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Supplementary Information

Tetraphenylethylene Tethered Phenothiazine-Based Double-Anchored Sensitizers for High Performance Dye-Sensitized Solar Cells

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Experimental Section

General Information. The reactions were carried out using standard Schlenk techniques and under nitrogen atmosphere, and the solvents used were purified by standard procedures. Column chromatography was performed using silica gel (230-400 mesh, Macherey-Nagel GmbH & Co.) as stationary phase. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVIII-400 or AV-500 spectrometer. Electronic absorption spectra were recorded by a Dynamica DB-20 UV-visible spectrophotometer, and emission spectra were recorded on a Hitachi F-4500 or Fluorolog FL3-21 (Horiba Jobin Yvon) spectrofluorometer. Cyclic voltammetry experiments were performed at room temperature with a CHI-621B electrochemical analyzer equipped with a conventional three-electrode unit consisting of platinum working and auxiliary electrodes and a nonaqueous $Ag/AgNO_3$ reference electrode. The $E_{1/2}$ values were determined as $1/2(E_p^a + E_p^c)$, where E_p^a and E_p^c were the anodic and cathodic peak potentials, respectively. The solvent in all experiments was CH_2Cl_2 and the supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate. For FAB-mass spectra, the source accelerating voltage was operated at 10 kV with a Xe gun, using 3-nitrobenzyl alcohol as the matrix. Elementary analyses were performed on a Perkin-Elmer 2400 CHN analyzer.

(4-(3,7-Dibromo-10*H*-phenothiazin-10-yl)phenyl)(phenyl)methanone (1).

To a flask containing 3,7-dibromo-10*H*-phenothiazine (6.60 g, 18.4 mmol) and *t*-BuOK (2.50 g, 22 mmol) was added THF (20.0 mL) and the resulting mixture was heated at 60 ^{o}C for 10 min. (4-Fluorophenyl) (phenyl)methanone (3.7 g, 1.8 mmol) was then added and the solution and then refluxed at 80 ^{o}C for 16 h. After removal of the solvent, the residue was extracted with dichlorometane (300 mL) and washed with brine (200 mL). The combined organic extract was dried over anhydrous $MgSO_4$ and filtered. The filtrate was pumped dry and the crude product was further purified by column chromatography using EA/hexanes (1:4 by vol.) as the eluent. The desired product was isolated as a green powder in 58% yield (5.7g). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.93 (d, J_{HH} = 8.5 Hz, 2H), 7.81 (d, J_{HH} = 7.2 Hz, 2H), 7.60 (t, J_{HH} = 7.2 Hz, 1H), 7.49 (t, J_{HH} = 7.8 Hz, 2H), 7.31(d, J_{HH} = 8.5 Hz, 2H), 7.28 (d, J_{HH} = 2.3 Hz, 2H), 7.13 (dd, J_{HH} = 8.7; 2.2 Hz, 2H), 6.48 (d, J_{HH} = 8.7 Hz, 2H). ^{13}C NMR (125 Hz, $CDCl_3$): δ 195.5, 145.7, 141.9, 137.5, 135.4, 132.8, 132.7, 130.3, 130.1, 128.6, 126.9, 125.1, 121.2, 116.9. MS-HR-EI (*m/z*): $[M]^+$ calcd for $C_{25}H_{15}Br_2NOS$: 534.9241; found: 536.9217.

3,7-Dibromo-10-(4-(1,2,2-triphenylvinyl)phenyl)-10*H*-phenothiazine (2).

To a flask containing diphenylmethane (1.0 mL, 5.9 mmol) was added dried THF (6.0 mL), and the solution was prechiled to -78 ^{o}C. After dropwise addition of *n*-butyllithium (1.6 M *n*-BuLi in hexane, 3.5 mL), the solution was stirred at 0 ^{o}C for 1 h. A dried THF solution (6.0 mL) of **1** prechilled to 0 ^{o}C was then slowly added. The solution was warmed to room temperature and stirred for 12 h. After removal of the solvent, the residue was extracted with dichlorometane (200 mL) and brine (100 mL). The combined organic extract was dried over

anhydrous $MgSO_4$ and filtered. The filtrate was concentrated and transferred to a reaction flask equipped with a Dean Stark trap. *p*-Toluenesulfonic acid monohydrate (0.28 g, 1.5 mmol) and toluene (50 mL) were added, and the resulting solution was refluxed at 110 °C for 3 h. After removal of the solvent, the residue was extracted with dichlorometane (200 mL) and washed with brine (100 mL). The combined organic extract was dried over anhydrous $MgSO_4$ and filtered. The filtrate was pumped dry and the crude product was further purified by column chromatography using hexanes as the eluent. Compound **2** was isolated as a yellow-green powder in 50% yield (1.92 g). ^{1}H NMR (400 MHz, THF-d_8): δ 7.29 (d, J_{HH} = 8.3 Hz, 2H), 7.13−7.05 (m, 19H), 6.98 (dd, J_{HH} = 8.8; 2.2 Hz, 2H), 5.98 (d, J_{HH} = 9.3 Hz, 2H). ^{13}C NMR (100 Hz, THF): δ 144.9, 143.6, 143.1, 143.1, 142.8, 142.6, 140.1, 138.1, 134.1, 131.5, 131.4, 130.0, 130.0, 129.8, 128.9, 128.1, 127.9, 127.8, 127.0, 121.3, 117.1, 114.8. HR-MS-MALDI (*m/z*): $[M]^+$ calcd for $C_{38}H_{25}Br_2NS$, 685.0074; found, 687.0053. The identity of compound **2** was also confirmed by ^{1}H−^{1}H COSY,DEPT ^{13}C. ^{1}H−^{13}C HSQC and ^{1}H−^{13}C HMBC NMR spectra, as shown in Figure S10−S13.

5,5'-(10-(4-(1,2,2-Triphenylvinyl)phenyl)-10*H*-phenothiazine-3,7-diyl)bis(thiophene-2-carbaldehyde) (YL1al).

To a flask containing **2** (0.50 g, 0.72 mmol), $Pd(PPh_3)_2Cl_2$ (14 mg, 0.021 mmol), (5-(1,3-dioxolan-2-yl)thiophen-2-yl)tributylstannan (0.97 g, 2.1 mmol) and PPh_3 (11 mg, 0.042 mmol) was added dried DMF (6.6 mL) and the resulting mixture was refluxed for 16 h. Dichloromethane (10 mL) and HCl (4N, 20 mL) were added and the solution was reacted for another 3 h. The solution was pumped dry, and the residue was extracted with dichlorometane (100 mL) and washed with brine (100 mL). The combined organic extract was dried over anhydrous $MgSO_4$ and filtered. The filtrate was pumped dry and the crude product was further purified by column chromatography using dichloromethane as the eluent. Compound **YL1al** was isolated as an orange-red powder in 49% yield (0.26 g). ^{1}H NMR (400 MHz, THF-d_8): δ 9.81 (s, 2H), 7.77 (d, J_{HH} = 3.4 Hz, 2H), 7.43 (d, J_{HH} = 3.4 Hz, 2H), 7.39 (s, 2H), 7.34 (d, J_{HH} = 7.7 Hz, 2H), 7.23 (d, J_{HH} = 8.7 Hz, 2H), 7.24−7.09 (m, 17H), 6.11 (d, J_{HH} = 8.5 Hz, 2H). ^{13}C NMR (100 Hz, THF-d_8): δ 152.8, 146.1, 144.9, 144.6, 143.9, 143.6, 143.4, 141.2, 139.1, 138.2, 135.0, 132.3, 132.1, 130.9, 129.0, 128.8, 128.6, 127.6, 126.0, 124.8, 124.4, 120.9, 117.0. MS-HR-MALDI (m/z): $[M]^+$ calcd for $C_{48}H_{31}NO_2S_3$, 749.1517; found, 749.1520.

(2*E*,2'*E*)-3,3'-((10-(4-(1,2,2-Triphenylvinyl)phenyl)-10*H*-phenothiazine-3,7-diyl)bis(thio-phene-5,2-diyl))bis(2-cyanoacrylic acid) (YL1).

To a flask containing **YL1al** (0.15 g, 0.20 mmol), cyanoacetic acid (0.17 g, 2.0 mmol) and ammonium acetate (46 mg, 0.60 mmol) was added acetic acid (3.0 mL), and the resulting mixture was heated at 110 °C for 16 h. The solution was pumped dry, and the residue was extracted with EA (100 mL) and washed with brine (100 mL). The combined organic extract was dired over anhydrous $MgSO_4$ and filtered. The filtrate was pumped dry and the crude product was recrystallized from THF and hexanes to afford **YL1** as a dark purple powder in 68% yield

(0.12 g). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.00 (s, 2H), 7.63 (d, J_{HH} =3.3 Hz, 2H), 7.51 (d, J_{HH} = 3.3 Hz, 2H), 7.38 (s, 2H), 7.28−7.11 (m, 17H), 7.05−7.01 (m, 4H), 5.99 (d, J_{HH} = 8.6 Hz, 2H). ^{13}C NMR (100 Hz, DMSO-d_6): δ 164.4, 163.5, 147.1, 144.6, 143.4, 143.1, 142.8, 142.2, 140.3, 137.9, 136.3, 134.0, 131.3, 131.1, 130.2, 128.5, 128.4, 128.3, 127.3, 125.4, 124.3, 123.8, 119.9, 119.5, 116.4, 110.2. MS-HR-MALDI (*m/z*): $[M]^+$ calcd for $C_{54}H_{33}N_3O_4S_3$, 883.1633; found, 883.1623. Anal. calcd for $C_{54}H_{33}N_3O_4S_3$: C, 73.37; H, 3.76; N, 4.75. Found: C, 73.31; H, 3.77; N, 4.89.

5,5'-(10-(4-(1,2,2-Triphenylvinyl)phenyl)l-10*H*-phenothiazine-3,7-diyl)bis(3-hexylthio-phene-2-carbaldehyde) (YL2al).

To a flask containing **2** (0.30 g, 0.44 mmol)、$Pd(PPh_3)_4$ (61 mg, 0.052 mmol) and (5-(1,3-dioxolan-2-yl)-4-hexylthiophen-2-yl)tributylstannane (0.69 g, 1.3 mmol) was added dried toluene (2.0 mL) and the resulting mixture was refluxed for 16 h. Dichloromethane (10 mL) and HCl (4N, 20 mL) were added and the solution was reacted for another 3 h. The solution was pumped dry, and the residue was extracted with dichlorometane (100 mL) and brine (100 mL). The combined organic extract was dehydrated by anhydrous $MgSO_4$ and filtered. The filtrate was pumped dry and the crude product was further purified by column chromatography using dichloromethane/hexanes (1:6 by vol.) as the eluent. Compound **YL2al** was isolated as a red powder in 18% yield (70 mg). ^{1}H NMR (500 MHz, THF-d_8): δ 9.99 (s, 2H), 7.37 (s, 2H), 7.37 (d, J_{HH} = 8.2 Hz, 2H), 7.34 (d, J_{HH} = 7.7 Hz, 2H), 7.30 (s, 2H), 7.21−7.15 (m, 11H), 7.11−7.08 (m, 6H), 6.09 (d, J_{HH} = 8.6 Hz, 2H), 2.97 (t, J_{HH} = 7.7 Hz, 4H), 1.36−1.29 (m, 16H), 0.92−0.89 (m, 6H). ^{13}C NMR (125 Hz, THF-d_8): δ 181.8, 154.3, 151.7, 146.1, 144.9, 144.7, 144.2, 144.0, 143.7, 141.3, 139.2, 137.4, 135.1, 132.5, 132.3, 132.2, 131.0, 129.2, 128.9, 128.7, 127.9, 127.8, 126.9, 126.0, 124.7, 120.9, 117.1, 32.8, 32.5, 30.8, 30.2, 29.3, 23.6, 14.6, 1.5. MS-HR-MALDI (m/z): $[M]^+$ calcd for $C_{60}H_{55}NO_2S_3$, 917.3395; found, 917.3400.

(2*E*,2'*E*)-3,3'-((10-(4-(1,2,2-Triphenylvinyl)phenyl)-10*H*-phenothiazine-3,7-diyl)bis(3-he- xylthiophene-5,2-diyl))bis(2-cyanoacrylic acid) (YL2).

The reaction procedures are similar to those for **YL1**, inplace of **YL1al**, **YL2al** was used. Compound **YL2** was isolated as a dark purple powder in 68% yield. ^{1}H NMR (400 MHz, THF-d_8): δ 8.39 (s, 2H), 7.40 (d, J_{HH} = 5.7 Hz, 4H), 7.34 (d, J_{HH} = 8.1 Hz, 2H), 7.26 (d, J_{HH} = 8.1 Hz, 2H), 7.19−7.10 (m, 19H), 6.12 (d, J_{HH} = 8.7 Hz, 2H), 1.73−1.67 (m, 4H), 1.40−1.34 (m, 12H), 0.90−0.90 (m, 10H). ^{13}C NMR (100 Hz, THF-d_8): δ 156.5, 151.7, 146.2, 145.0, 144.7, 144.3, 144.1, 143.8, 143.6, 141.2, 139.1, 135.2, 132.5, 132.3, 131.0, 130.2, 128.9, 128.8, 128.7, 127.9, 127.7, 126.4, 126.0, 124.7, 120.9, 117.2, 117.0, 114.9, 98.2, 32.7, 32.3, 30.1, 29.9, 26.0, 23.6, 14.6. MS-HR-MALDI (m/z): $[M]^+$ calcd for $C_{66}H_{57}N_3O_4S_3$, 1051.3511; found, 1051.3495. Anal. calcd for $C_{66}H_{57}N_3O_4S_3$: C, 75.33; H, 5.46; N, 3.99. Found: C, 75.26; H, 5.64; N, 4.04.

3,7-Bis(4'-hexyl-[2,2'-bithiophen]-5-yl)-10-(4-(1,2,2-triphenylvinyl)phenyl)-10*H*-pheno-thiazine (3).

To a flask containing **2** (0.30 g, 0.44 mmol), tributyl(4'-hexyl-[2,2'-bithiophen]-5-yl)stannane (0.70 g, 1.31 mmol) and $Pd(PPh_3)_4$ (61 mg, 0.052 mmol) was added toluene (2.0 mL) and the resulting mixture was refluxed for 16 h. After removal of the solvent, the residue was extracted with dichlorometane (100 mL) and washed with brine (100 mL). The combined organic extract was dried over anhydrous $MgSO_4$ and filtered. The filtrate was pumped dry and the crude product was further purified by column chromatography using dichloromethane/hexanes (1:2 by vol.) as the eluent. Compound **3** was isolated as a yellow powder in 67% yield (0.30 g). ^{1}H NMR (400 MHz, acetone-d_6): δ 7.39 (d, J_{HH} = 8.2 Hz, 2H), 7.32 (s, 2H), 7.30 (d, J_{HH} = 3.4 Hz, 2H), 7.26−7.14 (m, 21H), 7.02 (s, 2H), 6.13 (d, J_{HH} = 8.5 Hz, 2H), 2.62 (t, J_{HH} = 7.7 Hz, 4H), 1.67−1.62 (m, 4H), 1.39−1.27 (m, 12H), 0.92−0.89 (m, 6H). ^{13}C NMR (100 Hz, acetone-d_6): δ 145.2, 143.9, 137.3, 134.8, 132.2, 132.0, 131.0, 129.8, 128.9, 128.8, 127.8, 126.0, 125.4, 125.2, 124.5, 124.0, 120.4, 117.1, 32.5, 29.4, 14.4.

5',5'''-(10(4-(1,2,2-Triphenylvinyl)phenyl)-10*H*-phenothiazine-3,7-diyl)bis(4-hexyl-[2,2'-bithiophene]-5-carbaldehyde) (YL3al).

To a solution of **3** (0.30 g, 0.29 mmol) in DMF (2.5 mL) prechilled to 0 ^{o}C was added $POCl_3$ (0.14 mL, 1.5 mmol) dropwise. After being stirred for 30 min., the solution was warmed to room temperature and then heated at 80 ^{o}C for 12 h. After the solution was pumped dry, aqueous NaOAc (1M, 10 ml) was added to the residue and the mixture was stirred for 0.5 h, extracted with dichlorometane (100 mL) and washed with brine (100 mL). The combined organic extract was dried over anhydrous $MgSO_4$ and filtered. The filtrate was pumped dry and the crude product was further purified by column chromatography using dichloromethane/hexanes (2:1 by vol.) as the eluent. Compound **YL3al** was isolated as a red powder in 41% yield (0.13 g). ^{1}H NMR (400 MHz, THF-d_8): δ 9.98 (s, 2H), 7.37 (d, J_{HH} = 3.9 Hz, 2H, J_{HH} = 8.4 Hz, 2H), 2.96 (t, J_{HH} = 7.8 Hz, 4H), 1.41−1.37 (m, 4H), 1.34−1.28 (m, 12H), 0.91−0.87 (m, 6H). ^{13}C NMR (100 Hz, THF-d_8): δ 183.4, 164.5, 158.7, 148.7, 147.6, 145.4, 144.6, 144.5, 144.3, 144.1, 143.8, 141.2, 139.5, 134.6, 132.1, 131.9, 131.8, 130.9, 130.0, 128.1, 127.7, 127.4, 125.1, 123.9, 123.7, 121.4, 119.8, 118.5, 116.9, 38.3, 32.3, 25.3, 23.2. MS-HR-FAB (m/z): $[M]^+$ calcd for $C_{68}H_{59}NO_2S_5$, 1081.3149; found, 1082.3207.

(2*E*,2'*E*)-3,3'-((10-(4-(1,2,2-Triphenylvinyl)phenyl)-10*H*-phenothiazine-3,7-diyl)bis(4-he-xyl-[2,2'-bithiophene]-5',5-diyl))bis(2-cyanoacrylic acid) (YL3).

The reaction procedures are similar to those for **YL1**, inplace of **YL1al**, **YL3al** was used. Compound **YL3** was isolated as a dark purple powder in 75% yield. ^{1}H NMR (500 MHz, THF-d_8): δ 8.38 (s, 2H), 7.46 (d, J_{HH} = 5.0 Hz, 2H), 7.35−7.33 (m, 6H), 7.29 (s, 2H), 7.18−7.09 (m, 19H), 6.10 (d, J_{HH} = 8.6Hz, 2H), 2.83 (t, J_{HH} = 7.6Hz, 4H), 1.69−1.65 (m, 4H), 1.41−1.33 (m, 12H), 0.92−0.88 (m, 6H). ^{13}C NMR (125Hz, THF-d_8): δ 164.8, 156.4, 146.0, 144.8, 144.4, 144.1, 143.6, 141.4, 139.5, 135.4, 135.1, 132.6, 132.3, 131.2, 130.2, 129.5, 129.0, 128.8, 127.8, 126.8, 125.4, 125.0, 124.4, 121.1, 117.2, 98.8, 32.8, 32.3, 30.9, 30.1, 29.9, 23.7, 14.6. MS-HR-FAB (m/z):

$[M]^+$ calcd for $C_{74}H_{61}N_3O_4S_5$, 1215.3266; found, 1215.3270. Anal. calcd for $C_{74}H_{61}N_3O_4S_5$: C, 73.06; H, 5.05; N, 3.45. Found: C, 72.90; H, 5.14; N, 3.61.

3,7-Bis(4,4-dihexyl-4*H*-cyclopenta[2,1-*b*:3,4-*b*']dithiophen-2-yl)-10-(4-(1,2,2-triphenyl-vi nyl)phenyl)-10*H*-phenothiazine (4)

To a flask containing **2** (0.20 g, 0.29 mmol), $Pd(PPh_3)_4$ (13 mg, 0.012 mmol) and tributyl(4,4-dihexyl-4*H*-cyclopenta[2,1-*b*:3,4-*b*']dithiophen-2-yl)stannane[13] (0.55 g, 0.87 mmol) was added dried toluene (2.0 mL), and the solution was refluxed for 16 h. After removal of the solvent, the residue was extracted with dichlorometane (100 mL) and washed with brine (100 mL). The combined organic extract was dried over anhydrous $MgSO_4$ and filtered. The filtrate was pumped dry and the crude product was further purified by column chromatography using dichloromethane/hexanes (1:1 by vol.) as the eluent. Compound **4** was isolated as a yellow powder in 77% yield (0.27 g). ^{1}H NMR (400 MHz, acetone-d_6): δ 7.40−7.39 (m, 3H), 7.37−7.35 (m, 5H), 7.25−7.13 (m, 19H), 7.09 (d, J_{HH} = 4.8 Hz, 2H), 6.13 (d, J_{HH} = 8.5 Hz, 2H), 1.94 (t, J_{HH} = 8.0 Hz, 8H), 1.19−1.09 (m, 24H), 0.99−0.94 (m, 8H), 0.80 (t, J_{HH} = 6.5 Hz, 12H). ^{13}C NMR (100 Hz, acetone-d_6): δ 159.7, 158.4, 145.1, 144.1, 143.7, 143.5, 143.3, 142.9, 140.9, 139.1, 136.8, 135.6, 134.3, 131.8, 131.6, 130.5, 130.4, 128.5, 128.3, 127.3, 125.9, 124.2, 123.2, 122.4, 120.3, 118.0, 116.7, 54.6, 54.3, 38.2, 32.0, 24.9, 22.9, 14.0. MS-HR-MALDI (m/z): $[M]^+$ calcd for $C_{80}H_{83}NS_5$, 1217.5129; found, 1217.5124.

6,6'-(10-(4-(1,2,2-Triphenylvinyl)phenyl)-10*H*-phenothiazine-3,7-diyl)bis(4,4-dihexyl-4*H*-cyclopenta[2,1-*b*:3,4-*b*']dithiophene-2-carbaldehyde) (YL4al).

The reaction procedures are similar to those for **YL3al**, instead of compound **3**, compound **4** was used. The eluent used for column chromatography was dichloromethane/hexanes (5:1 by vol.). Compound **YL4al** was isolated as a red powder in 51% yield. ^{1}H NMR (400 MHz, acetone-d_6): δ 9.84 (s, 2H), 7.85 (s, 2H), 7.42 (s, 2H), 7.28-7.26 (m, 4H), 7.14−7.05 (m, 19H), 6.04 (d, J_{HH} = 7.9 Hz, 2H), 1.98−1.93 (m, 8H), 1.15−1.11 (m, 24H), 0.99−0.95 (m, 8H), 0.767−0.74 (m, 12H). ^{13}C NMR (100 Hz, acetone-d_6): δ 183.1, 164.4, 158.6, 148.5, 147.5, 145.6, 144.6, 144.4, 143.9, 143.6, 143.3, 141.0, 138.9, 134.7, 132.1, 131.9, 131.6, 130.7, 130.1, 128.8, 128.6, 128.6, 127.6, 125.1, 123.96, 120.5, 118.4, 117.0, 55.1, 38.2, 30.4, 25.3, 23.3, 14.4. MS-HR-FAB (m/z): $[M]^+$ calcd for $C_{82}H_{83}NO_2S_5$, 1273.5027; found,1274.6035.

(2*E*,2'*E*)-3,3'-((10-(4-(1,2,2-Triphenylvinyl)phenyl)-10*H*-phenothiazine-3,7-diyl)bis(4,4-dihexyl-4*H*-cyclopenta[2,1-*b*:3,4-*b*']dithiophene-6,2-diyl))bis(2-cyanoacrylic acid) (YL4).

The reaction procedures are similar to those for **YL1**, instead of compound **YL1al**, compound **YL4al** was used. Compound **YL4** was isolated as a dark purple powder in 71% yield. ^{1}H NMR (400 MHz, THF-d_8): δ 8.29 (s, 2H), 7.72 (s, 2H), 7.33−7.30 (m, 6H), 7.13−7.06 (m, 19H), 6.07 (d, J_{HH} = 8.6 Hz, 2H), 2.00−1.85 (m, 8H), 1.13−1.13 (m, 24H), 0.97−0.97 (m, 8H), 0.79−0.76 (m, 12H). ^{13}C NMR (100 Hz, THF-d_8): δ 164.5, 164.3, 158.5, 149.5,

149.3, 143.7, 137.5, 135.0, 134.7, 132.1, 131.9, 130.6, 130.0, 128.6, 128.3, 124.9, 123.7, 120.5, 117.2, 116.8, 95.8, 54.8, 38.4, 32.3, 30.4, 23.3, 14.1. MS-HR-MALDI (m/z): $[M]^+$ calcd for $C_{88}H_{85}N_3O_4S_5$, 1407.5144; found, 1408.5185. Anal. calcd for $C_{88}H_{85}N_3O_4S_5$: C, 75.02; H, 6.08; N, 2.98. Found: C, 75.17; H, 5.98; N, 3.03.

(*E*)-3,7-dibromo-10-(4-(1,2-diphenylvinyl)phenyl)-10*H*-phenothiazine (5).

To a flask containing **1** (1.0 g, 1.9 mmol) was added dried THF (5.0 mL), and the solution was prechiled to 0 ^oC. After dropwise addition of benzylmagnesium chloride (1 M in THF, 2 mL, 2.0 mmol), the solution was stirred at 0 ^oC for 1 h then warme to room temperature and stirred for 12 h. After removal of the solvent, the residue was extracted with dichlorometane (50 mL) and washed with brine (50 mL). The combined organic extract was dried over anhydrous $MgSO_4$ and filtered. The filtrate was concentrated and transferred to a reaction flask equipped with a Dean Stark trap. *p*-Toluenesulfonic acid monohydrate (36 mg, 0.2 mmol) and toluene (50 mL) were added, and the resulting solution was refluxed for 16 h. After removal of the solvent, the residue was extracted with dichlorometane (100 mL) and washed with brine (100 mL). The combined organic extract was dried over anhydrous $MgSO_4$ and filtered. The filtrate was pumped dry and the crude product was further purified by column chromatography using hexanes as the eluent. Compound **5** was isolated as a white powder in 76% yield (1.1 g). ^1H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, J_{HH} = 8.5 Hz, 1H), 7.43−7.35 (m, 5H), 7.28−7.23 (m, 3H), 7.15−7.03 (m, 8H), 6.98 (dd, J_{HH} = 8.8, 2.3 Hz 1H), 6.92 (dd, J_{HH} = 8.8, 2.3 Hz, 1H), 6.10 (d, J_{HH} = 8.8 Hz, 1H), 6.07 (d, J_{HH} = 8.8 Hz, 1H). ^{13}C NMR (100 Hz, $CDCl_3$): δ 143.8, 143.2, 142.5, 141.9, 141.4, 141.3, 139.9, 139.5, 137.4, 137.1, 133.5, 130.9, 130.5, 130.3, 130.1, 129.9, 129.8, 129.6, 129.3, 129.1, 128.6, 128.2, 127.9, 127.7, 127.3, 127.3, 121.8, 127.9, 127.7, 127.3, 121.8, 121.7, 117.5, 115.0, 115.0. HR-MS-FAB (*m/z*): $[M]^+$ calcd for $C_{32}H_{21}Br_2NS$, 608.9761; found, 687.5676.

(*E*)-10-(4-(1,2-diphenylvinyl)phenyl)-3,7-bis(4-hexylthiophen-2-yl)-10*H*-phenothiazine (6)

To a flask containing **5** (0.30 g, 0.44 mmol), tributyl(4-hexylthiophen-2-yl)stannane (0.70 g, 1.31 mmol) and $Pd(PPh_3)_4$ (61 mg, 0.052 mmol) was added dried toluene (2.0 mL) and the resulting mixture was refluxed for 16 h. After removal of the solvent, the residue was extracted with dichlorometane (100 mL) and washed with brine (100 mL). The combined organic extract was dried over anhydrous $MgSO_4$ and filtered. The filtrate was pumped dry and the crude product was further purified by column chromatography using dichloromethane/hexanes (1:2 by vol.) as the eluent. Compound **6** was isolated as a yellow powder in 67% yield (0.30 g). ^1H NMR (400 MHz, acetone-d_6): δ 7.64 (d, J_{HH} = 6.8 Hz, 1H), 7.49−7.10 (m, 20H), 6.96 (d, J_{HH} = 6.3 Hz, 2H), 6.31 (d, J_{HH} = 8.7 Hz, 1H), 6.24 (d, J_{HH} = 8.7 Hz, 1H), 2.61−2.56 (m, 4H), 1.65−1.61 (m, 4H), 1.35−1.30 (m, 12H), 0.89−0.86 (m, 6H). ^{13}C NMR (100 Hz, acetone-d_6): δ 145.1, 144.2, 143.9, 143.7, 143.6, 143.4, 143.2, 142.7, 142.3, 141.9, 141.0, 140.8, 140.6, 138.2, 138.1, 134.0, 133.9, 131.8, 131.2, 131.1, 131.0, 130.6, 130.5, 130.5, 130.0, 129.8, 129.6, 129.3, 128.9, 128.6, 128.3, 128.0, 127.9, 127.6, 125.1, 124.9, 124.8, 124.2, 123.7, 121.2, 121.0, 119.9, 117.5,

117.3, 117.2, 32.4, 31.2, 31.2, 23.4, 14.4. MS-HR-FAB (m/z): $[M]^+$ calcd for $C_{52}H_{51}NS_3$, 785.3184; found, 785.3187.

(*E*)-5,5'-(10-(4-(1,2-diphenylvinyl)phenyl)-10*H*-phenothiazine-3,7-diyl)bis(3-hexylthiophene-2-carbaldehyde) (YL5al)

The reaction procedures are similar to those for **YL3al**, inplce of compound **3**, compound **6** was used. The eluent used for column chromatography was dichloromethane/hexanes (3:1 by vol.). Compound **YL5al** was isolated as a red powder in 51% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.97 (s, 1H), 9.95 (s, 1H), 7.58 (d, J_{HH} = 8.4 Hz, 1H), 7.47 (d, J_{HH} = 8.3 Hz, 1H), 7.40−7.25 (m, 9H), 7.18−7.05 (m, 10H), 6.21 (d, J_{HH} = 8.6 Hz, 1H), 6.18 (d, J_{HH} = 8.6 Hz, 1H), 2.93−2.88 (m, 4H), 1.72−1.66 (m, 4H), 1.36−1.23 (m, 12H), 0.89−0.84 (m, 6H). ^{13}C NMR (100 Hz, $CDCl_3$): δ 181.7, 154.2, 151.8, 151.7, 144.2, 144.1, 144.0, 142.4, 141.7, 141.6, 141.3, 139.8, 139.0, 138.8, 137.3, 137.0, 136.0, 135.9, 133.5, 131.0, 130.5, 130.4, 130.2, 129.7, 129.3, 129.0, 128.6, 128.2, 128.1, 128.0, 127.9, 127.6, 127.3, 125.6, 125.6, 125.3, 124.2, 124.1, 120.0, 120.0, 116.2, 116.1, 31.7, 31.5, 29.1, 28.7, 22.6, 14.2. MS-HR-FAB (m/z): $[M]^+$ calcd for $C_{54}H_{51}NO_2S_3$, 841.3082; found, 842.3162.

(2*E*,2'*E*)-3,3'-((10-(4-((*E*)-1,2-diphenylvinyl)phenyl)-10*H*-phenothiazine-3,7-diyl)bis(3-hexylthiophene-5,2-diyl))bis(2-cyanoacrylic acid) YL5

The reaction procedures are similar to those for **YL1**, inplce of compound **YL1al**, compound **YL5al** was used. Compound **YL5** was isolated as a dark purple powder in 75% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.29 (s, 1H), 8.28 (s, 1H), 7.64−7.60 (m, 3H), 7.51−7.38 (m, 10H), 7.32−7.06 (m, 8H), 6.21 (d, J_{HH} = 8.8 Hz, 1H), 6.17 (d, J_{HH} = 8.8 Hz, 1H), 2.80−2.75 (m, 4H), 1.64−1.59 (m, 4H), 1.32−1.29 (m, 12H), 0.87−0.85 (m, 6H). ^{13}C NMR (100Hz, DMSO-d_6): δ 163.9, 156.2, 149.8, 143.2, 143.0, 141.6, 140.9, 140.5, 139.4, 138.3, 136.7, 136.6, 133.1, 130.8, 130.2, 129.7, 129.4, 129.3, 129.1, 128.5, 128.0, 128.0, 127.0, 127.0, 126.2, 125.6, 125.6, 123.7, 119.2, 119.0, 116.6, 116.2, 116.0, 96.2, 30.8, 30.4, 28.3, 21.9, 13.8. MS-HR-MALDI (m/z): $[M]^+$ calcd for $C_{60}H_{53}N_3O_4S_3$, 975.3198; found, 975.3174.

Quantum chemistry computation

The computation was performed with Gaussian 09 program package. Molecular geometry optimization of the molecules were performed using hybrid B3LYP functional level and 6-311G(d,P) basis set. For each molecule, a number of possible conformations were examined and the one with the lowest energy was used. The same functional was also applied for the calculation of excited states using time-dependent density functional theory (TD–DFT). In this work, we also use TD–DFT to visualize the extent of transition moments as well as their charge-transfer characters.

DSSCs' fabrication and analyses

Fluorine–doped tin oxide (FTO, TEC-7, 7 Ω square^{-1}, NSG America Inc., New Jersey, USA) conductive glasses were sequentially cleaned via the ultra-sonication in the bathes of neutral cleaner, de-ionized water, acetone, and isopropanol. A 15 μm-thick TiO_2 film, containing a 10 μm-thick transparent layer (Solarnix transparent paste) and a 5 μm-thick scattering layer (home-made scattering paste), was casted on the cleaned FTO via the doctor-blade technique with a controlled area of 0.20 cm^2. Each layer was sintered in a closed oven at 450 ^{o}C for 30 min in an air atmosphere before use. After that, the TiO_2 film was immersed in a 70 mM of $TiCl_4$ solution (de-ionized water/ethanol = 9/1 v/v) at 70 ^{o}C for 30 min, followed by the same sintering process. Then the as-prepared TiO_2 film was immersed in 3×10^{-4} M of dye solution at room temperature for 1 day using a tri-solvent system of acetonitrile/*tert*-butanol/ dimethyl sulfoxide having the volume ratio of 3/3/4 (for **YL1**, **YL2**, **YL3**, and **YL5**) or 3.5/3.5/3 (for **YL4**, **DCE4**, and **HL5**). Finally, a dye-adsorbed TiO_2 film was assembled with a sputtered-platinum/carbon cloth counter electrode using a 25 μm-thick Surlyn® (SX1170-25, Solaronix S. A., Switzerland) as the cell spacer. The iodide-based electrolyte, containing 0.1 M lithium iodide (LiI), 1.0 M 1,2-dimethyl-3-propylimidazolium iodide (DMPII), 0.04 M iodine (I_2), and 0.5 M 4–*tert*–butylpyridine (TBP) in acetonitrile/3-methoxypropionitrile (ACN/MPN = 8:2, in volume ratio), was injected into the cell gap between these two electrodes by capillarity.

Photovoltaic performance of DSSCs was measured by a potentiostat/galvanostat (650B, CH Instruments, Inc.) at AM 1.5G sun light illumination by using a class A quality solar simulator (XES–40S2–CE, San–Ei Electric Co., Ltd., Osaka, Japan). The incident light intensity of 100 mW cm^{-2} was calibrated with a standard Si cell (Oriel 91150, Newport Corp.). Incident photon–to–current conversion efficiencies (IPCE) of DSSCs were recorded by another potentiostat/galvanostat (PGSTAT101, Autolab, Eco–Chemie, Utrecht, the Netherlands) under monochromatic light illumination in a wavelength range of 400-800 nm using the same solar simulator equipped with a monochromator. The incident radiation flux (φ) was calibrated by a silicon solar cell. Electrochemical impedance spectra (EIS) of DSSCs were recorded by the CHI potentiostat/galvanostat equipped with a FRA2 module in a frequency range of 10 mHz−65 kHz and AC amplitude of ±10 mV. Under dark condition, the EIS spectra were measured at an applied bias of –0.65 V.

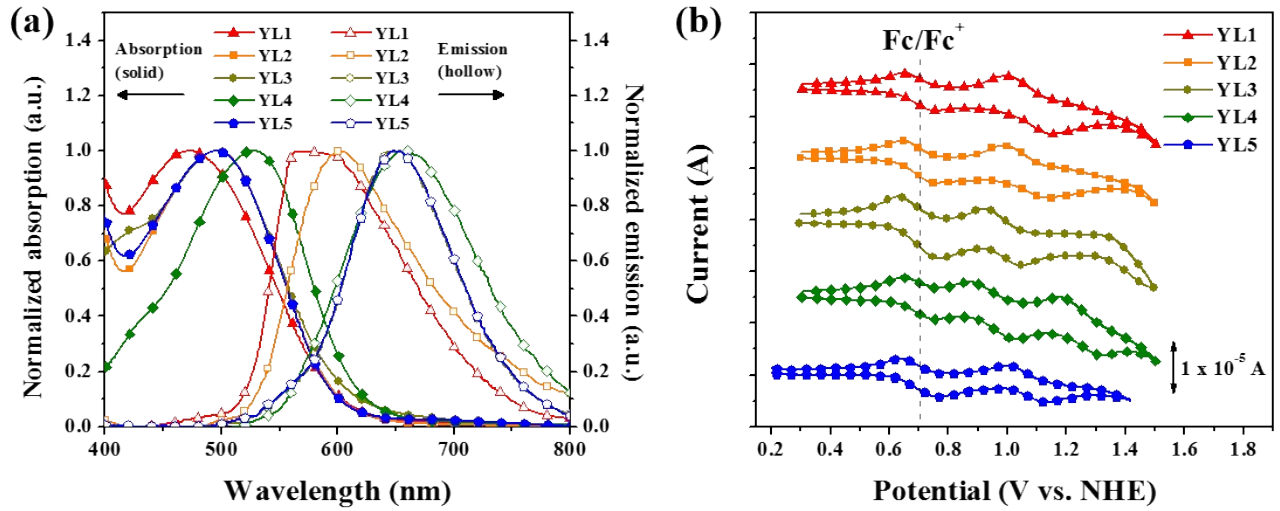


Figure S1. (a) Normalized absorption (solid) and emission spectra (hollow) of **YL** dyes (10 mM in THF). (b) Cyclic voltammograms of **YL** dyes (10 mM in THF). An internal reference (ferrocene/ferrocenium) with a standard potential of 0.7 V vs. NHE was applied.

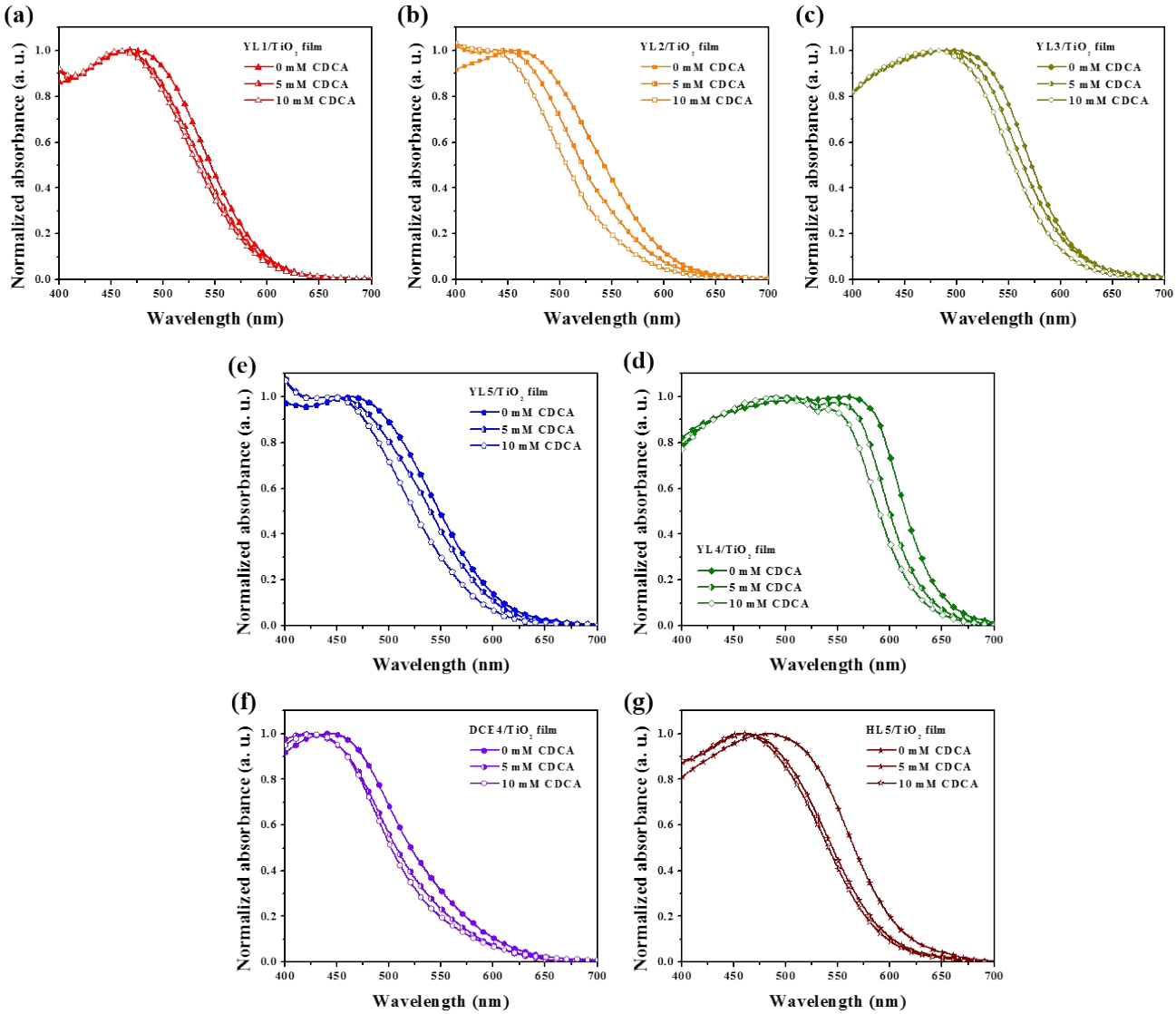


Figure S2. Normalized absorption spectra of **YL** dyes adsorbed on a TiO_2 film (4 μm) with 0 (solid), 5 (half solid), or 10 (hollow) mM of chenodeoxycholic acid.

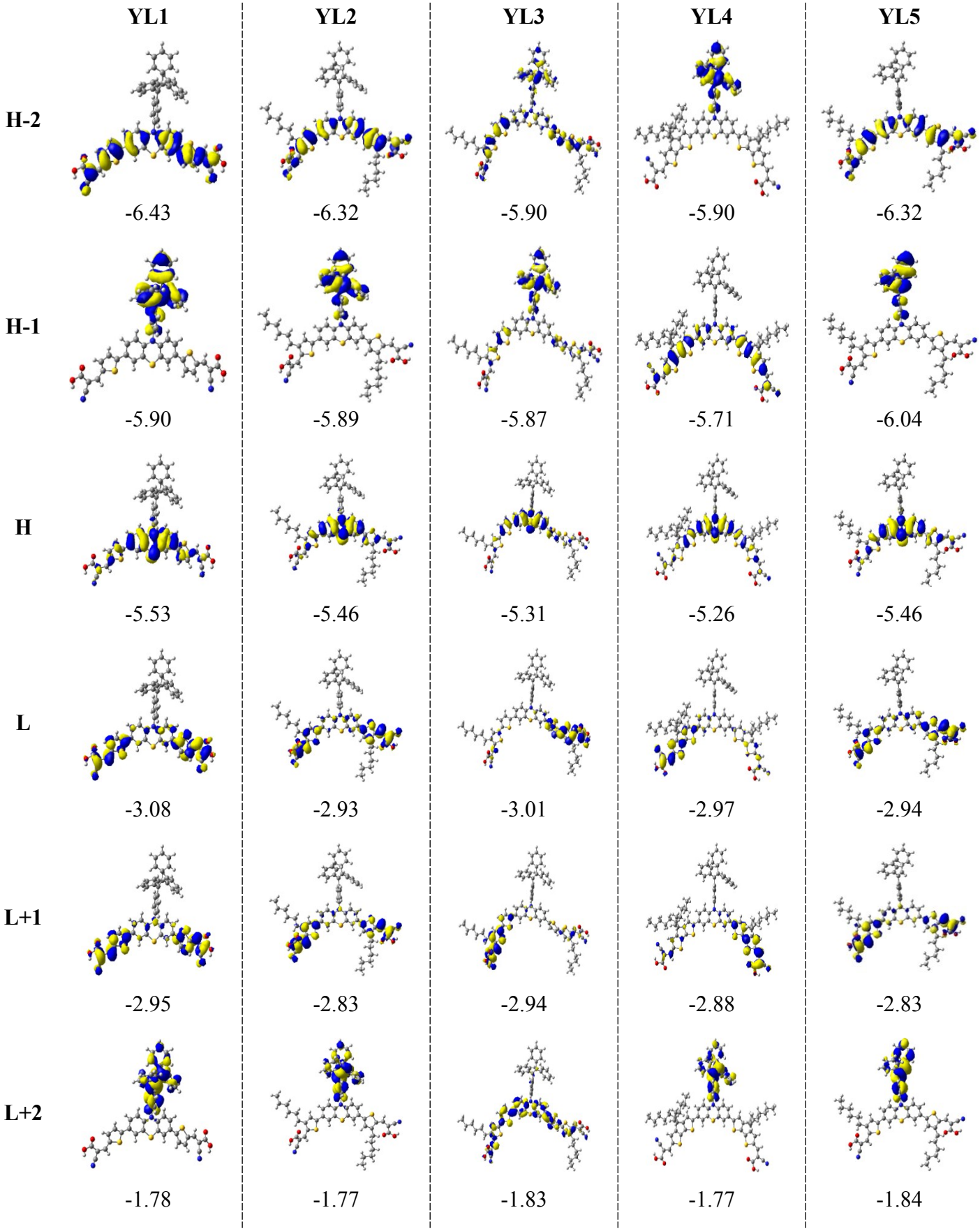


Figure S3. Frontier molecular orbitals of **YL** dyes; the calculated HOMOs and LUMOs energies (eV) of the **YL** dyes in THF are listed below.

Table S1. Calculated excitation energies for **YL** dyes in THF solution.

Dyes	N_States	*E* (ev)	WL (nm)	*f*	Major Contributions
	1	2.07	596.93	0.8757	H→L (99%)
	2	2.29	539.57	0.1982	H→L+1 (99%)
	3	2.57	481.71	0.0029	H-1→L (99%)
	4	2.70	458.04	0.0022	H-1→L+1 (100%)
YL1	5	3.06	404.50	0.7509	H-3→L (91%)
	6	3.12	396.59	0.4521	H-2→L (99%)
	7	3.21	385.55	0.4059	H-2→L+1 (89%)
	8	3.23	383.30	0.1256	H-3→L+1 (96%)
	9	3.27	378.48	0.0184	H→L+2 (88%)
	10	3.43	361.41	0.0085	H→L+3 (83%)
	1	2.14	577.93	0.8281	H→L (98%)
	2	2.33	530.68	0.1611	H→L+1 (99%)
	3	2.70	457.84	0.0055	H-1→L (99%)
	4	2.82	439.18	0.0054	H-1→L+1 (99%)
YL2	5	3.06	404.81	0.7229	H-3→L (46%), H-2→L (33%)
	6	3.09	400.08	0.4705	H-3→L (24%), H-2→L (59%)
	7	3.21	385.91	0.0919	H-3→L (27%), H-2→L+1 (67%)
	8	3.22	384.56	0.0055	H→L+2 (82%), H→L+3 (10%)
	9	3.25	380.45	0.02	H-3→L+1 (90%)
	10	3.34	371.08	0.0031	H→L+2 (12%), H→L+3 (80%)
	1	1.98	623.91	0.9722	H→L (91%)
	2	2.11	585.77	0.2866	H→L+1 (92%)
	3	2.63	471.42	0.3141	H-1→L (92%)
	4	2.66	465.93	0.2535	H-2→L (83%)
YL3	5	2.67	463.71	0.8186	H-2→L+1 (44%), H-1->L+1 (39%)
	6	2.74	451.01	0.0309	H-2→L+1 (46%), H-1->L+1 (53%)
	7	2.87	431.89	0.2825	H-3→L (93%)
	8	2.95	419.19	0.0844	H-3→L+1 (95%)
	9	3.02	409.60	0.0896	H→L+2 (90%)
	10	3.15	393.01	0.0166	H→L+3 (96%)
	1	1.99	621.90	1.1500	H→L (93%)
	2	2.15	574.92	0.4166	H→L+1 (94%)
	3	2.54	486.49	0.7936	H-1→L (97%)
	4	2.61	473.81	0.7509	H-1→L+1 (95%)
YL4	5	2.73	454.18	0.0066	H-2→L (99%)
	6	2.78	444.87	0.2884	H-3→L (96%)
	7	2.81	440.50	0.0026	H-2→L+1 (99%)
	8	2.89	428.87	0.2288	H-3→L+1 (97%)
	9	3.06	404.21	0.0083	H→L+2 (87%)
	10	3.16	391.73	0.0413	H→L+3 (84%)
	1	2.14	579.09	0.8551	H→L (98%)
	2	2.33	530.90	0.1649	H→L+1 (98%)
	3	2.85	433.78	0.0144	H-1→L (99%)
	4	2.97	416.93	0.0321	H-1→L+1 (99%)
YL5	5	3.05	405.87	0.6777	H-3→L (39%), H-2→L (42%)
	6	3.09	400.32	0.4885	H-3→L (31%), H-2→L (50%),
	7	3.15	392.91	0.0043	H→L+2 (95%)
	8	3.20	386.62	0.0921	H-3→L (26%), H-2→L+1 (70%)
	9	3.25	380.80	0.0247	H-3→L+1 (91%)
	10	3.32	373.44	0.0028	H→L+3 (89%)

WL: wavelength; *f*: oscillator strength; H: HOMO; H-n: HOMO-n; L: LUMO; L+n: LUMO+n.

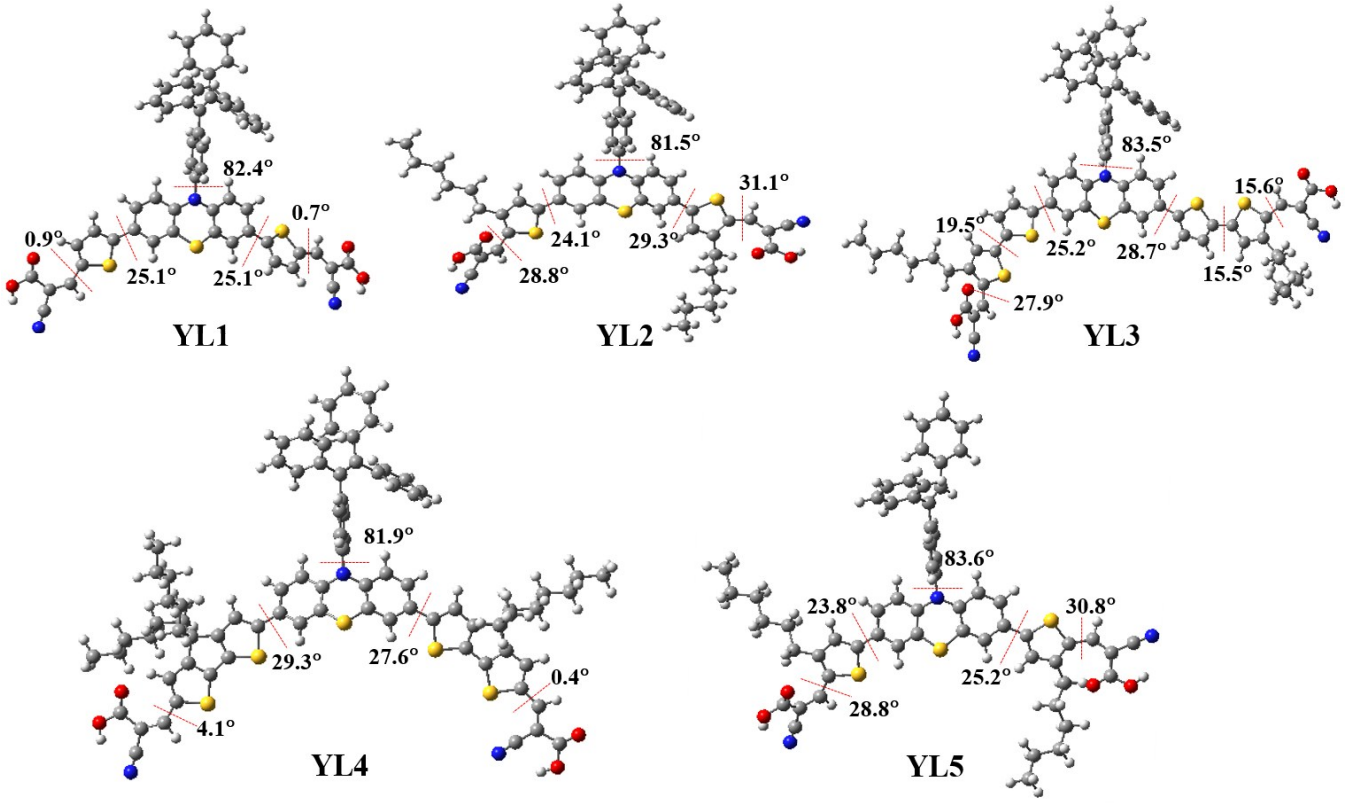


Figure S4. Optimized geometries with dihedral angles of YL dyes

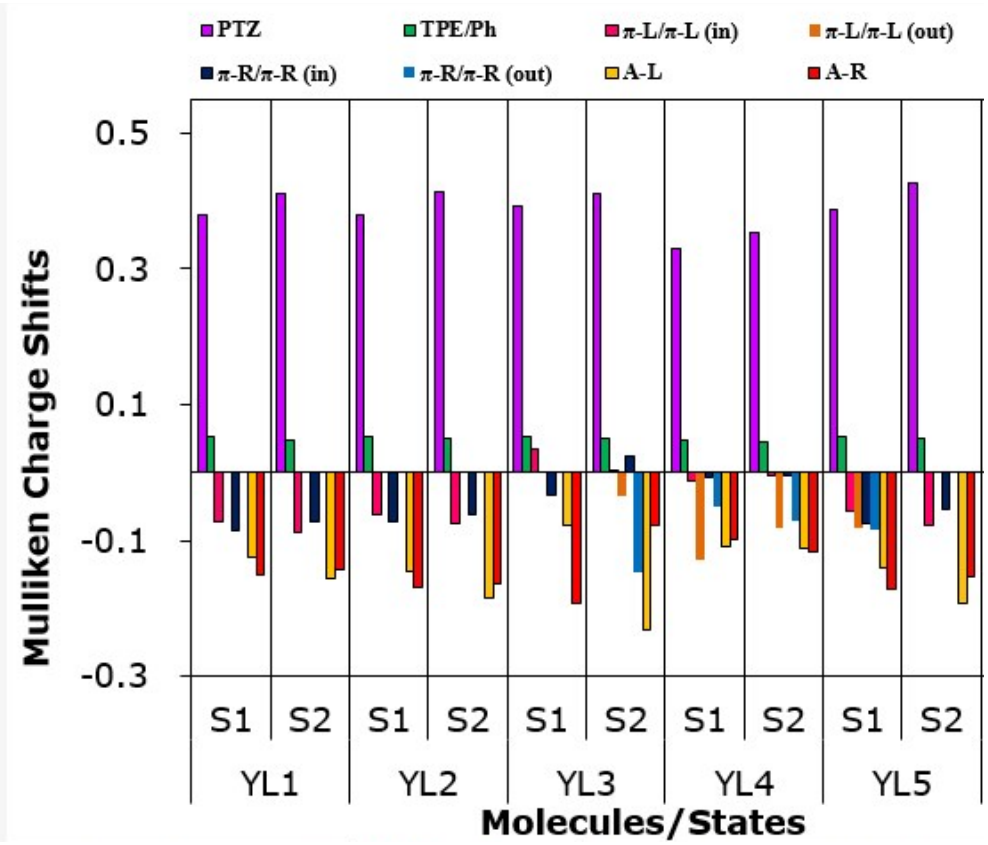


Figure S5. Plot of the difference in the Mulliken charges in **YL** dyes between the ground and excited states.

Table S2. Calculated Mulliken charges difference (Δq) between the excited-state and ground states for different segments of the **YL** dyes calculated from the B3LYP/6-311G(d,p) for the S_1 and S_2 states.

Dye	State	f [a]	Δ(Mulliken charge),[b]|e| (Δq)		$f \times$ |(Δq)|[c]	Dye	State	f [a]	Δ(Mulliken charge),[b]|e| (Δq)		$f \times$ |(Δq)|[c]
YL1	S_1	0.87	PTZ	0.38	0.35	**YL2**	S_1	0.83	PTZ	0.38	0.30
			TPE	0.05	0.03				TPE	0.05	0.03
			π-L	-0.07					π-L	-0.06	
			π-R	-0.08					π-R	-0.07	
			A-L	-0.13					A-L	-0.15	
			A-R	-0.15					A-R	-0.17	
	S_2	0.20	PTZ	0.41	0.07		S_2	0.16	D	0.41	0.07
			TPE	0.05	0.01				TPE	0.05	0.01
			π-L	-0.09					π-L	-0.07	
			π-R	-0.07					π-R	-0.06	
			A-L	-0.15					A-L	-0.18	
			A-R	-0.14					A-R	-0.16	
YL3	S_1	0.97	PTZ	0.39	0.52	**YL4**	S_1	1.15	PTZ	0.33	0.39
			TPE	0.05	0.11				TPE	0.05	0.07
			π-L (in)	0.03					π-L (in)	-0.01	
			π-L (out)	-0.04					π-L (out)	-0.08	
			π-R (in)	-0.03					π-R (in)	-0.01	
			π-R (out)	-0.15					π-R (out)	-0.07	
			A-L	-0.08					A-L	-0.11	
			A-R	-0.19					A-R	-0.10	
	S_2	0.28	PTZ	0.41	0.62		S_2	0.42	PTZ	0.35	0.15
			TPE	0.05	0.23				TPE	0.04	0.02
			π-L (in)	0.00					π-L (in)	-0.00	
			π-L (out)	-0.13					π-L (out)	-0.08	
			π-R (in)	0.02					π-R (in)	-0.00	
			π-R (out)	-0.05					π-R (out)	-0.08	
			A-L	-0.23					A-L	-0.11	
			A-R	-0.08					A-R	-0.12	
YL5	S_1	0.86	PTZ	0.39	0.31						
			TPE	0.05	0.02						
			π-L	-0.06							
			π-R	-0.07							
			A-L	-0.14							
			A-R	-0.17							
	S_2	0.16	PTZ	0.43	0.07						
			TPE	0.05	0.01						
			π-L	-0.08							
			π-R	-0.05							
			A-L	-0.19							
			A-R	-0.15							

[a]Oscillator strength; [b]The difference of the Mulliken charge between the ground state and excited state; [c]The product of the oscillator strength and the Mulliken charge of the donor (D) and acceptor (A). D: phenothiazine, TPE entity; A: 2-cyanoacrylic acid; *π*-L/ *π*-L (in)/ *π*-L (out): *π* spacer at the left-hand side/ *π* spacer at the left-hand side near to core/ *π* spacer at the left-hand side away from core; *π*-R/ *π*-R (in)/ *π*-R (out): *π* spacer at the right-hand side/ *π* spacer at the right-hand side near to core/ *π* spacer at the right-hand side away from core.

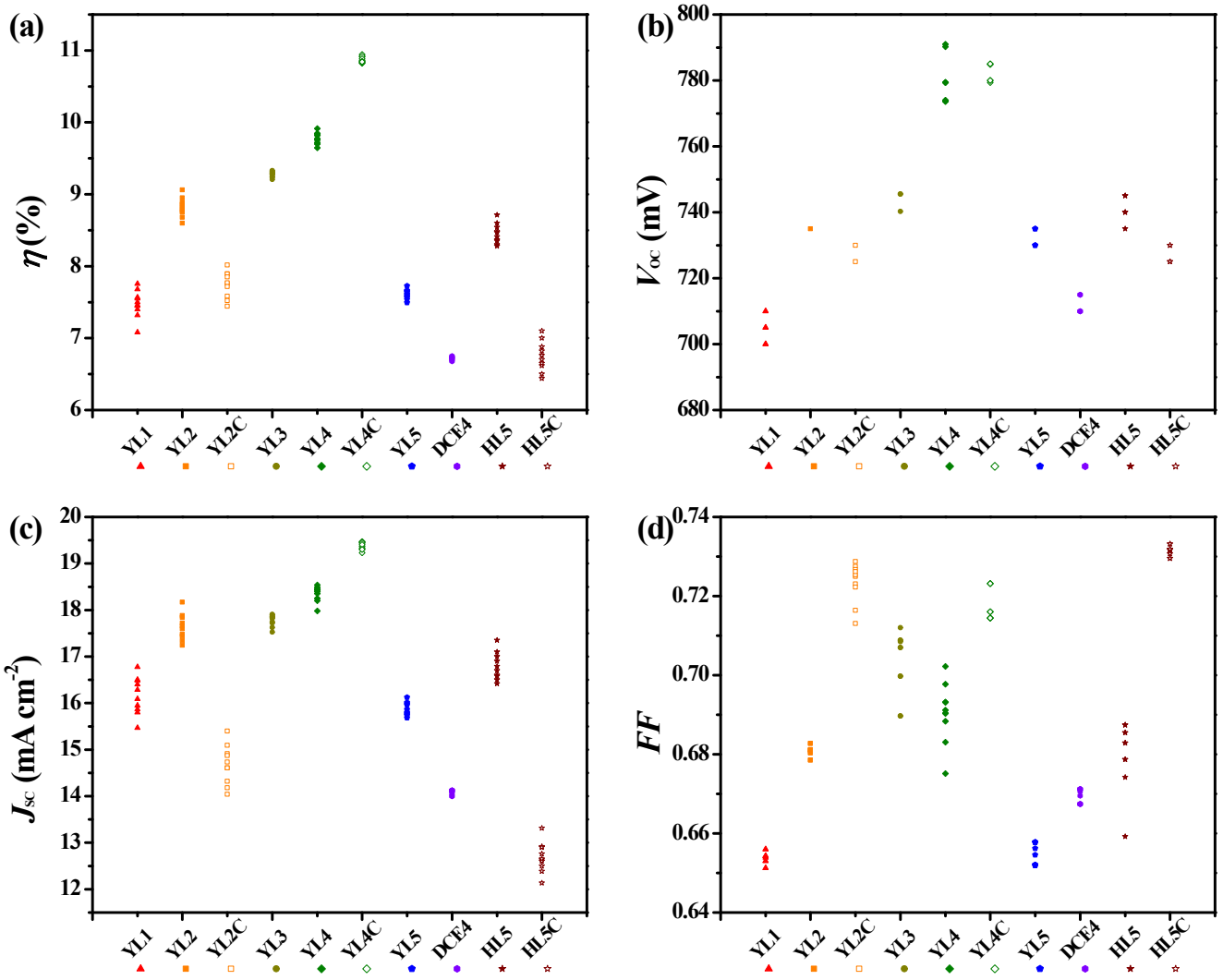


Figure S6. Photovoltaic performace of the DSSCs with **YL** dyes, **DCE4**, and **HL5** based on I^-/I_3^- redox mediator, where **YL2C**, **YL4C**, and **HL5C** means the addition of 10 mM of CDCA as the co-adsorbent. The statistic data of (a) efficiency (η), (b) V_{OC}, (c) J_{SC}, and (d) *FF* were obtained based on 10 cells for each dye.

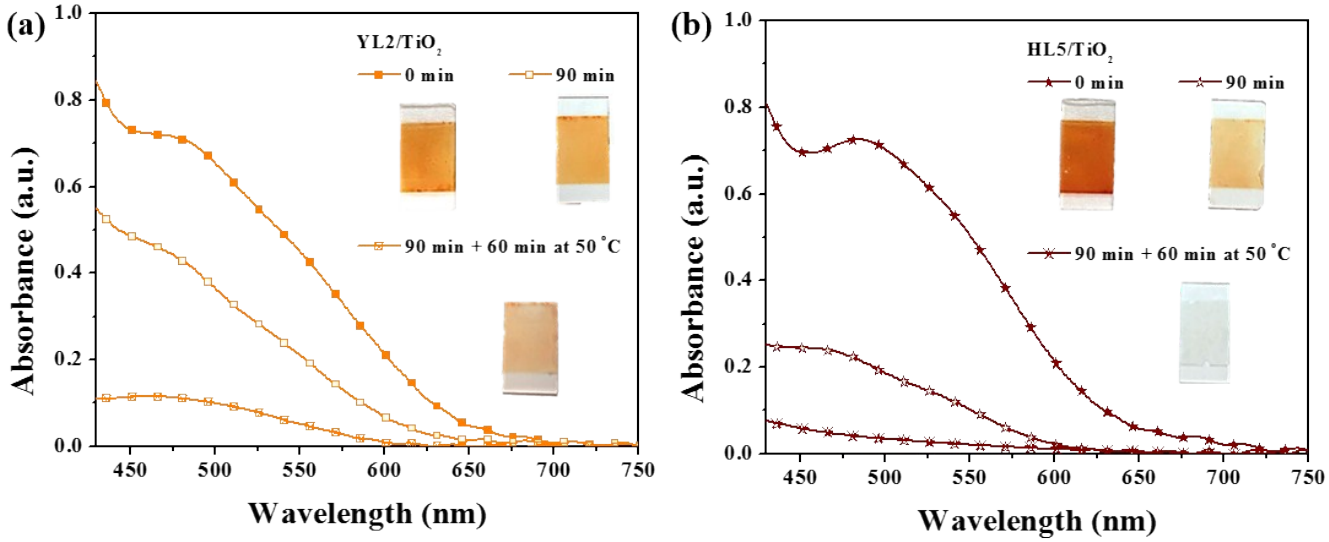


Figure S7. Absorbance spectra of (a) **YL2**-adsorbed TiO_2 film and (b) **HL5**-adsorbed TiO_2 film, soaking in a dye leaching solution (saturated KOH in ethanol) for 0, 90, and 90+60 min, where the last 60 min was at 50 oC.

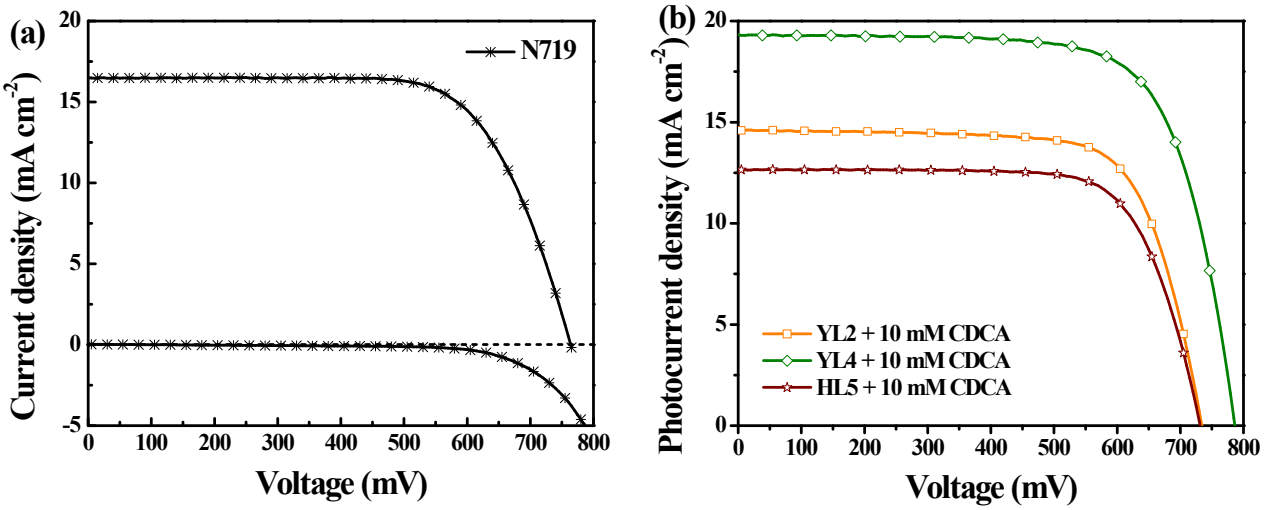


Figure S8. *J-V* plots of the DSSC with N719 based on iodide electrolyte (measured at 1 sun or dark).

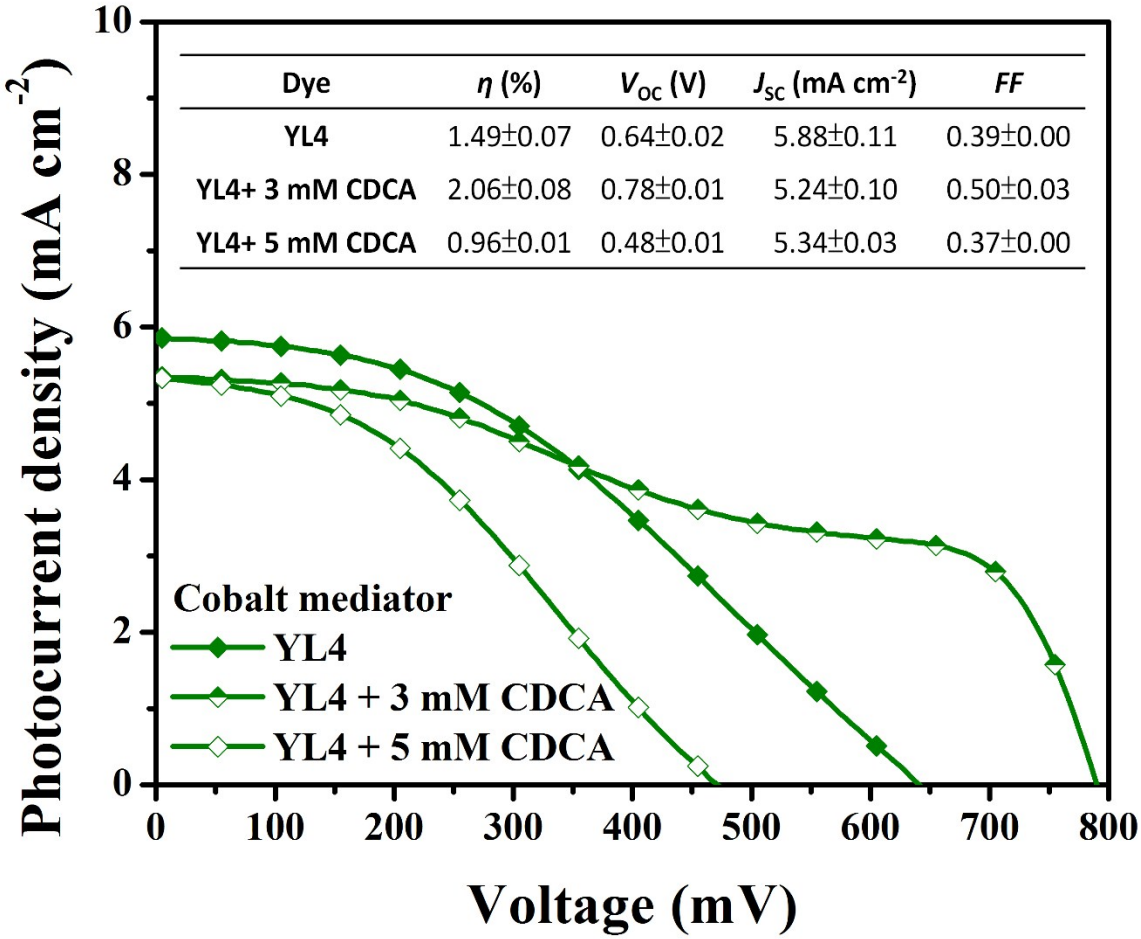


Figure S9. Photovoltaic performace of the DSSCs using **YL4** with 0, 3, 5 mM of CDCA as the co-adsorbent, measured under 1 sun in a cobalt-based redox mediator (tris(1,10-phenanthroline)cobalt(II/III) (bi/tri)-fluoromethanesulfonimide salt, Co-phen^{2+}/Co-phen^{3+}).

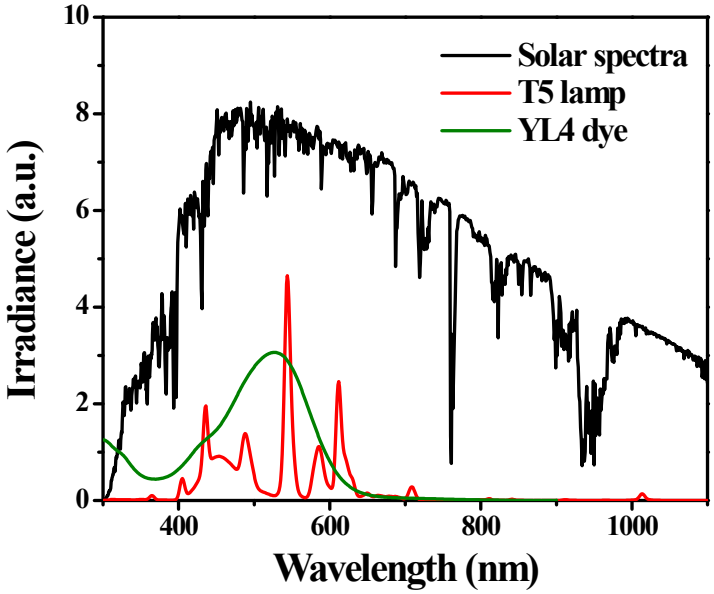


Figure S10. Solar spectrum, emission spectrum of t Philips T5 lamp, and the absorption spectrum of **YL4**.

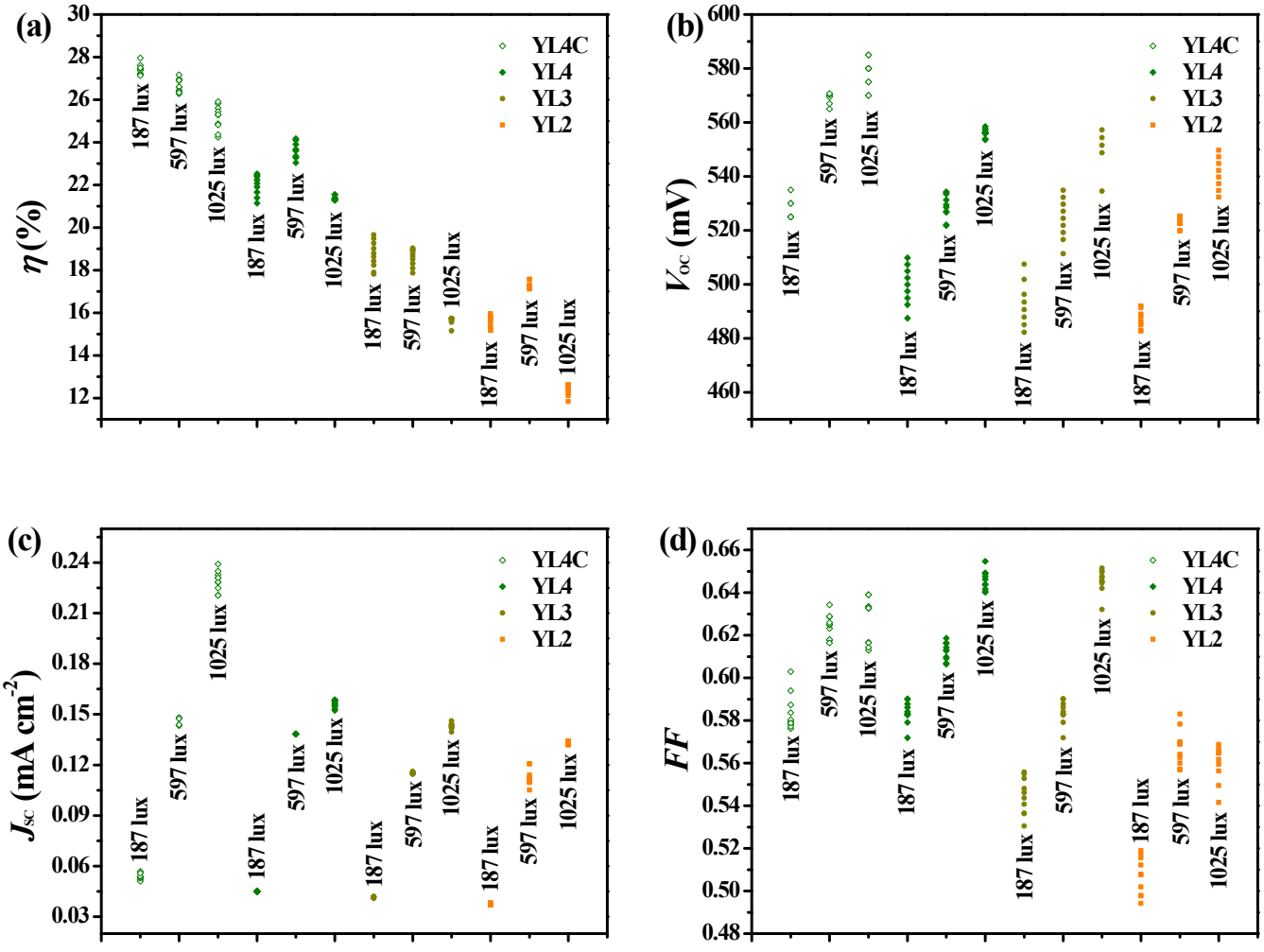
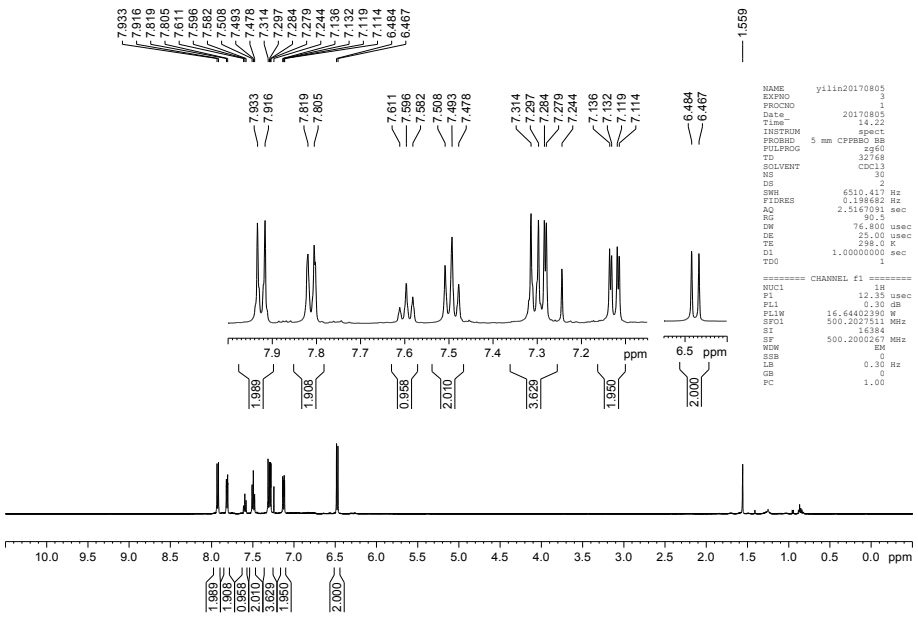
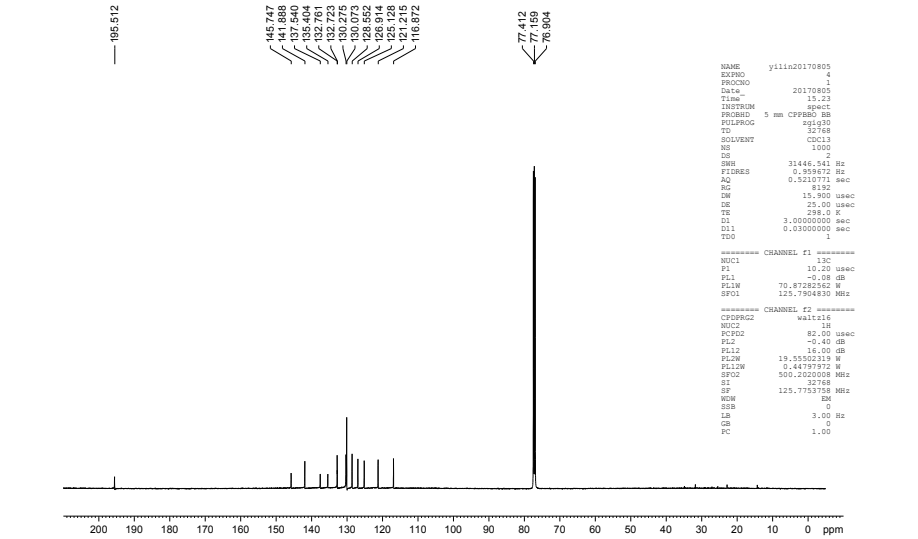


Figure S11. Photovoltaic performace of the DSSCs using **YL2**–**YL4** and **YL4** with 10 mM of CDCA, measured using T5 fluorescent light. The statistic data of (a) efficiency (η), (b) V_{OC}, (c) J_{SC}, and (d) *FF* were obtained based on 10 cells for each dye and light illuminances (187, 597, or 1025 lux).

(a)



(b)



(c)

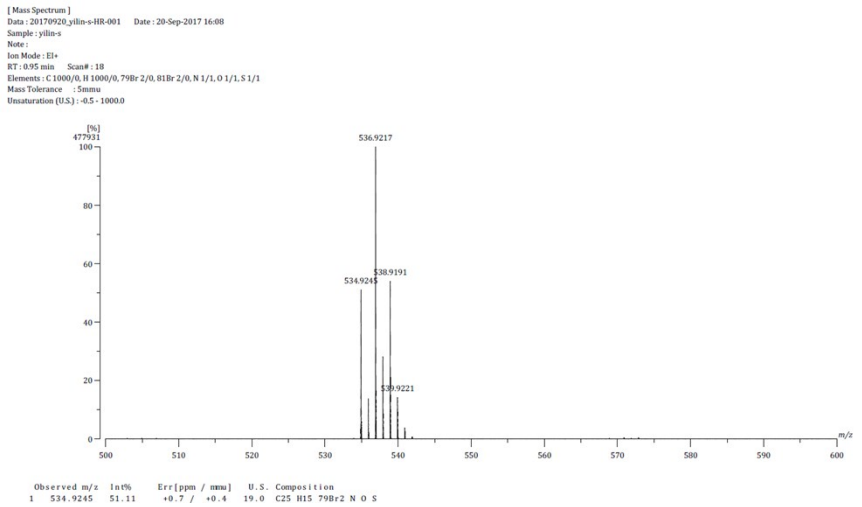
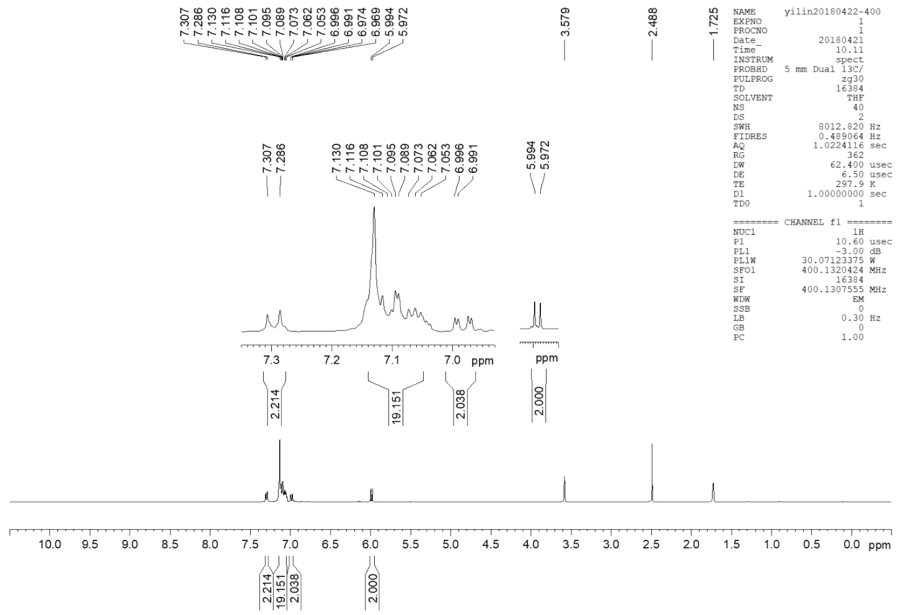
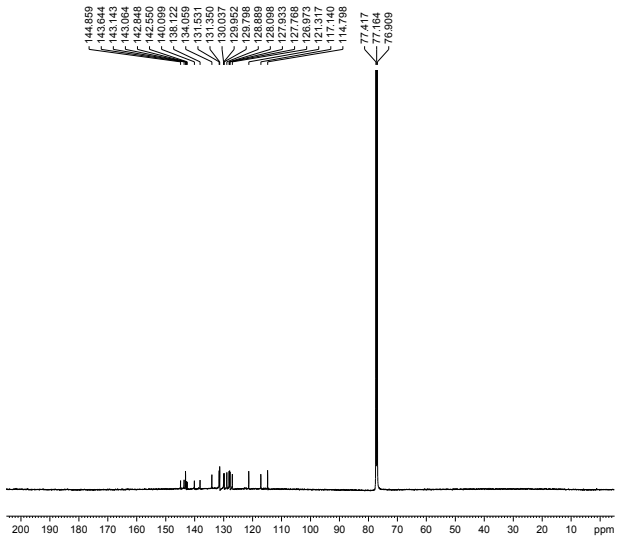


Figure S12. (a) ^{1}H NMR, (b) ^{13}C NMR and (c) Mass spectra of **1**.

(a)



(b)



(c)

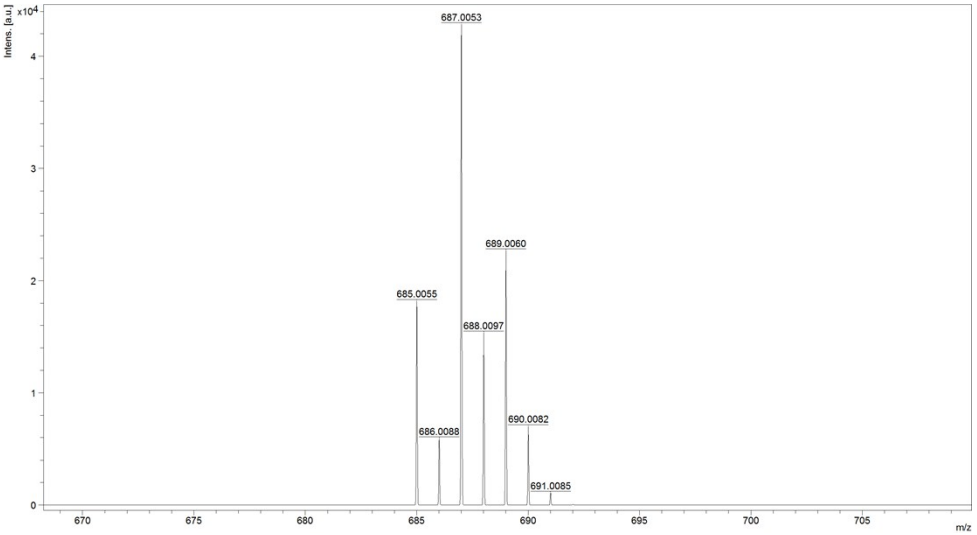


Figure S13. (a) ^{1}H NMR, (b) ^{13}C NMR and (c) Mass spectra of **2**.

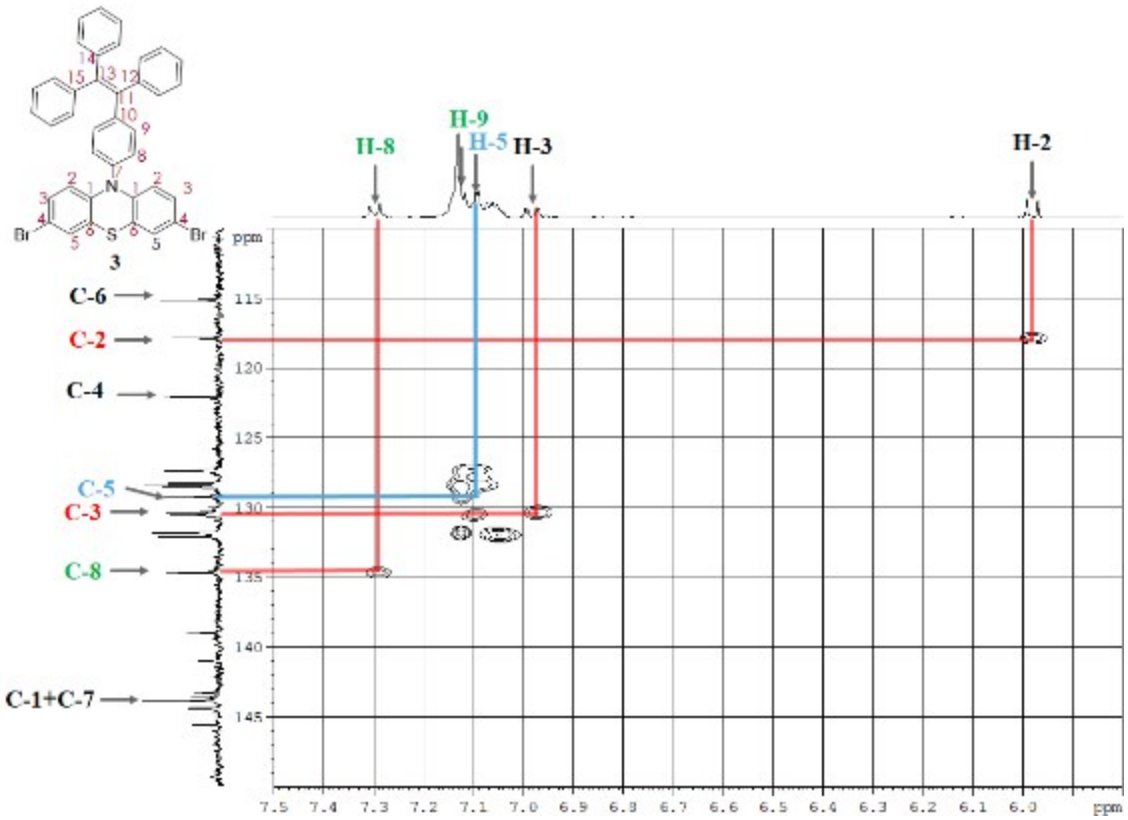


Figure S14. $^{1}H-{}^{1}H$ COSY NMR spectrum of **2**.

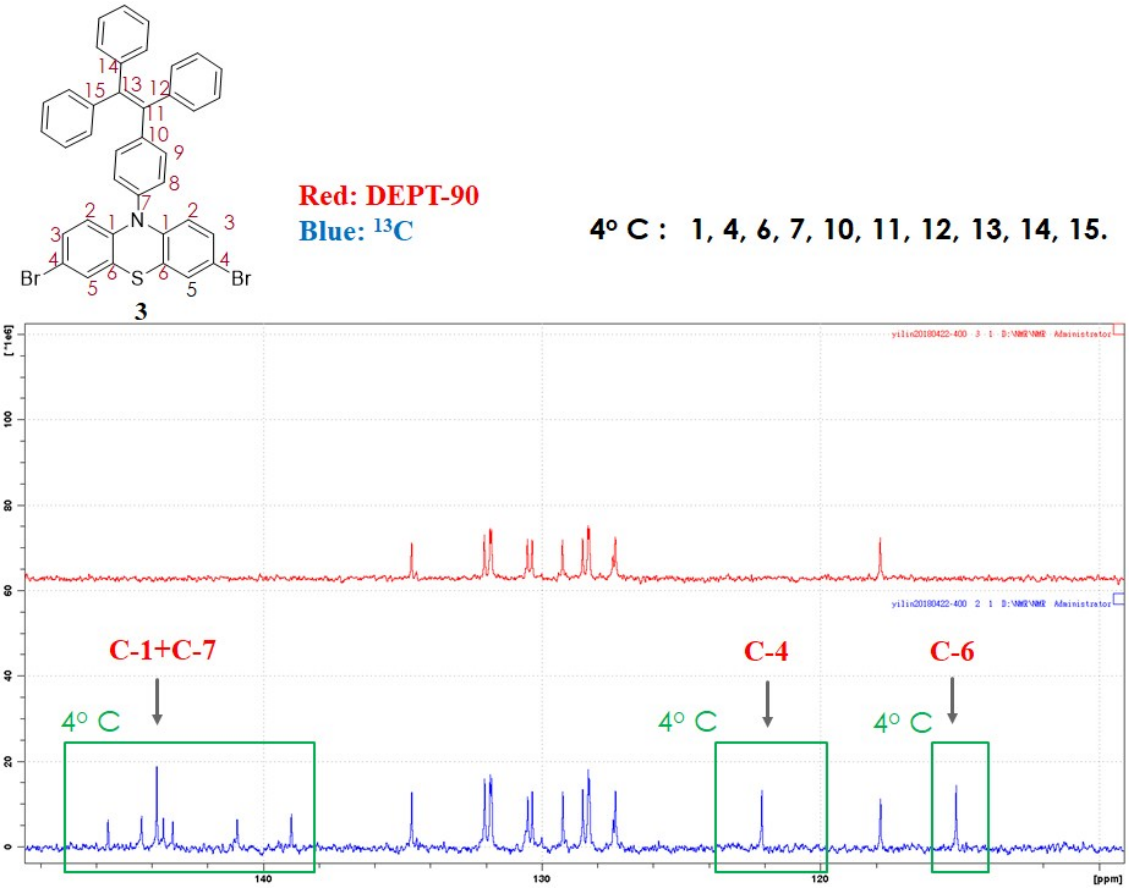


Figure S15. DEPT NMR spectrum of **2**.

Figure S16. $^{1}H-^{13}C$ HSQC NMR spectrum of **2**.

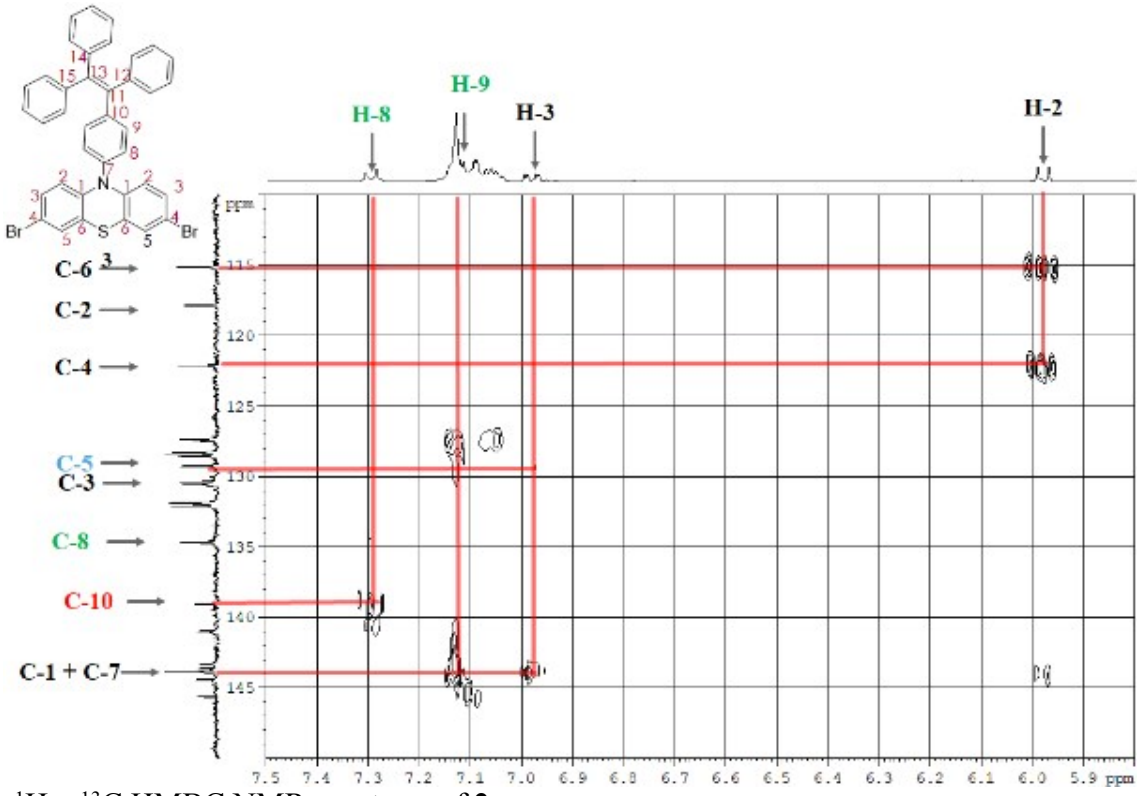
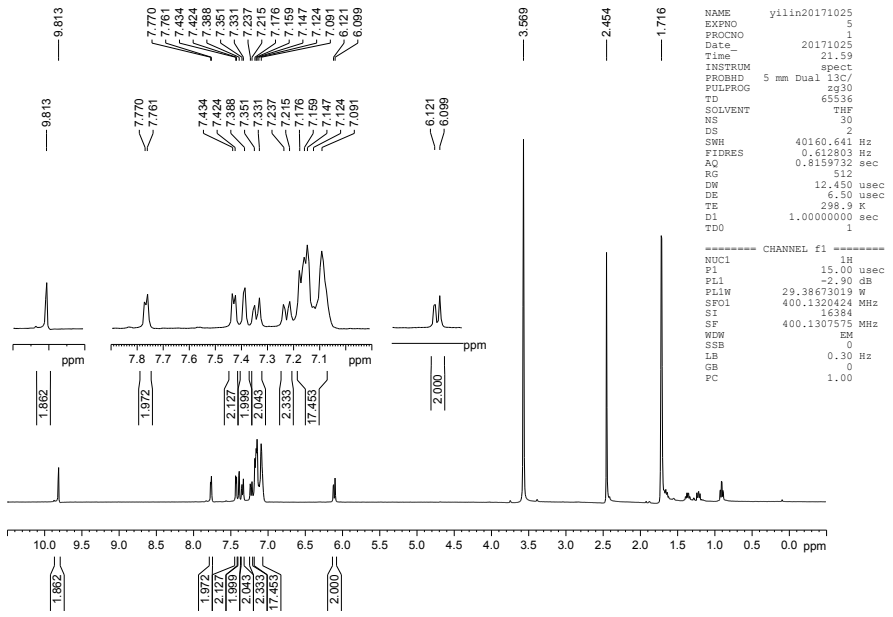
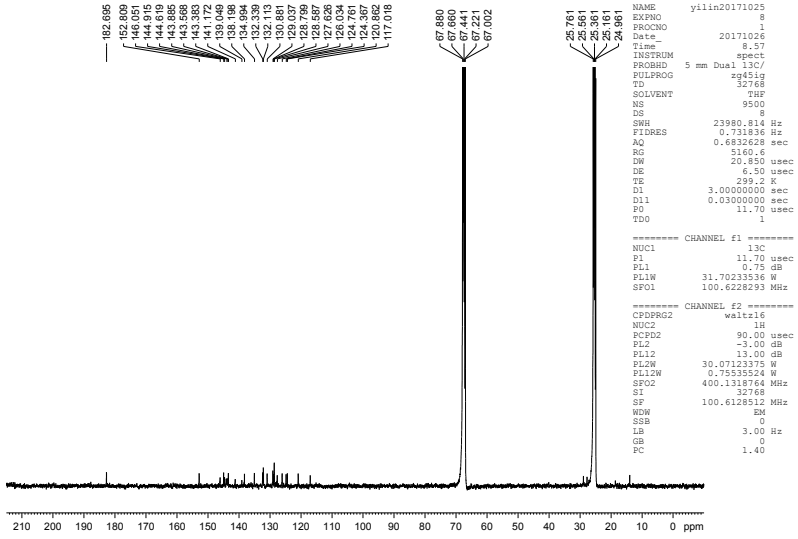


Figure S17. $^{1}H-^{13}C$ HMBC NMR spectrum of **2**.

(a)



(b)



(c)

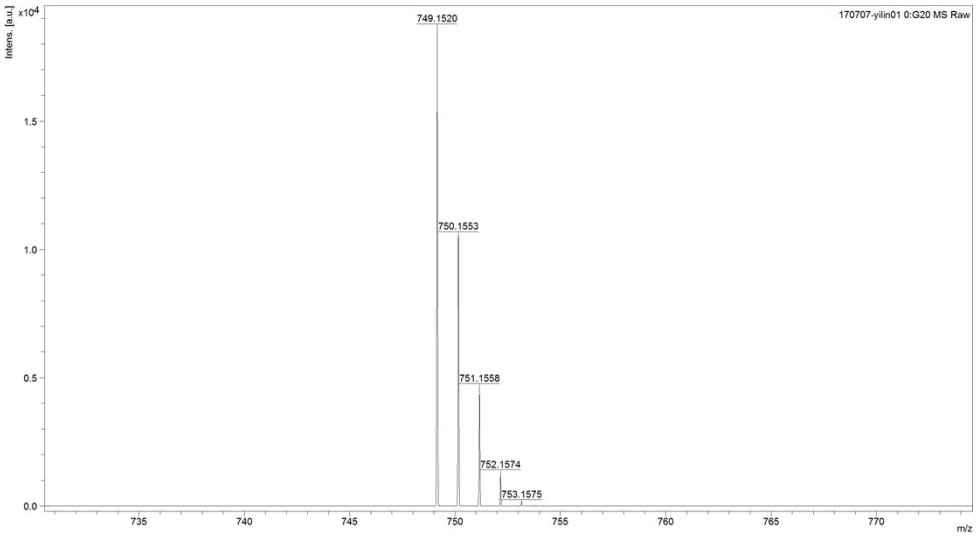
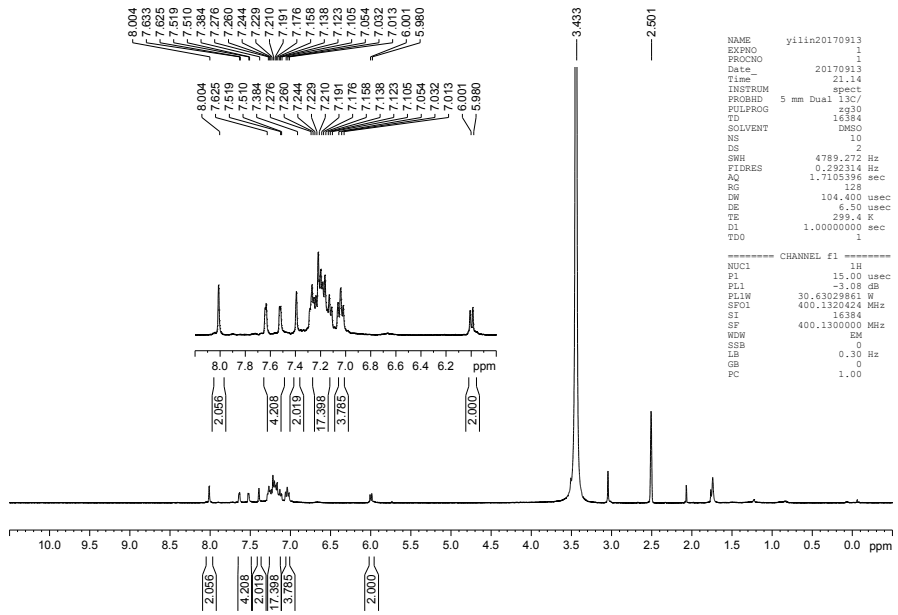
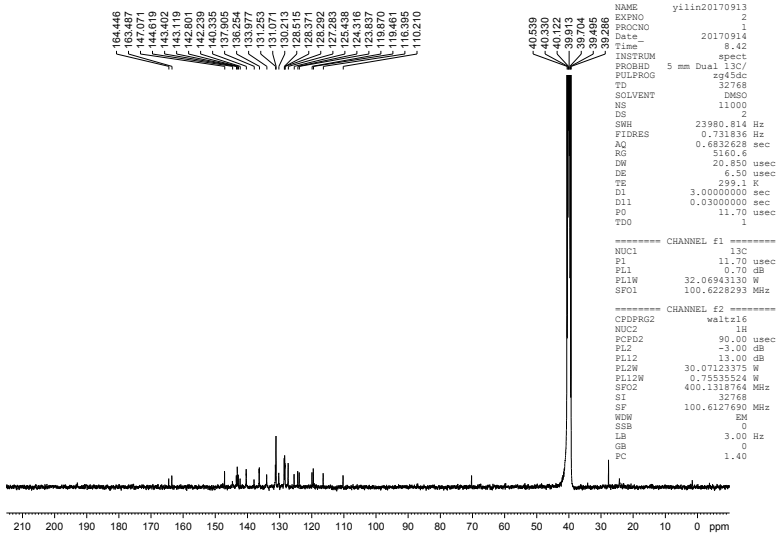


Figure S18. (a) ^{1}H NMR, (b) ^{13}C NMR and (c) Mass spectra of **YL1al**.

(a)



(b)



(c)

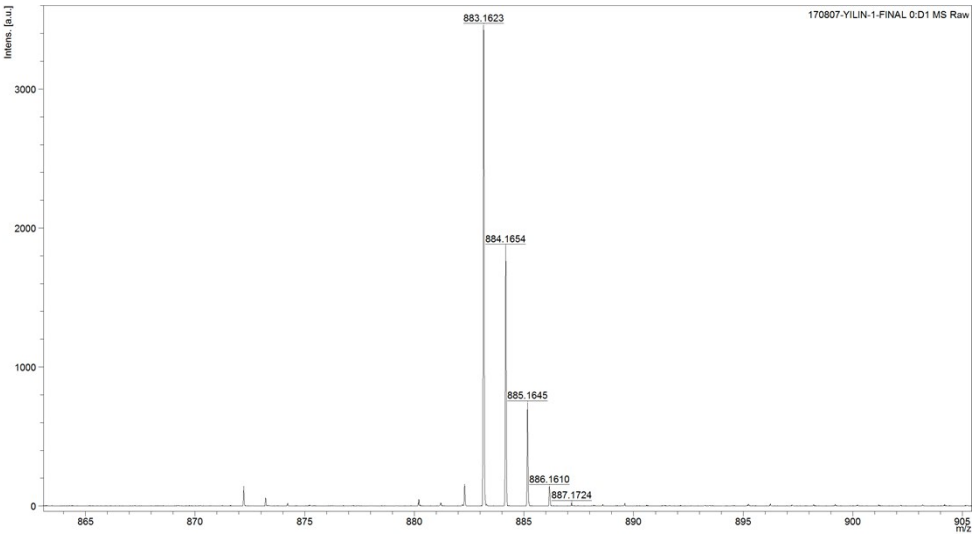
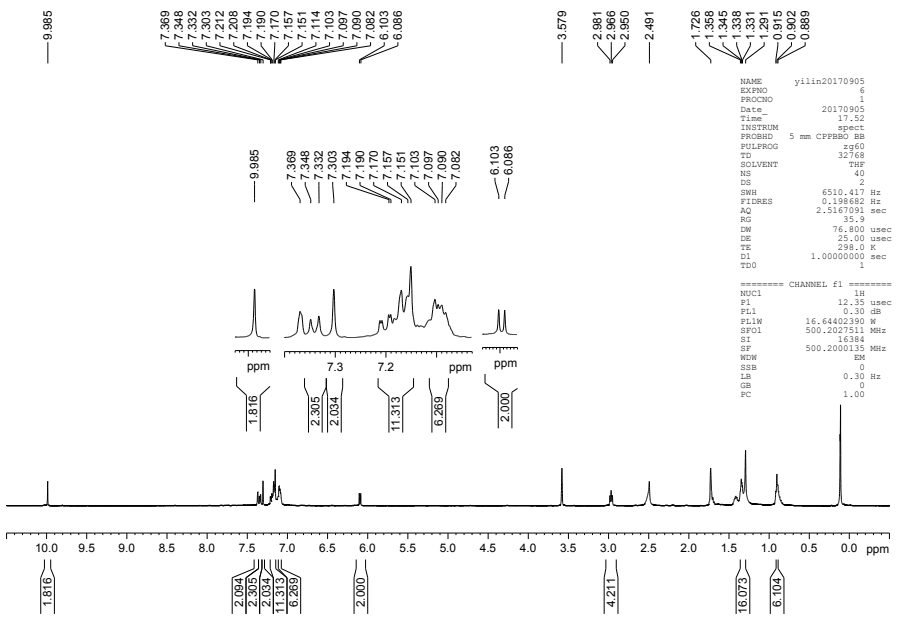
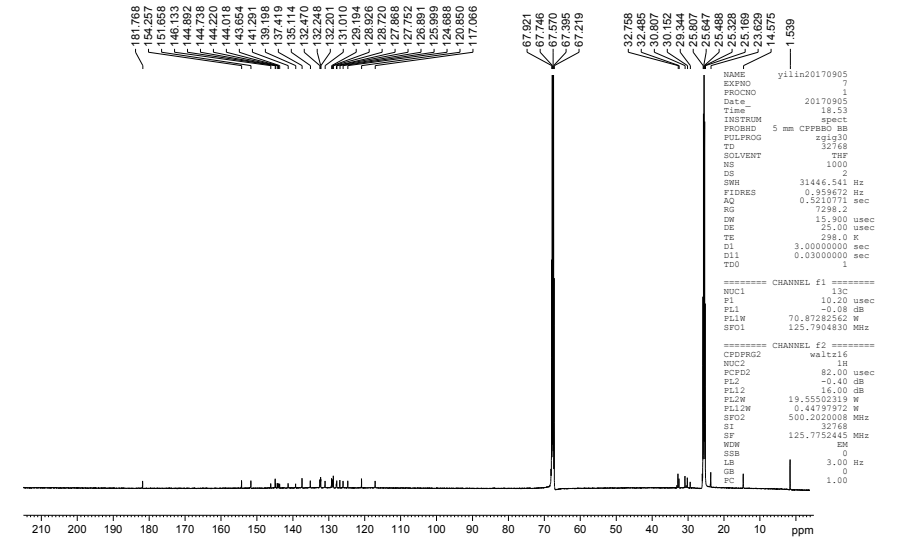


Figure S19. (a) ^{1}H NMR, (b) ^{13}C NMR and (c) Mass spectra of **YL1**.

(a)



(b)



(c)

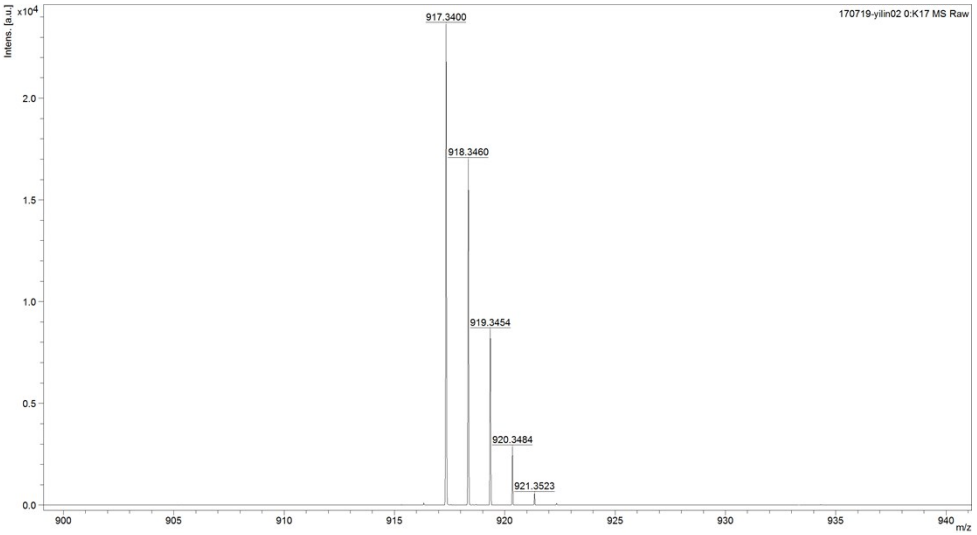
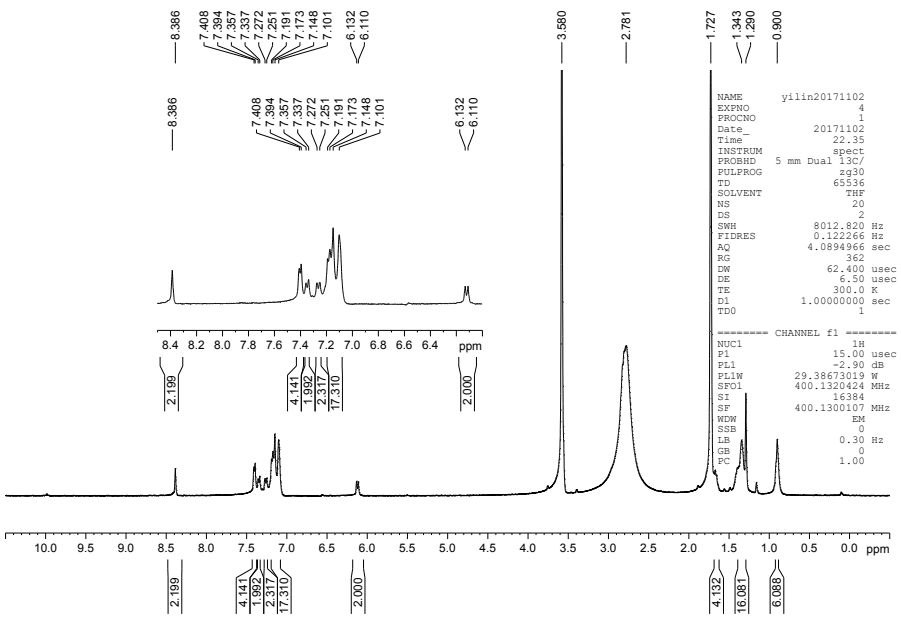
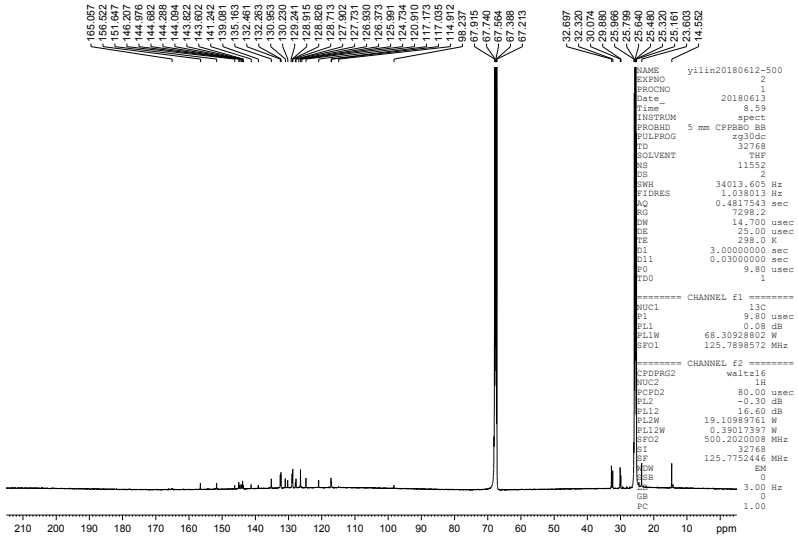


Figure S20. (a) ^{1}H NMR, (b) ^{13}C NMR and (c) Mass spectra of **YL2al**

(a)



(b)



(c)

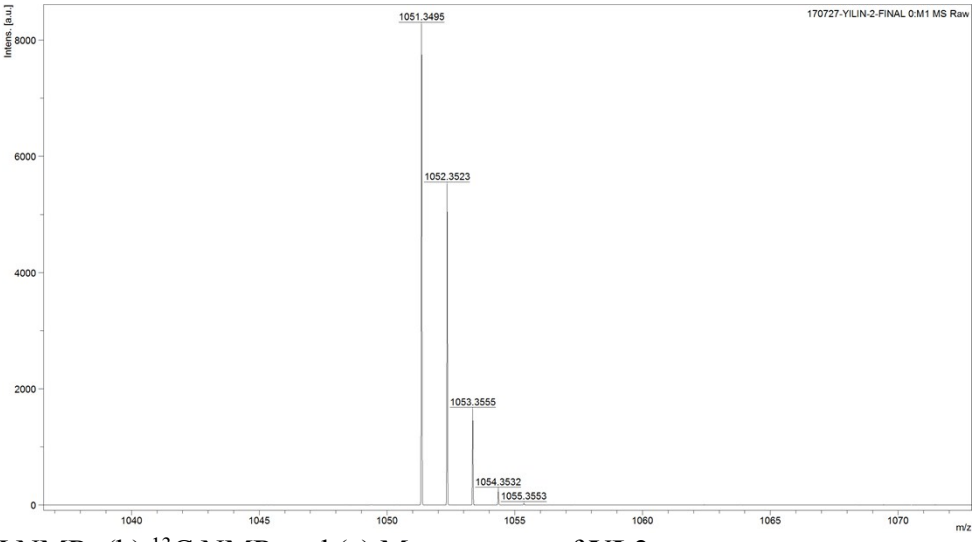
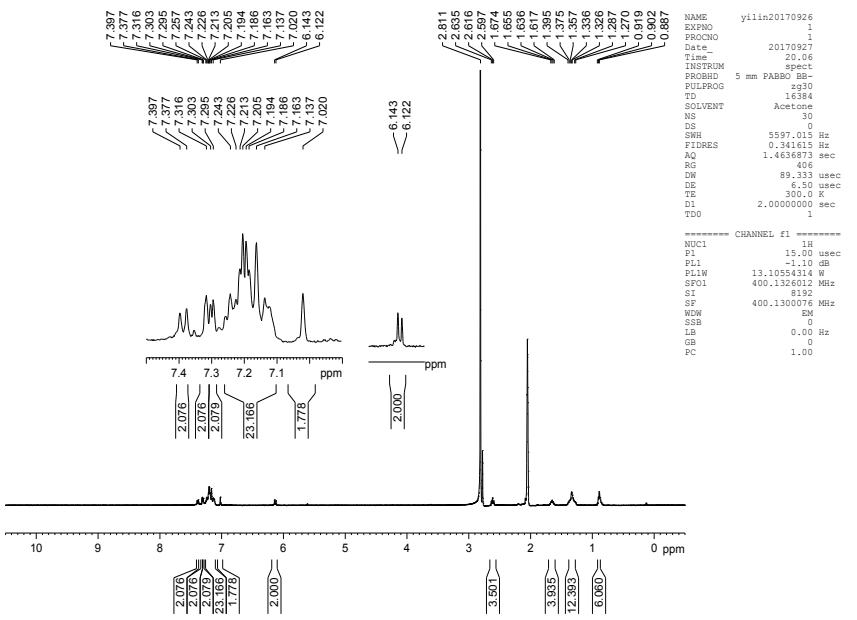
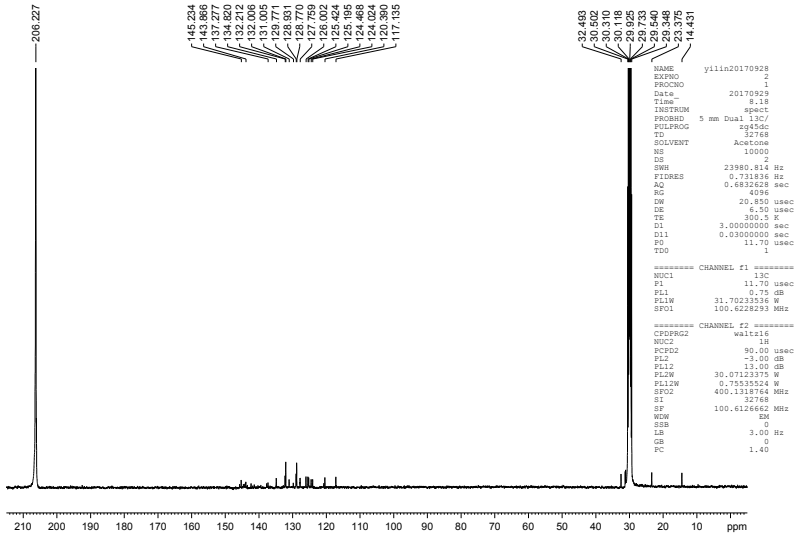


Figure S21. (a) ^{1}H NMR, (b) ^{13}C NMR and (c) Mass spectra of **YL2**.

(a)



(b)



(c)

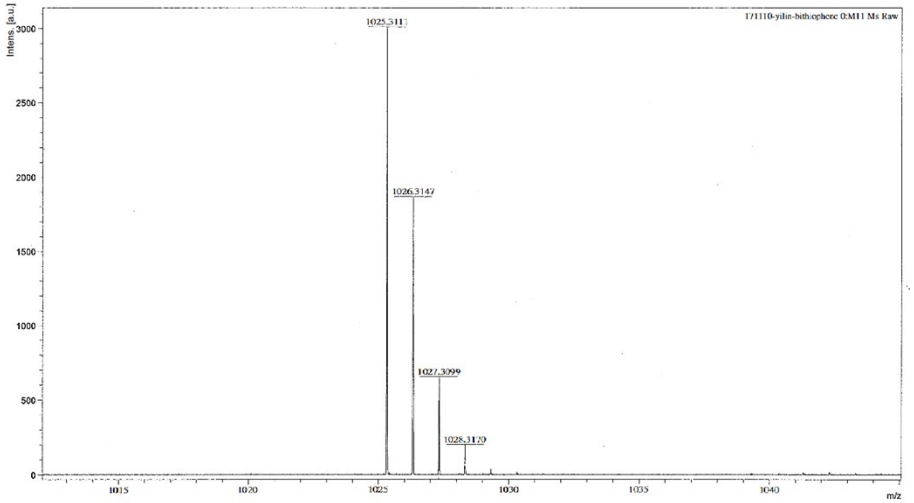
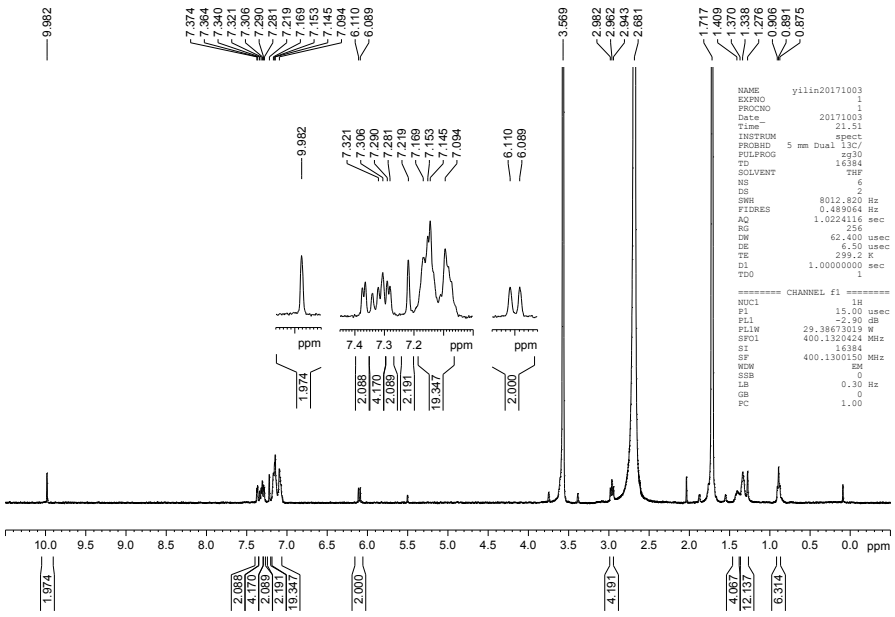
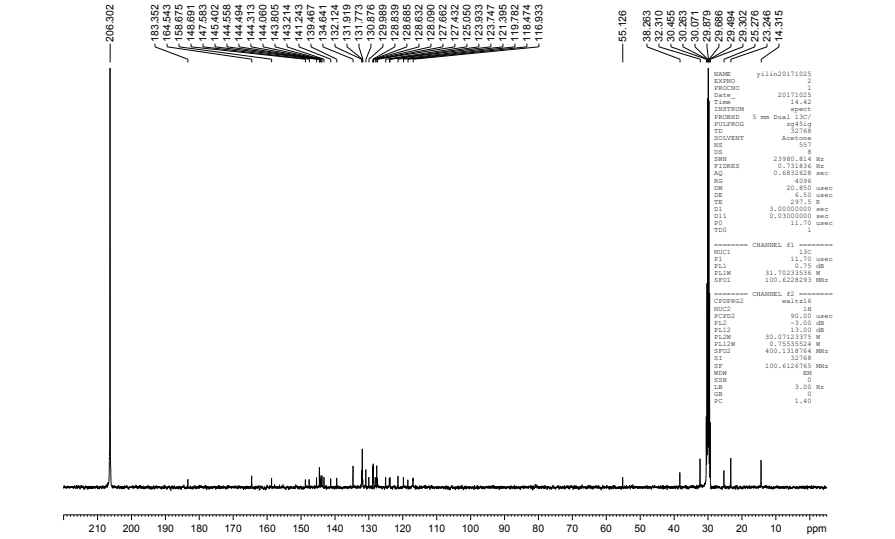


Figure S22. (a) ^{1}H NMR, (b) ^{13}C NMR and (c) Mass spectra of **3**.

(a)



(b)



(c)

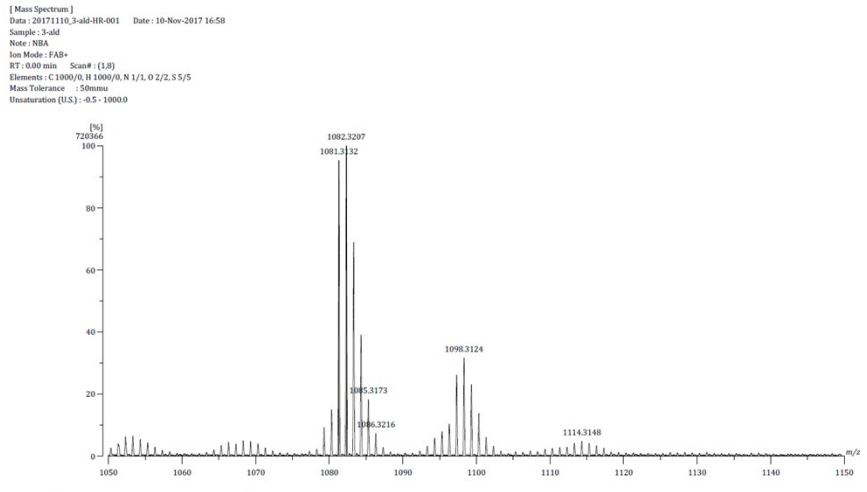
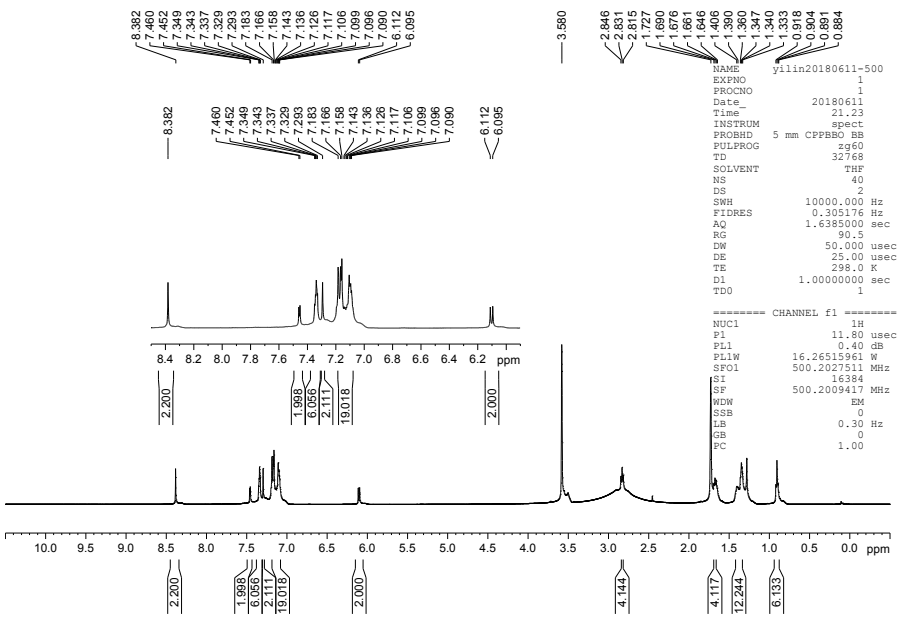
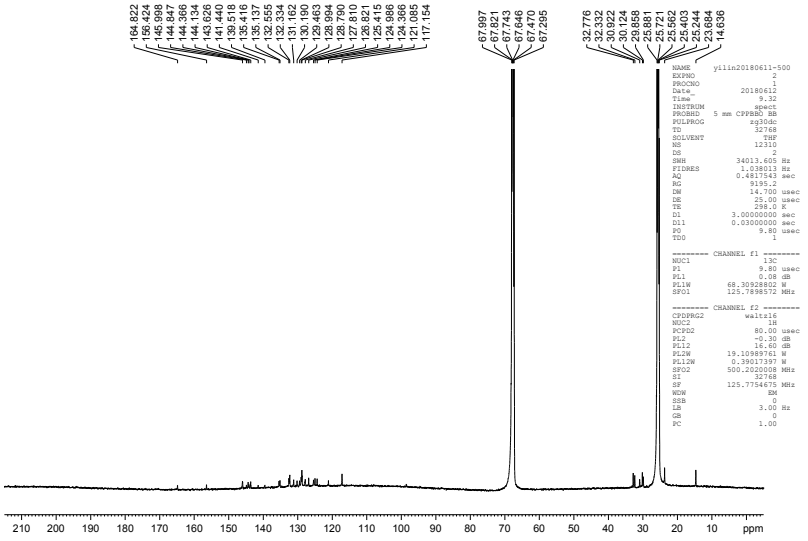


Figure S23. (a) ^{1}H NMR, (b) ^{13}C NMR and (c) Mass spectra of **YL3al**.

(a)



(b)



(c)

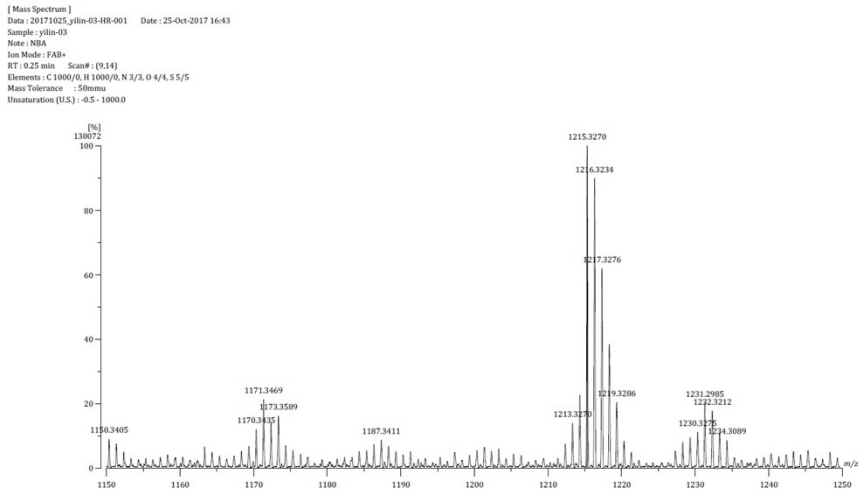
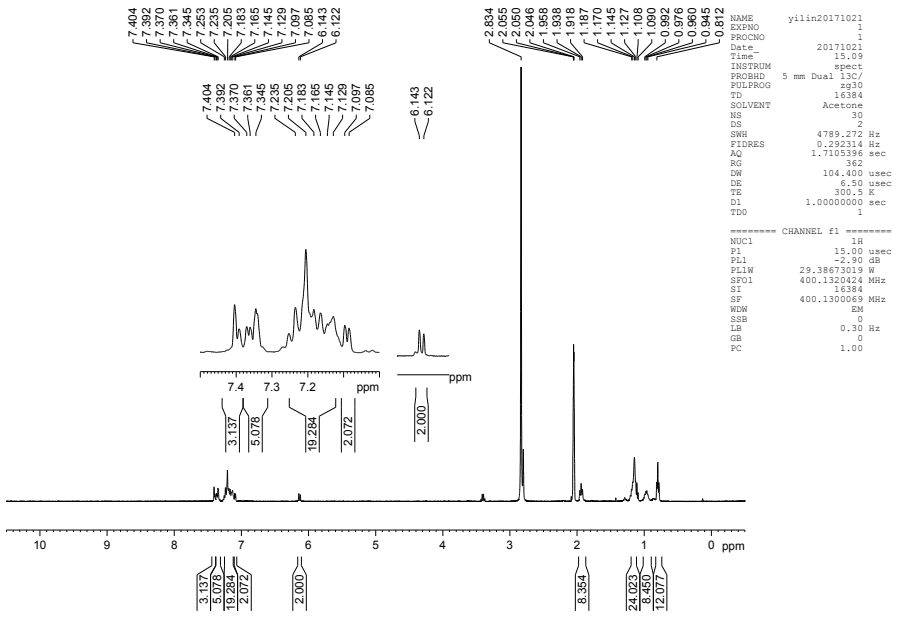
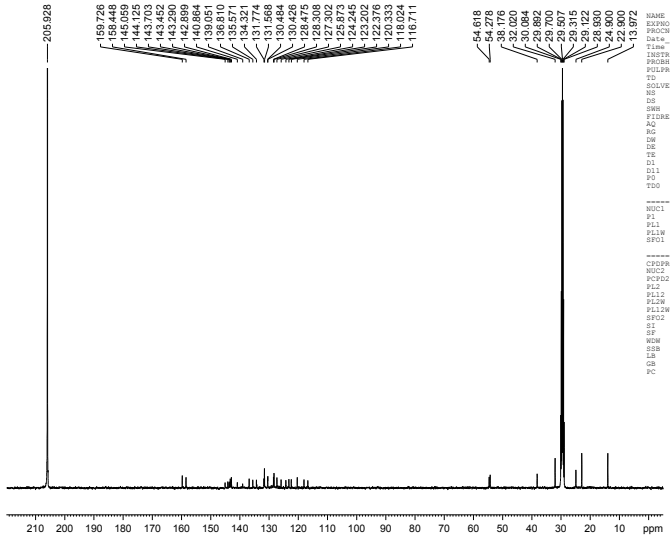


Figure S24. (a) ^{1}H NMR, (b) ^{13}C NMR and (c) Mass spectra of **YL3**.

(a)



(b)



(c)

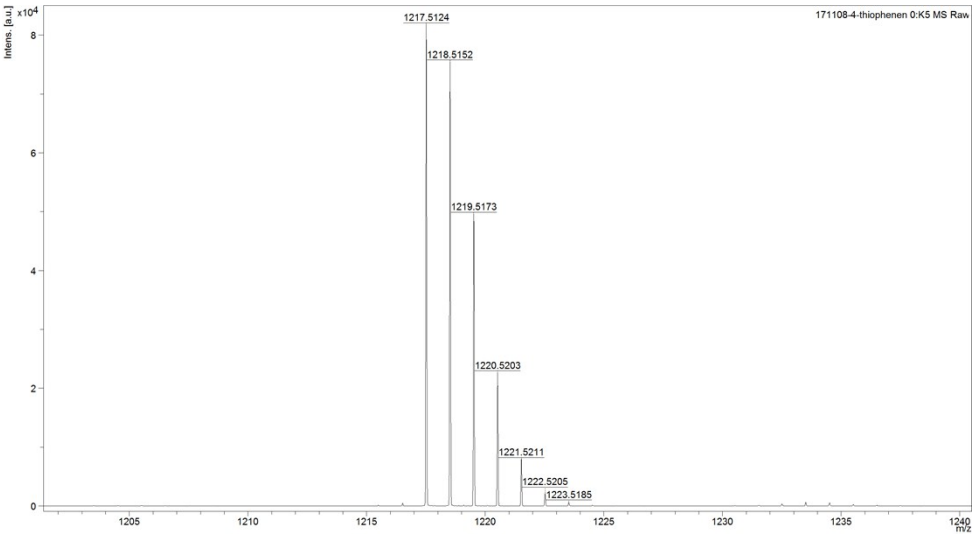
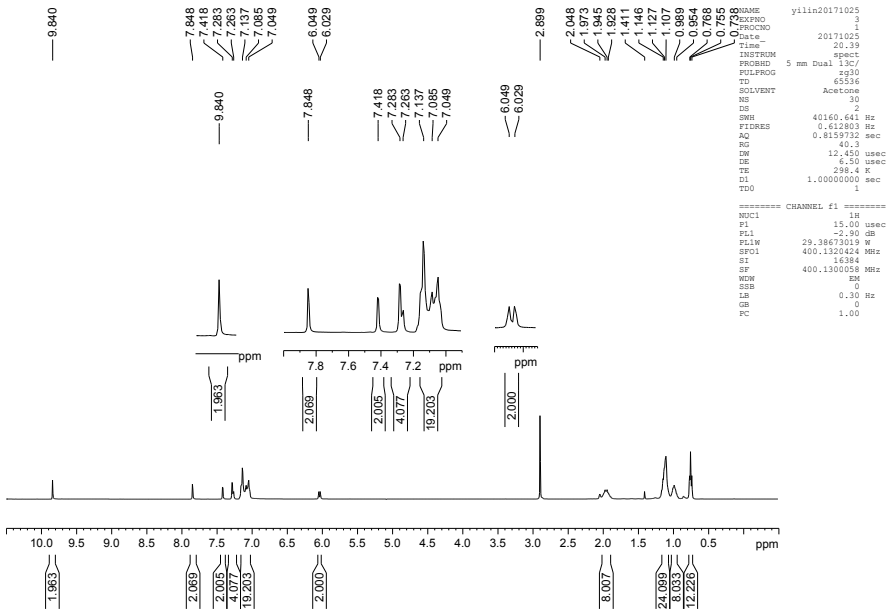
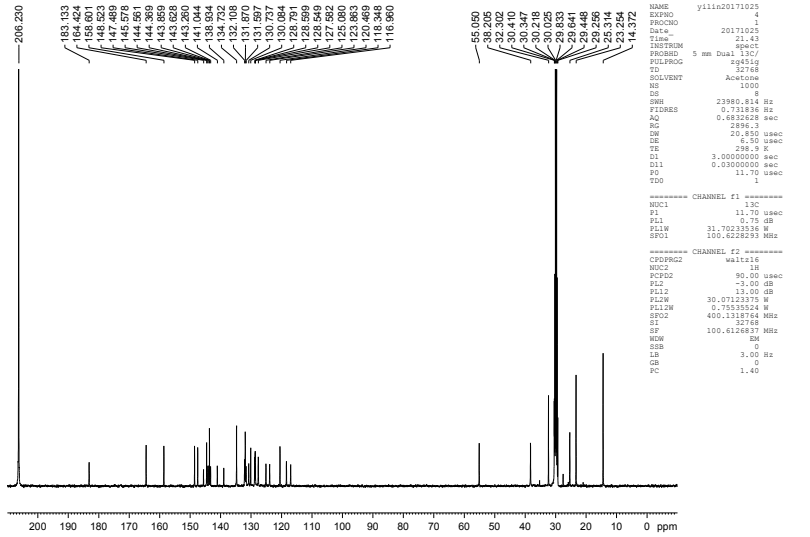


Figure S25. (a) ^{1}H NMR, (b) ^{13}C NMR and (c) Mass spectra of **4**.

(a)



(b)



(c)

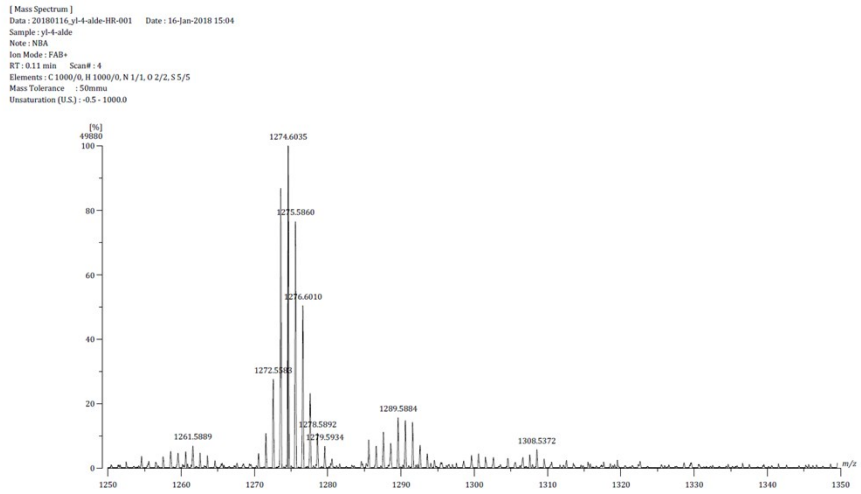
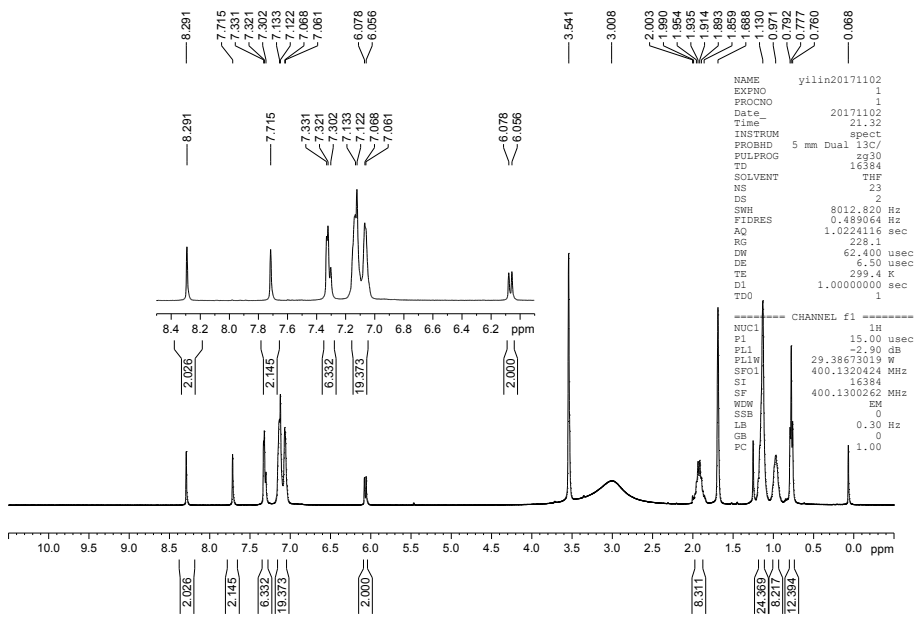
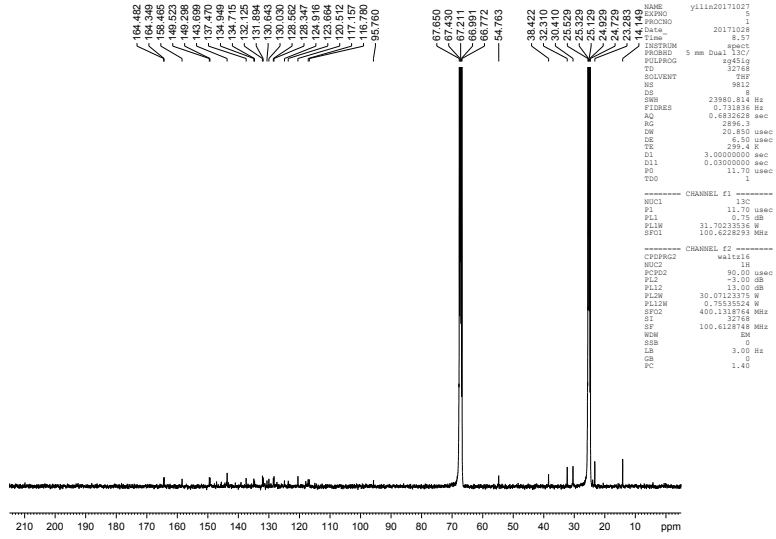


Figure S26. (a) ^{1}H NMR, (b) ^{13}C NMR and (c) Mass spectra of **YL4al**.

(a)



(b)



(c)

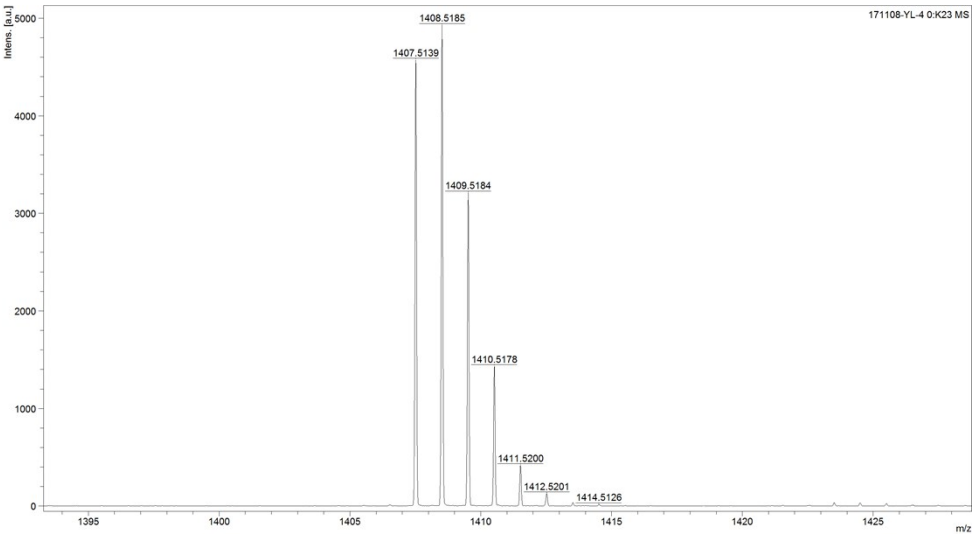
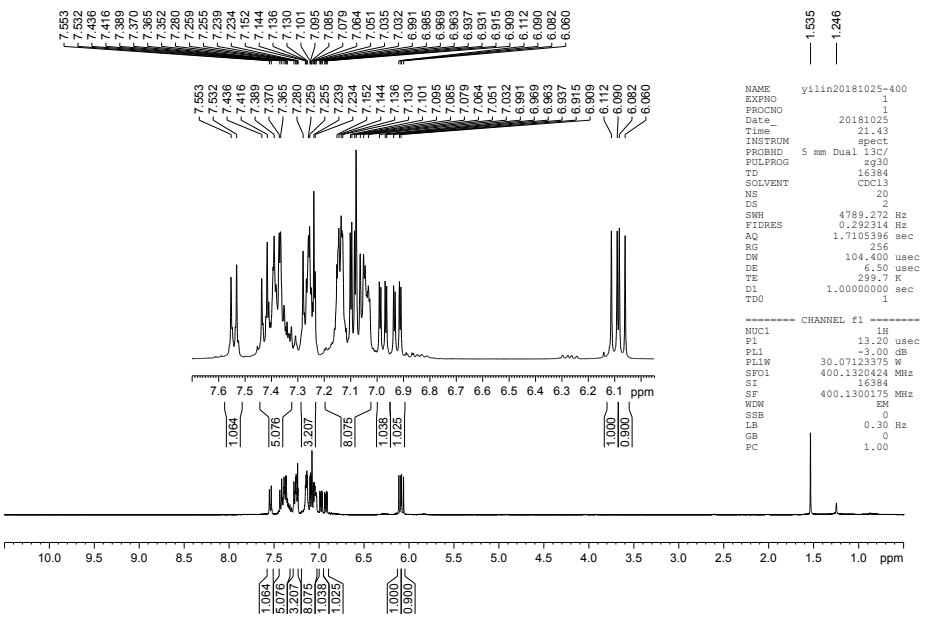
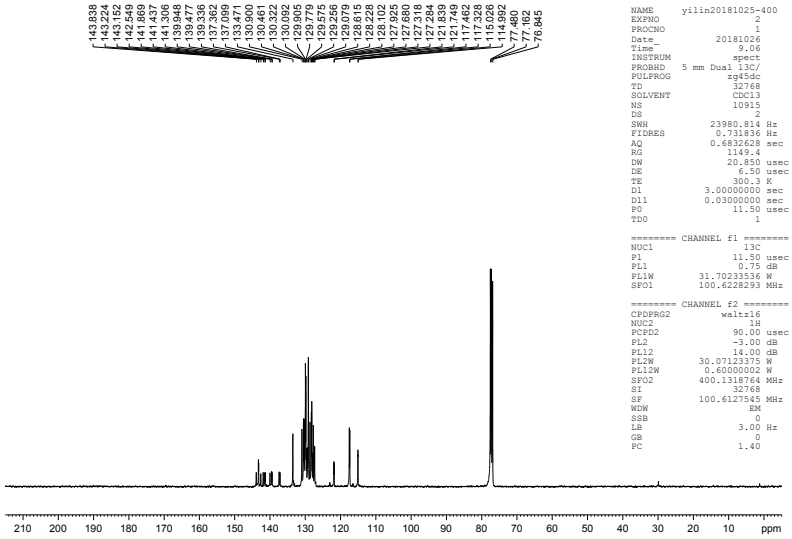


Figure S27. (a) ^{1}H NMR, (b) ^{13}C NMR and (c) Mass spectra of **YL4**.

(a)



(b)



(c)

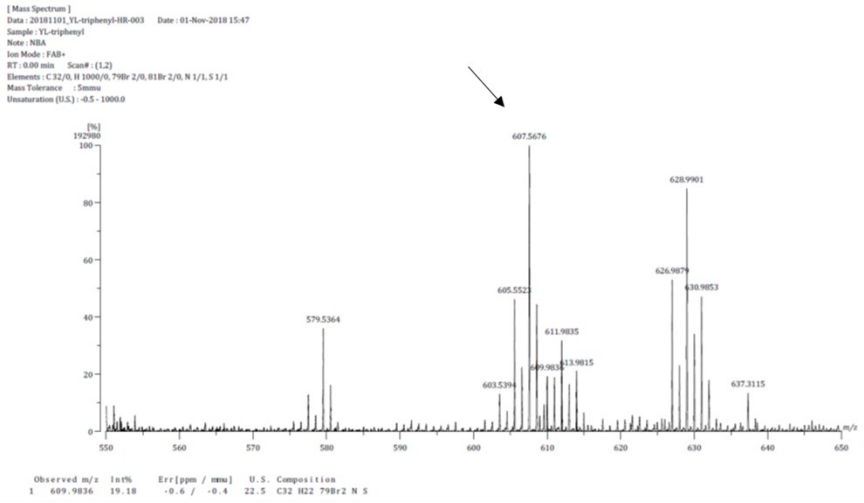
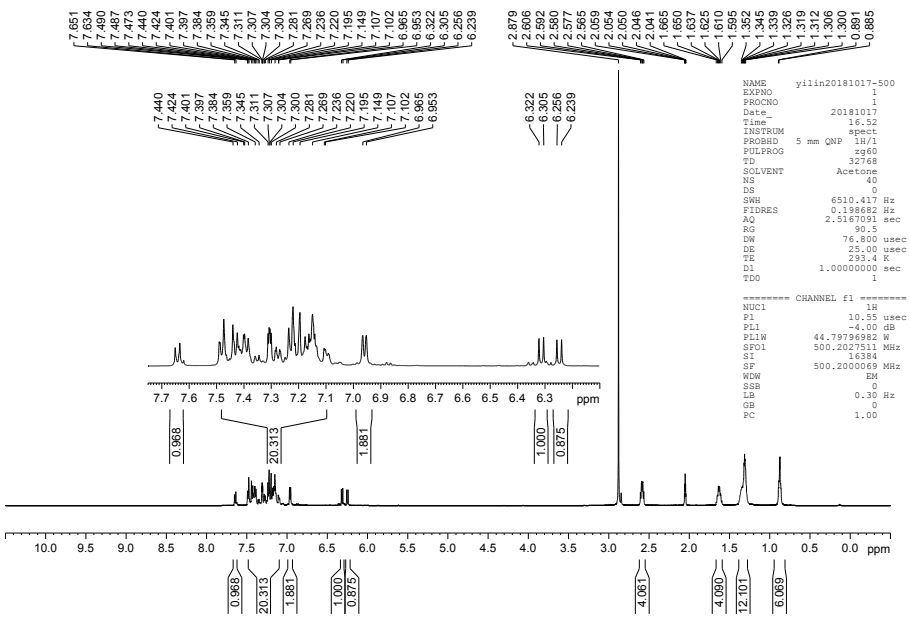
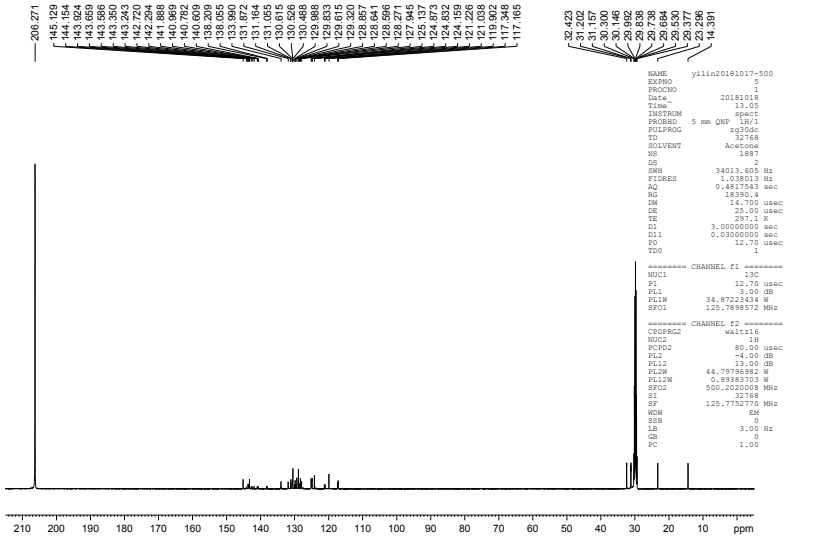


Figure S28. (a) ^{1}H NMR, (b) ^{13}C NMR and (c) Mass spectra of **5**.

(a)



(b)



(c)

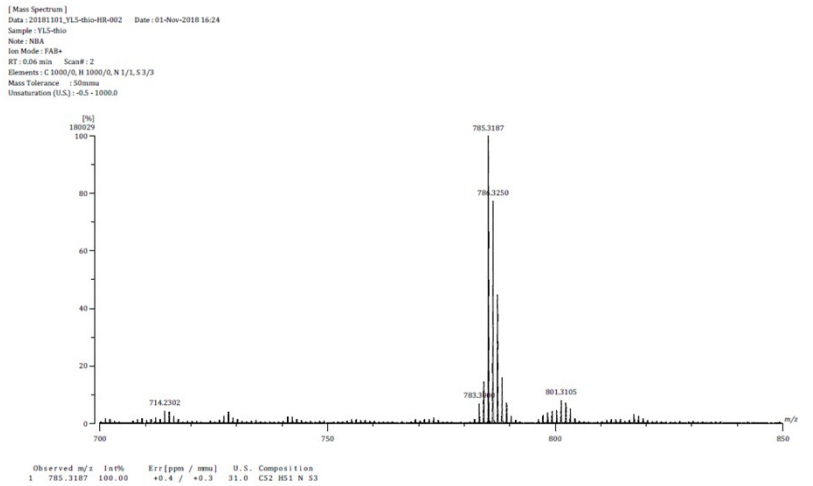
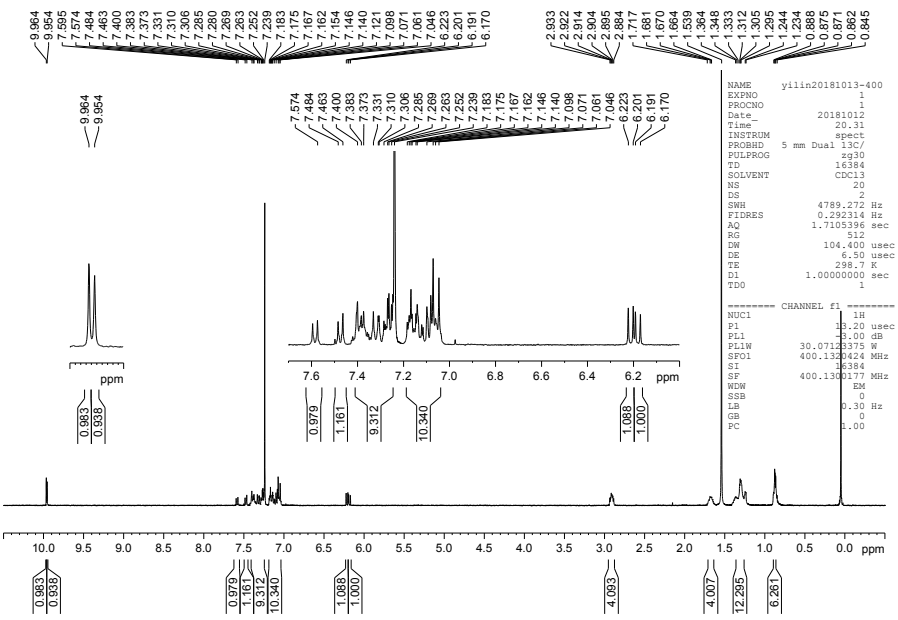
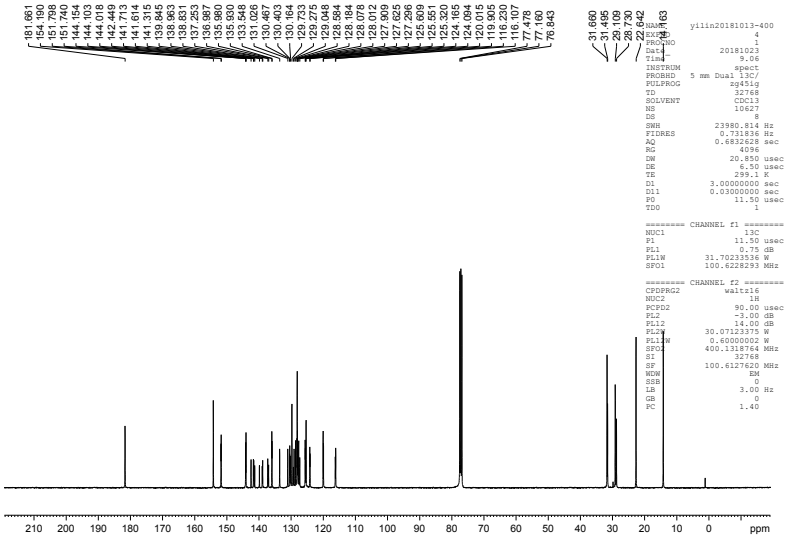


Figure S29. (a) ^{1}H NMR, (b) ^{13}C NMR and (c) Mass spectra of **6**.

(a)



(b)



(c)

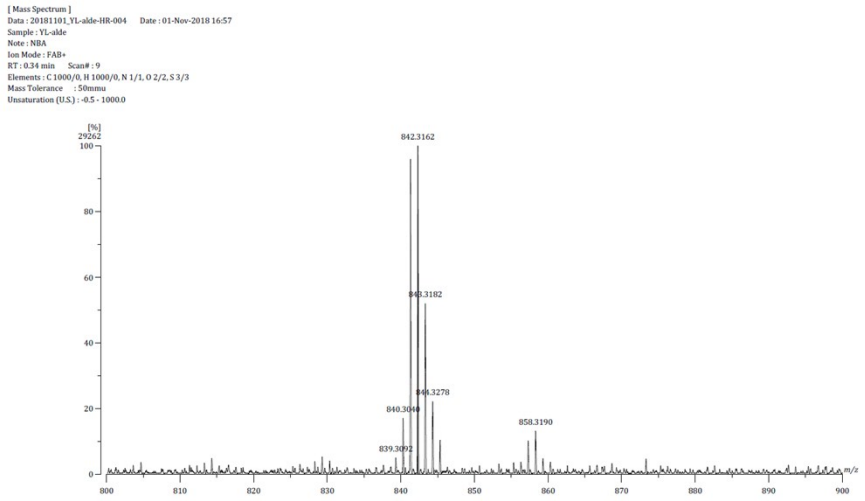
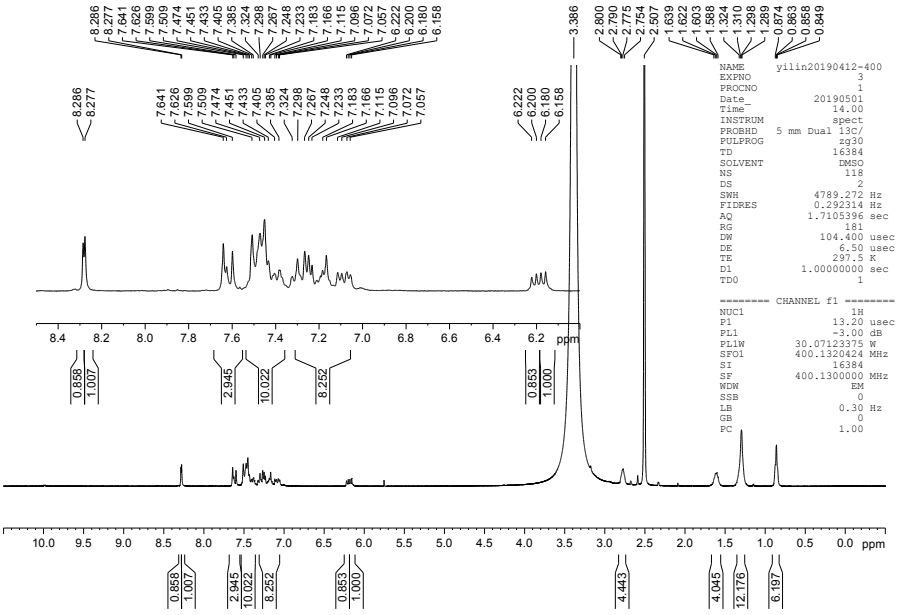
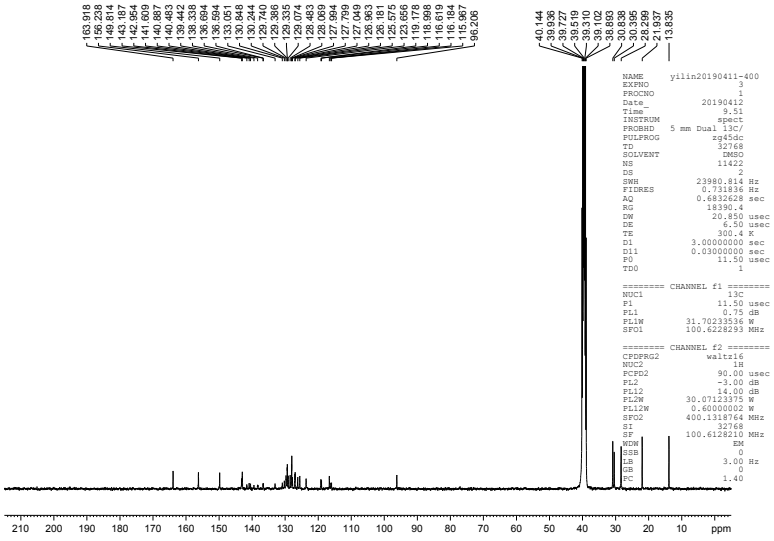


Figure S30. (a) ^{1}H NMR, (b) ^{13}C NMR and (c) Mass spectra of **YL5al**.

(a)



(b)



(c)

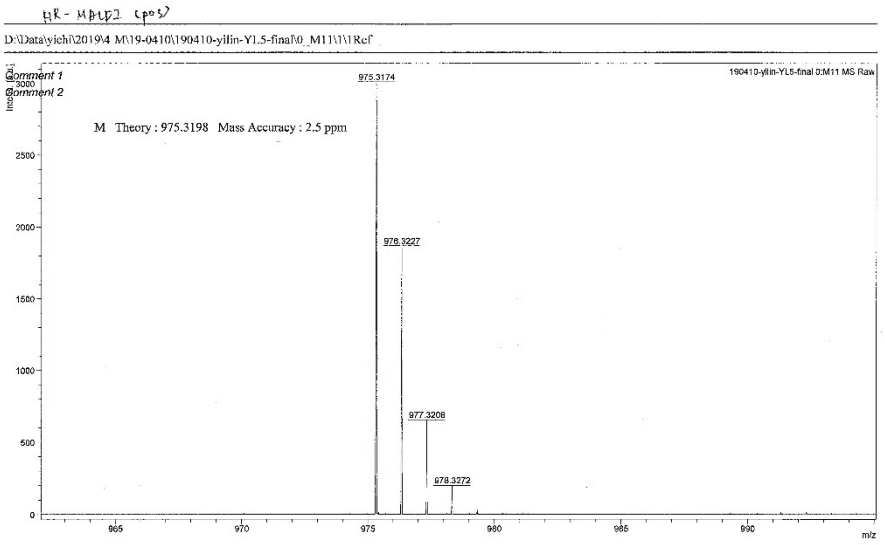


Figure S31. (a) ^{1}H NMR, (b) ^{13}C NMR and (c) Mass spectra of **YL5**.