), 140.63 (C-6"), 139.48 (Th), 138.87 (C-4",8"), 138.76 (Th), 138.64 (Th), 130.75 (C-4,8 or C-5,7), 130.71 (C-4,8 or C-5,7), 130.27 (C-5",7"), 120.24 (C-2 or C-2"), 118.16 (C-1",3"), 114.46 (C-2 or C-2"), 100.05 (C-1,3), 64.95 ($OCH_2$), 64.41 ($OCH_2$), 60.37 ($CO_2Et$), 59.79 ($CO_2Et$), 14.75 ($CO_2Et$), 14.13 ($CO_2Et$) ppm; HR-FAB-MS: calcd for $C_{38}H_{35}NO_{10}S^+$ $[M]^+$ 697.1982; found: 697.1995.

**2'-(Azulen-2-yl)-5'-[1",3"-bis(ethoxycarbonyl)azulen-2"-yl]thiophene (22)**




To a solution of **2** (307 mg, 1.00 mmol), **18** (210 mg, 1.00 mmol), $PCy_3 \cdot HBF_4$ (37 mg, 0.10 mmol), PivOH (31 mg, 0.30 mmol) and $K_2CO_3$ (207 mg, 1.50 mmol) in toluene (3 mL) was added $Pd(OAc)_2$ (11 mg, 0.05 mmol). The resulting mixture was stirred at 100 °C for 12 h under an Ar atmosphere. The reaction mixture was poured into water and extracted with toluene. The organic layer was washed with brine, dried with $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography with $CH_2Cl_2$ to give **22** (417 mg, 87%) as brown crystals.

M.p. 148.0–149.0 °C ($CHCl_3$/EtOH); IR (KBr disk): $\nu_{max}$ = 2978 (w), 1684 (s), 1577 (w), 1533 (w), 1510 (w), 1480 (w), 1453 (m), 1431 (m), 1413 (s), 1379 (m), 1316 (w), 1299 (w), 1265 (w), 1245 (w), 1188 (s), 1115 (m), 1094 (w), 1057 (m), 1028 (m), 948 (w), 898 (w), 885 (w), 847 (w), 811 (m), 750 (w), 726 (m), 698 (w), 681 (w), 653 (w) $cm^{-1}$; UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ (log ε) = 237 (4.53), 272 (4.51), 313 (4.77), 323 (4.77), 352 sh (4.24), 402 sh (4.34), 428 (4.46), 546 sh (3.09), 610 sh (2.77), 633 sh (2.50) nm; $^1$H NMR (500 MHz, $CDCl_3$): $\delta_H$ = 9.54 (d, 2H, *J* = 10.0 Hz, 4",8"-H), 8.21 (d, 2H, *J* = 10.0 Hz, 4,8-H), 7.93 (t, 1H, *J* = 10.0 Hz, 6"-H), 7.72 (t, 2H, *J* = 10.0 Hz, 5",7"-H), 7.61 (d, 1H, *J* = 4.0 Hz, 3'-H of Th), 7.56 (s, 2H, 1,3-H), 7.46 (t, 1H, *J* = 10.0 Hz, 6-H), 7.14 (t, 2H, *J* = 10.0 Hz, 5,7-H), 7.11 (d, 1H, *J* = 4.0 Hz, 4'-H of Th), 4.24 (q, 4H, *J* = 7.0 Hz, $CO_2Et$), 1.11 (t, 6H, *J* = 7.0 Hz, $CO_2Et$) ppm; $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta_C$ = 165.55 ($CO_2Et$), 146.23 (C-2"), 143.33 (C-2), 142.24 (C-3"a,8"a), 141.85 (C-2' or C-5' of Th), 141.31 (C-3a,8a), 140.53 (C-6"), 139.92 (C-2' or C-5' of Th), 138.89 (C-4",8"), 135.84 (C-6), 135.17 (C-4,8), 130.27 (C-5",7"), 129.22 (C-4' of Th), 125.13 (C-3' of Th), 124.12 (C-5,7), 118.23 (C-1",3"), 113.77 (C-1,3), 60.37 ($CO_2Et$), 13.84 ($CO_2Et$) ppm; HR-EI-MS: calcd for $C_{30}H_{24}O_4S^+$ $[M]^+$ 480.1395; found: 480.1398.

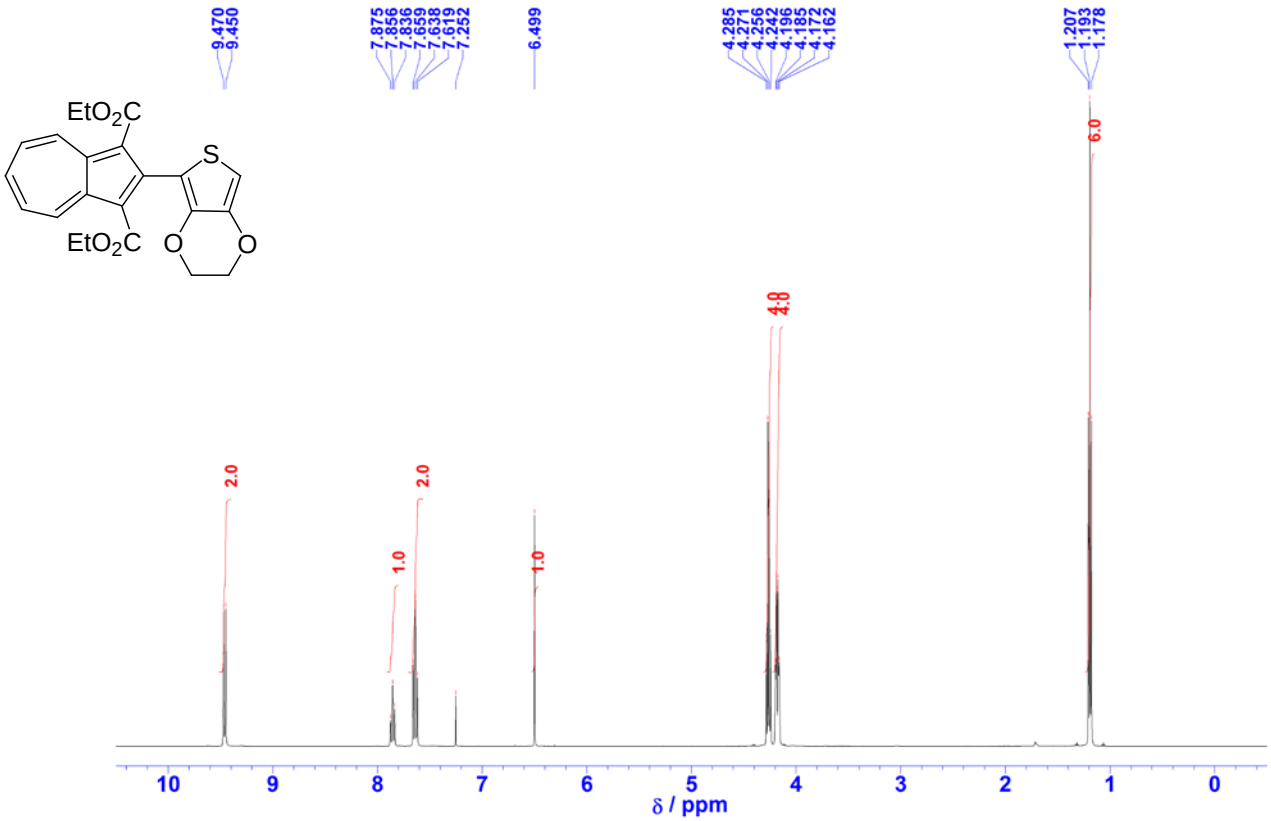



**Figure S–1.** $^{1}$H NMR spectrum of **9** in $CDCl_3$ (500 MHz).

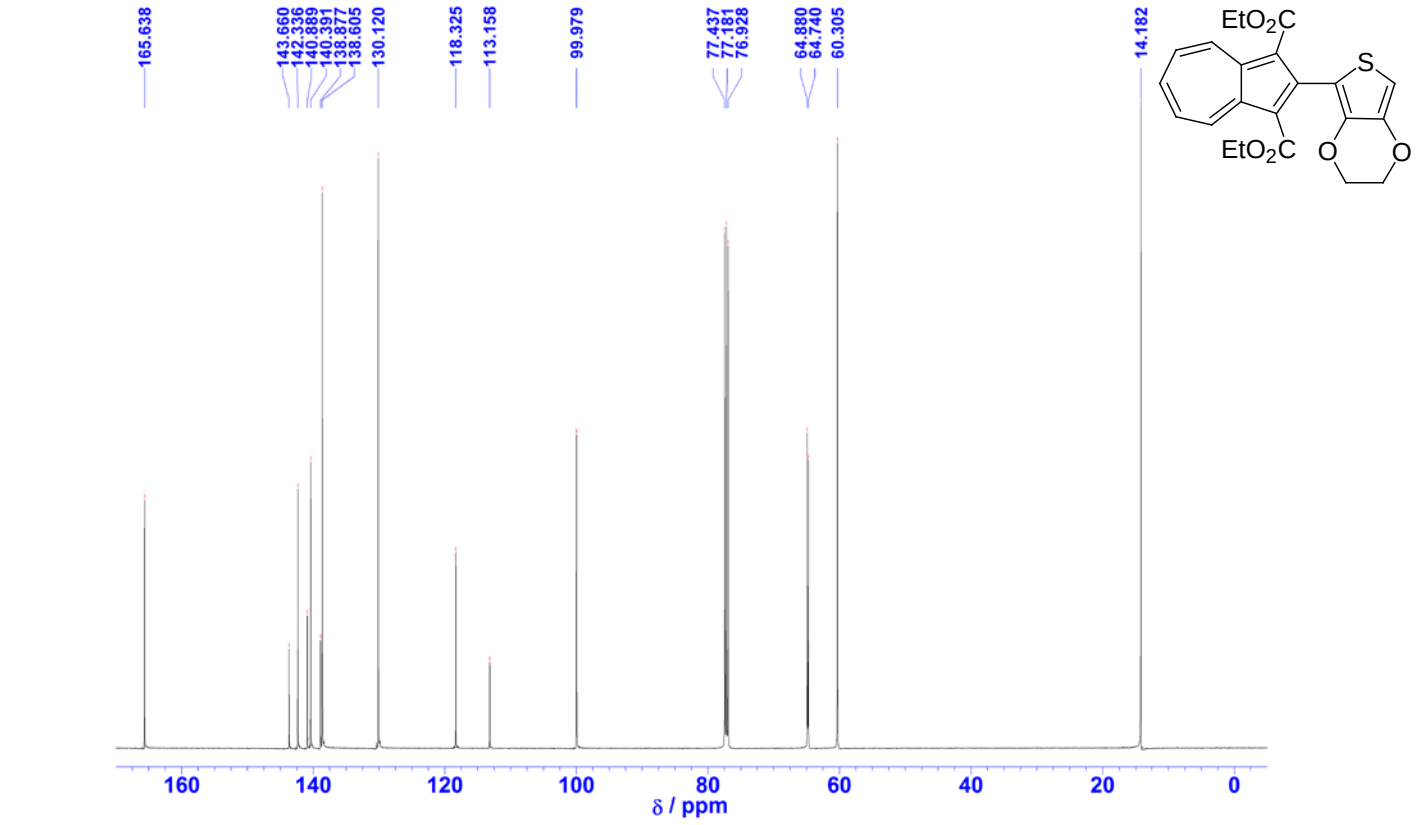



**Figure S–2.** $^{13}$C NMR spectrum of **9** in $CDCl_3$ (125 MHz).

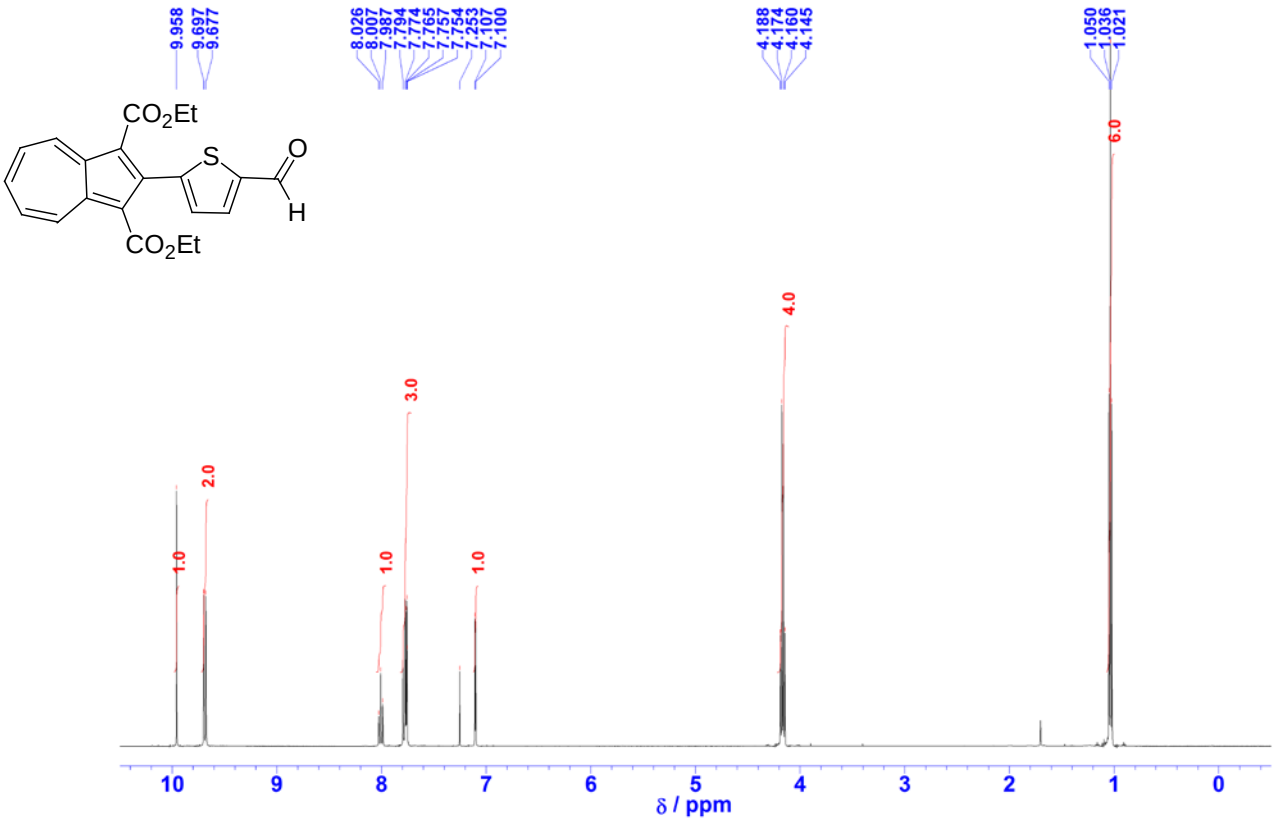



**Figure S–3.** $^{1}$H NMR spectrum of **10** in $CDCl_3$ (500 MHz).

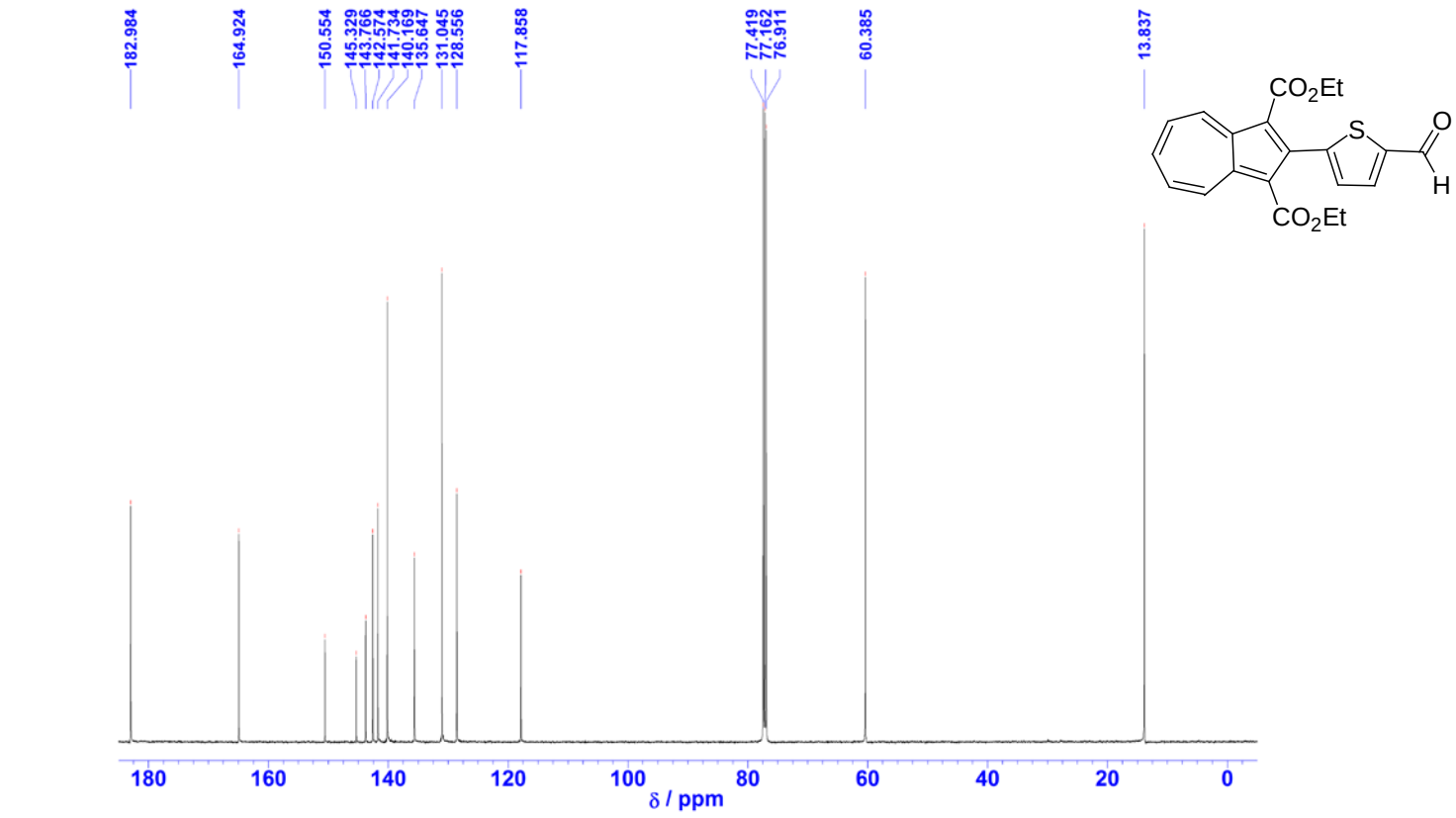



**Figure S–4.** $^{13}$C NMR spectrum of **10** in $CDCl_3$ (125 MHz).

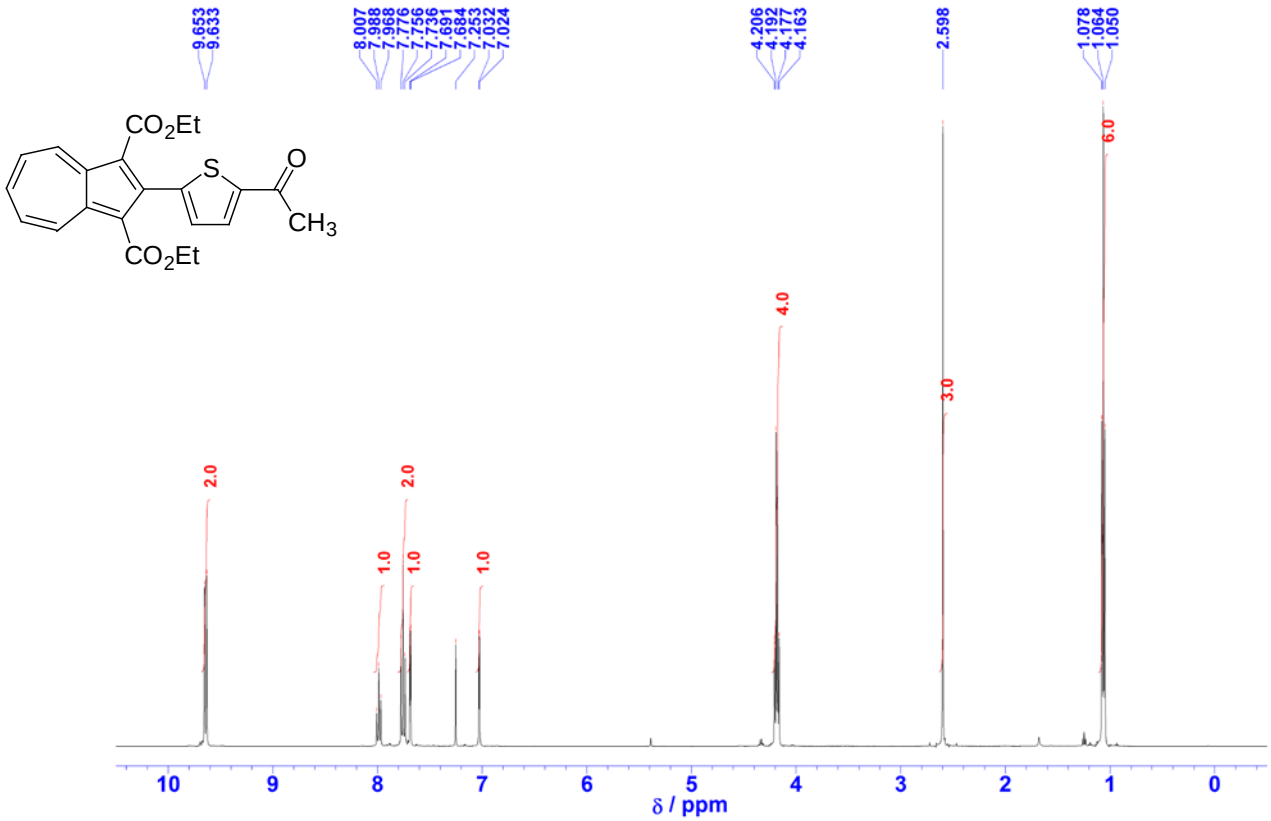



**Figure S–5.** $^{1}$H NMR spectrum of **11** in $CDCl_3$ (500 MHz).

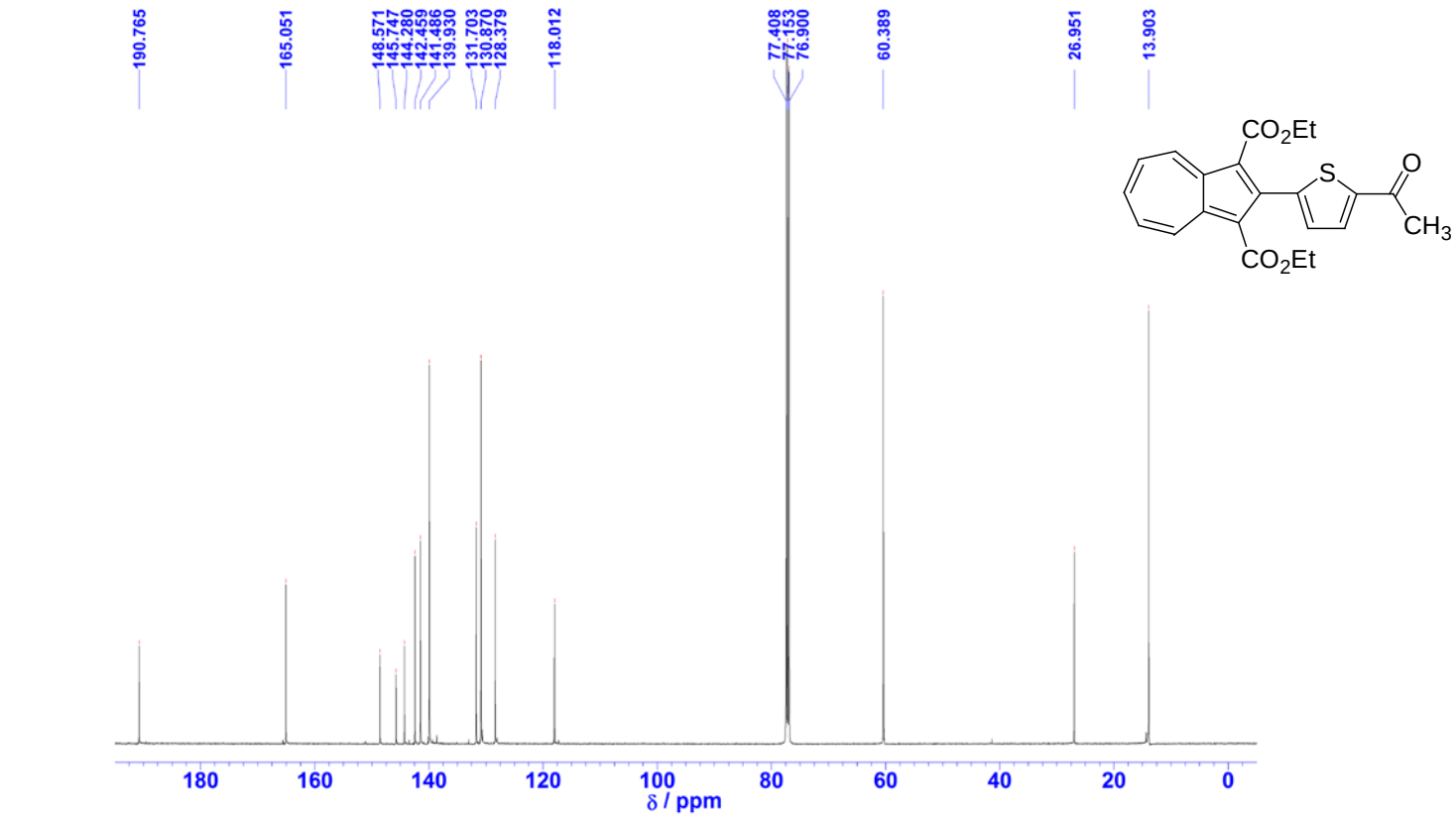



**Figure S–6.** $^{13}$C NMR spectrum of **11** in $CDCl_3$ (125 MHz).

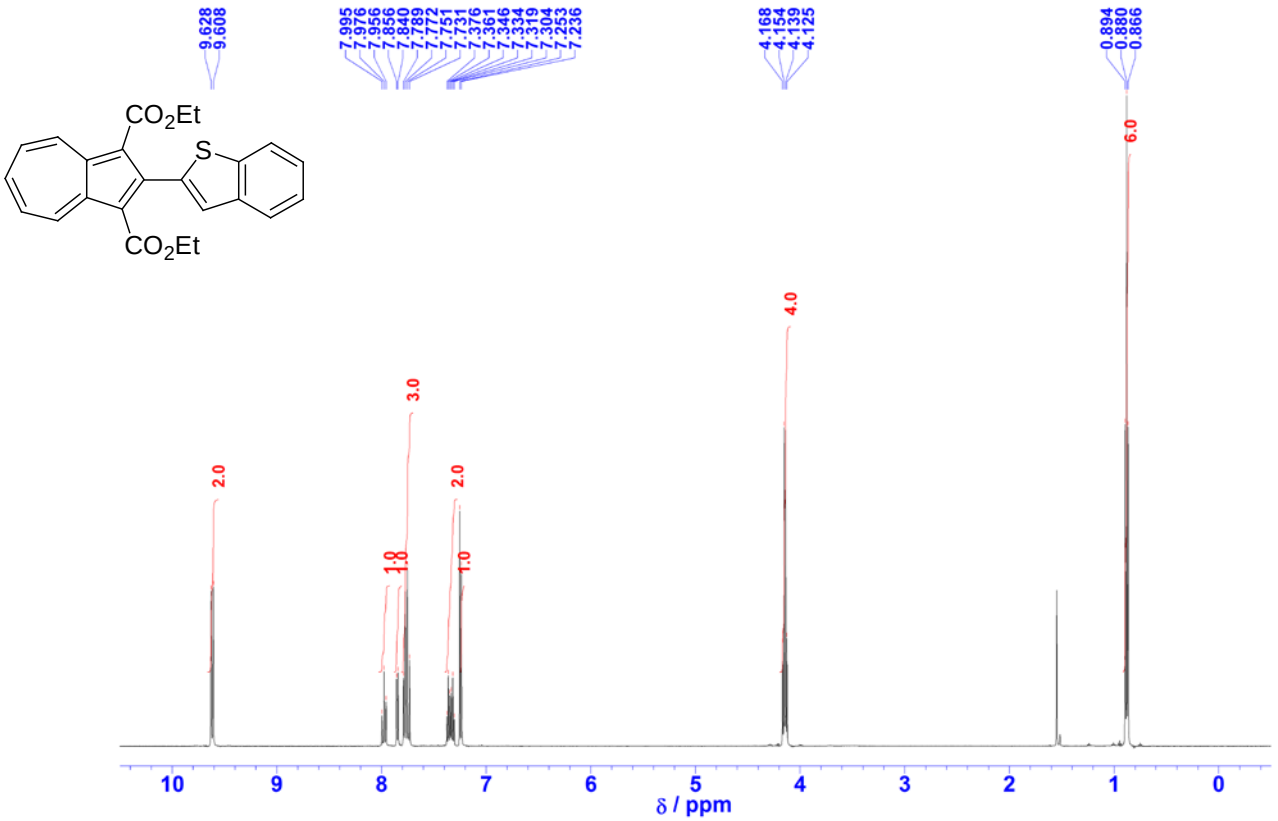



**Figure S–7.** $^{1}$H NMR spectrum of **12** in $CDCl_3$ (500 MHz).

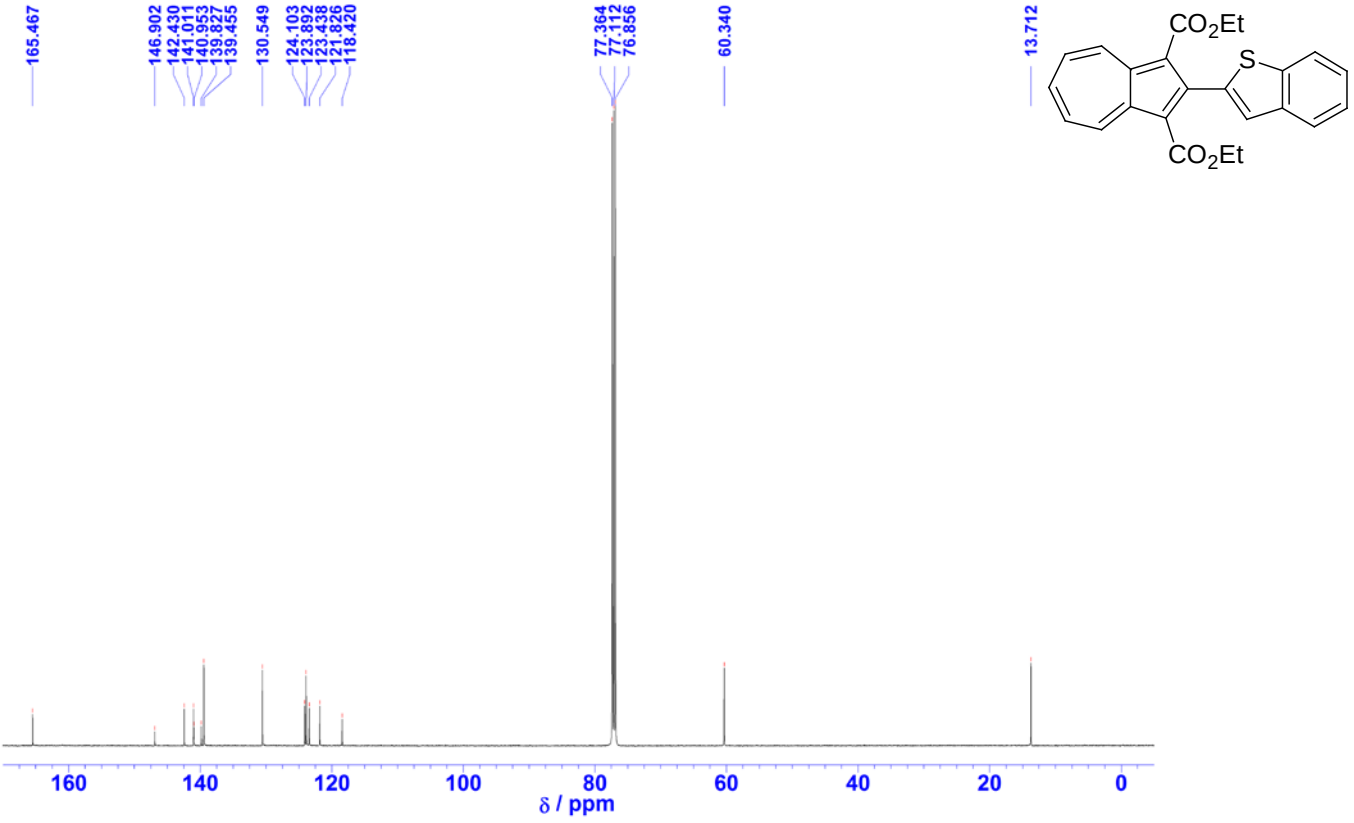



**Figure S–8.** $^{13}$C NMR spectrum of **12** in $CDCl_3$ (125 MHz).

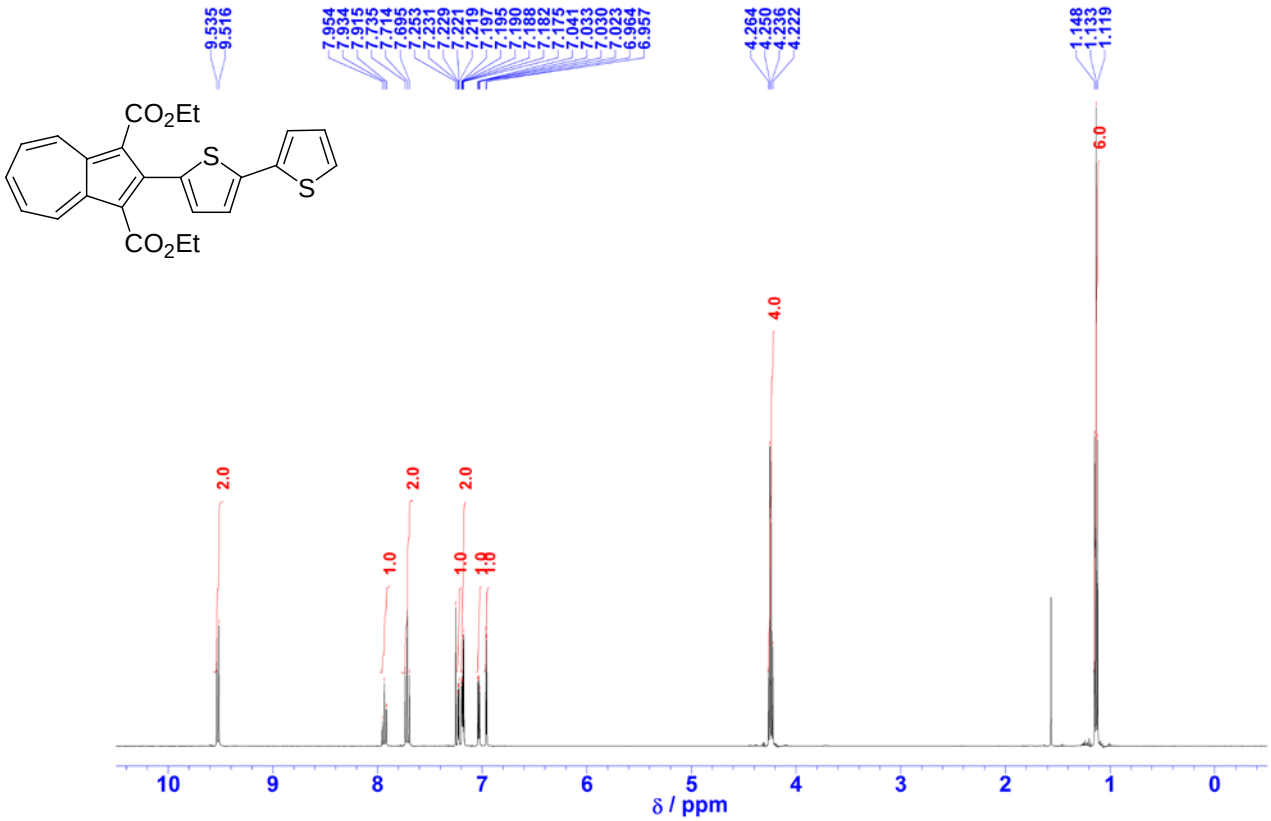



**Figure S–9.** $^{1}$H NMR spectrum of **13** in $CDCl_3$ (500 MHz).

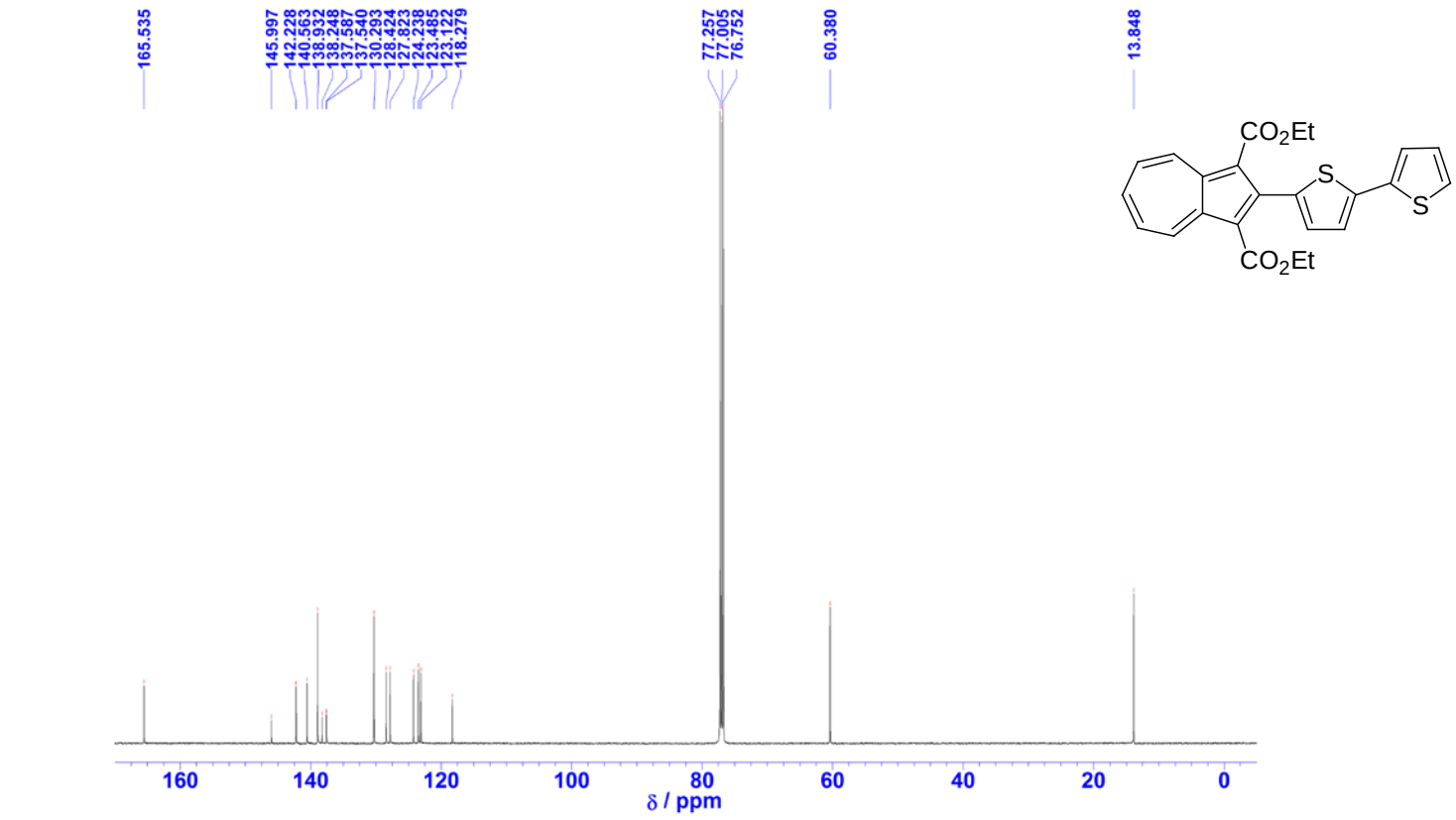



**Figure S–10.** $^{13}$C NMR spectrum of **13** in $CDCl_3$ (125 MHz).

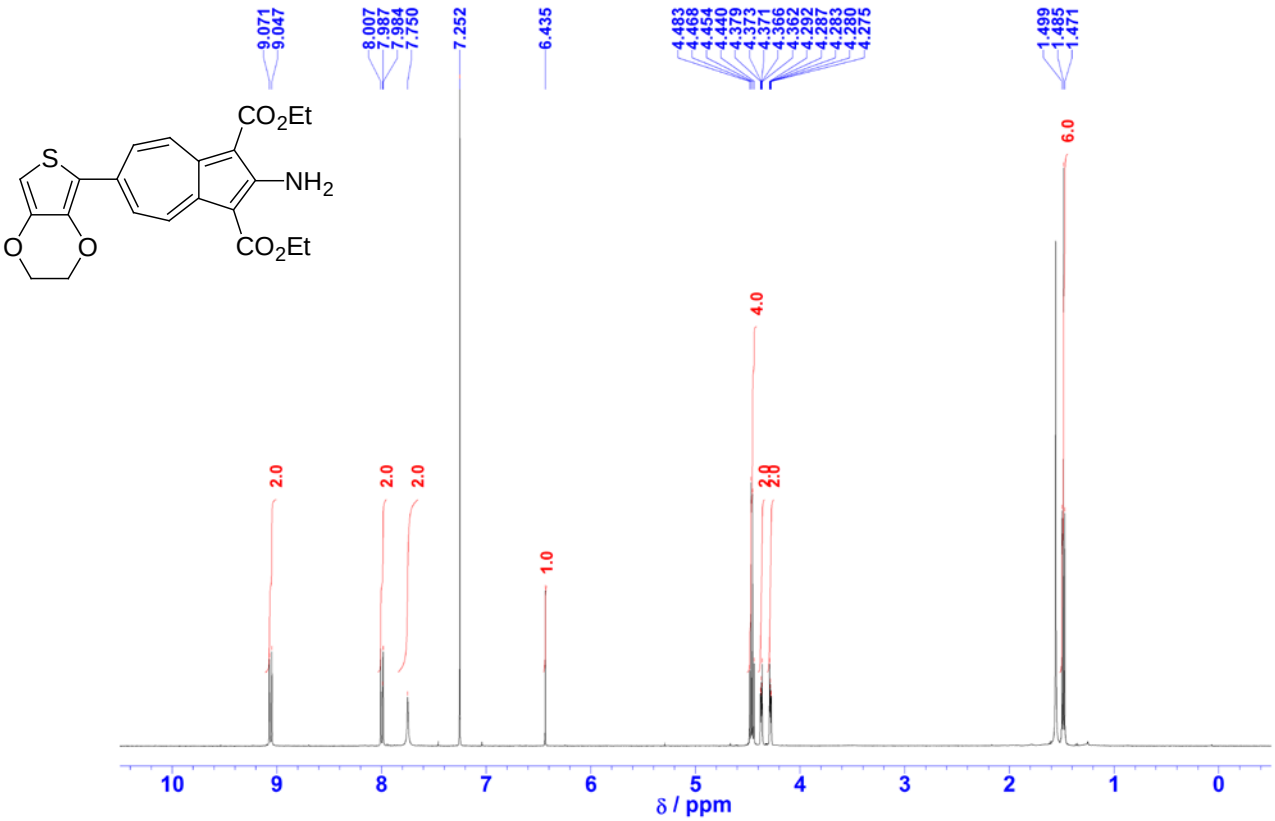



**Figure S–11.** $^{1}$H NMR spectrum of **14** in $CDCl_3$ (500 MHz).

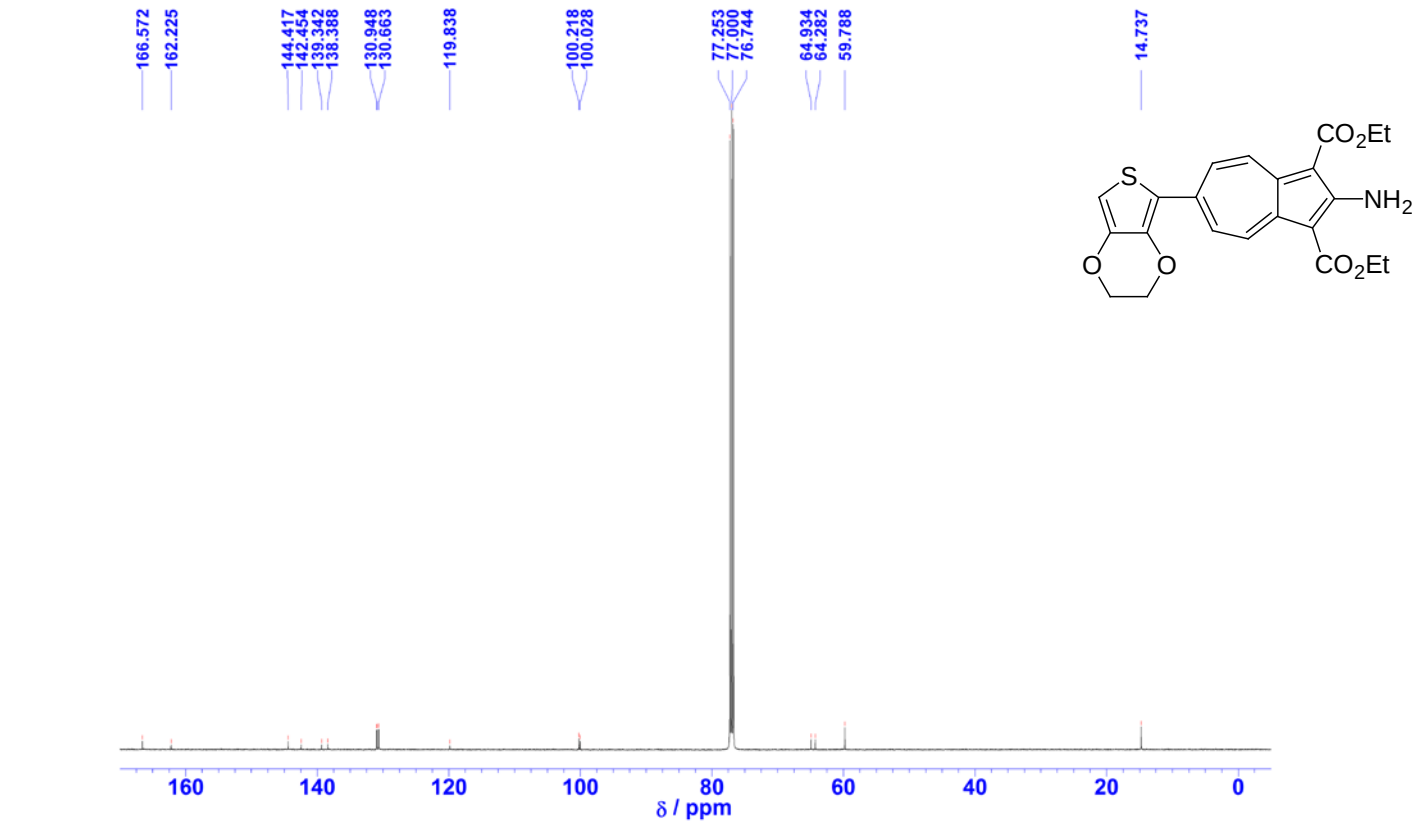



**Figure S–12.** $^{13}$C NMR spectrum of **14** in $CDCl_3$ (125 MHz).

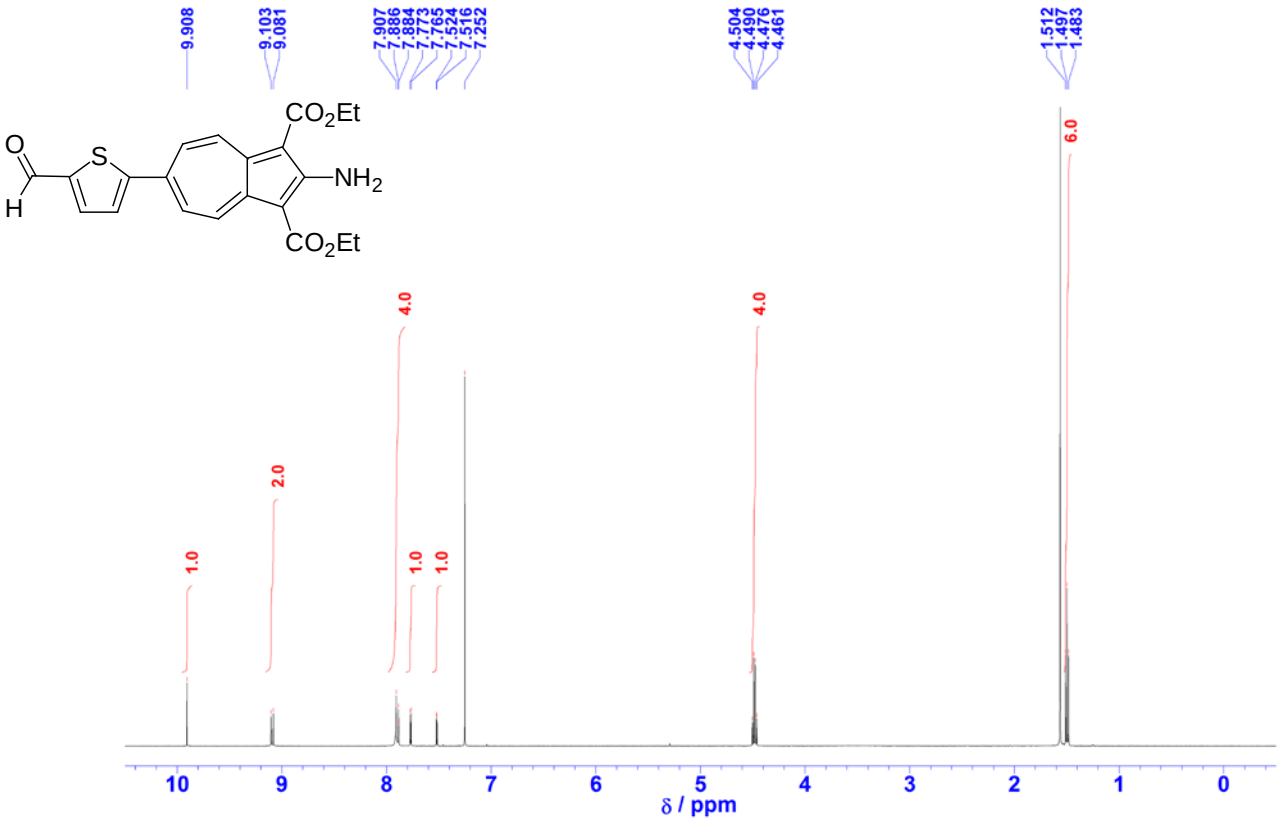



**Figure S–13.** $^{1}$H NMR spectrum of **15** in $CDCl_3$ (500 MHz).

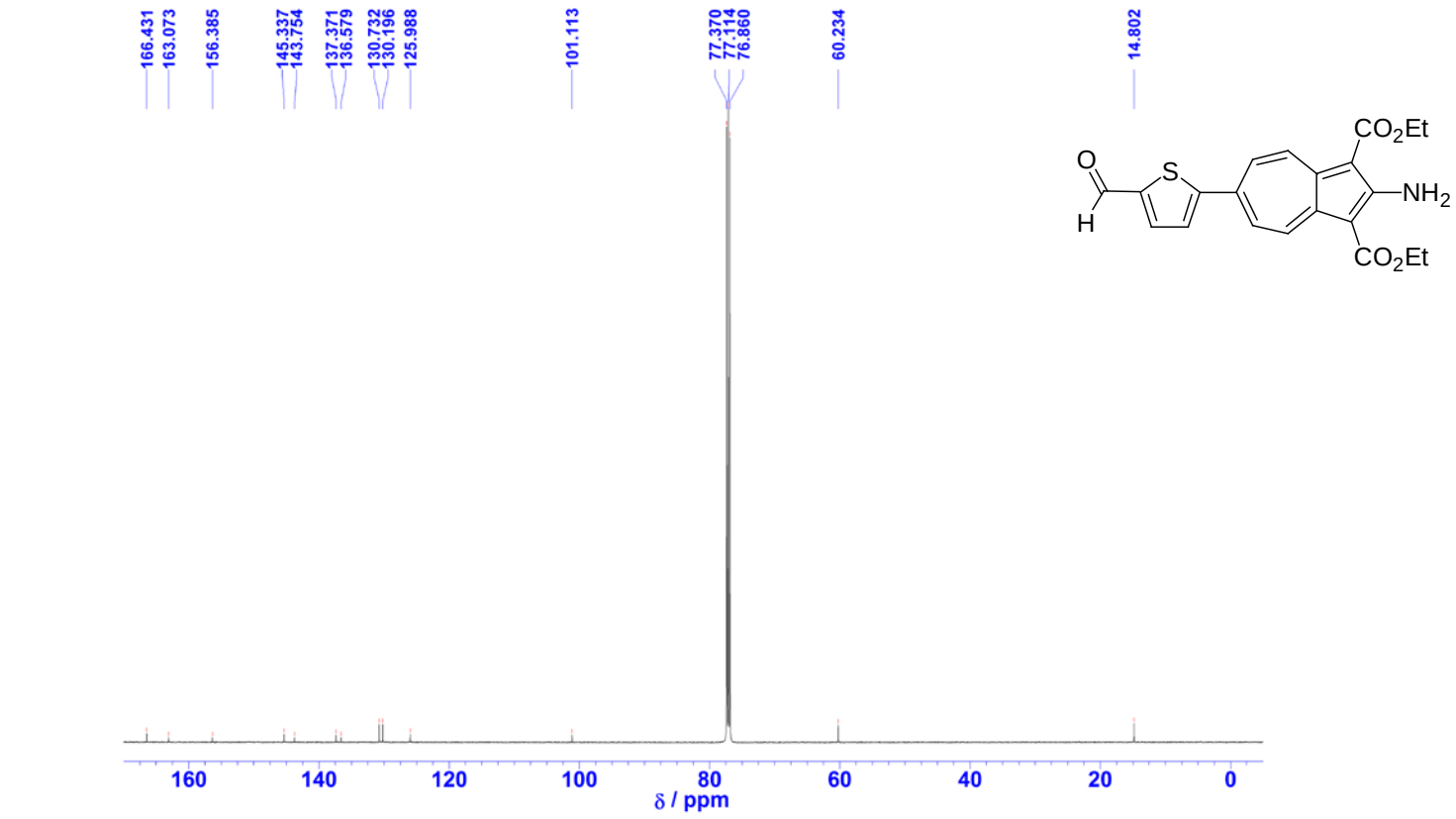



**Figure S–14.** $^{13}$C NMR spectrum of **15** in $CDCl_3$ (125 MHz).

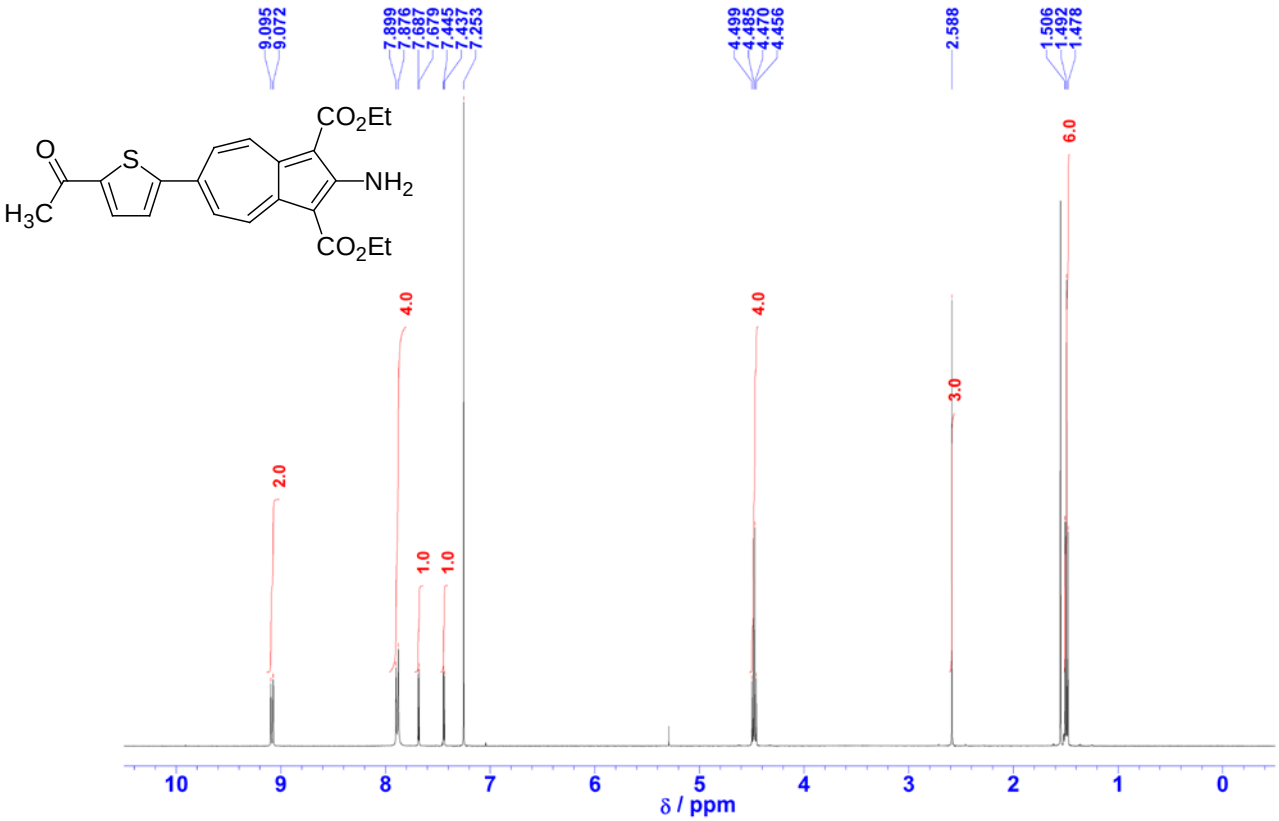



**Figure S–15.** $^{1}$H NMR spectrum of **16** in $CDCl_3$ (500 MHz).

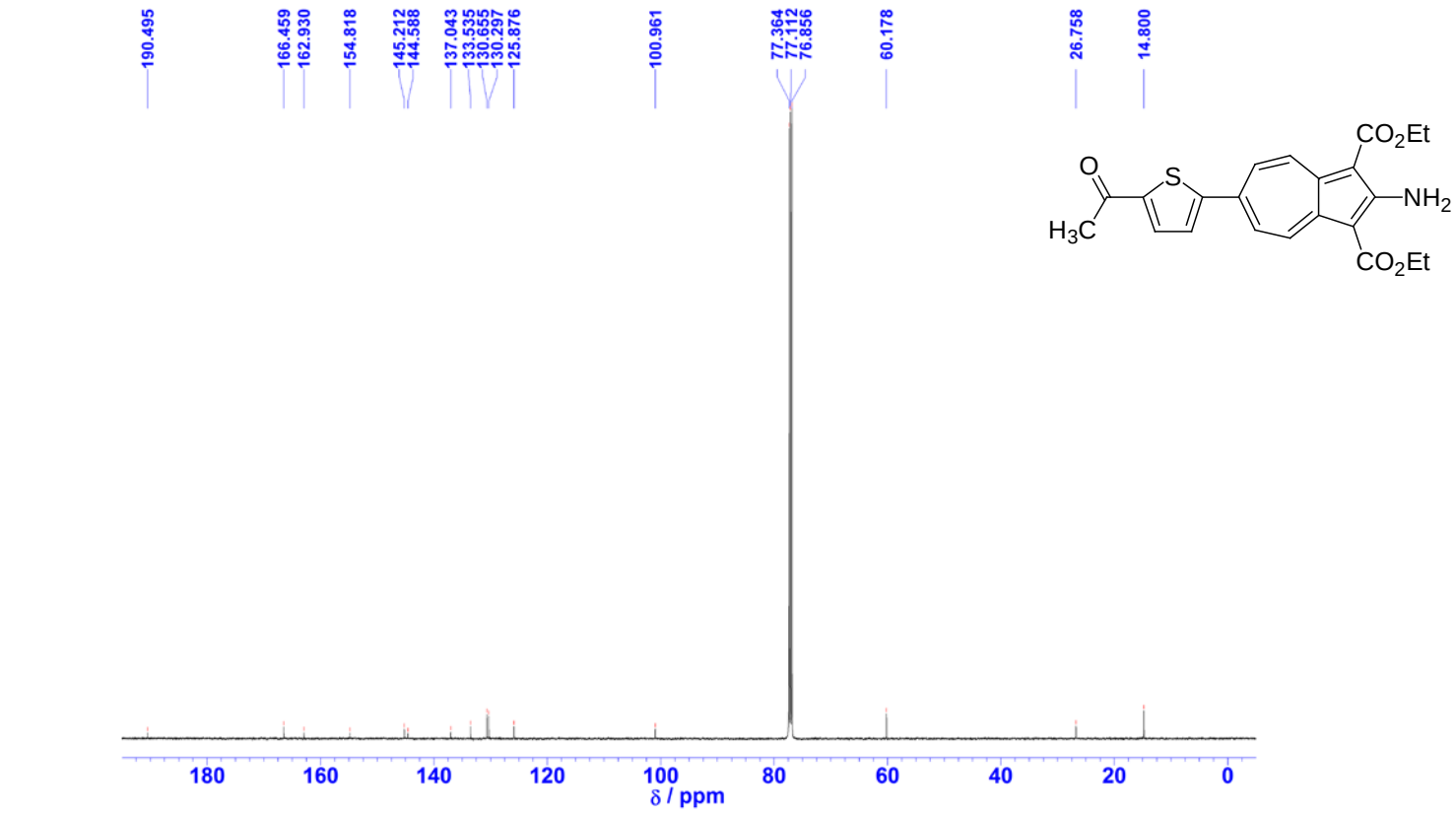



**Figure S–16.** $^{13}$C NMR spectrum of **16** in $CDCl_3$ (125 MHz).

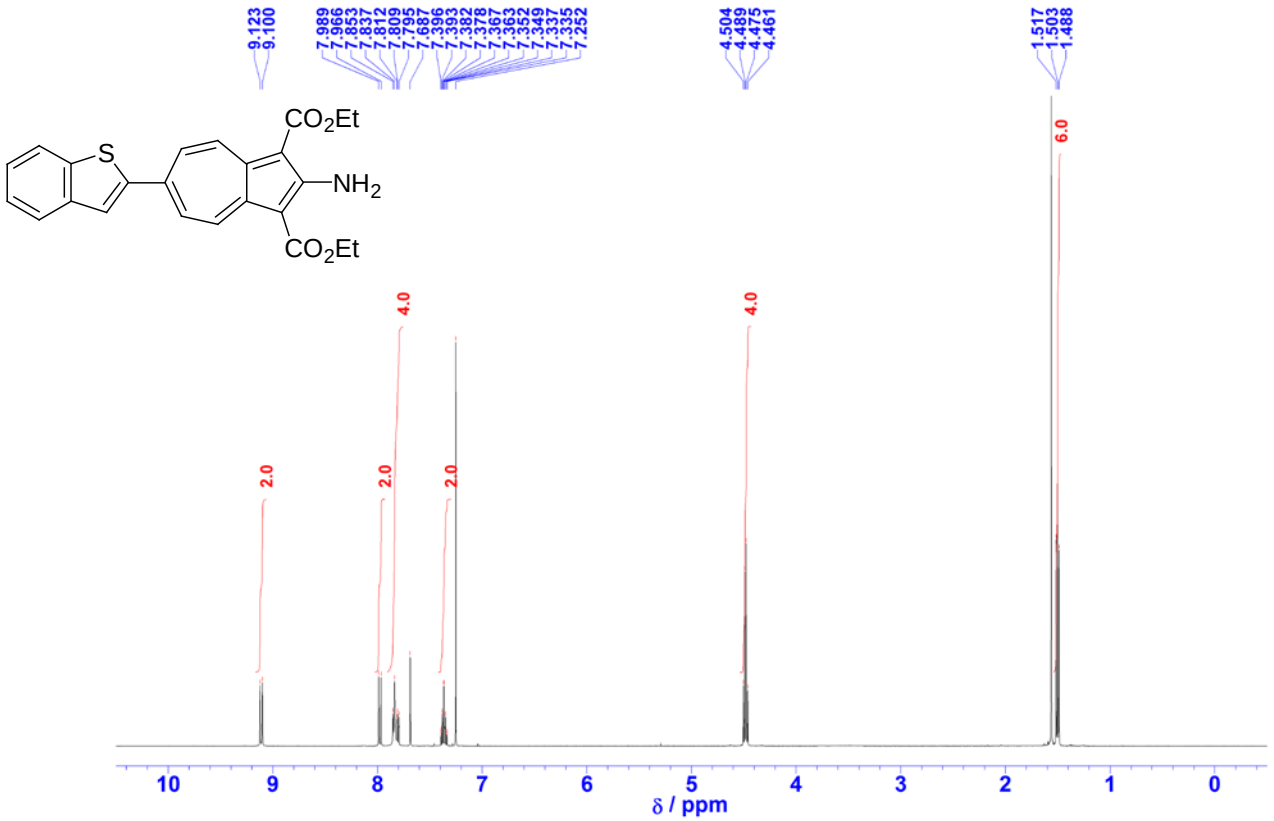



**Figure S–17.** $^{1}$H NMR spectrum of **17** in $CDCl_3$ (500 MHz).

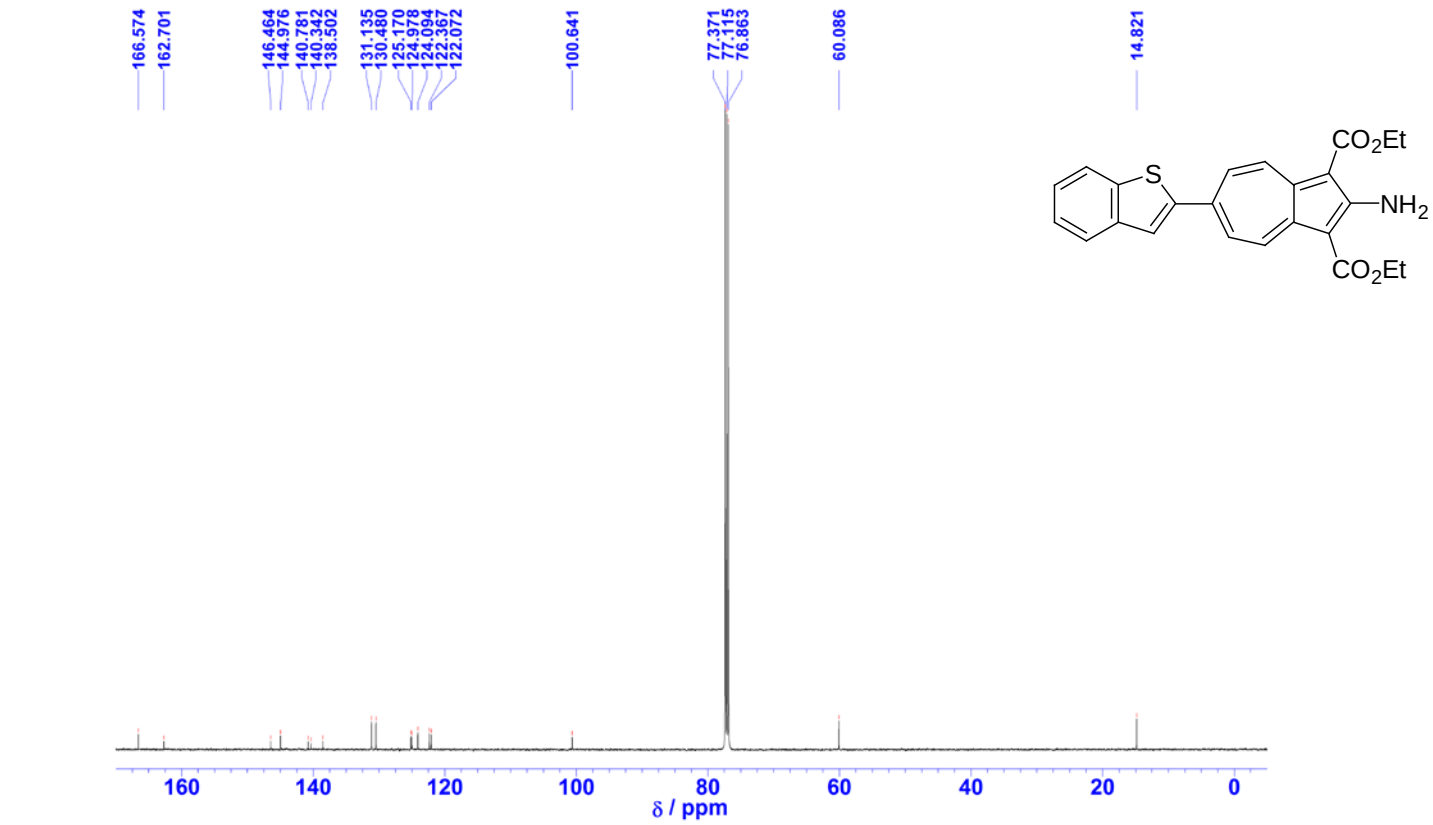



**Figure S–18.** $^{13}$C NMR spectrum of **17** in $CDCl_3$ (125 MHz).

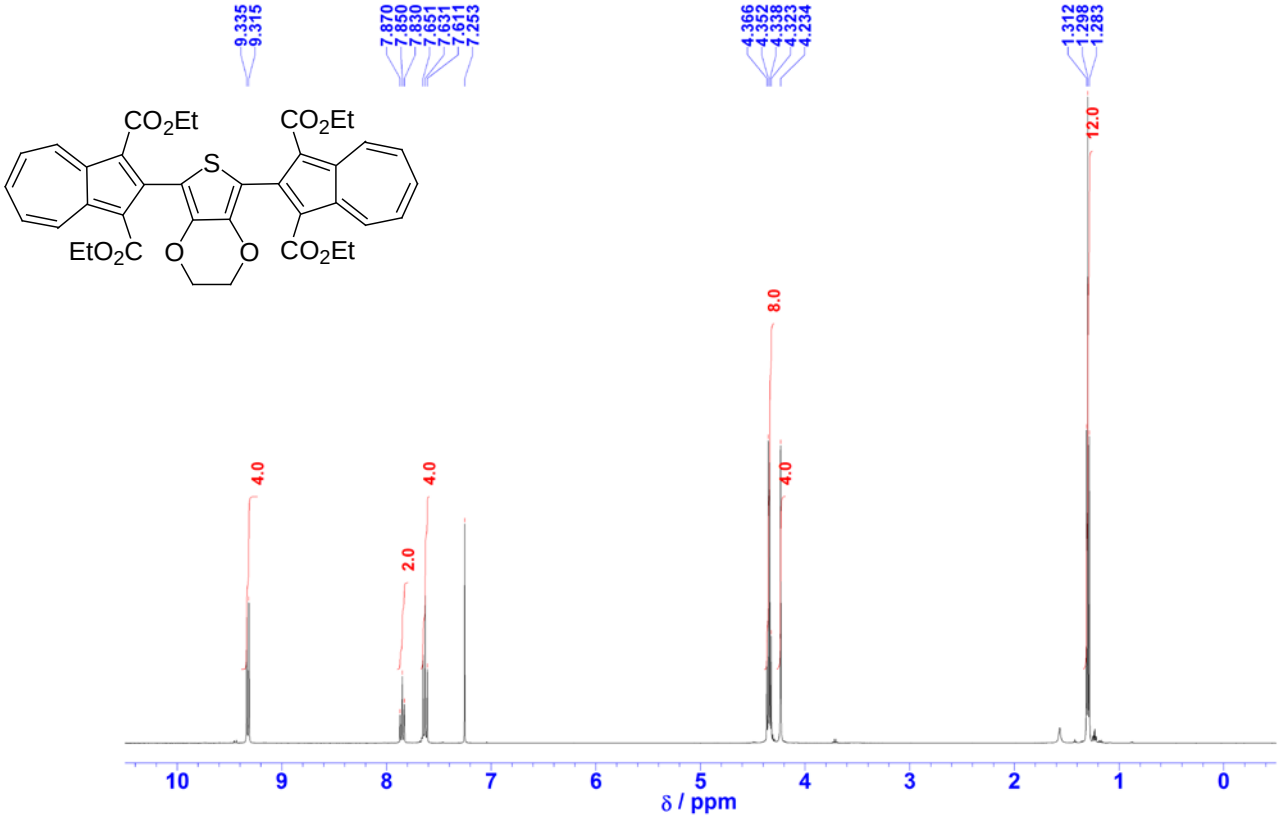



**Figure S–19.** $^{1}$H NMR spectrum of **19** in $CDCl_3$ (500 MHz).

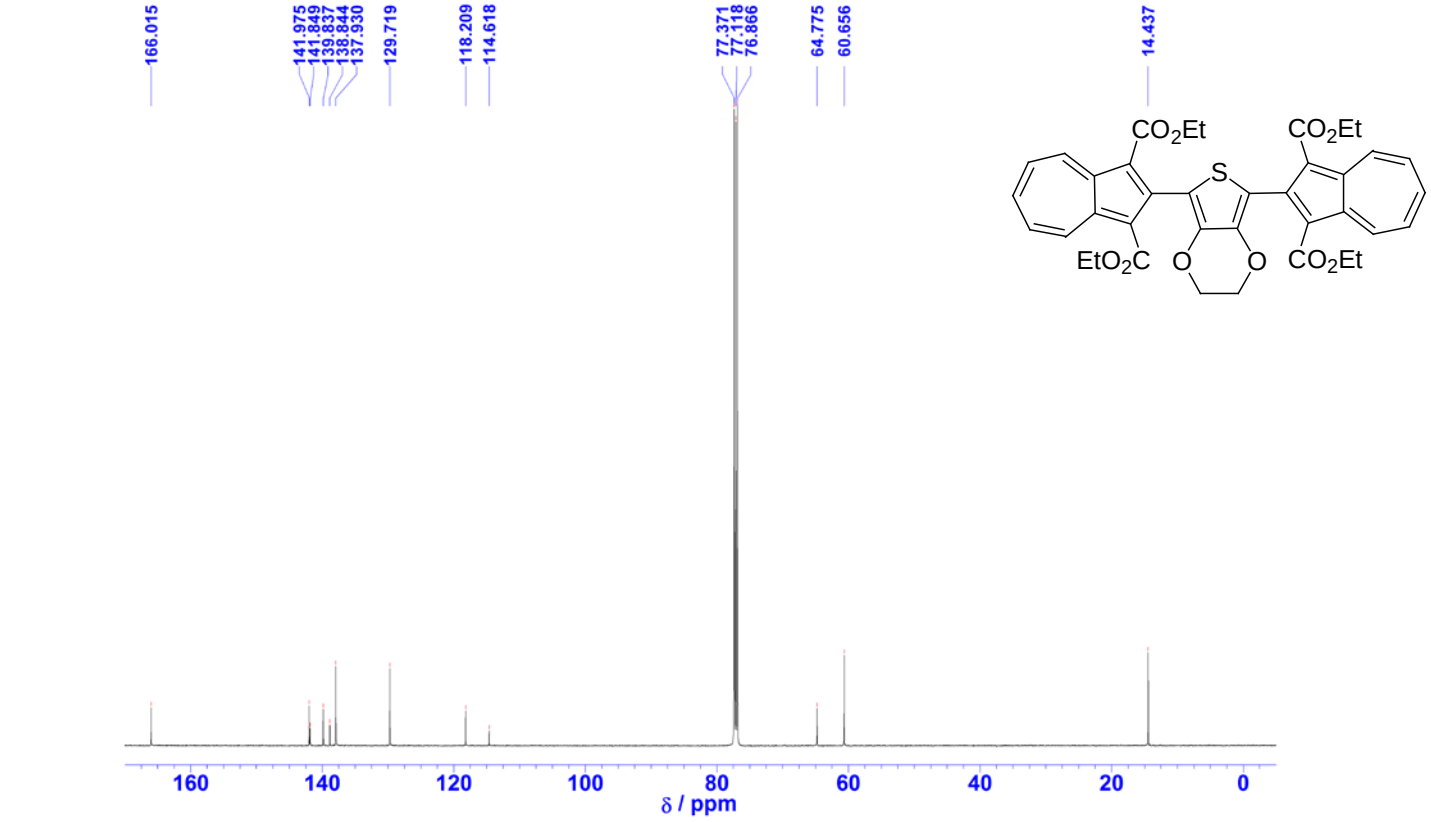



**Figure S–20.** $^{13}$C NMR spectrum of **19** in $CDCl_3$ (125 MHz).

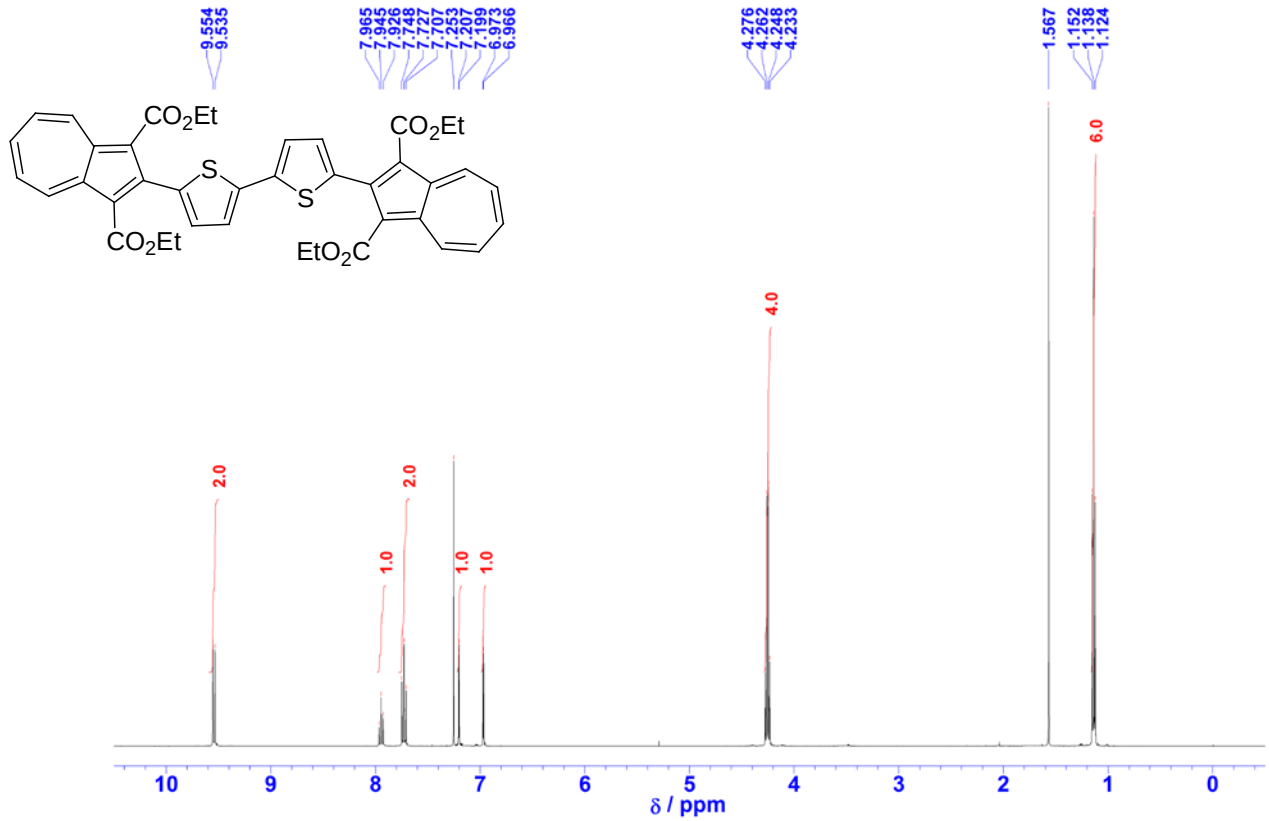



**Figure S–21.** $^{1}$H NMR spectrum of **20** in $CDCl_3$ (500 MHz).

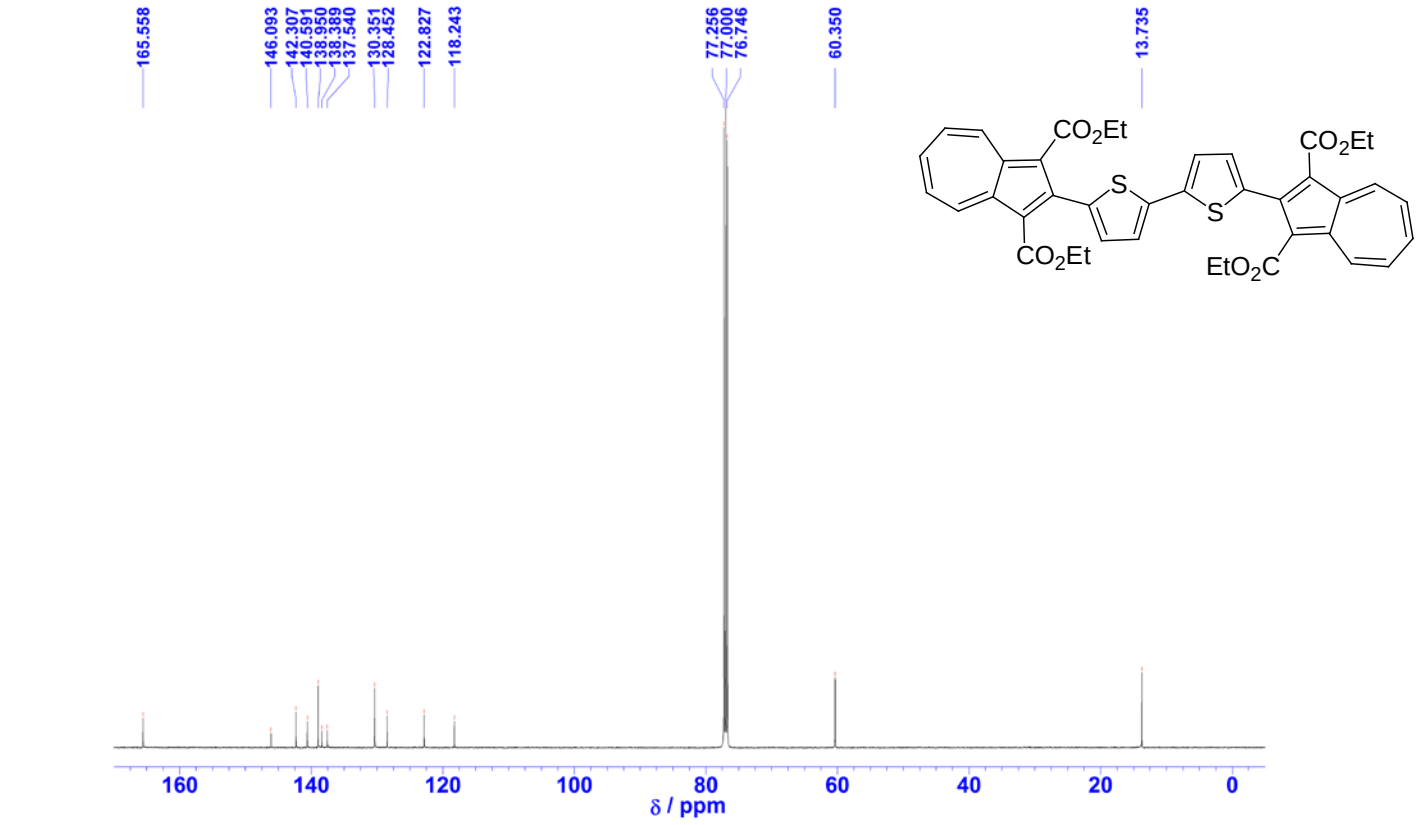



**Figure S–22.** $^{13}$C NMR spectrum of **20** in $CDCl_3$ (125 MHz).

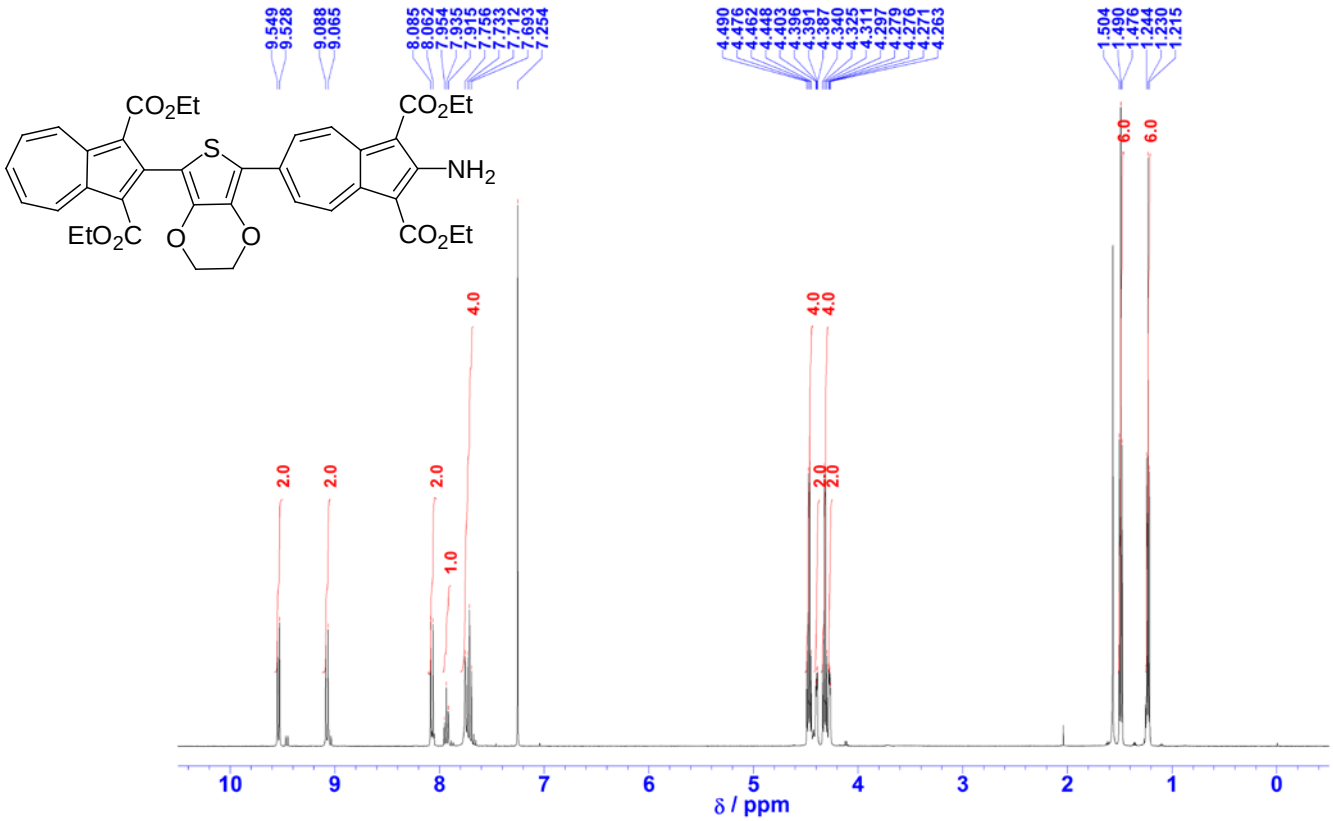



**Figure S–23.** $^{1}$H NMR spectrum of **21** in $CDCl_3$ (500 MHz).

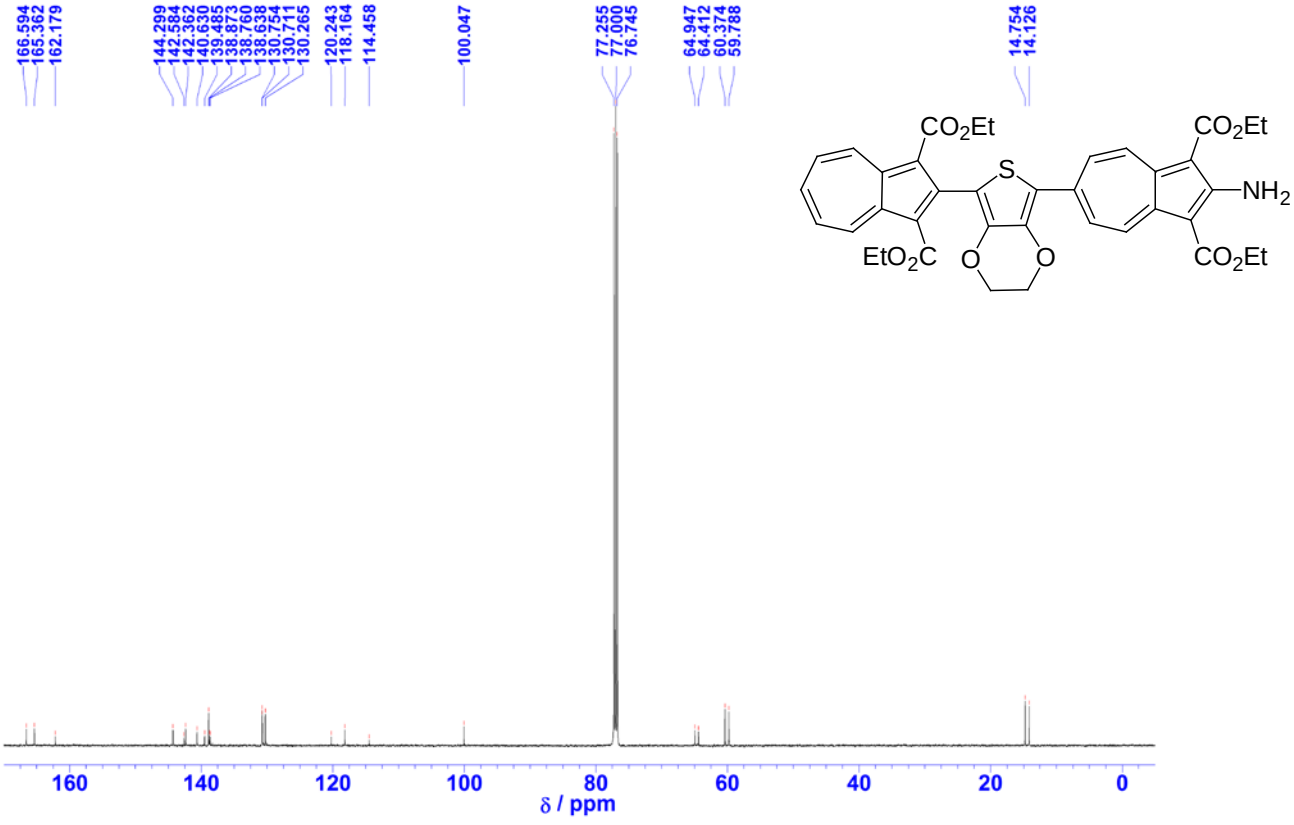



**Figure S–24.** $^{13}$C NMR spectrum of **21** in $CDCl_3$ (125 MHz).

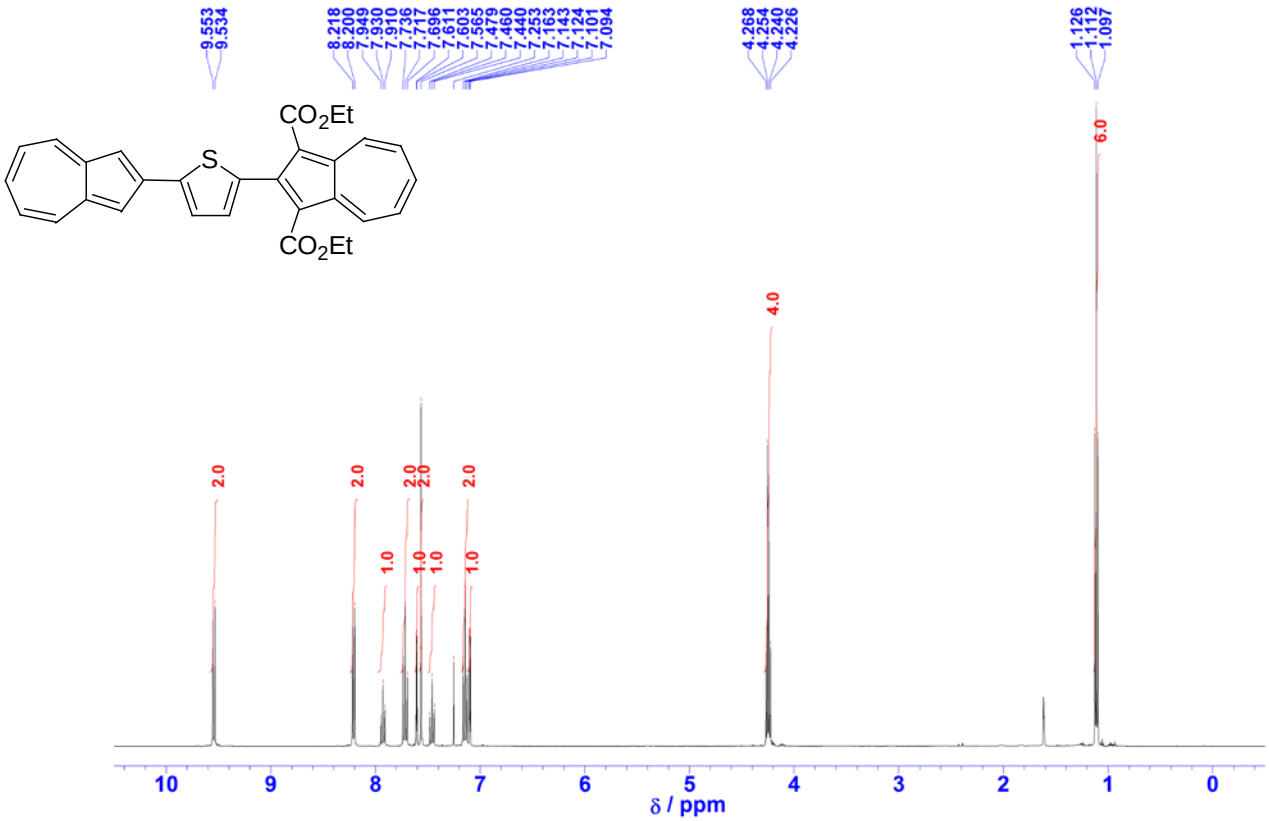



**Figure S–25.** $^{1}$H NMR spectrum of **22** in $CDCl_3$ (500 MHz).

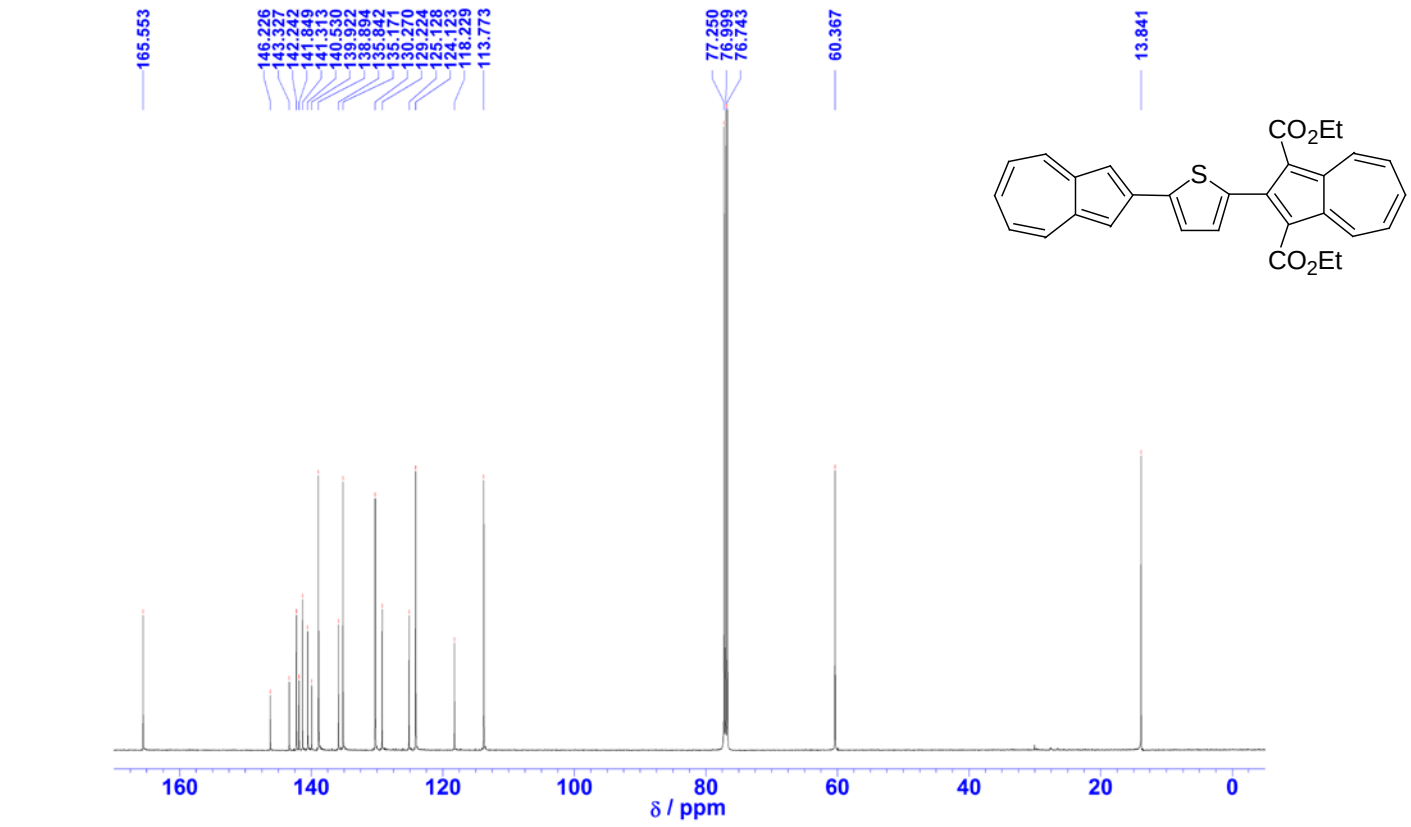



**Figure S–26.** $^{13}$C NMR spectrum of **22** in $CDCl_3$ (125 MHz).

**Table S–1**. Absorption maxima [nm] and their coefficients (log ε) in visible region of thienylazulene derivatives **9–17** and di(azulenyl)thiophenes **19–22** in $CH_2Cl_2$, and **1** and **23** for references

| Sample | λmax (log ε) |
|---|---|
| **9** | 419 (3.81), 528 (2.79) |
| **10** | 525 (2.86) |
| **11** | 514 (2.85) |
| **12** | 392 (3.61), 522 (2.82) |
| **13** | 426 (3.92), 541 sh (2.82) |
| **14** | 433 sh (4.42), 451 (4.51) |
| **15** | 457 (4.48) |
| **16** | 455 (4.48) |
| **17** | 430 sh (4.41), 451 (4.51) |
| **19** | 463 (4.38) |
| **20** | 446 (4.26) |
| **21** | 479 (4.58) |
| **22** | 402 sh (4.34), 428 (4.46), 546 sh (3.09), 610 sh (2.77), 633 sh (2.50) |
| **1** | 388 (3.85), 404 sh (3.76), 452 (3.37) |
| **23** | 505 (2.81), 534 sh (2.75) |

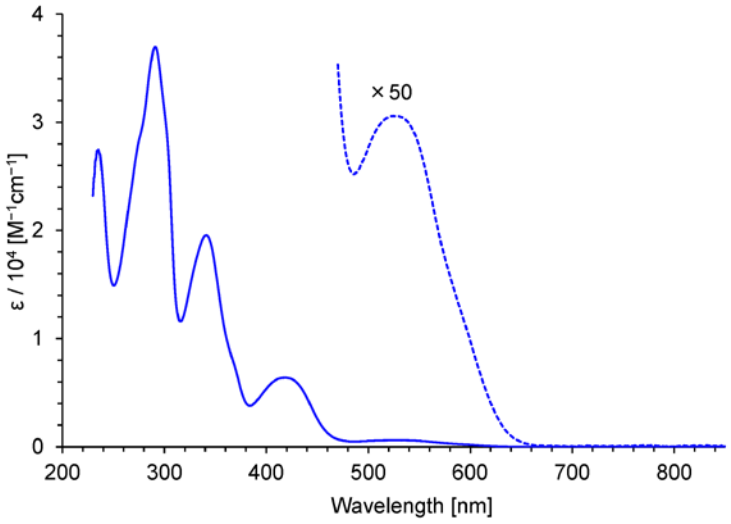



**Figure S–27.** UV/Vis spectra of **9** in CH2Cl2.

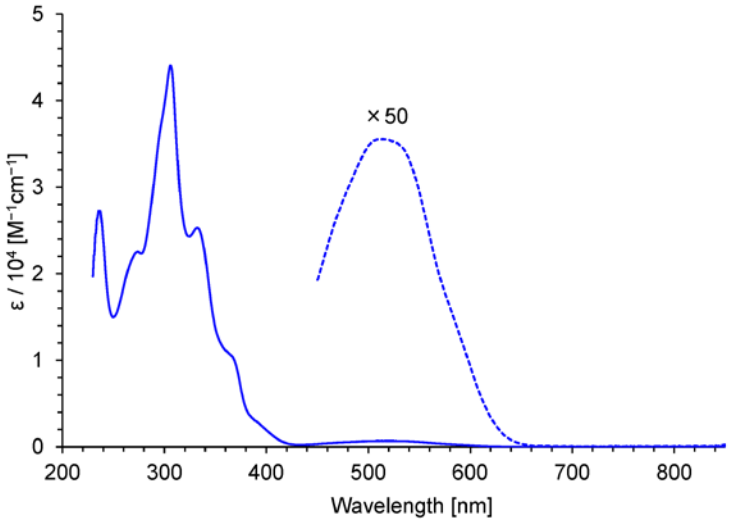



**Figure S–28.** UV/Vis spectra of **10** in CH2Cl2.

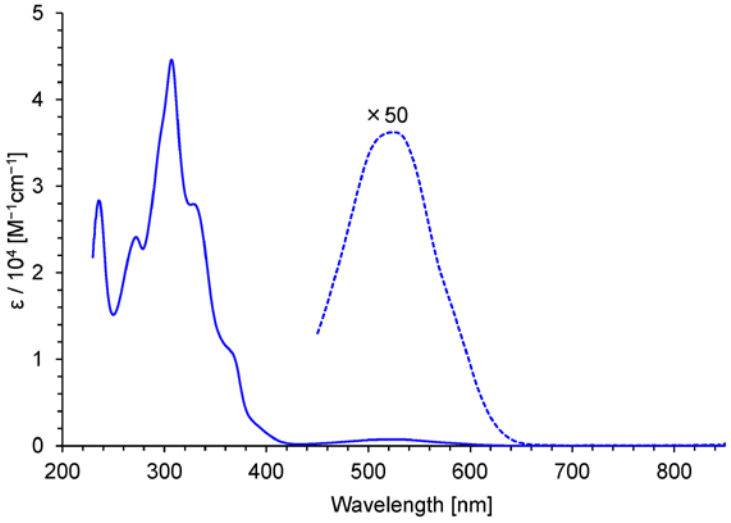



**Figure S–29.** UV/Vis spectra of **11** in CH2Cl2.

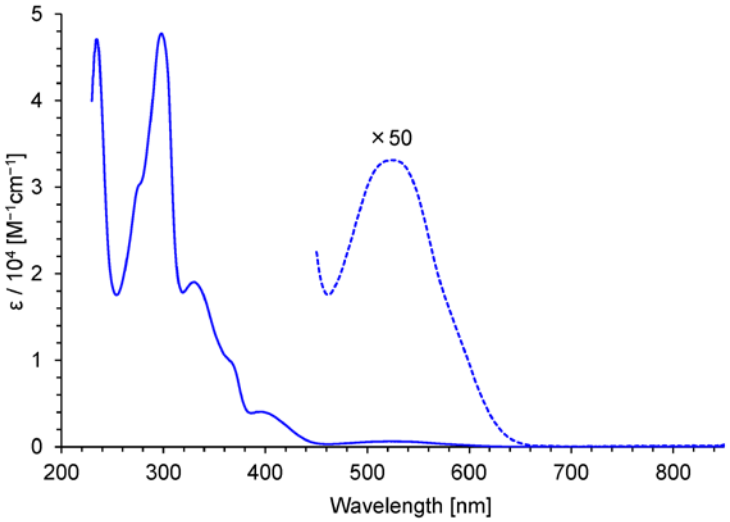



**Figure S–30.** UV/Vis spectra of **12** in $CH_2Cl_2$.

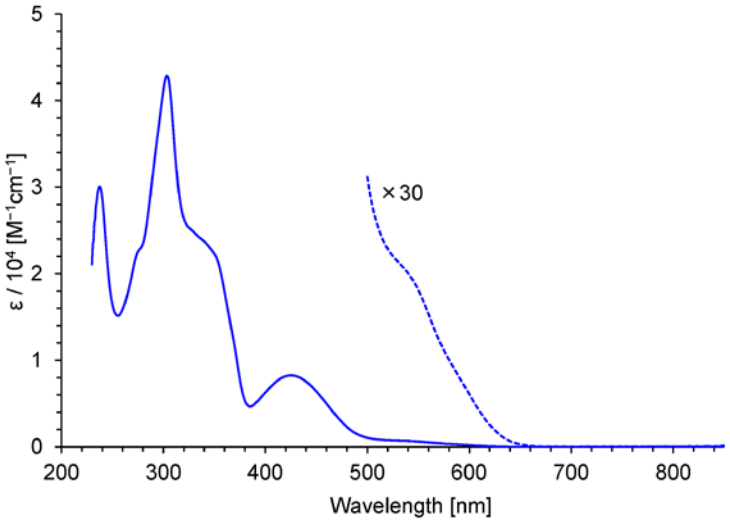



**Figure S–31.** UV/Vis spectra of **13** in $CH_2Cl_2$.

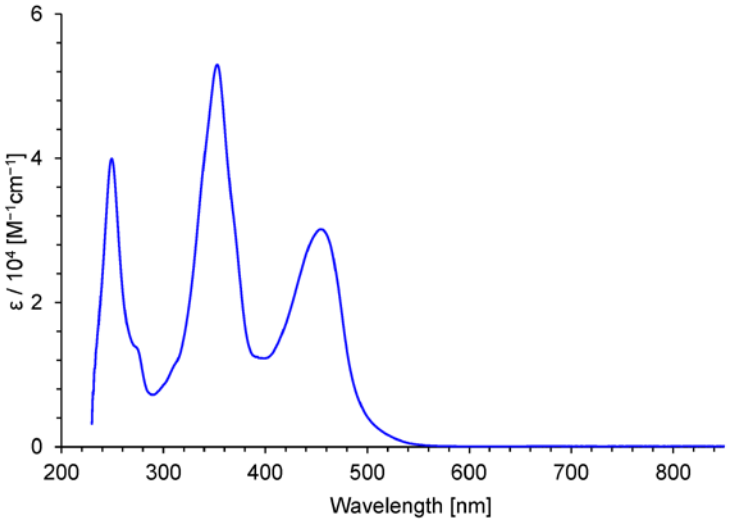



**Figure S–32.** UV/Vis spectra of **15** in $CH_2Cl_2$.

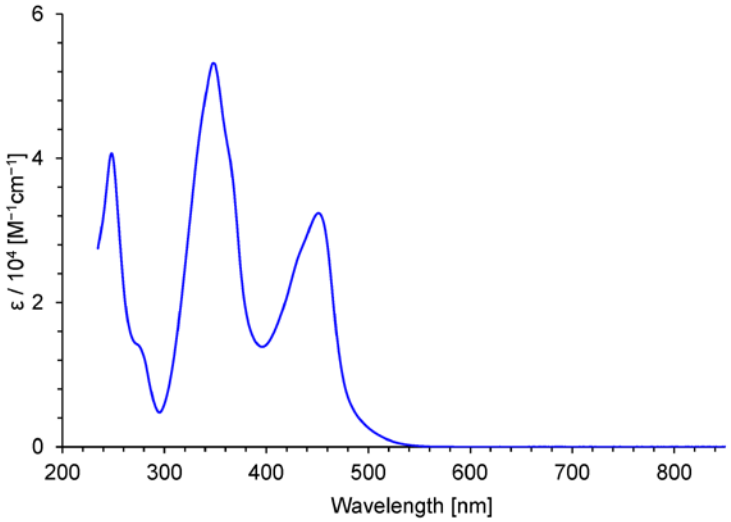



**Figure S–33.** UV/Vis spectra of **16** in $CH_2Cl_2$.

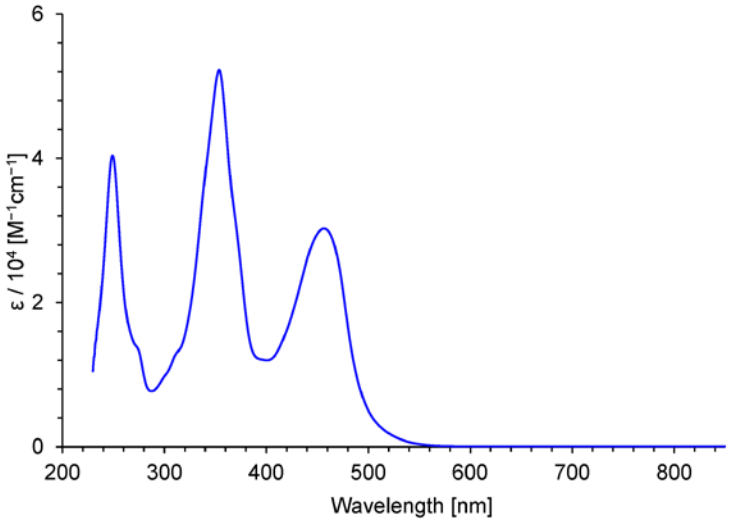



**Figure S–34.** UV/Vis spectra of **17** in $CH_2Cl_2$.

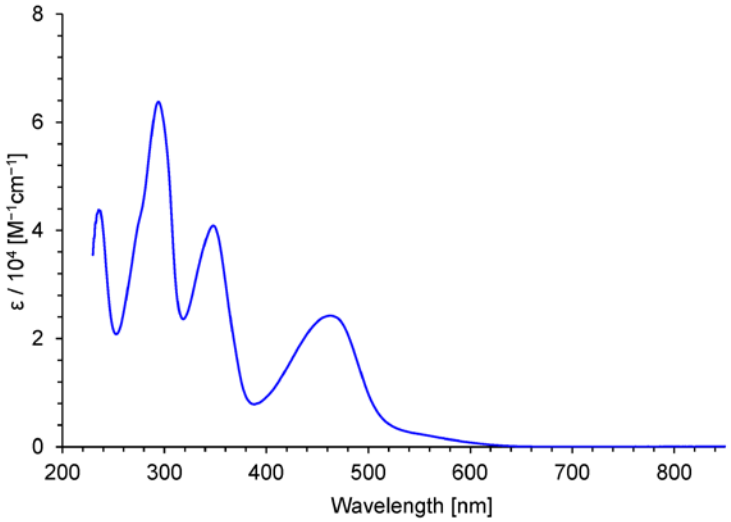



**Figure S–35.** UV/Vis spectra of **19** in $CH_2Cl_2$.

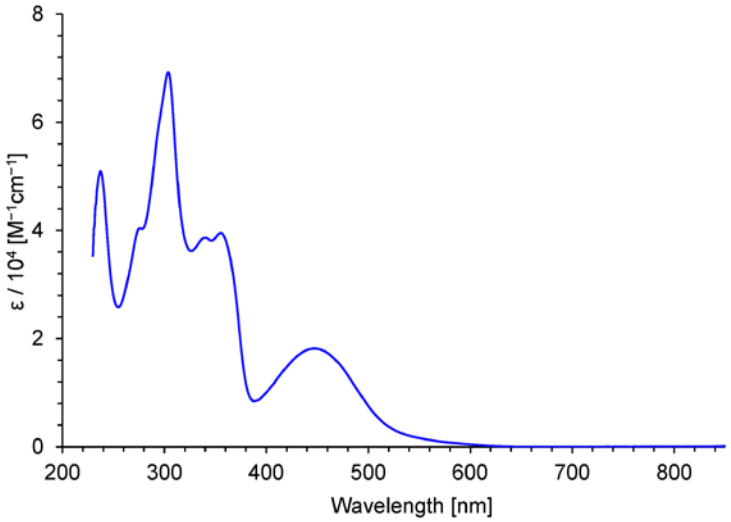



**Figure S–36.** UV/Vis spectra of **20** in $CH_2Cl_2$.

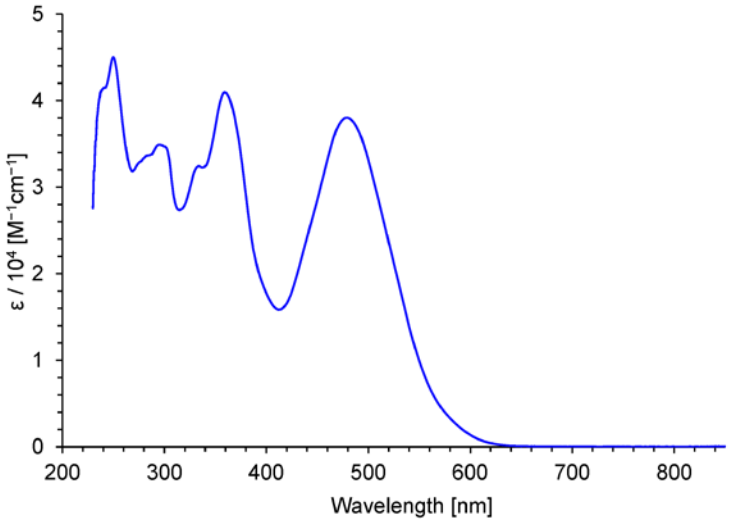



**Figure S–37.** UV/Vis spectra of **21** in $CH_2Cl_2$.

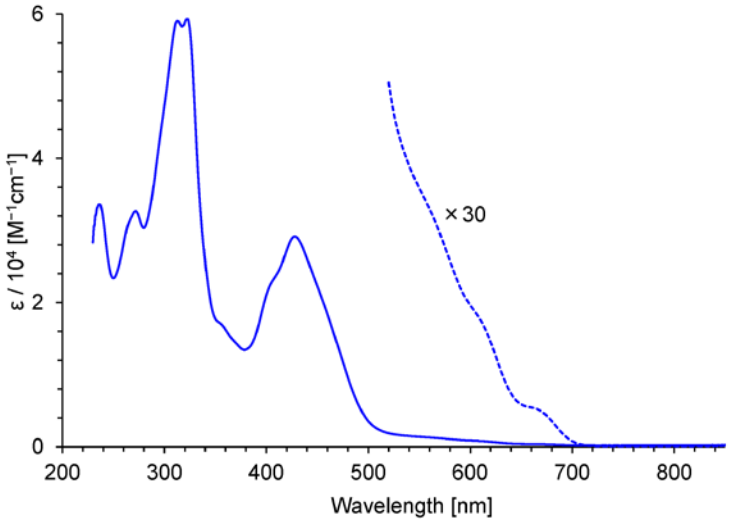



**Figure S–38.** UV/Vis spectra of **22** in $CH_2Cl_2$.

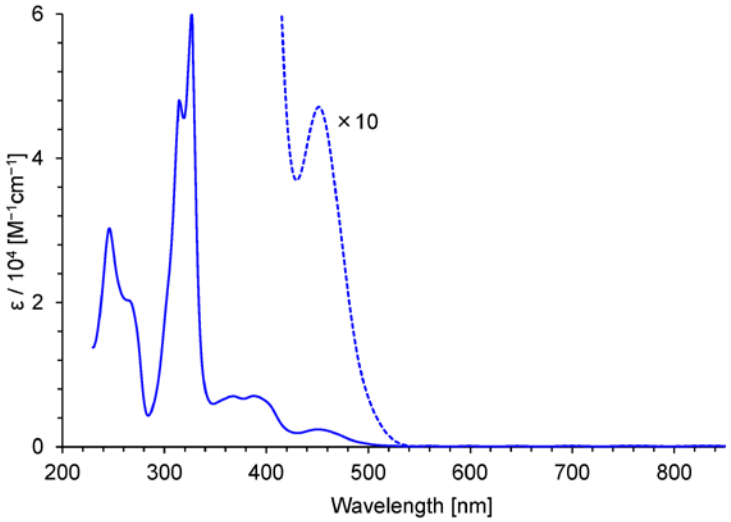



**Figure S–39.** UV/Vis spectra of **1** in $CH_2Cl_2$.

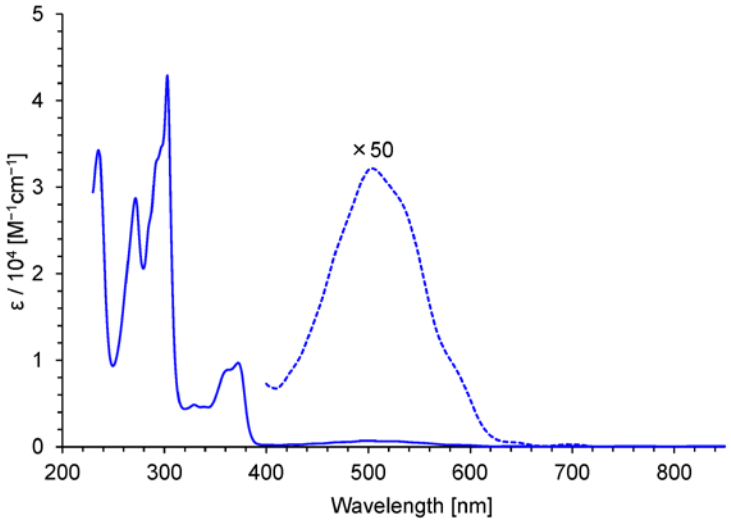
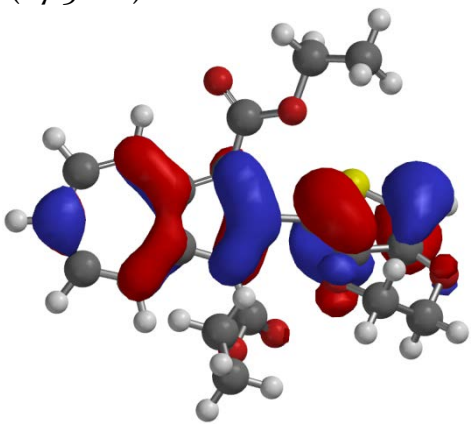
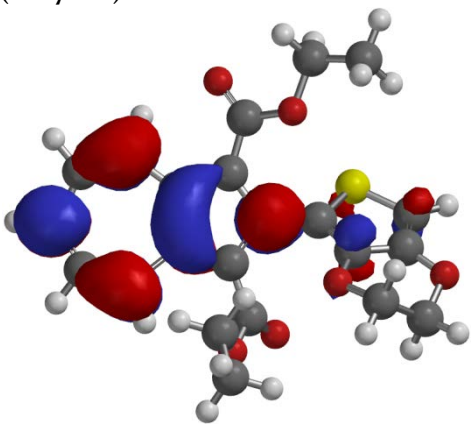



**Figure S–40.** UV/Vis spectra of **23** in $CH_2Cl_2$.

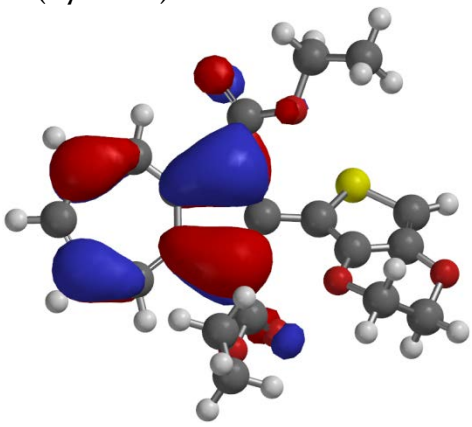
HOMO (–7.51 eV)



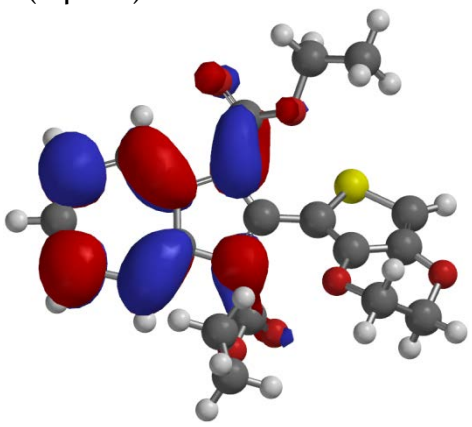
LUMO (0.67 eV)



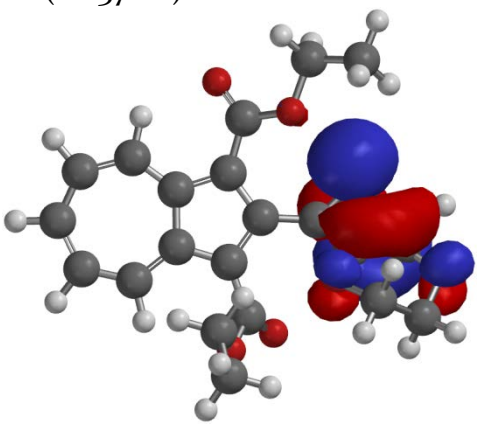
HOMO–1 (–7.61 eV)



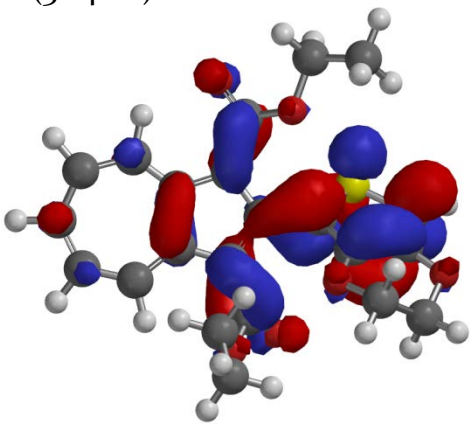
LUMO+1 (1.42 eV)



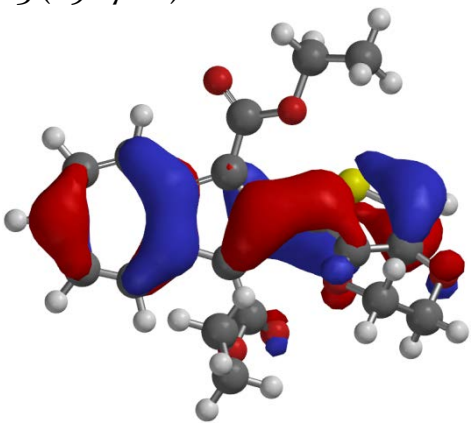
HOMO–2 (–8.37 eV)



LUMO+2 (3.24 eV)



HOMO–3 (–9.27 eV)



LUMO+3 (4.42 eV)

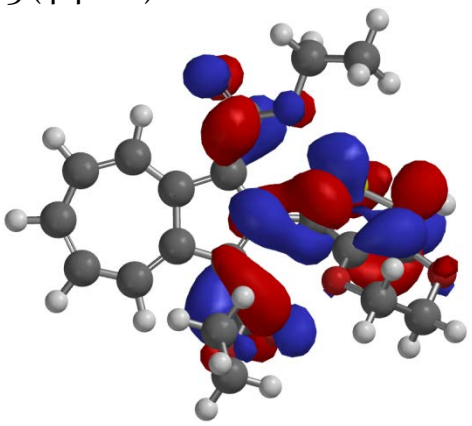
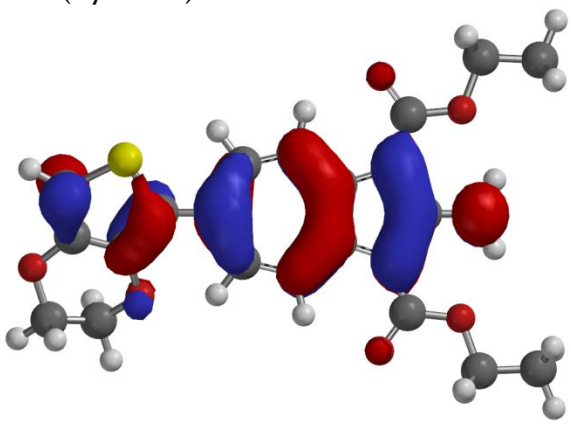
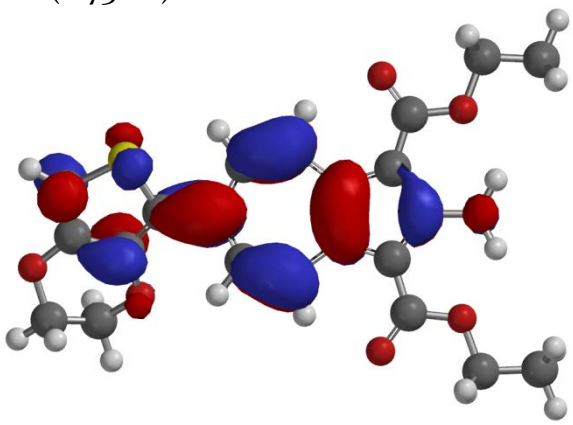


**Figure S-41.** Frontier Kohn–Sham orbitals of **9** at the B3LYP/6-31G** level.

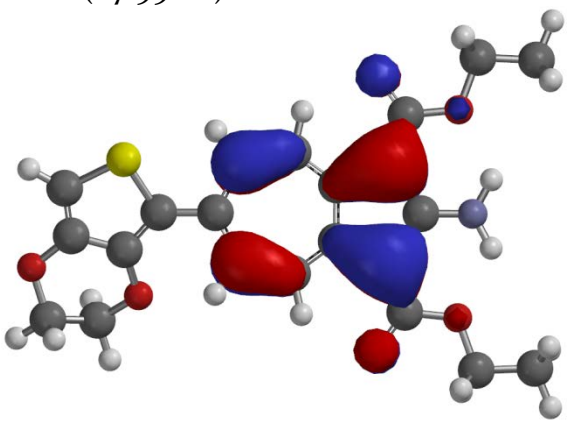
HOMO (–7.16 eV)



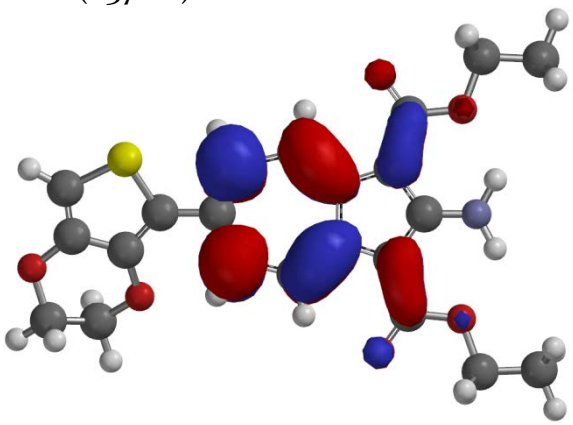
LUMO (0.73 eV)



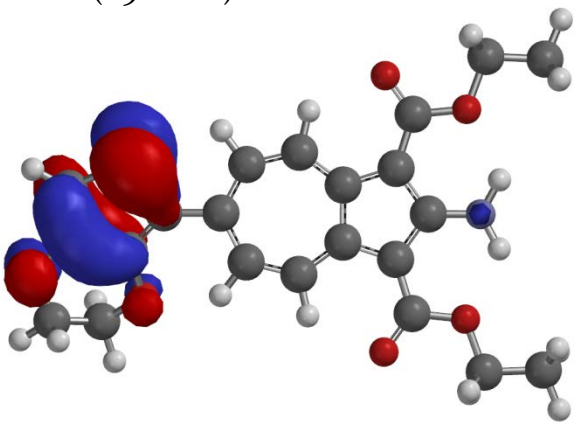
HOMO–1 (–7.99 eV)



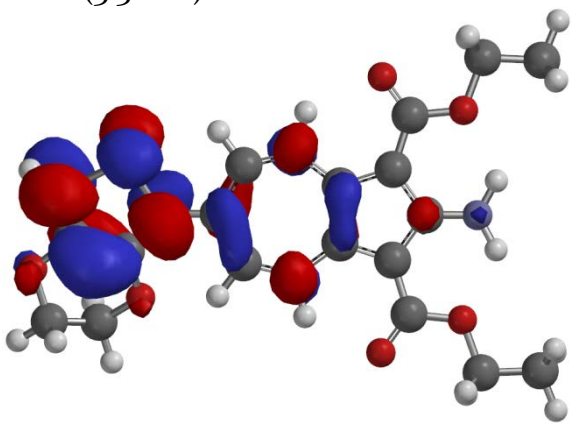
LUMO+1 (1.37 eV)



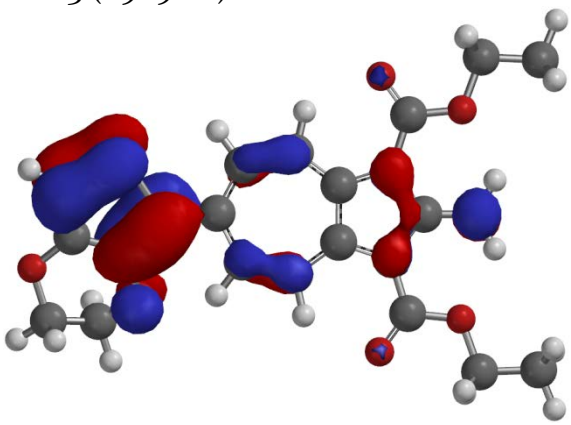
HOMO–2 (–9.02 eV)



LUMO+2 (3.38 eV)



HOMO–3 (–9.19 eV)



LUMO+3 (3.81 eV)

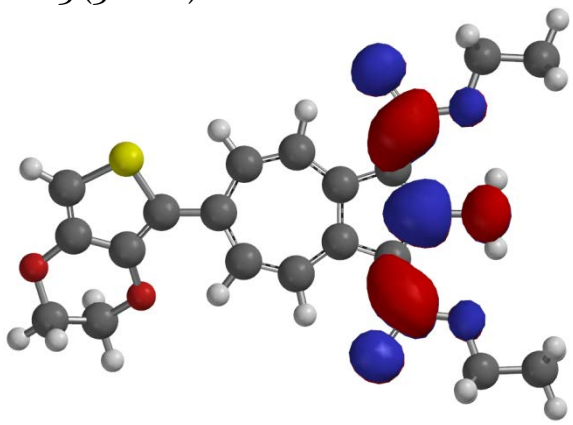
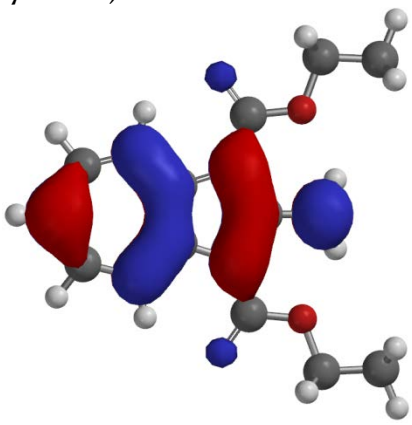
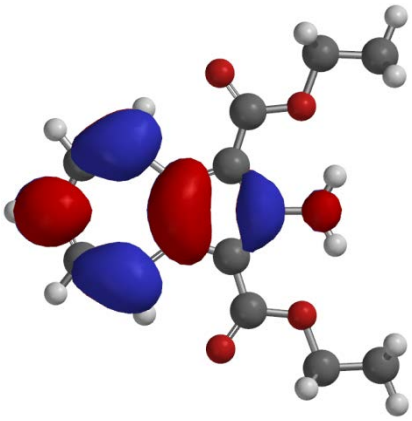


**Figure S-42.** Frontier Kohn–Sham orbitals of **14** at the B3LYP/6-31G** level.

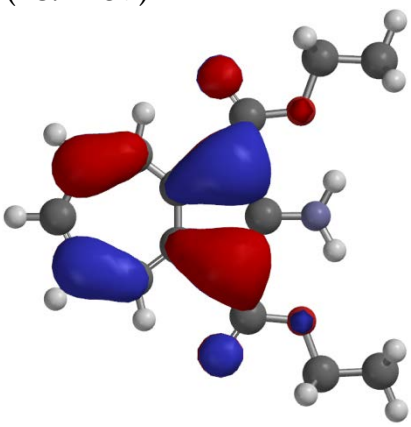
HOMO (–7.62 eV)



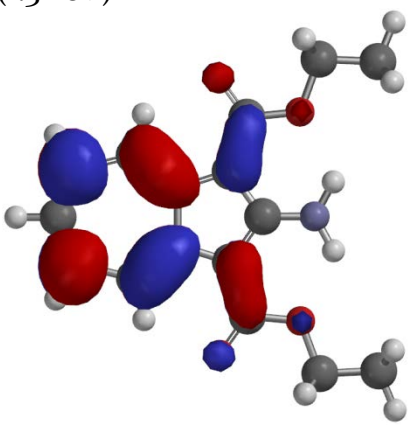
LUMO (1.20 eV)



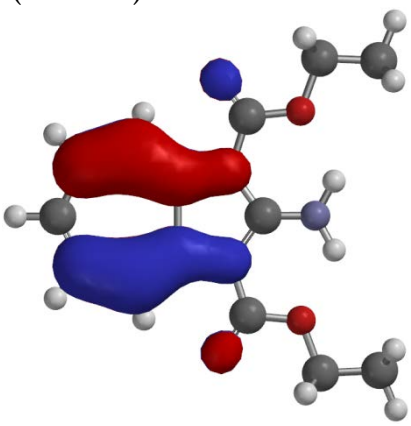
HOMO–1 (–8.06 eV)



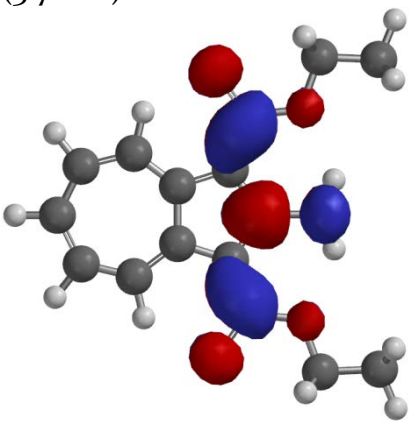
LUMO+1 (1.30 eV)



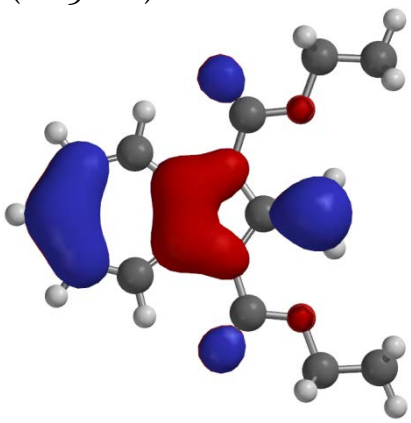
HOMO–2 (–11.11 eV)



LUMO+2 (3.72 eV)



HOMO–3 (–11.58 eV)



LUMO+3 (5.98 eV)

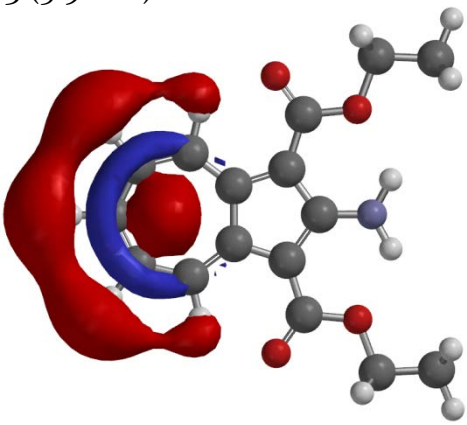
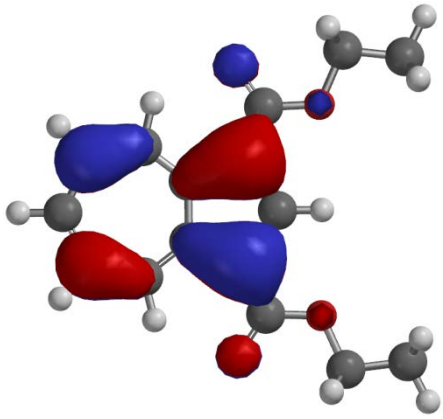
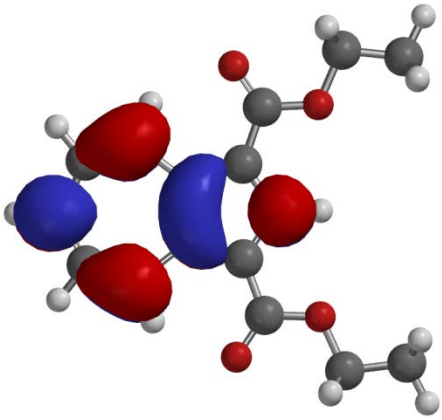


**Figure S-43.** Frontier Kohn–Sham orbitals of **1** at the B3LYP/6-31G** level.

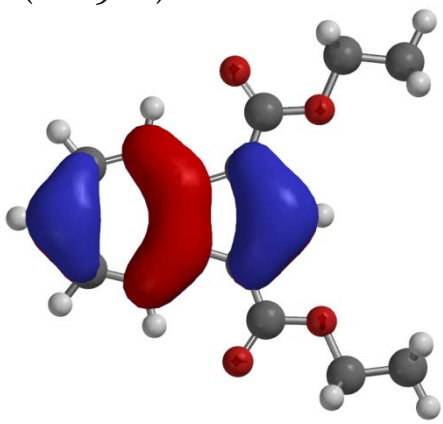
HOMO (–7.90 eV)



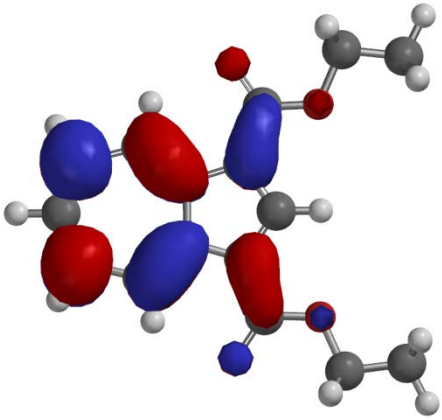
LUMO (0.78 eV)



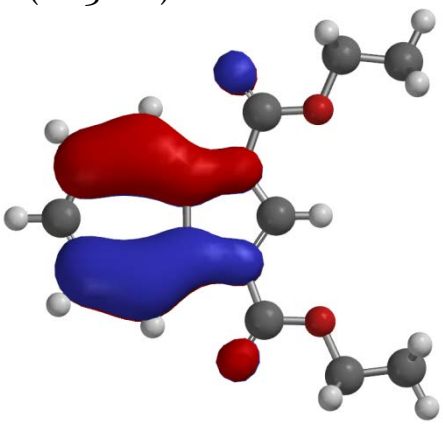
HOMO–1 (–8.89 eV)



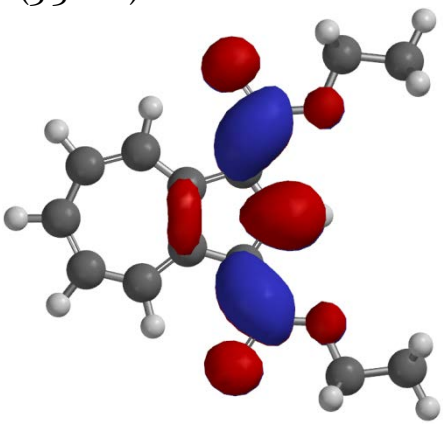
LUMO+1 (1.11 eV)



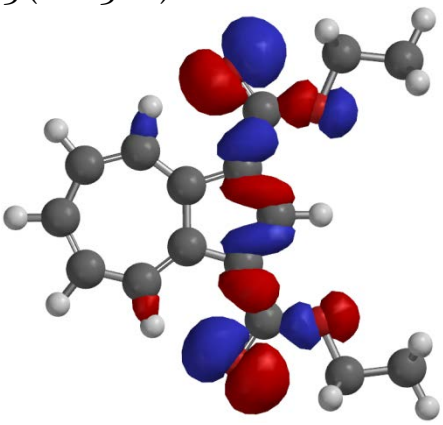
HOMO–2 (–11.32 eV)



LUMO+2 (3.38 eV)



HOMO–3 (–11.83 eV)



LUMO+3 (5.75 eV)

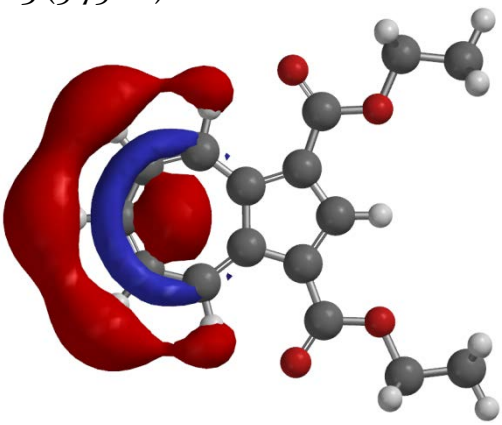


**Figure S-44.** Frontier Kohn–Sham orbitals of **23** at the B3LYP/6-31G** level.

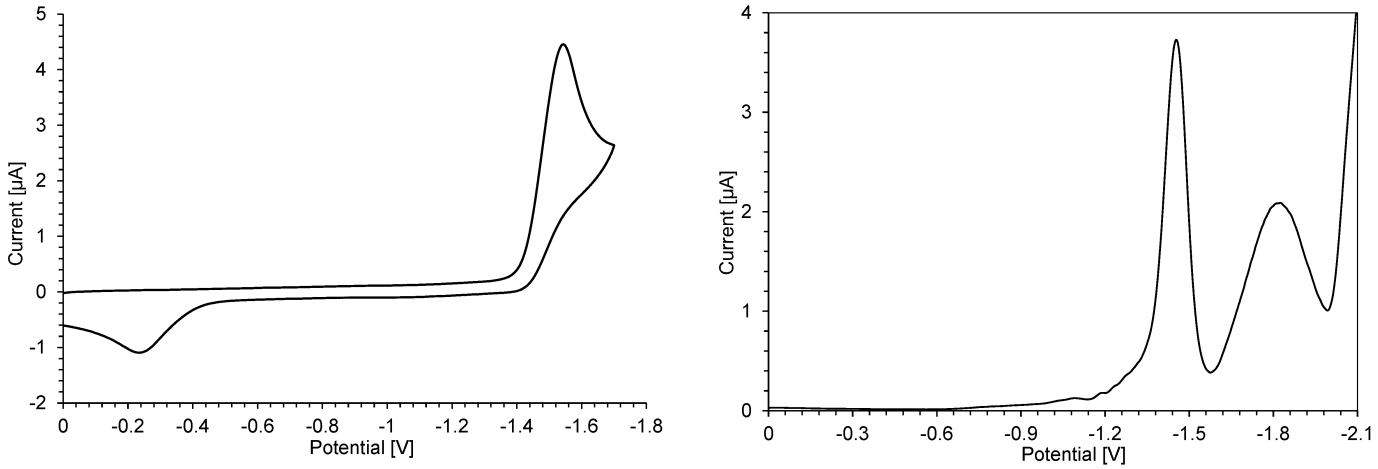



**Figure S-45.** Cyclic voltammogram (left) and differential pulse voltammogram (right) of **9** (1 mM) in benzonitrile containing $Et_4NClO_4$ (0.1M) as the supporting electrolyte.

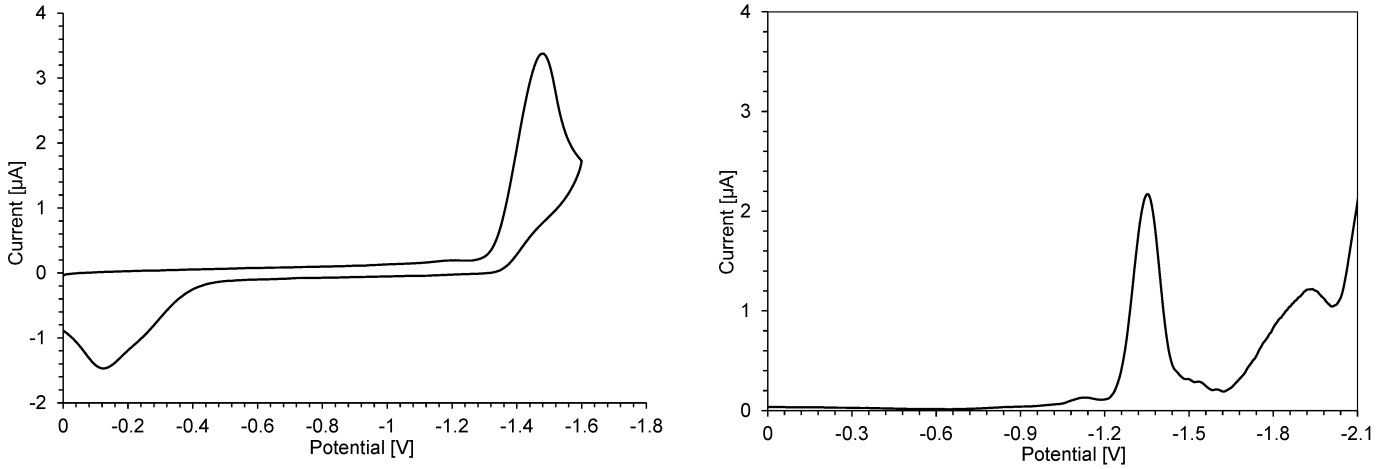



**Figure S-46.** Cyclic voltammogram (left) and differential pulse voltammogram (right) of **10** (1 mM) in benzonitrile containing $Et_4NClO_4$ (0.1M) as the supporting electrolyte.

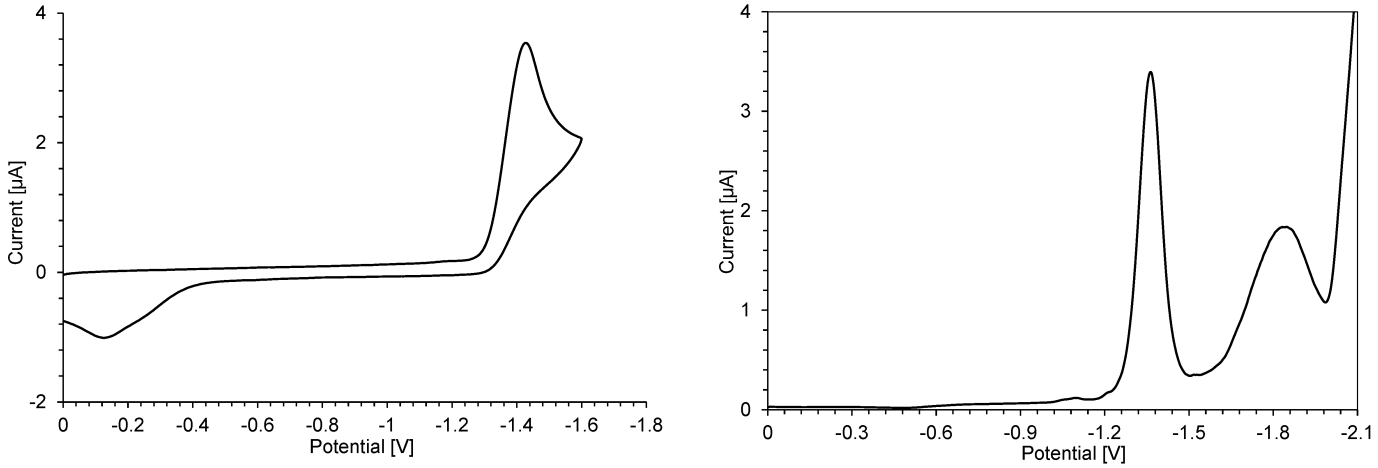



**Figure S-47.** Cyclic voltammogram (left) and differential pulse voltammogram (right) of **11** (1 mM) in benzonitrile containing $Et_4NClO_4$ (0.1M) as the supporting electrolyte.

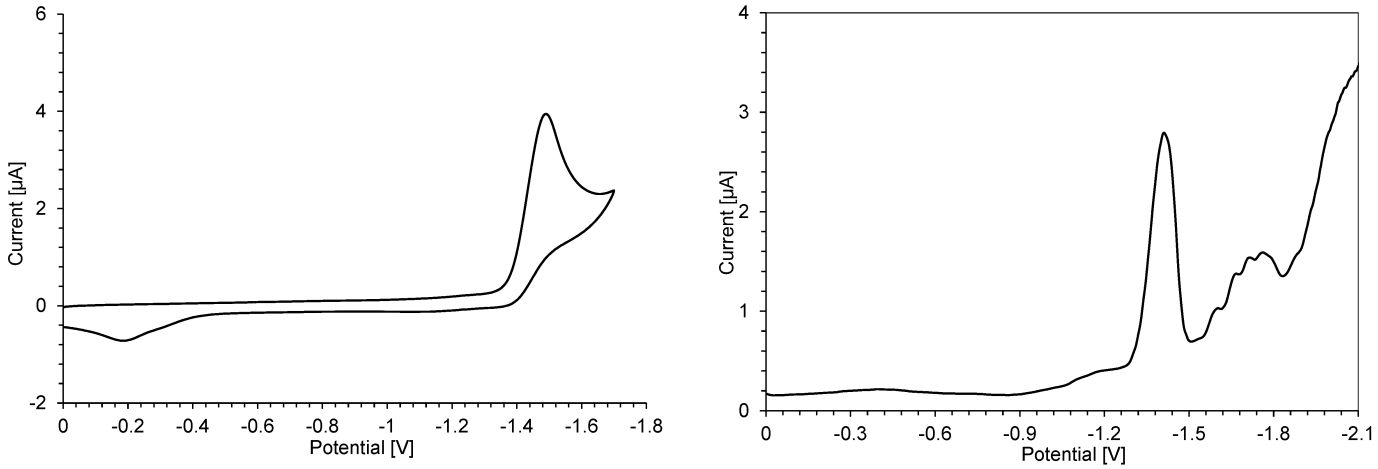



**Figure S-48.** Cyclic voltammogram (left) and differential pulse voltammogram (right) of **12** (1 mM) in benzonitrile containing $Et_4NClO_4$ (0.1M) as the supporting electrolyte.

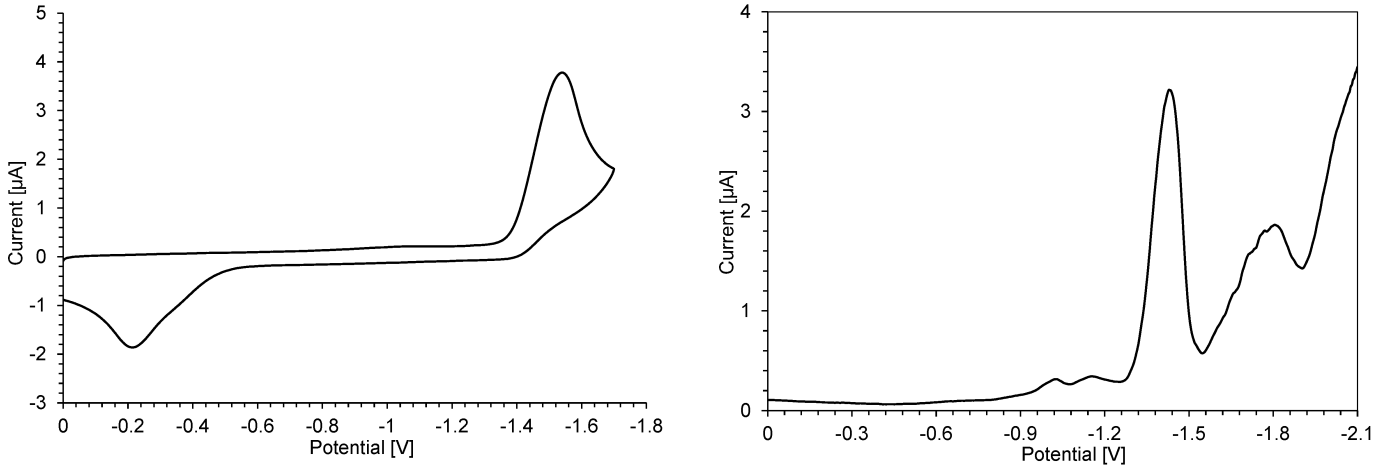



**Figure S-49.** Cyclic voltammogram (left) and differential pulse voltammogram (right) of **13** (1 mM) in benzonitrile containing $Et_4NClO_4$ (0.1M) as the supporting electrolyte.

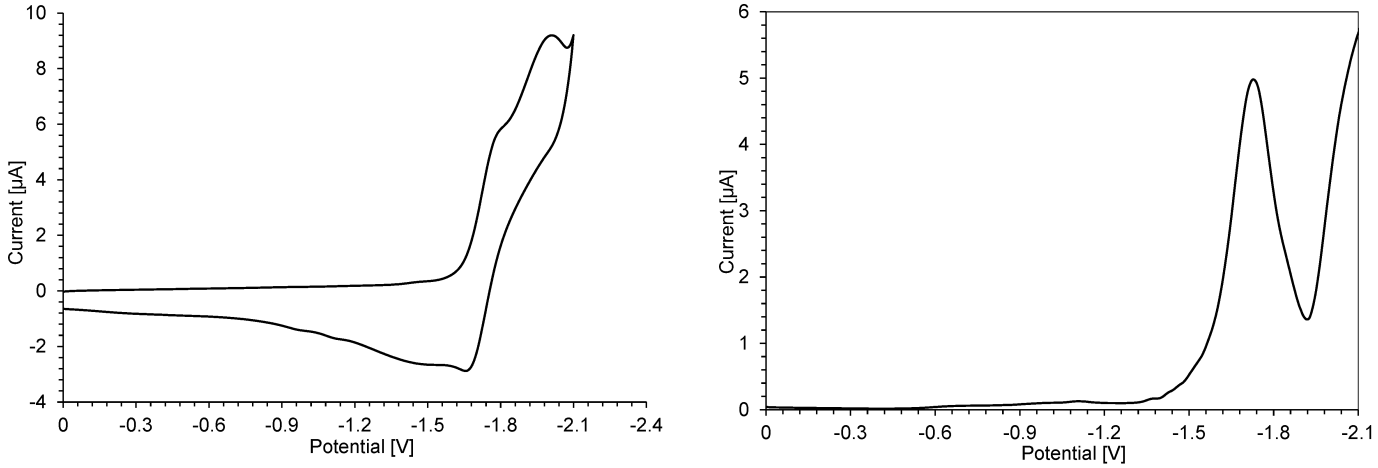



**Figure S-50.** Cyclic voltammogram (left) and differential pulse voltammogram (right) of **14** (1 mM) in benzonitrile containing $Et_4NClO_4$ (0.1M) as the supporting electrolyte.

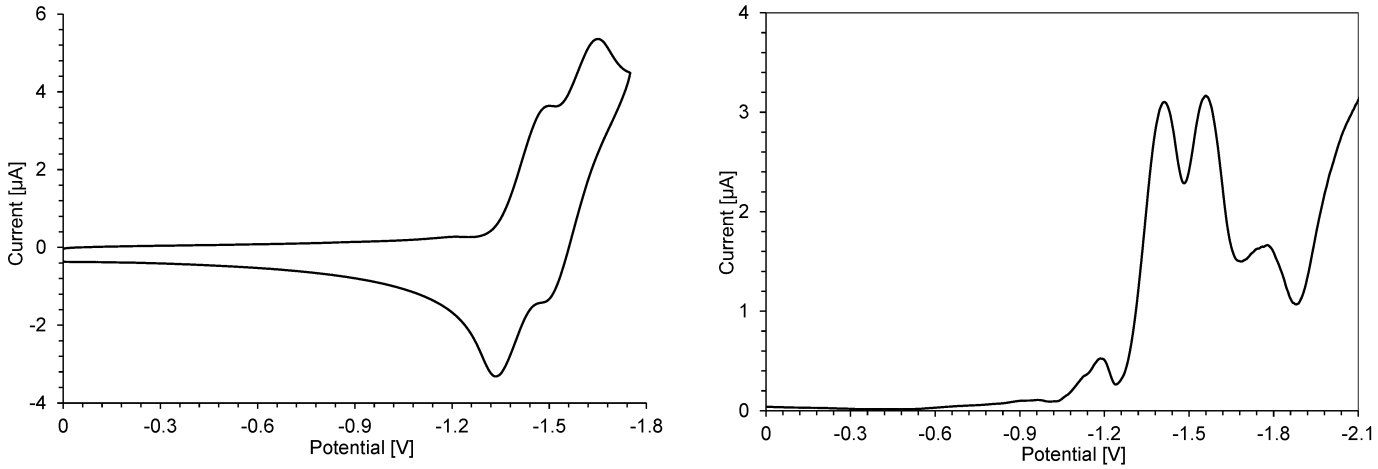



**Figure S-51.** Cyclic voltammogram (left) and differential pulse voltammogram (right) of **15** (1 mM) in benzonitrile containing $Et_4NClO_4$ (0.1M) as the supporting electrolyte.

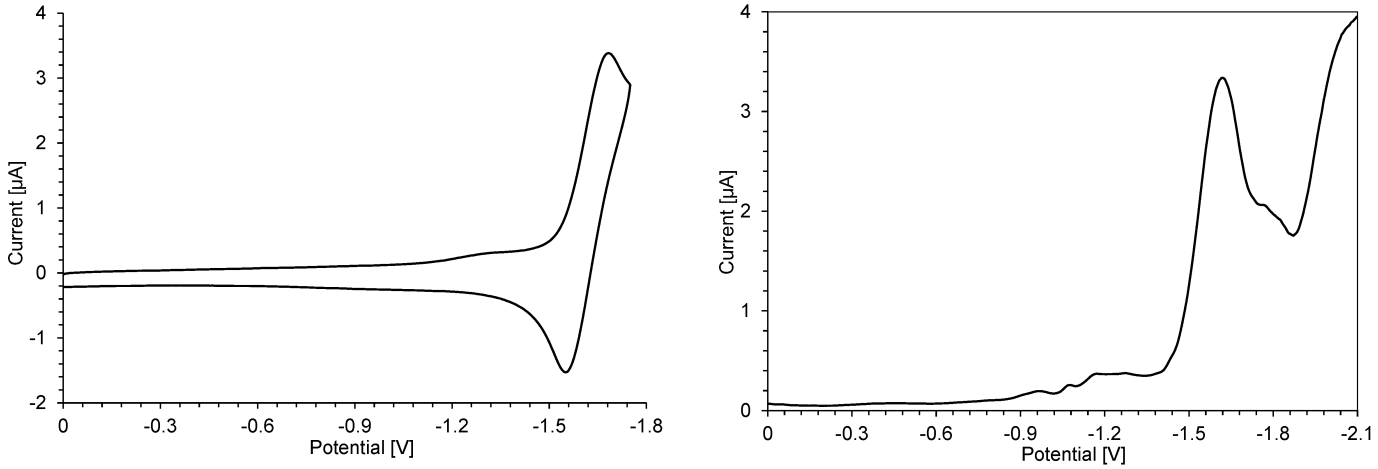



**Figure S-52.** Cyclic voltammogram (left) and differential pulse voltammogram (right) of **17** (1 mM) in benzonitrile containing $Et_4NClO_4$ (0.1M) as the supporting electrolyte.

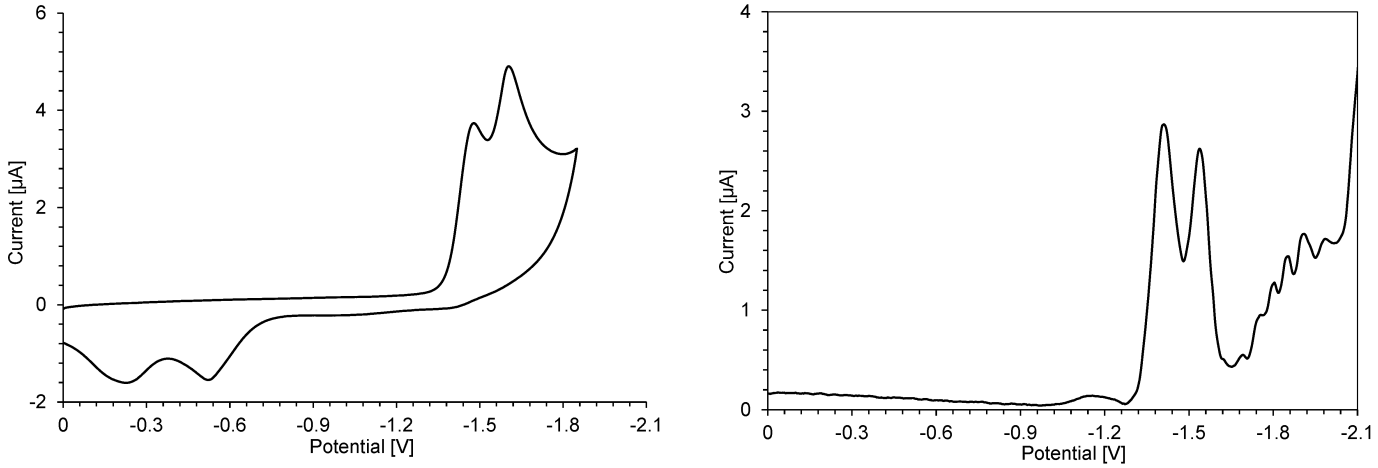



**Figure S-53.** Cyclic voltammogram (left) and differential pulse voltammogram (right) of **19** (1 mM) in benzonitrile containing $Et_4NClO_4$ (0.1M) as the supporting electrolyte.

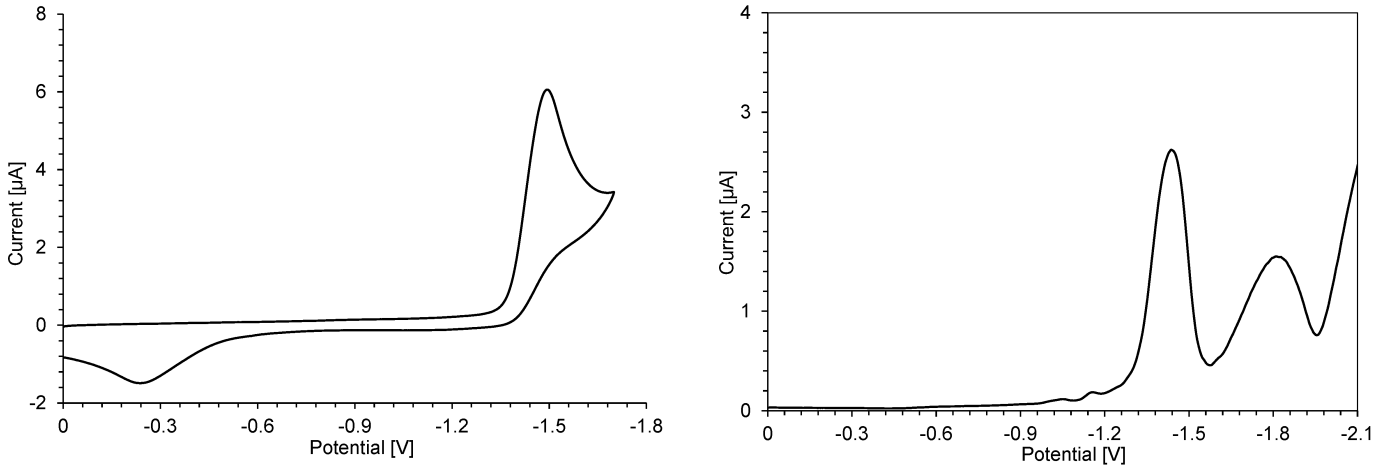



**Figure S-54.** Cyclic voltammogram (left) and differential pulse voltammogram (right) of **20** (1 mM) in benzonitrile containing $Et_4NClO_4$ (0.1M) as the supporting electrolyte.

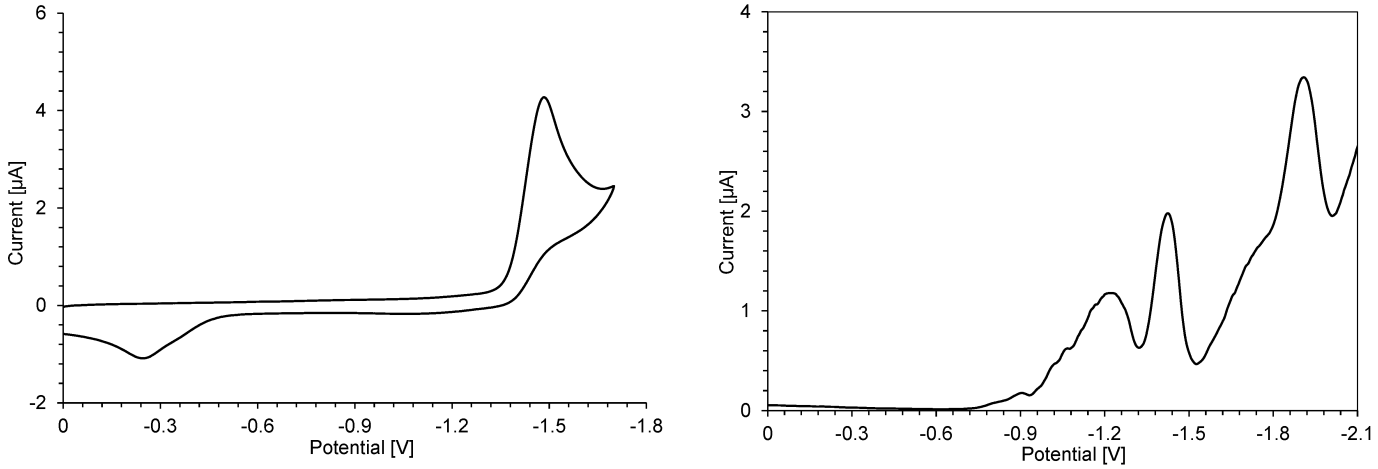



**Figure S-55.** Cyclic voltammogram (left) and differential pulse voltammogram (right) of **22** (1 mM) in benzonitrile containing $Et_4NClO_4$ (0.1M) as the supporting electrolyte.