Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Electronic Supplementary Information (ESI)

Synthesis of azulenophthalimides by phosphine-mediated annulation of 1,2-diformylazulenes with maleimides

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➢ *Contents*

1. Copies of ^{1}H NMR, ^{13}C NMR, COSY and HRMS of reported compounds (Figures S1−S51).

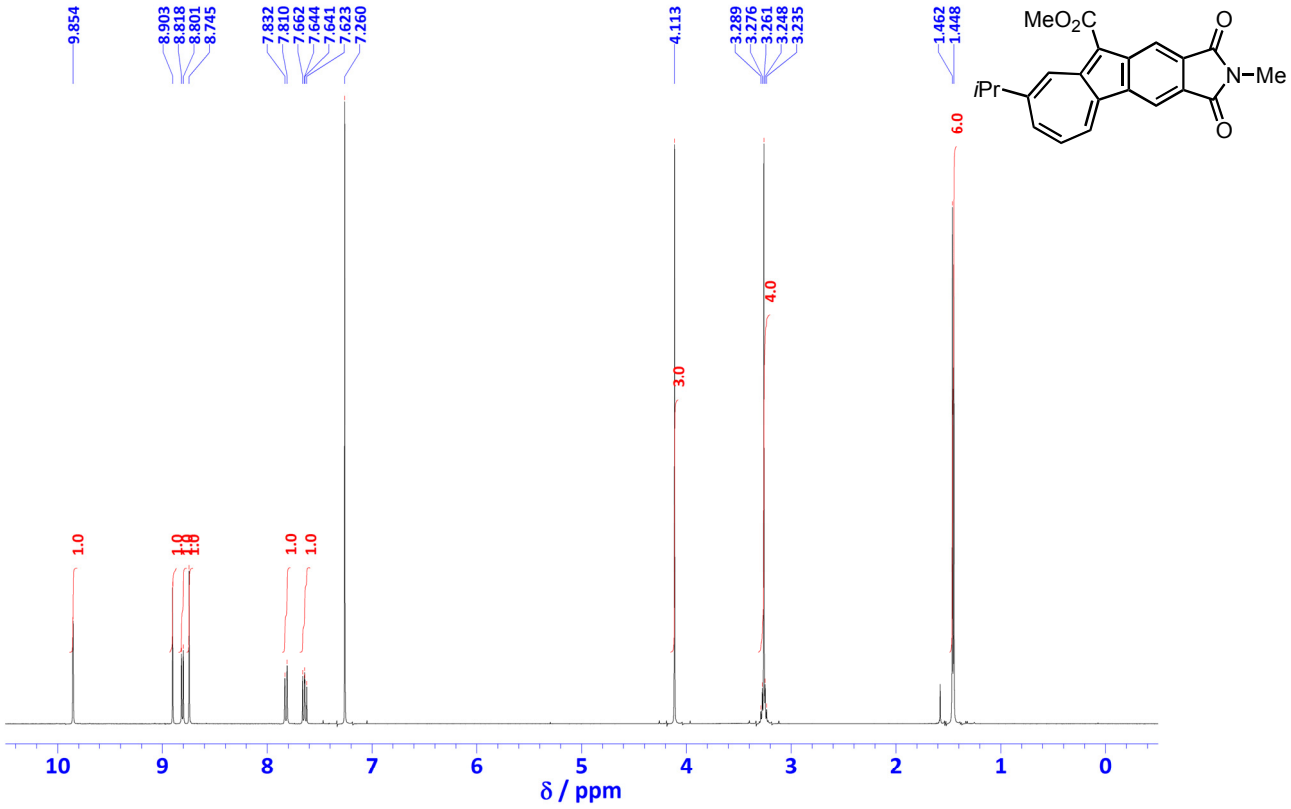


Figure S1. ^{1}H NMR spectrum of **4a** in $CDCl_3$ (500 MHz).

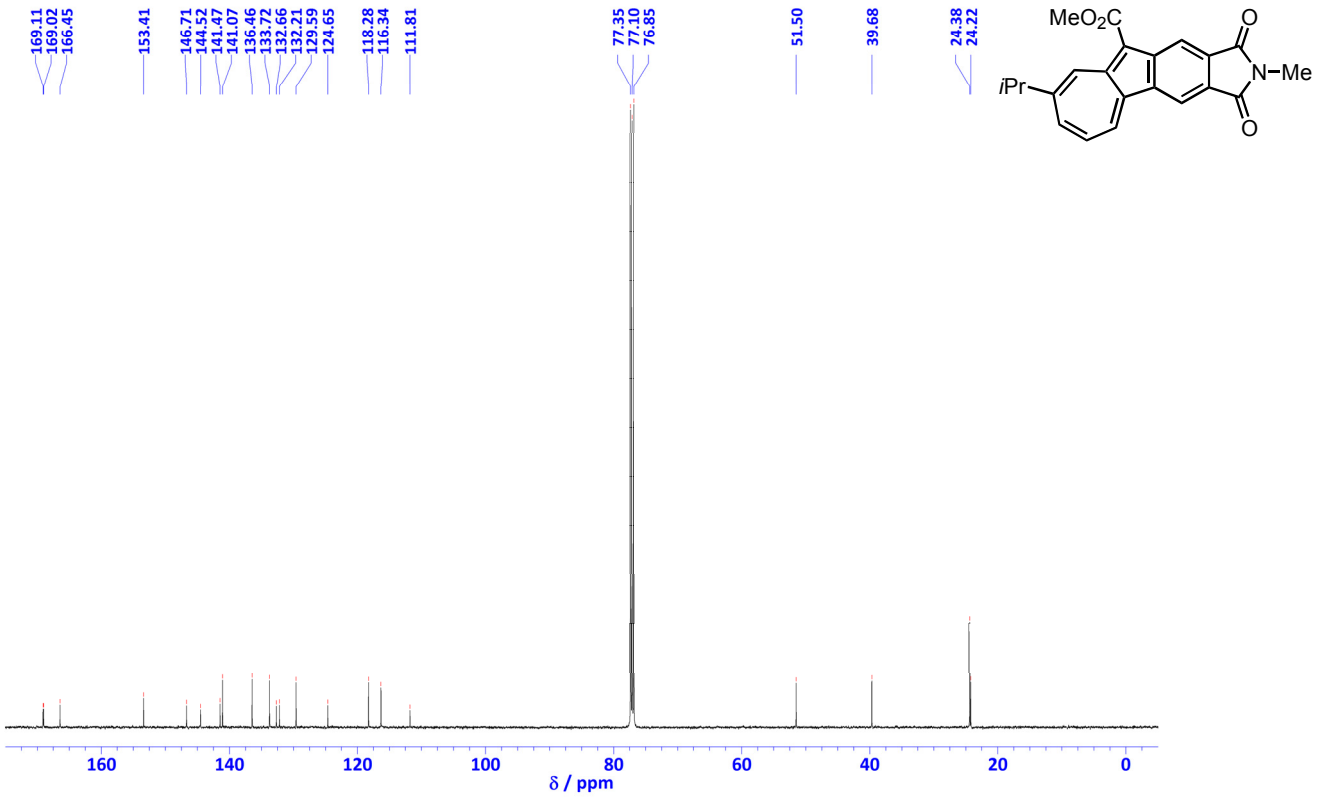


Figure S2. ^{13}C NMR spectrum of **4a** in $CDCl_3$ (125 MHz).

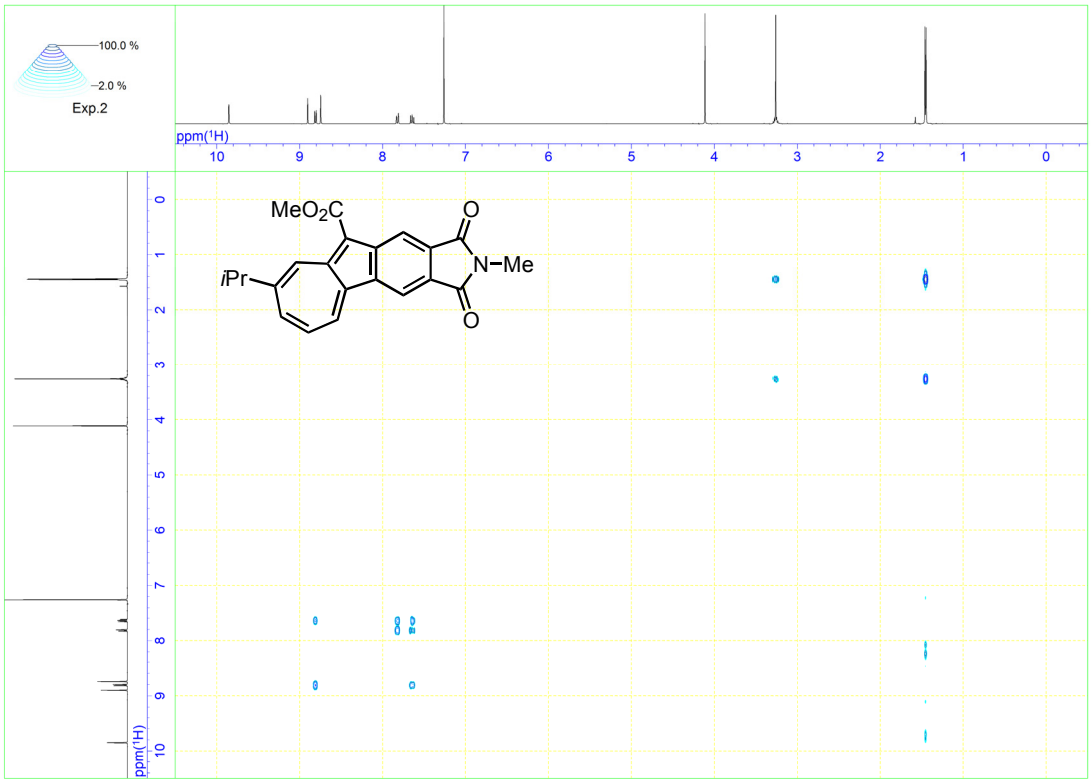


Figure S3. COSY spectrum of **4a** in $CDCl_3$ (500 MHz).

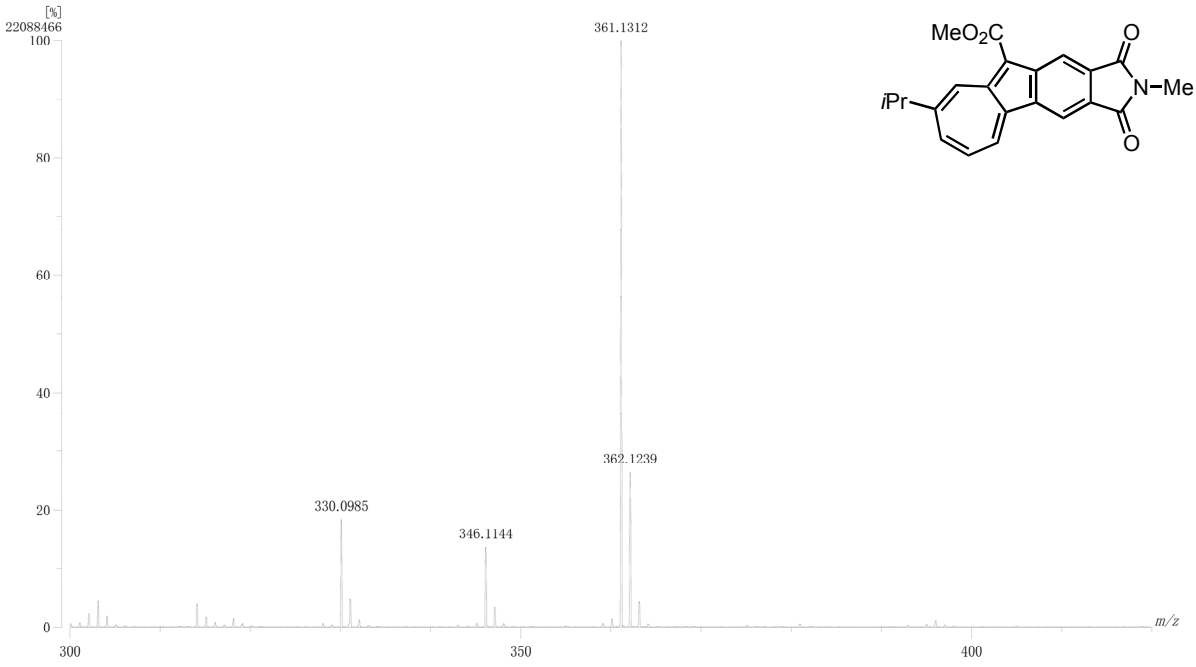


Figure S4. HRMS (FAB-double-focusing, positive) of **4a**.

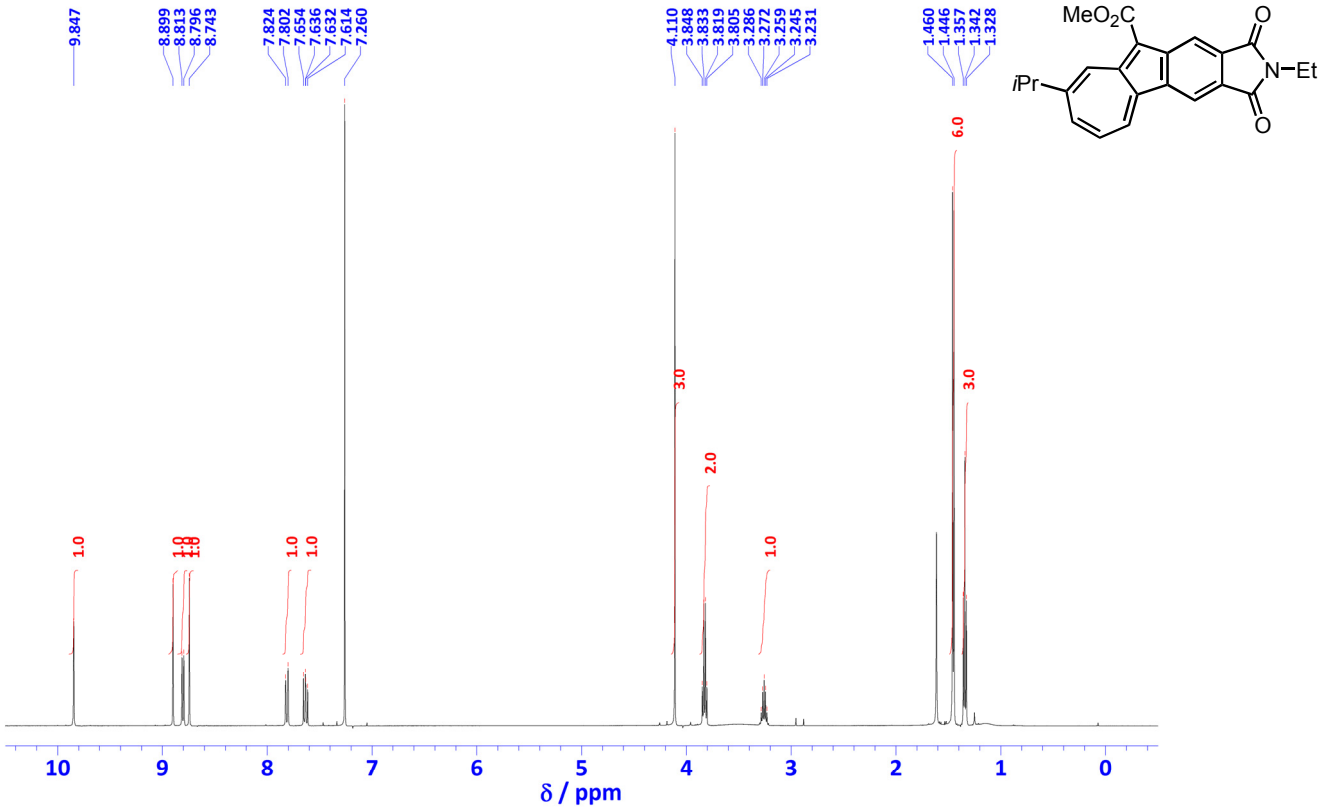


Figure S5. ^{1}H NMR spectrum of **4b** in $CDCl_3$ (500 MHz).

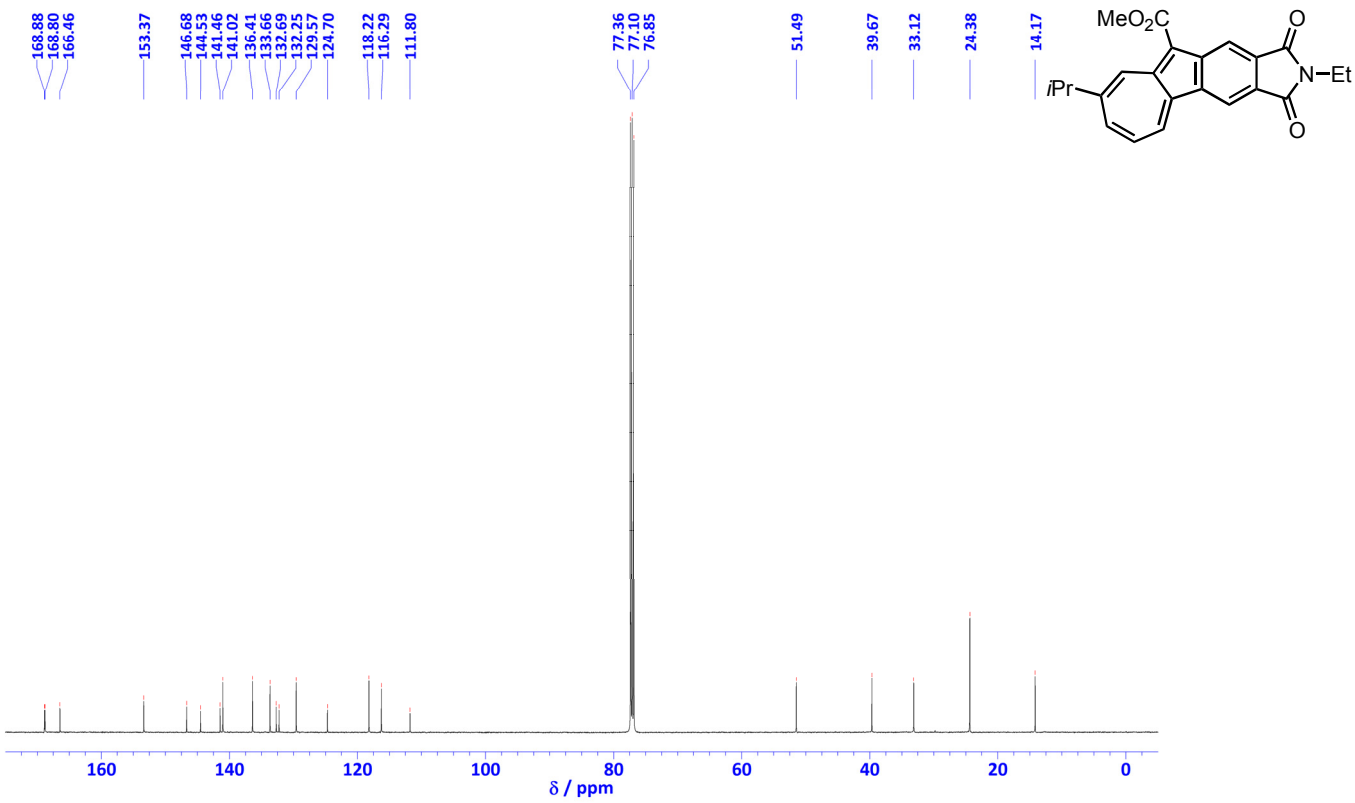


Figure S6. ^{13}C NMR spectrum of **4b** in $CDCl_3$ (125 MHz).

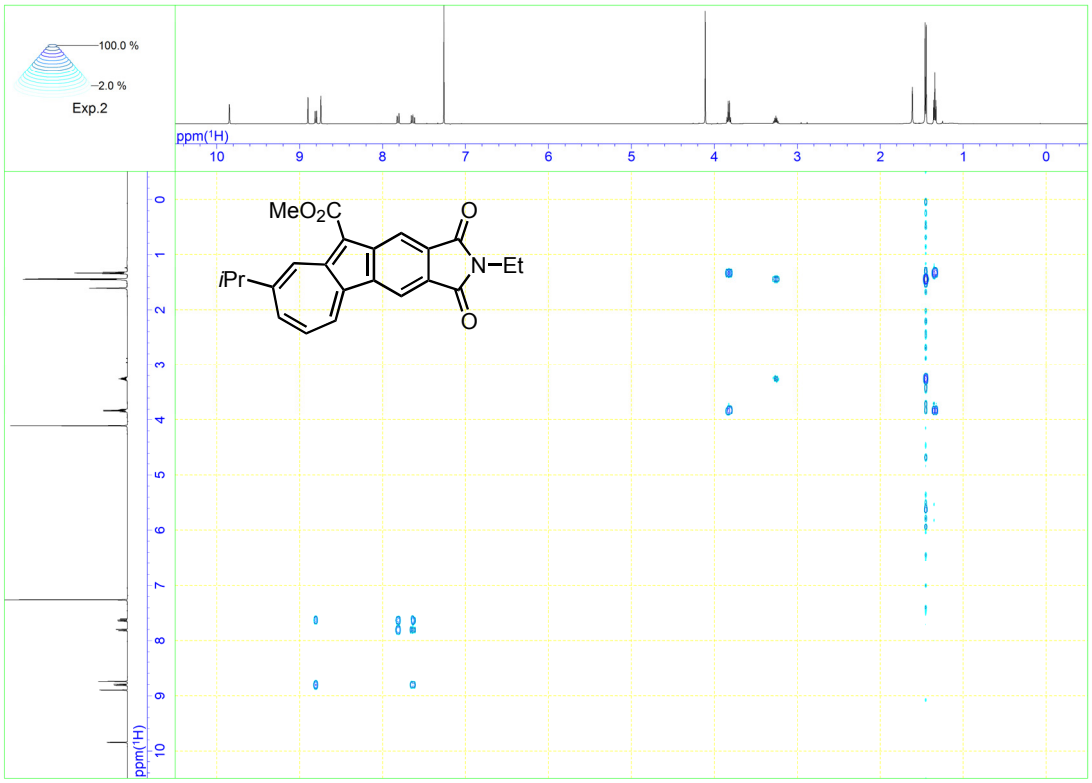


Figure S7. COSY spectrum of **4b** in $CDCl_3$ (500 MHz).

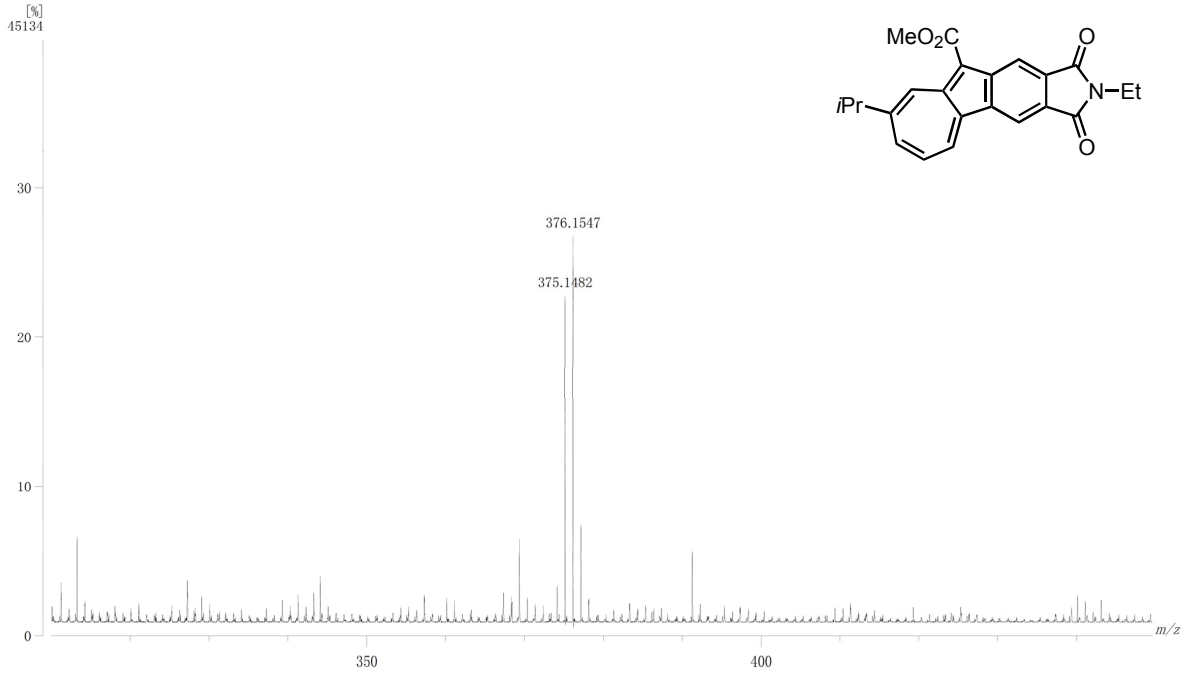


Figure S8. HRMS (FAB-double-focusing, positive) of **4b**.

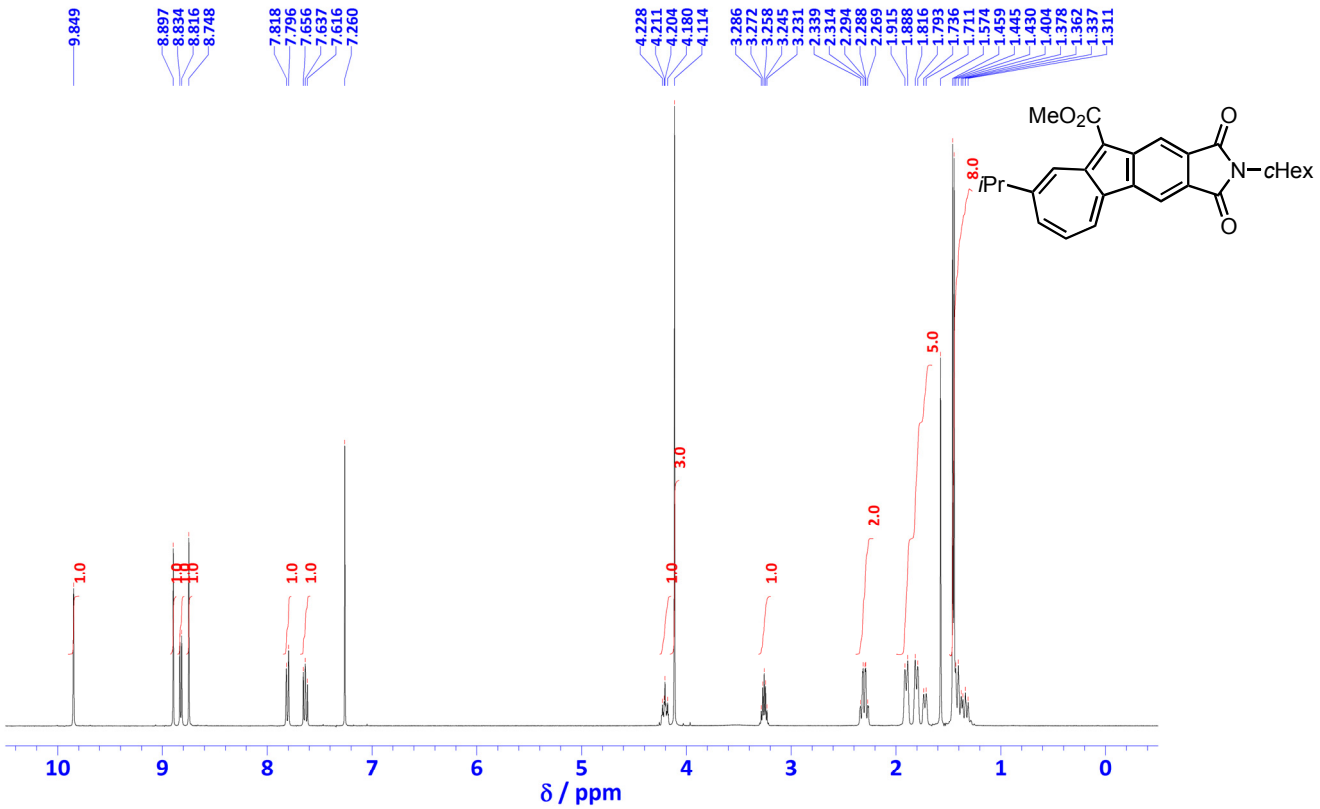


Figure S9. ^{1}H NMR spectrum of **4c** in $CDCl_3$ (500 MHz).

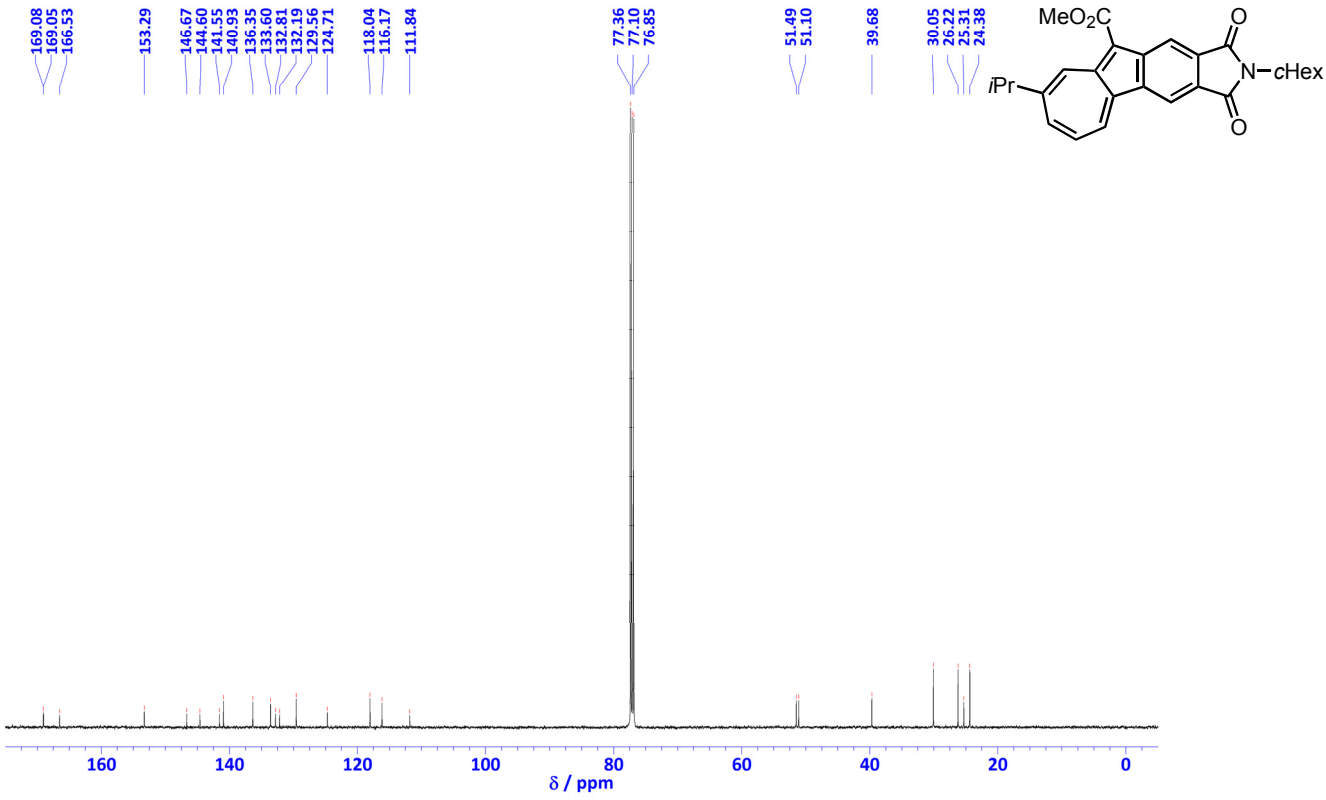


Figure S10. ^{13}C NMR spectrum of **4c** in $CDCl_3$ (125 MHz).

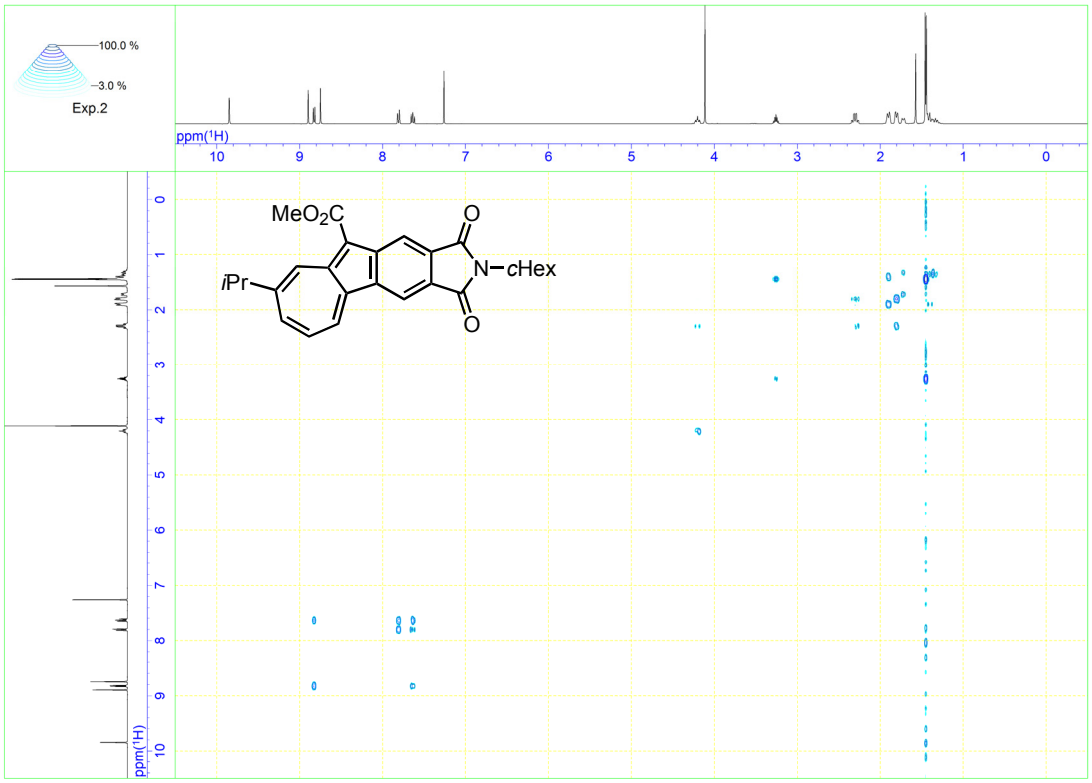


Figure S11. COSY spectrum of **4c** in $CDCl_3$ (500 MHz).

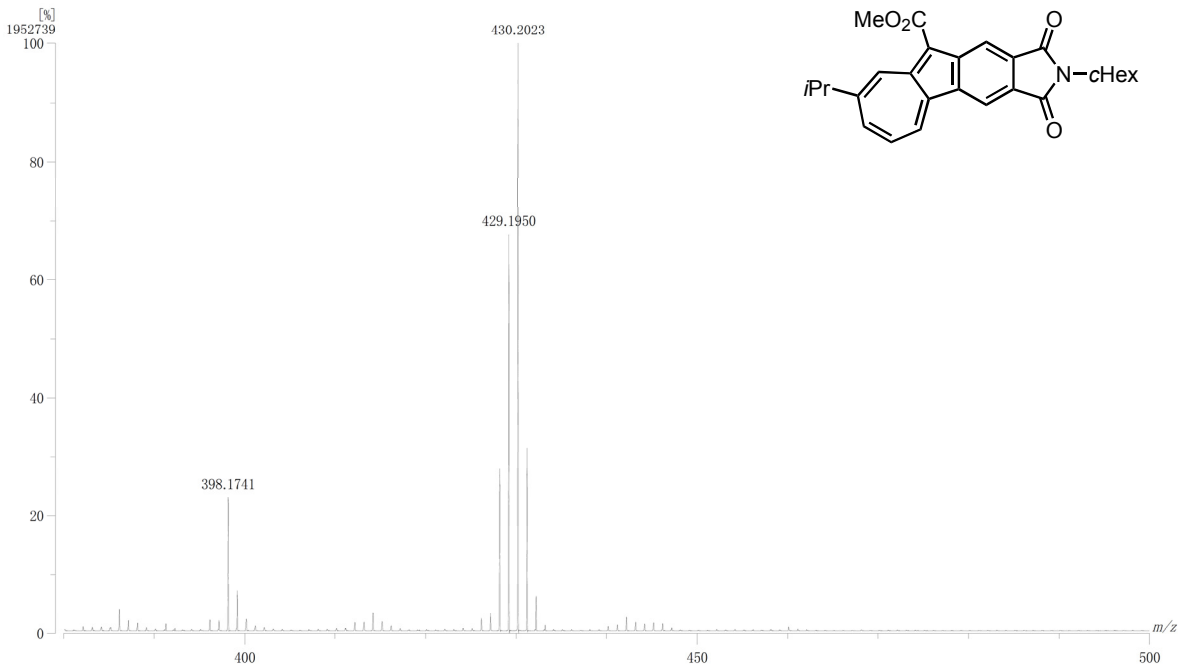


Figure S12. HRMS (FAB-double-focusing, positive) of **4c**.

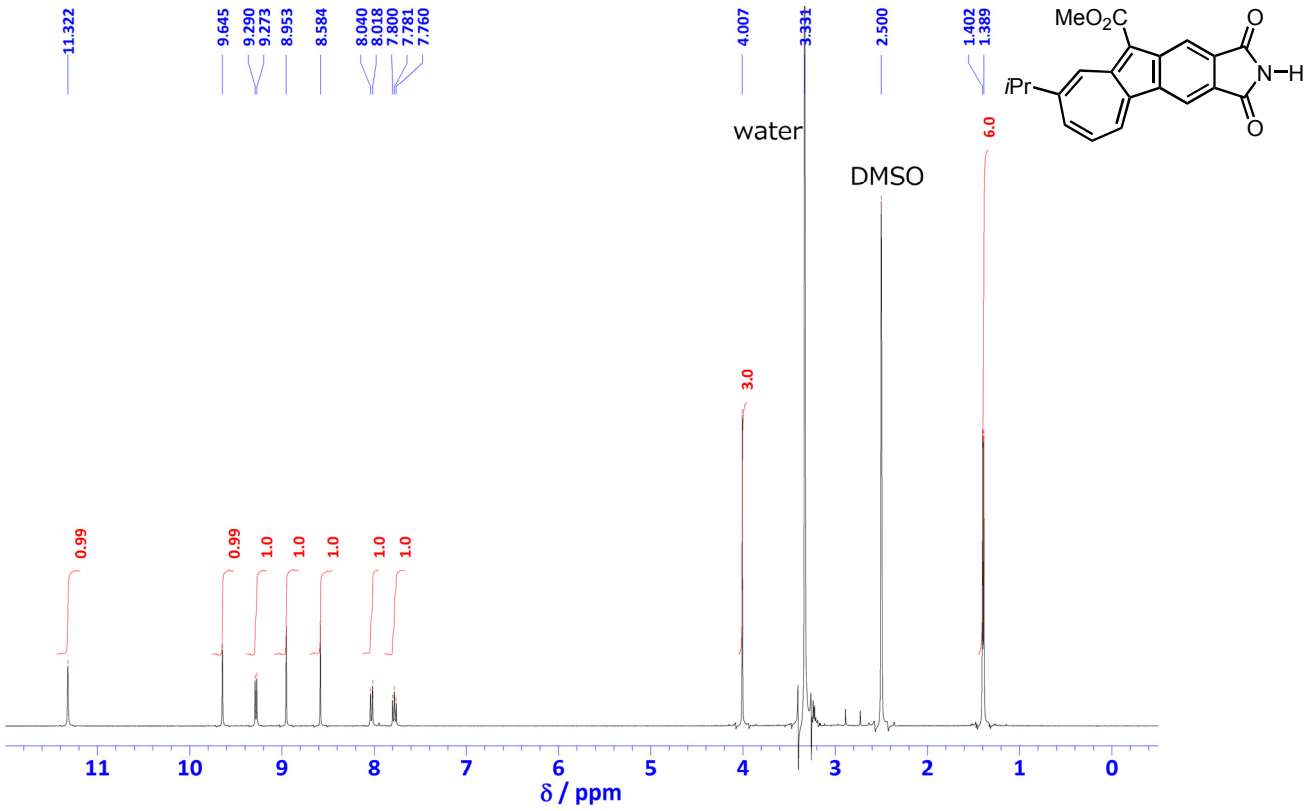


Figure S13. ^{1}H NMR spectrum of **4d** in DMSO-d_6 (500 MHz, 140 °C).

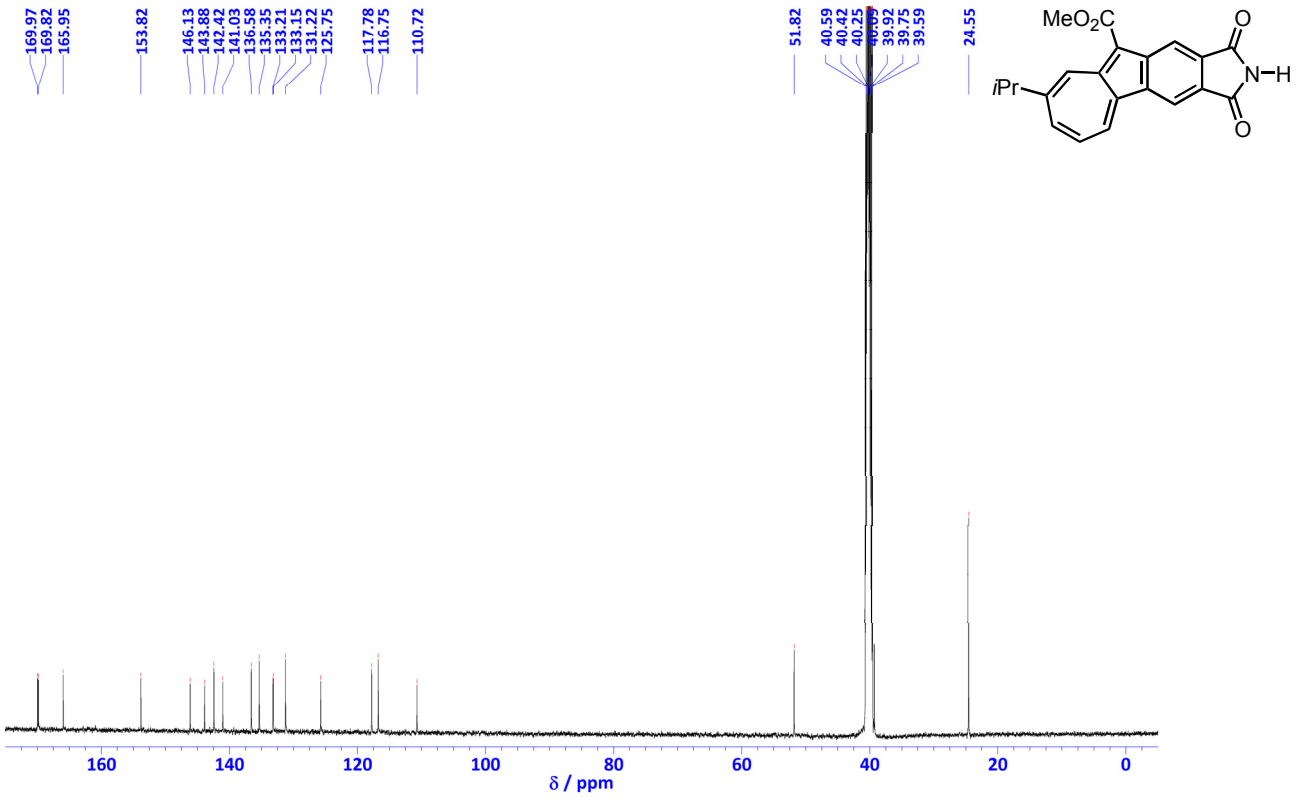


Figure S14. ^{13}C NMR spectrum of **4d** in DMSO-d_6 (125 MHz, 140 °C).

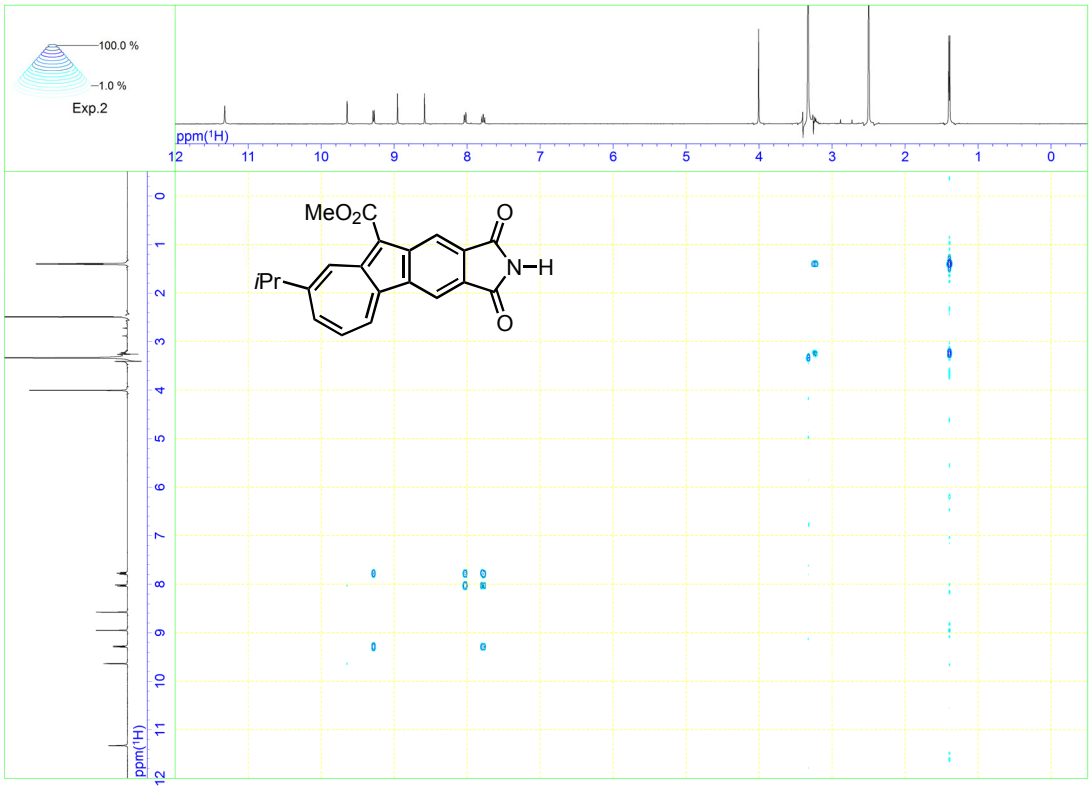


Figure S15. COSY spectrum of **4d** in DMSO-d_6 (500 MHz, 140 °C).

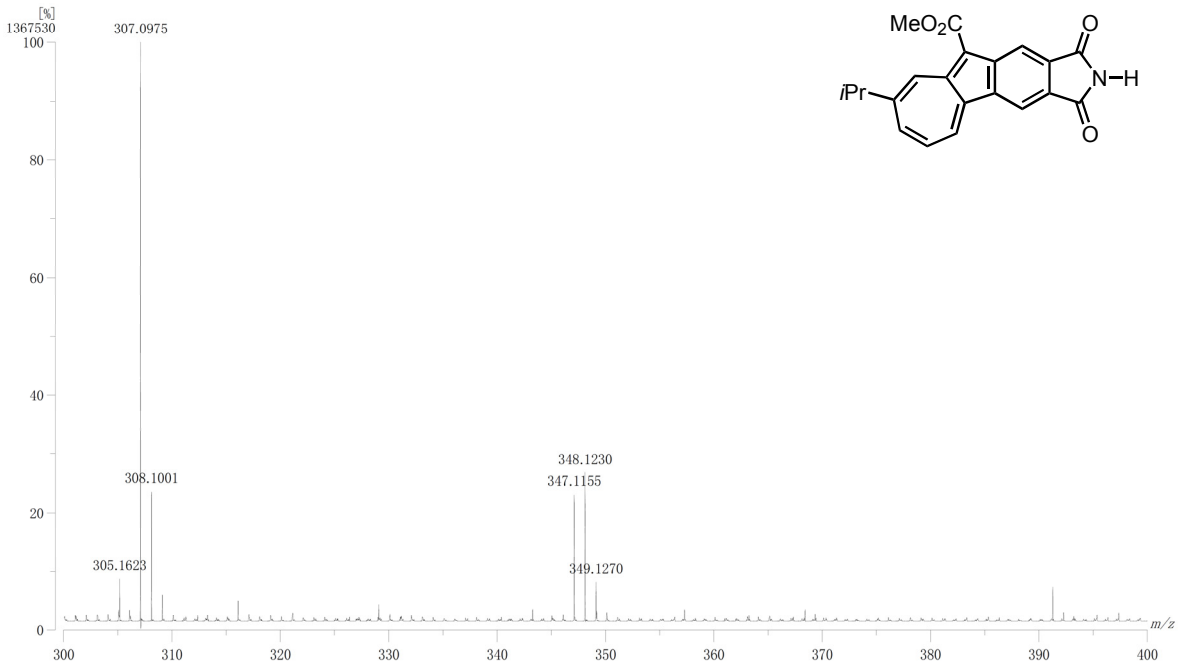


Figure S16. HRMS (FAB-double-focusing, positive) of **4d**.

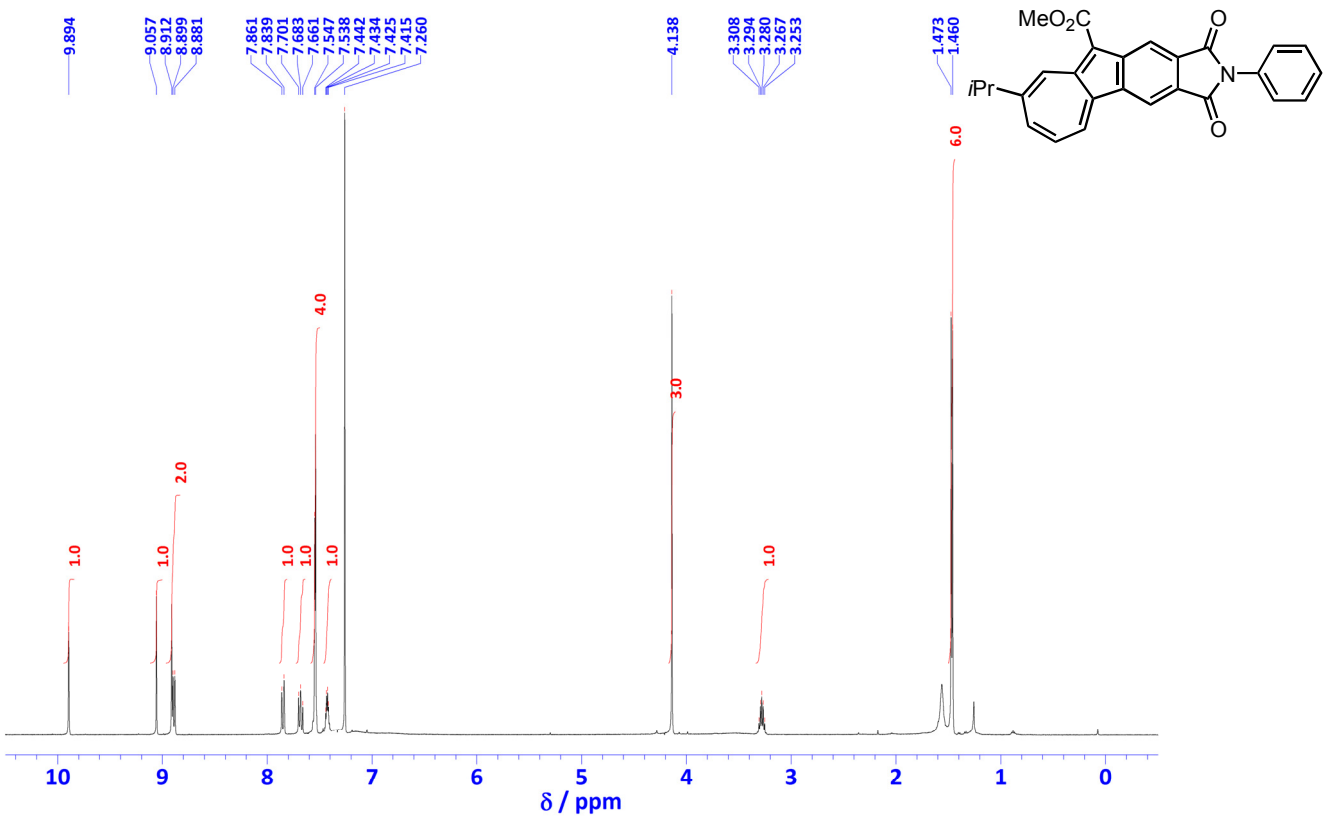


Figure S17. ^{1}H NMR spectrum of **4e** in $CDCl_3$ (500 MHz).

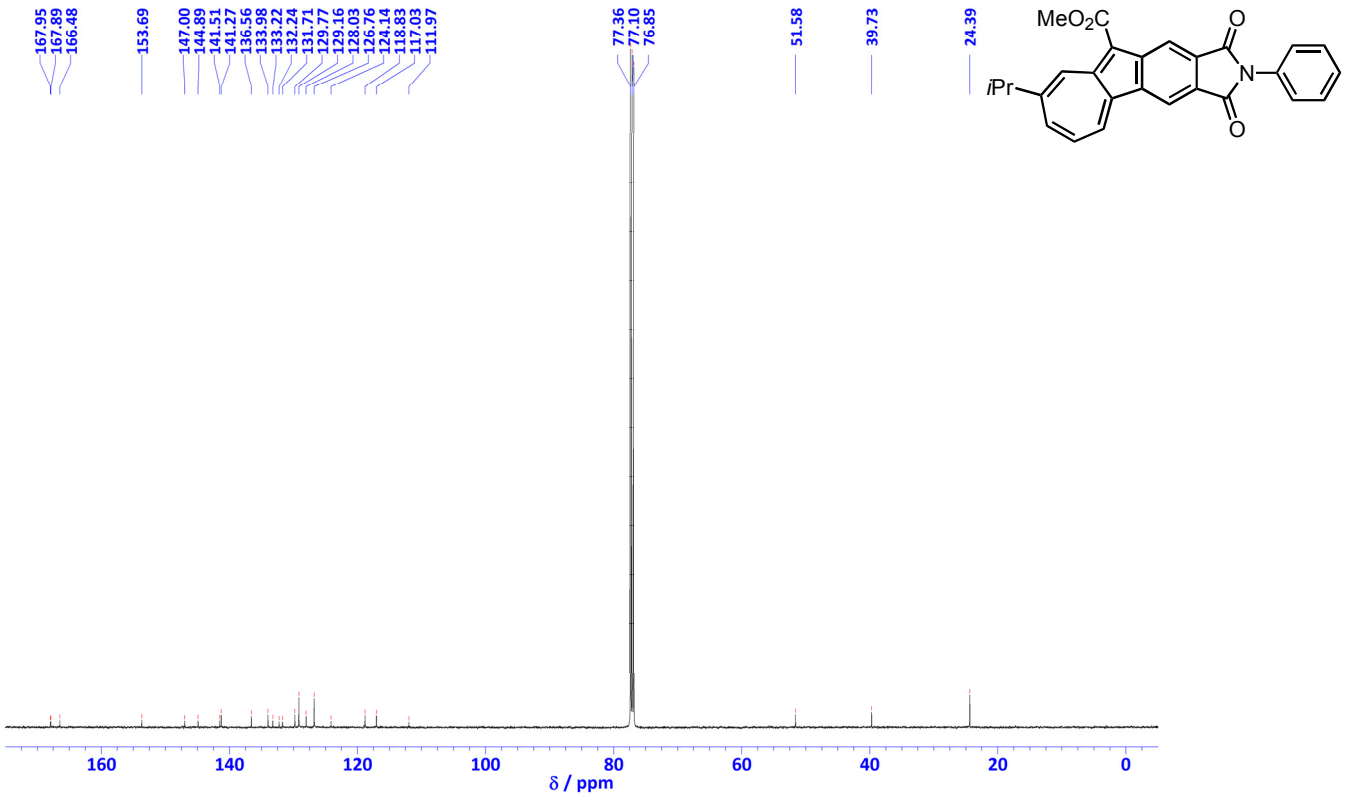


Figure S18. ^{13}C NMR spectrum of **4e** in $CDCl_3$ (125 MHz).

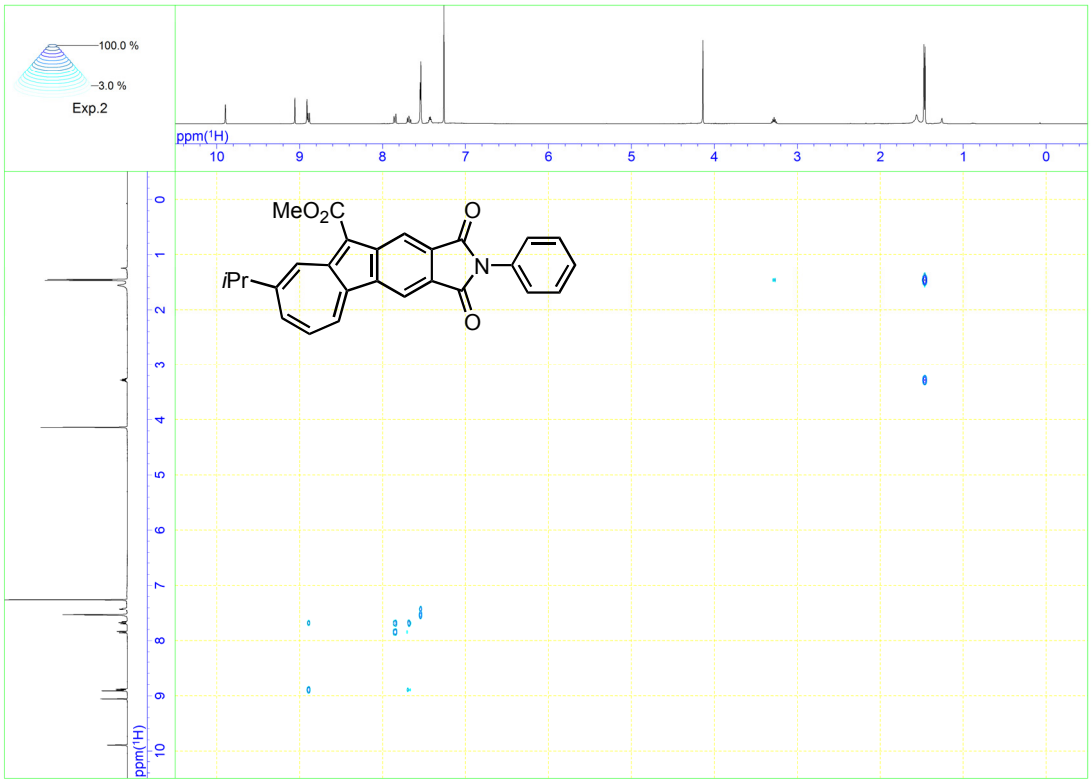


Figure S19. COSY spectrum of **4e** in $CDCl_3$ (500 MHz).

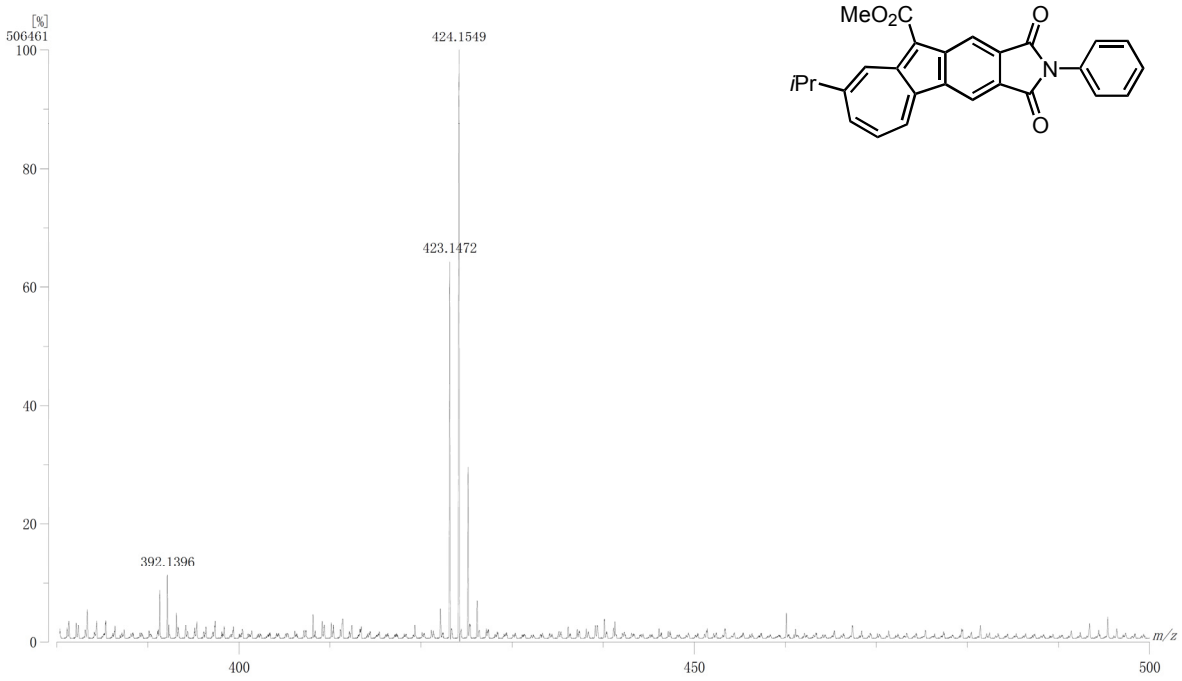


Figure S20. HRMS (FAB-double-focusing, positive) of **4e**.

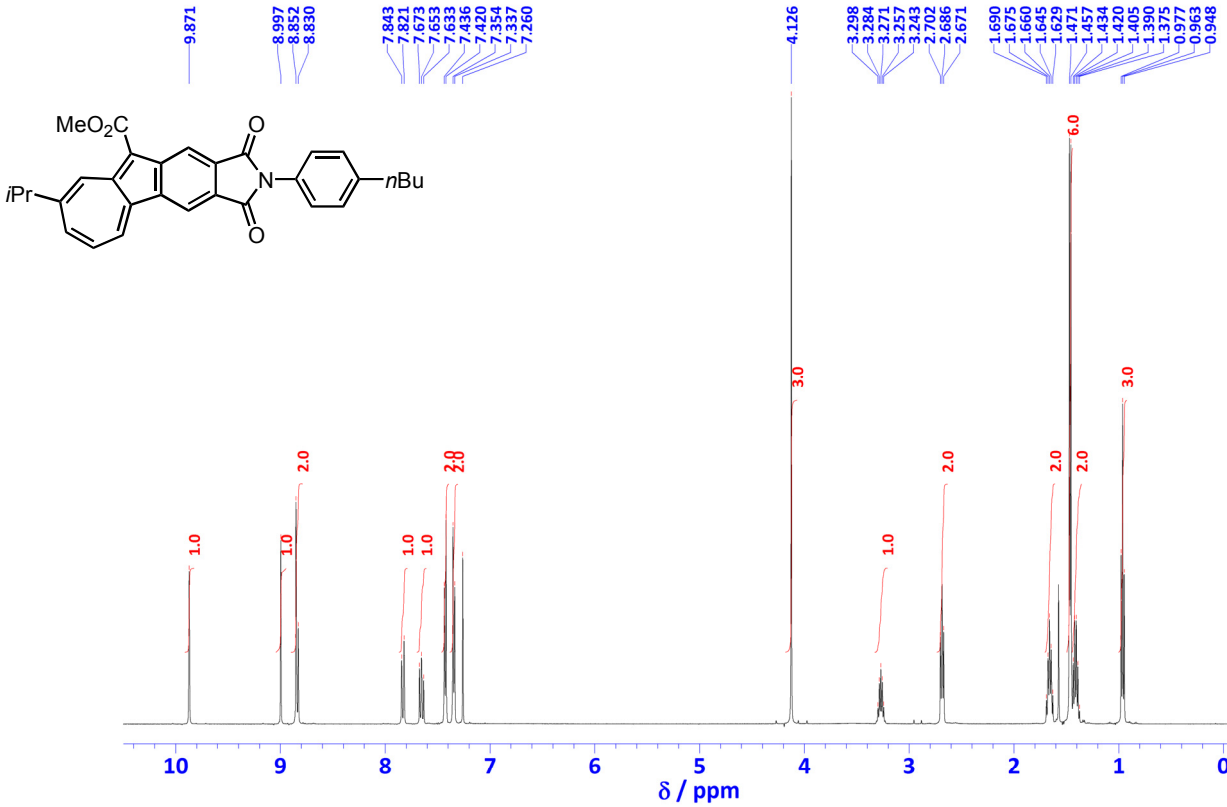


Figure S21. ^{1}H NMR spectrum of **4f** in $CDCl_3$ (500 MHz).

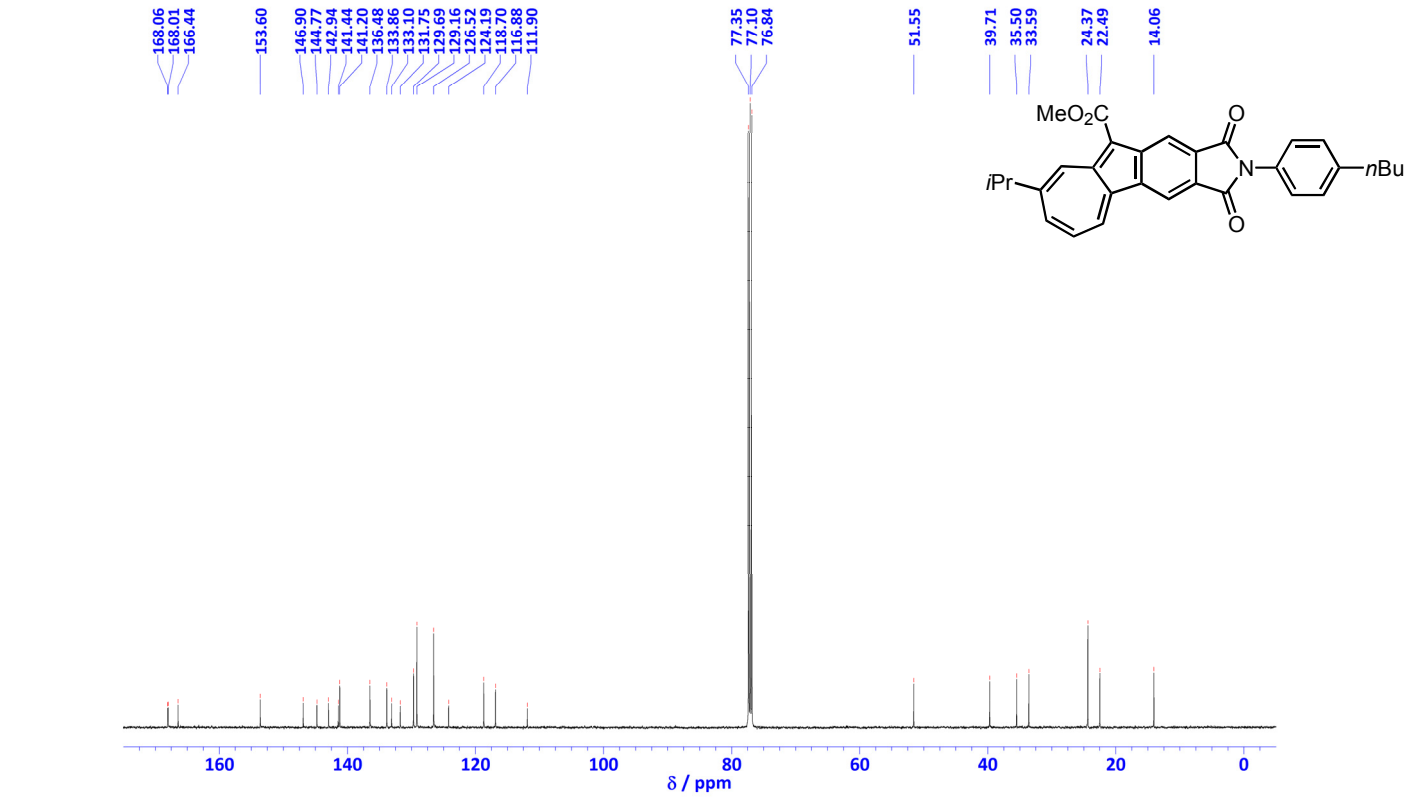


Figure S22. ^{13}C NMR spectrum of **4f** in $CDCl_3$ (125 MHz).

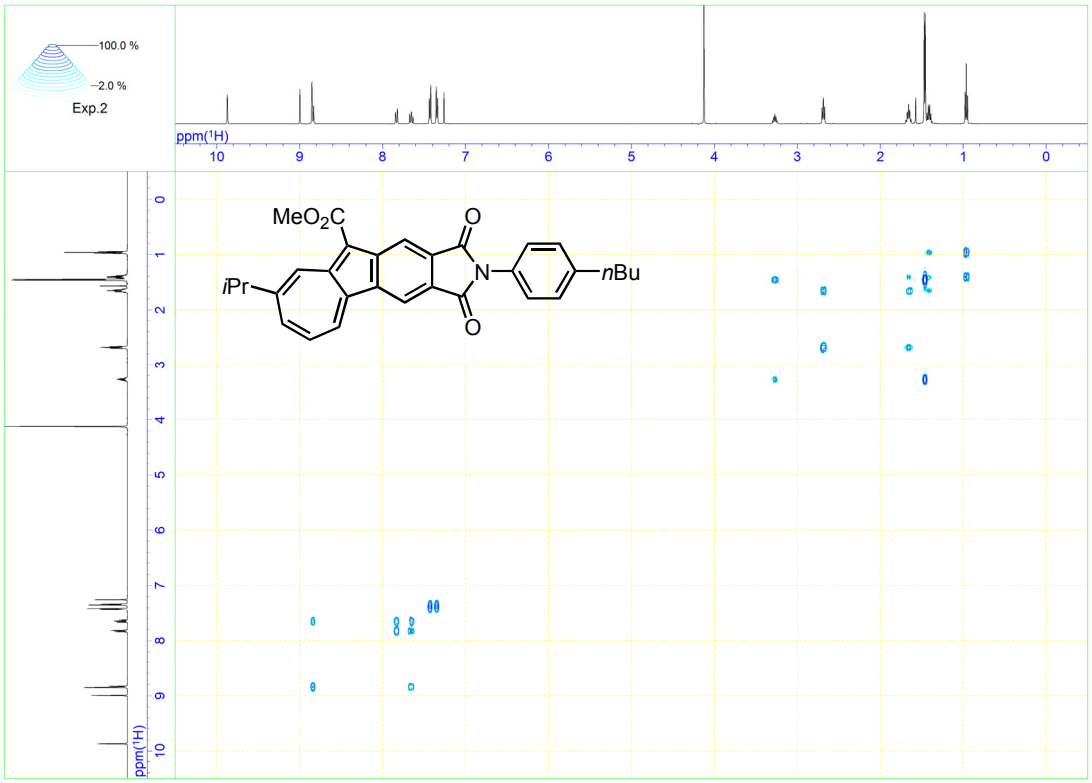


Figure S23. COSY spectrum of **4f** in $CDCl_3$ (500 MHz).

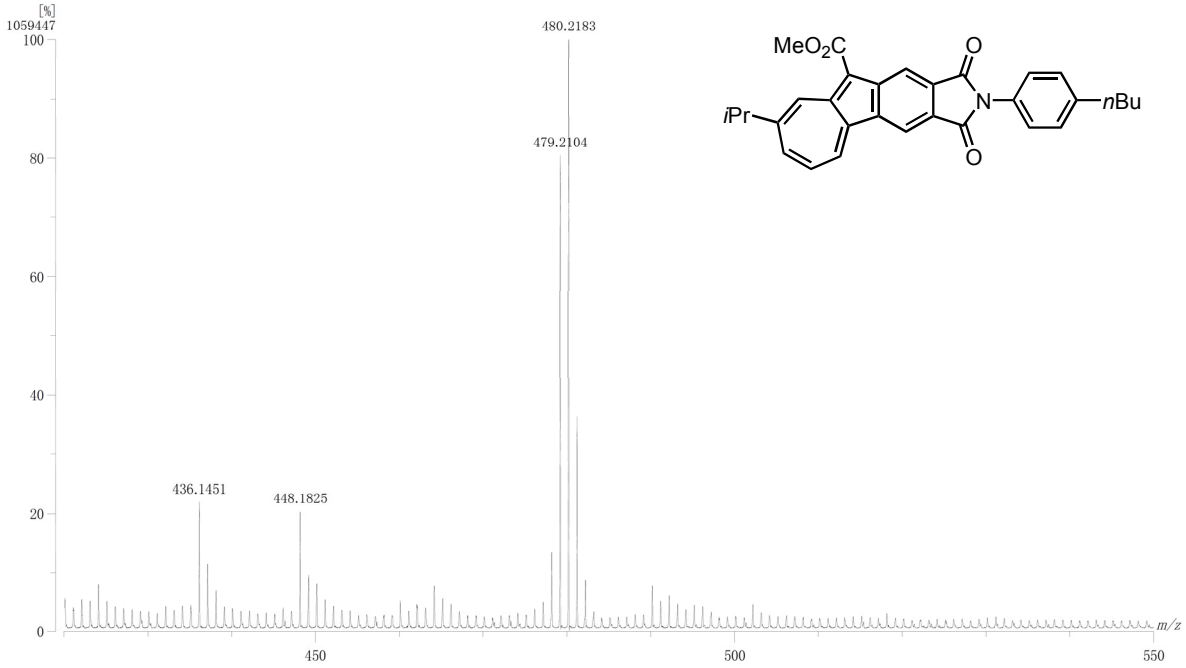


Figure S24. HRMS (FAB-double-focusing, positive) of **4f**.

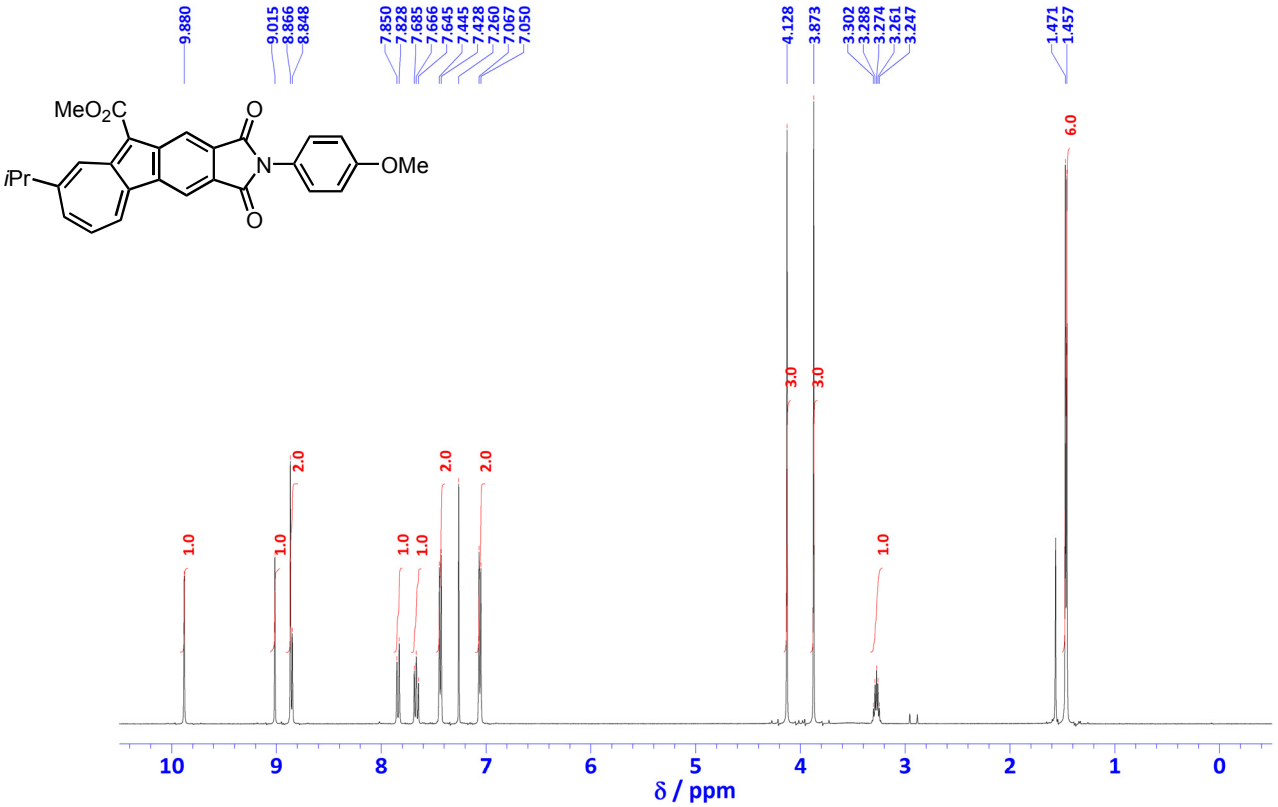


Figure S25. ^{1}H NMR spectrum of **4g** in $CDCl_3$ (500 MHz).

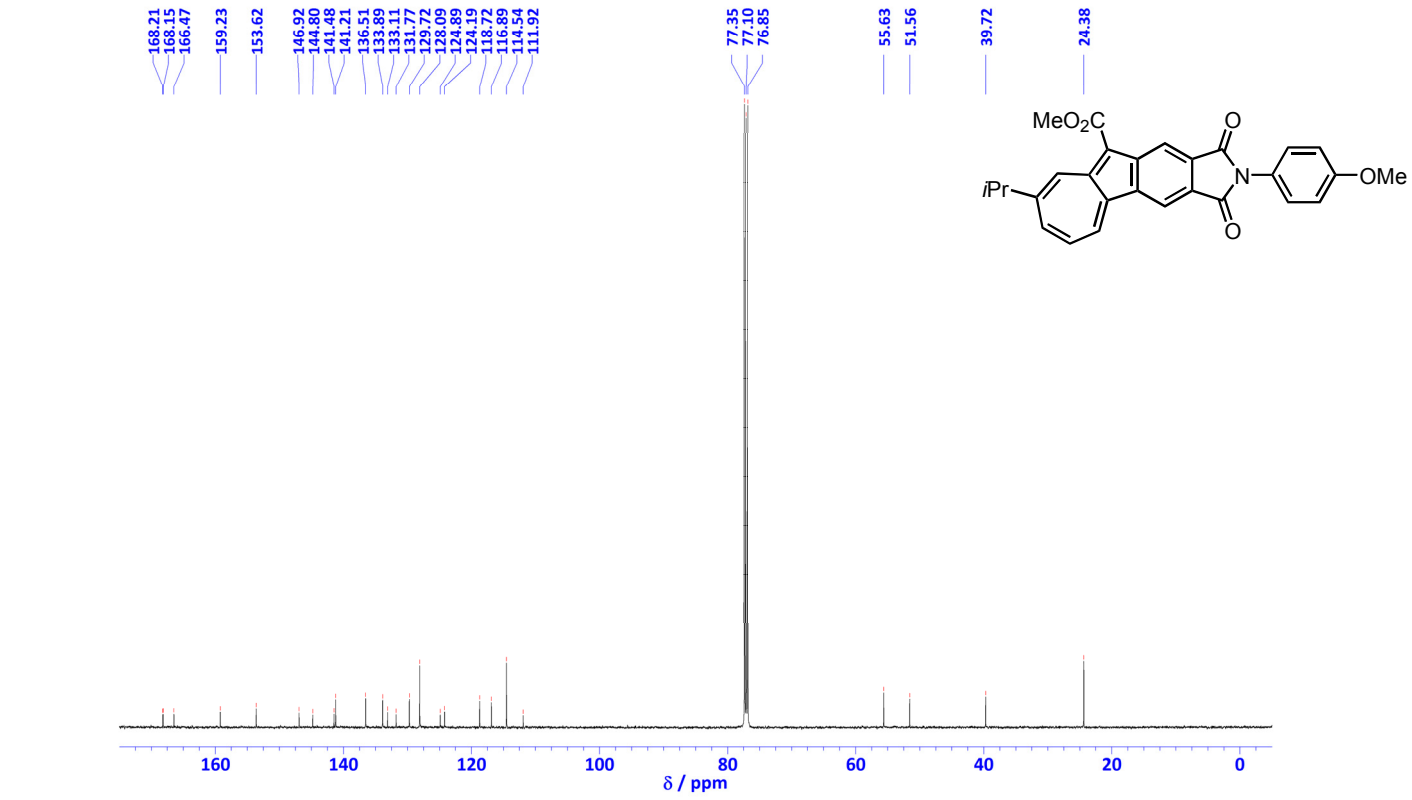


Figure S26. ^{13}C NMR spectrum of **4g** in $CDCl_3$ (125 MHz).

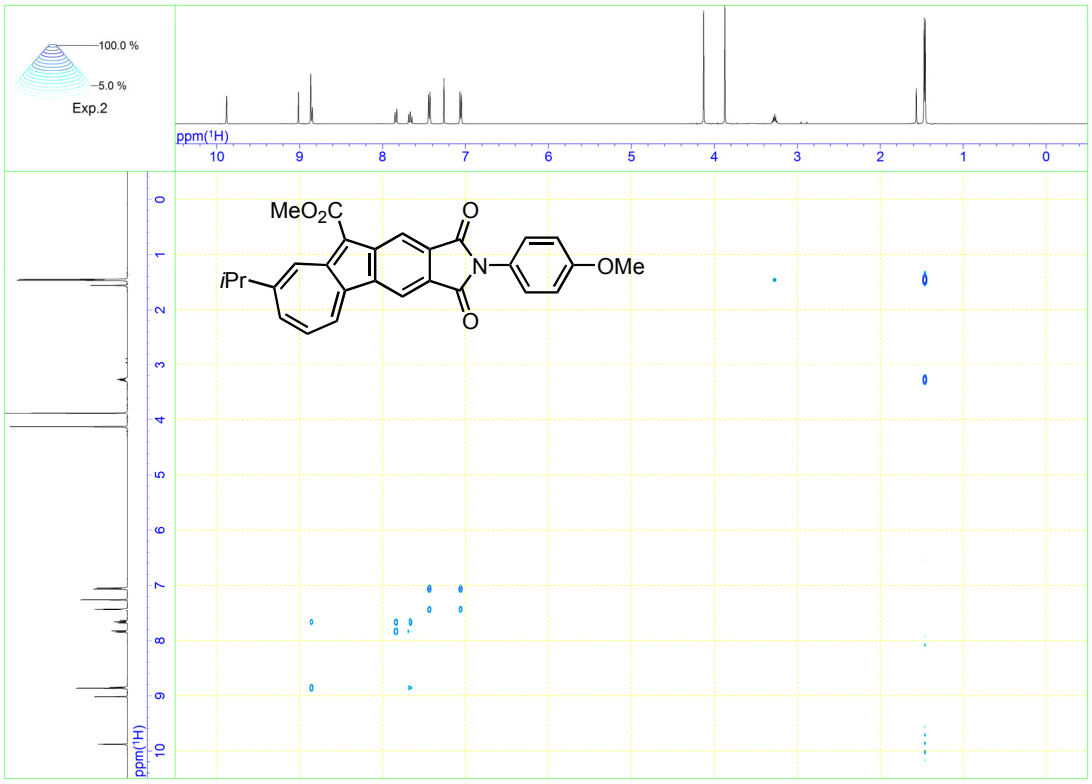


Figure S27. COSY spectrum of **4g** in $CDCl_3$ (500 MHz).

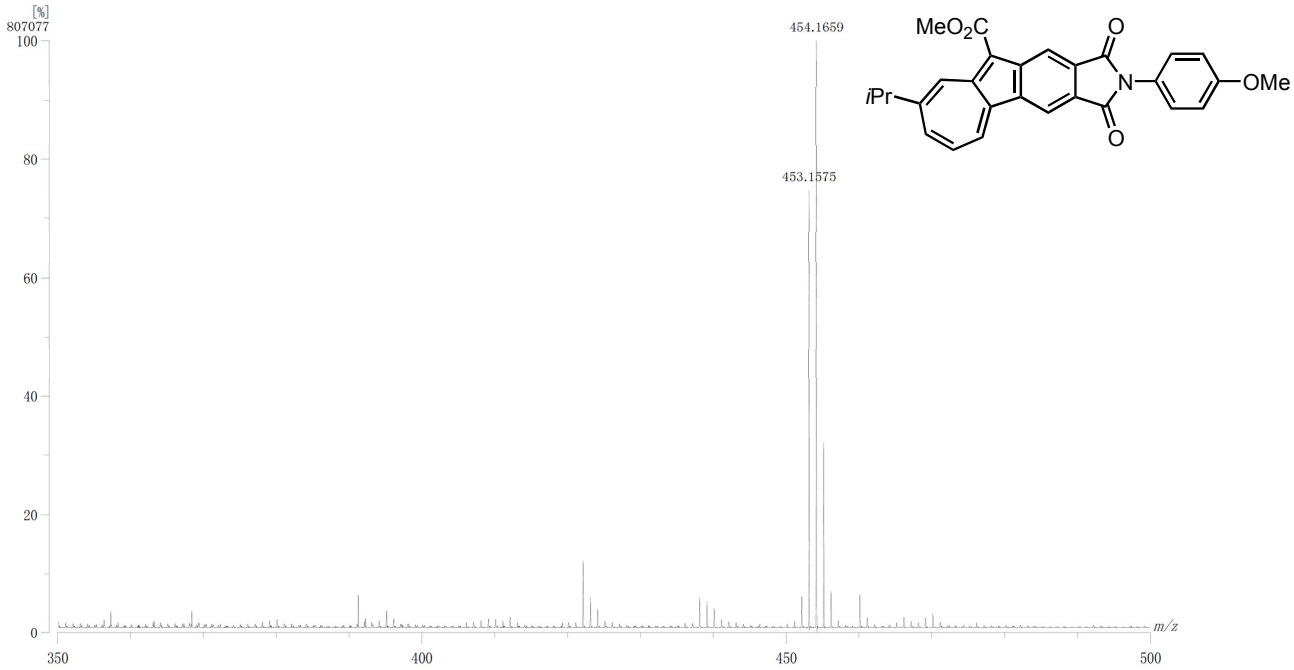


Figure S28. HRMS (FAB-double-focusing, positive) of **4g**.

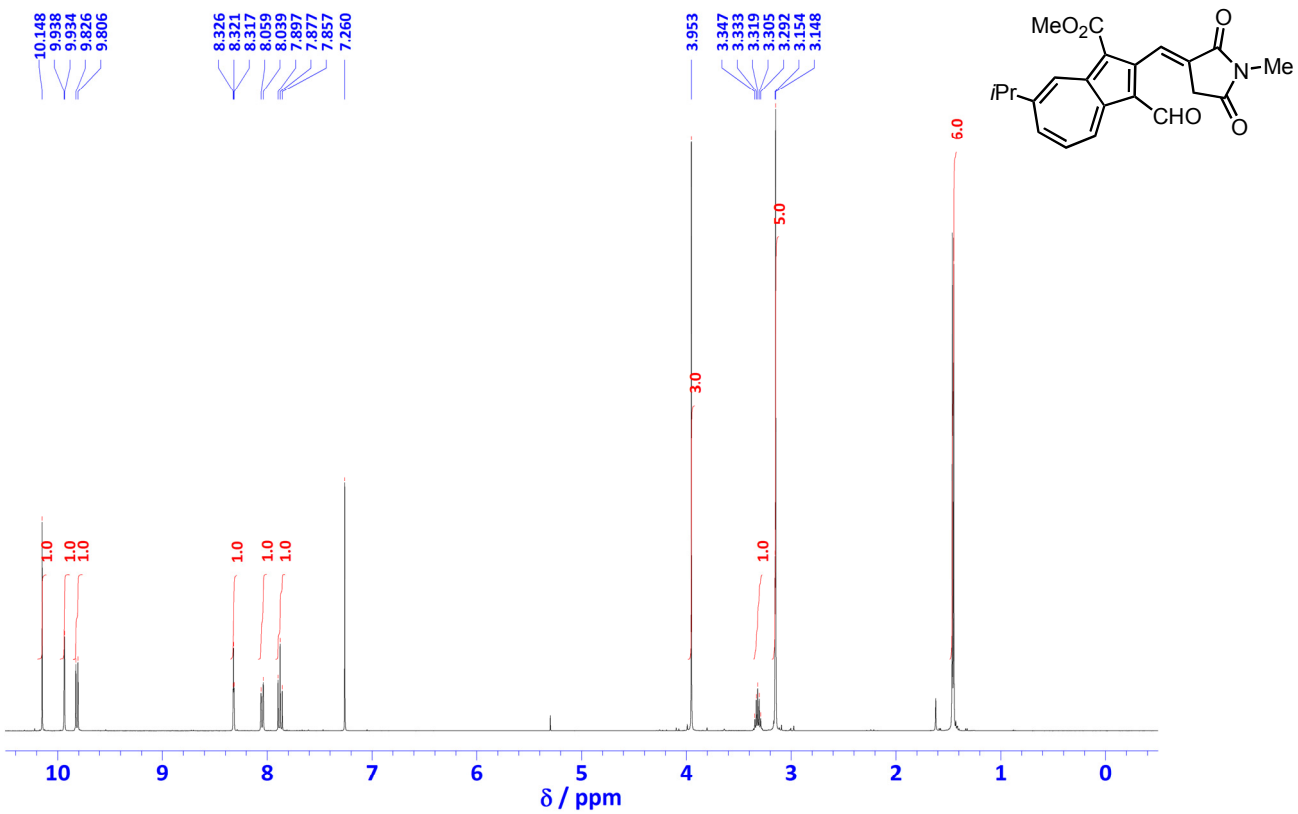


Figure S29. ^{1}H NMR spectrum of **5** in $CDCl_3$ (500 MHz).

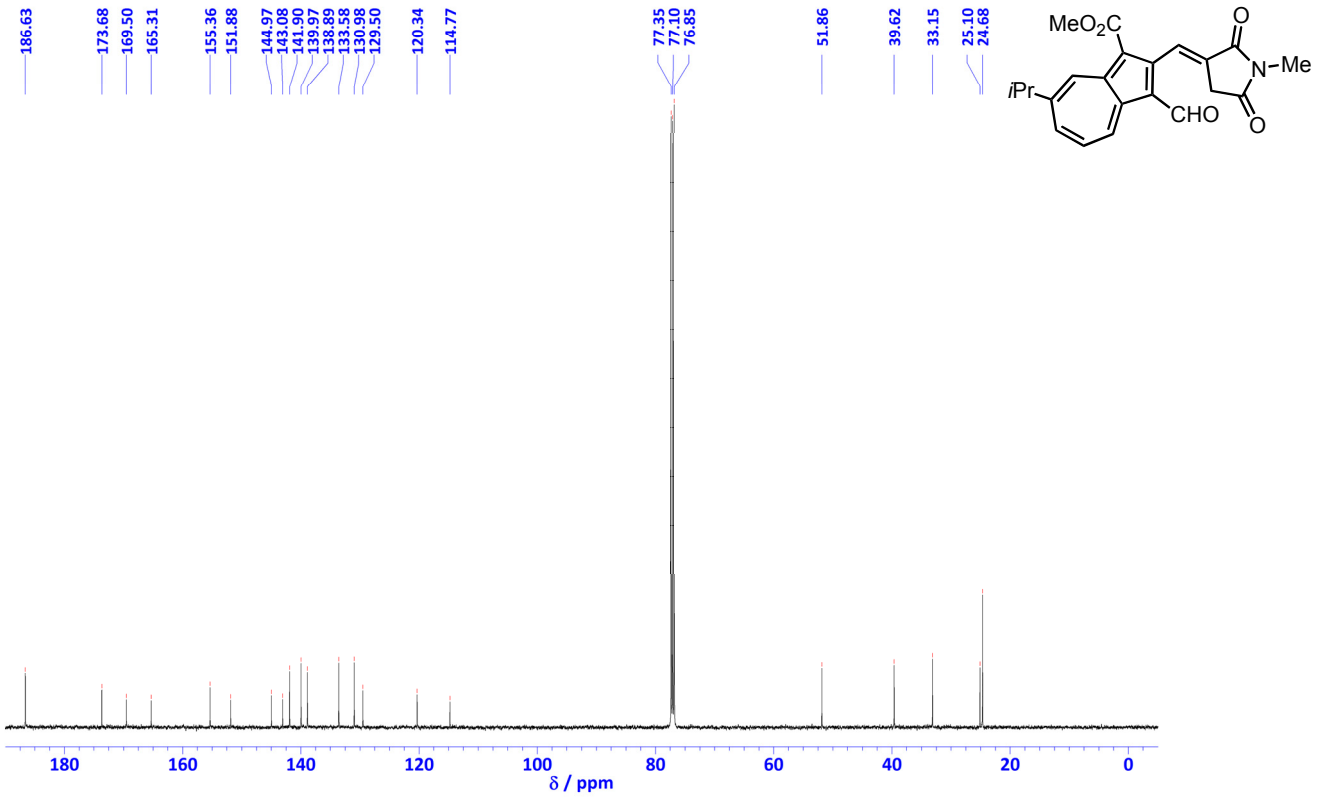


Figure S30. ^{13}C NMR spectrum of **5** in $CDCl_3$ (125 MHz).

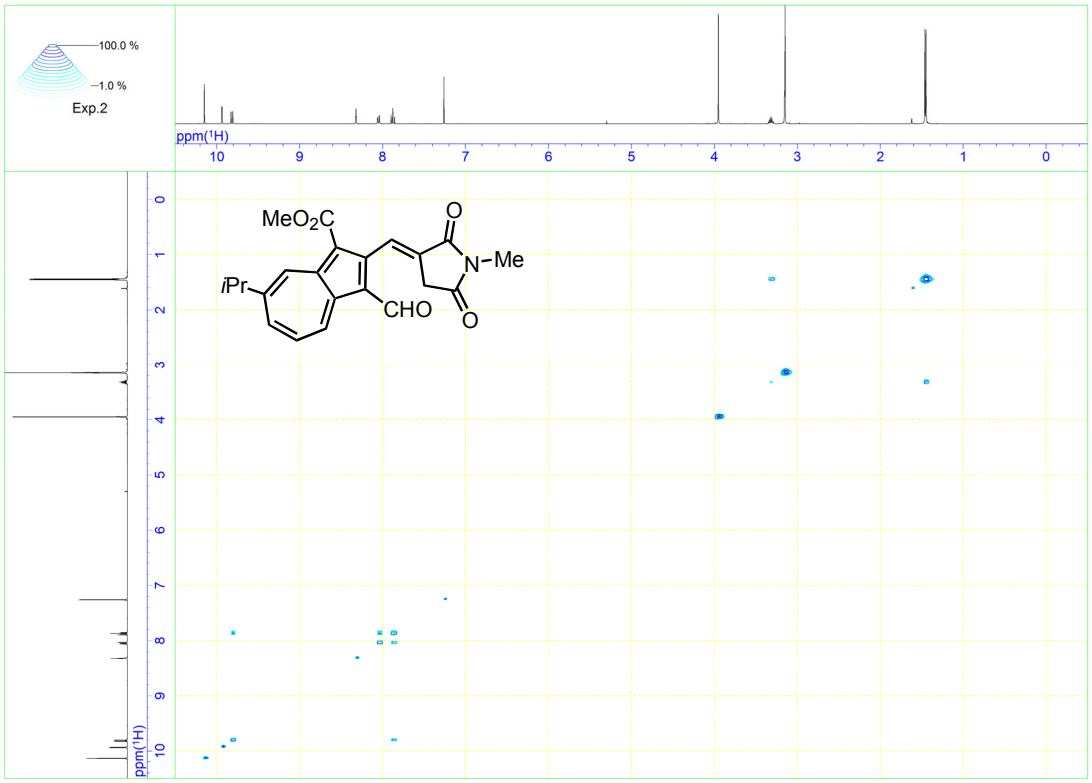


Figure S31. COSY spectrum of **5** in $CDCl_3$ (500 MHz).

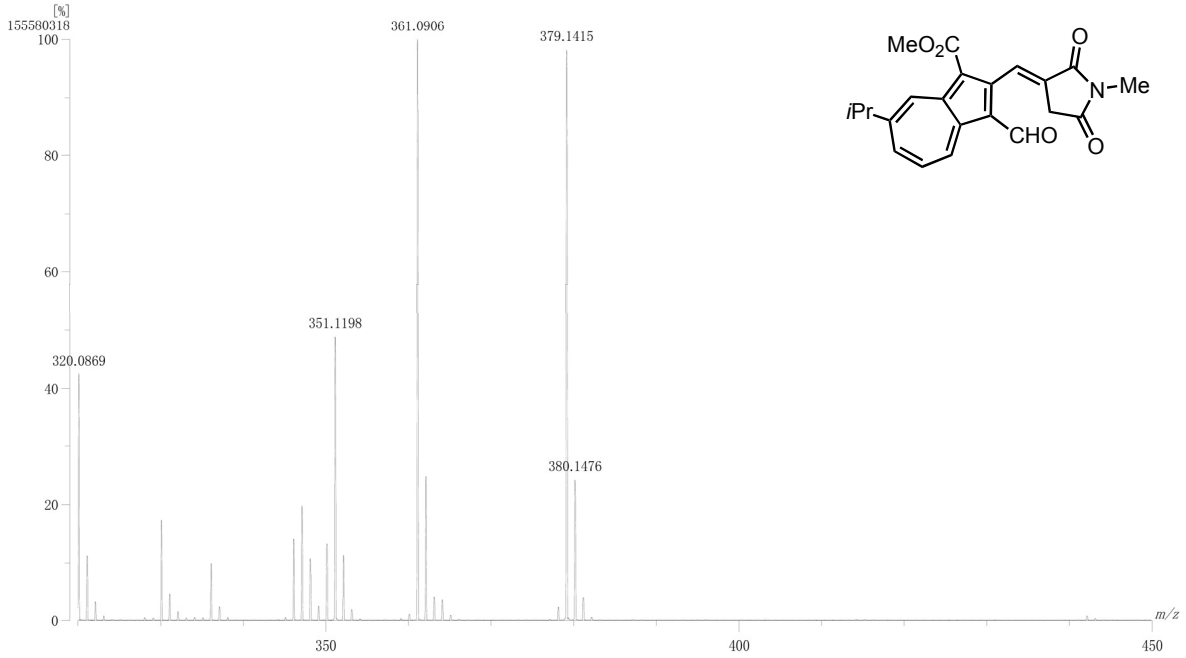


Figure S32. HRMS (FAB-double-focusing, positive) of **5**.

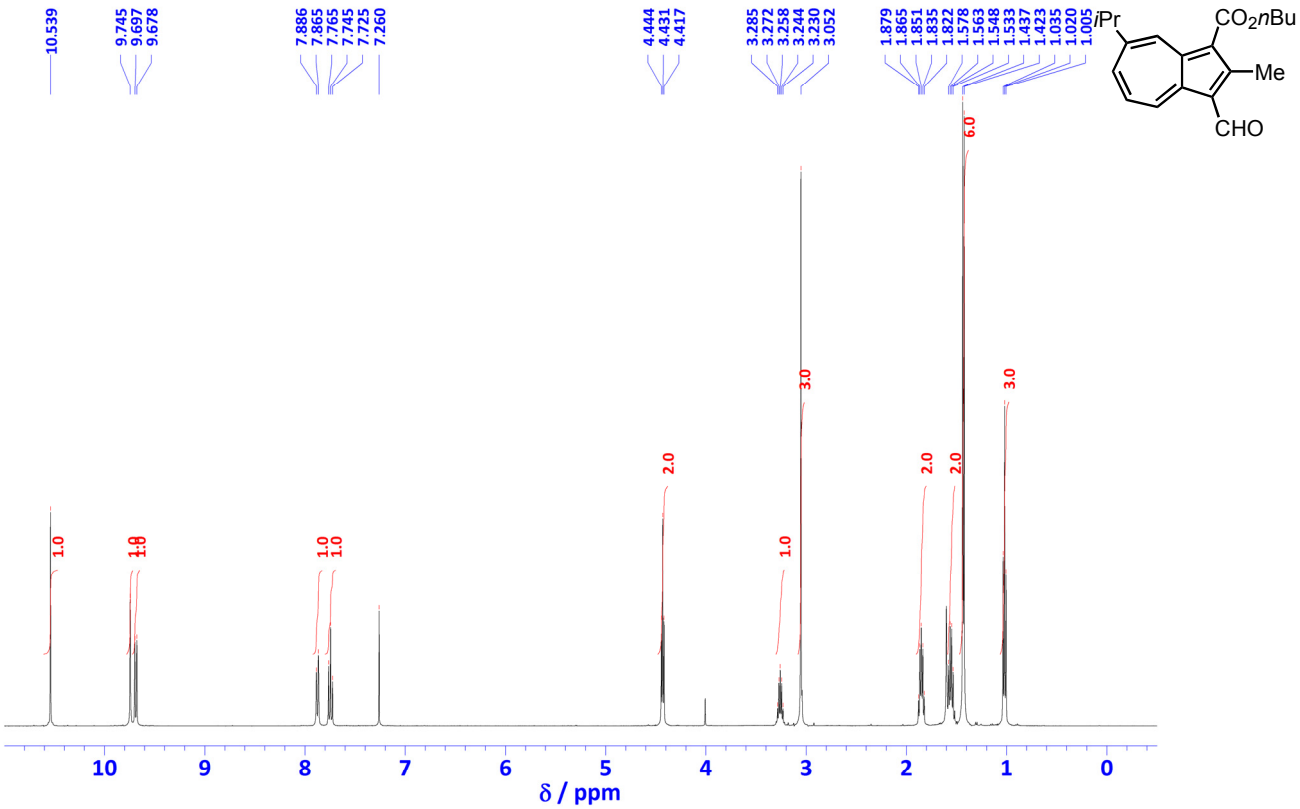


Figure S33. ^{1}H NMR spectrum of **8** in $CDCl_3$ (500 MHz).

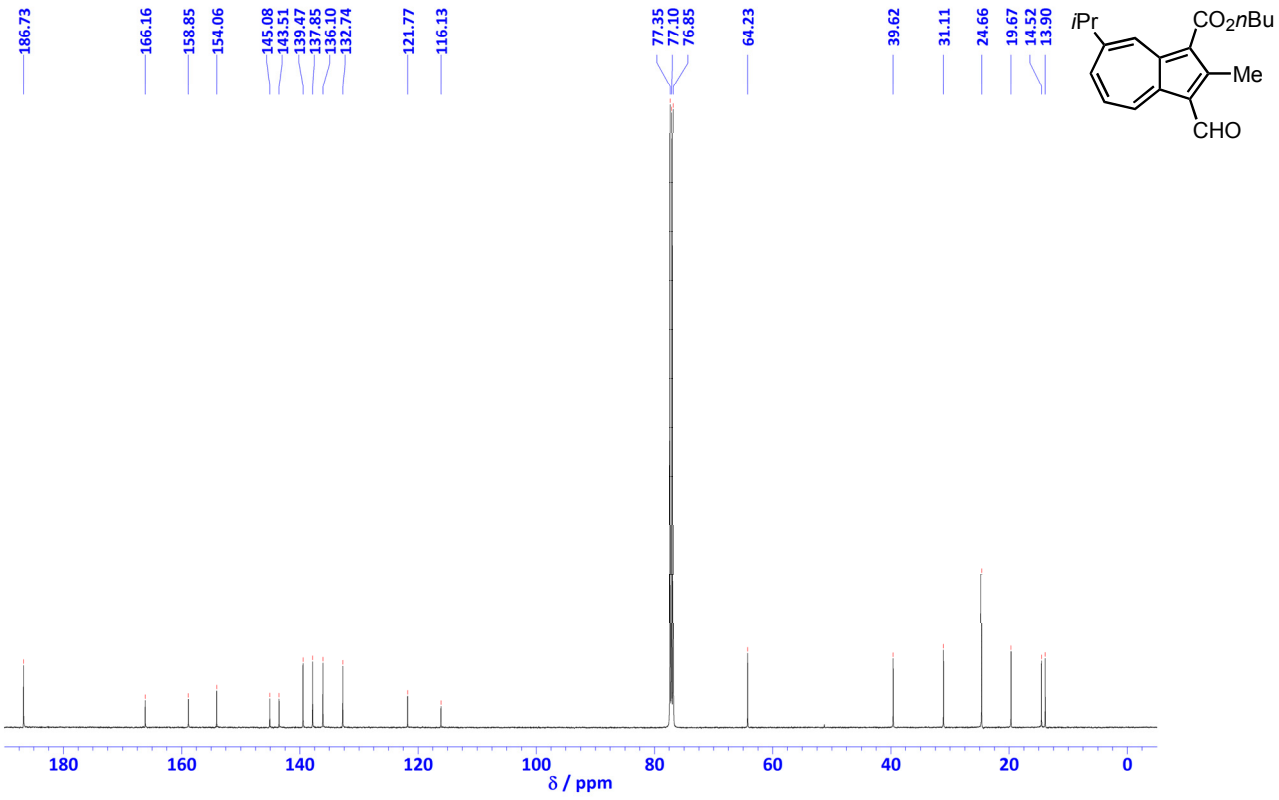


Figure S34. ^{13}C NMR spectrum of **8** in $CDCl_3$ (125 MHz).

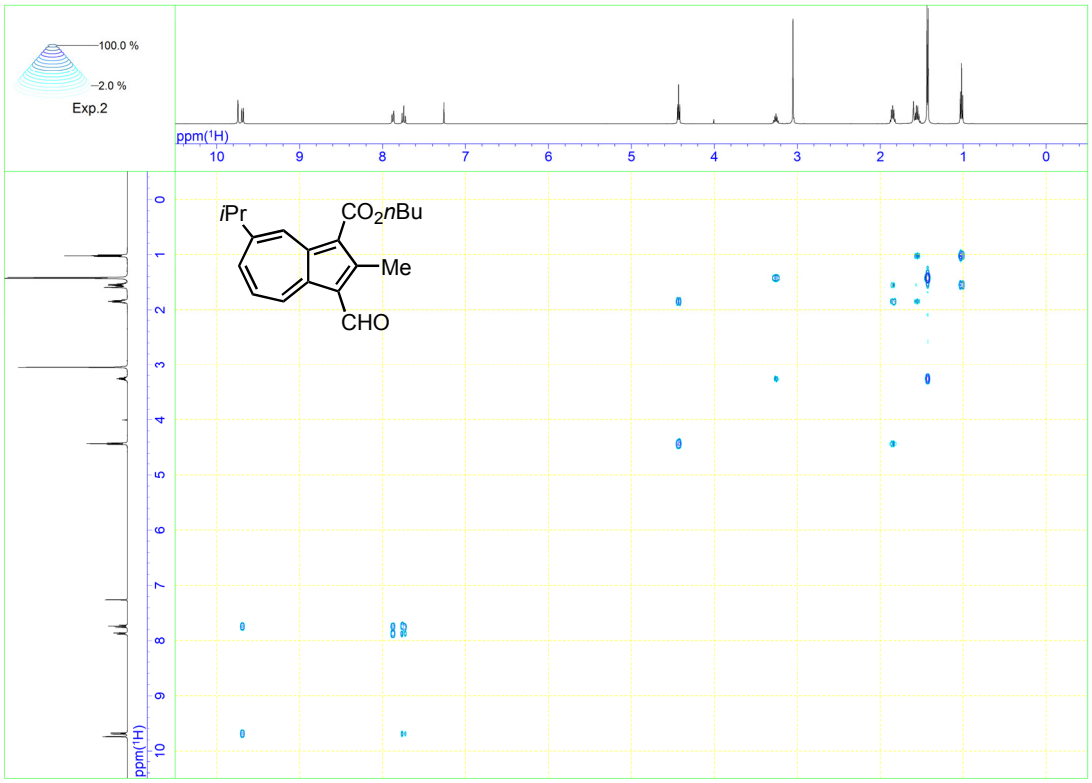


Figure S35. COSY spectrum of **8** in $CDCl_3$ (500 MHz).

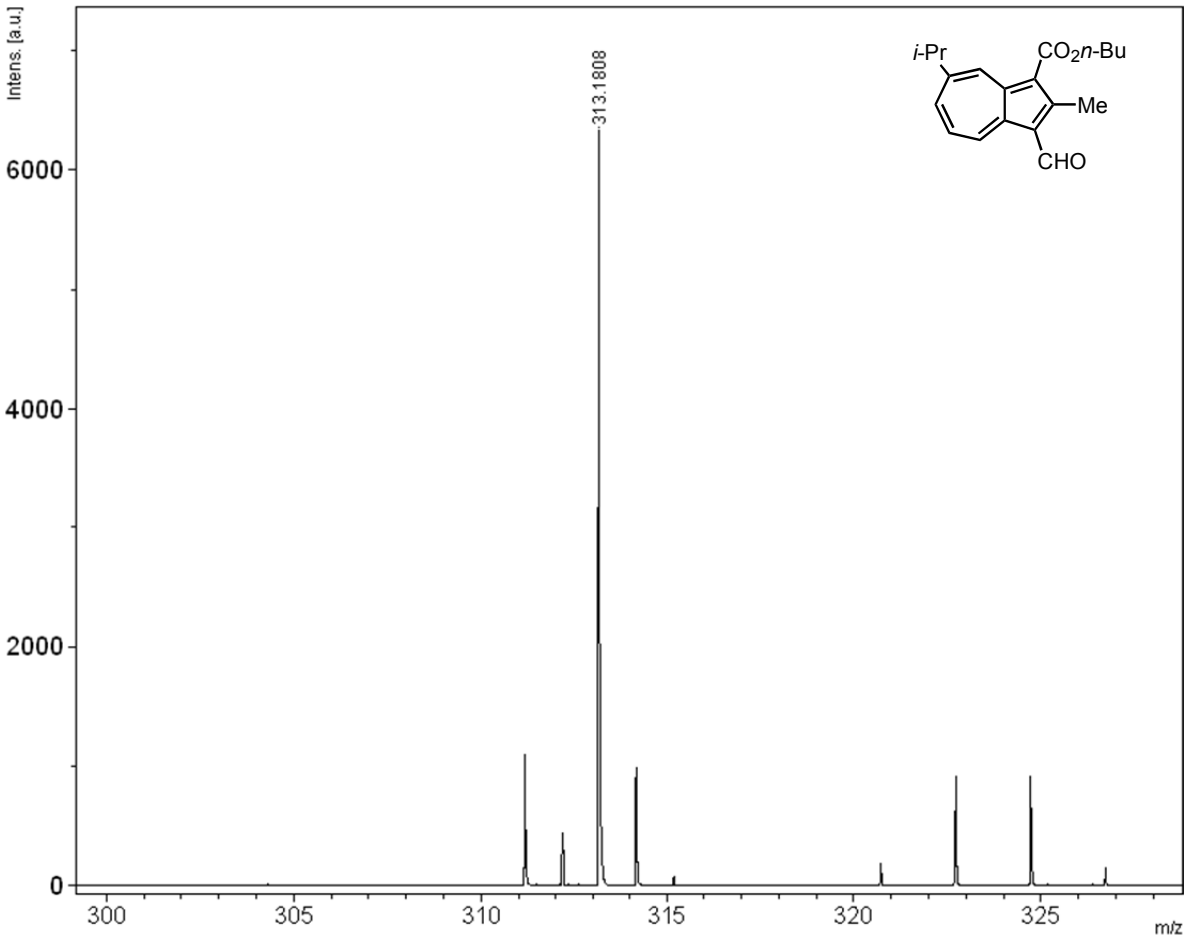


Figure S36. HRMS (MALDI-TOF, positive) of **8**.

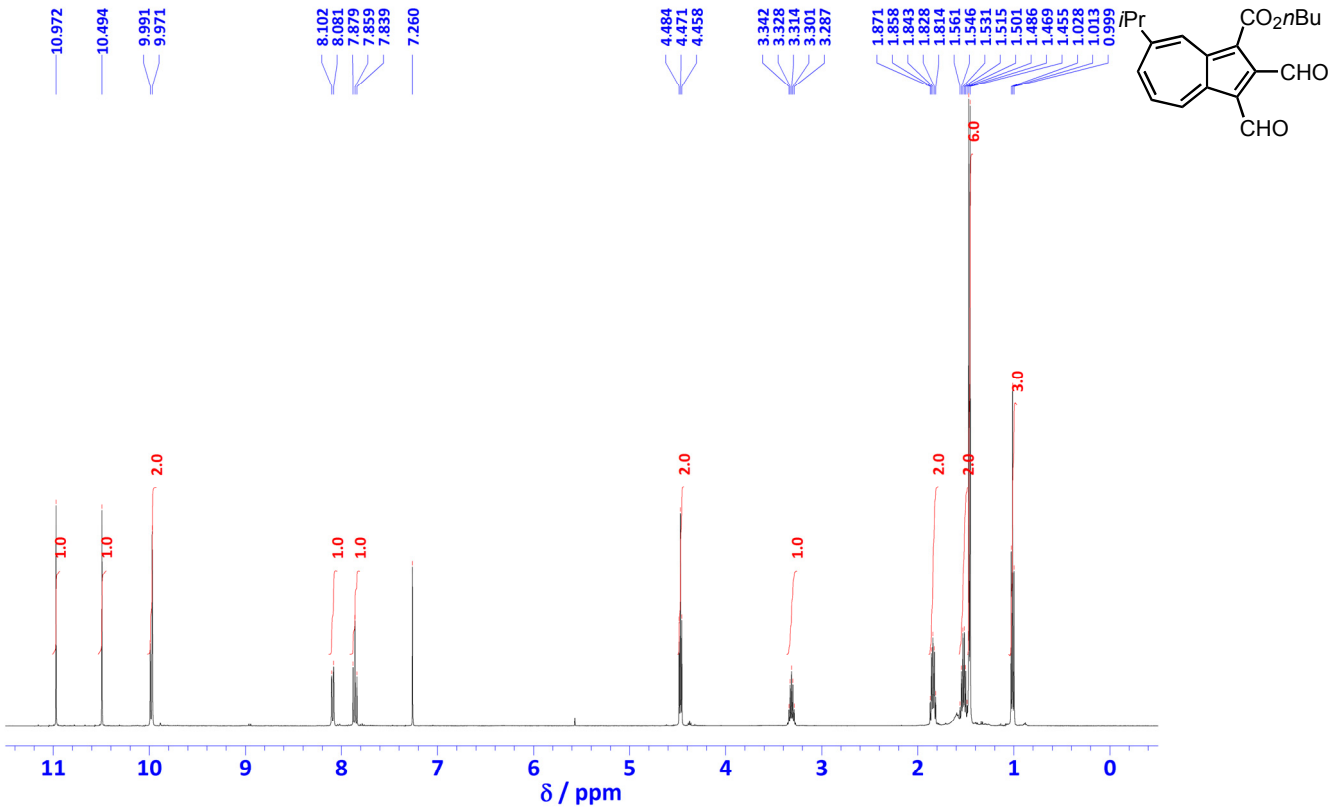


Figure S37. ^{1}H NMR spectrum of **9** in $CDCl_3$ (500 MHz).

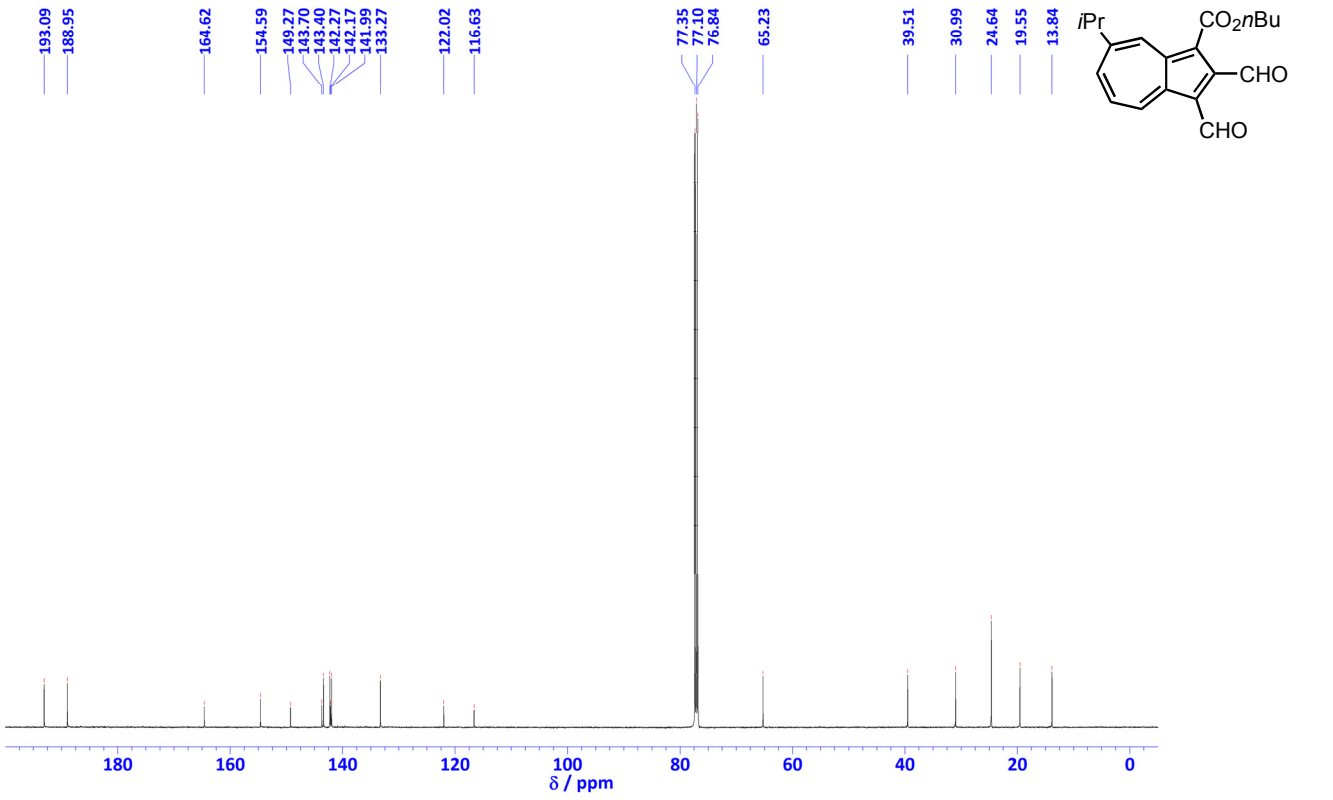


Figure S38. ^{13}C NMR spectrum of **9** in $CDCl_3$ (125 MHz).

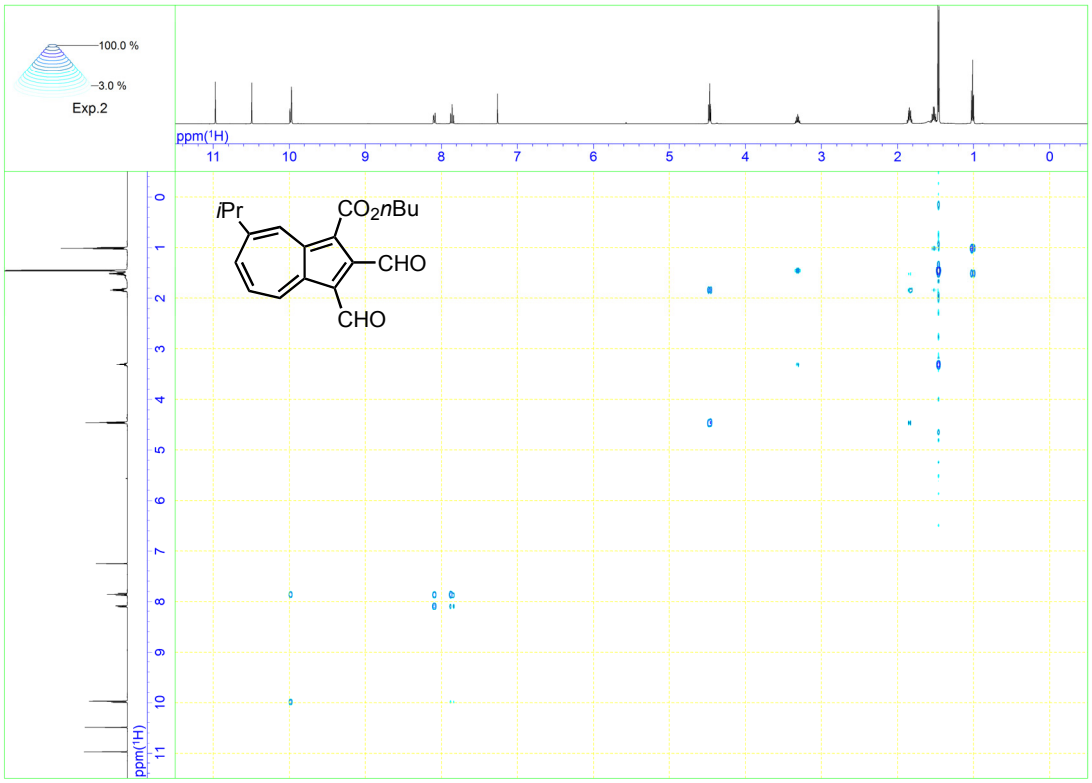


Figure S39. COSY spectrum of **9** in $CDCl_3$ (500 MHz).

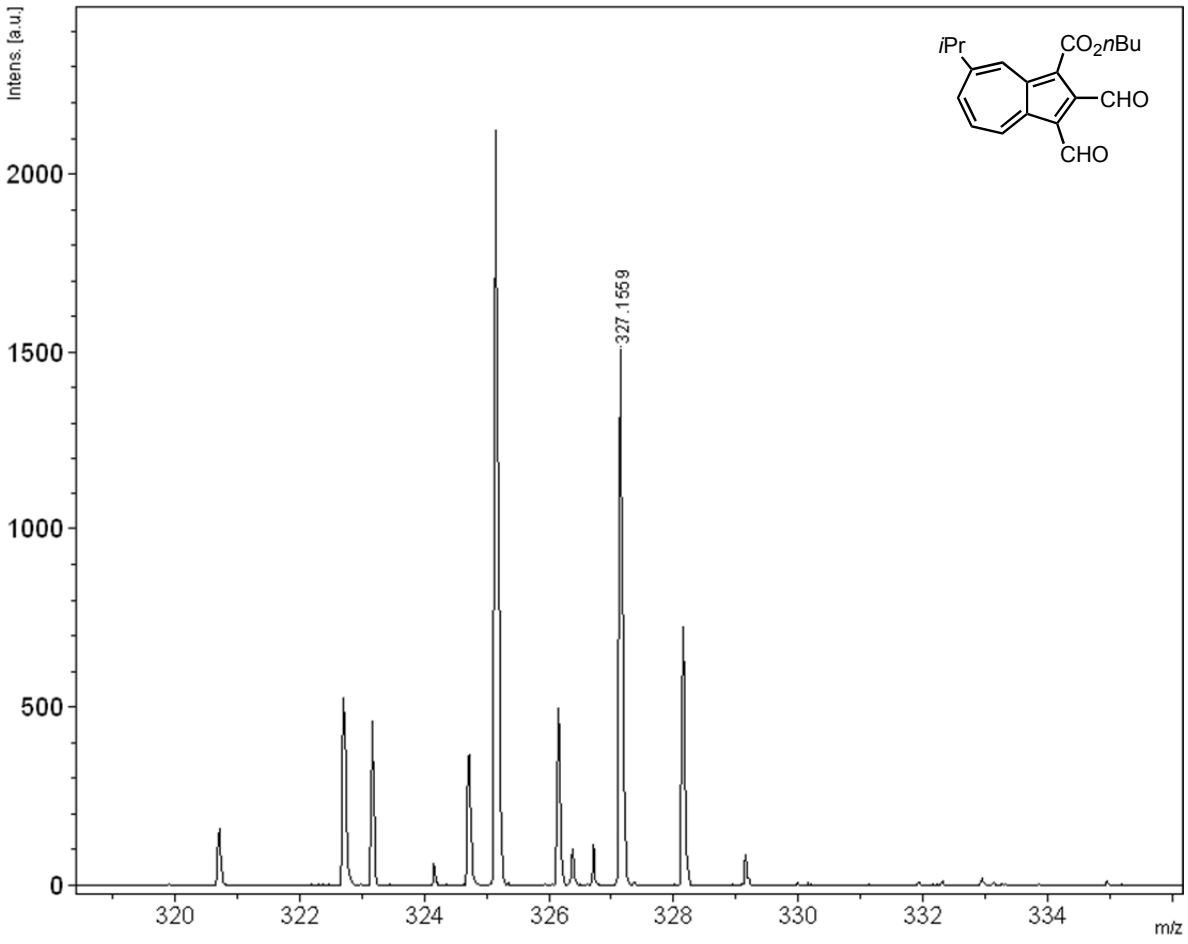


Figure S40. HRMS (MALDI-TOF, positive) of **9**.

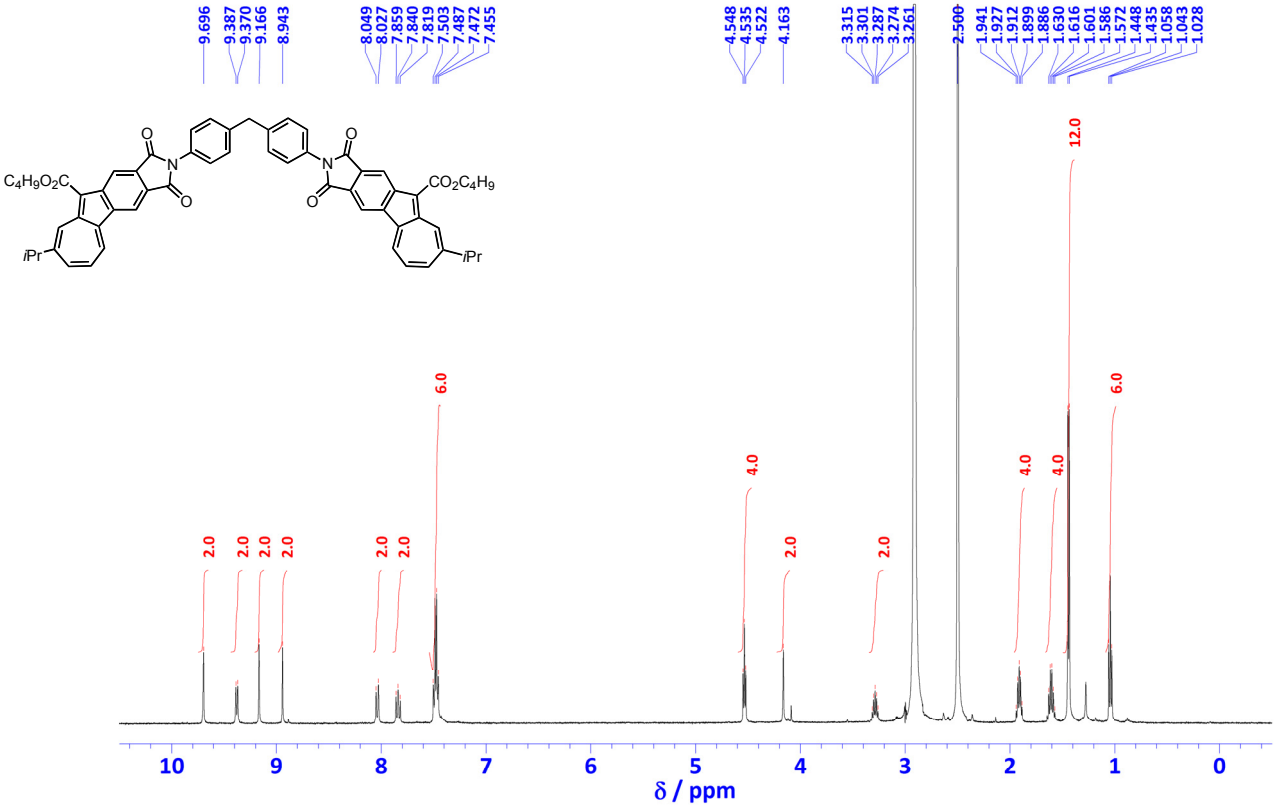


Figure S41. ^{1}H NMR spectrum of **10** in DMSO-d_6 (500 MHz, 140°C).

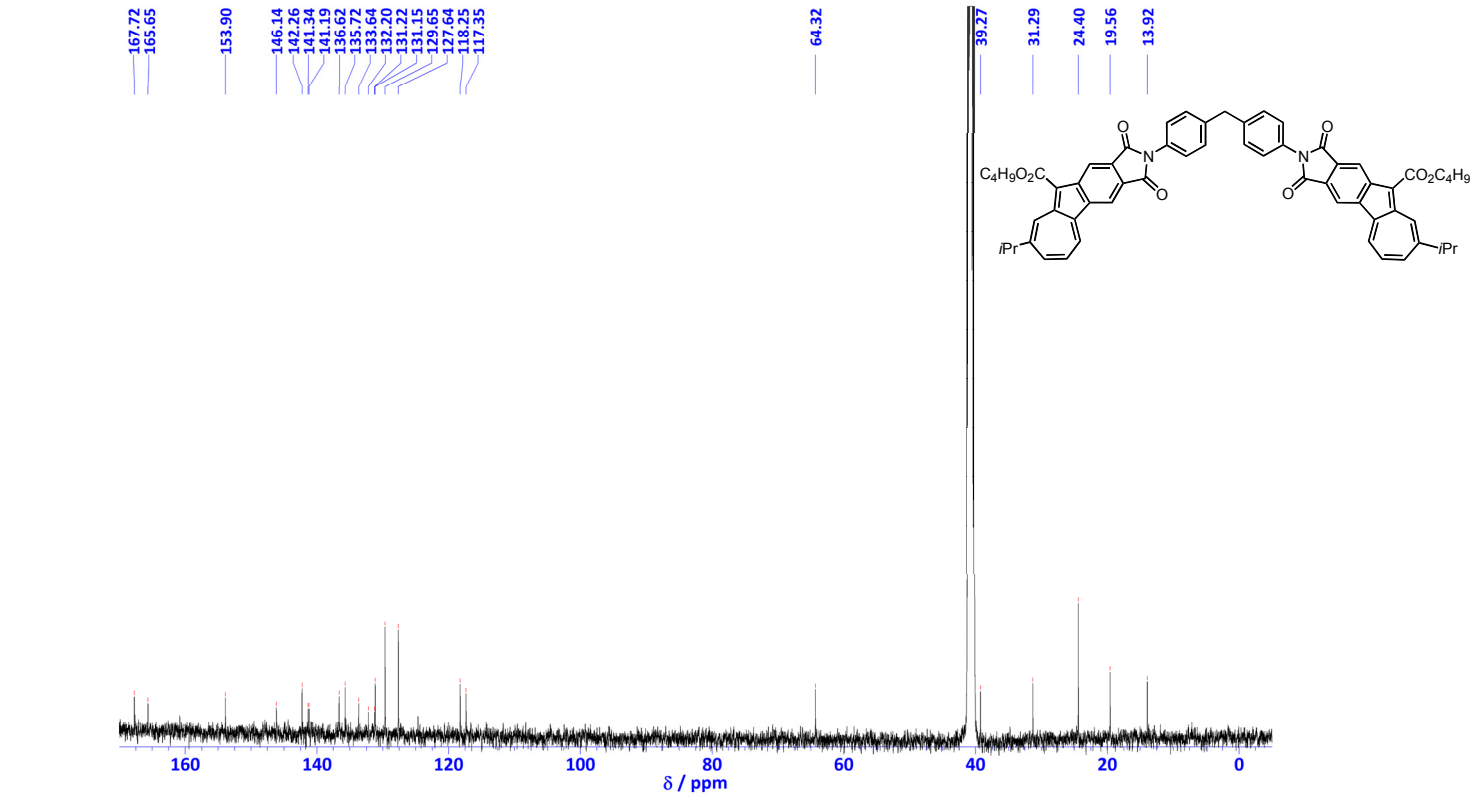


Figure S42. ^{13}C NMR spectrum of **10** in DMSO-d_6 (500 MHz, 140°C).

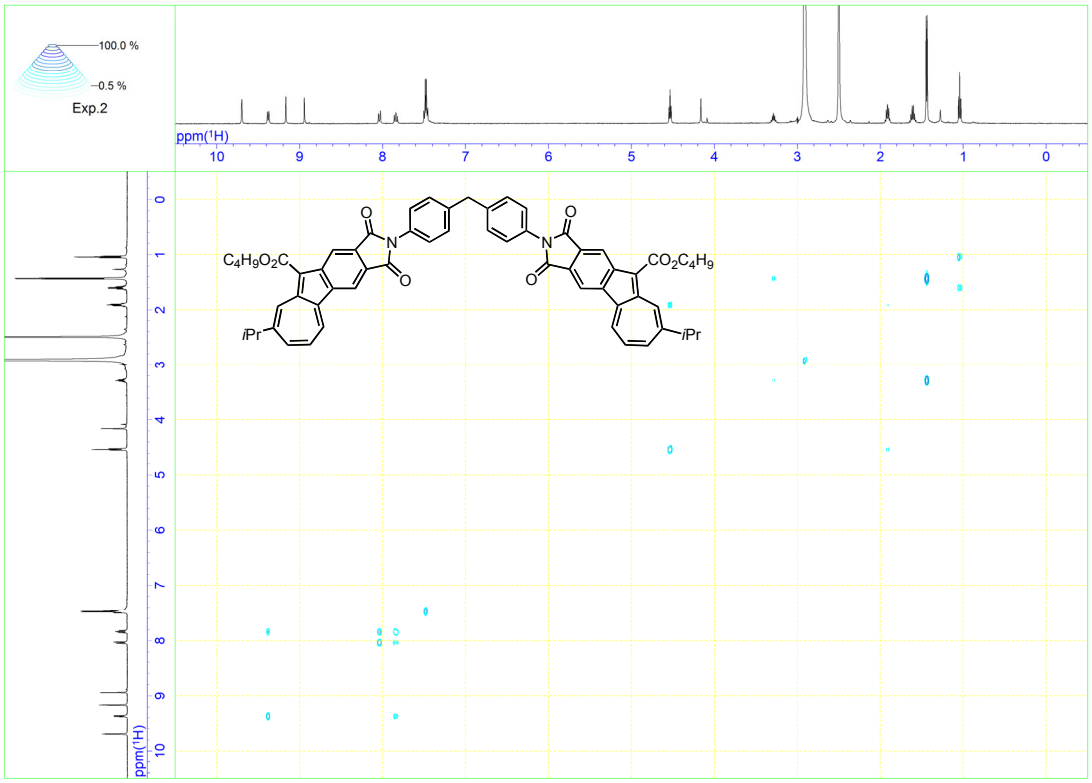


Figure S43. COSY spectrum of **10** in DMSO-d_6 (500 MHz, 140°C).

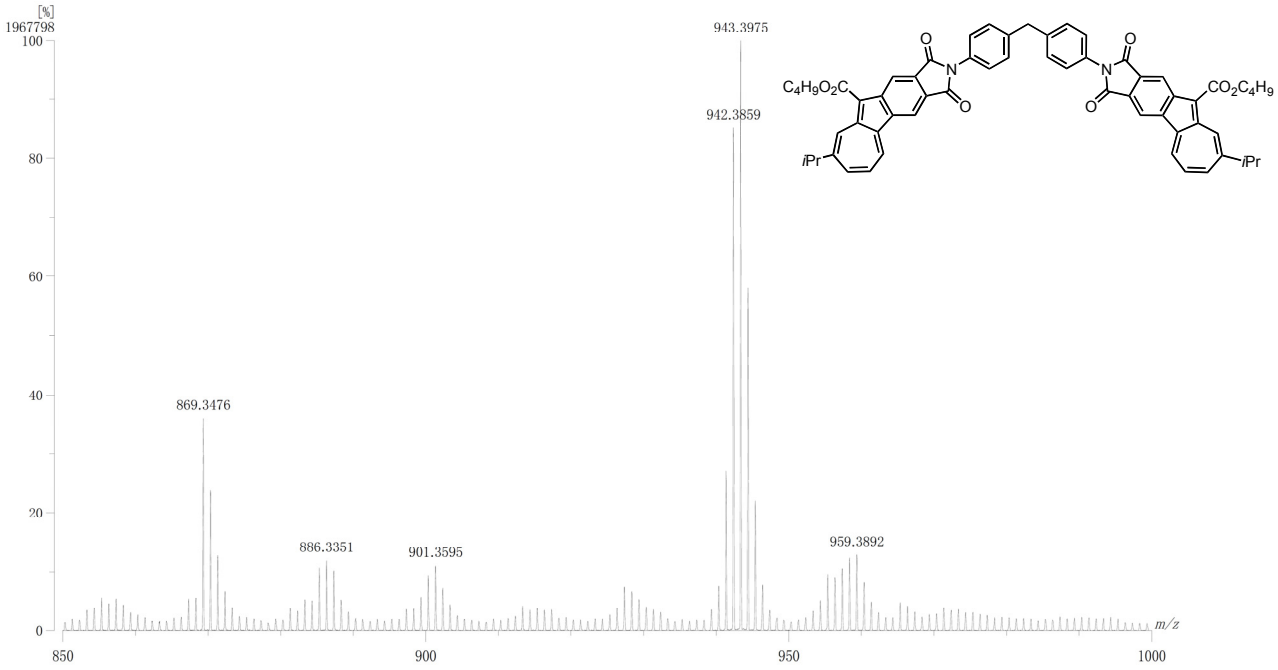


Figure S44. HRMS (FAB-double-focusing, positive) of **10**.

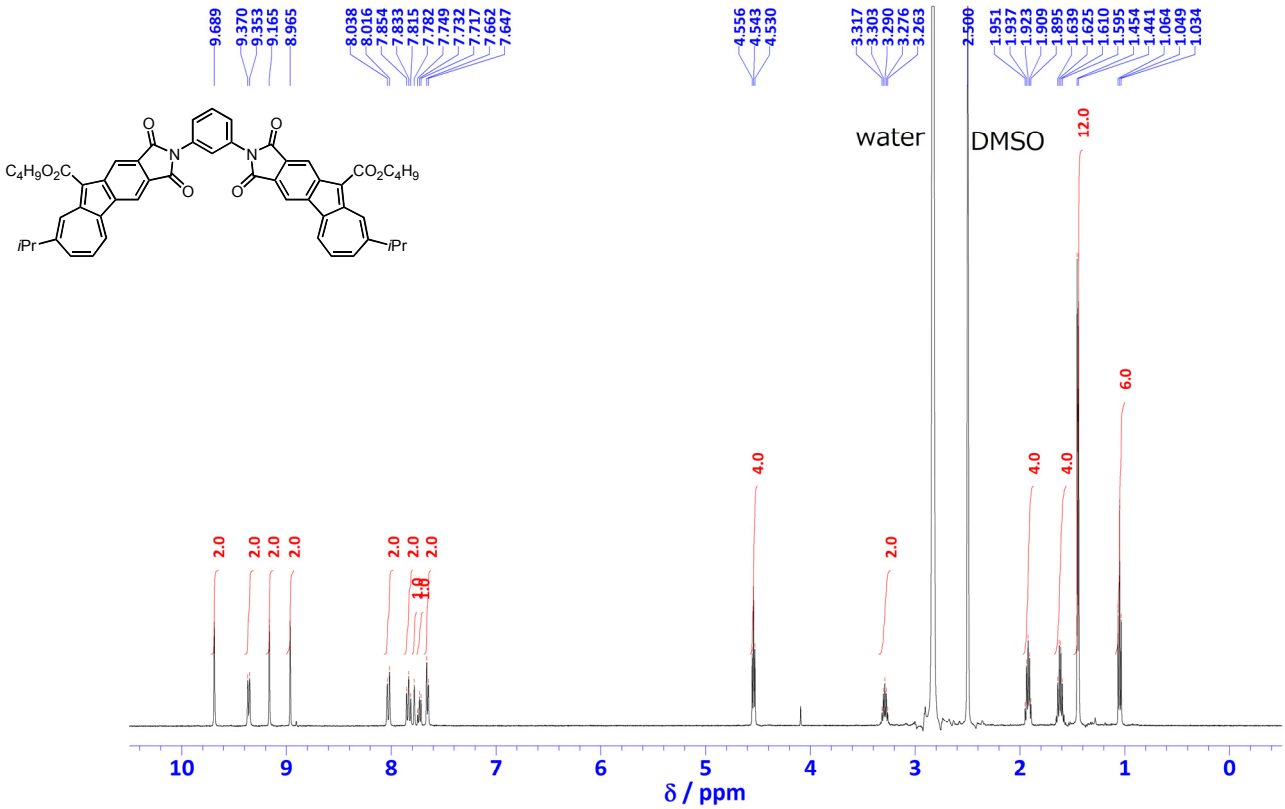


Figure S45. ^{1}H NMR spectrum of **11** in DMSO-d_6 (500 MHz, 140°C).

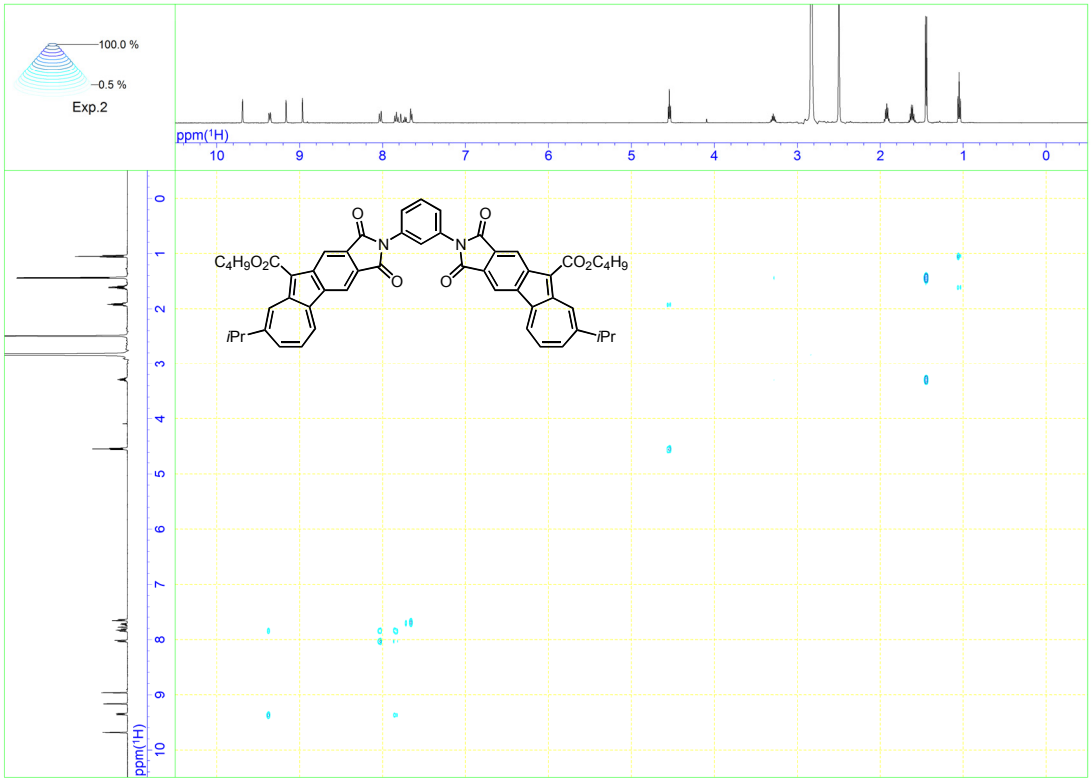


Figure S46. COSY spectrum of **11** in DMSO-d_6 (500 MHz, 140°C).

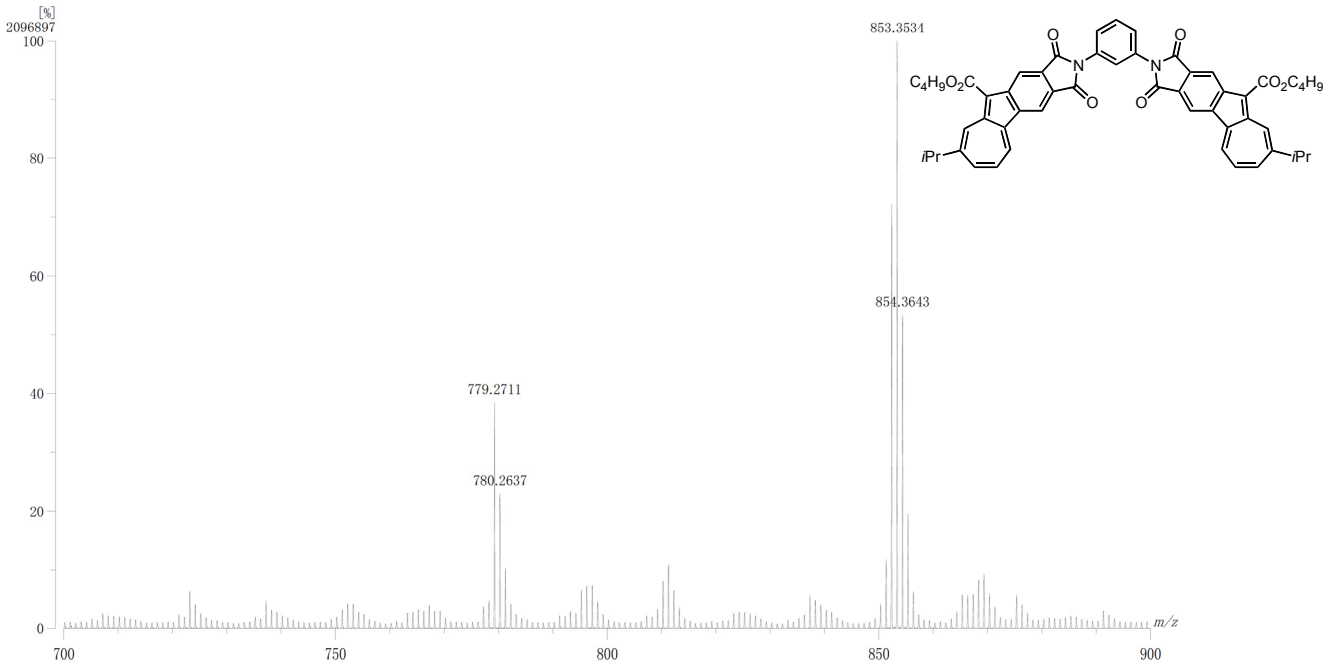


Figure S47. HRMS (FAB-double-focusing, positive) of **11**.

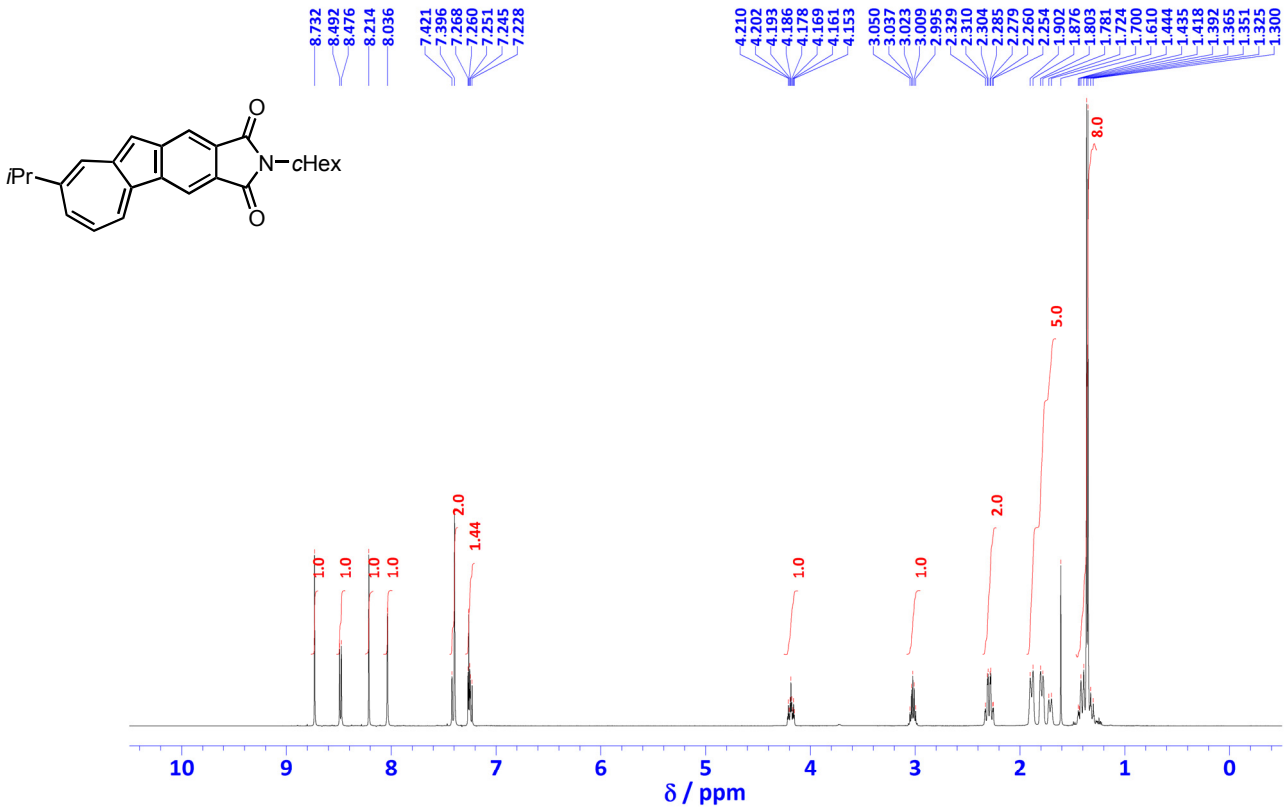


Figure S48. ^{1}H NMR spectrum of **12** in $CDCl_3$ (500 MHz).

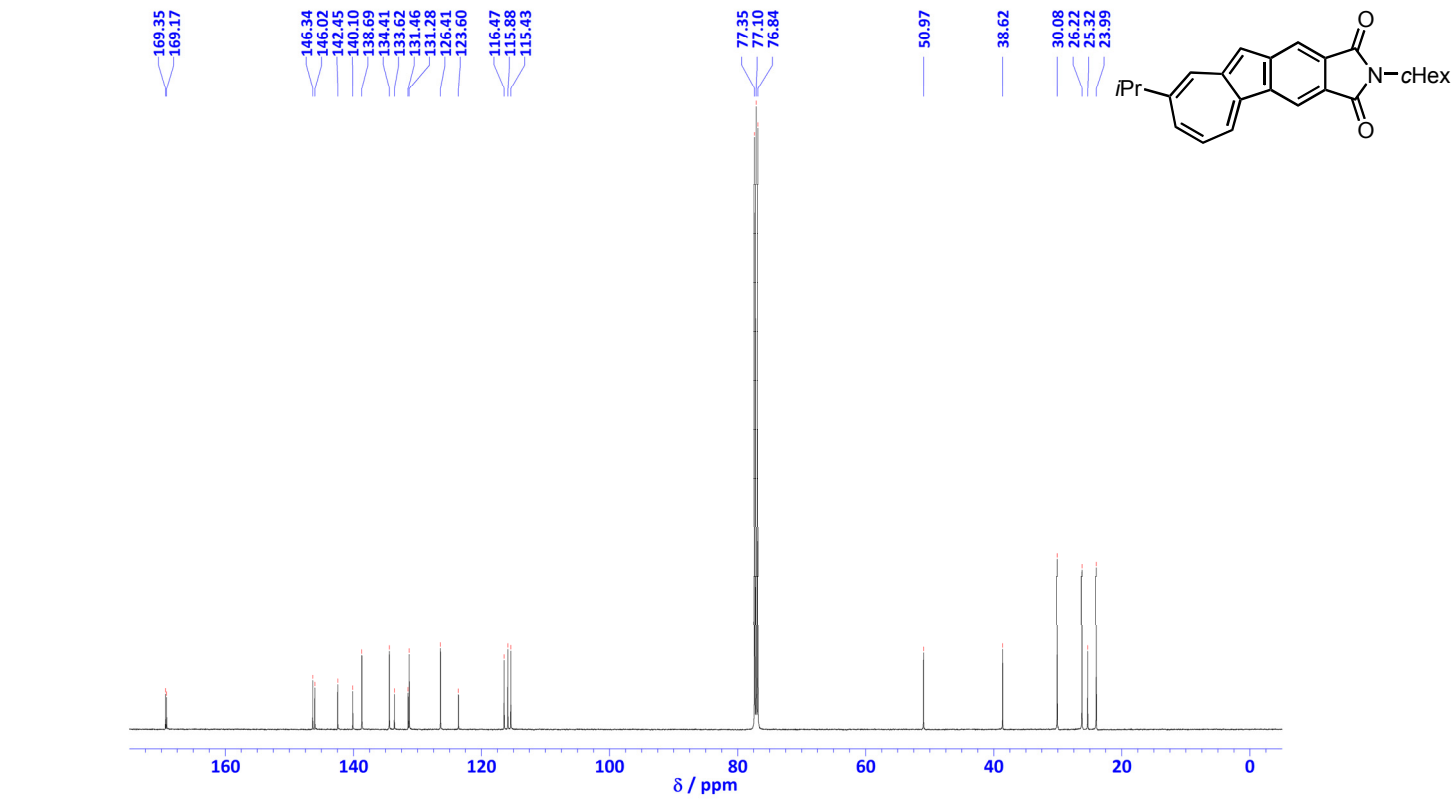


Figure S49. ^{13}C NMR spectrum of **12** in $CDCl_3$ (125 MHz).

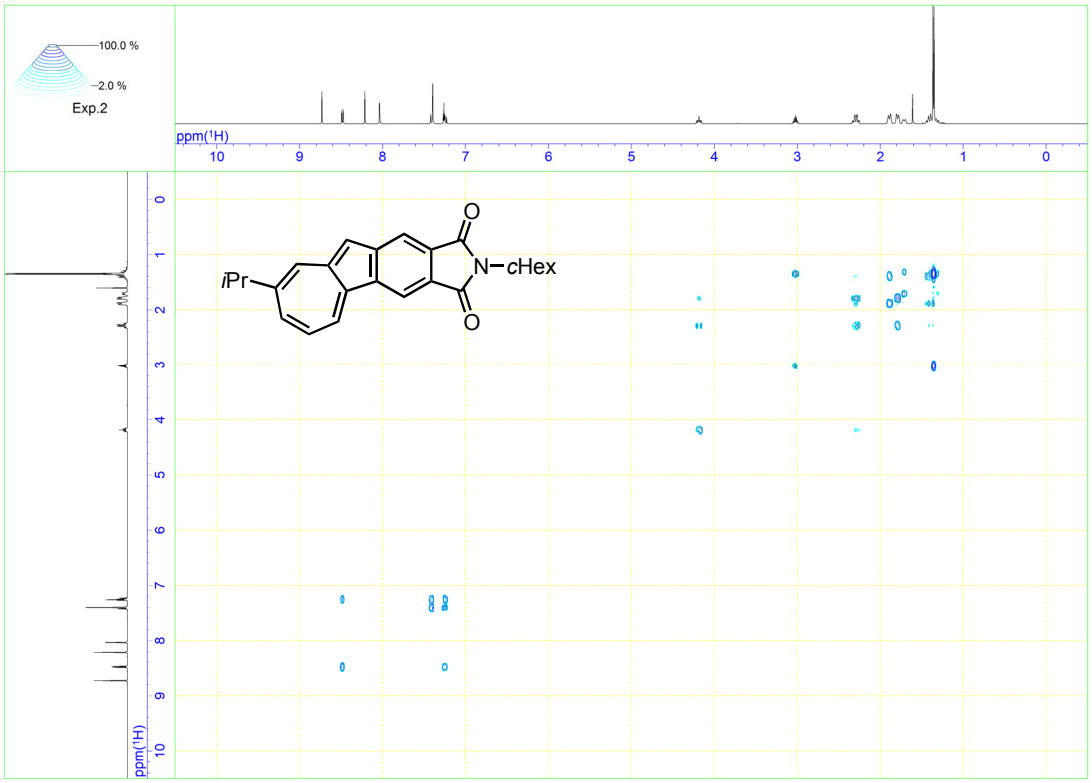


Figure S50. COSY spectrum of **12** in $CDCl_3$ (500 MHz).

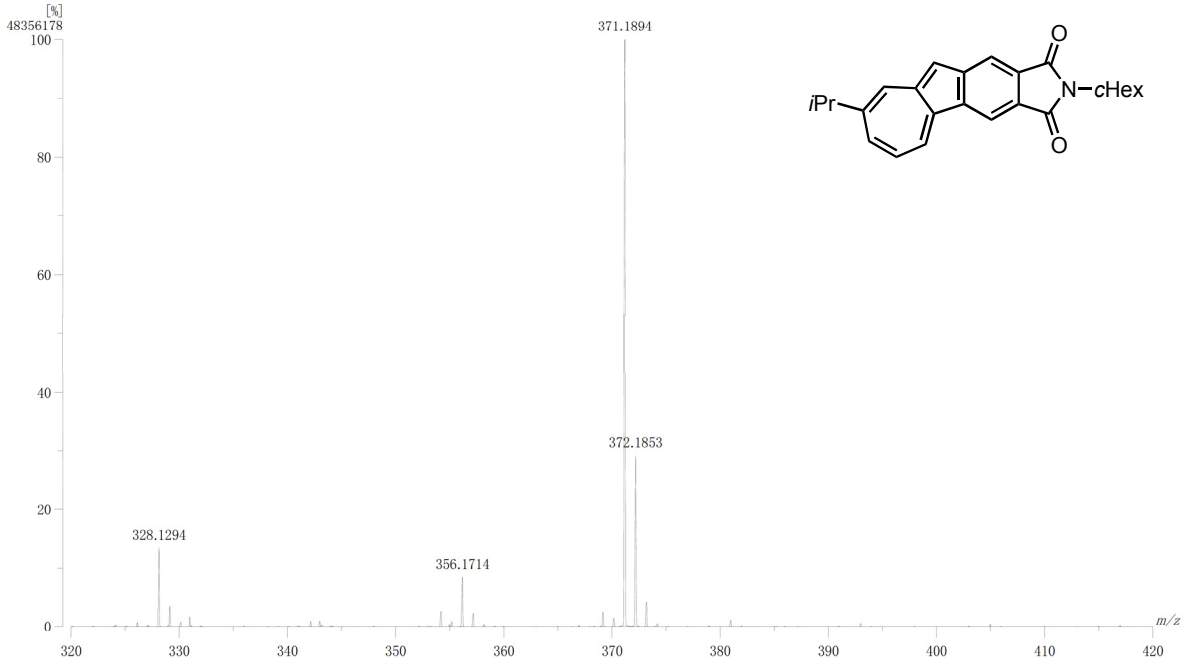


Figure S51. HRMS (FAB-double-focusing, positive) of **12**.

2. UV/Vis spectra and continuous change in the visible spectra of azulenophthalimide derivatives 4a−4g and 12 (Figures S52−S69).

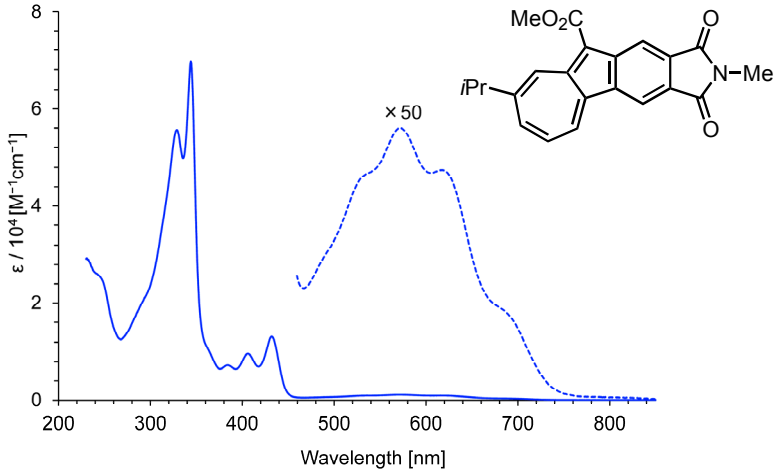


Figure S52. UV/Vis spectrum of **4a** in CH_2Cl_2; the dotted line represents that of 50 magnifications.

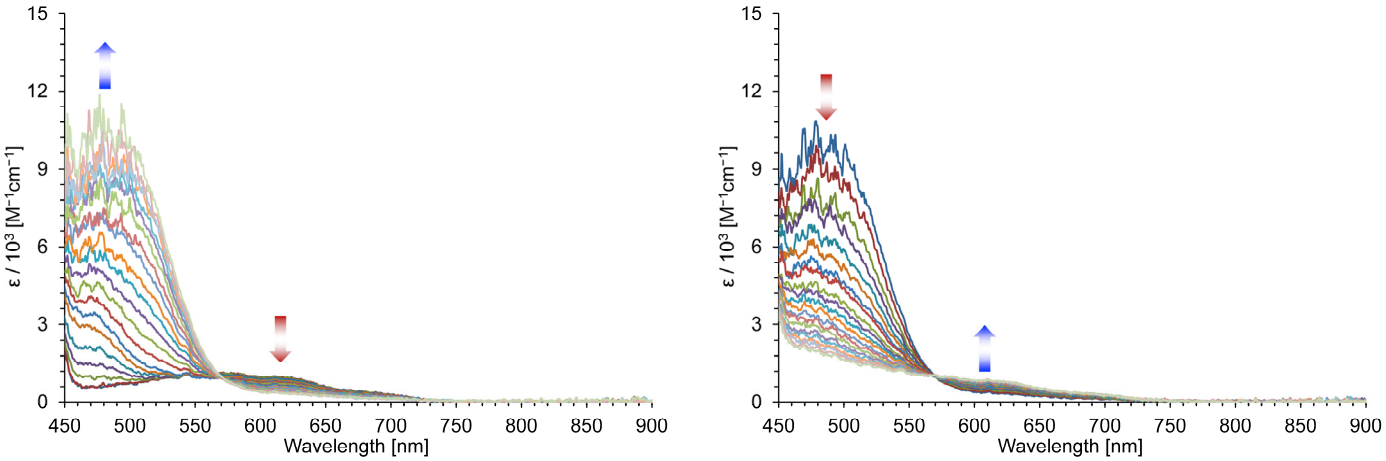


Figure S53. Continuous change in the visible spectrum of **4a**: constant-voltage electrochemical reduction at −1.40 V (left) and oxidation of the reduced species at ±0.00 V (right) in benzonitrile containing Et_4NClO_4 (0.1 M) at 20 sec intervals.

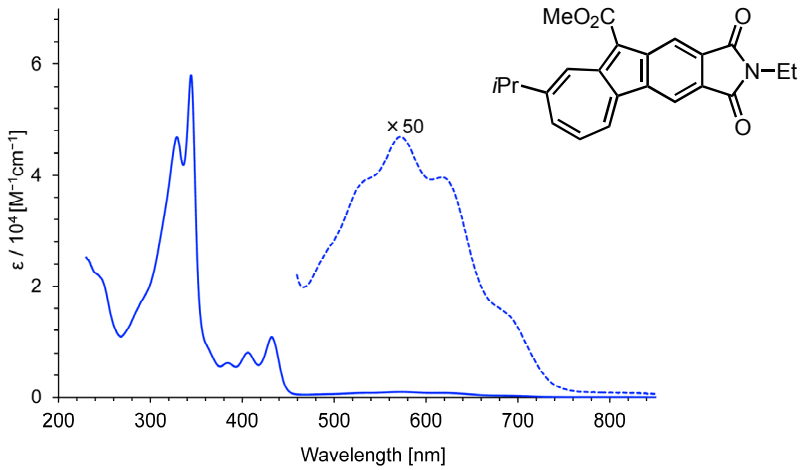


Figure S54. UV/Vis spectrum of **4b** in CH_2Cl_2; the dotted line represents that of 50 magnifications.

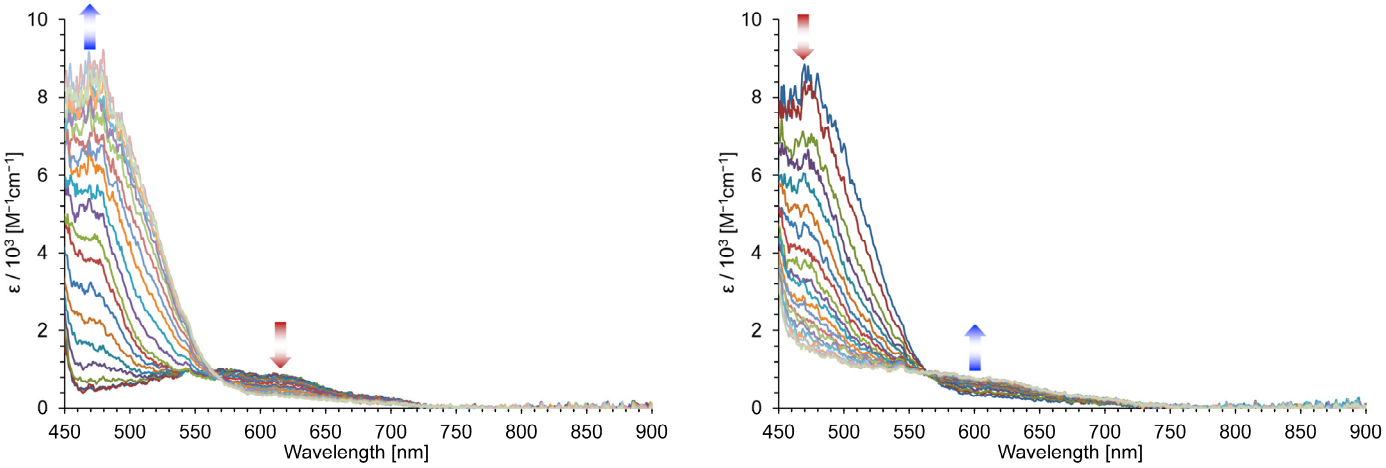


Figure S55. Continuous change in the visible spectrum of **4b**: constant-voltage electrochemical reduction at −1.40 V (left) and oxidation of the reduced species at ±0.00 V (right) in benzonitrile containing Et_4NClO_4 (0.1 M) at 20 sec intervals.

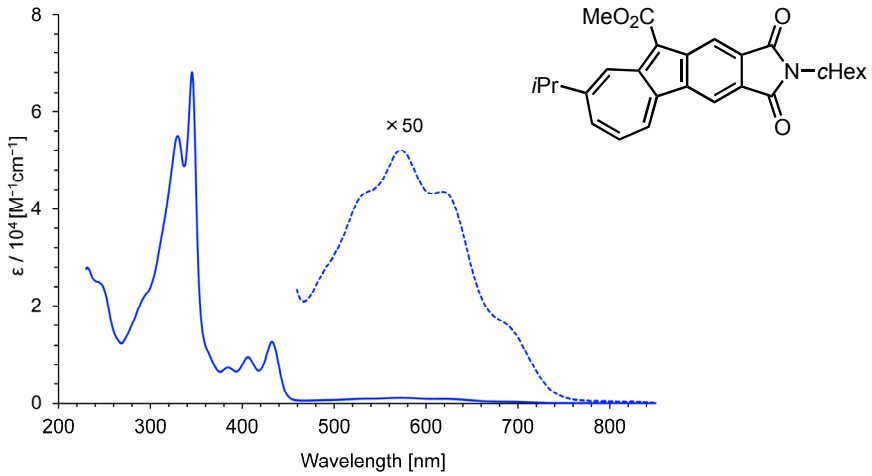


Figure S56. UV/Vis spectrum of **4c** in CH_2Cl_2; the dotted line represents that of 50 magnifications.

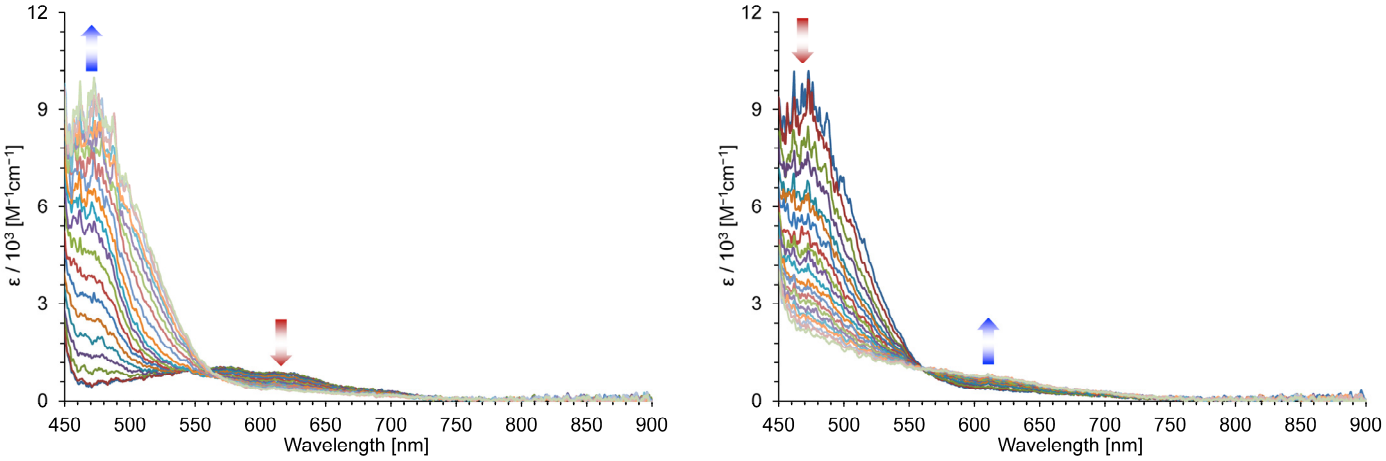


Figure S57. Continuous change in the visible spectrum of **4c**: constant-voltage electrochemical reduction at −1.40 V (left) and oxidation of the reduced species at ±0.00 V (right) in benzonitrile containing Et_4NClO_4 (0.1 M) at 20 sec intervals.

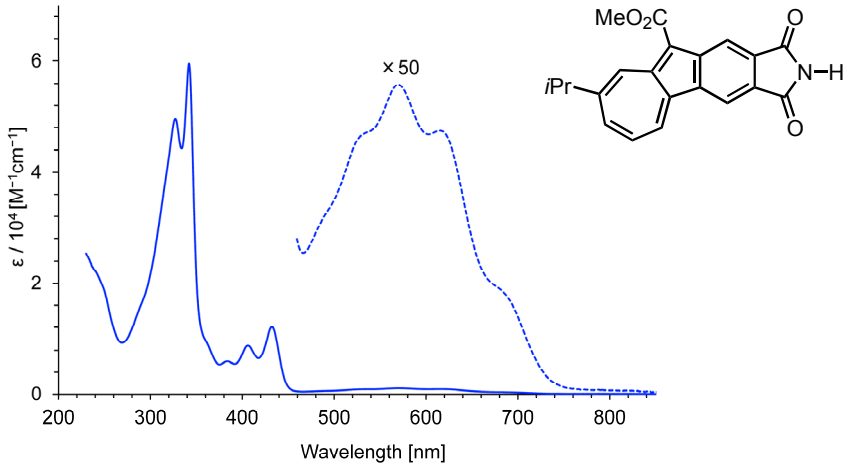


Figure S58. UV/Vis spectrum of **4d** in CH_2Cl_2; the dotted line represents that of 50 magnifications.

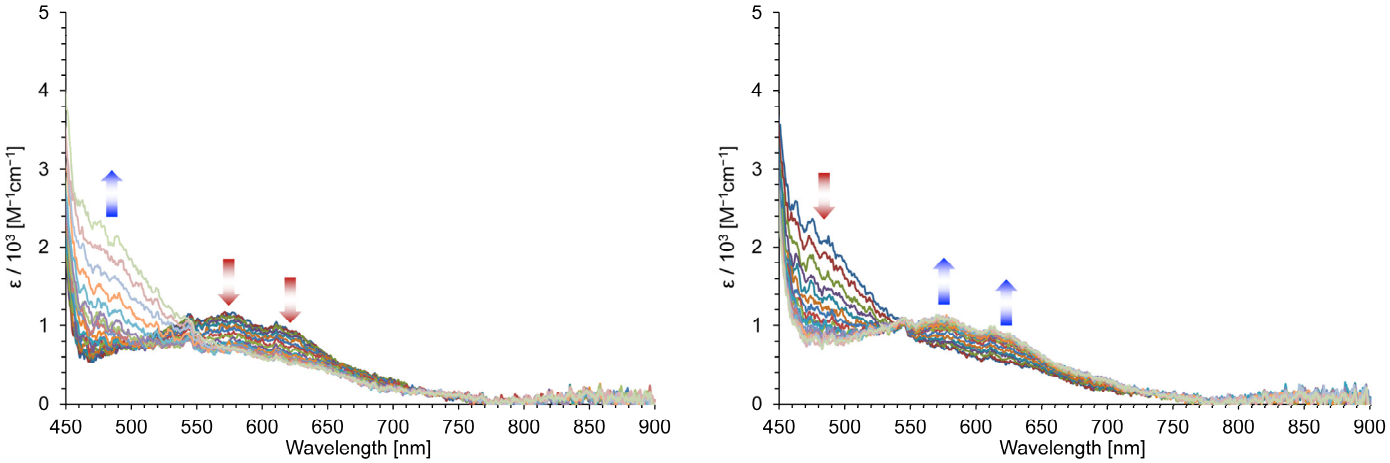


Figure S59. Continuous change in the visible spectrum of **4d**: constant-voltage electrochemical reduction at −1.40 V (left) and oxidation of the reduced species at ±0.00 V (right) in benzonitrile containing Et_4NClO_4 (0.1 M) at 20 sec intervals.

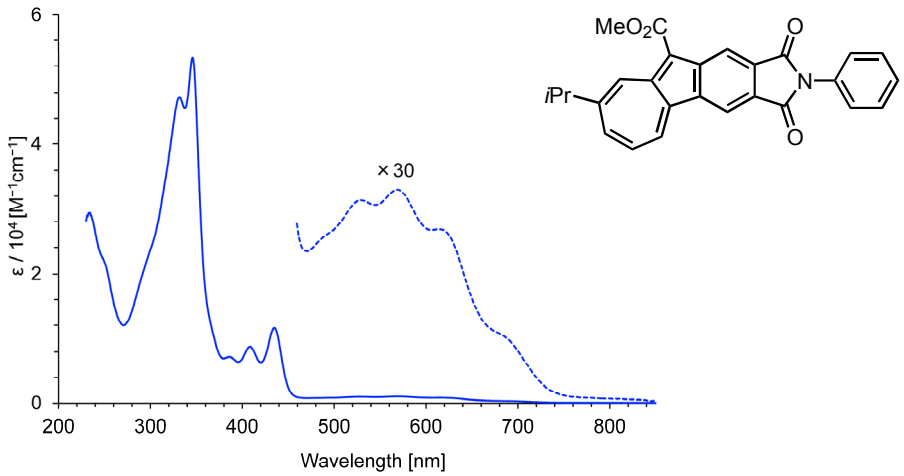


Figure S60. UV/Vis spectrum of **4e** in CH_2Cl_2; the dotted line represents that of 50 magnifications.

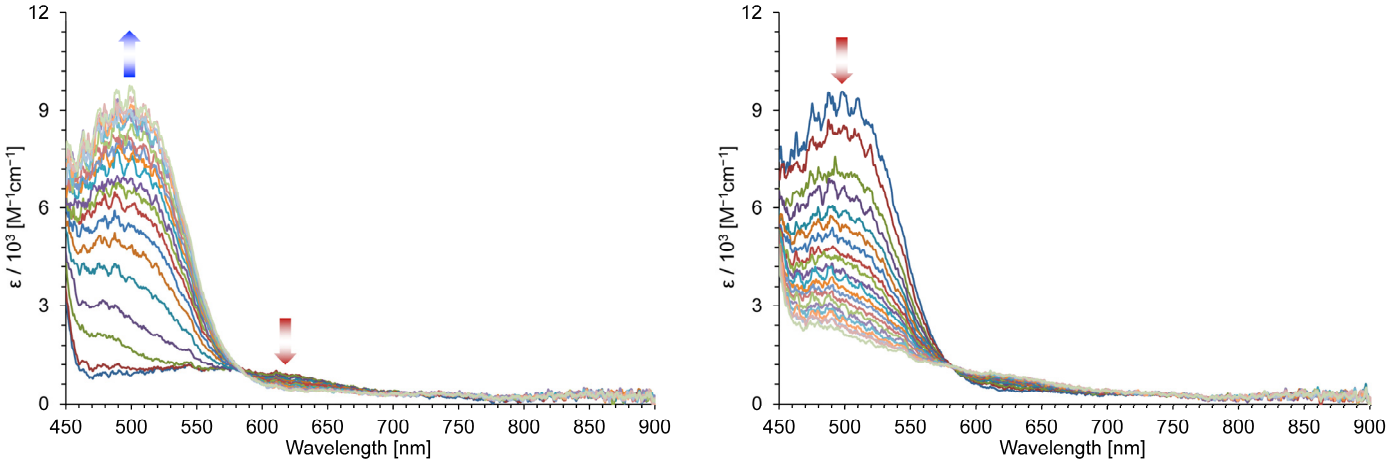


Figure S61. Continuous change in the visible spectrum of **4e**: constant-voltage electrochemical reduction at −1.40 V (left) and oxidation of the reduced species at ±0.00 V (right) in benzonitrile containing Et_4NClO_4 (0.1 M) at 10 sec intervals.

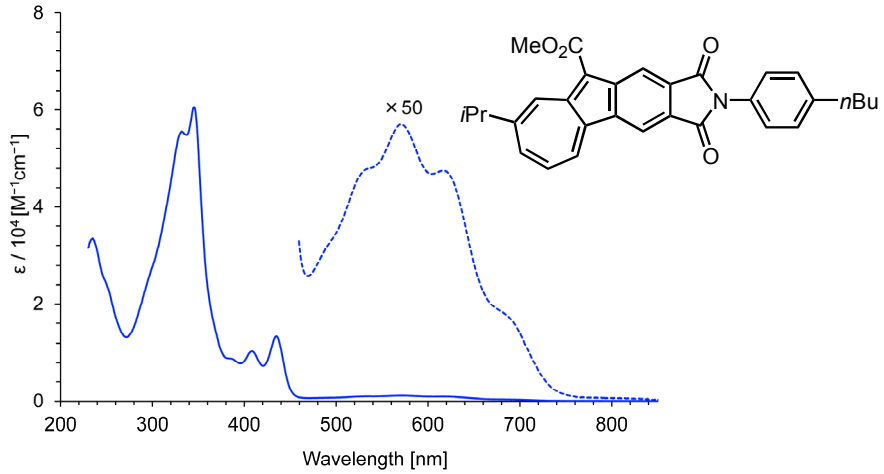


Figure S62. UV/Vis spectrum of **4f** in CH_2Cl_2; the dotted line represents that of 50 magnifications.

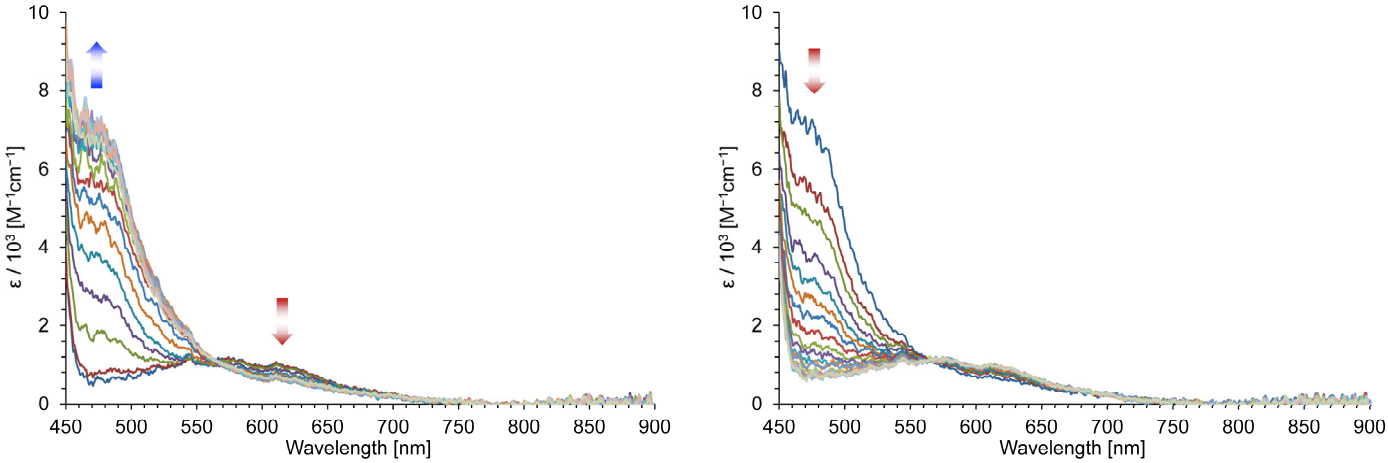


Figure S63. Continuous change in the visible spectrum of **4f**: constant-voltage electrochemical reduction at −1.40 V (left) and oxidation of the reduced species at ±0.00 V (right) in benzonitrile containing Et_4NClO_4 (0.1 M) at 10 sec intervals.

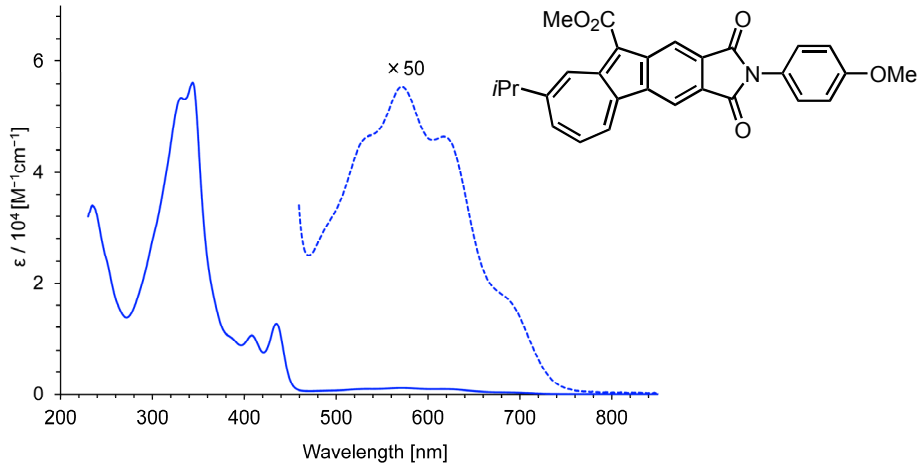


Figure S64. UV/Vis spectrum of **4g** in CH_2Cl_2; the dotted line represents that of 50 magnifications.

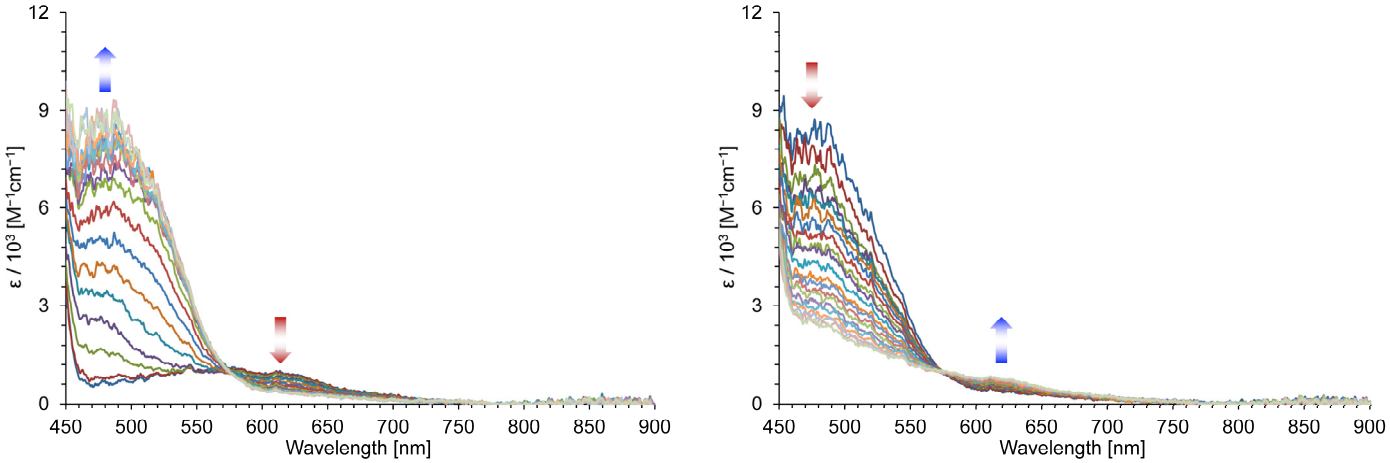


Figure S65. Continuous change in the visible spectrum of **4g**: constant-voltage electrochemical reduction at −1.40 V (left) and oxidation of the reduced species at ±0.00 V (right) in benzonitrile containing Et_4NClO_4 (0.1 M) at 10 sec intervals.

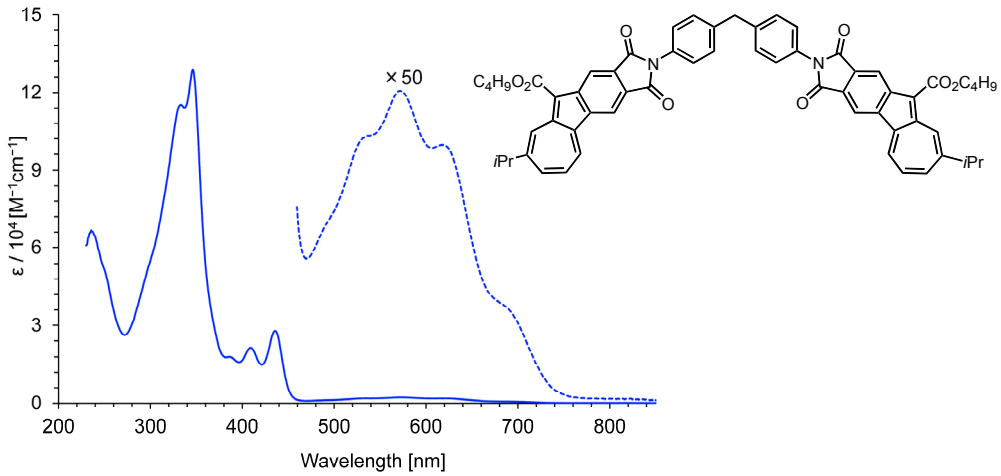


Figure S66. UV/Vis spectrum of **10** in CH_2Cl_2; the dotted line represents that of 50 magnifications.

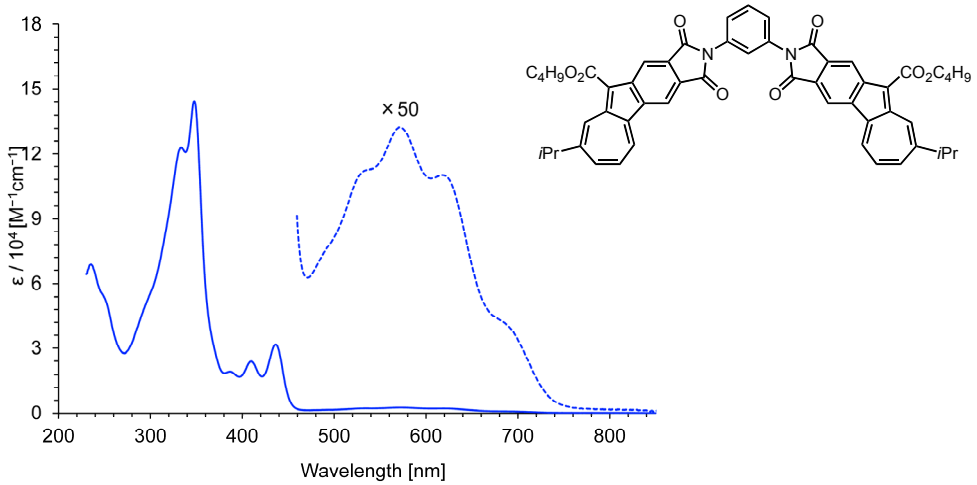


Figure S67. UV/Vis spectrum of **11** in CH_2Cl_2; the dotted line represents that of 50 magnifications.

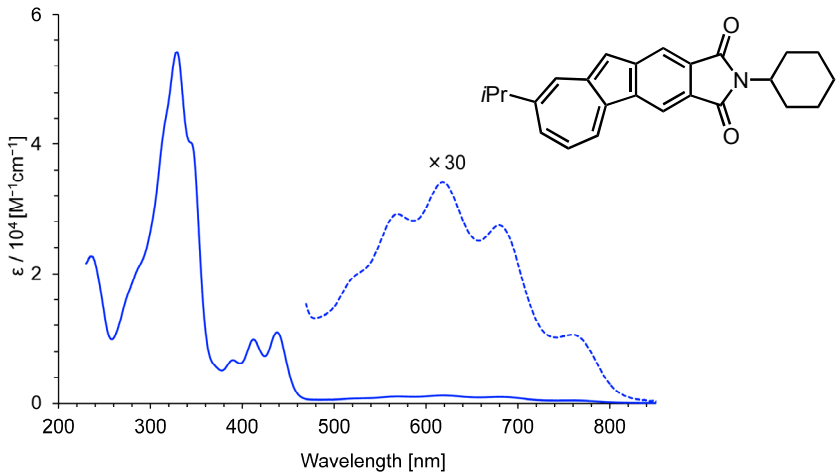


Figure S68. UV/Vis spectrum of **12** in CH_2Cl_2; the dotted line represents that of 50 magnifications.

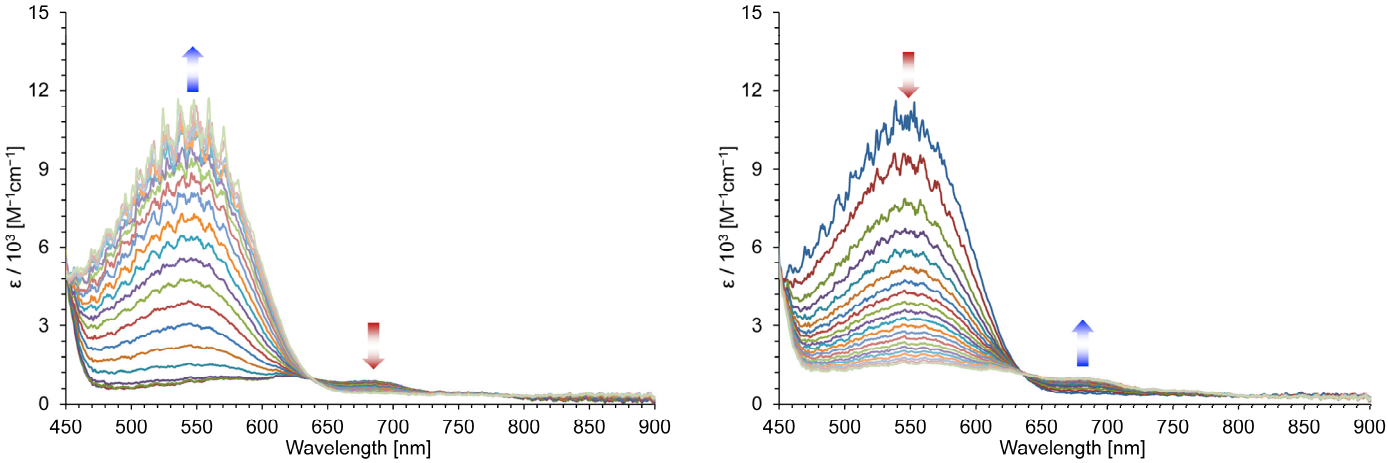
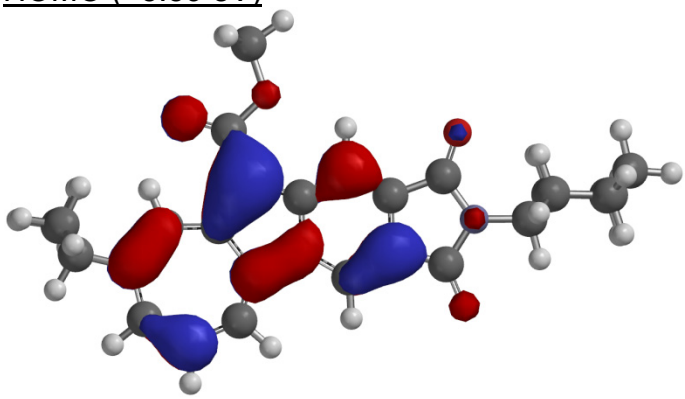


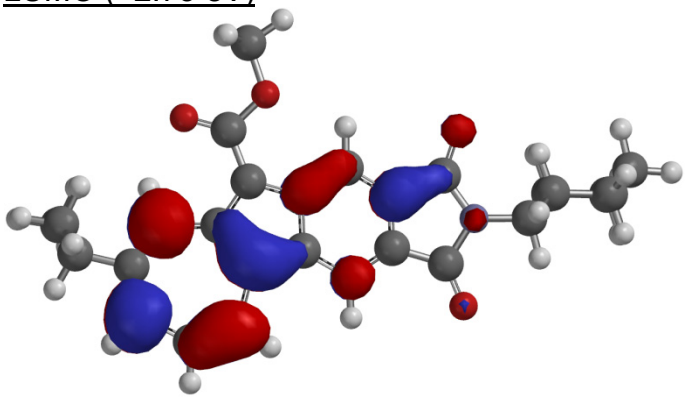
Figure S69. Continuous change in the visible spectrum of **12**: constant-voltage electrochemical reduction at −1.40 V (left) and oxidation of the reduced species at ±0.00 V (right) in benzonitrile containing Et_4NClO_4 (0.1 M) at 10 sec intervals.

3. Frontier Kohn–Sham orbitals of compounds 4c, 4e and 12 (Figures S70−S72).

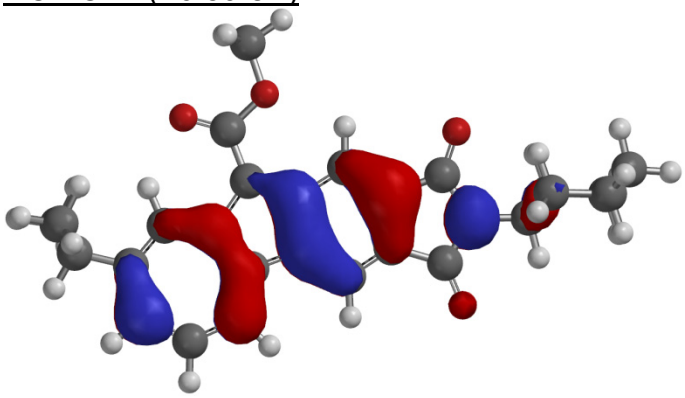
HOMO (−5.59 eV)



LUMO (−2.73 eV)



HOMO−1 (−6.59 eV)



LUMO+1 (−2.10 eV)

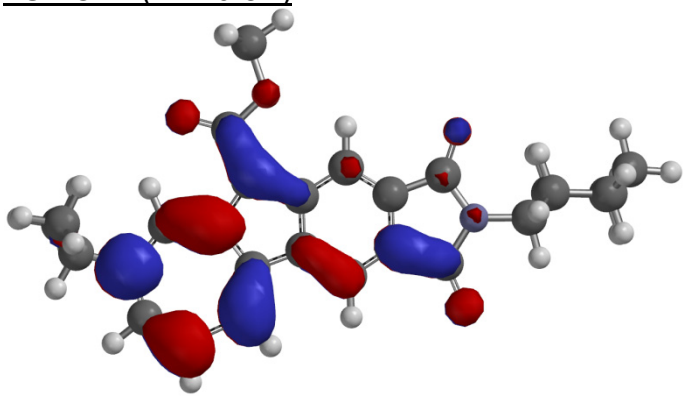
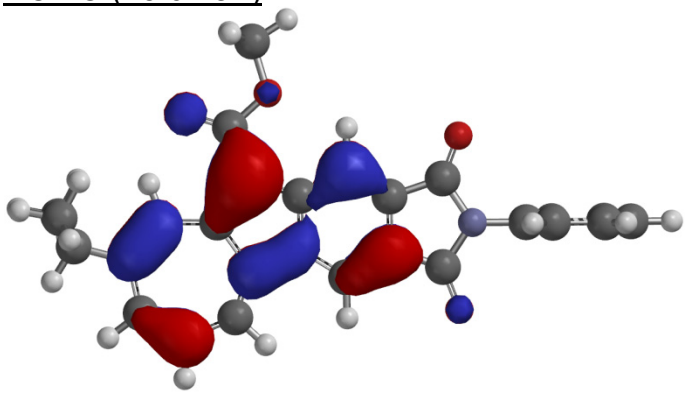
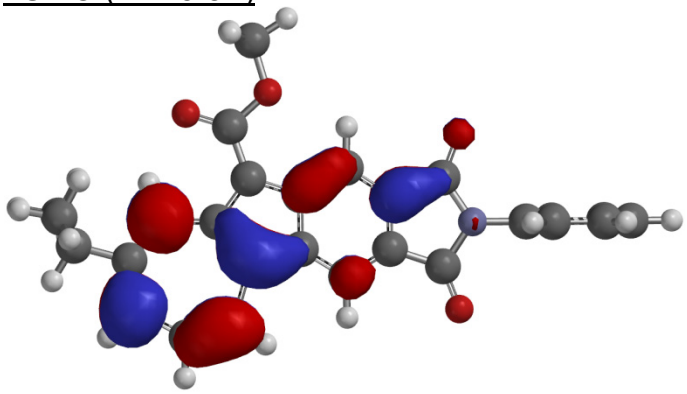


Figure S70. Frontier Kohn–Sham orbitals of **4c** at the B3LYP/6-31G** level.

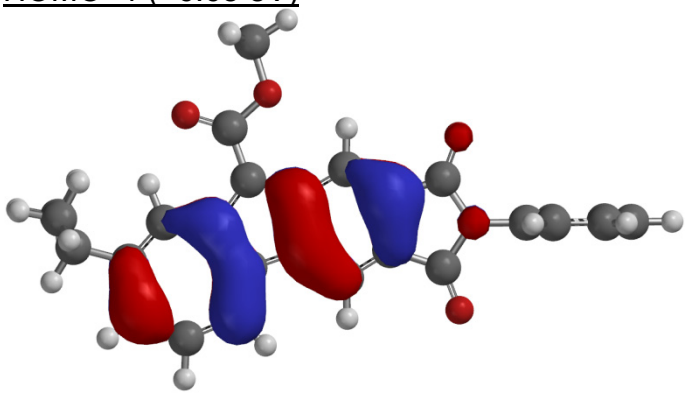
HOMO (−5.61 eV)



LUMO (−2.75 eV)



HOMO−1 (−6.68 eV)



LUMO+1 (−2.11 eV)

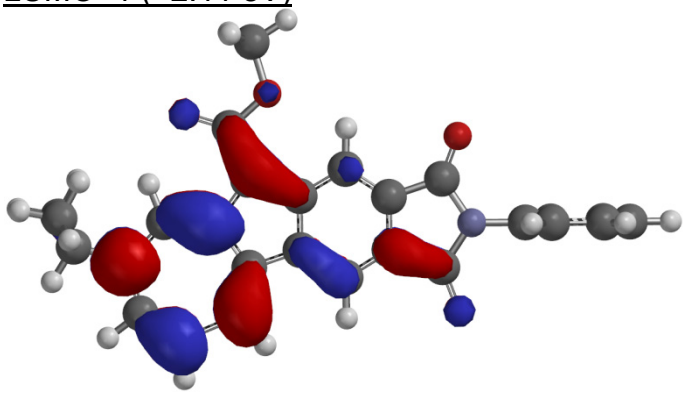
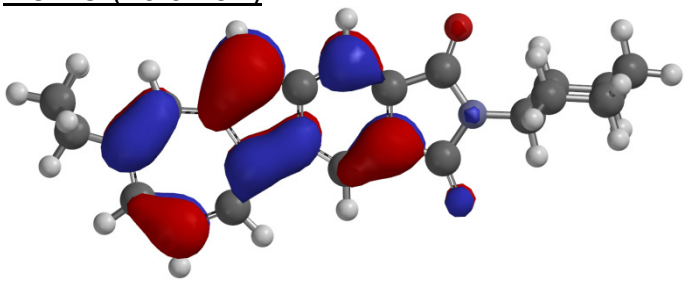
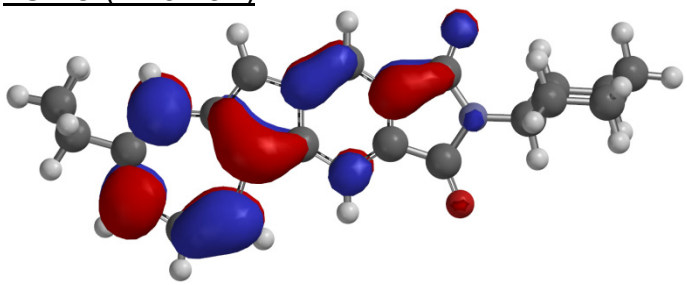


Figure S71. Frontier Kohn–Sham orbitals of **4e** at the B3LYP/6-31G** level.

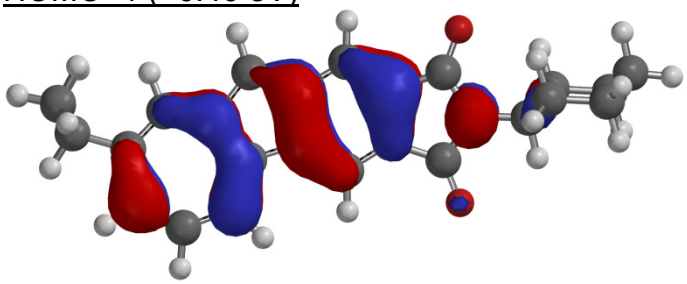
HOMO (−5.34 eV)



LUMO (−2.57 eV)



HOMO−1 (−6.46 eV)



LUMO+1 (−1.89 eV)

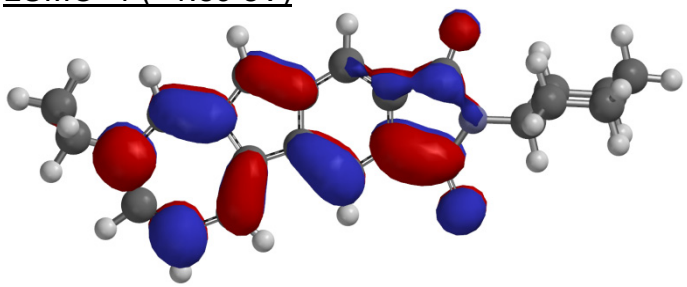
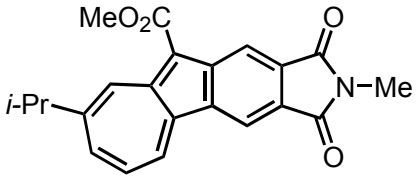


Figure S72. Frontier Kohn–Sham orbitals of **12** at the B3LYP/6-31G** level.

4. Cyclic and differential pulse voltammograms of azulenophthalimide derivatives 4a−4g and 12 (Figures S73−S80).



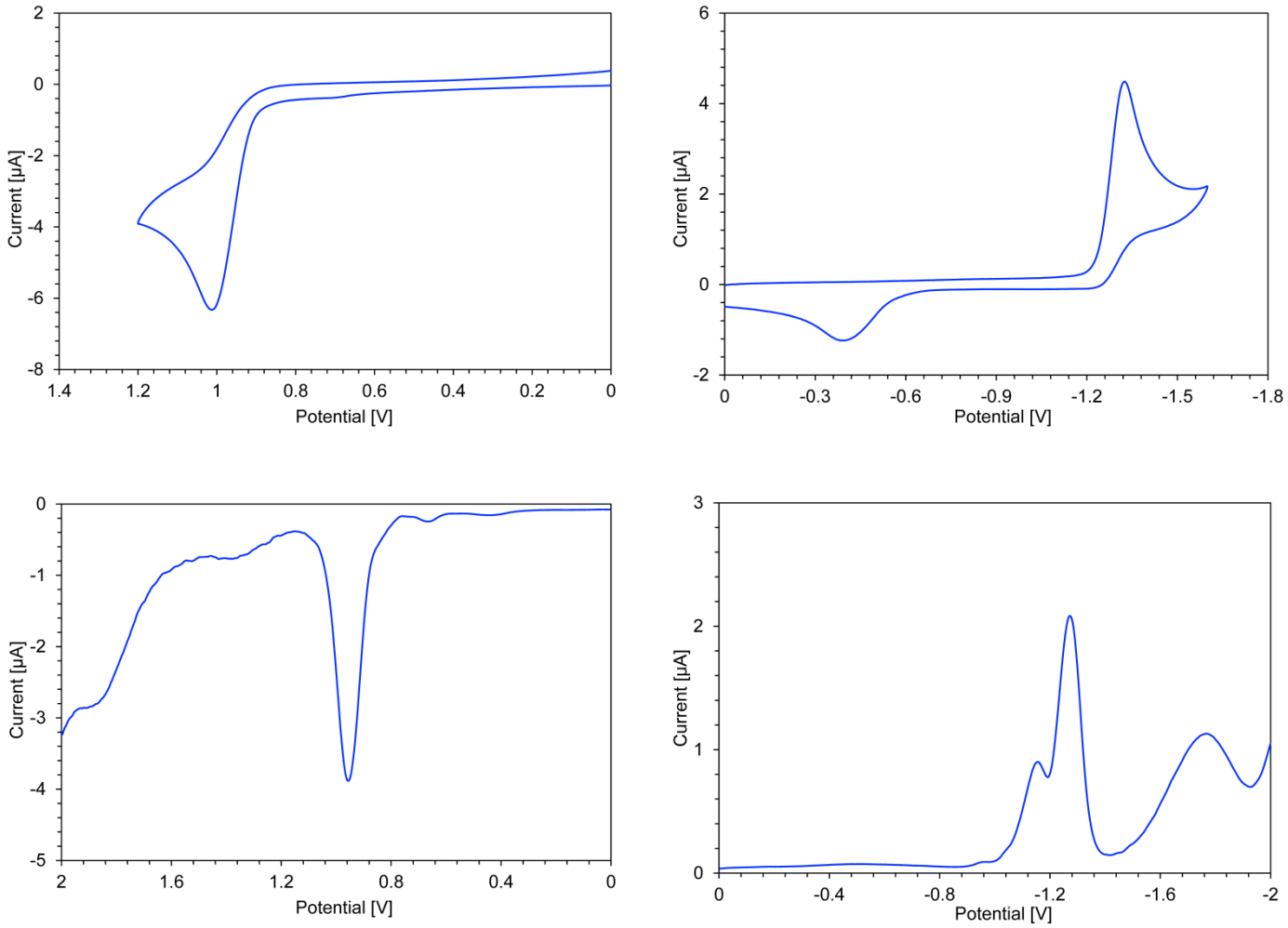
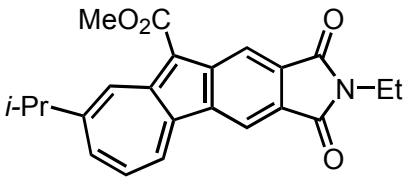


Figure S73. Cyclic voltammogram for oxidation (top, left) and reduction (top, right), and differential pulse voltammograms for oxidation (bottom, left) and reduction (bottom, right) of **4a** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as the supporting electrolyte; scan rate: CV = 100 mVs^{-1}, DPV = 20 mVs^{-1}.



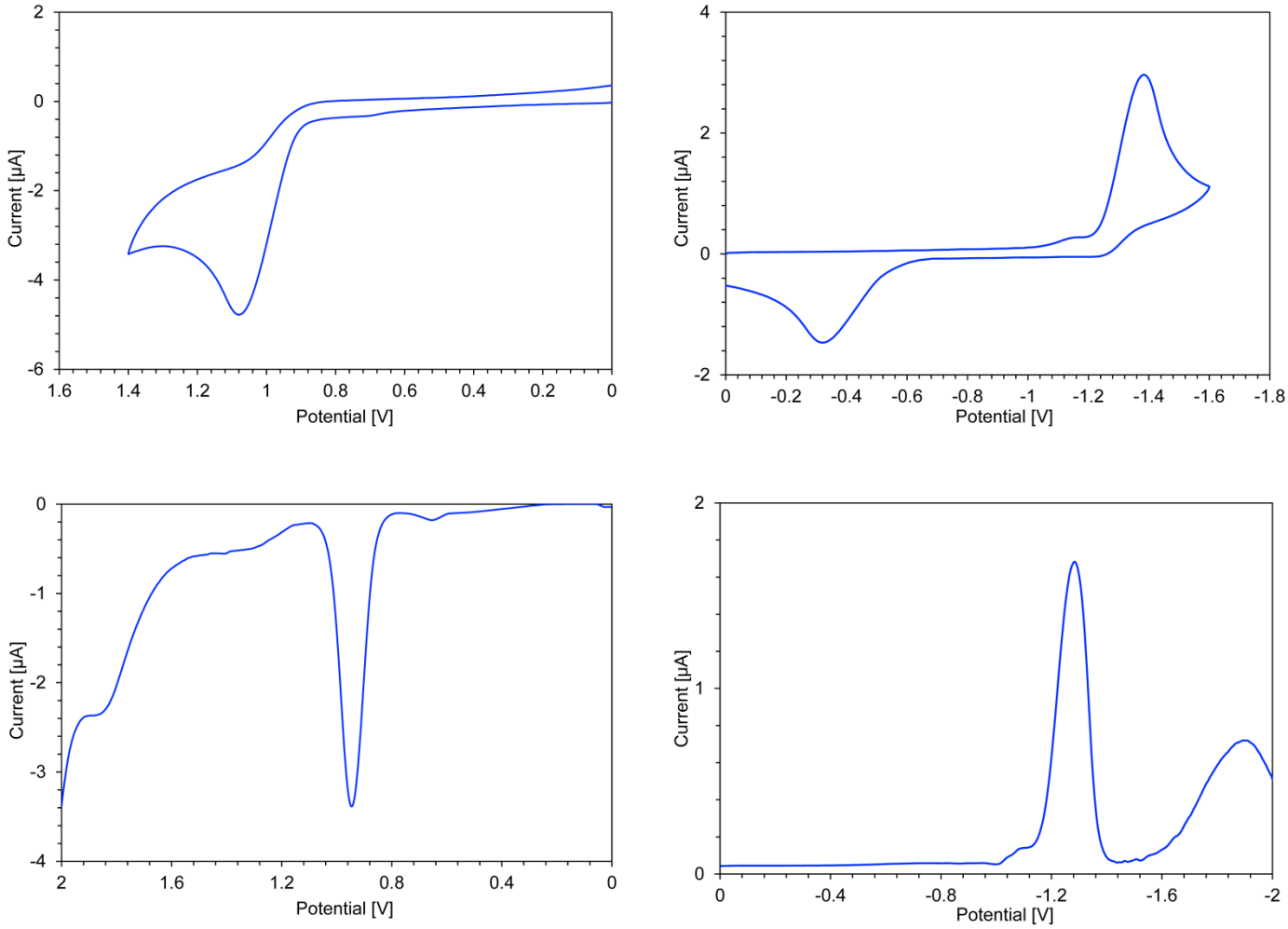


Figure S74. Cyclic voltammogram for oxidation (top, left) and reduction (top, right), and differential pulse voltammograms for oxidation (bottom, left) and reduction (bottom, right) of **4b** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as the supporting electrolyte; scan rate: CV = 100 mVs^{-1}, DPV = 20 mVs^{-1}.

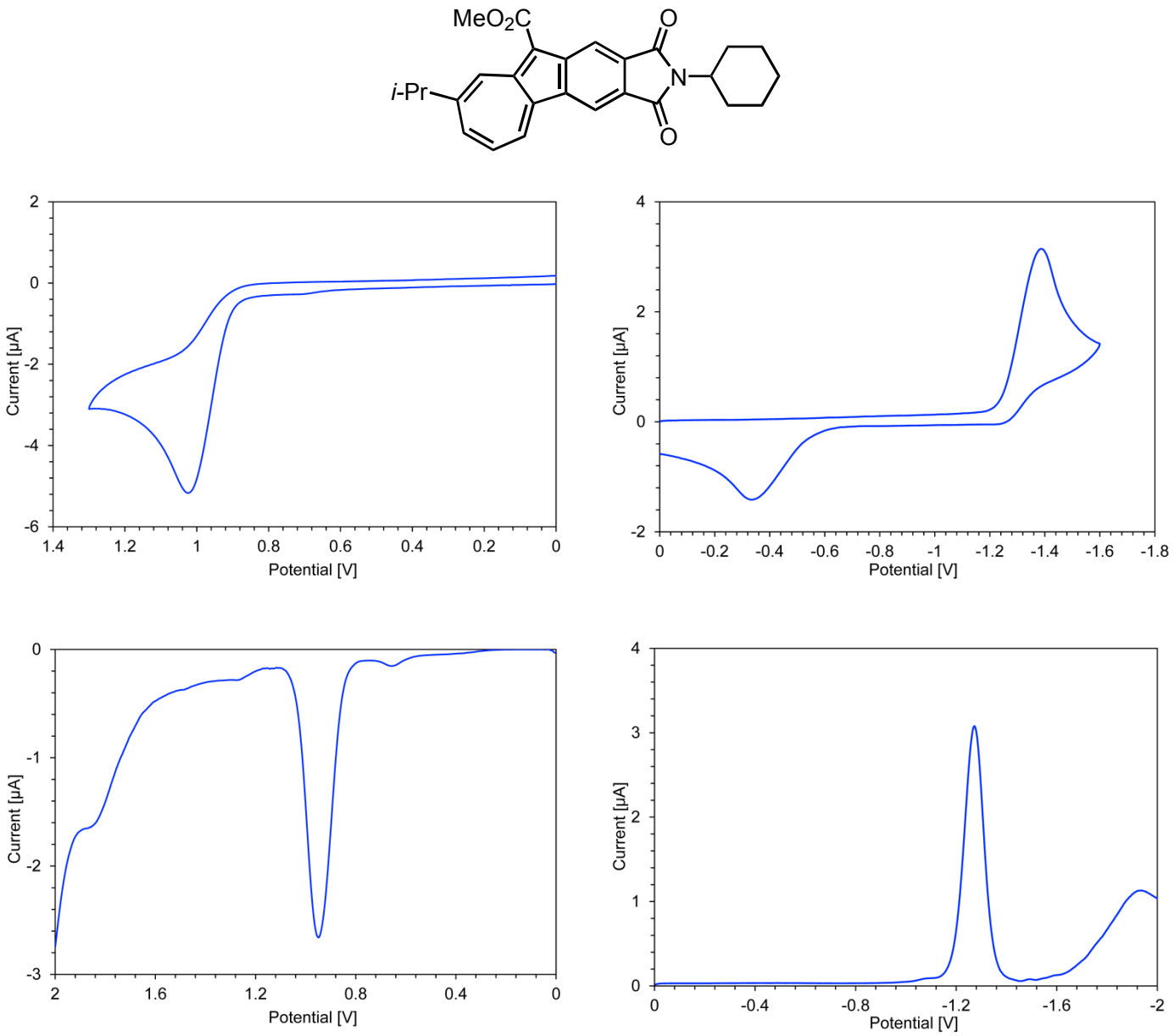


Figure S75. Cyclic voltammogram for oxidation (top, left) and reduction (top, right), and differential pulse voltammograms for oxidation (bottom, left) and reduction (bottom, right) of **4c** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as the supporting electrolyte; scan rate: CV = 100 mVs^{-1}, DPV = 20 mVs^{-1}.

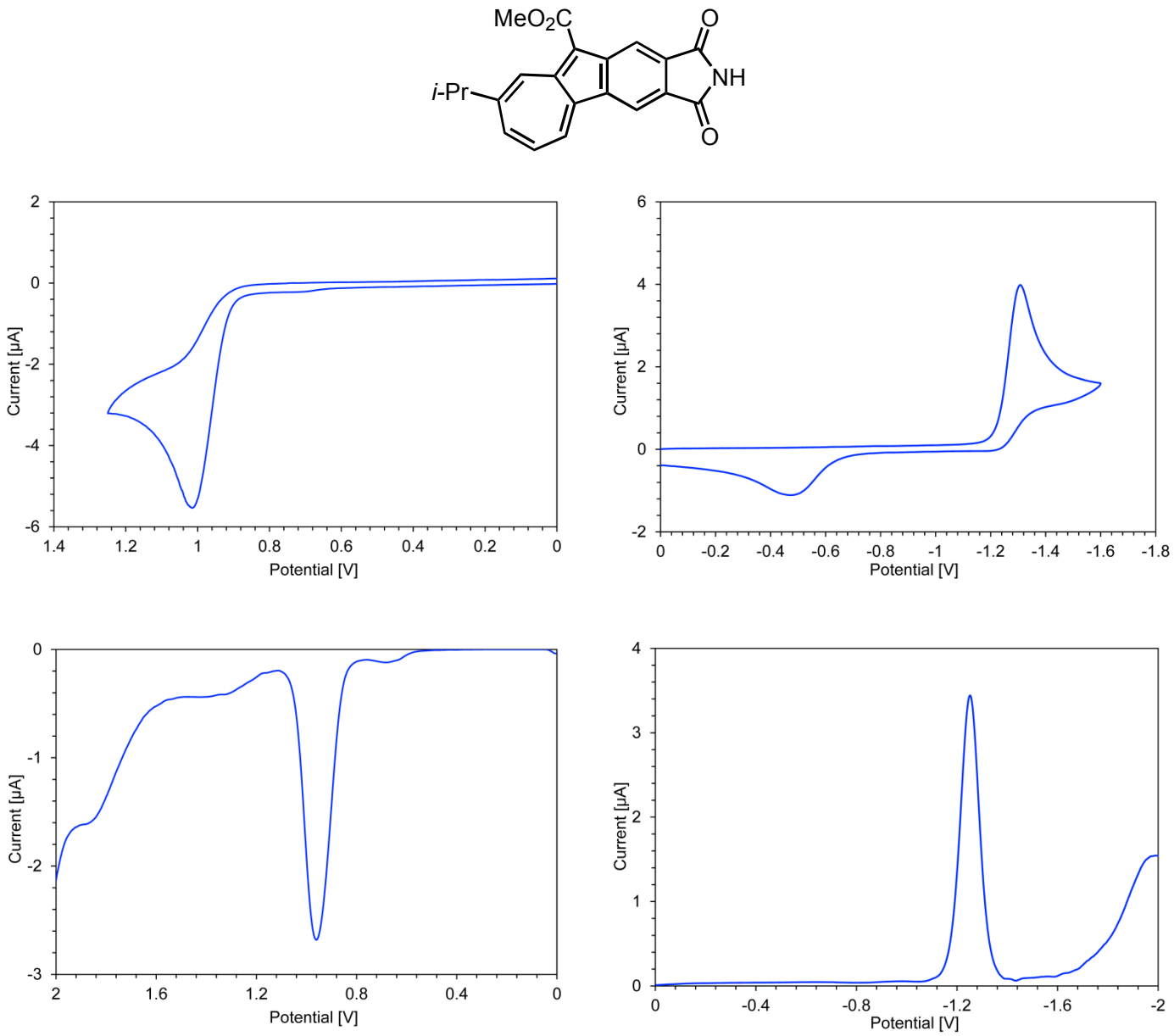


Figure S76. Cyclic voltammogram for oxidation (top, left) and reduction (top, right), and differential pulse voltammograms for oxidation (bottom, left) and reduction (bottom, right) of **4d** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as the supporting electrolyte; scan rate: CV = 100 mVs^{-1}, DPV = 20 mVs^{-1}.

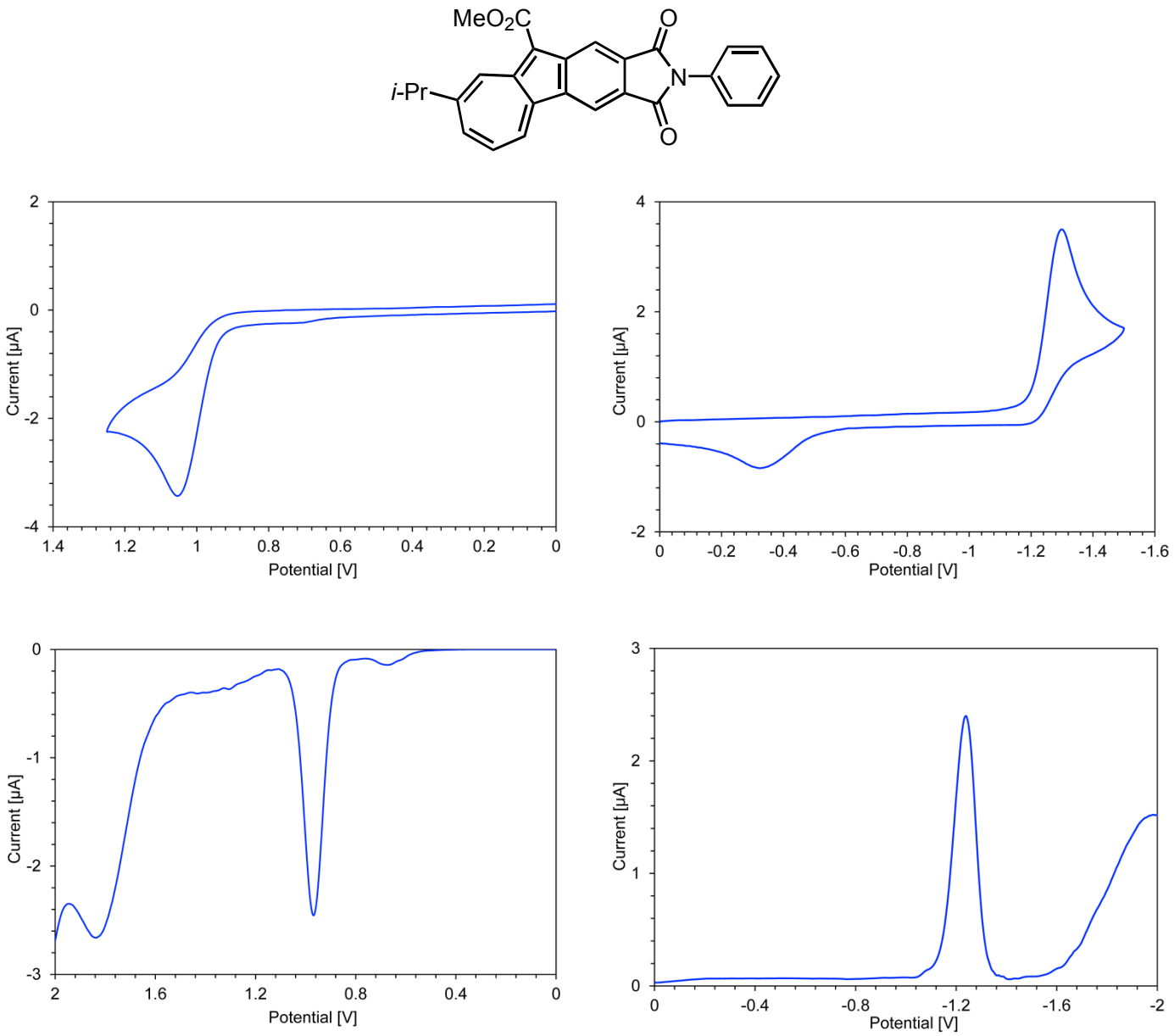


Figure S77. Cyclic voltammogram for oxidation (top, left) and reduction (top, right), and differential pulse voltammograms for oxidation (bottom, left) and reduction (bottom, right) of **4e** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as the supporting electrolyte; scan rate: CV = 100 mVs^{-1}, DPV = 20 mVs^{-1}.

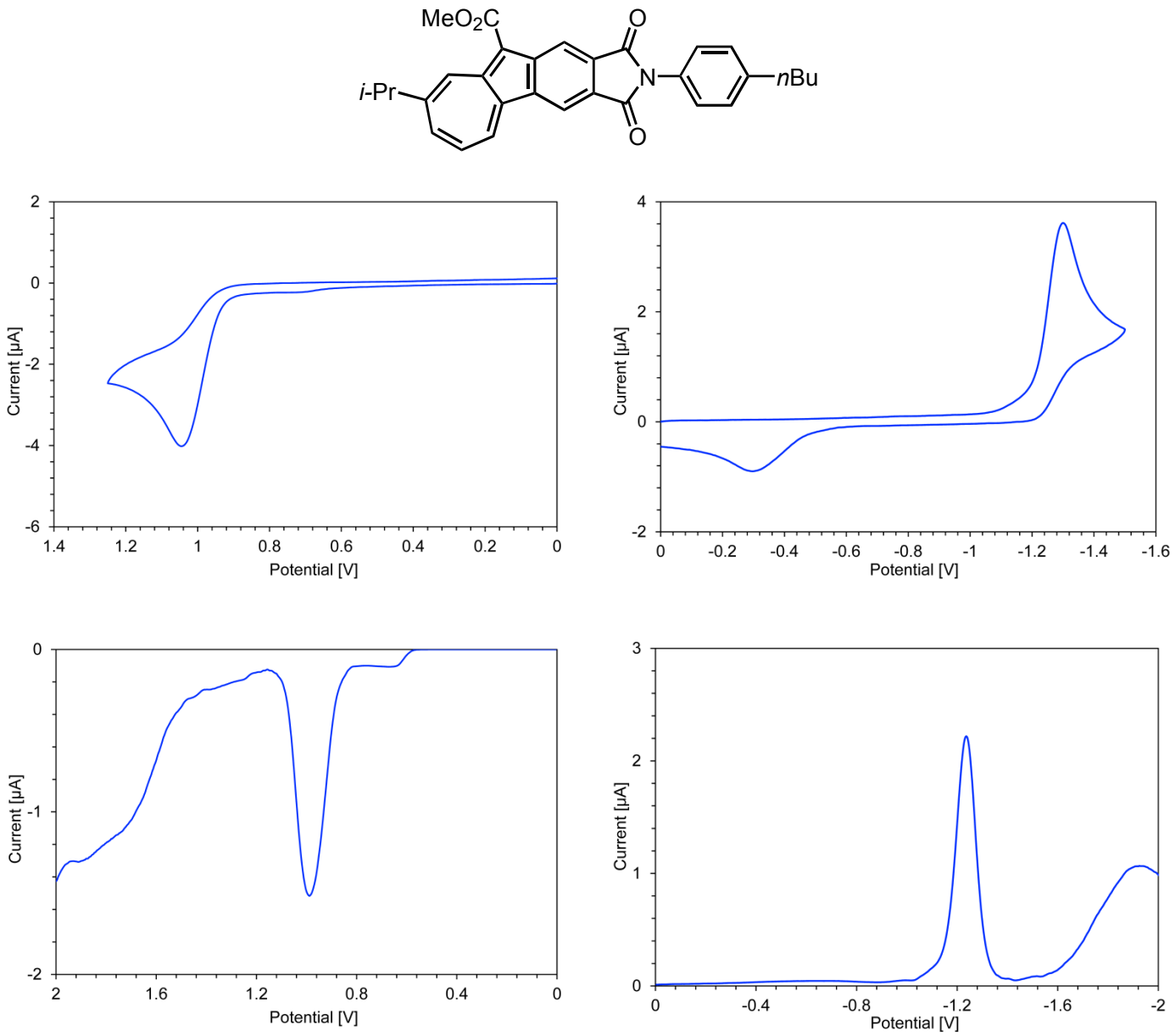


Figure S78. Cyclic voltammogram for oxidation (top, left) and reduction (top, right), and differential pulse voltammograms for oxidation (bottom, left) and reduction (bottom, right) of **4f** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as the supporting electrolyte; scan rate: CV = 100 mVs^{-1}, DPV = 20 mVs^{-1}.

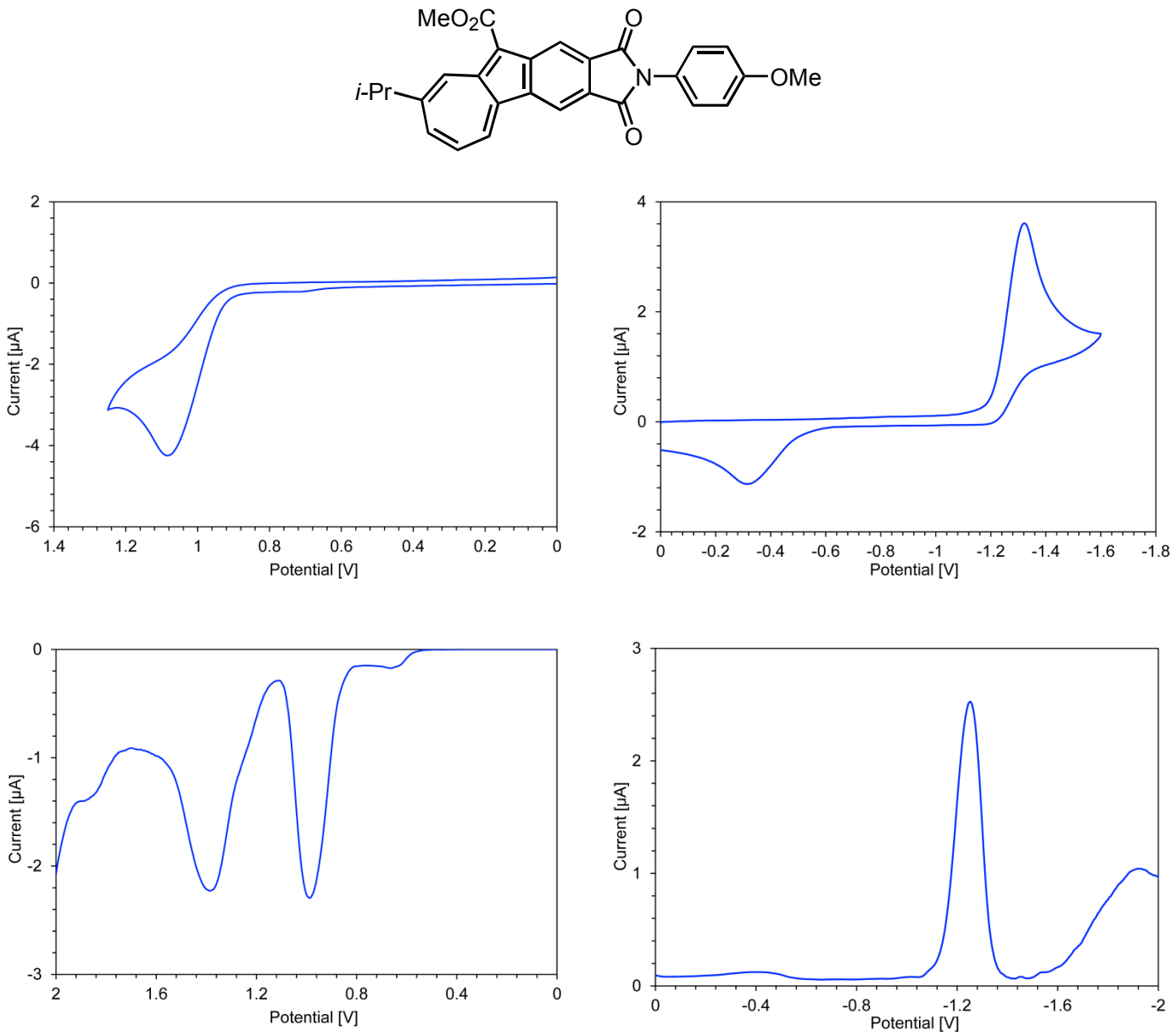


Figure S79. Cyclic voltammogram for oxidation (top, left) and reduction (top, right), and differential pulse voltammograms for oxidation (bottom, left) and reduction (bottom, right) of **4g** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as the supporting electrolyte; scan rate: CV = 100 mVs^{-1}, DPV = 20 mVs^{-1}.

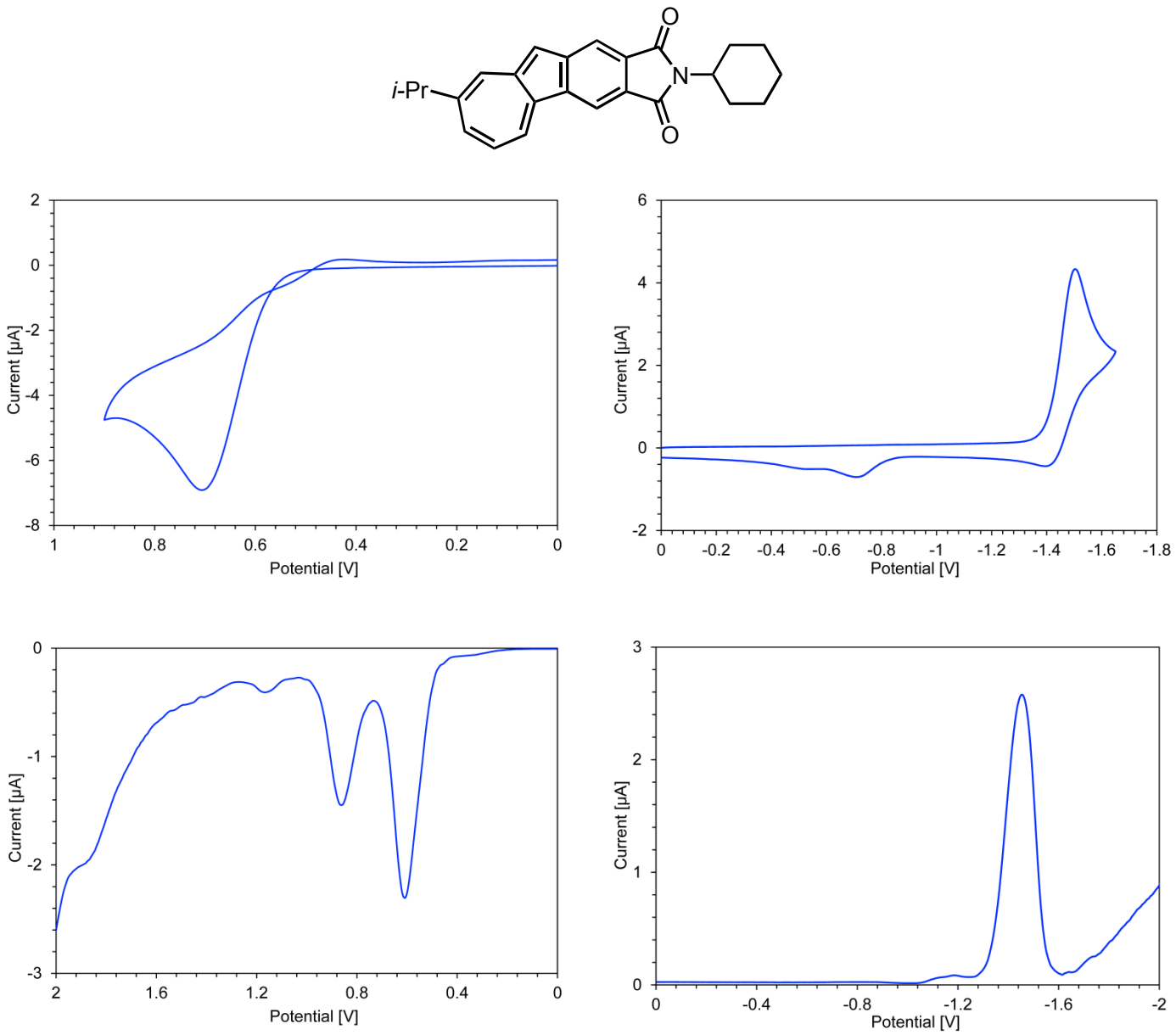
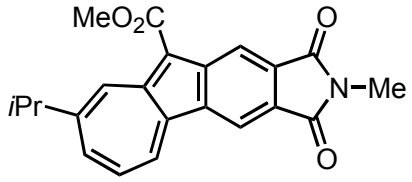


Figure S80. Cyclic voltammogram for oxidation (top, left) and reduction (top, right), and differential pulse voltammograms for oxidation (bottom, left) and reduction (bottom, right) of **12** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as the supporting electrolyte; scan rate: CV = 100 mVs^{-1}, DPV = 20 mVs^{-1}.

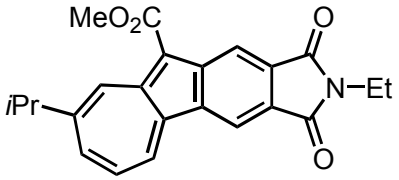
5. Experimental detail

Compound 4a



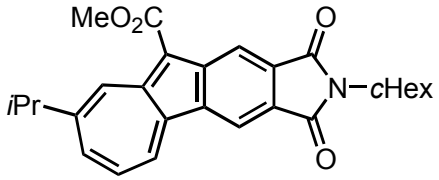
PPh_3 (205 mg, 0.782 mmol) was added to a solution of **3** (143 mg, 0.503 mmol) and *N*-methylmaleimide (70 mg, 0.630 mmol) in DMF (5 mL). The resulting mixture was stirred at 100 °C under an Ar atmosphere for 21 h. The reaction mixture was diluted with MeOH. The precipitate was collected by filtration, washed with a mixed solvent of EtOH/H_2O and hexane to give **4a** (147 mg, 81%) as green solid. m.p. 280−282 °C (decomp.); IR (AT−IR): ν_{max} = 2970 (w), 2941 (w), 2883 (w), 1761 (m), 1698 (s), 1672 (s), 1613 (w), 1474 (m), 1456 (m), 1441 (m), 1423 (s), 1383 (m), 1360 (m), 1335 (w), 1311 (w), 1269 (m), 1239 (w), 1215 (w), 1188 (m), 1157 (s), 1116 (s), 1087 (m), 1069 (w), 1019 (w), 985 (w), 971 (m), 930 (w), 897 (w), 872 (w), 846 (w), 816 (m), 783 (w), 758 (w), 741 (s), 708 (w), 668 (m), 658 (m) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 247 sh (4.40), 292 sh (4.31), 329 (4.75), 344 (4.84), 365 sh (3.99), 385 (3.86), 406 (3.99), 432 (4.12), 530 sh (2.96), 572 (3.05), 618 sh (2.98), 691 (2.54) nm; ^1H NMR (500 MHz, $CDCl_3$): δ_H = 9.85 (s, 1H, H_8), 8.90 (s, 1H, Bz), 8.81 (d, 1H, *J* = 8.9 Hz, H_4), 8.75 (s, 1H, Bz), 7.82 (d, 1H, *J* = 11.2 Hz, H_6), 7.64 (dd, 1H, *J* = 11.2, 8.9 Hz, H_5), 4.11 (s, 3H, CO_2Me), 3.29−3.23 (m, 4H, Me and *i*Pr), 1.45 (d, 6H, *J* = 7.2 Hz, *i*Pr) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 168.91, 168.83, 166.49, 153.40, 146.70, 144.55, 141.48, 141.04, 136.43, 133.68, 132.71, 132.27, 129.59, 124.72, 118.23, 116.30, 111.81, 51.48, 39.66, 33.11, 24.36, 14.15 ppm; HRMS (FAB−MS, positive): calcd for $C_{22}H_{19}NO_4^{\cdot+}$ $[M]^{\cdot+}$ 361.1309; found: 361.1312.

Compound 4b



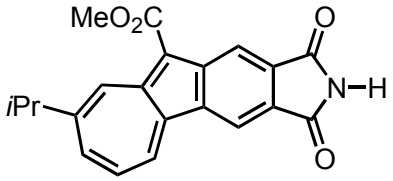
PPh_3 (199 mg, 0.759 mmol) was added to a solution of **3** (144 mg, 0.506 mmol) and *N*-ethylmaleimide (79 mg, 0.631 mmol) in DMF (5 mL). The resulting mixture was stirred at 100 °C under an Ar atmosphere for 23 h. The reaction mixture was diluted with MeOH. The precipitate was collected by filtration, washed with a mixed solvent of EtOH/H_2O and hexane to give **4b** (150 mg, 79%) as green solid. m.p. 240−242 °C (decomp.); IR (AT−IR): ν_{max} = 2953 (w), 2872 (w), 1760 (m), 1698 (s), 1684 (s), 1622 (w), 1608 (w), 1575 (w), 1480 (m), 1459 (m), 1435 (w), 1398 (m), 1376 (m), 1354 (m), 1334 (m), 1303 (w), 1255 (w), 1229 (m), 1200 (m), 1170 (m), 1121 (m), 1063 (m), 1010 (m), 921 (w), 906 (m), 889 (w), 849 (w), 810 (w), 799 (w), 780 (w), 757 (w), 745 (m), 704 (w), 679 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 247 sh (4.40), 292 sh (4.31), 329 (4.67), 345 (4.76), 365 sh (3.95), 385 (3.79), 407 (3.91), 432 (4.03), 530 sh (2.89), 573 (2.97), 618 sh (2.90), 691 (2.47) nm; ^1H NMR (500 MHz, $CDCl_3$): δ_H = 9.85 (s, 1H, H_8), 8.90 (s, 1H, Bz), 8.81 (d, 1H, *J* = 8.9 Hz, H_4), 8.74 (s, 1H, Bz), 7.81 (d, 1H, *J* = 10.9 Hz, H_6), 7.63 (dd, 1H, *J* = 10.9, 8.9 Hz, H_5), 4.11 (s, 3H, CO_2Me), 3.83 (q, 2H, *J* = 7.2 Hz, Et), 3.26 (sept, 1H, *J* = 6.9 Hz, *i*Pr), 1.45 (d, 6H, *J* = 6.9 Hz, *i*Pr), 1.34 (t, 3H, *J* = 7.2 Hz, Et) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 168.91, 168.83, 166.49, 153.40, 146.70, 144.55, 141.48, 141.04, 136.43, 133.68, 132.71, 132.27, 129.59, 124.72, 118.23, 116.30, 111.81, 51.48, 39.66, 33.11, 24.36, 14.15 ppm; HRMS (FAB−MS, positive): calcd for $C_{23}H_{21}NO_4^{\cdot+}$ $[M]^{\cdot+}$ 375.1466; found: 375.1482, calcd for $C_{23}H_{22}NO_4^{\cdot+}$ $[M + H]^{\cdot+}$ 376.1544; found: 376.1547.

Compound 4c



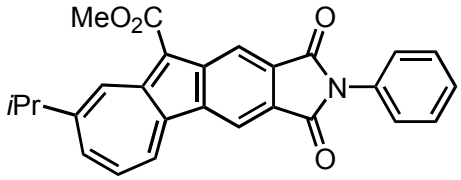
PPh_3 (201 mg, 0.766 mmol) was added to a solution of **3** (143 mg, 0.503 mmol) and *N*-(cyclohexyl)maleimide (113 mg, 0.631 mmol) in DMF (5 mL). The resulting mixture was stirred at 100 °C under an Ar atmosphere for 21 h. The reaction mixture was diluted with MeOH. The precipitate was collected by filtration, washed with a mixed solvent of EtOH/H_2O and hexane to give **4c** (179 mg, 83%) as green solid. m.p. 279−281 °C (decomp.); IR (AT−IR): ν_{max} = 2949 (w), 2931 (w), 2853 (w), 1754 (m), 1698 (s), 1608 (w), 1576 (w), 1505 (w), 1479 (m), 1457 (m), 1434 (w), 1393 (m), 1381 (m), 1362 (s), 1298 (w), 1255 (w), 1229 (m), 1213 (w), 1188 (w), 1170 (s), 1123 (s), 1087 (w), 1064 (w), 1012 (w), 960 (w), 895 (w), 874 (w), 848 (w), 806 (w), 781 (w), 757 (w), 745 (m), 706 (w), 679 (w), 655 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 243 sh (4.40), 292 sh (4.33), 330 (4.74), 346 (4.83), 384 (3.87), 407 (3.98), 432 (4.10), 530 sh (2.93), 573 (3.02), 618 sh (2.94), 691 (2.50) nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 9.85 (s, 1H, H_8), 8.90 (s, 1H, Bz), 8.83 (d, 1H, *J* = 8.6 Hz, H_4), 8.75 (s, 1H, Bz), 7.81 (d, 1H, *J* = 11.2 Hz, H_6), 7.62−7.66 (dd, 1H, *J* = 11.2, 8.6 Hz, H_8), 4.23−4.18 (m, 1H, *c*Hex), 4.11 (s, 3H, CO_2Me), 3.25 (sept, 1H, *J* = 6.9 Hz, *i*Pr), 2.34−2.26 (m, 2H, *c*Hex), 1.91−1.71 (m, 5H, *c*Hex), 1.46−1.31 (m, 9H, *i*Pr and *c*Hex) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 169.08, 166.56, 153.31, 146.69, 144.62, 141.57, 140.95, 136.37, 133.62, 132.83, 132.20, 129.58, 124.72, 118.06, 116.18, 111.86, 51.48, 51.10, 39.67, 30.04, 26.20, 25.30, 24.37 ppm; HRMS (FAB−MS, positive): calcd for $C_{27}H_{27}NO_4^{\cdot+}$ $[M]^{\cdot+}$ 429.1935; found: 429.1950, calcd for $C_{27}H_{28}NO_4^{\cdot+}$ $[M + H]^{\cdot+}$ 430.2013; found: 430.2023.

Compound 4d



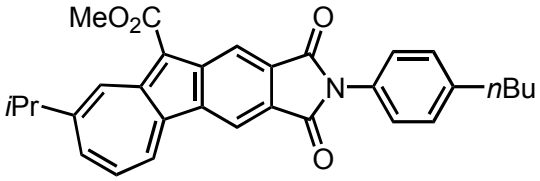
PPh_3 (402 mg, 1.53 mmol) was added to a solution of **3** (146 mg, 0.514 mmol) and maleimide (63 mg, 0.649 mmol) in DMF (5 mL). The resulting mixture was stirred at 100 °C under an Ar atmosphere for 23 h. The reaction mixture was diluted with MeOH. The precipitate was collected by filtration, washed with a mixed solvent of EtOH/H_2O and hexane to give **4d** (114 mg, 64%) as green solid. m.p. 294−295 °C (decomp.); IR (AT−IR): ν_{max} = 3188 (w), 3062 (w), 2968 (w), 2949 (w), 2872 (w), 1760 (s), 1704 (s), 1676 (s), 1637 (w), 1606 (w), 1573 (w), 1477 (m), 1454 (m), 1437 (w), 1426 (w), 1387 (m), 1357 (w), 1321 (m), 1305 (m), 1284 (w), 1266 (m), 1228 (w), 1186 (w), 1163 (m), 1133 (s), 1117 (m), 1087 (w), 1041 (w), 1019 (w), 987 (w), 923 (w), 903 (w), 872 (w), 815 (m), 783 (m), 768 (m), 759 (m), 746 (m), 709 (w), 689 (w), 661 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 247 sh (4.30), 289 sh (4.19), 327 (4.69), 342 (4.77), 361 sh (3.98), 384 (3.78), 406 (3.95), 432 (4.08), 533 sh (2.97), 570 (3.05), 616 (2.98), 689 sh (2.55) nm; ^{1}H NMR (500 MHz, DMSO-d_6): δ_H = 11.29 (s, 1H, NH), 9.61 (s, 1H, H_8), 9.25 (d, 1H, *J* = 8.9 Hz, H_4), 8.92 (s, 1H, Bz), 8.55 (s, 1H, Bz), 8.00 (d, 1H, *J* = 10.9 Hz, H_6), 7.75 (dd, 1H, *J* = 10.9, 8.9 Hz, H_5), 3.97 (s, 3H, CO_2Me), 3.21 (sept, 1H, *J* = 6.9 Hz, *i*Pr), 1.36 (d, 6H, *J* = 6.9 Hz, *i*Pr) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ_C = 169.97, 169.82, 165.95, 153.82, 146.13, 143.88, 142.42, 141.03, 136.58, 135.35, 133.21, 133.15, 131.22, 125.75, 117.78, 116.75, 110.72, 51.82, 24.55 ppm, one signal is overlapped with the solvent signals; HRMS (FAB−MS, positive): calcd for $C_{21}H_{17}NO_4^{\cdot+}$ $[M]^{\cdot+}$ 347.1153; found: 347.1155, calcd for $C_{21}H_{18}NO_4^{\cdot+}$ $[M + H]^{\cdot+}$ 348.1226; found: 348.1230.

Compound 4e



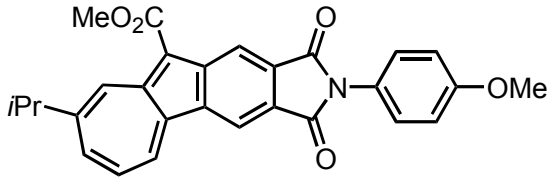
PPh_3 (202 mg, 0.770 mmol) was added to a solution of **3** (145 mg, 0.510 mmol) and *N*-phenylmaleimide (110 mg, 0.635 mmol) in DMF (5 mL). The resulting mixture was stirred at 100 °C under an Ar atmosphere for 23 h. The reaction mixture was diluted with MeOH. The precipitate was collected by filtration, washed with a mixed solvent of EtOH/H_2O and hexane to give **4e** (166 mg, 77%) as green solid. m.p. 264−266 °C; IR (AT−IR): ν_{max} = 2959 (w), 1767 (w), 1704 (s), 1672 (m), 1606 (w), 1501 (m), 1480 (w), 1453 (w), 1435 (w), 1389 (m), 1269 (w), 1185 (m), 1171 (m), 1116 (m), 1100 (w), 1066 (w), 1010 (w), 899 (w), 880 (w), 866 (w), 844 (w), 807 (w), 783 (w), 759 (m), 740 (m), 720 (m), 707 (m), 689 (m), 654 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 234 (4.43), 250 sh (4.30), 293 sh (4.27), 332 (4.63), 346 (4.69), 386 (3.82), 409 (3.90), 435 (4.02), 529 (3.00), 568 (3.02), 618 sh (2.93), 691 (2.53) nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 9.90 (s, 1H, H_8), 9.06 (s, 1H, Bz), 8.91−8.88 (m, 2H, H_4 and Bz), 7.85 (d, 1H, *J* = 10.9 Hz, H_6), 7.68 (dd, 1H, *J* = 10.9, 8.9 Hz, H_5), 7.54−7.53 (m, 4H, *o,m*-Ph), 7.44−7.40 (m, 1H, *p*-Ph), 4.14 (s, 3H, CO_2Me), 3.28 (t, 1H, *J* = 6.9 Hz, *i*Pr), 1.46 (d, 6H, *J* = 6.9 Hz, *i*Pr) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 167.98, 167.92, 166.51, 153.71, 147.03, 144.92, 141.53, 141.29, 136.58, 134.00, 133.24, 132.26, 131.73, 129.79, 129.18, 128.04, 126.78, 124.15, 118.85, 117.05, 111.98, 51.58, 39.72, 24.37 ppm; HRMS (FAB−MS, positive): calcd for $C_{27}H_{21}NO_4^{\cdot+}$ $[M]^{\cdot+}$ 423.1466; found: 423.1472, calcd for $C_{27}H_{22}NO_4^{\cdot+}$ $[M + H]^{\cdot+}$ 424.1544; found: 424.1549.

Compound 4f



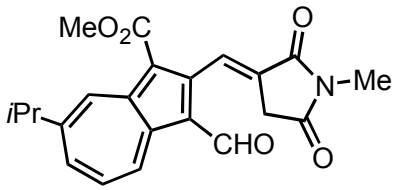
PPh_3 (202 mg, 0.770 mmol) was added to a solution of **3** (144 mg, 0.506 mmol) and *N*-(4-*n*-butylphenyl)maleimide (145 mg, 0.632 mmol) in DMF (5 mL). The resulting mixture was stirred at 100 °C under an Ar atmosphere for 24 h. The reaction mixture was diluted with MeOH. The precipitate was collected by filtration, washed with a mixed solvent of EtOH/H_2O and hexane to give **4f** as green solid (199 mg, 82%). m.p. 276−278 °C; IR (AT−IR): ν_{max} = 2957 (w), 2928 (w), 2871 (w), 1766 (w), 1708 (s), 1681 (s), 1609 (w), 1516 (w), 1479 (w), 1459 (m), 1434 (w), 1391 (m), 1377 (m), 1355 (w), 1303 (w), 1256 (w), 1235 (w), 1219 (w), 1189 (m), 1169 (s), 1123 (s), 1065 (w), 1011 (w), 964 (w), 918 (w), 907 (w), 889 (w), 829 (w), 807 (w), 787 (w), 762 (w), 745 (w), 711 (w), 695 (w), 668 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 235 (4.52), 250 sh (4.38), 293 sh (4.37), 332 (4.74), 346 (4.78), 385 (3.95), 409 (4.02), 435 (4.12), 533 sh (2.98), 571 (3.06), 615 (2.98), 695 sh (2.50) nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 9.87 (s, 1H, H_8), 9.00 (s, 1H, Bz), 8.84 (m, 2H, H_4 and Bz), 7.83 (d, 1H, *J* = 10.9 Hz, H_6), 7.65 (dd 1H, *J* = 10.9, 8.9 Hz, H_5), 7.43 (d, 2H, *J* = 8.0 Hz, *o*-Ph), 7.35 (d, 2H, *J* = 8.0 Hz, *m*-Ph), 4.12 (s, 3H, CO_2Me), 3.27 (sept, 1H, *J* = 6.9 Hz, *i*Pr), 2.68 (t, 2H, *J* = 7.7 Hz, *n*Bu), 1.65 (quint, 2H, *J* = 7.7 Hz, *n*Bu), 1.46 (d, 6H, *J* = 6.9 Hz, *i*Pr), 1.40 (sext, 2H, *J* = 7.7 Hz, *n*Bu), 0.96 (t, 3H, *J* = 7.7 Hz, *n*Bu) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 168.09, 168.04, 166.47, 153.63, 146.92, 144.79, 142.96, 141.46, 141.22, 136.50, 133.87, 133.12, 131.76, 129.70, 129.18, 126.54, 124.20, 118.72, 116.89, 111.91, 51.54, 39.69, 35.48, 33.58, 24.35, 22.47, 14.04 ppm; HRMS (FAB−MS, positive): calcd for $C_{31}H_{29}NO_4^{\cdot+}$ $[M]^{\cdot+}$ 479.2092; found: 479.2104, calcd for $C_{31}H_{30}NO_4^{\cdot+}$ $[M + H]^{\cdot+}$ 480.2175; found: 480.2183.

Compound 4g



PPh_3 (199 mg, 0.759 mmol) was added to a solution of **3** (143 mg, 0.503 mmol) and *N*-(4-methoxyphenyl)maleimide (128 mg, 0.630 mmol) in DMF (5 mL). The resulting mixture was stirred at 100 °C under an Ar atmosphere for 22 h. The reaction mixture was diluted with MeOH. The precipitate was collected by filtration, washed with a mixed solvent of EtOH/H_2O and hexane to give **4g** (185 mg, 81%) as green solid. m.p. 274−275 °C; IR (AT−IR): ν_{max} = 2978 (w), 2951 (w), 2865 (w), 2842 (w), 1762 (w), 1700 (s), 1682 (m), 1608 (w), 1588 (w), 1515 (s), 1477 (m), 1456 (m), 1433 (w), 1416 (w), 1382 (m), 1358 (m), 1300 (w), 1250 (s), 1227 (m), 1214 (w), 1182 (m), 1163 (s), 1123 (s), 1083 (w), 1027 (w), 955 (w), 935 (w), 909 (w), 894 (w), 881 (w), 865 (w), 833 (w), 815 (m), 788 (w), 757 (w), 742 (m), 709 (w), 687 (w), 667 (w), 657 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 235 (4.53), 332 (4.73), 344 (4.75), 388 sh (4.00), 408 (4.03), 435 (4.10), 533 sh (2.97), 571 (3.04), 617 (2.97), 689 sh (2.52) nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 9.88 (s, 1H, H_8), 9.02 (s, 1H, Bz), 8.86 (m, 2H, H_4 and Bz), 7.84 (d, 1H, *J* = 10.9 Hz, H_6), 7.67 (dd, 1H, *J* = 10.9, 8.9 Hz, H_5), 7.44 (d, 2H, *J* = 8.9 Hz, *o*-Ph), 7.06 (d, 2H, *J* = 8.9 Hz, *m*-Ph), 4.13 (s, 3H, CO_2Me), 3.87 (s, 3H, OMe), 3.27 (sept, 1H, *J* = 6.9 Hz, *i*Pr), 1.46 (d, 6H, *J* = 6.9 Hz, *i*Pr) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 168.24, 168.18, 166.50, 159.26, 153.65, 146.95, 144.82, 141.50, 141.24, 136.53, 133.91, 133.13, 131.79, 129.74, 128.11, 124.91, 124.21, 118.73, 116.91, 114.56, 111.93, 77.36, 77.10, 76.85, 55.63, 51.56, 39.71, 24.37 ppm; HRMS (FAB−MS, positive): calcd for $C_{28}H_{23}NO_5^{\cdot+}$ $[M]^{\cdot+}$ 453.1571; found: 453.1575, calcd for $C_{28}H_{24}NO_5^{\cdot+}$ $[M + H]^{\cdot+}$ 454.1649; found: 454.1659.

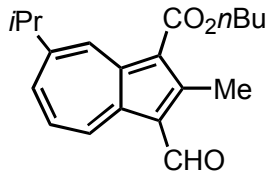
Compound 5



1-Methyl-3-(triphenylphosphoranylidene)-2,5-pyrrolidinedione (189 mg, 0.506 mmol) was added to a solution of **3** (72 mg, 0.253 mmol) in DMF (3 mL). The resulting mixture was stirred at 100 °C under an Ar atmosphere for 48 h. The reaction mixture was diluted with MeOH. The precipitate was collected by filtration, washed with a mixed solvent of EtOH/H_2O and hexane to give **5** (52 mg, 54%) as red crystals. m.p. 193−195 °C; IR (AT−IR): ν_{max} = 2964 (w), 2863 (w), 1770 (w), 1703 (s), 1685 (m), 1665 (w), 1645 (m), 1575 (w), 1521 (w), 1486 (w), 1436 (s), 1385 (m), 1328 (w), 1312 (w), 1279 (m), 1251 (w), 1227 (m), 1185 (w), 1159 (w), 1139 (w), 1120 (w), 1110 (w), 1084 (w), 1041 (w), 993 (m), 967 (w), 943 (w), 909 (w), 869 (w), 813 (w), 794 (w), 769 (w), 748 (w), 698 (w), 665 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ_H = 10.15 (s, 1H, CHO), 9.94 (d, 1H, *J* = 1.7 Hz, H_8), 9.82 (d, 1H, *J* = 10.2 Hz, H_4), 8.32 (dd, 1H, *J* = 2.3, 2.3 Hz, CH), 8.05 (d, 1H, *J* = 10.2 Hz, H_6), 7.88 (t, 1H, *J* = 10.2 Hz, H_5), 3.95 (s, 3H, CO_2Me), 3.32 (sept, 1H, *J* = 6.9 Hz, *i*Pr), 3.15 (m, 5H, Me and CH_2), 1.45 (d, 6H, *J* = 6.9 Hz, *i*Pr) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 186.63, 173.68, 169.50, 165.31, 155.36, 151.88, 144.97, 143.08, 141.90, 139.97, 138.89, 133.58, 130.98, 129.50, 120.34, 114.77, 51.86, 39.62, 33.15, 25.10, 24.68 ppm; HRMS (FAB−MS, positive): calcd for $C_{22}H_{21}NO_5^{\cdot+}$ $[M]^{\cdot+}$ 379.1415; found: 379.1415.

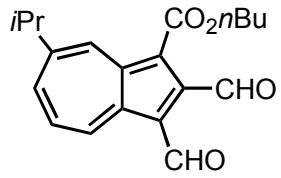
Reaction of 5 with PPh_3: PPh_3 (106 mg, 0.404 mmol) was added to a solution of **5** (118 mg, 0.311 mmol) in DMF (3 mL). The resulting mixture was stirred at 100 °C under an Ar atmosphere for 48 h. The reaction mixture was diluted with MeOH. The precipitate was collected by filtration, washed with a mixed solvent of EtOH/H_2O and hexane to give **4a** (57 mg, 51%) as green solid.

Compound 8



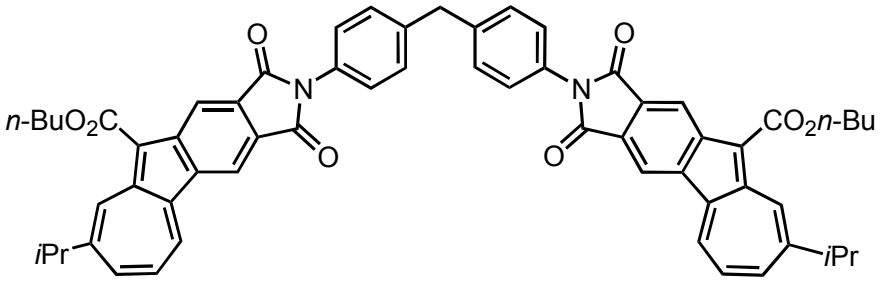
$POCl_3$ (3.88 g, 25.3 mmol) in DMF (25 mL) was added to the solution of **8** (2.40 g, 8.44 mmol) in DMF (85 mL). The resulting mixture was stirred at room temperature for 7 h under an Ar atmosphere. The reaction mixture was poured into ice-cooled water, neutralized with 10% K_2CO_3 aq., extracted with AcOEt, washed with brine and dried with Na_2SO_4. The organic layer was concentrated under reduced pressure. The crude product was purified by recrystallization from AcOEt to give the **9** (2.57 g, 97%) as red crystals. m.p. 84−85 °C; IR (AT−IR): ν_{max} = 2960 (m), 2934 (w), 2868 (w), 1682 (m), 1639 (s), 1626 (m), 1599 (w), 1574 (w), 1523 (w), 1505 (m), 1474 (m), 1436 (s), 1412 (m), 1401 (m), 1386 (m), 1371 (m), 1304 (w), 1281 (w), 1226 (s), 1210 (m), 1178 (m), 1132 (m), 1114 (m), 1092 (m), 1046 (m), 989 (m), 971 (w), 937 (w), 905 (w), 815 (m), 807 (m), 786 (m), 740 (w), 699 (w), 665 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ_H = 10.54 (s, 1H, CHO), 9.75 (s, 1H, H_8), 9.69 (d, 1H, *J* = 10.0 Hz, H_4), 7.88 (d, 1H, *J* = 10.0 Hz, H_6), 7.74 (t, 1H, *J* = 10.0 Hz, H_5), 4.43 (t, 2H, *J* = 7.4 Hz, *n*Bu), 3.26 (sept, 1H, *J* = 6.9 Hz, *i*Pr), 3.05 (s, 3H, Me), 1.85 (quint, 2H, *J* = 7.4 Hz, *n*Bu), 1.55 (sext, 1H, *J* = 7.4 Hz, *n*Bu), 1.43 (d, 6H, *J* = 6.9 Hz, *i*Pr), 1.02 (t, 3H, *J* = 7.4 Hz, *n*Bu) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 186.73, 166.16, 158.85, 154.06, 145.08, 143.51, 139.47, 137.85, 136.10, 132.74, 121.77, 116.13, 64.23, 39.62, 31.11, 24.66, 19.67, 14.52, 13.90 ppm; HRMS (MALDI-TOF, positive): calcd for $C_{20}H_{24}O_3+H^+$ $[M + H]^+$ 313.1798; found: 313.1808.

Compound 9



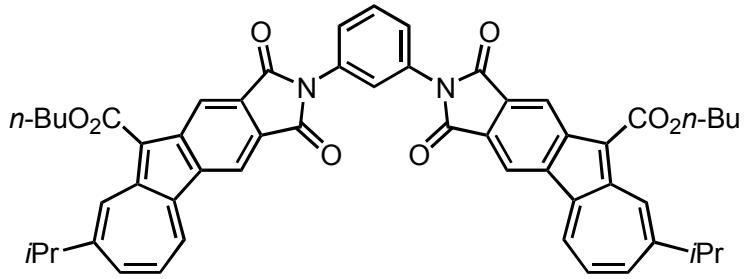
DMFDMA (1.87 g, 15.7 mmol) was added to a solution of **9** (2.45 g, 7.84 mmol) in DMF (8 mL). The resulting mixture was refluxed for 3 h. The reaction mixture was then poured into water and extracted with CH_2Cl_2. The organic layer was washed with brine, dried with Na_2SO_4, and concentrated under reduced pressure to give the crude enamine product (3.05 g) as dark-red oil. Sodium periodate (5.04 g, 23.5 mmol) was added to the crude enamine product in a mixed solvent of THF (20 mL) and H_2O (20 mL) and the resulting mixture was stirred at room temperature for 4 h. The reaction mixture was then filtered and the filtrate was extracted with CH_2Cl_2. The organic layer was dried with Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by recrystallization from CH_2Cl_2/hexane to give **10** (2.21 g, 86%) as purple crystals. m.p. 128−129 °C; IR (AT−IR): ν_{max} = 2961 (m), 2873 (w), 1749 (w), 1685 (s), 1665 (s), 1522 (w), 1496 (m), 1465 (m), 1428 (m), 1384 (m), 1340 (w), 1310 (w), 1272 (w), 1233 (m), 1210 (m), 1184 (m), 1117 (m), 1090 (m), 1066 (m), 1021 (w), 984 (m), 948 (w), 937 (w), 904 (w), 853 (w), 818 (m), 778 (w), 762 (w), 730 (w), 691 (w), 669 (m), 657 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ_H = 10.97 (s, 1H, CHO), 10.50 (s, 1H, CHO), 9.98 (m, 2H, $H_{4,8}$), 8.09 (d, 1H, *J* = 10.2 Hz, H_6), 7.86 (t, 1H, *J* = 10.2 Hz, H_5), 4.47 (t, 2H, *J* = 7.4 Hz, *n*Bu), 3.32 (sept, 1H, *J* = 6.9 Hz, *i*Pr), 1.84 (quint, 2H, *J* = 7.4 Hz, *n*Bu), 1.53 (sext, 2H, *J* = 7.4 Hz, *n*Bu), 1.46 (d, 6H, *J* = 6.9 Hz, *i*Pr), 1.01 (t, 3H, *J* = 7.4 Hz, *n*Bu) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 193.09, 188.95, 164.62, 154.59, 149.27, 143.70, 143.40, 142.27, 142.17, 141.99, 133.27, 122.02, 116.63, 65.23, 39.51, 30.99, 24.64, 19.55, 13.84 ppm; HRMS (MALDI-TOF, positive): calcd for $C_{20}H_{22}O_4+H^+$ $[M + H]^+$ 327.1591; found: 327.1559.

Compound 10



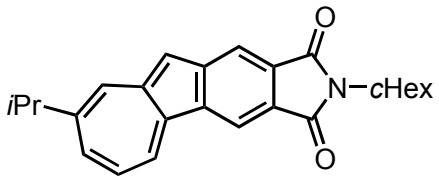
PPh_3 (183 mg, 0.70 mmol) was added to a solution of **10** (166 mg, 0.51 mmol) and 4,4-bismaleimide diphenylmethane (82 mg, 0.23 mmol) in DMF (3.0 mL). The resulting mixture was stirred at 100 °C under an Ar atmosphere for 22 h. The reaction mixture was diluted with MeOH. The precipitate was collected by filtration, washed with a mixed solvent of EtOH/H_2O and hexane. The obtained crude solid was purified by column chromatography on silica gel with CH_2Cl_2/EtOAc (20/1) to give **11** (50 mg, 23%) as green solid. m.p. 270−272 °C; IR (AT−IR): ν_{max} = 3058 (w), 2960 (w), 2933 (w), 2869 (w), 1768 (m), 1709 (s), 1683 (s), 1670 (s), 1619 (w), 1606 (m), 1514 (m), 1478 (m), 1450 (m), 1435 (m), 1366 (s), 1335 (w), 1266 (m), 1228 (w), 1195 (m), 1170 (s), 1119 (s), 1064 (m), 1022 (w), 995 (w), 968 (w), 928 (w), 912 (w), 888 (w), 813 (m), 783 (m), 759 (w), 745 (m), 720 (w), 709 (w), 697 (w), 684 (w), 671 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 234 (4.82), 252 sh (4.70), 295 sh (4.69), 333 (5.06), 346 (5.11), 381 (4.25), 409 (4.33), 436 (4.44), 531 sh (3.31), 572 (3.38), 619 (3.30), 692 sh (2.85) nm; ^{1}H NMR (500 MHz, DMSO-d_6): δ_H = 9.67 (s, 2H, H_8), 9.35 (d, 2H, *J* = 8.6 Hz, H_4), 9.14 (s, 2H, Bz), 8.91 (s, 2H, Bz), 8.01 (d, 2H, *J* = 11.2 Hz, H_6), 7.81 (dd, 2H, *J* = 11.2, 8.6 Hz, H_5), 7.45 (m, 8H, *o,m*-Ph), 4.50 (t, 4H, *J* = 7.4 Hz, *n*Bu), 4.13 (s, 2H, CH_2), 3.26 (sept, 2H, *J* = 6.9 Hz, *i*Pr), 1.91−1.85 (m, 4H, *n*Bu), 1.60−1.54 (m, 4H, *n*Bu), 1.41 (d, 12H, *J* = 6.9 Hz, *i*Pr), 1.01 (t, 6H, *J* = 7.4 Hz, *n*Bu) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ_C = 167.73, 165.66, 153.91, 146.15, 142.26, 141.35, 141.20, 136.63, 135.72, 133.64, 132.20, 131.15, 129.65, 127.64, 118.25, 117.35, 64.30, 39.24, 31.26, 24.37, 19.53, 13.88 ppm; HRMS (FAB−MS, positive): calcd for $C_{61}H_{54}N_2O_8^{\cdot+}$ $[M]^{\cdot+}$ 942.3875; found: 942.3859.

Compound 11



PPh_3 (70 mg, 0.27 mmol) was added to a solution of **10** (71 mg, 0.25 mmol) and 4,4-bismaleimide diphenylmethane (43 mg, 0.12 mmol) in DMF (5.0 mL). The resulting mixture was stirred at 100 °C under an Ar atmosphere for 22 h. The reaction mixture was diluted with MeOH. The precipitate was collected by filtration, washed with a mixed solvent of EtOH/H_2O and hexane. The obtained crude solid was purified by column chromatography on silica gel with CH_2Cl_2/EtOAc (10/1) to give **12** (22 mg, 21%) as green solid. m.p. >300 °C; IR (AT−IR): ν_{max} = 2962 (w), 2935 (w), 2871 (w), 1763 (m), 1711 (s), 1605 (m), 1575 (w), 1496 (m), 1480 (m), 1455 (m), 1434 (m), 1381 (m), 1347 (s), 1288 (m), 1267 (m), 1227 (m), 1206 (m), 1170 (s), 1116 (s), 1099 (m), 1065 (m), 1019 (w), 977 (w), 947 (w), 903 (w), 876 (w), 813 (m), 790 (m), 757 (m), 744 (m), 725 (m), 707 (m), 687 (w), 668 (w), 658 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 236 (4.84), 252 sh (4.72), 293 sh (4.68), 334 (5.09), 348 (5.16), 386 (4.29), 410 (4.38), 437 (4.50), 530 sh (3.35), 572 (3.42), 618 sh (3.34), 692 sh (2.90) nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 9.66 (s, 2H, H_8), 9.33 (d, 2H, *J* = 8.6 Hz, H_4), 9.13 (s, 2H, Bz), 8.93 (s, 2H, Bz), 8.00 (d, 2H, *J* = 10.9 Hz, H_6), 7.80 (dd, 2H, *J* = 10.9, 8.6 Hz, H_5), 7.75 (s, 1H, Ph), 7.70 (t, 1H, *J* = 7.6 Hz, Ph), 7.62 (d, 2H, *J* = 7.6 Hz, Ph), 4.51 (t, 4H, *J* = 7.3 Hz, *n*Bu), 3.26 (sept, 2H, *J* = 6.6 Hz, *i*Pr), 1.89 (quint, 4H, *J* = 7.3 Hz, *n*Bu), 1.58 (sext, 4H, *J* = 7.3 Hz, *n*Bu), 1.41 (d, 12H, *J* = 6.6 Hz, *i*Pr), 1.02 (t, 6H, *J* = 7.3 Hz, *n*Bu) ppm; Low solubility hampered the measurement of ^{13}C NMR; HRMS (FAB−MS, positive): calcd for $C_{54}H_{49}N_2O_8^{\cdot+}$ $[M + H]^{\cdot+}$ 853.3479; found: 853.3534.

Compound 12



A solution of **4c** (215 mg, 0.501 mmol) in 100% H_3PO_4 (10 mL) was stirred at 100 °C for 30 min. After the reaction mixture was cooled, it was poured into water, extracted with $CHCl_3$ and dried with Na_2SO_4. The crude product was purified by silica gel column chromatography with toluene as the eluent to afford **13** (184 mg, 99%) as green solid. m.p. 202−203 °C; IR (AT−IR): ν_{max} = 2953 (w), 2920 (w), 2851 (w), 1754 (w), 1690 (s), 1607 (w), 1590 (w), 1541 (w), 1505 (w), 1488 (w), 1467 (w), 1392 (w), 1374 (w), 1360 (m), 1315 (w), 1285 (w), 1254 (w), 1218 (w), 1187 (w), 1165 (w), 1142 (w), 1096 (m), 1080 (w), 1067 (w), 1033 (w), 1016 (w), 957 (w), 936 (w), 916 (w), 892 (w), 863 (w), 828 (w), 805 (w), 754 (w), 744 (w), 733 (w), 700 (w), 679 (w), 668 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 236 (4.35), 283 sh (4.30), 314 sh (4.61), 329 (4.73), 345 sh (4.60), 390 (3.83), 412 (3.99), 438 (4.04), 520 sh (2.81), 569 (2.99), 618 (3.06), 680 (2.96), 760 (2.55) nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 8.73 (s, 1H, Bz), 8.48 (d, 1H, *J* = 8.6 Hz, H_4), 8.21 (s, 1H, Bz), 8.04 (s, 1H, H_8), 7.41 (d, 1H, *J* = 11.5 Hz, H_6), 7.40 (s, 1H, H_1), 7.25 (dd, 1H, *J* = 11.5, 8.6 Hz, H_5), 4.21−4.16 (m, 1H, *c*Hex), 3.02 (sept, 1H, *J* = 6.9 Hz, *i*Pr), 2.33−2.25 (m, 2H, *c*Hex), 1.90−1.87 (m, 2H, *c*Hex), 1.80−1.78 (m, 2H, *c*Hex), 1.71 (d, 1H, *J* = 12.0 Hz, *c*Hex), 1.44−1.33 (m, 9H, *i*Pr and *c*Hex) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 169.35, 169.17, 146.35, 146.02, 142.45, 140.10, 138.69, 134.41, 133.62, 131.46, 131.28, 126.41, 123.60, 116.47, 115.88, 115.43, 50.97, 38.62, 30.08, 26.22, 25.32, 23.99 ppm; HRMS (FAB−MS, positive): calcd for $C_{25}H_{25}NO_2^{\cdot+}$ $[M]^{\cdot+}$ 371.1885; found: 371.1894.