Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Thiophene fused indenocorannulenes

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1. Materials and methods

1.1 General and instruments

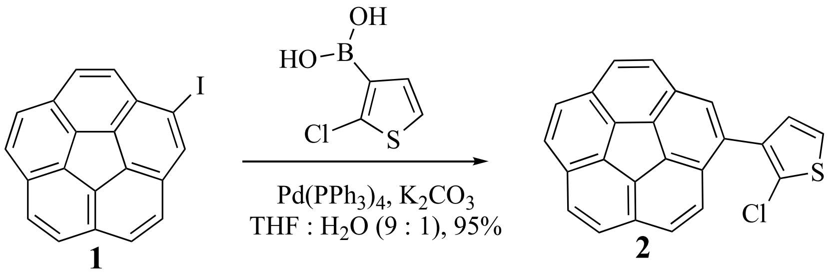
Unless otherwise stated, all commercially available reagents and solvents were used as received without further purification. Flash chromatography was performed on silica gel 100-200 m. Thin layer chromatography (TLC) was performed on glass backed plates pre-coated with silica (GF254), which were developed using standard visualizing agents. All optical measurements were performed in HPLC grade dichloromethane. UV-Vis measurements were carried out on HITACHI U-3900. Infrared spectra (IR) were recorded on a *JASCO FT/IR-4100 Fourier Transform Infrared Spectrometer*. IR frequencies are given in cm^{-1}. Signal intensities are presented as weak (w), medium (m), strong (s) and very strong (vs). NMR spectra were recorded on *Bruker AV-400/600* (400/600 MHz) instruments. The chemical shift (δ) is shown in ppm and referenced against the corresponding solvent peaks (for $CDCl_3$, ^{1}H-NMR: 7.26 ppm; ^{13}C-NMR: 77.16 ppm). Data is reported as follows: chemical shift in ppm, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, dt = doublet of triplet), coupling constant (*J*) in Hz, and integration. Fluorescence excitation/emission measurements were carried on *Edinburgh FLS980* spectrophotometer, using 450W Xenon arc lamp, with excitation and emission slit widths at 1 nm. Emission spectra were obtained by exciting at the longest wavelength excitation maximum. Fluorescence lifetimes were measured using nanosecond flash lamp with computer controlled power supply, for solutions with O.D. ~ 0.1. Absolute quantum yields were measured using an integrating sphere accessory. Microwave reactions were performed in a *CEM Discover Microwave Reactor* with integrated active cooling. All cyclic voltammetry measurements were performed using a *CHI600E Electrochemical Analyzer, CH Instruments, Inc.* and in THF solvent with a scan rate of 0.1 V/s. THF was of HPLC grade and distilled over CaH_2 prior to its use. Tetrabutylammonium hexafluorophosphate (TBAH) was used as an electrolyte. Non-Aqueous Ag/Ag+ was used as reference electrode (10 mM $AgNO_3$ in 0.1 M Bu_4NPF_6 in acetonitrile), platinum wire as counter electrode and glassy carbon as working electrode for all measurements. All $E_{1/2}$ potentials are directly obtained from cyclic voltammetric curves as averages of the cathodic and anodic peak potentials. Ferrocene was used as an internal standard. The standard potential of ferrocinium/ferrocene couple in THF (+0.085 V) was used to calibrate all voltammetry plots. High-resolution mass spectra (HRMS) recorded for accurate mass analysis, were performed on either a Q-TOF micro (Bruker Compass Data Analysis 4.0) spectrometer. The ECD spectrometer was purged with nitrogen before recording each spectrum, which was baseline subtracted. The baseline was always measured for the same solvent and in the same cell as the samples. The spectra are presented without smoothing and further data processing. VCD spectra were measured on ChiralIR-2X with 300 μm cell, $CHBr_3$ as solvent. The crystal structures were obtained from Rigaku XtalAB PRO MM007 DW.

1.2 Computational data

The structural and energetic analyses of the molecular systems for all compounds described in this study were carried out with the B97-D dispersion enabled density functional method,[1,2] using an ultrafine grid, together with the Def2-TZVPP basis set.[3] Full geometry optimizations were performed and uniquely characterized via second derivatives (Hessian) analysis to establish stationary points and effects of zero point and thermal energy contributions. Absorption energies were computed in acetonitrile at the TD-wB97xD[4]/Def2-TZVPP(ACN) level of theory. From the TD-DFT results, spectra were simulated from the excitation energies and rotation lengths by overlapping Gaussian functions f or each transition. VCD was performed in bromoform at the B97-D/Def2-TZVPP($CHBr_3$) level of theory. The simulated VCD spectrum consists of a sum of Lorentzian distributions centered on the computed frequencies, with fixed width and with the height proportional to the computed rotational constant. Reduction potential data was determined in tetrahydrofuran at the B97-D/Def2-TZVPP(THF) level of theory, using $E° = -\Delta H/nF$, where $n = 1$, $F = 1$ eV, and referenced to Ag/AgCl. The Strumm and Morgan correction[5] for 0.1 M AgCl/Ag of 0.29 was used in combination with the value for the SHE electrode, giving 4.73 = 4.44 (SHE) + 0.29 (0.1 M AgCl/Ag), for the reference value. Effects of solvent employed the COSMO:*ab initio* continuum method[6,7] using a dielectric as in experiment, and radii of Klamt.[8] Visualization and analysis of structural and property results were obtained using Avogadro[9] and GaussView (for spectra).[10]

2. Synthetic procedures and analyses

2.1 Synthesis of compound 2



40 mg (0.107 mmol, 1 eq) of iodocorannulene **1**, 35 mg (0.214 mmol, 2 eq) of 2-chlorothiophene-3-boronic acid, 6.2 mg (0.00535 mmol, 0.05 eq) of tetrakis(triphenyl-phosphine)palladium, 45 mg (0.321 mmol, 3 eq) of potassium carbonate, and a total 1 mL of 9:1 ratio of THF to water were added to a sealed tube. The reaction mixture was degassed using nitrogen and then heated to 100°C for 22 h. When the reaction is completed, the reaction mixture was cooled to room temperature then 5 mL water and 5 mL ethyl acetate was added, dichloromethane was used to wash the aqueous phase (twice), the organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The product was purified by silica column chromatography to give 37 mg of **2** as a yellow solid (95%).

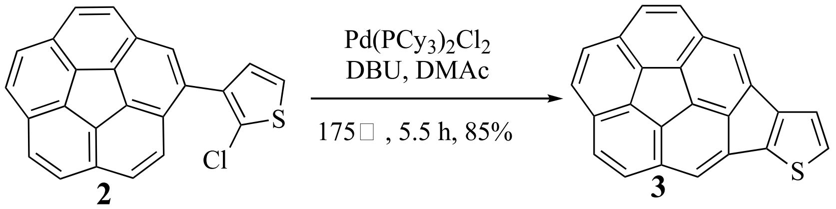
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 (s, 1H), 7.85 (s, 2H), 7.83 (s, 2H), 7.82 – 7.81 (m, 2H), 7.79 (d, J = 8.8, 1H), 7.69 (d, J = 8.8, 1H), 7.27 (d, J = 6, 1H), 7.19 (d, J = 6, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 136.85, 136.15, 135.92, 135.85. 135.56, 135.47, 132.98, 130.96, 130.88, 130.38, 130.01, 129.83, 127.49, 127.37, 127.32, 127.26, 127.19, 127.11, 127.02, 126.98, 126.98, 126.88, 126.78, 122.81.

HRMS-ESI (+): Calculated for $C_{24}H_{11}ClNaS$ [M+Na$^+$] 389.01676; found389.0162.

IR (film): 3458.5 (m), 3109.8 (w), 3031.7 (w), 1628.7 (m), 1420.3 (w), 1247.6 (m), 1023.2 (m), 910.0 (w), 847.7 (w), 834.4 (s), 819.7 (m),733.3 (m), 693.8 (w), 680.4 (w).

2.2 Synthesis of compound 3



A dry, sealed tube containing a magnetic stirring bar was charged with 2 (9.5 mg 0.026 mmol, 1 eq), Pd(PCy$_3$)$_2$Cl$_2$, (3.9 mg, 0.00538 mmol, 0.2 eq), DBU (0.024 mL, 0.156 mmol, 6 eq) and dimethylacetamide (1 ml). The reaction vessel was sealed, evacuated, purged with nitrogen and heated at 175 °C for 5.5 hours. The reaction mixture was allowed to cool and was then diluted with 10 mL of dichloromethane. The organic solution was washed with 10% HCl, water, and brine and was then dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure. The residue was subjected to silica gel flash column chromatography to give 3 (7.5 mg, 85%).

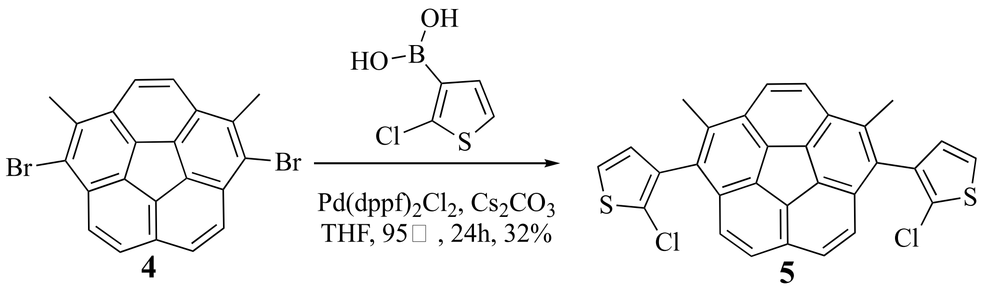
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 – 7.47 (m, 4H), 7.41 (s, 2H), 7.36 (s, 1H), 7.32 (s, 1H), 7.15 (d, *J* = 4.9 Hz, 1H), 7.11 (d, *J* = 5.0 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.04, 145.16, 141. 25, 139.15, 138.18, 138.16, 138.07, 137.49, 137.09, 137.03, 136.95, 136.87, 129.90, 129.82, 128.60, 128.13, 128.01, 127.12, 127.08, 126.80, 126.76, 121.66, 121.53, 119.91.

HRMS-ESI (+): Calculated for $C_{24}H_{11}S$ [M+H$^+$] 331.0576; found 331.0576.

IR (film): 3744.0 (m), 3091.1 (w), 3032.1 (w), 2378.0 (m), 2311.0 (m), 1750.8 (s), 1698.9 (m), 1641.9 (w), 1512.1 (w), 1321.2 (m), 1297.9 (m), 1127.2 (w), 1082.4 (w), 866.5 (s), 817.7 (s), 668.5 (m), 629.8 (m), 564.5(m).

2.3 Synthesis of compound 5



Compound 4 (100 mg, 0.23 mmol, 1 eq), Pd(dppf)Cl$_2$ (34 mg, 0.046 mmol, 0.2 eq), Cs$_2$CO$_3$ (900 mg, 2.76 mmol, 12 eq), and (2-chlorothiophen-3-yl)boronic acid (150 mg, 0.92 mmol, 4 eq) was transferred into a sealed tube. Dry and degassed THF (23 mL) was added and the mixture was heated to 95 °C for 24 hours. After TLC trace showed complete consumption of 4, the reaction mixture was quenched with water (25 mL) and extracted with CH_2Cl_2 (3 × 25 mL). The organic phase was dried over anhydrous Na_2SO_4 and concentrated via rotary evaporator. The crude product was purified through column and recrystallized in CH_2Cl_2/ CH_3OH to afford the pure 5 as white powder (38 mg, 32% yield).

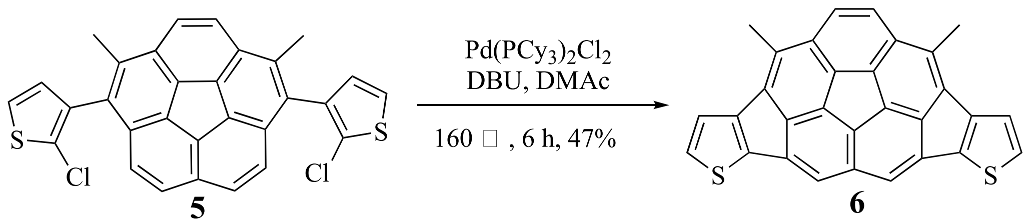
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 (s, 2H), 7.68 (d, *J* = 8.8 Hz, 2H), 7.33 (dd, *J* = 8.8, 2.5 Hz, 2H), 7.29 (dd, *J* = 5.9, 0 Hz, 2H), 6.97 (dd, *J* = 34.4, 4.4 Hz, 2H), 2.68 (s, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 136.25, 136.22, 135.73, 135.20, 135.18, 134.66, 134.48, 131.01, 130.00, 130.79, 130.29, 129.97, 129.80, 129.77, 127.84, 127.78, 127.28, 127.26, 126.01, 125.31, 122.68, 122.62, 15.90. [This compound exists as a mixture of rotamers, the rate of interconversion is slow on the NMR timescale at room temperature.]

HRMS-ESI (+): Calculated for $C_{30}H_{17}Cl_2S_2$ [M+H$^+$] 513.0114; found 513.0112.

IR (film): 3865.1 (w), 3108.3 (m), 2919.2 (s), 1451.2 (m), 1422.1 (m), 1403.9 (m), 1030.3 (s), 868.0 (s), 825.1 (w), 808.7 (s), 798.8 (s), 700.1 (m), 633.3 (s).

2.4 Synthesis of compound 6



Compound 5 (20 mg, 0.039 mmol, 1 eq) was reacted with 1,8-diazabicyclo[5.4.0]-7-undecene (0.08 mL, 0.546 mmol, 14 eq) and $Pd(PCy_3)_2Cl_2$ (12 mg, 0.0156 mmol, 0.4 eq) in dry N,N-dimethylacetamide (2 mL). The reaction mixture was degassed with nitrogen gas and heated to 160 °C in a sealed tube for 5-6 hours. After TLC trace showed complete consumption of 5, the mixture was diluted with CH_2Cl_2 (20 mL) and washed with H_2O (3 × 40 mL). 2 M HCl was added dropwise to neutralize the aqueous phase while washing. The organic phase was dried over Na_2SO_4 and concentrated via rotary evaporator. The crude product was then purified through column using 10:1

hexane/ CH_2Cl_2 followed by 5:1 hexane/ CH_2Cl_2 as eluent. It was then recrystallized with CH_2Cl_2/CH_3OH to afford the 8 mg pure 6 as orange solid (47% yield).

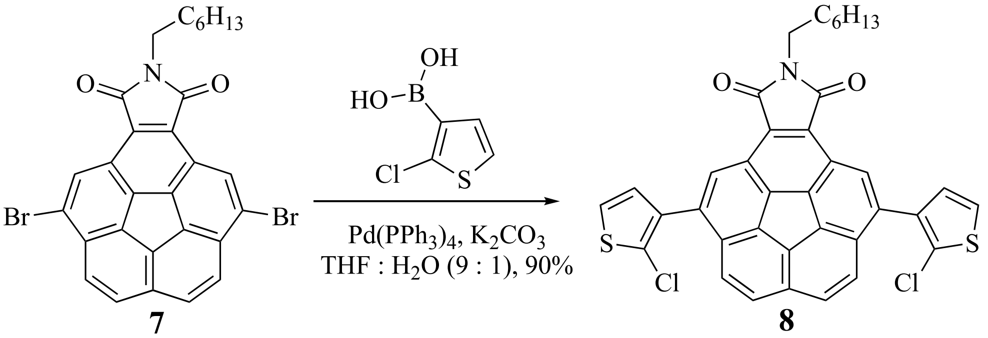
^{1}H NMR (600 MHz,) δ 7.55 (s, 2H), 7.24 (d, *J* = 4.9 Hz, 2H), 7.20 (s, 2H), 7.19 (d, *J* = 5.2 Hz, 2H), 2.57 (s, 6H).

^{13}C NMR (151 MHz,) δ 144.20, 142.96, 141.73, 140.52, 138.39, 138.39, 136.48, 136.33, 134.73, 133.99, 132.53, 128.61, 125.19, 122.64, 121.04, 15.05.

HRMS-ESI (+): Calculated for $C_{30}H_{15}S_2$ [M+H$^+$] 439.0610; found 439.0607.

IR (film): 3437.2 (m), 2926.3 (s), 2848.8 (m), 1635.4 (w), 1445.1 (w), 1174.0 (w), 1003.9 (w), 735.7 (w).

2.5 Synthesis of compound 8



Compound 7 (110 mg, 0.191 mmol, 1 eq), $Pd(PPh_3)_4$ (24 mg, 0.02 mmol, 0.1 eq), K_2CO_3 (133 mg, 0.96 mmol, 5 eq), and (2-chlorothiophen-3-yl)boronic acid (128 mg, 0.788 mmol, 4 eq) was transferred into a sealed tube. Dry and degassed 5mL THF: H_2O (9:1) was added and the mixture was heated to 100 °C for 1 hour. After TLC trace showed complete consumption of 7, the reaction mixture was quenched with water (25 mL) and extracted with CH_2Cl_2 (3 × 25 mL). The organic phase was dried over anhydrous Na_2SO_4 and concentrated via rotary evaporator. The crude product was purified through column to afford the pure 8 as yellow solid (112 mg, 90% yield).

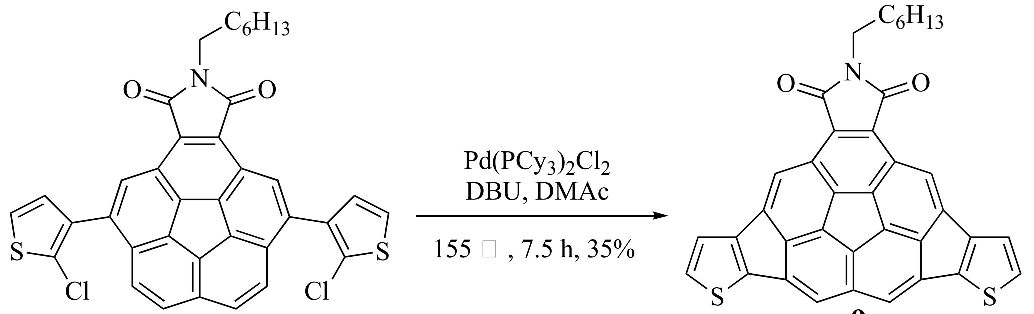
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.51 (s, 2H), 7.83 (d, *J* = 8.8 Hz, 2H), 7.71 (d, *J* = 8.8 Hz, 2H), 7.30 (d, *J* = 5.7 Hz, 2H), 7.19 (d, *J* = 5.7 Hz, 2H), 3.76 (t, *J* = 7.3 Hz, 2H), 1.77 – 1.69 (m, 2H), 1.41 – 1.32 (m, 4H), 1.30 – 1.24 (m, 4H), 0.87 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.28, 138.00, 135.99, 135.89, 135.62, 135.60, 131.73, 131.11, 130.93, 129.76, 128.83, 127.59, 127.59, 125.85, 124.72, 123.23, 37.97, 31.70, 28.85, 28.82, 26.87, 22.56, 14.05.

HRMS-ESI (+): Calculated for $C_{37}H_{25}Cl_2NNaO_2S_2$ [M+Na$^+$] 672.0598; found 672.0596.

IR (film): 2926.4 (m), 2854.6 (m), 1760.5 (m), 1703.0 (s), 1436.3 (m), 1399.1 (m), 1369.2 (w), 1072.7 (w), 1027.5 (m), 881.1 (w), 845.2 (w), 827.8(w), 728.9 (w).

2.6 Synthesis of compound 9



8 **9**

A dry, sealed tube containing a magnetic stirring bar was charged with 8 (20 mg 0.0308 mmol, 1 eq), Pd(PCy$_3$)$_2$Cl$_2$, (9.1 mg, 0.123 mmol, 0.4 eq), DBU (0.028 mL, 0.185 mmol, 6 eq) and dimethylacetamide (2 mL). The reaction vessel was sealed, evacuated, purged with nitrogen and heated at 155 °C for 7.5 hours. The reaction mixture was allowed to cool and was then diluted with 20 mL of dichloromethane. The organic solution was washed with 10% HCl, water, and brine and was then dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was subjected to silica gel flash column chromatography to give 9 (6.2 mg, 35%).

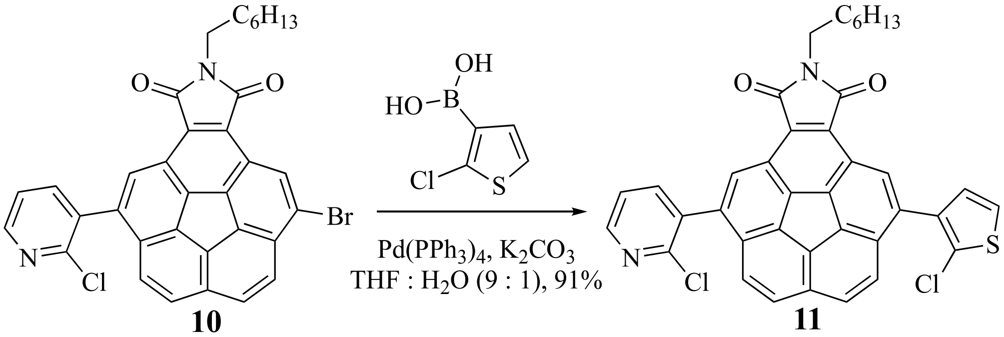
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (s, 2H), 7.18 (d, *J* = 5.0 Hz, 2H), 7.09 (d, *J* = 4.9 Hz, 2H), 6.98 (s, 2H), 3.61 (t, *J* = 7.3 Hz, 2H), 1.65 – 1.60 (m, 2H), 1.29 (d, *J* = 6.7 Hz, 8H), 0.85 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.66, 144.47, 143.56, 142.29, 142.17, 139.96, 139.02, 138.30, 137.27, 137.10, 131.77, 129.31, 129.08, 123.57, 120.48, 119.41, 37.74, 31.68, 28.84, 28.78, 26.84, 22.57, 14.04.

HRMS-ESI (+): Calculated for $C_{37}H_{24}NO_2S_2$ [M+H$^+$] 579.1277; found 579.1281

IR (film): 3438.8 (m), 2924.8 (s), 2853.1 (m), 1756.9 (m), 1698.7 (s), 1438.8 (w), 1397.4 (m), 1364.3 (w), 1296.6 (w), 1081.7 (m), 884.1 (m), 755.2 (w), 699.0 (w).

2.7 Synthesis of compound 11



Compound 10 (159 mg, 0.262 mmol, 1 eq), $Pd(PPh_3)_4$ (30 mg, 0.0262 mmol, 0.1 eq), K_2CO_3 (180 mg, 1.30 mmol, 5 eq), and (2-chlorothiophen-3-yl)boronic acid (84 mg, 0.524mmol, 2 eq) was transferred into a sealed tube. Dry and degassed 2 mL THF: H_2O (9:1) was added and the mixture was heated to 100 °C for 1 hour. After TLC trace showed complete consumption of 10, the reaction mixture was quenched with water (25 mL) and extracted with CH_2Cl_2 (3 × 25 mL). The organic phase was dried over anhydrous Na_2SO_4 and concentrated via rotary evaporator. The crude product was purified through column to afford the pure 11 as yellow solid (154 mg, 91% yield).

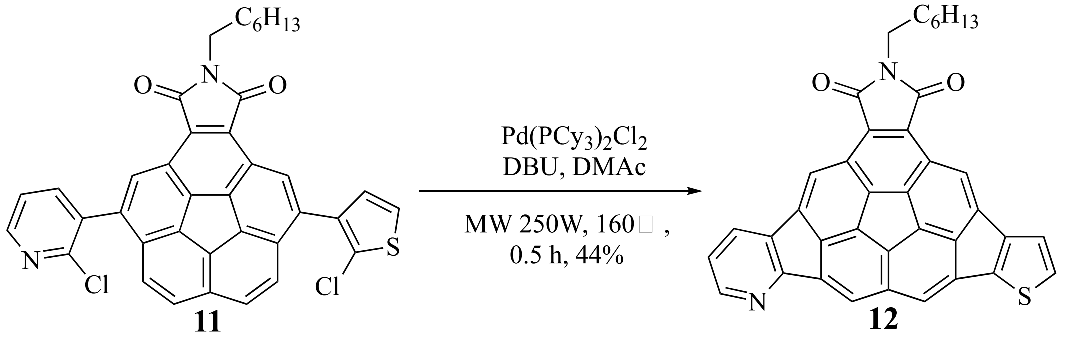
^1H NMR (600 MHz, Chloroform-*d*) δ 8.58 (dd, $J = 4.8, 1.9$ Hz, 1H), 8.52 (s, 1H), 8.39 (s, 1H), 7.82 (t, $J = 8.6$ Hz, 2H), 7.76 (dd, $J = 7.5, 2.0$ Hz, 1H), 7.72 (d, $J = 8.8$ Hz, 1H), 7.49 (d, $J = 8.8$ Hz, 1H), 7.42 (dd, $J = 7.5, 4.8$ Hz, 1H), 7.30 (d, $J = 5.6$ Hz, 1H), 7.20 (d, $J = 5.7$ Hz, 1H), 3.75 (t, $J = 7.3$ Hz, 2H), 1.76-1.71 (m, 2H), 1.40 – 1.34 (m, 4H), 1.31 – 1.27 (m, 4H), 0.87 (t, $J = 6.8$ Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 169.26, 169.17, 150.80, 149.61, 140.70, 138.99, 138.44, 138.18, 135.91, 135.89, 135.72, 135.21, 134.21, 131.87, 131.80, 131.25, 130.97, 130.94, 129.73, 129.73, 129.05, 128.91, 127.73, 127.68, 126.66, 126.45, 125.92, 125.02, 124.56, 123.30, 122.57, 38.00, 31.68, 28.83, 28.80, 26.85, 22.54, 14.02.

HRMS-ESI (+): Calculated for $C_{38}H_{26}Cl_2N_2O_2Na$ [M+Na$^+$] 667.0977; found 667.098.

IR (film): 2924.6 (s), 2853.5 (m), 1758.6 (m), 1705.4 (s), 1457.0 (w), 1436.2 (m), 1399.6 (s), 1371.0 (m), 1028.8 (m), 885.7 (m), 841.0 (w), 826.3 (m).

2.8 Synthesis of compound 12



A dry, sealable microwave reaction vessel containing a Teflon coated magnetic stirring bar was charged with 11 (12 mg 0.0186 mmol, 1 eq), $Pd(PCy_3)_2Cl_2$, (4.1 mg, 0.00555 mmol, 0.4 eq), DBU (0.017ml, 0.112 mmol, 6 eq) and dimethylacetamide (2.2 ml). The reaction vessel was sealed, evacuated, purged with nitrogen and heated in a CEM Discovery microwave reactor at 150 °C for 30 min. The reaction mixture was allowed to cool and was then diluted with 20 mL of dichloromethane. The organic solution was washed with 10% HCl, water, and brine and was then dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was subjected to silica gel flash column chromatography to give 12 (4.7 mg, 44%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.40 (dd, *J* = 5.0, 1.6 Hz, 1H), 8.09 (s, 1H), 7.90 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.85 (s, 1H), 7.79 (s, 1H), 7.23 (s, 1H), 7.20 (d, *J* = 5.0 Hz, 1H), 7.14 (dd, *J* = 7.6, 5.2 Hz, 1H), 7.11 (d, *J* = 5.2 Hz, 1H), 7.12 – 7.10 (m, 1H), 3.65 (t, *J* = 7.3 Hz, 2H), 1.64 (t, *J* = 7.3 Hz, 2H), 1.26 (s, 8H), 0.87 – 0.83 (m, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.45, 168.41, 158.43, 148.91, 144.75, 144.66, 142.04, 141.34, 140.38, 139.49, 139.24, 139.03, 138.94, 138.75, 137.42, 137.11, 133.44, 131.78, 131.68, 129.69, 129.69, 129.42, 129.42, 129.37, 128.89, 125.74, 123.98, 122.51, 121.01, 120.55, 119.71, 37.84, 31.70, 28.84, 28.79, 26.86, 22.58, 14.04.

HRMS-ESI (+): Calculated for $C_{38}H_{25}N_2O_2S$ [M+H$^+$] 573.1632; found 573.1601.

IR (film): 3439.3 (s), 2923.3 (s), 2852.7 (m), 1756.7 (w), 1697.6 (s), 1555.1 (w), 1438.1 (m), 1397.9 (s), 1371.6 (m), 1119.8 (w), 1083.8 (w), 886.1 (m), 803.3 (m), 722.5 (w,), 541.9 (m).

3. Cyclic voltammetric measurements

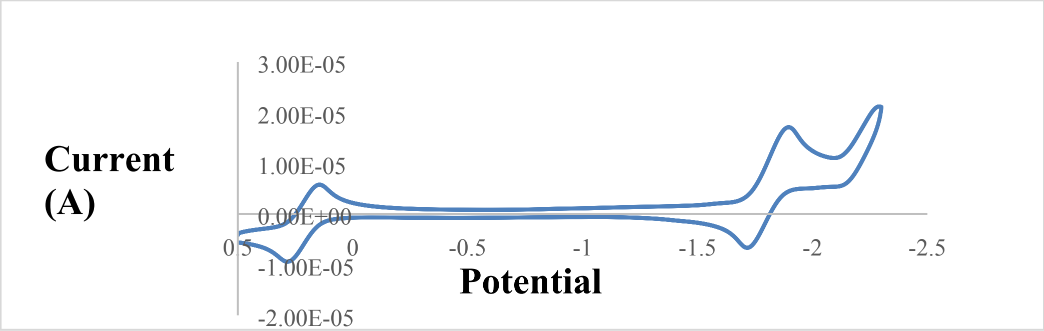


Figure S1: Reduction CV plot for 3.

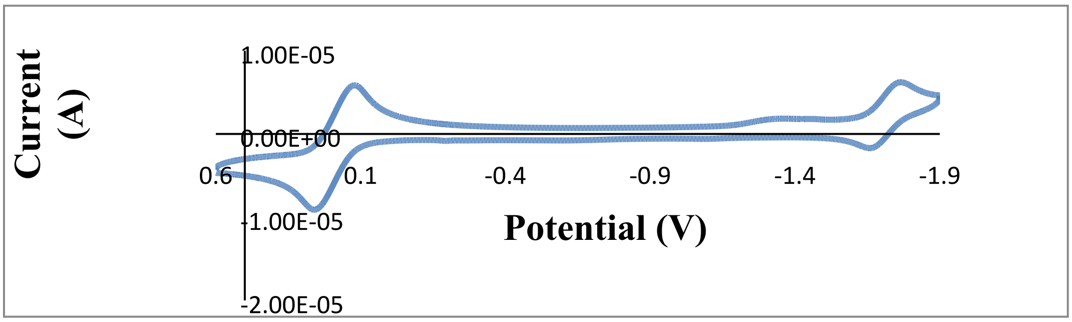


Figure S2: Reduction CV plot for 6.

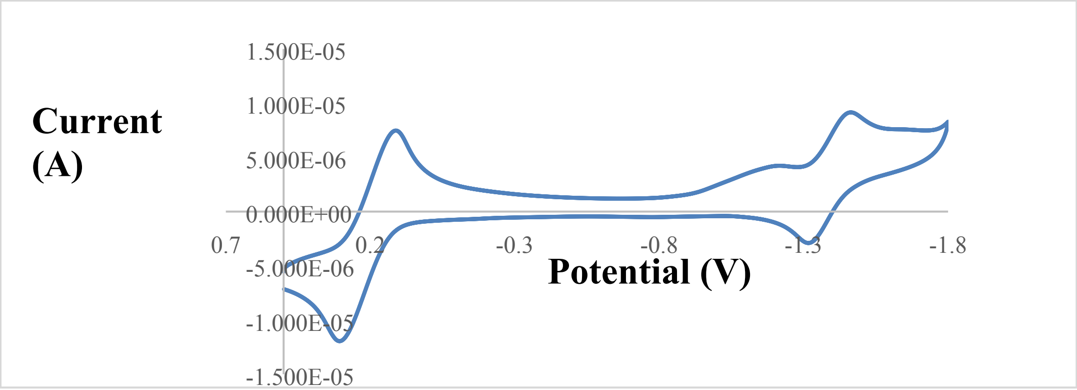


Figure S3: Reduction CV plot for 9.

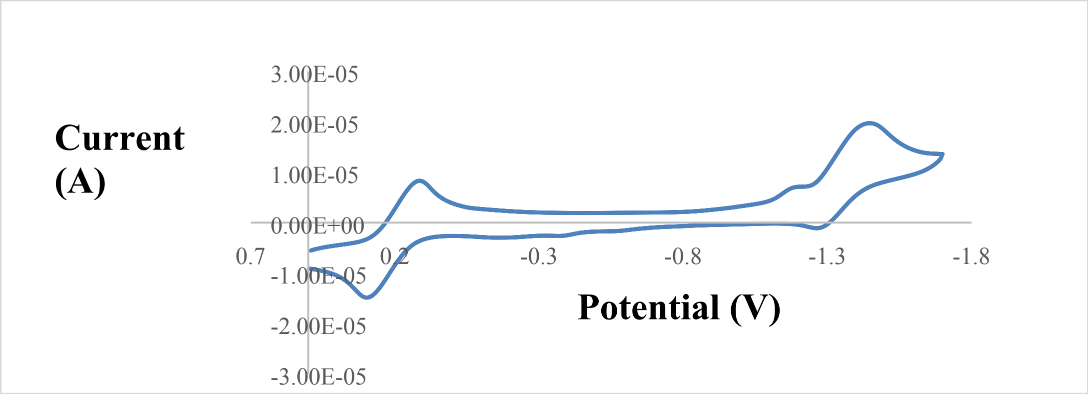


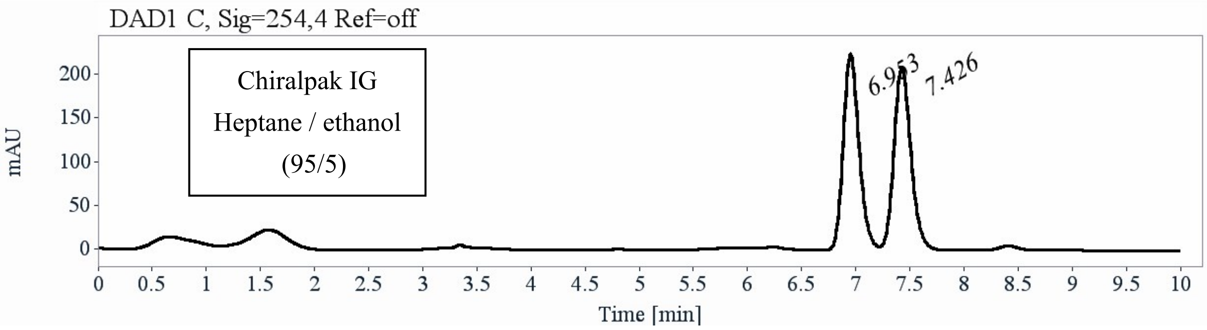
Figure S4: Reduction CV plot for 12.

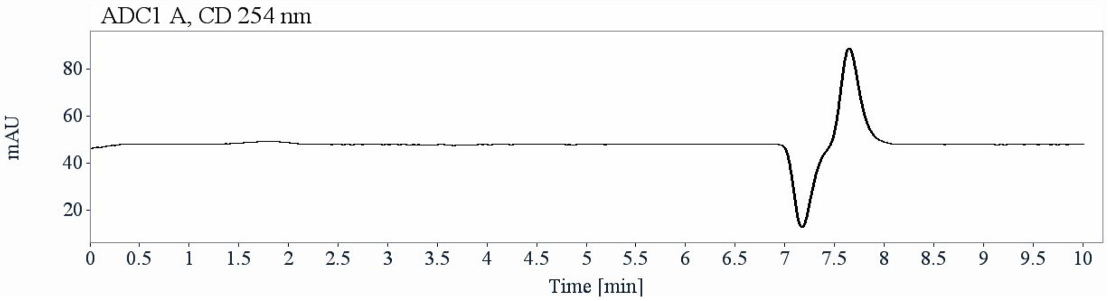
4. Enantiomeric separation of 3a/3b

4.1 Analytical HPLC separation for the enantiomers 3a/3b

- The sample is dissolved in dichloromethane, injected on the chiral columns, and detected with an UV detector at 254 nm and with dichroism circular at 254 nm. The flow-rate is 1 ml/min.

Column	**Mobile Phase**	**t1**	**k1**	**t2**	**k2**	**α**	**Rs**
Chiralpak IG	Heptane / ethanol (95/5)	6.95 (-)	1.36	7.43 (+)	1.52	1.12	1.72

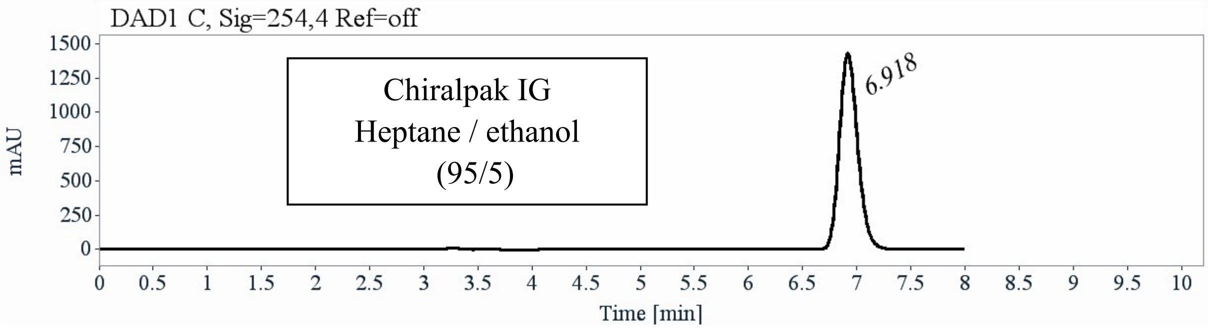




RT [min]	**Area**	**Area%**	**Capacity Factor**	**Enantioselectivity**	**Resolution (USP)**
6.95	2275	49.86	1.36		
7.43	2288	50.14	1.52	1.12	1.72
Sum	4562	100.00			

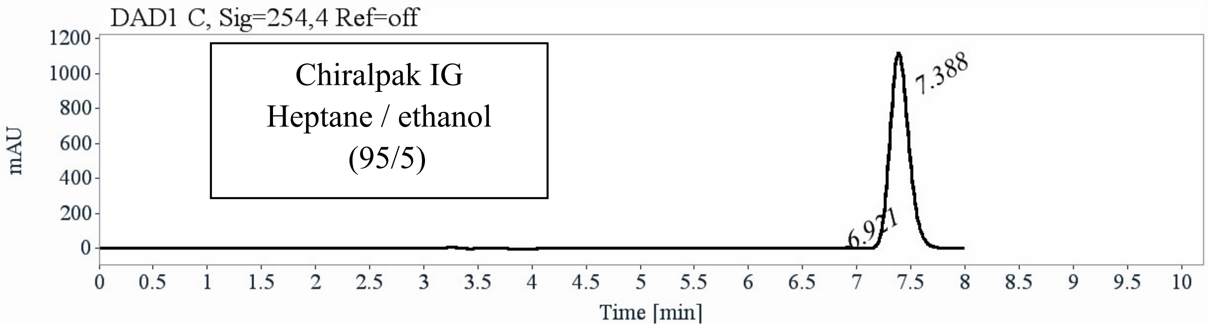
4.2 Semi-preparative separation of enantiomers 3a/3b

- Sample preparation: About 43 mg of compound **3a/3b** are dissolved in 28 mL of a mixture of dichloromethane and hexane (36/64).
- Chromatographic conditions: Chiralpak IG (250 x 10 mm), hexane / ethanol (95/5) as mobile phase, flow-rate = 5 mL/min, UV detection at 290 nm.
- Injections (stacked): 560 times 0.05ml, every 1.5minutes.
- First fraction(**3a**): 17 mg of the first eluted enantiomer with ee > 99.5%



RT [min]	Area	Area%
6.92	15030	100.00
Sum	15030	100.00

- Second fraction(**3b**): 16 mg of the second eluted enantiomer with ee > 99 %



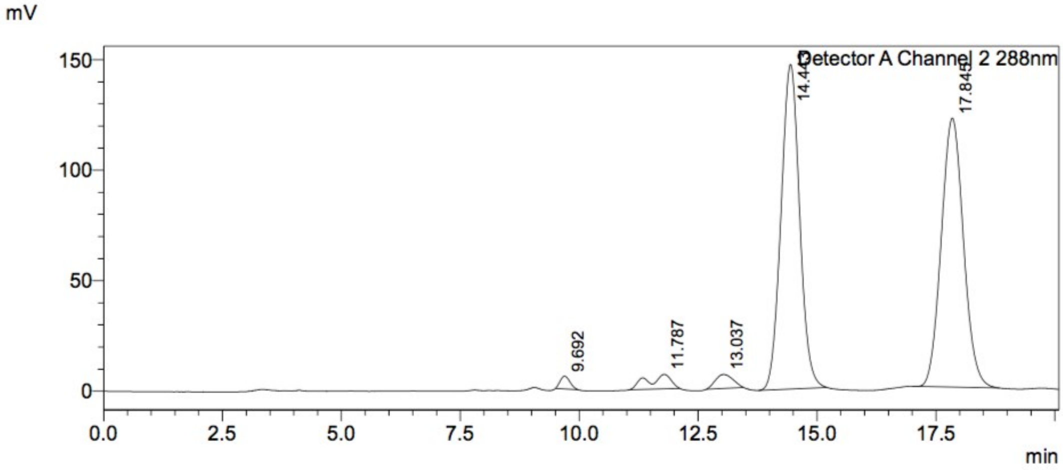
RT [min]	Area	Area%
6.92	53	0.38
7.39	13702	99.62
Sum	13754	100.00

5. Enantiomeric separation of 12a/12b

5.1 Analytical HPLC separation of the enantiomers12a/12b

- A sample of **12a**/**12b** is dissolved in dichloromethane, injected on the Chiralpak ID column, and detected with an UV detector at 288 nm. Mobile Phase is DCM： iPrOH： Hexane (15:15:70). The flow-rate is 1 ml/min.

Chromatogram:



Peak Table:

Detector A Channel 2 288nm

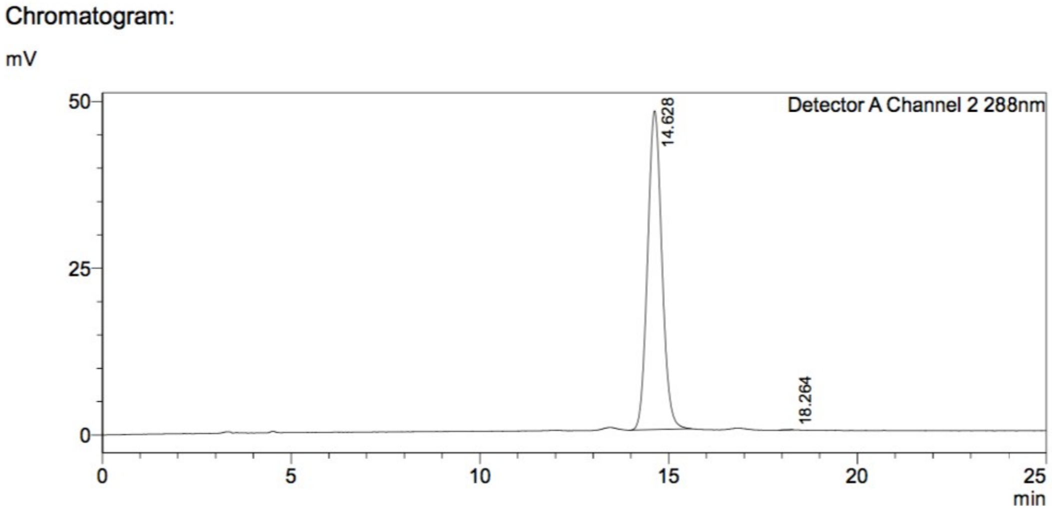
Peak	Ret. Time	Area	Height	Area%	Compound Name
1	9.692	82917	5782	0.986	
2	11.787	218339	6551	2.596	
3	13.037	162315	6336	1.930	
4	14.443	3988269	146837	47.425	
5	17.845	3957807	121658	47.063	
Total		8409647	287164	100.000	

Figure S5: Analytical HPLC trace of **12a**/**12b**.

5.2 Semi-preparative separation of enantiomers 12a/12b

- Sample preparation: About 40 mg of compound **12a/12b** are dissolved in 12 mL of dichloromethane.
- Chromatographic conditions: Chiralpak ID (250 x 10 mm), hexane / iPrOH / dichloromethane (70/15/15) as mobile phase, flow-rate = 5 mL/min, UV detection at 288 nm.
- Injections (stacked): 20 times, 0.6ml
- First fraction(**12a**): 16 mg of the first eluted with ee > 99.5%

- Second fraction(**12b**): 17 mg of the second eluted with ee >99.5%
- Chromatograms of the collected fractions:

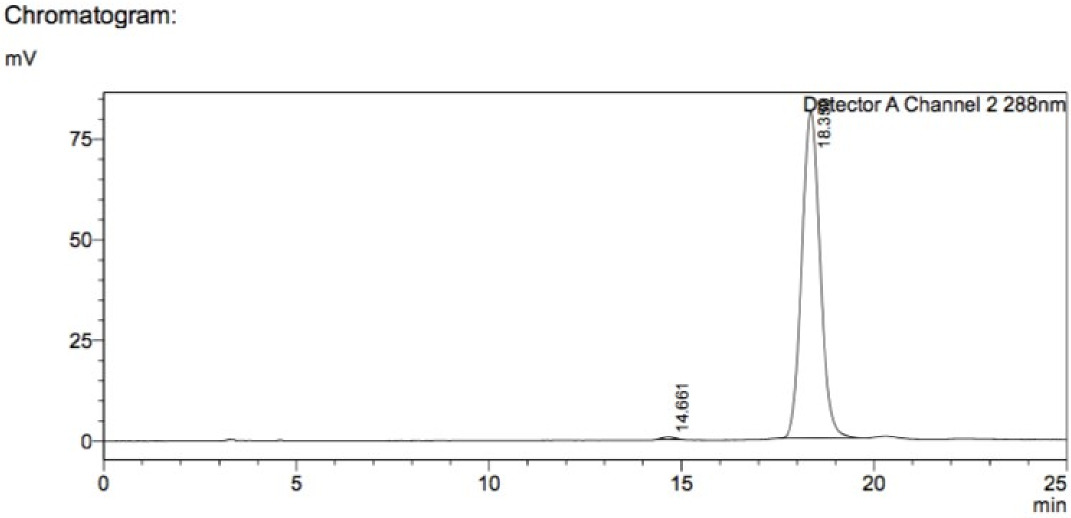


Peak Table:

Detector A Channel 2 288nm

Peak	Ret. Time	Area	Height	Area%	Compound Name
1	14.628	1254428	47788	99.986	
2	18.264	172	11	0.014	
Total		1254600	47800	100.000	

Figure S6: HPLC trace of **12a** (after semi-preparative separation).



Peak Table:

Detector A Channel 2 288nm

Peak	Ret. Time	Area	Height	Area%	Compound Name
1	14.661	12701	620	0.471	
2	18.359	2686071	81295	99.529	
Total		2698771	81915	100.000	

Figure S7: HPLC trae of the **12b** (after semi-preparative separation).

6. Optical rotations

Optical rotations were measured on a 241 Perkin-Elmer polarimeter with a sodium lamp (589 nm), a mercury lamp (578 and 546 nm) and a double-jacketed 10 cm cell at 25°C.

Table S1. $[\alpha]_\lambda^{25}$ of **3a** and **3b** at different wavelength in CH_2Cl_2

λ (nm)	first eluted (**3a**) on Chiralpak IG $[\alpha]_\lambda^{25}$ (CH_2Cl_2)	second eluted (**3b**) on Chiralpak IG $[\alpha]_\lambda^{25}$ (CH_2Cl_2)
589	- 1150 (c = 0.037)	+ 1150 (c = 0.039)
578	- 1300 (c = 0.037)	+ 1300 (c = 0.039)
546	- 2600 (c = 0.037)	+ 2600 (c = 0.039)

7. Kinetic studies of enantiomerization

About 0.35 mg of the 2nd eluted enantiomer **3b** is heated in about 20 mL of ethanol at 78°C. 0.02ml are taken and then injected on Chiralpak IG (95:5, heptane / ethanol, 1 mL/min, UV 254 nm). The percentage decrease of the 2nd eluted enantiomer (**3b**) is monitored.

Table S2. Percentage of **3b** at different time in ethanol.

Time (min)	% **2nd** eluted enantiomer (**3b**)	ln ((%t-50%)/(%(t=0)-50%))
0	97.13	0.0000
20	90.55	-0.1504
41	84.50	-0.3120
55	80.94	-0.4209
75	76.49	-0.5761
95	72.68	-0.7314

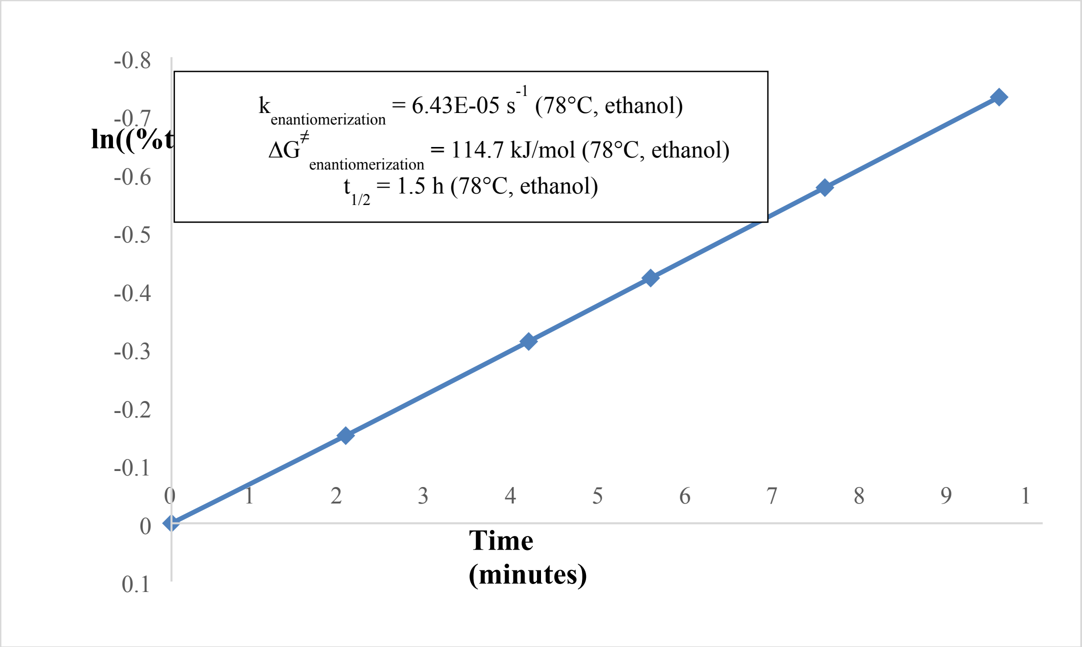


Figure S8. Kinetics of **3b** enantiomerization in enthanol at 78°C

About 0.3 mg of the 2nd eluted enantiomer (**3b**) is heated in about 20 mL of cyclohexane at 80.7°C. 0.02ml are taken and then injected on Chiralpak IG (95:5, heptane / ethanol, 1 mL/min, UV 254 nm). The percentage decrease of the 2nd eluted enantiomer (**3b**) is monitored.

Table S3. Percentage of **3b** at different time in cyclohexane.

Time (min)	% **2nd** eluted enantiomer (**3b**)	ln ((%t-50%)/(%(t=0)-50%))
0	99.02	0.0000
10	96.86	-0.0451
15	95.84	-0.0671
20	94.87	-0.0885
30	92.96	-0.1320
40	91.11	-0.1760
50	89.33	-0.2202
60	87.69	-0.2628
80	84.57	-0.3492
100	81.64	-0.4378
120	79.04	-0.5236
140	76.61	-0.6109
160	74.39	-0.6981

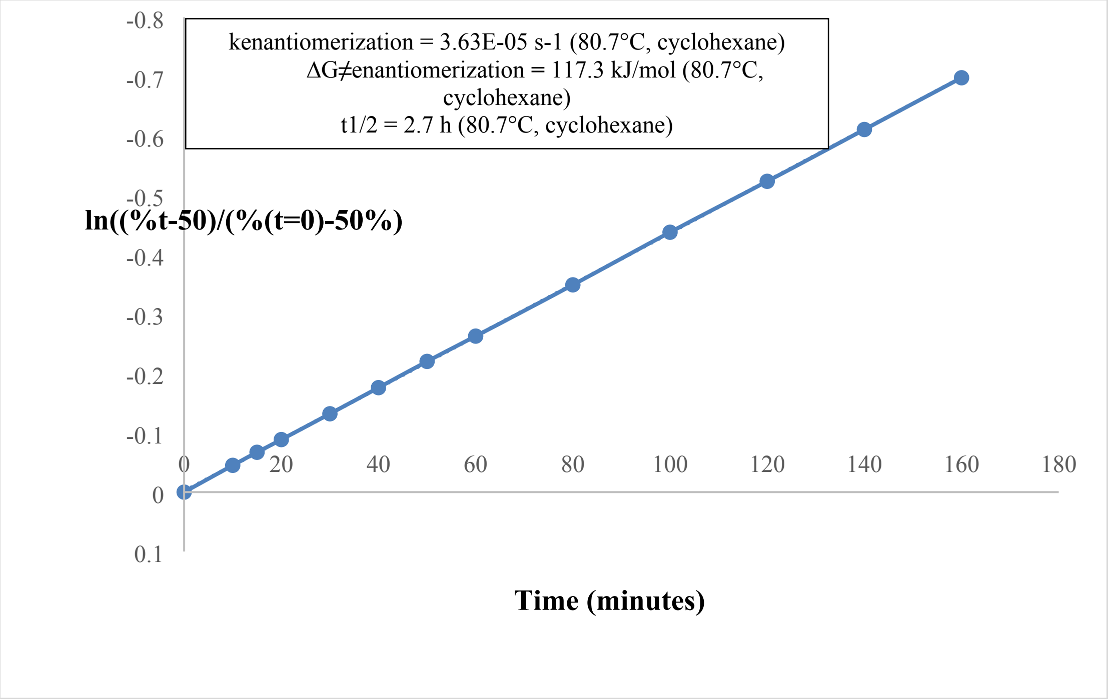


Figure S9. Kinetics of **3b** enantiomerization in cyclohexane at 80.7°C

About 0.25 mg of the 2nd eluted enantiomer **3b** is heated in about 15 mL of CCl_4 at 77 °C. 0.02 ml are taken and then injected on Chiralpak IG (95:5 heptane / ethanol, 1 mL/min, UV 254 nm). The percentage decrease of the 2nd eluted enantiomer **3b** is monitored.

Table S4. Percentage of **3b** at different time in CCl_4.

Time (min)	% 2nd eluted enantiomer (**3b**)	ln ((%t-50%)/(%(t=0)-50%))
0	99.21	0.0000
5	98.14	-0.0220
10	97.09	-0.0440
15	96.05	-0.0664
20	95.05	-0.0883
30	93.07	-0.1333
45	90.30	-0.1997
60	87.66	-0.2675
75	85.22	-0.3345
95	82.20	-0.4241
115	79.44	-0.5137
135	74.92	-0.6032
155	74.63	-0.6921

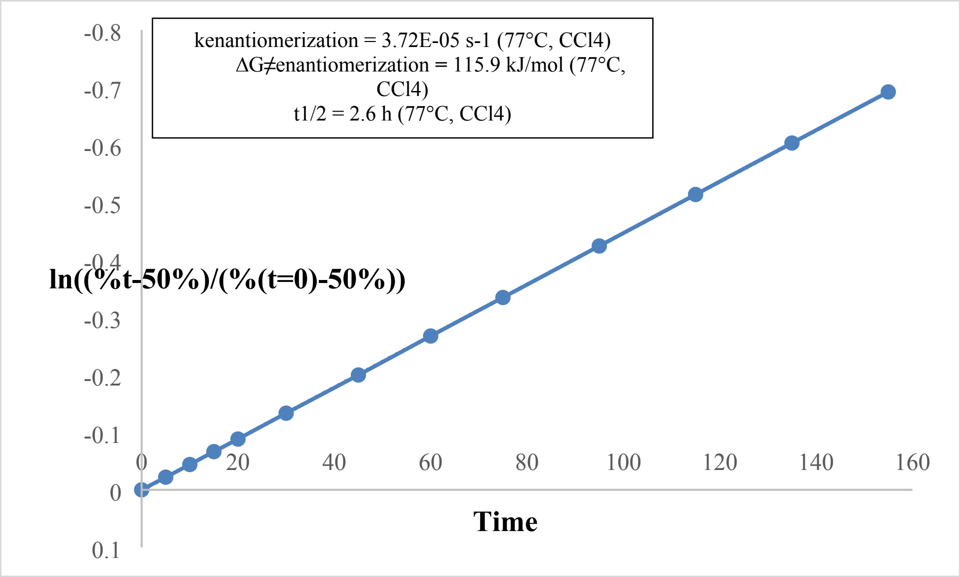


Figure S10. Kinetics of **3b** enantiomerization in CCl_4 at 77°C

About 0.3 mg of the 2nd eluted enantiomer **12b** is heated in about 15 mL of diphenyl ether at 228 °C. 0.02 ml is taken and then injected on Chiralpak ID, hexane / iPrOH / dichloromethane (70/15/15). The percentage decrease of the 2nd eluted enantiomer **12b** is monitored.

Table S5. Percentage of **12b** at different time in diphenyl ether

Time (h)	% 2nd eluted enantiomer (**12b**)	ln (1/(1-2X))
0	99.53	0.009444460
12	99.40	0.012072581
24	98.93	0.0216323
36	98.59	0.028605257

49	98.20	0.036663984
60	98.06	0.039572775
72	97.49	0.051503843
84	97.15	0.058688996
96	96.77	0.066781034
111	96.55	0.071496002
120	96.28	0.077313103

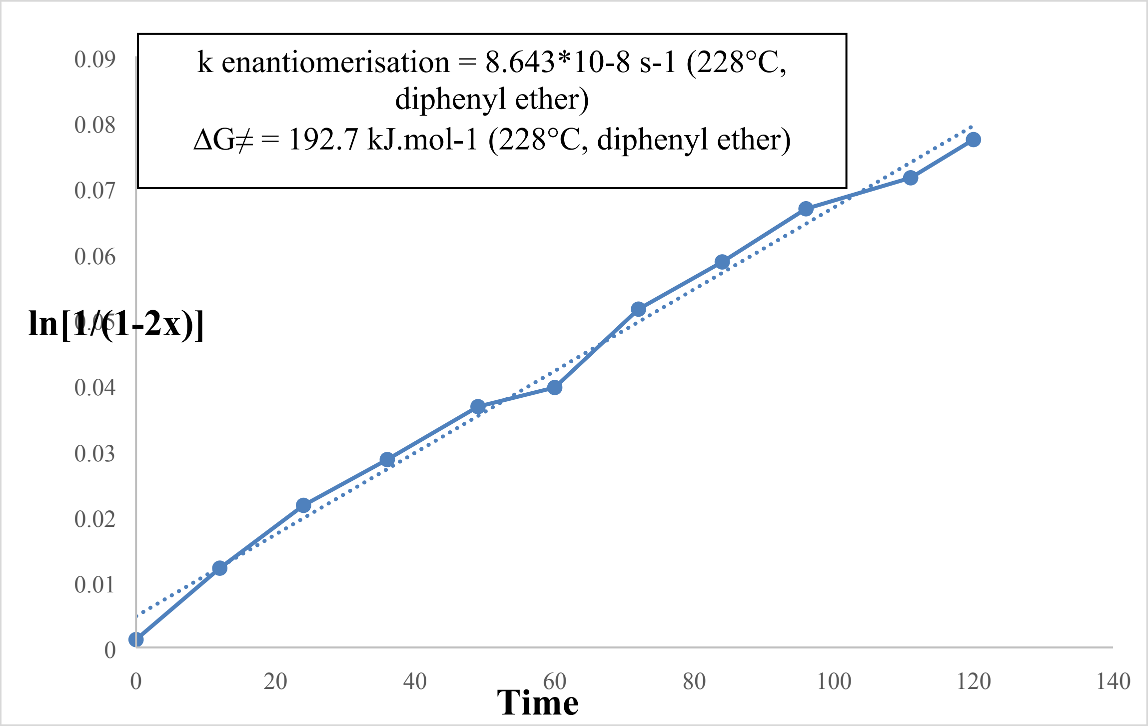


Figure S11. Kinetics of **12b** enantiomerization in diphenyl ether at 228°C

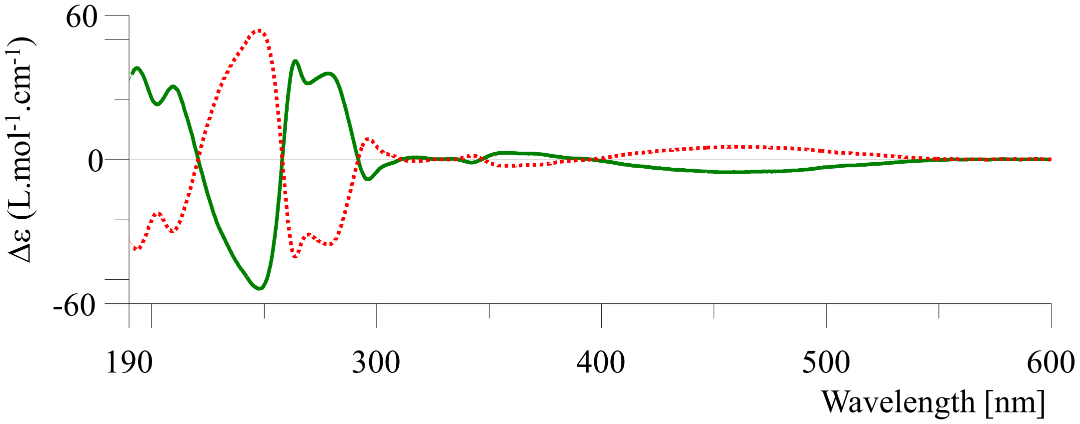
8. Electronic circular dichroism

ECD and UV spectra were measured on a JASCO J-815 spectrometer equipped with a JASCO Peltier cell holder PTC-423 to maintain the temperature at 25.0 ± 0.2°C. A CD quartz cell of 1 mm of optical pathlength was used. The CD spectrometer was purged with nitrogen before recording each spectrum, which was baseline subtracted.

The baseline was always measured for the same solvent and in the same cell as the samples.

The spectra are presented without smoothing and further data processing.

Acquisition parameters: 0.1 nm as intervals, scanning speed 50 nm/min, band width 2 nm, and 3 accumulations per sample.



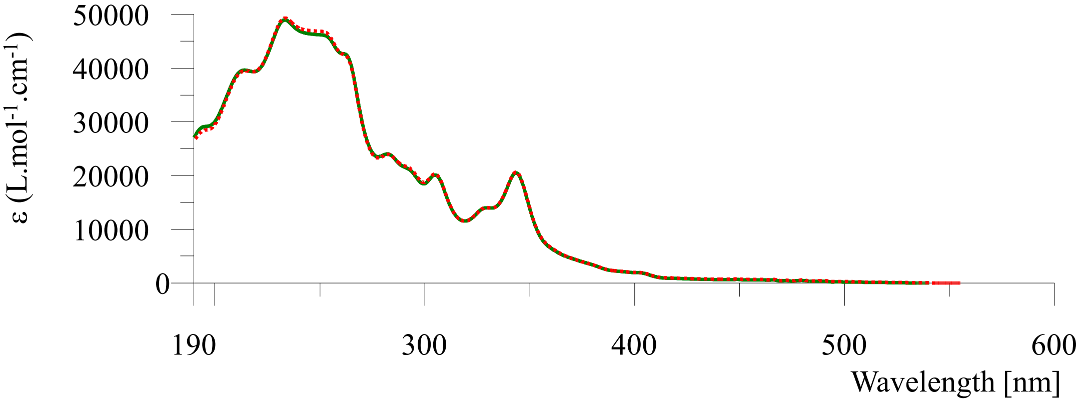


Figure S12. ECD and UV-vis of **3a** and **3b** in ACN (1st eluted enantiomer(**3a**): green solid line, concentration = 0.335 mmol.L^{-1} in acetonitrile. 2nd eluted enantiomer(**3b**): red dotted line, concentration = 0.333 mmol.L^{-1} in acetonitrile).

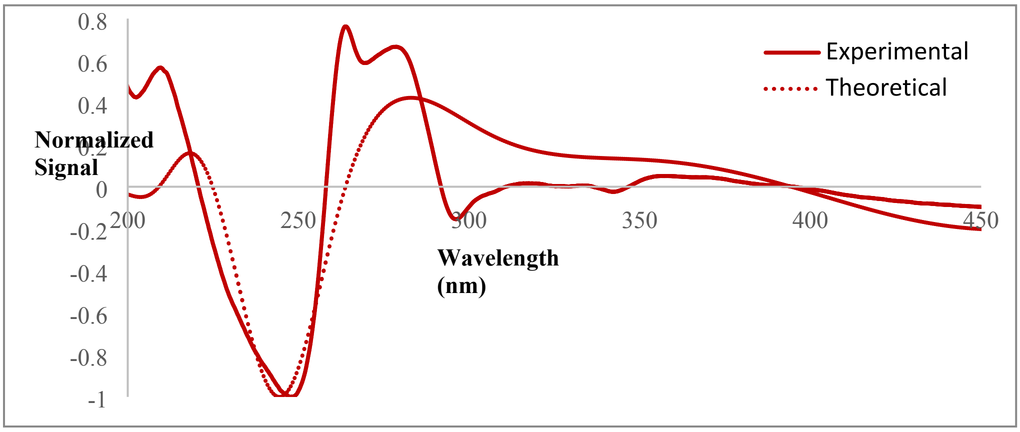


Figure S13. Experimental (1st eluted) and TD-CAMB3LYP/Def2-TZVP//B97-D/Def2-TZVPP ECD spectra of **3.**

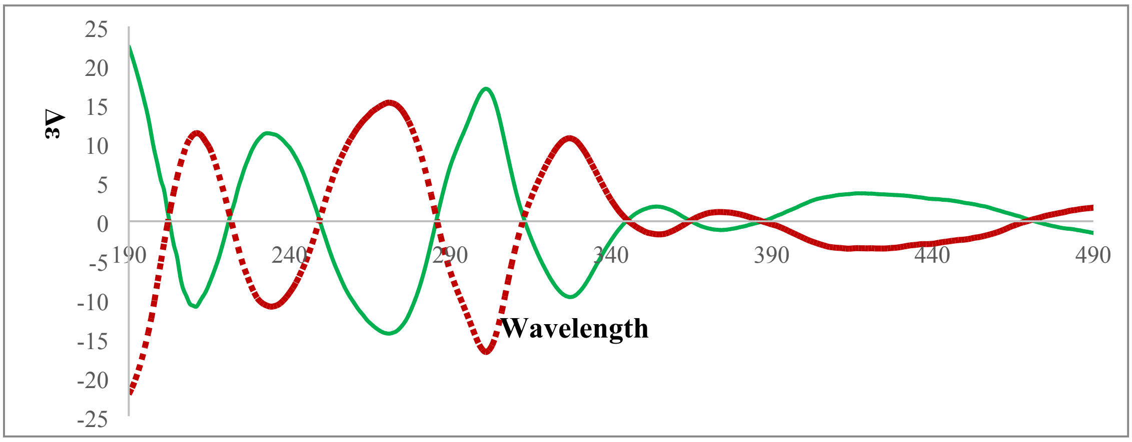


Figure S14. ECD spectra of **12a** and **12b** (1st eluted enantiomer: green solid line. 2nd eluted enantiomer: red dotted line).

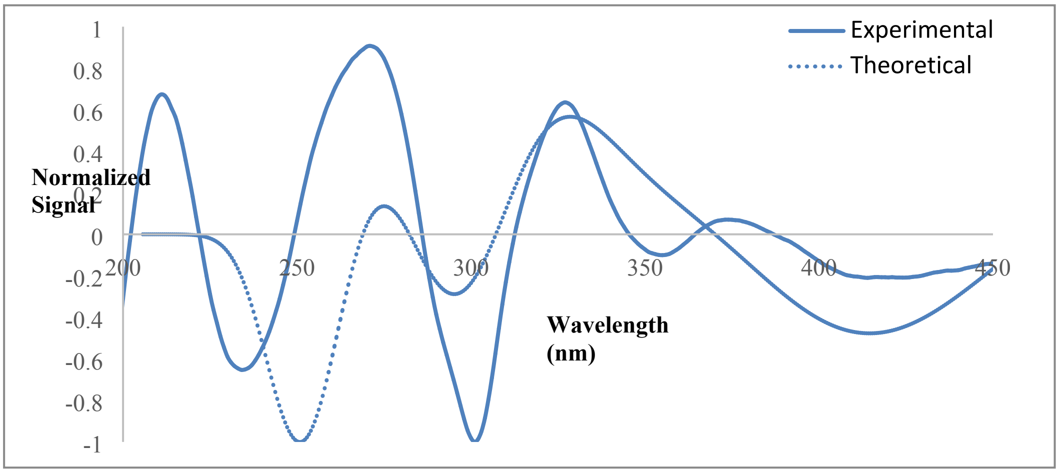


Figure S15. Experimental (2nd eluted) and TD-CAMB3LYP/Def2-TZVP//B97-D/Def2-TZVPP ECD spectra of **12.**

9. Vibrational circular dichroism

The VCD spectra were measured on the BioTools Chiral IR-2X (Dual PEM) with 300 µm cell, $CHBr_3$ as solvent.

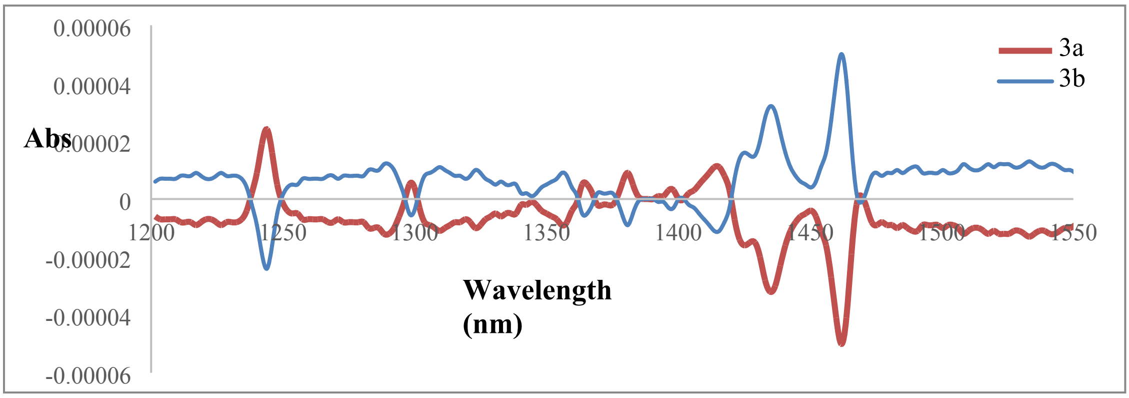


Figure S16. VCD spectra of **3a**/**3b**

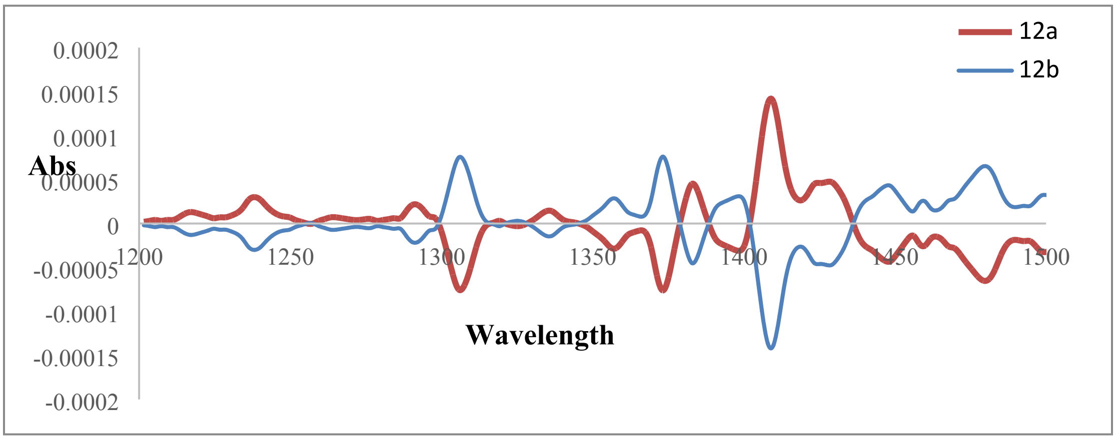


Figure S17. VCD spectra of **12a**/**12b**

10. X-ray crystal structure

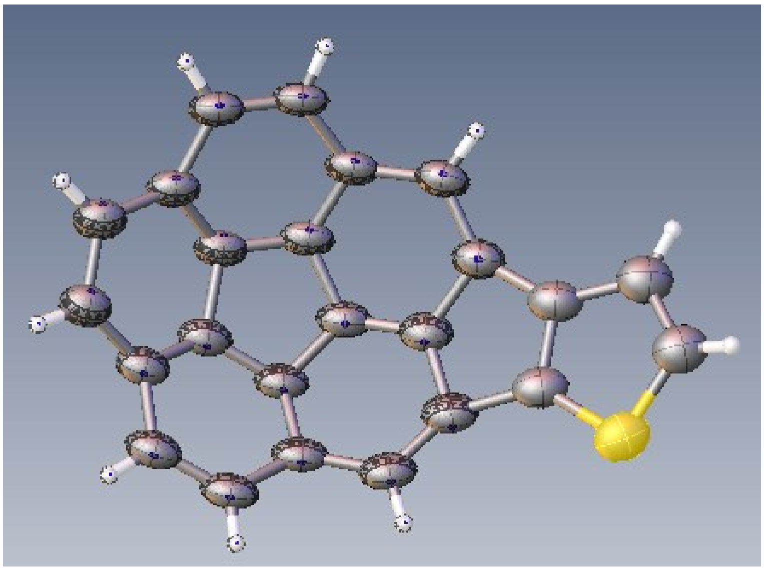


Figure S18. Crystal structure of mono thiophene-indenocorannulene **3**

Table 4-9. Crystal data of mono thiophene-indenocorannulene **3**

Identification code	**3**
Empirical formula	$C_{24}H_{10}S$
Formula weight	330.38
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	$Pna2_1$
a/Å	23.621(3)
b/Å	16.2578(9)
c/Å	3.8910(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1494.2(2)
Z	4
ρ_{calc}g/cm^3	1.469
μ/mm^{-1}	1.910
F(000)	680.0
Crystal size/mm^3	0.02 × 0.05 × 0.10
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.256 to 133.766
Index ranges	$-28 \leq h \leq 27$, $-19 \leq k \leq 19$, $-4 \leq l \leq 4$
Reflections collected	3485

Independent reflections	3485 [R_{int} = ?, R_{sigma} = 0.0147]
Data/restraints/parameters	3485/4964/345
Goodness-of-fit on F^2	1.229
Final R indexes [I>=2σ (I)]	$R_1 = 0.0895$, $wR_2 = 0.2712$
Final R indexes [all data]	$R_1 = 0.1030$, $wR_2 = 0.2863$
Largest diff. peak/hole / e Å^{-3}	0.28/-0.26
Flack parameter	0.45(10)

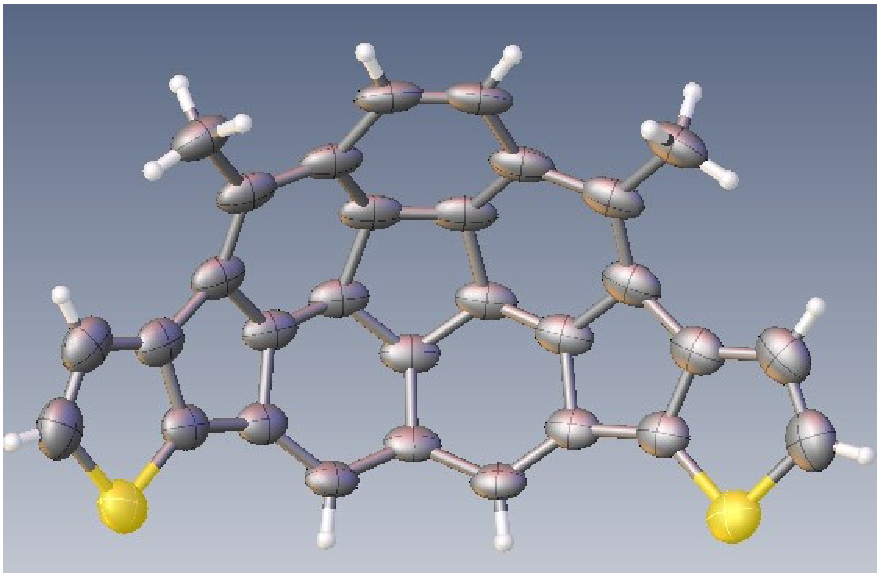


Figure S19. Crystal structure of dimethyl thiophene-diindenocorannulene **6**

Table 4-10. Crystal data of dimethyl thiophene-diindenocorannulene **6**

Identification code	**6**
Empirical formula	$C_{30}H_{14}S_2$
Formula weight	438.58
Temperature/K	159.99(10)
Crystal system	orthorhombic
Space group	*Pnma*
a/Å	8.06299(16)
b/Å	24.9602(6)
c/Å	9.47610(18)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1907.10(7)
Z	4
ρ_{calc}g/cm^3	1.5274

μ/mm^{-1}	2.653
F(000)	908.9
Crystal size/mm^3	0.04 × 0.03 × 0.01
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.08 to 148.7
Index ranges	$-10 \le h \le 9$, $-31 \le k \le 27$, $-6 \le l \le 11$
Reflections collected	9656
Independent reflections	1926 [R_{int} = 0.0326, R_{sigma} = 0.0244]
Data/restraints/parameters	1926/0/149
Goodness-of-fit on F^2	1.075
Final R indexes [I>=2σ (I)]	R_1 = 0.0508, wR_2 = 0.1335
Final R indexes [all data]	R_1 = 0.0601, wR_2 = 0.1411
Largest diff. peak/hole / e Å^{-3}	0.31/-0.36

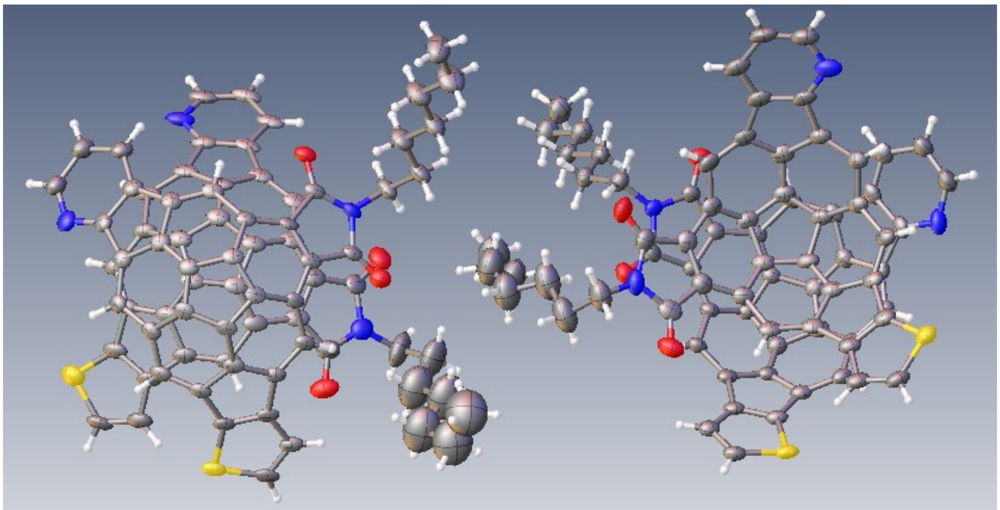


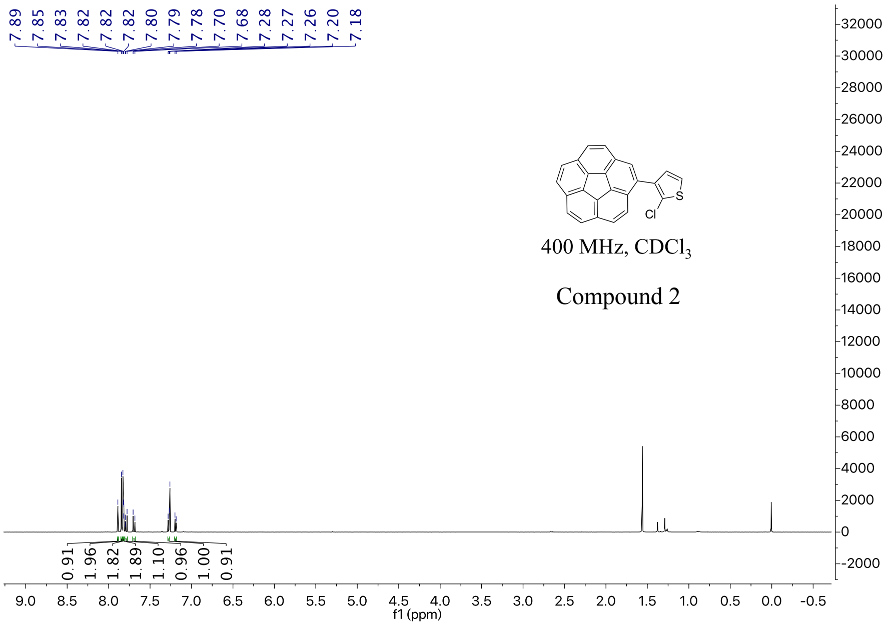
Figure S20. Crystal structure of **12a**

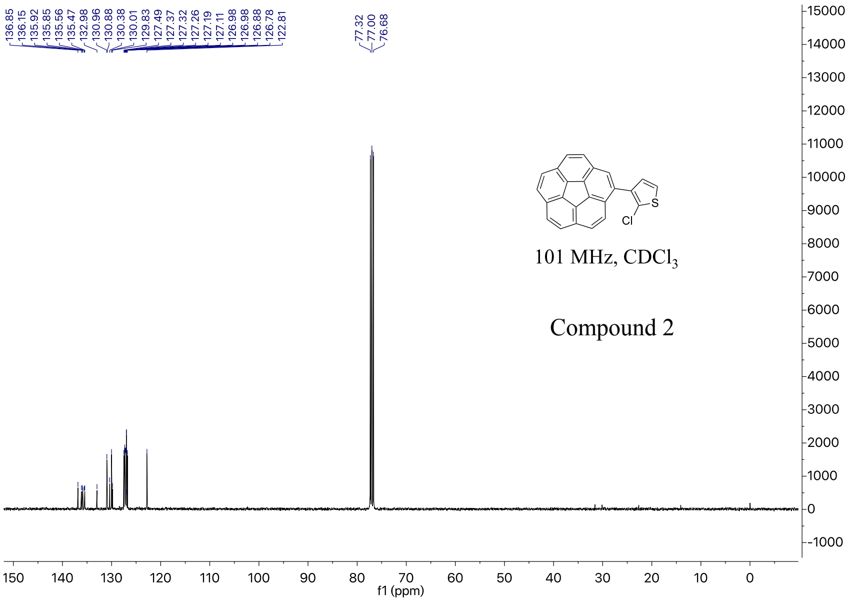
Table 4-11. Crystal data of **12a**

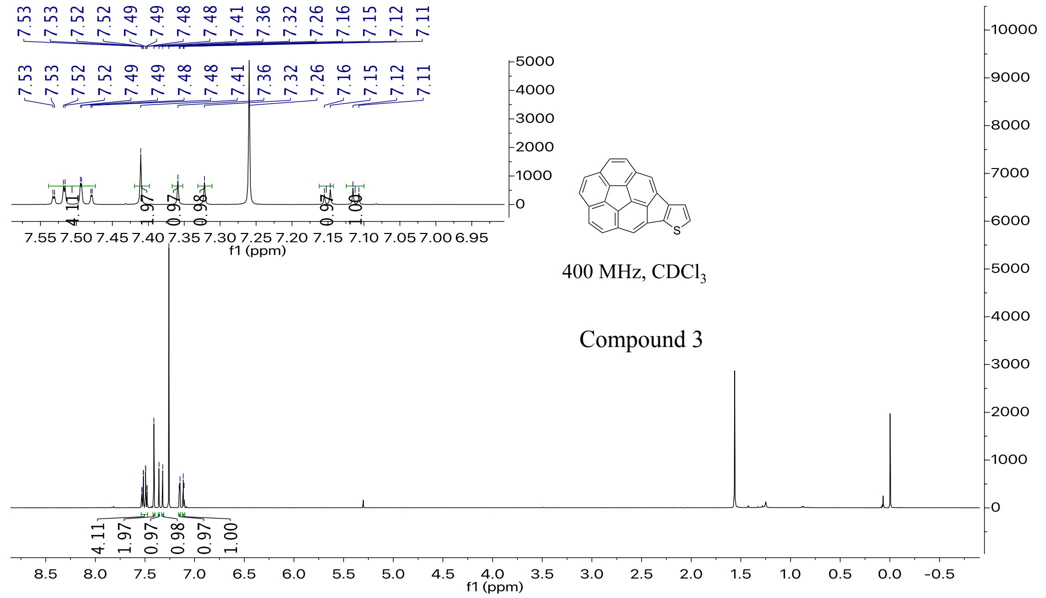
Identification code	**12a**
Empirical formula	$C_{38}H_{24}N_2O_2S$
Formula weight	572.65
Temperature/K	115.00(14)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	7.76820(10)
b/Å	24.6364(4)
c/Å	29.2589(5)
α/°	90
β/°	94.119(2)
γ/°	90

Volume/Å^3	5585.12(15)
Z	8
ρ_{calc}g/cm^3	1.362
μ/mm^{-1}	1.340
F(000)	2384.0
Crystal size/mm^3	0.09 × 0.06 × 0.03
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	4.694 to 133.202
Index ranges	$-9 \leq h \leq 9$, $-29 \leq k \leq 29$, $-34 \leq l \leq 34$
Reflections collected	94635
Independent reflections	19718 [R_{int} = 0.1337, R_{sigma} = 0.0885]
Data/restraints/parameters	19718/2854/1549
Goodness-of-fit on F^2	1.053
Final R indexes [I>=2σ (I)]	R_1 = 0.0889, wR_2 = 0.2530
Final R indexes [all data]	R_1 = 0.1196, wR_2 = 0.2780
Largest diff. peak/hole / e Å^{-3}	0.62/-0.44
Flack parameter	0.06(4)

11. ^{1}H-NMR and ^{13}C-NMR

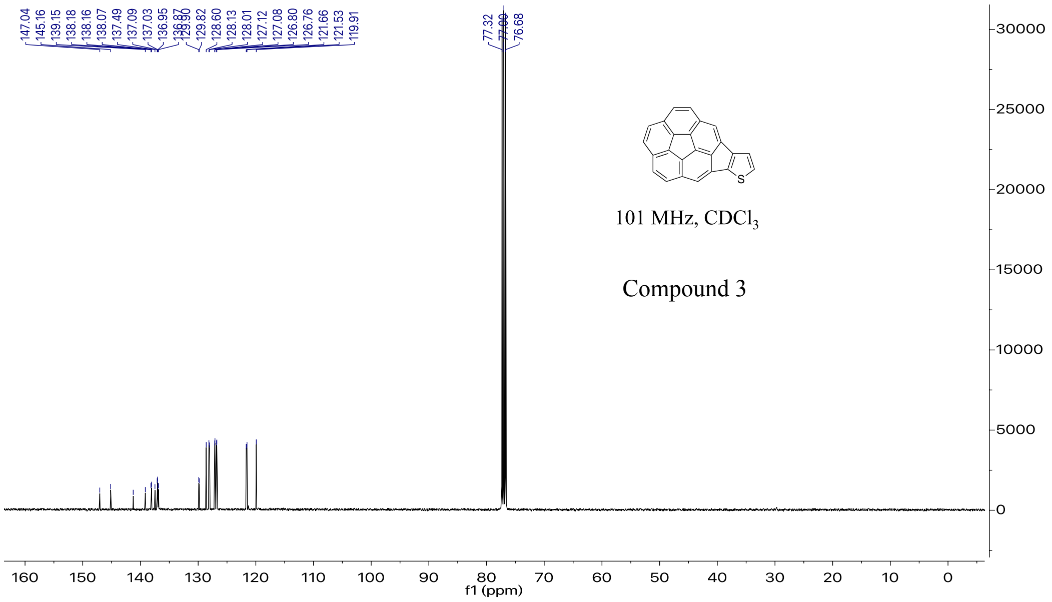






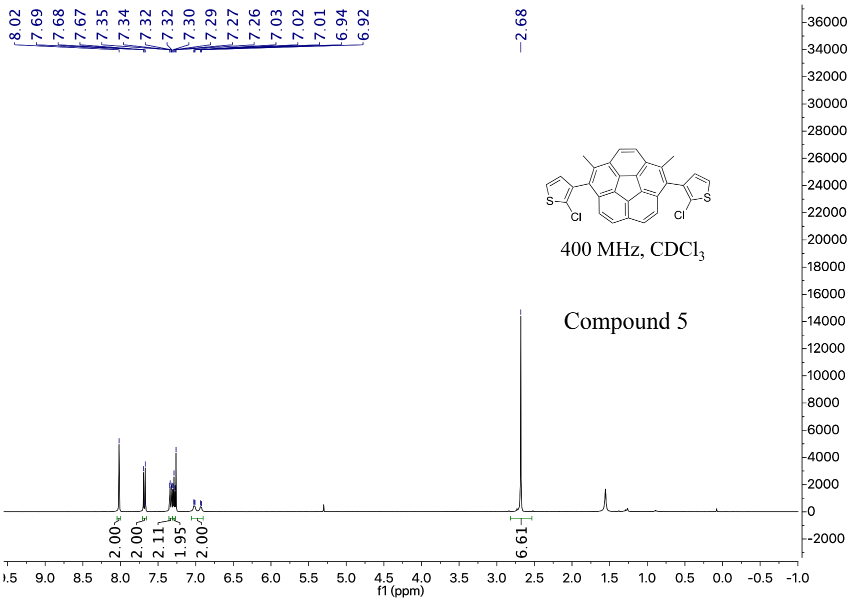
400 MHz, $CDCl_3$

Compound 3



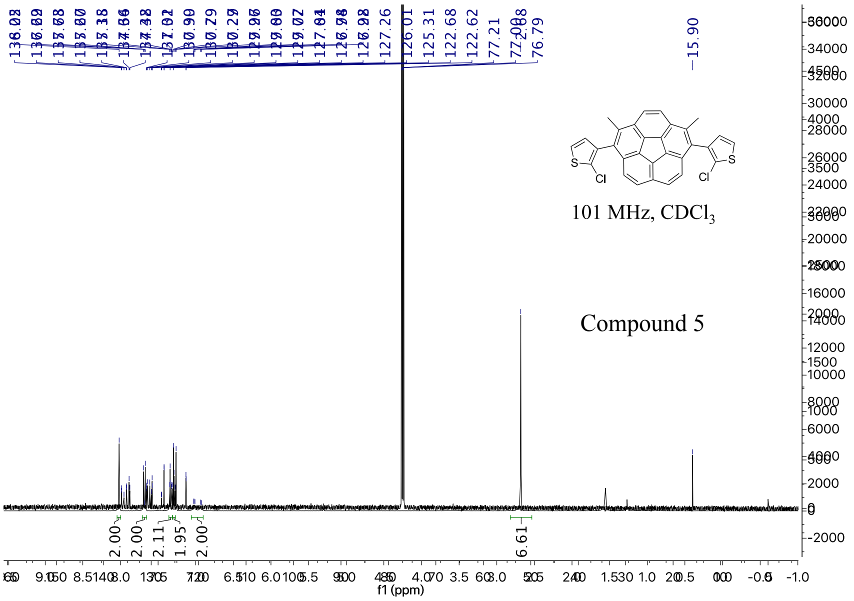
101 MHz, $CDCl_3$

Compound 3



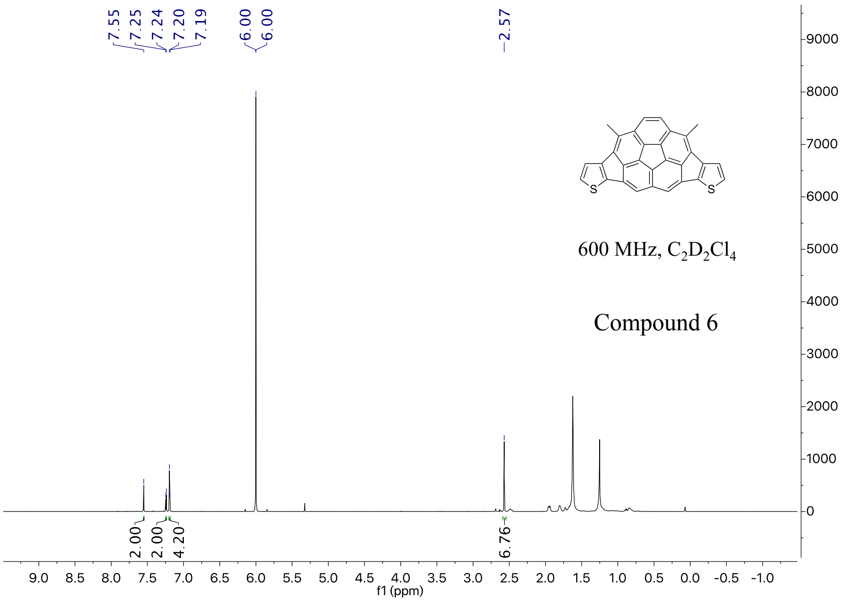
400 MHz, $CDCl_3$

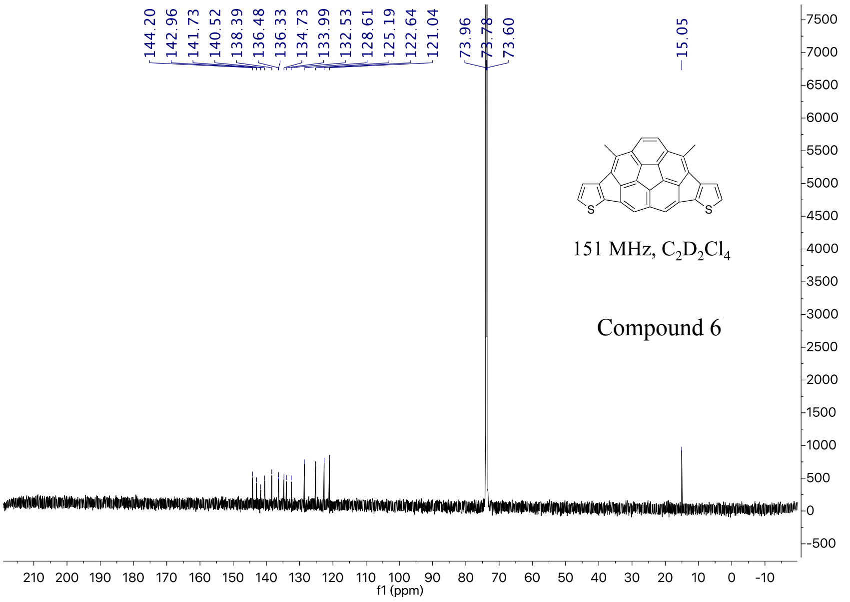
Compound 5

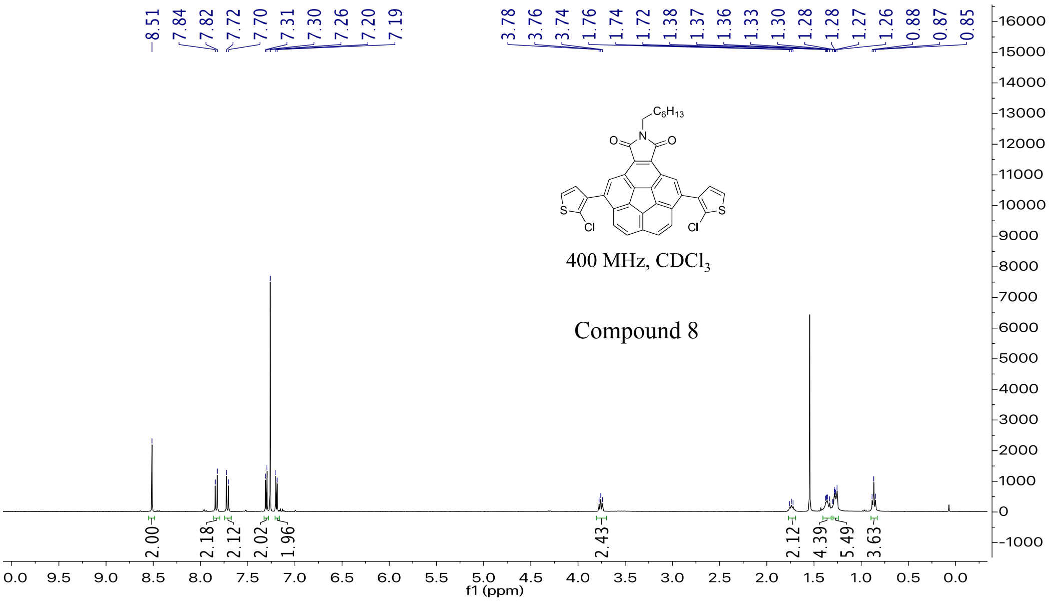


101 MHz, $CDCl_3$

Compound 5

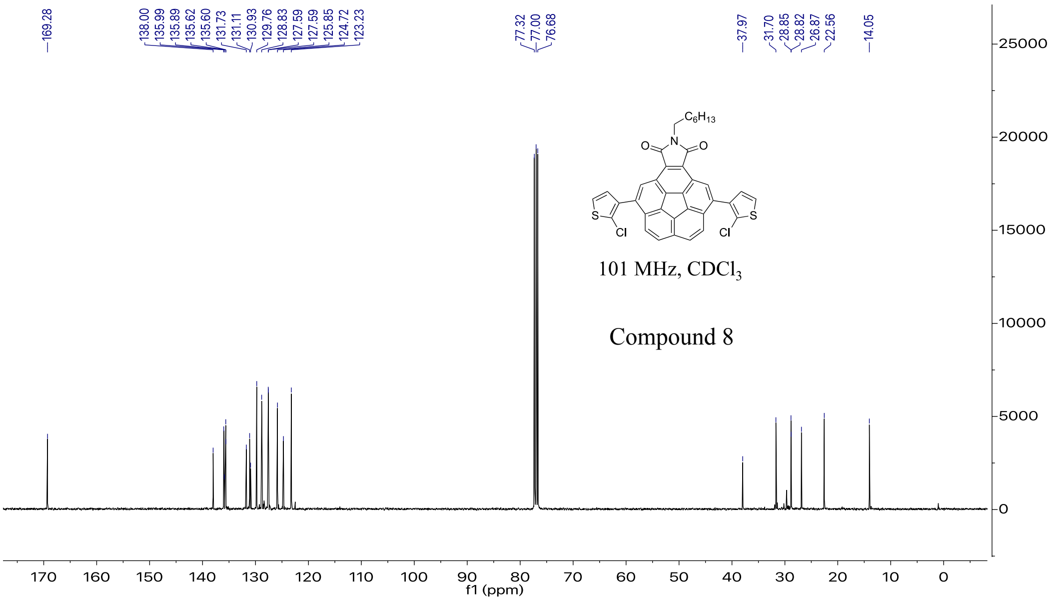

7.55
7.25
7.24
7.20
7.19
6.00
6.00
2.57
2.00
2.00
4.20
6.76
600 MHz, $C_2D_2Cl_4$
Compound 6
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
S
S


144.20
142.96
141.73
140.52
138.39
136.48
136.33
134.73
133.99
132.53
128.61
125.19
122.64
121.04
73.96
73.78
73.60
15.05
151 MHz, $C_2D_2Cl_4$
Compound 6
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
S
S



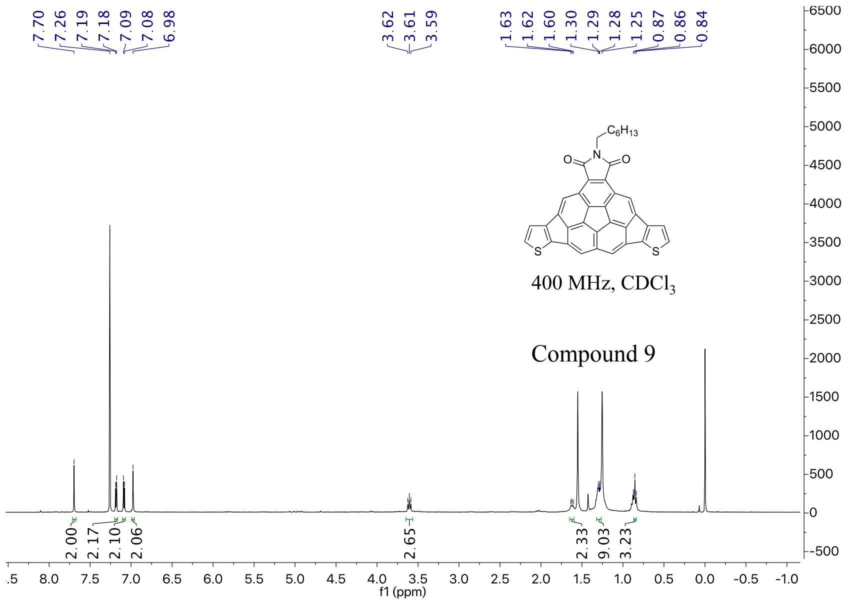
400 MHz, $CDCl_3$

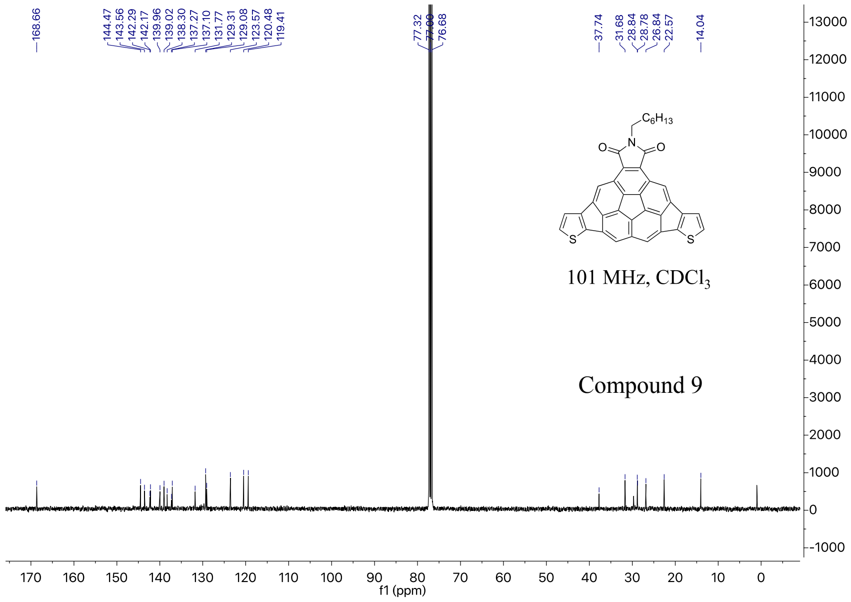
Compound 8

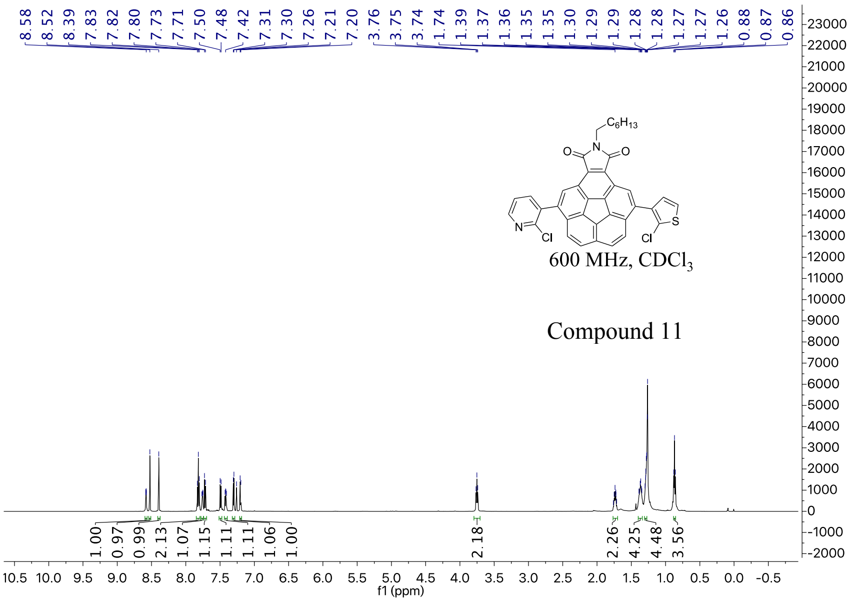


101 MHz, $CDCl_3$

Compound 8

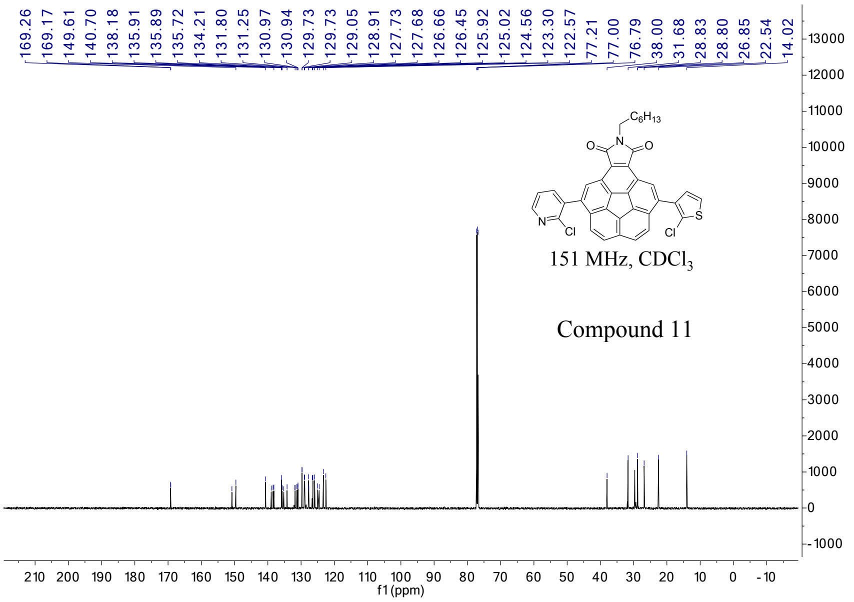

7.70
7.26
7.19
7.18
7.09
7.08
6.98
3.62
3.61
3.59
1.63
1.62
1.60
1.30
1.29
1.28
1.25
0.87
0.86
0.84
C6H13
N
O
O
S
S
400 MHz, CDCl3
Compound 9
2.00
2.17
2.10
2.06
2.65
2.33
9.03
3.23
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500


168.66
144.47
143.56
142.29
142.17
139.96
139.02
138.30
137.27
137.10
131.77
129.31
129.08
123.57
120.48
119.41
77.32
77.00
76.68
37.74
31.68
28.84
28.78
26.84
22.57
14.04
C6H13
N
O
O
S
S
101 MHz, CDCl3
Compound 9
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000



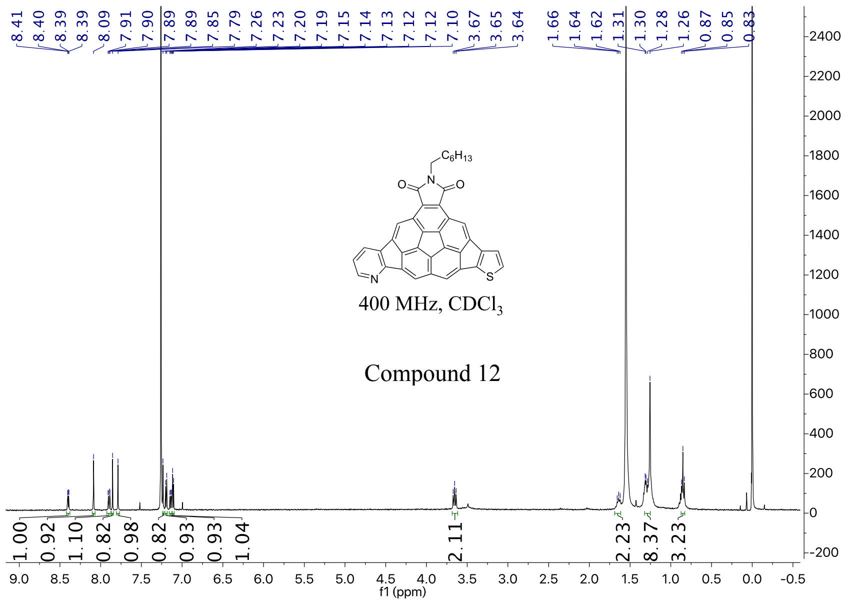
600 MHz, $CDCl_3$

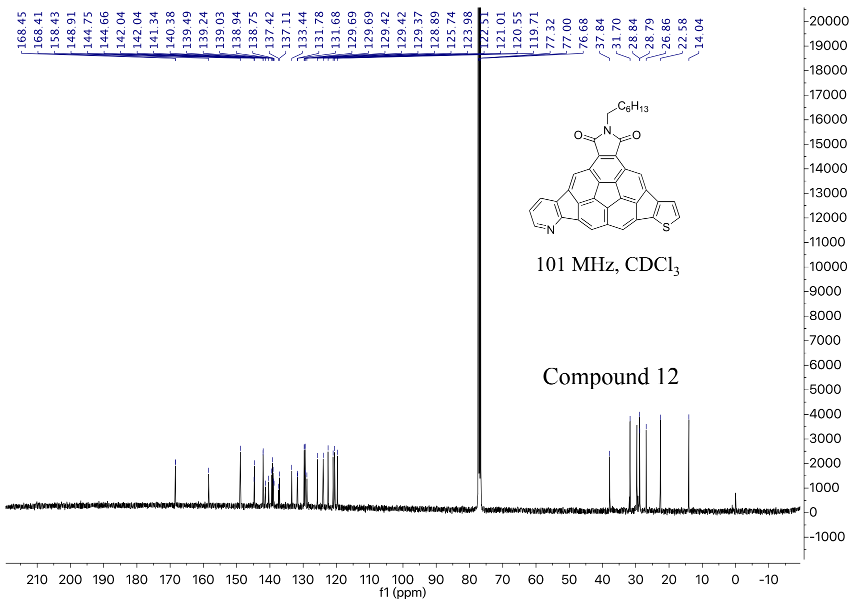
Compound 11



151 MHz, $CDCl_3$

Compound 11





12. Onset wavelength (λ_{onset}) determination

Onset wavelength is found by drawing a trend line on the UV absorption spectrum and a baseline, then the wavelength at the intercept point was used as λ_{onset}.

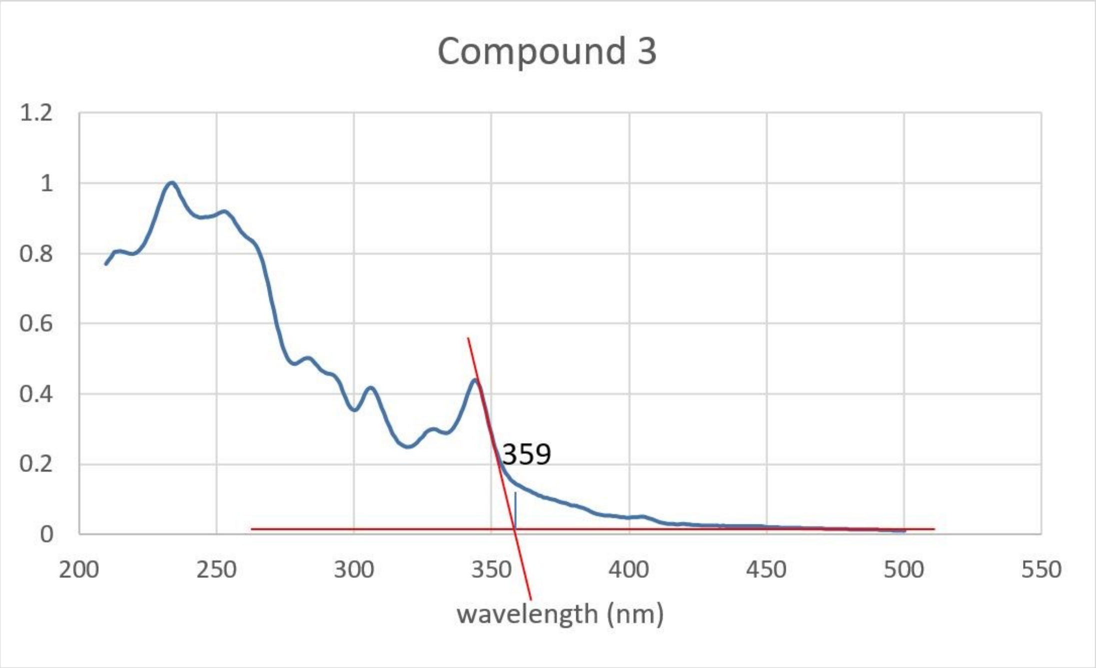


Figure S21. Onset wavelength determination of **3**

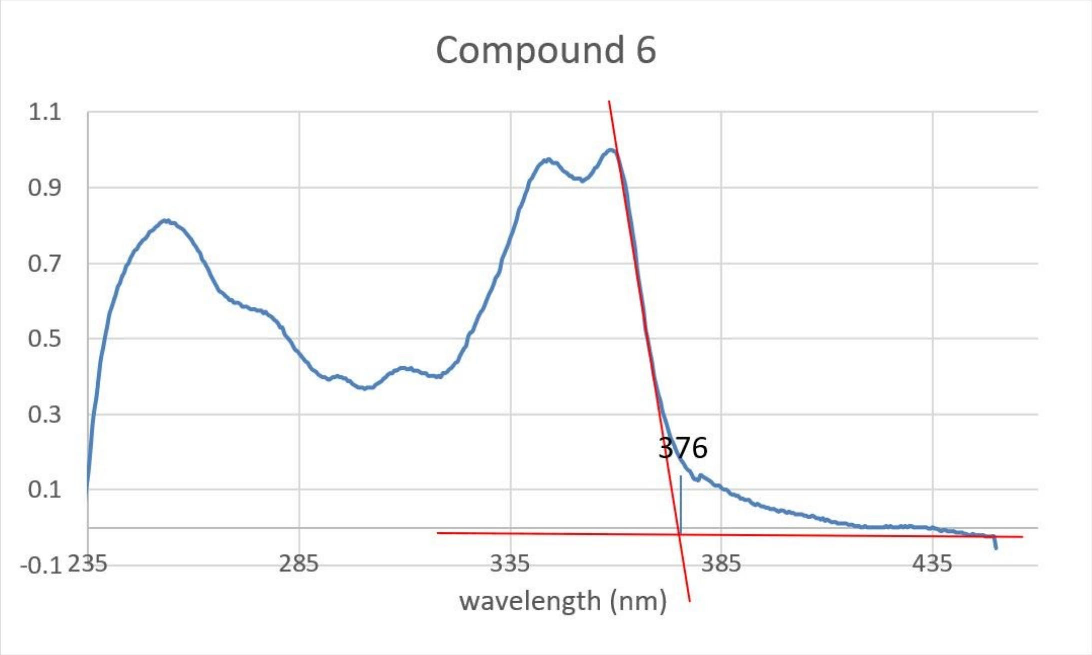


Figure S22. Onset wavelength determination of **6**

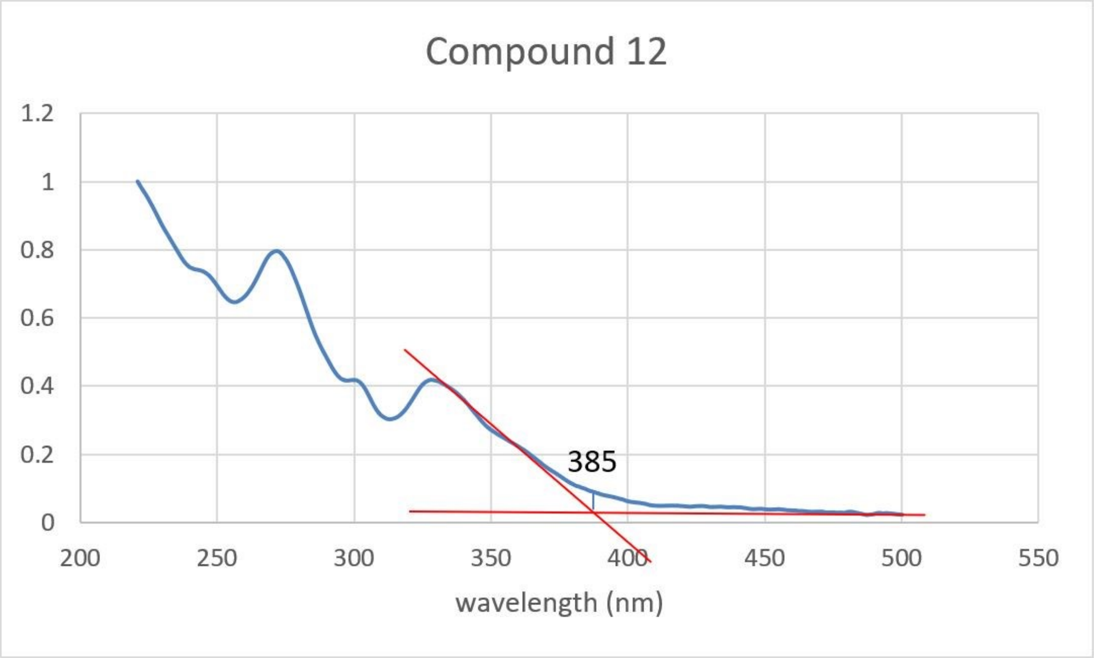


Figure S22. Onset wavelength determination of **12**

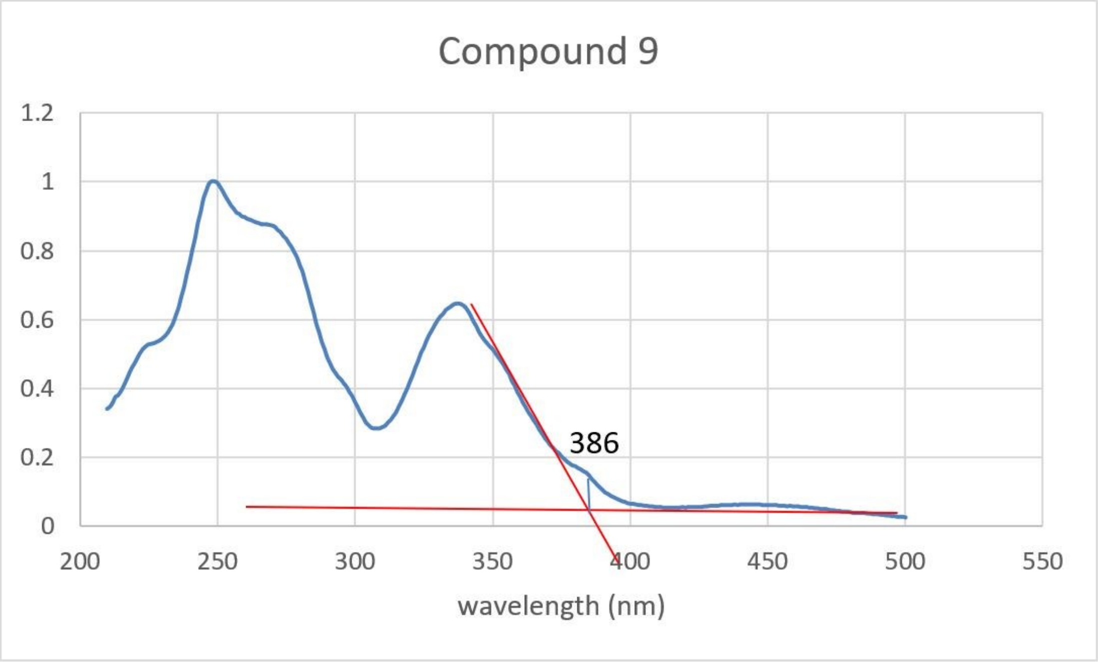


Figure S23. Onset wavelength determination of **9**

13. Literature

(1) S. Grimme, *J. Comput. Chem.* **2006**, *27*, 1787-1799.

(2) S. Grimme, *J. Chem. Phys.* **2006**, *124*, 034108-034115.

(3) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, 7, 3297-3305.

(4) J. D. Chai, M. Head-Gordon, *J. Chem. Phys.* **2008**, *128*, 084106.

(5) W. Strumm, J. J. Morgan, *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*, Wiley-Interscience, New York, 1996.

(6) A. Klamt, G. Schüürmann, *J. Chem. Soc. Perkin Trans.* **1993**, *2*, 799.

(7) K. K. Baldridge, A. Klamt, *J. Chem. Phys.* **1997**, *106*, 6622-6633.

(8) A. Klamt, V. Jonas, T. Bürger, C. W. Lohrenz *J. Phys. Chem.* **1997**, *102*, 5074.

(9) M. D. Hanwell, D. E. Curtis, D. C. Lonie, T. Vandermeersch, E. Zurek, G. R. Hutchison, *J. Cheminform*. **2012**, *4*, 17.

(10) R. Dennington, T. Keith, J. Millam, *GaussView, Version 5*, Semichem Inc., Shawnee Mission, KS, 2009.