Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Electronic Supplementary Information (ESI)

Synthesis of Azuleno[2,1-b]thiophenes by Cycloaddition of Azulenylalkynes with Elemental Sulfur and Their Structural, Optical and Electrochemical Properties

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General: Melting points were determined with a Yanagimoto MPS3 micromelting apparatus and are uncorrected. High-resolution mass spectra were obtained with a Bruker Daltonics APEX III instrument (dithranol as a matrix substance and/or CF_3CO_2Ag as an auxiliary agent). IR and UV/Vis spectra were measured with JASCO FT/IR-4100 and Shimadzu UV-2550 spectrophotometers. ^{1}H and ^{13}C NMR spectra were recorded with a JEOL ECA500 at 500 MHz and 125 MHz, respectively. Voltammetry measurements were carried out with a BAS 100B/W electrochemical workstation equipped with Pt working and auxiliary electrodes and a reference electrode formed from $Ag/AgNO_3$ (0.01 M) in acetonitrile containing tetrabutylammonium perchlorate (0.1 M).

1. Copies of ^{1}H NMR, ^{13}C NMR, COSY and HRMS of new compounds (Figures S1−S92).

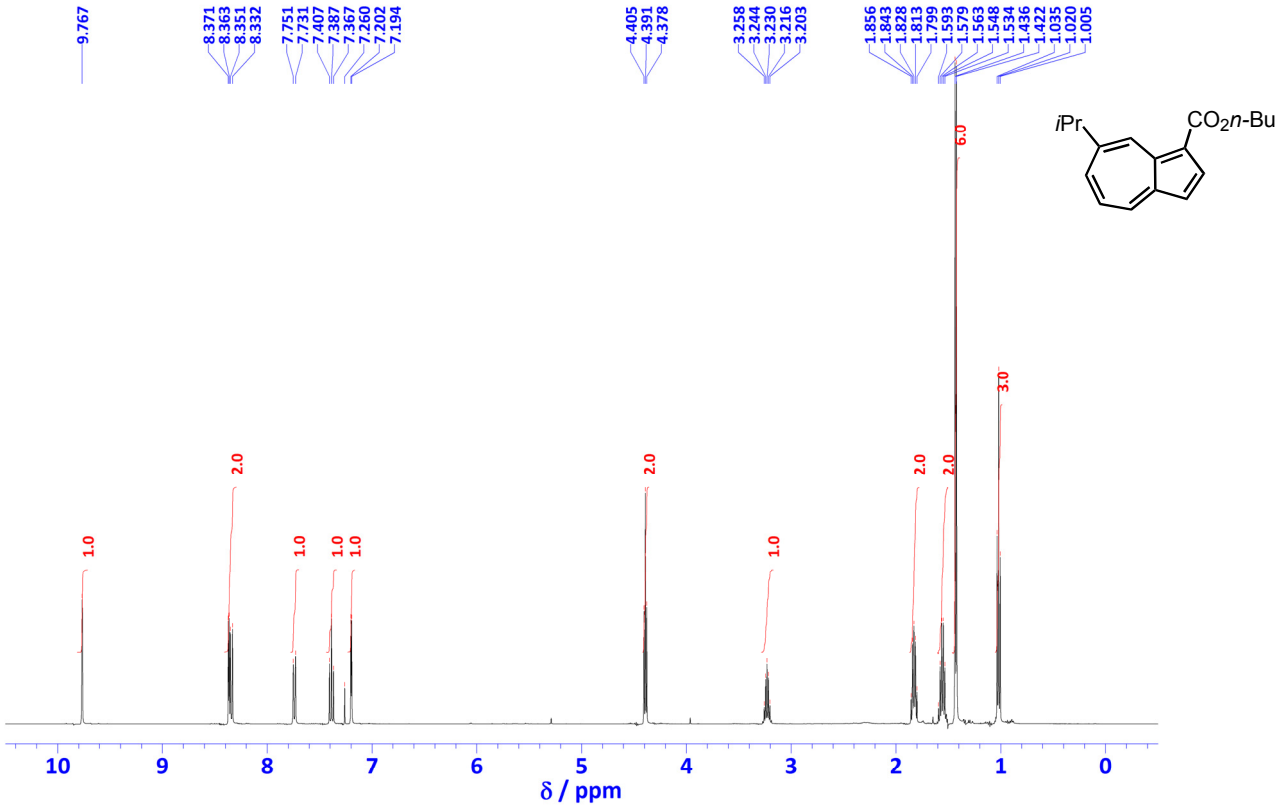


Figure S1. ^{1}H NMR spectrum of 1-butoxycarbonyl-7-isopropylazulene in $CDCl_3$ (500 MHz).

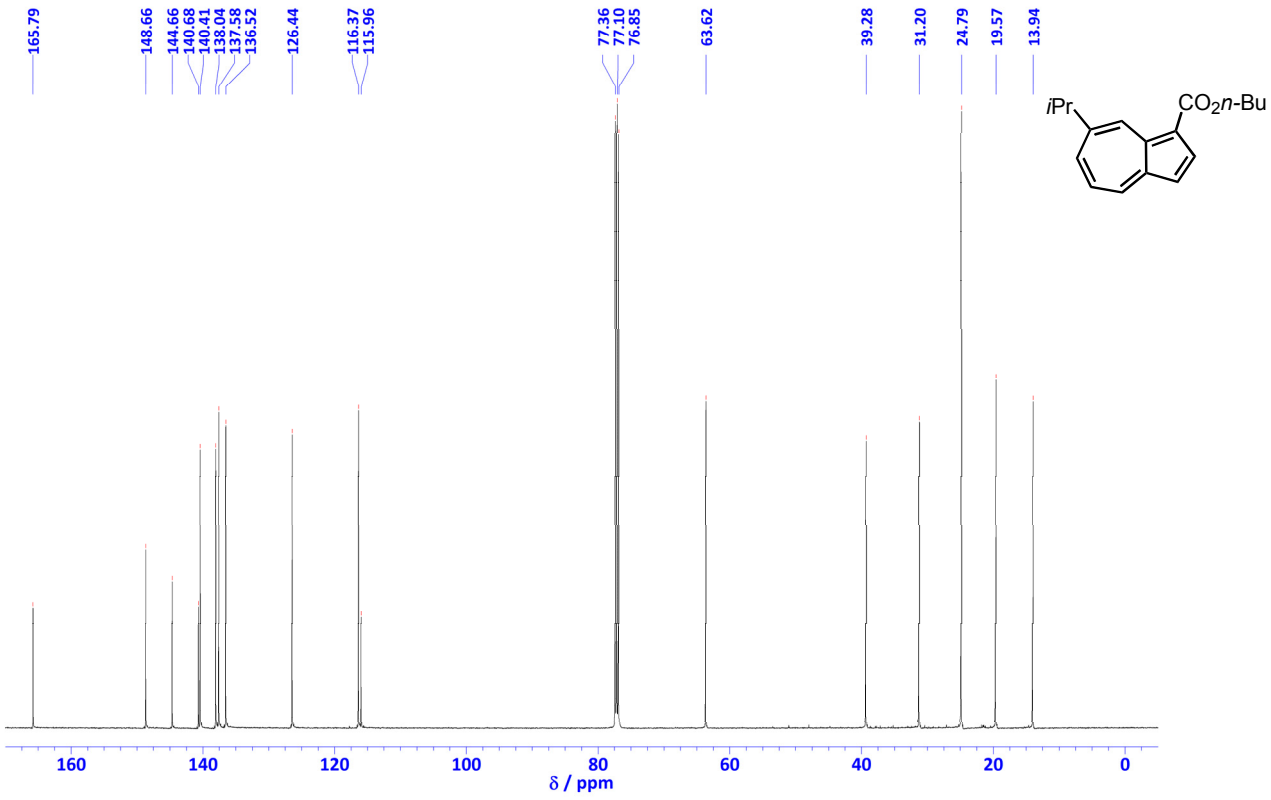


Figure S2. ^{13}C NMR spectrum of 1-butoxycarbonyl-7-isopropylazulene in $CDCl_3$ (125 MHz).

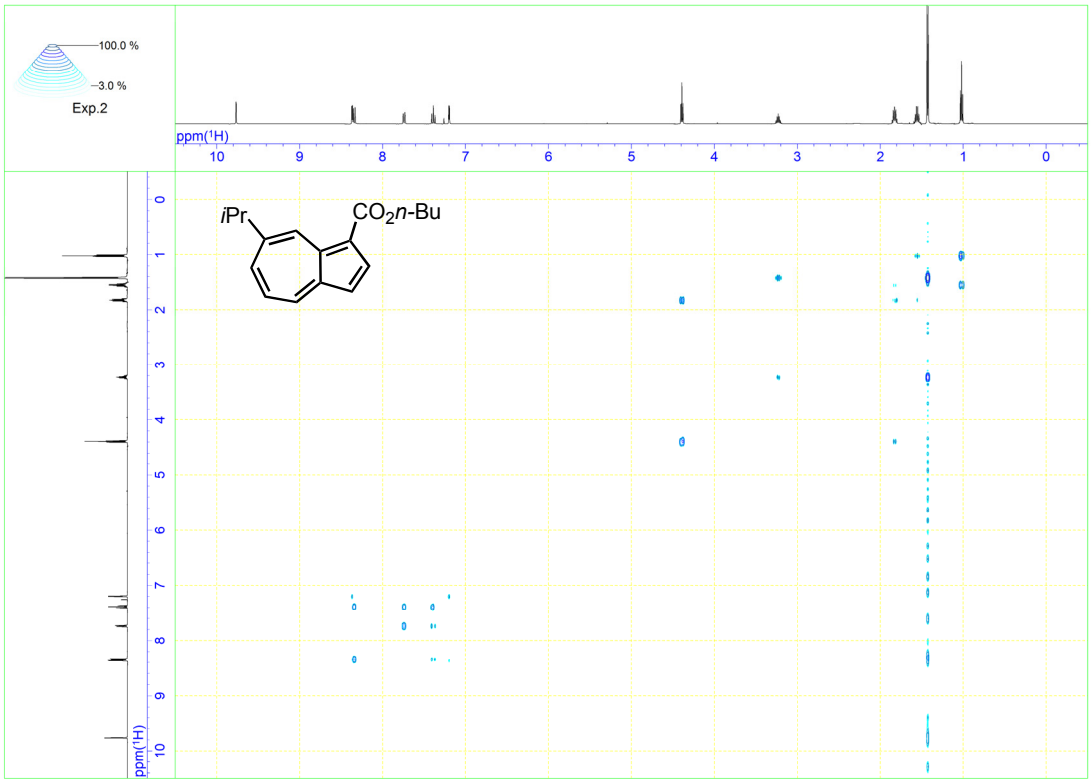


Figure S3. COSY spectrum of 1-butoxycarbonyl-7-isopropylazulene in $CDCl_3$ (500 MHz).

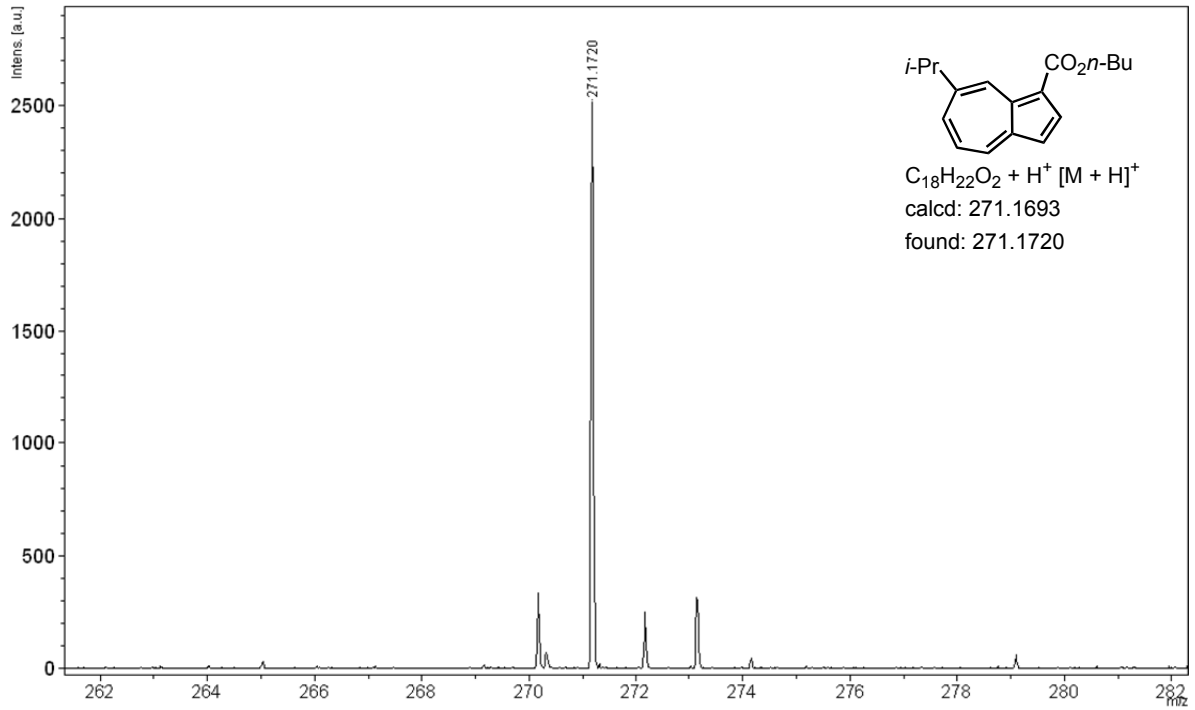


Figure S4. HRMS (MALDI-TOF, positive) of 1-butoxycarbonyl-7-isopropylazulene.

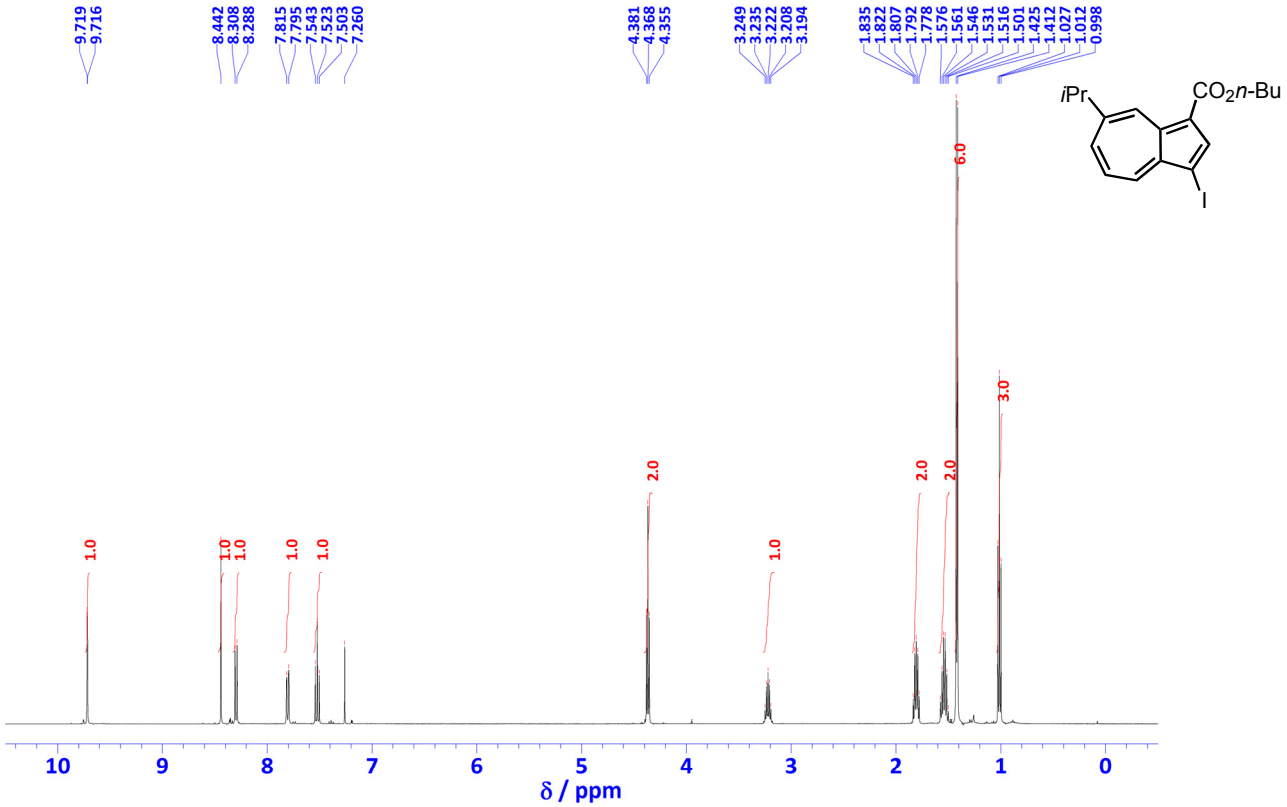


Figure S5. ^{1}H NMR spectrum of 1-butoxycarbonyl-3-iodo-7-isopropylazulene in $CDCl_3$ (500 MHz).

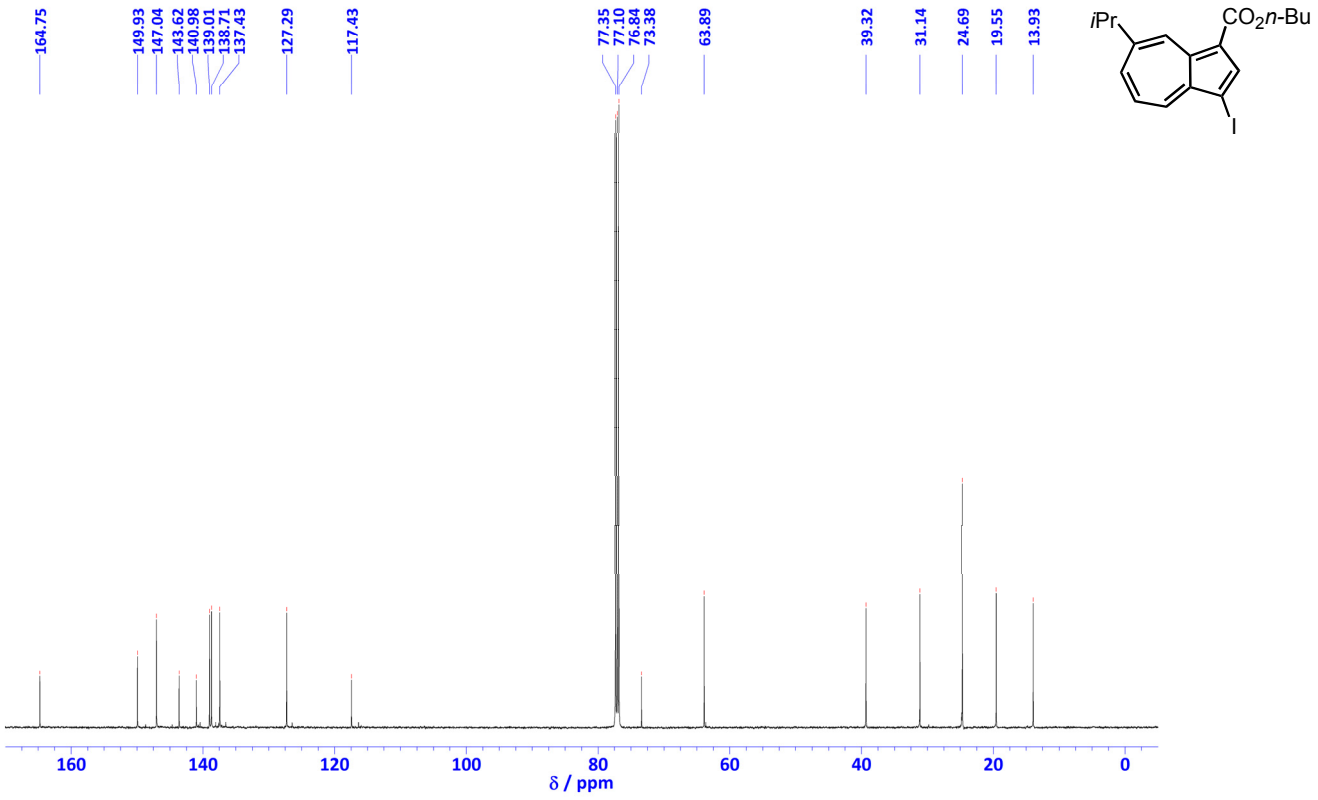


Figure S6. ^{13}C NMR spectrum of 1-butoxycarbonyl-3-iodo-7-isopropylazulene in $CDCl_3$ (125 MHz).

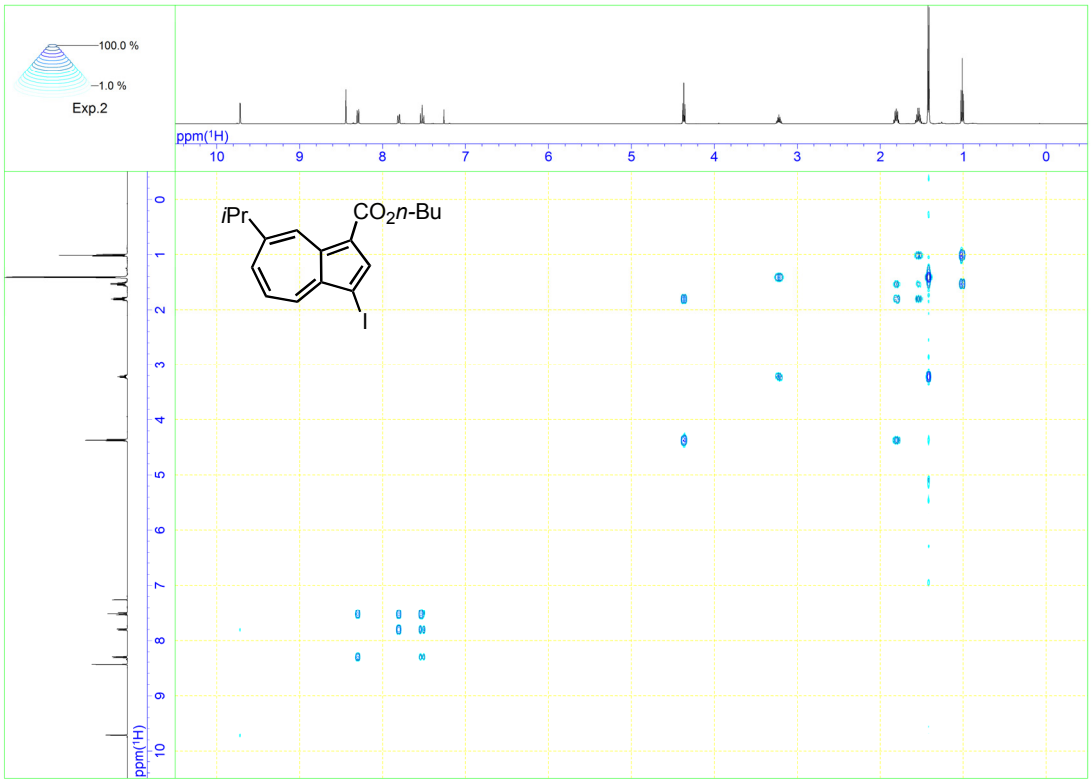


Figure S7. COSY spectrum of 1-butoxycarbonyl-3-iodo-7-isopropylazulene in $CDCl_3$ (500 MHz).

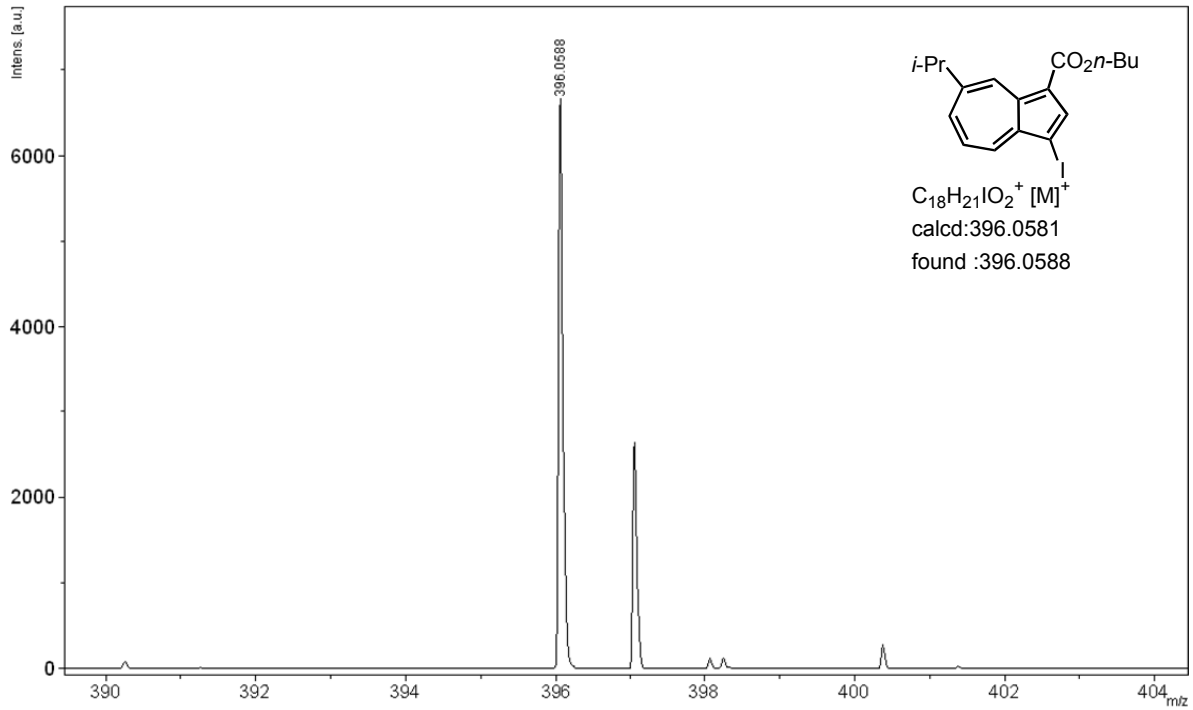


Figure S8. HRMS (MALDI-TOF, positive) of 1-butoxycarbonyl-3-iodo-7-isopropylazulene.

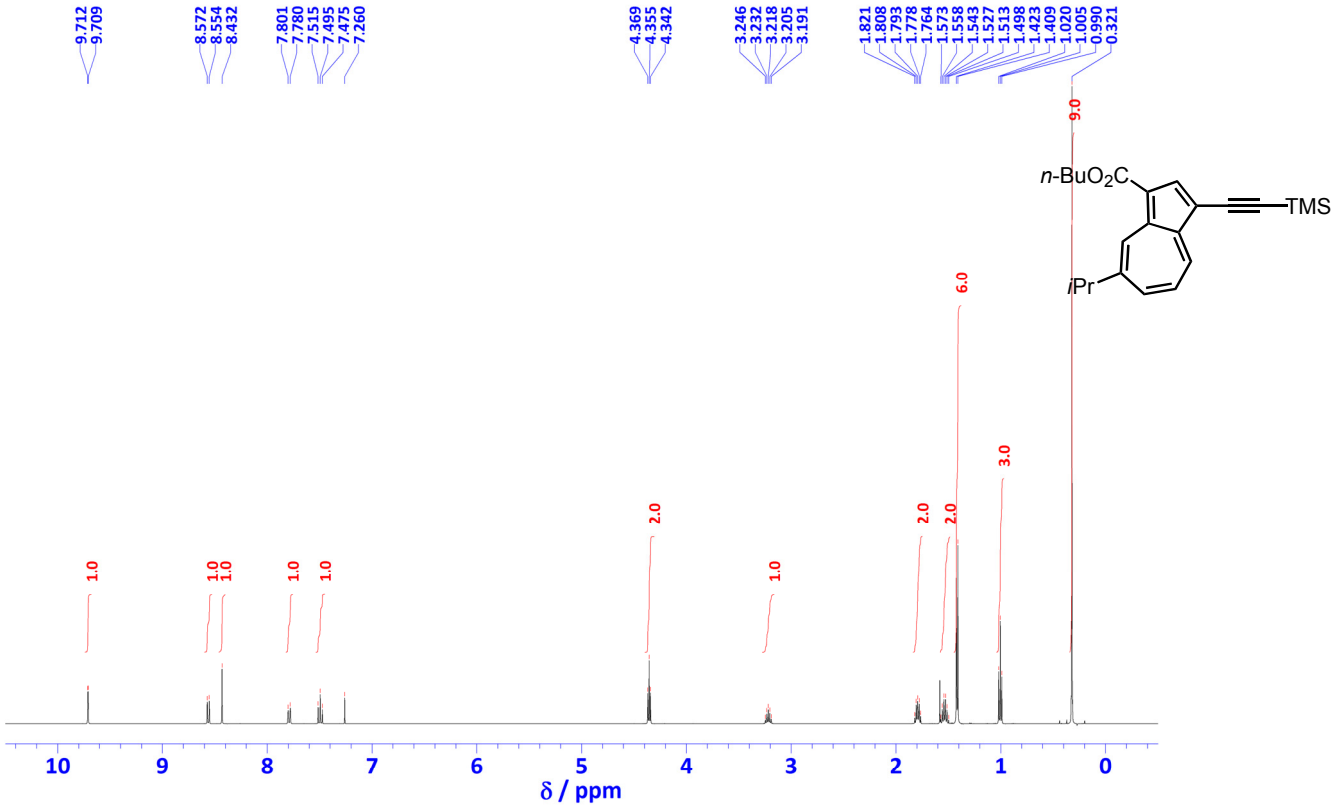


Figure S9. ^{1}H NMR spectrum of 1-butoxycarbonyl-3-trimethylsilylethynyl-7-isopropylazulene in $CDCl_3$ (500 MHz).

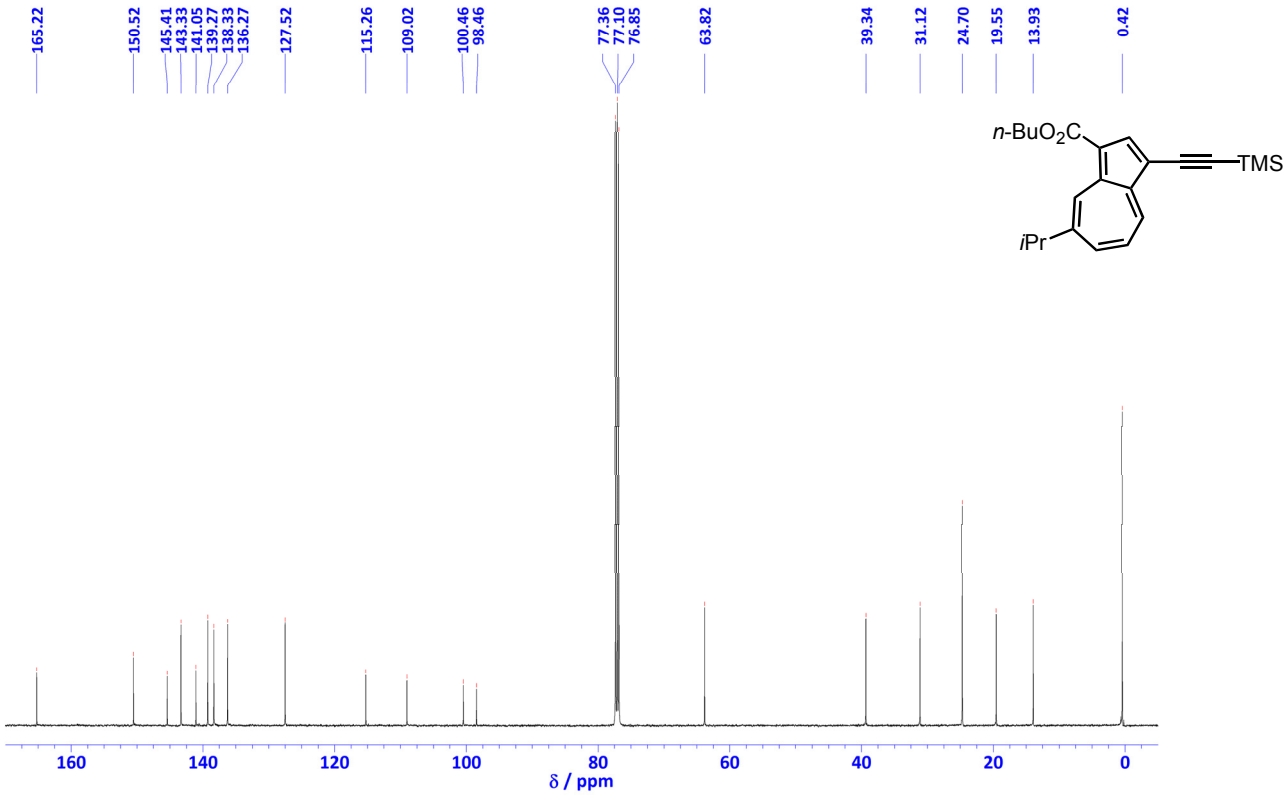


Figure S10. ^{13}C NMR spectrum of 1-butoxycarbonyl-3-trimethylsilylethynyl-7-isopropylazulene in $CDCl_3$ (125 MHz).

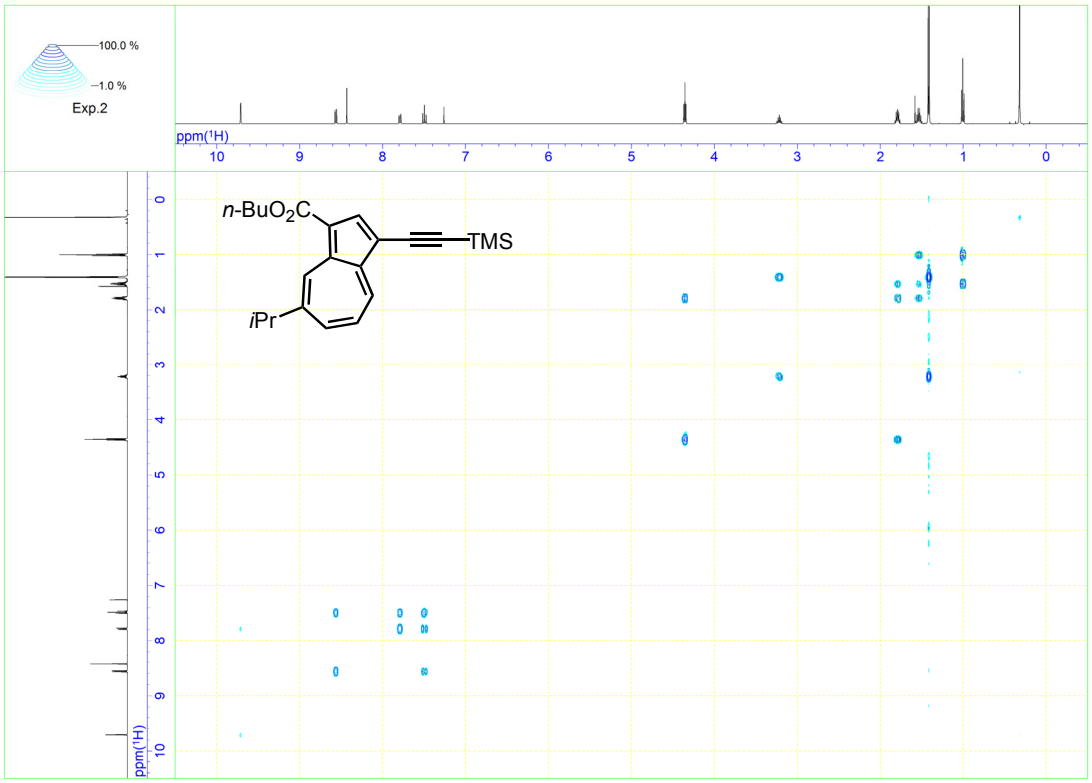


Figure S11. COSY spectrum of 1-butoxycarbonyl-3-trimethylsilylethynyl-7-isopropylazulene in $CDCl_3$ (500 MHz).

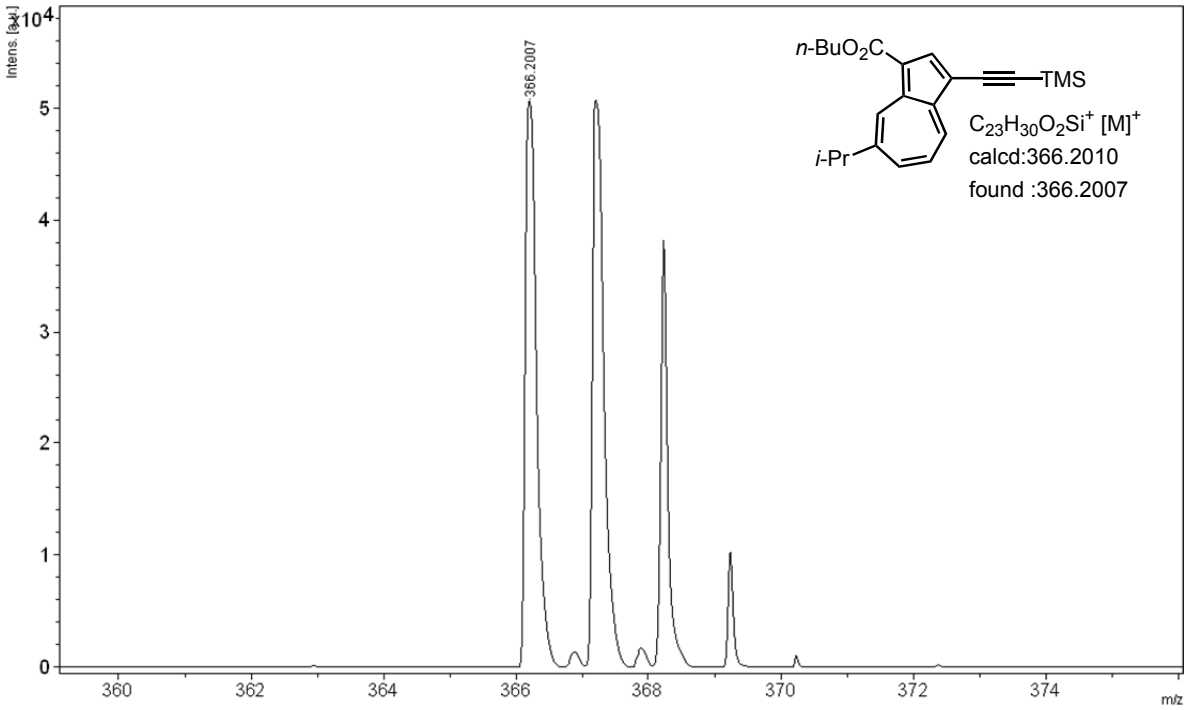


Figure S12. HRMS (MALDI-TOF, positive) of 1-butoxycarbonyl-3-trimethylsilylethynyl-7-isopropylazulene.

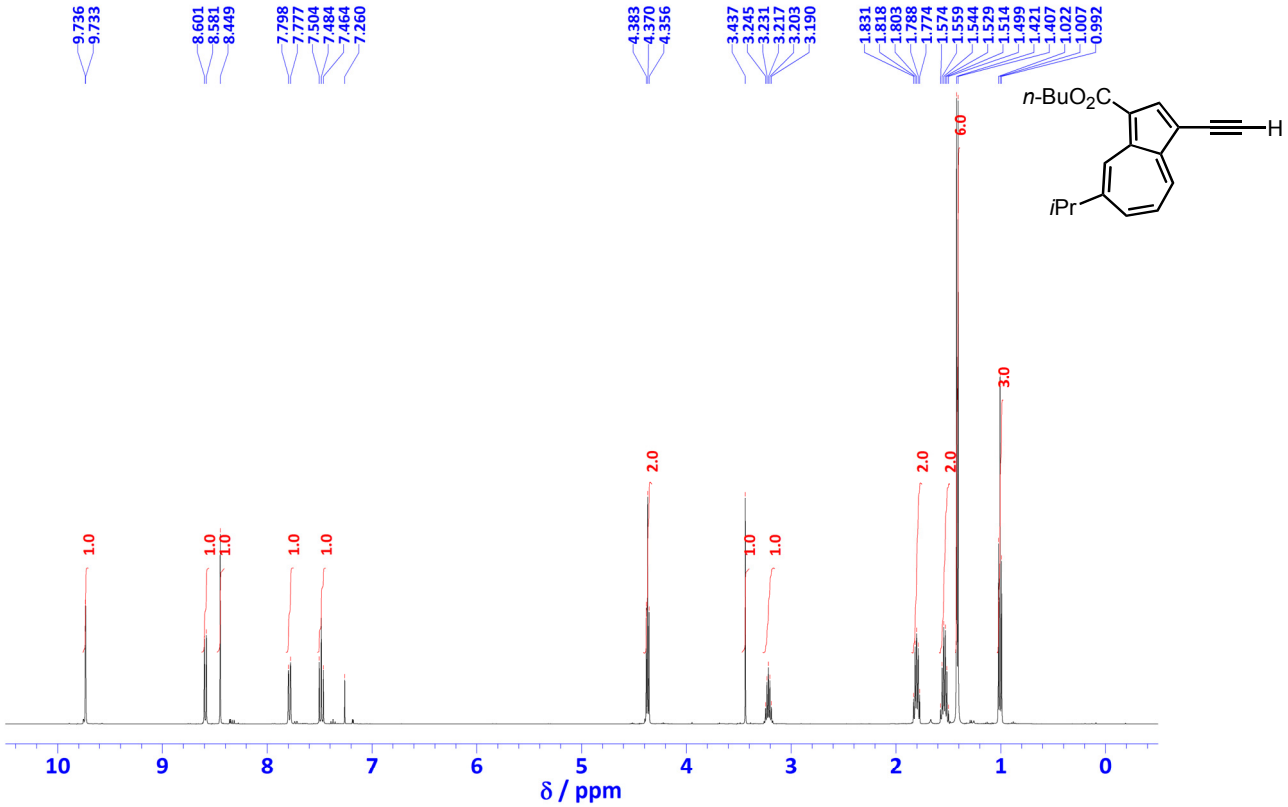


Figure S13. ^{1}H NMR spectrum of 1-butoxycarbonyl-3-ethynyl-7-isopropylazulene in $CDCl_3$ (500 MHz).

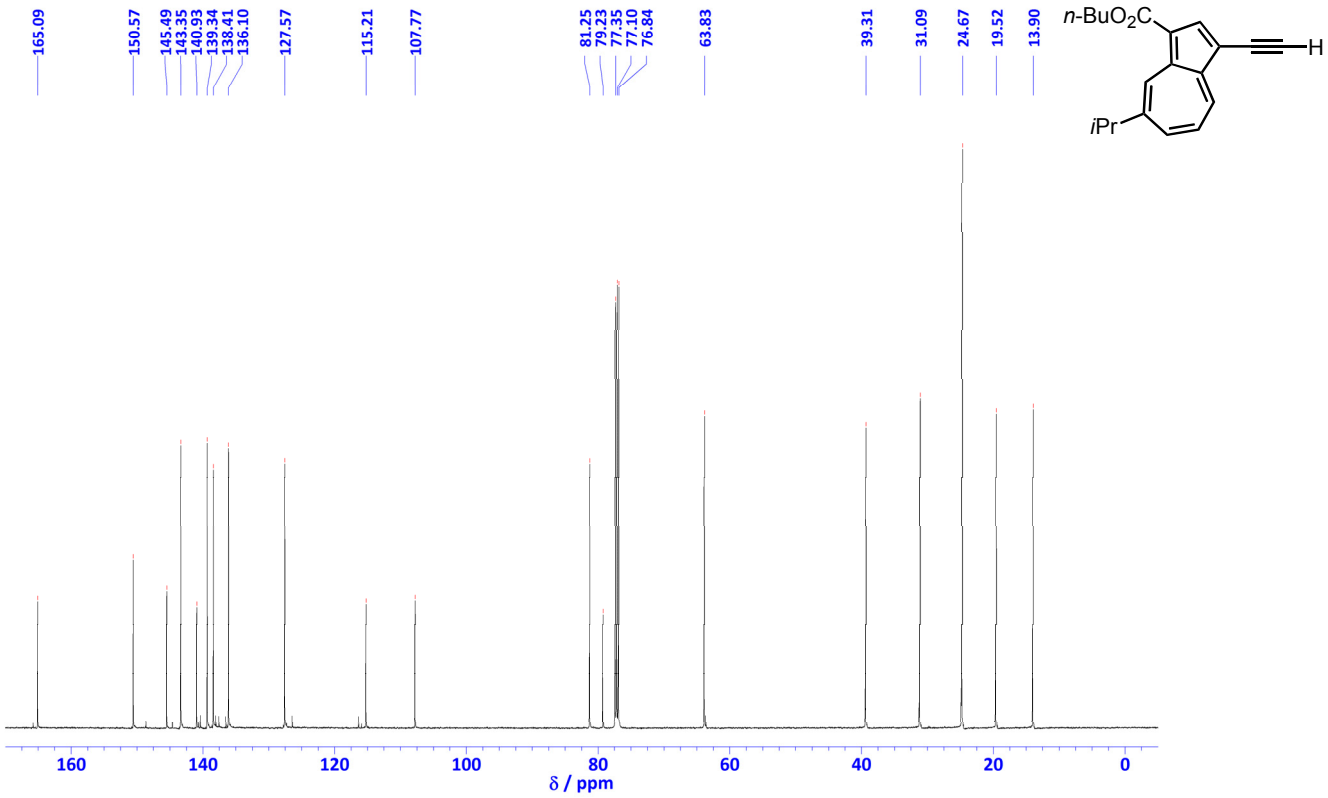


Figure S14. ^{13}C NMR spectrum of 1-butoxycarbonyl-3-ethynyl-7-isopropylazulene in $CDCl_3$ (125 MHz).

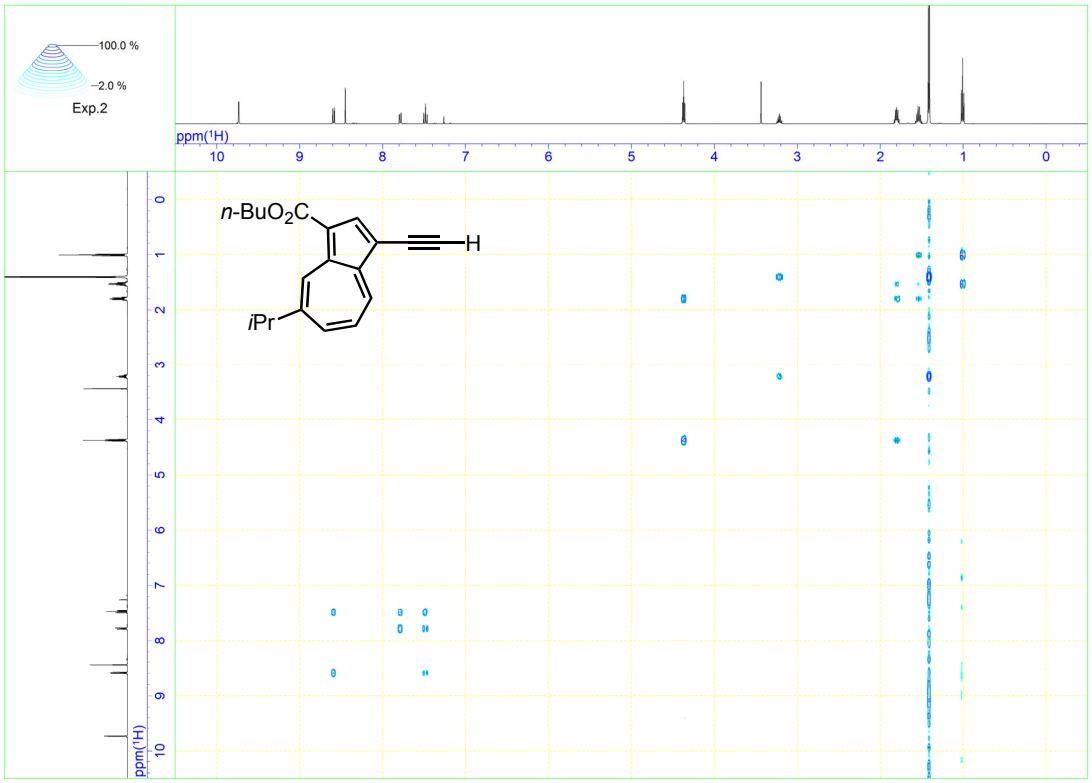


Figure S15. COSY spectrum of 1-butoxycarbonyl-3-ethynyl-7-isopropylazulene in $CDCl_3$ (500 MHz).

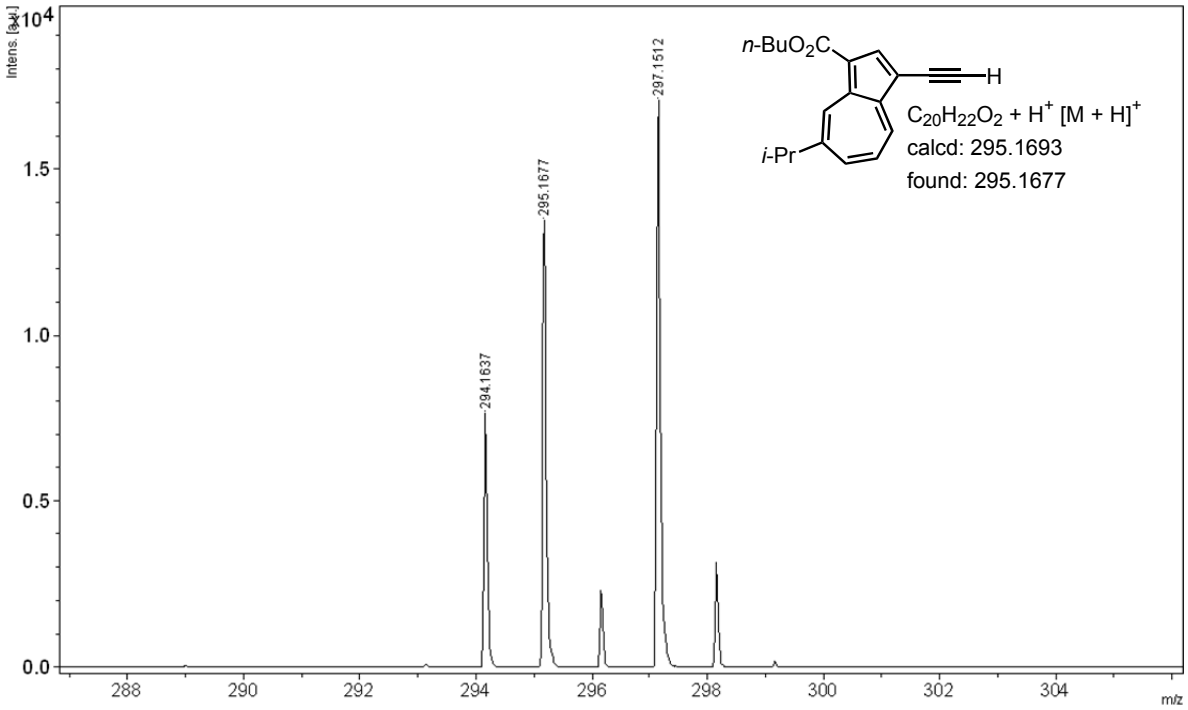


Figure S16. HRMS (MALDI-TOF, positive) of 1-butoxycarbonyl-3-ethynyl-7-isopropylazulene.

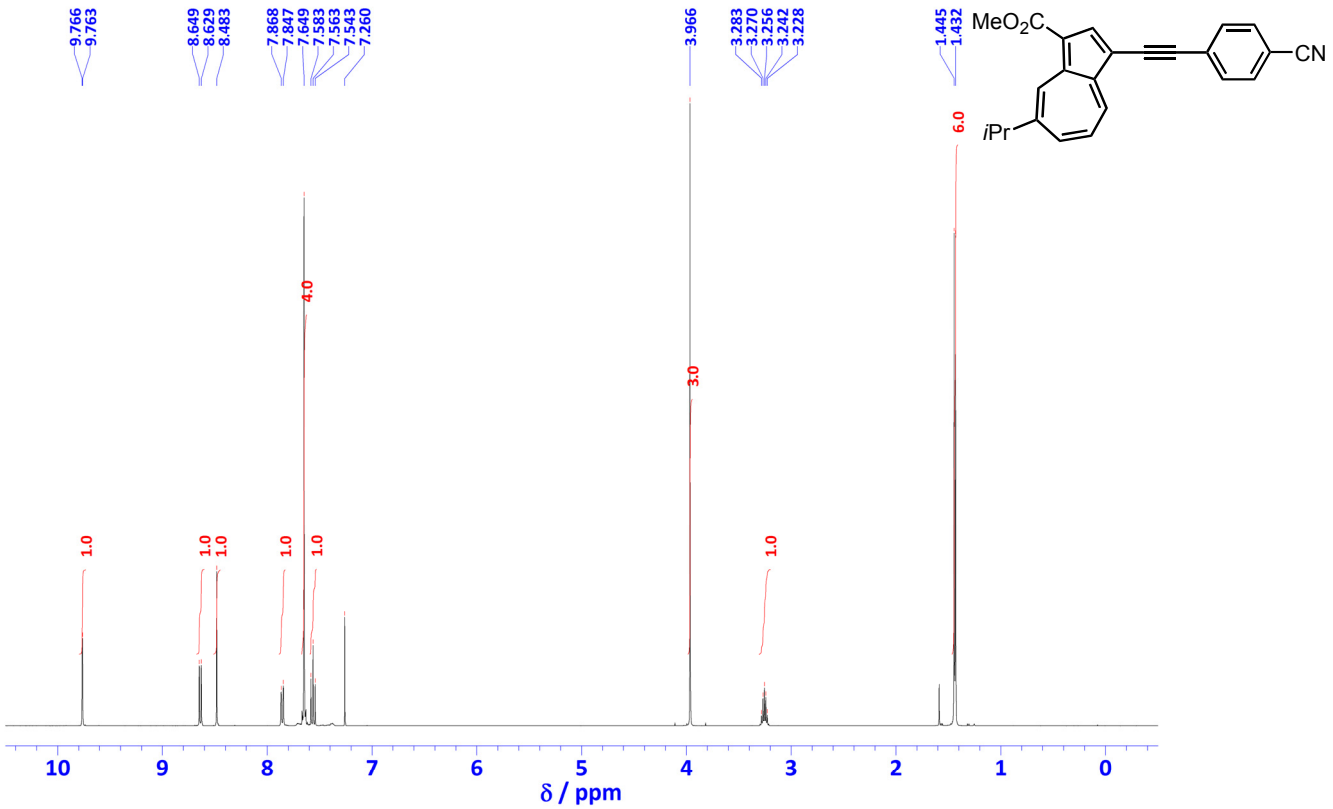


Figure S17. ^{1}H NMR spectrum of **3** in $CDCl_3$ (500 MHz).

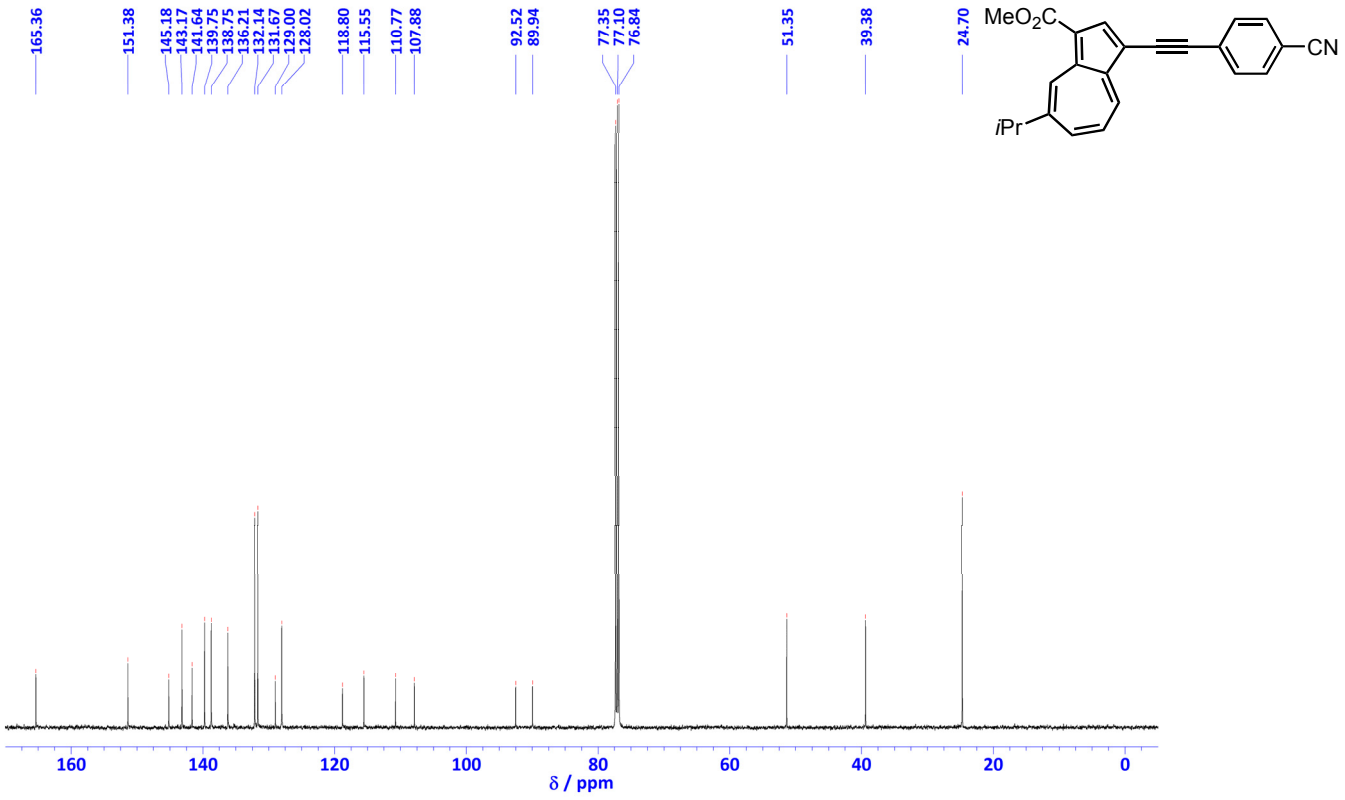


Figure S18. ^{13}C NMR spectrum of **3** in $CDCl_3$ (125 MHz).

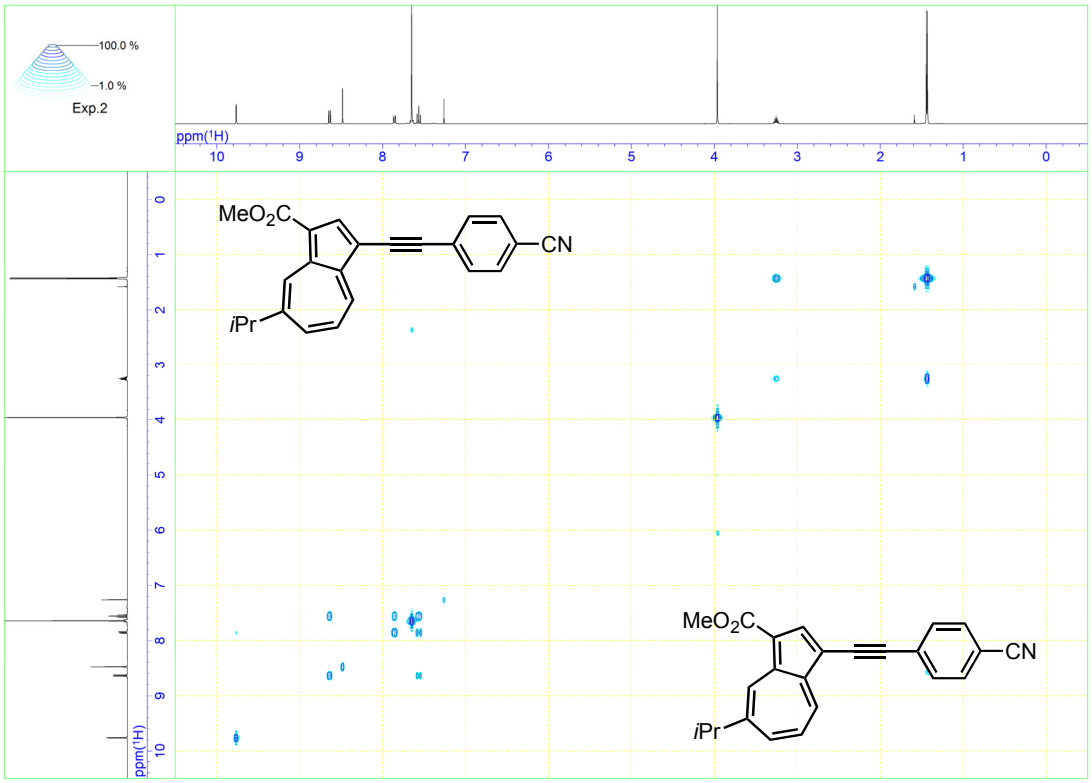


Figure S19. COSY spectrum of **3** in $CDCl_3$ (500 MHz).

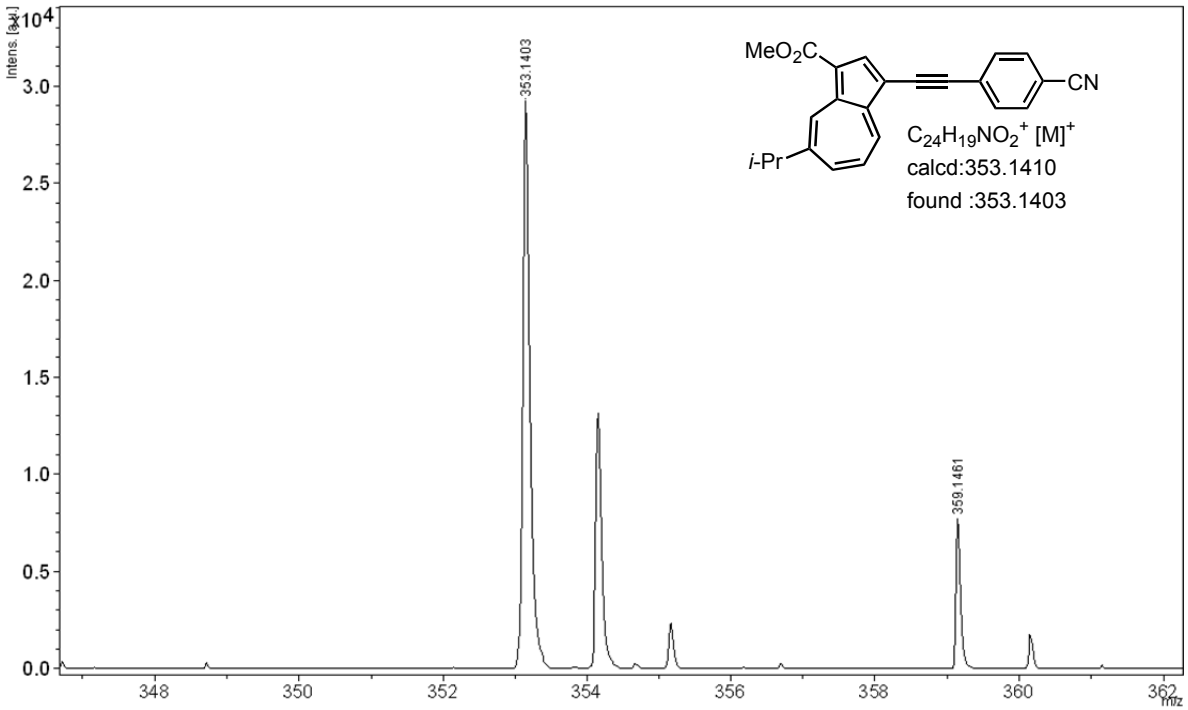


Figure S20. HRMS (MALDI-TOF, positive) of **3**.

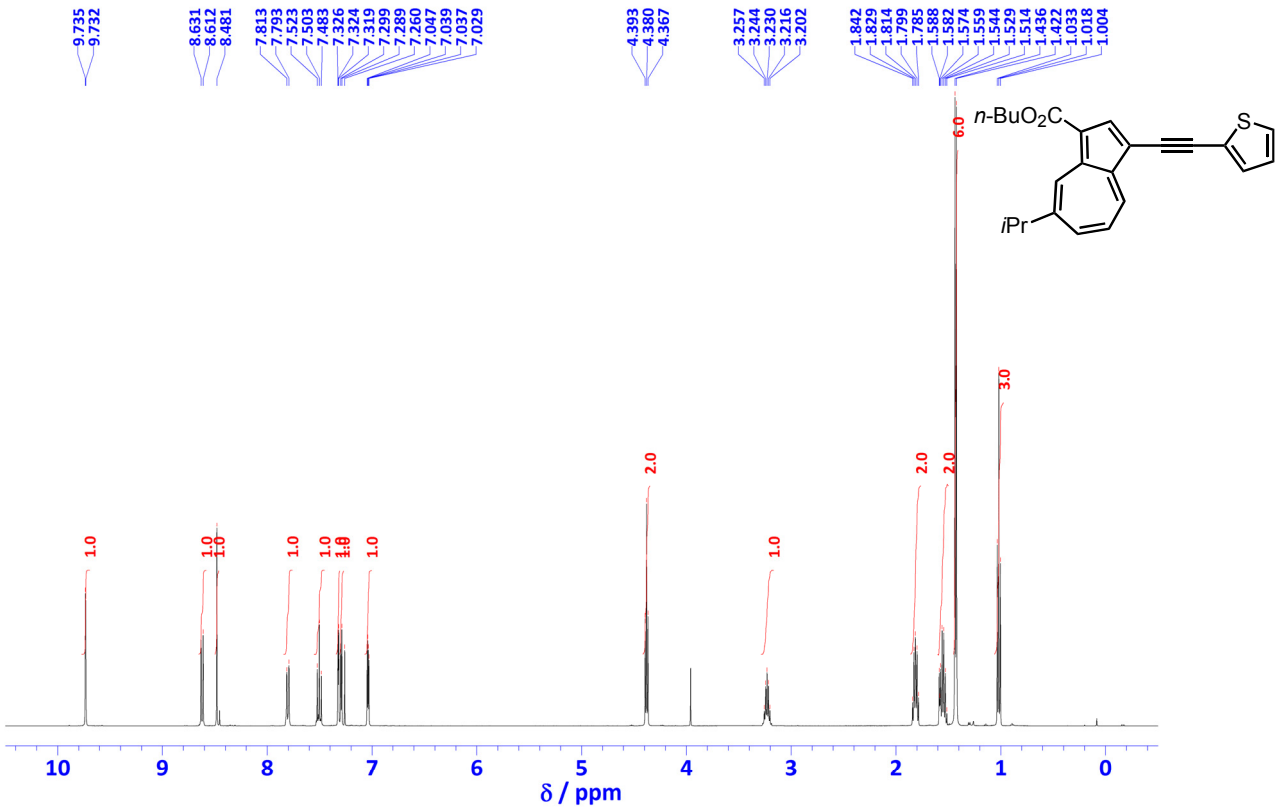


Figure S21. ^{1}H NMR spectrum of **7b** in $CDCl_3$ (500 MHz).

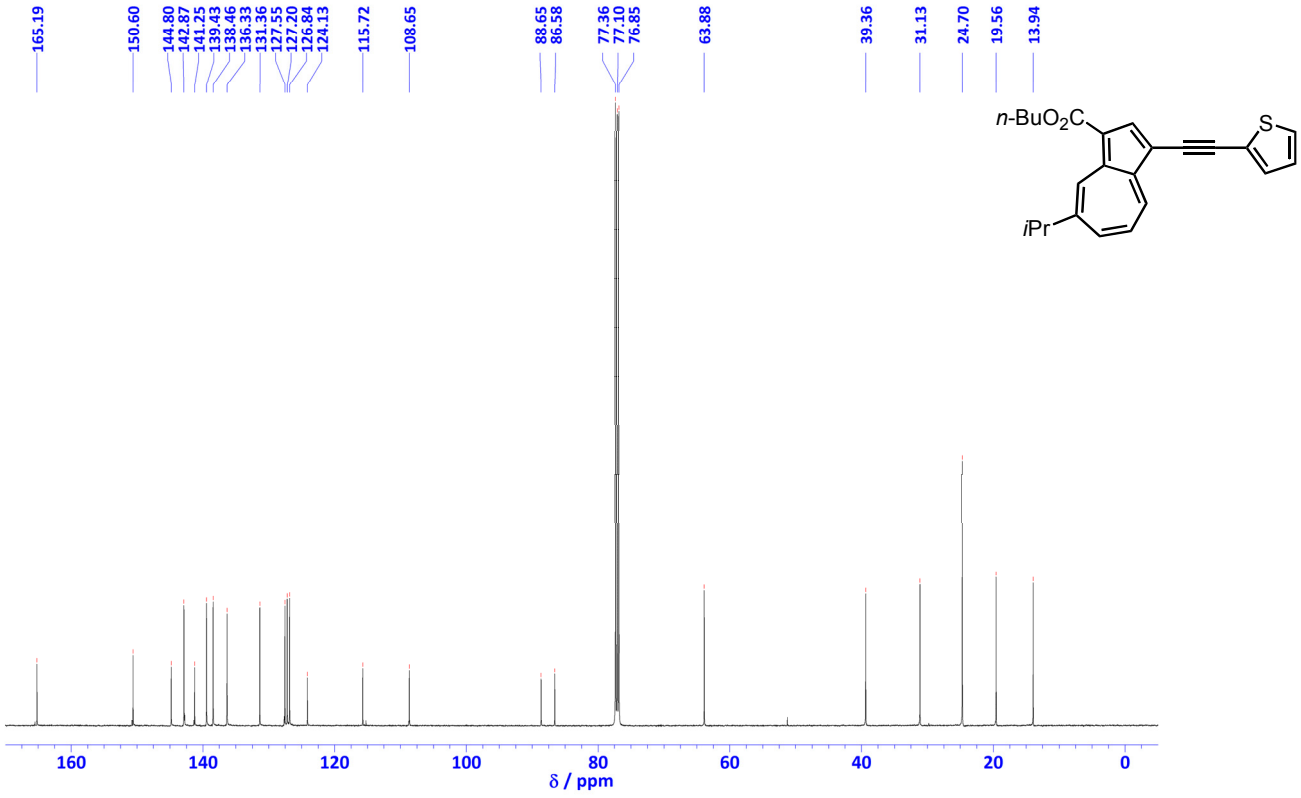


Figure S22. ^{13}C NMR spectrum of **7b** in $CDCl_3$ (125 MHz).

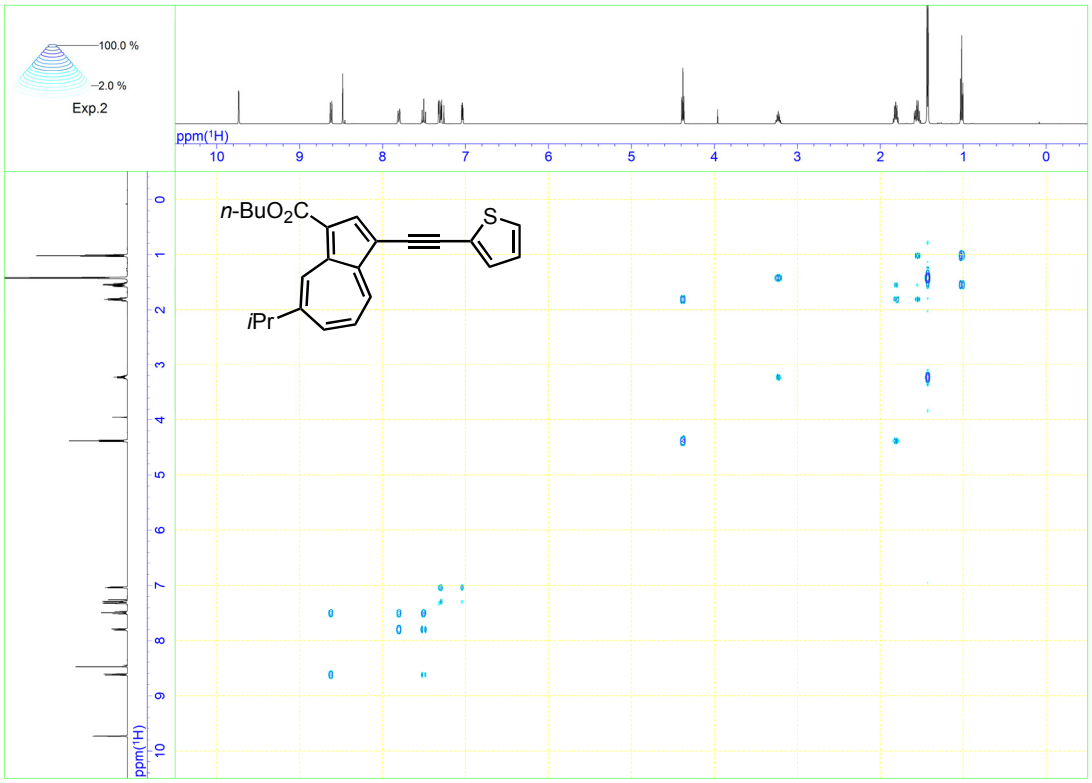


Figure S23. COSY spectrum of **7b** in $CDCl_3$ (500 MHz).

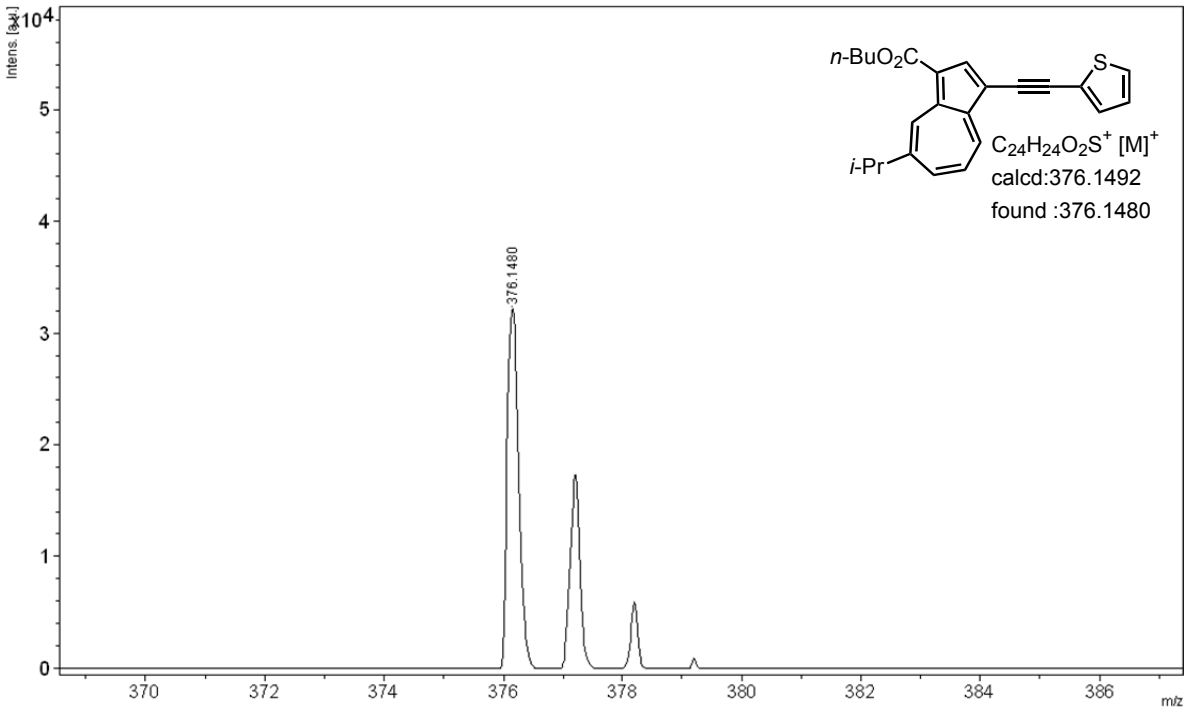


Figure S24. HRMS (MALDI-TOF, positive) of **7b**.

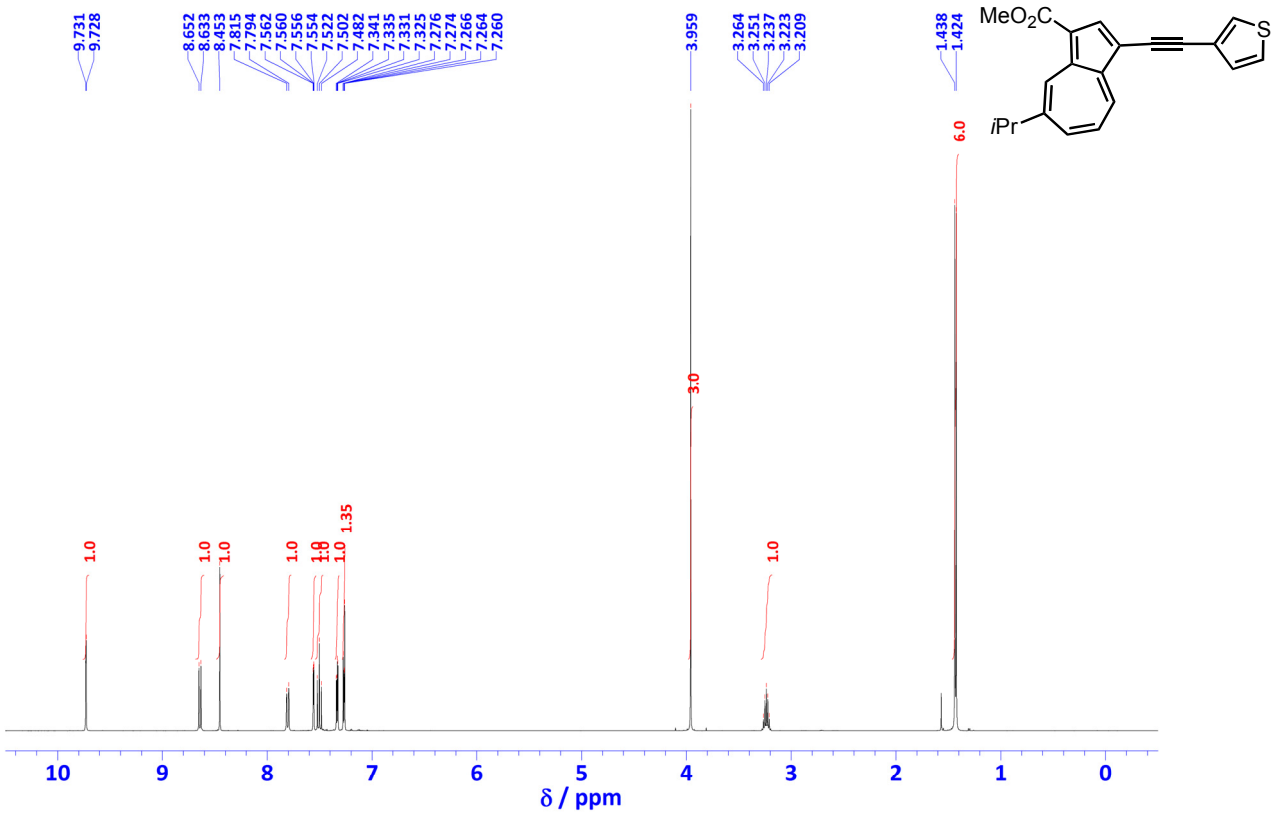


Figure S25. ^{1}H NMR spectrum of **8a** in $CDCl_3$ (500 MHz).

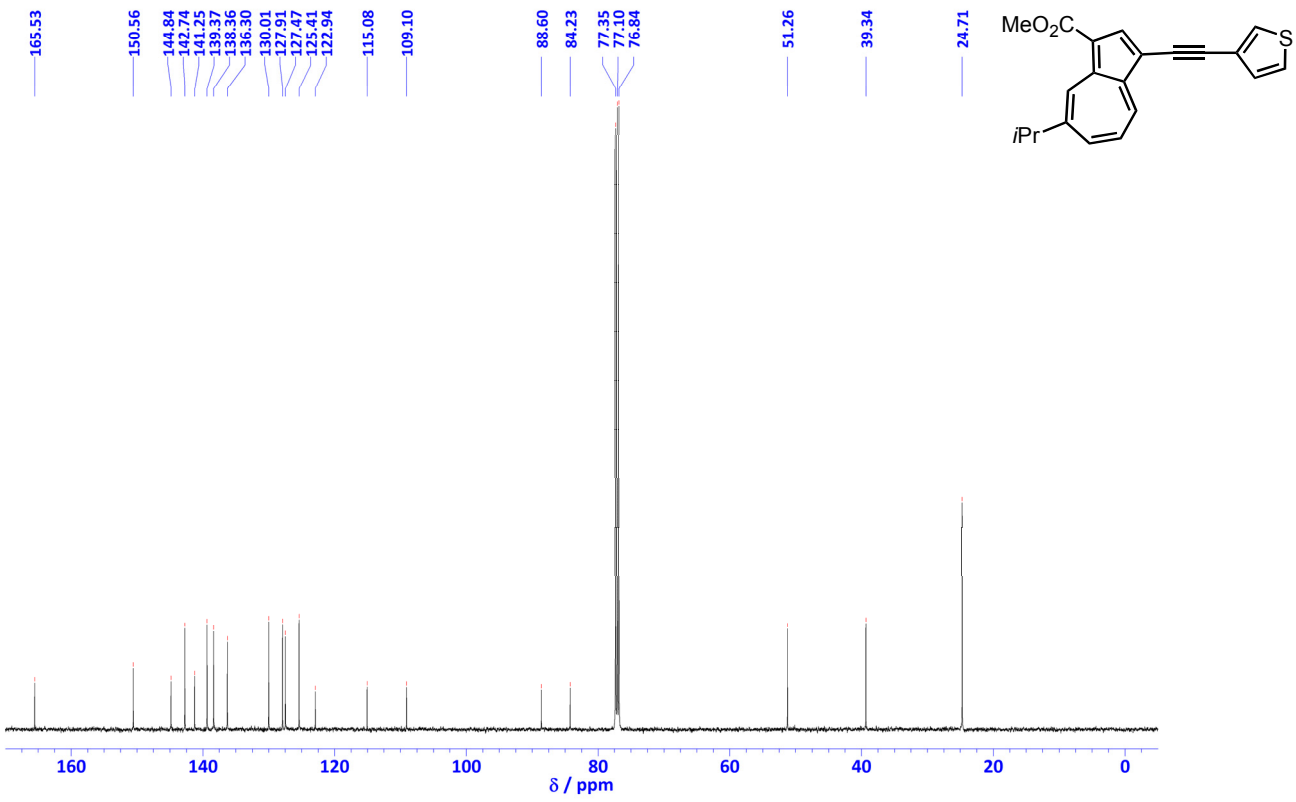


Figure S26. ^{13}C NMR spectrum of **8a** in $CDCl_3$ (125 MHz).

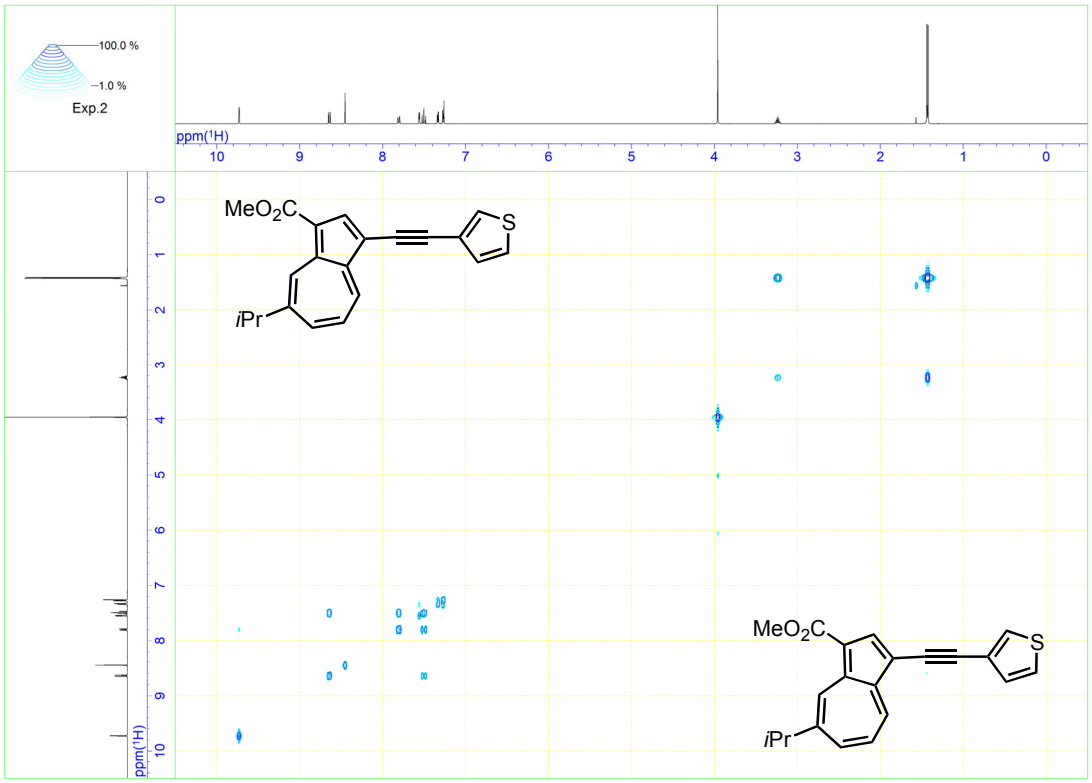


Figure S27. COSY spectrum of **8a** in $CDCl_3$ (500 MHz).

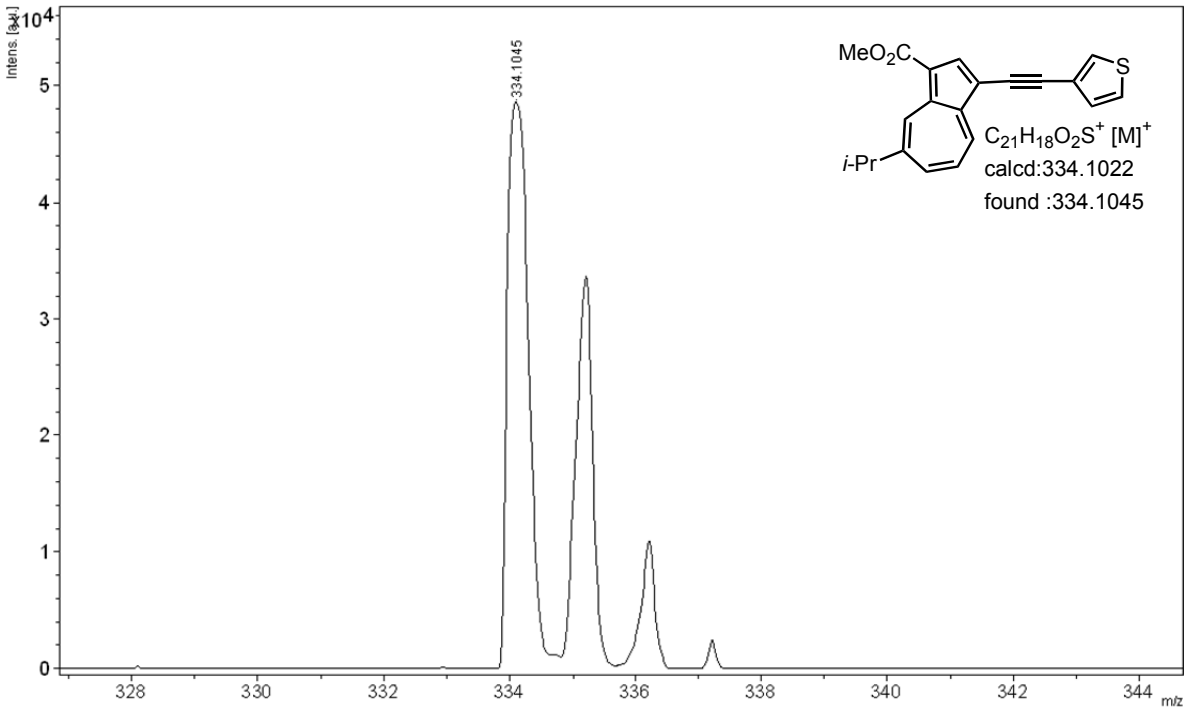


Figure S28. HRMS (MALDI-TOF, positive) of **8a**.

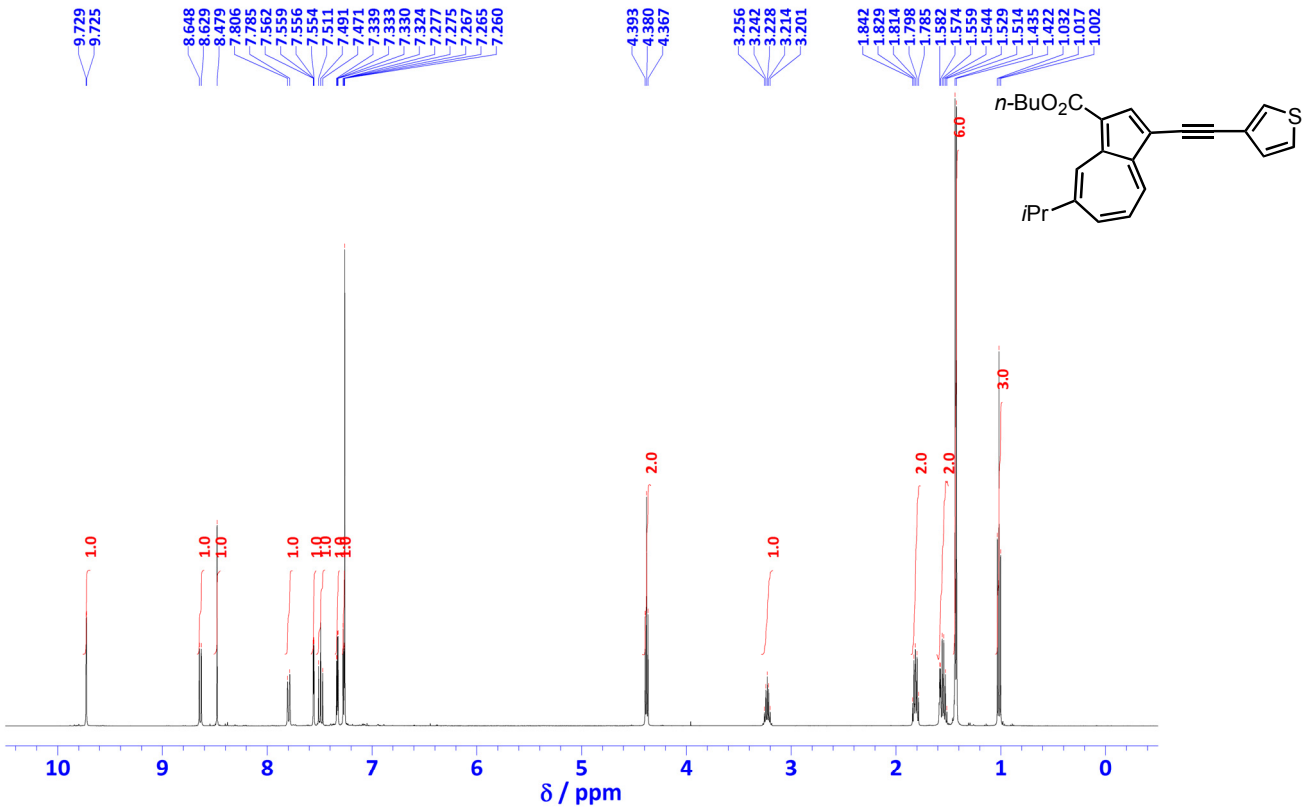


Figure S29. ^{1}H NMR spectrum of **8b** in $CDCl_3$ (500 MHz).

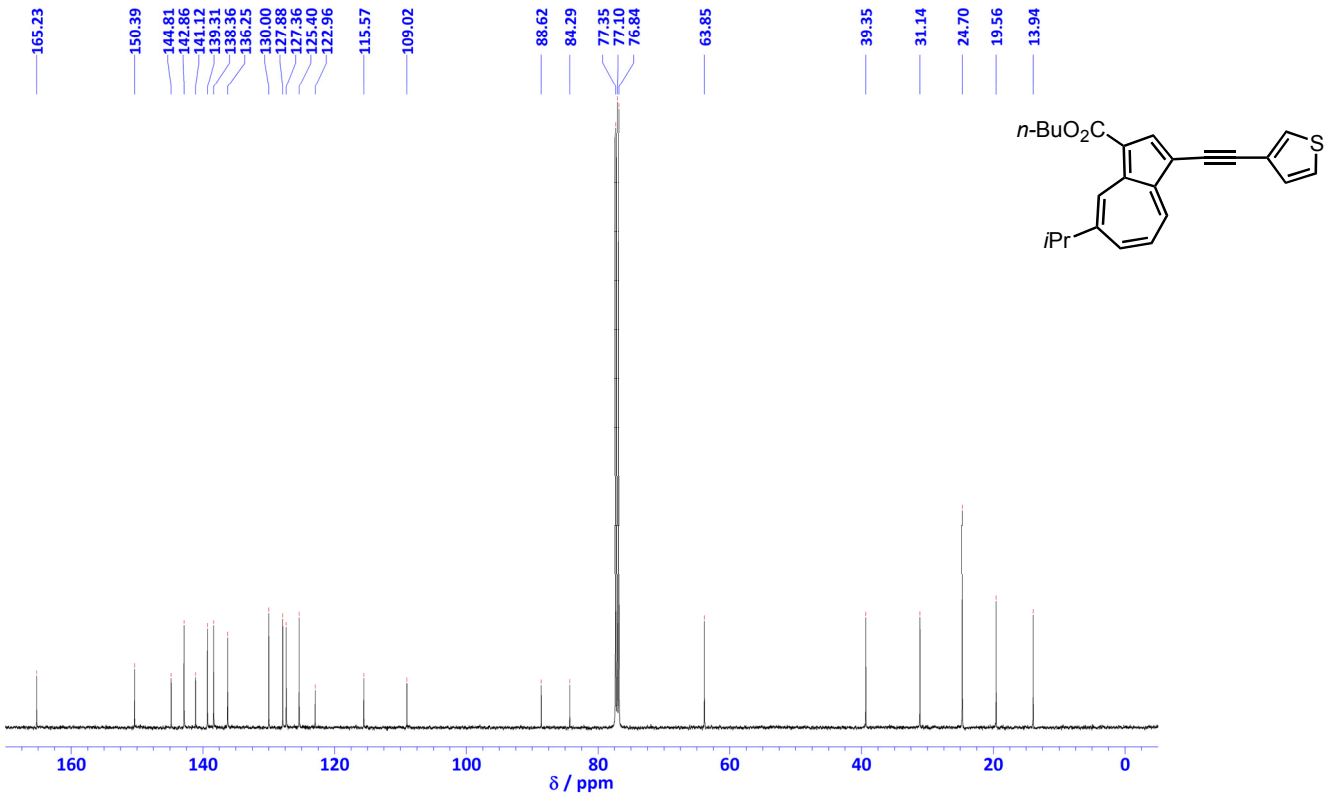


Figure S30. ^{13}C NMR spectrum of **8b** in $CDCl_3$ (125 MHz).

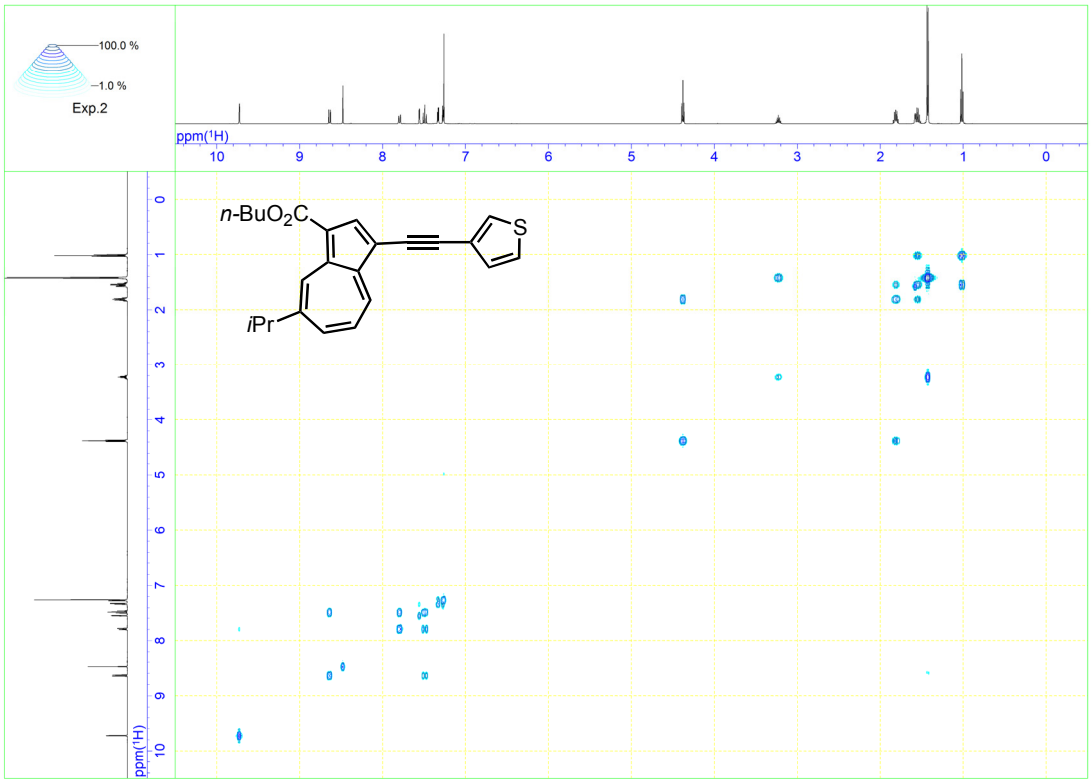


Figure S31. COSY spectrum of **8b** in $CDCl_3$ (500 MHz).

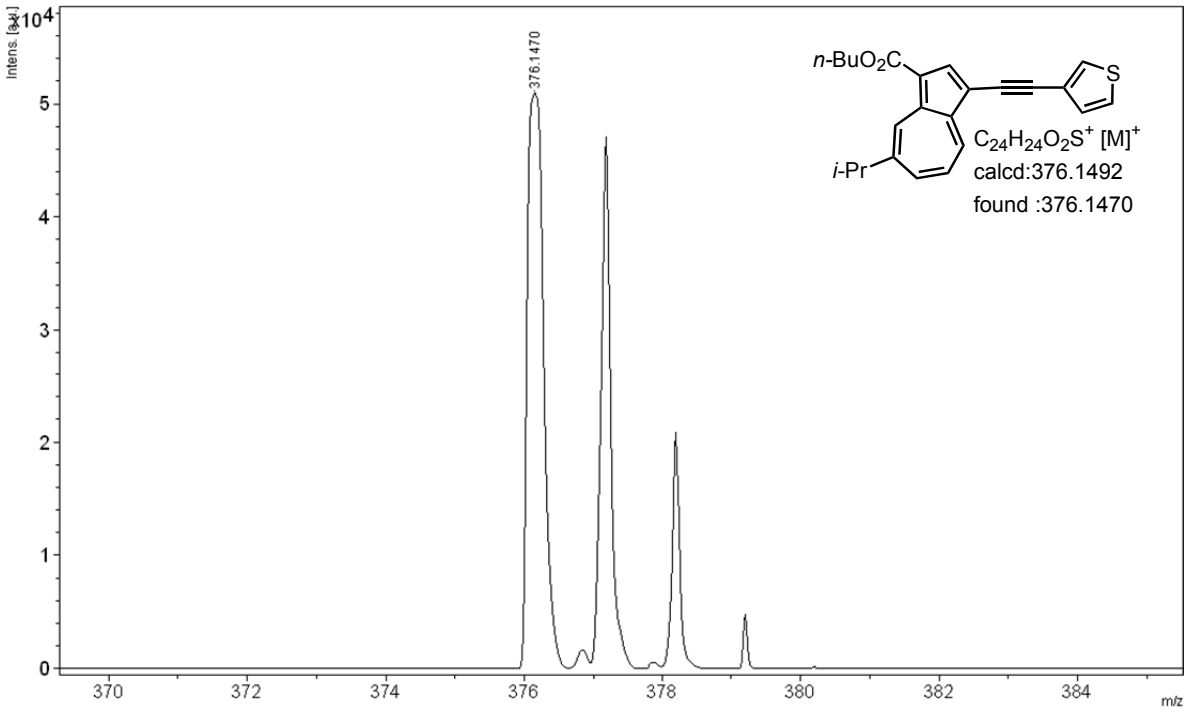


Figure S32. HRMS (MALDI-TOF, positive) of **8b**.

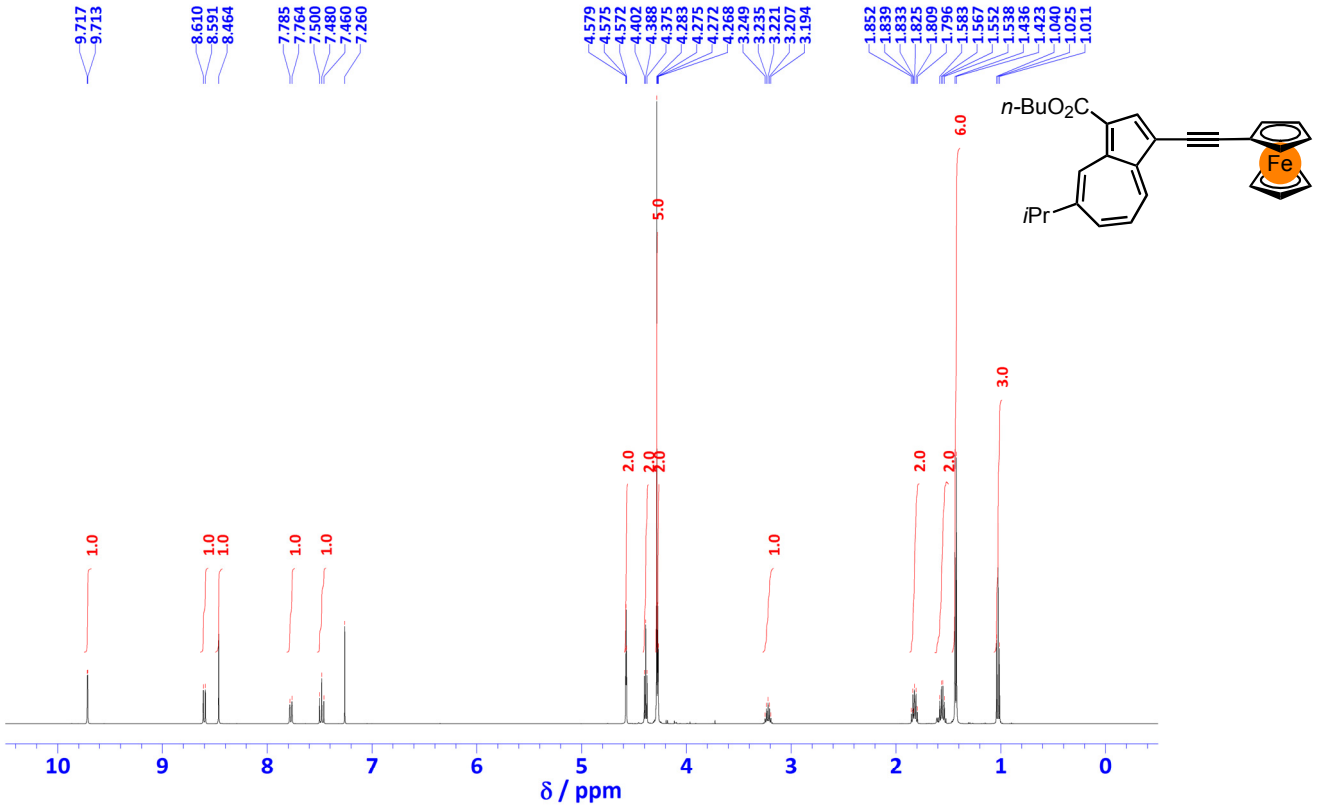


Figure S33. ^{1}H NMR spectrum of **9b** in $CDCl_3$ (500 MHz).

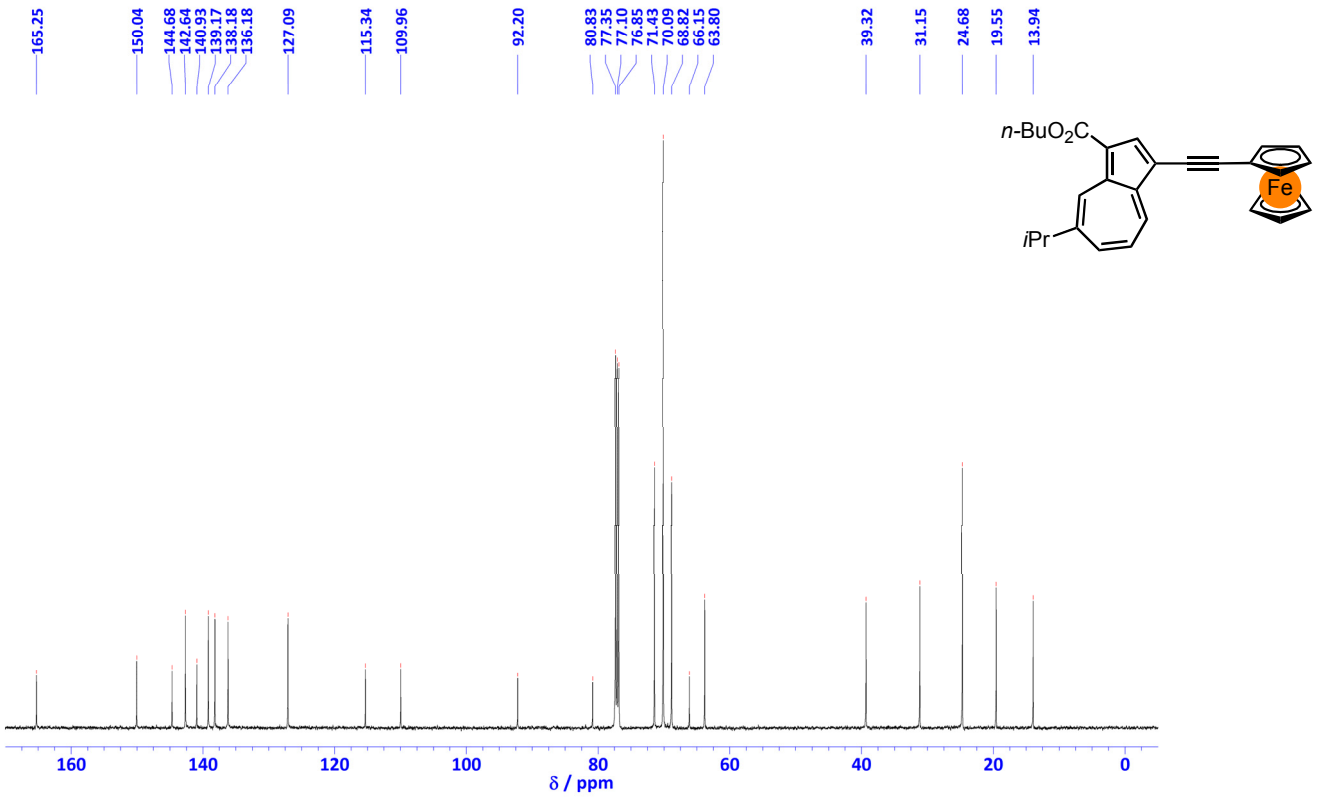


Figure S34. ^{13}C NMR spectrum of **9b** in $CDCl_3$ (125 MHz).

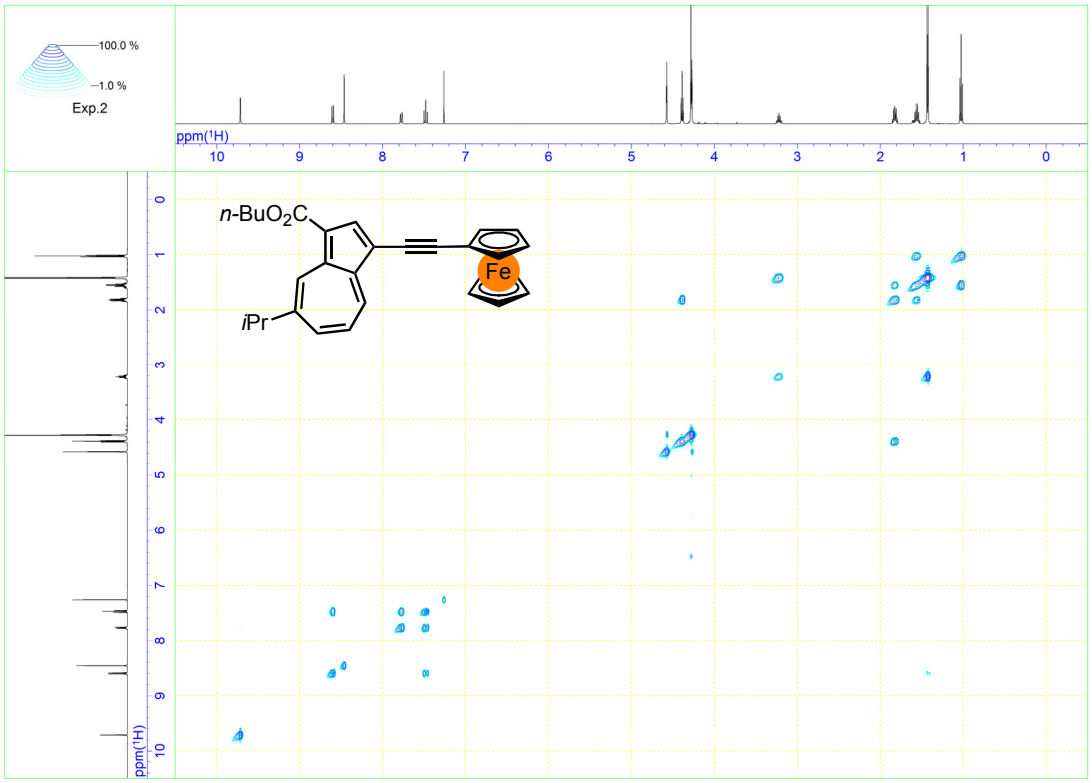


Figure S35. COSY spectrum of **9b** in $CDCl_3$ (500 MHz).

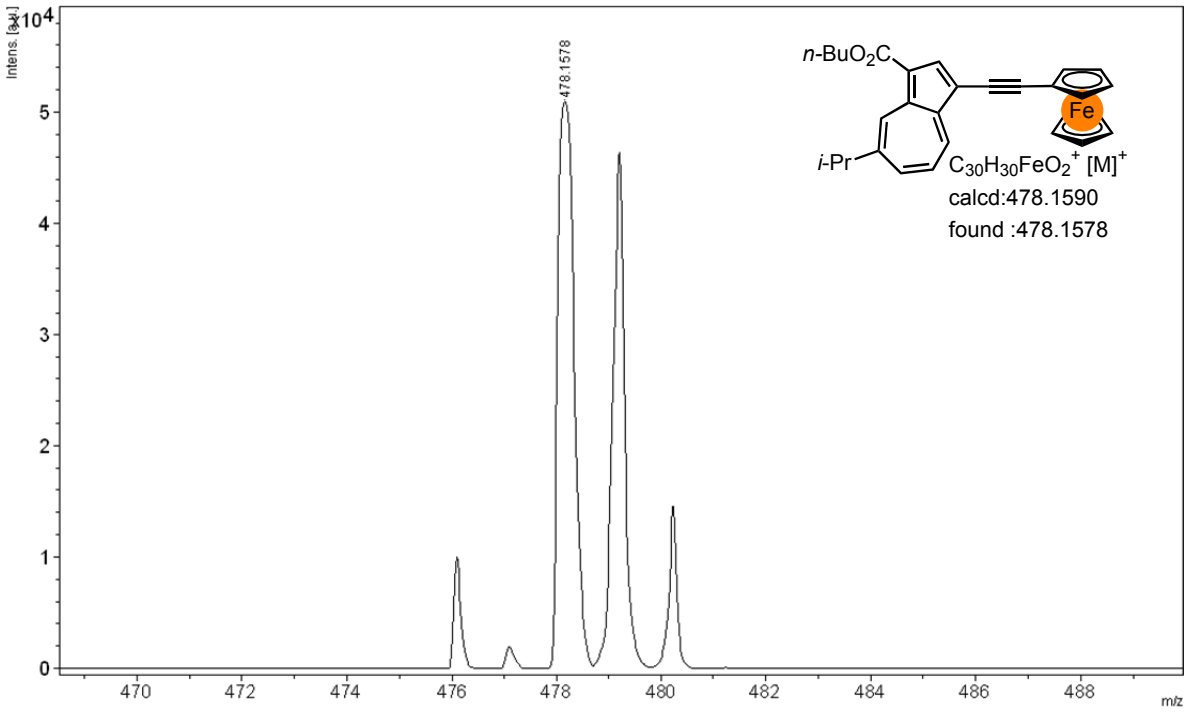


Figure S36. HRMS (MALDI-TOF, positive) of **9b**.

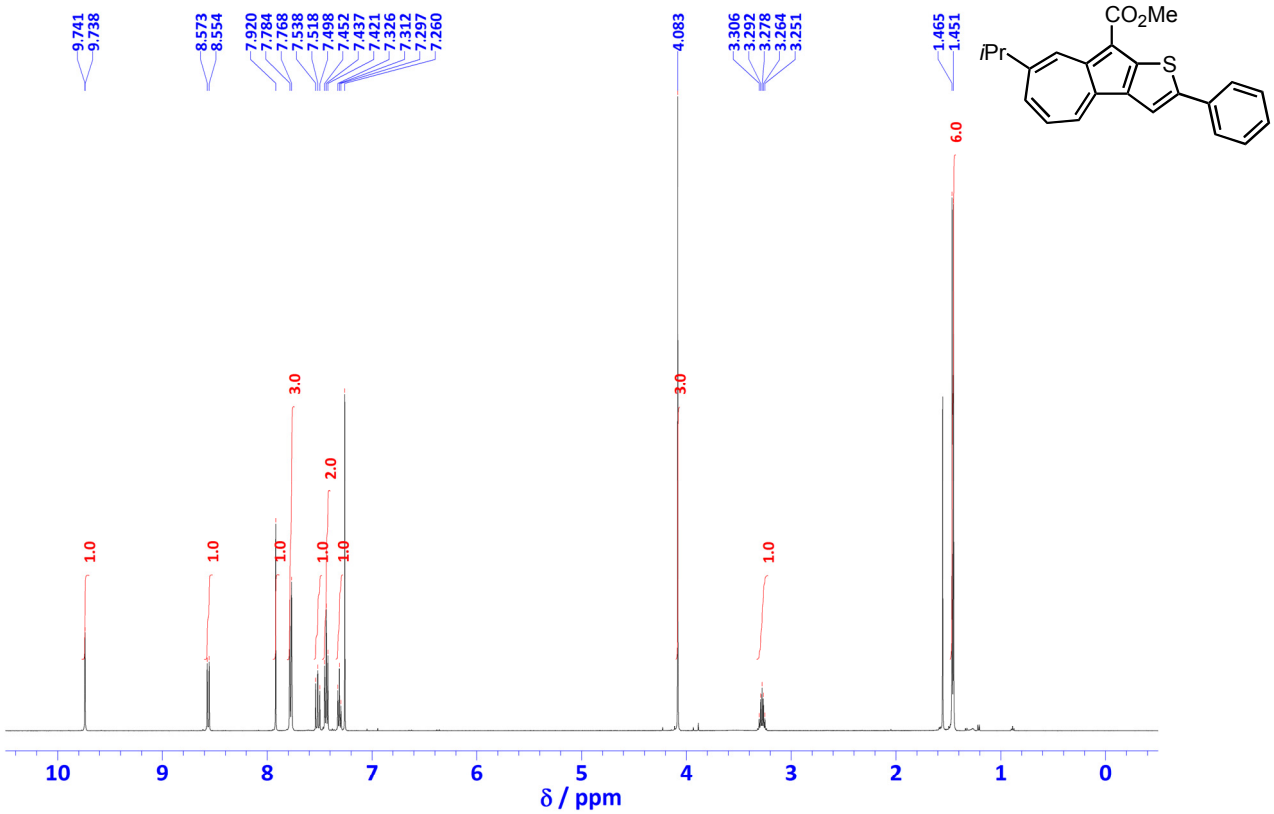


Figure S37. ^{1}H NMR spectrum of **11** in $CDCl_3$ (500 MHz).

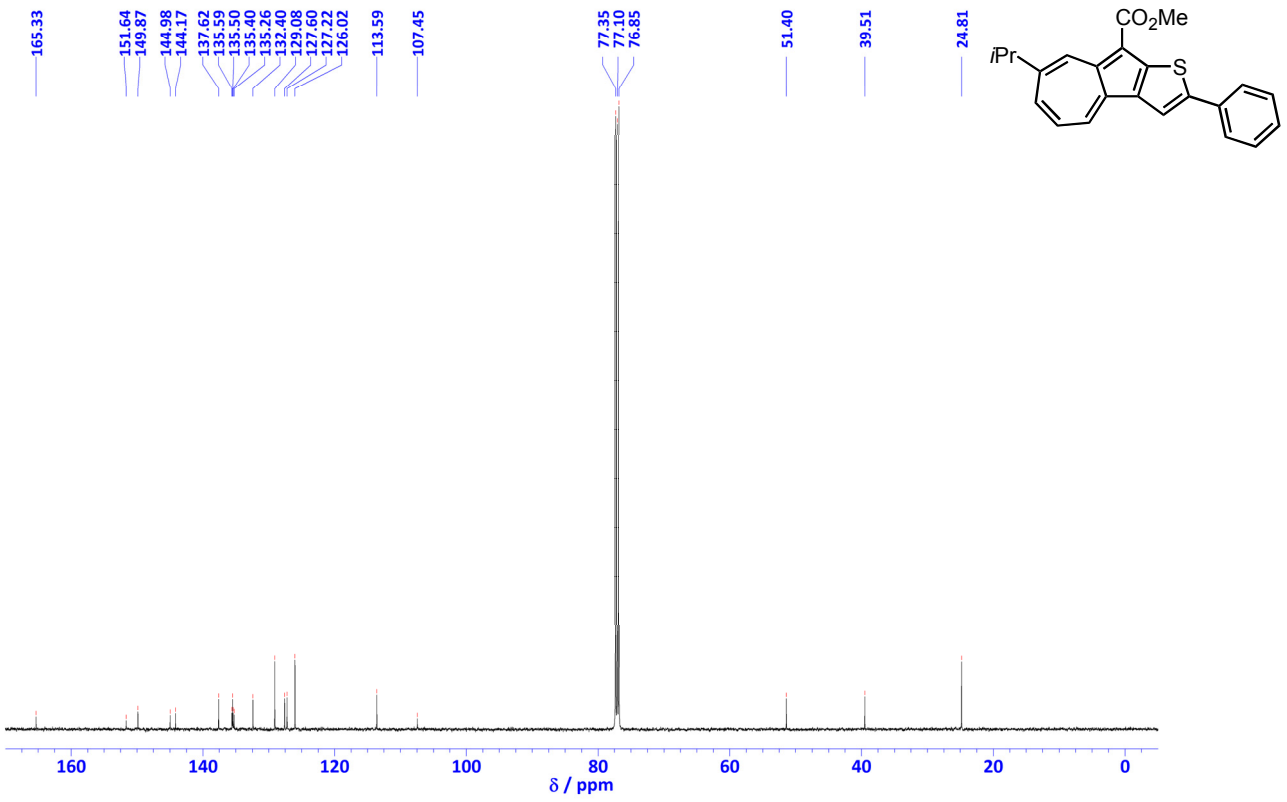


Figure S38. ^{13}C NMR spectrum of **11** in $CDCl_3$ (125 MHz).

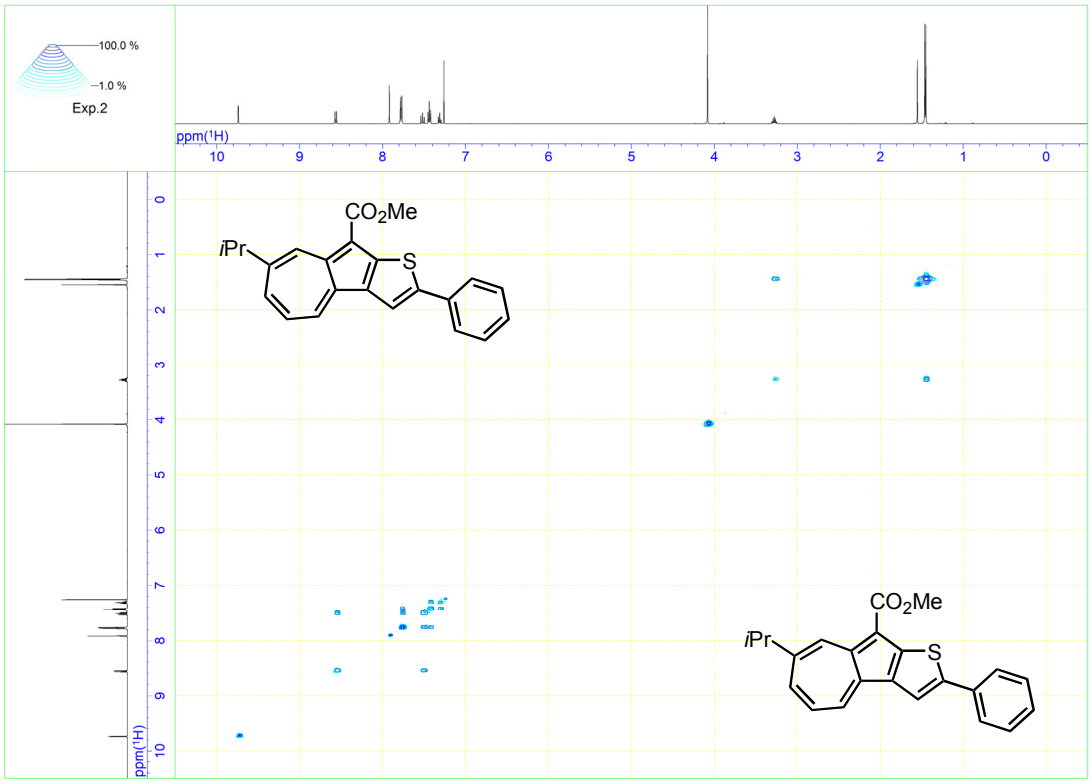


Figure S39. COSY spectrum of **11** in $CDCl_3$ (500 MHz).

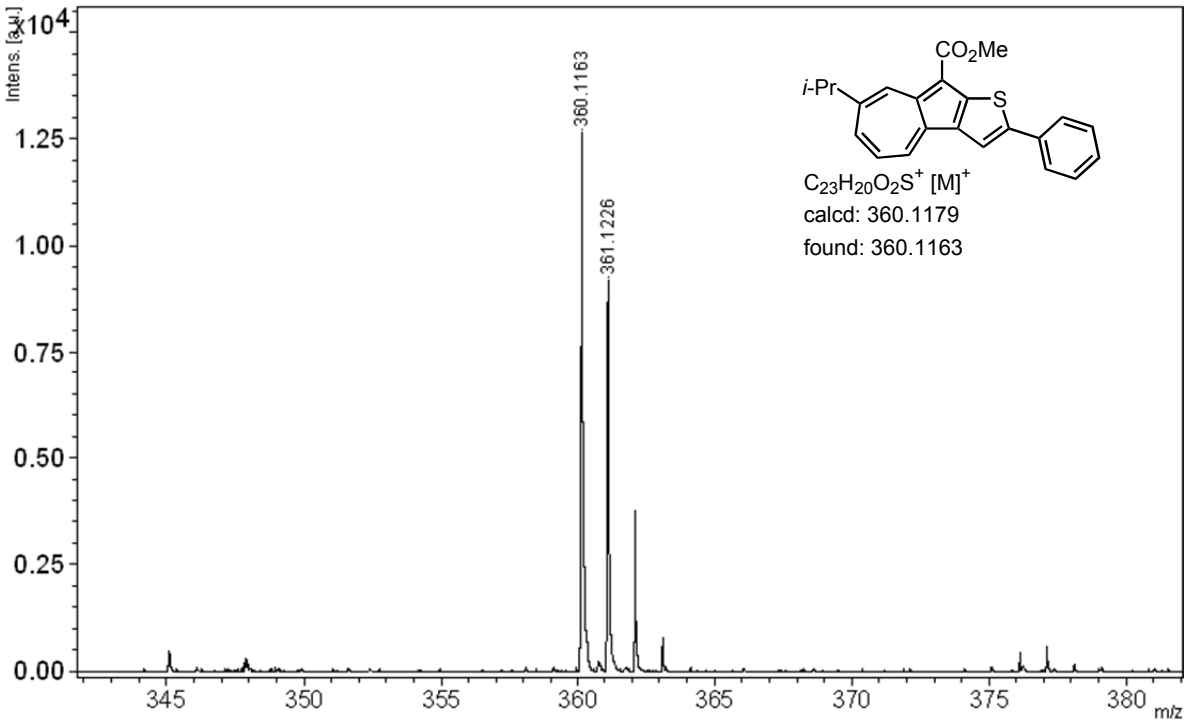


Figure S40. HRMS (MALDI-TOF, positive) of **11**.

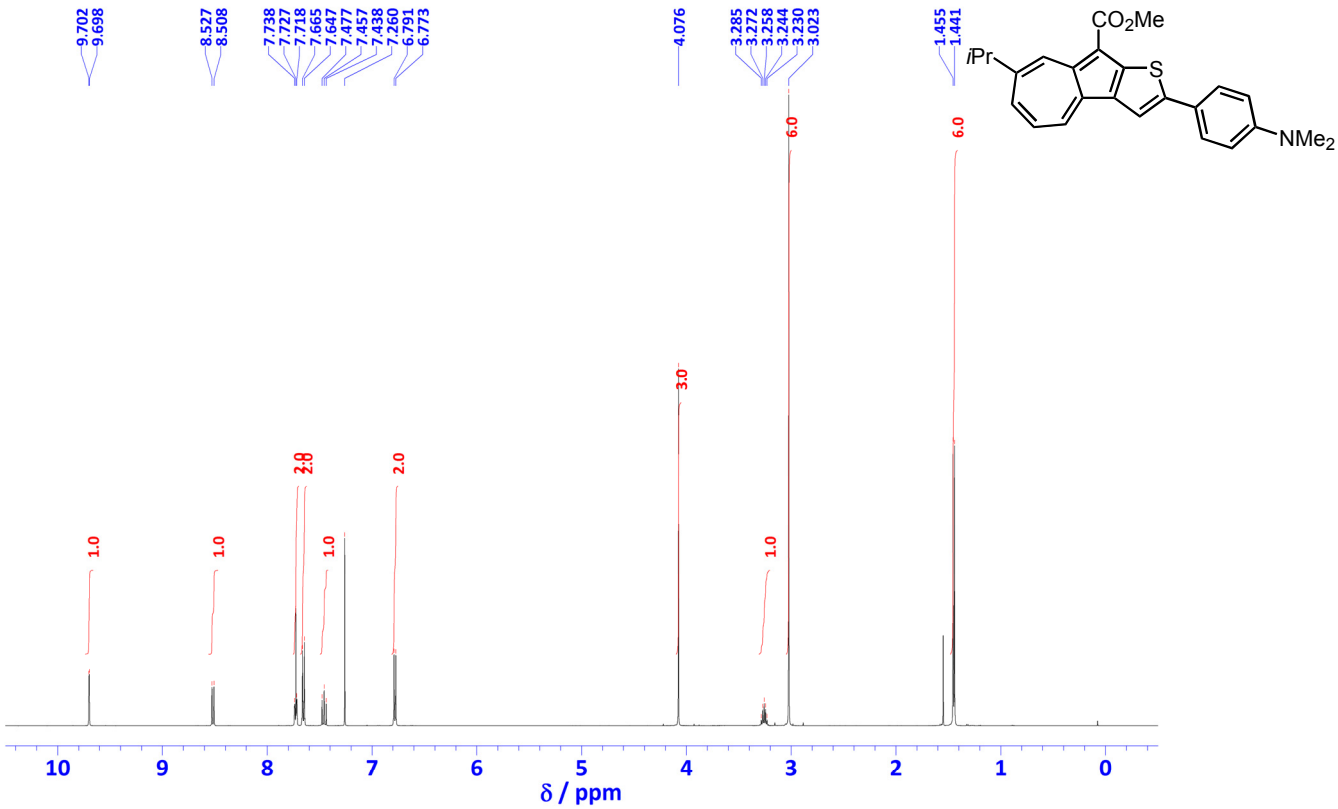


Figure S41. ^{1}H NMR spectrum of **12** in $CDCl_3$ (500 MHz).

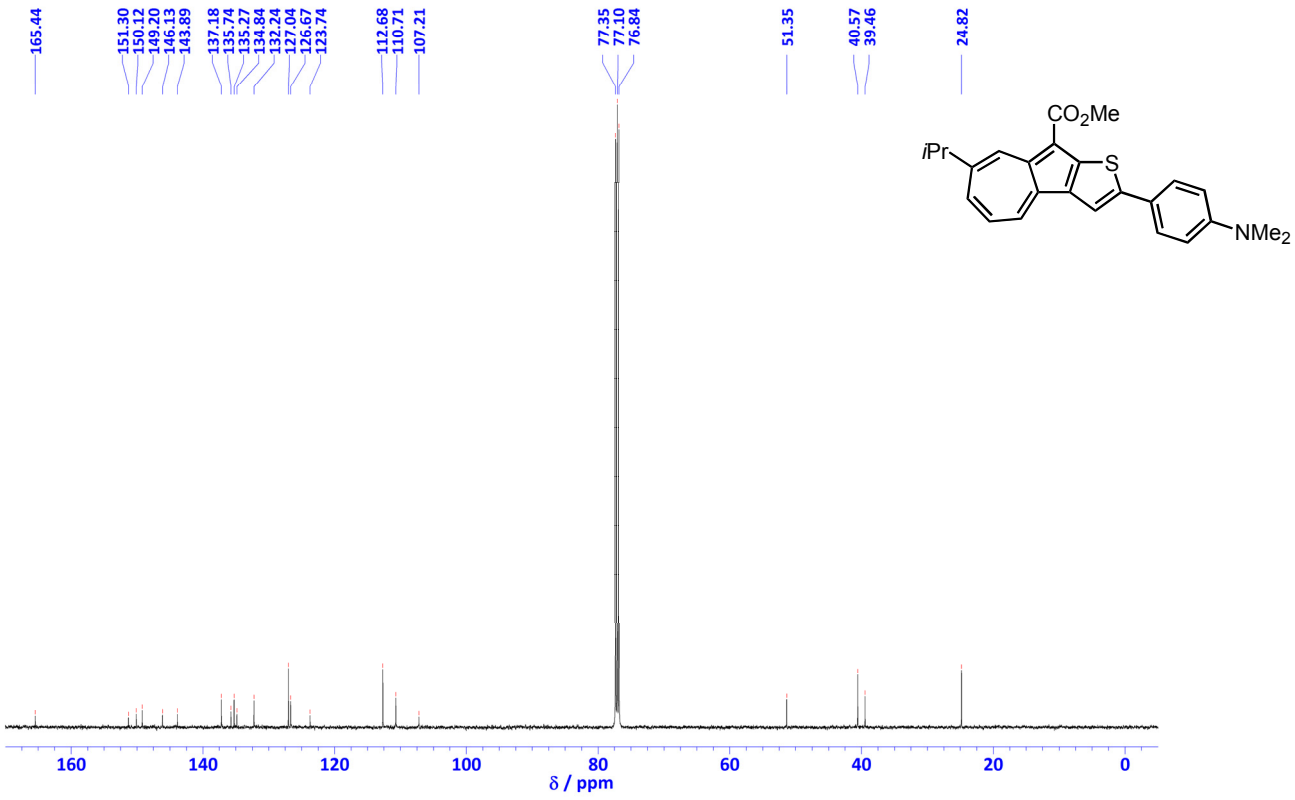


Figure S42. ^{13}C NMR spectrum of **12** in $CDCl_3$ (125 MHz).

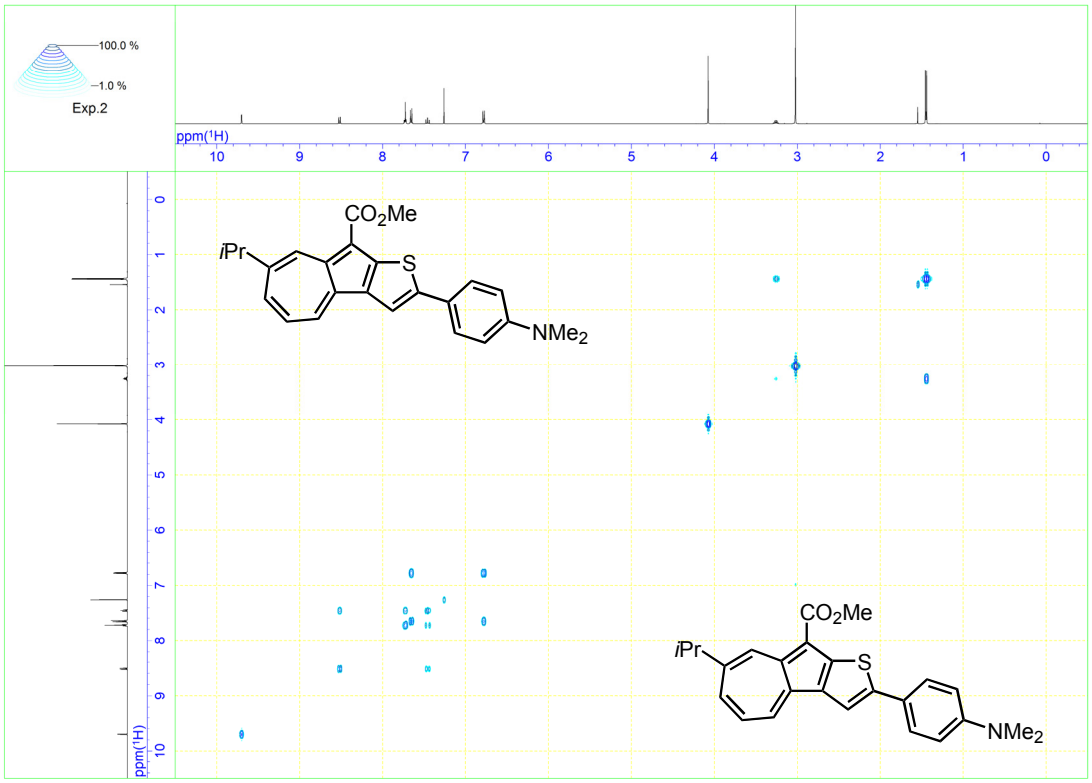


Figure S43. COSY spectrum of **12** in $CDCl_3$ (500 MHz).

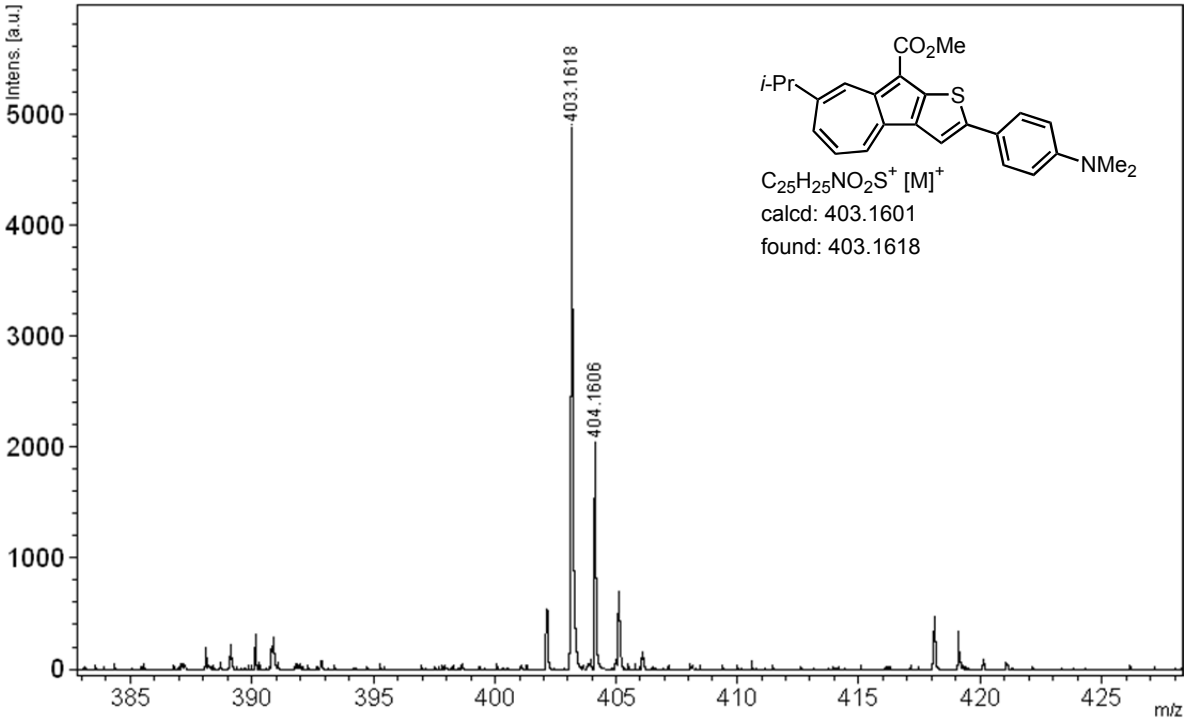


Figure S44. HRMS (MALDI-TOF, positive) of **12**.

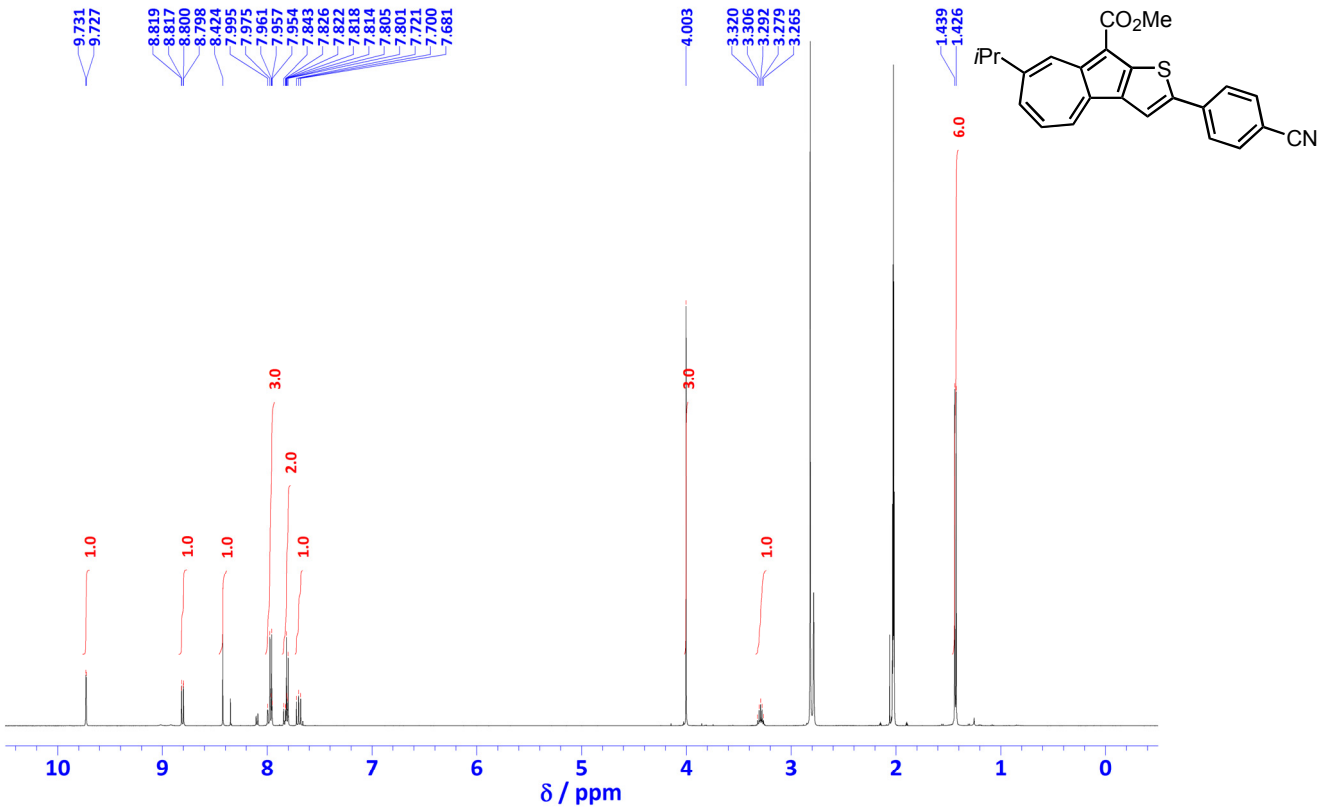


Figure S45. ^{1}H NMR spectrum of **13** in acetone-d_6 (500 MHz).

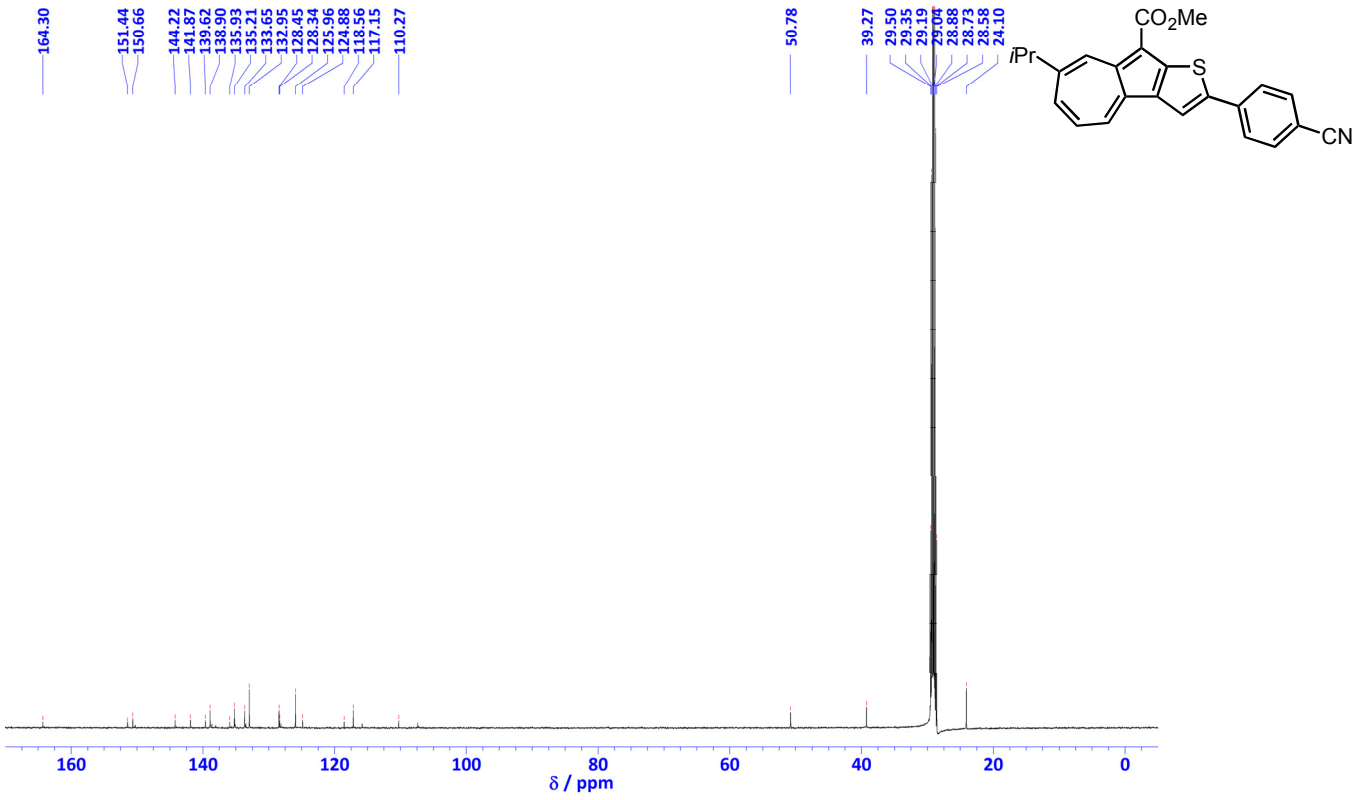


Figure S46. ^{13}C NMR spectrum of **13** in acetone-d_6 (125 MHz).

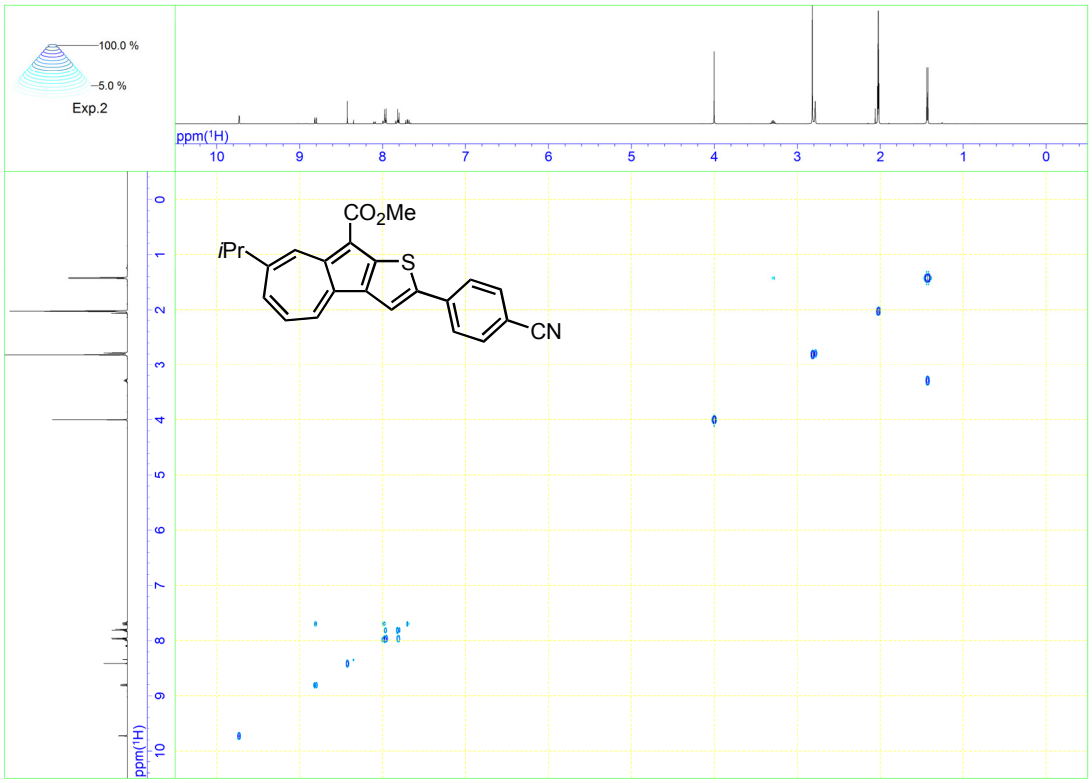


Figure S47. COSY spectrum of **13** in acetone-d_6 (500 MHz).

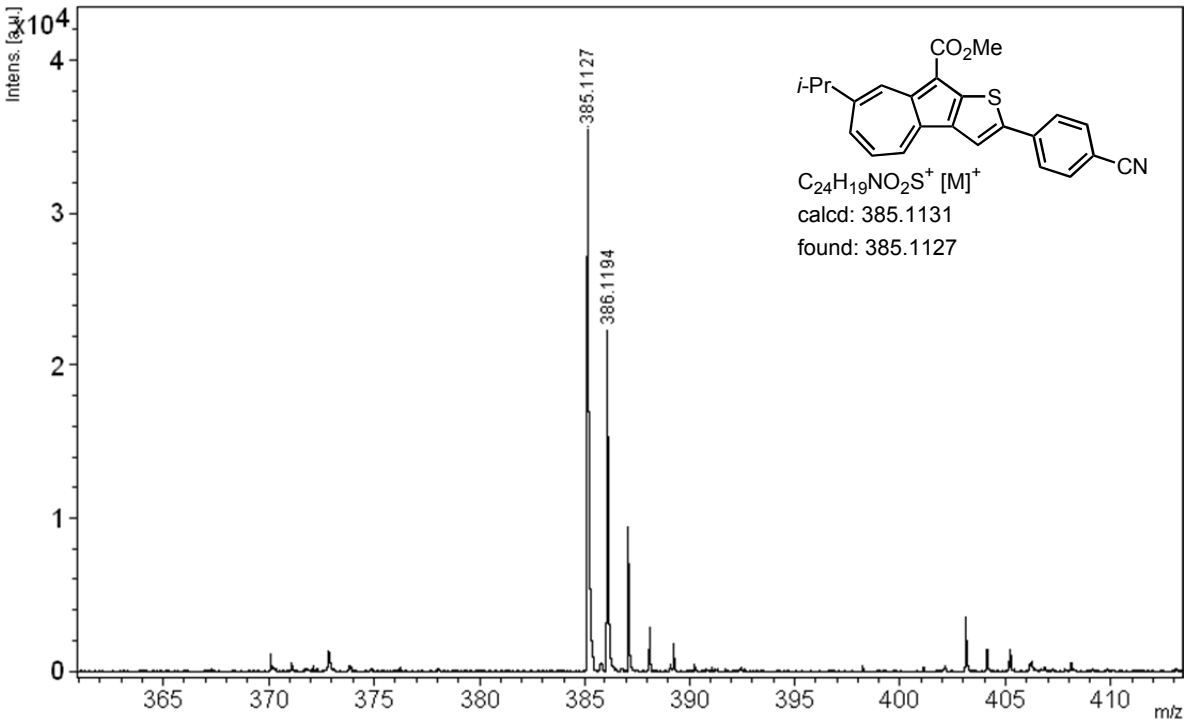


Figure S48. HRMS (MALDI-TOF, positive) of **13**.

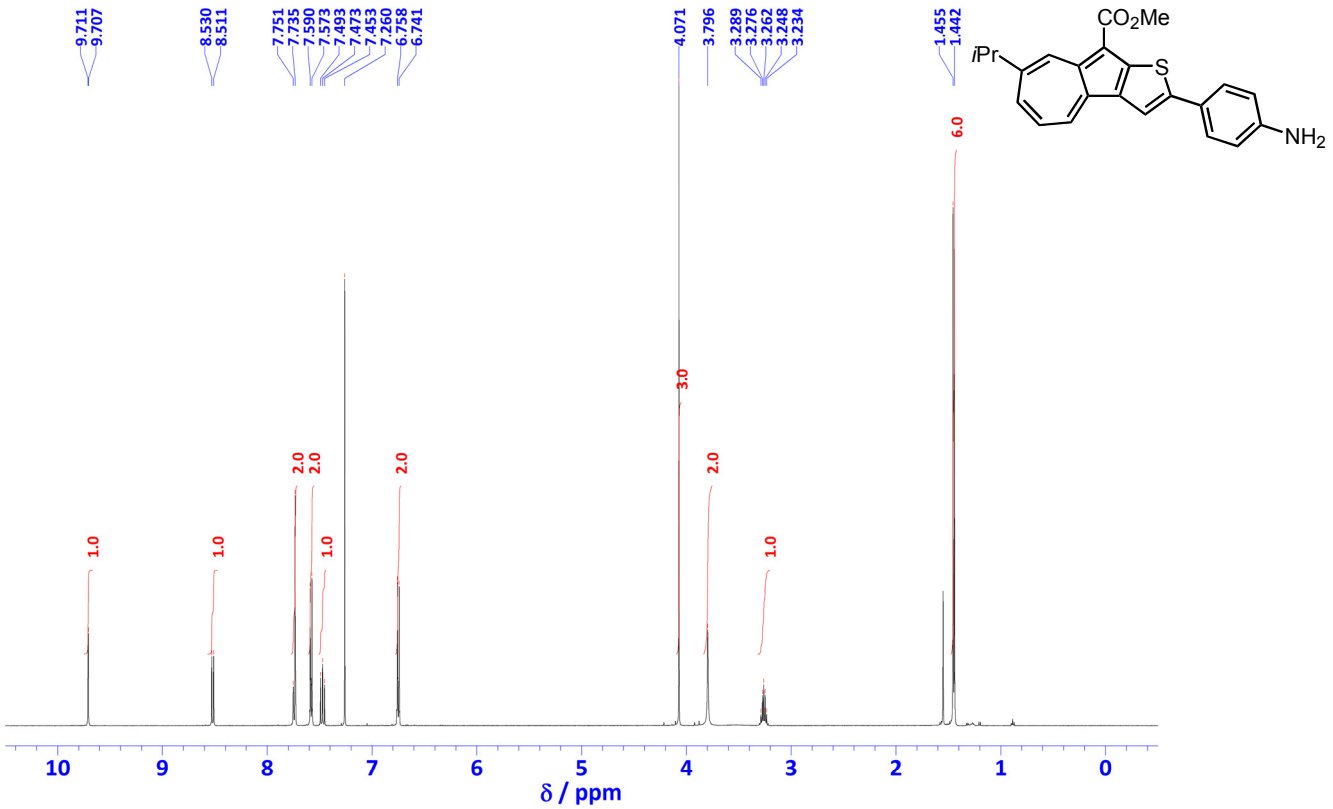


Figure S49. ^{1}H NMR spectrum of **14** in $CDCl_3$ (500 MHz).

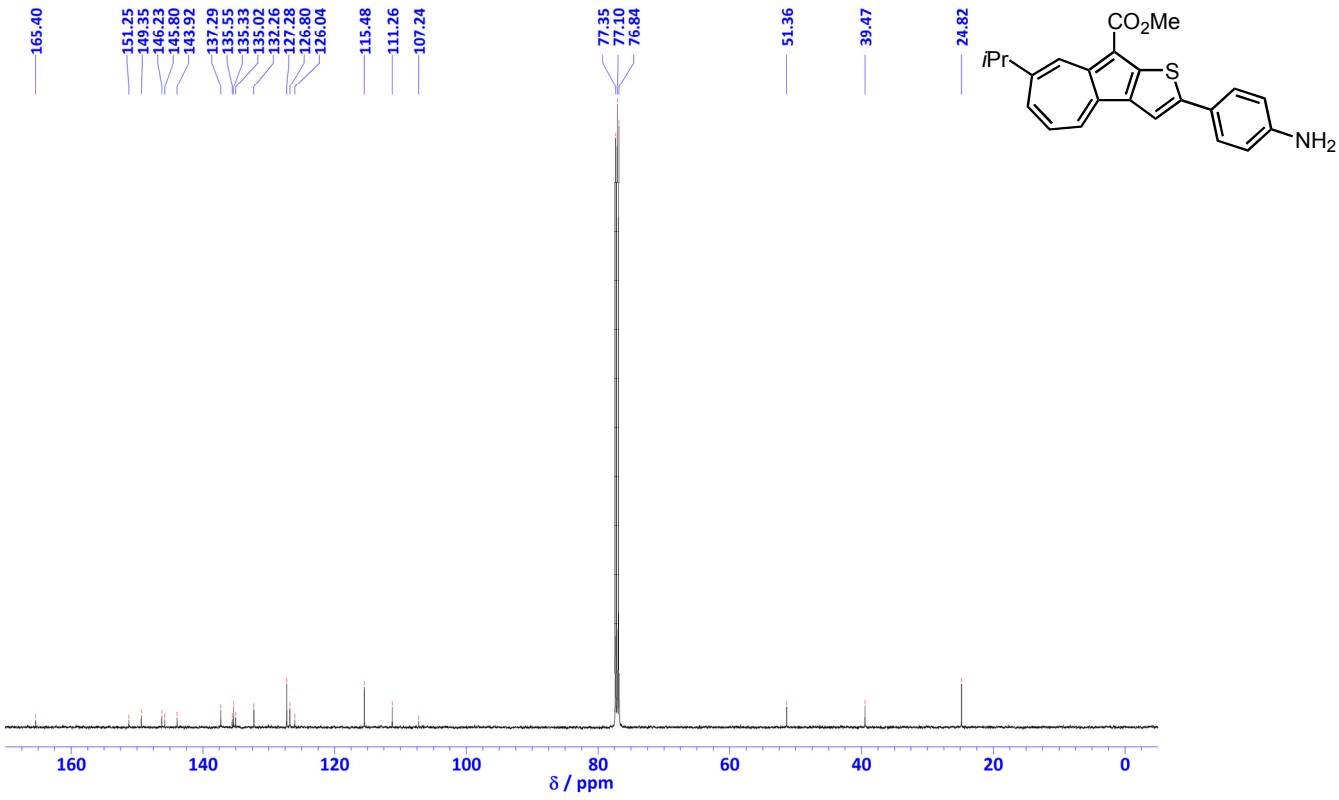


Figure S50. ^{13}C NMR spectrum of **14** in $CDCl_3$ (125 MHz).

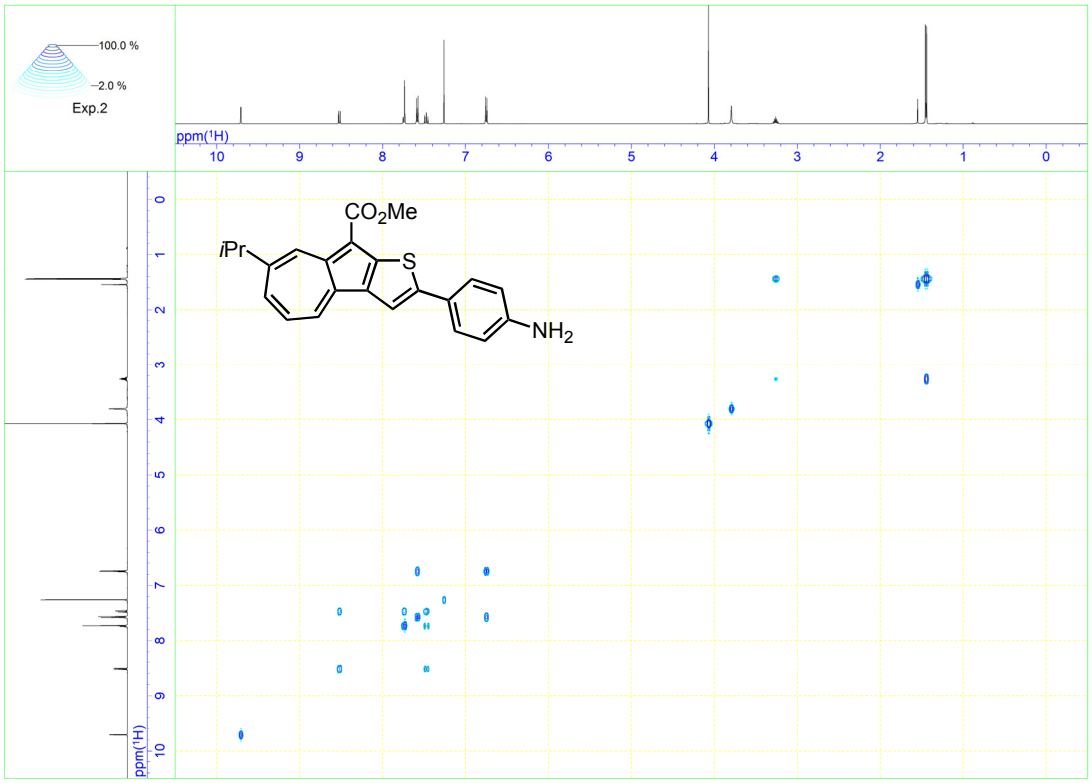


Figure S51. COSY spectrum of **14** in $CDCl_3$ (500 MHz).

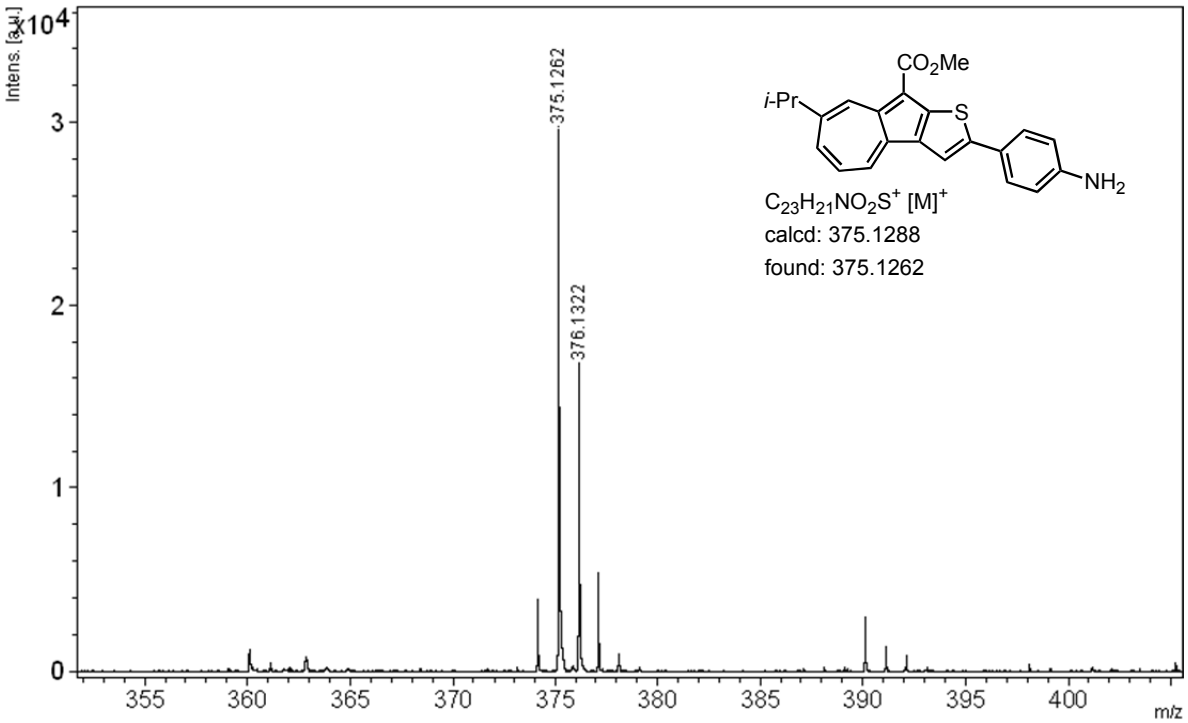


Figure S52. HRMS (MALDI-TOF, positive) of **14**.

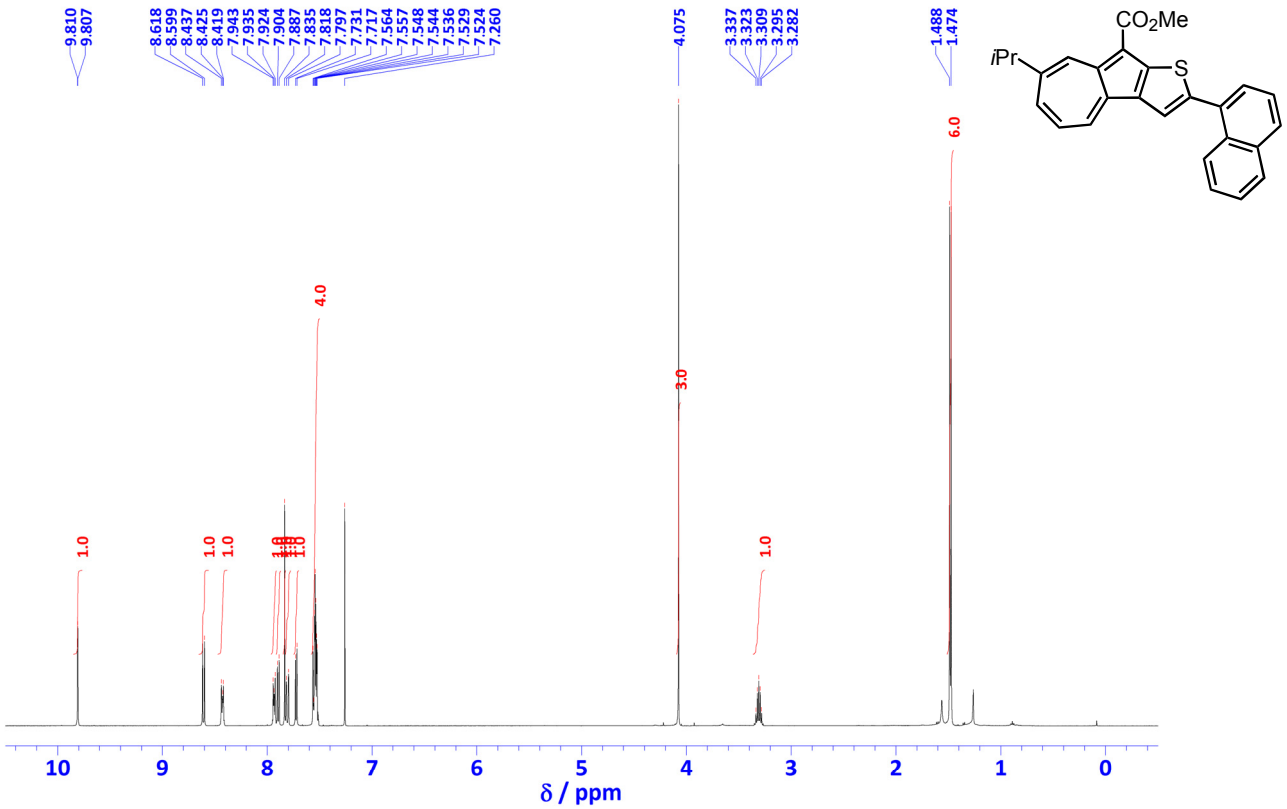


Figure S53. ^{1}H NMR spectrum of **15** in $CDCl_3$ (500 MHz).

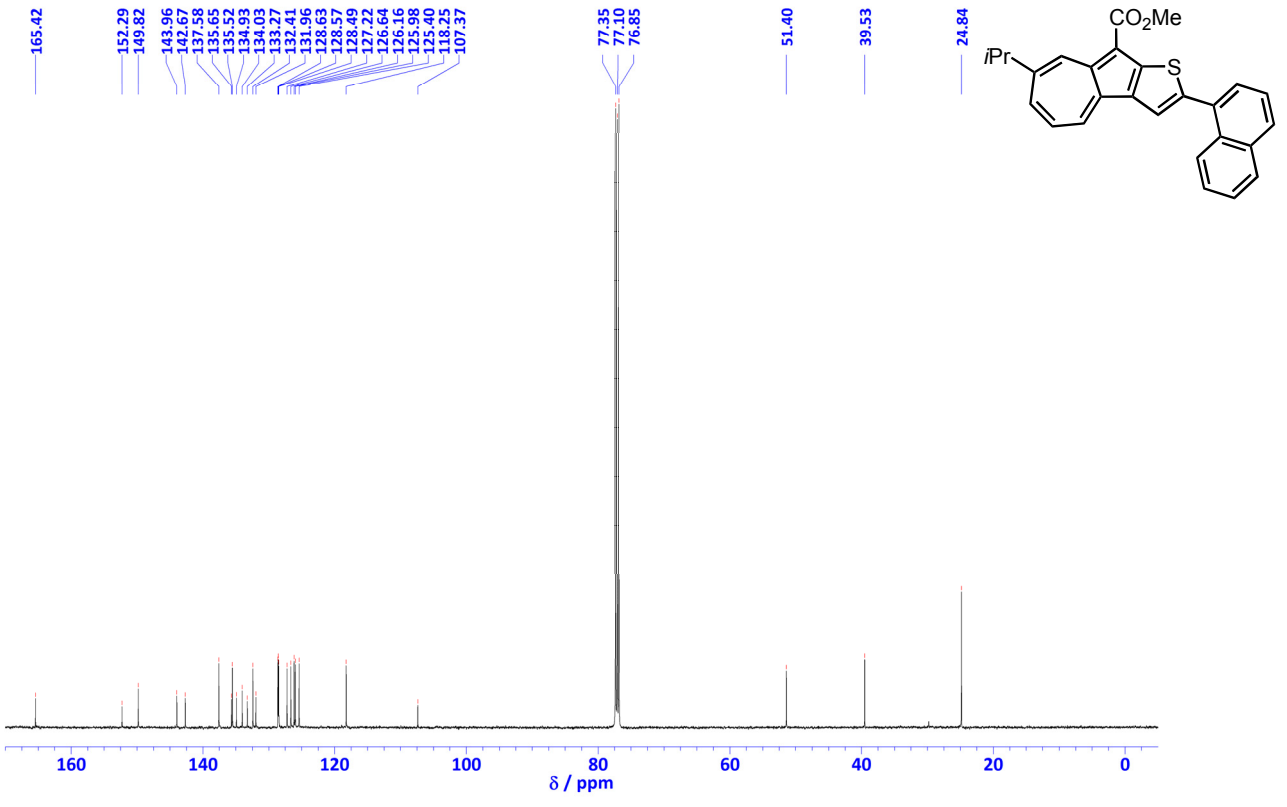


Figure S54. ^{13}C NMR spectrum of **15** in $CDCl_3$ (125 MHz).

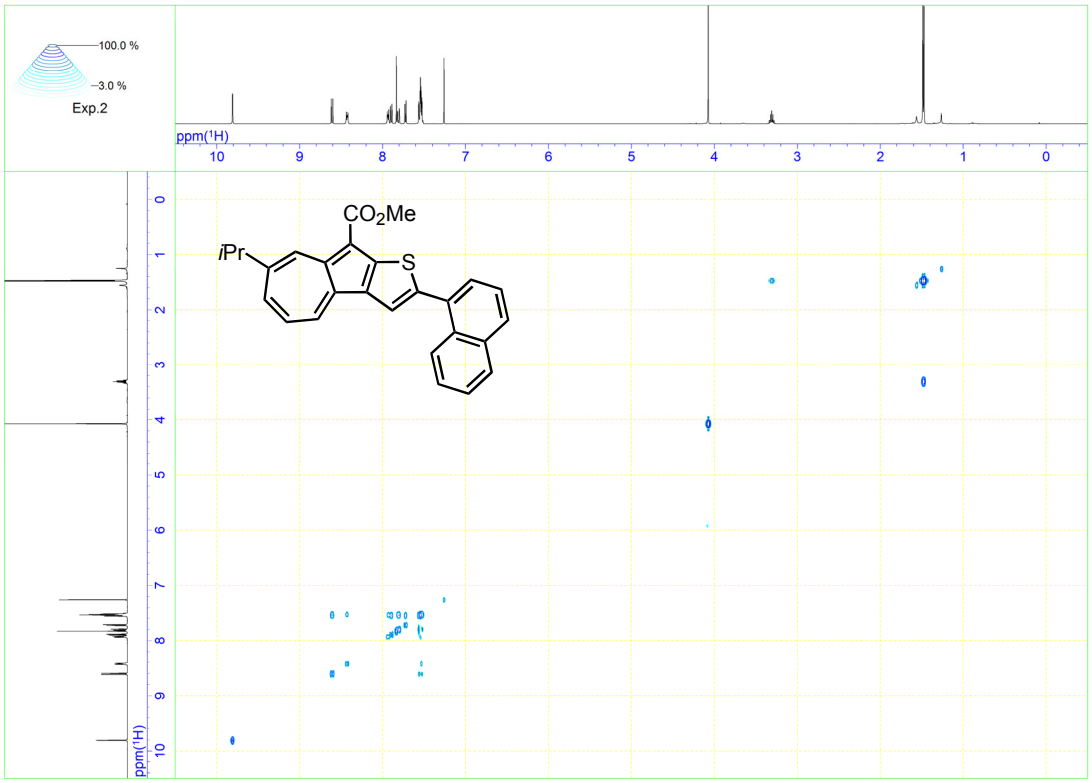


Figure S55. COSY spectrum of **15** in $CDCl_3$ (500 MHz).

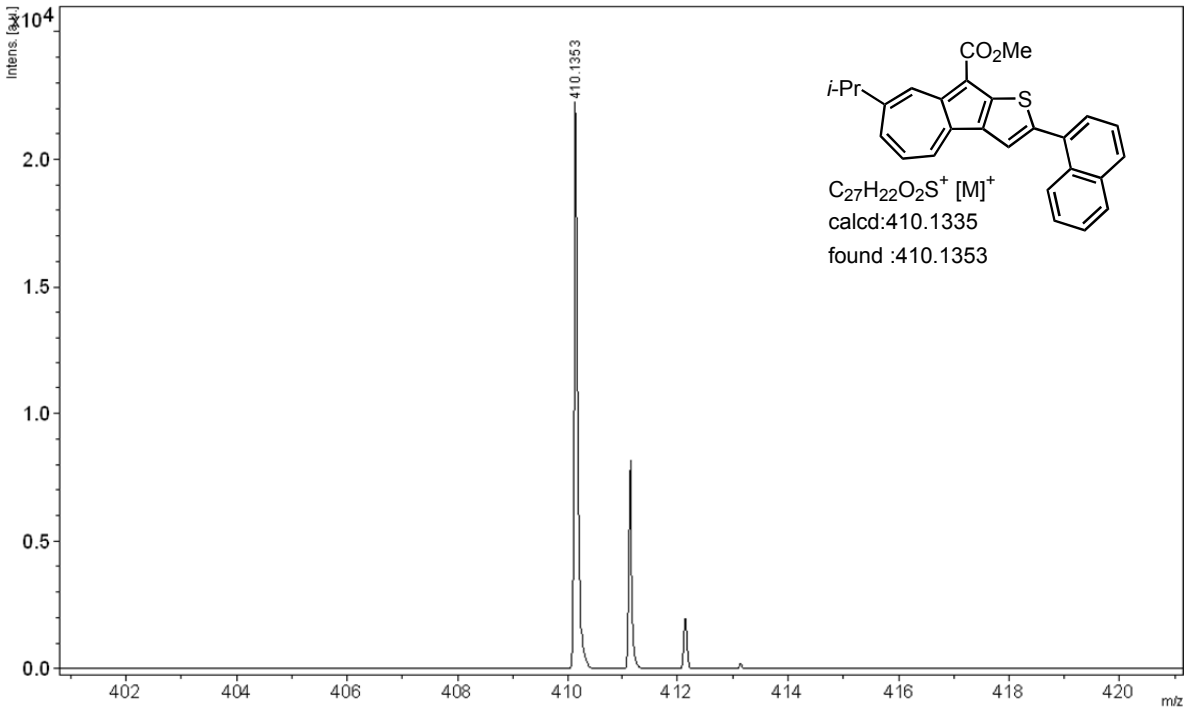


Figure S56. HRMS (MALDI-TOF, positive) of **15**.

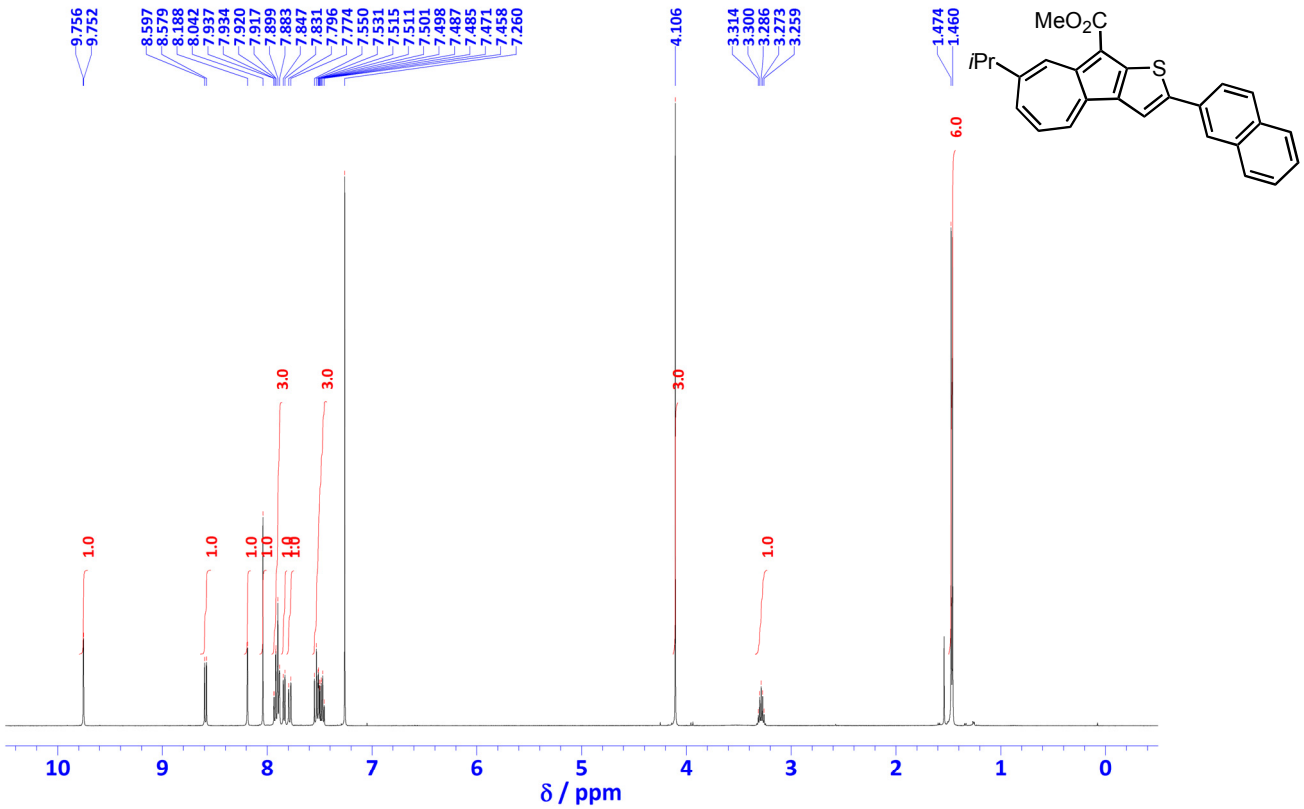


Figure S57. ^{1}H NMR spectrum of **16** in $CDCl_3$ (500 MHz).

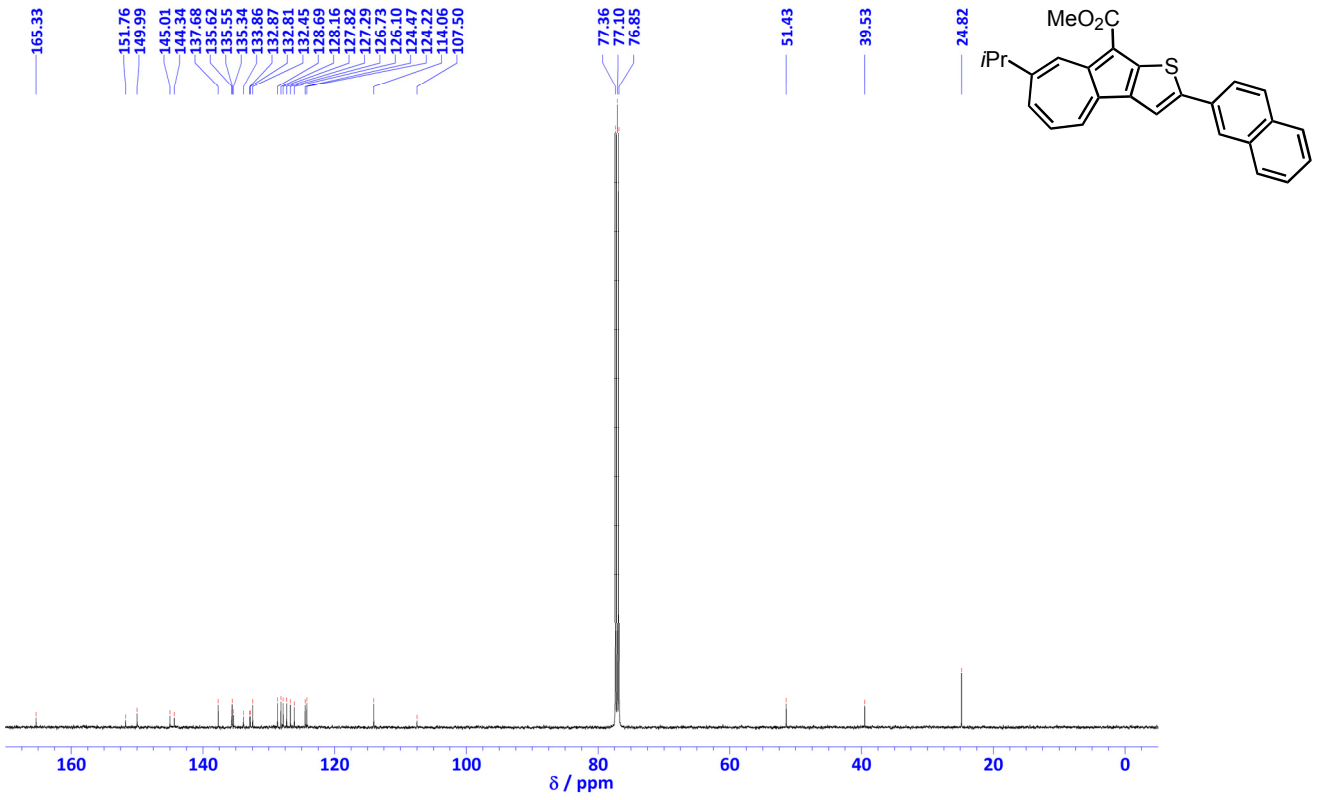


Figure S58. ^{13}C NMR spectrum of **16** in $CDCl_3$ (125 MHz).

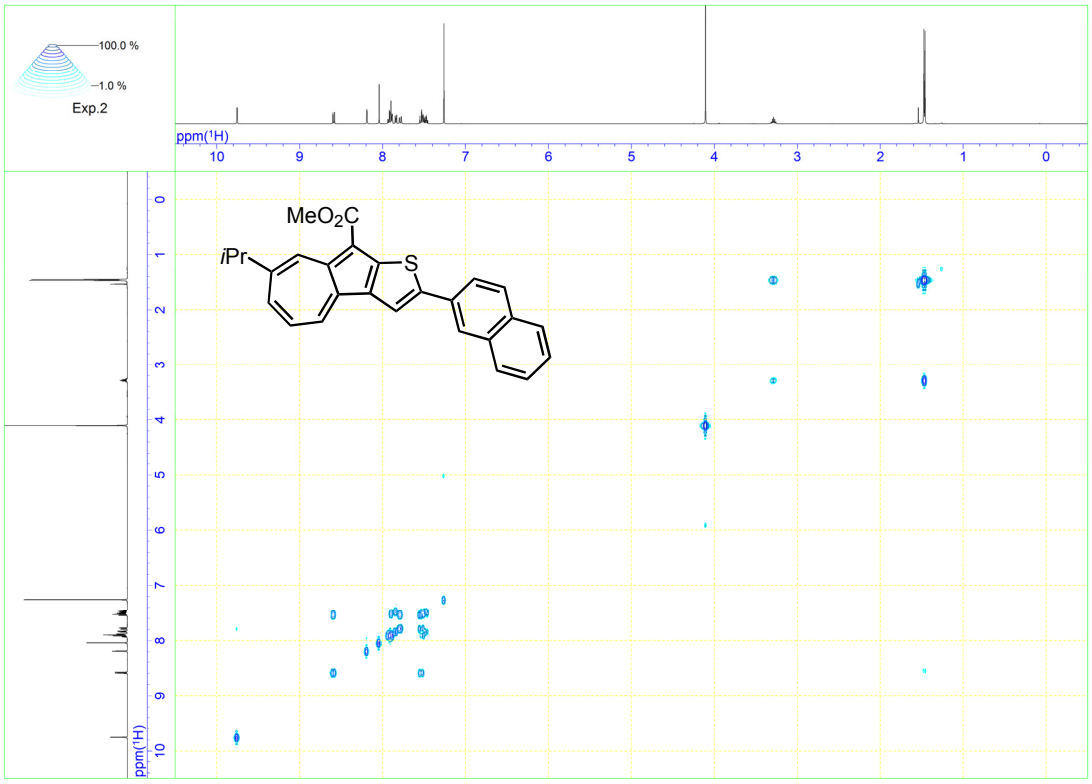


Figure S59. COSY spectrum of **16** in $CDCl_3$ (500 MHz).

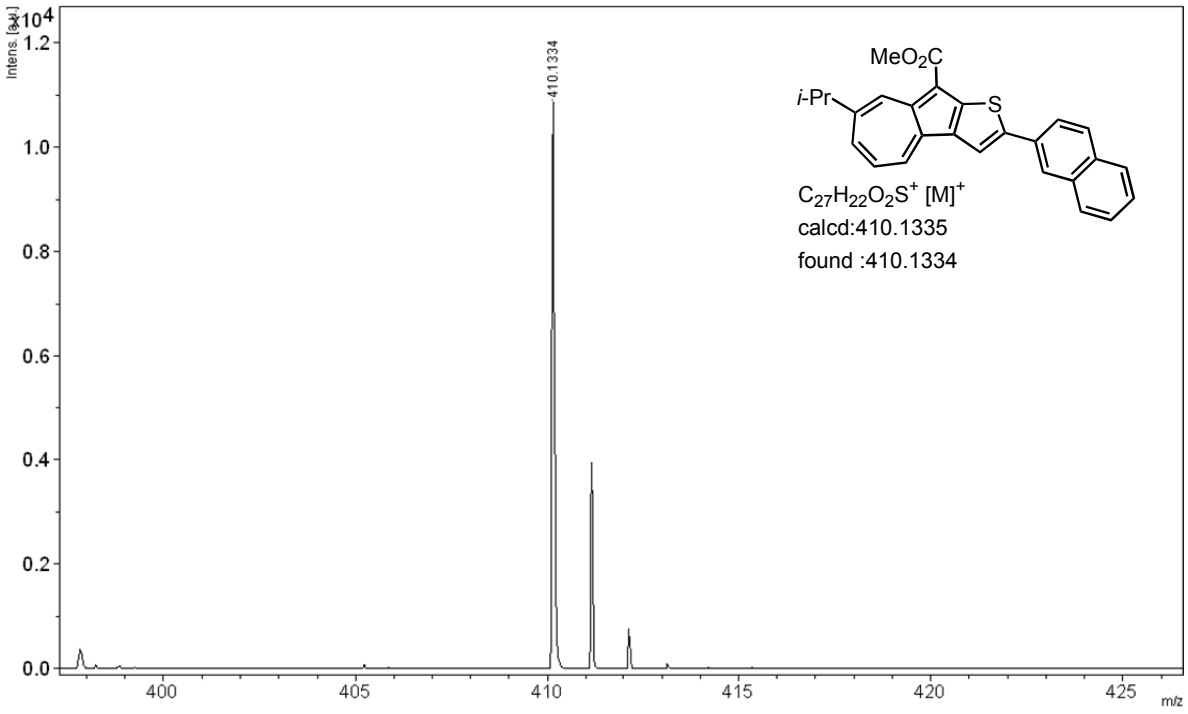


Figure S60. HRMS (MALDI-TOF, positive) of **16**.

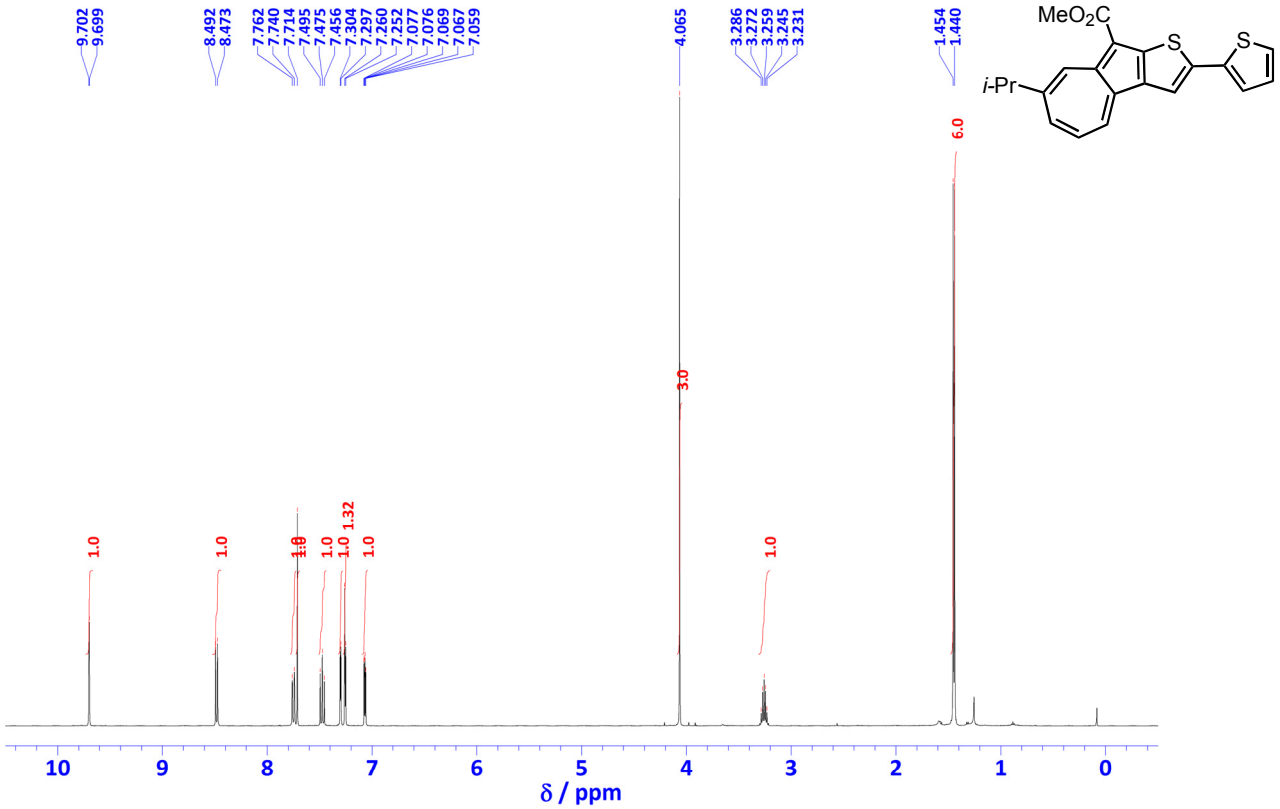


Figure S61. ^{1}H NMR spectrum of **17a** in $CDCl_3$ (500 MHz).

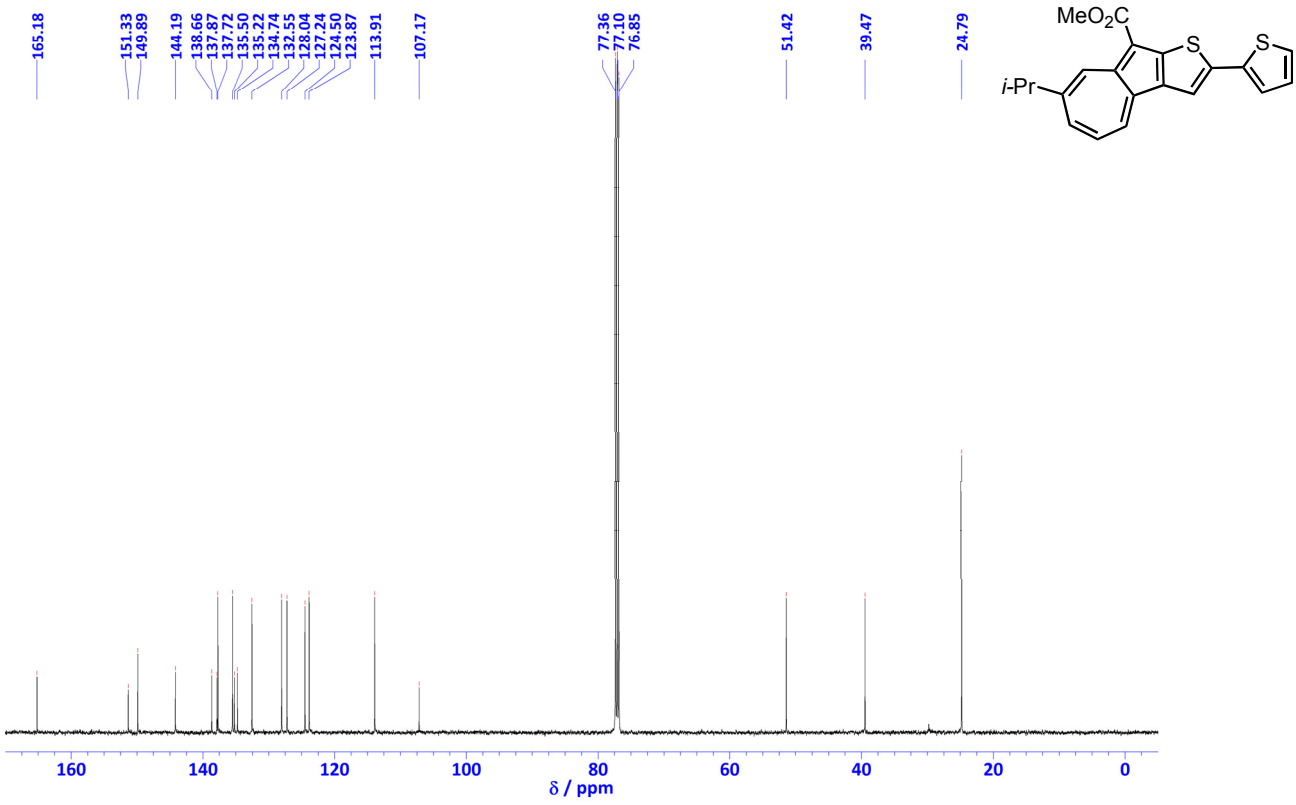


Figure S62. ^{13}C NMR spectrum of **17a** in $CDCl_3$ (125 MHz).

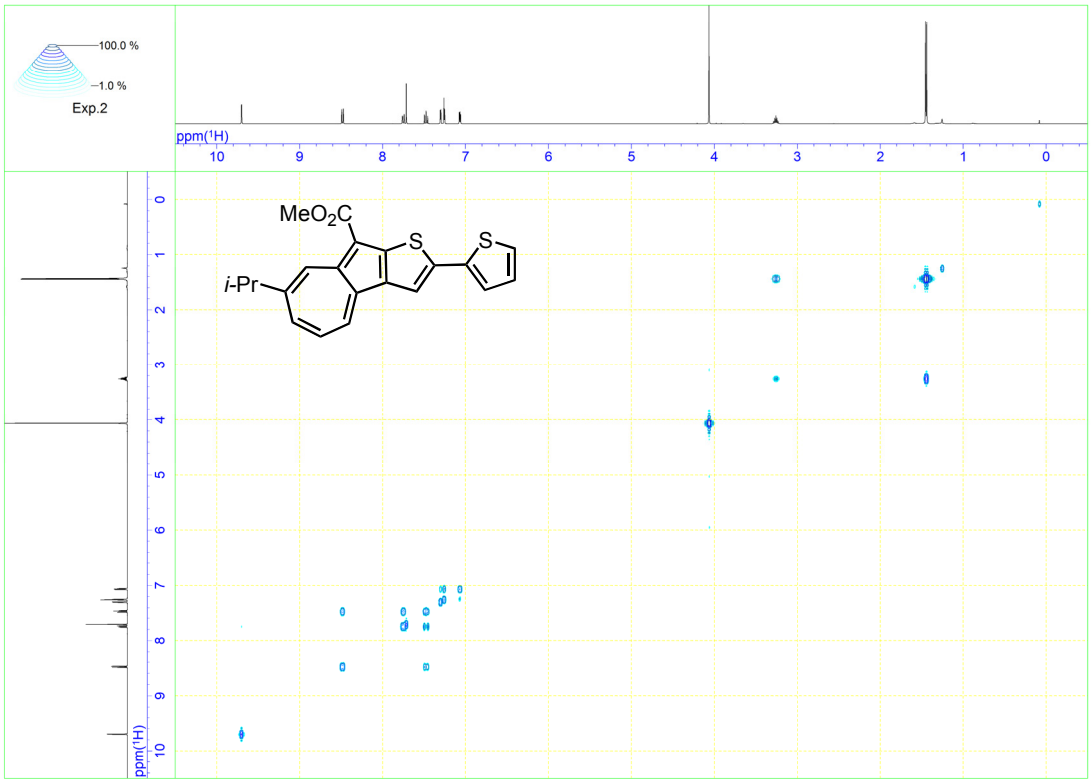


Figure S63. COSY spectrum of **17a** in $CDCl_3$ (500 MHz).

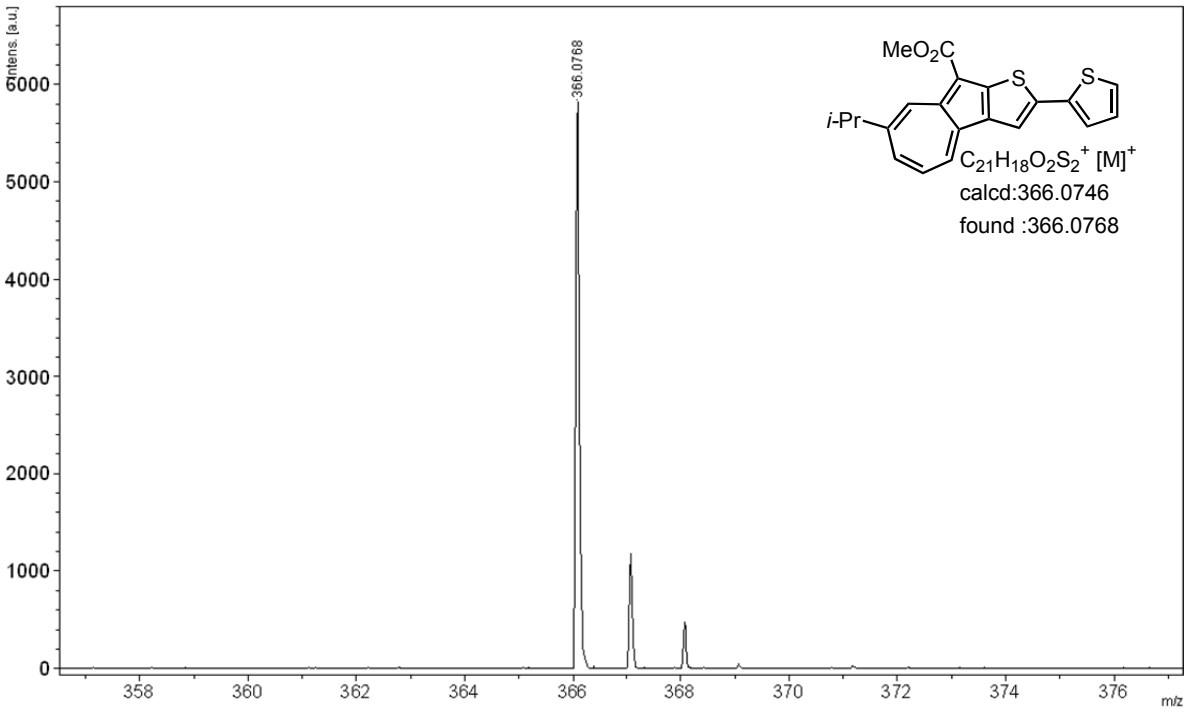


Figure S64. HRMS (MALDI-TOF, positive) of **17a**.

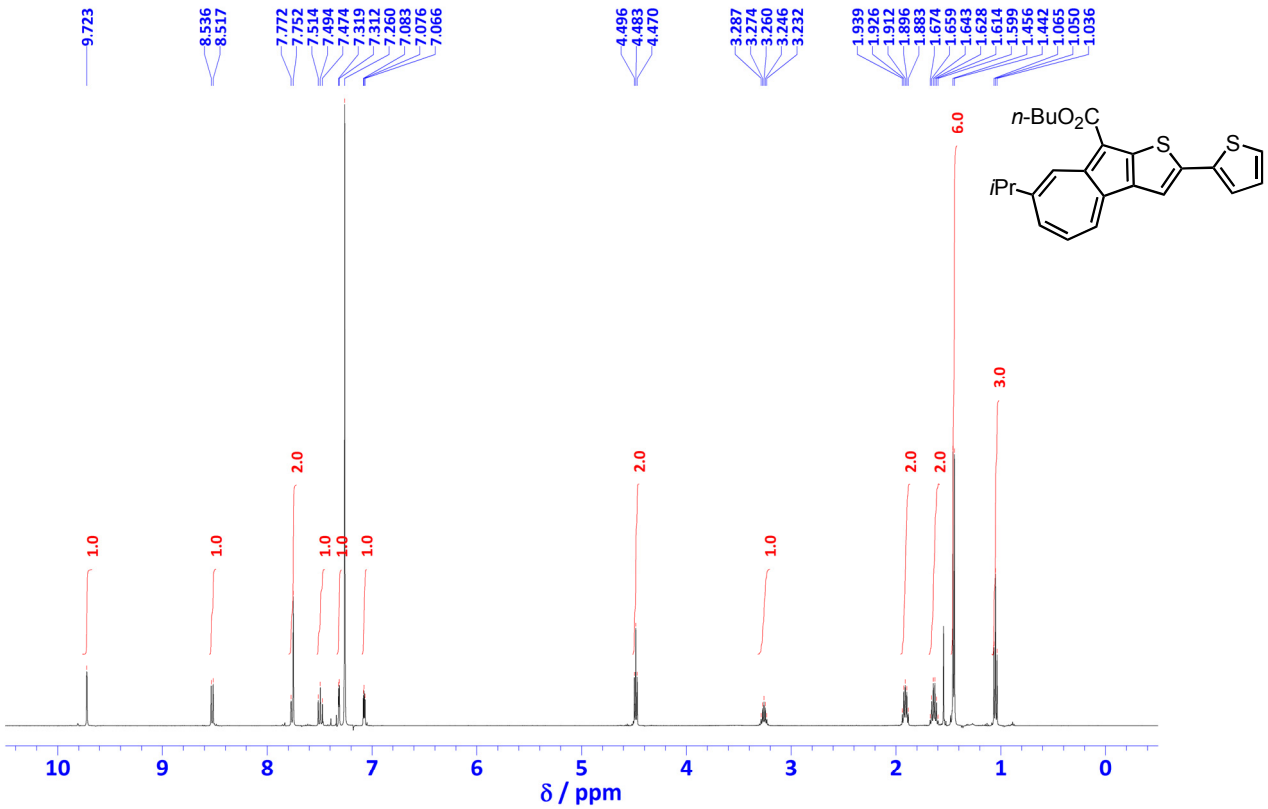


Figure S65. ^{1}H NMR spectrum of **17b** in $CDCl_3$ (500 MHz).

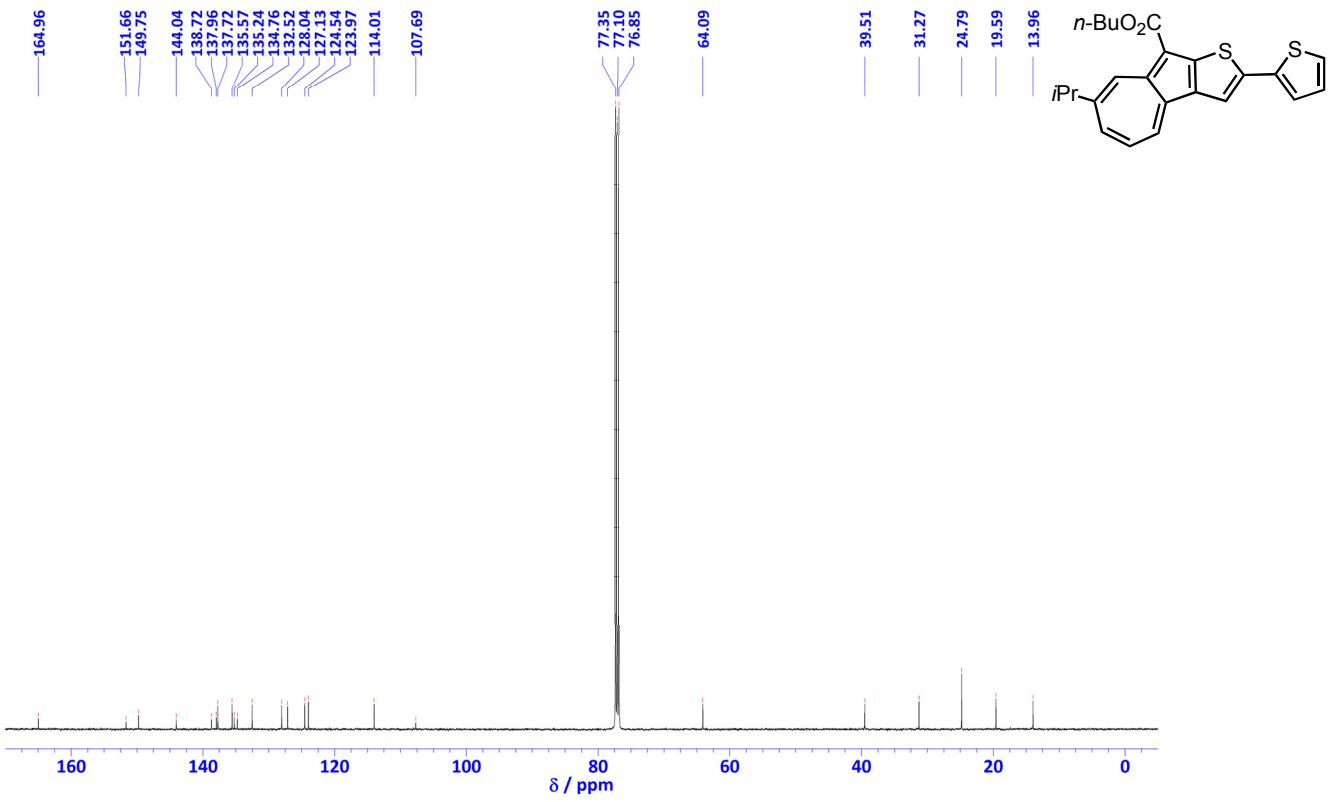


Figure S66. ^{13}C NMR spectrum of **17b** in $CDCl_3$ (125 MHz).

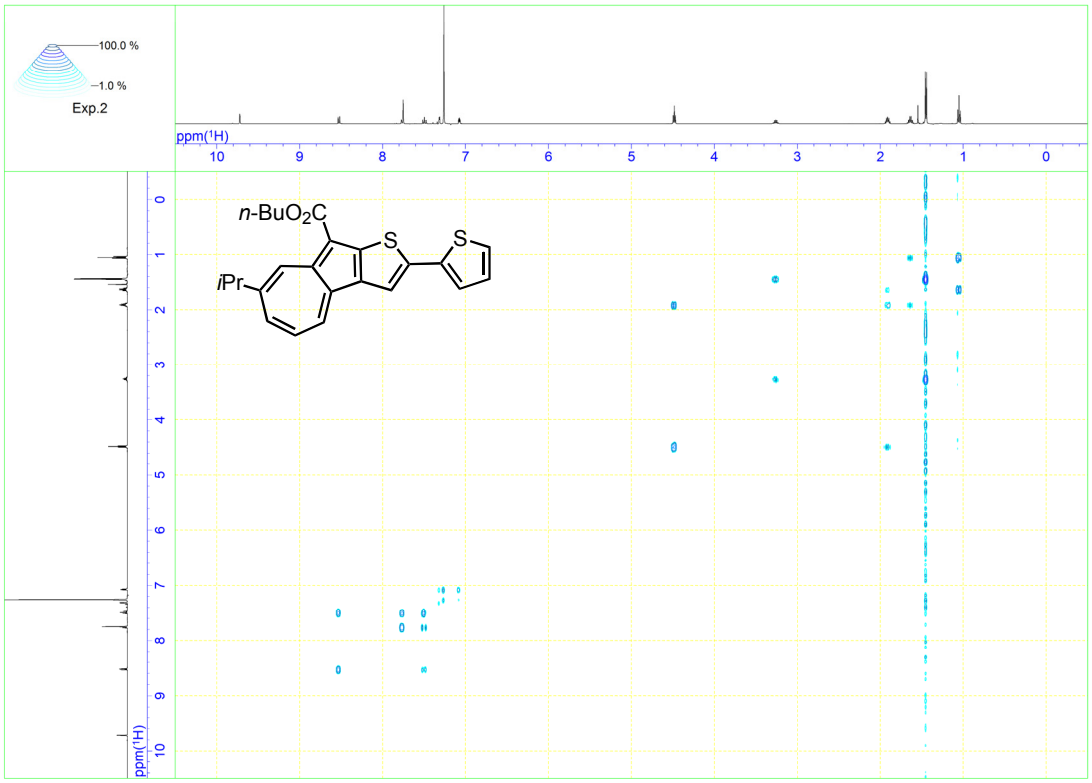


Figure S67. COSY spectrum of **17b** in $CDCl_3$ (500 MHz).

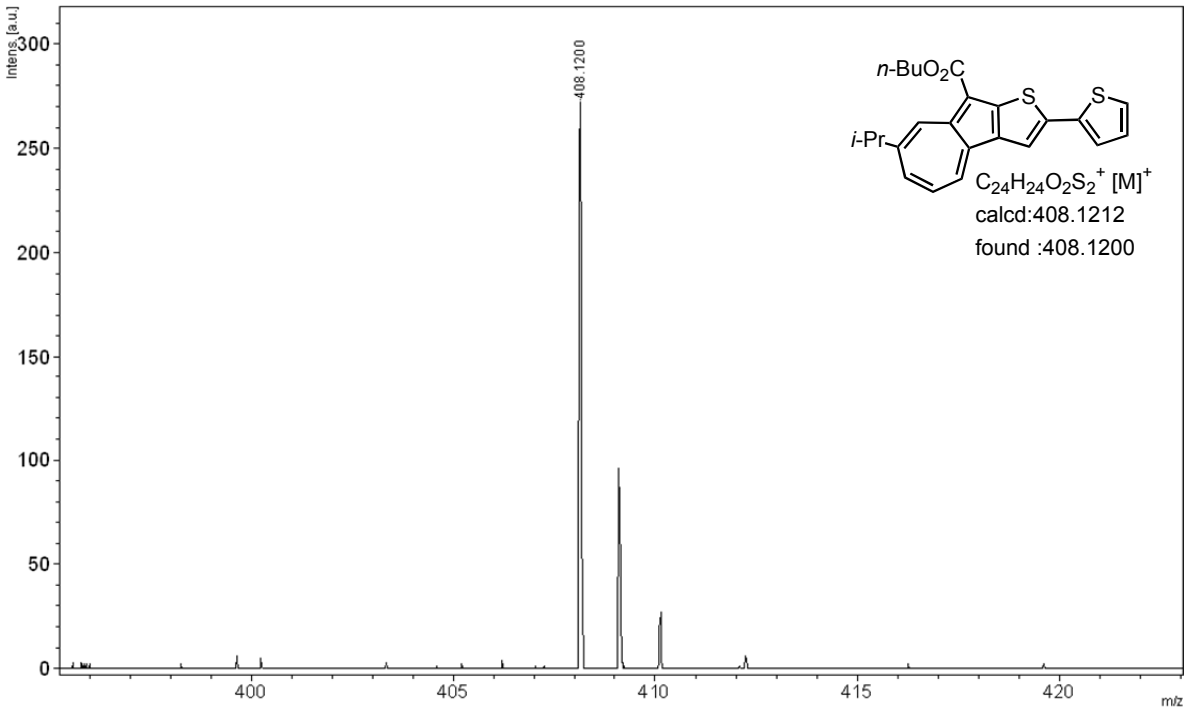


Figure S68. HRMS (MALDI-TOF, positive) of **17b**.

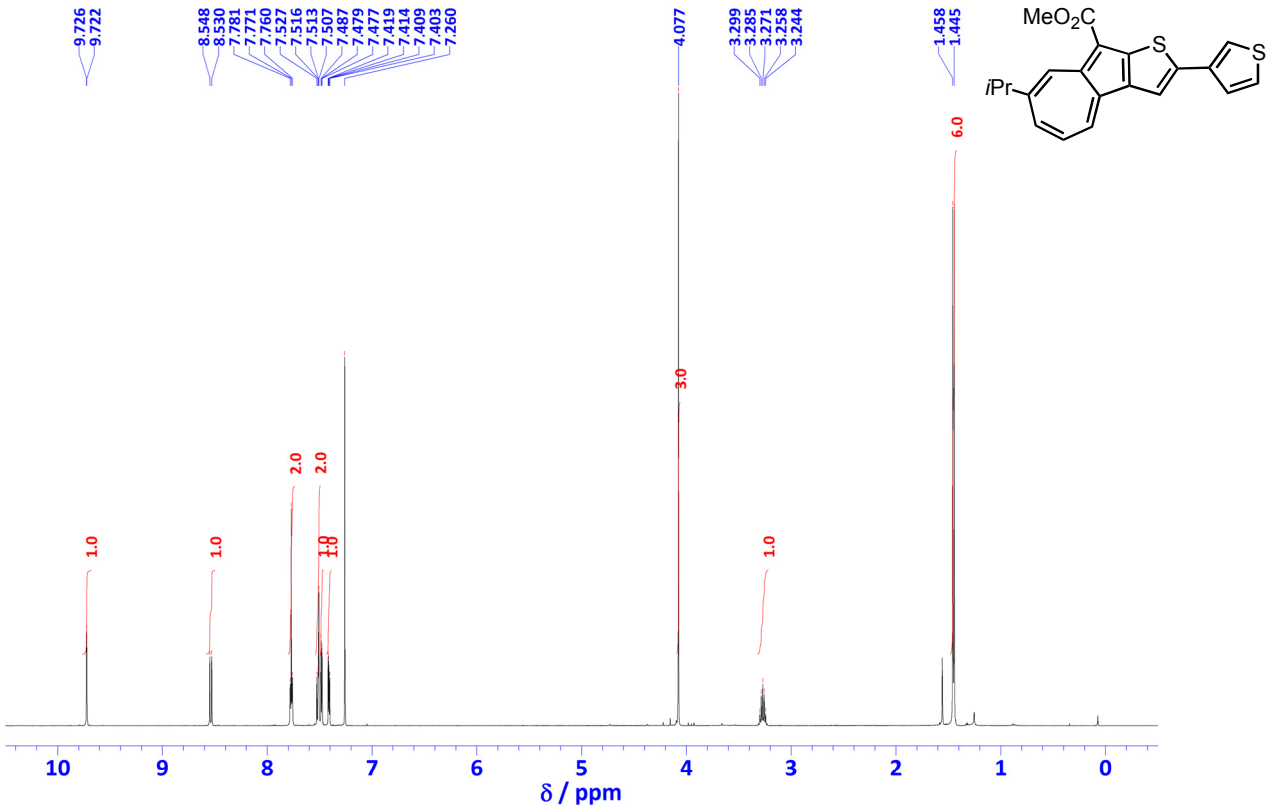


Figure S69. ^{1}H NMR spectrum of **18a** in $CDCl_3$ (500 MHz).

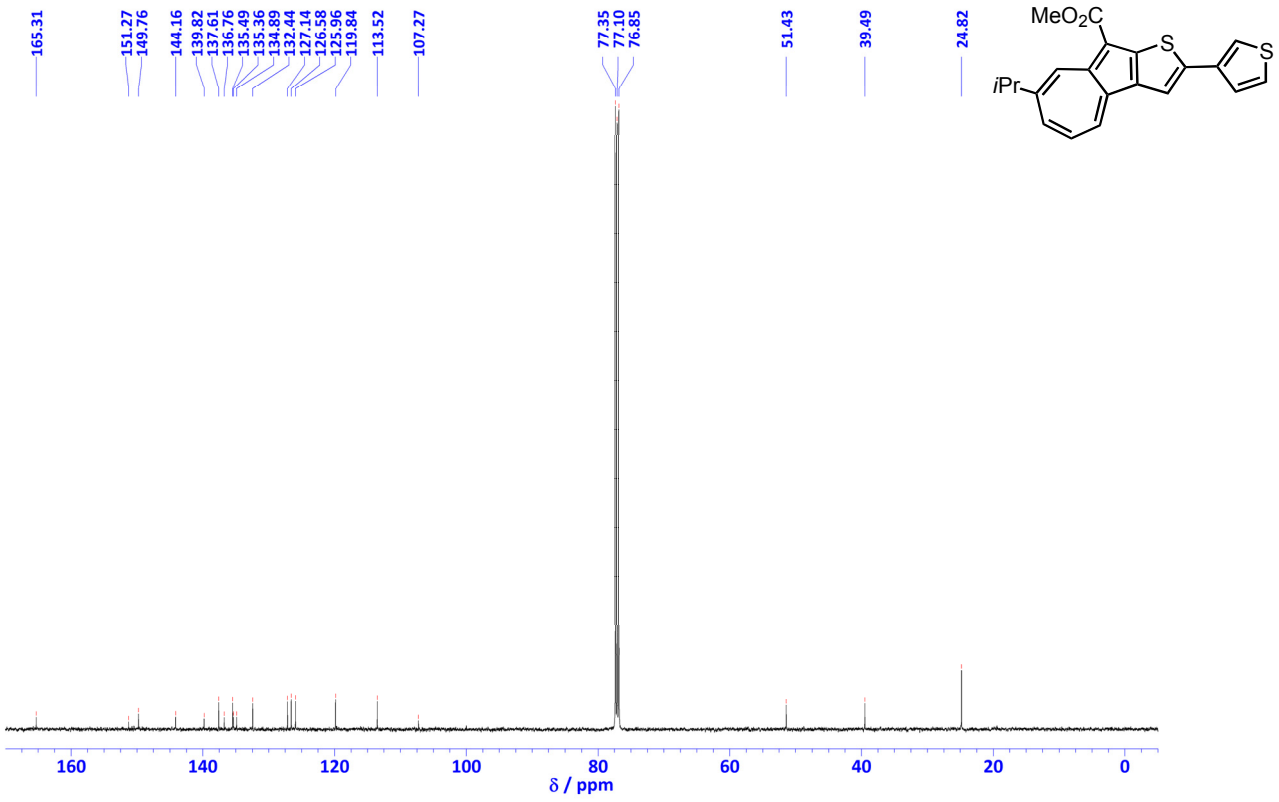


Figure S70. ^{13}C NMR spectrum of **18a** in $CDCl_3$ (125 MHz).

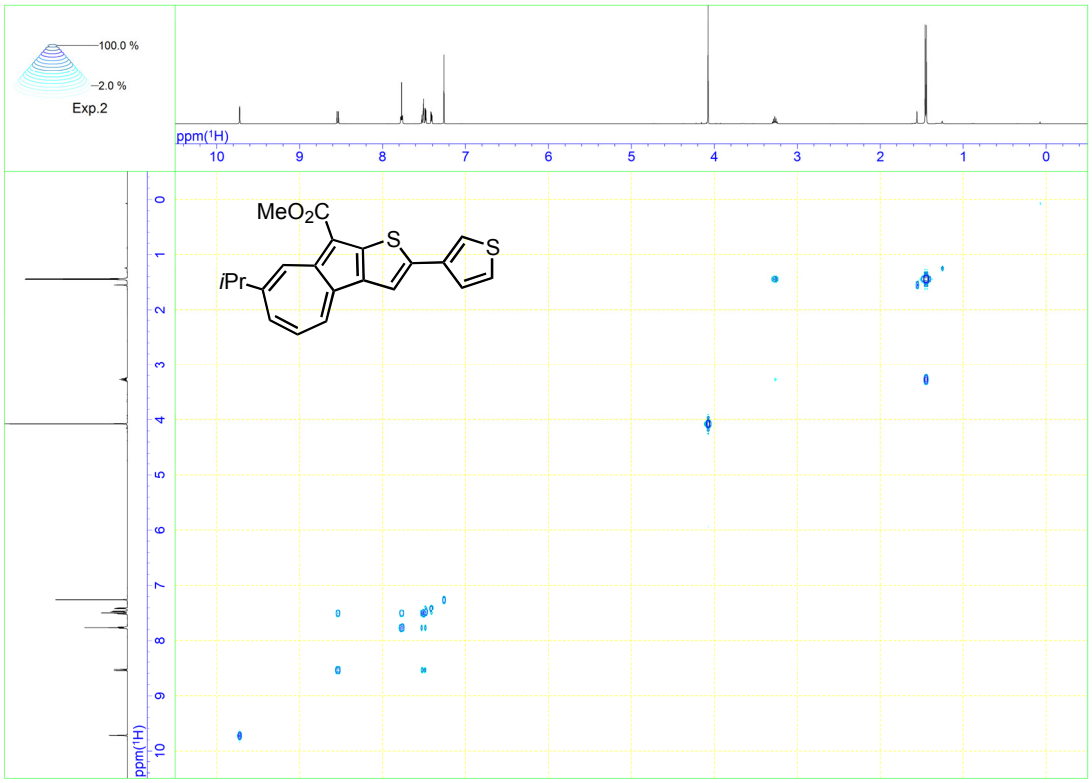


Figure S71. COSY spectrum of **18a** in $CDCl_3$ (500 MHz).

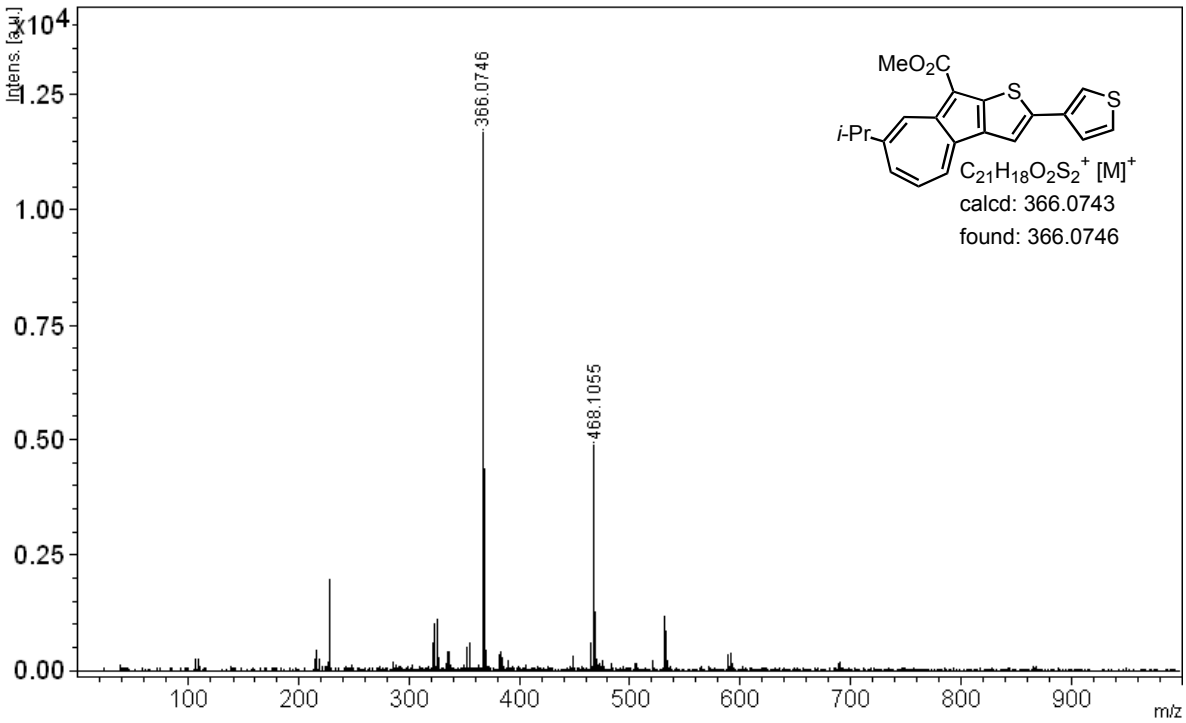


Figure S72. HRMS (MALDI-TOF, positive) of **18a**.

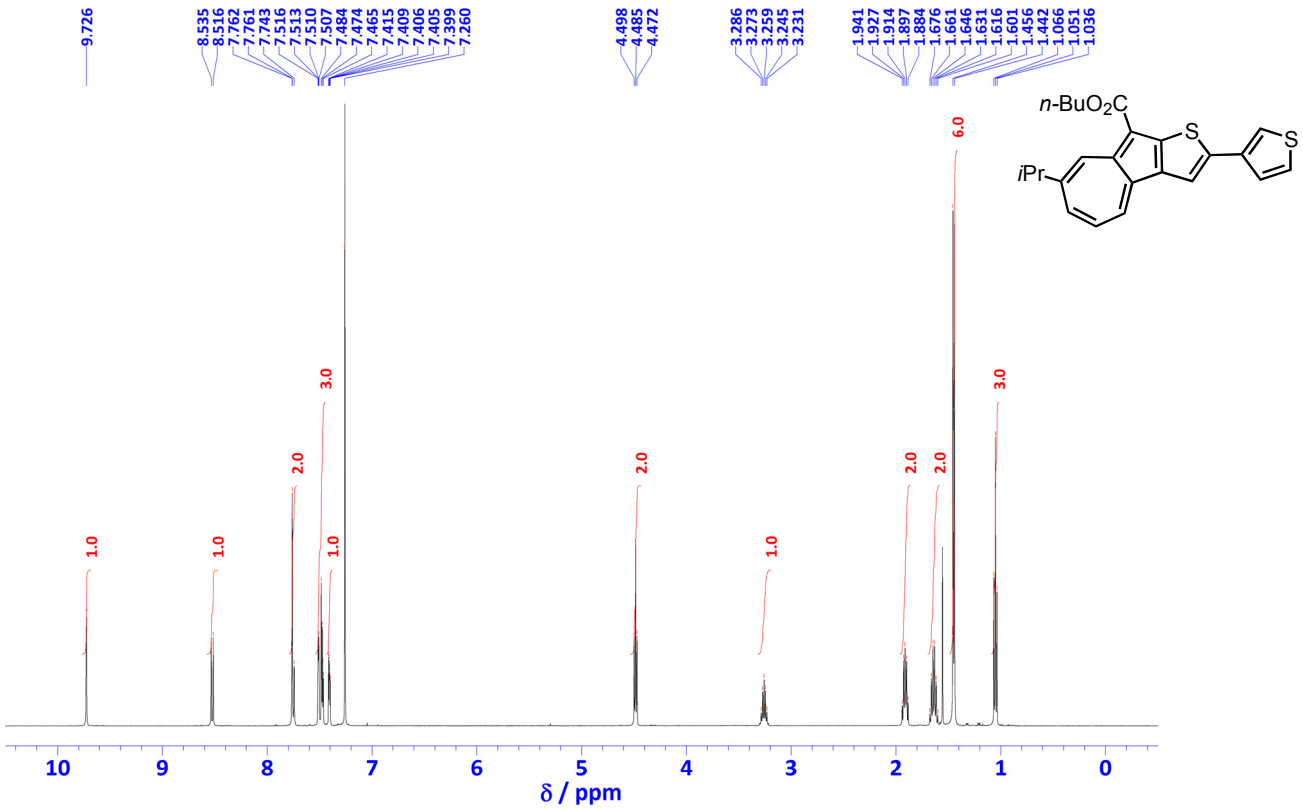


Figure S73. ^{1}H NMR spectrum of **18b** in $CDCl_3$ (500 MHz).

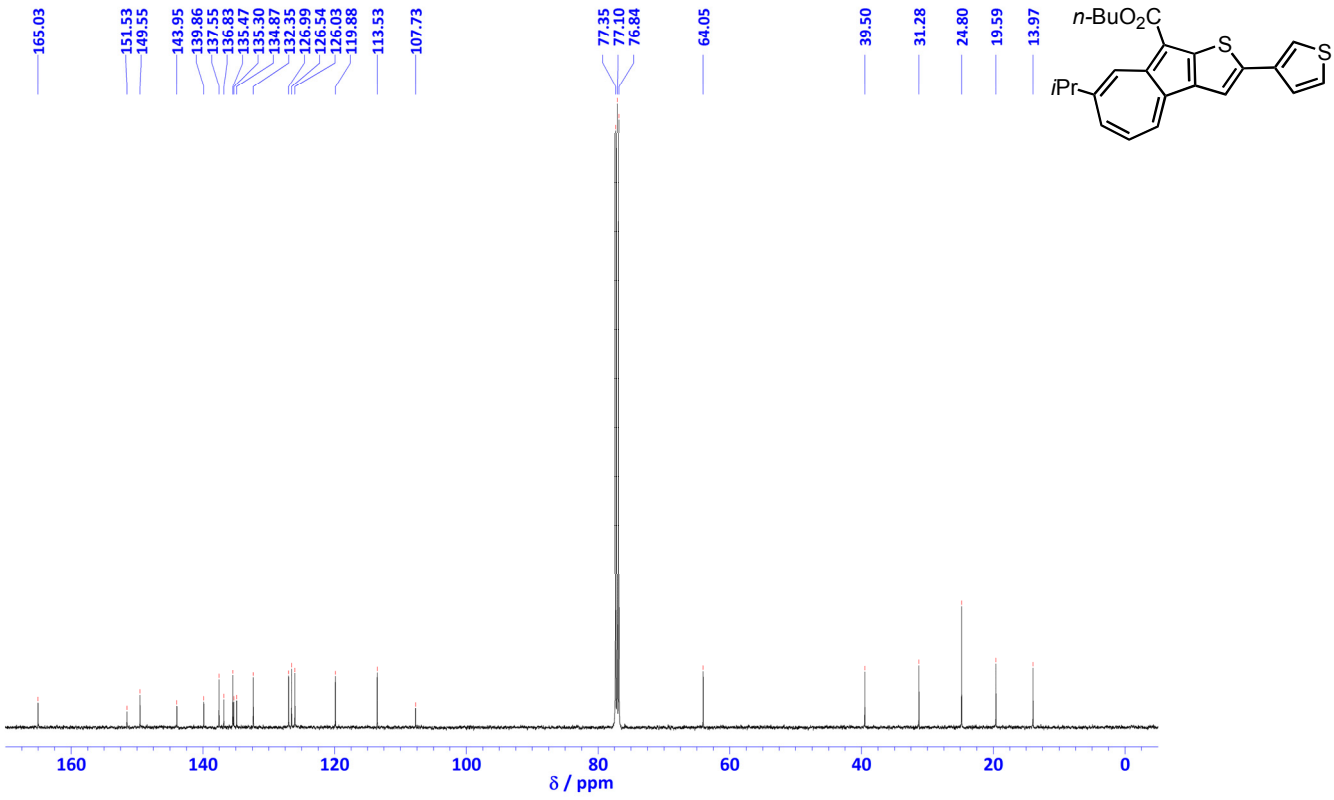


Figure S74. ^{13}C NMR spectrum of **18b** in $CDCl_3$ (125 MHz).

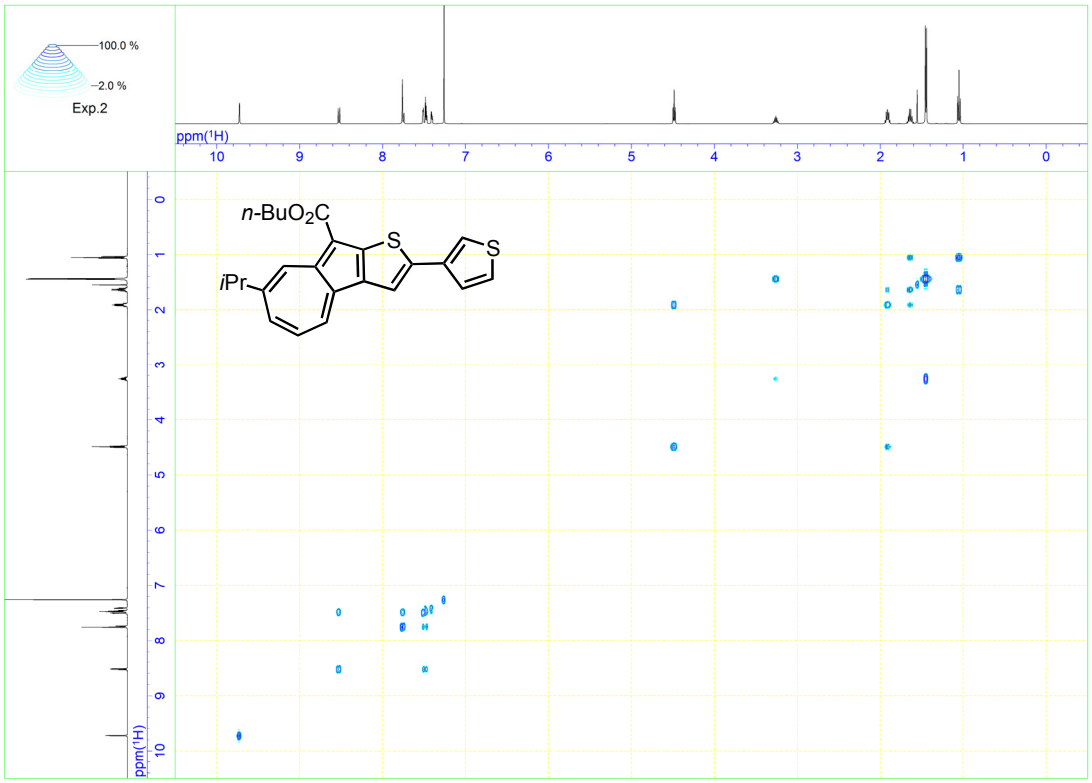


Figure S75. COSY spectrum of **18b** in $CDCl_3$ (500 MHz).

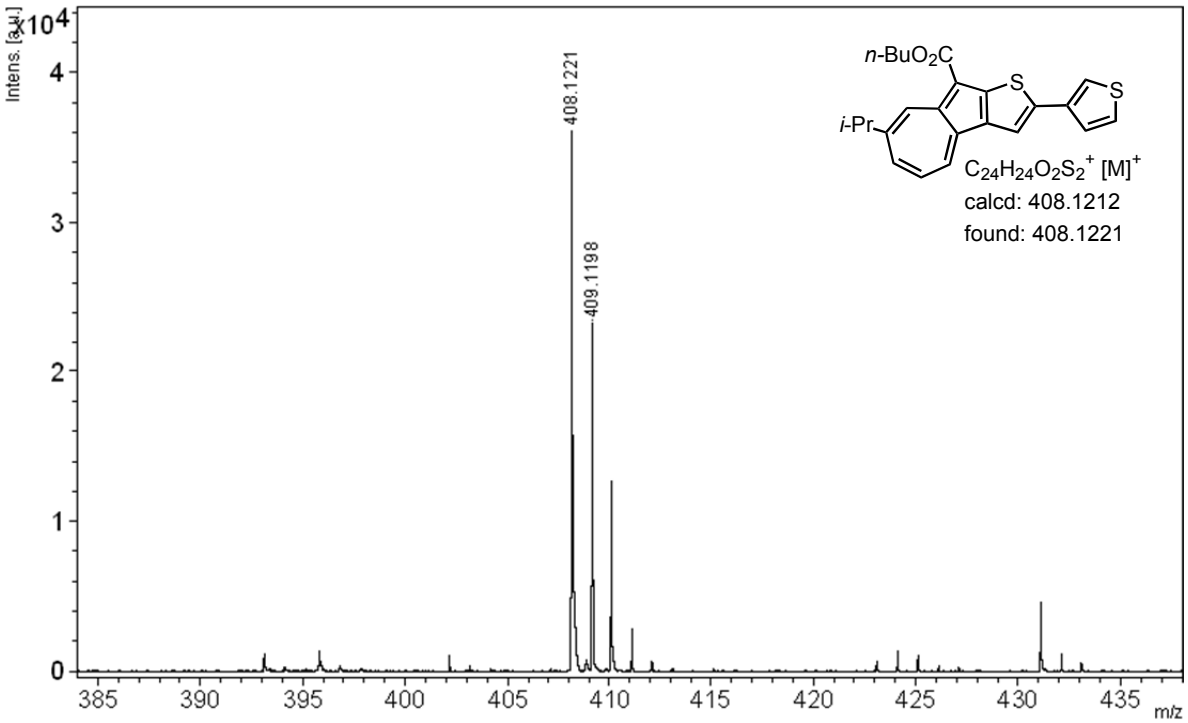


Figure S76. HRMS (MALDI-TOF, positive) of **18b**.

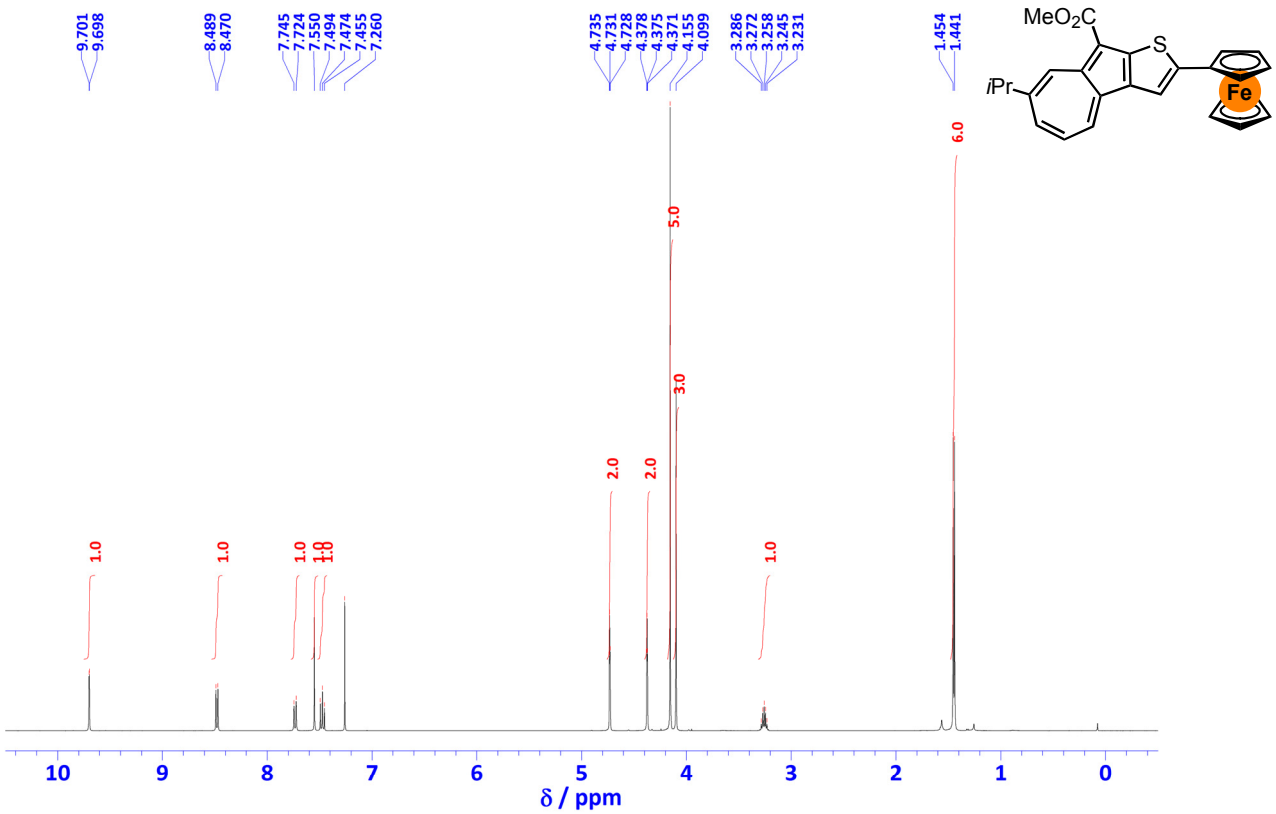


Figure S77. ^{1}H NMR spectrum of **19a** in $CDCl_3$ (500 MHz).

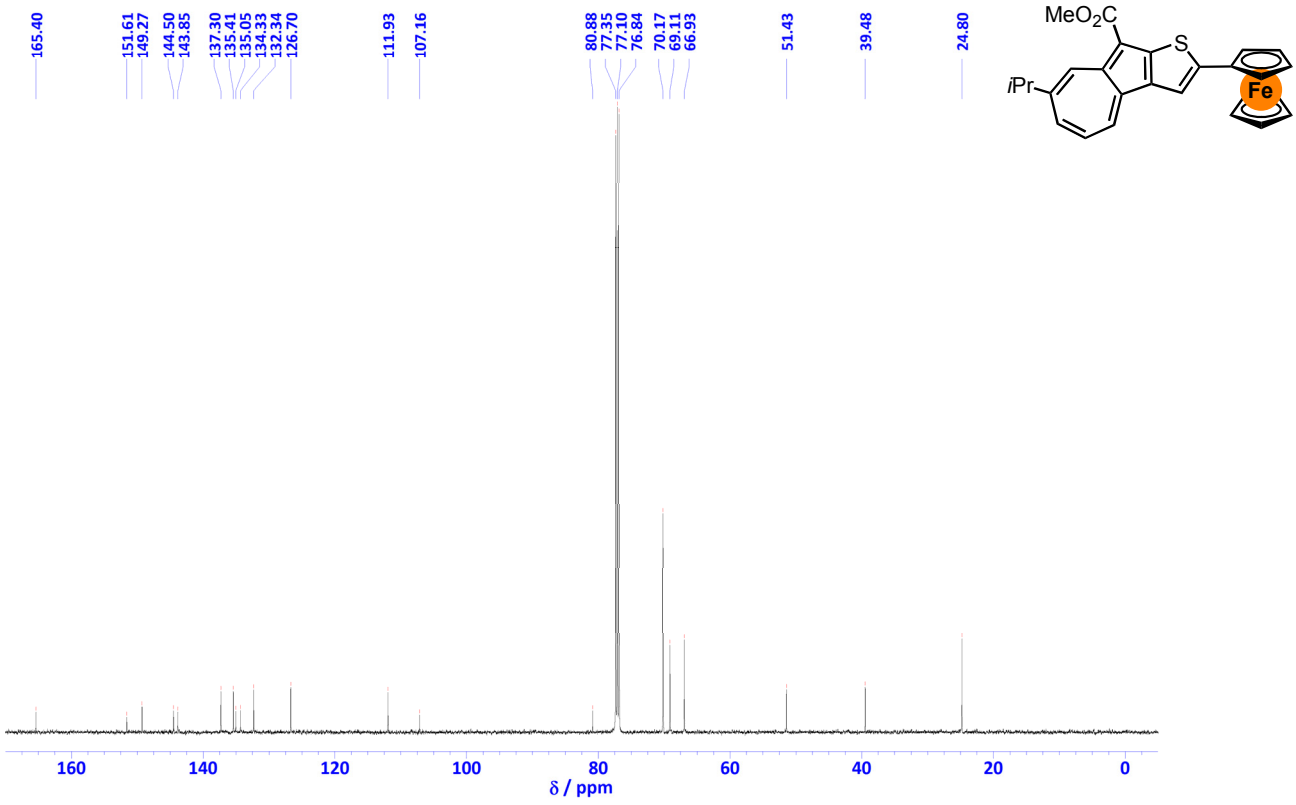


Figure S78. ^{13}C NMR spectrum of **19a** in $CDCl_3$ (125 MHz).

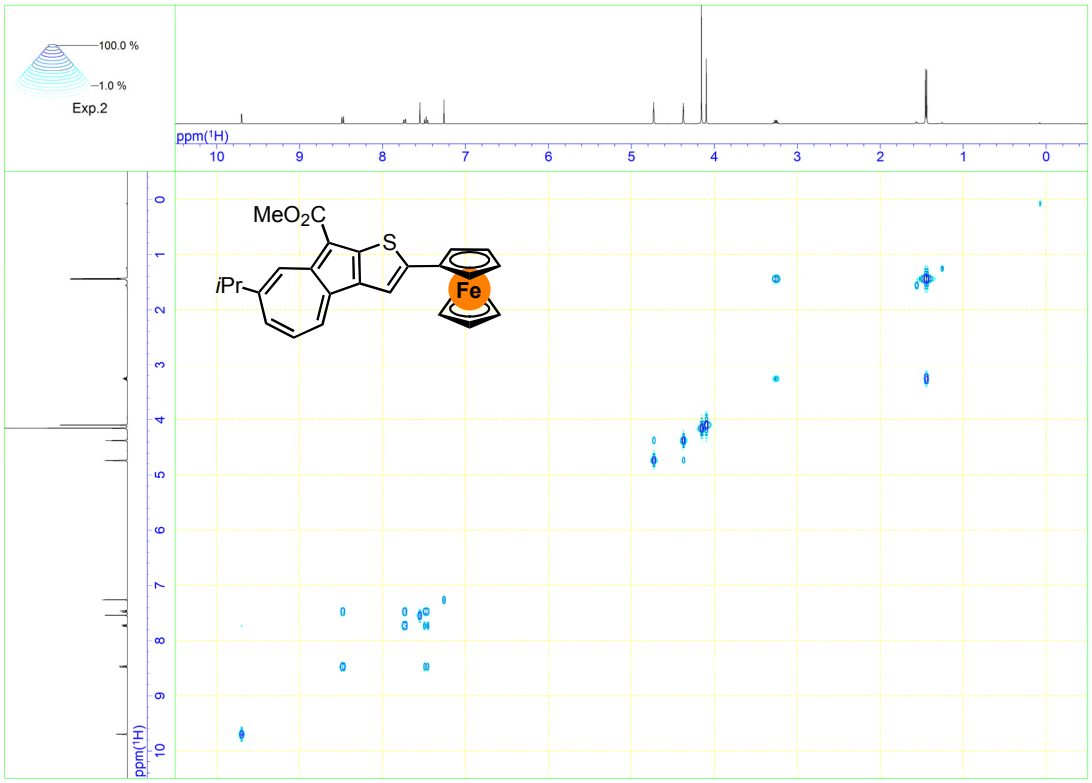


Figure S79. COSY spectrum of **19a** in $CDCl_3$ (500 MHz).

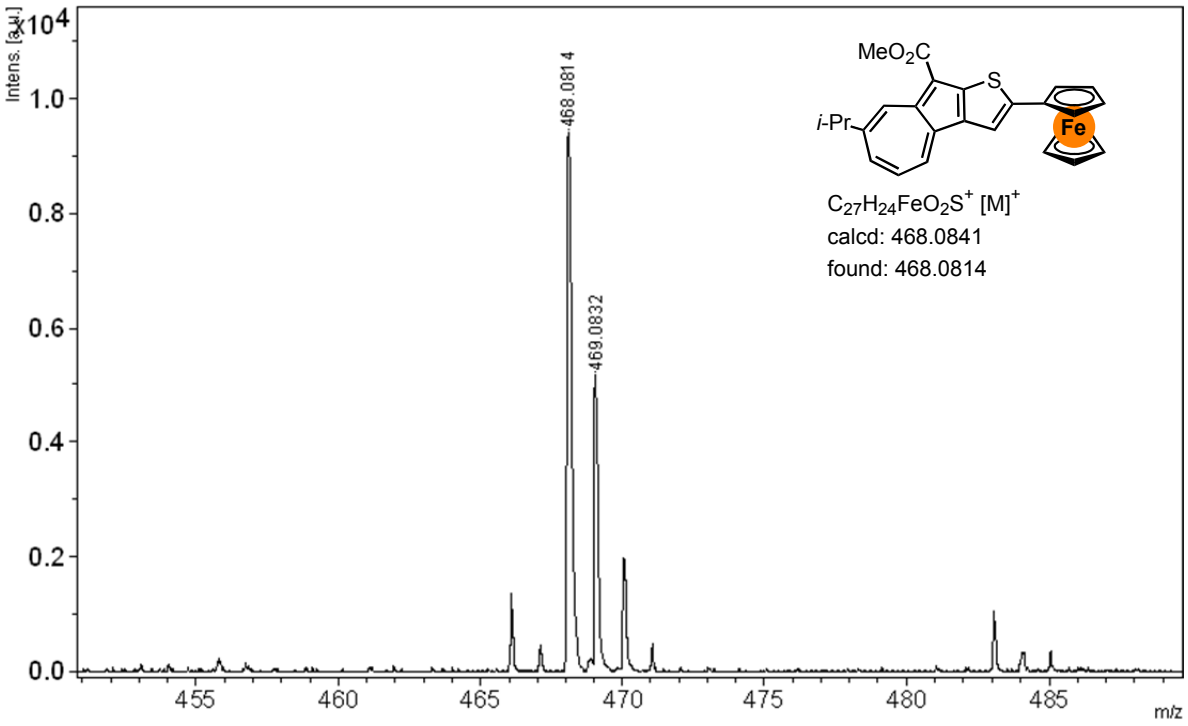


Figure S80. HRMS (MALDI-TOF, positive) of **19a**.

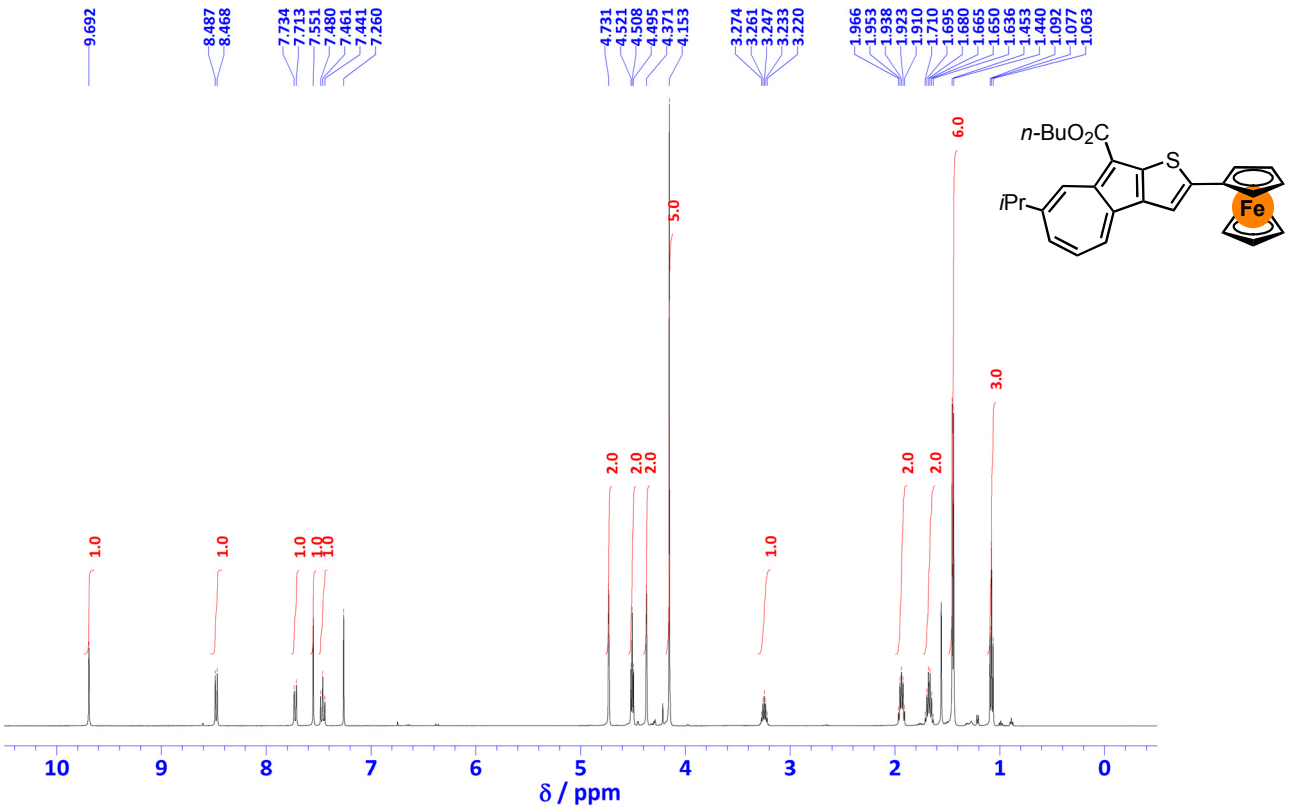


Figure S81. ^{1}H NMR spectrum of **19b** in $CDCl_3$ (500 MHz).

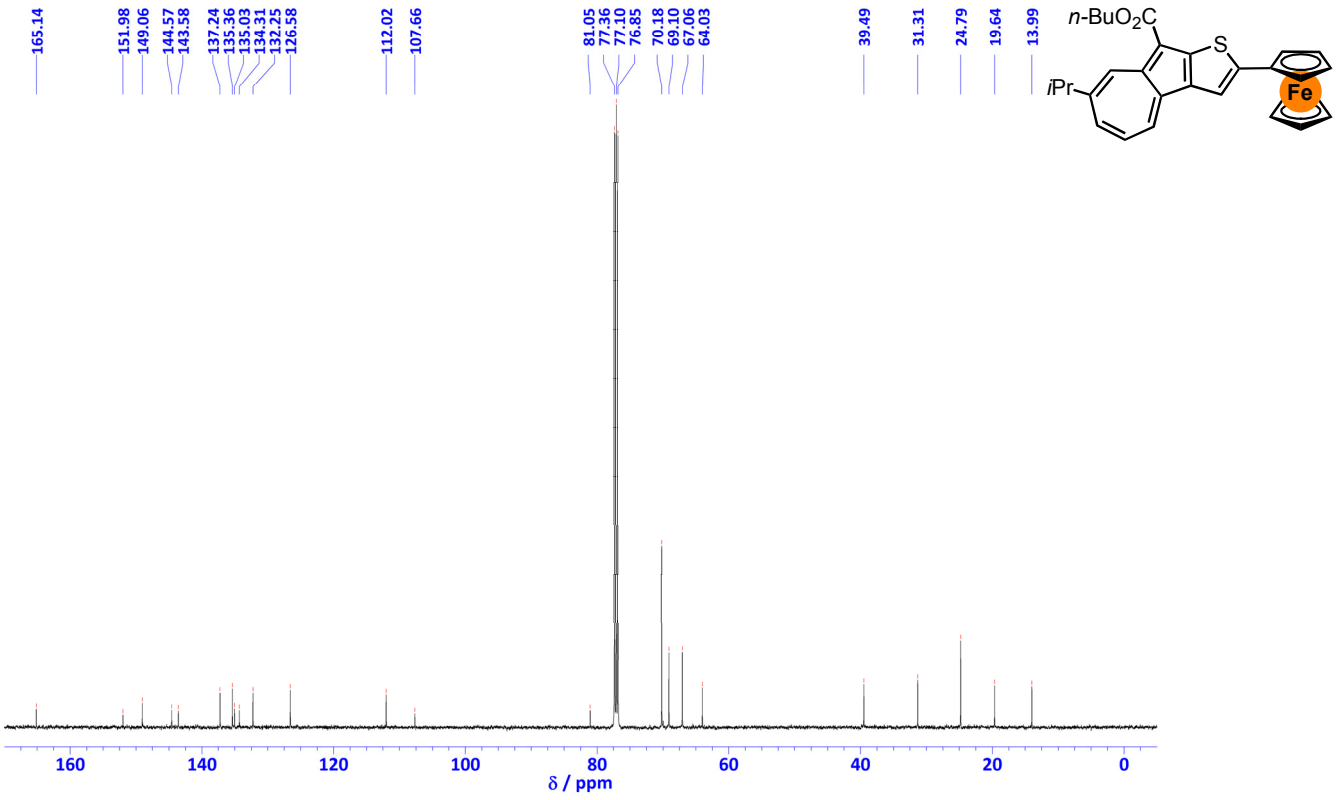


Figure S82. ^{13}C NMR spectrum of **19b** in $CDCl_3$ (125 MHz).

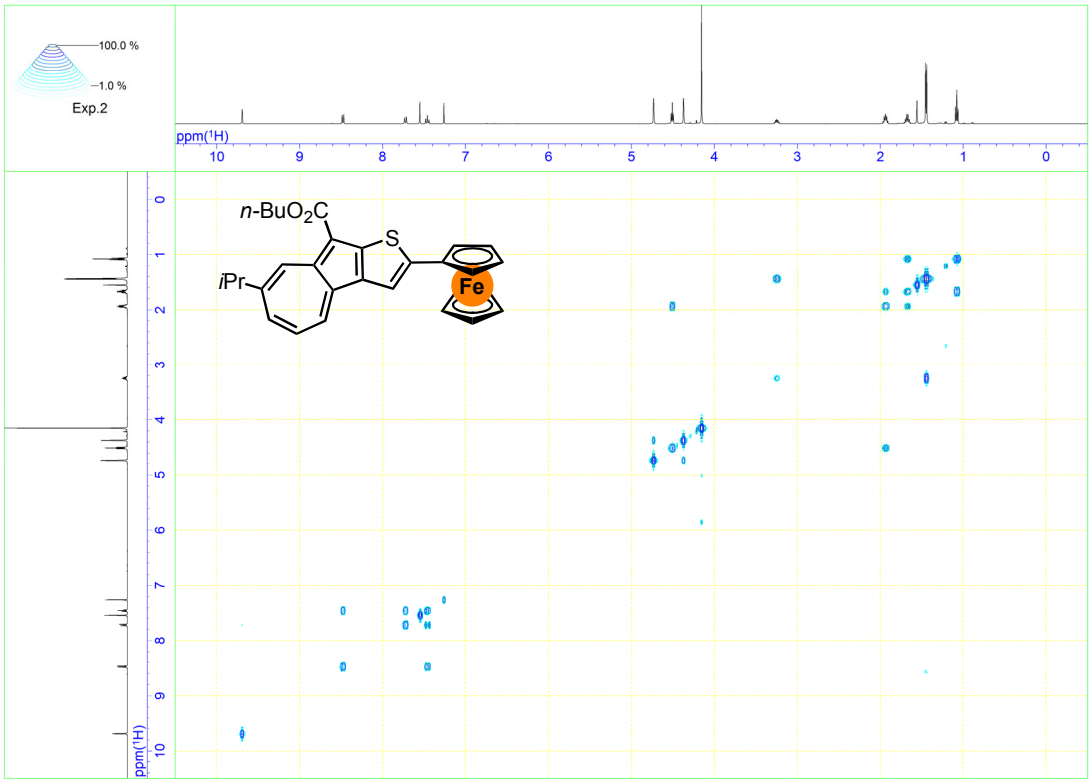


Figure S83. COSY spectrum of **19b** in $CDCl_3$ (500 MHz).

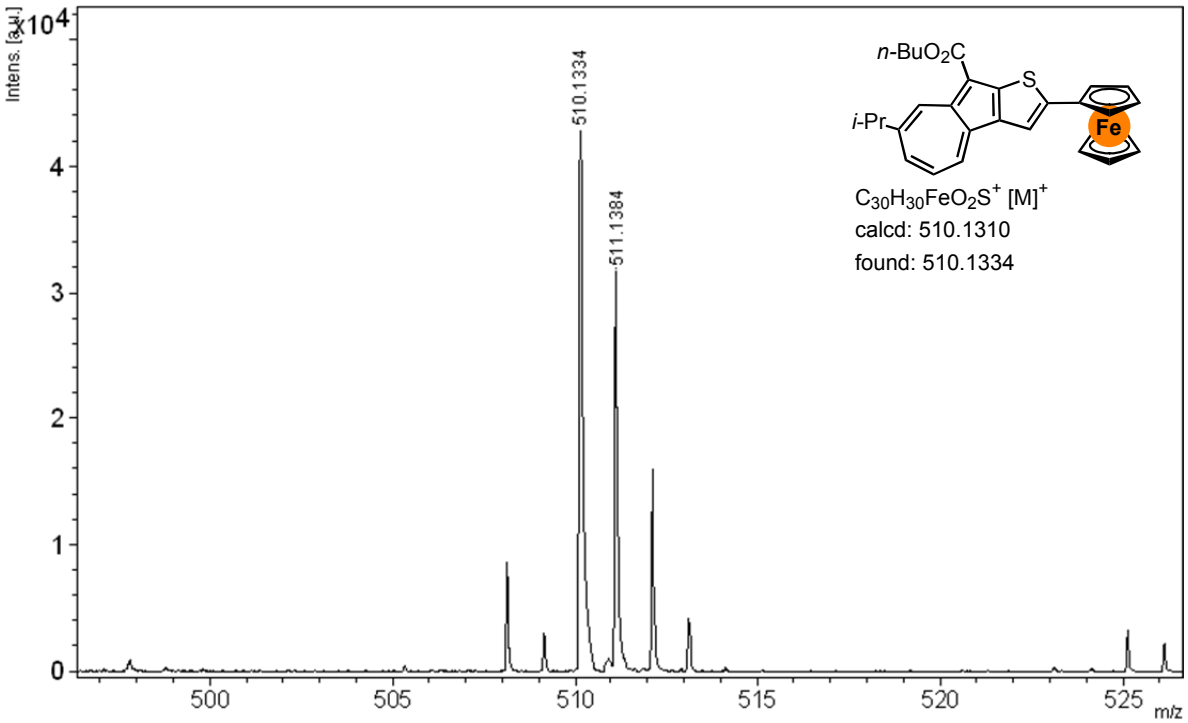


Figure S84. HRMS (MALDI-TOF, positive) of **19b**.

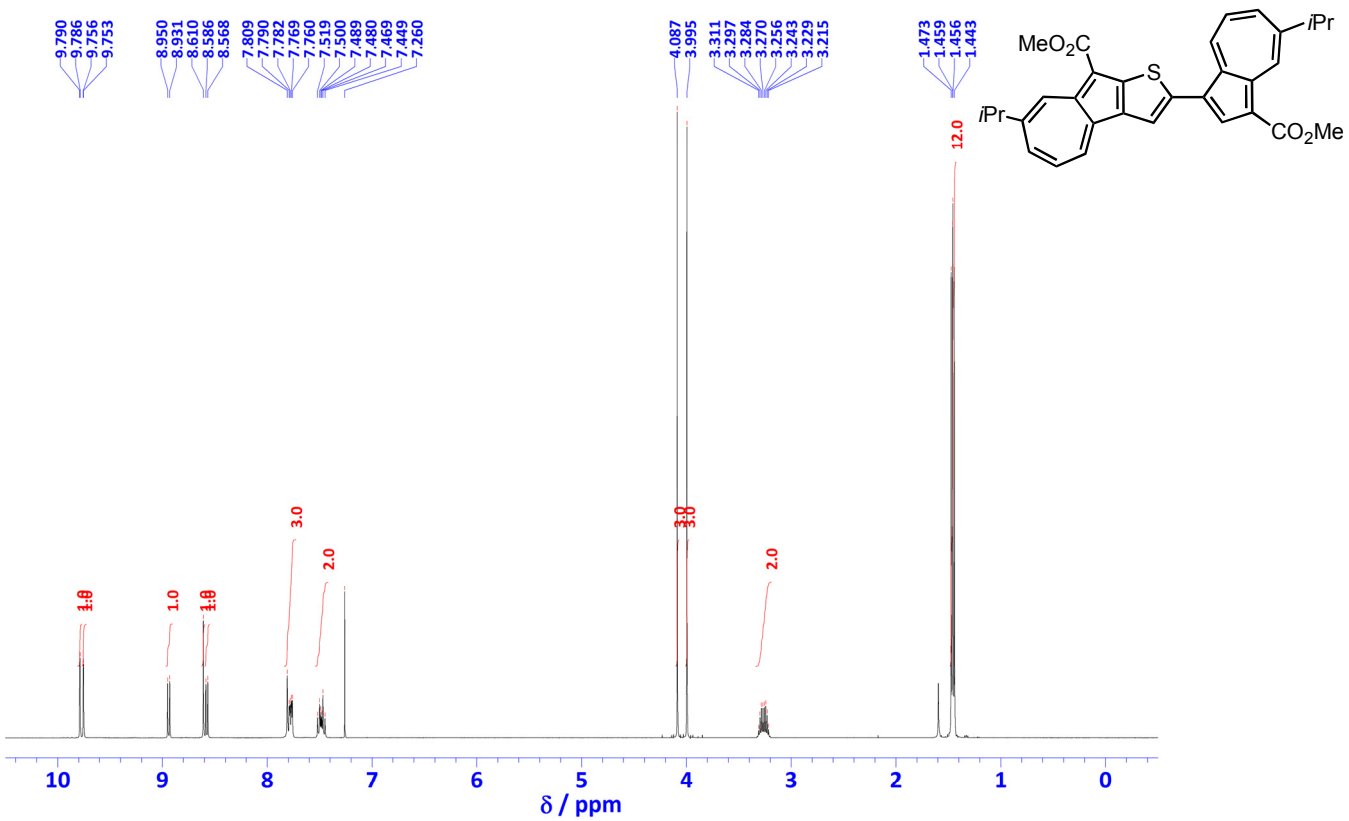


Figure S85. ^{1}H NMR spectrum of **20** in $CDCl_3$ (500 MHz).

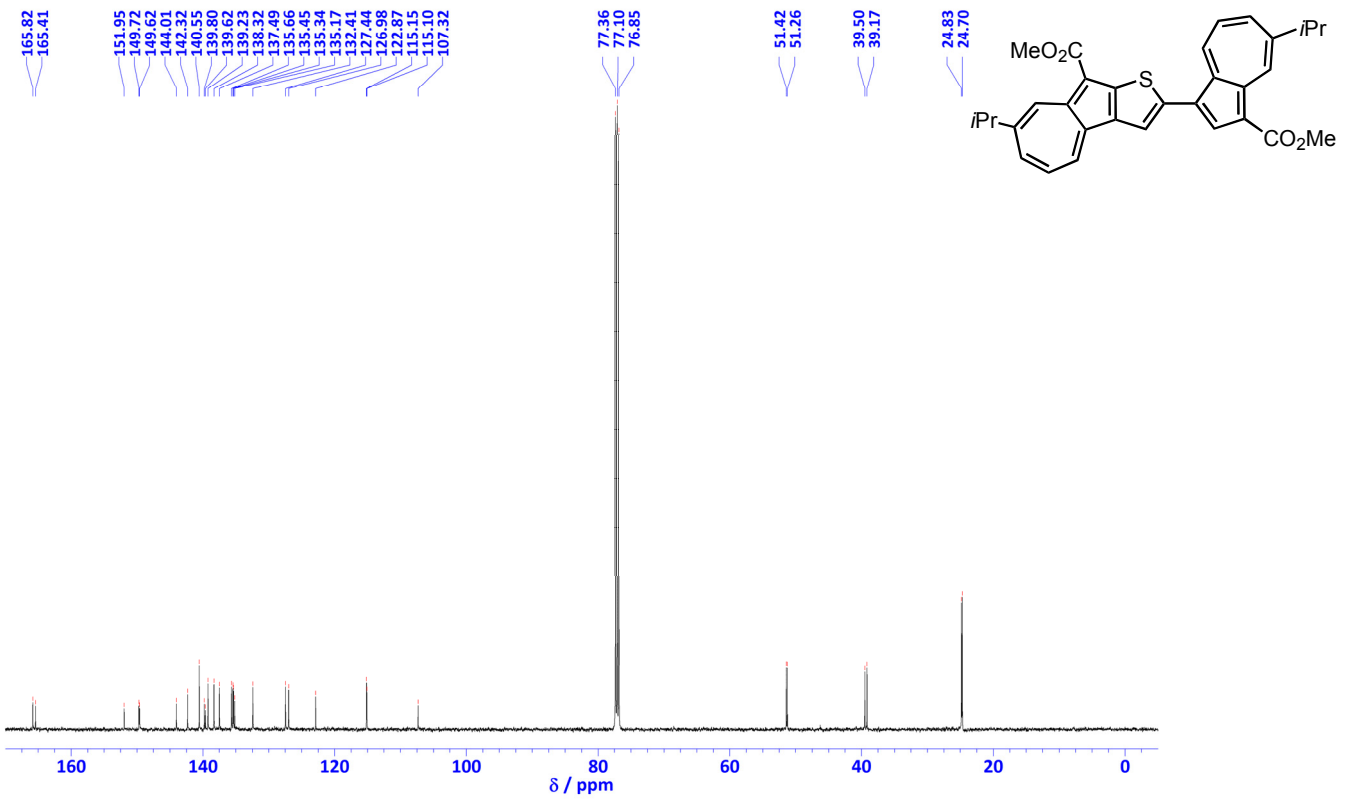


Figure S86. ^{13}C NMR spectrum of **20** in $CDCl_3$ (125 MHz).

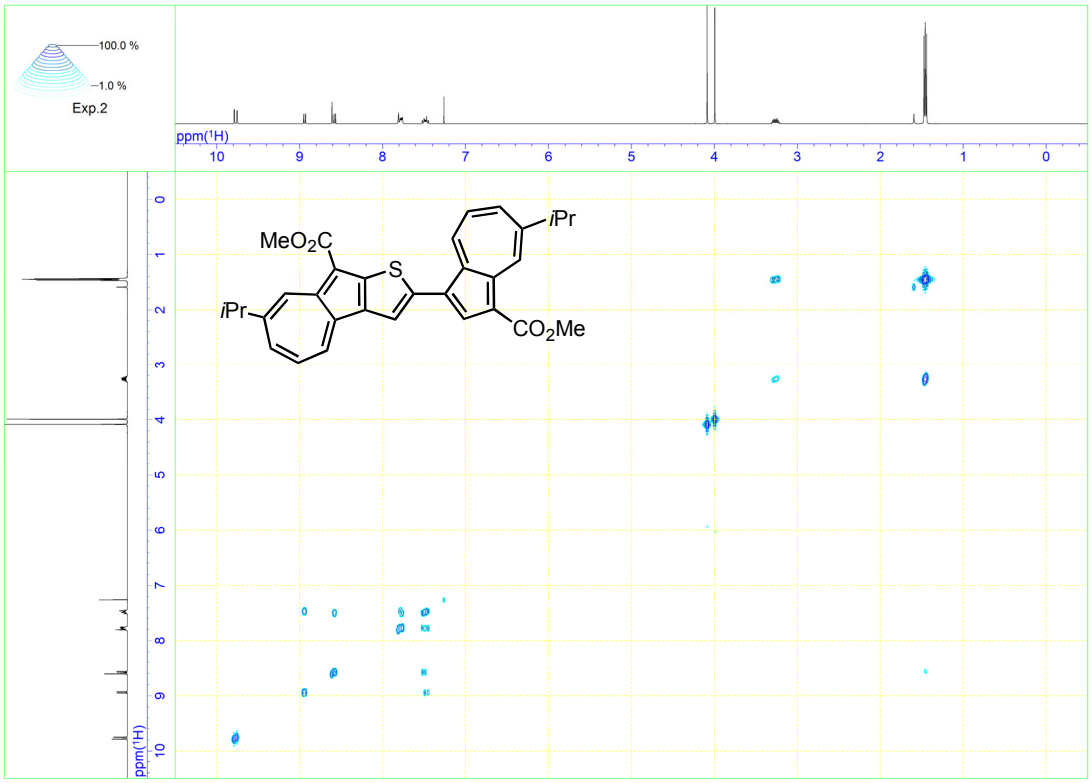


Figure S87. COSY spectrum of **20** in $CDCl_3$ (500 MHz).

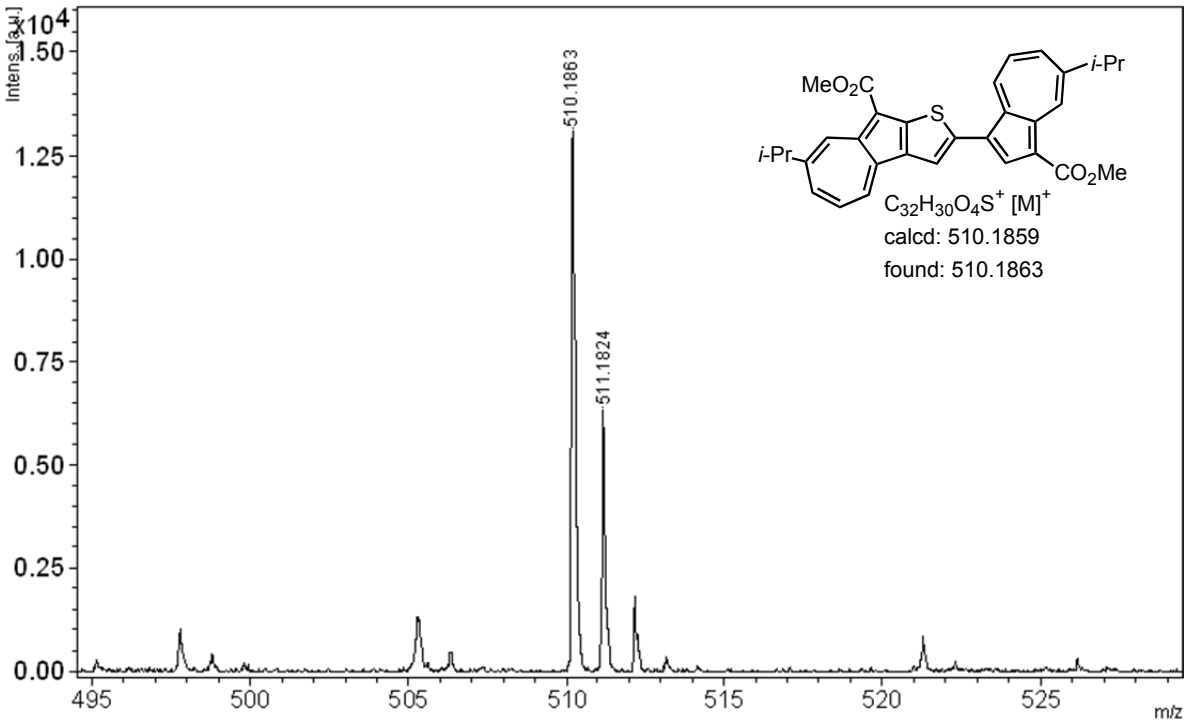


Figure S88. HRMS (MALDI-TOF, positive) of **20**.

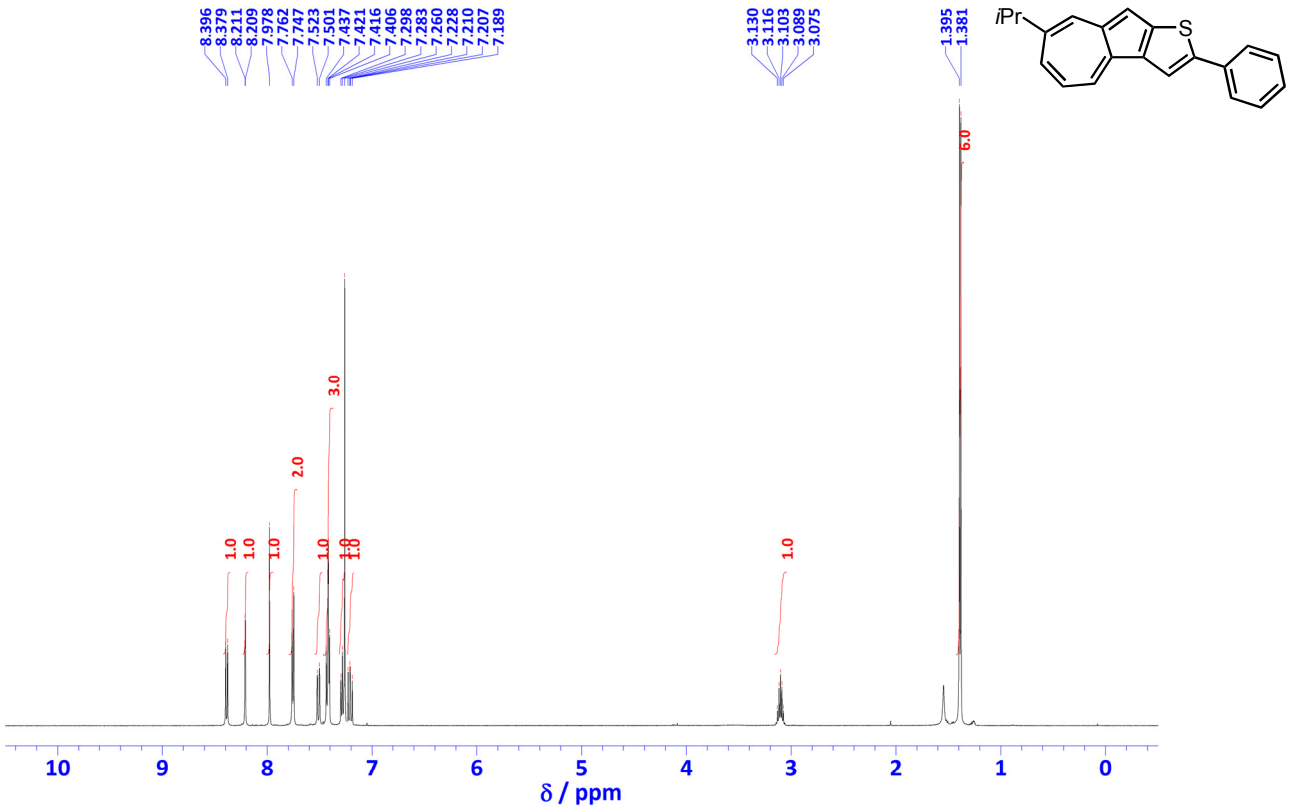


Figure S89. ^{1}H NMR spectrum of **21** in $CDCl_3$ (500 MHz).

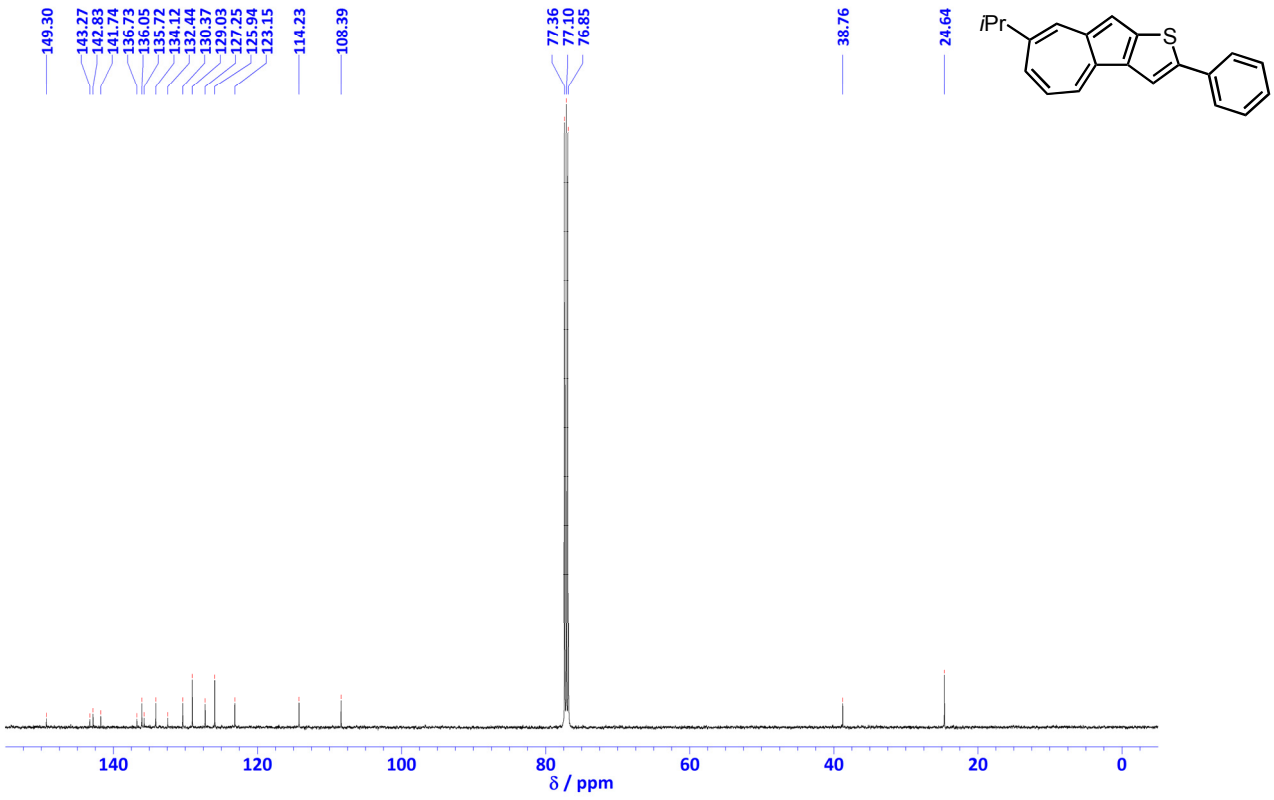


Figure S90. ^{13}C NMR spectrum of **21** in $CDCl_3$ (125 MHz).

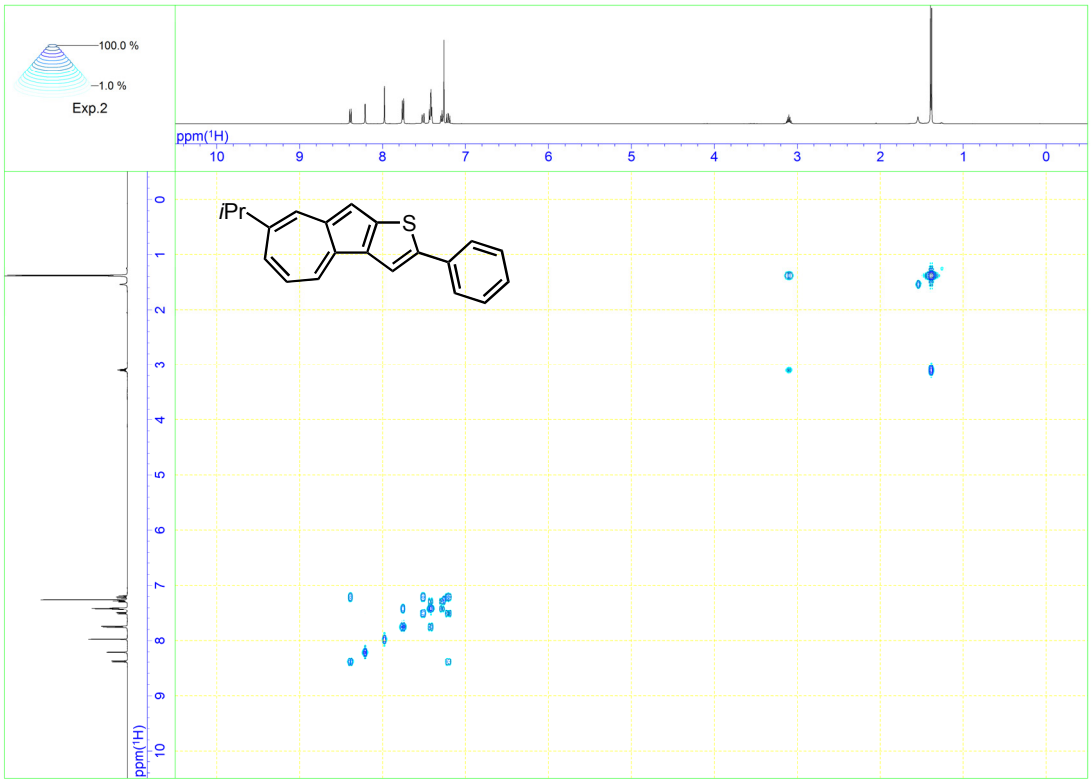


Figure S91. COSY spectrum of **21** in $CDCl_3$ (500 MHz).

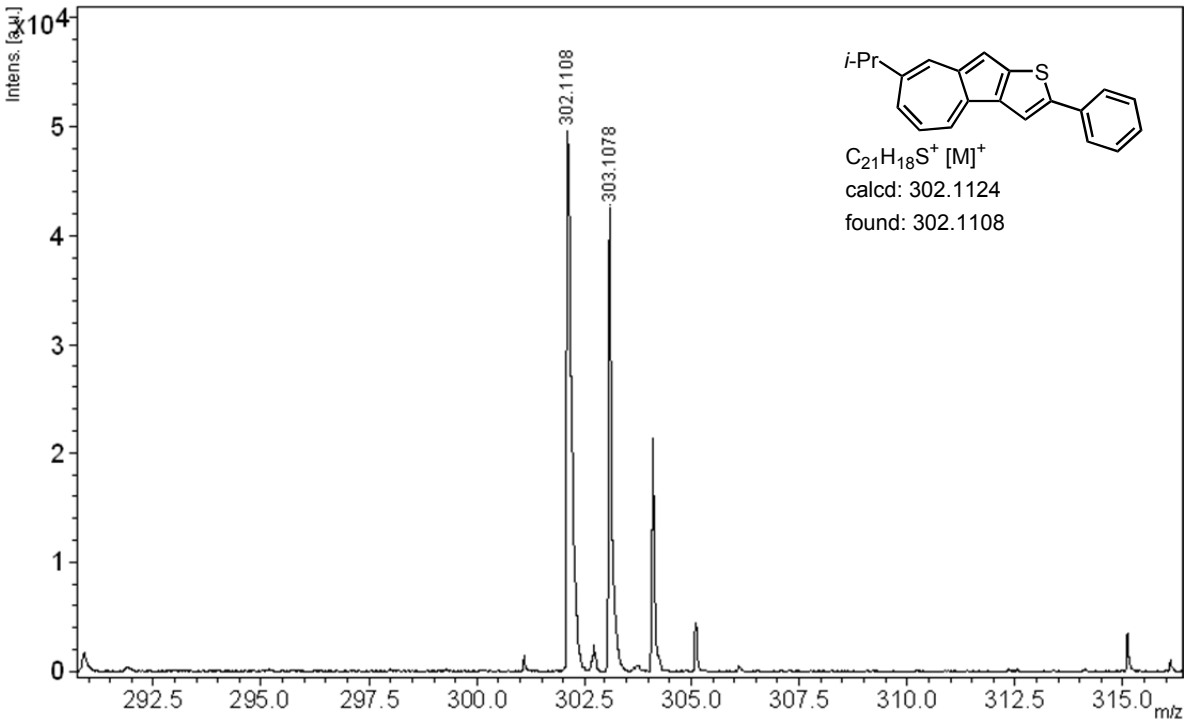


Figure S92. HRMS (MALDI-TOF, positive) of **21**.

2. UV/Vis spectra and continuous change in the visible spectra of 11−20 (Figures S93−S124).

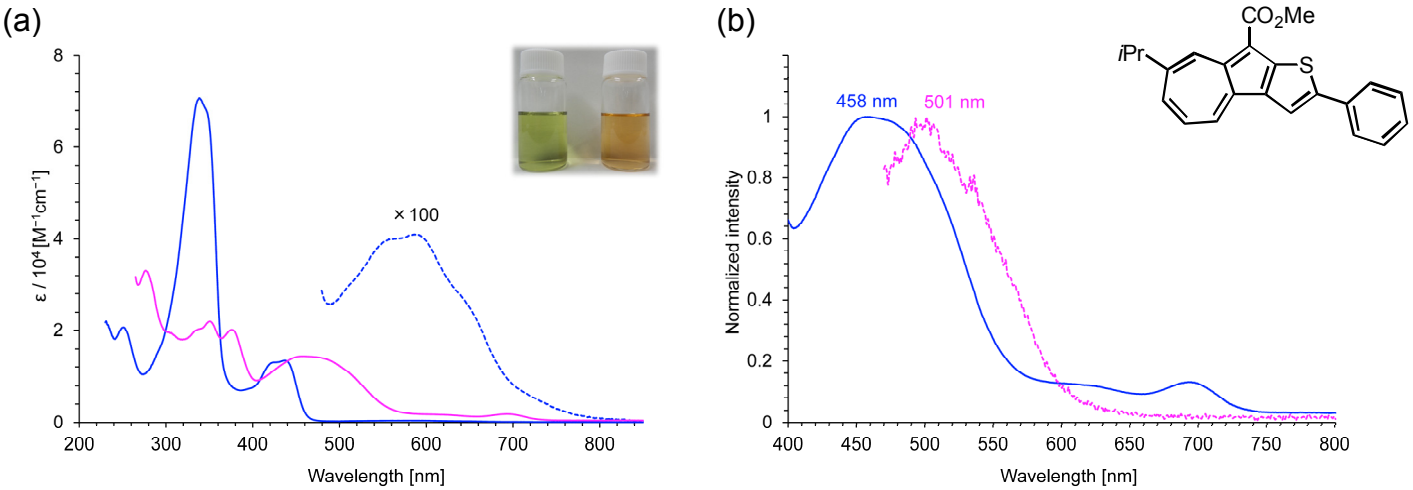


Figure S93. (a) UV/Vis spectra of **11** (blue line, left photo) in CH_2Cl_2 and in 30% CF_3CO_2H/CH_2Cl_2 (pink line, right photo); the dotted lines represent the magnification (×100) of the spectrum of **11** in the visible region. (b) UV/Vis spectrum (blue line) and fluorescence spectrum (pink dot-line) of **11** in 30% CF_3CO_2H/CH_2Cl_2.

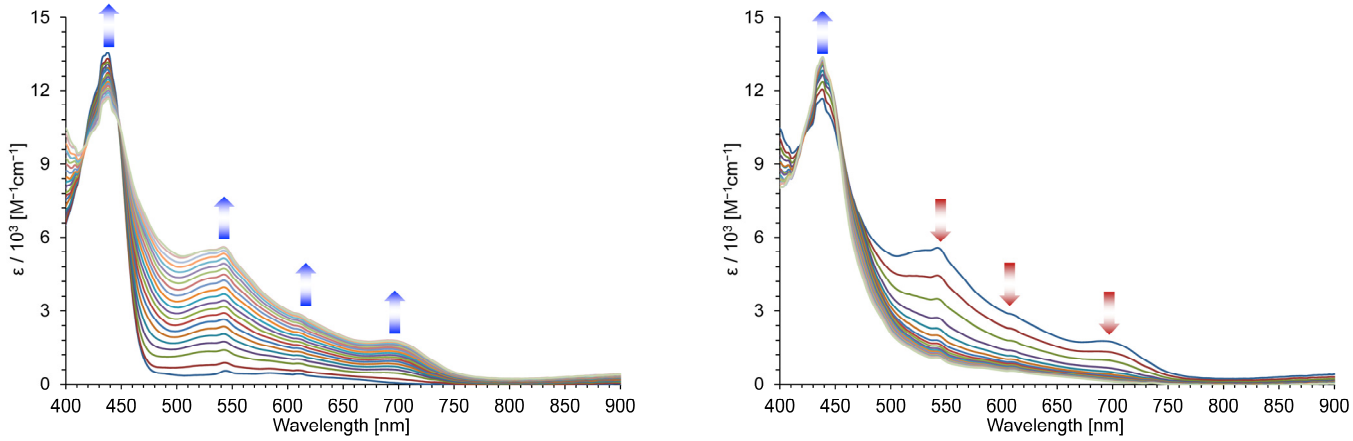


Figure S94. Continuous change in the visible spectrum of **11**: constant-voltage electrochemical oxidation at +0.85 V (left) and reduction of the oxidized species at ±0.00 V (right) in benzonitrile containing Et_4NClO_4 (0.1 M) at 20 sec intervals.

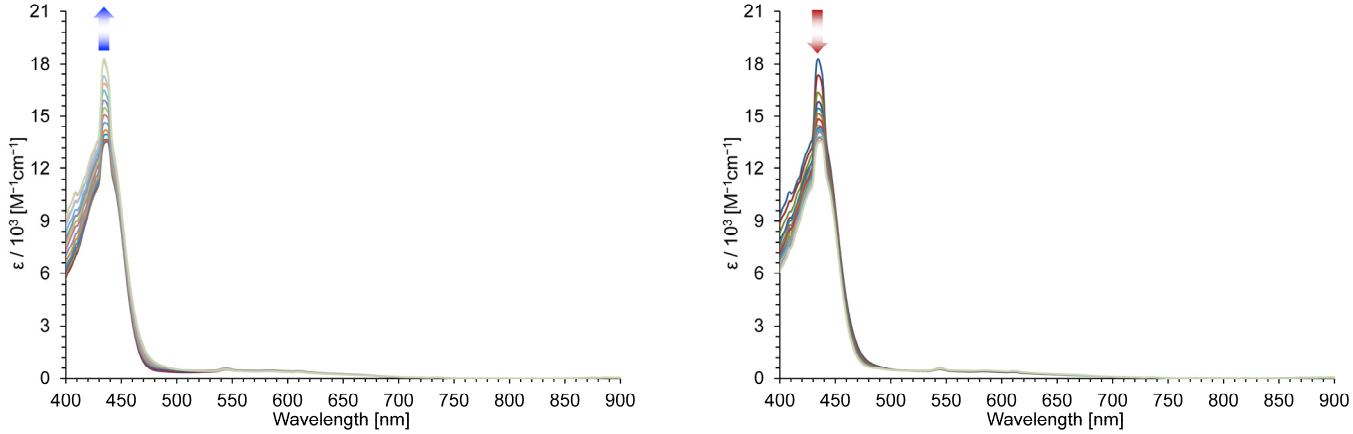


Figure S95. Continuous change in the visible spectrum of **11**: constant-voltage electrochemical reduction at −2.00 V (left) and oxidation of the reduced species at ±0.00 V (right) in benzonitrile containing Et_4NClO_4 (0.1 M) at 20 sec intervals.

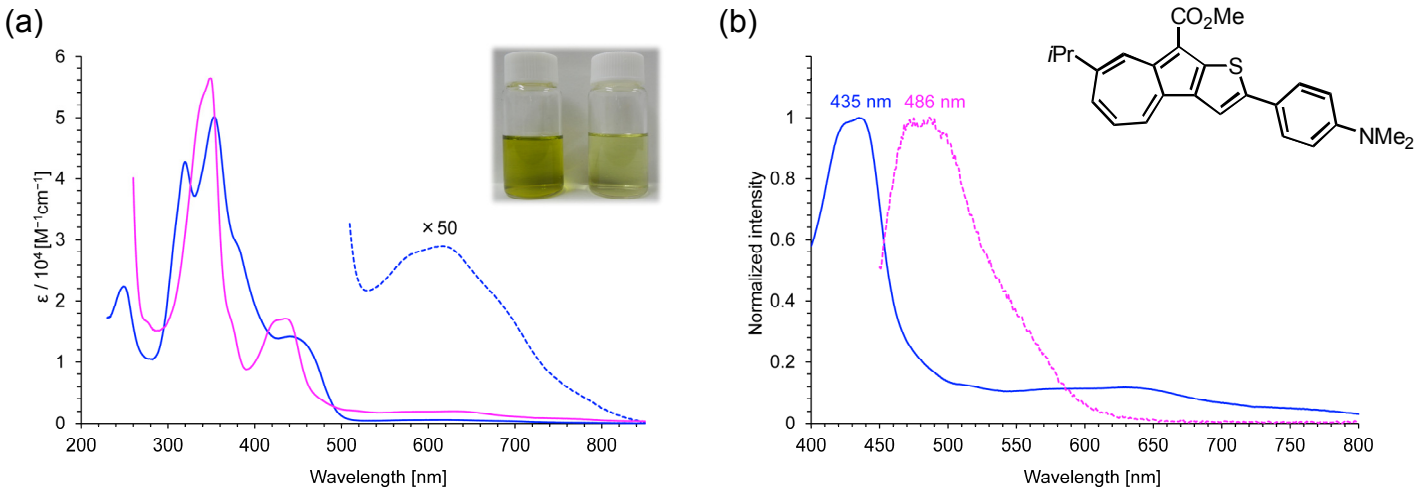


Figure S96. (a) UV/Vis spectra of **12** (blue line, left photo) in CH_2Cl_2 and in 30% CF_3CO_2H/CH_2Cl_2 (pink line, right photo); the dotted lines represent the magnification (×50) of the spectrum of **12** in the visible region. (b) UV/Vis spectrum (blue line) and fluorescence spectrum (pink dot-line) of **12** in 30% CF_3CO_2H/CH_2Cl_2.

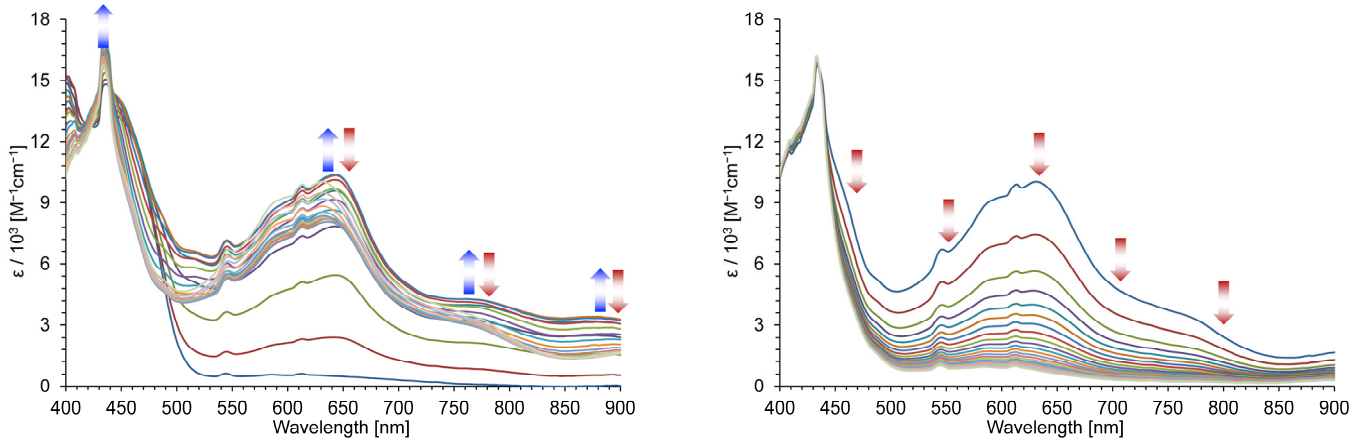


Figure S97. Continuous change in the visible spectrum of **12**: constant-voltage electrochemical oxidation at +0.45 V (left) and reduction of the oxidized species at ±0.00 V (right) in benzonitrile containing Et_4NClO_4 (0.1 M) at 20 sec intervals.

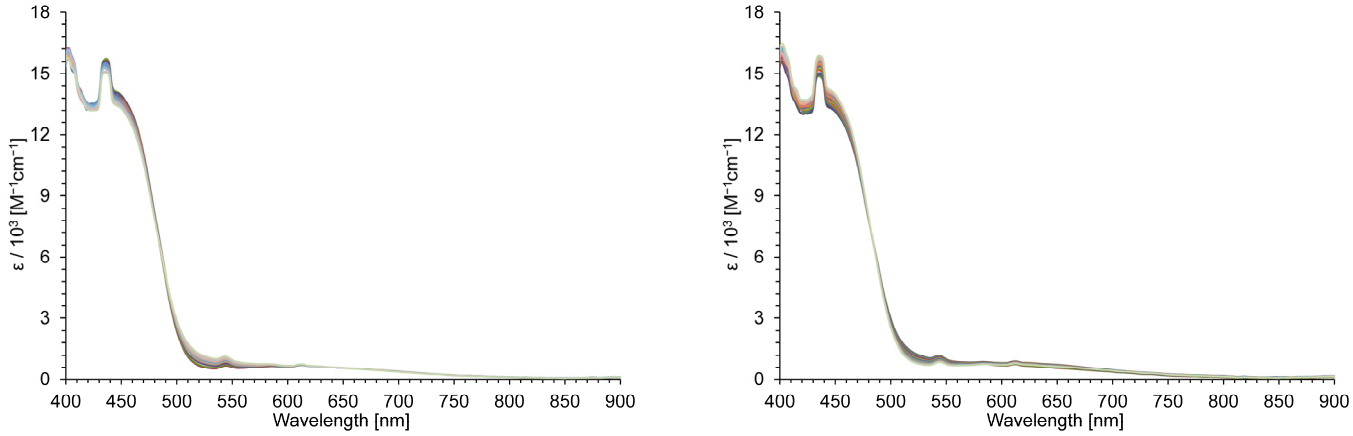


Figure S98. Continuous change in the visible spectrum of **12**: constant-voltage electrochemical reduction at −2.00 V (left) and oxidation of the reduced species at ±0.00 V (right) in benzonitrile containing Et_4NClO_4 (0.1 M) at 20 sec intervals.

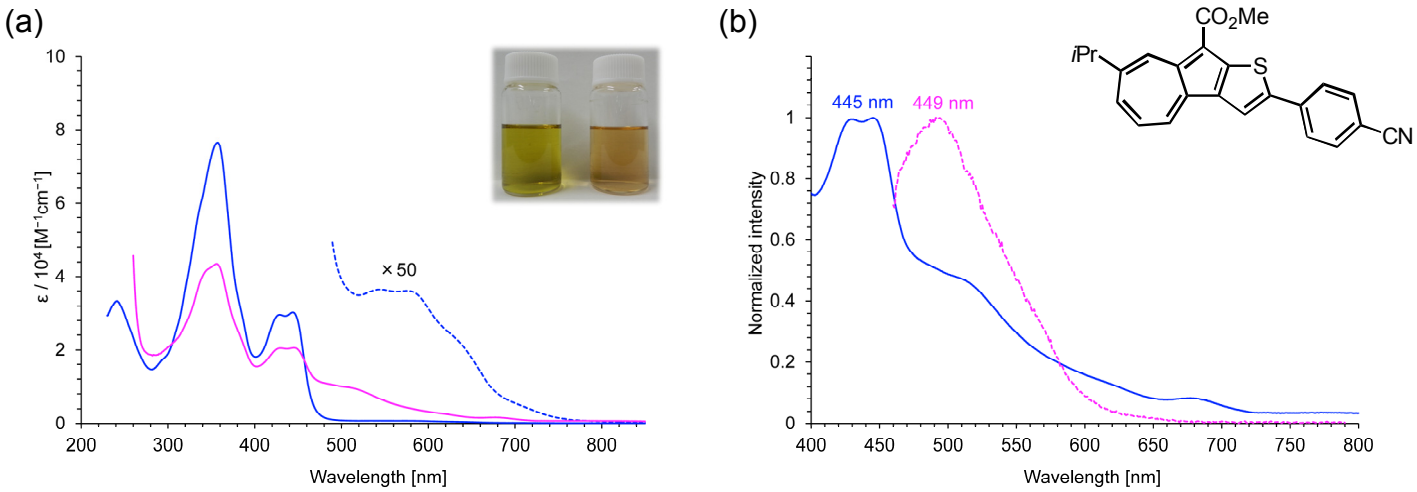


Figure S99. (a) UV/Vis spectra of **13** (blue line, left photo) in CH_2Cl_2 and in 30% CF_3CO_2H/CH_2Cl_2 (pink line, right photo); the dotted lines represent the magnification (×50) of the spectrum of **13** in the visible region. (b) UV/Vis spectrum (blue line) and fluorescence spectrum (pink dot-line) of **13** in 30% CF_3CO_2H/CH_2Cl_2.

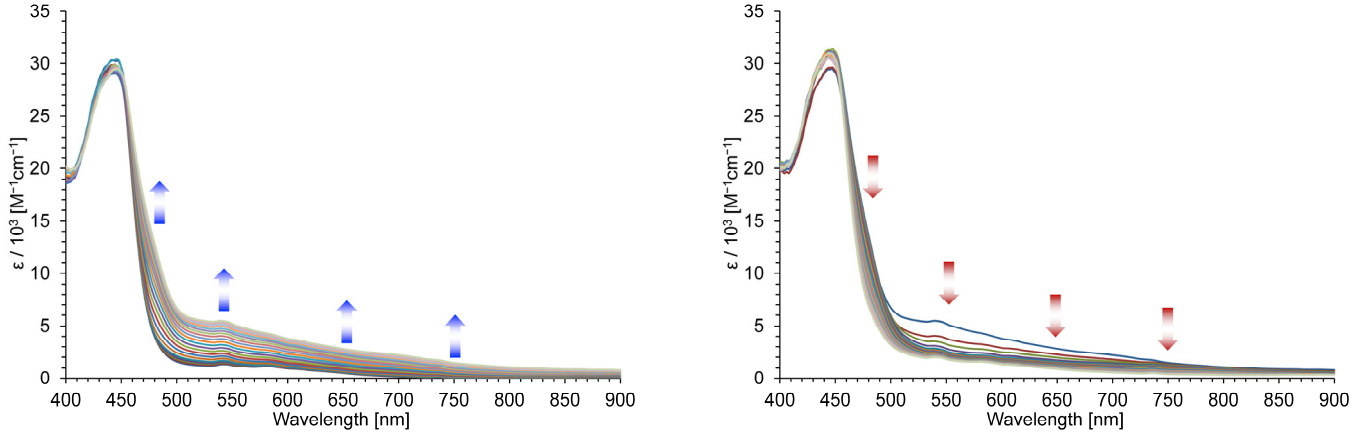


Figure S100. Continuous change in the visible spectrum of **13**: constant-voltage electrochemical oxidation at +1.30 V (left) and reduction of the oxidized species at ±0.00 V (right) in benzonitrile containing Et_4NClO_4 (0.1 M) at 20 sec intervals.

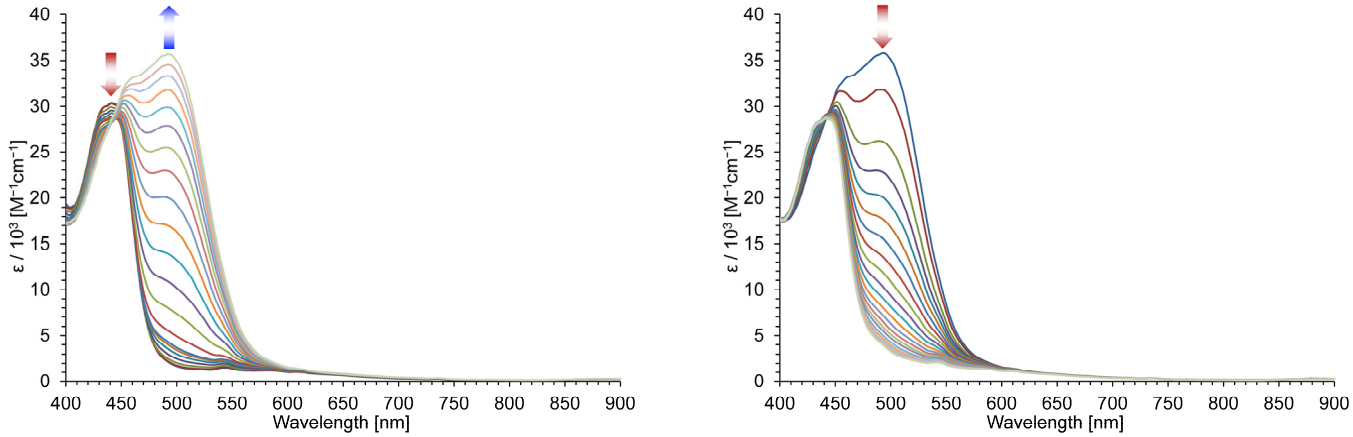


Figure S101. Continuous change in the visible spectrum of **13**: constant-voltage electrochemical reduction at −1.70 V (left) and oxidation of the reduced species at ±0.00 V (right) in benzonitrile containing Et_4NClO_4 (0.1 M) at 20 sec intervals.

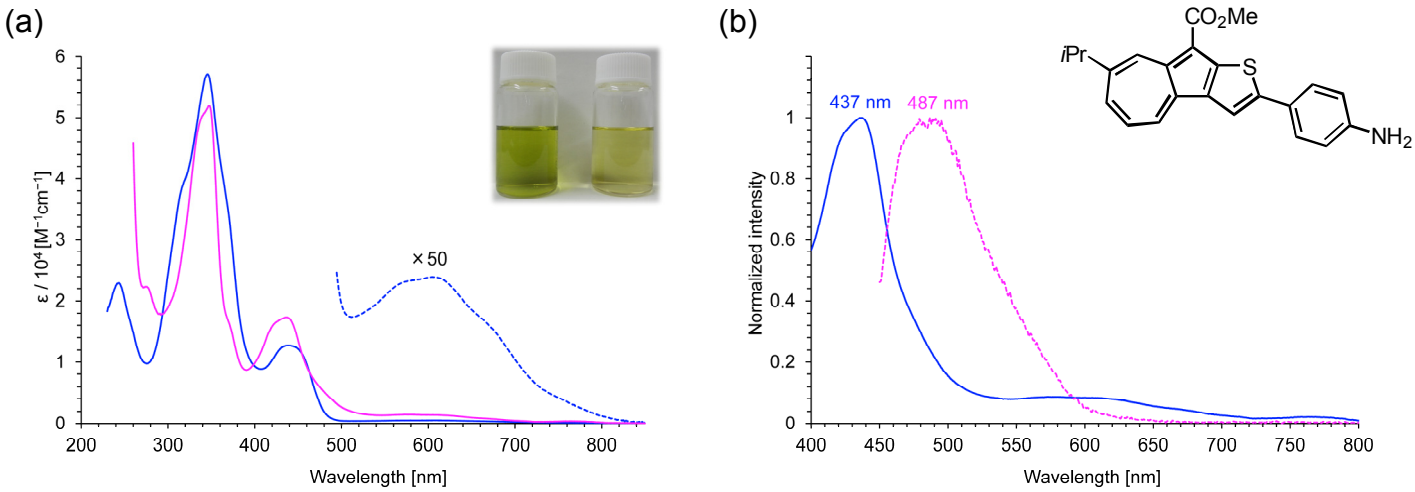


Figure S102. (a) UV/Vis spectra of **14** (blue line, left photo) in CH_2Cl_2 and in 30% CF_3CO_2H/CH_2Cl_2 (pink line, right photo); the dotted lines represent the magnification (×50) of the spectrum of **14** in the visible region. (b) UV/Vis spectrum (blue line) and fluorescence spectrum (pink dot-line) of **14** in 30% CF_3CO_2H/CH_2Cl_2.

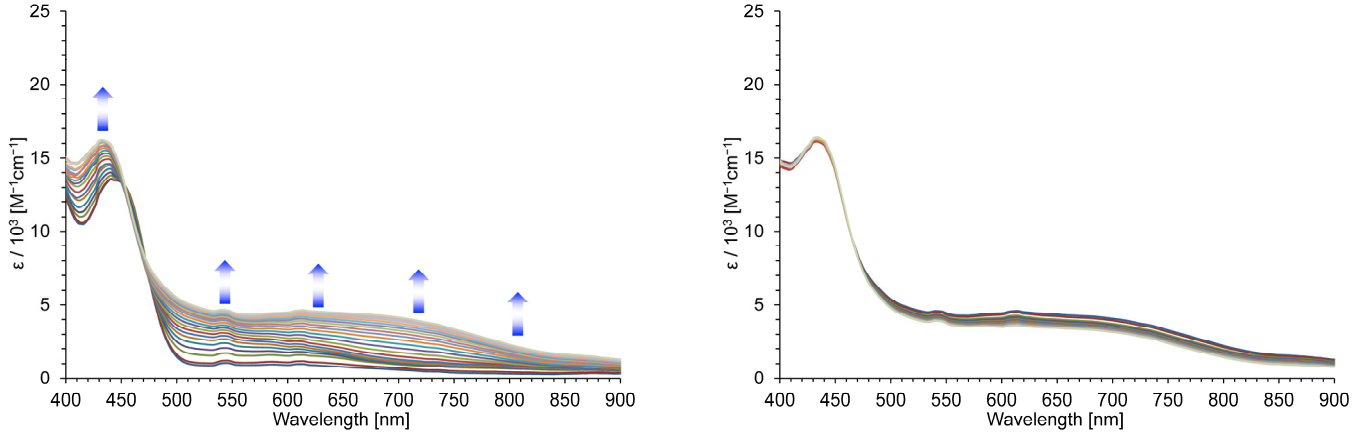


Figure S103. Continuous change in the visible spectrum of **14**: constant-voltage electrochemical oxidation at +0.70 V (left) and reduction of the oxidized species at ±0.00 V (right) in benzonitrile containing Et_4NClO_4 (0.1 M) at 20 sec intervals.

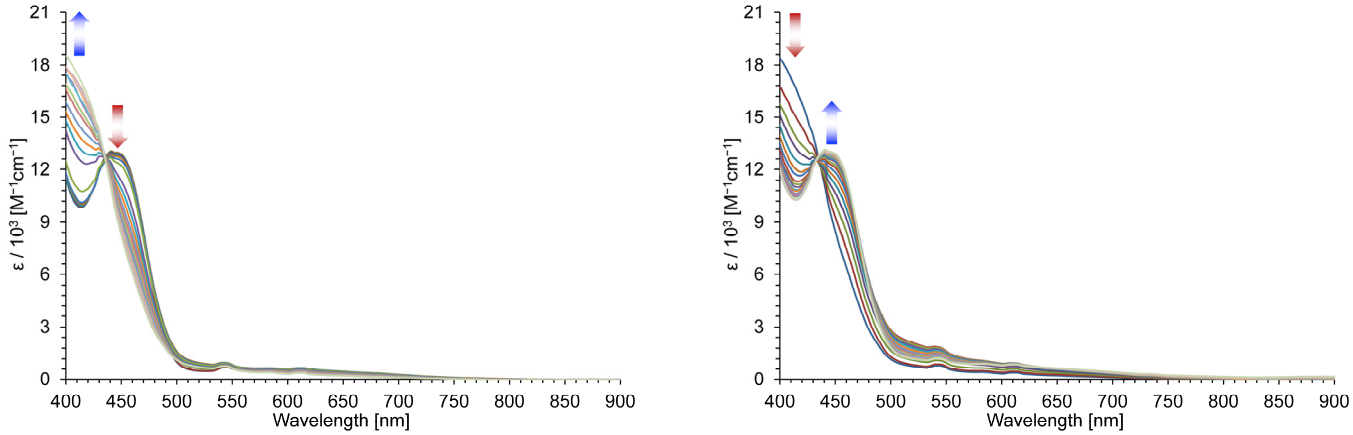


Figure S1043. Continuous change in the visible spectrum of **14**: constant-voltage electrochemical reduction at −1.70 V (left) and oxidation of the reduced species at ±0.00 V (right) in benzonitrile containing Et_4NClO_4 (0.1 M) at 20 sec intervals.

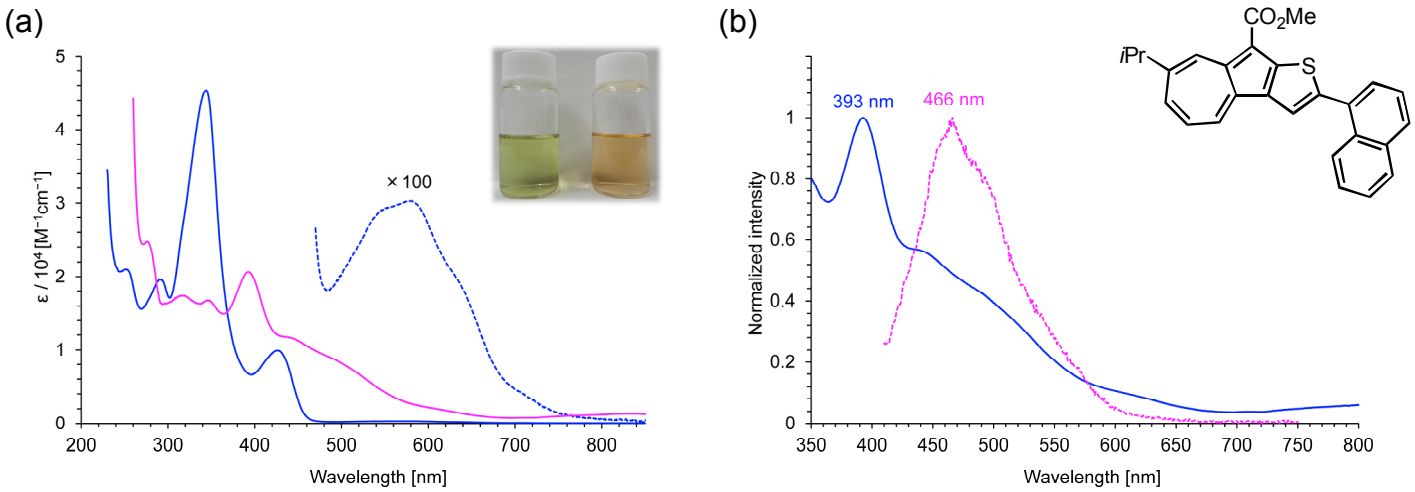


Figure S105. (a) UV/Vis spectra of **15** (blue line, left photo) in CH_2Cl_2 and in 30% CF_3CO_2H/CH_2Cl_2 (pink line, right photo); the dotted lines represent the magnification (×100) of the spectrum of **15** in the visible region. (b) UV/Vis spectrum (blue line) and fluorescence spectrum (pink dot-line) of **15** in 30% CF_3CO_2H/CH_2Cl_2.

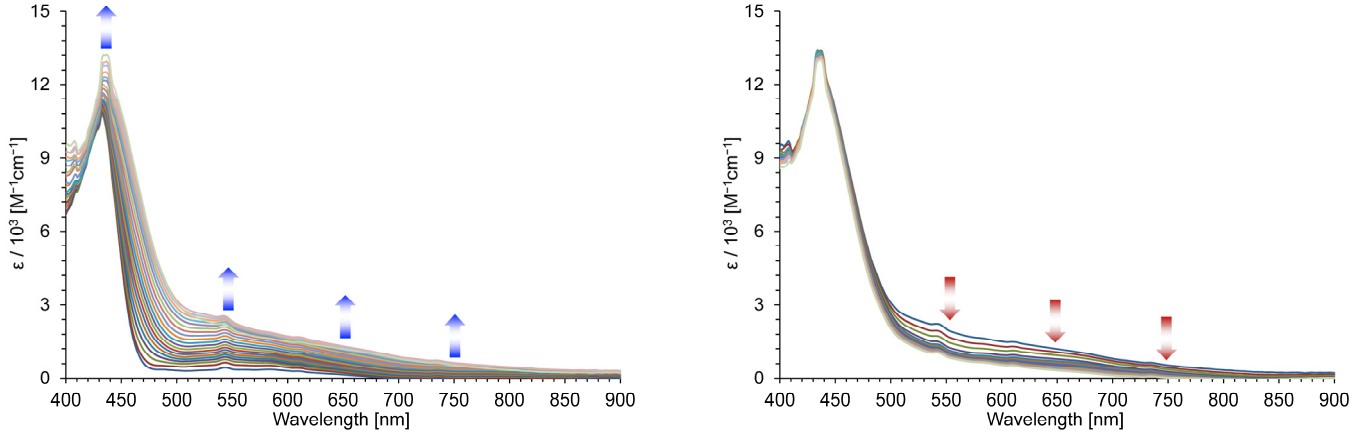


Figure S106. Continuous change in the visible spectrum of **15**: constant-voltage electrochemical oxidation at +0.85 V (left) and reduction of the oxidized species at ±0.00 V (right) in benzonitrile containing Et_4NClO_4 (0.1 M) at 20 sec intervals.

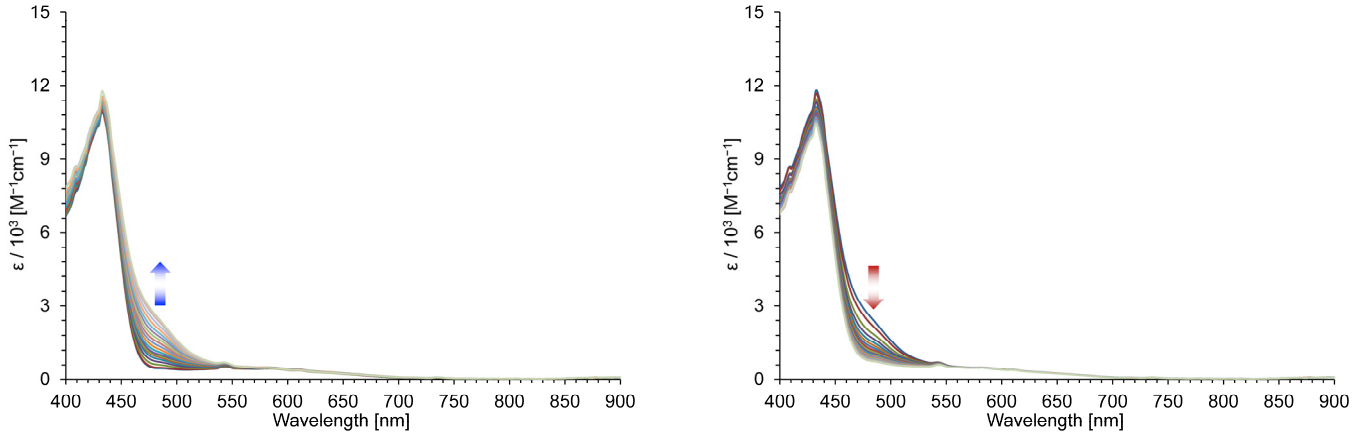


Figure S107. Continuous change in the visible spectrum of **15**: constant-voltage electrochemical reduction at −2.00 V (left) and oxidation of the reduced species at ±0.00 V (right) in benzonitrile containing Et_4NClO_4 (0.1 M) at 20 sec intervals.

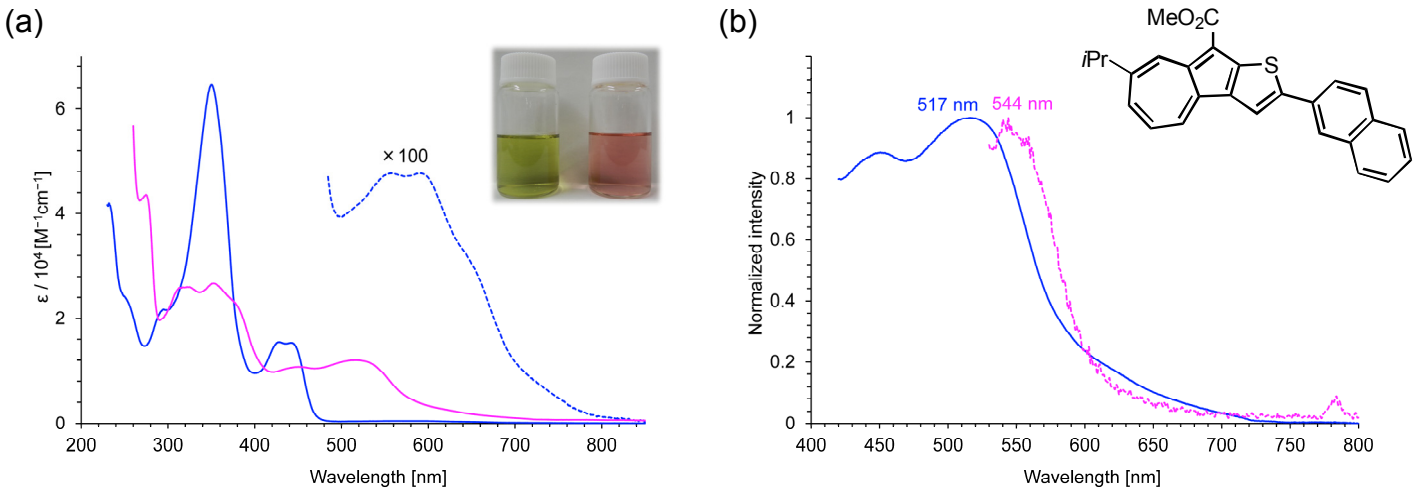


Figure S108. (a) UV/Vis spectra of **16** (blue line, left photo) in CH_2Cl_2 and in 30% CF_3CO_2H/CH_2Cl_2 (pink line, right photo); the dotted lines represent the magnification (×100) of the spectrum of **16** in the visible region. (b) UV/Vis spectrum (blue line) and fluorescence spectrum (pink dot-line) of **16** in 30% CF_3CO_2H/CH_2Cl_2.

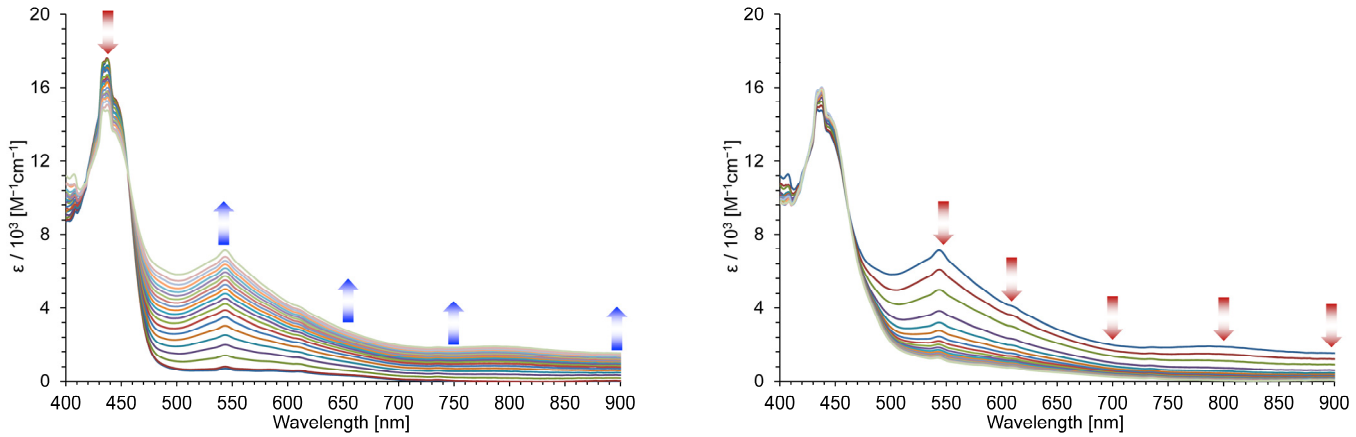


Figure S109. Continuous change in the visible spectrum of **16**: constant-voltage electrochemical oxidation at +0.85 V (left) and reduction of the oxidized species at ±0.00 V (right) in benzonitrile containing Et_4NClO_4 (0.1 M) at 20 sec intervals.

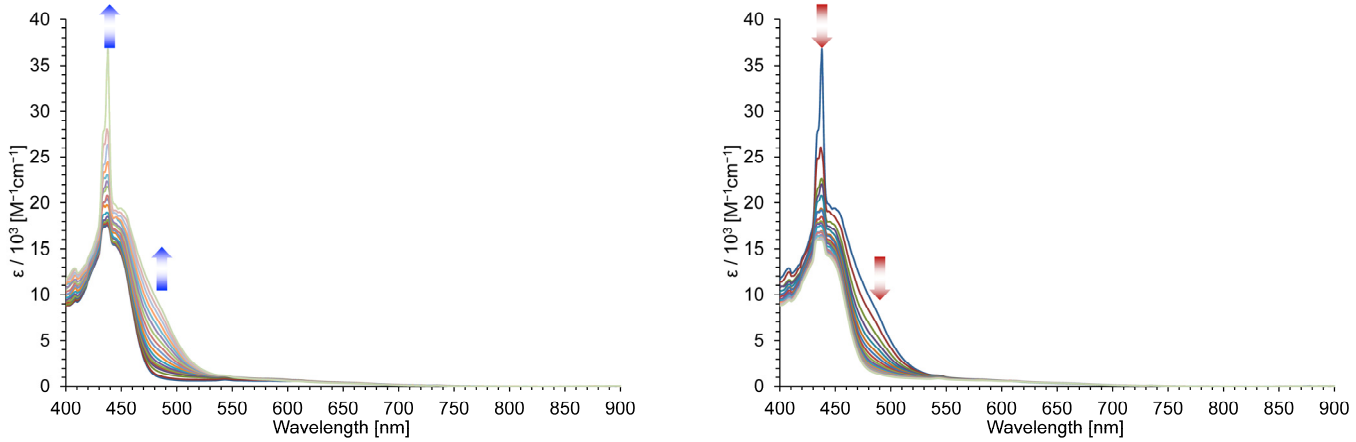


Figure S110. Continuous change in the visible spectrum of **16**: constant-voltage electrochemical reduction at −2.00 V (left) and oxidation of the reduced species at ±0.00 V (right) in benzonitrile containing Et_4NClO_4 (0.1 M) at 20 sec intervals.

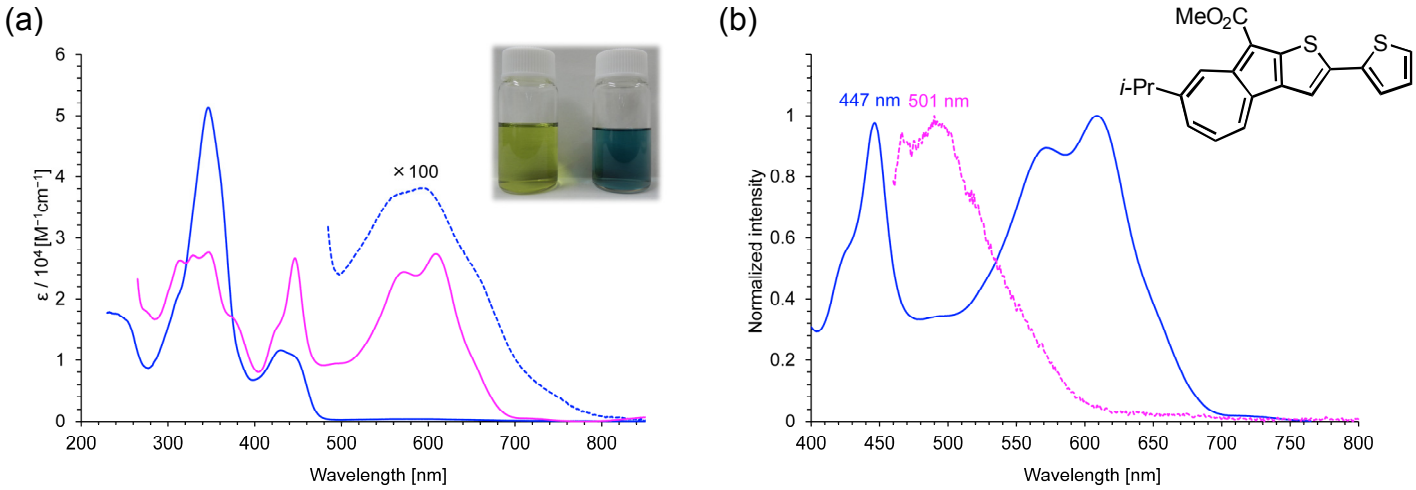


Figure S111. (a) UV/Vis spectra of **17a** (blue line, left photo) in CH_2Cl_2 and in 30% CF_3CO_2H/CH_2Cl_2 (pink line, right photo); the dotted lines represent the magnification (×100) of the spectrum of **17a** in the visible region. (b) UV/Vis spectrum (blue line) and fluorescence spectrum (pink dot-line) of **17a** in 30% CF_3CO_2H/CH_2Cl_2.

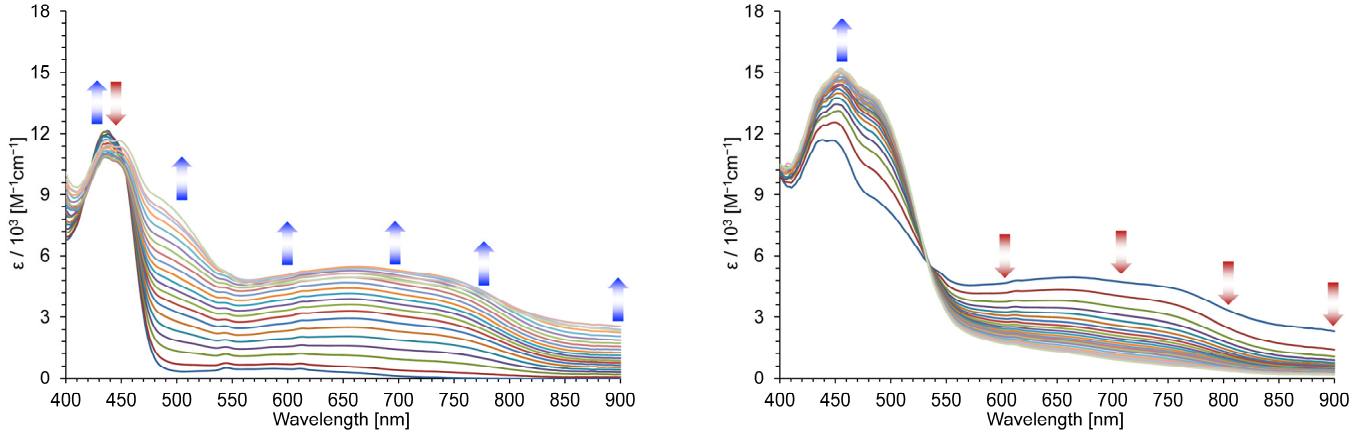


Figure S112. Continuous change in the visible spectrum of **17a**: constant-voltage electrochemical oxidation at +0.85 V (left) and reduction of the oxidized species at ±0.00 V (right) in benzonitrile containing Et_4NClO_4 (0.1 M) at 20 sec intervals.

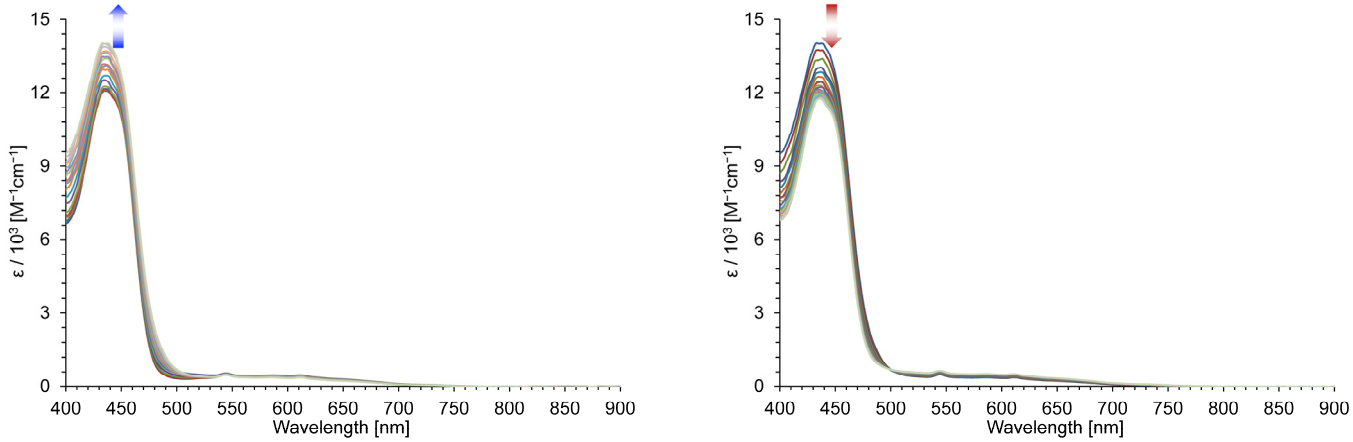


Figure S113. Continuous change in the visible spectrum of **17a**: constant-voltage electrochemical reduction at −2.00 V (left) and oxidation of the reduced species at ±0.00 V (right) in benzonitrile containing Et_4NClO_4 (0.1 M) at 20 sec intervals.

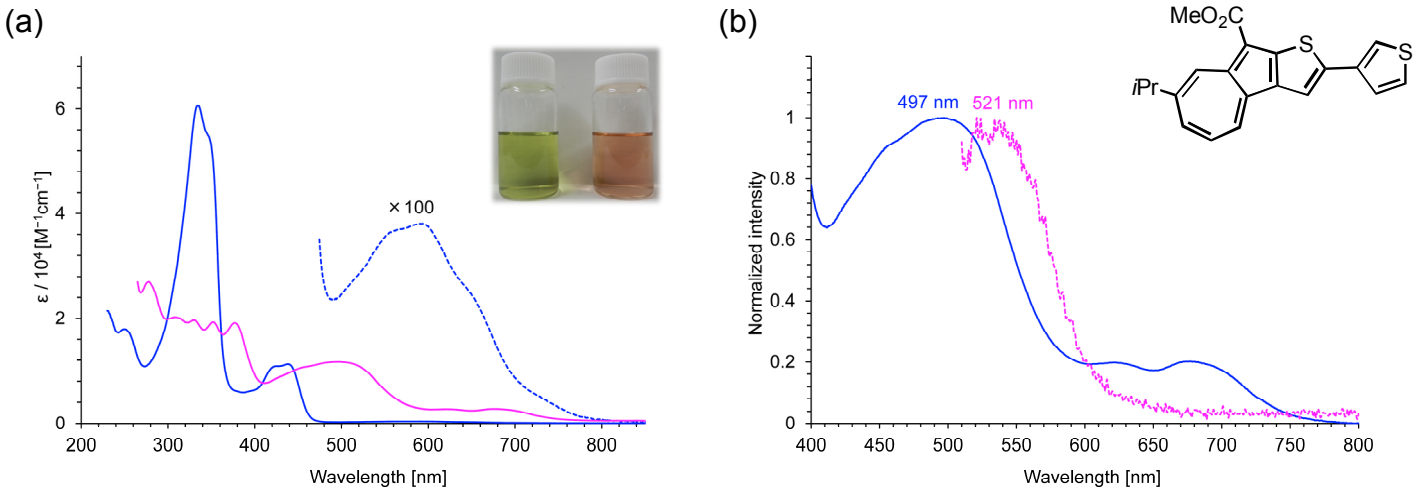


Figure S114. (a) UV/Vis spectra of **18a** (blue line, left photo) in CH_2Cl_2 and in 30% CF_3CO_2H/CH_2Cl_2 (pink line, right photo); the dotted lines represent the magnification (×100) of the spectrum of **18a** in the visible region. (b) UV/Vis spectrum (blue line) and fluorescence spectrum (pink dot-line) of **18a** in 30% CF_3CO_2H/CH_2Cl_2.

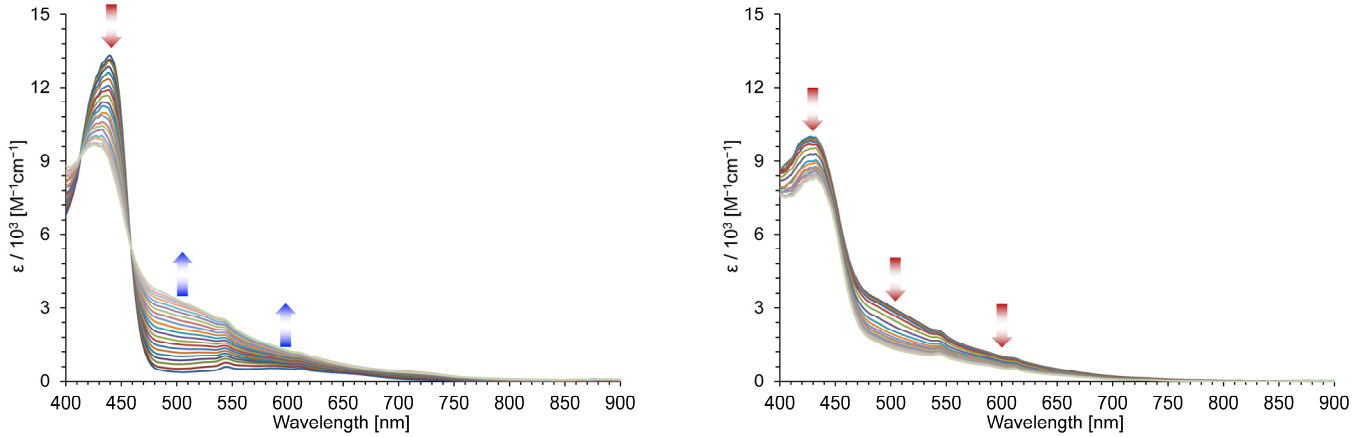


Figure S115. Continuous change in the visible spectrum of **18a**: constant-voltage electrochemical oxidation at +0.85 V (left) and reduction of the oxidized species at ±0.00 V (right) in benzonitrile containing Et_4NClO_4 (0.1 M) at 20 sec intervals.

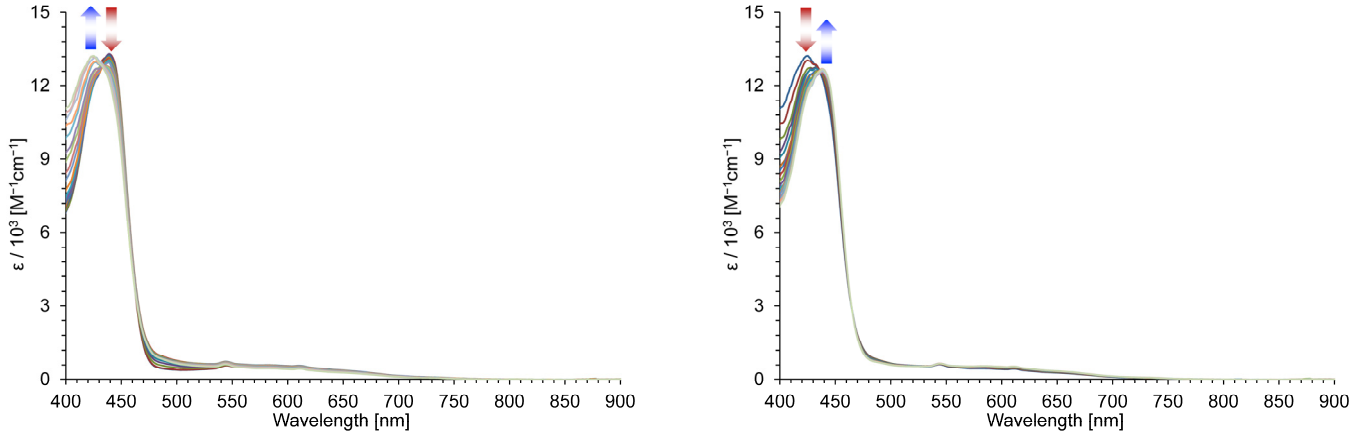


Figure S116. Continuous change in the visible spectrum of **18a**: constant-voltage electrochemical reduction at −2.00 V (left) and oxidation of the reduced species at ±0.00 V (right) in benzonitrile containing Et_4NClO_4 (0.1 M) at 20 sec intervals.

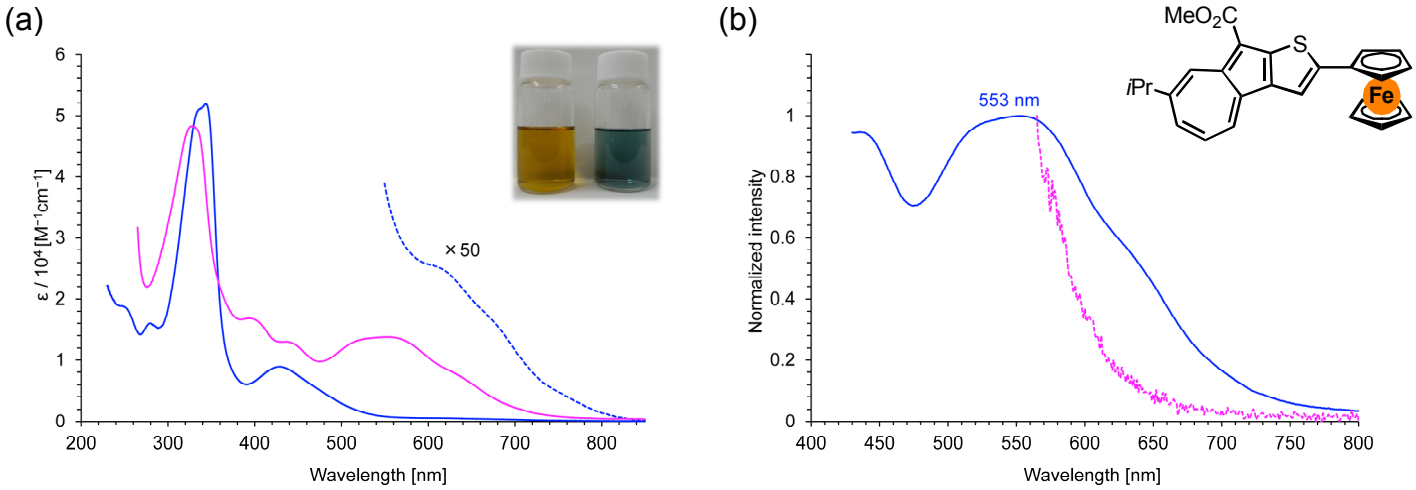


Figure S117. (a) UV/Vis spectra of **19a** (blue line, left photo) in CH_2Cl_2 and in 30% CF_3CO_2H/CH_2Cl_2 (pink line, right photo); the dotted lines represent the magnification (×100) of the spectrum of **19a** in the visible region. (b) UV/Vis spectrum (blue line) and fluorescence spectrum (pink dot-line) of **19a** in 30% CF_3CO_2H/CH_2Cl_2.

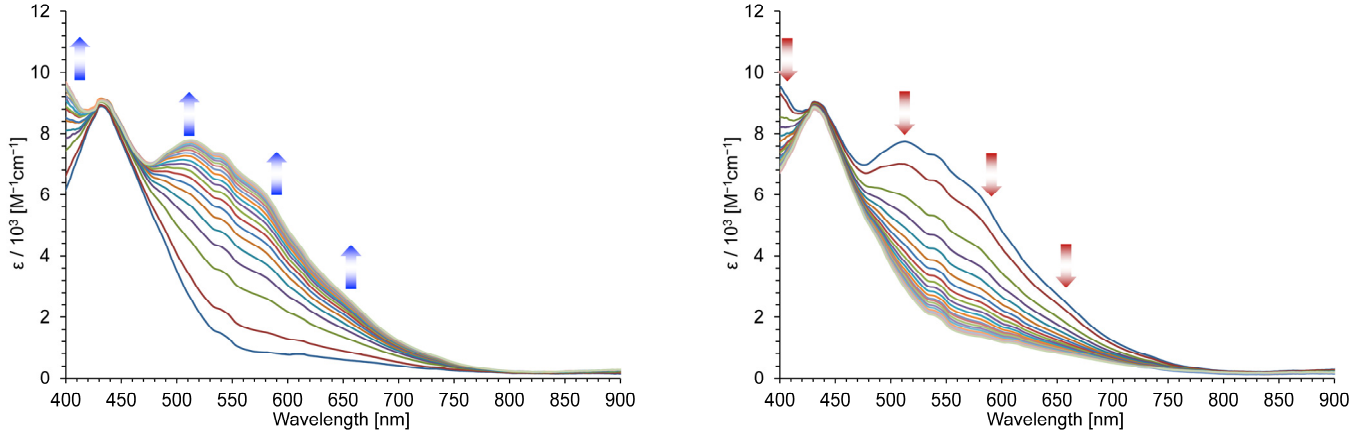


Figure S118. Continuous change in the visible spectrum of **19a**: constant-voltage electrochemical oxidation at +0.50 V (left) and reduction of the oxidized species at −0.50 V (right) in benzonitrile containing Et_4NClO_4 (0.1 M) at 20 sec intervals.

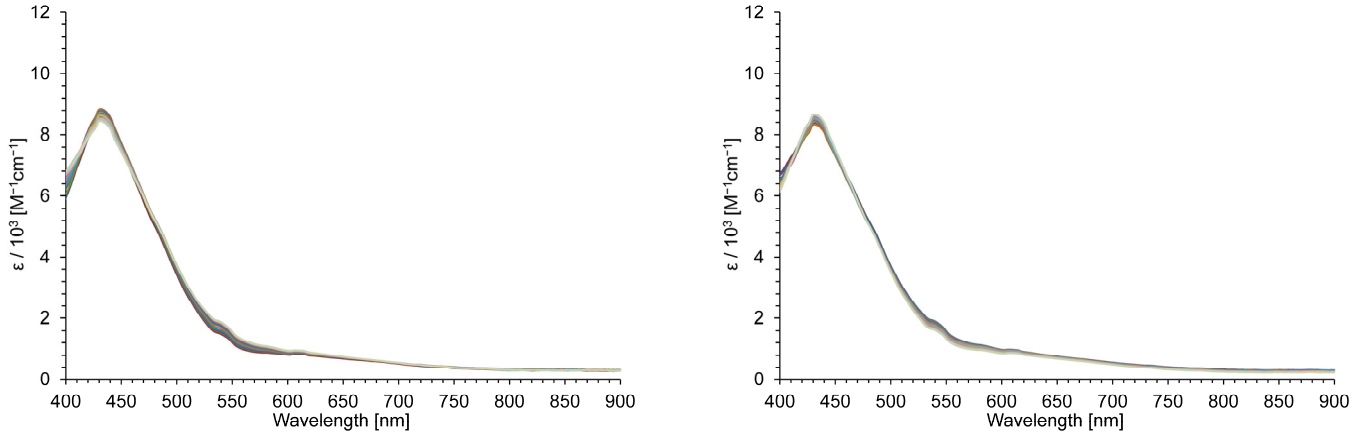


Figure S119. Continuous change in the visible spectrum of **19a**: constant-voltage electrochemical reduction at −1.90 V (left) and oxidation of the reduced species at ±0.00 V (right) in benzonitrile containing Et_4NClO_4 (0.1 M) at 20 sec intervals.

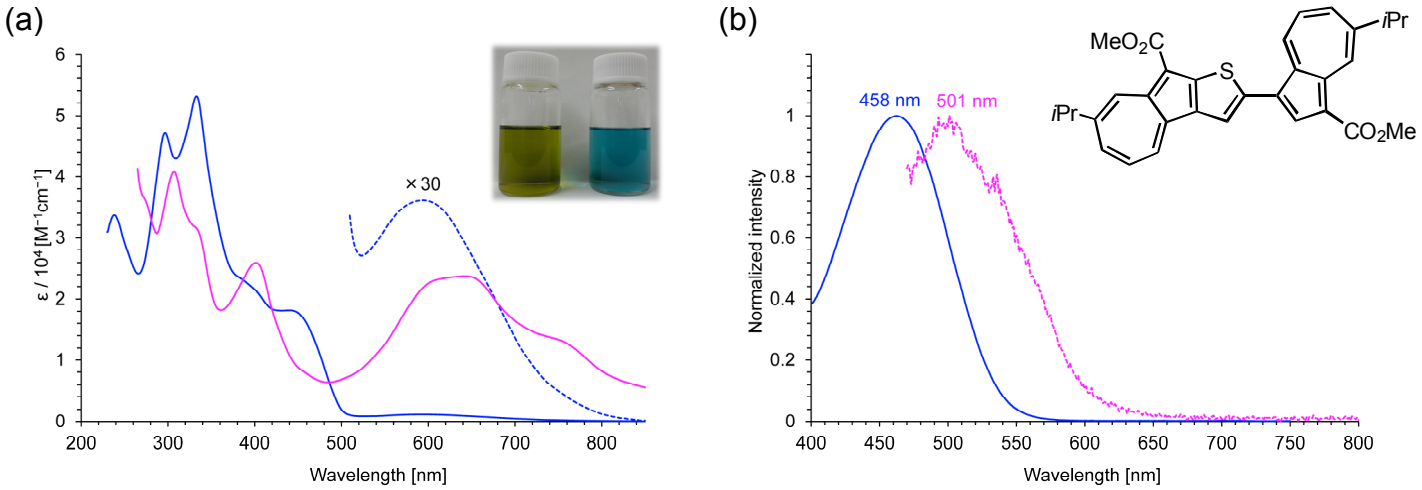


Figure S120. (a) UV/Vis spectra of **20** (blue line, left photo) in CH_2Cl_2 and in 30% CF_3CO_2H/CH_2Cl_2 (pink line, right photo); the dotted lines represent the magnification (×30) of the spectrum of **20** in the visible region. (b) UV/Vis spectrum (blue line) and fluorescence spectrum (pink dot-line) of **20** in 30% CF_3CO_2H/CH_2Cl_2.

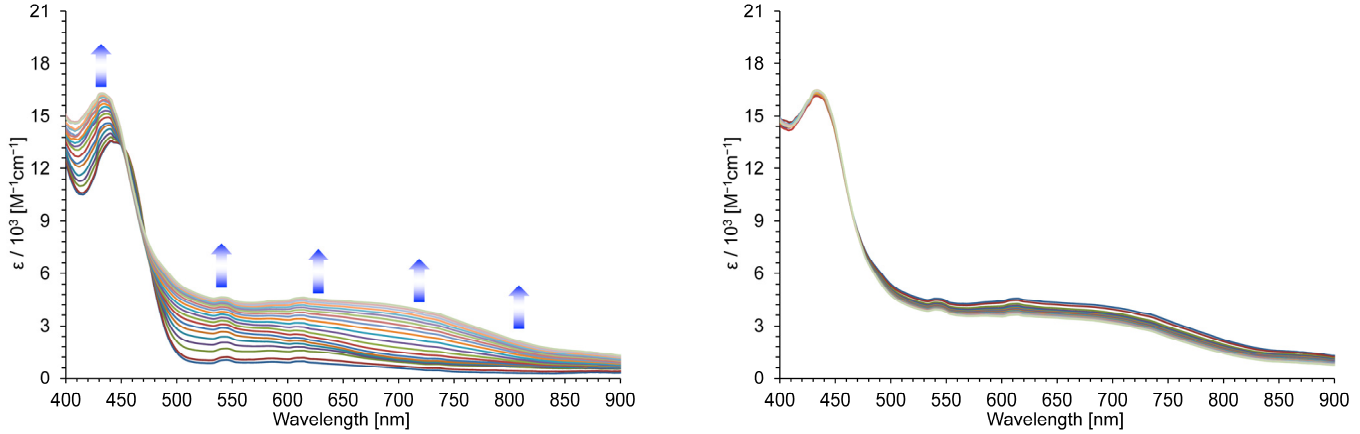


Figure S121. Continuous change in the visible spectrum of **20**: constant-voltage electrochemical oxidation at +0.70 V (left) and reduction of the oxidized species at ±0.00 V (right) in benzonitrile containing Et_4NClO_4 (0.1 M) at 20 sec intervals.

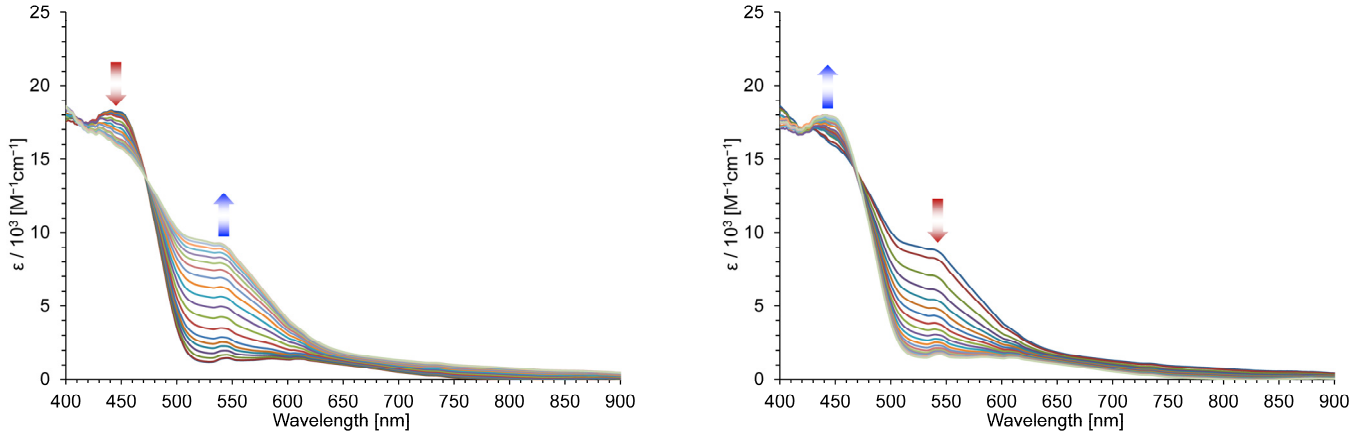


Figure S122. Continuous change in the visible spectrum of **20**: constant-voltage electrochemical reduction at −1.70 V (left) and oxidation of the reduced species at ±0.00 V (right) in benzonitrile containing Et_4NClO_4 (0.1 M) at 20 sec intervals.

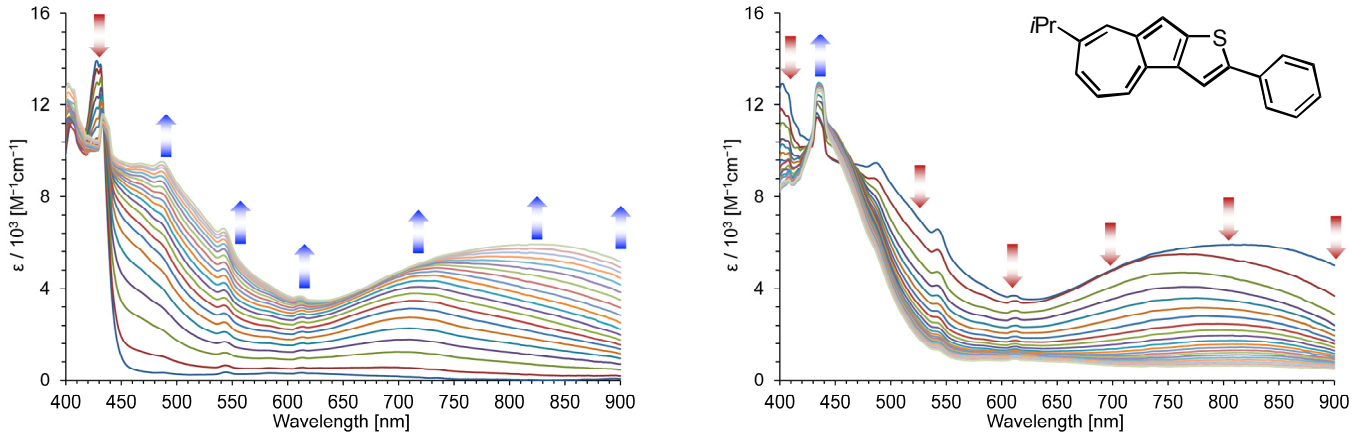


Figure S123. Continuous change in the visible spectrum of **21**: constant-voltage electrochemical oxidation at +0.75 V (left) and reduction of the oxidized species at ±0.00 V (right) in benzonitrile containing Et_4NClO_4 (0.1 M) at 20 sec intervals.

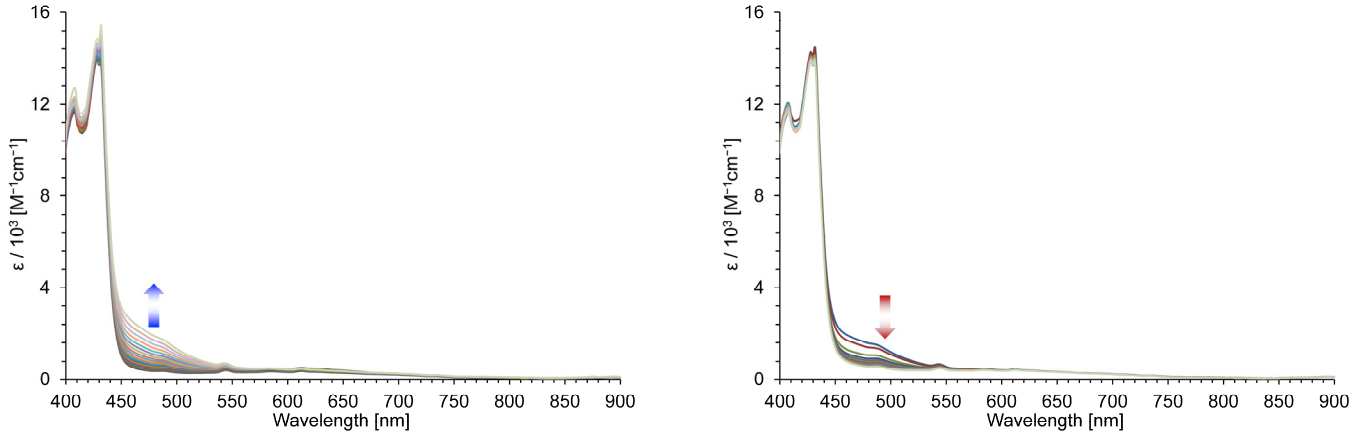
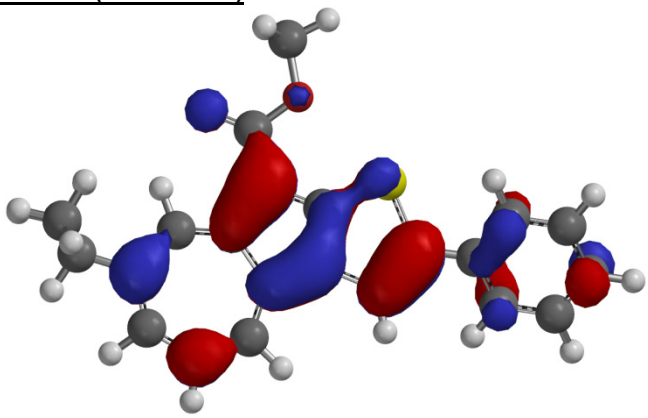


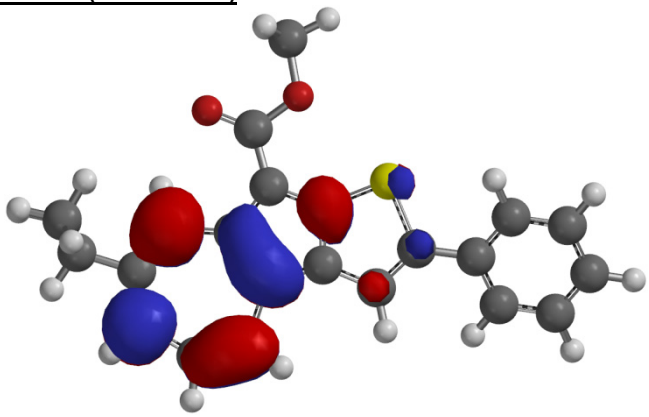
Figure S124. Continuous change in the visible spectrum of **21**: constant-voltage electrochemical reduction at −2.00 V (left) and oxidation of the reduced species at ±0.00 V (right) in benzonitrile containing Et_4NClO_4 (0.1 M) at 20 sec intervals.

3. Frontier Kohn–Sham orbitals of 11–14 and 21 (Figures S125–S129).

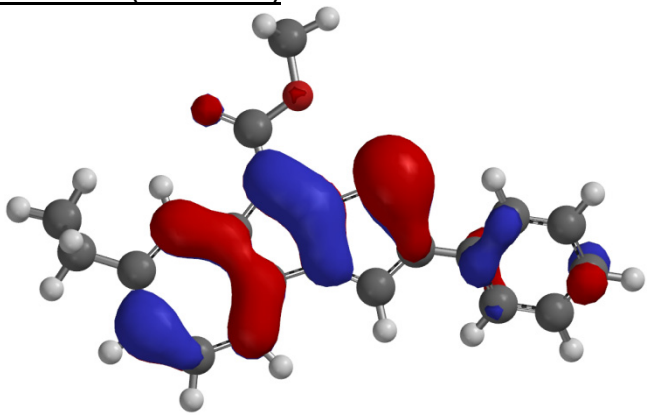
HOMO (−5.23 eV)



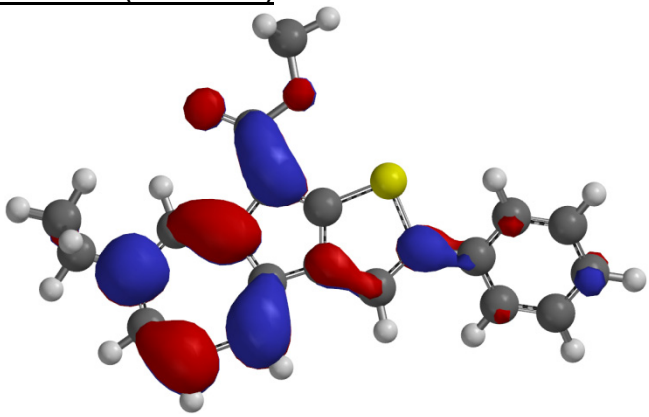
LUMO (−2.32 eV)



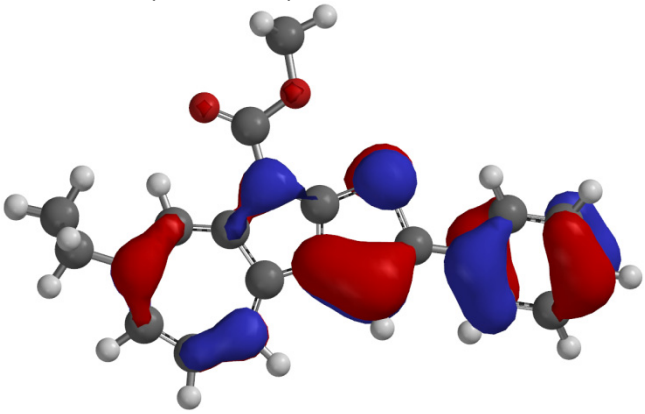
HOMO−1 (−6.20 eV)



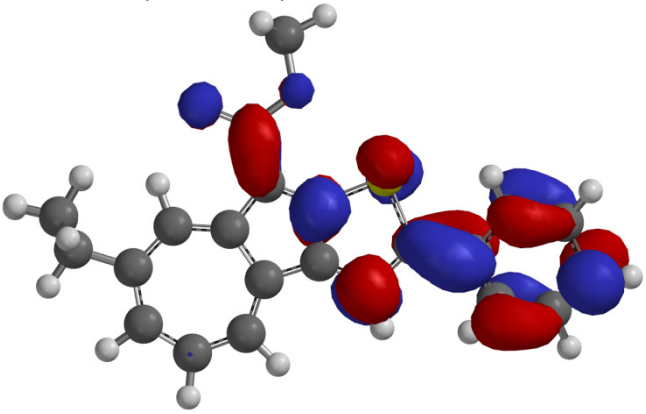
LUMO+1 (−1.93 eV)



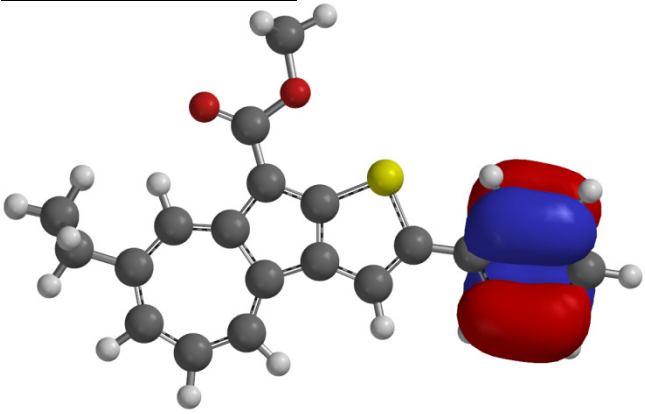
HOMO−2 (−6.89 eV)



LUMO+2 (−1.00 eV)



HOMO−3 (−7.08 eV)



LUMO+3 (−0.38 eV)

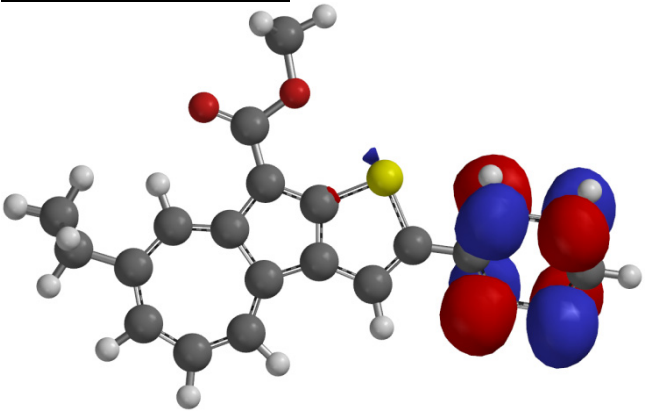
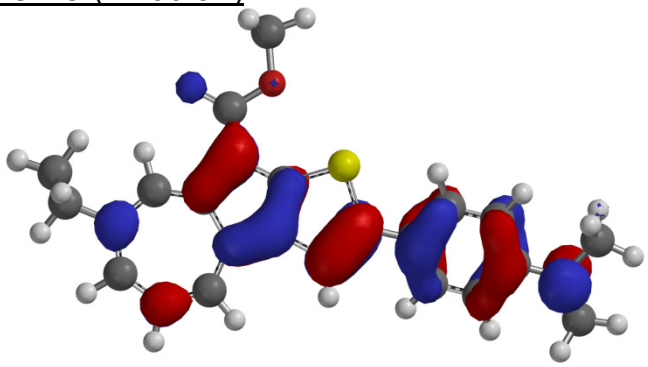
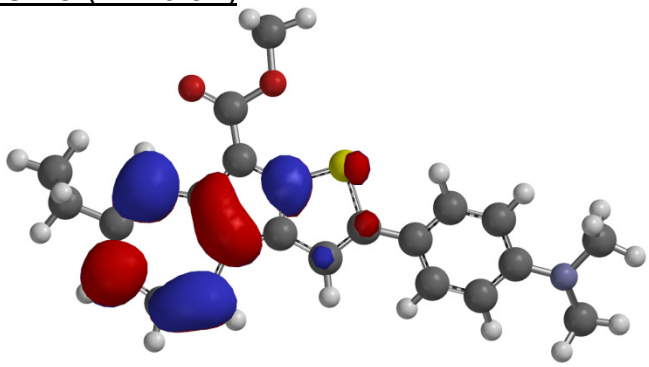


Figure S125. Frontier Kohn–Sham orbitals of **11** at the B3LYP/6-311G* level.

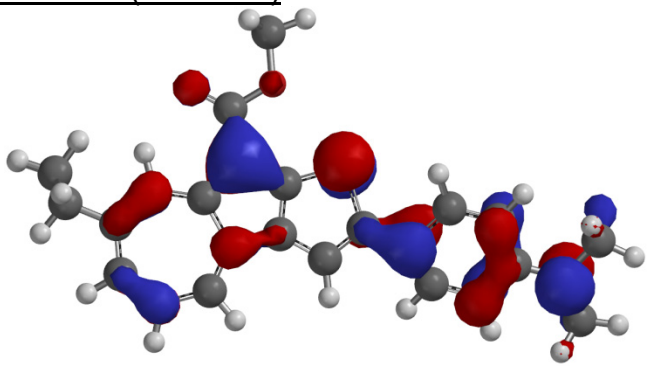
HOMO (−4.90 eV)



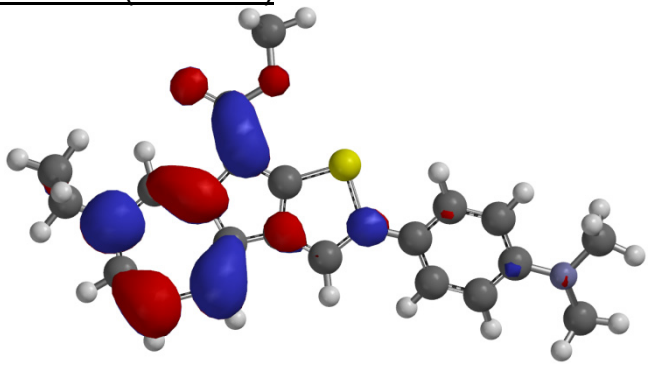
LUMO (−2.26 eV)



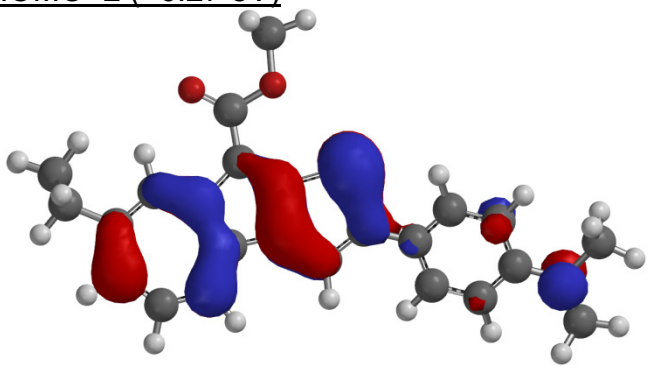
HOMO−1 (−5.74 eV)



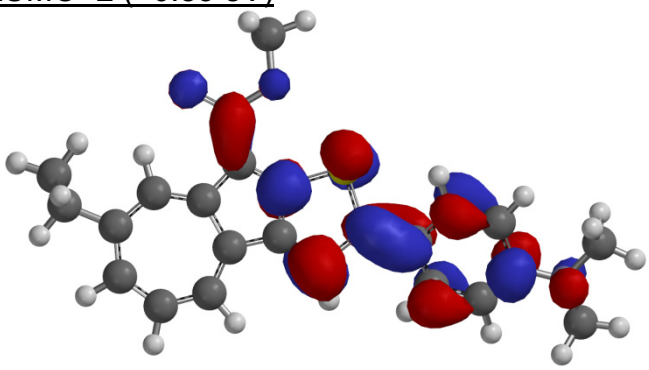
LUMO+1 (−1.86 eV)



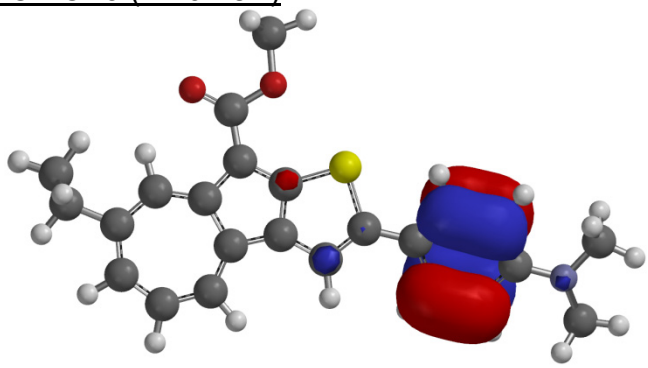
HOMO−2 (−6.27 eV)



LUMO+2 (−0.83 eV)



HOMO−3 (−7.02 eV)



LUMO+3 (−0.43 eV)

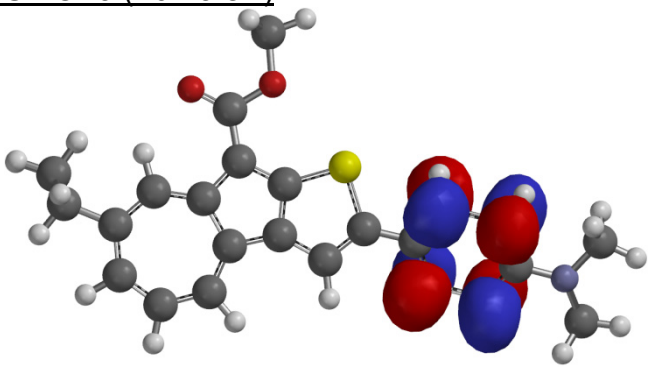
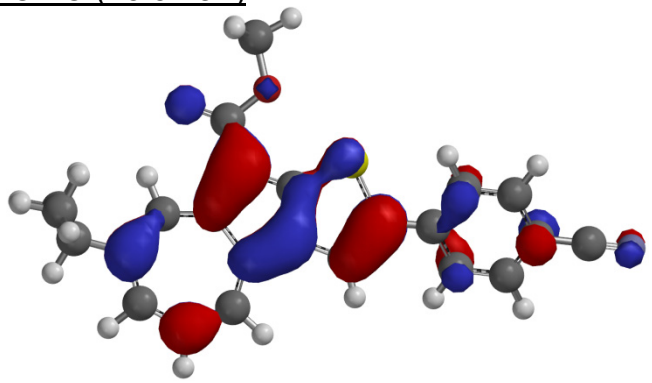
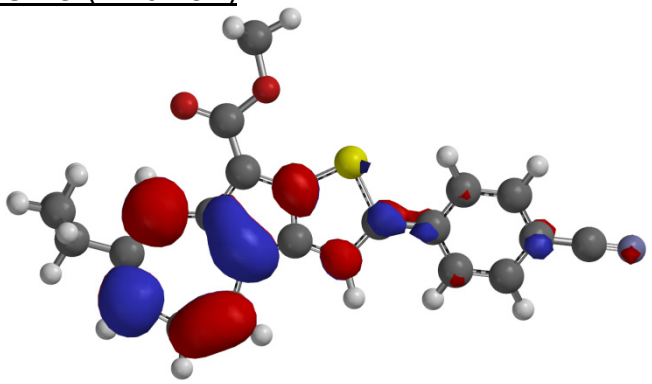


Figure S126. Frontier Kohn–Sham orbitals of **12** at the B3LYP/6-311+G** level.

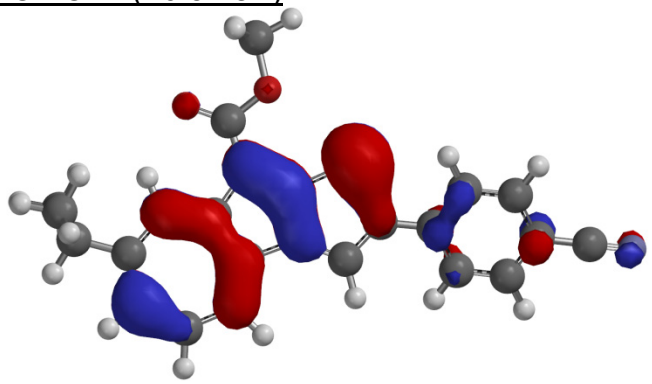
HOMO (−5.54 eV)



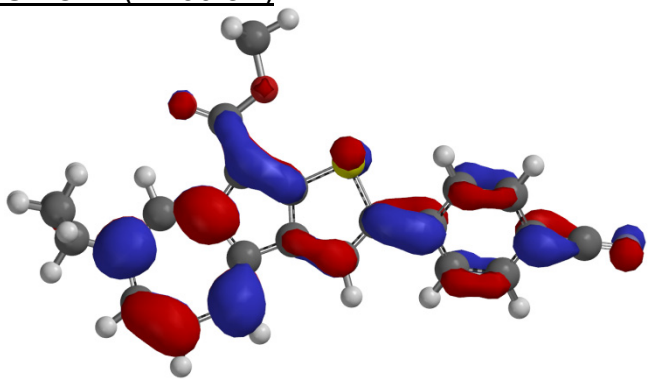
LUMO (−2.62 eV)



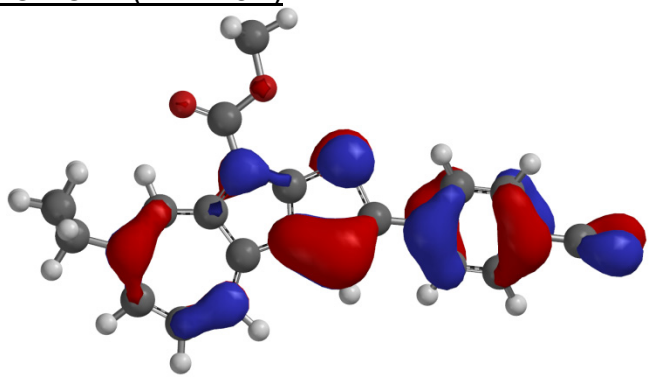
HOMO−1 (−6.51 eV)



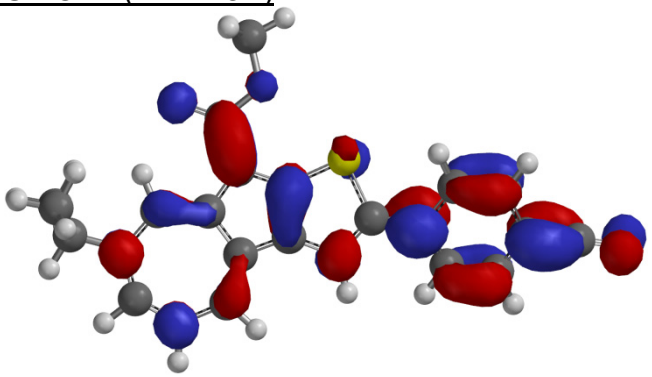
LUMO+1 (−2.30 eV)



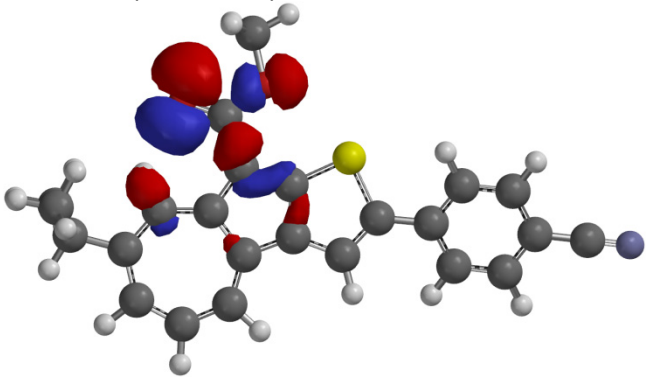
HOMO−2 (−7.22 eV)



LUMO+2 (−1.72 eV)



HOMO−3 (−7.62 eV)



LUMO+3 (−0.92 eV)

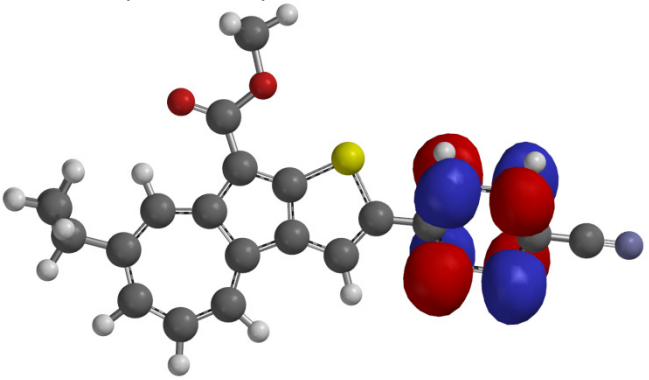
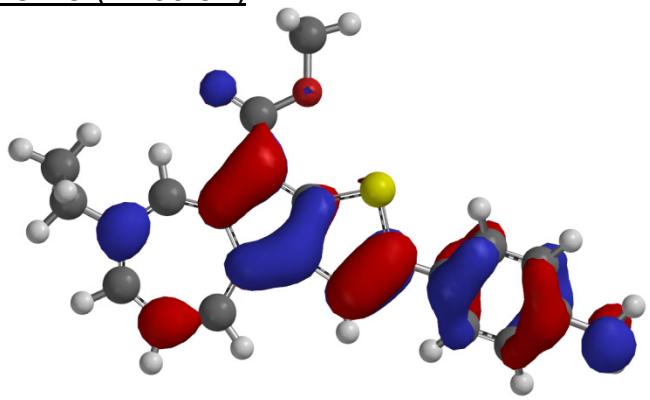
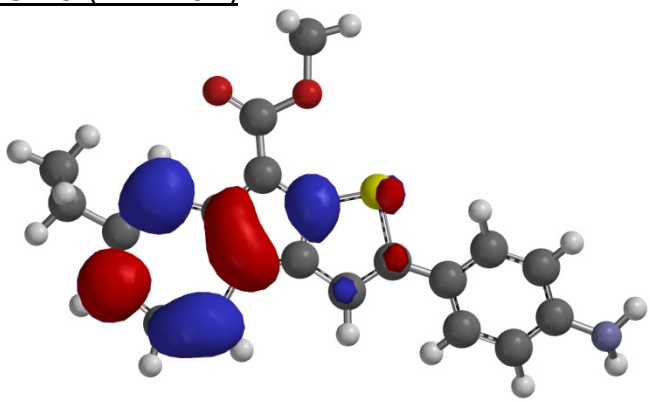


Figure S127. Frontier Kohn–Sham orbitals of **13** at the B3LYP/6-311G* level.

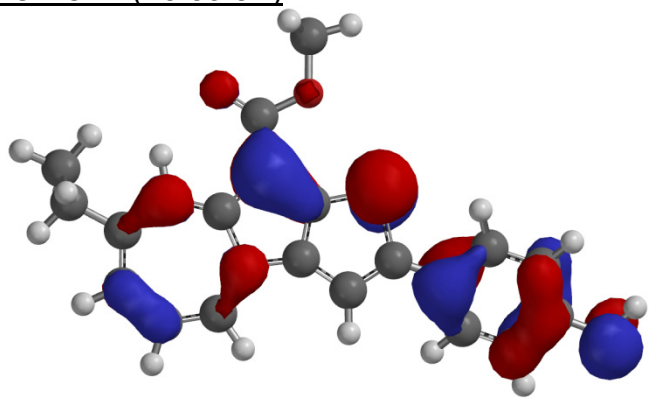
HOMO (−4.93 eV)



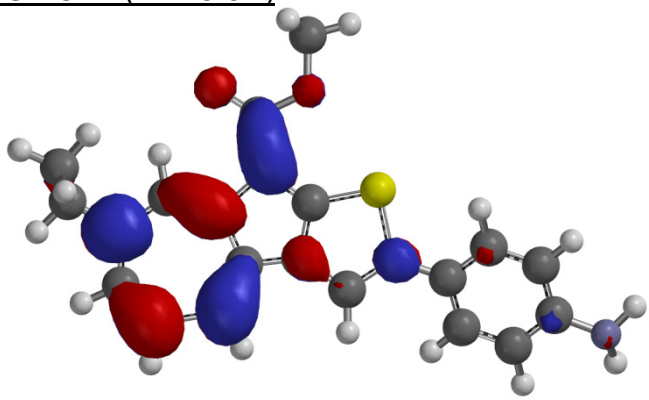
LUMO (−2.17 eV)



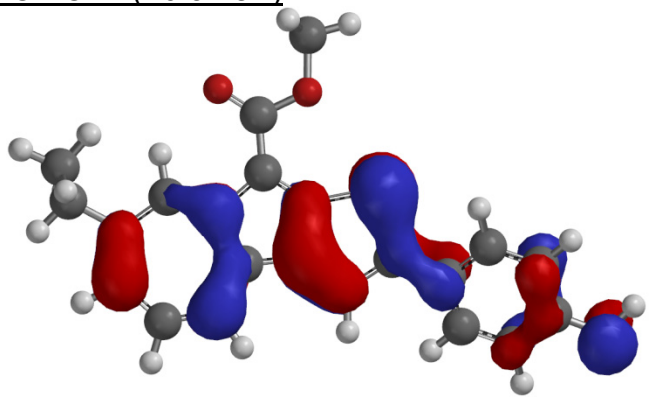
HOMO−1 (−5.83 eV)



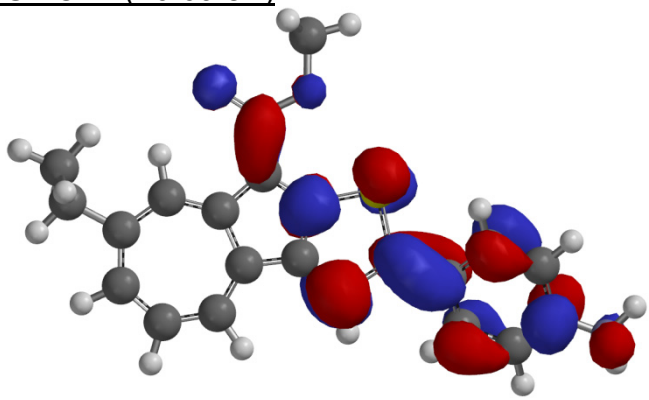
LUMO+1 (−1.78 eV)



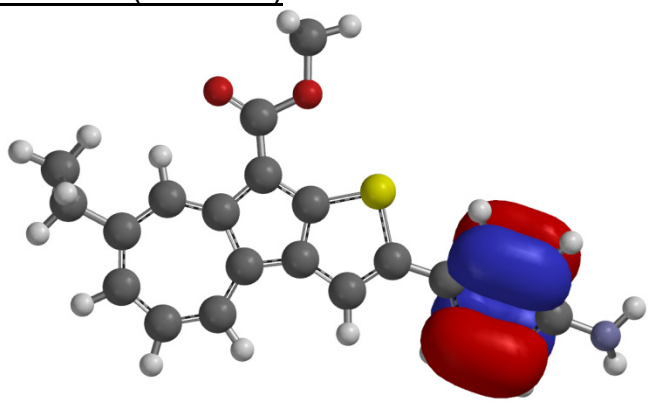
HOMO−2 (−6.32 eV)



LUMO+2 (−0.69 eV)



HOMO−3 (−7.02 eV)



LUMO+3 (−0.31 eV)

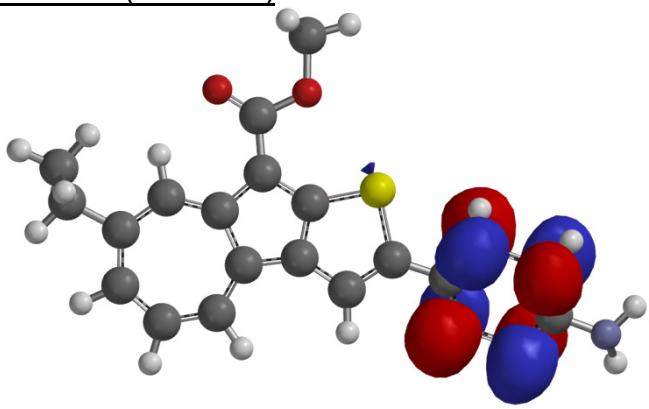
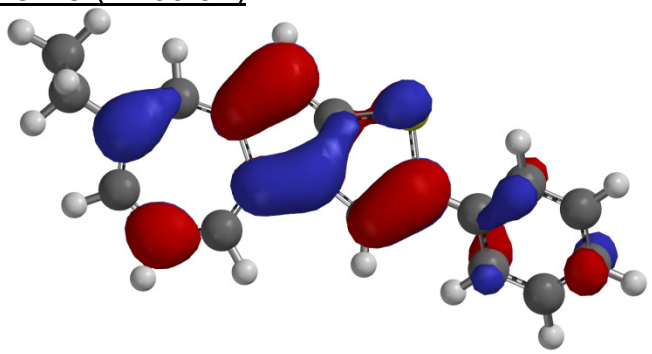
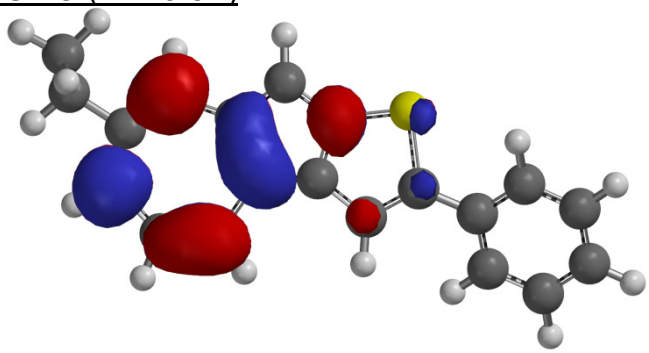


Figure S128. Frontier Kohn–Sham orbitals of **14** at the B3LYP/6-311G* level.

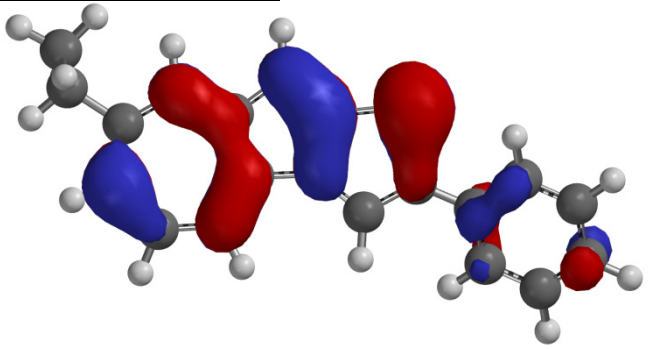
HOMO (−4.99 eV)



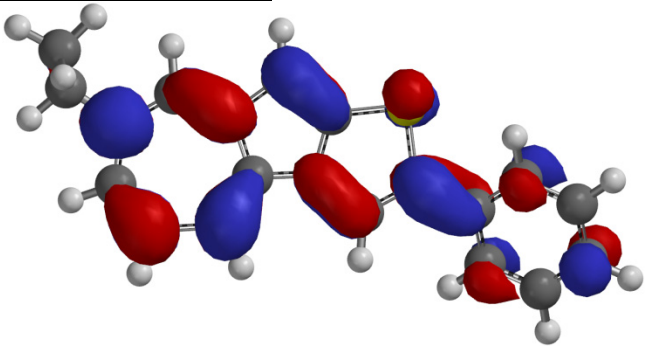
LUMO (−2.13 eV)



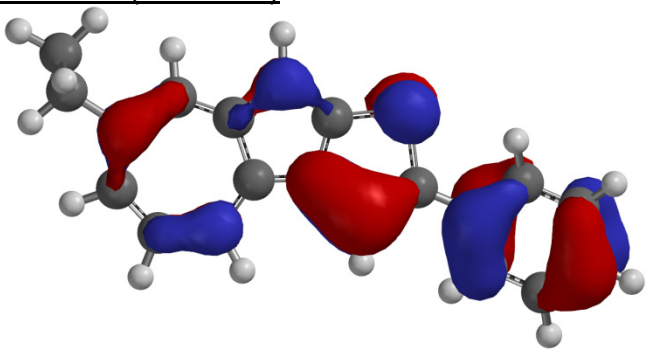
HOMO−1 (−6.02 eV)



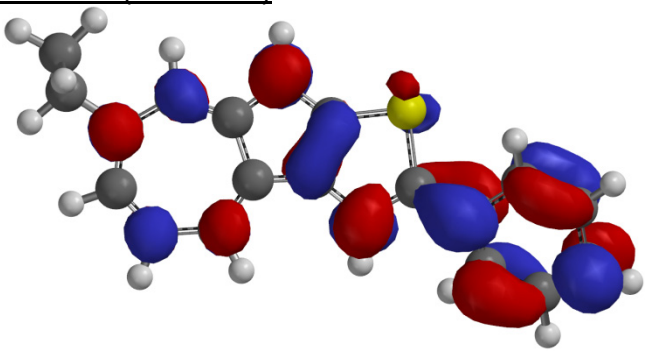
LUMO+1 (−1.62 eV)



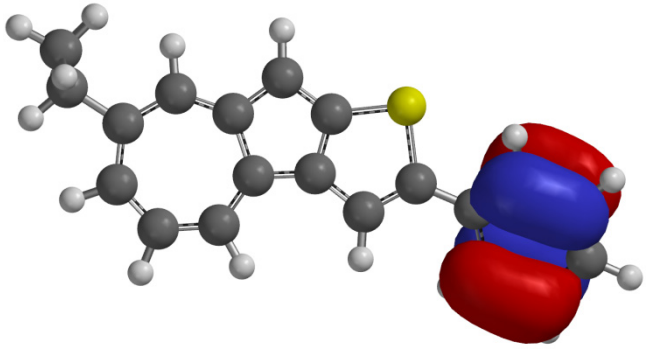
HOMO−2 (−6.80 eV)



LUMO+2 (−0.60 eV)



HOMO−3 (−7.03 eV)



LUMO+3 (−0.33 eV)

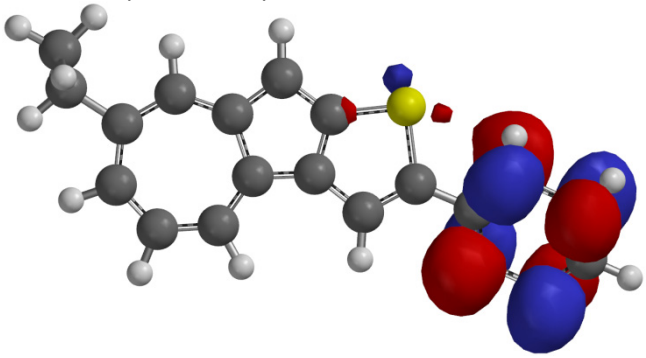


Figure S129. Frontier Kohn–Sham orbitals of **21** at the B3LYP/6-311G* level.

4. Cyclic and differential pulse voltammograms of 11−21 (Figures S130−S140).

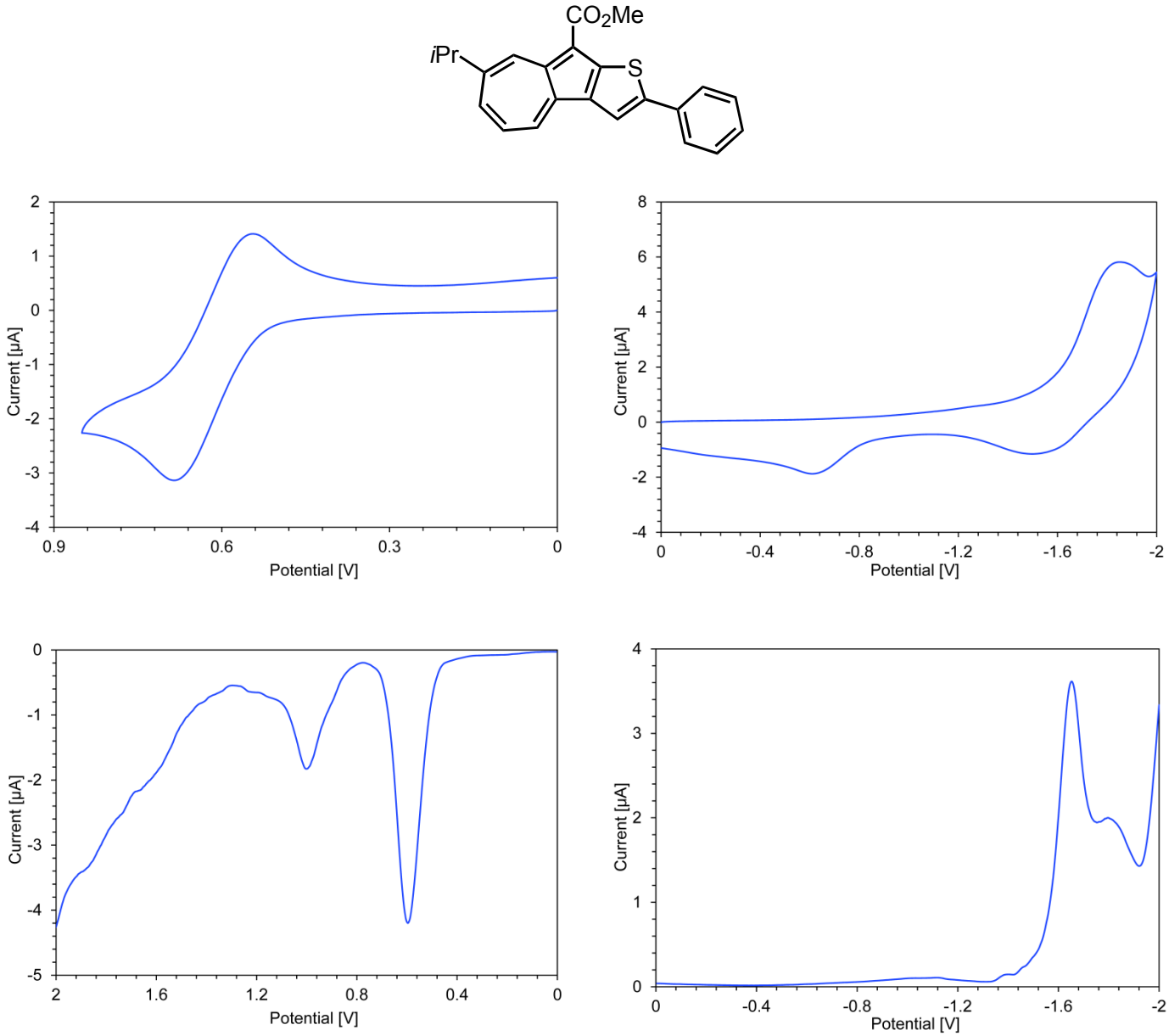


Figure S130. Cyclic voltammogram for oxidation (top, left) and reduction (top, right), and differential pulse voltammograms for oxidation (bottom, left) and reduction (bottom, right) of **11** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as the supporting electrolyte; scan rate: CV = 100 mVs^{-1}, DPV = 20 mVs^{-1}.

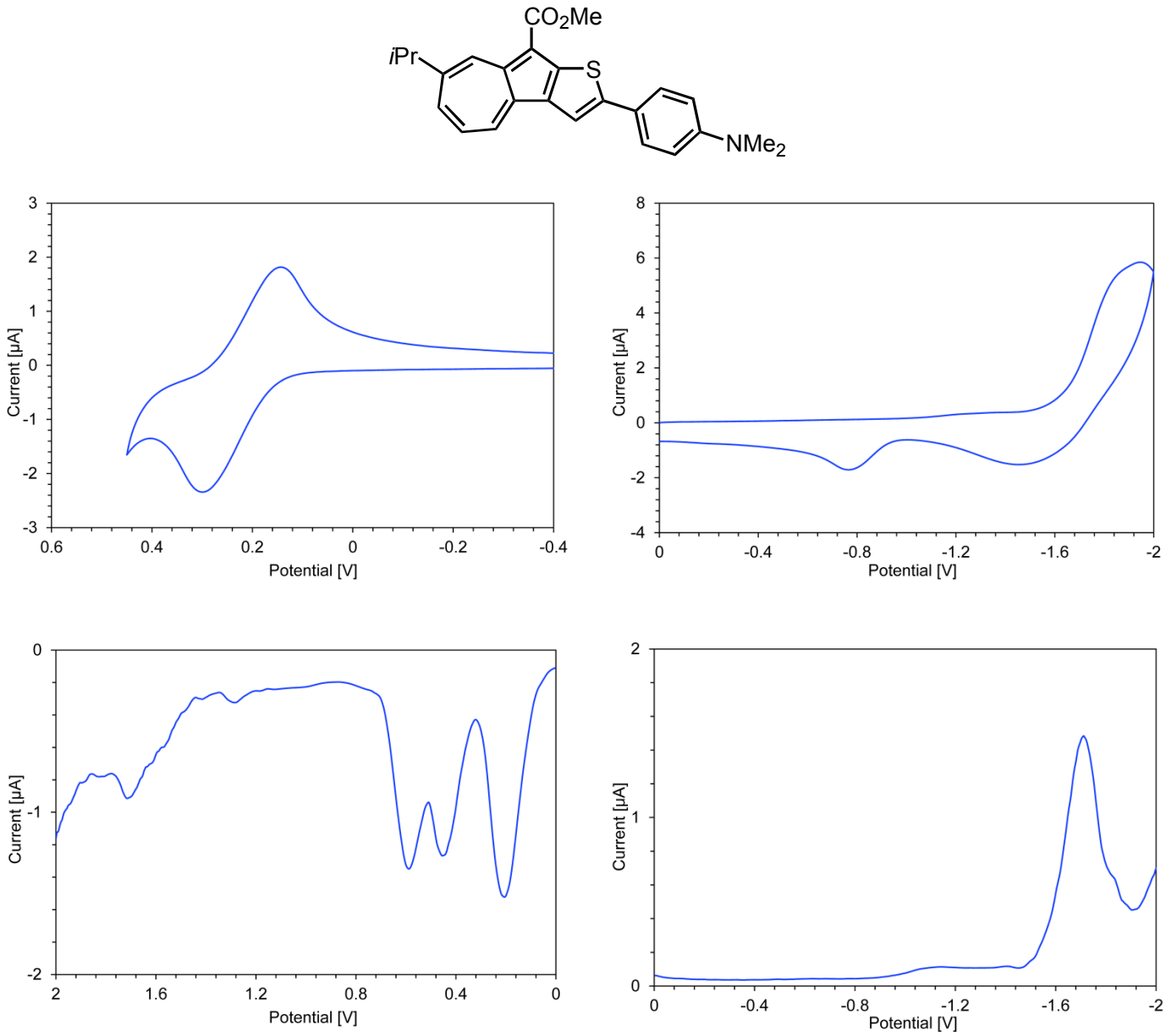


Figure S131. Cyclic voltammogram for oxidation (top, left) and reduction (top, right), and differential pulse voltammograms for oxidation (bottom, left) and reduction (bottom, right) of **12** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as the supporting electrolyte; scan rate: CV = 100 mVs^{-1}, DPV = 20 mVs^{-1}.

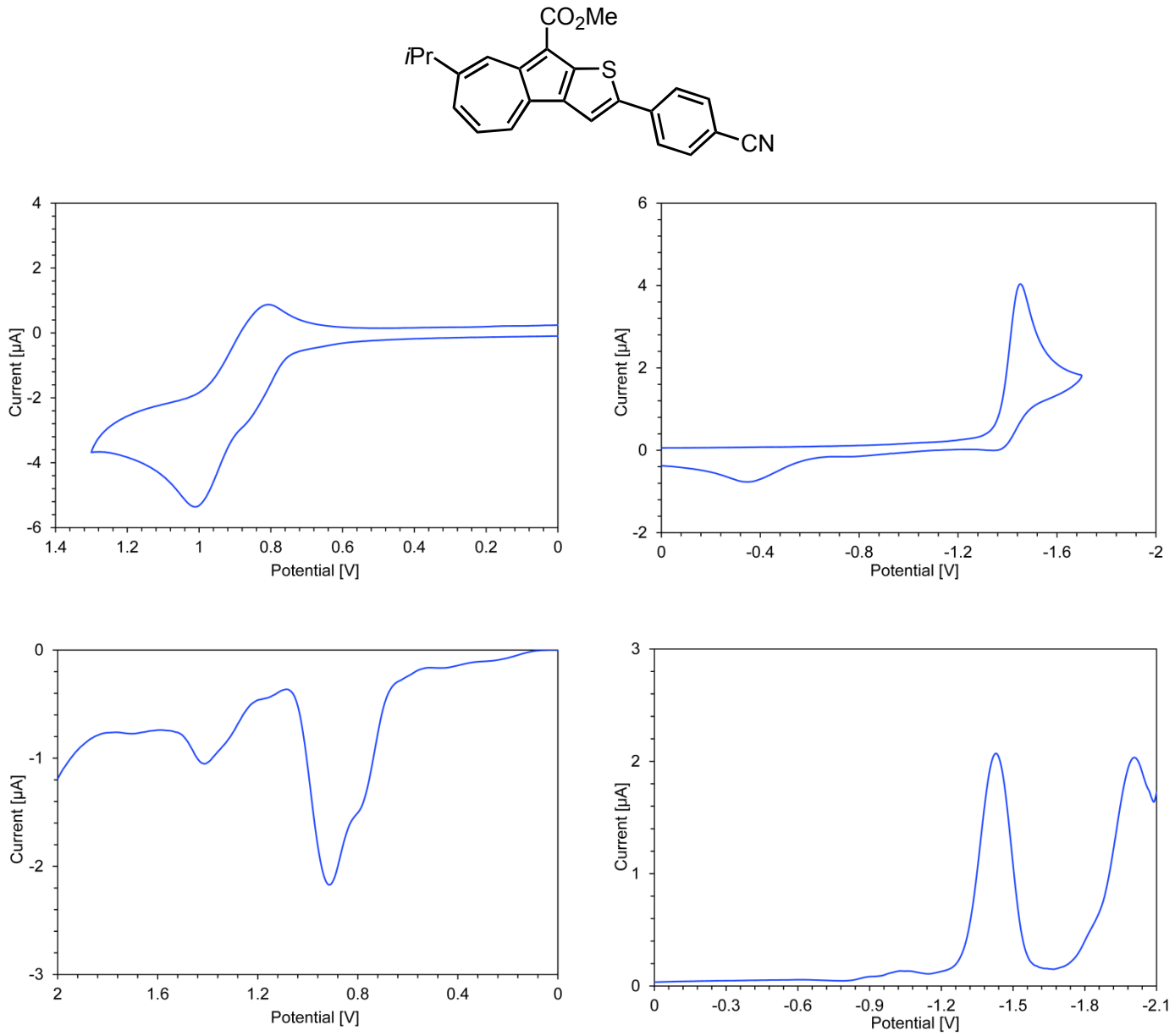


Figure S132. Cyclic voltammogram for oxidation (top, left) and reduction (top, right), and differential pulse voltammograms for oxidation (bottom, left) and reduction (bottom, right) of **13** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as the supporting electrolyte; scan rate: CV = 100 mVs^{-1}, DPV = 20 mVs^{-1}.

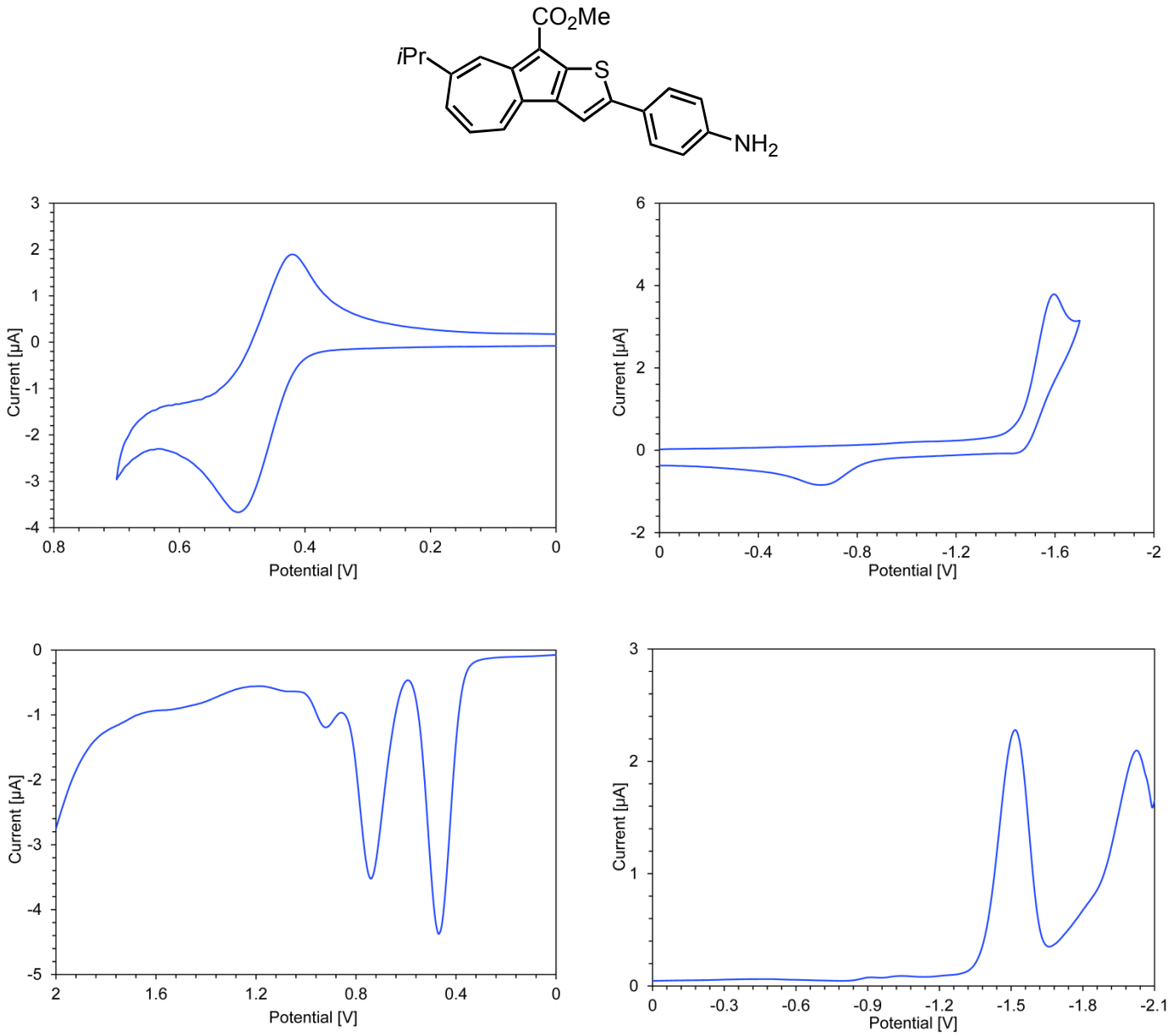


Figure S133. Cyclic voltammogram for oxidation (top, left) and reduction (top, right), and differential pulse voltammograms for oxidation (bottom, left) and reduction (bottom, right) of **14** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as the supporting electrolyte; scan rate: CV = 100 mVs^{-1}, DPV = 20 mVs^{-1}.

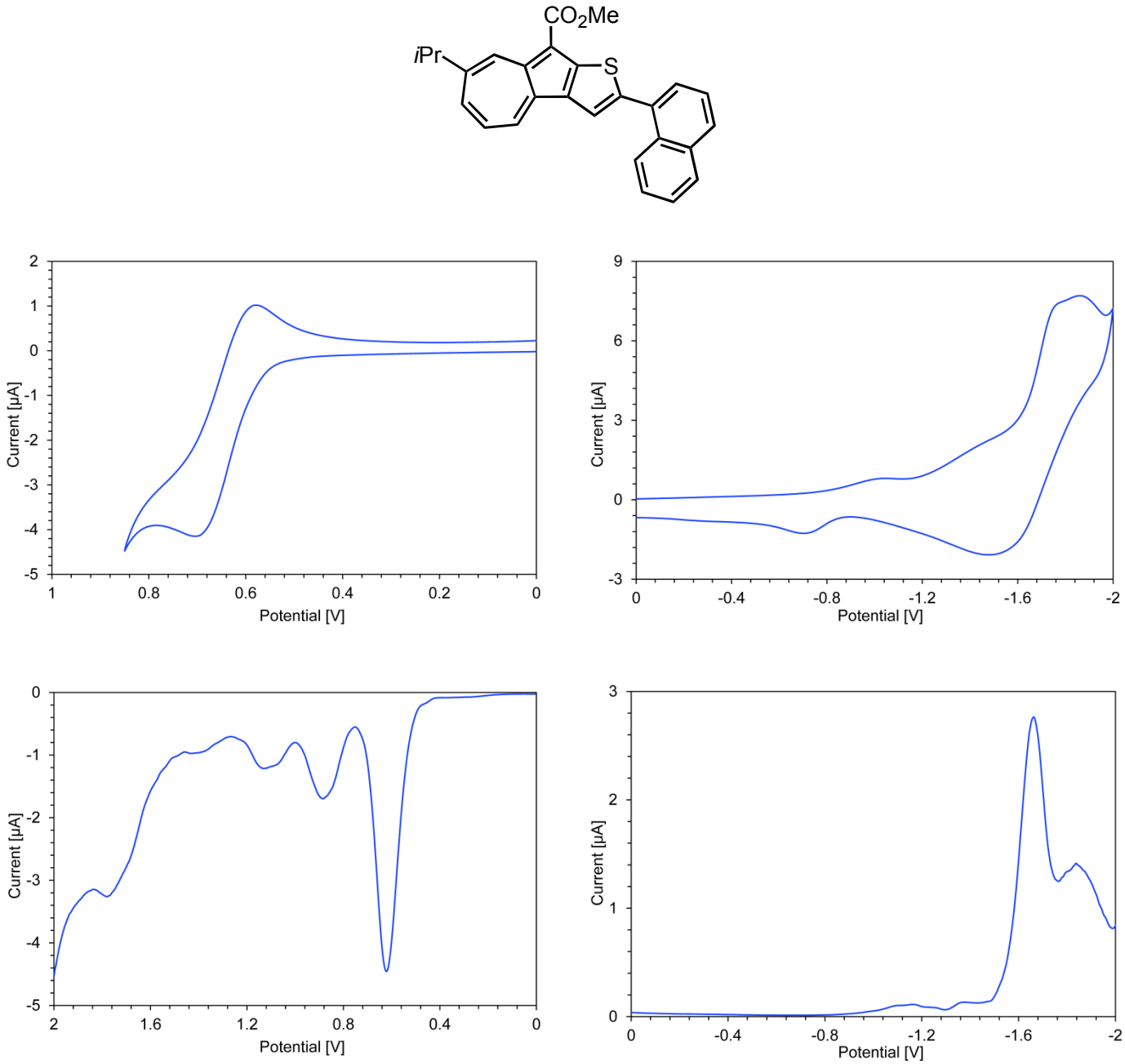


Figure S134. Cyclic voltammogram for oxidation (top, left) and reduction (top, right), and differential pulse voltammograms for oxidation (bottom, left) and reduction (bottom, right) of **15** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as the supporting electrolyte; scan rate: CV = 100 mVs^{-1}, DPV = 20 mVs^{-1}.

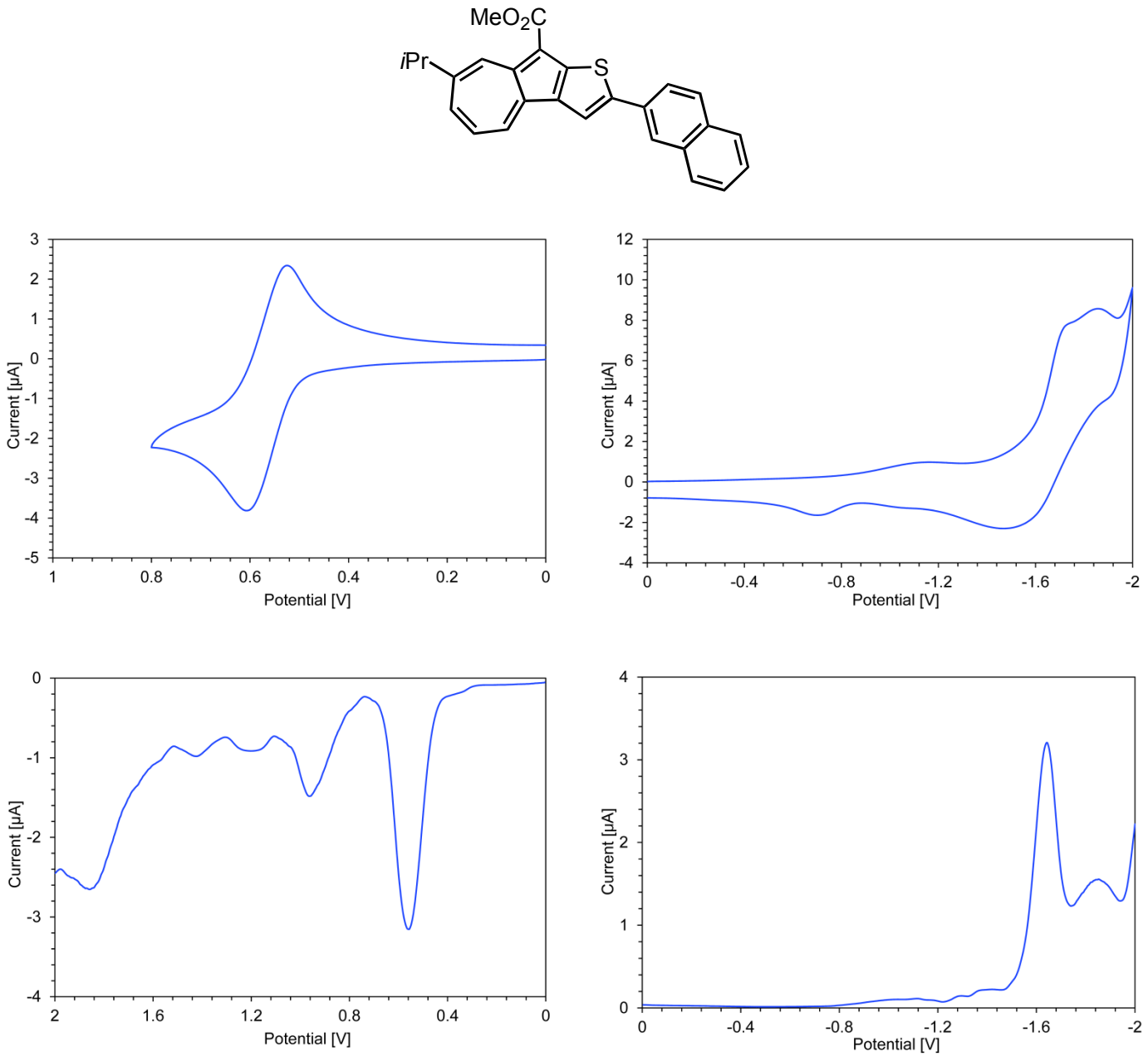


Figure S135. Cyclic voltammogram for oxidation (top, left) and reduction (top, right), and differential pulse voltammograms for oxidation (bottom, left) and reduction (bottom, right) of **16** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as the supporting electrolyte; scan rate: CV = 100 mVs^{-1}, DPV = 20 mVs^{-1}.

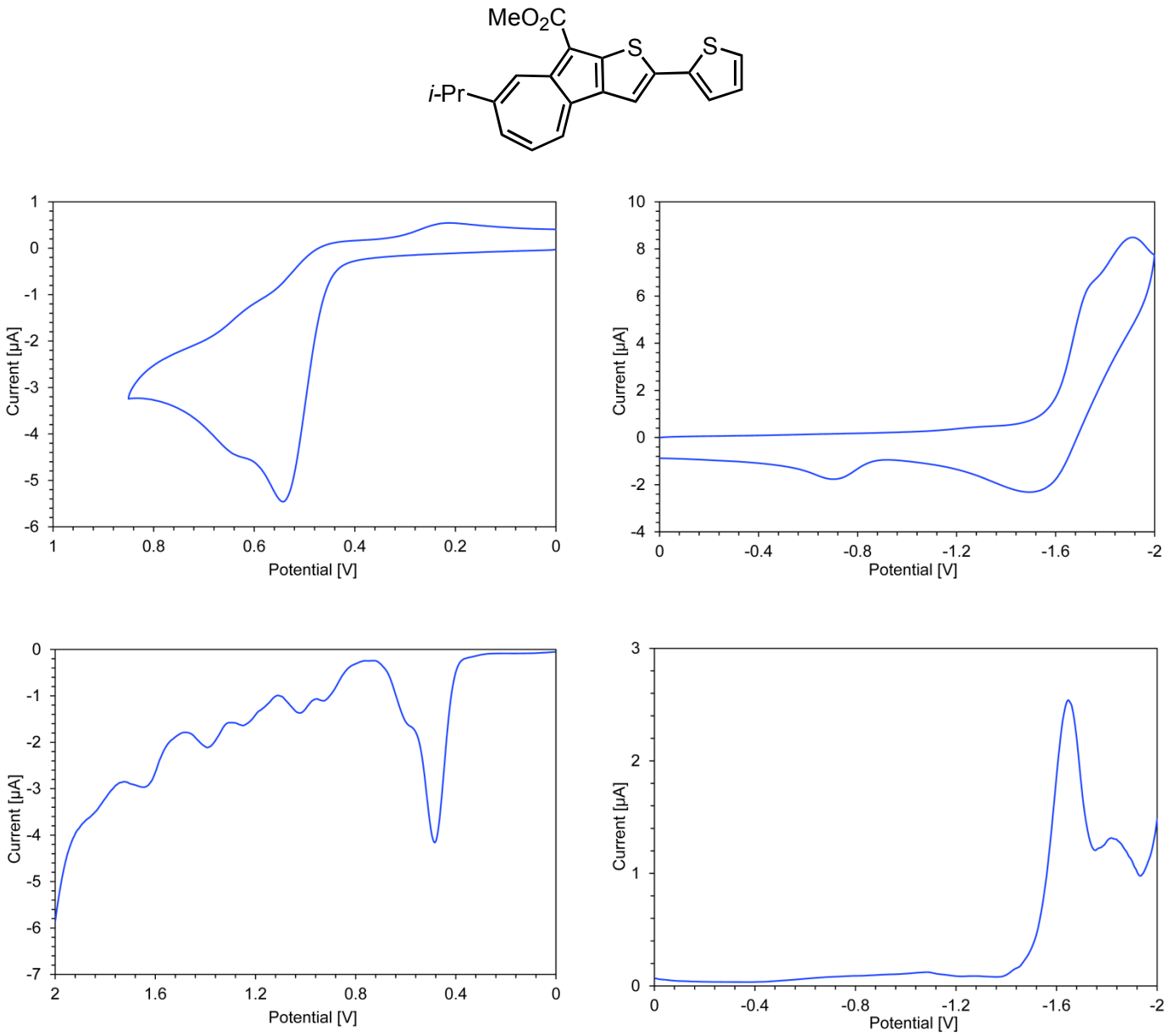


Figure S136. Cyclic voltammogram for oxidation (top, left) and reduction (top, right), and differential pulse voltammograms for oxidation (bottom, left) and reduction (bottom, right) of **17a** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as the supporting electrolyte; scan rate: CV = 100 mVs^{-1}, DPV = 20 mVs^{-1}.

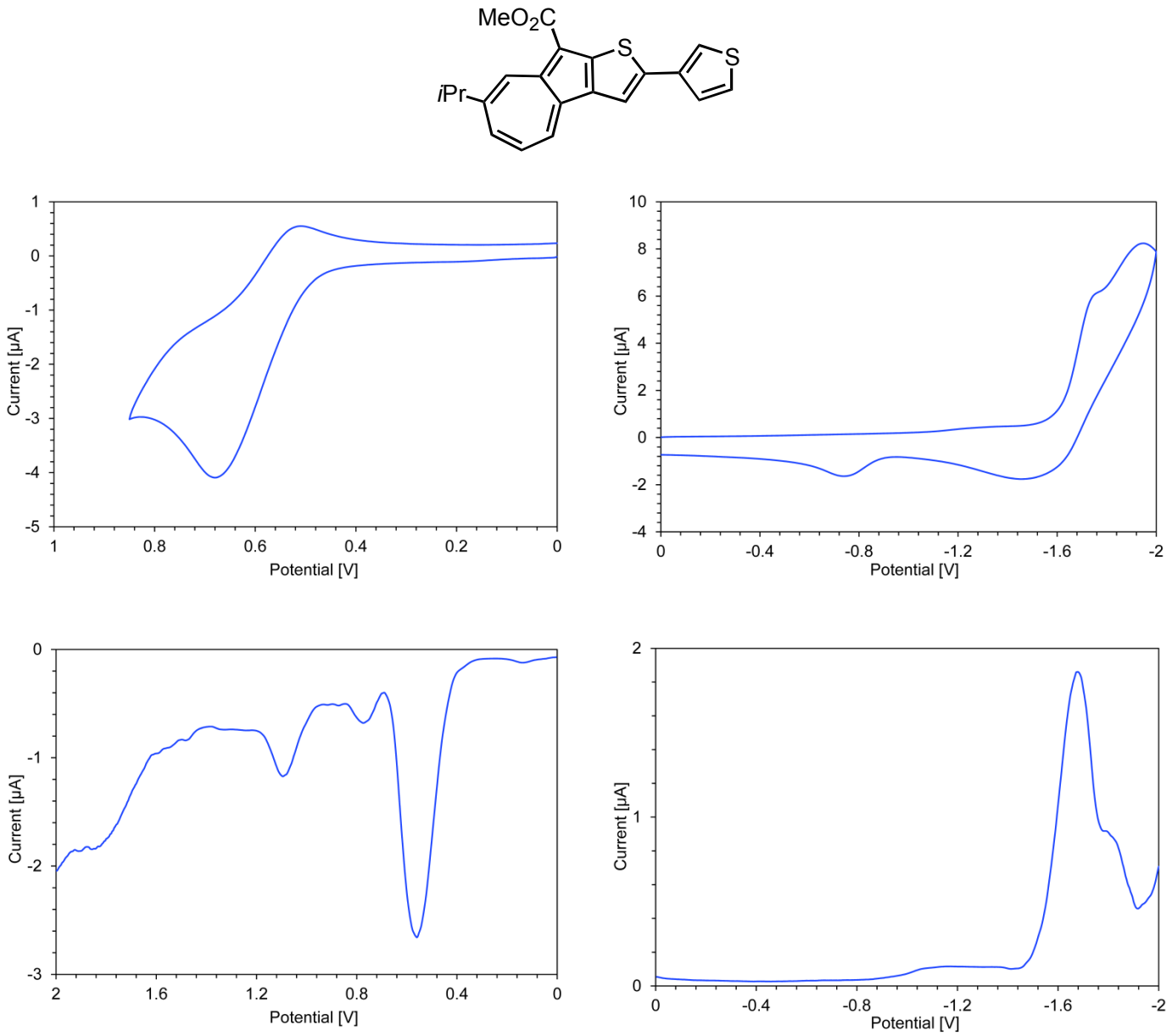


Figure S137. Cyclic voltammogram for oxidation (top, left) and reduction (top, right), and differential pulse voltammograms for oxidation (bottom, left) and reduction (bottom, right) of **18a** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as the supporting electrolyte; scan rate: CV = 100 mVs^{-1}, DPV = 20 mVs^{-1}.

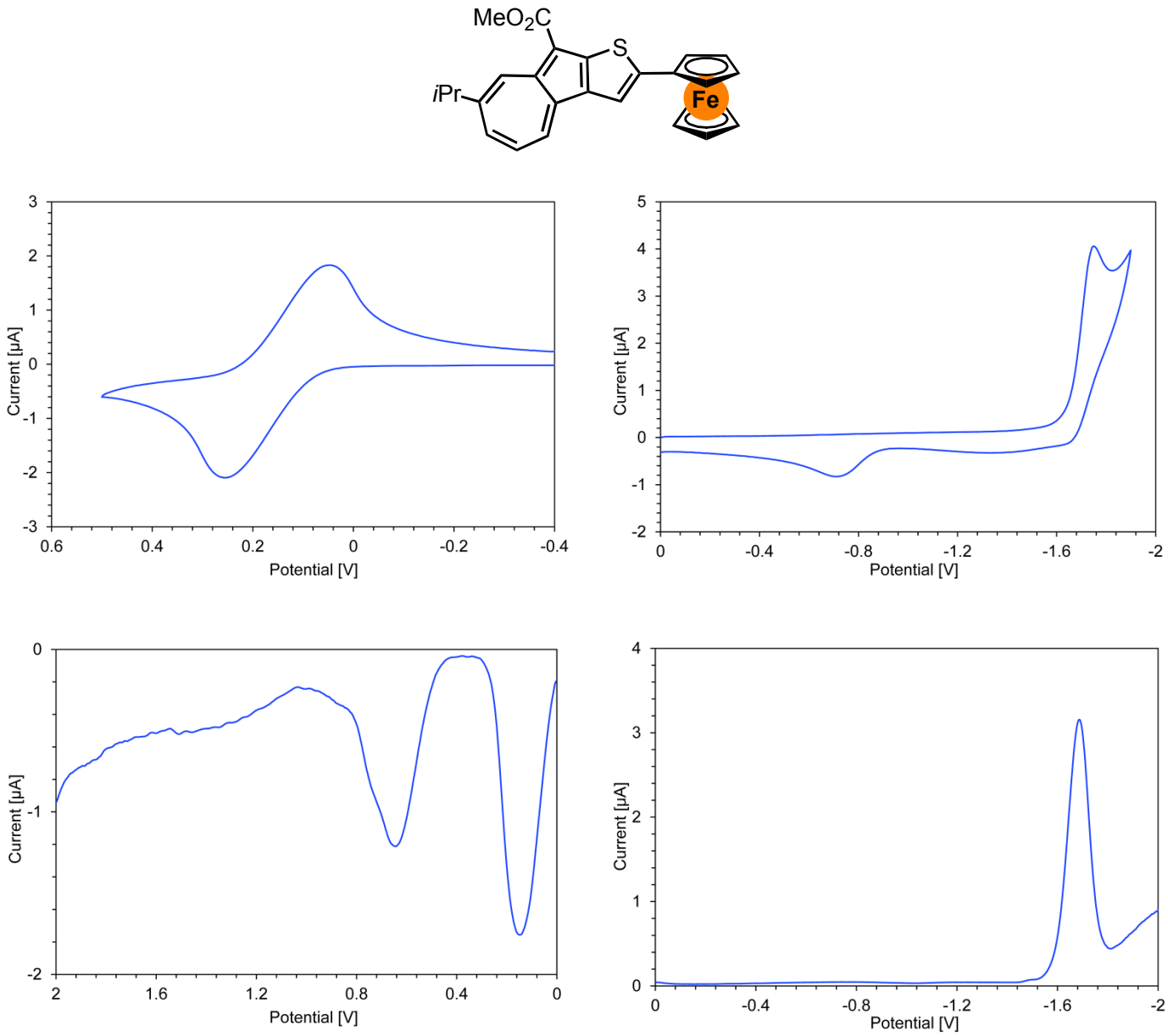


Figure S138. Cyclic voltammogram for oxidation (top, left) and reduction (top, right), and differential pulse voltammograms for oxidation (bottom, left) and reduction (bottom, right) of **19a** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as the supporting electrolyte; scan rate: CV = 100 mVs^{-1}, DPV = 20 mVs^{-1}.

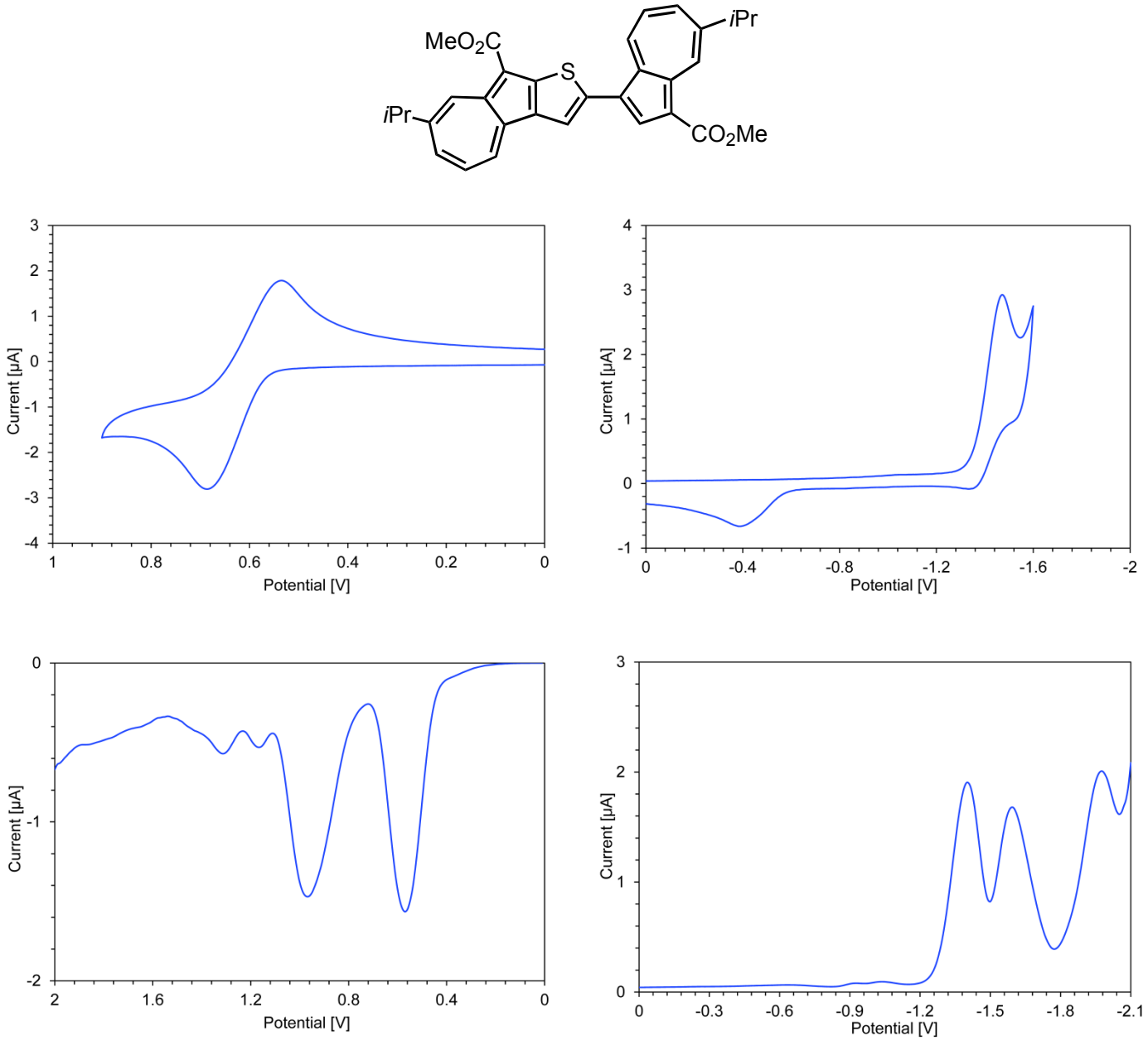


Figure S139. Cyclic voltammogram for oxidation (top, left) and reduction (top, right), and differential pulse voltammograms for oxidation (bottom, left) and reduction (bottom, right) of **20** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as the supporting electrolyte; scan rate: CV = 100 mVs^{-1}, DPV = 20 mVs^{-1}.

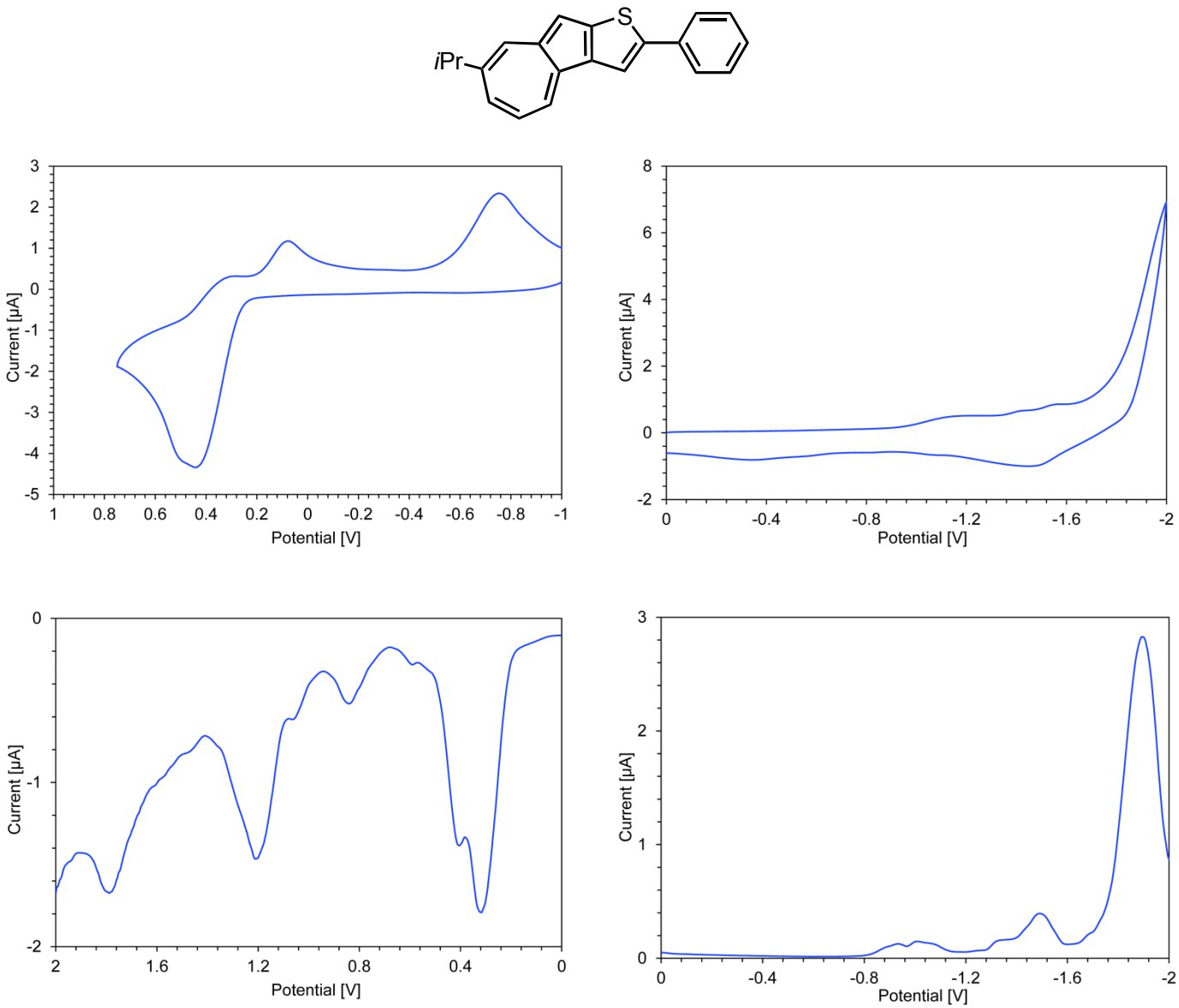


Figure S140. Cyclic voltammogram for oxidation (top, left) and reduction (top, right), and differential pulse voltammograms for oxidation (bottom, left) and reduction (bottom, right) of **21** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as the supporting electrolyte; scan rate: CV = 100 mVs^{-1}, DPV = 20 mVs^{-1}.

5. ORTEP Drawing of 12, 17b, 19a and 20 (Figures S141−S144).

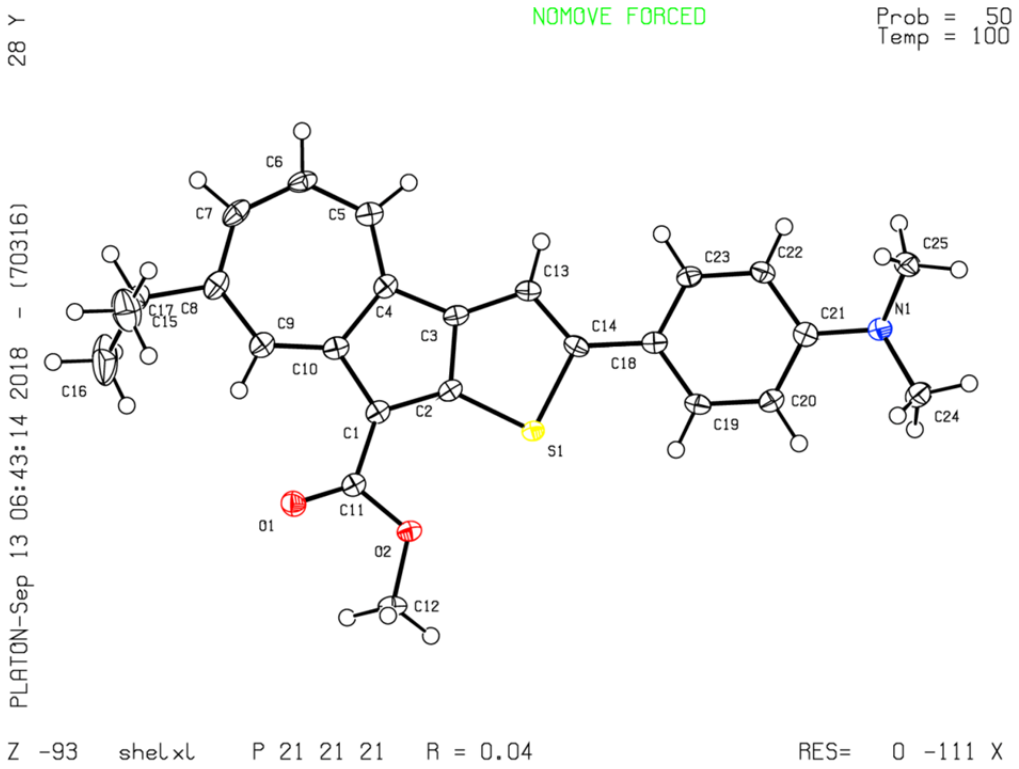


Figure S141. ORTEP diagrams of **12** (CCDC 1868701); ellipsoids are drawn at the 50% probability level; recrystallized from CH_2Cl_2/MeOH.

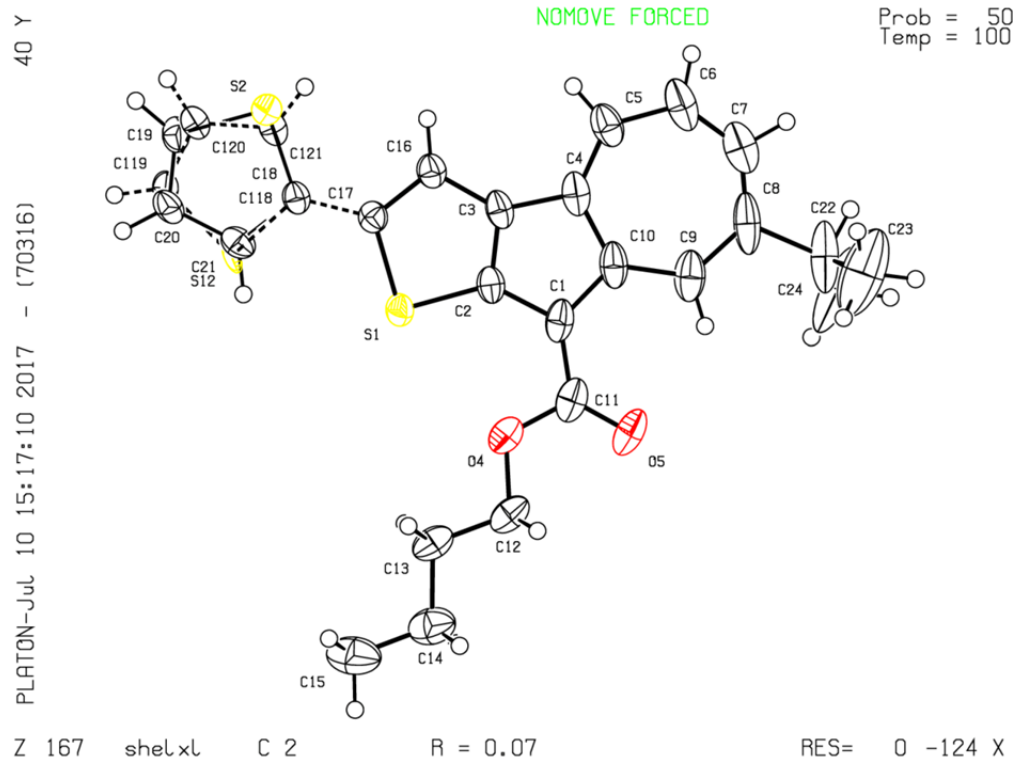


Figure S142. ORTEP diagrams of **17b** (CCDC 1561681); ellipsoids are drawn at the 50% probability level; recrystallized from CH_2Cl_2/MeOH.

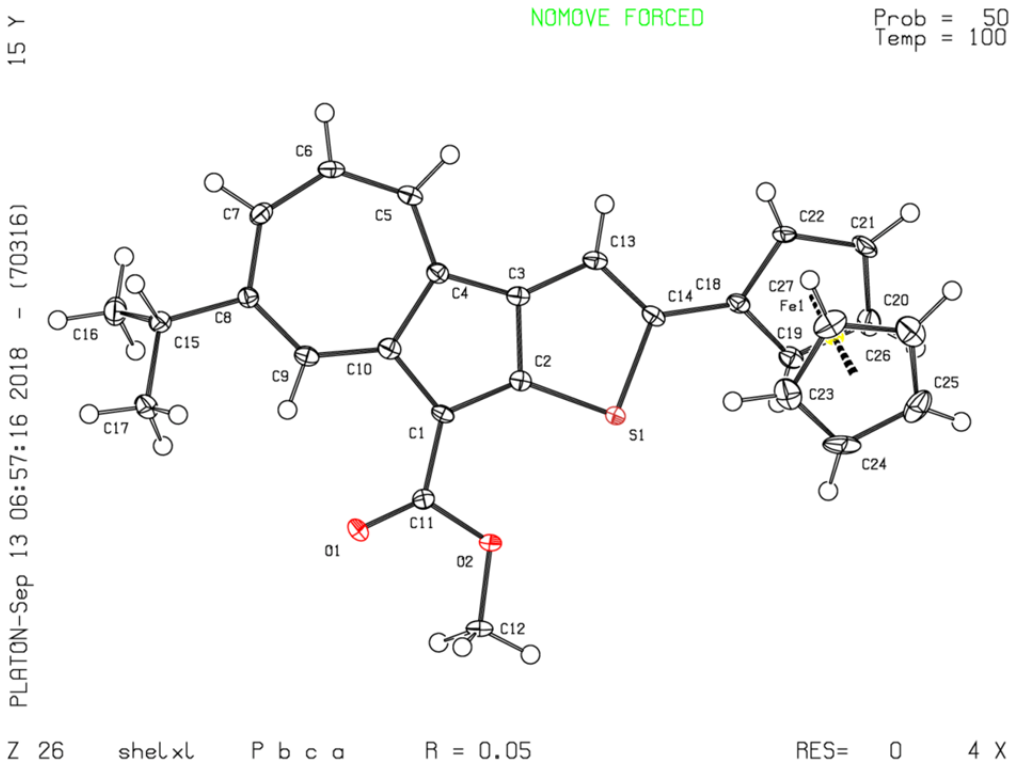


Figure S143. ORTEP diagrams of **19a** (CCDC 1868702); ellipsoids are drawn at the 50% probability level; recrystallized from CH_2Cl_2/EtOH.

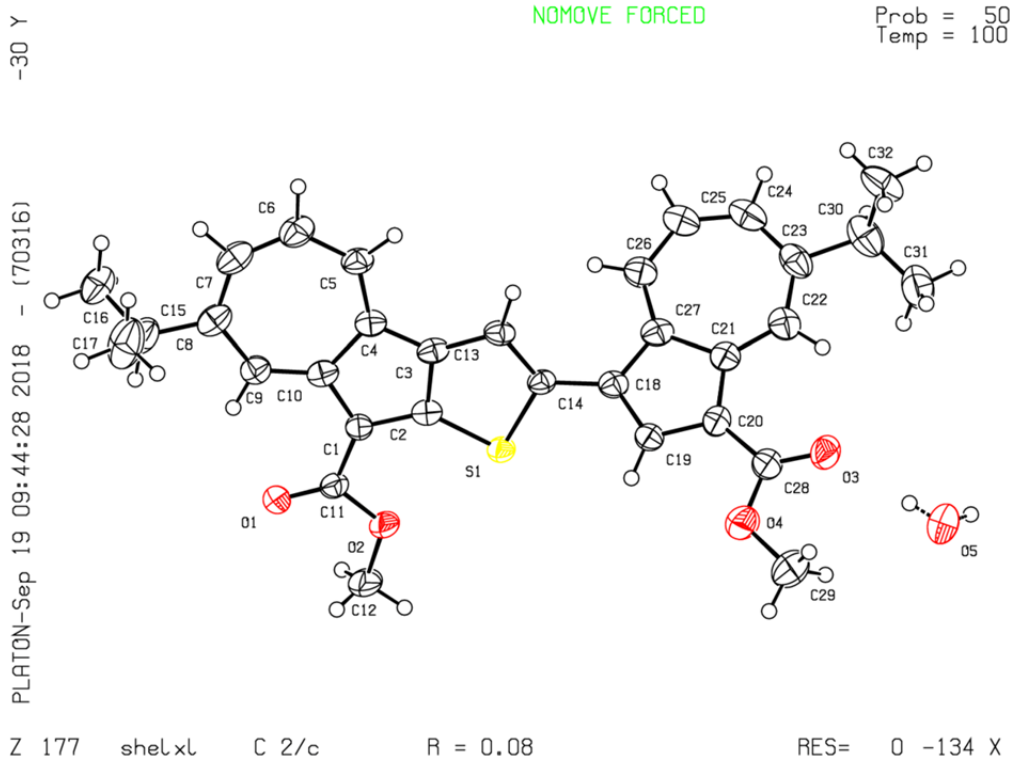
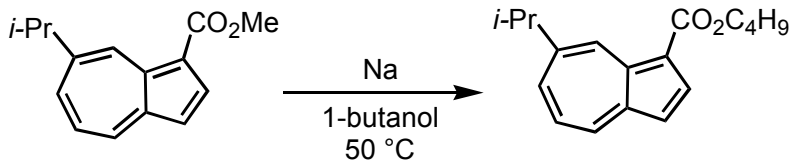


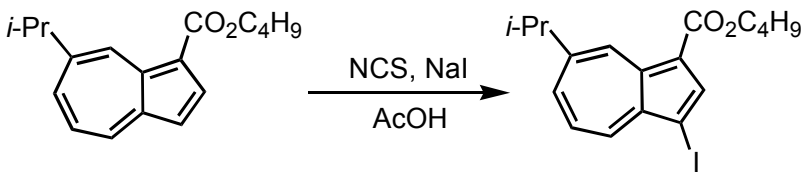
Figure S144. ORTEP diagrams of **20** (CCDC 1868703); ellipsoids are drawn at the 50% probability level; recrystallized from CH_2Cl_2/EtOH.

Synthesis of 1-*n*-butoxycarbonyl-7-isopropylazulene



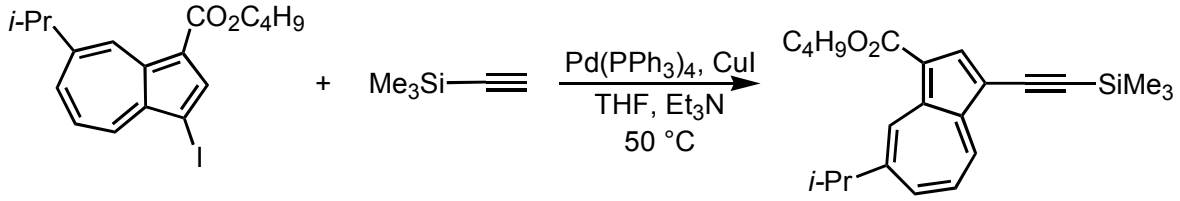
To a solution of 1-methoxycarbonyl-7-isopropylazulene (2.21 g, 9.76 mmol) in 1-butanol (100 mL) was added sodium (1.04 g, 45.2 mmol) and the resulting mixture was stirred at 50 °C for 18 h under a nitrogen atmosphere. The reaction mixture was poured into water and extracted with toluene. The organic layer was washed with brine, dried with Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/AcOEt (20 : 1) to give 1-*n*-butoxycarbonyl-7-isopropylazulene (2.26 g, 86%) as purple oil. IR (AT-IR): ν_{max} = 2959 (w), 2871 (w), 2143 (w), 1684 (m), 1596 (w), 1508 (w), 1431 (s), 1377 (w), 1305 (w), 1248 (w), 1215 (s), 1171 (w), 1129 (w), 1071 (w), 1053 (w), 989 (w), 966 (w), 933 (w), 917 (w), 887 (w), 853 (s), 840 (s), 805 (w), 777 (m), 766 (m), 739 (w), 722 (w), 702 (w), 673 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ_H = 9.77 (s, 1H, H_8), 8.37 (d, 1H, *J* = 4.0 Hz, H_2), 8.34 (d, 1H, *J* = 10.0 Hz, H_4), 7.74 (d, 1H, *J* = 10.0 Hz, H_6), 7.39 (t, 1H, *J* = 10.0 Hz, H_5), 7.20 (d, 1H, *J* = 4.0 Hz, H_3), 4.39 (t, 2H, *J* = 7.4 Hz, *n*Bu), 3.23 (sept, 1H, *J* = 6.9 Hz, *i*Pr), 1.85−1.80 (m, 2H, *n*Bu), 1.59−1.53 (m, 2H, *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 = 165.79, 148.66, 144.66, 140.68, 140.41, 138.04, 137.58, 136.52, 126.44, 116.37, 115.96, 63.62, 39.28, 31.20, 24.79, 19.57, 13.94 ppm; HRMS (MALDI-TOF, positive): calcd for $C_{18}H_{22}O_2$ + H^+ $[M + H]^+$, 271.1693; found: 271.1720.

Synthesis of 1-*n*-butoxycarbonyl-3-iodo-7-isopropylazulene



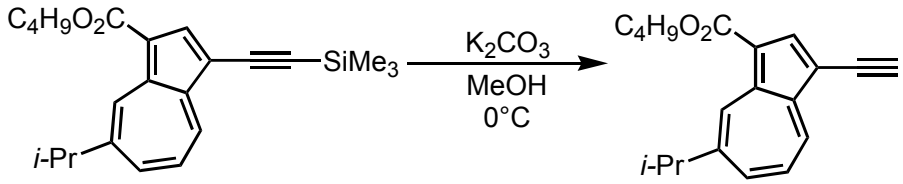
To a mixture of NCS (990 mg, 7.41 mmol) and NaI (1.45 g, 9.67 mmol) in AcOH (20 mL) was added a solution of 1-*n*-butoxycarbonyl-7-isopropylazulene (1.30 g, 4.82 mmol) in AcOH (10 mL). The reaction mixture was stirred at room temperature for 3 hours. The reaction mixture was poured into saturated aq. Na_2SO_3, extracted with hexane. The organic layer was washed with 10% NaOH, brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/AcOEt (20 : 1) to give 1-*n*-butoxycarbonyl-3-iodo-7-isopropylazulene (1.82 g, 95%) as purple solid. m.p. 52−53 °C; IR (AT-IR): ν_{max} = 2957 (w), 2929 (w), 2871 (w), 1673 (s), 1577 (w), 1521 (w), 1492 (w), 1451 (m), 1417 (m), 1377 (w), 1328 (w), 1299 (w), 1263 (w), 1211 (s), 1192 (m), 1168 (w), 1128 (w), 1063 (w), 1046 (w), 958 (w), 934 (w), 915 (w), 881 (w), 854 (w), 794 (w), 773 (m), 741 (w), 717 (w), 689 (w), 666 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ_H = 9.72 (d, 1H, *J* = 1.7 Hz, H_8), 8.44 (s, 1H, H_2), 8.30 (d, 1H, *J* = 10.0 Hz, H_4), 7.81 (d, 1H, *J* = 10.0 Hz, H_6), 7.52 (t, 1H, J = 10.0 Hz, H_5), 4.37 (t, 2H, *J* = 7.4 Hz, *n*Bu), 3.21 (sept, 1H, *J* = 6.9 Hz, *i*Pr), 1.83−1.78 (m, 2H, *n*Bu), 1.57−1.51 (m, 2H, *n*Bu), 1.42 (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= 164.75, 149.93, 147.04, 143.62, 140.98, 139.01, 138.71, 137.43, 127.29, 117.43, 73.38, 63.89, 39.32, 31.14, 24.69, 19.55, 13.93 ppm; HRMS (MALDI-TOF, positive): calcd for $C_{18}H_{21}IO_2^+$ $[M]^+$, 396.0581; found :396.0588.

Synthesis of 1-*n*-butoxycarbonyl-3-trimethylsilylethynyl-7-isopropylazulene



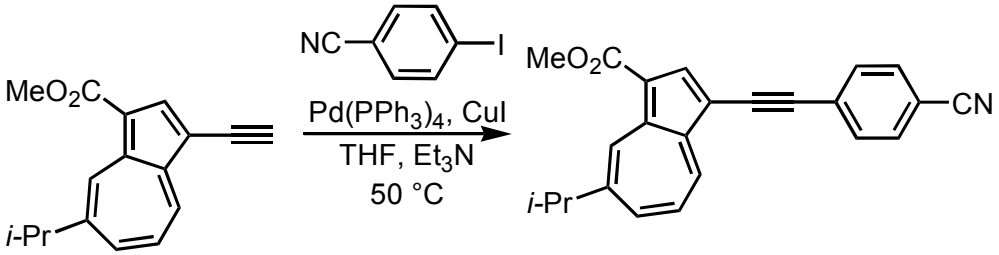
To a degassed solution of 1-*n*-butoxycarbonyl-3-iodo-7-isopropylazulene (2.11 g, 5.34 mmol), trimethylsilylacetylene (787 mg, 8.01 mmol), and CuI (101 mg, 0.534 mmol) in trimethylamine (25 mL) and THF (25 mL) was added tetrakis(triphenylphosphine)palladium(0) (196 mg, 0.160 mmol). The resulting mixture was stirred at 50 °C for 16 h under an Ar atmosphere. The reaction mixture was poured into a sat.NH_4Cl solution and extracted with toluene. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/AcOEt (20 : 1) to give 1-*n*-butoxycarbonyl-3-trimethylsilylethynyl-7-isopropylazulene (1.93 g, 99 %) as purple crystals. m.p. 93−94 °C; IR (AT-IR): ν_{max} = 2959 (w), 2871 (w), 2143 (w), 1684 (m), 1596 (w), 1508 (w), 1431 (s), 1377 (w), 1305 (w), 1248 (w), 1215 (s), 1171 (w), 1129 (w), 1071 (w), 1053 (w), 989 (w), 966 (w), 933 (w), 917 (w), 887 (w), 853 (s), 840 (s), 805 (w), 777 (m), 766 (m), 739 (w), 722 (w), 702 (w), 673 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ_H= 9.71 (d, 1H, *J* = 1.7 Hz, H_8), 8.56 (d, 1H, *J* = 10.0 Hz, H_4), 8.43 (s, 1H, H_2), 7.79 (d, 1H, *J* = 10.0 Hz, H_6), 7.50 (t, 1H, *J* = 10.0 Hz, H_5), 4.35 (t, 2H, *J* = 7.3 Hz, *n*Bu), 3.22 (sept, 1H, *J* = 6.9 Hz, *i*Pr), 1.82−1.76 (m, 2H, *n*Bu), 1.56−1.51 (m, 2H, *n*Bu), 1.41 (d, 6H, *J* = 6.9 Hz, *i*Pr), 1.00 (t, 3H, *J* = 7.3 Hz, *n*Bu), 0.32 (s, 9H, $SiMe_3$) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C= 165.22, 150.52, 145.41, 143.33, 141.05, 139.27, 138.33, 136.27, 127.52, 115.26, 109.02, 100.46, 98.46, 63.82, 39.34, 31.12, 24.70, 19.55, 13.93, 0.42 ppm; HRMS (MALDI-TOF, positive): calcd for $C_{23}H_{30}O_2Si^+$ $[M]^+$, 366.2010; found :366.2007.

Synthesis of 1-*n*-butoxycarbonyl-3-ethynyl-7-isopropylazulene



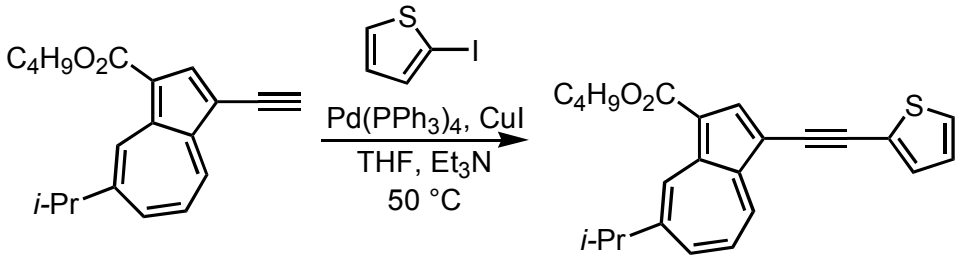
To a solution of 1-*n*-butoxycarbonyl-3-trimethylsilylethynyl-7-isopropylazulene (1.54 g, 4.19 mmol) in MeOH (30 mL) and THF (5 mL) was added K_2CO_3 (1.76 g, 12.7 mmol). The resulting mixture was stirred at 0°C for 1h. The reaction mixture was poured into water and extracted with AcOEt. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/AcOEt (15 : 1) to give 1-*n*-butoxycarbonyl-3-ethynyl-7-isopropylazulene (1.19 g, 96%) as purple oil. IR (AT-IR): ν_{max} = 2960 (w), 2931 (w), 2871 (w), 2099 (w), 1687 (m), 1597 (w), 1523 (w), 1508 (w), 1463 (w), 1430 (s), 1378 (m), 1335 (w), 1307 (w), 1264 (w), 1209 (s), 1170 (m), 1122 (m), 1072 (w), 1044 (m), 958 (w), 917 (w), 893 (w), 803 (w), 776 (m), 728 (w), 689 (w), 677 (w), 659 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ_H= 9.74 (d, 1H, *J* = 1.7 Hz, H_8), 8.59 (d, 1H, *J* = 10.0 Hz, H_4), 8.45 (s, 1H, H_2), 7.79 (d, 1H, *J* = 10.0 Hz, H_6), 7.48 (t, 1H, *J* = 10.0 Hz, H_5), 4.37 (t, 2H, *J* = 7.4 Hz, *n*Bu), 3.44 (s, 1H, C≡CH), 3.22 (sept, 1H, *J* = 6.9 Hz, *i*Pr), 1.83−1.77 (m, 2H, *n*Bu), 1.57−1.51 (m, 2H, *n*Bu), 1.41 (d, 6H, *J* = 6.9 Hz, *i*Pr), 1.00 (t, 3H, *J* = 7.4 Hz, *n*Bu) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C= 165.09, 150.57, 145.49, 143.35, 140.93, 139.34, 138.41, 136.10, 127.57, 115.21, 107.77, 81.25, 79.23, 63.83, 39.31, 31.09, 24.67, 19.52, 13.90 ppm; HRMS (MALDI-TOF, positive): calcd for $C_{20}H_{22}O_2 + H^+$ $[M + H]^+$, 295.1693; found: 295.1677.

Synthesis of 1-*n*-butoxycarbonyl-3-(*p*-cyanophenylethynyl)-7-isopropylazulene (3)



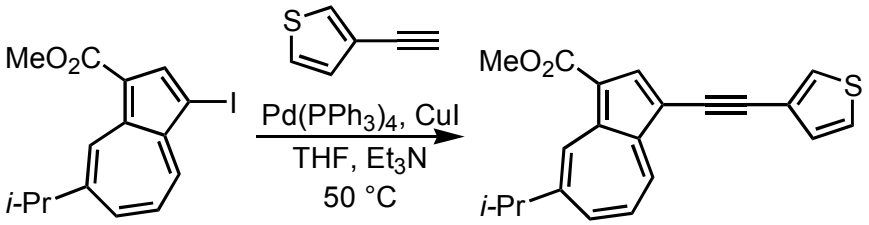
To a degassed solution of 1-methoxycarbonyl-3-ethynyl-7-isopropylazulene (711 mg, 2.01 mmol), *p*-iodobenzonitrile (378 mg, 2.97 mmol,), and CuI (55 mg, 0.289 mmol) in trimethylamine (10 mL) and THF (10 mL) was added tetrakis(triphenylphosphine)palladium(0) (136 mg, 0.118 mmol). The resulting mixture was stirred at 50 °C for 12 h under an Ar atmosphere. The reaction mixture was poured into a sat.NH_4Cl solution and extracted with AcOEt. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/AcOEt (4 : 1) to give **3** (606 mg, 85 %) as purple solid. m.p. 131−132 °C; IR (AT-IR): ν_{max} = 2962 (w), 2949 (w), 2223 (w), 2195 (m), 1699 (s), 1602 (m), 1495 (m), 1445 (m), 1411 (m), 1374 (m), 1327 (w), 1276 (w), 1249 (m), 1203 (s), 1169 (m), 1122 (m), 1099 (m), 1070 (m), 1042 (w), 1023 (w), 998 (w), 961 (w), 920 (w), 875 (m), 841 (m), 827 (m), 801 (m), 774 (m), 750 (m), 706 (m), 691 (m), 673 (w), 661 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ_H = 9.76 (d, 1H, *J* = 1.7 Hz, H_8), 8.64 (d, 1H, *J* = 10.0 Hz H_4), 8.48 (s, 1H, H_2), 7.86 (d, 1H, *J* = 10.0 Hz, H_6), 7.65 (br.s, 4H, *p*-CNPh), 7.56 (t, 1H, *J* = 10.0 Hz, H_5), 3.96 (s, 3H, CO_2Me), 3.25 (sept, 1H, *J* = 6.9 Hz, *i*Pr), 1.44 (d, 6H, *J* = 6.9 Hz, *i*Pr) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C= 165.36, 151.38, 145.18, 143.17, 141.65, 139.75, 138.75, 136.21, 132.14, 131.67, 129.00, 128.02, 118.80, 115.55, 110.77, 107.88, 92.52, 89.94, 51.35, 39.38, 24.70 ppm; HRMS (MALDI-TOF, positive): calcd for $C_{24}H_{19}NO_2^+$ $[M]^+$, 353.1410; found :353.1403.

Synthesis of 1-*n*-butoxycarbonyl-3-(2-thienylethynyl)-7-isopropylazulene (7b)



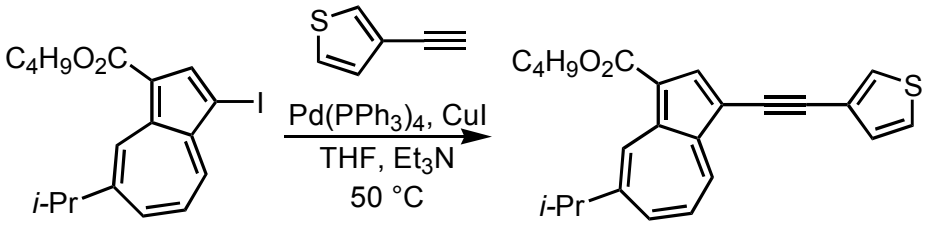
To a degassed solution of 1-*n*-butoxycarbonyl-3-ethynyl-7-isopropylazulene (593 mg, 2.01 mmol), 2-iodothiophene (634 mg, 3.02 mmol), and CuI (40 mg, 0.210 mmol) in trimethylamine (10 mL) and THF (10 mL) was added tetrakis(triphenylphosphine)palladium(0) (118 mg, 0.10 mmol). The resulting mixture was stirred at 50 °C for 18 h under an Ar atmosphere. The reaction mixture was poured into a sat.NH_4Cl solution and extracted with AcOEt. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/AcOEt (20 : 1) to give **7b** (590 mg 78 %) as green oil. IR (AT-IR): ν_{max} = 2959 (m), 2929 (w), 2871 (w), 2194 (w), 1689 (m), 1577 (w), 1501 (w), 1445 (m), 1420 (m), 1376 (m), 1341 (w), 1307 (w), 1235 (m), 1209 (s), 1166 (m), 1129 (m), 1116 (m), 1071 (m), 1046 (m), 959 (w), 917 (m), 889 (w), 849 (m), 825 (w), 802 (w), 775 (m), 697 (m), 666 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ_H= 9.73 (d, 1H, *J* = 1.4 Hz, H_8), 8.62 (d, 1H, *J* = 10.0 Hz, H_4), 8.48 (s, 1H, H_2), 7.80 (d, 1H, *J* = 10.0 Hz, H_6), 7.50 (t, 1H, *J* = 10.0 Hz, H_5), 7.32 (dd, 1H, *J* = 3.7, 0.9 Hz, H_3 of Thiophene), 7.29 (d, 1H, *J* = 5.2 Hz, H_5 of Thiophene), 7.04 (dd, 1H, *J* = 5.0, 3.7 Hz, H_4 of Thiophene), 4.38 (t, 2H, *J* = 7.3 Hz, *n*Bu), 3.23 (sept, 1H, *J* = 6.9 Hz, *i*Pr), 1.84−1.78 (m, 2H, *n*Bu), 1.59−1.53 (m, 2H, *n*Bu), 1.43 (d, 6H, *J* = 6.9 Hz, *i*Pr), 1.02 (t, 3H, *J* = 7.3 Hz, *n*Bu) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C= 165.18, 150.60, 144.80, 142.87, 141.24, 139.43, 138.46, 136.33, 131.36, 127.55, 127.20, 126.83, 124.13, 115.72, 108.65, 88.65, 86.58, 63.87, 39.36, 31.13, 24.70, 19.56, 13.94 ppm; HRMS (MALDI-TOF, positive): calcd for $C_{24}H_{24}O_2S^+$ $[M]^+$, 376.1492; found :376.1480.

Synthesis of 1-methoxycarbonyl-3-(3-thienylethynyl)-7-isopropylazulene (8a)



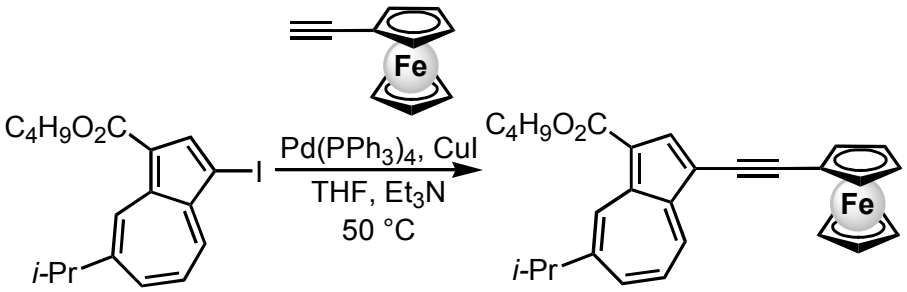
To a degassed solution of 1-methoxycarbonyl-3-iodo-7-isopropylazulene (719 mg, 2.03 mmol), 3-ethynylthiophene (324 mg, 3.00 mmol), and CuI (40 mg, 0.210 mmol) in trimethylamine (10 mL) and THF (10 mL) was added tetrakis(triphenylphosphine)palladium(0) (141 mg, 0.122 mmol). The resulting mixture was stirred at 50 °C for 21 h under an Ar atmosphere. The reaction mixture was poured into a sat.NH_4Cl solution and extracted with AcOEt. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/AcOEt (15 : 1) to give **8a** (666 mg, 98 %) as purple oil. IR (AT-IR): ν_{max} = 2959 (w), 2931 (w), 2871 (w), 2194 (w), 1689 (s), 1577 (w), 1501 (w), 1445 (m), 1420 (s), 1376 (w), 1341 (w), 1307 (w), 1265 (w), 1235 (m), 1209 (s), 1166 (m), 1129 (m), 1116 (w), 1071 (w), 1046 (w), 959 (w), 917 (w), 889 (w), 849 (w), 825 (w), 802 (w), 775 (m), 740 (w), 697 (m), 666 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ_H= 9.73 (d, 1H, *J* = 1.7 Hz, H_8), 8.64 (d, 1H, *J* = 10.0 Hz, H_4), 8.45 (s, 1H, H_2), 7.81 (d, 1H, *J* = 10.0 Hz, H_6), 7.56 (dd, 1H, *J* = 3.0, 1.0 Hz, H_2 of Thiophene), 7.50 (t, 1H, *J* = 10.0 Hz, H_5), 7.33 (dd, 1H, *J* = 5.0, 3.0 Hz, H_4 of Thiophene), 7.27 (dd, 1H, *J* = 5.0, 1.0 Hz, H_5 of Thiophene), 3.96 (s, 3H, CO_2Me), 3.24 (sept, 1H, *J* = 6.9 Hz, *i*Pr), 1.43 (d, 6H, *J* = 6.9 Hz, *i*Pr) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C= 165.53, 150.56, 144.84, 142.74, 141.25, 139.37, 138.36, 136.30, 130.01, 127.92, 127.47, 125.41, 122.95, 115.08, 109.10, 88.60, 84.23, 51.26, 39.34, 24.71 ppm; HRMS (MALDI-TOF, positive): calcd for $C_{21}H_{18}O_2S^+$ $[M]^+$, 334.1022; found :334.1045.

Synthesis of 1-*n*-butoxycarbonyl-3-(3-thienylethynyl)-7-isopropylazulene (8b)



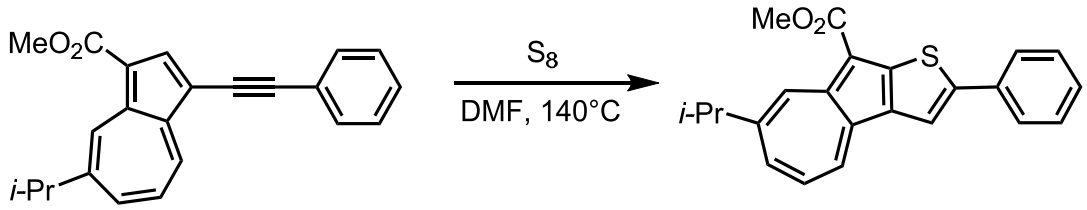
To a degassed solution of 1-*n*-butoxycarbonyl-3-iodo-7-isopropylazulene (797 mg, 2.01 mmol), 3-ethynylthiophene (324 mg, 3.00 mmol), and CuI (39 mg, 0.204 mmol) in trimethylamine (10 mL) and THF (10 mL) was added tetrakis(triphenylphosphine)palladium(0) (121 mg, 0.105 mmol). The resulting mixture was stirred at 50 °C for 19 h under an Ar atmosphere. The reaction mixture was poured into a sat.NH_4Cl solution and extracted with AcOEt. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/AcOEt (15 : 1) to give **8b** (756 mg, 100 %) as purple oil. IR (AT-IR): ν_{max} = 2959 (w), 2871 (w), 2203 (w), 1687 (s), 1577 (w), 1502 (w), 1442 (s), 1417 (m), 1376 (w), 1307 (w), 1229 (m), 1208 (s), 1166 (m), 1130 (w), 1119 (w), 1071 (w), 1044 (w), 962 (w), 914 (w), 889 (w), 864 (w), 826 (w), 800 (w), 776 (s), 739 (w), 688 (w), 670 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ_H = 9.72 (d, 1H, *J* = 1.7 Hz, H_8), 8.64 (d, 1H, *J* = 10.0 Hz, H_4), 8.45 (s, 1H, H_2), 7.80 (d, 1H, *J* = 10.0 Hz, H_6), 7.55 (dd, 1H, *J* = 3.0, 1.0 Hz, H_2 of Thiophene), 7.50 (t, 1H, *J* = 10.0 Hz, H_5), 7.33 (dd, 1H, *J* = 5.0, 3.0 Hz, H_4 of Thiophene), 7.26 (dd, 1H, *J* = 5.0, 1.0 Hz, H_5 of Thiophene), 3.95 (s, 3H, CO_2Me), 3.23 (sept, 1H, *J* = 6.9 Hz, *i*Pr), 1.42 (d, 6H, *J* = 6.9 Hz, *i*Pr) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C= 165.23, 150.39, 144.81, 142.87, 141.12, 139.32, 138.37, 136.26, 130.00, 127.89, 127.36, 125.40, 122.96, 115.57, 109.02, 88.62, 84.29, 63.85, 39.35, 31.14, 24.70, 19.56, 13.94 ppm; HRMS (MALDI-TOF, positive): calcd for $C_{24}H_{24}O_2S^+$ $[M]^+$, 376.1492; found :376.1470.

Synthesis of 1-*n*-butoxycarbonyl-3-(ferrocenylethynyl)-7-isopropylazulene (9b)



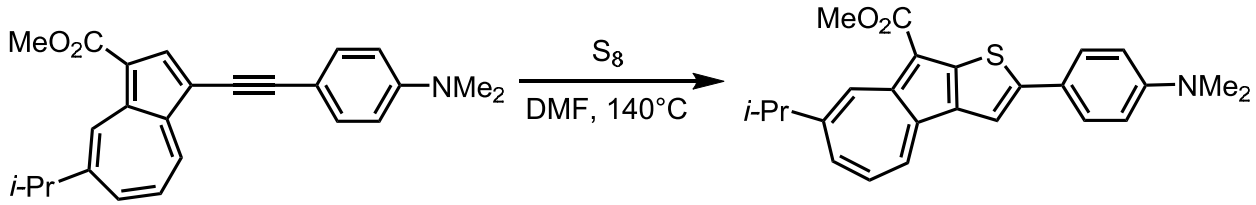
To a degassed solution of 1-*n*-butoxycarbonyl-3-iodo-7-isopropylazulene (811 mg, 2.05 mmol), ethynylferrocene (641 mg, 3.05 mmol), and CuI (42 mg, 0.221 mmol) in trimethylamine (10 mL) and THF (10 mL) was added tetrakis(triphenylphosphine)palladium(0) (118 mg, 0.102 mmol). The resulting mixture was stirred at 50 °C for 12 h under an Ar atmosphere. The reaction mixture was poured into a sat.NH_4Cl solution and extracted with Hexane. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/AcOEt (15 : 1) to give **9b** (918 mg 94 %) as brown solid. m.p. = 127−128 °C; IR (AT-IR): ν_{max} = 2959 (w), 2929 (w), 2869 (w), 2205 (w), 1688 (s), 1577 (w), 1527 (w), 1473 (m), 1426 (s), 1376 (m), 1306 (w), 1247 (m), 1208 (s), 1194 (s), 1168 (m), 1121 (m), 1107 (m), 1070 (m), 1055 (m), 1025 (m), 1003 (m), 959 (w), 913 (m), 819 (m), 775 (m), 756 (m), 687 (w), 675 (w), 666 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ_H = 9.72 (d, 1H, *J* = 1.7 Hz, H_8), 8.60 (d, 1H, *J* = 9.8 Hz, H_4), 8.46 (s, 1H, H_2), 7.77 (d, 1H, *J* = 9.8 Hz, H_6), 7.48 (t, 1H, *J* = 9.8 Hz, H_5), 4.57 (t, 2H, *J* = 1.7 Hz, Cp), 4.39 (t, 2H, , *J* = 7.4 Hz, *n*Bu), 4.28 (s, 5H, Cp), 4.27 (t, 1H, *J* = 1.7 Hz, Cp), 3.22 (t, 1H, *J* = 6.9 Hz, *i*Pr), 1.85−1.79 (m, 2H, *n*Bu), 1.58−1.54 (m, 2H, *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= 165.25, 150.04, 144.68, 142.64, 140.93, 139.17, 138.18, 136.18, 127.09, 115.34, 109.96, 92.20, 80.83, 71.43, 70.09, 68.82, 66.15, 63.80, 39.32, 31.15, 24.68, 19.55, 13.94 ppm; HRMS (MALDI-TOF): calcd for $C_{30}H_{30}FeO_2^+$ $[M]^+$, 478.1590; found :478.1578.

Compound 11



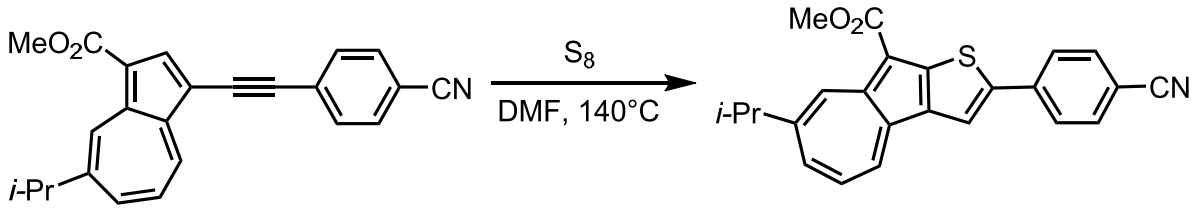
To a solution of **1** (298 mg, 0.910 mmol) in DMF (10 mL) was added S_8 (232 mg, 0.910 mmol). The resulting mixture was stirred at 110 °C for 30 h. The reaction mixture was poured into water and extracted with $CHCl_3$. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/AcOEt (10 : 1) to give **11** (218 mg, 67%) as green solid. M.p. 151−152 °C; IR (AT-IR): ν_{max} = 2957 (w), 1690 (s), 1596 (w), 1529 (w), 1478 (w), 1463 (m), 1446 (m), 1397 (m), 1312 (w), 1207 (m), 1194 (m), 1174 (m), 1136 (w), 1079 (m), 1014 (w), 954 (w), 902 (w), 828 (w), 794 (w), 775 (m), 756 (s), 728 (w), 705 (w), 687 (m), 674 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 251 (4.32), 339 (4.85), 346 sh (4.84), 421 sh (4.11), 438 (4.13), 565 (2.62), 590 (2.63), 655 sh (2.40) nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 9.74 (d, 1H, *J* = 1.4 Hz, H_8), 8.56 (d, 1H, *J* = 9.2 Hz, H_4), 7.92 (s, 1H, H_3 of thiophene), 7.79−7.77 (m, 3H, H_6 and *o*-Ph), 7.52 (t, 1H, *J* = 9.9 Hz, H_5), 7.44 (t, 2H, *J* = 7.5 Hz, *m*-Ph), 7.31 (t, 1H, *J* = 7.5 Hz, *p*-Ph), 4.08 (s, 3H, CO_2Me), 3.28 (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 = 165.33, 151.64, 149.87, 144.98, 144.17, 137.62, 135.59, 135.50, 135.40, 135.26, 132.40, 129.08, 127.60, 127.22, 126.02, 113.59, 107.45, 51.40, 39.51, 24.81 ppm; HRMS (MALDI-TOF): calcd for $C_{23}H_{20}O_2S^+$ $[M]^+$, 360.1179; found: 360.1163.

Compound 12



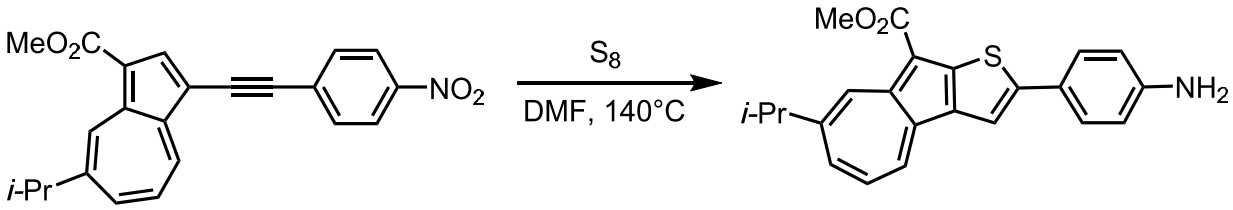
To a solution of **2** (190 mg, 0.511 mmol) in DMF (5 mL) was added S_8 (138 mg, 0.540 mmol). The resulting mixture was stirred at 140 °C for 24 h. The reaction mixture was poured into water and extracted with $CHCl_3$. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/AcOEt (4 : 1) to give **12** (80 mg, 39%) as green solid. M.p. 179−180 °C; IR (AT-IR): ν_{max} = 2960 (w), 1685 (s), 1608 (m), 1534 (m), 1498 (w), 1484 (m), 1454 (s), 1396 (m), 1383 (m), 1362 (m), 1311 (w), 1261 (w), 1225 (m), 1199 (s), 1173 (s), 1123 (m), 1077 (s), 1015 (m), 949 (m), 910 (w), 881 (w), 804 (s), 791 (s), 775 (m), 746 (w), 727 (w), 717 (w), 675 (w), 665 (w), 654 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 249 (4.35), 320 (4.63), 354 (4.70), 383 sh (4.46), 441 (4.16), 570 sh (2.75), 617 (2.79), 690 sh (2.61) nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 9.70 (d, 1H, *J* = 1.7 Hz, H_8), 8.52 (d, 1H, *J* = 9.2 Hz, H_4), 7.74-7.72 (m, 2H, H_6 and H_3 of thiophene), 7.66 (d, 2H, *J* = 8.9 Hz, *o*-Ph), 7.46 (t, 1H, *J* = 9.9 Hz, H_5), 6.78 (d, 2H, *J* = 8.9 Hz, *m*-Ph), 4.07 (s, 3H, CO_2Me), 3.26 (sept, 1H, *J* = 6.9 Hz, *i*Pr), 3.02 (s, 6H, NMe_2), 1.45 (d, 6H, *J* = 6.9 Hz, *i*Pr) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 165.44, 151.30, 150.12, 149.20, 146.13, 143.89, 137.18, 135.74, 135.27, 134.84, 132.24, 127.04, 126.67, 123.73, 112.68, 110.71, 107.21, 51.35, 40.57, 39.46, 24.82 ppm; HRMS (MALDI-TOF): calcd for $C_{25}H_{25}NO_2S^+$ $[M]^+$, 403.1601; found: 403.1618.

Compound 13



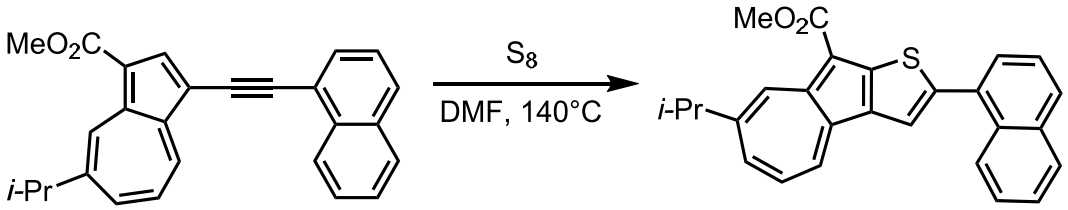
To a solution of **3** (181 mg, 0.512 mmol) in DMF (5 mL) was added S_8 (260 mg, 1.02 mmol). The resulting mixture was stirred at 140 °C for 7 h. The reaction mixture was poured into water and extracted with $CHCl_3$. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/AcOEt (4 : 1) to give **13** (120 mg, 61%) as green solid. M.p. 220−221 °C; IR (AT-IR): ν_{max} = 2957 (w), 2218 (m), 1693 (s), 1599 (s), 1551 (w), 1525 (m), 1491 (m), 1479 (m), 1448 (m), 1404 (m), 1362 (w), 1310 (w), 1280 (w), 1248 (w), 1205 (s), 1193 (m), 1174 (s), 1124 (w), 1080 (s), 1012 (w), 968 (w), 943 (w), 912 (w), 880 (w), 847 (w), 827 (m), 790 (m), 771 (m), 758 (w), 727 (w), 687 (w), 675 (w), 665 (w), 655 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 241 (4.52), 335 sh (4.75), 357 (4.88), 429 (4.47), 444 (4.48), 544 (2.87), 575 (2.87), 642 sh (2.63) nm; ^{1}H NMR (500 MHz, acetone-d_6): δ_H = 9.73 (d, 1H, *J* = 1.7 Hz, H_8), 8.81 (dd, 1H, *J* = 9.2, 0.9 Hz, H_4), 8.43 (s, 1H, H_3 of thiophene), 8.00−7.96 (m, 3H, H_6 and *m*-Ph), 7.81 (d, 2H, *J* = 8.6 Hz, *m*-Ph), 7.70 (dd, 1H, *J* = 10.3, 9.5 Hz, H_5), 4.00 (s, 3H, CO_2Me), 3.29 (sept, 1H, *J* = 6.9 Hz, *i*Pr), 1.43 (d, 6H, *J* = 6.9 Hz, *i*Pr) ppm; ^{13}C NMR (125 MHz, acetone-d_6): δ_C = 164.30, 151.44, 150.66, 144.22, 141.87, 139.62, 138.90, 135.93, 135.21, 133.65, 132.95, 128.45, 128.34, 125.96, 124.88, 118.56, 117.15, 110.27, 50.78, 39.27, 24.10 ppm; HRMS (MALDI-TOF): calcd for $C_{24}H_{19}NO_2S^+$ $[M]^+$, 385.1131; found: 385.1127.

Compound 14



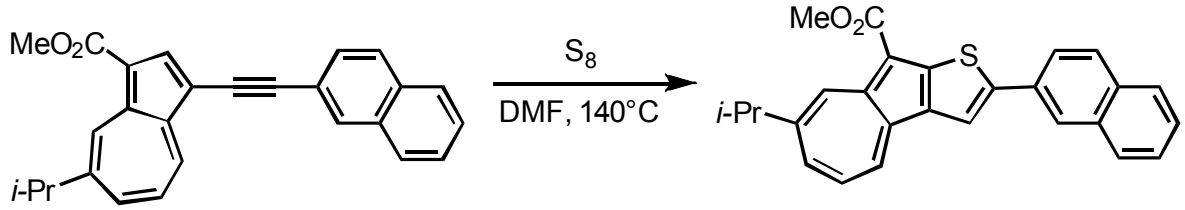
To a solution of **4** (79 mg, 0.212 mmol) in DMF (4 mL) was added S_8 (122 mg, 0.477 mmol). The resulting mixture was stirred at 140 °C for 24 h. The reaction mixture was poured into water and extracted with $CHCl_3$. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/AcOEt (1 : 1) to give **14** (18 mg, 23%) as green solid. M.p. 203−204 °C; IR (AT-IR): ν_{max} = 3467 (w), 3364 (w), 2953 (w), 1673 (s), 1621 (m), 1606 (m), 1534 (w), 1519 (w), 1483 (m), 1457 (s), 1447 (s), 1393 (s), 1381 (m), 1371 (m), 1308 (m), 1294 (m), 1205 (s), 1181 (s), 1122 (w), 1078 (s), 1009 (w), 940 (w), 911 (w), 818 (m), 802 (m), 792 (m), 776 (s), 719 (w), 668 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 243 (4.37), 315 sh (4.58), 346 (4.76), 438 (4.11), 556 sh (2.66), 605 (2.71), 681 sh (2.50) nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 9.71 (d, 1H, *J* = 1.4 Hz, H_8), 8.52 (d, 1H, *J* = 9.5 Hz, H_4), 7.75−7.73 (m, 2H, H_6 and H_3 of thiophene), 7.58 (d, 2H, *J* = 8.3 Hz, *o*-Ph), 7.47 (t, 1H, *J* = 9.9 Hz, H_5), 6.75 (d, 2H, *J* = 8.3 Hz, *m*-Ph), 4.07 (s, 3H, CO_2Me), 3.79 (s, 2H, NH_2), 3.26 (sept, 1H, *J* = 6.9 Hz, *i*Pr), 1.45 (d, 6H, *J* = 6.9 Hz, *i*Pr) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 165.40, 151.25, 149.35, 146.23, 145.80, 143.92, 137.29, 135.55, 135.33, 135.02, 132.26, 127.28, 126.80, 126.04, 115.48, 111.26, 107.24, 51.36, 39.47, 24.82 ppm; HRMS (MALDI-TOF): calcd for $C_{23}H_{21}NO_2S^+$ $[M]^+$, 375.1288; found: 375.1262.

Compound 15



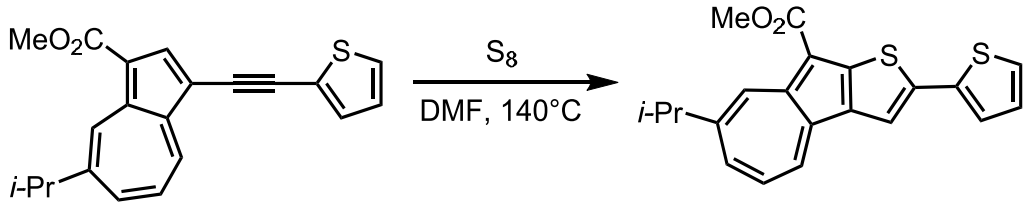
To a solution of **5** (200 mg, 0.528 mmol) in DMF (5 mL) was added S_8 (271 mg, 1.06 mmol). The resulting mixture was stirred at 140 °C for 10 h. The reaction mixture was poured into water and extracted with $CHCl_3$. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/AcOEt (7 : 1) to give **15** (144 mg, 66%) as green oil. IR (AT-IR): ν_{max} = 2959 (w), 1686 (s), 1589 (w), 1525 (w), 1507 (w), 1482 (w), 1465 (m), 1451 (s), 1398 (s), 1382 (m), 1335 (w), 1310 (w), 1267 (w), 1204 (s), 1174 (s), 1133 (w), 1076 (s), 1016 (w), 956 (w), 930 (w), 908 (w), 865 (w), 840 (w), 817 (w), 792 (s), 775 (s), 754 (s), 717 (w), 677 (w), 666 (w), 657 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 253 (4.33), 291 (4.30), 344 (4.66), 426 (4.00), 535 sh (2.46), 580 (2.50), 647 sh (2.26) nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 9.81 (d, 1H, *J* = 1.7 Hz, H_8), 8.61 (d, 1H, *J* = 9.2 Hz, H_4), 8.44−8.42 (m, 1H, naphthalene), 7.94−7.92 (m, 1H, naphthalene), 7.90 (d, 1H, *J* = 8.0 Hz, H_4 of naphthalene), 7.83 (s, 1H, H_3 of thiophene), 7.81 (d, 1H, *J* = 10.9 Hz, H_6), 7.72 (d, 1H, *J* = 6.9 Hz, H_8 of naphthalene), 7.56−7.52 (m, 4H, H_5 and naphthalene), 4.07 (s, 3H, CO_2Me), 3.30 (sept, 1H, *J* = 6.9 Hz, *i*Pr), 1.48 (d, 6H, *J* = 6.9 Hz, *i*Pr) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 165.42, 152.29, 149.82, 143.96, 142.67, 137.58, 135.65, 135.52, 134.93, 134.03, 133.27, 132.41, 131.96, 128.63, 128.57, 128.49, 127.22, 126.64, 126.16, 125.98, 125.40, 118.25, 107.37, 51.40, 39.53, 24.84 ppm; HRMS (MALDI-TOF): calcd for $C_{27}H_{22}O_2S^+$ $[M]^+$, 410.1335; found :410.1353.

Compound 16



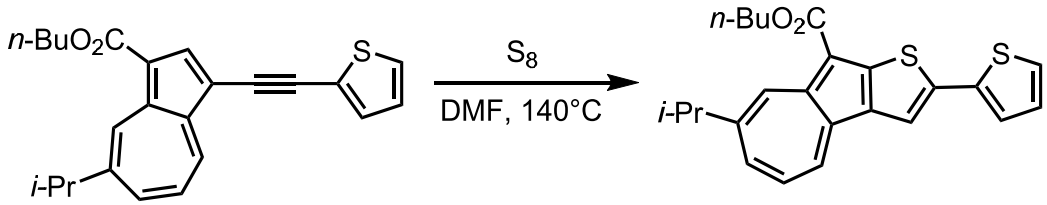
To a solution of **6** (212 mg, 0.560 mmol) in DMF (5 mL) was added S_8 (256 mg, 1.00 mmol). The resulting mixture was stirred at 140 °C for 2.5 h. The reaction mixture was poured into water and extracted with $CHCl_3$. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/AcOEt (6 : 1) to give **16** (110 mg, 48%) as green solid. M.p. 178−179 °C; IR (AT-IR): ν_{max} =3053 (w), 2956 (w), 2867 (w), 1688 (m), 1670 (m), 1624 (w), 1597 (w), 1525 (w), 1488 (w), 1451 (s), 1396 (m), 1382 (m), 1310 (w), 1276 (w), 1262 (w), 1207 (s), 1191 (s), 1135 (w), 1080 (m), 1039 (w), 1017 (w), 950 (w), 929 (w), 886 (w), 858 (w), 818 (s), 805 (m), 774 (m), 747 (m), 708 (w), 688 (w), 669 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 252 sh (4.38), 295 (4.34), 350 (4.81), 429 (4.19), 442 (4.19), 560 (2.69), 590 (2.69), 661 sh (2.46) nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 9.75 (d, 1H, *J* = 1.7 Hz, H_8), 8.59 (dd, 1H, *J* = 9.3, 0.7 Hz, H_4), 8.19 (s, 1H, H_1 of naphthalene), 8.04 (s, 1H, H_3 of thiophene), 7.94−7.88 (m, 3H, naphthalene), 7.84 (d, 1H, *J* = 8.0 Hz, naphthalene), 7.79 (d, 1H, *J* = 10.9 Hz, H_6), 7.55−7.46 (m, 3H, H_5 and naphthalene), 4.10 (s, 3H, CO_2Me), 3.28 (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 = 165.33, 151.76, 149.99, 145.01, 144.34, 137.68, 135.62, 135.55, 135.34, 133.86, 132.87, 132.81, 132.45, 128.69, 128.16, 127.82, 127.29, 126.73, 126.10, 124.47, 124.22, 114.06, 107.50, 51.43, 39.53, 24.82 ppm; HRMS (MALDI-TOF): calcd for $C_{27}H_{22}O_2S^+$ $[M]^+$, 410.1335; found :410.1334.

Compound 17a



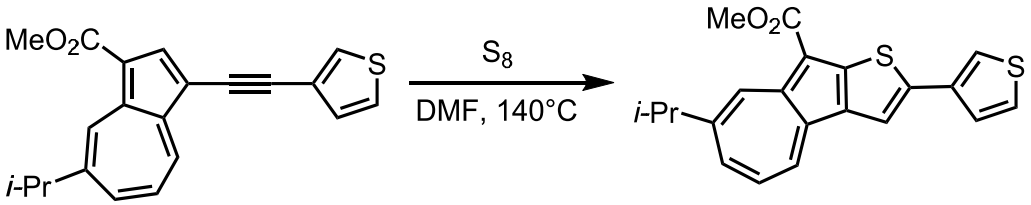
To a solution of **7a** (383 mg, 1.15 mmol) in DMF (10 mL) was added S_8 (330 mg, 1.29 mmol). The resulting mixture was stirred at 110 °C for 9 h. The reaction mixture was poured into water and extracted with $CHCl_3$. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/AcOEt (7 : 1) to give **17a** (88 mg, 21%) as green solid. M.p. 108−109 °C; IR (AT-IR): ν_{max} = 2958 (w), 1688 (s), 1519 (w), 1497 (w), 1480 (m), 1462 (s), 1448 (s), 1420 (m), 1398 (m), 1381 (m), 1339 (w), 1309 (w), 1199 (s), 1175 (s), 1133 (w), 1076 (s), 1043 (w), 1013 (w), 958 (w), 923 (w), 878 (w), 842 (w), 793 (m), 775 (m), 691 (m), 673 (w), 662 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 252 sh (4.22), 309 sh (4.29), 347 (4.71), 430 (4.07), 447 sh (4.03), 556 sh (2.59), 596 (2.61), 662 sh (2.40) nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 9.70 (d, 1H, *J* = 1.7 Hz, H_8), 8.48 (d, 1H, *J* = 9.5 Hz, H_4), 7.75 (d, 1H, *J* = 10.6 Hz, H_6), 7.71 (s, 1H, H_3 of thiophene), 7.48 (t, 1H, *J* = 9.9 Hz, H_5), 7.30 (d, 1H, *J* = 3.4 Hz, $H_{3'}$ of thiophene), 7.26 (d, 1H, *J* = 4.3 Hz, $H_{5'}$ of thiophene), 7.08−7.06 (m, 1H, $H_{4'}$ of thiophene), 4.06 (s, 3H, CO_2Me), 3.26 (sept, 1H, *J* = 6.9 Hz, *i*Pr), 1.44 (d, 6H, *J* = 6.9 Hz, *i*Pr) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 165.18, 151.33, 149.89, 144.19, 138.66, 137.87, 137.71, 135.50, 135.22, 134.74, 132.55, 128.04, 127.23, 124.50, 123.87, 113.90, 107.17, 51.42, 39.46, 24.79 ppm; HRMS (MALDI-TOF): calcd for $C_{21}H_{18}O_2S_2^+$ $[M]^+$, 366.0746; found :366.0768.

Compound 17b



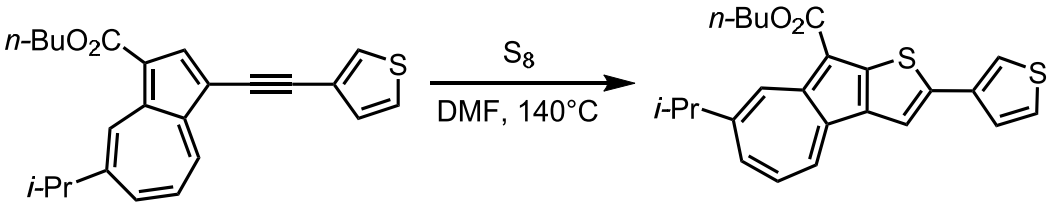
To a solution of **7b** (371 mg, 0.908 mmol) in DMF (10 mL) was added S_8 (239 mg, 0.934 mmol). The resulting mixture was stirred at 140 °C for 22 h. The reaction mixture was poured into water and extracted with AcOEt. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/AcOEt (10 : 1) to give **17b** (179 mg, 48%) as green solid. M.p. 110−112 °C; IR (AT-IR): ν_{max} = 2959 (m), 2930 (w), 2870 (w), 1686 (s), 1541 (w), 1519 (w), 1477 (m), 1461 (m), 1445 (m), 1422 (m), 1406 (m), 1381 (m), 1307 (w), 1267 (w), 1202 (m), 1177 (s), 1133 (m), 1076 (s), 1038 (w), 1016 (w), 998 (m), 966 (w), 949 (w), 876 (w), 840 (m), 833 (m), 814 (m), 795 (m), 777 (m), 740 (w), 728 (w), 688 (s), 657 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 241 (4.41), 311 sh (4.47), 347 (4.87), 430 (4.23), 447 sh (4.19), 552 sh (2.74), 596 (2.76), 661 sh (2.57) nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 9.72 (d, 1H, *J* = 1.1 Hz, H_8), 8.53 (d, 1H, *J* = 9.5 Hz, H_4), 7.76 (d, 1H, *J* = 10.0 Hz, H_6), 7.75 (s, 1H, H_3 of thiophene),7.49 (t, 1H, *J* = 9.9 Hz, H_5), 7.32 (d, 1H, *J* = 3.6 Hz, H_5 of thiophene), 7.26 (d, 1H, *J* = 4.9 Hz, H_3 of thiophene), 7.07 (dd, 1H, *J* = 4.9, 3.6 Hz, H_4 of thiophene), 4.48 (t, 2H, *J* = 7.4 Hz, *n*Bu), 3.26 (sept, 1H, *J* = 6.9 Hz, *i*Pr), 1.90 (q, 2H, *J* = 7.4 Hz, *n*Bu), 1.63 (q, 2H, *J* = 7.4 Hz, *n*Bu), 1.45 (d, 6H, *J* = 6.9 Hz, *i*Pr), 1.05 (t, 3H, *J* = 7.4 Hz, *n*Bu) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 164.96, 151.66, 149.75, 144.04, 138.72, 137.96, 137.72, 135.57, 135.24, 134.76, 132.52, 128.04, 127.13, 124.54, 123.97, 114.01, 107.69, 64.09, 39.51, 31.27, 24.79, 19.59, 13.96 ppm; HRMS (MALDI-TOF): calcd for $C_{24}H_{24}O_2S_2^+$ $[M]^+$, 408.1212; found :408.1200.

Compound 18a



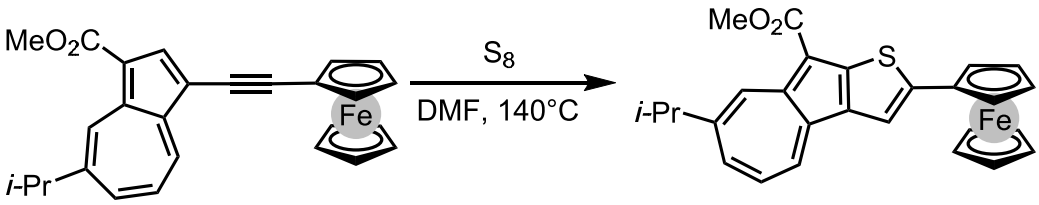
To a solution of **8a** (170 mg, 0.508 mmol) in DMF (5 mL) was added S_8 (141 mg, 0.551 mmol). The resulting mixture was stirred at 140 °C for 24 h. The reaction mixture was poured into water and extracted with $CHCl_3$. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with toluene to give **18a** (45 mg, 24%) as green oil. IR (AT-IR): ν_{max} = 2956 (w), 1685 (s), 1602 (w), 1518 (w), 1481 (w), 1448 (s), 1396 (m), 1363 (w), 1354 (w), 1309 (w), 1204 (s), 1185 (m), 1172 (m), 1134 (w), 1076 (m), 1039 (w), 1013 (w), 984 (w), 955 (w), 930 (w), 877 (w), 854 (w), 830 (w), 816 (w), 793 (m), 772 (s), 728 (w), 698 (w), 689 (w), 655 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 250 (4.26), 335 (4.78), 348 sh (4.74), 421 sh (4.03), 438 (4.06), 522 sh (2.47), 592 (2.59), 657 sh (2.38) nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 9.73 (d, 1H, *J* = 1.7 Hz, H_8), 8.54 (d, 1H, *J* = 9.2 Hz, H_4), 7.78−7.76 (m, 2H, H_6 and H_3 of thiophene), 7.53−7.51 (m, 2H, H_5 and $H_{2'}$ of thiophene), 7.48 (dd, 1H, *J* = 4.9, 0.9 Hz, $H_{5'}$ of thiophene), 7.41 (dd, 1H, *J* = 4.9, 2.9 Hz, $H_{4'}$ of thiophene), 4.08 (s, 3H, CO_2Me), 3.27 (sept, 1H, *J* = 6.9 Hz, *i*Pr), 1.45 (d, 6H, *J* = 6.9 Hz, *i*Pr) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 165.31, 151.27, 149.76, 144.16, 139.82, 137.61, 136.76, 135.49, 135.36, 134.89, 132.44, 127.14, 126.58, 125.96, 119.84, 113.52, 107.27, 51.43, 39.49, 24.82 ppm; HRMS (MALDI-TOF): calcd for $C_{21}H_{18}O_2S_2^+$ $[M]^+$, 366.0743; found: 366.0746.

Compound 18b



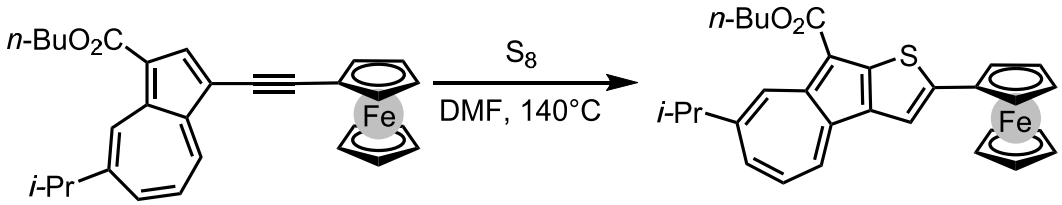
To a solution of **8b** (330 mg, 0.876 mmol) in DMF (10 mL) was added S_8 (243 mg, 0.949 mmol). The resulting mixture was stirred at 140 °C for 19.5 h. The reaction mixture was poured into water and extracted with AcOEt. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/AcOEt (12 : 1) to give **18b** (209 mg, 58%) as green solid. M.p. 136−137 °C; IR (AT-IR): ν_{max} = 2960 (w), 2870 (w), 1686 (s), 1519 (w), 1477 (m), 1456 (m), 1413 (m), 1382 (m), 1308 (w), 1267 (w), 1247 (w), 1206 (s), 1177 (s), 1133 (w), 1075 (s), 1037 (w), 998 (m), 966 (w), 949 (w), 901 (w), 873 (w), 855 (m), 837 (w), 825 (m), 795 (m), 770 (s), 740 (w), 728 (w), 687 (w), 653 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 249 (4.32), 335 (4.85), 349 sh (4.79), 422 sh (4.10), 439 (4.12), 550 sh (2.62), 593 (2.65), 655 sh (2.46) nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 9.73 (s, 1H, H_8), 8.53 (d, 1H, *J* = 9.5 Hz, H_4), 7.76−7.74 (m, 2H, H_6 and H_3 of thiophene), 7.52−7.47 (m, 3H, H_5 and $H_{2',5'}$ of thiophene), 7.41 (dd, 1H, *J* = 5.0, 0.9 Hz, $H_{4'}$ of thiophene), 4.49 (t, 2H, *J* = 7.3 Hz, *n*Bu), 3.26 (sept, 1H, *J* = 6.9 Hz, *i*Pr), 1.94−1.88 (m, 2H, *n*Bu), 1.67−1.60 (m, 2H, *n*Bu), 1.45 (d, 6H, *J* = 6.9 Hz, *i*Pr), 1.05 (t, 3H, *J* = 7.3 Hz, *n*Bu) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 165.03, 151.53, 149.55, 143.95, 139.86, 137.55, 136.83, 135.47, 135.30, 134.87, 132.35, 126.99, 126.54, 126.03, 119.88, 113.53, 107.73, 64.06, 39.50, 31.28, 24.80, 19.59, 13.97 ppm; HRMS (MALDI-TOF): calcd for $C_{24}H_{24}O_2S_2^+$ $[M]^+$, 408.1212; found: 408.1221.

Compound 19a



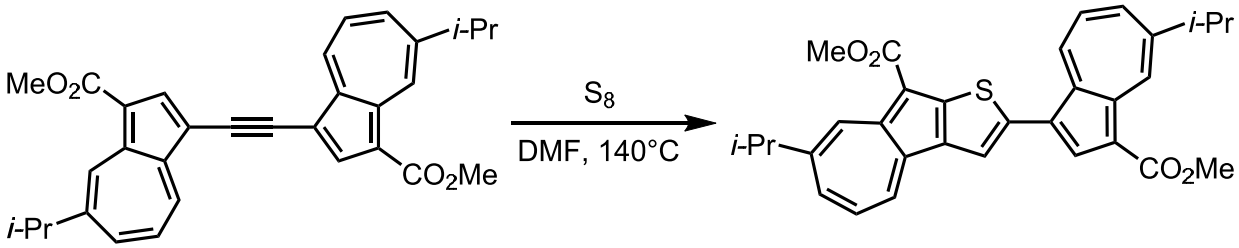
To a solution of **9a** (220 mg, 0.504 mmol) in DMF (5 mL) was added S_8 (146 mg, 0.570 mmol). The resulting mixture was stirred at 140 °C for 24 h. The reaction mixture was poured into water and extracted with $CHCl_3$. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/AcOEt (7 : 1) to give **19a** (57 mg, 24%) as brown solid. M.p. 185−186 °C; IR (AT-IR): ν_{max} = 2960 (w), 1678 (s), 1515 (w), 1487 (w), 1454 (s), 1402 (m), 1379 (w), 1309 (w), 1218 (s), 1189 (m), 1131 (w), 1105 (w), 1078 (s), 1054 (w), 1027 (w), 1001 (w), 953 (w), 865 (w), 821 (m), 806 (m), 795 (m), 774 (s), 722 (w), 687 (w), 679 (w), 667 (w), 656 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 247 sh (4.28), 279 (4.20), 335 sh (4.71), 344 (4.72), 429 (3.95), 611 sh (2.73), 688 sh (2.49) nm; ^1H NMR (500 MHz, $CDCl_3$): δ_H = 9.70 (d, 1H, *J* = 1.4 Hz, H_8), 8.48 (d, 1H, *J* = 9.2 Hz, H_4), 7.73 (d, 1H, *J* = 10.6 Hz, H_6), 7.55 (s, 1H, H_3 of thiophene), 7.47 (t, 1H, *J* = 9.9 Hz, H_5), 4.73 (t, 2H, *J* = 1.7 Hz, Cp of ferrocene), 4.37 (t, 2H, *J* = 1.7 Hz, Cp of ferrocene), 4.15 (s, 5H, Cp of ferrocene), 4.10 (s, 3H, CO_2Me), 3.26 (sept, 1H, *J* = 6.9 Hz, *i*Pr), 1.44 (d, 6H, *J* = 6.9 Hz, *i*Pr) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 165.40, 151.61, 149.27, 144.51, 143.85, 137.30, 135.41, 135.05, 134.33, 132.34, 126.70, 111.93, 107.16, 80.88, 70.17, 69.11, 66.94, 51.43, 39.48, 24.80 ppm; HRMS (MALDI-TOF): calcd for $C_{27}H_{24}FeO_2S^+$ $[M]^+$ 468.0841; found: 468.0814.

Compound 19b



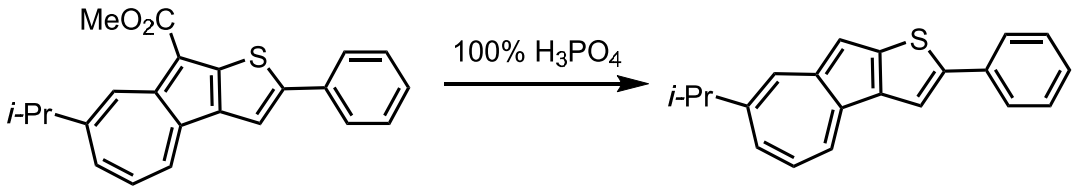
To a solution of **9b** (483 mg, 1.01 mmol) in DMF (10 mL) was added S_8 (265 mg, 1.04 mmol). The resulting mixture was stirred at 140 °C for 20.5 h. The reaction mixture was poured into water and extracted with AcOEt. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/AcOEt (10 : 1) to give **19b** (171 mg, 33%) as brown solid. M.p. 119−120 °C; IR (AT-IR): ν_{max} = 2960 (w), 2865 (w), 1685 (s), 1519 (w), 1469 (m), 1440 (s), 1408 (m), 1379 (m), 1217 (m), 1195 (s), 1176 (m), 1123 (w), 1106 (w), 1070 (m), 1057 (m), 1028 (m), 999 (m), 959 (w), 848 (w), 831 (w), 819 (m), 808 (m), 795 (m), 778 (m), 767 (m), 737 (w), 690 (w), 666 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 248 (4.30), 279 (4.24), 335 sh (4.72), 343 (4.73), 429 (3.98), 616 sh (2.73), 678 sh (2.55) nm; ^1H NMR (500 MHz, $CDCl_3$): δ_H = 9.72 (d, 1H, *J* = 1.7 Hz, H_8), 8.60 (d, 1H, *J* = 9.2 Hz, H_4), 8.46 (s, 1H, H_3 of thiophene), 7.77 (d, 1H, *J* = 10.3 Hz, H_6), 7.48 (t, 1H, *J* = 9.9 Hz, H_5), 4.57 (t, 2H, *J* = 1.7 Hz, Cp of ferrocene), 4.39 (t, 2H, *J* = 7.4 Hz, *n*Bu), 4.28 (s, 5H, Cp of ferrocene), 4.27 (t, 2H, *J* = 1.7 Hz, Cp of ferrocene), 3.22 (sept, 1H, *J* = 6.9 Hz, *i*Pr), 1.85−1.79 (m, 2H, *n*Bu), 1.58−1.54 (m, 2H, *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 = 165.25, 150.04, 144.68, 142.64, 140.93, 139.17, 138.18, 136.18, 127.09, 115.34, 109.96, 92.20, 80.83, 71.43, 70.09, 68.82, 66.15, 63.80, 39.32, 31.15, 24.68, 19.55, 13.94 ppm; HRMS (MALDI-TOF): calcd for $C_{30}H_{30}FeO_2S^+$ $[M]^+$, 510.1310; found: 510.1334.

Compound 20



To a solution of **10** (212 mg, 0.440 mmol) in DMF (5 mL) was added S_8 (226 mg, 0.833 mmol). The resulting mixture was stirred at 140 °C for 10 h. The reaction mixture was poured into water and extracted with $CHCl_3$. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with toluene to give **20** (102 mg, 45%) as green solid. M.p. 173−174 °C; IR (AT-IR): ν_{max} = 2956 (w), 1674 (s), 1577 (w), 1521 (w), 1500 (w), 1450 (s), 1417 (m), 1399 (m), 1381 (m), 1349 (w), 1310 (w), 1236 (m), 1210 (s), 1174 (s), 1126 (m), 1077 (m), 1051 (w), 1014 (m), 965 (w), 946 (w), 895 (m), 876 (w), 858 (w), 822 (w), 807 (m), 790 (w), 775 (s), 735 (w), 687 (w), 654 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 238 (4.53), 297 (4.67), 333 (4.73), 396 sh (4.35), 440 (4.26), 593 (3.68) nm; ^1H NMR (500 MHz, $CDCl_3$): δ_H = 9.79 (d, 1H, *J* = 1.7 Hz, H_8 or $H_{8'}$), 9.76 (d, 1H, *J* = 1.7 Hz, H_8 or $H_{8'}$), 8.94 (d, 1H, *J* = 9.5 Hz, $H_{4'}$), 8.61 (s, 1H, $H_{2'}$), 8.58 (dd, 1H, *J* = 9.3, 0.7 Hz, H_8), 7.81 (s, 1H, H_3 of thiophene), 7.79−7.76 (m, 2H, H_6 and $H_{6'}$), 7.52−7.45 (m, 2H, H_5 and $H_{5'}$), 4.09 (s, 3H, CO_2Me), 3.99 (s, 3H, CO_2Me), 3.32−3.20 (m, 2H, *i*Pr), 1.47−1.44 (m, 12H, *i*Pr) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 165.82, 165.41, 151.95, 149.72, 149.62, 144.01, 142.32, 140.55, 139.80, 139.62, 139.22, 138.32, 137.49, 135.66, 135.45, 135.34, 135.17, 132.41, 127.44, 126.98, 122.87, 115.15, 115.10, 107.32, 51.42, 51.26, 39.50, 39.17, 24.83, 24.70 ppm; HRMS (MALDI-TOF): calcd for $C_{32}H_{30}O_4S^+$ $[M]^+$, 510.1859; found: 510.1863.

Compound 21



A solution of **11** (103 mg, 0.286 mmol) in 100% H_3PO_4 (10 mL) was stirred at 90 °C for 30 min. After the reaction mixture was cooled and it was poured into ice-cooled water. The precipitate was collected by filtration to give **21** (60 mg, 69%) as green solid. M.p. 168−169 °C; IR (AT-IR): ν_{max} = 2952 (w), 2863 (w), 1595 (w), 1574 (w), 1521 (m), 1469 (m), 1443 (m), 1400 (w), 1376 (m), 1361 (w), 1338 (w), 1289 (w), 1245 (w), 1216 (w), 1200 (w), 1158 (w), 1101 (w), 1071 (w), 1051 (w), 1033 (w), 1004 (w), 937 (w), 923 (w), 914 (w), 896 (w), 843 (w), 834 (w), 784 (s), 754 (s), 722 (m), 686 (m), 668 (m), 660 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 239 (4.10), 338 (4.73), 387 (3.97), 403 (4.08), 425 (4.12), 528 sh (2.15), 595 (2.32), 631 (2.35), 700 (2.17), 785 sh (1.68) nm; UV/Vis (30% CF_3CO_2H/CH_2Cl_2): λ_{max} (log ε) = 274 (4.56), 303 sh (4.11), 371 (4.23), 463 (4.25) nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 8.39 (d, 1H, *J* = 8.9 Hz, H_4), 8.21 (d, 1H, *J* = 1.4 Hz, H_8), 7.98 (s, 1H, H_3 of thiophene), 7.75 (d, 2H, *J* = 7.3 Hz, *o*-Ph), 7.51 (d, 1H, *J* = 10.9 Hz, H_6), 7.44−7.41 (m, 3H, H_3 and *m*-Ph), 7.28 (t, 1H, *J* = 7.3 Hz, *p*-Ph), 7.21 (dd, 1H, *J* = 10.9, 8.9 Hz, H_5), 3.10 (sept, 1H, *J* = 6.9 Hz, *i*Pr), 1.39 (d, 6H, *J* = 6.9 Hz, *i*Pr) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 149.30, 143.27, 142.83, 141.74, 136.73, 136.05, 135.72, 134.12, 132.44, 130.37, 129.03, 127.25, 125.93, 123.15, 114.23, 108.38, 38.76, 24.64 ppm; HRMS (MALDI-TOF): calcd for $C_{21}H_{18}S^+$ $[M]^+$, 302.1124; found: 302.1108.