Electronic Supplementary Information (ESI)

Triphenylamine-based π-Conjugated Dendrimers: Convenient Synthesis, Easy Solution Processability, and Good Hole-Transporting Property

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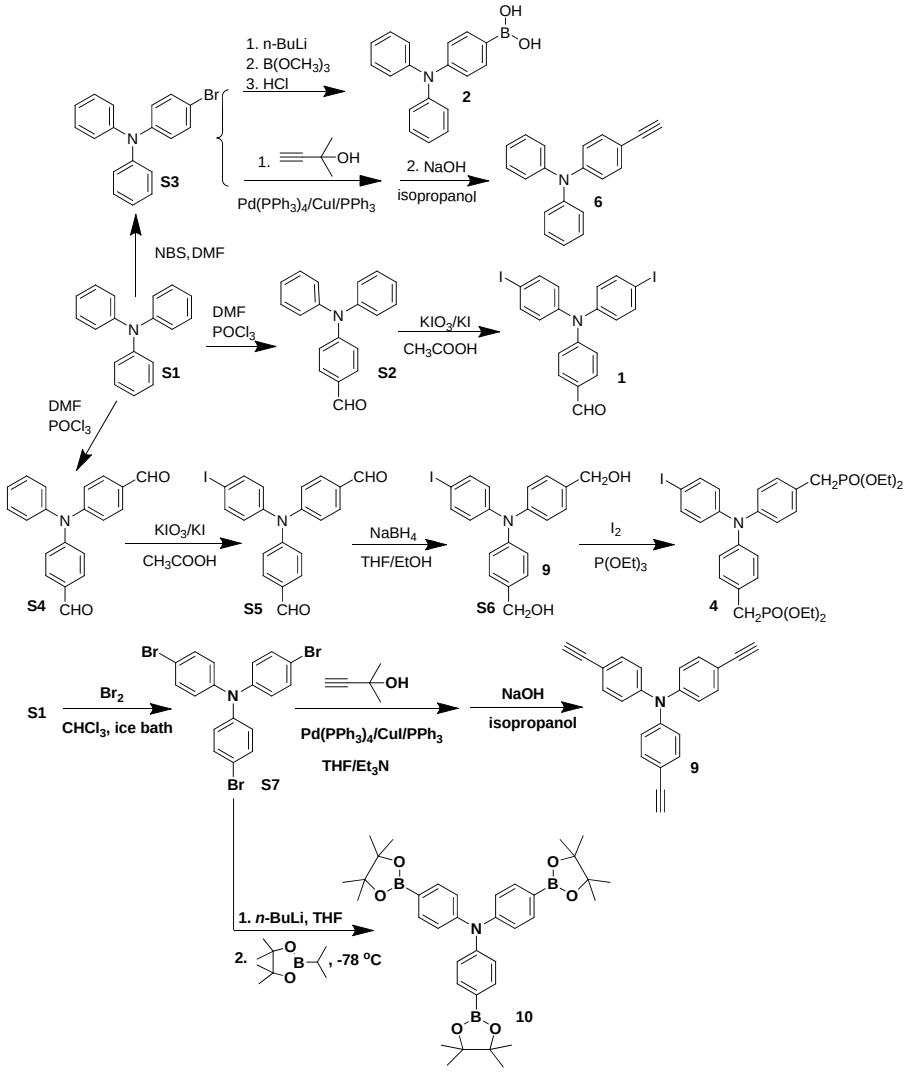

Scheme S1. The synthetic route of monomers.

Experimental Section

Materials.

Tetrahydrofuran (THF) was dried over and distilled from K-Na alloy under an atmosphere of dry nitrogen. Triethylamine (Et_3N) was distilled under normal pressure and kept over potassium hydroxide. Compound **S2** and **S4** were prepared in our previous work.[1] All other reagents were used as received.

Instrumentation.

The ^1H NMR and ^{13}C NMR spectra were measured on a Varian Mercury300 spectrometer or Bruker ARX 400 spectrometer using tetramethylsilane (TMS; δ = 0 ppm) as internal standard. Elemental analyses were performed by a CARLOERBA-1106 micro-elemental analyzer.

Synthesis of 4-Bromo-*N,N*-diphenylaniline (S3).

Triphenylamine (**S1**) (5.00 g, 20.38 mmol) and anhydrous dimethyl formamide (DMF) (40 mL) were added to 100-mL 3-necked flask at 0 ^oC. Then, *N*-bromosuccinimide (NBS) (3.99 g, 22.42 mmol) in 15 mL anhydrous DMF was slowly added to this solution using dropping funnel, and stirred for 1 h at room temperature. Then the reaction was terminated with a 2 M HCl, extracted with ethyl ether and dried with anhydrous $NaSO_4$. The product was recrystallized in ethylacetate and hexane (1:10) to afford white solid **S3** (4.85 g, 73.5 %). ^1H NMR (300 M Hz, $CDCl_3$, 298 K) δ (ppm): 6.92 (d, J = 9.0 Hz, 2H, ArH), 7.05 (m, 6H, ArH), 7.30 (m, 6H, ArH).

Synthesis of Triphenylamine Boronic Acid (2).[2]

A solution of compound **S3** (2.60 g, 8.02 mmol) in THF (10 mL) was added dropwise to a solution of *n*-BuLi (3.8 mL in n-hexane, 8.20 mmol, Aldrich) in THF (12 mL) at -78 ^oC under nitrogen, the mixture was stirred for 1 h, then trimethyl borate (0.9 mL) was added dropwise, the reaction mixture was stirred for another one hour at -78 ^oC, then stirred over night at room

temperature. Hydrochloric acid (2 M) was then added into the mixture, the mixture stirred for 30 min. The resultant mixture was extracted with ether, and washed with distilled water for three times. The organic layer was dried over magnesium sulfate and evaporated to dryness. The crude product was purified by column chromatography on silica gel using ethyl acetate/petroleum ether (2:1) as eluent to afford white powder **2** (1.20 g, 51.7 %). ^{1}H NMR (300 M Hz, $CDCl_3$, 298 K) δ (ppm): 7.06-7.15 (m, 6H, ArH), 7.30 (m, 6H, ArH), 8.00 (d, J = 7.8 Hz, 2H, ArH).

Synthesis of 4-Ethynyl-*N,N*-diphenylaniline (6).

A mixture of compound **S3** (2.59 g, 8.00 mmol), 2-methylbut-3-yn-2-ol (0.86 mL, 8.89 mmol), cuprous iodide (CuI**)** (0.18 g, 0.94 mmol), triphenylphosphine (PPh_3) (0.25 g, 0.95 mmol), triphenylphosphine and tetrakis(triphenylphosphine)palladium ($Pd(PPh_3)_4$) (0.10 g, 0.086 mmol) was carefully degassed and charged with nitrogen. THF (20 mL)/Et_3N (10 mL) was then added. The reaction was refluxed for 30 h and terminated with water. The mixture was extracted with $CHCl_3$, washed with water, dried over anhydrous Na_2SO_4, and evaporated to dryness. The crude product was purified by column chromatography on silica gel using ethyl acetate/petroleum ether (2/1, V/V) as eluent to afford 2-methyl-4-(p-*N,N*-diphenylaminophenyl)-3-butyn-2-ol (1.64 g, 62.8 %). ^{1}H NMR (300 M Hz, $CDCl_3$, 298 K) δ (ppm): 1.61 (s, 6H, -CH_3), 6.92 (d, J = 9.0 Hz, 2H, ArH), 7.05 (m, 6H, ArH), 7.30 (m, 6H, ArH).

To a solution of 2-methyl-4-(p-*N,N*-diphenylaminophenyl)-3-butyn-2-ol (1.64 g, 5.02 mmol) in isopropanol (20 mL) was added NaOH (0.6 g, 15.00 mmol). The mixture was refluxed at 80 ^{o}C for 3 h, and then extracted with chloroform, washed with brine, dried over anhydrous Na_2SO_4, and evaporated to dryness. The crude product was purified by column chromatography on silica gel using chloroform/petroleum ether (1/2, V/V) as eluent to afford buff solid **6**.^{1}H NMR (300 M Hz, $CDCl_3$, 298 K) δ (ppm): 3.02 (s, 1H, -C≡CH), 6.93 (m, 2H, ArH), 7.05 (m, 6H, ArH), 7.30 (m, 6H,

ArH).

Synthesis 4-(bis(4-iodophenyl)amino)benzaldehyde (1).[3]

Compound **S2** (5.26 g, 19.27 mmol) was dissolved in 75 mL of glacial acetic acid, and then KI (6.50 g, 85.53 mmol) and KIO_3 (12.47 g, 55.67 mmol) were added. The reaction mixture was stirred for 3 h at 70 °C. After cooling, the salts were filtered off and washed thoroughly with water and dichloromethane. The aqueous phase was extracted several times with dichloromethane. The combined organic phases were washed with a diluted ammonia solution until pH≈8, with a $NaHSO_3$ solution, and with brine and dried over $MgSO_4$. After removal of the solvents, the crude compound was stirred for 15 min in 500 mL of boiling ethanol. After the solution was cooled to room temperature, the pure product was isolated by filtration as yellow solid **1** (9.07 g, 89.7 %). ^{1}H NMR (300 M Hz, $CDCl_3$, 298 K) δ (ppm): 6.88 (d, J = 8.1 Hz, 4H, ArH), 7.04 (d, J = 8.7 Hz, 2H, ArH), 7.62 (d, J = 9.0 Hz, 4H, ArH), 7.70 (d, J = 9.0 Hz, 4H, ArH), 9.85 (s, 1H, -CHO).

Synthesis of 4-[*N*,*N*-di(4-iodophenyl)amino]benzaldehyde (S5).

Compound **S4** (1.04 g, 3.46 mmol) was dissolved in 25 mL of glacial acetic acid, and then KI (0.58 g, 3.49 mmol) and KIO_3 (1.04 g, 3.45 mmol) were added. The reaction mixture was stirred for 3 h at 70 °C. After cooled to room temperature, the salts were filtered off and washed thoroughly with water and dichloromethane. The aqueous phase was extracted several times with dichloromethane. The combined organic phases were washed with a diluted ammonia solution until pH≈8, with a $NaHSO_3$ solution, and with brine and dried over $MgSO_4$. After removal of the solvents, the crude compound was stirred for 15 min in 500 mL of boiling ethanol. After the solution was cooled to room temperature, and the pure product was isolated by filtration as yellow solid **S5** (1.48 g, 98.0 %). ^{1}H NMR (300 M Hz, $CDCl_3$, 298 K) δ (ppm): 6.91 (d, J = 8.1 Hz, 2H, ArH), 7.16 (d, J = 8.7 Hz, 4H, ArH), 7.67 (d, J = 8.7 Hz, 2H, ArH),7.77 (d, J = 8.7 Hz, 4H, ArH), 9.90 (s, 2H, -CHO).

Synthesis of compound S6.

Compound **S5** (1.45 g, 3.4 mmol) and $NaBH_4$ (0.31 g, 8.16 mmol) was dissolved in dried THF, and stirred at room temperature for 2 h. Then the reaction mixture was refluxed overnight. After the reaction was cooled to room temperature, the diluted HCl solution was added into the above mixture to adjust the pH≈7, and then extracted with $CHCl_3$, washed with water, dried over anhydrous Na_2SO_4, and evaporated to dryness to afford white solid **S6**. The crude product was not purified and used directly in the next reaction (1.45 g, 100 %). ^{1}H NMR (300 M Hz, $CDCl_3$, 298 K) δ (ppm): 4.64 (s, 4H, -CH_2OH), 6.80 (d, J = 6.6 Hz, 2H, ArH), 7.04 (d, J = 9.2 Hz, 4H, ArH), 7.24 (d, J = 6.0 Hz, 4H, ArH),7.48 (d, J = 6.6 Hz, 2H, ArH).

Synthesis of compound 4.

To a mixture of compound **S6** (0.47 g, 1.1 mmol) in 3.2 mL of triethyl phosphite was added iodine (0.56 g, 2.2 mmol) at 0 °C. The reaction mixture was stirred for 36 h, and the excess of triethyl phosphate was evaporated under vacuum. The crude product was purified by column chromatography on silica gel using ethyl acetate/methanol (10/1, V/V) as eluent to afford white solid **4** (0.33 g, 44.7 %). ^{1}H NMR (300 M Hz, $CDCl_3$, 298 K) δ (ppm): 1.26 (t, J = 7.2 Hz, 12H, -CH_3), 3.06 (d, J = 22.2 Hz, 4 H, -CH_2P-), 4.04 (m, 8H, -OCH_2-), 6.77 (d, J = 9.0 Hz, 2H, ArH), 6.97 (d, J = 8.1Hz, 4H, ArH), 7.16 (d, J = 6.6 Hz, 4H, ArH), 7.47 (d, J = 8.7 Hz, 2H, ArH). ^{13}C NMR (75 M Hz, $CDCl_3$, 298 K) δ (ppm): 16.59, 32.32, 34.15, 62.35, 124.65, 125.58, 126.43, 130.96, 138.28, 146.14, 147.64. $C_{28}H_{36}INO_6P_2$ (EA) (%, found/calcd): C, 49.55/50.09; H, 5.47/5.40; N, 1.80/2.09.

Synthesis of compound tris(4-bromophenyl)amine (S7).

To a solution of **S1** (2.45 g, 10.0 mmol) in $CHCl_3$ (25 mL), 1.9 mL of Br_2 in $CHCl_3$ (5 mL) was added slowly in an ice bath. The mixture was stirred at room temperature overnight, then a lot of hydrous solution of $NaHSO_3$ was added. The organic layer was collected and evaporated to dryness.

The crude product was purified by crystallization in ethanol to afford white solid **S7** (4.19 g, 86.9 %). ^{1}H NMR (300 M Hz, $CDCl_3$, 298 K) δ (ppm): 7.35 (d, J = 8.4 Hz, 6H), 6.92 (d, J = 8.4 Hz, 6H).

Synthesis of compound tris(4-ethynylphenyl)amine (9).[4]

A mixture of compound **S7** (1.93 g, 4.0 mmol), 2-methylbut-3-yn-2-ol (1.50 g, 17.8 mmol), cuprous iodide (CuI) (0.23 g, 1.20 mmol), triphenylphosphine (PPh_3) (0.31 g, 1.20 mmol), triphenylphosphineand tetrakis(triphenylphosphine)palladium ($Pd(PPh_3)_4$) (0.14 g, 0.12 mmol) was carefully degassed and charged with nitrogen. THF (15 mL)/Et_3N (15 mL) was then added. The reaction was stirred for 3 days at room temperature. The mixture was extracted with $CHCl_3$, washed with water, dried over anhydrous Na_2SO_4, and evaporated to dryness. The crude product was purified by column chromatography on silica gel using ethyl acetate/petroleum ether (4/5) as eluent to afford buff solid *4,4′,4″*-(*4,4′,4″*-Nitrilotris(benzene-4,1-diyl))tris(2-methylbut-3-yn-2-ol) (0.62 g, 31.6 %). ^{1}H NMR (300 M Hz, $CDCl_3$, 298 K) δ (ppm): 1.61 (s, 18H, -CH_3), 6.95 (d, J = 8.7 Hz, 6H, ArH), 7.28 (d, J = 8.1 Hz, 6H, ArH).

To a solution of *4,4′,4″*-(*4,4′,4″*-Nitrilotris(benzene-4,1-diyl))tris(2-methylbut-3-yn-2-ol) (0.51 g, 1.04 mmol) in *iso*-propanol (12 mL) was added NaOH (0.37 g, 9.25 mmol). The mixture was refluxed at 80 ^{o}C overnight, and then extracted with chloroform, washed with brine and dried over anhydrous Na_2SO_4, and evaporated to dryness. The crude product was purified by column chromatography on silica gel using chloroform as eluent to afford yellow solid **9** (0.27 g, 79.0 %). ^{1}H NMR (300 M Hz, $CDCl_3$, 298 K) δ (ppm): 3.05 (s, 3H, -C≡CH), 6.98 (d, J = 8.7 Hz, 6H, ArH), 7.36 (d, J = 8.1 Hz, 6H, ArH).

Synthesis of tris{4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolane)phenyl}amine (10).[5]

To a solution of **S7** (0.60 g, 1.24 mmol) in 10 mL of dry THF at -78 ^{o}C, 1.65 mL of *n*-butyllithium (2.6 M in hexane, 4.29 mmol) was added dropwise. The mixture was stirred at -78 ^{o}C

for 2 h. Then, 1.0 mL of 2-isopropoxy-4,4,5,5,-tetramethyl-1,3,2-dioxaborolane (4.96 mmol) was added rapidly to the above solution and the mixture went to stir for 2 h. The resultant mixture was warmed up to room temperature and stirred for 36 h, then poured into water, and extracted with ether. The combined extract was washed with brine, dried over anhydrons Na_2SO_4, and concentrated. The crude product was purified by column chromatography on silica gel using ethyl acetate/petroleum ether (1:10) as eluent to afford white powder **10** (0.12 g, 15.5 %). ^{1}H NMR (300 M Hz, $CDCl_3$, 298 K) δ (ppm): 1.34 (s, 36H, -CH_3), 7.06 (d, J = 8.4 Hz, 6H, ArH), 7.67 (d, J = 7.8 Hz, 6H, ArH).

Reference.

1. Gong, W.; Li, Q.; Li, Suyue; Lu, C.; Li, Z.; Zhu, J.; Zhu, Z.; Li, Z.; Wang, Q.; Cui, Y.; Qin, J. *Mater. Lett.* **2007**, *61*, 1151-1153.
2. Morandeira, A.; Lopez-Duarte, I.; O'Regan, B.; Martinez-Diaz, M. V.; Forneli, A.; Palomares, E.; Torres, T.; Durrant, J. R. *J. Mater. Chem.* **2012**, *19*, 5016-5026.
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4. Niklas, P.; Arnulf, R.; Valentin, S.; Volker, S.; Georg, G.; Jurgen S.; Robert, L. *Macromolecules* **2009**, *42*, 6519-6528.
5. Sahu, D.; Tsai, C.-H.; Wei, H.-Y.; Ho, K.-C.; Chang, F.-C.; Chu, C.-W. *J. Mater. Chem.* **2012**, *22*, 7945-7953.

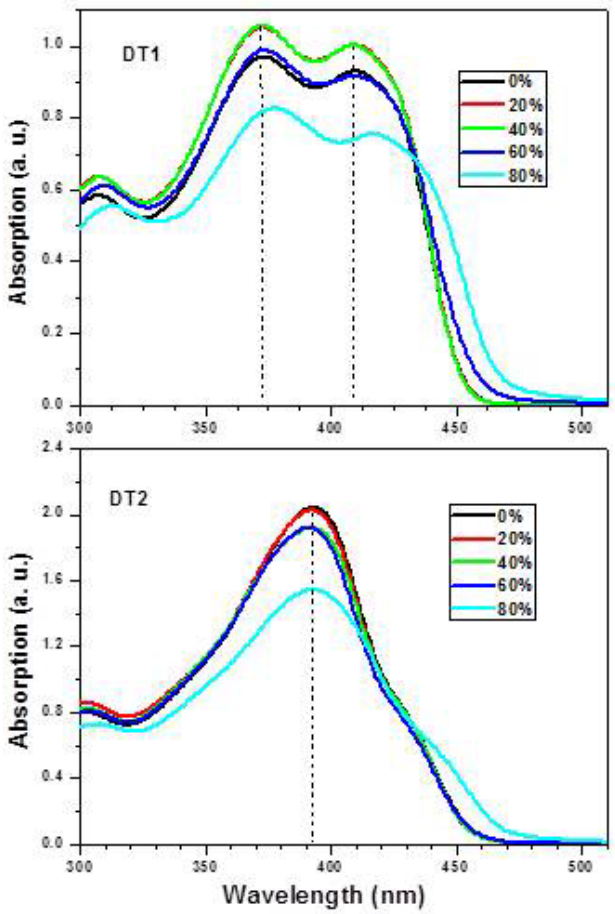

Figure S1. Absorption spectra of dendrimers measured in various composition ratios of cyclohexane in THF solutions from 0 to 80%.

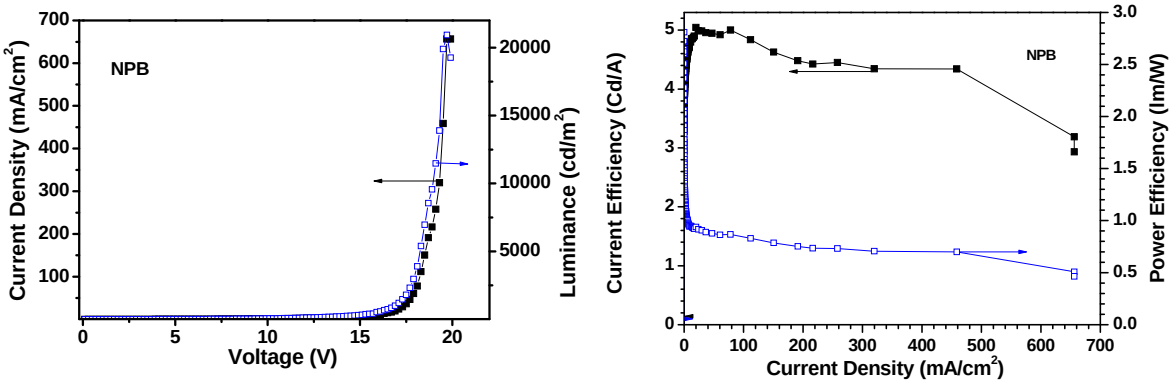

Figure S2. The luminance and current density as a function of applied voltage (left) and the current and power efficiency as a function of current density (right) of NPB-based Alq_3 emitting device.

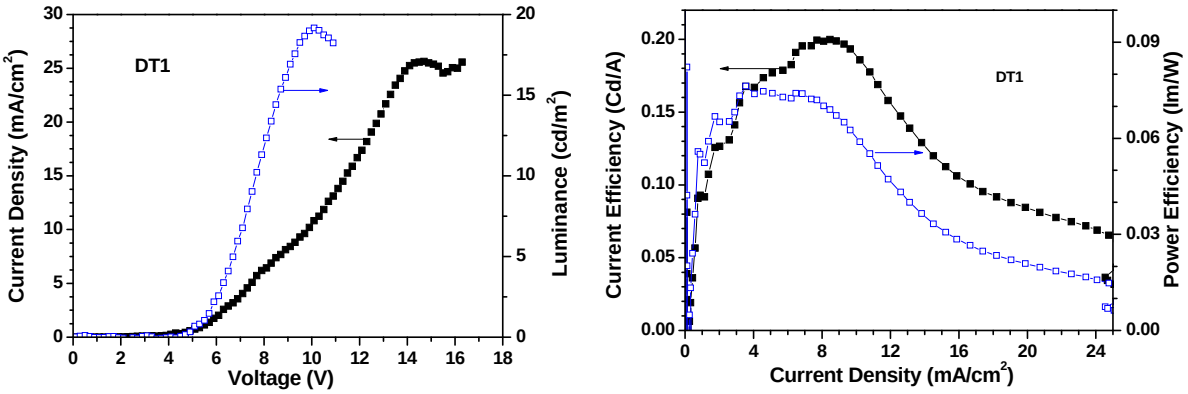

Figure S3. The luminance and current density as a function of applied voltage (left) and the current and power efficiency as a function of current density (right) of **DT1**-based Alq_3 emitting device.

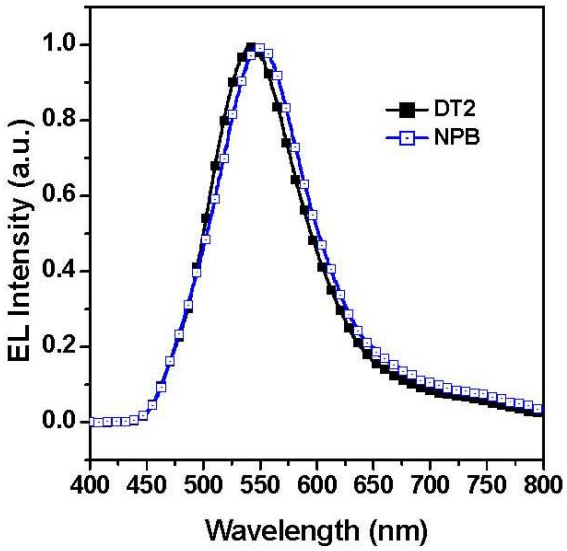

Figure S4. The EL spectra of **DT2**- or NPB- based Alq3 emitting device.

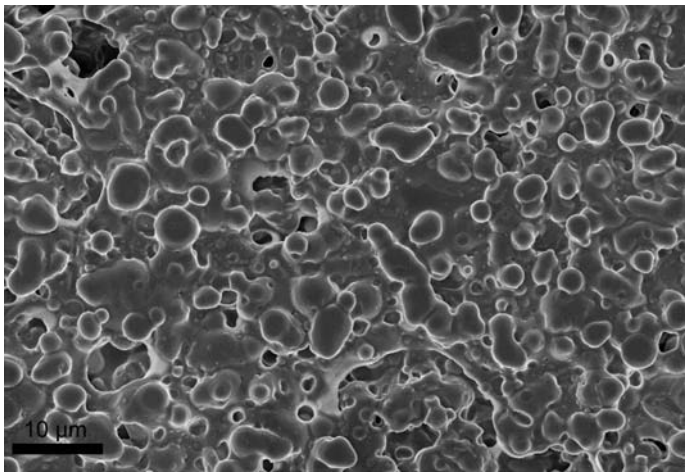

Figure S5. Topographic images of the thin film of **DT2** on ITO surface obtained by SEM

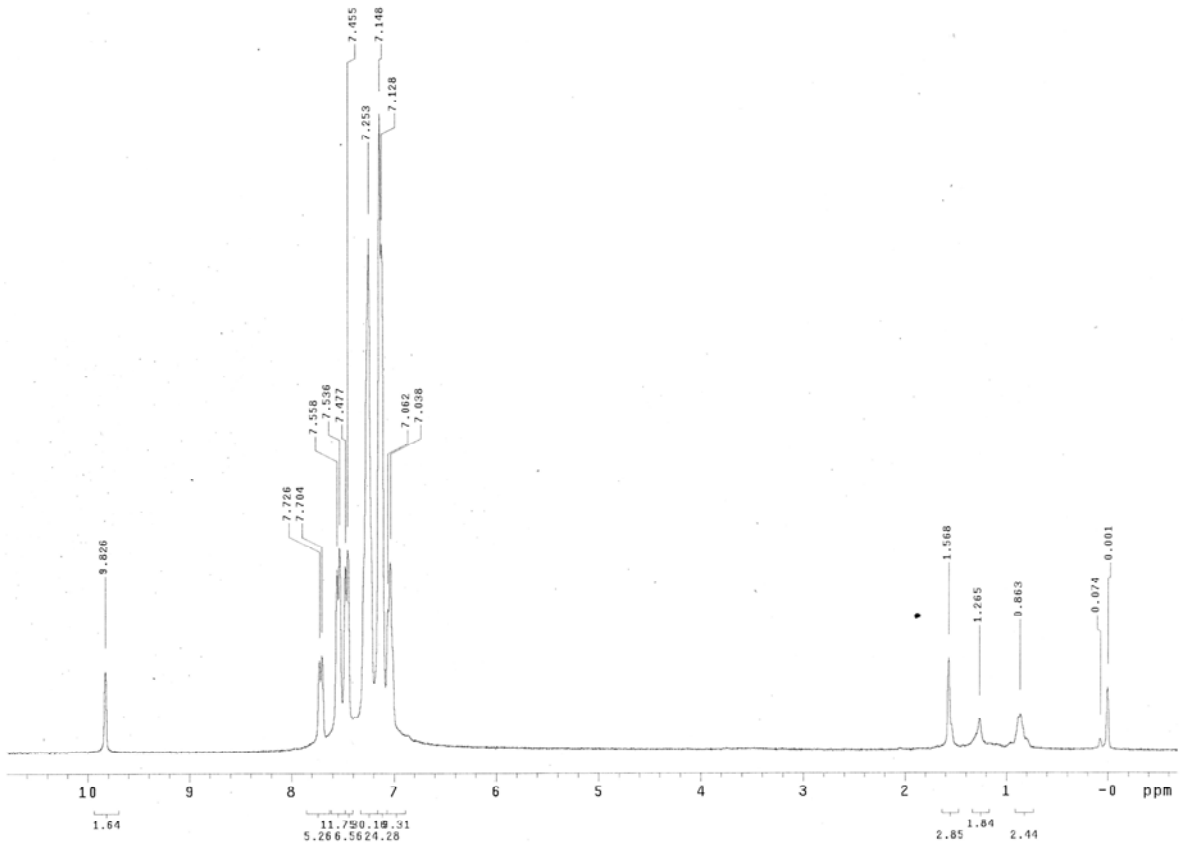

Figure S6. The [1]H NMR spectrum of **3** conducted in *d*-chloroform.

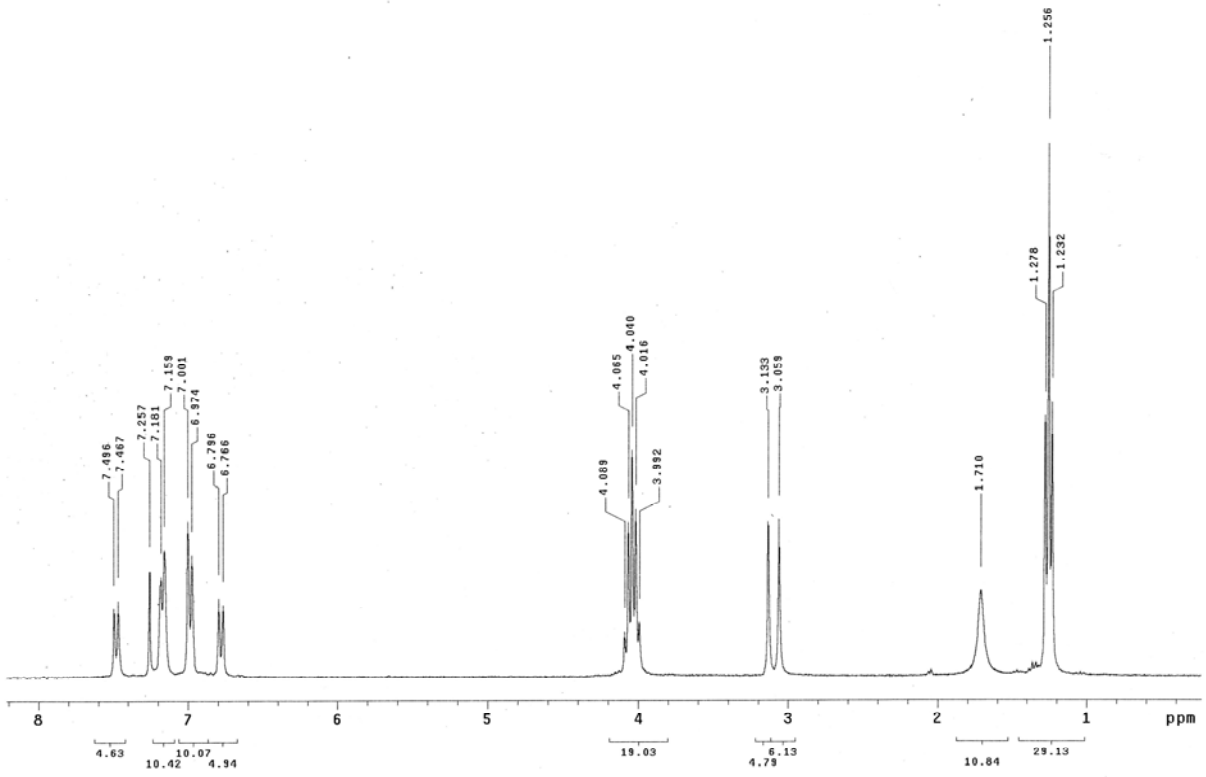

Figure S7. The [1]H NMR spectrum of **4** conducted in *d*-chloroform.

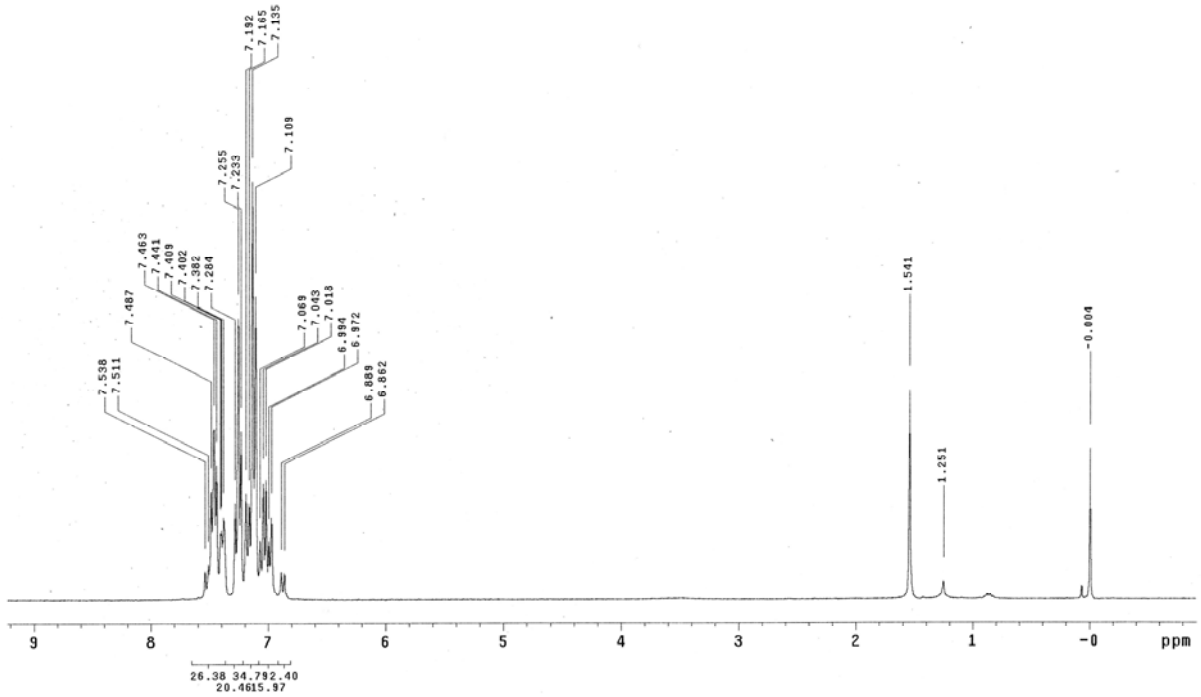

Figure S8. The [1]H NMR spectrum of **5** conducted in *d*-chloroform.

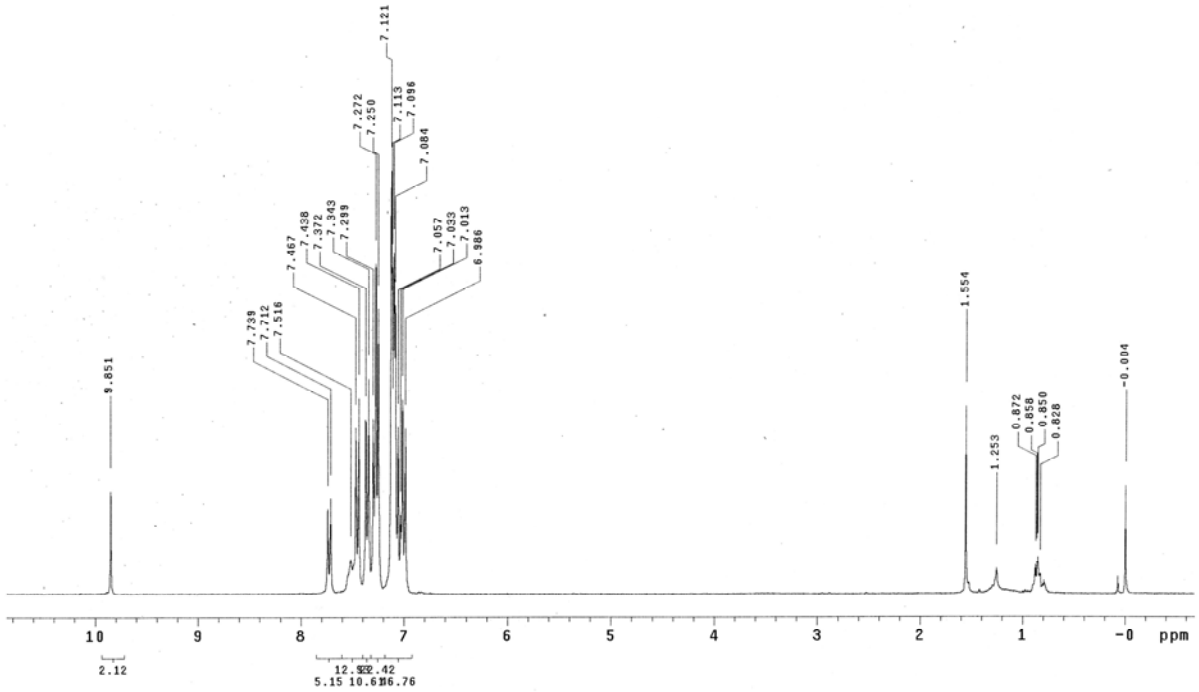

Figure S9. The [1]H NMR spectrum of **7** conducted in *d*-chloroform.

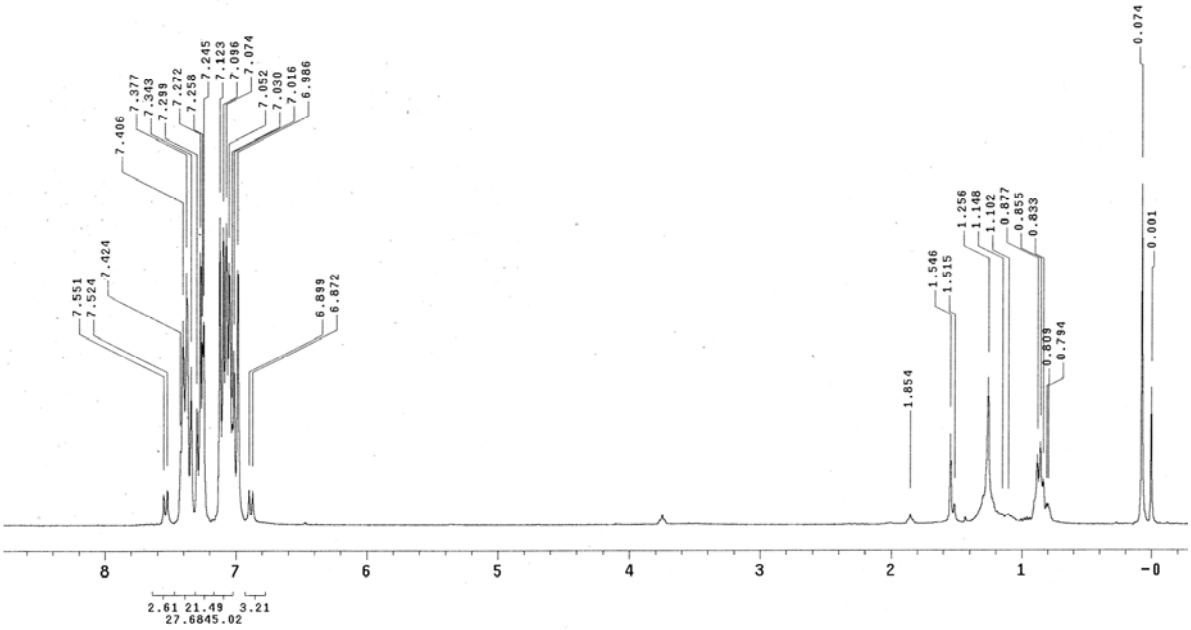

Figure S10. The ^{1}H NMR spectrum of **8** conducted in *d*-chloroform.

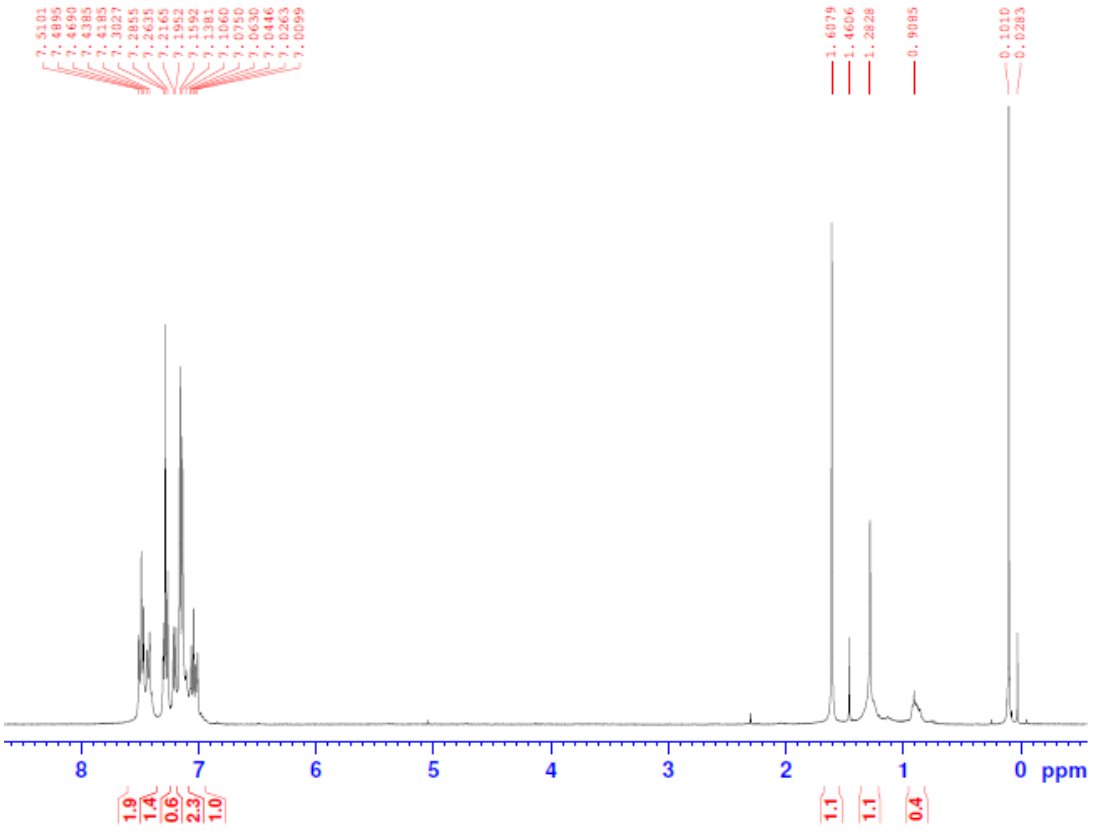

Figure S11. The ^{1}H NMR spectrum of **DT1** conducted in *d*-chloroform.

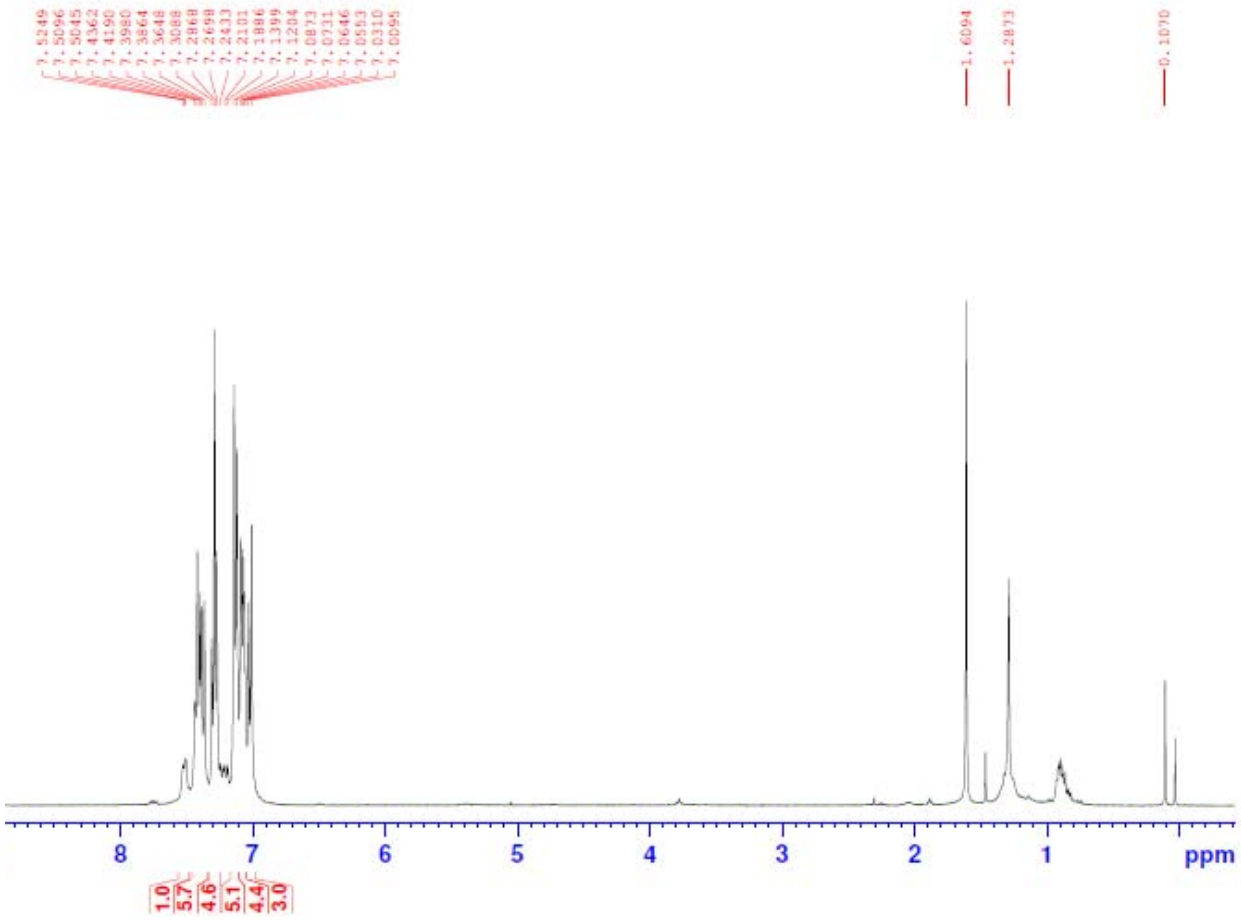

Figure S12. The ^{1}H NMR spectrum of **DT2** conducted in *d*-chloroform.

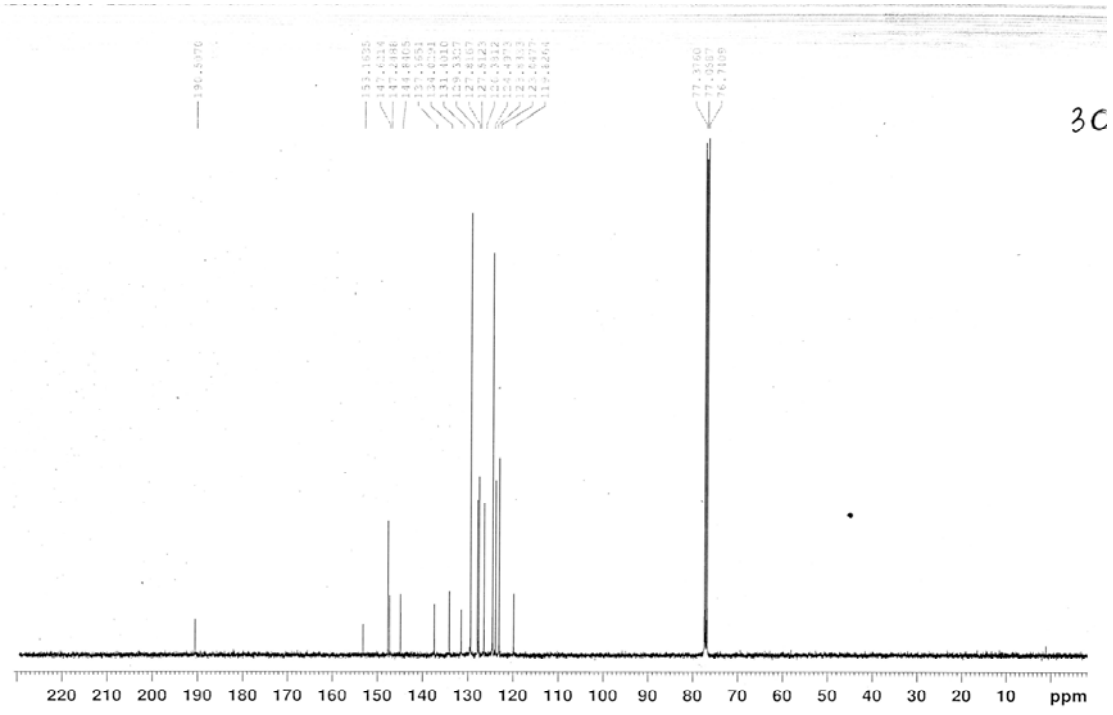

Figure S13. The ^{13}C NMR spectrum of **3** conducted in *d*-chloroform.

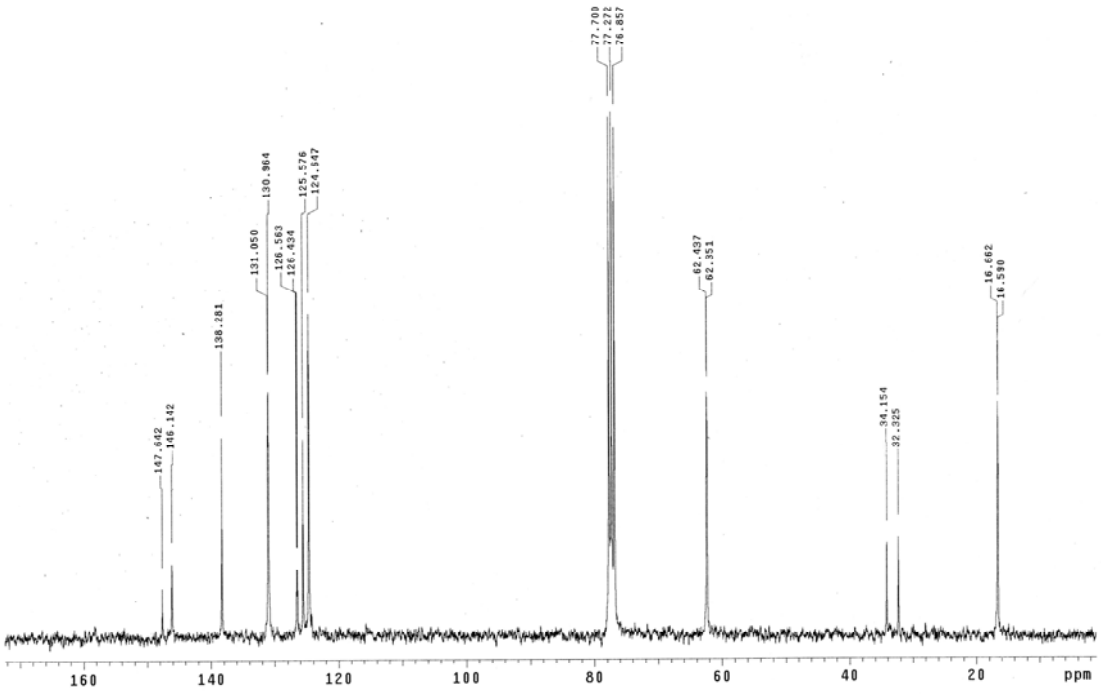

Figure S14. The ^{13}C NMR spectrum of **4** conducted in *d*-chloroform.

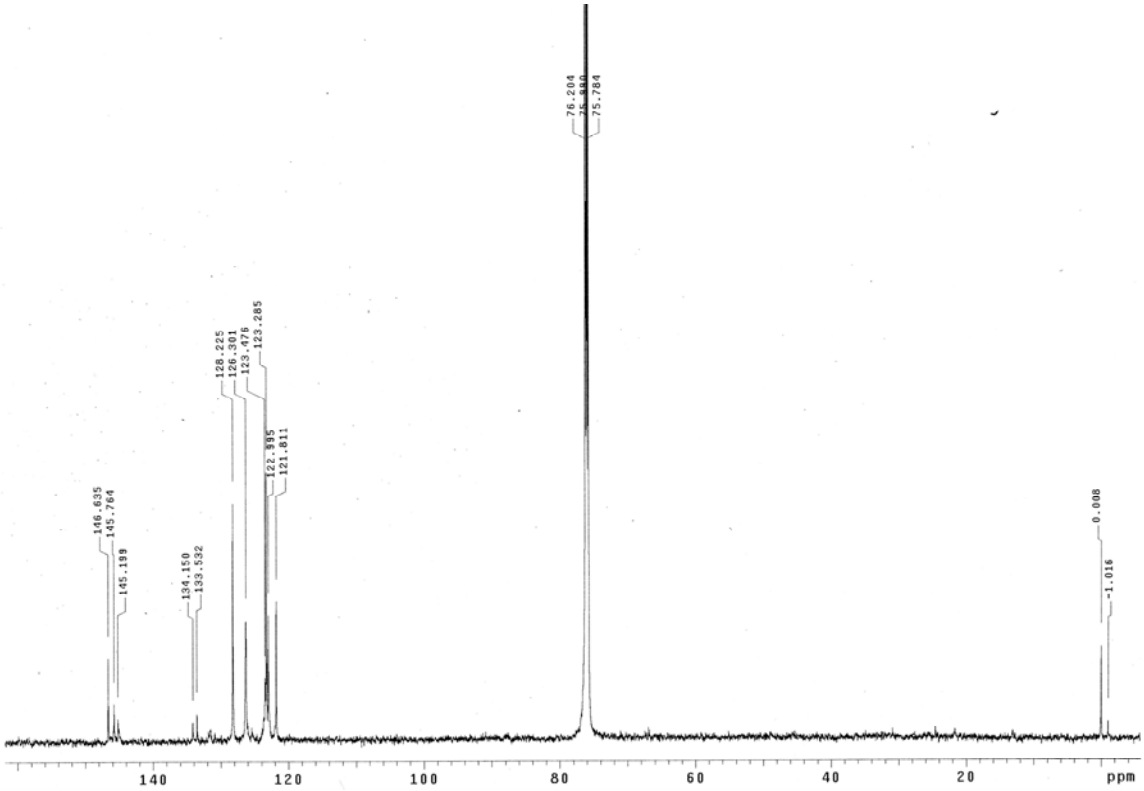

Figure S15. The ^{13}C NMR spectrum of **5** conducted in *d*-chloroform.

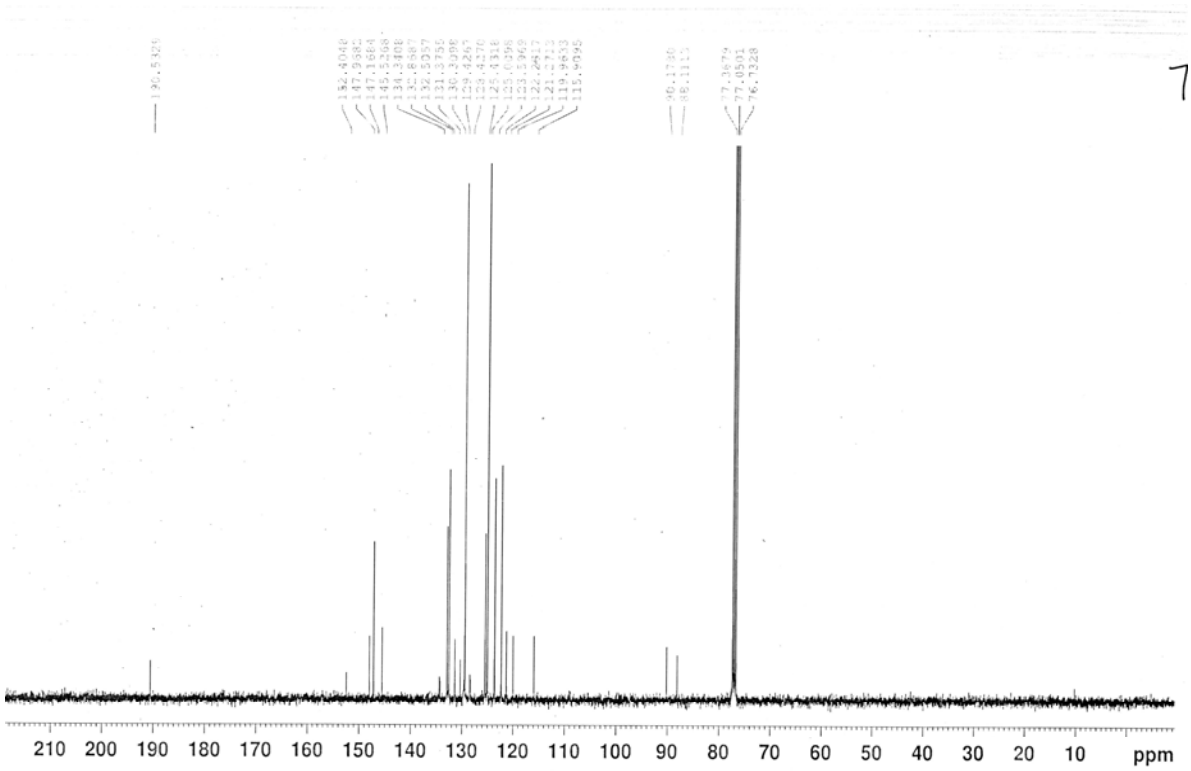

Figure S16. The ^{13}C NMR spectrum of **7** conducted in *d*-chloroform.

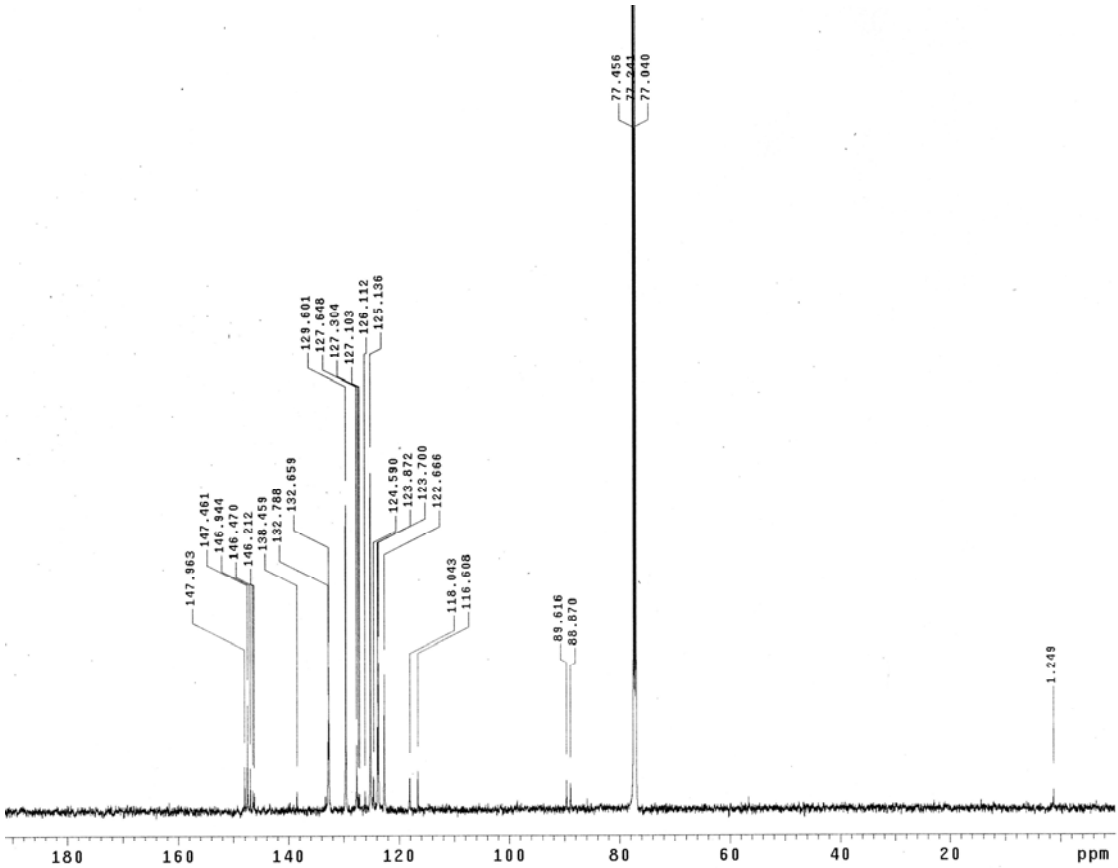

Figure S17. The ^{13}C NMR spectrum of **8** conducted in *d*-chloroform.

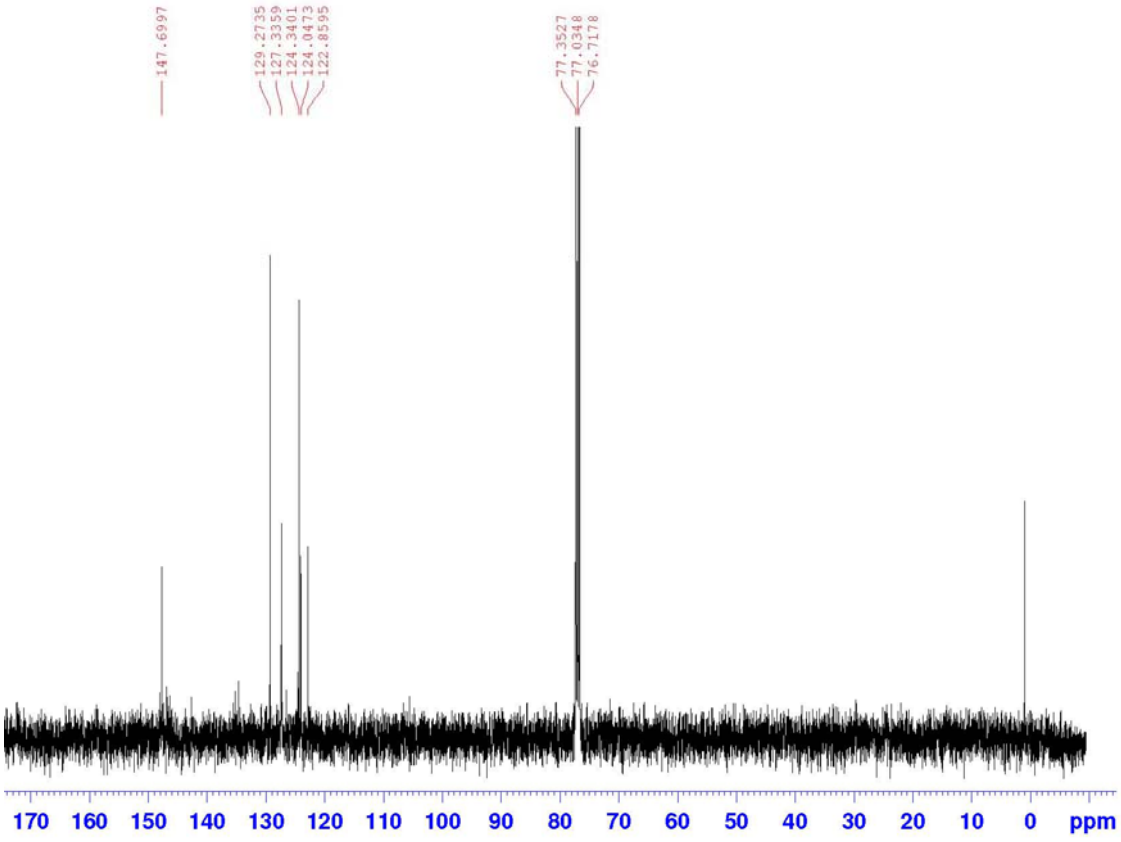

Figure S18. The ^{13}C NMR spectrum of **DT1** conducted in *d*-chloroform

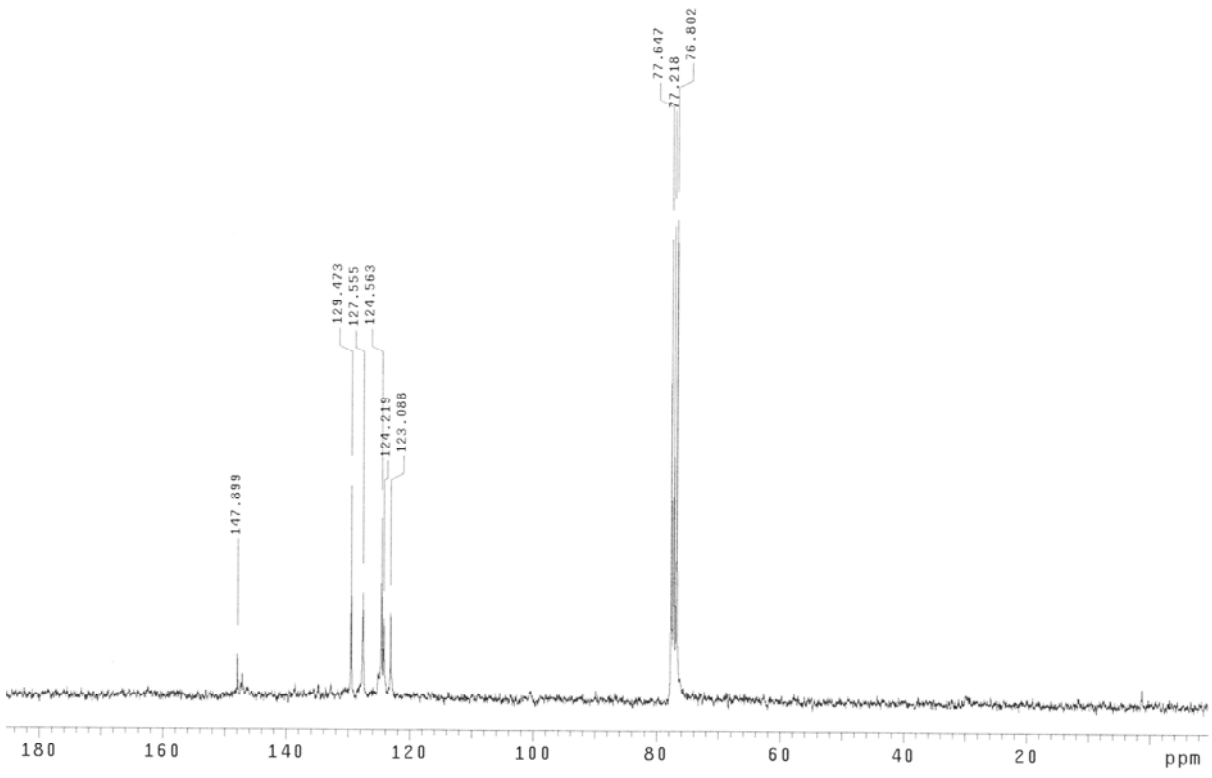

Figure S19. The ^{13}C NMR spectrum of **DT2** conducted in *d*-chloroform.