Supporting Information

Palladium-catalyzed sequential [3+2] cyclization/C-H activation of *o*-iodostyrenes with cyclopropenones as C2 synthons

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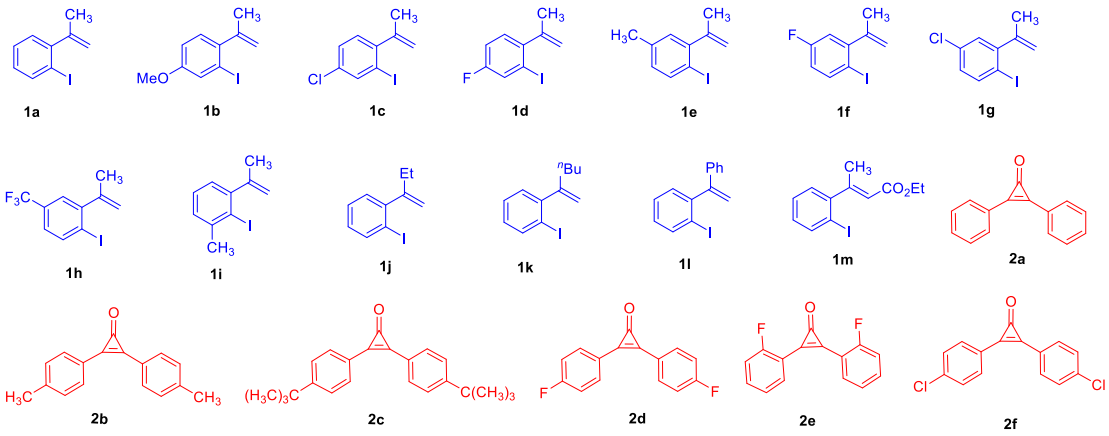
Table of Contents

1. General Considerations

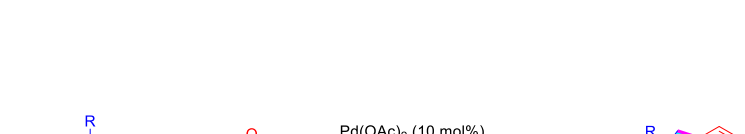
All reactions were carried out under N_2 atmosphere. Materials were obtained from commercial suppliers or prepared according to standard procedures unless otherwise noted. Solvents were purified and dried according to standard methods prior to use. For product purification by flash column chromatography, silica gel (200~300 mesh) and light petroleum ether (bp. 60~90) are used. ^{1}H NMR spectra were recorded on a Bruker advance III 400 MHz in $CDCl_3$ and $^{13}C\{^1H\}$ NMR spectra were recorded on 101 MHz in $CDCl_3$ using TMS as internal standard. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, dd = doublet of doublet, dt = triplet of doublets, ddd = doublet of doublet of doublets, coupling constant (s) in Hz, integration). Data for ^{13}C NMR is reported in terms of chemical shift (δ, ppm). High-resolution mass spectral analysis (HRMS) data were measured on a Bruker Apex II.

2. Preparation of Substrates

Substrates **1** were synthesized according to the known literature.[1-5] Substrates **2** were prepared through the known literatures.[6]

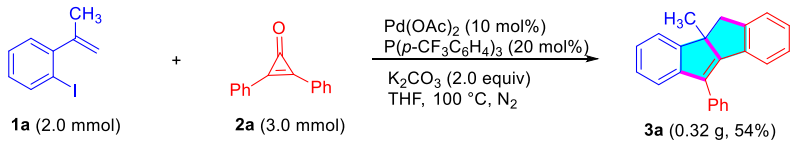


3. Experiment Procedure



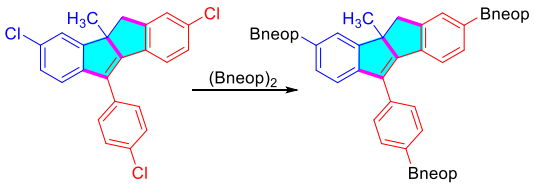
O-iodostyrenes **1** (0.2 mmol, 1.0 equiv), cyclopropenones **2** (0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (10 mol%), $P(p\text{-}CF_3C_6H_4)_3$ (20 mol%), K_2CO_3 (0.4 mmol, 2.0 equiv) were added to a sealed tube, THF (4.0 mL, 0.05 M) were added via syringe. The mixture was flushed with N_2 and heated at 100 ℃ in an oil bath until only trace amounts of solvent remained. After cooling at room temperature, CH_2Cl_2 (5 mL) was added and the mixture was evaporated under reduced pressure. The residue was purified through silica gel chromatography to afford the products **3**.

4. Scale-Up Reaction



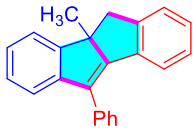
O-iodostyrenes **1a** (2.0 mmol, 1.0 equiv), cyclopropenones **2a** (3.0 mmol, 1.5 equiv), $Pd(OAc)_2$ (10 mol%), $P(p\text{-}CF_3C_6H_4)_3$ (20 mol%), K_2CO_3 (4.0 mmol, 2.0 equiv) were added to a sealed tube, THF (40 mL, 0.05 M) were added via syringe. The mixture was flushed with N_2 and heated at 100 ℃ in an oil bath until only trace amounts of solvent remained. After cooling at room temperature, CH_2Cl_2 (50 mL) was added and the reaction mixture was filtered through celite. The solvent in the filtrate was evaporated under reduced pressure. The residue was purified through silica gel chromatography to afford the products **3a** with 54% yield.

5. Synthesis of Polyboron Tetracyclic Product 4



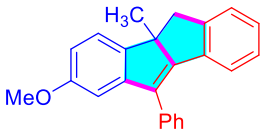
Under nitrogen atmosphere, **3u** (79.4 mg, 0.2 mmol), $(Bneop)_2$ (203.4 mg, 0.9 mmol), $Pd(PCy_3)_2Cl_2$ (7.5 mol%), KOAc (180 mg, 1.8 mmol), and xylene (3 mL) were added to a Schlenk flask. The reaction mixture was stirred under 140 ℃ for 24 h. After the indicated time the reaction mixture was quenched with water and extracted with EA. The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, and concentrated at the reduced pressure. The residue was purified by flash silica gel column chromatography to provide the pure product **4** (45% yield).

6. Spectra Data



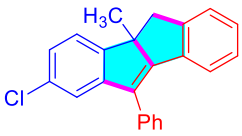
3a

4b-methyl-10-phenyl-4b,5-dihydroindeno[2,1-a]indene ***(3a)***: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a pale yellow solid, Mp = 115-117 ℃, 40 mg, 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 7.5, 1.7 Hz, 2H), 7.45 (d, *J* = 7.5 Hz, 1H), 7.41-7.26 (m, 5H), 7.20-7.10 (m, 3H), 7.03 (dt, *J* = 20.8, 7.3 Hz, 2H), 2.94 (d, *J* = 14.4 Hz, 1H), 2.73 (d, *J* = 14.4 Hz, 1H), 1.34 (d, *J* = 1.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 151.5, 151.4, 146.7, 135.7, 134.9, 133.2, 129.4, 128.5, 127.8, 127.5, 127.0, 126.8, 126.2, 125.1, 122.9, 122.8, 121.5, 62.0, 40.4, 27.2. HRMS (APCI-TOF) calcd for $C_{23}H_{19}$ $[M+H]^+$: 295.1481, found: 295.1479.



3b

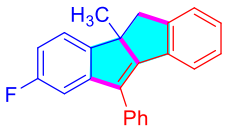
2-methoxy-4b-methyl-10-phenyl-4b,5-dihydroindeno[2,1-a]indene ***(3b)***: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1~50:1, v/v) affords the title compound as a yellow solid, Mp = 131-133 ℃, 40 mg, 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.50 (m, 2H), 7.46-7.38 (m, 3H), 7.31 (d, *J* = 7.4 Hz, 1H), 7.23 (dd, *J* = 18.2, 7.7 Hz, 2H), 7.07-6.99 (m, 2H), 6.87 (d, *J* = 2.4 Hz, 1H), 6.69 (dd, *J* = 8.1, 2.4 Hz, 1H), 3.71 (s, 3H), 2.93 (d, *J* = 14.4 Hz, 1H), 2.71 (d, *J* = 14.4 Hz, 1H), 1.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.2, 159.4, 151.4, 148.2, 143.8, 135.8, 134.9, 133.1, 129.4, 128.5, 127.8, 127.6, 126.8, 126.2, 123.3, 122.8, 110.4, 107.4, 61.3, 55.6, 40.7, 27.3. HRMS (APCI-TOF) calcd for $C_{24}H_{21}O$ $[M+H]^+$: 325.1587, found: 325.1590.



3c

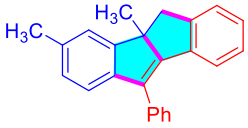
2-chloro-4b-methyl-10-phenyl-4b,5-dihydroindeno[2,1-a]indene ***(3c)***: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow solid, Mp = 65-67 ℃, 39 mg, 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.3 Hz, 2H), 7.43 (q, *J* = 7.3 Hz, 3H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.27-7.25 (m, 2H), 7.22 (d, *J* = 7.3 Hz, 1H), 7.12-7.08 (m, 2H), 7.04 (d, *J* = 7.5 Hz, 1H), 2.96 (d, *J* = 14.4 Hz, 1H), 2.73 (d, *J* = 14.5 Hz, 1H), 1.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 151.3, 149.6, 148.6, 135.4, 134.3, 133.0, 132.3, 129.3, 128.6, 128.1, 128.0, 127.0, 126.3, 124.9, 123.8, 123.0, 121.6, 61.6,

40.4, 27.2. HRMS (APCI-TOF) calcd for $C_{23}H_{18}Cl$ $[M+H]^+$: 329.1092, found: 329.1090.



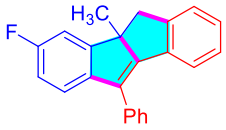
3d

2-fluoro-4b-methyl-10-phenyl-4b,5-dihydroindeno[2,1-a]indene ***(3d)***: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a pale yellow solid, Mp = 79-81 ℃, 32 mg, 52% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.49 (m, 2H), 7.47-7.38 (m, 3H), 7.32 (d, *J* = 7.4 Hz, 1H), 7.28-7.20 (m, 2H), 7.08 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.05-6.97 (m, 2H), 6.80 (ddd, *J* = 9.2, 8.1, 2.4 Hz, 1H), 2.94 (d, *J* = 14.4 Hz, 1H), 2.72 (d, *J* = 14.5 Hz, 1H), 1.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9 (d, *J* = 243.2 Hz), 160.9, 151.4, 148.8 (d, *J* = 8.5 Hz), 146.8 (d, *J* = 2.4 Hz), 135.5, 134.4, 129.3, 128.6, 128.0, 127.9, 127.0, 126.3, 123.6, 123.5, 122.9, 111.5 (d, *J* = 23.0 Hz), 108.6 (d, *J* = 23.5 Hz), 61.5, 40.5, 27.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.95. HRMS (APCI-TOF) calcd for $C_{23}H_{18}F$ $[M+H]^+$: 313.1387, found: 313.1379.



3e

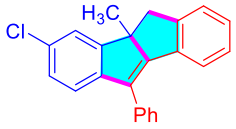
3,4b-dimethyl-10-phenyl-4b,5-dihydroindeno[2,1-a]indene ***(3e)***: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a pale yellow solid, Mp = 126-128 ℃, 42 mg, 69% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.51 (m, 2H), 7.47-7.43 (m, 1H), 7.39 (dd, *J* = 8.4, 6.7 Hz, 2H), 7.33-7.27 (m, 1H), 7.20 (d, *J* = 7.9 Hz, 3H), 7.07-6.99 (m, 3H), 2.93 (d, *J* = 14.4 Hz, 1H), 2.74 (d, *J* = 14.4 Hz, 1H), 2.35 (s, 3H), 1.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 151.8, 151.2, 144.1, 135.9, 135.1, 135.0, 133.3, 129.4, 128.4, 127.72, 127.66, 127.4, 126.8, 126.2, 124.0, 122.7, 121.2, 61.8, 40.4, 27.3, 21.7. HRMS (APCI-TOF) calcd for $C_{24}H_{21}$ $[M+H]^+$: 309.1638, found: 309.1640.



3f

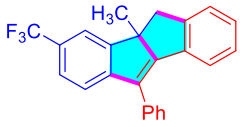
3-fluoro-4b-methyl-10-phenyl-4b,5-dihydroindeno[2,1-a]indene ***(3f)***: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a pale white solid, Mp = 114-116 ℃, 27 mg, 43% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.6 Hz, 2H), 7.47-7.35 (m, 3H), 7.33-7.27 (m, 1H), 7.21 (dd, *J* = 8.3, 5.7 Hz, 2H), 7.09-6.98 (m, 3H), 6.87 (m, 1H), 2.93 (d, *J* = 14.4 Hz, 1H), 2.74 (d, *J* = 14.4 Hz, 1H), 1.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.7 (d, *J* = 245.4 Hz), 158.4 (d, *J* = 4.0 Hz), 153.6 (d, *J* = 7.7 Hz), 150.9, 142.5 (d, *J* = 2.4 Hz), 135.6, 134.7, 132.6, 129.4, 128.5, 127.9, 127.6, 126.9, 126.2, 122.6,

122.0 (d, *J* = 8.6 Hz), 113.7 (d, *J* = 22.6 Hz), 110.9 (d, *J* = 22.9 Hz), 61.8 (d, *J* = 2.3 Hz), 40.2, 27.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.47. HRMS (APCI-TOF) calcd for $C_{23}H_{18}F$ $[M+H]^+$: 313.1387, found: 313.1383.



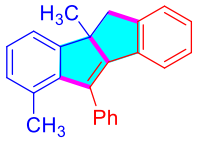
3g

3-chloro-4b-methyl-10-phenyl-4b,5-dihydroindeno[2,1-a]indene ***(3g)***: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a colorless solid, Mp = 92-94 ℃, 42 mg, 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (dt, *J* = 6.3, 1.3 Hz, 2H), 7.47-7.38 (m, 3H), 7.34-7.28 (m, 2H), 7.21 (dd, *J* = 7.9, 2.7 Hz, 2H), 7.16 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.09 (td, *J* = 7.5, 1.3 Hz, 1H), 7.05-7.00 (m, 1H), 2.94 (d, *J* = 14.5 Hz, 1H), 2.74 (d, *J* = 14.5 Hz, 1H), 1.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 153.1, 151.0, 145.2, 135.5, 134.5, 132.5, 131.1, 129.4, 128.6, 128.0, 127.8, 127.2, 127.0, 126.3, 123.6, 122.8, 122.2, 61.9, 40.2, 27.2. HRMS (APCI-TOF) calcd for $C_{23}H_{18}Cl$ $[M+H]^+$: 329.1092, found: 329.1092.



3h

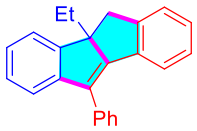
4b-methyl-10-phenyl-3-(trifluoromethyl)-4b,5-dihydroindeno[2,1-a]indene ***(3h)***: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1~50:1, v/v) affords the title compound as a white solid, Mp = 156-158 ℃, 28 mg, 39% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.52 (d, *J* = 7.0 Hz, 2H), 7.45 (dt, *J* = 15.2, 7.5 Hz, 4H), 7.39-7.32 (m, 2H), 7.25 (d, *J* = 7.4 Hz, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 3.01 (d, *J* = 14.5 Hz, 1H), 2.77 (d, *J* = 14.5 Hz, 1H), 1.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.7, 151.6, 151.5, 150.2 (d, *J* = 1.6 Hz), 135.2, 134.3, 132.3, 129.4, 128.7, 128.3, 128.2, 127.1, 126.4, 124.5 (q, *J* = 4.0 Hz), 123.1, 121.3, 119.6 (q, *J* = 3.7 Hz), 62.1, 40.2, 27.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.30. HRMS (APCI-TOF) calcd for $C_{24}H_{18}F_3$ $[M+H]^+$: 363.1355, found: 363.1357.



3i

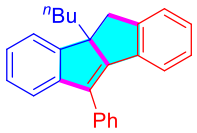
1,4b-dimethyl-10-phenyl-4b,5-dihydroindeno[2,1-a]indene ***(3i)***: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a white solid, Mp = 132-134 ℃, 35 mg, 57% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 6.8 Hz, 1H), 7.41 (dd, *J* = 8.4, 6.4 Hz, 1H), 7.31-7.23 (m, 2H), 7.19 (dd, *J* = 7.3, 5.5 Hz, 2H), 7.16-7.12 (m, 1H), 7.06-7.00 (m, 2H), 6.98-6.87 (m, 3H), 2.95 (dd, *J* = 14.5, 1.6 Hz, 1H),

2.74 (d, *J* = 14.3 Hz, 1H), 1.90 (s, 3H), 1.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 152.2, 150.9, 144.5, 137.5, 135.9, 134.7, 132.9, 130.7, 130.0, 128.9, 128.2, 128.0, 127.4, 127.2, 126.8, 126.0, 125.1, 122.7, 120.6, 61.1, 40.6, 27.3, 20.4. HRMS (APCI-TOF) calcd for $C_{24}H_{21}$ $[M+H]^+$: 309.1638, found: 309.1636.



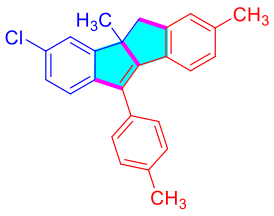
3j

4b-ethyl-10-phenyl-4b,5-dihydroindeno[2,1-a]indene ***(3j)***: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow solid, Mp = 165-167 ℃, 37 mg, 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.52 (m, 2H), 7.46-7.39 (m, 3H), 7.34-7.28 (m, 3H), 7.23-7.18 (m, 2H), 7.13-6.99 (m, 3H), 2.99 (d, *J* = 14.5 Hz, 1H), 2.77 (d, *J* = 14.5 Hz, 1H), 1.95 (dt, *J* = 13.3, 7.3 Hz, 1H), 1.69 (dq, *J* = 14.4, 7.3 Hz, 1H), 0.48 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.9, 151.8, 149.7, 148.1, 136.1, 135.0, 134.6, 129.5, 128.5, 127.8, 127.5, 127.0, 126.8, 126.1, 124.9, 123.1, 122.6, 121.1, 65.8, 39.7, 33.2, 9.0. HRMS (APCI-TOF) calcd for $C_{24}H_{21}$ $[M+H]^+$: 309.1638, found: 309.1638.



3k

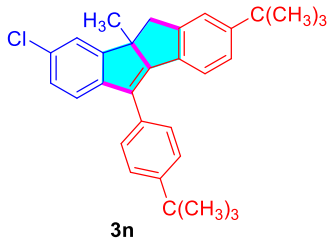
4b-butyl-10-phenyl-4b,5-dihydroindeno[2,1-a]indene ***(3k)***: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a colorless solid, Mp = 167-169 ℃, 36 mg, 54% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.52 (m, 2H), 7.47-7.39 (m, 3H), 7.35-7.28 (m, 3H), 7.19 (ddd, *J* = 8.8, 7.3, 1.6 Hz, 2H), 7.15-7.11 (m, 1H), 7.08-6.99 (m, 2H), 2.99 (d, *J* = 14.5 Hz, 1H), 2.75 (d, *J* = 14.5 Hz, 1H), 1.96-1.87 (m, 1H), 1.63 (td, *J* = 13.3, 12.5, 4.0 Hz, 1H), 1.06-0.94 (m, 3H), 0.76-0.68 (m, 1H), 0.62 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3, 151.8, 150.1, 147.9, 136.2, 135.0, 134.5, 129.5, 128.5, 127.8, 127.5, 127.0, 126.8, 126.1, 124.9, 123.1, 122.6, 121.1, 65.5, 40.2, 40.0, 26.6, 23.2, 14.1. HRMS (APCI-TOF) calcd for $C_{26}H_{25}$ $[M+H]^+$: 337.1951, found: 337.1946.



3m

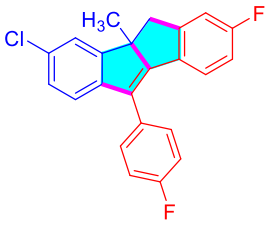
3-chloro-4b,7-dimethyl-10-(p-tolyl)-4b,5-dihydroindeno[2,1-a]indene ***(3m)***: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title

compound as a yellow solid, Mp = 182-184 ℃, 41 mg, 58% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.7 Hz, 2H), 7.37-7.30 (m, 2H), 7.18 (ddd, *J* = 22.1, 8.0, 4.8 Hz, 4H), 7.05 (s, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 2.89 (d, *J* = 14.4 Hz, 1H), 2.71 (d, *J* = 14.5 Hz, 1H), 2.35 (s, 3H), 2.25 (s, 3H), 1.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 153.0, 151.3, 145.5, 137.8, 137.6, 132.9, 131.63, 131.55, 130.7, 129.22, 129.19, 127.7, 127.1, 127.0, 123.4, 122.6, 122.0, 61.8, 40.1, 27.3, 21.7, 21.5. HRMS (APCI-TOF) calcd for $C_{25}H_{22}Cl$ $[M+H]^+$: 357.1405, found: 357.1408.



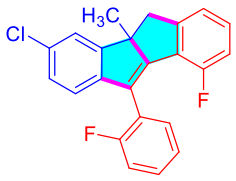
3n

7-(tert-butyl)-10-(4-(tert-butyl)phenyl)-3-chloro-4b-methyl-4b,5-dihydroindeno[2,1-a]indene (***3n***): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a pale blue solid, Mp = 89-91 ℃, 46 mg, 52% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.40 (m, 5H), 7.33 (d, *J* = 2.0 Hz, 1H), 7.28-7.24 (m, 2H), 7.18-7.14 (m, 1H), 7.10 (dd, *J* = 8.0, 1.8 Hz, 1H), 2.96-2.70 (m, 2H), 1.35 (s, 3H), 1.30 (s, 9H), 1.22 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 153.2, 151.2, 151.1, 150.8, 131.7, 131.6, 130.7, 129.0, 127.0, 125.4, 124.0, 123.5, 123.3, 122.3, 122.2, 62.0, 40.4, 34.92, 34.86, 31.6, 31.5, 27.4. HRMS (APCI-TOF) calcd for $C_{31}H_{34}Cl$ $[M+H]^+$: 441.2344, found: 441.2337.



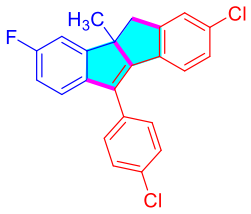
3o

3-chloro-7-fluoro-10-(4-fluorophenyl)-4b-methyl-4b,5-dihydroindeno[2,1-a]indene (***3o***): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a pale yellow solid, Mp = 121-123 ℃, 36 mg, 49% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.42 (m, 2H), 7.36-7.30 (m, 2H), 7.18-7.07 (m, 4H), 6.96-6.92 (m, 1H), 6.74 (td, *J* = 8.8, 2.4 Hz, 1H), 2.93 (d, *J* = 14.7 Hz, 1H), 2.74 (d, *J* = 14.7 Hz, 1H), 1.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9 (d, *J* = 248.9 Hz), 162.5 (d, *J* = 248.3 Hz), 157.8, 153.4 (d, *J* = 8.3 Hz), 152.7, 145.0, 131.3 (d, *J* = 2.8 Hz), 131.2, 131.0 (d, *J* = 1.6 Hz), 130.93, 130.85, 130.3 (d, *J* = 3.3 Hz), 127.3, 123.6, 123.5, 122.0, 115.8, 115.6, 114.0 (t, *J* = 23.1 Hz), 62.2, 40.2 (d, *J* = 2.0 Hz), 27.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.31, -113.41. HRMS (APCI-TOF) calcd for $C_{23}H_{16}F_2Cl$ $[M+H]^+$: 365.0903, found: 365.0911.



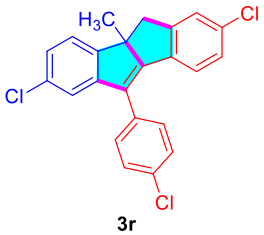
3p

3-chloro-9-fluoro-10-(2-fluorophenyl)-4b-methyl-4b,5-dihydroindeno[2,1-a]indene ***(3p)***: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a white solid, Mp = 135-137 ℃, 29 mg, 41% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.26 (m, 2H), 7.25-6.84 (m, 7H), 6.77 (t, *J* = 8.6 Hz, 1H), 2.97 (d, *J* = 14.5 Hz, 1H), 2.78 (d, *J* = 14.5 Hz, 1H), 1.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.6 (d, *J* = 248.9 Hz), 155.4 (d, *J* = 268.5 Hz), 152.0, 145.3, 131.9, 131.3, 130.7, 129.8 (d, *J* = 8.1 Hz), 129.5, 127.4, 123.8, 123.3, 122.7, 122.4, 122.0, 115.8, 115.6, 114.5, 62.8, 40.1(d, *J* = 2.0 Hz), 27.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.90, -111.72. HRMS (APCI-TOF) calcd for $C_{23}H_{16}F_2Cl$ $[M+H]^+$: 365.0903, found: 365.0907.



3q

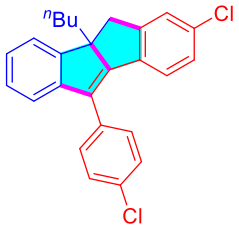
7-chloro-10-(4-chlorophenyl)-3-fluoro-4b-methyl-4b,5-dihydroindeno[2,1-a]indene ***(3q)***: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a pale yellow solid, Mp = 146-148 ℃, 35 mg, 46% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (q, *J* = 8.5 Hz, 4H), 7.29 (d, *J* = 8.2 Hz, 1H), 7.22 (s, 1H), 7.18-7.14 (m, 1H), 7.05 (ddd, *J* = 20.0, 8.3, 2.2 Hz, 2H), 6.91 (td, *J* = 8.8, 2.4 Hz, 1H), 2.94 (d, *J* = 14.7 Hz, 1H), 2.74 (d, *J* = 14.7 Hz, 1H), 1.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.0 (d, *J* = 246.3 Hz), 157.4 (d, *J* = 4.2 Hz), 153.2 (d, *J* = 7.8 Hz), 152.6, 141.9 (d, *J* = 2.5 Hz), 133.9, 133.6, 132.9, 132.0, 130.5, 128.9, 127.3, 126.6, 123.2, 122.0 (d, *J* = 8.7 Hz), 113.9 (d, *J* = 22.8 Hz), 111.0 (d, *J* = 23.1 Hz), 62.0 (d, *J* = 2.3 Hz), 40.1, 27.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.67. HRMS (APCI-TOF) calcd for $C_{23}H_{16}FCl_2$ $[M+H]^+$: 381.0608, found: 381.0610.



3r

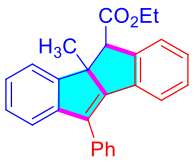
2,7-dichloro-10-(4-chlorophenyl)-4b-methyl-4b,5-dihydroindeno[2,1-a]indene ***(3r)***: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow solid, Mp = 88-90 ℃, 31 mg, 40% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 0.9 Hz, 4H), 7.27 (dd, *J* = 14.1, 8.0 Hz, 2H), 7.23-7.19 (m, 2H), 7.12 (dd, *J* = 7.9,

1.9 Hz, 1H), 7.02 (dd, *J* = 8.2, 2.0 Hz, 1H), 2.94 (d, *J* = 14.7 Hz, 1H), 2.71 (d, *J* = 14.7 Hz, 1H), 1.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4, 153.0, 149.2, 148.0, 134.02, 133.97, 133.6, 133.3, 132.5, 131.6, 130.5, 129.0, 127.4, 126.7, 125.3, 123.9, 123.6, 121.5, 61.9, 40.2, 27.1. HRMS (APCI-TOF) calcd for $C_{23}H_{16}Cl_3$ $[M+H]^+$: 397.0312, found: 397.0309.



3s

4b-butyl-7-chloro-10-(4-chlorophenyl)-4b,5-dihydroindeno[2,1-a]indene (***3s***): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow solid, Mp = 57-59 ℃, 40 mg, 50% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.30 (dd, *J* = 13.7, 7.7 Hz, 2H), 7.21 (dt, *J* = 13.9, 3.8 Hz, 3H), 7.17-7.13 (m, 1H), 7.02-6.98 (m, 1H), 2.97 (d, *J* = 14.8 Hz, 1H), 2.72 (d, *J* = 14.7 Hz, 1H), 1.89 (ddd, *J* = 13.2, 11.1, 4.4 Hz, 1H), 1.60 (td, *J* = 12.7, 4.0 Hz, 1H), 1.04-0.90 (m, 3H), 0.63 (t, *J* = 7.0 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3, 153.5, 149.8, 147.3, 134.4, 133.7, 133.4, 133.2, 132.9, 130.6, 128.9, 128.8, 127.2, 127.1, 126.5, 125.3, 123.2, 123.1, 121.0, 65.8, 40.1, 39.8, 26.6, 23.1, 14.1. HRMS (APCI-TOF) calcd for $C_{26}H_{23}Cl_2$ $[M+H]^+$: 405.1171, found: 405.1171.

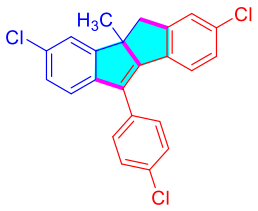


3t, 1.8:1 dr

ethyl 4b-methyl-10-phenyl-4b,5-dihydroindeno[2,1-a]indene-5-carboxylate (***3t***, *major)*: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1~30:1, v/v) affords the title compound as a pale red solid, Mp = 135-137 ℃, 33 mg, 45% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.46 (m, 3H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.39-7.27 (m, 4H), 7.22-7.10 (m, 4H), 4.04 (s, 1H), 3.73 (dq, *J* = 10.7, 7.1 Hz, 1H), 3.43 (dq, *J* = 10.7, 7.1 Hz, 1H), 1.38 (s, 3H), 0.56 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 156.7, 148.9, 147.8, 147.3, 136.1, 134.9, 134.3, 129.2, 128.6, 128.4, 127.9, 127.8, 127.3, 126.5, 125.2, 123.19, 123.15, 121.5, 64.6, 60.4, 57.2, 28.0, 13.7. HRMS (APCI-TOF) calcd for $C_{26}H_{23}O_2$ $[M+H]^+$: 367.1693, found: 367.1693.

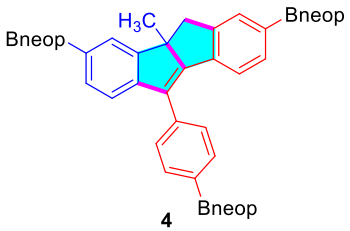
ethyl 4b-methyl-10-phenyl-4b,5-dihydroindeno[2,1-a]indene-5-carboxylate (***3t***, *minor)*: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a pale red solid, Mp = 131-133 ℃, 18 mg, 25% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.3 Hz, 1H), 7.57-7.48 (m, 3H), 7.43 (q, *J* = 7.9 Hz, 3H), 7.32 (dd, *J* = 10.8, 7.4 Hz, 2H), 7.25-7.16 (m, 3H), 7.09 (t, *J* = 7.5 Hz, 1H), 4.44 (dq, *J* = 10.9, 7.1 Hz, 1H), 4.33 (dq, *J* = 10.8, 7.2 Hz, 1H), 3.74 (s, 1H), 1.42 (t, *J* = 7.2 Hz, 3H), 1.31 (s, 3H). ^{13}C NMR (101

MHz, $CDCl_3$) δ 171.5, 155.9, 149.9, 147.3, 146.6, 135.4, 134.4, 129.5, 128.5, 128.0, 127.8, 127.73, 127.70, 127.6, 125.5, 124.2, 122.4, 121.5, 64.4, 61.1, 52.9, 23.1, 14.7. HRMS (APCI-TOF) calcd for $C_{26}H_{23}O_2$ $[M+H]^+$: 367.1693, found: 367.1695.



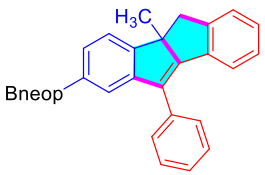
3u

3,7-dichloro-10-(4-chlorophenyl)-4b-methyl-4b,5-dihydroindeno[2,1-a]indene ***(3u)***: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow blue solid, Mp = 119-121 ℃, 37 mg, 47% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.36 (m, 4H), 7.33 (d, *J* = 1.8 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 1H), 7.23 (d, *J* = 2.0 Hz, 1H), 7.20-7.15 (m, 2H), 7.03 (dd, *J* = 8.2, 2.0 Hz, 1H), 2.94 (d, *J* = 14.7 Hz, 1H), 2.73 (d, *J* = 14.7 Hz, 1H), 1.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0, 152.7, 152.7, 144.6, 134.0, 133.8, 133.7, 132.7, 131.9, 131.5, 130.5, 129.0, 127.4, 127.4, 126.7, 123.7, 123.4, 122.1, 62.1, 40.1, 27.1. HRMS (APCI-TOF) calcd for $C_{23}H_{16}Cl_3$ $[M+H]^+$: 397.0312, found: 397.0308.



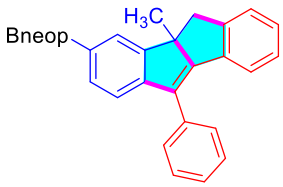
4

2,2'-(5-(4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)phenyl)-9b-methyl-9b,10-dihydroindeno[2,1-a]indene-2,8-diyl)bis(5,5-dimethyl-1,3,2-dioxaborinane) ***(4)***: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50:1~10:1, v/v) affords the title compound as a pale yellow solid, Mp = 191-193 ℃, 57 mg, 45% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.7 Hz, 2H), 7.80 (s, 1H), 7.66 (t, *J* = 4.0 Hz, 2H), 7.54 (d, *J* = 7.8 Hz, 2H), 7.46 (s, 2H), 7.31 (d, *J* = 7.7 Hz, 1H), 3.74-3.66 (m, 12H), 2.97 (d, *J* = 14.4 Hz, 1H), 2.74 (d, *J* = 14.4 Hz, 1H), 1.36 (s, 3H), 0.97 (d, *J* = 4.2 Hz, 12H), 0.93 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.8, 138.0, 137.3, 134.0, 133.9, 133.1, 132.6, 131.4, 128.7, 127.9, 122.4, 120.9, 72.5, 72.5, 62.1, 40.4, 32.1, 32.0, 27.2, 22.1, 22.0. HRMS (APCI-TOF) calcd for $C_{38}H_{46}O_6B_3$ $[M+H]^+$: 631.3568, found: 631.3574.



5

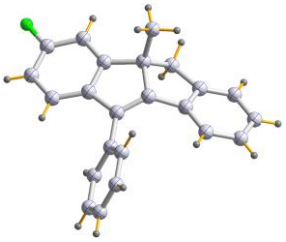
5,5-dimethyl-2-(4b-methyl-10-phenyl-4b,5-dihydroindeno[2,1-a]inden-2-yl)-1,3,2-dioxaborinane ***(5)***: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50:1~20:1, v/v) affords the title compound as a viscous gelatinous state, 56 mg, 69% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.72 (dd, *J* = 7.3, 1.0 Hz, 1H), 7.68-7.61 (m, 2H), 7.55-7.44 (m, 4H), 7.42-7.36 (m, 1H), 7.29 (d, *J* = 7.3 Hz, 1H), 7.17-7.08 (m, 2H), 3.74 (s, 4H), 3.04 (d, *J* = 14.4 Hz, 1H), 2.83 (d, *J* = 14.4 Hz, 1H), 1.43 (s, 3H), 1.00 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 154.3, 151.2, 146.2, 135.9, 135.1, 133.6, 131.2, 129.6, 128.5, 127.7, 127.4, 126.8, 126.7, 126.2, 122.8, 122.4, 72.4, 61.9, 40.3, 32.0, 27.2, 22.0. HRMS (APCI-TOF) calcd for $C_{28}H_{28}O_2B$ $[M+H]^+$: 407.2177, found: 407.2176.



6

5,5-dimethyl-2-(4b-methyl-10-phenyl-4b,5-dihydroindeno[2,1-a]inden-3-yl)-1,3,2-dioxaborinane ***(6)***: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50:1~20:1, v/v) affords the title compound as a pale white solid, Mp = 187-189 ℃, 49 mg, 61% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.75 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.66-7.60 (m, 2H), 7.56-7.47 (m, 3H), 7.42-7.36 (m, 2H), 7.31 (d, *J* = 7.4 Hz, 1H), 7.19-7.09 (m, 2H), 3.81 (s, 4H), 3.05 (d, *J* = 14.4 Hz, 1H), 2.83 (d, *J* = 14.5 Hz, 1H), 1.45 (s, 3H), 1.06 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3, 151.7, 150.6, 149.3, 135.8, 135.0, 133.4, 133.0, 129.5, 128.5, 127.9, 127.8, 127.7, 126.8, 126.3, 122.9, 120.8, 72.5, 62.0, 40.5, 32.1, 27.2, 22.1. HRMS (APCI-TOF) calcd for $C_{28}H_{28}O_2B$ $[M+H]^+$: 407.2177, found: 407.2183.

7. Crystallographic Data of 3f



structure of 3f CCDC: 2390990

Datablock:

Bond precision:	C-C = 0.0022 A		Wavelength = 0.71073
Cell:	a = 11.689(2)	b=17.293(3)	c=8.4188(14)
	alpha=90	beta=102.698(2)	gamma=90
Temperature:	296 K		
	Calculated		Reported
Volume	1660.1(5)		1660.1(5)
Space group	p 21/c		p 21/c
Hall group	-p 2ybc		-p 2ybc
Moiety formula	C23H17F		
Sum formula	C23H17F		C23H17F
Mr	312.37		312.36
Dx,g cm-3	1.250		1.250
Z	4		4
Mu (mm-1)	0.079		0.079
F000	656.0		656.0
F000’	656.29		
h,k,lmax	15,22,10		15,22,10
Nref	3835		3816
Tmin,Tmax			
Tmin’			

Correction method = Not given

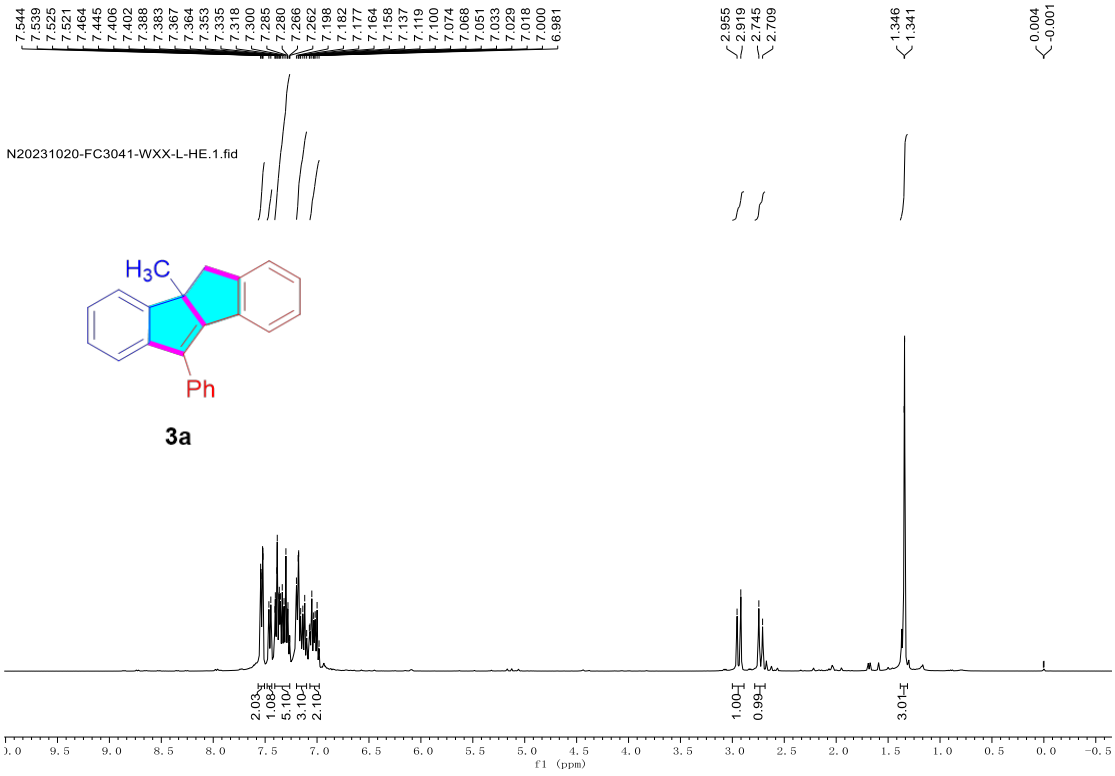
Data completeness = 0.995	Theta (max) = 27.575
R (reflections) = 0.0491(2825)	wR2 (reflections) = 0.1773(3816)
S = 1.273	Npar = 218

8. Reference

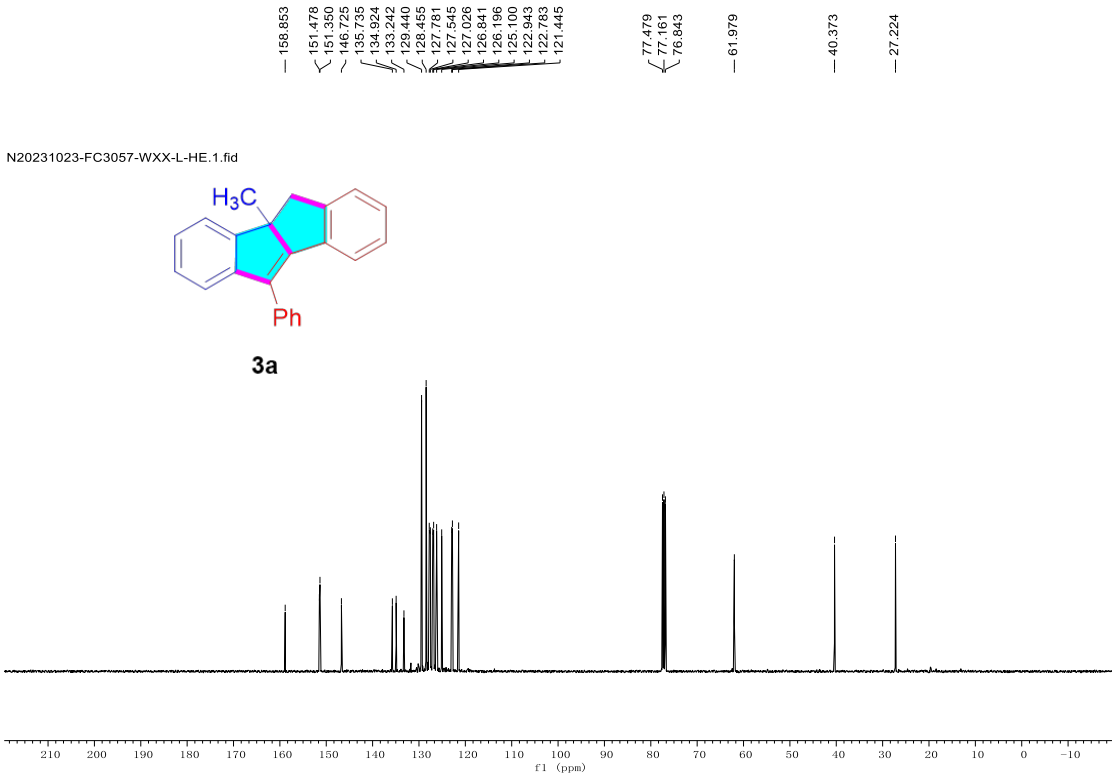
(1) Li, J.; Chen, J.; Wang, L.; Shi, Y. *Org. Lett.* **2021**, *23*, 3646-3651.
(2) Huang, Q.; Larock, R. C. *J. Org. Chem*. **2003**, *68*, 7342.
(3) Yao, T.; Zhang, H.; Zhao, Y. *Org. Lett.* **2016**, *18*, 2532.
(4) Emer, E.; Pfeifer, L.; Brown, J. M.; Gouverneur, V. *Angew. Chem. Int. Ed.* **2014**, *53*, 4181.
(5) Lou, Z.; Zhang, S.; Chen, C.; Pang, X.; Li, M.; Wen, L. *Adv. Synth. Catal.* **2014**, *356*, 153.
(6) Yao, L.; Hu, Q.; Bao, L.; Zhu, W.; Hu, Y. *Org. Lett.* **2021**, *23*, 4971.

9. NMR Spectra

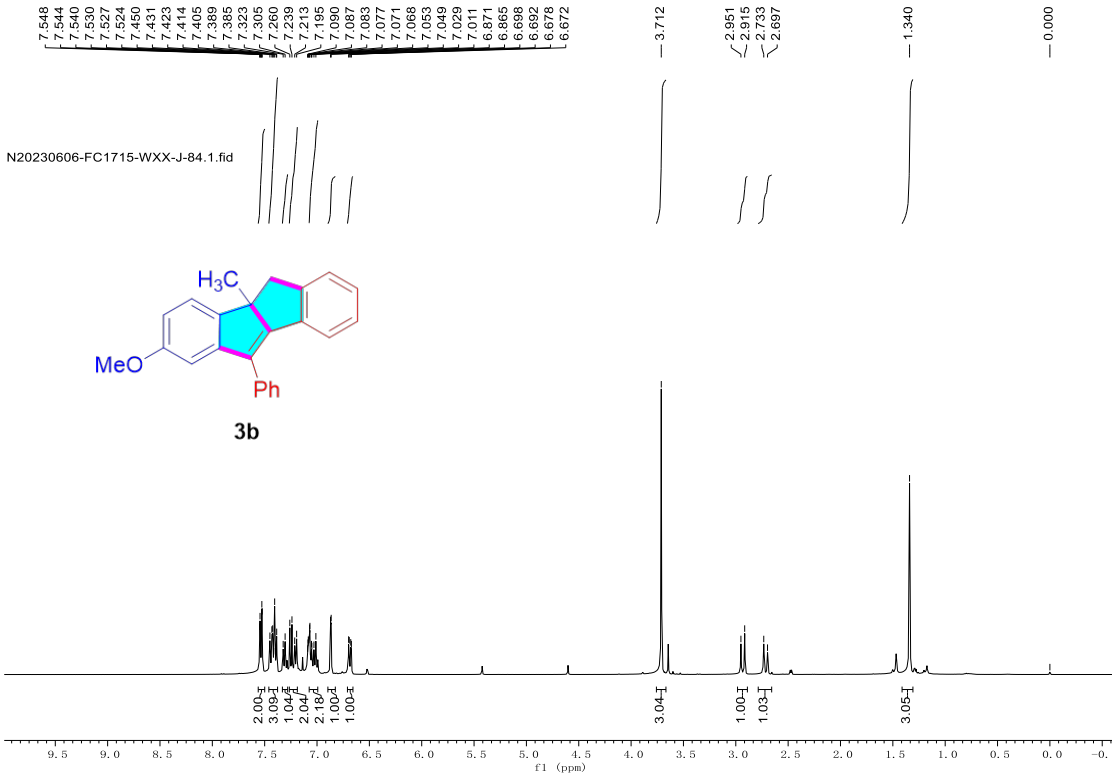
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3a**



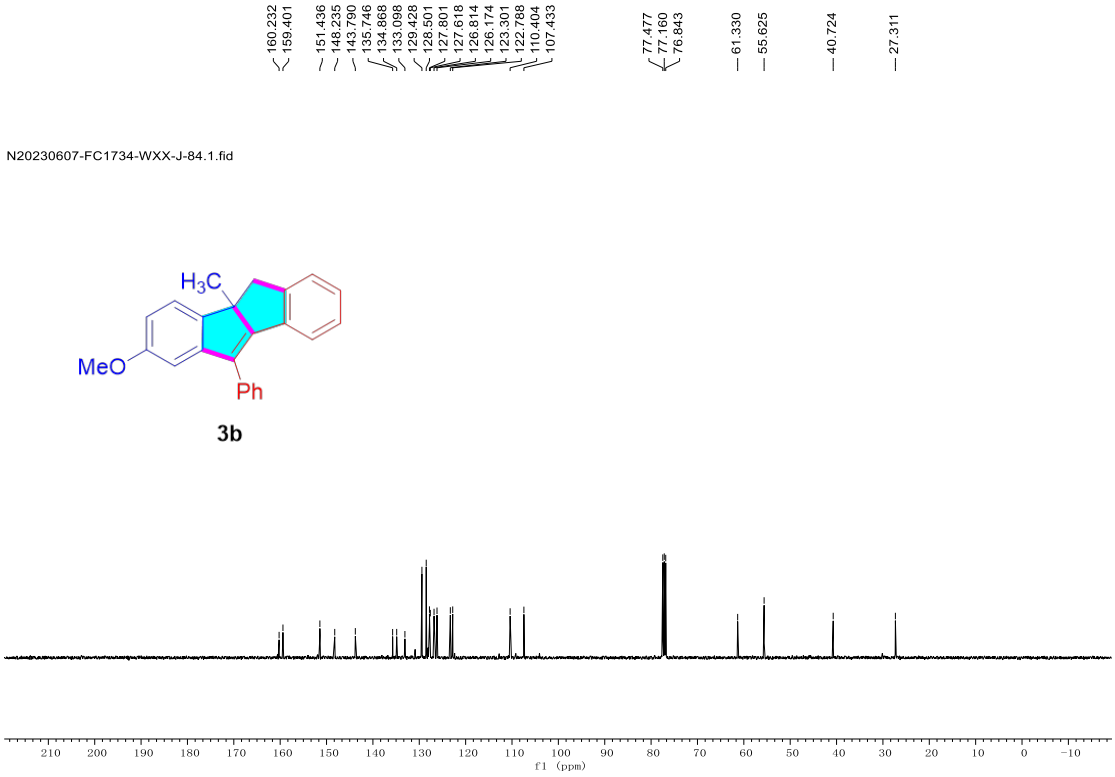
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **3a**



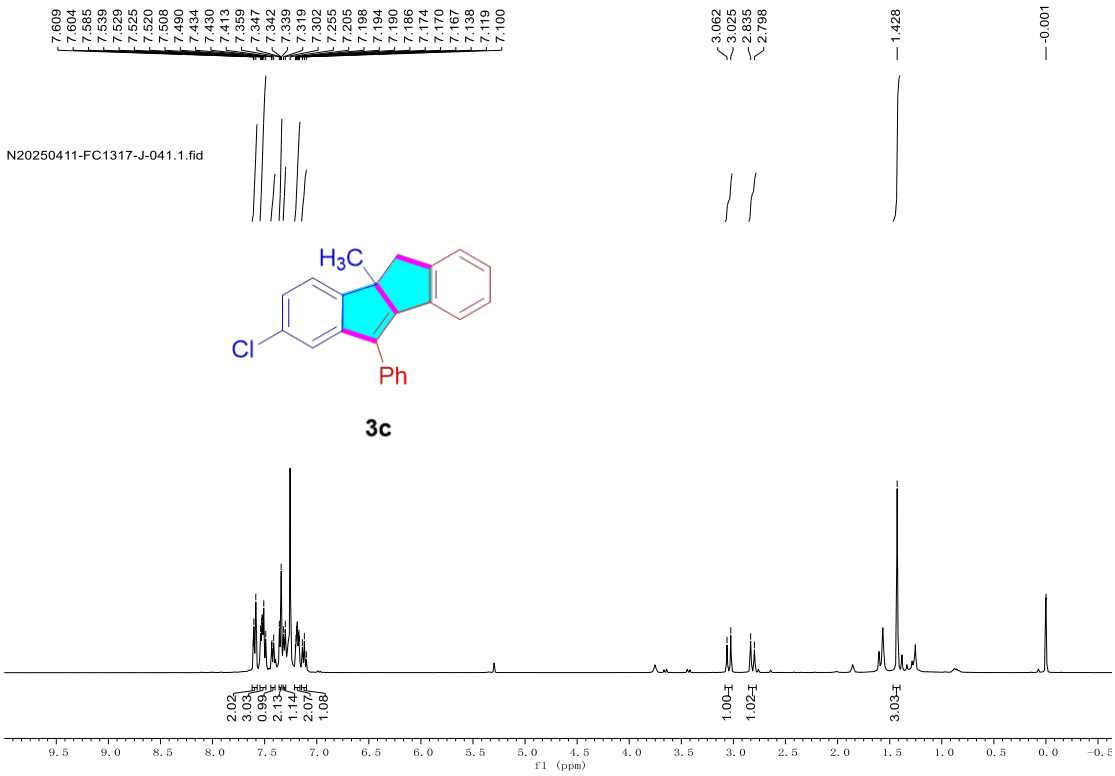
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3b**



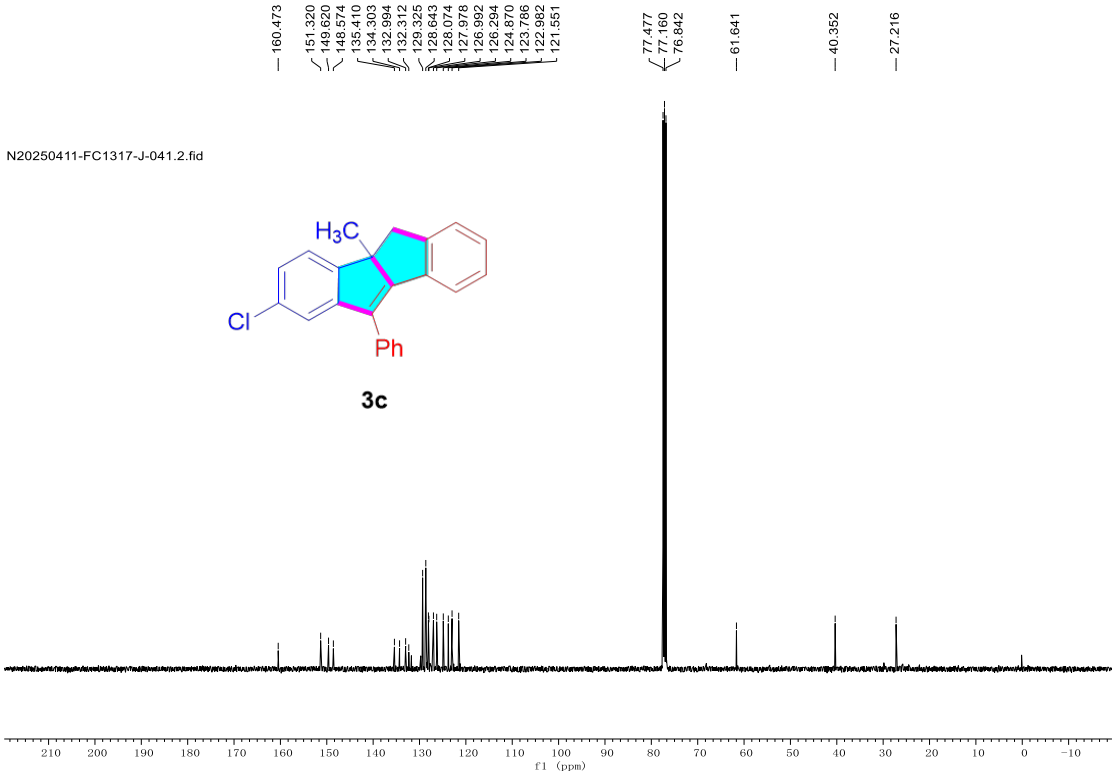
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **3b**



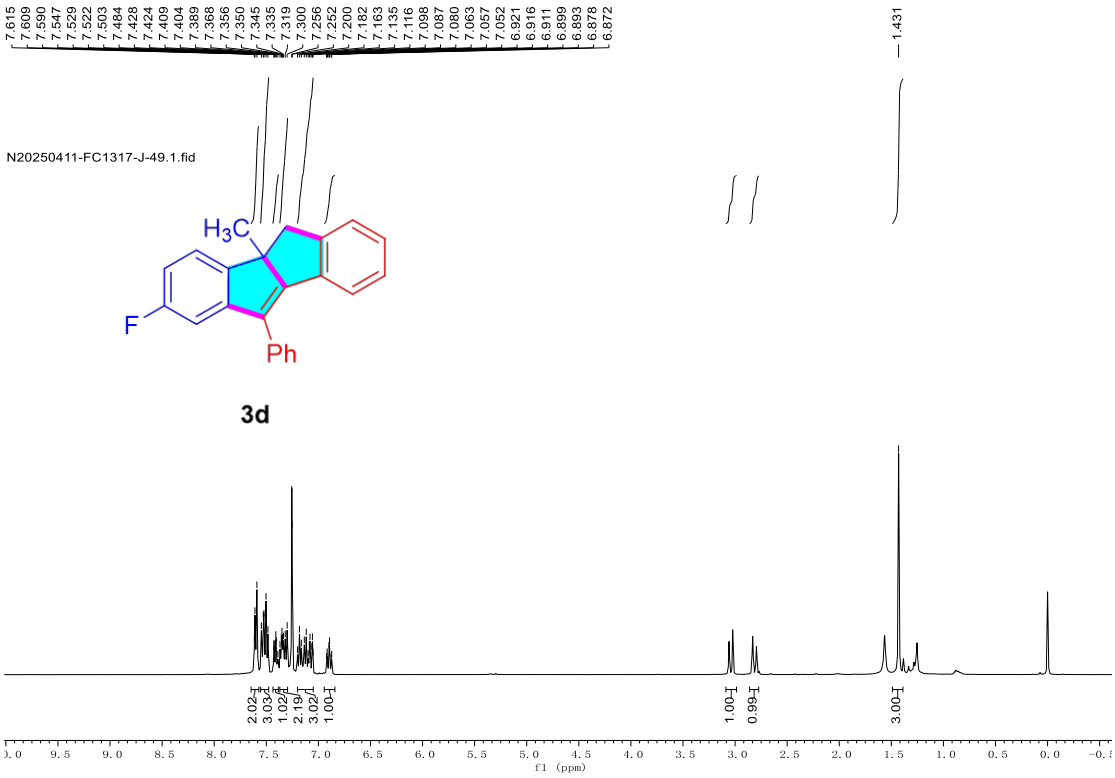
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3c**



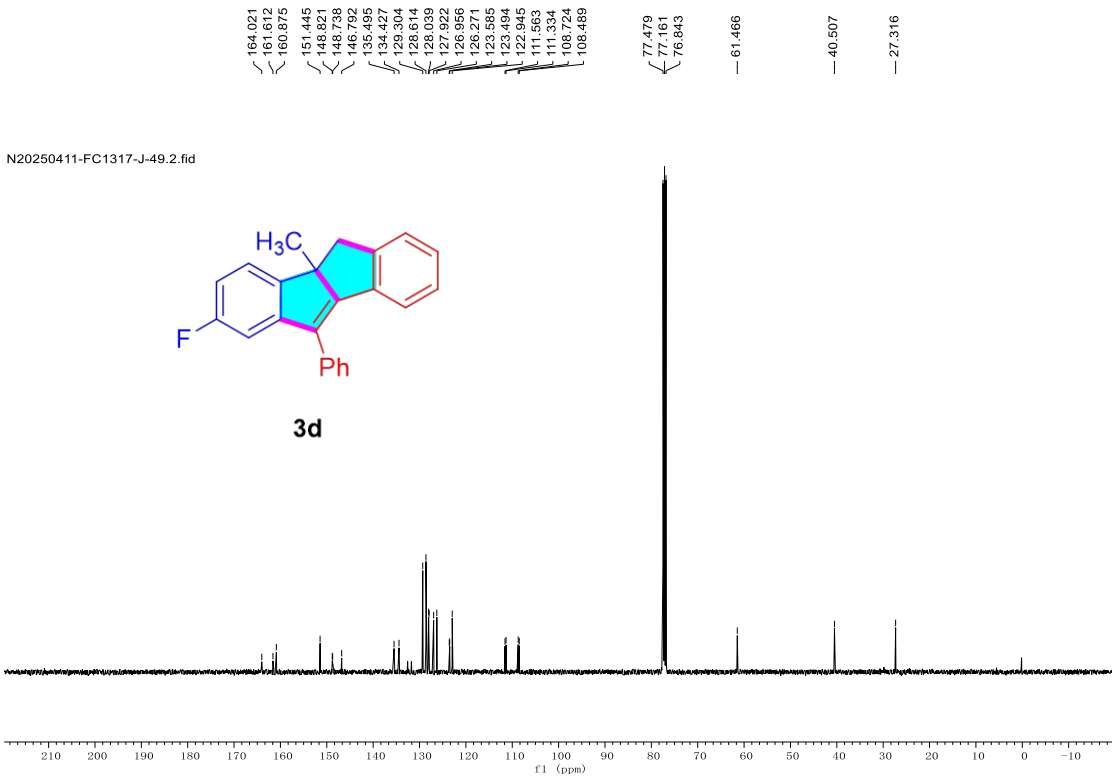
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **3c**



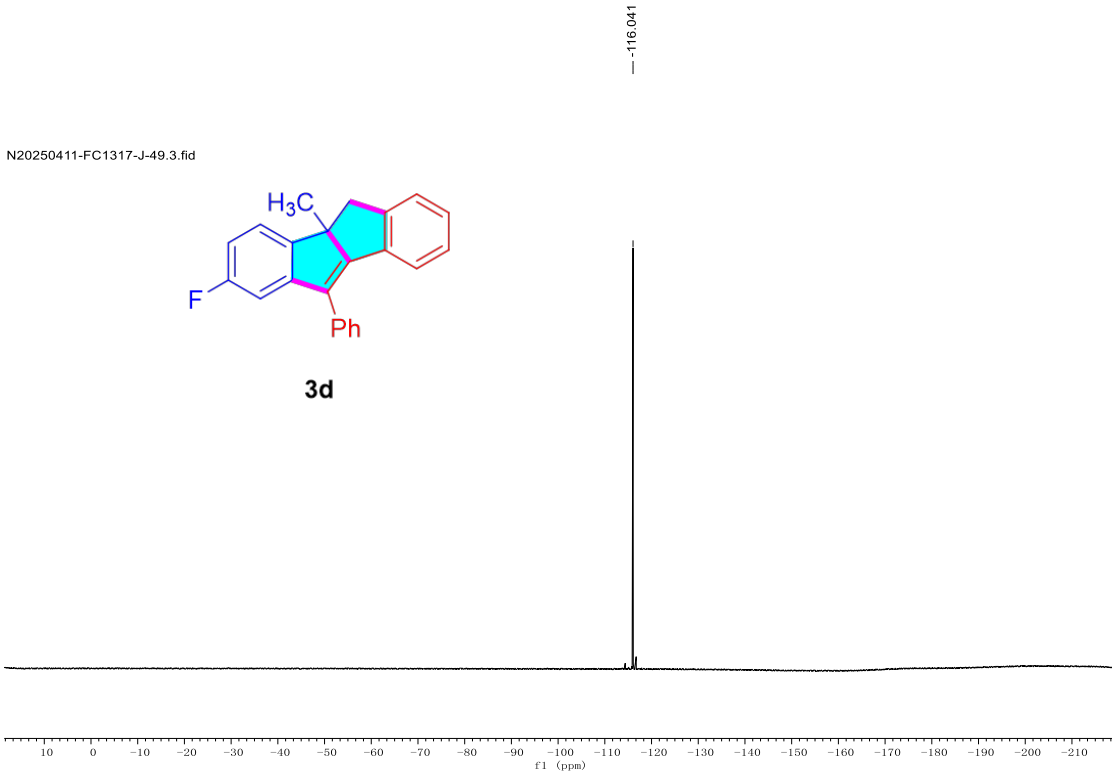
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3d**



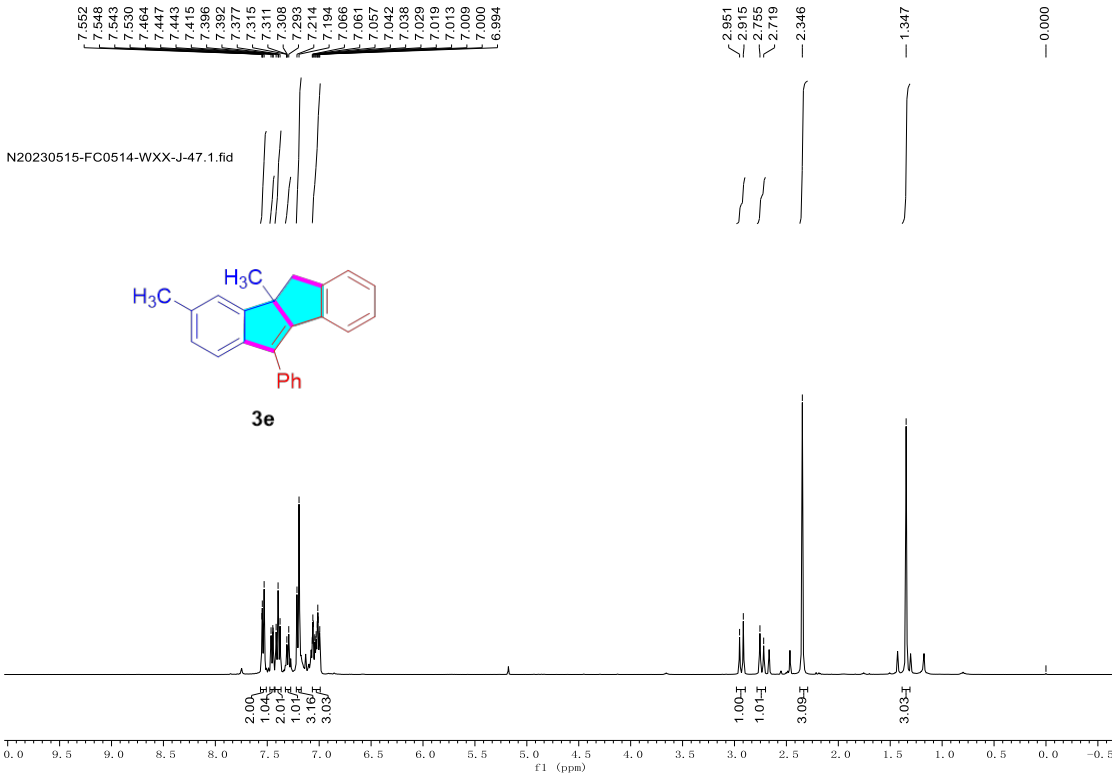
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **3d**



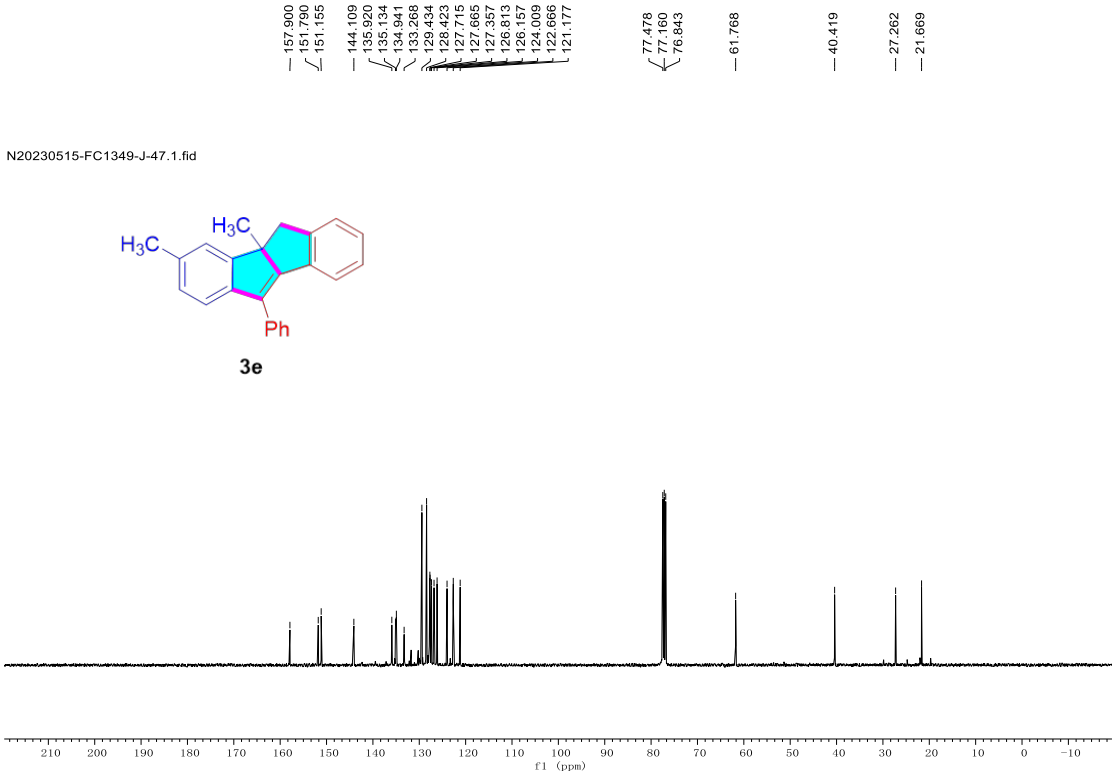
^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of **3d**



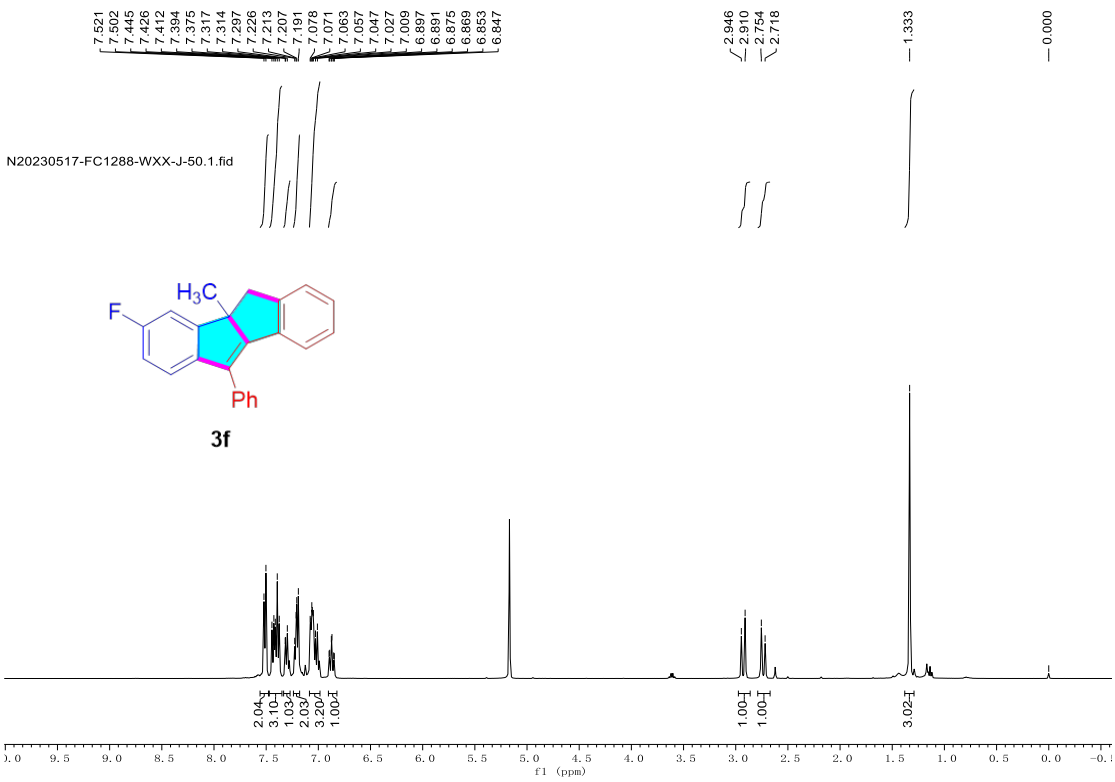
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3e**



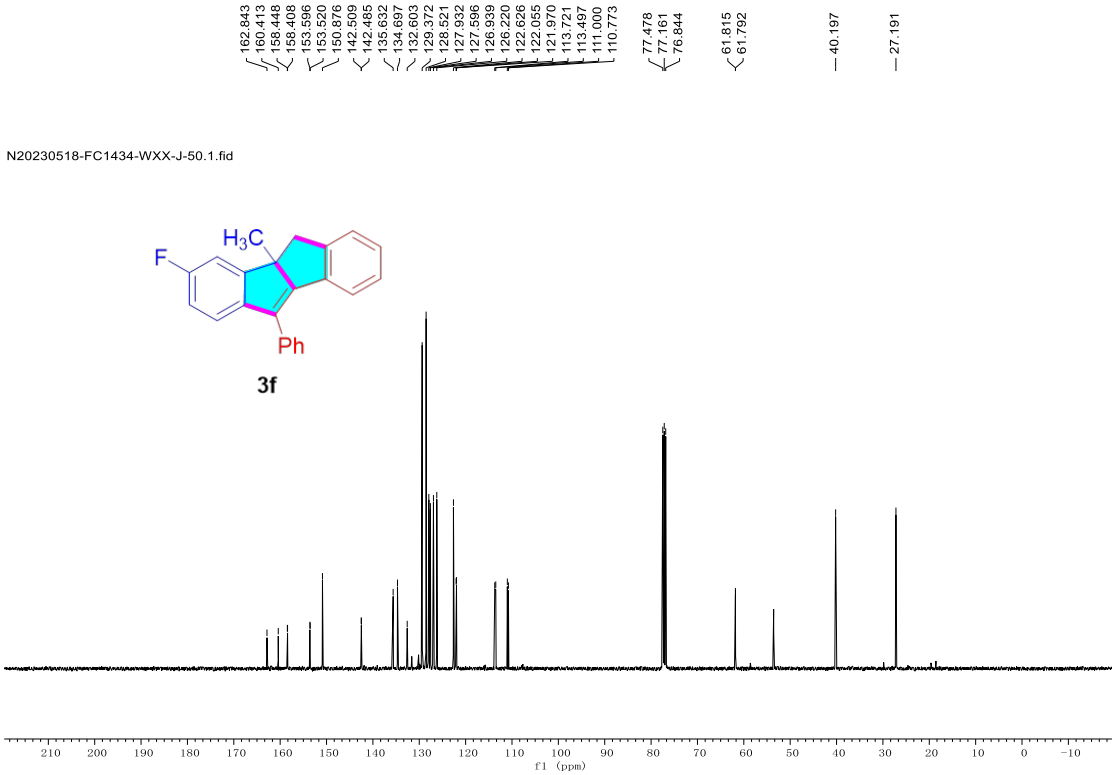
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **3e**



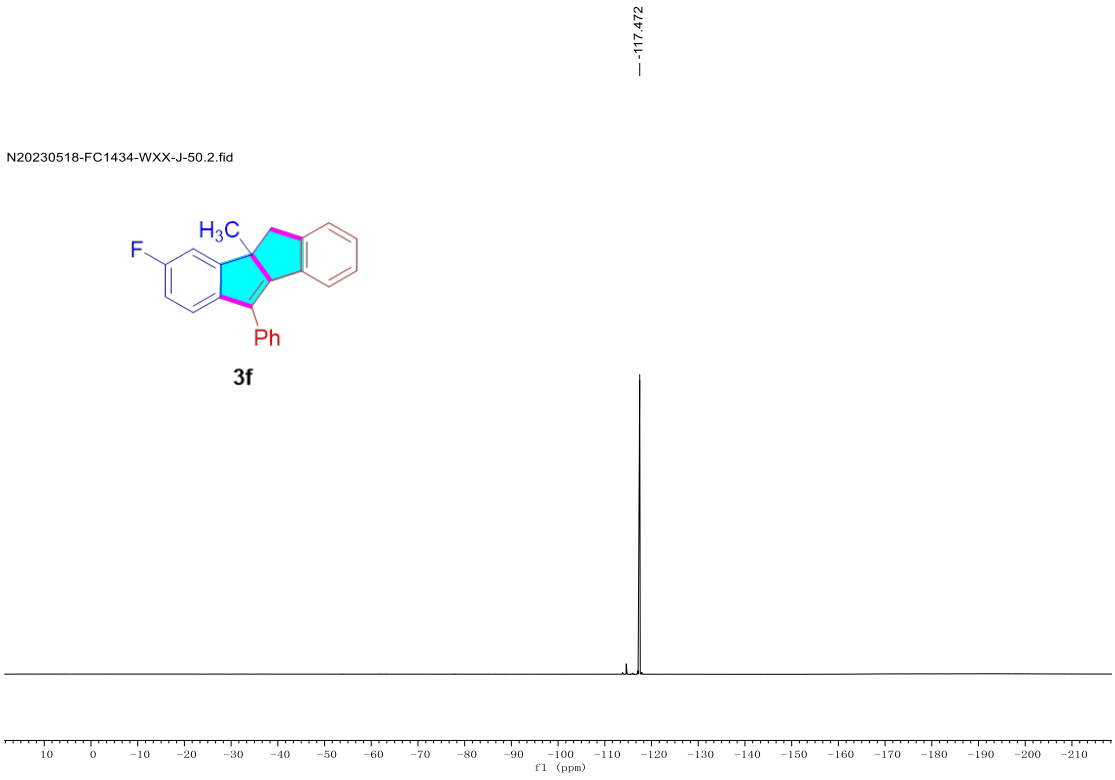
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3f**



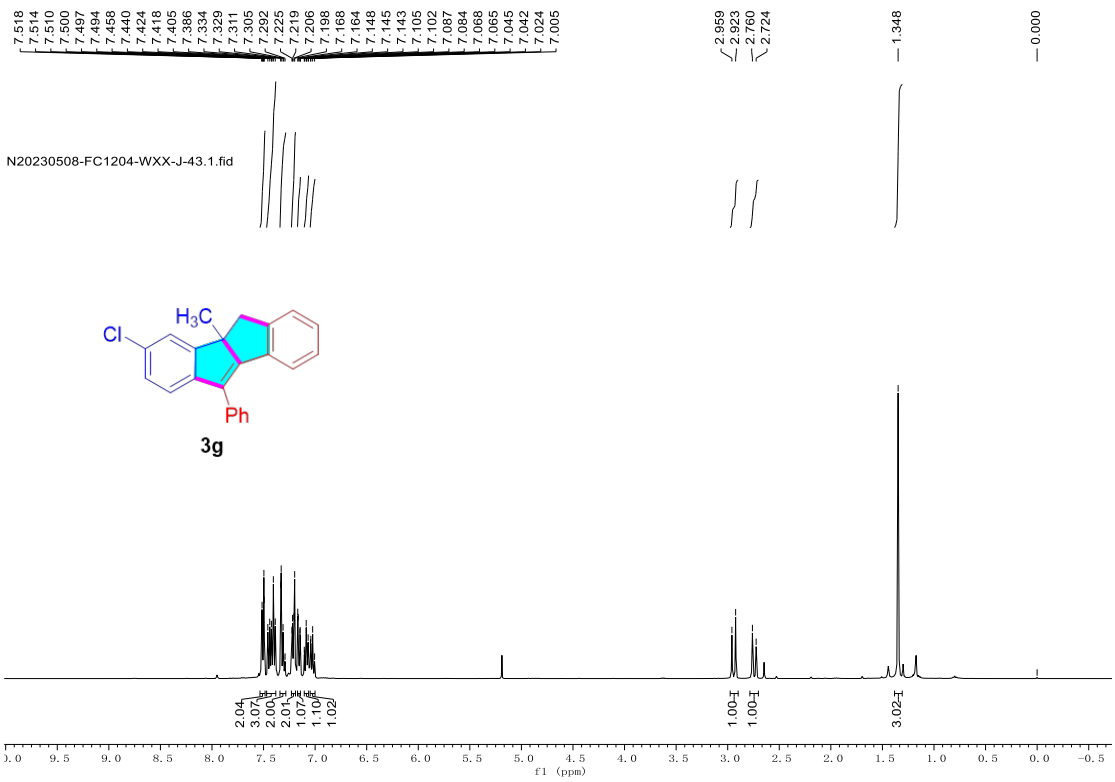
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **3f**



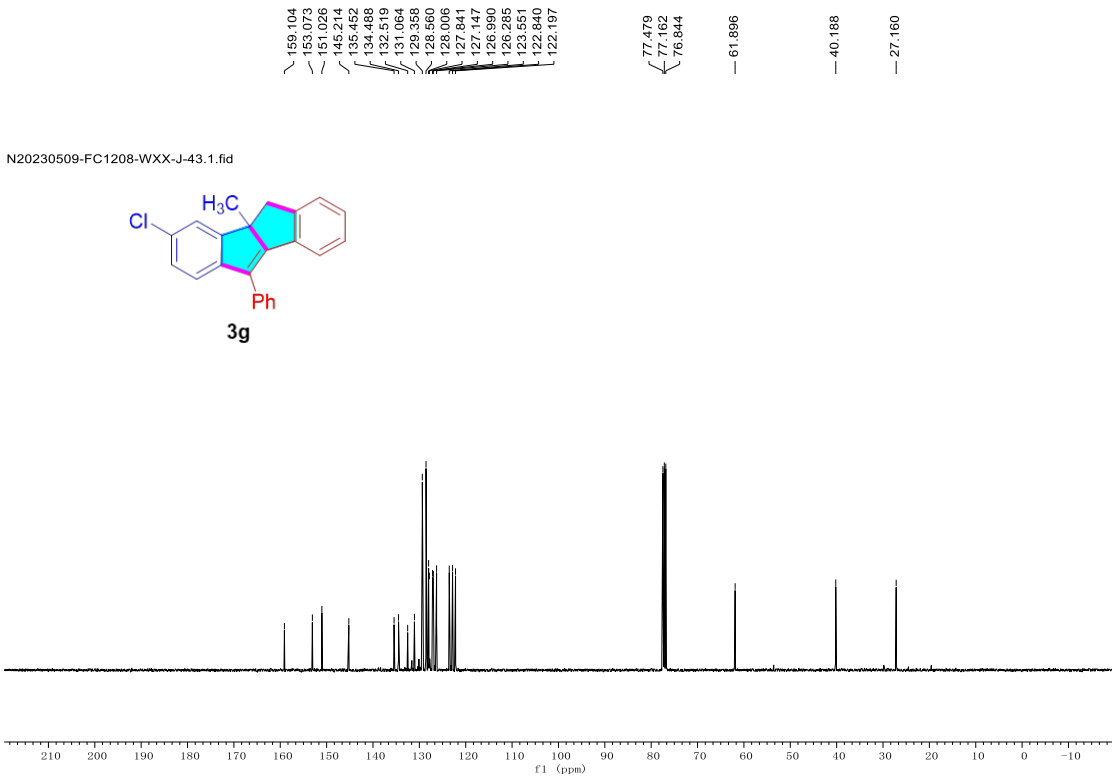
^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of **3f**



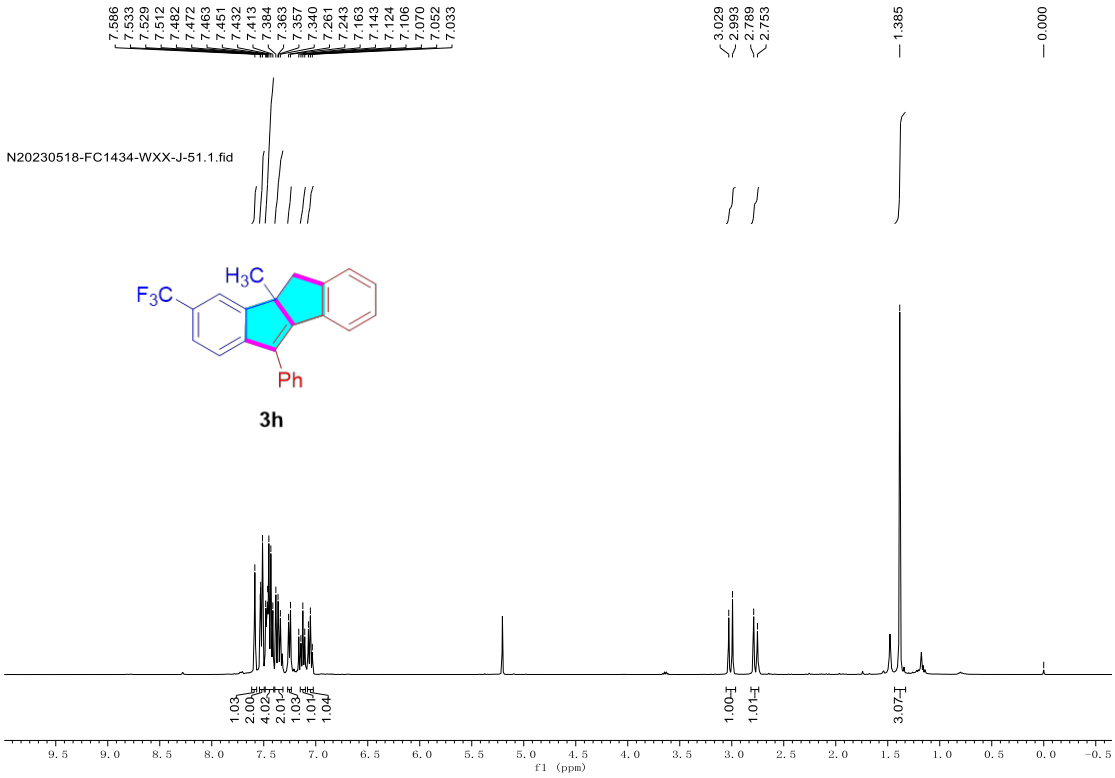
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3g**



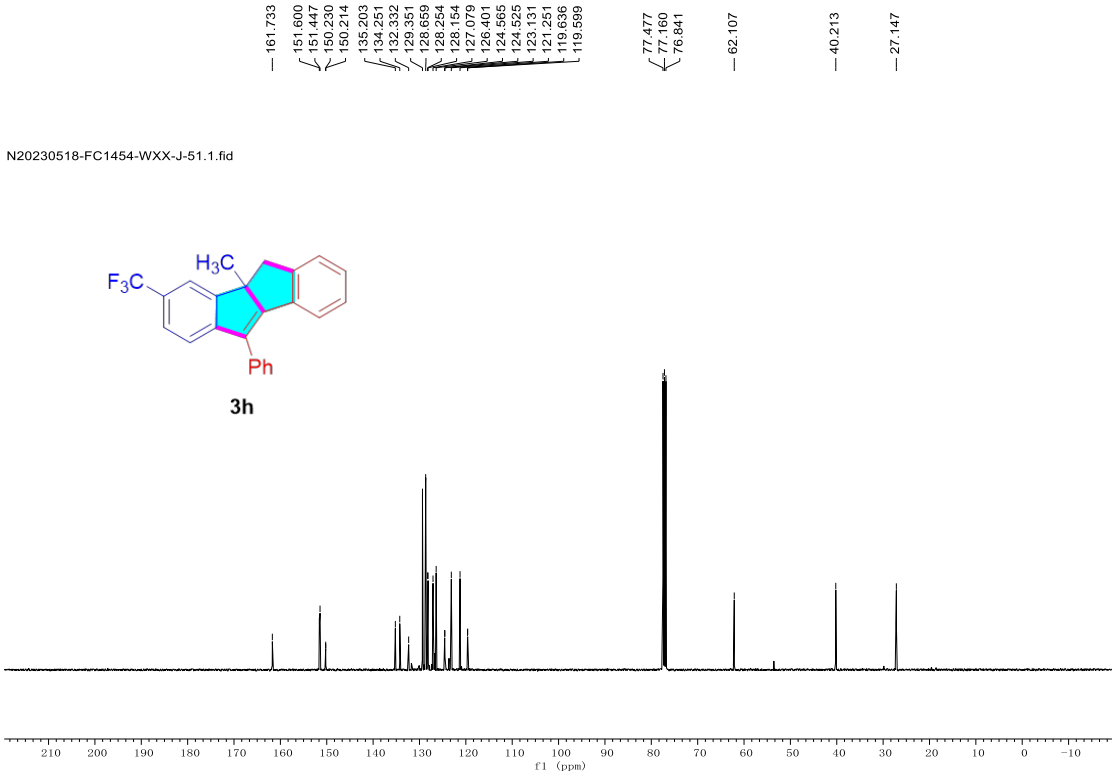
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **3g**



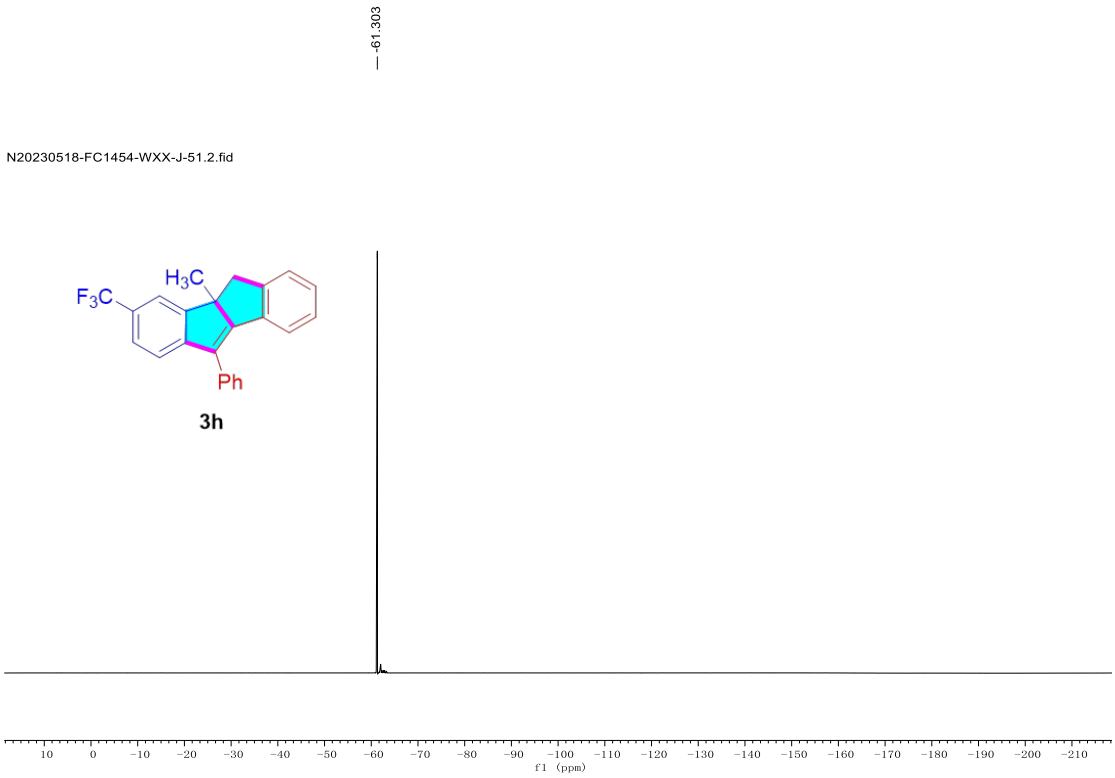
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3h**



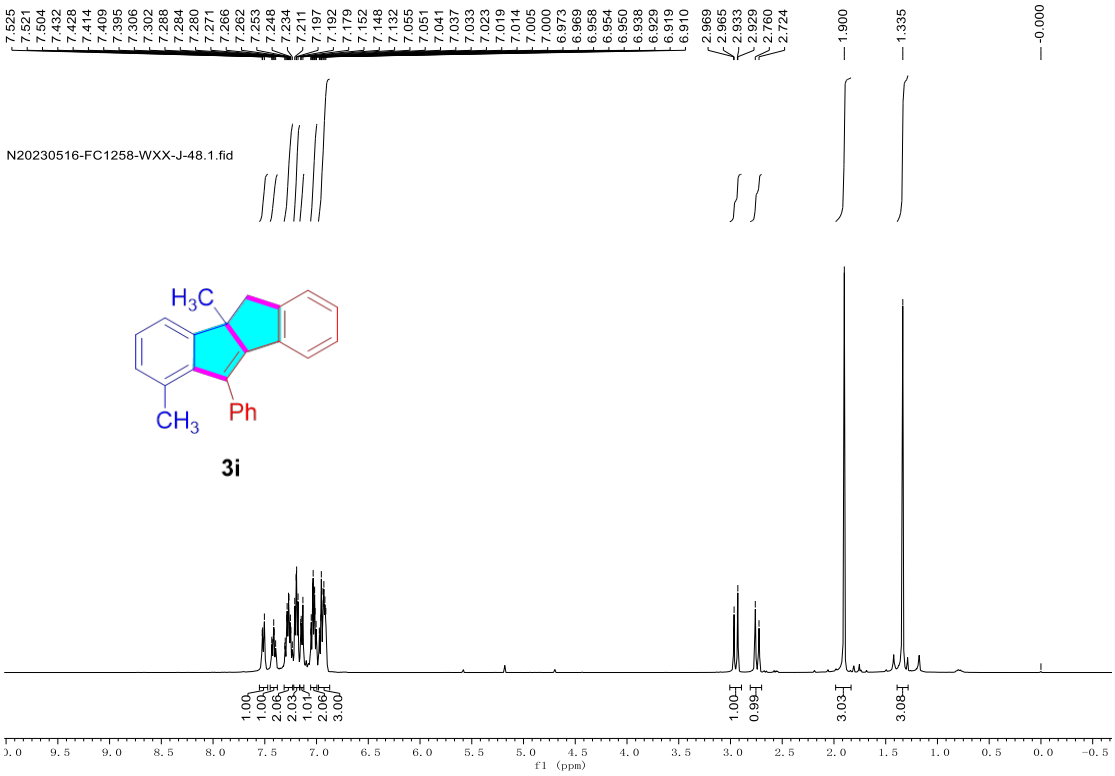
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **3h**



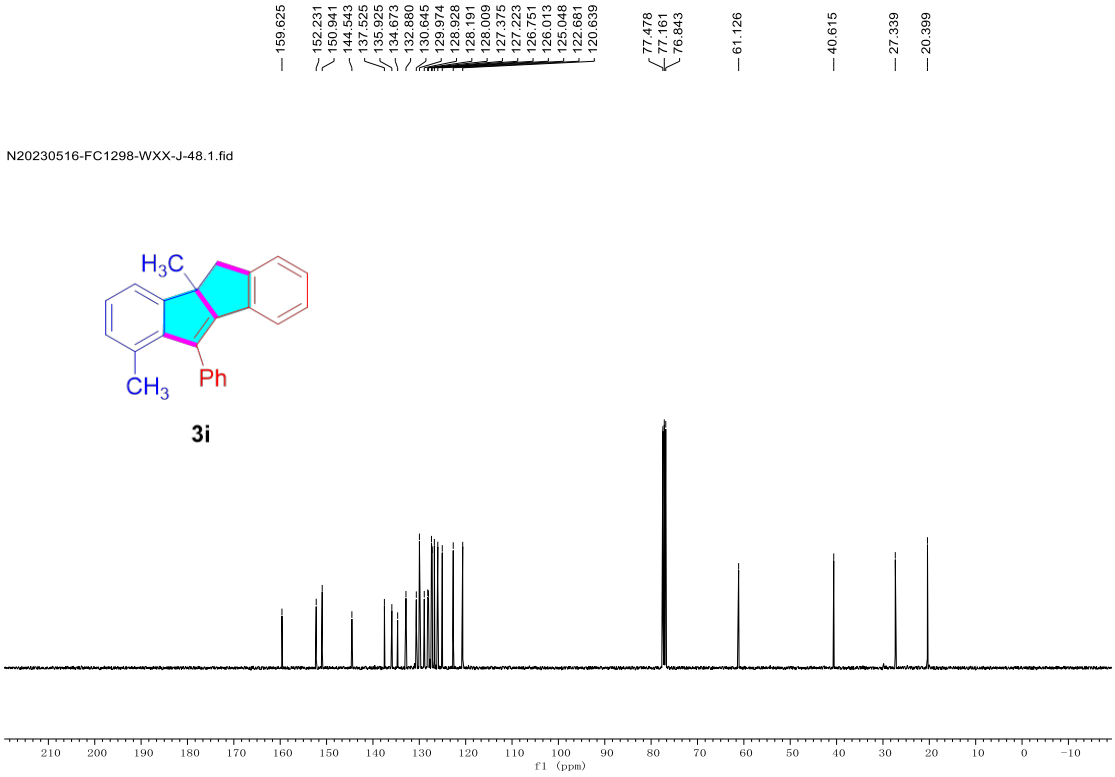
^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of **3h**



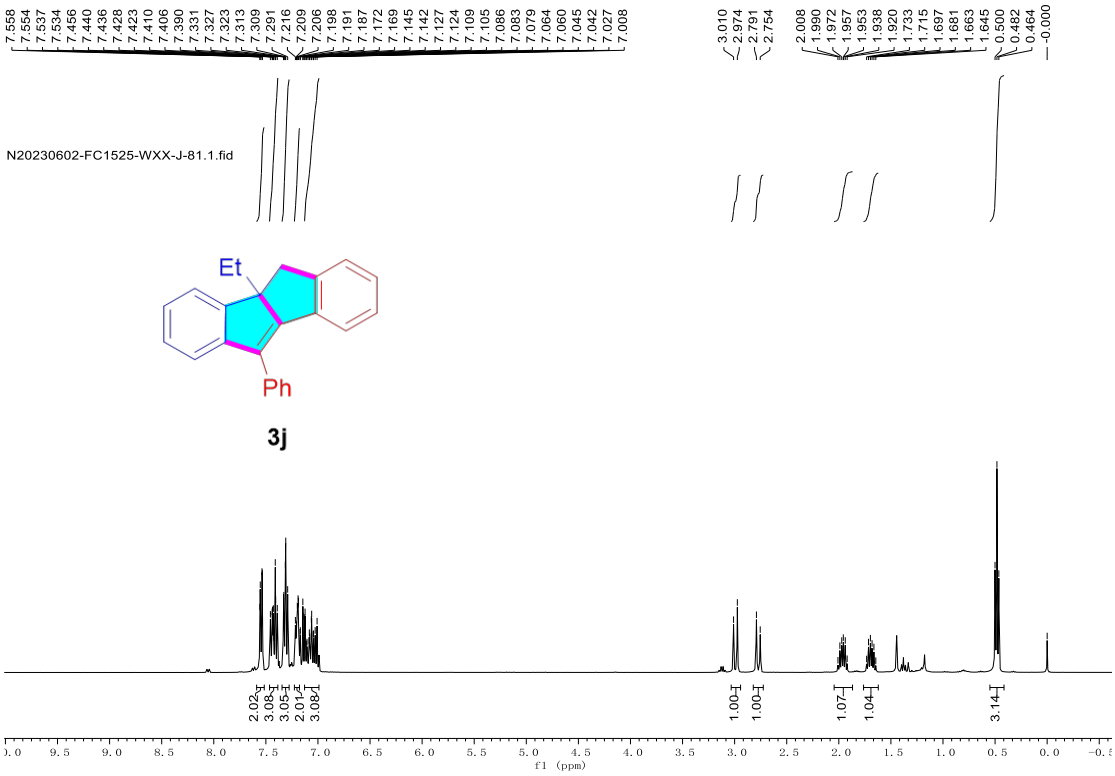
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3i**



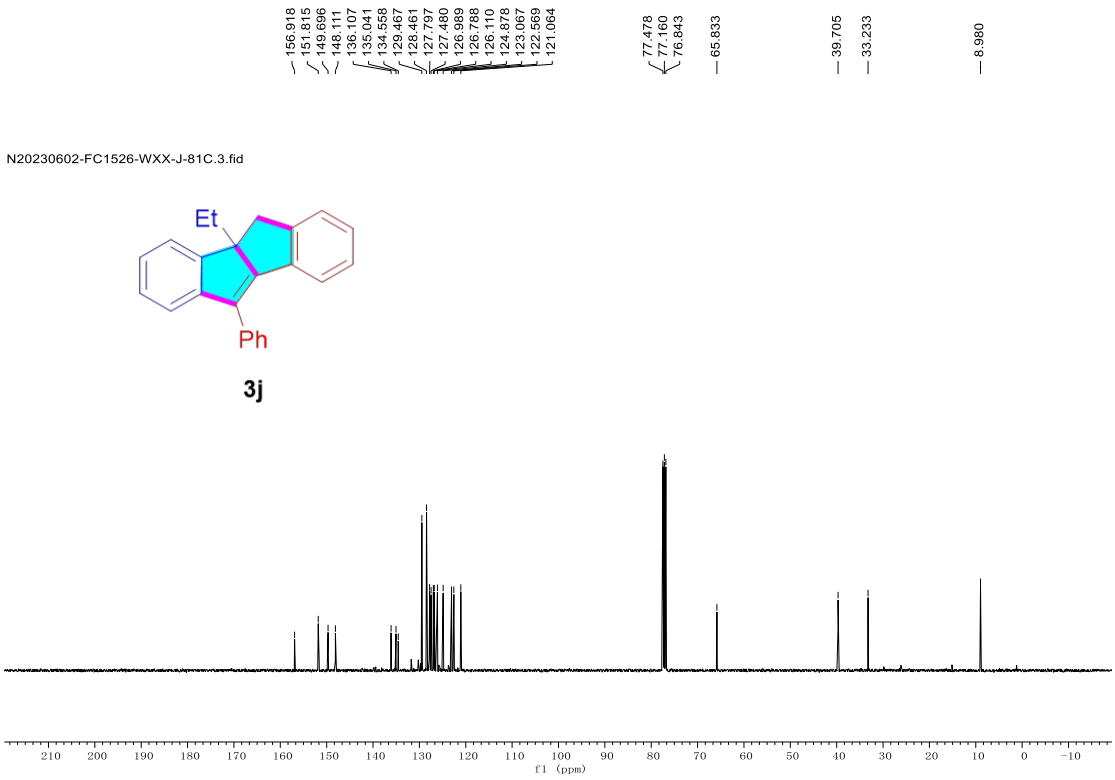
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **3i**



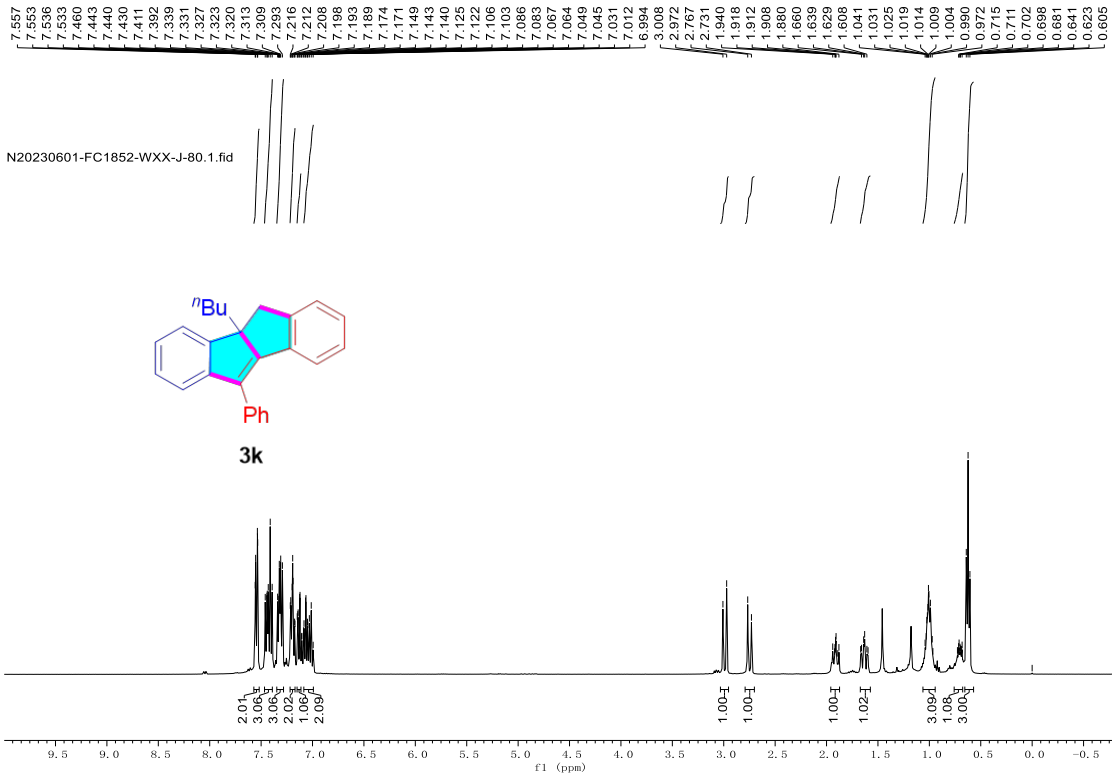
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3j**



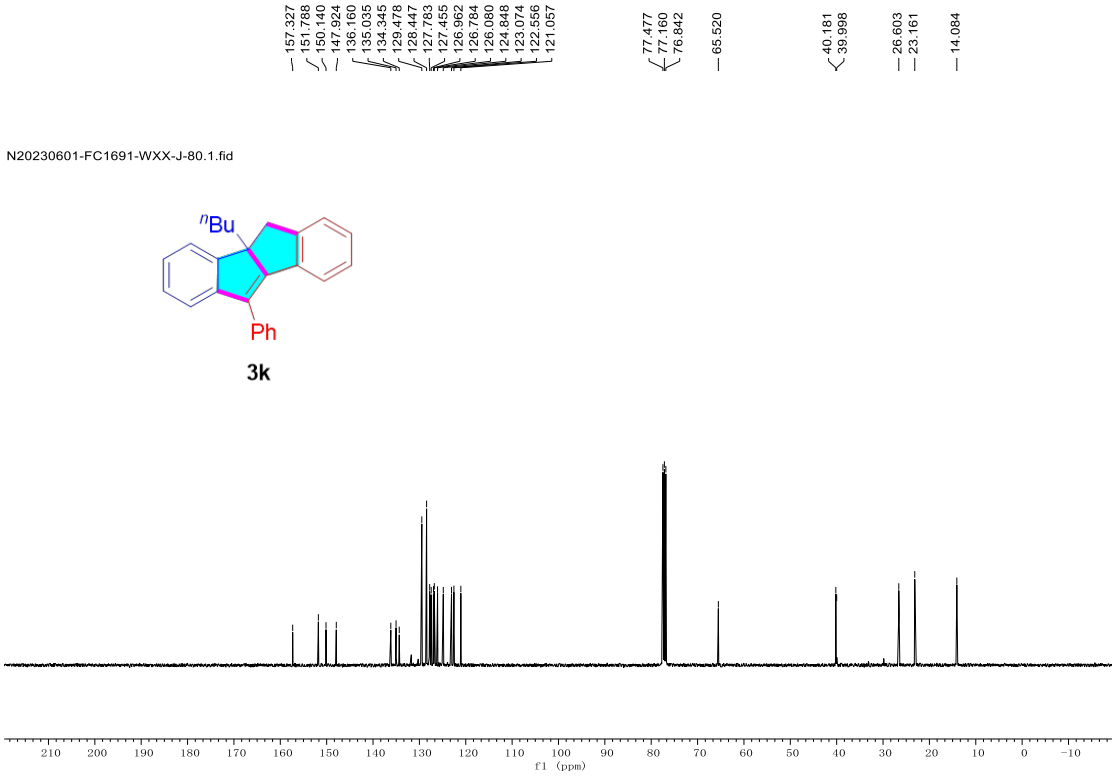
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **3j**



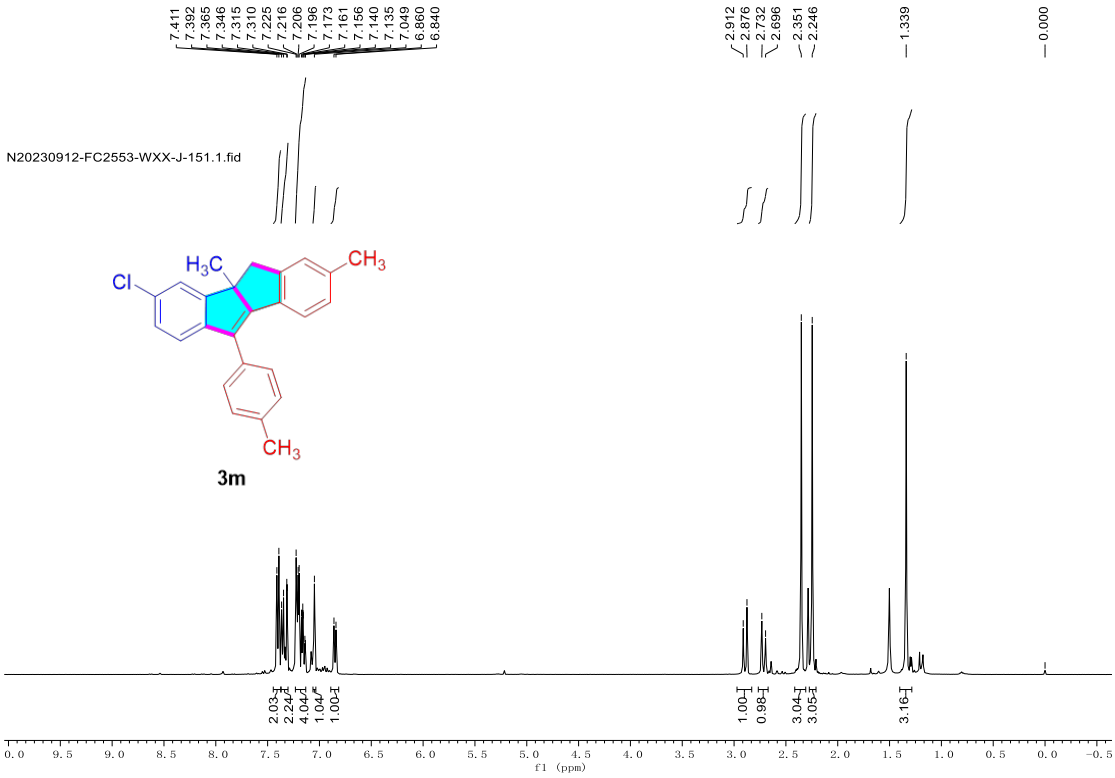
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3k**



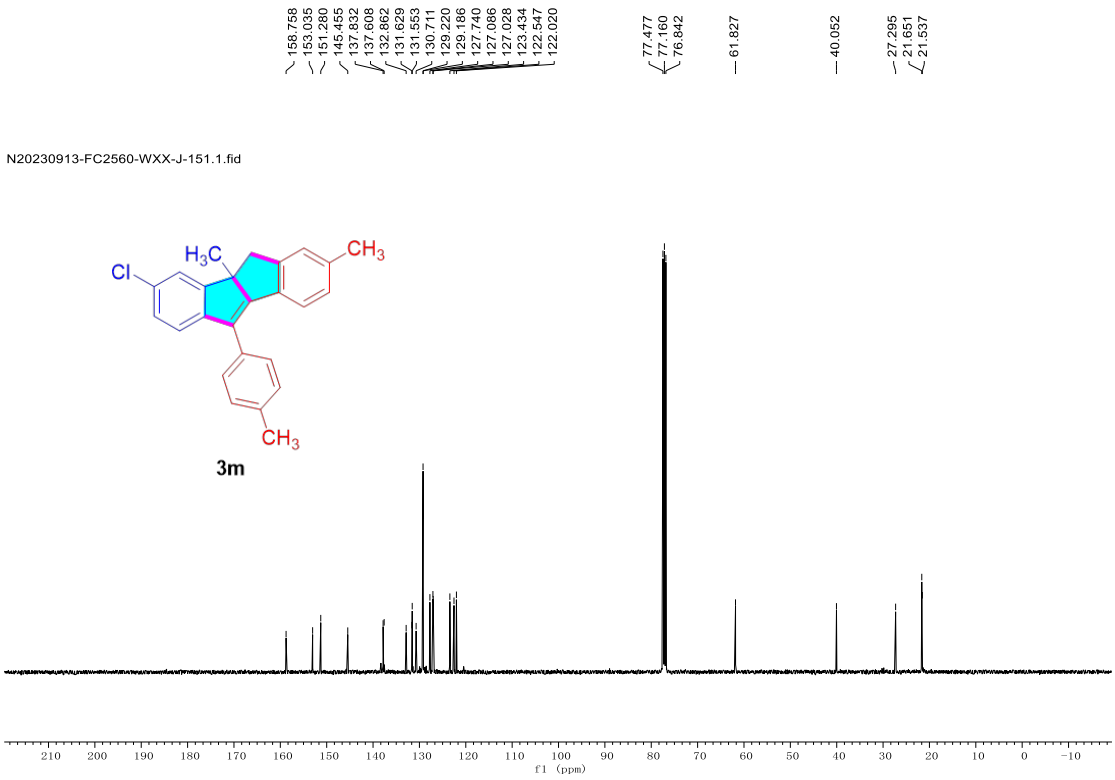
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **3k**



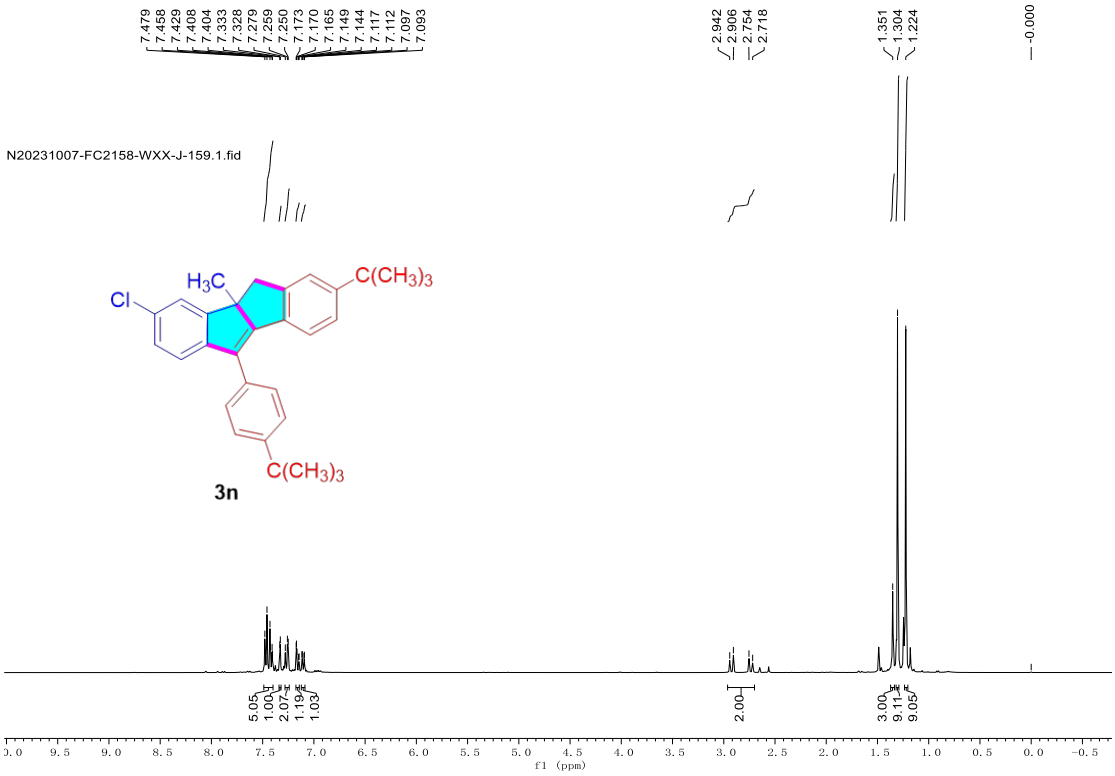
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3m**



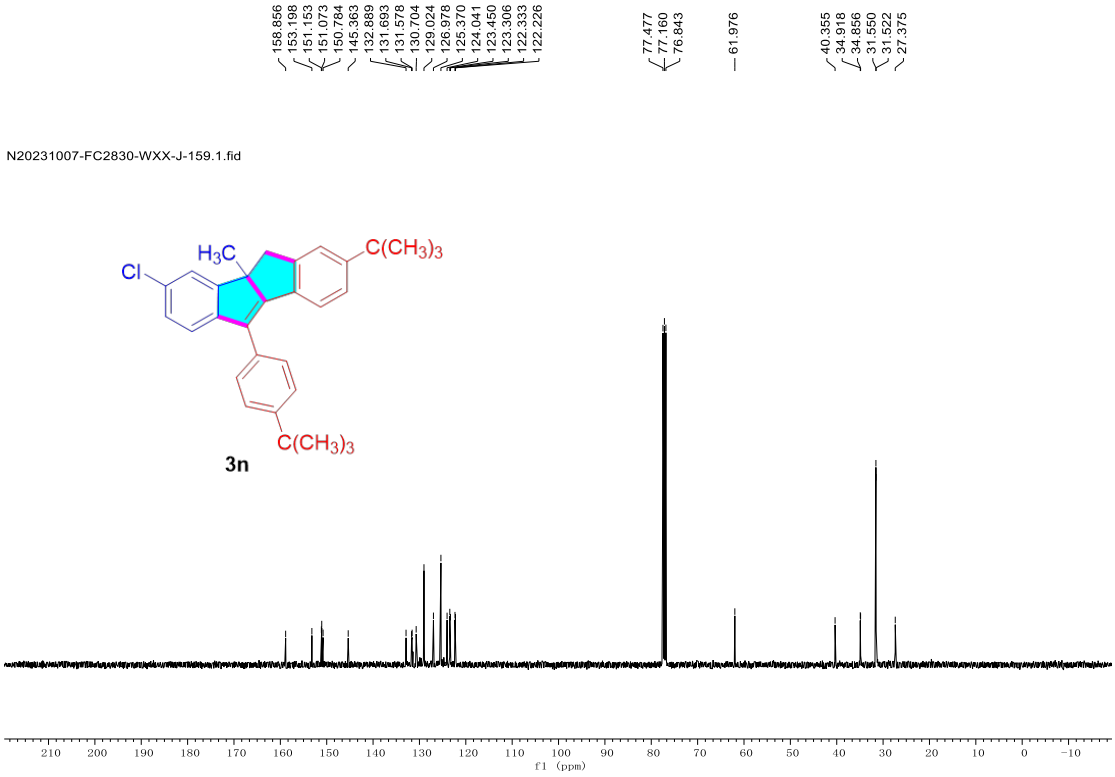
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **3m**



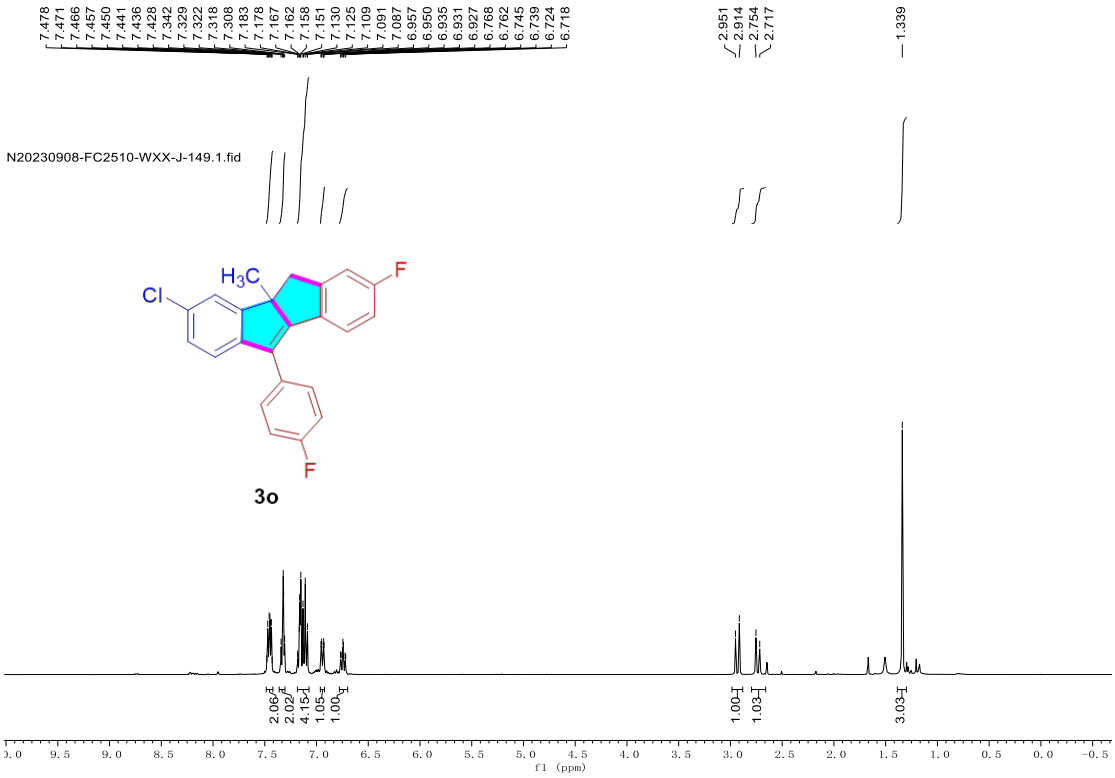
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3n**



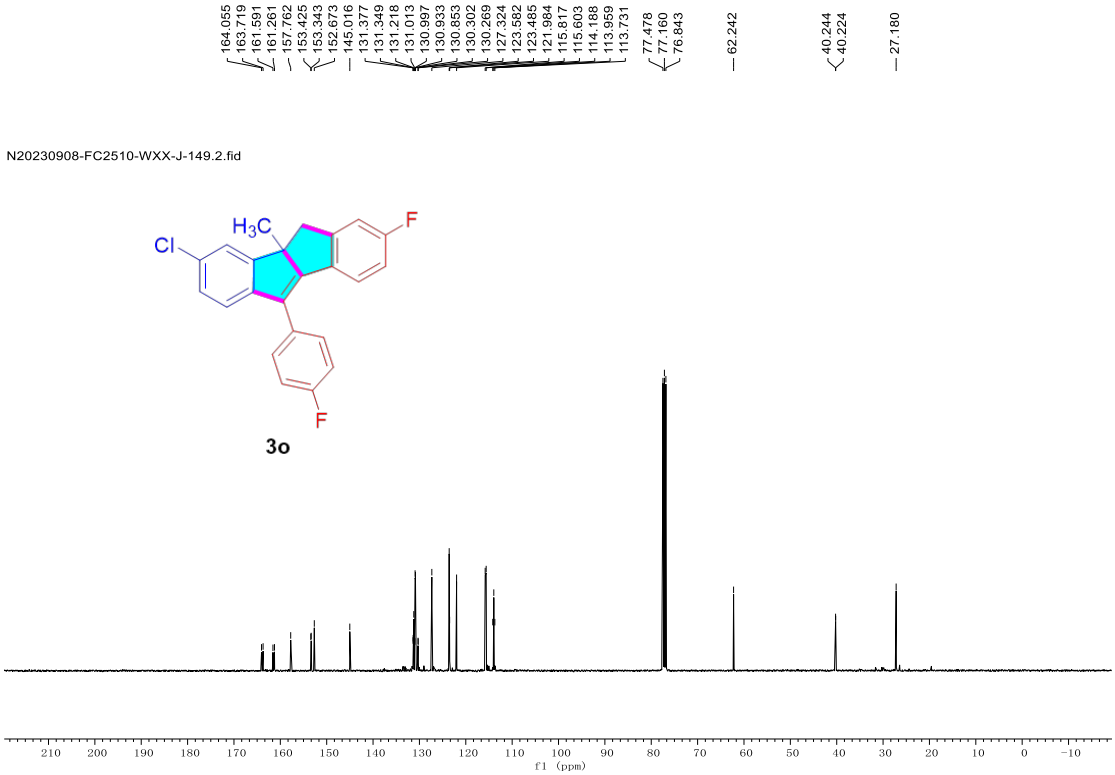
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **3n**



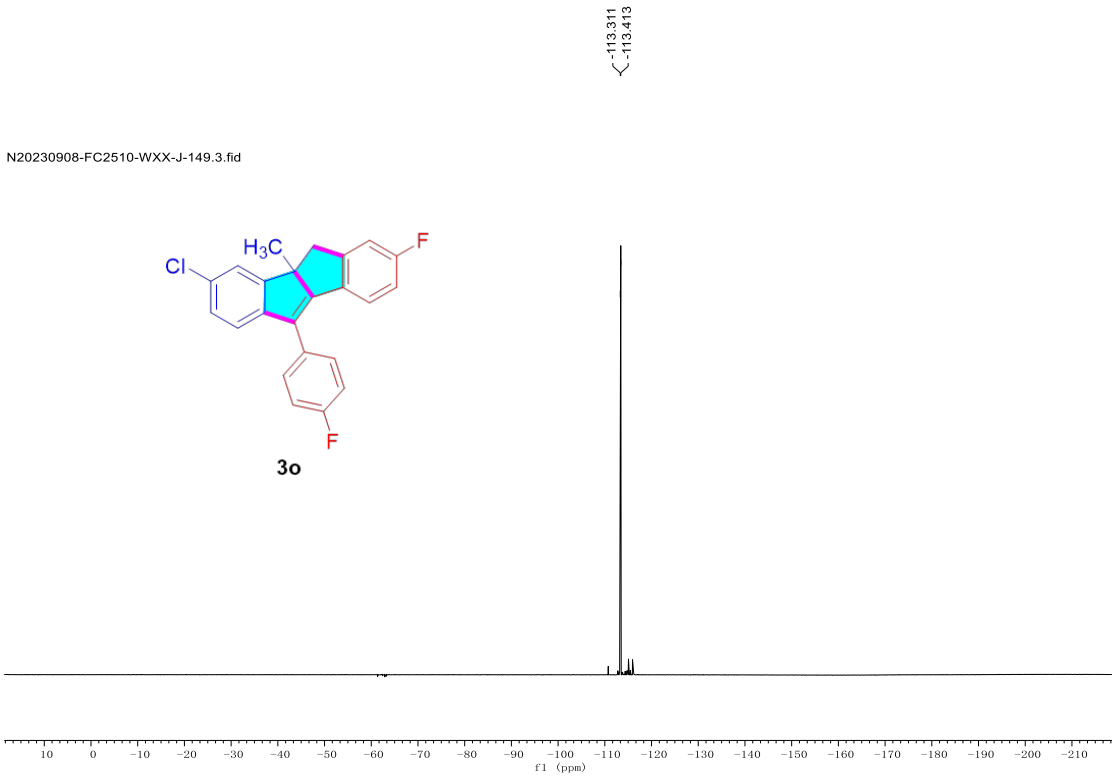
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3o**



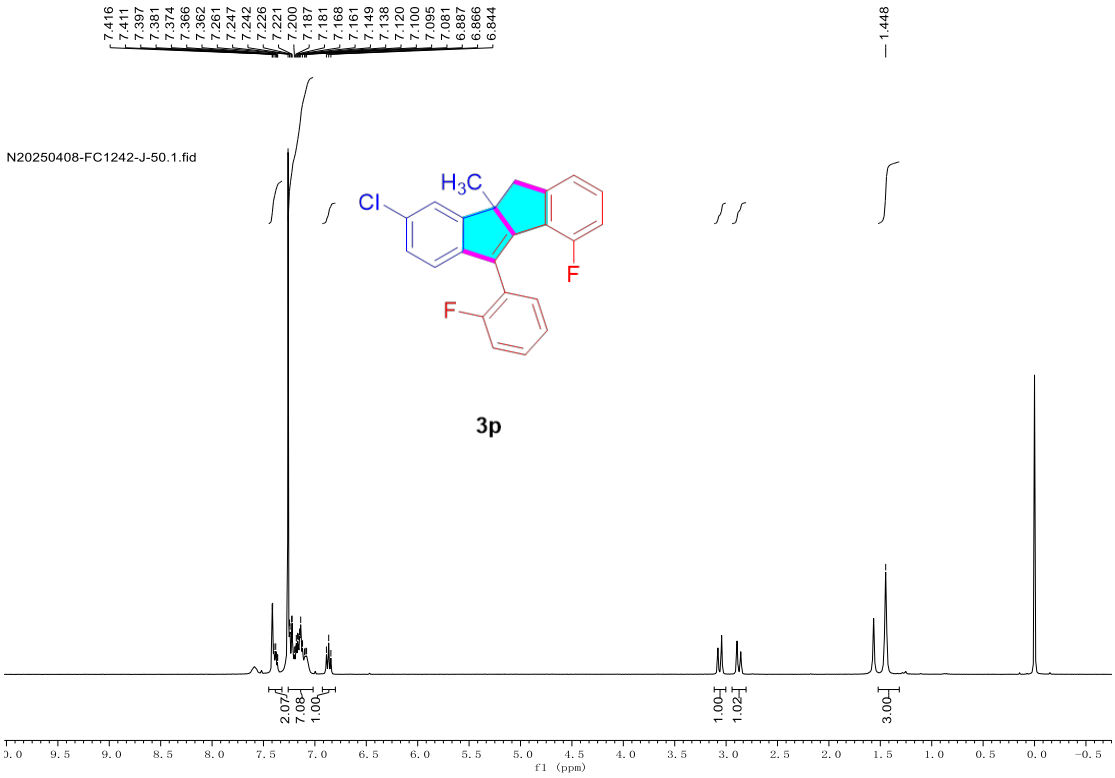
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **3o**



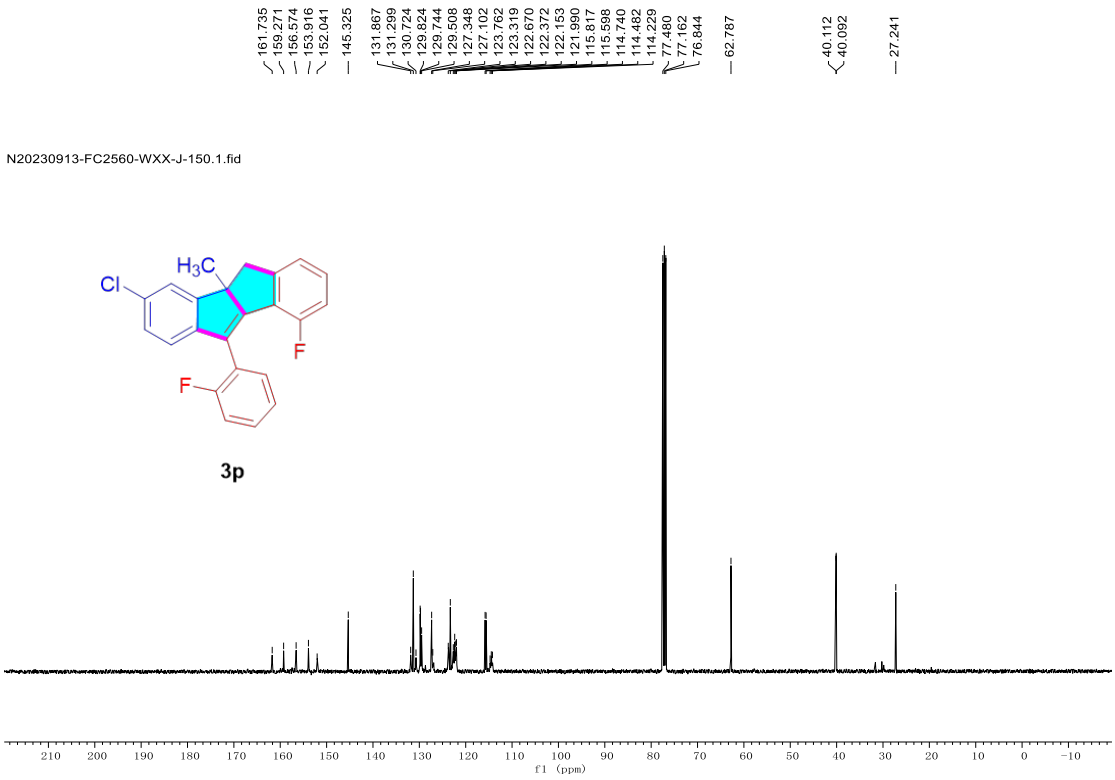
^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of **3o**



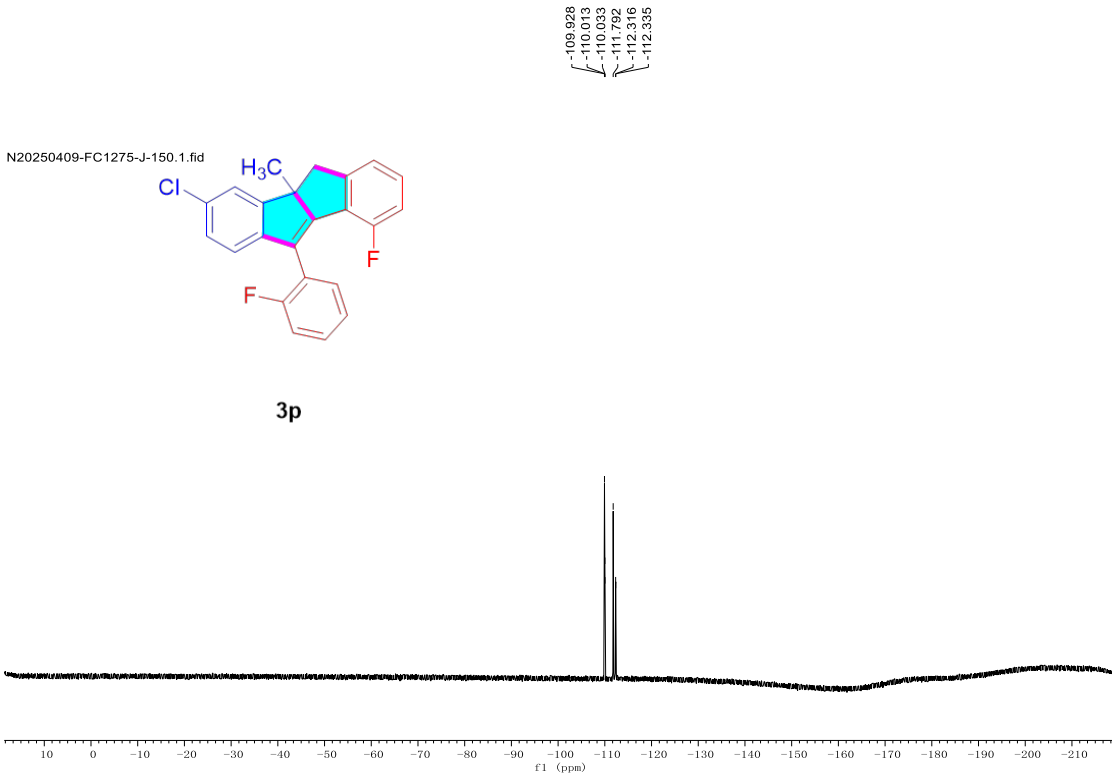
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3p**



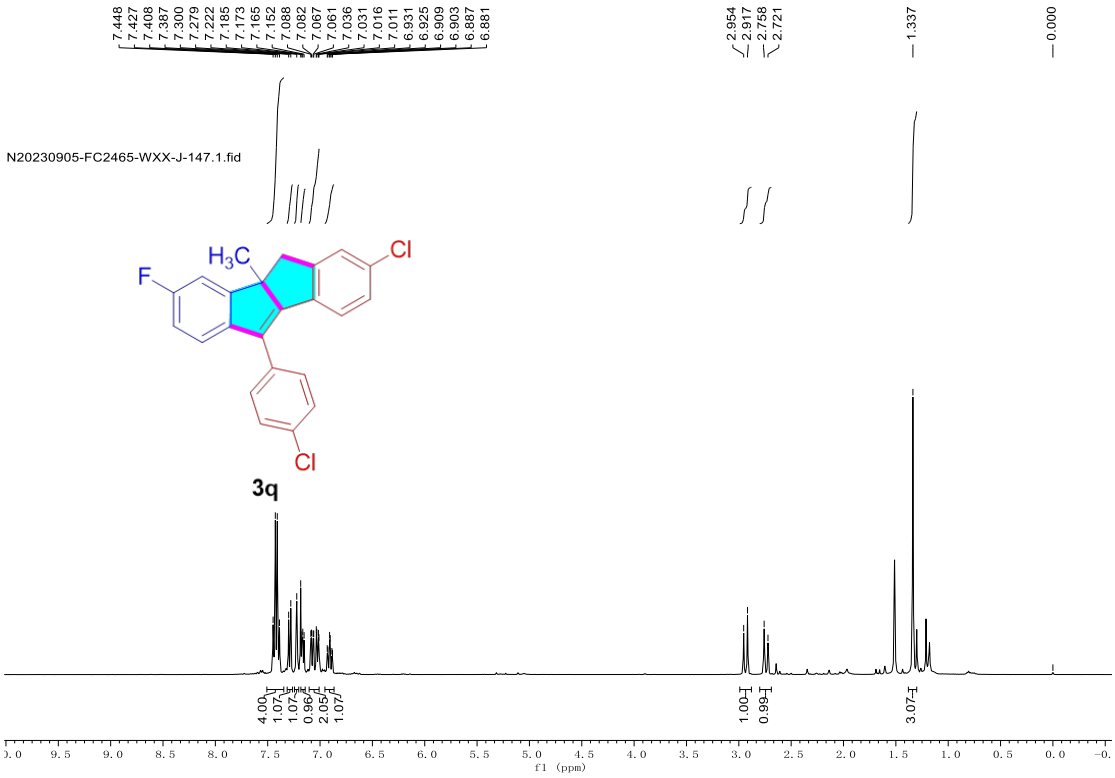
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **3p**



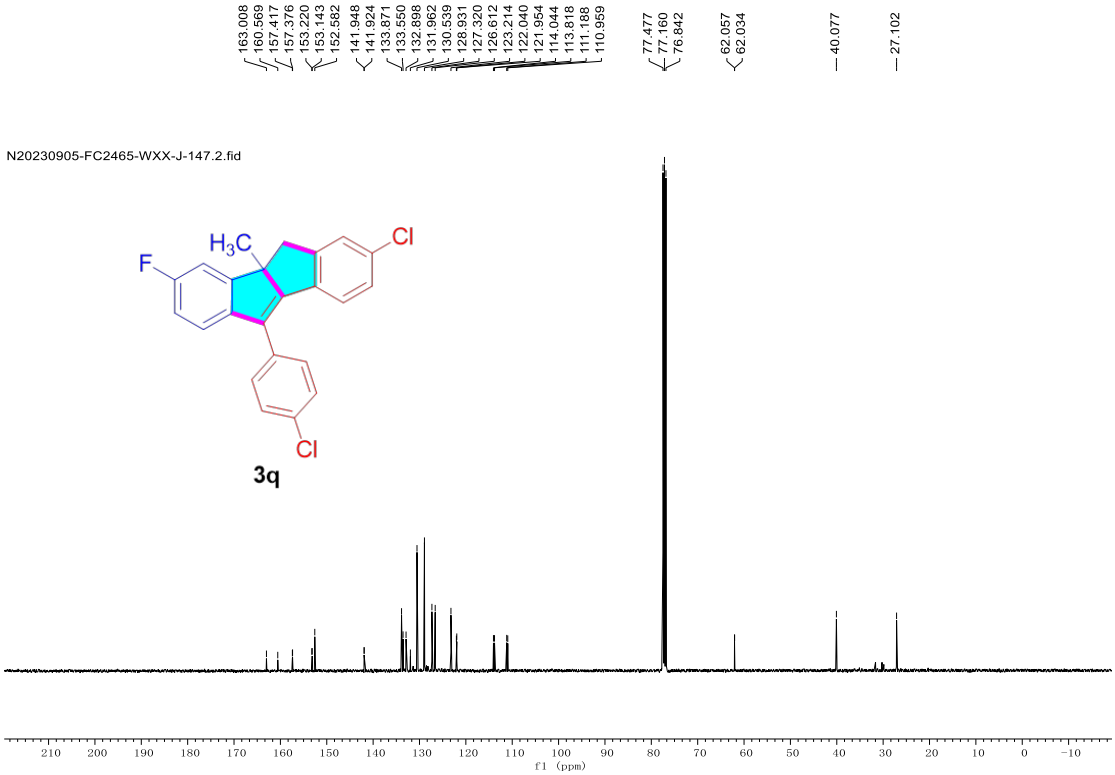
^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of **3p**



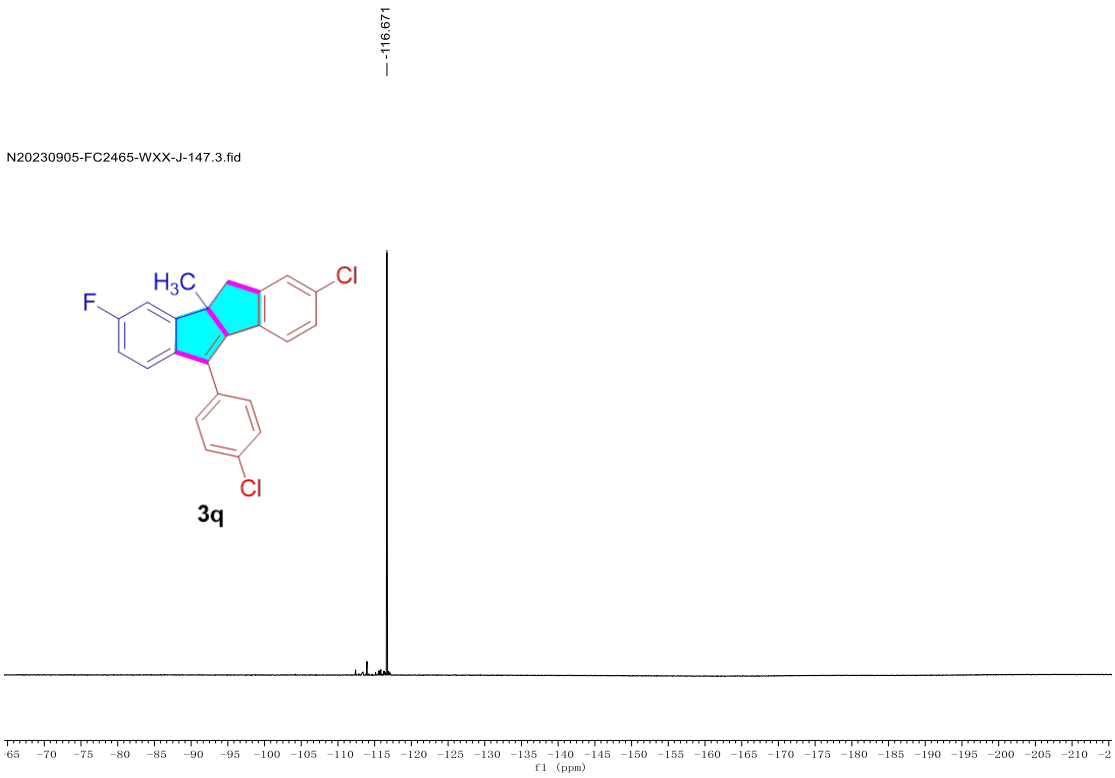
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3q**



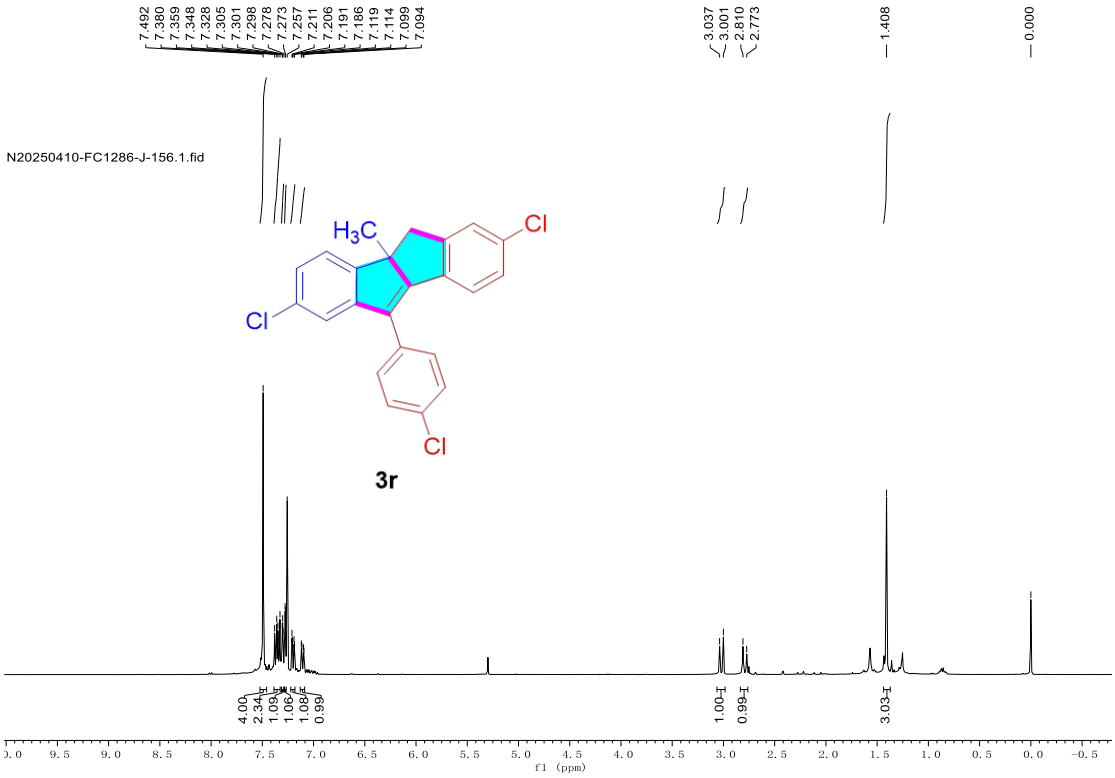
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **3q**



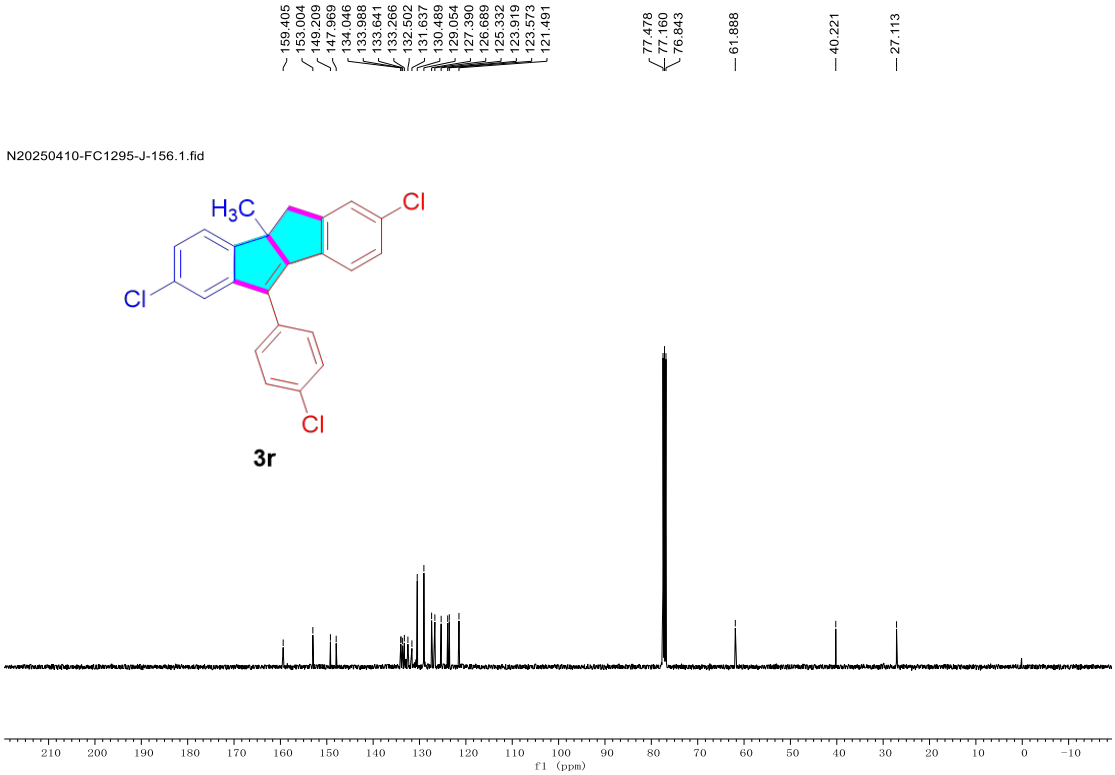
^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of **3q**



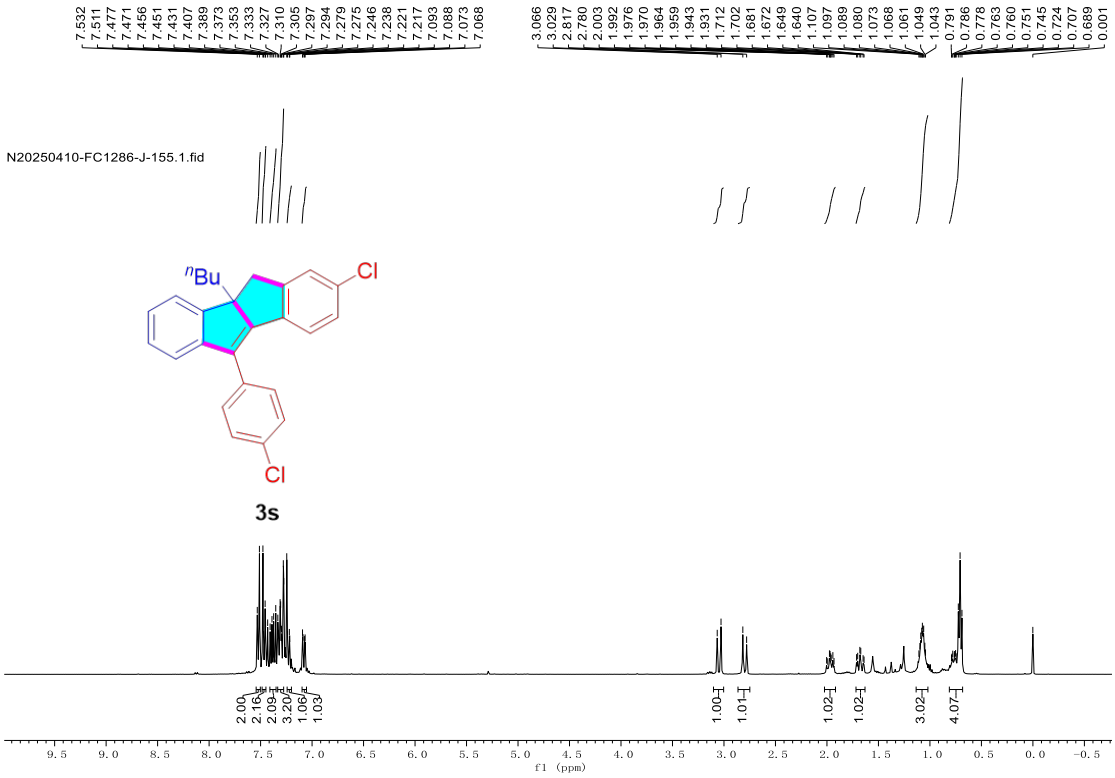
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3r**



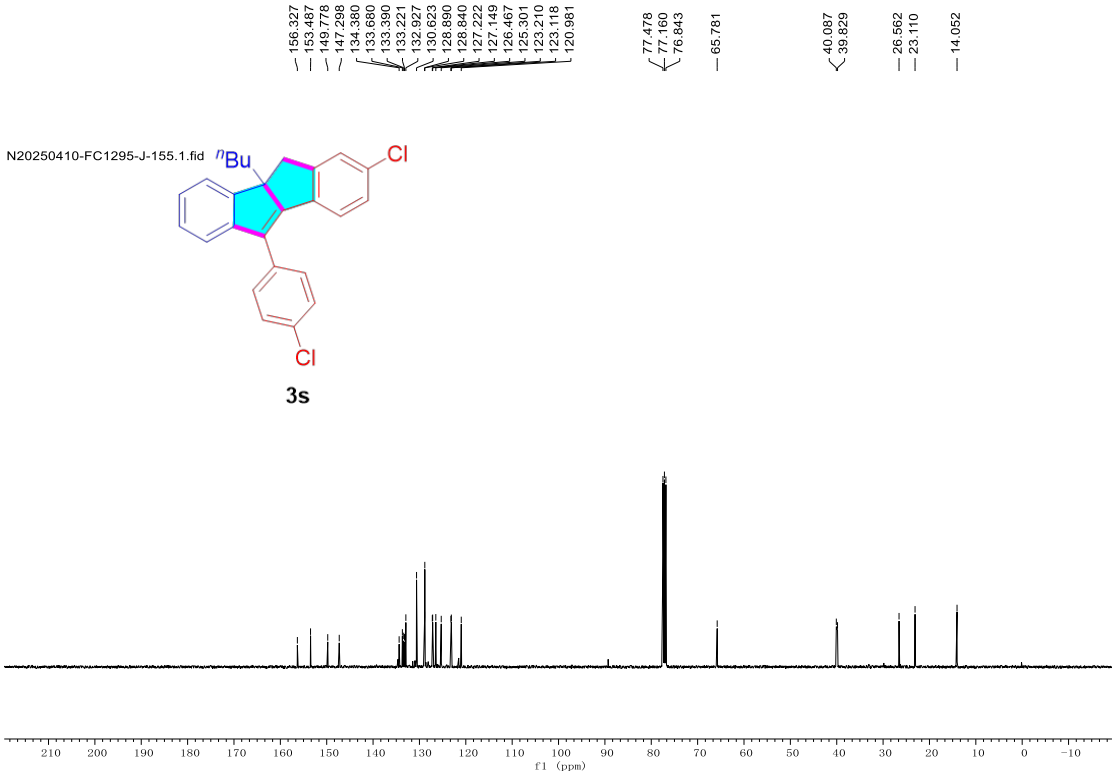
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **3r**



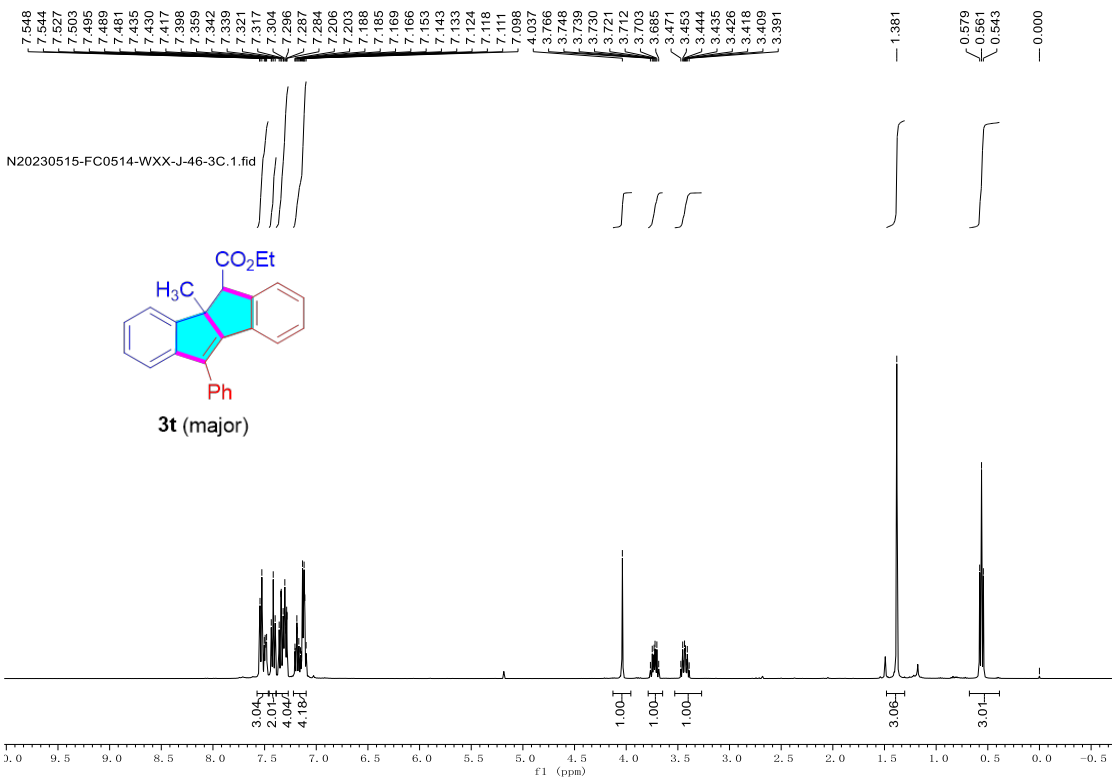
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3s**



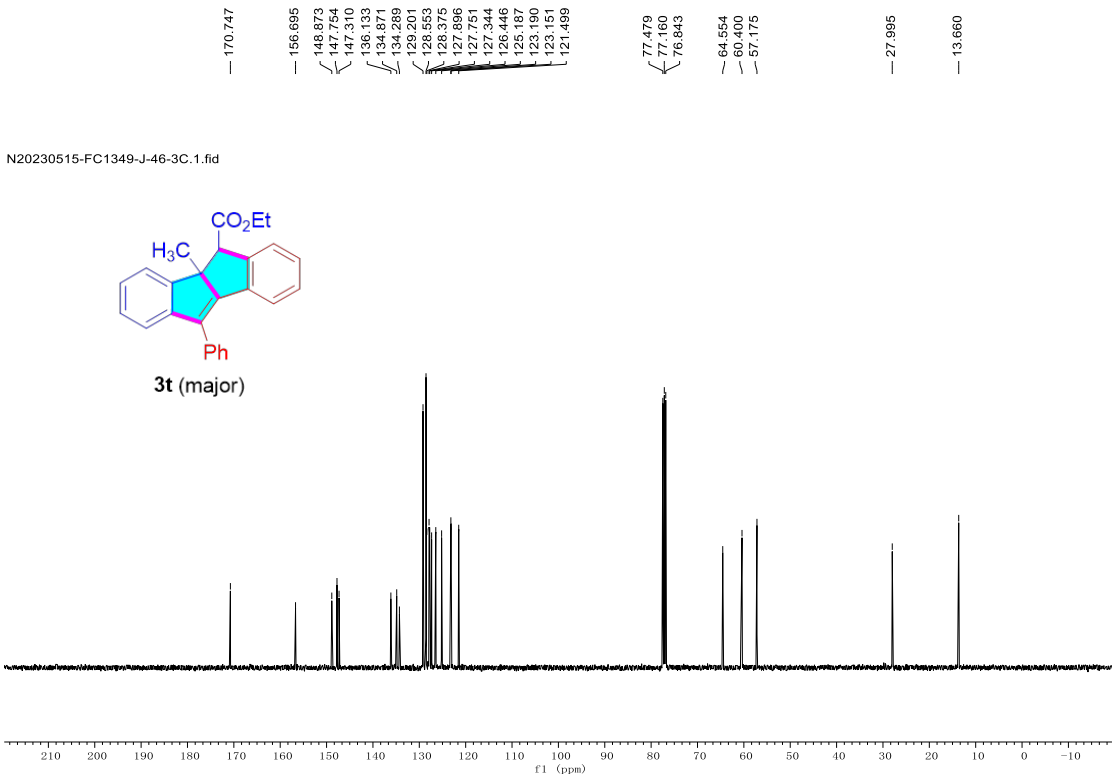
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **3s**



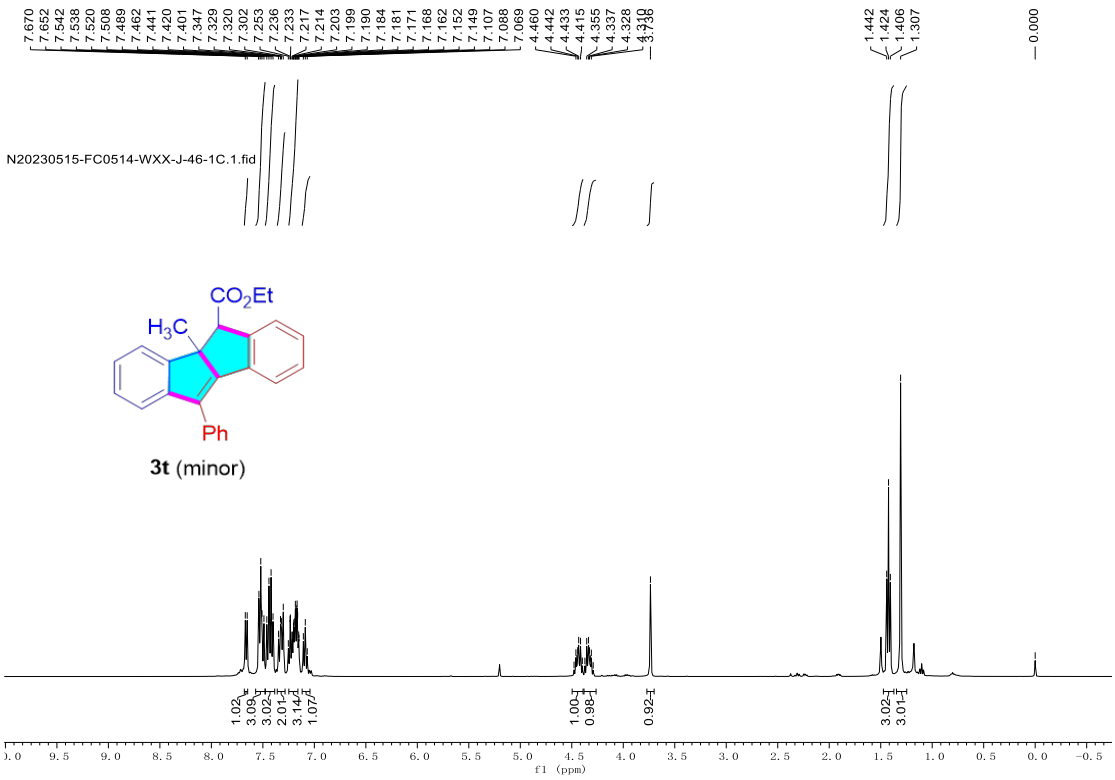
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3t**



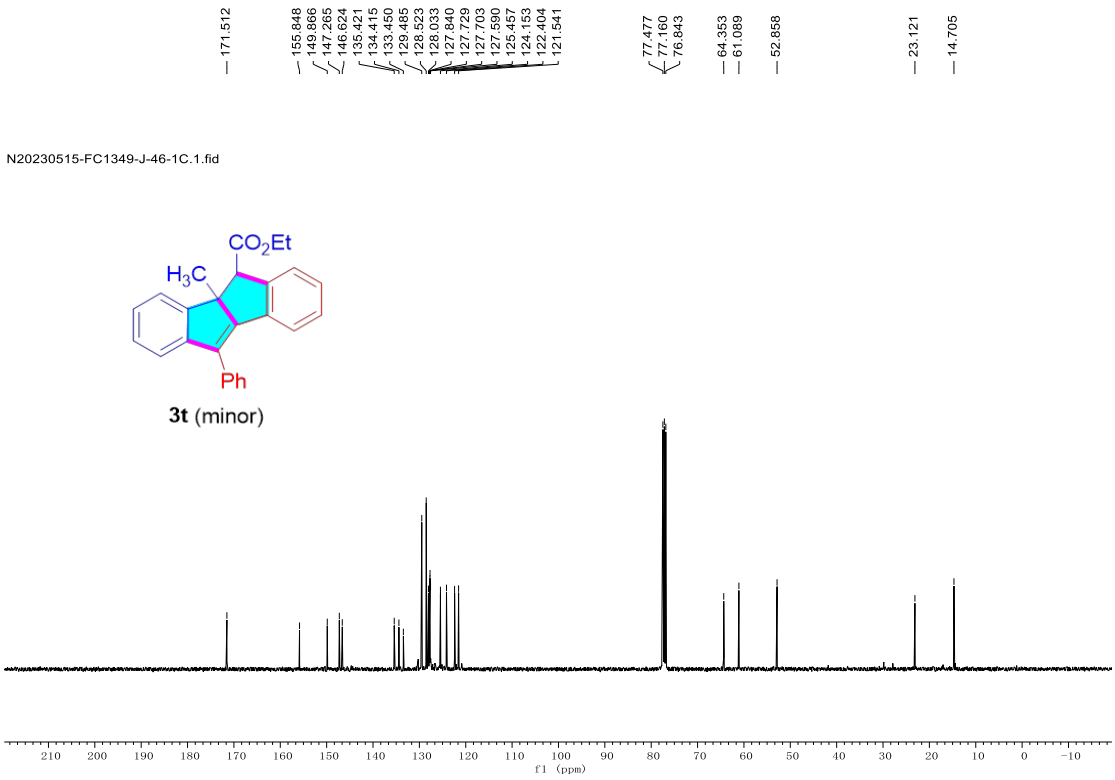
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **3t**



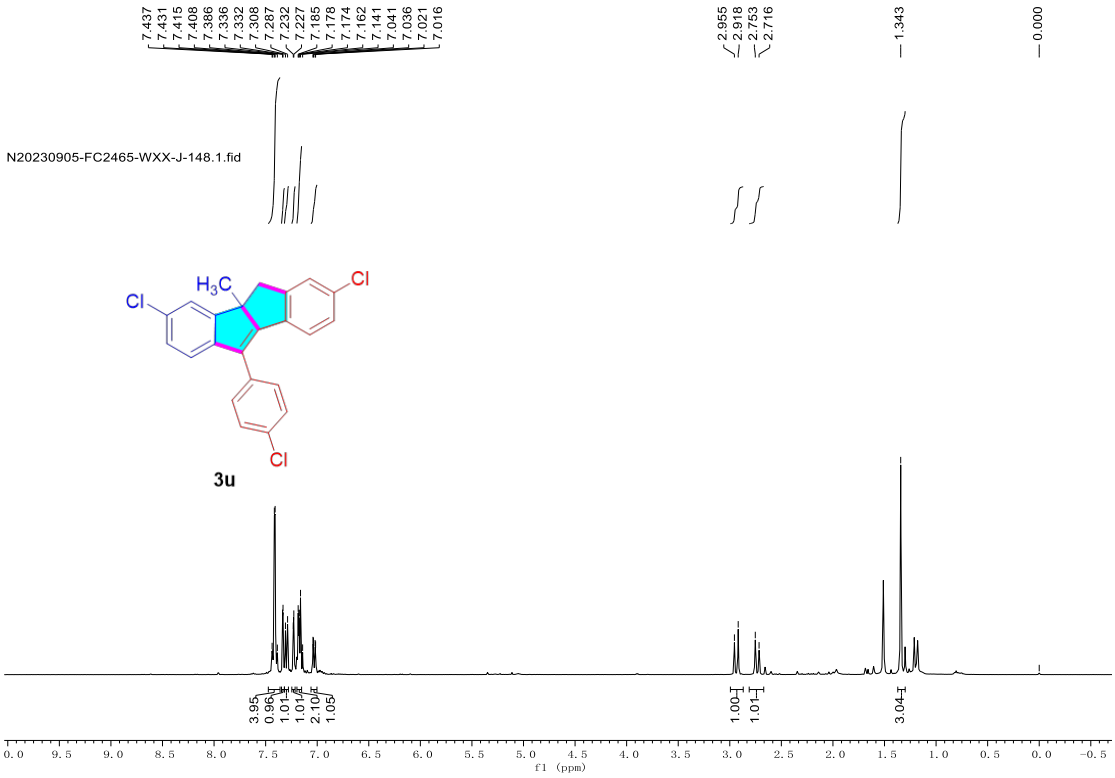
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3t**



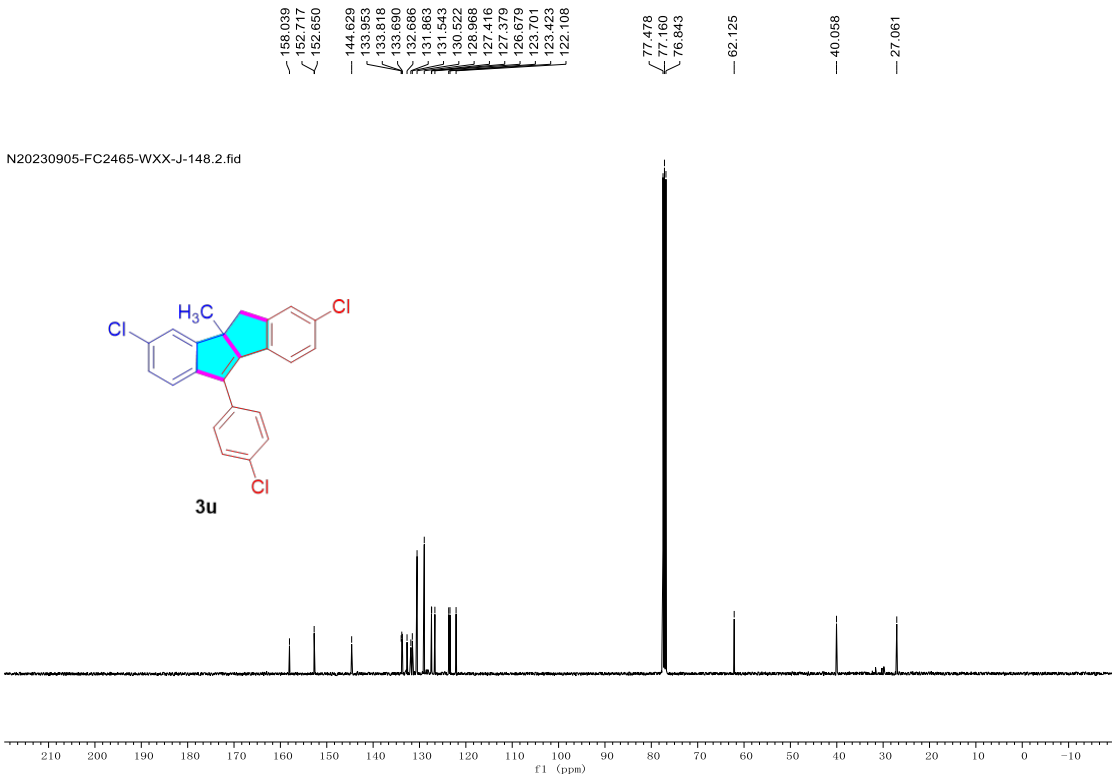
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **3t**



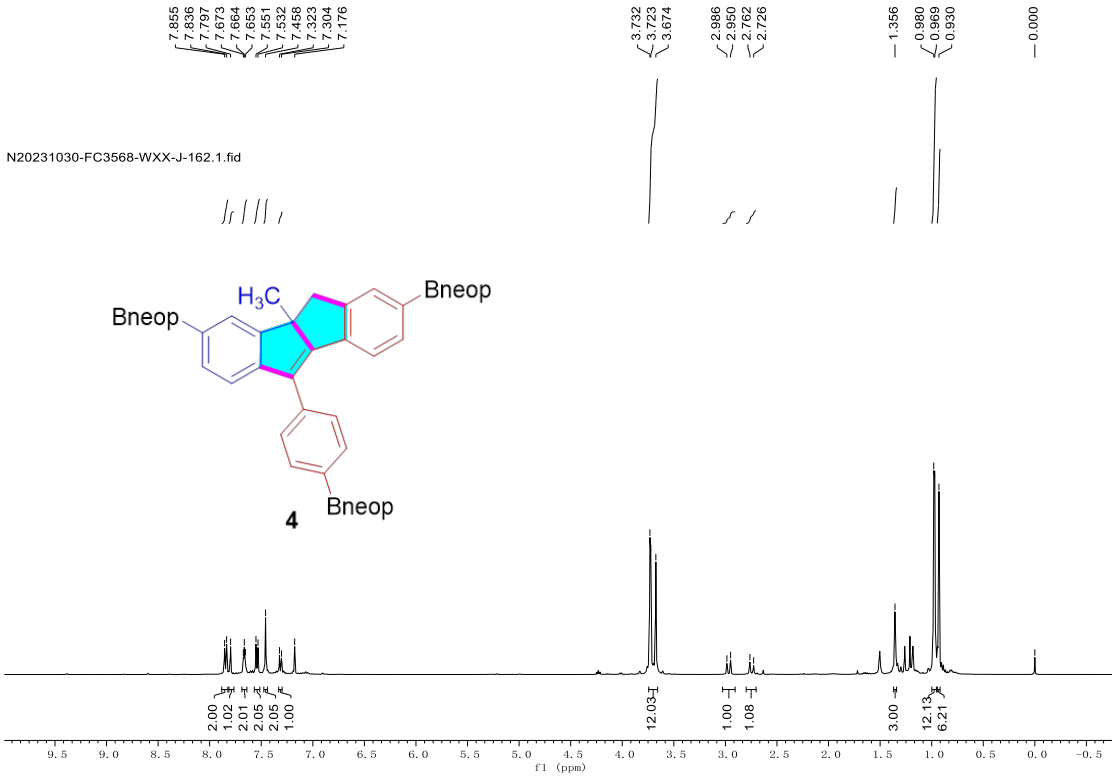
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3u**



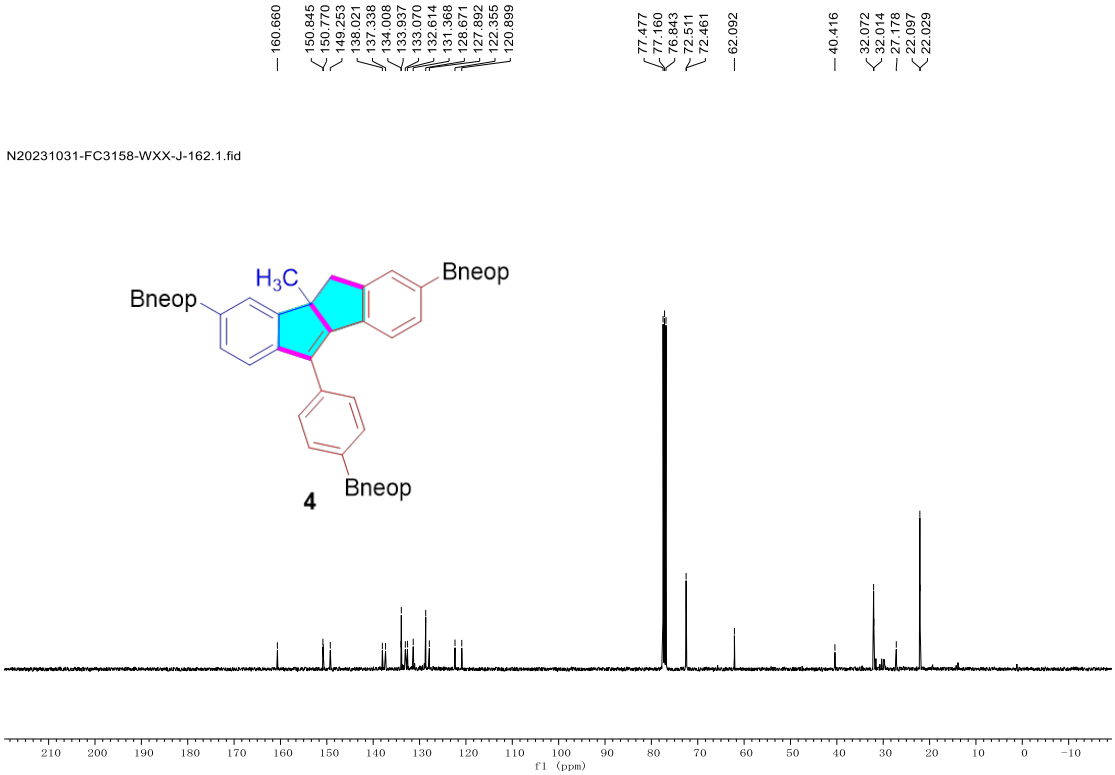
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **3u**



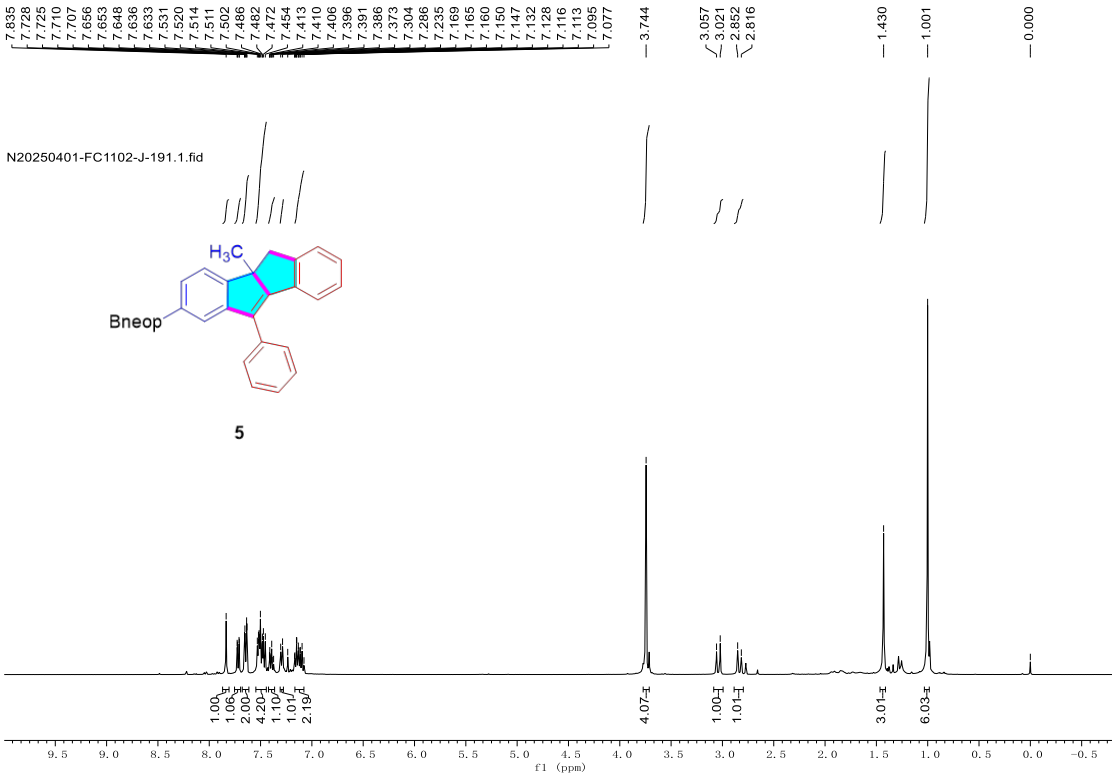
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4**



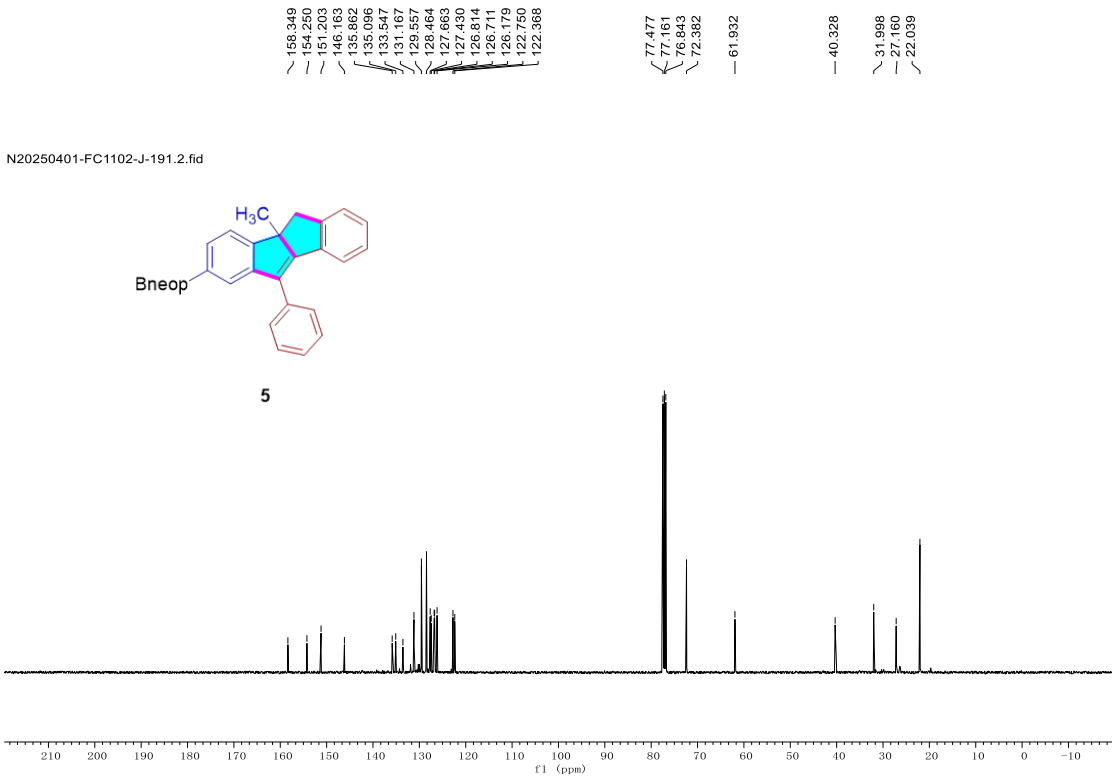
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **4**



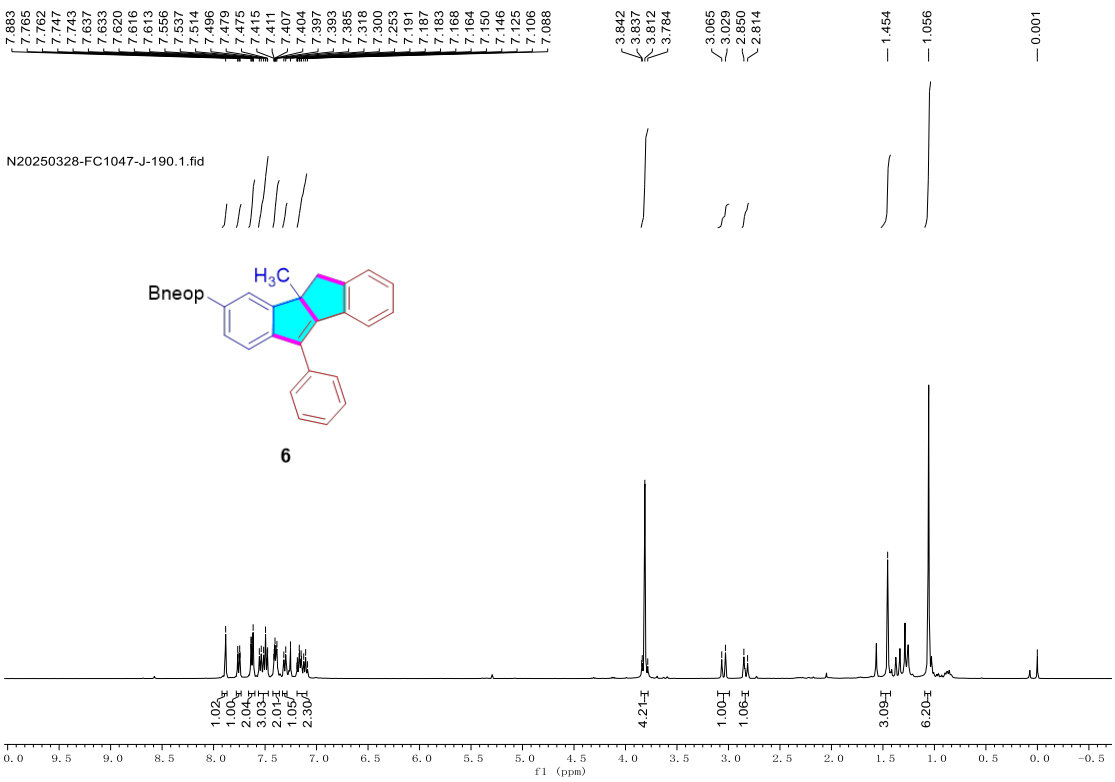
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **5**



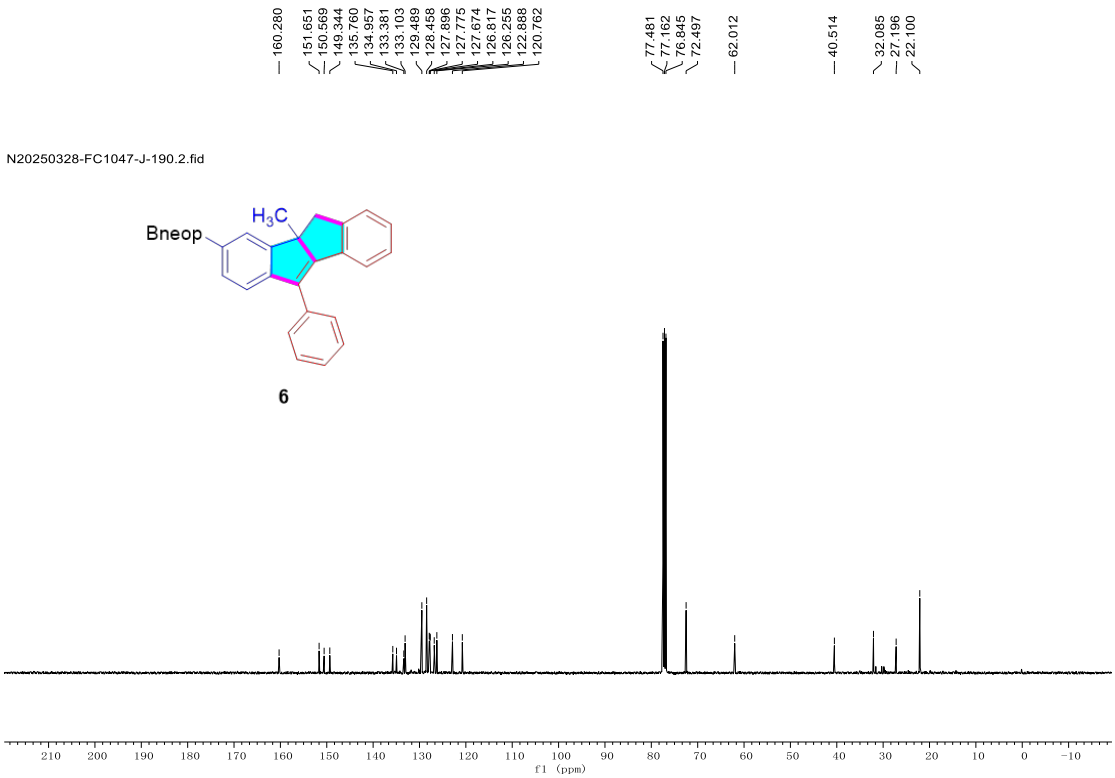
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **5**



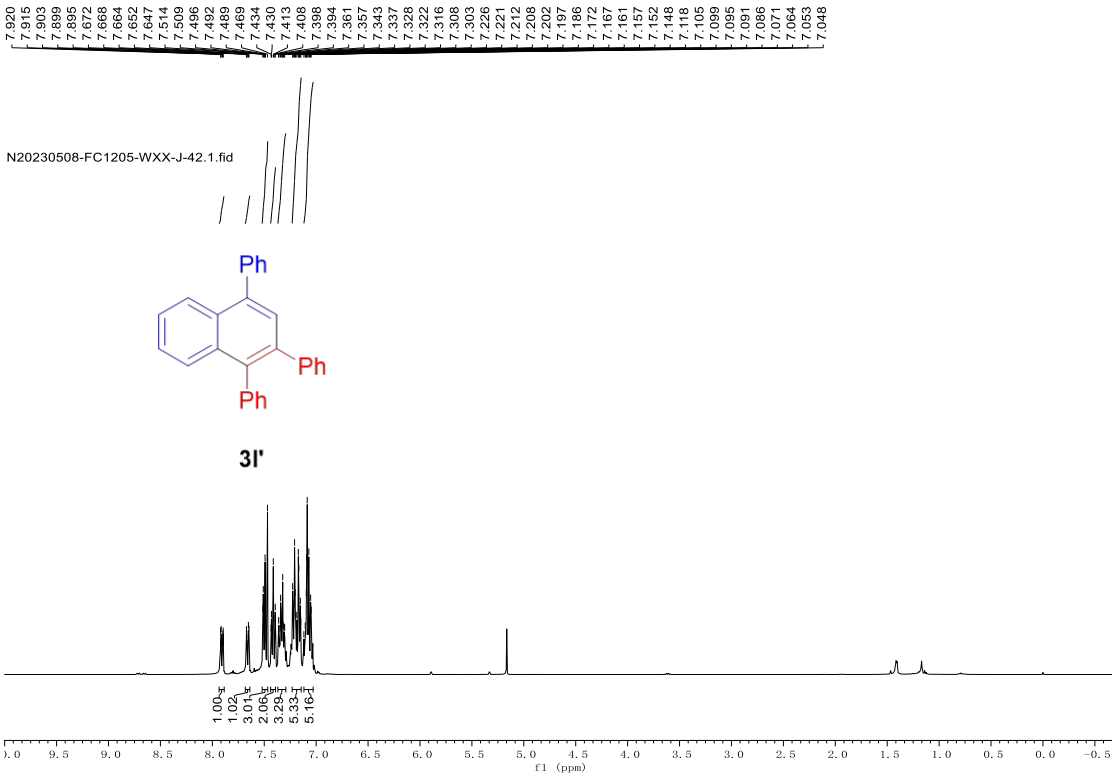
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **6**



^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **6**



^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3l'**



^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **3l'**