Supporting Information

Bromide-Selective Suzuki Cross-coupling of Bromoaryl Triflates Enabled by Bidentate Diimine-Pd Complexes

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Contents

1. General experimental information..... S1
2. Synthesis procedure for the catalysts..... S1-S4
3. General procedure for Pd catalyzed Suzuki reactions.....S5-S6
4. Characterization data of the Suzuki coupled products..... S6-S10
5. NMR spectrums of the catalysts and reaction products..... S10-S58
6. References.....S58

1. General experimental information

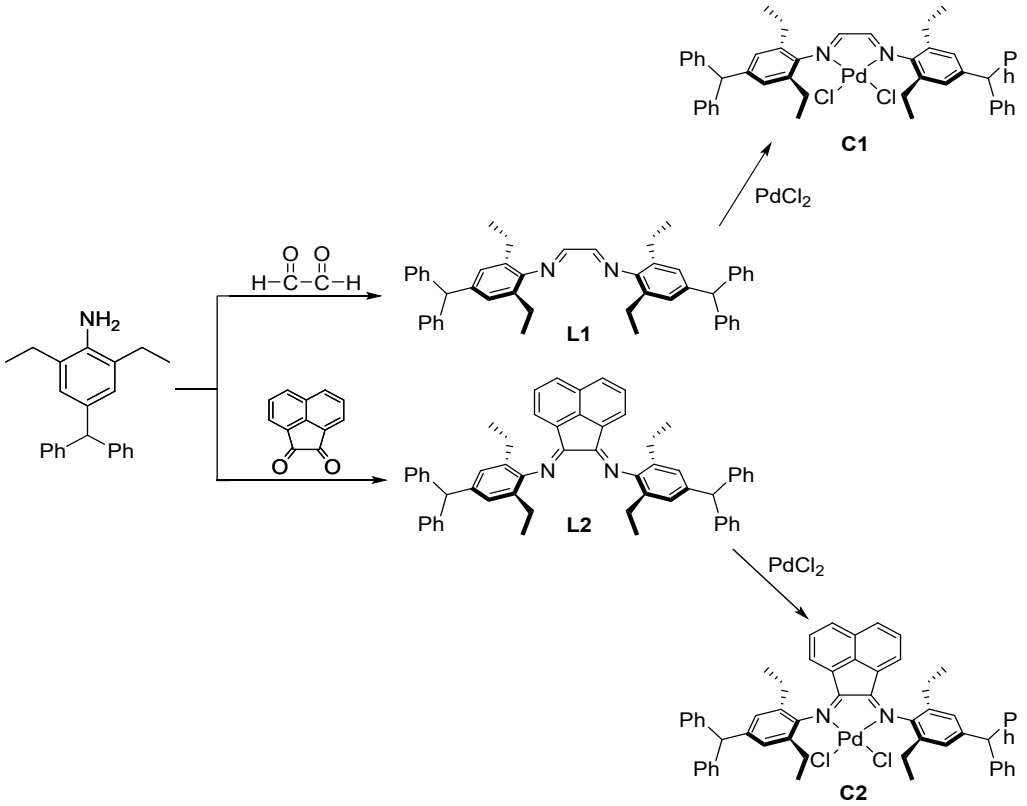
All bromoaryl triflate and aryl boronic acids were purchased from Aldrich Chemical. Aryl amines, glyoxal, acenaphthenequinone, and palladium (II) chloride were also commercially obtained from Aldrich Chemical. Inorganic bases were purchased from Darui Chemical Reagent Factory. Isopropyl alcohol and other solvents were obtained from Guangzhou Chemical Reagent Factory and used directly. Complexes **C1**-**C2** were prepared following the procedures described below. **C3**-**C10** were synthesized according to the previous literature.[1-2]

The NMR data of the compounds were acquired on a Varian Mercury-Plus 400 MHz spectrometer at room temperature, unless stated otherwise. The decoupled nucleus was used, with $CDCl_3$ as the solvent and TMS as the reference standard. *J* values are given in Hz. GC yields for optimization studies were obtained using a Shimadzu GC-2010 Plus instrument.

All Suzuki coupling reactions were carried out using a parallel reaction apparatus (WP-RH-1020, WATTECS) under air conditions. The subsequent work-up and purification procedures were performed using reagent-grade solvents obtained from Guangzhou Chemical Reagent Factory. Purification was achieved through standard column chromatography techniques employing silica gel.

2. Synthesis procedure for the catalysts

The synthetic routes for complexes **C1** and **C2**, depicted in Scheme 1, were modified based on previous methods.[1-2] These complexes were obtained in good to high yields and isolated as air-stable yellow solids. Their chemical structures were confirmed using ^{1}H and ^{13}C NMR spectroscopy.



Scheme 1. The synthetic procedure of the investigated Pd-diimine complexes **C1**-**C2**.

Procedure for the Synthesis of α-Diimine Compounds L1-L2. Under N_2 atmosphere, 4-(diphenylmethyl)-2,6-diethylaniline (20 mmol, 6.30 g), 40% glyoxal solution (10 mmol, 1.44 g), anhydrous ethanol (30 mL) and acetic acid (3 mL) were transferred into a flask and the resulting mixture was allowed to stir at room temperature under air for 24 hours. Upon reaction completion, collect the yellow precipitate by suction filtration. Dry the solid, then recrystallize from dichloromethane/anhydrous ethanol to obtain the titled compound **L1** as a yellow solid in 85% yield (8.5 mmol, 5.5 g).

L1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 2H), 7.25 –7.18 (m, 10H), 7.07 (d, J = 7.5 Hz, 10H), 6.77 (s, 4H), 5.43 (s, 2H), 2.37 (q, J = 7.5 Hz, 8H), 1.00 (t, J = 7.5 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.26, 147.51, 144.23, 140.32, 132.38, 129.48, 128.29, 127.68, 126.24, 56.58, 22.71, 14.47.

4-(diphenylmethyl)-2,6-diethylaniline (22 mmol, 6.90 g), acenaphthenequinone (10 mmol, 1.82 g), anhydrous zinc chloride (23 mmol, 3.20 g) and acetic acid (25 mL) were combined in a flask under N_2 atmosphere and the mixture was allowed to heat at 140 ^{o}C for 5 h. After completion of the reaction, cool the mixture to room temperature, and

collect the reddish-orange solid via filtration using a Büchner funnel. The obtained solid was washed by acetic acid, dried by oven and redissolved in CH_2Cl_2. Potassium oxalate (4.60 g, 25 mmol) in 150 mL H_2O was added into the CH_2Cl_2 solution, and the resulting mixture was allowed to stir at RT for 24 h. Upon completion of the stirring, the reaction mixture was filtered to remove white solid and the filtrate was stewed and layered. The organic layer was then dried over anhydrous sodium sulfate, filtered, concentrated under vacuum and recrystallized from CH_2Cl_2/ethanol. The titled compound **L2** was obtained as orange/reddish solids 6.99 g (9.0 mmol, 90% yield). The NMR data for **L2** are consistent with those previously reported in the literature.[3]

Procedures for the Synthesis of Pd-Diimine Compounds C1-C2. Under nitrogen atmosphere, a mixture of **L1** (0.5 mmol, 0.326 g), $PdCl_2$ (0.55 mmol, 0.0975 g), and 10 mL of methanol was heated slowly to 60°C and stirred at 60°C for 24 h. After completion, the solution was cooled to room temperature. Purify the crude product by dry-column flash chromatography using dichloromethane as the eluent. Concentrate the collected fractions under reduced pressure, then recrystallize from dichloromethane/n-hexane to afford the desired complex **C1**.

C1 was obtained as bright-yellow solids in 70% yield (0.29 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 2H), 7.24 (dd, J = 9.5, 5.3 Hz, 8H), 7.17 (d, J = 7.3 Hz, 4H), 7.06 (d, J = 7.3 Hz, 8H), 6.71 (s, 4H), 5.44 (s, 2H), 2.50−2.48 (m, 8H), 0.96 (t, J = 7.5 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.03, 142.91, 142.59, 141.82, 134.35, 128.42, 127.32, 125.86, 125.37, 55.55, 23.83, 12.93.

C2 was synthesized according to the same procedure and obtained as yellow-orange solids in 80% yield (0.38 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 8.3 Hz, 2H), 7.48 (t, J = 7.8 Hz, 2H), 7.35 (t, J = 7.5 Hz, 8H), 7.28−7.24 (m, 4H), 7.20 (d, J = 7.2 Hz, 8H), 7.03 (s, 4H), 6.55 (d, J = 7.2 Hz, 2H), 5.63 (s, 2H), 2.94−2.85 (m, 4H), 2.75−2.63 (m, 4H), 1.17 (t, J = 7.5 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.69, 144.49, 143.62, 140.88, 135.02, 132.65, 129.54, 129.32, 127.86, 126.56, 125.43, 124.86, 56.78, 24.94, 13.91.

3. General procedure for Pd-diimine catalyzed Suzuki reactions

General procedure for Pd-diimine catalyzed Suzuki reactions of bromoaryl triflates. Under an air atmosphere, bromoaryl triflate (0.25 mmol), arylboronic acid (0.26 mmol), base (0.5 mmol), palladium α-diimine complex (0.25 mol%), and solvent (1 mL) were sequentially added into a parallel reaction tube. The resulting mixture was allowed to stir at 80 ^{o}C for 4 h. After completion, the reaction mixture was cooled to room temperature and followed by extraction with ethyl acetate three times (3 × 10 mL). The organic layers were combined and dried with anhydrous sodium sulfate, filtered, and subsequently analyzed by gas chromatography (GC) to determine the GC yield. The solvent was removed by rotary evaporation under reduced pressure. The residue was purified by thin-layer chromatography (TLC) or silica-gel column chromatography to afford the products. The isolated yields of coupled products were calculated based on the feedings of the bromophenyl triflates.

General procedure for Pd-NHC catalyzed Suzuki reactions of aryl triflates. Under an air atmosphere, aryl triflate (0.25 mmol), arylboronic acid (0.26 mmol), potassium carbonate (0.5 mmol), Pd-NHC complex (0.000625 mmol, 0.25 mol%), and MeOH (1 mL) were sequentially added into a parallel reaction tube. The resulting mixture was allowed to stir at 80^{o}C for 4 h. After completion, the reaction mixture was cooled to room temperature and followed by extraction with ethyl acetate three times (3 × 10 mL). The organic layers were combined and dried with anhydrous sodium sulfate, filtered, and concentrated. The resulting residue was then purified by thin-layer chromatography on silica-gel using petroleum ether/ethyl acetate to afford the corresponding products. The isolated yields of coupled products were calculated based on the feedings of the aryl triflates.

Reaction procedure for Pd-diimine catalyzed Competitive Suzuki reactions. Under an air atmosphere, bromobenzene (0.50 mmol, 0.079 g), phenyl

triflate (0.50 mmol, 0.11 g), *p*-tolylboronic acid (0.52 mmol, 0.07 g), potassium carbonate (0.5 mmol, 0.14 g), complex **C3** (0.25 mol%, 0.0014 g), and ^{i}PrOH/H_2O (19:1, 1 mL) were sequentially added into a parallel reaction tube. The mixture was stirred at 80 °C for 4 h. After cooling to ambient temperature, 1,3,5-trimethoxybenzene (84 mg, 0.50 mmol) was added as an internal standard to the mixture and stirred for 30 min. The mixture was then concentrated under reduced pressure. ^{1}H and ^{19}F NMR spectroscopy was performed on the residue.

4. Characterization data of the Coupled products

4'-methyl-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate **(3a)** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.8 Hz, 2H), 7.45 (d, J = 8.1 Hz, 2H), 7.32 (d, J = 8.8 Hz, 2H), 7.28 (s, 2H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.74, 141.65, 138.02, 136.41, 129.73, 128.66, 127.03, 121.59, 118.80 (q, J = 319.0 Hz), 21.15. ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.77.

3'-methyl-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate **(3b)** ^{1}H NMR (400 MHz $CDCl_3$) δ 7.57 (d, J = 6.0 Hz, 2H), 7.31 (m, 5H), 7.19 (m, 1H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.54, 142.47, 139.91, 139.31, 129.50, 128.61, 124.94, 124.26, 122.20, 119.47 (q, J = 319.0 Hz), 22.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.77.

2'-methyl-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate **(3c)** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.7 Hz, 2H), 7.35−7.33 (m, 2H), 7.30 (d, J = 3.6 Hz, 2H), 7.28 (s, 1H), 7.22 (d, J = 7.2 Hz, 1H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.52, 142.39, 139.93, 135.25, 131.01, 130.55, 129.67, 127.99, 126.01, 121.03, 118.80 (q, J = 319.0 Hz), 20.40. ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.82.

4'-ethyl-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate **(3d)** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67−7.62 (m, 2H), 7.49 (d, J = 8.1 Hz, 2H), 7.35−7.33 (m, 4H), 2.72 (q, J = 7.6 Hz, 2H), 1.30 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.76, 144.37, 141.69, 136.67, 128.69, 128.56, 127.14, 121.60, 118.83 (q, J = 319.0 Hz), 28.55, 15.56. ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.78.

2'-ethyl-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate **(3e)** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.8 Hz, 2H), 7.35−7.27 (m, 4H), 7.25−7.20 (m, 1H), 7.15 (d, J = 7.0 Hz, 1H), 2.56 (q, J = 7.6 Hz, 2H), 1.09 (t, J = 7.5 Hz, 3H). ^{13}C NMR (100 MHz,

$CDCl_3$) δ 149.22, 143.09, 142.15, 140.26, 131.67, 130.48, 129.45, 128.86, 126.45, 121.61, 119.48 (q, J = 321.2 Hz), 26.72, 16.19. ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.82. HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{15}H_{13}F_3NaO_3S$, 353.0435; found, 353.0425.

4'-(tert-butyl)-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate **(3f)** ^1H NMR (400 MHz, $CDCl_3$) δ 7.67−7.62 (m, 2H), 7.50 (s, 4H), 7.34 (d, J = 8.7 Hz, 2H), 1.37 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.24, 148.77, 141.57, 136.39, 128.70, 126.87, 125.99, 121.59, 118.80 (q, J = 319.0 Hz), 34.64, 31.33. ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.78.

4'-methoxy-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate **(3g)** ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.5 Hz, 2H), 7.49 (d, J = 8.5 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 6.99 (d, J = 8.4 Hz, 2H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.71, 148.50, 141.32, 131.76, 128.37, 128.29, 121.60, 118.79 (q, J = 319.0 Hz), 114.43, 55.40. ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.77.

3'-methoxy-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate **(3h)** ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.8 Hz, 2H), 7.38−7.29 (m, 3H), 7.11 (d, J = 7.3 Hz, 1H), 7.08−7.04 (m, 1H), 6.92 (d, J = 8.2 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.72, 149.64, 142.18, 141.37, 130.68, 129.55, 122.24, 120.26, 119.45 (q, J = 322.2 Hz), 113.95, 113.68, 55.91. ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.76.

2'-methoxy-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate **(3i)** ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.8 Hz, 2H), 7.39−7.33 (m, 1H), 7.30 (d, J = 8.7 Hz, 3H), 7.07−6.98 (m, 2H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.31, 148.49, 138.97, 131.35, 130.76, 129.46, 128.61, 120.99, 120.81, 118.80 (q, J = 319.0 Hz), 111.28, 55.53. ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.83.

4'-(methylthio)-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate **(3j)** ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.8 Hz, 2H), 7.48 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.5 Hz, 4H), 2.52 (d, J = 3.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.82, 141.03, 138.90, 135.87, 128.54, 127.50, 126.78, 121.72, 118.79 (q, J = 319.0 Hz), 15.64. ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.75. HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{14}H_{12}F_3O_3S_2$, 349.0180; found, 349.0183.

4'-ethoxy-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate **(3k)** ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.7 Hz, 2H), 7.48 (d, J = 8.6 Hz, 2H), 7.31 (d, J = 8.7 Hz, 2H), 6.98 (d, J = 8.7 Hz, 2H), 4.08 (d, J = 7.0 Hz, 2H), 1.45 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.10, 148.47, 141.36, 131.56, 128.33, 128.25, 121.58, 118.80 (q, J = 319.0 Hz), 114.95, 63.59, 14.85. ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.77.

4'-phenoxy-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate **(3l)** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.7 Hz, 2H), 7.52 (d, J = 8.6 Hz, 2H), 7.39 (t, J = 7.9 Hz, 2H), 7.34 (d, J = 8.7 Hz, 2H), 7.16 (t, J = 7.4 Hz, 1H), 7.09 (dd, J = 8.0, 6.4 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.67, 156.77, 148.76, 141.06, 134.14, 129.92, 128.60, 128.56, 123.75, 121.69, 119.30, 119.02, 118.82 (q, J = 319.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.75. HRMS (ESI) m/z: $[M+H]^+$calcd. for $C_{19}H_{14}F_3O_4S$, 395.0565; found, 395.0556.

4'-(trifluoromethyl)-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate **(3m)** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.3 Hz, 2H), 7.66 (d, J = 8.8 Hz, 4H), 7.39 (dd, J = 6.7, 4.8 Hz, 2H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 149.50, 142.78, 140.23, 129.83, 129.16, 127.57, 126.01, 124.10 (q, J = 270.0 Hz), 121.98, 118.78 (q, J = 319.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.55, -72.73.

4'-fluoro-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate **(3n)** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.7 Hz, 2H), 7.55−7.48 (m, 2H), 7.34 (d, J = 8.7 Hz, 2H), 7.15 (t, J = 8.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.86 (d, J = 247.8 Hz), 148.92, 140.73, 128.83, 128.79, 121.75, 118.79 (q, J = 319.0 Hz), 116.08, 115.87. ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.76, -114.34.

3',5'-bis(trifluoromethyl)-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate **(3o)** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 2H), 7.92 (s, 1H), 7.69 (d, J = 8.8 Hz, 2H), 7.44 (d, J = 8.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.66, 142.13, 139.39, 133.19 (q, J = 34.0 Hz), 129.94, 128.06, 123.92 (q, J = 272.0 Hz), 123.02, 122.48, 119.50（q, J = 322.2 Hz）. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.91, -72.73.

4'-chloro-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate **(3p)** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.7 Hz, 2H), 7.49 (d, J = 8.6 Hz, 2H), 7.43 (d, J = 8.5 Hz, 2H), 7.35 (d, J = 8.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.10, 140.48, 137.73, 134.34, 129.21, 128.79, 128.46, 121.83, 118.78 (q, J = 319.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.74.

methyl 4'-(((trifluoromethyl)sulfonyl)oxy)-[1,1'-biphenyl]-4-carboxylate **(3q)** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 8.8 Hz, 2H), 7.63 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 8.7 Hz, 2H), 3.95 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.78, 149.45, 143.59, 140.50, 130.31, 129.70, 129.13, 127.19, 121.89, 118.78 (q, J = 319.0 Hz), 52.30. ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.73.

[1,1'-biphenyl]-4-yl trifluoromethanesulfonate **(3r)** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 8.7 Hz, 2H), 7.56 (d, J = 7.5 Hz, 2H), 7.47 (t, J = 7.5 Hz, 2H), 7.40 (d, J = 7.3

Hz, 1H), 7.35 (d, J = 8.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.95, 141.72, 139.31, 129.02, 128.91, 128.09, 127.22, 121.66, 118.80 (q, J = 319.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.76.

4-(benzofuran-2-yl)phenyl trifluoromethanesulfonate **(3s)** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.9 Hz, 2H), 7.58 (d, J = 8.6 Hz, 1H), 7.51 (d, J = 9.0 Hz, 1H), 7.31 (m, 3H), 7.27−7.21 (m, 1H), 7.02 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.73, 154.44, 149.84, 131.48, 129.52, 127.21, 125.66, 123.94, 122.52, 121.92, 119.44（q, J = 322.0 Hz）, 111.97, 103.44. ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.70. HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{15}H_{10}F_3O_4S$, 343.0252; found, 343.0260.

4-(thiophen-3-yl)phenyl trifluoromethanesulfonate **(3t)** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 8.8 Hz, 2H), 7.48 (dd, J = 2.9, 1.3 Hz, 1H), 7.42 (dd, J = 5.0, 3.0 Hz, 1H), 7.36 (dd, J = 5.0, 1.2 Hz, 1H), 7.30 (d, J = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.53, 140.39, 136.30, 128.10, 126.92, 126.14, 121.74, 121.52, 118.78 (q, J = 319.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.74. HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{11}H_8F_3O_3S_2$, 308.9867; found, 308.9857.

4-(naphthalen-1-yl)phenyl trifluoromethanesulfonate **(3u)** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92−7.84 (m, 2H), 7.77 (d, J = 8.0 Hz, 1H), 7.54−7.48 (m, 3H), 7.48−7.40 (m, 2H), 7.39−7.32 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.53, 141.88, 138.76, 134.46, 132.47, 131.94, 129.11 (d, J = 4.0 Hz), 128.55, 127.80, 127.16, 126.74, 126.48, 126.03 (d, J = 7.0 Hz), 121.90, 119.53 (q, J = 322.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.75.

4'-methoxy-[1,1'-biphenyl]-3-yl trifluoromethanesulfonate **(3v)** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 7.9 Hz, 1H), 7.54−7.46 (m, 3H), 7.47−7.42 (m, 1H), 7.20 (dd, J = 8.1, 1.7 Hz, 1H), 7.00 (d, J = 8.8 Hz, 2H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.94, 150.07, 143.59, 131.46, 130.46, 128.29, 126.58, 119.45, 119.15, 118.80 (q, J = 319.0 Hz), 114.49, 55.41. ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.82.

4'-methyl-[1,1'-biphenyl]-3-yl trifluoromethanesulfonate **(3w)** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 7.8 Hz, 1H), 7.49 (m, 4H), 7.28 (d, J = 7.9 Hz, 2H), 7.23 (dd, J = 8.1, 2.0 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.05, 143.93, 138.37, 136.15, 130.46, 129.80, 127.02, 126.86, 119.75, 119.52, 118.80 (q, J = 319.0 Hz), 21.17. ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.80.

2'-methyl-[1,1'-biphenyl]-3-yl trifluoromethanesulfonate **(3x)** ^{1}H NMR (400 MHz,

$CDCl_3$) δ 7.49 (t, J = 8.0 Hz, 1H), 7.35 (d, J = 7.6 Hz, 1H), 7.31−7.23 (m, 5H), 7.20 (d, J = 7.2 Hz, 1H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.36, 144.55, 139.67, 135.27, 130.64, 129.93, 129.61, 129.27, 128.18, 126.08, 122.14, 119.64, 118.81 (q, J = 319.0 Hz), 20.29. ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.80.

[1,1'-biphenyl]-3-yl trifluoromethanesulfonate **(3y)** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 7.8 Hz, 1H), 7.59−7.55 (m, 2H), 7.53 (d, J = 8.1 Hz, 1H), 7.48 (t, J = 7.9 Hz, 3H), 7.41 (t, J = 7.2 Hz, 1H), 7.26 (d, J = 4.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.03, 143.99, 139.03, 130.53, 129.09, 128.38, 127.20, 127.10, 120.00, 119.85, 118.80 (q, J = 319.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.78.

4'-methoxy-[1,1'-biphenyl]-2-yl trifluoromethanesulfonate **(3z)** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46−7.41 (m, 2H), 7.42−7.35 (m, 4H), 6.99 (d, J = 8.7 Hz, 2H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.67, 146.94, 135.26, 131.94, 130.59, 128.54, 127.92, 122.09, 119.97, 118.38 (q, J = 318.0 Hz), 113.98, 55.32. ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.04.

2'-methoxy-[1,1'-biphenyl]-2-yl trifluoromethanesulfonate **(4a)** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47−7.38 (m, 4H), 7.34 (ddd, J = 7.8, 4.8, 2.6 Hz, 1H), 7.24 (dd, J = 7.5, 1.6 Hz, 1H), 7.07−6.97 (m, 2H), 3.79 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.27, 148.45, 133.17, 131.98, 130.80, 130.11, 129.67, 128.77, 125.28, 121.83, 121.22, 119.04 (q, J = 318.0 Hz), 111.46, 56.05. ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.61.

4'-methoxy-5-methyl-[1,1'-biphenyl]-2-yl trifluoromethanesulfonate **(4b)** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 8.8 Hz, 2H), 7.24 (t, J = 6.5 Hz, 2H), 7.16 (dd, J = 8.4, 1.6 Hz, 1H), 6.97 (d, J = 8.8 Hz, 2H), 3.85 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.61, 144.90, 138.55, 134.84, 132.40, 130.53, 129.01, 128.12, 121.76, 118.40 (q, J = 318.0 Hz), 113.94, 55.30, 20.94. ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.82.

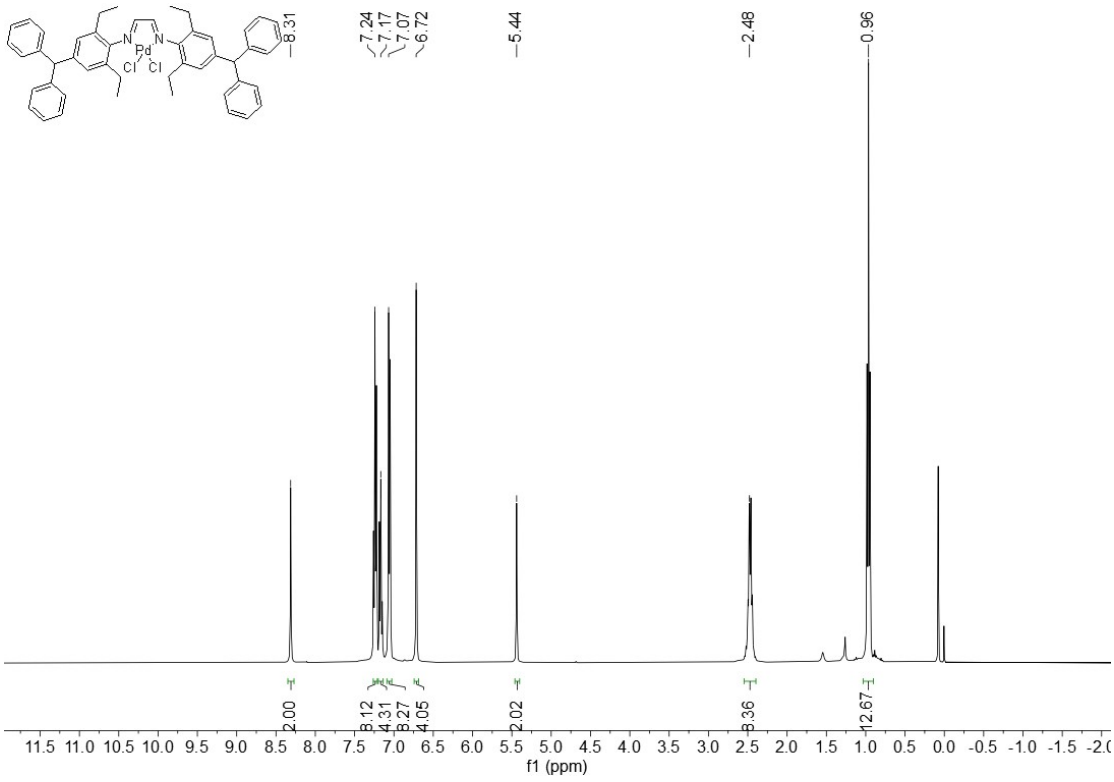
3-(4'-methyl-[1,1'-biphenyl]-4-yl)thiophene (**5a**) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (q, J = 8.4 Hz, 4H), 7.52 (d, J = 8.1 Hz, 2H), 7.49−7.46 (m, 1H), 7.44−7.37 (m, 2H), 7.24 (s, 2H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.64, 140.52, 138.46, 137.82, 135.21, 130.22, 127.97, 127.47, 126.97, 126.95, 120.86, 100.66, 21.81. HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{17}H_{15}S$, 251.0894; found, 251.0889.

2-(4'-methyl-[1,1'-biphenyl]-4-yl)benzofuran (**5b**) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.8 Hz, 2H), 7.61 (d, J = 7.6 Hz, 2H), 7.53 (m, 1H), 7.48 (m, 3H), 7.18 (m, 4H),

6.98 (s, 1H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.45, 155.59, 141.85, 138.20, 138.14, 130.28, 129.97, 129.77, 127.91, 127.49, 125.99, 124.93, 123.63, 121.55, 111.85, 101.96, 21.84.

4-fluoro-4''-methyl-1,1':4',1''-terphenyl (**5c**) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (m, 8H), 7.20 (m, 2H), 7.06 (m, 2H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.50 (d, J = 244.0 Hz), 140.09, 138.86, 137.71, 137.26, 136.91, 129.60, 128.54, 127.38, 127.35, 115.81, 115.60, 21.18. HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{19}H_{16}F_2$, 263.1236; found, 263.1238.

5. NMR spectrums of the catalysts and reaction products



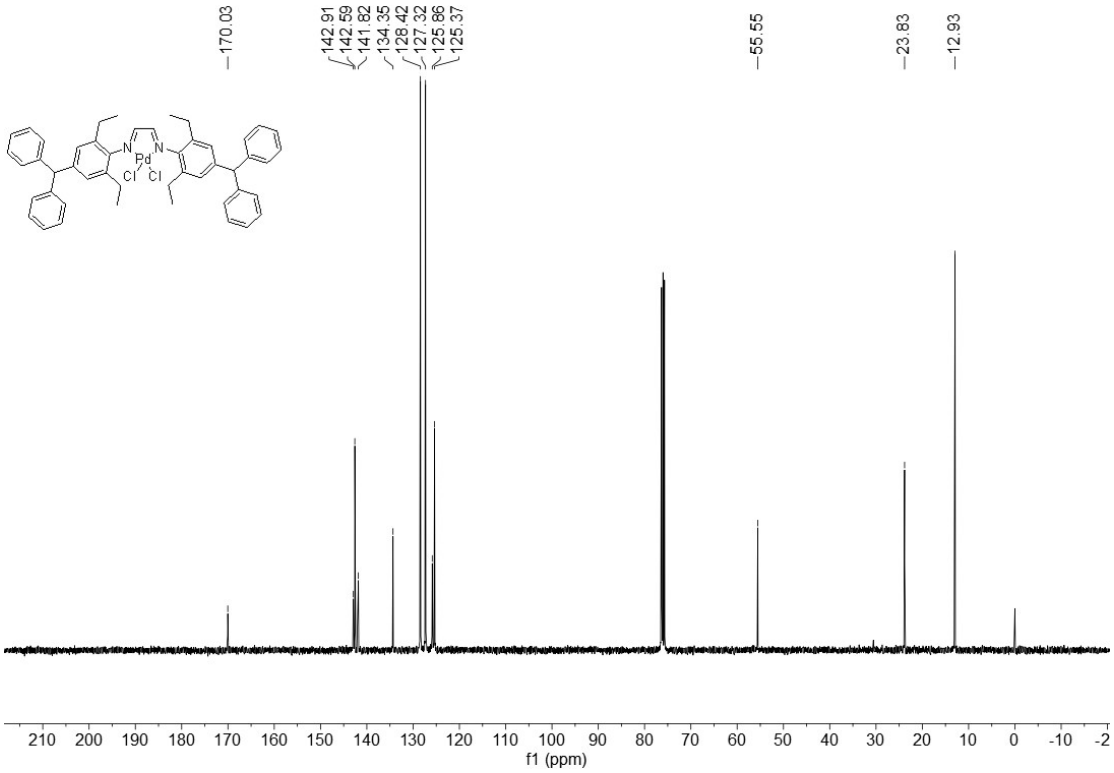
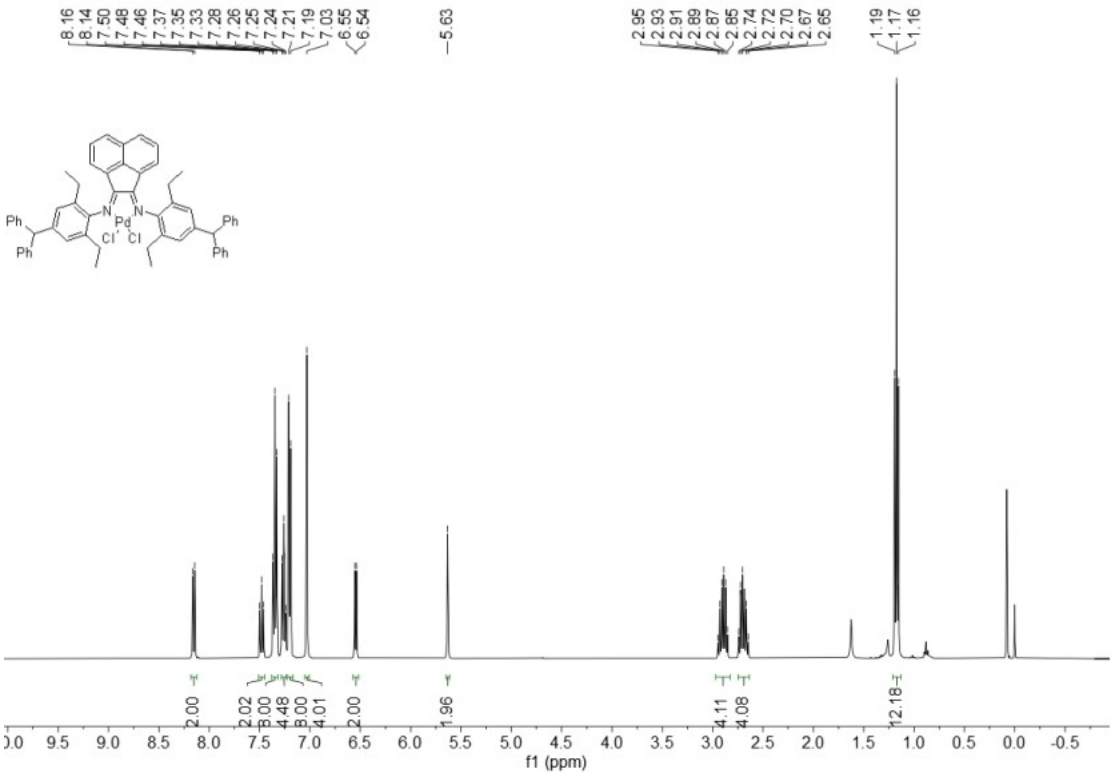


Figure S1. The NMR spectrums of **C1**



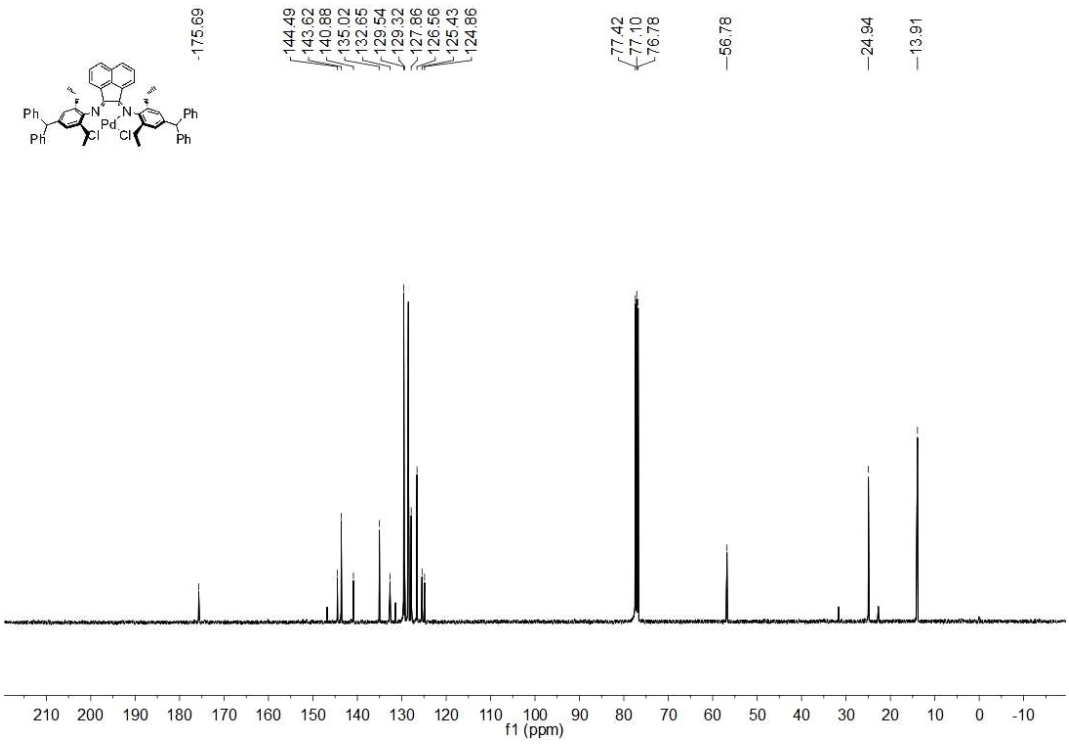
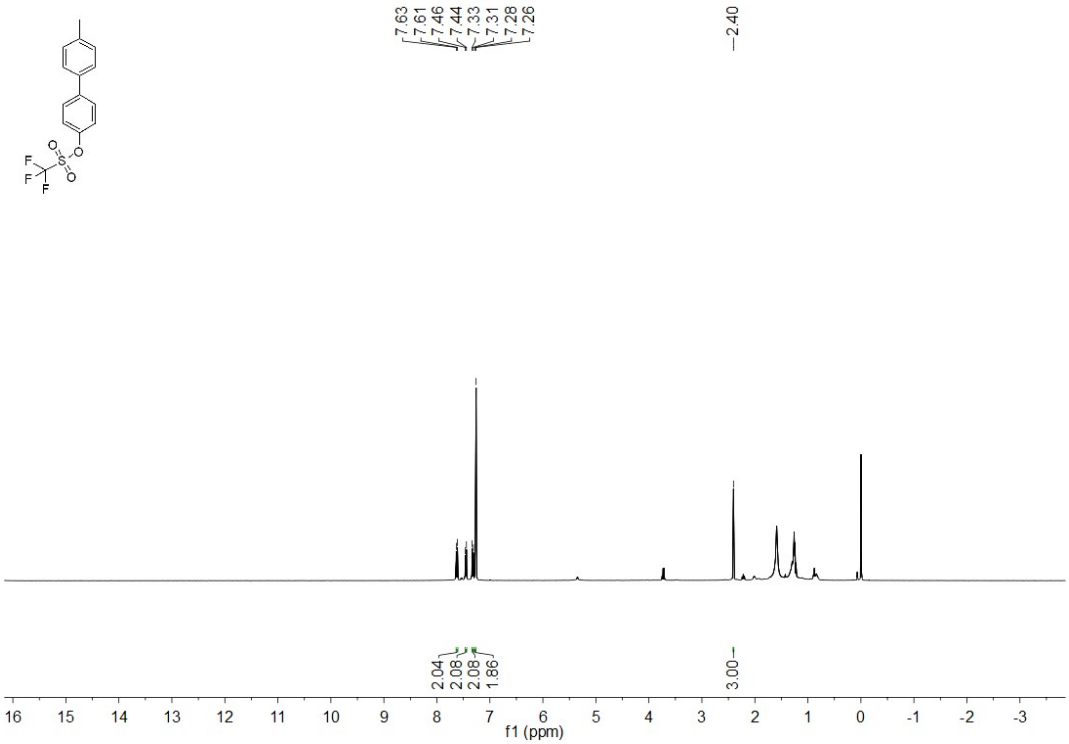
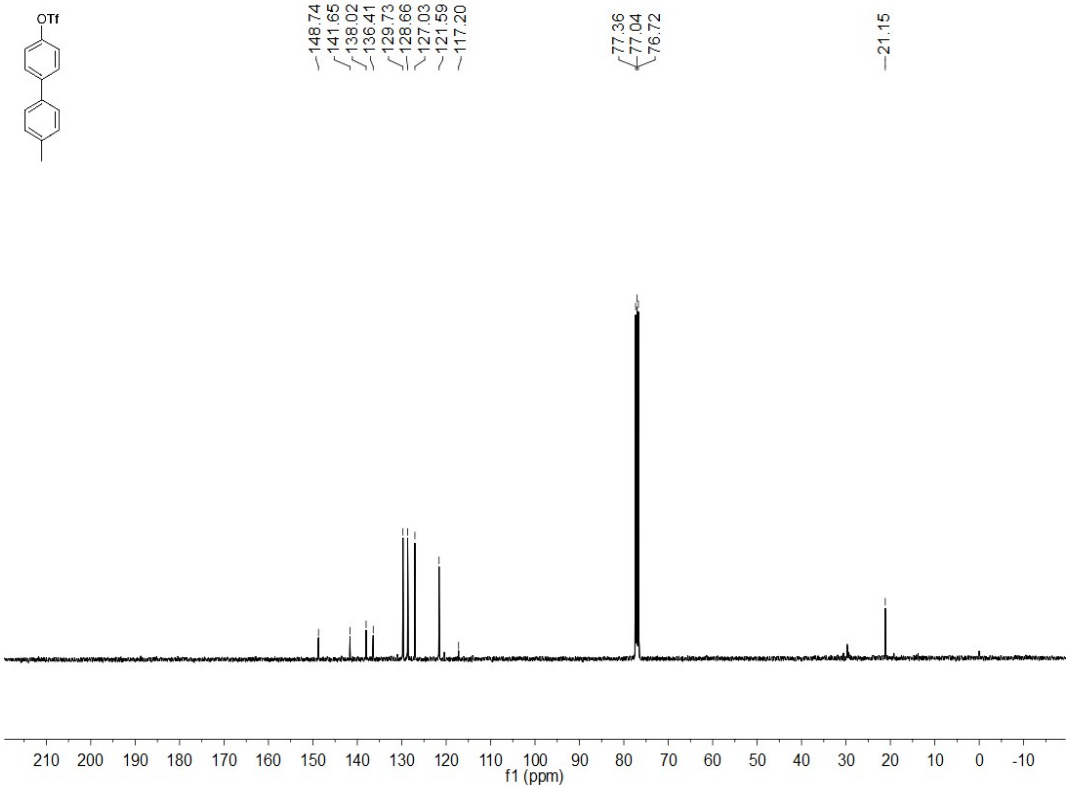


Figure S2. The NMR spectrums of **C2**


7.63
7.61
7.46
7.44
7.33
7.31
7.28
7.26
2.40
2.04
2.08
2.08
1.86
3.00
f1 (ppm)


OTf
148.74
141.65
138.02
136.41
129.73
128.66
127.03
121.59
117.20
77.36
77.04
76.72
21.15
f1 (ppm)

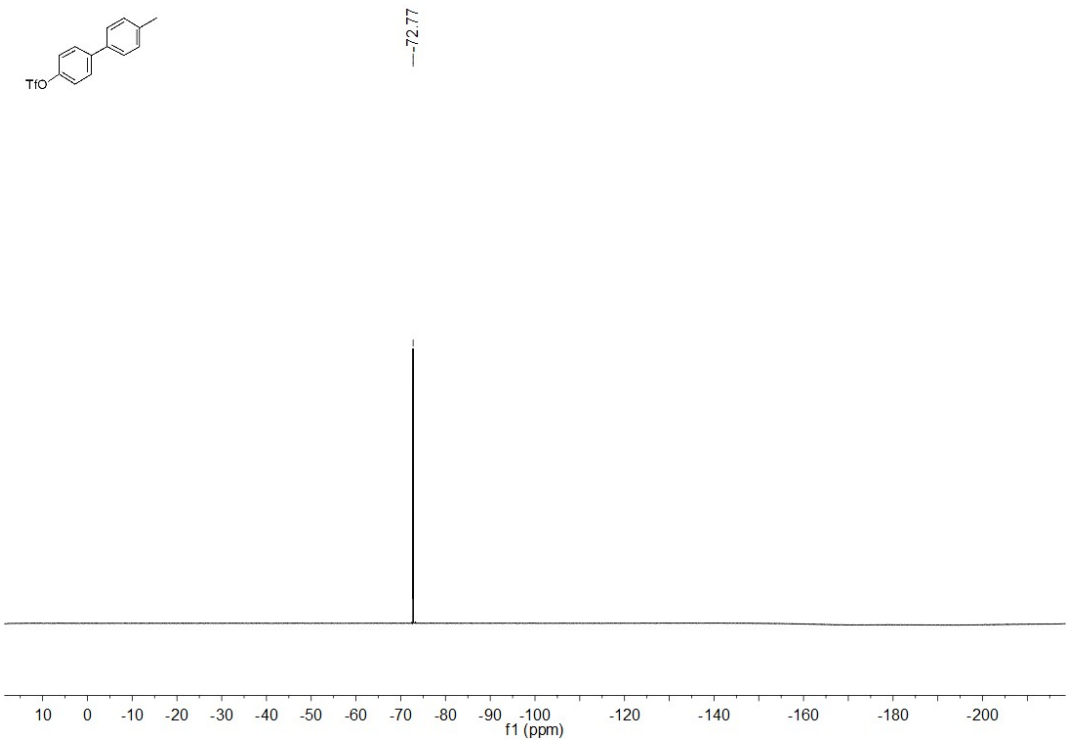
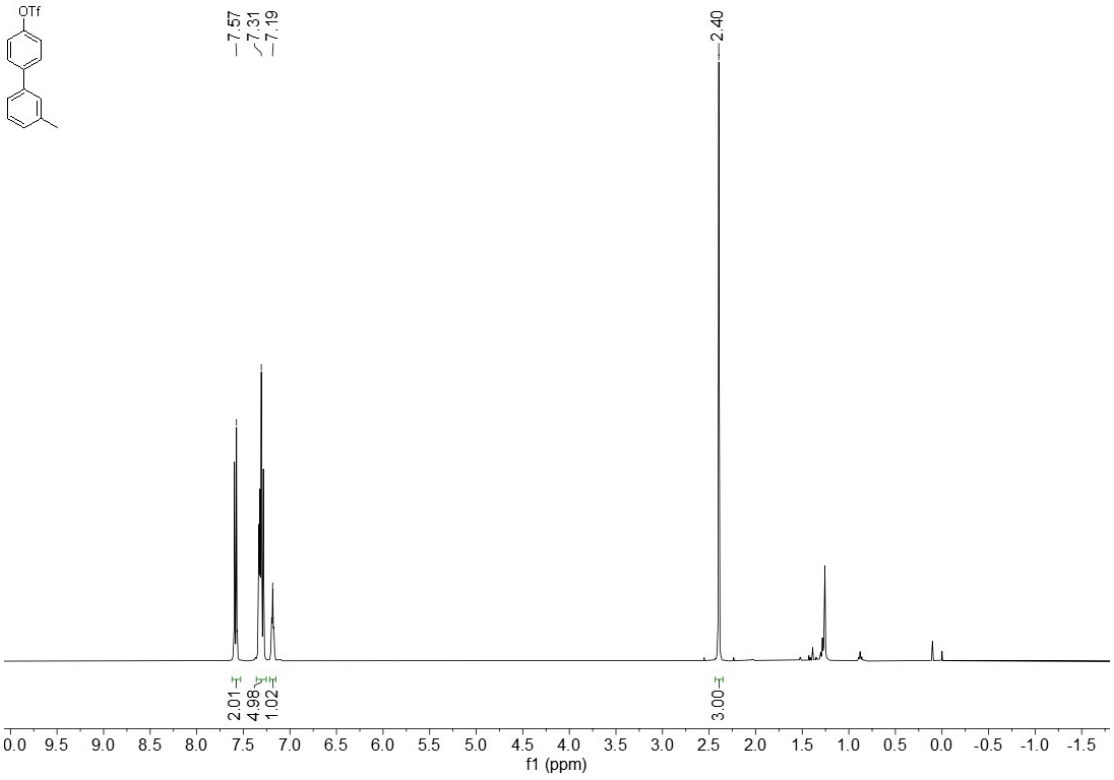
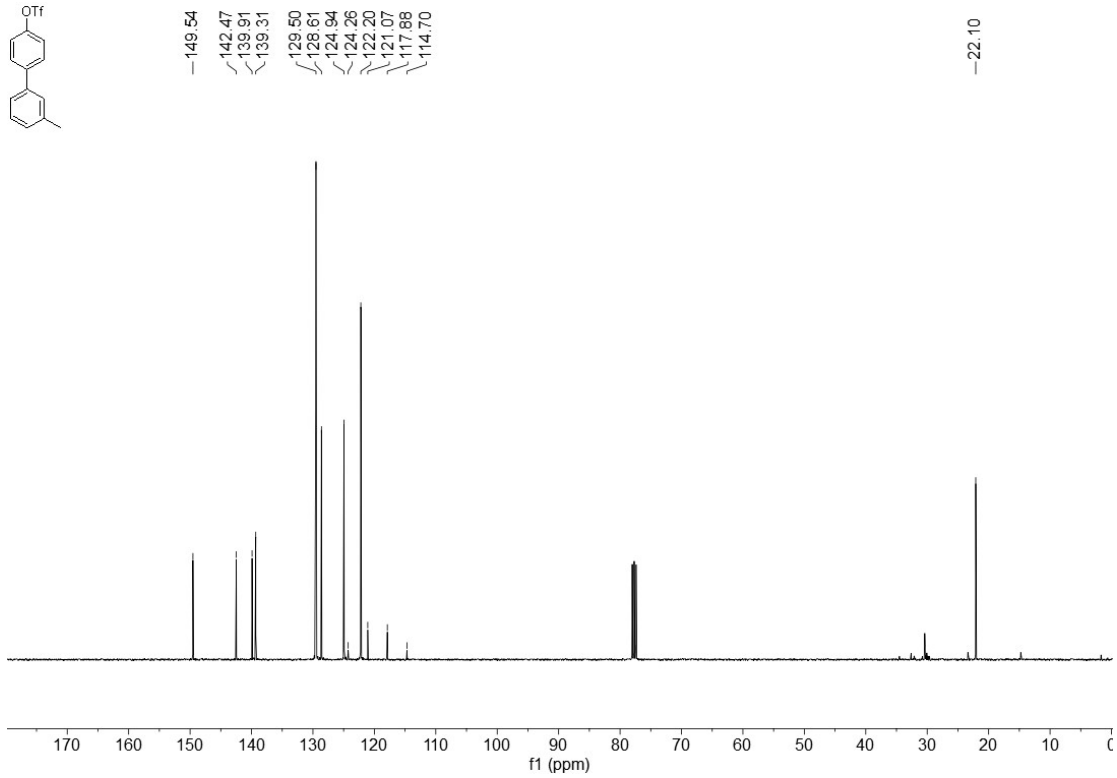


Figure S3. The NMR spectrums of **3a**





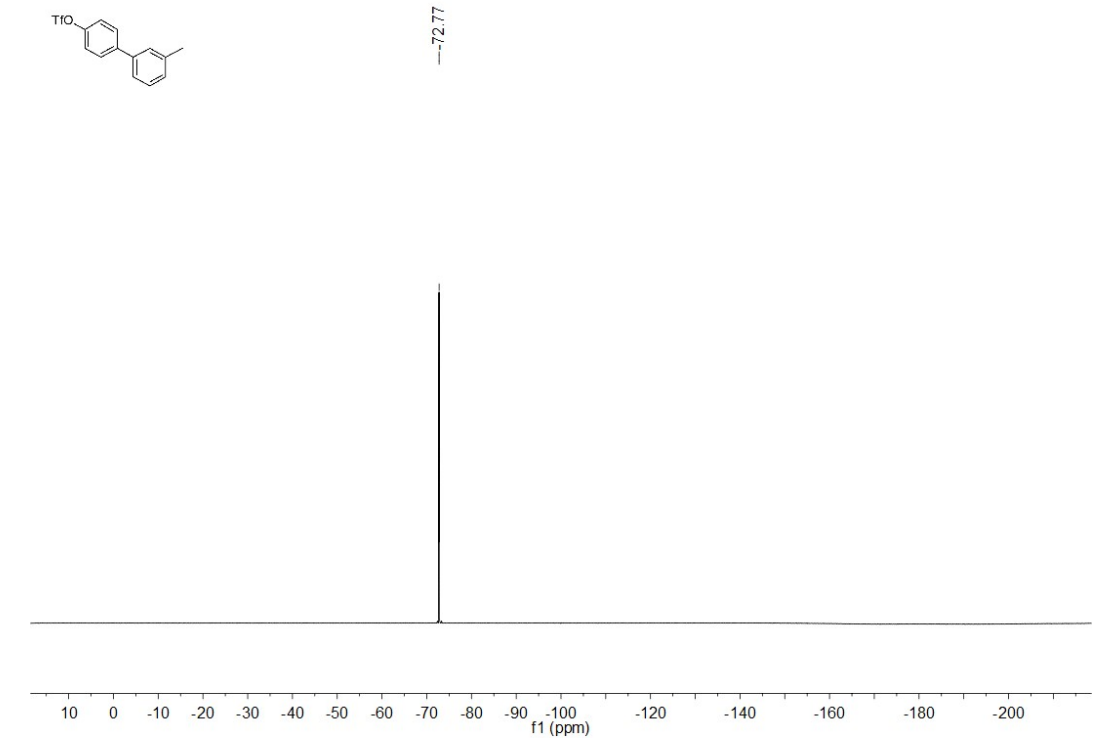
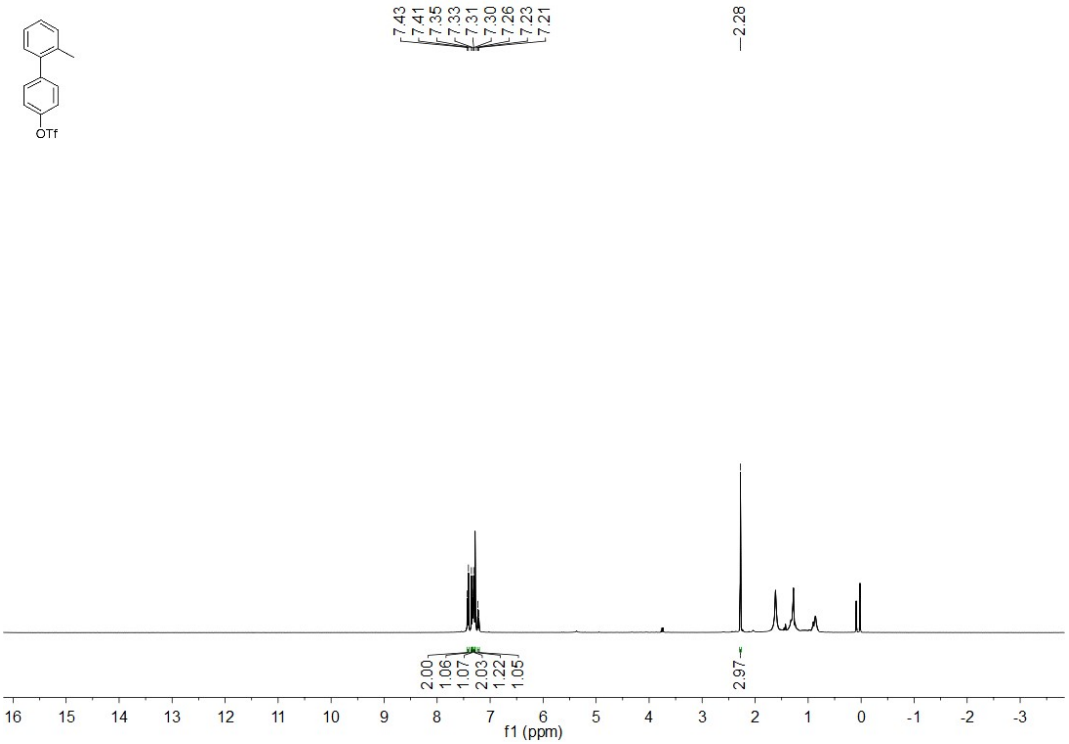
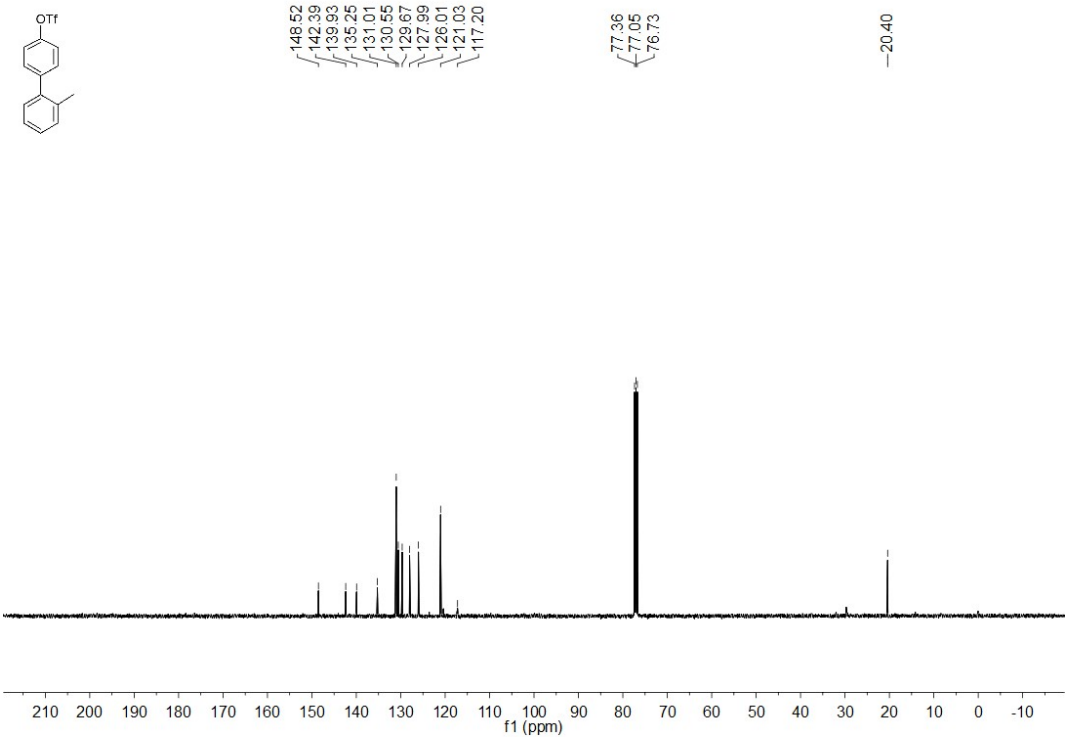


Figure S4. The NMR spectrums of **3b**


OTf
7.43
7.41
7.35
7.33
7.31
7.30
7.26
7.23
7.21
2.28
2.00
1.06
1.07
2.03
1.22
1.05
2.97
f1 (ppm)


OTf
148.52
142.39
139.93
135.25
131.01
130.55
129.67
127.99
126.01
121.03
117.20
77.36
77.05
76.73
20.40
f1 (ppm)

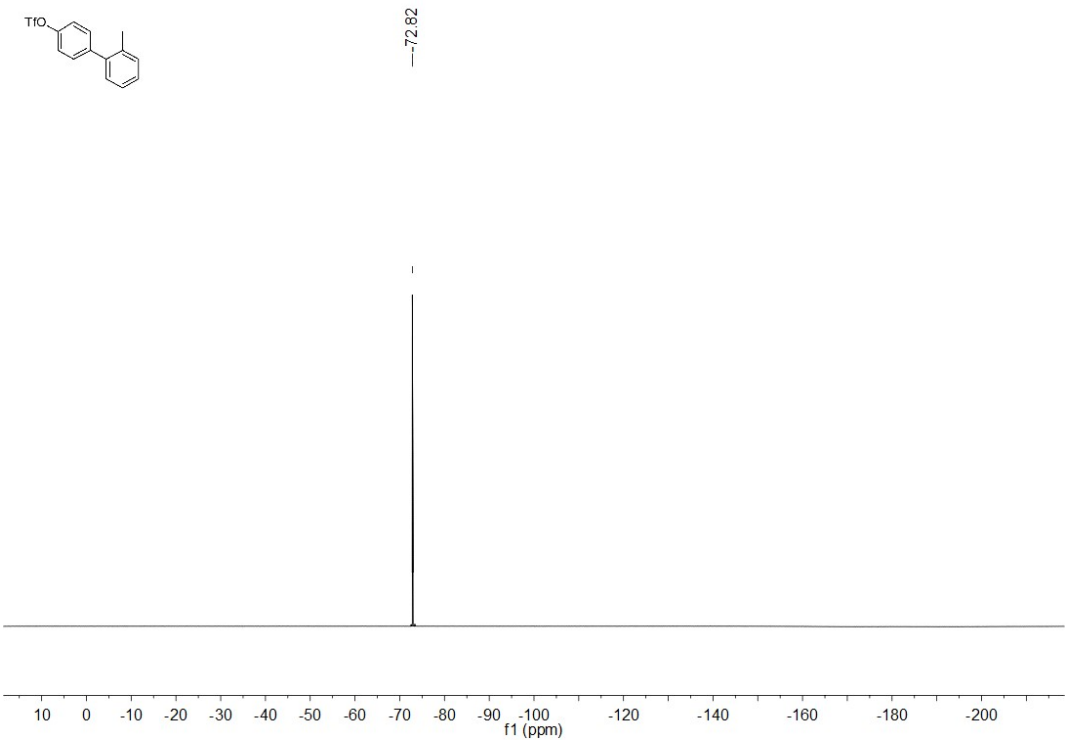
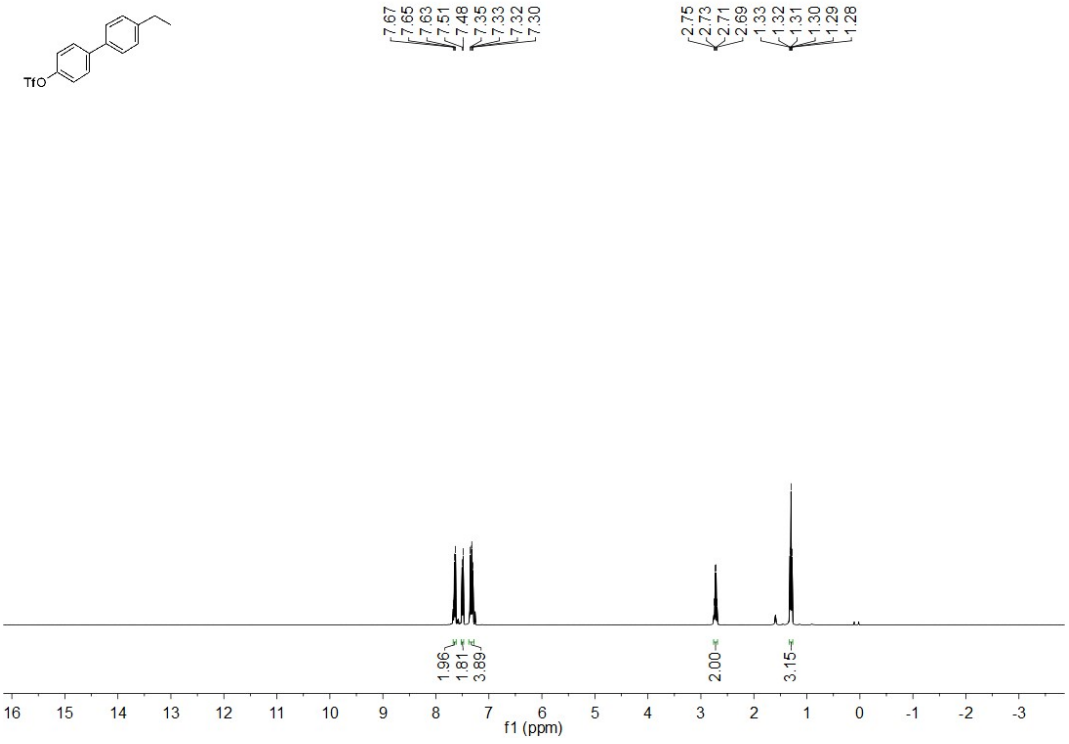
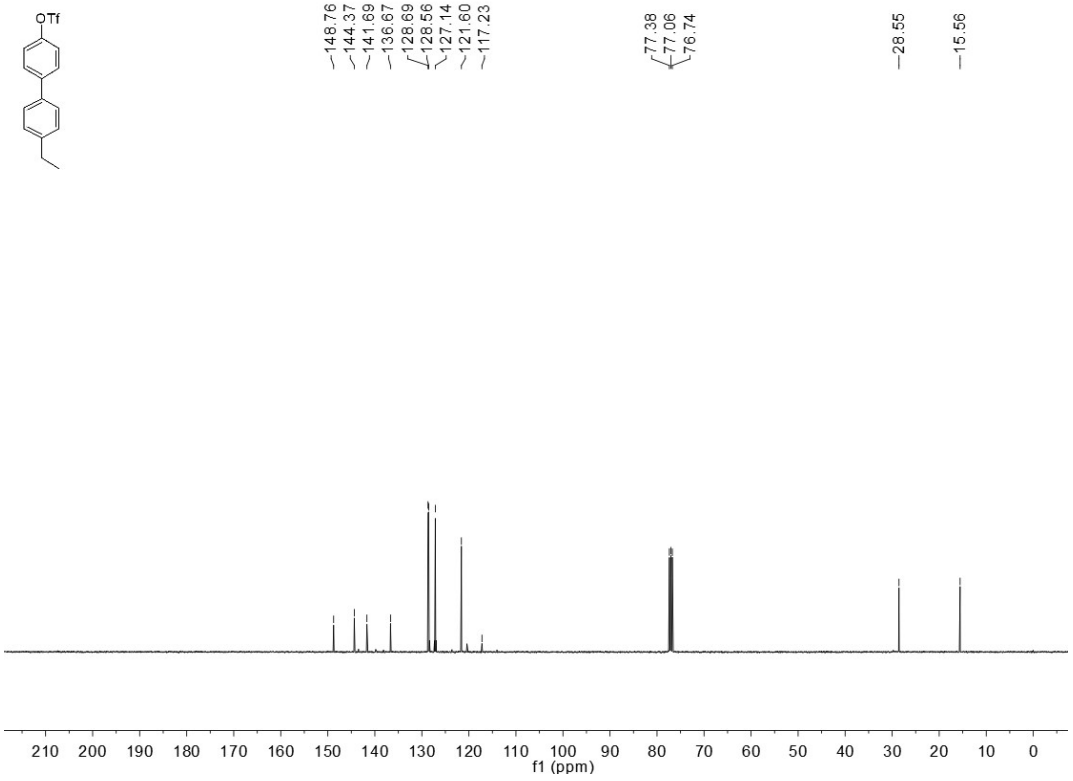


Figure S5. The NMR spectrums of **3c**





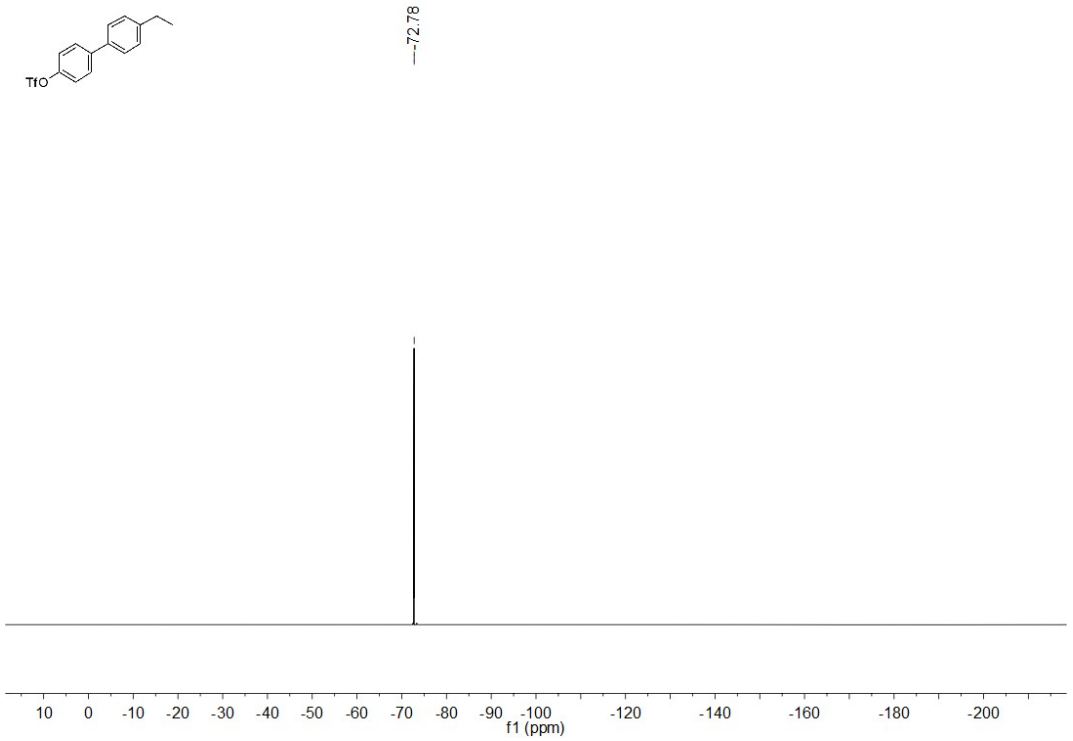
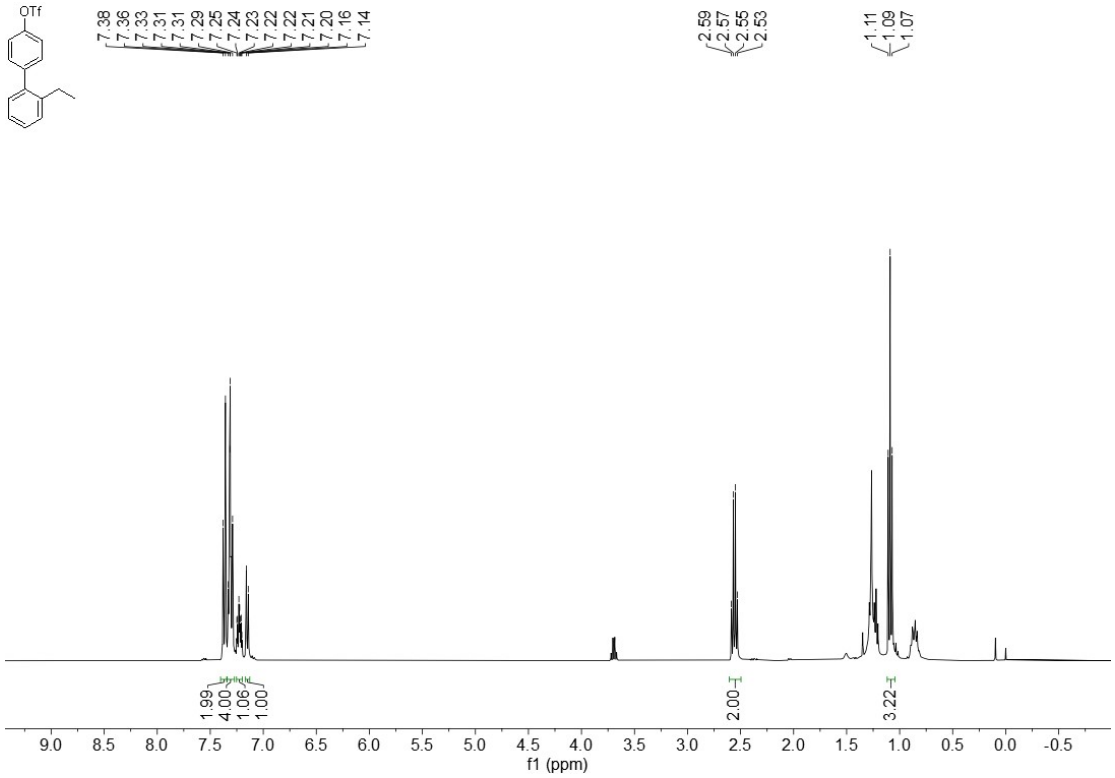
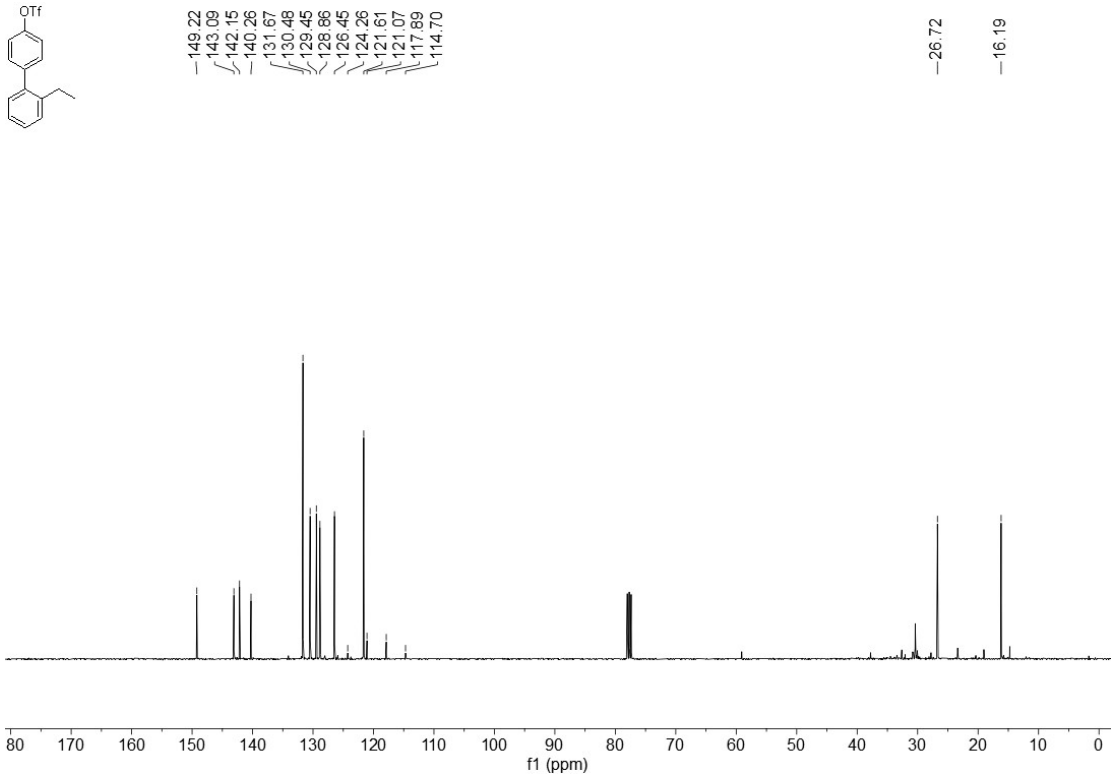


Figure S6. The NMR spectrums of **3d**


OTf
7.38
7.36
7.33
7.31
7.31
7.29
7.25
7.24
7.23
7.22
7.22
7.21
7.20
7.16
7.14
2.59
2.57
2.55
2.53
1.11
1.09
1.07
1.99
4.00
1.06
1.00
2.00
3.22
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


OTf
149.22
143.09
142.15
140.26
131.67
130.48
129.45
128.86
126.45
124.26
121.61
121.07
117.89
114.70
26.72
16.19
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

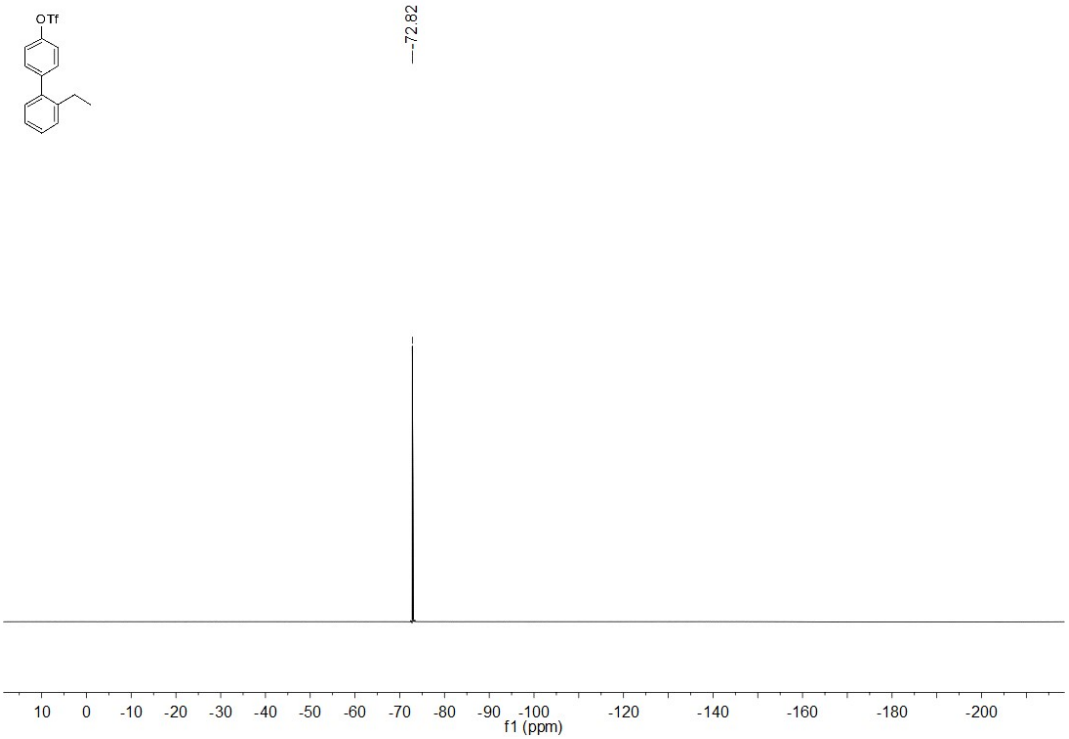
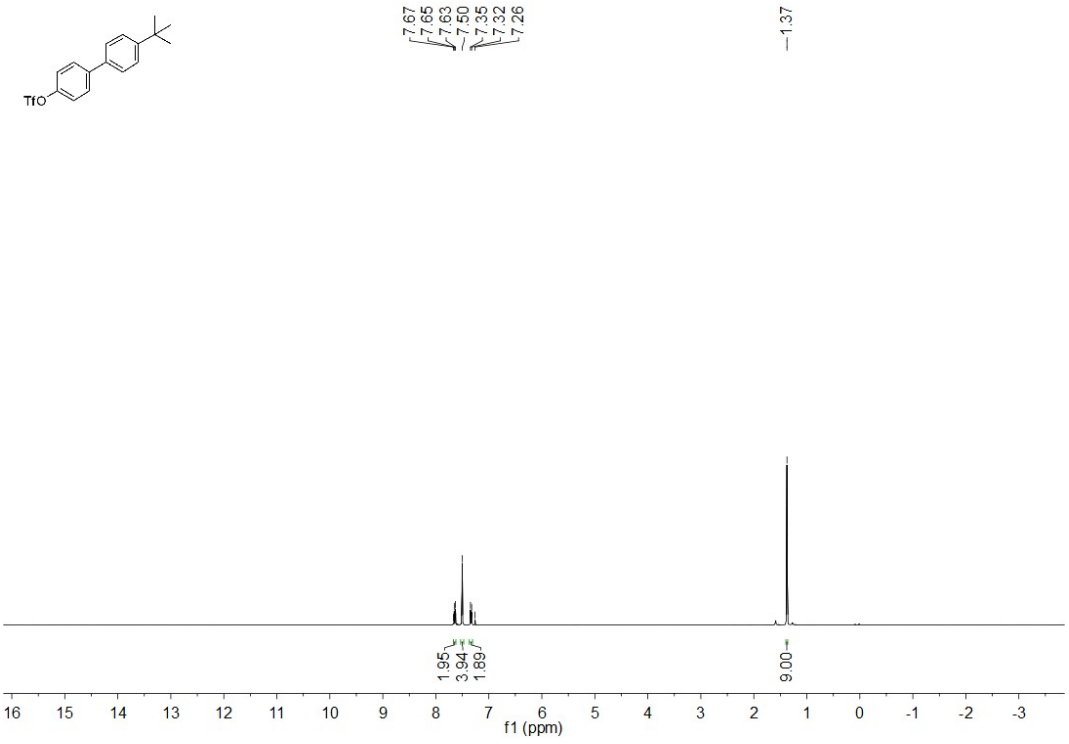
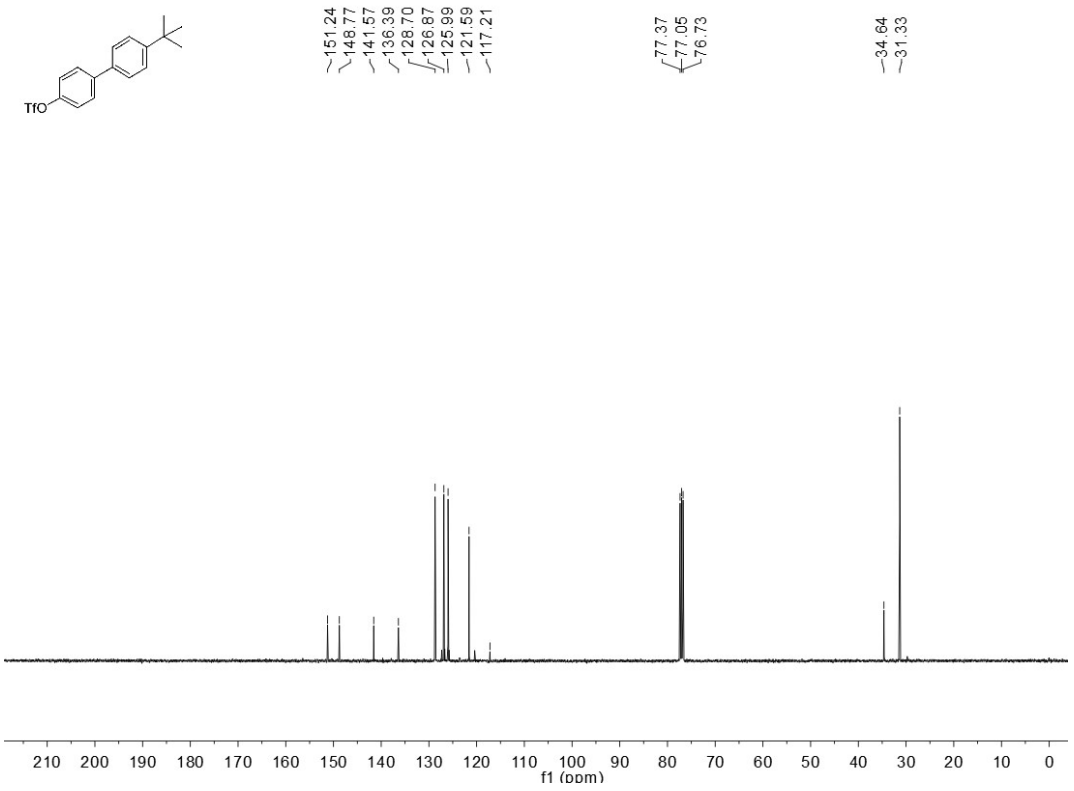


Figure S7. The NMR spectrums of **3e**





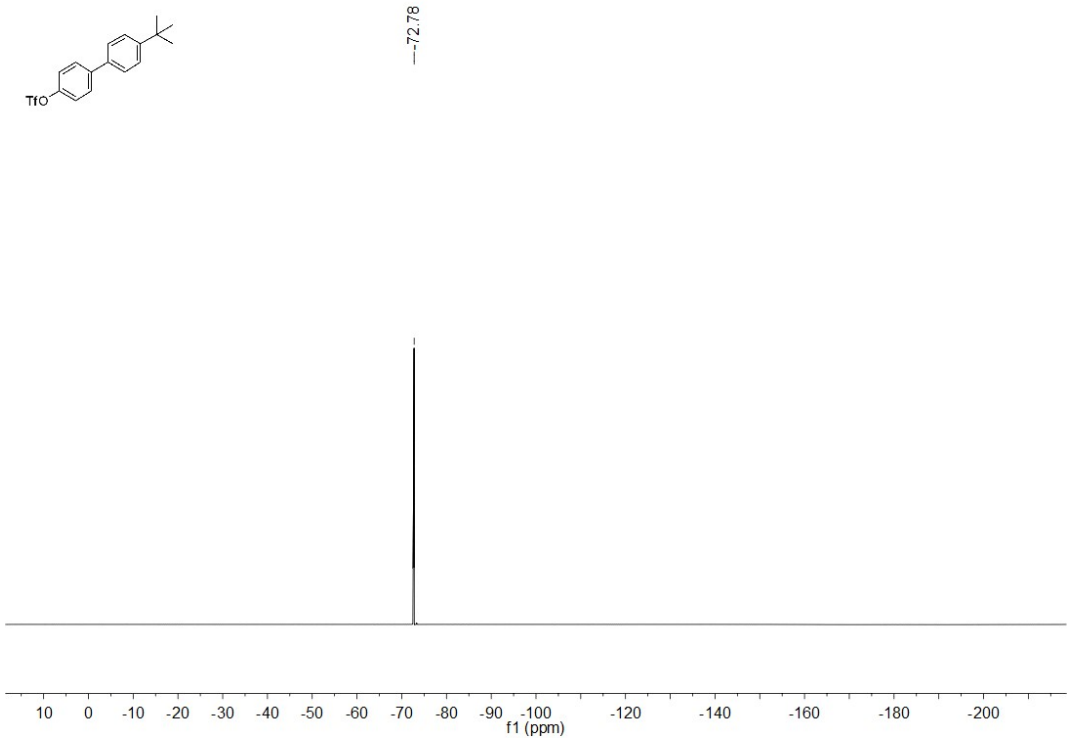
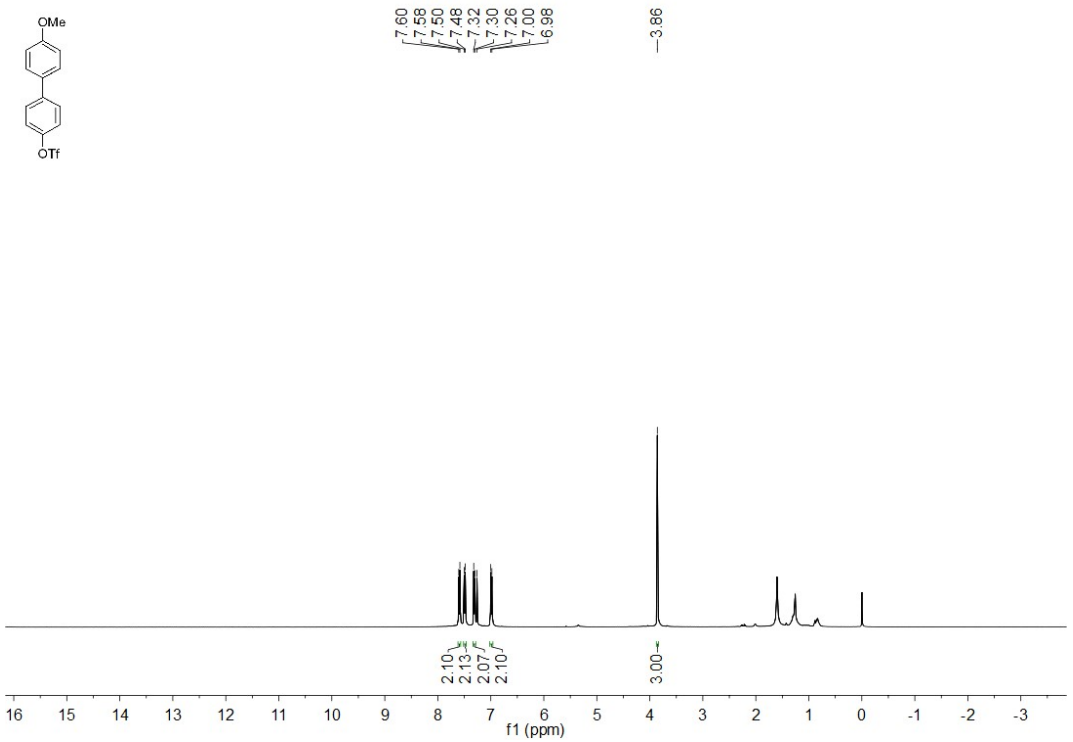


Figure S8. The NMR spectrums of **3f**


OMe
OTf
7.60
7.58
7.50
7.48
7.32
7.30
7.26
7.00
6.98
3.86
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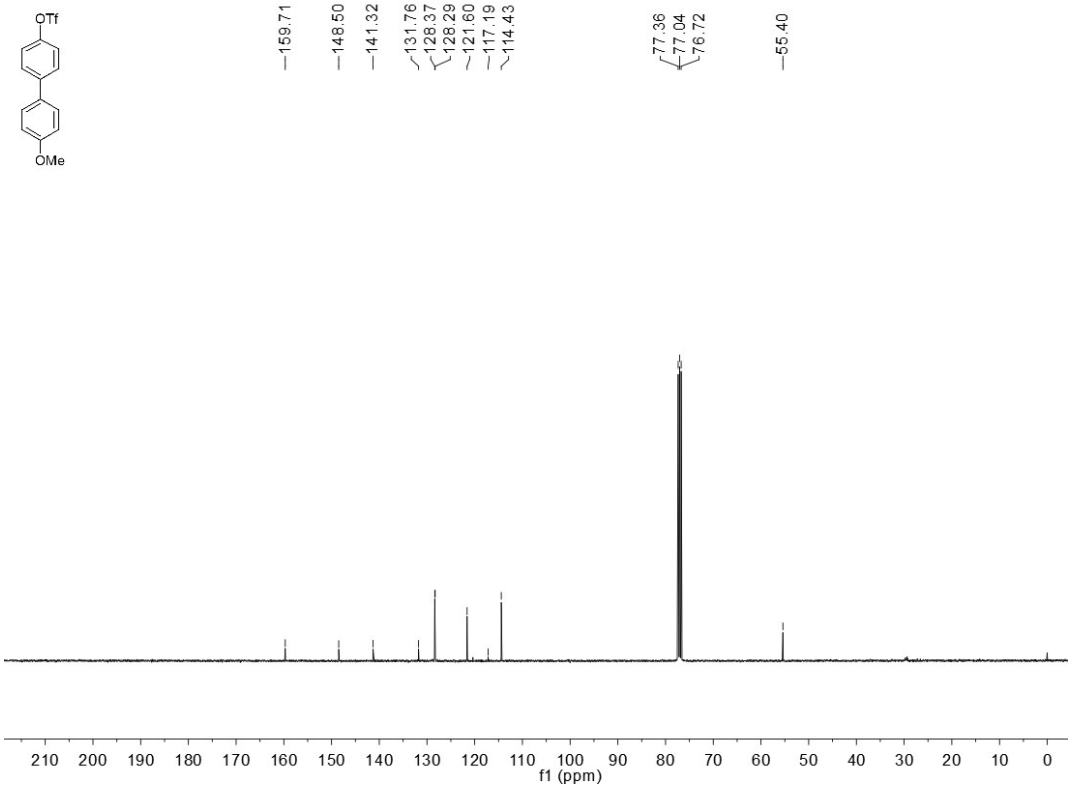
2.13
2.07
2.10
3.00
f1 (ppm)


OTf
OMe
159.71
148.50
141.32
131.76
128.37
128.29
121.60
117.19
114.43
77.36
77.04
76.72
55.40
f1 (ppm)

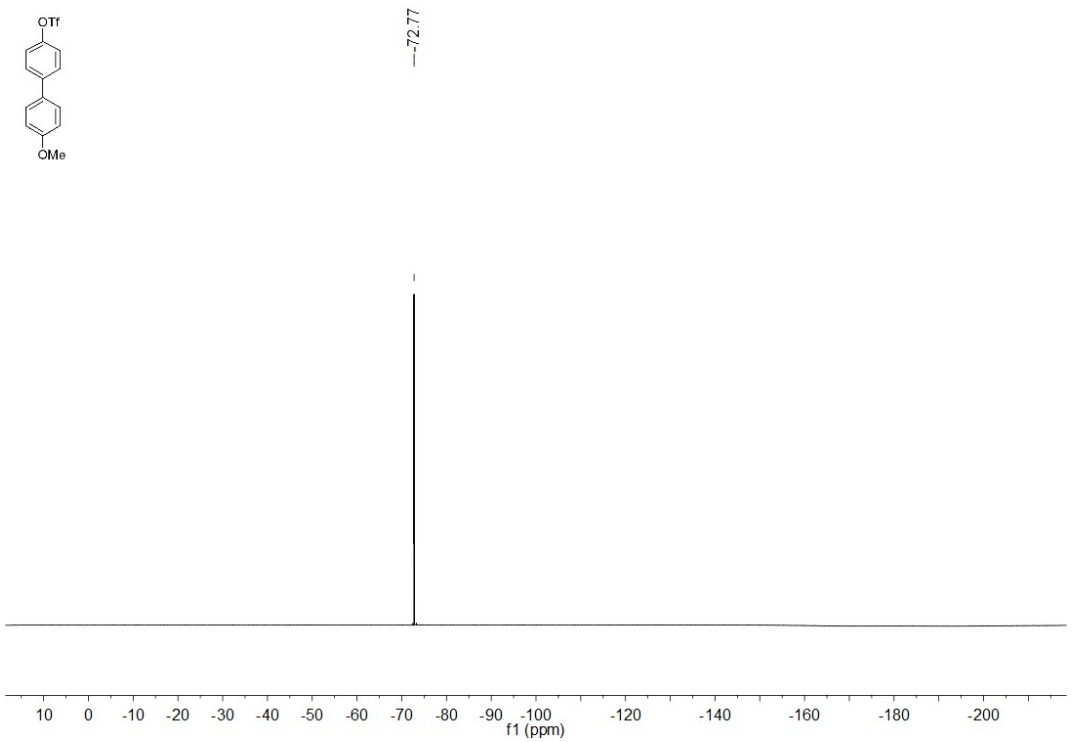
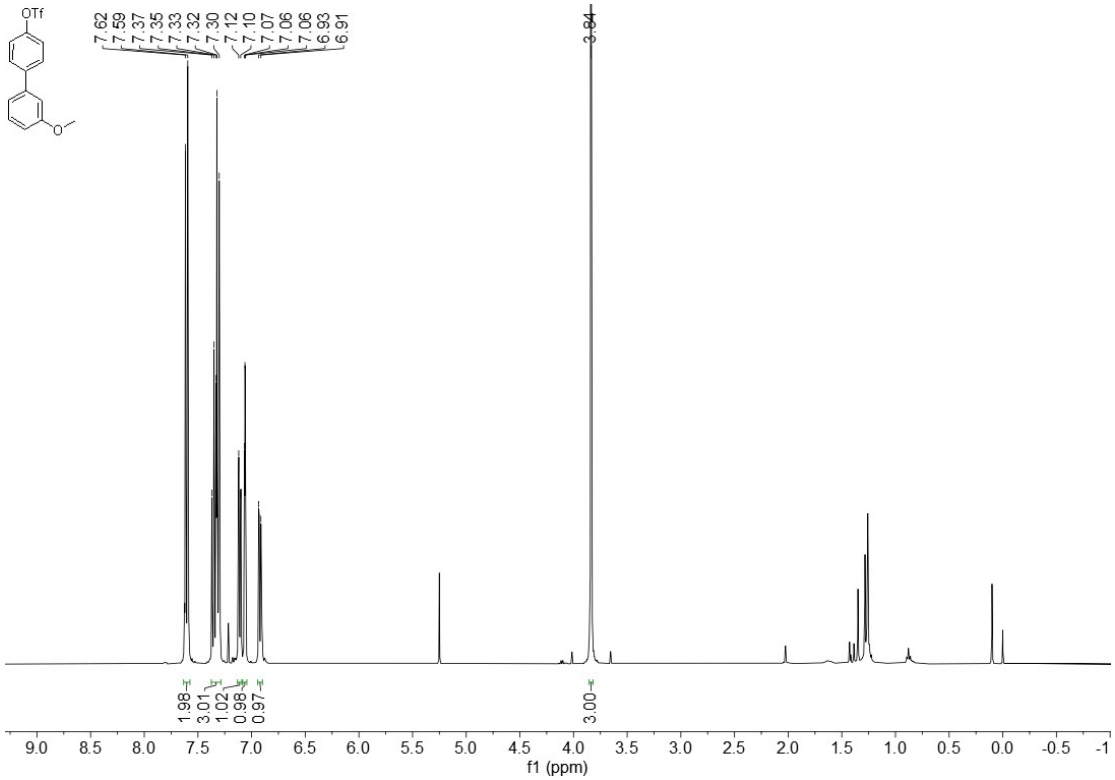
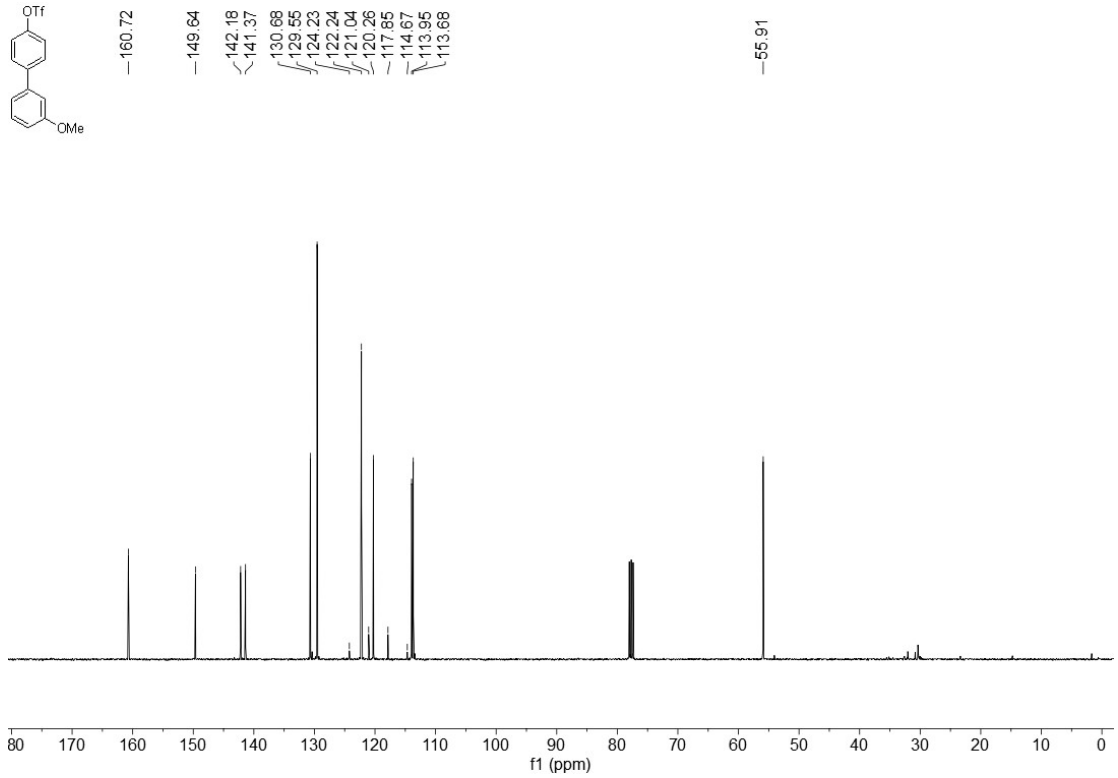


Figure S9. The NMR spectrums of **3g**





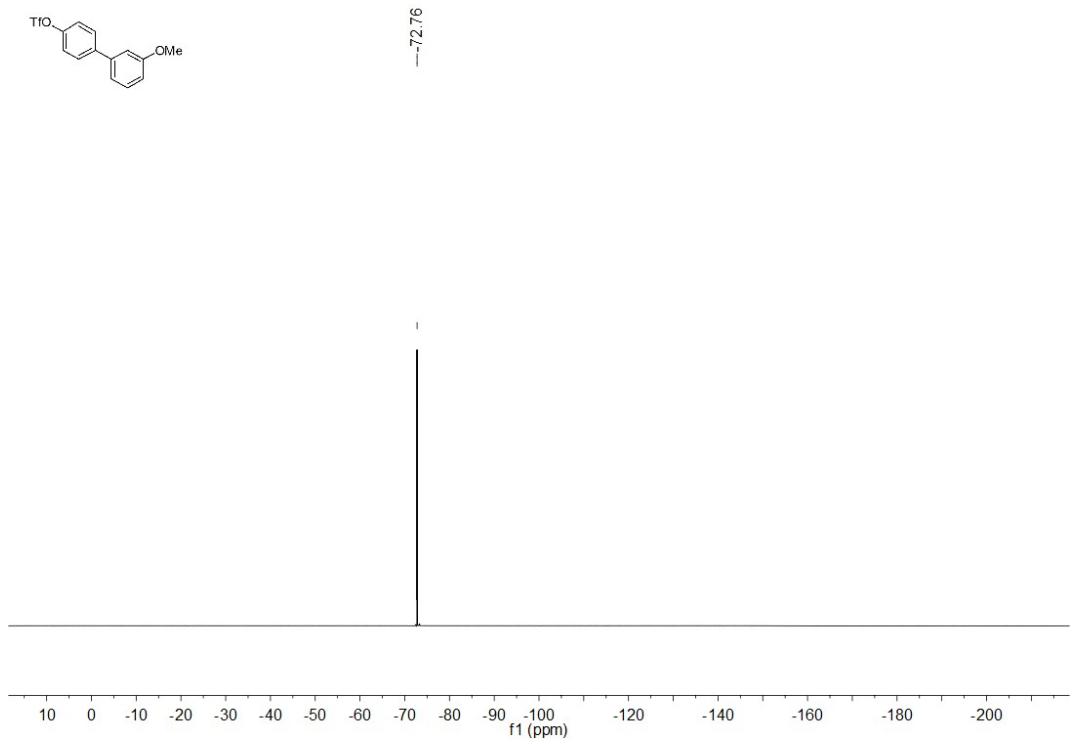
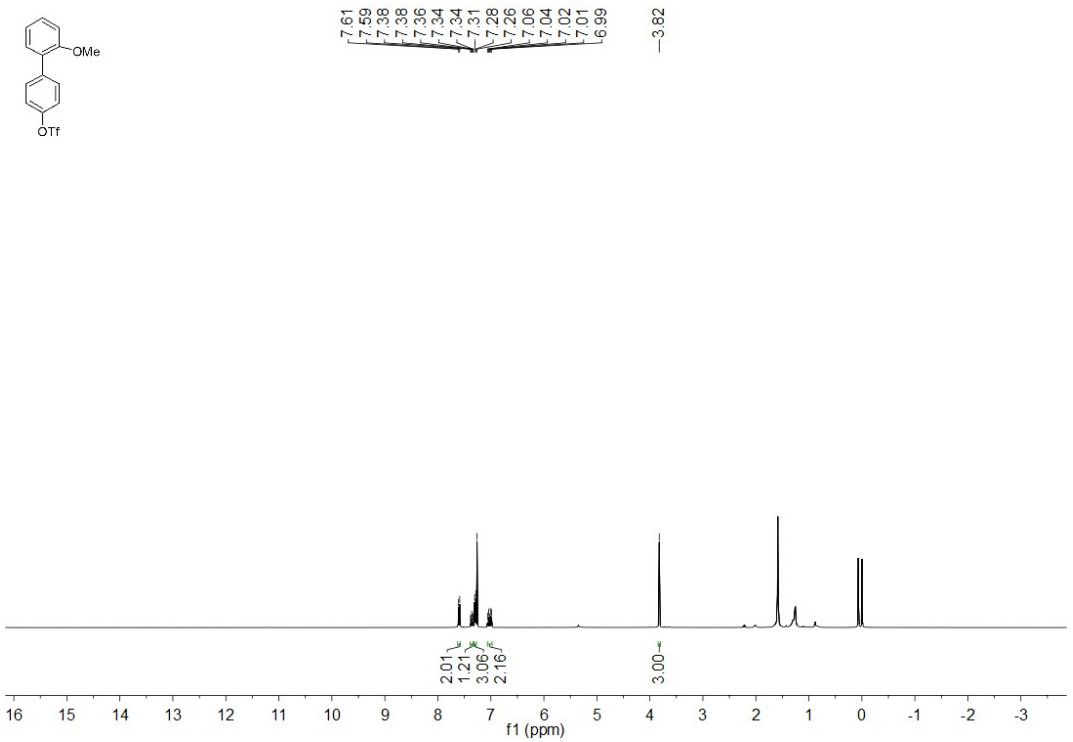


Figure S10. The NMR spectrums of **3h**


OMe
OTf
7.61
7.59
7.38
7.38
7.36
7.34
7.34
7.31
7.28
7.26
7.06
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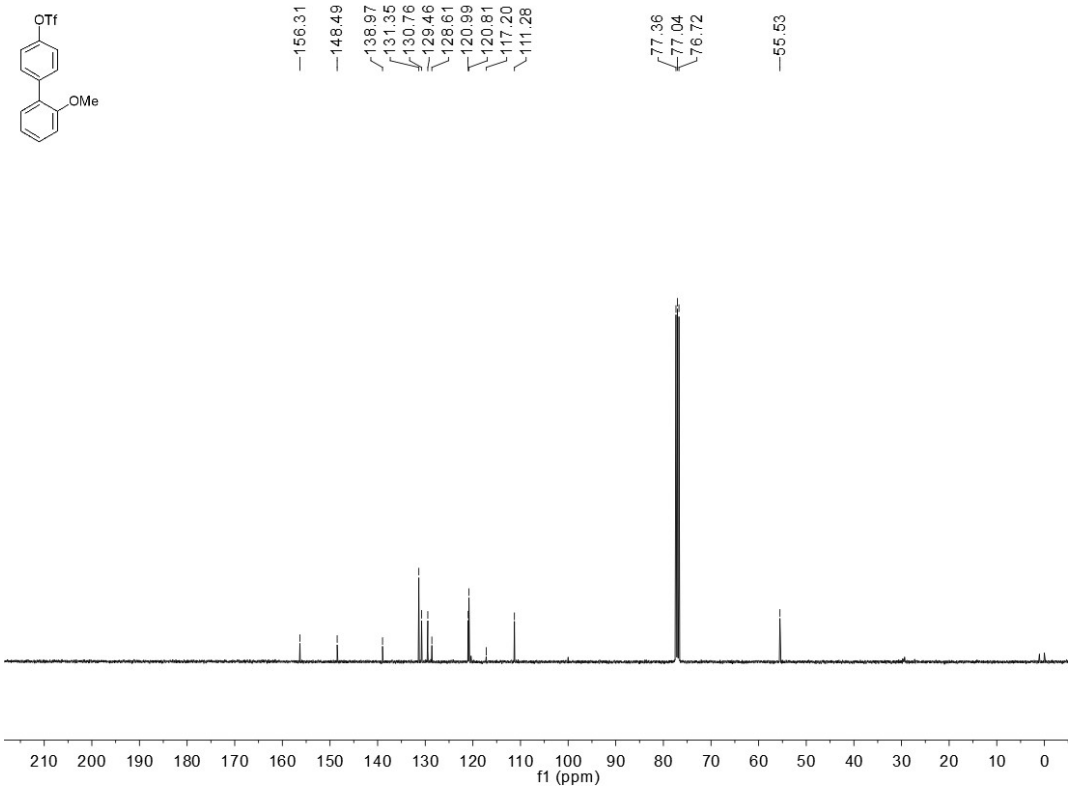
3.82
2.01
1.21
3.06
2.16
3.00
f1 (ppm)


OTf
OMe
156.31
148.49
138.97
131.35
130.76
129.46
128.61
120.99
120.81
117.20
111.28
77.36
77.04
76.72
55.53
f1 (ppm)

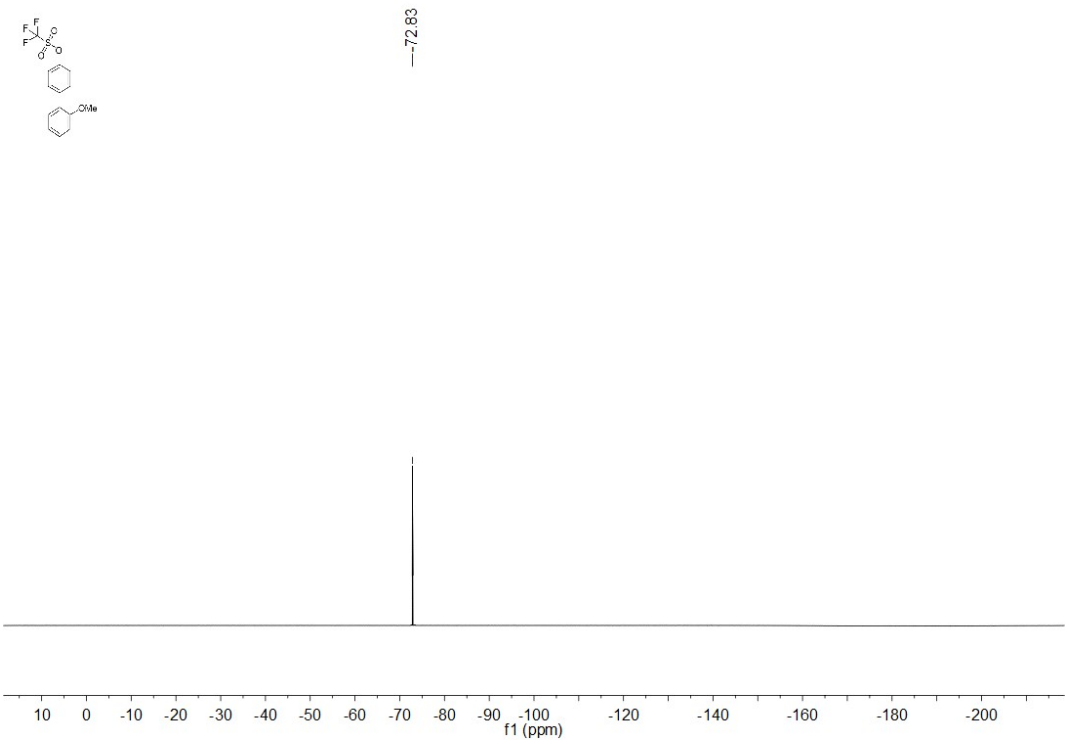
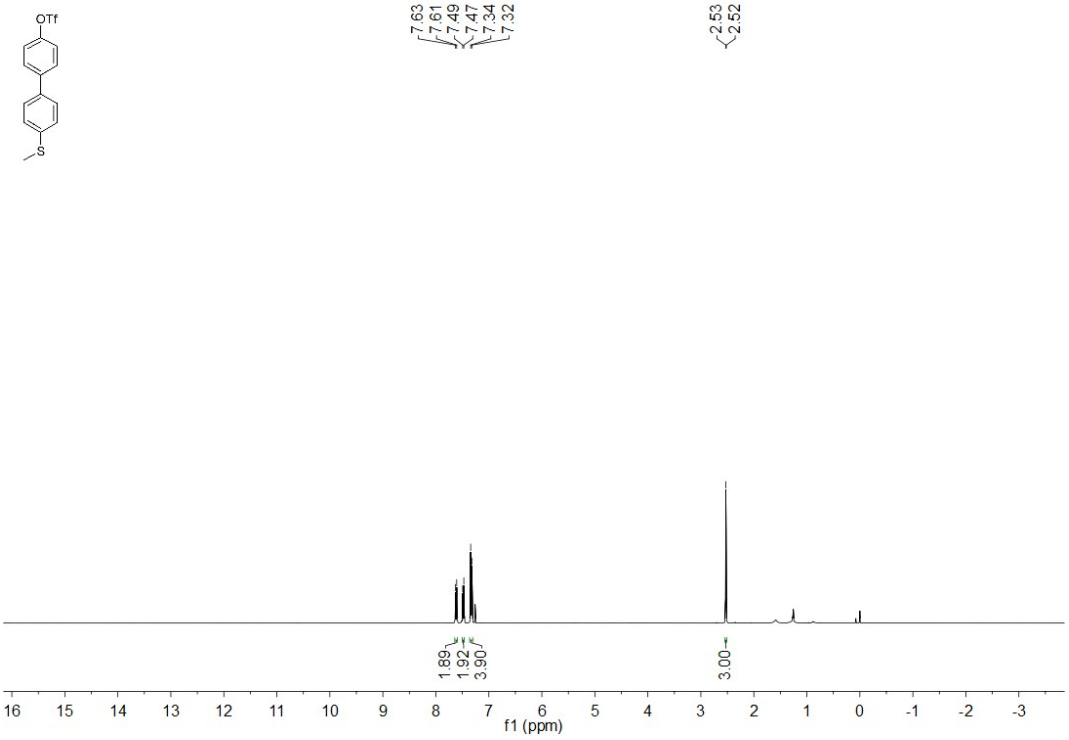
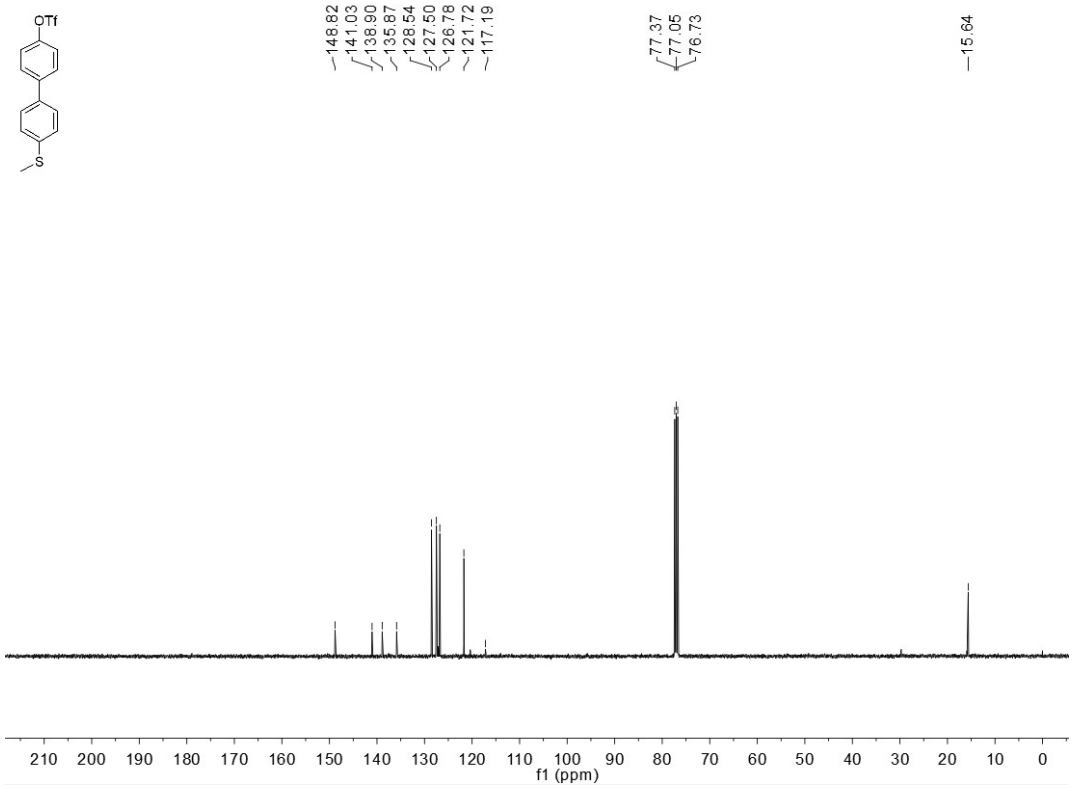


Figure S11. The NMR spectrums of **3i**





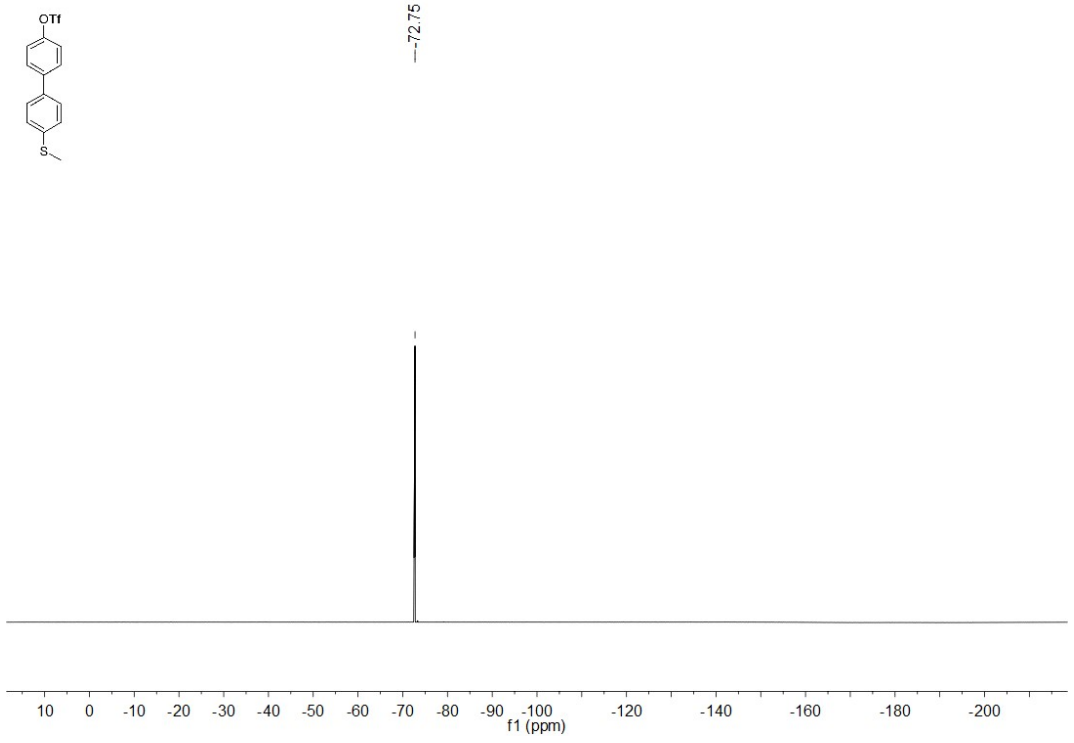
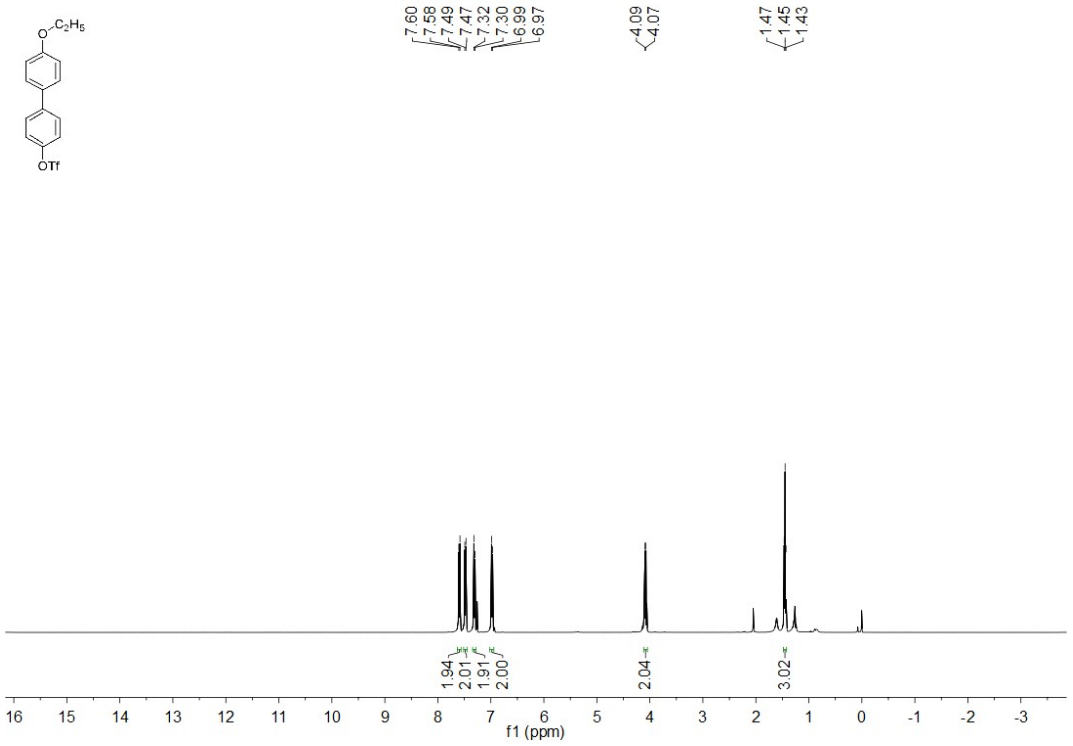


Figure S12. The NMR spectrums of **3j**


7.60
7.58
7.49
7.47
7.32
7.30
6.99
6.97
4.09
4.07
1.47
1.45
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1.94
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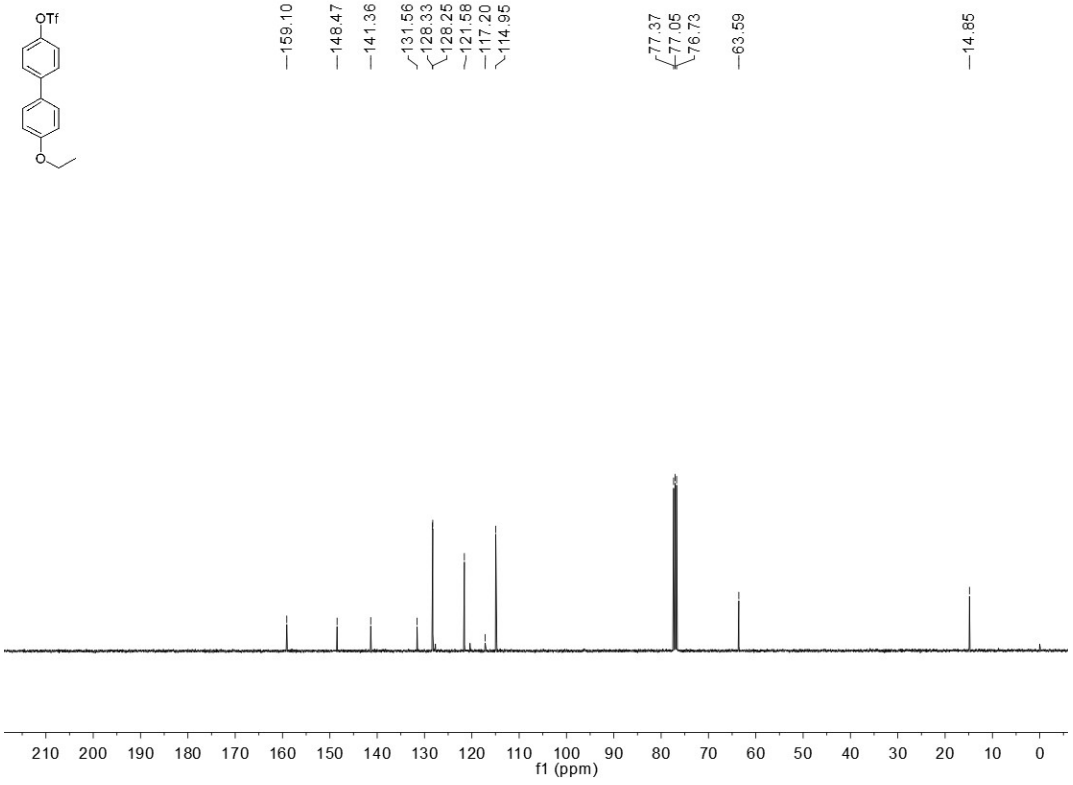
1.91
2.00
2.04
3.02
f1 (ppm)


159.10
148.47
141.36
131.56
128.33
128.25
121.58
117.20
114.95
77.37
77.05
76.73
63.59
14.85
f1 (ppm)

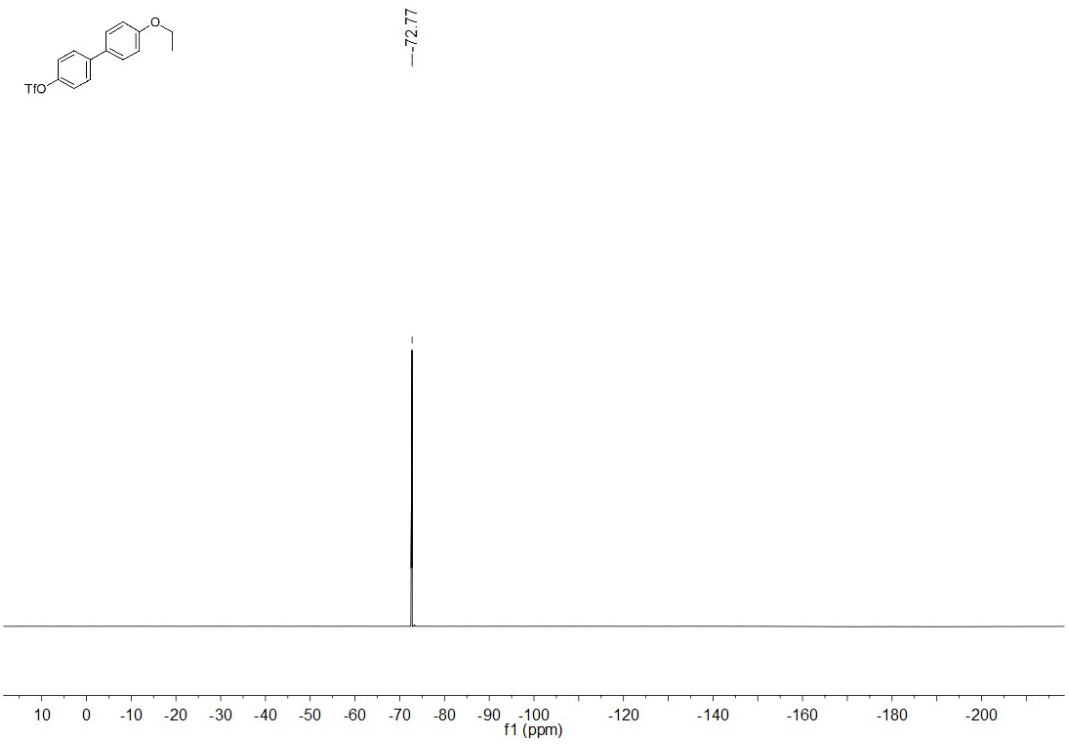
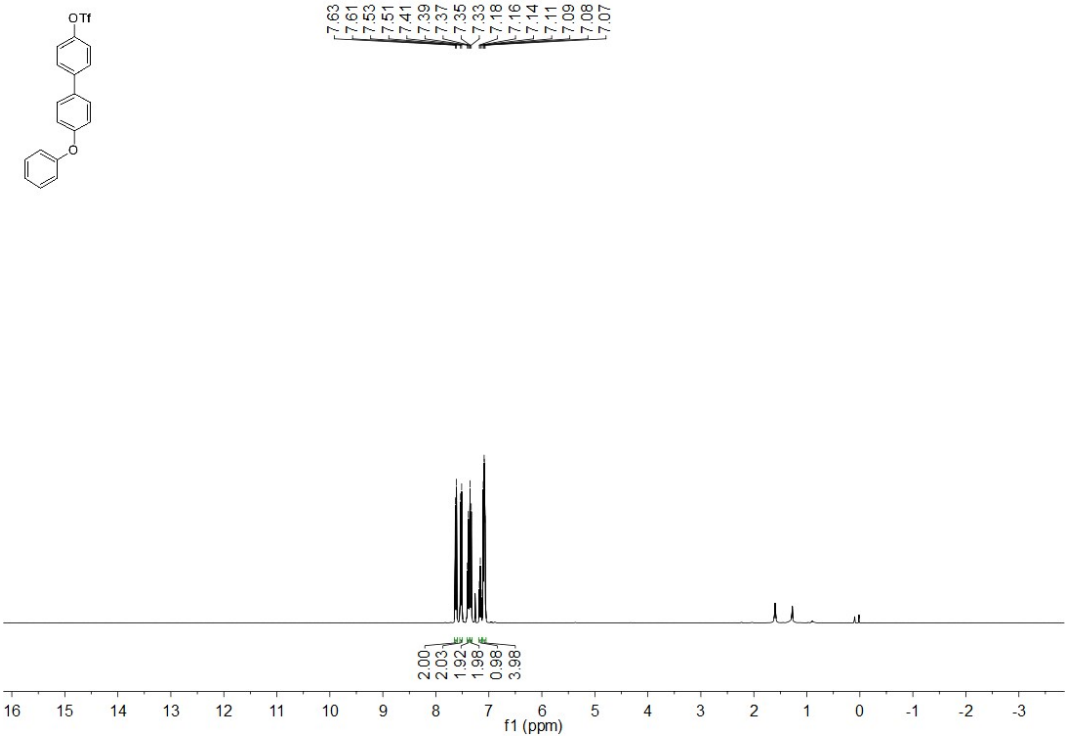


Figure S13. The NMR spectrums of **3k**



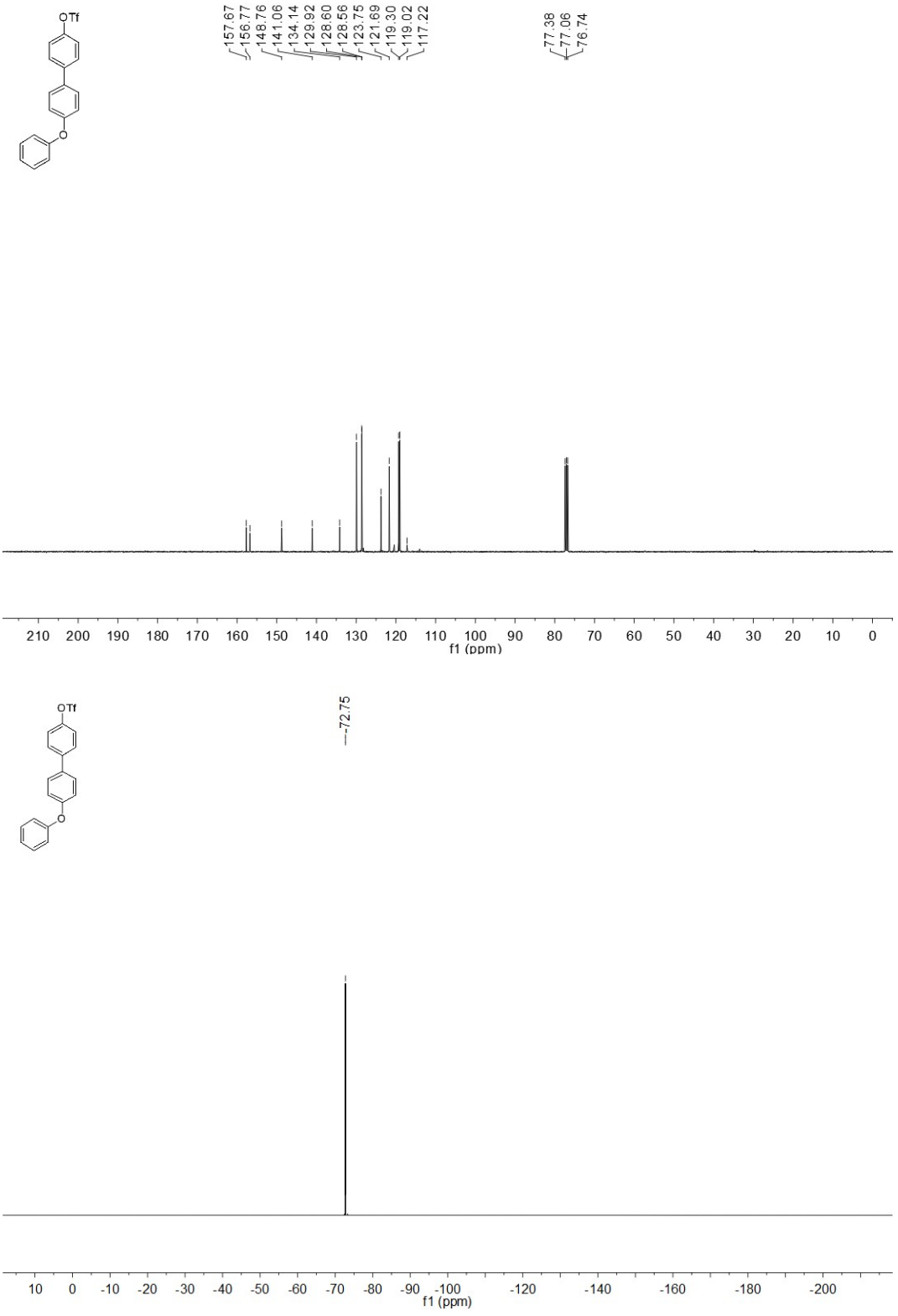
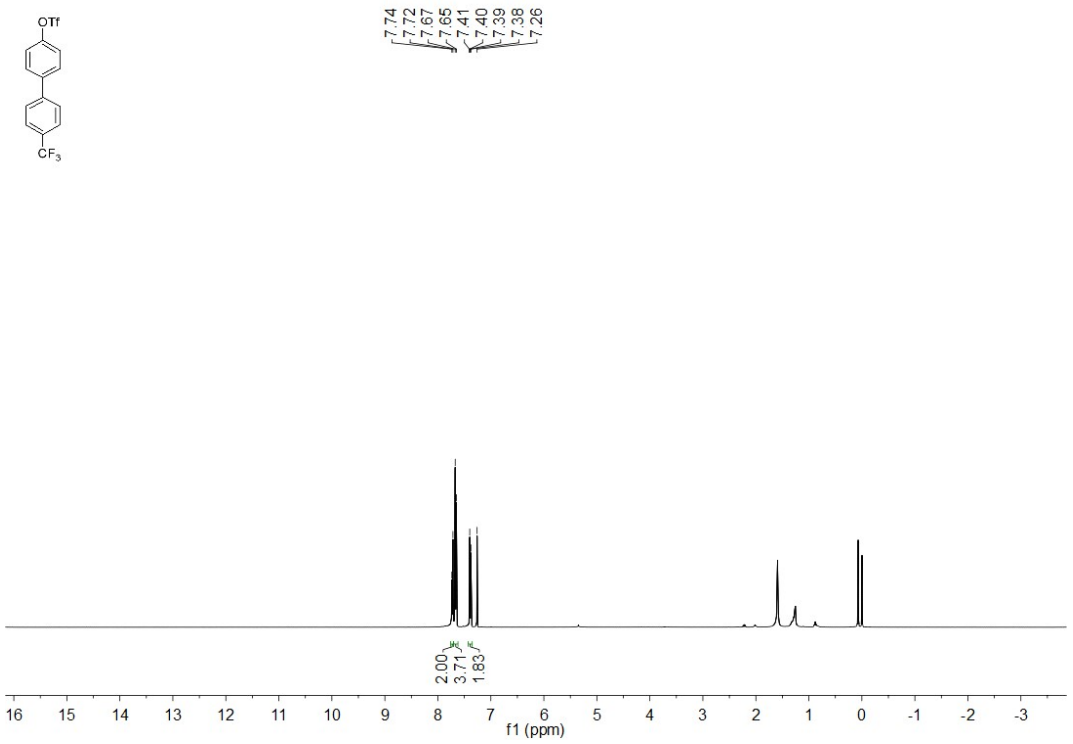
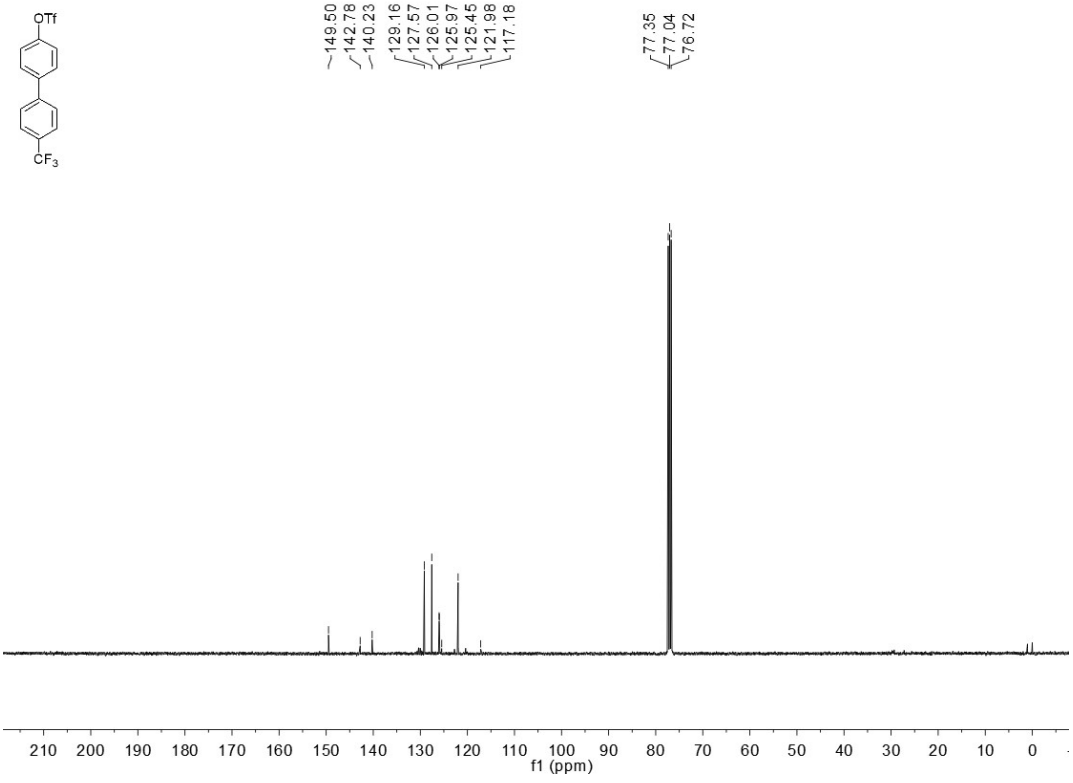


Figure S14. The NMR spectrums of **3l**


OTf
CF3
7.74
7.72
7.67
7.65
7.41
7.40
7.39
7.38
7.26
2.00
3.71
1.83
f1 (ppm)


OTf
CF3
149.50
142.78
140.23
129.16
127.57
126.01
125.97
125.45
121.98
117.18
77.35
77.04
76.72
f1 (ppm)

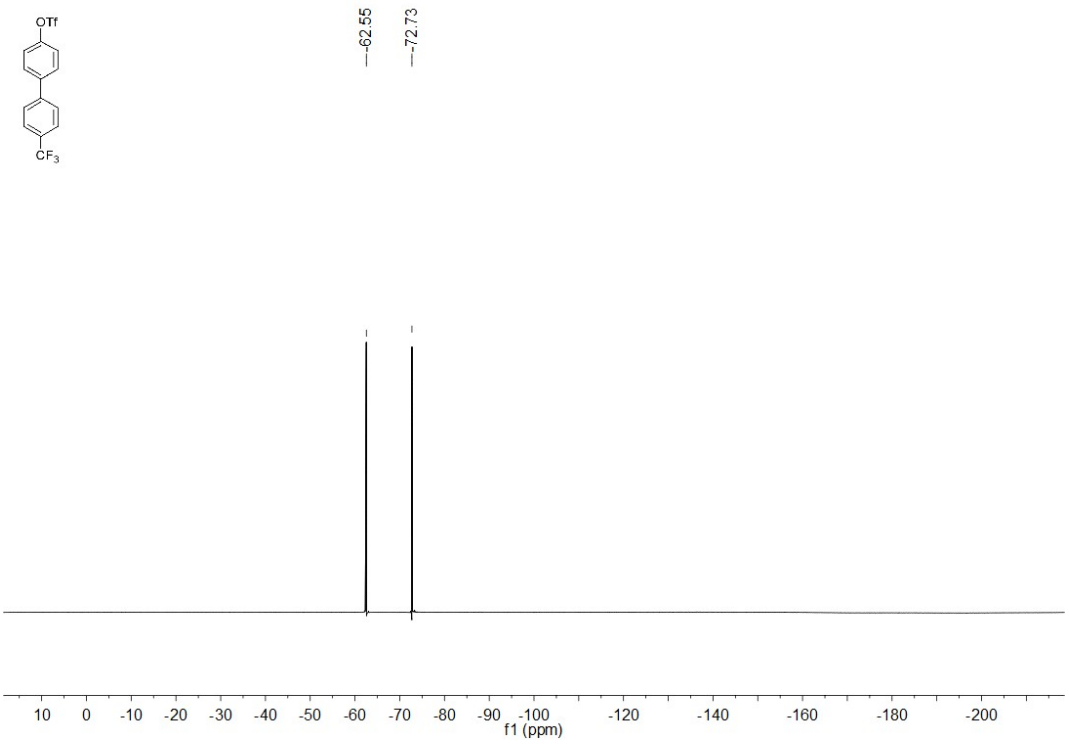
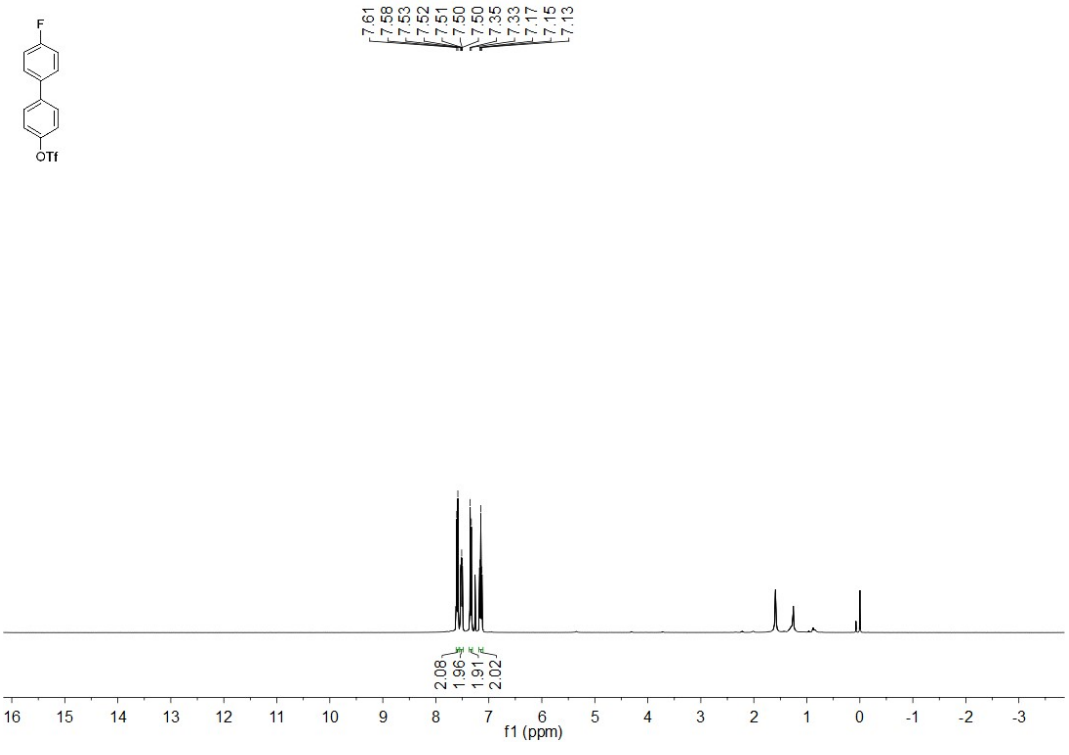


Figure S15. The NMR spectrums of **3m**



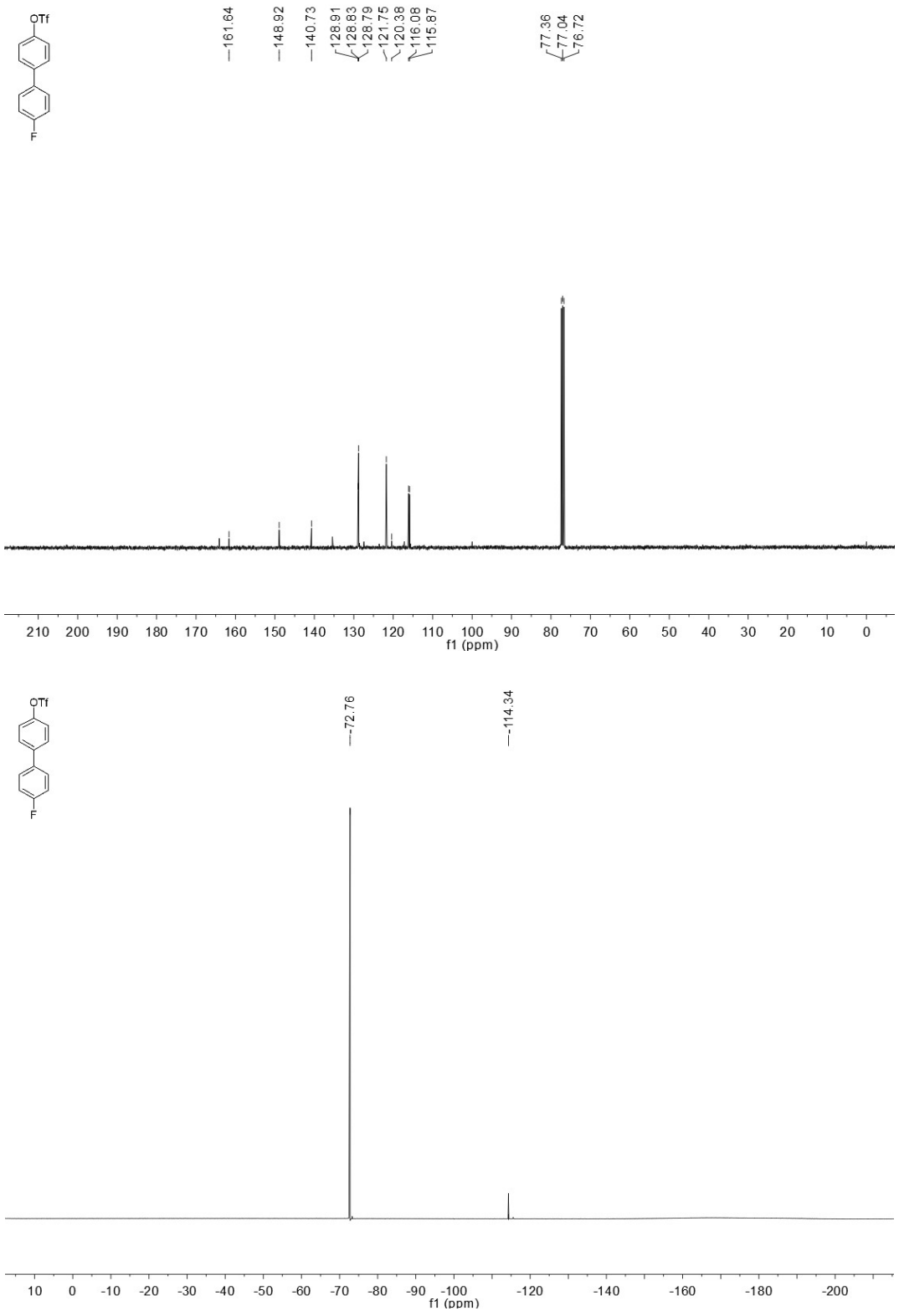
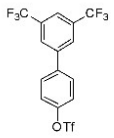
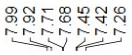
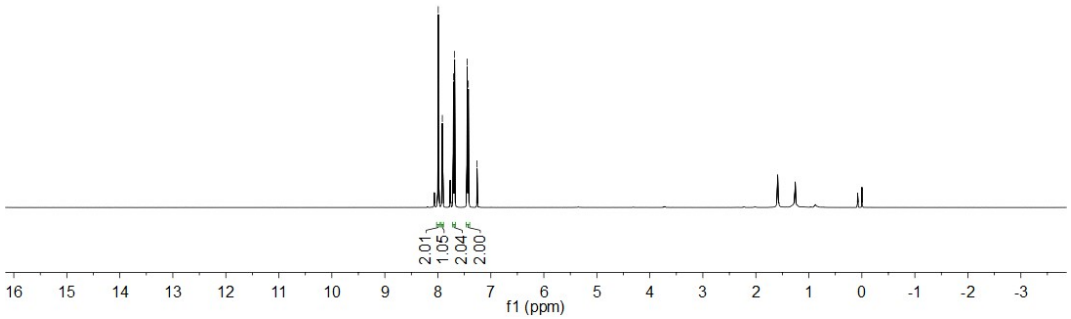
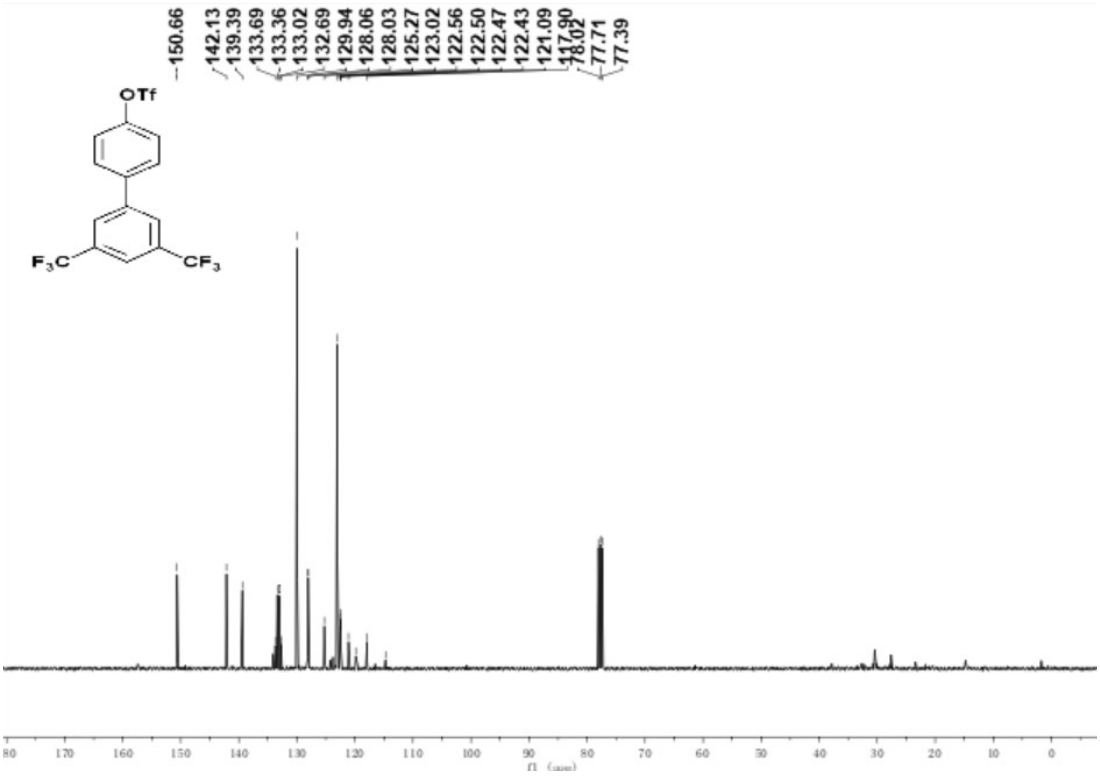


Figure S16. The NMR spectrums of **3n**


F3C
CF3
OTf


7.99
7.92
7.71
7.68
7.45
7.42
7.26


2.01
1.05
2.04
2.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


150.66
142.13
139.39
133.69
133.36
133.02
132.69
129.94
128.06
128.03
125.27
123.02
122.56
122.50
122.47
122.43
121.09
117.90
78.02
77.71
77.39
OTf
F3C
CF3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

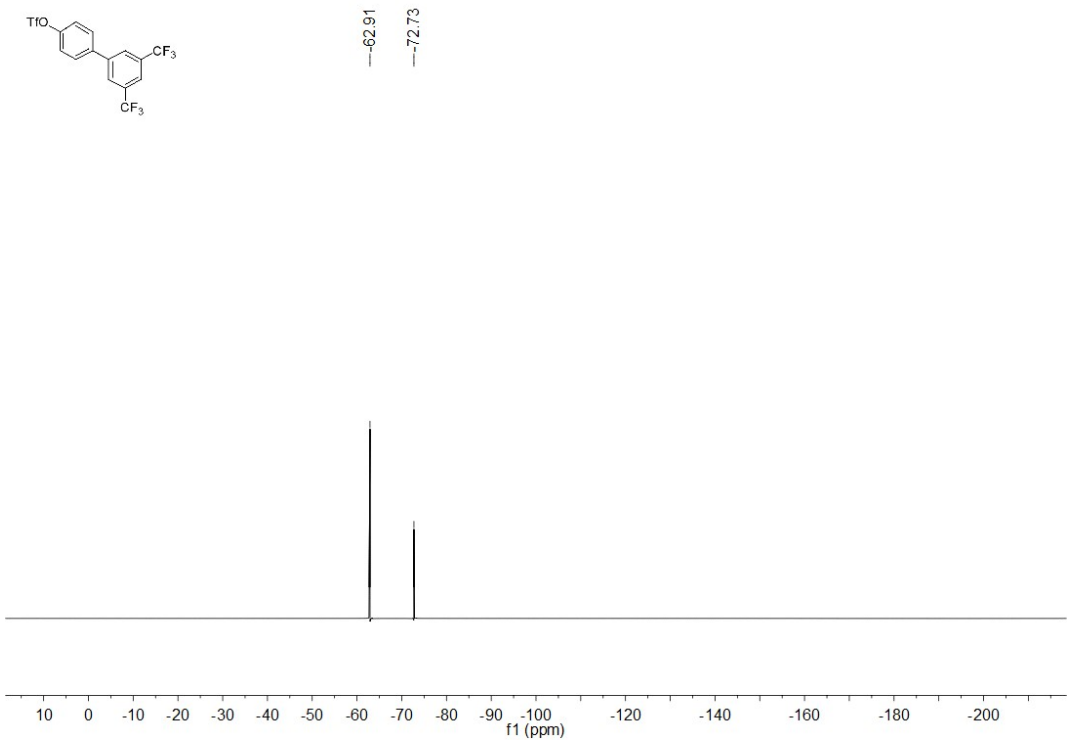
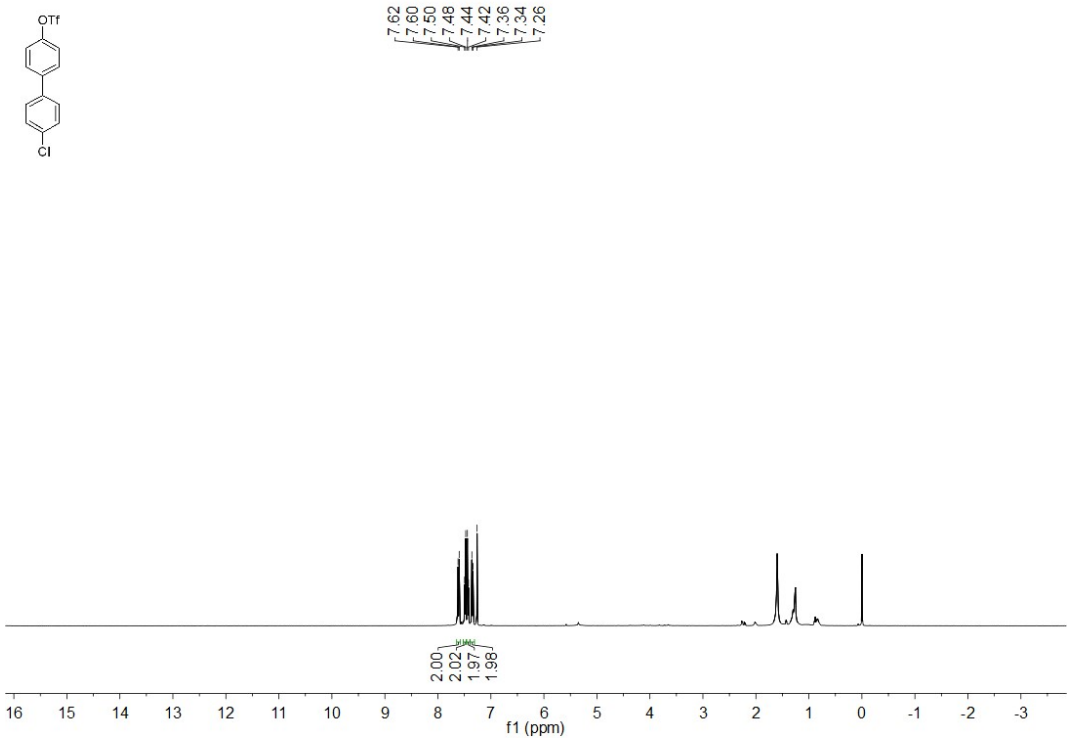
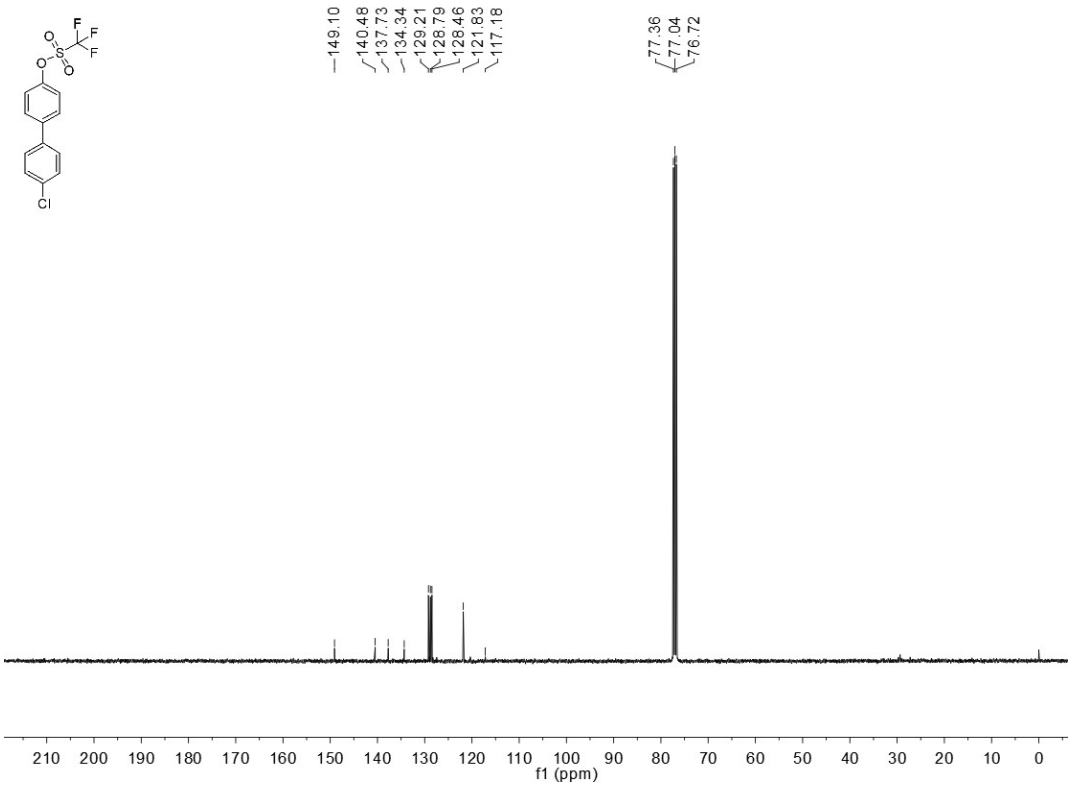


Figure S17. The NMR spectrums of **3o**





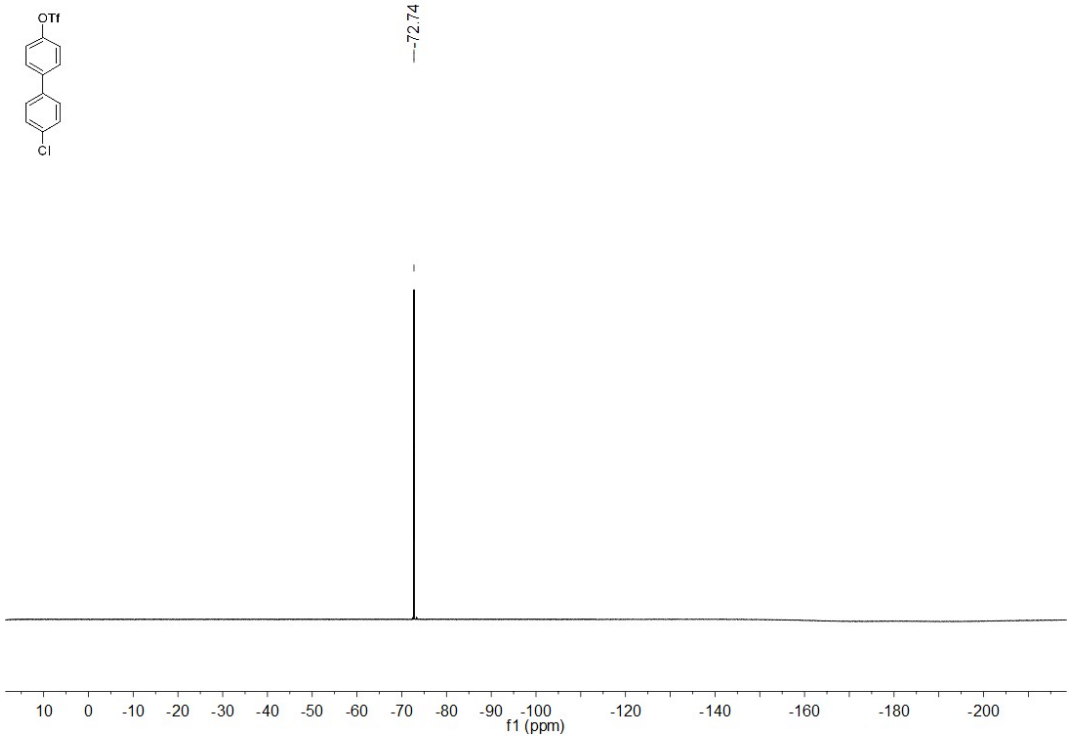
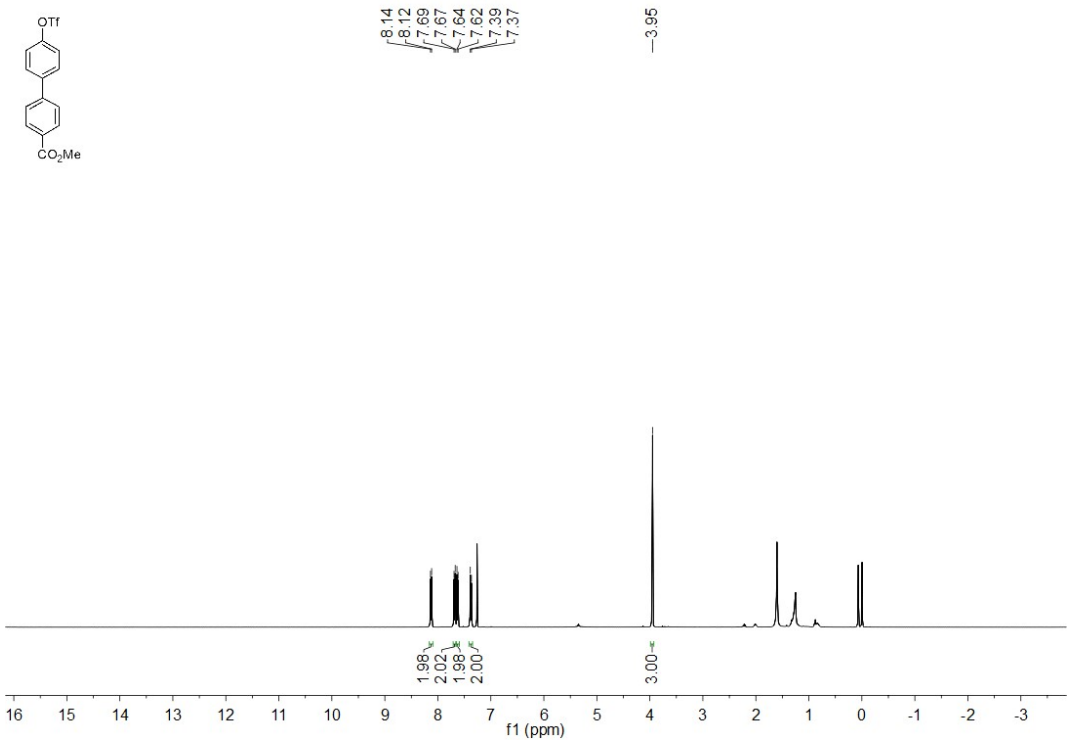
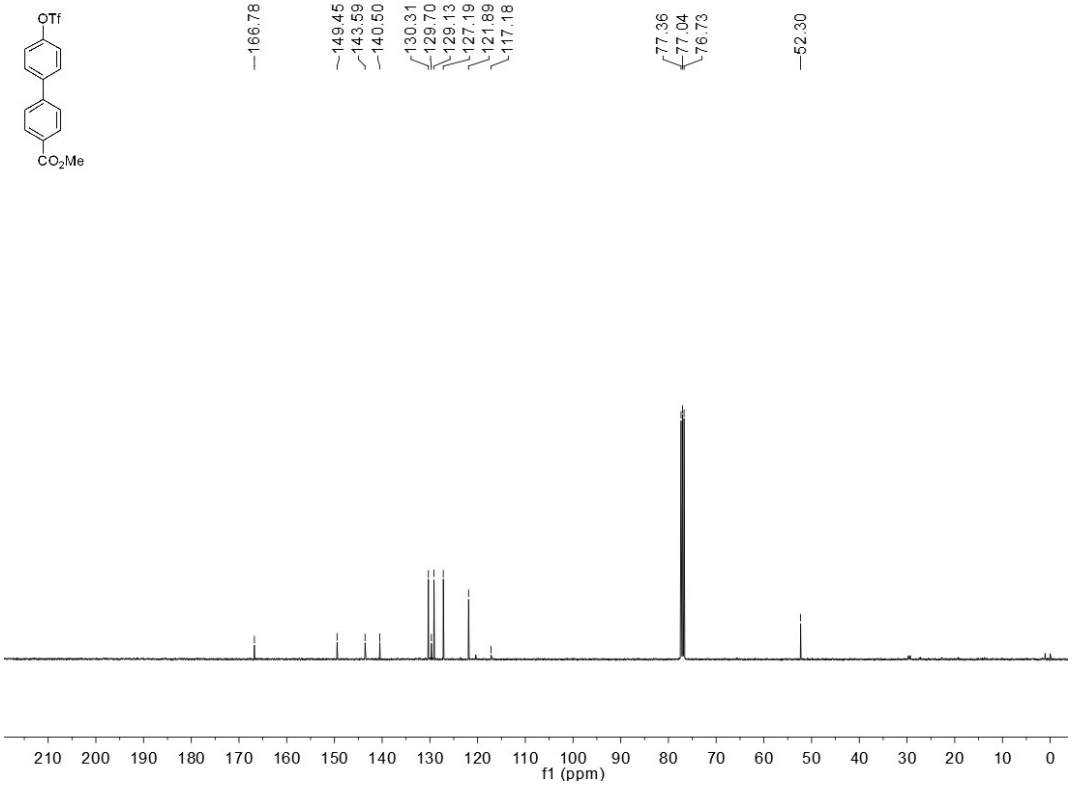


Figure S18. The NMR spectrums of **3p**


OTf
CO2Me
8.14
8.12
7.69
7.67
7.64
7.62
7.39
7.37
3.95
1.98
2.02
1.98
2.00
3.00
f1 (ppm)


OTf
CO2Me
166.78
149.45
143.59
140.50
130.31
129.70
129.13
127.19
121.89
117.18
77.36
77.04
76.73
52.30
f1 (ppm)

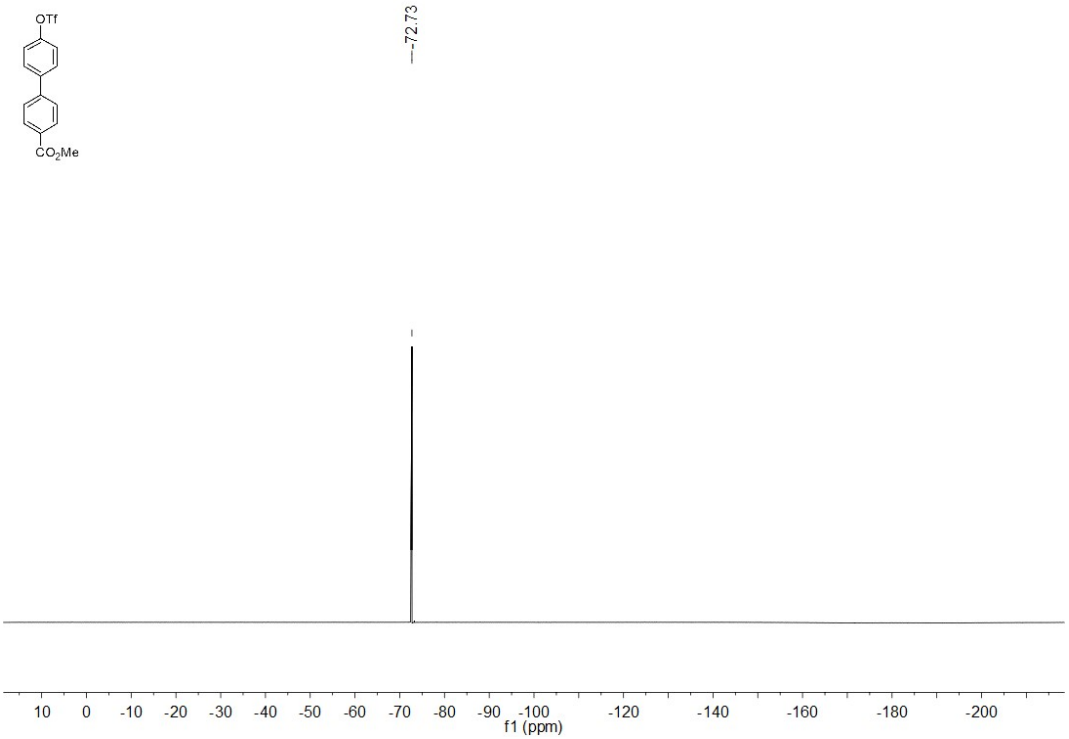
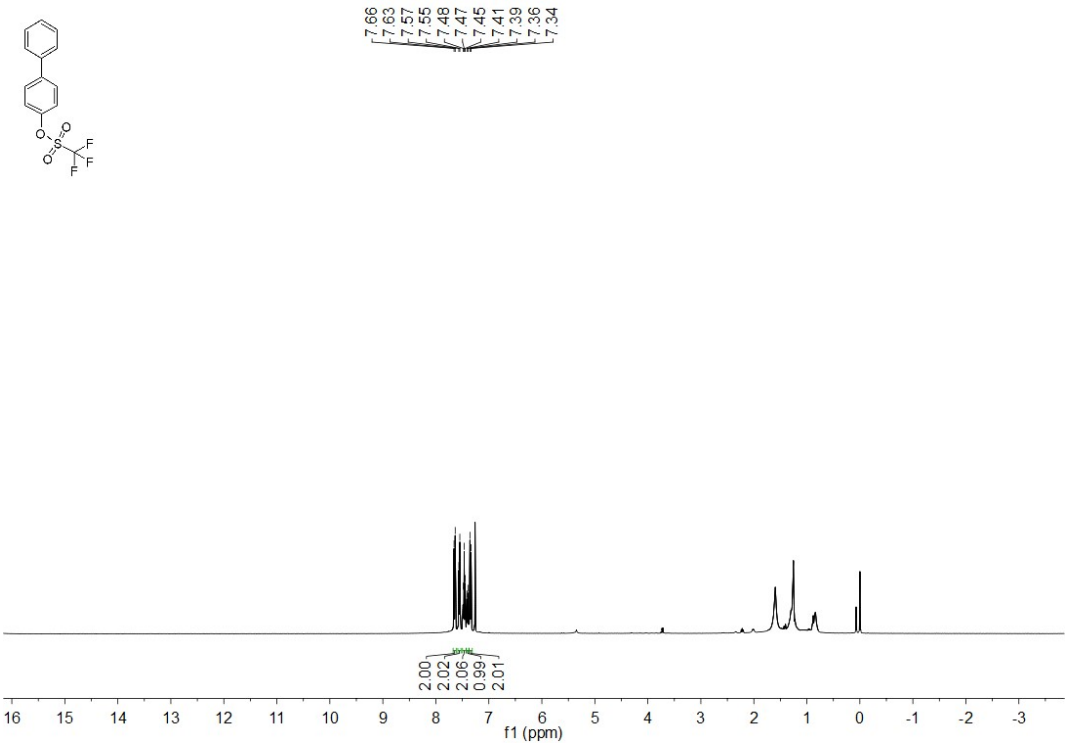


Figure S19. The NMR spectrums of **3q**



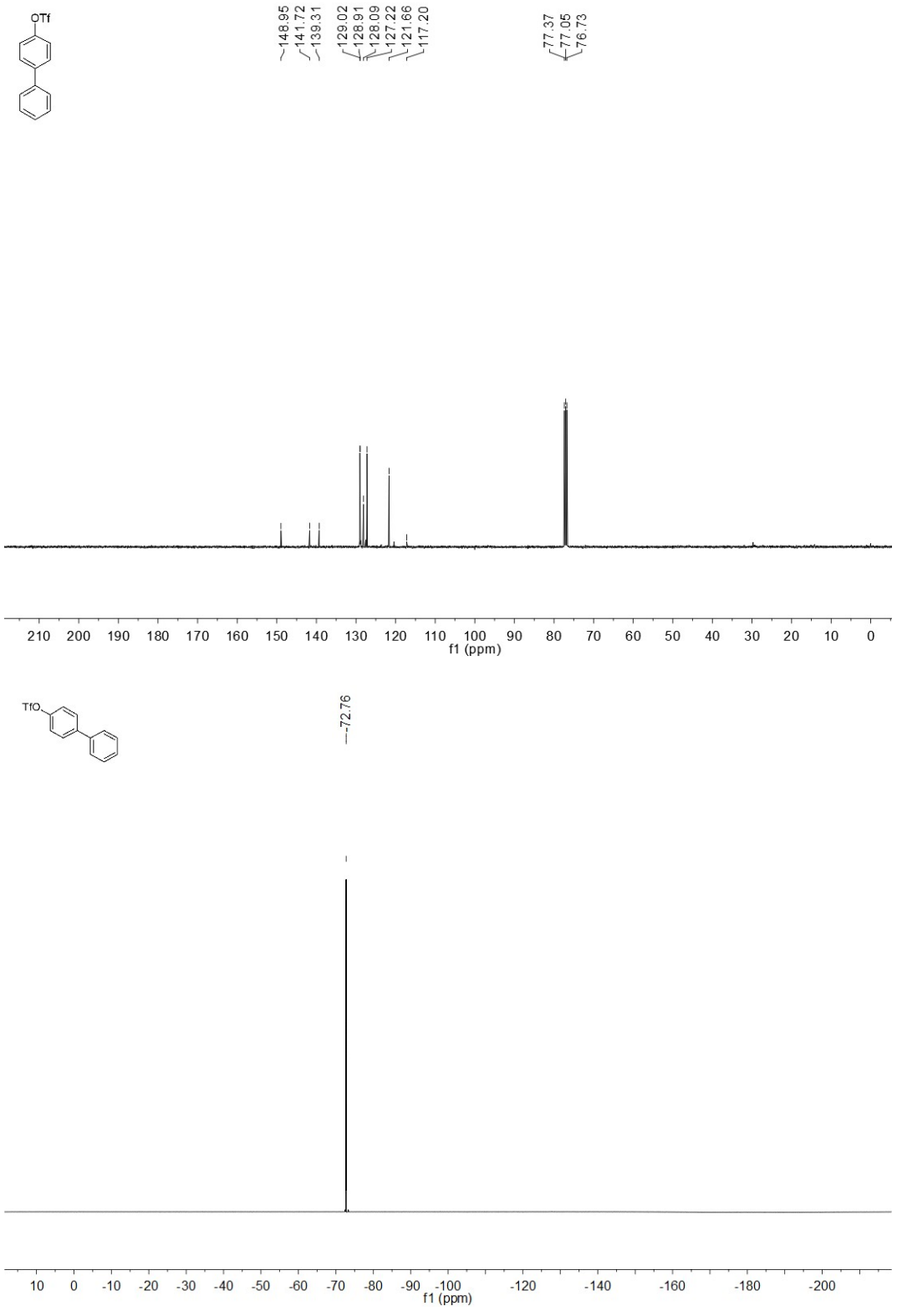
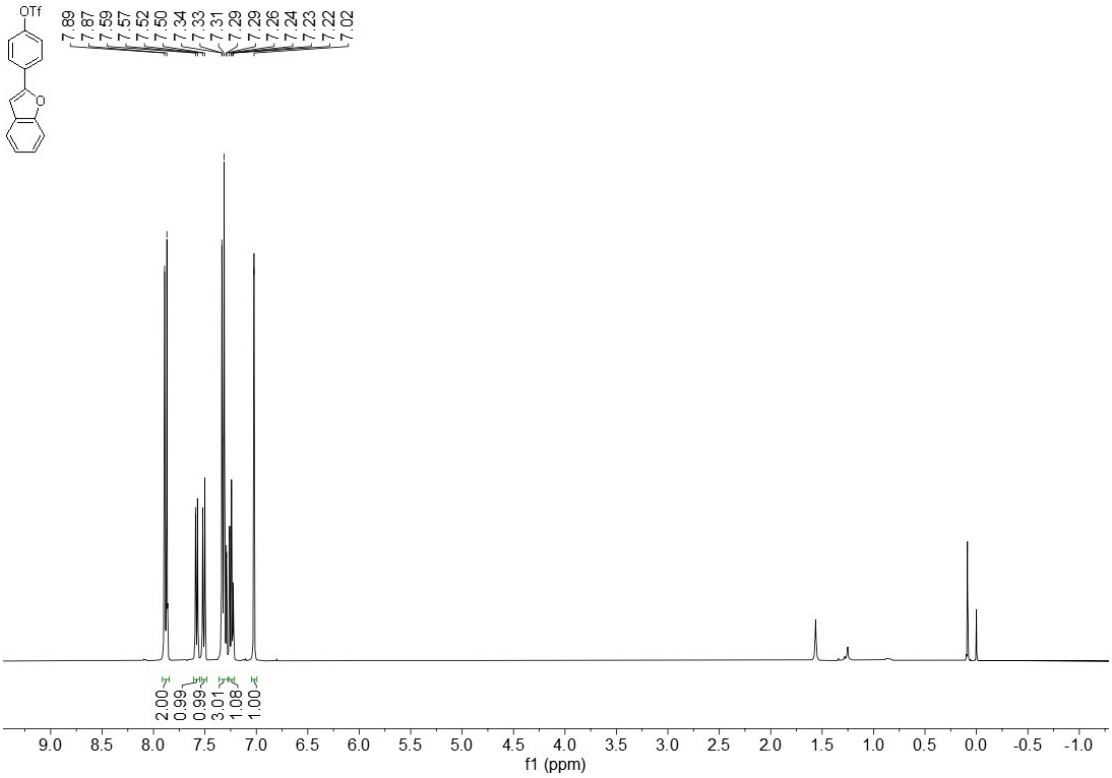
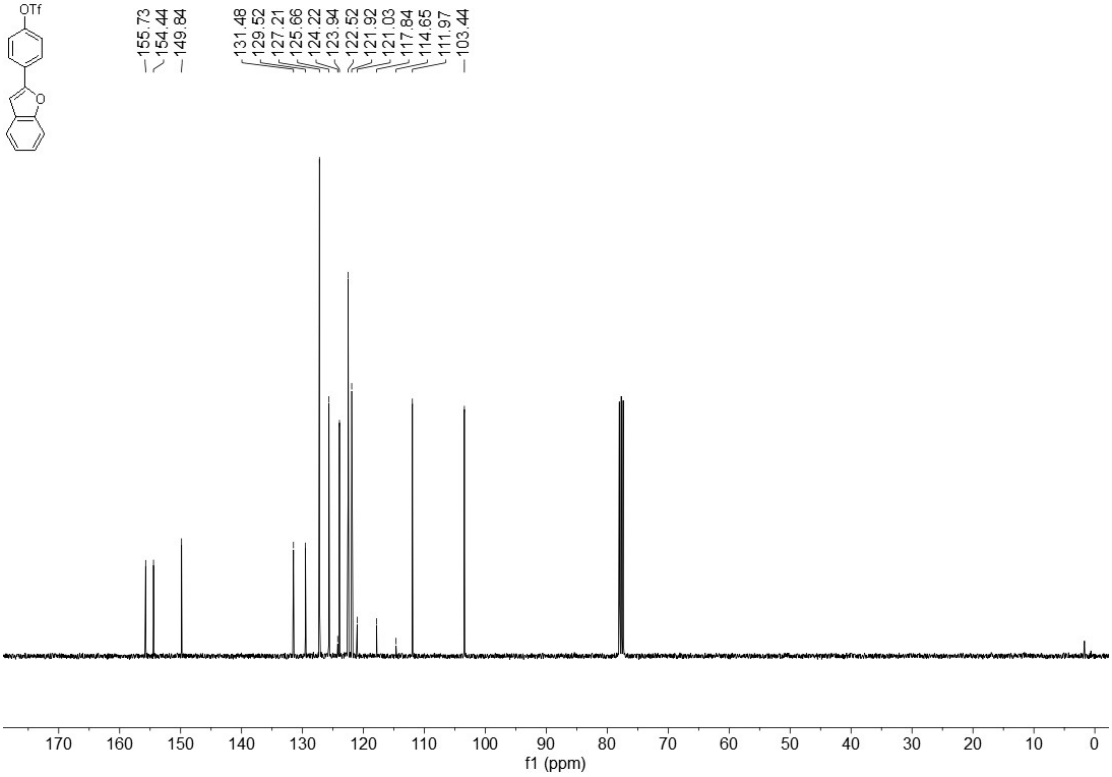


Figure S20. The NMR spectrums of **3r**


OTf
7.89
7.87
7.59
7.57
7.52
7.50
7.34
7.33
7.31
7.29
7.29
7.26
7.24
7.23
7.22
7.02
2.00
0.99
0.99
3.01
1.08
1.00
f1 (ppm)


OTf
155.73
154.44
149.84
131.48
129.52
127.21
125.66
124.22
123.94
122.52
121.92
121.03
117.84
114.65
111.97
103.44
f1 (ppm)

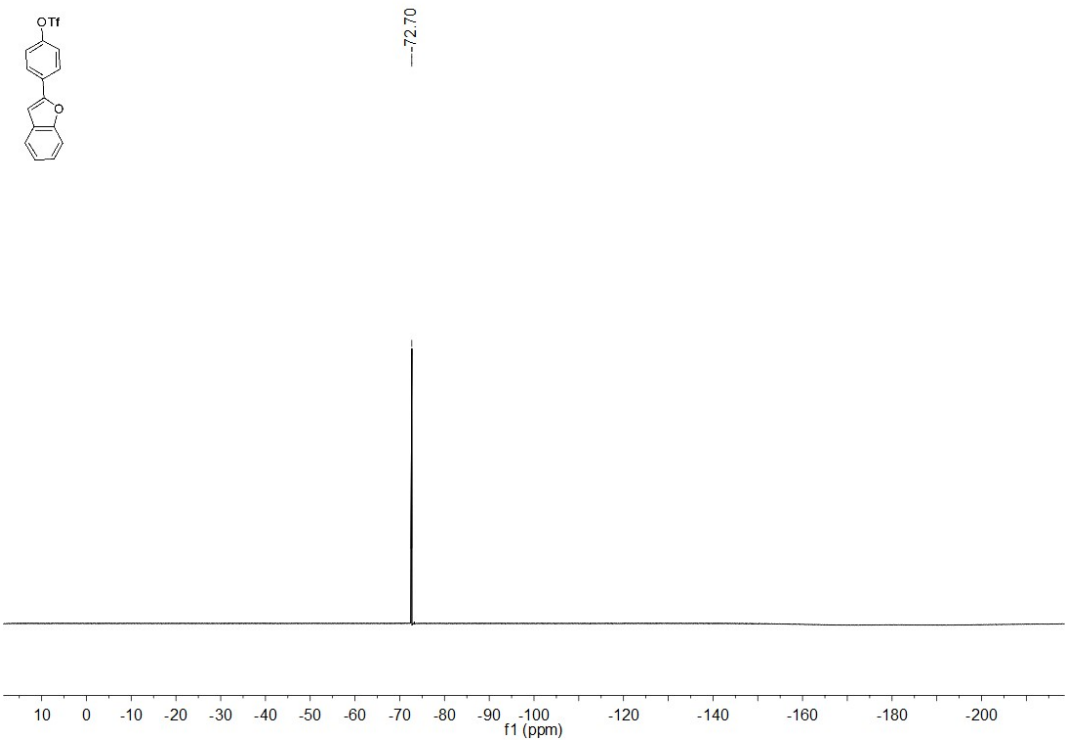
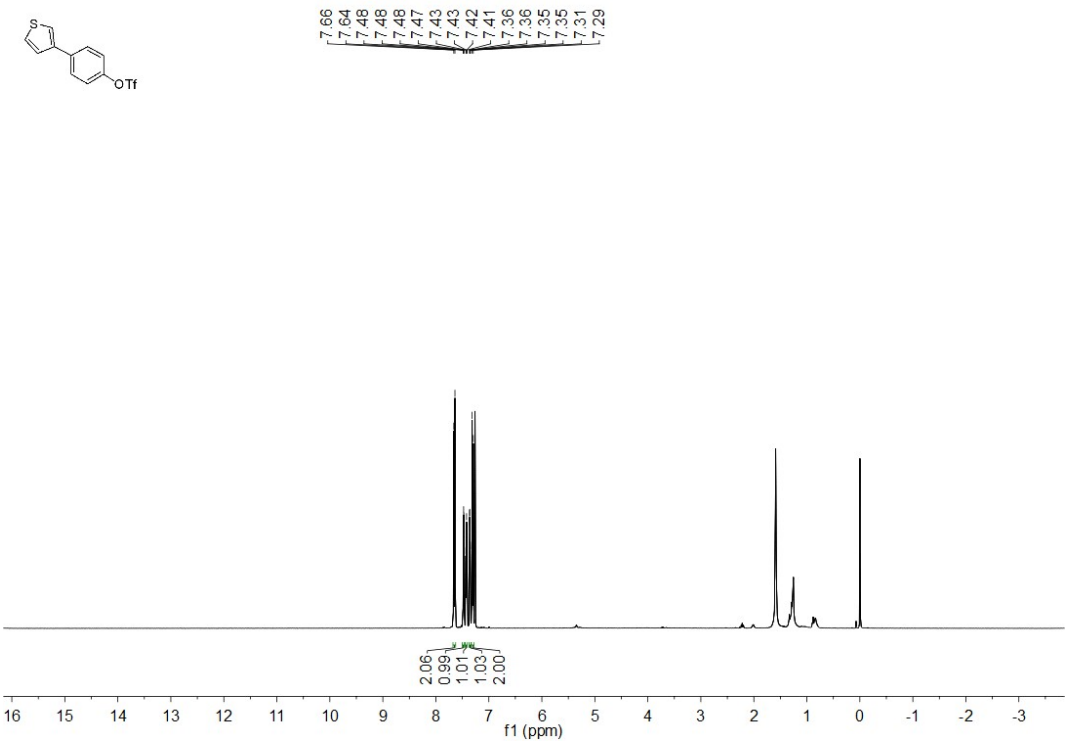
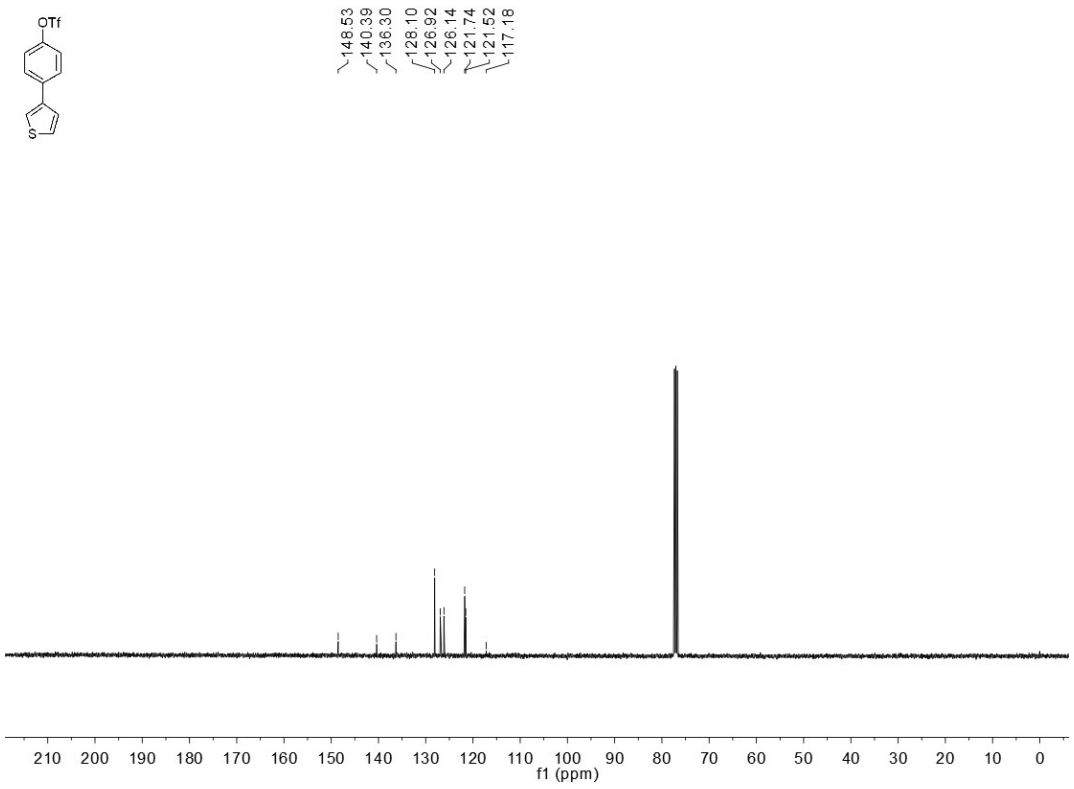


Figure S21. The NMR spectrums of **3s**





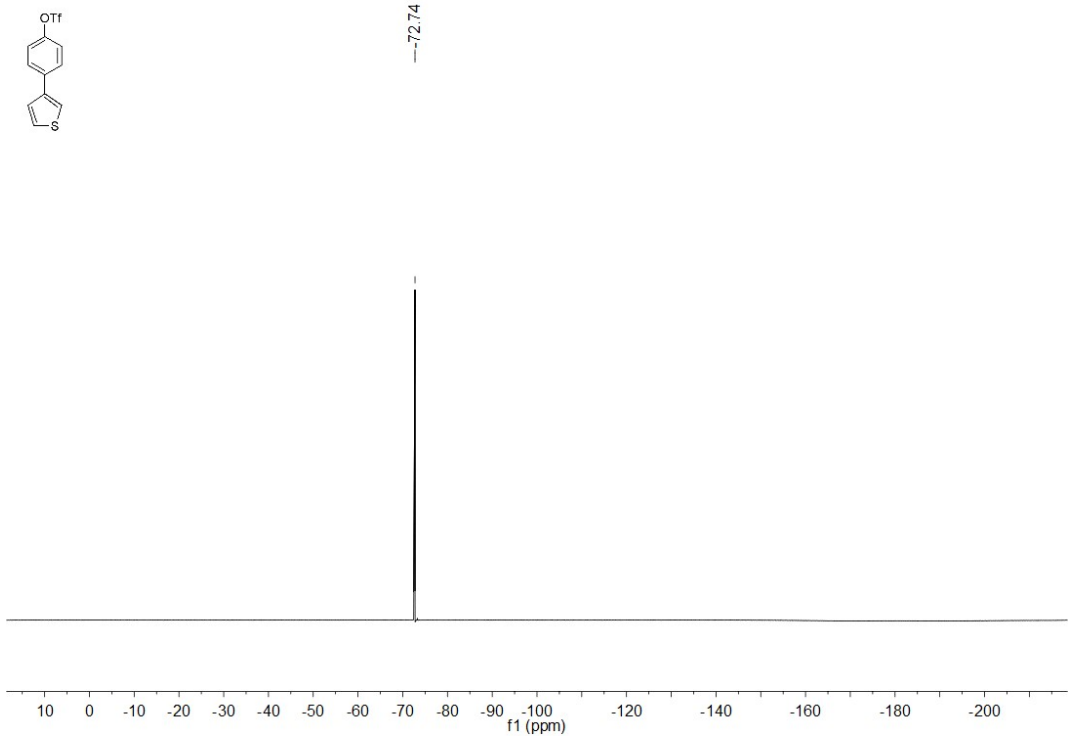
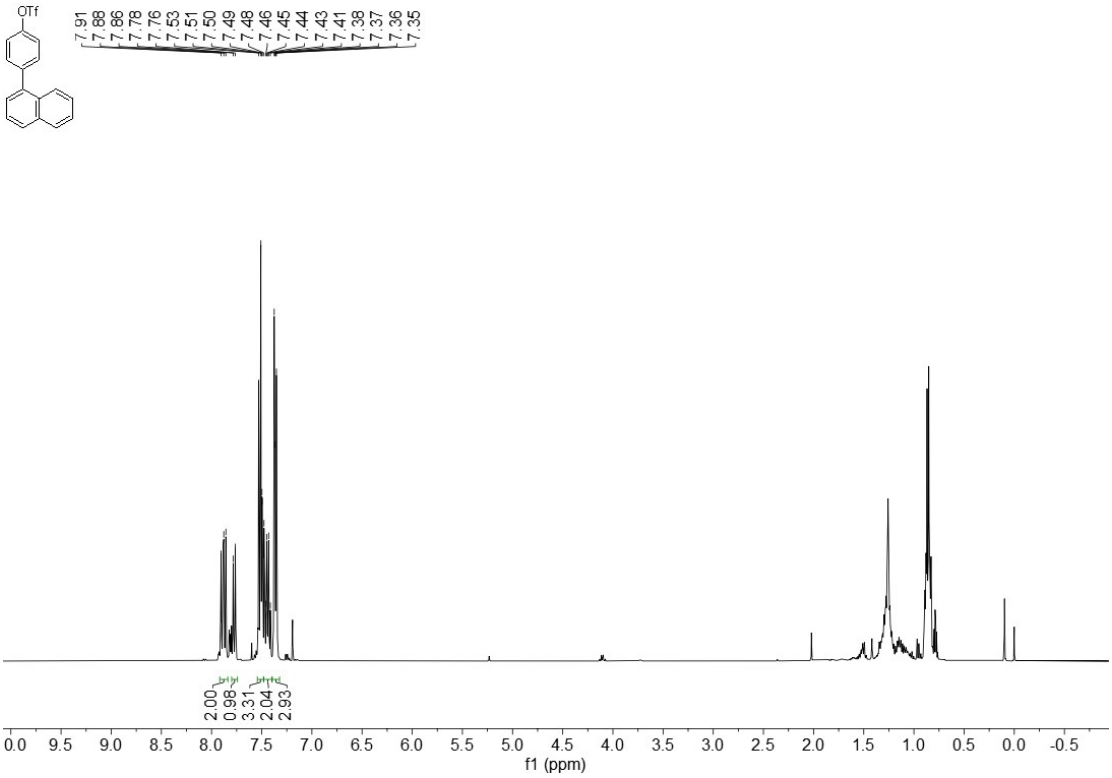
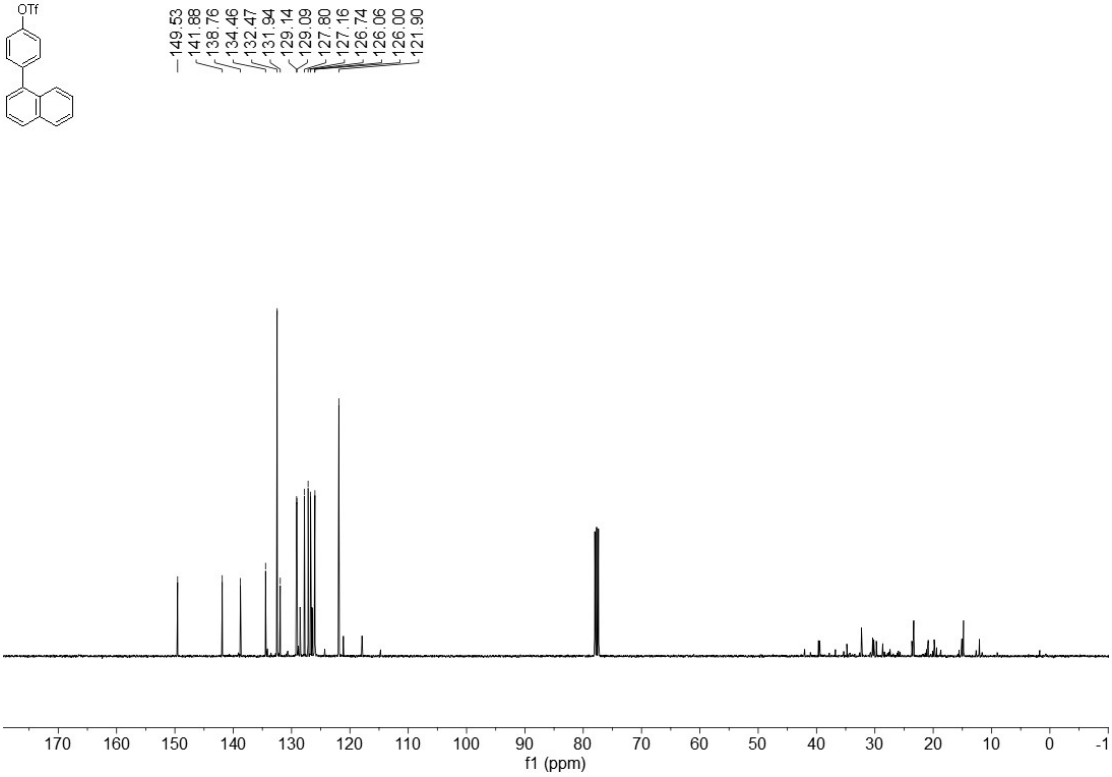


Figure S22. The NMR spectrums of **3t**


OTf
7.91
7.88
7.86
7.78
7.76
7.53
7.51
7.50
7.49
7.48
7.46
7.45
7.44
7.43
7.41
7.38
7.37
7.36
7.35
2.00
0.98
3.31
2.04
2.93
f1 (ppm)


OTf
149.53
141.88
138.76
134.46
132.47
131.94
129.14
129.09
127.80
127.16
126.74
126.06
126.00
121.90
f1 (ppm)

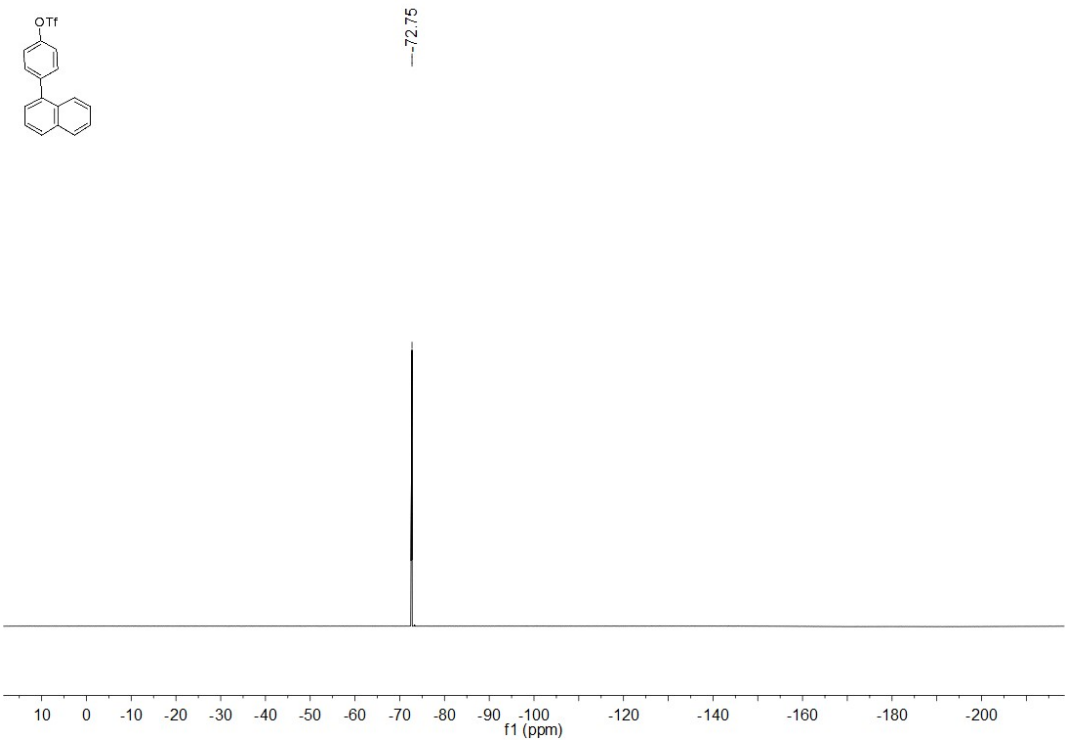
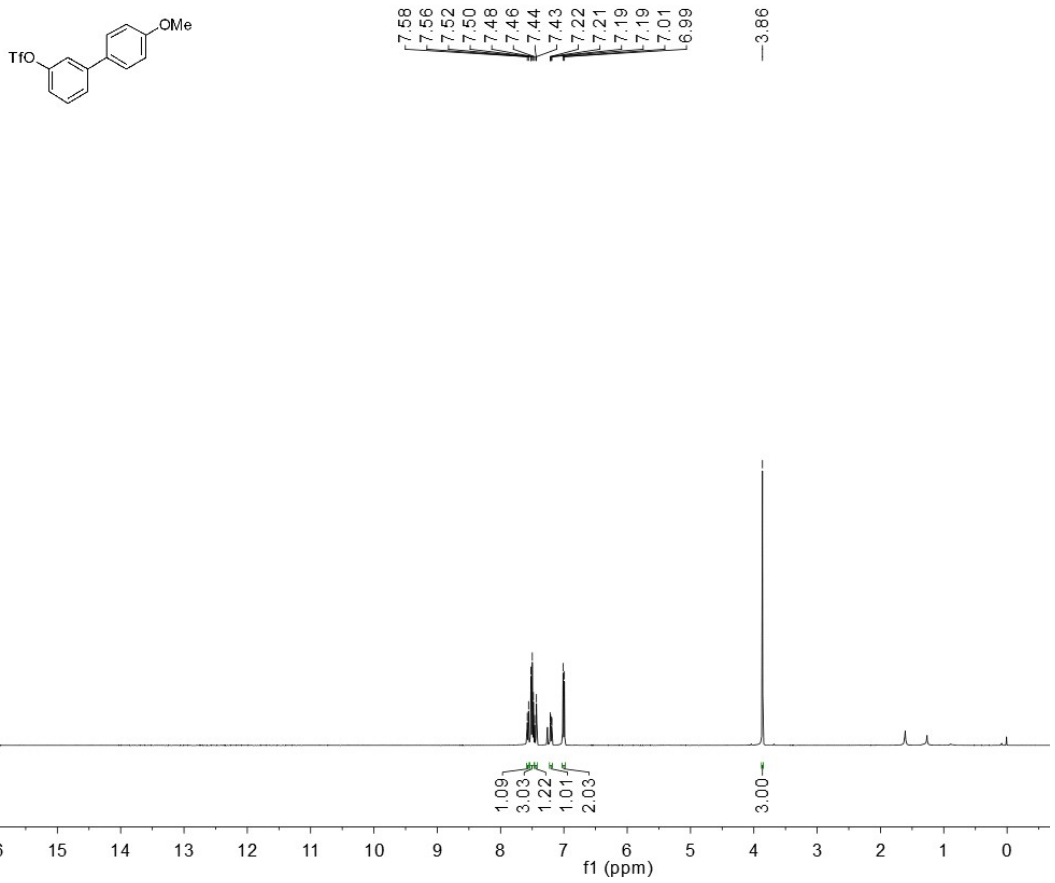


Figure S23. The NMR spectrums of **3u**



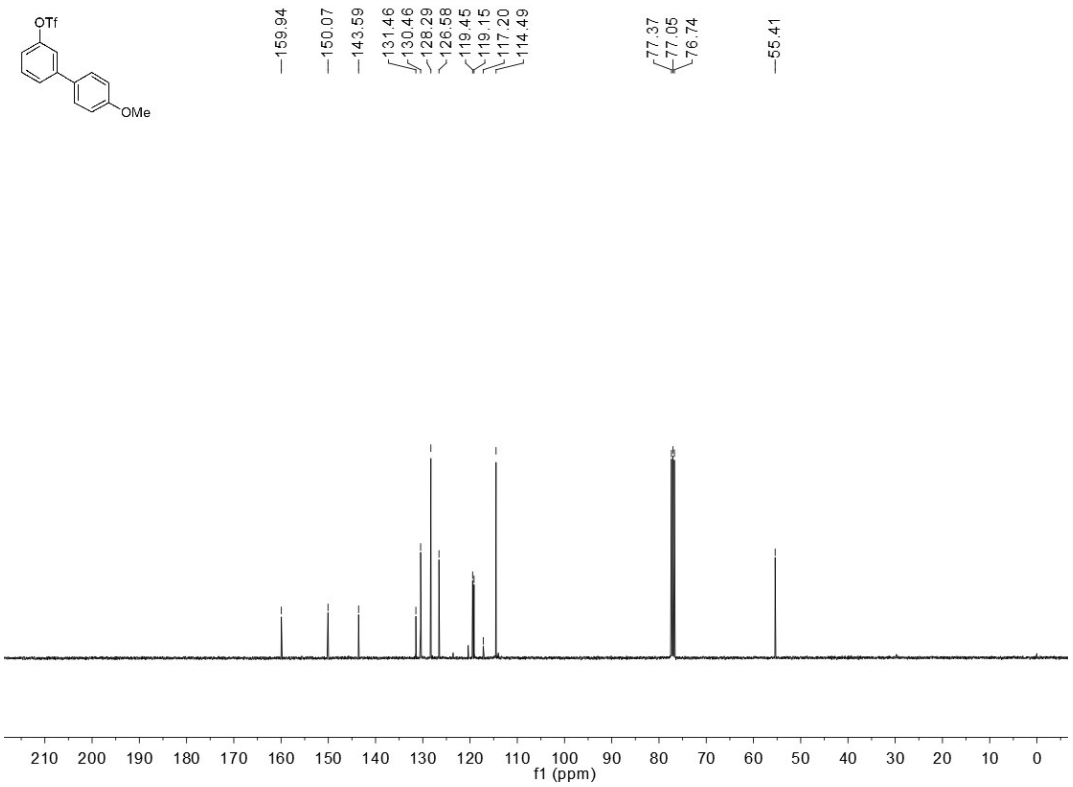
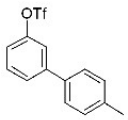
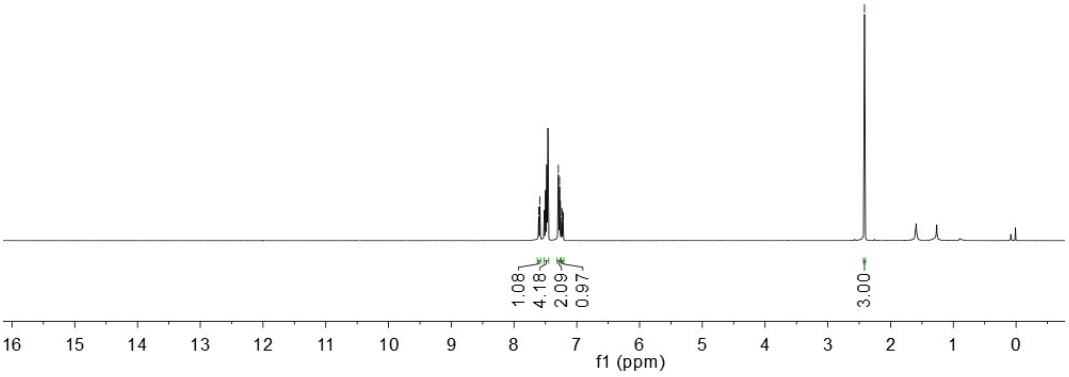


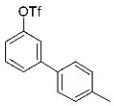
Figure S24. The NMR spectrums of **3v**

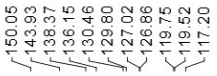

OTf


7.61
7.59
7.29
7.27
7.26
7.24
7.24
7.22
7.22


2.42

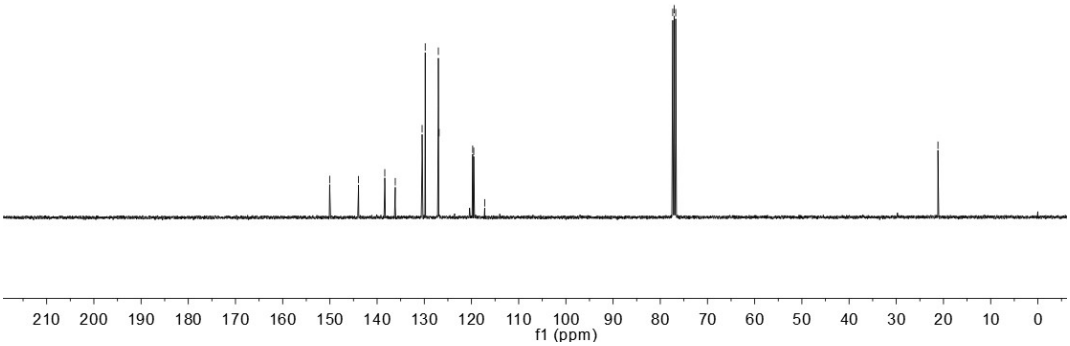

1.08
4.18
2.09
0.97
3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)


OTf


150.05
143.93
138.37
136.15
130.46
129.80
127.02
126.86
119.75
119.52
117.20


77.37
77.05
76.73


21.17


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

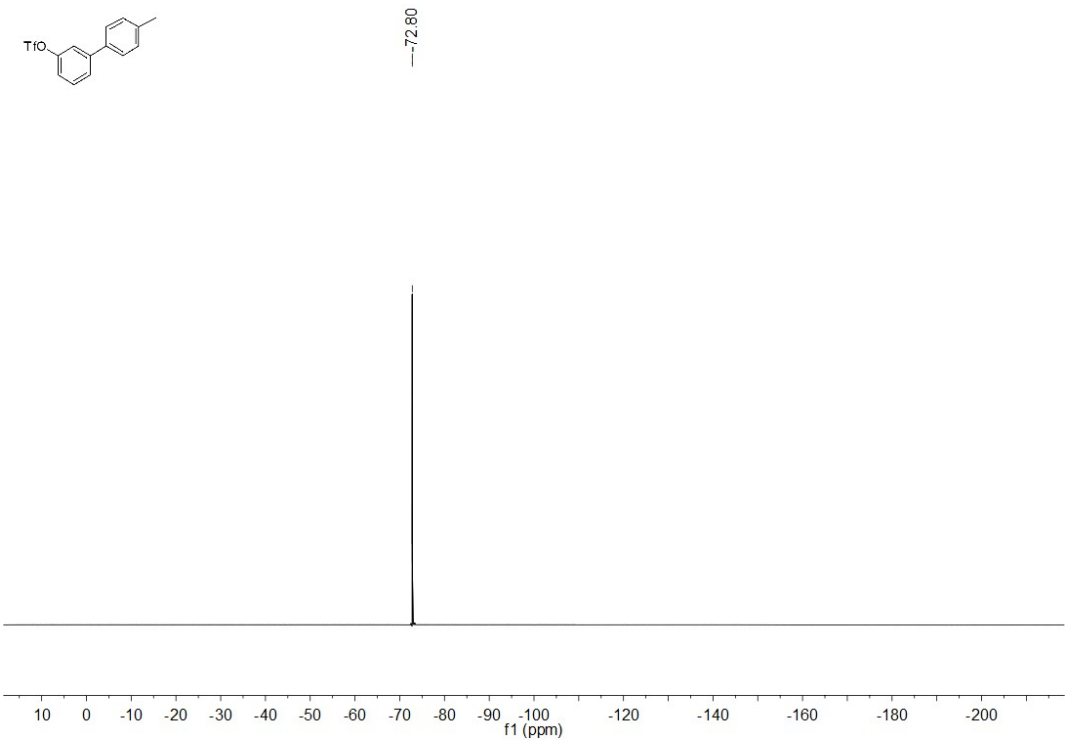
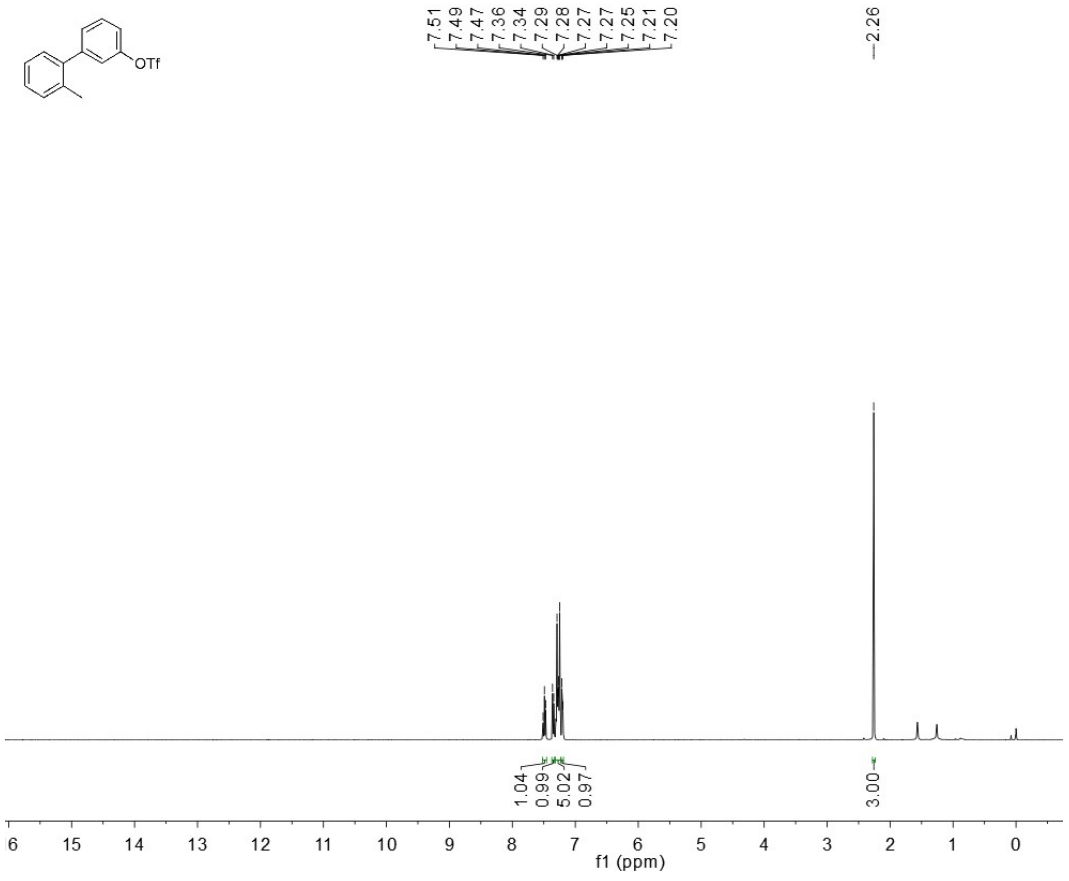


Figure S25. The NMR spectrums of **3w**



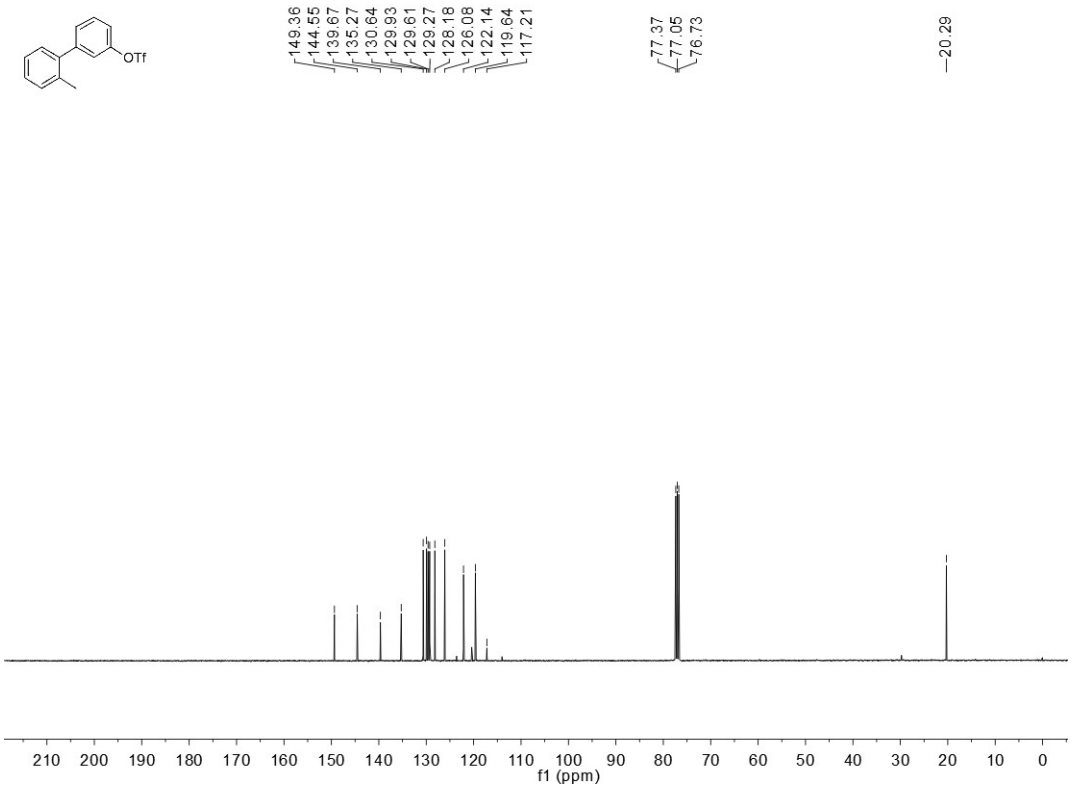
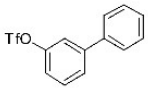
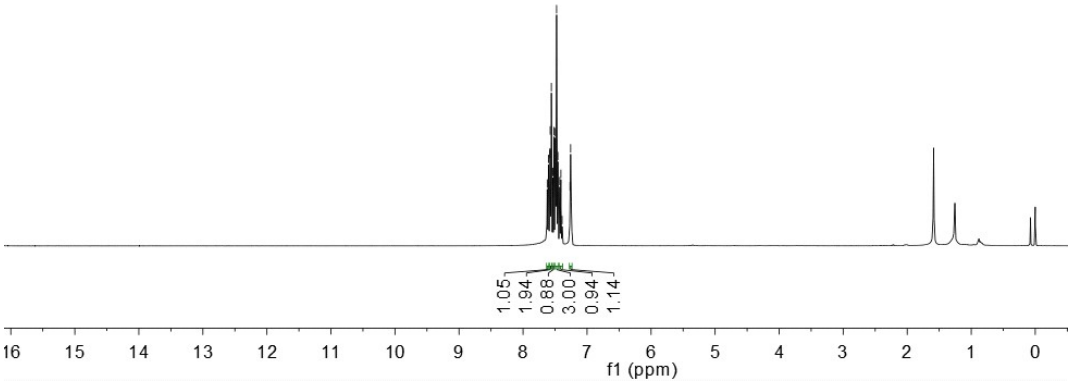
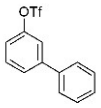


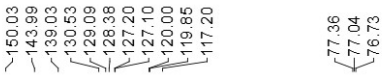
Figure S26. The NMR spectrums of **3x**


TfO

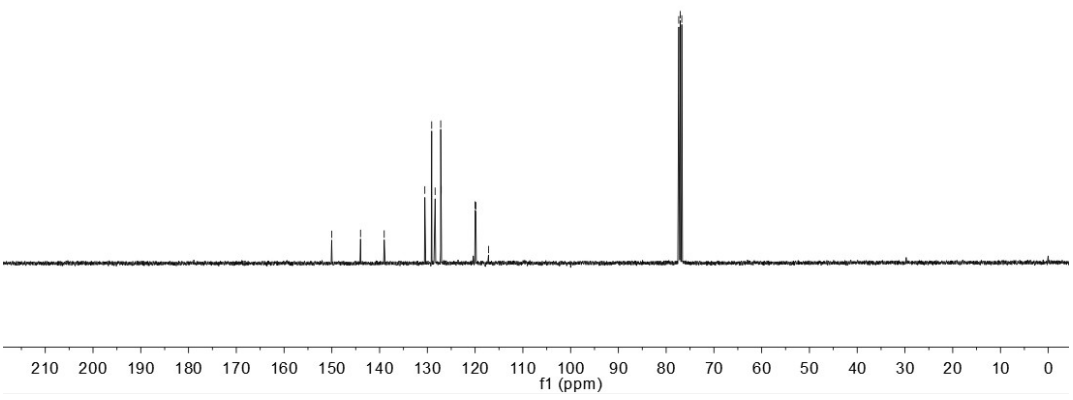

7.62
7.60
7.58
7.58
7.56
7.54
7.52
7.50
7.48
7.46
7.43
7.41
7.39
7.27
7.26


1.05
1.94
0.88
3.00
0.94
1.14
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)


OTf


150.03
143.99
139.03
130.53
129.09
128.38
127.20
127.10
120.00
119.85
117.20

77.36
77.04
76.73


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

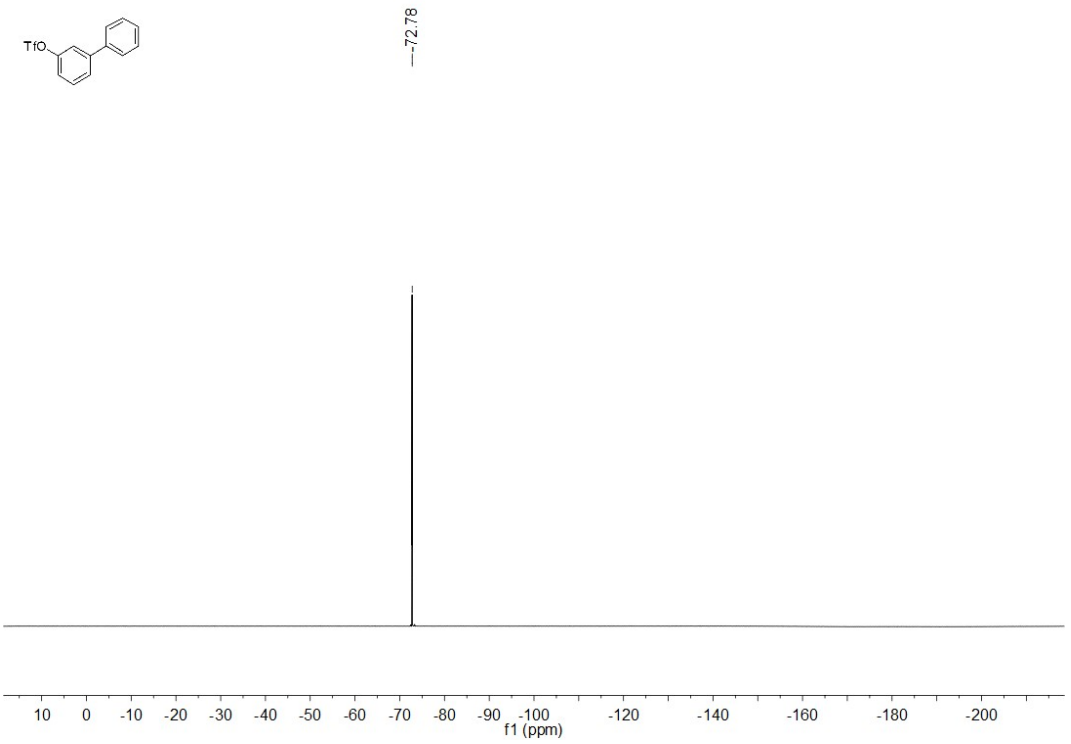
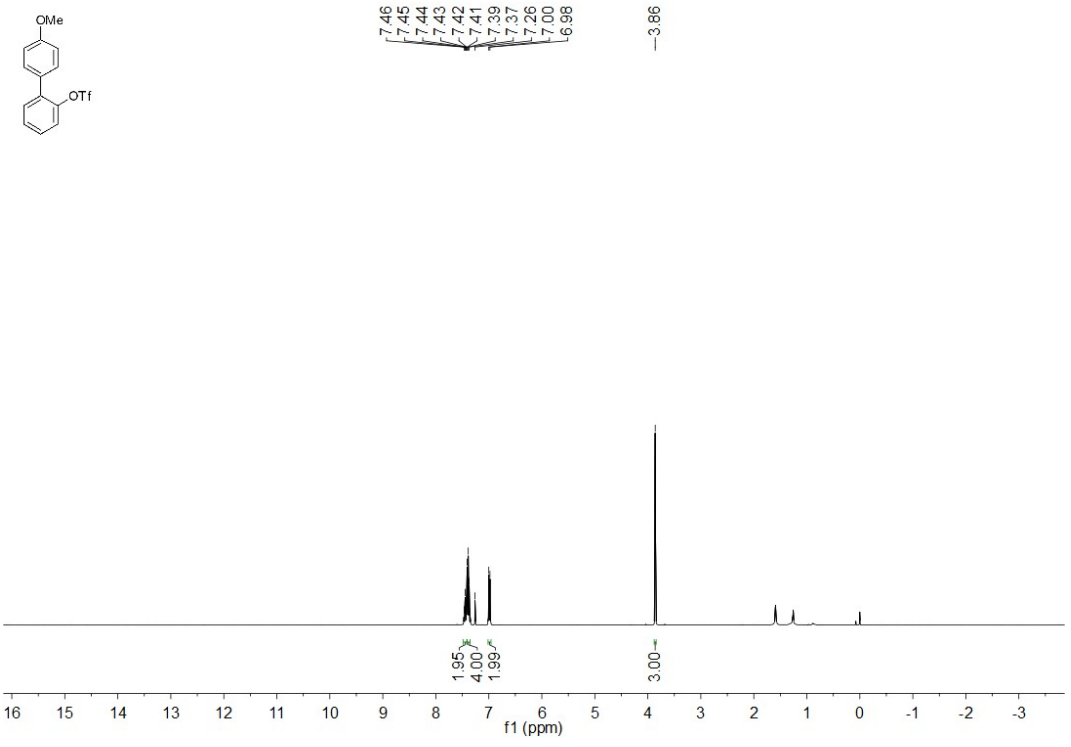


Figure S27. The NMR spectrums of **3y**



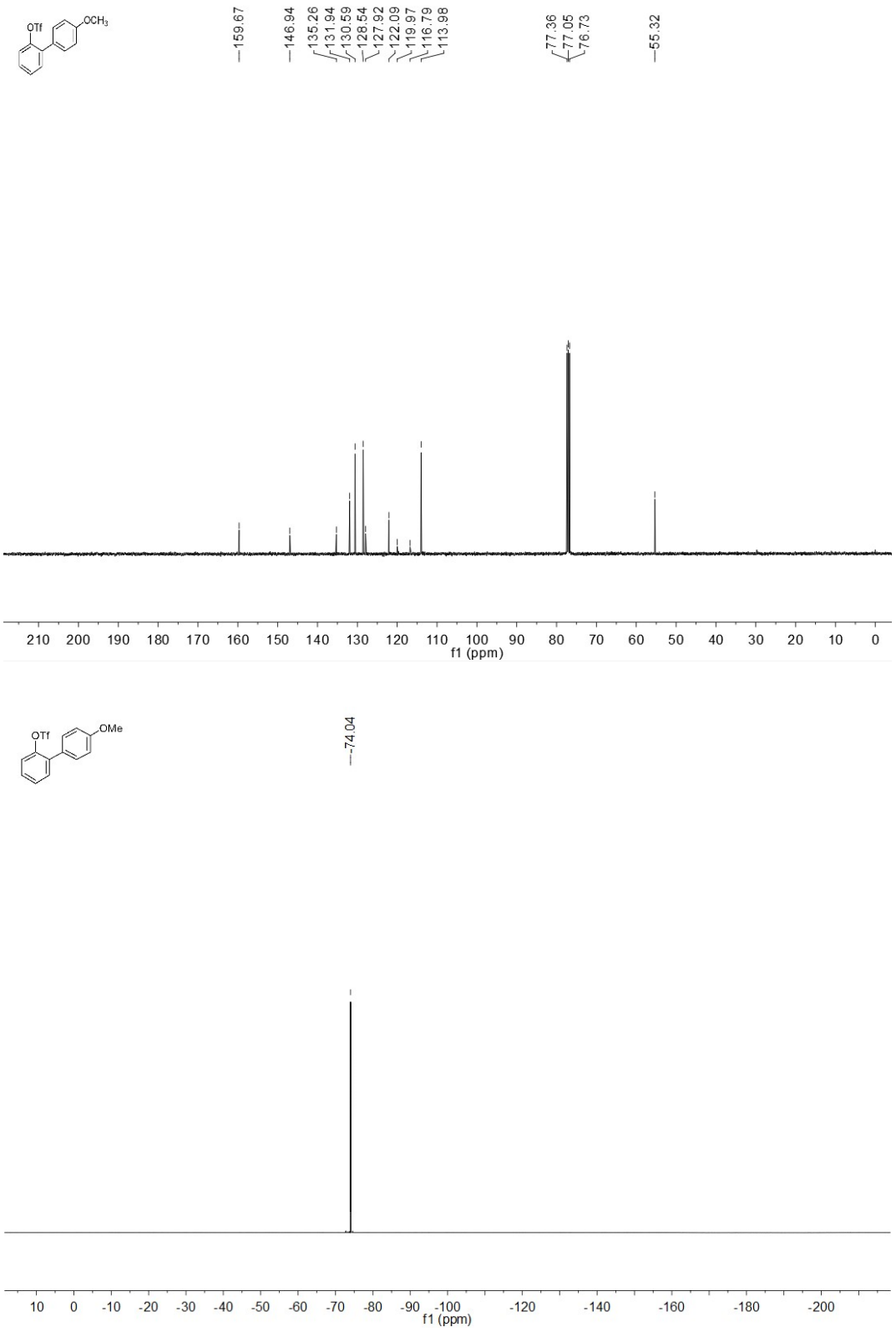
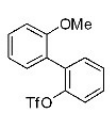
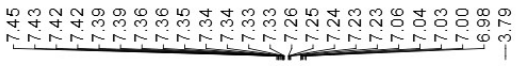
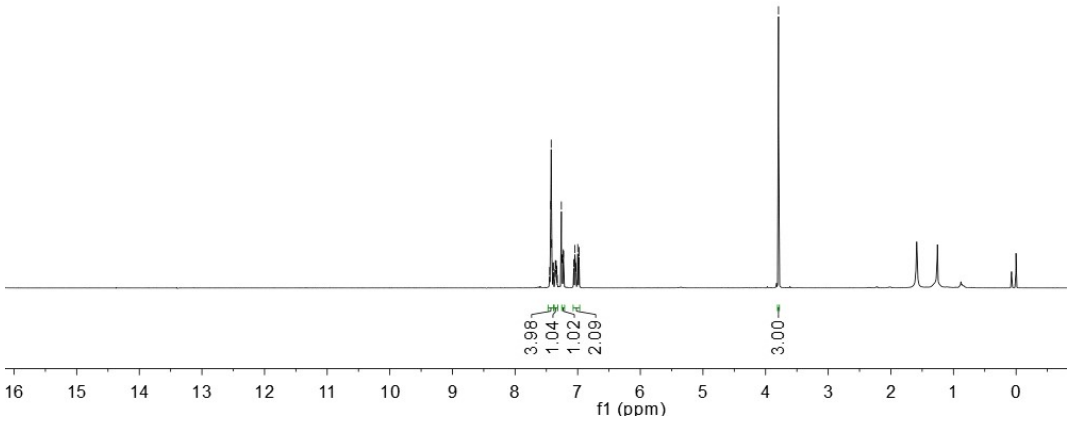
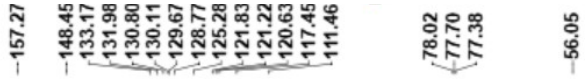


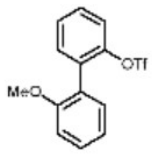
Figure S28. The NMR spectrums of **3z**

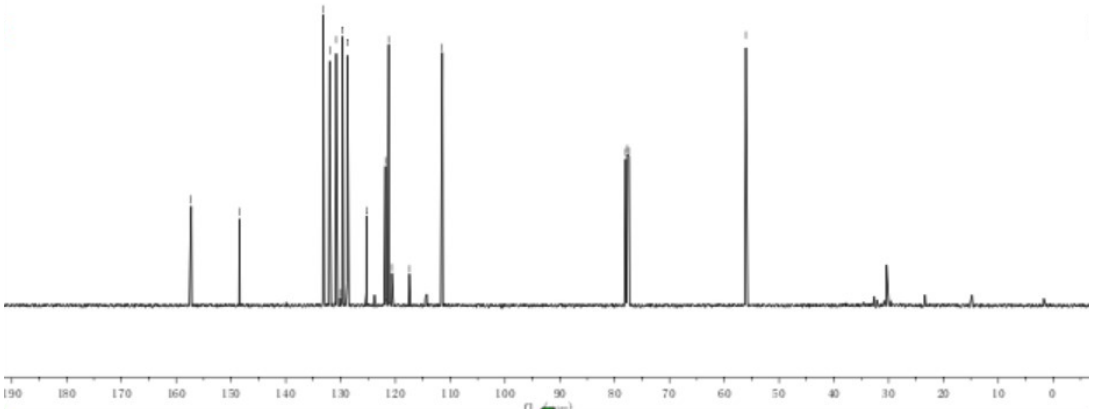

OMe
TfO


7.45
7.43
7.42
7.42
7.39
7.39
7.36
7.36
7.35
7.34
7.34
7.33
7.33
7.26
7.25
7.24
7.23
7.23
7.06
7.04
7.03
7.00
6.98
3.79


3.98
1.04
1.02
2.09
3.00
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


157.27
148.45
133.17
131.98
130.80
130.11
129.67
128.77
125.28
121.83
121.22
120.63
117.45
111.46
78.02
77.70
77.38
56.05


OTf
MeO


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

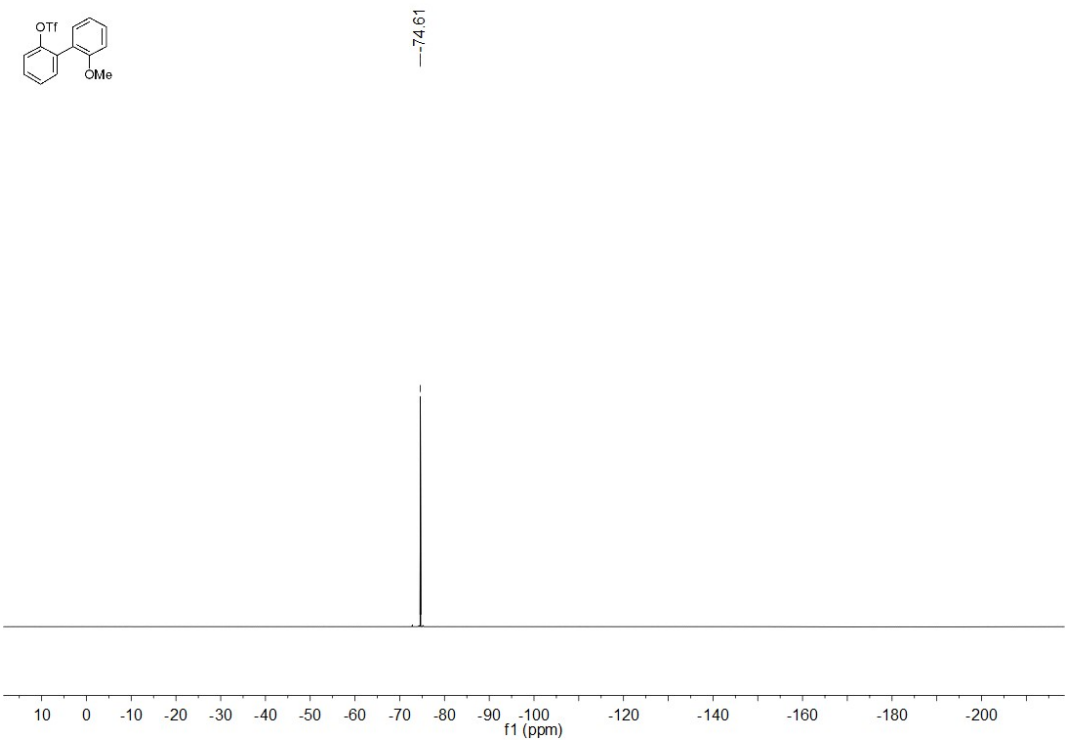
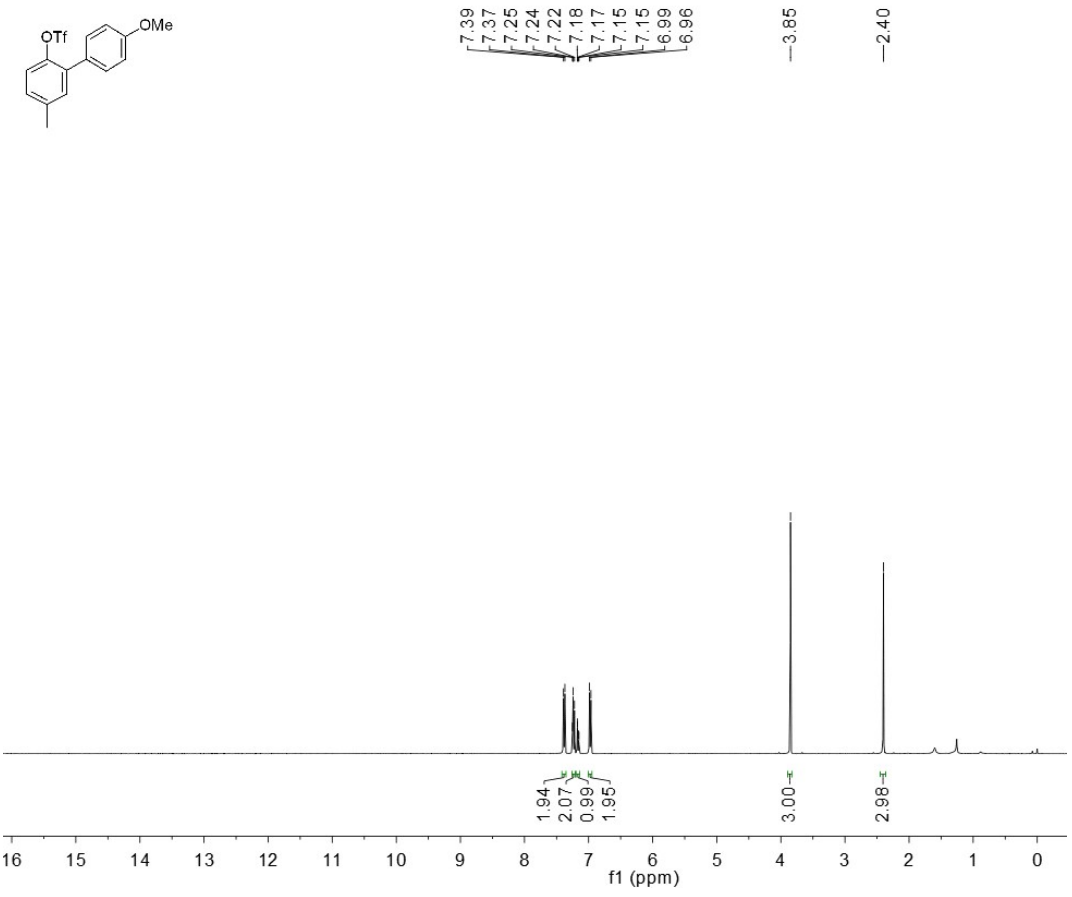
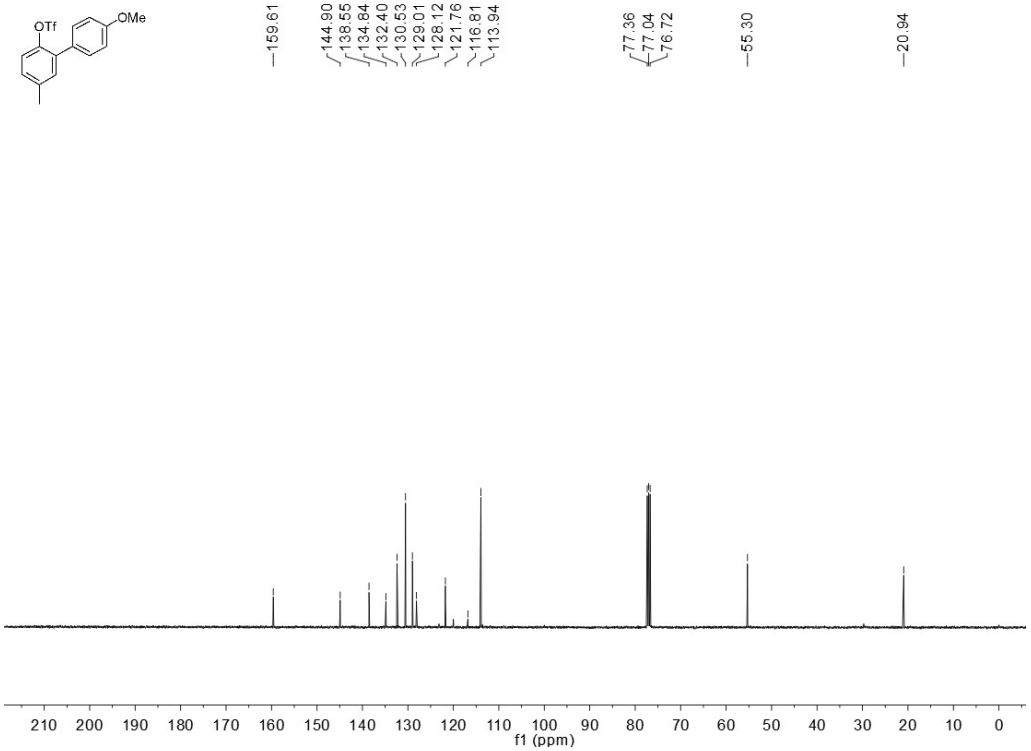


Figure S29. The NMR spectrums of **4a**





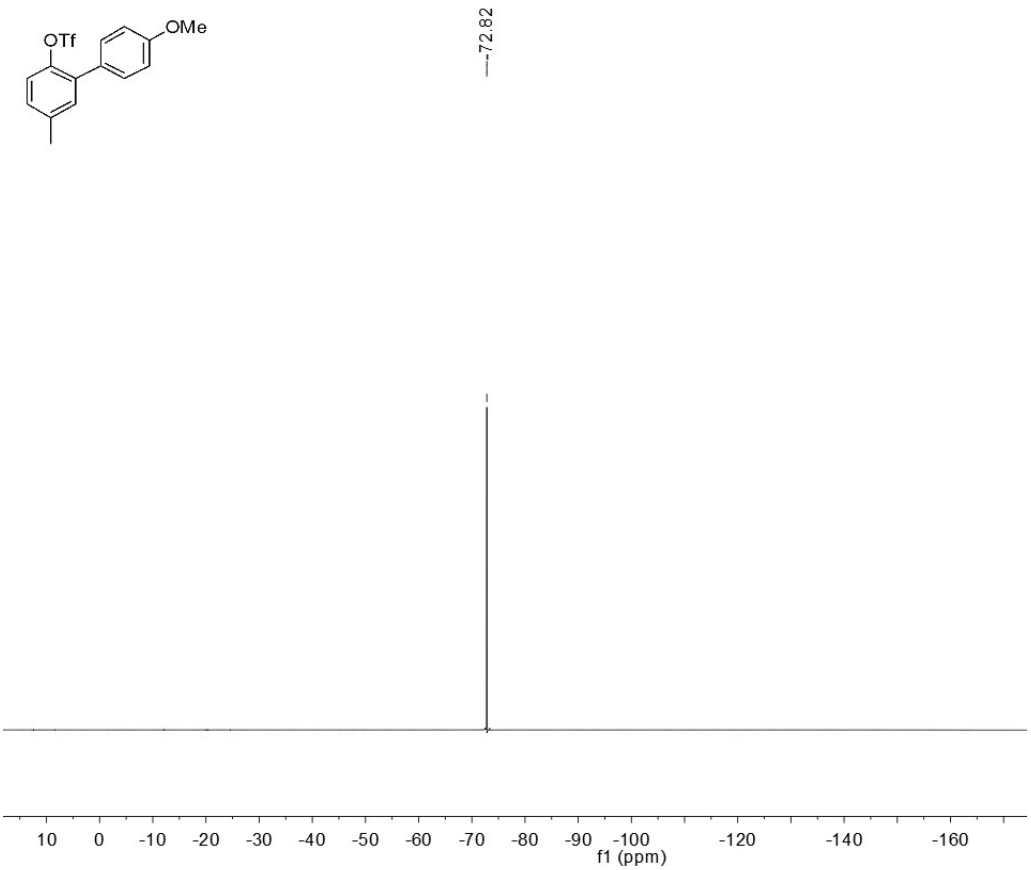


Figure S30. The NMR spectrums of **4b**

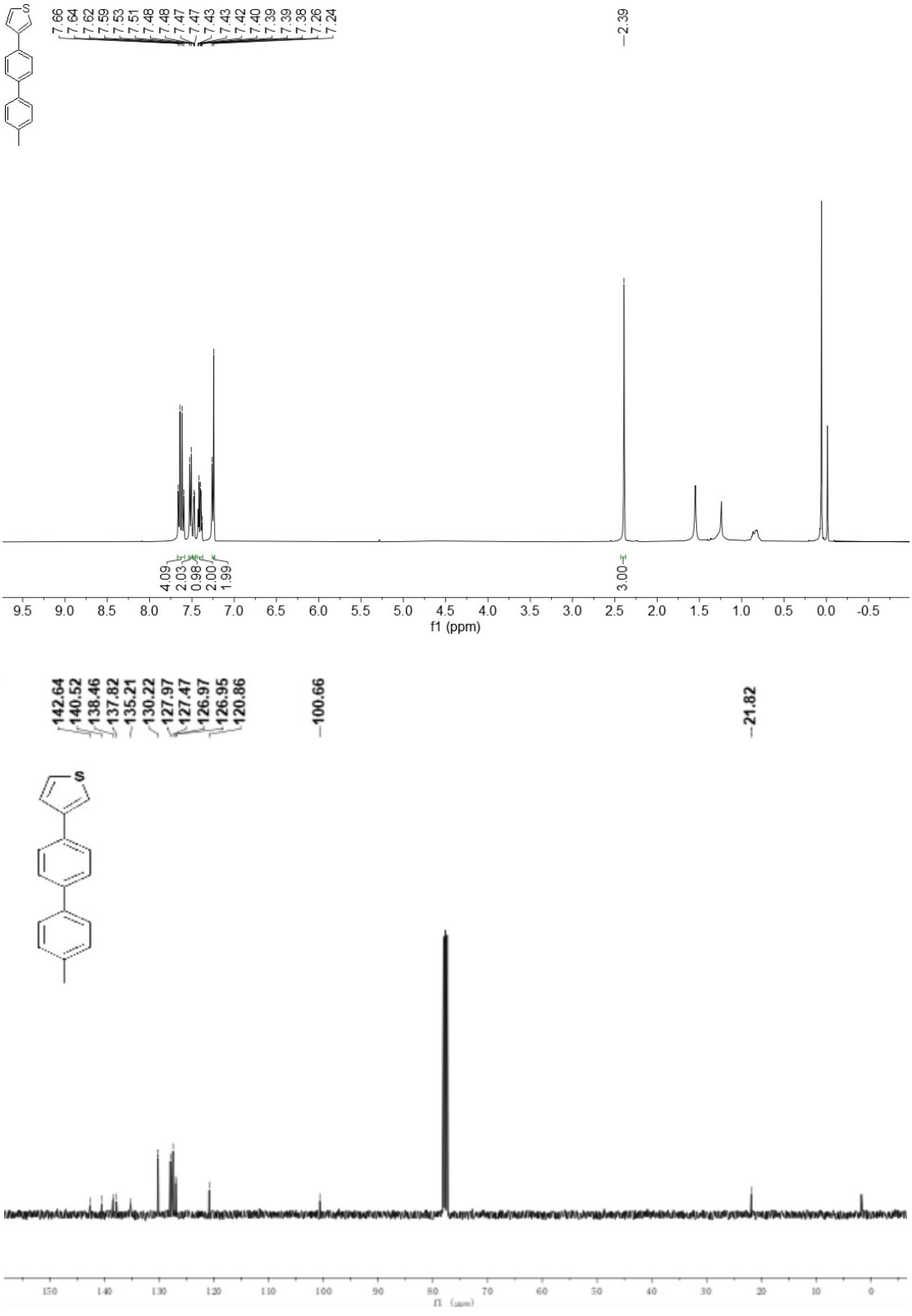
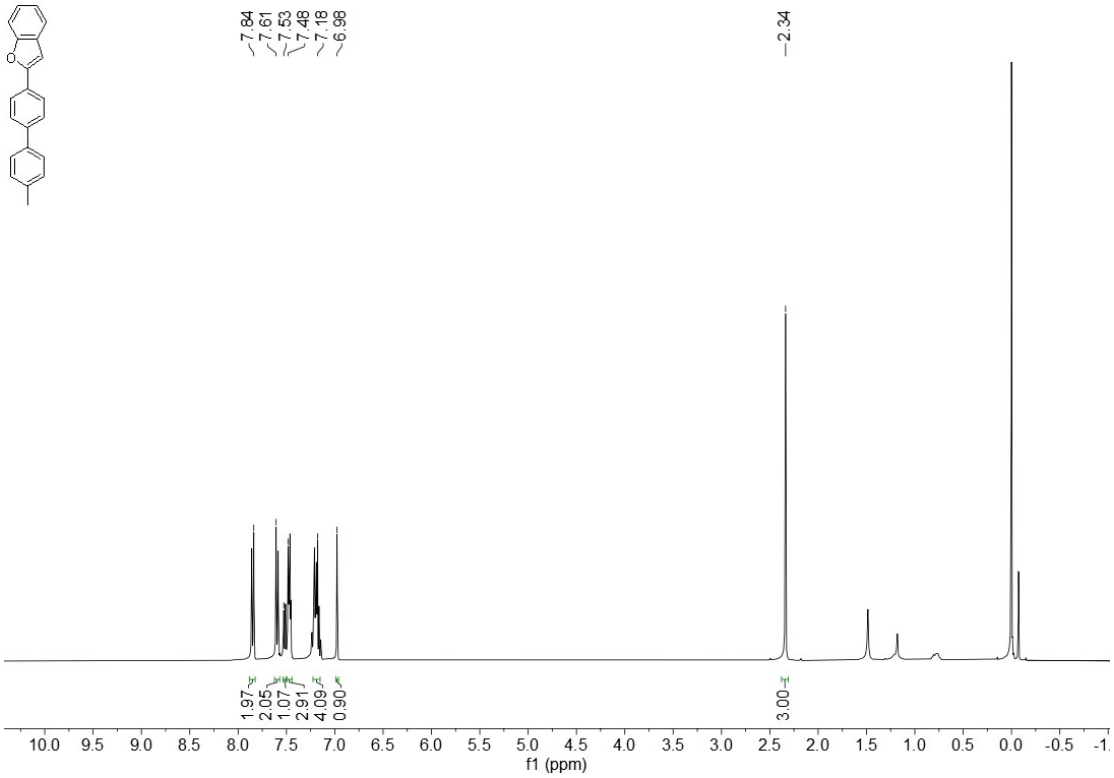


Figure S31. The NMR spectrums of **5a**



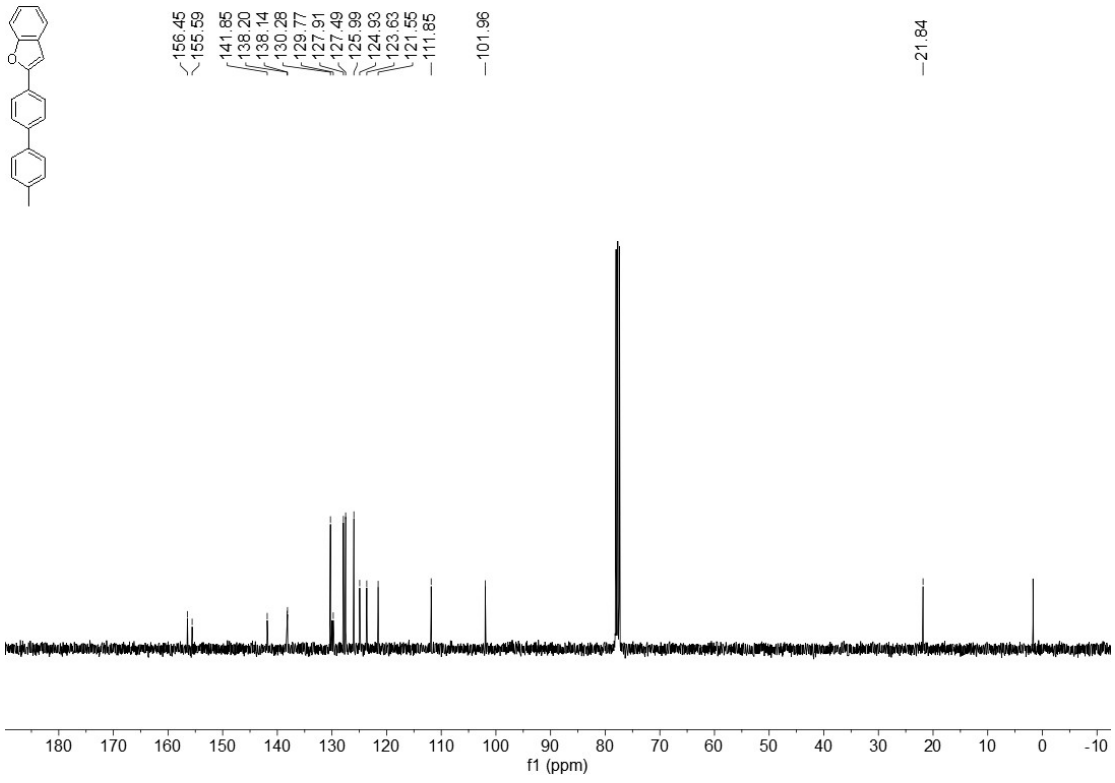
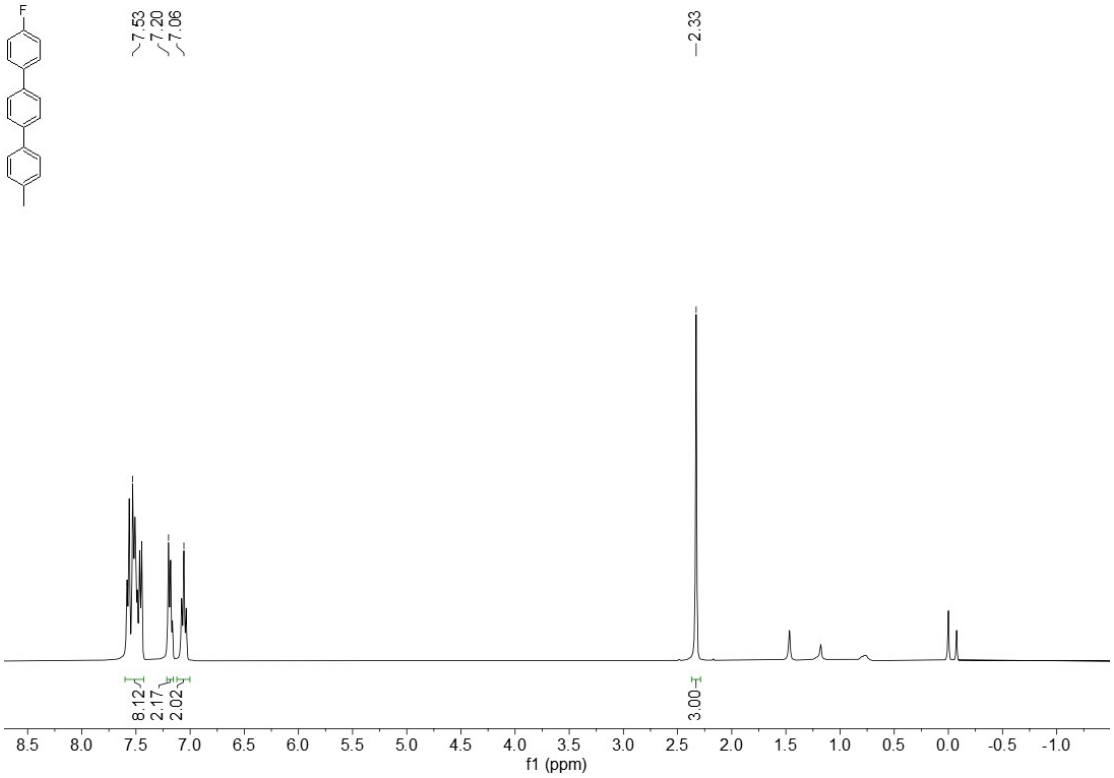


Figure S32. The NMR spectrums of **5b**



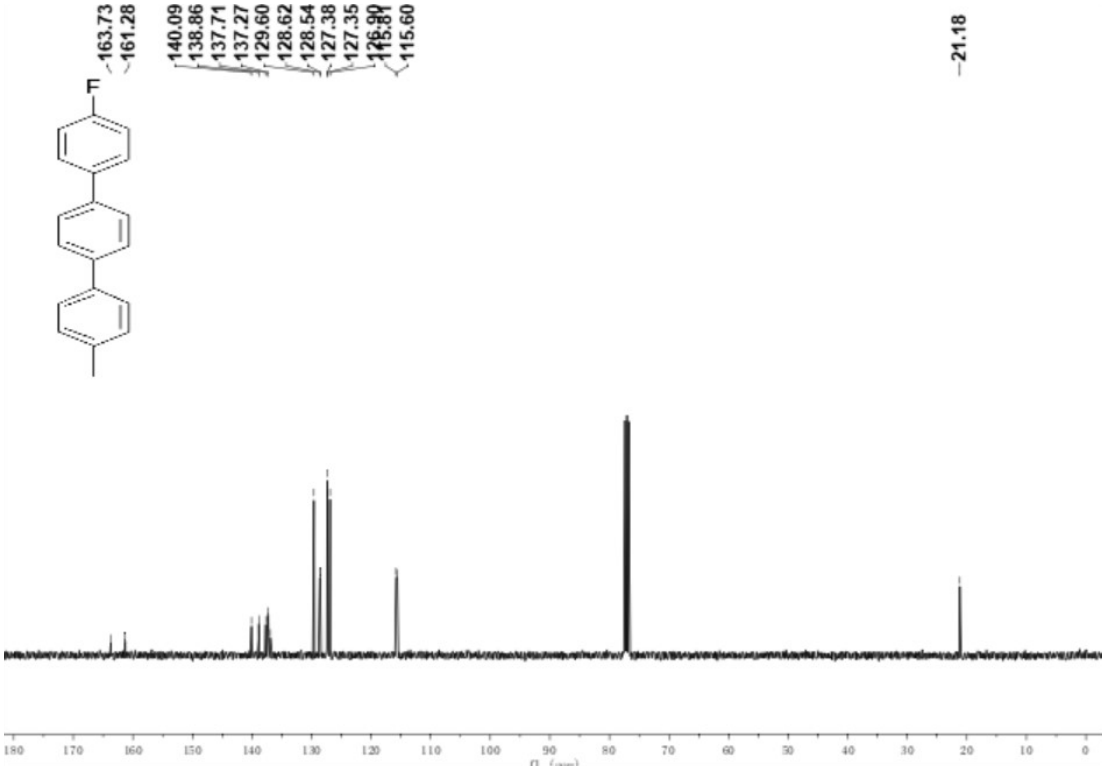


Figure S33. The NMR spectrums of **5c**

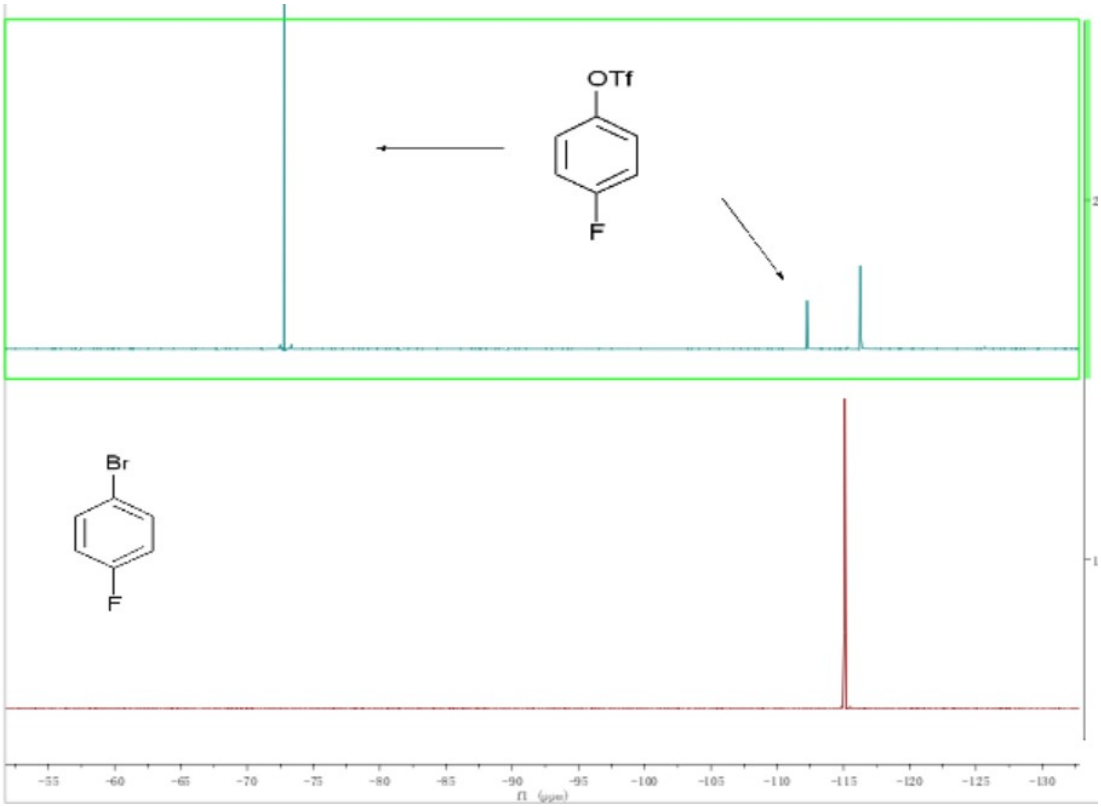


Figure S34. The ^{19}F NMR spectrums of 1-bromo-4-fluorobenzene (lower) and the crude product of competitive Suzuki reaction (upper)

6. References

1. J.-S. Ouyang, Y.-F. Li, D.-S. Shen, Z. Ke and F.-S. Liu, *Dalton Trans.*, 2016, **45**, 14919-14927
2. F.-M. Chen, D.-D. Lu, L.-Q. Hu, J. Huang and F.-S. Liu, *Org. Biomol. Chem.*, 2017, **15**, 5731-5736.
3. L.-Q. Hu, R.-L. Deng, Y.-F. Li, C.-J. Zeng, D.-S. Shen and F.-S. Liu, *Organometallics*, 2018, **37**, 214-226.