Supplementary Information

Synthesis of dithienofurans via cascade copper catalysed dual C-S coupling and ring closure reactions under mild conditions

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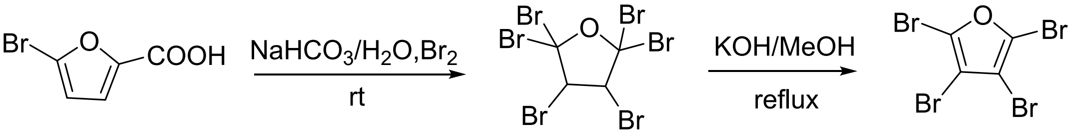
1. General Information

All reagents were purchased from commercial suppliers and used without further purification unless otherwise specified. Thin layer chromatography (TLC) was performed using TLC silica gel 60 F254 glass plates. Silica gel 60 (200-300 mesh) was used for column chromatography. Proton nuclear magnetic resonance (^{1}H NMR) and carbon nuclear magnetic resonance (^{13}C NMR) spectra were measured on JEOL 400YH spectrometers. Chemical shifts for hydrogens are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane (δ = 0), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), and coupling constant (Hz). HRMS spectra were determined on Thermo Fisher Q Exactive Focus LCMSMS Fourier transform ion cyclotron resonance mass spectrometer (ESI).

2. General procedure A for Sonogashira coupling

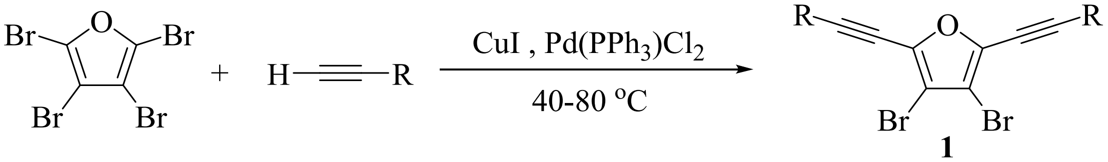


Scheme S1. Synthesis route of perbromofuran

5-Bromo-2-furancarboxylic acid (50.0 g, 262 mmol) and KOH (80 g, 952 mmol) were dissolved in 300 mL of water, heated to 70 °C and stirred for 30 minutes, then cooled to room temperature. Br_2 (43 mL, 836 mmol) was added dropwise in an ice water bath and stirred for 12 h at room temperature. The unreacted Br_2 was quenched by adding an appropriate amount of $NaHSO_3$ solution. Then the precipitate was filtered off and washed with water, affording 2,2,3,4,5,5-hexabromotetrahydrofuran (102 g, 187 mmol, 71%) as a white solid which contains *cis*-*trans* isomers.

KOH (4.12 g, 73.4 mmol) was added in 50 mL of methanol solution, and 2,2,3,4,5,5-hexabromotetrahydrofuran (10.0 g, 18.4 mmol) obtained above was added.

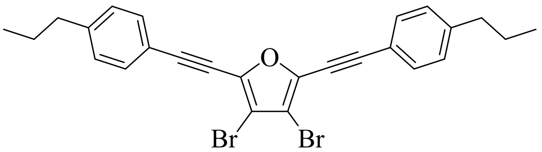
The reaction mixture and heated to 67 °C for 3 hours. The reaction mixture was cooled with liquid nitrogen and then filtered and washed with water. The crude product was recrystallized in ethanol to give the target compound perbromofuran (2.47 g, 6.44 mmol, 35%) as white needle-like solid. ^{13}C NMR (101 MHz, $CDCl_3$): δ 123.35. 107.25. HR-MS (ESI): m/z calcd for C_4Br_4O $[M]^+$ 379.6683, found 379.6683.



Scheme S2. Synthesis route of substrates for ring-closure reaction through Sonogashira coupling reaction

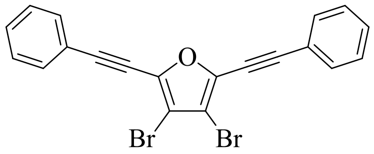
Perbromofuran (1 eq) was put into a two-necked flask, evacuated and refilled with nitrogen three times, then NEt_3 and THF (v/v, 1:1) were added and bubbled for 30 min with nitrogen. Then CuI (0.08-0.2 eq), $Pd(PPh_3)_2Cl_2$ (0.04-0.1 eq) and terminal alkyne (2.2-2.5 eq) were added under the protection of nitrogen, and then the reaction mixture was reacted at room temperature or enhanced temperature. The reaction mixture was stirred until the reaction was completed based on TLC analysis, NEt_3 and THF were evaporated under reduced pressure. By extraction with dichloromethane, the organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residual crude product was finally purified by flash silica gel column chromatography and recrystallization to afford the corresponding compound **1**.

3,4-dibromo-2,5-bis((4-propylphenyl)ethynyl)furan **(1a)**



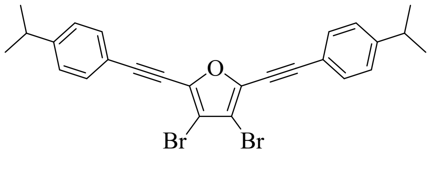
The general procedure A was followed with perbromofuran (5 g, 13 mmol), 1-ethynyl-4-propylbenzene (4.1 ml, 28.6 mmol), CuI (198 mg, 1.0 mmol) and $Pd(PPh_3)_2Cl_2$ (365 mg, 0.5 mmol) in NEt_3/THF (50 mL/50 mL) at 40 °C for 36 h. The residual crude product was purified by flash silica gel column chromatography (eluted with petroleum ether) and recrystallized in ethanol to afford compound **1a** (5.15 g, 10.1 mmol, 78%) as white needle solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, *J* = 8.0 Hz, 4H), 7.19 (d, *J* = 8.0 Hz, 4H), 2.61 (t, *J* = 8.0 Hz, 4H), 1.70-1.55 (m, 4H), 0.94 (t, *J* = 8.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.78, 136.86, 131.83, 128.83, 118.61, 109.42, 99.05, 76.91, 38.21, 24.43, 13.94. HR-MS (ESI): m/z calcd for $C_{26}H_{22}Br_2O$ $[M]^+$ 508.0037, found 508.0041.

3,4-dibromo-2,5-bis(phenylethynyl)furan **(1b)**



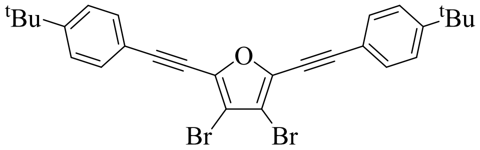
The general procedure A was followed with perbromofuran (300 mg, 0.78 mmol), phenylacetylene (0.2 mL, 1.7 mmol), CuI (12.2 mg, 0.06 mmol) and $Pd(PPh_3)_2Cl_2$ (22.5 mg, 0.03 mmol) in NEt_3/THF (10 mL/10 mL) at 40 °C for 36 h. The residual crude product was purified by flash silica gel column chromatography (eluted with petroleum ether) and recrystallized in ethanol to afford compound **1b** (222.7 mg, 0.523 mmol, 67%) as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60-7.54 (m, 4H), 7.44-7.35 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 136.76, 131.86, 129.65, 128.64, 121.36, 109.71, 98.63, 77.26. HR-MS (ESI): m/z calcd for $C_{20}H_{10}Br_2O$ $[M]^+$ 423.9098, found 423.9091.

3,4-dibromo-2,5-bis((4-isopropylphenyl)ethynyl)furan **(1c)**



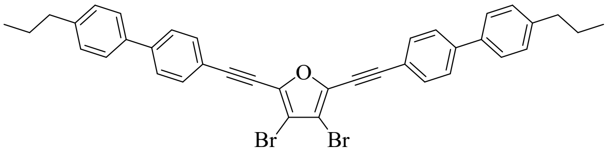
The general procedure A was followed with perbromofuran (1 g, 2.6 mmol), 4'-isopropylphenyl acetylene (937 mg, 5.7 mmol), CuI (40 mg, 0.2 mmol) and $Pd(PPh_3)_2Cl_2$ (73 mg, 0.1 mmol) in NEt_3/THF (30 mL/30 mL) at 40 °C for 36 h. The residual crude product was purified by flash silica gel column chromatography (eluted with petroleum ether and dichloromethane) and recrystallized in petroleum ether to afford compound **1c** (862 mg, 1.69 mmol, 65%) as white solid. ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 7.49 (d, *J* = 8.3 Hz, 4H), 7.24 (d, *J* = 8.1 Hz, 4H), 2.96-2.90 (m, 2H), 1.26 (d, *J* = 6.9 Hz, 12H). ^{13}C NMR (101 MHz, $(CD_3)_2CO$): δ 151.40, 136.70, 131.85, 127.08, 118.18, 109.25, 98.94, 76.13, 34.10, 23.16. HR-MS (ESI): m/z calcd for $C_{26}H_{22}Br_2O$ $[M]^+$ 508.0037, found 508.0037.

3,4-dibromo-2,5-bis((4-(tert-butyl)phenyl)ethynyl)furan **(1d)**



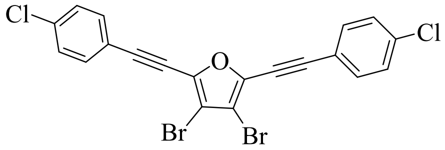
The general procedure A was followed with perbromofuran (1 g, 2.6 mmol), 4-(*tert*-tutyl)phenylacetylene (905 mg, 5.7 mmol), CuI (40 mg, 0.2 mmol) and $Pd(PPh_3)_2Cl_2$ (73 mg, 0.1 mmol) in NEt_3/THF (30 mL/30 mL) at 60 °C for 24 h. The residual crude product was purified by flash silica gel column chromatography (eluted with petroleum ether) and recrystallized in ethanol to afford compound **1d** (645 mg, 1.2 mmol, 46%) as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, *J* = 8.6 Hz, 4H), 7.40 (d, *J* = 8.4 Hz, 4H), 1.33 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.14, 136.79, 131.65, 125.65, 118.34, 109.35, 98.83, 77.10, 35.05, 31.20. HR-MS (ESI): m/z calcd for $C_{28}H_{26}Br_2O$ $[M]^+$ 536.0350, found 536.0350.

3,4-dibromo-2,5-bis((4'-propyl-[1,1'-biphenyl]-4-yl)ethynyl)furan **(1e)**



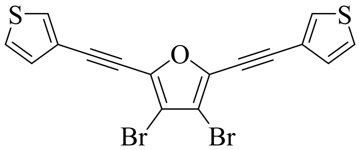
The general procedure A was followed with perbromofuran (1 g, 2.6 mmol), 4-ethynyl-4'-propyl-1,1'-biphenyl (1.43 g, 6.5 mmol), CuI (40 mg, 0.2 mmol) and $Pd(PPh_3)_2Cl_2$ (73 mg, 0.1 mmol) in NEt_3/THF (30 mL/30 mL) at 60 °C for 24 h. The residual crude product was purified by flash silica gel column chromatography (eluted with petroleum ether and dichloromethane) and recrystallized in petroleum ether and dichloromethane cosolvent to afford compound **1e** (689 mg, 1.04 mmol, 40%) as yellow solid. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.66 – 7.56 (m, 8H), 7.53 (d, *J* = 8.3 Hz, 4H), 7.27 (d, *J* = 8.4 Hz, 4H), 2.64 (t, *J* = 8.0 Hz, 4H), 1.73-1.64 (m, 4H), 0.98 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 142.82, 142.33, 137.44, 136.82, 132.26, 129.19, 127.08, 126.99, 119.79, 109.67, 98.81, 77.83, 37.81, 24.65, 13.99. HR-MS (ESI): m/z calcd for $C_{38}H_{30}Br_2O$ [M]$^+$ 660.0663, found 660.0661.

3,4-dibromo-2,5-bis((4-chlorophenyl)ethynyl)furan **(1f)**



The general procedure A was followed with perbromofuran (1 g, 2.6 mmol), 4-chlorophenylacetylene (781 mg, 5.7 mmol), CuI (40 mg, 0.2 mmol) and Pd(PPh$_3$)$_2$Cl$_2$ (73 mg, 0.1 mmol) in NEt$_3$/THF (30 mL/30 mL) at 60 °C for 24 h. The residual crude product was purified by flash silica gel column chromatography (eluted with petroleum ether and dichloromethane) and recrystallized in trichloromethane and ethanol cosolvent to afford compound **1f** (594 mg, 1.2 mmol, 46%) as yellow solid. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.49 (d, *J* = 8.3 Hz, 4H), 7.36 (d, *J* = 8.3 Hz, 4H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 136.73, 135.93, 132.99, 129.05, 119.82, 110.04, 97.58, 78.08. HR-MS (ESI): m/z calcd for $C_{20}H_8Br_2Cl_2O$ [M]$^+$ 491.8319, found 491.8315.

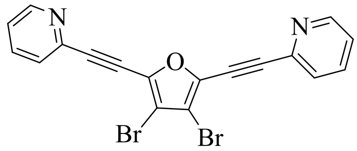
3,4-dibromo-2,5-bis(thiophen-3-ylethynyl)furan **(1g)**



The general procedure A was followed with perbromofuran (1 g, 2.6 mmol), 3-ethynylthiophene (703 mg, 6.5 mmol), CuI (40 mg, 0.2 mmol) and Pd(PPh$_3$)$_2$Cl$_2$ (73 mg, 0.1 mmol) in NEt$_3$/THF (30 mL/30 mL) at 40 °C for 48 h. The residual crude product was purified by flash silica gel column chromatography (eluted with petroleum ether and dichloromethane cosolvent) and recrystallized in toluene to afford compound

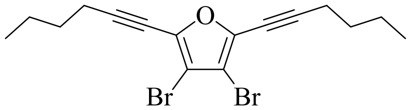
1g (866 mg, 1.98 mmol, 76%) as brown solid. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.64 (dd, *J* = 3.0, 1.1 Hz, 2H), 7.33 (dd, *J* = 5.0, 3.0 Hz, 2H), 7.22 (dd, *J* = 5.0, 1.1 Hz, 2H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 136.71, 130.91, 129.81, 126.03, 120.43, 109.49, 93.78, 76.85. HR-MS (ESI): m/z calcd for $C_{16}H_6Br_2OS_2$ [M]$^+$ 435.8227, found 435.8230.

2,2'-((3,4-dibromofuran-2,5-diyl)bis(ethyne-2,1-diyl))dipyridine **(1h)**



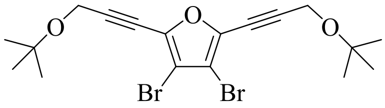
The general procedure A was followed with perbromofuran (1 g, 2.6 mmol), 2-ethynylpyridine (590 mg, 5.8 mmol), CuI (99 mg, 0.52 mmol) and Pd(PPh$_3$)$_2$Cl$_2$ (182 mg, 0.26 mmol) in NEt$_3$/THF (30 mL/30 mL) at 80 °C for 24 h. The residual crude product was purified by flash silica gel column chromatography (eluted with petroleum ether and ethyl acetate cosolvent) and recrystallized in petroleum ether and dichloromethane cosolvent to afford compound **1h** (356 mg, 0.832 mmol, 32%) as brown solid. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.75-8.54 (m, 1H), 7.73 (td, *J* = 7.8, 1.9 Hz, 1H), 7.59 (dd, *J* = 0.8, 7.6 Hz, 1H), 7.40 – 7.28 (m, 1H). ^{13}C NMR (101 MHz, (CD$_3$)$_2$CO): δ 150.72, 141.32, 136.80, 136.71, 127.92, 124.53, 110.97, 98.00, 75.06. HR-MS (ESI): m/z calcd for $C_{18}H_8Br_2N_2O$ [M]$^+$ 425.9003, found 425.9004.

3,4-dibromo-2,5-di(hex-1-yn-1-yl)furan **(1i)**



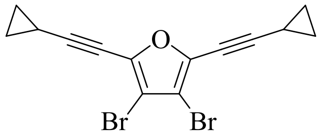
The general procedure A was followed with perbromofuran (767 g, 2.0 mmol), 1-hexyne (410 mg, 5.0 mmol), CuI (30 mg, 0.16 mmol) and Pd(PPh$_3$)$_2$Cl$_2$ (56 mg, 0.08 mmol) in NEt$_3$/THF (20 mL/20 mL) at 40 °C for 24 h. The residual crude product was purified by flash silica gel column chromatography (eluted with petroleum ether) to afford compound **1i** (486 mg, 1.26 mmol, 63%) as yellow oily liquid. ^{1}H NMR (400 MHz, CDCl$_3$): δ 2.48 (t, *J* = 7.0 Hz, 4H), 1.66-1.54 (m, 4H), 1.54-1.41 (m, 4H), 0.94 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 136.26, 107.89, 100.27, 69.09, 30.22, 21.98, 19.43, 13.63. HR-MS (ESI): m/z calcd for $C_{16}H_{18}Br_2O$ $[M]^+$ 383.9724, found 383.9725.

3,4-dibromo-2,5-bis(3-(tert-butoxy)prop-1-yn-1-yl)furan **(1j)**



The general procedure A was followed with perbromofuran (767 g, 2.0 mmol), 3-(tert-butoxy)prop-1-yne (673 mg, 6.0 mmol), CuI (61 mg, 0.32 mmol) and $Pd(PPh_3)_2Cl_2$ (112.4 mg, 0.16 mmol) in NEt_3/THF (20 mL/20 mL) at 65 °C for 24 h. The residual crude product was purified by flash silica gel column chromatography (eluted with petroleum ether) and recrystallized in petroleum ether to afford compound **1j** (419 mg, 0.94 mmol, 47%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.36 (s, 4H), 1.28 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 136.27, 109.65, 97.18, 75.17, 72.81, 51.08, 27.67. HR-MS (ESI): m/z calcd for $C_{18}H_{22}Br_2O_3$ $[M]^+$ 443.9936, found 443.9939.

3,4-dibromo-2,5-bis(cyclopropylethynyl)furan **(1k)**

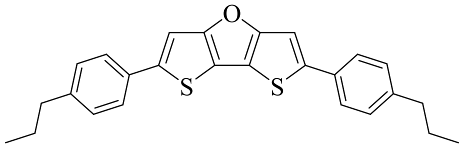


The general procedure A was followed with perbromofuran (767 mg, 2.0 mmol), ethynylcyclopropane (397 mg, 6.0 mmol), CuI (30.5 mg, 0.16 mmol) and $Pd(PPh_3)_2Cl_2$ (56.2 mg, 0.08 mmol) in NEt_3/THF (20 mL/20 mL) at 25 °C for 24 h. The residual crude product was purified by flash silica gel column chromatography (eluted with petroleum ether) and recrystallized in petroleum ether to afford compound **1k** (290 mg, 0.82 mmol, 41%) as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.57-1.48 (m, 2H), 1.01-0.91 (m, 4H), 0.90-0.86 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 136.22, 108.16, 103.39, 63.97, 9.40, 0.43. HR-MS (ESI): m/z calcd for $C_{14}H_{10}Br_2O$ $[M]^+$ 351.9098, found 351.9099.

3. General procedure B for the synthesis of DTFs

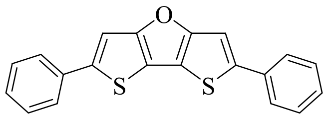
The synthesis of DTFs (**2a**-**2l**) were based on the corresponding 3,4-dibromo-2,5-dialkynylfuran (**1a**-**1l**) as the starting substrate. Under nitrogen atmosphere, the substrate (**1a**-**1l**, 0.2 mmol), the catalyst $Cu(OAc)_2 \cdot H_2O$ (0.01 mmol), the base $K_3PO_4 \cdot H_2O$ (0.4 mmol), the ligand 4,7-diphenyl-1,10-phenanthroline (DPPhen, 0.02 mmol) and the sulfur source $Na_2S \cdot 9H_2O$ (0.6 mmol) were added to a 25 ml Schlenk tube, and then it was evacuated and refilled with nitrogen three times. Then NMP (5 mL) was added as the solvent, and the reaction mixture was heated for 12-24 hours. The solvent NMP was evaporated under reduced pressure, and the residual crude product was purified by flash silica gel column chromatography and recrystallization to afford the corresponding compounds **2**.

2,6-bis(4-propylphenyl)dithieno[3,2-*b*:2',3'-*d*]furan **(2a)**



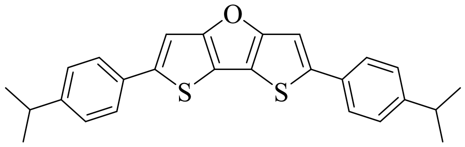
Following general procedure B, the reaction was carried out at 80 °C for 12 h and the residual crude product was purified by flash silica gel column chromatography (eluting with petroleum ether and dichloromethane cosolvent) and recrystallized in trichloromethane and ethanol cosolvent to afford compound **2a** (58 mg, 0.14 mmol, 70%) as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 8.2 Hz, 4H), 7.33 (s, 2H), 7.21 (d, *J* = 8.2 Hz, 4H), 2.61 (t, *J* = 7.3 Hz, 4H), 1.71 – 1.62 (m, 4H), 0.97 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.50, 143.09, 142.68, 132.49, 129.24, 125.30, 117.72, 107.44, 37.83, 24.56, 13.89. HR-MS (ESI): m/z calcd for $C_{26}H_{24}OS_2$ $[M]^+$ 416.1269, found 416.1267.

2,6-diphenyldithieno[3,2-*b*:2',3'-*d*]furan **(2b)**



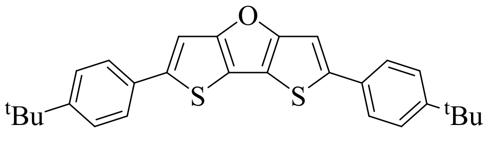
Following general procedure B, the reaction was carried out at 80 °C for 12 h and the residual crude product was purified by flash silica gel column chromatography (eluting with petroleum ether and dichloromethane cosolvent) and recrystallized in trichloromethane to afford compound **2b** (17 mg, 0.052 mmol, 26%) as yellow solid. ^{1}H NMR (400 MHz, $CDCl_2CDCl_2$, 90 °C): δ 7.65 (d, *J* = 8.1 Hz, 4H), 7.44 (t, *J* = 7.5 Hz, 4H), 7.40 (s, 2H), 7.34 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_2CDCl_2$, 90 °C): δ 160.83, 143.41, 135.11, 129.24, 128.04, 125.65, 118.36, 108.16. HR-MS (ESI): m/z calcd for $C_{20}H_{12}OS_2$ $[M]^+$ 332.0330, found 332.0322.

2,6-bis(4-isopropylphenyl)dithieno[3,2-*b*:2',3'-*d]*furan **(2c)**



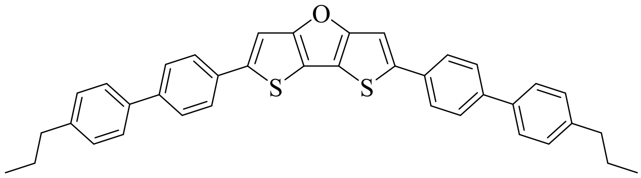
Following general procedure B, the reaction was carried out at 80 °C for 12 h and the residual crude product was purified by flash silica gel column chromatography (eluting with petroleum ether and dichloromethane cosolvent) and recrystallized in trichloromethane and ethanol cosolvent to afford compound **2c** (35 mg, 0.084 mmol, 42%) as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, *J* = 8.3 Hz, 4H), 7.33 (s, 2H), 7.27 (d, *J* = 8.2 Hz, 4H), 2.97-2.90 (m, 2H), 1.28 (d, *J* = 6.9 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.50, 148.85, 143.05, 132.64, 127.21, 125.43, 117.76, 107.47, 33.98, 23.98. HR-MS (ESI): m/z calcd for $C_{26}H_{24}OS_2$ $[M]^+$ 416.1269, found 416.1271.

2,6-bis(4-(tert-butyl)phenyl)dithieno[3,2-*b*:2',3'-*d*]furan **(2d)**



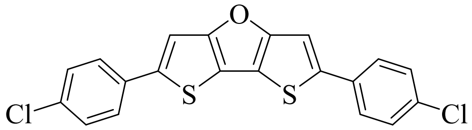
Following general procedure B, the reaction was carried out at 80 °C for 12 h and the residual crude product was purified by flash silica gel column chromatography (eluting with petroleum ether and dichloromethane cosolvent) and recrystallized in trichloromethane and ethanol cosolvent to afford compound **2d** (52 mg, 0.116 mmol, 58%) as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 8.5 Hz, 4H), 7.43 (d, *J* = 8.6 Hz, 4H), 7.34 (s, 2H), 1.35 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.51, 151.09, 142.95, 132.25, 126.09, 125.15, 117.80, 107.51, 34.76, 31.35. HR-MS (ESI): m/z calcd for $C_{28}H_{28}OS_2$ $[M]^+$ 444.1582, found 444.1583.

2,6-bis(4'-propyl-[1,1'-biphenyl]-4-yl)dithieno[3,2-*b*:2',3'-*d*]furan**(2e)**



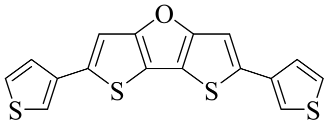
Following general procedure B, the reaction was carried out at 80 °C for 23 h and the residual crude product was purified by flash silica gel column chromatography (eluting with petroleum ether and dichloromethane cosolvent) and recrystallized in trichloromethane and ethanol cosolvent to afford compound **2e** (40 mg, 0.07 mmol, 35%) as yellow solid. ^{1}H NMR (400 MHz, $CDCl_2CDCl_2$, 90 °C): δ 7.71 (d, *J* = 7.7 Hz, 4H), 7.64 (d, *J* = 8.2 Hz, 4H), 7.56 (d, *J* = 7.8 Hz, 4H), 7.35 (s, 2H), 7.27 (d, *J* = 8.4 Hz, 4H), 2.66 (t, *J* = 8.1 Hz, 4H), 1.77-1.67 (m, 4H), 1.01 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_2CDCl_2$, 90 °C): δ 143.59, 142.26, 140.44, 137.82, 133.22, 129.83, 129.52, 128.67, 127.46, 126.86, 126.77, 126.16, 37.82, 24.32, 13.92.

2,6-bis(4-chlorophenyl)dithieno[3,2-*b*:2',3'-d]furan **(2f)**



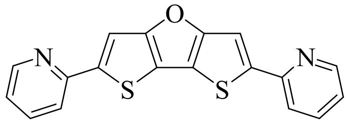
Following general procedure B, the reaction was carried out at 80 °C for 12 h and the residual crude product was purified by flash silica gel column chromatography (eluting with petroleum ether and dichloromethane cosolvent) and recrystallized in trichloromethane and ethanol cosolvent to afford compound **2f** (34 mg, 0.084 mmol, 42%) as yellow solid. ^{1}H NMR (400 MHz, $CDCl_2CDCl_2$, 90 °C): δ 7.55 (d, *J* = 8.1 Hz, 4H), 7.40 (d, *J* = 8.2 Hz, 4H), 7.36 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_2CDCl_2$, 90 °C): δ 160.87, 142.15, 133.91, 133.63, 129.45, 126.80, 120.54, 118.59. HR-MS (ESI): m/z calcd for $C_{20}H_{10}Cl_2OS_2$ $[M]^+$ 399.9550, found 399.9554.

2,6-di(thiophen-3-yl)dithieno[3,2-*b*:2',3'-*d*]furan **(2g)**



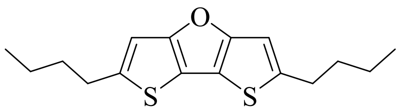
Following general procedure B, the reaction was carried out at 80 °C for 12 h and the residual crude product was purified by flash silica gel column chromatography (eluting with toluene) and recrystallized in toluene to afford compound **2g** (34 mg, 0.098 mmol, 49%) as brown solid. ^{1}H NMR (400 MHz, $(CD_3)_2SO$, 90 °C): δ 7.73 (dd, *J* = 2.9, 1.2 Hz, 2H), 7.62 (dd, *J* = 4.9, 2.7 Hz, 2H), 7.60 (s, 2H), 7.45 (dd, *J* = 5.0, 1.6 Hz, 2H). HR-MS (ESI): m/z calcd for $C_{16}H_8OS_4$ $[M]^+$ 343.9458, found 343.9458.

2,6-di(pyridin-2-yl)dithieno[3,2-*b*:2',3'-*d*]furan **(2h)**



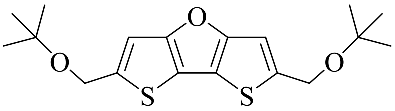
Following general procedure B, the reaction was carried out at 80 °C for 12 h and the residual crude product was purified by flash silica gel column chromatography (eluting with ethyl acetate and toluene cosolvent) and recrystallized in toluene to afford compound **2h** (20 mg, 0.06 mmol, 30%) as yellow solid. ^{1}H NMR (400 MHz, $(CD_3)_2SO$, 90 °C): δ 8.52 (d, *J* = 4.8 Hz, 2H), 8.03 (s, 2H), 7.92 (d, *J* = 7.9 Hz, 2H), 7.81 (t, *J* = 7.1 Hz, 2H), 7.27-7.23 (m, 2H). ^{13}C NMR (101 MHz, $(CD_3)_2SO$, 90 °C): δ 161.08, 152.61, 144.83, 137.64, 120.91, 119.48 119.07, 112.21, 110.35. HR-MS (ESI): m/z calcd for $C_{18}H_{10}N_2OS_2$ $[M]^+$ 334.0235, found 334.0235.

2,6-dibutyldithieno[3,2-*b*:2',3'-*d*]furan **(2i)**



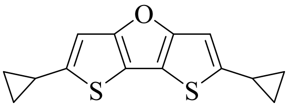
Following general procedure B, the reaction was carried out at 100 °C for 12 h and the residual crude product was purified by flash silica gel column chromatography (eluting with petroleum ether) to afford compound **2i** (7 mg, 0.024 mmol, 12%) as offwhite solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.82 (s, 2H), 2.85 (t, J = 7.6 Hz, 4H), 1.73-1.65 (m, 4H), 1.46-1.37 (m, 4H), 0.94 (t, J = 7.3 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.74, 144.14, 116.16, 109.29, 33.82, 31.19, 22.17, 13.88. HR-MS (ESI): m/z calcd for $C_{16}H_{20}OS_2$ $[M]^+$ 292.0956, found 292.0954.

2,6-bis(tert-butoxymethyl)dithieno[3,2-*b*:2',3'-*d*]furan **(2j)**



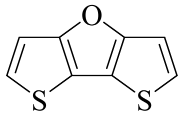
Following general procedure B, the reaction was carried out at 100 °C for 12 h and the residual crude product was purified by flash silica gel column chromatography (eluting with petroleum ether and dichloromethane cosolvent) to afford compound **2j** (11 mg, 0.032 mmol, 16%) as offwhite solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.02 (s, 2H), 4.64 (s, 4H), 1.31 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.88, 141.67, 118.28, 110.24, 76.80, 60.47, 27.75. HR-MS (ESI): m/z calcd for $C_{18}H_{24}O_3S_2$ $[M]^+$ 352.1167, found 352.1165.

2,6-dicyclopropyldithieno[3,2-*b*:2',3'-*d*]furan **(2k)**



Following general procedure B, the reaction was carried out at 80 °C for 12 h and the residual crude product was purified by flash silica gel column chromatography (eluting with petroleum ether) to afford compound **2k** (18 mg, 0.069 mmol, 32%) as offwhite solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.81 (s, 2H), 2.15-2.08 (m, 2H), 1.06-0.97 (m, 4H), 0.82-0.74 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.55, 146.71, 115.42, 108.37, 12.39, 9.71. HR-MS (ESI): m/z calcd for $C_{14}H_{12}OS_2$ $[M]^+$ 260.0330, found 260.0326.

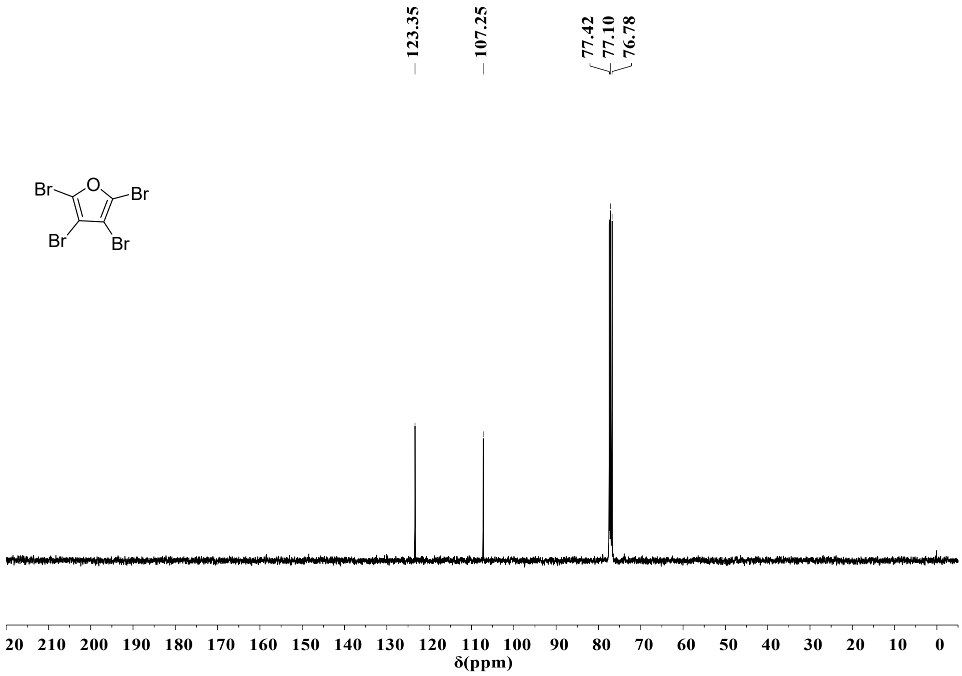
dithieno[3,2-*b*:2',3'-*d*]furan **(2l)**



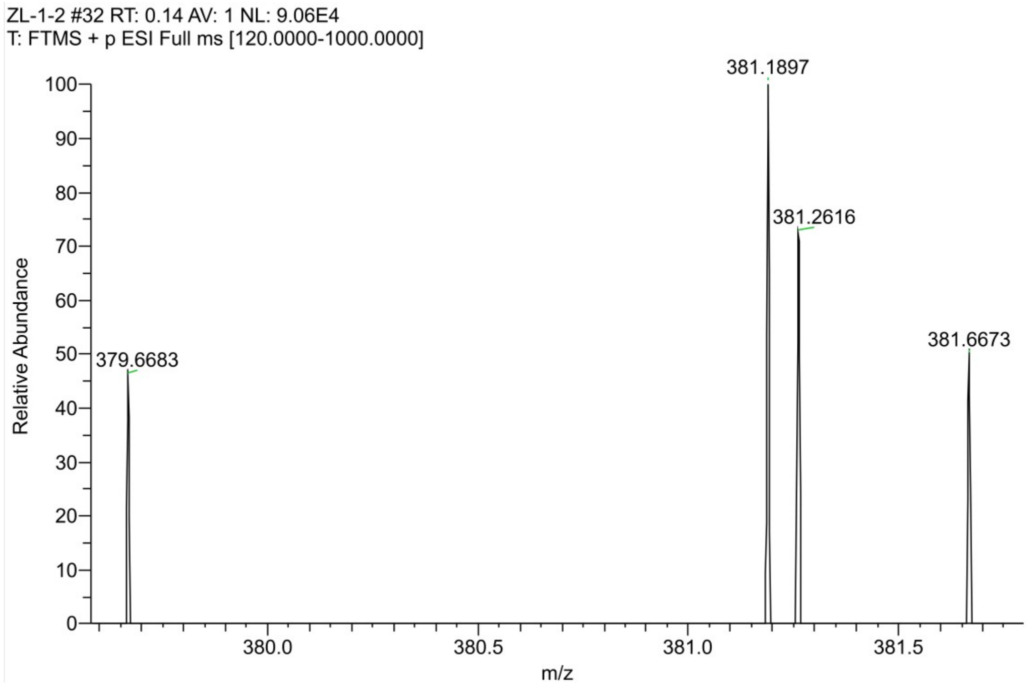
The general procedure A was followed with perbromofuran (2.5 g, 6.5 mmol), trimethylsilylacetylene (1.6 g, 16.3 mmol), CuI (99 mg, 0.52 mmol) and Pd(PPh_3)$_2$$Cl_2$ (182 mg, 0.26 mmol) in NEt_3/THF (25 mL/25 mL) at 65 °C for 12 h， then the solvent NEt_3 and THF were evaporated under reduced pressure. Next general procedure B were followed, $Cu(OAc)_2 \cdot H_2O$ (65.5 mg, 0.325 mmol), 4,7-diphenyl-1,10-phenanthroline (218 mg, 0.65 mmol), $K_3PO_4 \cdot H_2O$ (4.5 g, 19.5 mmol), $Na_2S \cdot 9H_2O$ (4.7 g, 19.5 mmol) and NMP (25 ML) were used, the reaction mixture was stirred at 80 °C for 12 h. The residual crude product was purified by flash silica gel column chromatography (eluting with petroleum ether) and recrystallized in ethanol to afford compound **2l** (117 mg, 0.65 mmol, 10%) as offwhite solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (d, *J* = 5.4 Hz, 2H), 7.15 (d, *J* = 5.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.11, 123.86, 118.63, 112.06. HR-MS (ESI): m/z calcd for $C_8H_4OS_2$ $[M]^+$179.9704, found 179.9702.

4. ^{1}H and ^{13}C NMR spectra and HRMS spectra

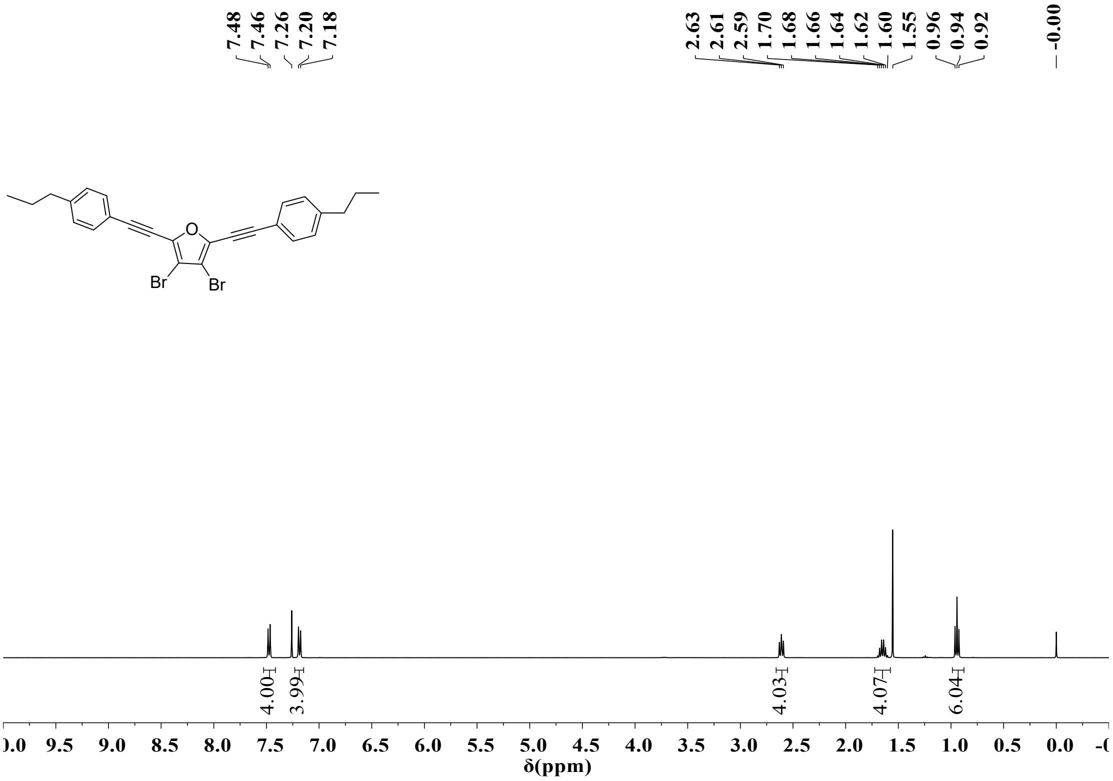
^{13}C NMR spectrum for perbromofuran



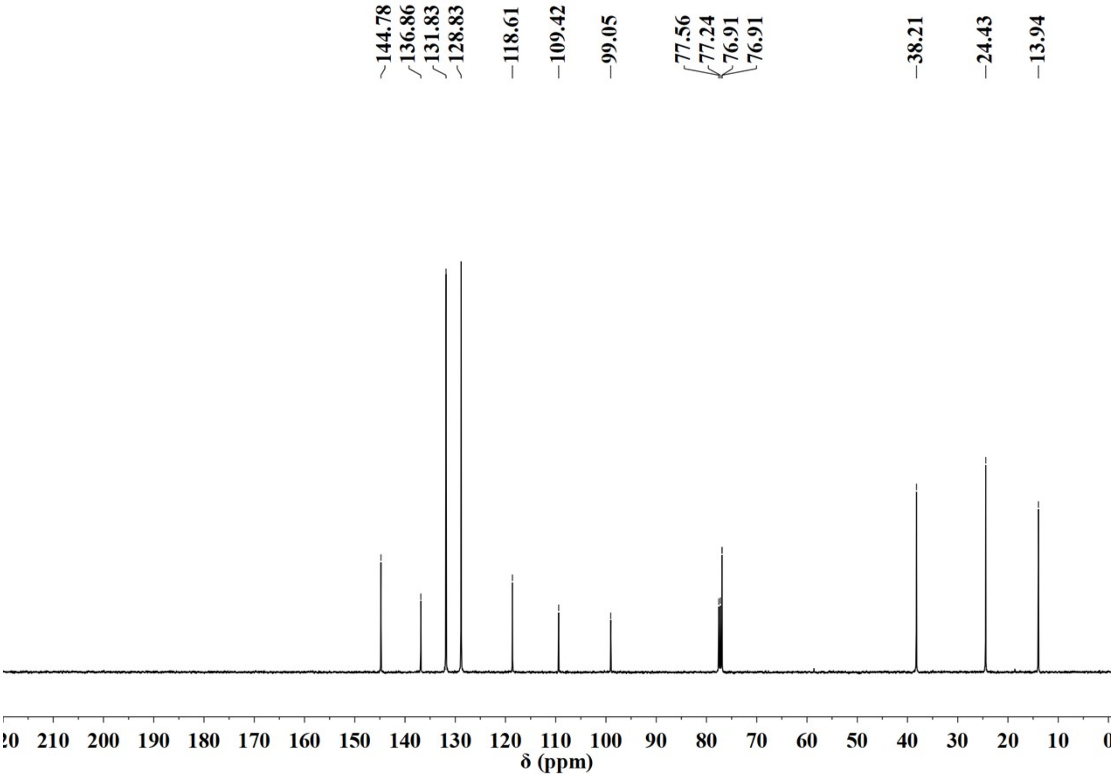
HR-MS spectrum for perbromofuran



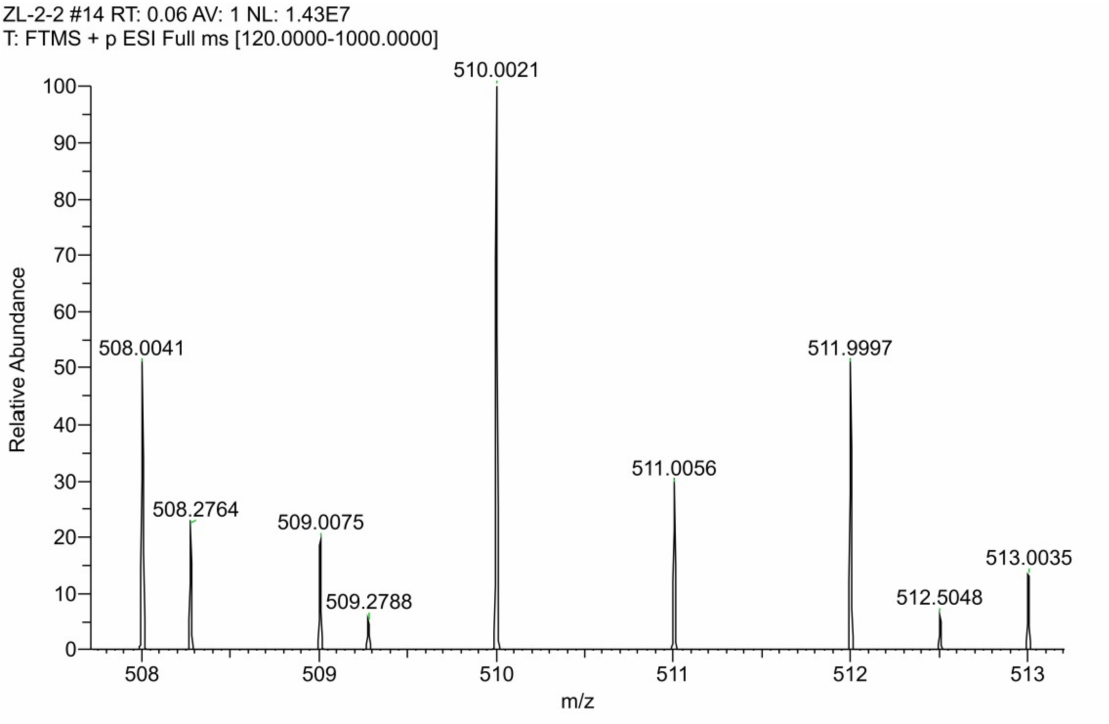
^{1}H NMR spectrum for **1a**



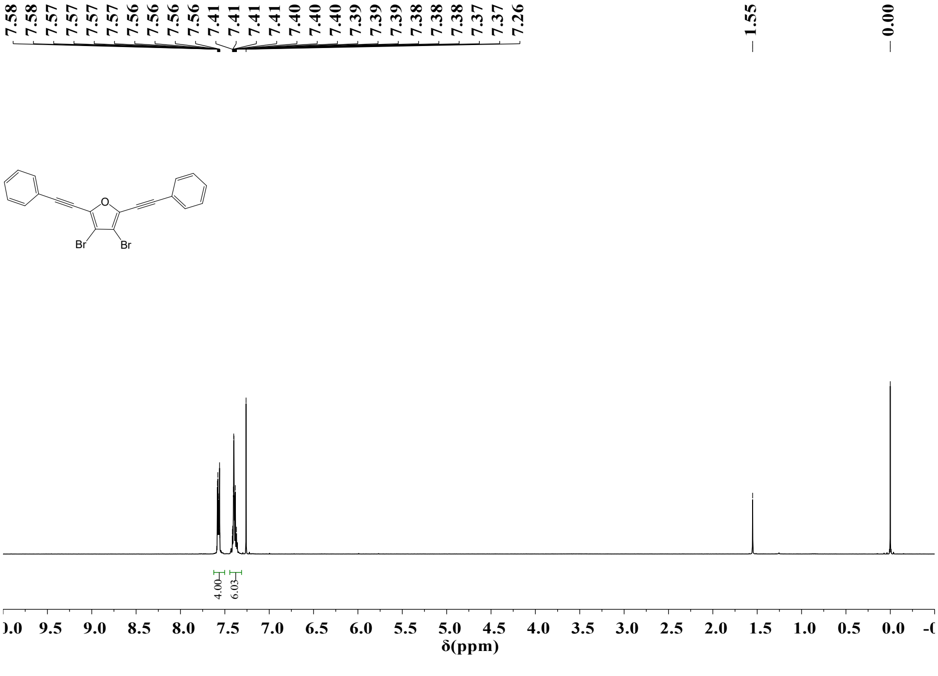
^{13}C NMR spectrum for **1a**



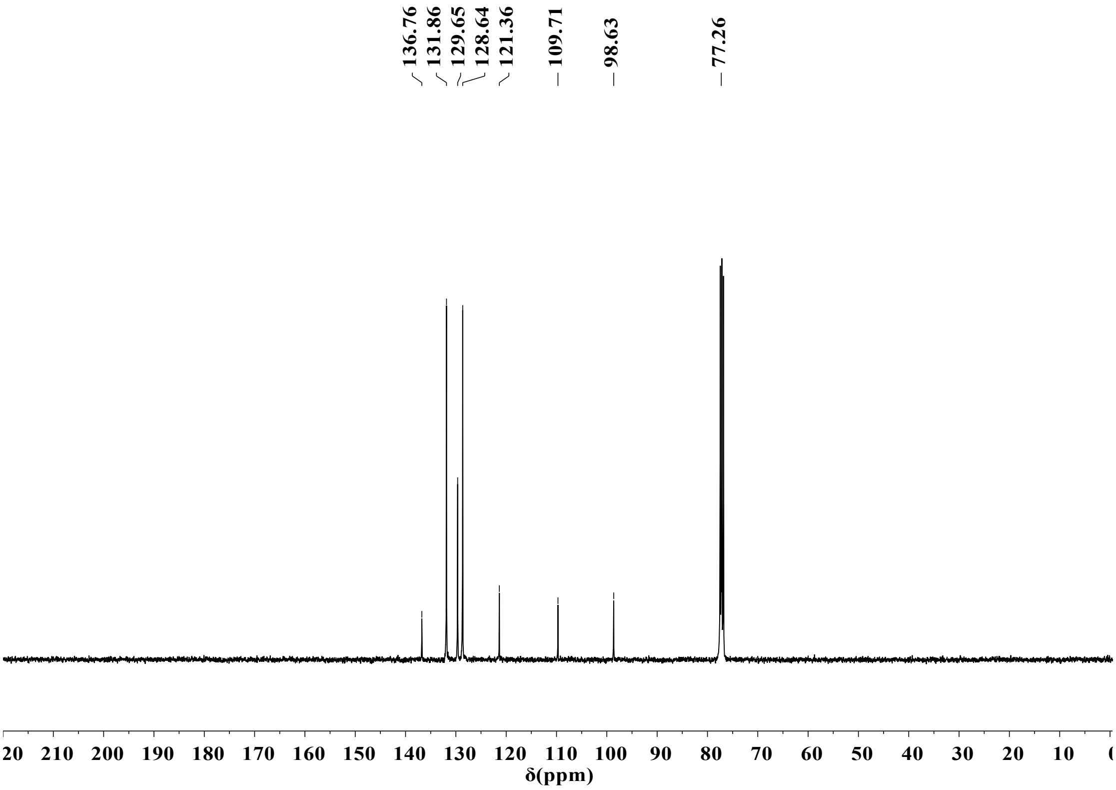
HR-MS spectrum for **1a**



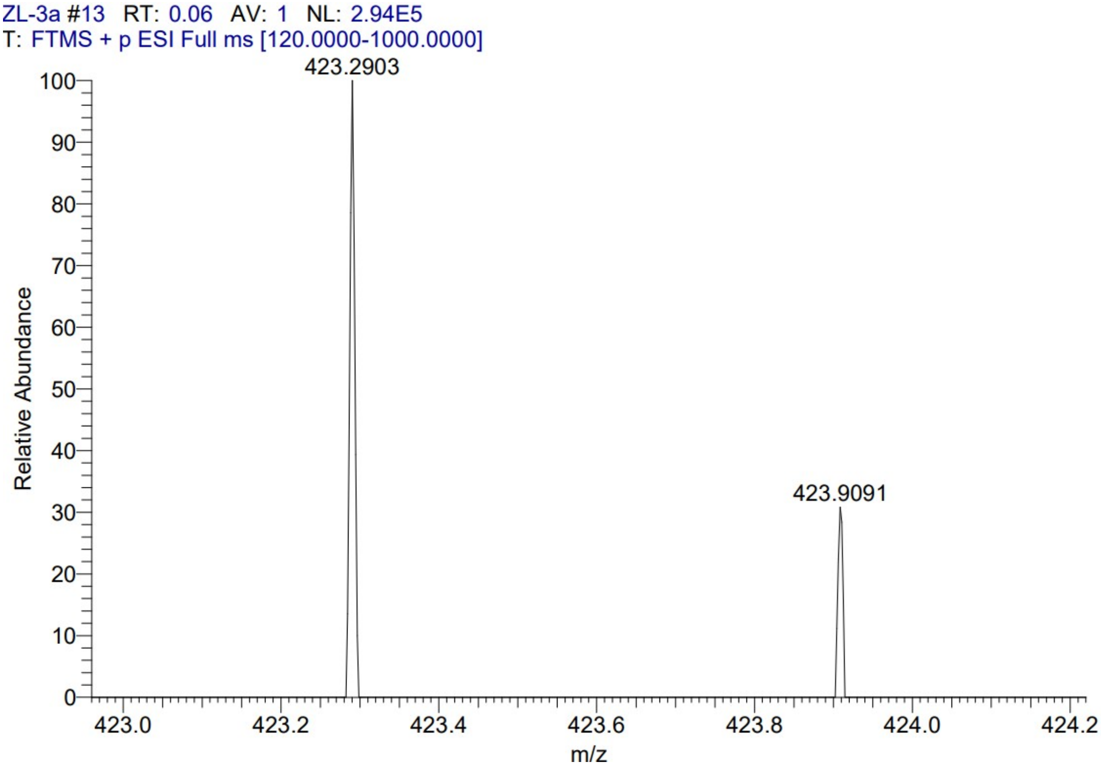
^{1}H NMR spectrum for **1b**



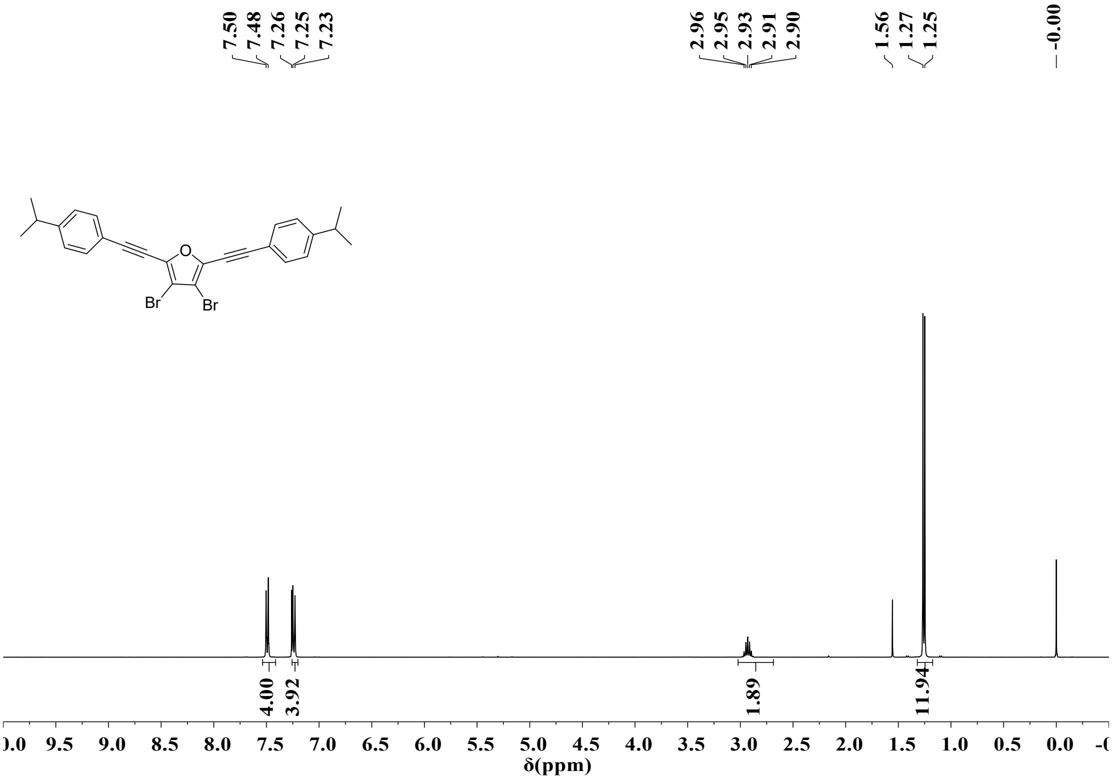
^{13}C NMR spectrum for **1b**



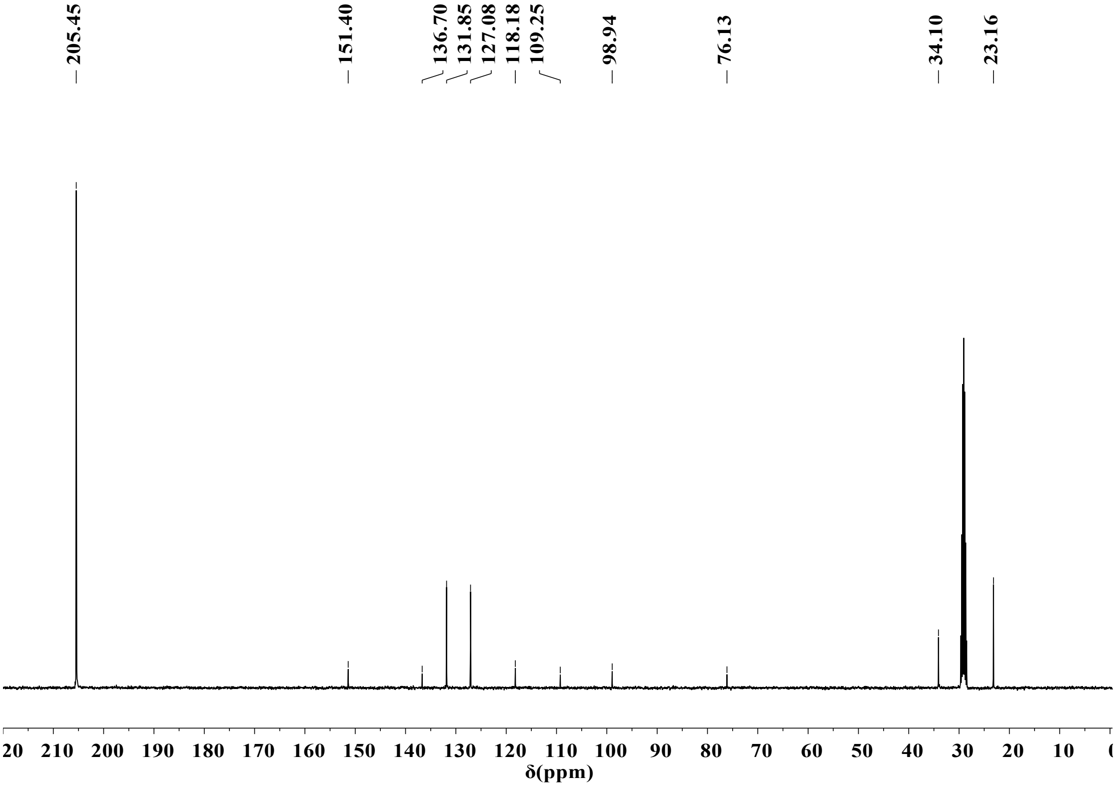
HR-MS spectrum for **1b**



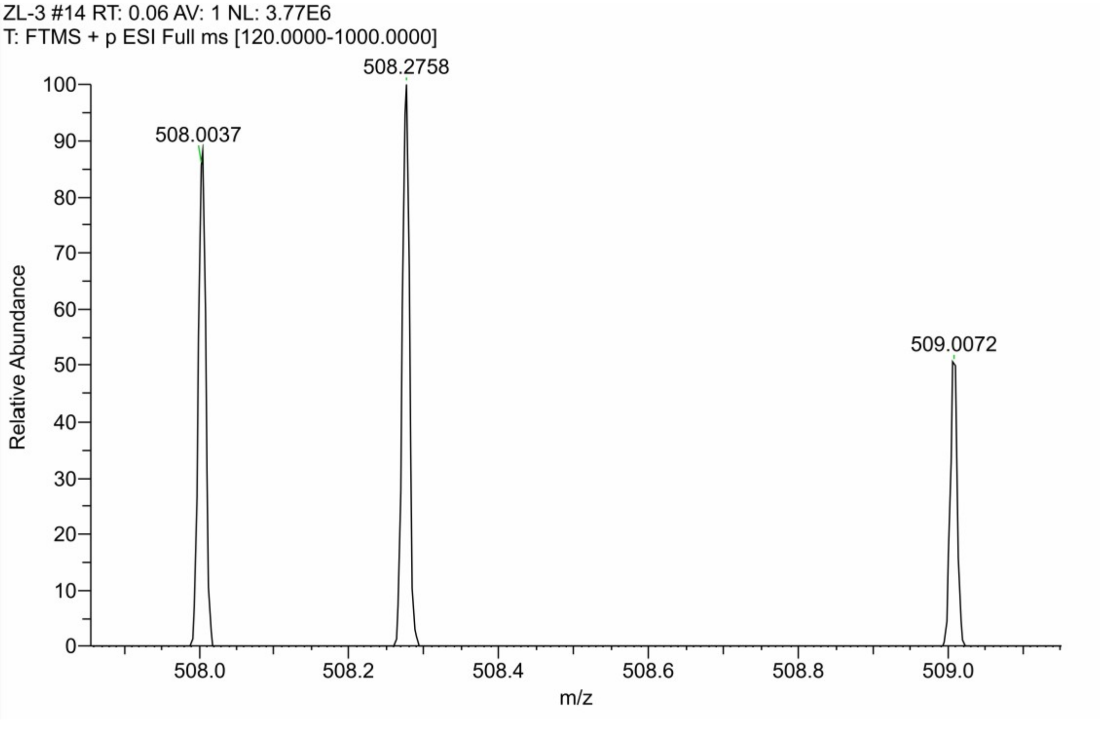
^{1}H NMR spectrum for **1c**



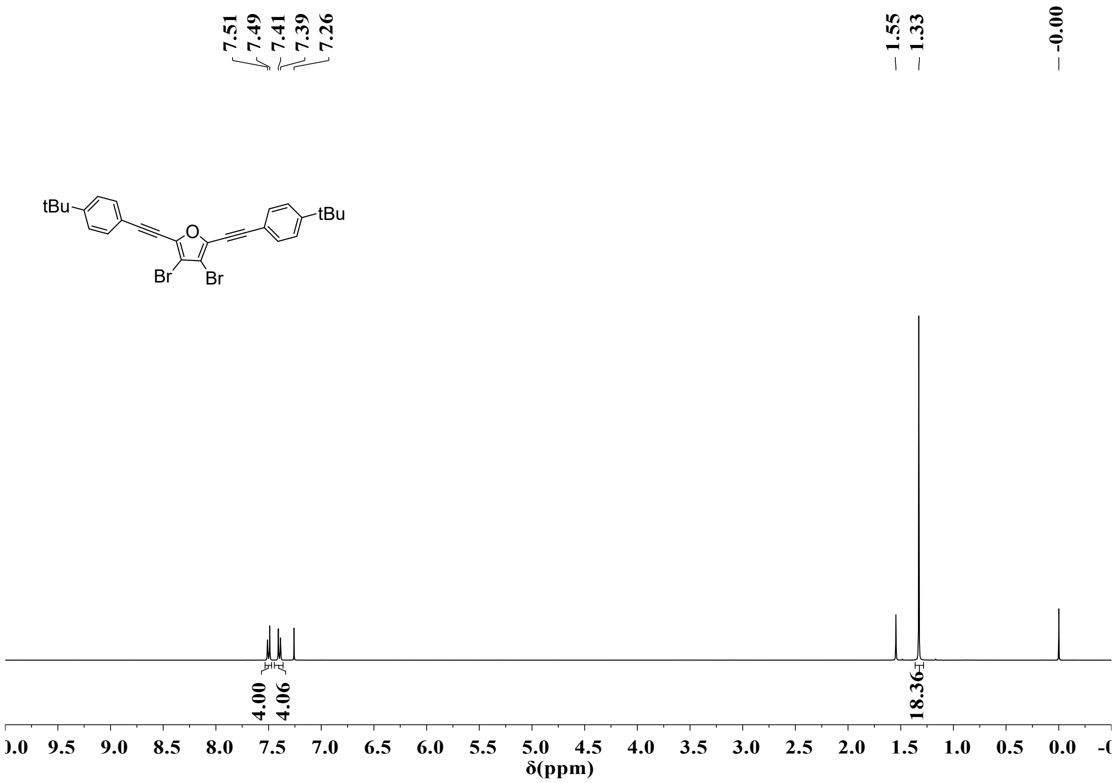
^{13}C NMR spectrum for **1c**



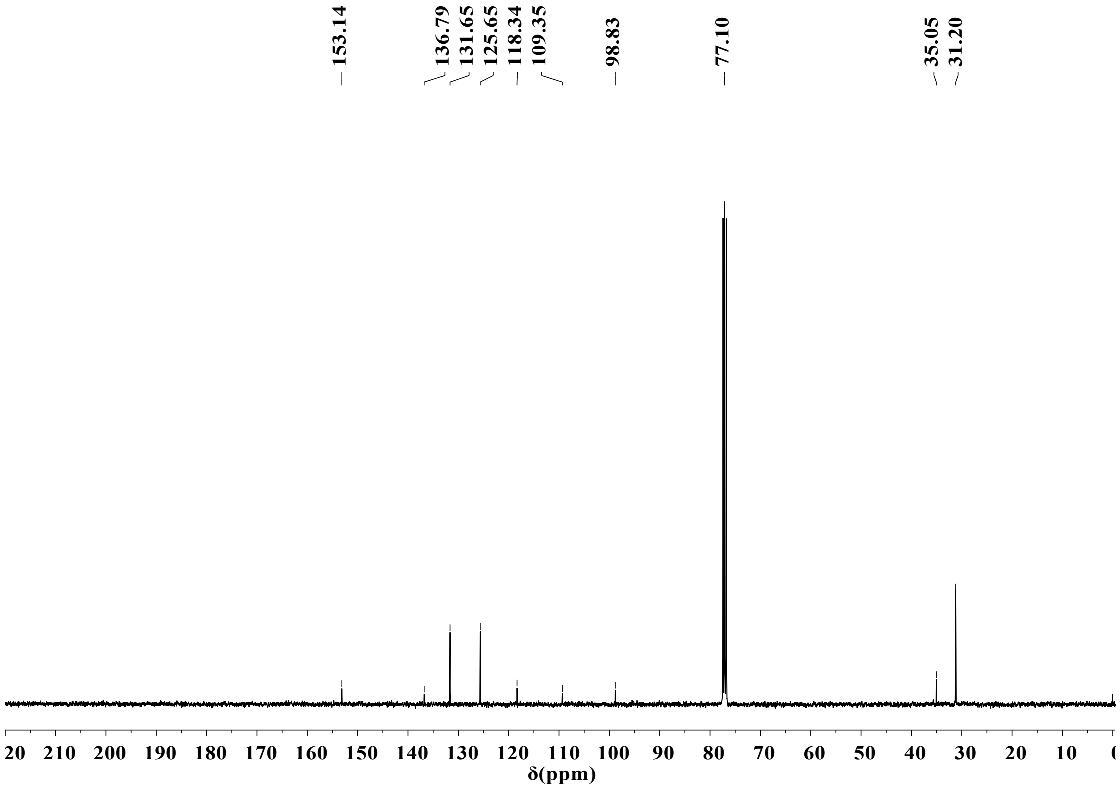
HR-MS spectrum for **1c**



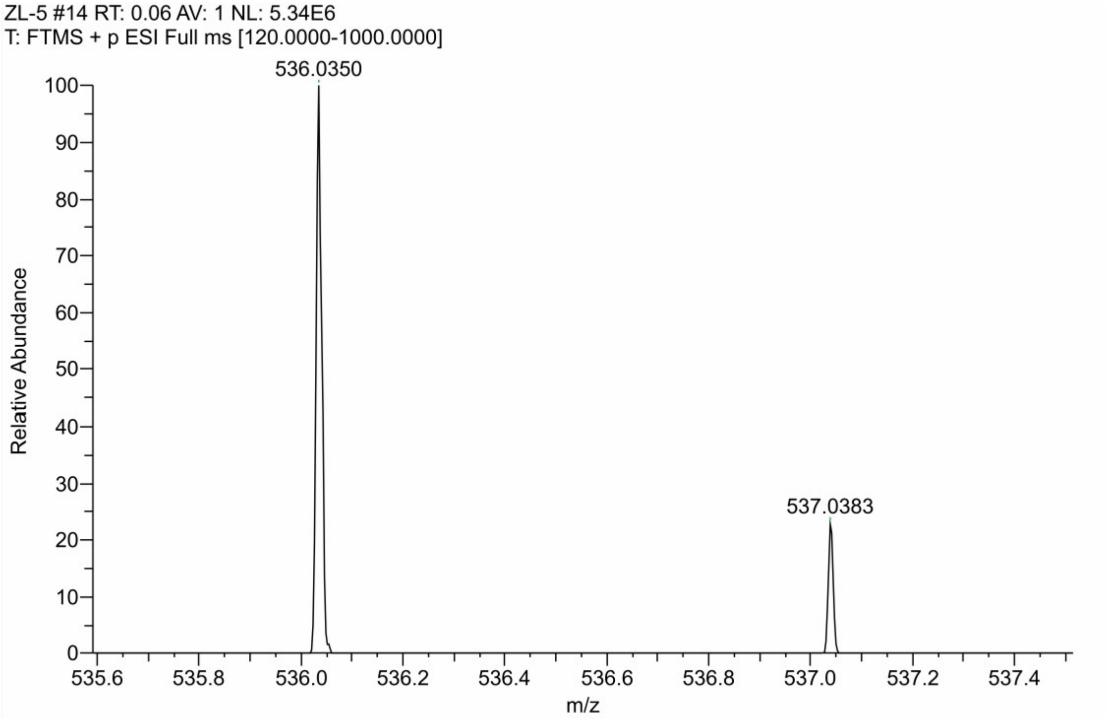
^{1}H NMR spectrum for **1d**



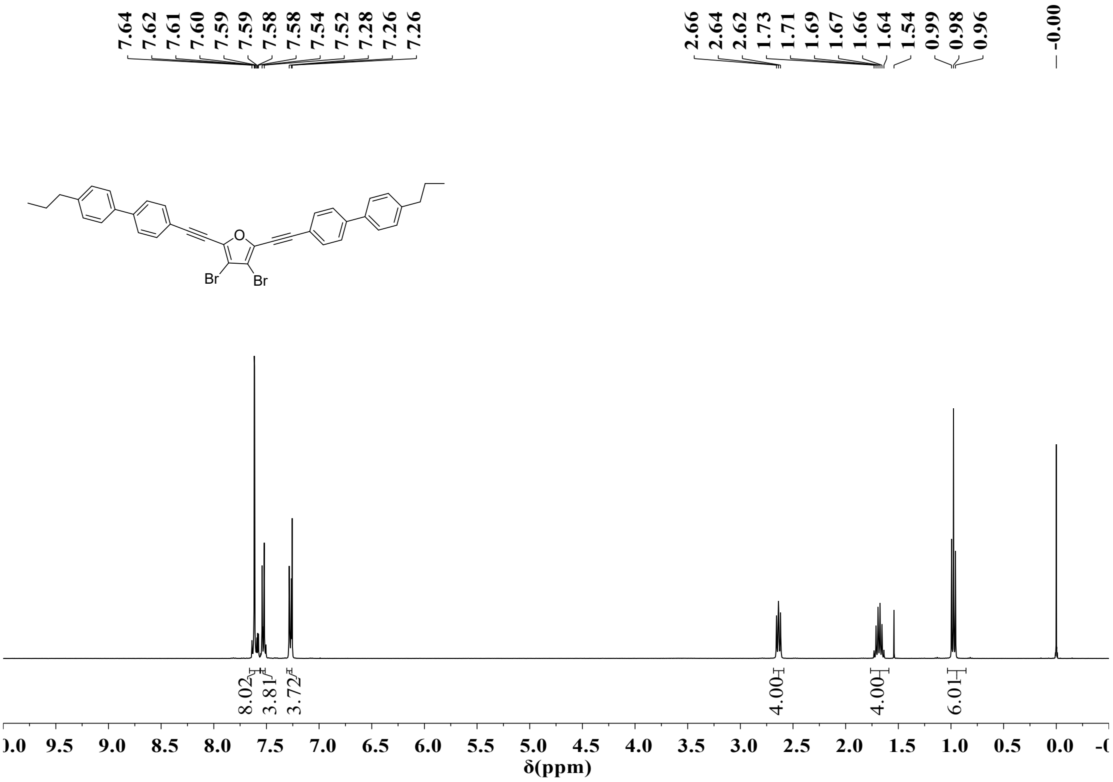
^{13}C NMR spectrum for **1d**



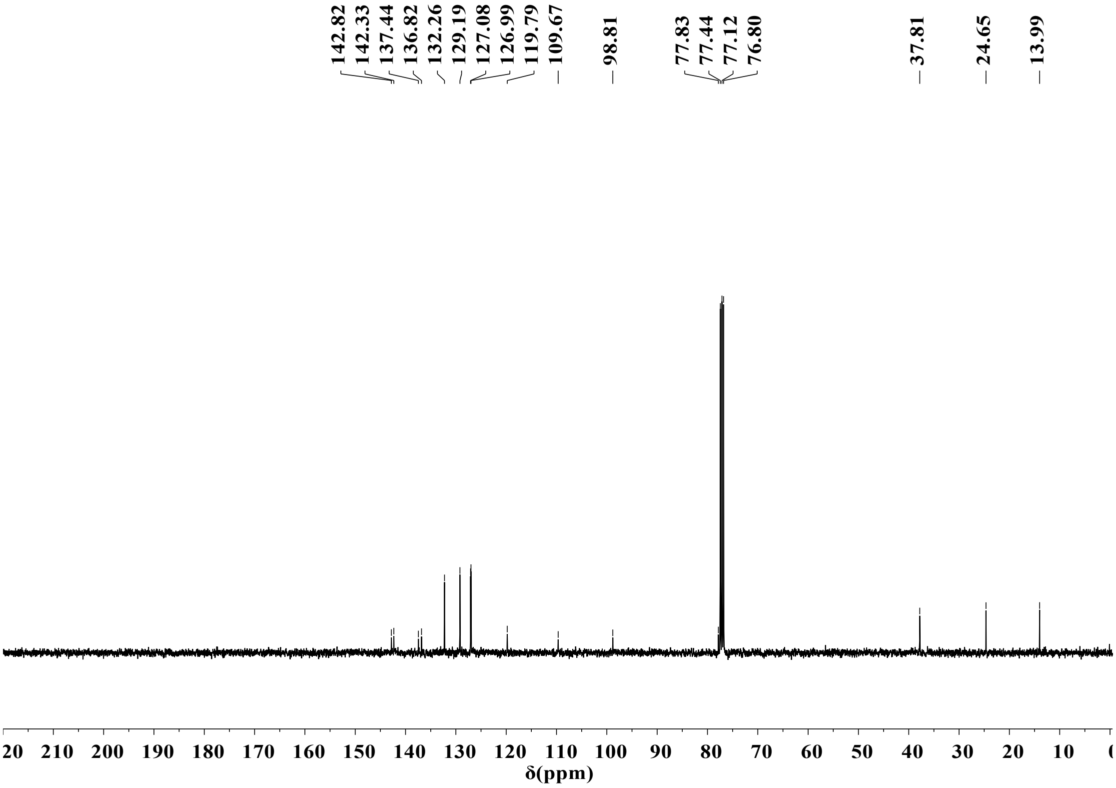
HR-MS spectrum for **1d**



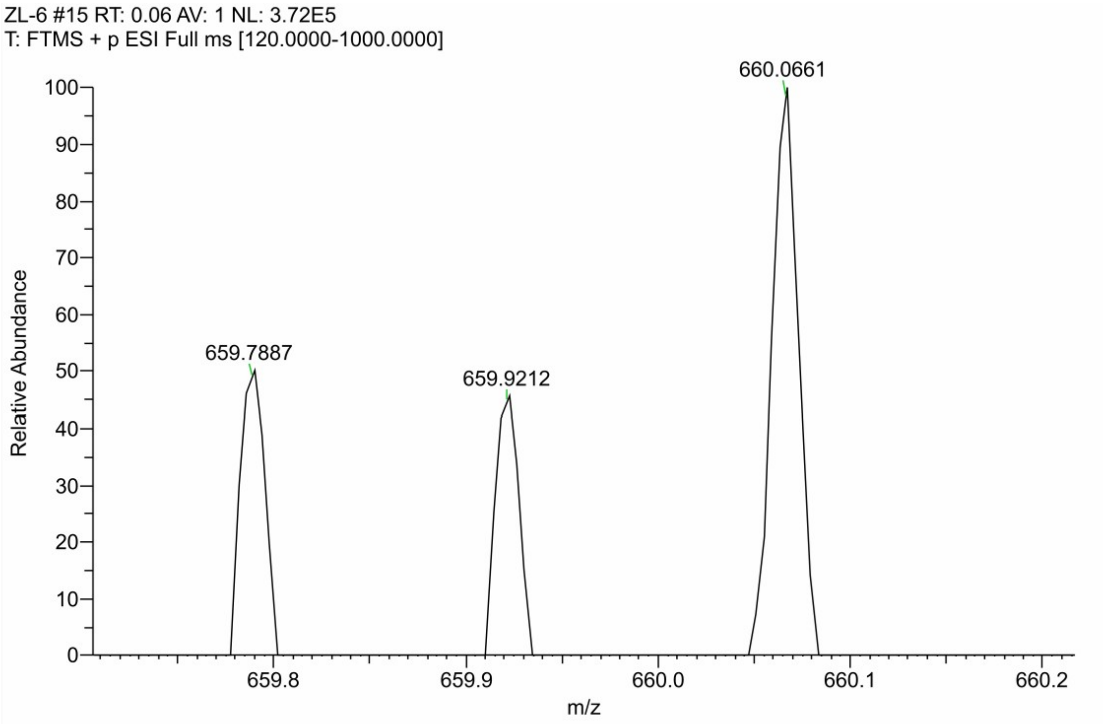
^{1}H NMR spectrum for **1e**



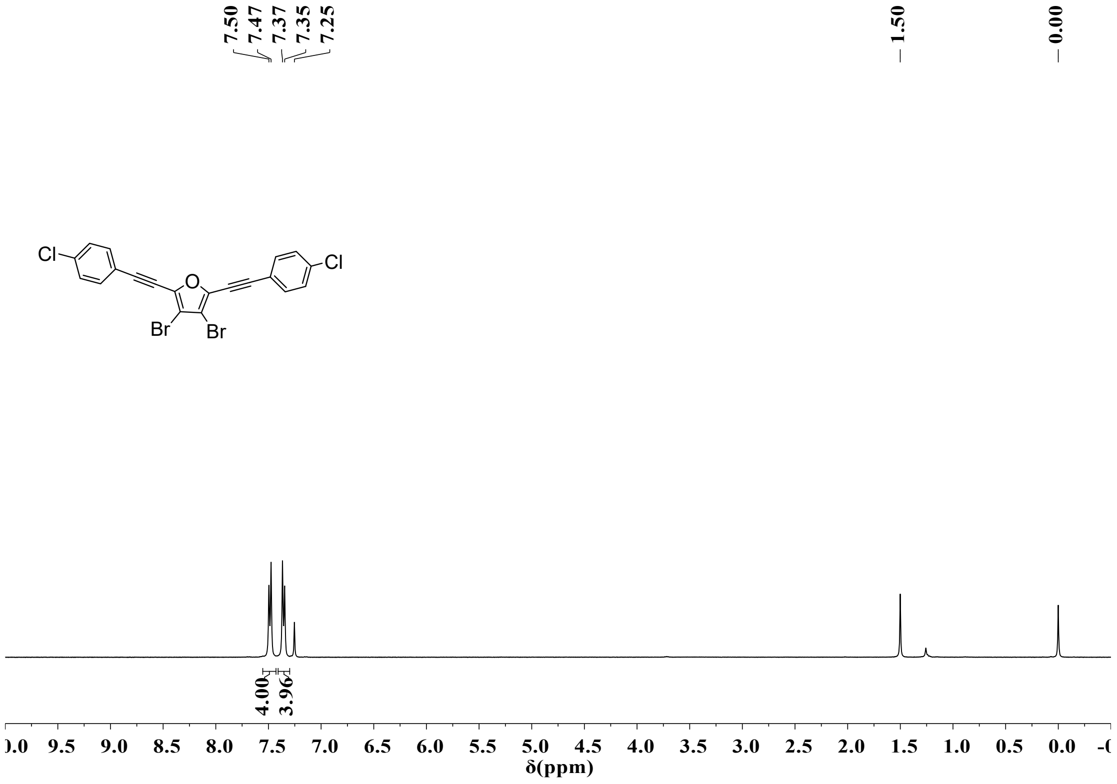
^{13}C NMR spectrum for **1e**



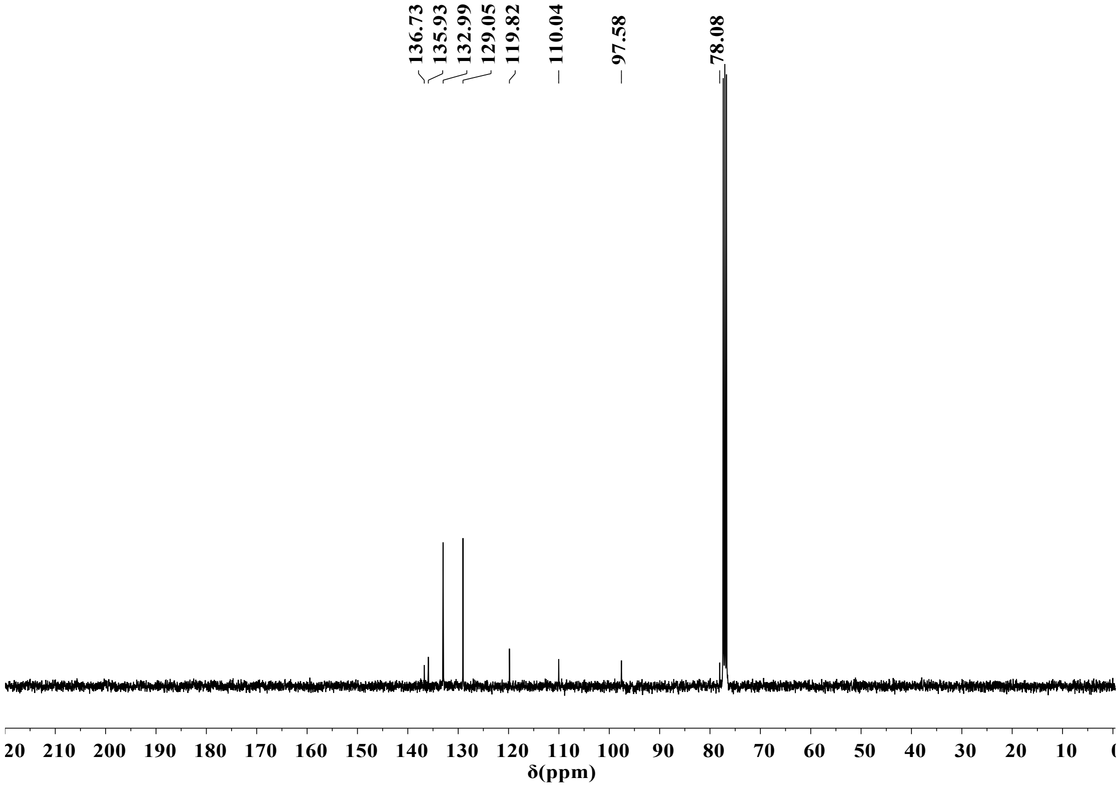
HR-MS spectrum for **1e**



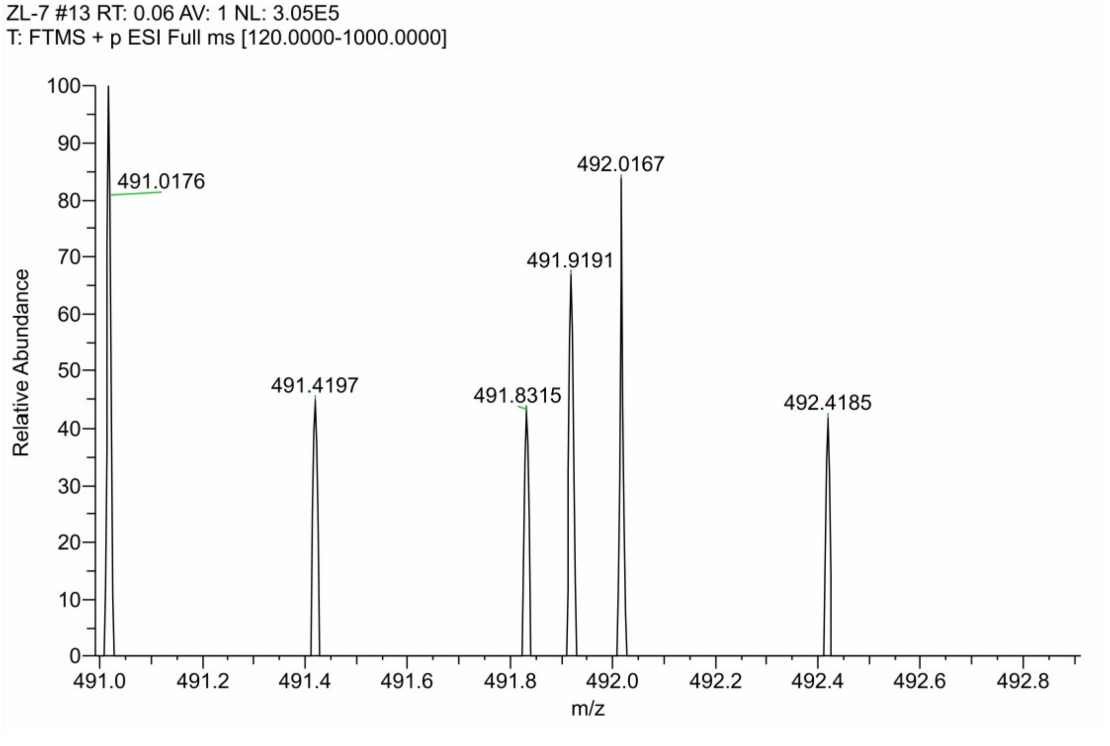
^{1}H NMR spectrum for **1f**



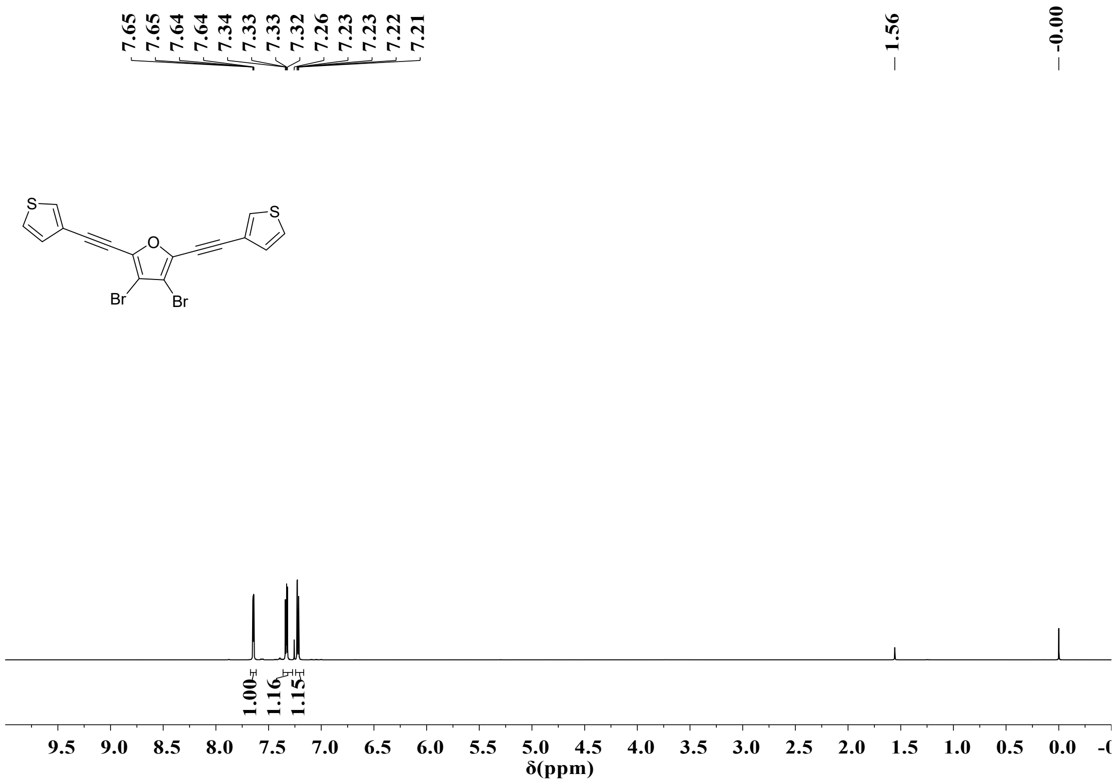
^{13}C NMR spectrum for **1f**



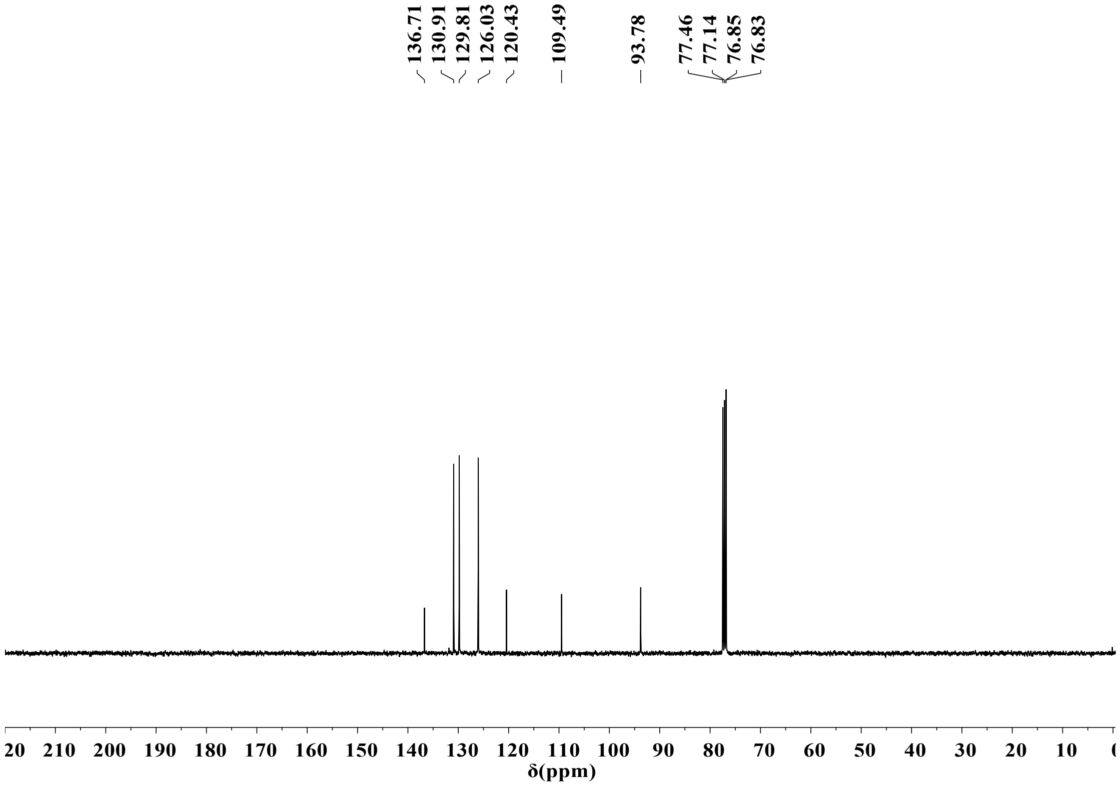
HR-MS spectrum for **1f**



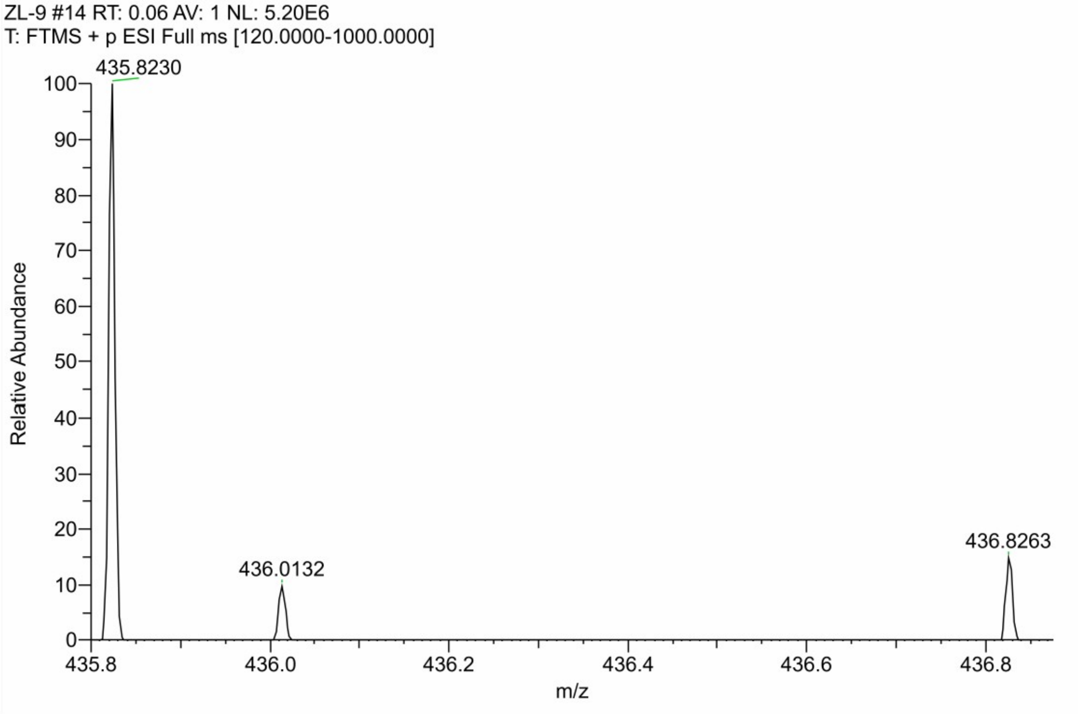
^{1}H NMR spectrum for **1g**



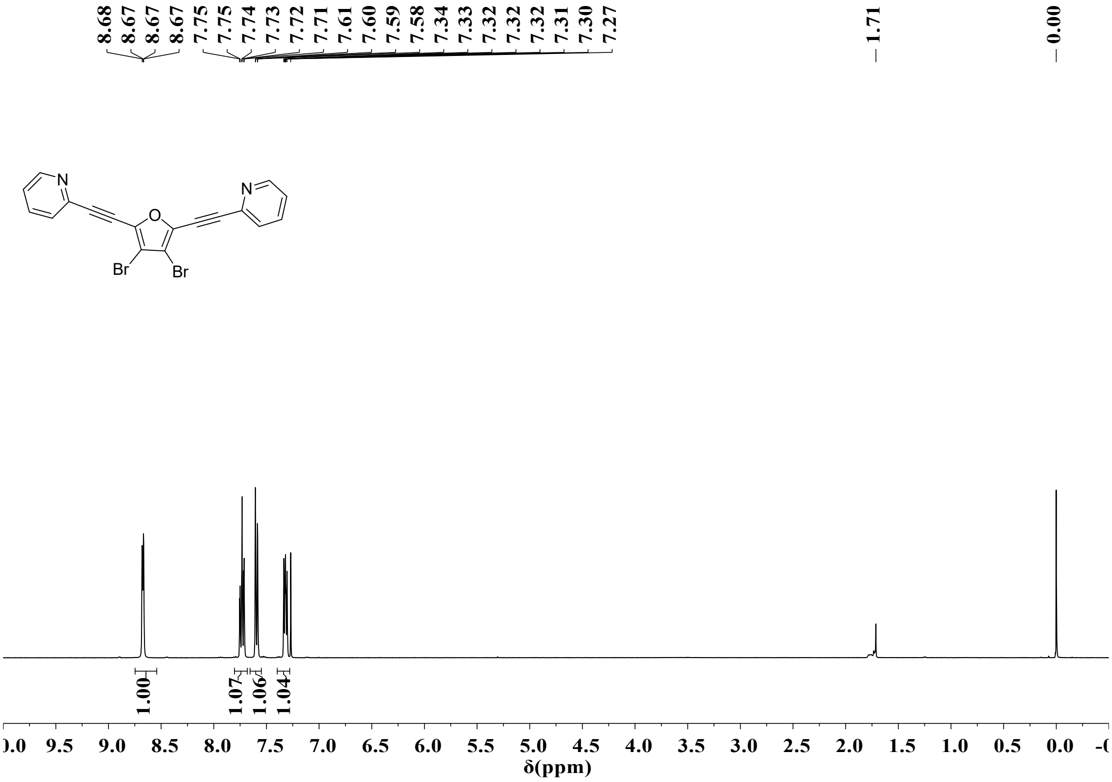
^{13}C NMR spectrum for **1g**



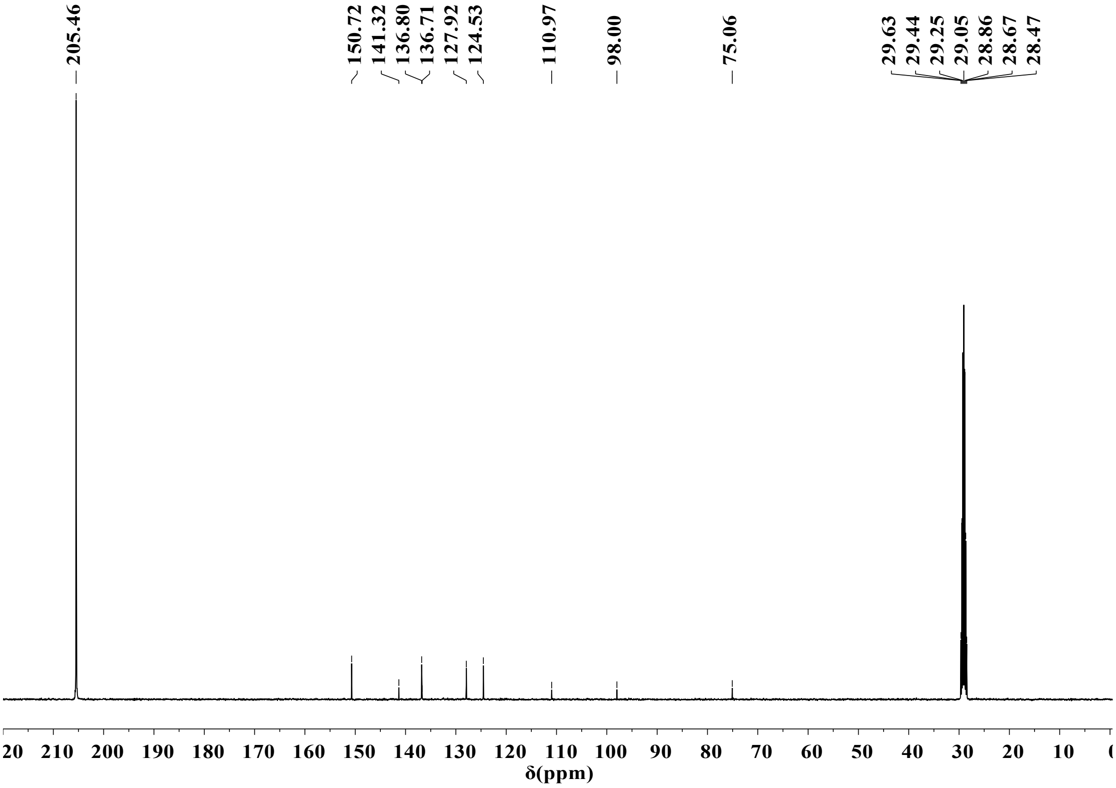
HR-MS spectrum for **1g**



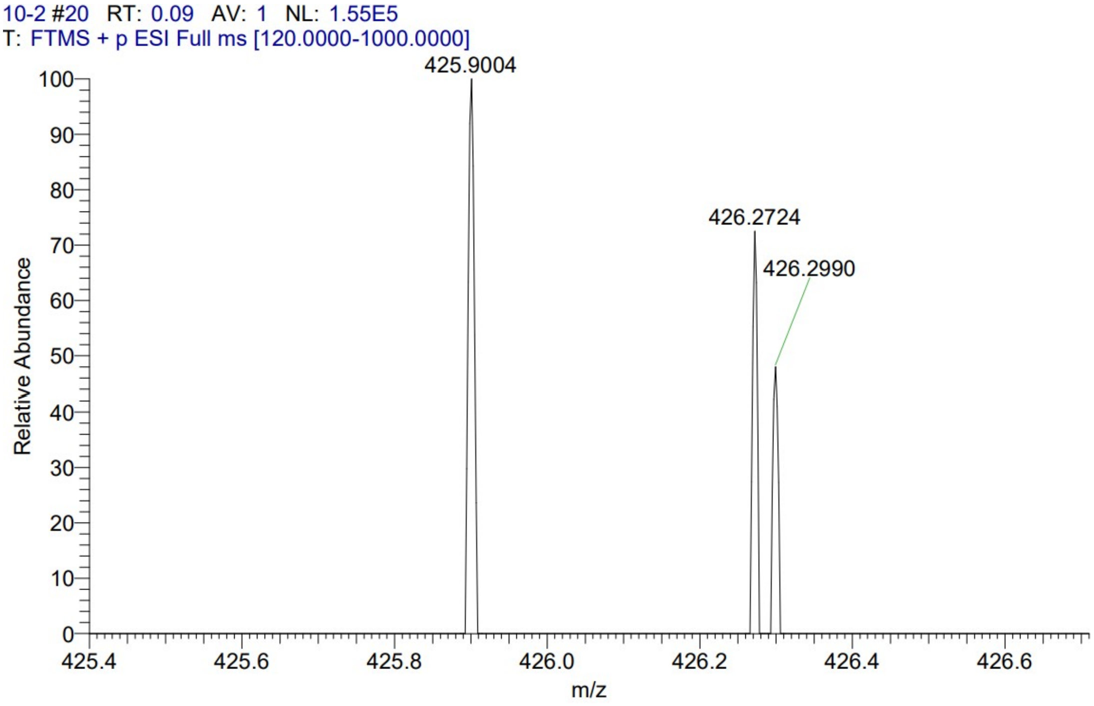
^{1}H NMR spectrum for **1h**



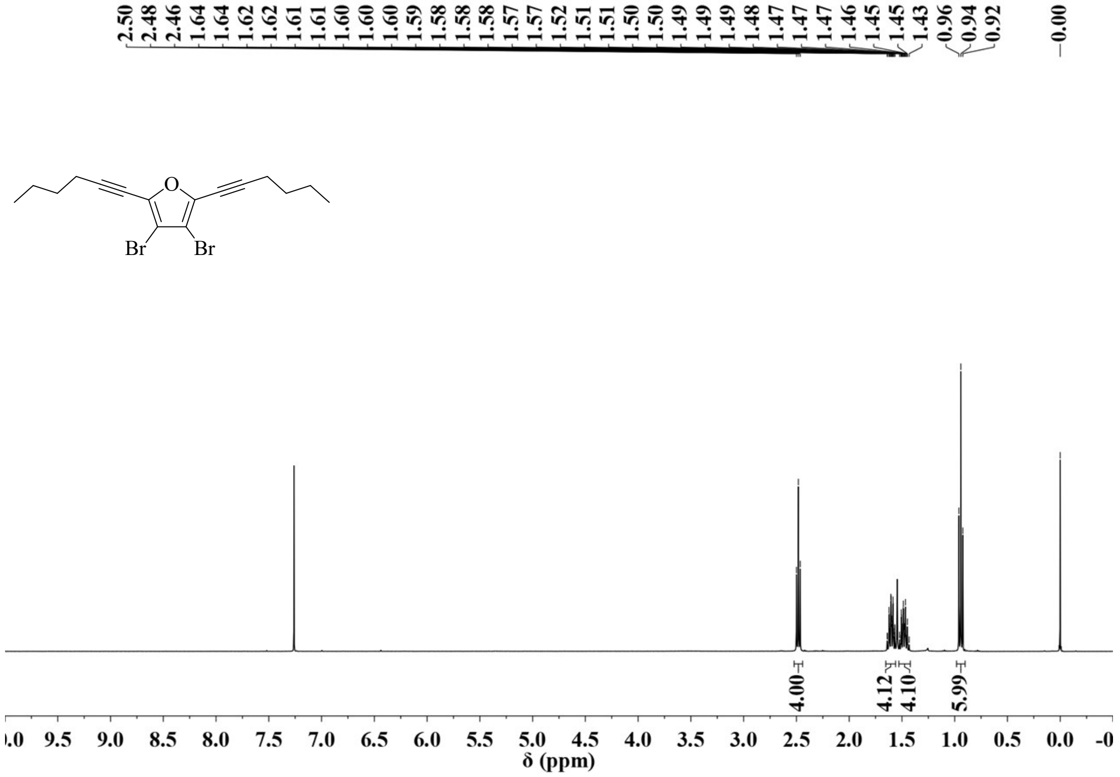
^{13}C NMR spectrum for **1h**



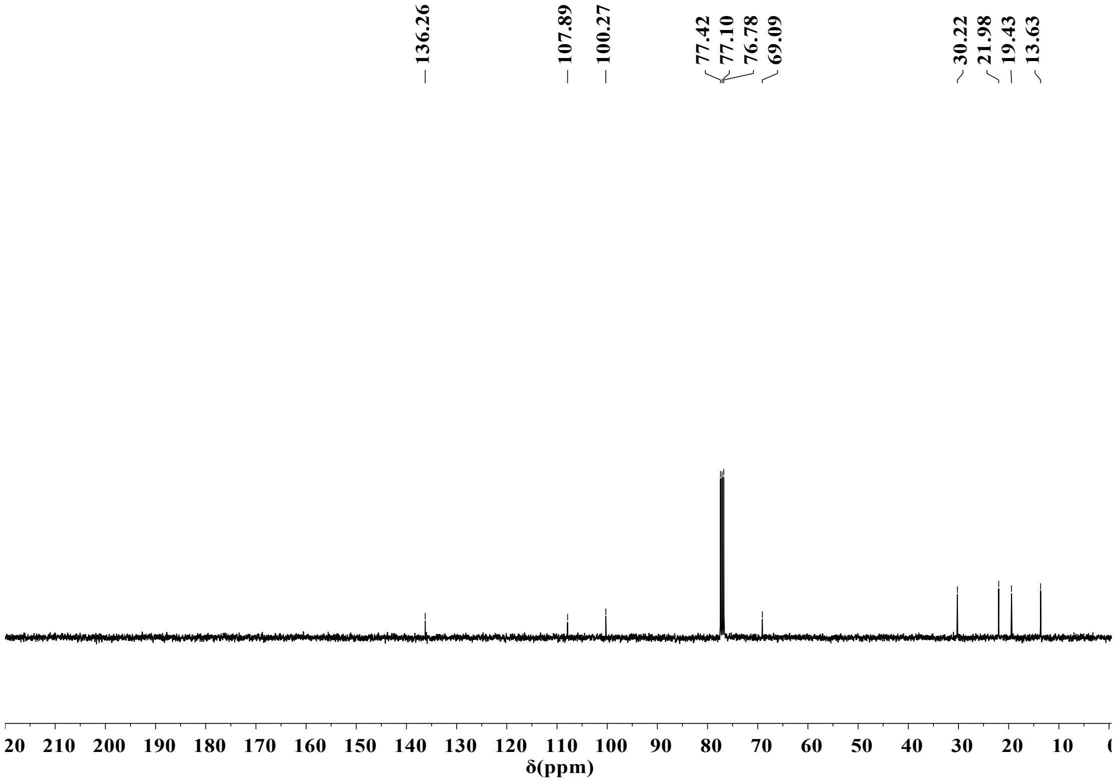
HR-MS spectrum for **1h**



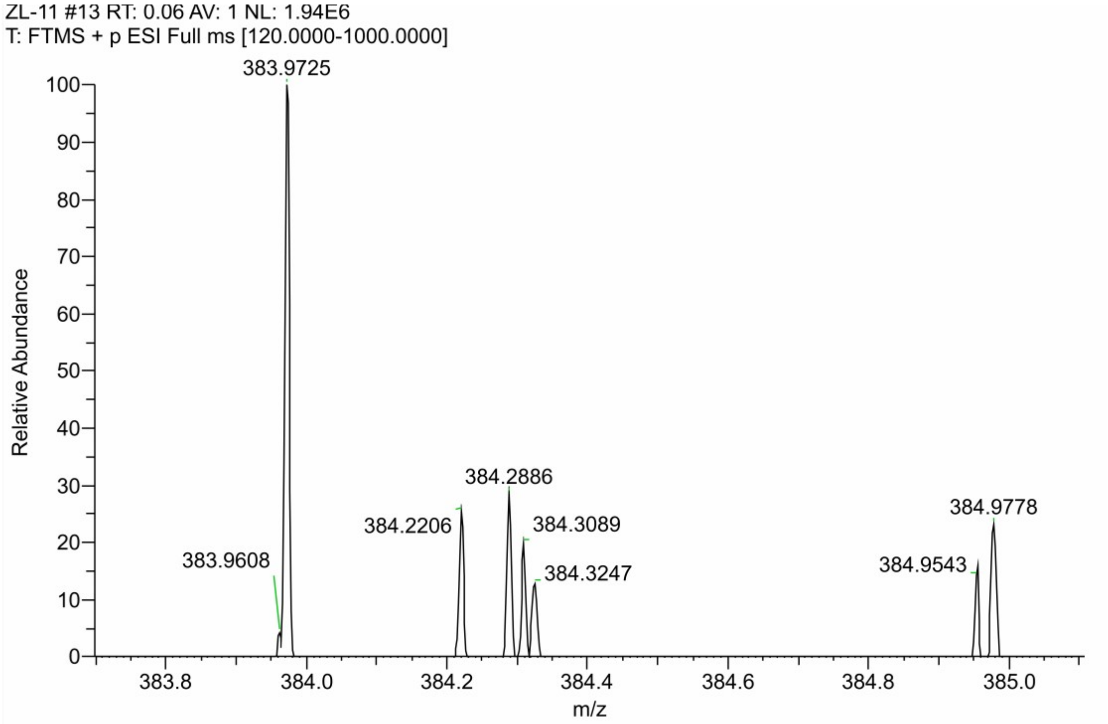
^{1}H NMR spectrum for **1i**



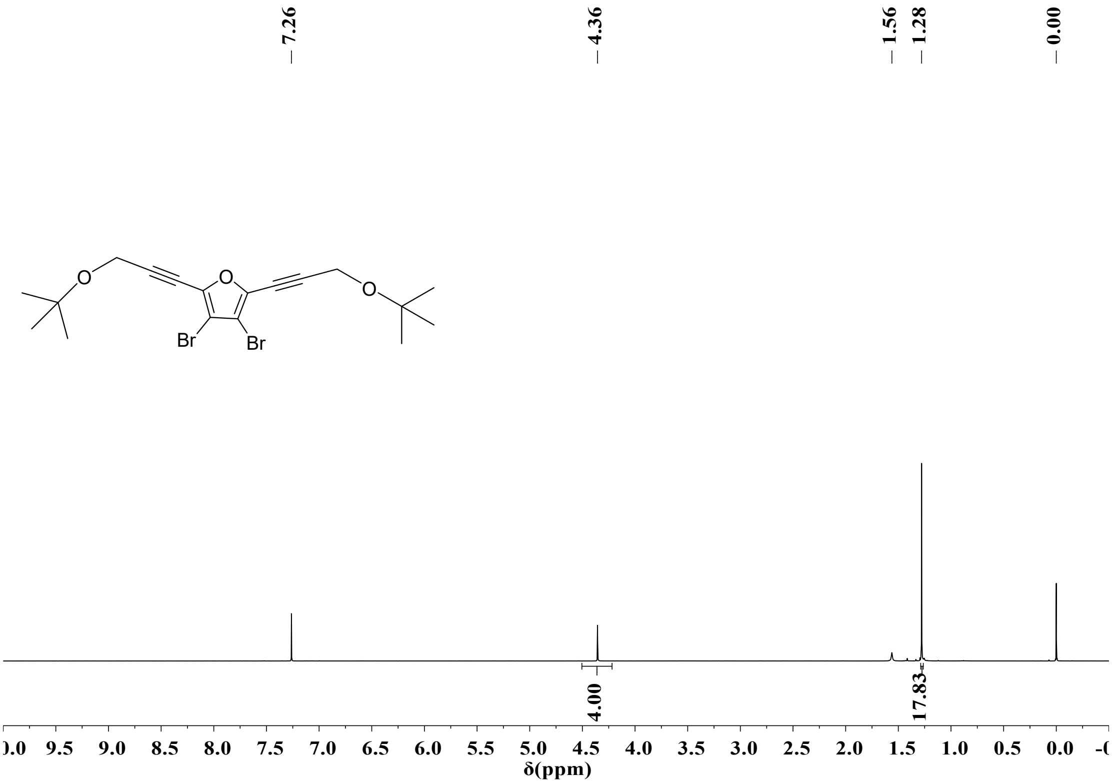
^{13}C NMR spectrum for **1i**



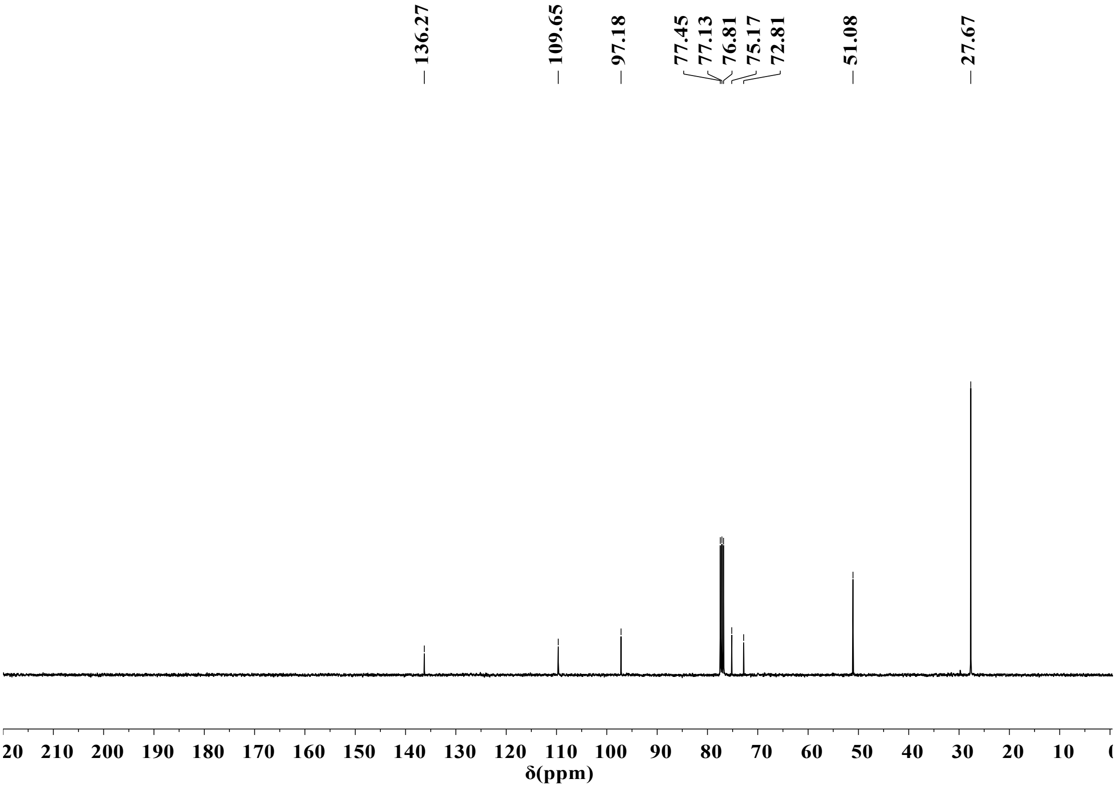
HR-MS spectrum for **1i**



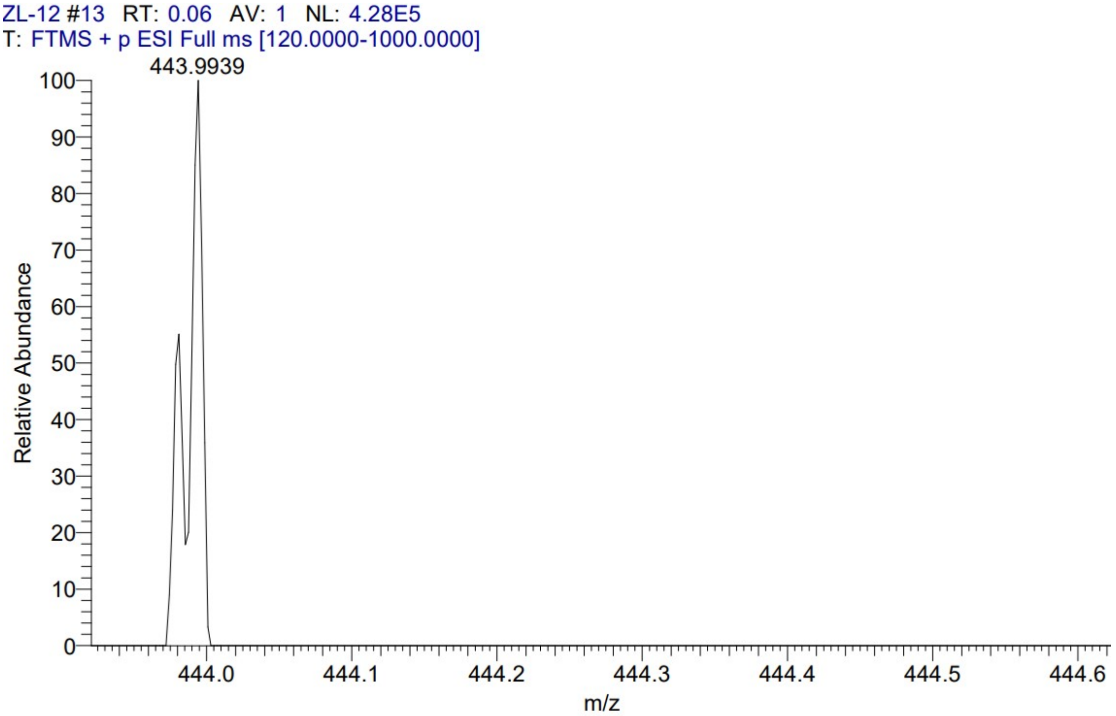
^{1}H NMR spectrum for **1j**



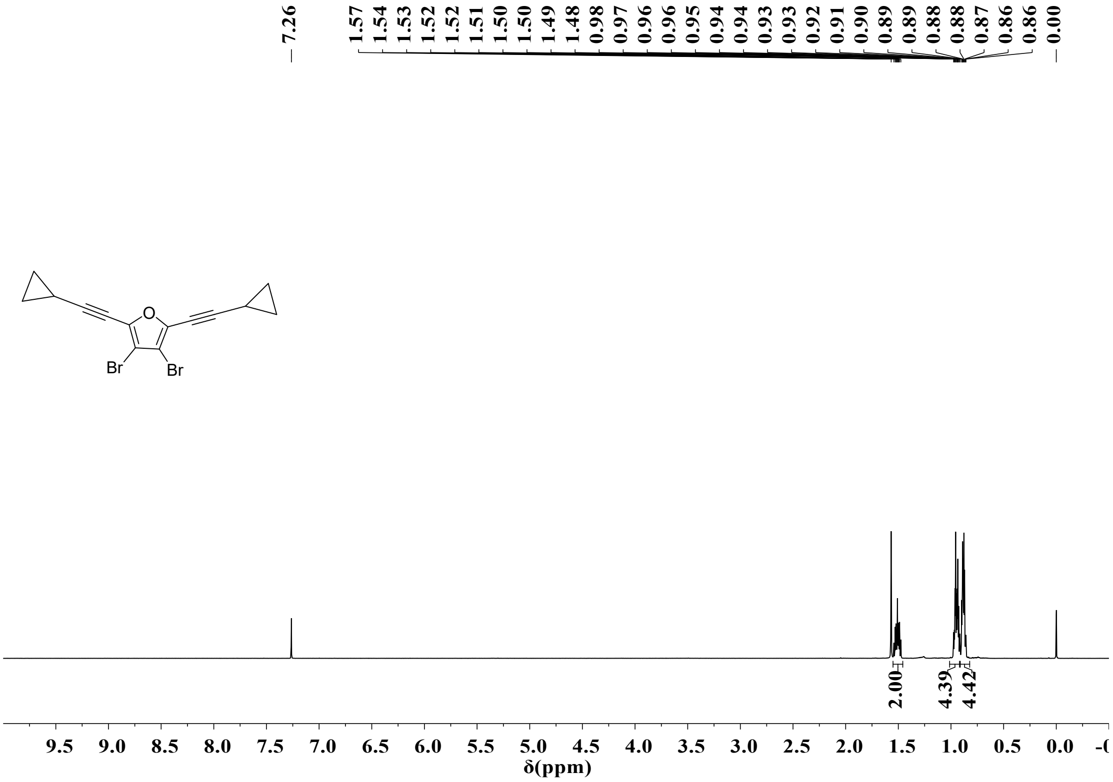
^{13}C NMR spectrum for **1j**



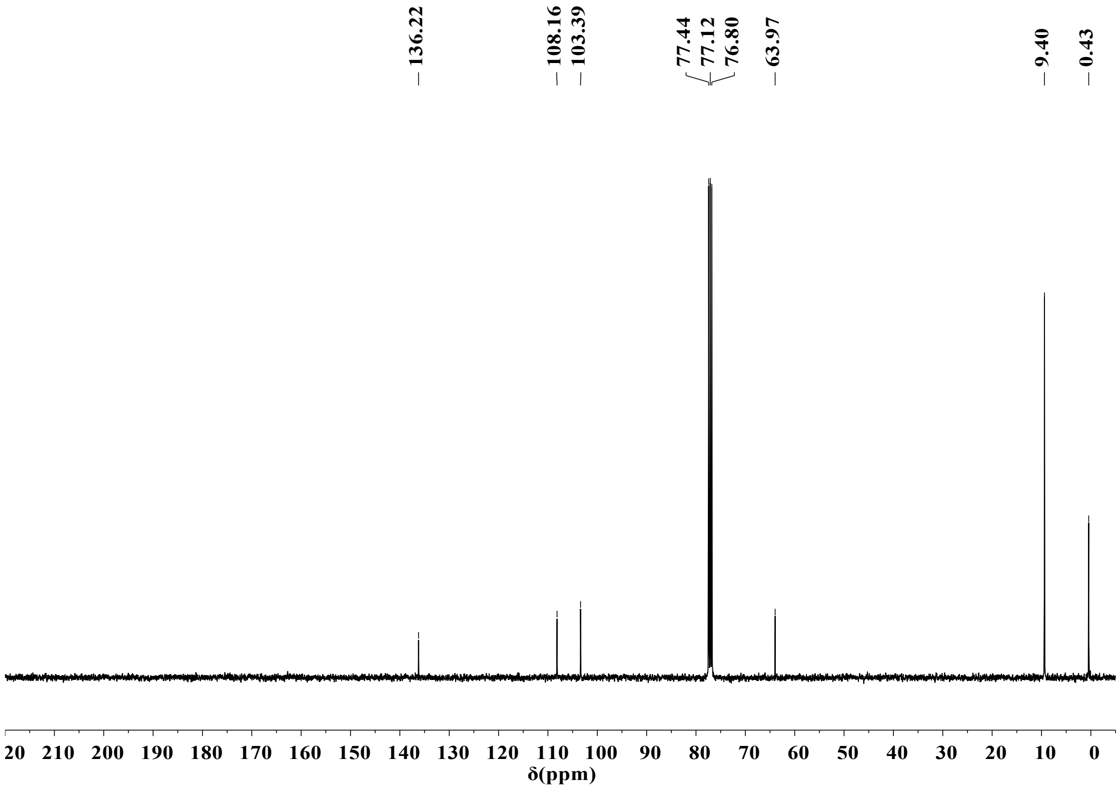
HR-MS spectrum for **1j**



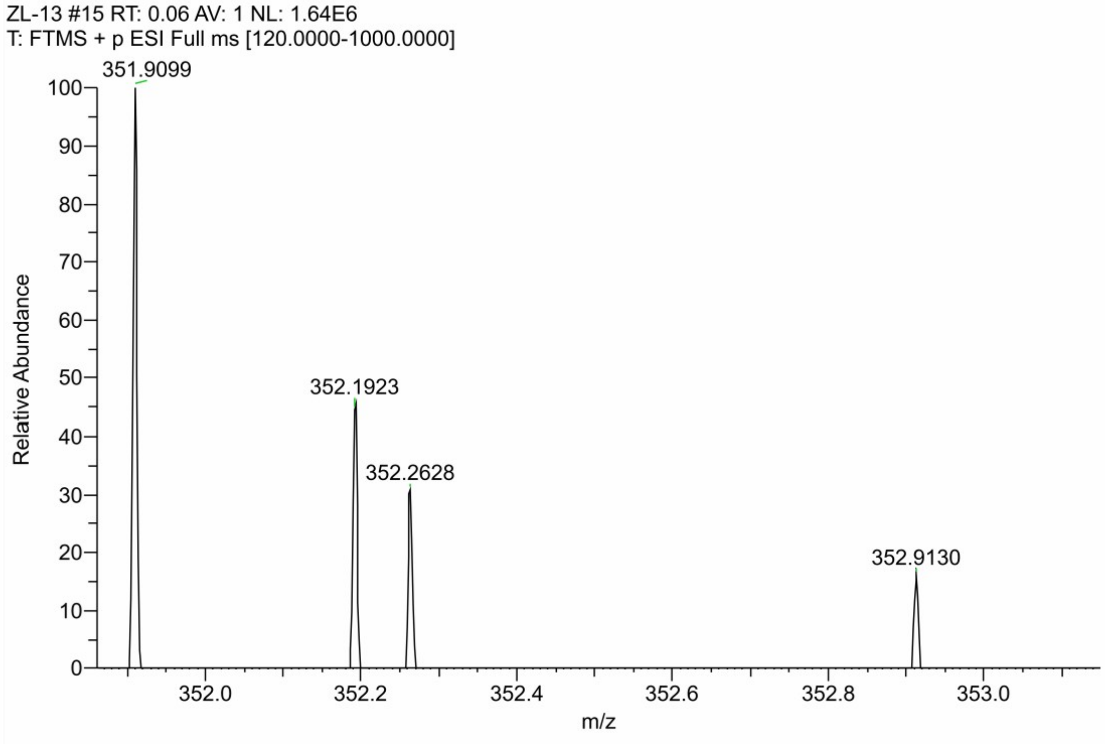
^{1}H NMR spectrum for **1k**



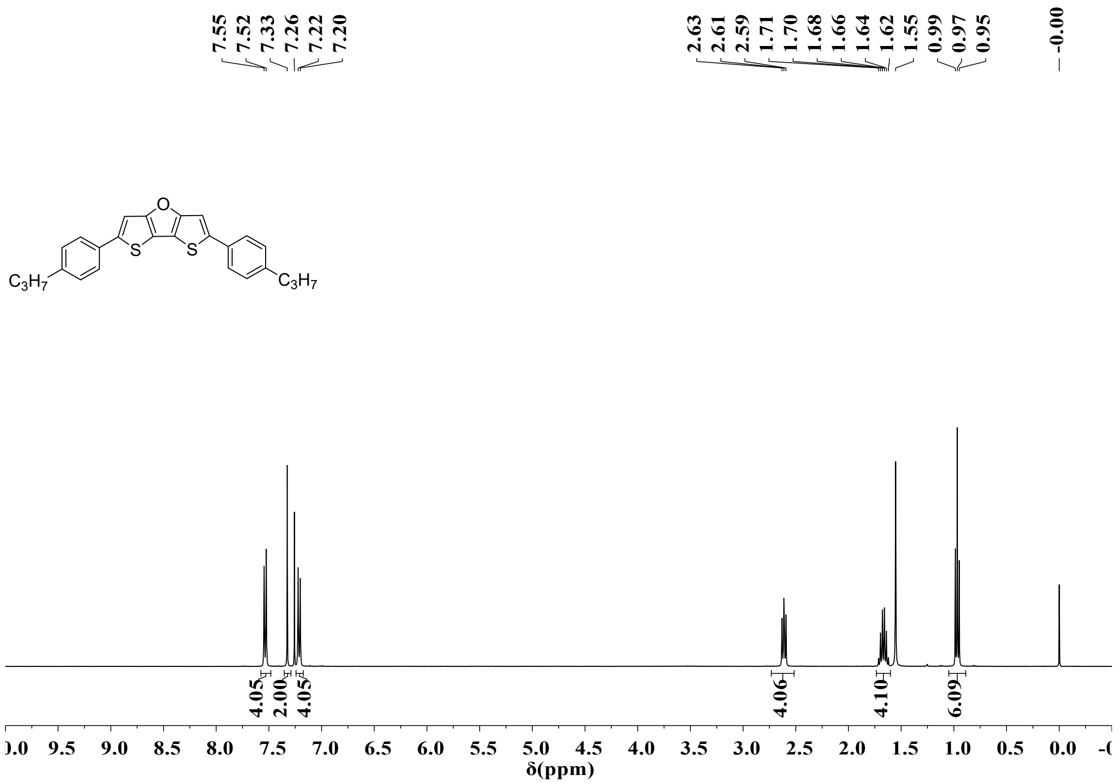
^{13}C NMR spectrum for **1k**



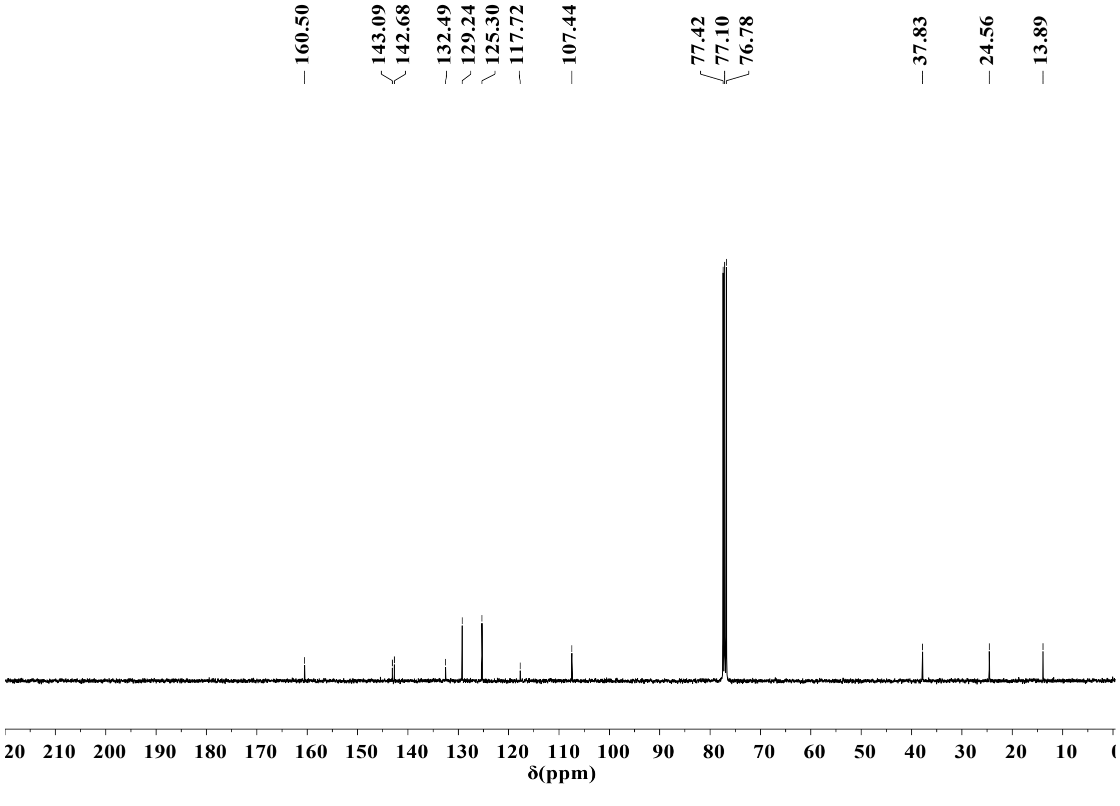
HR-MS spectrum for **1k**



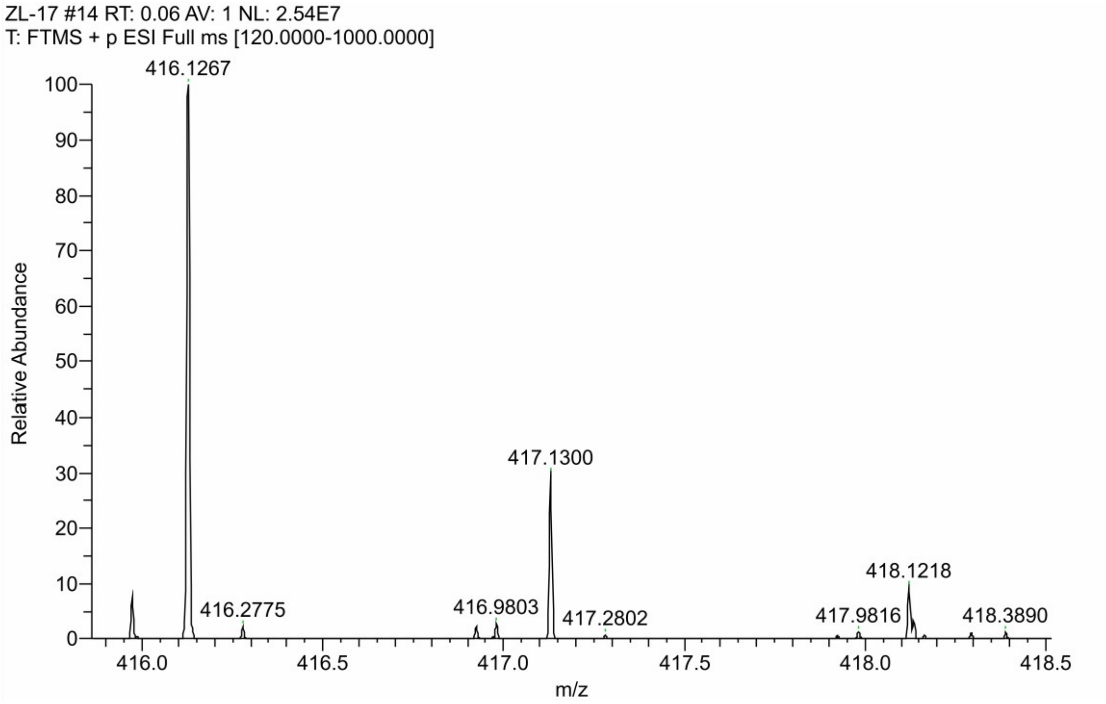
^{1}H NMR spectrum for **2a**



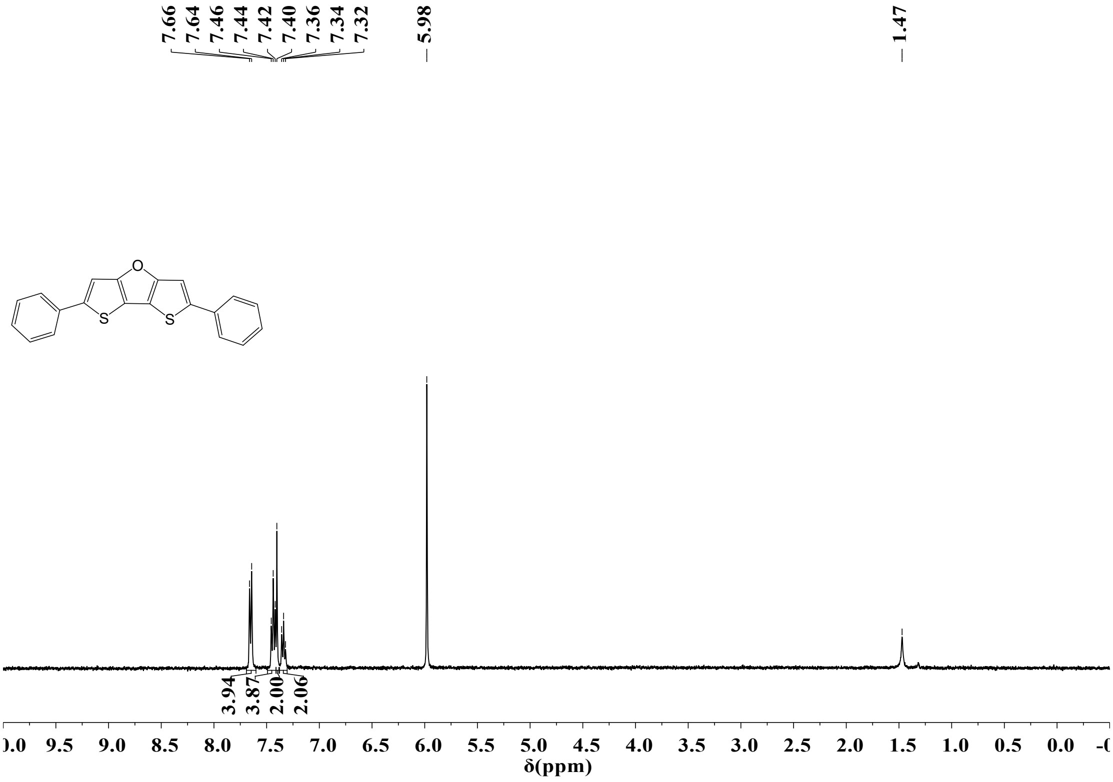
^{13}C NMR spectrum for **2a**



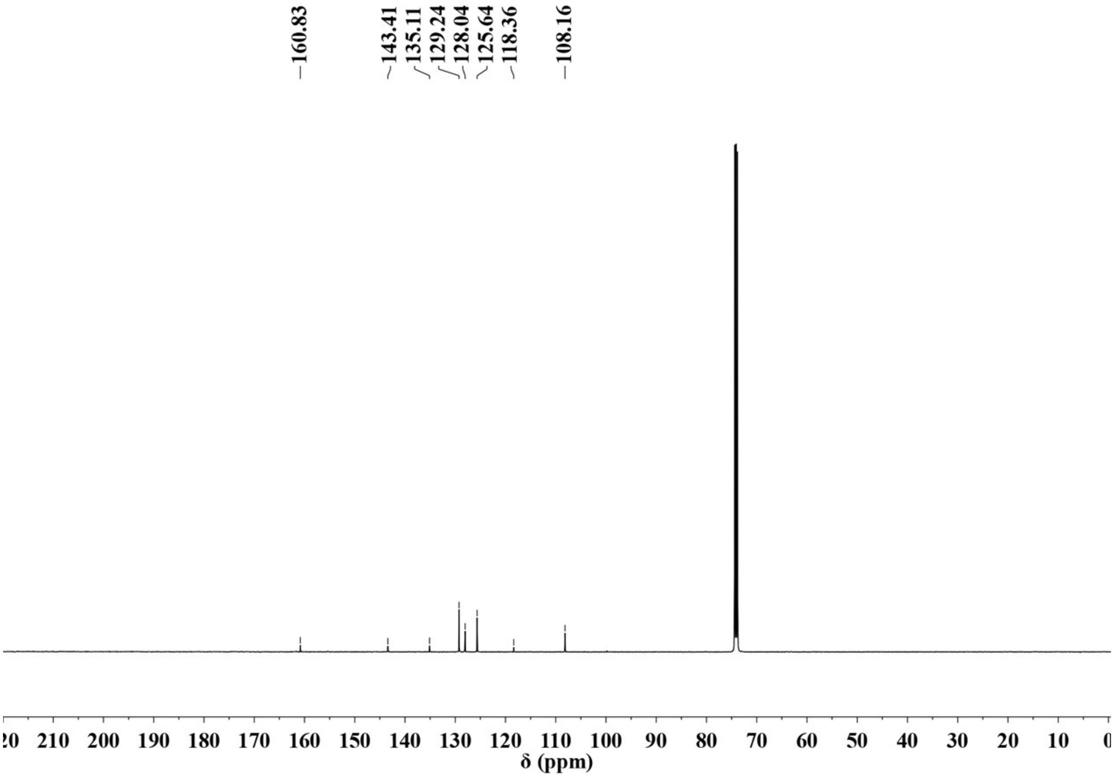
HR-MS spectrum for **2a**



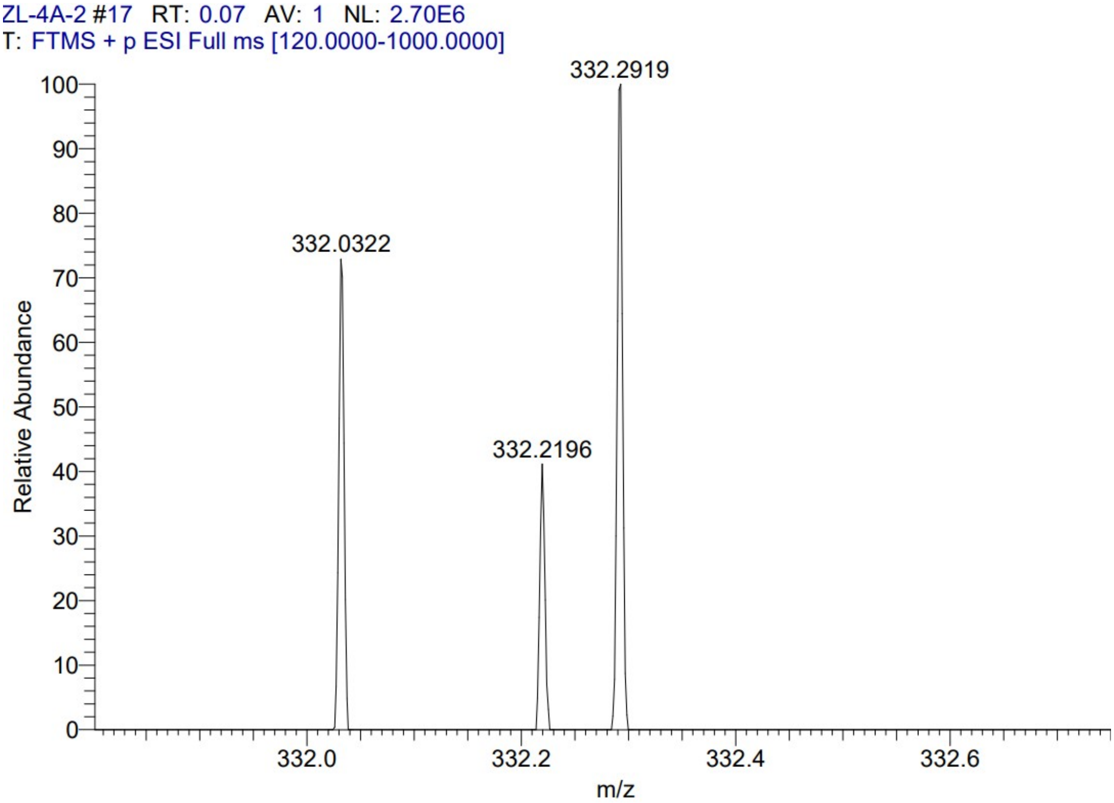
^{1}H NMR spectrum for **2b**



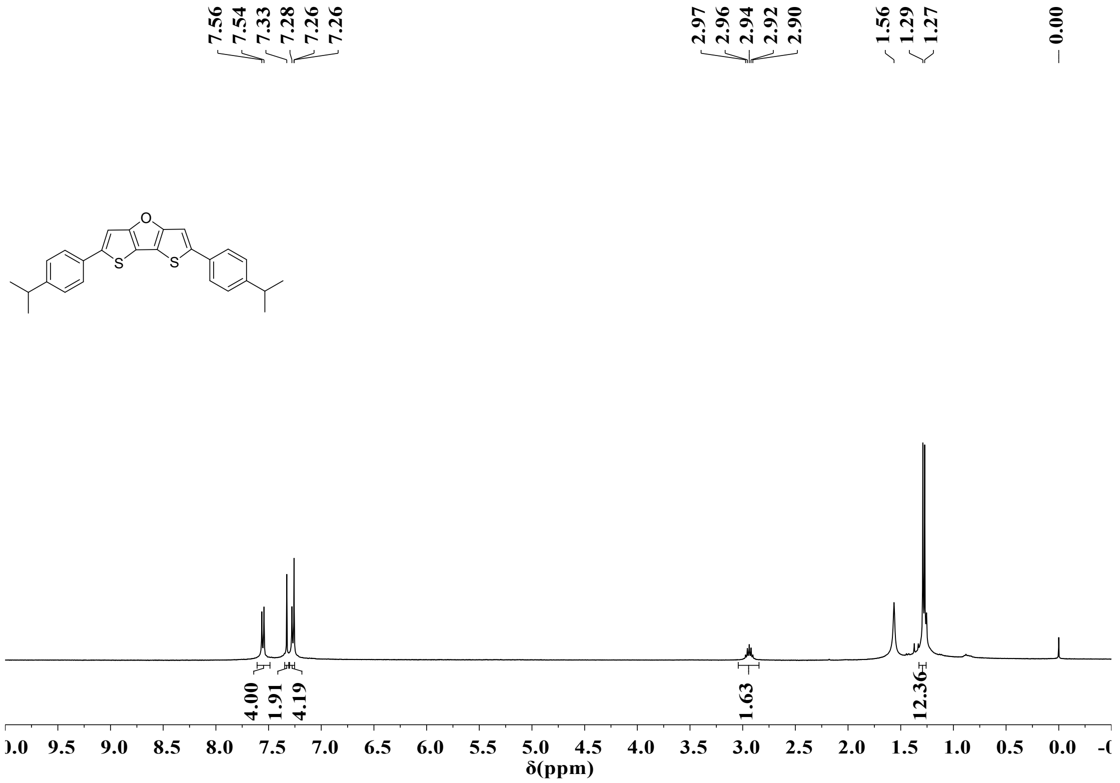
^{13}C NMR spectrum for **2b**



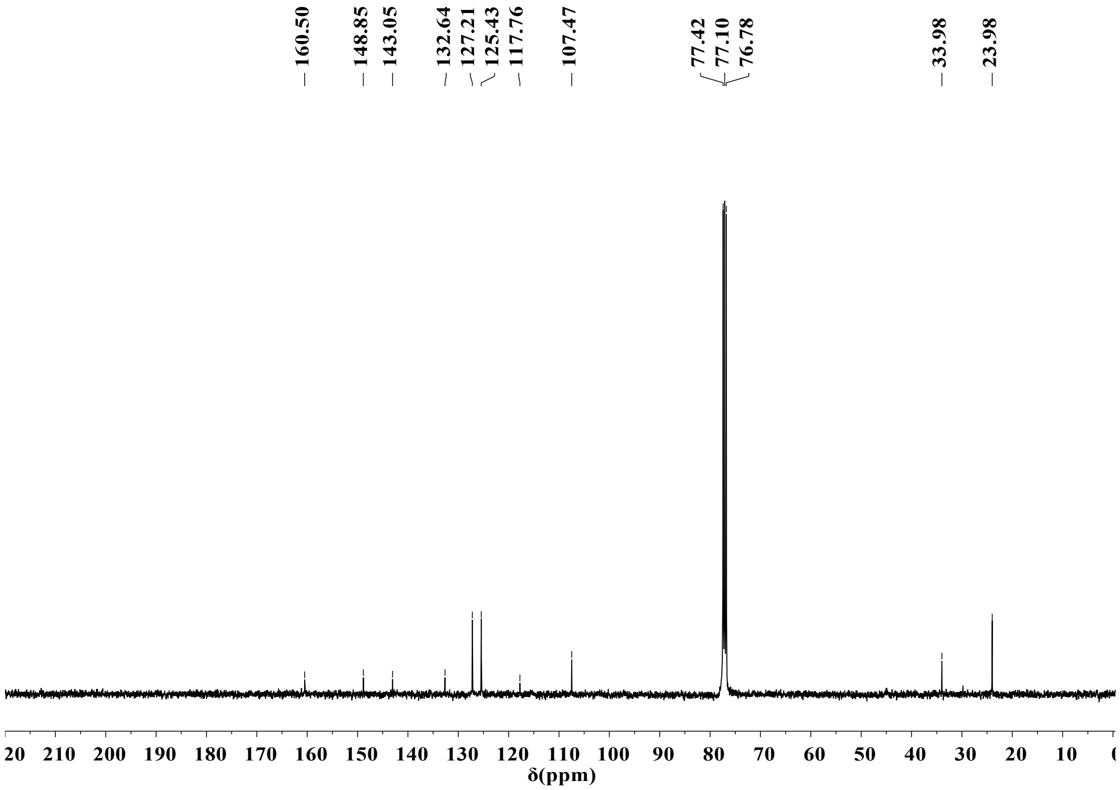
HR-MS spectrum for **2b**



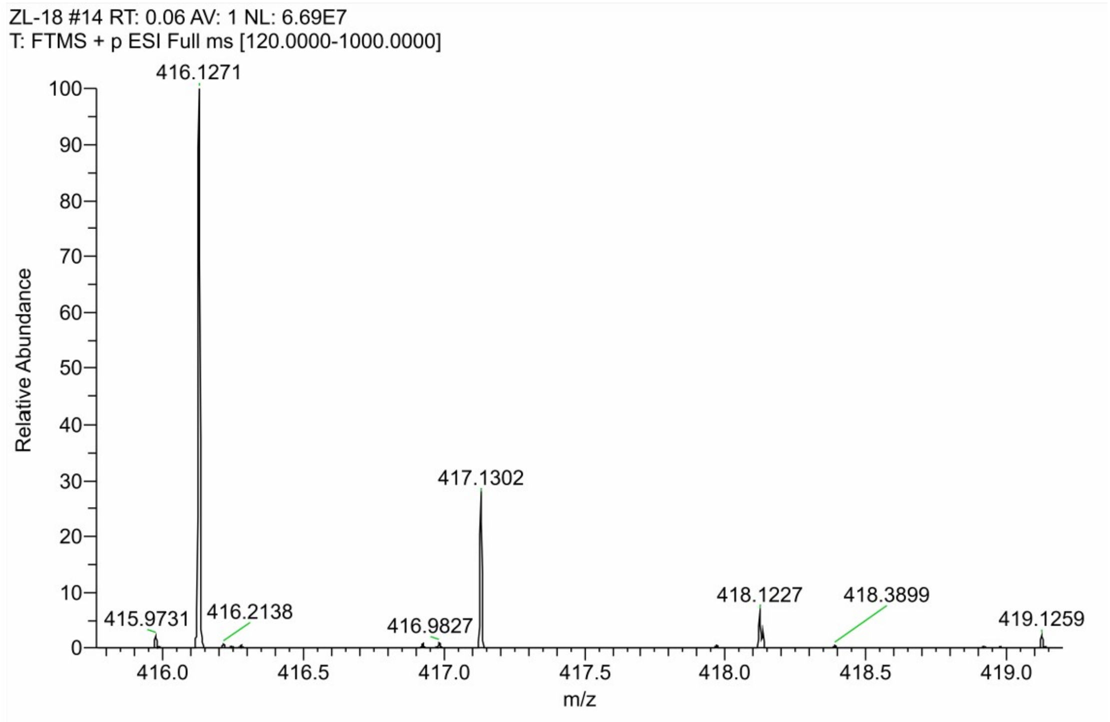
^{1}H NMR spectrum for **2c**



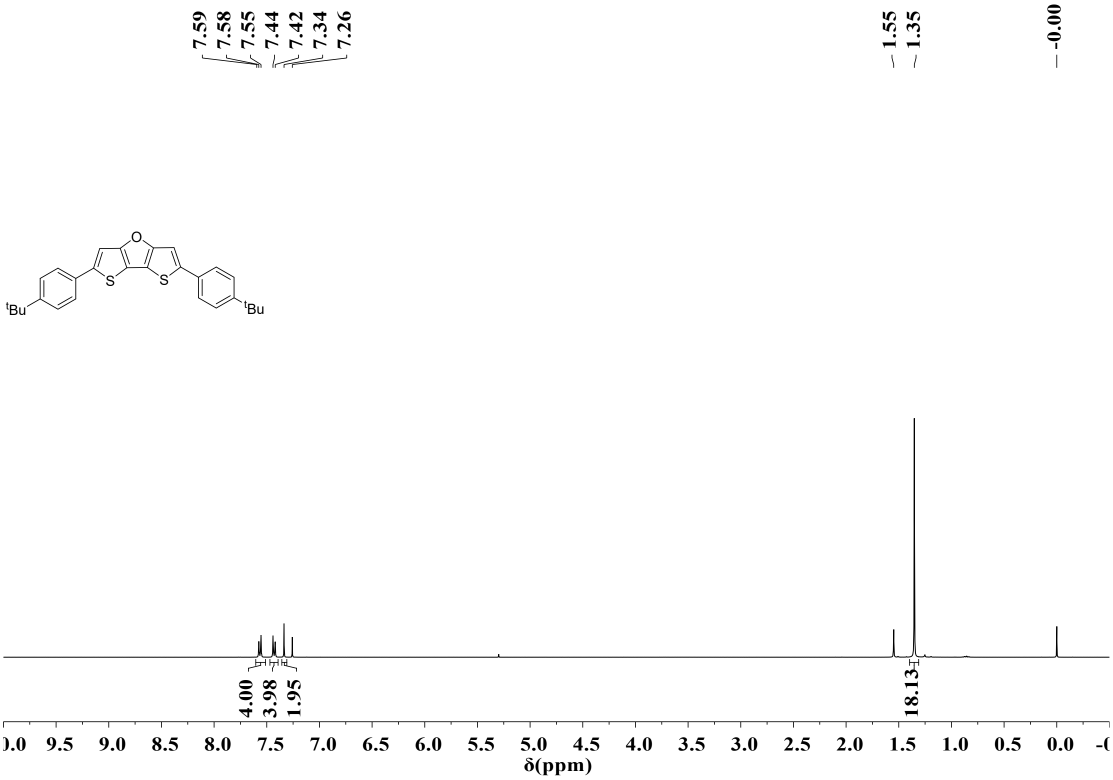
^{13}C NMR spectrum for **2c**



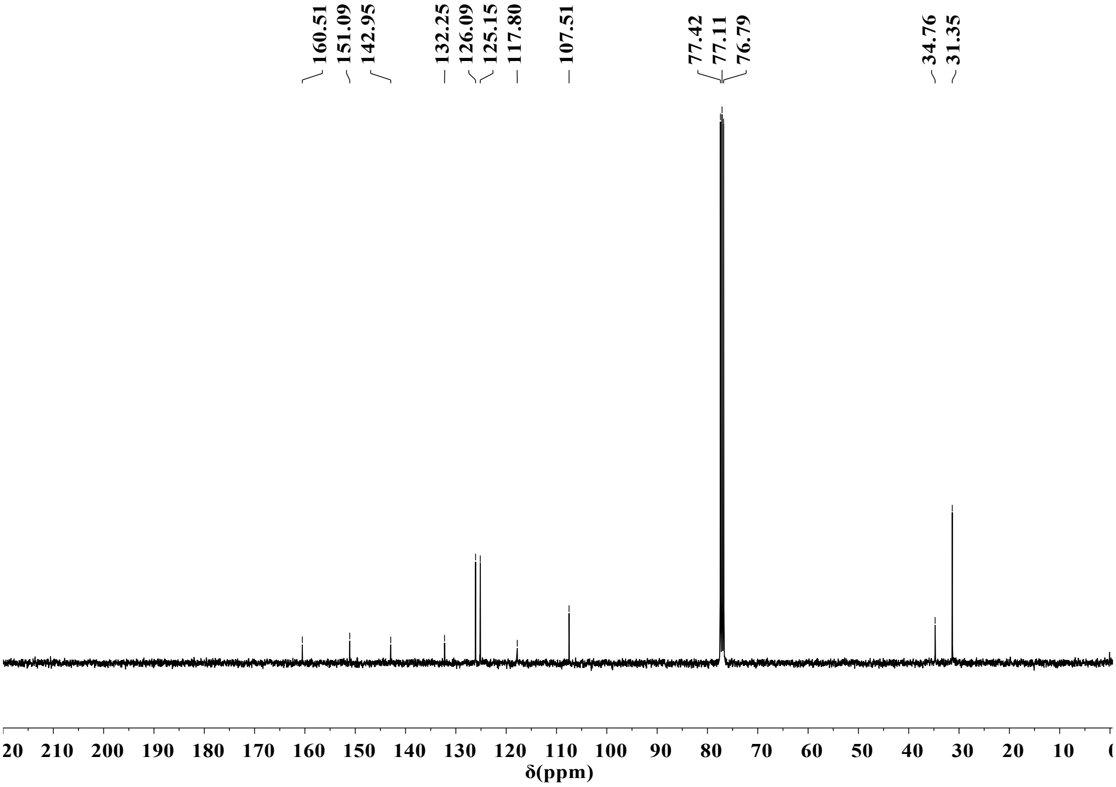
HR-MS spectrum for **2c**



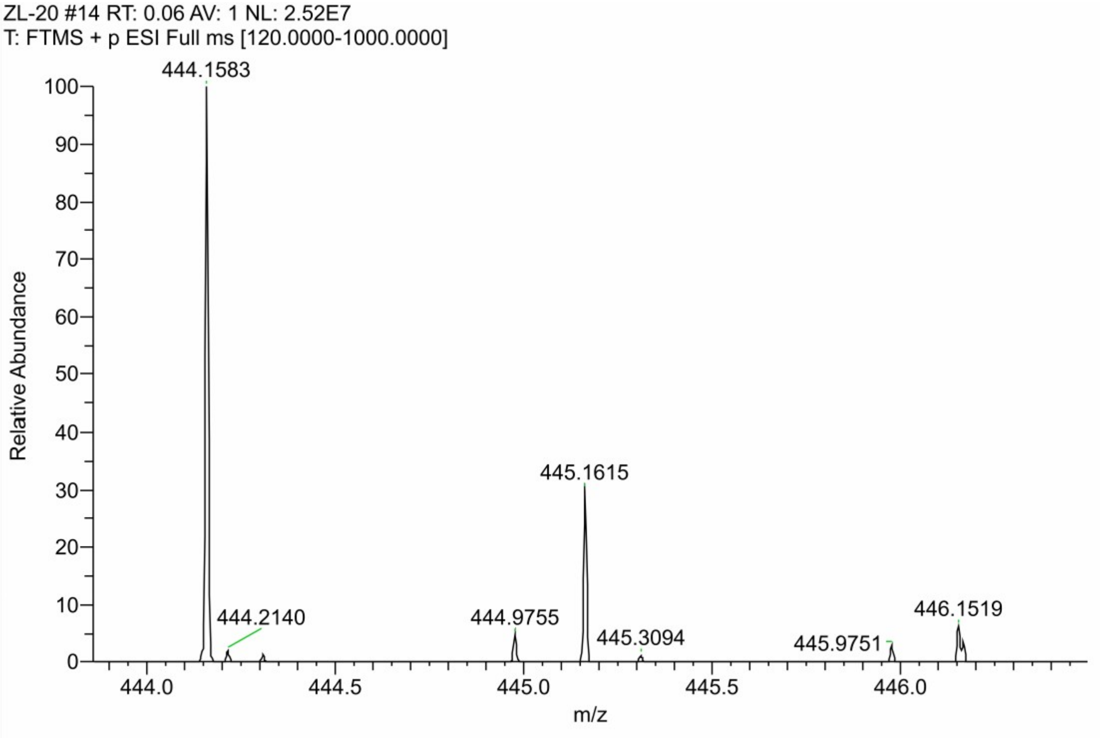
^{1}H NMR spectrum for **2d**



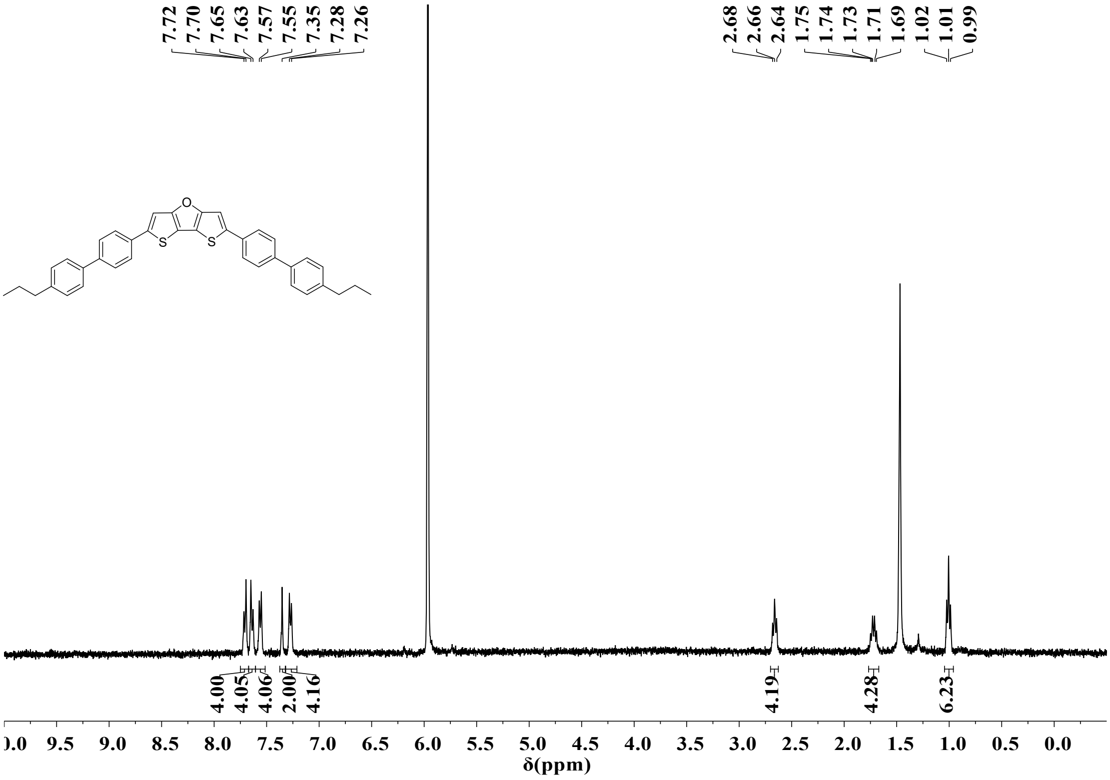
^{13}C NMR spectrum for **2d**



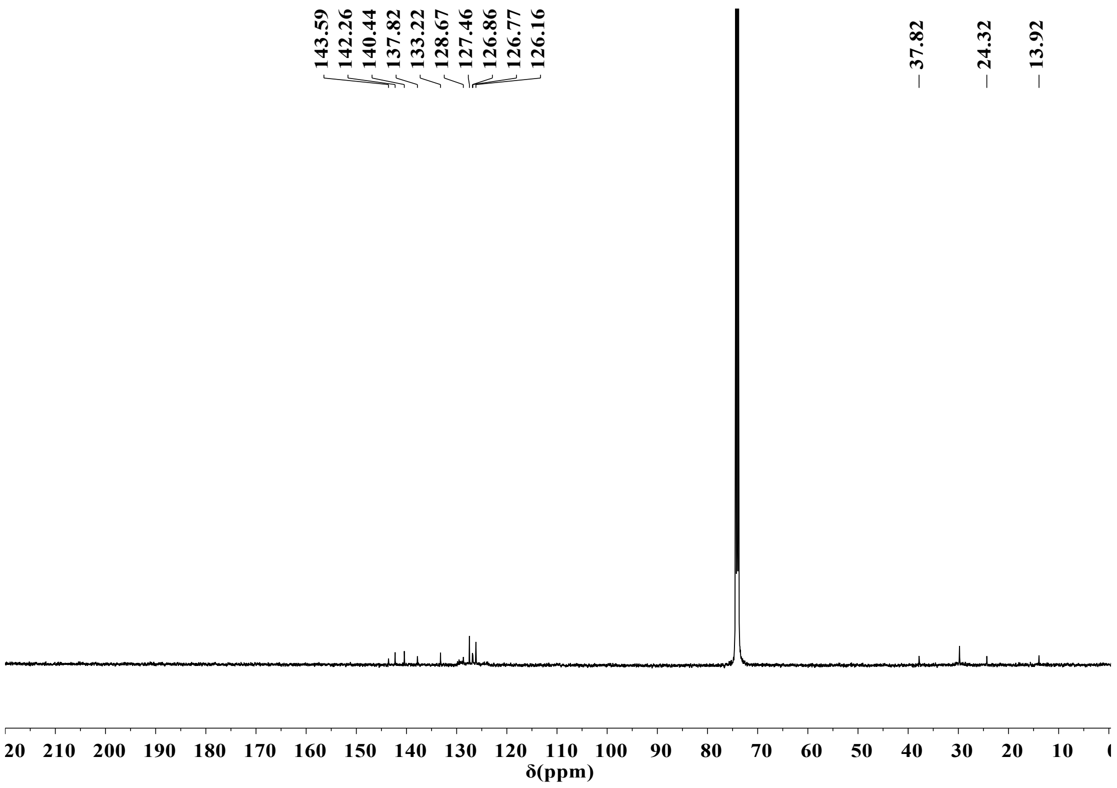
HR-MS spectrum for **2d**



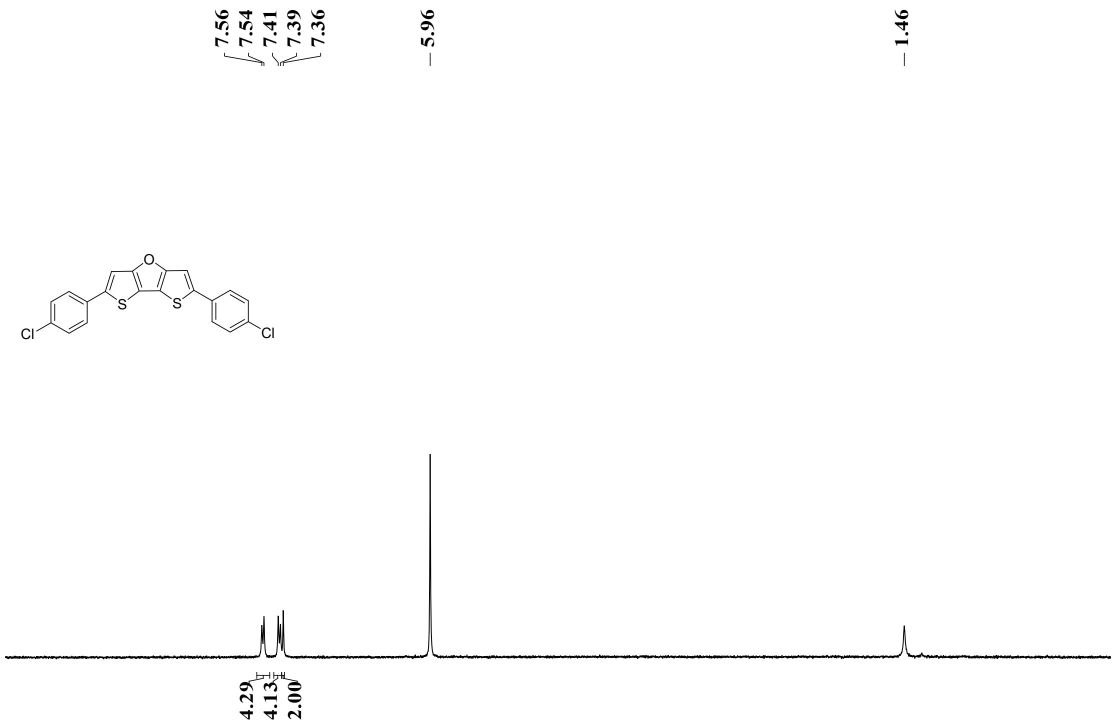
^{1}H NMR spectrum for **2e**



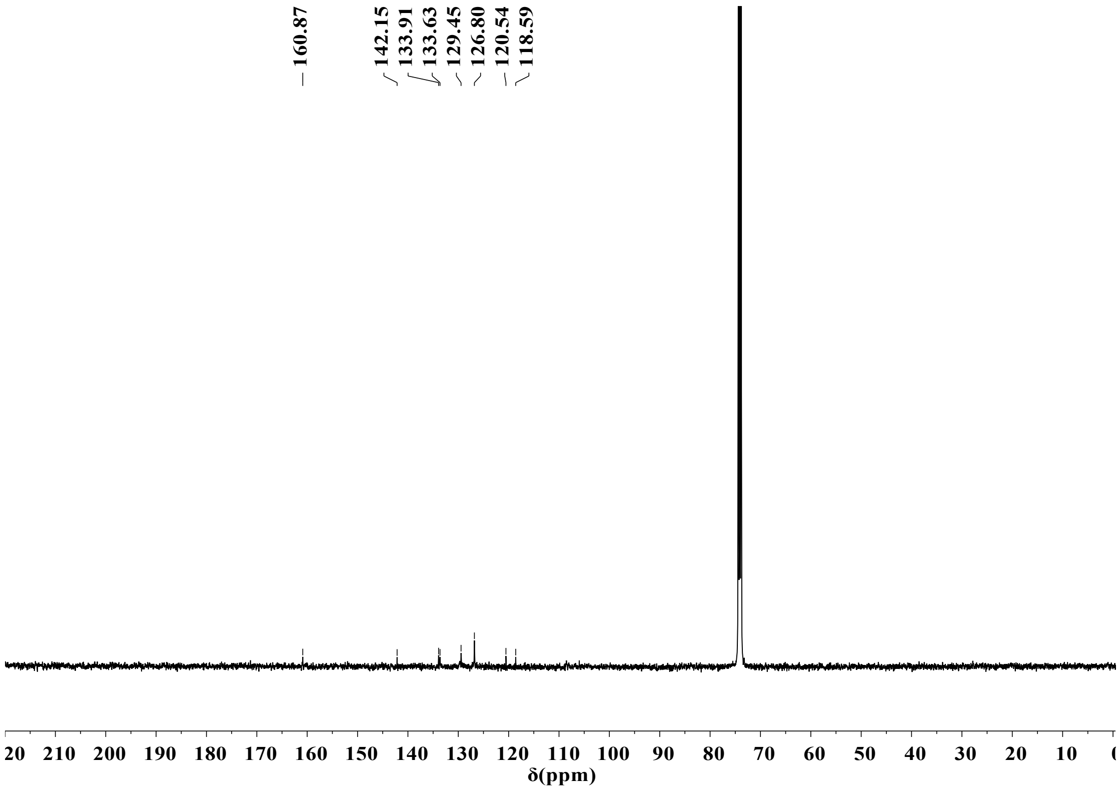
^{13}C NMR spectrum for **2e**



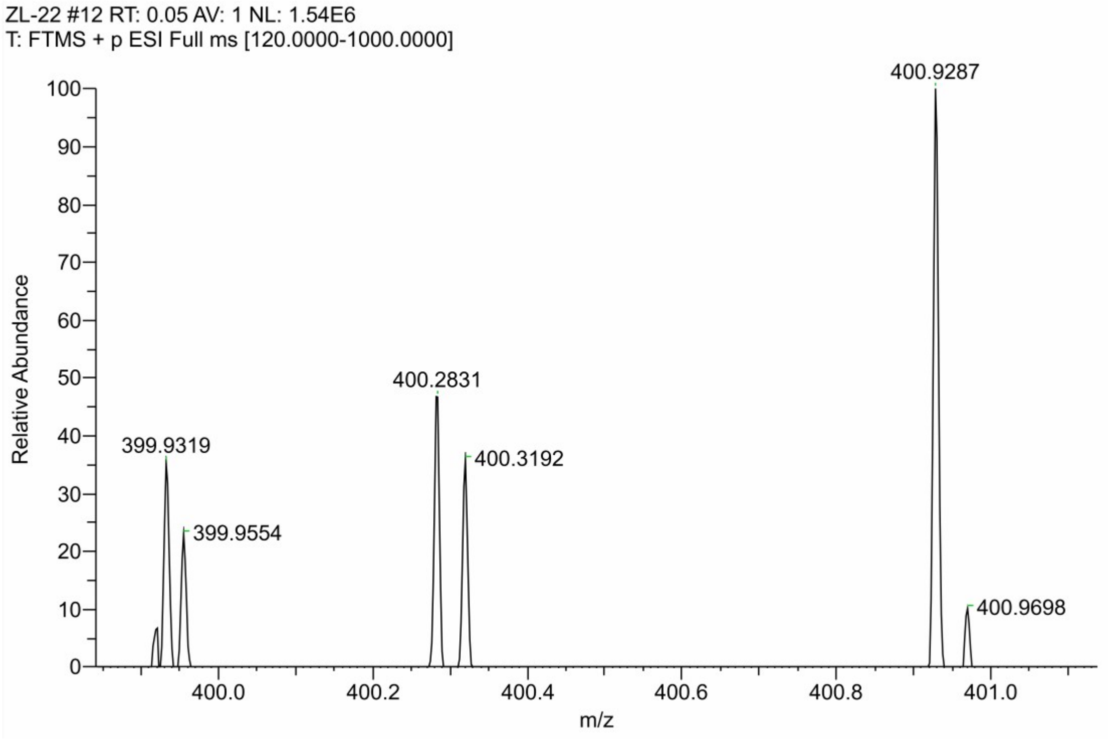
^{1}H NMR spectrum for **2f**



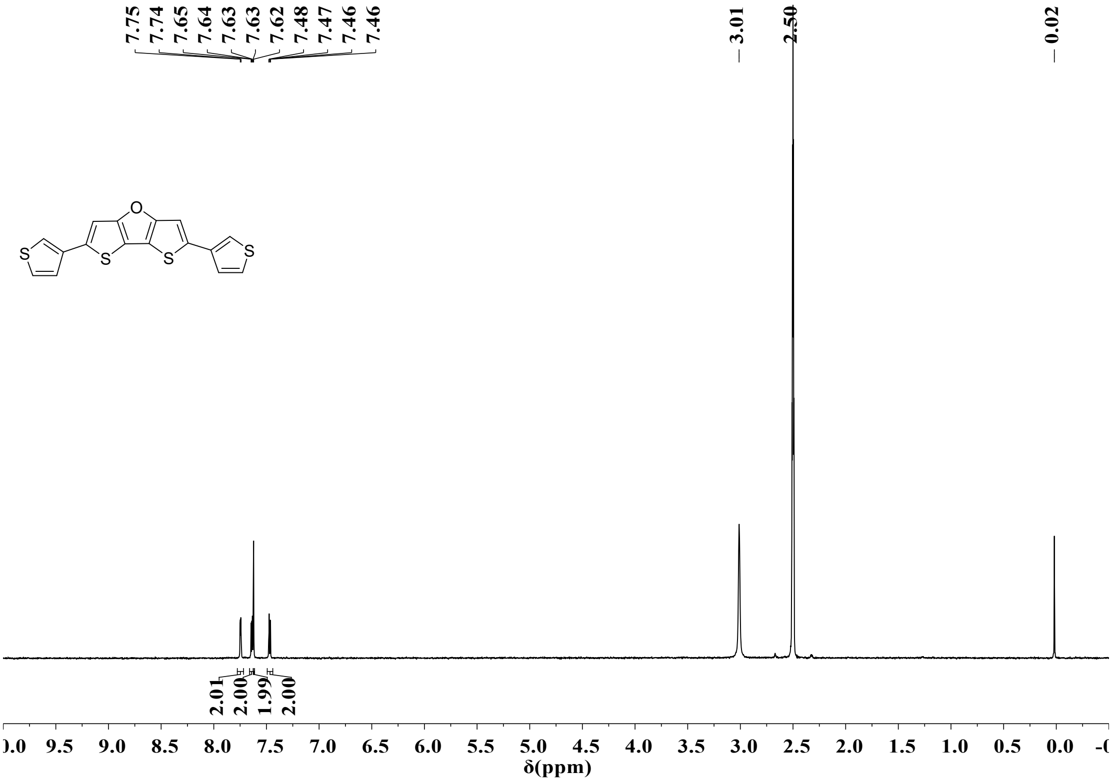
^{13}C NMR spectrum for **2f**



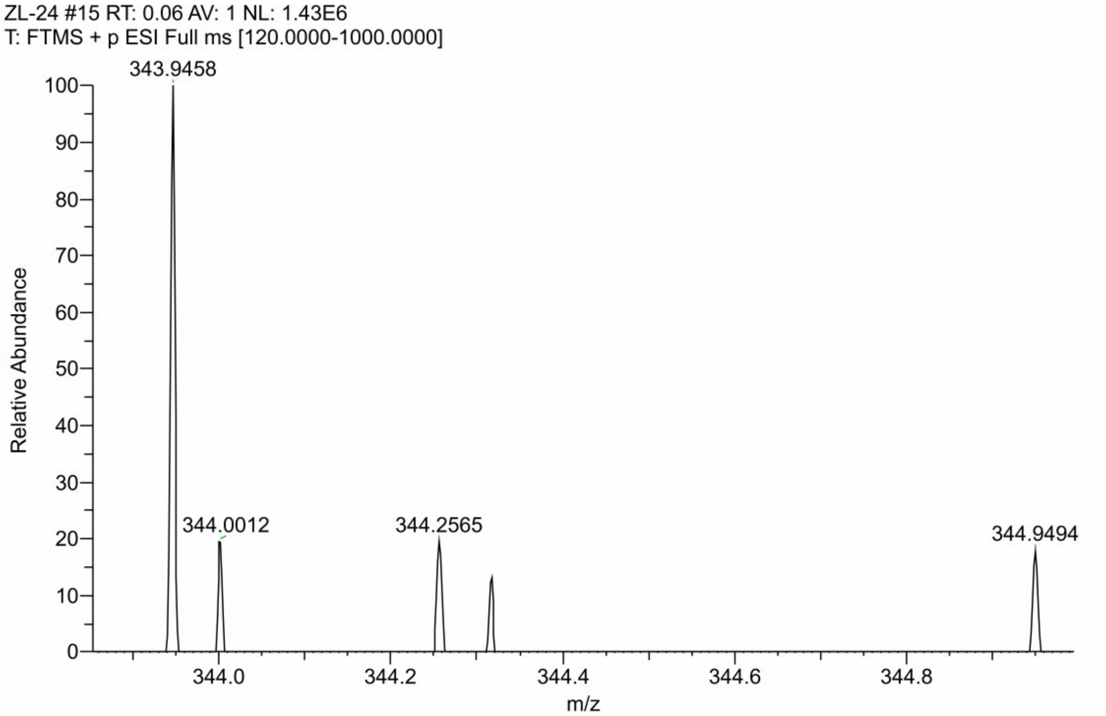
HR-MS spectrum for **2f**



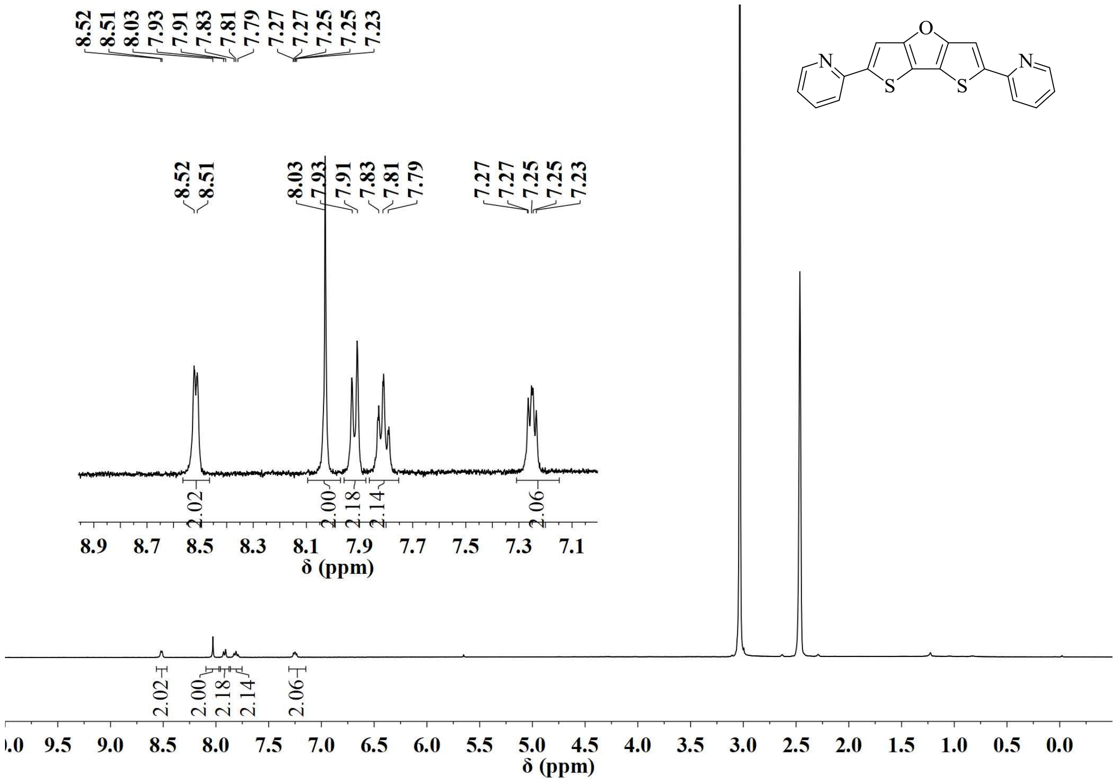
^{1}H NMR spectrum for **2g**



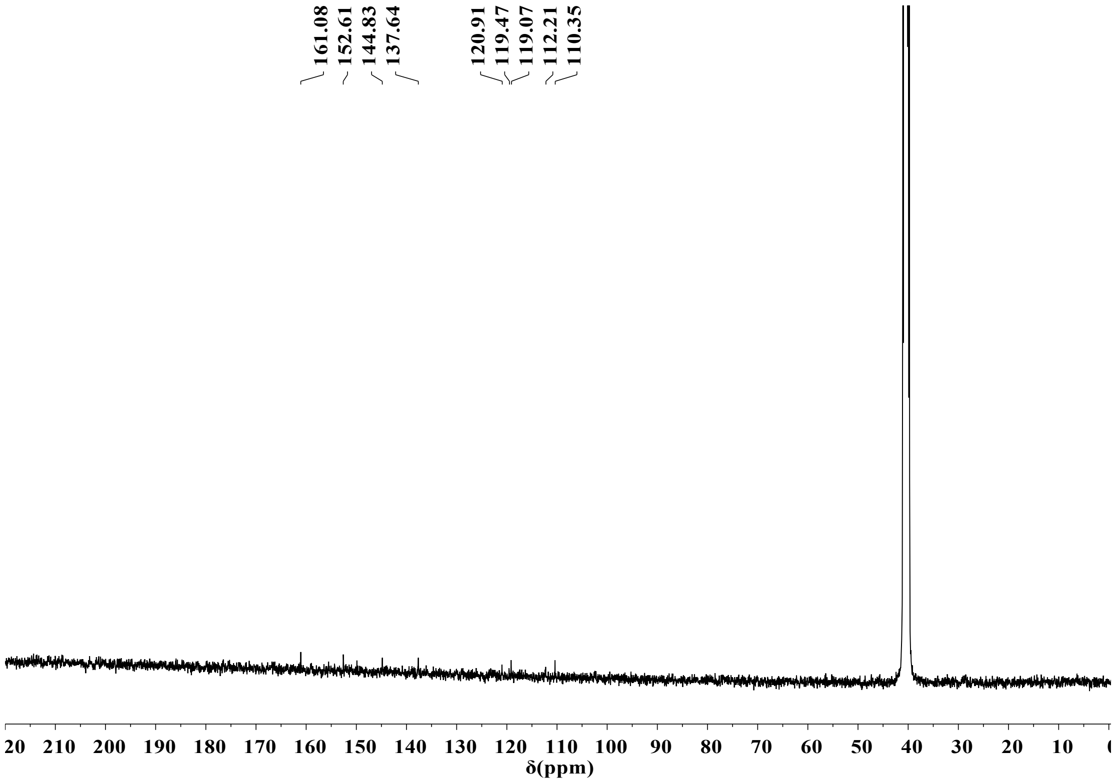
HR-MS spectrum for **2g**



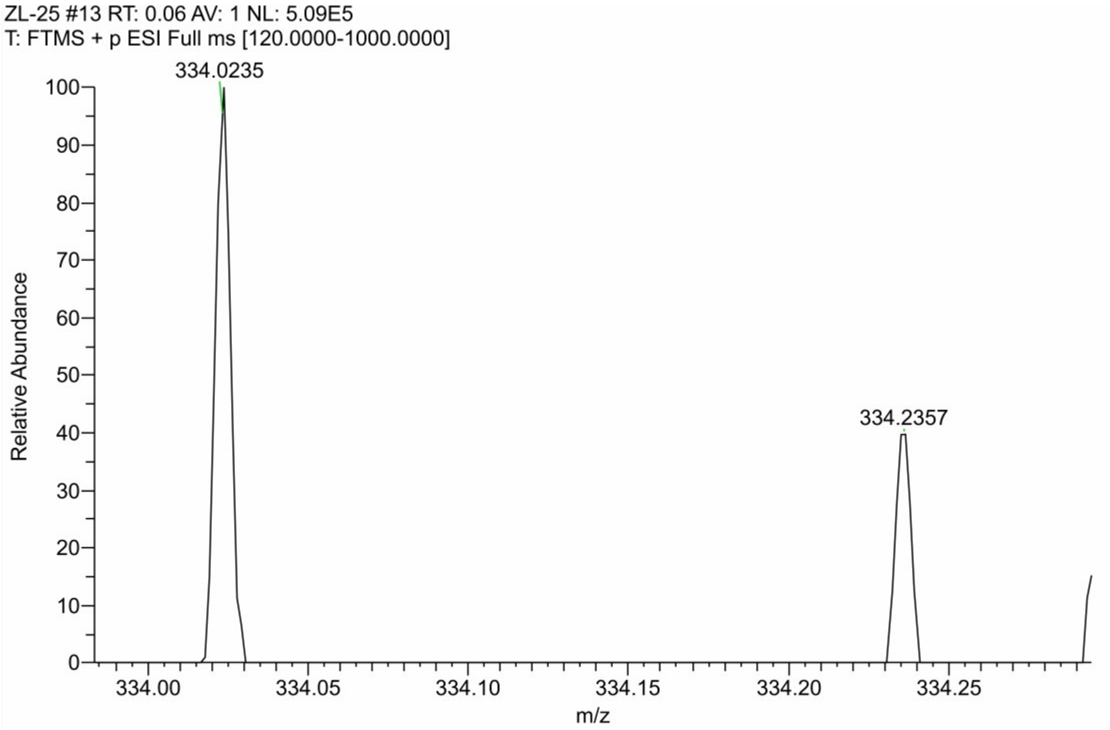
^{1}H NMR spectrum for **2h**



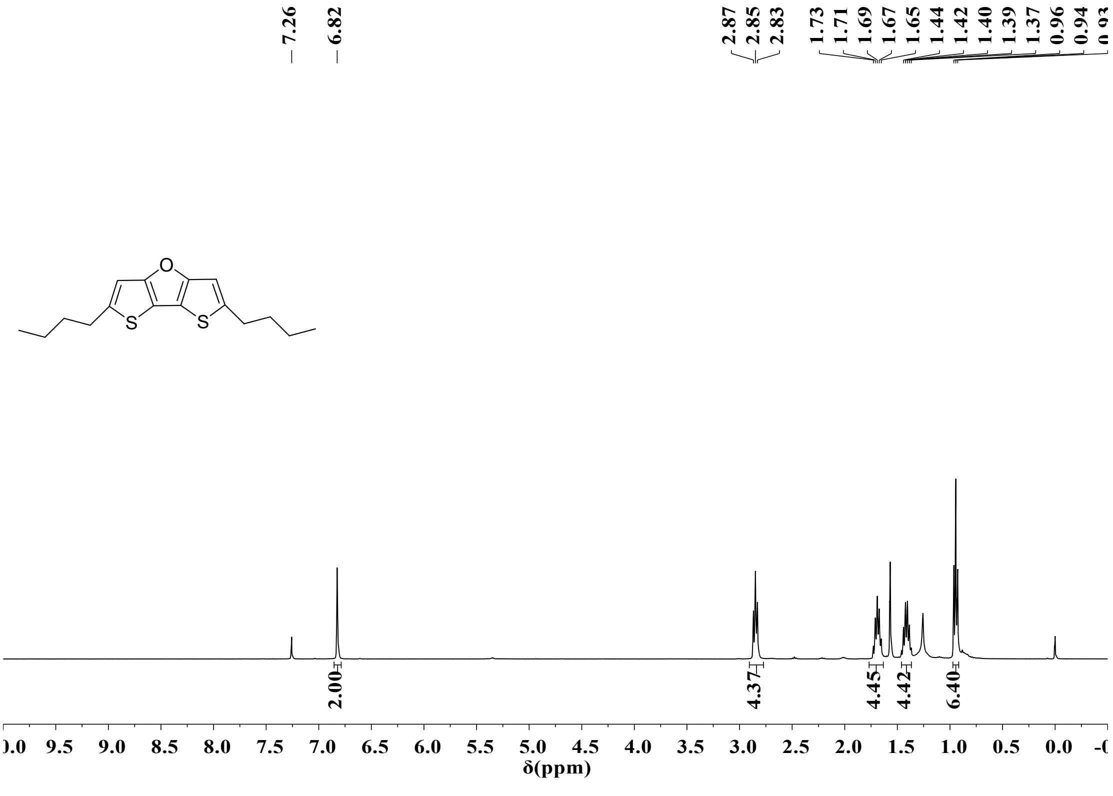
^{13}C NMR spectrum for **2h**



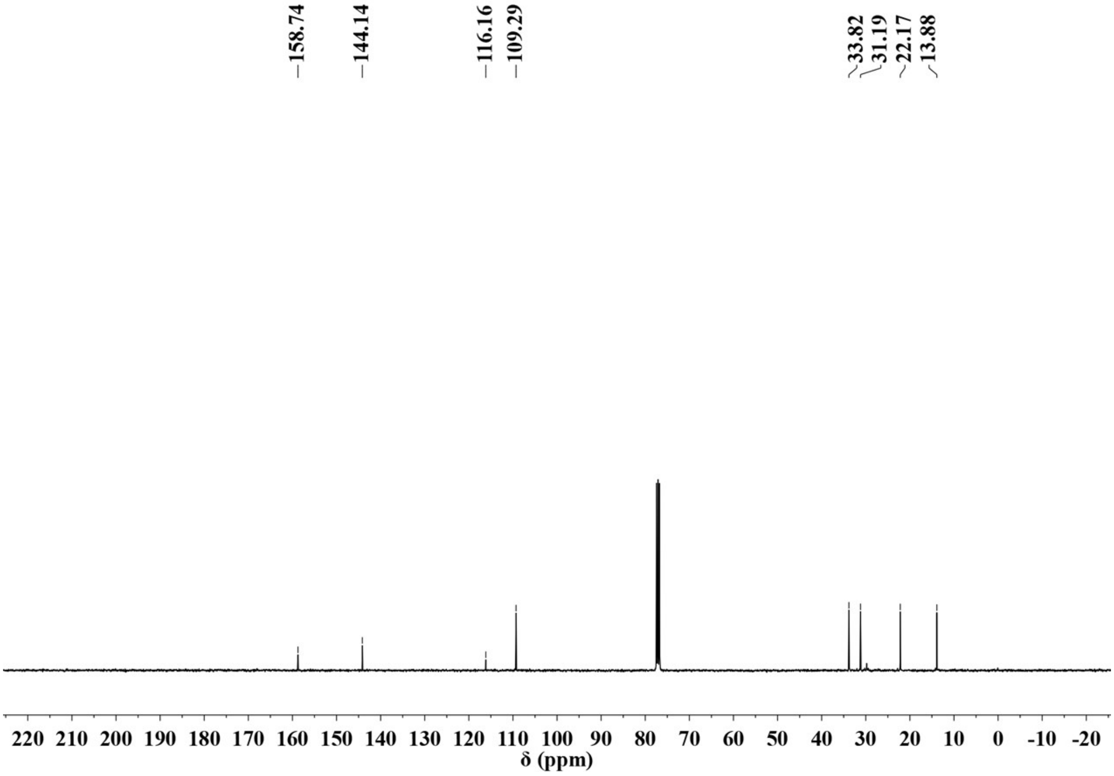
HR-MS spectrum for **2h**



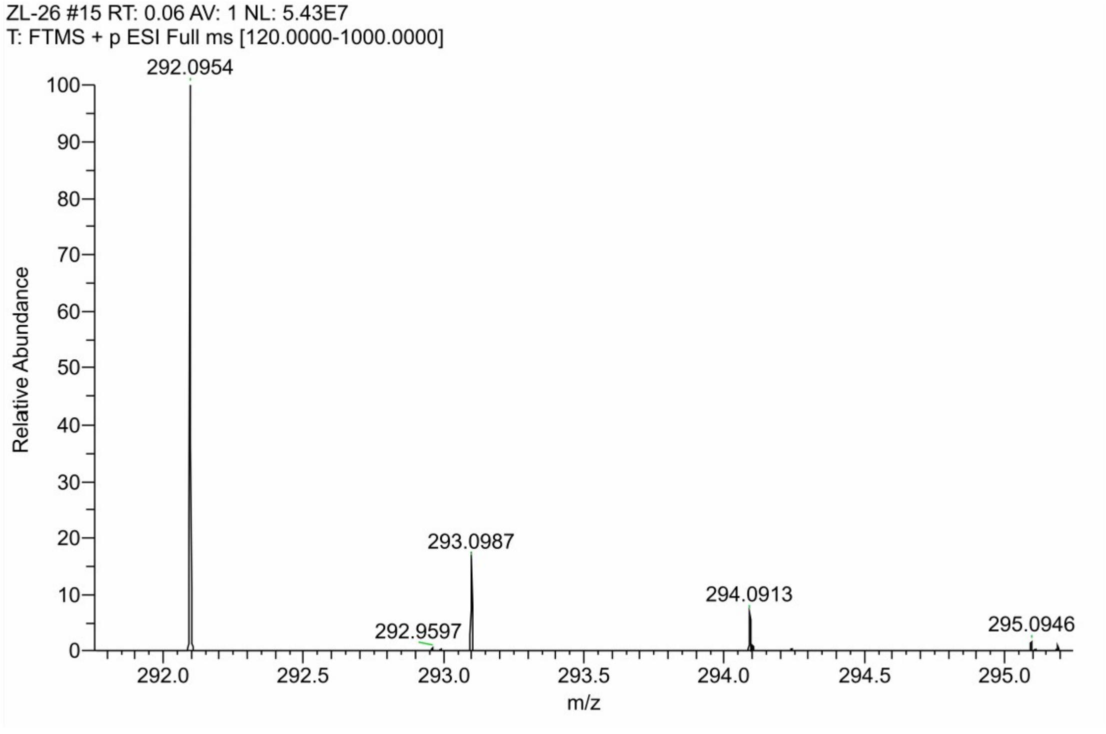
^{1}H NMR spectrum for **2i**



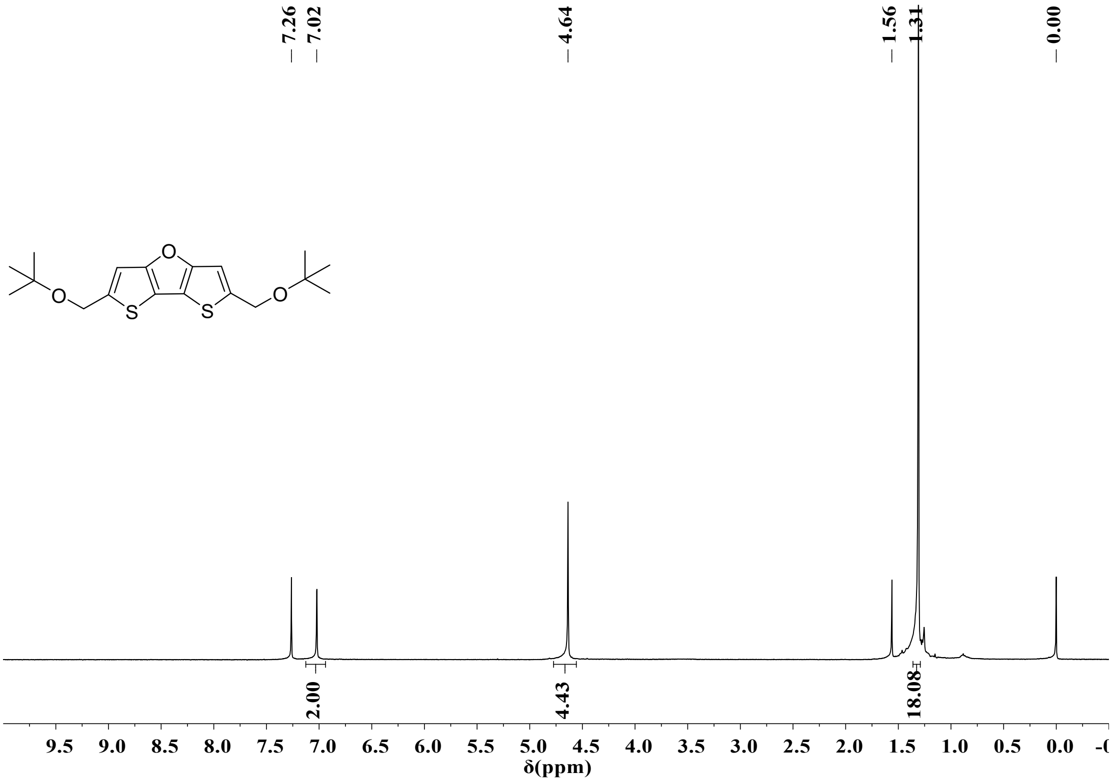
^{13}C NMR spectrum for **2i**



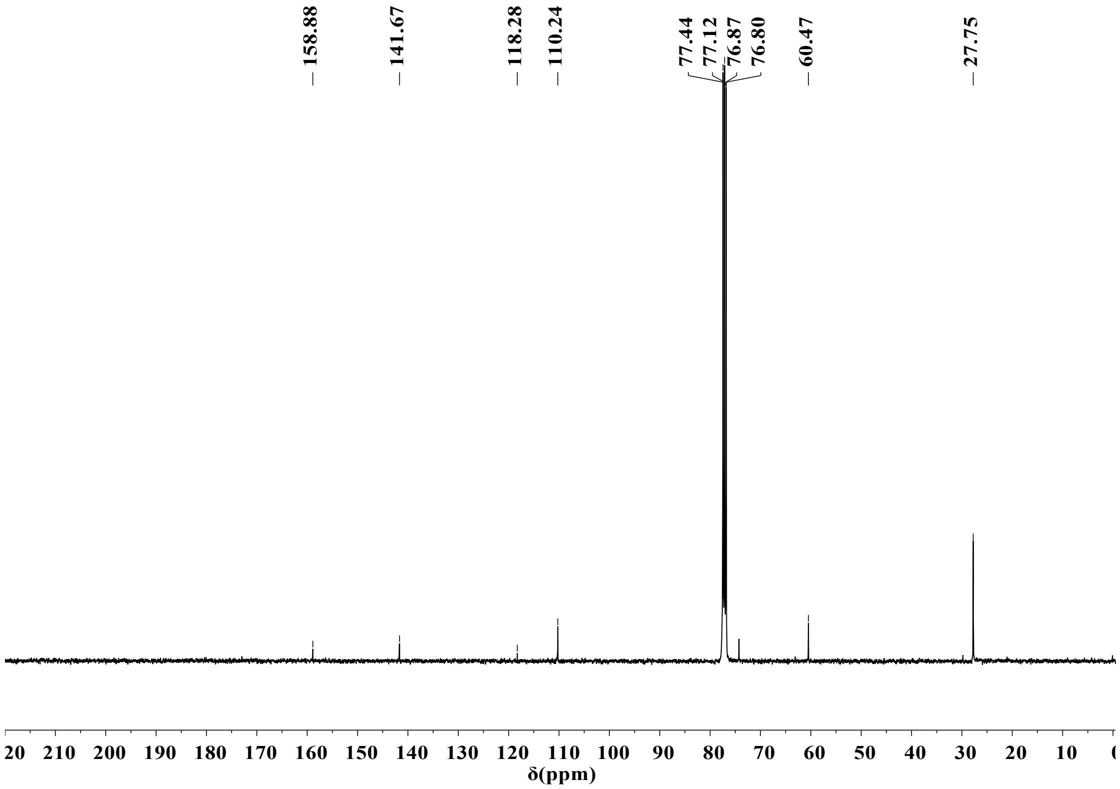
HR-MS spectrum for **2i**



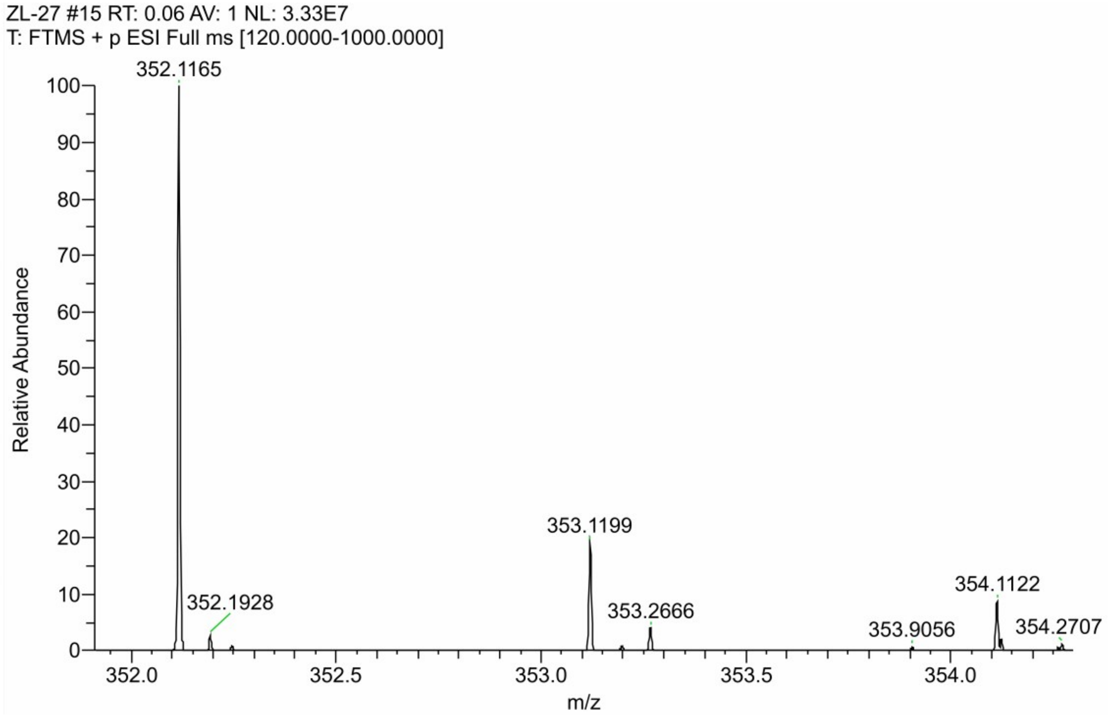
^{1}H NMR spectrum for **2j**



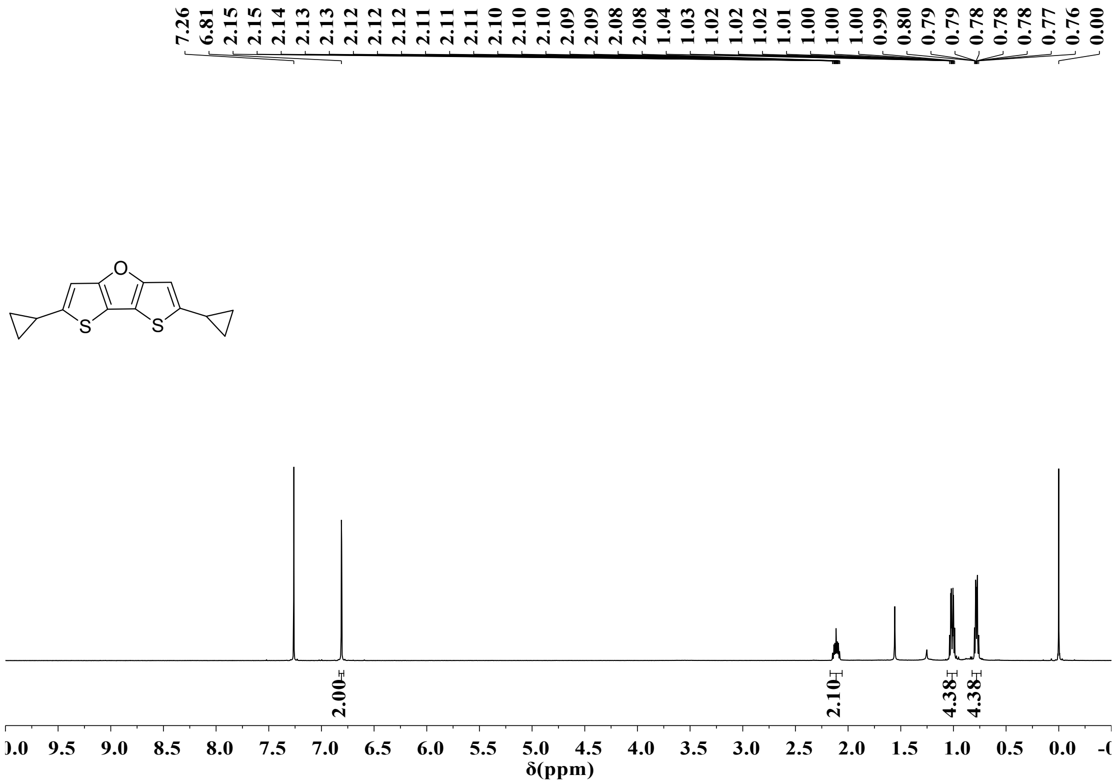
^{13}C NMR spectrum for **2j**



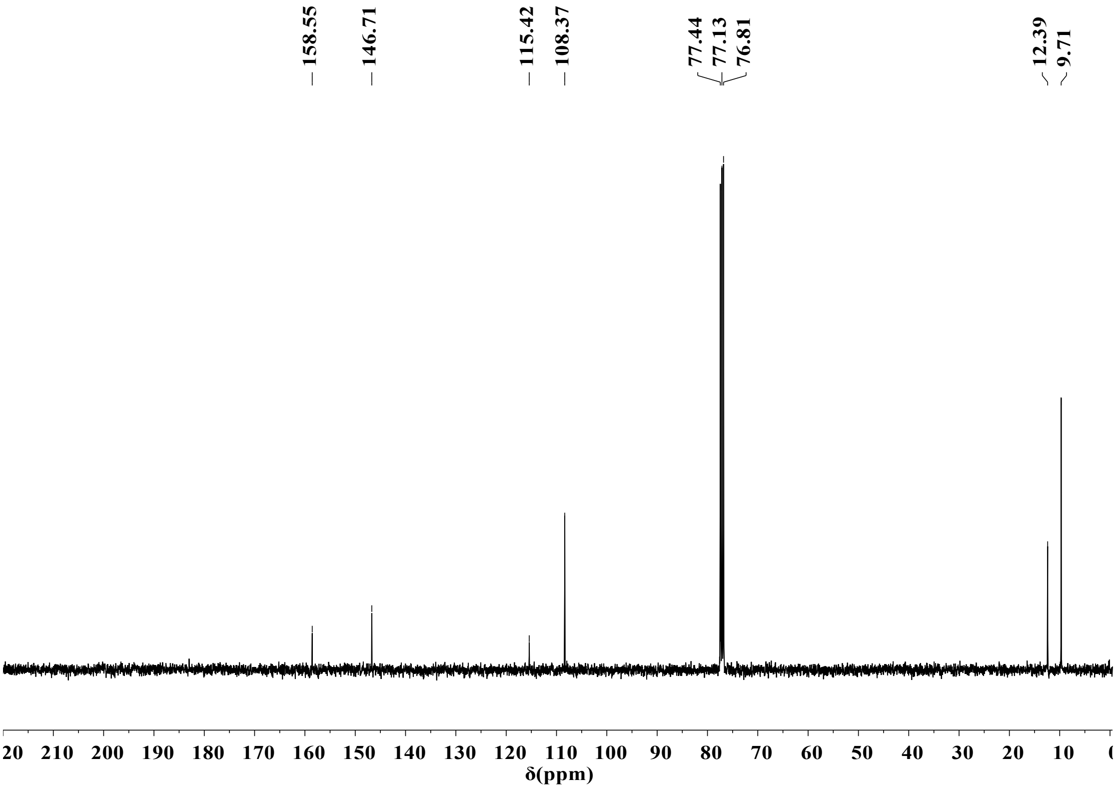
HR-MS spectrum for **2j**



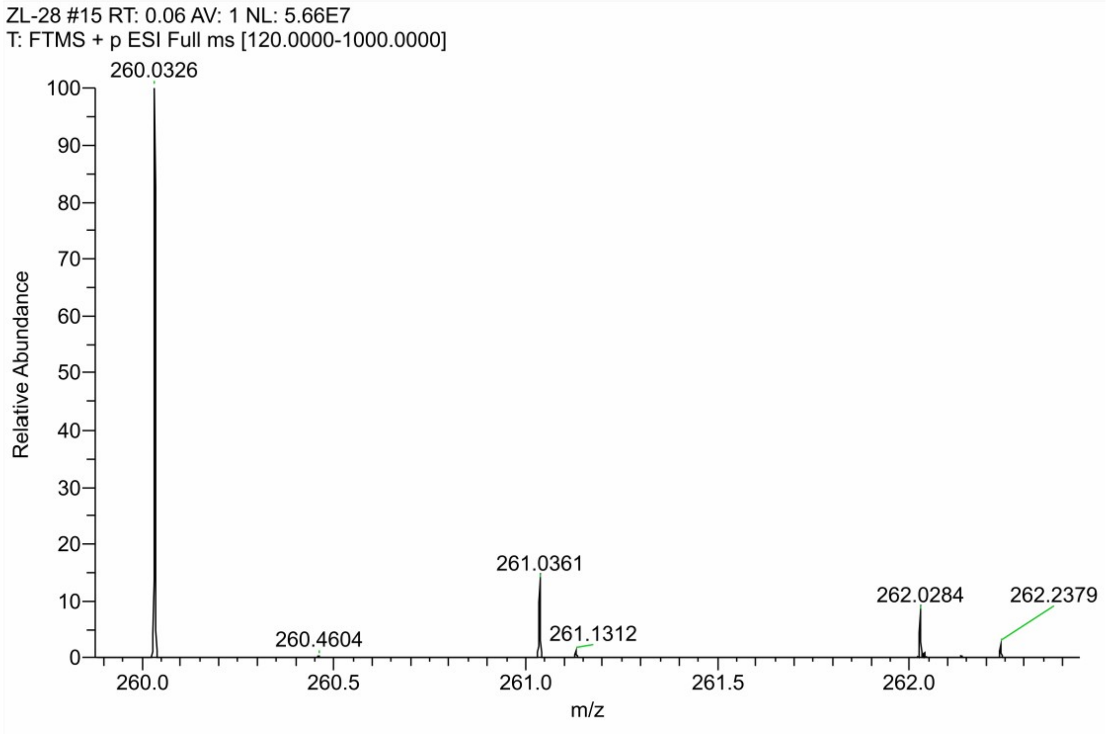
^{1}H NMR spectrum for **2k**



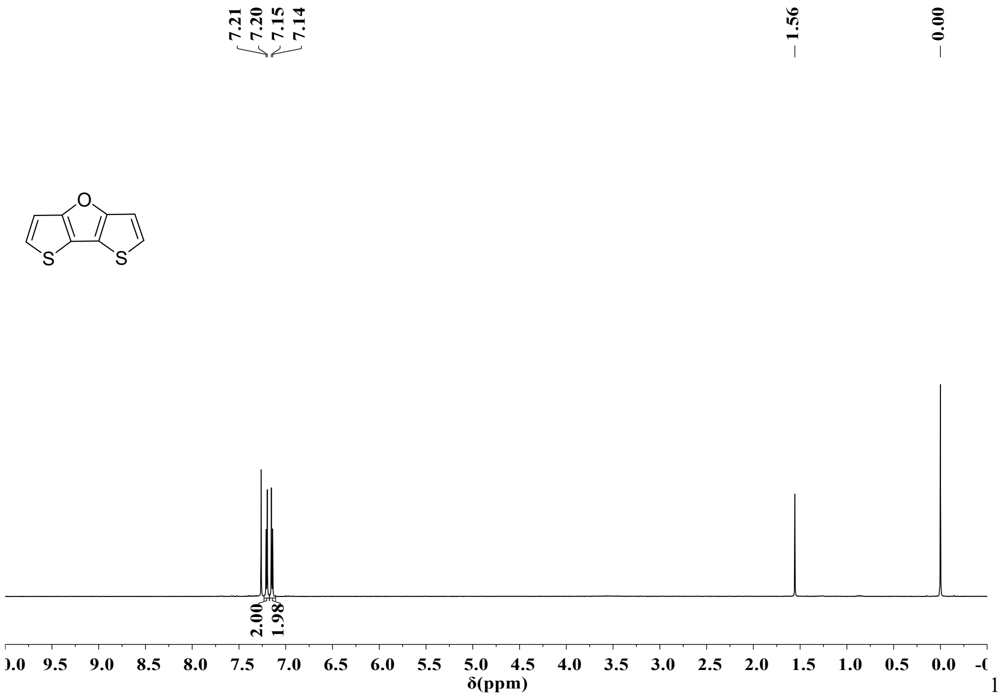
^{13}C NMR spectrum for **2k**



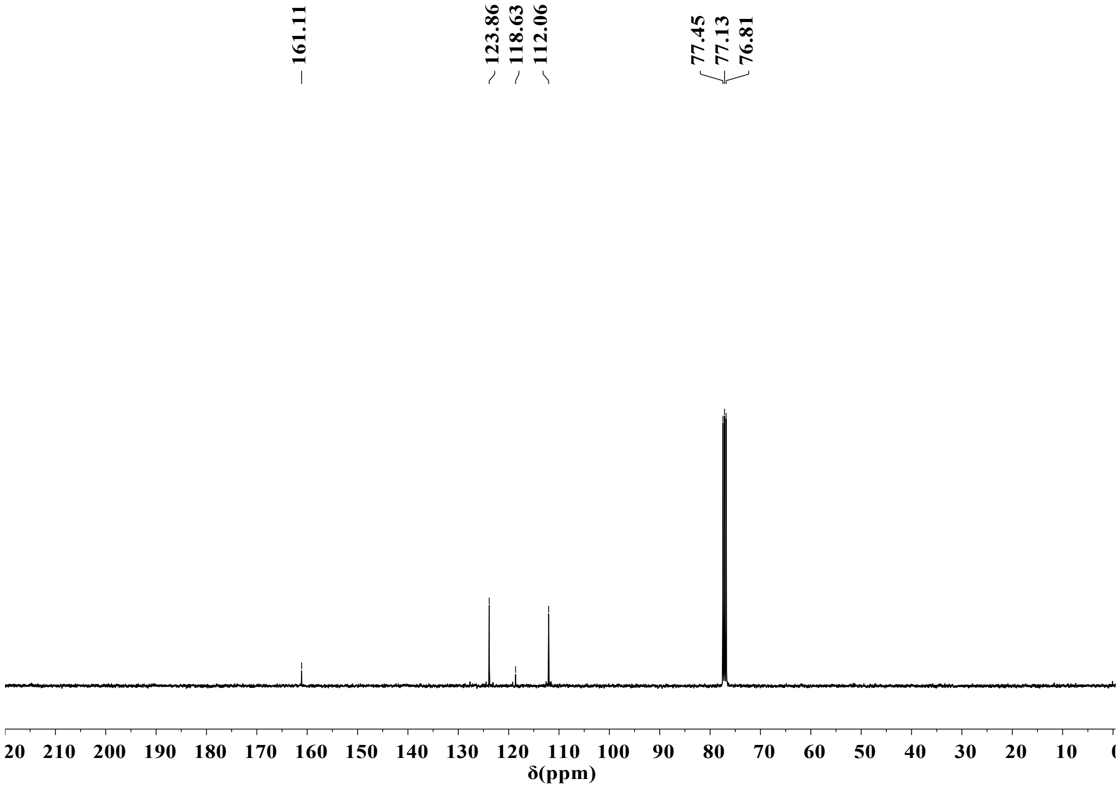
HR-MS spectrum for **2k**



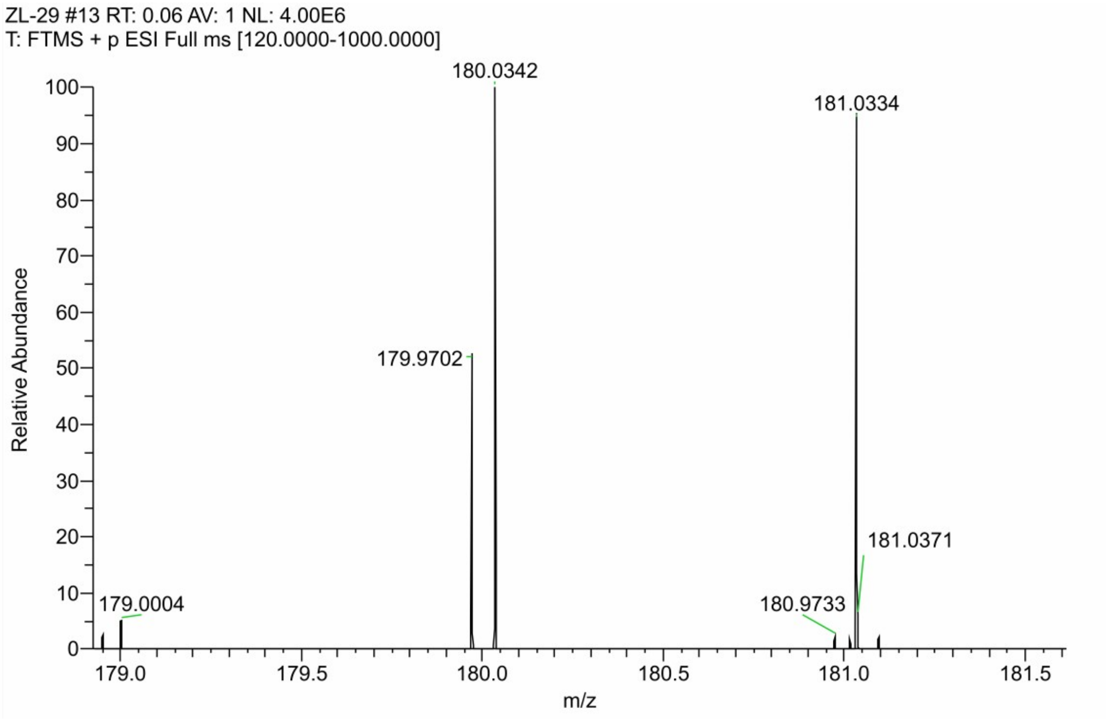
^{1}H NM spectrum for **2l**



^{13}C NMR spectrum for **2l**



HR-MS spectrum for **2l**



5. Thermogravimetric Analysis of 2a and 2d

The thermal decomposition temperature (T_d, the temperature corresponding to 5% loss of initial weight) of **2a** and **2d** is 362 °C and 344 °C, respectively, which are all over 300 °C, indicating that they all have good thermal stability.

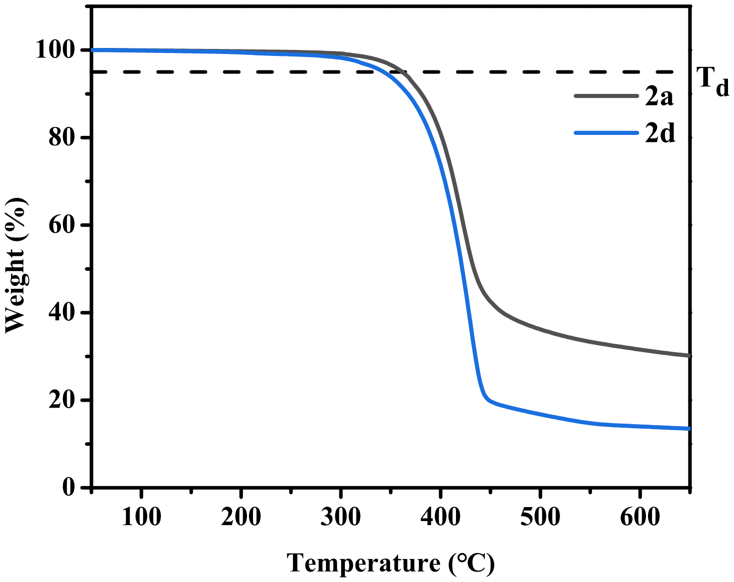


Figure S1 TGA traces of **2a** and **2d** measured in nitrogen atmosphere.

6. Single crystal X-ray crystallographic analysis of 2b and 2c

Compound	**2b**	**2c**
CCDC No	2094066	2094067
Empirical formula	$C_{20}H_{12}OS_2$	$C_{26}H_{24}OS_2$
Formula weight	332.42	416.57
Temperature/K	150.00(10)	150.01(10)
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/c$	$P2_12_12_1$
a/Å	16.763(2)	5.6526(2)
b/Å	5.6910(10)	10.0371(3)
c/Å	7.7824(11)	36.8324(15)
α/°	90	90
β/°	97.279(14)	90
γ/°	90	90
Volume/$Å^3$	736.4(2)	2089.71(13)
Z	2	4
$\rho_{calc}g/cm^3$	1.499	1.324
μ/mm^{-1}	0.362	2.411
F(000)	344.0	880.0
Crystal size/mm^3	0.14 × 0.13 × 0.12	0.13 × 0.12 × 0.09
Radiation	Mo Kα (λ = 0.71073)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	4.9 to 58.596	4.798 to 147.376
Index ranges	$-20 \le h \le 23, -7 \le k \le 7, -10 \le l \le 8$	$-4 \le h \le 6, -12 \le k \le 8, -45 \le l \le 41$
Reflections collected	3848	5045
Independent reflections	1776 [R_{int} = 0.0241, R_{sigma} = 0.0462]	3352 [R_{int} = 0.0326, R_{sigma} = 0.0543]
Data/restraints/parameters	1776/186/184	3352/0/266
Goodness-of-fit on F^2	1.046	1.084
Final R indexes [I>=2σ (I)]	R_1 = 0.0610, wR_2 = 0.1248	R_1 = 0.0480, wR_2 = 0.1297
Final R indexes [all data]	R_1 = 0.0940, wR_2 = 0.1449	R_1 = 0.0533, wR_2 = 0.1337
Largest diff. peak/hole / e $Å^{-3}$	0.30/-0.33	0.34/-0.38

Flack parameter		0.032(18)

Single crystals of **2b** (CCDC 2094066) were obtained by vacuum sublimation, while single crystals of **2c** (CCDC 2094067) were obtained in toluene solution. The single crystal structures were revealed by X-ray diffraction analysis. Both compounds show good symmetry and planarity, and both are stacked in herringbone patterns (see Figure 1 and Figure 2 in the main text).