Electronic Supplementary Material (ESI) for ChemComm.

Ruthenium-catalyzed Fluorination of Alkenes

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Supporting Information

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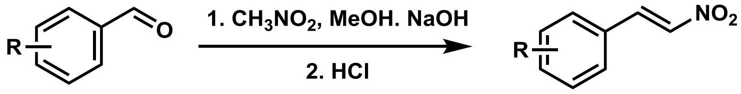
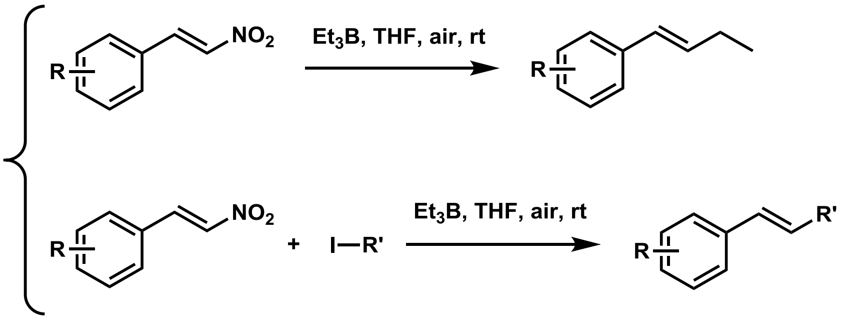
General Methods and Materials:

All other reagents were purchased and used without further purification unless specified otherwise. Solvents for chromatography were technical grade and distilled prior to use. Flash chromatography was performed using 200-300 mesh silica gel (Qingdao Haiyang Chemical HG/T2354-92) with the indicated solvent system according to standard techniques. Analytical thin-layer chromatography (TLC) was performed using Huanghai silica gel plates with HSGF 254. Visualization of the developed chromatogram was performed by UV absorbance (254 nm) or appropriate stains. NMR data were recorded on Bruker 400M nuclear resonance spectrometers (400 MHz for ^{1}H; 376 MHz for ^{19}F; 100 MHz for ^{13}C) unless otherwise specified. Chemical shifts (δ) in ppm are reported as quoted relative to the residual signals of chloroform (^{1}H 7.26 ppm or ^{13}C 77.16 ppm). Multiplicities are described as: s (singlet), bs (broad singlet), d (doublet), t (triplet), q (quartet), m (multiplet); and coupling constants (*J*) are reported in Hertz (Hz). ^{13}C NMR spectra were recorded with total proton decoupling. HRMS (APCI) analysis was performed by The Analytical Instrumentation Center at Peking University; Shenzhen Graduate School and the data were reported with ion mass/charge (m/z) ratios as values in atomic mass units.

General Procedure for 1,2-disubstituted Alkenes





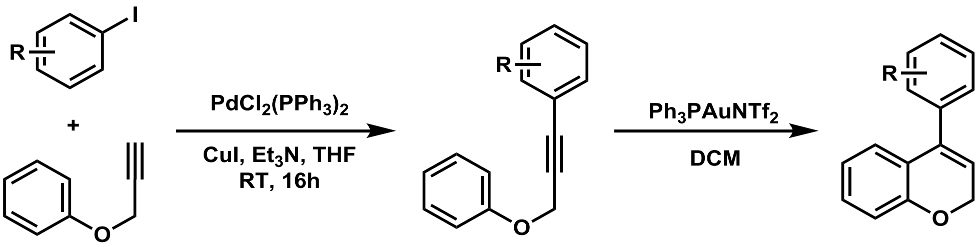
To a mixture of aldehyde (1 equiv) and nitromethane (1 equiv) in methanol at 0 ℃, a solution of NaOH in H_2O (1.2 equiv) was added dropwise. Further methanol was added and the resulting slurry stirred at that temperature for 1 h. Water (30 mL) was added and the clear solution was poured into hydrochloric acid (5 M) and stirred for 15 min. The aqueous mixture was extracted with DCM (20 mL x 3), the combined organic layers dried over magnesium sulfate and the solvent removed unsing a rotary evaporator. The residue was purified by column chromatography (petrolether/EtOAc) to yield nitroalkenes.[1]

Ethyl-substitutedalkenes:
Nitroalkene (1 equiv) and Et_3B (3 equiv) stirred in THF at r.t. The solution was bubbled with the air that filled in the balloon. After 10 min, the solution was evaporated and the oily residue was purified by flash column chromatography by hexane.

Other alkyl-substitutedalkenes:
Nitroalkene (1 equiv) and alkyl iodide (20 equiv) stirred in THF at r.t. The solution was bubbled with the air that filled in the balloon. Meantime, Et_3B (3 equiv) was added. After 10 min to 1 h, the solution was evaporated and the oily residue was purified by flash column chromatography by hexane.

The spectroscopic data for substrates **2e-2i** were identical to those described in reference 2. Other styrenes were purchased from Energy Chemical.

General Procedure for Chromene Derivatives

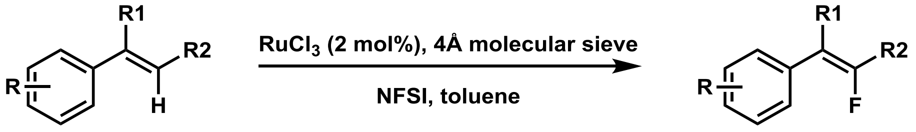


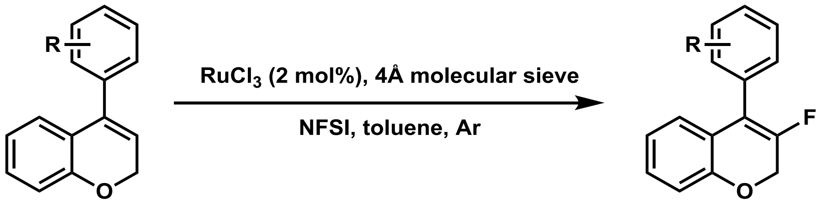
To a suspension of *trans*-dichloro-*bis*-(triphenylphosphine)palladium(II) (1-5 mol%) and copper(I) iodine (2-10 mol%) in tetrahydrofuran (0.2 M) was added the appropriate iodoarene (1.0 equiv.) and triethylamine (7.0 equiv.). The corresponding alkyne (1.1 equiv.) was added and the reaction mixture stirred at room temperature for the specified length of time. The reaction mixture was concentrated *in vacuo* and filtered through a plug of celite and silica, eluting with diethyl ether (3 × 25 mL). The solvent was removed *in vacuo* and the crude residue was purified by flash chromatography to yield the corresponding alkyne.[3]

The above alkyne (1 equiv) and catalyst (0.05 equiv) stirred in DCM at r.t. for 30 min to 4 h. When the reaction completed, the solution was evaporated and the oily residue was purified by flash column chromatography by hexane.[4]

The spectroscopic data for substrates **3a**-**3c**, **3e**-**3f** were identical to those described in reference 5. Analytic data for compound 3d (new compound) is presented on pages 7-8 (copies of NMR: pages 27-28).

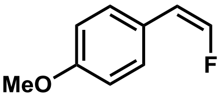
General Procedure for the Synthesis of Fluoroalkene and Fluorochromene Derivatives:





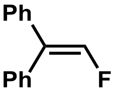
A reaction tube was charged with ruthenium(III) chloride (2 mol%), molecular sieve and NFSI (1.2 equiv.). A solution of the corresponding alkene (1.0 equiv.) in toluene (0.2 M) was added, and the reaction mixture stirred at the specified temperature for the specified length of time. When the reaction completed, the reaction mixture was cooled to room temperature. The reaction mixture was filtered through a plug of silica, eluting with diethyl ether. The solvent was removed *in vacuo* and the crude residue was purified by flash chromatography to yield the corresponding product. The spectral data for **2a**[6] and **2j**[7] were identical to those reported in the literature.

Characterization of the Products



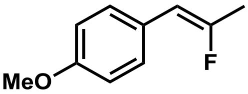
(Z)-1-(2-fluorovinyl)-4-methoxybenzene (2b):

75% yield, colourless liquid. $R_f = 0.5$ (EtOAc:Hexane = 1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.8 Hz, 2H), 6.90 – 6.87 (m, 2H), 6.60 (dd, *J* = 83.1, 5.3 Hz, 1H), 5.56 (dd, *J* = 45.2, 5.3 Hz, 1H), 3.83 (s, 3H). 13C NMR (101 MHz, $CDCl_3$) δ 158.88, 147.00 (d, *J* = 267.6 Hz), 130.12 (d, *J* = 7.1 Hz), 127.56 – 125.03 (m), 113.91, 110.21, 55.25. ^{19}F NMR (376 MHz, $CDCl_3$) δ -125.36. HRMS (APCI) Calcd. for $C_9H_{10}FO$ ($[M+H]^+$): 153.0710; Found: 153.0712.



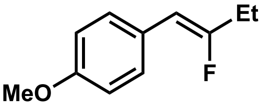
(2-fluoroethene-1,1-diyl)dibenzene (2c):

51% yield, colourless liquid. $R_f = 0.5$ (EtOAc:Hexane = 1:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (ddd, *J* = 11.8, 4.6, 1.7 Hz, 9H), 7.26 – 7.24 (m, 1H), 6.98 (d, *J* = 83.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.80 (d, *J* = 268.4 Hz), 137.02 (d, *J* = 8.2 Hz), 135.16, 129.78 (d, *J* = 4.3 Hz), 128.70 (d, *J* = 3.1 Hz), 128.53, 128.32 – 128.13 (m), 127.81 (d, *J* = 4.0 Hz), 126.26 (d, *J* = 5.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -128.09. HRMS (APCI) Calcd. for $C_{14}H_{12}F$ ($[M+H]^+$): 199.0918; Found: 199.0914.



(Z)-1-(2-fluoroprop-1-en-1-yl)-4-methoxybenzene (2d):

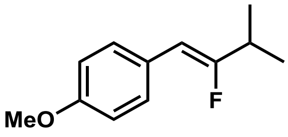
93% yield, colourless liquid. $R_f = 0.5$ (EtOAc:Hexane = 1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.9 Hz, 2H), 5.41 (d, *J* = 39.2 Hz, 1H), 3.81 (s, 3H), 2.06 (dd, *J* = 16.8, 0.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.21 (d, J = 2.7 Hz), 156.38 (d, J = 261.4 Hz), 129.32 (d, *J* = 7.3 Hz), 126.68 (d, *J* = 2.5 Hz), 113.82, 105.66 (d, *J* = 9.2 Hz), 55.23, 18.94 (d, *J* = 29.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -97.42. HRMS (APCI) Calcd. for $C_{10}H_{12}FO$ ($[M+H]^+$): 167.0867; Found: 167.0863.



(Z)-1-(2-fluorobut-1-en-1-yl)-4-methoxybenzene (2e):

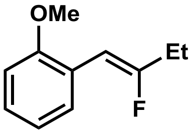
89% yield, colourless liquid. $R_f = 0.5$ (EtOAc:Hexane = 1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 5.41 (d, *J* = 40.0 Hz, 1H), 3.82 (s, 3H), 2.36 (dq, *J* = 15.0, 7.4 Hz, 2H), 1.18 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.50, 159.04 (d, *J* =

168.3 Hz), 129.45 (d, *J* = 7.4 Hz), 126.81 (d, *J* = 33.1 Hz), 113.81, 104.01 (d, *J* = 9.2 Hz), 55.24, 26.20 (d, *J* = 27.7 Hz), 11.01 (d, *J* = 3.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -103.60. HRMS (APCI) Calcd. for $C_{11}H_{14}FO$ ($[M+H]^+$): 181.1023; Found: 181.1021.



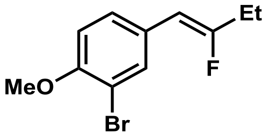
(Z)-1-(2-fluoro-3-methylbut-1-en-1-yl)-4-methoxybenzene (2f):

91% yield, colourless liquid. R_f = 0.5 (EtOAc:Hexane = 1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.8 Hz, 2H), 6.88 – 6.85 (m, 2H), 5.42 (d, *J* = 40.6 Hz, 1H), 3.82 (s, 3H), 2.56 (ddt, *J* = 20.6, 13.7, 6.9 Hz, 1H), 1.19 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.48 (d, *J* = 265.8 Hz), 158.17, 129.54 (d, *J* = 7.5 Hz), 126.84 (d, *J* = 36.2 Hz), 113.81, 102.67 (d, *J* = 9.5 Hz), 55.24, 31.96 (d, *J* = 26.0 Hz), 19.82 (d, *J* = 2.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.38. HRMS (APCI) Calcd. for $C_{12}H_{16}FO$ ($[M+H]^+$): 195.1180; Found: 195.1175.



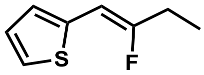
(Z)-1-(2-fluorobut-1-en-1-yl)-2-methoxybenzene (2g):

91% yield, colourless liquid. R_f = 0.5 (EtOAc:Hexane = 1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.20 (d, *J* = 7.3 Hz, 2H), 6.97 – 6.92 (m, 1H), 6.89 – 6.84 (m, 1H), 5.88 (d, *J* = 40.7 Hz, 1H), 3.84 (s, 3H), 2.47 – 2.33 (m, 2H), 1.20 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.73 (d, *J* = 221.6 Hz), 155.82, 129.74 (d, *J* = 12.5 Hz), 128.70 (d, *J* = 48.3 Hz), 127.72, 120.60, 110.38, 98.01 (d, *J* = 7.3 Hz), 55.52, 26.54 (d, *J* = 27.8 Hz), 11.01 (d, *J* = 3.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -102.51. HRMS (APCI) Calcd. for $C_{11}H_{14}FO$ ($[M+H]^+$): 181.1023; Found: 181.1020.



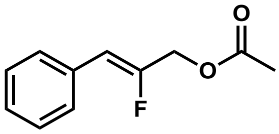
(Z)-2-bromo-4-(2-fluorobut-1-en-1-yl)-1-methoxybenzene (2h):

75% yield, pale yellow liquid. R_f = 0.4 (EtOAc:Hexane = 1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 2.0 Hz, 1H), 7.38 (dd, *J* = 8.6, 2.1 Hz, 1H), 6.85 (d, *J* = 8.6 Hz, 1H), 5.35 (d, *J* = 39.2 Hz, 1H), 3.90 (s, 3H), 2.34 (dt, *J* = 15.0, 7.5 Hz, 2H), 1.17 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.11 (d, *J* = 265.4 Hz), 154.39, 132.99 (d, *J* = 7.9 Hz), 130.50 – 125.58 (m), 111.60 (d, *J* = 18.0 Hz), 103.00 (d, *J* = 9.1 Hz), 56.24, 26.16 (d, *J* = 27.4 Hz), 10.90 (d, *J* = 3.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -101.68. HRMS (APCI) Calcd. for $C_{11}H_{13}BrFO$ ($[M+H]^+$): 259.0128; Found: 259.0131.



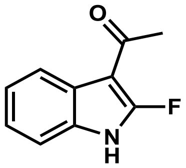
(Z)-2-(2-fluorobut-1-en-1-yl)thiophene (2i):

46% yield, pale yellow liquid. R_f = 0.5 (EtOAc:Hexane = 1:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 5.0 Hz, 1H), 7.00 (d, *J* = 2.8 Hz, 1H), 6.99 – 6.94 (m, 1H), 5.80 (d, *J* = 38.6 Hz, 1H), 2.37 (dd, *J* = 14.7, 7.3 Hz, 2H), 1.18 (d, *J* = 7.4 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.34 (d, *J* = 265.2 Hz), 136.25, 126.67, 125.63 (d, *J* = 3.7 Hz), 124.89 (d, *J* = 9.0 Hz), 99.61 (d, *J* = 12.8 Hz), 25.70 (d, *J* = 26.5 Hz), 10.86 (d, *J* = 3.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -97.31. HRMS (APCI) Calcd. for $C_8H_{10}FS$ ($[M+H]^+$): 157.0482; Found: 157.0479.



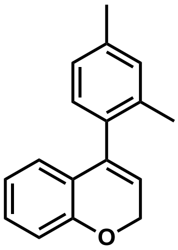
(Z)-2-fluoro-3-phenylallyl acetate (2k):

50% yield, white solid. R_f = 0.4 (EtOAc:Hexane = 1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.49 (m, 2H), 7.35 (dd, *J* = 10.5, 4.4 Hz, 2H), 7.29 (d, *J* = 7.3 Hz, 1H), 5.85 (d, *J* = 37.4 Hz, 1H), 4.74 (d, *J* = 17.8 Hz, 2H), 2.15 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.44, 154.01 (d, *J* = 266.1 Hz), 132.26 (d, *J* = 3.2 Hz), 128.90 (d, *J* = 7.4 Hz), 128.55, 127.95 (d, *J* = 2.3 Hz), 127.10, 111.02 (d, *J* = 6.7 Hz), 62.92 (d, *J* = 30.9 Hz), 20.82. ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.26. HRMS (APCI) Calcd. for $C_{11}H_{12}FO_2$ ($[M+H]^+$): 195.0816; Found: 195.0811.



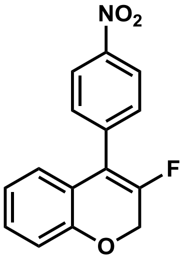
1-(2-fluoro-1H-indol-3-yl)ethan-1-one (2l):

80% yield, white solid. R_f = 0.5 (EtOAc:Hexane = 1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (s, 1H), 7.72 (dd, *J* = 8.2, 0.8 Hz, 1H), 7.41 – 7.33 (m, 2H), 7.17 (ddd, *J* = 8.0, 6.5, 1.3 Hz, 1H), 2.66 (d, *J* = 2.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.49, 148.13 (d, *J* = 262.6 Hz), 133.69, 127.74, 121.09, 119.71 (d, *J* = 20.4 Hz), 119.47 (d, *J* = 2.8 Hz), 116.46 (d, *J* = 16.1 Hz), 112.53, 27.99 (d, *J* = 4.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -154.79. HRMS (APCI) Calcd. for $C_{10}H_9FNO$ ($[M+H]^+$): 178.0663; Found: 178.0662.



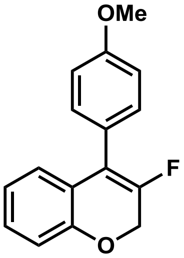
4-(2,4-dimethyl)-2H-chromene (3d):

82% yield, colourless liquid. R_f = 0.5 (EtOAc:Hexane = 1:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.08 (m, 4H), 6.92 (d, *J* = 8.1 Hz, 1H), 6.82 (td, *J* = 7.5, 1.1 Hz, 1H), 6.68 (dd, *J* = 7.6, 1.4 Hz, 1H), 5.70 (t, *J* = 3.7 Hz, 1H), 4.96 (t, *J* = 3.2 Hz, 2H), 2.42 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.13, 137.51, 136.64, 136.37, 134.99, 130.87, 129.73, 129.15, 126.59, 125.64, 123.96, 121.29, 120.40, 116.01, 65.55, 21.22, 19.82. HRMS (APCI) Calcd. for $C_{17}H_{16}O$ ($[M+H]^+$): 237.1279; Found: 237.1283.



3-fluoro-4-(4-nitrophenyl)-2H-chromene (4a):

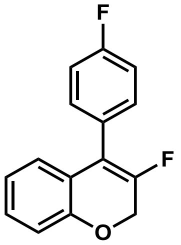
71% yield, yellow solid. R_f = 0.4 (EtOAc:Hexane = 1:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.8 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.20 – 7.12 (m, 1H), 6.98 – 6.87 (m, 2H), 6.81 (dd, *J* = 7.7, 1.5 Hz, 1H), 4.93 (d, *J* = 3.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.89, 148.35 (d, *J* = 153.2 Hz), 138.14, 131.00 (d, *J* = 2.1 Hz), 128.76 (d, *J* = 2.3 Hz), 125.34 (d, *J* = 6.6 Hz), 123.77, 122.26, 121.88, 116.33, 113.22 (d, *J* = 9.4 Hz), 63.80 (d, *J* = 36.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.85. HRMS (APCI) Calcd. for $C_{15}H_{11}FNO_3$ ($[M+H]^+$): 272.0717; Found: 272.0710.



3-fluoro-4-(4-methoxyphenyl)-2H-chromene (4b):

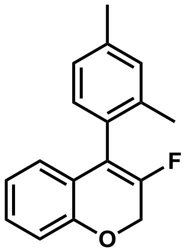
75% yield, colourless liquid. R_f = 0.5 (EtOAc:Hexane = 1:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.3 Hz, 2H), 7.15 – 7.09 (m, 1H), 6.99 (d, *J* = 8.8 Hz, 2H), 6.93 – 6.86 (m, 3H), 4.91 (d, *J* = 3.0 Hz, 2H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.37, 151.99, 149.11 (d, *J* = 270.6

Hz), 131.14 (d, *J* = 1.8 Hz), 127.96 (d, *J* = 2.3 Hz), 125.78 (d, *J* = 6.7 Hz), 123.34 (d, *J* = 3.4 Hz), 123.11, 121.89, 115.84, 113.99, 64.01 (d, *J* = 37.2 Hz), 55.30. ^{19}F NMR (376 MHz, $CDCl_3$) δ -119.90. HRMS (APCI) Calcd. for $C_{16}H_{14}FO_2$ ($[M+H]^+$): 257.0972; Found: 257.0971.



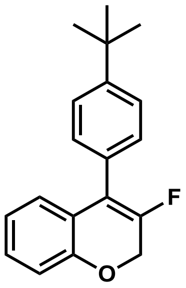
3-fluoro-4-(4-fluorophenyl)-2H-chromene (4c):

62% yield, white solid. R_f = 0.5 (EtOAc:Hexane = 1:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 8.3, 5.5 Hz, 2H), 7.17 – 7.10 (m, 3H), 6.94 – 6.83 (m, 3H), 4.91 (d, *J* = 3.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.49 (d, *J* = 247.5 Hz), 151.89, 149.49 (d, *J* = 272.1 Hz), 131.70 (d, *J* = 8.1 Hz), 128.21 (d, *J* = 2.3 Hz), 126.89, 125.58 (d, *J* = 6.6 Hz), 123.53 (d, *J* = 124.5 Hz), 122.01, 115.97, 115.60 (d, *J* = 21.5 Hz), 113.68 (d, *J* = 10.0 Hz), 63.92 (d, *J* = 36.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.49, -118.31. HRMS (APCI) Calcd. for $C_{15}H_{11}F_2O$ ($[M+H]^+$): 245.0772; Found: 245.0767.



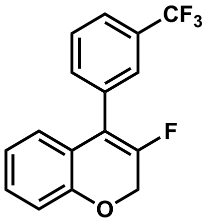
4-(2,4-dimethylphenyl)-3-fluoro-2H-chromene (4d):

72% yield, white solid. R_f = 0.5 (EtOAc:Hexane = 1:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (s, 1H), 7.12 – 7.07 (m, 3H), 6.92 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.84 (t, *J* = 7.5 Hz, 1H), 6.63 (dd, *J* = 7.6, 1.5 Hz, 1H), 4.97 (d, *J* = 1.7 Hz, 2H), 2.40 (s, 3H), 2.19 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.48, 149.16 (d, *J* = 268.9 Hz), 138.14, 137.27, 131.11, 130.22, 127.95 (d, *J* = 2.4 Hz), 127.40, 126.72, 125.46 (d, *J* = 6.7 Hz), 123.09 (d, *J* = 3.9 Hz), 121.95, 115.65, 63.92 (d, *J* = 37.3 Hz), 21.24, 19.60. ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.23. HRMS (APCI) Calcd. for $C_{17}H_{16}FO$ ($[M+H]^+$): 255.1180; Found: 255.1184.



4-(4-(tert-butyl)phenyl)-3-fluoro-2H-chromene (4e):

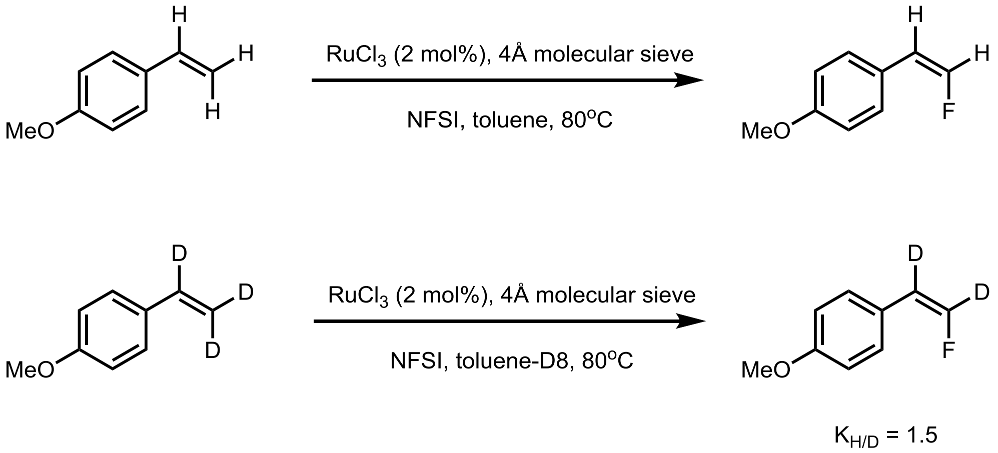
75% yield, white solid. R_f = 0.5 (EtOAc:Hexane = 1:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.15 – 7.09 (m, 1H), 6.98 – 6.84 (m, 3H), 4.92 (d, *J* = 3.0 Hz, 2H), 1.37 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.96, 151.02, 149.18 (d, *J* = 271.1 Hz), 129.58 (d, *J* = 1.8 Hz), 127.95 (d, *J* = 2.6 Hz), 125.94 (d, *J* = 6.6 Hz), 125.40, 123.23 (d, *J* = 3.3 Hz), 121.86, 115.82, 114.37 (d, *J* = 10.2 Hz), 64.00 (d, *J* = 37.2 Hz), 34.68, 31.34. ^{19}F NMR (376 MHz, $CDCl_3$) δ -118.77. HRMS (APCI) Calcd. for $C_{19}H_{20}FO$ ($[M+H]^+$): 283.1493; Found: 283.1490.



3-fluoro-4-(3-(trifluoromethyl)phenyl)-2H-chromene (4f):

54% yield, colourless liquid. R_f = 0.5 (EtOAc:Hexane = 1:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.62 (m, 2H), 7.56 (dd, *J* = 11.3, 7.6 Hz, 2H), 7.18 – 7.13 (m, 1H), 6.94 (dd, *J* = 8.1, 1.0 Hz, 1H), 6.90 (t, *J* = 7.5 Hz, 1H), 6.81 (dd, *J* = 7.7, 1.6 Hz, 1H), 4.93 (d, *J* = 3.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.86, 150.00 (d, *J* = 274.0 Hz), 133.36, 131.97, 131.07 (d, *J* = 32.5 Hz), 129.76, 129.06, 128.46 (d, *J* = 2.3 Hz), 126.81 (dd, *J* = 3.6, 2.2 Hz), 125.39 (d, *J* = 6.6 Hz), 124.99 (dd, *J* = 7.4, 3.7 Hz), 122.16, 116.13, 113.55 (d, *J* = 9.8 Hz), 63.85 (d, *J* = 36.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.63, -117.39. HRMS (APCI) Calcd. for $C_{16}H_{11}F_4O$ ($[M+H]^+$): 295.0741; Found: 295.0736.

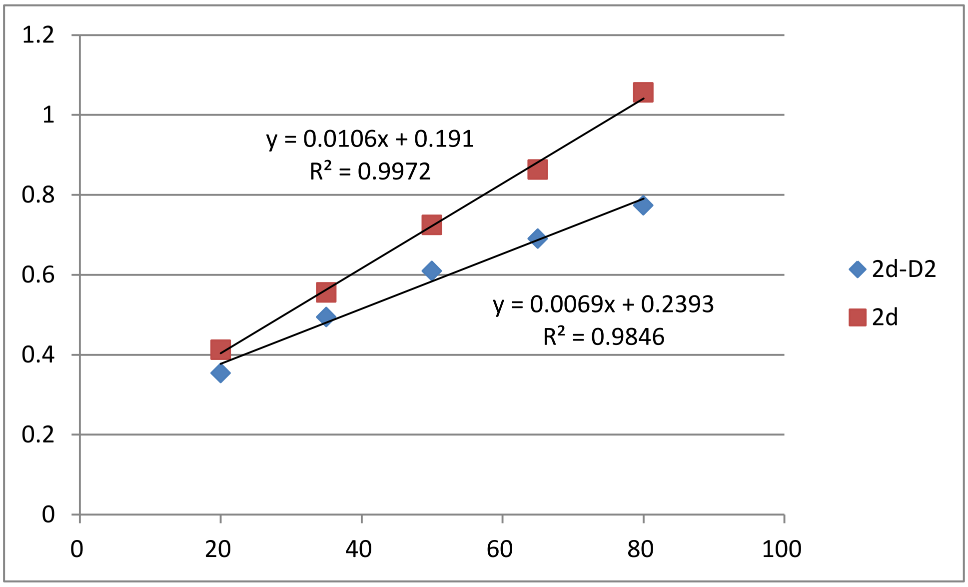
Deuterium kinetic isotope effect (DKIE) measurements



A sample experimental set-up is as follows: A reaction tube was charged with ruthenium(III) chloride (2 mol%), molecular sieve and NFSI (1.5 equiv.). A solution of the corresponding alkene or alkene-d3 (0.4 mmol, 1.0 equiv.) in toluene or toluene-d8 (0.2 M) was added. The tube was put into a oil bath (80 °C) to react to initiate the reaction and signify time zero (t =0). Aliquots (~ 0.05 mL) were removed at 15 min intervals for the first 80 mins. Each aliquot was filtered through a plug of silica, eluting with diethyl ether and analyzed by GC. A sample plot of the initial rate data for reactions of both 2b and 2b-D2 are shown below.

The isotope effect $K_{H/D}$ was calculated as 1.5.

Chart S1. Plot of initial rates for DKIE measurements.



References

1. Trost, B. M.; Müller, C. *J. Am. Chem. Soc.* **2008**, *130*, 2438.

2. Liu, J.; Jang, Y.; Shih, Y.; Hu, S.; Chu, C.; Yao, C. *J. Org. Chem.* **2001**, *66*, 6021

3. Walkinshaw, A. J.; Xu, W.; Suero, M. G.; Gaunt, M. J. *J. Am. Chem. Soc.* **2013**, *135,* 12532.

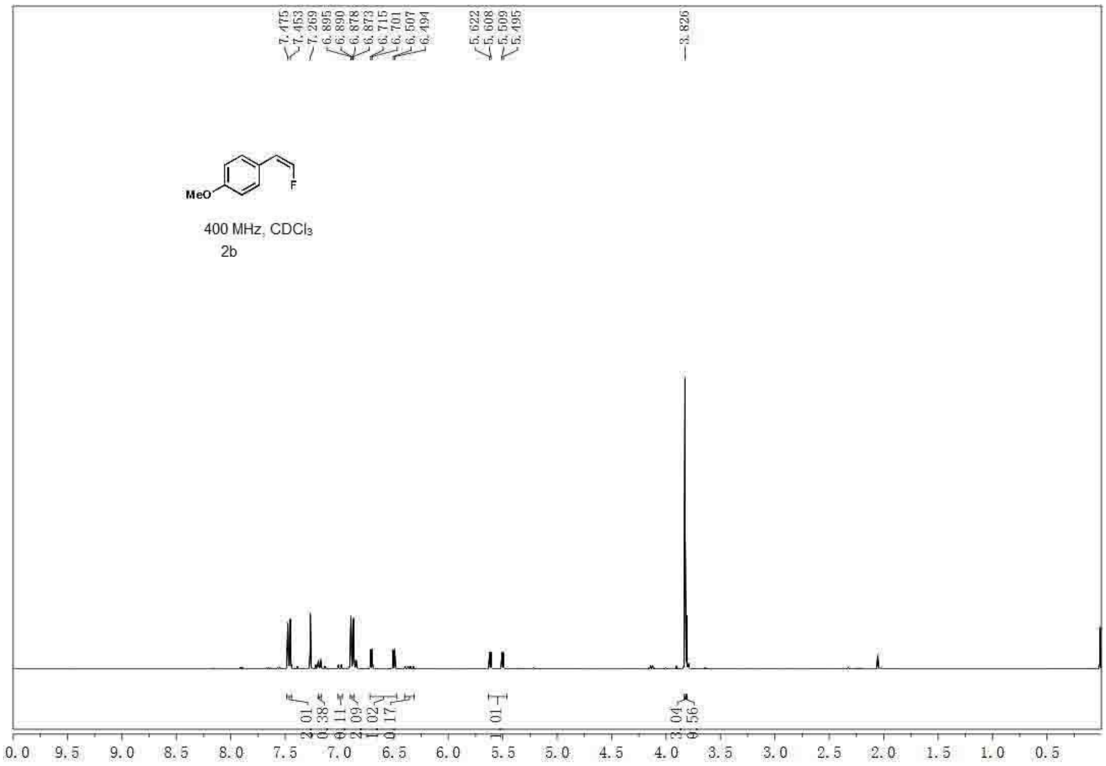
4. Lykakis, I. N.; Efe, C.; Gryparis, C.; Stratakis, M. *Eur. J. Org. Chem.* **2011**, 2334.

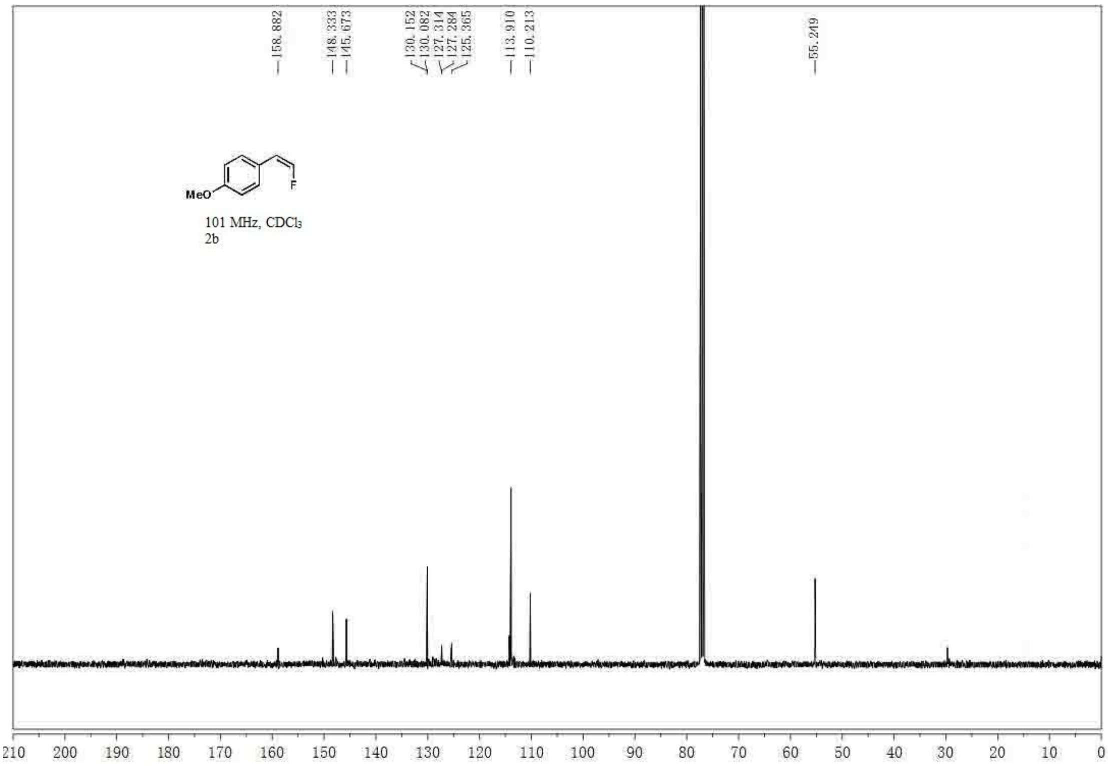
5. Aponick, A.; Biannic, B.; Jong, M. R. *Chem. Commun.* **2010**, *46*, 6849; Arcadi, A.; Blesi, F.; Cacchi, S.; Fabrizi, G. Goggiamani, A.; Marinelli, F. *Org. Biomol. Chem.* **2012**, *10,* 9700; Eguchi, T.; Hoshino, Y.; Ayame, A. *B. Chem. Soc. Jpn.* **2002**, *75,* 581.

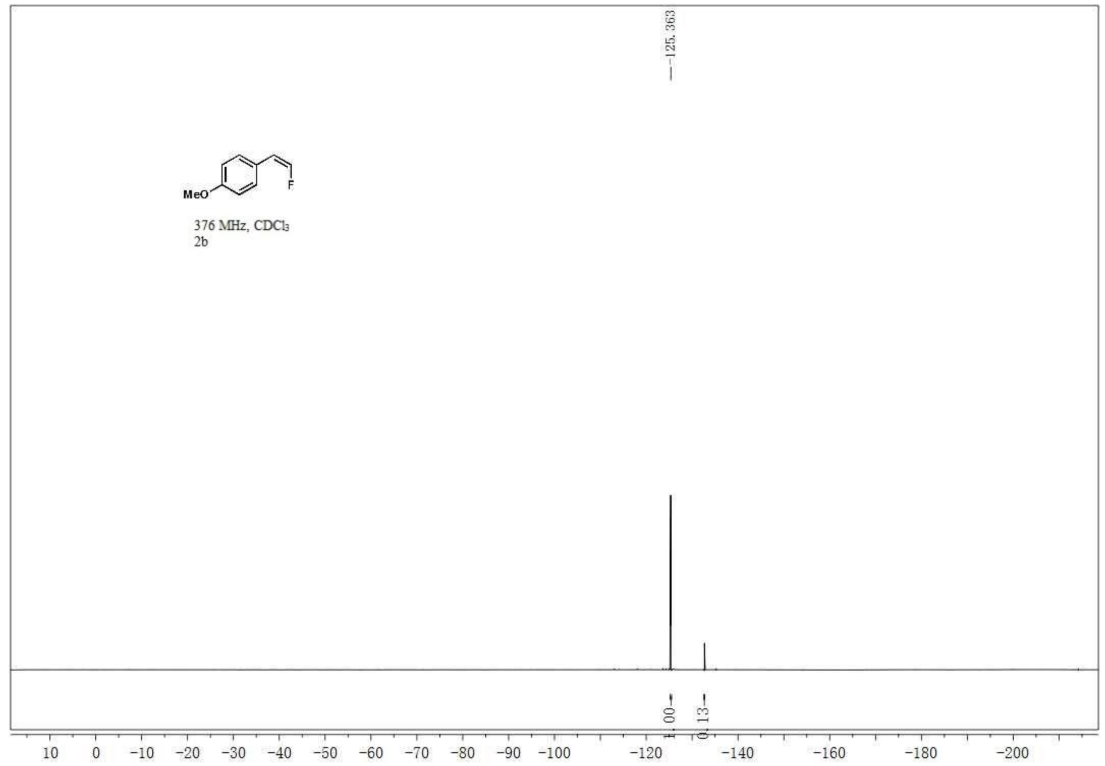
6. Isogai, K.; Nishizawa, N.; Saito, t.; Sakai, J. *Bull. Chem. Soc. Jpn.* **1983**, 1555.

7. Yoshida, M.; Komata, A.; Hara, S. *Tetrahedron* **2006**, *62*, 8636.

NMR Spectra Images







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2b
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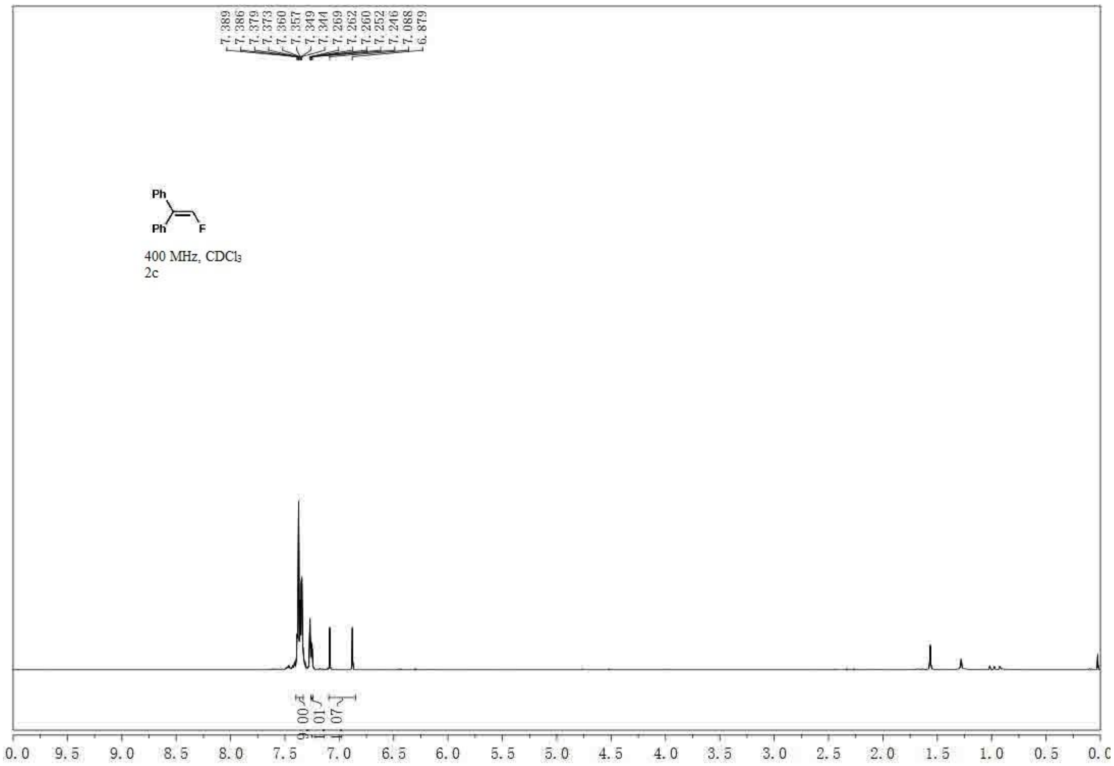
0.13
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200



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7.386
7.379
7.373
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7.357
7.349
7.344
7.269
7.262
7.260
7.252
7.246
7.088
6.879
Ph
Ph
F
400 MHz, CDCl3
2c
9.00
1.01
1.07
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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4.0
3.5
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2.0
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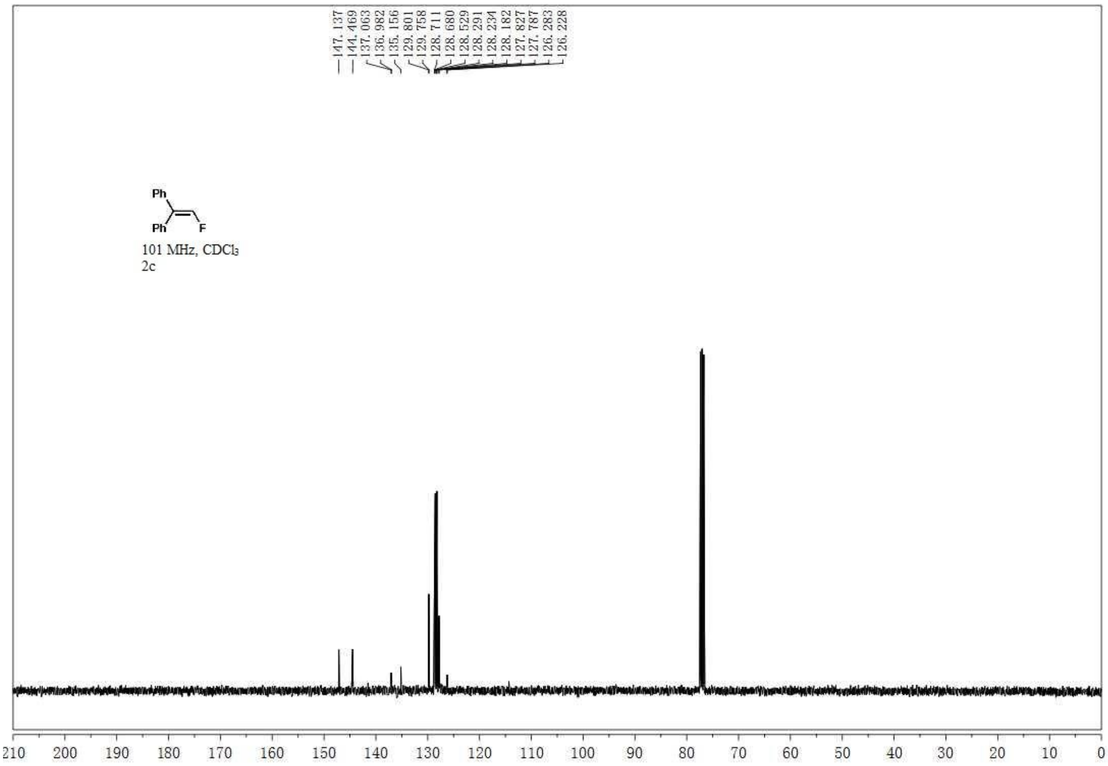
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128.182
127.827
127.787
126.283
126.228
Ph
Ph
F
101 MHz, CDCl3
2c
210
200
190
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150
140
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120
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100
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30
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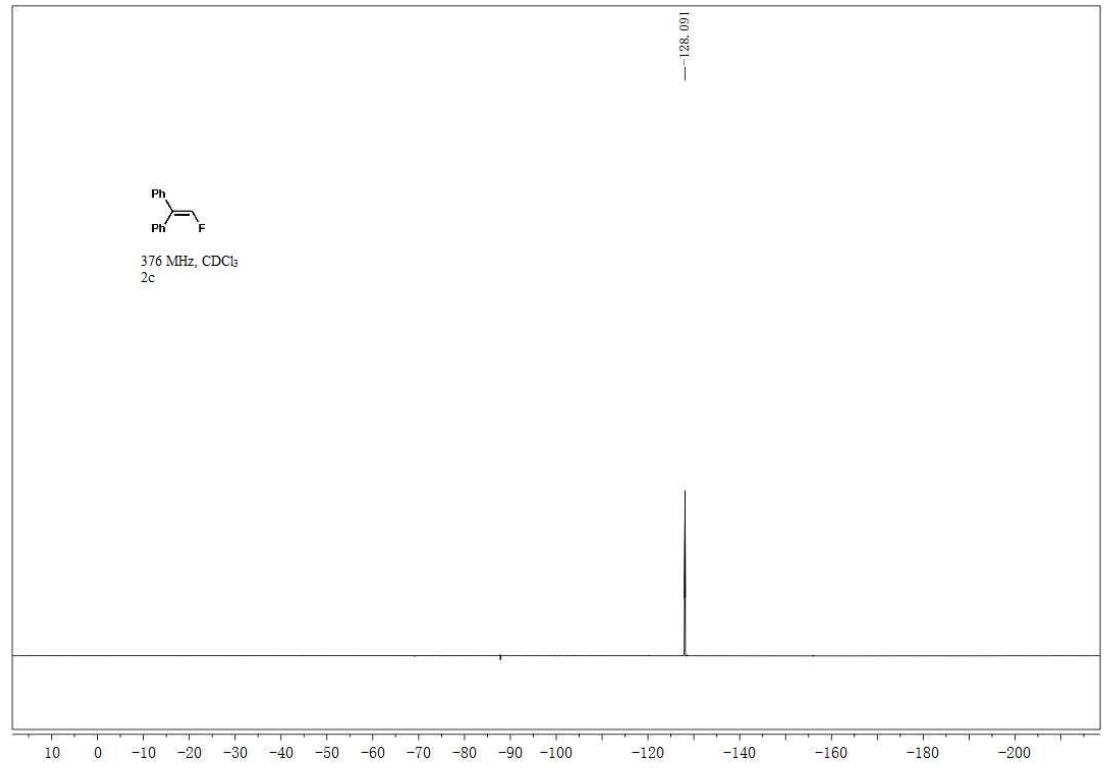
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2c
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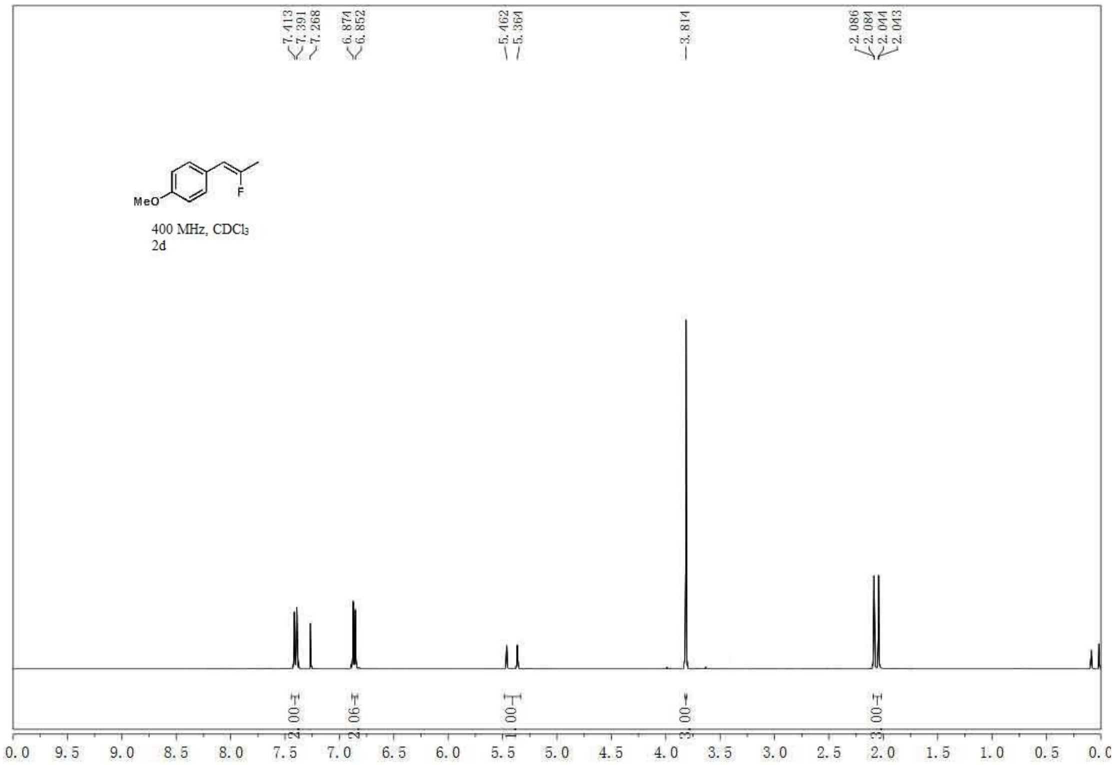
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5.462
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MeO
F
400 MHz, CDCl3
2d
2.00
2.06
1.00
3.00
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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2.0
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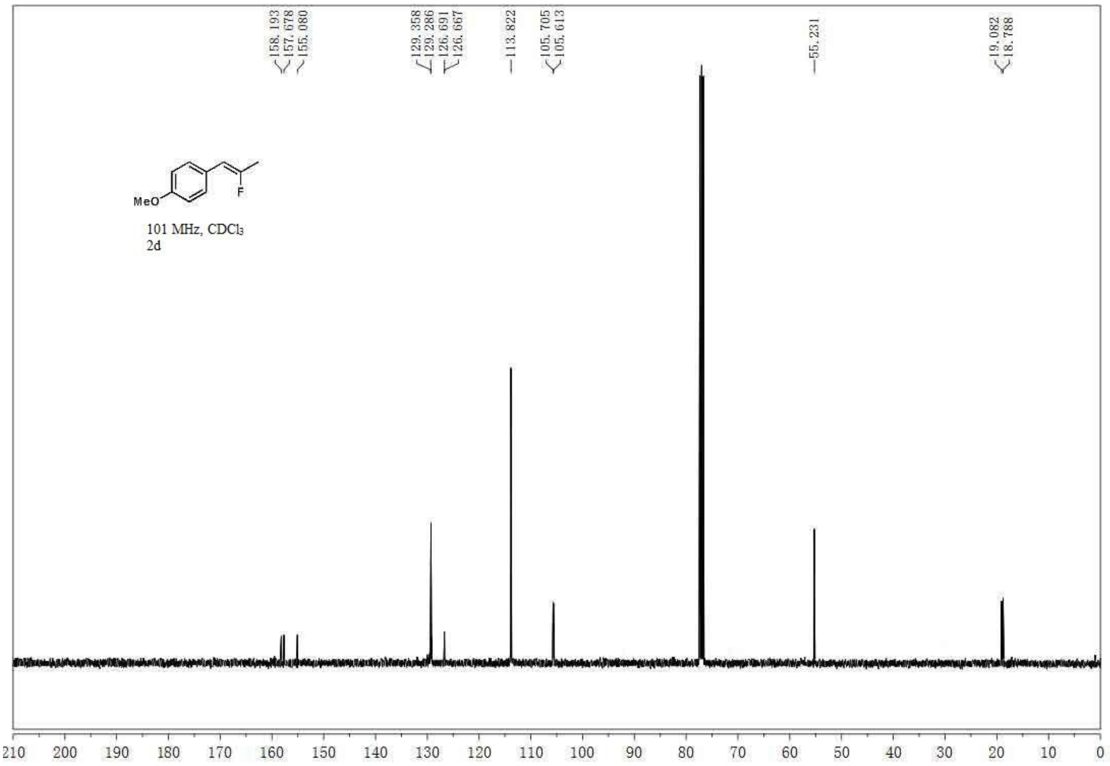
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18.788
MeO
F
101 MHz, CDCl3
2d
210
200
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150
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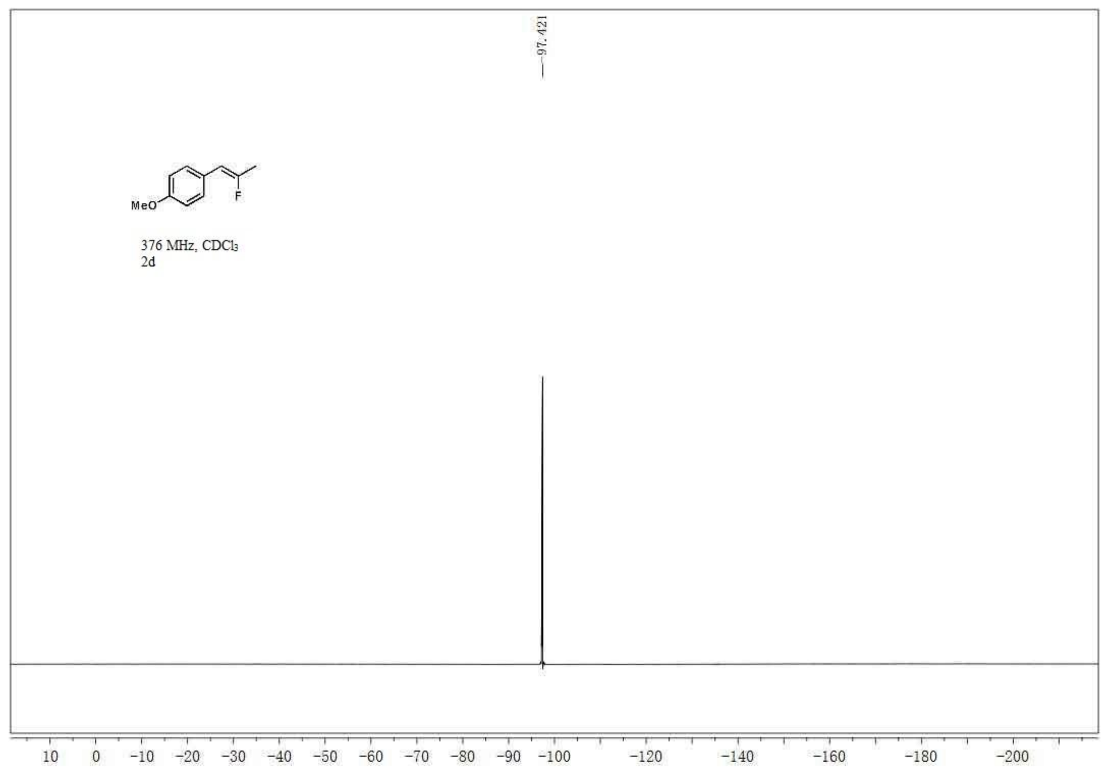
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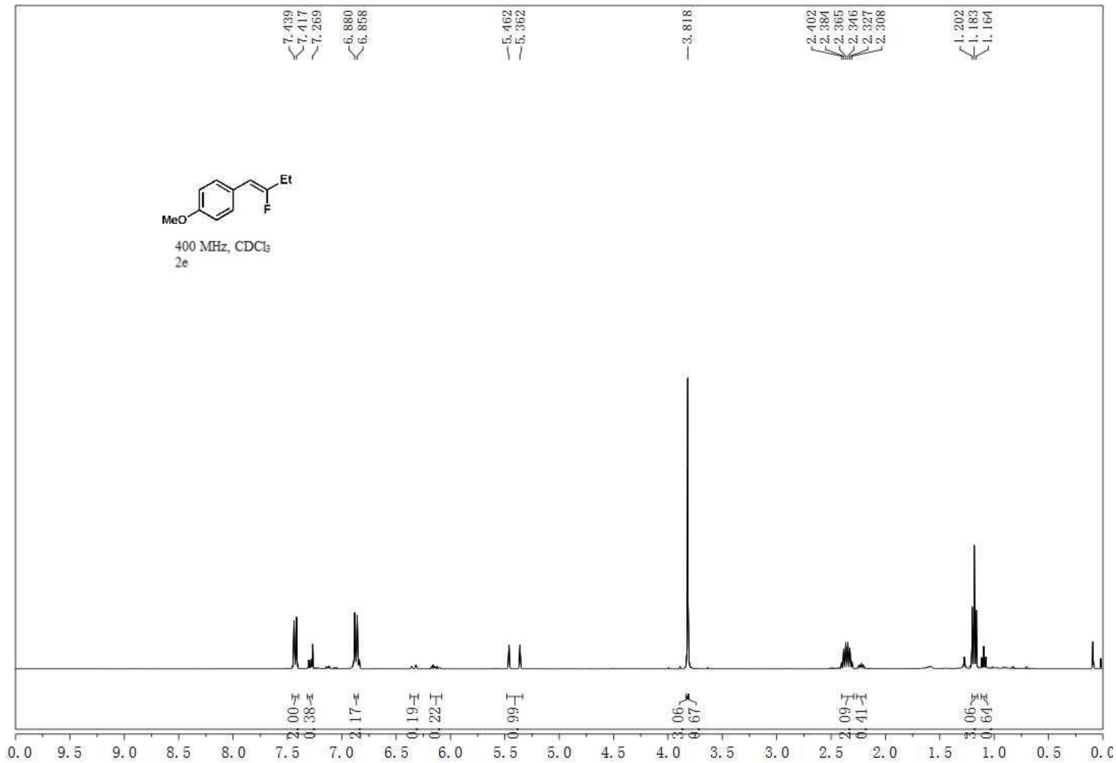
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2.327
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1.202
1.183
1.164
Et
F
MeO
400 MHz, CDCl3
2e
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2.17
0.19
0.22
0.99
3.06
0.67
2.09
0.41
3.06
0.64
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8.0
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7.0
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2.0
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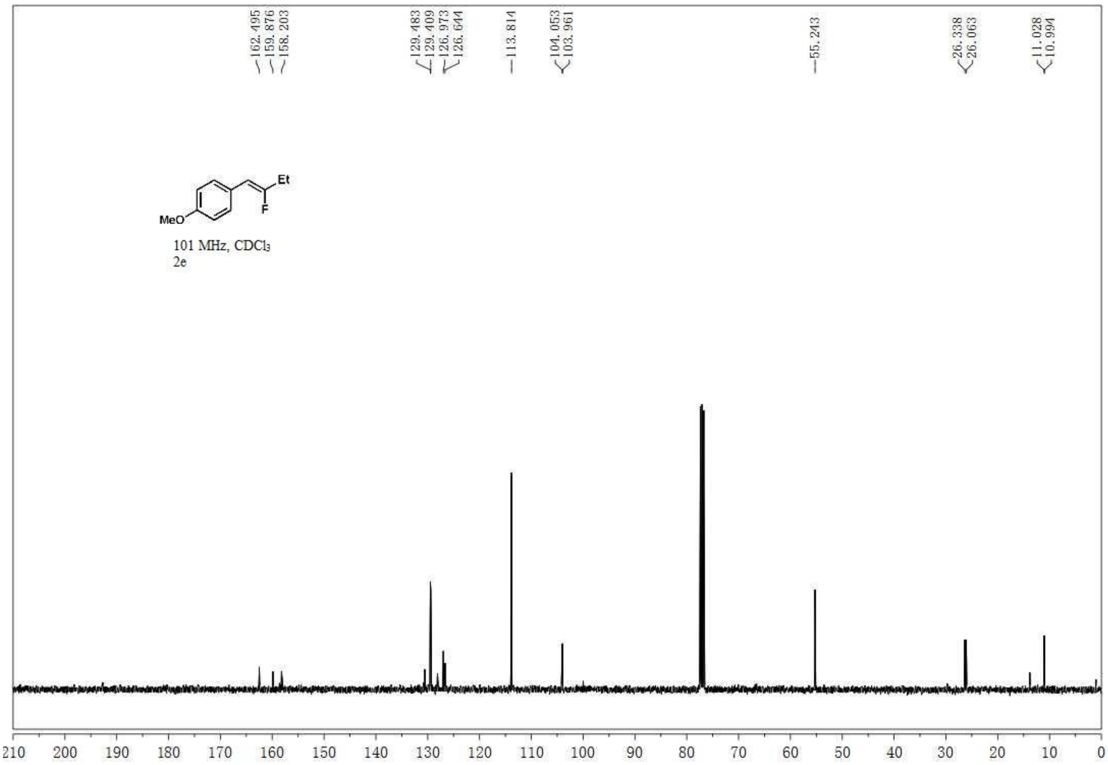
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26.063
11.028
10.994
Et
F
MeO
101 MHz, CDCl3
2e
210
200
190
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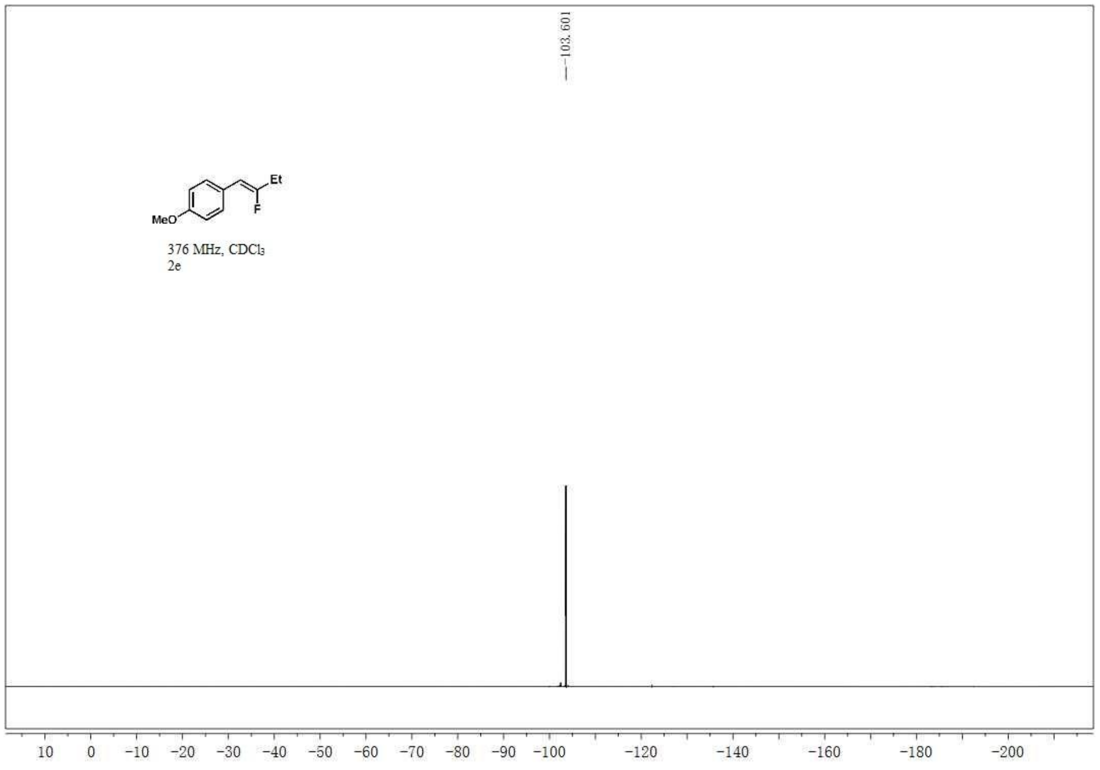
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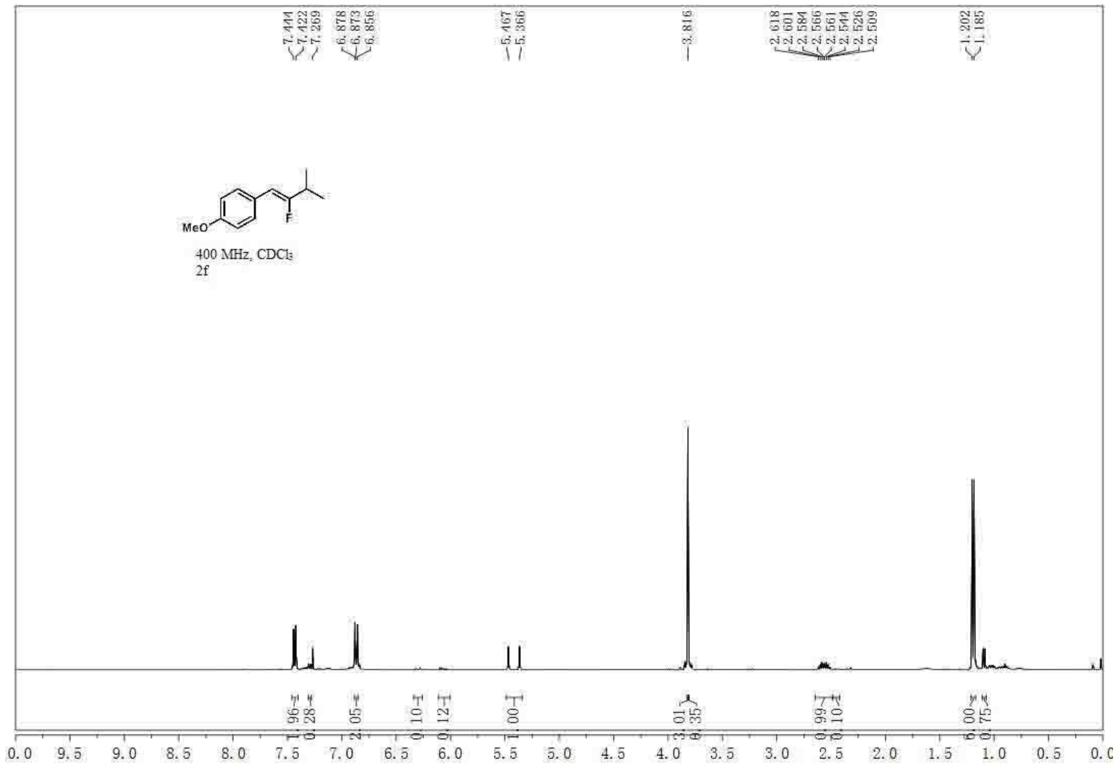
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2.561
2.544
2.526
2.509
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1.185
MeO
F
400 MHz, CDCl3
2f
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0.28
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0.10
0.12
1.00
3.01
0.35
0.99
0.10
6.00
0.75
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8.0
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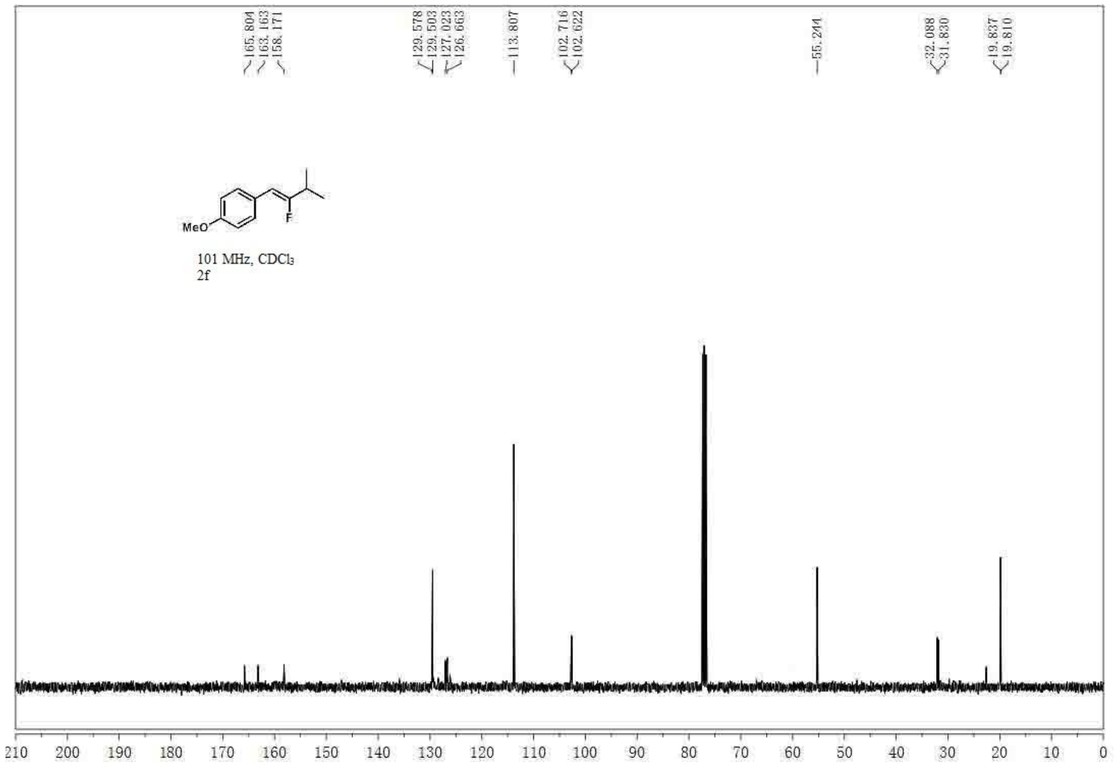
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101 MHz, CDCl3
2f
210
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10
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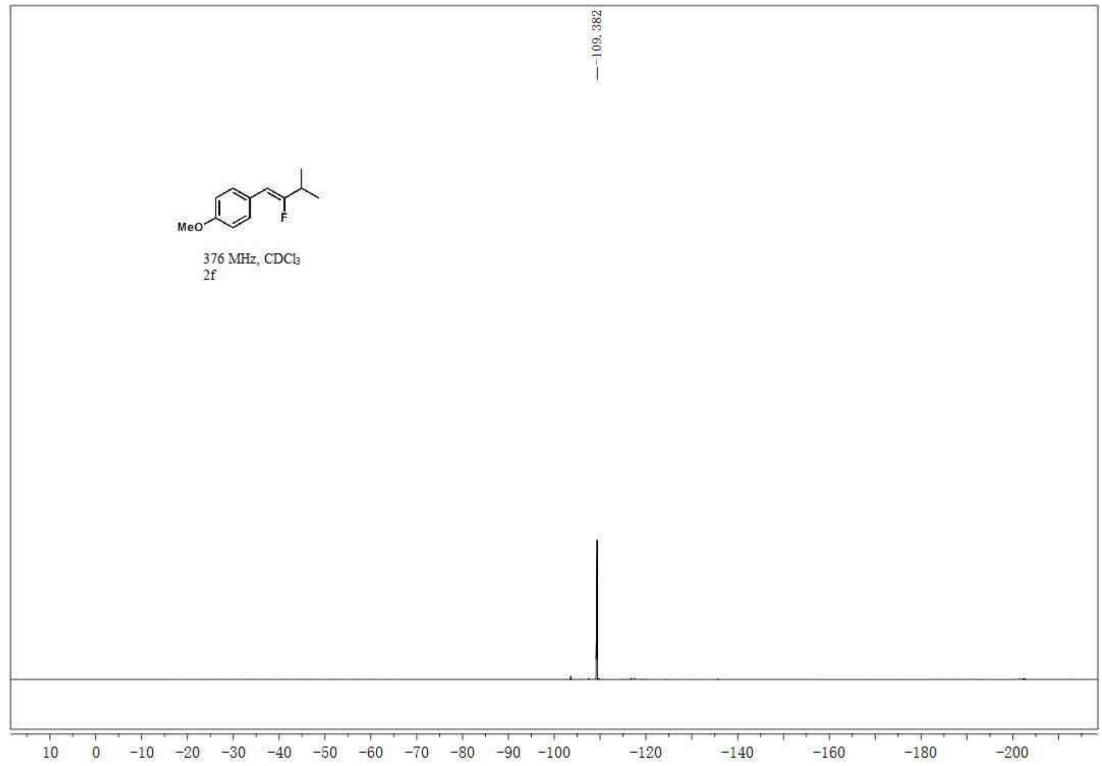

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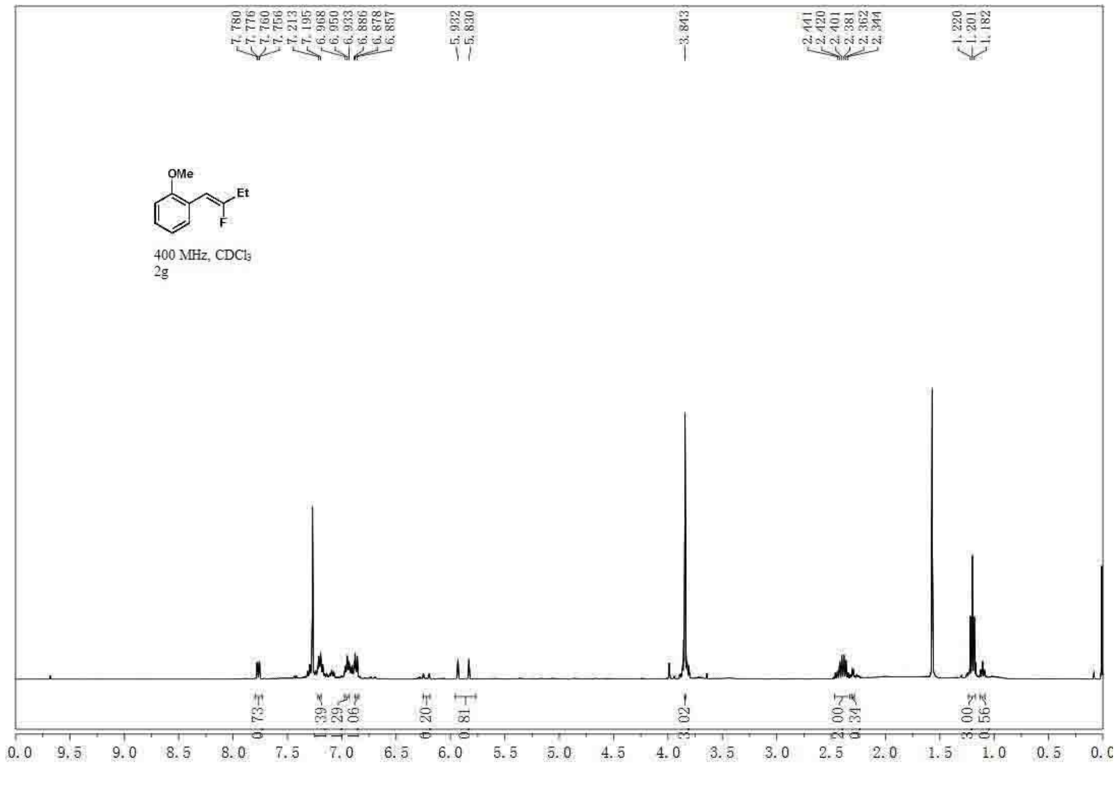

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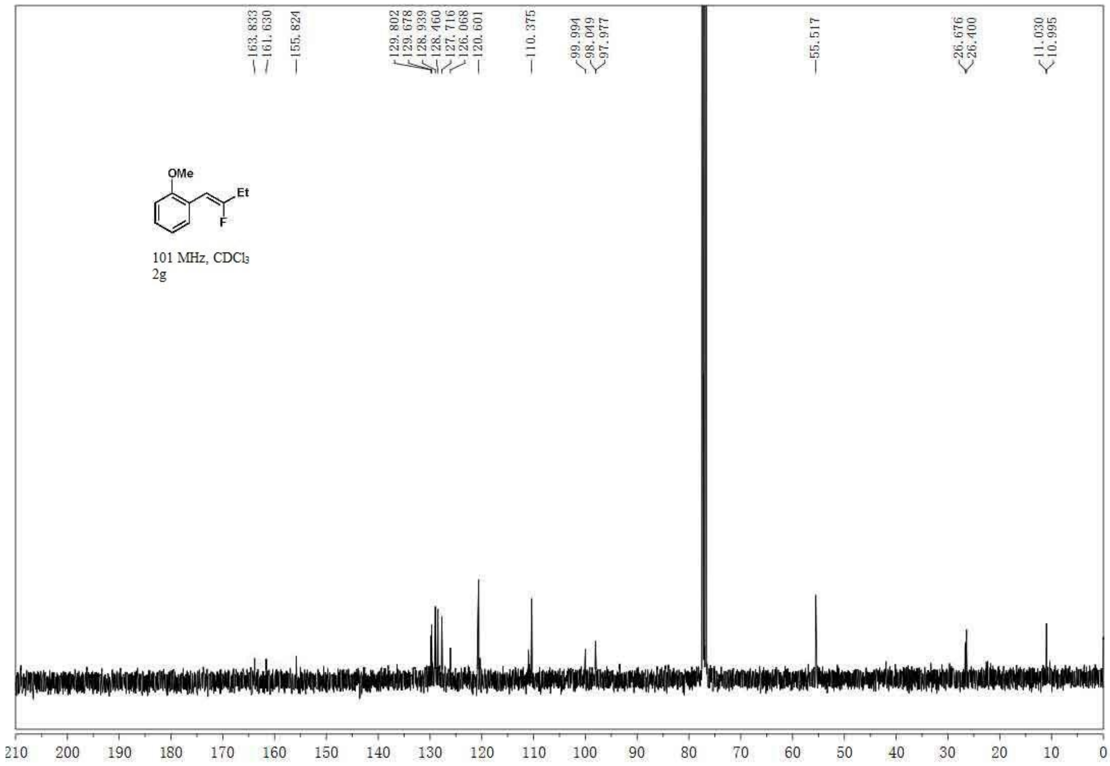
5.932 5.830
3.843
2.441 2.420 2.401 2.381 2.362 2.344
1.220 1.201 1.182
OMe
Et
F
400 MHz, CDCl3
2g
0.73 1.39 1.29 1.06 0.20 0.81 3.02 2.00 0.34 3.00 0.56
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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2g
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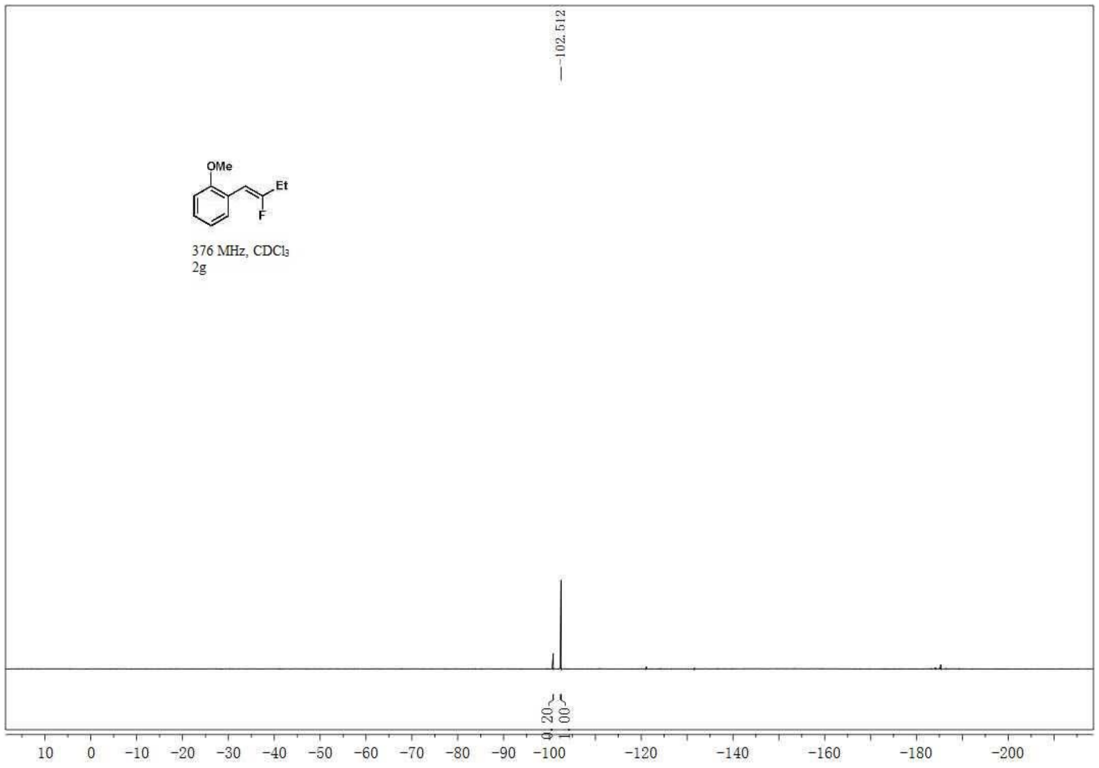
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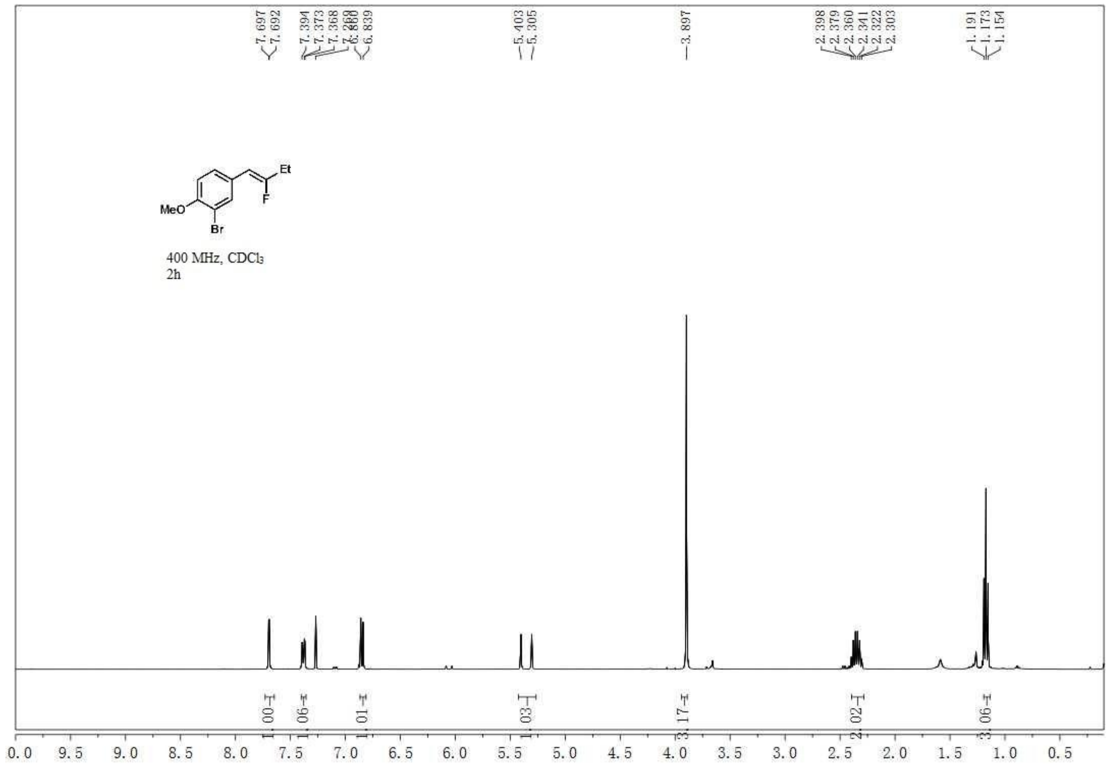
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2.360
2.341
2.322
2.303
1.191
1.173
1.154
MeO
Br
F
Et
400 MHz, CDCl3
2h
1.00
1.06
1.01
1.03
3.17
2.02
3.06
0.0
9.5
9.0
8.5
8.0
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7.0
6.5
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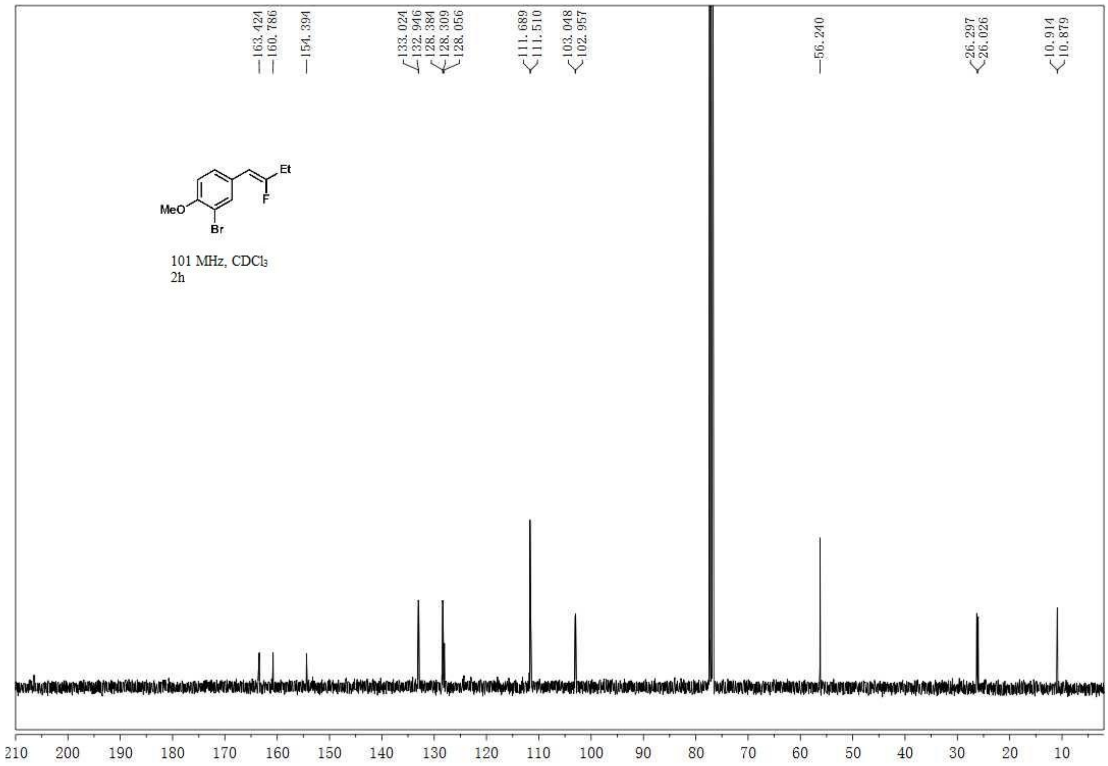
1.0
0.5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56.240
26.297
26.026
10.914
10.879
MeO
Br
F
Et
101 MHz, CDCl3
2h
210
200
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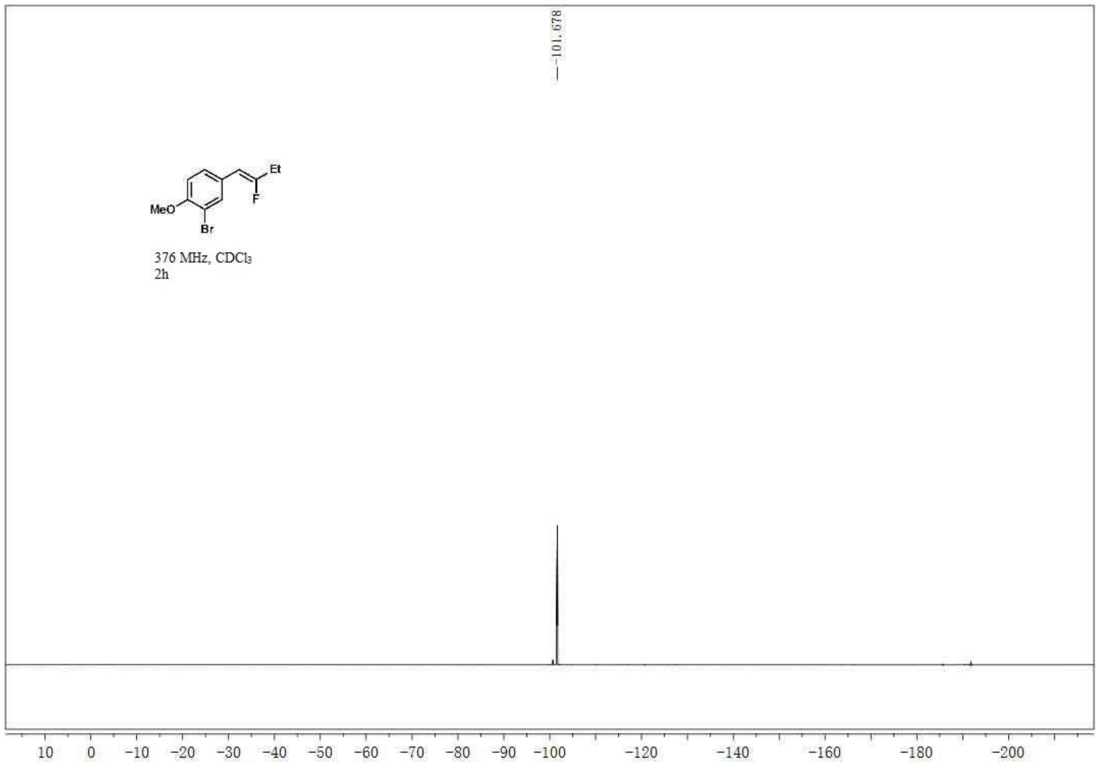

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Et
MeO
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376 MHz, CDCl3
2h
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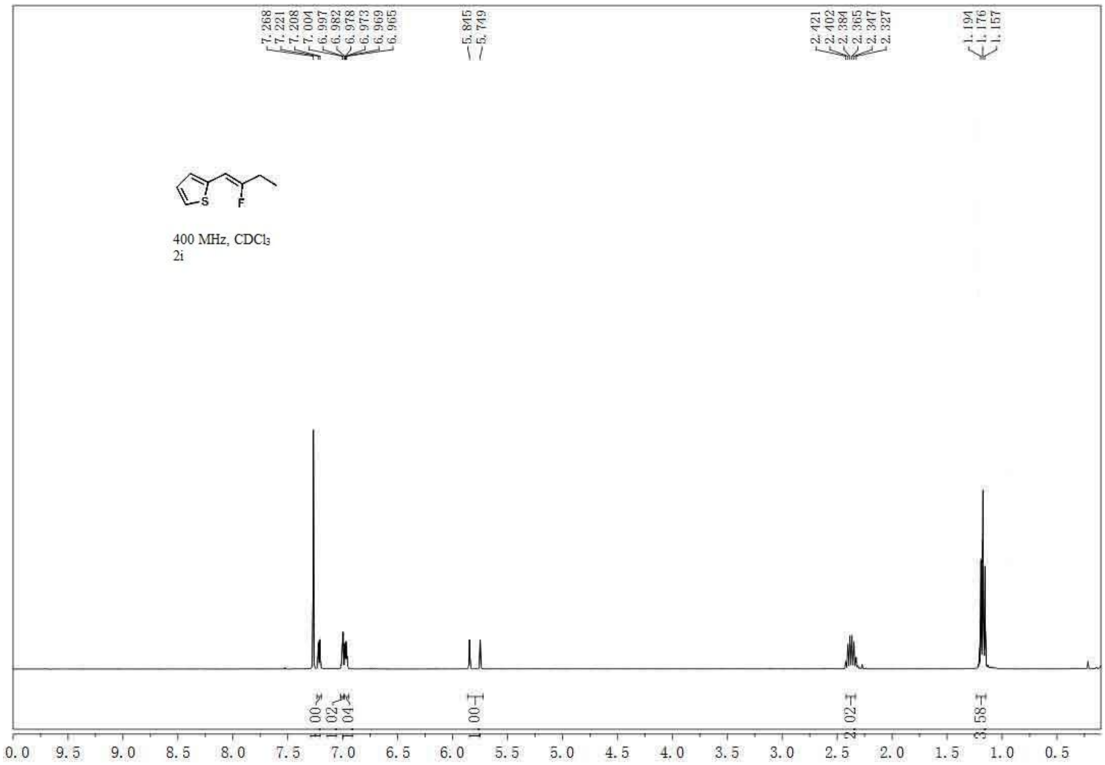

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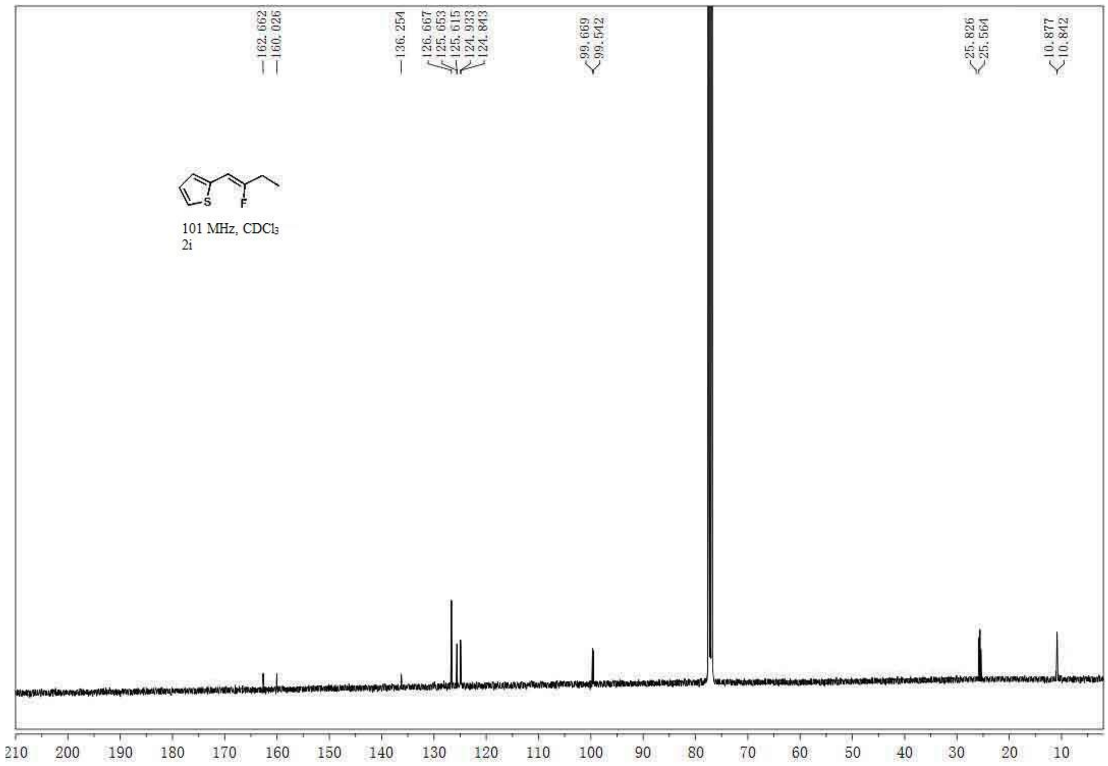
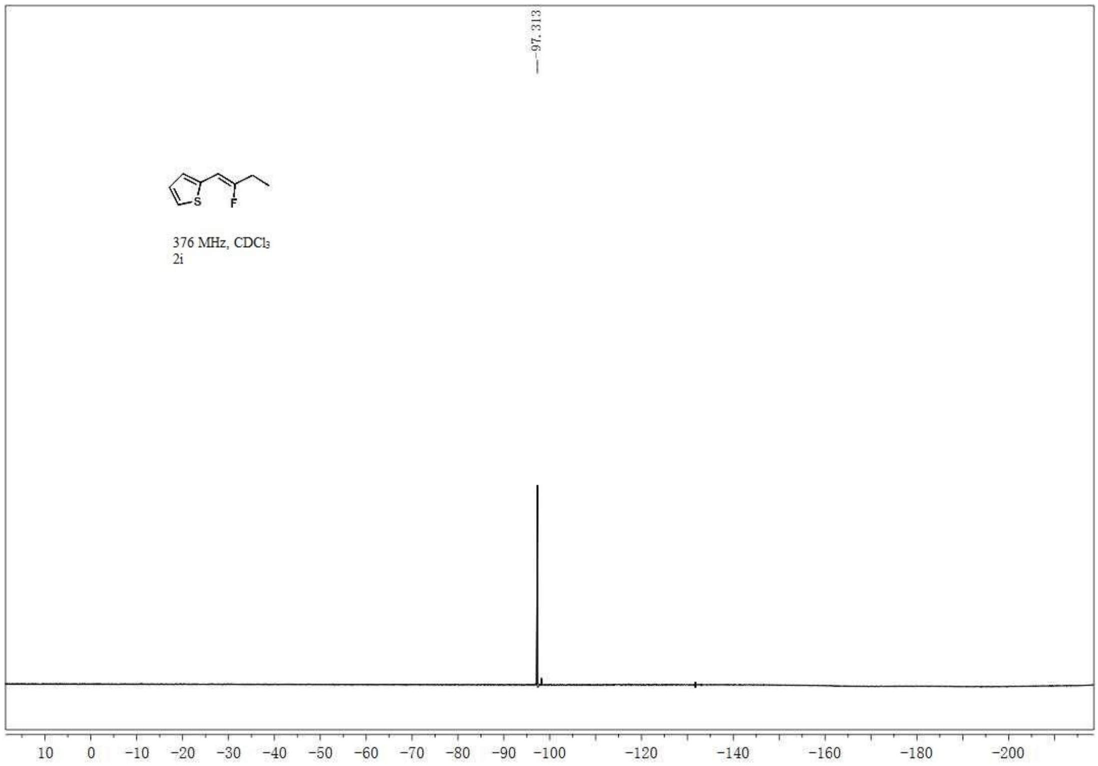
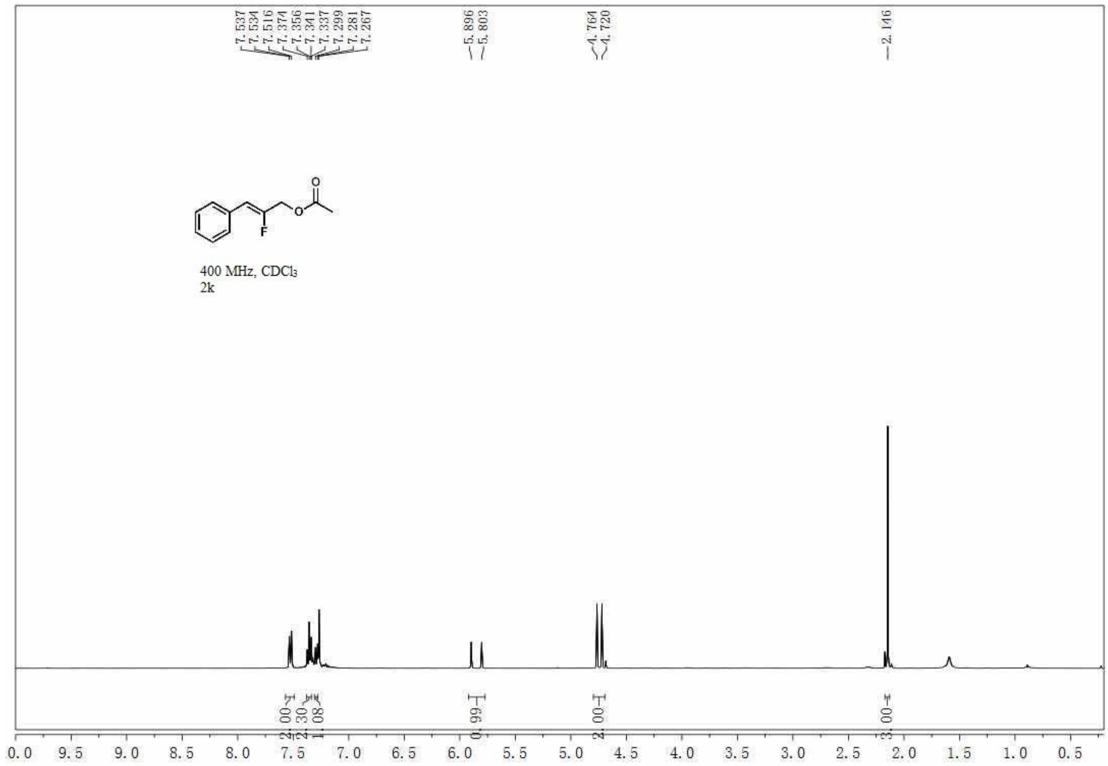
S
F
400 MHz, CDCl3
2i
1.00
1.02
1.04
1.00
2.02
3.58
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5

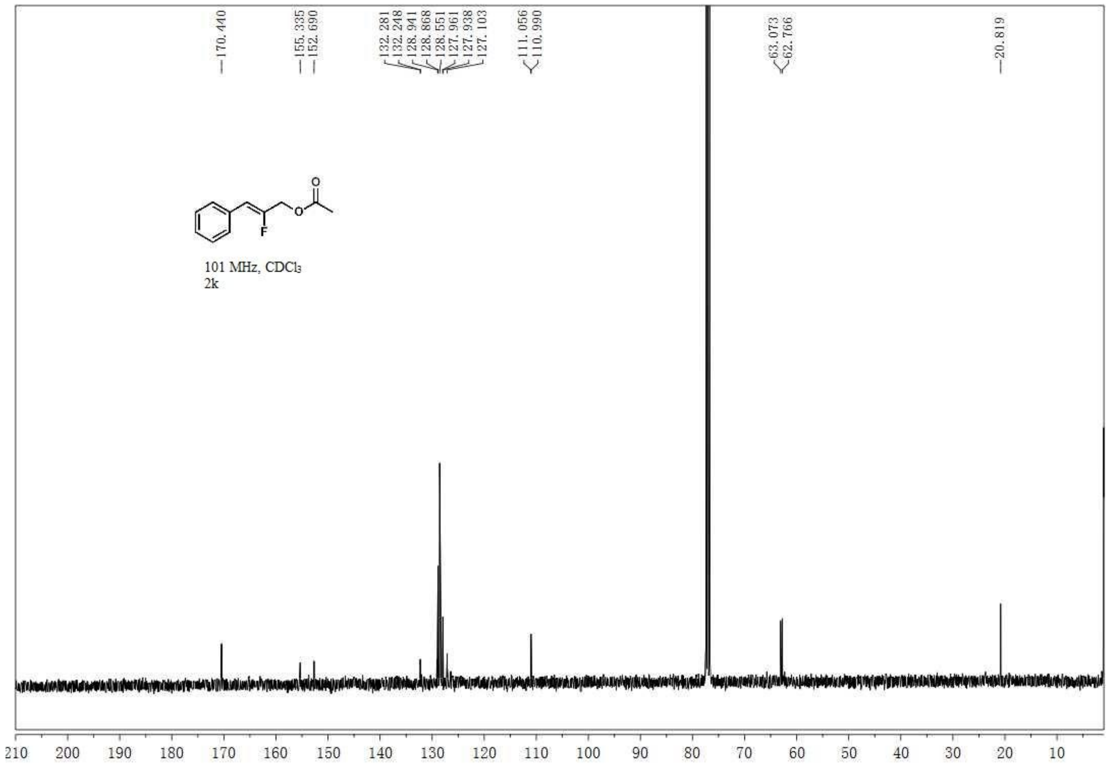


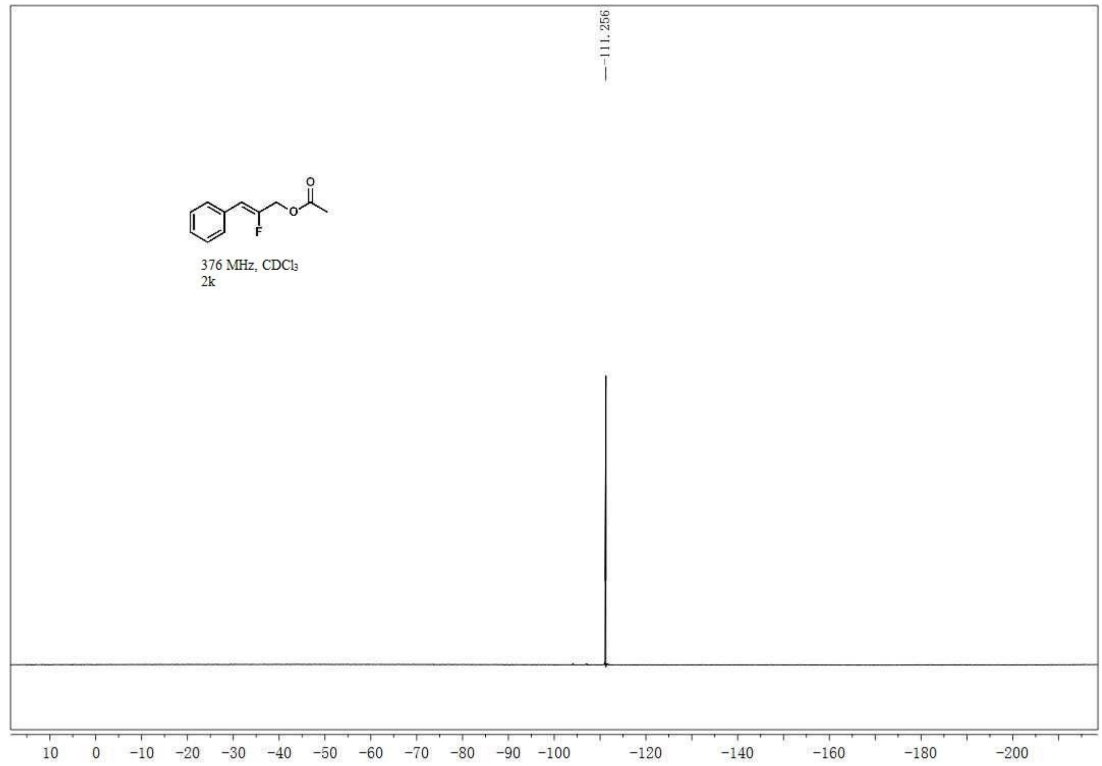
162.662
160.026
136.254
126.667
125.653
125.615
124.933
124.843
99.669
99.542
25.826
25.564
10.877
10.842
S
F
101 MHz, CDCl3
2i
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

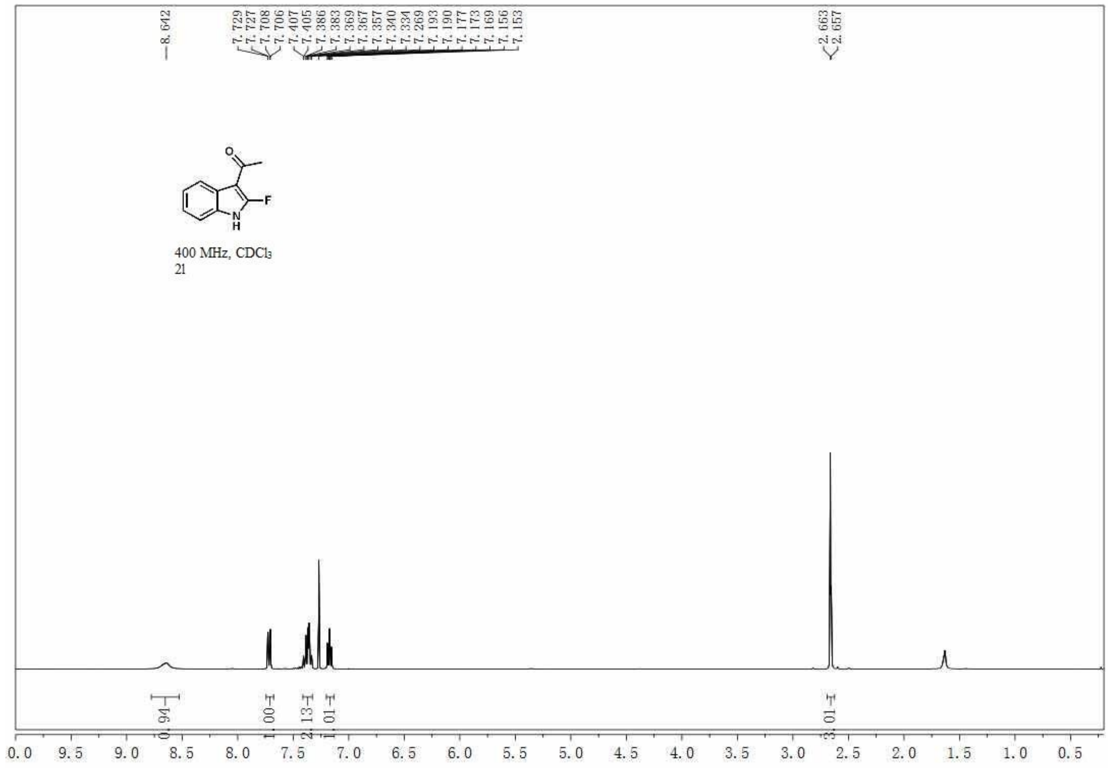


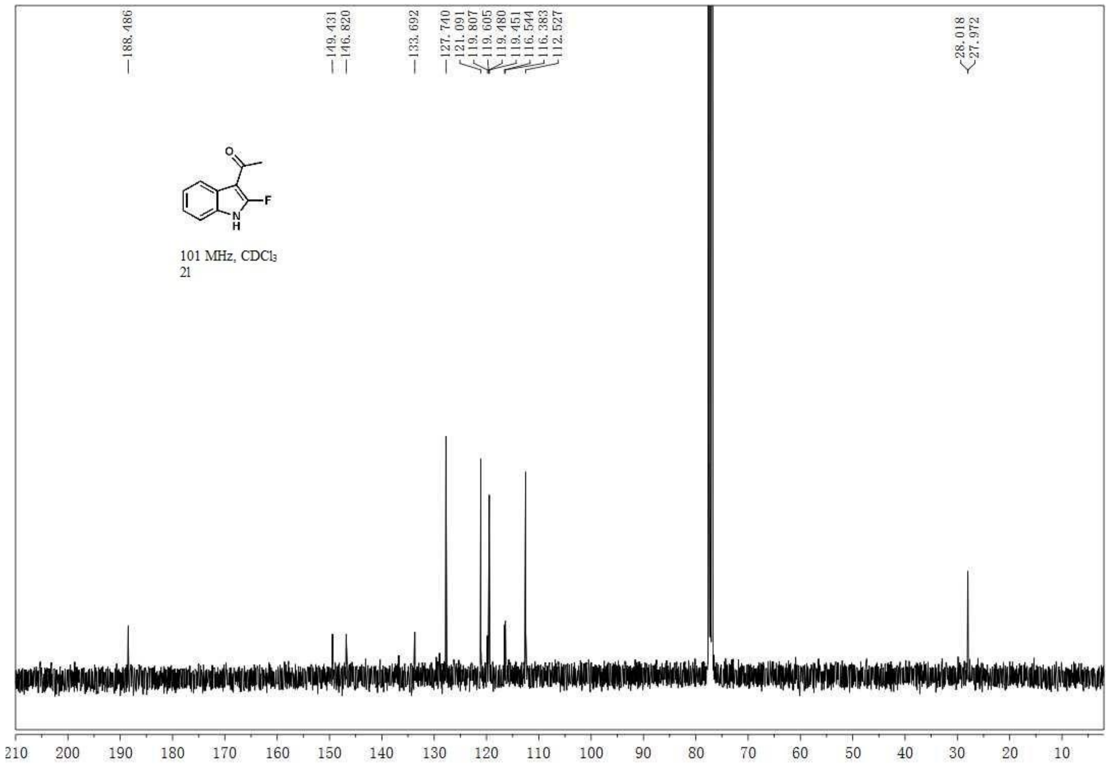
-97.313
S
F
376 MHz, CDCl3
2i
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200

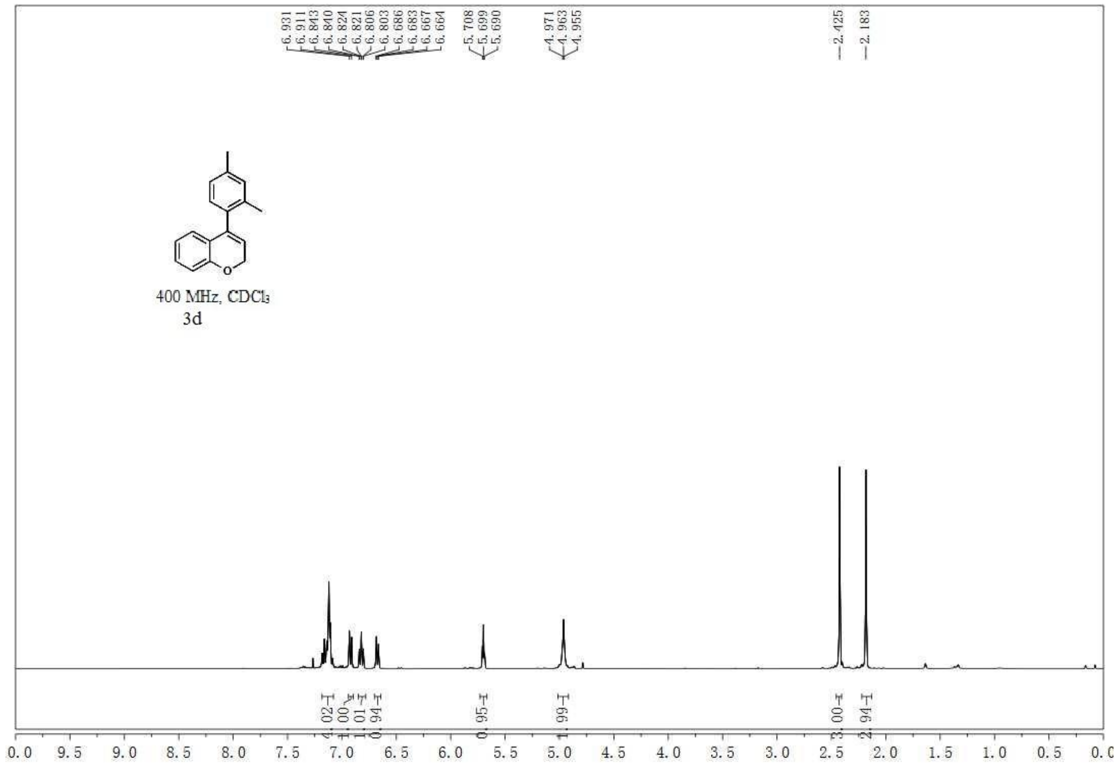

7.537
7.534
7.516
7.374
7.356
7.341
7.337
7.299
7.281
7.267
5.896
5.803
4.764
4.720
2.146
O
F
400 MHz, CDCl3
2k
2.00
2.30
1.08
0.99
2.00
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

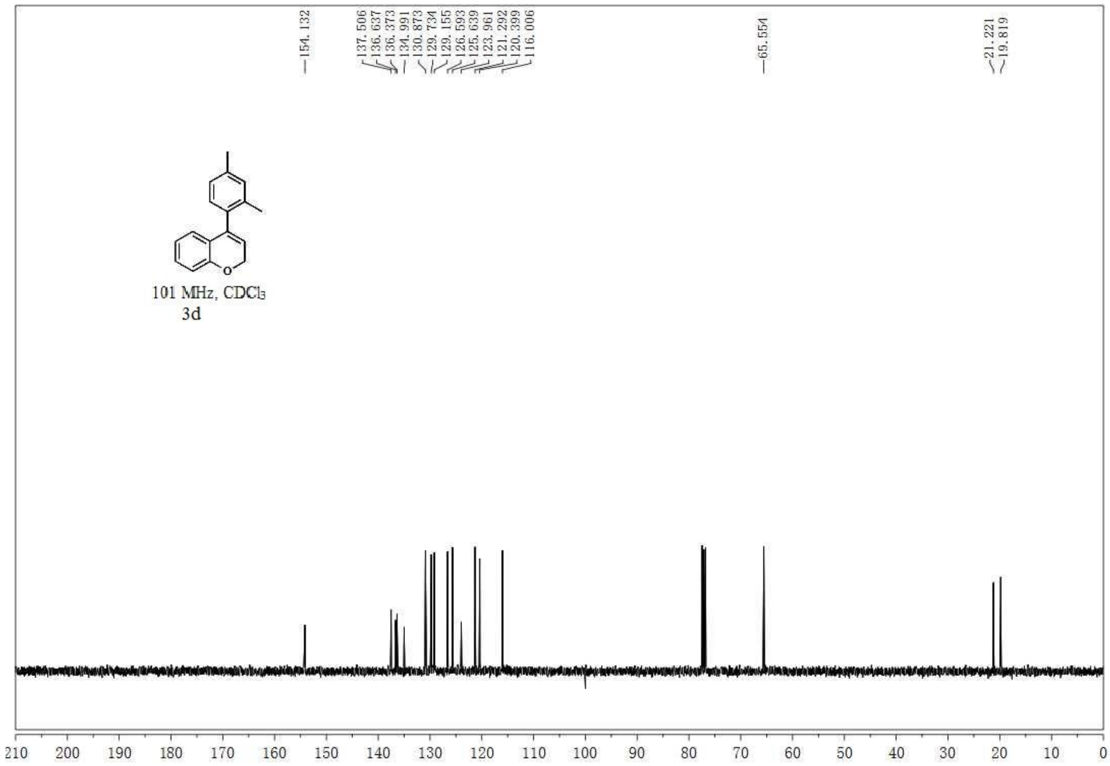

170.440
155.335
152.690
132.281
132.248
128.941
128.868
128.551
127.961
127.938
127.103
111.056
110.990
63.073
62.766
20.819
O
F
101 MHz, CDCl3
2k
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


-111.256
376 MHz, CDCl3
2k
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200

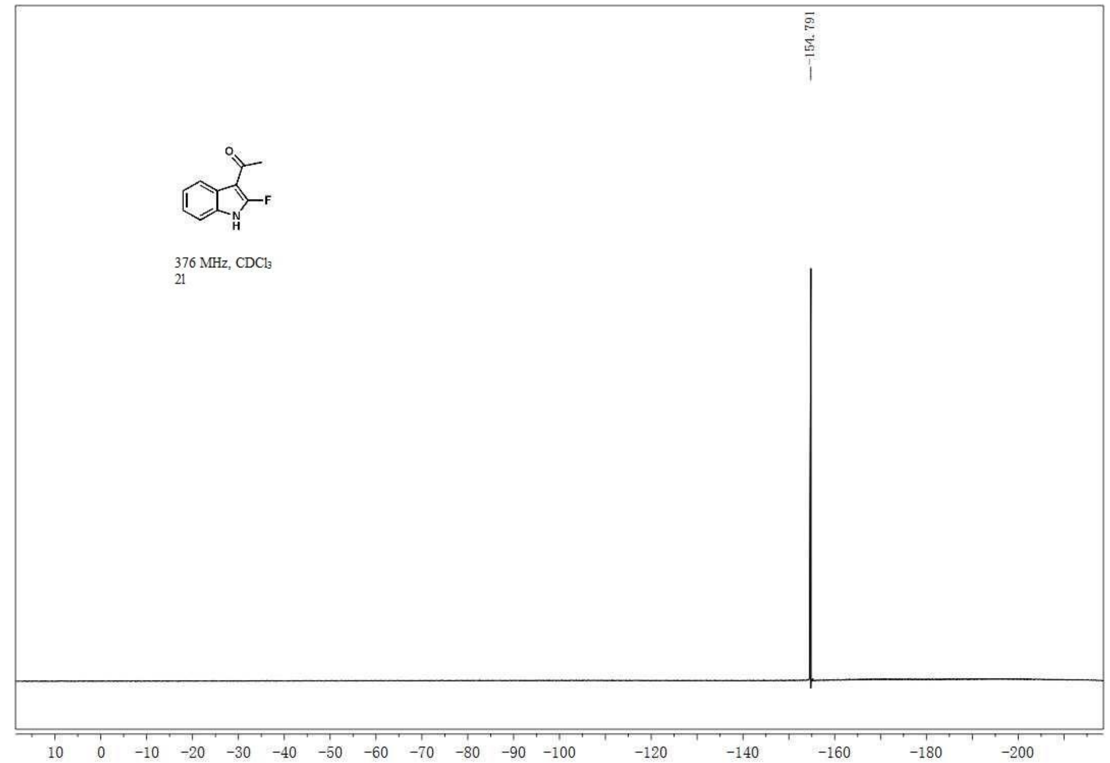

8.642
7.729
7.727
7.708
7.706
7.407
7.405
7.386
7.383
7.369
7.367
7.357
7.340
7.334
7.269
7.193
7.190
7.177
7.173
7.169
7.156
7.153
2.663
2.657
400 MHz, CDCl3
2l
0.94
1.00
2.13
1.01
3.01
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


188.486
149.431
146.820
133.692
127.740
121.091
119.807
119.605
119.480
119.451
116.544
116.383
112.527
28.018
27.972
O
F
N
H
101 MHz, CDCl3
2l
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

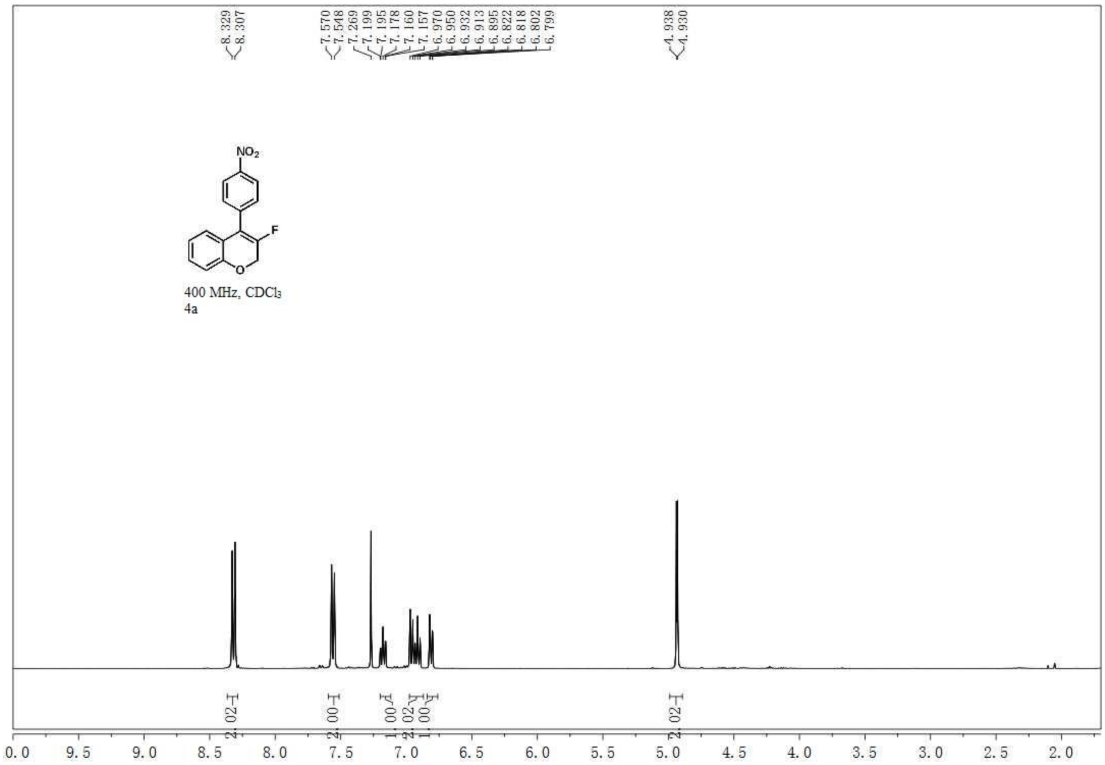

6.931
6.911
6.843
6.840
6.824
6.821
6.806
6.803
6.686
6.683
6.667
6.664
5.708
5.699
5.690
4.971
4.963
4.955
2.425
2.183
O
400 MHz, CDCl3
3d
4.02
1.00
1.01
0.94
0.95
1.99
3.00
2.94
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

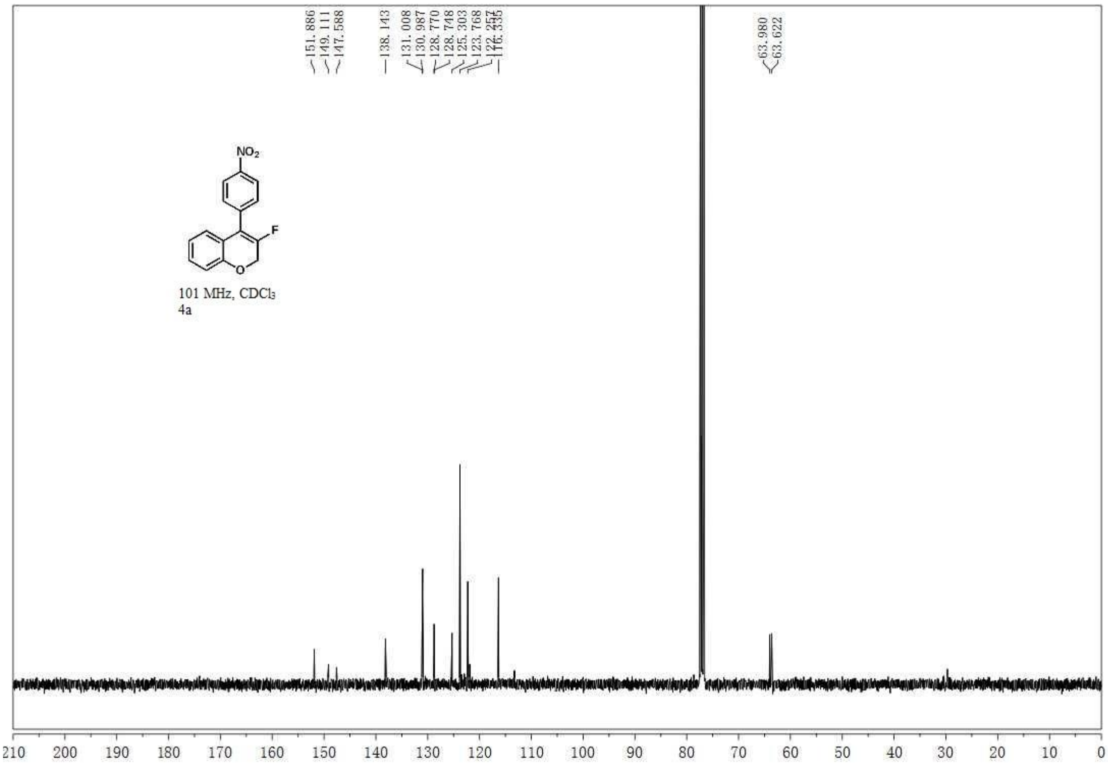


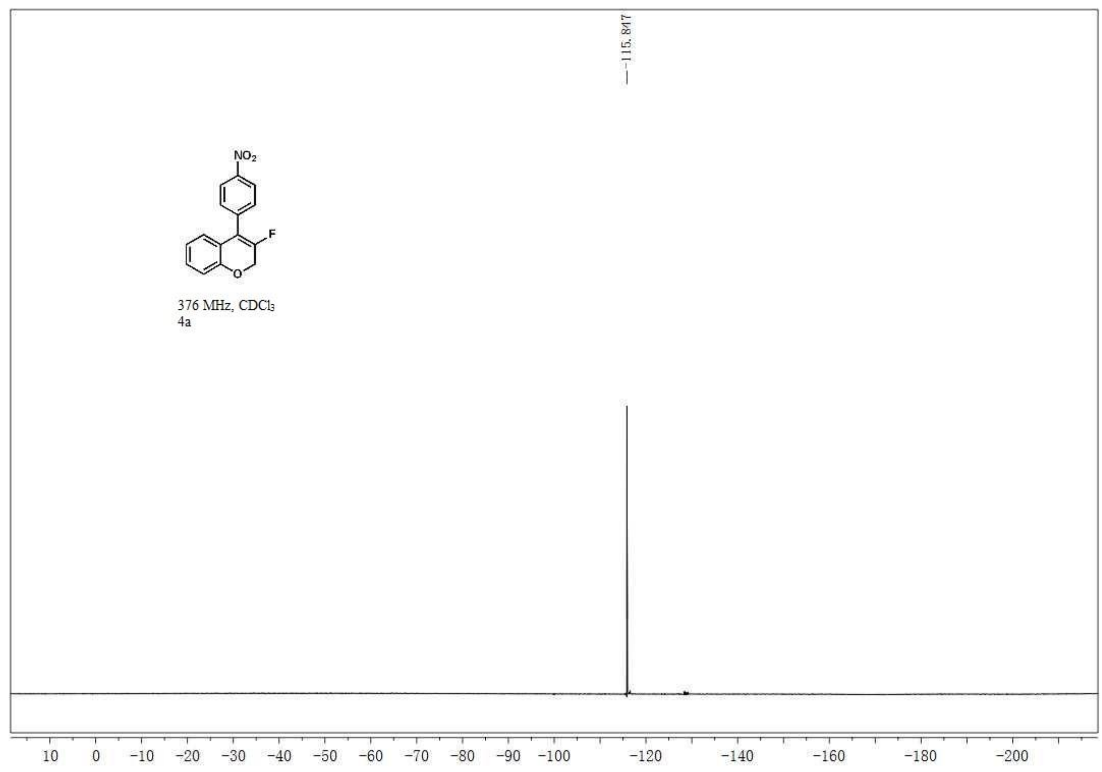
154.132
137.506
136.637
136.373
134.991
130.873
129.734
129.155
126.593
125.639
123.961
121.292
120.399
116.006
65.554
21.221
19.819
O
101 MHz, CDCl3
3d
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



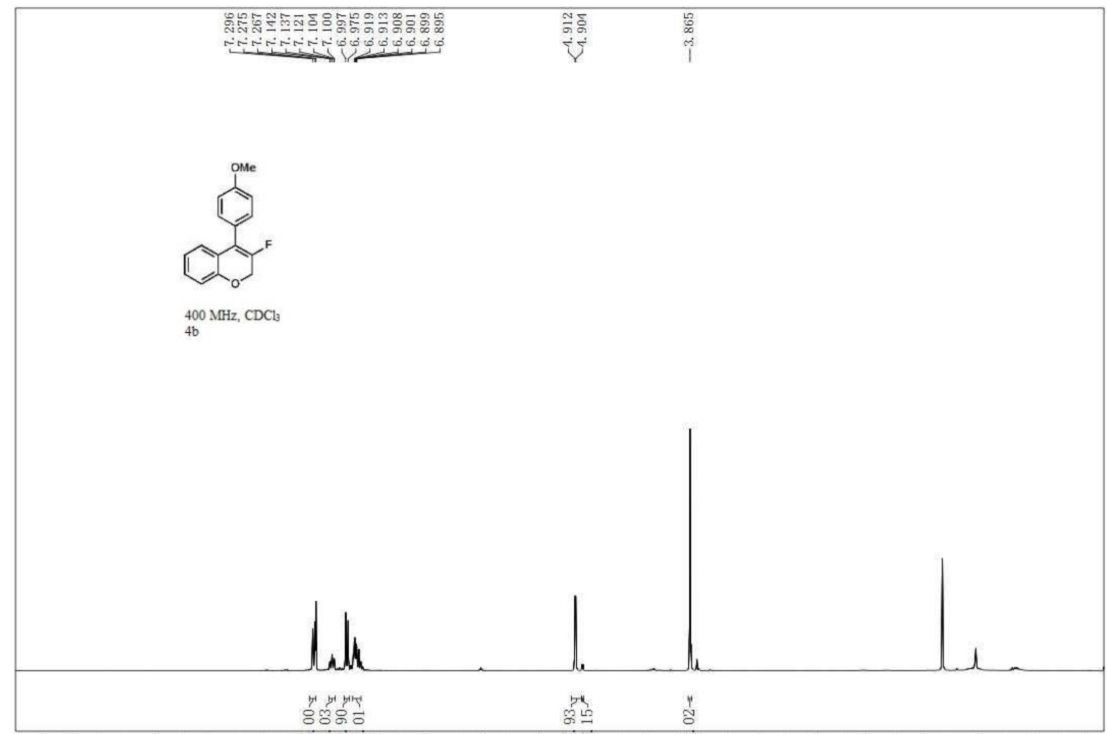
-154.791
O
F
N
H
376 MHz, CDCl3
2l
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200


8.329
8.307
7.570
7.548
7.269
7.199
7.195
7.178
7.160
7.157
6.970
6.950
6.932
6.913
6.895
6.822
6.818
6.802
6.799
4.938
4.930
NO2
F
O
400 MHz, CDCl3
4a
2.02
2.00
1.00
2.02
1.00
2.02
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0

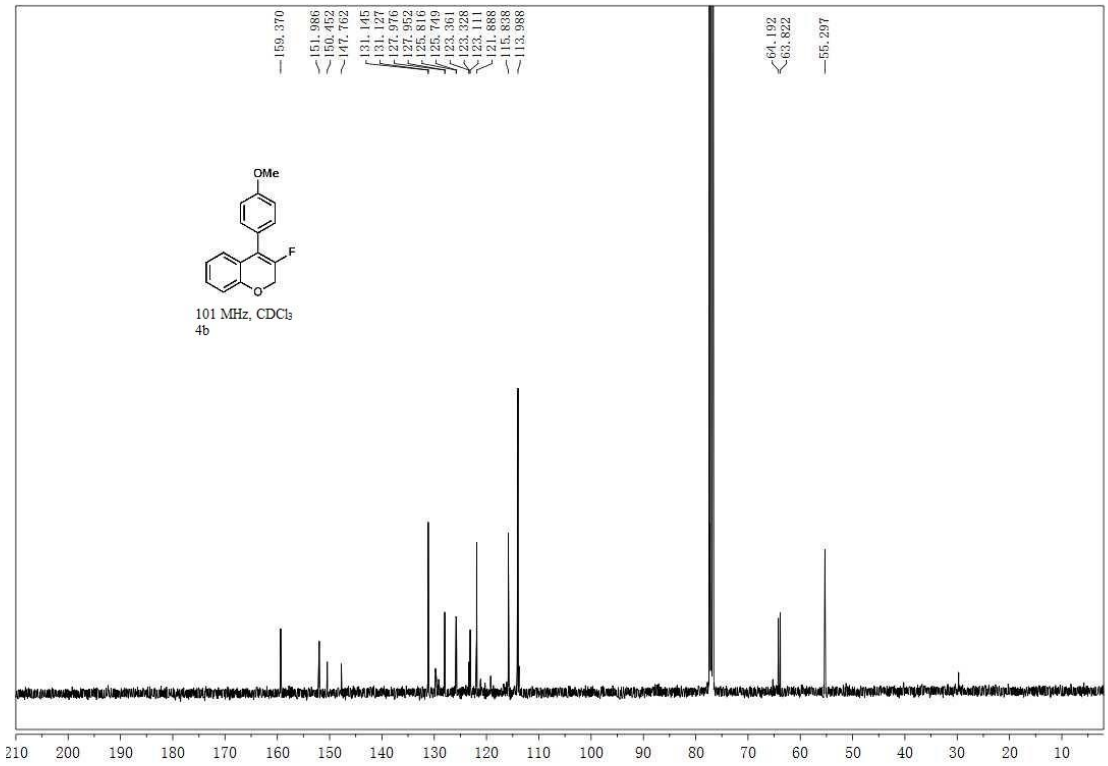

151.886
149.111
147.588
138.143
131.008
130.987
128.770
128.748
125.303
123.768
122.257
116.335
63.980
63.622
NO2
F
O
101 MHz, CDCl3
4a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

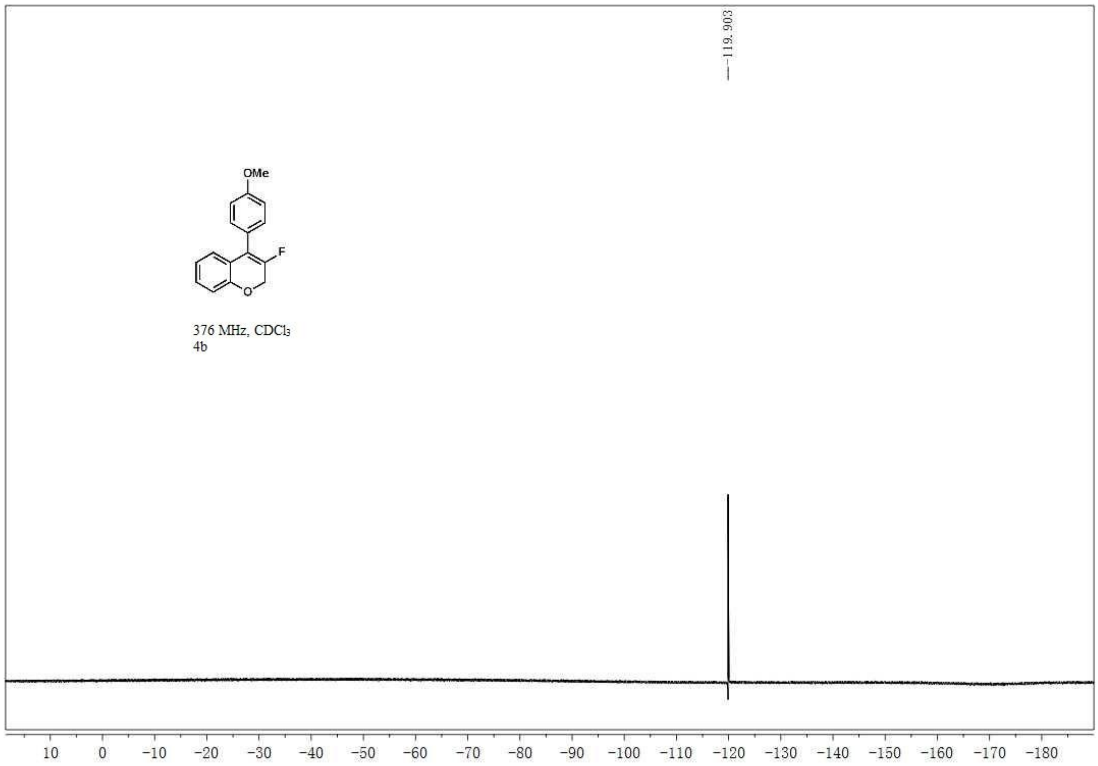


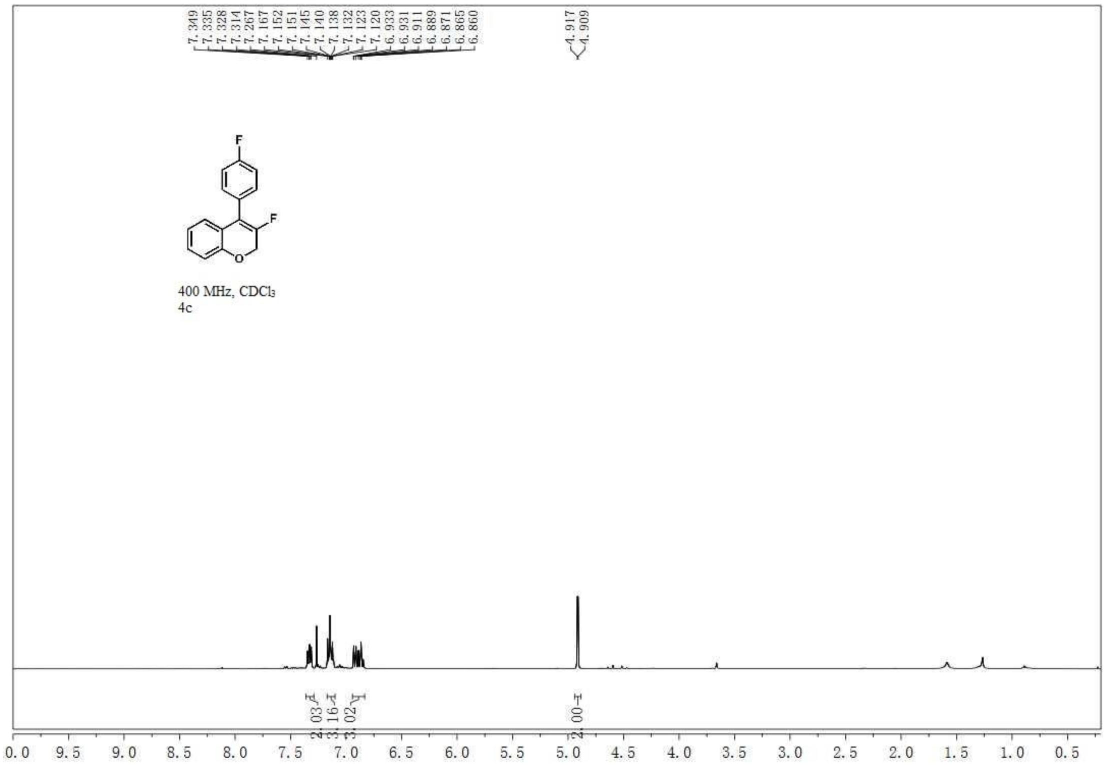
-115.847
NO2
F
O
376 MHz, CDCl3
4a
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200

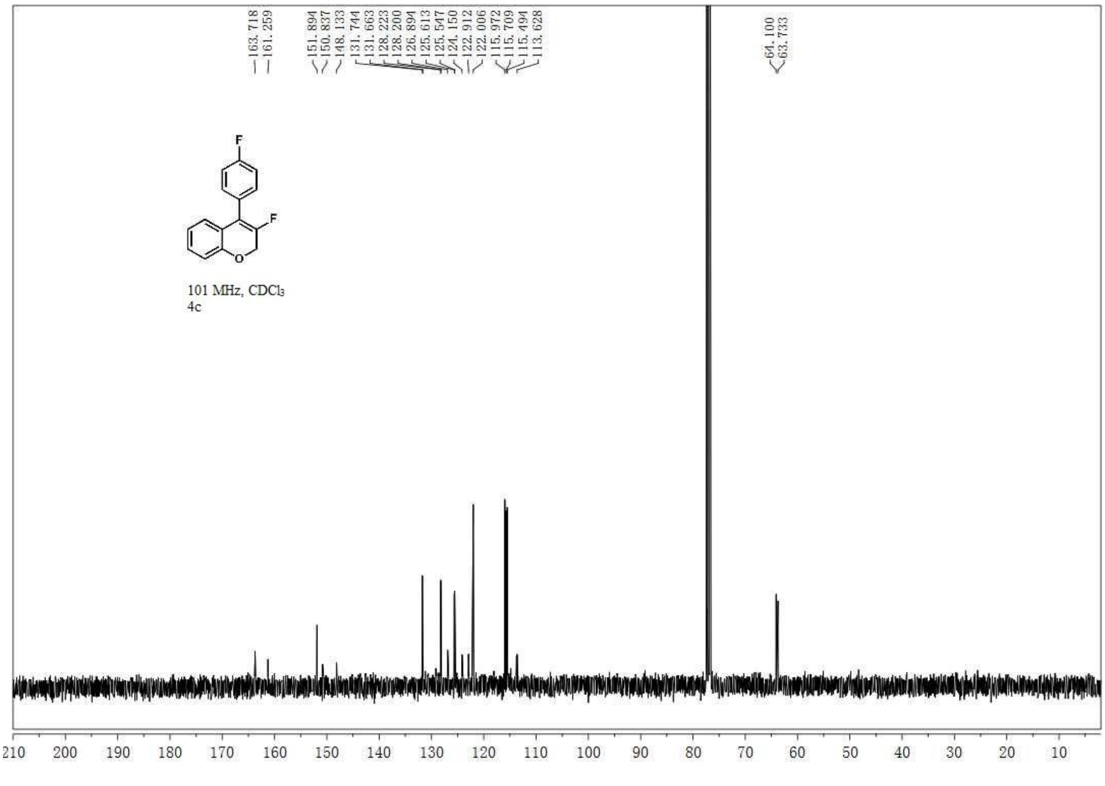


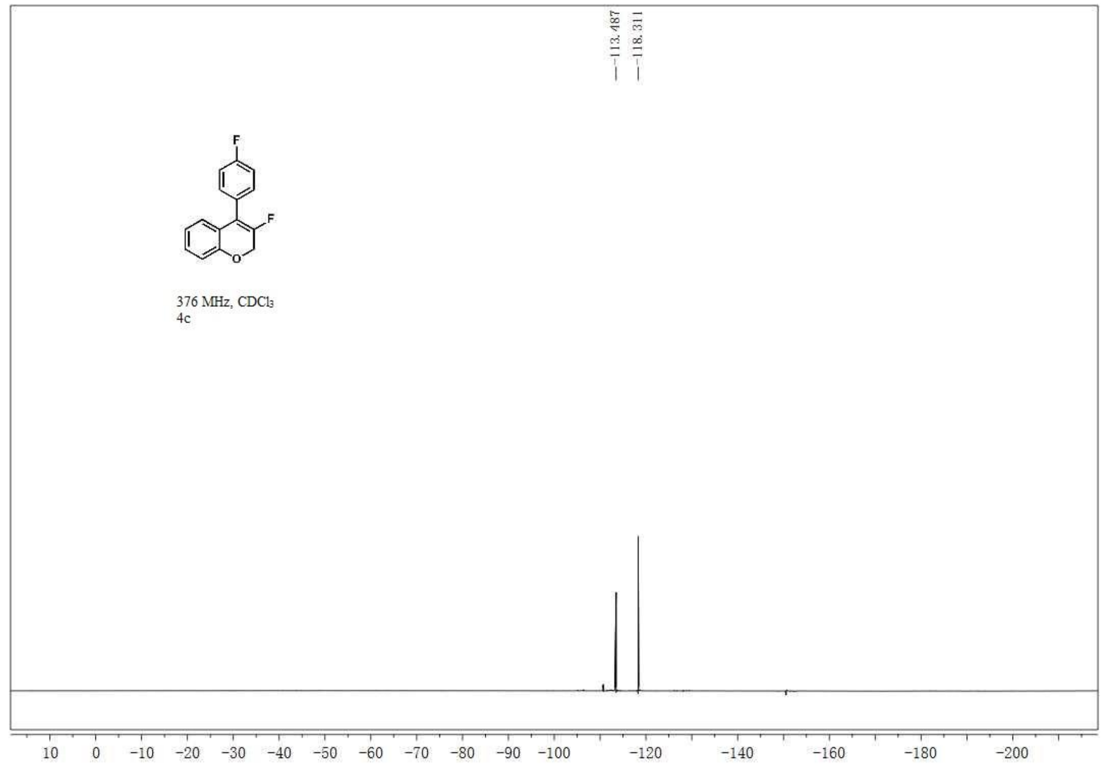
7.296
7.275
7.267
7.142
7.137
7.121
7.104
7.100
6.997
6.975
6.919
6.913
6.908
6.901
6.899
6.895
4.912
4.904
3.865
OMe
F
O
400 MHz, CDCl3
4b
2.00
1.03
1.90
3.01
1.93
0.15
3.02
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


159.370
151.986
150.452
147.762
131.145
131.127
127.976
127.952
125.816
125.749
123.361
123.328
123.111
121.888
115.838
113.988
64.192
63.822
55.297
OMe
F
O
101 MHz, CDCl3
4b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

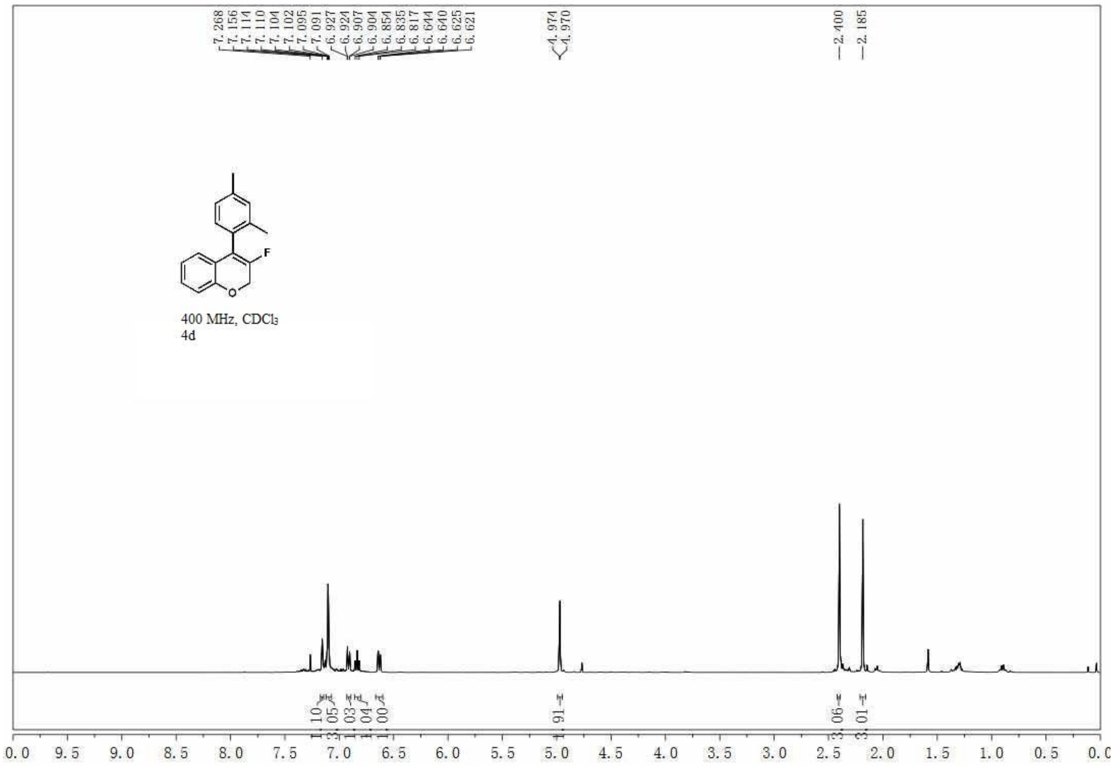

-119.903
OMe
F
O
376 MHz, CDCl3
4b
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180


7.349
7.335
7.328
7.314
7.267
7.167
7.152
7.151
7.145
7.140
7.138
7.132
7.123
7.120
6.933
6.931
6.911
6.889
6.871
6.865
6.860
4.917
4.909
F
F
O
400 MHz, CDCl3
4c
2.03
3.16
3.02
2.00
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

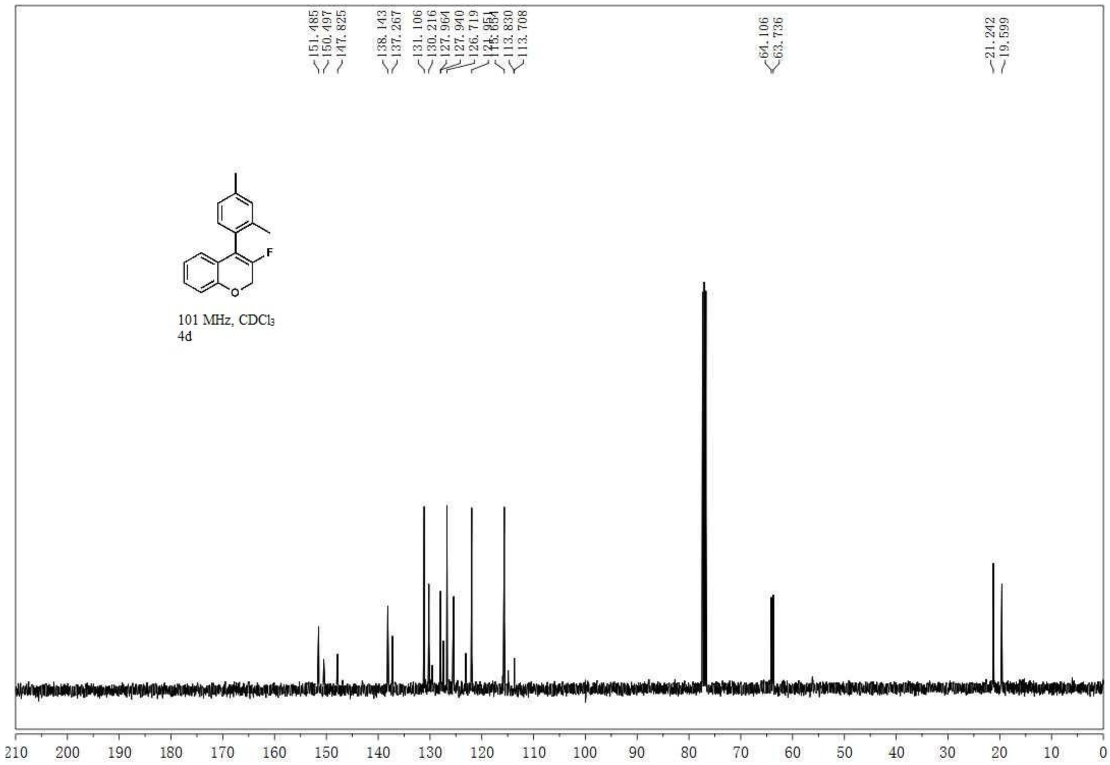

163.718
161.259
151.894
150.837
148.133
131.744
131.663
128.223
128.200
126.894
125.613
125.547
124.150
122.912
122.006
115.972
115.709
115.494
113.628
64.100
63.733
F
F
O
101 MHz, CDCl3
4c
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10



376 MHz, $CDCl_3$
4c



400 MHz, $CDCl_3$
4d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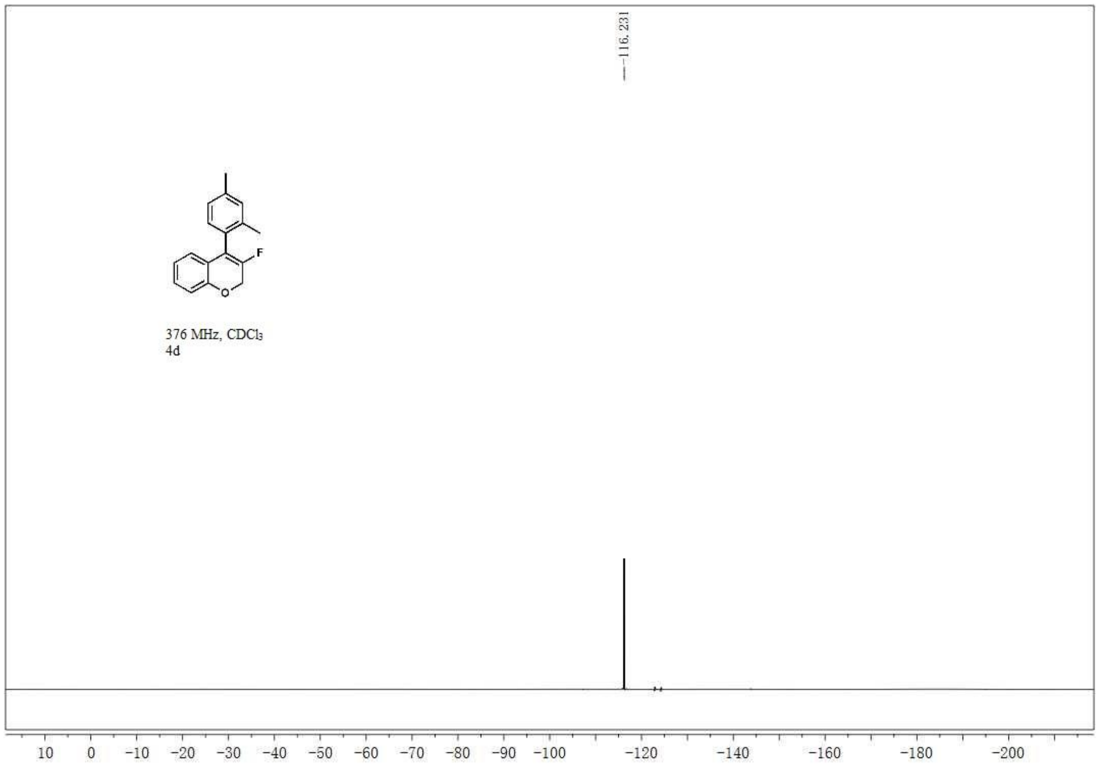
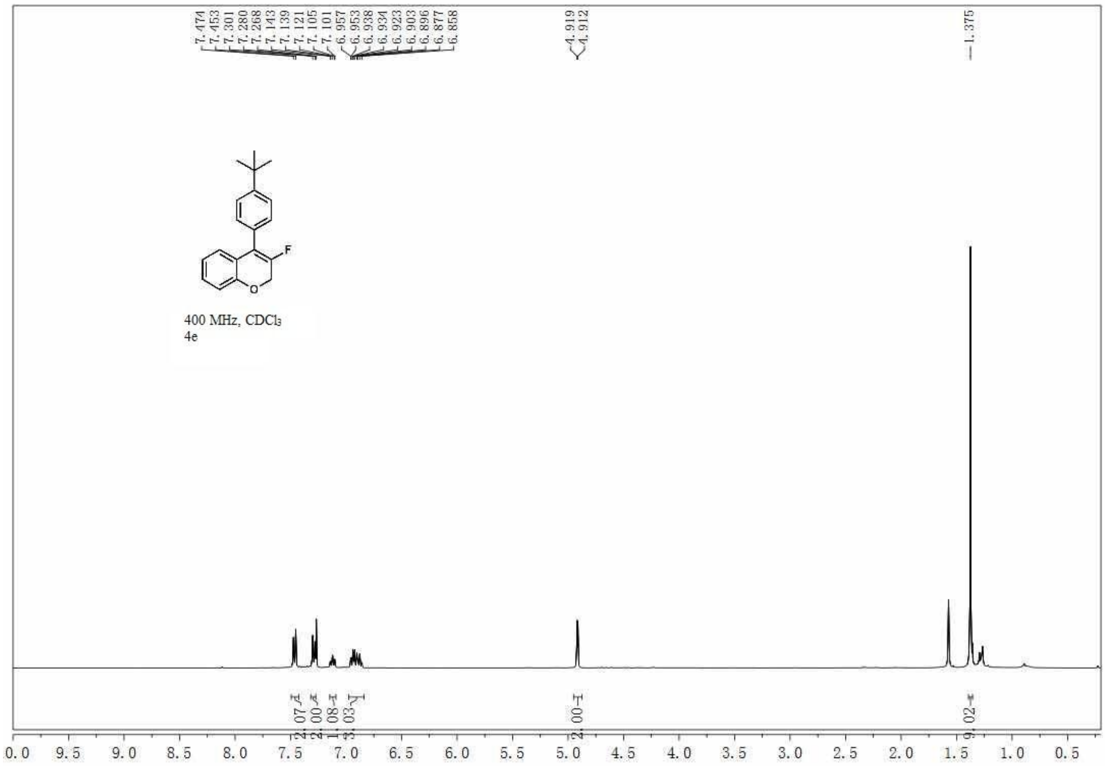
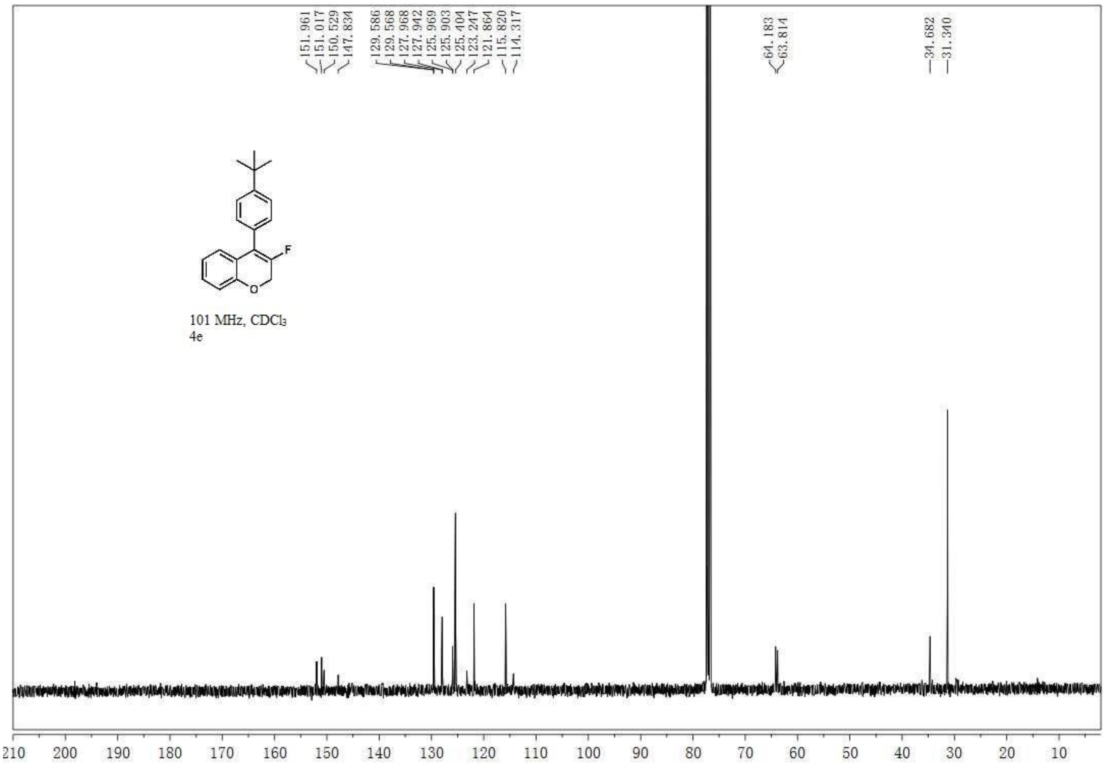
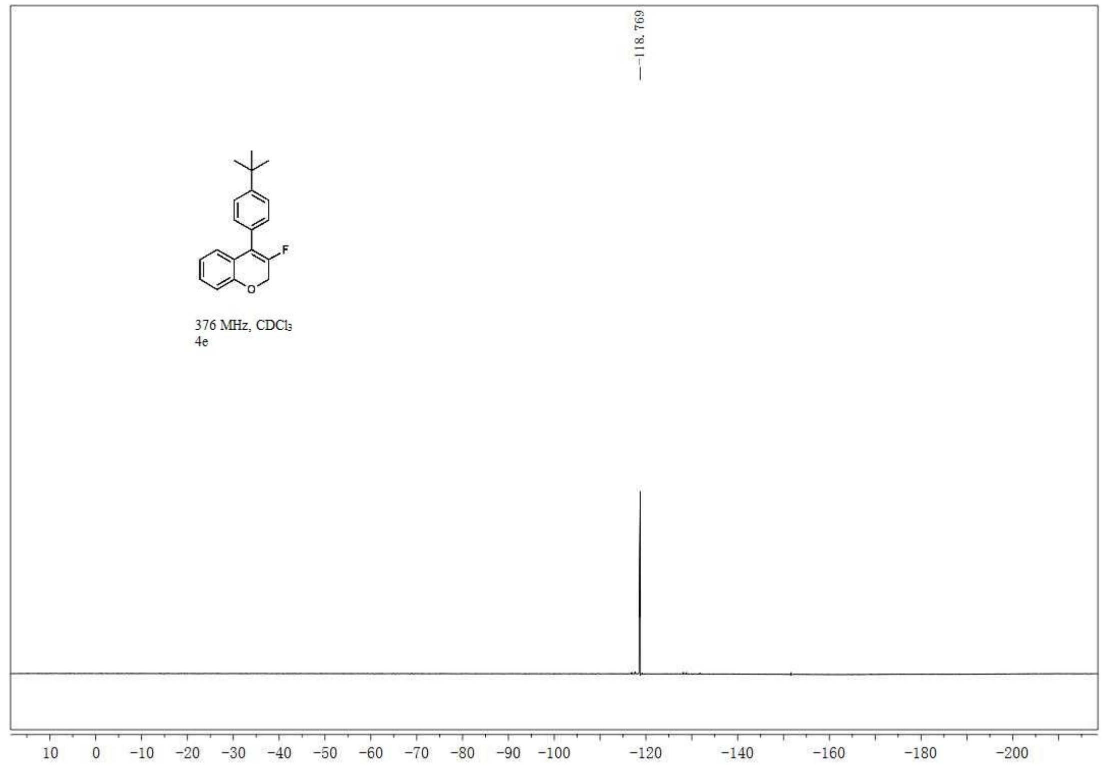
150.497
147.825
138.143
137.267
131.106
130.216
127.964
127.940
126.719
121.951
115.654
113.830
113.708
64.106
63.736
21.242
19.599
F
O
101 MHz, CDCl3
4d
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

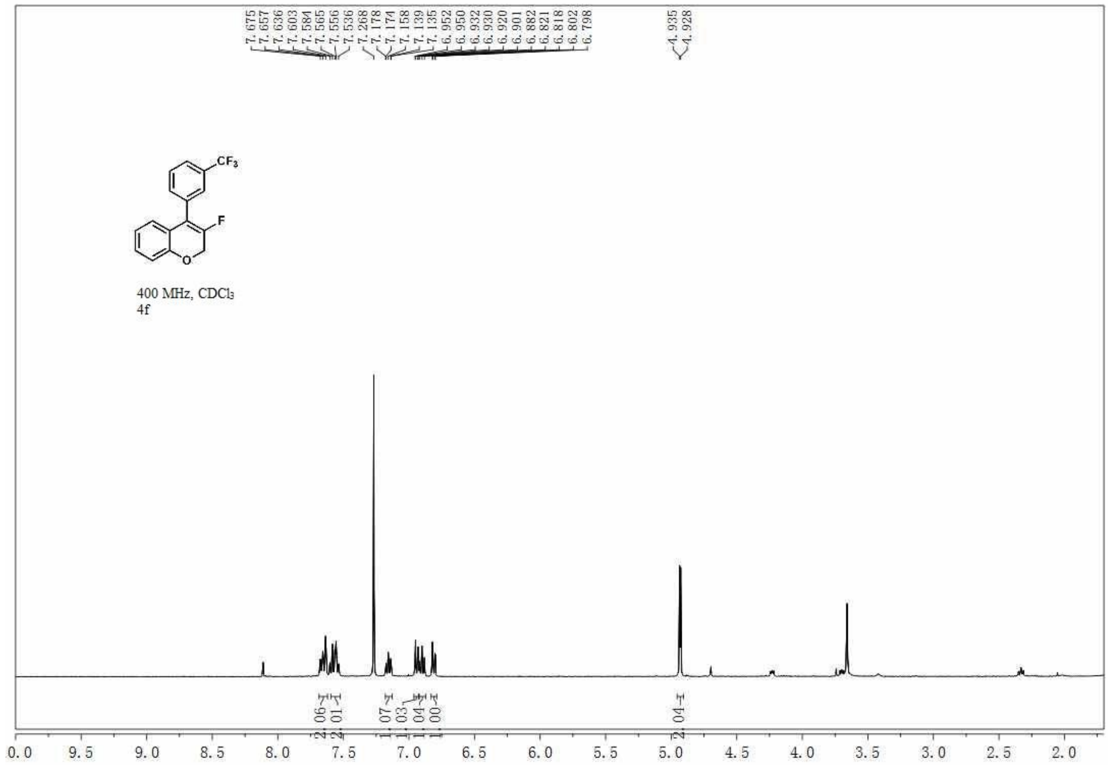

116.231
F
O
376 MHz, CDCl3
4d
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−120
−140
−160
−180
−200


7.474
7.453
7.301
7.280
7.268
7.143
7.139
7.121
7.105
7.101
6.957
6.953
6.938
6.934
6.923
6.903
6.896
6.877
6.858
4.919
4.912
1.375
F
O
400 MHz, CDCl3
4e
2.07
2.00
1.08
3.03
2.00
9.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

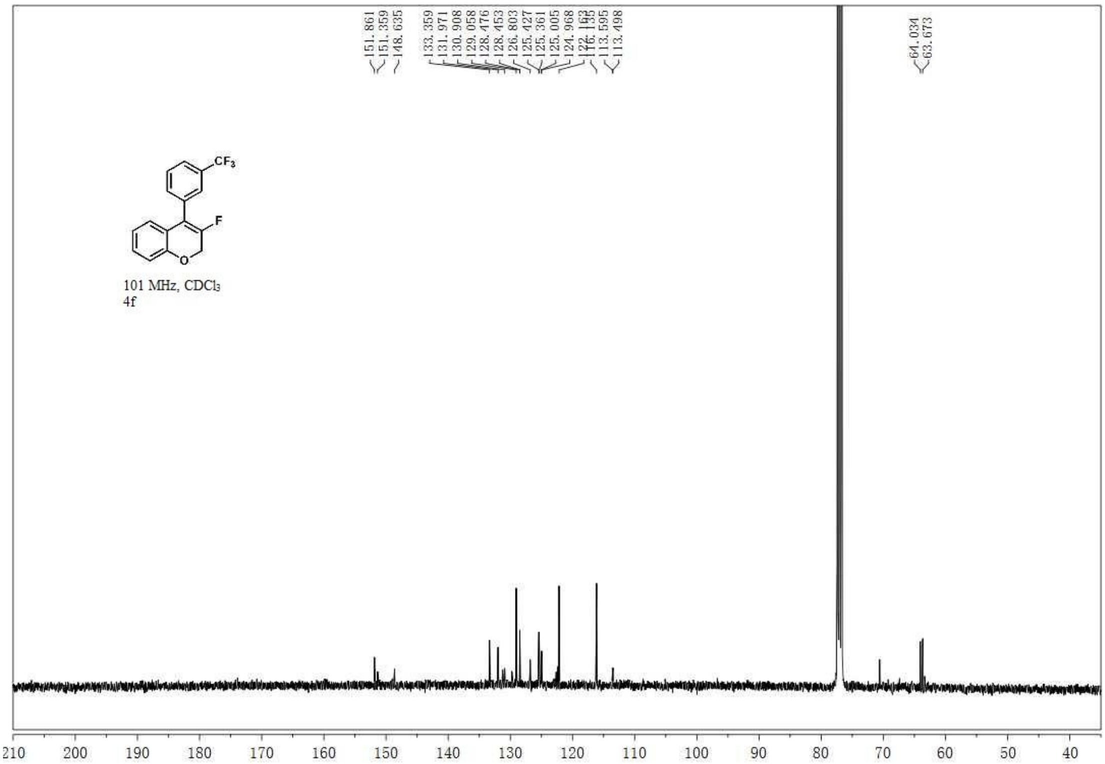

151.961
151.017
150.529
147.834
129.586
129.568
127.968
127.942
125.969
125.903
125.404
123.247
121.864
115.820
114.317
64.183
63.814
34.682
31.340
F
O
101 MHz, CDCl3
4e
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

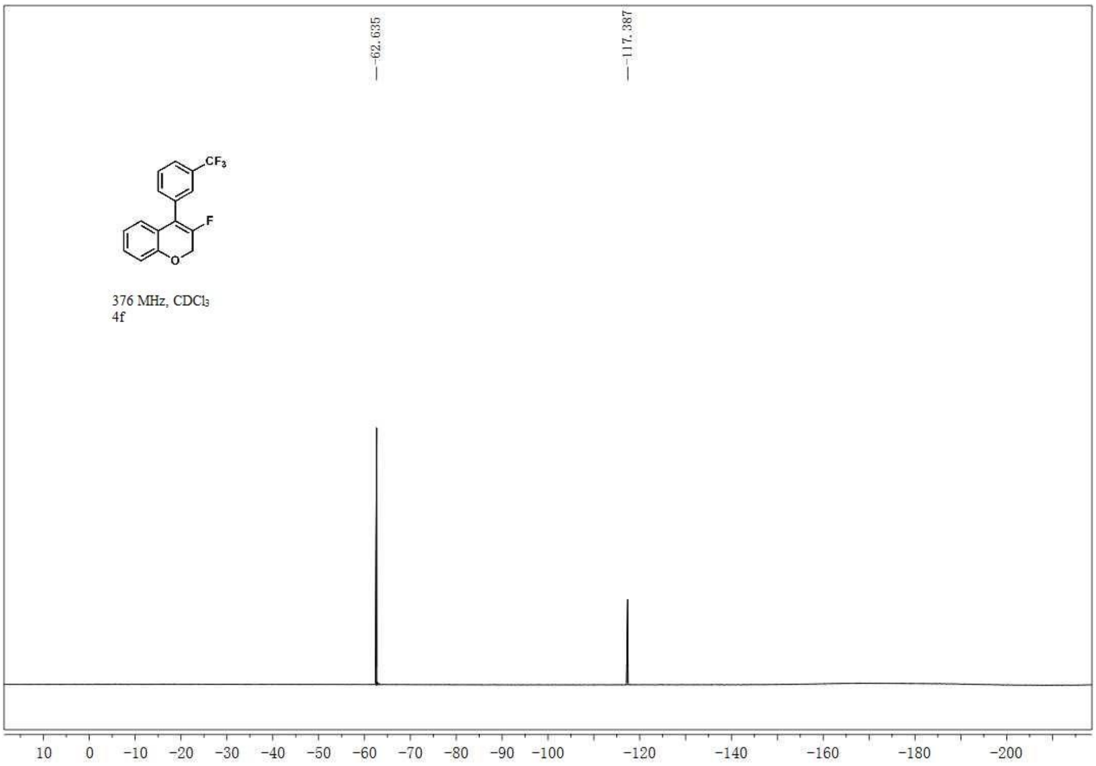


376 MHz, CDCl$_3$
4e



400 MHz, CDCl$_3$
4f


151.861
151.359
148.635
133.359
131.971
130.908
129.058
128.476
128.453
126.803
125.427
125.361
125.005
124.968
122.163
116.135
113.595
113.498
64.034
63.673
CF3
F
O
101 MHz, CDCl3
4f
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40


-62.635
-117.387
CF3
F
O
376 MHz, CDCl3
4f
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−120
−140
−160
−180
−200