Supporting Information

Synthesis of Regioregular π-Conjugated Polymers Consisting of Lactam Moiety via Direct Heteroarylation Polymerization

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Table S1. Correlation between molar ratio of Pd catalyst and molecular weight.

Polymers	**Catalyst %**	**Mn (**KDa)	**Mw (**KDa)	**PDI**
PTN-RR	Pd-2%	13.1	20.5	1.56
PTN-RR	Pd-5%	9.6	18.1	1.88
PTN-RR	Pd-10%	10.1	19.3	1.76
PTN-RA	Pd-5%	4.6	10.0	2.17
PTNBT-RR	Pd-2%	3.9	10.2	2.59
PTNBT-RR	Pd-5%	5.7	13.2	2.37
PTNBT-RR	Pd-10%	11.1	23.8	2.12
PTNBT-RA	Pd-10%	4.4	12.5	2.82

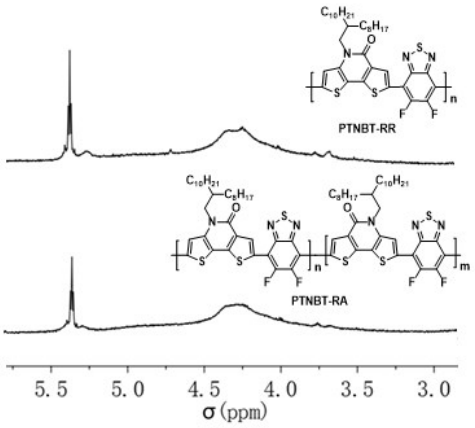


Figure S1. ^{1}H NMR spectra of PTNBT-RR and PTNBT-RA.

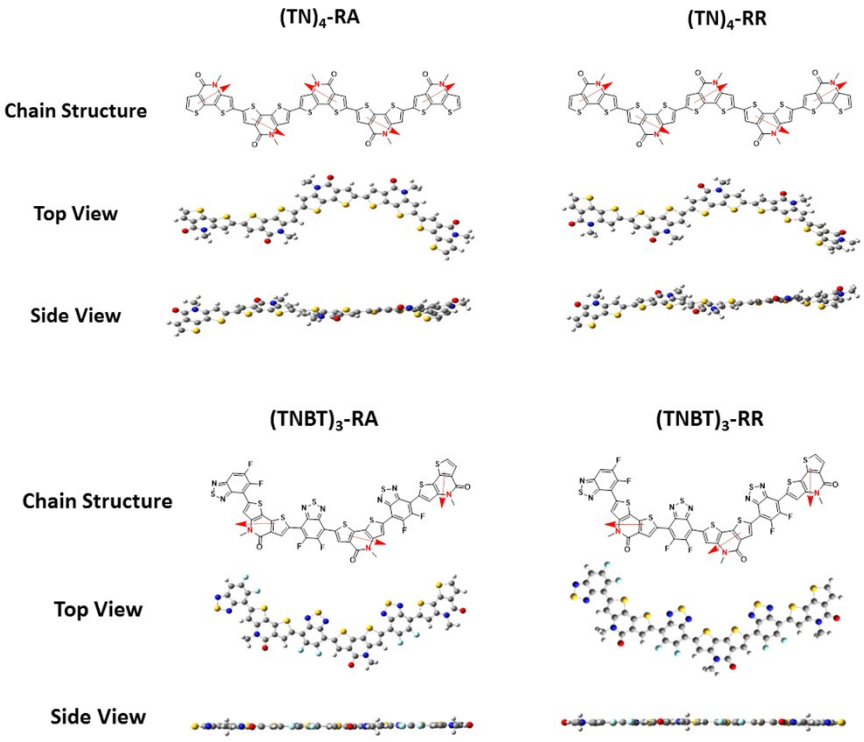


Figure S2. Molecular structures and the calculated geometry of model compounds.

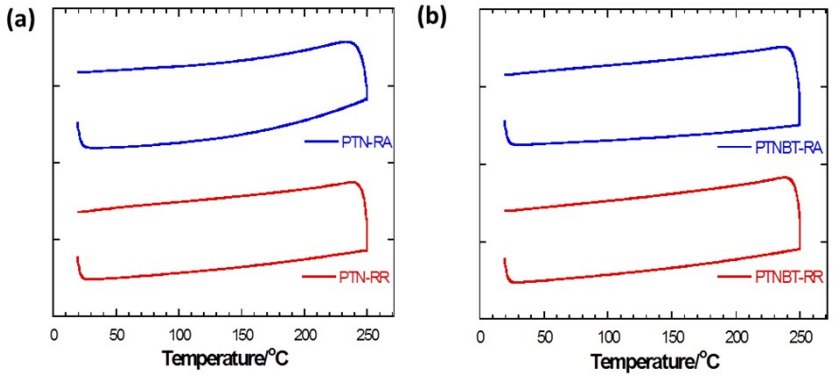


Figure S3. DSC traces of the polymers.

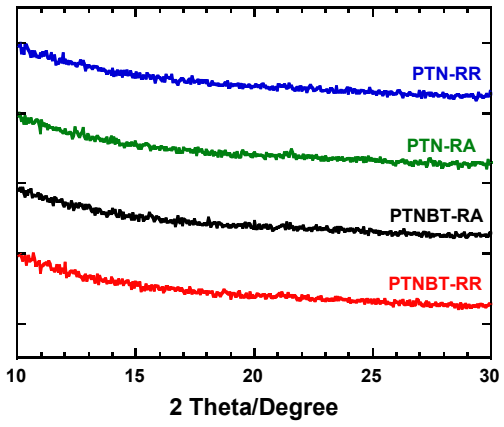


Figure S4. X-ray diffraction patterns of polymers on ITO substrate.

General Experimental Procedures

^{1}H-NMR and ^{13}C-NMR spectra were collected on Bruker AV500 spectrometers in deuterated chloroform solution using tetramethyl silane as the reference. THF was freshly distilled over sodium before use and MeCN was dried by calcium hydride. Xylene(Super Dry) is purchased from Sigma Aldrich.

Scheme S1 Synthesis to monomers and polymers.

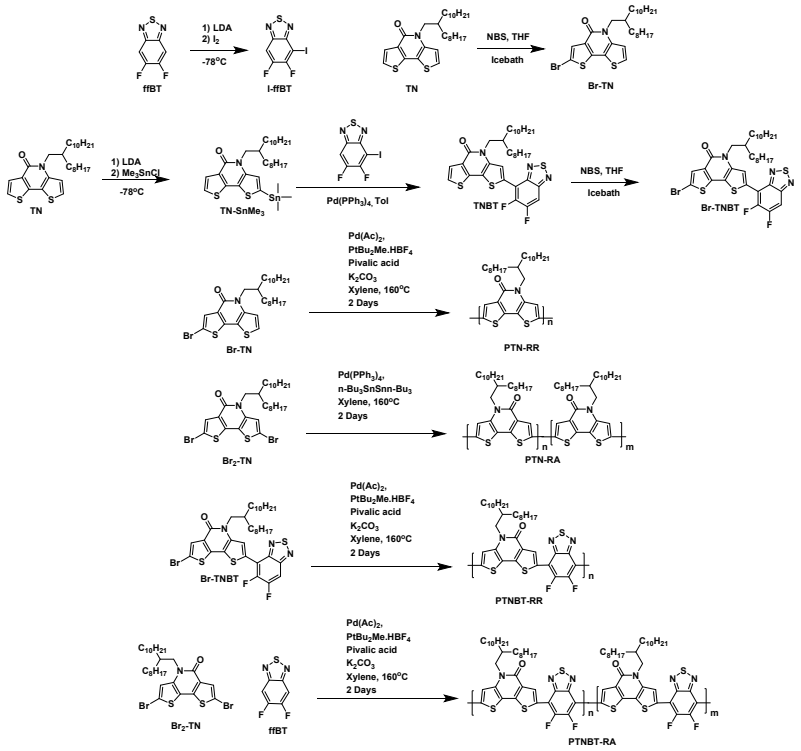
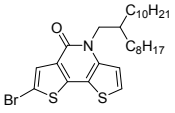
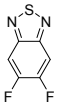
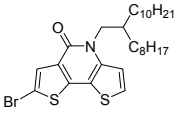
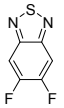
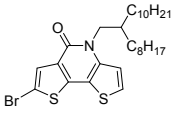
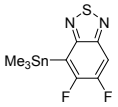
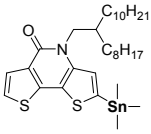
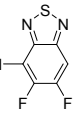


Table S2. Attempts tried for synthesizing **Br-TNBT**(Entry 1) or **TNBT**(Entry 2,3,4)

Entry	Reactants		Coupling Condition	Yield and notes
1			$Pd(Ac)_2$, Ag_2O DMSO 80°C	No target chemical.
2			$Pd(Ac)_2$, $PtBu_2Me.HBF_4$ Pivalic acid K_2CO_3, Toluene,120°C	Trace target chemical. The homo-coupling of TN prevails.
3			$Pd(PPh_3)_4$ Toluene 125°C, MW	Trace target chemical.
4			$Pd(PPh_3)_4$ Xylene 100°C	Yield: 46%

5,6-Difluoro-4-iodobenzo[*c*][1,2,5]thiadiazole (I-ffBT)

Under the protection of Ar, ffBT (1.24 g, 7.2 mmol) was dissolved into 10 mL THF, and the system was subsequently cooled down to -78 °C with stirring. Later 2M LDA solution (3.6 mL, 7.2 mmol) was slowly injected into the solution. After the addition was completed, the system was kept under -78 °C for another four hours. Then iodine (2 g, 8 mmol) was added in one portion at -78 °C and the system was slowly raised to R.T. and stirred overnight. The next day, Na_2SO_3 (aq.) was added to quench the reaction and the dichloromethane was added to extract the target compound for three times. The combine organic layers were then dried by $MgSO_4$ and concentrated under reduced pressure. The crude product was then purified by concentrated under vacuum. The crude product was purified by silica gel chromatography using PE/ dichloromethane = 10/1 (v/v) as eluent to yellow powder (1.78 g, yield = 83%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.74 (dd, *J* = 9.2, 7.5 Hz, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 156.06, 155.91, 155.50, 155.32, 154.35, 154.19, 154.02, 153.87, 153.42, 153.24, 152.54, 152.49, 152.27, 152.11, 150.28, 150.26, 150.24, 148.45, 148.36, 106.19, 106.17, 106.03, 106.01.

4-(2-Octyldodecyl)dithieno[3,2-*b*:2',3'-*d*]pyridin-5(4*H*)-one (TN) and 2,7-dibromo-4-(2-octyldodecyl)dithieno[3,2-*b*:2',3'-*d*]pyridin-5(4*H*)-one (Br_2-TN) were synthesized according to methods reported by Hao et al.[1]

7-Bromo-4-(2-octyldodecyl)dithieno[3,2-*b*:2',3'-*d*]pyridin-5(4*H*)-one (Br-TN)

TN(488mg,1mmol) was dissolved in 3 mL THF and placed in an icebath. Later NBS was added into the system by portions, altogether 178 mg, 1 mmol. After the addition, the solution was slowly raised to room temperature and stirred overnight. The next day, brine was added to quench the reaction and the dichloromethane was added to extract the target compound for three times. The combine organic layers were then dried by $MgSO_4$ and concentrated under reduced pressure. The crude product was then purified by concentrated under vacuum. The crude product was purified by silica gel chromatography using PE/ dichloromethane = 1/1 (v/v) as eluent to yellow oil (365 mg, yield = 64%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.65 (s, 1H), 7.45 (d, *J* = 5.5 Hz, 1H), 7.06 (d, *J* = 5.4 Hz, 1H), 4.30 – 4.09 (m, 2H), 1.96 (h, *J* = 6.9 Hz, 1H), 1.47 – 1.13 (m, 32H), 0.87 (m, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 152.86 , 137.88 , 136.13 , 124.06, 121.36 , 112.81 , 108.56 , 105.82 , 44.55 , 32.49 , 27.16, 26.78 , 25.20 , 24.88 , 24.82 , 24.77 , 24.60 , 24.53 , 21.88 , 17.94, 9.39 .

4-(2-Octyldodecyl)-2-(trimethylstannyl)dithieno[3,2-*b*:2',3'-*d*]pyridin-5(4*H*)-one (TN-$SnMe_3$)

Under the protection of Ar, TN (4.88 g, 10 mmol) was dissolved into 30 mL THF, and the system was subsequently cooled down to -78 °C with stirring. Later 2M LDA solution (6 mL, 12 mmol) was slowly injected into the solution. After the addition was completed, the system was kept under -78 °C for another four hours. Then Me_3SnCl (3 g, 15 mmol) was added in one portion at -78 °C and the system was slowly raised to room temperature and stirred overnight. The next day, brine was added to quench the reaction and the dichloromethane was added to extract the target compound for three times. The combine organic layers were then dried by $MgSO_4$ and concentrated under reduced pressure. The crude product was then purified by concentrated under vacuum. The crude product was used without further purification.

2-(5,6-Difluorobenzo[*c*][1,2,5]thiadiazol-4-yl)-4-(2-octyldodecyl)dithieno[3,2-*b*:2',3'-*d*]pyridin-5(4*H*)-one (TNBT)

In a reaction tube, Sn-TN (775 mg, 1 mmol) and I-ffBT (298 mg, 1 mmol) was dissolved into 5 mL toluene and bubbled with Ar for 10 min. Later 30 mg $Pd(PPh_3)_4$ was added into the reaction tube and the tube was sealed and heated to 100°C for 1 day. The next day, the system was concentrated under reduced pressure. The crude product was purified by silica gel chromatography using PE/dichloromethane = 1/1 (v/v) as eluent to orange solid (296 mg, yield = 46%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.42 (s, 1H), 7.74 – 7.67 (m, 2H), 7.30 (d, *J* = 5.2 Hz, 1H), 4.30 (s, 2H), 2.07 (p, *J* = 6.4 Hz, 1H), 1.50 – 1.15 (m, 32H), 0.85 (dt, *J* = 8.6, 7.0 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.80, 155.17, 155.02, 153.12, 152.97, 150.98, 150.78, 150.63, 150.53, 148.92, 148.65, 140.38, 140.06, 130.81, 129.93, 126.77, 123.85, 120.65, 117.30, 113.19, 104.79, 104.63, 48.92, 37.58, 31.90, 30.03, 29.65, 29.30, 26.85, 22.68, 14.11. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -126.51 (dd, *J* = 16.7, 7.7 Hz), -126.90 (dd, *J* = 16.7, 8.9 Hz).

7-Bromo-2-(5,6-difluorobenzo[*c*][1,2,5]thiadiazol-4-yl)-4-(2-octyldodecyl)dithieno[3,2-*b*:2',3'-*d*]pyridin-5(4H)-one (Br-TNBT)

TNBT (329 mg,0.5 mmol) was dissolved in 3 mL THF and placed in an ice bath. Then NBS was added into the system by portions, altogether 89mg. After the addition, the solution was slowly raised to room temperature and stirred overnight. The next day, brine was added to quench the reaction and the dichloromethane was added to extract the target compound for three times. The combine organic layers were then dried by $MgSO_4$ and concentrated under reduced pressure. The crude product was then purified by concentrated under vacuum. The crude product was purified by silica gel chromatography using PE/ dichloromethane = 1/1 as eluent to orange solid (266 mg, yield = 72%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.28 (d, *J* = 2.1 Hz, 1H), 7.63 (t, *J* = 8.1 Hz, 1H), 7.51 (d, *J* = 4.2 Hz, 1H), 4.17 (s, 2H), 1.94 (p, *J* = 6.6 Hz, 1H), 1.44 – 1.08 (m, 32H), 0.78 (q, *J* = 7.0 Hz, 6H).. ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.31, 153.90, 152.00, 150.06, 149.44, 147.97, 147.44, 140.41, 139.21, 130.40, 128.78, 127.99, 119.39, 114.95, 111.74, 110.88, 103.99, 103.83, 47.91, 36.53, 30.88, 30.69, 29.00, 28.61, 28.31, 25.80, 21.65, 21.63, 13.08. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -126.02 (dd, *J* = 16.2, 7.3 Hz), -126.79 (dd, *J* = 16.6, 8.7 Hz).

General Procedure of Synthesizing Regioregular Polymers(PTNBT-RR and PTN-RR)

In a glove box, 0.1mmol monomer (Br-TN or Br-TNBT) was added into a reaction tube. Afterwards, 1eq pivalic acid, 3eq K_2CO_3, $Pd(Ac)_2$ (n%)and $P(t\text{-}Bu)_2Me{\cdot}HBF_4$ (2 mol%) were added. Before the reaction tube was sealed, 2ml xylene was added. The reaction tube was then heated with oil bath for two days and after the polymerization was completed, the mixture was cooled to room temperature and poured into methanol. After precipitation in MeOH, the precipitate was filtered and dried before purification via Soxhlet extraction. After being purified via Soxhletextraction for 12 h with MeOH, 12 h with hexane, 12 h with dichloromethane, (12 h with chloroform when necessary), the dichloromethane or chloroform solution was then concentrated by evaporation and precipitated into methanol (200 mL). The solid was collected and dried under vacuum.

Yields: PTN-RR: 29% for 2%Pd; 44% for 5%Pd; and 47% for 10%Pd.

PTNBT-RR: 64% for 2%Pd; 59% for 5%Pd; and 35% for 10%Pd.

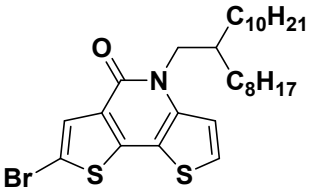
Synthesis of PTNBT-RA

In a glove box, 0.1mmol Br_2-TN and ffBT were added into a reaction tube. Afterwards, 2 eq pivalic acid, 6 eq K_2CO_3, $Pd(Ac)_2$ (10%)and $P(t\text{-}Bu)_2Me{\cdot}HBF_4$ (20%) were added. Before the reaction tube was sealed, 2ml xylene was added. The reaction tube was then heated with oil bath for two days and after the polymerization was completed, the mixture was cooled to room temperature and poured into methanol. After precipitation in MeOH, the precipitate was filtered and was not dried before purification via Soxhlet extraction. After being purified via Soxhlet extraction for 12 h with MeOH, 12 h with hexane, 12 h with dichloromethane, the dichloromethane was then concentrated by evaporation and precipitated into methanol (200 mL). The dark purple solid was collected and dry under vacuum, yield: 35%.

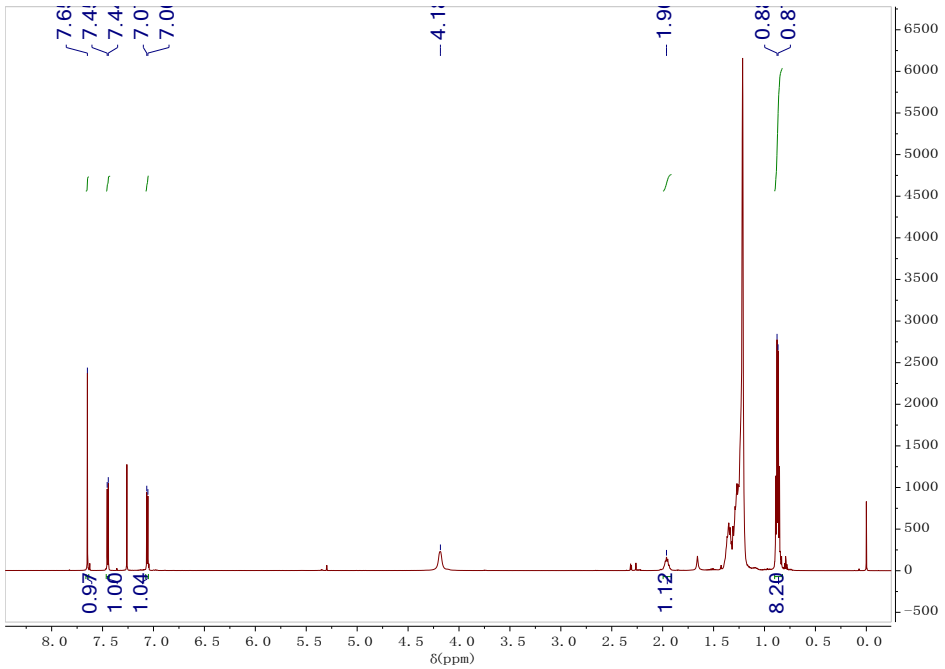
Synthesis of PTN-RA

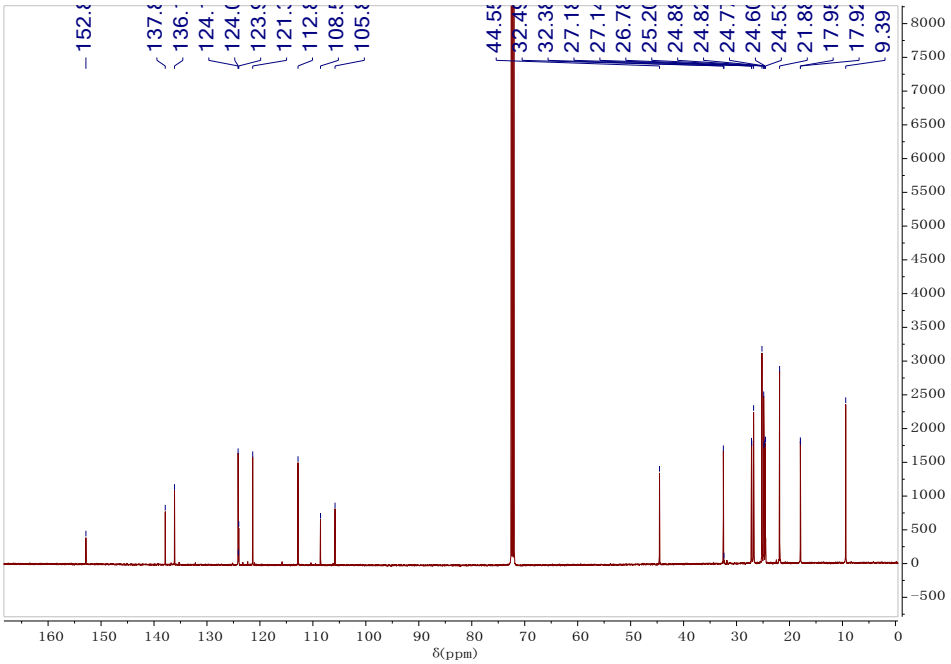
In a glove box, 0.1mmol Br_2-TN and 0.1mmol hexabutyldistannane were added into a reaction tube. Afterwards, $Pd(PPh_3)_4$ were added. Before the reaction tube was sealed, 2ml xylene was added. The reaction tube was then heated with oil bath for two days and after the polymerization was completed, the mixture was cooled to room temperature and poured into methanol. After precipitation in MeOH, the precipitate was filtered and was not dried before purification via Soxhlet extraction. After being purified via Soxhlet extraction for 12 h with MeOH, 12 h with hexane, 12 h with dichloromethane, the dichloromethane was then concentrated by evaporation and precipitated into methanol (200 mL). The dark purple solid was collected and dry under vacuum, yield: 41%.

NMR Spectra of Chemicals

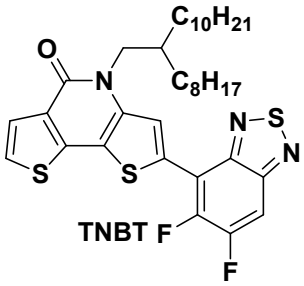


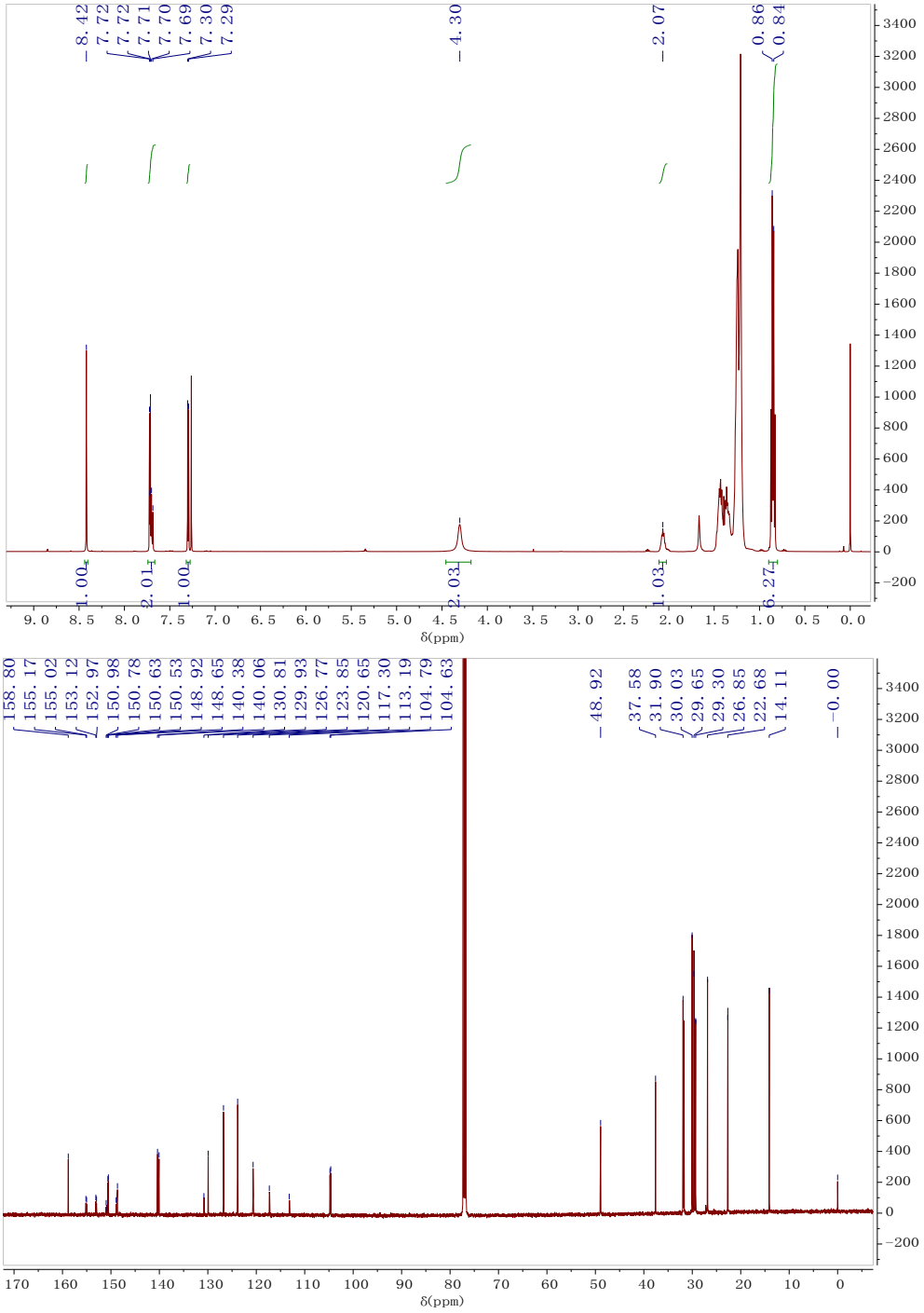
Br-TN



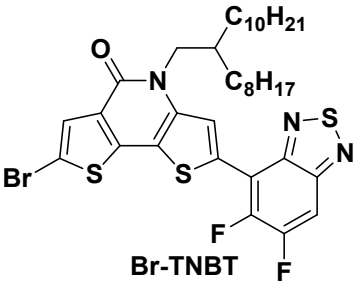


^{1}H and ^{13}C NMR of Br-TN

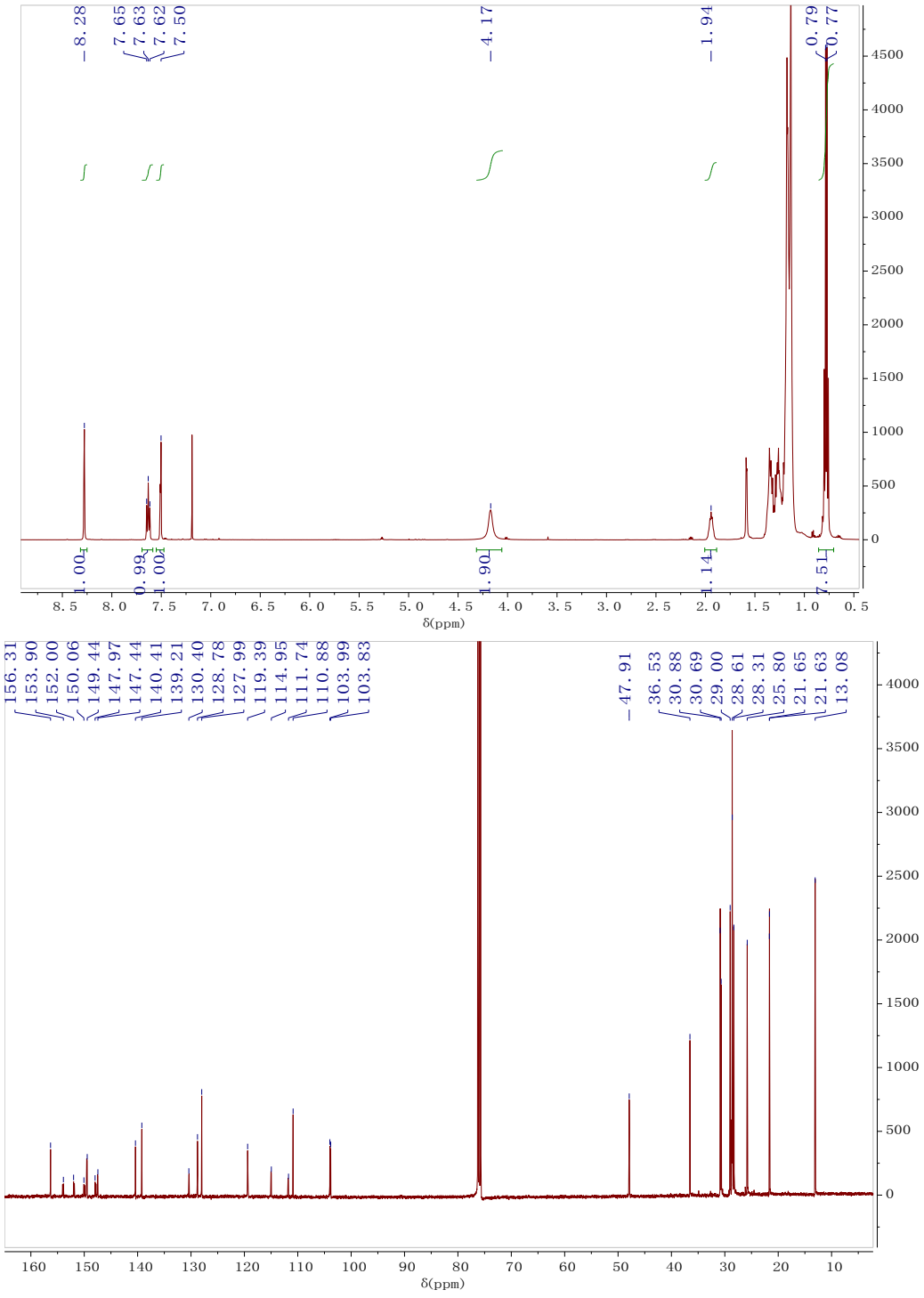




^{1}H and ^{13}C NMR of TNBT



Br-TNBT



^{1}H and ^{13}C NMR of Br-TNBT

Reference:

1. Hao, M.; Luo, G.; Shi, K.; Xie, G.; Wu, K.; Wu, H.; Yu, G.; Cao, Y.; C. Yang, *J. Mater. Chem. A*, **2015**, 3, 20516-20526.