Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Panchromatic Cross-Conjugated π-Bridge NIR Dyes for DSCs

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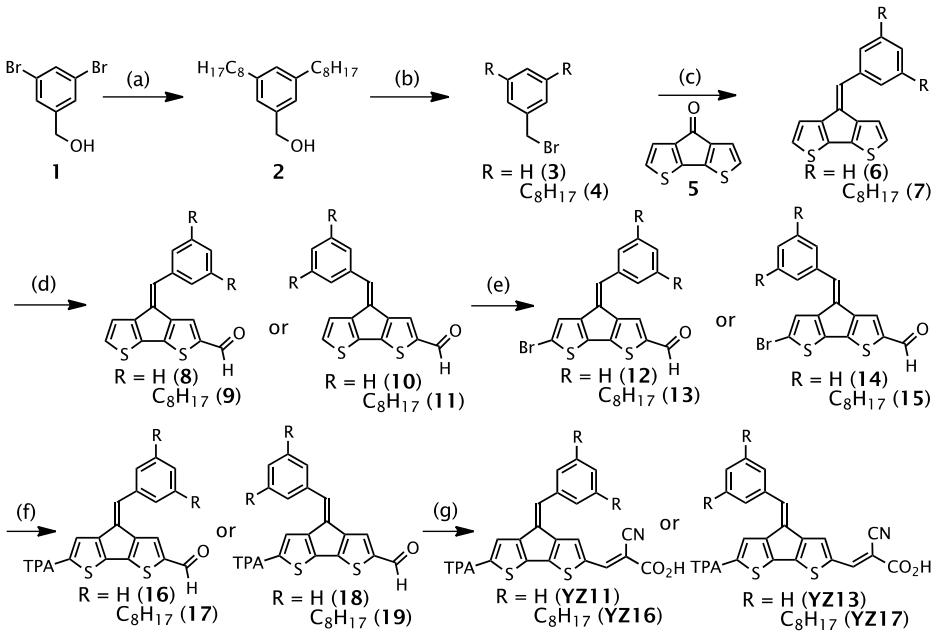
1. Synthetic Data.

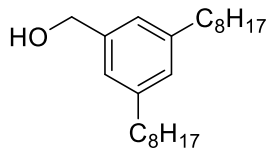
General Information: All commercially obtained reagents were used as received. 4,4,5,5 tetramethyl-2-{4-[N, N -bis(4-hexyloxyphenyl)amino]phenyl}jj-1,3,2-dioxaborolane,[1] 4H-cyclopenta[2,1-b:3,4-b']-dithiophen-4-one (CDTC=O),[2] 4-benzylidene-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene[3] and *n*-octylzinc bromide [4] were made according to previously reported literature procedures. Thin-layer chromatography (TLC) was conducted with Sorbtech silica XHL TLC plates and visualized with UV. Flash column chromatography was performed with Silicycle ultrapure silica gels P60, 40-63 μm (230-400 mesh). Reverse phase column chromatography was performed with premium grade C18 silica gel from Sorbent technologies. ^{1}H and ^{13}C NMR spectra were recorded on Bruker Advance 300 (300 MHz), Bruker Advance DRX 500 (500 MHz) and Bruker Ascend 600 (600 MHz) spectrometers and are reported in ppm using solvent as an internal standard (chloroform-*d* at 7.26 ppm, acetone-d_6 at 2.05 ppm, and methylene chloride-d_2 at 5.32 ppm). NMR data is reported as s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, b = broad, ap = apparent, dd = doublet of doublets, and coupling constant(s) are in Hertz, followed by integration information. UV−Vis-NIR spectra were measured with a Cary 5000 instrument. HRMS spectra were obtained with a QTOF HRMS utilizing nanospray ionization. The mass analyzer was set to the 400−2000 Da range. HPLC measurement were taken using an Agilent 1100A HPLC instrument, equipped with an Agilent Eclipse Plus C18 column and UV-vis detector. 90% isopropanol: 10% water was used as the mobile phase at 0.3 ml/min for all the measurement.

* For the case of the final dyes, many times heavily alkylated dyes with nitrogen containing functionality and carboxylic acids give peak broadened NMR spectrum in a host of solvents at a host of temperatures, with and without base or acid. The NMRs of some of the final dyes in this manuscript show significant peak broadening in many cases. As a measure of purity, HPLC analysis for final dyes and copies of HPLC data and NMR files are included in the supporting information to illustrate the line broadening issue. While we cannot confirm the dye purity definitively by NMR due to the broadening, only the dye related peaks broadens in these spectrum which allows us to see clearly resolved peaks for any non-dye impurities. The purpose of the NMRs in these cases is to observe any impurities, and the HPLC and TLC are then used to confirm only one dye is present.

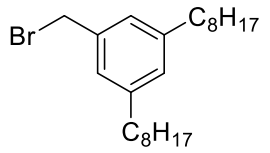


Scheme S1. Synthetic route to **YZ11**, **YZ13**, **YZ16** and **YZ17**.

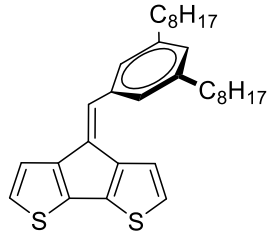
(a) Pd-PEPPSI-IPr (3.5 mol%), toluene/THF (1:3, 0.11 M), n-octylzinc bromide (0.5 M, 3.5 equiv.), r.t. to 60ºC, 62%. (b) CH_2Cl_2 (0.25 M), PBr_3 (1.35 equiv.), r.t., 16 hours. 73% (c) PPh_3 (1.04 equiv.), toluene (0.1 g/mL), 115 °C, 12 h; then **5** (0.95 equiv.), sodium ethoxide (~1.5 equiv.), EtOH (0.15-0.2 M), 60 °C, 16 h, **6:** 76%, **7:** 60%. (d) $POCl_3$ (1.2 equiv.), DMF (1.2 equiv.), DCM (0.39 M), r.t., overnight, **8:** 40%, **10:** 41%, **9:** 50%, **11:** 59%. (e) NBS (1.1 equiv.), DMF (0.3 M), r.t., overnight, **12:** 96%, **14:** 100%, **13:** 95%, **15:** 91%. (f) TPA-Bpin (1.2 equiv.), Pd(PPh3)4 (10 mol%), aq. K_2CO_3 (2.0 M), THF (0.025 M), reflux, overnight, **16:** 91%, **18:** 69%, **17:** 100%, **19:** 83%. (g) cyanoacetic acid (3.0 equiv.), piperdine (7.0 equiv.), $CHCl_3$ (0.25 M), 90ºC, 10 hours, **YZ11:** 87%, **YZ13:** 64%, **YZ16:** 20%, **YZ17:** 20%.



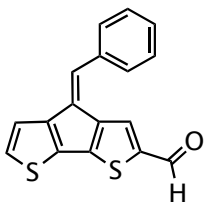
3,5-dioctylbenzyl alcohol (2): To a solution of 3,5-dibromobenzyl alcohol (**2**) (3.02 g, 11.4 mmol) and Pd-PEPPSI-IPr (0.235 g, 0.346 mmol,~3.5 mol%) in toluene (30 mL) under N_2 was added a THF solution (~0.50 M) of *n*-octylzinc bromide (81.0 mL, 40.5 mmol,~3.5 equiv.) dropwise at room temperature. After stirring for 16 h at room temperature, the reaction was heated to 60 °C and stirred for an additional 2 h. Upon cooling, the reaction mixture was quenched with saturated NH_4Cl (150 mL) and filtered through a Buchner funnel. The biphasic mixture was then poured into a separatory funnel, the water layer removed, and the organic phase washed with 3 × 100 mL 1 M Na_3EDTA (3 equiv. NaOH with EDTA), water (1 × 100 mL), and brine (1 × 100 mL). The organic solution was then dried with $MgSO_4$ and filtered through Celite. Volatiles were removed in vacuo and purification by flash chromatography on silica gel (hexanes to hexanes : ethyl acetate = 90 : 10 as the eluent) afforded a colorless oil (2.35 g, 62%). ^{1}H NMR (600 MHz, acetone-d_6) δ = 7.00 (s, 2H), 6.90 (s, 1 H), 4.57 (d, *J* = 5.4 Hz, 2H), 4.01 (t, *J* = 5.4 Hz, 1H), 2.58 (t, *J* = 7.8 Hz, 4H), 1.61 (p, 4H), 1.34 (m, 20H), 0.89 (t, *J* = 6.7 Hz, 6H). ^{13}C NMR (151 MHz, acetone-d_6) δ = 206.0, 143.3, 143.2, 127.9, 124.9, 64.9, 36.6, 32.7, 32.4, 30.2, 30.1, 30.1, 29.8, 23.3, 14.4. IR (neat, cm^{-1}) 3308, 2955, 2923, 2853, 1605, 1458, 1378, 1161, 1020, 870, 714. HRMS (ESI) *m/z* calc'd for $C_{23}H_{40}OCs$ $[M+Cs]^+$ 465.2134, found 465.2123.



3,5-dioctylbenzyl bromide (4): To a solution of 3,5-dibromobenzyl alcohol (**2**) (1.93 g, 5.80 mmol) in CH_2Cl_2 (20 mL) under N_2 at 0°C was added PBr_3 (0.750 mL, 7.90 mmol,~ 1.35 equiv.) dropwise. The reaction mixture was allowed to warm slowly to room temperature. After stirring 16 h at room temperature the reaction was cooled to 0 °C, quenched with DI water, and transferred to a separatory funnel. The organic layer was washed with saturated $NaHCO_3$ (1 x 50 mL), water (2 x 50 mL), and brine (1 x 50 mL). Drying over $MgSO_4$ followed by evaporation of the solvent *in vacuo* yielded a yellow oil. Purification was accomplished via flash chromatography (hexanes as the eluent), the product was isolated as a colorless oil (1.67 g, 73%). ^{1}H NMR (600 MHz, acetone-d_6) δ = 7.10 (s, 2H), 6.99 (s, 1 H), 4.58 (s, 2 H), 2.59 (t, *J* = 7.8 Hz, 4H), 1.62 (p, 4H), 1.34 (m, 20H), 0.88 (t, *J* = 6.7 Hz, 6H). ^{13}C NMR (151 MHz, acetone-d_6) δ = 144.1, 138.9, 129.5, 127.4, 36.3, 34.8, 32.6, 32.2, 30.2, 30.0, 30.0, 23.3, 14.4. IR (neat, cm^{-1}) 3025, 2922, 2852, 1062, 1493, 1453, 1377, 1209, 1030, 877, 756, 698. HRMS (ESI) *m/z* calc'd for $C_{23}H_{39}Br$ $[M]^+$ 394.2235, found 394.2394.

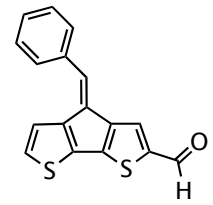


4-(3,5-dioctylbenzylidene)-4H-cyclopenta[2,1-b:3,4-b']dithiophene (7): In a nitrogen filled glove box, 3,5-dioctylbenzyl bromide (**4**) (1.23 g, 3.11 mmol) and triphenylphosphine (0.851 g, 3.24 mmol,~ 1.04 equiv.) were added to an oven-dried 40 mL reaction vial equipped with a stir bar. Toluene (15 mL) was added, the vessel sealed, and the mixture refluxed for 12 h. Upon cooling the solvent was removed *in vacuo* resulting in a waxy white solid. After pumping back into the glove box 4H-cyclopenta[2,1-b:3,4-b']dithiophen-4-one (**5**) (0.568 g, 2.95 mmol,~ 0.95 equiv.) and ethanol (20 mL) were added. The reaction mixture was heated to 60 °C and stirred for 0.5 h to dissolve the contents. A 60 °C solution of sodium ethoxide (0.323 g, 4.75 mmol,~1.53 equiv.) in ethanol was then added, resulting in an immediate color change to a deep red. After 16 h the reaction mixture was allowed to cool to room temperature, quenched with DI water (50 mL) and extracted with dichloromethane. The organic layer was washed with water (2 x 50 mL), brine (1 x 50 mL), then dried with $MgSO_4$. After gravity filtration the solvent was removed *in vacuo*. The compound was purified by flash chromatography (hexanes as the eluent) affording a red oil (0.916 g, 1.87 mmol, 60% yield) ^{1}H NMR (600 MHz, CD_2Cl_2) δ = 7.37 (s, 1H), 7.27 (s, 2H), 7.24 (d, *J* = 5.4 Hz, 1H), 7.15 (d, *J* = 4.8 Hz, 1H), 7.13 (d, *J* = 5.4 Hz, 1H), 7.05 (s, 1H), 7.00 (d, *J* = 5.4 Hz, 1H), 2.64 (t, *J* = 7.8 Hz, 4H), 1.66 (p, 4H), 1.2-1.4 (m, 20H), 0.89 (t, *J* = 6.7 Hz, 6H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ = 147.8, 143.6, 142.8, 140.8, 136.9, 136.6, 130.9, 130.4, 129.6, 127.5, 125.2, 124.1, 123.6, 120.2, 36.3, 32.4, 32.0, 29.9, 29.8, 29.7, 23.1, 14.3. IR (neat, cm^{-1}) 2950, 2921, 2812, 1628, 1594, 1464, 1370, 1092, 917, 877, 835, 803, 729, 667. HRMS (ESI) *m/z* calc'd for $C_{32}H_{42}S_2Cs$ $[M+Cs]^+$ 623.1782, found 623.1830.

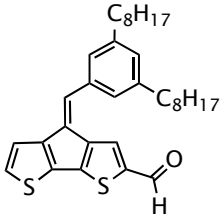


(*Z*)-4-benzylidene-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene-2 carbaldehyde (8): To a N_2 filled, flamed dried round bottom flask was added **6** (500 mg, 1.88 mmol),N,N-dimethylformamide (0.174 ml, 1.2 equiv.), dichloromethane (5.8 ml, 0.32 M), $POCl_3$ (0.21 ml, 1.2 equiv.) sequentially. Then, the round bottom flask was sealed with plastic cap and electric tape and reaction mixture was stirred at 0°C and warmed to room

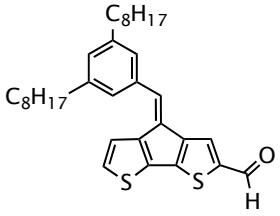
temperature overnight. During this time, the red solution turned into an orange solid. Saturated aqueous sodium acetate solution was added to quench the reaction and was stirred 2 hours at room temperature followed by extraction with dichloromethane and water. The organic layer was dried over anhydrous sodium sulfate and concentrated down to give an orange solid. The product was then purified through silica gel chromatography with 20% diethyl ether : hexane to give two different orange solid isomers (**8** and **10**). (222.0 mg, 0.75 mmol, 40%) ^{1}H NMR (500 MHz, $CDCl_3$) δ = 9.71 (s, 1H), 7.67 (s, 1H), 7.60 (d, *J* = 7.4 Hz, 2H), 7.55-7.41 (m, 3H), 7.45 (s, 1H), 7.37 (d, *J* = 4.8 Hz, 1H), 7.28 (d, *J* = 4.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 182.6, 150.9, 149.6, 142.6, 142.1, 135.8, 135.8, 132.0, 130.9, 130.0, 129.8, 129.4, 129.2, 128.8, 119.9. IR (neat, cm^{-1}): 3070, 3014, 2918, 2853, 2754, 2334, 2115, 1634, 1478, 1427, 1372, 1336, 1289, 1217, 1141, 1021, 922, 854. HRMS (ESI) *m/z* calc'd for $C_{17}H_{10}OS_2Cs$ $[M + Cs]^+$ 426.9228, found 426.9311.



(E)-4-benzylidene-4H-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene-2-carbaldehyde (10): This product was separated from the above reaction and purified through the same column as the other isomer. (**10**). (274 mg, 0.93 mmol, 50%). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.88 (s, 1H), 7.87 (s, 1H), 7.63 (d, *J* = 6.9 Hz, 2H), 7.58-7.39 (m, 4H), 7.23 (d, *J* = 4.8 Hz, 1H), 7.18 (d, *J* = 4.9 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 182.6, 146.9, 146.0, 143.3, 139.5, 135.8, 130.7, 129.9, 129.7, 129.1, 128.6, 128.4, 128.4, 123.2. IR (neat, cm^{-1}): 3359, 3180, 2931, 2875, 2789, 2656, 2334, 2109, 1642, 1484, 1435, 1373, 1345, 1202, 1147, 857. HRMS (ESI) *m/z* calc'd for $C_{17}H_{10}OS_2Cs$ $[M + Cs]^+$ 426.9228, found 426.9272.

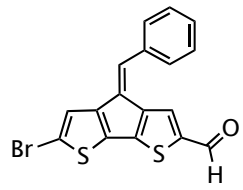


(Z)-4-(3,5-dioctylbenzylidene)-4H-cyclopenta[2,1-*b*:3,4-*b'*] dithiophene-2-carbaldehyde (9): The synthesis follows the same procedure as **8** except **7** was used in place of **6**. The crude mixture was purified through silica gel chromatography using 20% diethyl ether : hexane was the eluent to give two orange isomers. (94.3 mg, 0.13 mmol, 41%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 9.72 (s, 1H), 7.75 (s, 1H), 7.47 (s, 1H), 7.38 (d, *J* = 5.0 Hz, 1H), 7.30 (d, *J* = 5.0 Hz, 1H), 7.27 (s, 2H), 7.10 (s, 1H), 2.68 (t, *J* = 7.7 Hz, 4H), 1.86-1.60 (m, 4H), 1.57-1.18 (m, 20H), 0.92 (t, *J* = 6.5 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 182.4, 151.0, 149.4, 143.4, 143.2 142.5, 142.3, 135.6, 132.4, 131.8, 129.7, 129.6, 129.3, 127.3, 119.9, 35.9, 31.9, 31.6, 29.5, 29.5, 29.3, 22.7, 14.1. IR (neat, cm^{-1}): 3070, 3014, 2921, 2852, 2334, 2085, 1656, 1594, 1490, 1460, 1437, 1338, 1288, 1229, 1144. HRMS (ESI) *m/z* calc'd for $C_{33}H_{42}OS_2Cs$ $[M + Cs]^+$ 651.1732, found 651.1741.

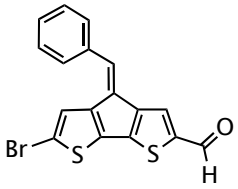


(E)-4-(3,5-dioctylbenzylidene)-4H-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene-2-carbaldehyde (11): This product was separated from the same reaction as **9** and purified through the same column as the other isomer **9**. (168 mg, 0.29 mmol, 59%). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.85 (s, 1H), 7.80 (s, 1H), 7.40 (s, 1H), 7.27 (s, 2H), 7.21 (s, 2H), 7.08 (s, 1H), 2.67 (t, *J* = 7.3 Hz, 4H), 1.95-1.63 (m, 4H), 1.51-1.09 (m, 20H), 0.92 (ap t, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 182.5, 147.1, 146.2, 145.5, 143.3, 139.2, 135.6, 131.6, 129.7, 129.4, 128.3, 128.2, 127.2, 123.3, 35.9, 31.9, 31.5, 29.5, 29.4, 29.3, 22.7, 14.2. IR (neat, cm^{-1}): 3319, 3085, 2942, 2921, 2851, 2335, 1654, 1594, 1496, 1443.5, 1392, 1373, 1352, 1300, 1218, 1145. HRMS (ESI)

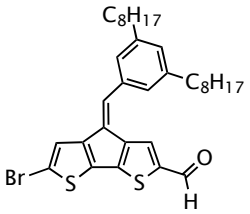
m/z calc'd for $C_{33}H_{42}OS_2Cs$ [M + Cs]$^+$ 651.1732, found 651.1741.



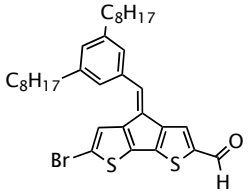
(E)-4-benzylidene-6-bromo-4H-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene-2-carbaldehyde (12): To a N_2 filled round bottom flask was added **8** (104 mg, 0.35 mmol, 1.0 equiv.), NBS (68.53 mg, 0.39 mmol, 1.1 equiv.), N,N-dimethylformamide (1.2 ml, 0.3 M). The flask was covered with aluminum foil stirred for 5 hours. The reaction mixture was extracted with dichloromethane and water. The organic layer was dried over anhydrous sodium sulfate and concentrated down. This product was used directly for next step without further purification. (126 mg, 0.34 mmol, 96%). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.72 (s, 1H), 7.67 (s, 1H), 7.60 (d, *J* = 6.8 Hz, 2H), 7.52-7.43 (m, 3H), 7.41 (s, 1H), 7.30 (s, 1H). HRMS (ESI) *m/z* calc'd for $C_{17}H_9OS_2BrCs$ [M + Cs]$^+$ 504.8333, found 504.8344.



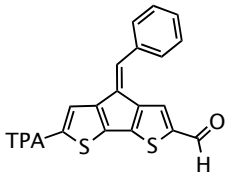
(Z)-4-benzylidene-6-bromo-4H-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene-2-carbaldehyde (14): The synthesis follows the same procedure as **12** except **10** was used in place of **8**. This product was used directly for next step without further purification. (127 mg, 0.34 mmol, 95%). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.89 (s, 1H), 7.88 (s, 1H), 7.60 (d, *J* = 6.1 Hz, 2H), 7.52-7.43 (m, 4H), 7.16 (s, 1H). HRMS (ESI) *m/z* calc'd for $C_{17}H_9OS_2BrCs$ [M + Cs]$^+$ 504.8333, found 504.8344.



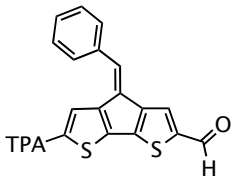
(E)-6-bromo-4-(3,5-dioctylbenzylidene)-4H-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene-2-carbaldehyde (13): The synthesis follows the same procedure as **12** except **9** was used in place of **8**. This product was used directly for next step without further purification. (65 mg, 0.10 mmol, 99%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 9.71 (s, 1H), 7.74 (s, 1H), 7.40 (s, 1H), 7.29 (s, 1H), 7.25 (s, 2H), 7.11 (s, 1H), 2.67 (t, *J* = 7.8 Hz, 4H), 1.81-1.60 (m, 4H), 1.56-1.19 (m, 20H), 0.91 (t, *J* = 7.1 Hz, 6H). HRMS (ESI) *m/z* calc'd for $C_{33}H_{41}OS_2BrCs$ [M + Cs]$^+$ 729.0837, found 729.0803.



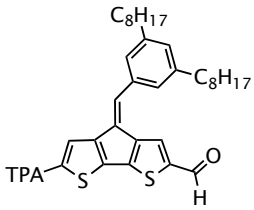
(Z)-6-bromo-4-(3,5-dioctylbenzylidene)-4H-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene-2-carbaldehyde (15): The synthesis follows the same procedure as **12** except **11** was used in place of **8**. This product was used directly for next step without further purification. (74 mg, 0.10 mmol, 91%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 9.87 (s, 1H), 7.83 (s, 1H), 7.44 (s, 1H), 7.25-7.17 (m, 3H), 7.10(s, 1H), 2.67 (t, J = 8.7 Hz, 4H), 1.81-1.57 (m, 4H), 1.57-1.13 (m, 20H), 0.92 (t, *J* = 6.5 Hz, 6H). HRMS (ESI) *m/z* calc'd for $C_{33}H_{41}OS_2BrCs$ [M + Cs]$^+$ 729.0837, found 729.0803.



(Z)-4-benzylidene-6-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)-4H-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene-2-carbaldehyde (16): To a N_2 filled pressure tube was added **12** (30 mg, 0.08 mmol, 1.0 equiv.), TPA-Bpin (55 mg, 0.1 mmol, 1.2 equiv.), $Pd(PPh_3)_4$ (9.3 mg, 0.01 mmol, 0.1 equiv.), aq. K_2CO_3 (0.32 ml, 2 M),Tetrahydrofuron (3.2 ml, 0.025 M), the reaction mixture was degassed with N_2 for 20 min and the pressure tube was sealed and reaction mixture was stirred under reflux overnight. The reaction mixture was then extracted with ethylacetate and dried with anhydrous Na_2SO_4. Note: care must be taken to ensure the column need to be run slowly, whereas streaking is apparent under longwave UV lamp irradiation. The filtrate was concentrated and purified by silica gel chromatography with 10% ethylacetate : hexane to give a red solid. (54 mg, 0.07 mmol, 91%). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.67 (s, 1H), 7.62 (d, *J* = 9.5 Hz, 3H), 7.50-7.40(m, 6H), 7.34 (s, 1H), 7.10 (d, *J* = 8.6 Hz, 4H), 6.94 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 4H), 3.97 (t, *J* = 6.3 Hz, 4H), 1.95-1.75 (m, 4H), 1.61-1.18 (m, 12H), 0.92 (ap t, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 182.3, 155.9, 151.8, 150.5, 149.9, 149.0, 142.0, 141.2, 140.1, 135.9, 133.4, 131.8, 130.8, 130.3, 129.8, 129.1, 128.8, 127.0, 126.3, 125.8, 119.9, 115.4, 114.0, 68.3, 31.6, 29.4, 25.8, 22.7, 14.1.). IR (neat, cm^{-1}): 3038, 2925, 2860, 1646, 1602, 1483, 1434, 1380, 1284, 1231, 1145, 1026, 823. HRMS (ESI) *m/z* calc'd for $C_{47}H_{47}O_3S_2NCs$ $[M + Cs]^+$ 870.2052, found 870.2081.

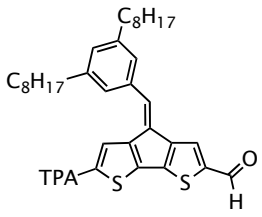


(E)-4-benzylidene-6-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)-4H-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene-2-carbaldehyde (18): The synthesis follows the same procedure as **16** except **14** was used in place of **12**. The crude purified by silica gel chromatography with 10% ethylacetate : hexane to give a red solid. (59 mg, 0.08 mmol, 100%). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.85 (s, 1H), 7.83 (s, 1H), 7.65 (d, *J* = 6.7 Hz, 2H), 7.56-7.40 (m, 4H), 7.29 (d, *J* = 6.8 Hz, 2H), 7.24 (s, 1H), 7.07 (d, *J* = 8.7 Hz, 4H), 6.90-6.84 (m, 6H), 3.95 (t, *J* = 6.4 Hz, 4H), 1.84-1.77 (m, 4H), 1.50-1.24 (m, 12H), 0.92 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 182.3, 155.9, 148.9, 148.8, 146.9, 146.8, 146.1, 142.8, 140.1, 137.0, 135.8, 130.7, 130.2, 129.8, 129.2, 128.6, 128.1, 126.9, 126.2, 125.7, 119.8, 117.3, 115.4, 68.3, 31.6, , 29.3, 25.8, 22.7, 14.1. IR (neat, cm^{-1}): 3039, 2924, 2858, 1647, 1602, 1497, 1474, 1388, 1285, 1230, 1186, 1144, 1026, 825. HRMS (ESI) *m/z* calc'd for $C_{47}H_{47}O_3S_2N$ $[M + Cs]^+$ 870.2052, found 870.2081.

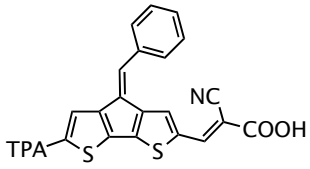


(Z)-6-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)-4-(3,5-dioctylbenzylidene)-4H-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene-2-carbaldehyde (17): The synthesis follows the same procedure as **16** except **13** was used in place of **12**. The crude was purified by silica gel chromatography with 10% ethylacetate : hexane to give a red solid. (39 mg, 0.04 mmol, 69%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 9.69 (s, 1H), 7.73 (s, 1H), 7.48 (s, 1H), 7.45 (d, *J* = 8.6 Hz, 2H), 7.38 (s, 1H), 7.29 (ap d, 2H, splitting could not be observed

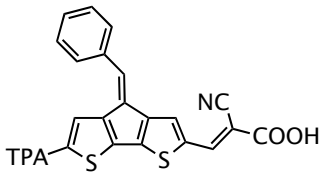
due to overlap with chloroform solvent signal), 7.11 (d, *J* = 8.9 Hz, 5H), 6.95 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 4H), 3.97 (t, *J* = 6.5 Hz, 4H), 2.68 (t, *J* = 7.5 Hz, 4H), 1.90-1.75 (m, 4H), 1.75-1.62 (m, 4H), 1.58-1.45 (m, 4H), 1.45-1.12 (m, 28H), 1.02-0.88 (ap t, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 182.1, 155.9, 152.0, 150.3, 149.8, 149.0, 143.4, 141.9, 141.5, 140.1, 135.7, 133.2, 132.3, 131.7, 129.9, 129.7, 127.3, 127.0, 126.3, 125.9, 119.9, 115.4, 114.0, 68.3, 35.9, 31.9, 31.6, 29.7, 29.5, 29.5, 29.3, 29.2, 25.8, 22.7, 22.6, 14.1, 14.1. IR (neat, cm^{-1}): 3307, 3003, 2958, 2924, 2855, 1655, 1600, 1500, 1381, 1286, 1237, 1143, 1028, 824. HRMS (ESI) *m/z* calc'd for $C_{47}H_{47}O_3S_2NCs$ $[M + Cs]^+$ 1094.4556, found 1094.4264.



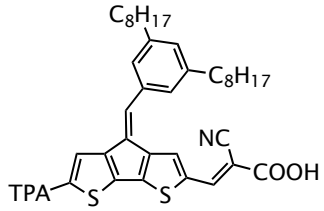
(E)-6-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)-4-(3,5-dioctylbenzylidene)-4H-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene-2-carbaldehyde (19): The synthesis follows the same procedure as **16** except **15** was used in place of **12**. The crude was purified by silica gel chromatography with 20% diethyl ether : hexane to give a red solid. (50 mg, 0.05 mmol, 83%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 9.86 (s, 1H), 7.83 (s, 1H), 7.43 (s, 1H), 7.34-7.29 (m, 5H), 7.08 (d, *J* = 8.4 Hz, 5H), 6.90 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 4H), 3.97 (t, *J* = 6.4 Hz, 4H), 2.67 (t, *J* = 7.6 Hz, 4H), 1.90-1.75 (m, 4H), 1.75-1.62 (m, 4H), 1.58-42 (m, 4H), 1.42-1.10 (m, 28H), 1.02-0.88 (ap t, , 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 182.3, 155.9, 148.9, 148.7, 147.2, 146.5, 146.3, 143.3, 142.7, 140.1, 136.8, 135.6, 131.7, 129.7, 129.7, 128.1, 127.2, 126.9, 126.1, 125.9, 119.9, 117.5, 115.3, 68.3, 36.0, 31.9, 31.8, 31.6, 29.7, 29.5, 29.3, 29.4, 29.3, 25.8, 22.7, 22.7, 14.1, 14.1. IR (neat, cm^{-1}): 3311, 3043, 2952, 2923, 2854, 1653, 1600, 1501, 1474, 1389, 1318, 1291, 1236, 1186, 1143, 1029, 825. HRMS (ESI) *m/z* calc'd for $C_{63}H_{80}O_3S_2N$ $[M+H]^+$ 962.5574, found 962.5579. (have to check with Dr. Delcamp, about mass)



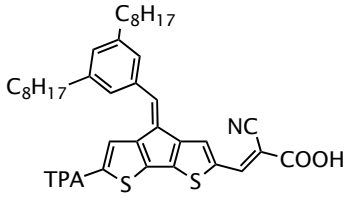
(E)-3-(4-((E)-benzylidene)-6-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)-4H-cyclopenta[2,1-*b*:3,4-*b*′]dithiophen-2-yl)-2-cyanoacrylic acid (YZ11): To a flame dried round bottom flask was added **16** (21 mg, 0.03 mmol, 1.0 equiv.) and Chloroform (0.12 ml, 0.25 M) and the mixture was degassed with N_2 for 30 min, followed by cyanoacetic acid (7.7 mg, 0.09 mmol, 3.0 equiv.) and piperidine (0.02 mL, 0.21 mmol, 7.0 equiv.). The flask was sealed with plastic cap and electric tape and stirred at 90 ^{0}C for 10 hours. The reaction mixture was directly purified through a silica gel plug using from 100% dichloromethane to 10% methanol: dichloromethane to 10% methanol:2% acetic acid: dichloromethane. The dye was extracted with hexane and water to remove acetic acid and trace silica gel particles. The organic layer was concentrated under reduced pressure to give a purple solid. The crude product was further purified through reverse phase column with 50% acetonitrile: methanol. Note: This dye was severely streaking in the column and has two major final isomers . The ratio of the isomers was determined by HPLC. (21 mg, 0.03 mmol, 87%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.5 (br s, 2H), 7.07-6.85 (br m, 19H), 3.95 (br s, 4H), 1.78-1.27 (br m, 16H) 0.93 (br m, 6H). IR (neat, cm^{-1}): 3411, 2926, 2858, 2338, 1602, 1464, 1387, 1336, 1255, 1178, 1150, 1040. HRMS (ESI) *m/z* calc'd for $C_{50}H_{47}O_4S_2N_2$ $[M-H]^+$ 803.3055, found 803.2930. UV-Vis (CH_2Cl_2): λ_{max} = 546 nm (ε = 15,000 M^{-1} cm^{-1}), λ_{onset} = 675 nm. CV (0.1 M Bu_4NPF_6 in CH_2Cl_2, sweep width 2.0-(-1.2.0), 0.1 Vs-1 scan rate) versus NHE: $E_{(S+/S)}$ = 0.87 V; E_g^{opt} = 1.84 eV. $E_{(S+/S*)}$ = –0.97 V [vs NHE, calculated from $E_{(S+/S*)} = (E_{(S+/S)} – E_g^{opt})$].



(E)-3-(4-((Z)-benzylidene)-6-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)-4H-cyclopenta[2,1-*b*:3,4-*b'*]dithiophen-2-yl)-2-cyanoacrylic acid (YZ13): The synthesis follows the same procedure **YZ11** except **18** was used. Final product is purple solid. (22 mg, 0.03 mmol, 64%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.5 (br s, 3H), 6.95-6.76 (br m, 18H), 3.92 (br s, 4H), 1.78-1.36 (br m, 16H), 0.93 (br m, 6H). IR (neat, cm^{-1}): 2926, 2859, 1597, 1502, 1477, 1375, 1285, 1237, 1026, 825. HRMS (ESI) *m/z* calc'd for $C_{50}H_{47}O_4S_2N_2$ $[M-H]^+$ 803.3055, , found 803.2983. UV-Vis (CH_2Cl_2): λ_{max} = 553 nm (ε = 15,000 M^{-1} cm^{-1}), λ_{onset} = 690 nm. CV (0.1 M Bu_4NPF_6 in CH_2Cl_2, sweep width 2.0-(-1.2.0), 0.1 Vs-1 scan rate) versus NHE: $E_{(S+/S)}$ = 0.89 V; E_g^{opt} = 1.80 eV. $E_{(S+/S*)}$ = –0.91 V [vs NHE, calculated from $E_{(S+/S*)} = (E_{(S+/S)} - E_g^{opt})$].



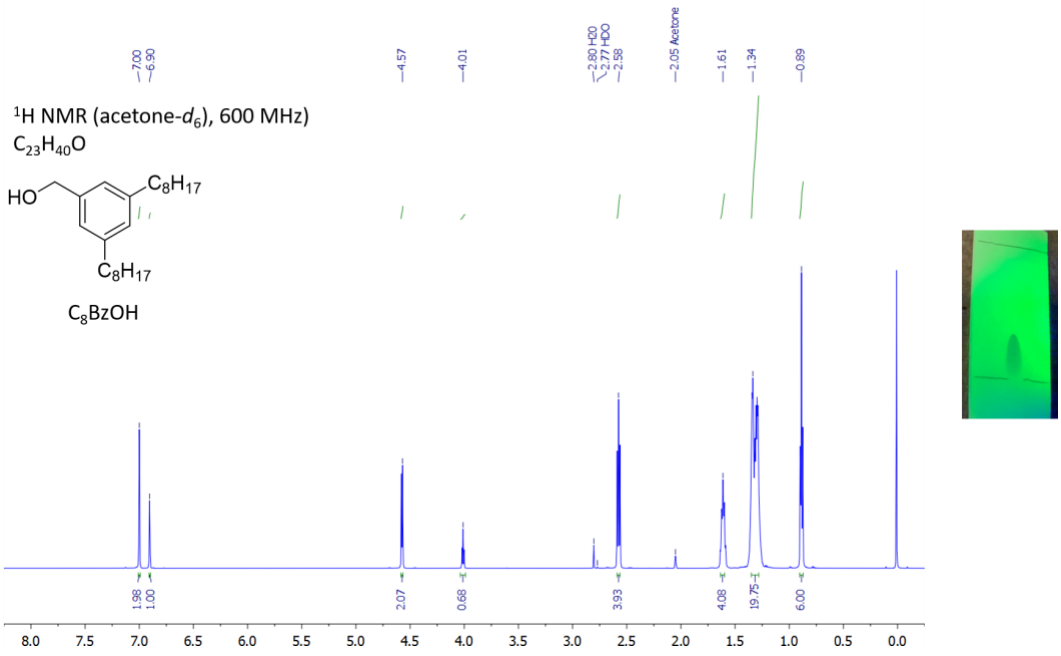
(E)-3-(6-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)-4-((E)-3,5-dioctylbenzylidene)-4H-cyclopenta[2,1-*b*:3,4-*b'*]dithiophen-2-yl)-2-cyanoacrylic acid (YZ16): The synthesis follows the same procedure **YZ11** except **17** was used. The crude product was further purified by 97% dichloromethane: methanol to 95% dichloromethane: methanol. Two major spots were collected which were **E** and **Z** isomers. (5.6 mg, 0.005 mmol, 20%) ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.15 (br s, 1H), 7.62 (br s, 1H), 7.50 (br s, 1H), 7.43 (br d, 2H), 7.35 (br s, 1H), 7.24 (br s, 2H), 7.10 (br d, 5H), 6.94 (br d, 2H), 6.87 (br d, 4H), 3.97 (br t, 4H), 2.68 (br t, 4H), 1.84-1.80 (br m, 4H), 1.64-1.60 (br m, 4H), 1.54-1.50 (br m, 4H), 1.37-1.30 (br m, 28H), 0.94-0.89 (br m, 12H). IR (neat, cm^{-1}): 2923, 2854, 2745, 2698, 2339, 1563, 1505, 1478, 1383, 1240, 1161, 1097, 817. HRMS (ESI) *m/z* calc'd for $C_{66}H_{79}O_4S_2N_2$ $[M-H]^+$ 1027.5560, found 1027.5358. UV-Vis (CH_2Cl_2): λ_{max} = 572 nm (ε = 15,000 M^{-1} cm^{-1}), λ_{onset} = 690 nm. CV (0.1 M Bu_4NPF_6 in CH_2Cl_2, sweep width 2.0-(-1.2.0), 0.1 Vs-1 scan rate) versus NHE: $E_{(S+/S)}$ = 0.89 V; E_g^{opt} = 1.80 eV. $E_{(S+/S*)}$ = –0.91 V [vs NHE, calculated from $E_{(S+/S*)} = (E_{(S+/S)} - E_g^{opt})$].



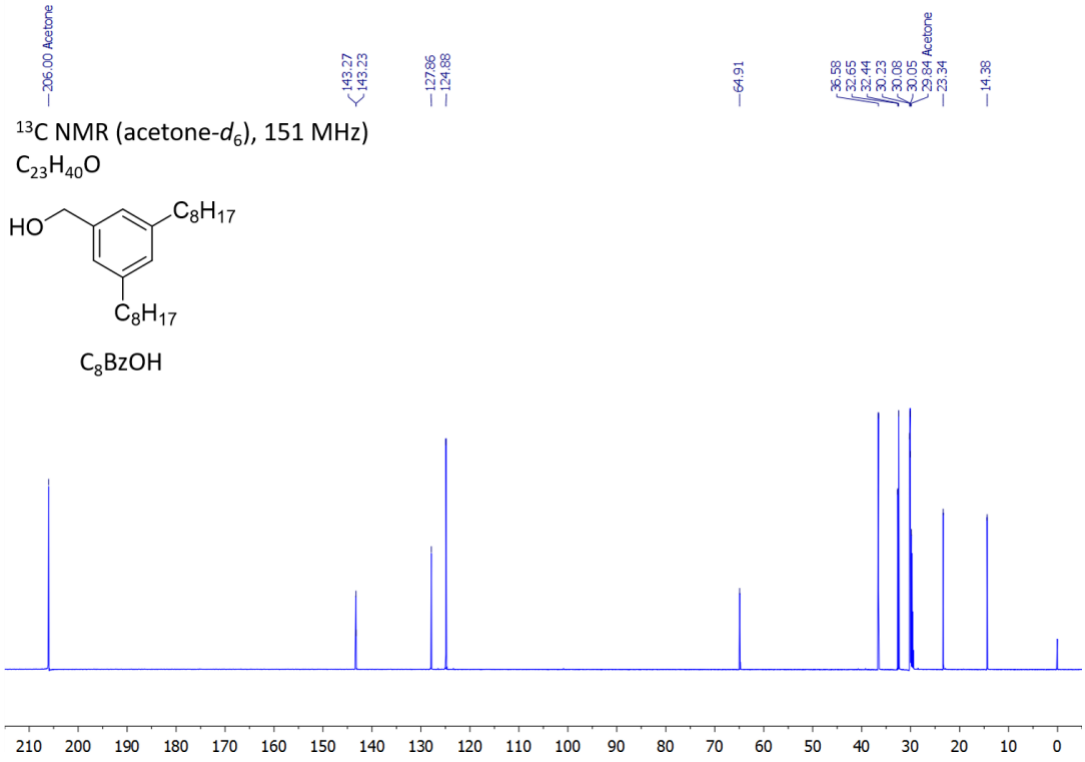
(E)-3-(6-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)-4-((Z)-3,5-dioctylbenzylidene)-4H-cyclopenta[2,1-*b*:3,4-*b'*]dithiophen-2-yl)-2-cyanoacrylic acid (YZ17): The synthesis follows the same procedure **YZ11** except **19** was used. The crude product was further purified by 97% dichloromethane: methanol to 95% dichloromethane: methanol. Two major spots were collected which were **E** and **Z** isomers. (5.6 mg, 0.005 mmol, 20%) ^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.78 (br m, 19H), 3.92 (br t, 4H), 2.68 (br t, 4H), 1.80 (br m, 4H), 1.64 (br m, 4H), 1.50 (br m, 4H), 1.37 (br m, 28H), 0.91 (br m, 12H). IR (neat, cm^{-1}): 2924, 2855, 1597, 1505, 1474, 1393, 1373, 1286, 1240, 1025, 826. HRMS (ESI) *m/z* calc'd for $C_{66}H_{79}O_4S_2N_2$ $[M-H]^+$ 1027.5560, found 1027.5541. UV-vis-NIR (λ_{max} (ε)) 557 nm (16,000); $E_{(S+/S)}$ 0.93V, $E_{(S+/S*)}$ -0.87V. UV-Vis (CH_2Cl_2): λ_{max} = 557 nm (ε = 16,000 M^{-1} cm^{-1}), λ_{onset} = 690 nm. CV (0.1 M Bu_4NPF_6 in CH_2Cl_2, sweep width 2.0-(-1.2.0), 0.1 Vs-1 scan rate) versus NHE: $E_{(S+/S)}$ = 0.93 V; E_g^{opt} = 1.80 eV. $E_{(S+/S*)}$ = –0.87 V [vs NHE, calculated from $E_{(S+/S*)} = (E_{(S+/S)} - E_g^{opt})$].

NMR spectra and HPLC traces on the following pages:

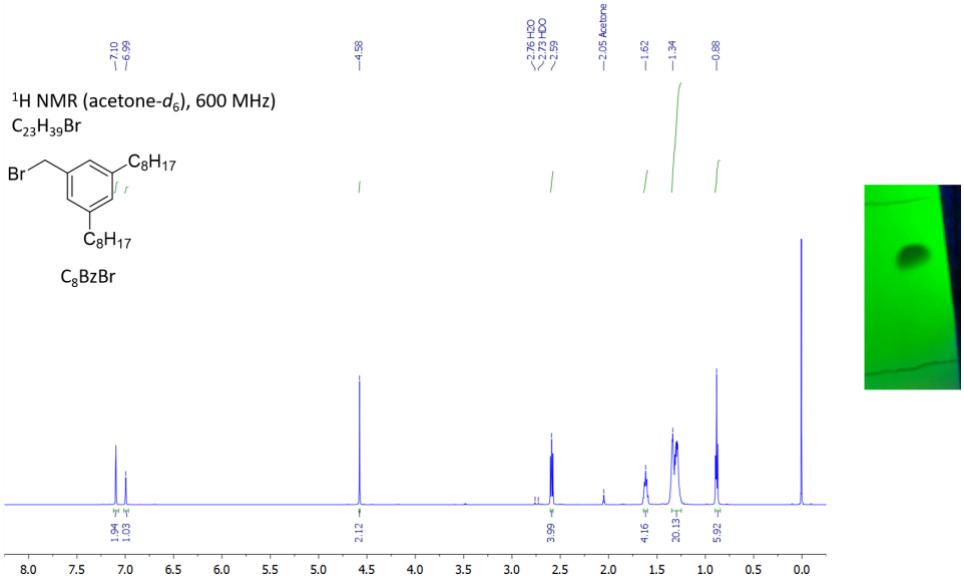
Compound **2**: ^{1}H NMR (Acetone-d$_6$), 600 MHz.



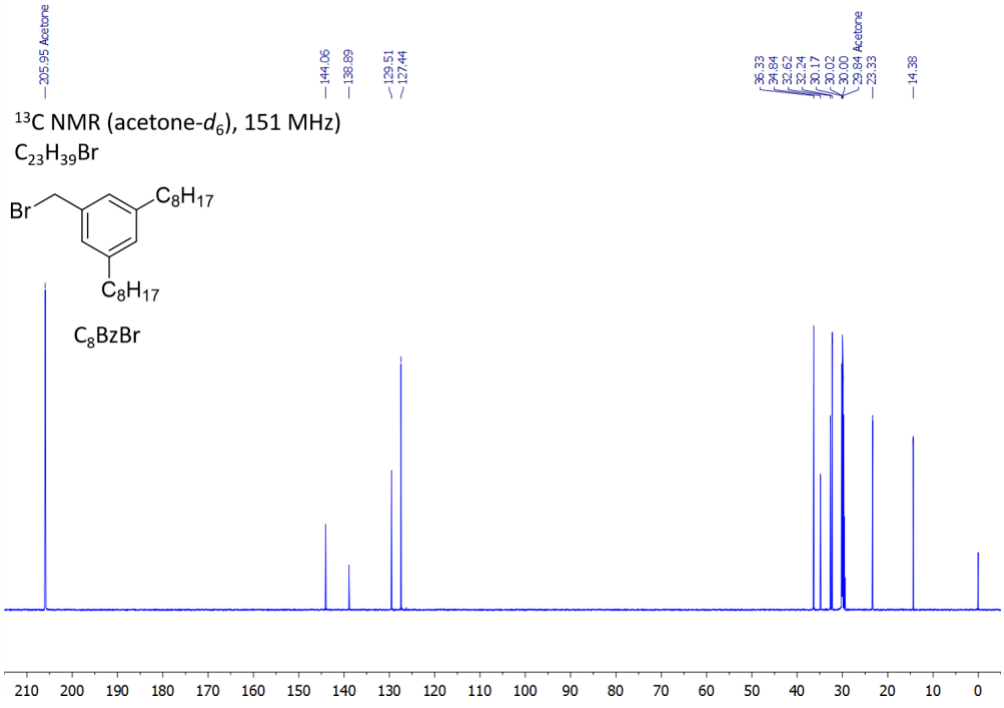
Compound **2**: ^{13}C NMR (Acetone-d$_6$), 151 MHz.



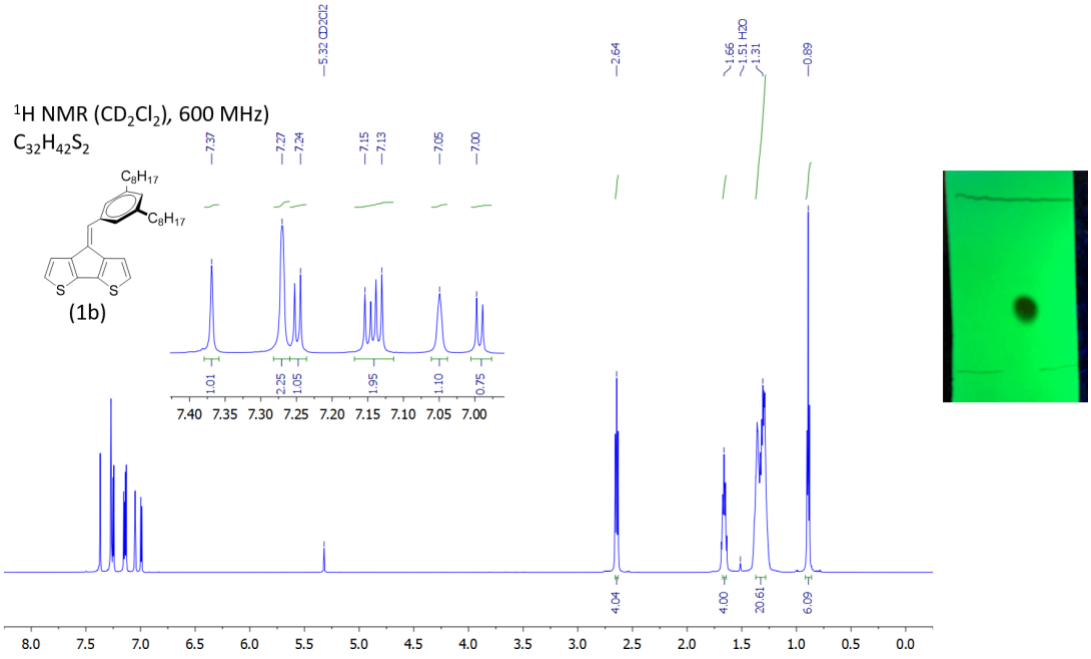
Compound **4**: ^{1}H NMR (Acetone-d$_6$), 600 MHz.



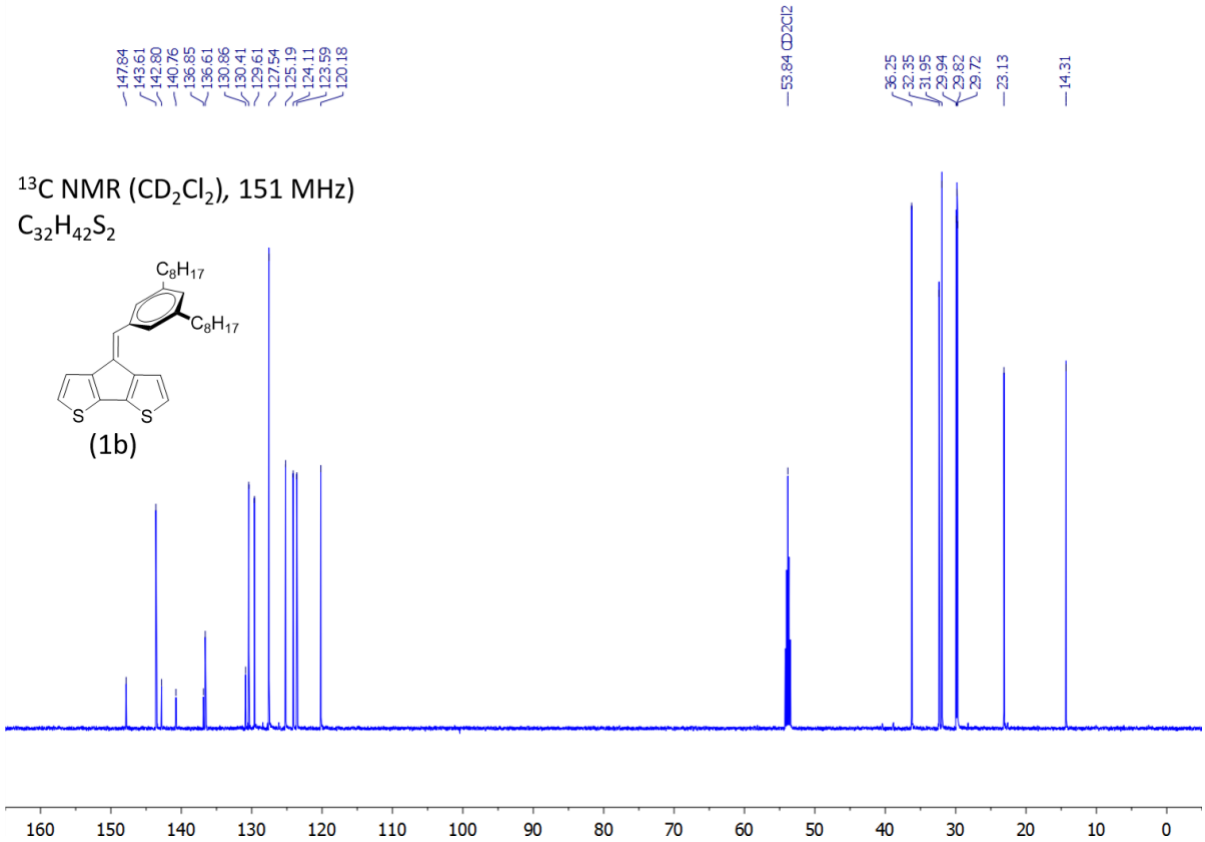
Compound **4**: ^{13}C NMR (Acetone-d$_6$), 151 MHz.



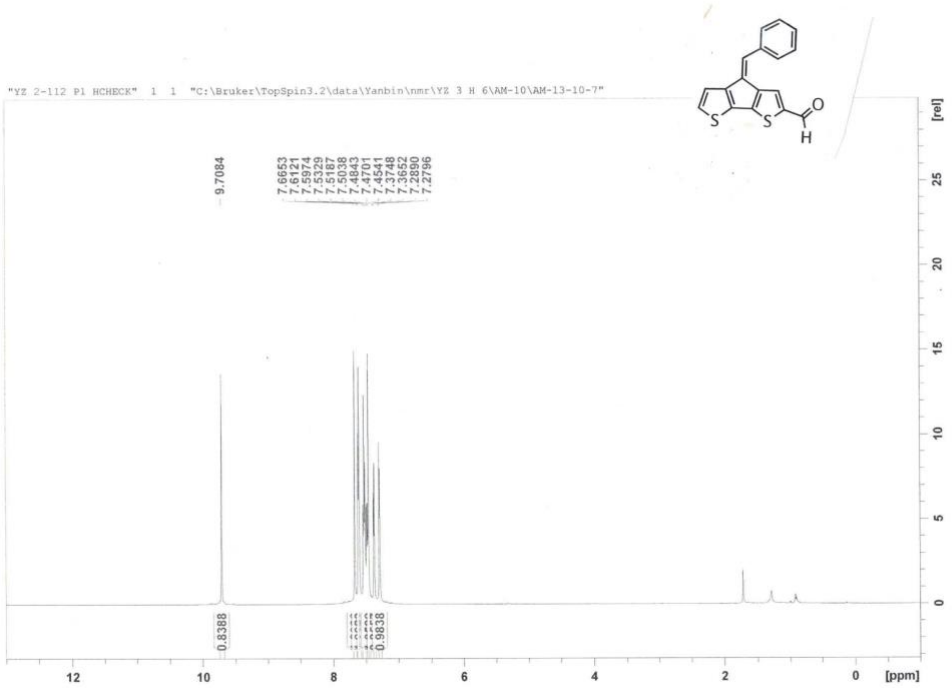
Compound **7**: ^{1}H NMR (CD_2Cl_2), 600 MHz.



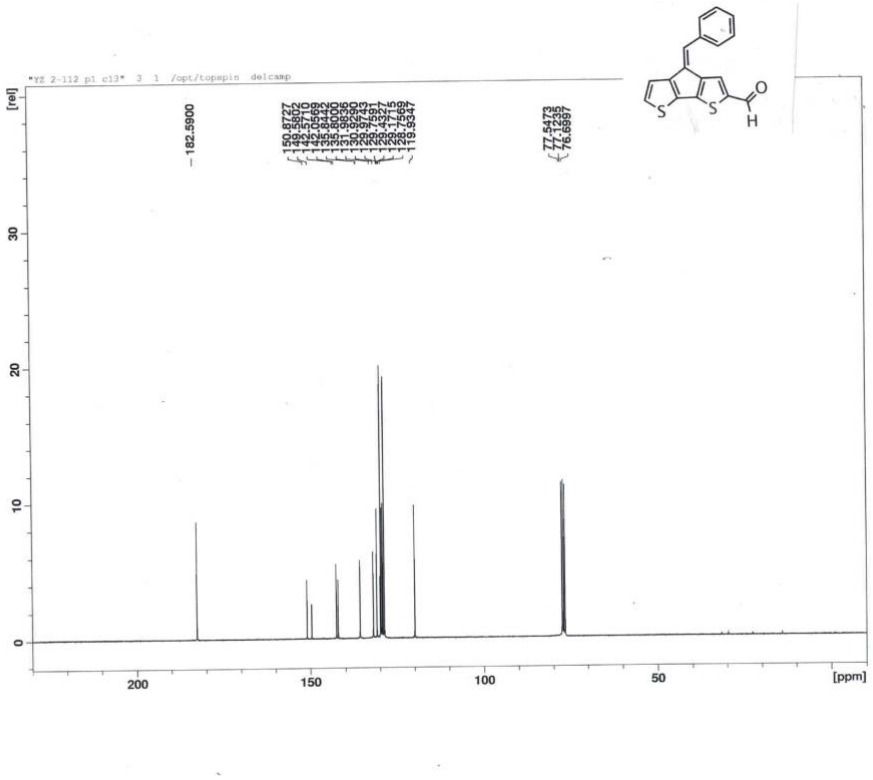
Compound **7**: ^{13}C NMR (CD_2Cl_2), 151 MHz.



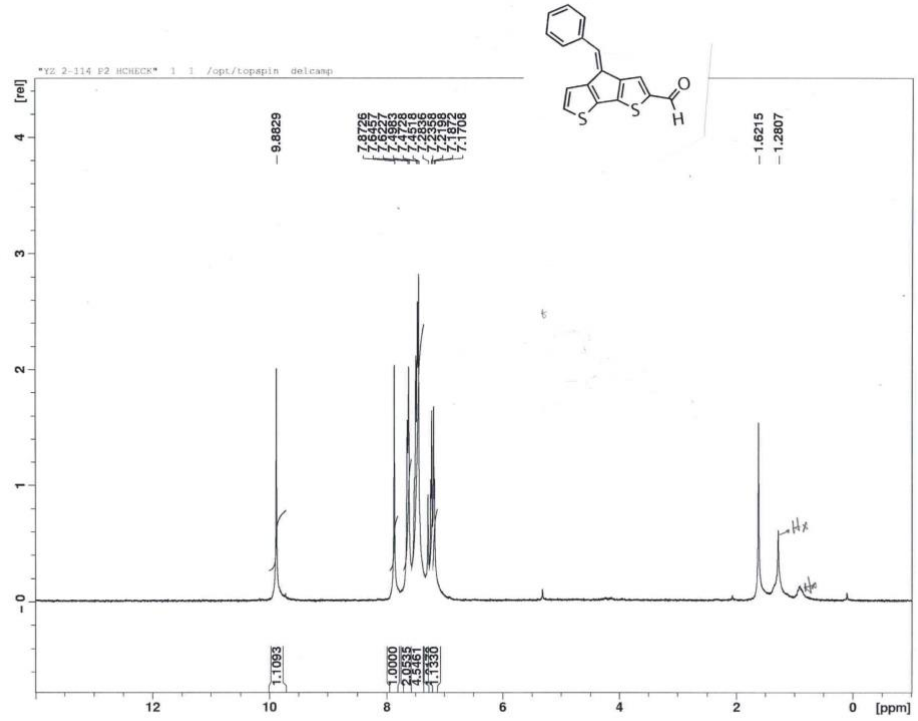
Compound **8**: ^{1}H NMR ($CDCl_3$), 500 MHz.



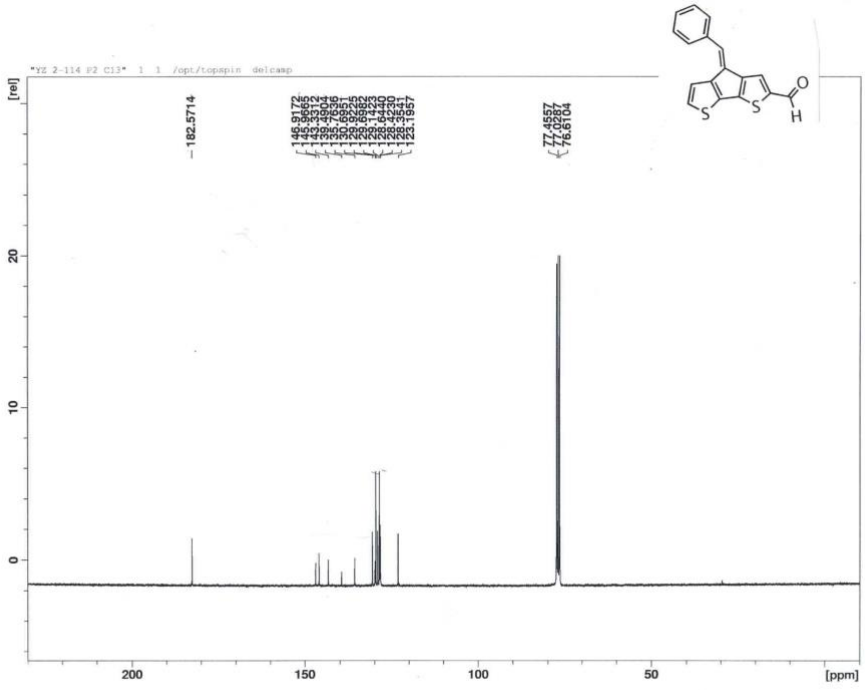
Compound **8**: ^{13}C NMR ($CDCl_3$), 125 MHz.



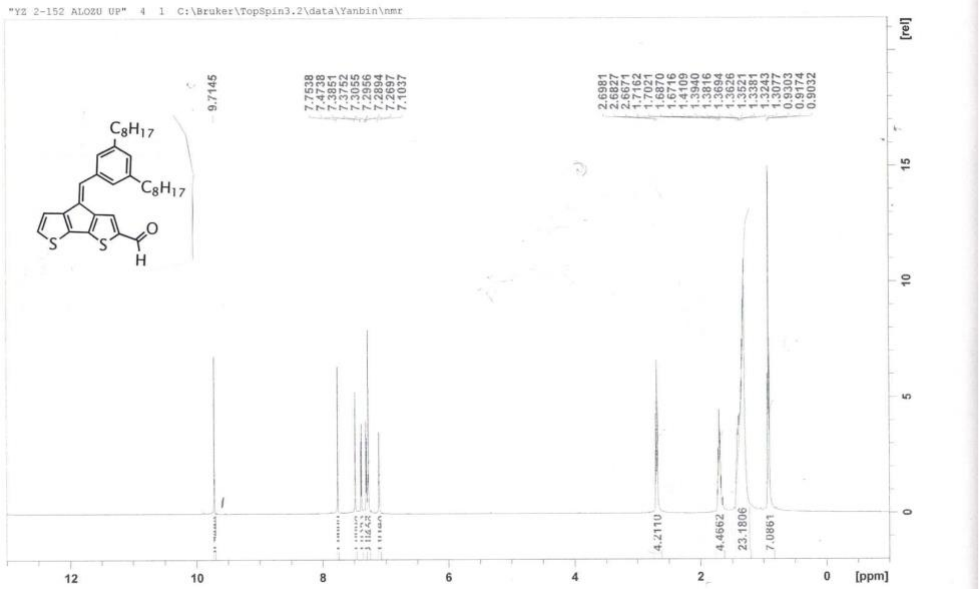
Compound **10**: ^{1}H NMR ($CDCl_3$), 300 MHz.



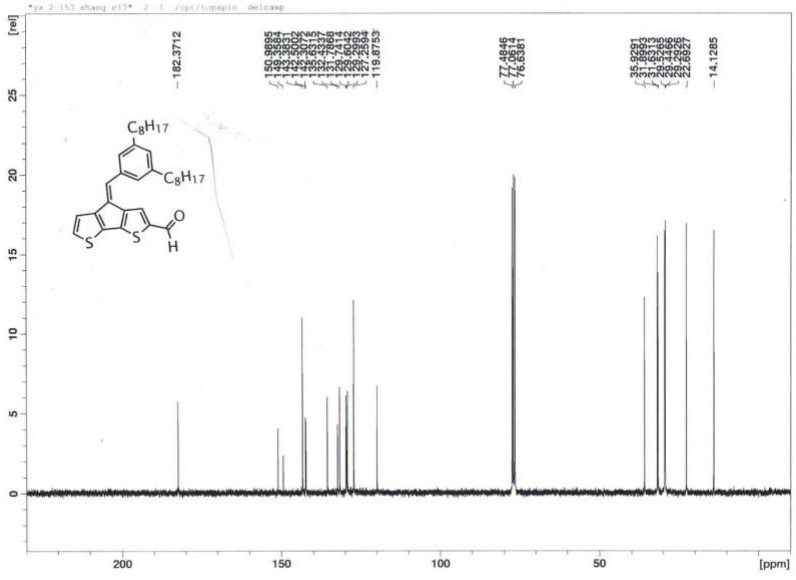
Compound **10**: ^{13}C NMR ($CDCl_3$), 75 MHz.



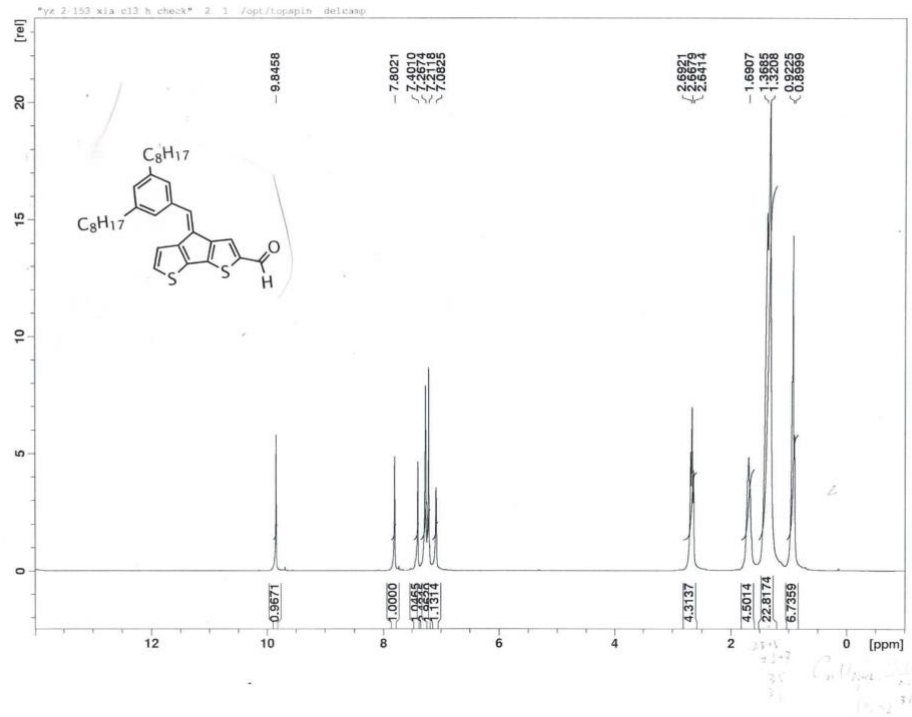
Compound **9**: ^{1}H NMR ($CDCl_3$), 500 MHz.



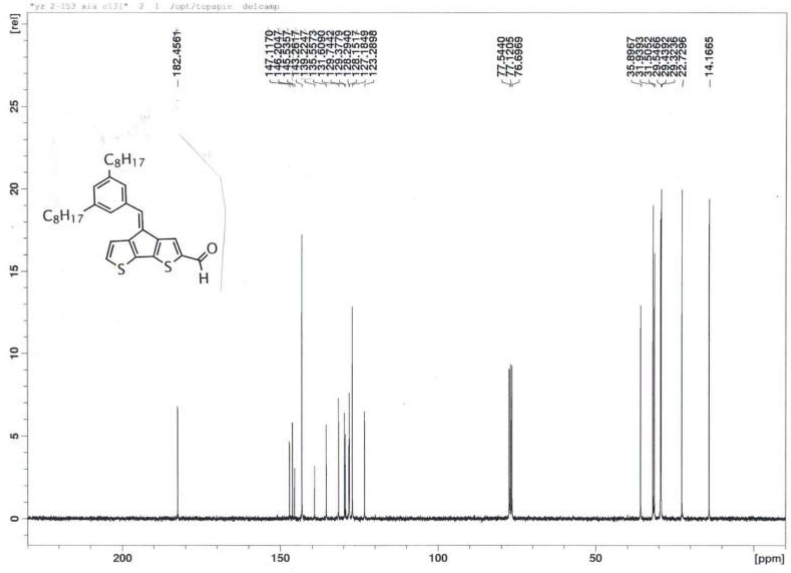
Compound **9**: ^{13}C NMR ($CDCl_3$), 75 MHz.



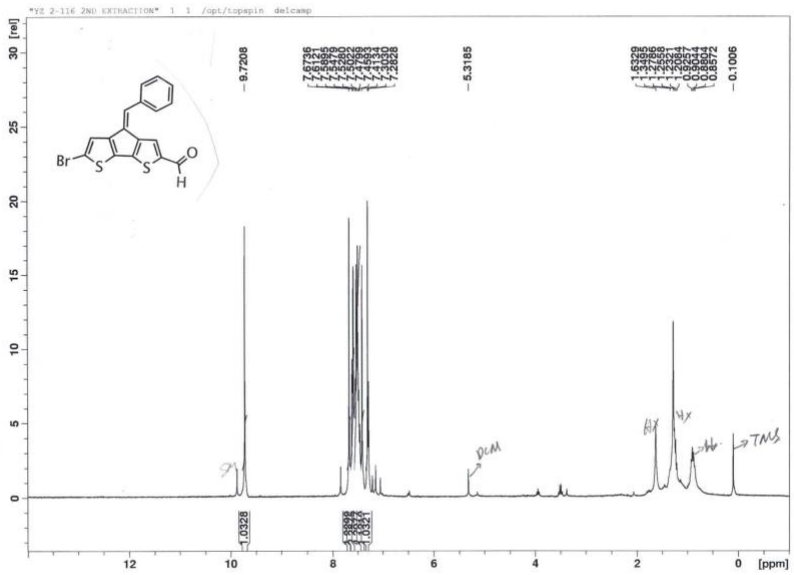
Compound **11**: ^{1}H NMR ($CDCl_3$), 300 MHz.



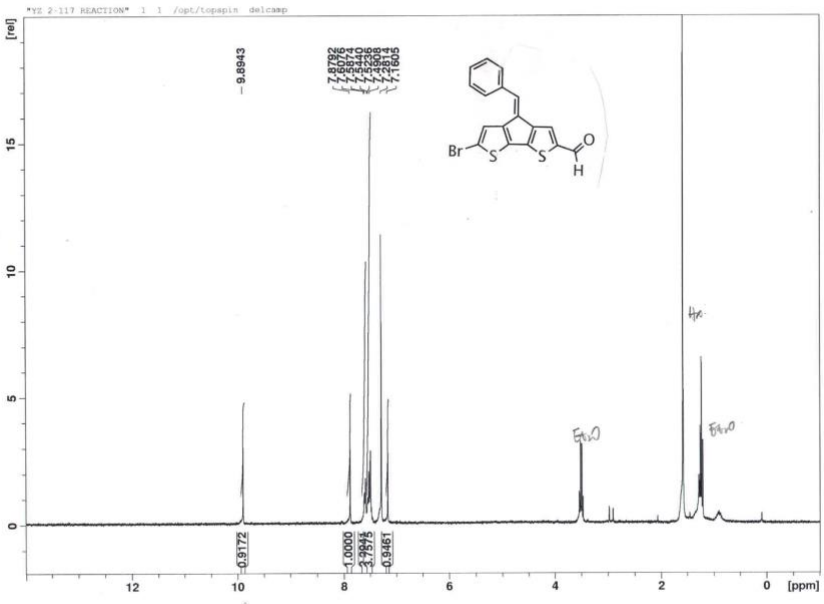
Compound **11**:^{13}C NMR ($CDCl_3$), 75 MHz.



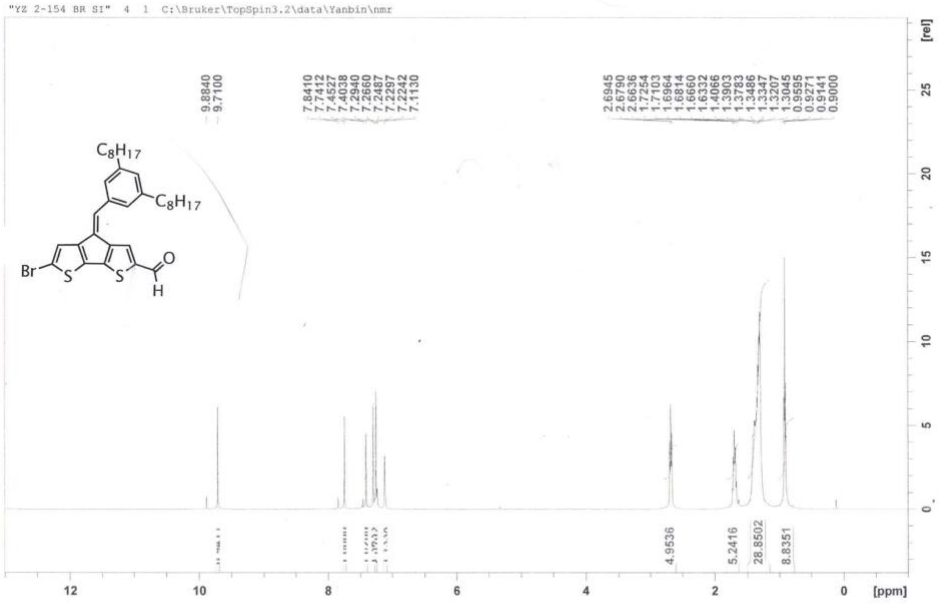
Compound **12**: ^{1}H NMR ($CDCl_3$), 300 MHz.



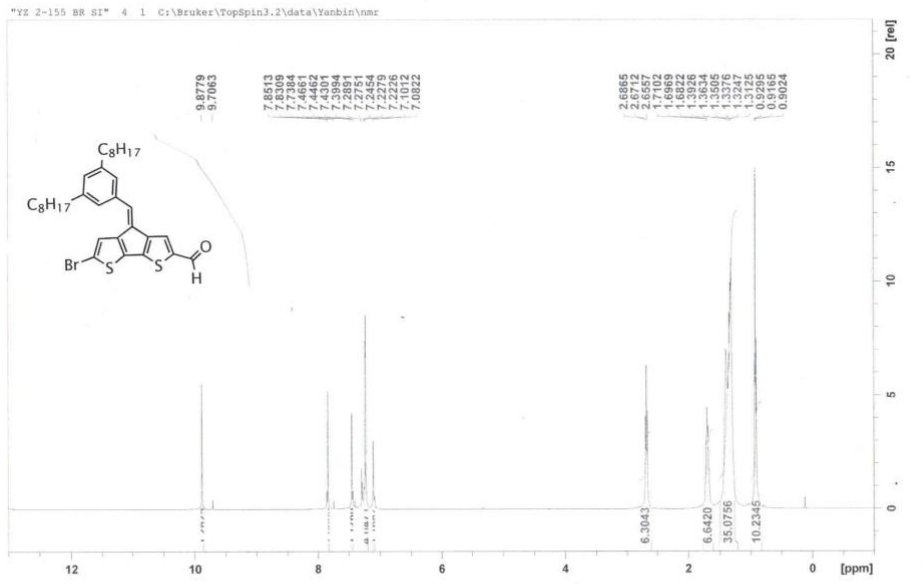
Compound **14**: ^{1}H NMR ($CDCl_3$), 300 MHz.



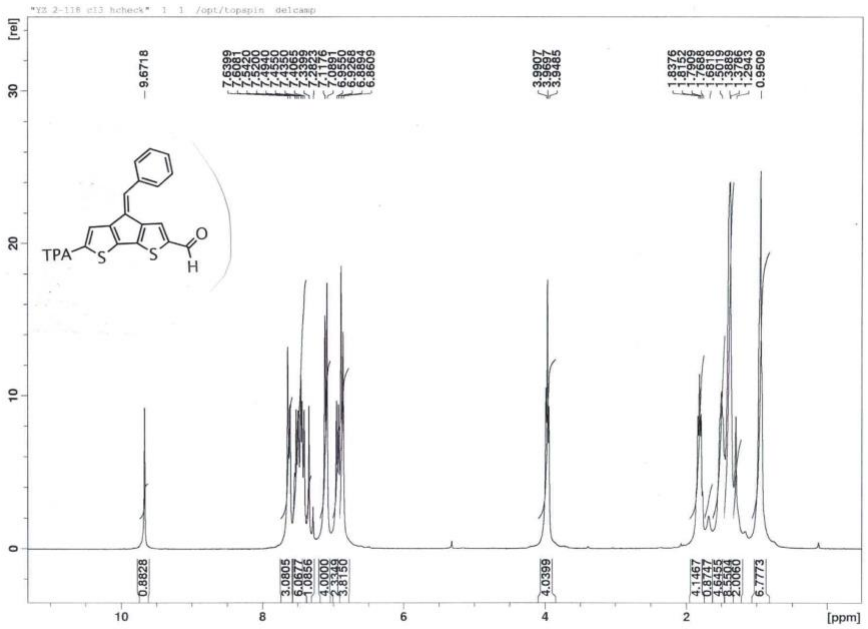
Compound **13**: ^{1}H NMR ($CDCl_3$), 300 MHz.



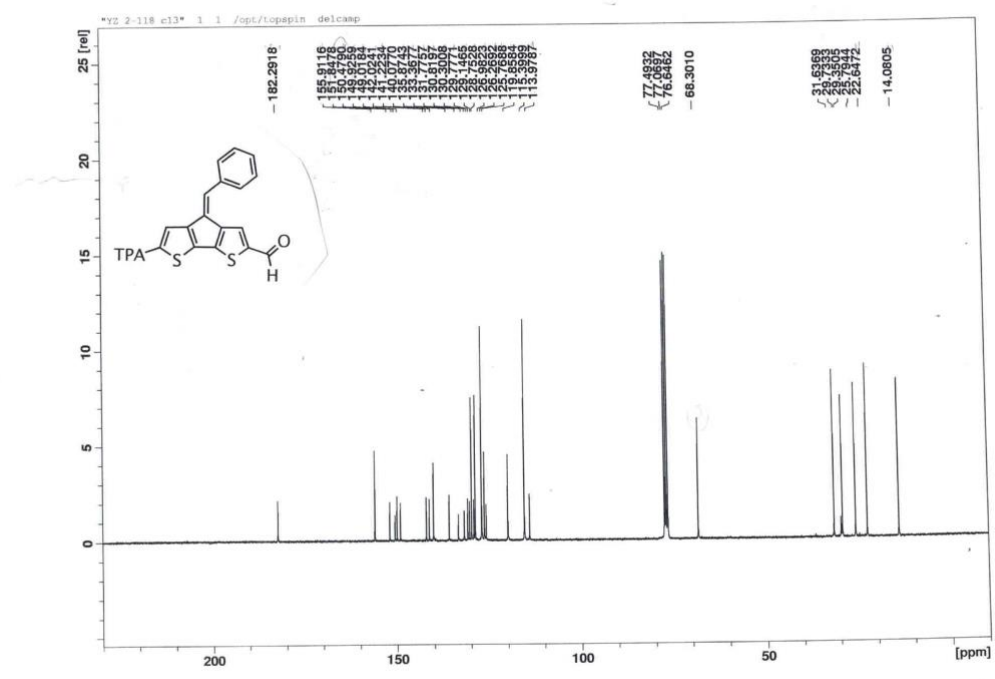
Compound **15**: ^{1}H NMR ($CDCl_3$), 500 MHz.



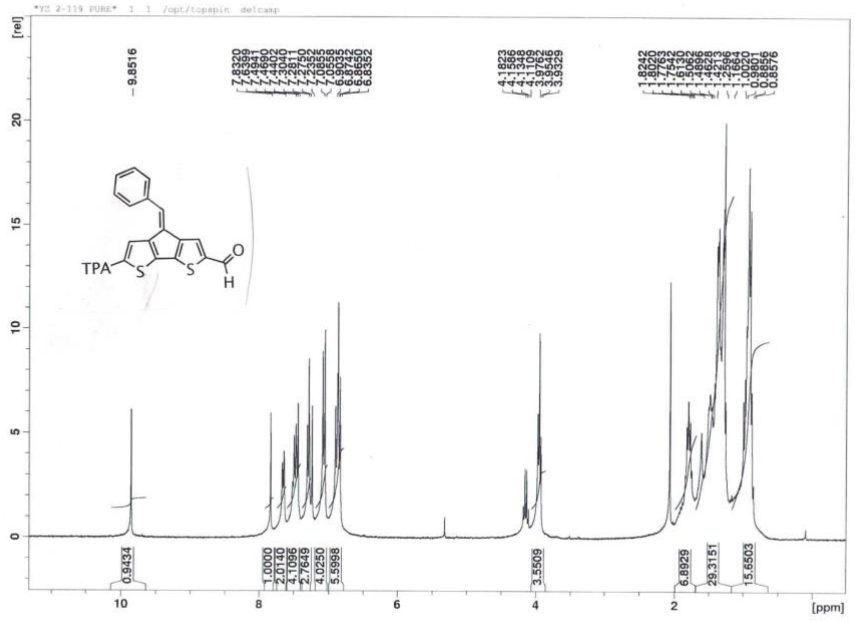
Compound **16**: ^{1}H NMR ($CDCl_3$), 300 MHz.



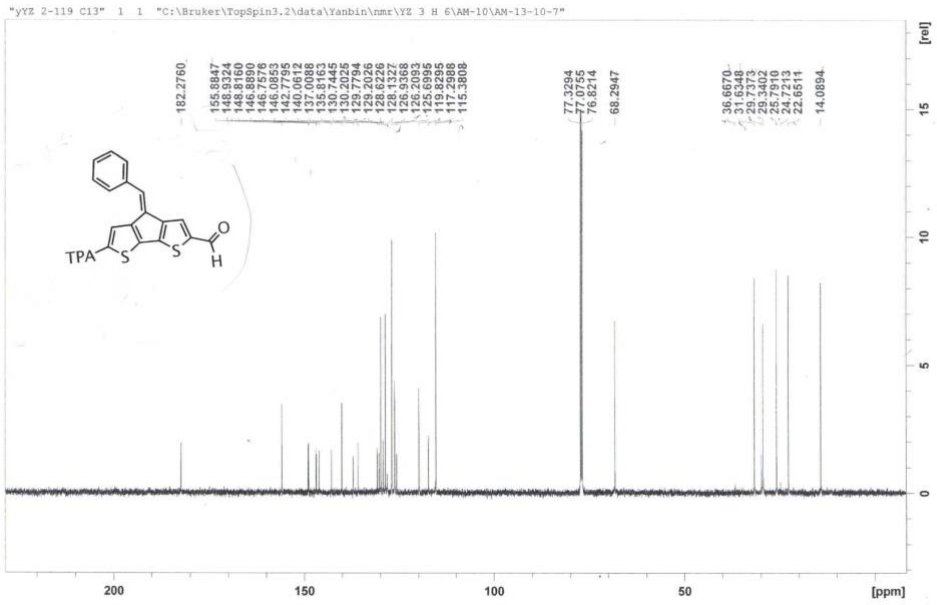
Compound **16**: ^{13}C NMR ($CDCl_3$), 75 MHz.



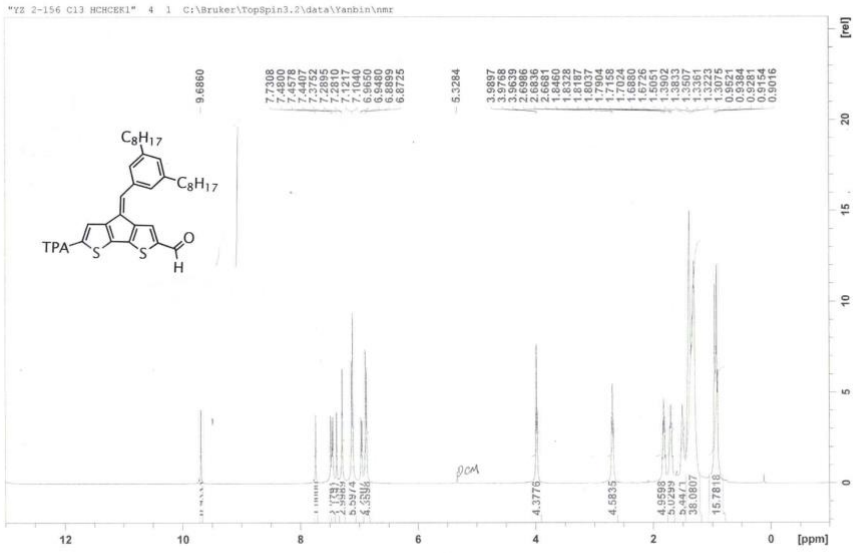
Compound **18**: ^{1}H NMR ($CDCl_3$), 300 MHz.



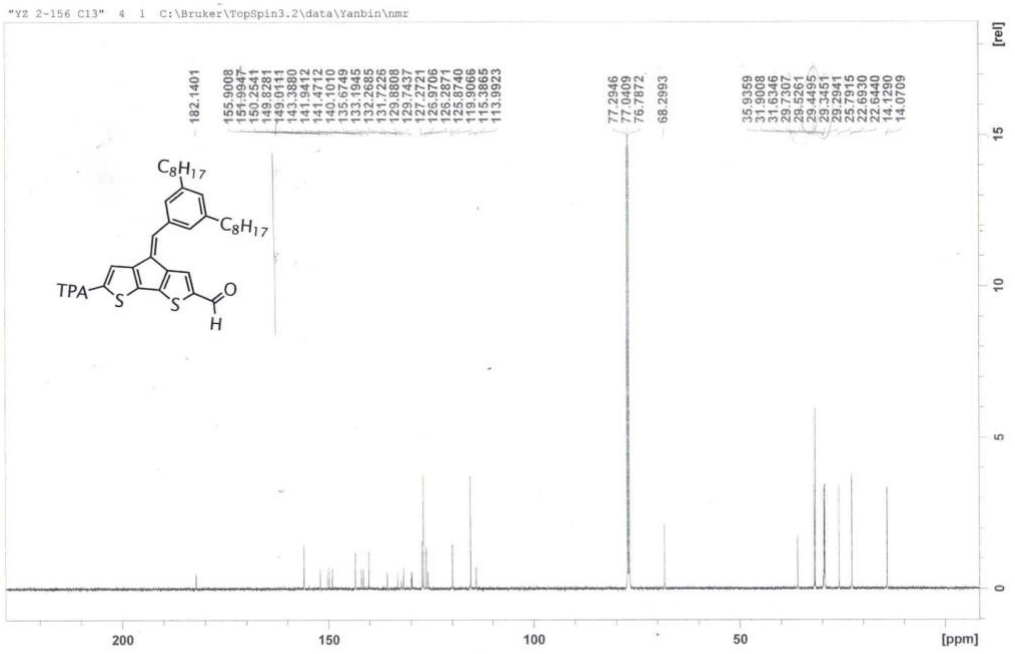
Compound **18**: ^{13}C NMR ($CDCl_3$), 75 MHz.



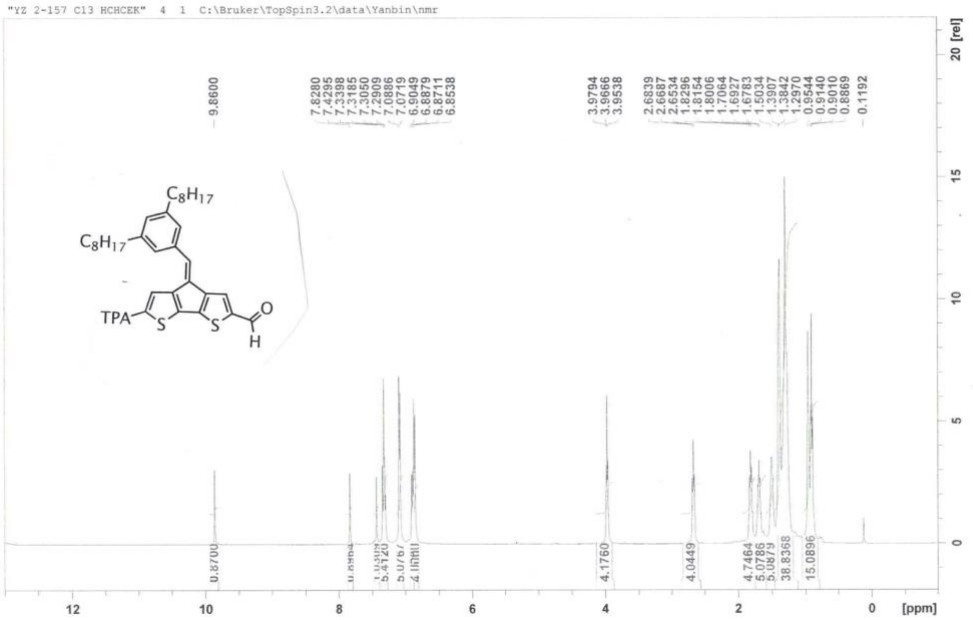
Compound **17**: ^{1}H NMR ($CDCl_3$), 500 MHz.



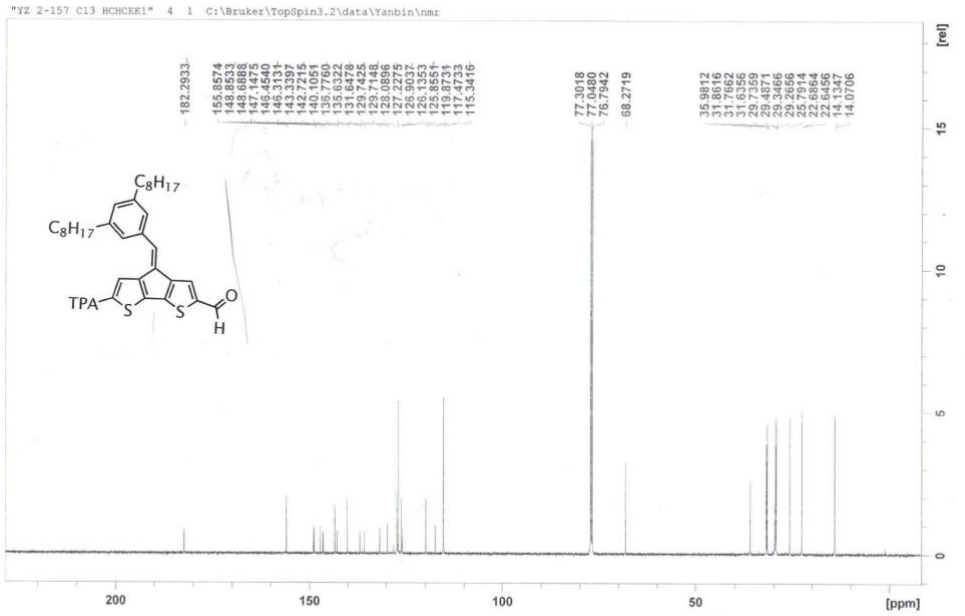
Compound **17**: ^{13}C NMR ($CDCl_3$), 125 MHz.



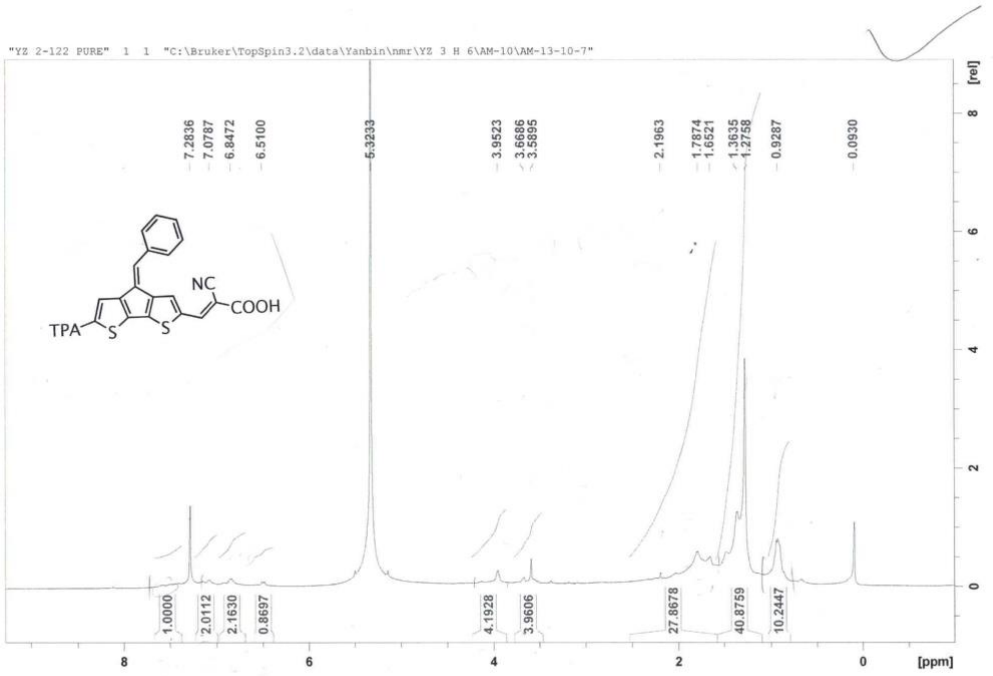
Compound **19**: ^{1}H NMR ($CDCl_3$), 500 MHz.

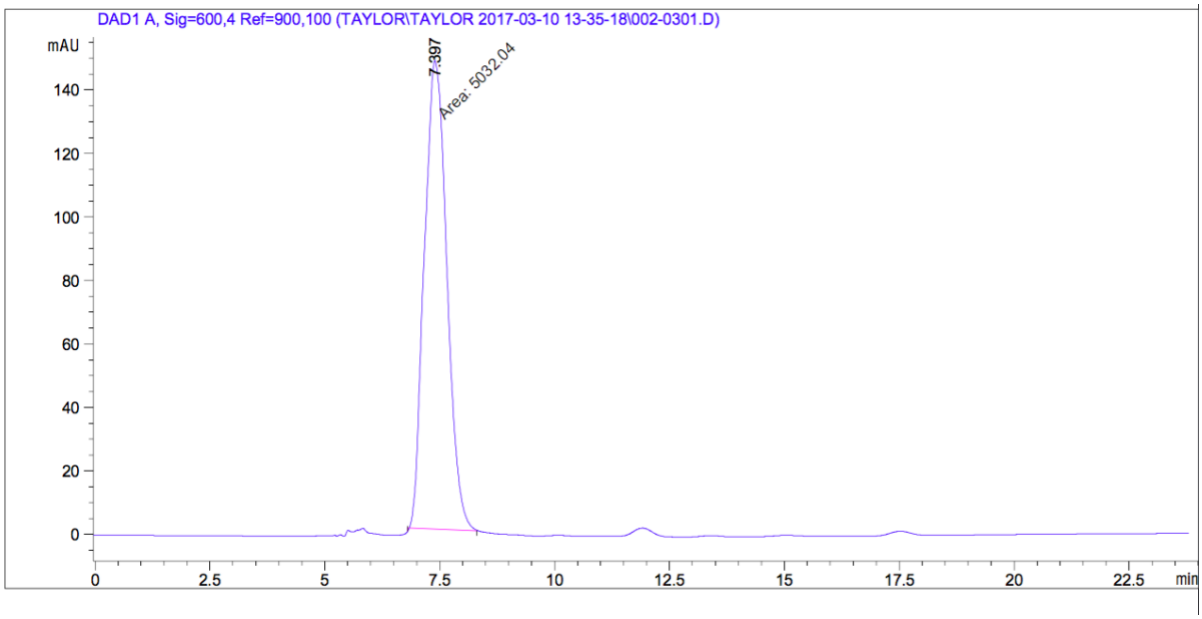


Compound **19**: ^{13}C NMR ($CDCl_3$), 125 MHz.

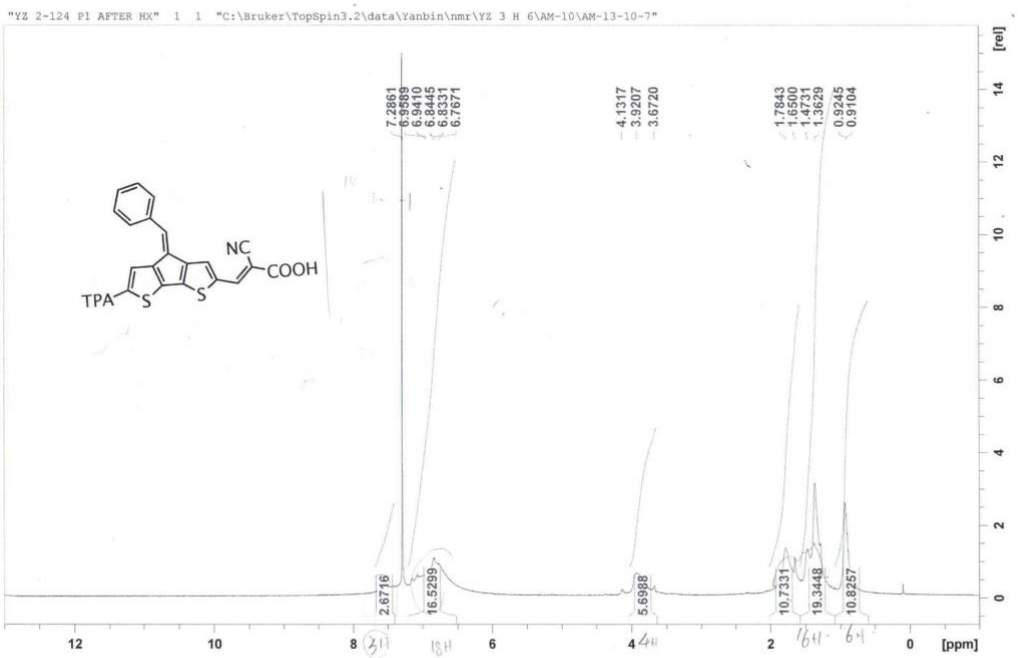


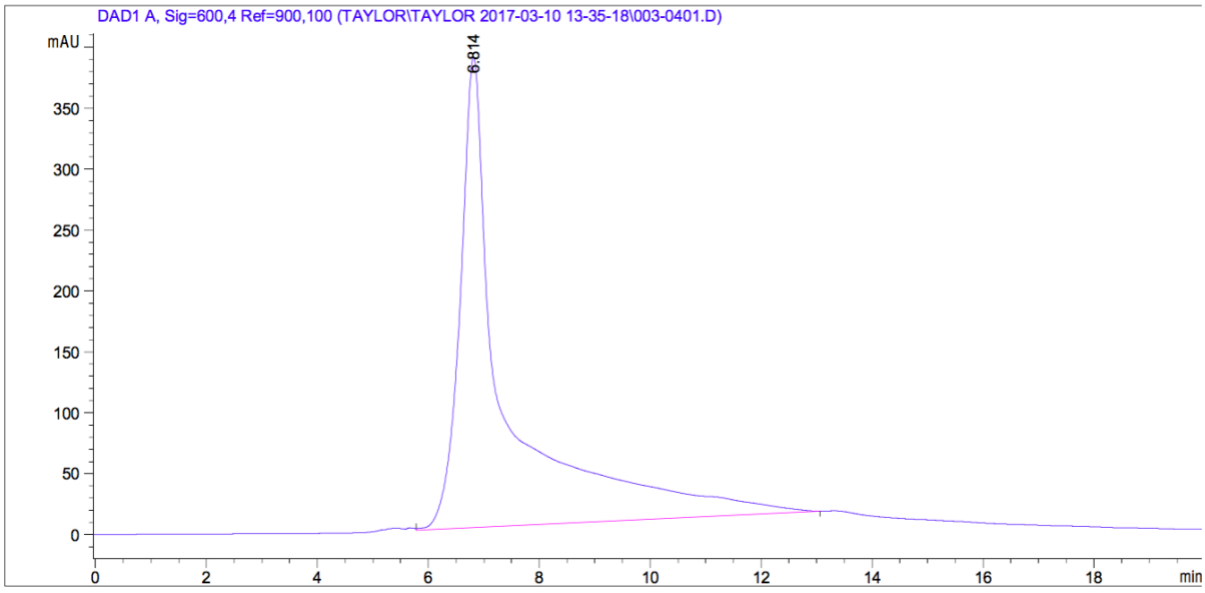
YZ11: ^{1}H NMR ($CDCl_3$), 500 MHz and HPLC spectrum.



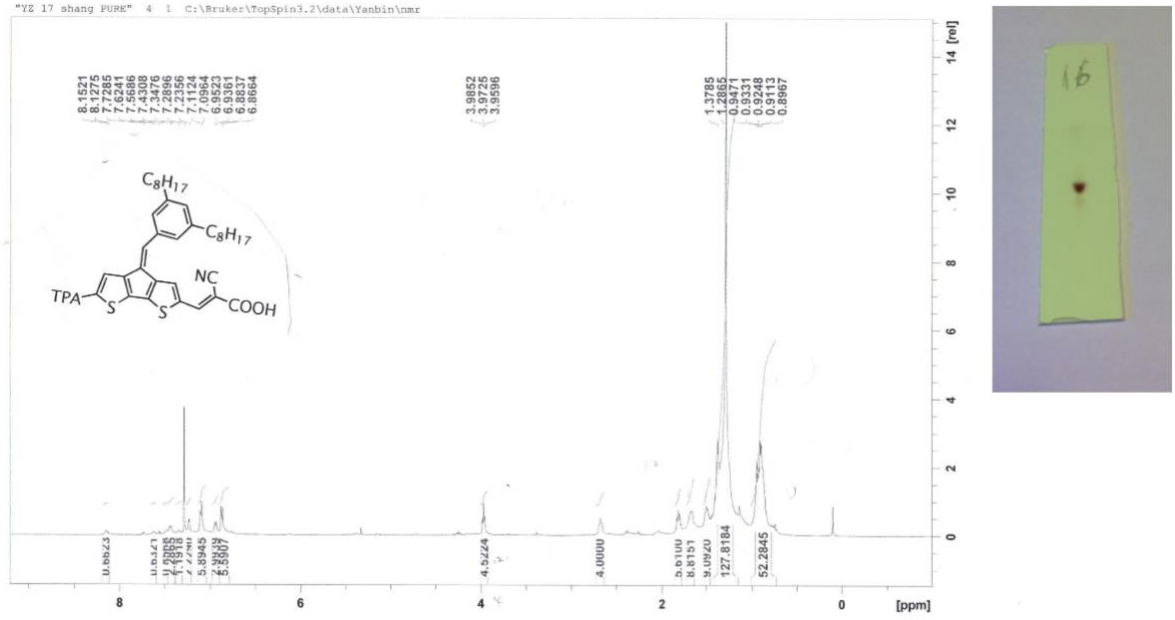


YZ13: ^{1}H NMR ($CDCl_3$), 500 MHz and HPLC spectrum.



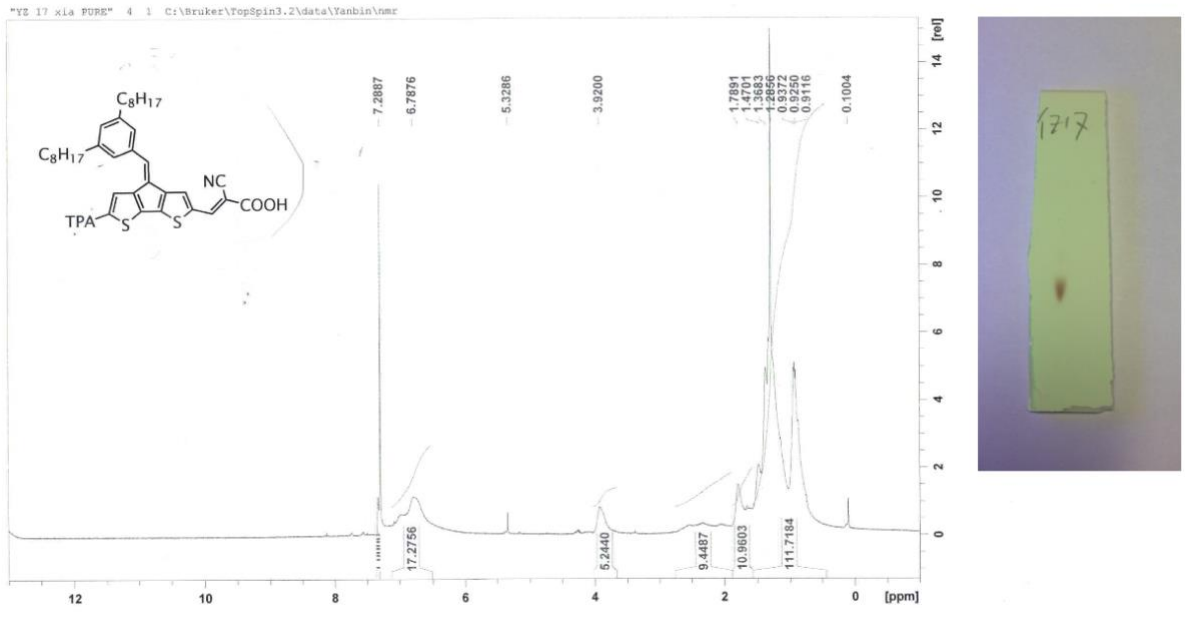


YZ16: ^{1}H NMR ($CDCl_3$), 500 MHz and TLC picture.



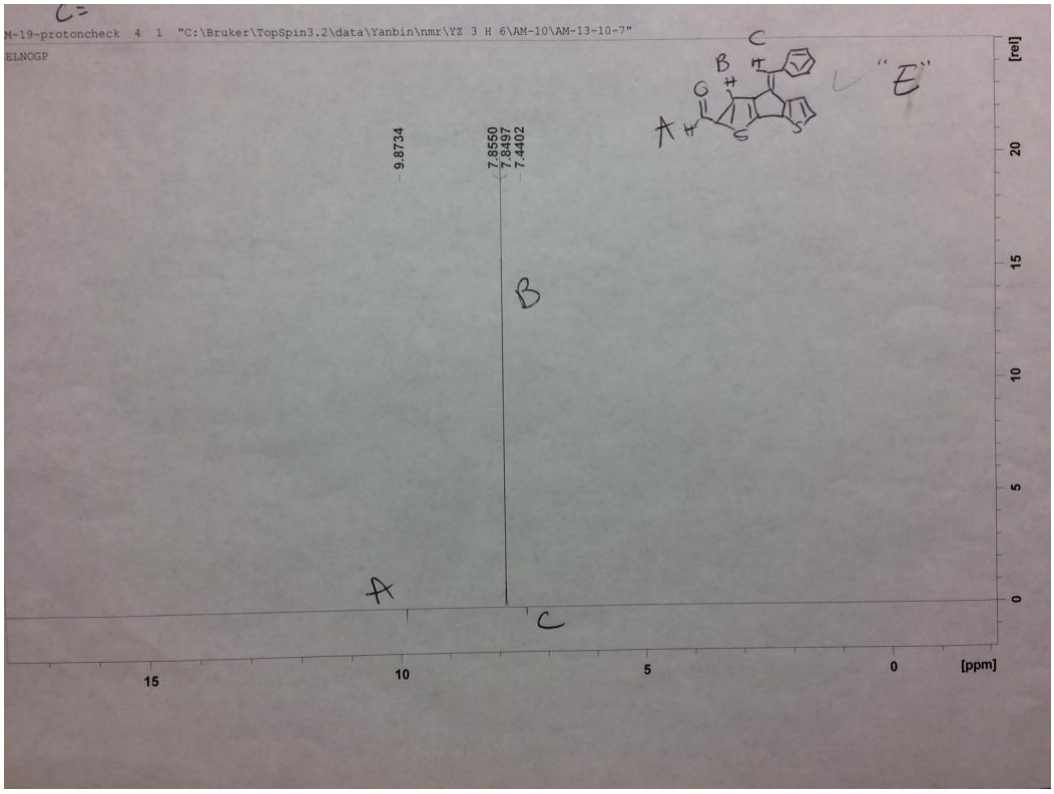
Note: TLC was taken in 97%DCM : 3%MeOH.

YZ17: ^{1}H NMR ($CDCl_3$), 500 MHz and TLC picture.

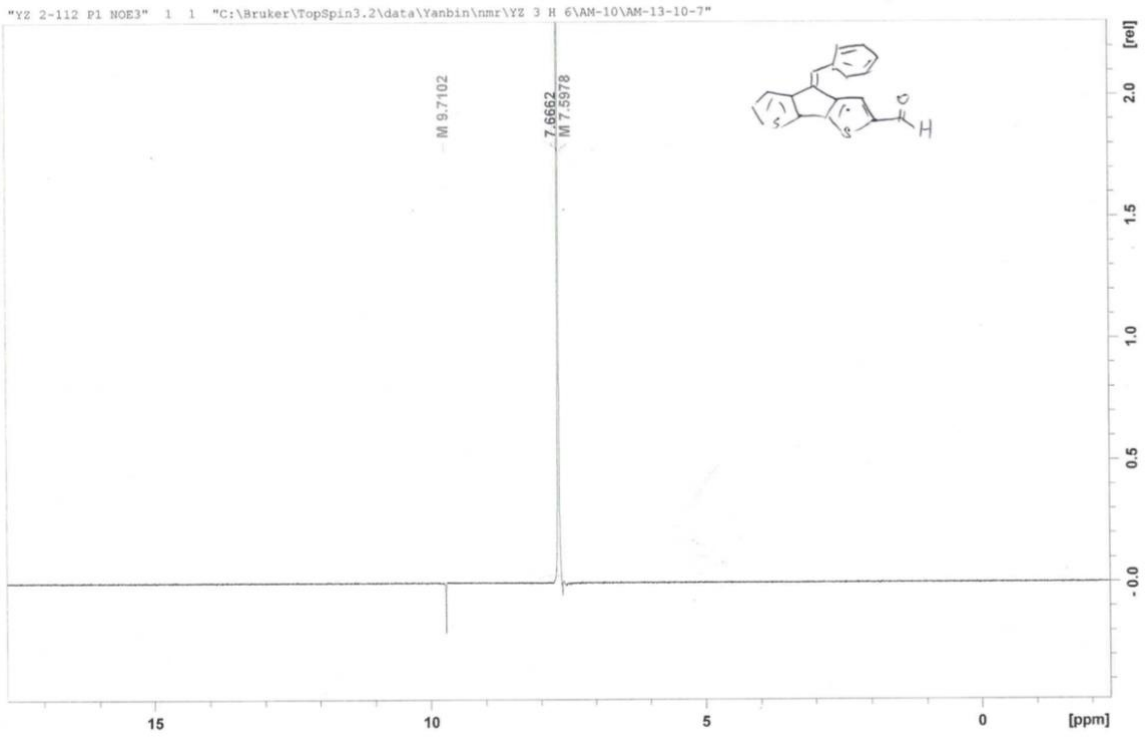


Note: TLC was taken in 97%DCM : 3%MeOH.

NOE spectrum for E isomer (10)

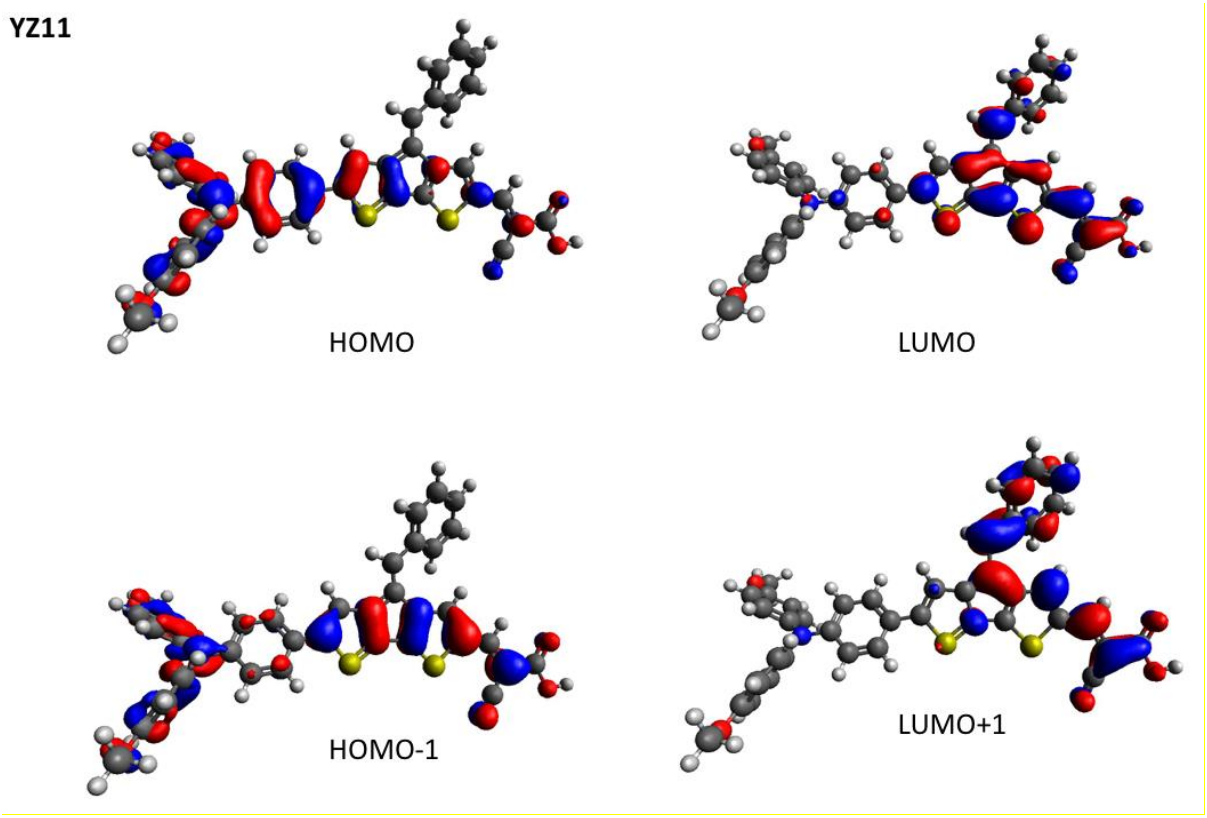


NOE spectrum for E isomer (8)

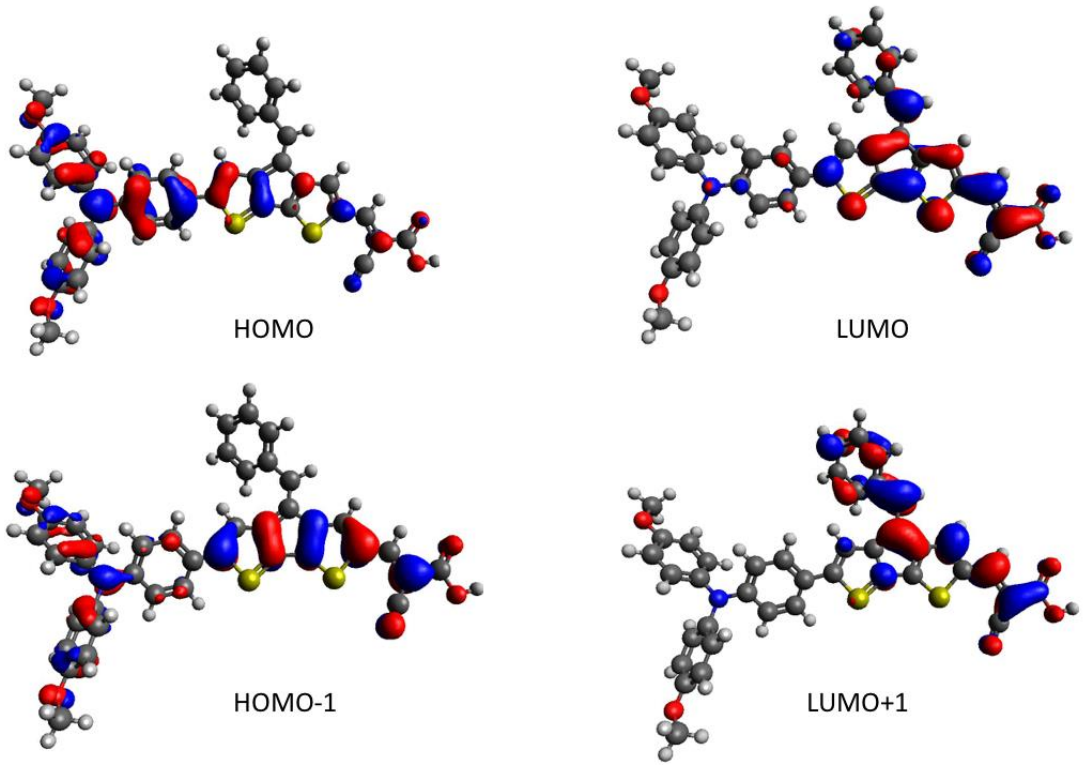


2. Computational Data

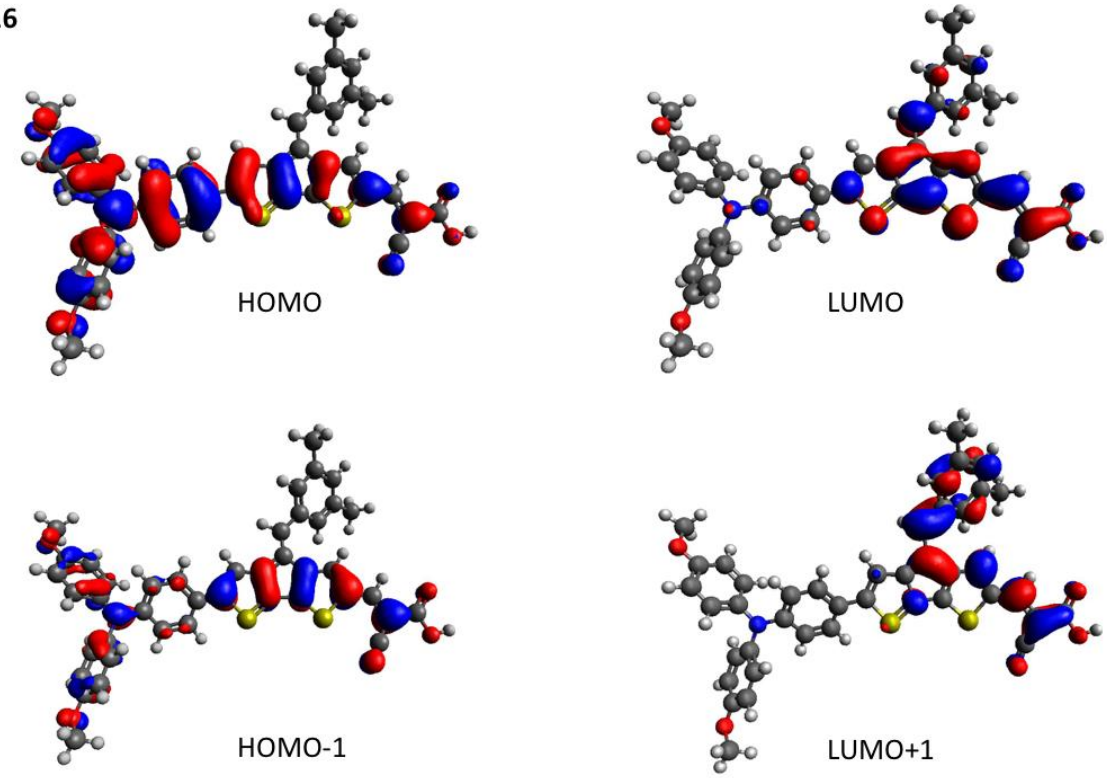
General Information: MM2 energy minimization in ChemBio3D Ultra (version:13.0.2.3021) was used for the initial energy minimization of **YZ11**, **YZ13**, **YZ16**, and **YZ17**. Dihedral angles for the relevant groups were set to values between the global minimum and the next local minimum on the conformation energy diagram as calculated by chemBio3D. Accurate geometry optimization were performed sequentially by density functional theory (DFT) using Guassian09 with the B3LYP functional with the following basis sets: first 3-21g, second 6-31g (d,p) and finally 6-311g (d,p). Time-dependent density functional theory (TD-DFT) computations were performed with optimized geometries and with the B3LYP functional and 6-311g (d.p) basis set to compute the vertical transition energies and oscillator strengths. Iso values are set to 0.3 for all structures and long alkyl chains are truncated to methyl groups.



YZ13



YZ16



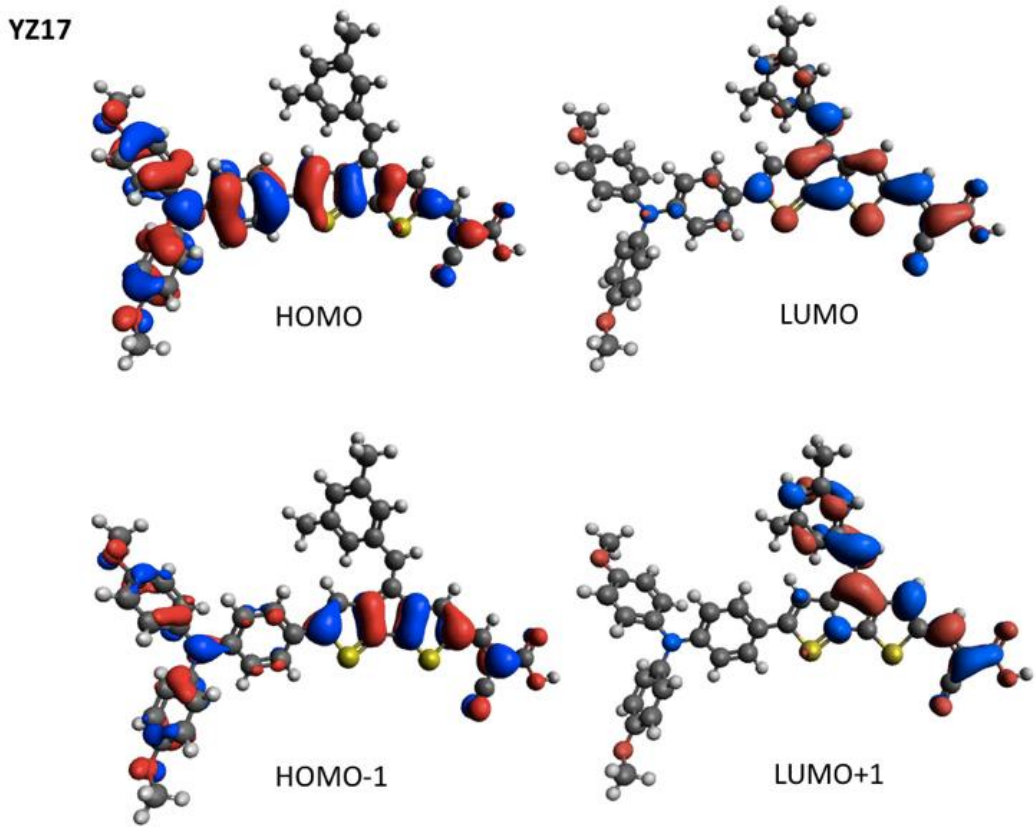


Figure S1: HOMO, LUMO, HOMO-1 and LUMO+1 orbitals for dyes **YZ11**, **YZ13**, **YZ16** and **YZ17**.

Table S1. Summary table for computational results: dihedral angles, orbital contributions to vertical transitions, vertical transition energies and oscillator strengths computed with DFT and TD-DFT analysis at the B3LYP/6-311(d,p) level

dye	angle 1 (°)	angle 2 (°)	transition	contrib. (%)	vert. trans. (nm/eV)	oscillator strength	energy (Hartrees)
YZ11	24.5	35.2	H → L	96%	640/1.93	0.5506	-2748.3620869
			H^{-1} → L	44%	458/2.71	0.5275	
			H → L^{+1}	51%			
YZ13	23.7	36.0	H → L	96%	654/1.89	0.5146	-2748.3619642
			H^{-1} → L	45%	462/2.68	0.6078	
			H^{-1} → L^{+1}	2%			
			H → L^{+1}	50%			
YZ16	25.8	38.5	H → L	96%	631/1.97	0.5895 0.5264	-2827.0179941
			H^{-1} → L	45%	453/2.74		
			H → L^{+1}	50%			
YZ17	24.7	35.6	H → L	96%	642/1.93	0.5379	-2827.0174338
			H^{-1} → L	44%	455/2.72	0.6317	
			H → L^{+1}	51%			

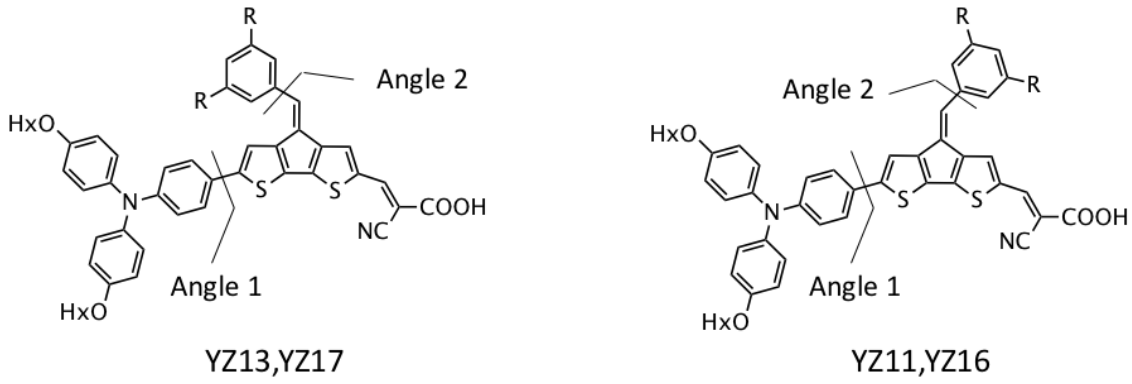


Figure S2. Position for dihedral angles

3. Photovoltaic Measurements and Device Fabrication

3. **1 DSC Device Fabrication:** For the photoanode, TEC 10 glass was purchased from Hartford Glass. Once cut into 2x2 cm squares, the substrate was submerged in a 0.2% Deconex 21 aqueous solution and sonicated for 15 minutes at room temperature. The electrodes were rinsed with water and sonicated in acetone for 10 minutes followed by sonication in ethanol for 10 minutes. Finally, the electrodes were placed under UV/ozone for 15 minutes (UV-Ozone Cleaning System, Model ProCleaner by UVFAB Systems). A compact TiO_2 underlayer is then applied by pretreatment of the substrate submerged in a 40 mM $TiCl_4$ solution in water (prepared from 99.9% $TiCl_4$ between 0-5 ^oC). The submerged substrates (conductive side up) were heated for 30 minutes at 70 ^oC. After heating, the substrates were rinsed first with water then with ethanol. The photoanode consists of thin TiO_2 electrodes comprised of a 10 μm mesoporous TiO_2 layer (particle size, 20 nm, Dyesol, DSL 18NR-T) for iodine cells and 5 μm mesoporous TiO_2 layer (particle size, 30 nm, Dyenamo, DN-GPS-30TS) for cobalt cells. All the photoanodes had 5.0 μm TiO_2 scattering layer (particle size, 100 nm, Solaronix R/SP). All the layers were screen printed from a Sefar screen (54/137–64W). Between each print, the substrate was heated for 7 minutes at 125 ^oC and the thickness was measured with a profilometer (Alpha-Step D-500 KLA Tencor). After all layers were deposited, the substrate was then sintered with progressive heating from 125^oC (5-minute ramp from r.t., 5 minute hold) to 325 ^oC (15 minute ramp from 125^oC, 5 minute hold) to 375 ^oC (5 minute ramp from 325 ^oC, 5 minute hold) to 450 ^oC (5 minute ramp from 375 ^oC, 15 minute hold) to 500 ^oC (5 minute ramp from 450 ^oC, 15 minute hold) using a programmable furnace (Vulcan® 3-Series Model 3-550). The cooled sintered photoanode was soaked 30 min at 70 ^oC in a 40 mM $TiCl_4$ water solution and heated again at

500 ^{o}C for 30 minutes prior to sensitization. The complete working electrode was prepared by immersing the TiO_2 film into the dye solution overnight. The solution is 0.3 mM of dye in MeCN:t-BuOH:THF mixture (1:1:1) with a 20:1 CDCA:dye ratio unless otherwise indicated. For preparing counter electrodes, 2x2 cm squares TEC 7 FTO glasses were drilled using Dremel-4000 with Dremel 7134 Diamond Taper Point Bit from the conductive and taped FTO side. The electrodes were washed with water followed by 0.1 M HCl in EtOH rinse and sonication in acetone bath for 10 minutes. The washed FTO electrodes were then dried at 400 ^{o}C for 15 minutes. A thin layer of Pt-paste (Solaronix, Platisol T/SP) was slot printed on the FTO and the printed electrodes were then cured at 450 ^{o}C for 10 minutes. After allowing them to cool to room temperature, the working electrodes were then sealed with a 25 μm thick hot melt film (Surlyn, Solaronix, "Meltonix 1170-25") by heating the system at 130 ^{o}C under 0.2 psi pressure for 1 minute. Devices were completed by filling the electrolyte by pre-drilled holes in the counter electrodes and finally the holes were sealed with a Surlyn pre-cut circle and a thin glass cover by heating at 130 ^{o}C under pressure 0.1 psi for 25 seconds. Finally, soldered contacts were added with a MBR Ultrasonic soldering machine (model USS-9210) with solder alloy (Cerasolzer wire dia 1.6 mm item # CS186-150). A circular black mask (active area 0.15 cm^2) punched from black tape was used in the subsequent photovoltaic studies.

3.1 Photovoltaic Measurements: Current-Voltage Curves: Photovoltaic characteristics were measured using a 150 W Xenon lamp (Model SF150B, SCIENCETECH Inc. Class ABA) solar simulator equipped with an AM 1.5 G filter for a less than 2% spectral mismatch. Prior to each measurement, the solar simulator output was calibrated with a KG5 filtered mono-crystalline silicon NREL calibrated reference cell from ABET Technologies (Model 15150-KG5). The current density-voltage characteristic of each cell was obtained with Keithley digital source meter (Model 2400). Device performances under AM 1.5G irradiation were analyzed based on the equation PCE = (J_{sc}*V_{oc}*FF)/I_0. The incident photon-to-current conversion efficiency was measured with an IPCE instrument manufactured by Dyenamo comprised of a 175 W Xenon lamp (CERMAX, Model LX175F), monochromator (Spectral Products, Model CM110, Czerny-Turner, dual-grating), filter wheel (Spectral Products, Model AB301T, fitted with filter AB3044 [440 nm high pass] and filter AB3051 [510 nm high pass]), a calibrated UV-enhanced silicon photodiode reference and Dyenamo issued software.

3.2 Electron lifetime measurements: Also known as small modulation photovoltage transient measurements, were carried out with a Dyenamo Toolbox (DN-AE01) instrument and software. The intensity of the LED light source (Seoul Semiconductors, Natural White, S42182H, 450 nm to 750 nm emission) is varied to modulate the device open-circuit voltage. The base light intensity was modulated by applied voltages of 2.80, 2.85, 2.90, 2.95 and 3.00 V applied to the LED with the 3.0 V bias approaching 1 sun intensity (97%). The direction of illumination was from the photoanode to the counter electrode, and the device was positioned 5 cm from the LED light source. The voltage rise and decay times are fitted with a Levenberg-Marquardt fitting algorithm via LabView, and the electron lifetime was obtained from the averaging of rise and decay times.

Cobalt Electrolyte: All devices in Table S2, Figure S2 and Figure S3 were prepared with $Co(bpy)_3(PF_6)_2$ (0.25 M), $Co(bpy)_3(PF_6)_3$ (0.05 M), TBP (0.25 M), LiTFSI (0.1 M), in acetonitrile. Electrodes use a 30 nm nanoparticle TiO_2 paste from Dyenamo.

Table S2. DSC devices under various conditions (a) dye deposition solvent, (b) CDCA:dye ratio for cobalt based electrolyte and 5 µm TiO_2 active layer.

dye	electrode variables	*Jsc* (mA/cm^2)	*Voc* (mV)	FF	PCE %
YZ11	(a) MeCN:*t*-BuOH:THF (1:1:1) (0.3 mM dye)	7.3	712	74	4.0
YZ13	(b) 0:1 CDCA:dye	5.5	647	73	2.7
YZ16		7.2	627	70	3.3
YZ17		8.8	760	68	4.8
YZ17	(a) MeCN:*t*-BuOH:THF (1:1:1) (0.3 mM dye) (b) 20:1 CDCA:dye	10	709	68	5.0
YZ17	(a) MeCN:*t*-BuOH:CB (1:2.5:2.5) (0.3 mM dye) (b) 20:1 CDCA:dye	9.1	731	73	5.0
YZ17	(a) MeCN:CB (1:1) (0.3 mM dye) (b) 20:1 CDCA:dye	8.6	742	75	5.0
C218	(a) MeCN:*t*-BuOH:THF (1:1:1) (0.3 mM dye) (b) 20:1 CDCA:dye	6.7	660	65.2	3.0
C218	(a) MeCN:*t*-BuOH (1:1) (0.3 mM dye) (b) 0:1 CDCA:dye	13.2	824	66.5	7.52

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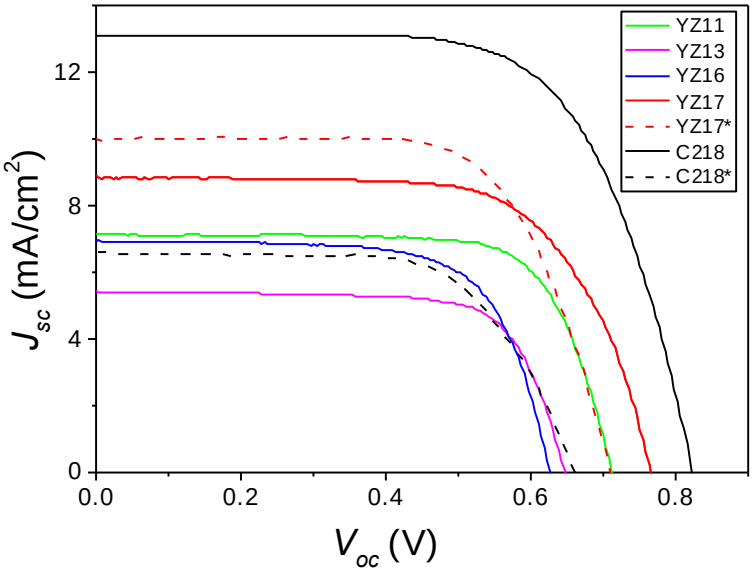

Figure S3: I-V curve for **YZ11**, **YZ13**, **YZ16**, **YZ17** and **C218**. Note: All the YZ dyes are in acetonitrile: tert-butanol: THF (1:1:1) (0.3 mM dye) with no CDCA (solid line), C218 (solid black line) in 1:1 acetonitrile: tert-butanol with no CDCA and with 20:1 CDCA:dye (dotted line). Comparing optimized conditions from Table S2.

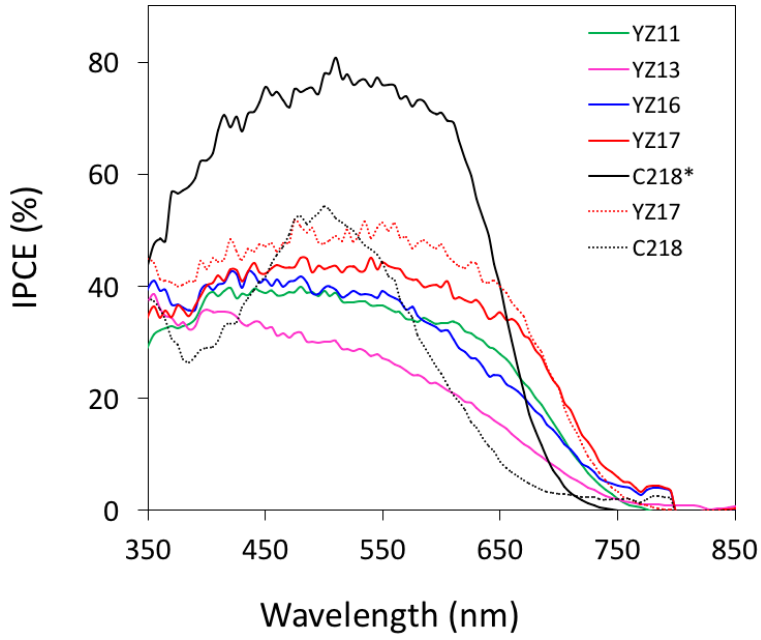

Figure S4: IPCE spectra for **YZ11**, **YZ13**, **YZ16**, **YZ17** and **C218** under the same condition as Figure S2.

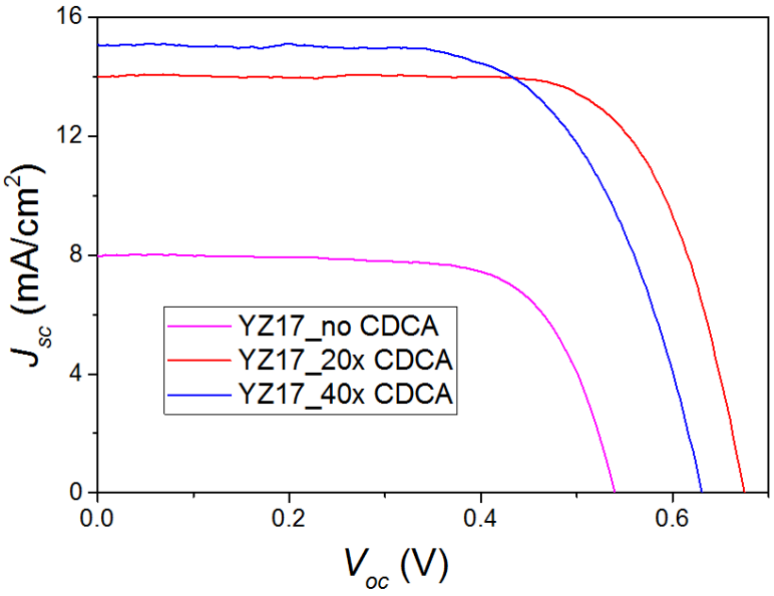

Figure S5. I-V curve of **YZ17** with 0:1 CDCA:dye (0 mM), 20:1 CDCA:dye (6 mM), 40:1 CDCA:dye (12 mM) addition in the acetonitrile: tert-butanol: THF (1:1:1) (0.3 mM dye) dipping solution. Devices were prepared with 1.0 M DMII (1,3-dimethylimidazolium iodide), 0.03 M iodine, 1.0 M LiI, 0.5 M TBP, 0.1 M guanidinium thiocyanide, acetonitrile:valeronitrile (85:15,v/v) solvent.

Table S3. Dye desorption study results. All films were prepared according to the conditions for devices reported in **Table 2** of the manuscript.

dye film	molar absorptivity ($M^{-1}cm^{-1}$)	λ_{max} (nm)	dye loading density (mol/cm^2)
YZ11	25,000	503	3.9 x 10^{-8}
YZ13	28,000	509	4.6 x 10^{-8}
YZ16	24,000	504	2.1 x 10^{-8}
YZ17	23,000	505	3.7 x 10^{-8}

Molar absorptivity values and absorption maximum were measured in 0.1 M TBAOH (tetrabutylammonium hydroxide) DMF solutions.

4. References

1. Zhu, Z.; Waller, D.; Gaudiana, R.; Morana, M.; Mühlbacher, D.; Scharber, M.; Brabec, C., *Macromolecules* **2007,** *40*, 1981.
2. Brzezinski, J. Z.; Reynolds, J. R., *Synthesis* **2002,** *8*, 1053.
3. Zotti, G.; Schiavon, G.; Zecchin, S.; Berlin, A.; Pagani, G., *Synth. Met.* **1994,** *66*, 149.
4. Foster, M. E.; Zhang, B. A.; Murtagh, D.; Liu, Y.; Sfeir, M. Y.; Wong, B. M.; Azoulay, J. D., *Macromol. Rapid Commun.* **2014,** *35*, 1516.