Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Facile and practical access to chiral benzofused oxa-heterocycles via asymmetric hydrogenation and intramolecular S_NAr cascade

Fangyuan Wang,†[a] Ting Wu,†[a] Bin Lu,†[a] Jianchao Yu,[a] Renwei Xiao,[a] Boxuan Yi,[a] Xumu Zhang,[a,*] Gen-Qiang Chen [a,b,*]

[a]*Medi-X Pingshan and Department of Chemistry, Southern University of Science and Technology, Shenzhen 518000, People's Republic of China;*

[b]*Academy for Advanced Interdisciplinary Studies and Guangdong Provincial Key Laboratory of Catalysis, Southern University of Science and Technology, Shenzhen 518055, People's Republic of China;*

†These authors contributed equally.

*Email: chengq@sustech.edu.cn; zhangxm@sustech.edu.cn

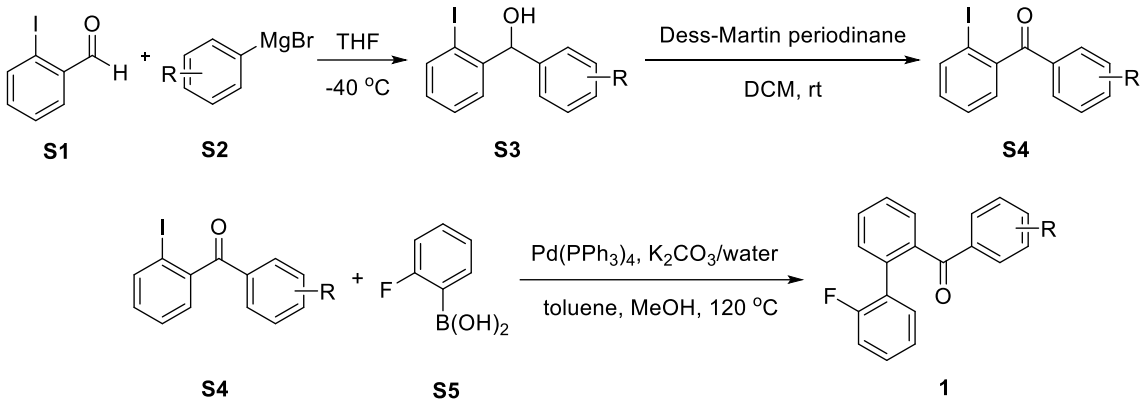
Content

1. General Information

Unless otherwise mentioned, all experiments were carried out under an atmosphere of argon or using standard Schlenk techniques. Solvents and reagents were purchased from commercial suppliers and used without further purification. Column Chromatography was performed with silica gel Merck 60 (300-400 mesh). NMR spectra were recorded on a Bruker DPX 400 spectrometer at 400 MHz for ^{1}H NMR, 101 MHz for ^{13}C NMR and a Bruker DPX 600 spectrometer at 600 MHz for ^{1}H NMR, 151 MHz for ^{13}C NMR. $CDCl_3$ and d^6-DMSO was the solvent used for the NMR analysis, with tetramethylsilane (TMS) as the internal standard. Chemical shifts are reported in ppm and coupling constants are given in Hz. Chemical shifts were reported relative to TMS (0.00 ppm) for ^{1}H NMR and relative to $CDCl_3$ (77.0 ppm) for ^{13}C NMR. HPLC analysis was carried out on Agilent 1260 Series instrument using a chiral stationary phase. PE refers to petroleum ether, and EA refers to ethyl acetate.

2. General Experimental Details

2.1 General Procedure for the Synthesis of Substrate



Scheme S1. Synthetic route of compound **1**.

Procedure A：Preparation of ketones 1.[1, 2]

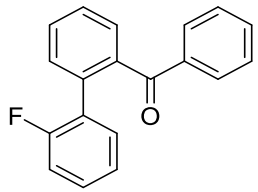
Step 1: To a solution of 2-Iodobenzaldehyde **S1** (2.32 g, 10 mmol, 1.0 equiv.) in THF (20 mL) was added 1 M PhMgBr **S2** (15 mL, 15 mmol, 1.5 equiv.) at -40℃. The mixture was stirred at -40℃ for 3 h until the start materials was consumed completely. The mixture was quenched by 1M HCl (10 mL) at 0℃, extracted by EtOAc (30 mL*2), the combined organic layer was washed by brine, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The crude product was purified by chromatography (PE:EA from 30:1 to 5:1). (2-iodophenyl)(phenyl)methanol **S3** was obtained. (90% ~ 99%).

Step 2: To a solution of (2-iodophenyl)(phenyl)methanol **S3** (10 mmol, 1.0 equiv.) in DCM (25 mL) was added Dess-Martin periodinane (5g, 12 mmol, 1.2 equiv.) at 0℃. The mixture was stirred at rt for 2 h until the start materials was consumed completely. The mixture was quenched by saturated $NaHCO_3$ (5ml), filtered and extracted by DCM (20 mL*2), the combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The crude product was purified by chromatography (PE:EA

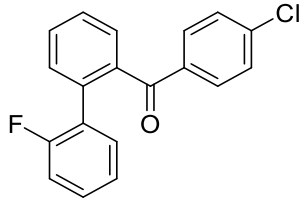
from 30:1 to 5:1). (2-iodophenyl)(phenyl)methanone **S4** was obtained with an equivalent yield.

Step 3: To a solution of (2-iodophenyl)(phenyl)methanone **S4** (5 mmol, 1.0 equiv.) , 2-Fluorophenylboronic acid **S5** (0.84 g, 6 mmol, 1.2 equiv.) and $Pd(PPh_3)_4$ (0.29 g, 5% mmol.) in toluene (80 mL) and MeOH (6.4 mL). The degassed K_2CO_3 aqueous (10ml, 1.38g/5ml water) was added. The mixture was stirred at 120℃ for 5 h until the start materials was consumed completely. The mixture was extracted by EtOAc (40 mL*2), the combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. Compound **1** was obtained with medium to high yield (75% ~ 96%).

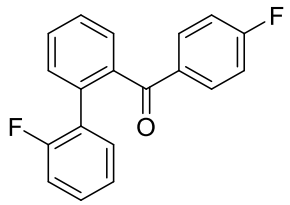
2.2 Characterization Data of Substrates



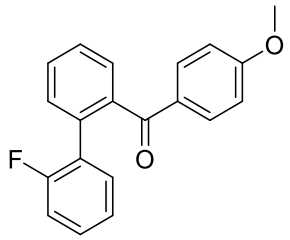
(2'-Fluoro-[1,1'-biphenyl]-2-yl)(phenyl)methanone (1a)[3]: Colourless oil, 1.35 g, 90% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.70 (d, 2H), 7.61 – 7.52 (m, 2H), 7.50 – 7.40 (m, 3H), 7.35 – 7.21 (m, 3H), 7.19 – 7.11 (m, 1H), 7.08 – 7.01 (m, 1H), 6.92 – 6.84 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 197.5, 159.0 (d, *J* = 247.4 Hz), 139.1, 137.2, 135.2, 132.7, 131.4 (d, *J* = 3.0 Hz), 131.1, 131.0, 130.5, 129.9, 129.4 (d, *J* = 8.1 Hz), 129.1, 128.0, 127.8, 127.5, 124.0 (d, *J* = 3.0 Hz), 115.4, 115.2. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -115.8. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{14}FO^+$ = 277.1023; Found 277.1023.



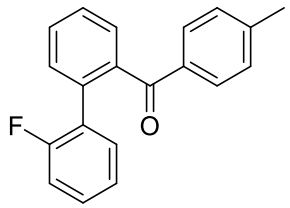
(4-Chlorophenyl)(2'-fluoro-[1,1'-biphenyl]-2-yl)methanone (1b)[1]: White solid, 0.57 g, 77% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.68 – 7.56 (m, 3H), 7.56 – 7.44 (m, 3H), 7.34 – 7.24 (m, 3H), 7.23 – 7.15 (m, 1H), 7.11 – 7.02 (t, 1H), 6.95 – 6.86 (t, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 196.3, 158.9 (d, *J* = 242.4 Hz), 139.1, 138.6, 135.6, 135.1, 131.4 (d, *J* = 10.1 Hz), 131.2, 131.1, 130.8, 129.6 (d, *J* = 10.0, 1.0 Hz), 129.0, 128.4, 127.8, 127.6, 124.2 (d, *J* = 3.0 Hz), 115.4 (d, *J* = 20.2 Hz). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -115.9. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{13}ClFO^+$ = 311.0633; Found 311.0631.



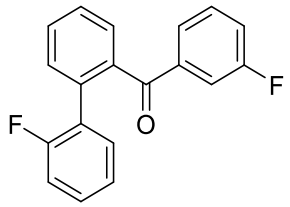
(2'-Fluoro-[1,1'-biphenyl]-2-yl)(4-fluorophenyl)methanone (**1c**)[1]: White solid, 0.87 g, 95% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.77 – 7.66 (m, 2H), 7.63 – 7.44 (m, 4H), 7.29 – 7.14 (m, 2H), 7.10 – 6.85 (m, 4H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 196.1, 165.5 (d, *J* = 252.5 Hz), 159.0 (d, *J* = 242.4 Hz), 138.9, 135.1, 133.7 (d, *J* = 3.0 Hz), 132.5 (d, *J* = 9.1 Hz), 131.4 (d, *J* = 3.0 Hz), 131.1, 130.7, 129.6 (d, *J* = 8.1 Hz), 129.0, 127.8 (d, *J* = 15.2 Hz), 127.7, 124.2 (d, *J* = 4.0 Hz), 115.6, 115.3, 115.1. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -105.5, -115.9. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{13}F_2O^+$ = 295.0929; Found 295.0927.



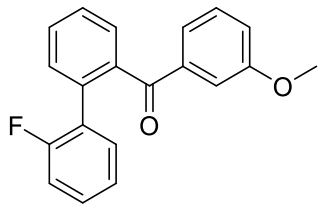
(2'-Fluoro-[1,1'-biphenyl]-2-yl)(4-methoxyphenyl)methanone (**1d**)[1]: Black solid, 1.52 g, 99% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 8.7 Hz, 2H), 7.60 – 7.42 (m, 4H), 7.25 (t, 1H), 7.22 – 7.14 (m, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.92 (t, 1H), 6.81 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 196.2, 163.3, 159.0 (d, *J* = 246.4 Hz), 139.5, 134.9, 132.3, 131.4 (d, *J* = 3.0 Hz), 131.0, 130.1, 129.4 (d, *J* = 8.1 Hz), 128.8, 127.9 (d, *J* = 15.2 Hz), 127.4, 124.0 (d, *J* = 3.0 Hz), 115.5, 115.3, 113.3, 55.4. **^{19}F NMR** (565 MHz, Chloroform-*d*) δ -115.9. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{16}FO_2^+$ = 307.1129; Found 307.1128.



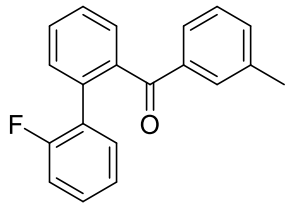
(2'-Fluoro-[1,1'-biphenyl]-2-yl)(p-tolyl)methanone (**1e**)[1]: White solid, 1.22 g, 84% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.66 – 7.50 (m, 4H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.29 – 7.22 (m, 1H), 7.22 – 7.10 (m, 3H), 7.06 (t, *J* = 7.1 Hz, 1H), 6.91 (t, 1H), 2.35 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 197.2, 159.0 (d, *J* = 252.5 Hz), 143.6, 139.4, 135.1, 134.7, 131.4 (d, *J* = 3.0 Hz), 131.1, 130.3, 130.1, 129.4 (d, *J* = 8.1 Hz), 129.0, 128.8, 127.9 (d, *J* = 15.3 Hz), 127.4, 124.0 (d, *J* = 3.0 Hz), 115.4 (d, *J* = 22.2 Hz), 21.6. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -115.9. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{16}FO^+$ = 291.1180; Found 291.1178.



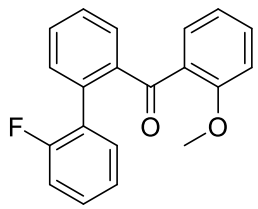
(2'-Fluoro-[1,1'-biphenyl]-2-yl)(3-fluorophenyl)methanone (**1f**)[1]: White solid, 0.52 g, 85% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.64 – 7.53 (m, 2H), 7.52 – 7.36 (m, 4H), 7.32 – 7.04 (m, 5H), 6.95 – 6.85 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 196.2, 162.3 (d, *J* = 252.5 Hz), 158.9 (d, *J* = 246.4 Hz), 139.4 (d, *J* = 7.1 Hz), 138.5, 135.2, 131.3 (d, *J* = 3.0 Hz), 131.1, 130.9, 129.7 (d, *J* = 4.0 Hz), 129.6 (d, *J* = 4.0 Hz), 129.1, 127.7 (d, *J* = 15.2 Hz), 127.6, 125.7 (d, *J* = 3.0 Hz), 124.2 (d, *J* = 4.0 Hz), 119.7 (d, *J* = 21.2 Hz), 116.3 (d, *J* = 23.2 Hz), 115.4 (d, *J* = 22.2 Hz). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -112.5, -115.8. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{13}F_2O^+$ = 295.0929; Found 295.0929.



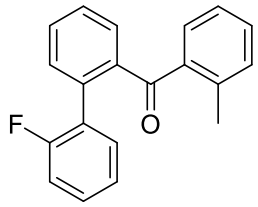
(2'-Fluoro-[1,1'-biphenyl]-2-yl)(3-methoxyphenyl)methanone (**1g**)[1]: White solid, 2.13 g, 81% yield. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.60 – 7.53 (m, 2H), 7.46 (t, *J* = 7.1 Hz, 2H), 7.28 – 7.15 (m, 5H), 7.08 – 7.03 (m, 1H), 7.02 – 6.98 (m, 1H), 6.91 (t, 1H), 3.77 (s, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 197.3, 159.0 (d, *J* = 246.1 Hz), 159.3, 139.1, 138.6, 135.2, 131.4 (d, *J* = 3.0 Hz), 131.1, 130.5, 129.4 (d, *J* = 9.1 Hz), 129.1, 129.0, 127.9 (d, *J* = 15.1 Hz), 127.4, 124.0 (d, *J* = 4.5 Hz), 123.0, 119.6, 115.4 (d, *J* = 22.6 Hz), 113.5, 55.3. **^{19}F NMR** (565 MHz, Chloroform-*d*) δ -115.8. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{16}FO_2^+$ = 307.1129; Found 307.1126.



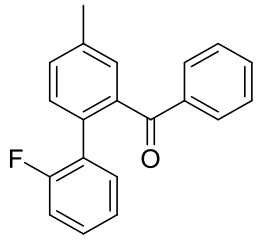
(2'-Fluoro-[1,1'-biphenyl]-2-yl)(m-tolyl)methanone (**1h**)[1]: Yellow oil, 1.1 g, 95% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.60 – 7.43 (m, 6H), 7.27 – 7.12 (m, 4H), 7.07 – 7.01 (m, 1H), 6.92 – 6.85 (m, 1H), 2.30 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 197.7, 159.0 (d, *J* = 246.4 Hz), 139.2, 137.7, 137.2, 135.2, 133.5, 131.4 (d, *J* = 4.0 Hz), 131.0, 130.4, 129.4 (d, *J* = 8.1 Hz), 129.2, 128.1, 127.9, 127.5, 127.2, 124.0 (d, *J* = 4.0 Hz), 115.4, 115.2, 21.1. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -115.6. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{16}FO^+$ = 291.1180; Found 291.1178.



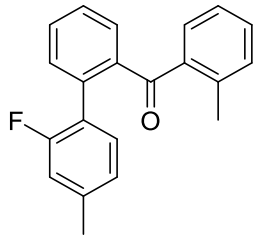
(2'-Fluoro-[1,1'-biphenyl]-2-yl)(2-methoxyphenyl)methanone (**1i**)[1]: Yellow liquid, 1.54 g, 95% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.62 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.54 – 7.48 (m, 1H), 7.44 – 7.33 (m, 3H), 7.28 – 7.23 (m, 1H), 7.20 – 7.07 (m, 2H), 7.02 – 6.95 (m, 1H), 6.86 – 6.77 (m, 2H), 6.68 (d, *J* = 8.4, 1.0 Hz, 1H), 3.57 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 196.9, 159.0 (d, *J* = 247.4 Hz), 158.0, 140.6, 135.0, 132.9, 131.4 (d, *J* = 4.0 Hz), 130.9, 130.7, 130.5, 129.2, 129.0 (d, *J* = 8.1 Hz), 128.3, 128.2 (d, *J* = 16.2 Hz), 127.5, 123.5 (d, *J* = 3.0 Hz), 119.9, 115.0 (d, *J* = 21.2 Hz), 111.0, 55.3. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -115.9. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{16}FO_2^+$ = 307.1129; Found 307.1127.



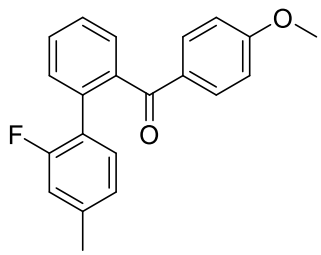
(2'-Fluoro-[1,1'-biphenyl]-2-yl)(o-tolyl)methanone (**1j**)[1]: White solid, 0.63 g, 75% yield. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.56 (t, *J* = 7.2 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.28 (d, *J* = 7.7 Hz, 1H), 7.24 – 7.19 (m, 2H), 7.18 – 7.13 (m, 1H), 7.10 – 7.03 (m, 3H), 6.87 (t, 1H), 2.38 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 199.3, 158.9 (d, *J* = 246.4 Hz), 140.1, 138.7, 137.7, 135.6, 131.1, 131.0, 131.0, 131.0, 130.7, 129.9, 129.3 (d, *J* = 7.1 Hz), 128.4, 128.2, 127.7, 124.9, 123.9 (d, *J* = 4.0 Hz), 115.2 (d, *J* = 22.2 Hz), 20.4. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -115.6. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{16}FO^+$ = 291.1180; Found 291.1177.



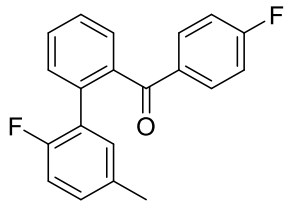
(2'-Fluoro-4-methyl-[1,1'-biphenyl]-2-yl)(phenyl)methanone (**1k**)[1]: White solid, 0.63 g, 95% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.69 (d, 2H), 7.45 – 7.36 (m, 2H), 7.30 (t, *J* = 8.4, 7.1 Hz, 2H), 7.20 (td, *J* = 7.6, 1.9 Hz, 1H), 7.15 – 7.05 (m, 3H), 7.00 (t, *J* = 7.5, 1.2 Hz, 1H), 6.86 (t, *J* = 9.7, 8.2, 1.2 Hz, 1H), 3.85 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 197.4, 159.1 (d, *J* = 242.4 Hz), 158.8, 140.1, 137.0, 132.7, 132.2, 131.5 (d, *J* = 3.0 Hz), 129.9, 129.0 (d, *J* = 8.1 Hz), 128.0, 127.6, 127.5, 127.4, 123.9 (d, *J* = 4.0 Hz), 116.3, 115.4, 115.2, 114.3, 55.5. **^{19}F NMR** (376 MHz,) δ -115.8. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{16}FO^+$ = 291.1180; Found 291.1179.



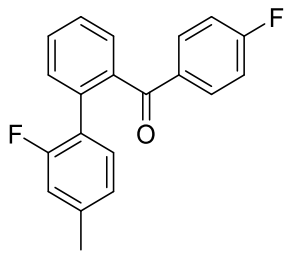
(2'-Fluoro-4'-methyl-[1,1'-biphenyl]-2-yl)(o-tolyl)methanone (**1l**)[1]: Colorless oil, 0.63 g, 80% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.58 – 7.50 (m, 2H), 7.43 – 7.37 (m, 2H), 7.30 (d, *J* = 7.7, 1.3 Hz, 1H), 7.28 – 7.21 (m, 1H), 7.14 – 7.04 (m, 3H), 6.88 (d, *J* = 7.7, 1.7, 0.8 Hz, 1H), 6.71 (d, *J* = 10.6, 1.4 Hz, 1H), 2.39 (s, 3H), 2.27 (s, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 199.4, 158.8 (d, *J* = 246.1 Hz), 140.1, 139.8 (d, *J* = 7.6 Hz), 138.8, 137.7, 135.8, 131.3, 131.2, 131.0 (d, *J* = 6.0 Hz), 130.9, 130.7 (d, *J* = 4.5 Hz), 130.0, 127.4, 125.3, 125.2, 124.9, 124.7 (d, *J* = 3.0 Hz), 115.8 (d, *J* = 22.6 Hz), 21.0, 20.5. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -116.7. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{18}OF^+$ = 305.1336; Found 305.1336.



(2'-Fluoro-4'-methyl-[1,1'-biphenyl]-2-yl)(4-methoxyphenyl)methanone (**1m**)[1]: Yellow solid, 0.61 g, 76% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 8.9 Hz, 2H), 7.57 – 7.41 (m, 4H), 7.13 (t, *J* = 7.9 Hz, 1H), 6.88 – 6.79 (m, 3H), 6.74 (d, 1H), 3.82 (s, 3H), 2.27 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 196.3, 163.3, 158.9 (d, *J* = 247.4 Hz), 139.9, 139.8, 139.5, 135.0, 132.4, 131.1, 131.0, 130.1, 130.0, 128.7, 127.1, 124.9, 124.8 (d, *J* = 3.0 Hz), 116.0, 115.8, 113.3, 55.4, 21.0. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -117.0. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{18}FO_2^+$ = 321.1285; Found 321.1284.



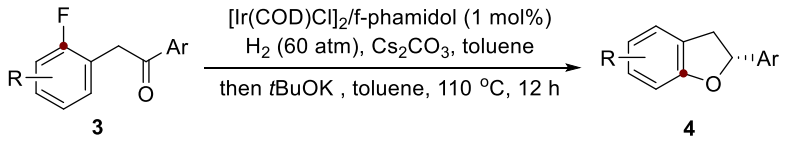
(2'-Fluoro-5'-methyl-[1,1'-biphenyl]-2-yl)(4-fluorophenyl)methanone (**1n**)[1]: White solid, 0.37 g, 50% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.80 – 7.67 (m, 2H), 7.62 – 7.43 (m, 4H), 7.10 – 6.92 (m, 4H), 6.78 (t, *J* = 9.9, 8.4 Hz, 1H), 2.26 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 196.2, 165.4 (d, *J* = 256.5 Hz), 157.2 (d, *J* = 244.4 Hz), 138.9, 135.4, 133.8, 133.6 (d, *J* = 4.0 Hz), 132.5 (d, *J* = 9.1 Hz), 131.8 (d, *J* = 3.0 Hz), 131.1, 130.7, 130.0 (d, *J* = 8.1 Hz), 129.0, 127.5, 127.3 (d, *J* = 16.2 Hz), 115.2 (d, *J* = 8.1 Hz), 115.0 (d, *J* = 8.1 Hz), 20.6. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -105.7, -121.4. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{15}F_2O^+$ = 309.1085; Found 309.1085.



(2'-Fluoro-4'-methyl-[1,1'-biphenyl]-2-yl)(4-fluorophenyl)methanone (**1o**)[1]: White solid, 0.37 g, 93% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.77 – 7.69 (m, 2H), 7.61 – 7.54 (m, 1H), 7.54 – 7.41 (m, 3H), 7.12 (t, *J* = 7.9 Hz, 1H), 7.04 – 6.95 (m, 2H), 6.87 (d, 1H), 6.73 (d, *J* = 11.2, 1.6 Hz, 1H), 2.27 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 196.2, 165.5 (d, *J* = 255.5 Hz), 158.8 (d, *J* = 246.4 Hz), 140.2 (d, *J* = 8.1 Hz), 138.9, 135.3, 133.7 (d, *J* = 3.0 Hz), 132.6 (d, *J* = 9.1 Hz), 131.2, 131.1 (d, *J* = 4.0 Hz), 130.6, 128.9, 127.4, 124.9 (d, *J* = 3.0 Hz), 124.7 (d, *J* = 15.2 Hz), 116.0 (d, *J* = 22.2 Hz), 115.2 (d, *J* = 22.2 Hz), 21.1. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -105.6, -117.0. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{15}F_2O^+$ = 309.1085; Found 309.1083.

3. General Procedure of Asymmetric Hydrogenation

General procedure: To a 4.0 mL vial was added the catalyst precursor $[Ir(COD)Cl]_2$ (6.7 mg, 0.01 mmol), f-phamidol (**L1**) (11.6 mg, 0.02 mmol) and anhydrous THF (1.0 mL) under argon atmosphere. The mixture was stirred for 2.0 h at 25℃ giving orange red solution in the argon-filled glovebox. The resulting solution (100 μL) transferred by syringe into a 5.0 mL vial charged with fresh distilled substrate α-aminoketones (0.2 mmol) and NaOMe (0.4 mmol, 21.6 mg, 2 equiv) in 2.0 mL anhydrous THF. The vials were transferred to an autoclave, which was then charged with 50 atm of H_2, stirred at room temperature for 12 h and further stirred at 80℃ for 4 h. The hydrogen gas was released slowly in a well-ventilated hood and the solution was concentrated and passed through a short column of silica gel to get the product. The product was analyzed by chiral HPLC for ee values.

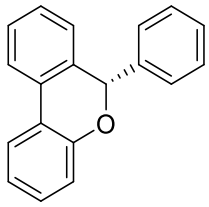


3 **4**

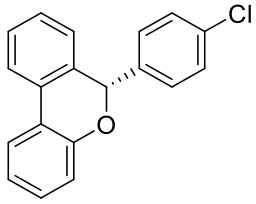
To a 10.0 mL vial equipped with a magnetic stir bar was added $[Ir(COD)_2Cl]_2$ (6.7 mg, 0.01 mmol) and f-phamidol (**L1**) (11.6 mg, 0.02 mmol) in dry toluene (10.0 mL) in an argon-filled glovebox. An Ir/*f*-phamidol-precatalyst solution (0.001 M) was formed after stirring for 30 min. To a 4.0 mL vial equipped with a magnetic stir bar was added ketones **3** (0.2 mmol, 1.0 eq.) and Cs_2CO_3 (195.5 mg, 0.6 mmol, 3.0 eq.) in an argon-filled glovebox. Then, a solution of Ir/*f*-phamidol-precatalyst (0.001 M, 1.0 mL) was added into the 4.0 mL vial, followed dried toluene (1.0 mL). The vial was transferred into the autoclave. The autoclave was quickly purged with hydrogen gas for three times, and then pressurized to 60 atm H_2. The reaction solution was stirred at room temperature for 48 h, and then the pressure was released carefully. Next, *t*BuOK (44.9 mg, 0.4 mmol) was

added into the system. The reaction was then heated to 110 °C for 12 h under Ar atmosphere. After that, the reaction system was cooled to room temperature and diluted with EtOAc (2.0 mL). Then, the solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica gel (silica: 200–300 mesh, eluent: petroleum ether) to afford the corresponding pure product **4**.

3.1 Characterization Data of Products

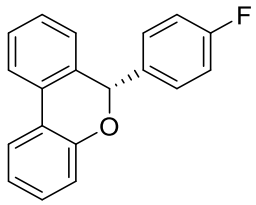


(*S*)-6-phenyl-6H-benzo[c]chromene (**2a**)[1]: Colorless liquid, 51 mg, 99% yield, 96% ee; $[\alpha]^{20}_{D}$ = +30.6 (c = 0.5, $CHCl_3$); **HPLC** (Chiralpak OD-3 column, hexane/isopropanol = 95/5; flow rate = 1.0 mL/min; UV detection at 220 nm; t_1 = 8.7 min (minor), t_2 = 9.6 min (major). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.76 (t, *J* = 8.2 Hz, 2H), 7.42 – 7.31 (m, 6H), 7.26 – 7.19 (m, 2H), 7.07 – 6.97 (m, 2H), 6.85 (d, *J* = 7.6 Hz, 1H), 6.16 (s, 1H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 153.6, 139.6, 134.0, 130.1, 129.6, 128.5, 128.5, 128.4, 128.2, 127.6, 126.3, 123.1, 122.8, 122.1, 117.9, 79.7.

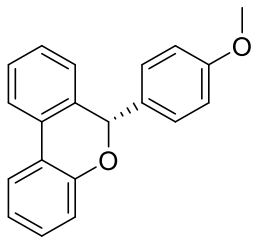


(*S*)-6-(4-chlorophenyl)-6H-benzo[c]chromene (**2b)**: Yellow solid, 58 mg, 99% yield, 85% ee; $[\alpha]^{20}_{D}$ = +12.6 (c = 1.0, $CHCl_3$); **HPLC** (Chiralpak OJ-3 column, hexane/isopropanol = 95/5; flow rate = 1.0 mL/min; UV detection at 220 nm; t_1 = 13.4 min (major), t_2 = 15.8 min (minor). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.77 – 7.70 (m,

2H), 7.39 (t, *J* = 7.6, 1.3 Hz, 1H), 7.28 (t, *J* = 2.1 Hz, 4H), 7.25 – 7.18 (m, 2H), 7.02 (t, *J* = 7.5, 1.2 Hz, 1H), 6.97 (d, *J* = 8.1, 1.3 Hz, 1H), 6.84 (d, *J* = 7.6 Hz, 1H), 6.12 (s, 1H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 153.2, 138.1, 134.2, 133.3, 129.9, 129.7, 129.4, 128.6, 128.6, 127.7, 126.1, 123.1, 122.6, 122.2 (d, *J* = 4.5 Hz), 117.9, 78.7.

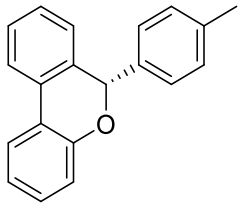


(*S*)-6-(4-fluorophenyl)-6H-benzo[c]chromene (**2c)**: Yellow solid, 55 mg, 99% yield, 95% ee; $[\alpha]^{20}_D$ = +21.6 (c = 1.45, $CHCl_3$); **HPLC** (Chiralpak OJ-3 column, hexane/isopropanol = 95/5; flow rate = 1.0 mL/min; UV detection at 220 nm; t_1 = 14.4 min (minor), t_2 = 15.3 min (major). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.74 (t, *J* = 8.1, 1.4 Hz, 2H), 7.42 – 7.27 (m, 3H), 7.27 – 7.16 (m, 2H), 7.05 – 6.95 (m, 4H), 6.83 (d, 1H), 6.13 (s, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 162.6 (d, *J* = 247.4 Hz), 153.3, 135.4 (d, *J* = 3.0 Hz), 133.6, 130.0, 129.9 (d, *J* = 8.1 Hz), 129.6, 128.6, 127.6, 126.1, 123.1, 122.7, 122.2 (d, *J* = 2.0 Hz), 117.9, 115.4, 115.2, 78.8. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -113.5. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{14}FO^+$ = 277.1023; Found 277.1020.

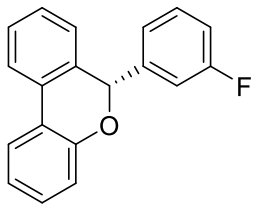


(*S*)-6-(4-methoxyphenyl)-6H-benzo[c]chromene (**2d)**[2]: Yellow oil, 56 mg, 98% yield, 89% ee; $[\alpha]^{20}_D$ = +14.0(c = 1.0, $CHCl_3$); **HPLC** (Chiralpak OJ-3 column, hexane/isopropanol = 70/30; flow rate = 1.0 mL/min; UV detection at 220 nm; t_1 = 16.2 min (major), t_2 = 20.0 min (minor). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.76 (t, *J* = 7.5,

5.8, 1.4 Hz, 2H), 7.39 (t, *J* = 7.7, 1.3 Hz, 1H), 7.29 (d, 2H), 7.24 – 7.18 (m, 2H), 7.03 (t, *J* = 7.5, 1.2 Hz, 1H), 6.97 (d, *J* = 8.0, 1.2 Hz, 1H), 6.90 – 6.84 (m, 3H), 6.13 (s, 1H), 3.79 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 159.6, 153.6, 134.2, 131.7, 130.1, 129.5, 129.5, 128.4, 127.6, 126.2, 123.0, 122.8, 122.0, 122.0, 117.9, 113.8, 79.3, 55.2.

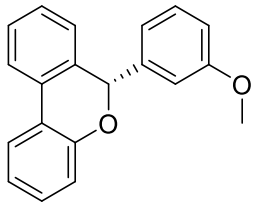


(*S*)-6-(p-tolyl)-6H-benzo[c]chromene (**2e**)[2]: White solid, 54 mg, 99% yield, 96% ee; $[\alpha]^{20}_D$ = +23.6(c = 1.0, $CHCl_3$); **HPLC** (Chiralpak OD-3 column, hexane/isopropanol = 90/10; flow rate = 1.0 mL/min; UV detection at 220 nm; t_1 = 5.6 min (major), t_2 = 6.2 min (minor). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.77 – 7.71 (m, 2H), 7.37 (t, *J* = 7.6, 1.3 Hz, 1H), 7.28 – 7.12 (m, 7H), 7.05 – 6.95 (m, 2H), 6.85 (d, *J* = 7.7, 0.9 Hz, 1H), 6.12 (s, 1H), 2.33 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 153.6, 138.1, 136.6, 134.1, 130.0, 129.5, 129.1, 128.3, 128.1, 127.5, 126.2, 123.0, 122.7, 122.0, 122.0, 117.9, 79.5, 21.2.

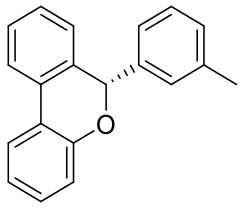


(*S*)-6-(3-fluorophenyl)-6H-benzo[c]chromene (**2f**): Yellow oil, 54 mg, 99% yield, 65% ee; $[\alpha]^{20}_D$ = - 0.93(c = 1.0, $CHCl_3$); **HPLC** (Chiralpak OJ-3 column, hexane/isopropanol = 95/5; flow rate = 1.0 mL/min; UV detection at 220 nm; t_1 = 13.5 min (major), t_2 = 16.0 min (minor). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.79 – 7.70 (m, 2H), 7.40 (t, *J* = 7.6, 1.3 Hz, 1H), 7.32 – 7.18 (m, 3H), 7.13 (d, *J* = 7.7, 1.2 Hz, 1H), 7.10 – 6.95 (m, 4H), 6.88 (d, *J* = 7.6 Hz, 1H), 6.14 (s, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 162.8 (d, *J* = 247.4 Hz), 153.2, 142.2 (d, *J* = 7.1 Hz), 133.1, 129.9 (d, *J* = 8.1 Hz), 129.7, 128.7, 127.7,

126.1, 123.6 (d, *J* = 2.0 Hz), 123.1, 122.6, 122.3, 122.2, 117.9, 115.3, 115.1 (d, *J* = 3.0 Hz), 114.9, 78.7 (d, *J* = 2.0 Hz). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -112.6. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{14}FO^+$ = 277.1023; Found 277.1021.

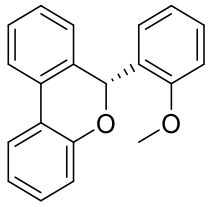


(*S*)-6-(3-methoxyphenyl)-6H-benzo[c]chromene (**2g**)[2]: Yellow oil, 57 mg, 99% yield, 90% ee; $[\alpha]^{20}_D$ = + 21.27 (c = 1.45, $CHCl_3$); **HPLC** (Chiralpak OJ-3 column, hexane/isopropanol = 70/30; flow rate = 1.0 mL/min; UV detection at 220 nm; t_1 = 18.4 min (major), t_2 = 23.2 min (minor). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.74 (t, *J* = 7.5, 5.4, 1.3 Hz, 2H), 7.38 (t, *J* = 7.6, 1.3 Hz, 1H), 7.28 – 7.19 (m, 3H), 7.06 – 6.98 (m, 2H), 6.95 (d, *J* = 5.0, 2.8 Hz, 2H), 6.86 (t, 2H), 6.12 (s, 1H), 3.74 (s, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 159.7, 153.6, 141.0, 133.8, 129.9, 129.6, 129.4, 128.4, 127.6, 126.2, 123.1, 122.7, 122.1, 122.0, 120.5, 117.8, 113.9, 113.5, 79.5, 55.2.

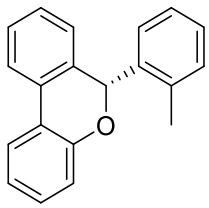


(*S*)-6-(m-tolyl)-6H-benzo[c]chromene (**2h)**: Yellow solid, 54 mg, 99% yield, 96% ee; $[\alpha]^{20}_D$ = + 13.2 (c = 1.45, $CHCl_3$); **HPLC** (Chiralpak OJ-3 column, hexane/isopropanol = 97/3; flow rate = 1.0 mL/min; UV detection at 220 nm; t_1 = 19.9 min (major), t_2 = 22.5 min (minor). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 7.7, 1.8 Hz, 2H), 7.36 (t, *J* = 7.6, 1.3 Hz, 1H), 7.25 – 7.10 (m, 7H), 7.05 – 6.97 (m, 2H), 6.81 (d, *J* = 7.6 Hz, 1H), 6.09 (s, 1H), 2.32 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 153.7, 139.4, 138.1, 134.1, 130.0, 129.5, 129.2, 128.8, 128.4, 128.3, 127.5, 126.2, 125.3, 123.1, 122.7, 122.0,

122.0, 117.8, 79.8, 21.4. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{17}O^+$ = 273.1274; Found 273.1269.

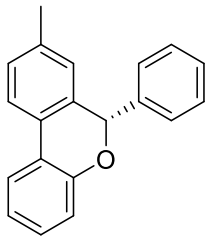


(*R*)-6-(2-methoxyphenyl)-6H-benzo[c]chromene (**2i)**: White solid, 57 mg, 99% yield, 68% ee; $[\alpha]^{20}_D$ = -13.7 (c = 1.0, $CHCl_3$); **HPLC** (Chiralpak OJ-3 column, hexane/isopropanol = 95/5; flow rate = 1.0 mL/min; UV detection at 220 nm; t_1 = 12.1 min (major), t_2 = 14.7 min (minor). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.77 (t, 2H), 7.39 – 7.29 (m, 3H), 7.24 – 7.16 (m, 2H), 7.06 (t, *J* = 7.6, 1.3 Hz, 1H), 7.01 – 6.91 (m, 3H), 6.76 (d, 1H), 6.63 (s, 1H), 3.87 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 157.1, 154.3, 134.2, 130.4, 129.5, 129.4, 129.0, 128.1, 127.8, 127.7, 125.8, 123.1, 122.9, 121.9, 121.8, 120.9, 117.7, 110.6, 73.5, 55.6. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{17}O_2^+$ = 289.1223; Found 289.1218.

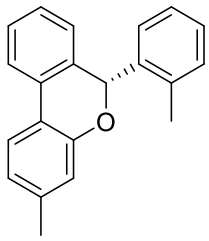


(*S*)-6-(o-tolyl)-6H-benzo[c]chromene (**2j)**: Brown oil, 54 mg, 99% yield, 94% ee; $[\alpha]^{20}_D$ = -1.6 (c = 1.0 , $CHCl_3$); **HPLC** (Chiralpak OJ-3 column, hexane/isopropanol = 95/5; flow rate = 1.0 mL/min; UV detection at 220 nm; t_1 = 8.9 min (major), t_2 = 11.0 min (minor). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.79 – 7.74 (m, 2H), 7.37 (t, *J* = 7.6, 1.3 Hz, 1H), 7.28 – 7.22 (m, 3H), 7.22 – 7.14 (m, 3H), 7.05 (t, *J* = 7.5, 1.3 Hz, 1H), 6.97 (d, *J* = 8.0, 1.3 Hz, 1H), 6.67 (d, *J* = 7.6, 1.1 Hz, 1H), 6.31 (s, 1H), 2.40 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 154.1, 137.1, 137.0, 133.8, 130.7, 130.5, 129.5, 128.7, 128.4,

128.4, 127.7, 126.1, 125.6, 123.1, 122.9, 122.1, 122.0, 117.6, 77.7, 19.6. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{18}O^+$ = 273.1274; Found 273.1268.

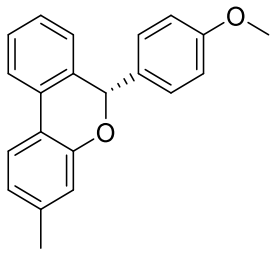


(*S*)-8-methyl-6-phenyl-6H-benzo[c]chromene (**2k)**: Yellow solid, 54 mg, 99% yield, 94% ee; $[\alpha]^{20}_D$ = +54.67 (c = 1.0, $CHCl_3$); **HPLC** (Chiralpak OD-3 column, hexane/isopropanol = 95/5; flow rate = 1.0 mL/min; UV detection at 220 nm; t_1 = 8.4 min (major), t_2 = 9.0 min (minor). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.67 (t, 2H), 7.47 – 7.23 (m, 5H), 7.15 (t, *J* = 7.8, 1.6 Hz, 1H), 7.08 – 6.83 (m, 3H), 6.39 (d, *J* = 2.6, 0.8 Hz, 1H), 6.10 (s, 1H), 3.72 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 159.3, 152.8, 139.4, 135.5, 128.5, 128.5, 128.4, 128.1, 123.5, 122.9, 122.8, 122.4, 122.1, 117.7, 113.7, 111.9, 79.6, 55.2. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{17}O^+$ = 273.1274; Found 273.1274.

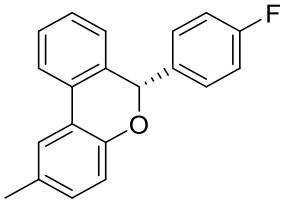


(*S*)-3-methyl-6-(o-tolyl)-6H-benzo[c]chromene (**2l)**: Colorless oil, 56 mg, 98% yield, 95% ee; $[\alpha]^{20}_D$ = - 22.5 (c = 1.0, $CHCl_3$); **HPLC** (Chiralpak OJ-3 column, hexane/isopropanol = 90/10; flow rate = 1.0 mL/min; UV detection at 220 nm; t_1 = 8.2 min (major), t_2 = 10.0 min (minor). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 7.8, 1.1 Hz, 1H), 7.64 (d, *J* = 7.9 Hz, 1H), 7.34 (t, *J* = 7.6, 1.2 Hz, 1H), 7.26 – 7.10 (m, 5H), 6.85 (d, *J* = 7.9, 1.6 Hz, 1H), 6.79 (s, 1H), 6.66 (d, *J* = 7.6 Hz, 1H), 6.28 (s, 1H), 2.40 (s,

3H), 2.29 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 154.0, 139.9, 137.2, 137.0, 133.4, 130.7, 128.7, 128.3, 128.3, 127.3, 126.1, 125.6, 123.0, 122.9, 121.7, 120.1, 118.0, 77.7, 21.3, 19.6. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{19}O^+$ = 287.1430; Found 287.1426.

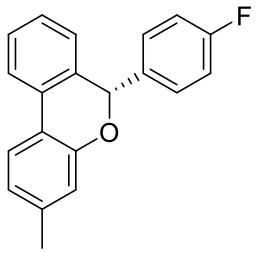


(*S*)-6-(4-methoxyphenyl)-3-methyl-6H-benzo[c]chromene (**2m**)[2]: Black solid, 59 mg, 98% yield, 92% ee; $[\alpha]^{20}_D$ = - 0.4 (c = 1.0, $CHCl_3$); **HPLC** (Chiralpak As-3 column, hexane/isopropanol = 95/5; flow rate = 1.0 mL/min; UV detection at 220 nm; t_1 = 5.2 min (minor), t_2 = 6.0 min (major). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 7.9, 1.2 Hz, 1H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.34 (t, *J* = 7.6, 1.3 Hz, 1H), 7.26 (d, 2H), 7.18 (t, 1H), 6.87 – 6.76 (m, 5H), 6.08 (s, 1H), 3.74 (s, 3H), 2.28 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 159.5, 153.4, 139.9, 133.7, 131.9, 130.2, 129.4, 128.3, 127.1, 126.1, 122.9, 122.8, 121.7, 119.9, 118.2, 113.8, 79.2, 55.2, 21.3.

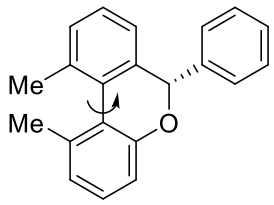


(*S*)-6-(4-fluorophenyl)-2-methyl-6H-benzo[c]chromene (**2n**): White solid, 31 mg, 54% yield, 94% ee; $[\alpha]^{20}_D$ = + 41.5 (c = 1.0, $CHCl_3$); **HPLC** (Chiralpak AD-3 column, hexane/isopropanol = 95/5; flow rate = 1.0 mL/min; UV detection at 220 nm; t_1 = 6.2 min (minor), t_2 = 6.8 min (major). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 7.8, 1.2 Hz, 1H), 7.59 (s, 1H), 7.48 – 7.33 (m, 3H), 7.29 (t, 1H), 7.13 – 6.99 (m, 3H), 6.97 – 6.82

(m, 2H), 6.15 (s, 1H), 2.39 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 162.6 (d, *J* = 248.5 Hz), 151.1, 135.5 (d, *J* = 3.0 Hz), 133.7, 131.4, 130.3, 130.1, 129.9 (d, *J* = 9.1 Hz), 128.5, 127.5, 126.1, 123.5, 122.3, 122.1, 117.6, 115.3 (d, *J* = 21.2 Hz), 78.8, 20.9. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -113.7. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{16}FO^+$ = 291.1180; Found 291.1176.

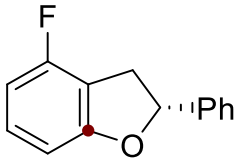


(*S*)-6-(4-fluorophenyl)-3-methyl-6H-benzo[c]chromene (**2o)**: Yellow solid, 58 mg, 99% yield, 95% ee; $[\alpha]^{20}_D$ = + 41.5 (c = 1.0, $CHCl_3$); **HPLC** (Chiralpak OJ-3 column, hexane/isopropanol = 95/5; flow rate = 1.0 mL/min; UV detection at 220 nm; t_1 = 12.5 min (major), t_2 = 21.2 min (minor). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 7.7 Hz, 1H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.46 – 7.34 (m, 3H), 7.29 – 7.23 (m, 1H), 7.07 (t, *J* = 8.7 Hz, 2H), 6.96 – 6.77 (m, 3H), 6.17 (s, 1H), 2.36 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 162.6 (d, *J* = 247.4 Hz), 153.2, 140.1, 135.6 (d, *J* = 3.0 Hz), 133.2, 130.1, 129.9 (d, *J* = 8.1 Hz), 128.5, 127.2, 126.1, 123.1, 122.9, 121.8, 119.9, 118.3, 115.3 (d, *J* = 22.2 Hz), 78.8, 21.3. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -113.7. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{16}FO^+$ = 291.1180; Found 291.1175.



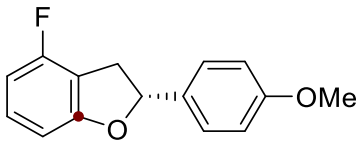
(*S*)-1,10-dimethyl-6-phenyl-6H-benzo[c]chromene (**2p)**: colorless oil, 52.7 mg, 92% yield, 3:1 d.r., 68% ee; $[\alpha]^{20}_D$ = + 20.1 (c = 1.0, $CHCl_3$); **HPLC** (Chiralpak OJ-3 column, hexane/isopropanol = 95/5; flow rate = 1.0 mL/min; UV detection at 254 nm; t_1 = 7.094

min (minor), t_2 = 12.900 min (major). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38-7.33 (m, 14H, major+minor), 7.26-6.99 (m, 18H, major+minor), 6.96-6.87 (m, 7H, major, 6H ; minor 1H), 6.74-6.65 (m, 2H, minor), 6.32 (d, *J* = 7.5 Hz, 3H, major), 6.10 (s, 1H, minor), 5.49 (s, 3H), 2.30 (s, 9H, major), 2.25 (s, 9H, major), 2.24 (s, 3H, minor), 2.15 (s, 3H, minor). **^{13}C NMR** (100 MHz,$CDCl_3$) δ 157.3 (major), 154.5 (minor), 141.0 (major), 138.7 (minor), 138.5 (major), 137.8 (minor), 136.0 (major), 135.5 (minor), 135.4 (minor), 134.3 (major), 131.2 (minor), 131.0 (major), 130.5 (major), 130.1 (minor), 128.5 (major), 128.4 (minor), 128.3 (major), 128.1 (minor), 127.9 (major), 127.8 (major+minor), 127.6 (minor), 126.6 (minor), 126.4 (major), 124.9 (minor), 124.7 (major), 124.5 (major), 124.3 (minor), 123.7 (minor), 122.3 (major), 115.4 (minor), 113.8 (major). **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{19}O^+$ = 287.1430; Found 287.1440.



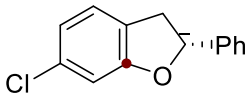
(*R*)-4-fluoro-2-phenyl-2,3-dihydrobenzofuran (4a)

Colorless oil, 40.3 mg, 94% yield, 99% ee. $[\alpha]_D^{20}$ = +3.80 (c = 0.50, $CHCl_3$). **HPLC:** The ee was determined by chiral HPLC (Chiralpak OD-3, n-hexane/isopropanol 98:2 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 ^oC). Retention times: t_R = 6.094 min (major), t_R = 9.415 min (minor). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.41-7.36 (m, 4H), 7.36-7.29 (m, 1H), 7.16-7.07 (m, 1H), 6.66 (d, *J* = 8.0 Hz, 1H), 6.59 (t, *J* = 8.4 Hz, 1H), 5.80 (dd, *J* = 9.3, 8.2 Hz, 1H), 3.66 (dd, *J* = 15.8, 9.5 Hz, 1H), 3.22 (dd, *J* = 15.8, 8.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 161.9 (d, *J* = 8.7 Hz), 159.3 (d, *J* = 247.1 Hz), 141.3, 129.6 (d, *J* = 8.8 Hz), 128.7, 128.2, 125.7, 112.9 (d, *J* = 21.5 Hz), 107.7 (d, *J* = 20.3 Hz), 105.3 (d, *J* = 4.5 Hz), 84.9, 35.0. **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) -116.80. **HRMS** (ESI) m/z: calcd for $C_{14}H_{10}FO^-$ $[M-H]^-$:213.0721, found: 213.0714.



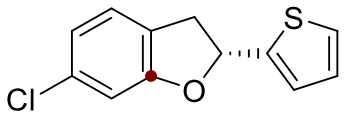
(*R*)-4-fluoro-2-(4-methoxyphenyl)-2,3-dihydrobenzofuran (4b)

Colorless oil, 45.4 mg, 93% yield, 98% ee. $[\alpha]_D^{20}$ = -49.00 (c = 0.50, $CHCl_3$). **HPLC:** The ee was determined by chiral HPLC (Chiralpak OD-3, n-hexane/isopropanol 98:2 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retention times: t_R = 7.592 min (major), t_R = 9.840 min (minor). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.35-7.30 (m, 2H), 7.15-7.07 (m, 1H), 6.94-6.88 (m, 2H), 6.63 (d, *J* = 8.0 Hz, 1H), 6.59 (t, *J* = 8.4 Hz, 1H), 5.82-5.72 (m, 1H), 3.81 (s, 3H), 3.63 (dd, *J* = 15.8, 9.4 Hz, 1H), 3.23 (dd, *J* = 15.8, 8.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 161.8 (d, *J* = 8.2 Hz), 159.6, 159.3 (d, *J* = 246.5 Hz), 133.1, 129.6 (d, *J* = 8.8 Hz), 127.3, 114.1, 113.1 (d, *J* = 20.8 Hz), 107.6 (d, *J* = 21.1 Hz), 105.3 (d, *J* = 3.6 Hz), 84.9, 55.3, 34.8. **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) -116.89. **HRMS** (ESI) m/z: calcd for $C_{15}H_{14}FO_2^+$ $[M+H]^+$:245.0972, found: 245.0974.



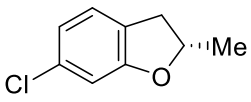
(*R*)-6-chloro-2-phenyl-2,3-dihydrobenzofuran (4c)

Colorless oil, 42.9 mg, 93% yield, 96% ee. $[\alpha]_D^{20}$ = -46.80 (c = 0.50, $CHCl_3$). **HPLC:** The ee was determined by chiral HPLC (Chiralpak OD-3, n-hexane/isopropanol 99:1 v/v, flow rate 1.0 mL/min, λ = 220 nm, 25 °C). Retention times: t_R = 8.344 min (major), t_R = 8.955 min (minor). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.38-7.34 (m, 4H), 7.34-7.27 (m, 1H), 7.09-7.03 (m, 1H), 6.84 (d, *J* = 7.1 Hz, 2H), 5.77 (dd, *J* = 9.4, 8.1 Hz, 1H), 3.57 (dd, *J* = 15.7, 9.5 Hz, 1H), 3.14 (dd, *J* = 15.7, 8.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 160.4, 141.4, 133.4, 128.7, 128.2, 125.7, 125.3, 125.2, 120.7, 110.1, 85.0, 37.7. **HRMS** (ESI) m/z: calcd for $C_{14}H_{10}ClO^-$ $[M-H]^-$:229.0426, found: 229.0419.



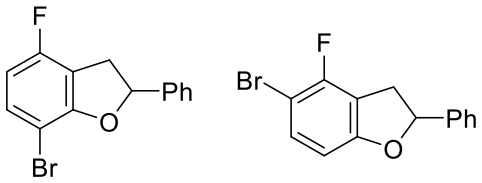
(*R*)-6-chloro-2-(thiophen-2-yl)-2,3-dihydrobenzofuran (4d)

Colorless oil, 43.5 mg, 92% yield, 98% ee. $[\alpha]_D^{20}$ = +61.60 (c = 0.50, $CHCl_3$). **HPLC:** The ee was determined by chiral HPLC (Chiralpak OD-3, n-hexane/isopropanol 98:2 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retention times: t_R = 7.940 min (major), t_R = 9.216 min (minor). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.30 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.12-7.08 (m, 2H), 6.99 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.86 (dd, *J* = 7.9, 1.8 Hz, 1H), 6.82 (d, *J* = 1.8 Hz, 1H), 6.03-5.97 (m, 1H), 3.59 (dd, *J* = 15.8, 9.2 Hz, 1H), 3.32 (ddd, *J* = 15.7, 7.8, 0.9 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 159.7, 143.9, 133.6, 126.8, 125.8, 125.4, 125.2, 124.9, 120.9, 110.4, 80.9, 37.8. **HRMS** (ESI) m/z: calcd for $C_{12}H_{10}ClOS^+$ $[M+H]^+$: 237.0135, found: 237.0138.



(*S*)-6-chloro-2-methyl-2,3-dihydrobenzofuran (4e)

Colorless oil, 31.4 mg, 93% yield, 34% ee. $[\alpha]_D^{20}$ = -12.0 (c = 0.50, $CHCl_3$). **HPLC:** The ee was determined by chiral HPLC (Chiralpak OD-3, n-hexane/isopropanol 98:2 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retention times: t_R = 11.892 min (major), t_R = 13.038 min (minor). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 6.91 (d, *J* = 7.9 Hz, 1H), 6.68 (dd, *J* = 7.9, 1.9 Hz, 1H), 6.63 (d, *J* = 1.8 Hz, 1H), 4.89-4.77 (m, 1H), 3.14 (dd, *J* = 15.5, 8.8 Hz, 1H), 2.64 (dd, *J* = 15.9, 8.0 Hz, 1H), 1.34 (d, *J* = 6.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 160.4, 133.1, 125.7, 125.3, 120.1, 110.0, 80.6, 77.3, 77.0, 76.7, 36.5, 21.6. **HRMS** (ESI) m/z: calcd for $C_9H_{10}ClO^+$ $[M+H]^+$: 169.0415, found: 169.0418.

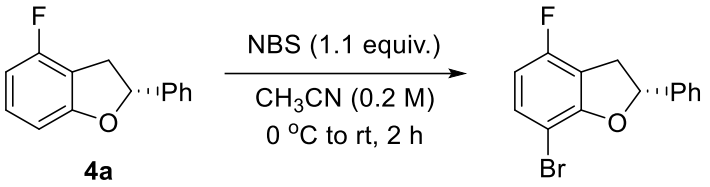


5a **5b**

A mixture of 5a and 5b

Colorless oil, 54.5 mg, 93% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.42-7.26 (m, 7H, major+minor), 6.56 (d, *J* = 8.5 Hz, 1H, major+minor), 5.92 (dd, J = 9.5, 7.9 Hz, 0.14H, minor), 5.82 (dd, J = 9.4, 8.1 Hz, 1H,major), 3.78 (ddt, J = 16.2, 9.5, 1.0 Hz, 0.16H, minor), 3.69 (dd, J = 16.0, 9.5 Hz, 1H, major), 3.34 (ddt, J = 16.1, 7.9, 1.1 Hz, 0.15H, minor), 3.25 (dd, J = 16.0, 8.0 Hz, 1H, major). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 161.1 (d, *J* = 7.1 Hz, major), 158.2 (d, *J* = 7.7 Hz, minor), 156.4 (major), 155.8 (minor), 154.0 (major), 153.4 (minor), 140.7 (major), 140.0 (minor), 134.7 (minor), 132.7 (major), 128.8 (minor), 128.8 (major), 128.6 (minor), 128.4 (major), 125.6 (major+minor), 115.3 (d, *J* = 23.2 Hz, minor), 114.6 (d, *J* = 22.6 Hz, major), 106.6 (d, *J* = 2.6 Hz, major+minor), 100.0 (d, *J* = 21.3 Hz, minor), 99.1 (d, *J* = 21.4 Hz, major), 85.9 (minor), 85.5 (major), 77.3, 77.0, 76.7, 36.4 (d, *J* = 2.1 Hz, minor), 35.4 (d, *J* = 1.9 Hz, major). **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) -110.13 (major), -111.56 (minor). **HRMS** (ESI) m/z: calcd for $C_{14}H_{11}BrFO^+$ $[M+H]^+$: 292.9972, found: 292.9968.

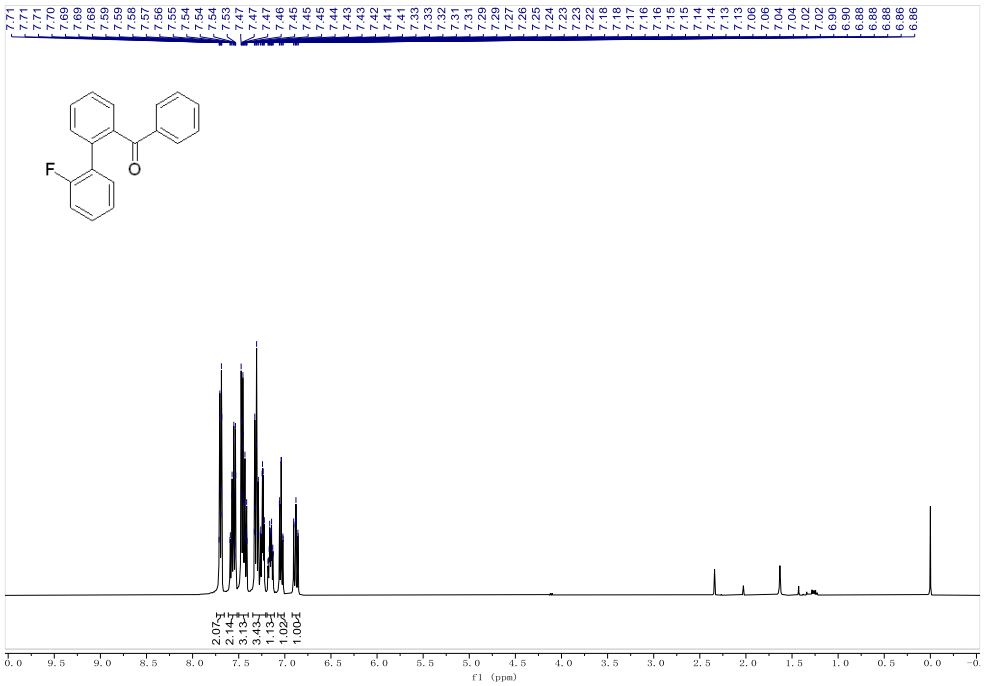
4. General Procedure of Transformation



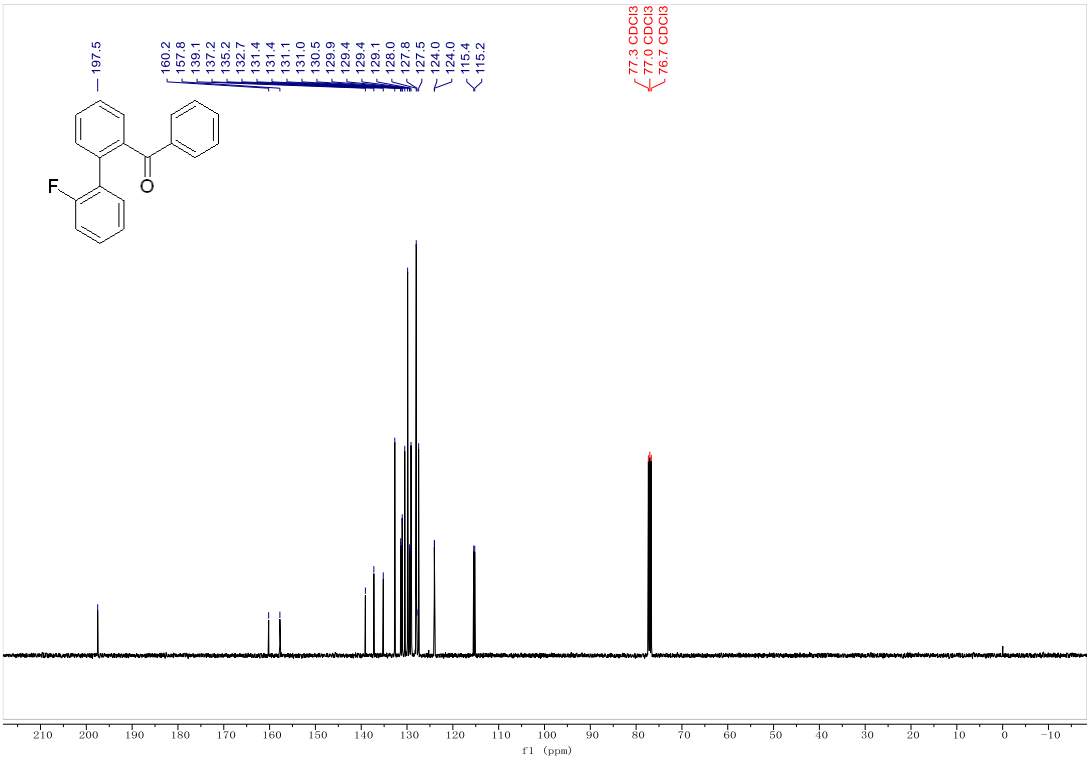
To a 15 ml round flask was added racemic **4a** (42.8mg, 0.2 mmol) in 2 mL CH_3CN, the flask was then cooled to 0 ℃ in a ice bath. Then, *N*-bromosuccinimide (39.1 mg, 0.22 mmol) was added into the system, warmed to room temperature. The solution was stirred at rt for 2 h. Then, the solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica gel (silica: 200–300 mesh, eluent: petroleum ether : EtOAc = 50:1-20: 1 v/v) to afford the corresponding product **5a** as a colorless oil with 93% yield.

5. NMR Spectroscopic Data

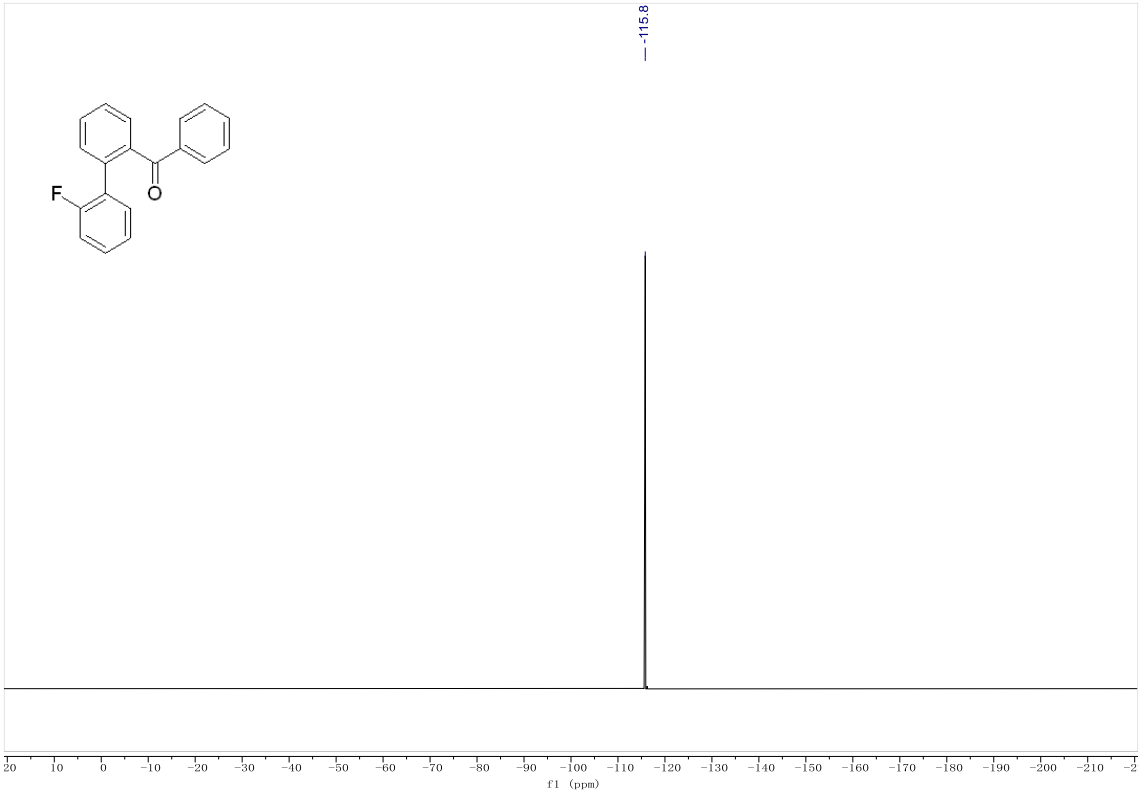
^{1}H NMR of 1a (400 MHz, Chloroform-*d*)



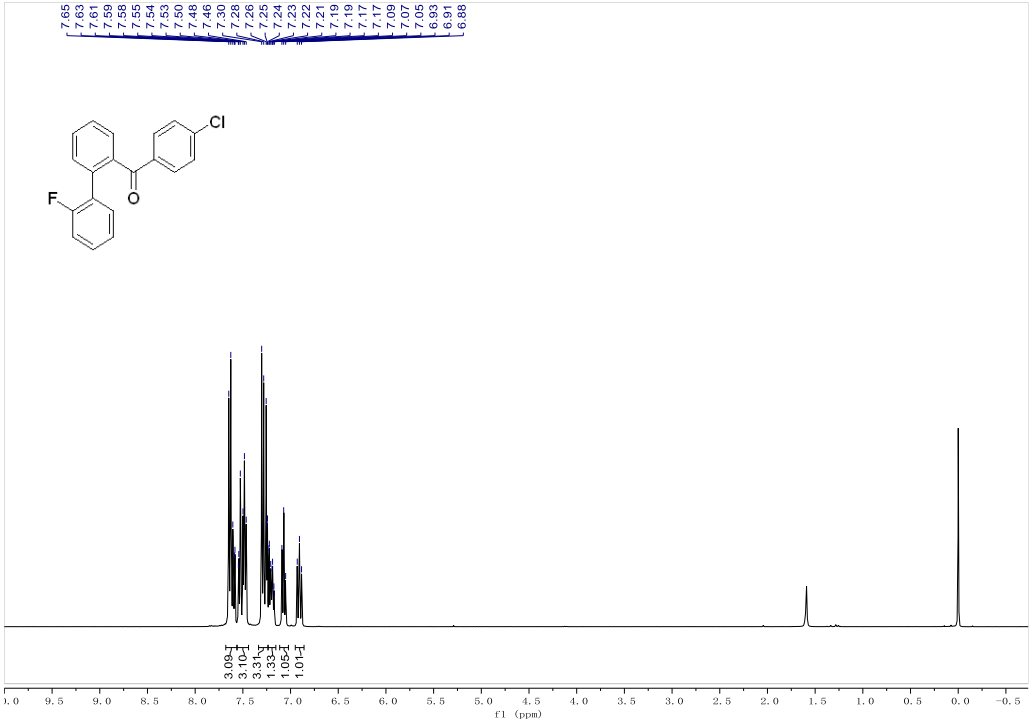
^{13}C NMR of 1a (101 MHz, Chloroform-*d*)



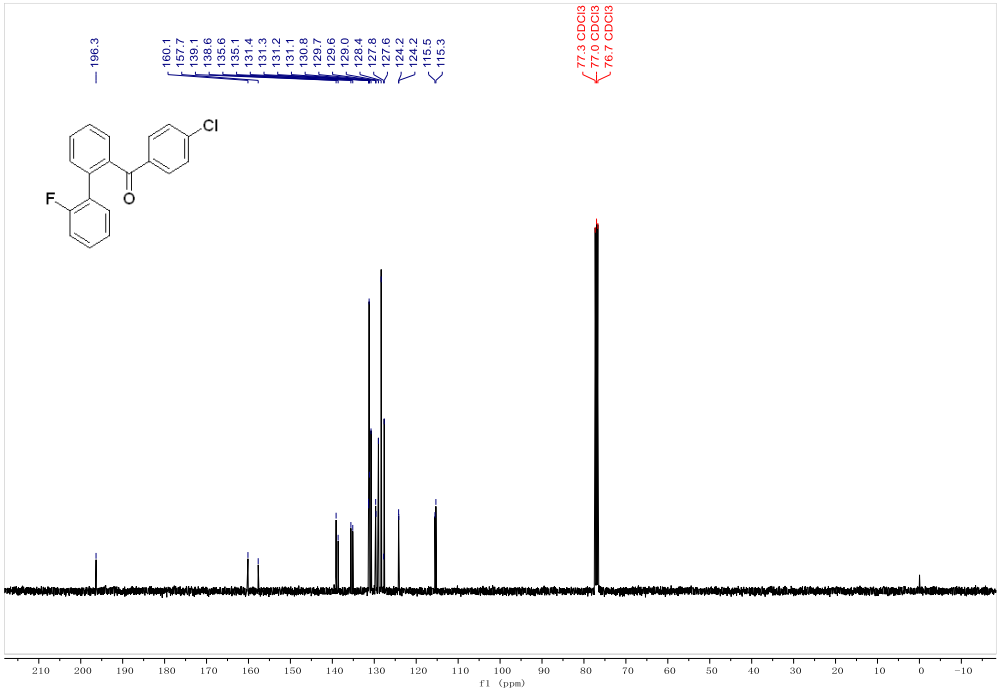
^{19}F NMR of 1a (400 MHz, Chloroform-*d*)



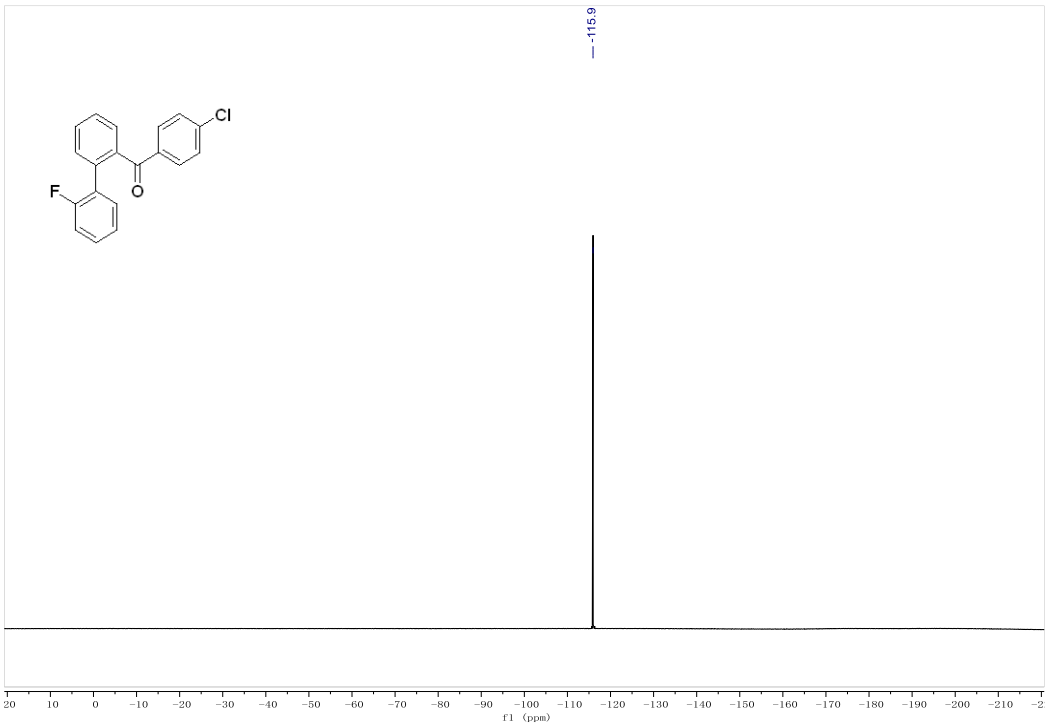
^{1}H NMR of 1b (400 MHz, Chloroform-*d*)



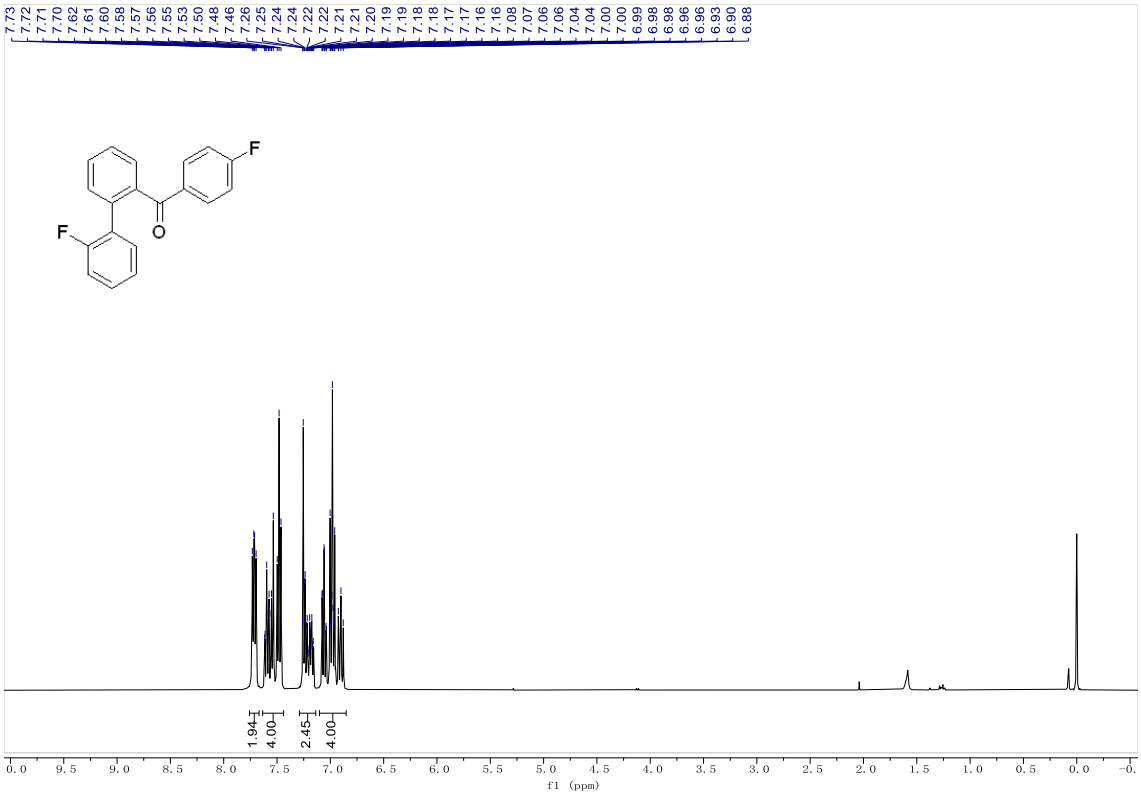
^{13}C NMR of 1b (101 MHz, Chloroform-*d*)



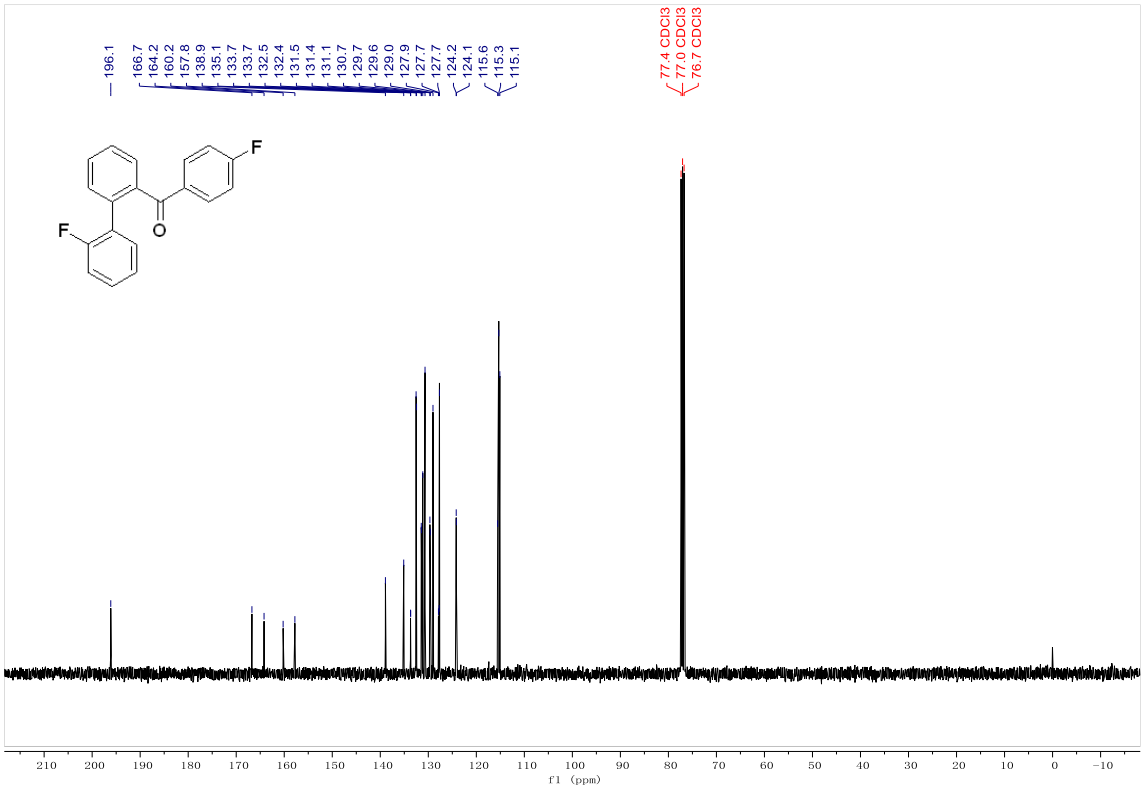
^{19}F NMR of 1b (400 MHz, Chloroform-*d*)



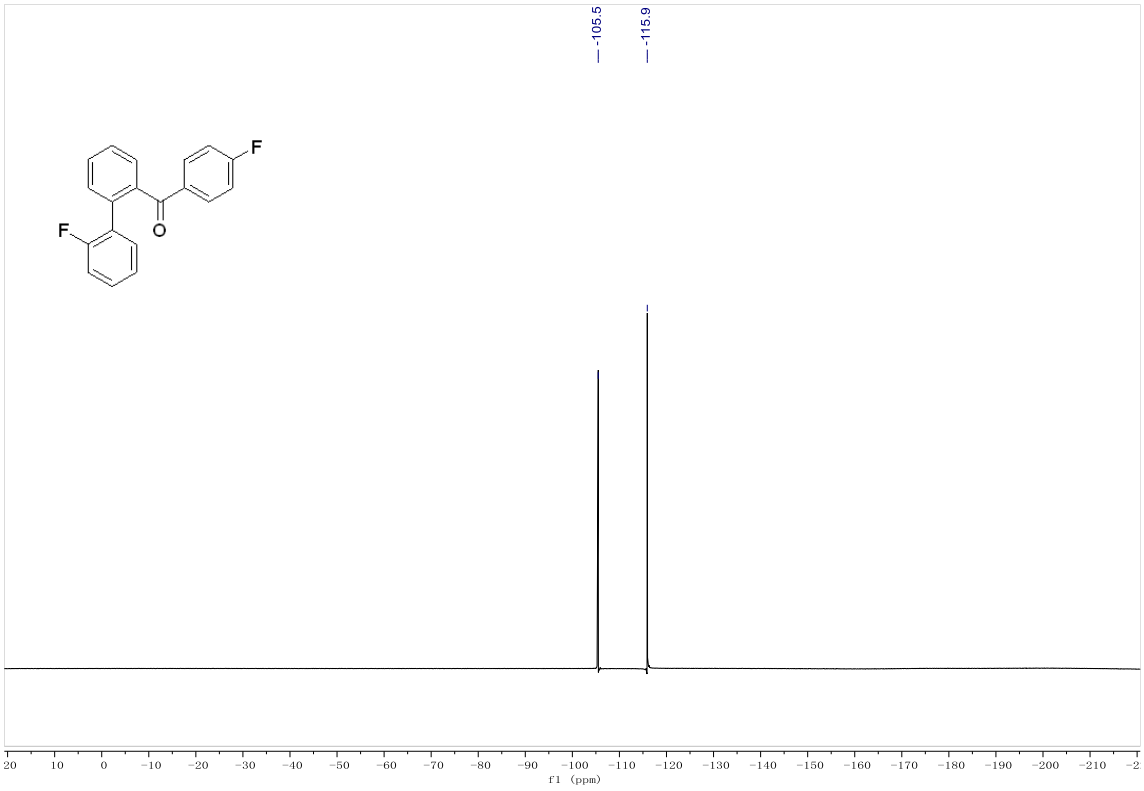
^{1}H NMR of 1c (400 MHz, Chloroform-*d*)



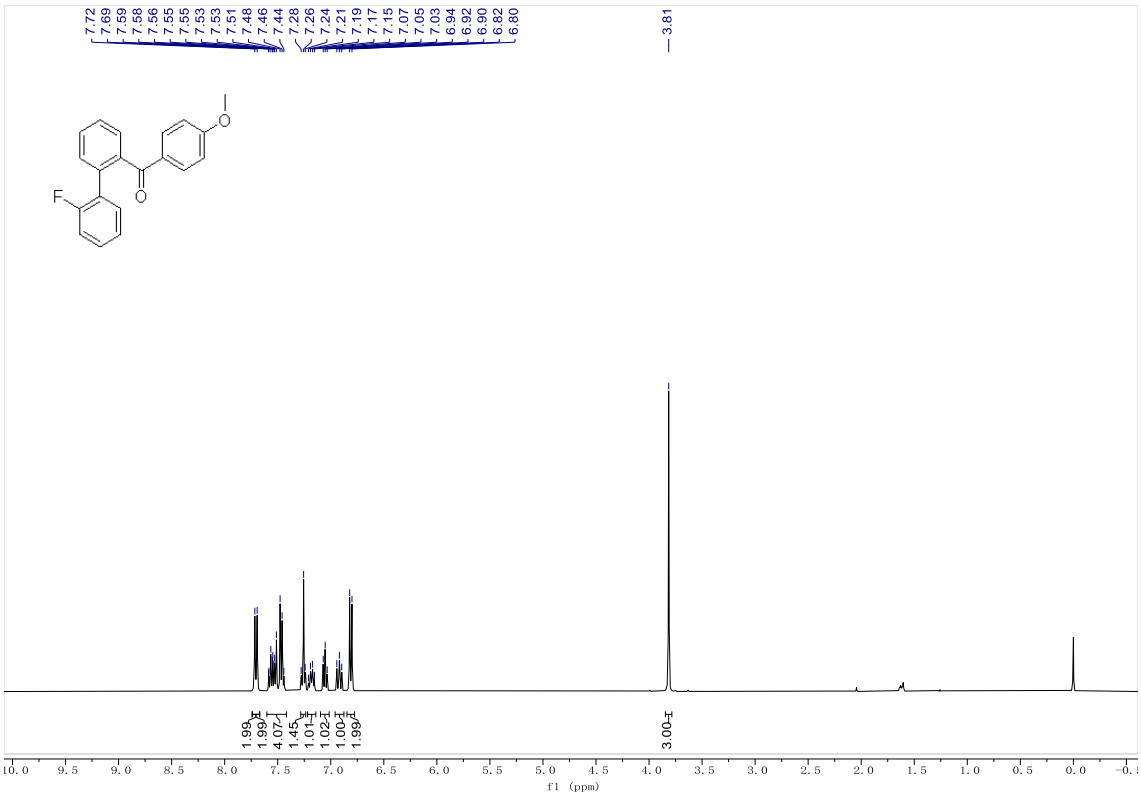
^{13}C NMR of 1c (101 MHz, Chloroform-*d*)



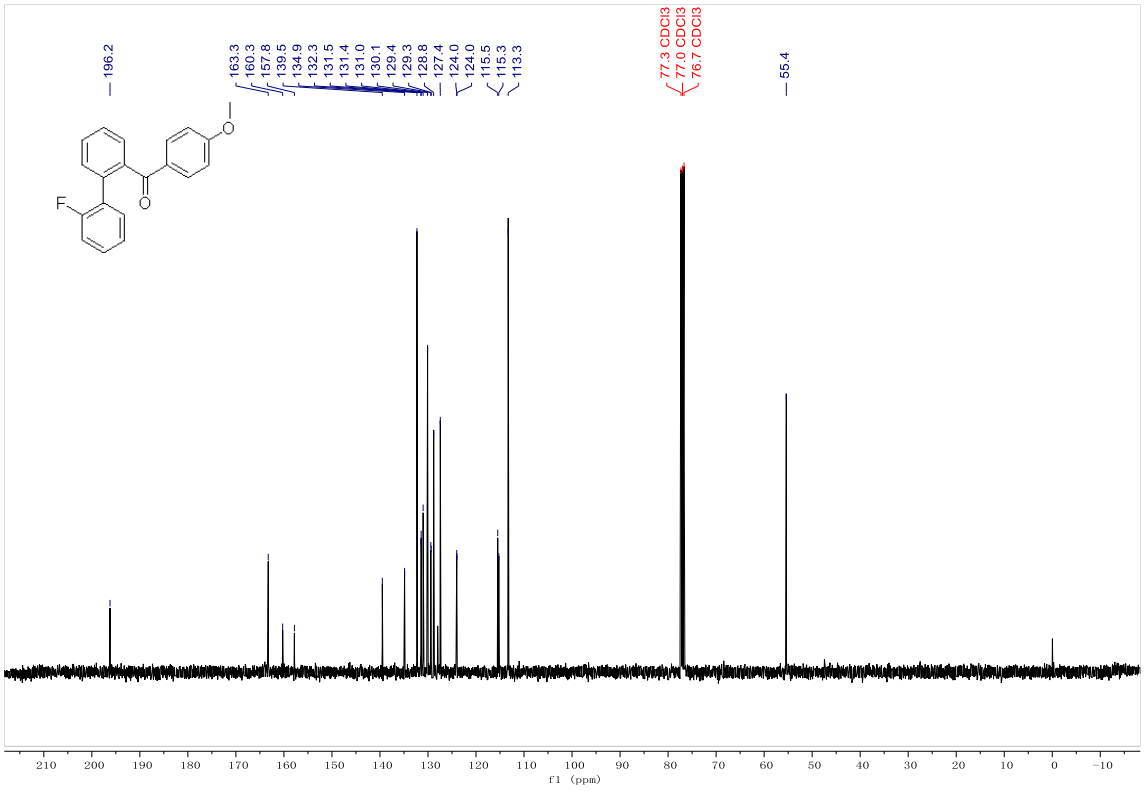
^{19}F NMR of 1c (400 MHz, Chloroform-*d*)



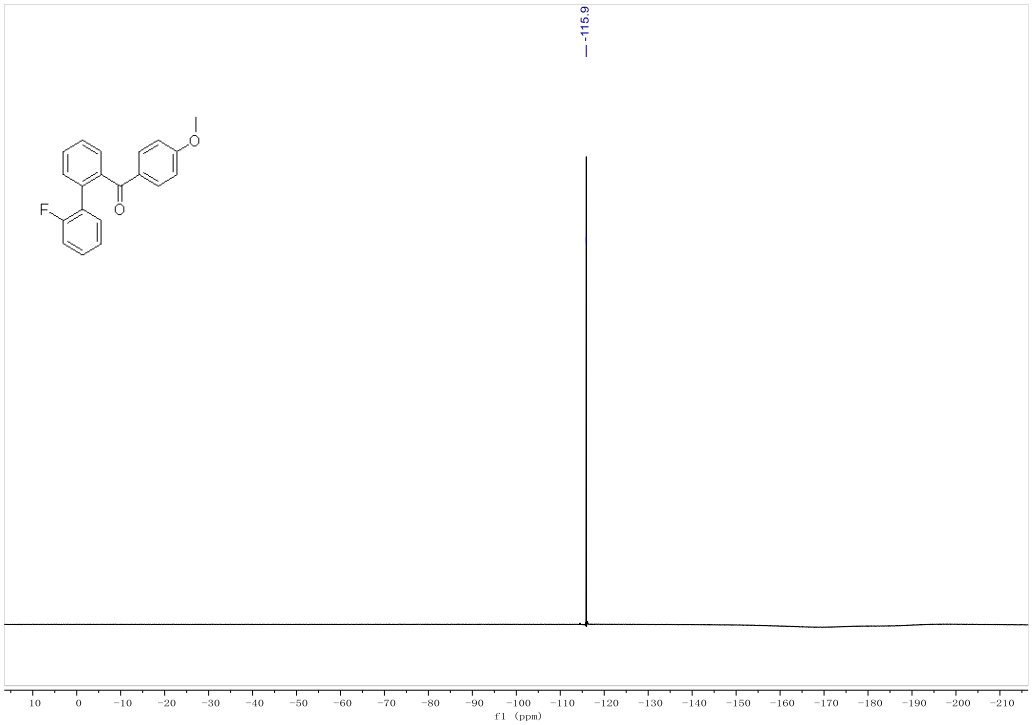
^{1}H NMR of 1d (400 MHz, Chloroform-*d*)



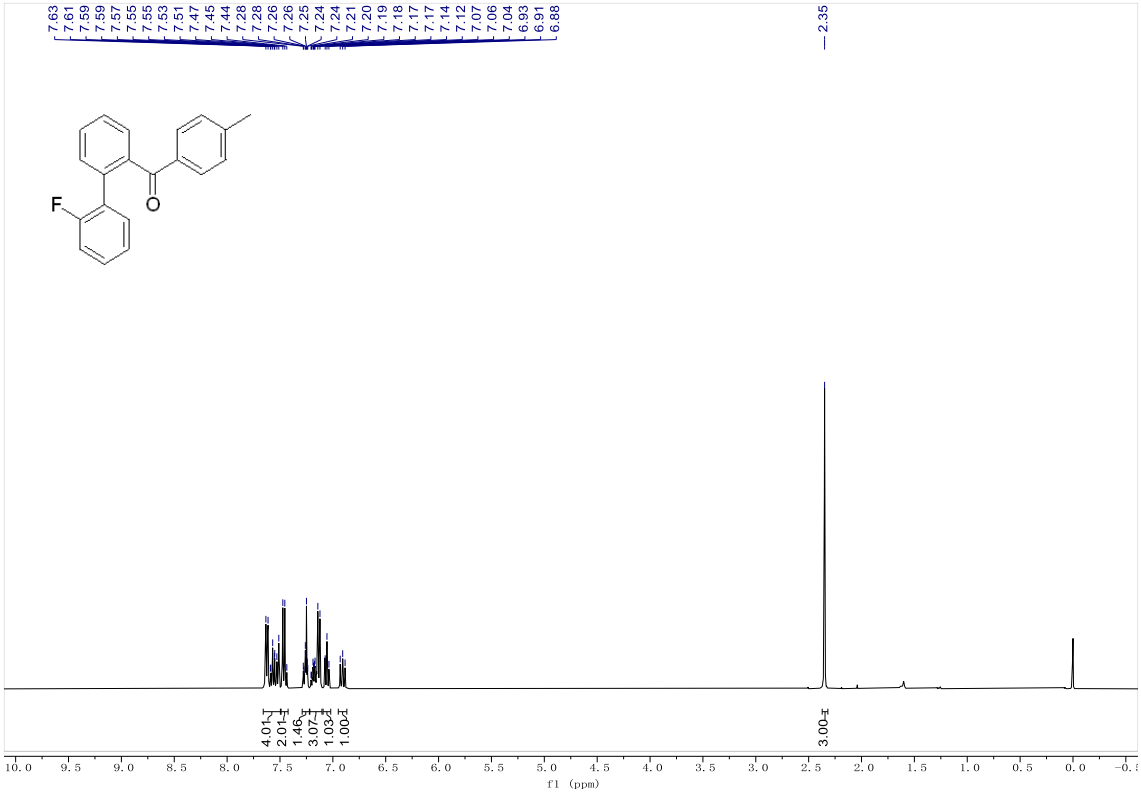
^{13}C NMR of 1d (101 MHz, Chloroform-*d*)



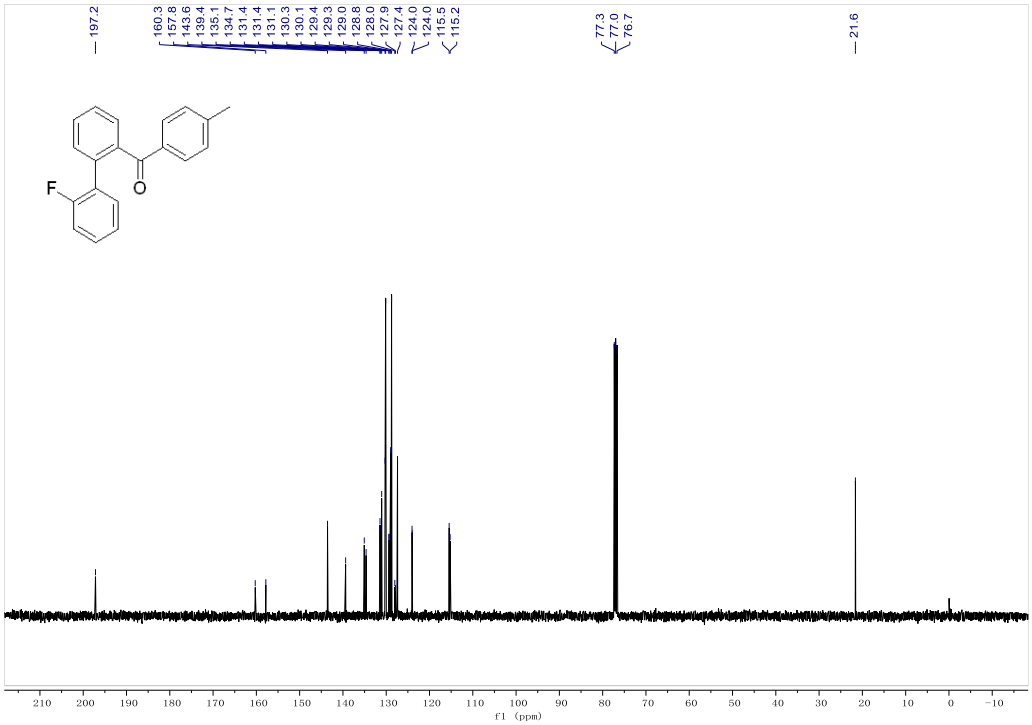
^{19}F NMR of 1d (400 MHz, Chloroform-*d*)



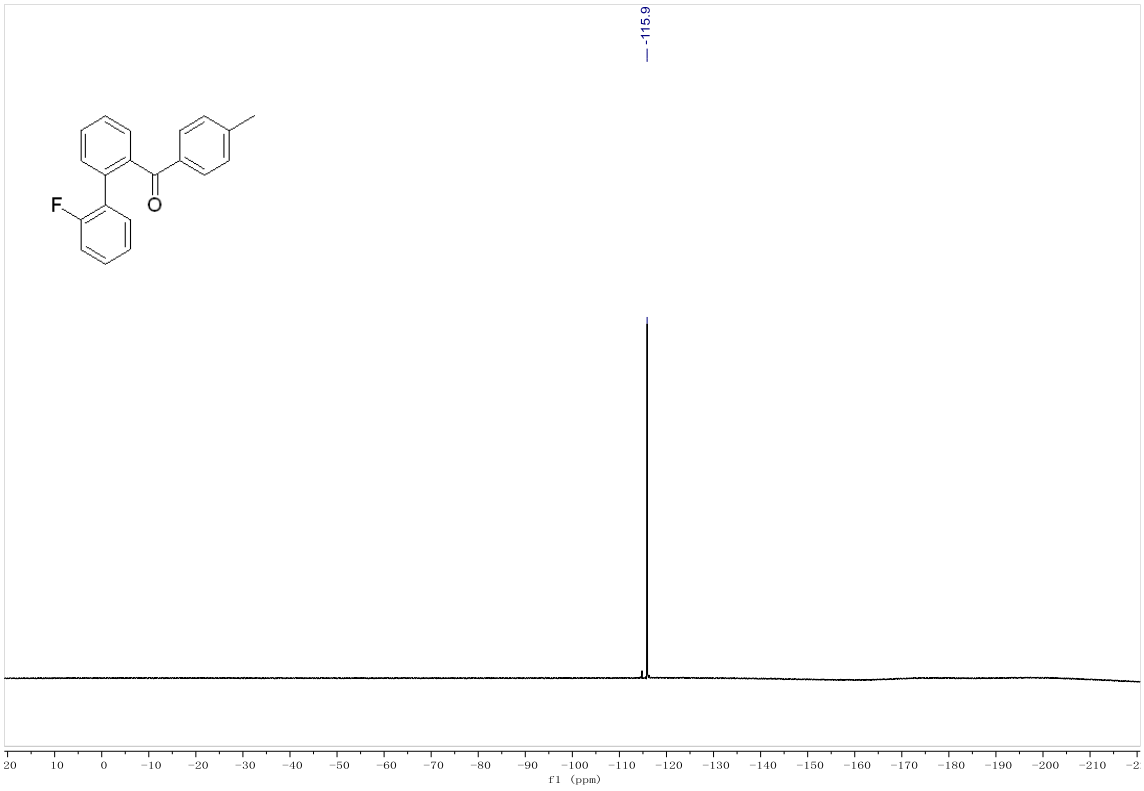
^{1}H NMR of 1e (400 MHz, Chloroform-*d*)



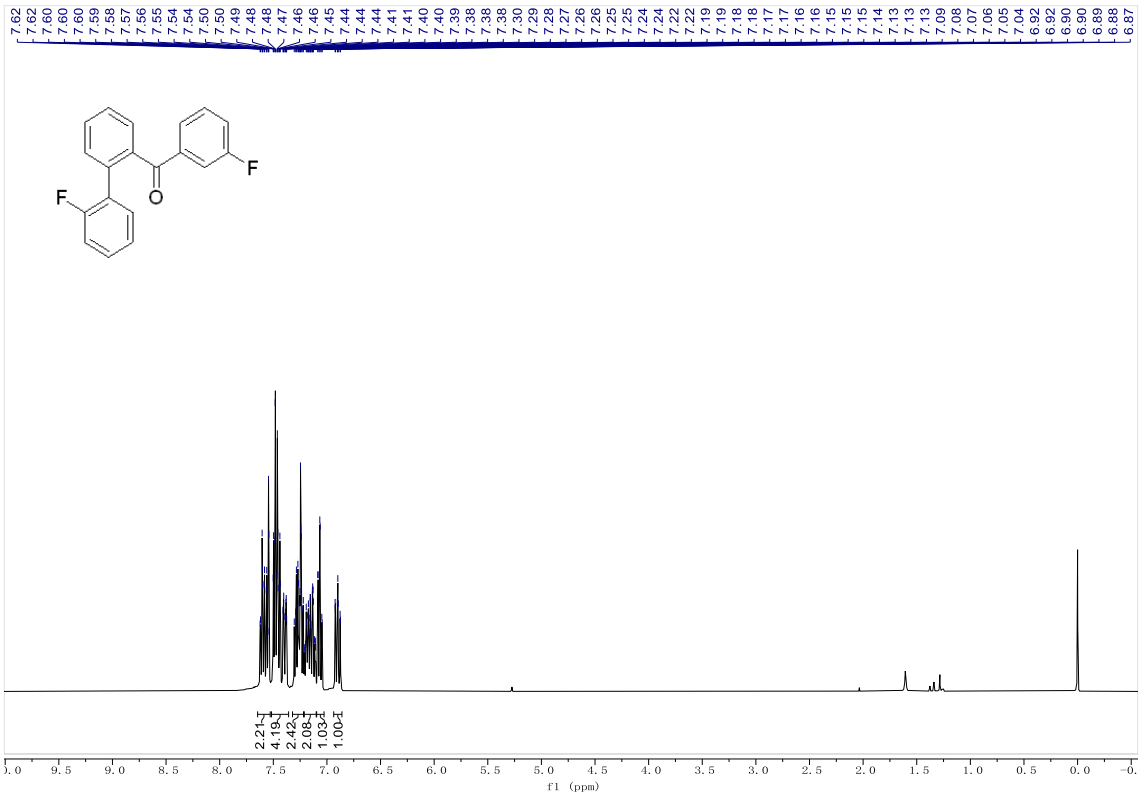
^{13}C NMR of 1e (101 MHz, Chloroform-*d*)



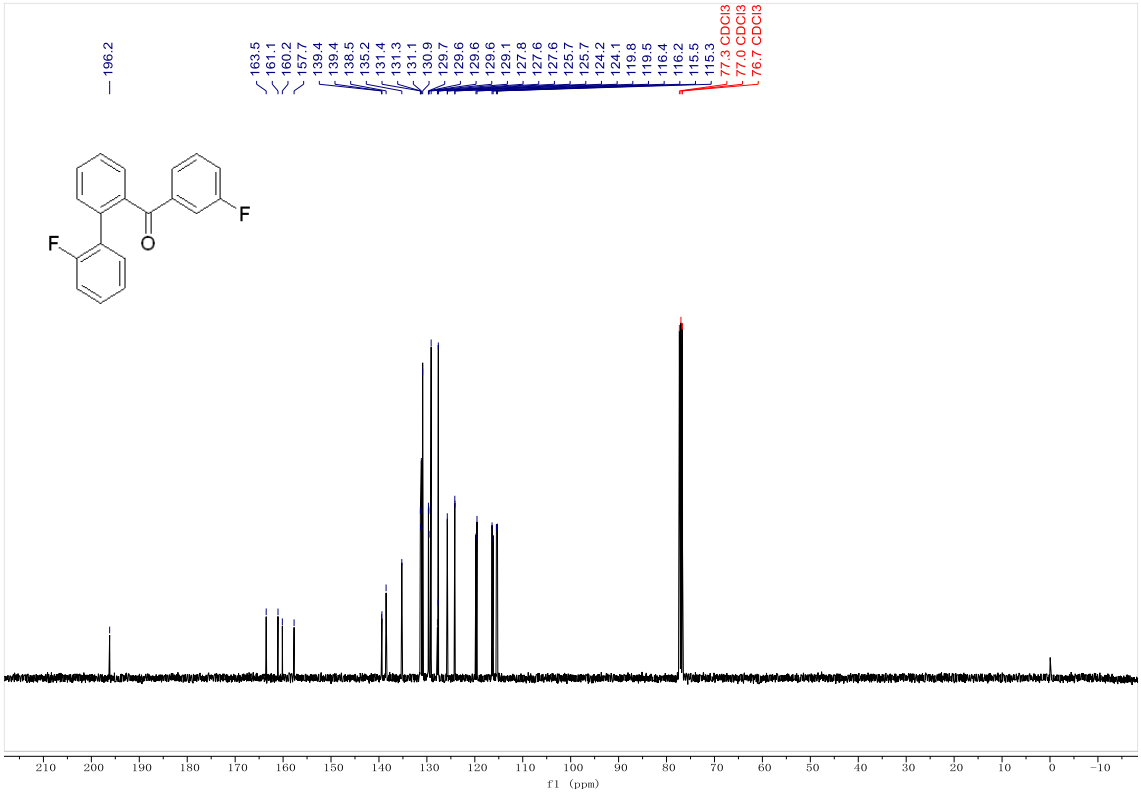
^{19}F NMR of 1e (400 MHz, Chloroform-*d*)



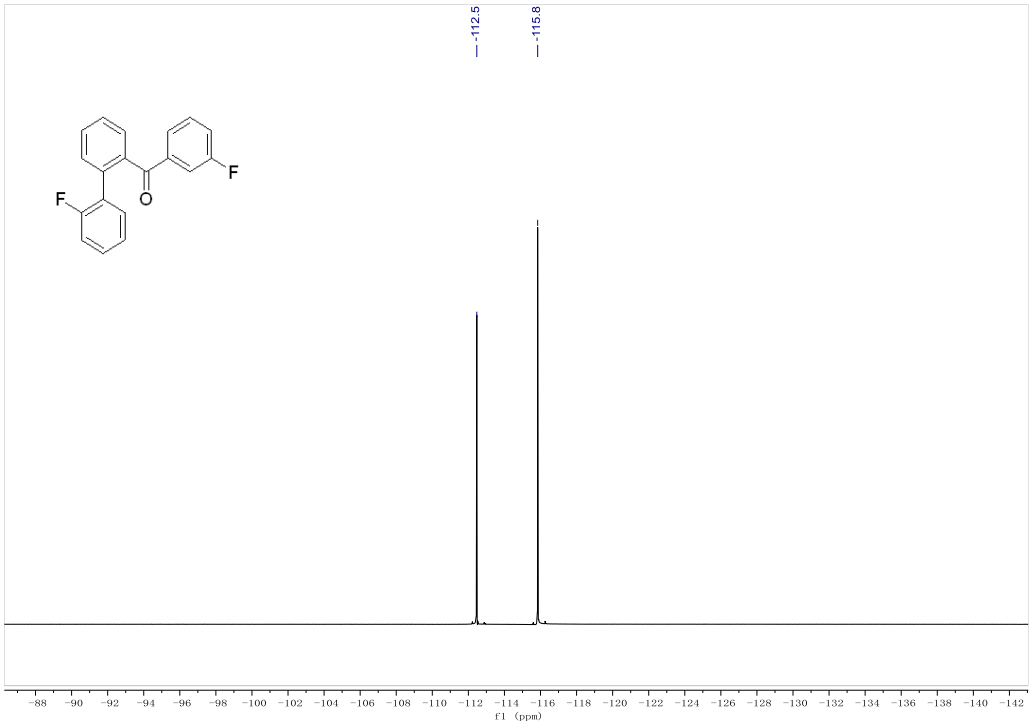
^{1}H NMR of 1f (400 MHz, Chloroform-*d*)



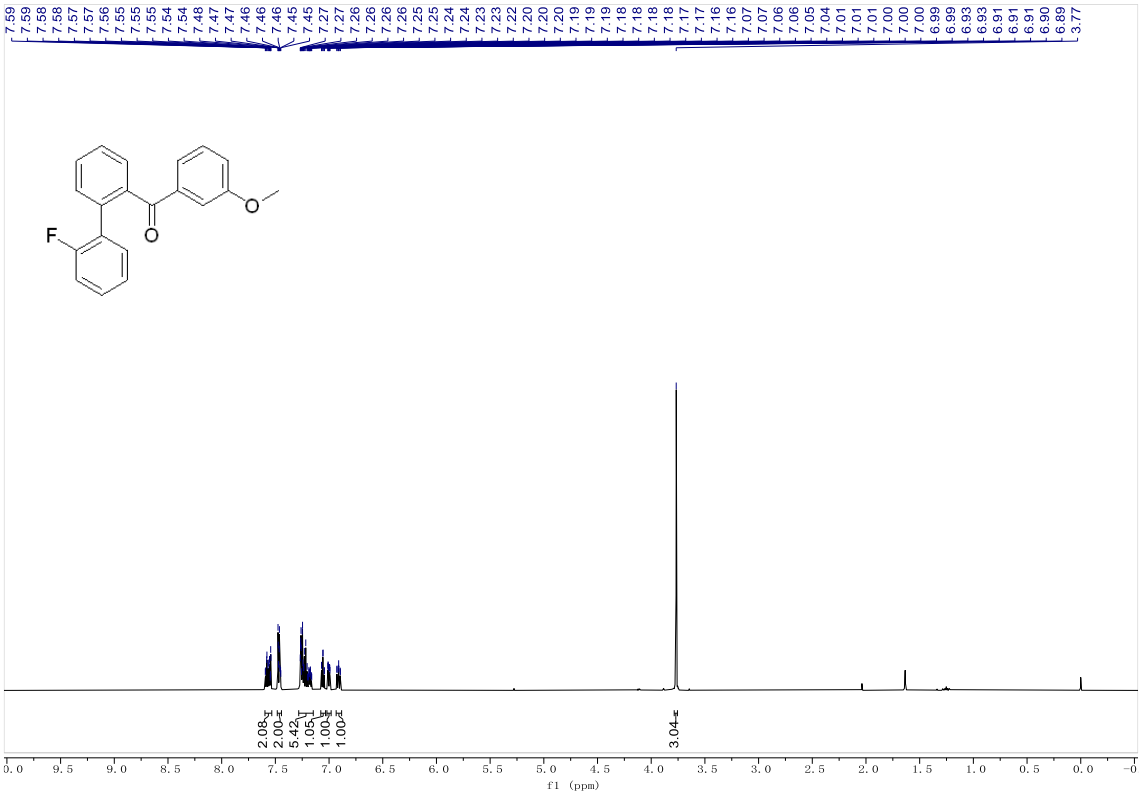
^{13}C NMR of 1f (101 MHz, Chloroform-*d*)



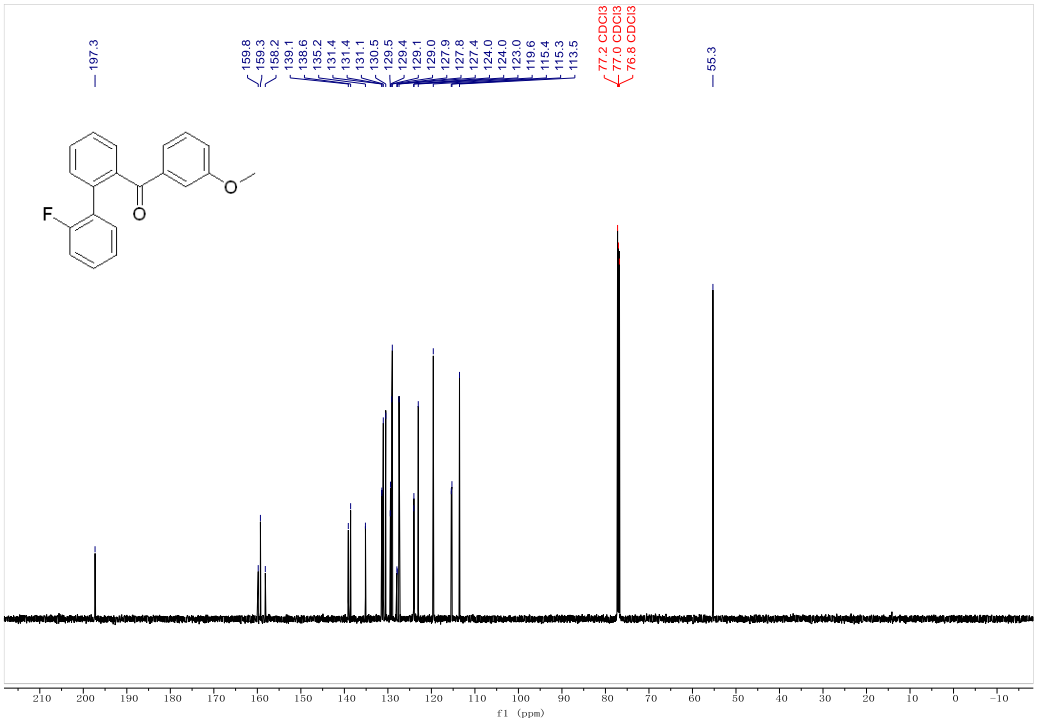
^{19}F NMR of 1f (400 MHz, Chloroform-*d*)



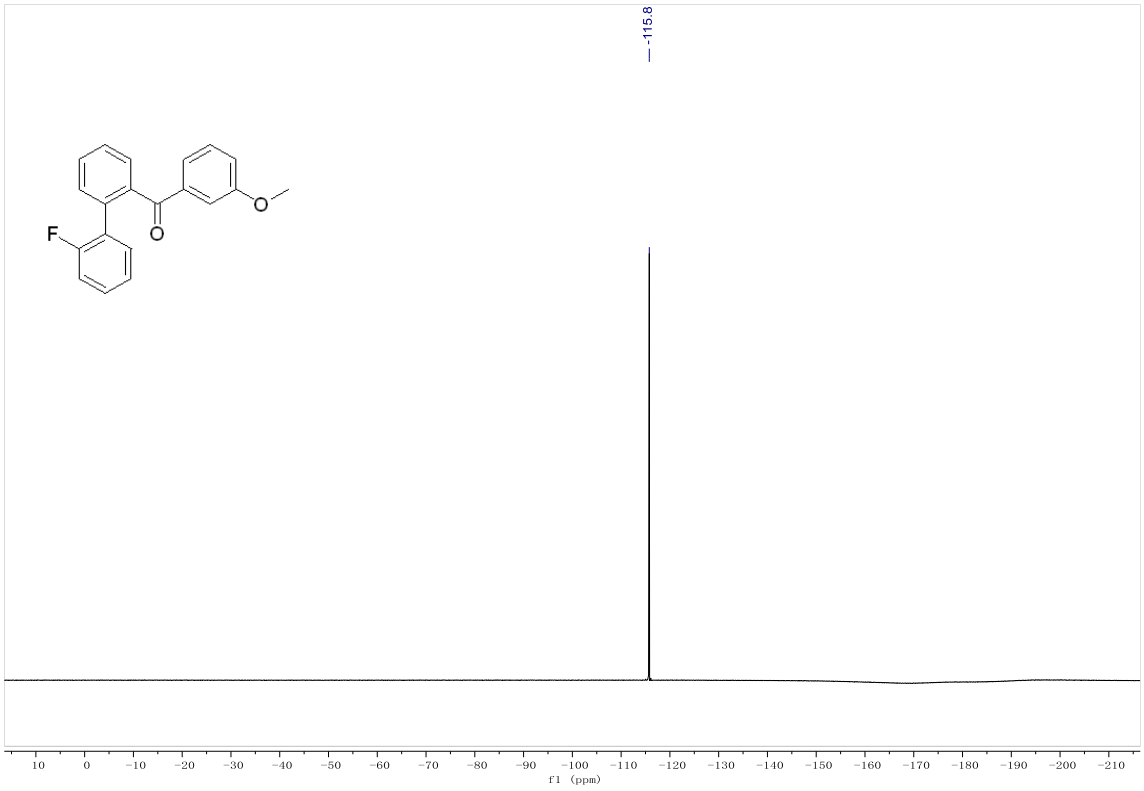
^{1}H NMR of 1g (400 MHz, Chloroform-*d*)



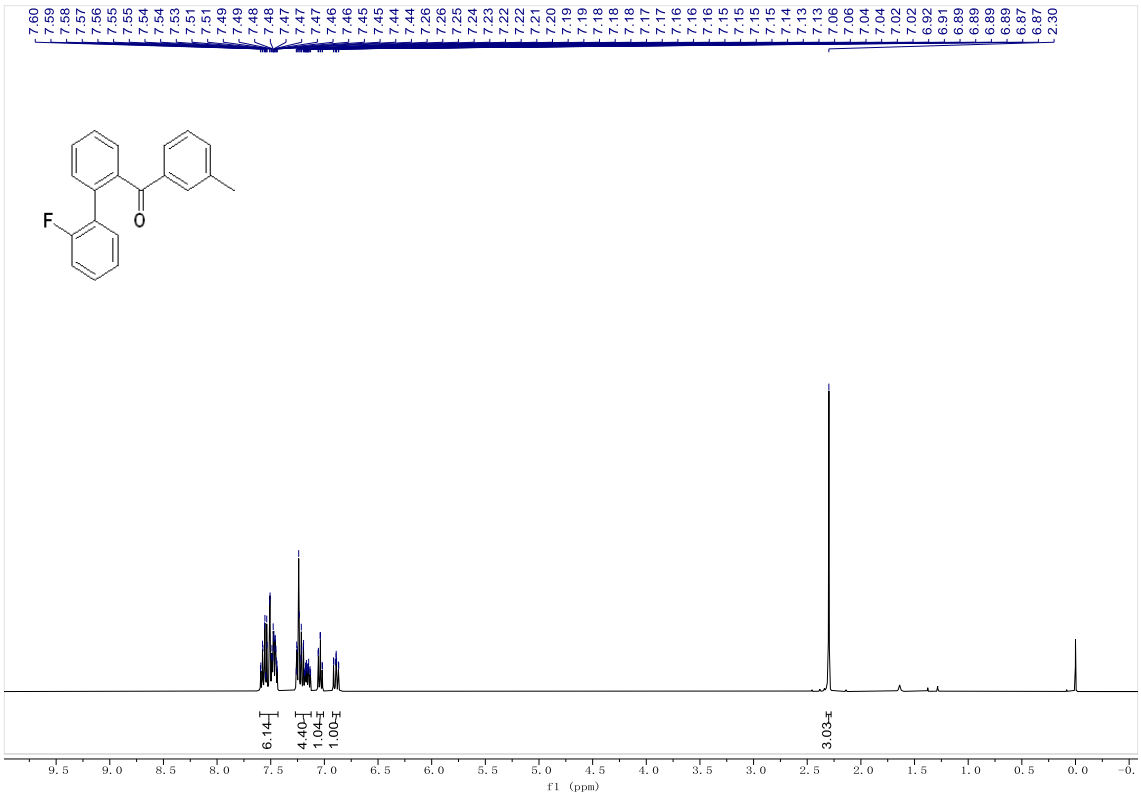
^{13}C NMR of 1g (151 MHz, Chloroform-*d*)



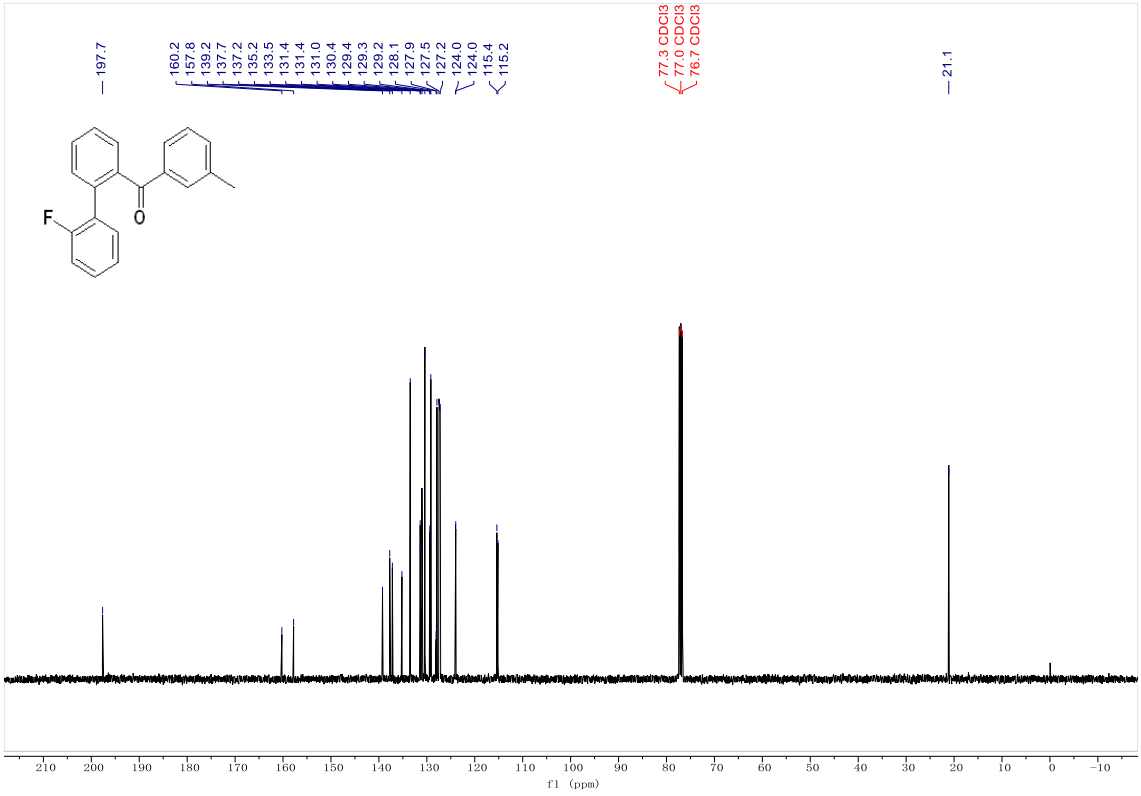
^{19}F NMR of 1g (400 MHz, Chloroform-*d*)



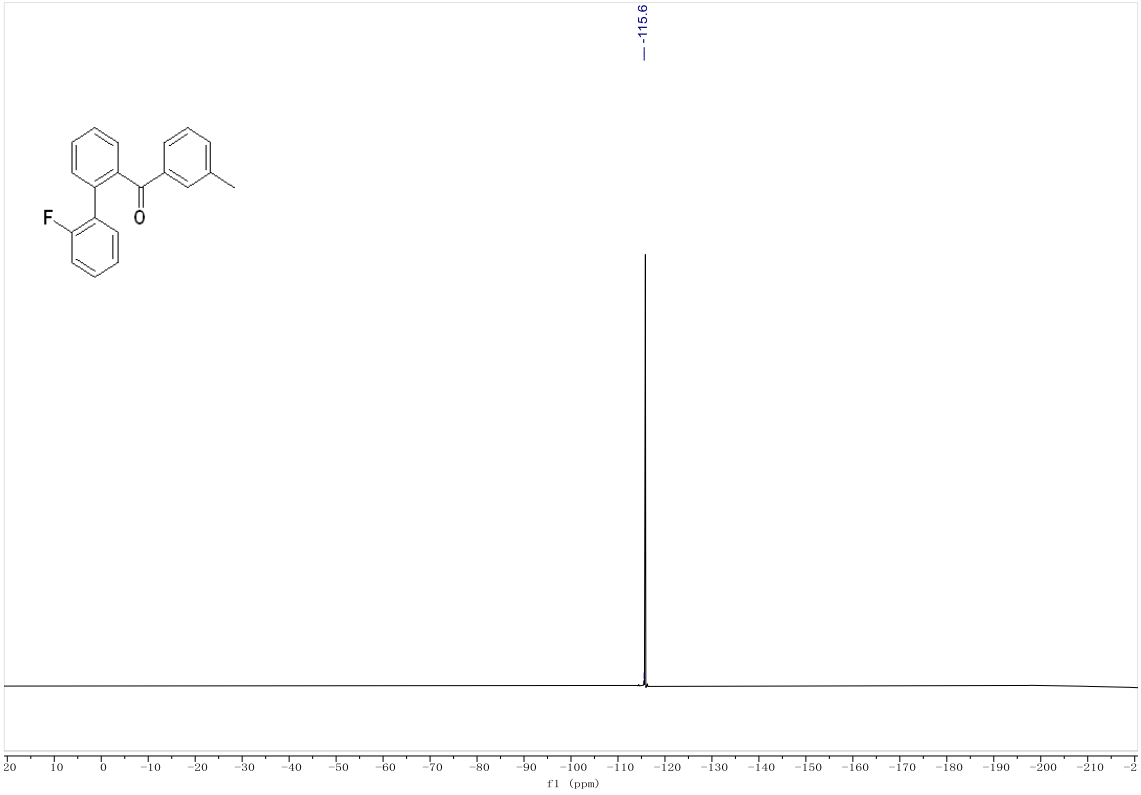
^{1}H NMR of 1h (400 MHz, Chloroform-*d*)



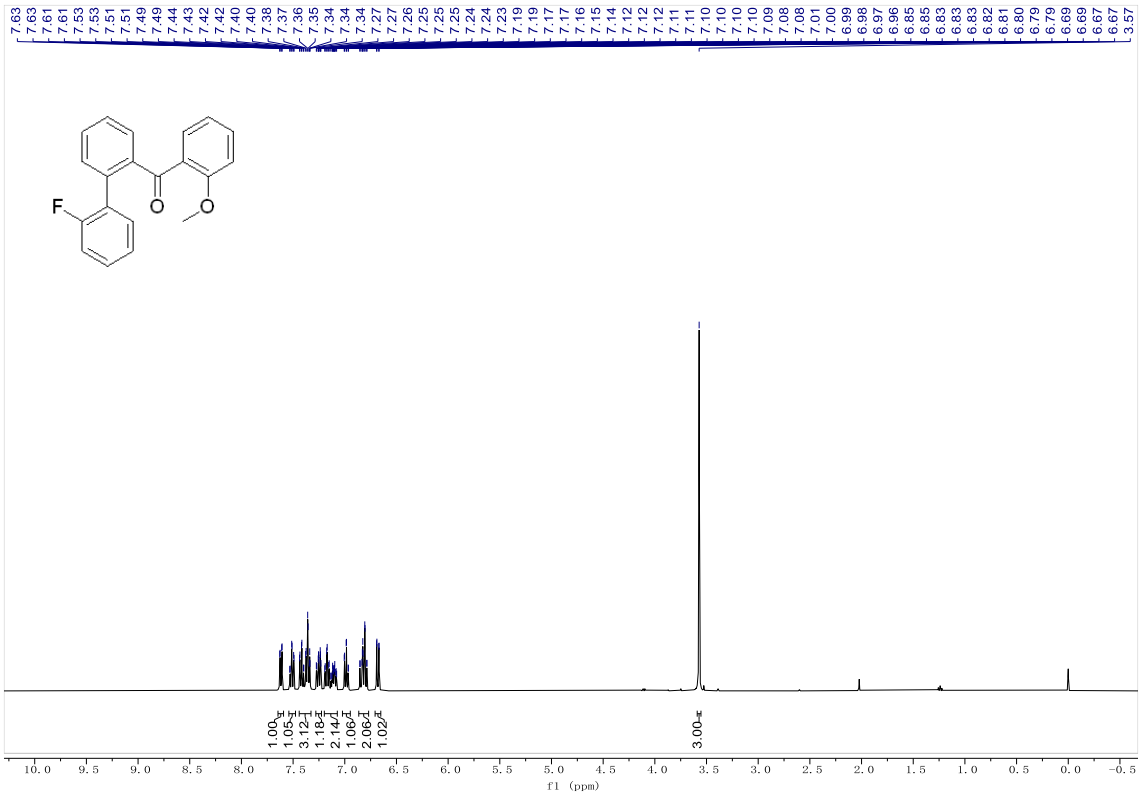
^{13}C NMR of 1h (101 MHz, Chloroform-*d*)



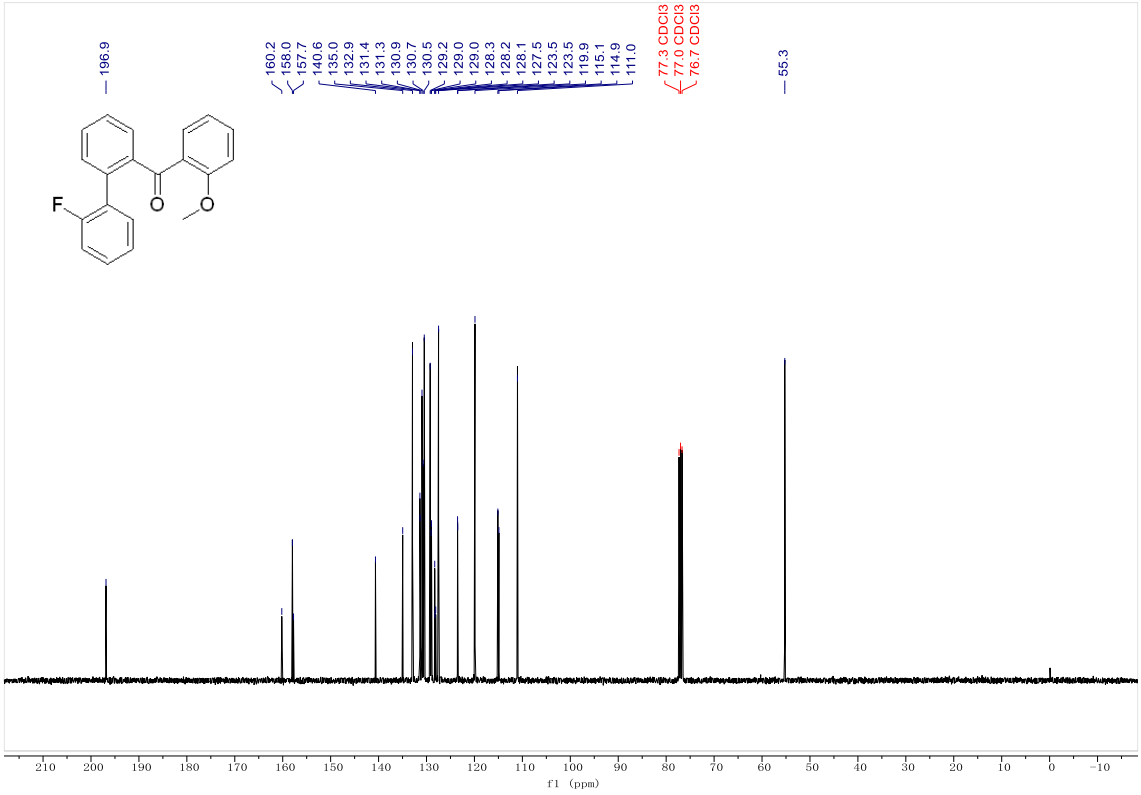
^{19}F NMR of 1h (400 MHz, Chloroform-*d*)



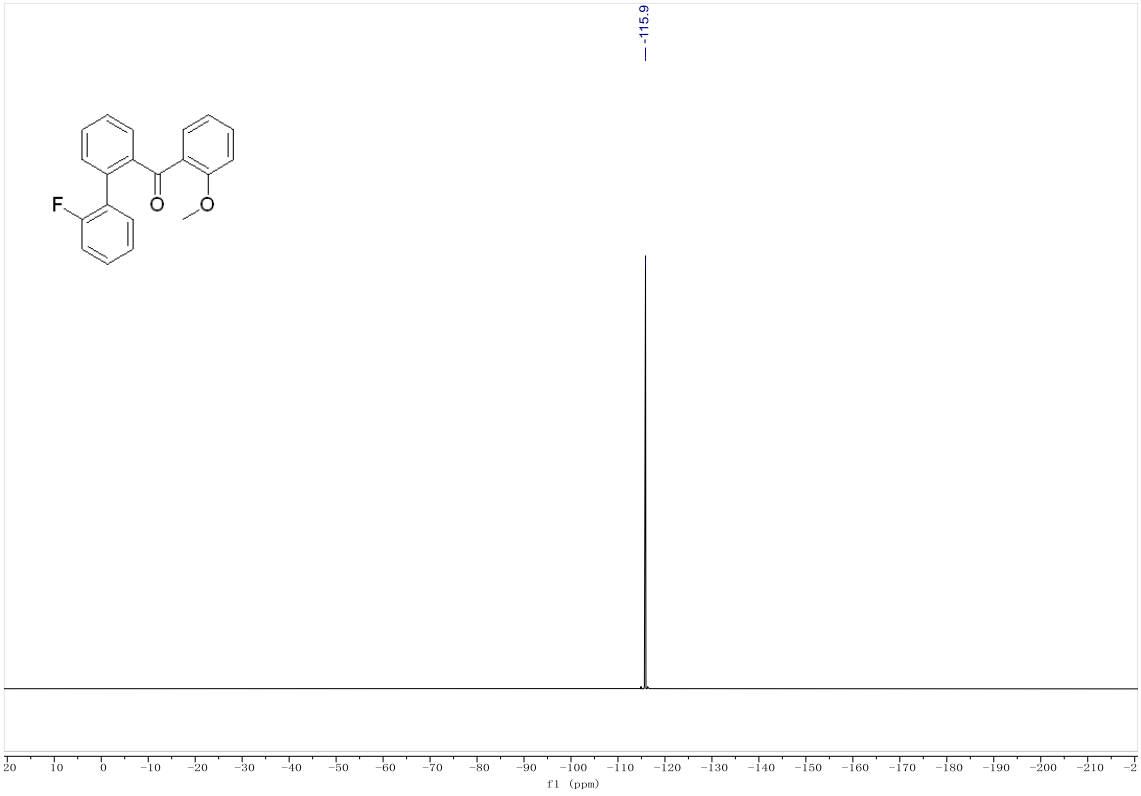
^{1}H NMR of 1i (400 MHz, Chloroform-*d*)



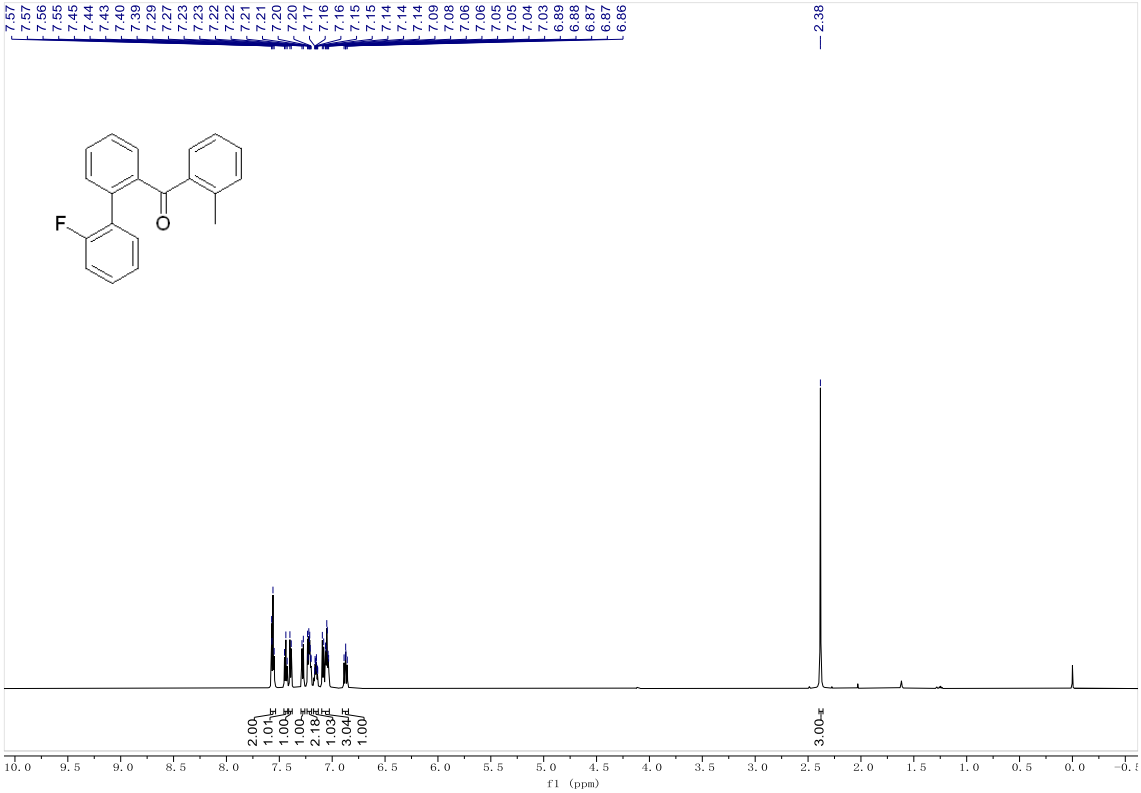
^{13}C NMR of 1i (101 MHz, Chloroform-*d*)



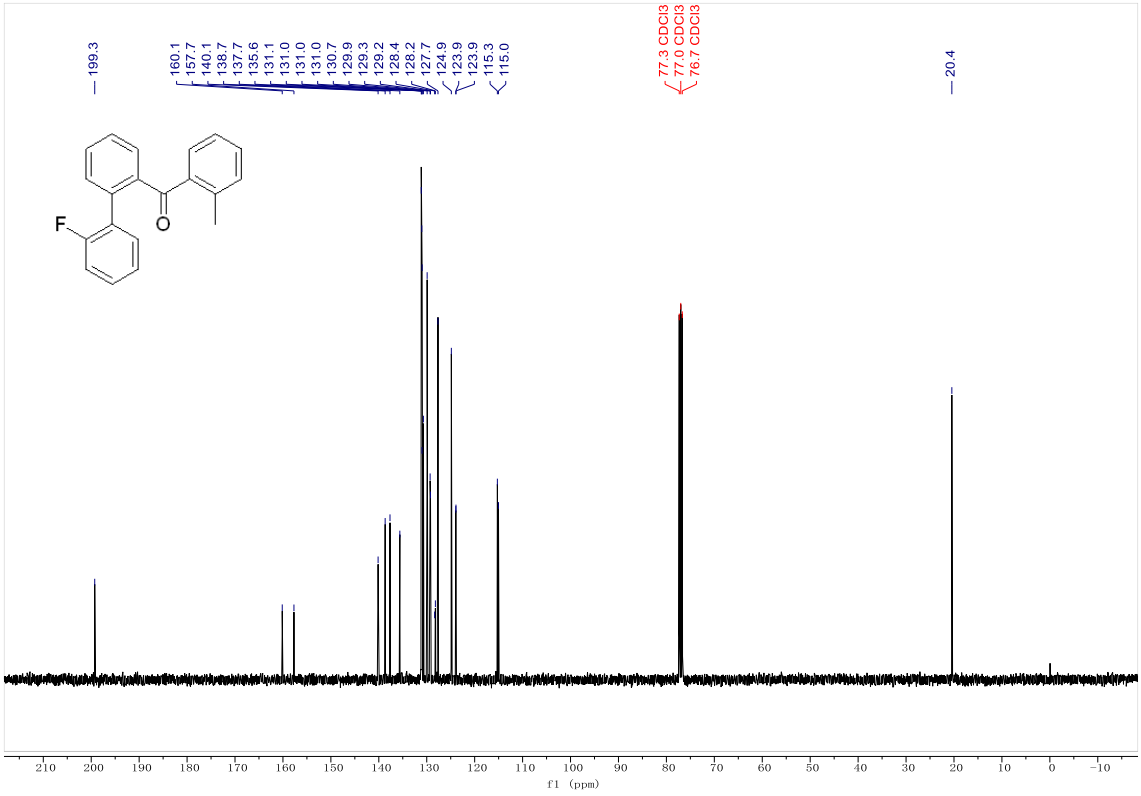
^{19}F NMR of 1i (400 MHz, Chloroform-*d*)



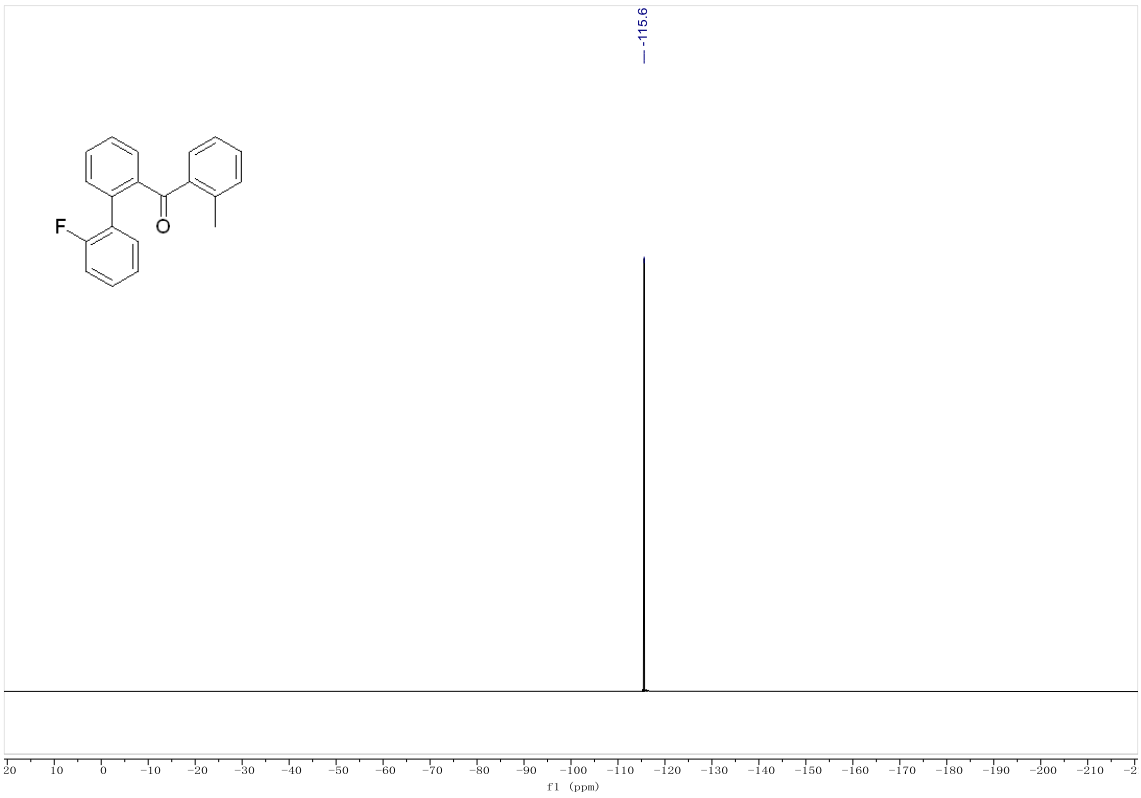
^{1}H NMR of 1j (400 MHz, Chloroform-*d*)



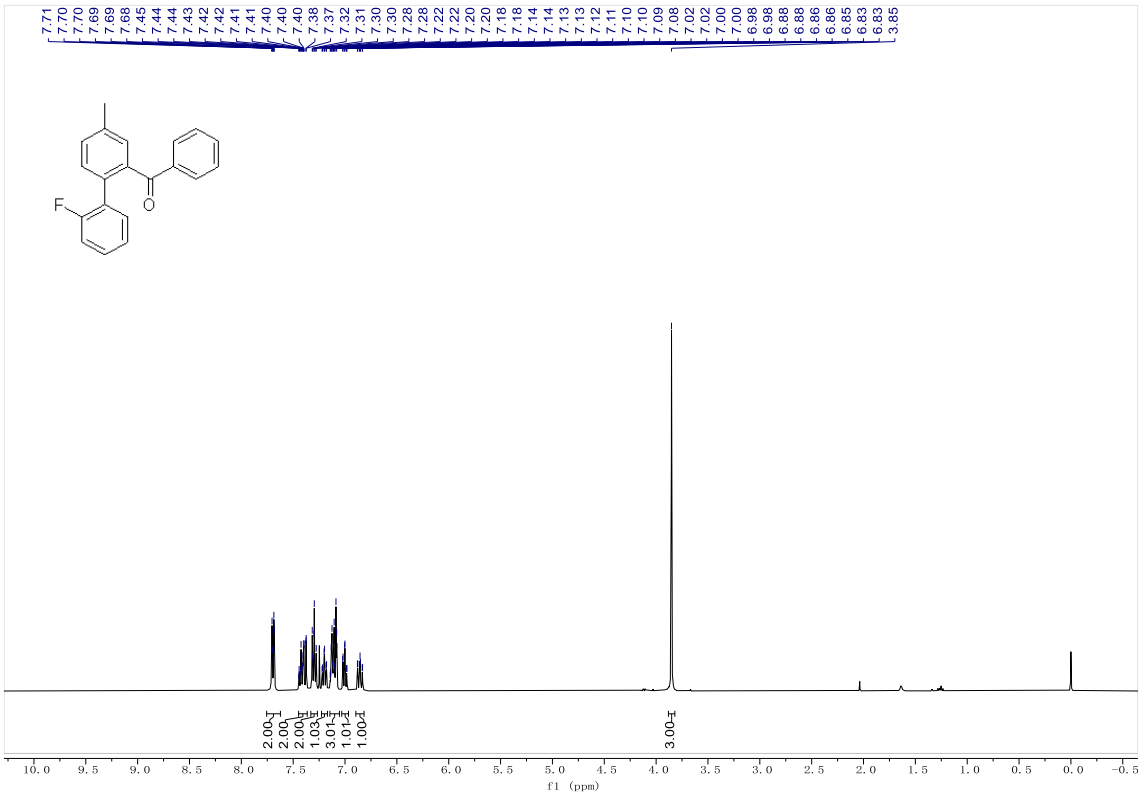
^{13}C NMR of 1j (101 MHz, Chloroform-*d*)



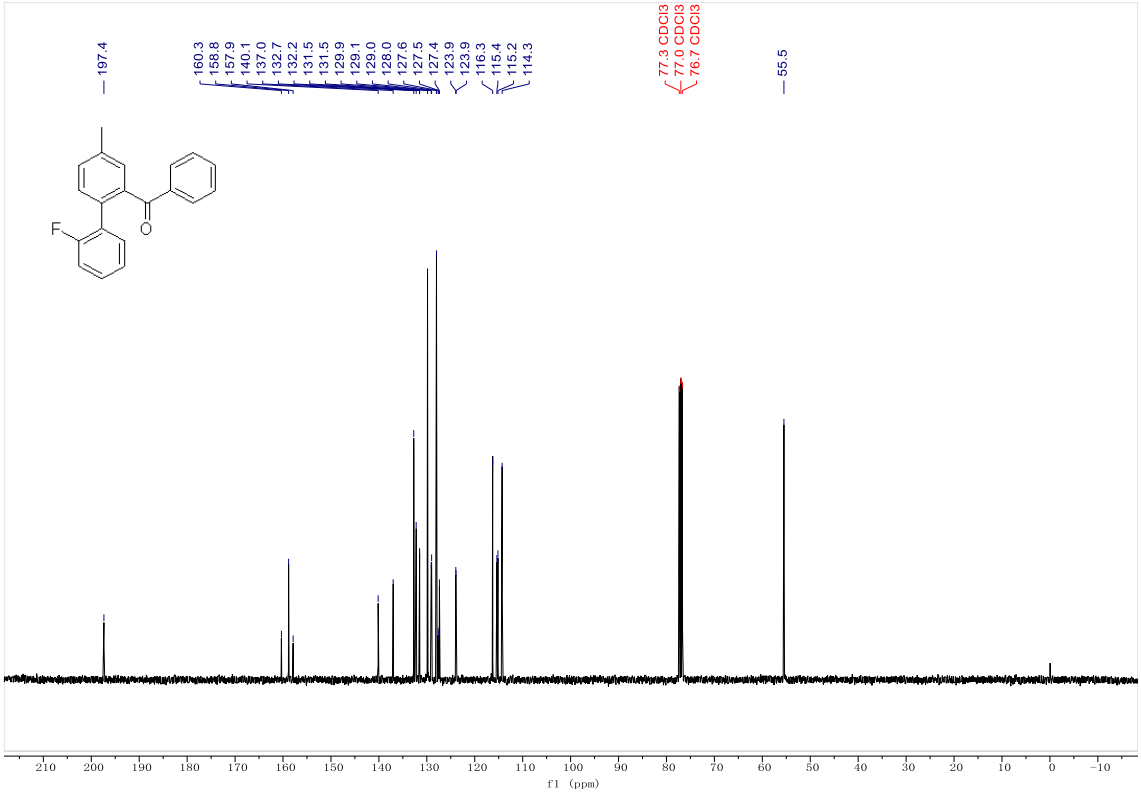
^{19}F NMR of 1j (400 MHz, Chloroform-*d*)



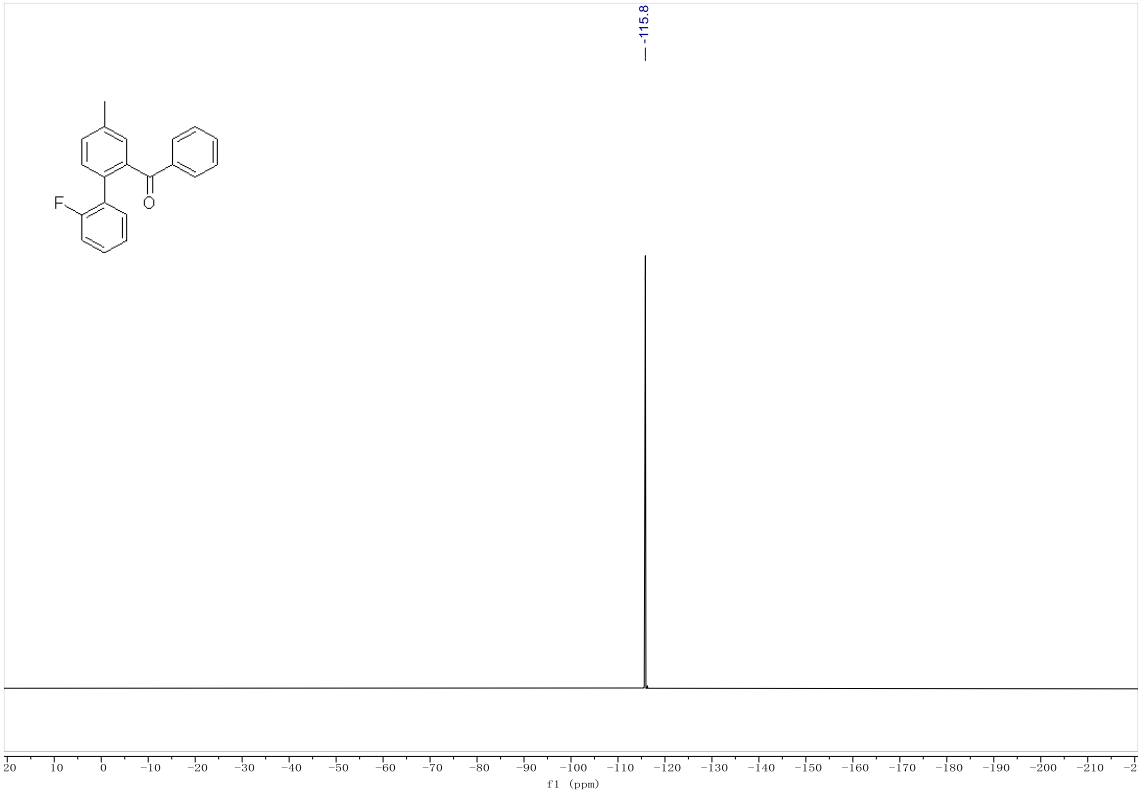
^{1}H NMR of 1k (400 MHz, Chloroform-*d*)



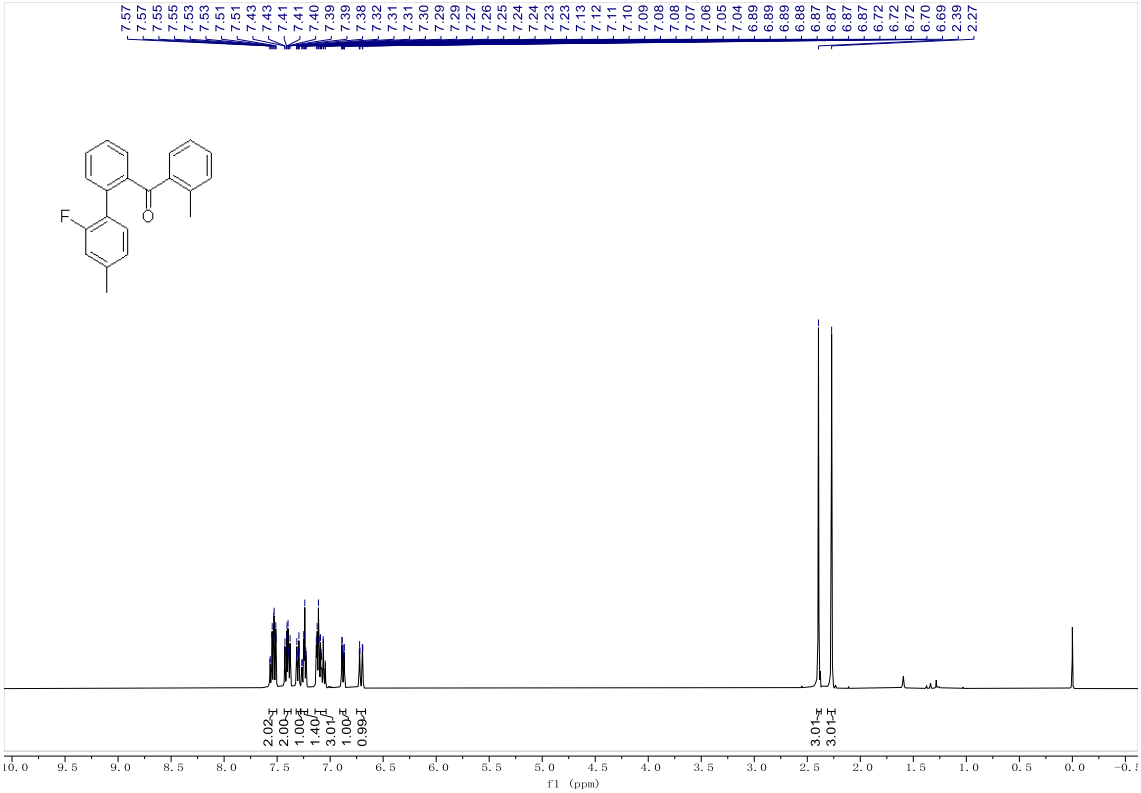
^{13}C NMR of 1k (101 MHz, Chloroform-*d*)



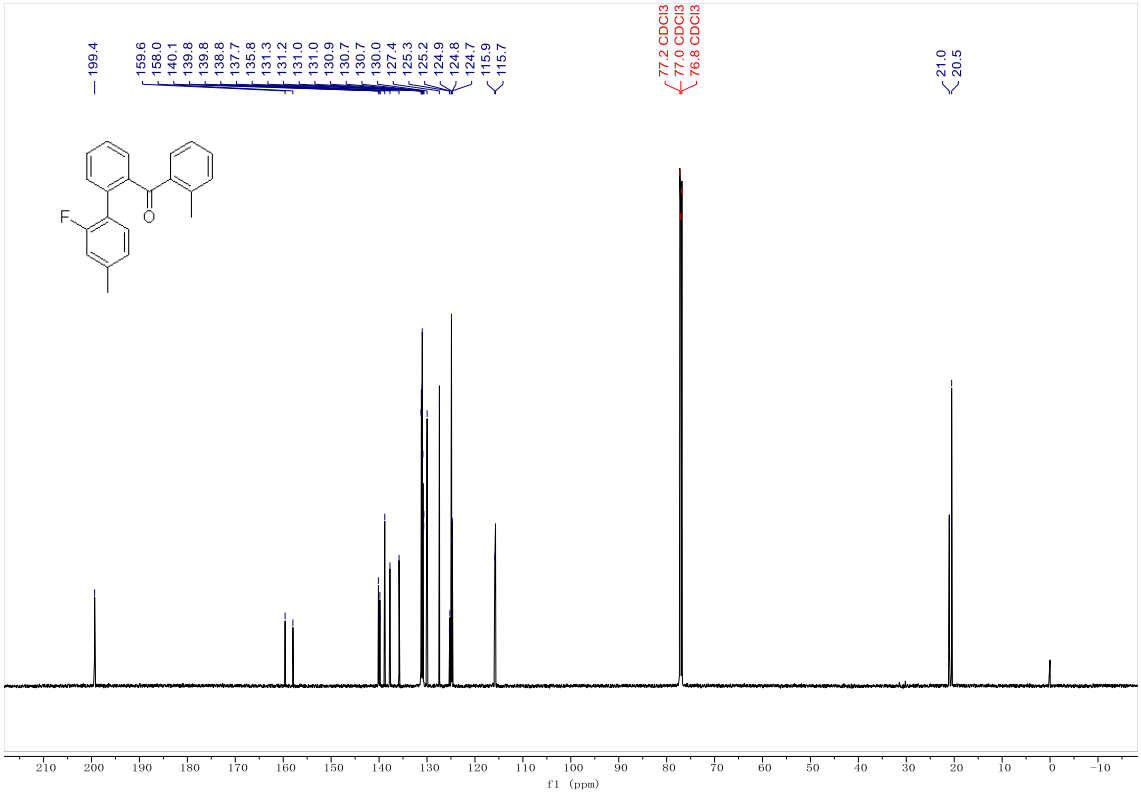
^{19}F NMR of 1k (400 MHz, Chloroform-*d*)



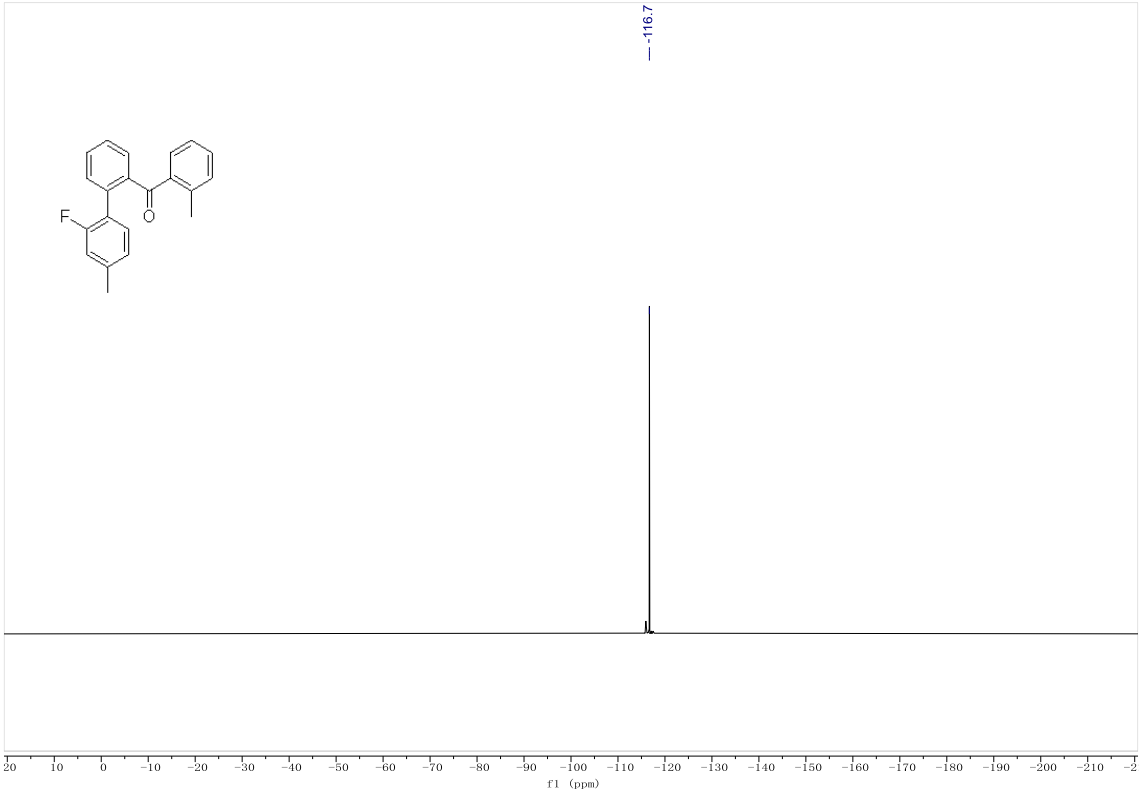
^{1}H NMR of 1l (400 MHz, Chloroform-*d*)



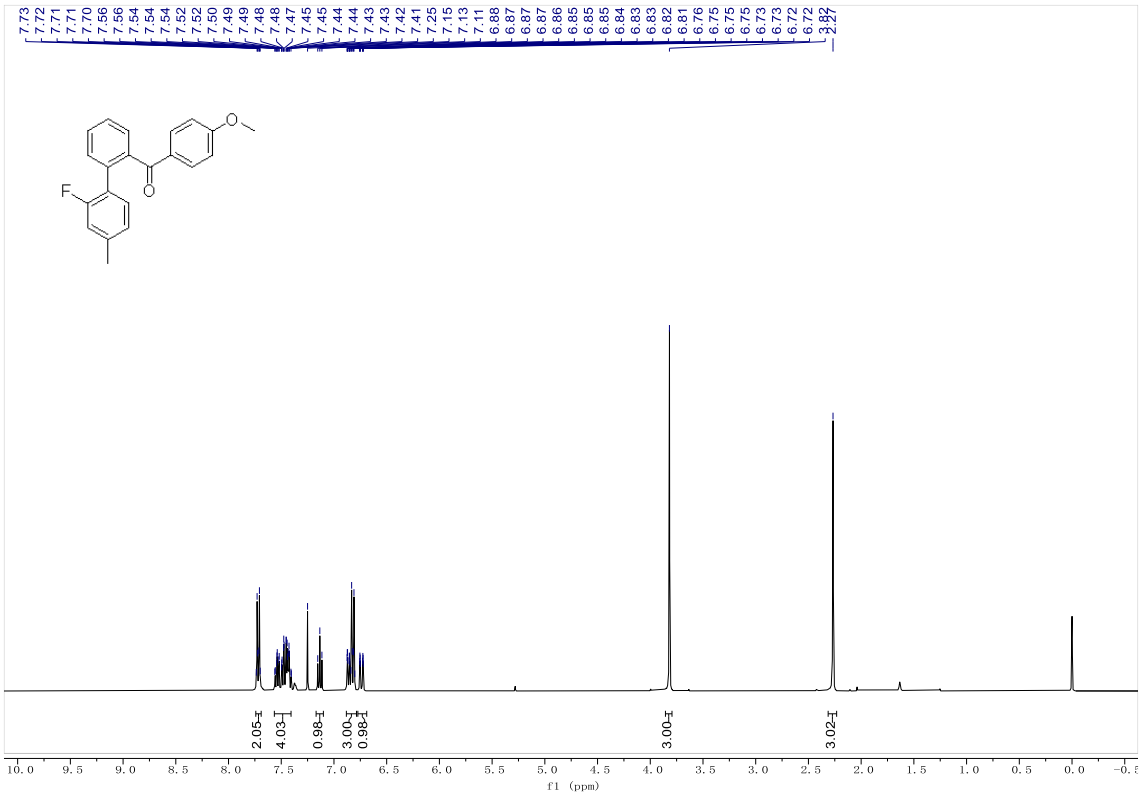
^{13}C NMR of 1l (101 MHz, Chloroform-*d*)



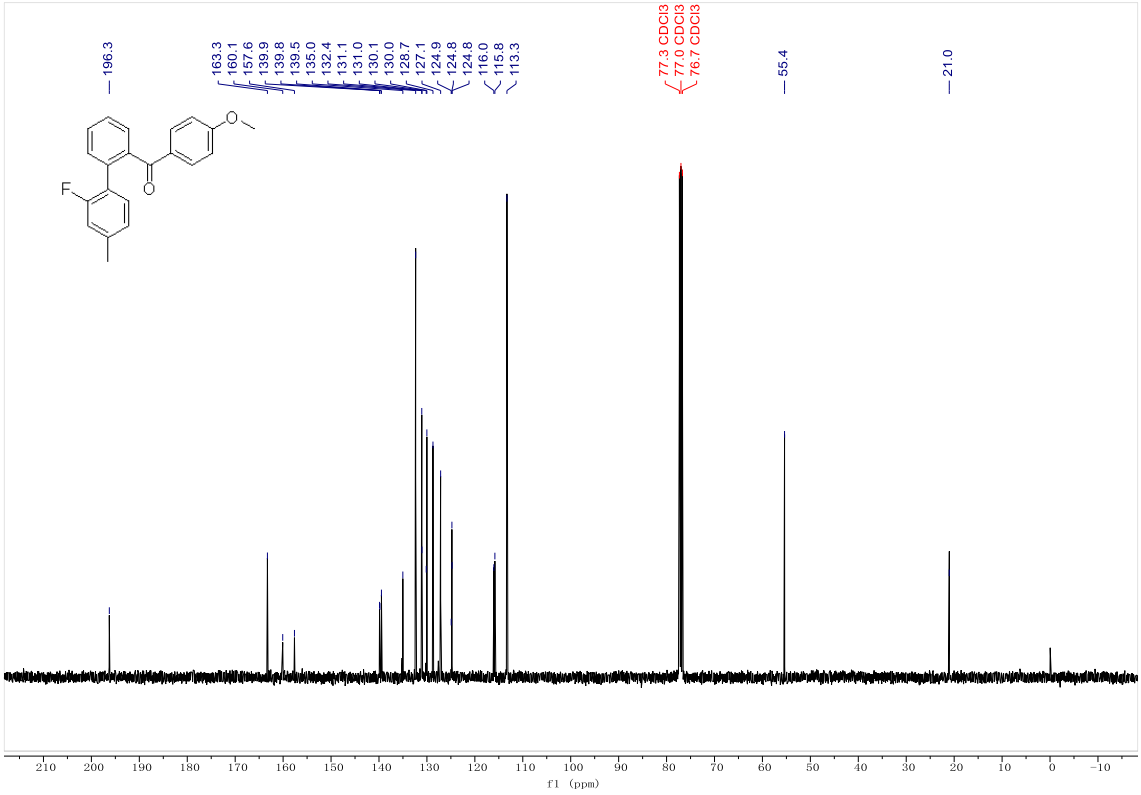
^{19}F NMR of 1l (400 MHz, Chloroform-*d*)



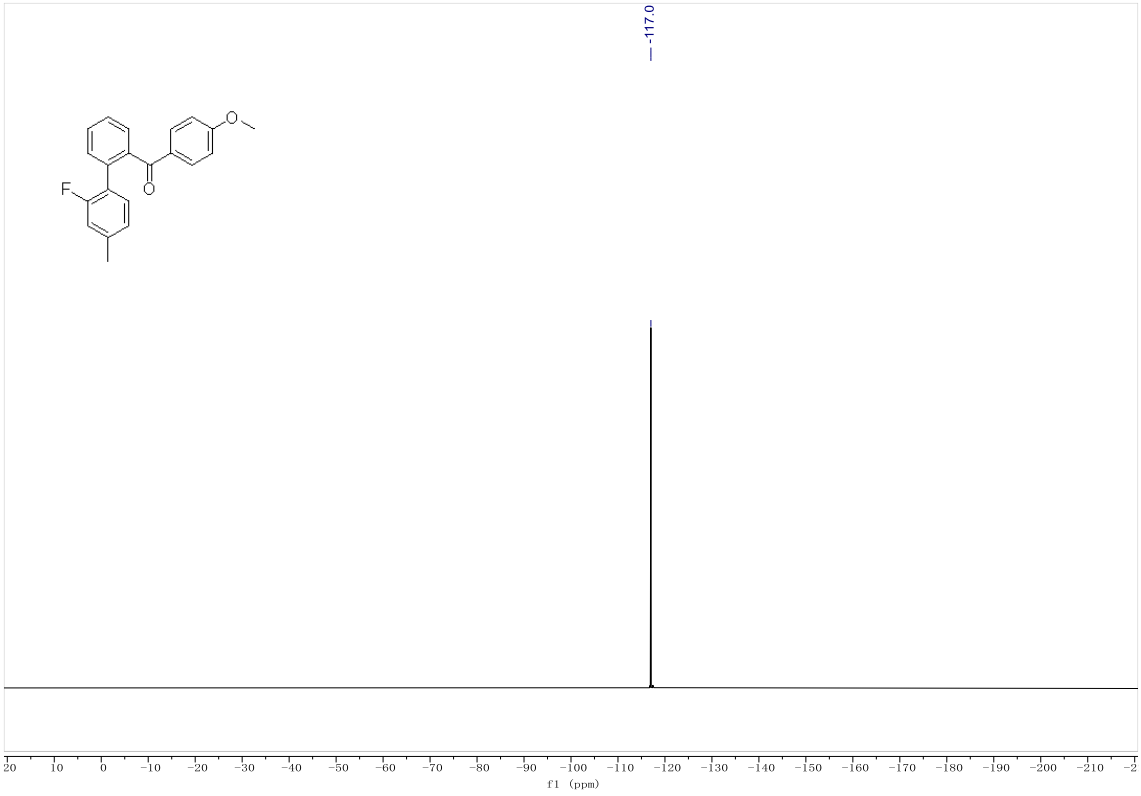
^{1}H NMR of 1m (400 MHz, Chloroform-*d*)



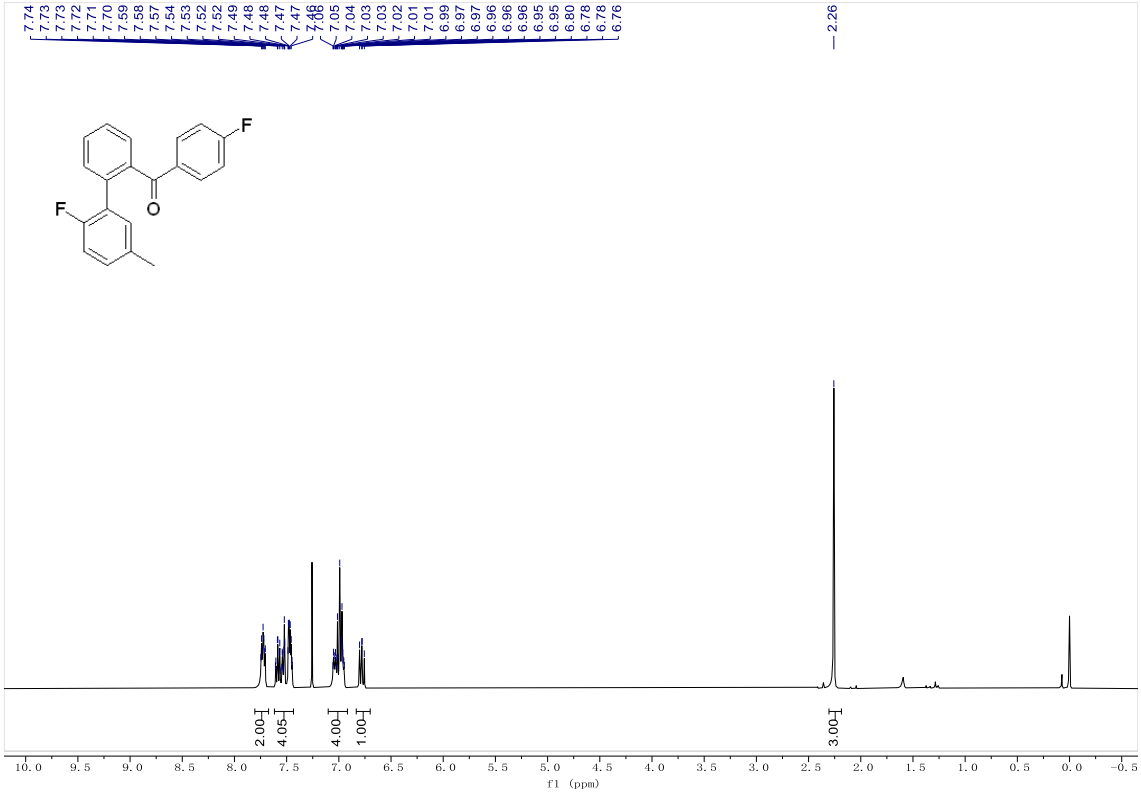
^{13}C NMR of 1m (101 MHz, Chloroform-*d*)



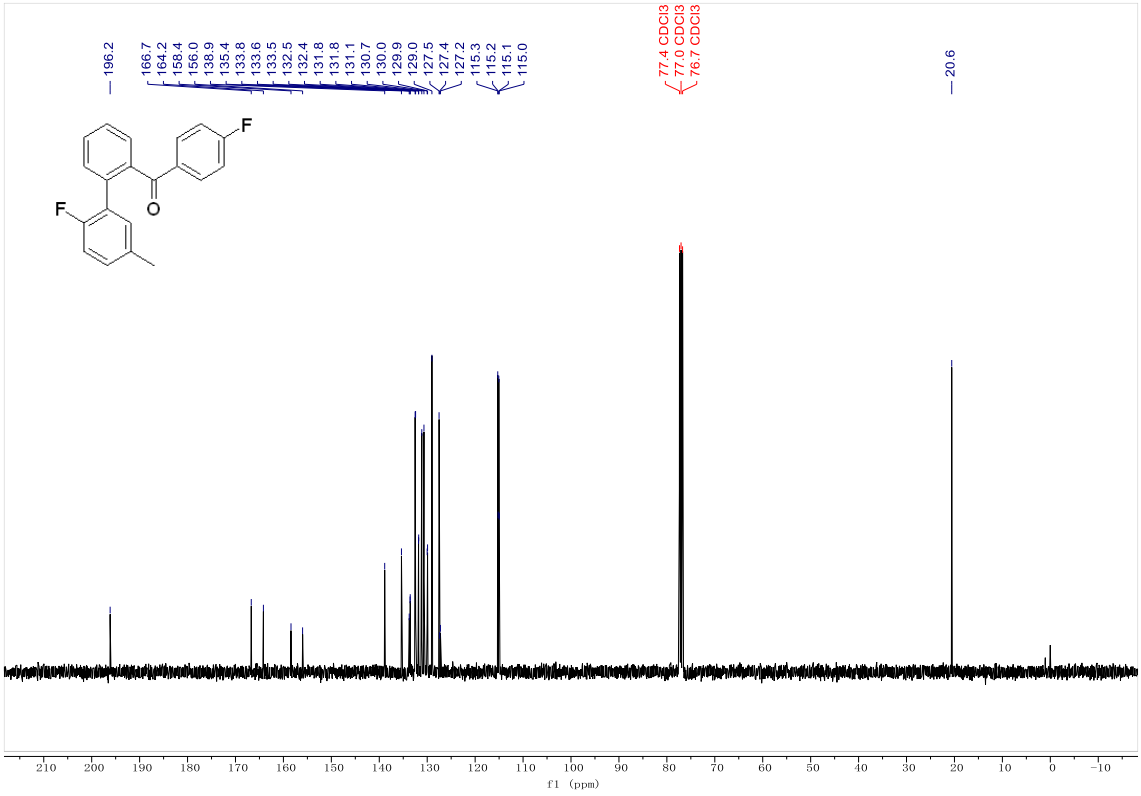
^{19}F NMR of 1m (400 MHz, Chloroform-*d*)



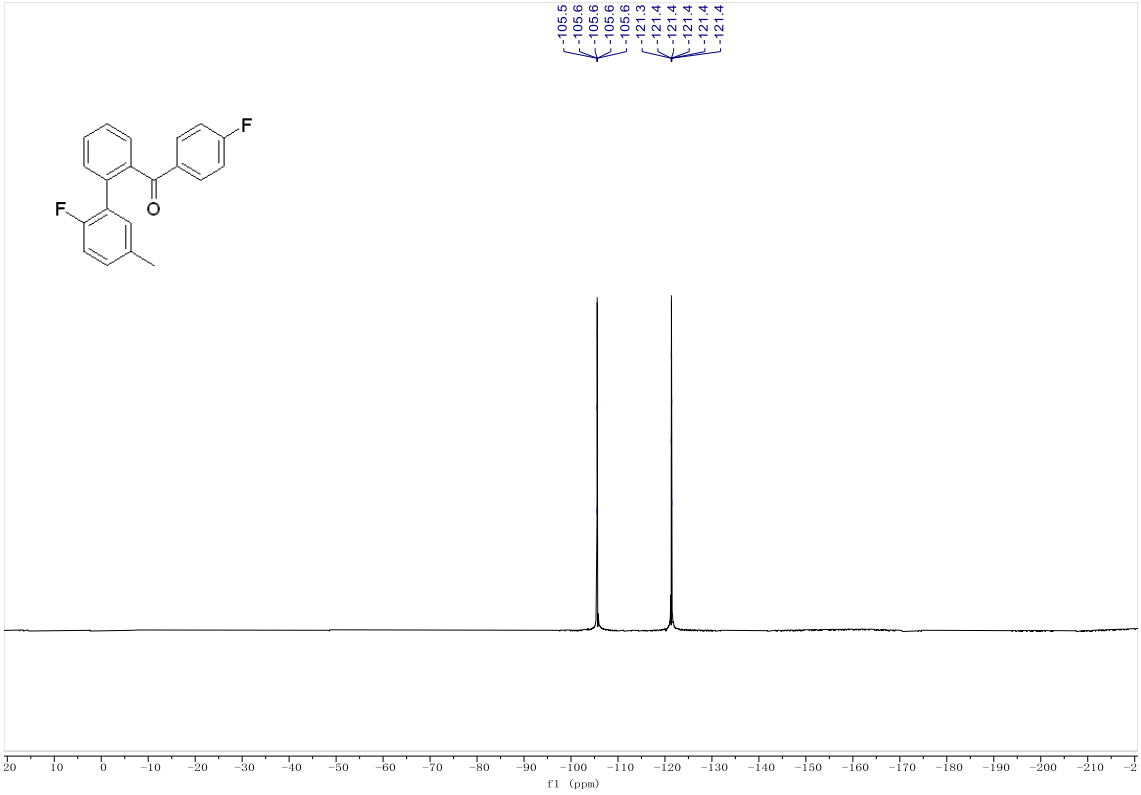
^{1}H NMR of 1n (400 MHz, Chloroform-*d*)



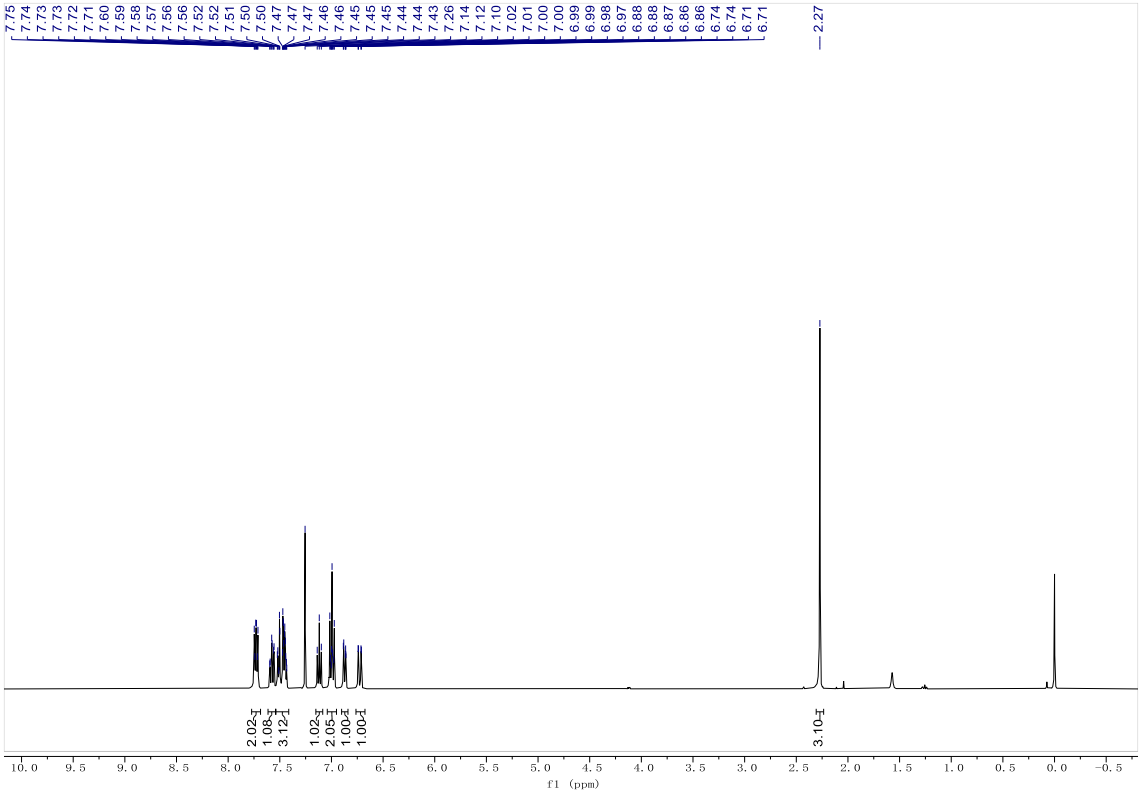
^{13}C NMR of 1n (101 MHz, Chloroform-*d*)



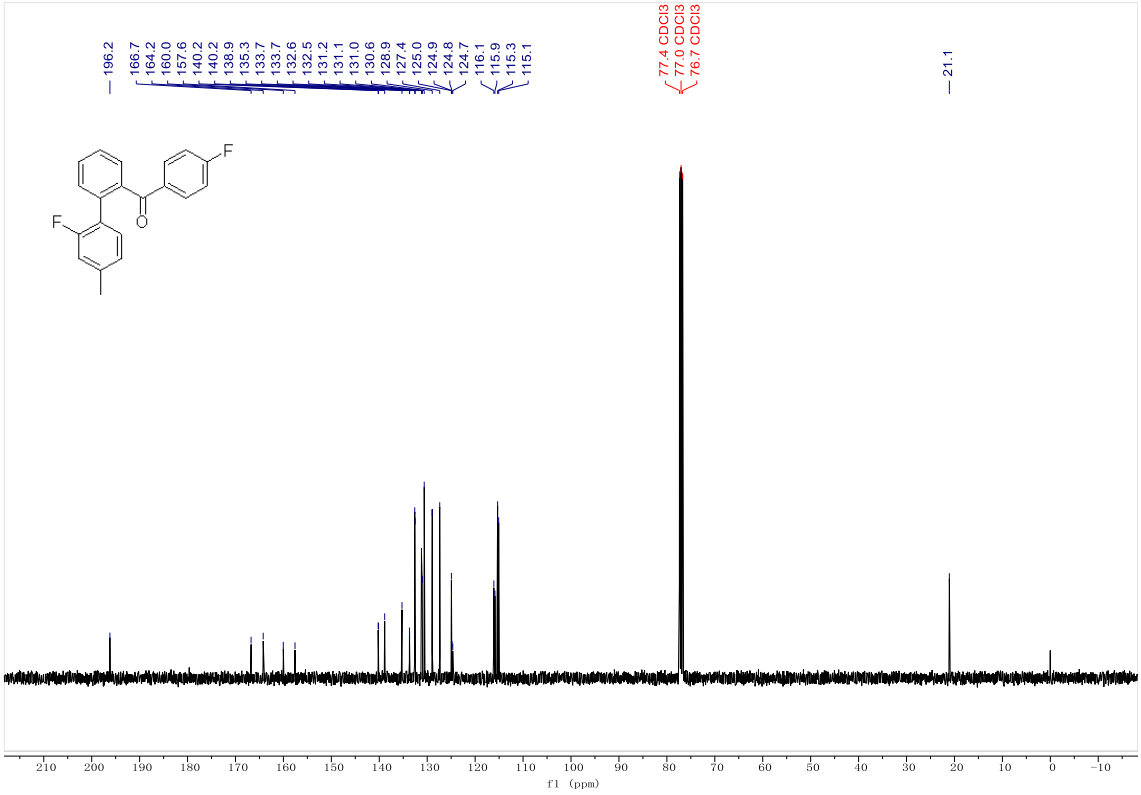
^{19}F NMR of 1n (400 MHz, Chloroform-*d*)



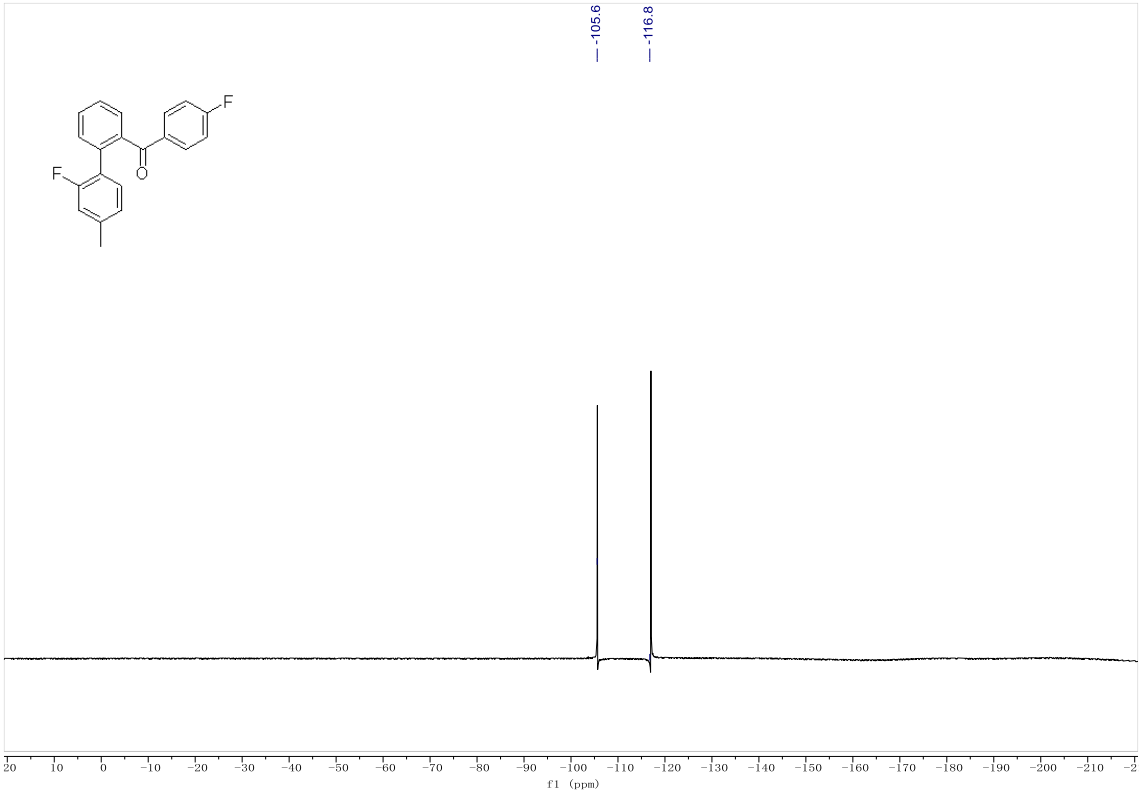
^{1}H NMR of 1o (400 MHz, Chloroform-*d*)



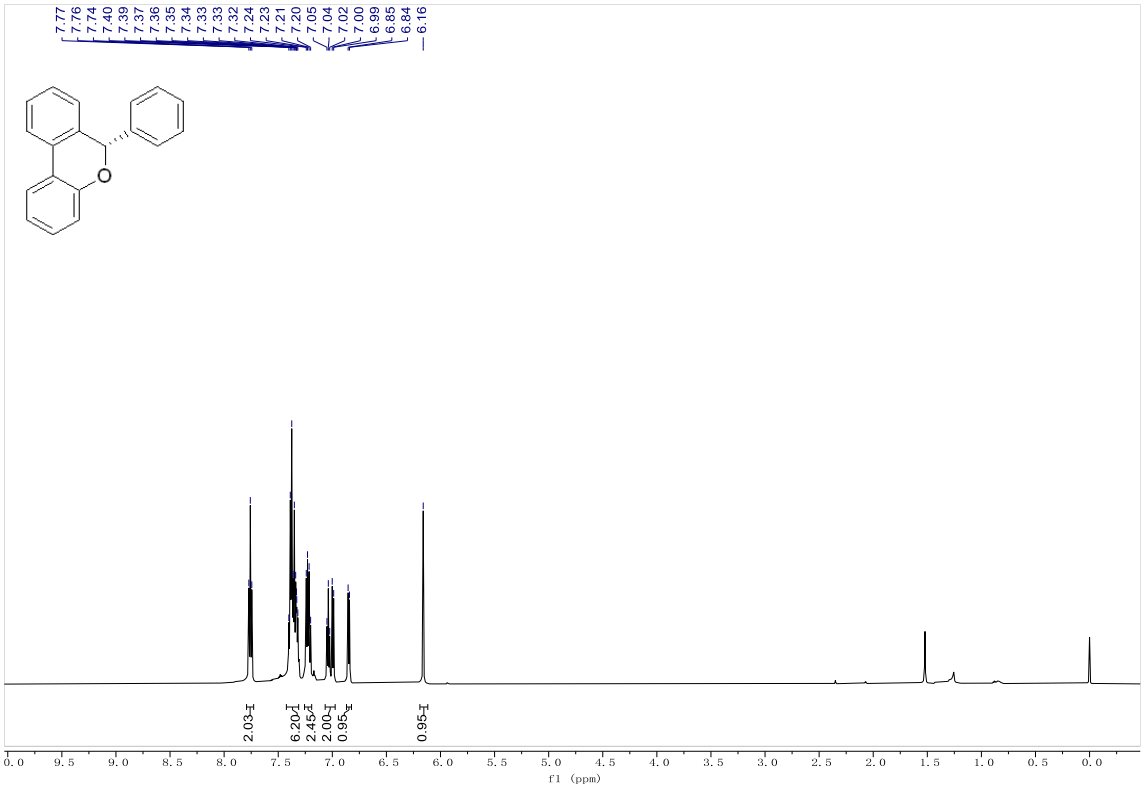
^{13}C NMR of 1o (101 MHz, Chloroform-*d*)



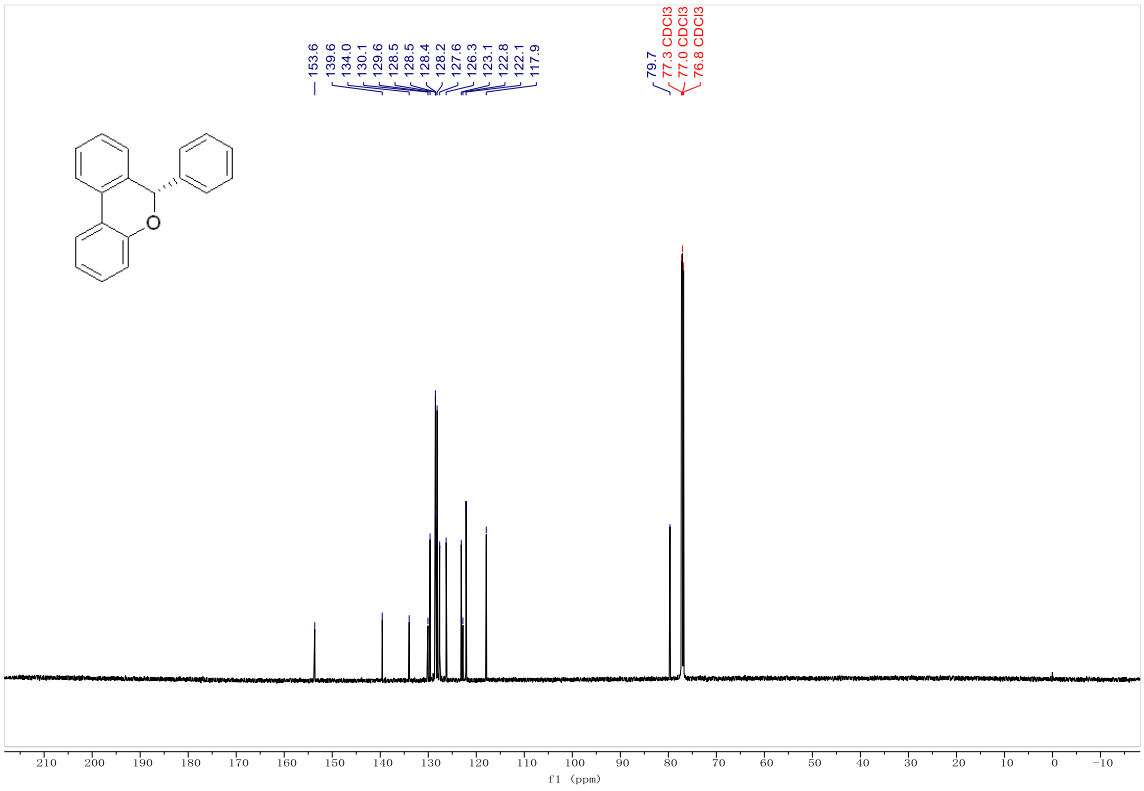
^{19}F NMR of 1o (400 MHz, Chloroform-*d*)



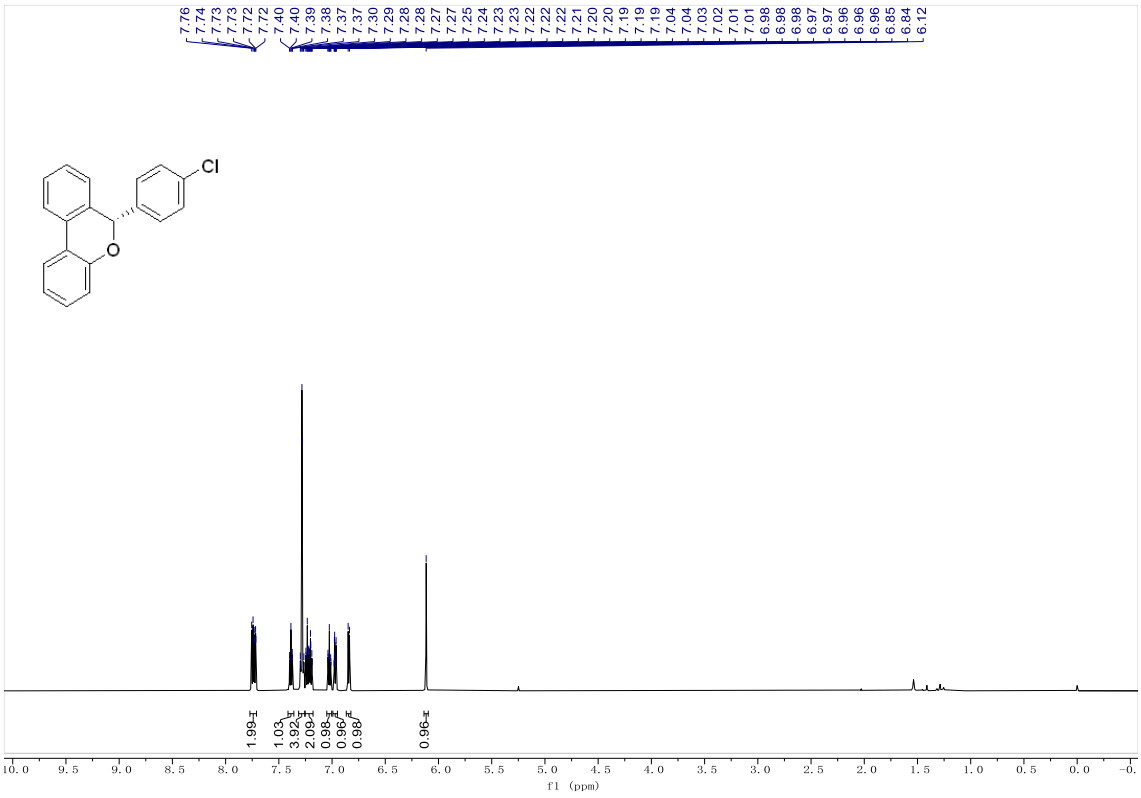
^{1}H NMR of 2a (400 MHz, Chloroform-*d*)



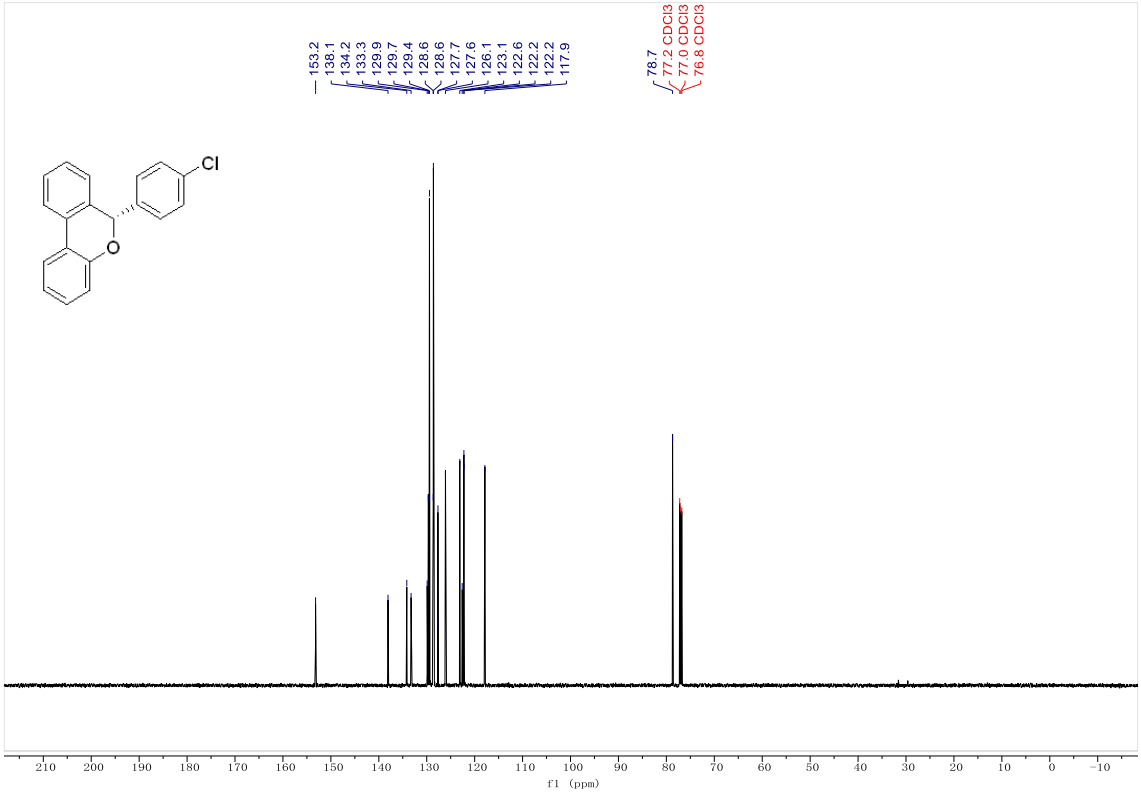
^{13}C NMR of 2a (151 MHz, Chloroform-*d*)



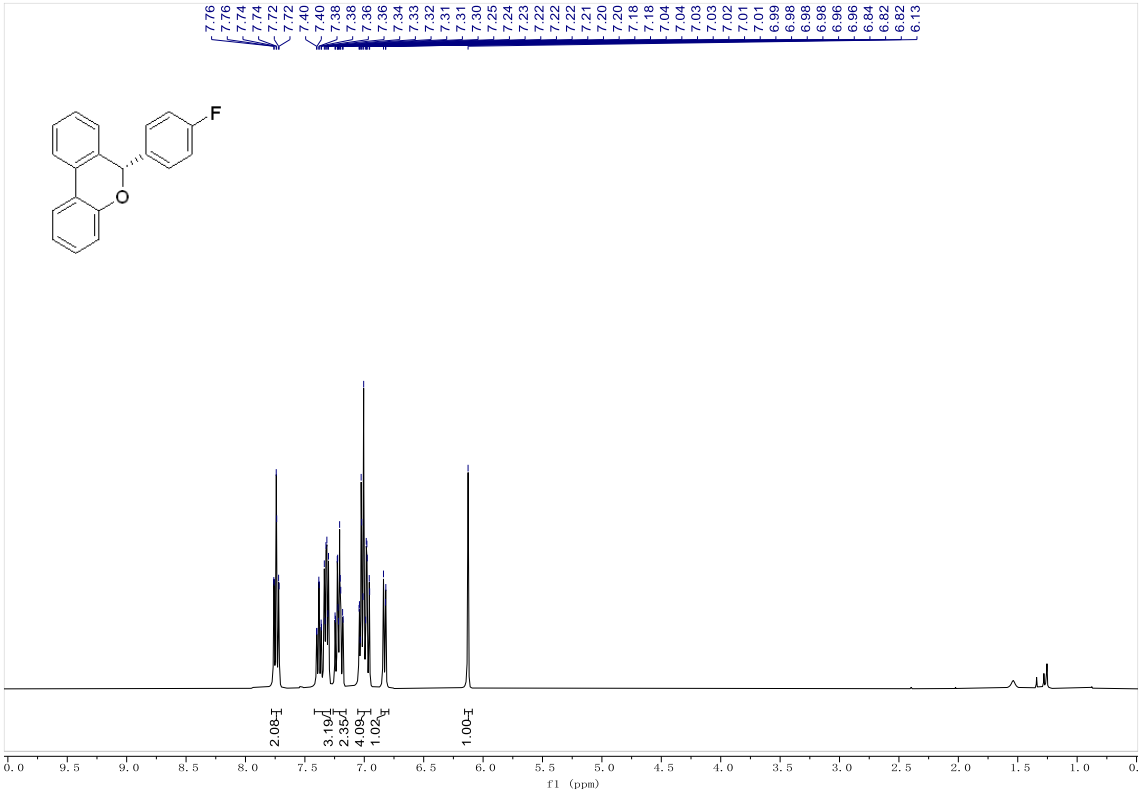
^{1}H NMR of 2b (400 MHz, Chloroform-*d*)



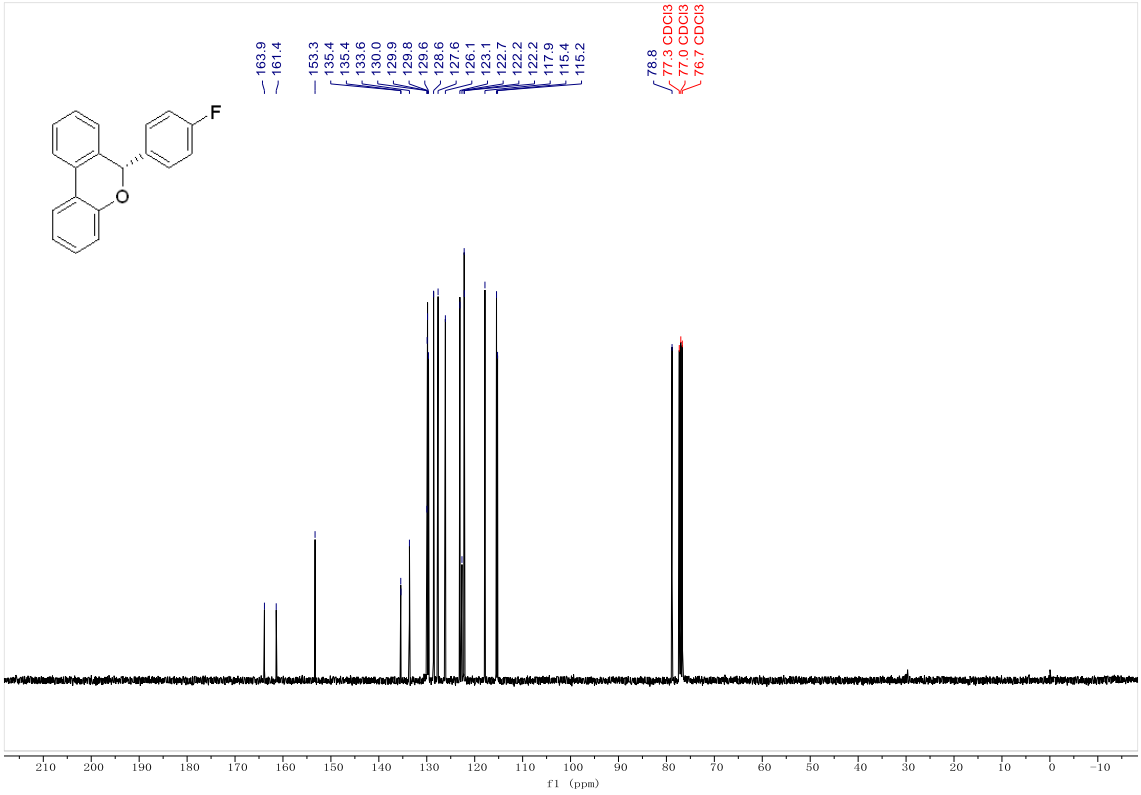
^{13}C NMR of 2b (151 MHz, Chloroform-*d*)



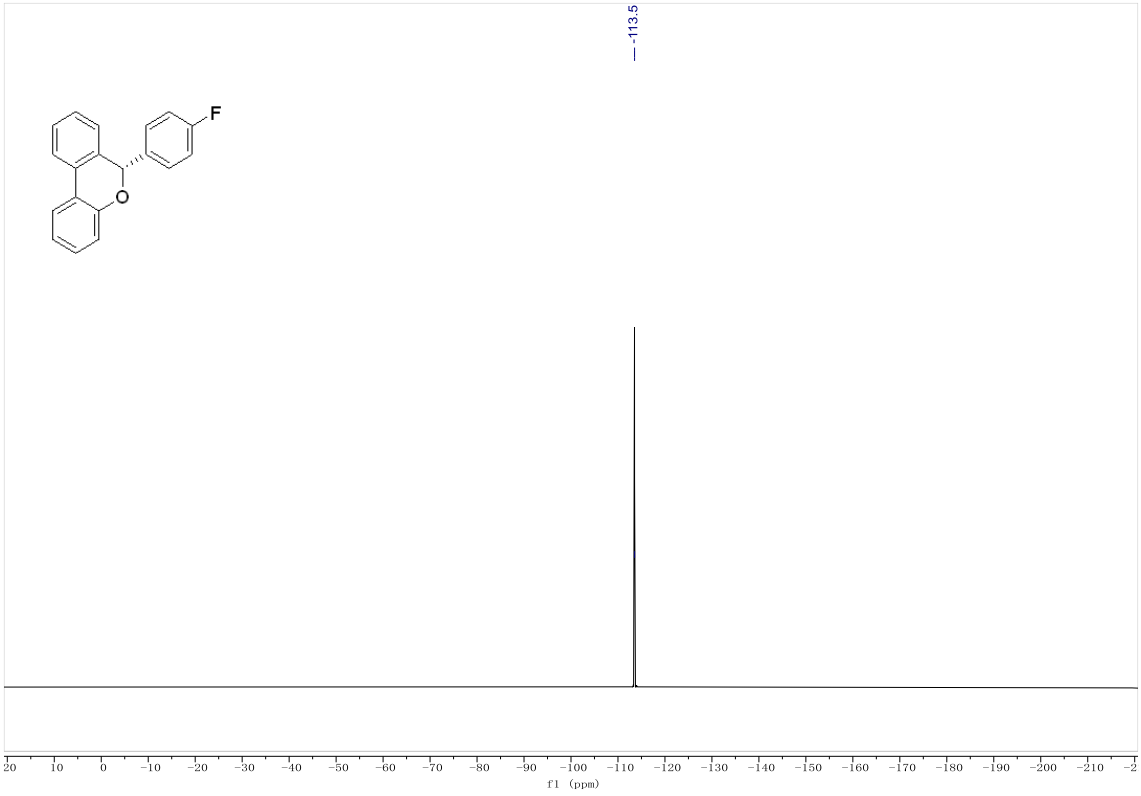
^{1}H NMR of 2c (400 MHz, Chloroform-*d*)



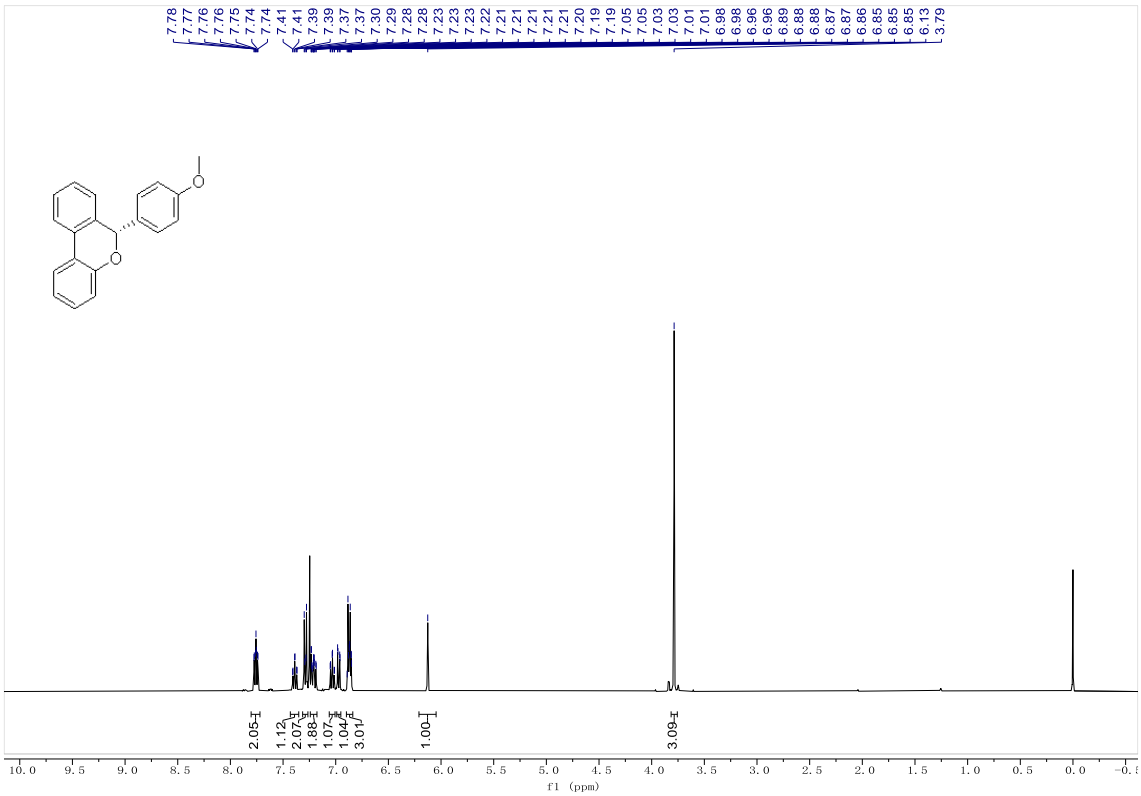
^{13}C NMR of 2c (101 MHz, Chloroform-*d*)



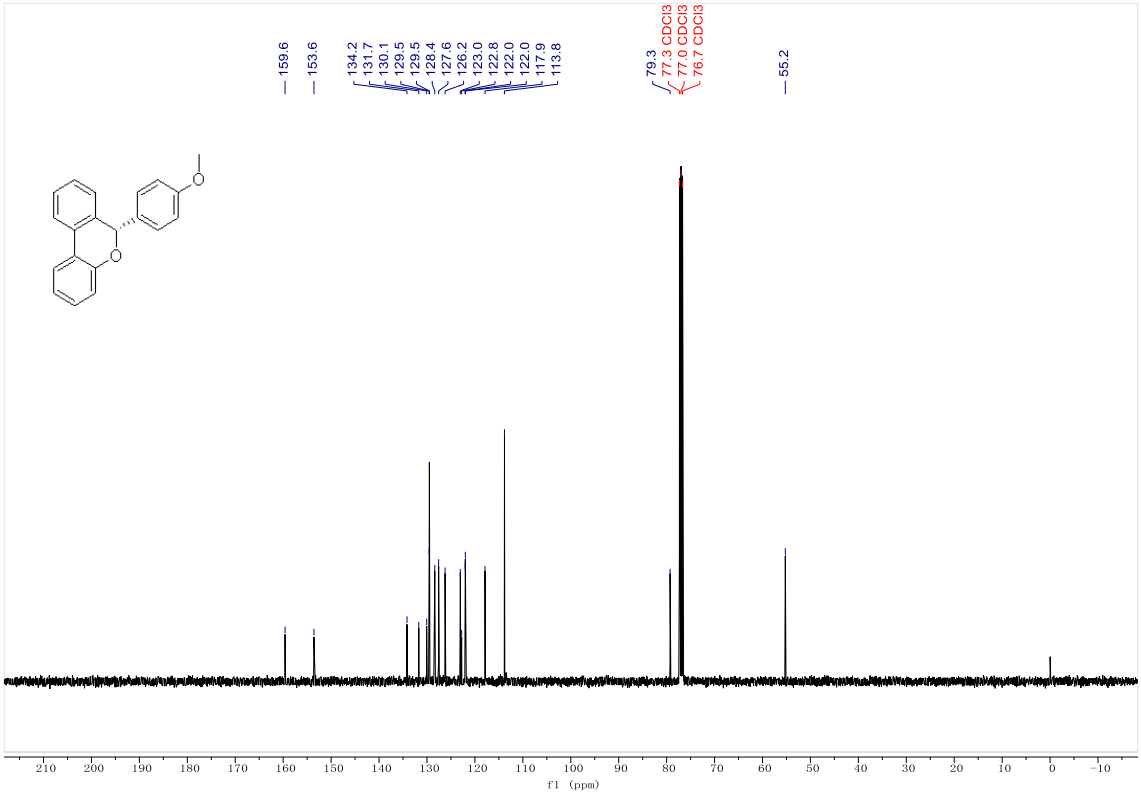
^{19}F NMR of 2c (400 MHz, Chloroform-*d*)



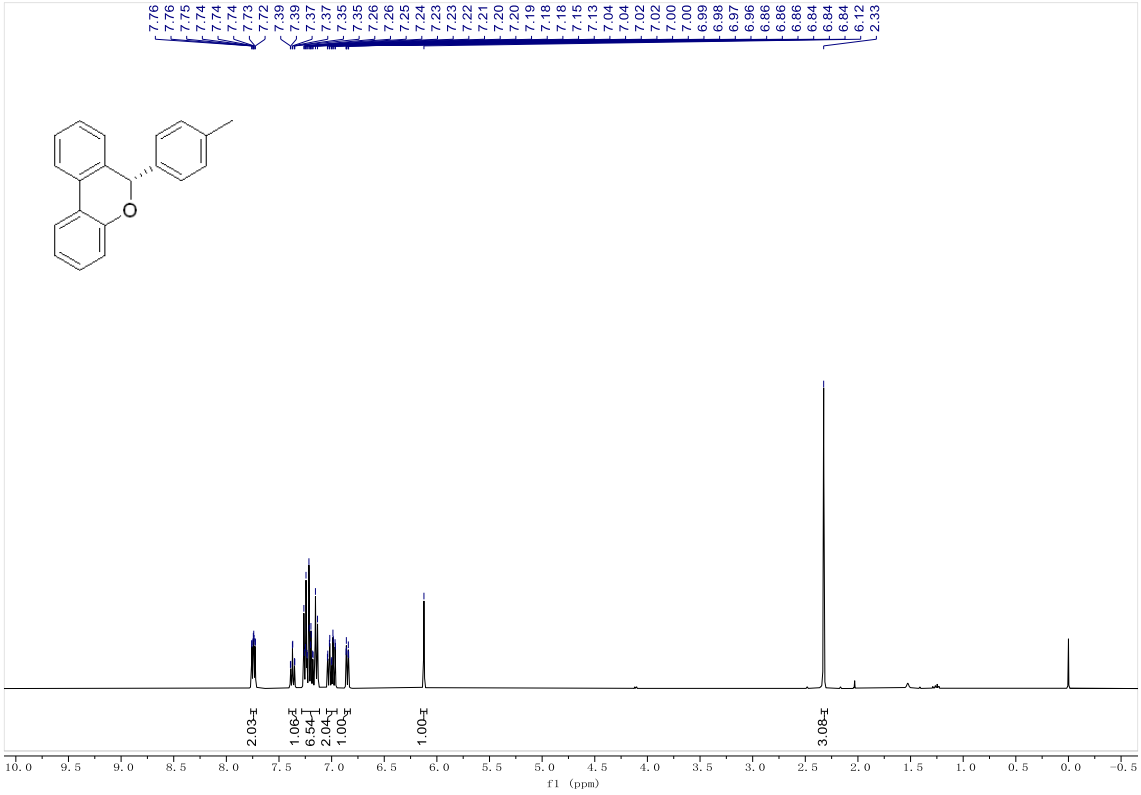
^{1}H NMR of 2d (400 MHz, Chloroform-*d*)



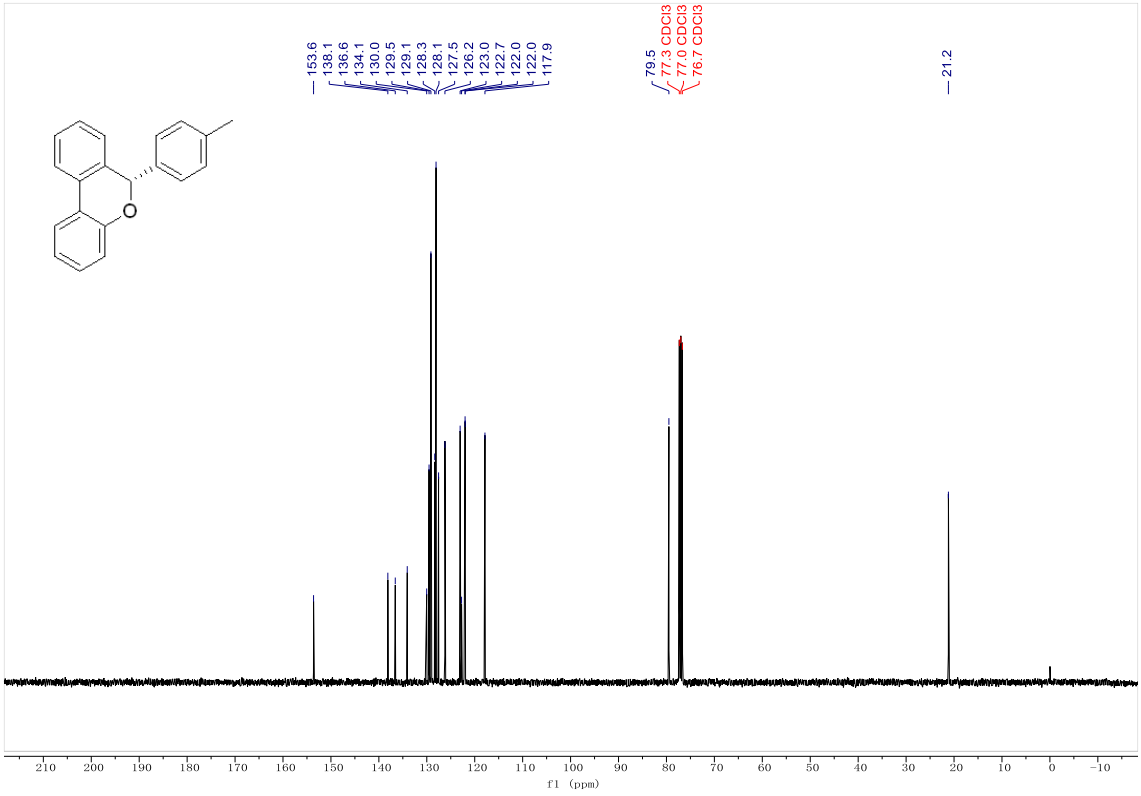
^{13}C NMR of 2d (101 MHz, Chloroform-*d*)



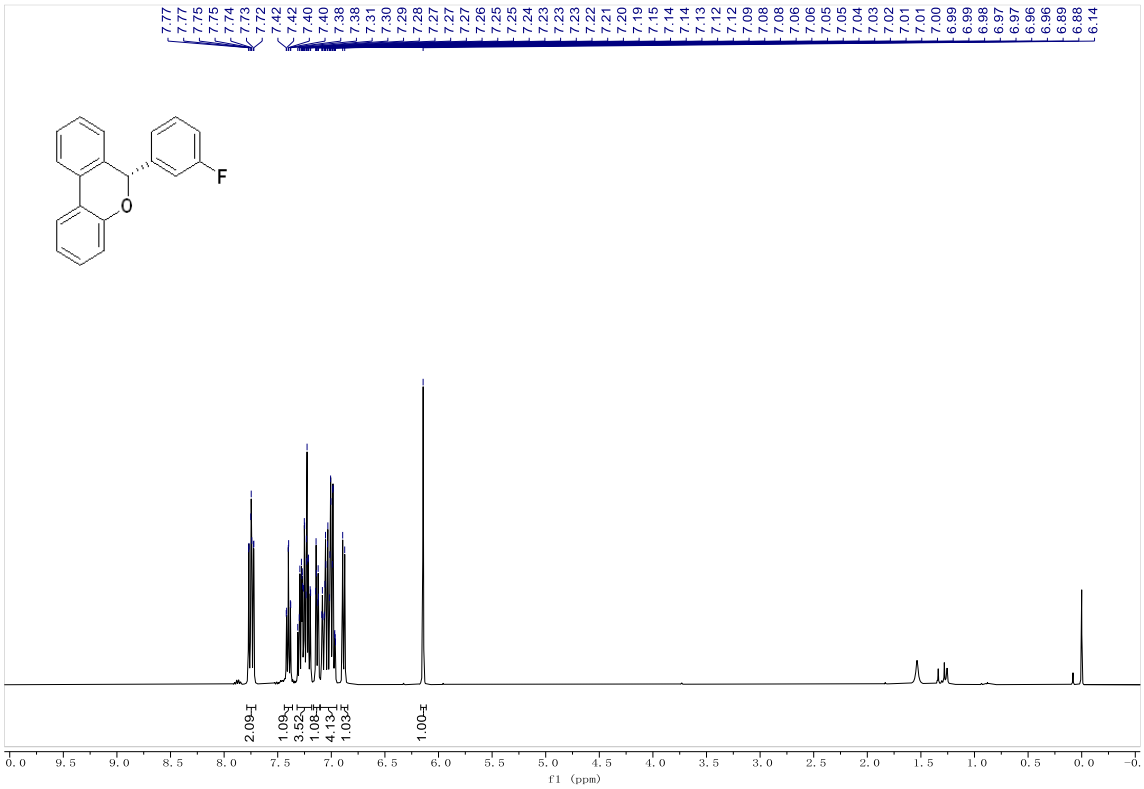
^{1}H NMR of 2e (400 MHz, Chloroform-*d*)



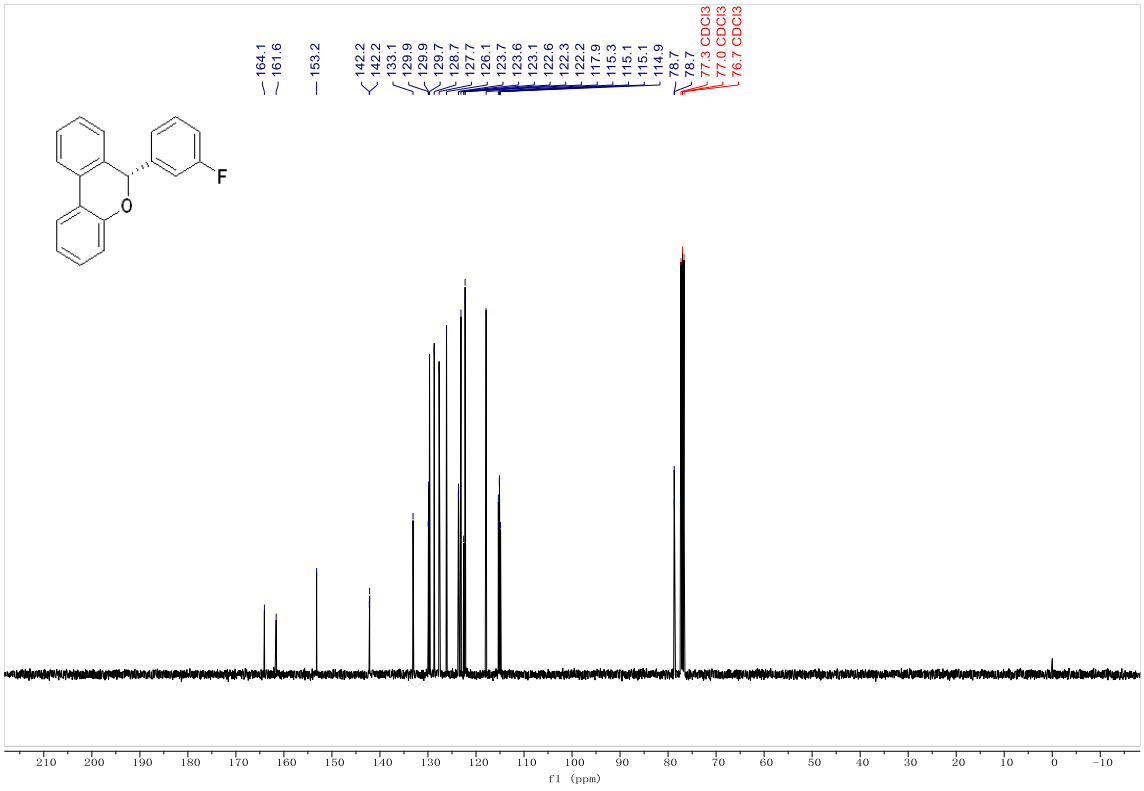
^{13}C NMR of 2e (101 MHz, Chloroform-*d*)



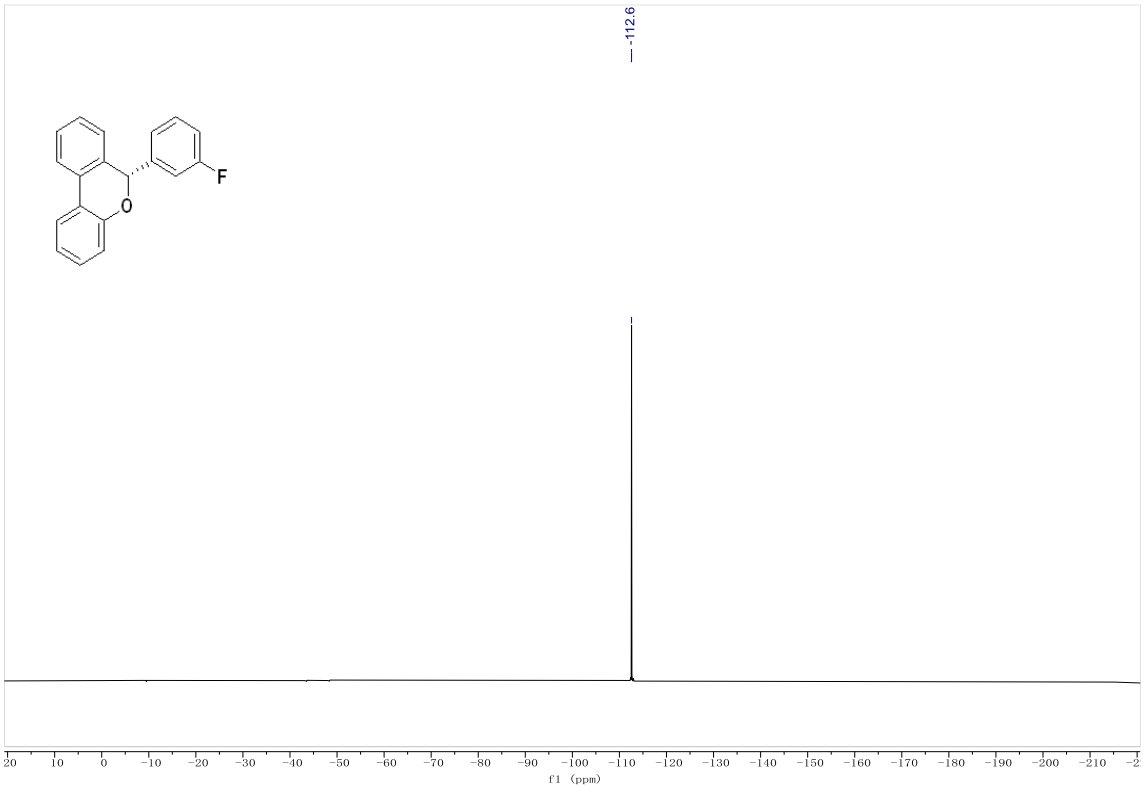
^{1}H NMR of 2f (400 MHz, Chloroform-*d*)



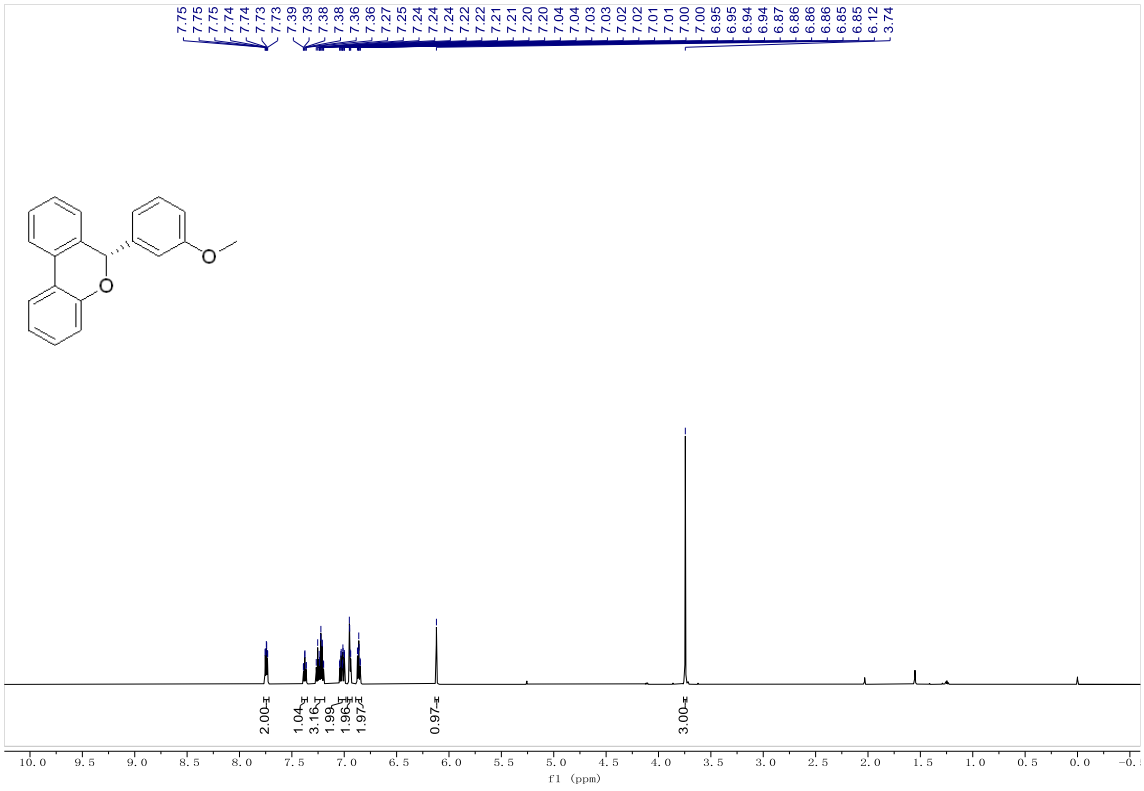
^{13}C NMR of 2f (101 MHz, Chloroform-*d*)



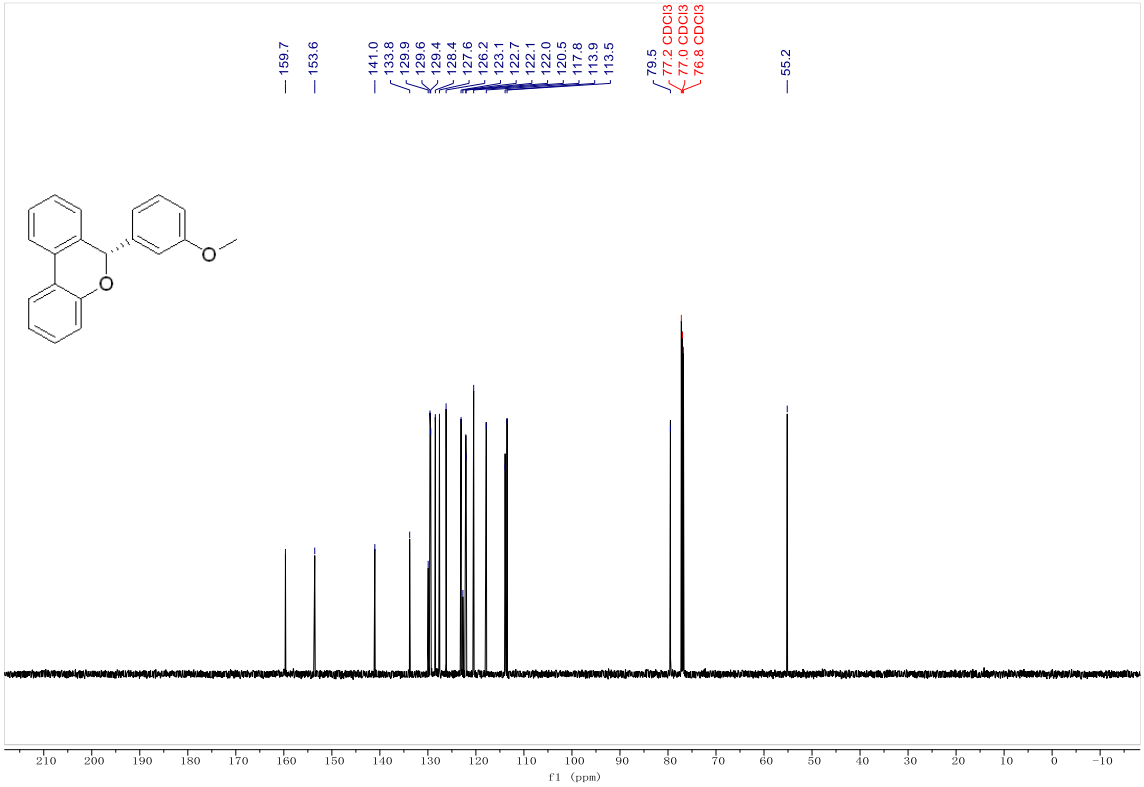
^{19}F NMR of 2f (400 MHz, Chloroform-*d*)



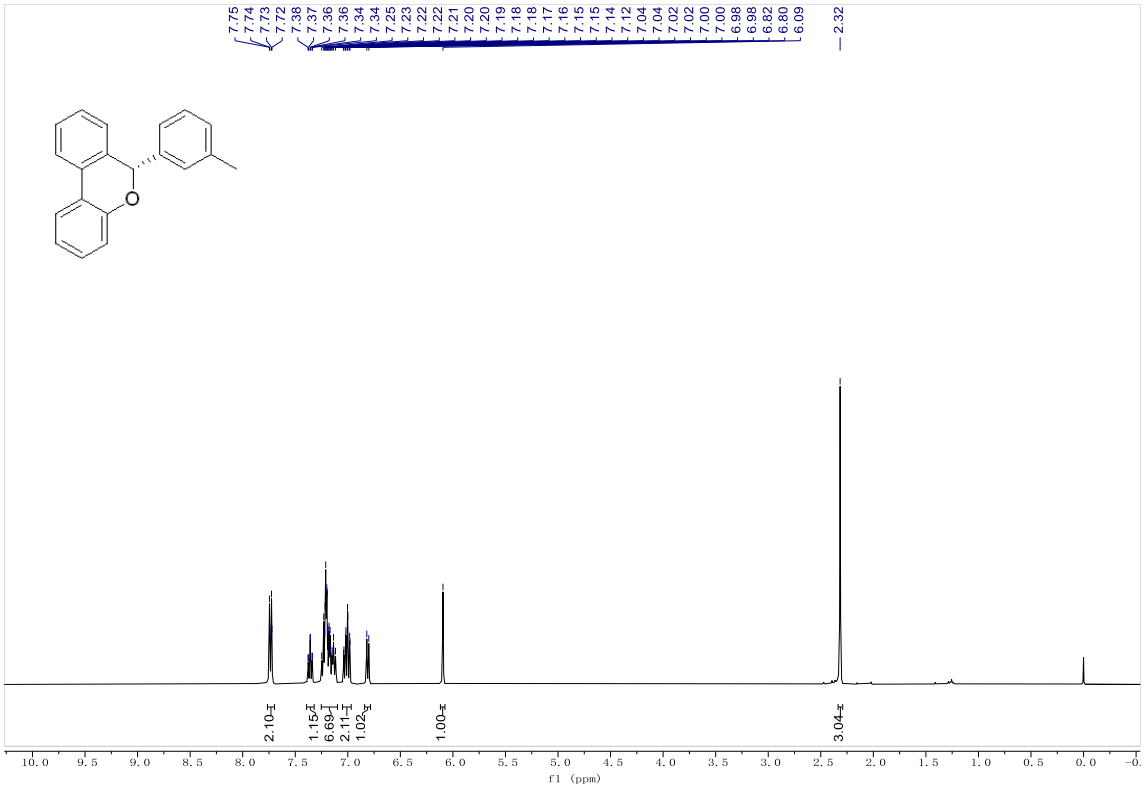
^{1}H NMR of 2g (400 MHz, Chloroform-*d*)



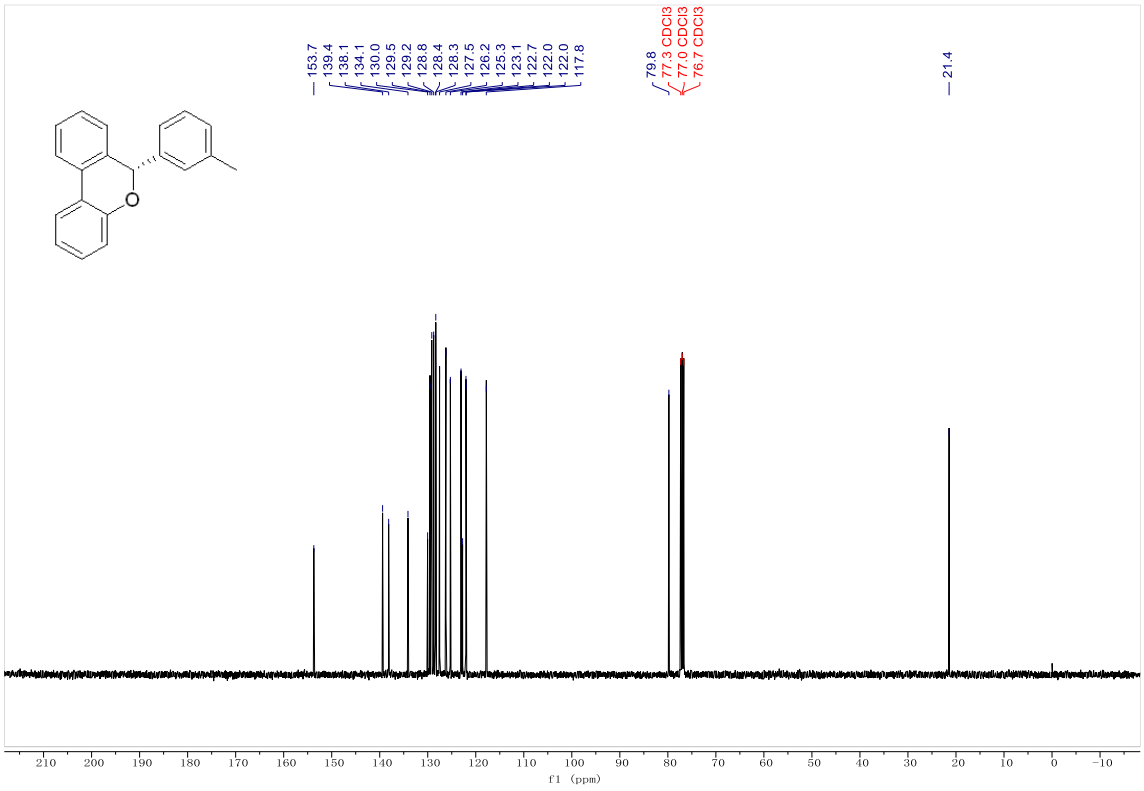
^{13}C NMR of 2g (101 MHz, Chloroform-*d*)



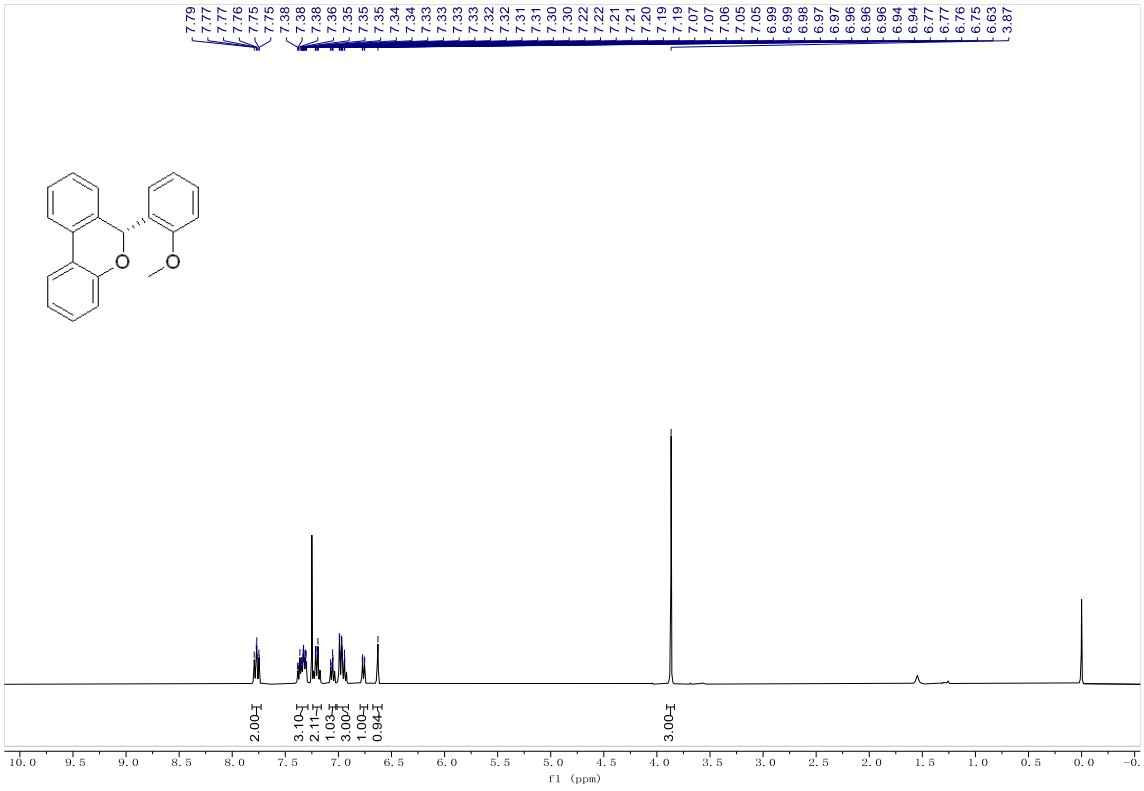
^{1}H NMR of 2h (400 MHz, Chloroform-*d*)



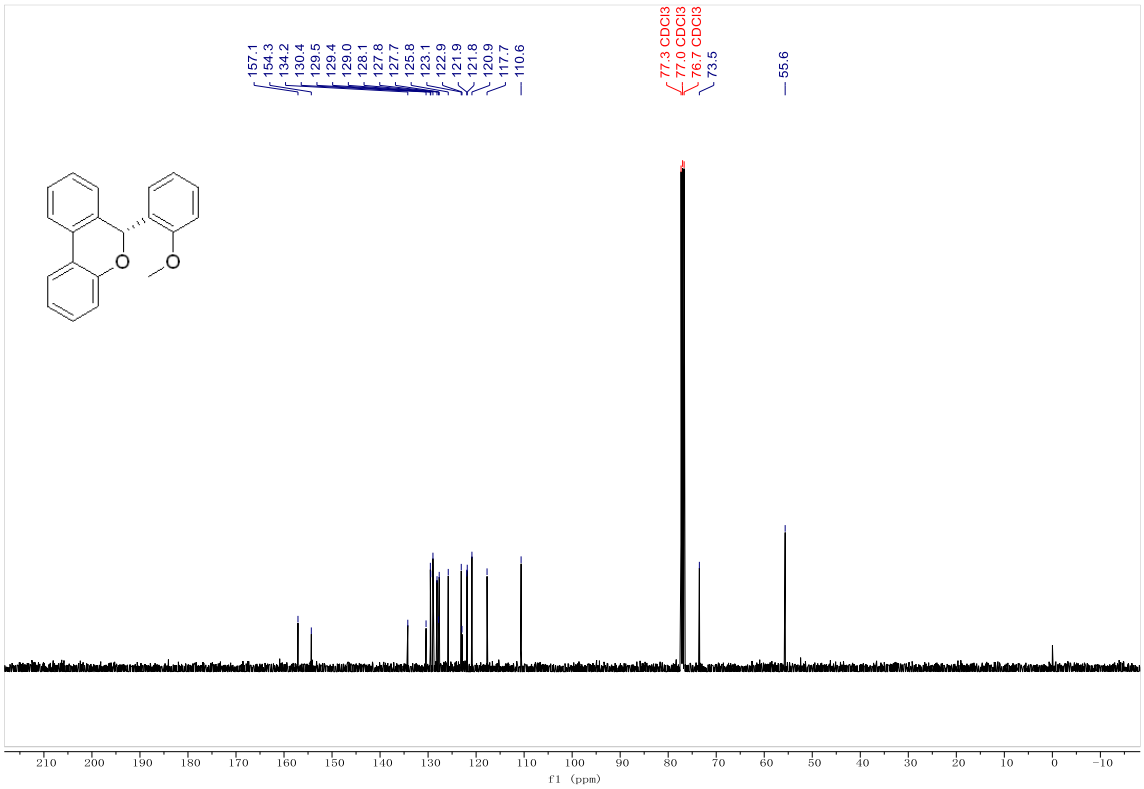
^{13}C NMR of 2h (101 MHz, Chloroform-*d*)



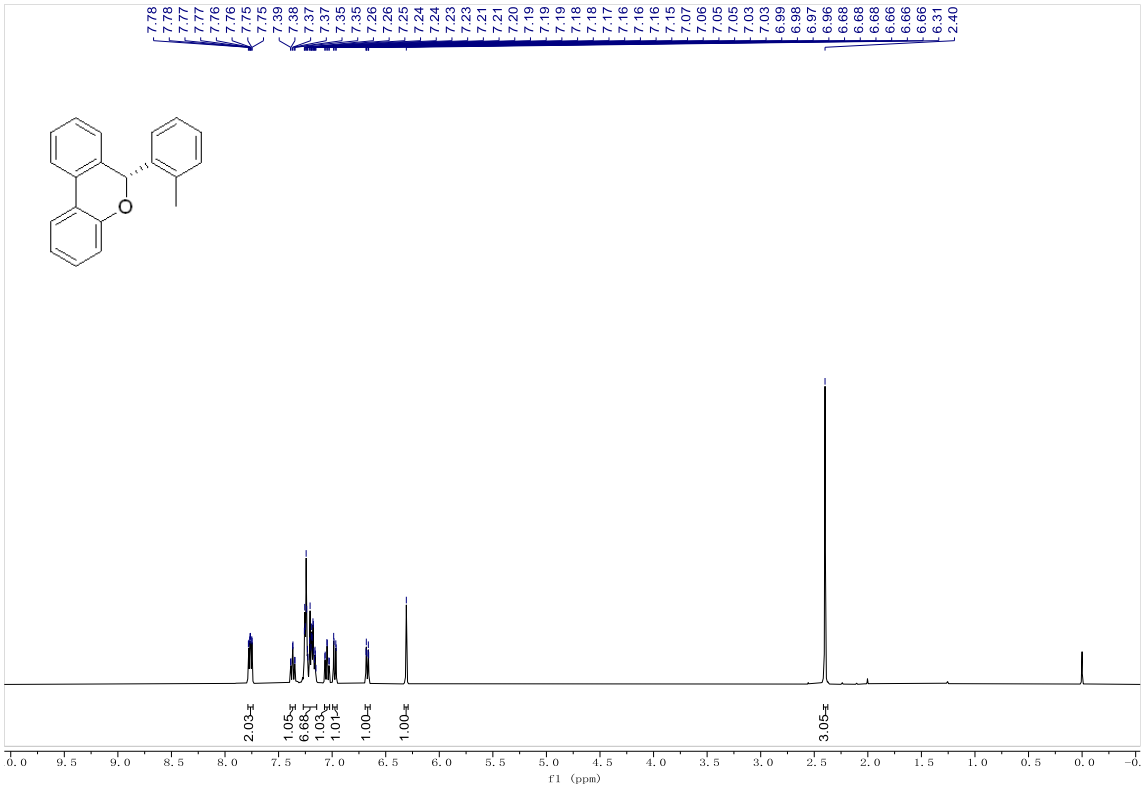
^{1}H NMR of 2i (400 MHz, Chloroform-*d*)



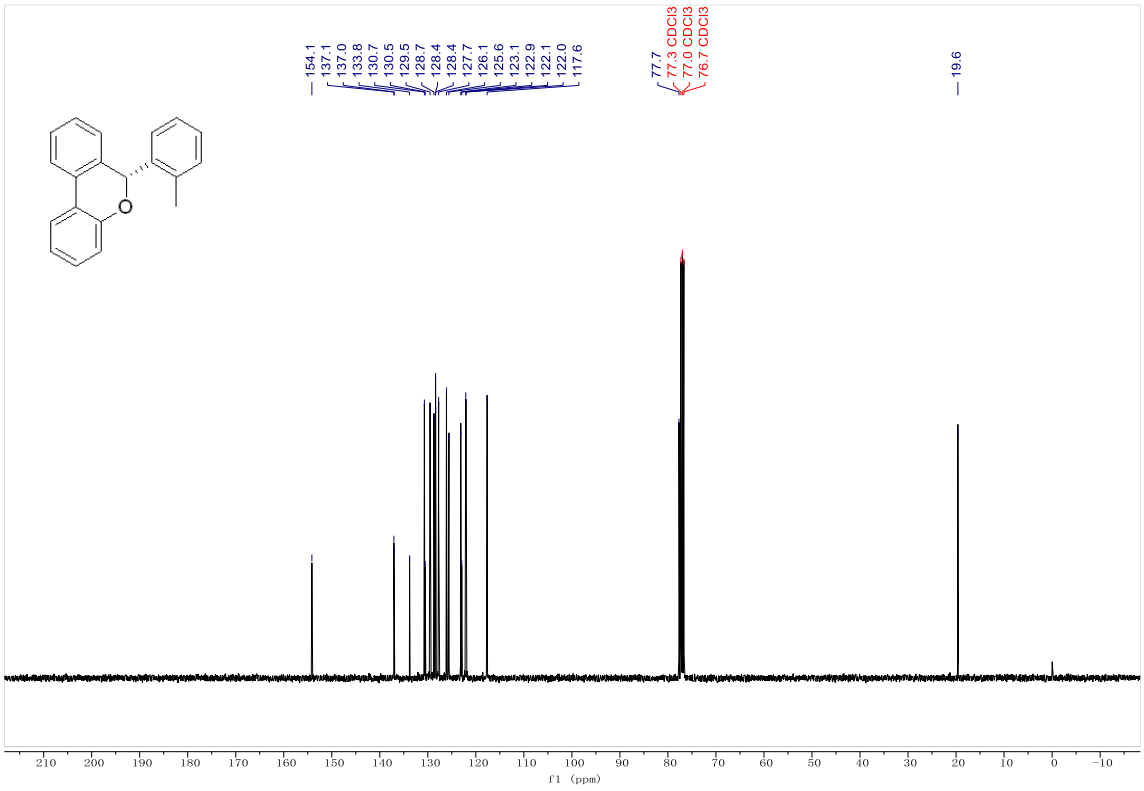
^{13}C NMR of 2i (101 MHz, Chloroform-*d*)



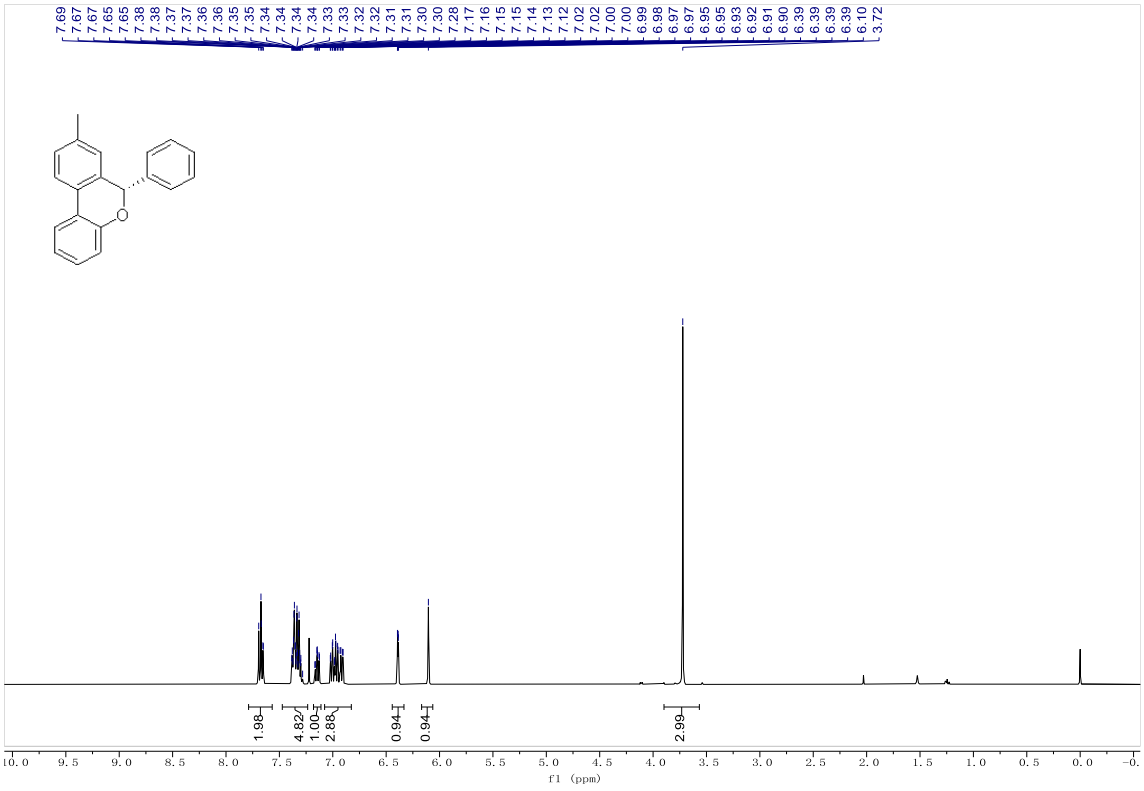
^{1}H NMR of 2j (400 MHz, Chloroform-*d*)



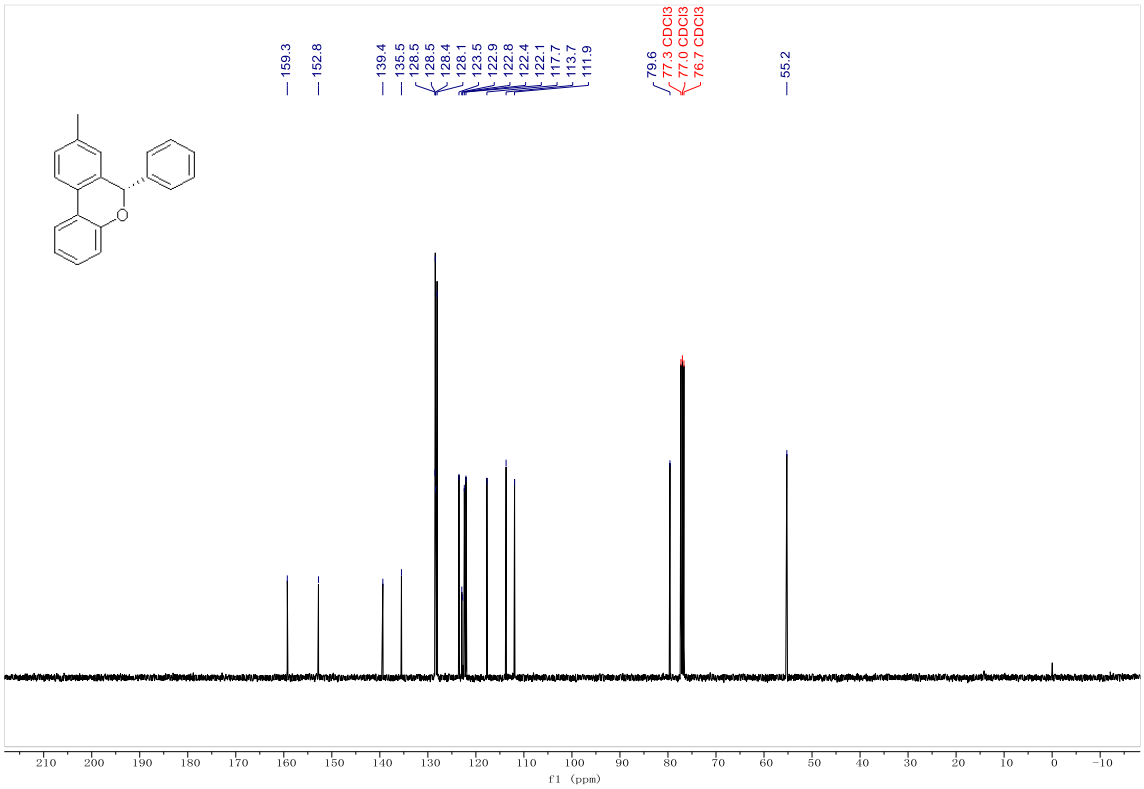
^{13}C NMR of 2j (101 MHz, Chloroform-*d*)



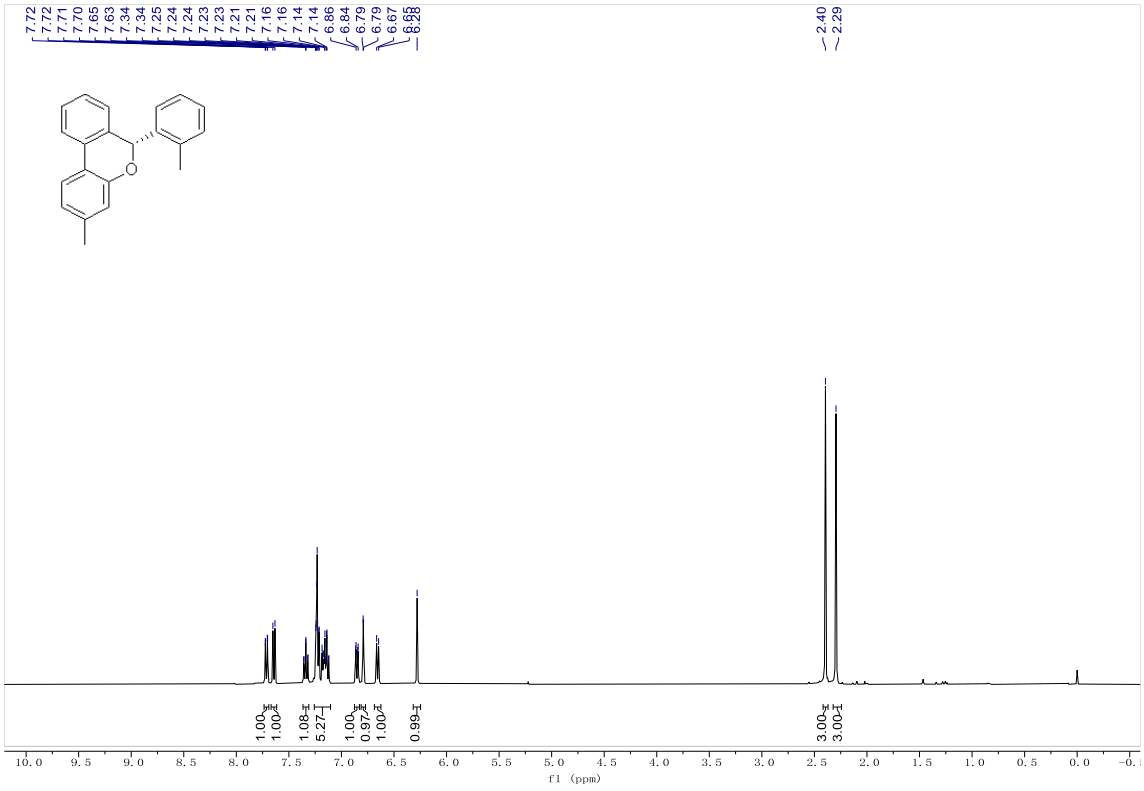
^{1}H NMR of 2k (400 MHz, Chloroform-*d*)



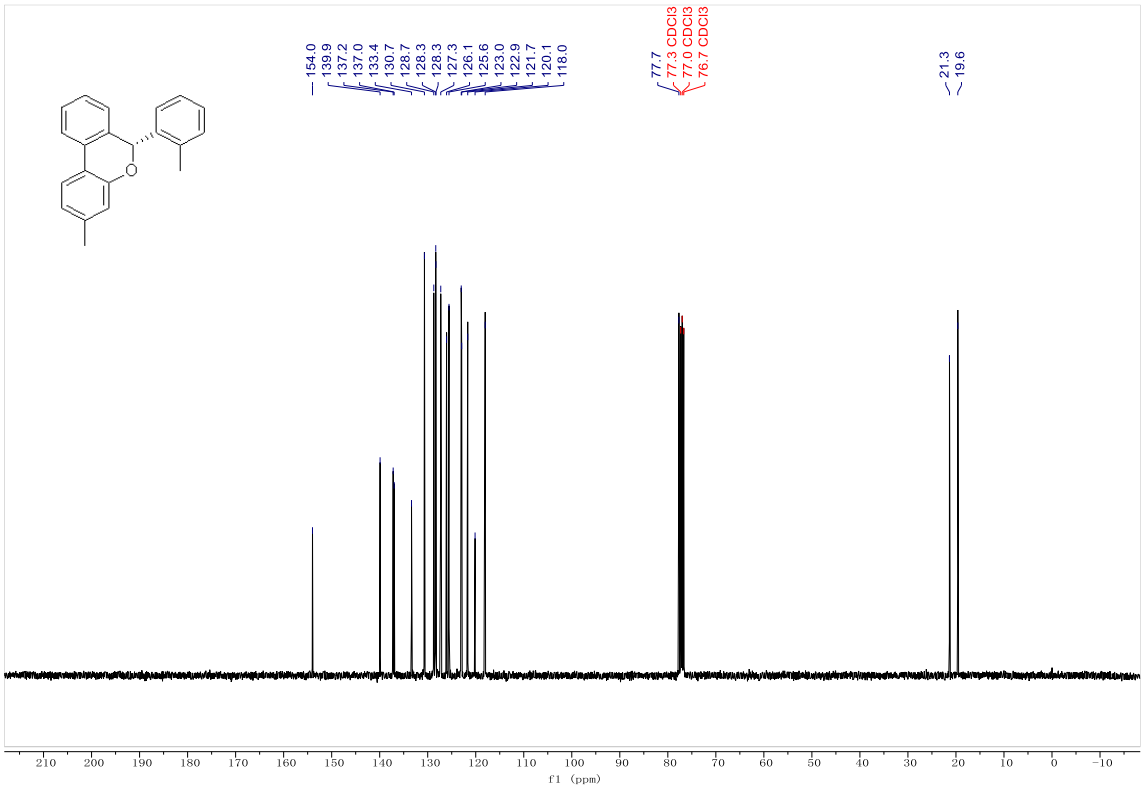
^{13}C NMR of 2k (101 MHz, Chloroform-*d*)



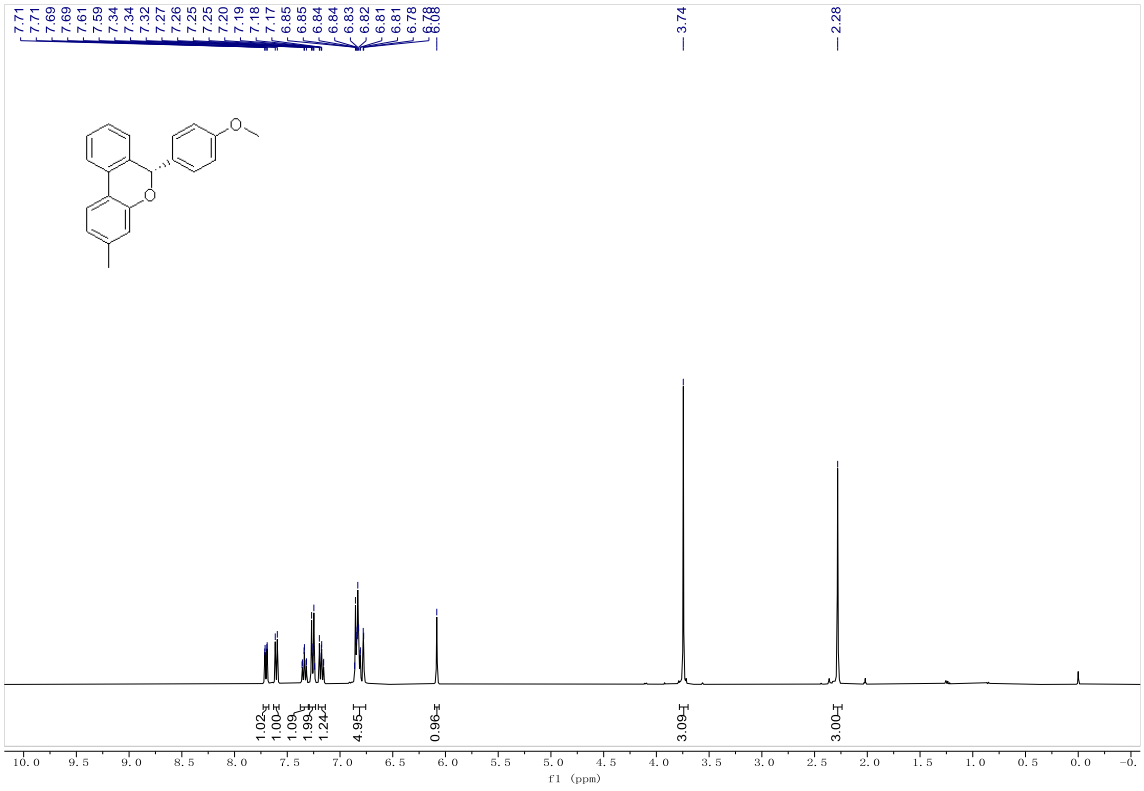
^{1}H NMR of 2l (400 MHz, Chloroform-*d*)



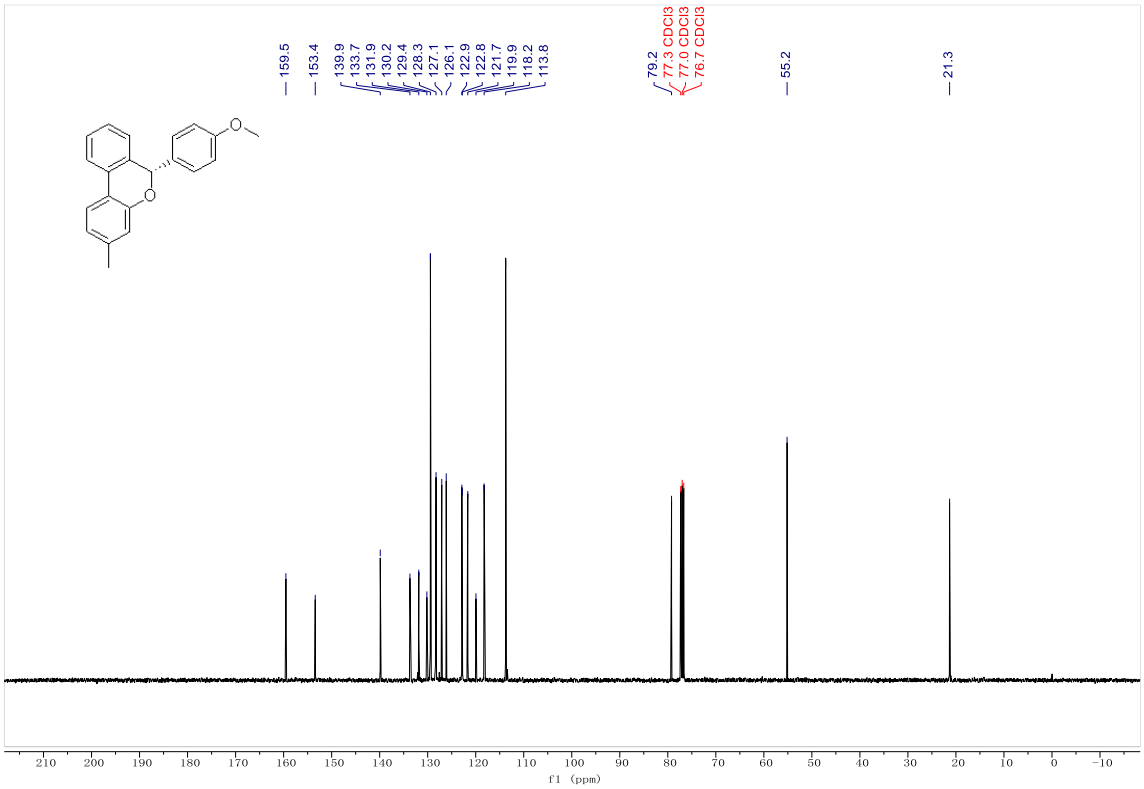
^{13}C NMR of 2l (101 MHz, Chloroform-*d*)



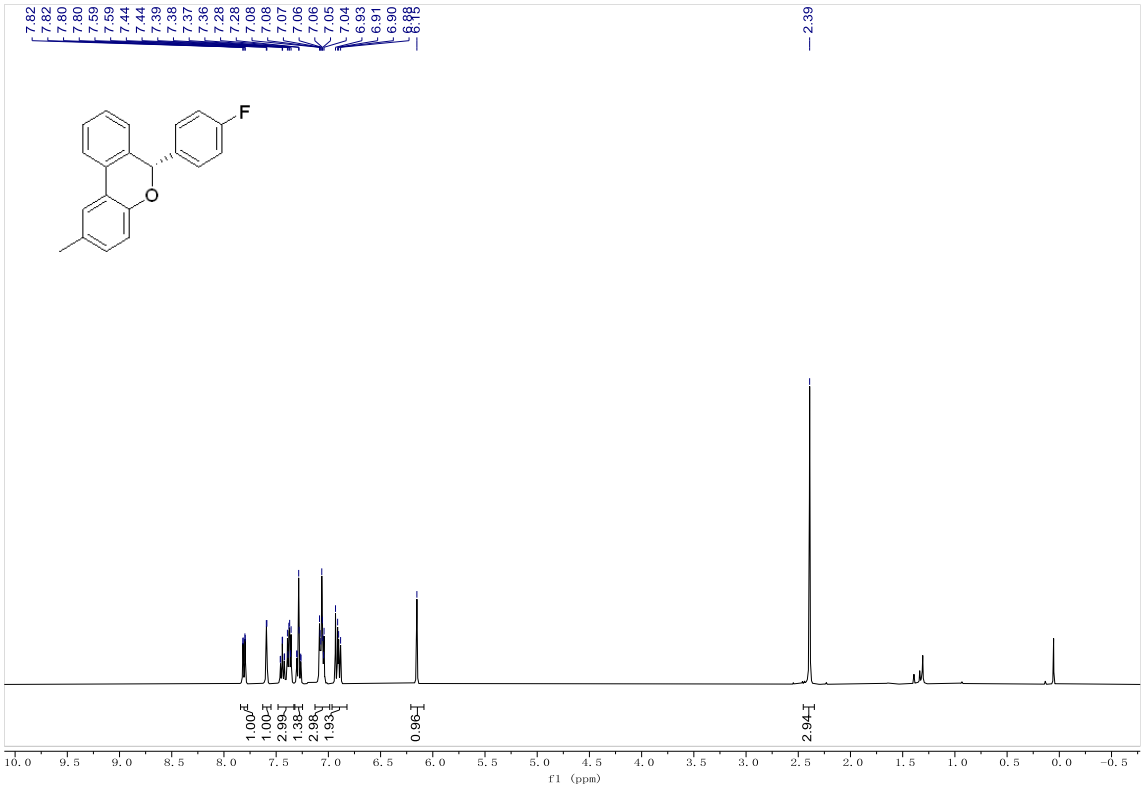
^{1}H NMR of 2i (400 MHz, Chloroform-*d*)



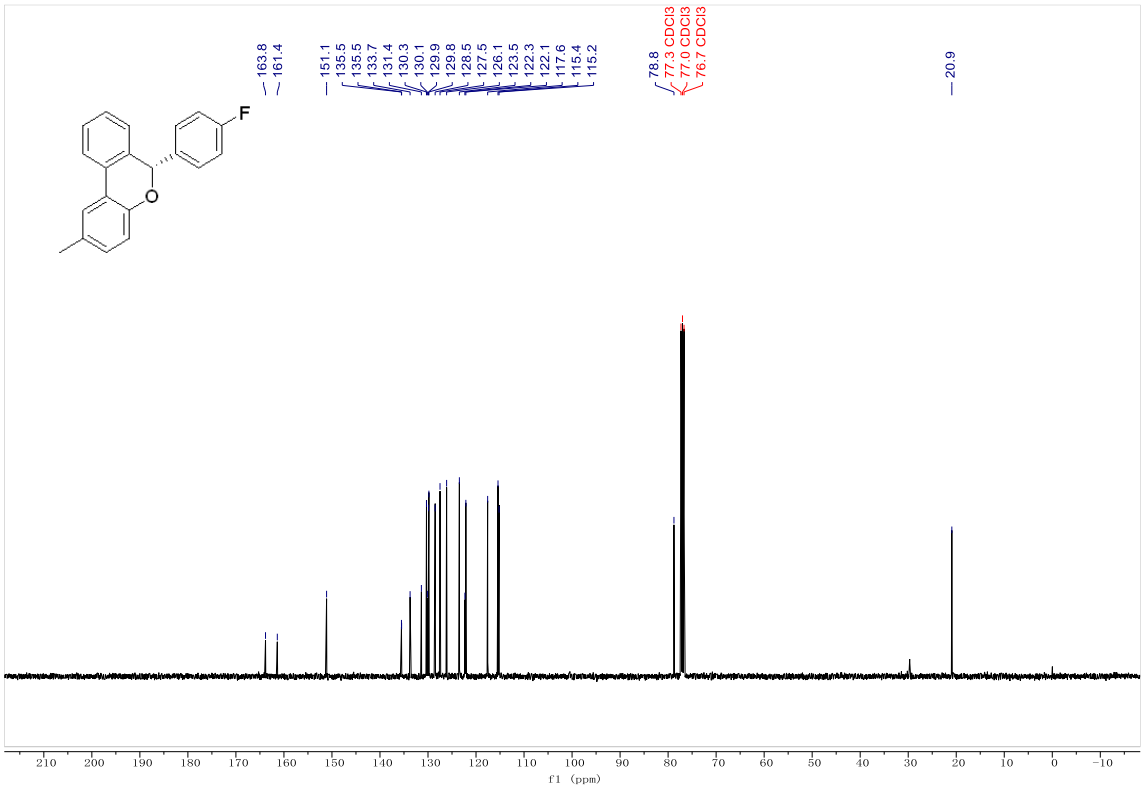
^{13}C NMR of 2i (101 MHz, Chloroform-*d*)



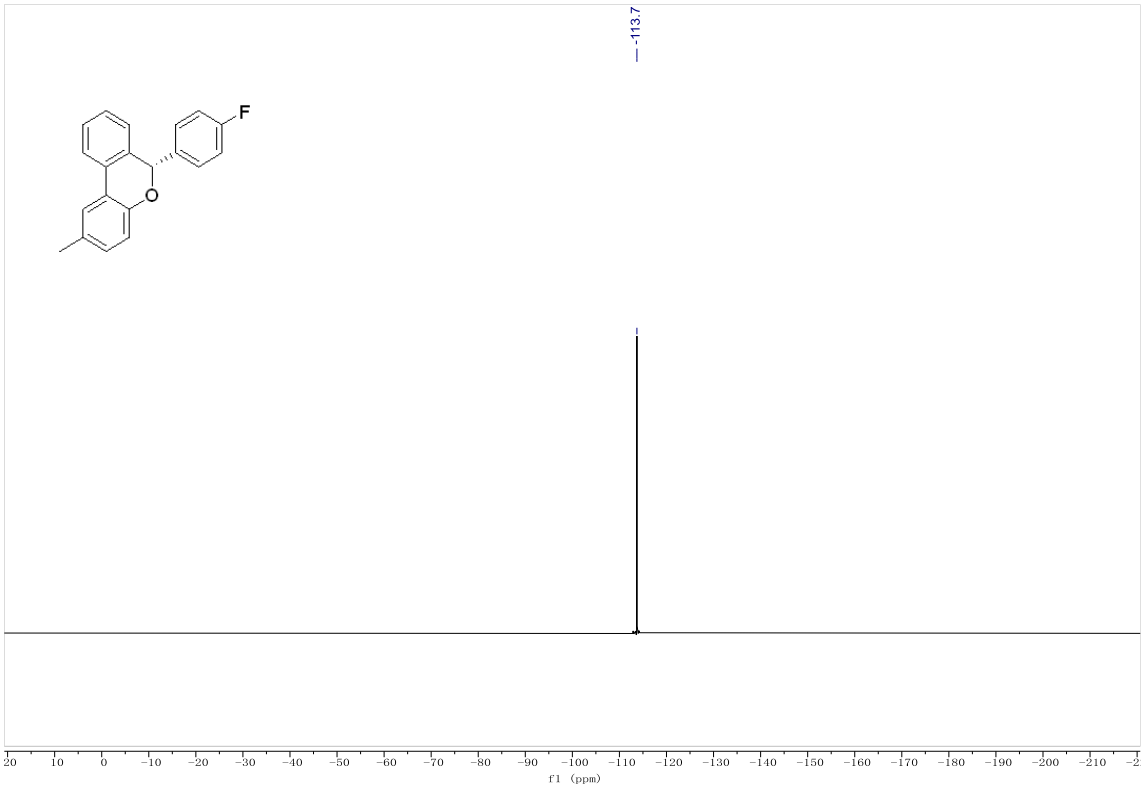
^{1}H NMR of 2j (400 MHz, Chloroform-*d*)



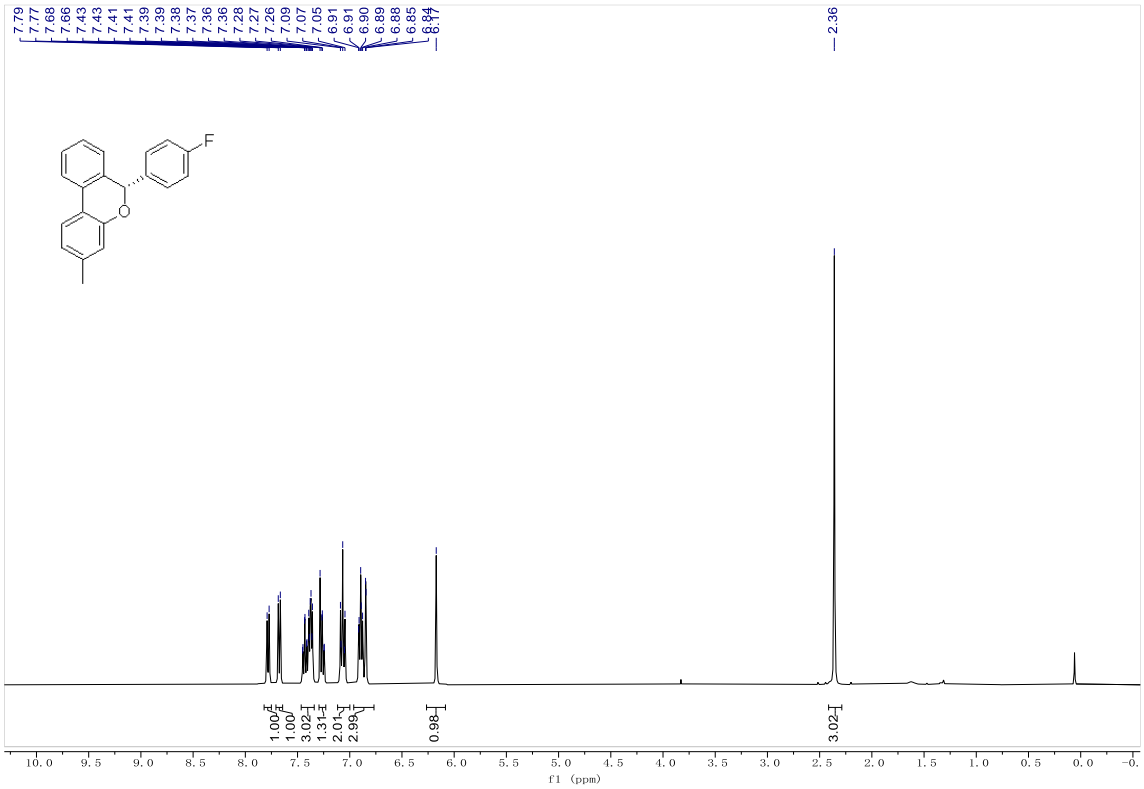
^{13}C NMR of 2j (101 MHz, Chloroform-*d*)



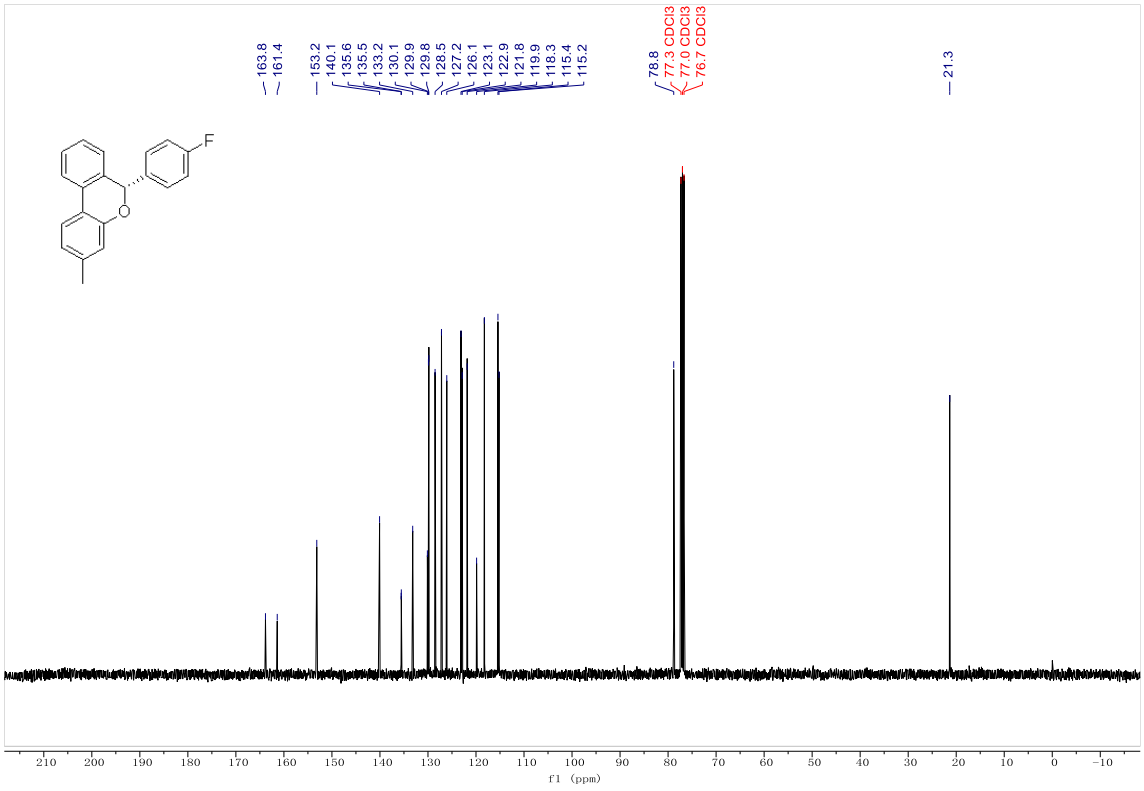
^{19}F NMR of 2j (400 MHz, Chloroform-*d*)



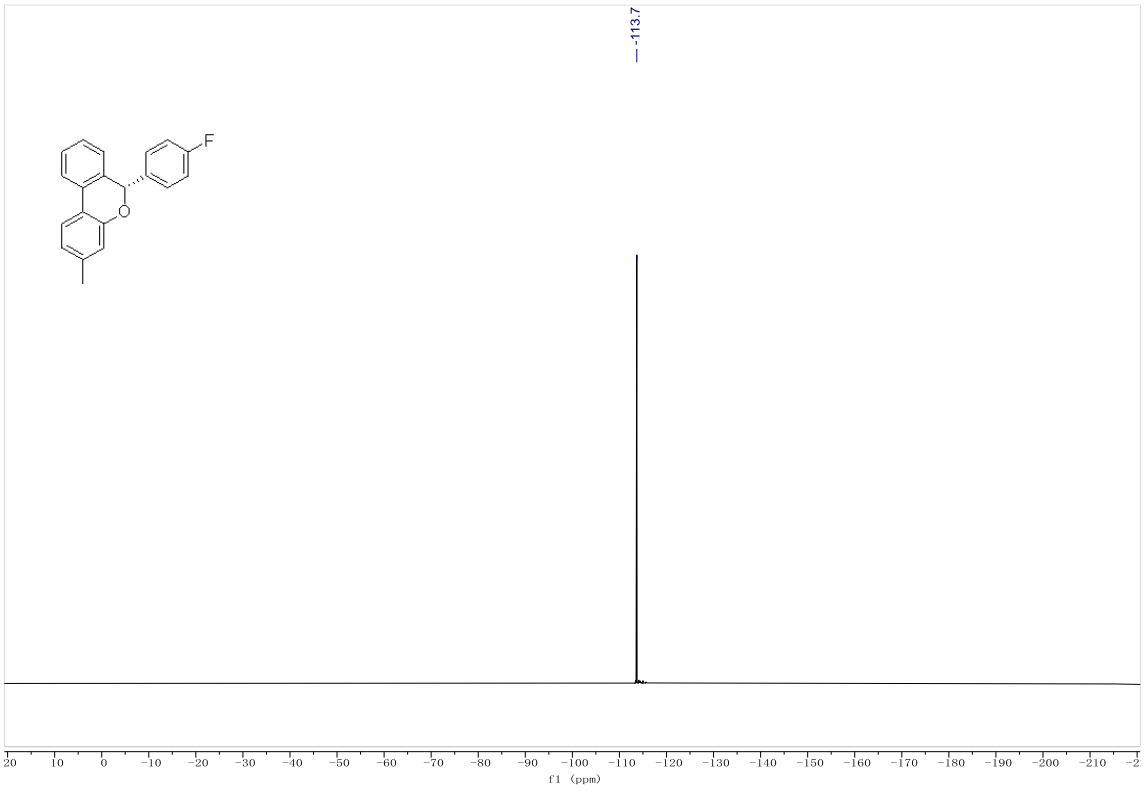
^{1}H NMR of 2i (400 MHz, Chloroform-*d*)



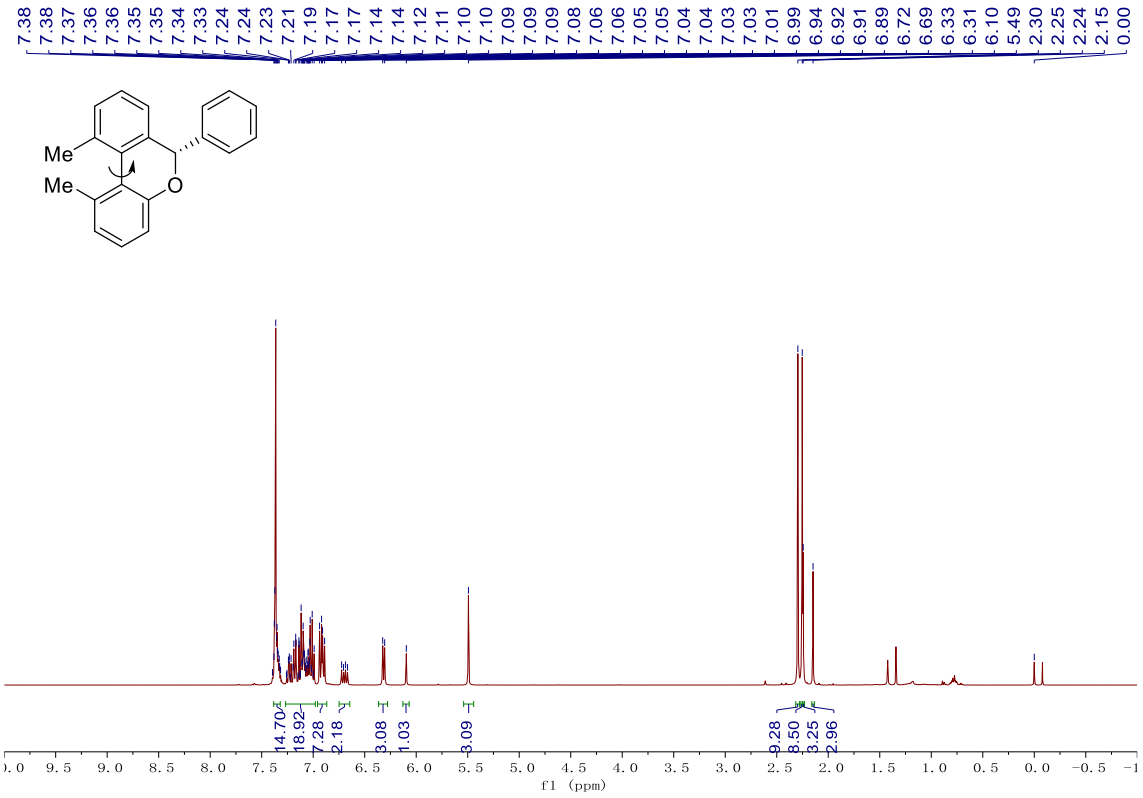
^{13}C NMR of 2i (101 MHz, Chloroform-*d*)



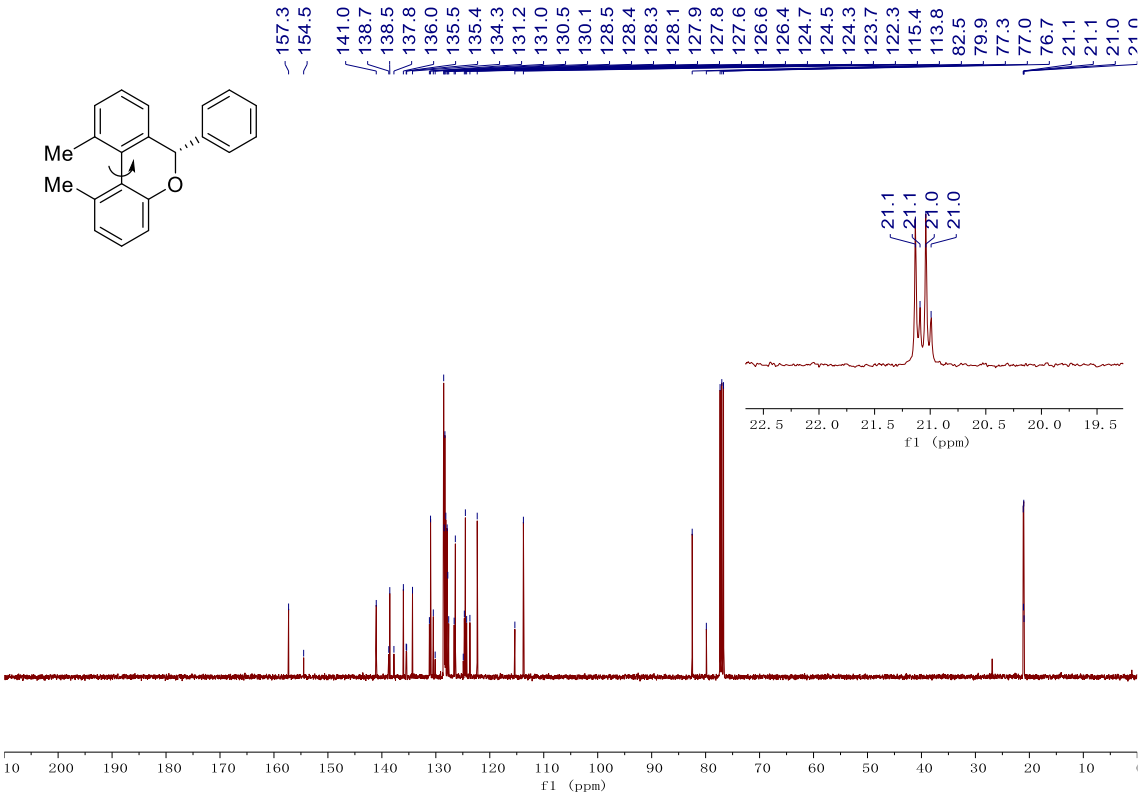
^{19}F NMR of 2a (400 MHz, Chloroform-*d*)



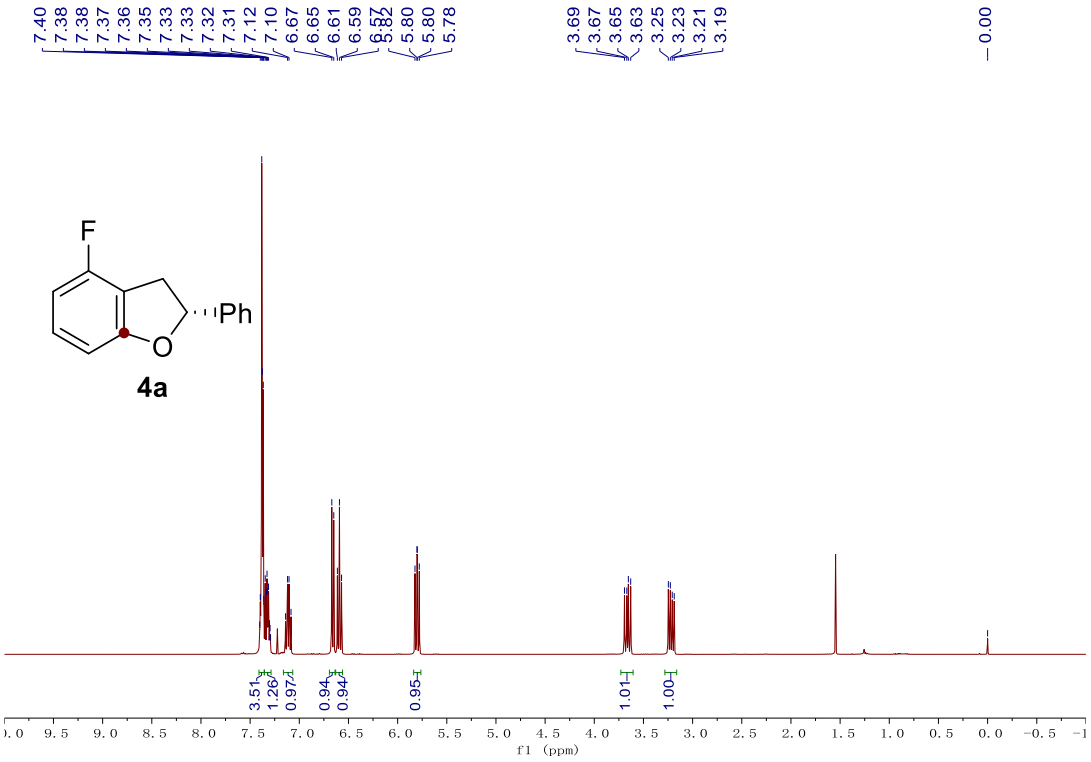
^{1}H NMR (400 MHz, $CDCl_3$) of **2p**



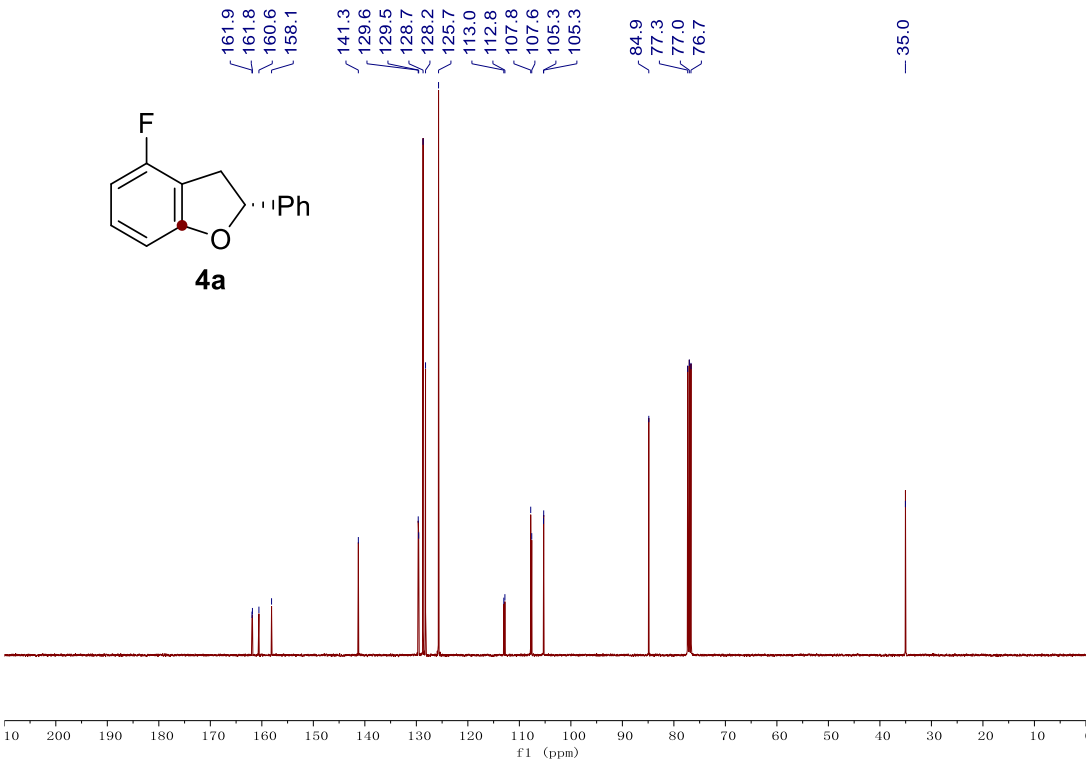
^{13}C NMR (100 MHz, $CDCl_3$) of **2p**



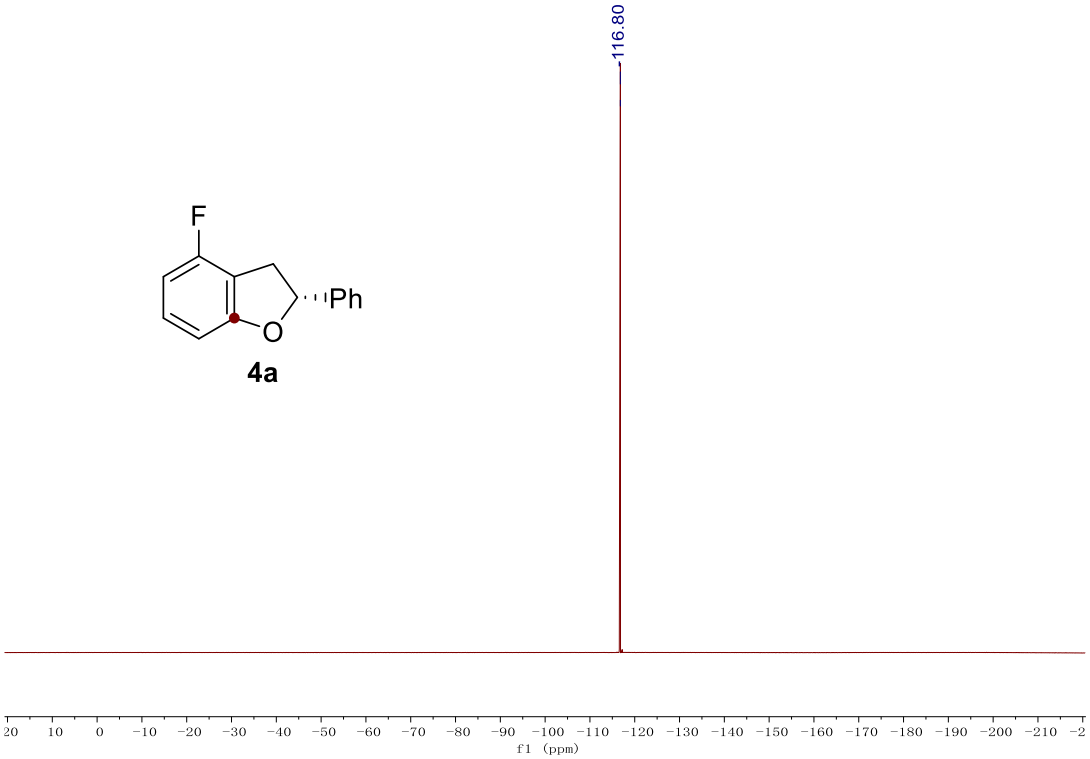
^{1}H NMR (400 MHz, $CDCl_3$) of **4a**



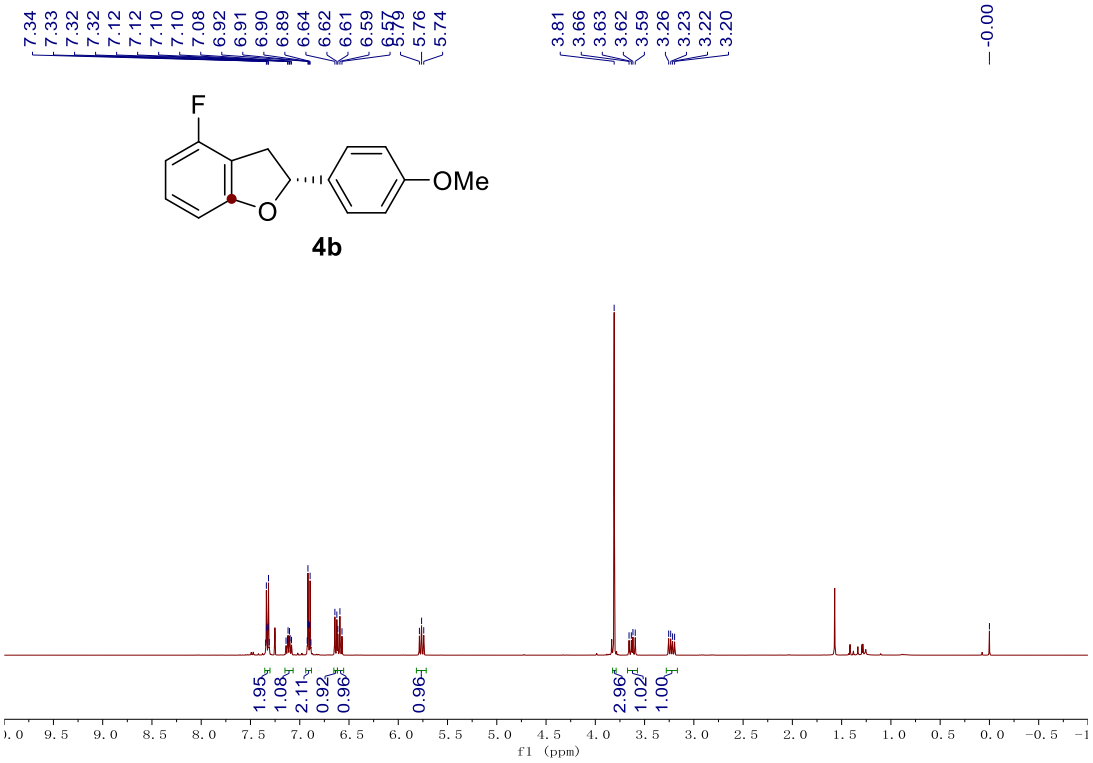
^{13}C NMR (100 MHz, $CDCl_3$) of **4a**



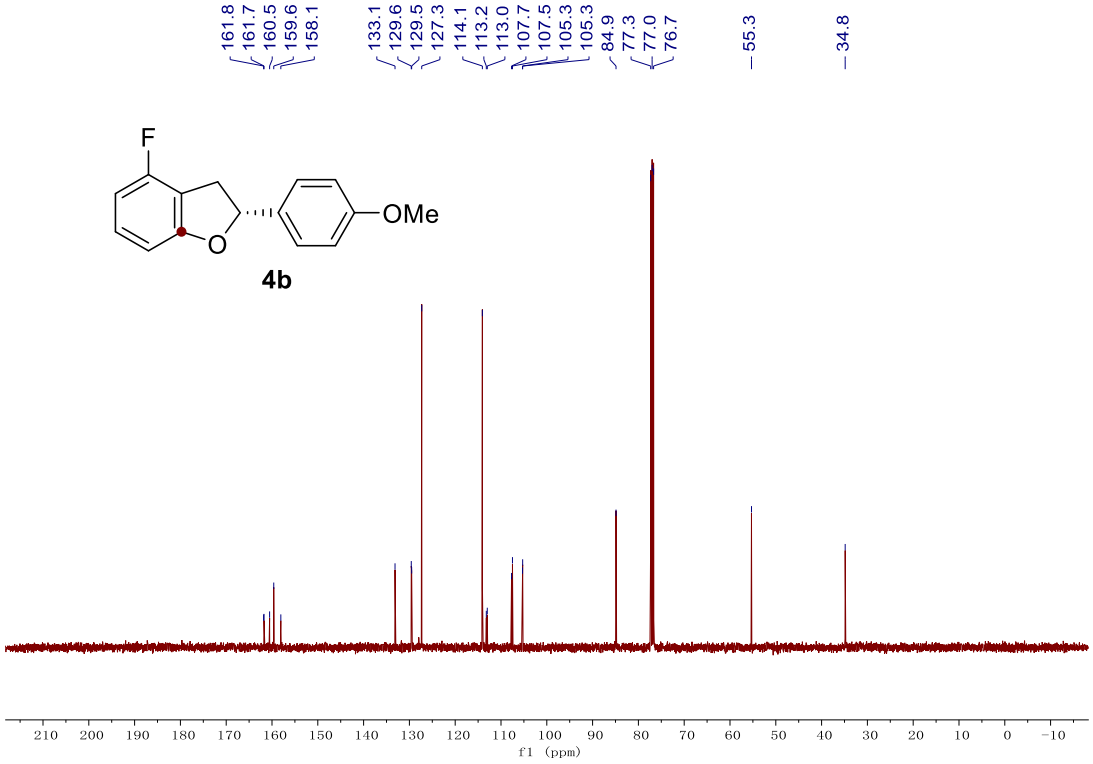
^{19}F NMR (376 MHz, $CDCl_3$) spectra of **4a**



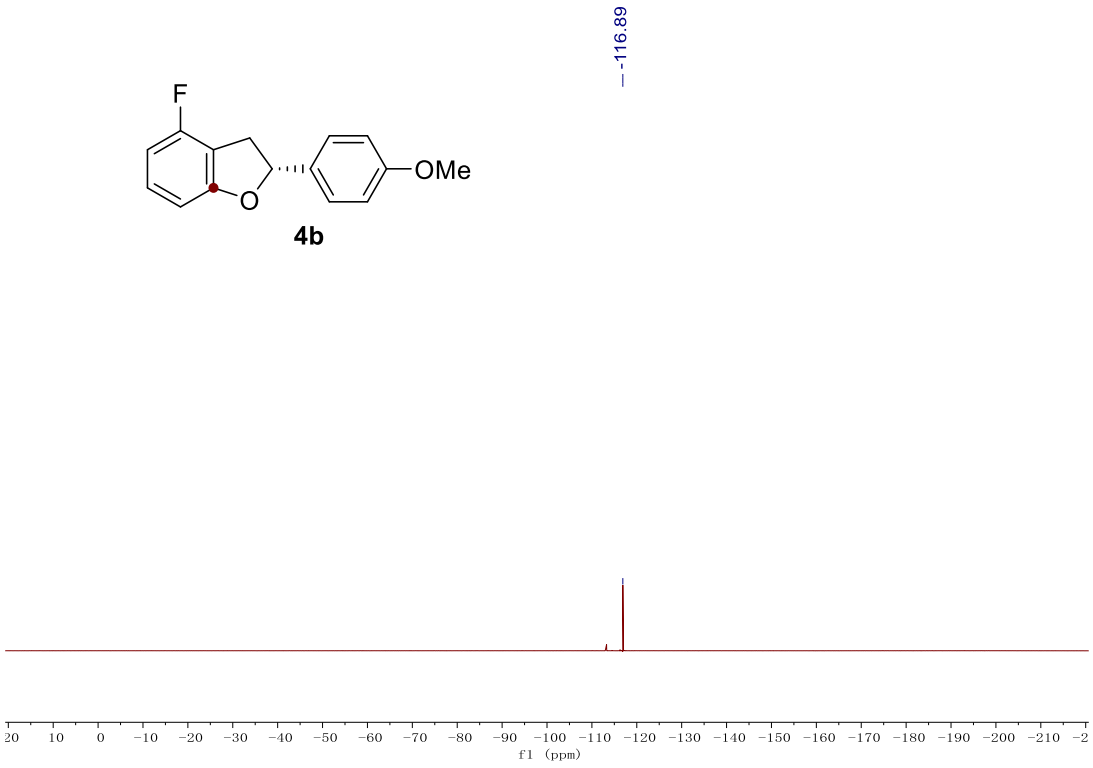
^{1}H NMR (400 MHz, $CDCl_3$) of **4b**



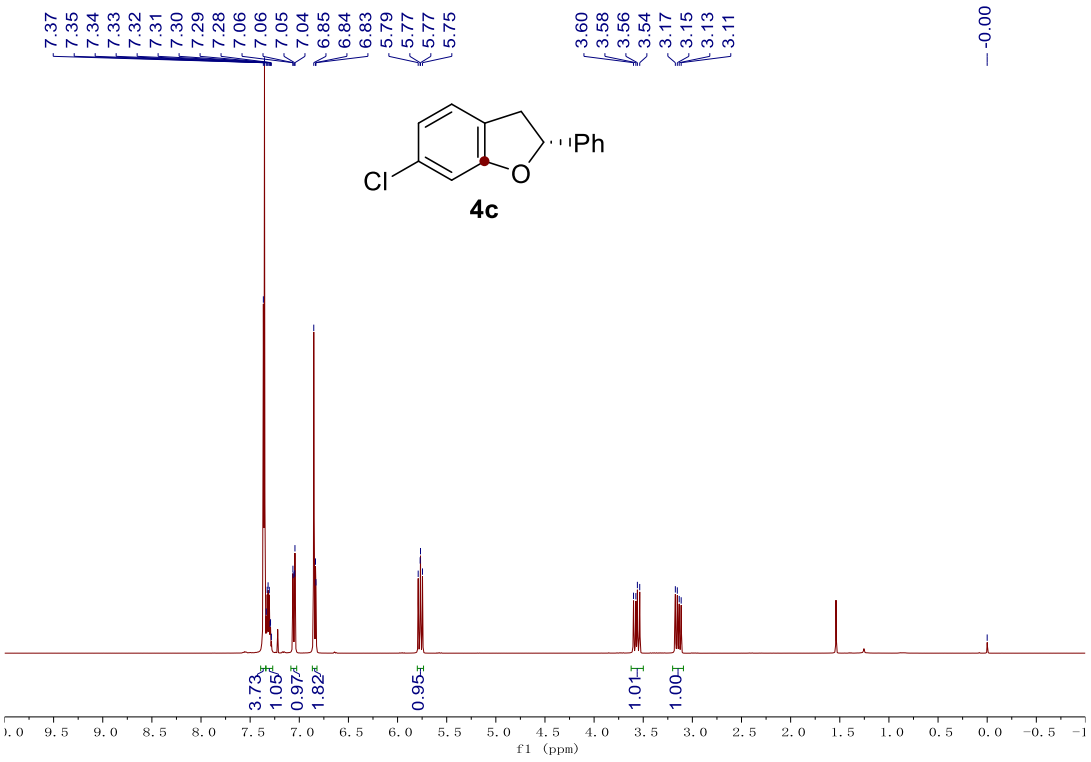
^{13}C NMR (100 MHz, $CDCl_3$) of **4b**



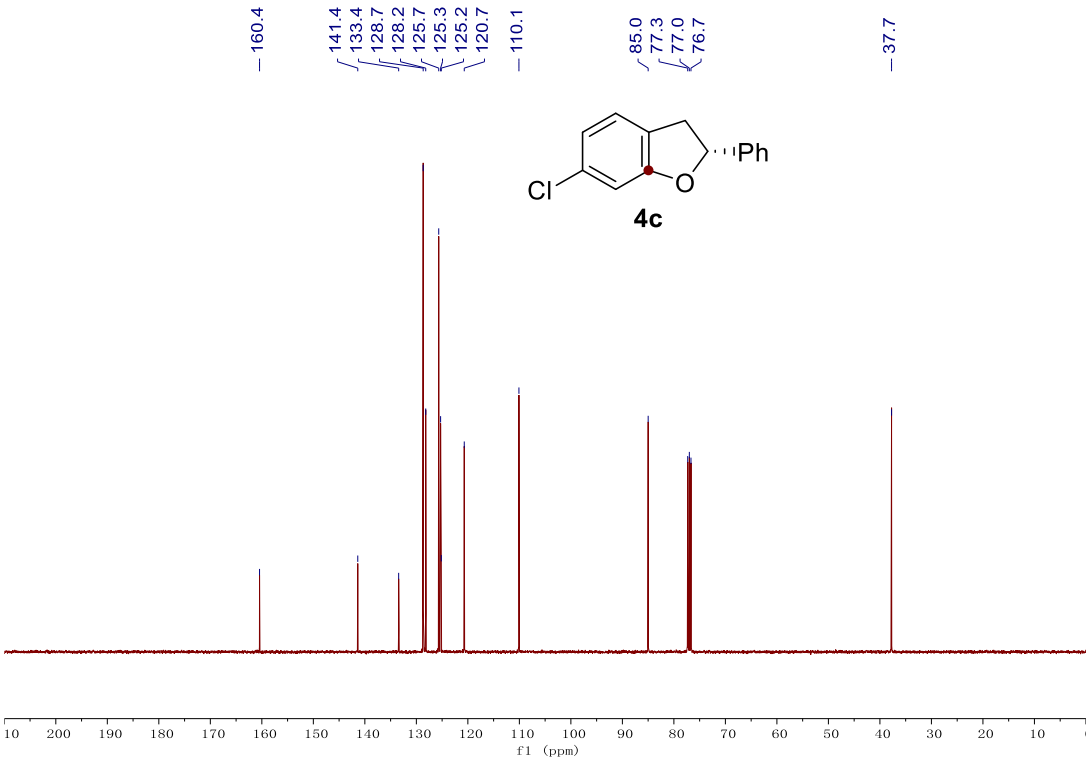
^{19}F NMR (376 MHz, $CDCl_3$) spectra of product **4b**



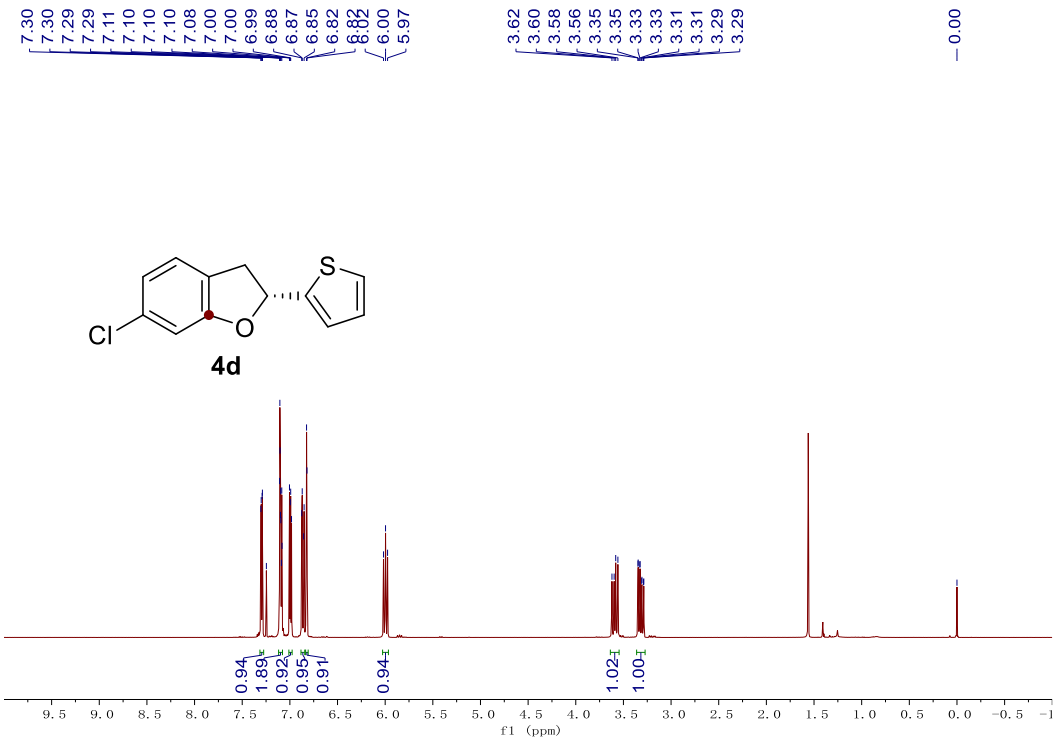
^{1}H NMR (400 MHz, $CDCl_3$) of **4c**



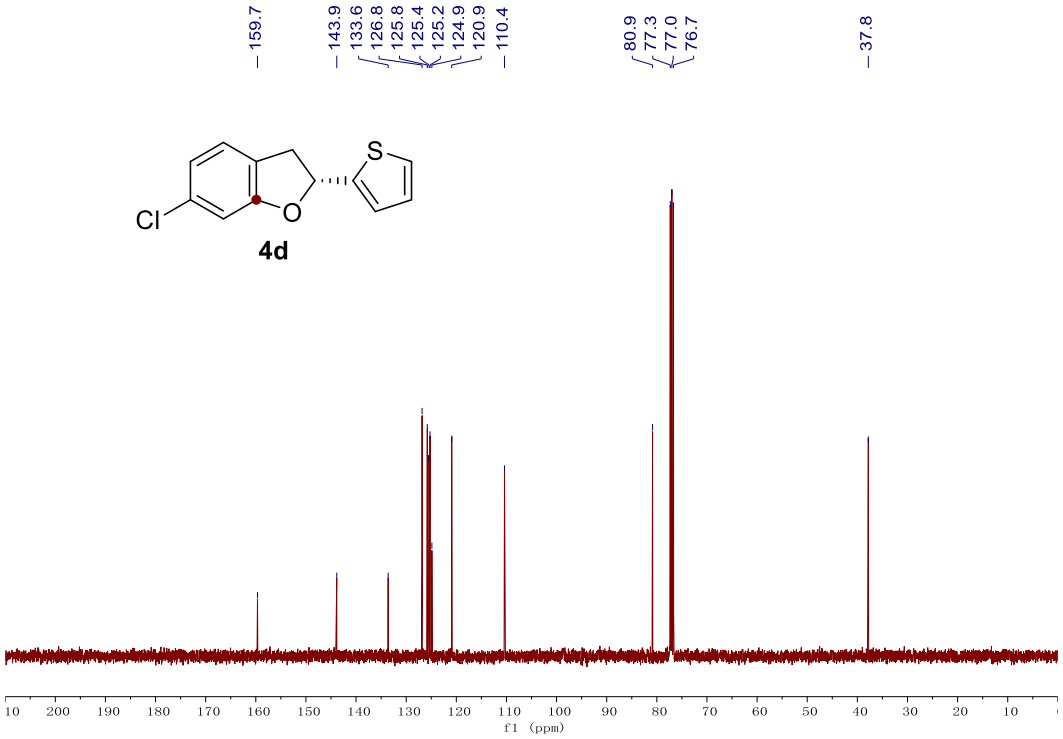
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **4c**



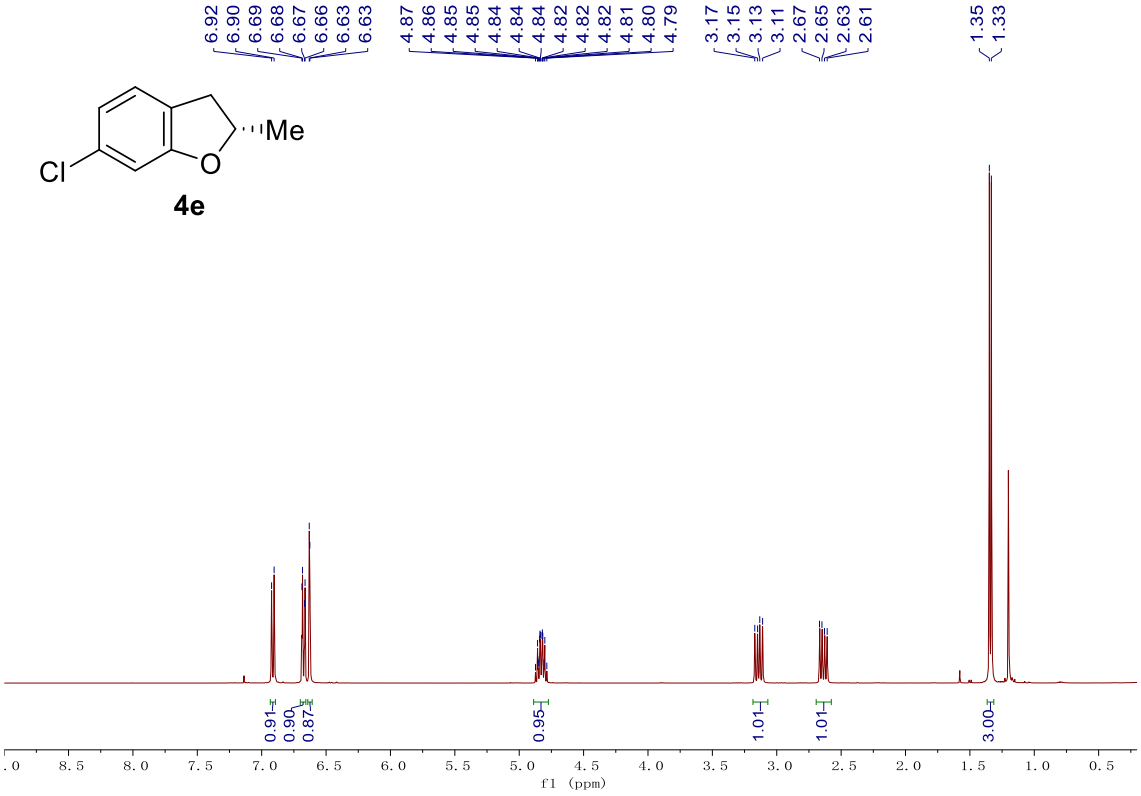
^{1}H NMR (400 MHz, $CDCl_3$) of **4d**



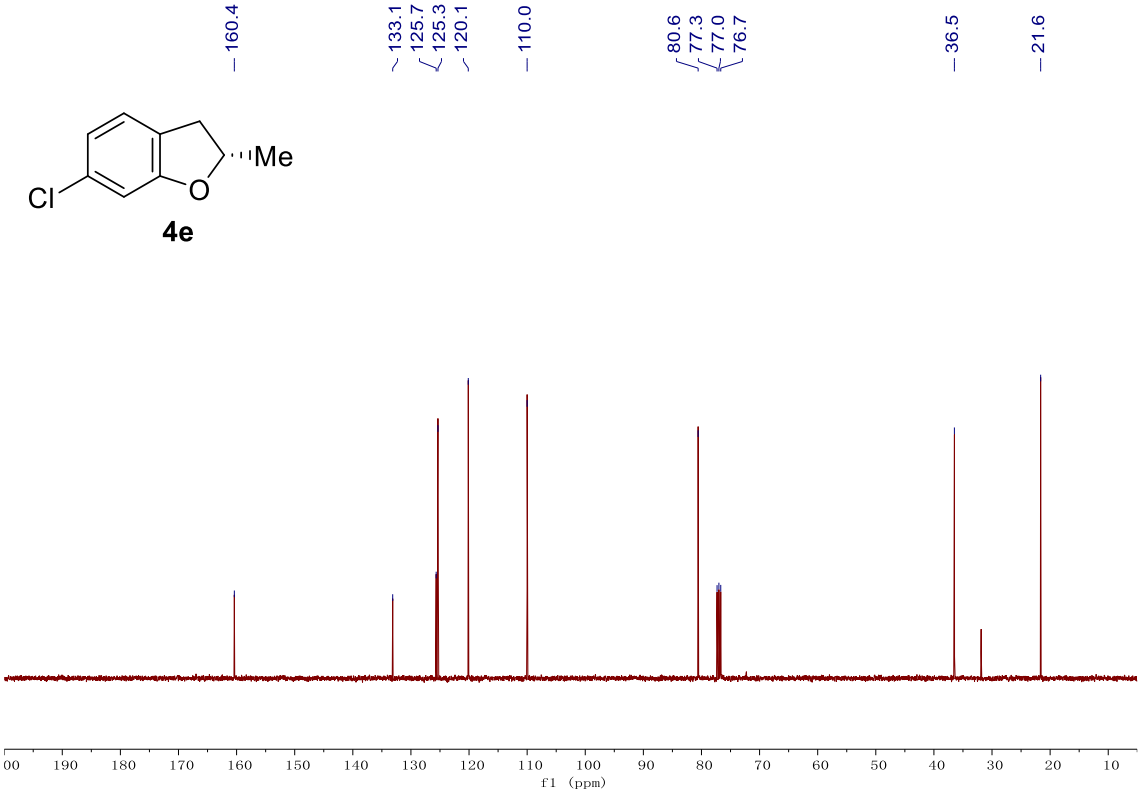
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **4d**



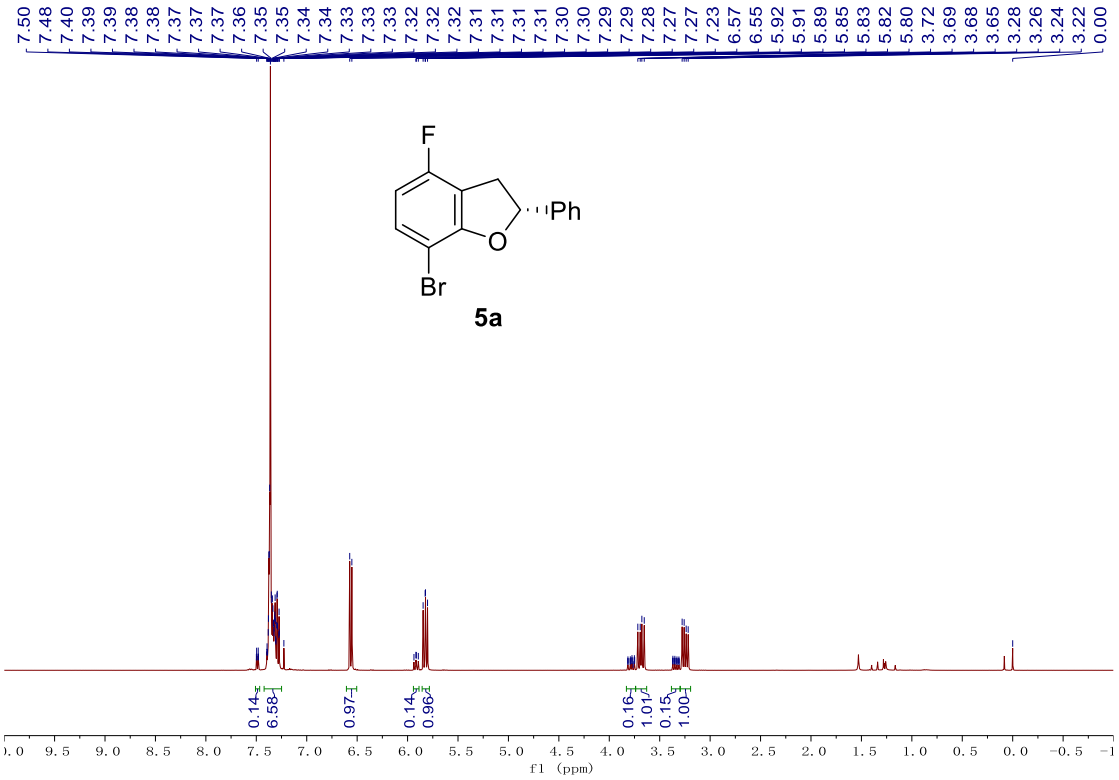
^{1}H NMR (400 MHz, $CDCl_3$) of **4e**



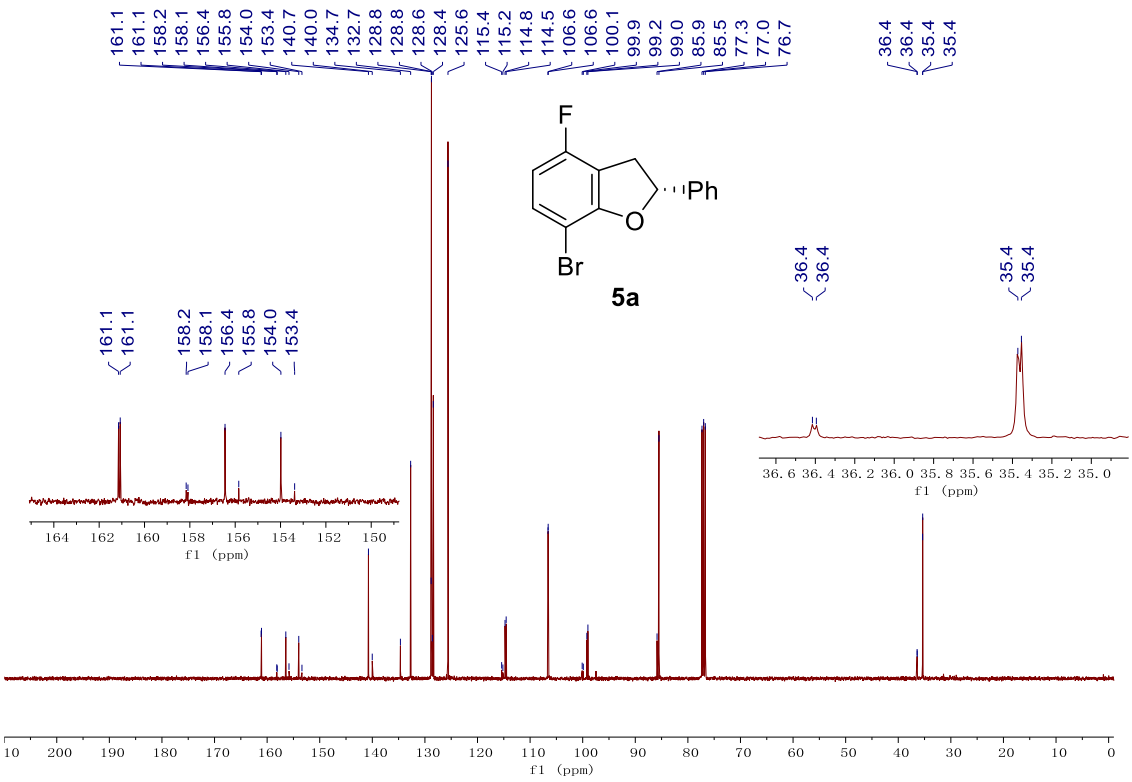
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **4e**



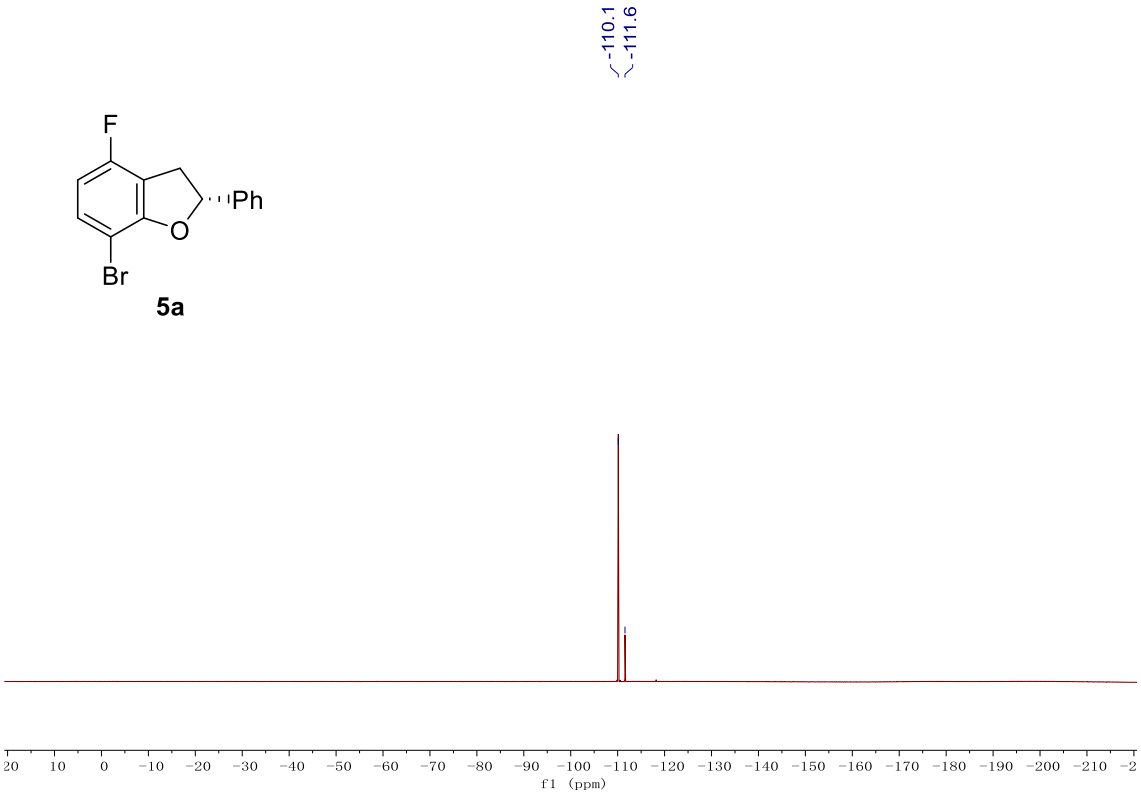
^{1}H NMR (400 MHz, $CDCl_3$) of **5a**



^{13}C NMR (400 MHz, $CDCl_3$) of **5a**

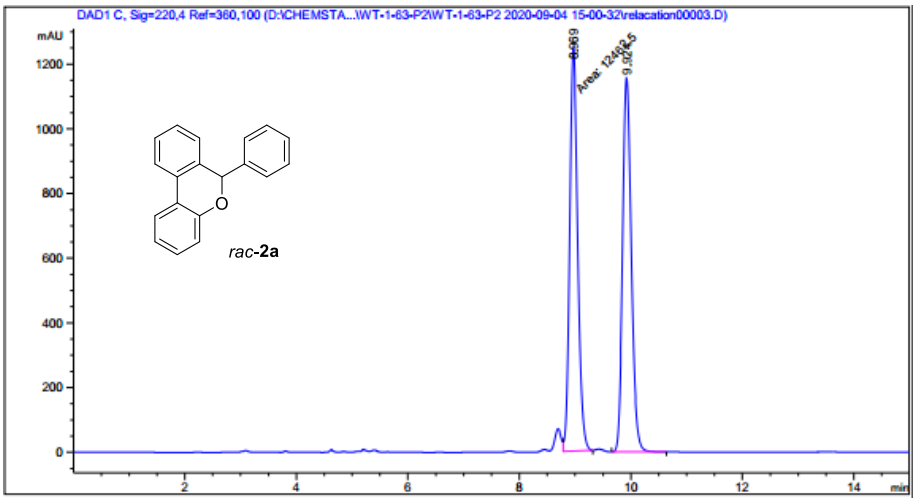


^{19}F NMR (400 MHz, $CDCl_3$) of **5a**



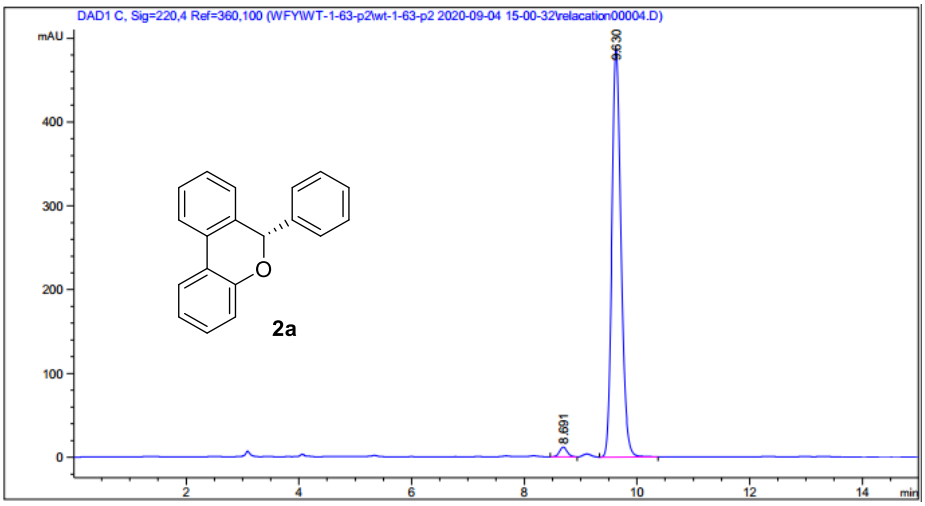
6. HPLC Spectra of the Products

HPLC spectra of **2a**



Signal 1: DAD1 C, Sig=220,4 Ref=360,100

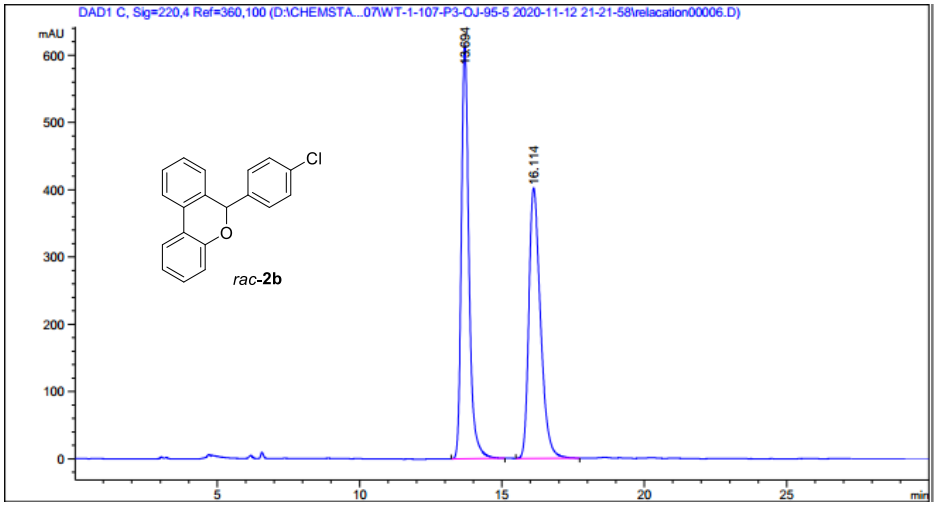
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.969	FM	0.1669	1.24625e4	1244.70911	49.9398
2	9.924	BB	0.1660	1.24926e4	1156.89917	50.0602



Signal 1: DAD1 C, Sig=220,4 Ref=360,100

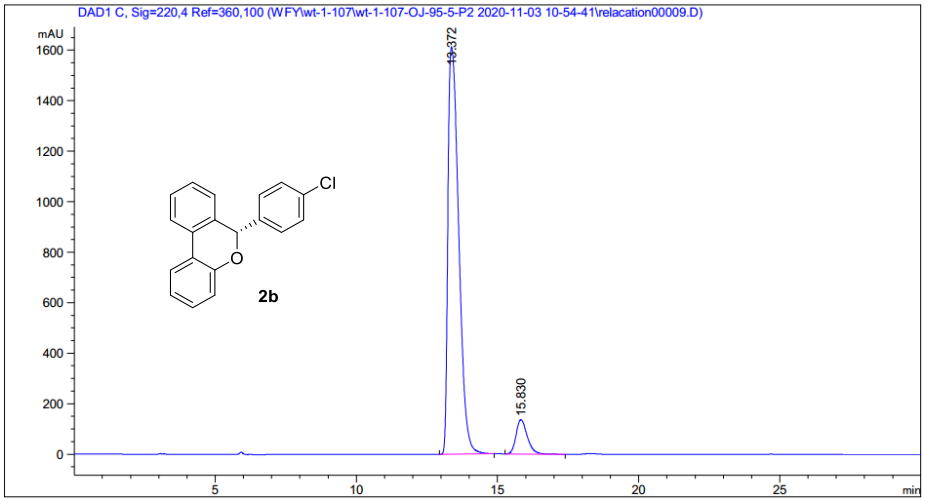
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.691	BV	0.1495	114.63356	11.78438	2.0500
2	9.630	BB	0.1735	5477.12744	486.02441	97.9500

HPLC spectra of **2b**



Signal 1: DAD1 C, Sig=220,4 Ref=360,100

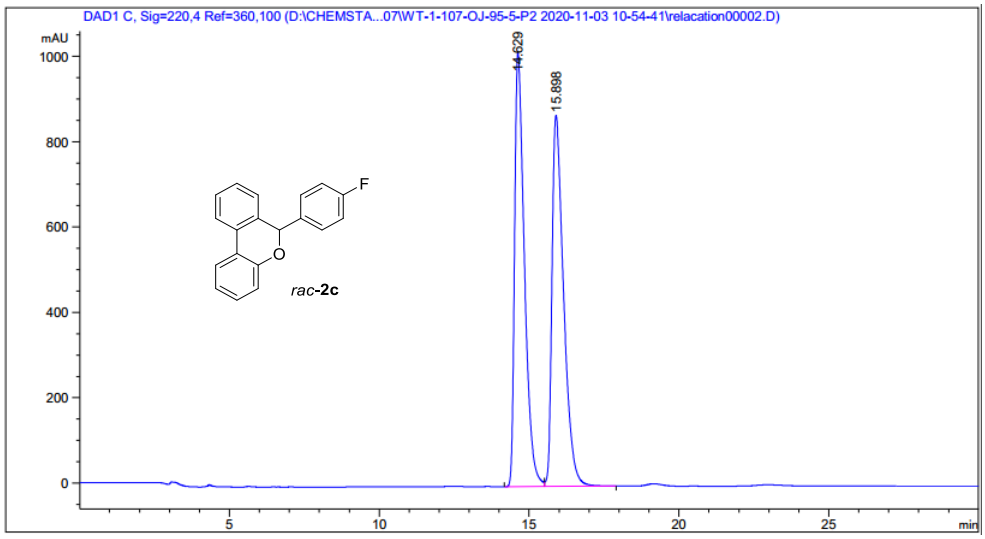
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.694	BB	0.2837	1.14168e4	611.70081	50.0571
2	16.114	BB	0.4347	1.13907e4	401.86435	49.9429



Signal 1: DAD1 C, Sig=220,4 Ref=360,100

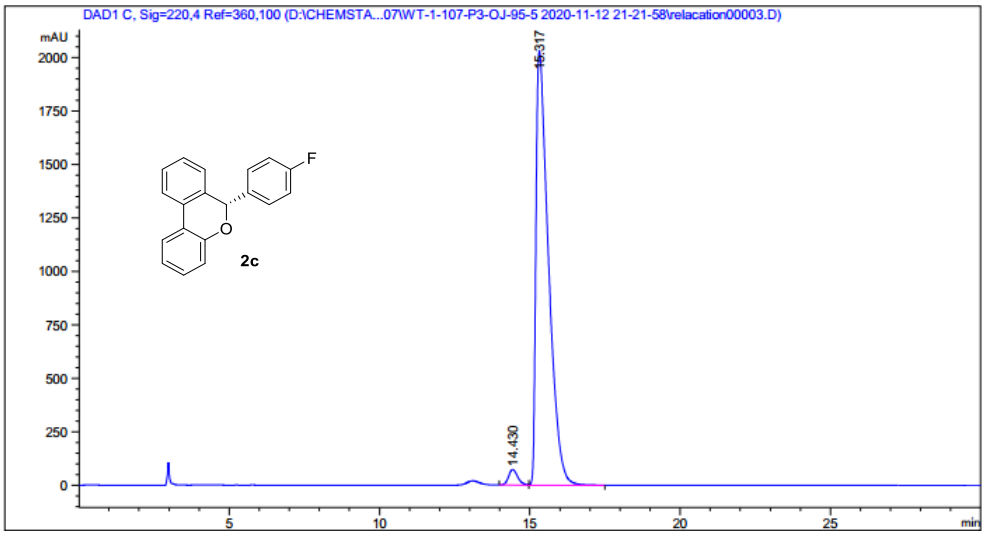
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.372	BB	0.4235	4.27678e4	1612.35168	91.9195
2	15.830	BB	0.4220	3759.62305	136.21463	8.0805

HPLC spectra of **2c**



Signal 1: DAD1 C, Sig=220,4 Ref=360,100

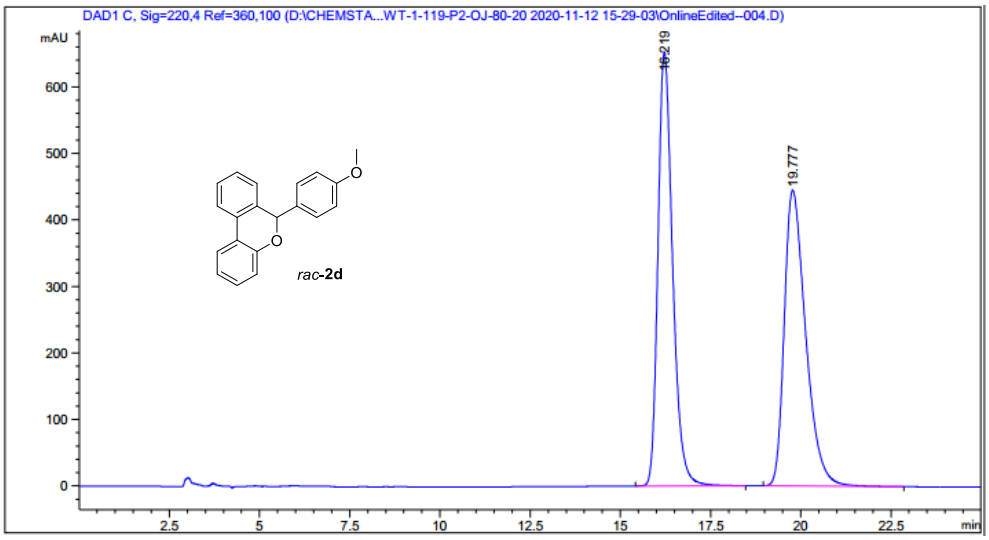
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.629	BV	0.3447	2.32466e4	1016.93384	49.8552
2	15.898	VB	0.4057	2.33816e4	869.68231	50.1448



Signal 1: DAD1 C, Sig=220,4 Ref=360,100

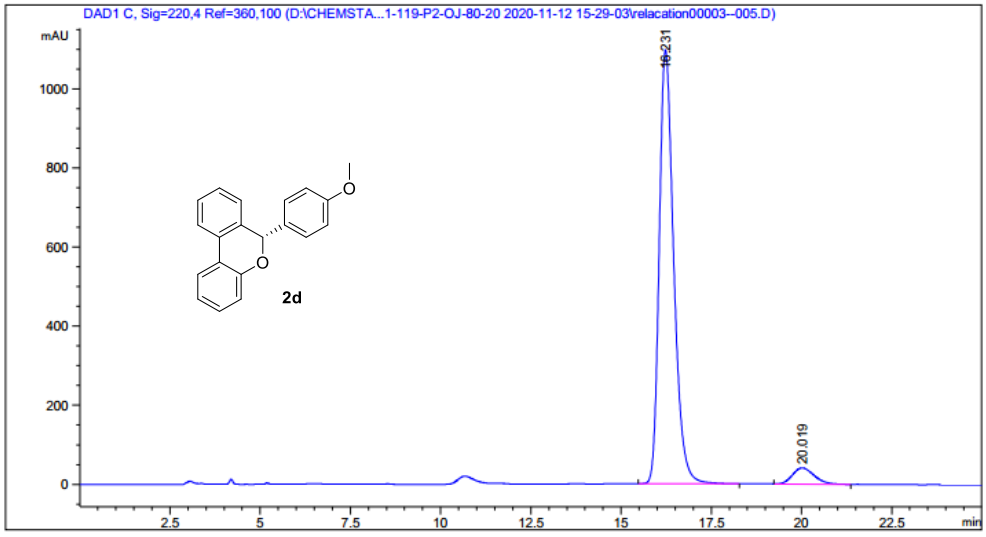
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.430	BV	0.3263	1543.90784	72.53063	2.5681
2	15.317	VB	0.4345	5.85745e4	2030.53772	97.4319

HPLC spectra of **2d**



Signal 1: DAD1 C, Sig=220,4 Ref=360,100

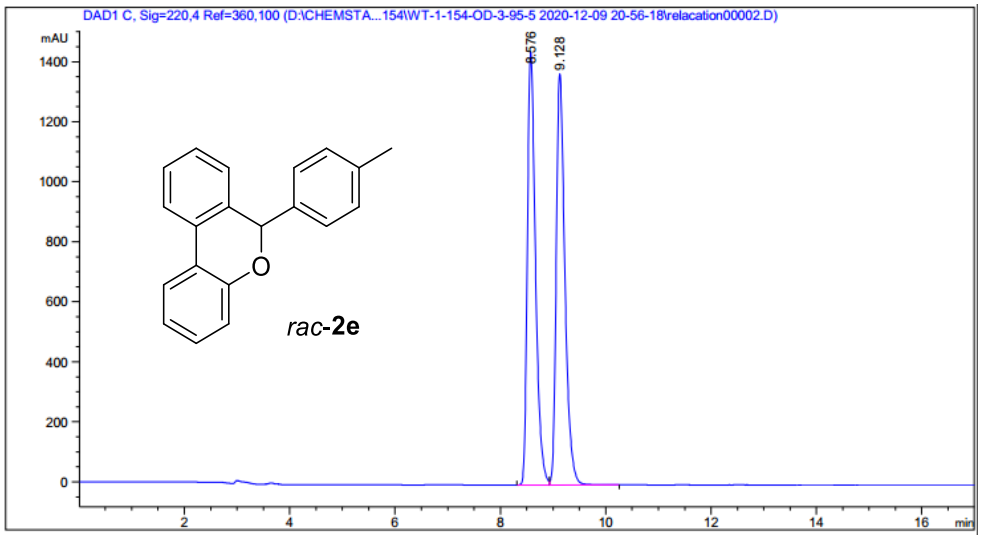
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.219	BB	0.4301	1.83458e4	652.30231	50.0650
2	19.777	BB	0.6302	1.82982e4	444.58417	49.9350



Signal 1: DAD1 C, Sig=220,4 Ref=360,100

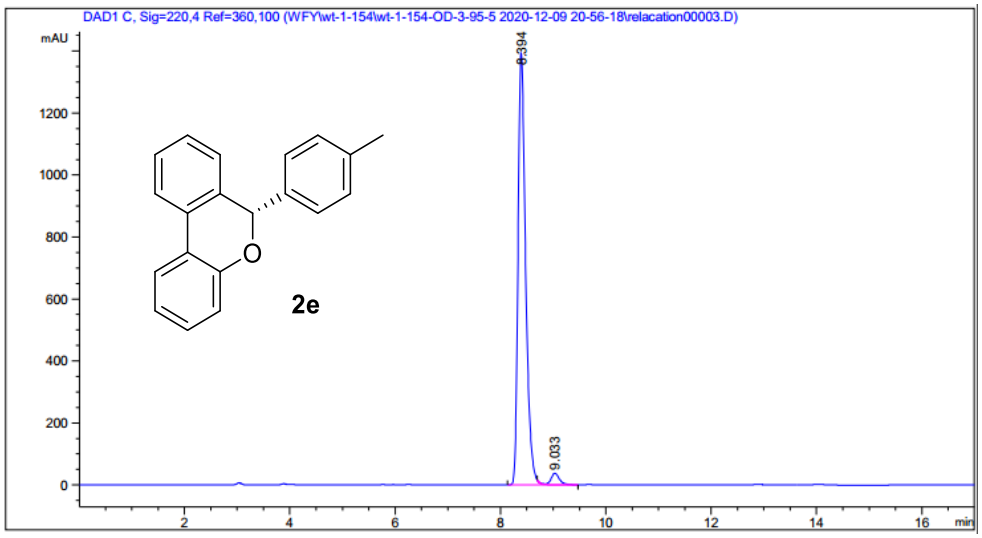
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.231	BB	0.4266	3.05123e4	1096.71619	94.6973
2	20.019	BB	0.6381	1708.56909	41.00250	5.3027

HPLC spectra of **2e**



Signal 1: DAD1 C, Sig=220,4 Ref=360,100

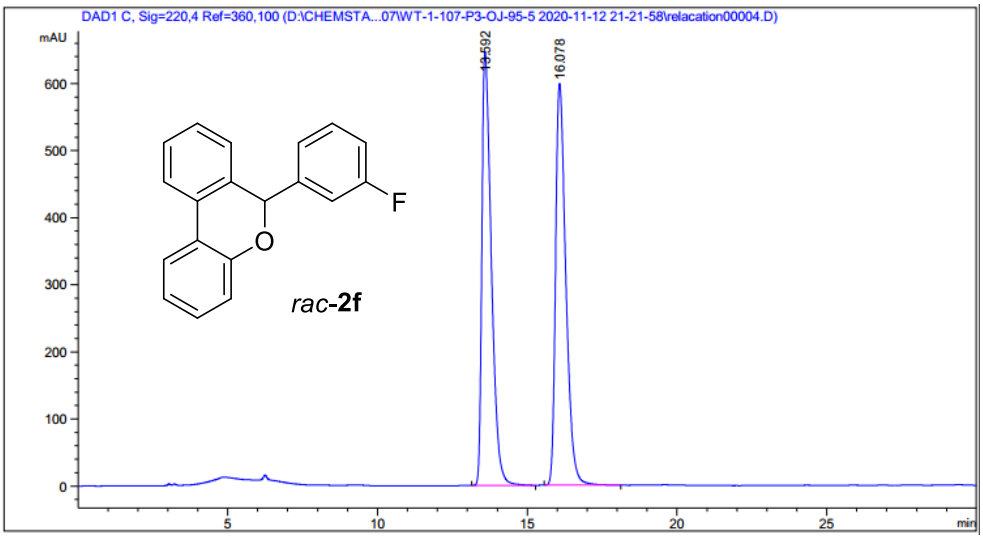
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.576	BV	0.1652	1.54951e4	1443.85791	49.7183
2	9.128	VB	0.1735	1.56707e4	1369.66626	50.2817



Signal 1: DAD1 C, Sig=220,4 Ref=360,100

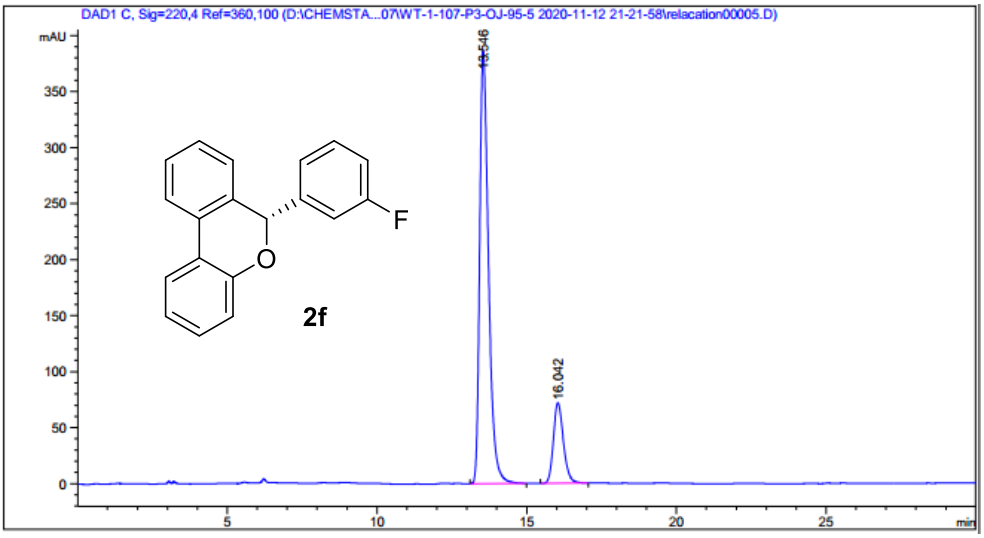
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.394	BV R	0.1528	1.39576e4	1394.38110	97.1610
2	9.033	VB E	0.1661	407.84030	37.14923	2.8390

HPLC spectra of **2f**



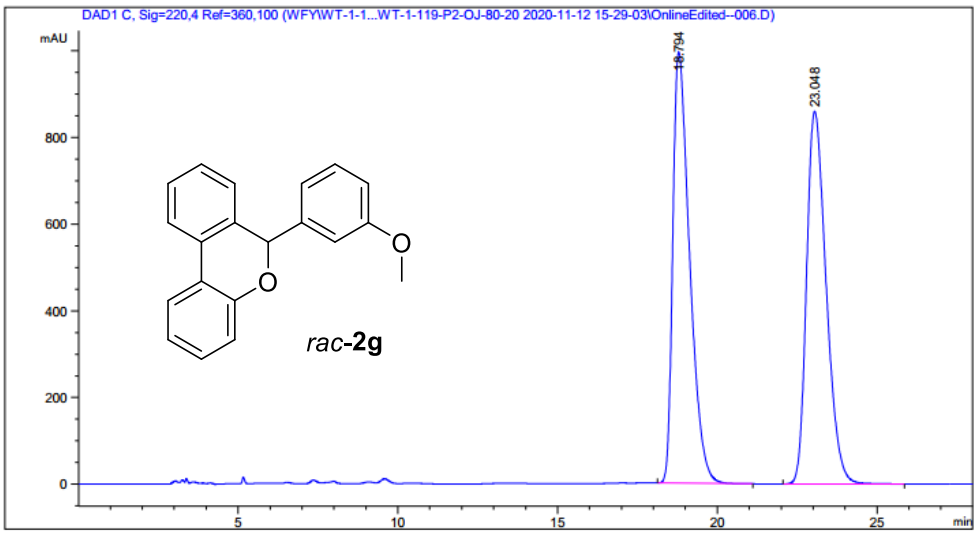
Signal 1: DAD1 C, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.592	BB	0.3364	1.41806e4	645.35284	49.8569
2	16.078	BB	0.3638	1.42620e4	598.89777	50.1431



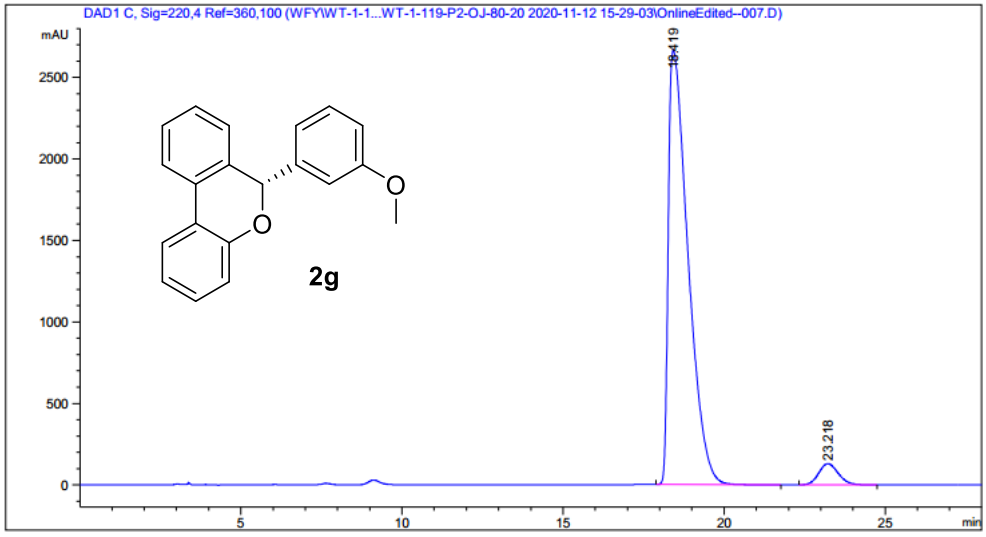
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.546	BB	0.3155	7932.94043	386.37384	82.5976
2	16.042	BB	0.3581	1671.38098	71.66966	17.4024

HPLC spectra of **2g**



Signal 1: DAD1 C, Sig=220,4 Ref=360,100

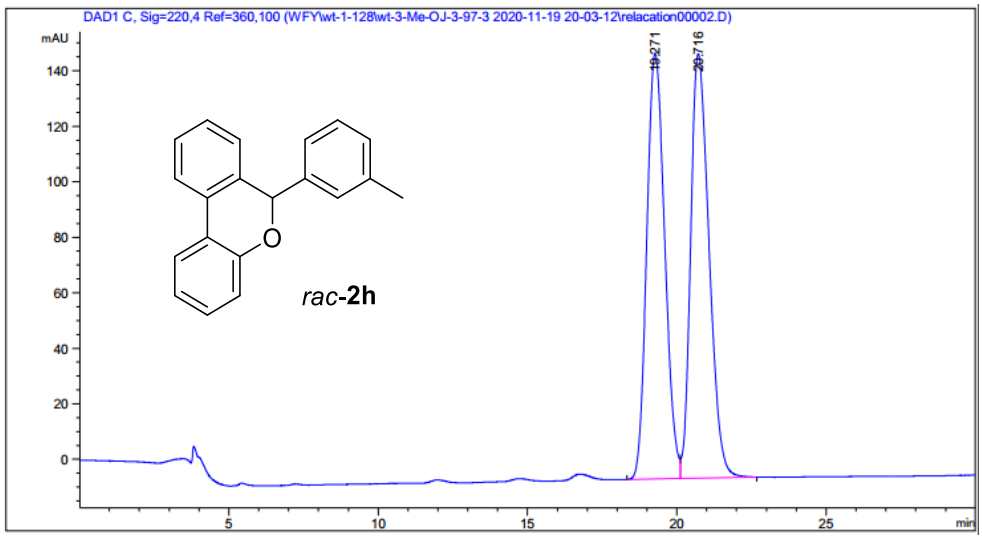
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.794	BB	0.5546	3.63708e4	994.73920	49.8204
2	23.048	BB	0.6547	3.66331e4	860.51050	50.1796



Signal 1: DAD1 C, Sig=220,4 Ref=360,100

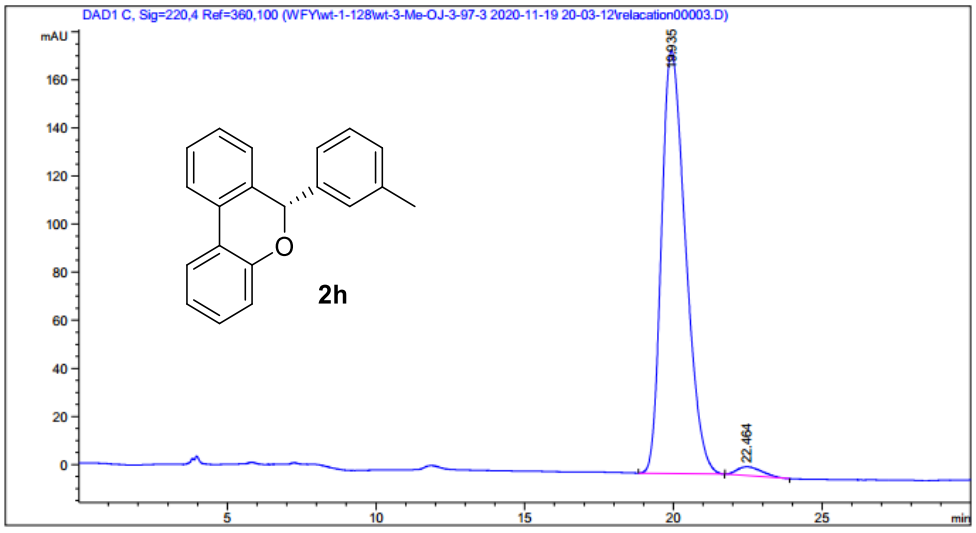
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.419	BB	0.5535	1.12854e5	2667.82666	95.3653
2	23.218	BB	0.6547	5484.62158	129.86960	4.6347

HPLC spectra of **2h**



Signal 1: DAD1 C, Sig=220,4 Ref=360,100

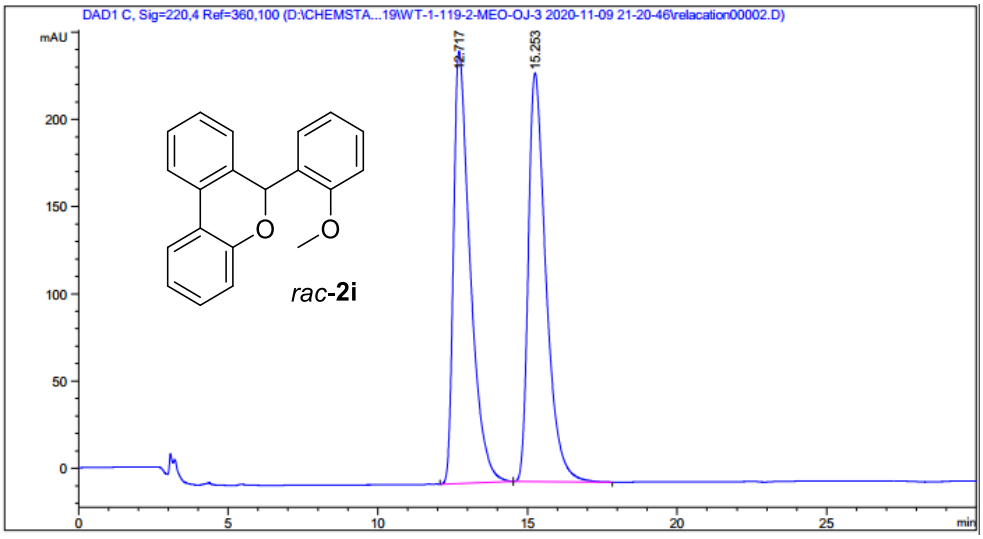
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.271	BV	0.6535	6411.57959	153.44704	49.5396
2	20.716	VB	0.6722	6530.75244	152.93167	50.4604



Signal 1: DAD1 C, Sig=220,4 Ref=360,100

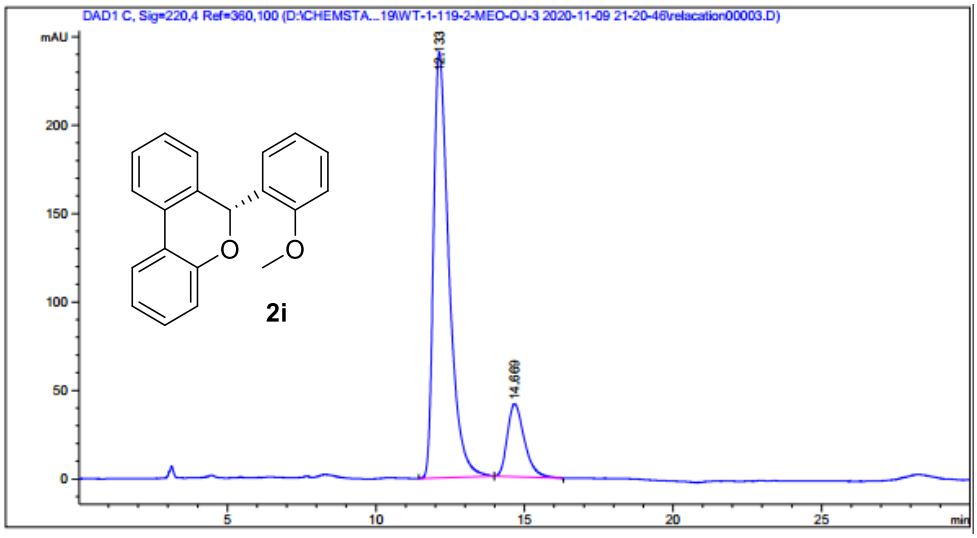
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.935	BB	0.8555	9887.25195	175.96992	97.8407
2	22.464	BB	0.7056	218.21060	3.72423	2.1593

HPLC spectra of **2i**



Signal 1: DAD1 C, Sig=220,4 Ref=360,100

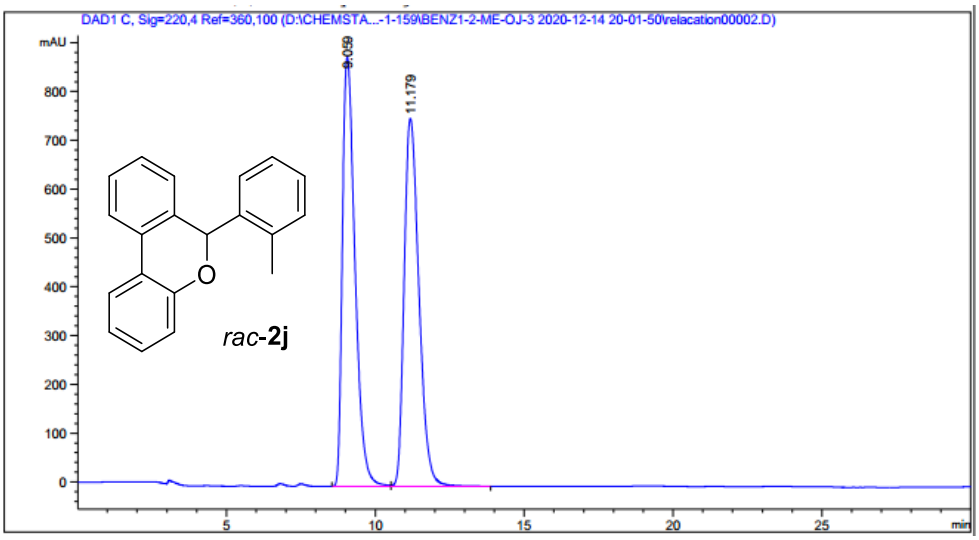
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.717	BB	0.5730	9582.91016	247.88930	49.9819
2	15.253	BB	0.6193	9589.83203	234.39232	50.0181



Signal 1: DAD1 C, Sig=220,4 Ref=360,100

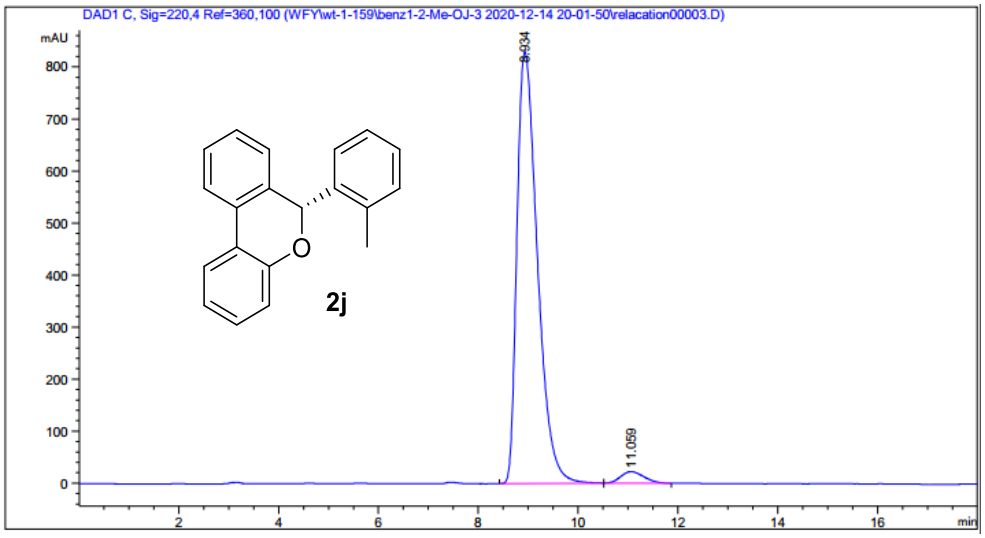
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.133	BB	0.5449	8686.54590	240.76474	84.1266
2	14.669	BB	0.6059	1639.01331	41.21609	15.8734

HPLC spectra of **2j**



Signal 1: DAD1 C, Sig=220,4 Ref=360,100

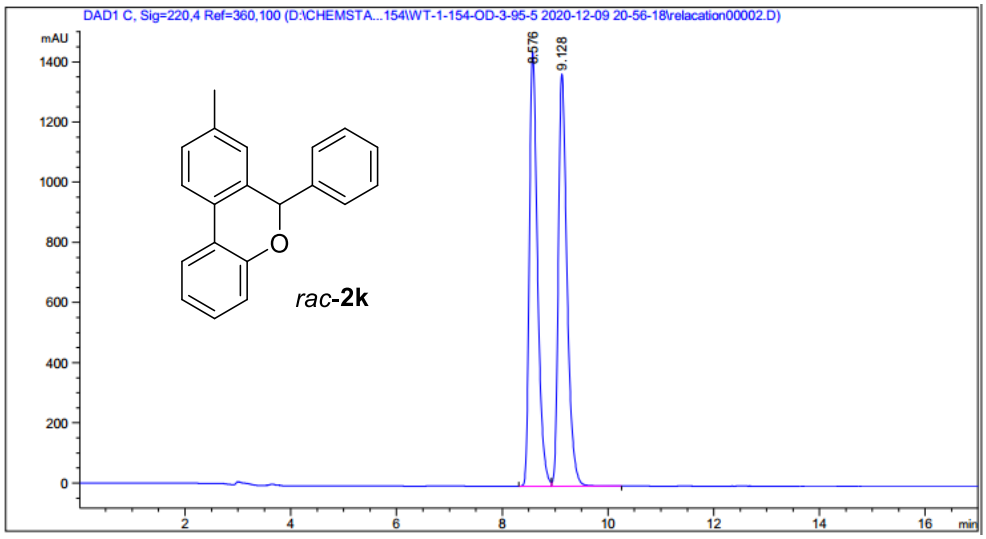
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.059	BV	0.4568	2.58529e4	879.91907	49.8954
2	11.179	VB	0.5379	2.59614e4	753.54535	50.1046



Signal 1: DAD1 C, Sig=220,4 Ref=360,100

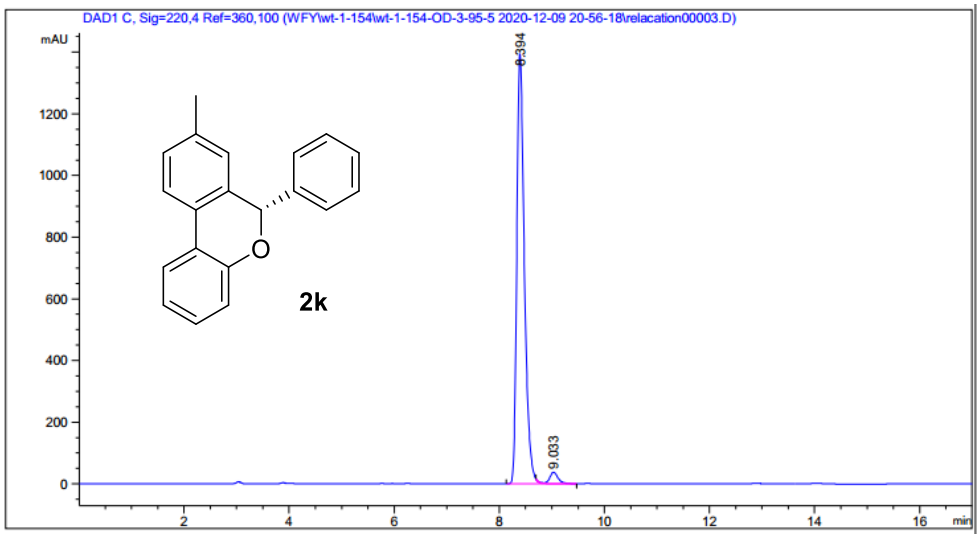
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.934	BB	0.4409	2.35340e4	829.82886	97.0631
2	11.059	BB	0.4939	712.07263	21.98534	2.9369

HPLC spectra of **2l**



Signal 1: DAD1 C, Sig=220,4 Ref=360,100

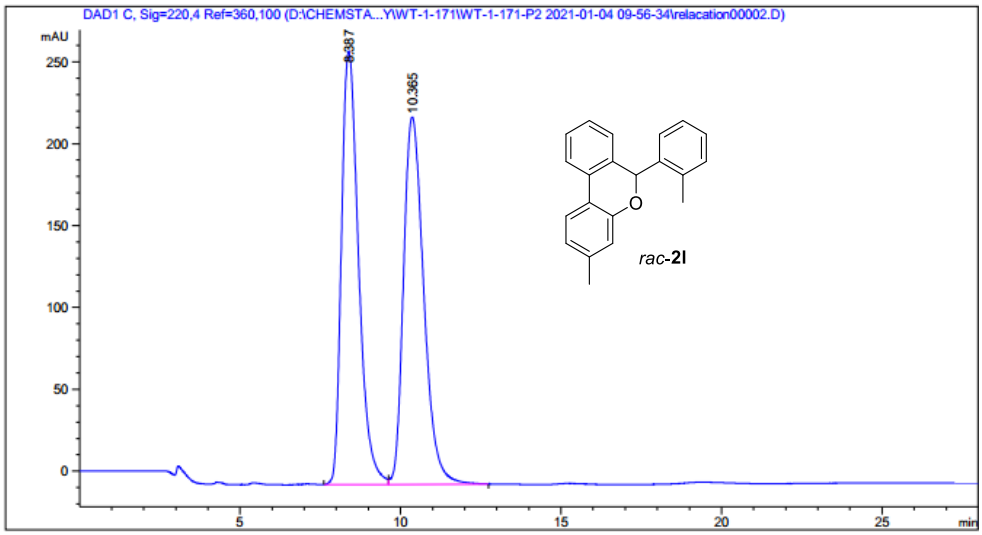
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.576	BV	0.1652	1.54951e4	1443.85791	49.7183
2	9.128	VB	0.1735	1.56707e4	1369.66626	50.2817



Signal 1: DAD1 C, Sig=220,4 Ref=360,100

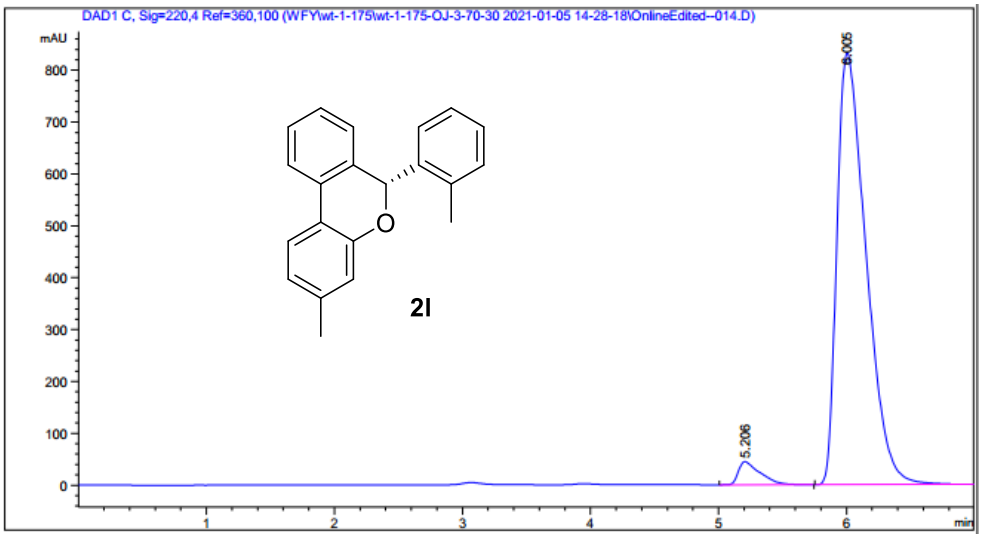
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.394	BV R	0.1528	1.39576e4	1394.38110	97.1610
2	9.033	VB E	0.1661	407.84030	37.14923	2.8390

HPLC spectra of **2l**



Signal 1: DAD1 C, Sig=220,4 Ref=360,100

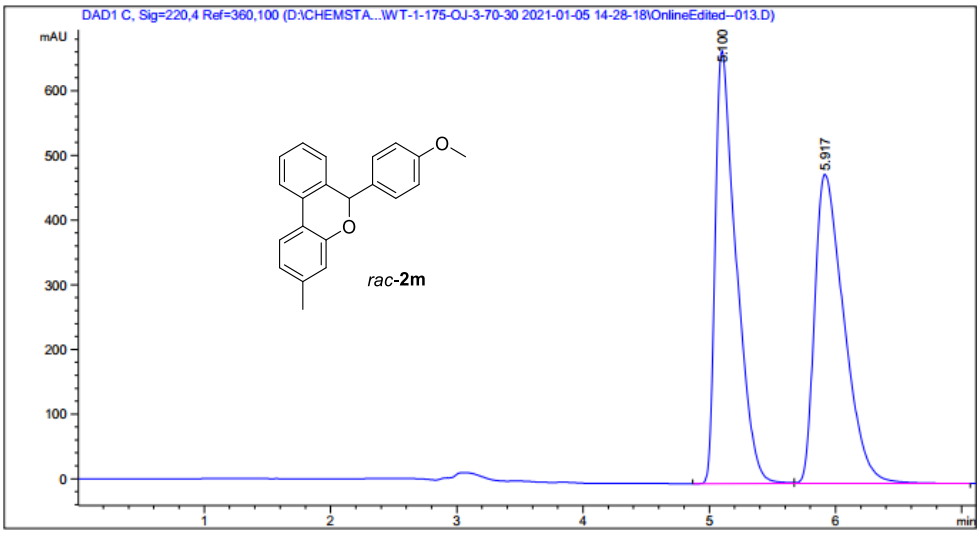
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.387	BV	0.5737	9792.11523	264.64941	49.8991
2	10.365	VB	0.6733	9831.71875	224.35379	50.1009



Signal 1: DAD1 C, Sig=220,4 Ref=360,100

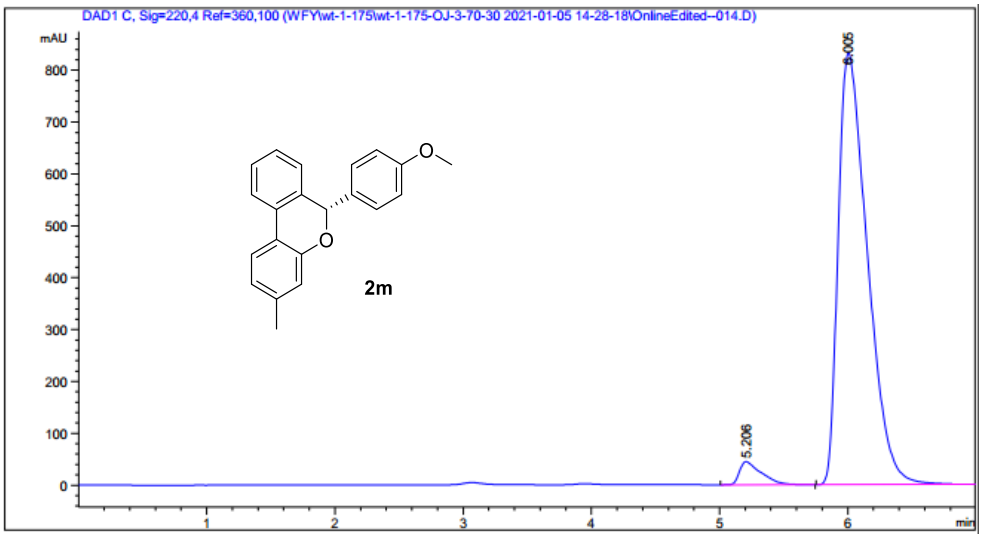
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.206	BB	0.1649	525.93671	44.81403	3.8558
2	6.005	BBA	0.2438	1.31142e4	832.27734	96.1442

HPLC spectra of **2m**



Signal 1: DAD1 C, Sig=220,4 Ref=360,100

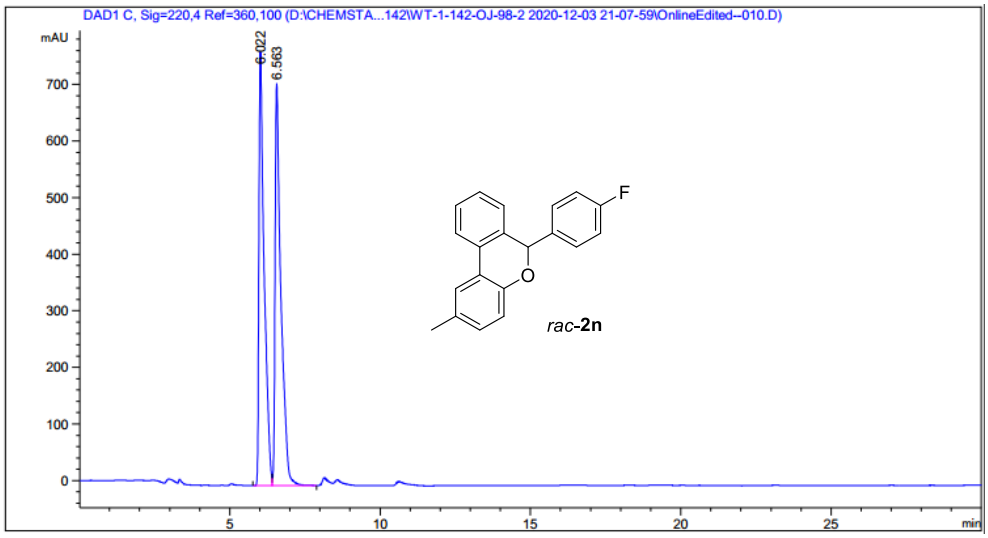
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.100	BV	0.1641	7688.05469	668.73840	49.9850
2	5.917	VB	0.2436	7692.67725	478.29132	50.0150



Signal 1: DAD1 C, Sig=220,4 Ref=360,100

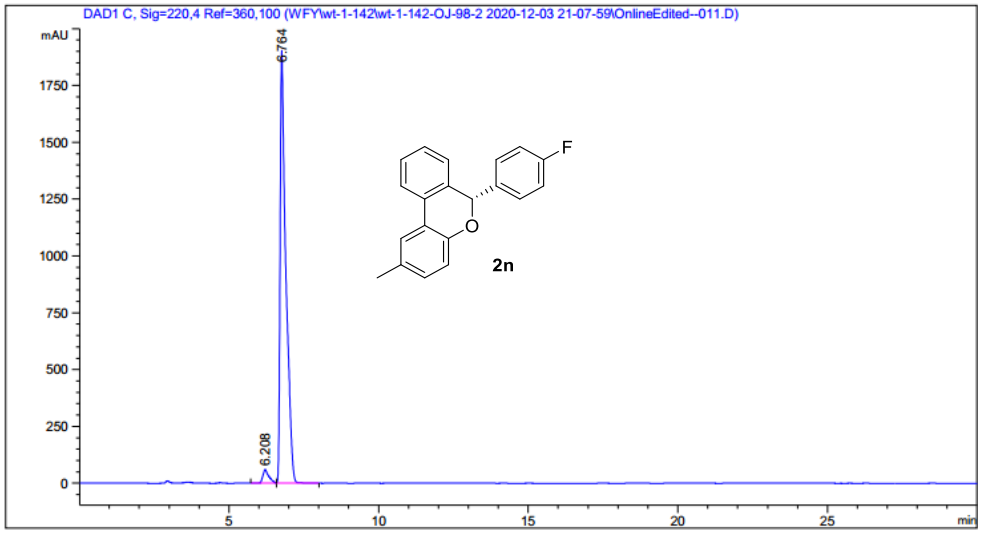
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.206	BB	0.1649	525.93671	44.81403	3.8558
2	6.005	BBA	0.2438	1.31142e4	832.27734	96.1442

HPLC spectra of **2n**



Signal 1: DAD1 C, Sig=220,4 Ref=360,100

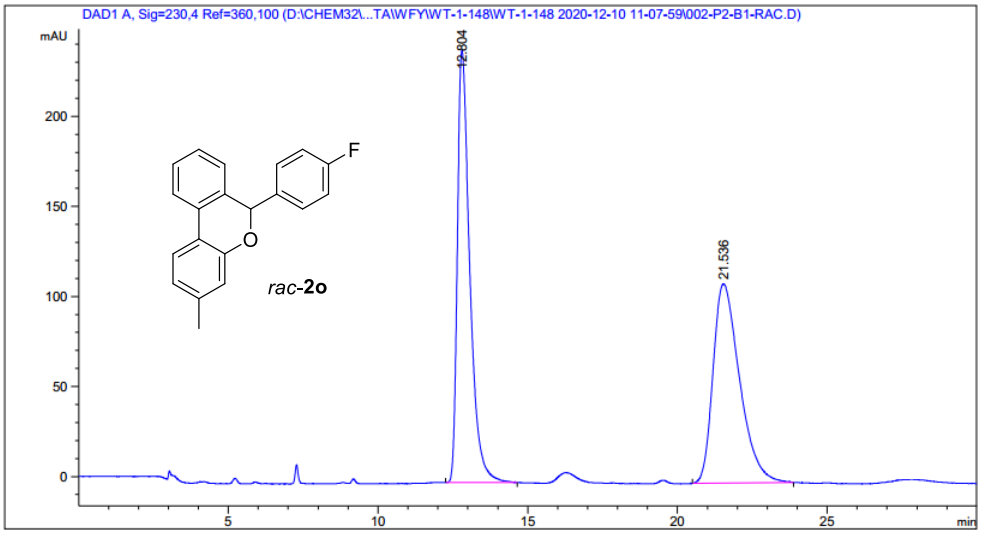
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.022	BV	0.1681	9217.93750	767.82147	49.1509
2	6.563	VB	0.1865	9536.43848	711.01819	50.8491



Signal 1: DAD1 C, Sig=220,4 Ref=360,100

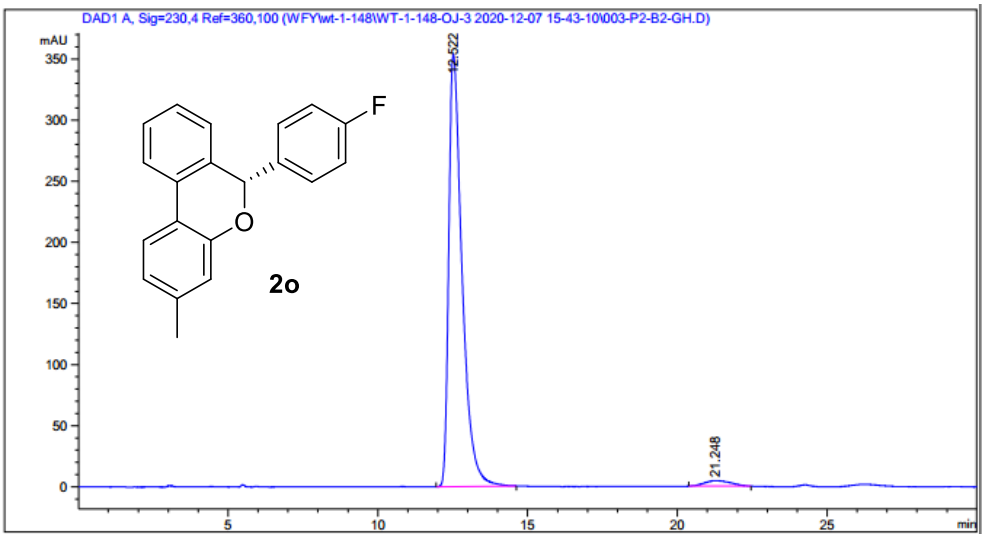
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.208	VV R	0.1888	840.06775	60.94250	3.1835
2	6.764	VB	0.1864	2.55479e4	1905.57568	96.8165

HPLC spectra of **2o**



Signal 1: DAD1 A, Sig=230,4 Ref=360,100

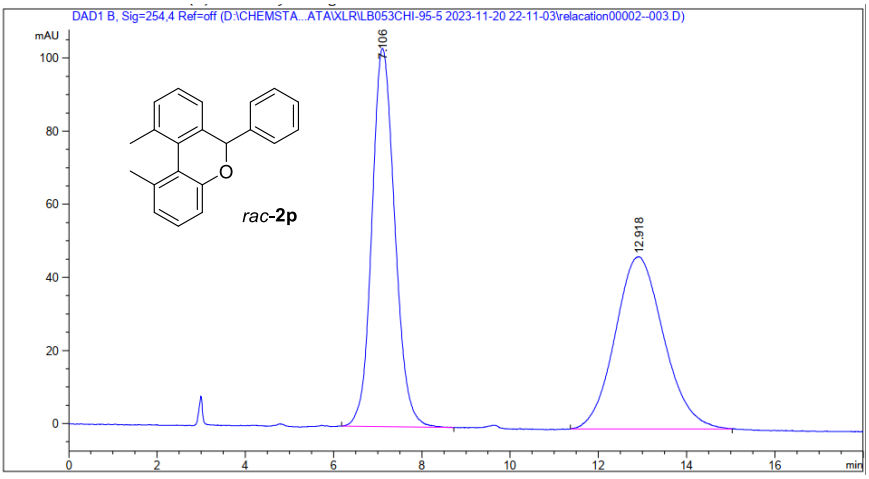
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.804	BB	0.4338	6906.73193	239.99565	50.3216
2	21.536	BB	0.8491	6818.44385	110.62206	49.6784



Signal 1: DAD1 A, Sig=230,4 Ref=360,100

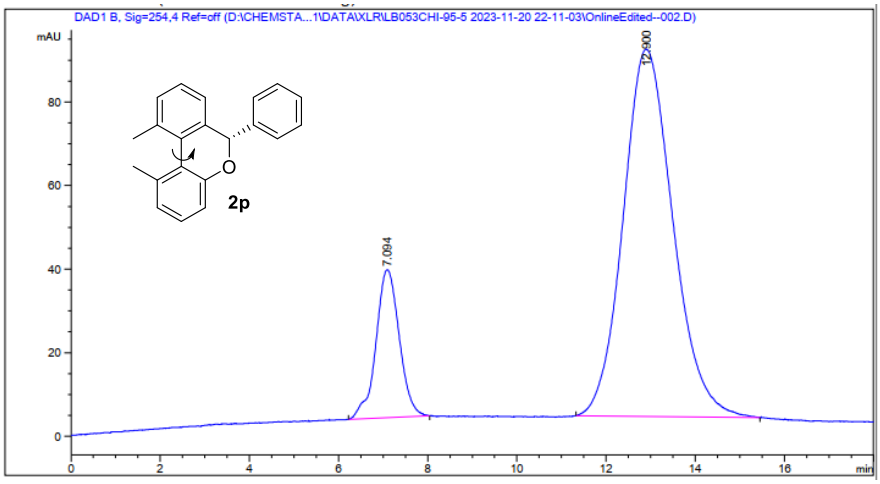
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.522	BB	0.4629	1.09407e4	353.68549	97.5156
2	21.248	BB	0.7192	278.73898	4.57257	2.4844

HPLC spectra of **2p**



Signal 1: DAD1 B, Sig=254,4 Ref=off

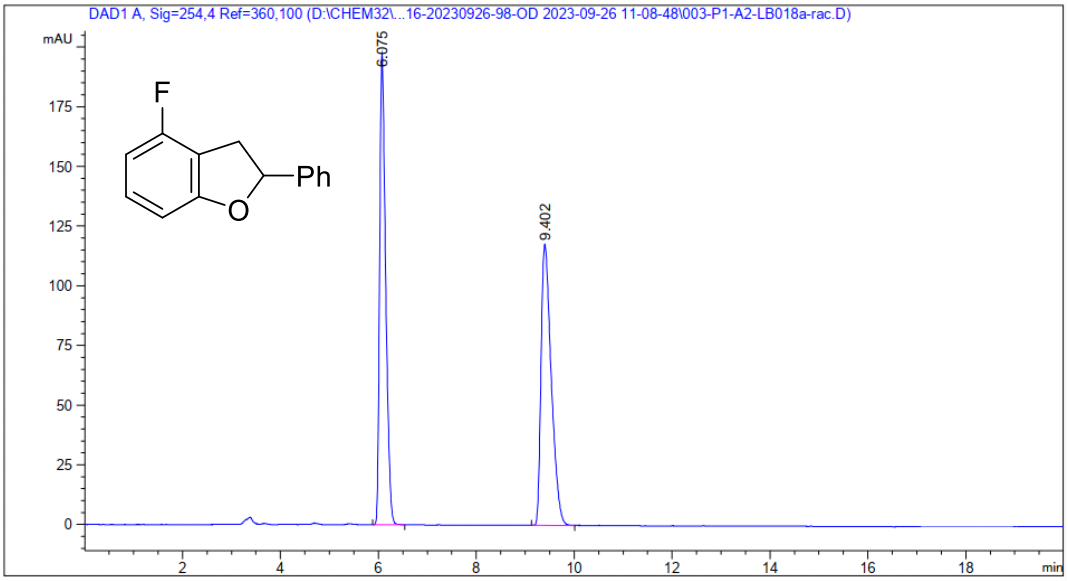
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.106	BB	0.5634	3735.50708	103.42138	50.9475
2	12.918	BB	0.9334	3596.55835	47.07096	49.0525



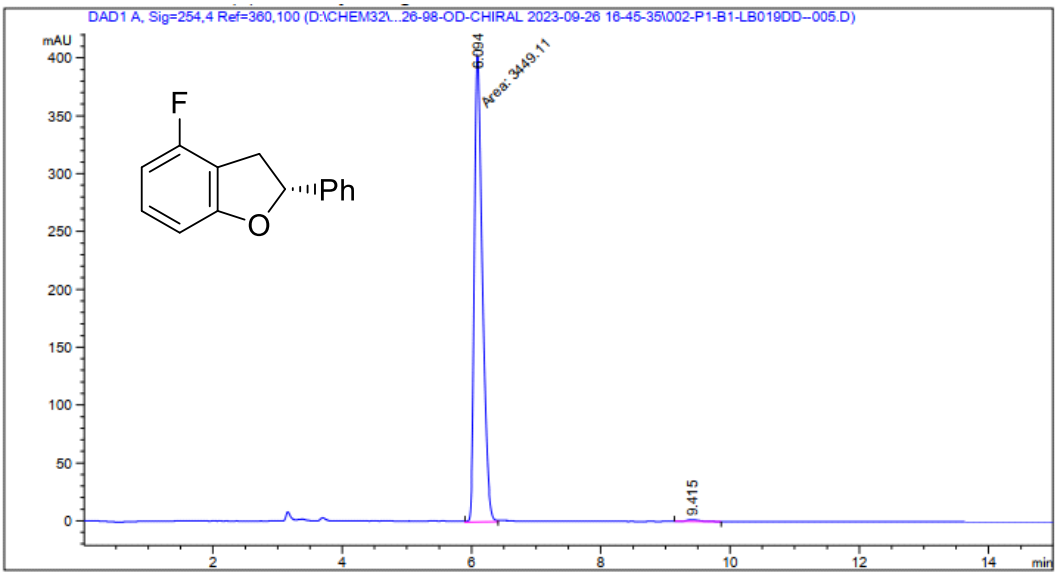
Signal 1: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.094	BB	0.5415	1284.99854	35.39694	15.8565
2	12.900	BB	0.9451	6818.91943	87.89438	84.1435

HPLC Spectra of **4a**

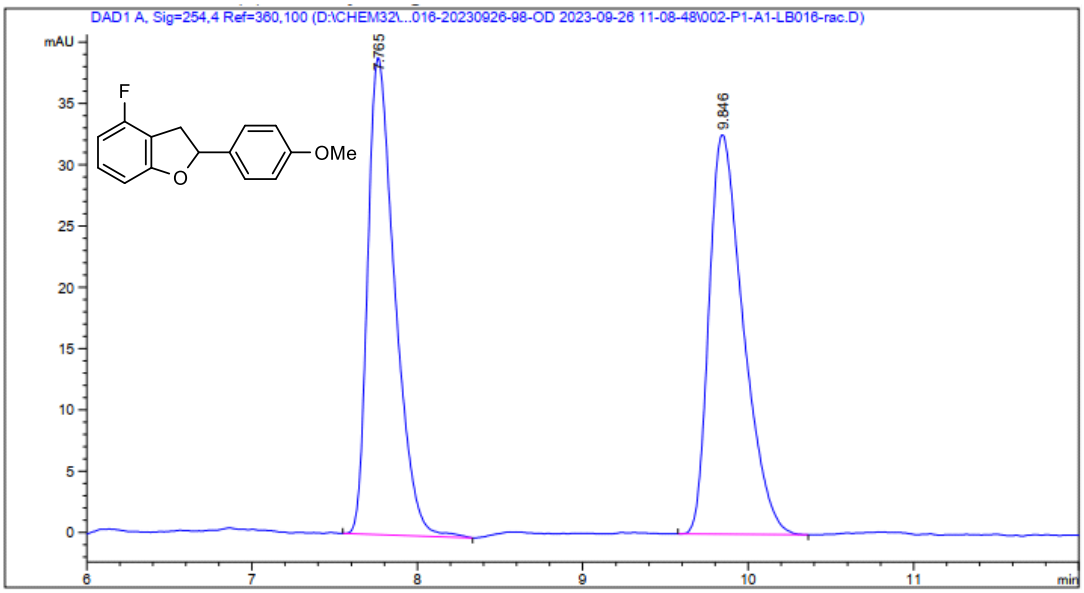


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.075	BB	0.1299	1688.23120	197.09761	49.7813
2	9.402	BB	0.2188	1703.06152	117.72148	50.2187

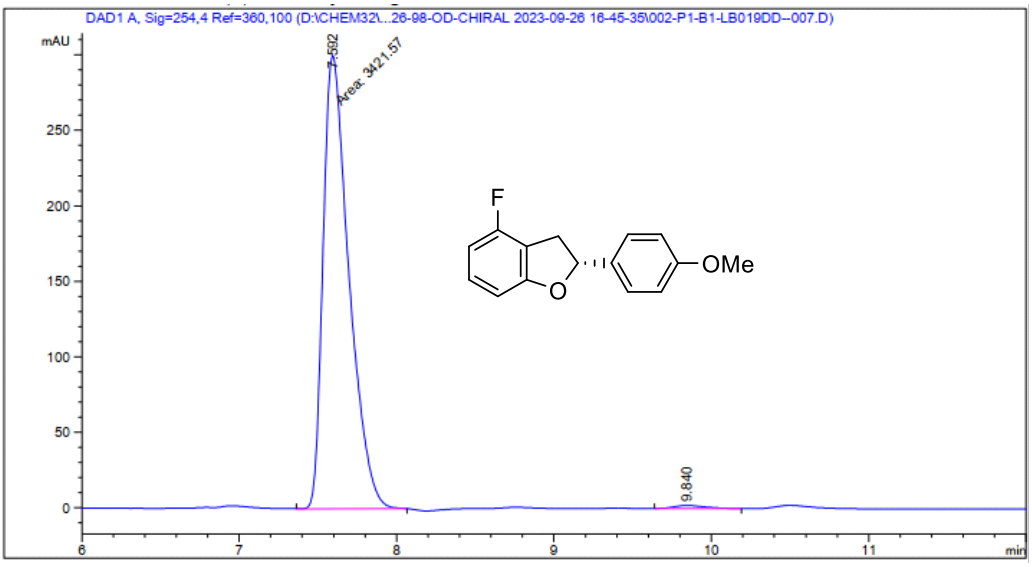


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.094	MM	0.1427	3449.10840	402.84155	99.3915
2	9.415	BB	0.2039	21.11502	1.50298	0.6085

HPLC spectra of **4b**

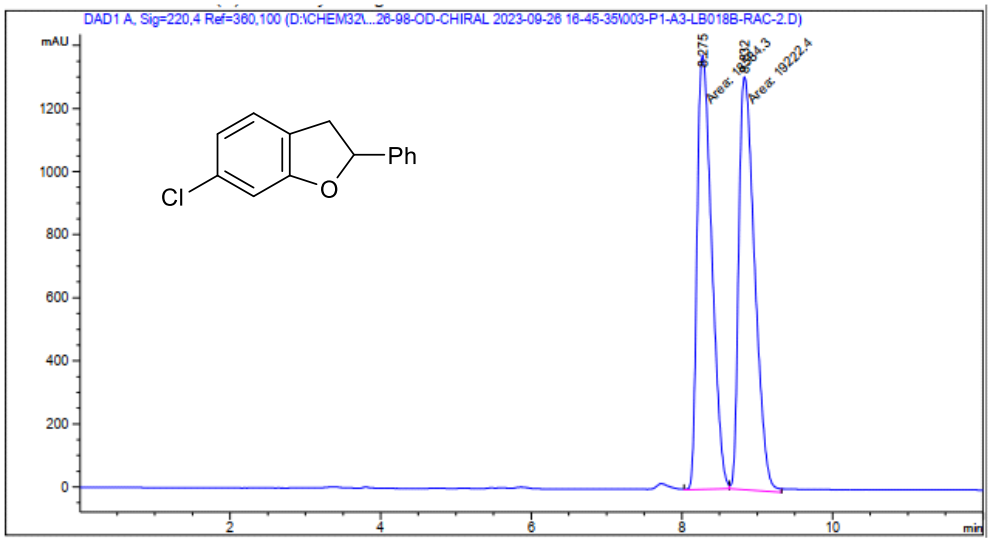


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.765	BB	0.1707	442.66223	38.91879	48.5392
2	9.846	BB	0.2178	469.30646	32.62306	51.4608

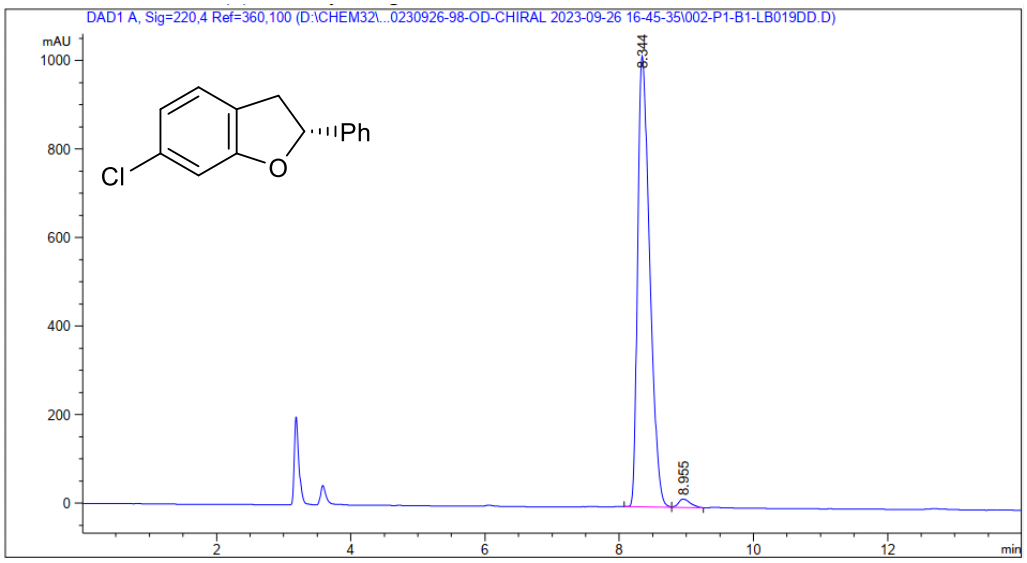


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.592	MM	0.1900	3421.56616	300.16470	99.1847
2	9.840	BB	0.1989	28.12538	2.03892	0.8153

HPLC spectra of **4c**

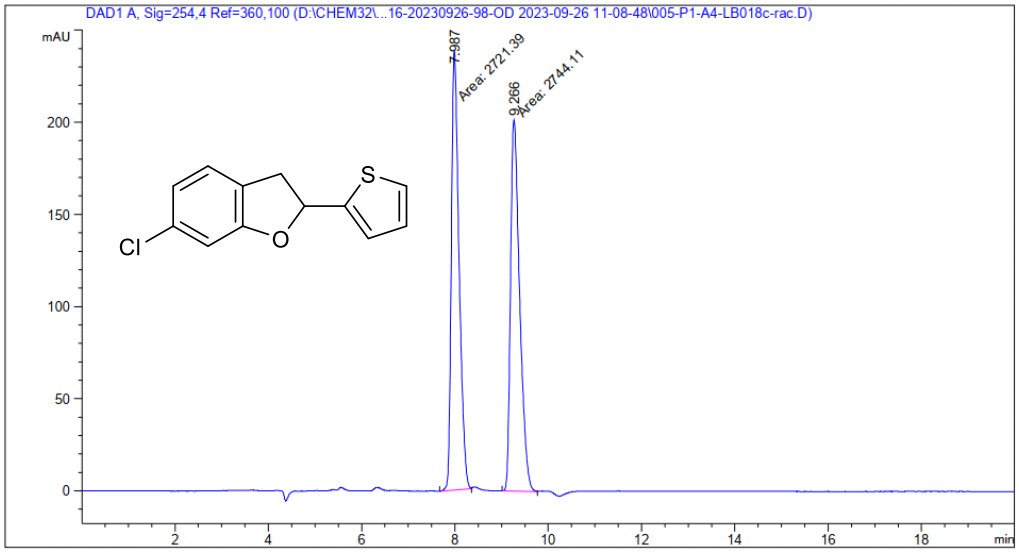


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.275	MM	0.2252	1.85843e4	1375.27368	49.1560
2	8.832	MM	0.2447	1.92224e4	1309.39771	50.8440

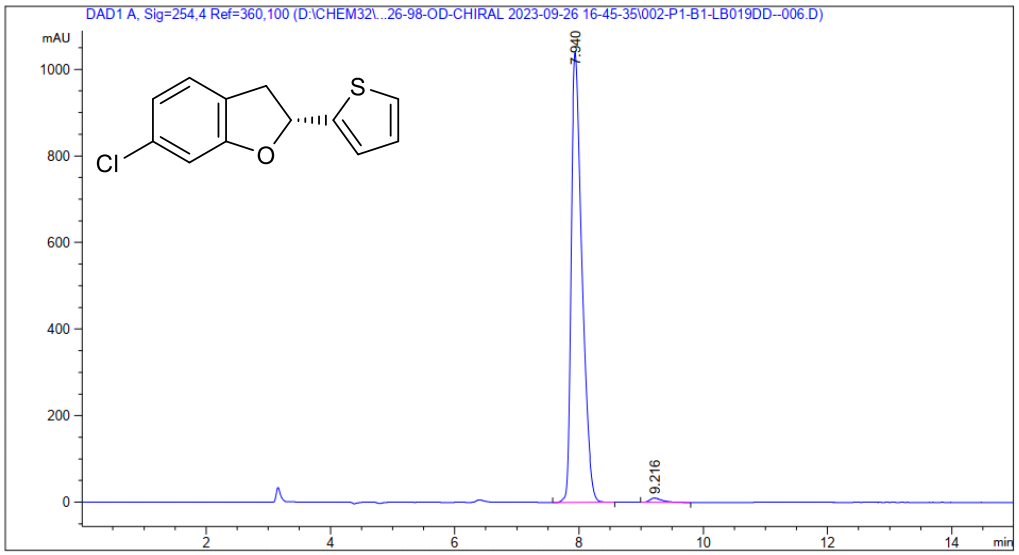


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.344	BV	0.1920	1.27389e4	1018.18463	98.2250
2	8.955	VB	0.1818	230.20641	18.94492	1.7750

HPLC spectra of **4d**

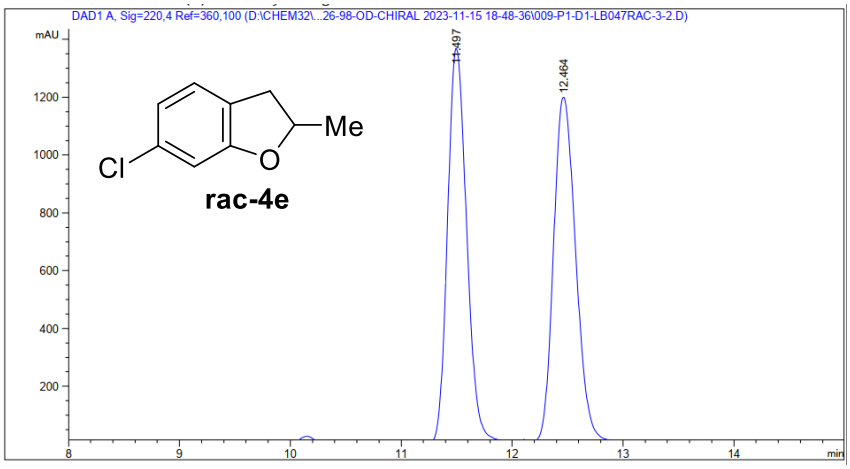


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.987	MM	0.1905	2721.38770	238.08713	49.7921
2	9.266	MM	0.2269	2744.11304	201.56805	50.2079

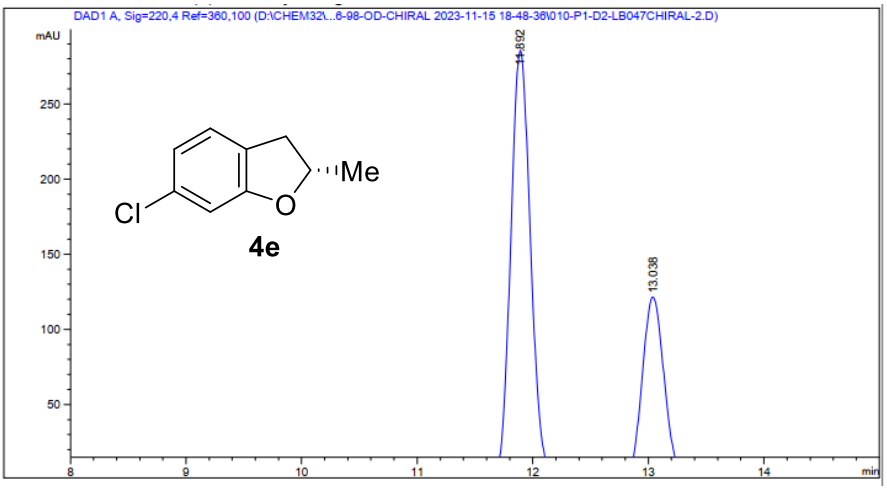


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.940	BB	0.1809	1.25469e4	1038.81799	98.9437
2	9.216	BB	0.1978	133.95139	9.90094	1.0563

HPLC spectra of **4e**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.497	BV	0.1893	1.65813e4	1369.40454	49.3418
2	12.464	VV R	0.2233	1.70237e4	1201.26953	50.6582



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.892	VV R	0.1896	3547.44092	288.18481	67.2370
2	13.038	BB	0.2179	1728.58154	124.56258	32.7630
Totals :				5276.02246	412.74739	

7. Crystallographic Information

The crystal data of compound **2j** has been deposited in CCDC with number 2079412.

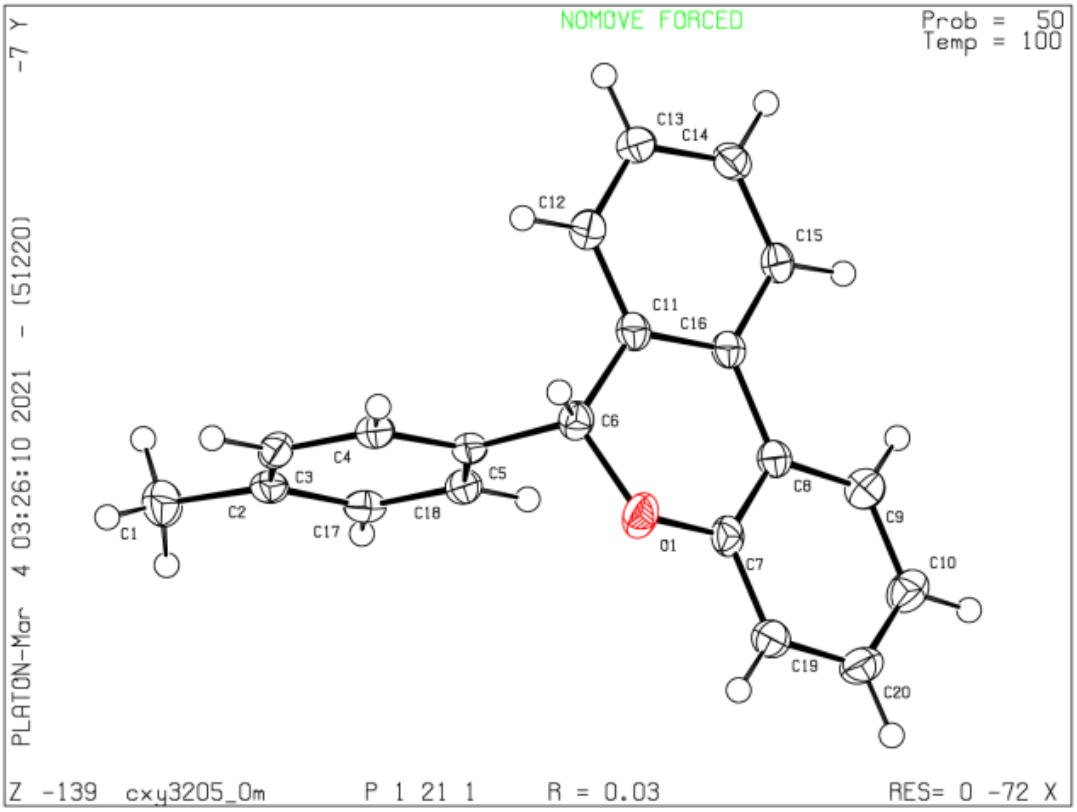


Table S3. Crystal data and structure refinement for cxy3205_0m.	
Identification code	cxy3205_0m
Empirical formula	$C_{20}H_{16}O$
Formula weight	272.33
Temperature/K	100.0
Crystal system	orthorhombic
Space group	$P2_1$
a/Å	8.9234(7)
b/Å	5.6665(4)
c/Å	14.4134(11)
α/°	90
β/°	106.079(3)

γ/°	90
Volume/Å^3	700.30(9)
Z	2
ρ_{calc}g/cm^3	1.291
μ/mm^{-1}	0.603
F(000)	288.0
Crystal size/mm^3	0.35 × 0.33 × 0.28
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/	6.382 to 136.36
Index ranges	-10≤h≤10, -6≤k≤6, -17≤l≤17
Reflections collected	13047
Independent reflections	2544 [R_{int}= 0.0301, R_{sigma}= 0.0213]
Data/restraints/parameters	2544/1/192
Goodness-of-fit on F^2	1.050
Final R indexes [I>=2σ (I)]	R_1 = 0.0258, wR_2 = 0.0693
Final R indexes [all data]	R_1 = 0.0260, wR_2 = 0.0695
Largest diff. peak/hole / e Å^{-3}	0.15/-0.11
Flack parameter	0.17(7)

Table S4. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for cxy3205_0m. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	3941.8(14)	7166(2)	7557.5(9)	31.0(3)
C1	8005(2)	5746(4)	4449.4(13)	34.8(4)
C2	7324.1(18)	6108(3)	5287.4(11)	23.8(4)
C3	7663.9(18)	8116(3)	5859.6(12)	23.3(4)
C4	7079.9(18)	8398(3)	6654.0(11)	21.5(3)
C5	6150.0(17)	6665(3)	6892.6(10)	19.0(3)
C6	5614.6(18)	6952(3)	7797.9(11)	22.3(4)
C7	3029.4(19)	5345(3)	7712.1(11)	22.9(4)
C8	3626.9(19)	3403(3)	8292.7(11)	21.2(4)
C9	2575(2)	1686(3)	8415.8(12)	25.9(4)
C10	987(2)	1916(4)	7990.5(13)	29.6(4)
C11	6268.8(19)	5039(3)	8531.9(11)	21.8(3)

C12	7870.0(19)	5016(3)	8965.1(12)	26.1(4)
C13	8538.6(19)	3316(4)	9640.9(12)	27.9(4)
C14	7604.0(19)	1621(3)	9895.8(11)	24.9(4)
C15	6009.9(19)	1618(3)	9462.4(11)	21.8(3)
C16	5317.9(18)	3310(3)	8766.6(11)	19.9(3)
C17	6356.1(18)	4399(3)	5517.7(11)	22.6(3)
C18	5786.0(17)	4659(3)	6313.5(11)	21.4(3)
C19	1433.8(19)	5594(3)	7290.5(12)	27.1(4)
C20	416(2)	3880(4)	7436.2(12)	29.0(4)

8. References

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