

Supporting Information

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1. General experimental procedures

Reagents were obtained from commercial suppliers and used without further purification. NMR spectra were recorded on Bruker Avance 400 MHz spectrometer. Spectra were recorded in deuteriochloroform referenced to residual CHCl₃ (1H, 7.26 ppm) or CDCl₃ (13C, 77.2 ppm). Chemical shifts (δ) are reported in ppm and coupling constants (J) are reported in Hz. The following abbreviations are used to describe multiplicity; s singlet, d-doublet, t-triplet, q-quartet, m-multiplet. HRMS experiments were carried out on a Waters Q-ToF 2 (ESI-Electrospray Ionization, ASAP-Atmospheric Solids Analysis Probe) spectrometer. Analytical TLC was carried out on Merck 60 F245 aluminium backed silica gel plates. Short wave UV radiation (245 nm), KMnO₄ and vanillin were used to visualize components. Compounds were purified by flash column chromatography using Geduran[®] silica gel 60 (0.040-0.063 nm).

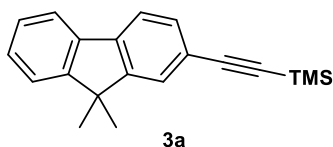
Single crystal diffraction data were collected at low temperature on a D8 Venture Bruker AXS CMOS diffractometer with multilayers monochromatized Mo K α radiation. Structures were solved by dual-space algorithm using SHELXT program. All non-hydrogen atoms were refined anisotropically by the full-matrix least-squares techniques using the program SHELXL-2018/3. Hydrogen atoms were located geometrically and treated using a riding model with isotropic atomic displacement parameter constrained to the equivalent adp of the bonded carbon atom. Powder X-ray diffraction data were obtained using a Bruker D8 Advance diffractometer working in the modified Bragg-Brentano geometry with a monochromatized Cu K α 1 radiation and equipped with a LynxEye fast detector. The

analysis of the powder X-ray diffraction patterns was performed by Rietveld refinement using the FullProf and WinPLOTR packages.

Cyclic voltammograms were recorded in dry CH₂Cl₂ solutions (containing 0.1 M [NⁿBu₄][PF₆], purged with nitrogen and maintained under an inert atmosphere) using a Pt disk as working electrode, a Pt wire as counter electrode and a SCE reference electrode; the FeCp₂^{0/+1} couple (E_{1/2}: 0.46 V,¹ ΔE_p = 0.09 V; I_{pa}/I_{pc} = 1) was used as an internal calibrant.

UV-visible spectra were recorded on a Jasco V-750 spectrophotometer using 1 cm² quartz cuvettes for solutions. The luminescence spectra were measured using Horiba-Jobin-Yvon Fluorolog-3 spectrofluorometers. The experiments were carried out using dilute solutions (A < 0.1 for the low-energy band, where the excitations are performed) to minimize inner-filter effects and intermolecular interactions. Powders were placed in quartz tubes inserted in a G8 GMP integrating sphere. The steady-state luminescence was excited with unpolarized light from a 450 W xenon CW lamp and detected at an angle of 90° with a Hamamatsu R928 photomultiplier tube (PMT) or a Peltier cooled R2658 PMT as specified. Long-pass filters were used to reject scattered light. Spectra were reference-corrected for both the excitation source light intensity variation (lamp and grating) and the emission spectral response (detector and grating). Fluorescence decays were obtained using an EDEPL375 pulsed laser diode producing an excitation at 375 nm associated with an Edinburgh FLS920 fluorometer that was equipped with a Peltier cooled Hamamatsu R928P PMT. Detection was performed at the emission maximum of the studied molecule using an emission slit width of 3 nm.

2. Synthesis



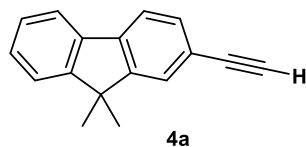
A solution of **2a** (916 mg, 3.353 mmol) in Et₃N (2 mL) and dry THF (20 mL) was treated with trimethylsilylacetylene (1 mL, 7.322 mmol), CuI (139 mg, 0.732 mmol), [PdCl₂(PPh₃)₂] (257 mg, 0.366 mmol) and PPh₃ (196 mg, 0.745 mmol). The reaction mixture was stirred at 80°C over 21 h, then evaporated and purified by column chromatography (pentane) to give alkyne **3a** (766 mg, 2.637 mmol, 78%) as a yellow/orange oil.

¹H NMR (400 MHz, CDCl₃) δ 7.73 – 7.68 (m, 1H), 7.65 (dd, J = 7.8, 0.7 Hz, 1H), 7.55 (dd, J = 1.5, 0.7 Hz, 1H), 7.46 (dd, J = 7.8, 1.5 Hz, 1H), 7.45 – 7.41 (m, 1H), 7.37 – 7.29 (m, 2H), 1.48 (s, 6H), 0.28 (s, 9H).

¹ N. G. Connelly, W. E. Geiger, *Chem. Rev.* **1996**, *96*, 877-910.

^{13}C NMR (101 MHz, CDCl_3) δ 154.1, 153.6, 139.8, 138.6, 131.3, 127.9, 127.2, 126.4, 122.8, 121.6, 120.4, 119.9, 106.1, 94.1, 47.0, 27.1, 0.2.

The spectroscopic data are in agreement with the literature.²

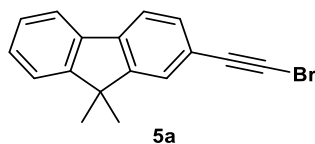


A solution of alkyne **3a** (559 mg, 1.924 mmol) in MeOH (4 mL) and THF (4 mL) was treated with K_2CO_3 (580 mg, 4.196 mmol). After 3 h at room temperature, the reaction was diluted with Et_2O , filtered through celite and concentrated under reduced pressure. The residue obtained was purified by column chromatography (cyclohexane:dichloromethane 1:0 to 95:5) to give alkyne **4a** (372 mg, 1.711 mmol, 89%) as a yellow oil.

^1H NMR (400 MHz, CDCl_3) δ 7.75 – 7.70 (m, 1H), 7.68 (dd, $J = 7.9, 0.8$ Hz, 1H), 7.58 (dd, $J = 1.5, 0.7$ Hz, 1H), 7.50 (dd, $J = 7.8, 1.5$ Hz, 1H), 7.47 – 7.43 (m, 1H), 7.39 – 7.31 (m, 2H), 3.14 (s, 1H), 1.49 (s, 6H).

^{13}C NMR (101 MHz, CDCl_3) δ 154.1, 153.7, 140.1, 138.5, 131.4, 128.0, 127.3, 126.6, 122.8, 120.6, 120.5, 120.0, 84.6, 77.2, 47.0, 27.1.

HRMS (ASAP) calculated for $\text{C}_{17}\text{H}_{15}$ $[\text{M}+\text{H}]^+$ 219.1168, found 219.1166



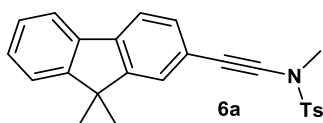
A solution of alkyne **4a** (130 mg, 0.596 mmol) in acetone (6 mL) was treated with N-bromosuccinimide (130.6 mg, 0.734 mmol) and AgNO_3 (10.5 mg, 0.062 mmol). After 15 h at room temperature in the dark, the reaction mixture was diluted with Et_2O and filtered through celite. The filtrate was concentrated under reduced pressure and purified by column chromatography (cyclohexane to cyclohexane:dichloromethane 1:0 to 9:1) to give brominated alkyne **5a** (136.9 mg, 0.462 mmol, 77%) as a yellow foiled solid.

^1H NMR (400 MHz, CDCl_3) δ 7.75 – 7.71 (m, 1H), 7.68 (dd, $J = 7.8, 0.7$ Hz, 1H), 7.56 (dd, $J = 1.5, 0.7$ Hz, 1H), 7.46 (ddd, $J = 7.3, 4.0, 1.1$ Hz, 2H), 7.39 – 7.34 (m, 2H), 1.50 (s, 6H).

^{13}C NMR (101 MHz, CDCl_3) δ 153.9, 153.6, 139.8, 138.3, 131.1, 127.8, 127.1, 126.4, 122.7, 121.1, 120.4, 119.9, 80.8, 49.4, 46.9, 27.0, 26.9.

² N. Guven, P. Camurlu, *J. Electrochem. Soc.*, **2015**, 162, H867-H876

HRMS (ESI MeOH/CH₂Cl₂ 90/10) calculated for C₁₇H₁₄⁷⁹Br [M+H]⁺ 297.0273, found 297.0275

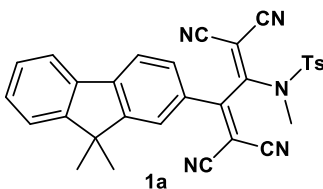


A solution of TsNHCH₃ (139 mg, 0.751 mmol), CuSO₄·5H₂O (39 mg, 0.160 mmol), 1,10-phenanthroline (50 mg, 0.277 mmol), K₂CO₃ (380 mg, 2.749 mmol) and brominated alkyne **5a** (202 mg, 0.682 mmol) in dry toluene (14 mL) was heated to 90 °C under a nitrogen atmosphere for 61 h. The reaction was then cooled to room temperature, diluted with EtOAc and filtered through celite. The filtrate was concentrated under reduced pressure and purified by column chromatography (cyclohexane:ethyl acetate 1:0 to 9:1) to give ynamide **6a** (216 mg, 0.538 mmol, 79%) as a yellow solid.

¹H NMR (400 MHz, CDCl₃) δ 7.90 – 7.84 (m, 2H), 7.72 – 7.68 (m, 1H), 7.64 (dd, *J* = 7.8, 0.7 Hz, 1H), 7.43 (ddd, *J* = 6.2, 2.1, 0.7 Hz, 2H), 7.41 – 7.37 (m, 2H), 7.37 – 7.30 (m, 3H), 3.18 (s, 3H), 2.47 (d, *J* = 0.7 Hz, 3H), 1.47 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 153.8, 153.5, 144.8, 139.1, 138.5, 133.3, 130.6, 129.8, 127.9, 127.6, 127.1, 125.9, 122.6, 121.1, 120.2, 119.8, 83.9, 69.8, 46.8, 39.4, 27.0, 26.9, 21.7.

HRMS (ESI MeOH/CH₂Cl₂ 90/10) calculated for C₂₅H₂₃NO₂NaS [M+Na]⁺ 424.1342, found 424.1341

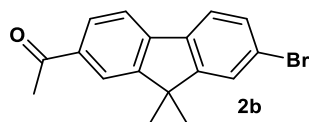


A solution of ynamide **6a** (80 mg, 0.199 mmol) and TCNE (39 mg, 0.304 mmol) in CH₂Cl₂ (3 mL) was stirred at room temperature for 16 h. The reaction mixture was purified by column chromatography (pentane:dichloromethane 1:1) to give TCBD **1a** (100 mg, 0.190 mmol, 95%) as a red solid.

¹H NMR (400 MHz, CDCl₃) δ 7.91 (dd, *J* = 8.0, 0.6 Hz, 1H), 7.87 – 7.85 (m, 1H), 7.84 – 7.81 (m, 1H), 7.78 – 7.72 (m, 2H), 7.65 (dd, *J* = 8.1, 1.9 Hz, 1H), 7.53 – 7.40 (m, 5H), 3.46 (s, 3H), 2.49 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 165.2, 164.2, 155.2, 155.1, 147.5, 146.4, 137.2, 132.4, 131.0, 130.2, 130.0, 129.8, 128.3, 127.8, 125.0, 123.2, 121.7, 121.3, 112.5, 112.3, 110.8, 110.7, 87.6, 80.6, 47.6, 41.1, 26.8, 22.0.

HRMS (ESI MeOH/CH₂Cl₂ 90/10) calculated for C₃₁H₂₃N₅O₂NaS [M+Na]⁺ 522.1465, found 522.1465

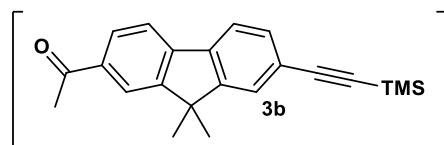


To a solution of 2-bromo-9,9-dimethylfluorene (2.0 g, 7.32 mmol) and acetyl chloride (1.1 mL, 15.47 mmol) in dichloromethane (30 mL) was added dropwise aluminium chloride (2.93 g, 21.96 mmol) at 0°C. The reaction mixture was then stirred at room temperature. After 1h15, the reaction mixture was quenched with 10 mL of HCl 1N with ice and extracted 3 times with dichloromethane (25 mL). Organic layers were dried over MgSO₄, filtered and concentrated. The residue obtained was purified by column chromatography (cyclohexane:dichloromethane 1:0 to 0:1) to give brominated alkyne **2b** (1.85 g, 5.89 mmol, 80%) as a yellow solid.

¹H NMR (400 MHz, CDCl₃) δ 8.04 (dd, *J* = 1.6, 0.7 Hz, 1H), 7.96 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.74 (dd, *J* = 8.0, 0.6 Hz, 1H), 7.63 (dd, *J* = 8.2, 0.5 Hz, 1H), 7.60 (dd, *J* = 1.8, 0.5 Hz, 1H), 7.50 (dd, *J* = 8.1, 1.8 Hz, 1H), 2.66 (s, 3H), 1.51 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 197.8, 156.8, 153.5, 143.0, 136.9, 136.4, 130.5, 128.4, 126.4, 122.7, 122.4, 122.3, 119.9, 47.3, 26.8, 26.8.

The spectroscopic data are in agreement with the literature.³



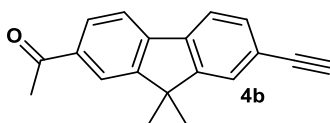
A solution of **2b** (164 mg, 0.522 mmol) in Et₃N (10 mL) was reacted with trimethylsilylacetylene (0.15 mL, 1.079 mmol), CuI (26 mg, 0.136 mmol) and [PdCl₂(PPh₃)₂] (39 mg, 0.056 mg). The reaction mixture was stirred at 85°C over 16 h. The reaction was quenched with 20 mL of water and extracted with 3 x 20 mL of EtOAc. The organic layers were dried over MgSO₄, filtered and concentrated under reduced pressure and purified by column chromatography (cyclohexane to cyclohexane:EtOAc 9:1) to give alkyne **3b** as an impure beige solid.

¹H NMR (400 MHz, CDCl₃) δ 8.04 (dd, *J* = 1.6, 0.7 Hz, 1H), 7.96 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.75 (dd, *J* = 7.9, 0.6 Hz, 1H), 7.70 (dd, *J* = 7.9, 0.7 Hz, 1H), 7.57 (dd, *J* = 1.5, 0.7 Hz, 1H), 7.49 (dd, *J* = 7.9, 1.4 Hz, 1H), 2.66 (s, 3H), 1.50 (s, 6H), 0.28 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 197.9, 154.6, 154.2, 143.3, 138.2, 136.4, 131.3, 128.3, 126.5, 123.0, 122.4, 120.8, 120.1, 105.5, 95.1, 47.0, 26.9, 26.8, 0.0.

³ X. Wu, J. Wu, Y. Liu, A. K-Y. Jen, *J. Am. Chem. Soc.*, **1999**, *121*, 472–473

HRMS (ESI MeOH/CH₂Cl₂ 90/10) calculated for C₂₂H₂₄ONaSi [M+Na]⁺ 355.1489, found 355.1491

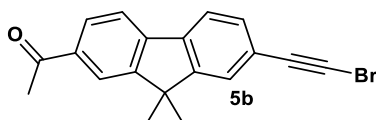


A solution of alkyne **3b** (0.522 mmol) in MeOH (2 mL) and THF (2 mL) was treated with K₂CO₃ (155 mg, 1.121 mmol). After 1 h at room temperature, the reaction was diluted with Et₂O, filtered through celite and concentrated under reduced pressure. The residue obtained was purified by column chromatography (cyclohexane:ethyl acetate 1:0 to 9:1) to give alkyne **4b** (42.5 mg, 0.163 mmol, 31% over 2 steps) as a yellow solid.

¹H NMR (400 MHz, CDCl₃) δ 8.05 (dd, *J* = 1.6, 0.6 Hz, 1H), 7.96 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.76 (dd, *J* = 8.0, 0.7 Hz, 1H), 7.72 (dd, *J* = 7.9, 0.7 Hz, 1H), 7.59 (dd, *J* = 1.5, 0.7 Hz, 1H), 7.51 (dd, *J* = 7.8, 1.5 Hz, 1H), 3.17 (s, 1H), 2.66 (s, 3H), 1.51 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 197.9, 154.7, 154.2, 143.2, 138.5, 136.5, 131.4, 128.3, 126.7, 122.4, 121.9, 120.9, 120.2, 84.1, 77.9, 47.1, 26.8, 26.8.

HRMS (ESI MeOH/CH₂Cl₂ 90/10) calculated for C₁₉H₁₆ONa [M+Na]⁺ 283.1093, found 283.1095

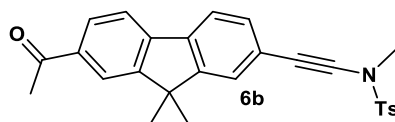


A solution of alkyne **4b** (40 mg, 0.154 mmol) in acetone (2 mL) was reacted with N-bromosuccinimide (33 mg, 0.185 mmol) and AgNO₃ (3 mg, 0.016 mmol). After 30 min at room temperature in the dark, the reaction mixture was diluted with pentane (10 mL) and the precipitate was filtered. The filtrate was concentrated under reduced pressure. The residue obtained was purified by column chromatography (cyclohexane:ethyl acetate 7:3) to give brominated alkyne **5b** (40 mg, 0.118 mmol, 77%) as a yellow solid.

¹H NMR (400 MHz, CDCl₃) δ 8.04 (dd, *J* = 1.6, 0.6 Hz, 1H), 7.96 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.75 (dd, *J* = 8.0, 0.6 Hz, 1H), 7.70 (dd, *J* = 7.9, 0.7 Hz, 1H), 7.55 (dd, *J* = 1.5, 0.7 Hz, 1H), 7.46 (dd, *J* = 7.9, 1.5 Hz, 1H), 2.66 (s, 3H), 1.50 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 197.8, 154.7, 154.1, 143.1, 138.4, 136.5, 131.3, 128.3, 126.5, 122.5, 122.4, 120.9, 120.2, 80.5, 50.6, 47.1, 26.9, 26.8.

HRMS (ESI MeOH/CH₂Cl₂ 90/10) calculated for C₁₉H₁₅O⁷⁹BrNa [M+Na]⁺ 361.0198, found 361.0196

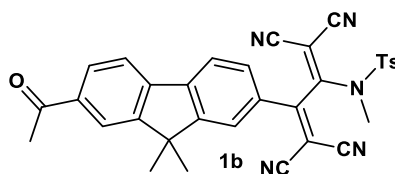


A solution of TsNHCH_3 (25 mg, 0.134 mmol), $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (5 mg, 0.020 mmol), 1,10-phenanthroline (12 mg, 0.472 mmol), K_2CO_3 (65 mg, 0.472 mmol) and alkyne **5b** (40 mg, 0.118 mmol) in dry toluene (2.0 mL) was heated to 90 °C under nitrogen atmosphere for 50 h. The reaction was then cooled to room temperature, concentrated under reduced pressure and purified by column chromatography (cyclohexane:ethyl acetate 9:1 to 8:2) to give ynamide **6b** (25 mg, 0.056 mmol, 48%) as a yellow solid.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.04 (dd, $J = 1.6, 0.6$ Hz, 1H), 7.96 (dd, $J = 7.9, 1.6$ Hz, 1H), 7.90 – 7.85 (m, 2H), 7.74 (dd, $J = 7.9, 0.6$ Hz, 1H), 7.69 (dd, $J = 7.8, 0.7$ Hz, 1H), 7.46 (dd, $J = 1.5, 0.7$ Hz, 1H), 7.42 – 7.35 (m, 3H), 3.18 (s, 3H), 2.66 (s, 3H), 2.47 (s, 3H), 1.50 (s, 6H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 198.0, 154.9, 154.2, 145.0, 143.5, 137.7, 136.4, 133.4, 130.8, 130.0, 128.5, 128.0, 125.9, 122.8, 122.5, 121.0, 120.1, 84.9, 69.8, 47.1, 39.4, 27.1, 26.9, 21.8.

HRMS (ESI MeOH/ CH_2Cl_2 90/10) calculated for $\text{C}_{27}\text{H}_{25}\text{NO}_3\text{NaS}$ $[\text{M}+\text{Na}]^+$ 466.1447, found 466.1448

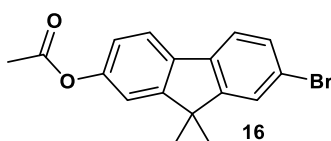


A solution of ynamide **6b** (25 mg, 0.057 mmol) and TCNE (7.3 mg, 0.057 mmol) in CH_2Cl_2 (2 mL) was stirred at room temperature for 16 h. The reaction mixture was purified by column chromatography (cyclohexane:ethyl acetate 1:0 7:3) to give TCBD **1b** (21.7 mg, 0.038 mmol, 67%) as an orange solid.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.10 (dd, $J = 1.6, 0.7$ Hz, 1H), 8.03 (dd, $J = 8.0, 1.6$ Hz, 1H), 7.97 (dd, $J = 8.1, 0.6$ Hz, 1H), 7.91 – 7.86 (m, 2H), 7.79 – 7.73 (m, 2H), 7.68 (dd, $J = 8.1, 1.9$ Hz, 1H), 7.48 – 7.42 (m, 2H), 3.45 (s, 3H), 2.69 (s, 3H), 2.50 (s, 3H), 1.59 (s, 6H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 197.6, 164.9, 163.5, 155.8, 155.0, 147.3, 144.2, 141.4, 137.7, 132.0, 130.7, 130.6, 129.8, 128.3, 128.0, 124.8, 122.5, 122.0, 121.3, 112.0, 111.7, 110.5, 110.2, 88.4, 80.5, 47.5, 40.7, 26.7, 26.4, 21.7.

HRMS (ASAP) calculated for $\text{C}_{33}\text{H}_{26}\text{N}_5\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$ 572.1751, found 572.1745

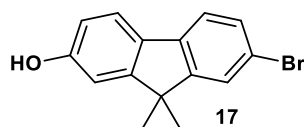


A solution of compound **2b** (603 mg, 1.91 mmol) in chloroform (20 mL) was treated with *meta*-chloroperbenzoic acid (695 mg, 3.10 mmol). The reaction mixture was stirred at rt for 89 h. The reaction was washed with 10 mL of a saturated aqueous solution of NaHCO₃, 10 mL of water and 10 mL of brine, then dried over N₂SO₄, filtered and concentrated under reduced pressure. The residue obtained was purified by column chromatography (cyclohexane:dichloromethane 1:0 to 3:7) to give compound **16** (541 mg, 1.63 mmol, 86%) as a beige solid.

¹H NMR (400 MHz, CDCl₃) δ 7.66 (dd, *J* = 8.2, 0.5 Hz, 1H), 7.57 – 7.50 (m, 2H), 7.45 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.14 (dd, *J* = 2.1, 0.5 Hz, 1H), 7.06 (dd, *J* = 8.2, 2.2 Hz, 1H), 2.33 (s, 3H), 1.47 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 169.4, 155.5, 154.6, 150.3, 137.3, 135.7, 130.0, 126.0, 121.1, 120.8, 120.5, 120.4, 116.0, 47.1, 26.8, 21.0.

HRMS (ESI MeOH) calculated for C₁₇H₁₅O₂⁷⁹BrNa [M+Na]⁺ 353.0148, found 353.0146

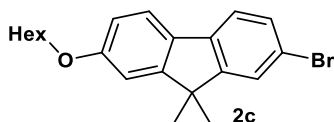


A solution of compound **16** (1.42 g, 4.29 mmol) in methanol/water (30 mL, v/v 1:1) was reacted with KOH (2.4 g, 4.29 mmol). The reaction mixture was stirred at 80°C for 15 h. The reaction was neutralized by conc. HCl and extracted with 2 x 40 mL of Et₂O. The organic layers were washed with 40 mL of water and 40 mL of brine, then dried over N₂SO₄, filtered and concentrated under reduced pressure. The residue obtained was purified by column chromatography (cyclohexane:dichloromethane 1:0 to 2:8) to give compound **17** (1.13 g, 3.73 mmol, 87%) as a pale yellow solid.

¹H NMR (400 MHz, CDCl₃) δ 7.54 (d, *J* = 8.2 Hz, 1H), 7.50 (d, *J* = 1.7 Hz, 1H), 7.47 (dt, *J* = 8.1, 0.6 Hz, 1H), 7.42 (ddd, *J* = 8.0, 1.8, 0.6 Hz, 1H), 6.89 (d, *J* = 2.4 Hz, 1H), 6.80 (ddd, *J* = 8.2, 2.4, 0.5 Hz, 1H), 4.90 (s, 1H), 1.45 (d, *J* = 0.5 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 155.5, 155.4, 155.0, 137.9, 131.0, 129.8, 125.8, 120.9, 120.3, 119.6, 114.2, 109.8, 46.8, 26.9.

HRMS (ESI MeOH/CH₂Cl₂ 90/10) calculated for C₁₅H₁₂O⁷⁹Br [M-H]⁻ 287.0077, found 287.0082

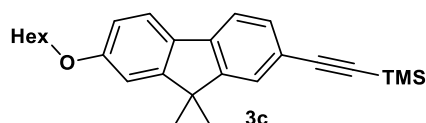


A solution of compound **17** (330 mg, 1.09 mmol) in acetonitrile (10 mL) was reacted with K_2CO_3 (304 mg, 2.20 mmol) and 1-bromohexane (0.17 mL, 1.21 mmol). The reaction mixture was stirred at reflux for 18 h. The reaction was quenched with 20 mL of water and extracted with 3 x 20 mL of Et_2O . The organic layers were washed with 20 mL of water and 20 mL of brine, then dried over N_2SO_4 , filtered and concentrated under reduced pressure. The residue obtained was purified by column chromatography (cyclohexane:dichloromethane 1:0 to 9:1) to give compound **2c** (323 mg, 0.865 mmol, 80%) as a yellow solid.

1H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, $J = 8.3$ Hz, 1H), 7.50 (d, $J = 1.8$ Hz, 1H), 7.47 (d, $J = 8.0$ Hz, 1H), 7.41 (dd, $J = 8.1, 1.7$ Hz, 1H), 6.94 (d, $J = 2.3$ Hz, 1H), 6.87 (dd, $J = 8.3, 2.3$ Hz, 1H), 4.01 (t, $J = 6.6$ Hz, 2H), 1.87 – 1.76 (m, 2H), 1.50 (t, $J = 7.6$ Hz, 2H), 1.45 (s, 6H), 1.37 (ddd, $J = 7.4, 4.6, 3.1$ Hz, 4H), 0.97 – 0.86 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 155.4, 155.3, 138.4, 131.0, 130.1, 126.1, 121.0, 120.6, 119.8, 113.4, 109.3, 68.5, 47.2, 31.8, 29.5, 27.3, 25.9, 22.8, 14.2.

HRMS (ASAP) calculated for $C_{21}H_{26}O^{79}Br$ $[M+H]^+$ 373.1161, found 373.1158

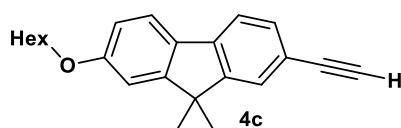


A solution of **2c** (251 mg, 0.672 mmol) in dry DMF (10 mL) was reacted with trimethylsilylacetylene (0.9 mL, 6.48 mmol), CuI (31 mg, 0.163 mmol), and $[PdCl_2(PPh_3)_2]$ (48 mg, 0.068 mmol). The reaction mixture was stirred at reflux over 30 h. The reaction mixture was concentrated under reduced pressure and purified by column chromatography (cyclohexane:dichloromethane 1:0 to 8:2) to give alkyne **3c** (184 mg, 0.471 mmol, 70%) as a yellow solid.

1H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, $J = 8.4$ Hz, 1H), 7.58 – 7.51 (m, 2H), 7.46 (dd, $J = 7.8, 1.5$ Hz, 1H), 6.98 (d, $J = 2.3$ Hz, 1H), 6.89 (dd, $J = 8.3, 2.3$ Hz, 1H), 4.03 (t, $J = 6.6$ Hz, 2H), 1.84 (dq, $J = 7.9, 6.6$ Hz, 2H), 1.55 – 1.50 (m, 2H), 1.48 (s, 6H), 1.43 – 1.36 (m, 4H), 1.01 – 0.90 (m, 3H), 0.31 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 156.1, 153.1, 139.9, 131.3, 131.3, 126.3, 121.3, 120.3, 119.0, 113.3, 109.3, 106.4, 93.6, 68.4, 46.9, 31.8, 29.5, 27.3, 27.1, 25.9, 22.8, 14.2, 0.2.

HRMS (ASAP) calculated for $C_{26}H_{35}OSi$ $[M+H]^+$ 391.2452, found 391.2458

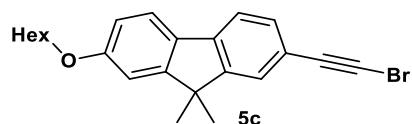


A solution of alkyne **3c** (561 mg, 1.436 mmol) in MeOH (8 mL) and THF (8 mL) was treated with K_2CO_3 (525 mg, 3.798 mmol). After 4 h at room temperature, the reaction was filtered and concentrated under reduced pressure. The residue obtained was purified by column chromatography (cyclohexane:dichloromethane 1:0 to 8:2) to give alkyne **4c** (418 mg, 1.31 mmol, 91%) as a yellow solid.

1H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, $J = 8.3$ Hz, 1H), 7.56 (dd, $J = 7.8, 0.7$ Hz, 1H), 7.51 (dd, $J = 1.4, 0.7$ Hz, 1H), 7.45 (dd, $J = 7.8, 1.5$ Hz, 1H), 6.96 (d, $J = 2.3$ Hz, 1H), 6.88 (dd, $J = 8.3, 2.3$ Hz, 1H), 4.02 (t, $J = 6.6$ Hz, 2H), 3.10 (s, 1H), 1.88 – 1.76 (m, 2H), 1.53 – 1.47 (m, 2H), 1.46 (s, 6H), 1.37 (ddd, $J = 7.4, 4.4, 3.0$ Hz, 4H), 0.97 – 0.86 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8, 156.1, 153.3, 140.2, 131.4, 131.2, 126.4, 121.3, 119.2, 119.1, 113.4, 109.3, 84.8, 68.5, 47.0, 31.8, 29.5, 27.3, 25.9, 22.8, 14.2.

HRMS (ASAP) calculated for $C_{23}H_{27}O$ $[M+H]^+$ 319.2056, found 319.2061

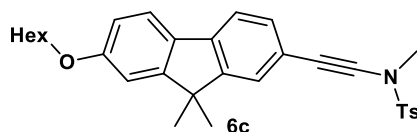


A solution of alkyne **4c** (196 mg, 0.615 mmol) in acetone (8 mL) was reacted with N-bromosuccinimide (132 mg, 0.742 mmol) and $AgNO_3$ (21 mg, 0.123 mmol). After 2 h at room temperature in the dark, the reaction mixture was filtered and concentrated under reduced pressure. The residue obtained was purified by column chromatography (cyclohexane:dichloromethane 1:0 to 9:1) to give brominated alkyne **5c** (140 mg, 0.352 mmol, 57%) as a yellow oil.

1H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, $J = 8.3$ Hz, 1H), 7.54 (dd, $J = 7.8, 0.7$ Hz, 1H), 7.48 (dd, $J = 1.5, 0.7$ Hz, 1H), 7.45 – 7.34 (m, 1H), 6.96 (d, $J = 2.3$ Hz, 1H), 6.87 (dd, $J = 8.3, 2.4$ Hz, 1H), 4.02 (t, $J = 6.6$ Hz, 2H), 1.87 – 1.76 (m, 2H), 1.52 – 1.47 (m, 6H), 1.45 (s, 6H), 1.37 (m, 4H), 0.97 – 0.84 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8, 156.1, 153.3, 140.1, 131.2, 131.2, 126.3, 121.3, 119.9, 119.1, 113.4, 109.3, 81.1, 68.5, 49.0, 47.0, 31.8, 29.5, 27.3, 27.1, 25.9, 22.8, 14.2.

HRMS (ASAP) calculated for $C_{23}H_{26}O^{79}Br$ $[M+H]^+$ 397.1162, found 397.1163

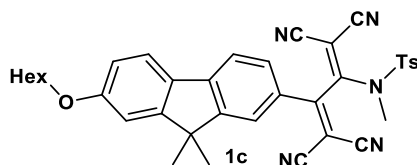


A solution of TsNHCH₃ (72 mg, 0.389 mmol), CuSO₄·5H₂O (9 mg, 0.036 mmol), 1,10-phenanthroline (11 mg, 0.063 mmol), K₂CO₃ (89 mg, 0.644 mmol) and alkyne **5c** (126 mg, 0.317 mmol) in dry toluene (4 mL) was heated to 90 °C under a nitrogen atmosphere for 41 h. The reaction was then cooled to room temperature, diluted with EtOAc and filtered through celite. The filtrate was concentrated under reduced pressure and purified by column chromatography (cyclohexane:dichloromethane 1:0 to 1:1) to give ynamide **6c** (133 mg, 0.265 mmol, 84%) as an orange solid.

¹H NMR (400 MHz, CDCl₃) δ 7.90 – 7.83 (m, 2H), 7.58 (d, *J* = 8.3 Hz, 1H), 7.53 (dd, *J* = 7.8, 0.7 Hz, 1H), 7.39 (d, *J* = 1.2 Hz, 2H), 7.31 (dd, *J* = 7.8, 1.5 Hz, 1H), 6.96 (d, *J* = 2.2 Hz, 1H), 6.87 (dd, *J* = 8.3, 2.3 Hz, 1H), 4.02 (t, *J* = 6.5 Hz, 2H), 3.17 (s, 3H), 2.47 (s, 3H), 1.87 – 1.76 (m, 2H), 1.53 – 1.47 (m, 2H), 1.45 (s, 6H), 1.36 (m, 4H), 0.96 – 0.88 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 159.7, 156.0, 153.3, 144.9, 139.4, 133.5, 131.4, 130.9, 129.9, 128.1, 126.0, 121.2, 119.8, 119.1, 113.4, 109.3, 83.6, 70.0, 68.5, 46.9, 39.5, 31.8, 29.5, 27.3, 25.9, 22.8, 21.8, 14.2.

HRMS (ESI MeOH/CH₂Cl₂ 90/10) calculated for C₃₁H₃₅NO₃NaS [M+Na]⁺ 524.2230, found 524.2230

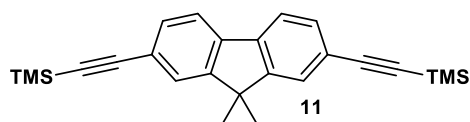


A solution of ynamide **6c** (123 mg, 0.245 mmol) and TCNE (32 mg, 0.5250 mmol) in CH₂Cl₂ (5 mL) was stirred at room temperature for 16 h. The reaction mixture was purified by column chromatography (cyclohexane:dichloromethane 1:0 to 3:7) to give TCBD **1c** (136 mg, 0.216 mmol, 88%) as a deep purple solid.

¹H NMR (400 MHz, CDCl₃) δ 7.83 (dd, *J* = 1.9, 0.6 Hz, 1H), 7.80 – 7.69 (m, 4H), 7.63 (dd, *J* = 8.1, 1.9 Hz, 1H), 7.48 – 7.39 (m, 2H), 7.00 (d, *J* = 2.3 Hz, 1H), 6.95 (dd, *J* = 8.4, 2.3 Hz, 1H), 4.06 (t, *J* = 6.5 Hz, 2H), 3.48 (s, 3H), 2.48 (s, 3H), 1.84 (dq, *J* = 8.4, 6.6 Hz, 2H), 1.53 (s, 6H), 1.51 (m, 2H), 1.38 (tdd, *J* = 6.9, 4.8, 2.4 Hz, 4H), 1.00 – 0.88 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 164.9, 164.4, 161.6, 157.6, 154.6, 147.4, 146.9, 132.4, 130.9, 130.6, 129.7, 128.5, 128.3, 124.7, 122.9, 120.3, 114.4, 112.8, 112.5, 110.9, 110.8, 109.1, 86.1, 80.3, 68.5, 47.4, 41.0, 31.7, 29.3, 26.9, 25.8, 22.7, 21.9, 14.1.

HRMS (ESI MeOH/CH₂Cl₂ 90/10) calculated for C₃₇H₃₅N₅O₃NaS [M+Na]⁺ 652.2353, found 652.2349

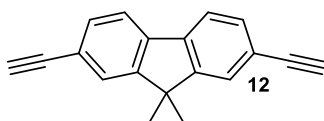


A solution of **10** (1 g, 2.840 mmol) in Et₃N (1.5 mL) and dry THF (1.5 mL) was treated with trimethylsilylacetylene (1.2 mL, 8.520 mmol), CuI (54 mg, 0.284 mmol) and [PdCl₂(PPh₃)₂] (100 mg, 0.142 mmol). The reaction mixture was stirred at 80°C over 72 h. 0.6 mL of trimethylsilylacetylene (4.260 mmol), 55 mg of CuI (0.142 mmol) and 169 mg of [PdCl₂(PPh₃)₂] (0.241 mmol) were added to the solution. The reaction mixture was stirred at 80°C over 24 h, then diluted with Et₂O (20 mL) and filtered through celite. The filtrate was concentrated under reduced pressure and purified by column chromatography (pentane to pentane:dichloromethane 95:5) to give alkyne **11** (749 mg, 1.939 mmol, 68%) as a yellow solid.

¹H NMR (400 MHz, CDCl₃) δ 7.61 (dd, *J* = 7.9, 0.7 Hz, 2H), 7.53 (dd, *J* = 1.5, 0.7 Hz, 2H), 7.45 (dd, *J* = 7.9, 1.4 Hz, 2H), 1.45 (s, 6H), 0.27 (s, 18H).

¹³C NMR (101 MHz, CDCl₃) δ 153.8, 138.8, 131.2, 126.3, 122.0, 120.1, 105.8, 94.5, 46.9, 26.8, 0.0

HRMS (ESI) calculated for C₂₅H₃₁Si₂ [M+H]⁺ 387.1964, found 387.1963

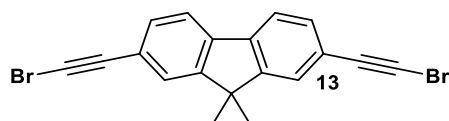


A solution of alkyne **11** (200 mg, 0.518 mmol) in MeOH (2 mL) and THF (2 mL) was treated with K₂CO₃ (286 mg, 2.072 mmol). After 2 h at room temperature, the reaction was diluted with Et₂O, filtered through celite and concentrated under reduced pressure. The residue obtained was purified by column chromatography (pentane to pentane:dichloromethane 9:1) to give alkyne **12** (125 mg, 0.467 mmol, 90%) as a brown solid.

¹H NMR (400 MHz, CDCl₃) δ 7.65 (dd, *J* = 7.8, 0.7 Hz, 2H), 7.56 (dd, *J* = 1.5, 0.7 Hz, 2H), 7.49 (dd, *J* = 7.8, 1.4 Hz, 2H), 3.14 (s, 2H), 1.47 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 153.8, 139.0, 131.4, 126.5, 121.1, 120.2, 84.3, 77.43, 46.9, 26.8

HRMS (ASAP) calculated for C₁₉H₁₅ [M+H]⁺ 243.1169, found 243.1168

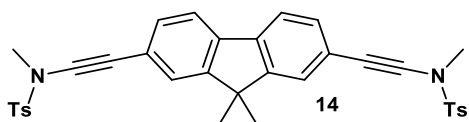


A solution of alkyne **12** (125 mg, 0.518 mmol) in acetone (5 mL) was reacted with N-bromosuccinimide (232 mg, 1.304 mmol) and AgNO₃ (20 mg, 0.118 mmol). After 2 h 30 at room temperature in the dark, the reaction mixture was filtered. The filtrate was concentrated under reduced pressure and purified by column chromatography (pentane) to give brominated alkyne **13** (94 mg, 0.236 mmol, 46%) as a yellow solid.

¹H NMR (400 MHz, CDCl₃) δ 7.63 (dd, *J* = 7.9, 0.7 Hz, 2H), 7.51 (dd, *J* = 1.5, 0.6 Hz, 2H), 7.43 (dd, *J* = 7.9, 1.5 Hz, 2H), 1.45 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 153.9, 138.9, 131.2, 126.4, 121.7, 120.3, 80.7, 50.0, 46.9, 26.8.

HRMS (ASAP) calculated for C₁₉H₁₃⁷⁹Br₂ [M+Na]⁺ 398.9384, found 398.9382

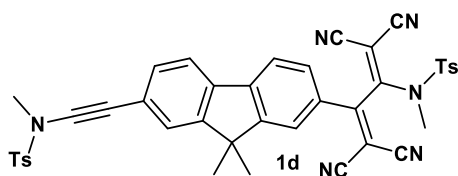


A solution of TsNHCH₃ (83 mg, 0.447 mmol), CuSO₄·5H₂O (5 mg, 0.020 mmol), 1,10-phenanthroline (14.5 mg, 0.080 mmol), K₂CO₃ (112 mg, 0.812 mmol) and alkyne **13** (81 mg, 0.203 mmol) in dry toluene (2.0 mL) was heated to 90 °C under nitrogen atmosphere for 22 h. The reaction was then cooled to room temperature, diluted with Et₂O (10 mL) and filtered through celite. The filtrate was concentrated under reduced pressure and purified by column chromatography (cyclohexane to cyclohexane:ethyl acetate 7:3) to give ynamide **14** (71 mg, 0.117 mmol, 58%) as a yellow solid.

¹H NMR (400 MHz, CDCl₃) δ 7.92 – 7.82 (m, 4H), 7.60 (dd, *J* = 7.8, 0.6 Hz, 2H), 7.44 – 7.36 (m, 6H), 7.34 (dd, *J* = 7.8, 1.5 Hz, 2H), 3.18 (s, 6H), 2.47 (s, 6H), 1.46 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 153.6, 144.6, 138.2, 133.2, 130.5, 129.7, 127.7, 125.6, 121.4, 119.9, 84.0, 69.5, 46.7, 39.2, 26.8, 21.5.

HRMS (ESI MeOH/CH₂Cl₂ 90/10) calculated for C₃₅H₃₂N₂O₄NaS₂ [M+Na]⁺ 631.1701, found 631.1698

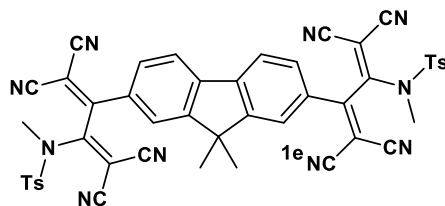


A solution of ynamide **14** (60 mg, 0.098 mmol) and TCNE (12.6 mg, 0.098 mmol) in CH₂Cl₂ (3 mL) was stirred at room temperature for 2 h. The reaction mixture was purified by column chromatography (cyclohexane:ethyl acetate 1:0 to 7:3) to give TCBD **1d** (29 mg, 0.039 mmol, 39%) as a dark red solid.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.91 – 7.82 (m, 4H), 7.79 – 7.70 (m, 3H), 7.65 (dd, $J = 8.1, 1.9$ Hz, 1H), 7.50 – 7.37 (m, 6H), 3.46 (s, 3H), 3.20 (s, 3H), 2.49 (s, 3H), 2.48 (s, 3H), 1.43z (s, 6H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 165.1, 164.1, 155.2, 155.1, 147.6, 145.6, 145.1, 136.6, 133.4, 132.4, 131.0, 130.9, 130.3, 130.0, 130.0, 128.3, 128.0, 125.9, 125.0, 124.3, 121.6, 121.4, 112.5, 112.2, 110.8, 110.7, 87.7, 85.8, 80.6, 69.8, 47.5, 41.1, 39.4, 27.0, 26.7, 22.0, 21.8.

HRMS (ESI MeOH/ CH_2Cl_2 90/10) calculated for $\text{C}_{41}\text{H}_{32}\text{N}_6\text{O}_4\text{NaS}_2$ $[\text{M}+\text{Na}]^+$ 758.1819, found 759.1818

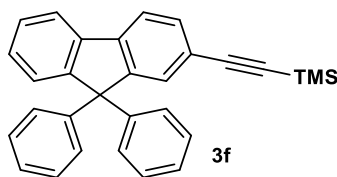


A solution of ynamide **14** (60 mg, 0.099 mmol) and TCNE (28 mg, 0.218 mmol) in CH_2Cl_2 (2.5 mL) was stirred at room temperature for 18 h. The reaction mixture was purified by column chromatography (cyclohexane:ethyl acetate 1:0 to 0:1) to give TCBD **1e** (61.4 mg, 0.076 mmol, 77%) as a yellow/brown solid.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.03 (dd, $J = 8.1, 0.6$ Hz, 2H), 7.91 (dd, $J = 1.9, 0.6$ Hz, 2H), 7.80 – 7.75 (m, 4H), 7.72 (dd, $J = 8.1, 1.8$ Hz, 2H), 7.49 – 7.43 (m, 4H), 3.44 (s, 6H), 2.51 (s, 6H), 1.64 (s, 6H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 165.0, 163.7, 156.2, 147.8, 143.3, 132.3, 131.9, 131.1, 130.2, 128.3, 125.3, 122.8, 112.1, 111.9, 110.8, 110.5, 89.6, 80.9, 77.5, 77.2, 76.8, 48.3, 41.1, 27.1, 26.5, 22.0.

HRMS (ESI MeOH/ CH_2Cl_2 90/10) calculated for $\text{C}_{47}\text{H}_{32}\text{N}_{10}\text{O}_4\text{NaS}_2$ $[\text{M}+\text{Na}]^+$ 887.1947, found 887.1943

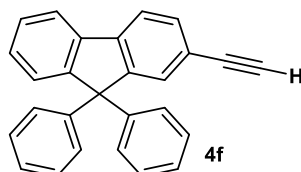


A solution of **2f** (1 g, 2.517 mmol) in Et_3N (2 mL) and dry THF (20 mL) was treated with trimethylsilylacetylene (0.70 mL, 5.055 mmol), CuI (49 mg, 0.257 mmol), PPh_3 (66 mg, 0.252 mmol) and $[\text{PdCl}_2(\text{PPh}_3)_2]$ (90 mg, 0.128 mmol). The reaction mixture was stirred at reflux over 63 h. The reaction mixture was concentrated under reduced pressure and purified by column chromatography (cyclohexane) to give alkyne **3f** (227 mg, 0.550 mmol, 22%) as a colorless solid.

¹H NMR (400 MHz, CDCl₃) δ 7.77 (ddd, *J* = 7.6, 1.3, 0.7 Hz, 1H), 7.74 – 7.70 (m, 1H), 7.51 (d, *J* = 7.6 Hz, 2H), 7.43 (ddd, *J* = 7.6, 1.2, 0.7 Hz, 1H), 7.39 (td, *J* = 7.5, 1.2 Hz, 1H), 7.31 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.29 – 7.19 (m, 10H), 0.26 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 151.8, 151.3, 145.5, 140.7, 139.5, 131.9, 129.8, 128.4, 128.3, 128.3, 127.7, 126.9, 126.4, 122.2, 120.6, 120.1, 105.9, 94.4, 65.6, 0.1.

HRMS (ASAP) calculated for C₃₀H₂₇S [M+H]⁺ 415.1877, found 415.1880

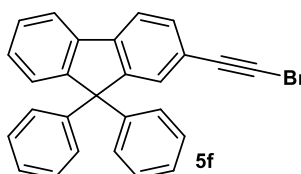


A solution of alkyne **3f** (213 mg, 0.524 mmol) in MeOH (2 mL) and THF (2 mL) was treated with K₂CO₃ (142 mg, 1.028 mmol). After 3 h at room temperature, the reaction was filtered with EtOAc and concentrated under reduced pressure. The residue obtained was purified by column chromatography (cyclohexane:ethyl acetate 1:0 to 9:1) to give alkyne **4f** (120 mg, 0.351 mmol, 68%) as a pale yellow solid.

¹H NMR (400 MHz, CDCl₃) δ 7.76 (ddd, *J* = 7.5, 1.2, 0.7 Hz, 1H), 7.72 (dd, *J* = 7.8, 0.7 Hz, 1H), 7.54 (dd, *J* = 1.5, 0.7 Hz, 1H), 7.51 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.42 (dt, *J* = 7.6, 0.9 Hz, 1H), 7.37 (td, *J* = 7.5, 1.2 Hz, 1H), 7.29 (td, *J* = 7.5, 1.2 Hz, 1H), 7.26 – 7.16 (m, 10H), 3.07 (s, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 151.7, 151.3, 145.5, 141.0, 139.4, 131.9, 130.1, 128.5, 128.2, 127.8, 126.9, 126.4, 121.1, 120.7, 120.2, 84.4, 77.4, 65.6.

The spectroscopic data are in agreement with the literature.⁴



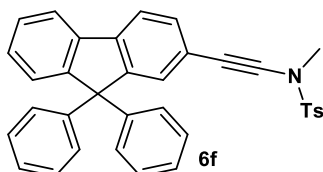
A solution of alkyne **4f** (111 mg, 0.324 mmol) in acetone (12 mL) was reacted with N-bromosuccinimide (70 mg, 0.393 mmol) and AgNO₃ (12 mg, 0.070 mmol). After 16 h at room temperature in the dark, the reaction mixture was filter and concentrated under reduced pressure. The residue obtained was purified by column chromatography (cyclohexane:ethyl acetate 1:0 to 9:1) to give brominated alkyne **5f** (156 mg, 0.323, 99%) as a yellow solid.

⁴ Z. Wang, T. Wang, C. Zhang, M. G. Humphrey, *Phys.Chem.Chem.Phys.*, **2017**, 19, 12928-12935

¹H NMR (400 MHz, CDCl₃) δ 7.75 (dt, *J* = 7.6, 1.0 Hz, 1H), 7.70 (dd, *J* = 7.9, 0.7 Hz, 1H), 7.49 (dd, *J* = 1.5, 0.7 Hz, 1H), 7.45 (dt, *J* = 7.8, 1.1 Hz, 1H), 7.41 (dt, *J* = 7.6, 1.0 Hz, 1H), 7.37 (td, *J* = 7.4, 1.2 Hz, 1H), 7.29 (td, *J* = 7.5, 1.2 Hz, 1H), 7.27 – 7.13 (m, 10H).

¹³C NMR (101 MHz, CDCl₃) δ 151.7, 151.4, 145.4, 140.9, 139.4, 131.7, 130.0, 128.5, 128.5, 128.2, 127.8, 127.0, 126.4, 121.7, 120.7, 120.2, 80.8, 65.6, 50.0.

HRMS (ASAP) calculated for C₂₇H₁₈⁷⁹Br [M+H]⁺ 421.05986 found 421.0590

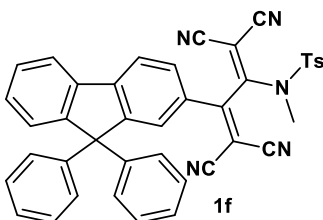


A solution of TsNHCH₃ (74 mg, 0.399 mmol), CuSO₄·5H₂O (13 mg, 0.053 mmol), 1,10-phenanthroline (26 mg, 0.144 mmol), K₂CO₃ (179 mg, 1.296 mmol) and alkyne **5f** (136 mg, 0.324 mmol) in dry toluene (6 mL) was heated to 90 °C under nitrogen atmosphere for 42 h. The reaction was then cooled to room temperature, diluted with EtOAc and filtered through celite. The filtrate was concentrated under reduced pressure and purified by column chromatography (cyclohexane:ethyl acetate 1:0 to 9:1) to give ynamide **6f** (112 mg, 0.212 mmol, 65%) as a yellow solid.

¹H NMR (400 MHz, CDCl₃) δ 7.84 – 7.79 (m, 2H), 7.74 (ddd, *J* = 7.6, 1.3, 0.7 Hz, 1H), 7.70 – 7.67 (m, 1H), 7.40 (ddd, *J* = 7.6, 1.2, 0.7 Hz, 1H), 7.38 – 7.35 (m, 3H), 7.35 – 7.31 (m, 2H), 7.30 – 7.25 (m, 1H), 7.25 – 7.16 (m, 10H), 3.13 (s, 3H), 2.44 (d, *J* = 0.7 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 151.6, 151.3, 145.6, 144.9, 140.2, 139.6, 133.3, 131.3, 129.9, 129.4, 128.4, 128.3, 128.2, 128.0, 127.8, 126.9, 126.4, 121.8, 120.5, 120.2, 84.3, 69.8, 65.6, 39.5, 21.8.

HRMS (ESI MeOH/CH₂Cl₂ 90/10) calculated for C₃₅H₂₇N₅O₂NaS [M+Na]⁺ 548.1655, found 548.1658

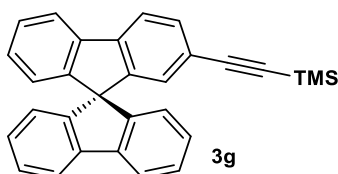


A solution of ynamide **6f** (50 mg, 0.095 mmol) and TCNE (13 mg, 0.099 mmol) in CH₂Cl₂ (2 mL) was stirred at room temperature for 16 h. The reaction mixture was purified by column chromatography (cyclohexane:ethyl acetate 1:0 to 8:2) to give TCBD **1f** (54 mg, 0.083 mmol, 87%) as a red solid.

¹H NMR (400 MHz, CDCl₃) δ 7.97 (dd, *J* = 8.1, 0.6 Hz, 1H), 7.90 – 7.85 (m, 1H), 7.81 (dd, *J* = 8.1, 1.9 Hz, 1H), 7.69 – 7.63 (m, 3H), 7.52 – 7.47 (m, 1H), 7.47 – 7.40 (m, 2H), 7.39 – 7.34 (m, 2H), 7.29 – 7.17 (m, 9H), 3.28 (s, 3H), 2.47 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 164.7, 164.5, 153.1, 152.7, 147.4, 147.1, 144.4, 138.1, 132.5, 131.0, 130.7, 130.4, 130.4, 128.8, 128.6, 128.3, 128.2, 128.1, 127.4, 126.7, 121.9, 121.6, 112.2, 112.2, 110.6, 110.5, 87.8, 80.9, 65.9, 41.3, 22.0.

HRMS (ESI MeOH/CH₂Cl₂ 90/10) calculated for C₄₁H₂₇N₅O₂NaS [M+Na]⁺ 676.1778, found 676.1783



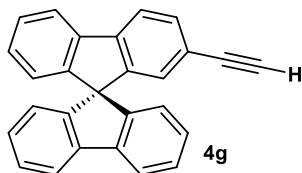
A solution of **2g** (1 g, 2.530 mmol) in Et₃N (2 mL) and dry THF (20 mL) was reacted with trimethylsilylacetylene (0.70 mL, 5.060 mmol), CuI (49 mg, 0.257 mmol), PPh₃ (72 mg, 0.274 mmol) and [PdCl₂(PPh₃)₂] (89 mg, 0.126 mmol). The reaction mixture was stirred at reflux over 16 h. The reaction mixture was concentrated under reduced pressure and purified by column chromatography (cyclohexane) to give alkyne **3g** (1.03 g, 2.496 mmol, 99%) as a yellow solid.

¹H NMR (400 MHz, CDCl₃) δ 7.85 (m, 3H), 7.79 (dd, *J* = 7.8, 0.7 Hz, 1H), 7.55 – 7.48 (m, 1H), 7.39 (m, 3H), 7.13 (td, *J* = 7.5, 1.1 Hz, 3H), 6.87 (dd, *J* = 1.4, 0.7 Hz, 1H), 6.74 (m, 3H), 0.18 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 149.3, 148.8, 148.3, 142.3, 141.9, 141.1, 132.0, 128.4, 128.0, 128.0, 124.2, 124.2, 122.2, 120.4, 120.2, 119.9, 94.5, 65.9, 0.1.

HRMS (ASAP) calculated for C₃₀H₂₅Si [M+H]⁺ 413.1720, found 413.1726

The spectroscopic data are in agreement with the literature.⁵



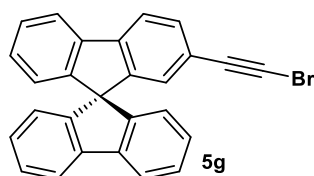
A solution of alkyne **3g** (1.03 g, 2.496 mmol) in MeOH (7.5 mL) and THF (10 mL) was treated with K₂CO₃ (696 mg, 5.036 mmol). After 3.5 h at room temperature, the reaction was filtered and concentrated under reduced pressure. The residue obtained was purified by column chromatography (cyclohexane) to give alkyne **4g** (476 mg, 1.397 mmol, 56%) as a pale yellow solid.

⁵ H. Jinhai, D. Lei, C. Jinxin, C. Lifei, PCT Int. Appl. (2013), WO 2013182046 A1 Dec 12, 2013

¹H NMR (400 MHz, CDCl₃) δ 7.91 – 7.76 (m, 4H), 7.51 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.38 (td, *J* = 7.5, 1.1 Hz, 3H), 7.13 (tdd, *J* = 7.6, 5.7, 1.2 Hz, 3H), 6.90 – 6.84 (m, 1H), 6.73 (tt, *J* = 7.6, 1.0 Hz, 3H), 2.96 (s, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 149.3, 149.0, 148.2, 142.5, 141.9, 141.0, 132.1, 128.6, 128.0, 128.0, 124.3, 124.2, 121.2, 120.5, 120.2, 120.0, 84.1, 65.9.

HRMS (ASAP) calculated for C₂₇H₁₇ [M+H]⁺ 341.1325, found 341.1328

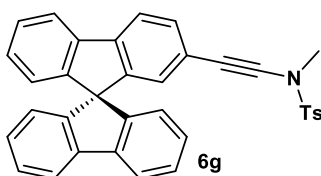


A solution of alkyne **4g** (465 mg, 1.366 mmol) in acetone (15 mL) was reacted with *N*-bromosuccinimide (296 mg, 1.663 mmol) and AgNO₃ (49 mg, 0.288 mmol). After 16 h at room temperature in the dark, the reaction mixture was filtered and concentrated under reduced pressure. The residue obtained was purified by column chromatography (cyclohexane) to give brominated alkyne **5g** (405 mg, 0.966 mmol, 71%) as a yellow solid.

¹H NMR (400 MHz, CDCl₃) δ 7.88 – 7.81 (m, 3H), 7.80 – 7.76 (m, 1H), 7.46 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.38 (td, *J* = 7.5, 1.1 Hz, 3H), 7.12 (tdd, *J* = 7.5, 6.5, 1.1 Hz, 3H), 6.85 – 6.80 (m, 1H), 6.73 (ddt, *J* = 12.1, 7.5, 0.9 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 149.2, 149.1, 148.2, 142.4, 141.9, 141.0, 131.8, 128.6, 128.0, 127.9, 124.3, 124.1, 121.8, 120.5, 120.2, 120.0, 80.5, 50.0.

HRMS (ASAP) calculated for C₂₇H₁₆⁷⁹Br [M+H]⁺ 419.0430, found 419.0433

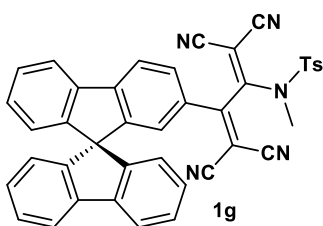


A solution of TsNHCH₃ (197 mg, 1.063 mmol), CuSO₄·5H₂O (27 mg, 0.113 mmol), 1,10-phenanthroline (55 mg, 0.398 mmol), K₂CO₃ (678 mg, 3.76 mmol) and alkyne **5g** (392 mg, 0.935 mmol) in dry toluene (20 mL) was heated to 90 °C under nitrogen atmosphere for 69 h. The reaction was then cooled to room temperature, diluted with EtOAc and filtered through celite. The filtrate was concentrated under reduced pressure and purified by column chromatography (cyclohexane:ethyl acetate 1:0 to 9:1) to give ynamide **6g** (434 mg, 0.828 mmol, 88%) as a yellow solid.

¹H NMR (400 MHz, CDCl₃) δ 7.86 (ddt, *J* = 7.6, 1.1, 0.6 Hz, 2H), 7.82 (dq, *J* = 7.7, 0.6 Hz, 1H), 7.77 (dt, *J* = 7.9, 0.6 Hz, 1H), 7.75 – 7.71 (m, 2H), 7.42 – 7.34 (m, 4H), 7.23 (dq, *J* = 7.9, 0.6 Hz, 2H), 7.17 – 7.09 (m, 3H), 6.73 (dt, *J* = 7.6, 1.2, 0.6 Hz, 3H), 6.70 (dt, *J* = 1.0, 0.5 Hz, 1H), 3.04 (d, *J* = 0.5 Hz, 3H), 2.41 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 149.1, 149.0, 148.4, 144.9, 141.9, 141.7, 141.2, 133.1, 131.4, 129.8, 128.3, 128.0, 128.0, 128.0, 127.4, 124.2, 121.9, 120.4, 120.2, 120.0, 84.3, 69.6, 65.9, 39.4, 21.8.

HRMS (ESI MeOH/CH₂Cl₂ 90/10) calculated for C₃₅H₂₅NO₂NaS [M+Na]⁺ 546.1498, found 546.1499;

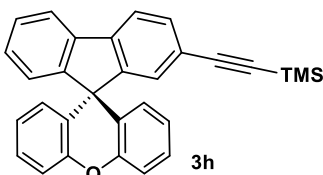


A solution of ynamide **6g** (116 mg, 0.221 mmol) and TCNE (29 mg, 0.222 mmol) in CH₂Cl₂ (3 mL) was stirred at room temperature for 16 h. The reaction mixture was purified by column chromatography (cyclohexane:ethyl acetate 1:0 to 8:2) to give TCBD **1g** (133 mg, 0.204 mmol, 92%) as a red solid.

¹H NMR (400 MHz, CDCl₃) δ 8.07 (dd, *J* = 8.1, 0.6 Hz, 1H), 7.99 – 7.93 (m, 2H), 7.88 (dq, *J* = 7.6, 0.8 Hz, 2H), 7.62 – 7.56 (m, 2H), 7.46 (td, *J* = 7.5, 1.0 Hz, 1H), 7.43 – 7.35 (m, 4H), 7.30 – 7.22 (m, 1H), 7.15 (td, *J* = 7.4, 1.0 Hz, 2H), 6.83 (dt, *J* = 7.6, 0.9 Hz, 1H), 6.76 (dt, *J* = 7.6, 0.9 Hz, 2H), 6.62 (dd, *J* = 1.9, 0.7 Hz, 1H), 2.91 (s, 3H), 2.47 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 164.7, 164.3, 150.7, 150.2, 148.4, 147.3, 147.1, 141.9, 139.7, 132.4, 131.3, 130.9, 130.6, 130.5, 128.6, 128.5, 128.3, 128.0, 125.9, 124.6, 124.2, 121.8, 121.5, 120.5, 112.2, 110.6, 110.2, 87.9, 82.2, 65.9, 40.7, 22.0.

HRMS (ESI MeOH/CH₂Cl₂ 90/10) calculated for C₄₁H₂₅N₅O₂NaS [M+Na]⁺ 647.1621, found 647.1623

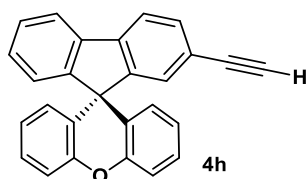


A solution of **2h** (500 mg, 1.215 mmol) in Et₃N (1 mL) and dry THF (10 mL) was reacted with trimethylsilylacetylene (0.35 mL, 2.530 mmol), CuI (31 mg, 0.163 mmol), PPh₃ (33 mg, 0.126 mmol) and [PdCl₂(PPh₃)₂] (46 mg, 0.065 mmol). The reaction mixture was stirred at reflux over 60 h. The reaction mixture was concentrated under reduced pressure and purified by column chromatography (cyclohexane) to give alkyne **3h** (509 mg, 1.189 mmol, 98%) as a yellow solid.

¹H NMR (400 MHz, CDCl₃) δ 7.78 (ddd, *J* = 7.6, 1.2, 0.7 Hz, 1H), 7.73 (dd, *J* = 7.9, 0.7 Hz, 1H), 7.50 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.38 (td, *J* = 7.4, 1.2 Hz, 1H), 7.27 (dd, *J* = 1.5, 0.7 Hz, 1H), 7.26 – 7.17 (m, 5H), 7.16 (ddd, *J* = 7.6, 1.2, 0.7 Hz, 1H), 6.78 (ddd, *J* = 7.9, 6.6, 1.9 Hz, 2H), 6.38 (ddd, *J* = 7.9, 1.5, 0.6 Hz, 2H), 0.19 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 155.7, 155.2, 151.4, 140.2, 139.0, 132.1, 129.5, 129.0, 128.4, 128.2, 128.1, 125.9, 124.3, 123.5, 122.8, 120.4, 119.9, 117.0, 105.5, 94.7, 54.2, 0.1.

HRMS (ESI MeOH/CH₂Cl₂ 90/10) calculated for C₃₀H₂₄ONaSi [M+Na]⁺ 451.1489, found 451.1487

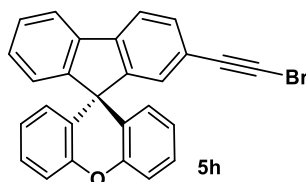


A solution of alkyne **3h** (500 mg, 1.166 mmol) in MeOH (5 mL) and THF (5 mL) was treated with K₂CO₃ (345 mg, 1.424 mmol). After 4.5 h at room temperature, the reaction mixture was diluted in dichloromethane (20 mL), filtered and concentrated under reduced pressure. The residue obtained was purified by column chromatography (cyclohexane:dichloromethane 1:0 to 9:1) to give alkyne **4h** (222 mg, 0.622 mmol, 53%) as a pale yellow solid.

¹H NMR (400 MHz, CDCl₃) δ 7.79 (dt, *J* = 7.7, 0.9 Hz, 1H), 7.75 (dd, *J* = 7.9, 0.7 Hz, 1H), 7.51 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.39 (td, *J* = 7.4, 1.2 Hz, 1H), 7.30 (dd, *J* = 1.5, 0.7 Hz, 1H), 7.25 – 7.15 (m, 6H), 6.78 (ddd, *J* = 7.8, 6.5, 1.9 Hz, 2H), 6.42 – 6.36 (m, 2H), 3.02 (s, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 155.4, 155.2, 151.5, 140.4, 139.1, 132.2, 129.7, 129.1, 128.4, 128.2, 128.0, 126.0, 124.3, 123.5, 121.8, 120.4, 120.0, 117.0, 84.0, 77.7, 54.3.

HRMS (ESI MeOH/CH₂Cl₂ 90/10) calculated for C₂₇H₁₆ONa [M+Na]⁺ 379.1093, found 379.1094;



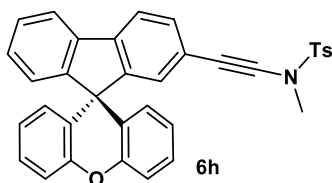
A solution of alkyne **4h** (214 mg, 0.600 mmol) in acetone (20 mL) was reacted with N-bromosuccinimide (232 mg, 1.303 mmol) and AgNO₃ (13 mg, 0.076 mmol). After 16 h at room temperature in the dark, the reaction mixture was filtered. The solid was washed with water and ethanol, then dissolved in dichloromethane and concentrated to give brominated alkyne **5h** (169 mg, 0.388 mmol, 65%) as a pale yellow solid.

¹H NMR (400 MHz, CDCl₃) δ 7.79 (ddd, *J* = 7.7, 1.1, 0.7 Hz, 1H), 7.73 (dd, *J* = 7.9, 0.7 Hz, 1H), 7.45 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.39 (td, *J* = 7.5, 1.2 Hz, 1H), 7.27 – 7.24 (m, 2H), 7.23 – 7.15 (m, 5H), 6.78 (ddd, *J* = 7.8, 6.5, 2.0 Hz, 2H), 6.38 (ddd, *J* = 7.9, 1.5, 0.5 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 155.4, 155.3, 151.4, 140.2, 139.1, 132.0, 129.6, 129.1, 128.5, 128.2, 128.0, 126.0, 124.3, 123.5, 122.4, 120.4, 120.1, 117.0, 80.5, 54.3, 50.3.

HRMS (ESI MeOH/CH₂Cl₂ 90/10) calculated for C₂₇H₁₅O⁷⁹BrNa [M+Na]⁺ 457.0199, found 457.0198

Crystal data (CCDC 2127295): C₂₇H₁₅BrO M = 435.30 g.mol⁻¹, T = 150 K, monoclinic, space group = P 2₁/n, a = 9.1558(5) Å, b = 14.5973(9) Å, c = 14.6262(10) Å, α = 90°, β = 101.237(2)°, γ = 90°, V = 1917.3(2) Å³, Z = 4, D_c = 1.508 g cm⁻³, absorption coefficient = 2.160 mm⁻¹, F(000) = 880, reflections collected = 18133, independent reflections = 4400 (R_{int} = 0.0505), data/restraints/parameters = 4400/0/262. Final R indices (I > 2 σ): R₁ = 0.0435, wR₂ = 0.1169, goodness-of-fit on F² of 0.988.

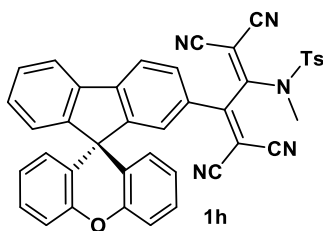


A solution of TsNHCH₃ (77 mg, 0.417 mmol), CuSO₄·5H₂O (10 mg, 0.038 mmol), 1,10-phenanthroline (28 mg, 0.152 mmol), K₂CO₃ (211 mg, 1.517 mmol) and alkyne **5h** (159 mg, 0.365 mmol) in dry toluene (12 mL) was heated to 90 °C under a nitrogen atmosphere for 60 h. The reaction was then cooled to room temperature, diluted with Et₂O (20 mL) and filtered through celite. The filtrate was concentrated under reduced pressure and purified by column chromatography (cyclohexane:dichloromethane 1:0 to 1:1) to give ynamide **6h** (156 mg, 0.290 mmol, 79%) as a yellow solid.

¹H NMR (400 MHz, CDCl₃) δ 7.80 – 7.74 (m, 3H), 7.71 (dd, *J* = 7.9, 0.7 Hz, 1H), 7.42 – 7.35 (m, 2H), 7.31 – 7.27 (m, 2H), 7.25 – 7.18 (m, 5H), 7.16 (ddd, *J* = 7.7, 1.3, 0.7 Hz, 1H), 7.11 (dd, *J* = 1.5, 0.7 Hz, 1H), 6.79 (ddd, *J* = 7.8, 6.6, 1.9 Hz, 2H), 6.39 (ddd, *J* = 7.8, 1.5, 0.5 Hz, 2H), 3.07z (s, 3H), 2.43 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 155.3, 155.3, 151.4, 144.9, 139.4, 139.3, 133.1, 131.5, 129.9, 129.0, 128.9, 128.4, 128.1, 128.1, 128.0, 126.0, 124.4, 123.5, 122.4, 120.3, 120.0, 117.0, 84.5, 69.6, 54.2, 39.4, 21.8.

HRMS (ESI MeOH/CH₂Cl₂ 90/10) calculated for C₃₅H₂₅NO₃NaS [M+Na]⁺ 562.1447, found 562.1449

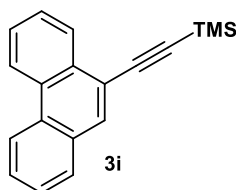


A solution of ynamide **6h** (50 mg, 0.093 mmol) and TCNE (12 mg, 0.097 mmol) in CH_2Cl_2 (2 mL) was stirred at room temperature for 16 h. The reaction mixture was purified by column chromatography (cyclohexane:dichloromethane 1:0 to 1:1) to give TCBD **1h** (56 mg, 0.084 mmol, 90%) as a red solid.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.03 (dd, $J = 8.1, 0.7$ Hz, 1H), 7.97 (dd, $J = 8.1, 1.8$ Hz, 1H), 7.90 (ddd, $J = 7.6, 1.2, 0.7$ Hz, 1H), 7.69 – 7.62 (m, 2H), 7.46 (td, $J = 7.5, 1.2$ Hz, 1H), 7.44 – 7.39 (m, 2H), 7.36 (td, $J = 7.5, 1.2$ Hz, 1H), 7.30 – 7.19 (m, 5H), 7.17 (dd, $J = 1.8, 0.6$ Hz, 1H), 6.85 (ddd, $J = 7.8, 6.8, 1.7$ Hz, 2H), 6.46 (ddd, $J = 7.8, 1.5, 0.5$ Hz, 2H), 3.02 (s, 3H), 2.49 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 164.7, 164.3, 156.0, 155.9, 151.5, 147.4, 146.6, 137.5, 132.5, 131.3, 131.1, 131.1, 131.0, 129.0, 128.7, 128.1, 127.8, 127.7, 126.1, 123.9, 123.6, 121.7, 121.6, 117.2, 112.2, 112.2, 110.6, 110.2, 88.2, 82.0, 54.7, 40.8, 22.0.

HRMS (ESI MeOH/ CH_2Cl_2 90/10) calculated for $\text{C}_{41}\text{H}_{25}\text{N}_5\text{O}_3\text{NaS}$ $[\text{M}+\text{Na}]^+$ 690.1570, found 690.1573;

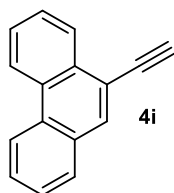


A solution of **2i** (1 g, 3.889 mmol) in Et_3N (8 mL) and dry THF (32 mL) was reacted with trimethylsilylacetylene (1.1 mL, 7.778 mmol), CuI (136 mg, 0.195 mmol), and $[\text{PdCl}_2(\text{PPh}_3)_2]$ (77 mg, 0.404 mmol). The reaction mixture was stirred at 85°C for 15 h. The reaction mixture was concentrated under reduced pressure. The residue was dissolved in dichloromethane (40 mL) and washed with Brine (40 mL). The aqueous solution was extracted with dichloromethane (2 x 40 mL). The organic layers were dried over MgSO_4 , filtered and concentrated under reduced pressure. The residue was purified by column chromatography (cyclohexane) to give alkyne **3i** (363 mg, 1.322 mmol, 33%) as a yellow oil.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.71 – 8.62 (m, 2H), 8.50 – 8.42 (m, 1H), 8.04 (s, 1H), 7.88 – 7.81 (m, 1H), 7.74 – 7.64 (m, 3H), 7.63 – 7.57 (m, 1H), 0.37 (s, 9H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 132.6, 131.2, 130.5, 130.1, 128.7, 127.7, 127.2, 127.1, 127.1, 122.9, 122.7, 119.6, 103.4, 99.3, 0.3.

The spectroscopic data are in agreement with the literature.⁶

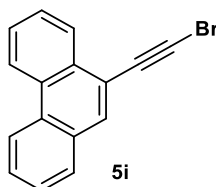


A solution of alkyne **3i** (363 mg, 1.323 mmol) in MeOH (6 mL) and THF (6 mL) was treated with K_2CO_3 (370 mg, 2.677 mmol). After 4 h at room temperature, K_2CO_3 (370 mg, 2.677 mmol) was added. The mixture was stirred for 6 h, then KF was added (1.11 g, 7.938). After 28h of reaction, KF was added (170 mg, 2.677 mmol) and after 1.5 h TBAF 1M in THF was added (2.8 mL, 2.8 mmol). After 48 h of reaction, the mixture was diluted with EtOAc and filtered and concentrated under reduced pressure. The residue obtained was purified by column chromatography (cyclohexane) to give alkyne **4i** (193 mg, 0.955 mmol, 72%) as a brown solid.

¹H NMR (400 MHz, $CDCl_3$) δ 8.74 – 8.64 (m, 2H), 8.51 – 8.45 (m, 1H), 8.10 – 8.06 (m, 1H), 7.86 (ddt, $J = 7.8, 1.2, 0.6$ Hz, 1H), 7.75 – 7.66 (m, 3H), 7.61 (ddd, $J = 8.2, 7.0, 1.2$ Hz, 1H), 3.49 (d, $J = 0.6$ Hz, 1H).

¹³C NMR (101 MHz, $CDCl_3$) δ 133.1, 131.2, 131.1, 130.6, 130.2, 128.7, 127.9, 127.3, 127.1, 127.0, 122.9, 122.8, 118.7, 82.1, 81.7.

The spectroscopic data are in agreement with the literature.⁷



A solution of alkyne **4i** (193 mg, 0.954 mmol) in acetone (10 mL) was reacted with N-bromosuccinimide (211 mg, 1.186 mmol) and $AgNO_3$ (16 mg, 0.095 mmol). After 2.5 h at room temperature in the dark, the reaction mixture was filtered through cotton. The filtrate was concentrated under reduced pressure and purified by column chromatography (cyclohexane) to give brominated alkyne **5i** (183 mg, 0.652 mmol, 68%) as a brown solid.

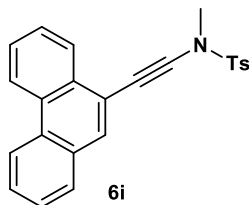
¹H NMR (400 MHz, $CDCl_3$) δ 8.73 – 8.61 (m, 2H), 8.44 – 8.37 (m, 1H), 8.02 (s, 1H), 7.84 (ddd, $J = 7.8, 1.4, 0.7$ Hz, 1H), 7.75 – 7.64 (m, 3H), 7.60 (ddd, $J = 8.1, 7.0, 1.2$ Hz, 1H).

⁶ M. Hassam, W.-S. Li, *Tetrahedron*, **2015**, 71, 2719-2723

⁷ V. Sharma, F. Chandra, D. Sahoo, A. L. Koner, *Eur. J. Org. Chem.*, **2017**, 6901–6905

^{13}C NMR (101 MHz, CDCl_3) δ 133.0, 131.3, 131.1, 130.5, 130.2, 128.7, 127.9, 127.3, 127.3, 127.2, 126.8, 122.9, 122.8, 119.3, 78.7, 53.8.

The spectroscopic data are in agreement with the literature.⁸

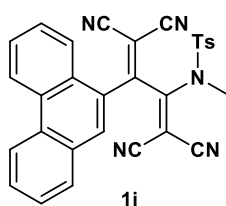


A solution of TsNHCH_3 (121 mg, 0.652 mmol), $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (4 mg, 0.016 mmol), 1,10-phenanthroline (47 mg, 0.260 mmol), K_2CO_3 (560 mg, 2.638 mmol) and alkyne **5i** (183 mg, 0.652 mmol) in dry toluene (10 mL) was heated to 90 °C under nitrogen atmosphere for 40 h. The reaction was then cooled to room temperature, diluted with dichloromethane (10 mL) and filtered through celite. The filtrate was concentrated under reduced pressure and purified by column chromatography (cyclohexane:ethyl acetate 1:0 to 9:1) to give ynamide **6i** (188 mg, 0.489 mmol, 75%) as a yellow oil.

^1H NMR (400 MHz, CDCl_3) δ 8.73 – 8.69 (m, 1H), 8.69 – 8.65 (m, 1H), 8.39 – 8.32 (m, 1H), 7.97 – 7.92 (m, 2H), 7.90 (s, 1H), 7.84 (dd, $J = 7.8, 1.5$ Hz, 1H), 7.75 – 7.64 (m, 3H), 7.61 (ddd, $J = 8.2, 7.0, 1.3$ Hz, 1H), 7.43 – 7.36 (m, 2H), 3.32 (s, 3H), 2.48 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 145.1, 133.5, 131.4, 131.3, 130.9, 130.2, 130.1, 130.1, 128.4, 128.0, 127.3, 127.2, 127.2, 127.1, 127.0, 122.9, 122.7, 119.3, 88.3, 67.9, 39.6, 21.8.

The spectroscopic data are in agreement with the literature.⁹



A solution of ynamide **6i** (176 mg, 0.455 mmol) and TCNE (58 mg, 0.455 mmol) in CH_2Cl_2 (5 mL) was stirred at room temperature for 16 h. The reaction mixture was purified by column chromatography (cyclohexane:ethyl acetate 1:0 to 7:3) to give TCBD **1i** (204 mg, 0.396 mmol, 87%) as a red solid.

^1H NMR (400 MHz, CDCl_3) δ 8.82 (d, $J = 8.3$, 1H), 8.73 (d, $J = 8.3$ Hz, 1H), 8.19 (s, 1H), 8.06 (dd, $J = 8.0, 1.3$ Hz, 1H), 7.86 (ddd, $J = 8.4, 7.1, 1.4$ Hz, 1H), 7.83 – 7.78 (m, 1H), 7.74 (dt, $J = 6.6, 1.1$ Hz, 3H), 7.72 – 7.69 (m, 2H), 7.46 – 7.36 (m, 2H), 2.87 (s, 3H), 2.47 (s, 3H).

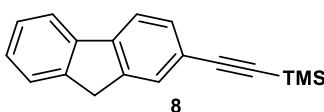
⁸ M. Elena de Orbe, M. Zanini, O. Quinonero, A. M. Echavarren *ACS Catal.*, **2019**, 9, 9, 7817-7822

⁹ B. Prabagar, S. Nayak, R. K. Mallick, R. Prasada, A. K. Sahoo, *Org. Chem. Front.*, **2016**, 3, 110–115

¹³C NMR (101 MHz, CDCl₃) δ 147.1, 132.3, 132.2, 131.1, 131.0, 130.7, 130.4, 130.1, 128.5, 128.4, 128.2, 128.1, 127.9, 124.3, 123.0, 111.8, 111.4, 111.2, 109.8, 94.9, 88.3, 40.5, 22.0.

HRMS (ESI) calculated for C₃₀H₁₉N₅O₂S [M+Na]⁺ 536.115, found 536.115

Crystal data (CCDC 2112157): C₃₀H₁₉N₅O₂S M = 513.56 g.mol⁻¹, T = 150 K, monoclinic, space group = P -1, a = 20.059(2) Å, b = 21.535(2) Å, c = 21.710(2) Å, α = 108.644°, β = 112.524(3)°, γ = 100.567(4)°, V = 7690.7(13) Å³, Z = 12, Dc = 1.331 g cm⁻³, absorption coefficient = 0.164 mm⁻¹, F(000) = 3192, reflections collected = 178052, independent reflections = 35393 (Rint = 0.0748), data/restraints/parameters = 35393/0/2065. Final R indices (I > 2 σ): R1 = 0.0631, wR2 = 0.1458, goodness-of-fit on F2 of 1.042.

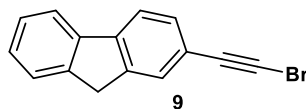


A solution of **7** (1 g, 4.080 mmol) in dry degassed THF (32 mL) and Et₃N (7 mL) was reacted with trimethylsilylacetylene (1.2 mL, 8.662 mmol), CuI (83 mg, 0.435 mmol), [PdCl₂(PPh₃)₂] (145 mg, 0.206 mg) and PPh₃ (206 mg, 0.783 mmol). The reaction mixture was stirred at reflux over 60 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. The residue was purified by column chromatography (cyclohexane) to give alkyne **8** (900 mg, 3.429 mmol, 84%) as a yellow solid.

¹H NMR (400 MHz, CDCl₃) δ 7.77 (ddt, J = 7.5, 1.2, 0.6 Hz, 1H), 7.71 (dt, J = 7.9, 0.6 Hz, 1H), 7.66 (dp, J = 1.5, 0.9 Hz, 1H), 7.55 (ddt, J = 7.3, 1.3, 0.7 Hz, 1H), 7.51 (ddd, J = 7.9, 1.5, 0.7 Hz, 1H), 7.39 (tdt, J = 6.9, 1.3, 0.6 Hz, 1H), 7.32 (tdd, J = 7.4, 1.2, 0.5 Hz, 1H), 3.88 (s, 2H), 0.28 (d, J = 0.6 Hz, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 143.6, 143.0, 142.1, 141.1, 130.9, 128.6, 127.2, 126.9, 125.1, 121.1, 120.2, 119.7, 105.9, 94.0, 36.7, 0.1.

The spectroscopic data are in agreement with the literature.¹⁰



A solution of alkyne **8** (1.37 g, 5.22 mmol) in acetone (50 mL) was reacted with N-bromosuccinimide (1.12 g, 6.26 mmol) and AgNO₃ (178 mg, 1.04 mmol). After 20 h at room temperature in the dark, the reaction mixture was filtered through cotton and concentrated under reduced pressure. The residue

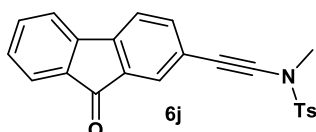
¹⁰ L. Liu, W.-Y. Wong, Y.-W. Lam, W.-Y. Tam, *Inorg. Chim. Acta*, **2007**, 360, 109-121

obtained was purified by column chromatography (pentane) to give brominated alkyne **9** (696mg, 2.58 mmol, 49%) as a brown oil.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.77 (dt, $J = 7.8, 0.9$ Hz, 1H), 7.72 (dd, $J = 7.8, 0.6$ Hz, 1H), 7.63 (td, $J = 1.6, 0.8$ Hz, 1H), 7.55 (dq, $J = 7.4, 1.0$ Hz, 1H), 7.48 (ddt, $J = 7.9, 1.5, 0.7$ Hz, 1H), 7.39 (dddd, $J = 7.5, 6.8, 1.4, 0.7$ Hz, 1H), 7.32 (td, $J = 7.4, 1.3$ Hz, 1H), 3.89 (s, 2H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 143.6, 143.1, 142.3, 140.9, 130.9, 128.6, 127.3, 127.0, 125.1, 120.7, 120.3, 119.7, 80.7, 49.4, 36.7.

HRMS (ESI MeOH/ CH_2Cl_2 90/10) calculated for $\text{C}_{15}\text{H}_{10}^{79}\text{Br}$ $[\text{M}+\text{H}]^+$ 268.9960, found 268.9960

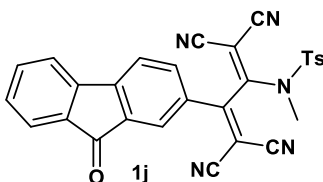


A solution of TsNHCH_3 (210 mg, 1.133 mmol), $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (51 mg, 0.209 mmol), 1,10-phenanthroline (76 mg, 0.419 mmol), K_2CO_3 (564 mg, 4.081 mmol) and alkyne **9** (277 mg, 1.029 mmol) in dry toluene (15 mL) was heated to 90 °C under nitrogen atmosphere for 42 h. The reaction was then cooled to room temperature and filtered through celite. The filtrate was concentrated under reduced pressure and purified by column chromatography (cyclohexane:dichloromethane 1:0 to 3:7) to give ynamide **6j** (311 mg, 0.803 mmol, 78%) as a yellow solid.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.87 – 7.82 (m, 2H), 7.65 (dt, $J = 7.4, 1.0$ Hz, 1H), 7.59 (dd, $J = 1.4, 0.7$ Hz, 1H), 7.52 – 7.48 (m, 2H), 7.48 – 7.43 (m, 2H), 7.42 – 7.36 (m, 2H), 7.30 (ddd, $J = 7.4, 5.5, 3.0$ Hz, 1H), 3.17 (s, 3H), 2.47 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 193.3, 145.2, 144.2, 143.4, 137.4, 135.1, 134.4, 134.3, 133.3, 130.1, 129.4, 128.0, 127.1, 124.6, 123.8, 120.7, 120.4, 85.7, 68.8, 39.4, 21.8.

HRMS (ESI MeOH/ CH_2Cl_2 90/10) calculated for $\text{C}_{23}\text{H}_{17}\text{NO}_3\text{NaS}$ $[\text{M}+\text{Na}]^+$ 410.0821, found 410.0820



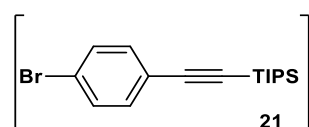
A solution of ynamide **6j** (49 mg, 0.133 mmol) and TCNE (19 mg, 0.152 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature for 15 h. The reaction mixture was purified by column chromatography (pentane:dichloromethane 1:1) to give TCBD **1j** (59 mg, 0.11 mmol, 90%) as an orange solid.

¹H NMR (400 MHz, CDCl₃) δ 8.06 (dd, *J* = 7.9, 1.9 Hz, 1H), 7.85 – 7.76 (m, 5H), 7.70 (dt, *J* = 7.6, 1.0 Hz, 1H), 7.64 (td, *J* = 7.4, 1.1 Hz, 1H), 7.55 – 7.46 (m, 3H), 3.48 (s, 3H), 2.54 (s, 3H).

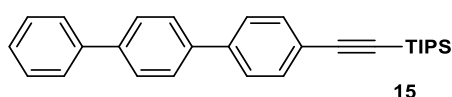
¹³C NMR (101 MHz, CDCl₃) δ 191.3, 164.2, 163.0, 149.6, 147.7, 142.6, 137.1, 135.5, 135.2, 134.6, 132.1, 131.8, 131.3, 131.0, 128.1, 125.1, 125.0, 123.0, 121.9, 121.6, 111.6, 111.6, 110.7, 110.2, 89.7, 80.5, 41.1, 26.9, 21.9.

HRMS (ESI MeOH/CH₂Cl₂ 90/10) calculated for C₂₉H₁₇N₅O₃NaS [M+Na]⁺ 538.0944, found 538.0944;

Crystal data (CCDC 2113145): C₃₀H₁₉Cl₂N₅O₃S M = 600.46 g.mol⁻¹, T = 150 K, triclinic, space group = P - 1, a = 10.6597(8) Å, b = 11.7525(11) Å, c = 12.8782(11) Å, α = 108.926(3)°, β = 101.465(3)°, γ = 103.504(3)°, V = 1416.3(2) Å³, Z = 2, D_c = 1.408 g cm⁻³, absorption coefficient = 0.345 mm⁻¹, F(000) = 616, reflections collected = 32506, independent reflections = 6451 (R_{int} = 0.0505), data/restraints/parameters = 6451/0/372. Final R indices (I > 2 σ): R₁ = 0.0412, wR₂ = 0.1021, goodness-of-fit on F² of 0.973.



A solution of **20** (1 g, 3.535 mmol) in degassed Et₃N (7 mL) was reacted with triisopropylsilylacetylene (0.9 mL, 3.888 mmol), CuI (21 mg, 0.110 mmol) and [PdCl₂(PPh₃)₂] (125 mg, 0.177 mmol). The reaction mixture was stirred at 40°C over 16 h. The reaction mixture was diluted with cyclohexane and filtered through celite. The filtrate was concentrated under reduced pressure and purified by column chromatography (cyclohexane) to give alkyne **21** as an impure colorless solid.¹¹



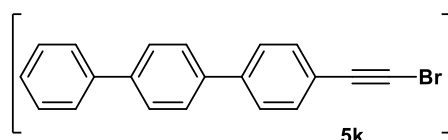
A solution of **18** (205 mg, 0.608 mmol) in degassed dimethoxyethane (3 mL) was reacted with 4-biphenylboronic acid (134 mg, 0.677 mmol), [Pd(dppf)Cl₂] (46 mg, 0.063 mmol) and Na₂CO₃ (2 mL, 2 M in water, 0.6 mmol). The reaction mixture was stirred at reflux over 60 h. The reaction mixture was diluted with water and extracted with dichloromethane. The organic layers were washed with water, dried over MgSO₄, filtered and concentrated under reduced pressure and purified by column chromatography (cyclohexane:ethyl acetate 1:0 to 9:1) to give alkyne **15** (112 mg, 0.273 mmol, 53% over 2 steps) as a colorless solid.

¹¹ Adapted from: J. Moreno, F. Schweighöfer, J. Wachtveitl, S. Hecht, *Chem. Eur. J.*, **2016**, 22, 1070 – 1075

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.68 (d, $J = 0.6$ Hz, 4H), 7.67 – 7.62 (m, 2H), 7.61 – 7.55 (m, 4H), 7.49 – 7.44 (m, 2H), 7.40 – 7.34 (m, 1H), 1.16 (s, 21H).

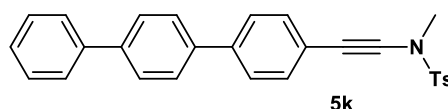
$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 140.7, 140.6, 139.4, 132.7, 129.0, 127.7, 127.6, 127.5, 127.2, 126.9, 122.7, 107.1, 91.5, 18.9, 11.5.

The spectroscopic data are in agreement with the literature.¹²



A solution of alkyne **15** (105 mg, 0.255 mmol) in acetone (12 mL) was reacted with N-bromosuccinimide (55 mg, 0.306 mmol) and AgF (39 mg, 0.306 mmol). After 23 h at room temperature in the dark, the reaction mixture was filtered and concentrated under reduced pressure. The residue obtained was purified by column chromatography (cyclohexane:dichloromethane 1:0 to 75:25) to give bromoalkyne **5k** (85 mg, not pure) as a pale yellow solid.

HRMS (ESI) calculated for $\text{C}_{20}\text{H}_{13}^{79}\text{Br}$ $[\text{M}+\text{H}]^+$ 333.027, found 333.028



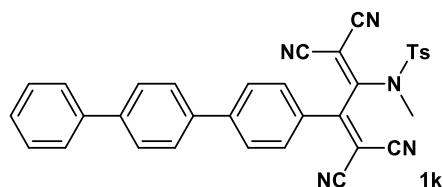
A solution of TsNHCH_3 (51 mg, 0.275 mmol), $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (7 mg, 0.028 mmol), 1,10-phenanthroline (22 mg, 0.122 mmol), K_2CO_3 (129 mg, 0.936 mmol) and alkyne **5k** (78 mg, not pure) in dry toluene (2 mL) was heated to 90 °C under a nitrogen atmosphere for 30 h. The reaction was then cooled to room temperature, diluted with dichloromethane and filtered through celite. The filtrate was concentrated under reduced pressure and purified by column chromatography (cyclohexane:dichloromethane 1:0 to 1:1) to give ynamide **6k** (34 mg, 0.077 mmol, 30% over 2 steps) as a colorless solid.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.91 – 7.84 (m, 2H), 7.72 – 7.63 (m, 6H), 7.62 – 7.56 (m, 2H), 7.52 – 7.42 (m, 4H), 7.42 – 7.32 (m, 3H), 3.18 (s, 3H), 2.48 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 145.0, 140.7, 140.6, 140.2, 139.3, 133.4, 132.0, 130.0, 129.0, 128.0, 127.7, 127.6, 127.4, 127.4, 127.2, 126.9, 121.8, 84.8, 69.1, 39.5, 21.8.

HRMS (ESI) calculated for $\text{C}_{28}\text{H}_{23}\text{NO}_2\text{S}$ $[\text{M}+\text{Na}]^+$ 460.134, found 460.134

¹² C. Quintana, M. Morshedi, H. Wang, J. Du, M. P. Cifuentes, M. G. Humphrey, *Nano Lett.*, **2019**, 19, 756–760



A solution of ynamide **6k** (33 mg, 0.075 mmol) and TCNE (10 mg, 0.075 mmol) in CH₂Cl₂ (2 mL) was stirred at room temperature for 16 h. The reaction mixture was purified by column chromatography (cyclohexane:dichloromethane 1:0 to 0:1) to give TCBD **1k** (35 mg, 0.062 mmol, 82%) as a red solid.

¹H NMR (400 MHz, CDCl₃) δ 7.91 – 7.85 (m, 2H), 7.85 – 7.80 (m, 2H), 7.80 – 7.74 (m, 6H), 7.71 – 7.65 (m, 2H), 7.53 – 7.44 (m, 4H), 7.44 – 7.38 (m, 1H), 3.49 (s, 3H), 2.51 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 164.7, 163.7, 147.6, 147.0, 142.1, 140.2, 137.5, 132.3, 131.0, 131.0, 130.0, 129.1, 128.3, 128.2, 128.0, 127.9, 127.8, 127.2, 112.1, 112.1, 110.9, 110.6, 88.6, 80.0, 41.2, 22.0.

HRMS (ESI) calculated for C₃₄H₂₃N₅O₂S [M+Na]⁺ 588.146, found 588.147

Crystal data (CCDC 2112158): C₆₉H₄₈Cl₂N₁₀O₄S₂ M = 1216.19 g.mol⁻¹, T = 150 K, monoclinic, space group = C 2/c, a = 30.7313(14) Å, b = 7.2123(4) Å, c = 28.6312(14) Å, α = 90°, β = 106.143(2)°, γ = 90°, V = 6095.7(5) Å³, Z = 4, D_c = 1.325 g cm⁻³, absorption coefficient = 0.234 mm⁻¹, F(000) = 2520, reflections collected = 21462, independent reflections = 6864 (R_{int} = 0.0447), data/restraints/parameters = 6864/0/408. Final R indices (I > 2 σ): R₁ = 0.0497, wR₂ = 0.1148, goodness-of-fit on F₂ of 1.009.

3. ^1H NMR and ^{13}C NMR spectra

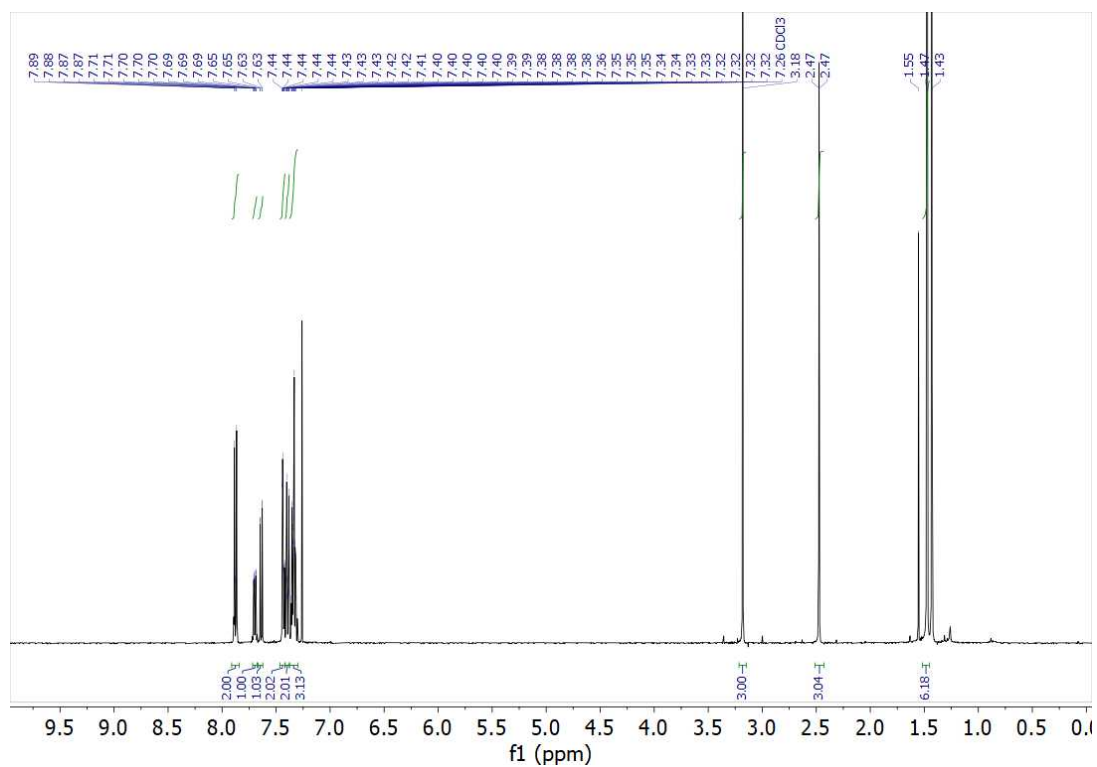


Figure S1. ^1H (400 MHz, CDCl_3) NMR spectrum of **6a** recorded at 25°C.

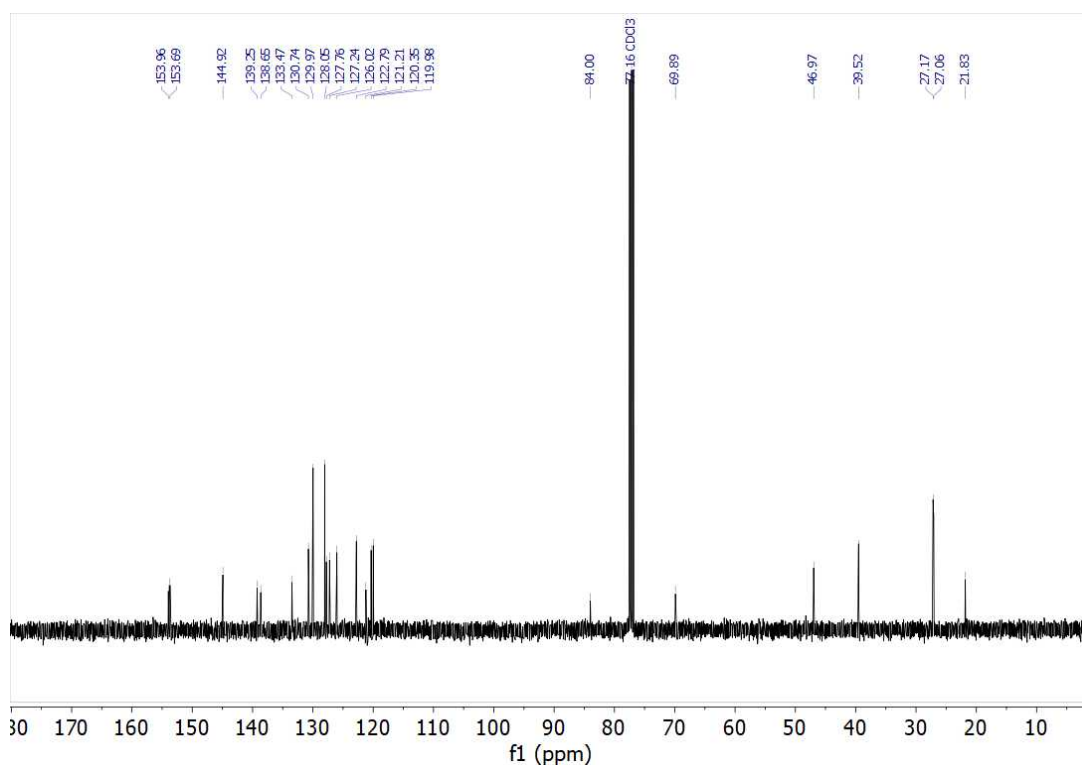


Figure S2. ^{13}C (101 MHz, CDCl_3) NMR spectrum of **6a** recorded at 25°C.

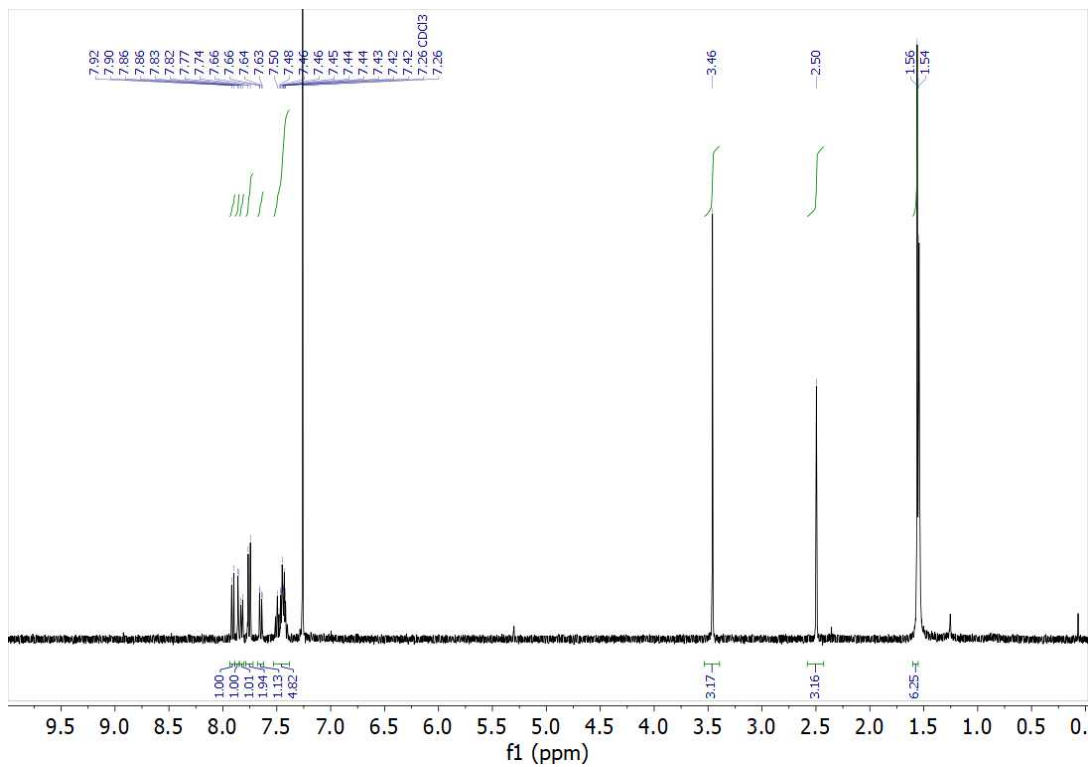


Figure S3. ¹H (400 MHz, CDCl₃) NMR spectrum of **1a** recorded at 25°C.

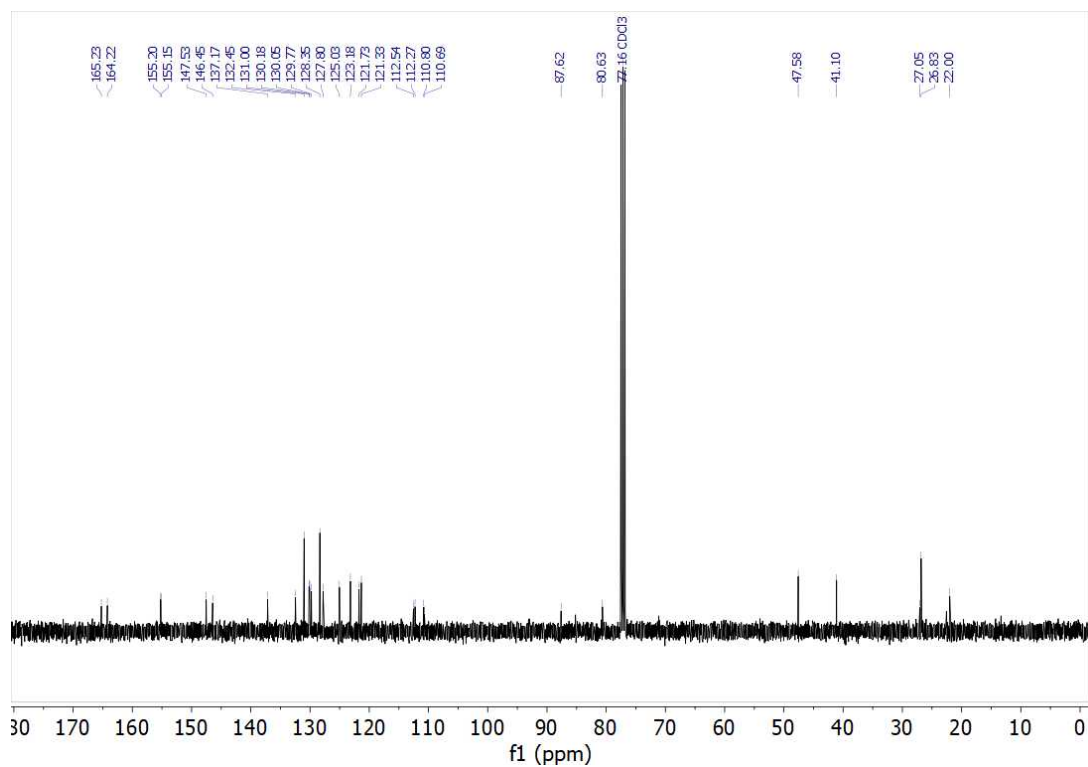


Figure S4. ¹³C (101 MHz, CDCl₃) NMR spectrum of **1a** recorded at 25°C.

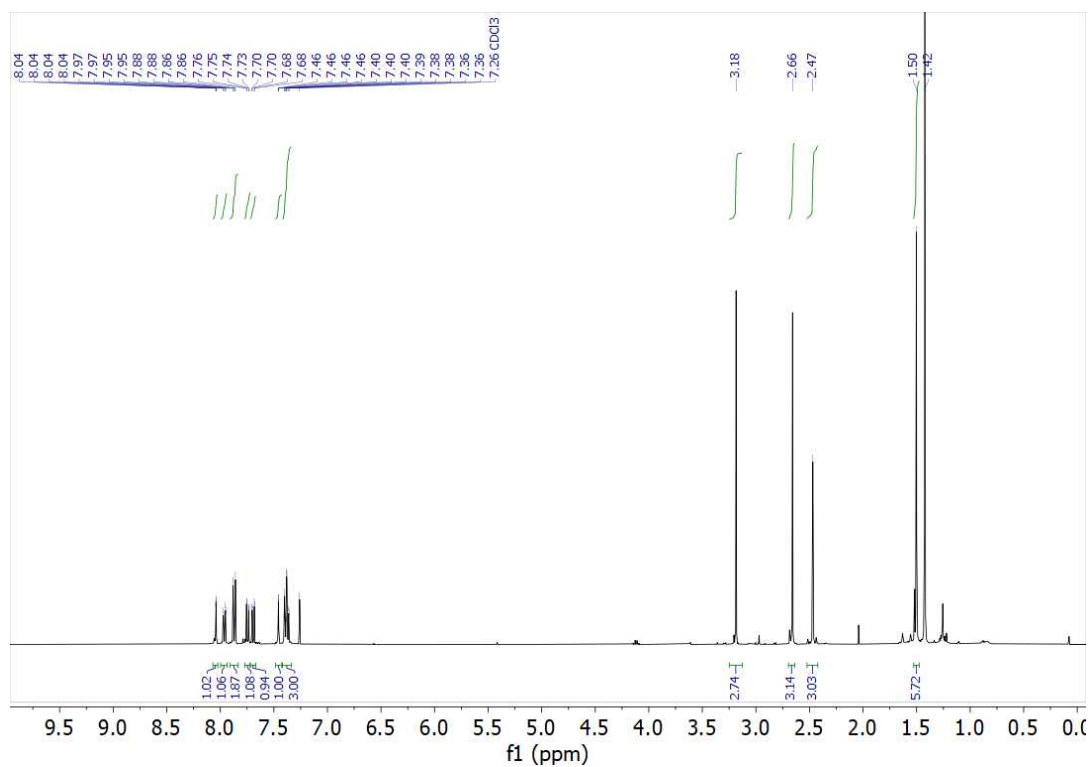


Figure S5. ¹H (400 MHz, CDCl₃) NMR spectrum of **6b** recorded at 25°C.

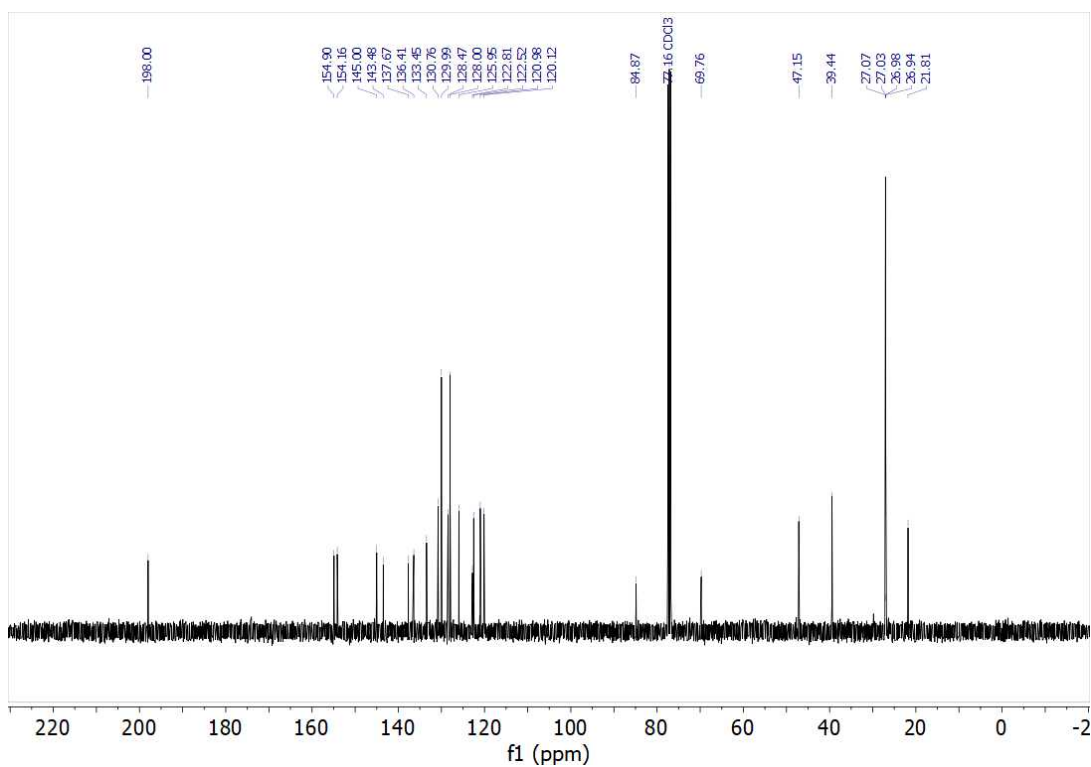


Figure S6. ¹³C (101 MHz, CDCl₃) NMR spectrum of **6b** recorded at 25°C.

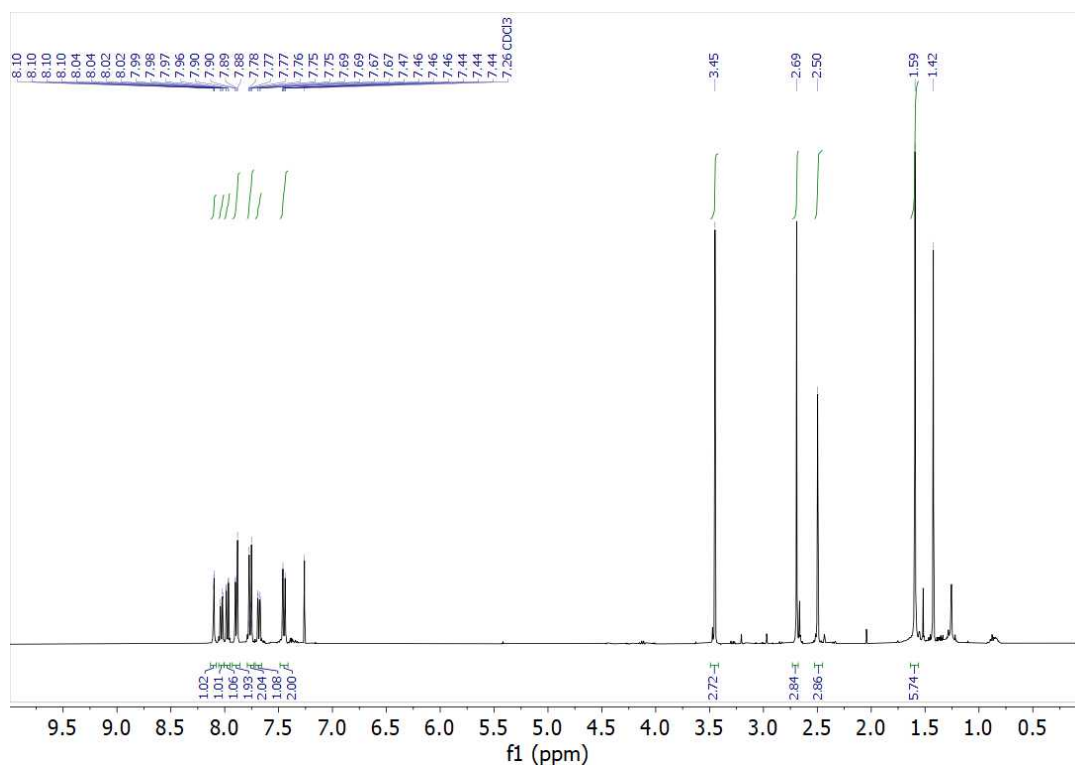


Figure S7. ¹H (400 MHz, CDCl₃) NMR spectrum of **1b** recorded at 25°C.

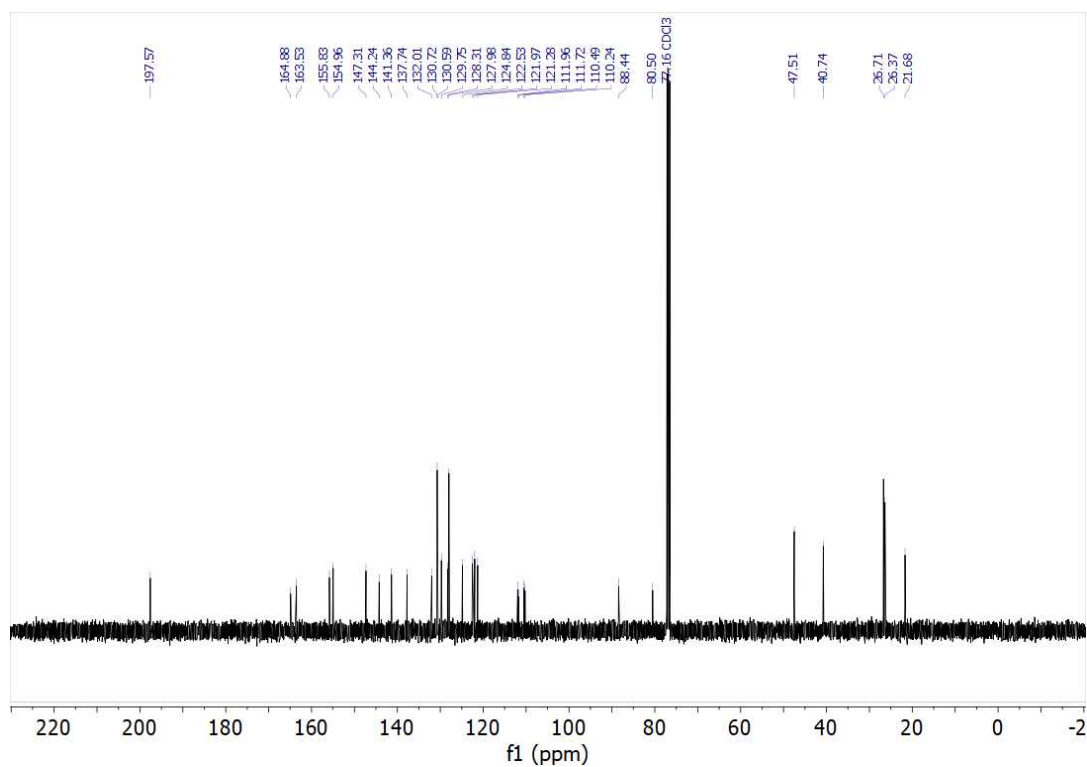


Figure S8. ¹³C (101 MHz, CDCl₃) NMR spectrum of **1b** recorded at 25°C.

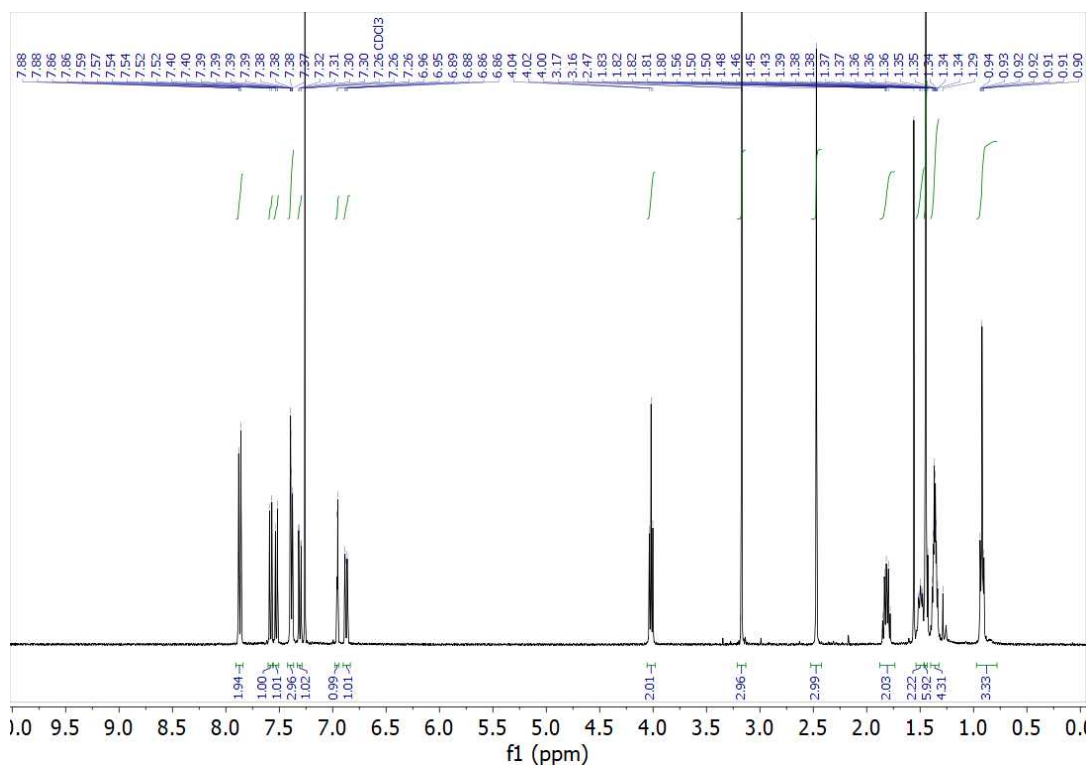


Figure S9. ^1H (400 MHz, CDCl_3) NMR spectrum of **6c** recorded at 25°C.

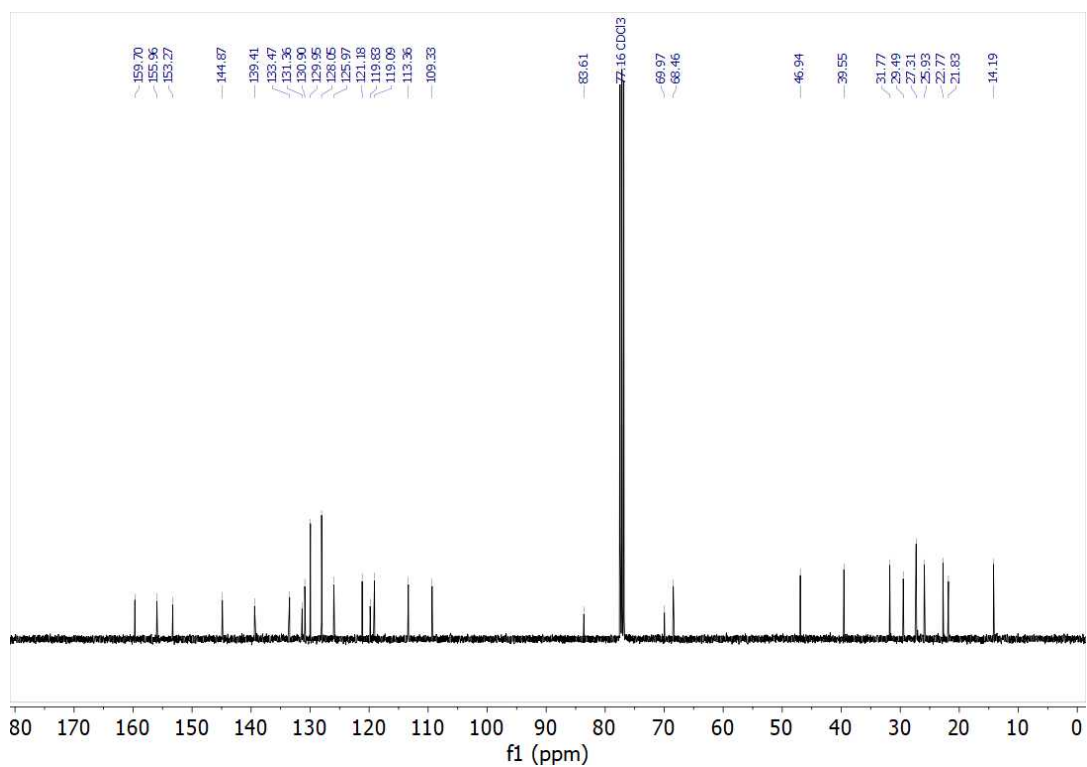


Figure S10. ^{13}C (101 MHz, CDCl_3) NMR spectrum of **6c** recorded at 25°C.

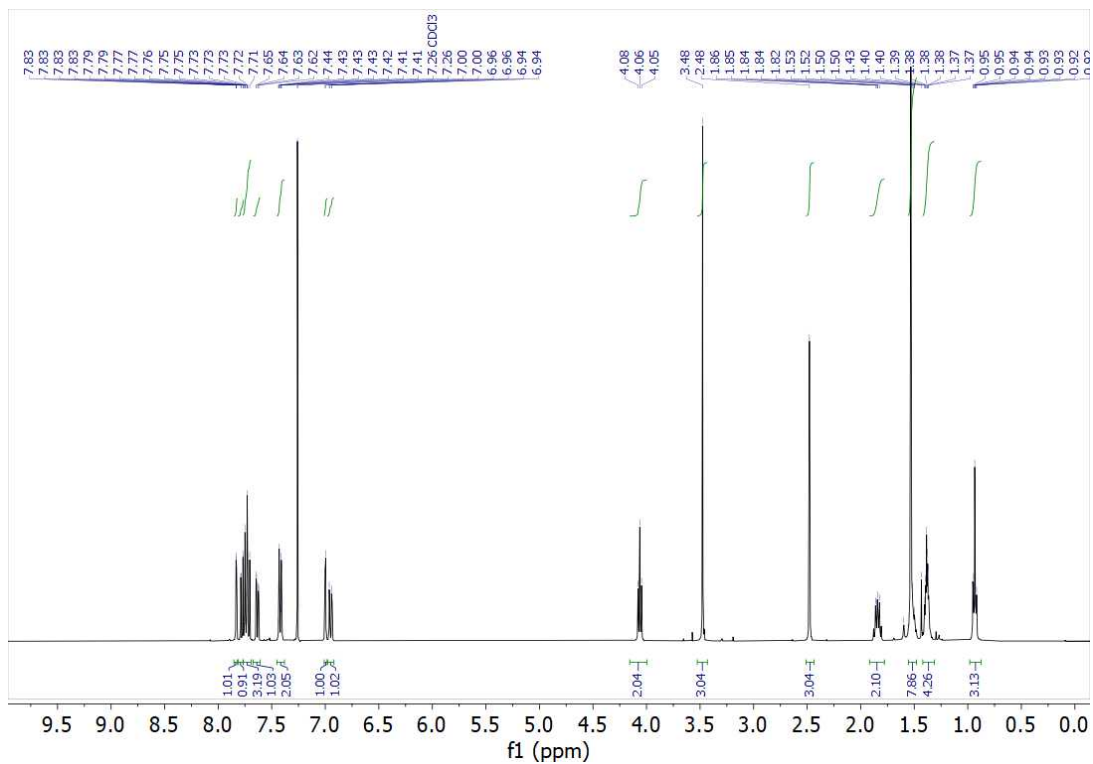


Figure S11. ¹H (400 MHz, CDCl₃) NMR spectrum of **1c** recorded at 25°C.

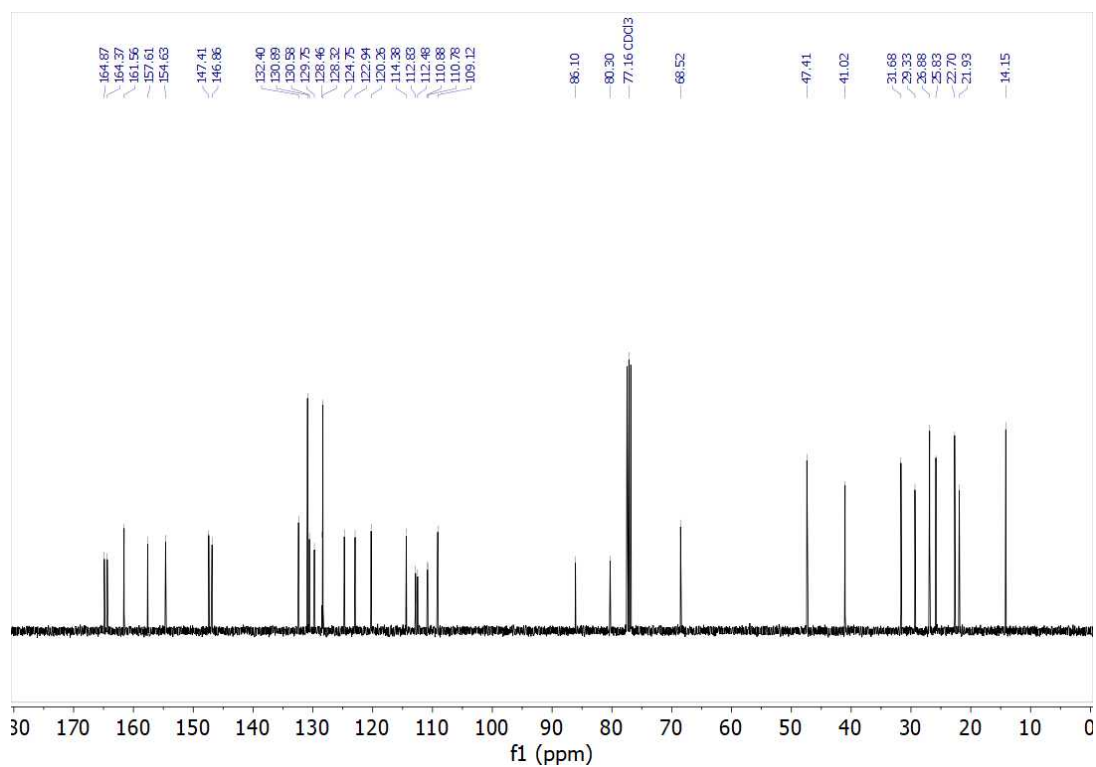


Figure S12. ¹³C (101 MHz, CDCl₃) NMR spectrum of **1c** recorded at 25°C.

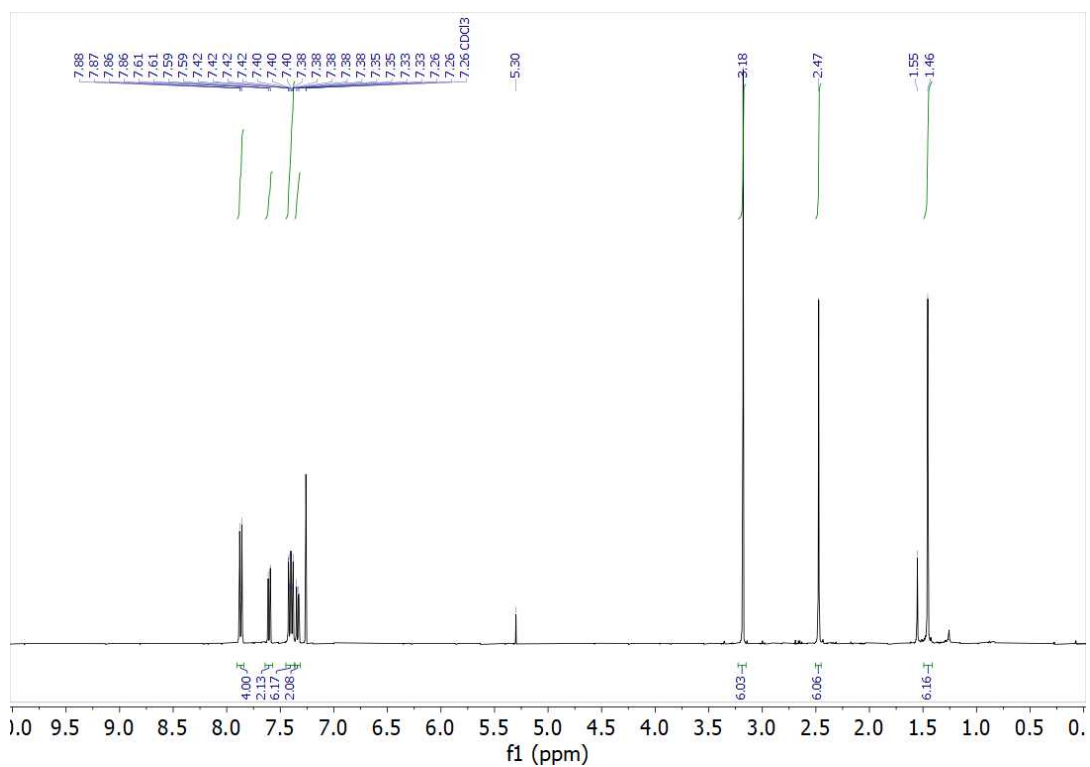


Figure S13. ¹H (400 MHz, CDCl₃) NMR spectrum of **14** recorded at 25°C.

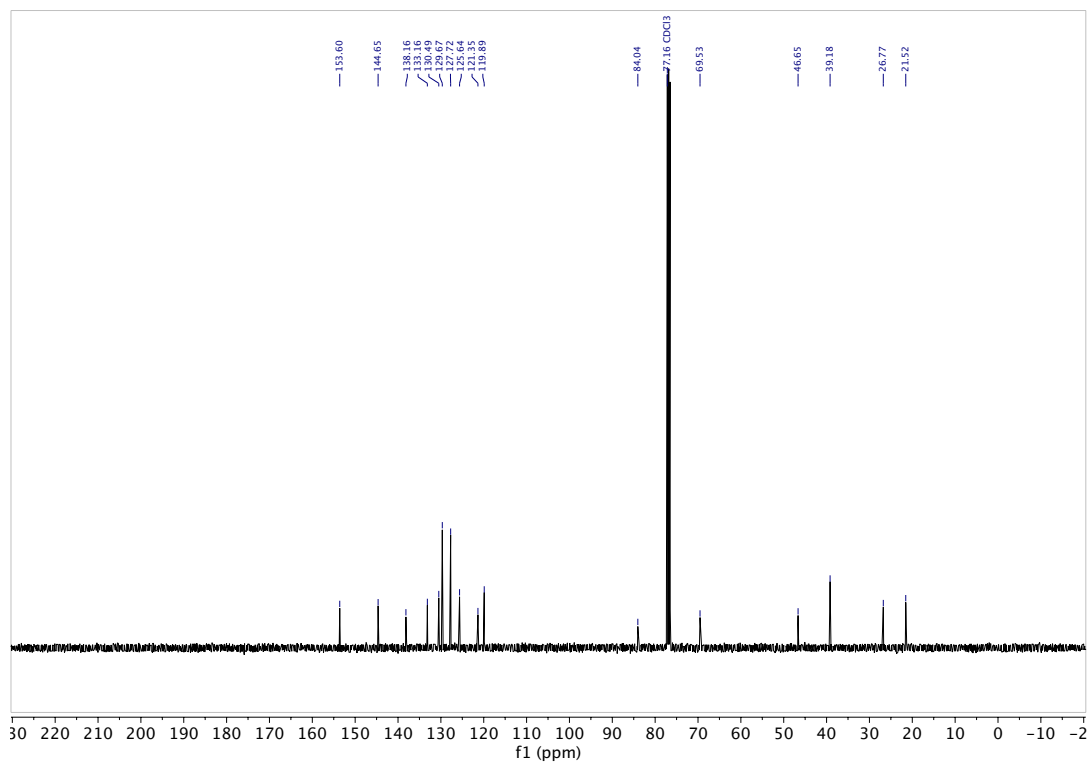


Figure S14. ¹³C (101 MHz, CDCl₃) NMR spectrum of **14** recorded at 25°C.

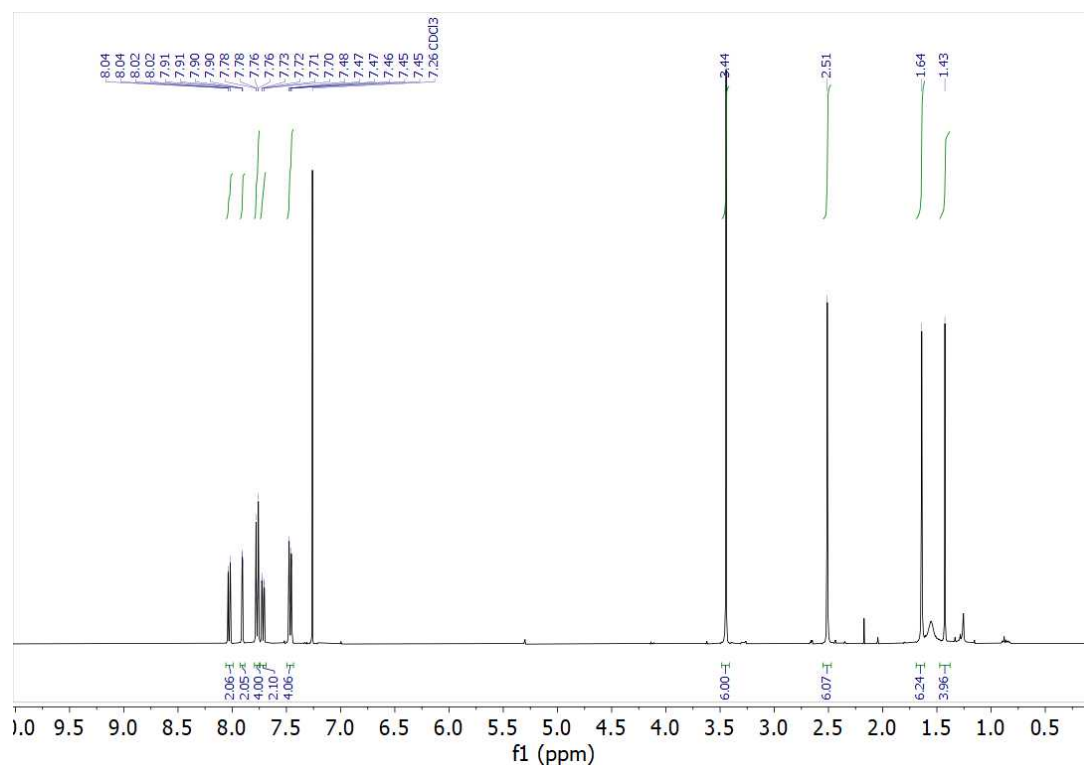


Figure S17. ¹H (400 MHz, CDCl₃) NMR spectrum of **1e** recorded at 25°C.

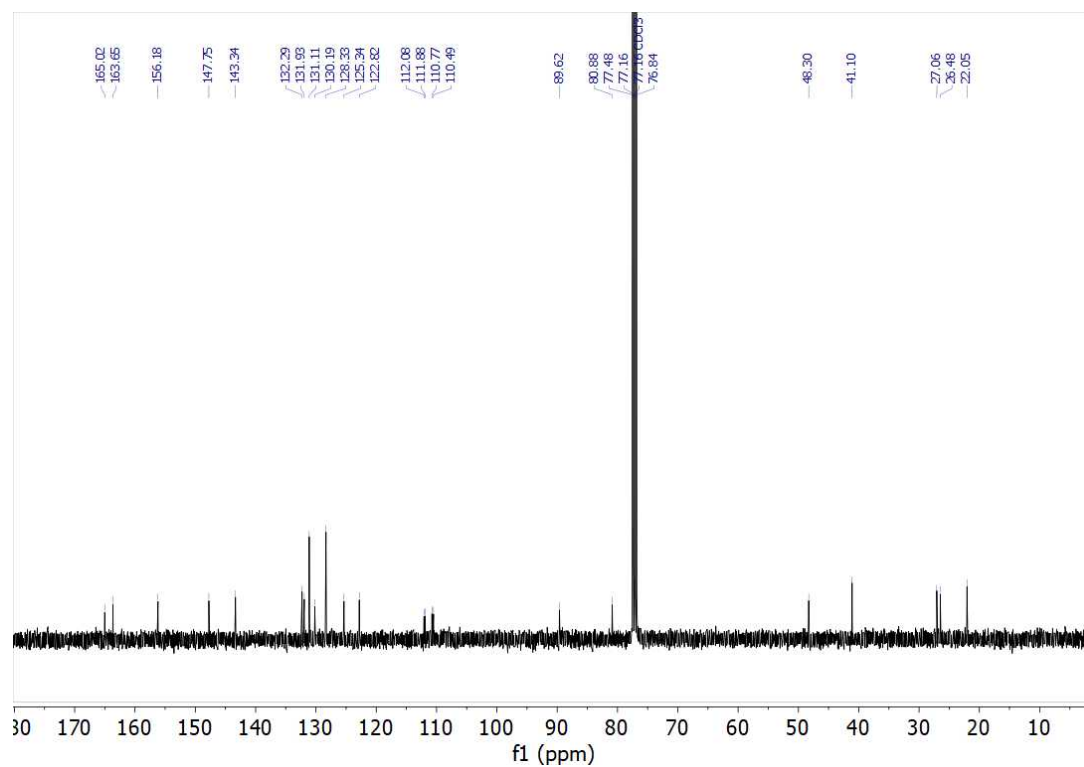


Figure S18. ¹³C (101 MHz, CDCl₃) NMR spectrum of **1e** recorded at 25°C.

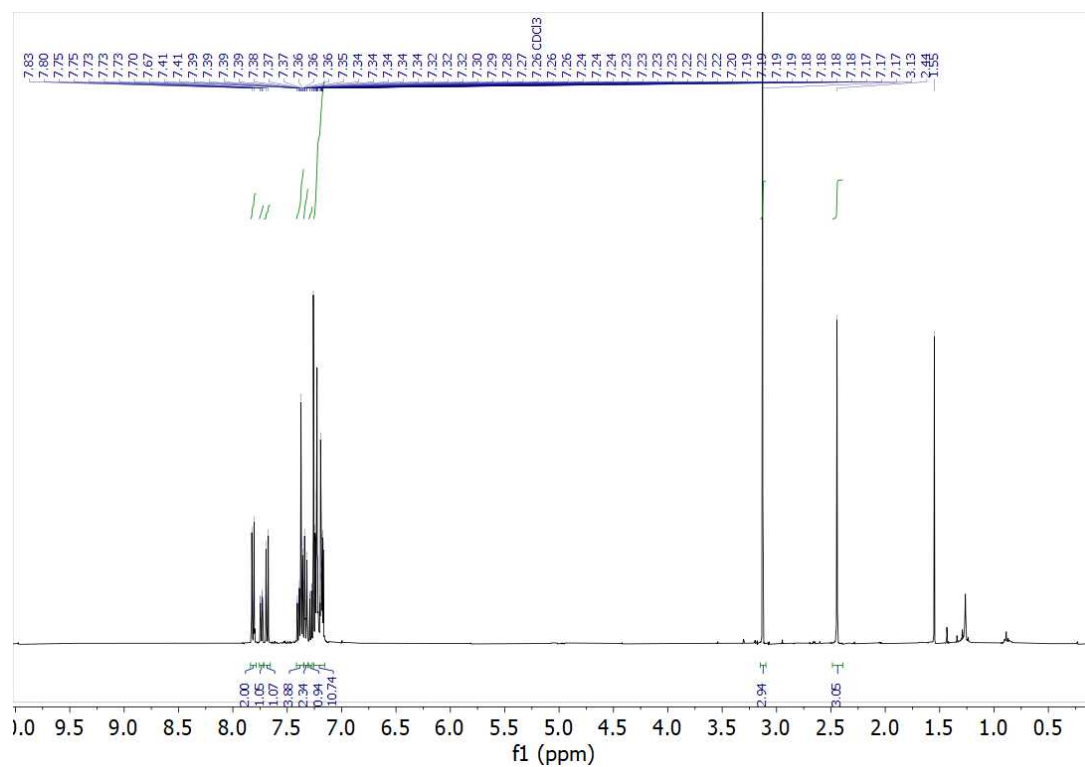


Figure S19. ^1H (400 MHz, CDCl_3) NMR spectrum of **6f** recorded at 25°C.

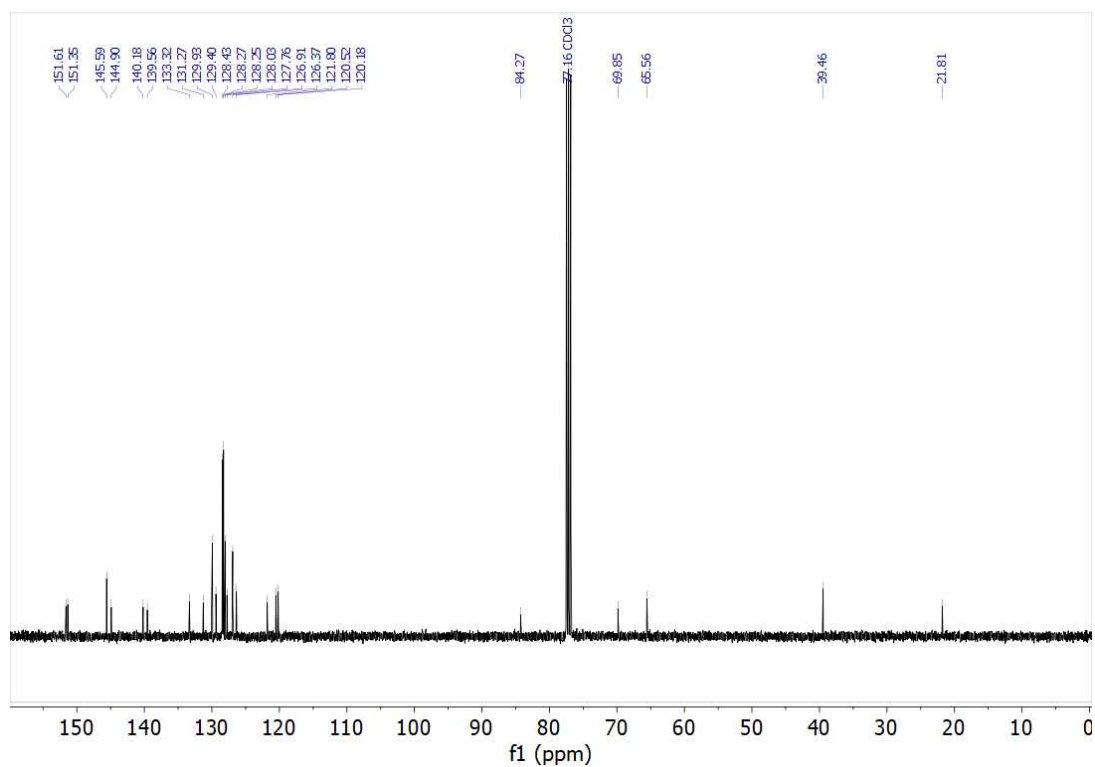


Figure S20. ^{13}C (101 MHz, CDCl_3) NMR spectrum of **6f** recorded at 25°C.

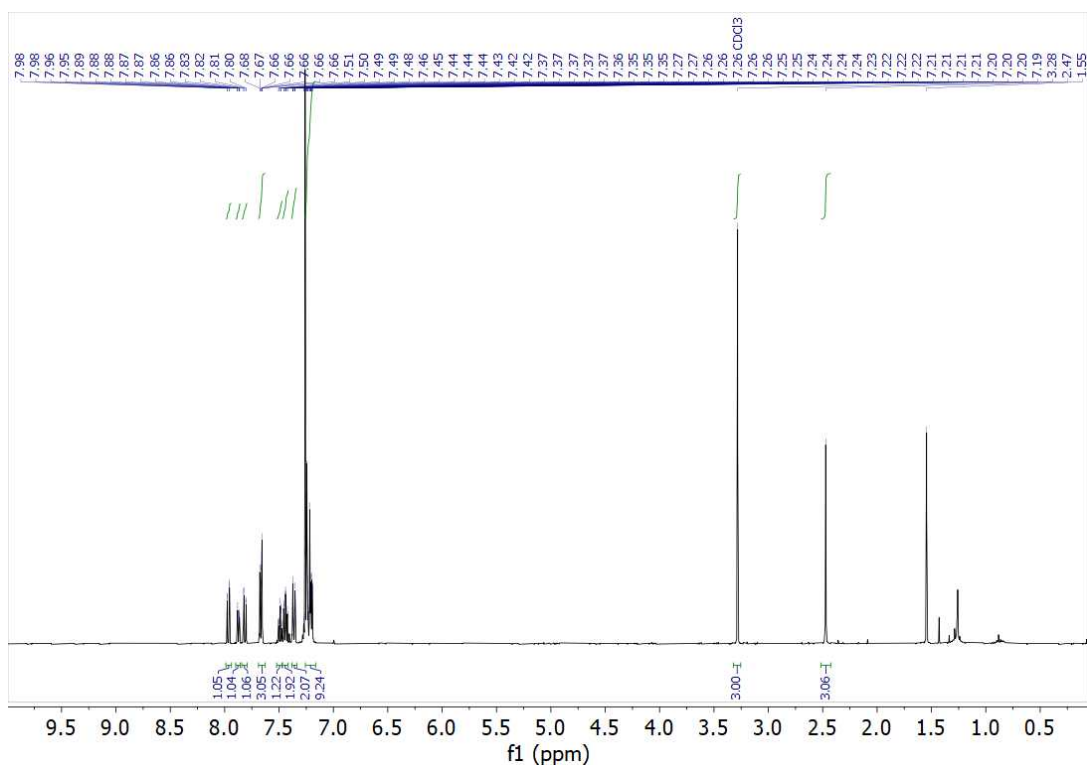


Figure S21. ^1H (400 MHz, CDCl_3) NMR spectrum of **1f** recorded at 25°C.

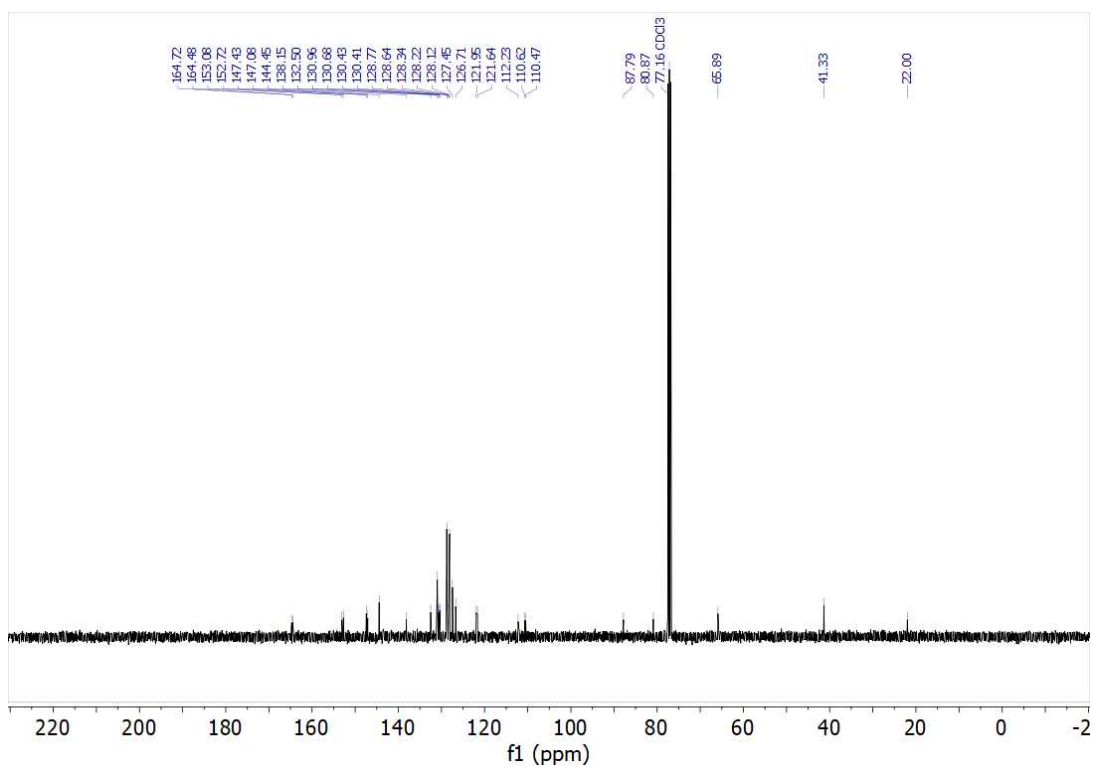


Figure S22. ^{13}C (101 MHz, CDCl_3) NMR spectrum of **1f** recorded at 25°C.

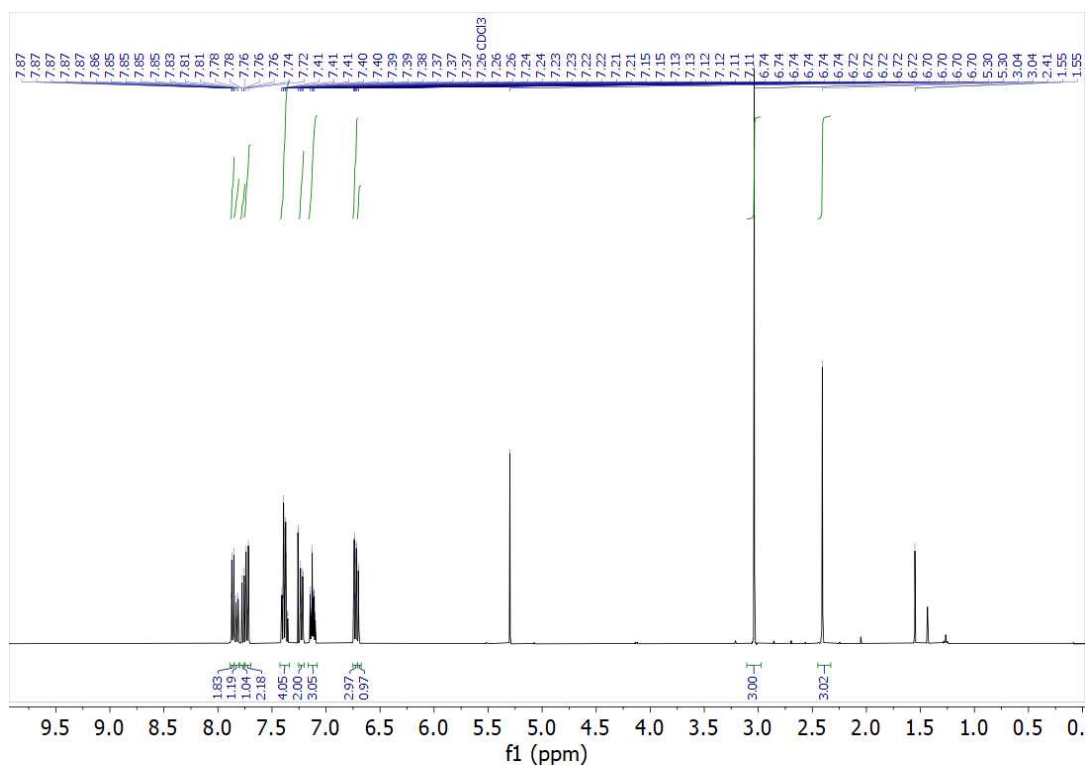


Figure S23. ^1H (400 MHz, CDCl_3) NMR spectrum of **6g** recorded at 25°C.

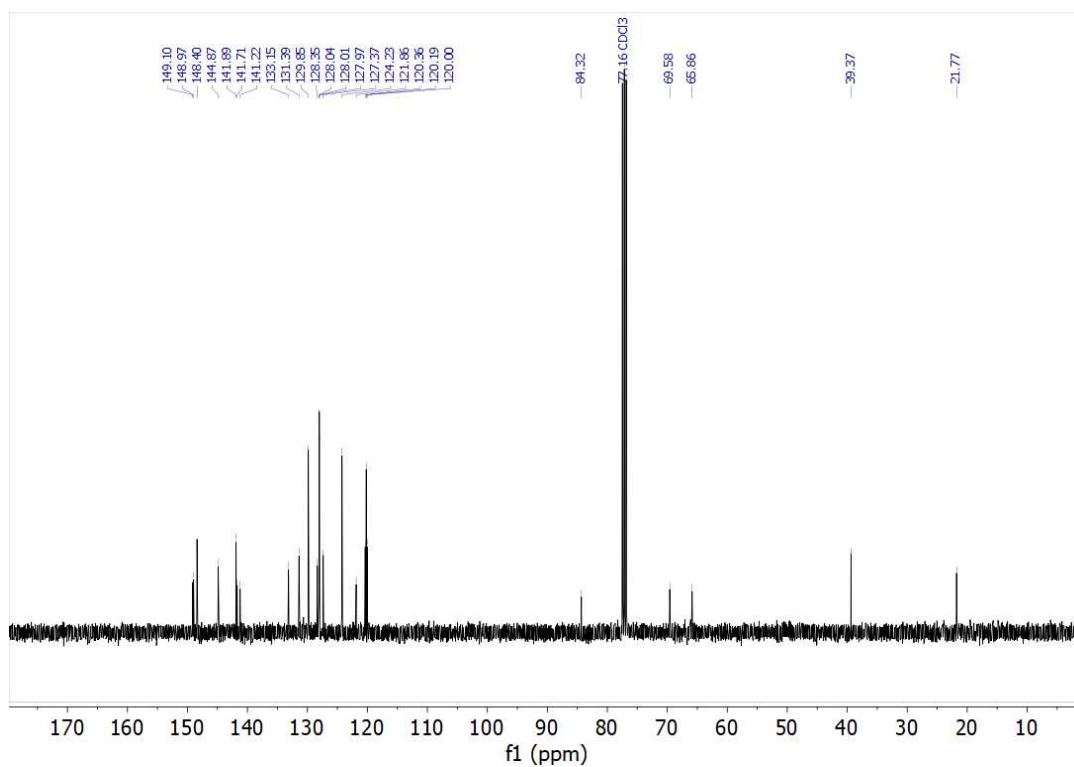


Figure S24. ^{13}C (101 MHz, CDCl_3) NMR spectrum of **6g** recorded at 25°C.

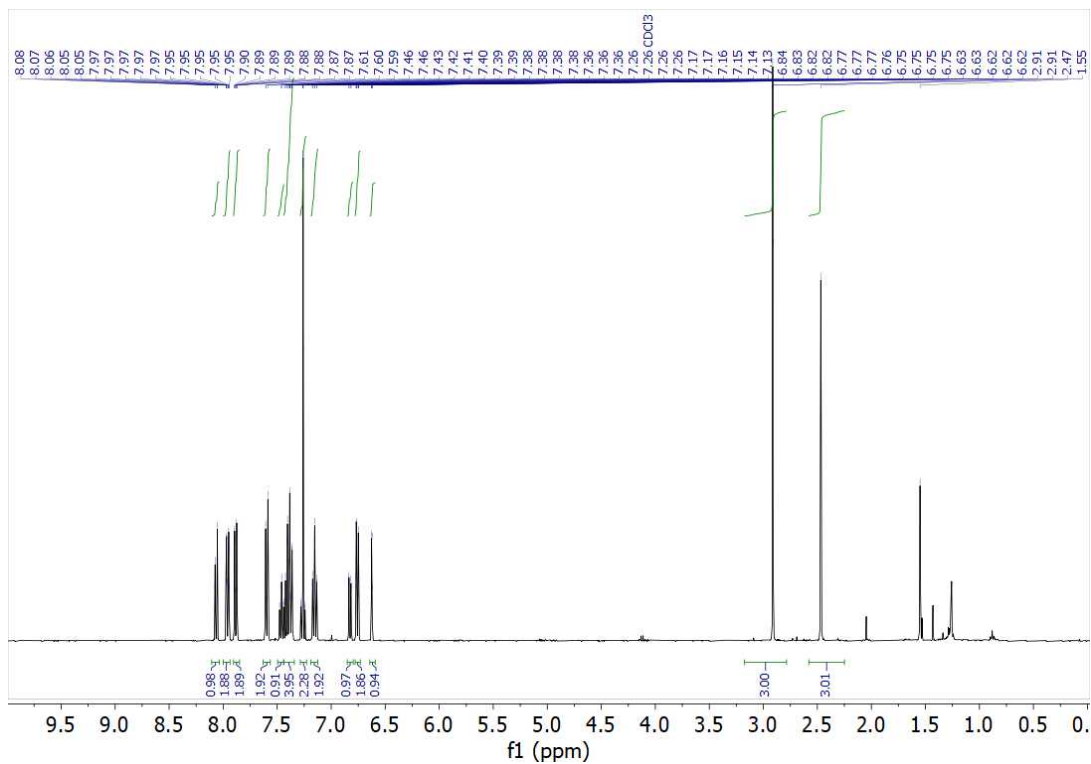


Figure S25. ^1H (400 MHz, CDCl_3) NMR spectrum of **1g** recorded at 25°C.

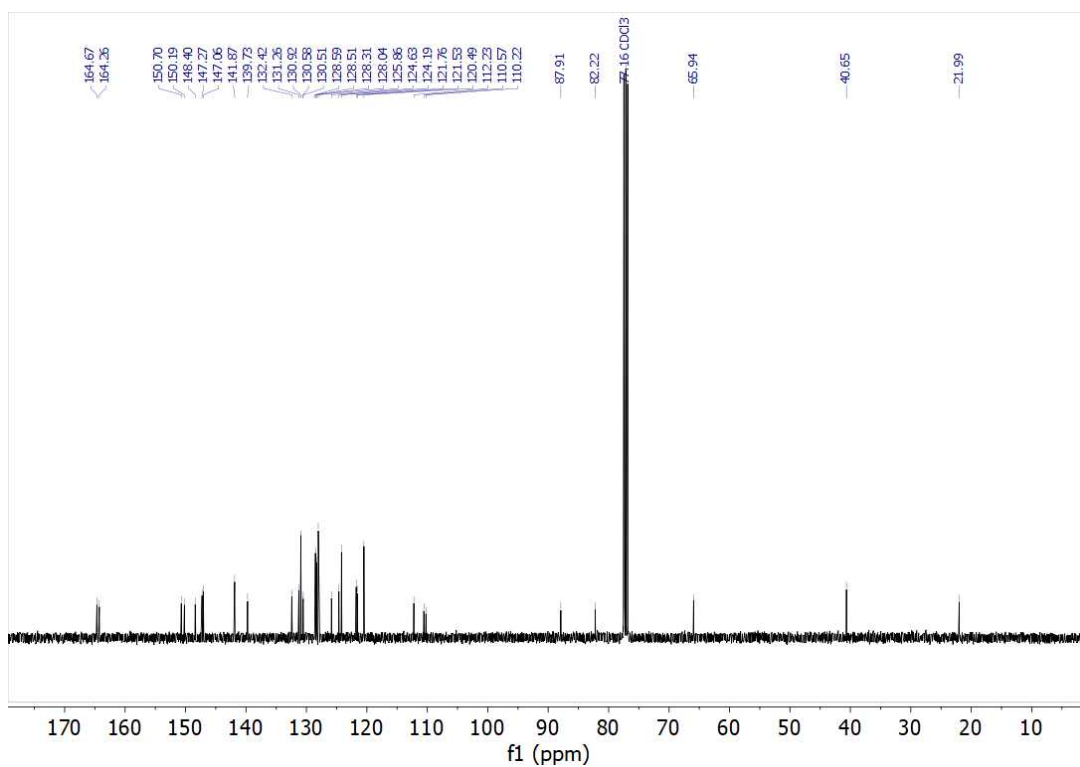


Figure S26. ^{13}C (101 MHz, CDCl_3) NMR spectrum of **1g** recorded at 25°C.

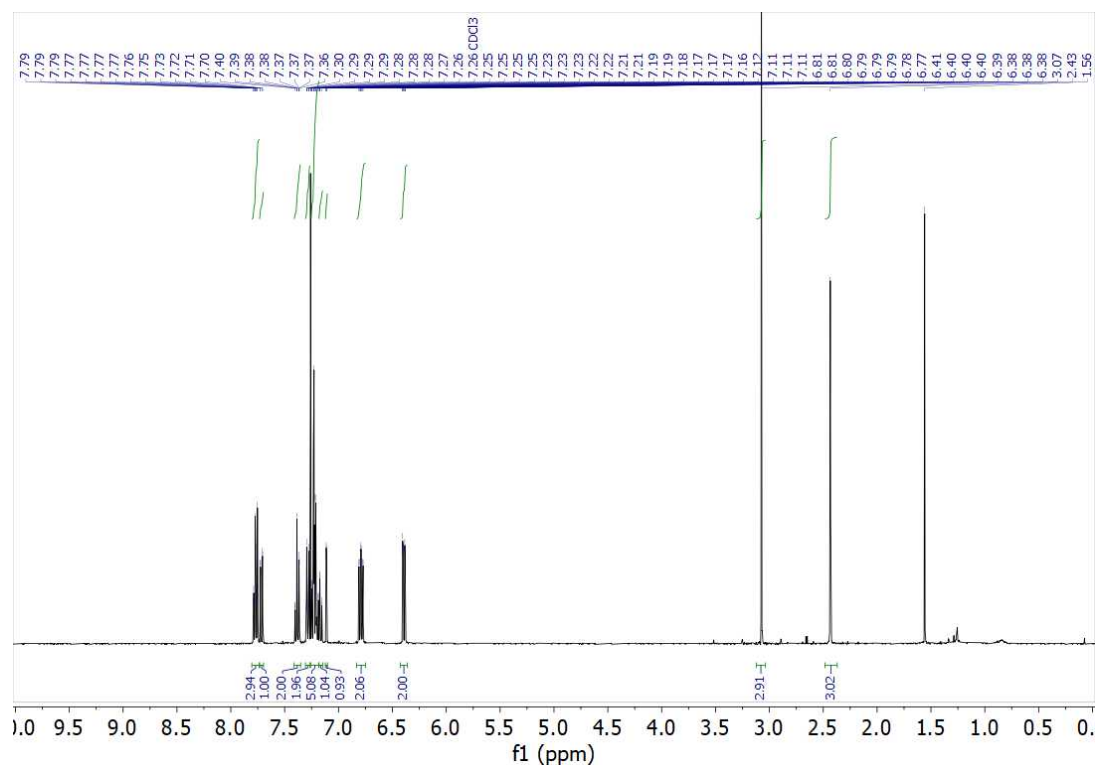


Figure S27. ^1H (400 MHz, CDCl_3) NMR spectrum of **6h** recorded at 25°C.

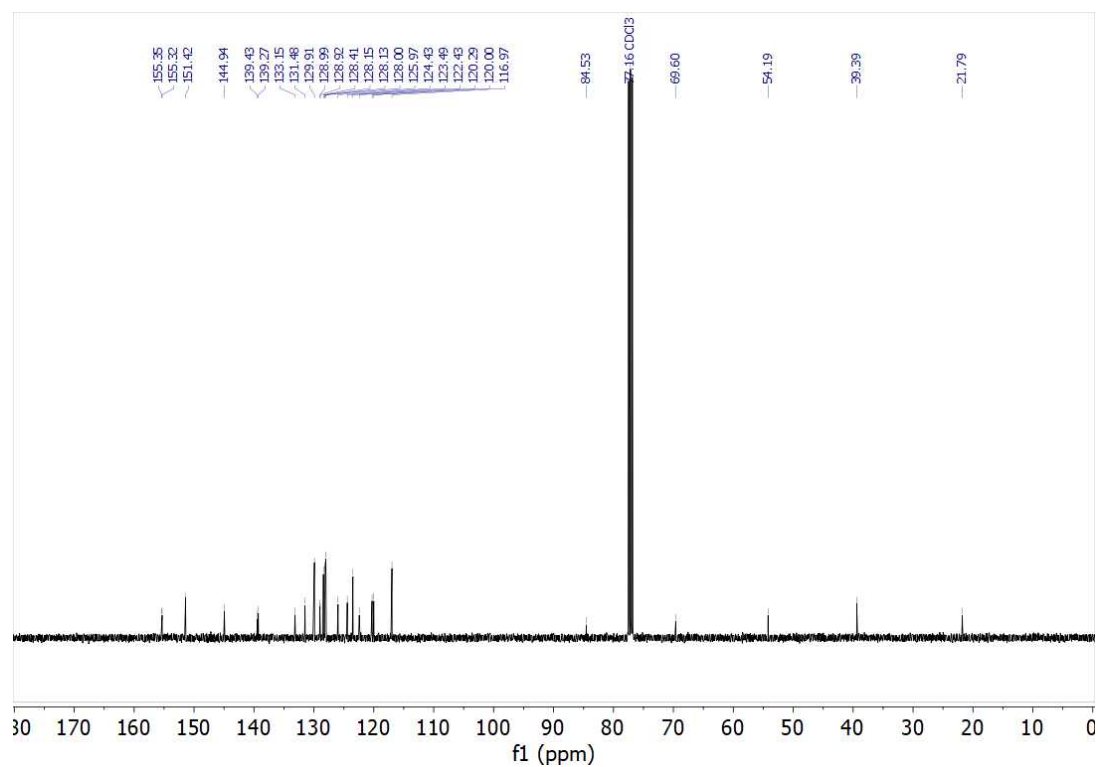


Figure S28. ^{13}C (101 MHz, CDCl_3) NMR spectrum of **6h** recorded at 25°C.

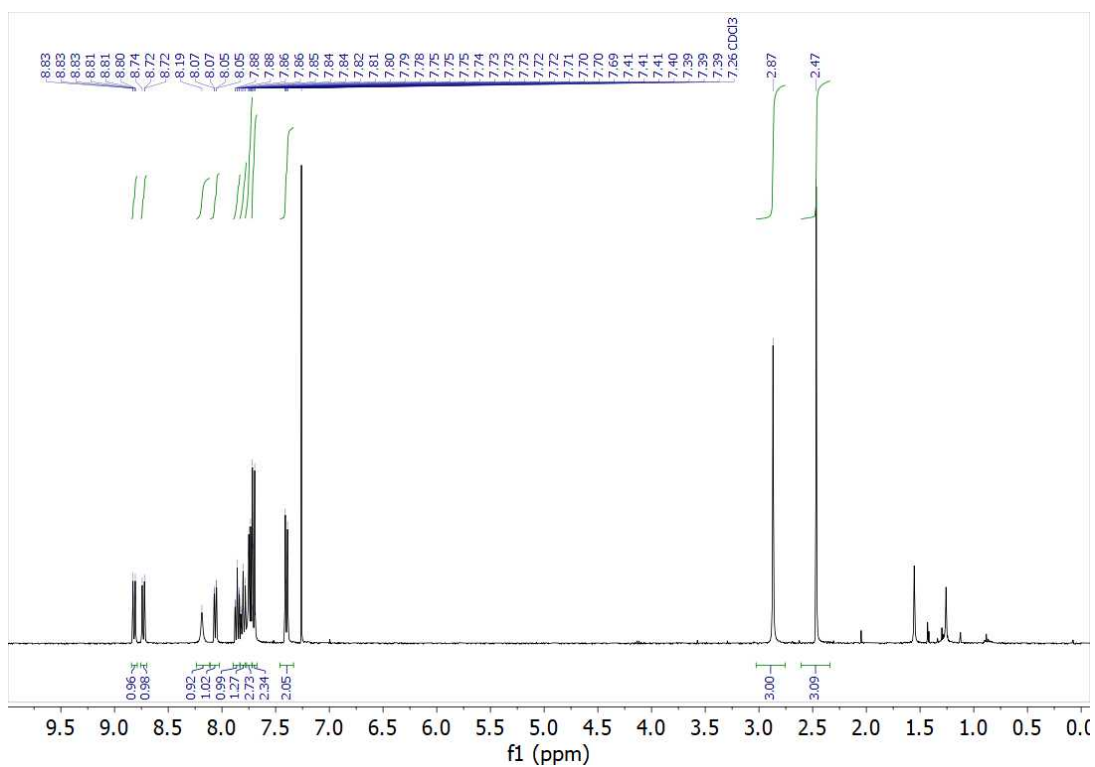


Figure S31. ^1H (400 MHz, CDCl_3) NMR spectrum of **1i** recorded at 25°C.

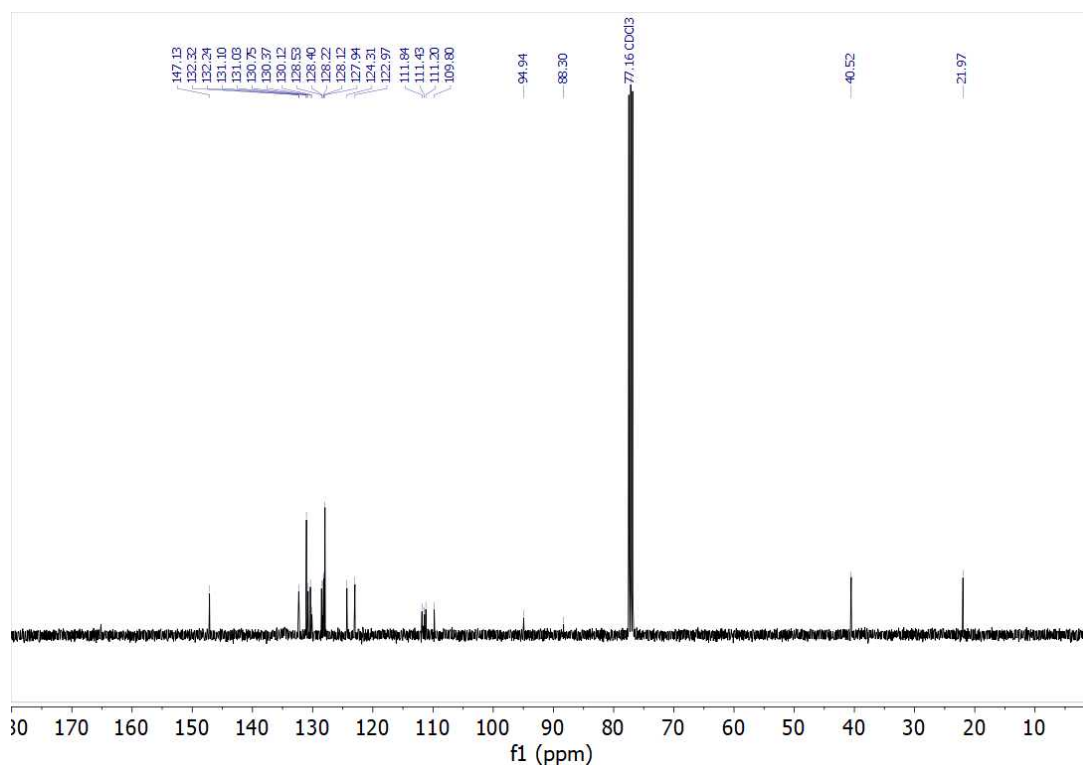


Figure S32. ^{13}C (101 MHz, CDCl_3) NMR spectrum of **1i** recorded at 25°C.

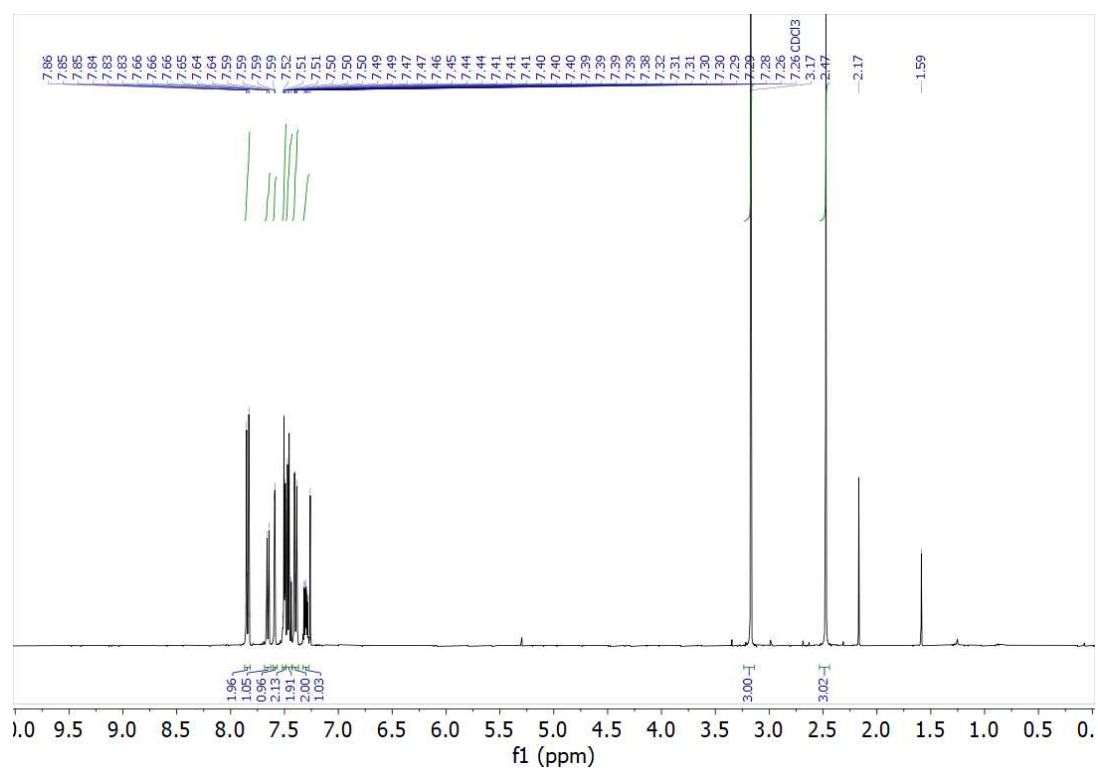


Figure S33. ^1H (400 MHz, CDCl_3) NMR spectrum of **6j** recorded at 25°C.

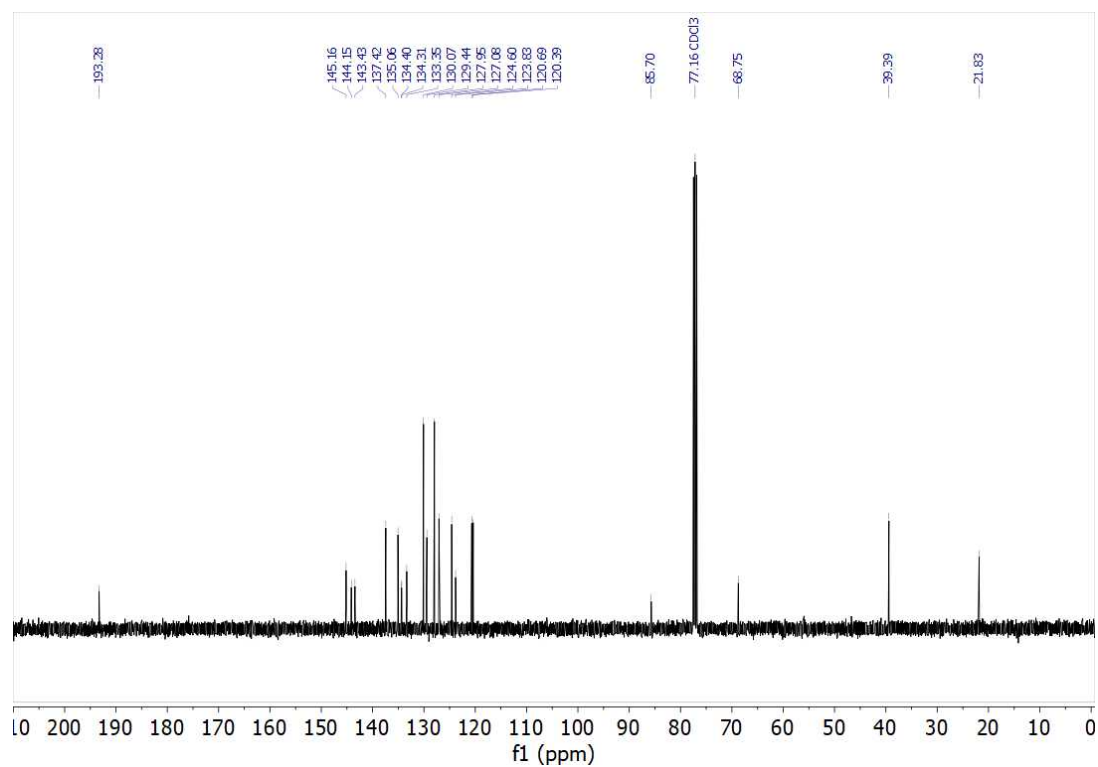


Figure S34. ^{13}C (101 MHz, CDCl_3) NMR spectrum of **6j** recorded at 25°C.

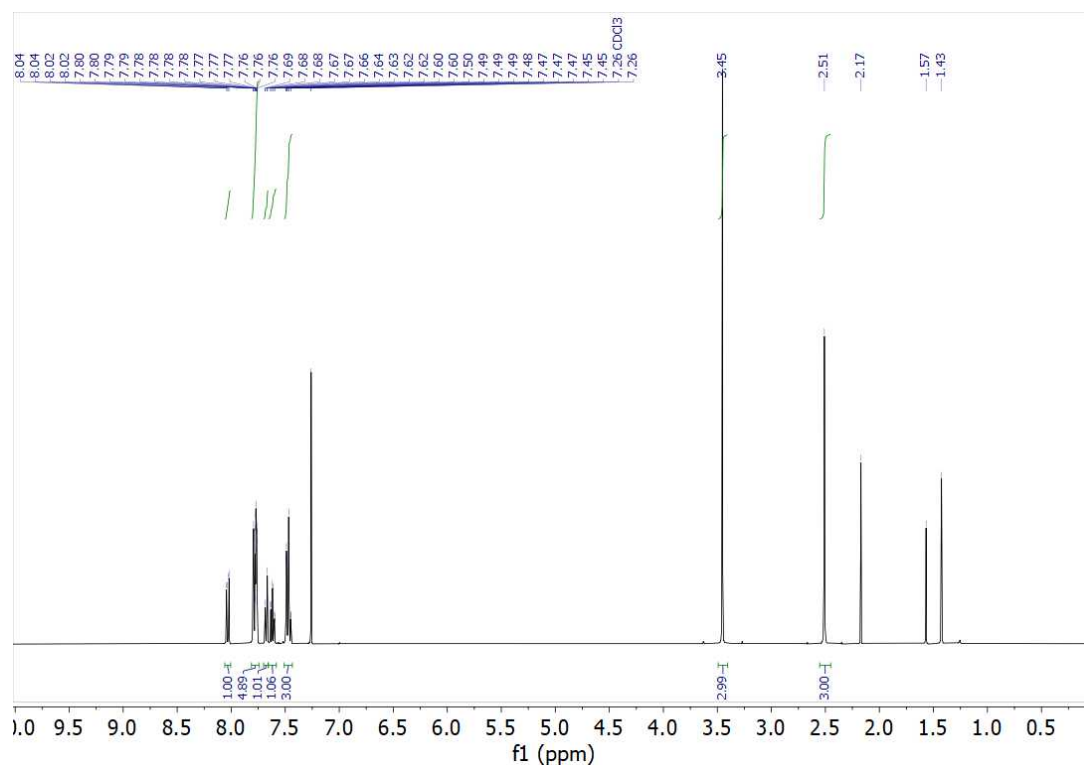


Figure S35. ¹H (400 MHz, CDCl₃) NMR spectrum of **1j** recorded at 25°C.

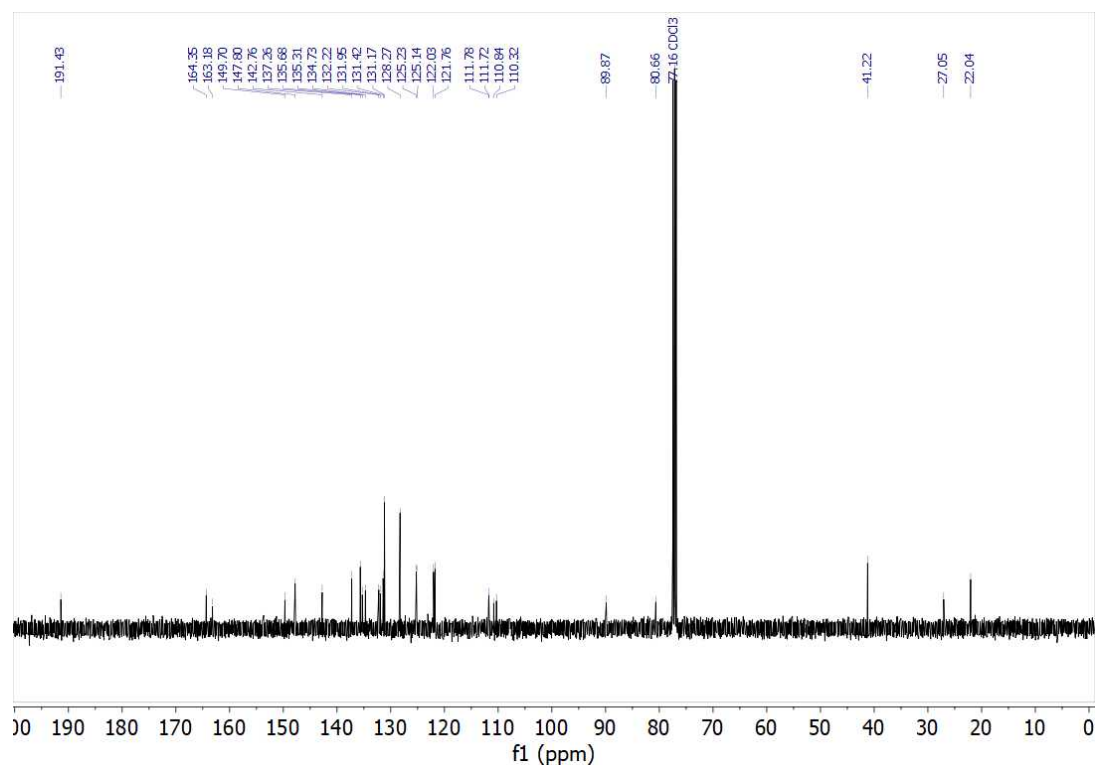


Figure S36. ¹³C (101 MHz, CDCl₃) NMR spectrum of **1j** recorded at 25°C.

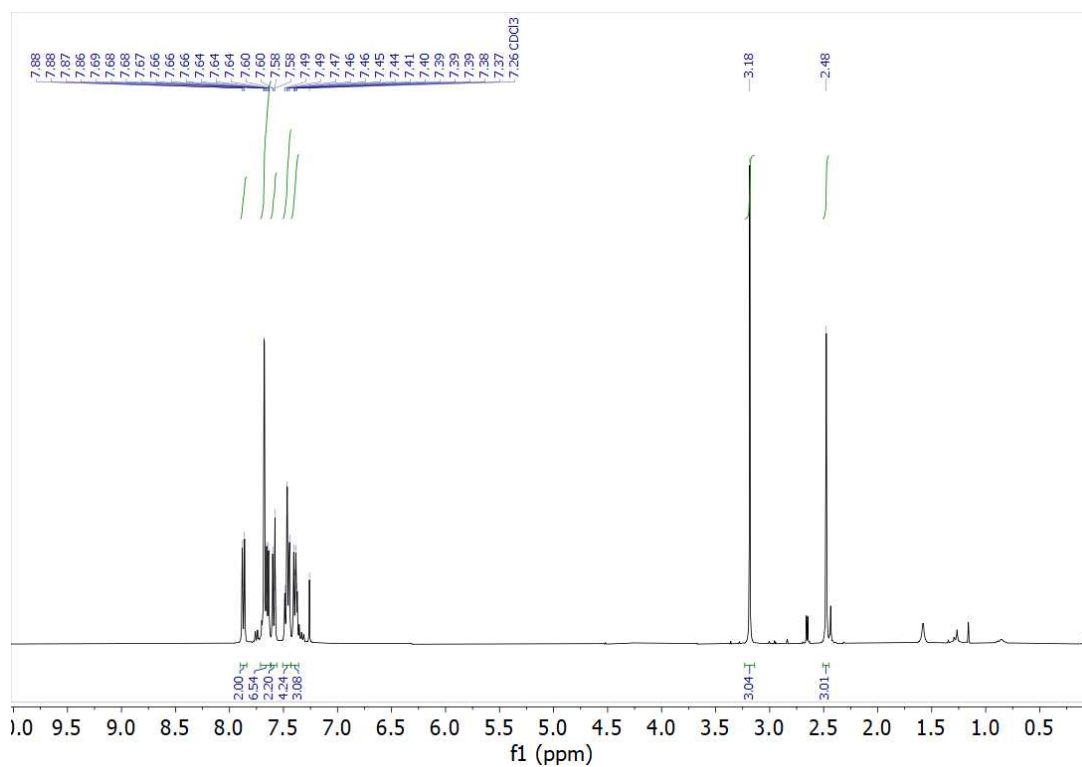


Figure S37. ^1H (400 MHz, CDCl_3) NMR spectrum of **6k** recorded at 25°C.

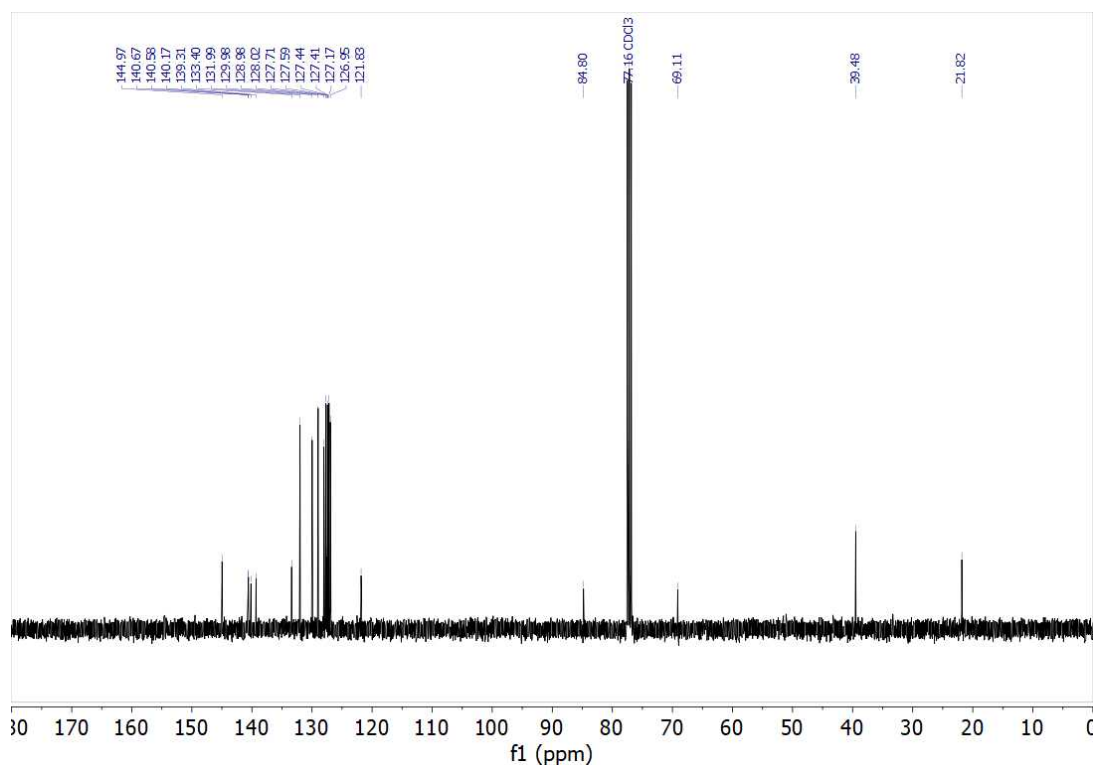


Figure S38. ^{13}C (101 MHz, CDCl_3) NMR spectrum of **6k** recorded at 25°C.

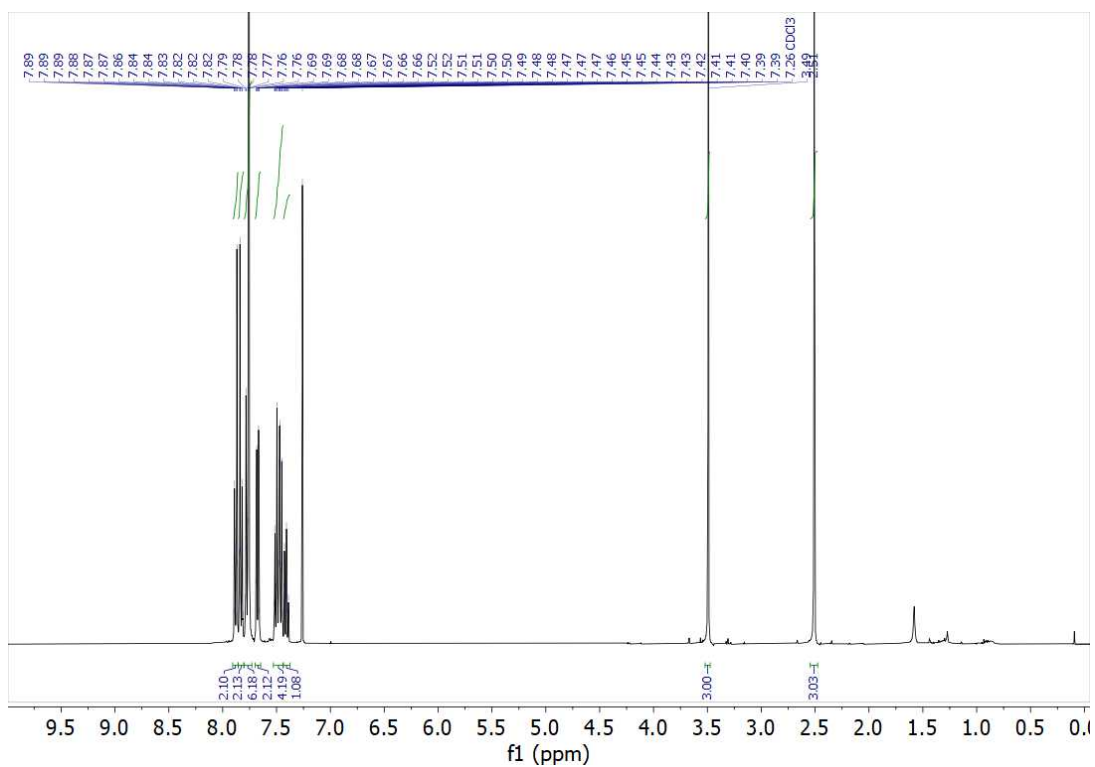


Figure S39. ^1H (400 MHz, CDCl_3) NMR spectrum of **1k** recorded at 25°C.

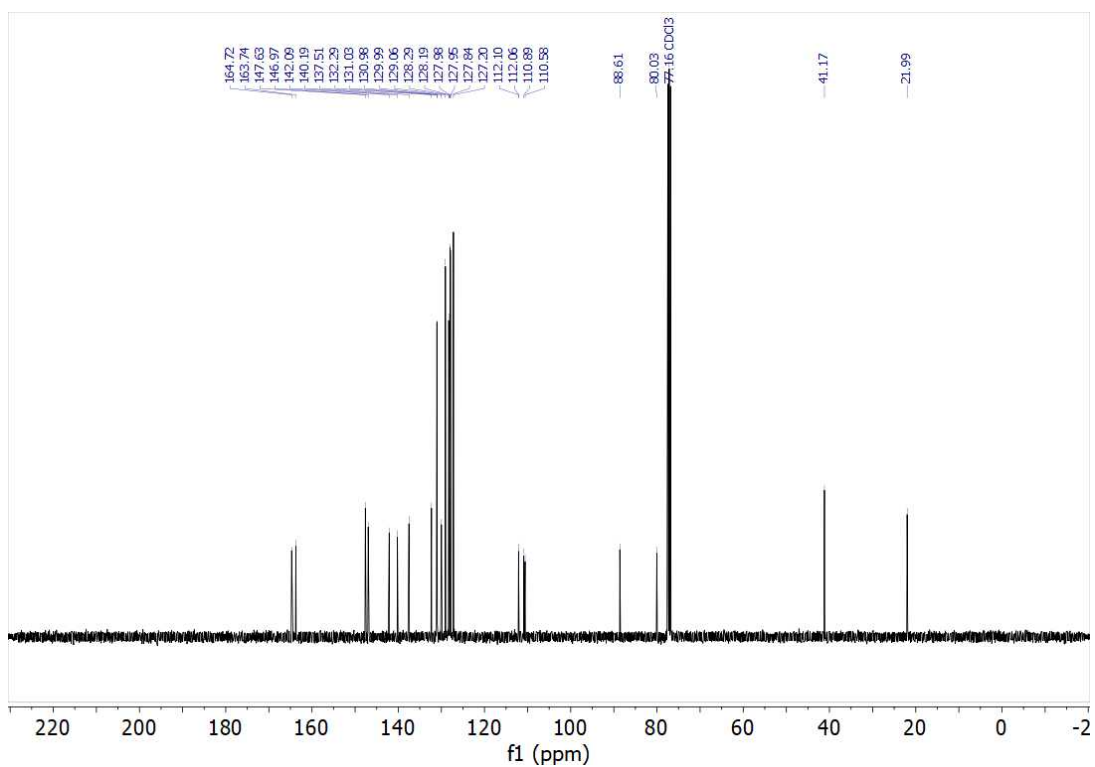


Figure S40. ^{13}C (101 MHz, CDCl_3) NMR spectrum of **1k** recorded at 25°C.

4. Electrochemical data

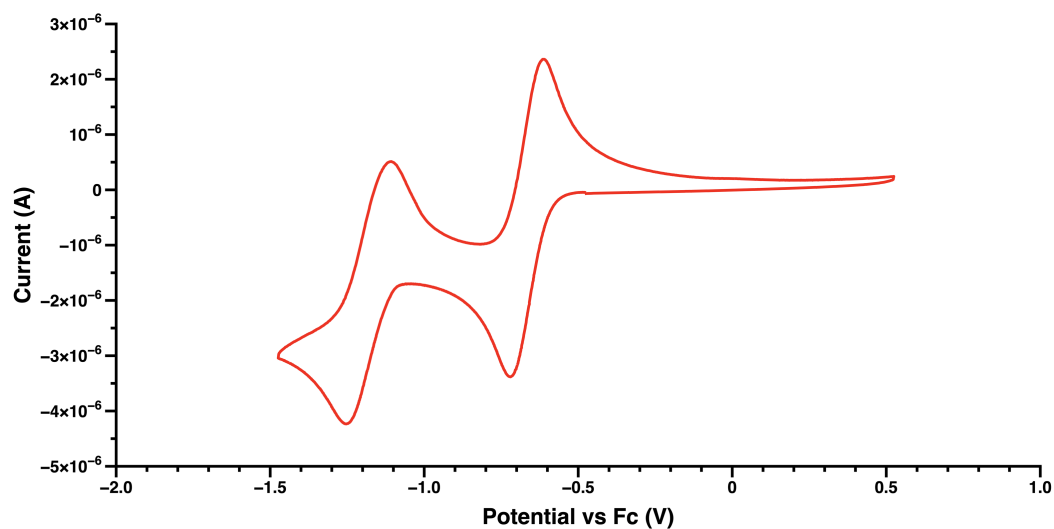


Figure S41. Cyclic voltammogram of **1a** in $\text{CH}_2\text{Cl}_2/[n\text{-Bu}_4\text{N}][\text{PF}_6]$ (0.1 M) at 25 °C at 0.1 V/s.

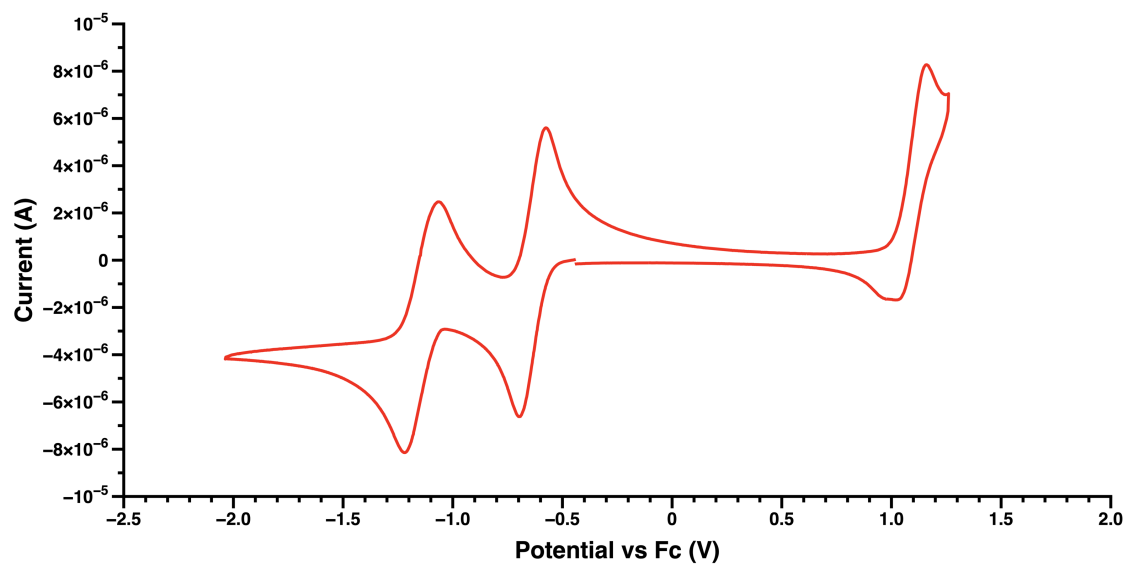


Figure S42. Cyclic voltammogram of **1c** in $\text{CH}_2\text{Cl}_2/[n\text{-Bu}_4\text{N}][\text{PF}_6]$ (0.1 M) at 25 °C at 0.1 V/s.

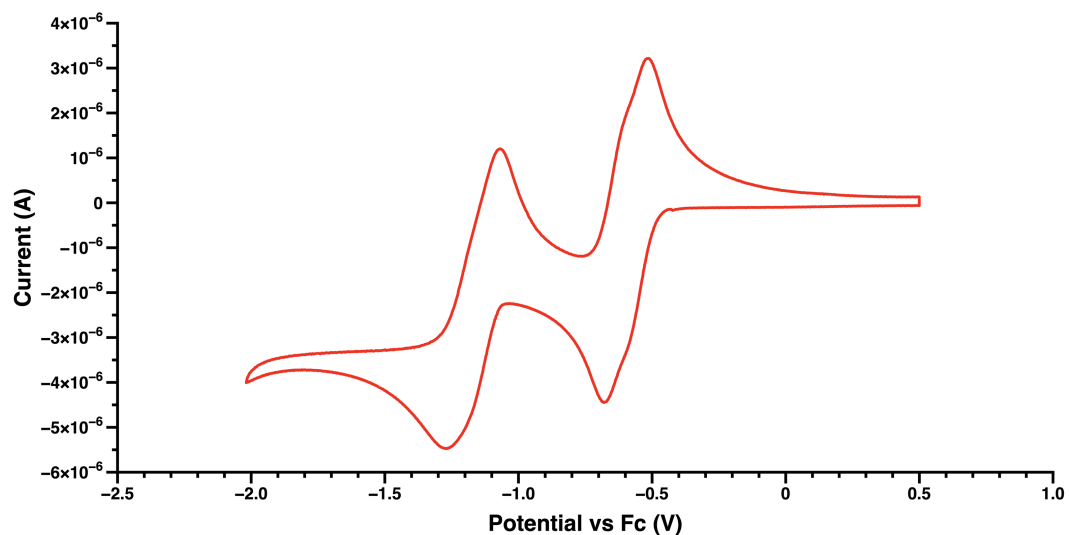


Figure S43. Cyclic voltammogram of **1e** in CH₂Cl₂/[*n*-Bu₄N][PF₆] (0.1 M) at 25 °C at 0.1 V/s.

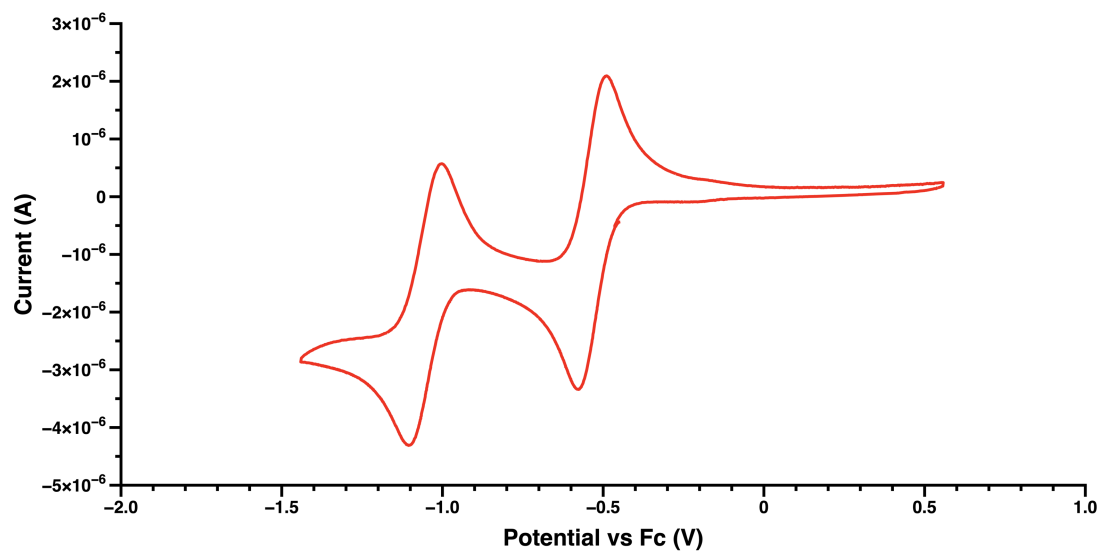


Figure S44. Cyclic voltammogram of **1j** in CH₂Cl₂/[*n*-Bu₄N][PF₆] (0.1 M) at 25 °C at 0.1 V/s.

5. Photophysical data

5.1. UV-vis absorption spectroscopy

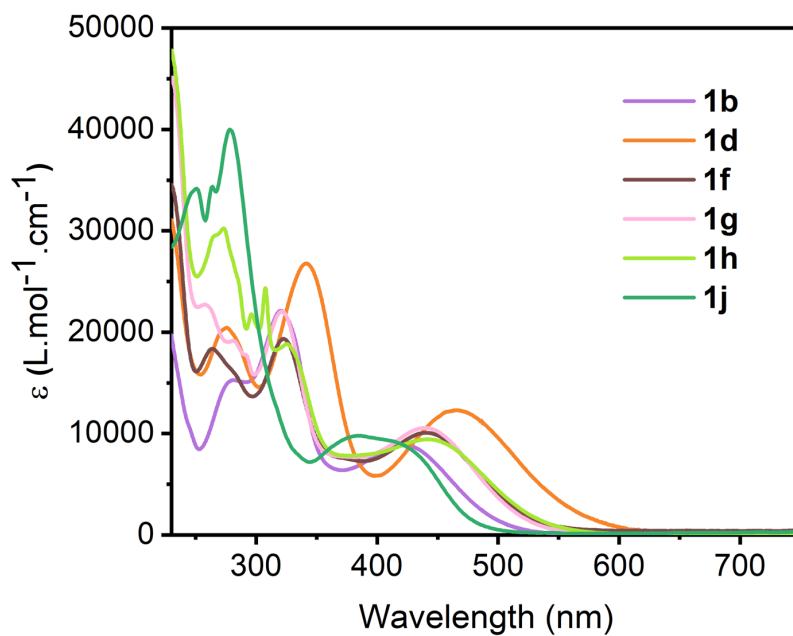


Figure S45 UV-visible absorption spectra of compounds **1b**, **1d**, **1f**, **1g**, **1h** and **1j** in dichloromethane.

5.2. Fluorescence spectroscopy

Considering the spectral characteristics and intensity of fluorescence of the family of compounds studied, to preserve consistency between the datasets all quantum yields were determined by the relative method using a select TCBD derivative, compound **1l**, as a secondary reference. The quantum yield of **1l** itself was found to be 6.9% (using the emission located below 800 nm) by comparison with 9,10-bis(phenylethynyl)anthracene (**BPEA**), as shown below.

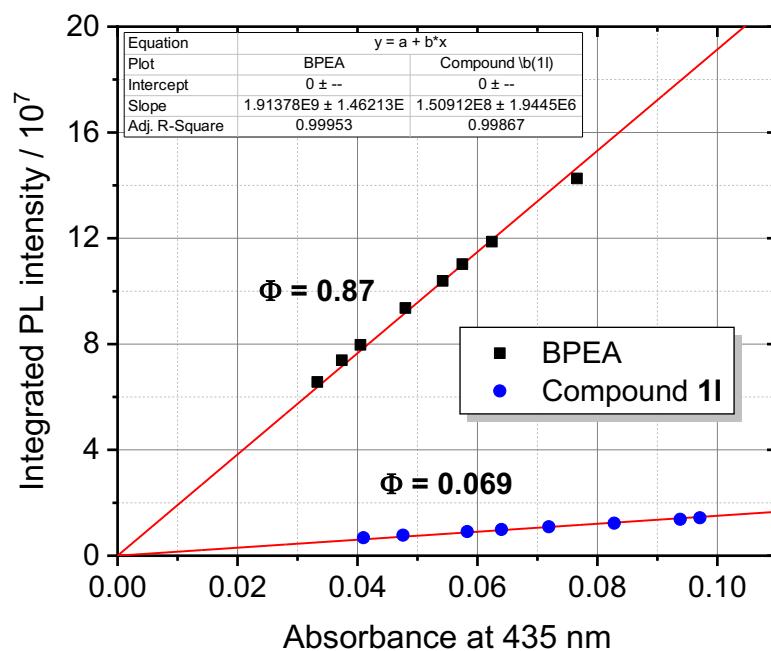


Figure S46. Linear plots used in the measurement of the quantum yield of compound **1l** in cyclohexane ($\Phi = 0.069$) with BPEA in cyclohexane as a reference ($\Phi = 0.87$)¹³

Table S1. Photoluminescence data of compounds **1a** to **1l** in dichloromethane.

	Dichloromethane		
	λ_{abs} (nm)	λ_{em} (nm)	ϕ (%)
1a	437	732	< 0.1 ^a
1b	420	697	< 0.1 ^b
1j	420	660	1.6 ^a

^a Quinine bisulfate in 0.5 M H₂SO₄ used as standard ($\phi = 54.6\%$)

^b **1l** in toluene used as standard

¹³ M. Levitus and M. A. Garcia-Garibay *J. Phys. Chem. A* **2000**, *104*, 8632–8637.

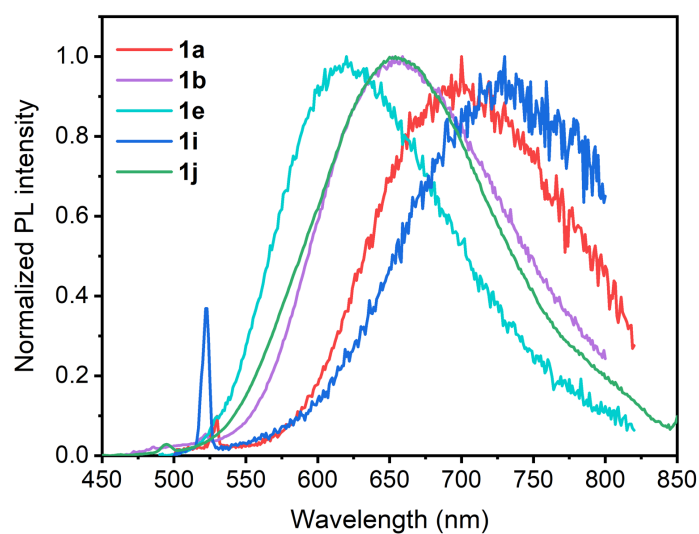


Figure S47. Photoluminescence spectra of compounds **1a**, **1b**, **1d**, **1i** and **1j** in toluene (λ_{exc} = 455, 455, 455, 455, and 430 nm, respectively).

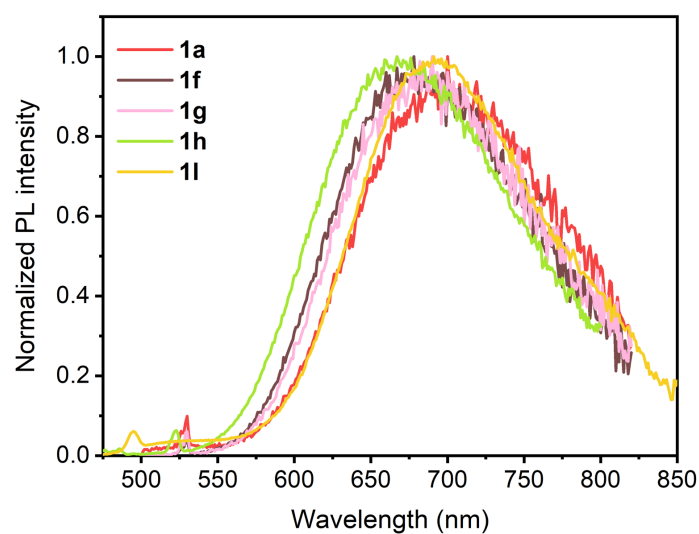


Figure S48. Photoluminescence spectra of compounds **1a**, **1f**, **1g**, **1h** and **1l** in toluene (λ_{exc} = 455, 455, 455, 455, and 455 nm, respectively).

Table S2. Photoluminescence spectral data of compounds **1a** to **1l** in toluene.

	Toluene	
	λ_{abs} (nm)	λ_{em} (nm)
1a	448	699
1b	432	653
1c	497	n.d.
1d	n.d.	n.d.
1e	450	620
1f	454	679
1g	446	684
1h	447	669
1i	465	729
1j	409	645
1k	428	712
1l	455	619

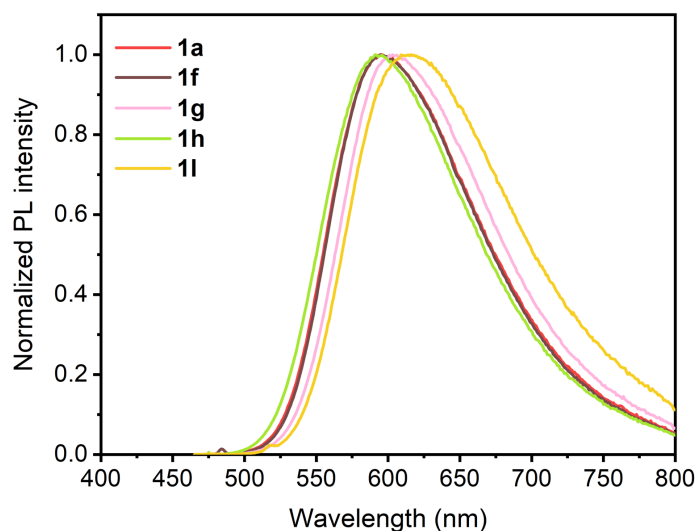


Figure S49. Photoluminescence spectra of compounds **1a**, **1f**, **1g**, **1h**, and **1l** in cyclohexane (λ_{exc} = 415, 425, 415, 415, and 454 nm, respectively).

Table S3. Absorption and emission maxima of the low-energy band of compounds **1a–l** in cyclohexane. The Stokes shifts $\Delta\nu_{\text{abs-vem}}$ are calculated from transition dipole moment representations^a

	Cyclohexane		
	λ_{abs} (nm)	λ_{em} (nm)	$\Delta\nu_{\text{abs-vem}}$ (cm^{-1})
1a	435	596	6900
1b	423	578	6920
1c	486	708	7350
1d	n.d.	n.d.	n.d.
1e	n.d.	n.d.	n.d.
1f	444	595	6520
1g	437	603	7160
1h	435	591	6730
1i	453	639	7170
1j	405	531	6570
1k	418	594	7830
1l	450	612	6880

^a G. Angulo, G. Grampp, A. Rosspeintner *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **2006**, *65*, 727–731.

Fluorescence lifetimes. The fluorescence decays were measured in cyclohexane at the maximum of emission of each compound using a 3-nm detection window. Surprisingly, they did not correspond to a monoexponential decay. The best fitting model was a sum of three exponentials in all cases, and the three components displayed lifetimes of the same order of magnitude. This complex decay was reproduced when exciting **1l** in the low-energy absorption band at 456 nm (instead of 375 nm), thus does not appear to vary with the initially populated state. The results obtained from this analysis are summarized in Table S4. While the longer component, which had a minor contribution and accounted for the noisy tail of the decay, did not show any clear tendency, the pre-exponential factors of the main components correlated well with the observed fluorescence quantum yield (Figure S50). A smaller contribution from the emissive state of shorter lifetime τ_1 , and conversely a more important contribution from τ_2 , are seemingly associated with larger values of quantum yield. It could be inferred that identifying and preventing the formation of the species responsible for τ_1 is an avenue worth exploring in the future in the design of bright fluorescent TCBD derivatives.

Table S4. Photoluminescence lifetimes τ_i of compounds **1a–l** in cyclohexane ($\lambda_{\text{exc}} = 375$ nm) obtained from the best fit (triexponential) and corresponding pre-exponential factors expressed as percentages (A_i).

	Triexponential fit						χ^2
	τ_1 (ns)	A_1 (%)	τ_2 (ns)	A_2 (%)	τ_3 (ns)	A_3 (%)	
1b	0.9	49	1.9	48	14.1	3	1.260
1c	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
1d	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
1e	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
1f	1.0	15	3.8	81	13.9	3	1.133
1g	1.2	33	4.8	40	9.1	27	1.153
1h	1.1	49	3.5	47	12.1	4	1.079
1i	1.1	59	3.6	32	10.9	9	1.144
1j	0.5	48	1.5	50	10.7	2	1.345
1k	1.1	27	2.8	70	13.7	3	1.126
1l	1.1	18	3.6	78	12.1	4	1.162

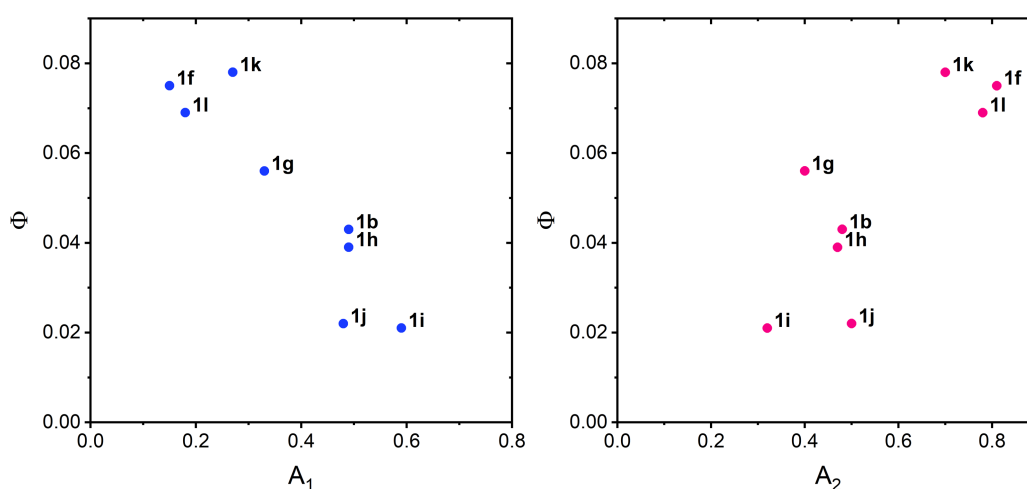


Figure S50. Fluorescence quantum yield of compounds **1a–l** in cyclohexane plotted against normalized pre-exponential factors A_1 et A_2 (see Table S3).

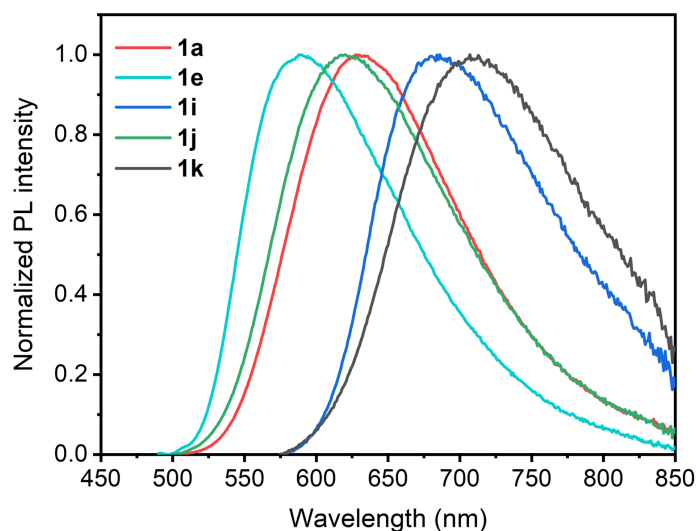


Figure S51. Photoluminescence spectra of compounds **1a**, **1e**, **1i**, **1j**, and **1k** in the solid state (powders; λ_{exc} = 475, 475, 550, 480 and 525 nm, respectively).

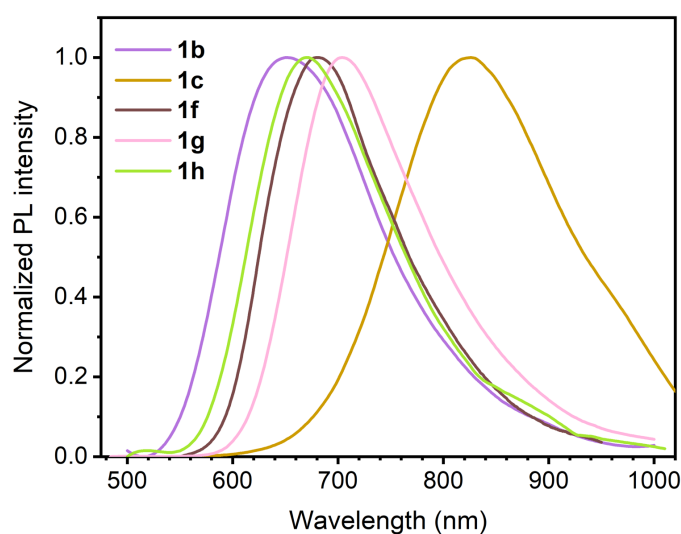


Figure S52. Photoluminescence spectra of compounds **1b**, **1c**, **1f**, **1g**, and **1h** in the solid state (powders; λ_{exc} = 420, 488, 525, 440 and 440 nm, respectively), measured through the NIR region using a R2658 detector. The weak signals produced noisy data that were smoothed using a Savitzky-Golay filter to facilitate their reading.