Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

for

Synthesis and optical properties of the photovoltaic materials based on dithienonaphthothiadiazole that have ambipolar nature for OPV application

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Contents

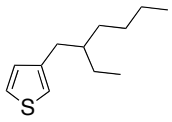
Experimental

General

All chemicals were purchased from commercial suppliers (Wako Pure Chemical, TCI, Kanto Chemical Co. Inc., and Aldrich) and used as received unless otherwise noted. Air- and moisture-sensitive reactions were carried out under an argon flow atmosphere by standard Schlenk techniques. Tetrahydrofuran (THF) (deoxidized, Wako Pure chemical) was used for preparation of Grignard reagents. *N*,*N*-dimethylacetamide (DMAc) (dehydrated, Wako Pure Chemical) were used for polymer syntheses. Column chromatography was conducted using silica gel N60 (spherical, neutralized) with particle size of 40–50 mm from Kanto Chemical Co. Inc.

Synthesis

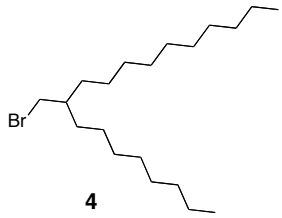
3-(2-Ethylhexyl)thiophene (3)



3

Magnesium, Turnings (6.07 g, 250 mmol) and iodine (402 mg, 1.6 mmol) were dissolved in THF (60 mL) under an Ar atmosphere. One third of 2-ethylhexyl bromide (39.1 g, 202 mmol) in THF (40 mL) was added and stirred for 10 min. Then, residual solution was added and mixture was refluxed for 1 h to give the Grignard reagent. 3-Bromothiophene (26.0 g, 159 mmol) and dichlorodiphenylprolylphosphine nickel(0) ($NiCl_2$(dppp)) (1.03 g, 1.89 mmol) was dissolved in 50 mL of THF and the Grignard solution was added slowly keeping with the reaction temperature at 0 °C. The reaction mixture was stirred at 0 °C for 30 min and stirred at room temperature overnight. The reaction was quenched with 2 M of hydrochloric acid (50 mL). Dichloromethane (DCM) was added and the organic layer was washed three times with water. The organic layer was dried over magnesium sulfate ($MgSO_4$) and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel using hexane as an eluent to give colorless oil (21.7 g, 55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.20 (dd, J = 4.8, 2.8 Hz, 1H), 6.88 (m, 2H), 2.55 (d, J = 7.2 Hz, 2H), 1.55 (m, 1H), 1.27 (m, 10 H), 0.87 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 142.01, 128.90, 124.92, 120.77, 40.53, 34.42, 32.64, 29.05, 25.76, 23.20, 14.29, 10.98. HRMS (EI) m/z calcd for $C_{12}H_{20}S$ 196.1286, found 196.1283.

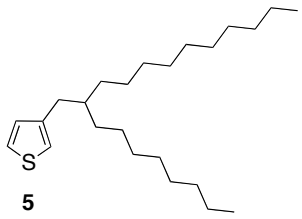
9-(bromomethyl)octadecane (4)



4

2-Octyldodecan-1-ol (12,9 g, 43 mmol), imidazole (3.55 g, 52 mmol), and triphenylphosphine (13.6 g, 52 mmol) was dissolved in 200 mL of DCM and the solution was bubbled with Ar for 10 min. Bromine (8.37 g, 52 mmol) was added at 0 °C and stirred at this temperature for 30 min and then at room temperature overnight. After removal of solvent, residue was filtrated and washed with hexane. The crude product was passed through two times a plug of silica gel using hexane as an eluent to give colorless oil (14.9 g, 96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.44 (d, J = 5.2 Hz, 2H), 1.60 (m, 1H), 1.28 (m, 32H), 0.89 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 39.78, 39.64, 32.72, 32.08, 32.06, 29.95, 29.80, 29.76, 29.73, 29.52, 29.48, 26.72, 22.85, 14.27. HRMS (EI) m/z calcd for $C_{20}H_{41}Br$ 360.2392, found 360.2399.

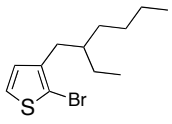
3-(2-Octyldodecyl)thiophene (5)



5

Magnesium, Turnings (1.31 g, 54 mmol) and iodine (343 mg, 1.4 mmol) was dissolved in 50 mL of THF under an Ar atmosphere. **4** (14.9 g, 41 mmol) in 25 mL was added over 10 min and the mixture was refluxed for 3 h to afford the Grignard reagent. 3-Bromothiophene (7.40 g, 45 mmol) and $NiCl_2$(dppp) (342 mg, 0.63 mmol) was dissolved in 25 mL of THF and the Grignard reagent was added slowly keeping with the reaction temperature at 0 °C. The reaction mixture was stirred at room temperature overnight. The reaction was quenched with 2 M of hydrochloric acid (30 mL). DCM was added and the organic layer was washed three times with water. The organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was passed through silica gel using hexane as an eluent. Further purification was performed by distillation at 210 °C, 10 mmHg to give colorless oil (3.26 g, 22 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.22 (dd, J =4.8, 3.2 Hz, 1H), 6.89 (m, 2H), 2.55 (d, J = 6.8 Hz, 2H), 1.59 (m, 1H), 1.25 (m, 34 H), 0.88 (t, J = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 142.06, 128.96, 124.91, 120.77, 39.08, 34.86, 33.46, 32.08, 30.16, 29.83, 29.81, 29.51, 26.76, 22.85, 14.29. HRMS (EI) m/z calcd for $C_{24}H_{44}S$ 364.3164, found 364.3153.

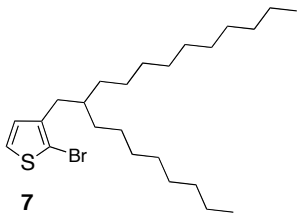
2-Bromo-3-(2-ethylhexyl)thiophene (6)



6

3 (7.50 g, 38 mmol) and *N*-bromosuccinimide (NBS; 7.11 g, 40 mmol) was dissolved in 100 mL of 1:1 mixture of acetic acid and chloroform (CF) and the mixture was stirred at room temperature overnight. Water was added to the reaction and the organic layer was washed with water and saturated sodium bicarbonate aqueous solution, and water. After the removal of solvent with rotary evaporator, the crude passed through a plug of silica gel with hexane. The product was distilled at 140 ˚C under 10 mmHg to afford colorless oil (6.11 g, 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.18 (d, J = 5.6 Hz, 1H), 6.76 (d, J = 5.6 Hz, 1H), 2.50 (d, J = 7.2 Hz, 2H), 1.60 (m, 1H), 1.28 (m, 10H), 0.88. ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 141.25, 128.89, 125.03, 109.52, 40.06, 33.69, 32.56, 28.87, 25.75, 23.13, 14.22, 10.91. HRMS (EI) m/z calcd for $C_{12}H_{19}BrS$ 274.0391, found 274.0868.

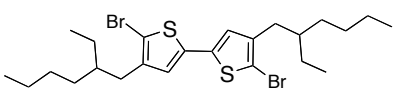
2-Bromo-3-(2-octyldodecyl)thiophene (7)



7

5 (1.12 g, 3.1 mmol) was dissolved in 40 mL of 1:1 mixture of CF and acetic acid and stirred at room temperature for 4 h. DCM and water was added and the organic layer was washed with water, saturated sodium bicarbonate aqueous solution, and water, and dried over $MgSO_4$. The solvent was removed under reduced pressure. The crude was purified by chromatography on silica gel using hexane as an eluent to give colorless oil (1.20 g, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.18 (d, J = 5.6 Hz, 1H), 6.78 (d, J = 6.0 Hz, 1H), 2.52 (d, J = 6.8 Hz, 2H), 1.68 (m, 1H), 1.30 (m, 34H), 0.92 (t, J = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 141.28, 128.93, 125.01, 109.60, 38.71, 34.19, 33.53, 32.12, 30.19, 29.86, 29.81, 29.57, 29.54, 26.71, 22.90, 14.32. HRMS (EI) m/z calcd for $C_{24}H_{43}BrS$ 442.2269, found 442.2265.

5,5'-Dibromo-4,4'-bis(2-ethylhexyl)-2,2'-bithiophene (8)

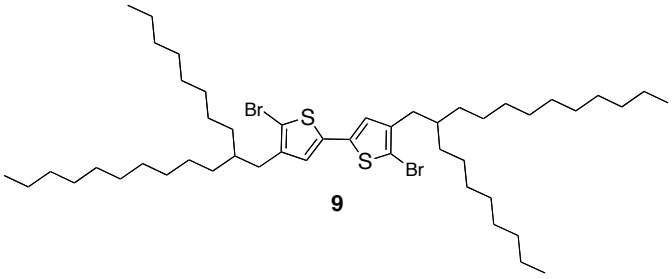


8

6 (3.15 g, 11.5 mmol) and bis(benzonitrile)dichloropalladium (II) ($PdCl_2(PhCN)_2$; 107 mg, 0.28 mmol) were dissolved in 40 mL of dehydrated dimethylsulfoxide (DMSO) under an Ar atmosphere.

The mixture was heated at 100 °C for 8 h, during which time potassium fluoride (KF; 1.55 g, 27 mmol) and silver nitrate ($AgNO_3$; 4.46 g, 26 mmol) was added in four portions every 2 h. After cooling to room temperature, the reaction mixture was filtrated through a celite pad. DCM and water was added and the organic layer was washed three times with water and dried over $MgSO_4$. The solvent was removed under reduced pressure. The crude product was purified by Gel permeation chromatography (GPC) with CF. The solvent was removed under vacuum to give the titled compound as colorless oil (1.44 g, 46 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.76 (s, 2H), 2.47 (d, J = 6.8 Hz, 4H), 1.62 (m, 2H), 1.32 (m, 20H), 0.91 (t, J = 7.6 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 141.32, 128.95, 125.08, 109.56, 40.11, 22.75, 32.61, 28.93, 25.80, 23.19, 14.27, 10.96. HRMS (APCI) m/z calcd for $C_{24}H_{37}Br_2S_2$ 547.0698, found 547.0700.

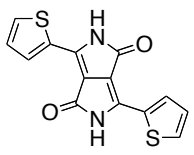
5,5'-Dibromo-4,4'-bis(2-octyldodecyl)-2,2'-bithiophene (9)



9

7 (329 mg, 0.74 mmol) was dissolved in 30 mL of DMSO and the solution was bubbled with Ar for 15 min. $PdCl_2(PhCN)_2$ (15.1 mg, 0.039 mmol) was added and the mixture was heated at 100 °C for 8 h, during which time KF (115 g, 2.0 mmol) and $AgNO_3$ (306 mg, 1.8 mmol) was added in four portions every 2 h and heated further overnight. After cooling to room temperature, hexane was added and the product was extracted with hexane three times and dried over $MgSO_4$. After removal of the solvent, the product was passed through silica gel plug using hexane was eluent. Further purification was performed by GPC with chloroform. The solvent was removed under vacuum to give the titled compound as colorless oil (97 mg, 30 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.74 (s, 2H), 2.45 (d, J = 7.2 Hz, 4H), 1.65 (m, 2H), 1.31 (m, 34H), 0.89 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 142.32, 136.14, 125.01, 108.62, 38.63, 34.33, 33.44, 32.10, 30.15, 29.85, 29.82, 29,77, 29.54, 29.52, 26.65, 22.86, 14.30. HRMS (APCI) m/z calcd for $C_{48}H_{85}Br_2S_2$ 883.4454, found 883.4455.

3,6-Di(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (10)

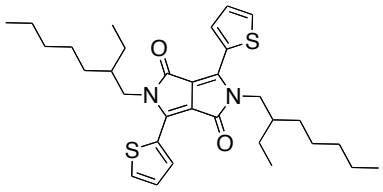


10

In the 300 mL of three-necked flask, 2-cyanothiophene (5.86 g, 53.7 mmol) and potassium

t-buthoxide (10.3 g, 91.7 mmol) in 50 mL of 2-methyl-2-butanol was added and the flask was heated at 100 °C. Dimethylsuccinate (3.50 g, 26.8 mmol) was added dropwise over 15 min with using dropping funnel and the mixture was stirred at that temperature equipped with Dean-stark condenser for 5 h. Acetic acid (30 mL) and methanol (100 mL) was added and the reaction solution was stirred further 1 h, allowing to cool to room temperature. The precipitate was filtrated and washed with large amount of methanol to give crude product (5.72 g, 71%). The crude product was used without further purification.

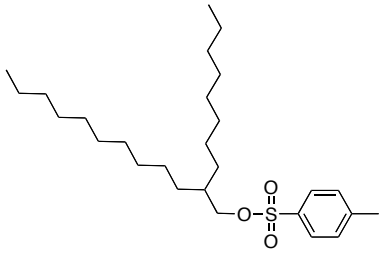
2,5-Bis(2-ethylhexyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (11)



11

10 (5.72 g, 19.0 mmol), potassium carbonate (K_2CO_3; 10.9 g, 78.8 mmol), and 2-ethylhexyl bromide (19.6 g, 101 mmol) were dissolved in 100 mL of dimethylformamide (DMF) and the mixture was bubbled with Ar for 15 min. The reaction solution was heated at 150 °C overnight. After removal of solvent, DCM was added and washed three times with water. Organic layer was dried over $MgSO_4$ and the solvent was removed with rotary evaporator. Column chromatography on silica gel using 6:4 mixture of hexane/DCM as an eluent gave titled compound as a purple powder (2.01 g, 20%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.89 (dd, J = 4.4, 1.2 Hz, 2H), 7.63 (dd, J = 5.2, 1.6 Hz, 2H), 7.27 (dd, J = 5.2, 3.6 Hz, 2H), 4.03 (m, 4H), 1.86 (m, 2H), 1.38–1.22 (m, 20H), 0.87 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 161.91, 140.58, 135.44, 130.68, 129.98, 128.58, 108.07, 46.00, 39.22, 30.36, 28.50, 23.67, 23.21, 14.18, 10.63. HRMS (APCI) *m*/*z* calcd for $C_{30}H_{41}O_2N_2S_2$ 525.2604, found 525.2602.

2-Octyldodecyl 4-methylbenzenesulfonate (12)

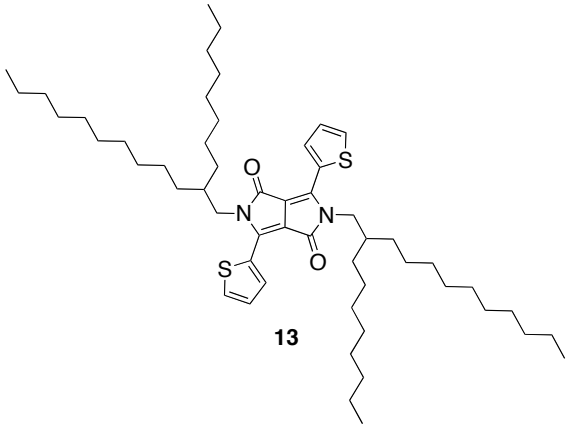


12

To 2-octyldodecan-1-ol (16.8 g, 56 mmol) and 50 mL of pyridine (622 mmol) in 300 mL of CH_2Cl_2, *p*-toluenesulfonyl chloride (10.9 g, 57 mmol) was added at 0 °C. The mixture was stirred at room temperature overnight. Water (100 mL) and hydrochloric acid (75 mL) was added. After removal of DCM by rotary evaporator, ethyl acetate (EA) was added and the organic layer was washed three

times with water. The organic layer was dried over $MgSO_4$ and the solvent was removed. The crude compound was purified by column chromatography on silica gel using 50:1 mixture of hexane/EA to give colorless oil (22.5 g, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.78 (d, J = 8.4 Hz 2H), 7.33 (d, J = 7.6 Hz, 2H), 3.90 (d, J = 5.6 Hz, 2H), 2.44 (s, 3H), 1.56 (m, 1H), 1.24 (m, 34H), 0.88 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 144.67, 133.25, 129.87, 128.05, 72.97, 37.70, 32.03, 32.00, 30.69, 29.91, 29.75, 29.62, 29.40, 26.57, 22.81, 22.78, 21.67, 14.24. HRMS (ESI) m/z calcd for $C_{27}H_{48}O_3NaS$ 475.3216, found 475.3219.

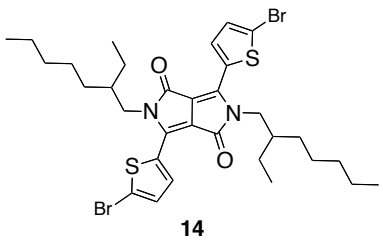
2,5-Bis(2-octyldodecyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (13)



13

10 (2.80 g, 9.3 mmol), **12** (9.31 g, 21mmol), K_2CO_3 (3.86 g, 28 mmol) in 50 mL of DMF was heated at 100 °C overnight. After removal of solvent, DCM and water was added and the organic layer was washed three times with water. The organic was evaporated under reduced pressure and the crude product was purified by column chromatography on silica gel with mixed solvent of hexane/DCM, in which the ratio of DCM was gradually increased from 30% to 50% to give target compound (667 mg, 8.3 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.88 (d, J = 4.0 Hz, 2H), 7.62 (d, J = 4.8 Hz, 2H), 7.26 (t, J = 4.6 Hz, 2H), 4.01 (d, J = 7.2 Hz, 4H), 1.90, (m, 2H), 1.25 (m, 68H), 0.85 (t, J = 6.6 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 161.87, 140.56, 135.38, 130.60, 129.97, 128.52, 108.12, 46.30, 32.06, 32.02, 31.30, 30.16, 29,77, 29.70, 29.64, 29.50, 29,44, 26.34, 22.83, 22.81, 14.27. HRMS (EI) m/z calcd for $C_{54}H_{89}O_2N_2S_2$ 861.6360, found 861.6354.

3,6-Bis(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-*c*]pyrrole-1,4(2H,5H)-dione (14)

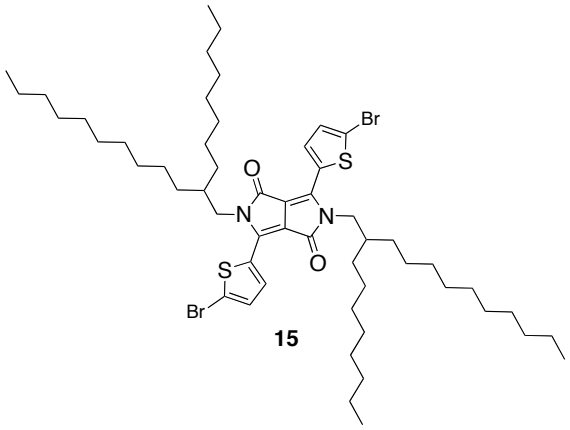


14

11 (1.13 g, 2.2 mmol) and NBS (796 mg, 4.5 mmol) was dissolved in mixture of 30 mL of CF and

20 mL of acetic acid. The mixture was stirred at room temperature for 7 h. Water was added to the reaction mixture and organic layer was washed with water, saturated sodium bicarbonate aqueous solution, and water. Organic layer was dried over $MgSO_4$ and the solvent was removed with rotary evaporator. The crude was chlomatographed on silica gel with 2:1 mixture of hexane/DCM to afford target compound as a purple powder (852 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.63 (d, J = 4.0 Hz, 2H), 7.22 (d, J = 4.0 Hz, 2H), 3.92 (m, 4H), 1.83 (m, 2H), 1.30 (m, 20H), 0.87 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 161.58, 139.57, 135.53, 131.63, 131.32, 119.16, 108.18, 46.17, 39.26, 30.32, 28.47, 23.71, 23.19, 14.17, 10.61. HRMS (APCI) m/z calcd for $C_{30}H_{39}O_2N_2Br_2S_2$ 681.0814, found 681.0811.

3,6-Bis(5-bromothiophen-2-yl)-2,5-bis(2-octyldodecyl)pyrrolo[3,4-*c*]pyrrole-1,4(2H,5H)-dione (15)



15

13 (627 mg, 0.73 mmol) and NBS (295 mg, 1.7 mmol) in mixture of CF (50 mL) and acetic acid (20 mL) stirred at room temperature overnight. Water was added and the organic layer was washed with water, saturated sodium bicarbonate aqueous solution, and water and dried over $MgSO_4$. The solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel using 7:3 mixture of hexane/DCM as an eluent to give titled compound (475 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.61 (d, J = 4.4 Hz, 2H), 7.19 (d, J = 4.4 Hz, 2H), 3.90 (d, J = 7.6 Hz, 4H), 1.86 (m, 2H), 1.21 (m, 68H), 0.86 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 161.43, 139.46, 135.47, 131.52, 131.29, 119.10, 108.05, 46.43, 37.85, 32.06, 32.02, 31.28, 31.17, 29.78, 29.70, 29.64, 29.51, 29.43, 26.29, 22.83, 22.81, 14.27. HRMS (APCI) m/z calcd for $C_{54}H_{87}O_2N_2Br_2S_2$ 1017.4570, found 1017.4558.

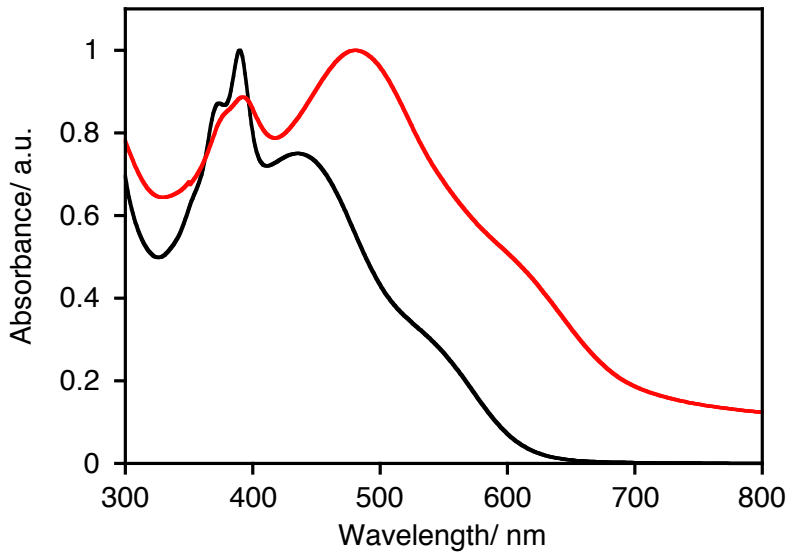


Figure S1. Absorption spectra of **PDTNT-BThEH** in *o*-DCB solution (black) and film (red).

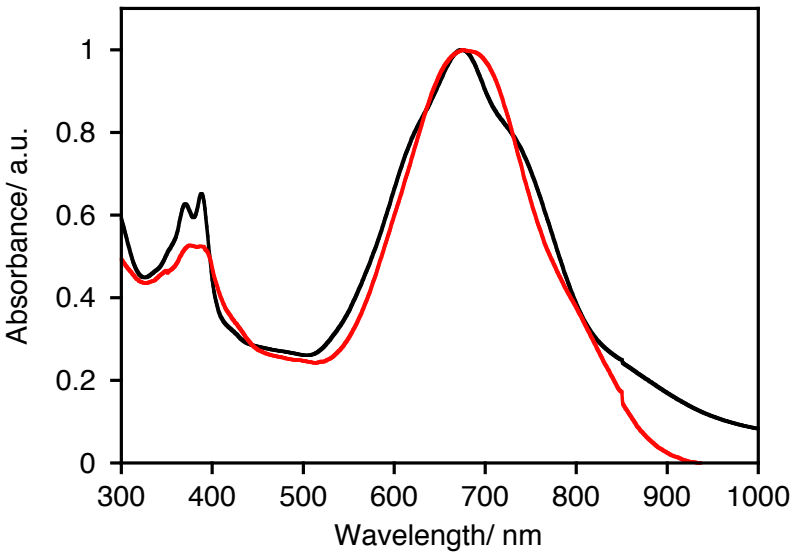


Figure S2. Absorption spectra of **PDTNT-DPPEH** in *o*-DCB solution (black) and film (red).

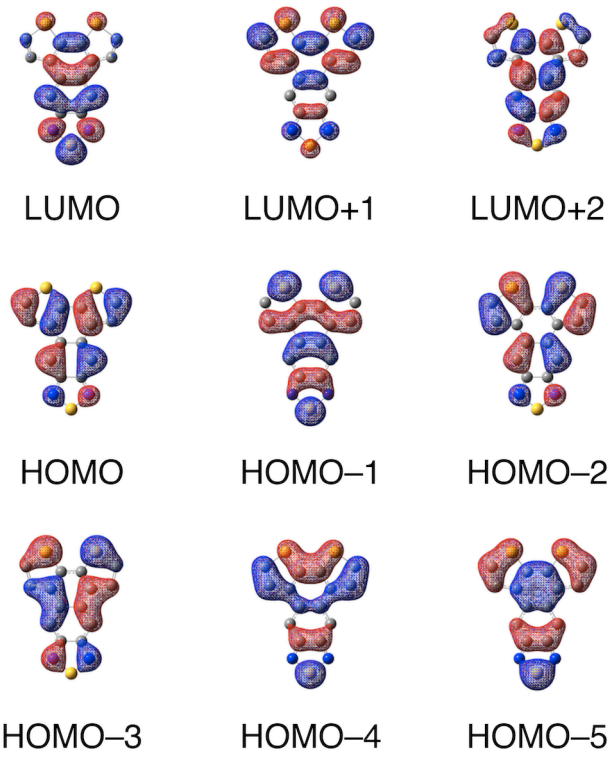


Figure S3. Molecular orbitals (from HOMO–5 to LUMO+2) of DTNT.

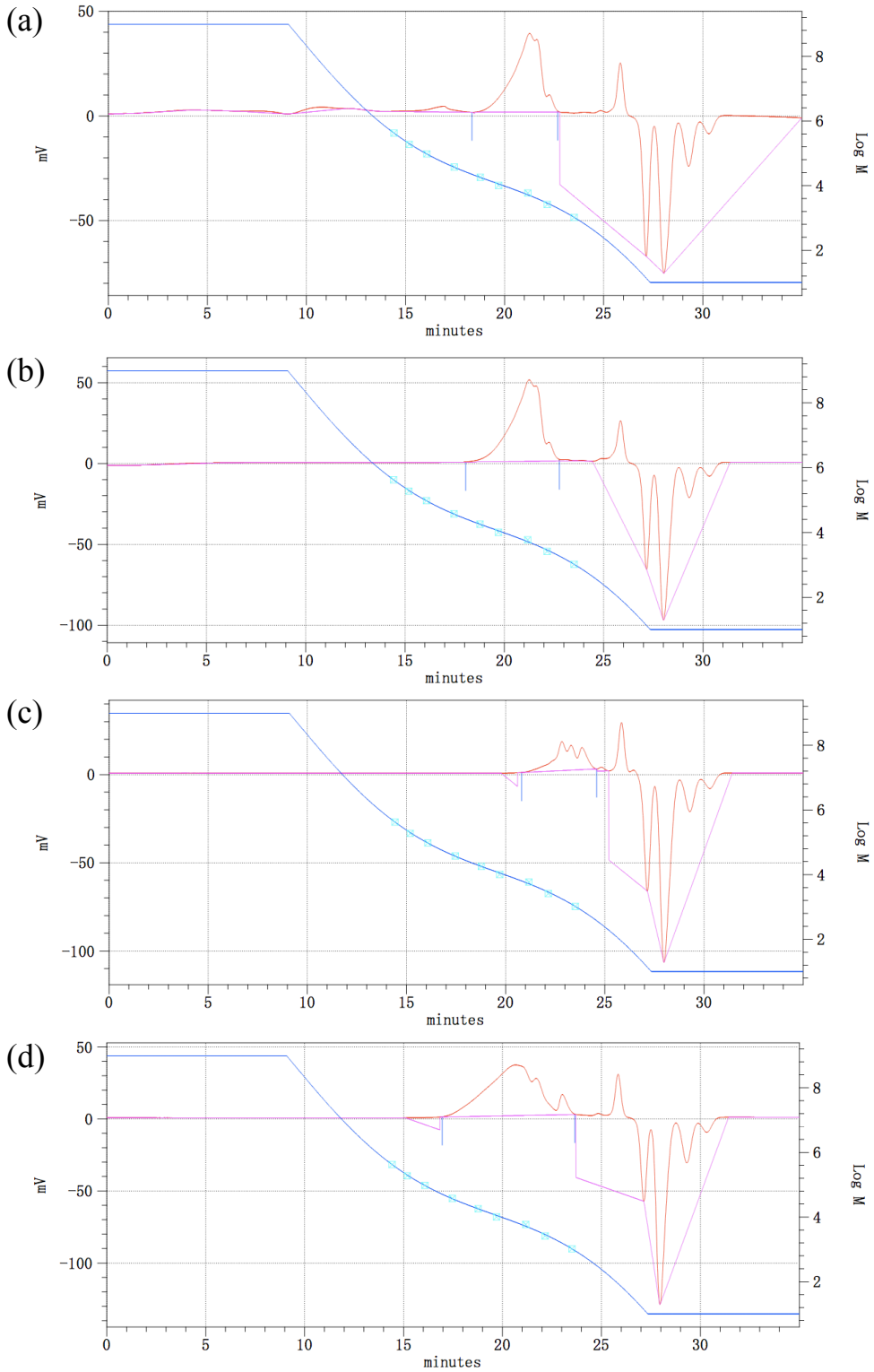


Figure S4. GPC chromatograms for (a) **PDTNT-BThEH**, (b) **PDTNT-BThOD**, (c) **PDTNT-DPPEH**, and (d) **PDTNT-DPPOD**.

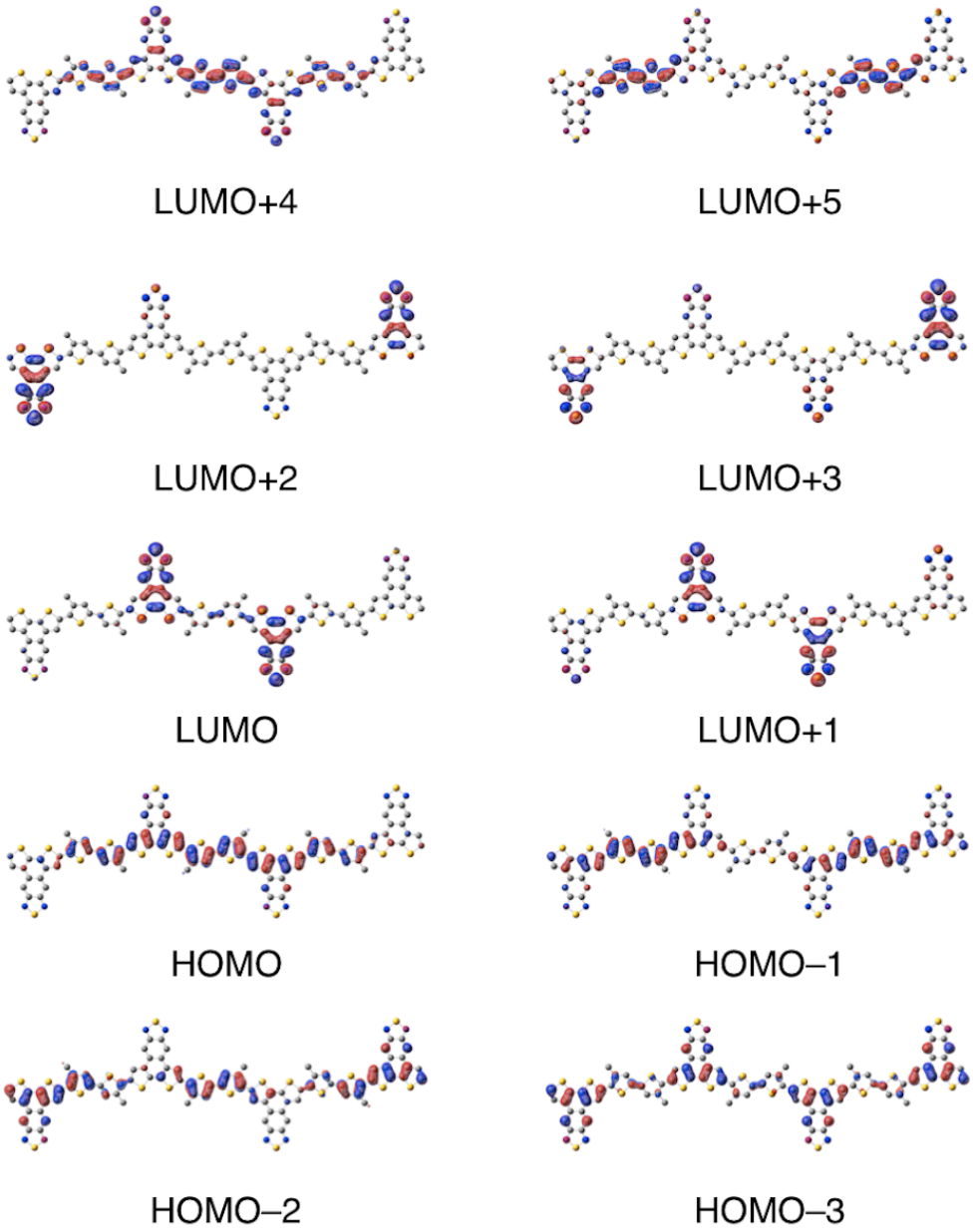


Figure S5. Molecular orbitals (from HOMO–3 to LUMO+5) of **PDTNT-BTh**.

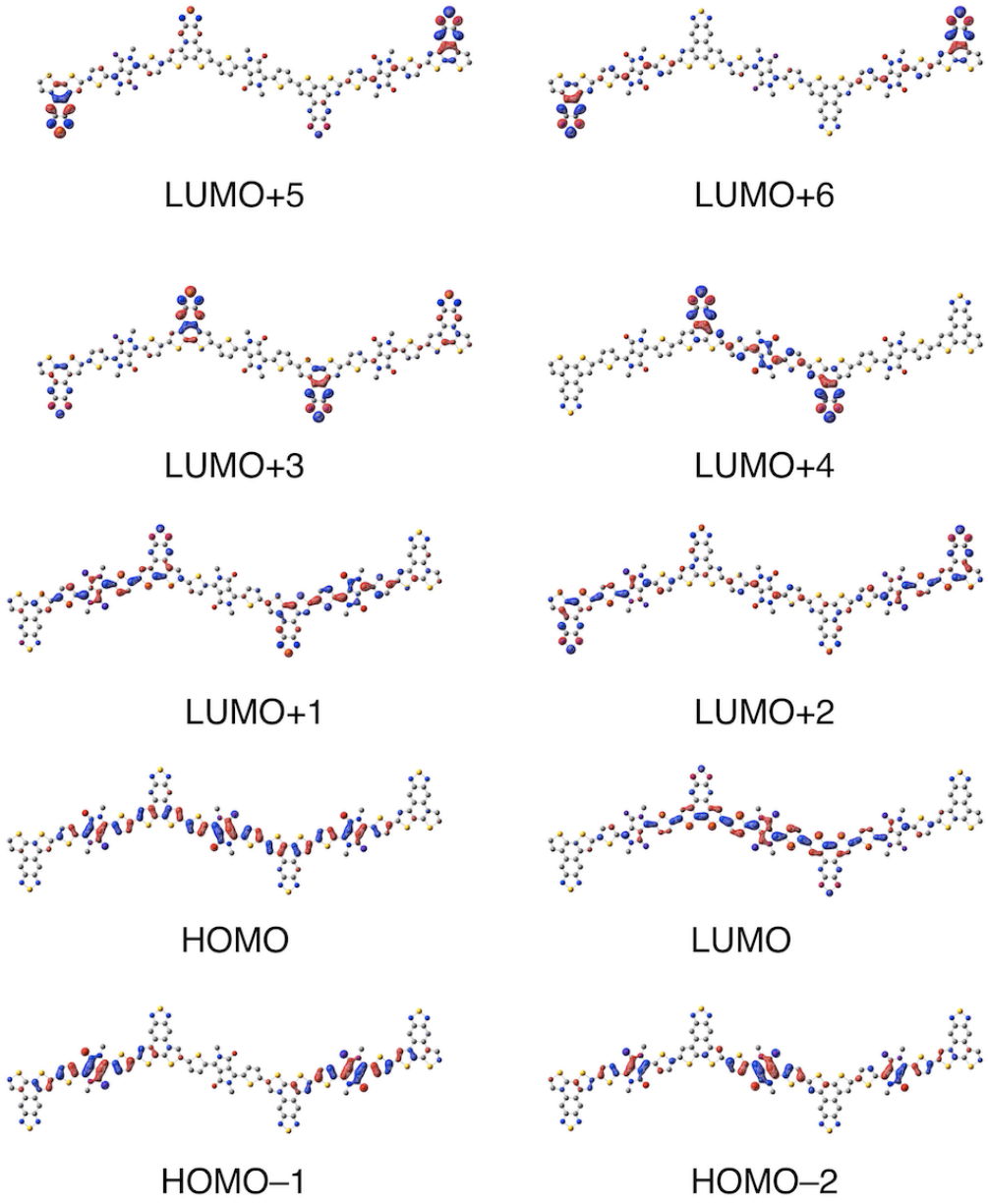


Figure S6. Molecular orbitals (from HOMO–2 to LUMO+6) of **PDTNT-DPP**.

Table S1. Selected results of the TD-DFT excited state transitions for DTNT

State	Excitation energy/ nm	Oscillator strength	MO transitions			Probability/ %
1	503.73	0.0387	HOMO	–>	LUMO	98.4
2	360.22	0.3186	HOMO–1	–>	LUMO	91.5
			HOMO	–>	LUMO+2	7.4
3	317.38	0.1184	HOMO	–>	LUMO+1	94.2
4	275.88	0.0133	HOMO–4	–>	LUMO	64.2
			HOMO–1	–>	LUMO+1	11.9
			HOMO	–>	LUMO+2	20.4
5	275.19	0.0115	HOMO–3	–>	LUMO	94.2
			HOMO–2	–>	LUMO+1	2.8
6	269.76	0.0152	HOMO–5	–>	LUMO	12.6
			HOMO–4	–>	LUMO	18.8
			HOMO–1	–>	LUMO+1	57.5
			HOMO	–>	LUMO+2	5.0
			HOMO	–>	LUMO+5	2.7
7	262.12	0.0800	HOMO–3	–>	LUMO	3.5
			HOMO–2	–>	LUMO+1	82.1
			HOMO–1	–>	LUMO+2	2.2
			HOMO	–>	LUMO+4	9.7

*TD-DFT calculation was conducted for the first ten lowest energies.

*Transitions with oscillator strength of zero are omitted for clarify.

Table S2. Selected results of the TD-DFT excited state transitions for **PDTNT-BTh**

State	Excitation energy/ nm	Oscillator strength	MO transitions			Probability/ %
1	720.84	1.3714	HOMO–1	–>	LUMO+1	8.8
			HOMO	–>	LUMO	87.0
2	652.86	0.2932	HOMO–2	–>	LUMO+2	3.2
			HOMO–1	–>	LUMO+2	3.1
			HOMO–1	–>	LUMO+3	16.1
			HOMO	–>	LUMO+2	71.7
3	651.52	0.0182	HOMO–2	–>	LUMO+3	3.1
			HOMO–1	–>	LUMO+2	16.9
			HOMO–1	–>	LUMO+3	3.2
			HOMO	–>	LUMO+1	6.6
			HOMO	–>	LUMO+3	66.3
4	602.90	0.0310	HOMO–2	–>	LUMO	2.1
			HOMO–1	–>	LUMO+1	80.9
			HOMO–1	–>	LUMO+3	3.2
			HOMO	–>	LUMO	8.3
			HOMO	–>	LUMO+4	3.1
5	588.10	1.8980	HOMO–2	–>	LUMO+2	2.3
			HOMO–1	–>	LUMO+1	3.5
			HOMO–1	–>	LUMO+3	19.2
			HOMO–1	–>	LUMO+5	3.9
			HOMO	–>	LUMO+2	14.8
			HOMO	–>	LUMO+4	50.8
6	586.91	0.0042	HOMO–2	–>	LUMO+3	7.8
			HOMO–1	–>	LUMO+2	61.9
			HOMO	–>	LUMO+1	2.2
			HOMO	–>	LUMO+3	22.5
7	586.09	0.8329	HOMO–2	–>	LUMO+2	6.1
			HOMO–1	–>	LUMO+3	42.3
			HOMO–1	–>	LUMO+5	2.7
			HOMO	–>	LUMO+2	10.2
			HOMO	–>	LUMO+4	34.3
8	545.40	0.0283	HOMO–3	–>	LUMO+1	4.0
			HOMO–2	–>	LUMO	89.1

*TD-DFT calculation was conducted for the first ten lowest energies.

*Transitions with oscillator strength of zero are omitted for clarify.

Table S3. Selected results of the TD-DFT excited state transitions for **PDTNT-DPP**

State	Excitation energy/ nm	Oscillator strength	MO transitions			Probability/ %
1	893.19	4.3024	HOMO–1	–>	LUMO+1	7.1
			HOMO	–>	LUMO	91.0
2	784.36	0.0007	HOMO–1	–>	LUMO	66.1
			HOMO	–>	LUMO+1	25.1
			HOMO	–>	LUMO+3	4.8
3	726.89	0.1208	HOMO–2	–>	LUMO	53.0
			HOMO–1	–>	LUMO+3	8.0
			HOMO	–>	LUMO+2	34.6
4	719.50	0.0021	HOMO–2	–>	LUMO	17.4
			HOMO–1	–>	LUMO+1	27.8
			HOMO–1	–>	LUMO+3	6.6
			HOMO–1	–>	LUMO	4.7
			HOMO	–>	LUMO+2	7.3
			HOMO	–>	LUMO+4	33.9
5	715.01	0.0003	HOMO–1	–>	LUMO+2	10.0
			HOMO–1	–>	LUMO+4	3.7
			HOMO	–>	LUMO+1	5.7
			HOMO	–>	LUMO+3	74.7
6	709.00	1.0389	HOMO–2	–>	LUMO	2.3
			HOMO–2	–>	LUMO+4	2.7
			HOMO–1	–>	LUMO+1	56.3
			HOMO	–>	LUMO	3.4
			HOMO	–>	LUMO+2	4.2
			HOMO	–>	LUMO+4	24.3
			HOMO	–>	LUMO+6	2.3
7	685.94	0.2033	HOMO–2	–>	LUMO	11.5
			HOMO–2	–>	LUMO+6	2.3
			HOMO–1	–>	LUMO+5	16.3
			HOMO	–>	LUMO+2	25.6
			HOMO	–>	LUMO+4	25.0
			HOMO	–>	LUMO+6	17.0

*TD-DFT calculation was conducted for the first ten lowest energies.

*Transitions with oscillator strength of zero are omitted for clarify.

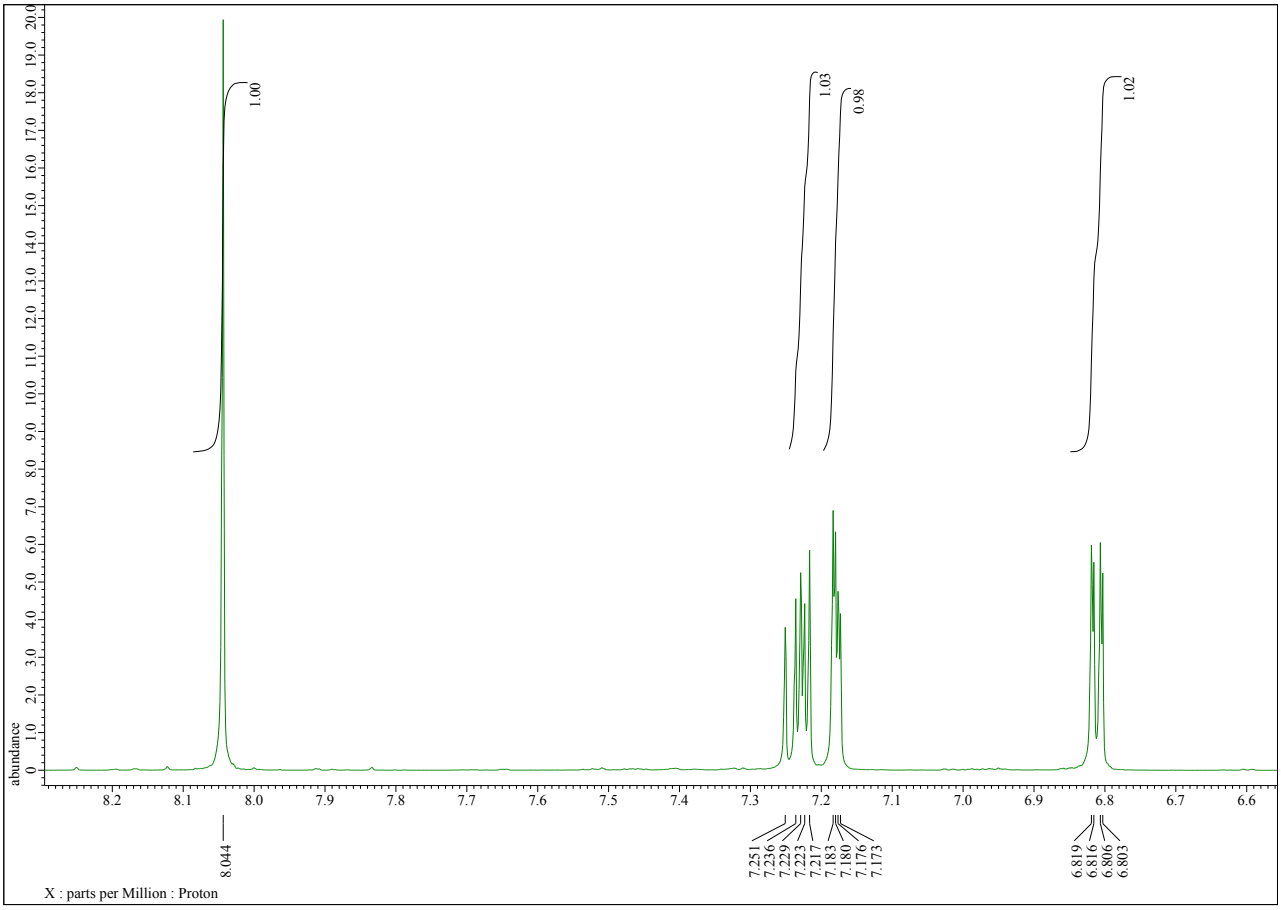


Figure S7. The ^{1}H NMR spectrum of **1**.

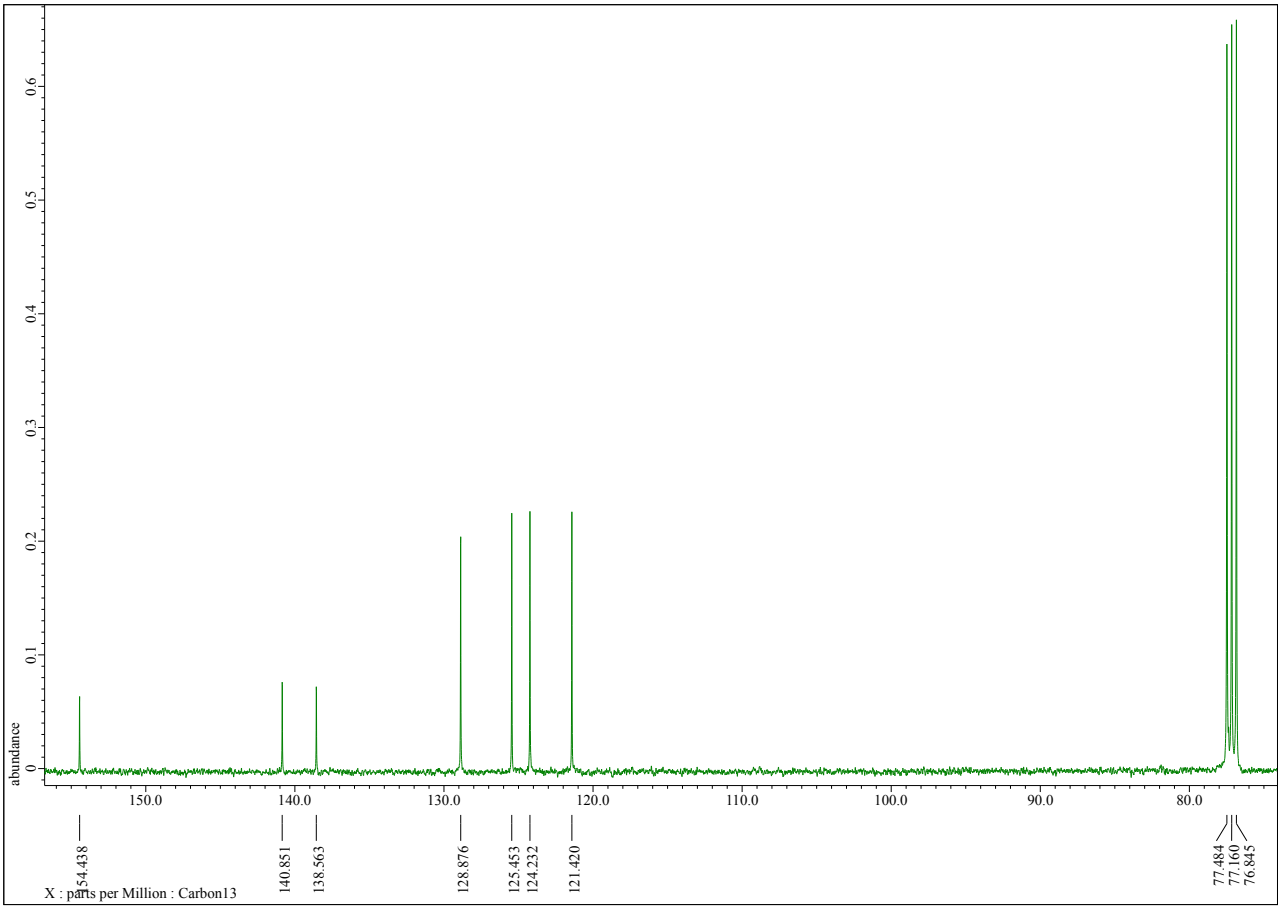


Figure S8. The ^{13}C NMR spectrum of **1**.

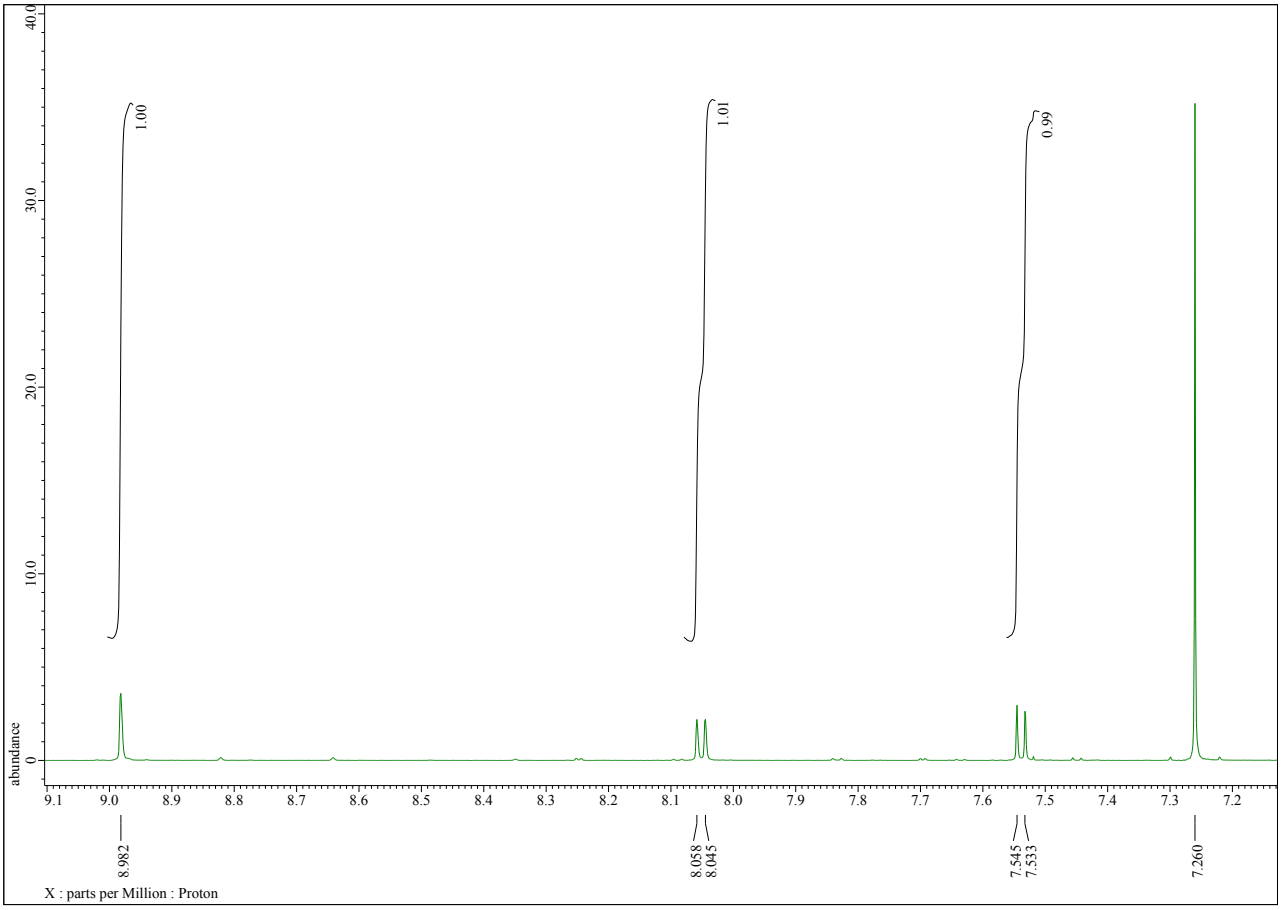


Figure S9. The ^{1}H NMR spectrum of **2**.

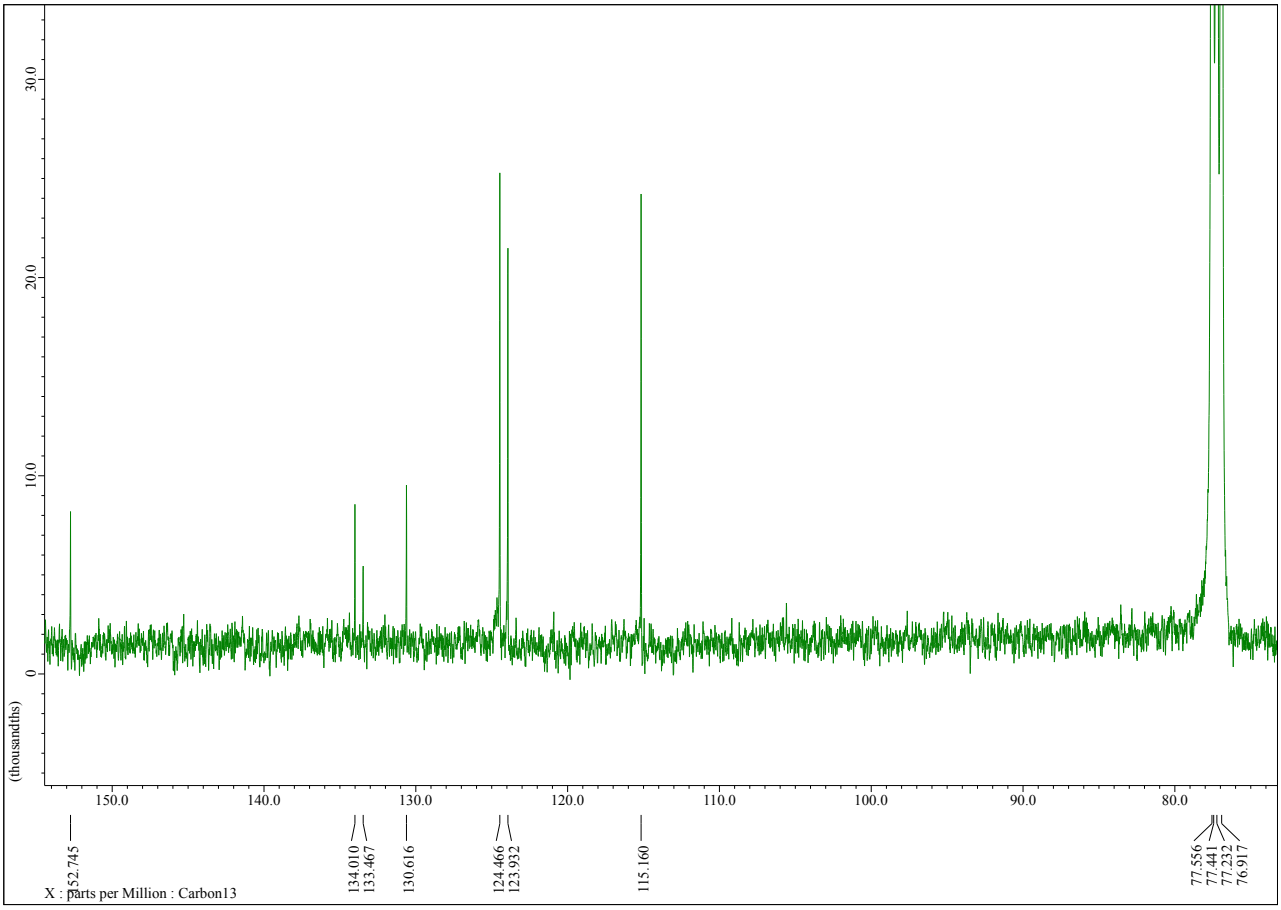


Figure S10. The ^{13}C NMR spectrum of **2**.

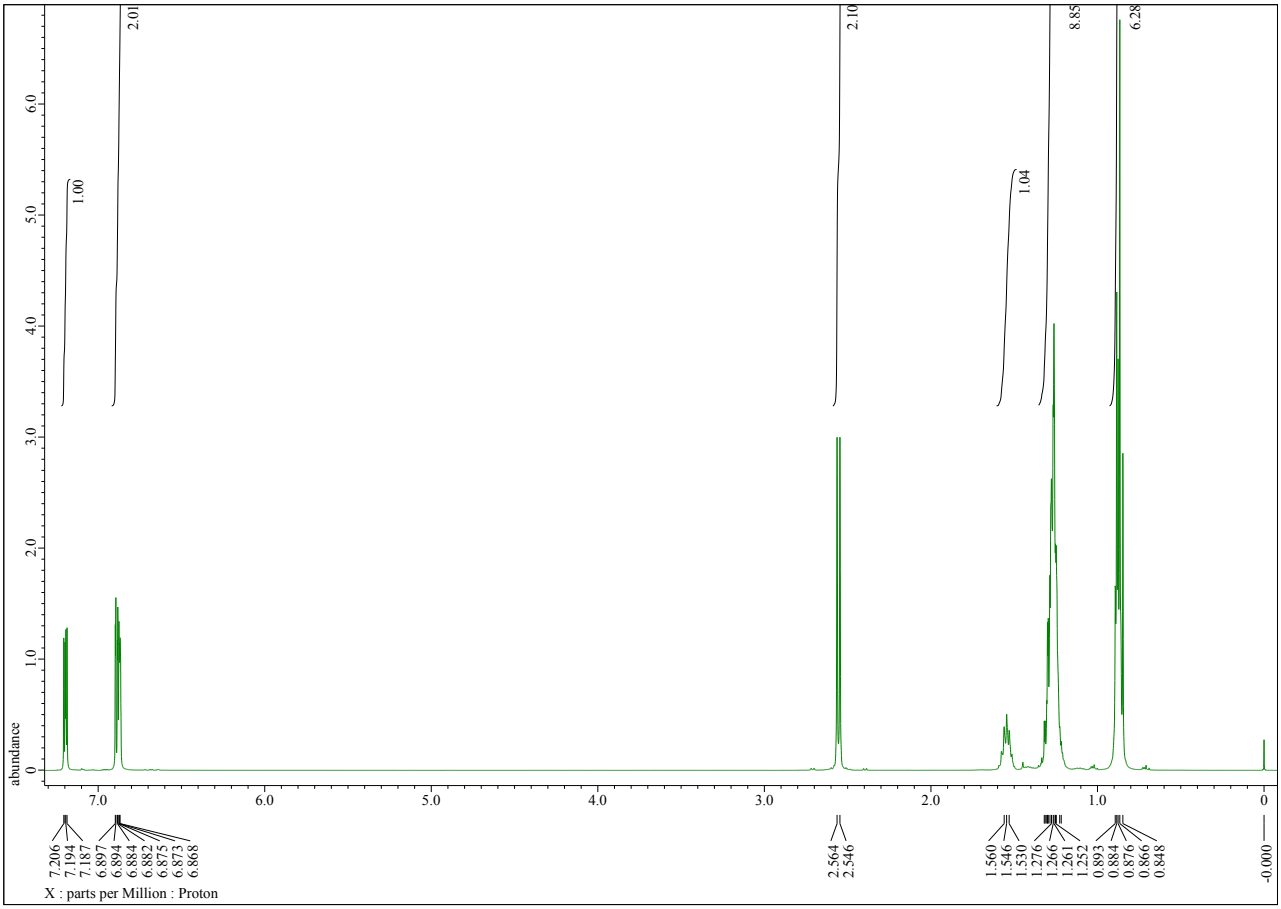


Figure S11. The ^{1}H NMR spectrum of **3**.

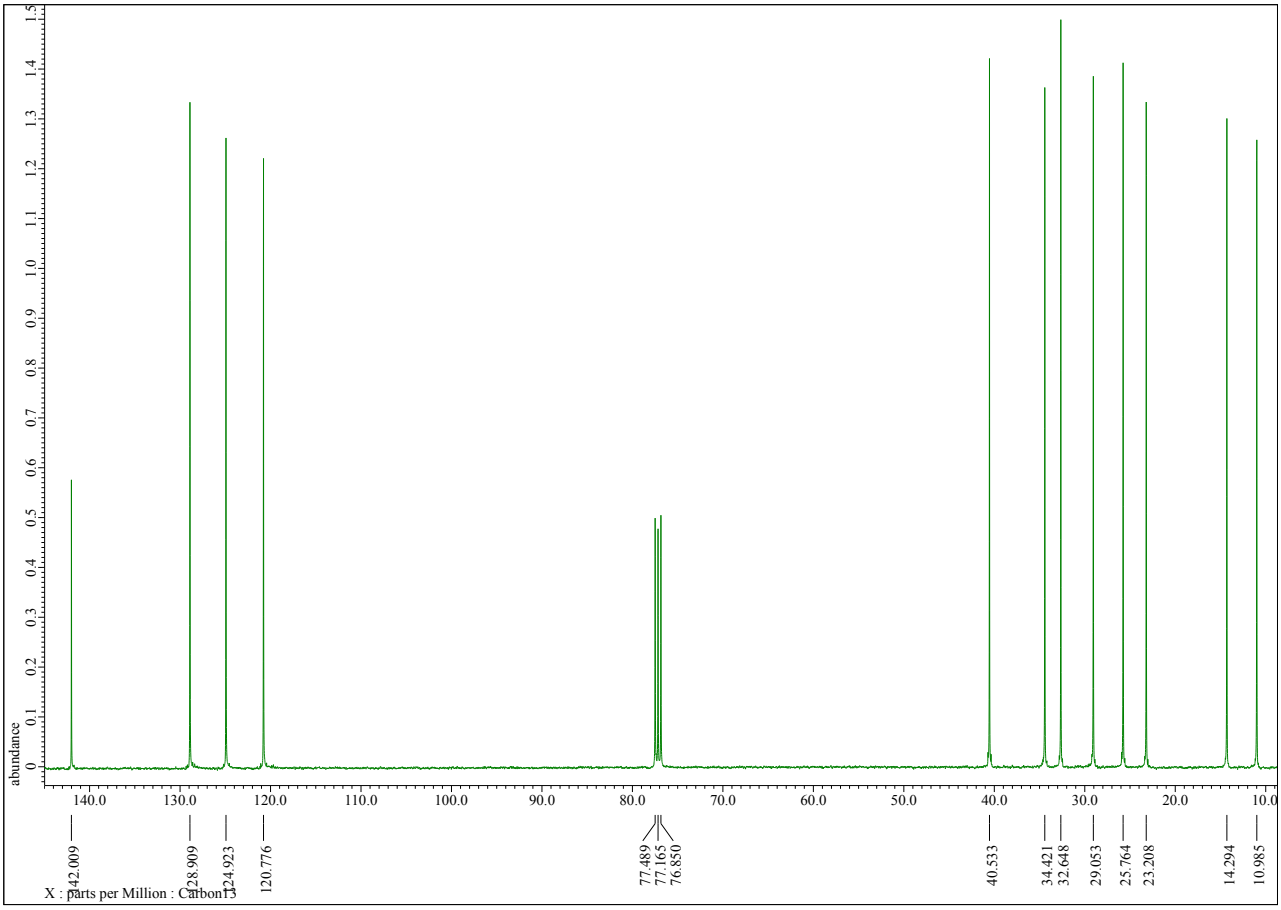


Figure S12. The ^{13}C NMR spectrum of **3**.

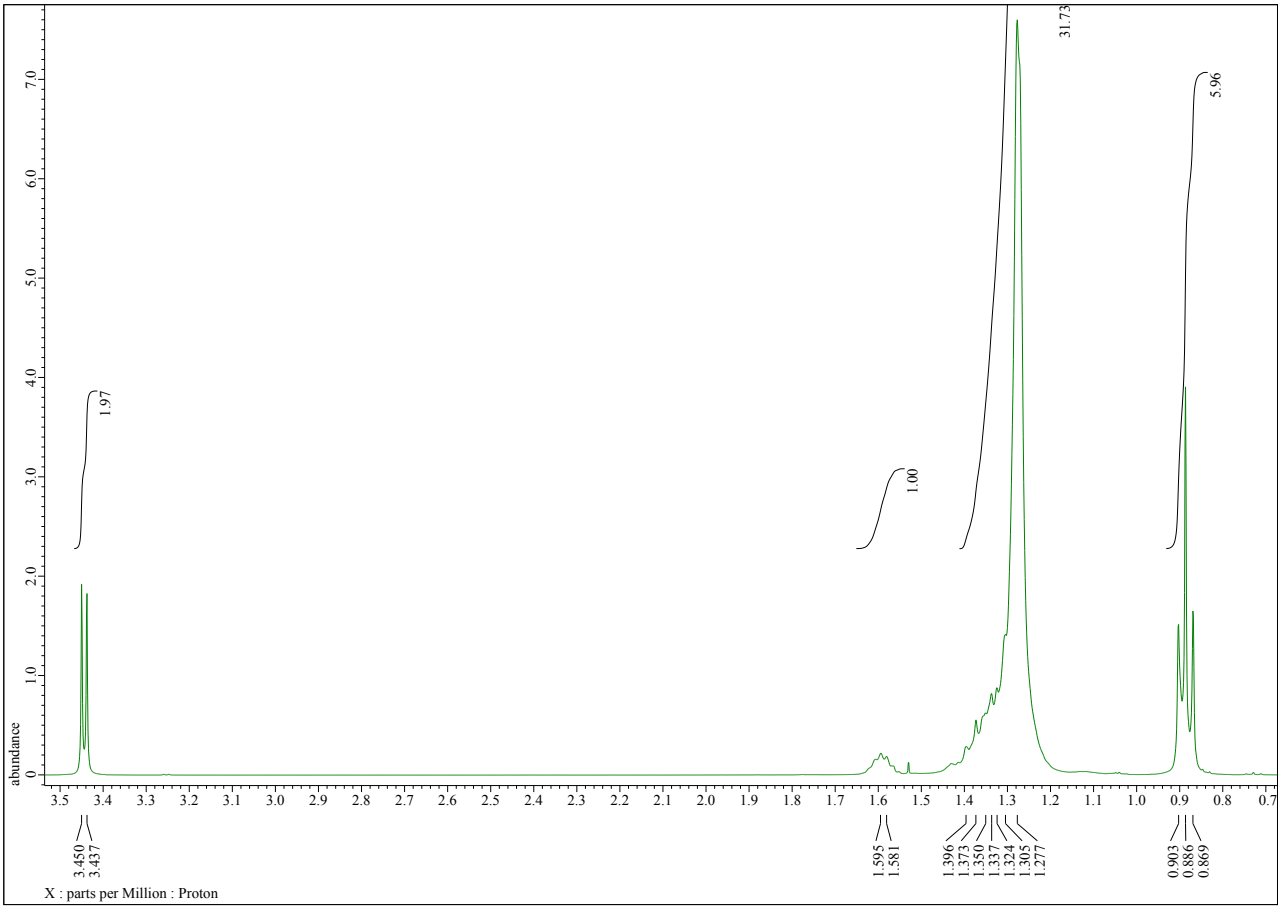


Figure S13. The ^{1}H NMR spectrum of **4**.

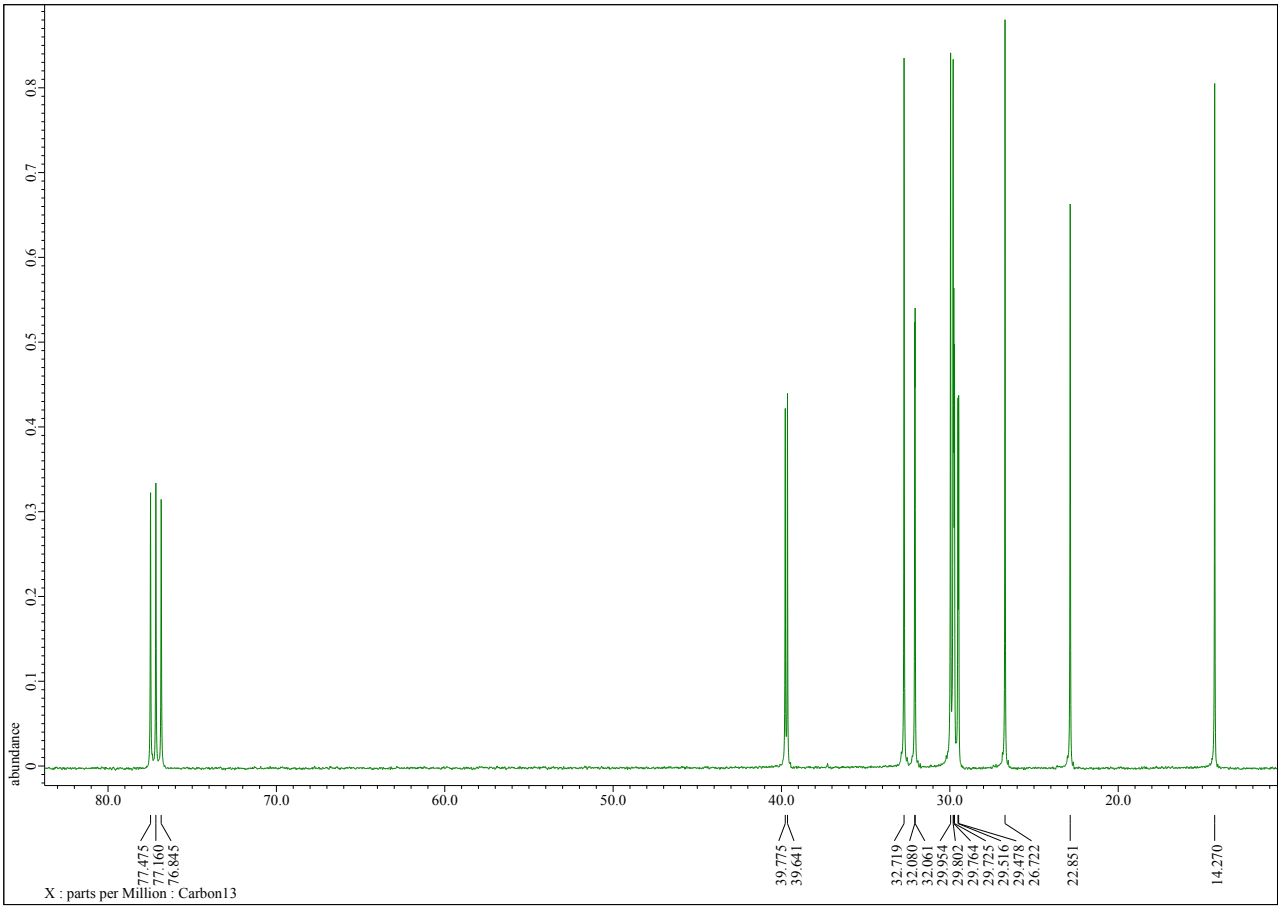


Figure S14. The ^{13}C NMR spectrum of **4**.

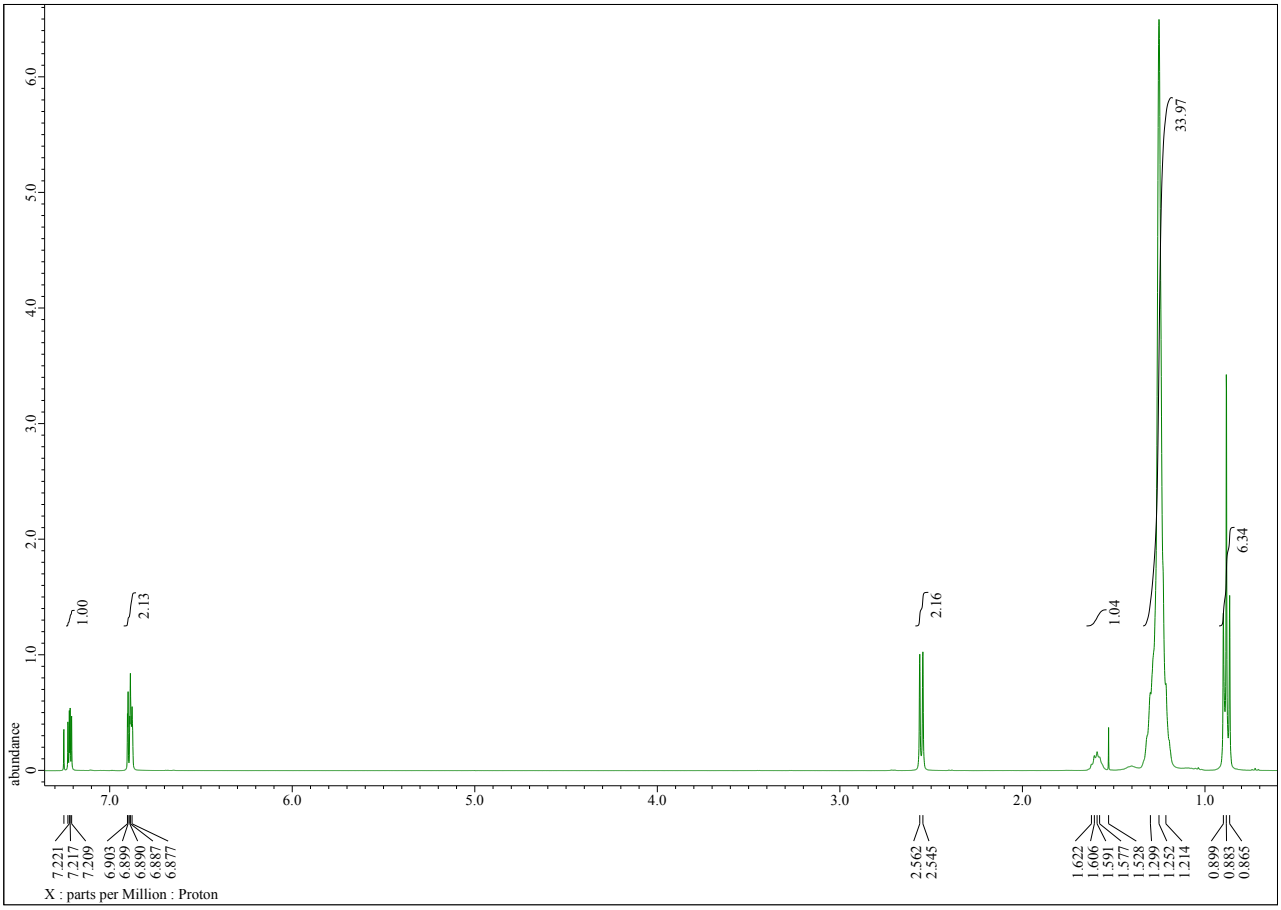


Figure S15. The ^{1}H NMR spectrum of **5**.

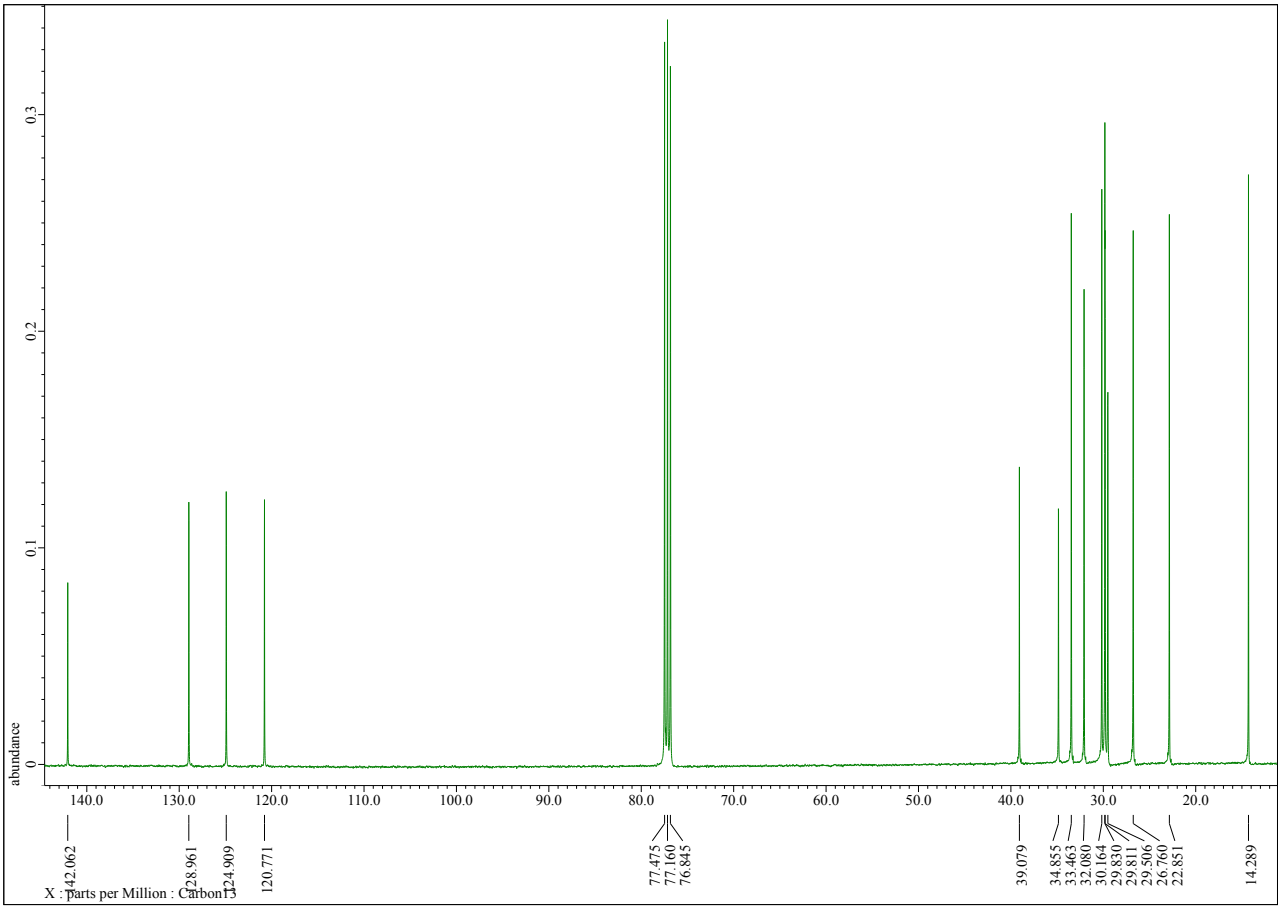


Figure S16. The ^{13}C NMR spectrum of **5**.

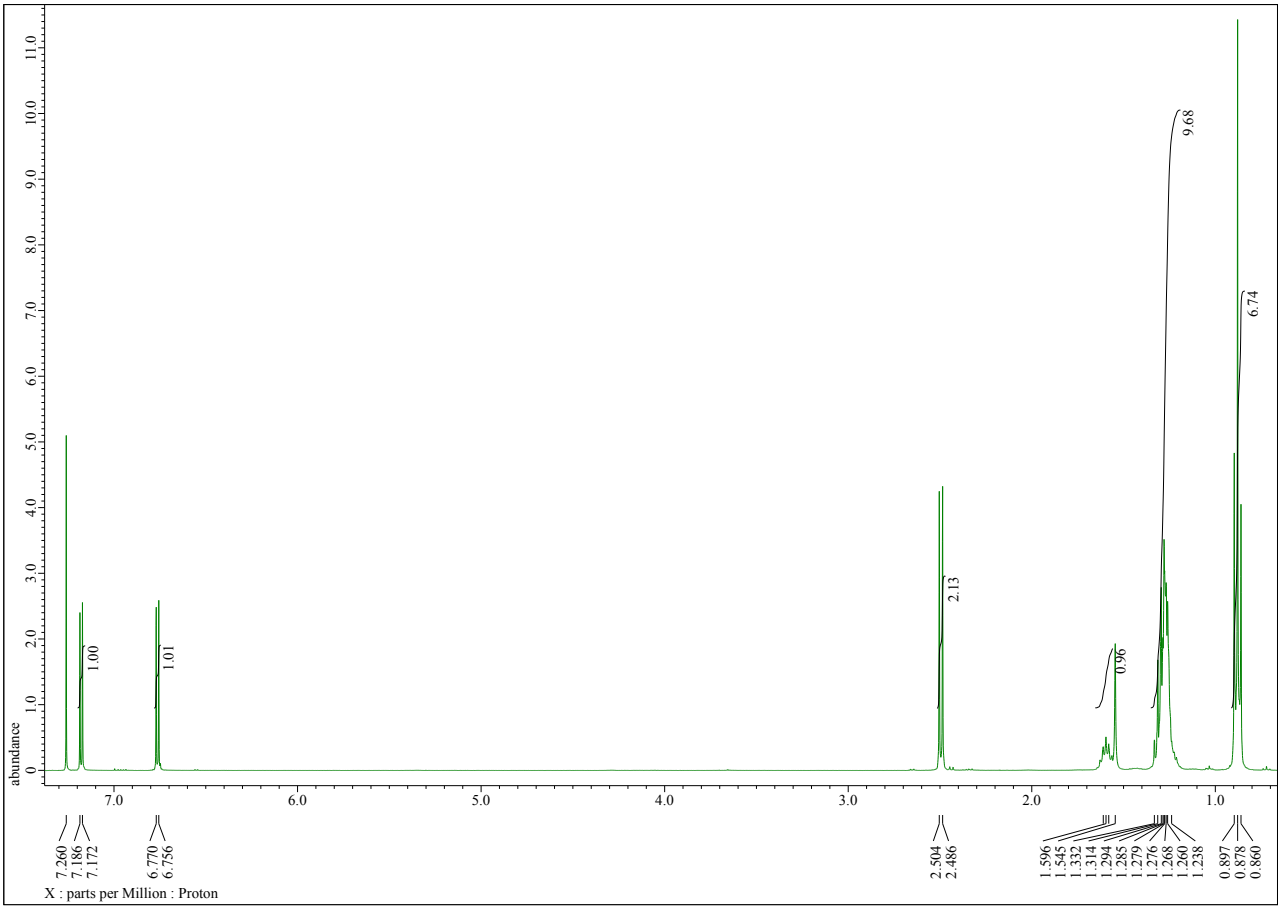


Figure S17. The ^{1}H NMR spectrum of **6**.

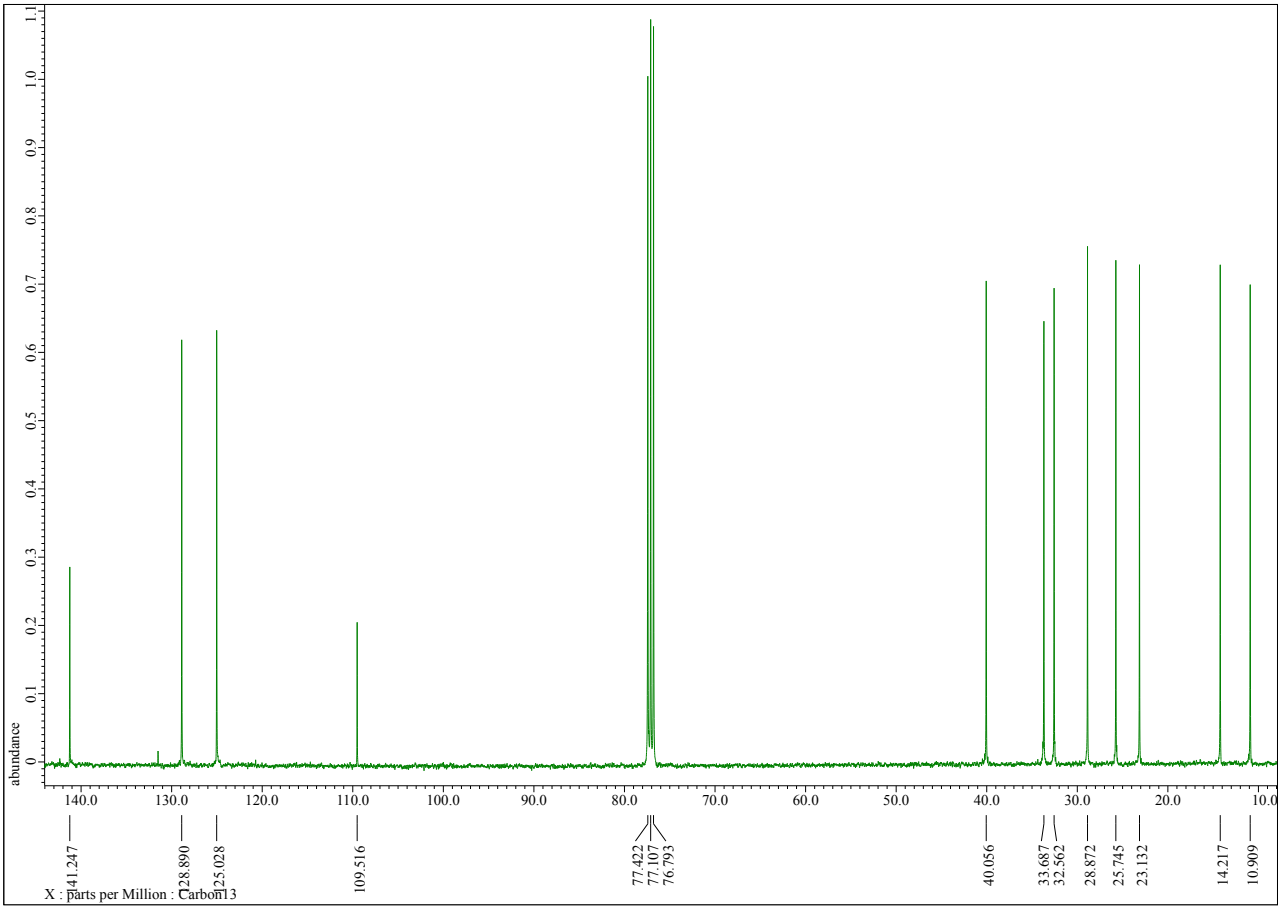


Figure S18. The ^{13}C NMR spectrum of **6**.

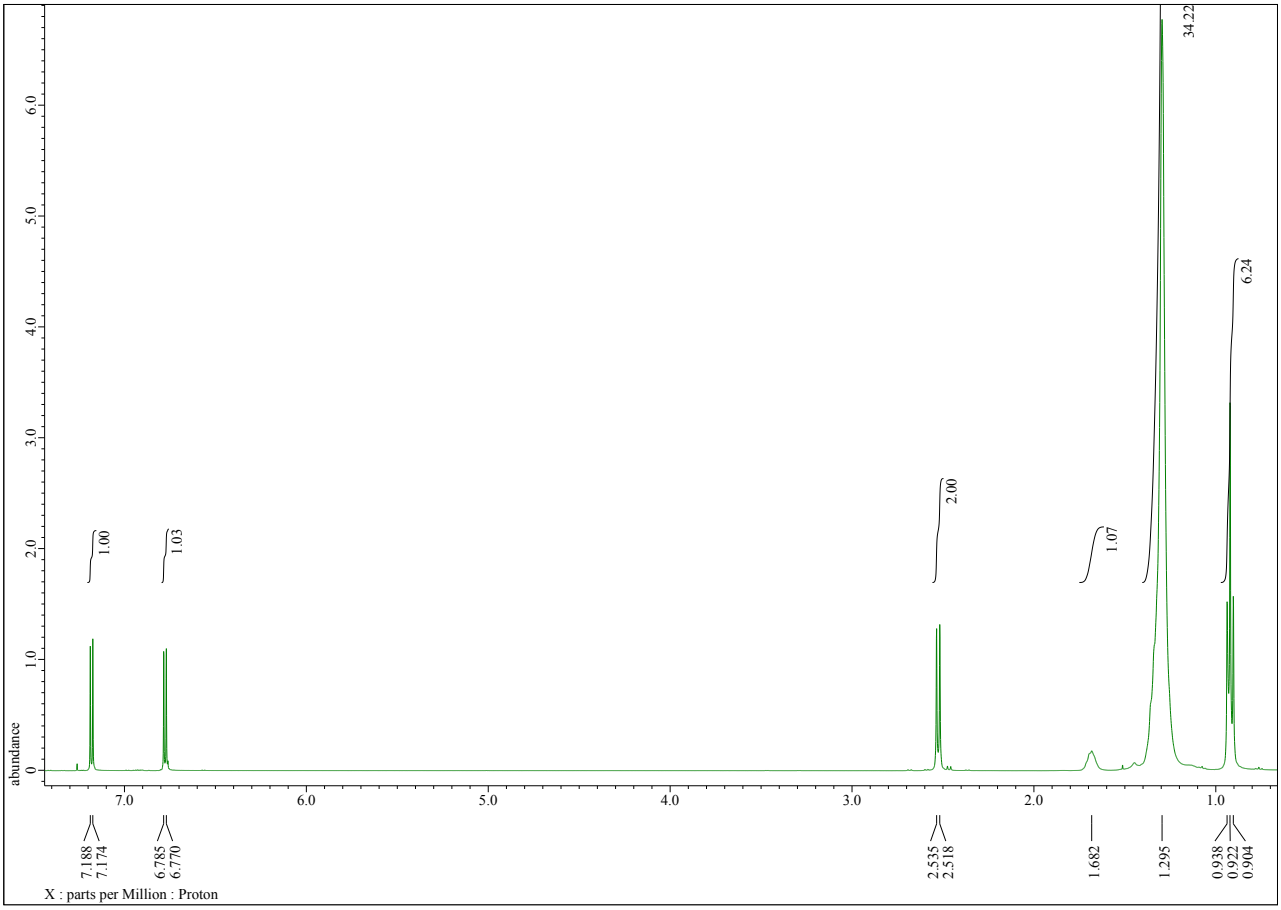


Figure S19. The ^{1}H NMR spectrum of **7**.

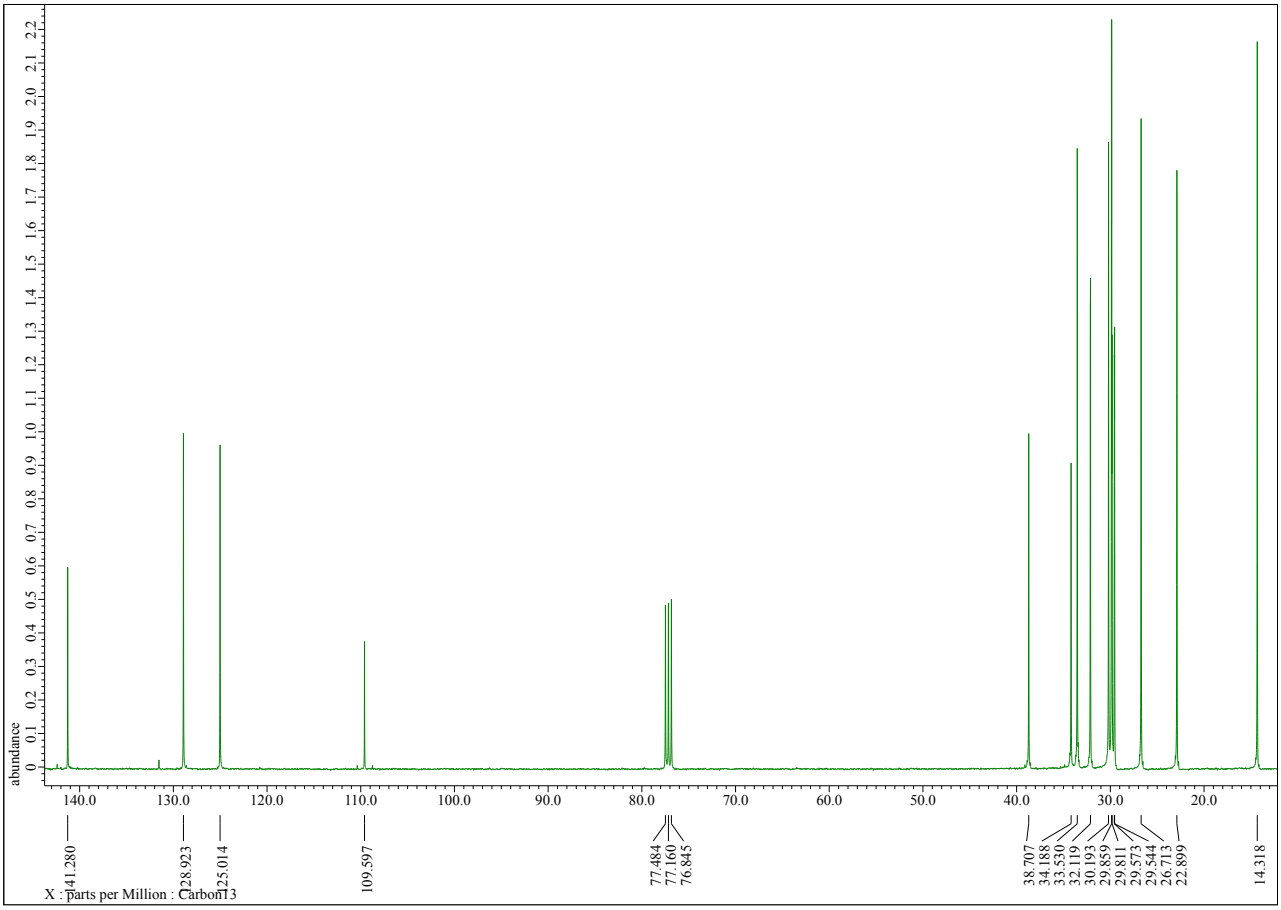


Figure S20. The ^{13}C NMR spectrum of **7**.

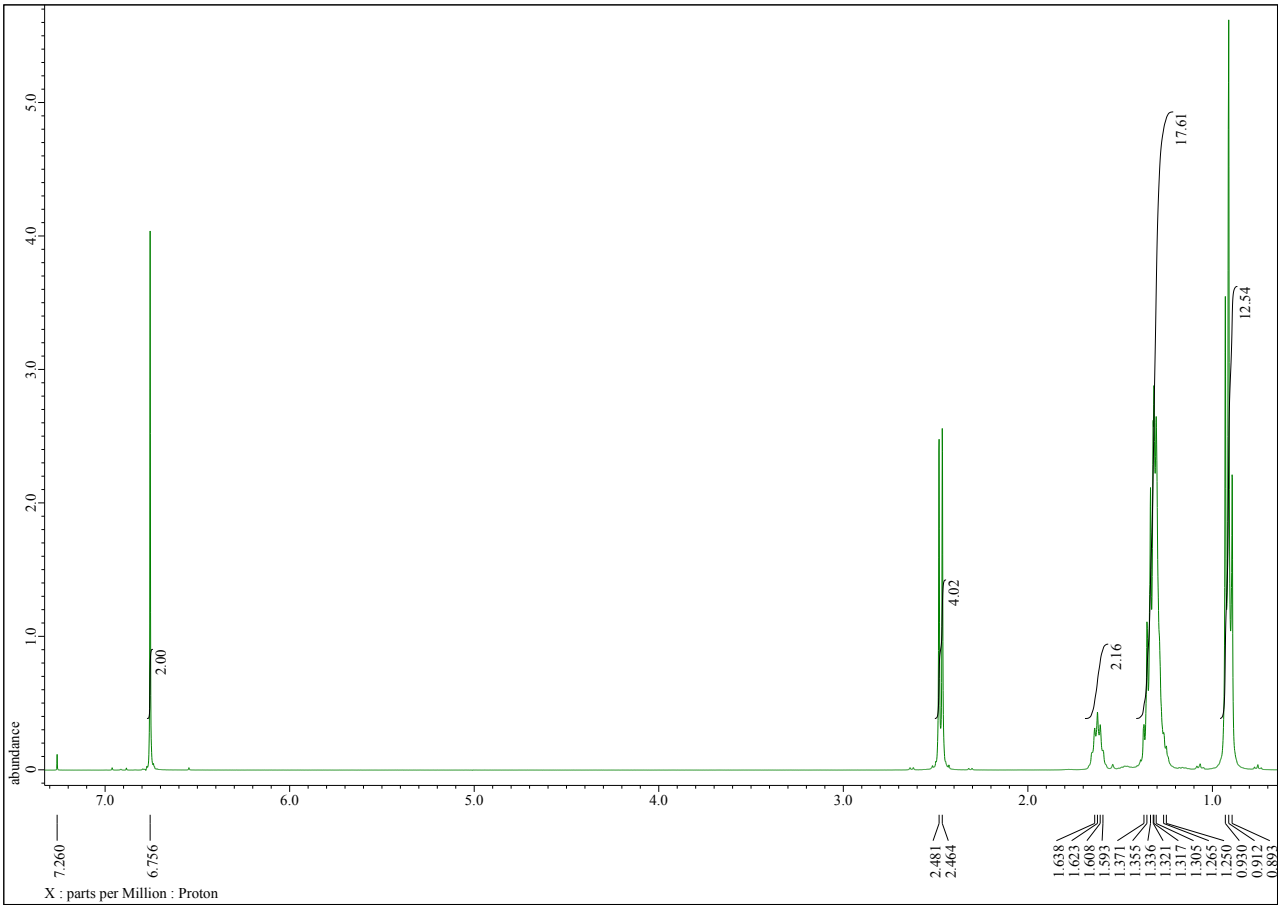


Figure S21. The ^{1}H NMR spectrum of **8**.

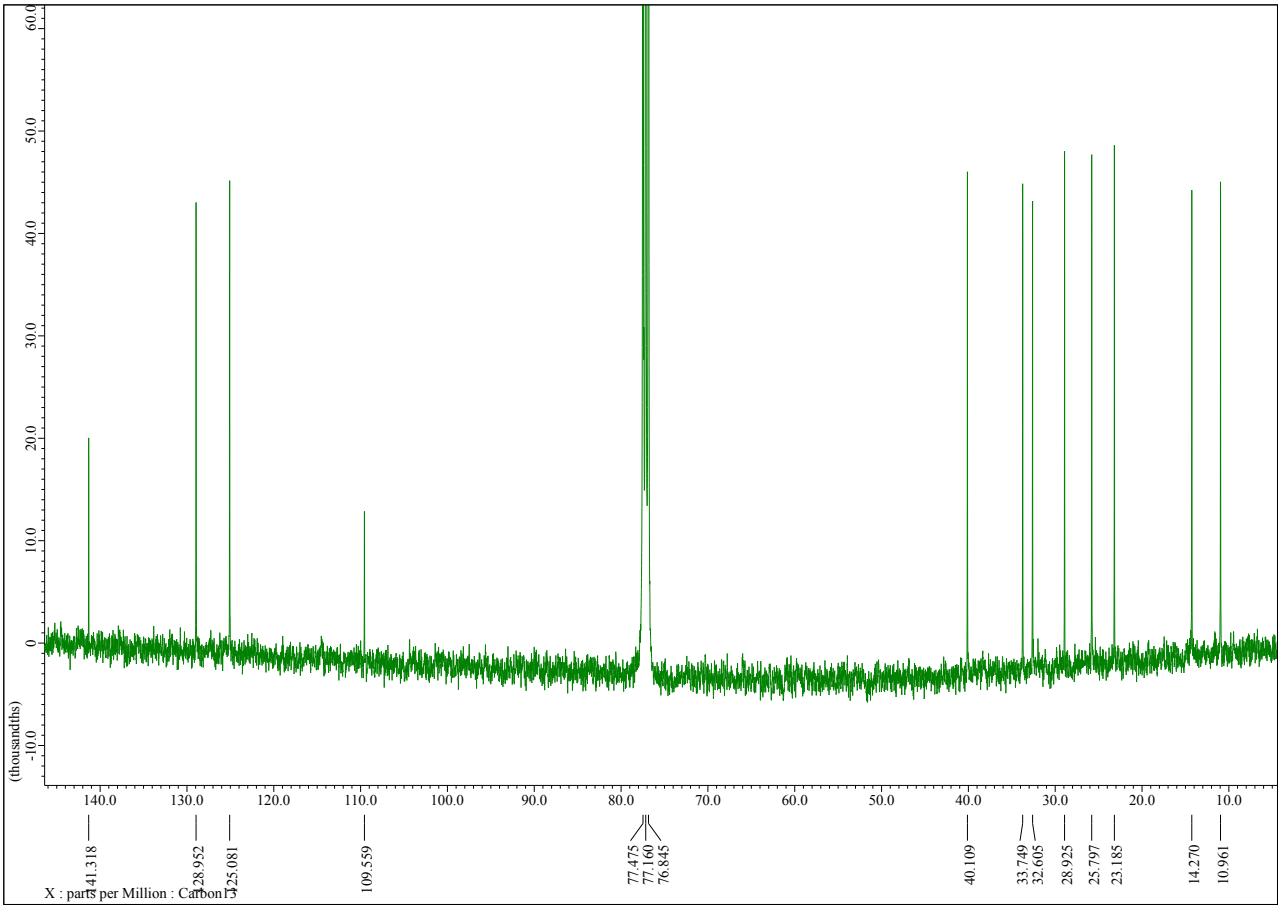


Figure S22. The ^{13}C NMR spectrum of **8**.

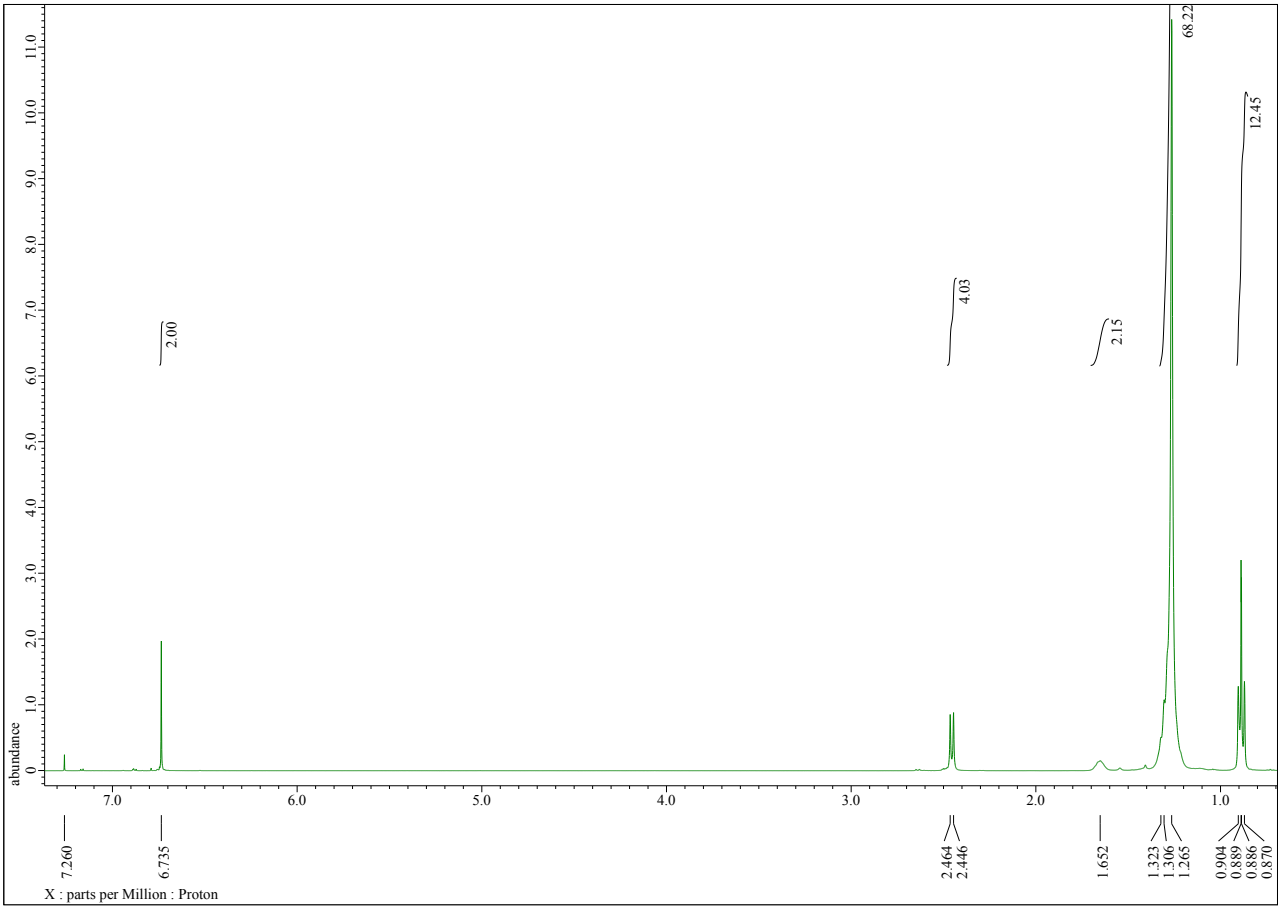


Figure S23. The ^{1}H NMR spectrum of **9**.

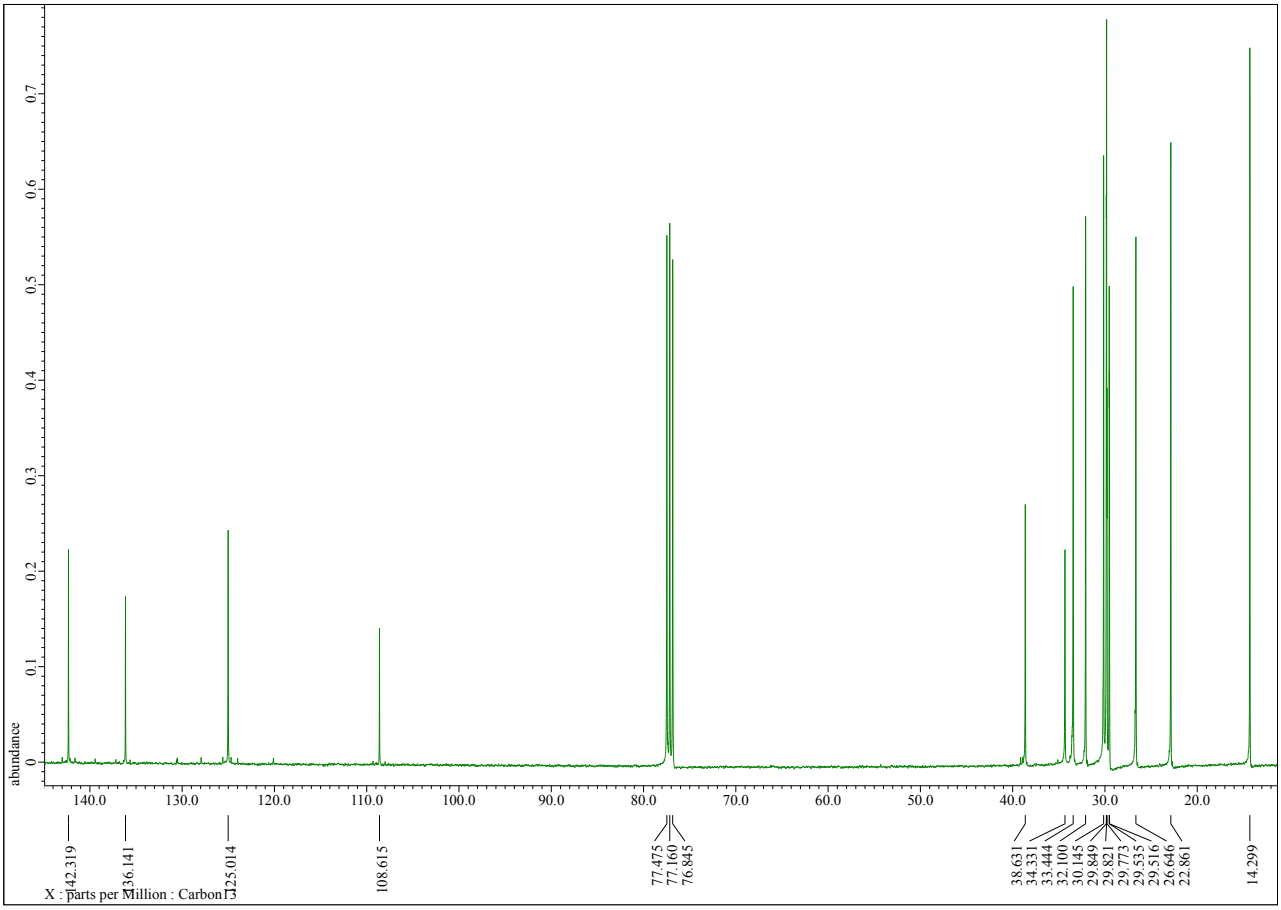


Figure S24. The ^{13}C NMR spectrum of **9**.

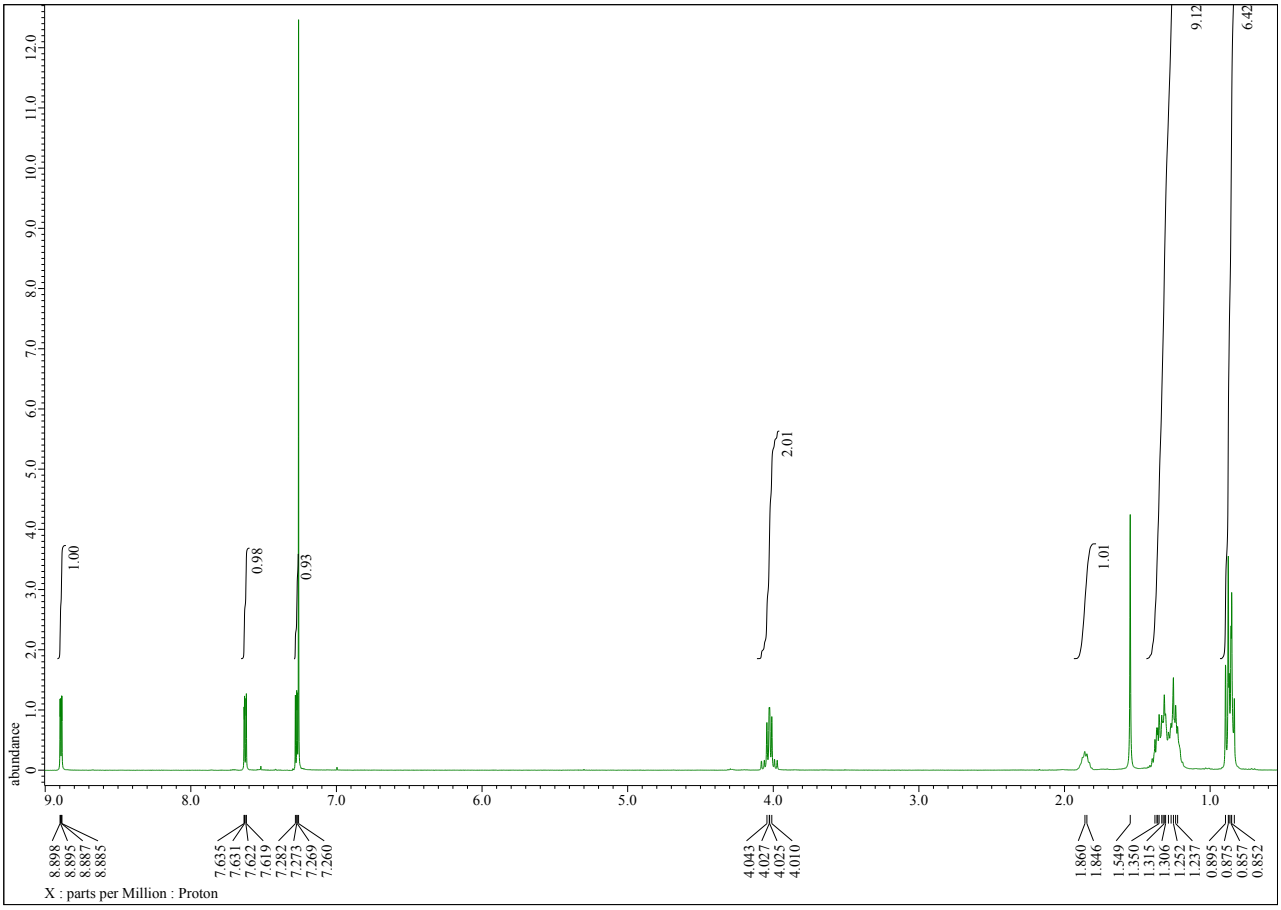


Figure S25. The ^{1}H NMR spectrum of **11**.

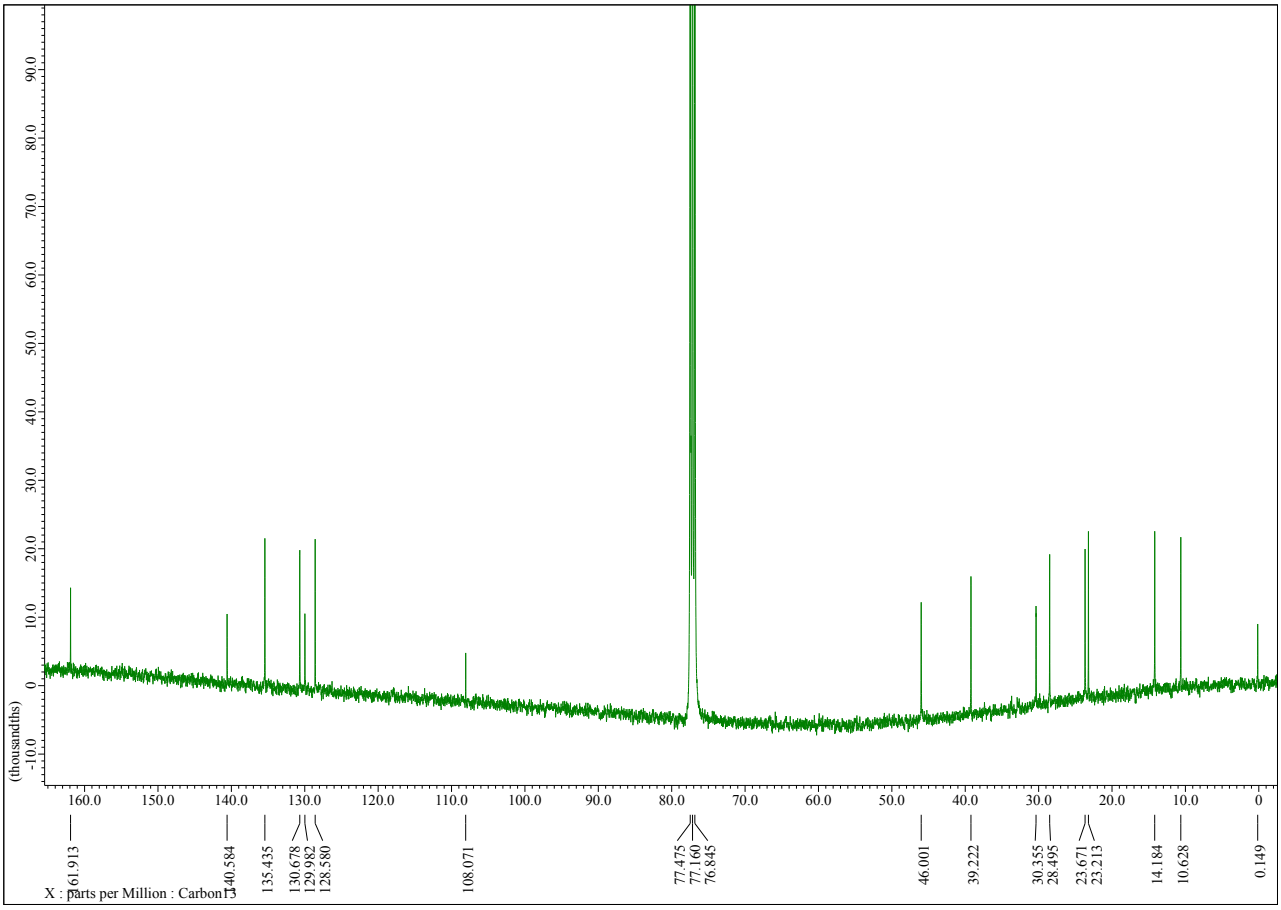


Figure S26. The ^{13}C NMR spectrum of **11**.

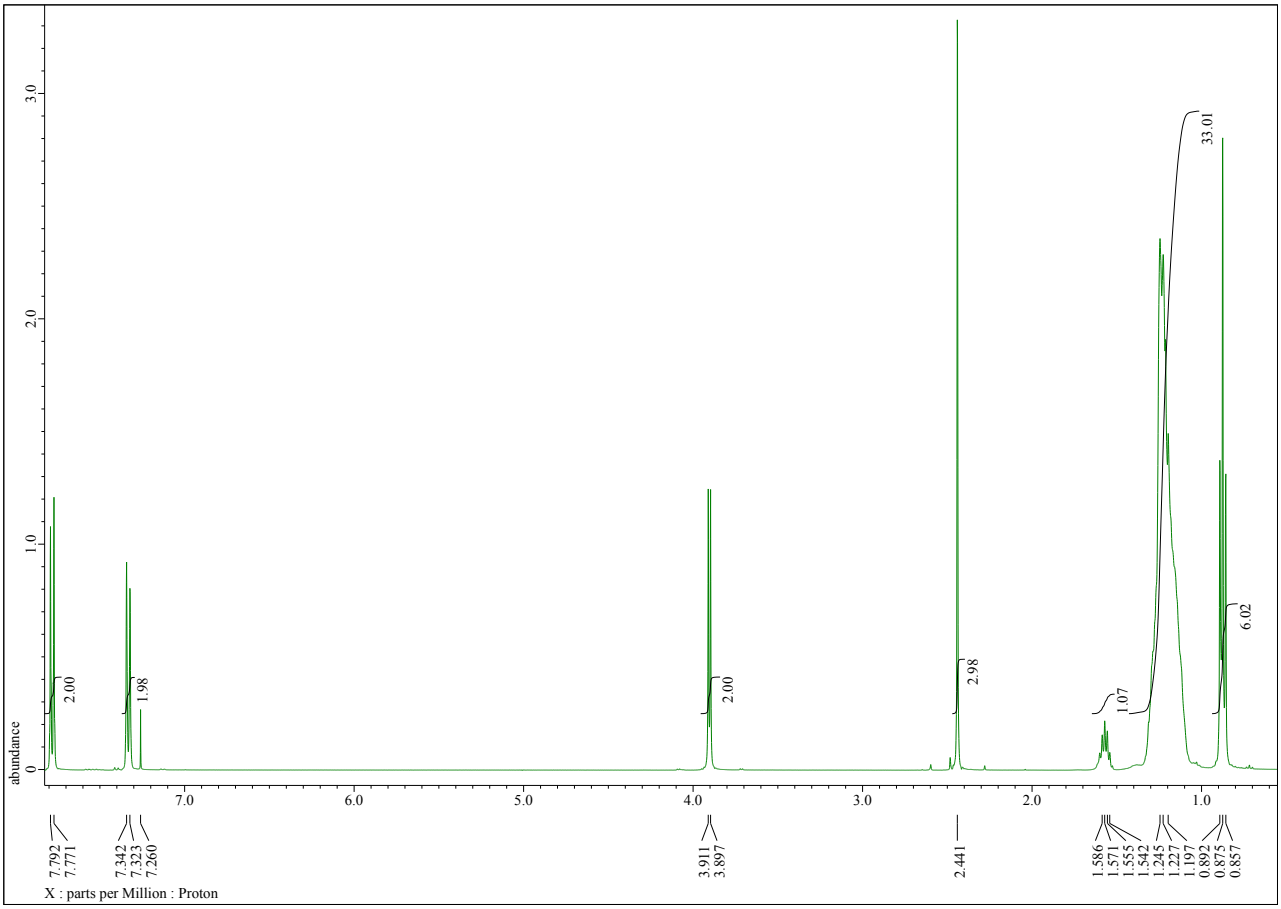


Figure S27. The ^{1}H NMR spectrum of **12**.

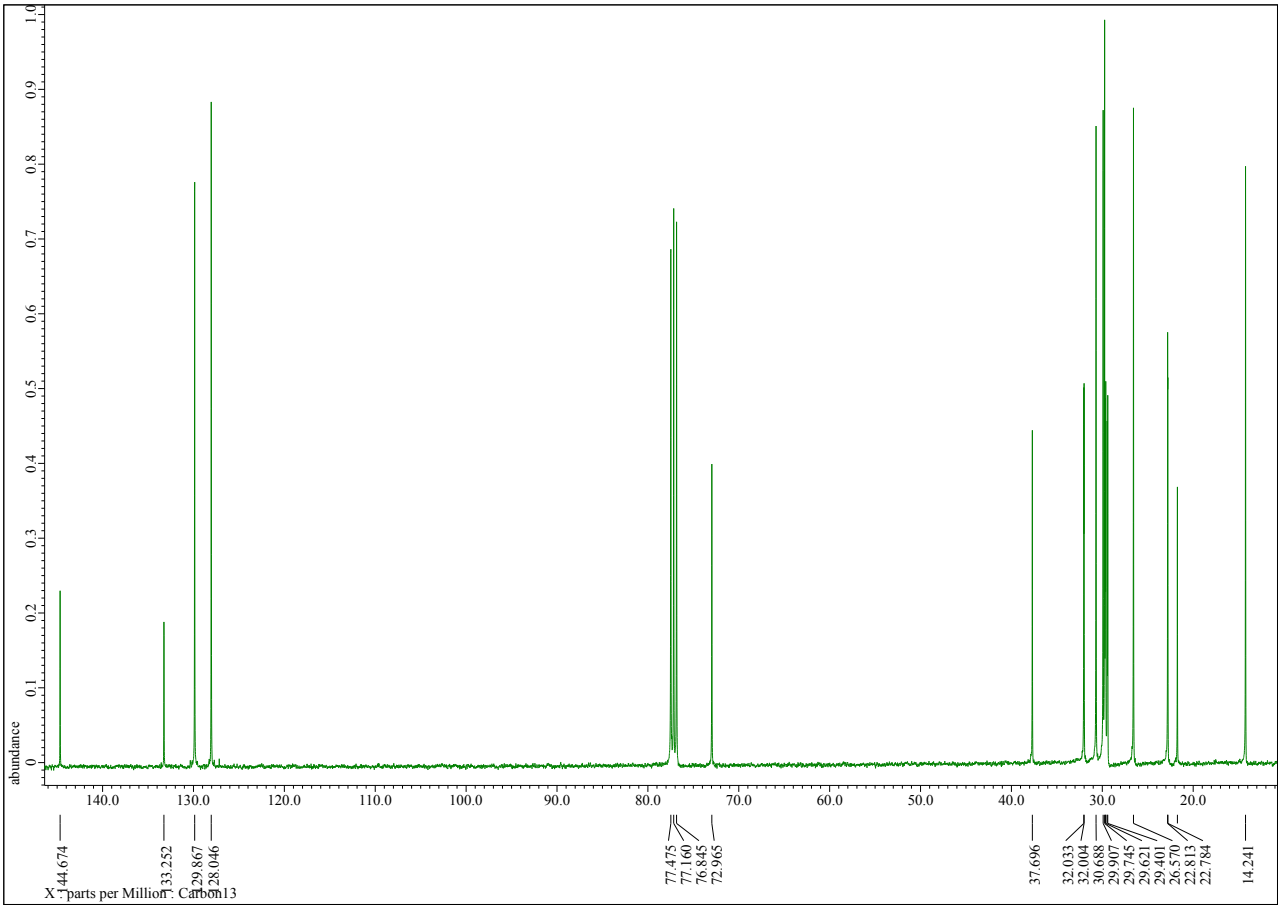


Figure S28. The ^{13}C NMR spectrum of **12**.

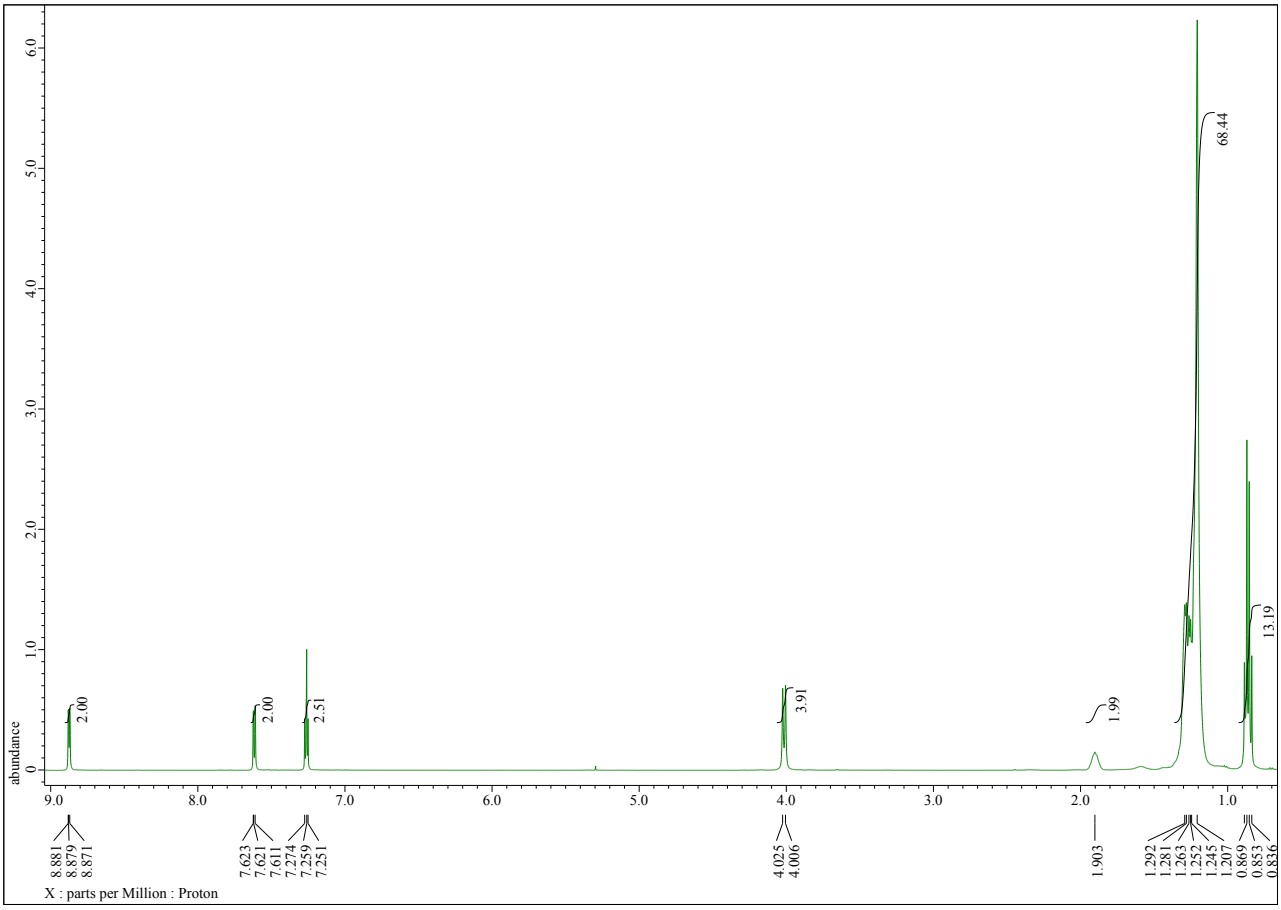


Figure S29. The ^{1}H NMR spectrum of **13**.

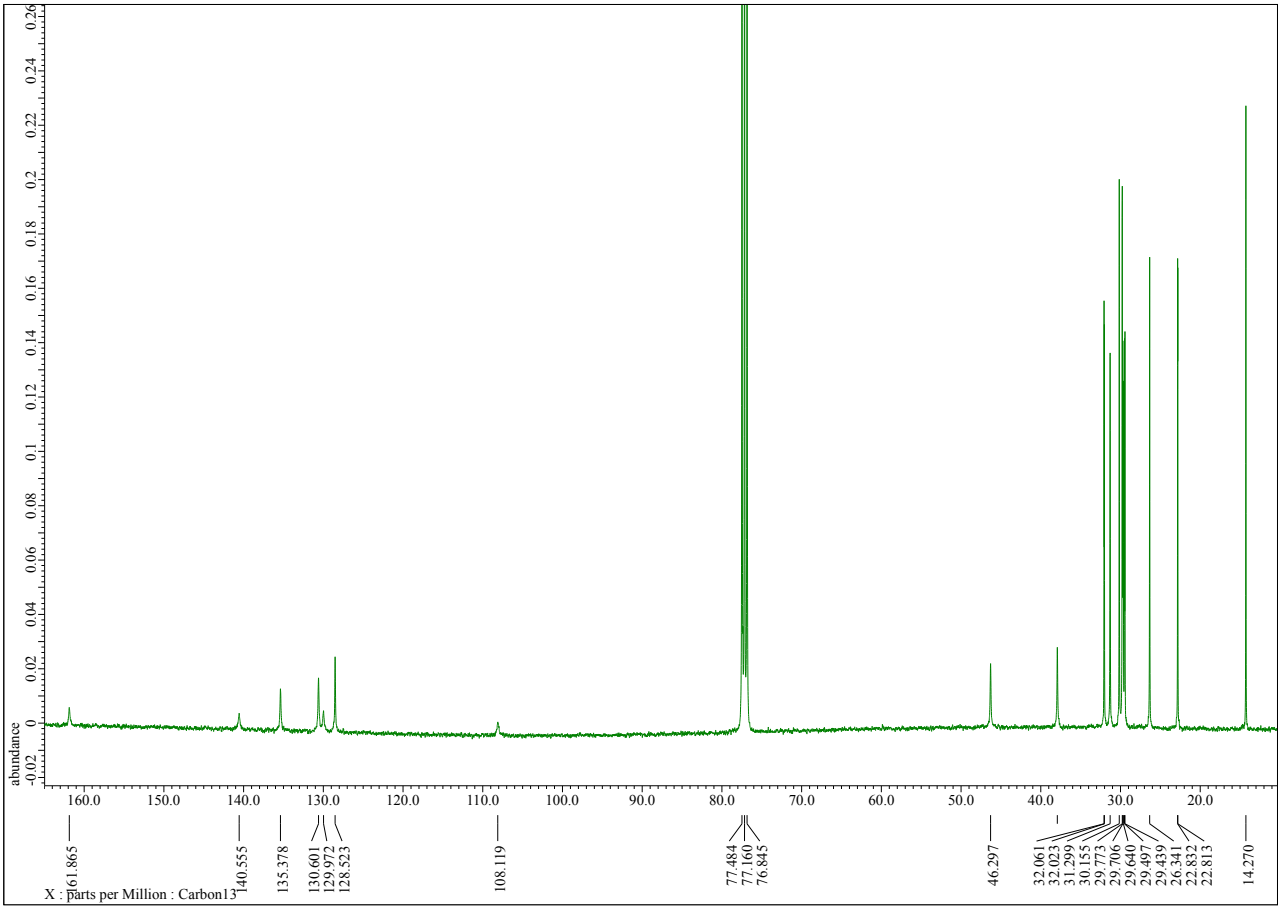


Figure S30. The ^{13}C NMR spectrum of **13**.

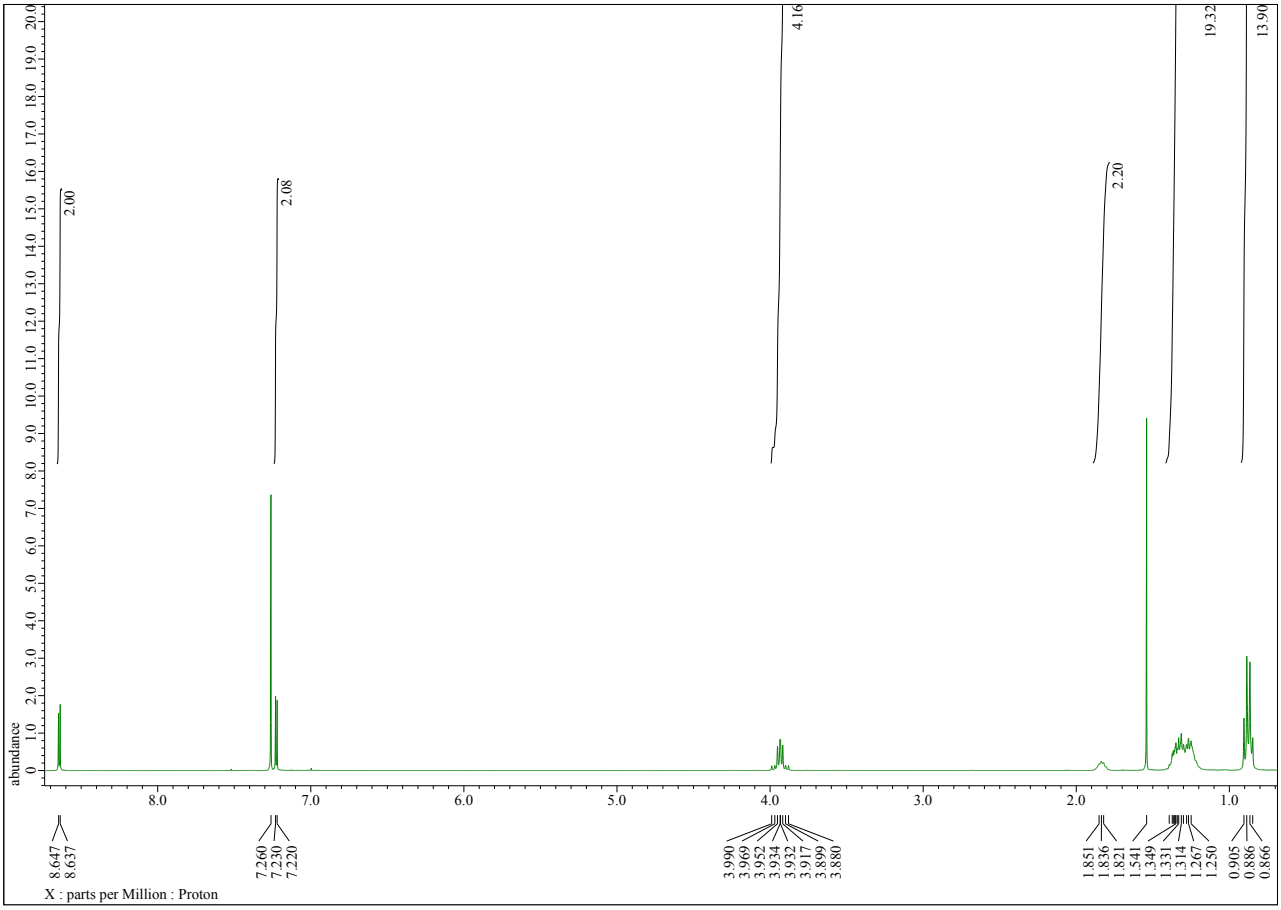


Figure S31. The ^{1}H NMR spectrum of **14**.

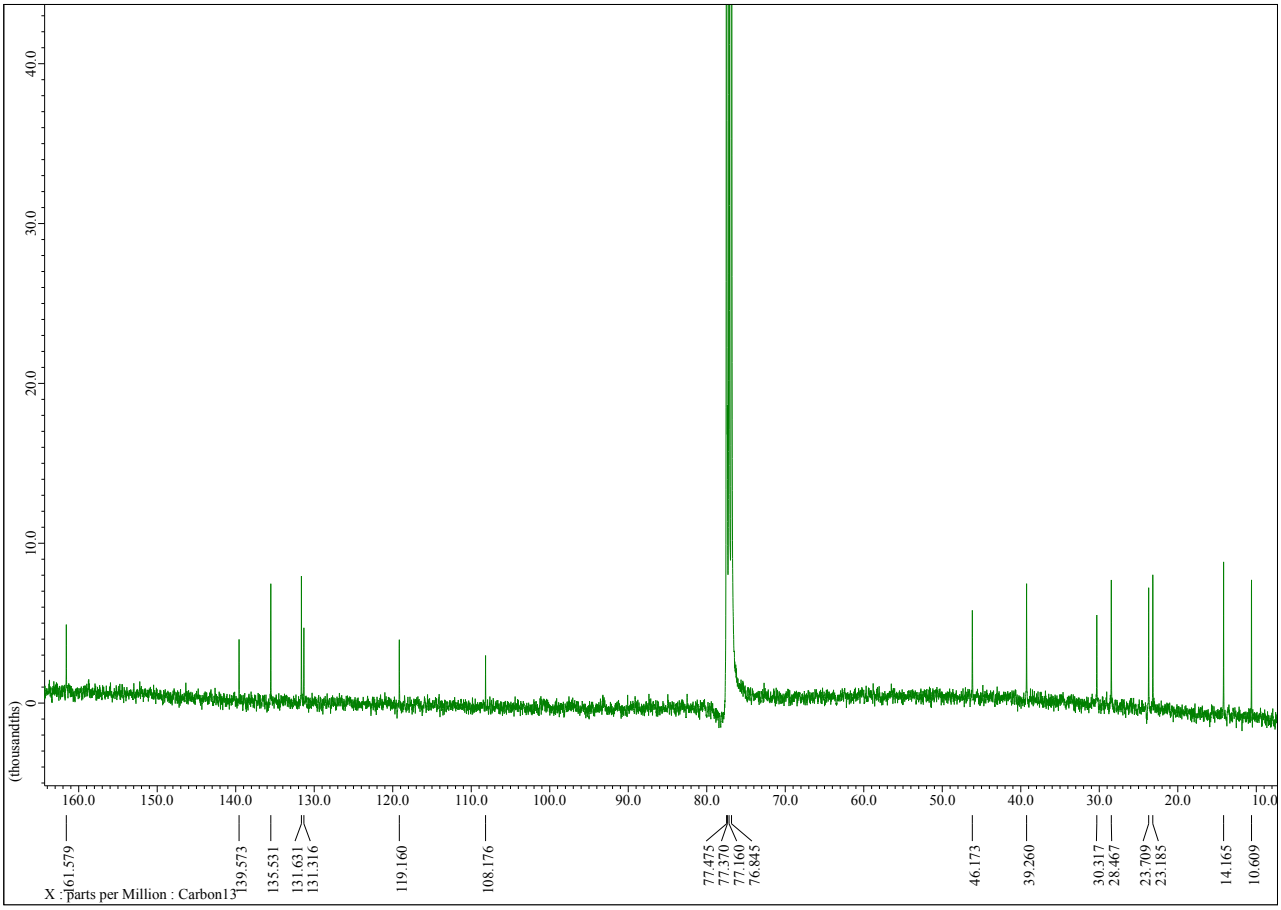


Figure S32. The ^{13}C NMR spectrum of **14**.

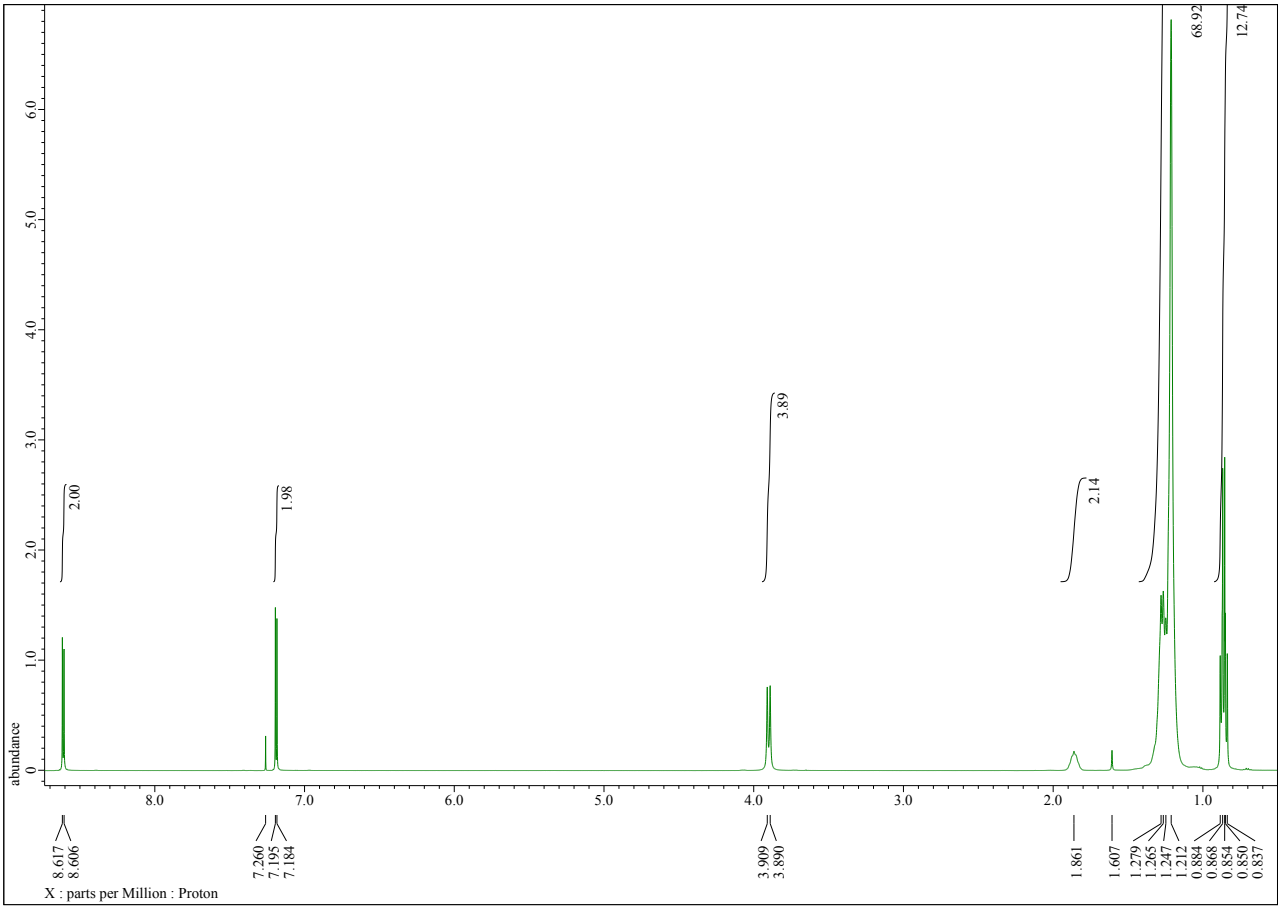


Figure S33. The ^{1}H NMR spectrum of **15**.

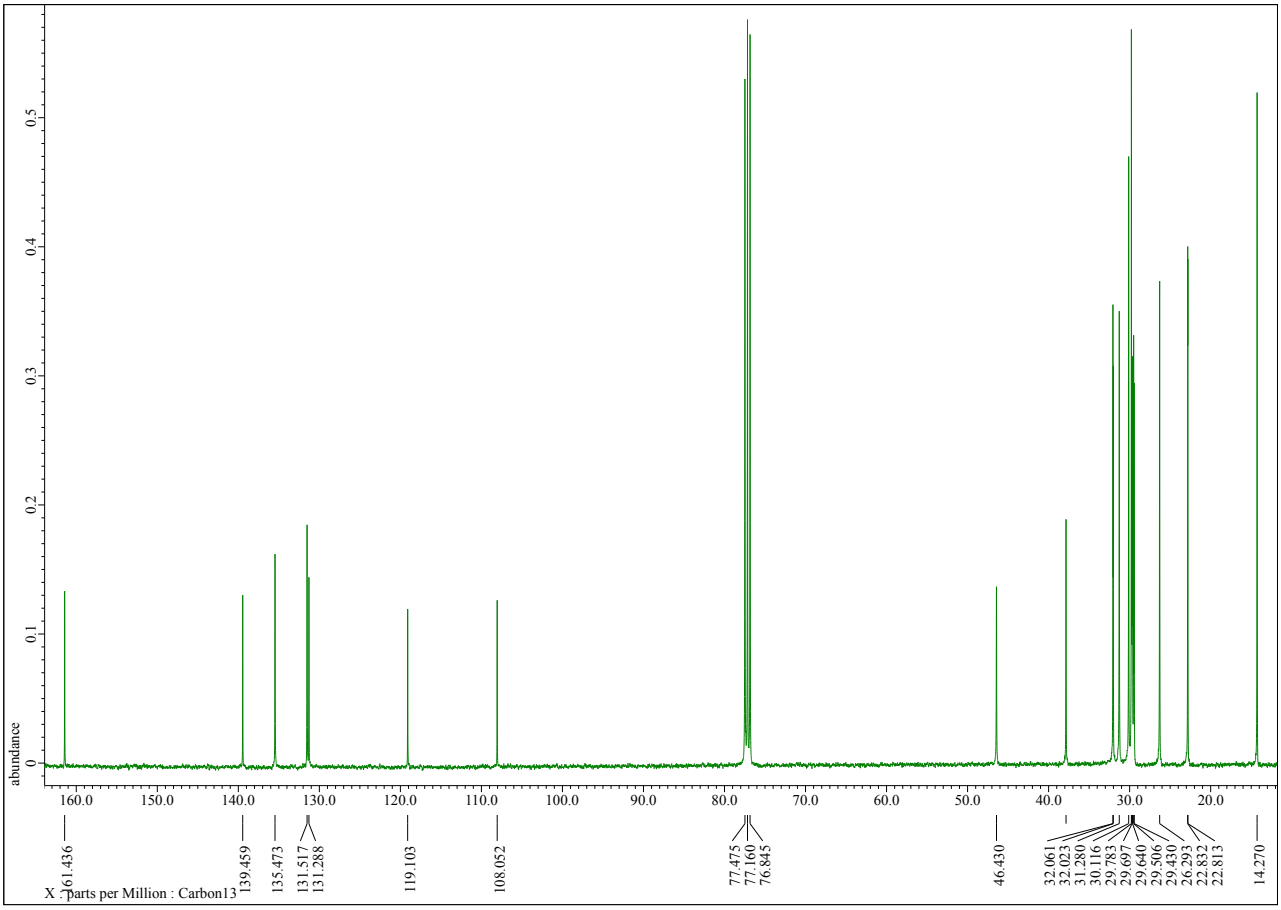


Figure S34. The ^{13}C NMR spectrum of **15**.

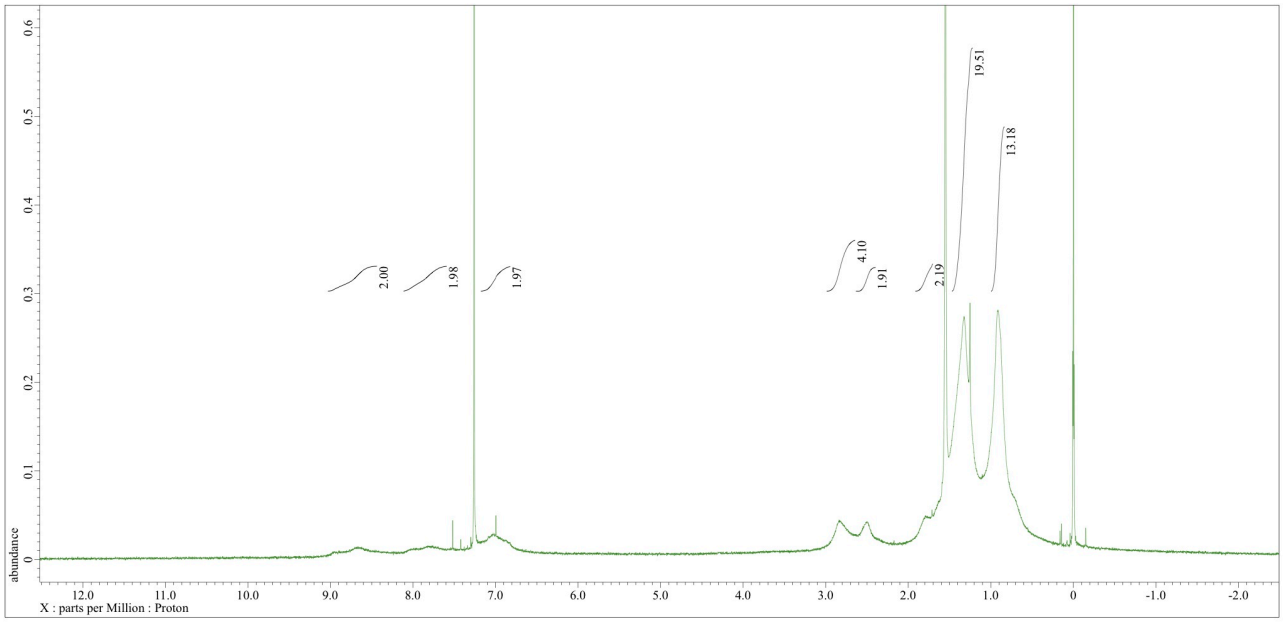


Figure S35. The ^{1}H NMR of **PDTNT-BThEH**.

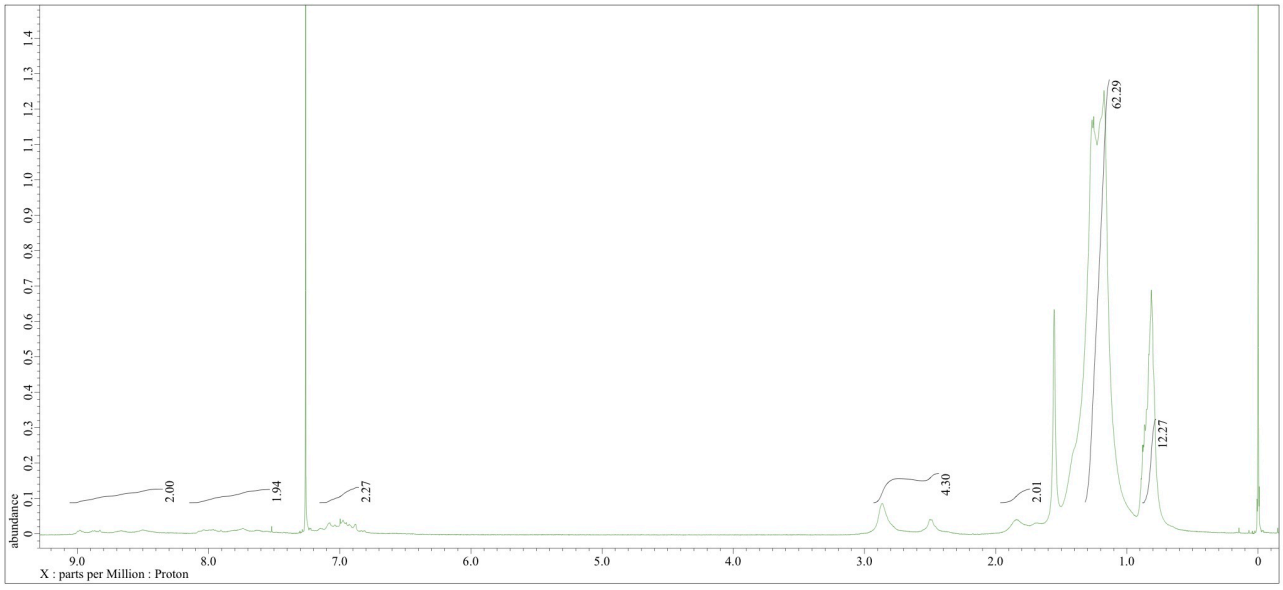


Figure S36. The ^{1}H NMR of **PDTNT-BThOD**.

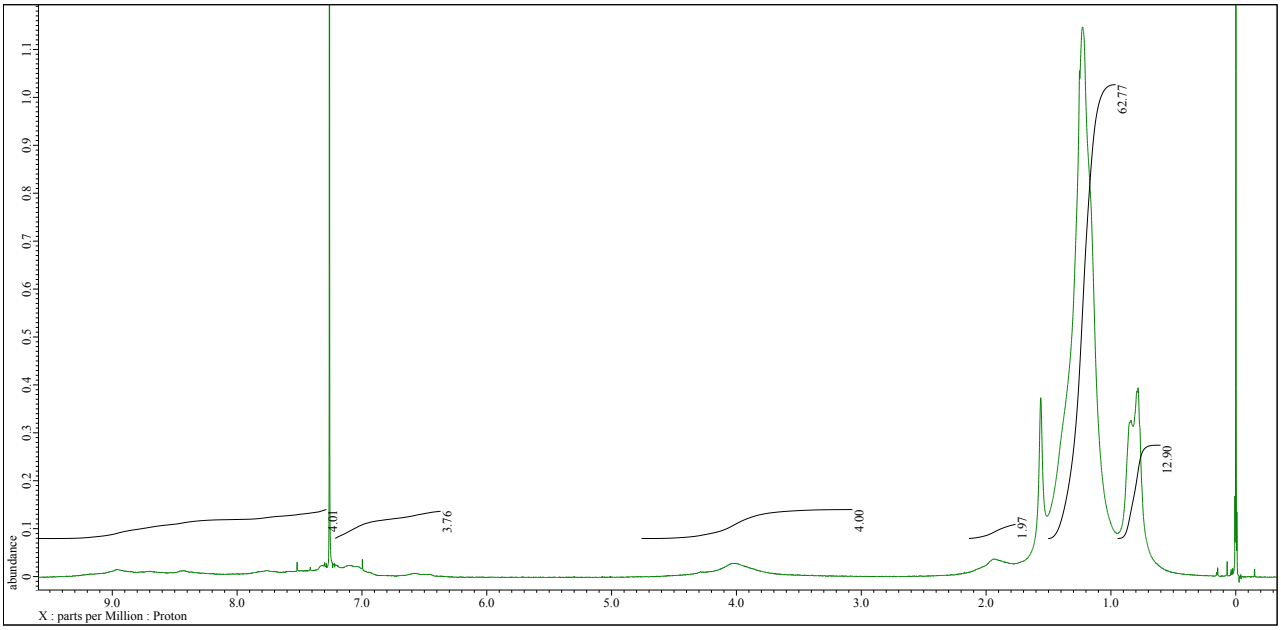


Figure S37. The ^{1}H NMR of **PDTNT-BThOD**.