Electronic Supplementary Information

Design and synthesis of triazoloquinoxaline polymers with positioning alkyl or alkoxyl chains for organic photovoltaics cells

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Contents

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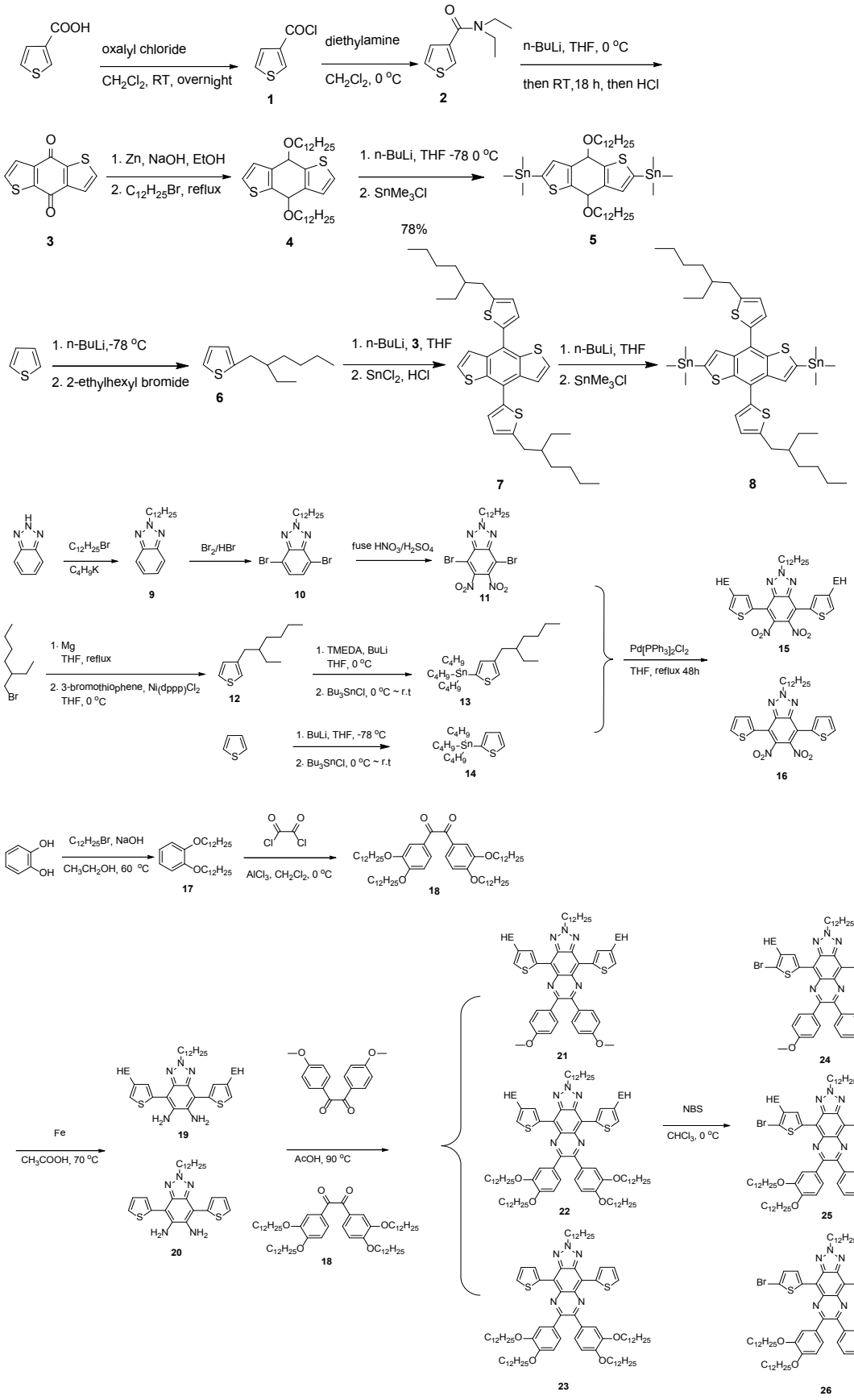
1. Synthetic procedures for monomers



Thiophene-3-carbonyl chloride (1).[S1] Thiophene-3-carboxylic acid (10.00 g, 78.03 mmol) was dissolved in 100 mL of anhydrous CH_2Cl_2. The mixture was cooled by ice-water bath, and then oxalyl chloride (19.81 g, 156.07 mmol) was added in one portion. The reactant was stirred overnight at room temperature (RT). After removing the solvent and unreacted oxalyl chloride by rotary evaporation, compound **1** was obtained as colorless solid (10.16 g, 69.31 mmol, 89%) and used directly without further purification.

N,N-Diethylthiophene-3-carboxamide (2).[S1] Compound **1** was dissolved in 60 mL of anhydrous CH_2Cl_2 then the solution was dropped into a 14.3 mL of diethylamine (10.14 g, 138.61 mmol) solution in 50 mL of anhydrous CH_2Cl_2 slowly in ice-water bath. After adding compound **1**, the ice bath was removed, and the reactant was stirred at RT for 30 min. Then, the reactant was washed by water several times and extracted by CH_2Cl_2. The organic layer was washed with water and brine, dried with $MgSO_4$, filtered, concentrated via rotary evaporation, the crude product was purified by distillation under vacuum, and compound **2** (10.00 g, 54.56 mmol, 79%) was obtained as a pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (dd, J = 2.9, 1.2 Hz, 1H), 7.30 (dd, J = 5.0, 2.9 Hz, 1H), 7.17 (dd, J = 5.0, 1.2 Hz, 1H), 3.43 (d, J = 68.5 Hz, 4H), 1.18 (s, 6H).

4,8-Dihydrobenzo[1,2-b:4,5-b']dithiophen-4,8-dione (3).[S1] Compound **2** (10.0 g, 54.56 mmol) was dissolved in 100 mL of anhydrous THF under an inert atmosphere. The solution was cooled down by an ice-water bath, and 22.9 mL of n-butyllithium (57.29 mmol, 2.5 M) was dropped into the solution within 30 min. Then, the reactant was stirred at RT for 30 min. The reactant was poured into 500 g of ice water and stirred for several hours. The mixture was filtrated, and the yellow precipitate was successively washed with water (200 mL), methanol (50 mL) and hexane (50 mL). Compound **3** was obtained as a yellow powder (5.00 g, 22.70 mmol, 83%). ^{1}H NMR (500 Hz, $CDCl_3$): δ (ppm) 7.68 (d, J = 5.0 Hz, 2H), 7.65 (d, J = 5.0 Hz, 2H).

4,8-Didodecyloxybenzo[1,2-b;3,4-b]dithiophene (4).[S1] Compound **3** (2.20 g, 10.00 mmol), zinc powder (1.44 g, 22.00 mmol), and 60 mL of water were put into a 100 mL flask; then NaOH (6.00 g, 149.82 mmol) was added into the mixture. The mixture was well stirred and heated to reflux for 1 h. Then, 1-bromododecane (7.47 g, 30.00 mmol) and a catalytic amount of tetrabutylammonium bromide were added into the flask. After being refluxed for 2 h, the reactant was poured into cold water and extracted by 200 mL of diethyl ether two times. The organic layer was washed with water and brine, dried with $MgSO_4$, filtered, concentrated via rotary evaporation, the crude product was purified by recrystallization from ethyl alcohol two times.

Compound **4** (4.40 g, 7.84 mmol, 89%) was obtained as colorless crystal. ^{1}H NMR (500 Hz, $CDCl_3$): δ (ppm) 7.48 (d, J = 5.5 Hz, 2H), 7.36 (d, *J* = 5.2 Hz, 2H), 4.27 (t, *J* = 6.6 Hz, 4H), 1.91-1.84 (m, 4H), 1.60-1.52 (m, 4H), 1.42-1.22 (m, 32H), 0.88 (t, *J* = 6.9 Hz, 6H).

2,6-Bis(trimethyltin)-4,8-didodecyloxybenzo[1,2-b;3,4-b]dithiophene (5).[S2] Compound **4** (0.50 g, 0.89 mmol) and 50 mL of anhydrous THF were added into a flask under an inert atmosphere. The solution was cooled down to -78 ° C and 0.9 mL of n-butyllithium (2.23 mmol, 2.5 M) was added dropwise. After being stirred at -78 °C for 1 h, then, 2.7 ml of trimethyltin chloride (2.67 mmol, 1 M) was added in one portion and the mixture was stirred at RT overnight. The mixture was poured into 200 mL of cool water and extracted by diethyl ether three times. The organic layer was washed with water and brine, dried with $MgSO_4$, filtered, concentrated via rotary evaporation, the residue was recrystallized by isopropanol yield the compound 5 as colorless needles (0.62 g, 0.70 mmol, 78%). ^{1}H NMR (500 Hz, $CDCl_3$): δ (ppm) 7.51 (s, 2H), 4.29 (t, *J* = 6.5 Hz, 4H), 1.93-1.85 (m, 4H), 1.64-1.54 (m, 4H), 1.45-1.21 (m, 32H), 0.88 (t, *J* = 6.8 Hz, 6H), 0.45 (s, 18H).

2-(2-Ethylhexyl)thiophene (6).[S3] Thiophene (8.00 g, 95.08 mmol) and 100 mL of anhydrous THF were added into a flask under an inert atmosphere. The solution was cooled down to -78 ° C and 40.0 mL of n-butyllithium (99.8 mmol, 2.5 M) was added dropwise. After being stirred at -78 °C for 1 h, then, 18.60 ml of 2-ethylhexyl bromide (104.59 mmol) was added in one portion and the mixture was stirred at -78 °C for 1 h and warmed up to RT overnight. The mixture was poured into 20 mL of cool water and extracted by diethyl ether three times. The organic layer was washed by water and then dried by anhydrous $MgSO_4$. After removing solvent under vacuum, the residue was vacuum distilled to yield the compound **6** as colorless needles (15.00 g, 76.39 mmol, 80%). ^{1}H NMR (500 Hz, $CDCl_3$): δ (ppm) 7.12 (d, *J* = 5.1 Hz, 1H), 6.93 (dd, *J* = 5.0, 3.5 Hz), 6.78 (d, *J* = 3.3 Hz, 1H), 3.48 (t, *J* = 4.2 Hz, 2H), 2.79 (d, *J* = 6.8 Hz, 2H), 1.65-1.58 (m, 1H), 1.41-1.25,(m, 10H), 0.97-0.86 (m, 6H).

4,8-Bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (7).[S4] 7.4 mL of n-Butyllithium (18.39 mmol, 2.5 M) was added dropwise to the mixture of compound **3** (3.57 g, 18.16 mmol) in 30 mL of anhydrous THF at 0 °C under argon atmosphere. The mixture was heated up to 50 °C for 3 h. then compound **6** (3.57 g, 18.16 mmol) was then added in portion, and the mixture was kept for 2 h at 50 °C. Cooling the mixture down to RT, $SnCl_2 \cdot 2H_2O$ (8.20 g, 36.32 mmol) in 20 mL of aqueous HCl (10%) was added, and the mixture was stirred overnight. The organic layer was washed with water and brine, dried with $MgSO_4$, filtered, concentrated via

rotary evaporation and purified by column chromatography on silica gel eluting with dichloromethane: petroleum ether (1:10, v/v) to give pure product as a yellow solid (1.20 g, 2.07 mmol, 46%). ^{1}H NMR (500 Hz, $CDCl_3$): δ (ppm) 7.64 (d, J = 5.7 Hz, 2H), 7.45 (d, J = 5.7 Hz, 2H), 7.29 (d, J = 3.5 Hz, 2H), 6.89 (d, J = 3.5 Hz, 2H), 2.86 (d, J = 6.8 Hz, 4H), 1.71-1.66 (m, 2H), 1.42-1.32,(br, 16H), 0.98-0.90 (m, 12H).

(4,8-Bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl) bis(trimethylstannane) (8).[S4] Compound **7** (0.50 g, 0.86 mmol) and 20 mL of anhydrous THF were added into a flask under an inert atmosphere. The solution was cooled to 0 ° C and 0.8 mL of n-butyllithium (1.90 mmol, 2.5 M) was added dropwise. The reaction mixture was then stirred for 2 h at room temperature, then the reaction mixture was cooled to 0 ° C and 3.0 ml of trimethyltin chloride (3.00 mmol, 1 M) was added in one portion and the mixture was stirred at RT overnight. The mixture was quenched by addition of 20 mL of water and extracted by diethyl ether three times. The organic layer was washed with water and brine, dried with $MgSO_4$, filtered, concentrated via rotary evaporation, the residue was recrystallized by isopropanol yield the compound **8** as pale yellow needles (0.63 g, 0.70 mmol, 82%). ^{1}H NMR (500 Hz, $CDCl_3$): δ (ppm) 7.69 (s, 2H), 7.32 (d, J = 3.5 Hz, 2H), 6.90 (d, J = 3.5 Hz, 2H), 2.89-2.87 (m, 4H), 1.72-1.68 (m, 2H), 1.38-1.31,(br, 16H), 0.98-0.95 (m, 12H), 0.40 (s, 18H).

2-Dodecylbenzotriazole (9).[S5] 1,2,3-Benzotriazole (2.50 g, 21.0 mmol), sodium tert-butoxide (2.12 g, 22.0 mmol), and bromododecane (6.05 g, 24.3 mmol) were dissolved in 30 mL of methanol. The mixture was refluxed for 12 h. After removal of the solvent by evaporation, the residue was dissolved in $CHCl_3$ and extracted with water. The organic layer was washed with water and brine, dried with $MgSO_4$, filtered, concentrated via rotary evaporation and purified by column chromatography on silica gel eluting with chloroform: petroleum ether (3:2, v/v) to obtain compound **9** as a colorless oil (2.32 g, 38%). ^{1}H NMR (500 Hz, $CDCl_3$): δ (ppm) 7.86 (dd, J = 6.5, 3.1 Hz, 2H), 7.37 (dd, J = 6.6, 3.1 Hz, 2H), 4.72 (t, J = 7.2 Hz, 2H), 2.11 (m, 2H), 1.28-1.19(m, 18H), 0.87 (t, J = 7.0 Hz, 3H).

4,7-Dibromo-2-dodecylbenzotriazole (10).[S5] Compound **9** (2.32 g, 8.05 mmol) and an aqueous HBr solution (30 mL) were added to a flask, and the mixture was stirred for 1 h at 100 °C. Bromine (1.37 g, 22.2 mmol) was added, and the mixture was stirred for 12 h at 135 °C. After the mixture was cooled to room temperature, an aqueous solution of $Na_2S_2O_3{\cdot}5H_2O$ was added and the product was extracted with $CHCl_3$. The organic layer was washed with water and brine, dried with $MgSO_4$, filtered, concentrated via rotary evaporation and purified by column chromatography

on silica gel eluting with chloroform: petroleum ether (3:4, v/v) to obtained compound **10** as pale yellow solid (1.42 g, 40%). ^{1}H NMR (500 Hz, $CDCl_3$): δ (ppm) 7.39 (s, 2H), 4.74 (t, *J* = 7.4 Hz, 2H), 2.10 (m, 2H), 1.30-1.16(m, 18H), 0.84 (t, *J* = 6.5 Hz, 3H).

4,7-Dibromo-2-dodecyl-5,6-dinitro-2H-benzo[d][1,2,3]triazole (11).[S6] A mixture of concentrated 40 mL of sulphuric acid and 40 mL of fuming nitric acid was cooled to 0 °C and compound **10** (6.14 g, 13.7 mmol) was added to the mixture in small portions to keep the temperature below 0 °C. After the addition was completed, the reaction mixture was stirred at 0 °C for 3 h and then poured into an ice-bath. The precipitate was collected by filtration and recrystallized with an acetone-water mixture to yield compound **11** as a yellow solid (4.0 g, 54%). ^{1}H NMR (500 Hz, $CDCl_3$): δ (ppm) 4.87 (t, *J* = 7.3 Hz, 2H), 2.20 (m, 2H), 1.43-1.24(m, 18H), 0.89 (t, *J* = 7.0 Hz, 3H).

3-(2-Ethylhexyl)thiophene (12).[S7] To magnesium turnings (1.98 g, 0.24 mmol) in anhydrous 20 mL of THF and a small amount of iodine in a 100 mL three-neck flask, a solution of 2-ethylhexyl bromide (15g, 77.7 mmol) in anhydrous 20 mL of anhydrous THF was added slowly under N_2 at a rate sufficient to maintain reflux. After refluxing for 1h, the Grignard reagent was then added dropwise through a canula to a mixture of 3-bromothiophene (9.38 g, 57.5 mmol), Ni(dppp)Cl_2 (312 mg, 0.58 mmol) and anhydrous 50 mL of THF placed in a 250 mL flask. The mixture was refluxed under argon and stirred overnight. Next, the mixture was hydrolyzed by careful addition of water followed by 38% aqueous HCl and extracted with CH_2Cl_2. The combined organic layer was washed with water and brine, dried with $MgSO_4$, filtered, concentrated via rotary evaporation and purified by column chromatography on silica gel eluting with petroleum ether to give compound **12** as colorless oil (6.9 g, 61%). ^{1}H NMR (500 Hz, $CDCl_3$): δ (ppm) 7.24-7.21 (m, 1H), 6.92-6.89 (m, 2H), 2.57 (d, *J* = 6.9 Hz, 2H), 1.59-1.53 (m, 1H), 1.32-1.22 (m, 8H), 0.92-0.82 (m, 6H).

2-(Tributylstannyl)-4-(2-ethylhexyl)thiophene (13).[S8] Compound **12** (6.9 g, 35.1 mmol) and N,N,N',N'-tetramethylethylenediamine (TMEDA) (5.8 mL, 38.7 mmol) in anhydrous 80 mL of anhydrous THF at 0 ºC was added dropwise 21.0 mL of n-butyllithium (52.7 mmol, 2.5 M) over 30 min. The resulting solution was stirred at 0 °C for 30 min and warmed to RT. The mixture was then cooled to 0 °C again before tributyltin chloride (17.2 mL, 63.3 mmol) was added dropwise within 30 minutes. After the addition the resulting mixture was stirred at 0 °C for 30 minutes and was allowed to warm to RT and kept at the temperature for further 1 hour. The mixture was then diluted with 50 mL of hexane and poured into 100 mL of water and

extracted with Et_2O. The combined organic layers were washed with saturated NH_4C1, water and brine, dried with $MgSO_4$, filtered, concentrated via rotary evaporation and purified by column chromatography on silica gel eluting with petroleum ether to give compound **13** as yellow oil (15.3 g, 90%). ^{1}H NMR (500 Hz, $CDCl_3$): δ (ppm) 7.16 (s, 1H), 6.93 (s, 1H), 2.60 (d, *J* = 6.9 Hz, 2H), 1.69-1.43 (m, 7H), 1.41-1.19 (m, 20H), 0.96-0.84 (m, 15H).

Tributyl(thiophen-2-yl)stannane (14).[S9] Thiophene (6.00 g, 71.31 mmol) in 100 mL of anhydrous THF at -78 ºC was added dropwise 32.8 mL of n-butyllithium (82.01 mmol, 2.5 M) over 1 hour. The resulting solution was stirred at -78 °C for 30 min before tributyltin chloride (22.24 mL, 82.01 mmol) was added dropwisely within 30 minutes. After the addition the resulting mixture was stirred at -78 °C for 30 minutes and was allowed to warm to RT overnight. The mixture was then poured into 100 mL of water and extracted with diethyl ether. The combined organic layer was washed with saturated NH_4C1, water and brine, dried with $MgSO_4$, filtered, concentrated via rotary evaporation and purified by column chromatography on silica gel eluting with petroleum ether to give compound **14** as yellow oil (24.00 g, 90%). ^{1}H NMR (500 Hz, $CDCl_3$): δ (ppm) 7.66 (dd, *J* = 4.7, 0.5 Hz, 1H), 7.27 (dd, *J* = 4.7, 3.2 Hz, 1H), 7.20 (dd, *J* = 3.2, 0.5 Hz, 1H), 1.60-1.53 (m, 6H), 1.38-1.31 (m, 6H), 1.14-1.08 (m, 6H), 0.90 (t, *J* = 7.3 Hz, 9H).

2-Dodecyl-4,7-bis(4-(2-ethylhexyl)thiophen-2-yl)-5,6-dinitro-2H-benzo[d][1,2,3]triazole (15).[S5] Compound **11** (3.00 g, 5.6 mmol), compound **13** (10.10 g, 13.5 mmol) and $Pd[PPh_3]_2Cl_2$ (157 mg ,0.22 mmol) were added into a round bottom flask purged with nitrogen. 80 mL of anhydrous THF was added and the reaction was heated under reflux for 2 days. The mixture was concentrated and extraction was carried out using CH_2Cl_2 and water. The combined organic layer was washed with water and brine, dried with $MgSO_4$, filtered, concentrated via rotary evaporation and purified by column chromatography purified by column chromatography on silica gel eluting with ethyl acetate: petroleum ether (1:20, v/v) to give compound **15** as brown oil (3.48g, 81%). ^{1}H NMR (500 Hz, $CDCl_3$): δ (ppm) 7.30 (s, 2H), 7.22 (s, 2H), 4.80 (t, *J* = 7.2 Hz, 2H), 2.60 (d, *J* = 6.8 Hz, 4H), 2.17-2.11 (m, 2H), 1.57-1.53 (m, 2H), 1.40-1.22 (m, 34H), 0.95-0.86 (m, 15H).

2-Dodecyl-5,6-dinitro-4,7-di(thiophen-2-yl)-2H-benzo[d][1,2,3]triazole (16).[S5] Compound **11** (5.40 g, 10.09 mmol), compound **14** (8.66 g, 23.20 mmol) and $Pd[PPh_3]_2Cl_2$ (450 mg ,0.45 mmol) were added into a round bottom flask purged with nitrogen. 80 mL of anhydrous THF was added and the reaction was heated under reflux for 2 days. The reaction mixture was concentrated and extraction was carried

out using CH_2Cl_2 and water. The combined organic layer was washed with water and brine, dried with $MgSO_4$, filtered, concentrated via rotary evaporation and purified by column chromatography purified by column chromatography on silica gel eluting with ethyl acetate: petroleum ether (1:10, v/v) to give compound **16** as brown solid (3.48g, 81%). ^{1}H NMR (500 Hz, $CDCl_3$): δ (ppm) 7.67 (dd, J = 5.1, 1.1 Hz, 2H), 7.53 (dd, J = 3.7, 1.1 Hz, 2H), 7.21 (dd, J = 5.1, 3.7 Hz, 2H), 4.81 (t, J = 7.3 Hz, 2H), 2.17-2.10 (m, 2H), 1.41-1.20 (m, 18H), 0.87 (t, J = 7.0 Hz, 3H).

1,2-Bis(dodecyloxy)benzene (17).[S10] NaOH (13.62 g, 340.57 mmol) was added to a solution catechol (15 g, 136.23 mmol) in 150 mL of EtOH. After stirring at 60 °C for 30 minutes, 82 mL of 1-bromododecane (340.57 mmol) was added dropwise into the reaction mixture and the reaction mixture was stirred at 60 °C overnight. After cooling down to RT, EtOH was removed on a rotary evaporator and the residue was extracted with CH_2Cl_2 and water. The organic layer was washed with water and brine, dried with $MgSO_4$, filtered, concentrated via rotary evaporation. The residue was washed with MeOH and dried to give **17** as a white solid (37.50 g, 62%). ^{1}H NMR (500 Hz, $CDCl_3$): δ (ppm) 6.89 (s, 4H), 3.99 (t, J = 6.7 Hz, 2H), 1.85-1.77 (m, 4H), 1.50-1.43 (m, 4H), 1.38-1.23 (m, 32H), 0.88 (t, J = 7.0 Hz, 6H).

1,2-Bis(3,4-bis(dodecyloxy)phenyl)ethane-1,2-dione (18).[S11] 1.93 mL of oxalyl chloride (2.90 g, 22.83 mmol) was added dropwise to the mixture of compound **17** (17.00 g, 38.05 mmol) in 100 mL of anhydrous CH_2Cl_2 by a microsyringe at 0 °C. The reaction mixture was kept at 0 °C for 10 min, and then aluminum chloride (2.54 g, 19.03 mmol) was added. After 30 min at 0 °C, the mixture was warmed gently to RT overnight. The reaction mixture was then poured into 100 mL of HCl solution (1 M). The organic layer was washed with water and brine, dried with $MgSO_4$, filtered, concentrated via rotary evaporation and purified by column chromatography on silica gel eluting with CH_2Cl_2 to give pure product compound **18** as a pale yellow solid (12.00 g, 12.6 mmol, 67%). ^{1}H NMR (500 Hz, $CDCl_3$): δ (ppm) 7.57 (d, J = 2.0 Hz, 2H), 7.43 (dd, J = 8.4, 2.0 Hz, 2H), 6.84 (d, J = 8.4 Hz, 2H), 4.08-4.03 (m, 8H), 1.87-1.80 (m, 8H), 1.50-1.43 (m, 8H), 1.34-1.21 (m, 64H), 0.90-0.86 (m, 12H).

2-Dodecyl-4,7-bis(4-(2-ethylhexyl)thiophen-2-yl)-2H-benzo[d][1,2,3]triazole-5, 6-diamine (19).[S5] Compound **15** (3.48 g, 4.54 mmol), iron powder (5.07 g, 90.85 mmol) and 100 mL of acetic acid were added into a round bottom flask purged with nitrogen. The mixture was stirred at 70 °C overnight, after which was allowed to cool to RT, poured into 200 mL of water and extracted using CH_2Cl_2. The organic layer was washed with water and brine, dried with $MgSO_4$, filtered, concentrated via rotary evaporation and purified by column chromatography on silica gel eluting with ethyl

acetate: petroleum ether (1:20, v/v) to give compound **19** as brown oil (2.64 g, 82%). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.24 (d, J = 1.3 Hz, 2H), 7.05 (s, 2H), 4.58 (t, J = 7.4 Hz, 2H), 4.20 (br, 4H), 2.63 (d, J = 6.8 Hz, 4H), 2.07-2.00 (m, 2H), 1.66-1.58 (m, 2H), 1.41-1.20 (m, 36H), 0.94-0.86 (m, 15H).

2-Dodecyl-4,7-di(thiophen-2-yl)-2H-benzo[d][1,2,3]triazole-5,6-diamine (20).[S5] Compound **16** (3.72 g, 6.87 mmol), iron powder (7.67 g, 137.35 mmol) and 100 mL of acetic acid were added into a round bottom flask purged with nitrogen. The reaction was stirred at 70 °C overnight, after which was allowed to cool to RT, poured into 200 mL of water and extracted using CH_2Cl_2. The organic layer was washed with water and brine, dried with $MgSO_4$, filtered, concentrated via rotary evaporation and purified by column chromatography on silica gel eluting with ethyl acetate: petroleum ether (1:20, v/v) to give compound **20** as brown solid (2.47 g, 5.13 mmol, 75%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50 (dd, J = 5.2, 1.1 Hz, 2H), 7.44 (dd, J = 3.5, 1.1 Hz, 2H), 7.23 (dd, J = 5.2, 3.5 Hz, 2H), 4.60-4.55 (m, 2H), 4.19 (s, 4H), 2.02 (dd, J = 14.7, 7.6 Hz, 2H), 1.37-1.19 (m, 24H), 0.87 (t, J = 7.0 Hz, 3H).

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2. NMR Spectra of intermediates

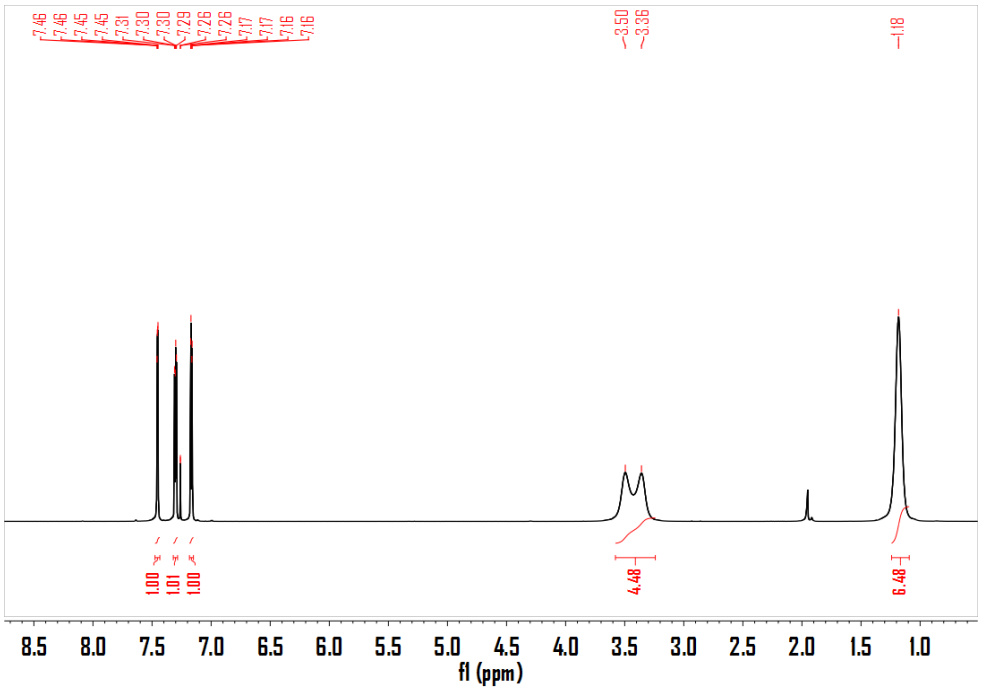


Fig. S1 ^{1}H NMR spectrum of **2**

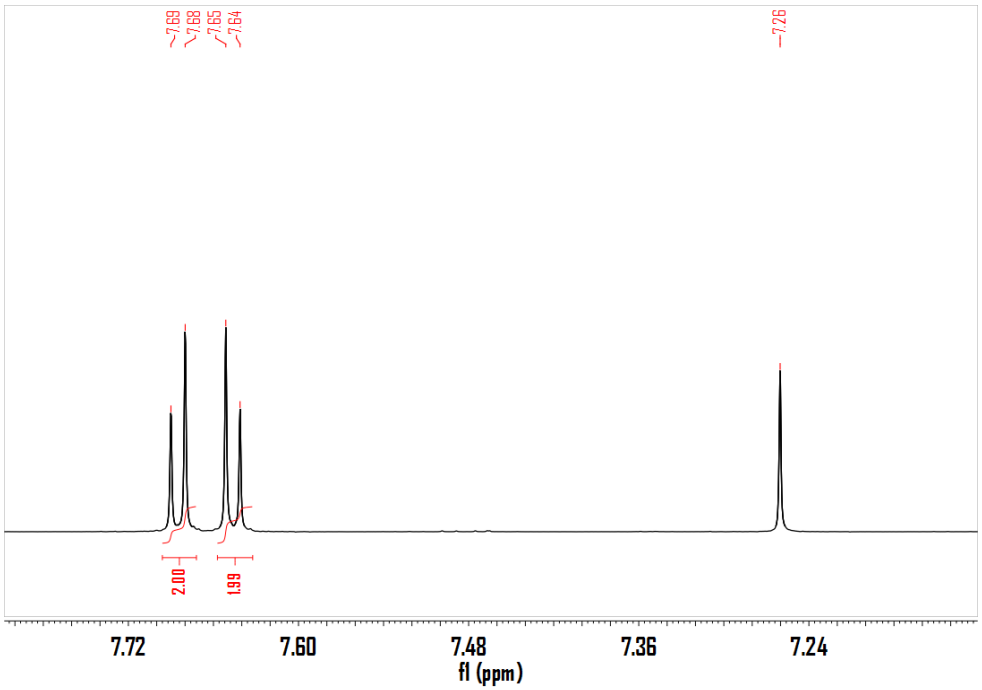


Fig. S2 ^{1}H NMR spectrum of **3**

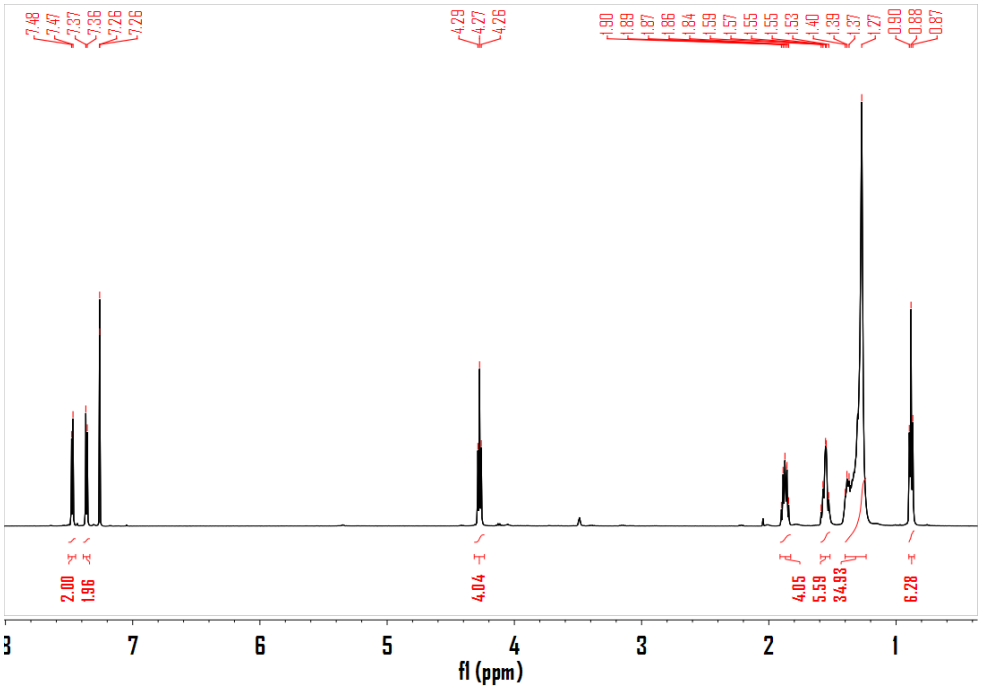


Fig. S3 ^{1}H NMR spectrum of **4**

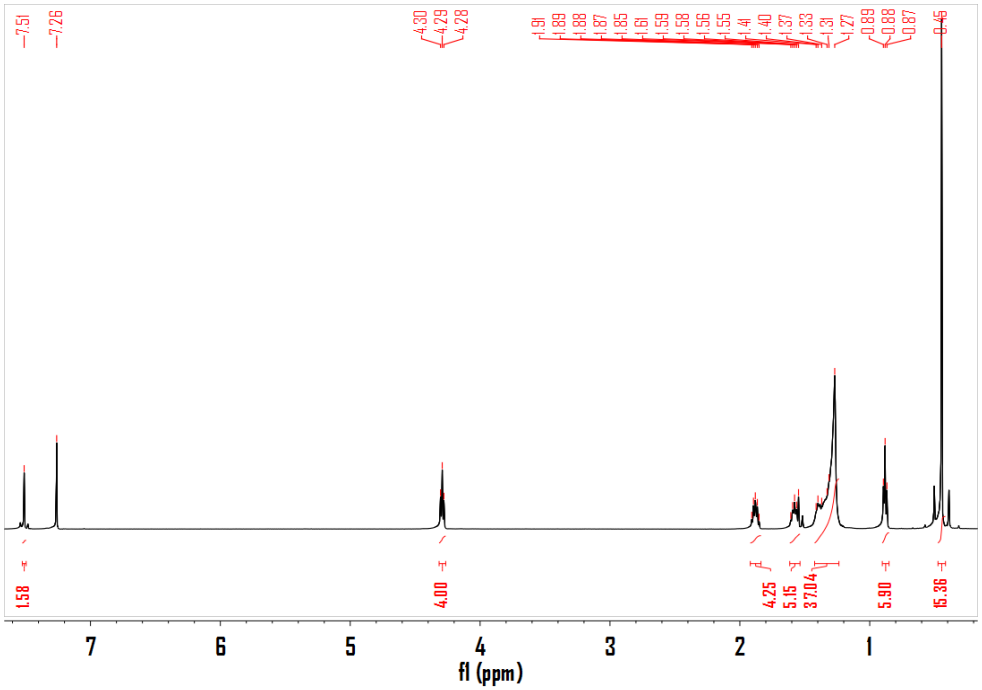


Fig. S4 ^{1}H NMR spectrum of **5**

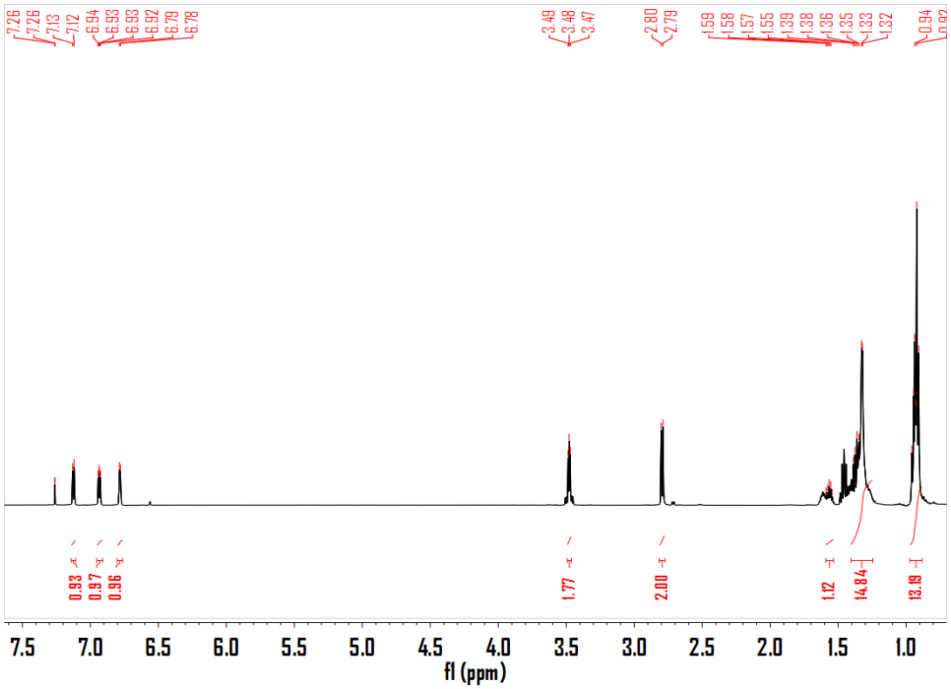


Fig. S5 ^{1}H NMR spectrum of **6**

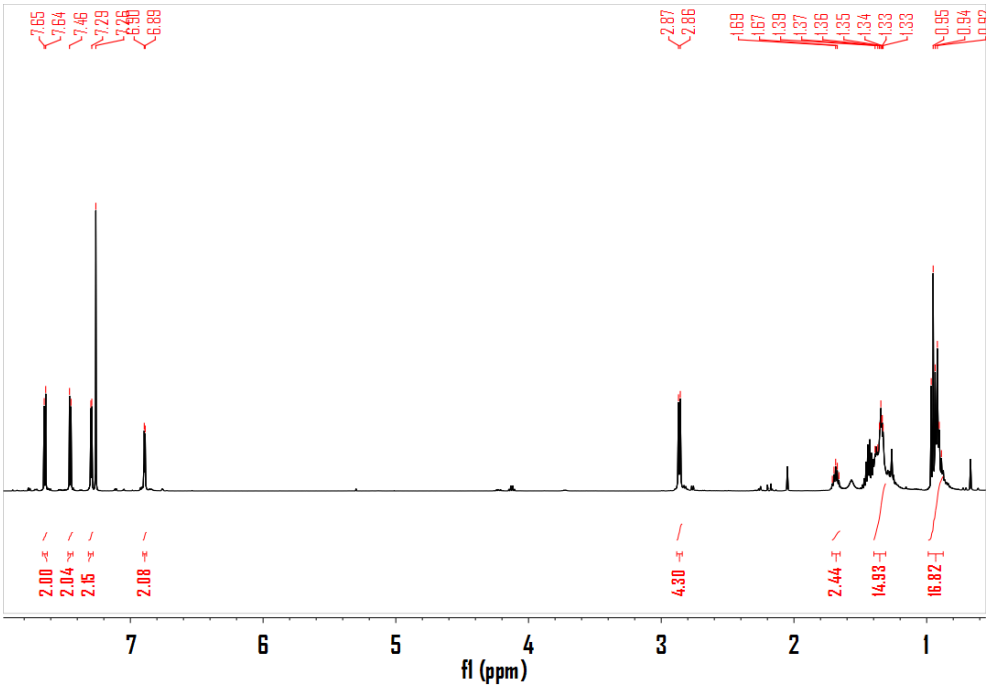


Fig. S6 ^{1}H NMR spectrum of **7**

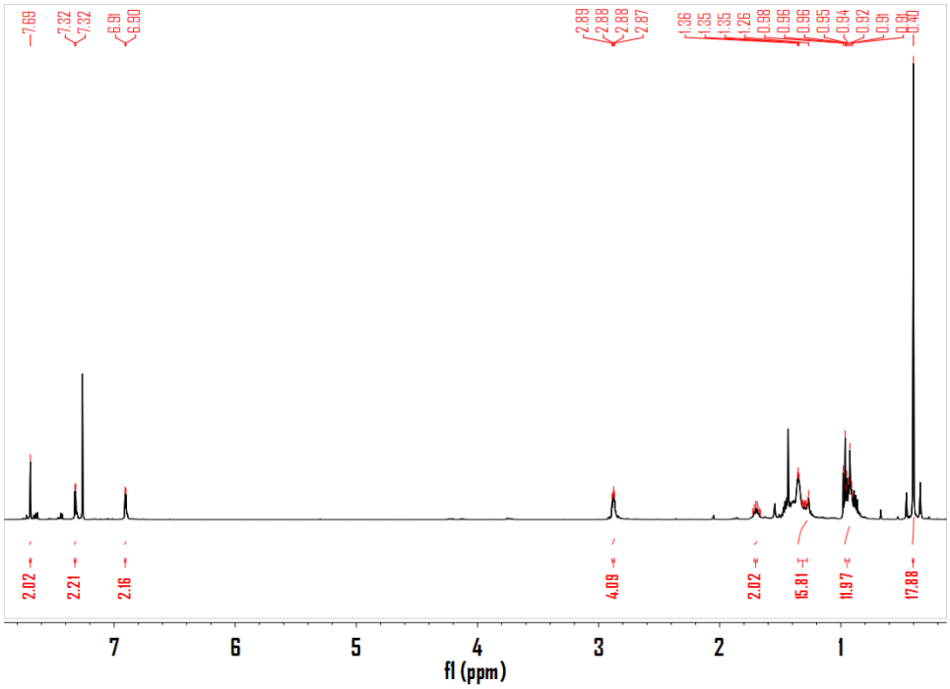


Fig. S7 ^{1}H NMR spectrum of **8**

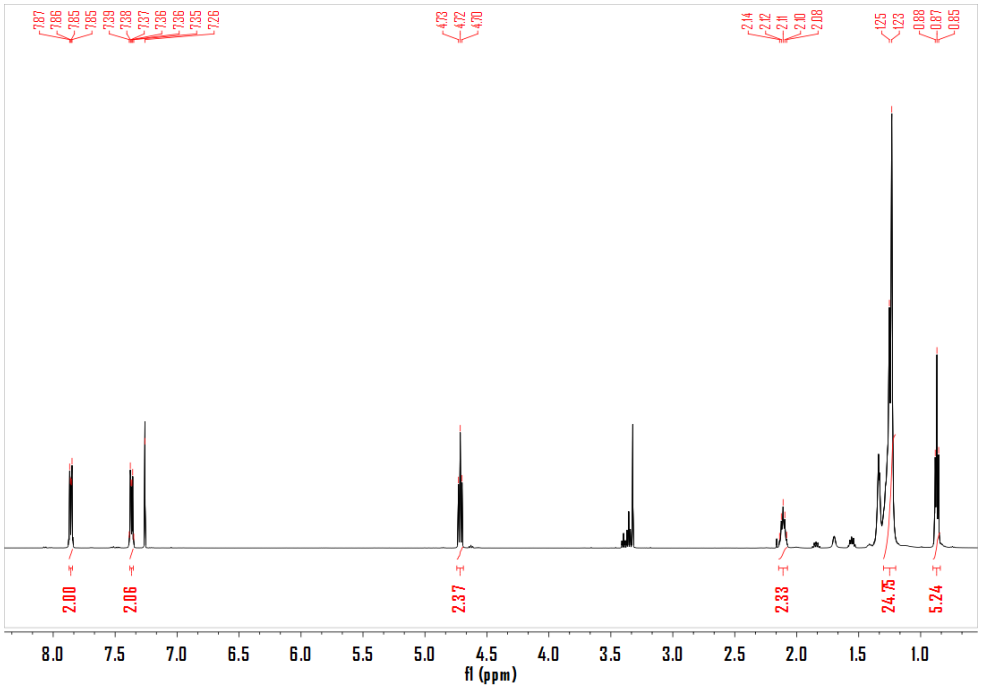


Fig. S8 ^{1}H NMR spectrum of **9**

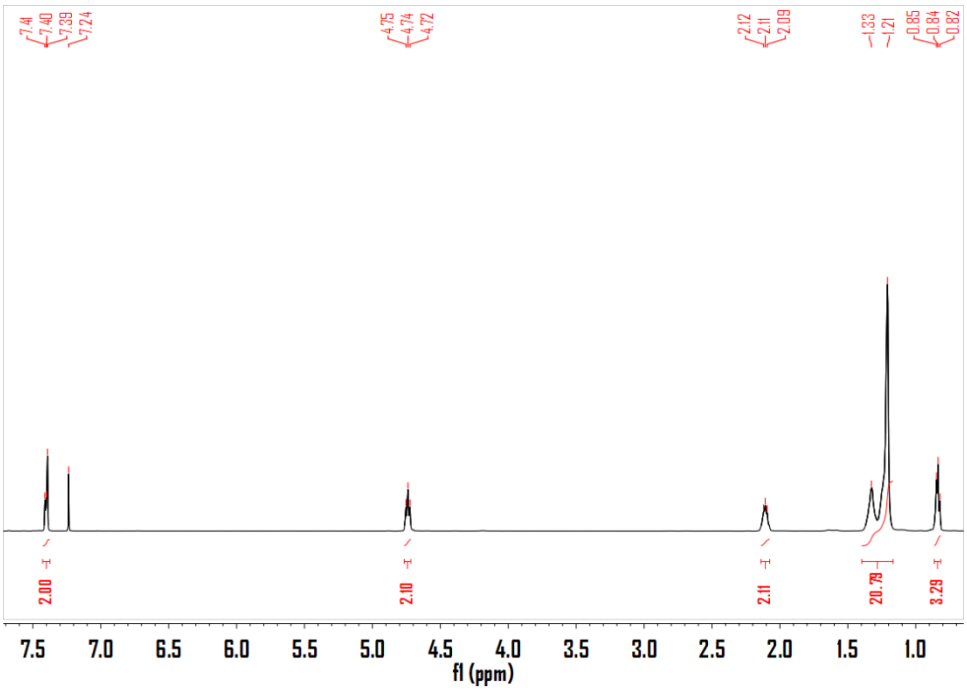


Fig. S9 ^{1}H NMR spectrum of **10**

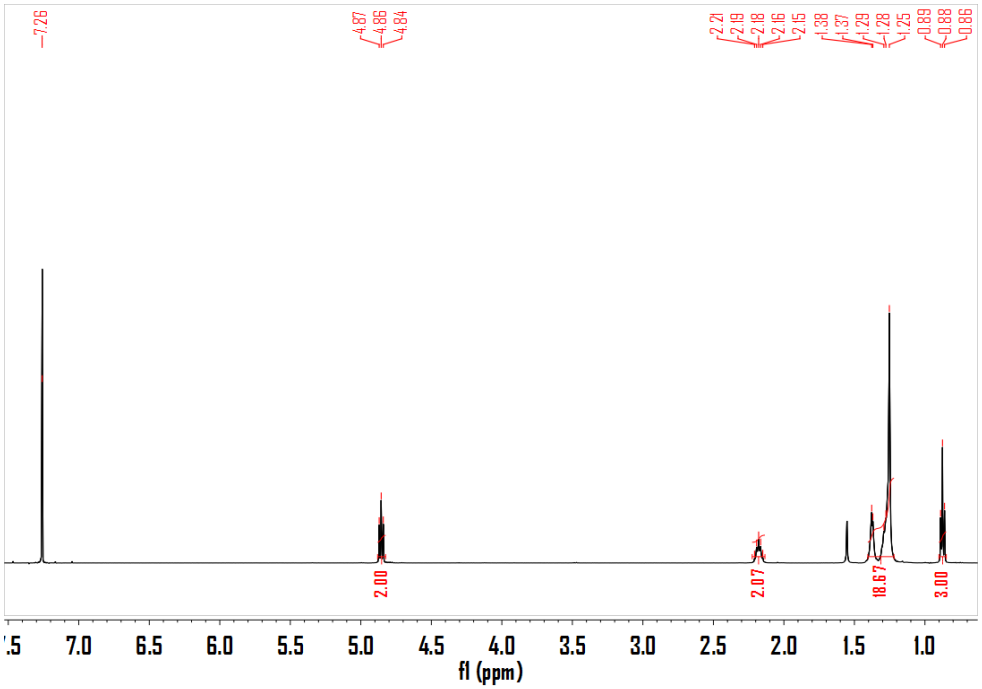


Fig. S10 ^{1}H NMR spectrum of **11**

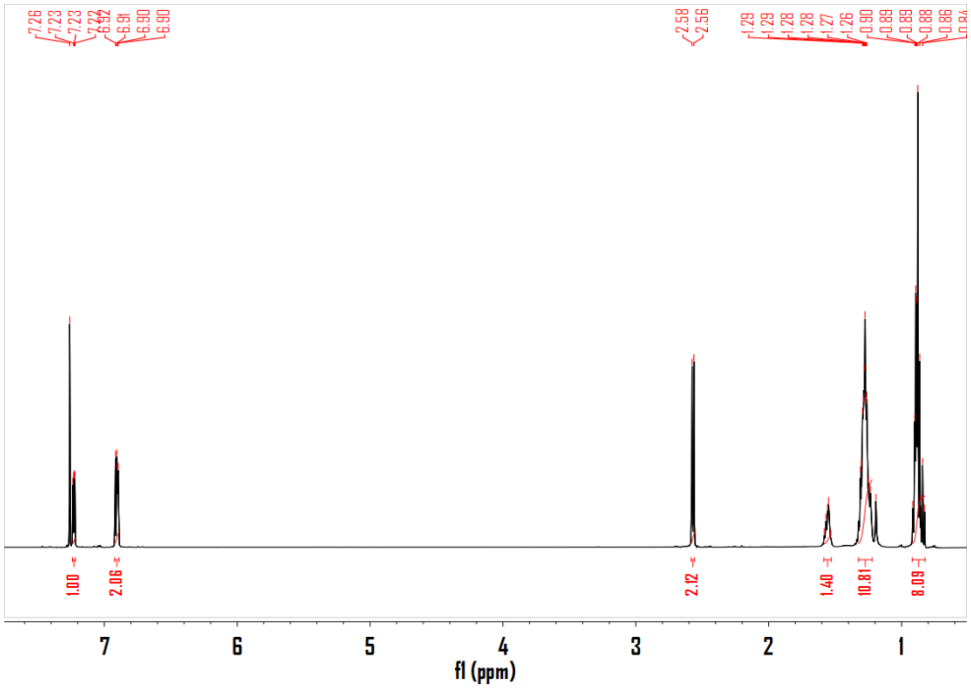


Fig. S11 ^{1}H NMR spectrum of **12**

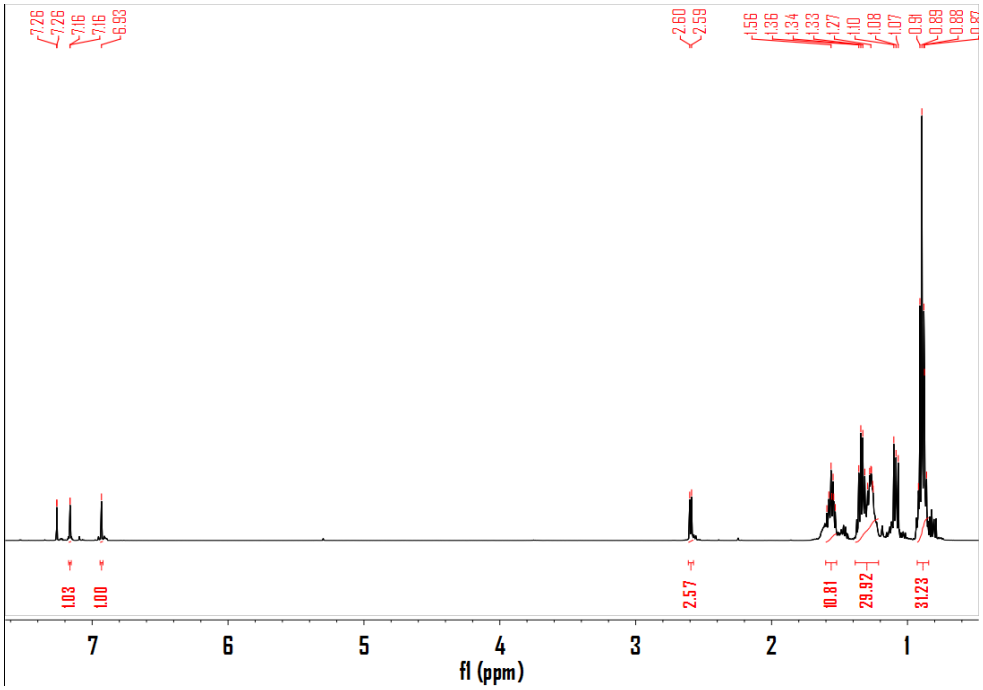


Fig. S12 ^{1}H NMR spectrum of **13**

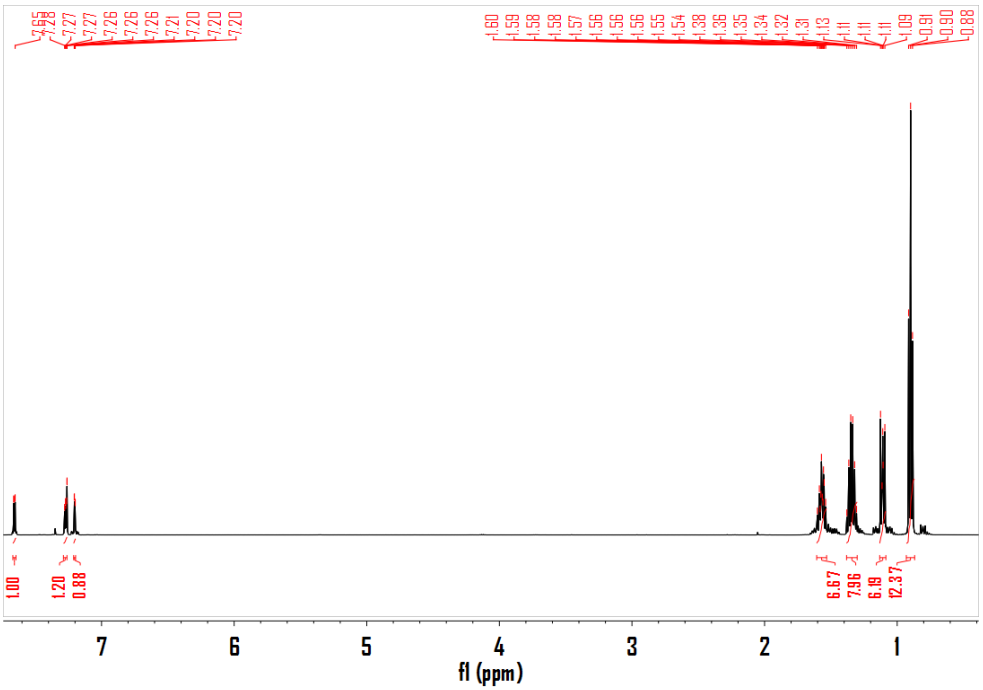


Fig. S13 ^{1}H NMR spectrum of **14**

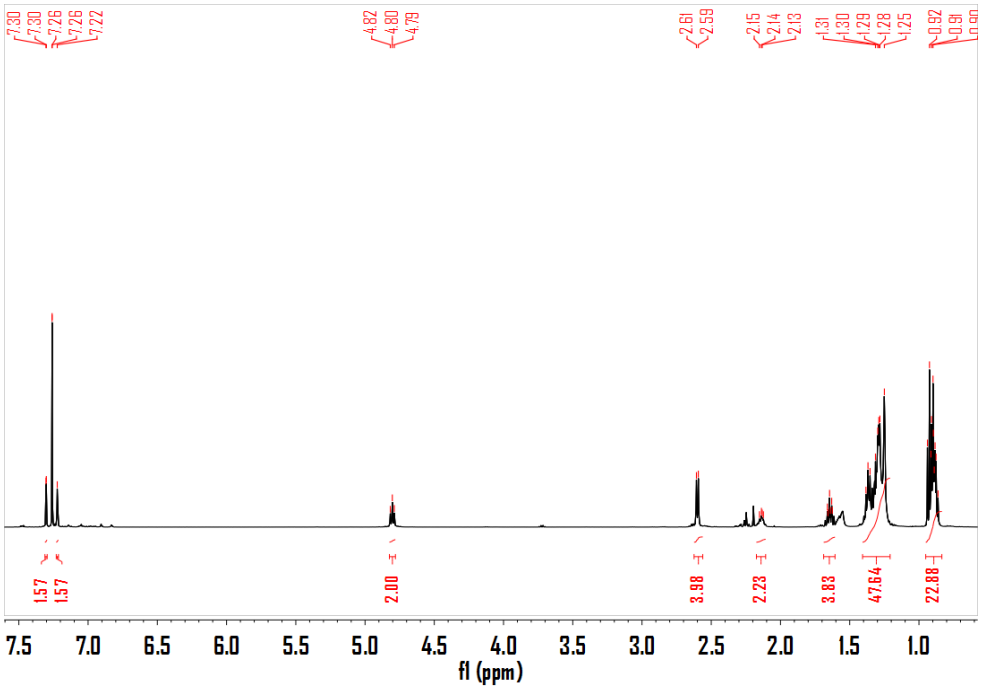


Fig. S14 ^{1}H NMR spectrum of **15**

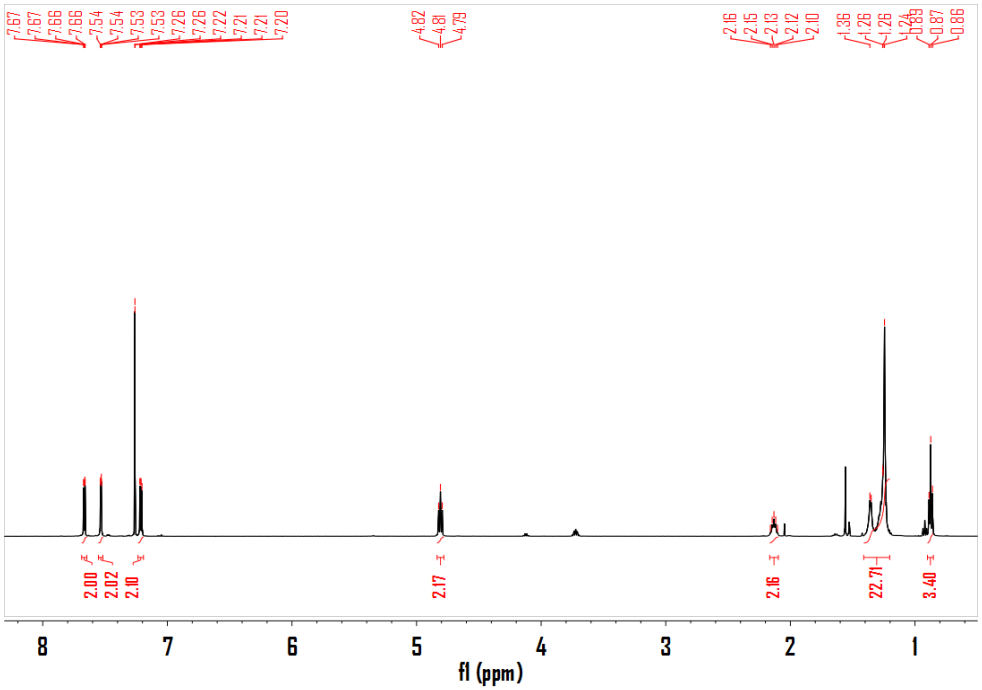


Fig. S15 ^{1}H NMR spectrum of **16**

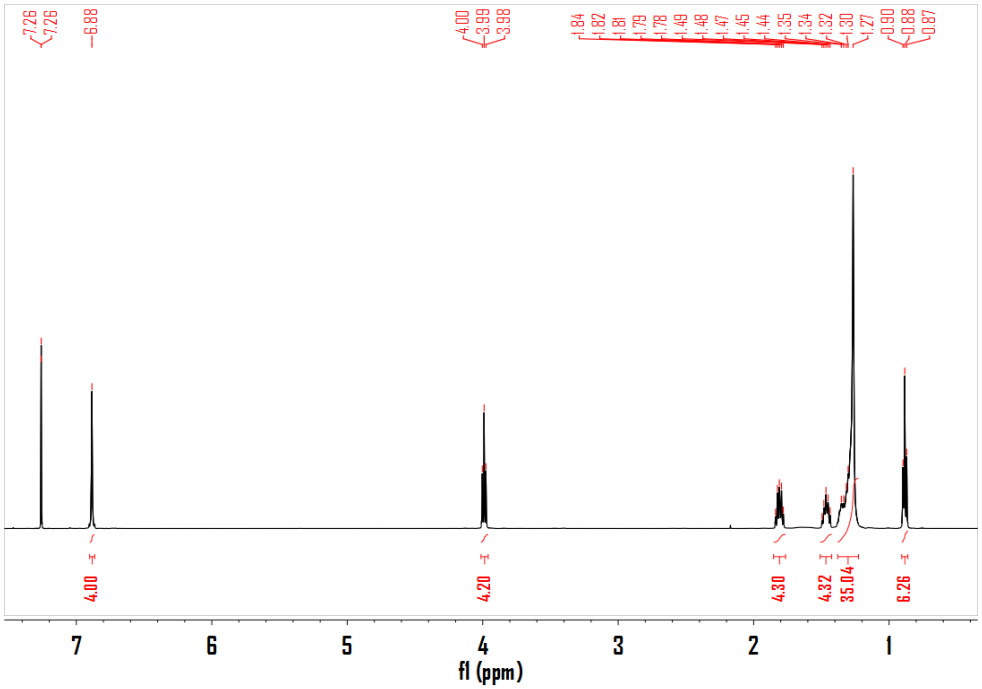


Fig. S16 ^{1}H NMR spectrum of **17**

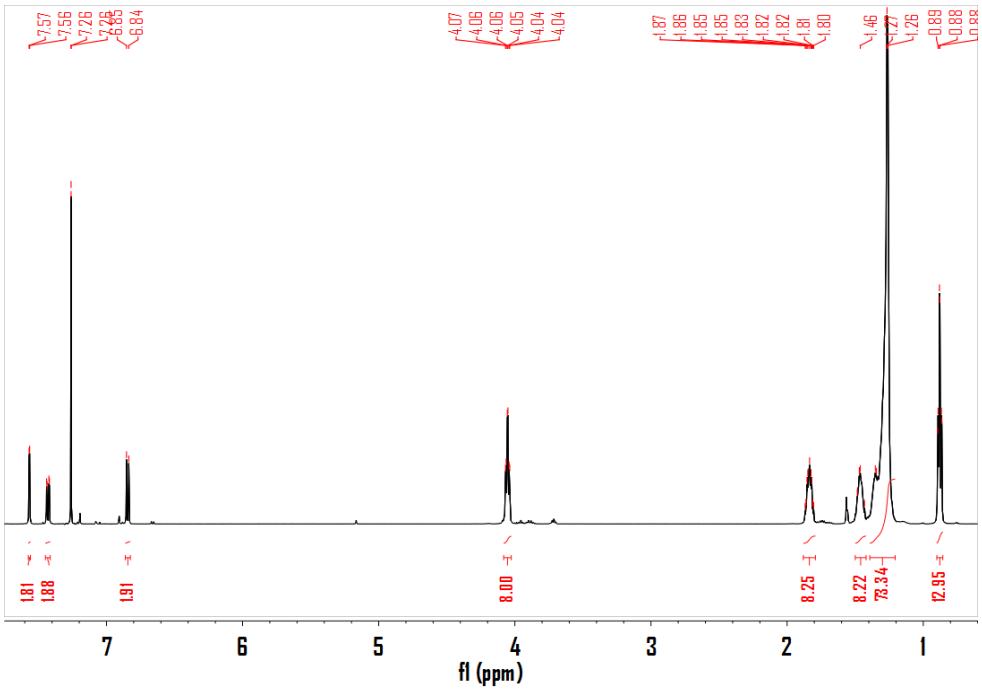


Fig. S16 ^{1}H NMR spectrum of **18**

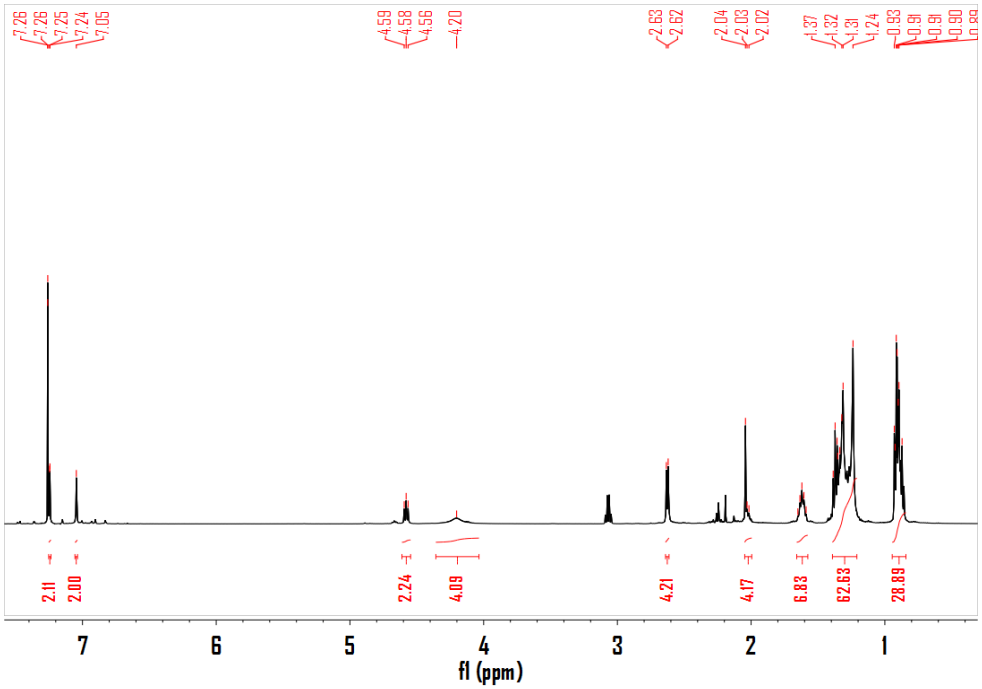


Fig. S18 ^{1}H NMR spectrum of **19**

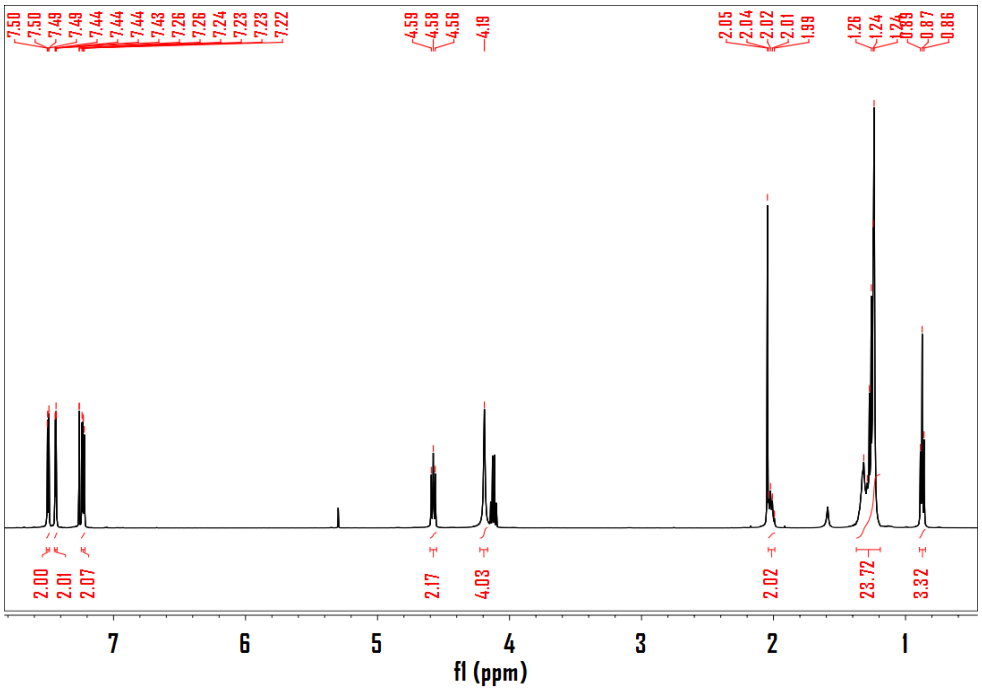


Fig. S19 ^{1}H NMR spectrum of **20**

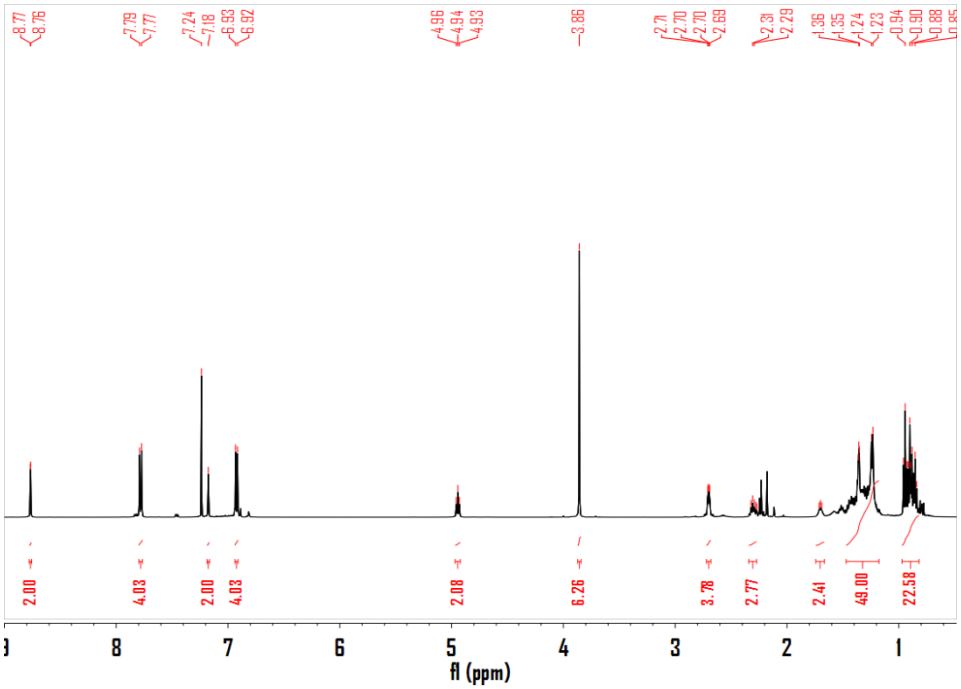


Fig. S20 ^{1}H NMR spectrum of **21**

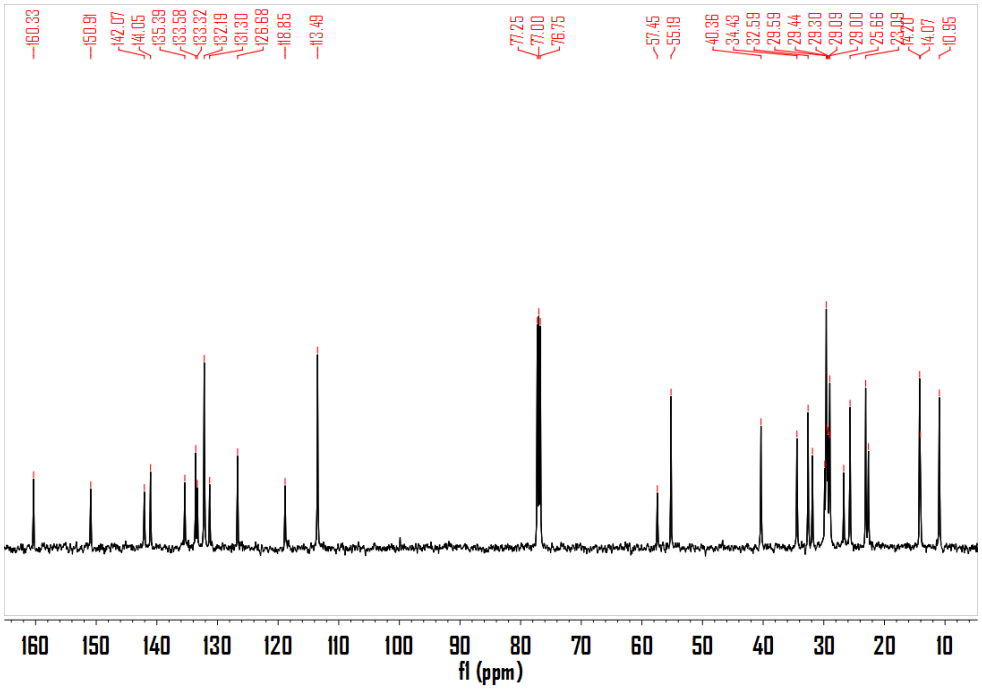


Fig. S21 ^{13}C NMR spectrum of **21**

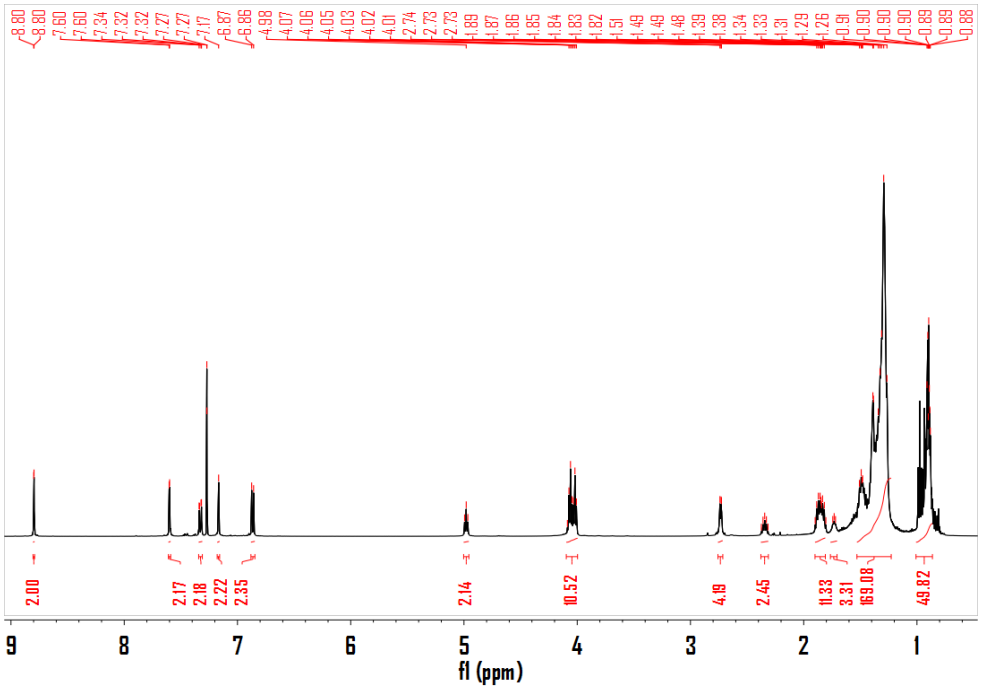


Fig. S22 ^{1}H NMR spectrum of **22**

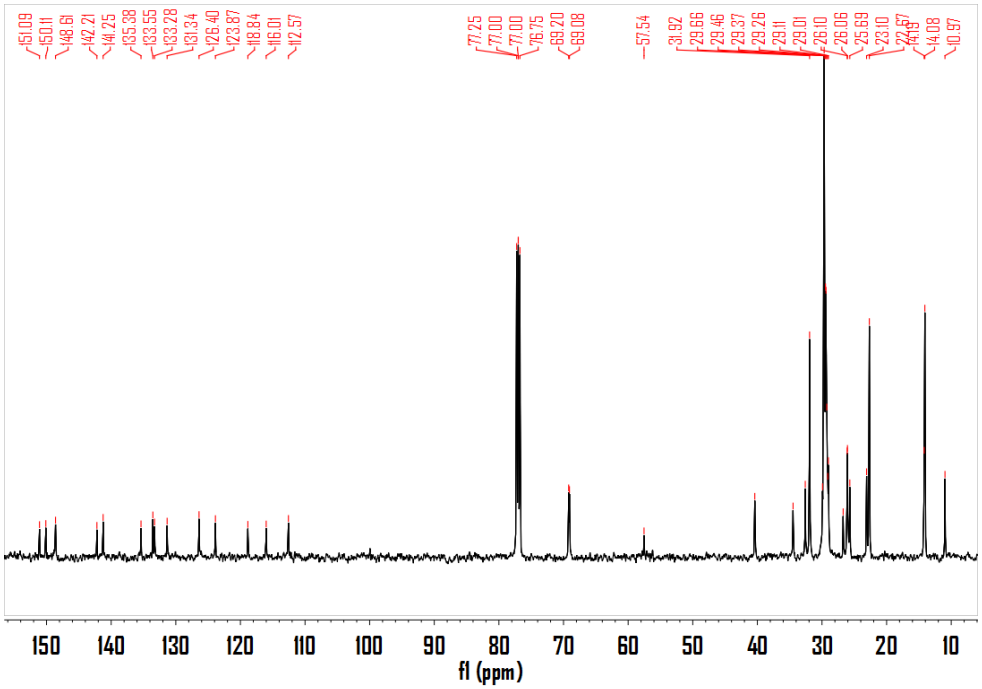


Fig. S23 ^{13}C NMR spectrum of **22**

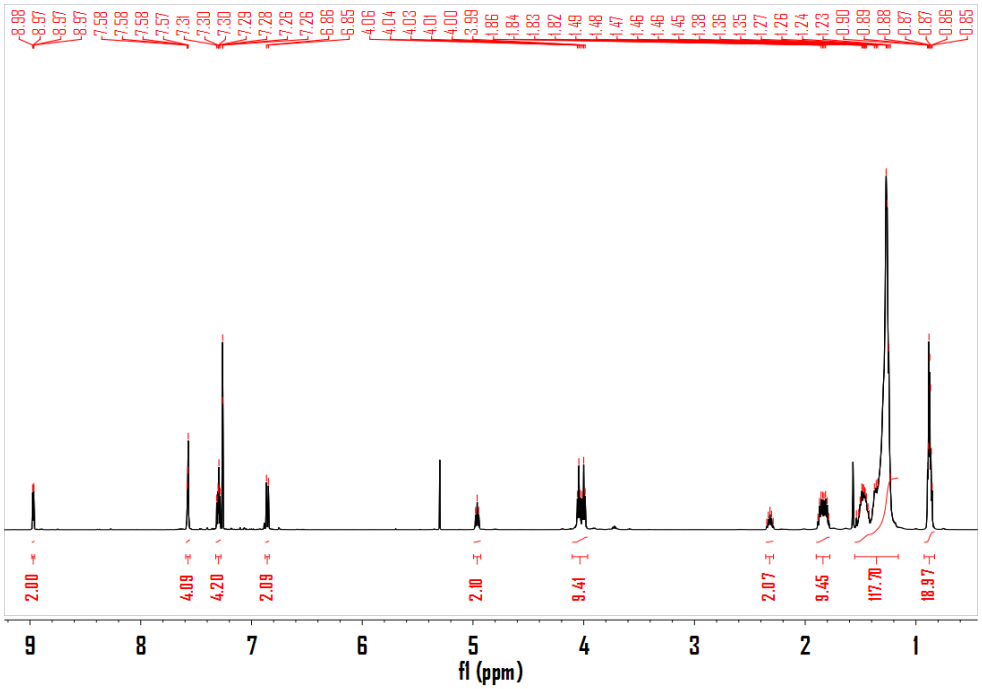


Fig. S24 ^{1}H NMR spectrum of **23**

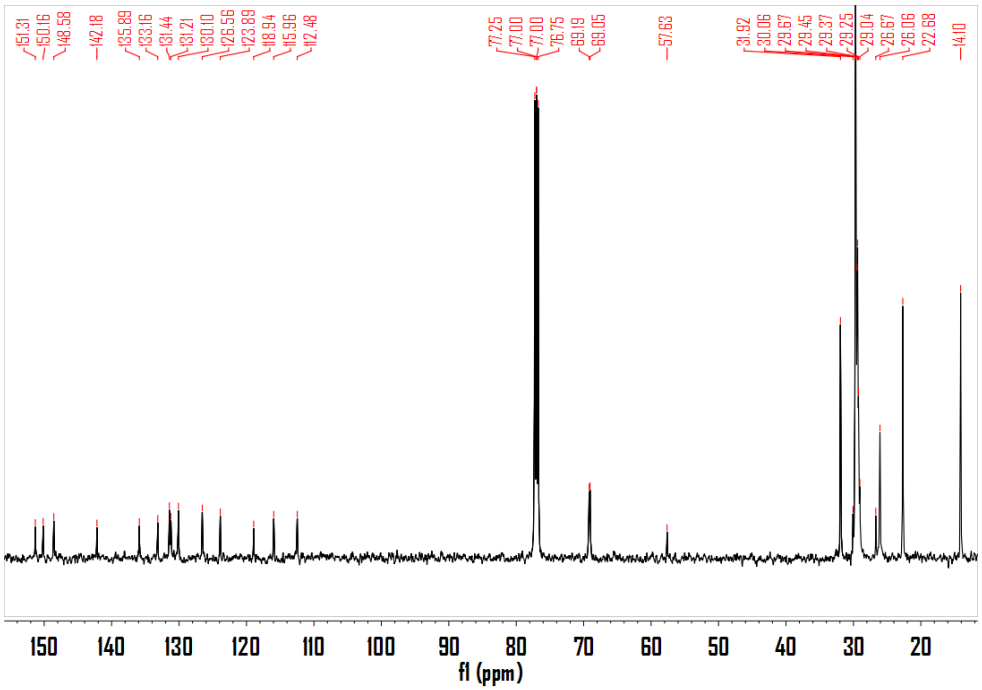


Fig. S25 ^{13}C NMR spectrum of **23**

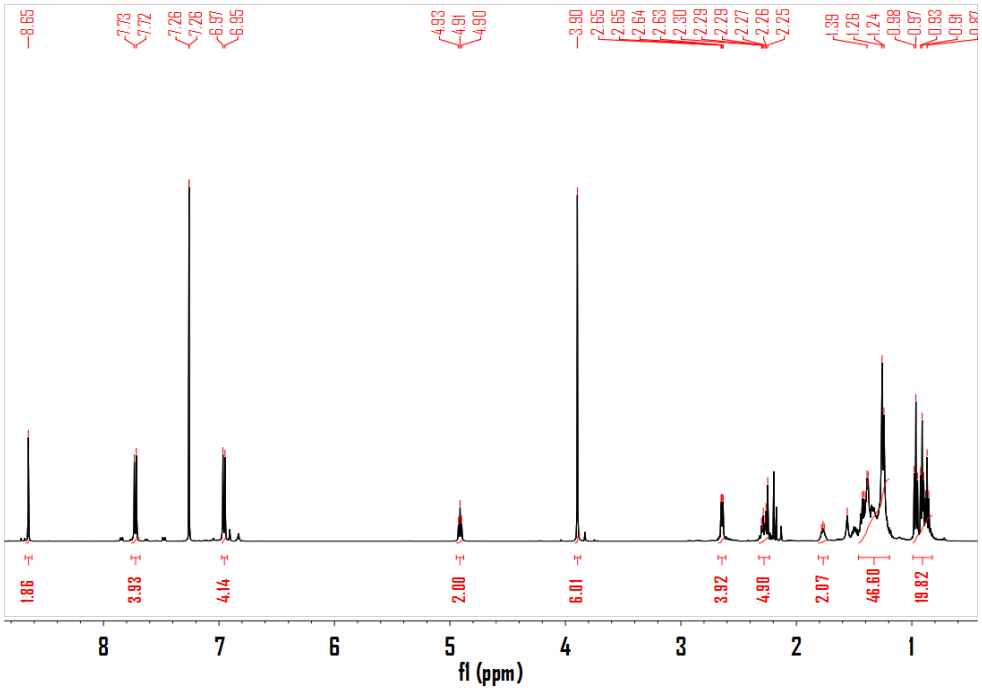


Fig. S26 ^{1}H NMR spectrum of **24**

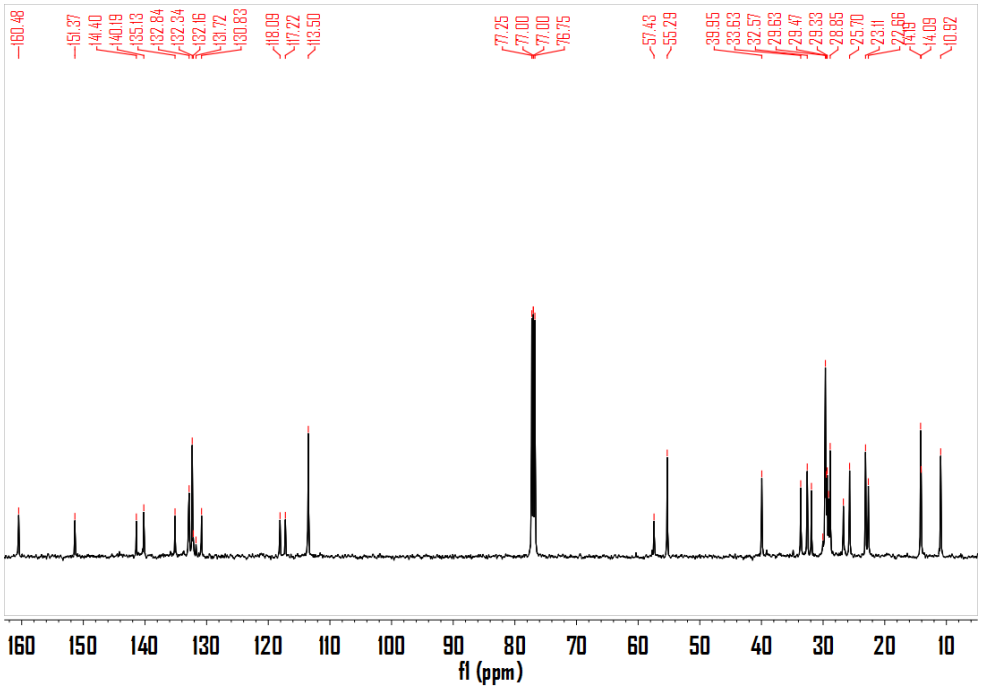


Fig. S27 ^{13}C NMR spectrum of **24**

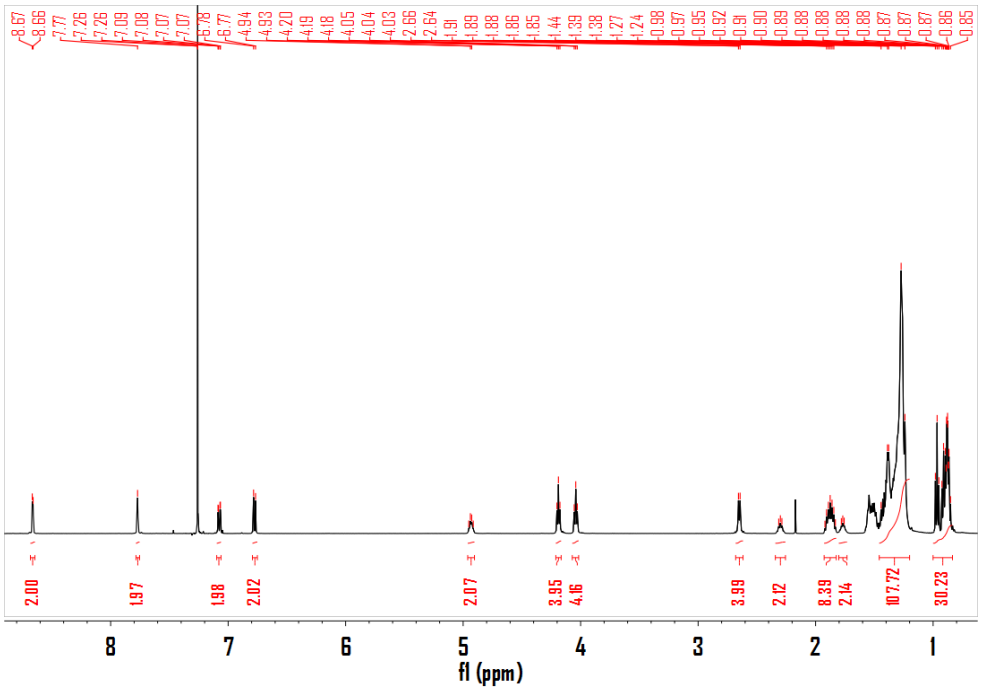


Fig. S28 ^{1}H NMR spectrum of **25**

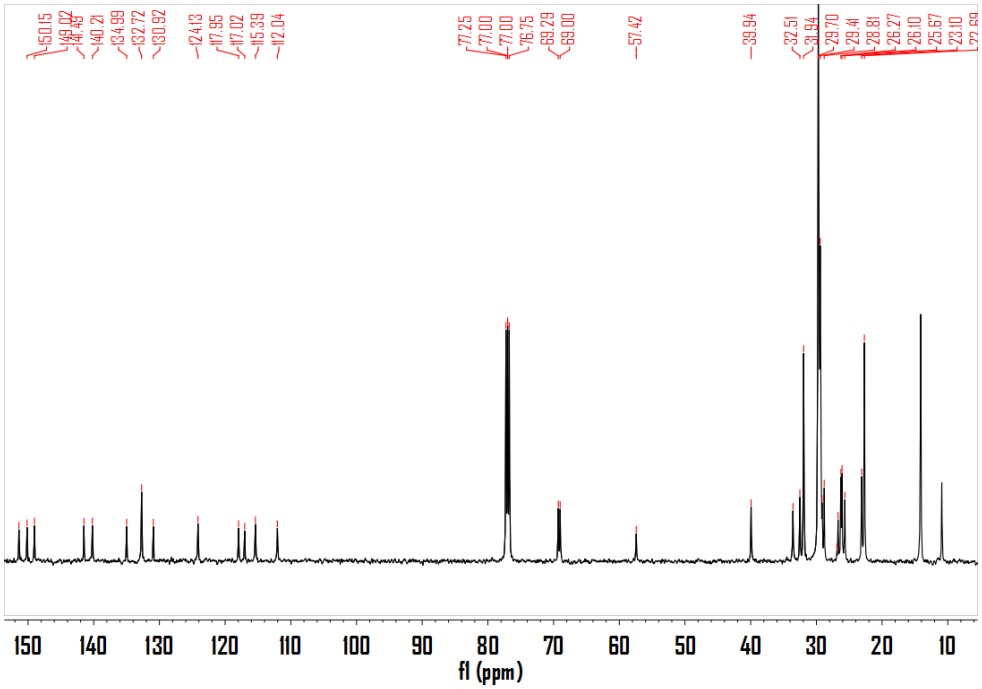


Fig. S29 ^{13}C NMR spectrum of **25**

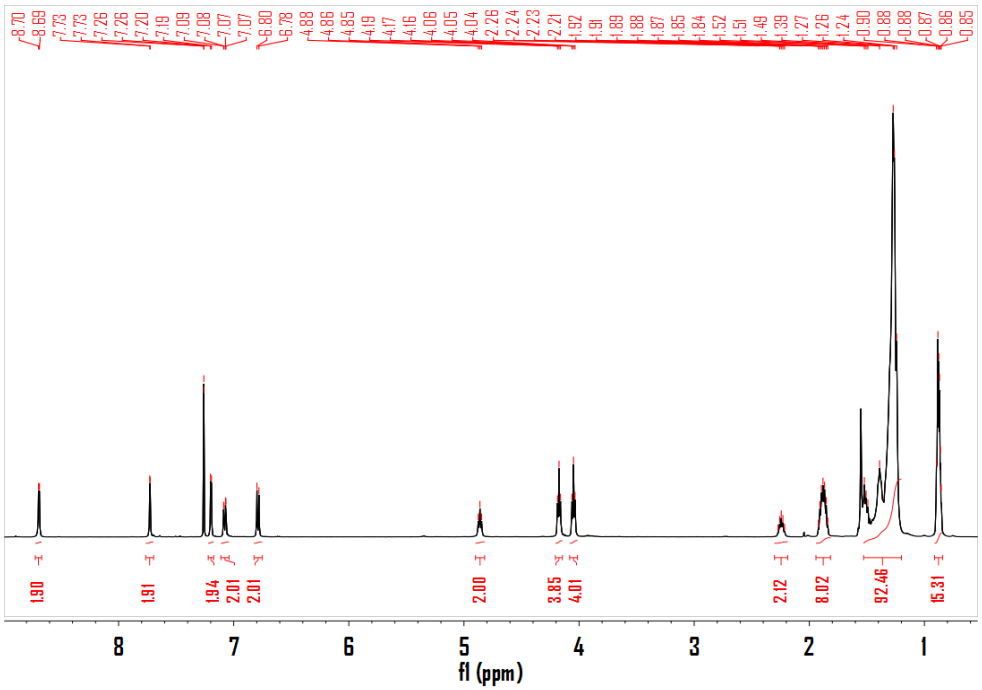


Fig. S30 ^{1}H NMR spectrum of **26**

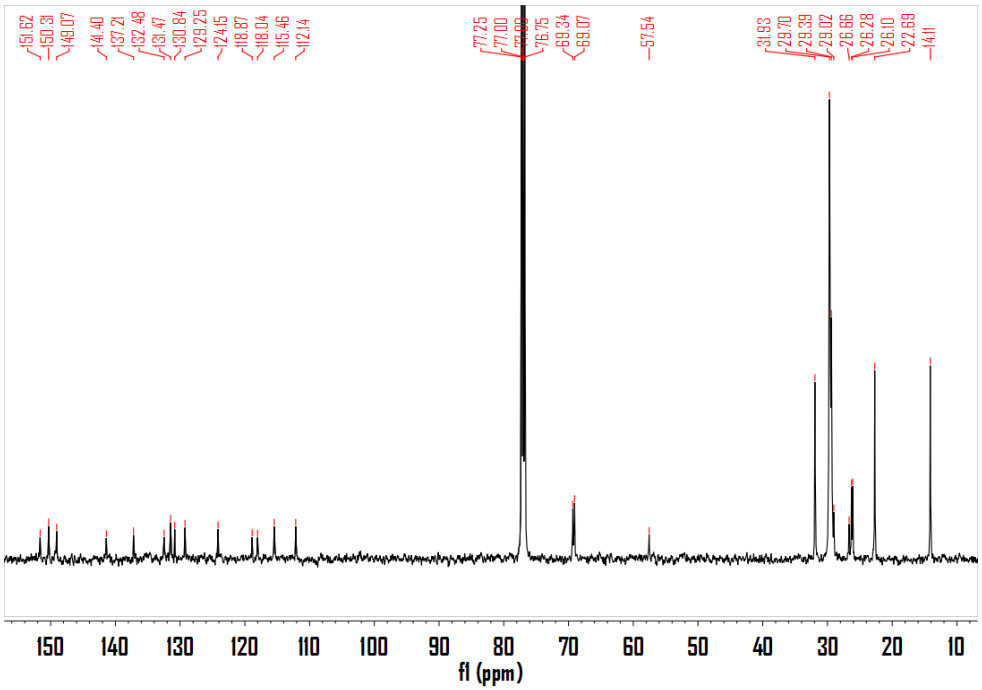
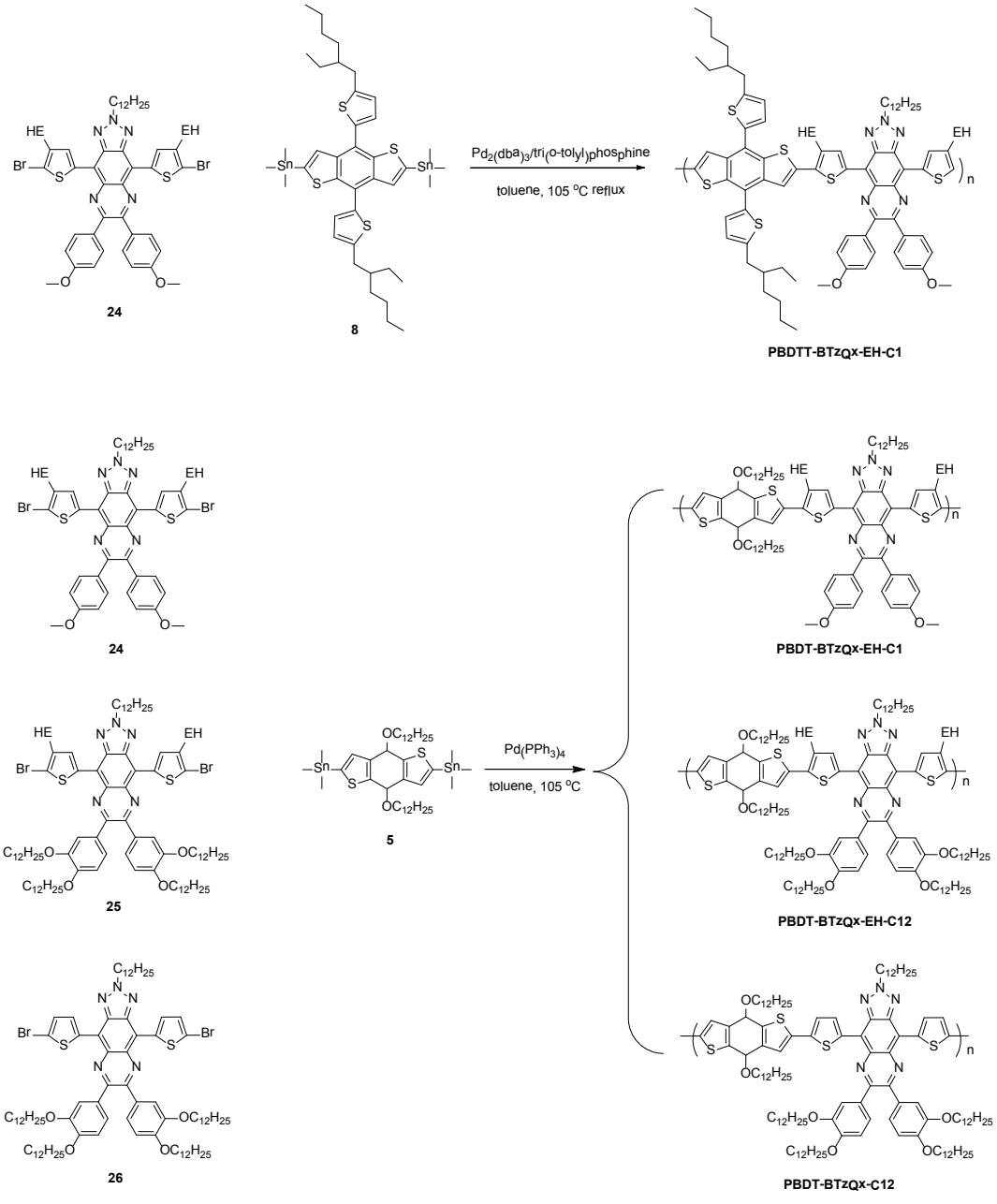


Fig. S31 ^{13}C NMR spectrum of **26**

3. General Procedures for Stille Coupling reaction

PBDTT-BTzQx-EH-C1, PBDT-BTzQx-EH-C1, PBDT-BTzQx-EH-C12, PBDT-BTzQx-C12 were prepared by coupling compound **24**, **25** or **26** with the corresponding bis(trimethylstannyl)-substituted BDT monomer by the same procedure.



4. NMR Spectra of copolymers

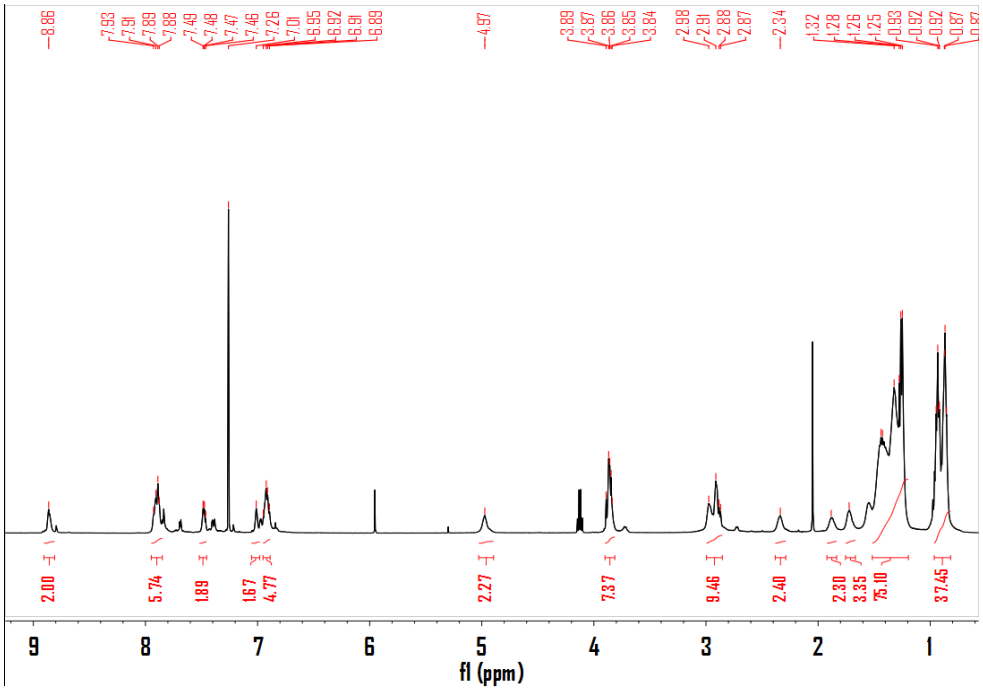


Fig. S32 ^{1}H NMR spectrum of **PBDTT-BTzQx-EH-C1**

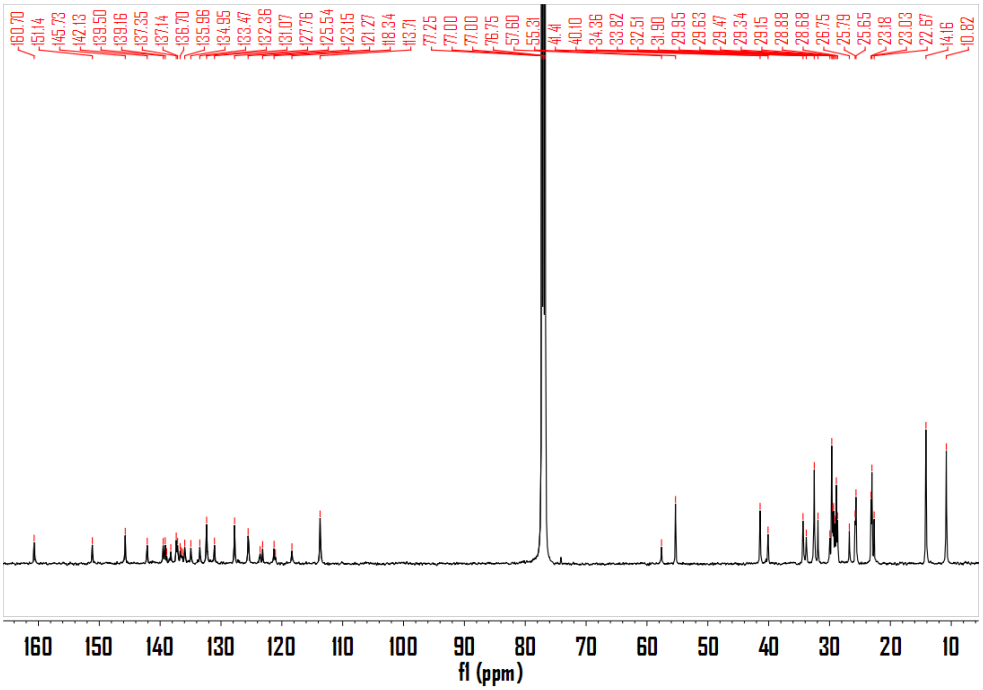


Fig. S33 ^{13}C NMR spectrum of **PBDTT-BTzQx-EH-C1**

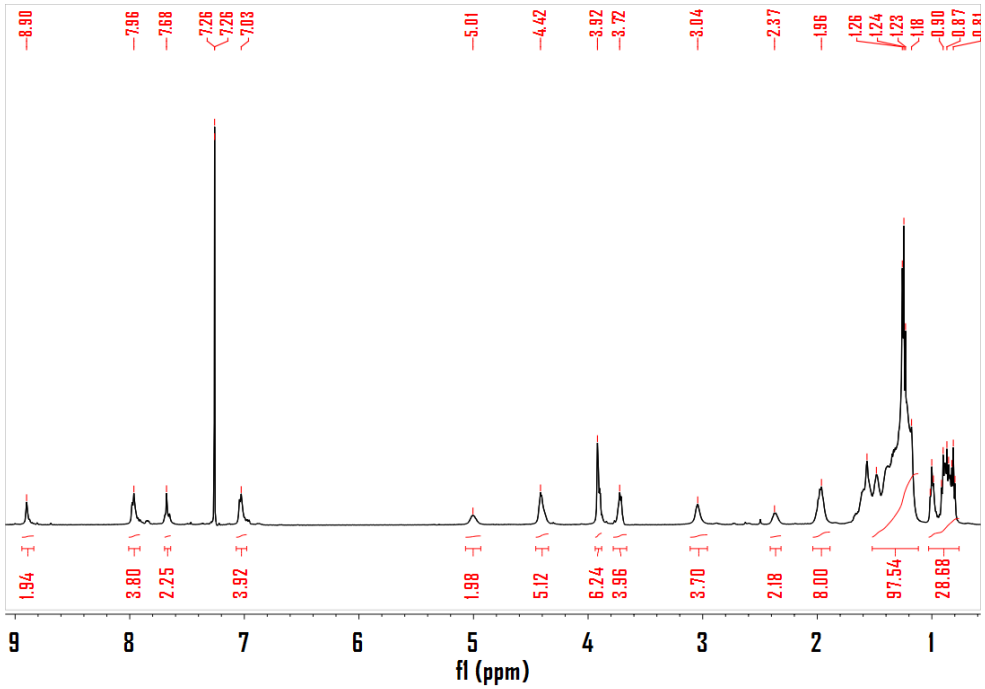


Fig. S34 ^{1}H NMR spectrum of **PBDT-BTzQx-EH-C1**

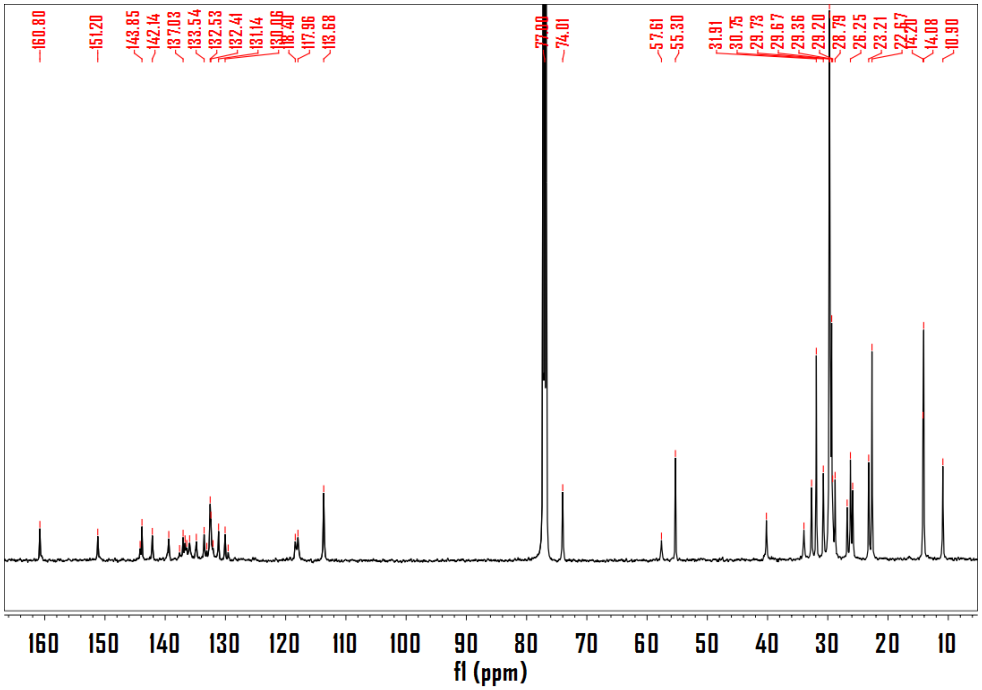


Fig. S35 ^{13}C NMR spectrum of **PBDT-BTzQx-EH-C1**

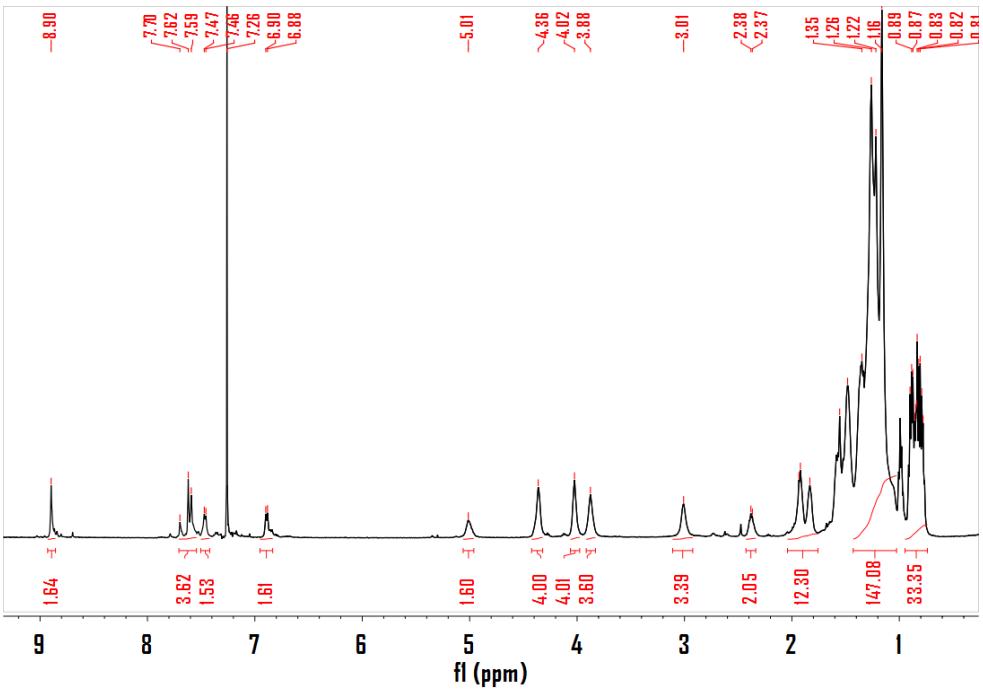


Fig. S36 ^{1}H NMR spectrum of **PBDT-BTzQx-EH-C12**

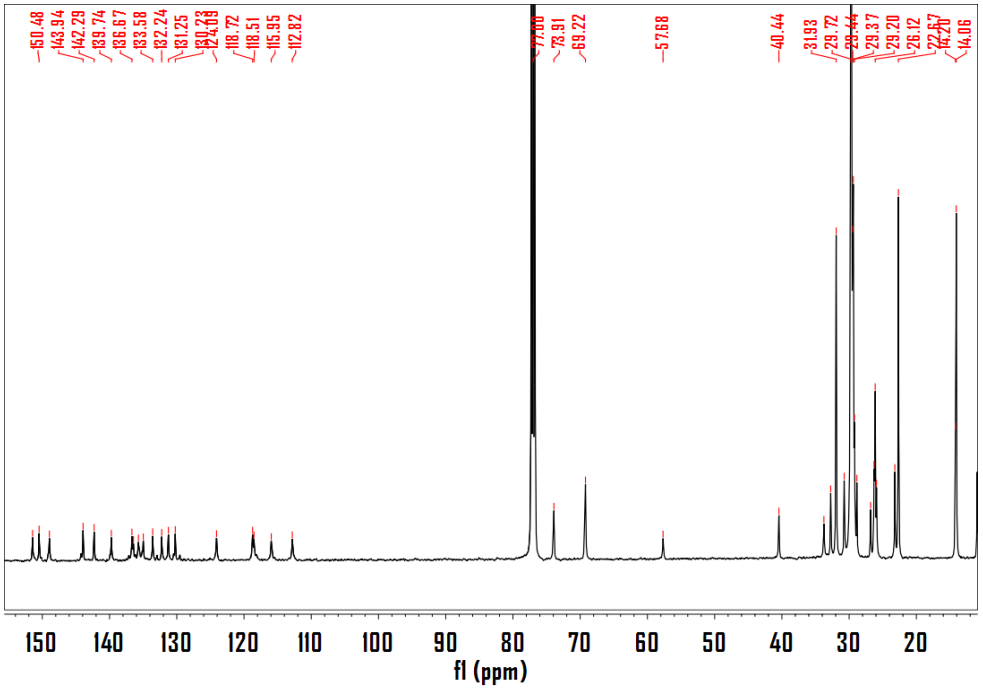


Fig. S37 ^{13}C NMR spectrum of **PBDT-BTzQx-EH-C12**

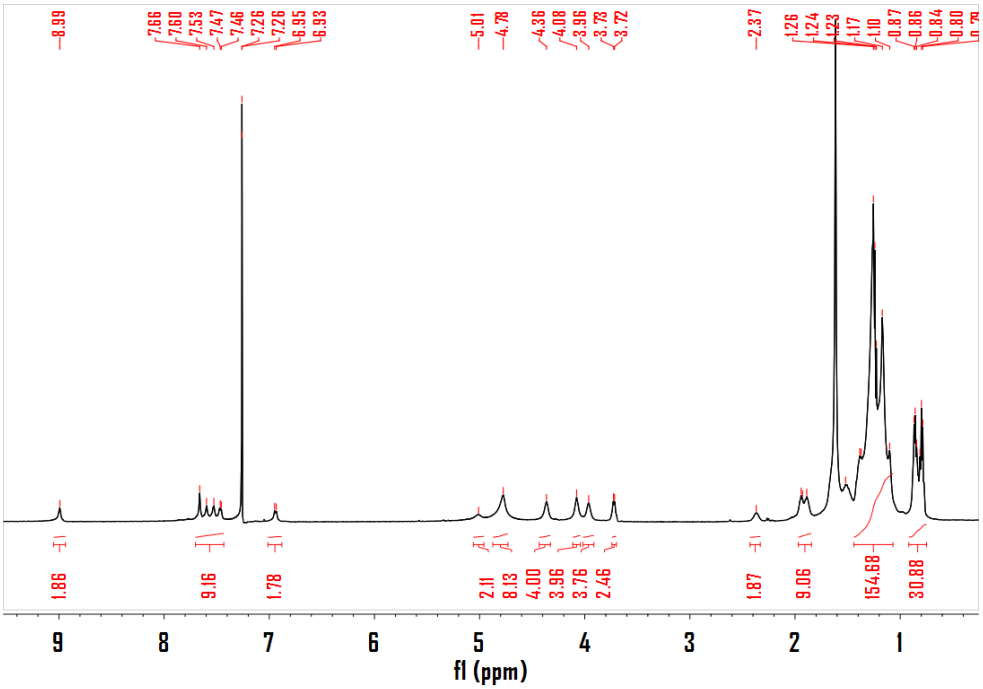


Fig. S38 ^{1}H NMR spectrum of **PBDT-BTzQx-C12**

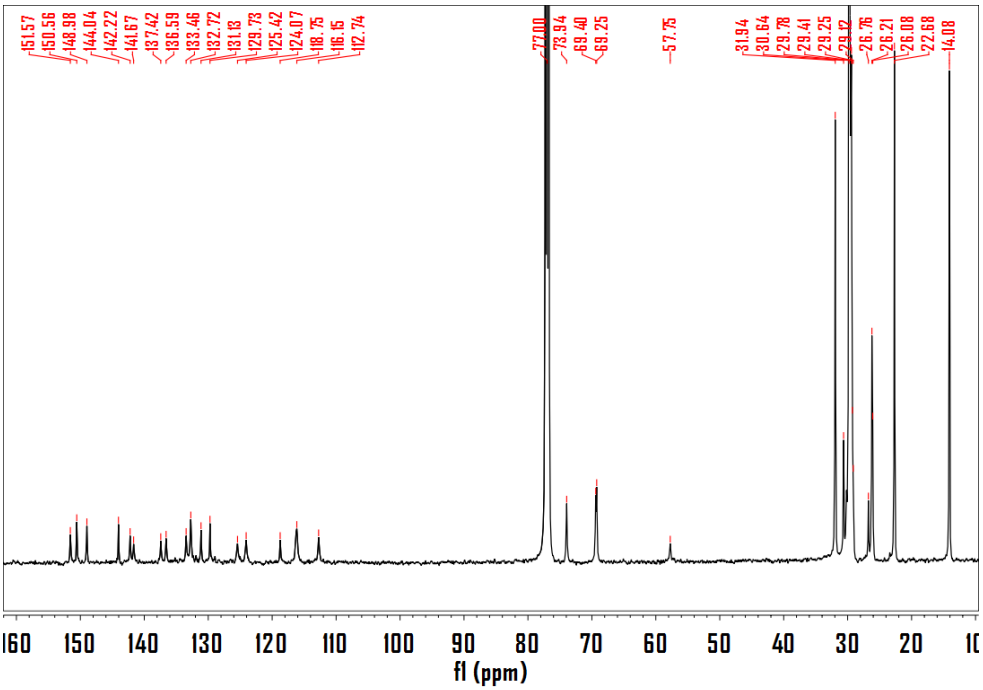


Fig. S39 ^{13}C NMR spectrum of **PBDT-BTzQx-C12**