

Supporting Information for

The Unprecedented Side Reactions in the Stille Coupling Reaction

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Supporting Information

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Section 1. General

All organic synthesis were carried out under an inert nitrogen atmosphere. Anhydrous tetrahydrofuran (THF) and toluene were distilled under a nitrogen atmosphere over sodium. 2-Thiophenyl tributylstanne, 3-hexyl-2-thiophenyl tributylstanne, 5-hexyl-2-thiophenyl tributylstanne, 2,2'-bis(trimethylstannyl)-thienothiophene, tributylstannyl chloride, 3-hexyl-2-brom-thiophene were purchased from Energy Chemical Company and used as delivered.

^1H NMR and ^{13}C NMR spectra were recorded using a 400 MHz Varian spectrometer in CDCl_3 at 298 K. Mass spectra (MS) of Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) analysis was performed using Bruker Autoflex II spectrometer.

General Mechanism of the Stille Reaction

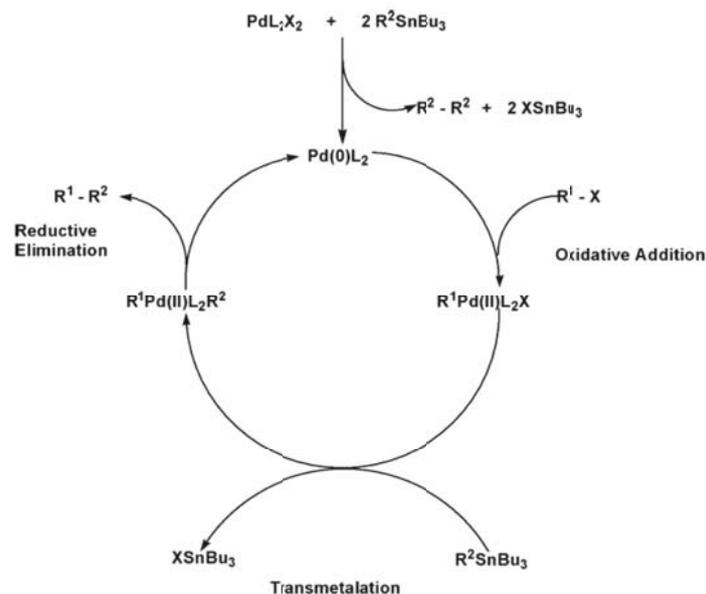


Figure S1. General catalytic cycle of the Stille Reaction¹

Section 2. Synthesis and characterization

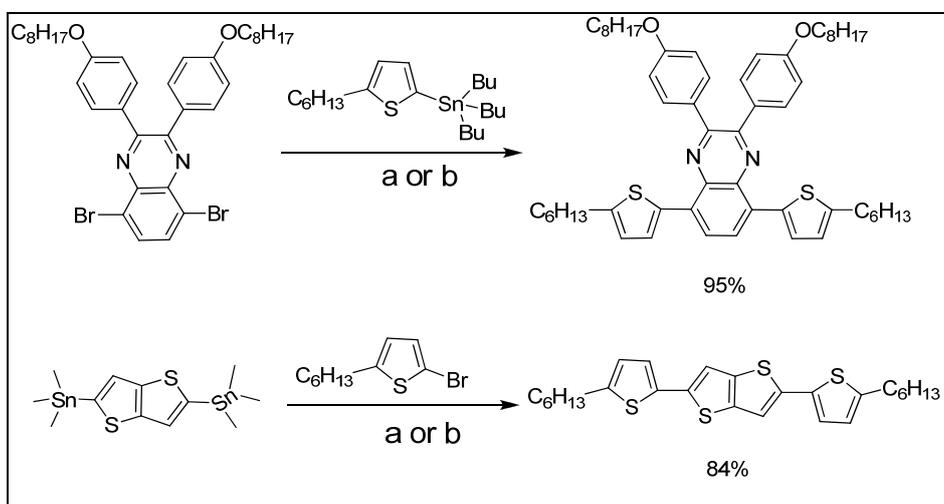
4,7-dibromoquinoline (BrQBr) were prepared according to known procedures with some optimization.² The scheme 2, 3 and 4 in the main manuscript are shown again to show the synthetic route of all compounds.

General synthetic procedures of Stille coupling reaction (I):

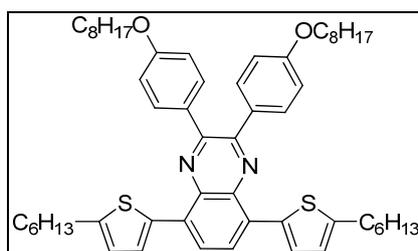
To a fresh-dried Schlenk tube, the organostannes and aryl halides were placed mixed in freshly distilled toluene (1 mmol/10 mL). The Schlenk tube and its contents were subjected to three pump/purge cycles with argon followed by addition of anhydrous and degassed toluene via a syringe. The catalysts of Pd₂(dba)₃ (2 mmol %, based on the reagent which used less) and P(*o*-tol)₃ (4 mmol %, based on the reagent used less) were added before the reaction system was sealed. The reaction mixture was stirred at 90~110 °C for 12~16 hr. After cooling to room temperature, the solvent was evaporated. Then, the products were isolated by silica column chromatography.

General synthetic procedures of the Stille coupling reaction (II):

To a fresh-dried Schlenk tube, organostannes and aryl halides were placed mixed in freshly distilled toluene (1 mmol/10 mL). The Schlenk tube and its contents were subjected to three pump/purge cycles with argon followed by addition of anhydrous and degassed toluene via a syringe. Pd(PPh₃)₄ (1~2 mmol %, based on the reagent used less) was added before the reaction system was sealed. The reaction mixture was stirred at 90~100 °C for 12~16 hr. After cooling to room temperature, the solvent was evaporated. The products were isolated by silica column chromatography.



Scheme S2. Synthetic route of compounds **7** and **8**. Conditions: a) Pd₂(dba)₃, P(*o*-tol)₃, toluene, 110 °C; b) Pd(PPh₃)₄, toluene, 110 °C



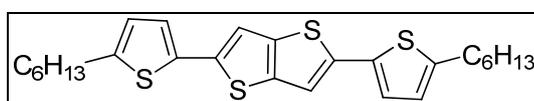
5,8-bis(5-hexylthiophen-2-yl)-2,3-bis(4-(octyloxy)phenyl)quinoxaline (7).

According to **General synthesis method (I)**:

A mixture of 5,8-dibromo-2,3-bis(4-(octyloxy)phenyl)quinoxaline (**BrQBr**) (696 mg, 1.0 mmol), 5-hexyl-2-thiophenyl tributylstanne (1008 mg, 2.2 mmol) and Pd₂(dba)₃ (18.3mg, 0.02 mmol)/P(*o*-tol)₃ (12.2 mg, 0.04 mmol) were heated to 100 °C in toluene (15 mL) for 15 hr in dark under argon atmosphere. After the reaction was confirmed to complete with thin layer chromatography (TLC), it was cooled to room temperature. The solvent was removed under vacuum. The residue was purified by silica gel column chromatography using petroleum ether and dichloromethane (PE/DCM) (6:1, v/v) as the eluent to give **7** as a yellow solid (827 mg, 95%). ¹H NMR (400 Hz, CDCl₃), δ (ppm): 7.94 (s, 3H), 7.48 (s, 3H), 3.96 (t, *J* = 7.5 Hz, 6H),

1.71 (br, 6H), 1.31-1.22 (m, 54H), 0.88 (t, $J = 7.0$ Hz, 9H); ^{13}C NMR (100 Hz, CDCl_3), δ (ppm): 139.95, 138.55, 124.85, 122.68, 118.52, 115.23, 114.40, 101.16, 46.82, 31.95, 30.19, 29.69, 29.67, 29.60, 29.58, 29.40, 29.31, 26.45, 22.73, 14.14. FAB-MS (m/z): calcd. for $\text{C}_{56}\text{H}_{74}\text{N}_2\text{O}_2\text{S}_2$: 1323.15. Found: 1323.0 (M^+), 1243.1 ($\text{M}^+ - \text{Br}$). Elemental Analysis: calcd. for $\text{C}_{56}\text{H}_{74}\text{N}_2\text{O}_2\text{S}_2$: C, 77.19; H, 8.56; N, 3.22. Found: C, 77.23; H, 8.50; N, 3.22.

When the synthesis of **7** was conducted according to **general synthesis method (II)**, the result was similar with a yield of ~95%.

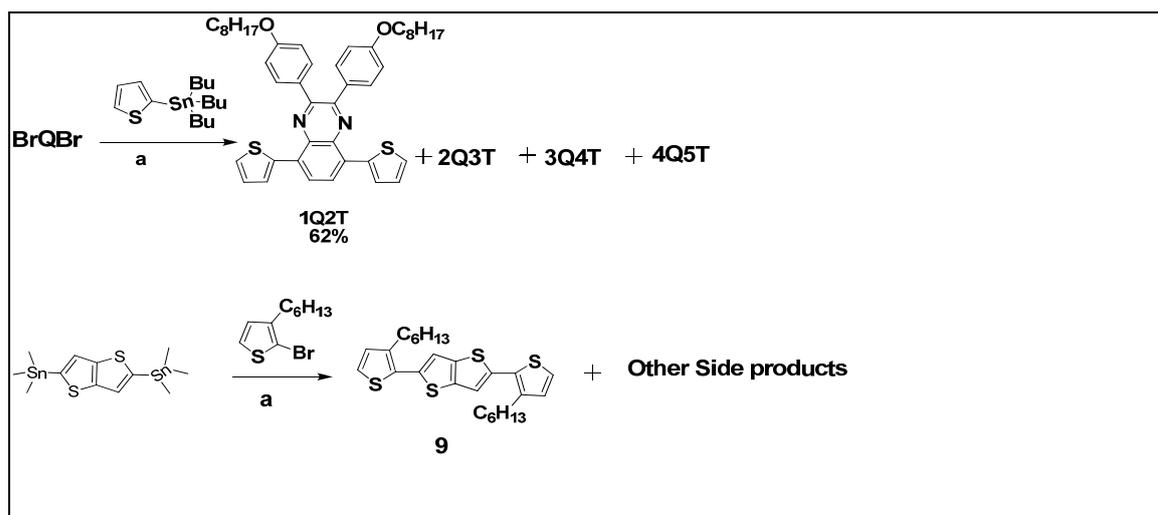


5,8-bis(5-hexylthiophen-2-yl)-2,2'-thienylthiophene (8).

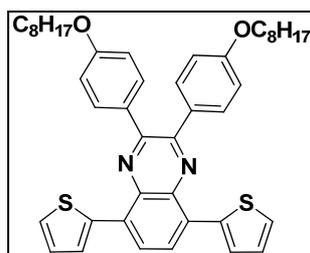
According to **General synthesis method (II)**:

A mixture of 2,2'-bis(trimethylstanne)-thienothiophene (930 mg, 2.0 mmol), 5-hexyl-2-thiophenyl bromide (1.06 g, 4.3 mmol) and $\text{Pd}_2(\text{dba})_3$ (36 mg, 0.04 mmol)/ $\text{P}(\text{o-tol})_3$ (24 mg, 0.08 mmol) were heated to 100 °C in toluene (15 mL) for 12 hr in dark under argon atmosphere. After the reaction was confirmed to complete with thin layer chromatography (TLC), it was cooled to room temperature. The solvent was removed under vacuum. The residue was purified by silica gel column chromatography using petroleum ether PE as the eluent to give **2** as a yellowish solid (793 mg, 84%). ^1H NMR (400 MHz, CDCl_3), δ (ppm): 7.19 (s, 2H), 7.00 (d, $J = 3.5$ Hz, 2H), 6.69 (d, $J = 3.5$ Hz, 2H), 2.80 (t, $J = 7.6$ Hz, 4H), 1.75 – 1.61 (m, 4H), 1.43 – 1.27 (m, 12H), 0.90 (t, $J = 7.0$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3), δ (ppm): 145.84, 139.09, 137.93, 135.04, 124.85, 123.18, 115.17, 31.59, 31.57, 30.22, 28.76, 22.60, 14.1.

When the synthesis of **8** was conducted according to **general synthesis method (I)**, the result was similar with a yield of ~85%.



Scheme S3. C-H direct-stannylation resulted side reactions, a) Pd₂(dba)₃, P(*o*-tol)₃, toluene, 110 °C, 16 hr.



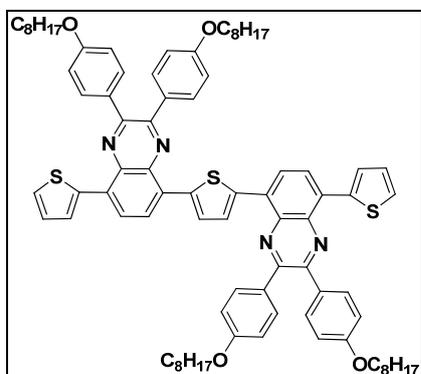
5,8-bis(hexylthiophen-2-yl)-2,3-bis(4-(octyloxy)phenyl)quinoxaline (1Q2T)

According to **General synthesis method (I)**:

A mixture of 5,8-dibromo-2,3-bis(4-(octyloxy)phenyl)quinoxaline (**BrQBr**) (696 mg, 1.0 mmol), 2-thiophenyl tributylstanne (823 mg, 2.2 mmol) and Pd₂(dba)₃ (18 mg, 0.02 mmol)/P(*o*-tol)₃ (12 mg, 0.04 mmol) were heated to 100 °C in toluene (15 mL) for 15 hr in dark under argon atmosphere. After the reaction was confirmed to complete with thin layer chromatography (TLC), it was cooled to room temperature. The solvent was removed under vacuum. The residue was purified by silica gel column chromatography using petroleum ether and dichloromethane (PE/DCM) (6:1, v/v) as the eluent to give **1Q2T** as a yellow solid (435 mg, 62%).

¹H NMR (400 MHz, CDCl₃), δ (ppm): 8.10 (s, 2H), 7.86 (d, *J* = 4.5 Hz, 2H), 7.73 (d, *J* = 11.4 Hz, 4H), 7.51 (d, *J* = 5.8 Hz, 2H), 7.18 (m, 2H), 6.90 (t, *J* = 11.5 Hz, 4H), 4.01 (t, *J* = 6.6 Hz, 4H), 1.93 – 1.73 (m, 4H), 1.52 – 1.24 (m, 20H), 0.90 (t, *J* = 6.8 Hz,

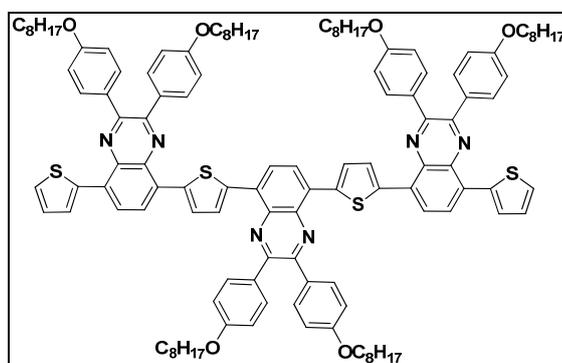
6H). ^{13}C NMR (100 MHz, CDCl_3), δ (ppm): 160.10, 151.28, 139.05, 137.07, 131.99, 131.16, 131.04, 128.70, 126.65, 126.53, 126.21, 114.24, 68.08, 31.86, 29.71, 29.38, 29.28, 29.26, 26.10, 22.65, 14.13, 14.11. MS (MALDI-TOF): calcd for $\text{C}_{44}\text{H}_{50}\text{N}_2\text{O}_2\text{S}_2$ $[\text{M}]^+$, 702.330; found, 702.192.



2Q3T (140 mg, 21%)

The yield was calculated based on **BrQBr**.

^1H NMR (400 MHz, CDCl_3), δ (ppm): 8.02 (s, 4H), 7.87 (s, 2H), 7.83 (d, $J = 3.3$ Hz, 2H), 7.72 (d, $J = 8.7$ Hz, 4H), 7.63 (d, $J = 8.7$ Hz, 4H), 7.51 (d, $J = 5.0$ Hz, 2H), 7.22 – 7.10 (m, 2H), 6.90 (d, $J = 8.8$ Hz, 4H), 6.71 (d, $J = 8.7$ Hz, 4H), 3.93 (dt, $J = 51.7, 6.6$ Hz, 8H), 1.88 – 1.65 (m, 8H), 1.55 – 1.24 (m, 48H), 0.91 (m, 12H). ^{13}C NMR (100 MHz, CDCl_3), δ (ppm): 159.95, 159.81, 151.08, 151.07, 141.57, 139.07, 137.29, 136.95, 131.90, 131.83, 131.45, 131.27, 131.08, 130.74, 128.59, 126.92, 126.54, 126.49, 126.08, 114.19, 114.09, 68.07, 68.03, 31.87, 31.85, 29.43, 29.33, 29.31, 29.29, 29.27, 26.12, 26.07, 22.70, 22.68, 14.14, 14.12. MS (MALDI-TOF): calcd for $\text{C}_{84}\text{H}_{96}\text{N}_4\text{O}_4\text{S}_3$ $[\text{M}]^+$, 1321.66; found, 1321.384.

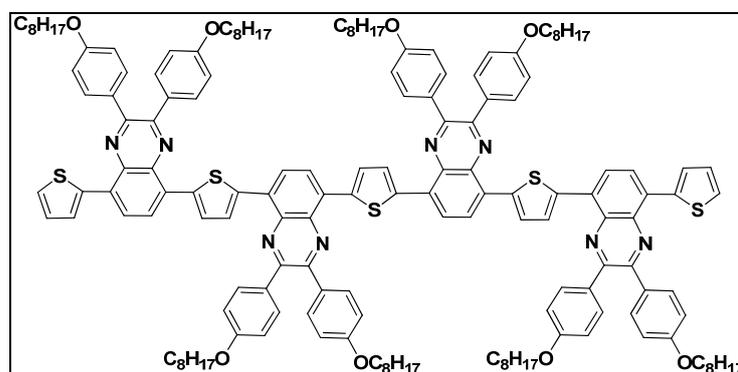


3Q4T (77.6 mg, 8%)

The yield was calculated based on **BrQBr**.

^1H NMR (400 MHz, CDCl_3), δ (ppm): 8.11 (d, $J = 9.2$ Hz, 6H), 7.97 (s, 4H), 7.86 (d, $J = 3.3$ Hz, 2H), 7.74 (d, $J = 8.7$ Hz, 4H), 7.70 – 7.62 (m, 8H), 7.52 (d, $J = 5.0$ Hz, 2H), 7.19 (m, 2H), 6.91 (d, $J = 8.8$ Hz, 4H), 6.74 (d, $J = 8.0$ Hz, 8H), 3.94 (dt, $J = 12.3, 6.4$ Hz, 12H), 1.83 – 1.70 (m, 12H), 1.48 – 1.26 (m, 72H) 0.96 – 0.78 (m, 18H).

^{13}C NMR (100MHz, CDCl_3), δ (ppm): 159.91, 159.79, 159.77, 150.99, 150.96, 150.79, 141.47, 141.46, 139.09, 137.33, 137.28, 136.93, 131.89, 131.84, 131.81, 131.41, 131.28, 131.23, 131.15, 131.13, 130.62, 128.58, 127.14, 126.94, 126.54, 126.43, 126.00, 114.15, 114.07, 114.04, 68.06, 68.02, 31.87, 31.86, 31.82, 29.46, 29.44, 29.43, 29.34, 29.29, 29.28, 29.25, 26.12, 26.10, 26.05, 22.70, 22.68, 22.65, 14.13, 14.12, 14.10. MS (MALDI-TOF): calcd for $\text{C}_{124}\text{H}_{142}\text{N}_6\text{O}_6\text{S}_4$ $[\text{M}]^+$, 1939.99; found, 1939.469.



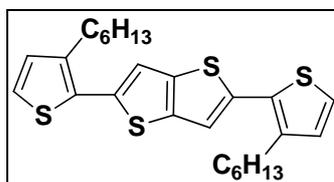
4Q5T (75 mg, 3 %)

The yield was calculated based on **BrQBr**.

^1H NMR (400 MHz, CDCl_3), δ (ppm): 7.95-7.87 (b, 8H), 7.84 (b, 4H), 7.79 (b, 4H), 7.72 (b, 4H), 7.70–7.52 (m, 12H), 7.42 (m, 2H), 7.19 (m, 2H), 6.85 (m, 4H), 6.68 (m, 12H), 3.94 (m, 4H), 3.90 (m, 12H), 1.83–1.70 (m, 16H), 1.48–1.26 (m, 82H), 0.96–0.78 (m, 24H). MS (MALDI-TOF): calcd for $\text{C}_{164}\text{H}_{188}\text{N}_8\text{O}_8\text{S}_5$ $[\text{M}]^+$, 2557.32; found, 2558.258.

When the reaction of **entry 2** was conducted according to **general synthesis**

method (I), the results were similar with yields variable.

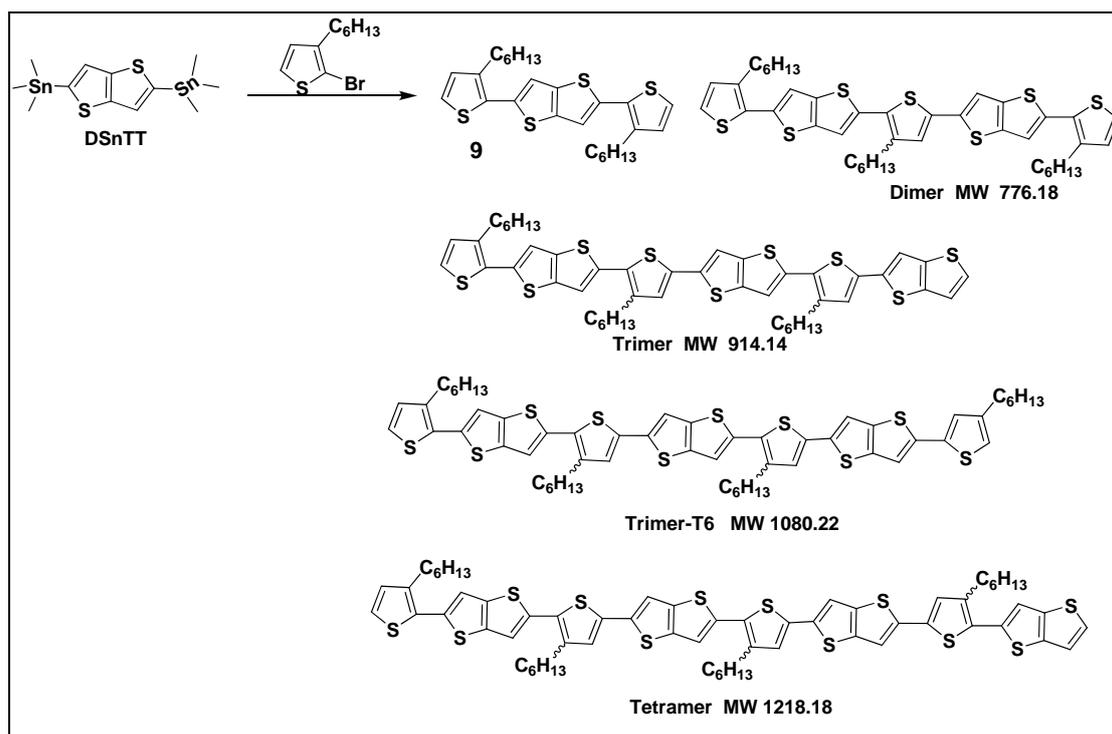


2,5-bis(3-hexylthiophen-2-yl)thieno[3,2-b]thiophene (9).

According to **General synthesis method (II)**:

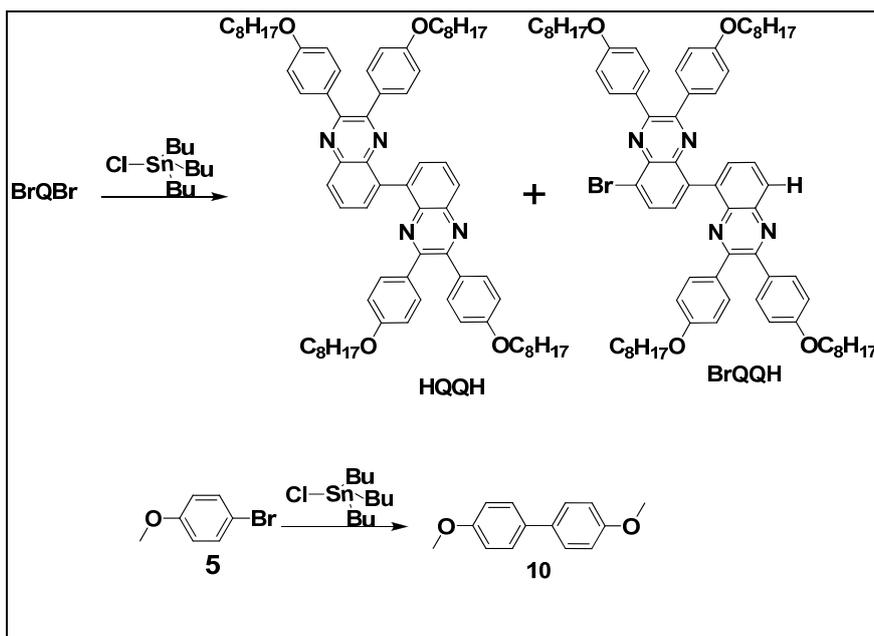
A mixture of 2,2'-bis(trimethylstanne)-thienothiophene (930 mg, 2.0 mmol), 3-hexyl-2-thiophenyl bromide (1.06 g, 4.3 mmol) and Pd₂(dba)₃ (36 mg, 0.02 mmol)/P(o-tol)₃ (24 mg, 0.08 mmol) were heated to 100°C in toluene (15 mL) for 12 hr in dark under argon atmosphere. After the reaction was confirmed to complete with thin layer chromatography (TLC), it was cooled to room temperature. The solvent was removed under vacuum. The residue was purified by silica gel column chromatography using petroleum ether PE as the eluent to give **9** as a yellowish solid (510 mg, 54%). ¹H NMR (400 MHz, CDCl₃), δ (ppm): 7.25 (s, 2H), 7.22 (d, *J* = 5.2 Hz, 2H), 6.97 (d, *J* = 5.2 Hz, 2H), 2.80 (t, *J* = 7.9 Hz, 4H), 1.69 – 1.63 (m, 4H), 1.39 – 1.31 (m, 12H), 0.90 (t, *J* = 6.9 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 140.33, 139.13, 137.61, 130.75, 130.01, 124.36, 118.07, 31.71, 30.79, 29.27, 22.66, 14.11.

When the synthesis of **1** was conducted according to **general synthesis method (I)**, the results were similar with the yields variable slightly.

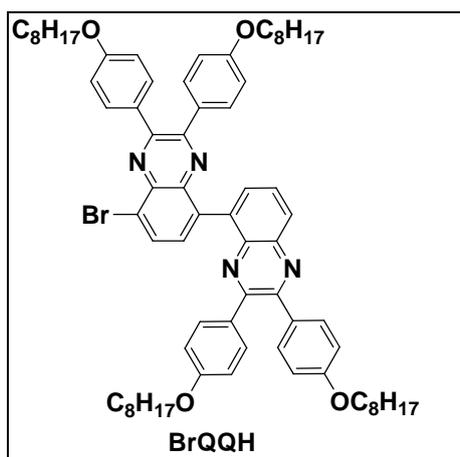


Scheme S3-1 the structures of possible side products for reaction of S3.b

Although **9** could be purified by silica gel column chromatography, most of other side products could not be separated very well by the same method, due to their poor solubility and low polarity. However, most portions of these side products could be collected from the column. By calculating the total weight of these side products, they accounted for 33% of the conversion of . In addition, their asymmetric structure also made it difficult to confirm their possible structures by proton NMR. Fortunately, their possible structures could be deduced by calculating the molecular weights and the measured molecular weights obtained through MALDI TOF MS. MS (MALDI-TOF): Dimer: calcd for $C_{42}H_{48}S_7$ $[M]^+$, 776.18; found, 776.115; Trimer: calcd for $C_{48}H_{50}S_9$ $[M]^+$, 914.14; found, 914.085; Trimer-T6: calcd for $C_{58}H_{64}S_{10}$ $[M]^+$, 1080.22; found, 1080.245; Tetramer: calcd for $C_{64}H_{66}S_{12}$ $[M]^+$, 1218.18; found, 1218.202.



Scheme S4. Reaction between tralkyl chloride/bromide with arylhalides, a) Pd₂(dba)₃, P(*o*-tol)₃, toluene, 110 °C, 16 hr.

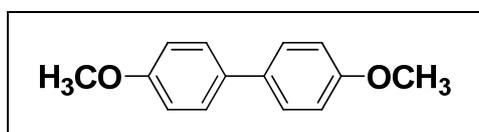


Synthesis of **BrQQH**

According to **General synthesis method (II)**:

A mixture of 5,8-dibromo-2,3-bis(4-(octyloxy)phenyl)quinoxaline (696 mg, 1.0 mmol), tributylstannyl bromide 407 mg, 1.1 mmol) and Pd₂(dba)₃ (18 mg, 0.02 mmol)/P(*o*-tol)₃ (12 mg, 0.04 mmol) were heated to 100 °C in toluene (15 mL) for 12 hr in dark under argon atmosphere. After the reaction was confirmed to complete with thin layer chromatography (TLC), it was cooled to room temperature. The solvent was removed under vacuum. The residue was purified by silica gel column

chromatography using petroleum ether PE as the eluent to give **BrQQH** as a waxy solid (958 mg, 83%). ^1H NMR (400 MHz, CDCl_3), δ (ppm): 8.05 (d, 2H), 8.00 (d, 2H), 7.60 (d, 4H), 7.53 (m, 1H), 7.51 (d, 4H), 6.88 (m, 8H), 4.00 (m, 8H), 1.83 (m, 8H), 1.49–1.26 (b, 40H), 0.90 (m, 12H). ^{13}C NMR (100 MHz, CDCl_3), δ (ppm): 160.20, 160.07, 153.54, 153.27, 141.59, 138.68, 131.70, 131.20, 130.98, 130.83, 129.52, 128.70, 123.96, 114.42, 114.25, 68.13, 68.09, 31.82, 29.37, 29.24, 29.23, 26.01, 22.71, 14.11. MS (MALDI-TOF): Dimer: calcd for $\text{C}_{72}\text{H}_{89}\text{BrN}_4\text{O}_4$, $[\text{M}]^+$, 1154.41; found, 1155.511.



Synthesis of **4,4'**-dimethoxybiphenyl (**10**)

According to **General synthesis method (II)**:

A mixture of 1-bromo-4-methoxybenzene (750 mg, 4 mmol), tributylstannyl bromide (820 mg, 2.2 mmol) and $\text{Pd}_2(\text{dba})_3$ (36 mg, 0.04 mmol)/ $\text{P}(\text{o-tol})_3$ (24 mg, 0.08 mmol) were heated to 100 °C in toluene (15 mL) for 12 hr in dark under argon atmosphere. After the reaction was confirmed to complete with TLC, it was cooled to room temperature. The solvent was removed under vacuum. The residue was purified by silica gel column chromatography using petroleum ether PE as the eluent to give **10** as a colorless oil (428mg, 91%). ^1H NMR (400 MHz, CDCl_3), δ (ppm): 7.25 (s, 2H), 7.22 (d, $J = 5.2$ Hz, 2H), 6.97 (d, $J = 5.2$ Hz, 2H), 2.80 (t, $J = 7.9$ Hz, 4H), 1.69 – 1.63 (m, 4H), 1.39 – 1.31 (m, 12H), 0.90 (t, $J = 6.9$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3), δ (ppm): 140.33, 139.13, 137.61, 130.75, 130.01, 124.36, 118.07, 31.71, 30.79, 29.27, 22.66, 14.11.

Section 3 Evidence to support the proposed mechanism

MALDI-TOF-MS measurement on Equation 3

To confirm the assumption on the possible mechanism, we measured the reaction mixture of **Equation 3** with MALDI-TOF-MS after **Equation 3** had been run for 25 min and 75 min. It was clearly found that 1Q2T, 2Q3T, 3Q4T and 4Q5T were formed. And the measured MALDI-TOF-MS spectra shown as Figure S26 and S27.

GC-MS measurement to confirm the stability of tributylstannyl chloride and 2,5-bis(trimethylstannyl)thieno[3,2-b]thiophene

To confirm the assumption on the stability issue of Bu_3SnCl and 2,5-bis(trimethylstannyl)thieno[3,2-b]thiophene, they both were heated with and without $\text{Pd}(\text{PPh}_3)_4$ (2% mol) in toluene at 110 °C for 30 min under argon atmosphere. It was found that, without Pd catalyst, both of them were stable enough. However, in present Pd catalyst, both of them were unstable, and many complex decomposed intermediates could be observed with GC trace. And all the measured structures and their molecular weights shown in **Figure S30, S31, S32 and S33**.

Section 4 References:

- 1 B. Carsten, F. He, H. J. Son, T. Xu and L. Yu, *Chem. Rev.*, 2011, **111**, 1493–528.
- 2 L. J. Lindgren, F. Zhang, M. Andersson, S. Barrau, S. Hellström, W. Mammo, E. Perzon, O. Inganäs and M. R. Andersson, *Chem. Mater.*, 2009, **21**, 3491–3502.

Section 5. NMR spectra

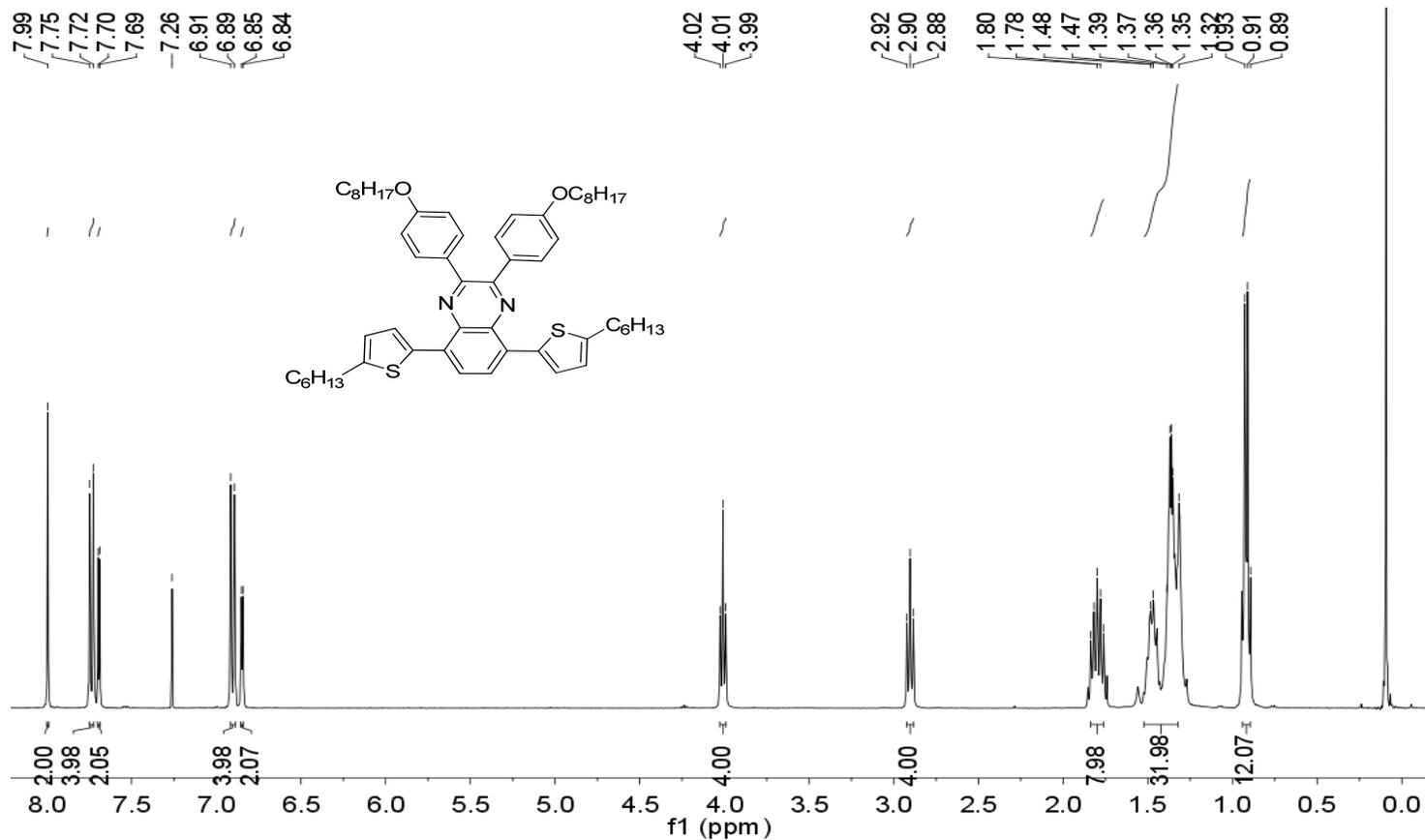


Figure S2. ^1H NMR of 7 in CDCl_3

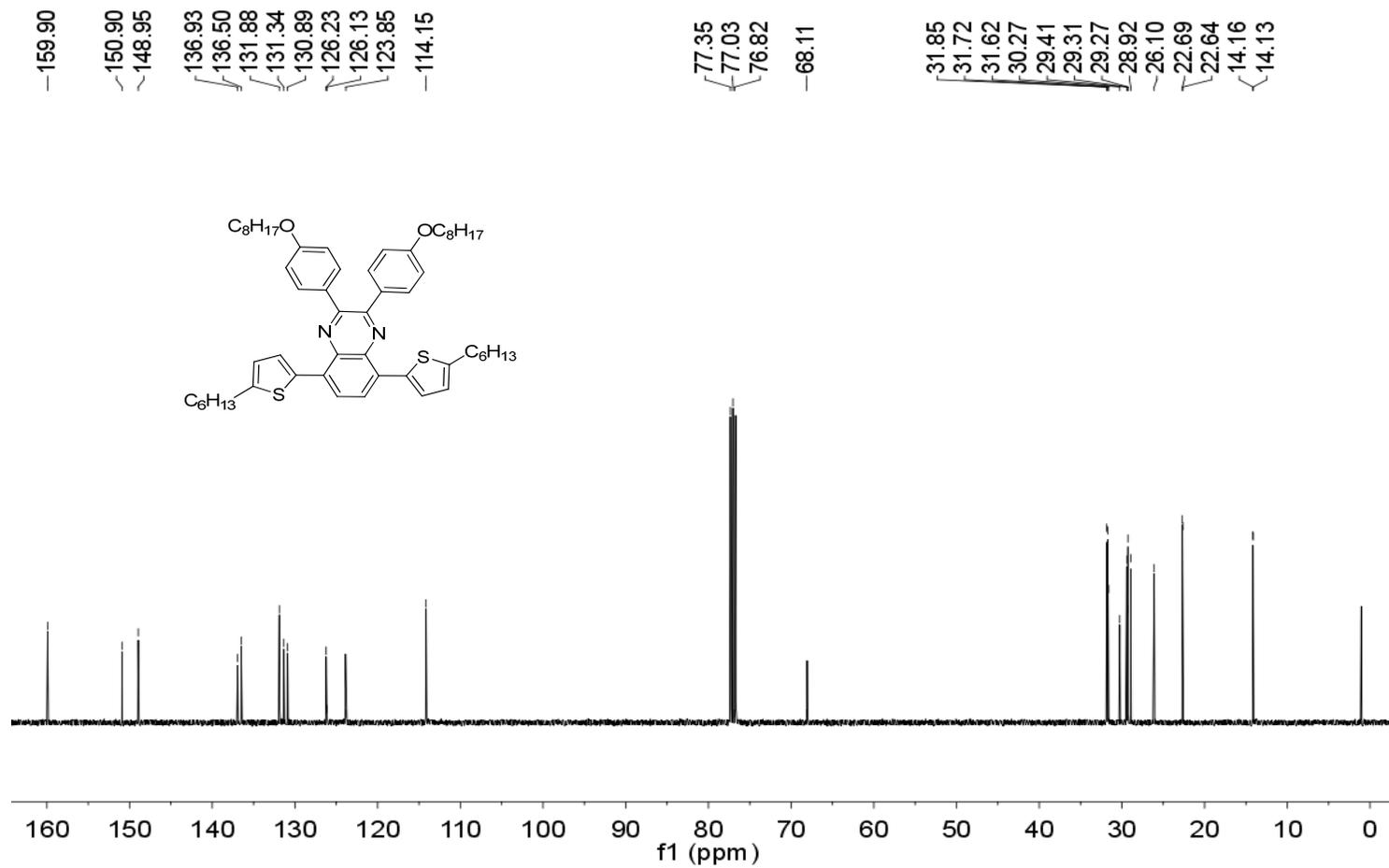


Figure S3. ^{13}C NMR of 7 in CDCl_3

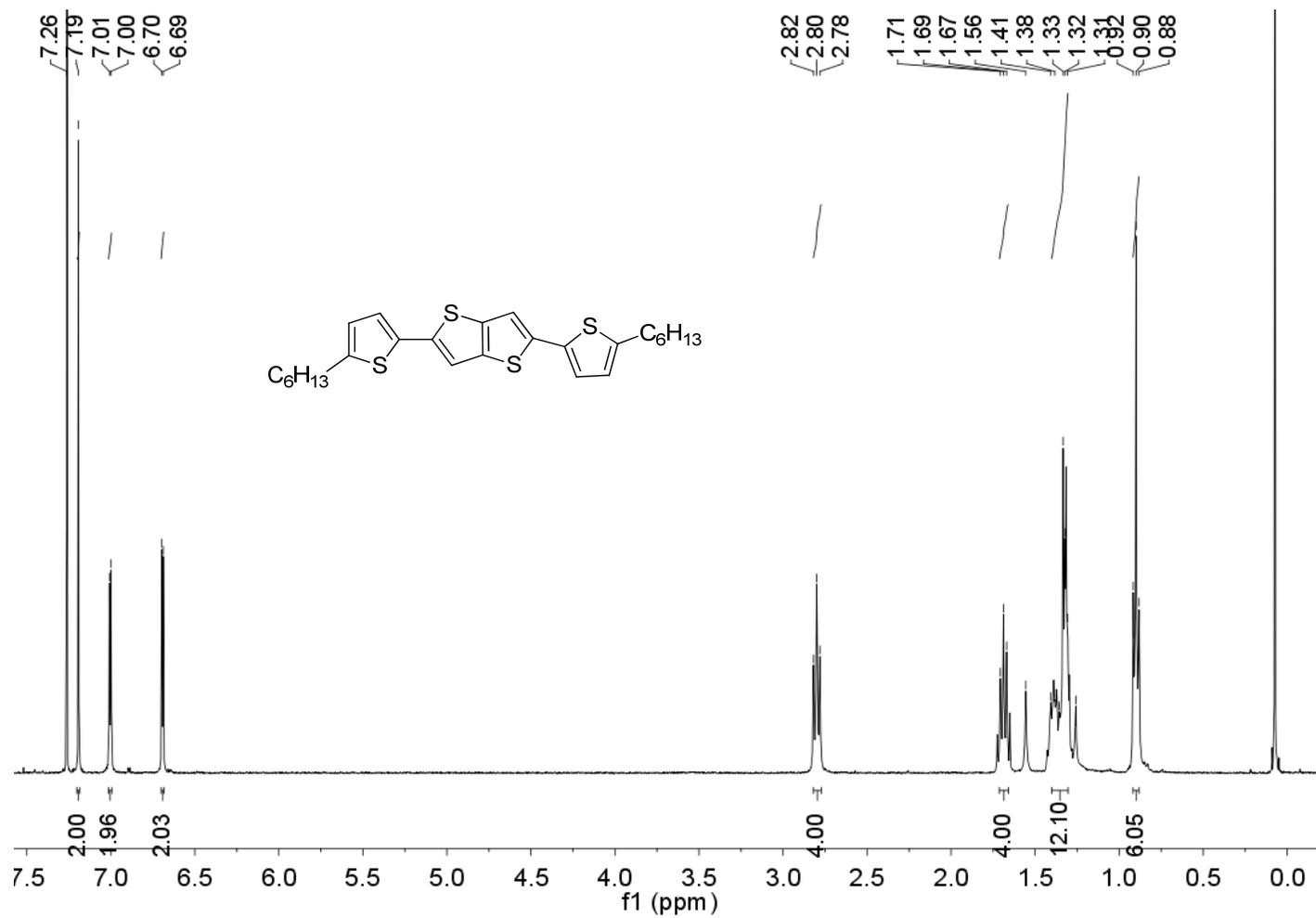


Figure S4. ^1H NMR of 8 in CDCl_3

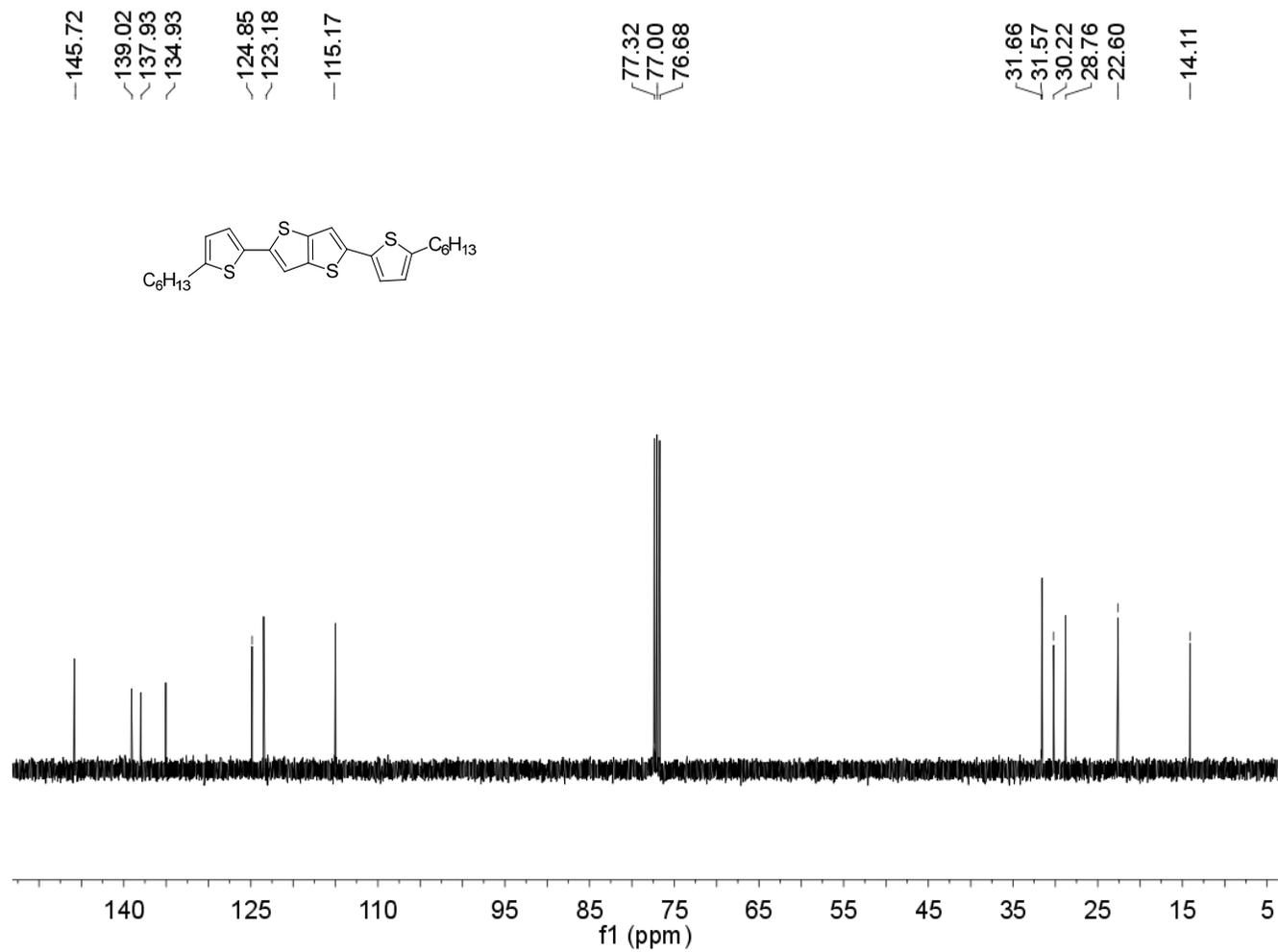


Figure S5. ^{13}C NMR of 8 in CDCl_3

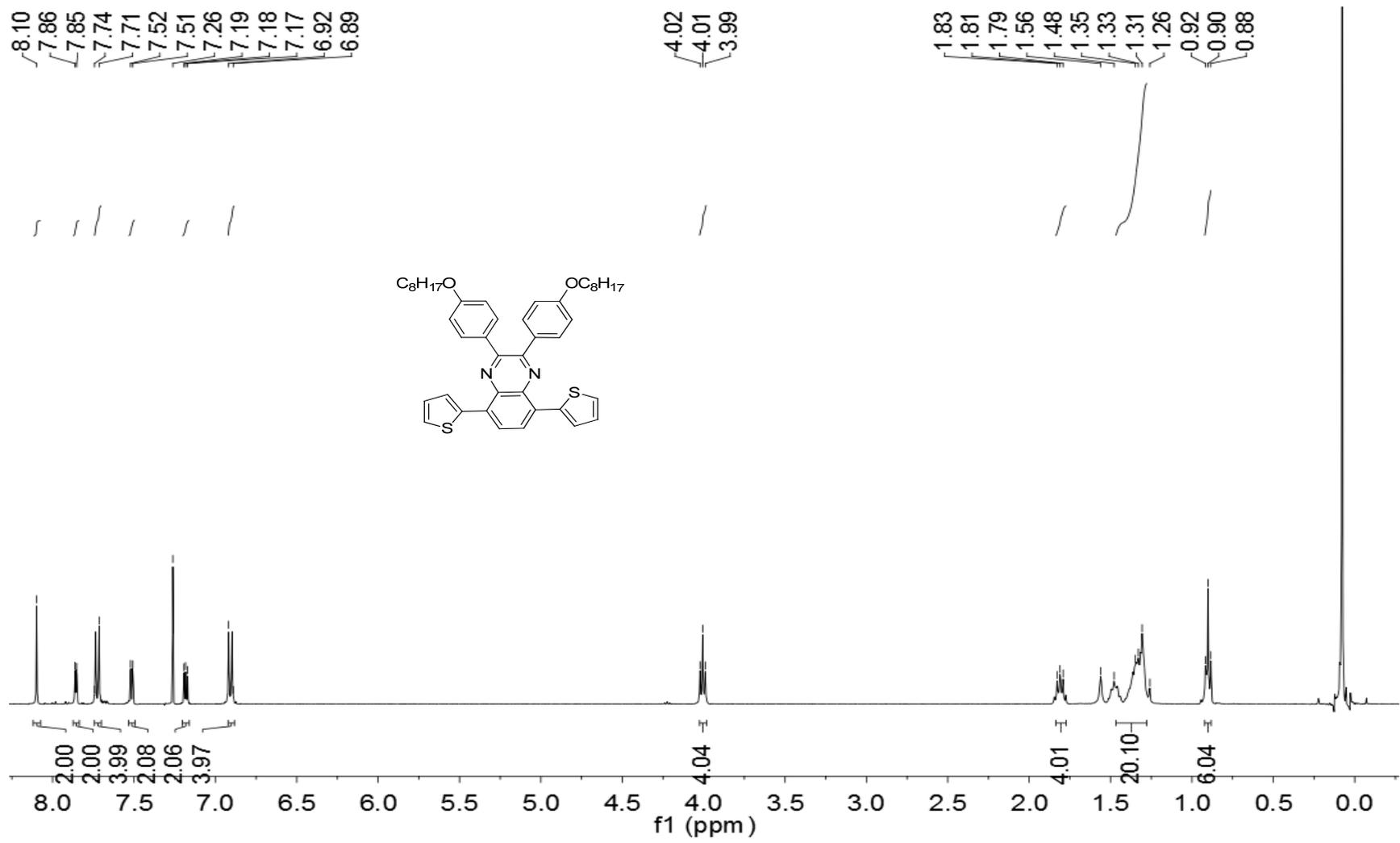


Figure S6. ¹H NMR of 1Q2T in CDCl₃

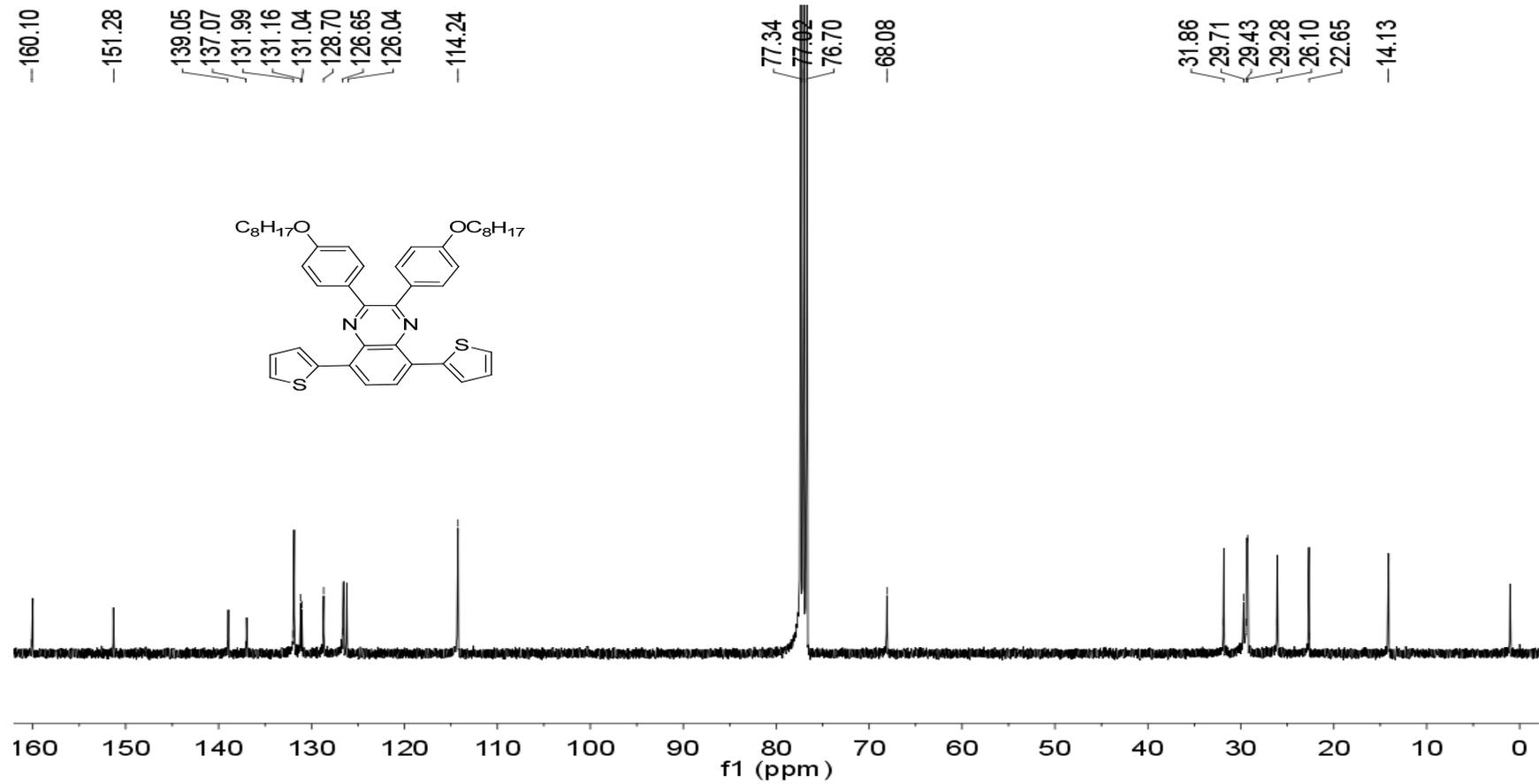


Figure S7. ¹³C NMR of 1Q2T in CDCl₃

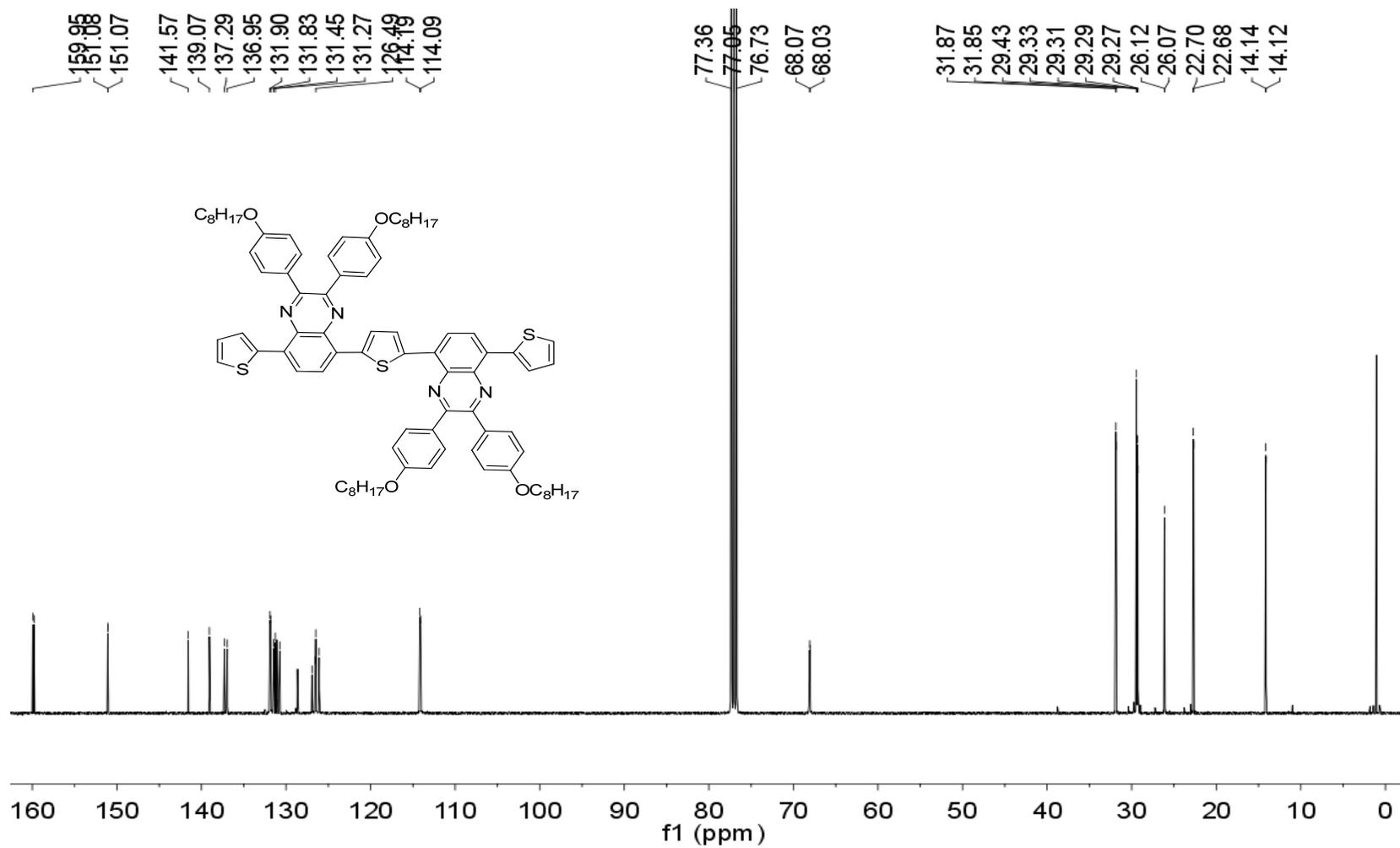


Figure S9. ¹³C NMR of 2Q3T in CDCl₃

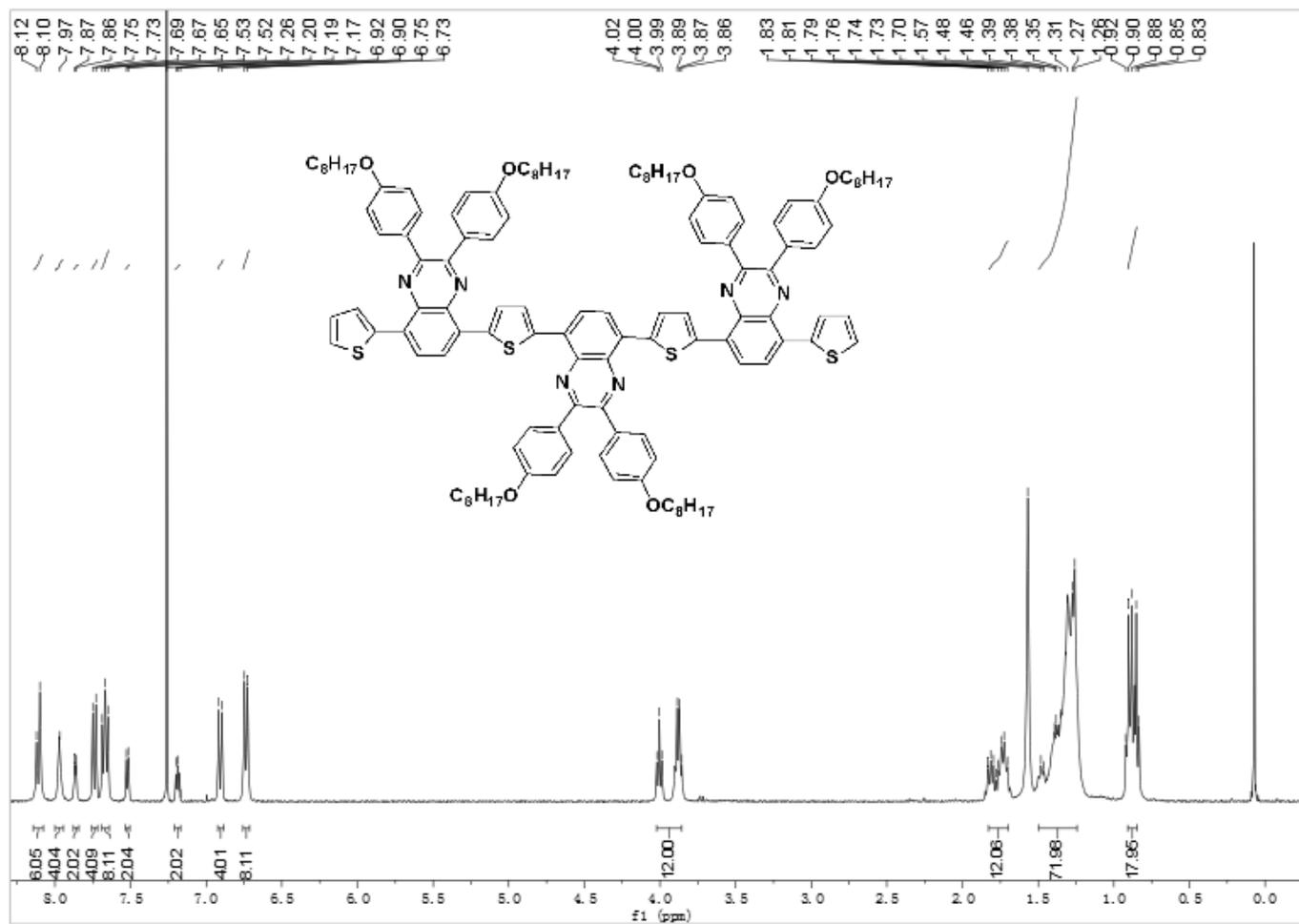
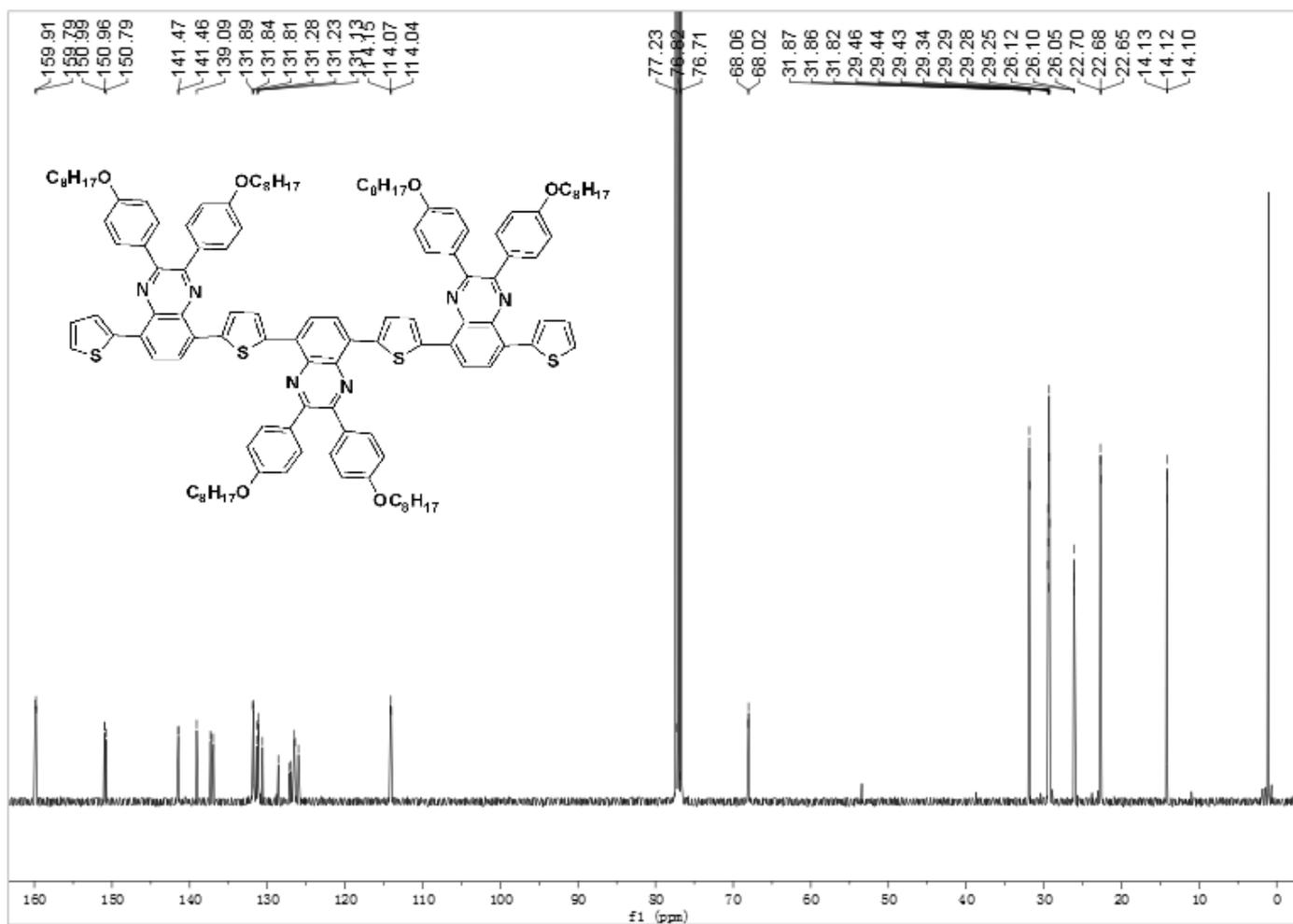


Figure S10. ¹H NMR of 3Q4T in CDCl₃



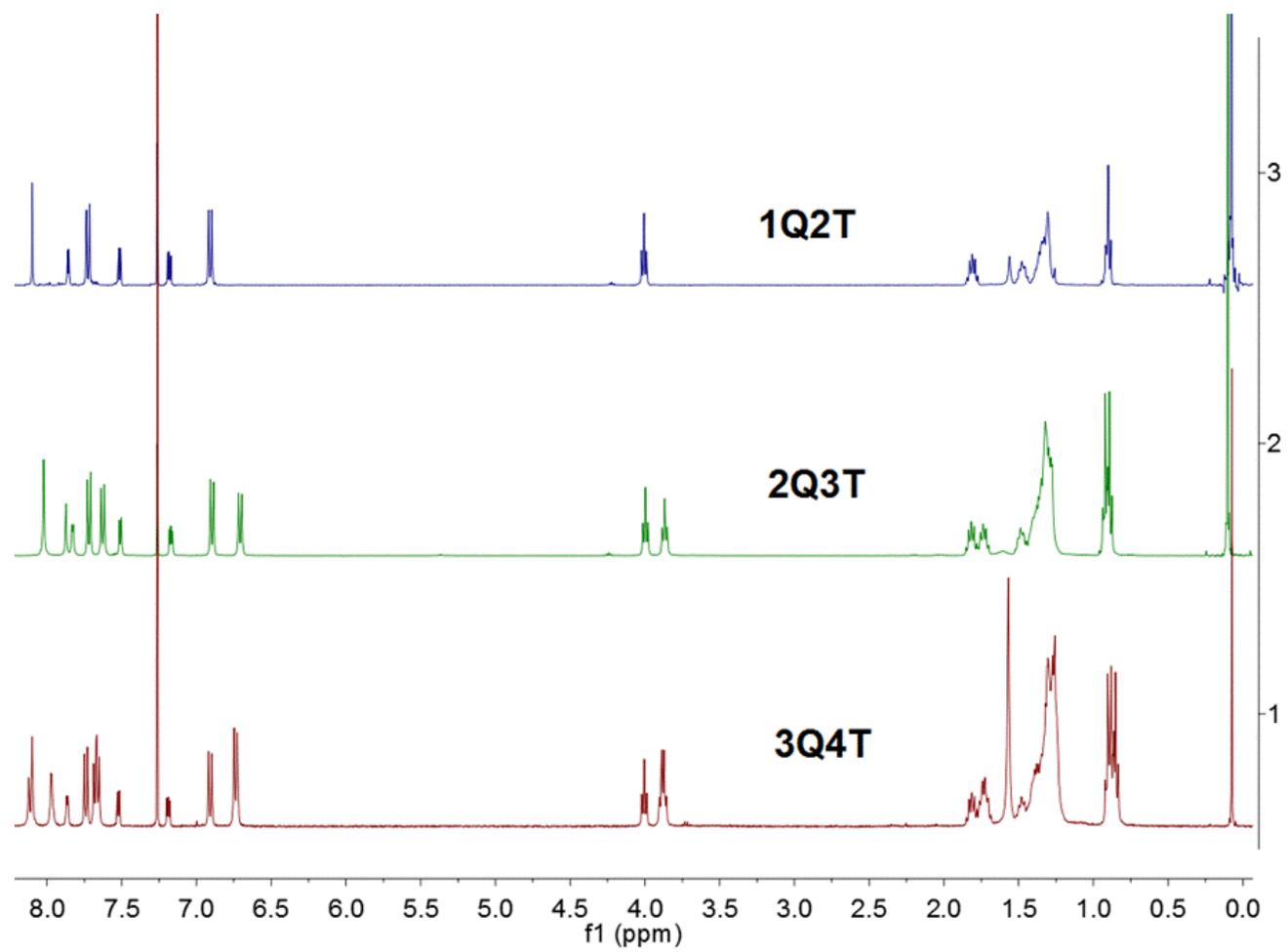


Figure S12. Stacked ^1H NMR of 1Q2T, 2Q3T and 3Q4T in CDCl_3

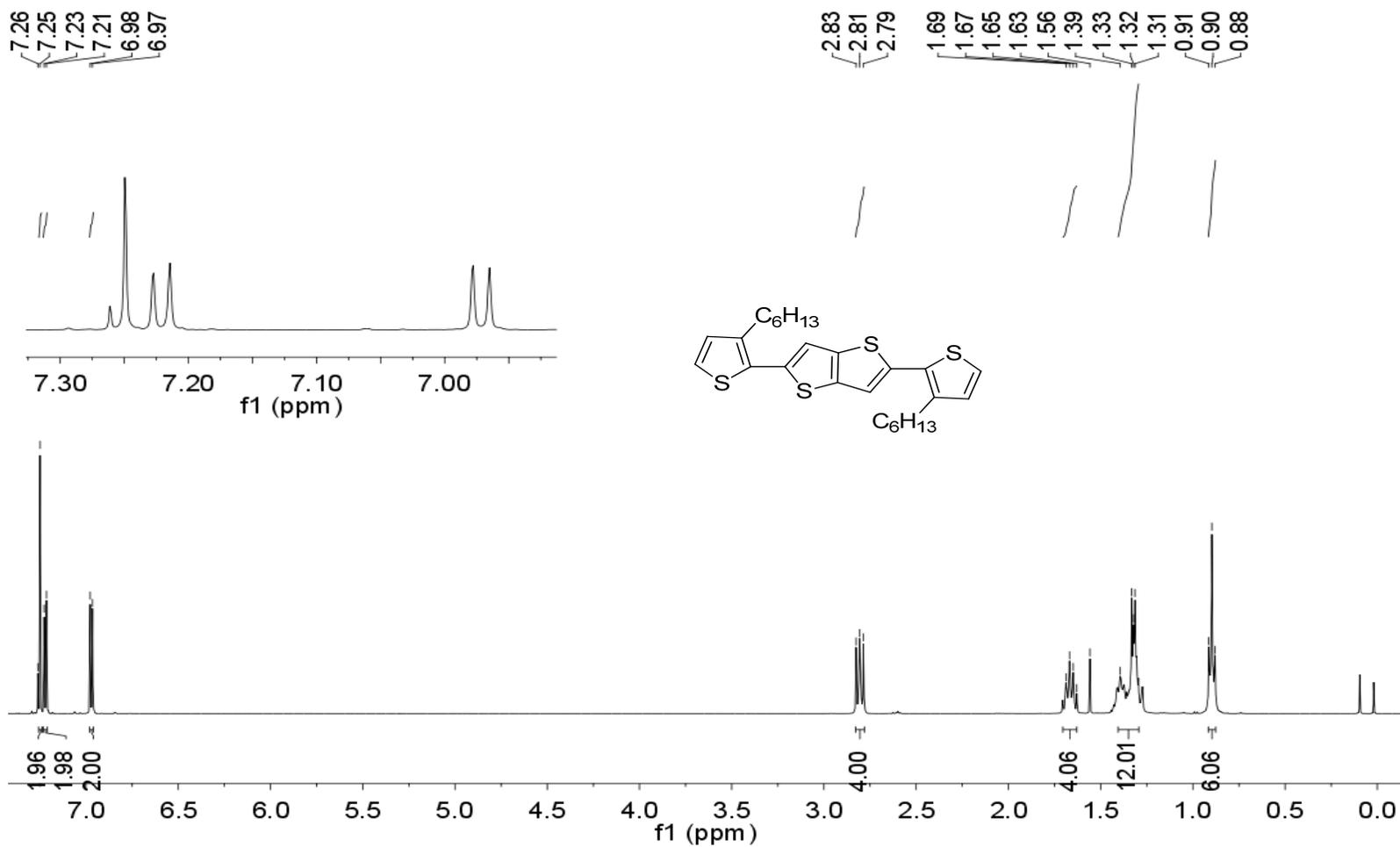
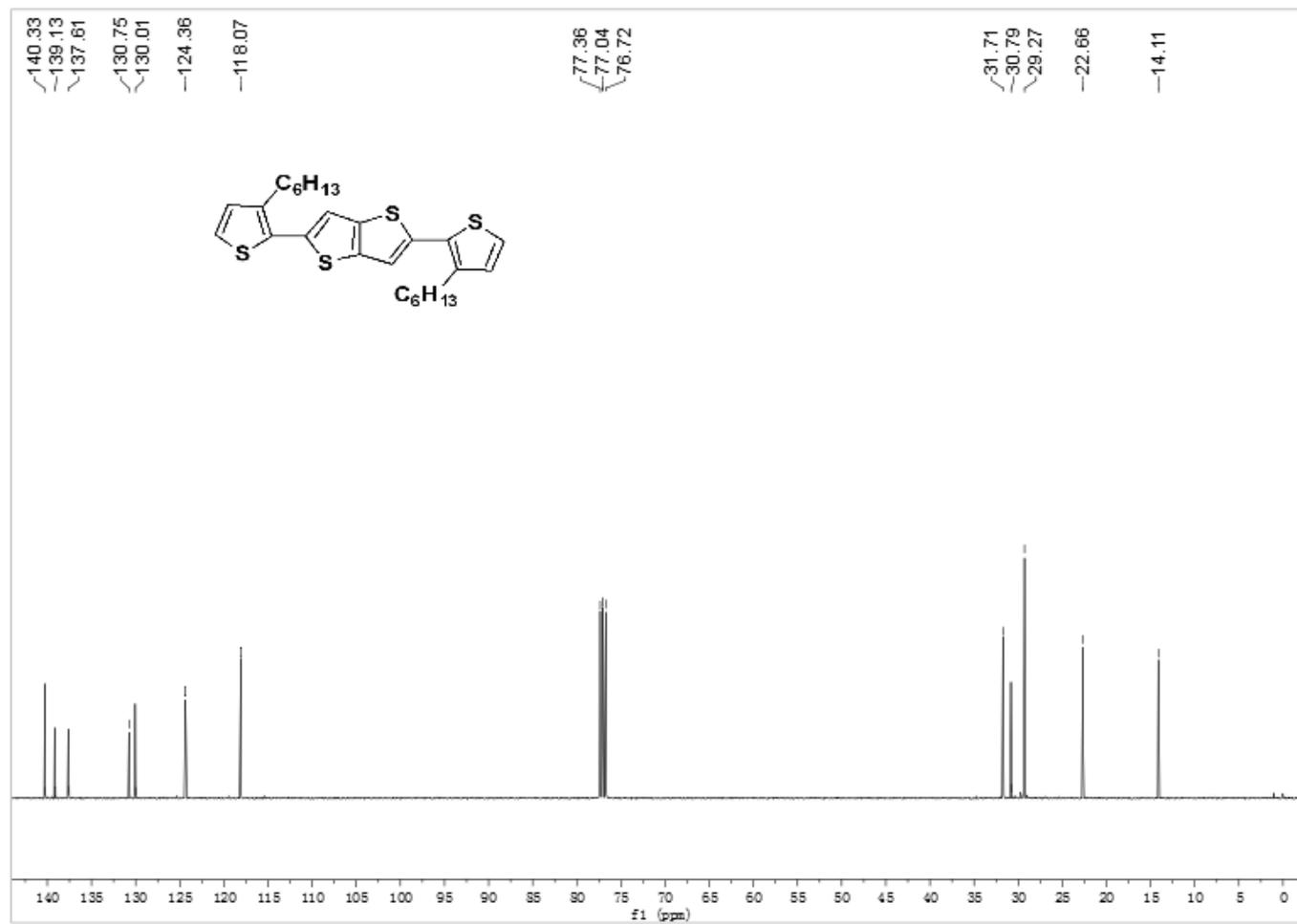


Figure S14. ¹H NMR of 9 in CDCl₃



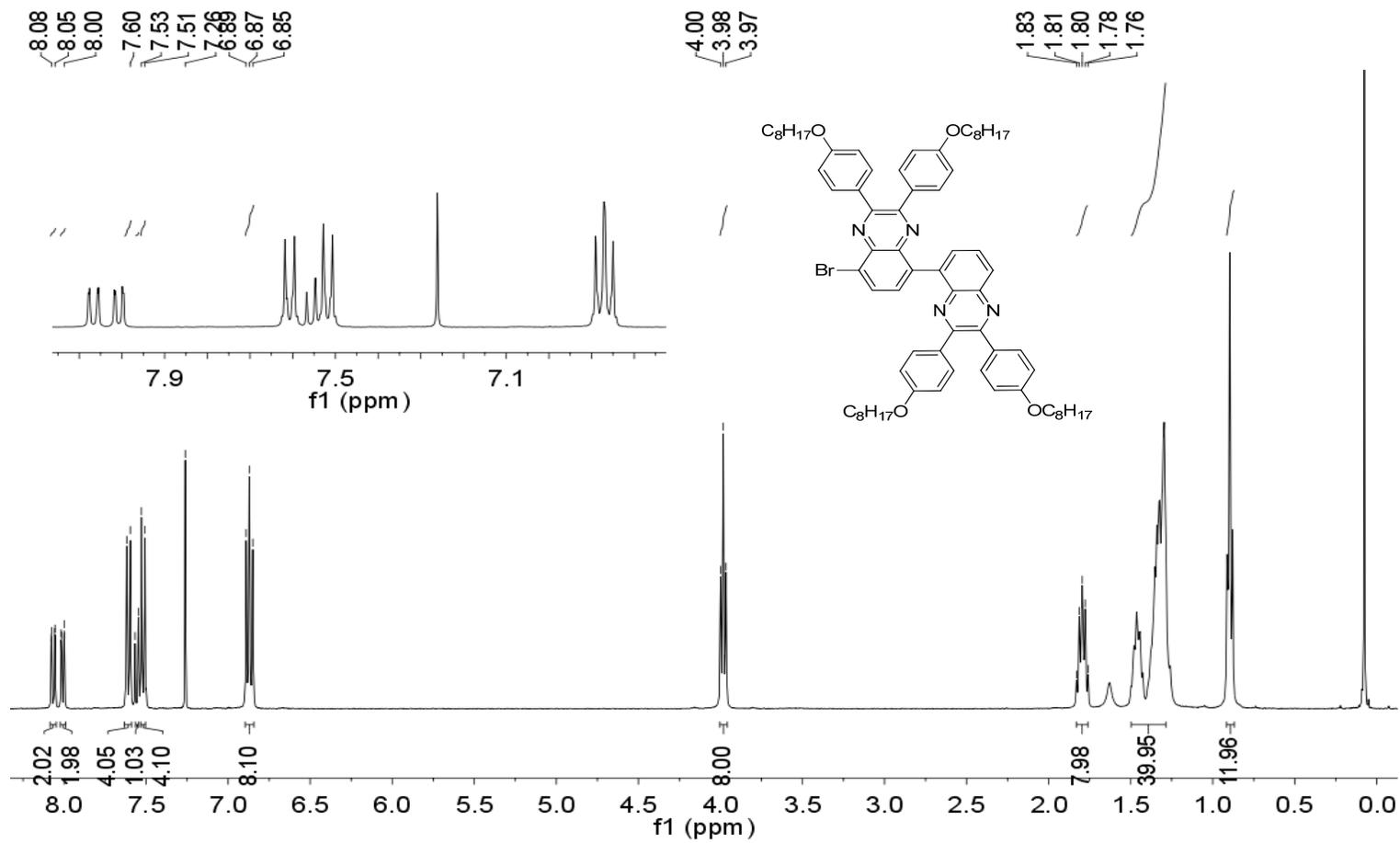


Figure S16. ¹H NMR of BrQQH in CDCl₃

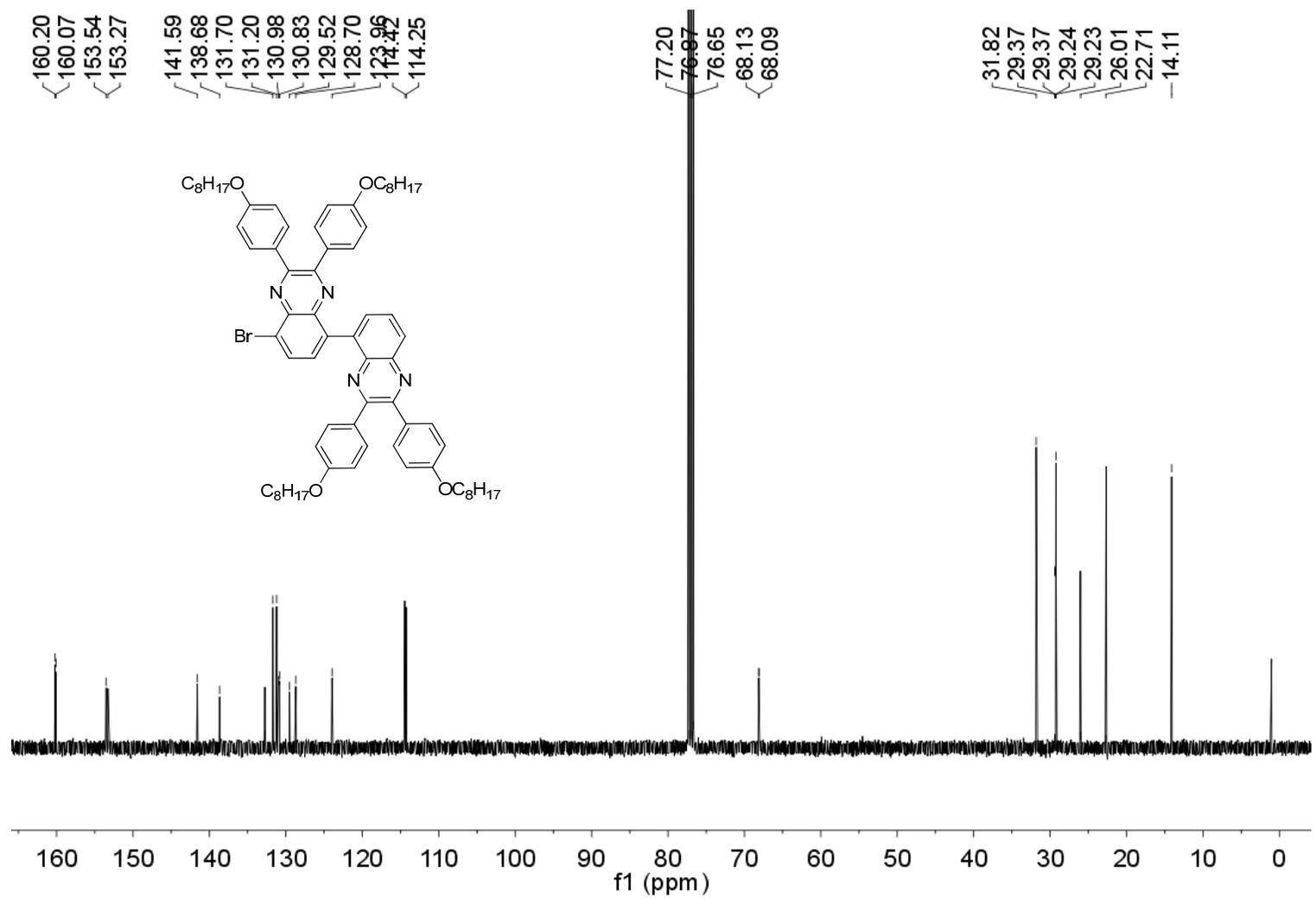


Figure S17. ¹³C NMR of BrQQH in CDCl₃

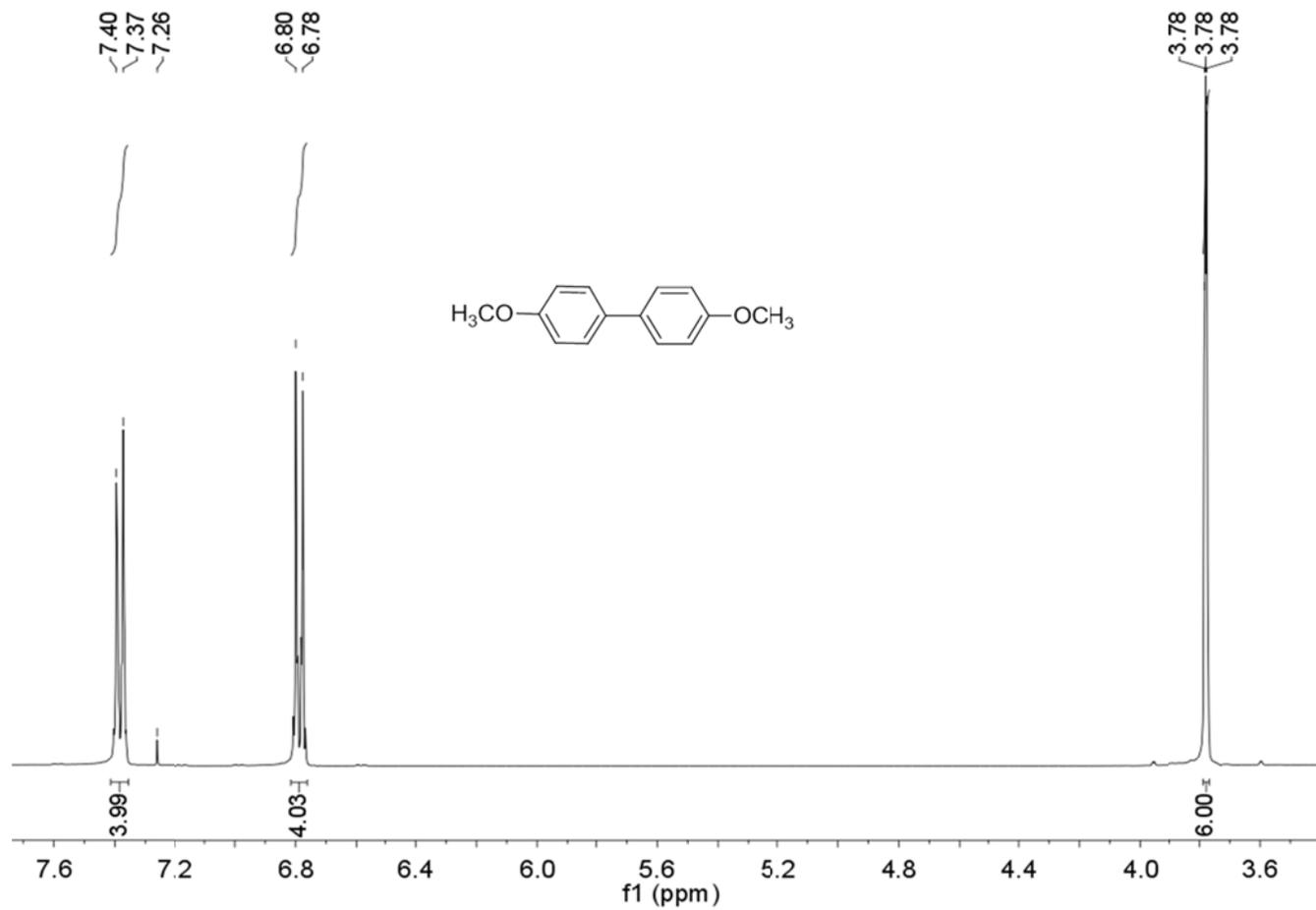


Figure S18. ^1H NMR of 4,4'-dimethoxybiphenyl in CDCl_3

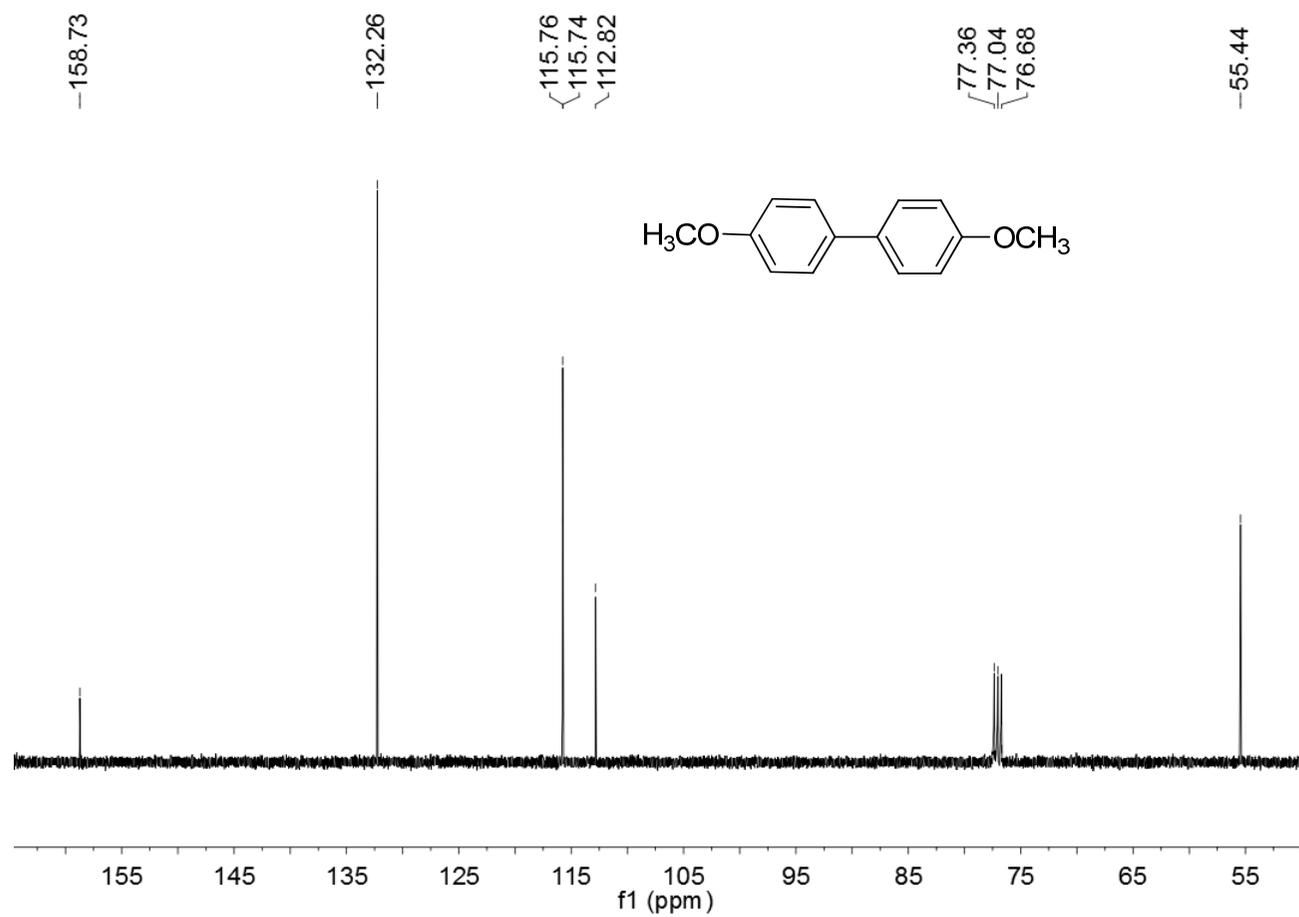


Figure S19. ¹³C NMR of 4,4'-dimethoxybiphenyl in CDCl₃

Section 6. MALDI-TOF MS spectra

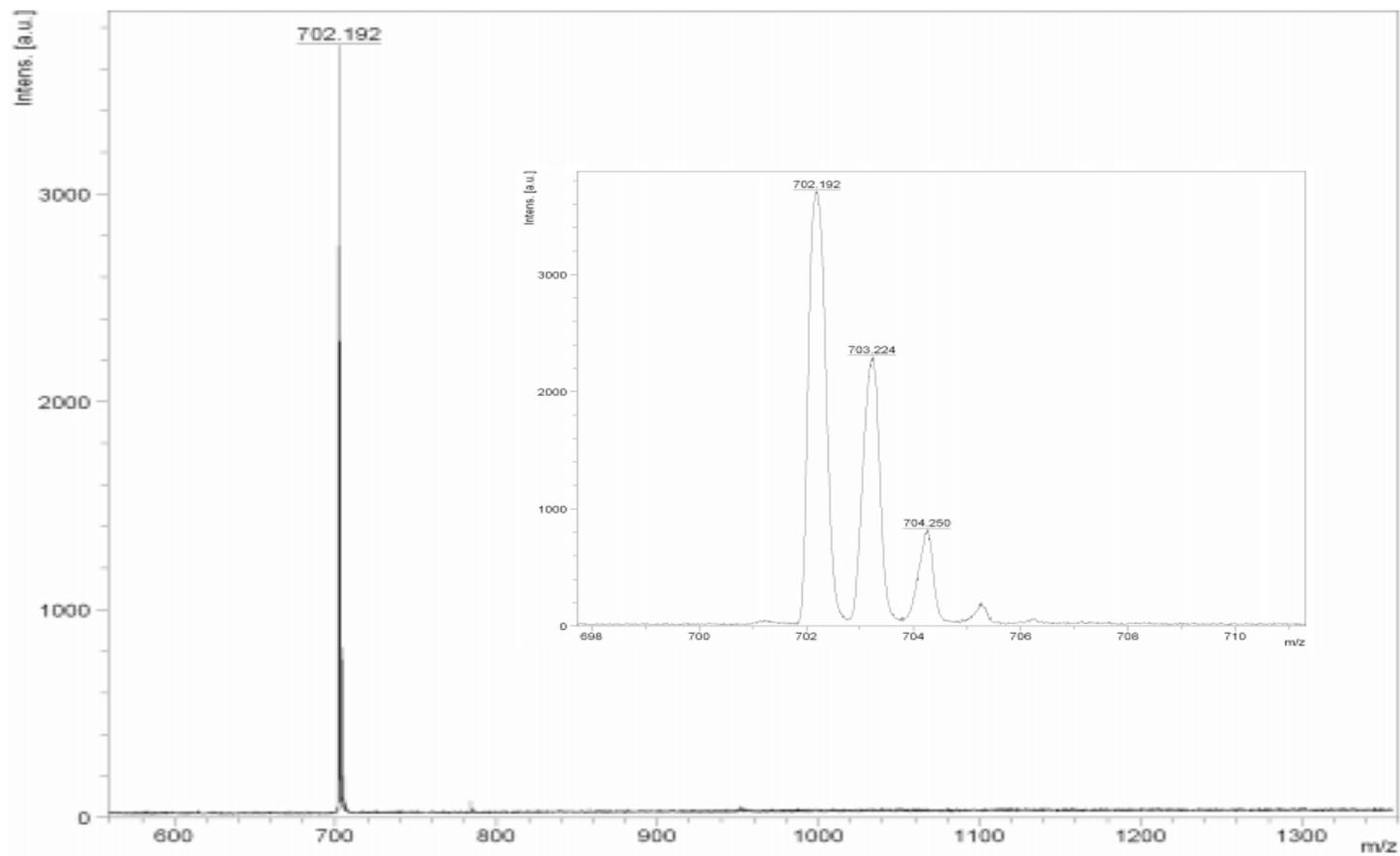


Figure S20. MS spectrum of 1Q2T

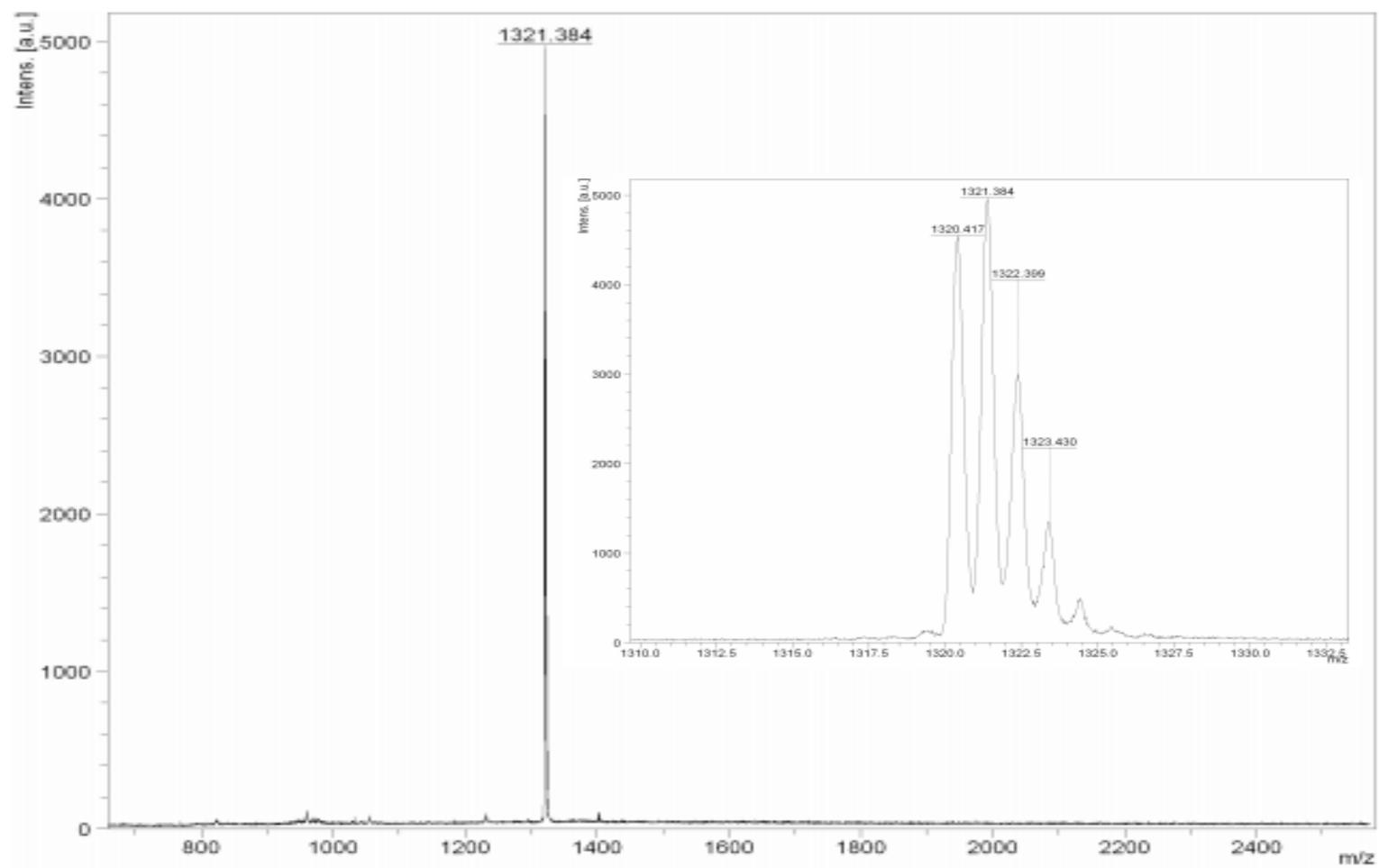


Figure S21. MS spectrum of the 2Q3T

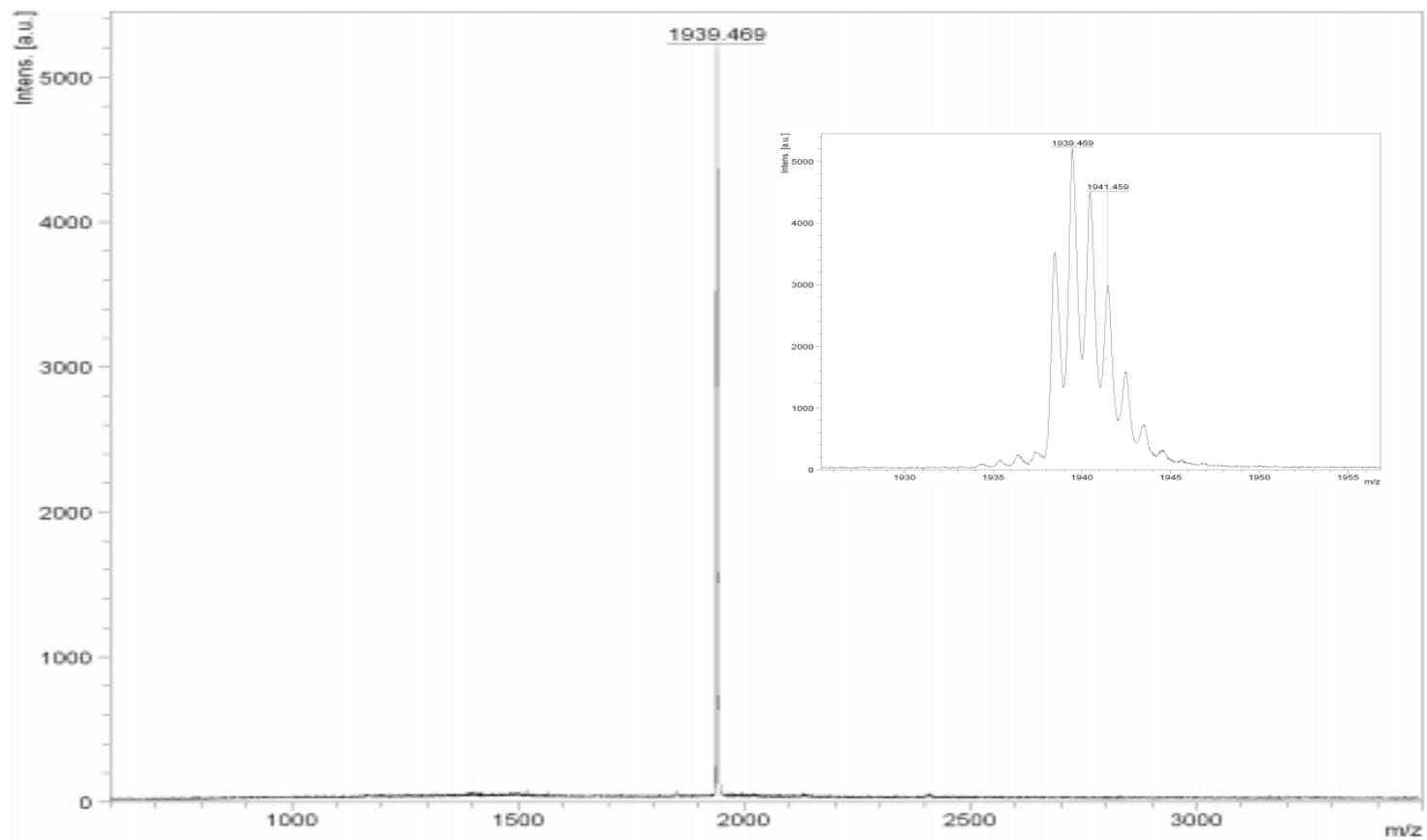


Figure S22. MS spectrum of the 3Q4T

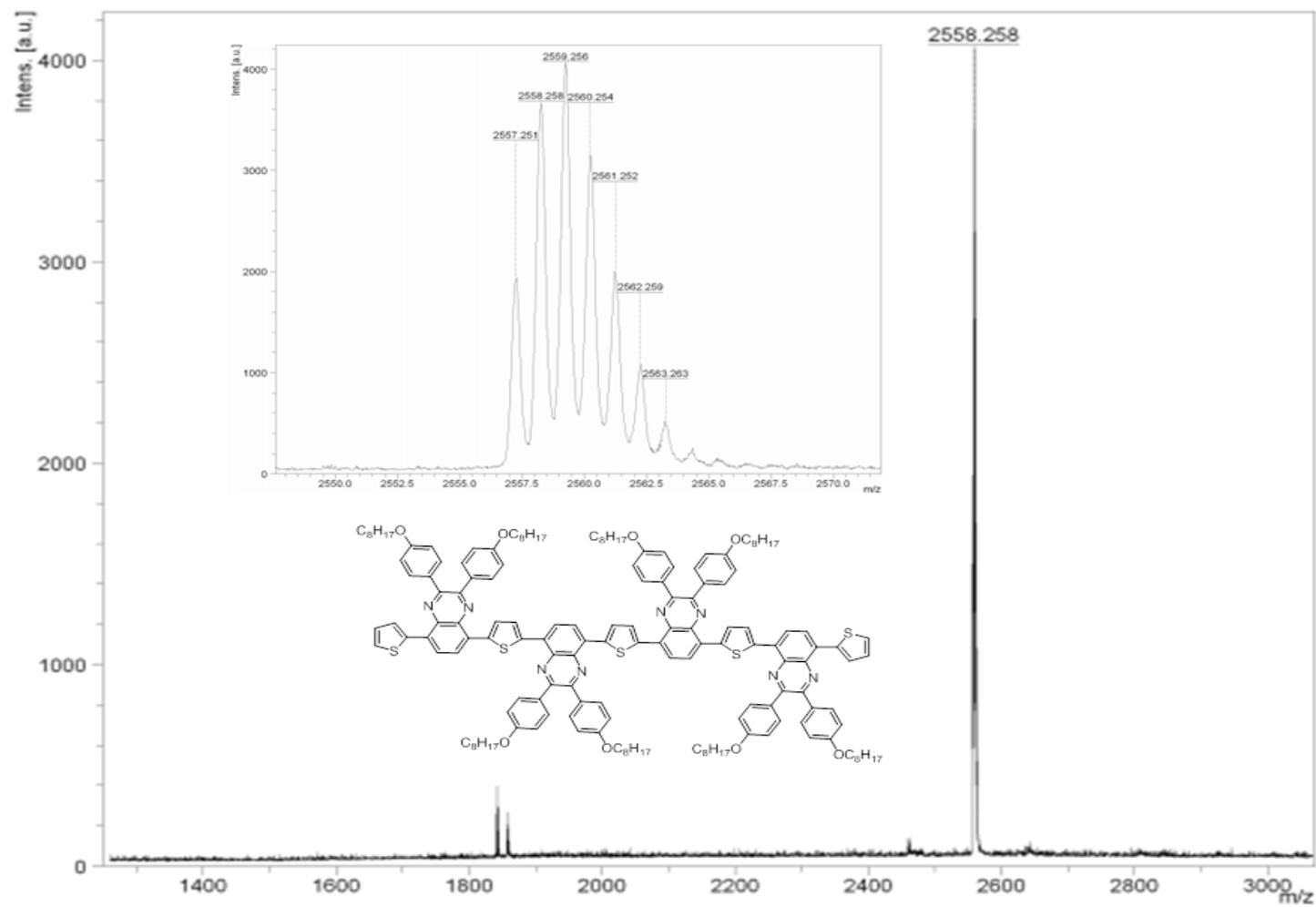


Figure S23. MS spectrum of the 4Q5T

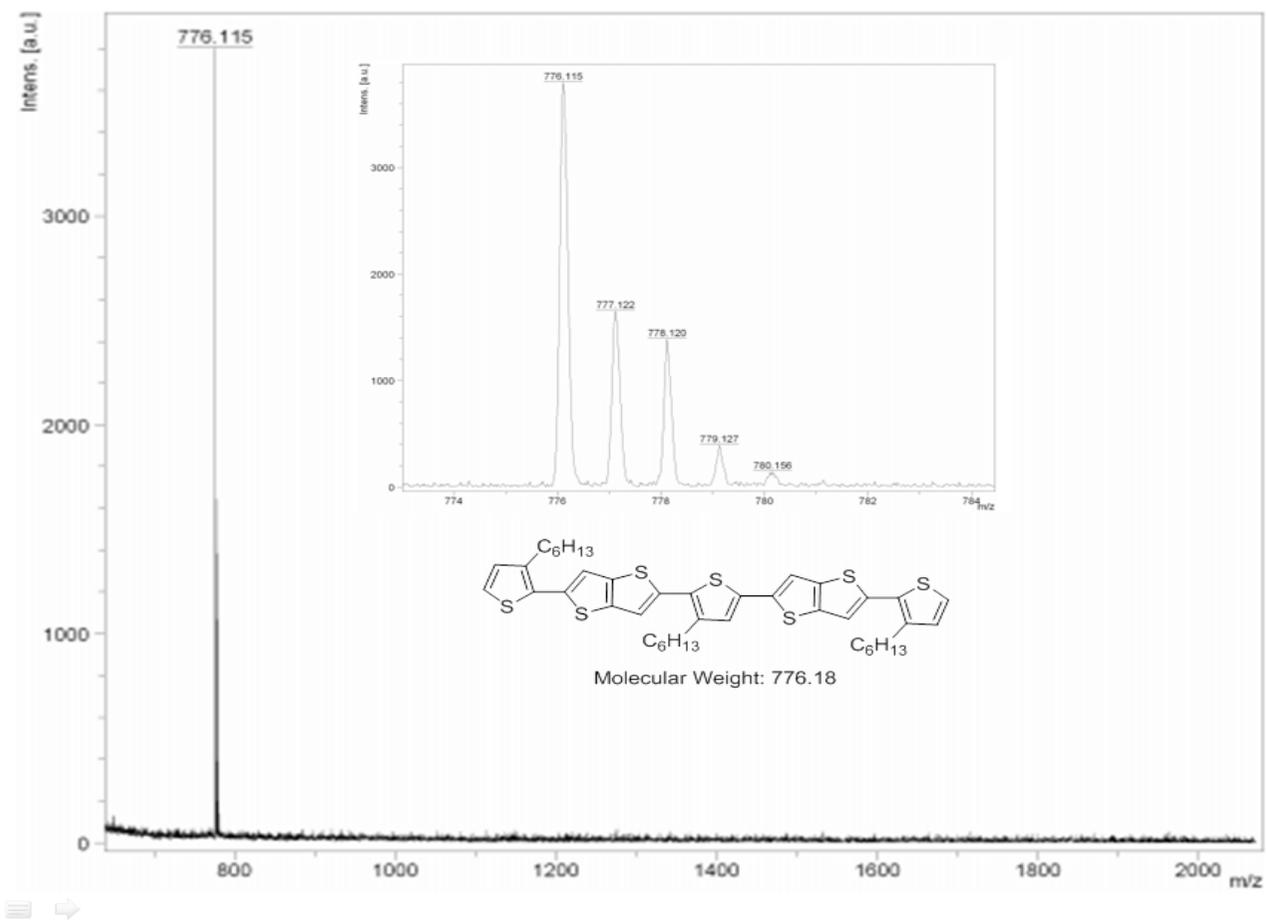


Figure S24-1. MS spectrum of the side-products of T6T-1

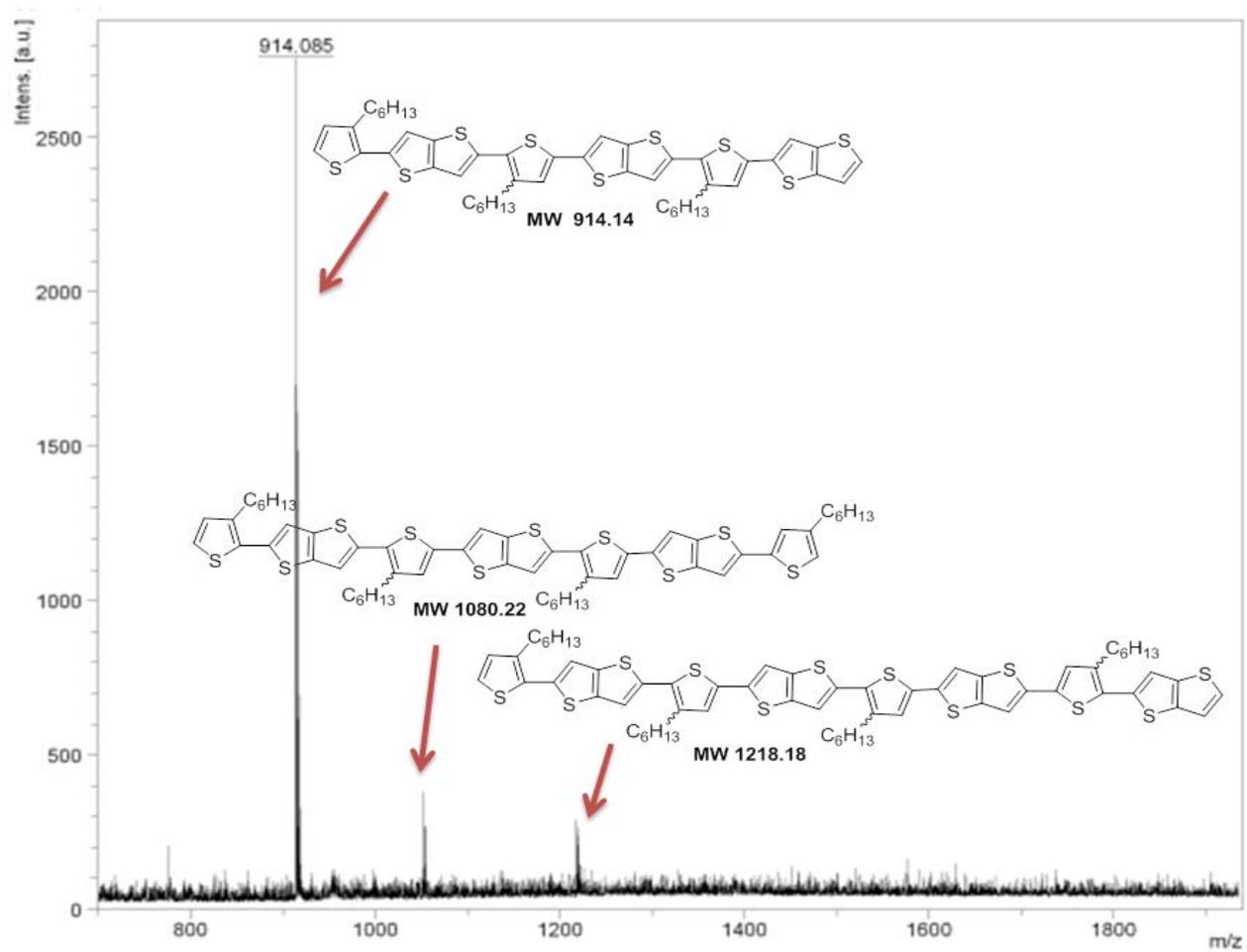


Figure S24-2. MS spectra of the side-products of reaction 3b

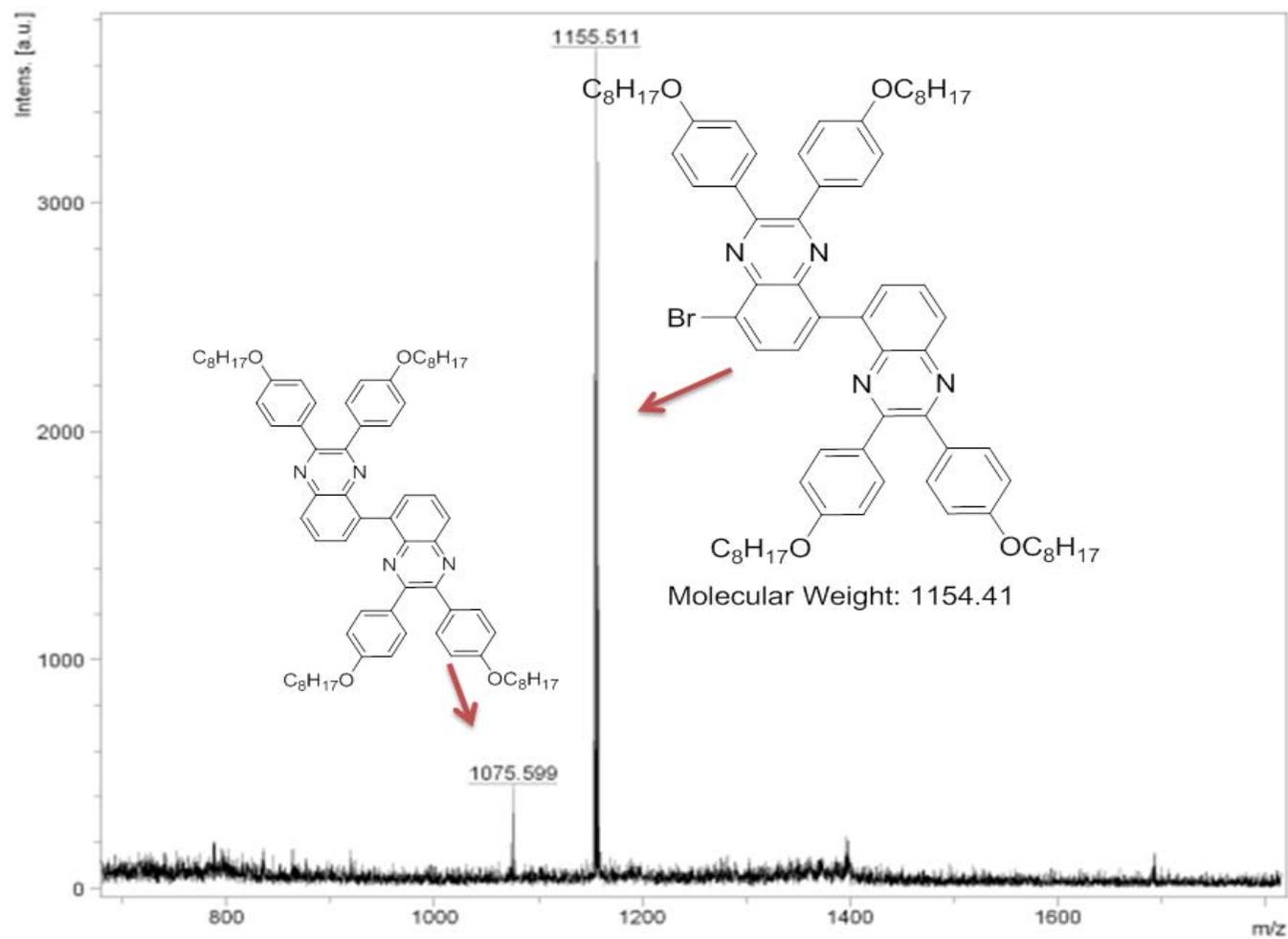


Figure S25. MS spectra of BrQQH and HQQH

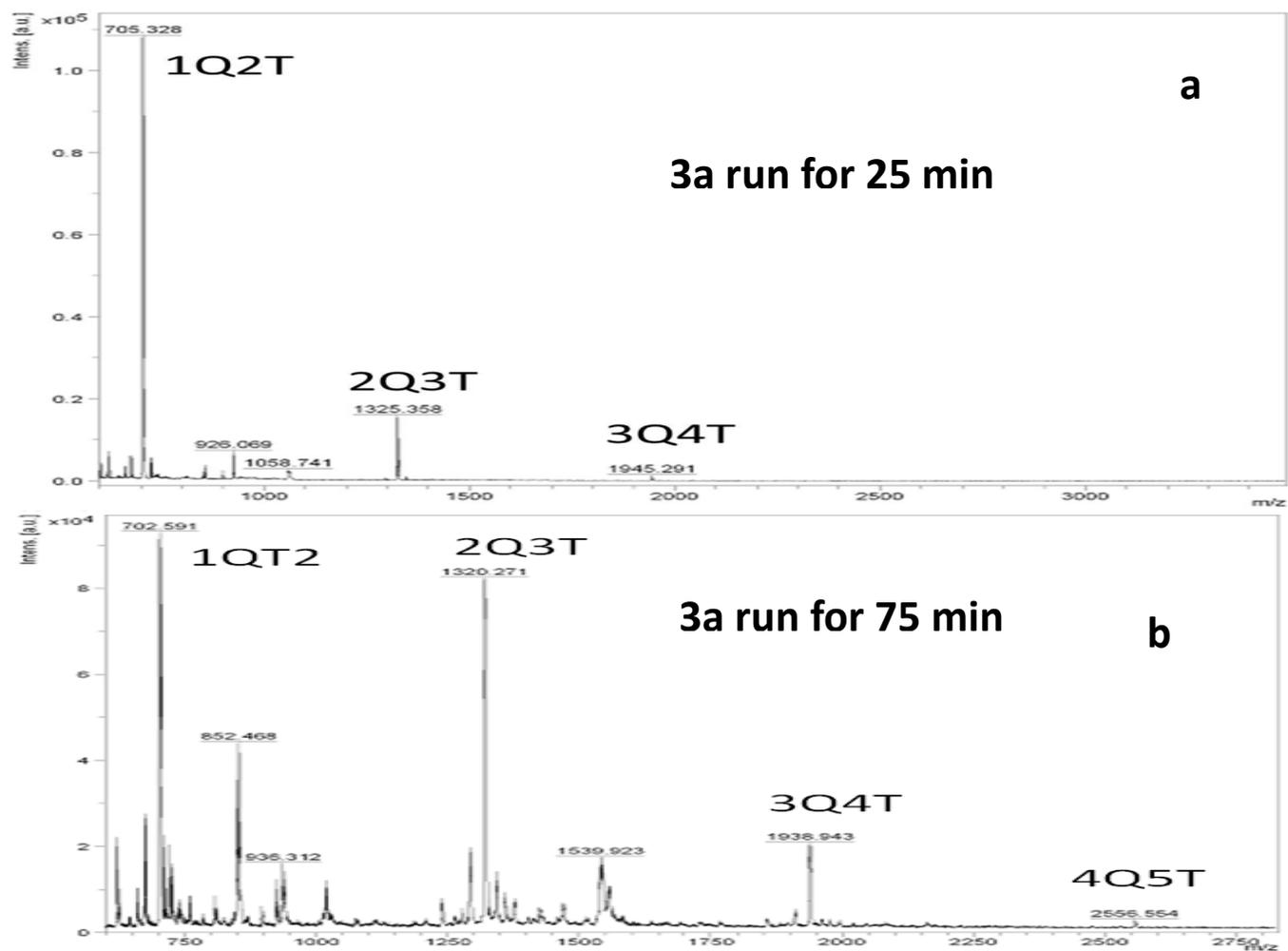


Figure S26. MALDI-TOF-MS spectra measured with the reaction mixture of Scheme 3a run for (a) 25 min and (b) 75 min.

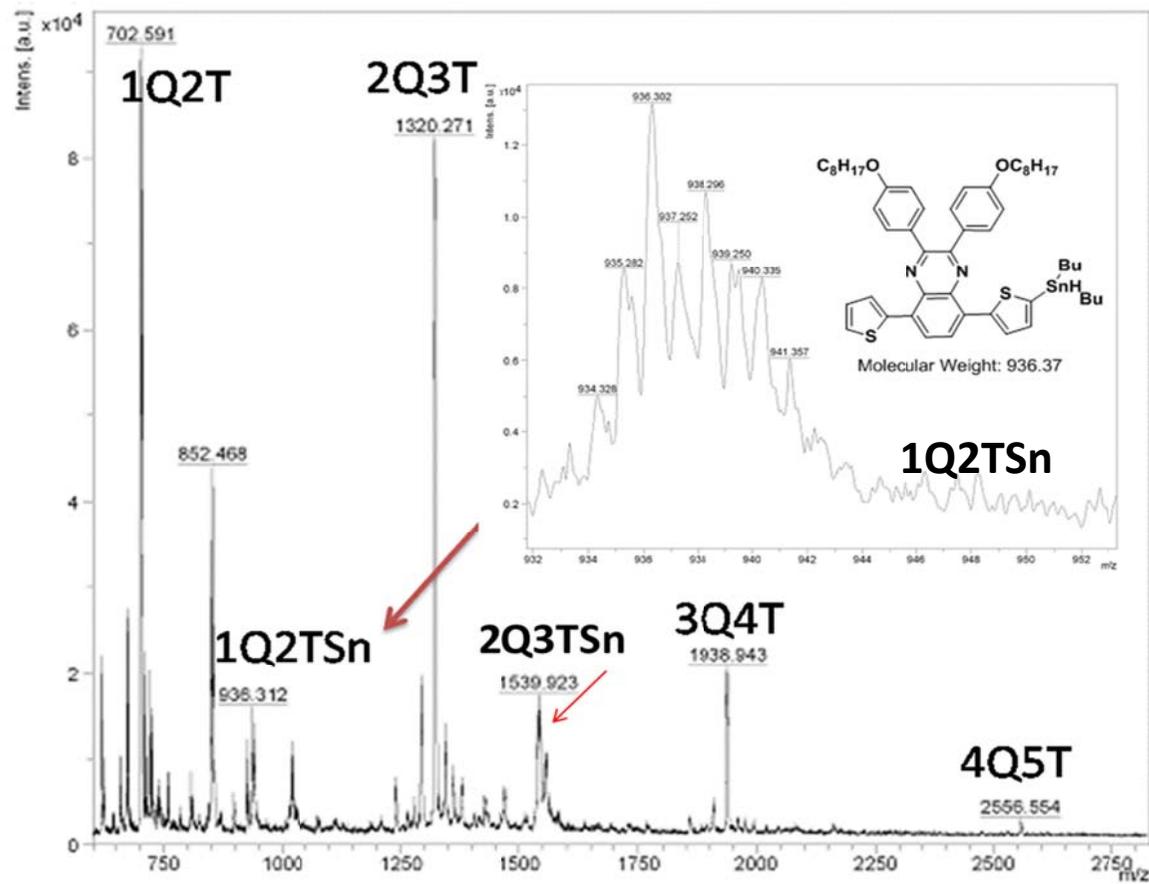


Figure S27. MALDI-TOF-MS spectra of 1Q2TSn and 2Q3TSn measured with the reaction mixture of Scheme 3a

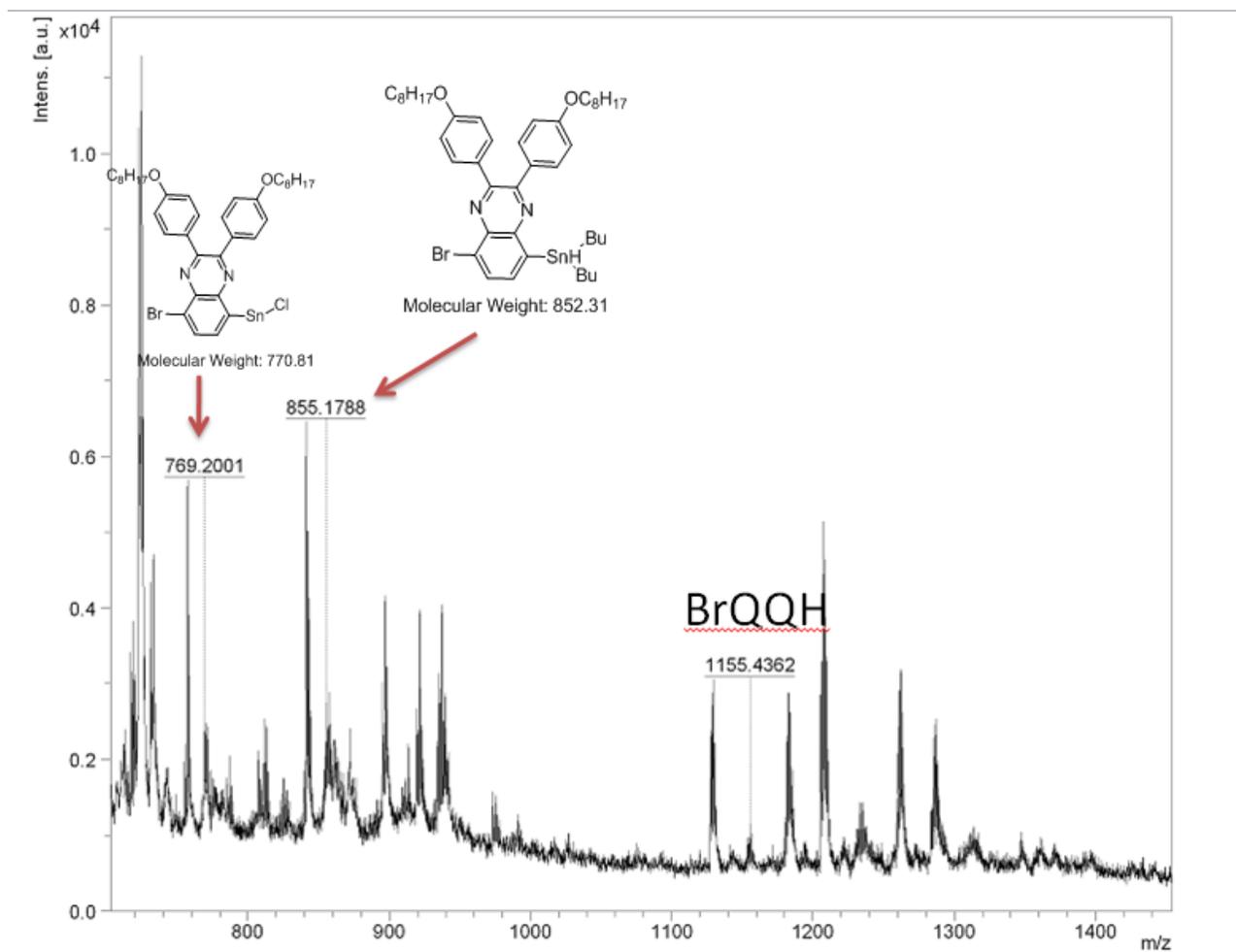


Figure S28. MALDI-TOF-MS spectra of 1Q2TSn and 2Q3TSn measured with the mixture of Equation 3.

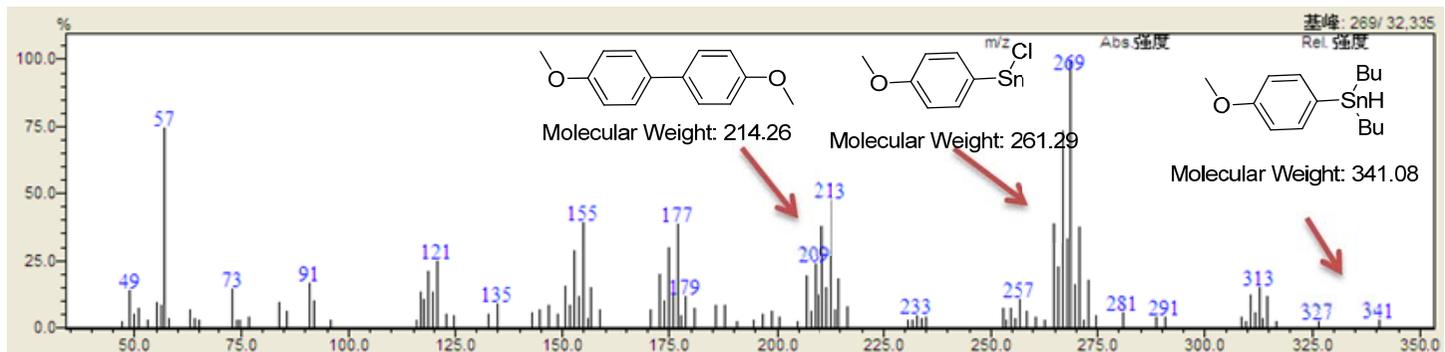


Figure S29. GC-MS spectra of 4,4'-dimethoxybiphenyl measured with the mixture of Equation 4.

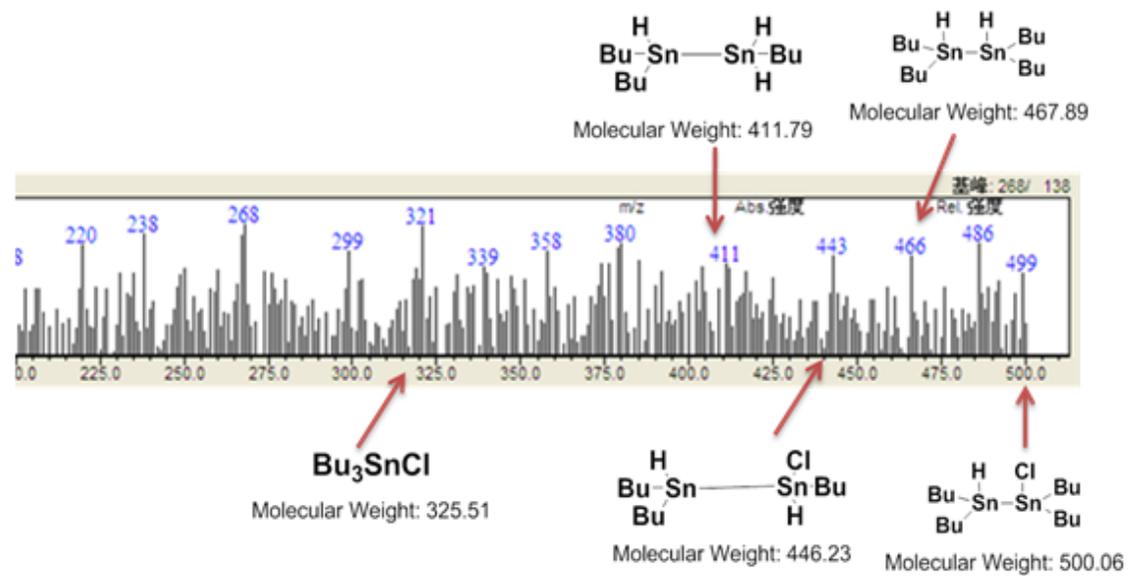


Figure S30. GC-MS spectrum of Bu₃SnCl heated with Pd(PPh₃)₄ for 30 min in toluene.

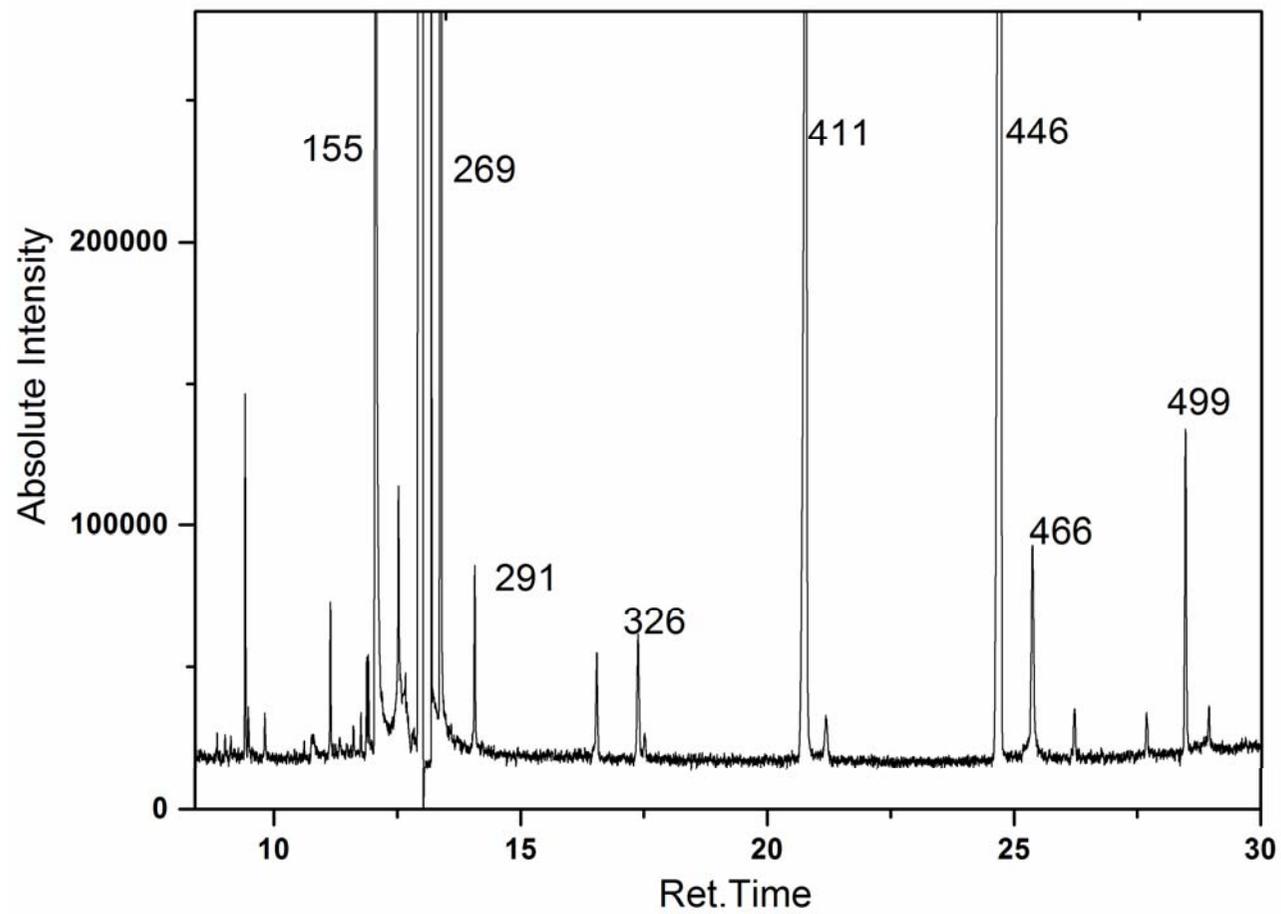


Figure S31. GC trace profile of Bu_3SnCl heated with $\text{Pd}(\text{PPh}_3)_4$ for 30 min in toluene. All numbers refer to molecular weight and the related molecular structures shown in Fig S30.

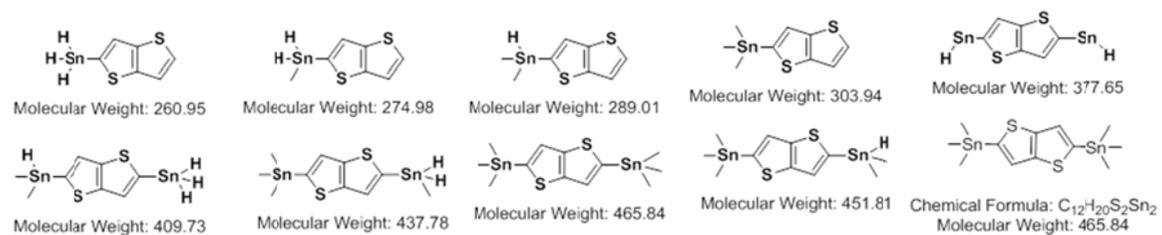


Figure S32. GC molecular weights and related molecular structures of 2,5-bis(trimethylstannyl)thieno[3,2-b]thiophene heated with Pd(PPh₃)₄ for 30 min in toluene. All numbers refer to molecular weight.

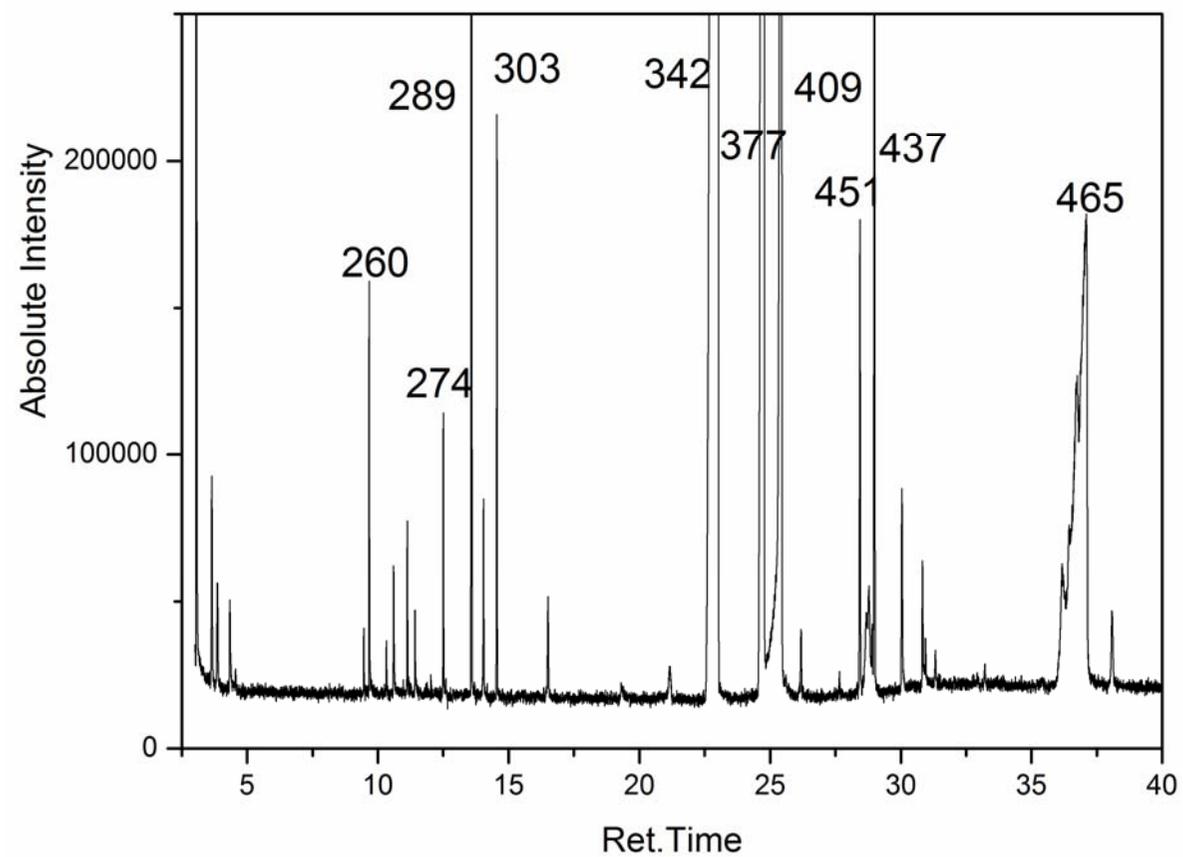


Figure S33. GC trace profile of 2,5-bis(trimethylstannyl)thieno[3,2-b]thiophene heated with Pd(PPh₃)₄ for 30 min in toluene. All numbers refer to molecular weight and the structures shown in Fig S32.