Supporting Information

Selective Monofluorination of Active Methylene Compounds: the Important Role of $ZnCl_2$ in Inhibiting Overfluorination

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General Methods:

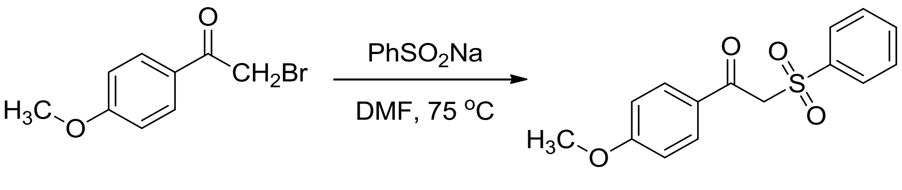
Unless otherwise mentioned, solvents and reagents were purchased from commercial sources and used without further purification. The solvent THF was refluxed with sodium and distilled. CH_3CN was distilled from CaH_2. ^1H, ^{13}C and ^{19}F NMR spectra were recorded on a 300MHz (Bruker AV300) or 400MHz (Agilent MR400) NMR spectrometer. ^1H NMR chemical shifts were determined relative to internal $(CH_3)_4Si$ (TMS) at δ 0.0 or to the signal of a residual protonated solvent: $CDCl_3$ δ 7.26 or $(CD_3)_2SO$ δ 2.50. ^{13}C NMR chemical shifts were determined relative to internal TMS at δ 0.0. ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ at δ 0.0. Data for ^1H, ^{13}C and ^{19}F NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, br = broad). Mass spectra were obtained on a mass spectrometer. High-resolution mass data were recorded on a high-resolution mass spectrometer in the EI or ESI mode.

Preparation of various methylene compounds:

Unless otherwise mentioned, starting materials were purchased from commercial sources and used as received (**1a-1i, 4e, 4g**). **1j, 4c, 4f, 4h, 4k** were prepared in Procedure A.[1] **4a, 4b, 4d, 4i, 4j** were prepared in Procedure B.[2]

Procedure A

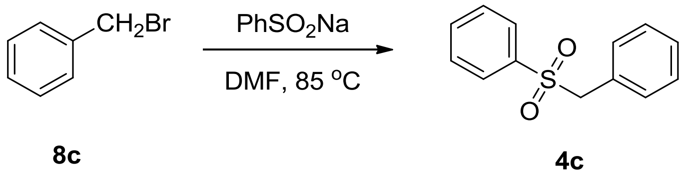
Preparation of 1-(4-methoxyphenyl)-2-(phenylsulfonyl)ethanone (1j):



7j **1j**

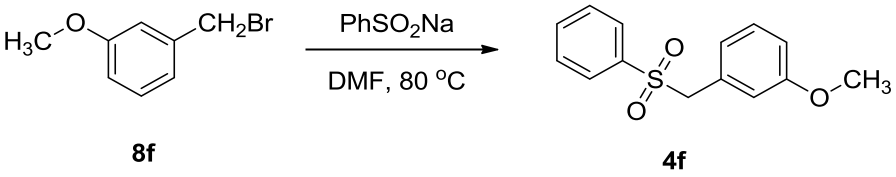
Sodium benzenesulfinate (98%, wt%, 1.1 equiv, 3.6850 g, 22 mmol) and 2-bromo-1-(4-methoxyphenyl)ethanone (**7j**) (98%, wt%, 1.0 equiv, 4.6751 g, 20 mmol) were dissolved in 34 mL DMF. The reaction mixture was stirred at 75 °C for 6 h under N_2 atmosphere until the almost completion of reaction monitored by TLC. The reaction was quenched by water. After extraction with EtOAc, the organic layer was washed with brine, and then dried over anhydrous Na_2SO_4, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with EtOAc/hexane to provide white solid (4.9196 g) in 85% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.6 Hz, 2H), 7.87 (d, J = 7.5 Hz, 2H), 7.65 (t, J = 7.1 Hz, 1H), 7.53 (t, J = 7.8 Hz, 2H), 6.93 (d, J = 8.7 Hz, 2H), 4.66 (s, 2H), 3.87 (s, 3H). MS (ESI, m/z): 291.1 ($M + H^+$), 313.1 ($M + Na^+$).

Preparation of (benzylsulfonyl)benzene (4c)



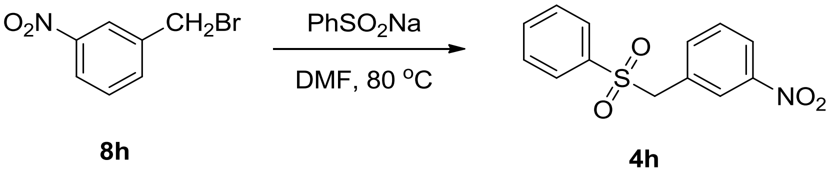
Sodium benzenesulfinate (98%, wt%, 1.05 equiv, 5.039 g, 30.7 mmol) and (bromomethyl)benzene (**8c**) (98%, wt%, 1.0 equiv, 5.0 g, 29.2 mmol) were dissolved in 50 mL DMF. The reaction mixture was stirred at 85 °C for 5 h under N_2 atmosphere until the almost completion of reaction monitored by TLC. The reaction was quenched by water. After extraction with EtOAc, the organic layer was washed with brine, and then dried over anhydrous Na_2SO_4, filtered and removed under vacuum. The crude product was recrystallization with EtOAc/hexane to provide white solid (5.89 g) in 87% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 – 7.56 (m, 3H), 7.50 – 7.41 (m, 2H), 7.36 – 7.22 (m, 3H), 7.08 (d, *J* = 6.7 Hz, 2H), 4.31 (s, 2H). MS (ESI, m/z): 233.1 (M + H^+), 250.1 (M + NH_4^+), 255.1 (M + Na^+).

Preparation of 1-methoxy-3-((phenylsulfonyl)methyl)benzene (4f)



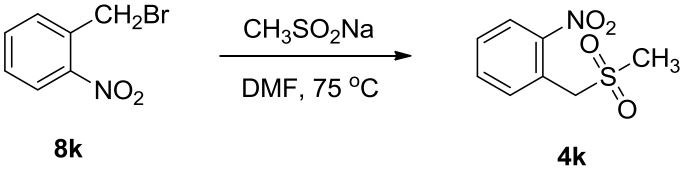
Sodium benzenesulfinate (98%, wt%, 1.1 equiv, 4.4957 g, 26.8 mmol) and 1-(bromomethyl)-3-methoxybenzene (**8f**) (98%, wt%, 1.0 equiv, 5.0 g, 24.4 mmol) were dissolved in 42 mL DMF. The reaction mixture was stirred at 80 °C for 6 h under N_2 atmosphere until the almost completion of reaction monitored by TLC. The reaction was quenched by water. After extraction with EtOAc, the organic layer was washed with brine, and then dried over anhydrous Na_2SO_4, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with EtOAc/hexane to provide white solid (5.5714 g) in 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.56 (m, 3H), 7.44 (t, *J* = 7.9 Hz, 2H), 7.14 (t, *J* = 7.9 Hz, 1H), 6.83 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.68 – 6.54 (m, 2H), 4.26 (s, 2H), 3.69 (s, 3H). MS (ESI, m/z): 263.1 (M + H^+), 280.0 (M + NH_4^+), 285.1 (M + Na^+).

Preparation of 1-nitro-3-((phenylsulfonyl)methyl)benzene (4h)



Sodium benzenesulfinate (98%, wt%, 1.05 equiv, 1.7588 g, 10.5 mmol) and 1-(bromomethyl)-3-nitrobenzene (**8h**) (97%, wt%, 1.0 equiv, 2.2271 g, 10 mmol) were dissolved in 17 mL DMF. The reaction mixture was stirred at 80 ^{o}C for 10 h under N_2 atmosphere until the almost completion of reaction monitored by TLC. The reaction was quenched by water. After extraction with EtOAc, the organic layer was washed with brine, and then dried over anhydrous Na_2SO_4, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with EtOAc/hexane to provide white solid (1.6502 g) in 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.1 Hz, 1H), 7.86 (s, 1H), 7.72 – 7.58 (m, 3H), 7.57 – 7.45 (m, 4H), 4.38 (s, 2H). MS (ESI, m/z): 278.1 (M + H^+), 295.1 (M + NH_4^+), 300.1 (M + Na^+).

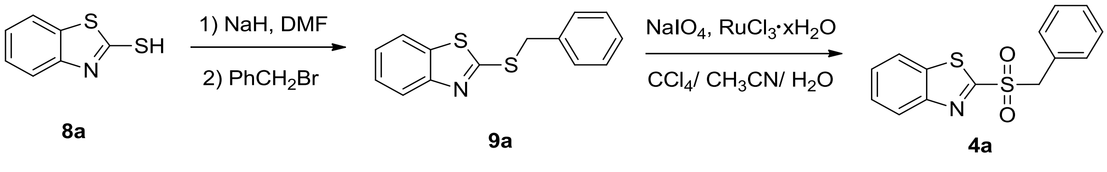
Preparation of 1-((methylsulfonyl)methyl)-2-nitrobenzene (4k)



Sodium methanesulfinate (85%, wt%, 1.0 equiv, 2.4021 g, 20 mmol) and 1-(bromomethyl)-2-nitrobenzene (**8k**) (97%, wt%, 1.0 equiv, 4.4542 g, 20 mmol) were dissolved in 34 mL DMF. The reaction mixture was stirred at 75 ^{o}C for 6 h under N_2 atmosphere until the almost completion of reaction monitored by TLC. The reaction was quenched by water. After extraction with EtOAc, the organic layer was washed with brine, and then dried over anhydrous Na_2SO_4, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with EtOAc/hexane to provide light green solid (4.1871 g) in 97% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.2 Hz, 1H), 7.76 – 7.62 (m, 2H), 7.62 – 7.53 (m, 1H), 4.78 (s, 2H), 2.89 (s, 3H). MS (ESI, m/z): 216.0 (M + H^+), 233.1 (M + NH_4^+), 238.0 (M + Na^+).

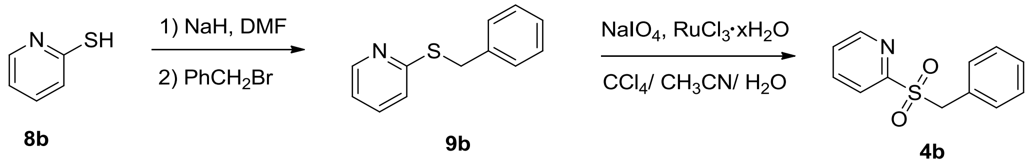
Procedure B

Preparation of 2-(benzylsulfonyl)benzothiazole (4a)



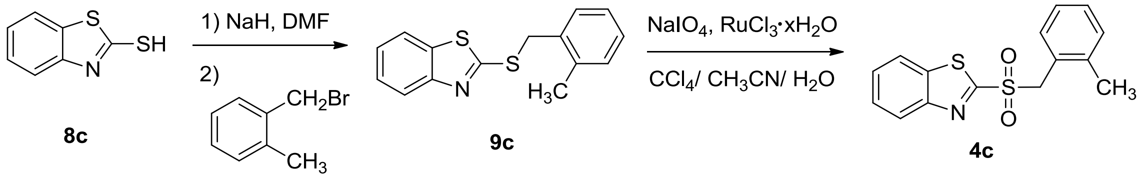
To a mixture of NaH (60%, wt%, 1.3 equiv, 1.0396 g, 26 mmol) and DMF (34 mL), benzothiazole-2-thiol (95%, 1.0 equiv, 3.5208 g, 20 mmol) was dissolved in under N_2 atmosphere. 10 minutes later, (bromomethyl)benzene (98%, wt%, 1.1 equiv, 3.8397 g, 22mmol) was added dropwise. The reaction was stirred at room temperature for 10 h until the almost completion of reaction monitored by TLC. The reaction was quenched by water. After extraction with EtOAc, the organic layer was washed with brine, and then dried over anhydrous Na_2SO_4, filtered and removed under vacuum. The crude product was then dissolved in the mixture of CCl_4 (30 mL), CH_3CN (30 mL) and H_2O (75 mL) without purification. $NaIO_4$ (8.5556 g, 40 mmol) and ruthenium trichloride hydrate (ca. 15 mg) was added and the mixture was stirred at room temperature for 5 h until the almost completion of reaction monitored by TLC. The reaction was filtered on diatomite and washed with CH_2Cl_2. The filtrate was evaporated under vacuum to remove CCl_4 and CH_3CN, then extraction with CH_2Cl_2. The organic layer was dried over anhydrous Na_2SO_4, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with EtOAc/hexane to provide white solid (3.4798g) in 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.3 Hz, 1H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.68 – 7.61 (m, 1H), 7.61 – 7.54 (m, 1H), 7.34 – 7.21 (m, 5H), 4.74 (s, 2H). MS (ESI, m/z): 290.0 (M + H^+), 312.0 (M + Na^+).

Preparation of 2-(benzylsulfonyl)pyridine (4b)



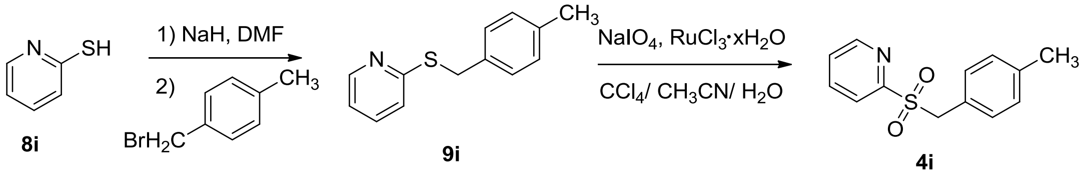
To a mixture of NaH (60%, wt%, 1.3 equiv, 1.0396 g, 26 mmol) and DMF (34 mL), pyridine-2-thiol (98%, wt%, 1.0 equiv, 2.2687 g, 20 mmol) was dissolved in under N_2 atmosphere. 10 minutes later, (bromomethyl)benzene (98%, wt%, 1.1 equiv, 3.8397 g, 22mmol) was added dropwise. The reaction was stirred at room temperature for 10 h until the almost completion of reaction monitored by TLC. The reaction was quenched by water. After extraction with EtOAc, the organic layer was washed with brine, and then dried over anhydrous Na_2SO_4, filtered and removed under vacuum. The crude product was then dissolved in the mixture of CCl_4 (30 mL), CH_3CN (30 mL) and H_2O (75 mL) without purification. $NaIO_4$ (8.5556 g, 40 mmol) and ruthenium trichloride hydrate (ca. 15 mg) was added and the mixture was stirred at room temperature for 5 h until the almost completion of reaction monitored by TLC. The reaction was filtered on diatomite and washed with CH_2Cl_2. The filtrate was evaporated under vacuum to remove CCl_4 and CH_3CN, then extraction with CH_2Cl_2. The organic layer was dried over anhydrous Na_2SO_4, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with CH_2Cl_2/hexane to provide white solid (4.1111 g) in 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (d, *J* = 4.6 Hz, 1H), 8.07 – 7.72 (m, 2H), 7.64 – 7.43 (m, 1H), 7.30 – 7.20 (m, 3H), 7.20 – 7.14 (m, 2H), 4.64 (s, 2H). MS (ESI, m/z): 234.1 (M + H^+), 256.1 (M + Na^+).

Preparation of 2-((2-methylbenzyl)sulfonyl)benzothiazole (4c)



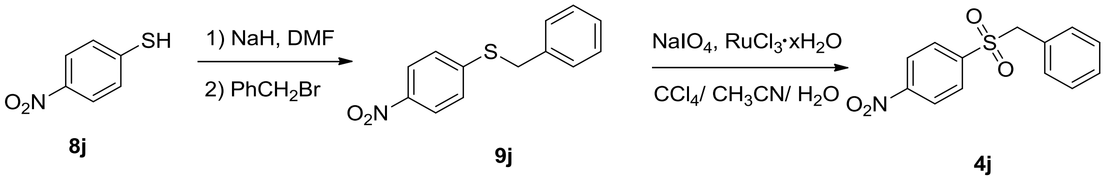
To a mixture of NaH (60%, wt%, 1.3 equiv, 1.0396 g, 26 mmol) and DMF (34 mL), benzothiazole-2-thiol (95%, wt%, 1.0 equiv, 3.5208 g, 20 mmol) was dissolved in under N_2 atmosphere. 10 minutes later, 1-(bromomethyl)-2-methylbenzene (98%, wt%, 1.1 equiv, 4.1544 g, 22mmol) was added dropwise. The reaction was stirred at room temperature for 10 h until the almost completion of reaction monitored by TLC. The reaction was quenched by water. After extraction with EtOAc, the organic layer was washed with brine, and then dried over anhydrous Na_2SO_4, filtered and removed under vacuum. The crude product was then dissolved in the mixture of CCl_4 (30 mL), CH_3CN (30 mL) and H_2O (75 mL) without purification. $NaIO_4$ (8.5556 g, 40 mmol) and ruthenium trichloride hydrate (ca. 15 mg) was added and the mixture was stirred at room temperature for 5 h until the almost completion of reaction monitored by TLC. The reaction was filtered on diatomite and washed with CH_2Cl_2. The filtrate was evaporated under vacuum to remove CCl_4 and CH_3CN, then extraction with CH_2Cl_2. The organic layer was dried over anhydrous Na_2SO_4, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with EtOAc/hexane to provide white solid (5.3698 g) in 89% yield. m.p.: 125-126 ^{o}C. IR (KBr): 3093, 3063, 3025, 2997, 2943, 2262, 2153, 1932, 1815, 1722, 1552, 1492, 1469, 1455, 1410, 1328, 1316, 1302, 1256, 1237, 1182, 1152, 1138, 1127, 1079, 1047, 1023, 854, 781, 767, 754, 735, 729, 711, 704, 691, 642, 586, 562, 534, 515, 491, 480, 433. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.1 Hz, 1H), 7.97 (d, *J* = 8.2 Hz, 1H), 7.71 – 7.63 (m, 1H), 7.63 – 7.56 (m, 1H), 7.26 – 7.13 (m, 3H), 7.08 (t, *J* = 7.0 Hz, 1H), 4.83 (s, 2H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.60, 152.59, 138.88, 137.10, 132.04, 131.03, 129.48, 128.06, 127.70, 126.31, 125.46, 124.70, 122.34, 58.39, 19.80. MS (ESI, m/z): 304.0 (M + H$^+$), 326.0 (M + Na$^+$). HRMS (ESI): calcd. For $C_{15}H_{13}N_1Na_1O_2S_2$ (M + H$^+$) 326.02799, found 326.02821.

Preparation of 2-((4-methylbenzyl)sulfonyl)pyridine (4i)



To a mixture of NaH (60%, wt%, 1.3 equiv, 1.0396 g, 26 mmol) and DMF (34 mL), pyridine-2-thiol (98%, wt%, 1.0 equiv, 2.2687 g, 20 mmol) was dissolved in under N_2 atmosphere. 10 minutes later, 1-(bromomethyl)-4-methylbenzene (98%, wt%, 1.1 equiv, 4.1544 g, 22 mmol) was added. The reaction was stirred at room temperature for 10 h until the almost completion of reaction monitored by TLC. The reaction was quenched by water. After extraction with EtOAc, the organic layer was washed with brine, and then dried over anhydrous Na_2SO_4, filtered and removed under vacuum. The crude product was then dissolved in the mixture of CCl_4 (30 mL), CH_3CN (30 mL) and H_2O (75 mL) without purification. $NaIO_4$ (8.5556 g, 40 mmol) and ruthenium trichloride hydrate (ca. 15 mg) was added and the mixture was stirred at room temperature for 5 h until the almost completion of reaction monitored by TLC. The reaction was filtered on diatomite and washed with CH_2Cl_2. The filtrate was evaporated under vacuum to remove CCl_4 and CH_3CN, then extraction with CH_2Cl_2. The organic layer was dried over anhydrous Na_2SO_4, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with CH_2Cl_2/hexane to provide white solid (4.4664 g) in 90% yield. m.p.: 98-99 ^{o}C. IR (KBr): 3060, 2999, 2928, 2260, 2188, 1611, 1575, 1561, 1513, 1456, 1425, 1386, 1300, 1289, 1248, 1161, 1149, 1125, 1113, 1104, 1082, 1046, 1025, 990, 977, 818, 782, 766, 741, 728, 698, 622, 603, 526, 505, 483. ^{1}H NMR (400 MHz, cdcl$_3$) δ 8.81 (d, *J* = 4.6 Hz, 1H), 7.94 – 7.70 (m, 2H), 7.59 – 7.46 (m, 1H), 7.05 (s, 4H), 4.60 (s, 2H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.29, 150.15, 138.66, 137.90, 130.80, 129.37, 127.39, 124.17, 123.15, 58.01, 21.19. MS (EI, m/z): 247 (M^+, 8.09), 105 (100.00), 182 (61.74), 77 (16.69), 78 (15.01), 79 (13.28), 103 (11.18), 51 (10.78), 167 (10.68). HRMS (EI): calcd. For $C_{13}H_{13}NO_2S$ (M^+) 247.0667, found 247.0668.

Preparation of 1-(benzylsulfonyl)-4-nitrobenzene (4j)



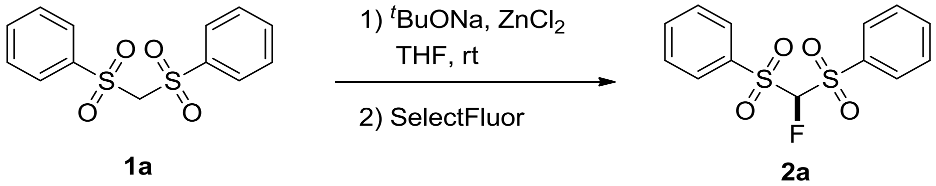
To a mixture of NaH (60%, wt%, 1.3 equiv, 1.0396 g, 26 mmol) and DMF (34 mL), 4-nitrobenzenethiol (98%, wt%, 1.0 equiv, 3.1668 g, 20 mmol) was dissolved in under N_2 atmosphere. 10 minutes later, (bromomethyl)benzene (98%, wt%, 1.1 equiv, 3.8397 g, 22mmol) was added dropwise. The reaction was stirred at room temperature for 10 h until the almost completion of reaction monitored by TLC. The reaction was quenched by water. After extraction with EtOAc, the organic layer was washed with brine, and then dried over anhydrous Na_2SO_4, filtered and removed under vacuum. The crude product was then dissolved in the mixture of CCl_4 (30 mL), CH_3CN (30 mL) and H_2O (75 mL) without purification. $NaIO_4$ (8.5556 g, 40 mmol) and ruthenium trichloride hydrate (ca. 15 mg) was added and the mixture was stirred at room temperature for 5 h until the almost completion of reaction monitored by TLC. The reaction was filtered on diatomite and washed with CH_2Cl_2. The filtrate was evaporated under vacuum to remove CCl_4 and CH_3CN, then extraction with CH_2Cl_2. The organic layer was dried over anhydrous Na_2SO_4, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with CH_2Cl_2/hexane to provide gray solid (3.2333 g) in 58% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.8 Hz, 2H), 7.78 (d, *J* = 8.8 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.28 (t, *J* = 7.7 Hz, 2H), 7.08 (d, *J* = 7.2 Hz, 2H), 4.37 (s, 2H). MS (ESI, m/z): 300.0 (M + Na$^+$).

Monofluorination of various methylene compounds:

1a-1j were monofluorinated in Condition A, and **4a-4k** were monofluorinated in Condition B. The equivalents of base (NaO^{t}Bu or LiHMDS) and $ZnCl_2$ were based on those of the starting methylene compounds.

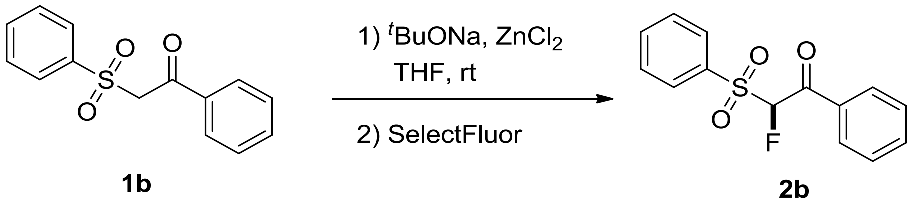
Condition A

Monofluorination of bis(phenylsulfonyl)methane (1a)



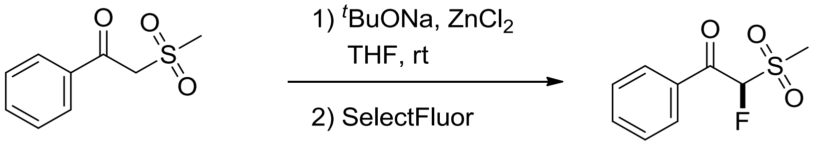
^{t}BuONa (2.5 equiv, 360.4 mg, 3.75 mmol) and anhydrous $ZnCl_2$ (2.5 equiv, 511.1 mg, 3.75 mmol) were dissolved in 12 mL THF. 5 minutes later, bis(phenylsulfonyl)methane (**1a**) (1.0 equiv, 444.0 mg, 1.5 mmol) was added into the mixture under N_2 atomosphere. The reaction was stirred for half an hour. Then SelectFluor (2.0 equiv, 1.0628g, 3.0 mmol) was added into the mixture in a flash. The reaction was allowed at room temperature for 2 h and quenched by 2M HCl until it became clear. After extraction with EtOAc, the organic layer was dried over anhydrous Na_2SO_4, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with EtOAc/hexane to provide white solid **2a** (377.0 mg) in 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.7 Hz, 4H), 7.77 (t, *J* = 7.1 Hz, 2H), 7.61 (t, *J* = 7.6 Hz, 4H), 5.73 (d, *J* = 45.8 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -168.19 (d, *J* = 45.9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.70, 135.25, 130.14, 129.47, 105.65 (d, *J* = 266.1 Hz). MS (ESI, m/z): 314.9 (M + H$^+$), 332.0 (M + NH_4^+), 337.0 (M + Na$^+$).

Monofluorination of 1-phenyl-2-(phenylsulfonyl)ethanone (1b)



^{t}BuONa (2.2 equiv, 317.1 mg, 3.3 mmol) and anhydrous $ZnCl_2$ (2.5 equiv, 511.1 mg, 3.75 mmol) were dissolved in 12 mL THF. 5 minutes later, 1-phenyl-2-(phenylsulfonyl)ethanone (**1b**) (1.0 equiv, 394.4 mg, 1.5 mmol) was added into the mixture under N_2 atomosphere. The reaction was stirred for half an hour. Then SelectFluor (2.0 equiv, 1.0628g, 3.0 mmol) was added into the mixture in a flash. The reaction was allowed at room temperature for 2 h and quenched by 2M HCl until it became clear. After extraction with EtOAc, the organic layer was dried over anhydrous Na_2SO_4, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with EtOAc/hexane to provide white solid **2b** (381.3 mg) in 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.7 Hz, 2H), 7.88 (d, *J* = 7.8 Hz, 2H), 7.74 (t, *J* = 7.1 Hz, 1H), 7.68 (t, *J* = 7.0 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 2H), 7.52 (t, *J* = 7.7 Hz, 2H), 6.35 (d, *J* = 48.0 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -179.60 (d, *J* = 48.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.43 (d, *J* = 17.6 Hz), 135.29, 135.03, 134.52, 133.88, 129.86, 129.76 (d, *J* = 2.7 Hz), 129.35, 128.84, 100.19 (d, *J* = 232.0 Hz). MS (EI, m/z): 278 (M^+, 1.36), 105 (100.00), 77 (65.92), 51 (18.08), 109 (14.77), 141 (8.50), 106 (7.91), 78 (5.67), 50 (5.64).

Monofluorination of 2-(methylsulfonyl)-1-phenylethanone (1c)

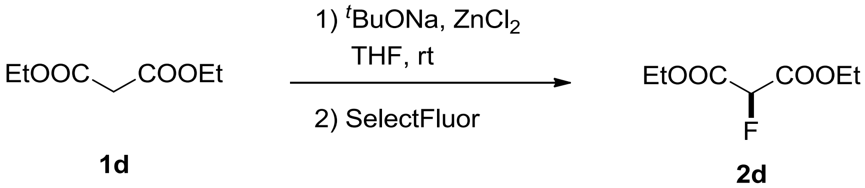


1c

2c

^{t}BuONa (1.8 equiv, 259.5 mg, 2.7 mmol) and anhydrous $ZnCl_2$ (2.5 equiv, 511.1 mg, 3.75 mmol) were dissolved in 12 mL THF. 5 minutes later, 2-(methylsulfonyl)-1-phenylethanone (**1c**) (1.0 equiv, 304.4 mg, 1.5 mmol) was added to the mixture under N_2 atomosphere. The reaction was stirred for half an hour. Then SelectFluor (2.0 equiv, 1.0628g, 3.0 mmol) was added into the mixture in a flash. The reaction was allowed at room temperature for 2 h and quenched by 2M HCl until it became clear. After extraction with EtOAc, the organic layer was dried over anhydrous Na_2SO_4, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with EtOAc/hexane to provide white solid **2c** (282.7 mg) in 87% yield. m.p.: 86-87 ^{o}C. IR (KBr): 3356, 3032, 3007, 2976, 2926, 1694, 1596, 1581, 1449, 1417, 1358, 1317, 1257, 1174, 1144, 1096, 1075, 1001, 983, 953, 847, 811, 768, 737, 684, 671, 631, 523, 487, 465, 420. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.8 Hz, 2H), 7.69 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 2H), 6.34 (d, *J* = 47.3 Hz, 1H), 3.05 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -182.53 (d, *J* = 47.4 Hz). MS (EI, m/z): 216 (M^+, 1.42), 105 (100.00), 77 (43.99), 109 (17.93), 51 (11.56), 106 (8.03), 50 (4.77), 78 (4.36), 83 (3.94). HRMS (EI): calcd. For $C_9H_9O_3FS$ (M^+) 216.0256, found 216.0257.

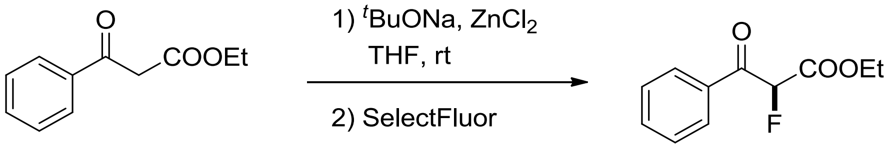
Monofluorination of diethyl malonate (1d)



1d **2d**

^{t}BuONa (1.5 equiv, 216.2 mg, 2.25 mmol) and anhydrous $ZnCl_2$ (2.5 equiv, 511.1 mg, 3.75 mmol) were dissolved in 12 mL THF. 5 minutes later, diethyl malonate (**1d**) (1.0 equiv, 240.3 mg, 1.5 mmol) was added into the mixture under N_2 atmosphere. The reaction was stirred for half an hour. Then SelectFluor (2.0 equiv, 1.0628g, 3.0 mmol) was added into the mixture in a flash. The reaction was allowed at room temperature for 2 h and quenched by 2M HCl until it became clear. After extraction with EtOAc, the organic layer was dried over anhydrous Na_2SO_4, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with EtOAc/hexane to provide colourless liquid **2d** (186.7 mg) in 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.26 (d, J = 48.2 Hz, 1H), 4.32 (qd, J = 7.1, 2.6 Hz, 4H), 1.32 (t, J = 7.1 Hz, 6H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -195.08 (d, J = 48.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.94 (d, J = 24.0 Hz), 85.27 (d, J = 196.4 Hz), 62.72, 13.96. MS (EI, m/z): 178 (M^+, 0.52), 78 (100.00), 105 (27.99), 106 (24.38), 60 (23.97), 133 (22.25), 77 (10.70), 45 (7.12), 49 (5.84).

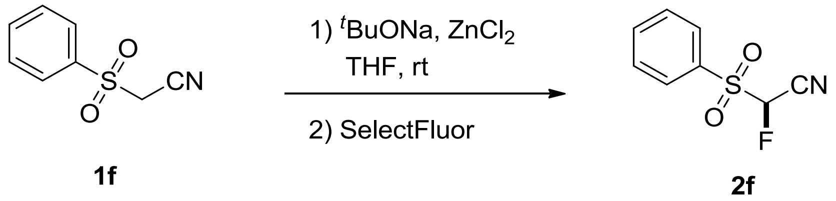
Monofluorination of ethyl 3-oxo-3-phenylpropanoate (1e)



1e **2e**

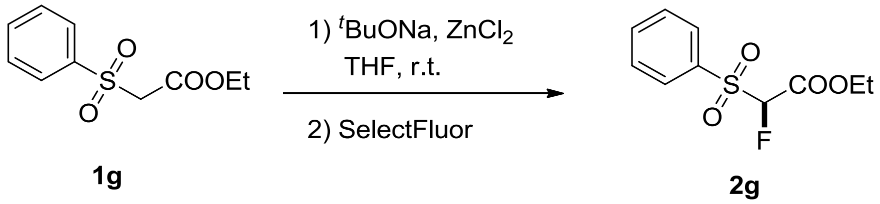
^{t}BuONa (1.5 equiv, 216.2 mg, 2.25 mmol) and anhydrous $ZnCl_2$ (3.0 equiv, 613.4 mg, 4.5 mmol) were dissolved in 12 mL THF. 5 minutes later, ethyl 3-oxo-3-phenylpropanoate (**1e**) (1.0 equiv, 303.5 mg, 1.5 mmol) was added into the mixture under N_2 atmosphere. The reaction was stirred for half an hour. Then SelectFluor (2.0 equiv, 1.0628g, 3.0 mmol) was added into the mixture in a flash. The reaction was allowed at room temperature for 2 h and quenched by 2M HCl until it became clear. After extraction with EtOAc, the organic layer was dried over anhydrous Na_2SO_4, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with EtOAc/hexane to provide colourless liquid **2e** (213.6 mg) in 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.1 Hz, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 7.8 Hz, 2H), 5.87 (d, J = 48.8 Hz, 1H), 4.30 (qd, J = 7.1, 1.4 Hz, 2H), 1.26 (t, J = 7.1 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -190.34 (d, J = 48.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.51 (d, J = 20.3 Hz), 164.89 (d, J = 24.2 Hz), 134.52 (s), 133.33 (s), 129.51 (d, J = 3.4 Hz), 128.81 (s), 90.05 (d, J = 197.6 Hz), 62.70 (s), 13.94 (s). MS (EI, m/z): 210 (M^+, 0.63), 105 (100.00), 77 (38.81), 51 (9.81), 106 (7.44), 109 (4.80), 78 (4.24), 50 (3.35), 118 (3.13).

Monofluorination of 2-(phenylsulfonyl)acetonitrile (1f)



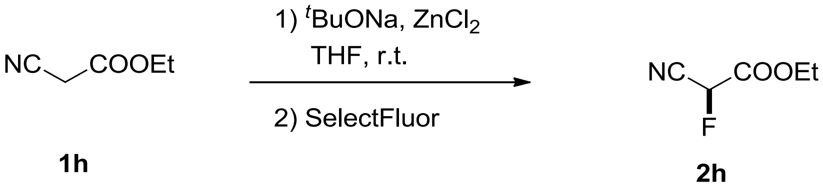
^{t}BuONa (2.2 equiv, 317.1 mg, 3.3 mmol) and anhydrous ZnCl$_2$ (2.2 equiv, 449.8 mg, 3.3 mmol) were dissolved in 12 mL THF. 5 minutes later, 2-(phenylsulfonyl)acetonitrile (**1f**) (1.0 equiv, 277.4 mg, 1.5 mmol) was added into the mixture under N$_2$ atmosphere. The reaction was stirred for half an hour. Then SelectFluor (2.0 equiv, 1.0628g, 3.0 mmol) was added into the mixture in a flash. The reaction was allowed at room temperature for 2 h and quenched by 2M HCl until it became clear. After extraction with EtOAc, the organic layer was dried over anhydrous Na$_2$SO$_4$, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with EtOAc/hexane to provide colourless liquid **2f** (275.5 mg) in 92% yield. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.04 (d, *J* = 7.7 Hz, 2H), 7.85 (t, *J* = 7.3 Hz, 1H), 7.69 (t, *J* = 7.6 Hz, 2H), 5.75 (d, *J* = 46.7 Hz, 1H). ^{19}F NMR (282 MHz, CDCl$_3$) δ -178.95 (d, *J* = 46.6 Hz). ^{13}C NMR (100 MHz, CDCl$_3$) δ 136.50, 132.16, 130.51, 129.90, 109.81 (d, *J* = 28.9 Hz), 88.03 (d, *J* = 230.9 Hz). MS (EI, m/z): 199 (M$^+$, 0.80), 77 (100.00), 141 (34.26), 51 (25.39), 50 (8.91), 78 (7.16), 74 (3.82), 58 (3.21), 142 (2.53)

Monofluorination of ethyl 2-(phenylsulfonyl)acetate (1g)



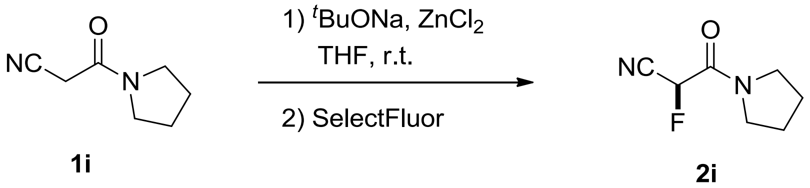
^{t}BuONa (2.5 equiv, 360.4 mg, 3.75 mmol) and anhydrous ZnCl$_2$ (2.2 equiv, 449.8 mg, 3.3 mmol) were dissolved in 12 mL THF. 5 minutes later, ethyl 2-(phenylsulfonyl)acetate (**1g**) (1.0 equiv, 349.4 mg, 1.5 mmol) was added into the mixture under N$_2$ atmosphere. The reaction was stirred for half an hour. Then SelectFluor (2.0 equiv, 1.0628g, 3.0 mmol) was added into the mixture in a flash. The reaction was allowed at room temperature for 2 h and quenched by 2M HCl until it became clear. After extraction with EtOAc, the organic layer was dried over anhydrous Na$_2$SO$_4$, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with EtOAc/hexane to provide colourless liquid **2g** (320.0 mg) in 87% yield. IR (film): 3069, 2984, 1760, 1584, 1476, 1449, 1396, 1372, 1343, 1313, 1275, 1244, 1201, 1159, 1111, 1081, 1022, 954, 856, 838, 763, 713, 687, 631, 597, 567, 543, 524. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.94 (d, *J* = 7.7 Hz, 2H), 7.75 (t, *J* = 7.5 Hz, 1H), 7.61 (t, *J* = 7.8 Hz, 2H), 5.57 (d, *J* = 48.0 Hz, 1H), 4.29 (q, J = 7.1 Hz, 2H), 1.28 (t, J = 7.1 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -180.39 (d, J = 48.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.98 (d, J = 23.4 Hz), 135.32, 134.52, 129.79, 129.40, 97.26 (d, J = 232.4 Hz), 63.51, 13.89. MS (EI, m/z): 246 (M^+, 1.37), 77 (100.00), 141 (62.49), 51 (21.81), 109 (13.71), 78 (13.56), 125 (6.75), 50 (5.98), 182 (5.62). HRMS (EI): m/z calcd. For $C_{10}H_{11}O_4FS$ (M^+) 246.0362, found 246.0365.

Monofluorination of ethyl 2-cyanoacetate (1h)



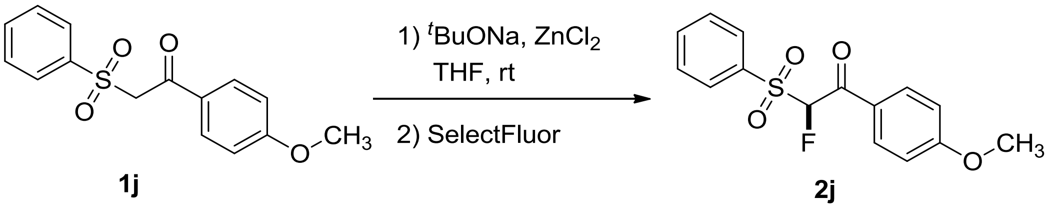
^{t}BuONa (2.2 equiv, 317.1 mg, 3.3 mmol) and anhydrous $ZnCl_2$ (3.5 equiv, 715.6 mg, 5.25 mmol) were dissolved in 12 mL THF. 5 minutes later, ethyl 2-cyanoacetate (**1h**) (1.0 equiv, 178.6 mg, 1.5 mmol) was added into the mixture under N_2 atmosphere. The reaction was stirred for half an hour. Then SelectFluor (2.0 equiv, 1.0628g, 3.0 mmol) was added into the mixture in a flash. The reaction was allowed at room temperature for 2 h and quenched by 2M HCl until it became clear. After extraction with EtOAc, the organic layer was dried over anhydrous Na_2SO_4, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with EtOAc/hexane to provide colourless liquid **2h** (118.2 mg) in 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.51 (d, J = 46.1 Hz, 1H), 4.40 (q, J = 7.1 Hz, 2H), 1.37 (t, J = 7.2 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -194.17 (d, J = 46.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.68 (d, J = 24.8 Hz), 111.69 (d, J = 29.7 Hz), 74.33 (d, J = 196.5 Hz), 64.31, 13.86. MS (ESI, m/z): 131.9 ($M + H^+$).

Monofluorination of 3-oxo-3-(pyrrolidin-1-yl)propanenitrile (1i)



^{t}BuONa (2.2 equiv, 317.1 mg, 3.3 mmol) and anhydrous $ZnCl_2$ (2.2 equiv, 449.8 mg, 3.3 mmol) were dissolved in 12 mL THF. 5 minutes later, 3-oxo-3-(pyrrolidin-1-yl)propanenitrile **(1i)** (1.0 equiv, 211.5 mg, 1.5 mmol) was added into the mixture under N_2 atmosphere. The reaction was stirred for half an hour. Then SelectFluor (2.0 equiv, 1.0628g, 3.0 mmol) was added into the mixture in a flash. The reaction was allowed at room temperature for 2 h and quenched by 2M HCl until it became clear. After extraction with EtOAc, the organic layer was dried over anhydrous Na_2SO_4, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with EtOAc/hexane to provide colourless liquid **2i** (221.2 mg) in 94% yield. IR (film): 3508, 2979, 2886, 1682, 1444, 1342, 1259, 1231, 1191, 1163, 1098, 1041, 1021, 995, 972, 932, 906, 827, 729, 518. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.62 (d, *J* = 46.8 Hz, 1H), 3.62 – 3.51 (m, 4H), 2.08 – 1.97 (m, 2H), 1.97 – 1.85 (m, 2H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -190.86 (d, *J* = 46.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.97 (d, *J* = 21.4 Hz), 112.33 (d, *J* = 30.3 Hz), 76.93 (d, *J* = 196.0 Hz), 47.36, 46.15 (d, *J* = 4.9 Hz), 26.18 (d, *J* = 1.3 Hz), 23.49. MS (EI, m/z): 156 (M^+, 43.27), 55 (100.00), 98 (91.95), 56 (39.57), 70 (28.57), 41 (26.73), 42 (23.53), 58 (18.95). HRMS (EI): m/z calcd. For $C_7H_9N_2OF$ (M^+) 156.0699, found 156.0700.

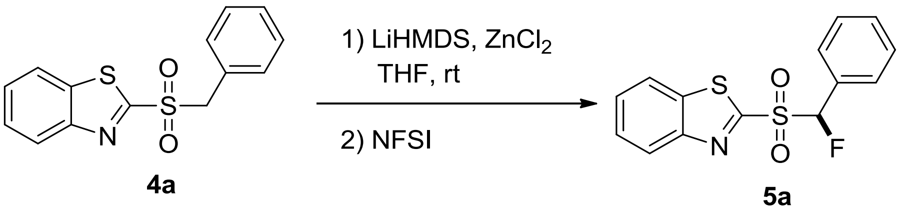
Monofluorination of 1-(4-methoxyphenyl)-2-(phenylsulfonyl)ethanone (1j)



^{t}BuONa (2.2 equiv, 317.1 mg, 3.3 mmol) and anhydrous $ZnCl_2$ (3.0 equiv, 613.4 mg, 4.5 mmol) were dissolved in 12 mL THF. 5 minutes later, 1-(4-methoxyphenyl)-2-(phenylsulfonyl)ethanone **(1j)** (1.0 equiv, 435.5 mg, 1.5 mmol) was added into the mixture under N_2 atmosphere. The reaction was stirred for half an hour. Then SelectFluor (2.0 equiv, 1.0628g, 3.0 mmol) was added into the mixture in a flash. The reaction was allowed at room temperature for 2 h and quenched by 2M HCl until it became clear. After extraction with EtOAc, the organic layer was dried over anhydrous Na_2SO_4, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with EtOAc/hexane to provide white solid **2j** (414.9 mg) in 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.6 Hz, 2H), 7.87 (d, *J* = 7.9 Hz, 2H), 7.73 (t, *J* = 7.5 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 2H), 6.98 (d, *J* = 8.9 Hz, 2H), 6.30 (d, *J* = 48.0 Hz, 1H), 3.91 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -179.34 (d, *J* = 48.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.28 (d, *J* = 17.3 Hz), 165.07, 135.19, 134.62, 132.39 (d, *J* = 2.8 Hz), 129.82, 129.30 , 126.92, 114.14, 100.20 (d, *J* = 231.6 Hz), 55.67. MS (EI, m/z): 308 (M^+, 5.84), 135 (100.00), 77 (22.91), 139 (15.48), 136 (9.43), 92 (6.84), 107 (6.36), 51 (6.33).

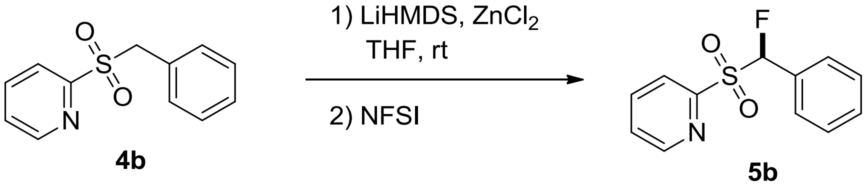
Condition B

Monofluorination of 2-(benzylsulfonyl)benzothiazole (4a)



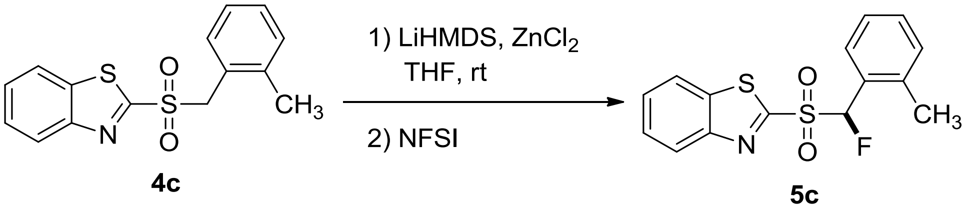
LiHMDS (2.2 equiv, 552.2 mg, 3.3 mmol) and anhydrous $ZnCl_2$ (3.5 equiv, 715.6 mg, 5.25 mmol) were dissolved in 12 mL THF. 5 minutes later, 2-(benzylsulfonyl)benzothiazole **(4a)** (1.0 equiv, 434.1 mg, 1.5 mmol) was added into the mixture under N_2 atmosphere. The reaction was stirred for half an hour. Then NFSI (2.0 equiv, 947.5 mg, 3.0 mmol) was added into the mixture in a flash. The reaction was allowed at room temperature for 0.5 h and quenched by 20mL 2M HCl. After extraction with EtOAc, the organic layer was dried over anhydrous Na_2SO_4, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with CH_2Cl_2/hexane to provide white solid **5a** (305.4 mg) in 66% yield. ^1H NMR (400 MHz,$CDCl_3$) δ 8.37 – 8.24 (m, 1H), 8.12 – 7.90 (m, 1H), 7.76 – 7.59 (m, 4H), 7.59 – 7.45 (m, 3H), 6.63 (d, *J* = 45.9 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -172.48 (d, *J* = 45.9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.72, 152.80, 137.53, 131.60 (d, *J* = 1.4 Hz), 128.87, 128.41 (d, *J* = 0.8 Hz), 128.34, 127.88, 126.23 (d, *J* = 19.4 Hz), 125.74, 122.34, 101.94 (d, *J* = 223.1 Hz). MS (ESI, m/z): 308.0 ($M + H^+$), 329.9 ($M + Na^+$). HRMS (ESI): m/z calcd. For $C_{14}H_{10}F_1N_1Na_1O_2S_2$ ($M + Na^+$) 330.00205, found 330.00308.

Monofluorination of 2-(benzylsulfonyl)pyridine (4b)



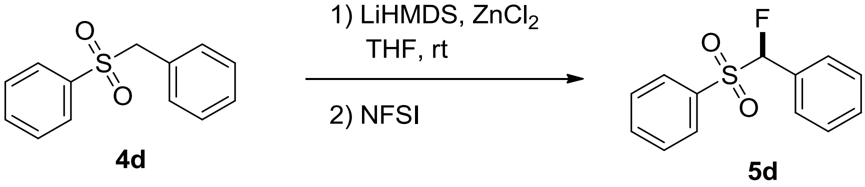
LiHMDS (2.5 equiv, 627.5 mg, 3.75 mmol) and anhydrous $ZnCl_2$ (2.2 equiv, 449.8 mg, 3.3 mmol) were dissolved in 12 mL THF. 5 minutes later, 2-(benzylsulfonyl)pyridine **(4d)** (1.0 equiv, 349.6 mg, 1.5 mmol) was added into the mixture under N_2 atmosphere. The reaction was stirred for half an hour. Then NFSI (2.0 equiv, 947.5 mg, 3.0 mmol) was added into the mixture in a flash. The reaction was allowed at room temperature for 0.5 h and quenched by 20mL 2M HCl. After extraction with EtOAc, the organic layer was dried over anhydrous Na_2SO_4, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with CH_2Cl_2/hexane to provide white solid **5d** (298.8 mg) in 79% yield. m.p.: 146-147 ^oC. IR (KBr): 3448, 3068, 2969, 1578, 1492, 1456, 1430, 1410, 1332, 1291, 1257, 1239, 1197, 1170, 1156, 1113, 1083, 1038, 1026, 990, 929, 850, 798, 777, 749, 733, 722, 695, 646, 616, 580, 557, 503, 444, 416, 403. ^1H NMR (400 MHz, $CDCl_3$) δ 8.84 (d, *J* = 3.8 Hz, 1H), 8.16 (d, *J* = 7.8 Hz, 1H), 8.00 (t, *J* = 7.8 Hz, 1H), 7.62 (d, *J* = 7.4 Hz, 3H), 7.56 – 7.40 (m, 3H), 6.70 (d, *J* = 46.0 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -175.32 (d, *J* = 46.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.87, 150.60, 138.23, 131.13 (d, *J* = 1.4 Hz), 128.66, 128.30 (d, *J* = 6.3 Hz), 127.98, 99.49 (d, *J* = 219.3 Hz). MS (ESI, m/z): 251.9 (M + H^+), 274.0 (M + Na^+). HRMS (ESI): calcd. For $C_{12}H_{11}F_1N_1O_2S$ (M + H^+) 252.04890, found 252.04934.

Monofluorination of 2-((2-methylbenzyl)sulfonyl)benzothiazole (4c)



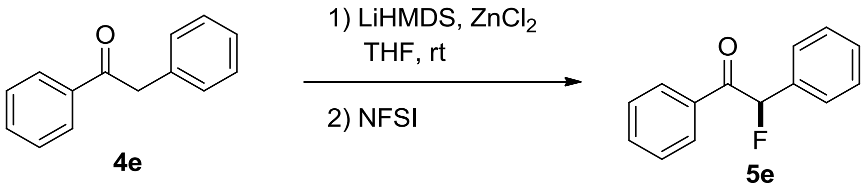
LiHMDS (3.0 equiv, 753.0 mg, 4.5 mmol) and anhydrous $ZnCl_2$ (3.5 equiv, 715.6 mg, 5.25 mmol) were dissolved in 12 mL THF. 5 minutes later, 2-((2-methylbenzyl)sulfonyl)benzothiazole **(4c)** (1.0 equiv, 455.1 mg, 1.5 mmol) was added into the mixture under N_2 atmosphere. The reaction was stirred for half an hour. Then NFSI (2.0 equiv, 947.5 mg, 3.0 mmol) was added into the mixture in a flash. The reaction was allowed at room temperature for 0.5 h and quenched by 20mL 2M HCl. After extraction with EtOAc, the organic layer was dried over anhydrous Na_2SO_4, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with CH_2Cl_2/hexane to provide white solid **5c** (370.8 mg) in 77% yield. m.p.: 148-150 °C. IR (KBr): 3029, 2987, 1464, 1348, 1317, 1154, 1125, 1113,1045, 1022, 761, 737, 716, 697, 652, 612, 594, 562, 544, 513, 485, 464. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 – 8.17 (m, 1H), 8.16 – 7.95 (m, 1H), 7.73 – 7.58 (m, 3H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 2H), 6.92 (d, *J* = 45.7 Hz, 1H), 2.60 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -170.51 (d, *J* = 45.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.16, 152.84, 138.36 (d, *J* = 4.7 Hz), 137.53, 131.45 (d, *J* = 1.7 Hz), 131.08, 128.57 (d, *J* = 7.8 Hz), 128.36, 127.84, 126.39, 125.74, 124.86 (d, *J* = 18.5 Hz), 122.35, 99.10 (d, *J* = 220.8 Hz), 19.64. MS (EI, m/z): 321 (M^+, 0.97), 123 (100.00), 103 (12.96), 77 (12.29), 256 (12.10), 124 (9.32), 236 (9.14), 242 (8.18), 257 (7.41). HRMS (EI): m/z calcd. For $C_{15}H_{12}NO_2FS_2$ (M^+) 321.0294, found 321.0290.

Monofluorination of (benzylsulfonyl)benzene (4d)



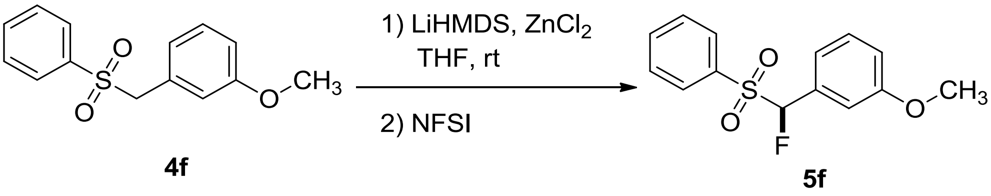
LiHMDS (2.5 equiv, 627.5 mg, 3.75 mmol) and anhydrous $ZnCl_2$ (1.0 equiv, 204.5 mg, 1.5 mmol) were dissolved in 12 mL THF. 5 minutes later, (benzylsulfonyl)benzene **(4d)** (1.0 equiv, 348.5 mg, 1.5 mmol) was added into the mixture under N_2 atmosphere. The reaction was stirred for half an hour. Then NFSI (2.0 equiv, 947.5 mg, 3.0 mmol) was added into the mixture in a flash. The reaction was allowed at room temperature for 0.5 h and quenched by 20mL 2M HCl. After extraction with EtOAc, the organic layer was dried over anhydrous Na_2SO_4, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with EtOAc/hexane to provide white solid **5c** (282.2 mg) in 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.7 Hz, 2H), 7.69 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 2H), 7.49 – 7.42 (m, 1H), 7.42 – 7.33 (m, 4H), 6.07 (d, *J* = 45.8 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -175.77 (d, *J* = 45.7 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.59, 134.53, 130.73, 129.92, 129.01, 128.40, 128.24, 127.53 (d, *J* = 6.7 Hz), 102.87 (d, *J* = 220.8 Hz). MS (ESI, m/z): 268.0 (M + NH_4^+), 273.0 (M + Na^+), 288.9 (M + K^+).

Monofluorination of 1,2-diphenylethanone (4e)



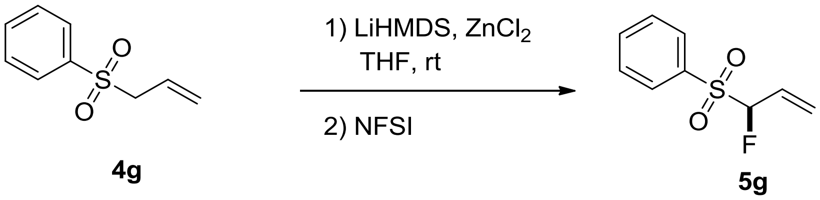
LiHMDS (2.2 equiv, 552.2 mg, 3.3 mmol) and anhydrous $ZnCl_2$ (2.2 equiv, 449.8 mg, 3.3 mmol) were dissolved in 12 mL THF. 5 minutes later, 1,2-diphenylethanone **(4e)** (1.0 equiv, 303.5 mg, 1.5 mmol) was added into the mixture under N_2 atmosphere. The reaction was stirred for half an hour. Then NFSI (2.0 equiv, 947.5 mg, 3.0 mmol) was added into the mixture in a flash. The reaction was allowed at room temperature for 0.5 h and quenched by 20mL 2M HCl. After extraction with EtOAc, the organic layer was dried over anhydrous Na_2SO_4, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with EtOAc/hexane to remove remaining NFSI and purified again with acetone/pentane to provide white solid **5e** (265.4 mg) in 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.8 Hz, 2H), 7.65 – 7.45 (m, 3H), 7.45 – 7.34 (m, 4H), 6.52 (d, *J* = 48.6 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -175.79 (d, *J* = 48.7 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.24 (d, *J* = 21.3 Hz), 134.20 (d, *J* = 19.9 Hz), 133.97, 133.75, 129.61 (d, *J* = 2.6 Hz), 129.07, 129.04, 128.66, 127.36 (d, *J* = 5.5 Hz), 93.92 (d, *J* = 185.7 Hz). MS (EI, m/z): 214 (M^+, 0.75), 105 (100.00), 77 (39.18), 109 (10.70), 51 (10.46), 106 (7.94), 83 (5.48), 50 (3.27), 78 (2.74).

Monofluorination of 1-methoxy-3-((phenylsulfonyl)methyl)benzene (4f)



LiHMDS (2.5 equiv, 627.5 mg, 3.75 mmol) and anhydrous $ZnCl_2$ (2.2 equiv, 449.8 mg, 3.3 mmol) were dissolved in 12 mL THF. 5 minutes later, 1-methoxy-3-((phenylsulfonyl)methyl)benzene **(4f)** (1.0 equiv, 393.5 mg, 1.5 mmol) was added into the mixture under N_2 atmosphere. The reaction was stirred for half an hour. Then NFSI (2.0 equiv, 947.5 mg, 3.0 mmol) was added into the mixture in a flash. The reaction was allowed at room temperature for 0.5 h and quenched by 20mL 2M HCl. After extraction with EtOAc, the organic layer was dried over anhydrous Na_2SO_4, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with EtOAc/hexane to provide white solid **5f** (281.5 mg) in 67% yield. m.p.: 122-123 ^oC. IR (KBr): 3064, 3017, 2962, 2933, 2833, 1610, 1588, 1488, 1458, 1448, 1435, 1323, 1291, 1272, 1234, 1151, 1085, 1071, 1060, 1036, 998, 905, 883, 768, 781, 719, 690, 650, 617, 572, 555, 543. ^1H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, 2H), 7.69 (t, J = 7.3 Hz, 1H), 7.53 (t, J = 7.7 Hz, 2H), 7.28 (t, 1H), 7.04 – 6.90 (m, 2H), 6.83 (s, 1H), 6.04 (d, J = 45.8 Hz, 1H), 3.74 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -175.17 (d, J = 45.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.44, 134.57, 129.96, 129.68 (d, J = 19.6 Hz), 129.49, 129.00, 119.97 (d, J = 6.8 Hz), 116.96, 116.95, 112.31 (d, J = 7.2 Hz), 102.81 (d, J = 221.3 Hz), 55.31. MS (EI, m/z): 280 (M^+, 3.64), 139 (100.00), 96 (13.41), 109 (12.94), 77 (10.54), 140 (9.23), 154 (6.67), 51 (6.43), 107 (4.68). HRMS (EI): calcd. For $C_{14}H_{13}O_3FS$ (M^+) 280.0569, found 280.0572.

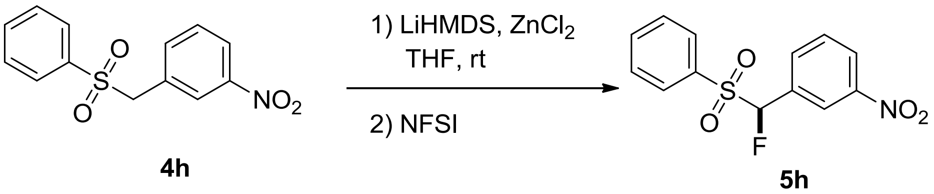
Monofluorination of (allylsulfonyl)benzene (4g)



LiHMDS (3.0 equiv, 753.0 mg, 4.5 mmol) and anhydrous $ZnCl_2$ (2.2 equiv, 449.8 mg, 3.3 mmol) were dissolved in 12 mL THF. 5 minutes later, (allylsulfonyl)benzene **(4g)** (1.0 equiv, 278.9 mg, 1.5 mmol) was added into the mixture under N_2 atmosphere. The reaction was stirred for half an hour. Then NFSI (2.0 equiv, 947.5 mg, 3.0 mmol) was added into the mixture in a flash. The reaction was allowed at room temperature for 0.5 h and quenched by 20mL 2M HCl. After extraction with EtOAc, the organic layer was dried over anhydrous Na_2SO_4, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with EtOAc/hexane to provide colourless liquid **4g** (198.9 mg) in 66% yield. IR (film): 3648, 3069, 1585, 1479, 1449, 1425, 1329, 1312, 1294, 1232, 1156, 1123, 1085, 1046, 1001, 984, 948, 823, 796, 756, 723, 701, 688, 651, 597, 548, 528, 509. ^1H NMR (400 MHz,$CDCl_3$) δ 7.93 (d, J = 7.9 Hz, 2H), 7.78 – 7.67 (m, 1H), 7.64 – 7.54 (m, 2H), 6.11 – 5.88 (m, 1H), 5.68 – 5.46 (m, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -178.13 (dd, J = 47.2, 17.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.68, 129.89, 129.13, 125.09 (d, J = 18.8 Hz), 124.87, 124.76, 101.82 (d, J = 219.7 Hz). MS (ESI, m/z):218.0 ($M + NH_4^+$), 222.9 ($M + Na^+$). HRMS (ESI): calcd. For $C_9H_9F_1Na_1O_2S_1$

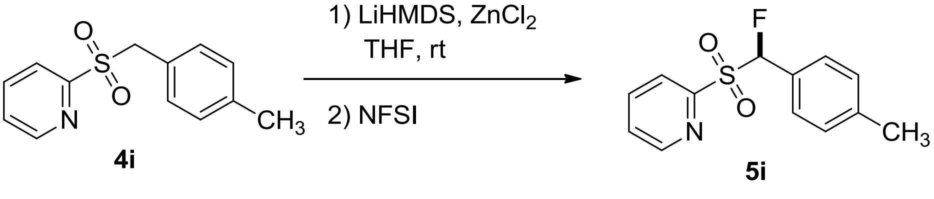
(M + Na$^+$) 223.01995, found 223.02029.

Monofluorination of 1-nitro-3-((phenylsulfonyl)methyl)benzene (4h)



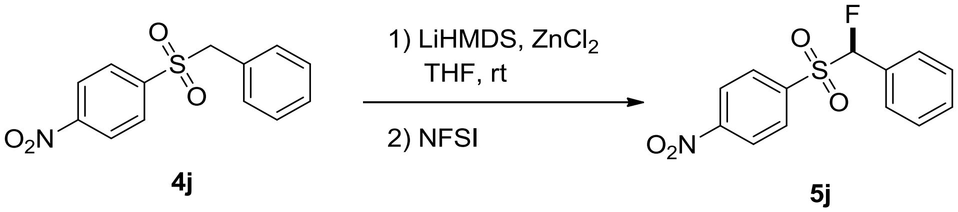
LiHMDS (2.2 equiv, 552.2 mg, 3.3 mmol) and anhydrous ZnCl$_2$ (1.8 equiv, 368.0 mg, 2.7 mmol) were dissolved in 12 mL THF. 5 minutes later, 1-nitro-3-((phenylsulfonyl)methyl)benzene **(4h)** (1.0 equiv, 416.0 mg, 1.5 mmol) was added into the mixture under N$_2$ atmosphere. The reaction was stirred for half an hour. Then NFSI (2.0 equiv, 947.5 mg, 3.0 mmol) was added into the mixture in a flash. The reaction was allowed at room temperature for 0.5 h and quenched by 20mL 2M HCl. After extraction with EtOAc, the organic layer was dried over anhydrous Na$_2$SO$_4$, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with CH$_2$Cl$_2$/hexane to provide **5h** white solid (417.4 mg) in 94% yield. m.p.: 155 ^{o}C. IR(KBr): 3451, 3095, 2957, 1584, 1532, 1449, 1356, 1328, 1311, 1233, 1085, 1046, 903, 830, 781, 756, 738, 717, 688, 641, 580, 559, 510. ^{1}H NMR (400 MHz, DMSO-D$_6$) δ 8.40 (d, J = 8.1 Hz, 1H), 8.23 (s, 1H), 7.95 – 7.84 (m, 4H), 7.81 (t, J = 7.9 Hz, 1H), 7.72 (t, J = 7.8 Hz, 2H), 7.21 (d, J = 44.6 Hz, 1H). ^{19}F NMR (282 MHz, DMSO-D$_6$) δ -177.23 (d, J = 44.6 Hz). ^{13}C NMR (100 MHz, DMSO-D$_6$) δ 147.90, 135.85, 134.68, 134.51 (d, J = 6.2 Hz), 130.83, 130.67 (d, J = 20.1 Hz), 130.17, 129.87, 126.09, 123.04 (d, J = 7.2 Hz), 100.62 (d, J = 216.0 Hz). MS (EI, m/z): 295 (M$^+$, 3.12), 154 (100.00), 108 (37.07), 107 (19.31), 77 (16.23), 51 (9.66), 155 (8.35), 109 (3.83), 50 (3.18). HRMS (EI): calcd. For $C_{13}H_{10}NO_4FS$ (M$^+$) 295.0315, found 295.0318.

Monofluorination of 2-((4-methylbenzyl)sulfonyl)pyridine (4i)



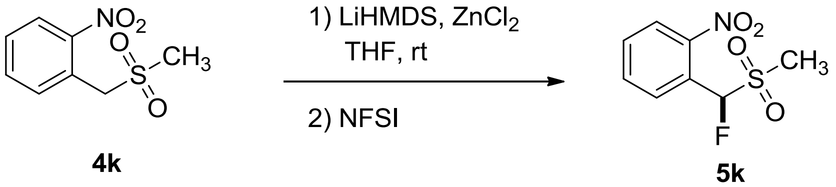
LiHMDS (2.5 equiv, 627.5 mg, 3.75 mmol) and anhydrous ZnCl$_2$ (1.5 equiv, 306.7 mg, 2.25 mmol) were dissolved in 12 mL THF. 5 minutes later, 2-((4-methylbenzyl)sulfonyl)pyridine **(4i)** (1.0 equiv, 371.0 mg, 1.5 mmol) was added into the mixture under N$_2$ atmosphere. The reaction was stirred for half an hour. Then NFSI (2.0 equiv, 947.5 mg, 3.0 mmol) was added into the mixture in a flash. The reaction was allowed at room temperature for 0.5 h and quenched by 20mL 2M HCl. After extraction with EtOAc, the organic layer was dried over anhydrous Na$_2$SO$_4$, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with CH_2Cl_2/hexane to provide white solid **5i** (310.8 mg) in 78% yield. m.p.: 139-140 ^oC. IR (KBr): 3822, 3651, 3057, 2962, 1613, 1577, 1560, 1513, 1449, 1427, 1327, 1238, 1184, 1164, 1152, 1110, 1081, 1040, 1021, 990, 831, 787, 777, 752, 735, 619, 637, 606, 562, 549, 503. ^1H NMR (400 MHz, $CDCl_3$) δ 8.83 (d, *J* = 3.9 Hz, 1H), 8.16 (d, *J* = 7.8 Hz, 1H), 8.00 (t, *J* = 7.7 Hz, 1H), 7.69 – 7.57 (m, 1H), 7.51 (d, *J* = 7.9 Hz, 2H), 7.35 – 7.22 (m, 2H), 6.67 (d, *J* = 45.9 Hz, 1H), 2.40 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -174.23 (d, *J* = 46.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.03, 150.59, 141.56, 138.19, 129.44, 128.31 (d, *J* = 6.1 Hz), 127.91, 124.63, 123.77 (d, *J* = 19.5 Hz), 99.53 (d, *J* = 218.8 Hz), 21.50. MS (ESI, m/z): 287.9 (M + Na^+), 552.9 (2M + Na^+). HRMS (ESI): calcd. For $C_{13}H_{12}F_1N_1Na_1O_2S_1$ (M + H^+) 288.04650, found 288.04662.

Monofluorination of 1-(benzylsulfonyl)-4-nitrobenzene (4j)



LiHMDS (2.5 equiv, 627.5 mg, 3.75 mmol) and anhydrous $ZnCl_2$ (3.0 equiv, 613.4 mg, 4.5 mmol) were dissolved in 12 mL THF. 5 minutes later, 1-(benzylsulfonyl)-4-nitrobenzene **(4j)** (1.0 equiv, 416.0 mg, 1.5 mmol) was added into the mixture under N_2 atomosphere. The reaction was stirred for half an hour. Then NFSI (2.0 equiv, 947.5 mg, 3.0 mmol) was added into the mixture in a flash. The reaction was allowed at room temperature for 0.5 h and quenched by 20mL 2M HCl. After extraction with EtOAc, the organic layer was dried over anhydrous Na_2SO_4, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with CH_2Cl_2/hexane to provide light green solid **5h** (393.2 mg) in 89% yield. m.p.: 167-168 ^oC. IR (KBr): 3103, 3067, 3038, 2957, 2875, 1963, 1901, 1812, 1608, 1537, 1491, 1480, 1457, 1402, 1347, 1336, 1314, 1223, 1234, 1197, 1154, 1112, 1082, 1046, 1030, 1014, 861, 844, 790, 754, 739, 719, 696, 678, 649, 585, 555, 504, 467, 442, 422. ^1H NMR (400 MHz, DMSO-D_6) δ 8.51 (d, *J* = 8.7 Hz, 2H), 8.16 (d, *J* = 8.6 Hz, 2H), 7.66 – 7.42 (m, 5H), 7.12 (d, *J* = 44.5 Hz, 1H). ^{19}F NMR (282 MHz, DMSO-D_6) δ -175.41 (d, *J* = 44.5 Hz). ^{13}C NMR (100 MHz, DMSO-D_6) δ 151.69, 140.88, 131.62, 131.56, 129.06, 128.54 (d, *J* = 6.4 Hz), 127.83 (d, *J* = 19.3 Hz), 125.15, 101.90 (d, *J* = 215.1 Hz). MS (ESI, m/z):312.9 (M + NH_4^+), 318.0 (M + Na^+). HRMS (ESI): calcd. For $C_{13}H_{10}F_1N_1Na_1O_4S_1$ (M + Na^+) 318.02068, found 318.02017.

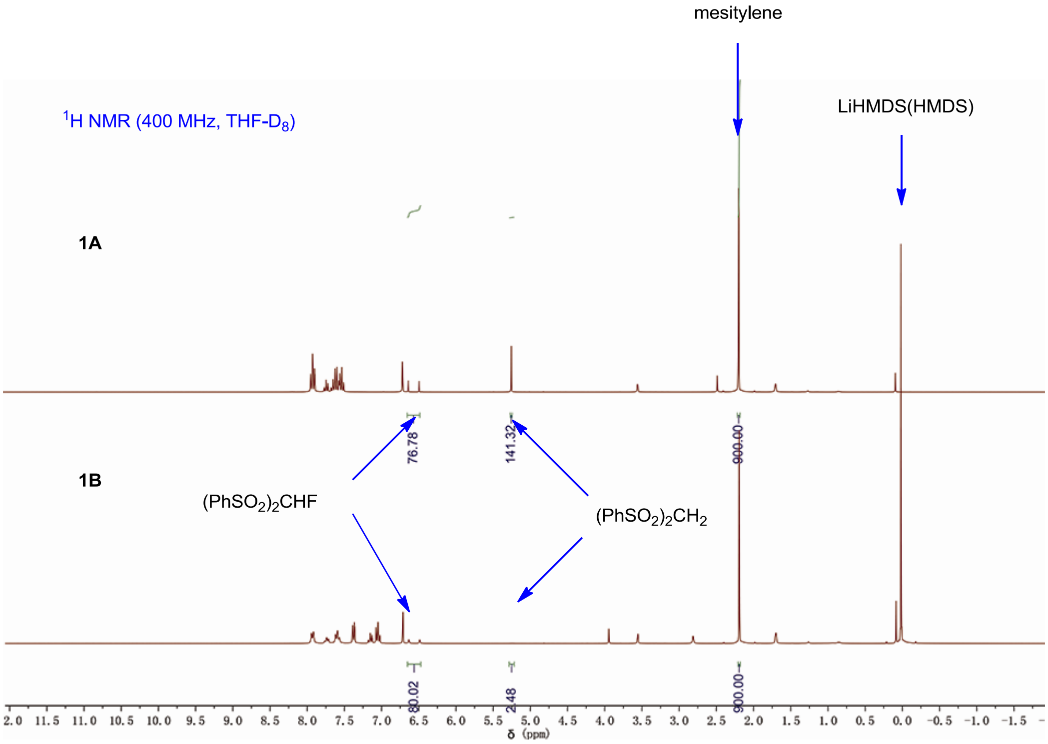
Monofluorination of 1-((methylsulfonyl)methyl)-2-nitrobenzene (4k)



LiHMDS (2.5 equiv, 627.5 mg, 3.75 mmol) and anhydrous $ZnCl_2$ (3.5 equiv, 715.6 mg, 5.25 mmol) were dissolved in 12 mL THF. 5 minutes later, 1-((methylsulfonyl)methyl)-2-nitrobenzene **(4k)** (1.0 equiv, 322.8 mg, 1.5 mmol) was added into the mixture under N_2 atmosphere. The reaction was stirred for half an hour. Then NFSI (2.0 equiv, 947.5 mg, 3.0 mmol) was added into the mixture in a flash. The reaction was allowed at room temperature for 0.5 h and quenched by 20mL 2M HCl. After extraction with EtOAc, the organic layer was dried over anhydrous Na_2SO_4, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with EtOAc/hexane to provide light green solid **5k** (329.7 mg) in 94% yield. m.p.: 151-152 ^oC. IR (KBr): 3114, 3032, 3017, 2937, 2870, 1611, 1580, 1527, 1482, 1443, 1410, 1350, 1330, 1315, 1300, 1237, 1188, 1143, 1091, 1057, 1040, 962, 887, 863, 838, 789, 760, 715, 684, 625, 534, 512, 467, 422, 409. ^1H NMR (400 MHz, DMSO-D_6) δ 8.21 (d, *J* = 8.3 Hz, 1H), 7.94 (t, *J* = 7.5 Hz, 1H), 7.83 (t, *J* = 7.0 Hz, 2H), 7.60 (d, *J* = 45.9 Hz, 1H), 3.28 (s, 3H). ^{19}F NMR (282 MHz, DMSO-D_6) δ -178.60 (d, *J* = 45.9 Hz). ^{13}C NMR (100 MHz, DMSO-D_6) δ 148.19 (d, *J* = 3.6 Hz), 134.55 (d, *J* = 1.0 Hz), 132.41, 129.13 (d, *J* = 12.3 Hz), 125.90, 122.68 (d, *J* = 20.8 Hz), 96.92 (d, *J* = 215.4 Hz), 38.50. MS (ESI, m/z): 250.9 (M + NH_4^+), 255.9 (M + Na^+). HRMS (ESI): calcd. For $C_8H_8F_1N_1Na_1O_4S_1$ (M + Na^+) 256.00503, found 252.00490.

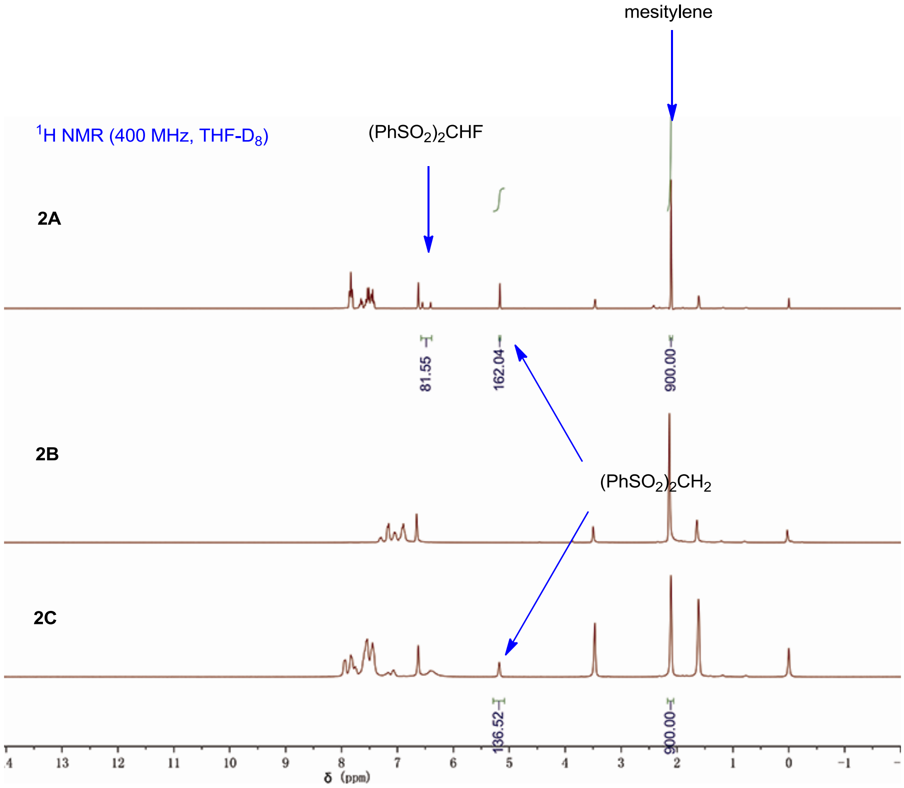
NMR experiments to gain insight into this $ZnCl_2$-mediated selective monofluorination

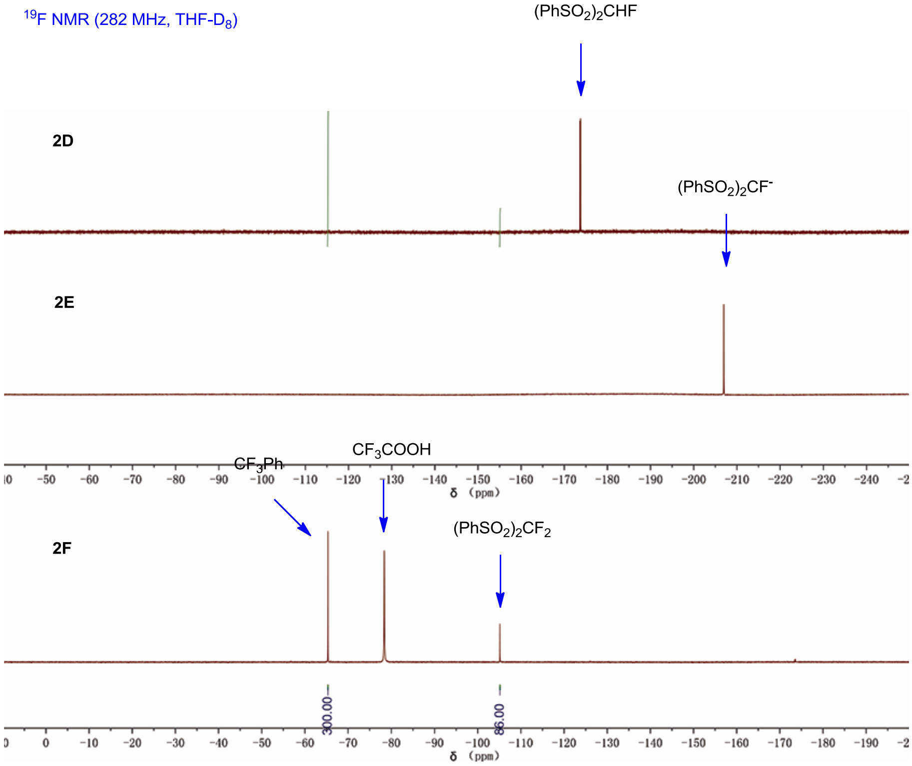
Experiment A Comparison of the tendency of deprontonation between $(PhSO_2)_2CH_2$ and $(PhSO_2)_2CHF$



$(PhSO_2)_2CH_2$ (29.6 mg, 0.1 mmol) and $(PhSO_2)_2CHF$ (31.4mg, 0.1 mmol) were dissolved in 2 mL THF-D_8 in the glove box. 19.5 mg mesitylene was added to the mixture as the internal standard. After 5 minutes, 0.5 mL of the solvent was taken out and indicated by ^{1}H NMR as a control experiment (entry 1A). Then LiHMDS (12.5 mg, 0.075 mmol) was added with extra 0.3 mL THF-D_8 to guarantee no remaining LiHMDS attached on the schlenk tube. 20 minutes later, 0.5 mL of the solvent was taken out indicated by ^{1}H NMR (entry 1B). The comparison of ^{1}H NMR peak integral between entry A and B showed that $(PhSO_2)_2CH_2$ was almost deprotonated, while $(PhSO_2)_2CHF$ was barely deprotonated. We made the conclusion that $(PhSO_2)_2CH_2$ has a stronger tendency of deprontonation than $(PhSO_2)_2CHF$.

Experiment B Comparison of the tendency of deprontonation between $(PhSO_2)_2CH_2$ and $(PhSO_2)_2CHF$



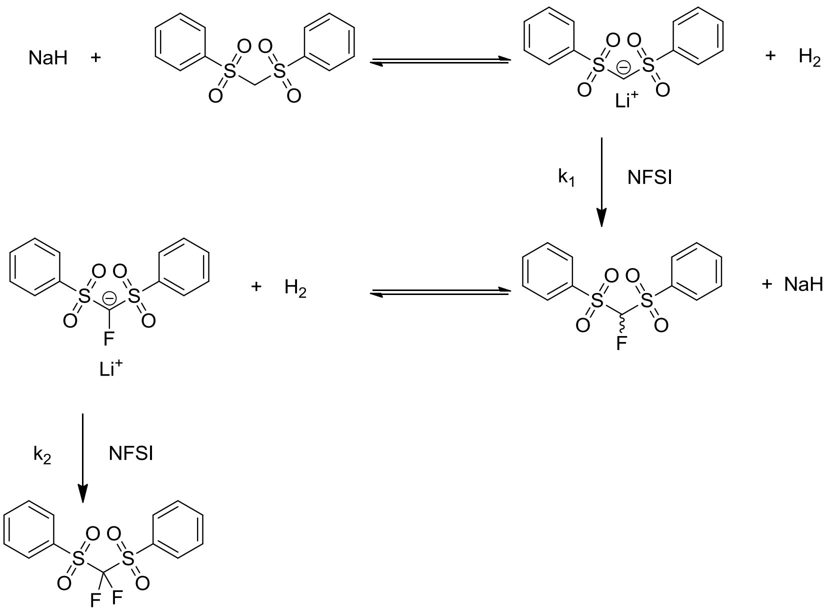


$(PhSO_2)_2CH_2$ (29.6 mg, 0.1 mmol) and $(PhSO_2)_2CHF$ (31.4mg, 0.1 mmol) were dissolved in 2 mL THF-D_8 in the glove box. 16.4 mg mesitylene was added to the mixture as the internal standard. After 5 minutes, 0.5 mL of the solvent was taken out and indicated by ^{1}H NMR and ^{19}F NMR as a control experiment (entry 2A and 2D). Then NaH (5.7 mg, 0.225 mmol) was added. 20 minutes later, 0.5 mL of the solvent was taken out and indicated by ^{1}H NMR and ^{19}F NMR (entry 2B and 2E). NFSI (15.8mg, 0.05mmol) was added and the mixture was stirred for 30 minutes. The reaction was quenched by 36.0 μL CF_3COOH and added in 14.2 mg CF_3Ph as the internal standard. 0.5 mL of the solvent was taken out and indicated by ^{1}H NMR and ^{19}F NMR (entry 2C and 2F). The crude calculation of fluorinated capability between $(PhSO_2)_2CH_2$ and $(PhSO_2)_2CHF$ were as follows:

(1) The comparison of ^{1}H NMR peak integral between entry 2A and 2B, ^{19}F NMR peak integral between entry 2D and 2E showed that $(PhSO_2)_2CH_2$ and $(PhSO_2)_2CHF$ were almost deprotonated.

(2) The comparison of ^{1}H NMR peak integral between entry 2A and 2C showed that after the reaction was quenched, the concentration of $(PhSO_2)_2CH_2$ was reduced by 15.7%, which meant 15.7% was converted into $(PhSO_2)_2CHF$. The amount was 15.7%*(1.0 ml/2.0 ml)*0.1 mmol = 0.0079 mmol.

(3) According to entry 2F of ^{19}F NMR peak integral, the amount of generation of $(PhSO_2)_2CF_2$ was 14.2 mg/(146.11 g/mol)*0.86/2 = 0.0418 mmol



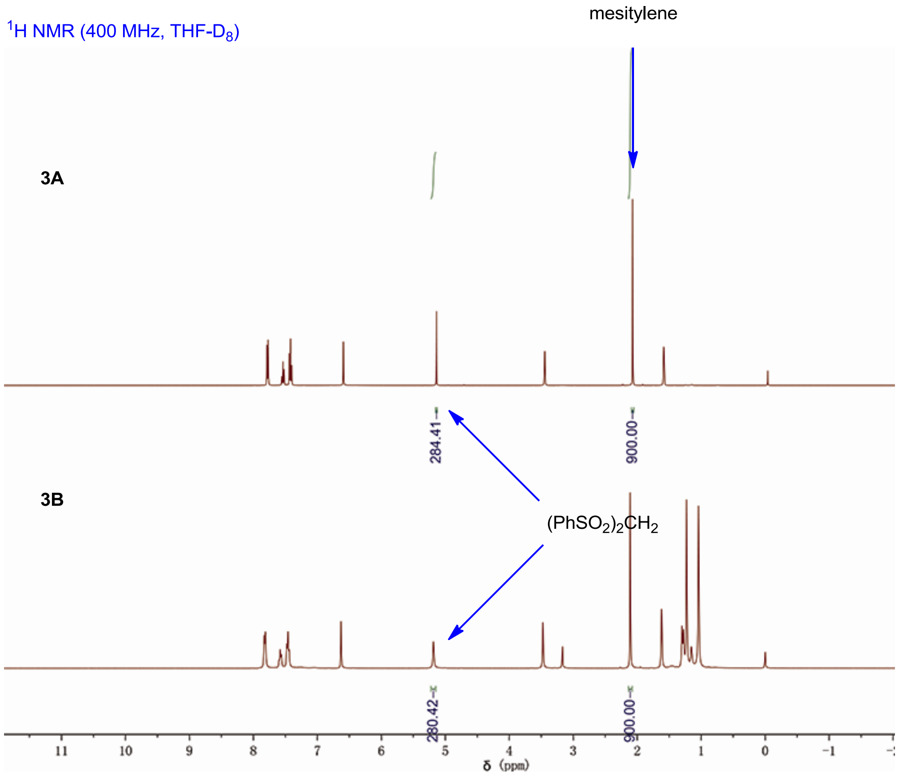
The reaction process was shown as above. We might as well compare the tendency for fluorination between $(PhSO_2)_2CH_2$ and $(PhSO_2)_2CHF$ through the average rate constants k_1 and k_2. The scope of k_2/k_1 could be esitmated as follows:

(1) If there were no further transformation of $(PhSO_2)_2CHF$ into $(PhSO_2)_2CF^-$ until the original $(PhSO_2)_2CF^-$ had been fluorinated. We would get the maximum ratio of k_2/k_1, which was (0.0418 mmol/ 0.0079 mmol) = 5.3

(2) If further transformation of $(PhSO_2)_2CHF$ into $(PhSO_2)_2CF^-$ finished before $(PhSO_2)_2CF^-$ had been fluorinated. We would get the minimum ratio of k_2/k_1. Since the amount of further transformation of $(PhSO_2)_2CHF$ into $(PhSO_2)_2CF^-$ could not pass 0.0079 mmol, the minimum ratio of k_2/k_1 was (0.05 mmol)/(0.05 mmol + 0.0079 mmol)* (0.0418 mmol/ 0.0079 mmol) = 4.6

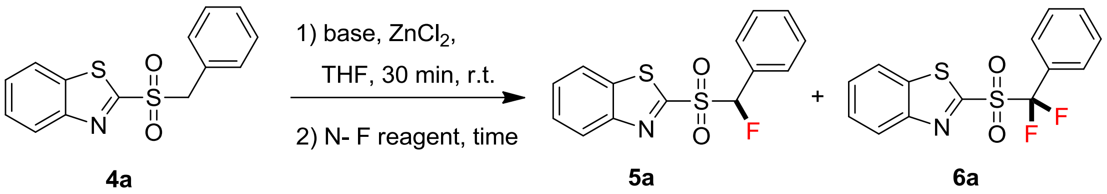
The result demonstrated that $(PhSO_2)_2CHF$ showed higher tendency for fluorination.

Experiment C Adding $(PhSO_2)_2CH_2$ into THF-D_8 under the optimized conditions (2.5 equiv of ^{t}BuONa and 2.5 equiv of $ZnCl_2$)



$(PhSO_2)_2CH_2$ (59.2 mg, 0.2 mmol) and anhydrous $ZnCl_2$ (68.2 mg, 0.5 mmol) were dissolved in 2 mL THF-D_8 in the glove box. 17.8 mg mesitylene was added to the mixture as the internal standard. After 5 minutes, 0.5 mL of the solvent was taken out and indicated by ^{1}H NMR as a control experiment (entry 3A). Then ^{t}BuONa (36.0 mg, 0.375 mmol) was added with extra 0.4 mL THF-D_8 to guarantee no remaining NaO^{t}Bu attached on the schlenk tube. 30 minutes later, 0.5 mL of the solvent was taken out indicated by ^{1}H NMR (entry 3B). The comparison of ^{1}H NMR peak integral between entry A and B showed that $(PhSO_2)_2CH_2$ was barely deprotonated.

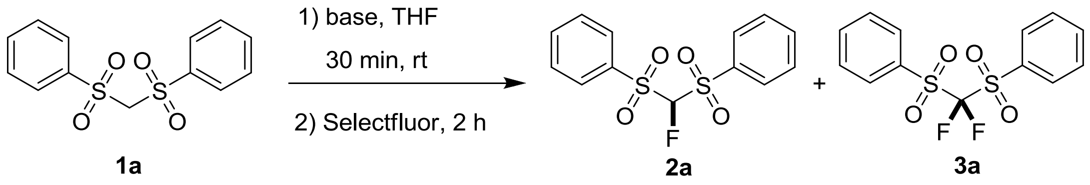
Table A. Optimized Conditions for Monofluorination of **4a** (R^1 =EWG, R^2 =Phenyl, Alkenyl)



entry	base (equiv)^a	ZnCl$_2$ (equiv)^a	time (h)	**5a** (%)^b	**6a** (%)^b
1	2.5 (^{t}BuONa)	2.5	2	-	-
2	2.5 (^{t}BuONa)	2.2	2	-	-
3	2.5 (^{t}BuONa)	1.8	2	-	-
4	2.5 (^{t}BuONa)	3.0	2	-	-
5	2.5 (LiHMDS)^c	2.5	2	-	-
6	2.5 (LiHMDS)^c	2.5	0.5	-	-
7	2.5 (LiHMDS)	2.2	0.5	-	-
8	2.5 (LiHMDS)	3.5	0.5	56	-
9	3.0 (LiHMDS)	3.5	0.5	27	-
10	2.2 (LiHMDS)	3.5	0.5	68	-
11	1.8 (LiHMDS)	3.5	0.5	53	-

[a] The equivalent is relative to that of **1a**. [b] Determined by ^{19}F NMR analysis of the crude reaction mixture using PhCF$_3$ as an internal standard. [c] Entry 5 used SelectFluor as fluorination reagent, while entry 6 NFSI.

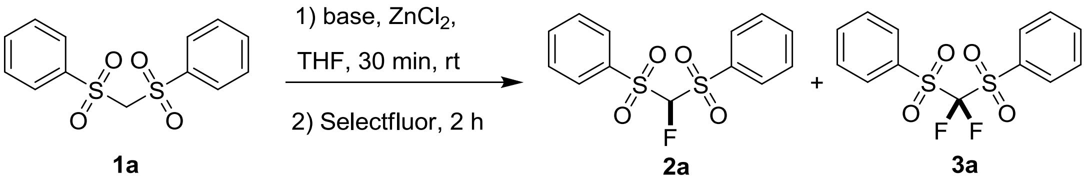
Table B. Screening of different bases.



entry	base^a	**2a** (%)^b	**3a** (%)^b
1	C_6H_5ONa	61	13
2	CH_3ONa	71	6
3	C_2H_5ONa	64	10
4	^{t}BuONa	73	2
5	NaHMDS	57	12

[a]The equivalent of base is 1 equiv relative to that of 1a. [b]Determined by ^{19}F NMR analysis of the crude reaction mixture using $PhCF_3$ as an internal standard.

Table C. Screening of different bases in the presence of $ZnCl_2$.



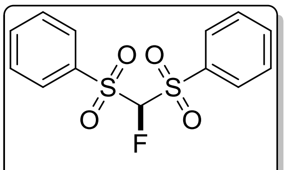
entry	base (equiv)[a]	$ZnCl_2$ (equiv)[a]	**2a** (%)[b]	**3a** (%)[b]
1	^{t}BuONa (2.5 equiv)	2.5	91	1
2	C_6H_5ONa (2.5 equiv)	2.5	-	-
3	CH_3ONa (2.5 equiv)	2.5	29	-
4	C_2H_5ONa (2.5 equiv)	2.5	39	-
5	C_2H_5ONa (2.5 equiv)	2.2	53	-
6	C_2H_5ONa (2.5 equiv)	1.8	82	19
7	NaHMDS (2.5 equiv)	2.5	15	39

[a]The equivalent is relative to that of 1a. [b]Determined by ^{19}F NMR analysis of the crude reaction mixture using $PhCF_3$ as an internal standard.

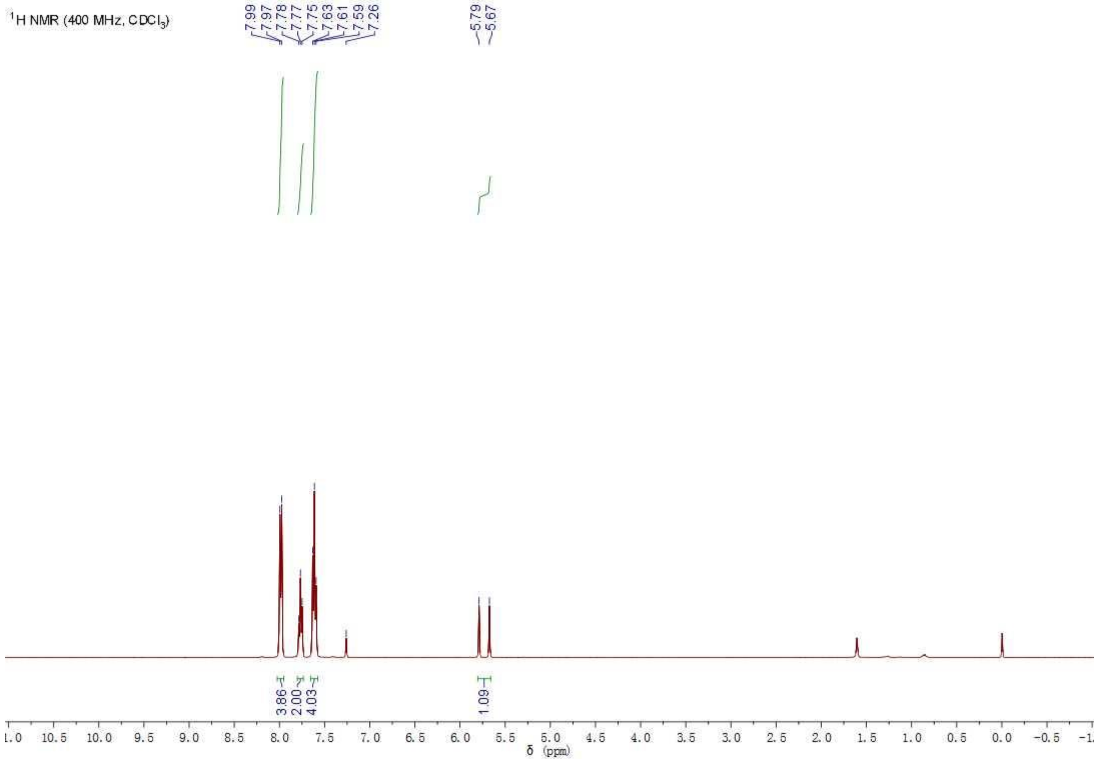
References

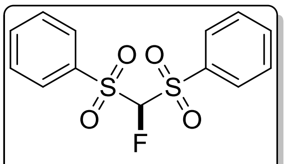
(1) Chang, Y.-F.; Jiang, Y.-R.; Cheng, W.-C. *Tetrahedron Lett.* **2008**, *49*, 543.

(2) Zhao, Y.; Huang, W.; Zhu, L.; Hu, J. *Org. Lett.* **2010**, *12*, 1444.

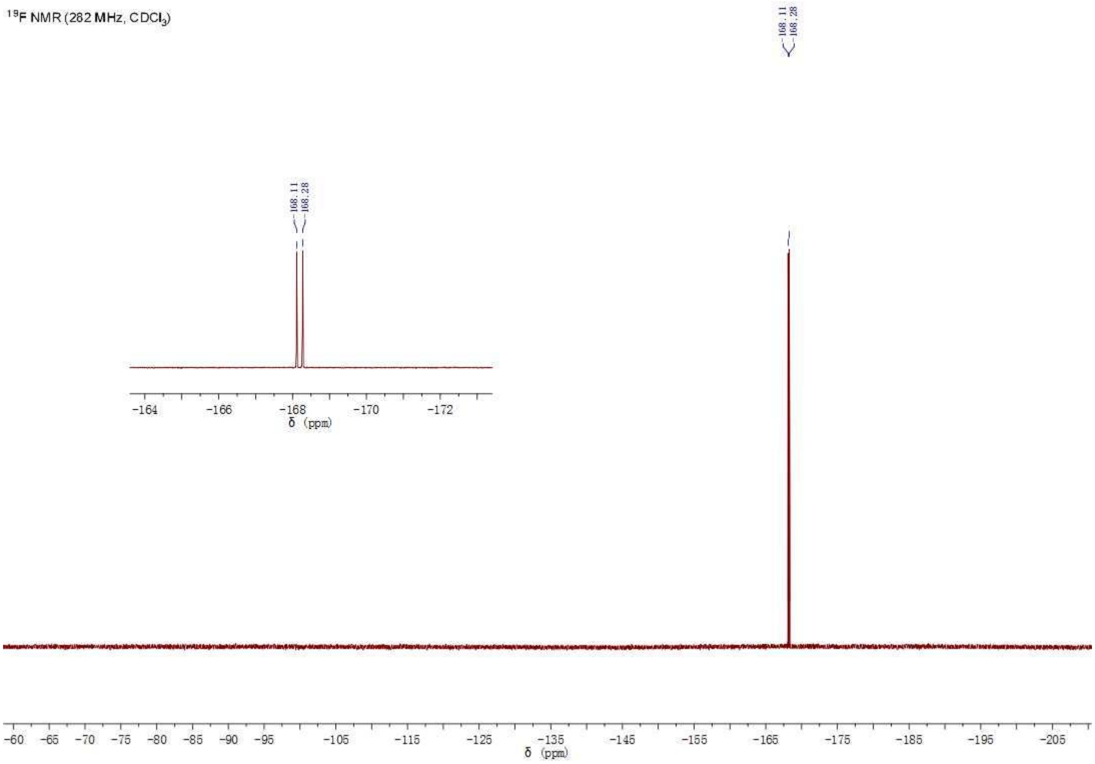


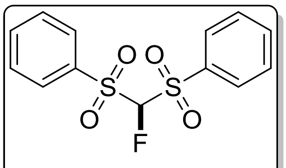
2a


^{1}H NMR (400 MHz, CDCl$_3$)
7.99
7.97
7.78
7.77
7.75
7.63
7.61
7.59
7.26
5.79
5.67
3.86
2.00
4.03
1.09
11.0 10.5 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 0.0 −0.5 −1
δ (ppm)

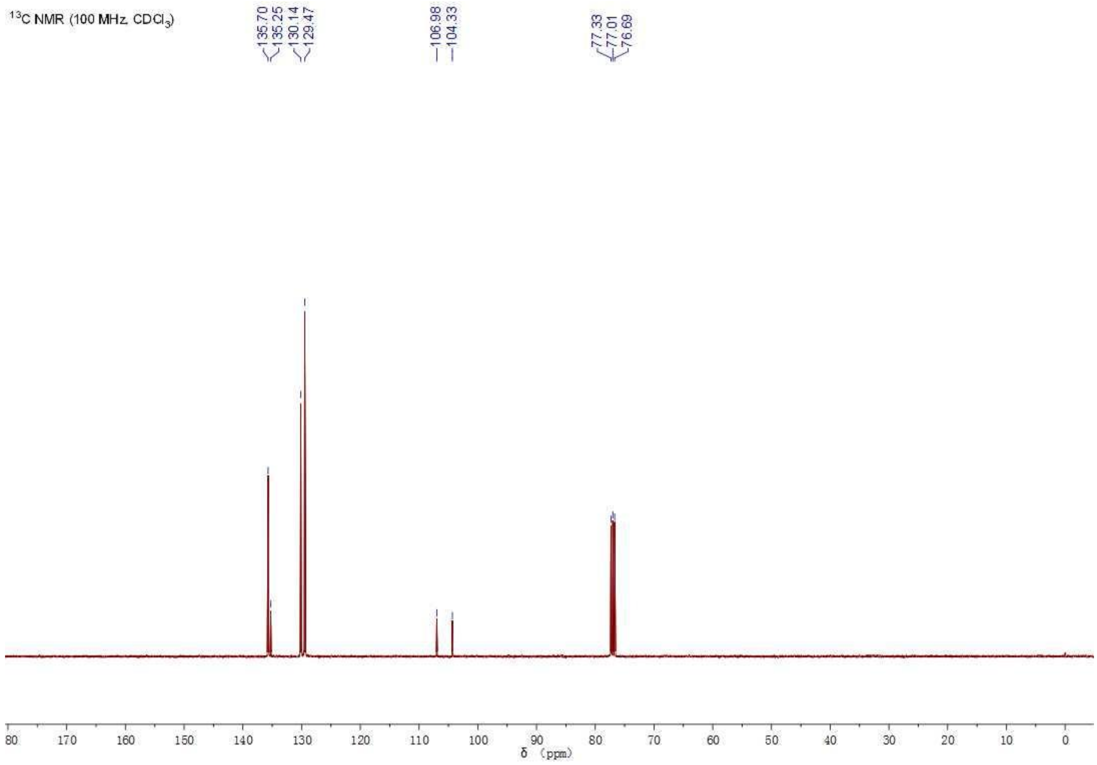

O
O
S
S
O
O
F

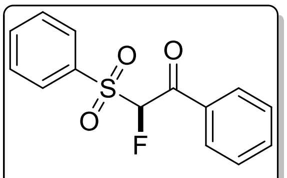
2a


^{19}F NMR (282 MHz, CDCl$_3$)
-168.11
-168.28
-164
-166
-168
-170
-172
δ (ppm)
-60
-65
-70
-75
-80
-85
-90
-95
-105
-115
-125
-135
-145
-155
-165
-175
-185
-195
-205
δ (ppm)

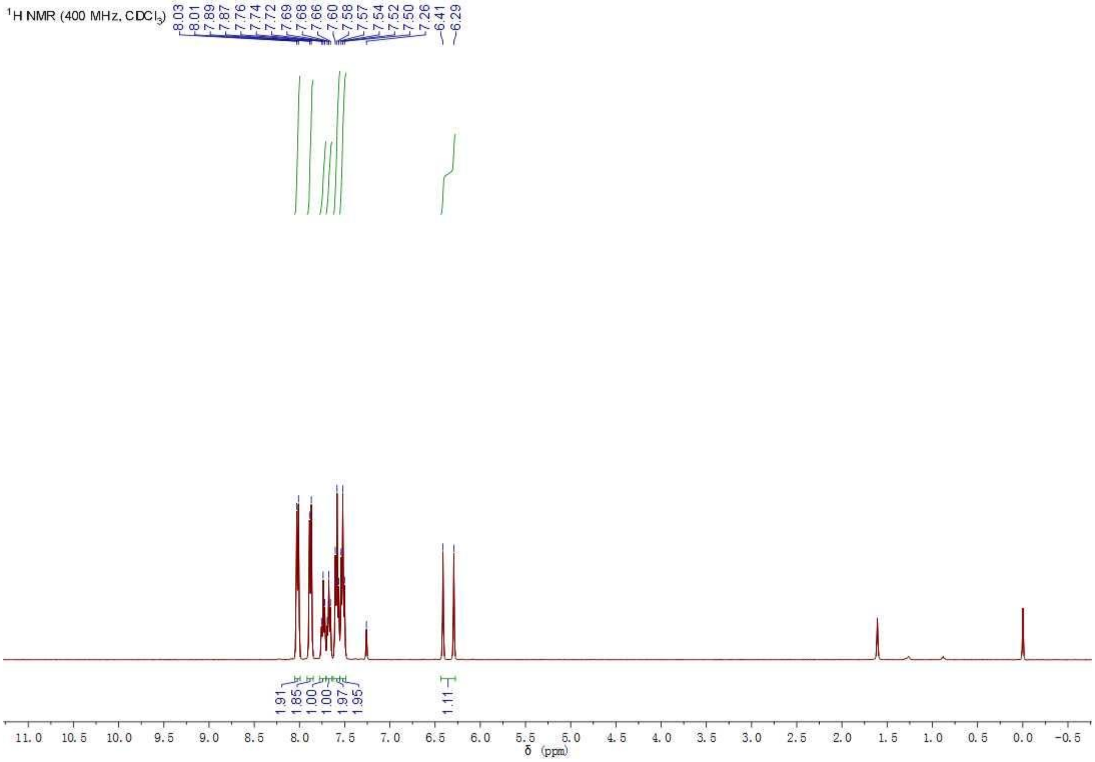


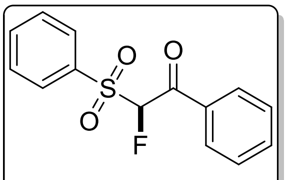
2a


^{13}C NMR (100 MHz, CDCl$_3$)
135.70
135.25
130.14
129.47
106.98
104.33
77.33
77.01
76.69
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

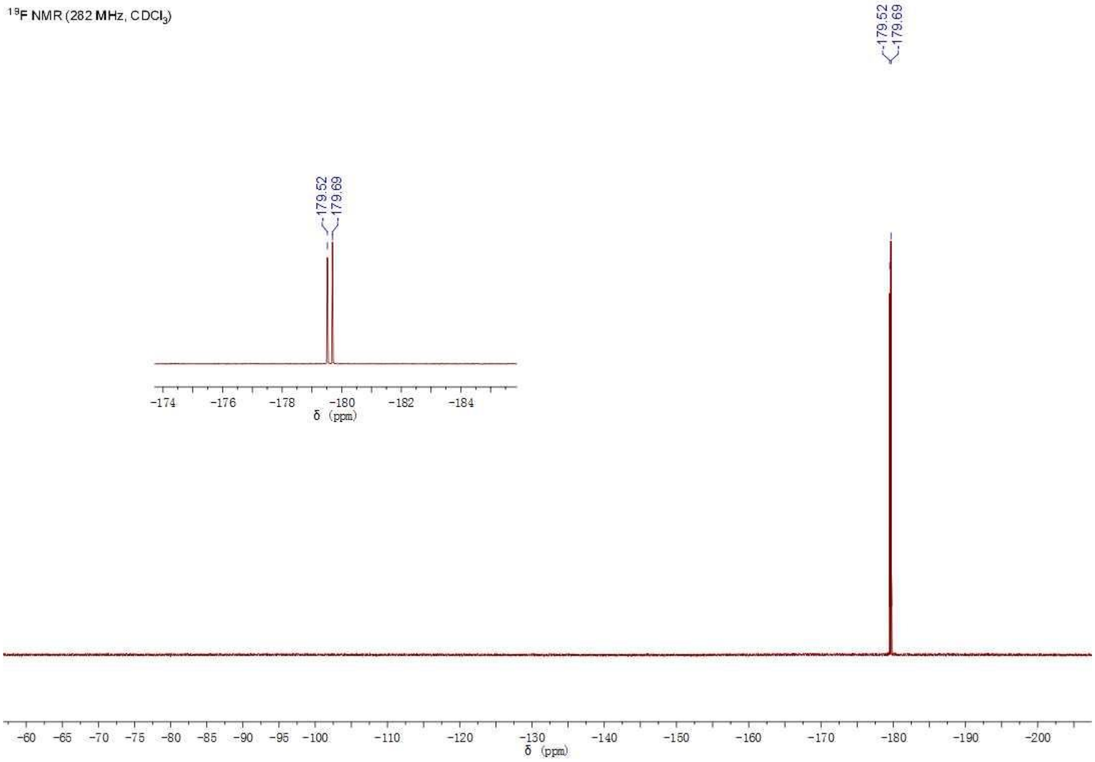

O
O
S
O
F

2b

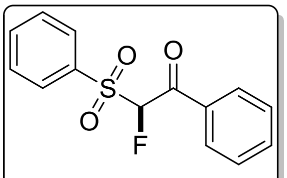

^{1}H NMR (400 MHz, CDCl$_3$)
8.03
8.01
7.89
7.87
7.76
7.74
7.72
7.69
7.68
7.66
7.60
7.58
7.57
7.54
7.52
7.50
7.26
6.41
6.29
1.91
1.85
1.00
1.00
1.97
1.95
1.11
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
δ (ppm)



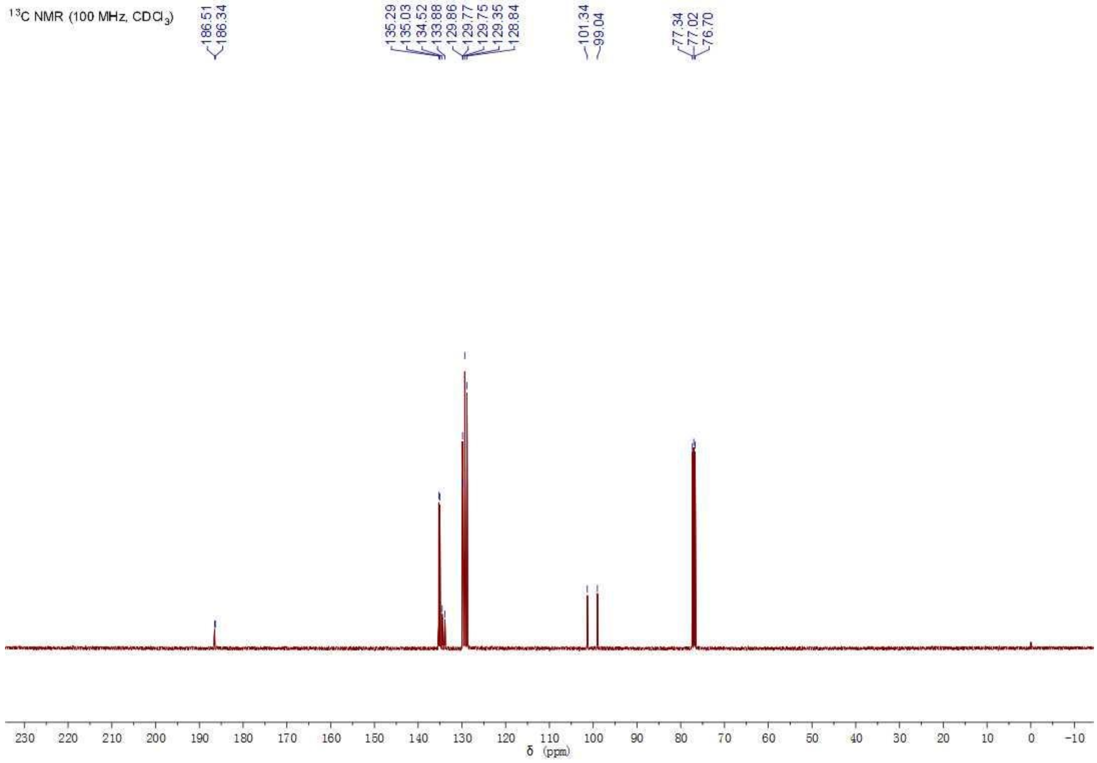
2b

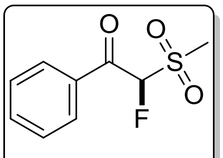


^{19}F NMR (282 MHz, $CDCl_3$)

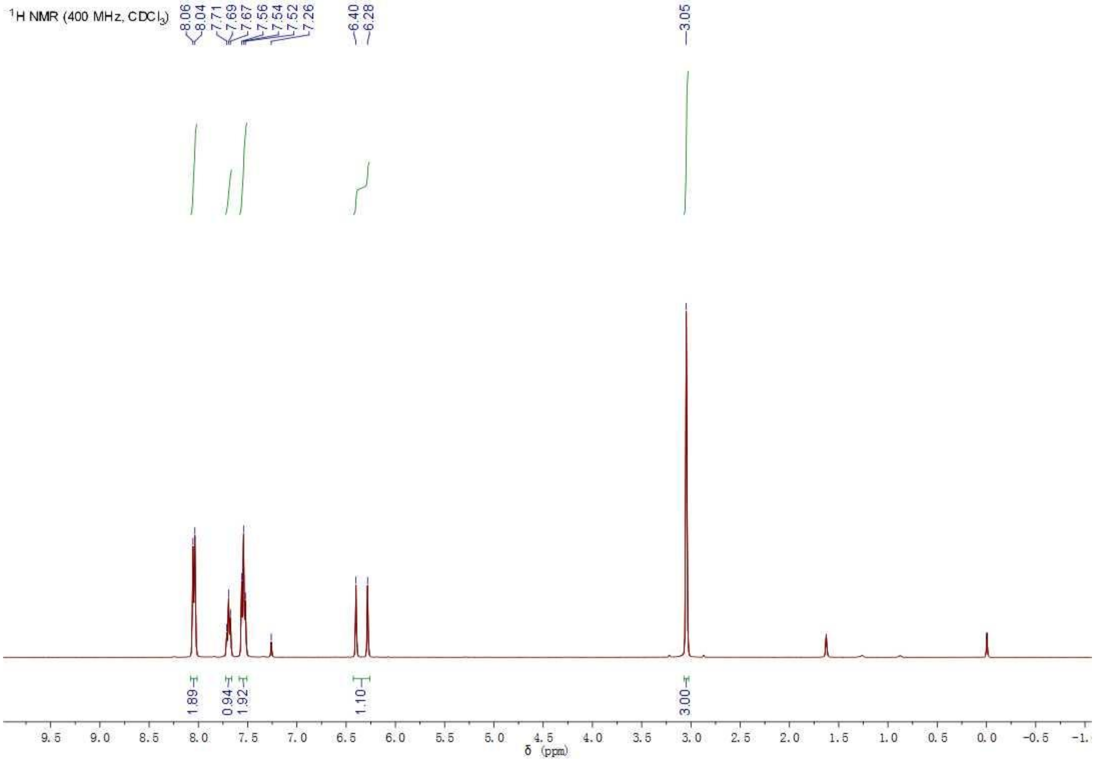

O
O
S
O
F

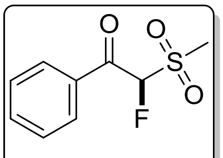
2b


13C NMR (100 MHz, CDCl3)
186.51
186.34
135.29
135.03
134.52
133.88
129.86
129.77
129.75
129.35
128.84
101.34
99.04
77.34
77.02
76.70
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
δ (ppm)

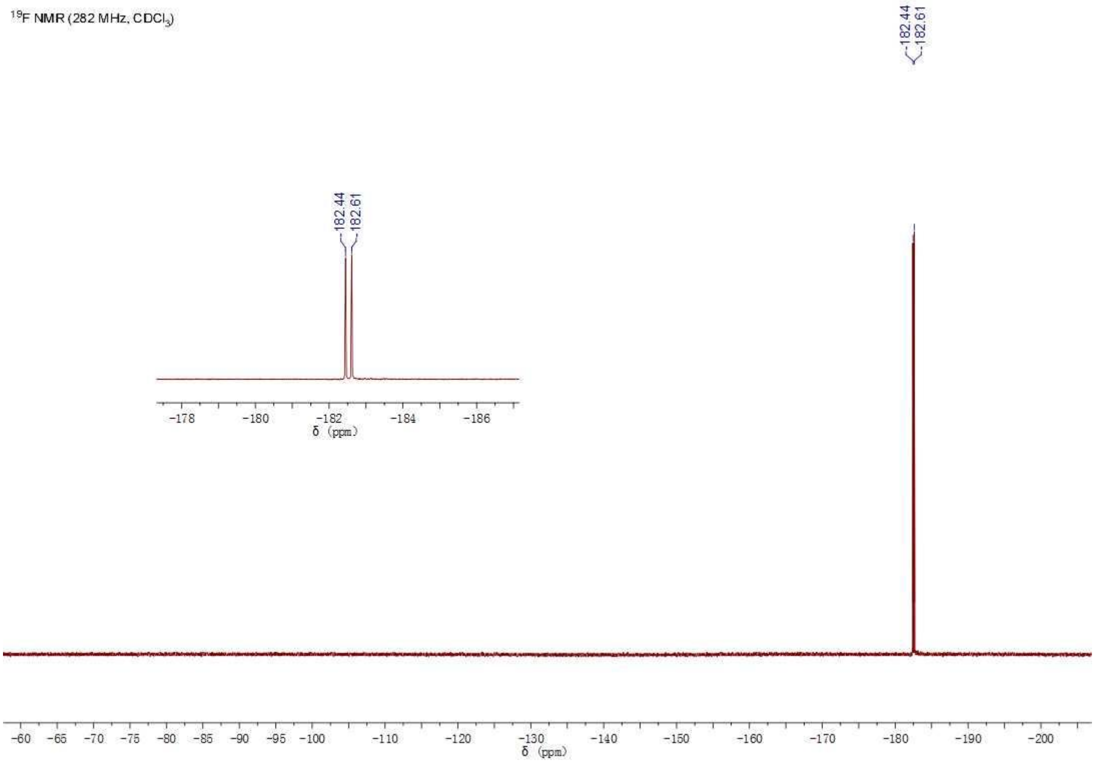


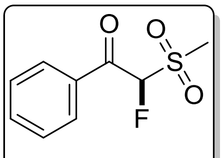
2c


¹H NMR (400 MHz, CDCl₃)
8.06
8.04
7.71
7.69
7.67
7.56
7.54
7.52
7.26
6.40
6.28
3.05
1.89
0.94
1.92
1.10
3.00
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
−0.5
−1.
δ (ppm)

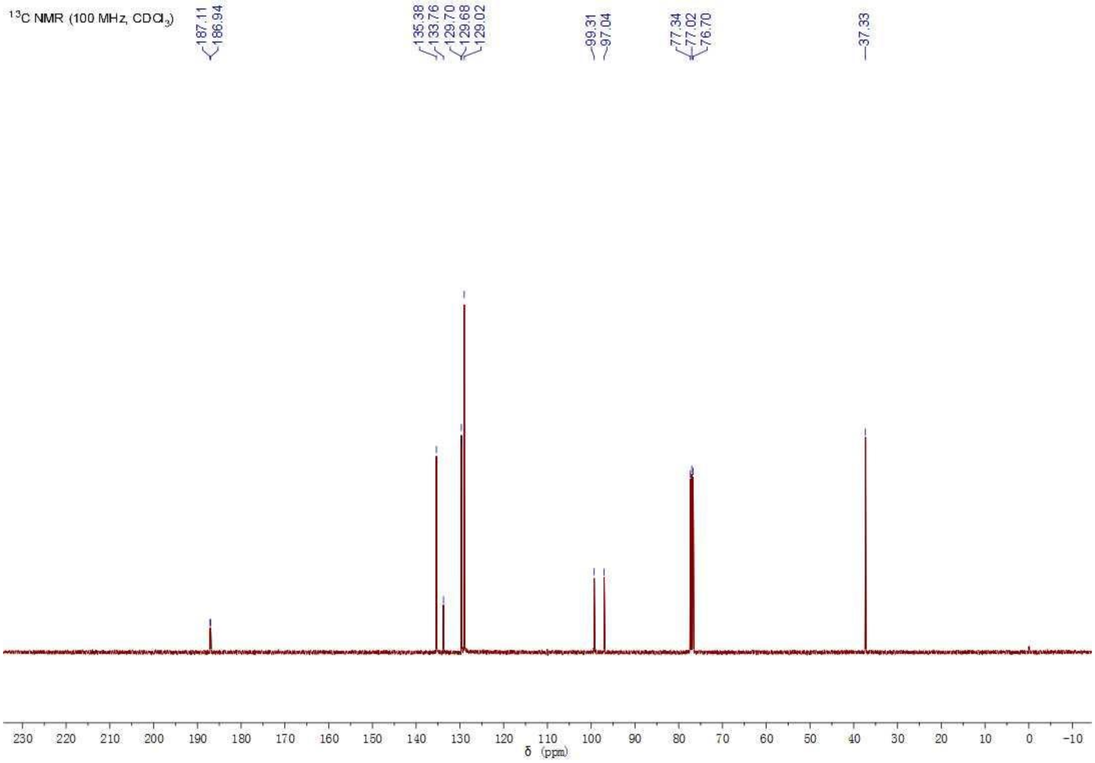

O
O
S
O
F

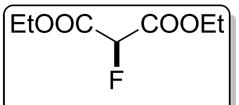
2c


^{19}F NMR (282 MHz, CDCl$_3$)
-182.44
-182.61
-182.44
-182.61
−178
−180
−182
−184
−186
δ (ppm)
−60
−65
−70
−75
−80
−85
−90
−95
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
δ (ppm)

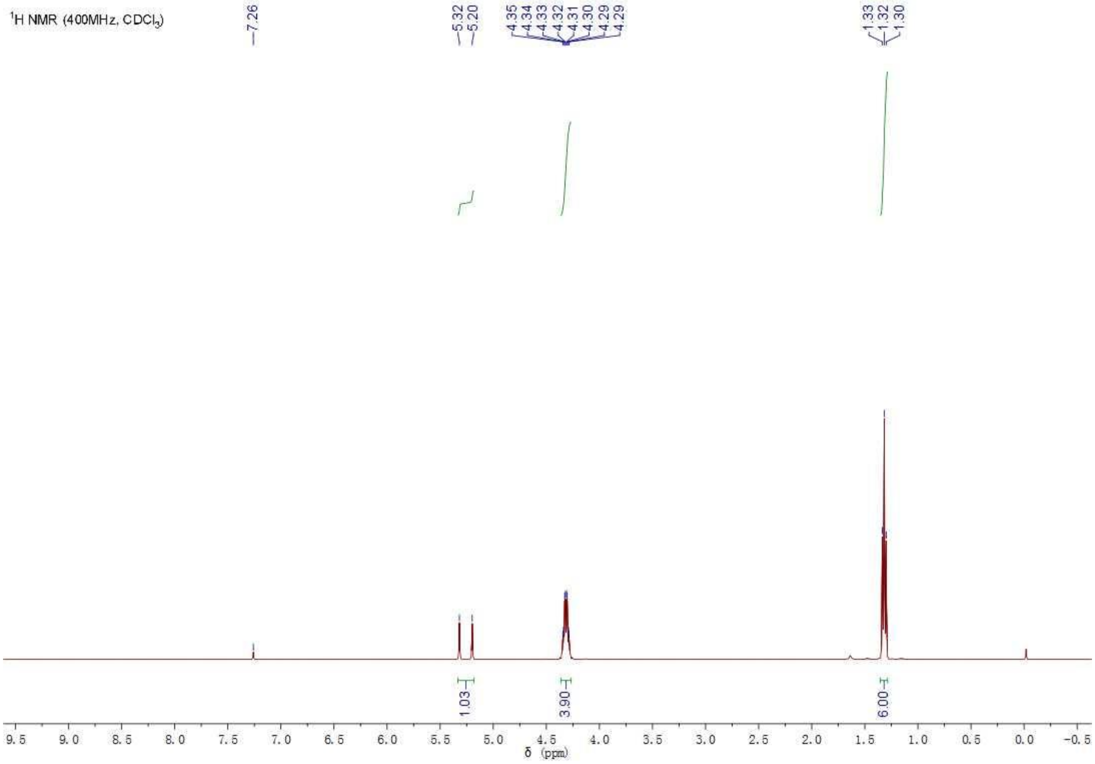


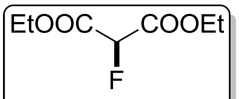
2c


13C NMR (100 MHz, CDCl3)
187.11
186.94
135.38
133.76
129.70
129.68
129.02
99.31
97.04
77.34
77.02
76.70
37.33
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
δ (ppm)

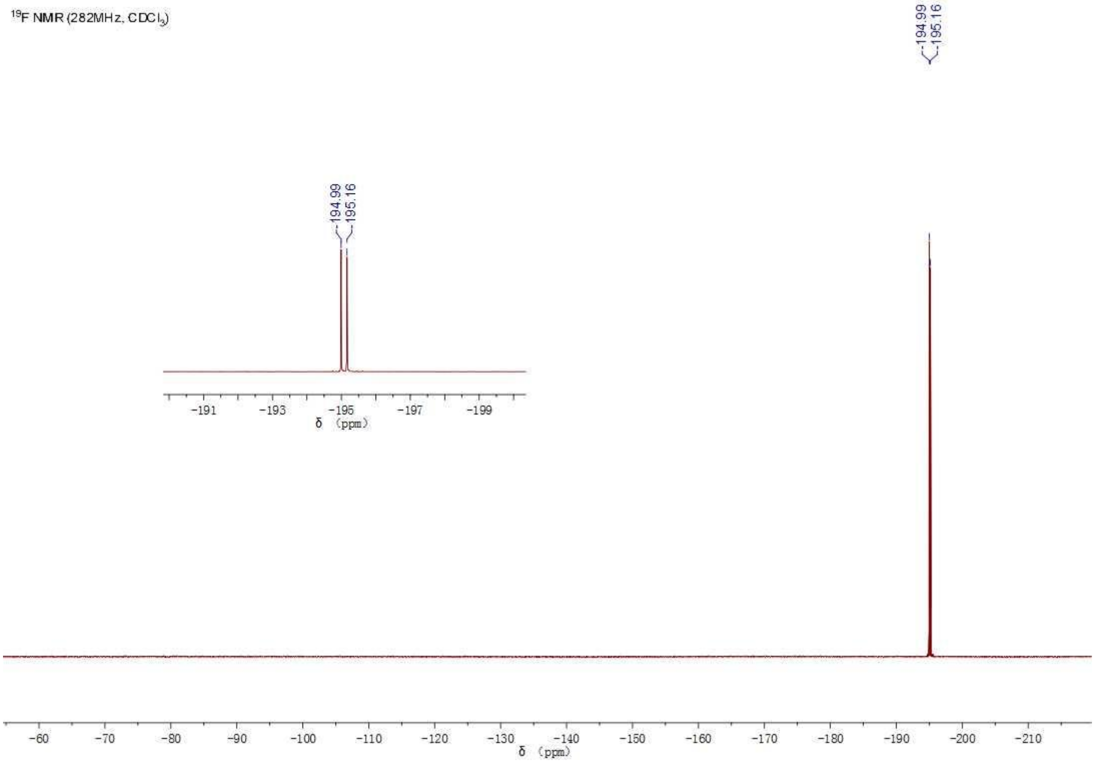


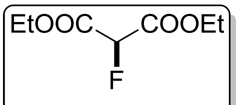
2d


^{1}H NMR (400MHz, CDCl$_3$)
7.26
5.32
5.20
4.35
4.34
4.33
4.32
4.31
4.30
4.29
4.29
1.33
1.32
1.30
1.03
3.90
6.00
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 −0.5
δ (ppm)

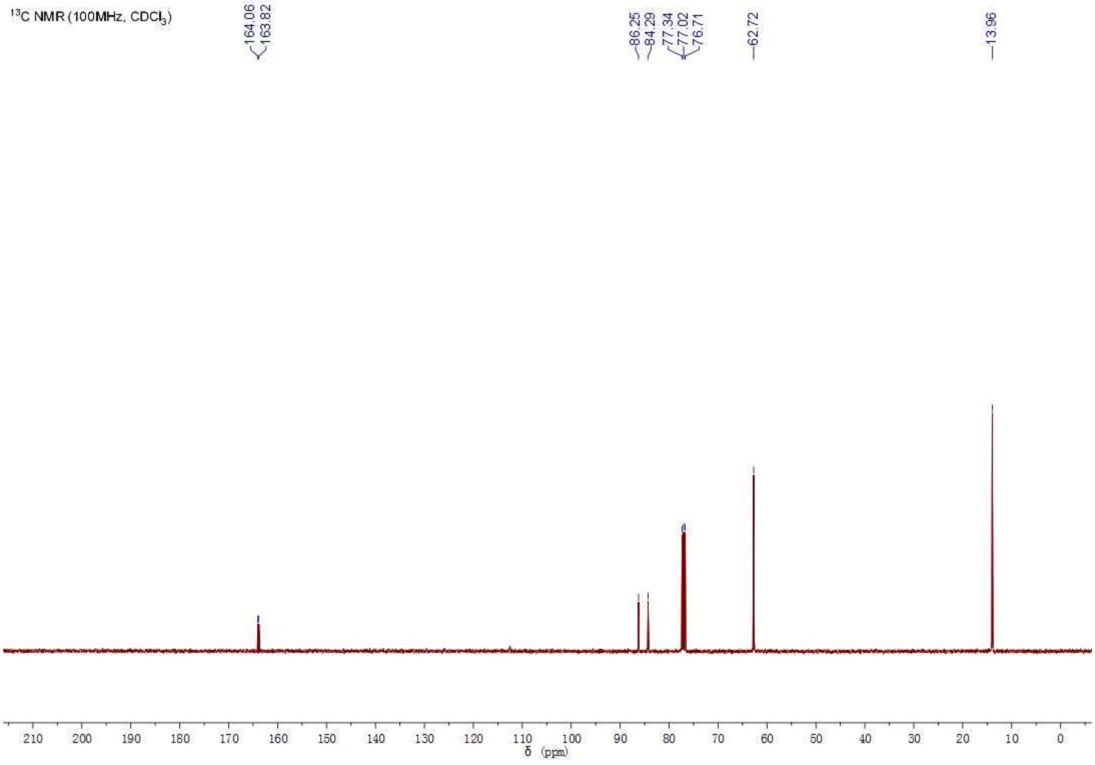

EtOOC
COOEt
F

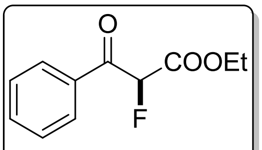
2d


^{19}F NMR (282MHz, CDCl$_3$)
-194.99
-195.16
-194.99
-195.16
-191
-193
-195
-197
-199
δ (ppm)
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
δ (ppm)

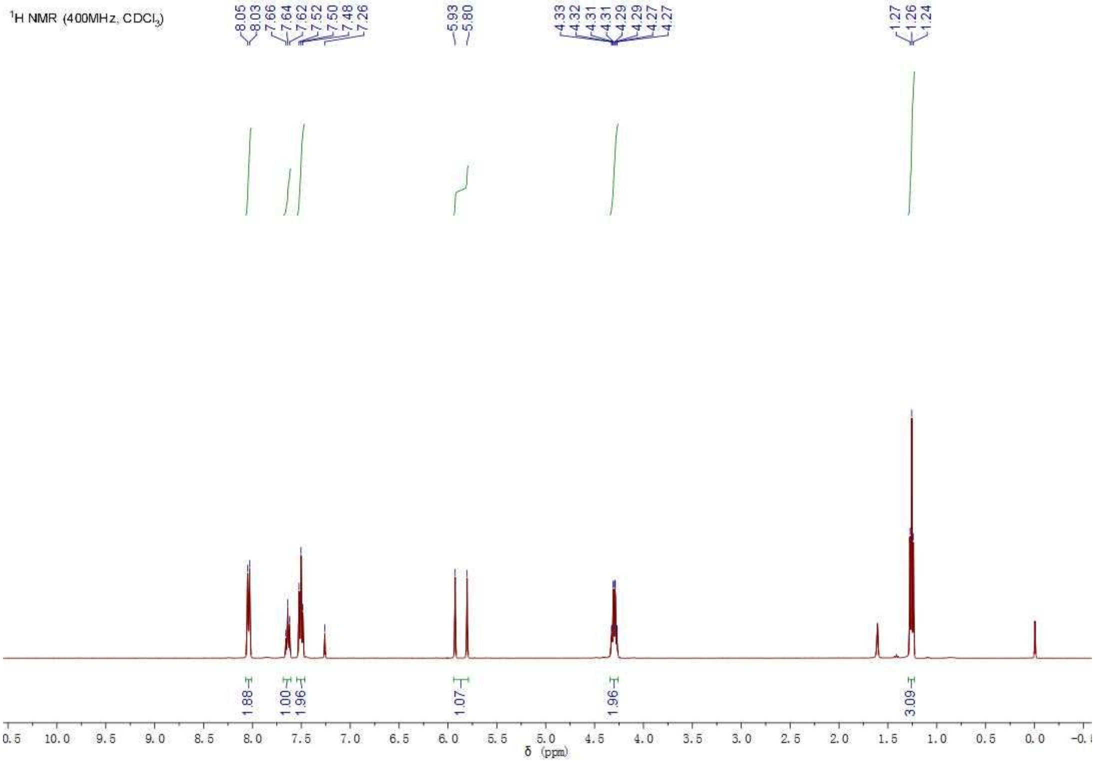

EtOOC
COOEt
F

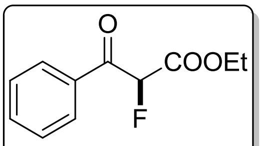
2d


^{13}C NMR (100MHz, CDCl$_3$)
164.06
163.82
86.25
84.29
77.34
77.02
76.71
62.72
13.96
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

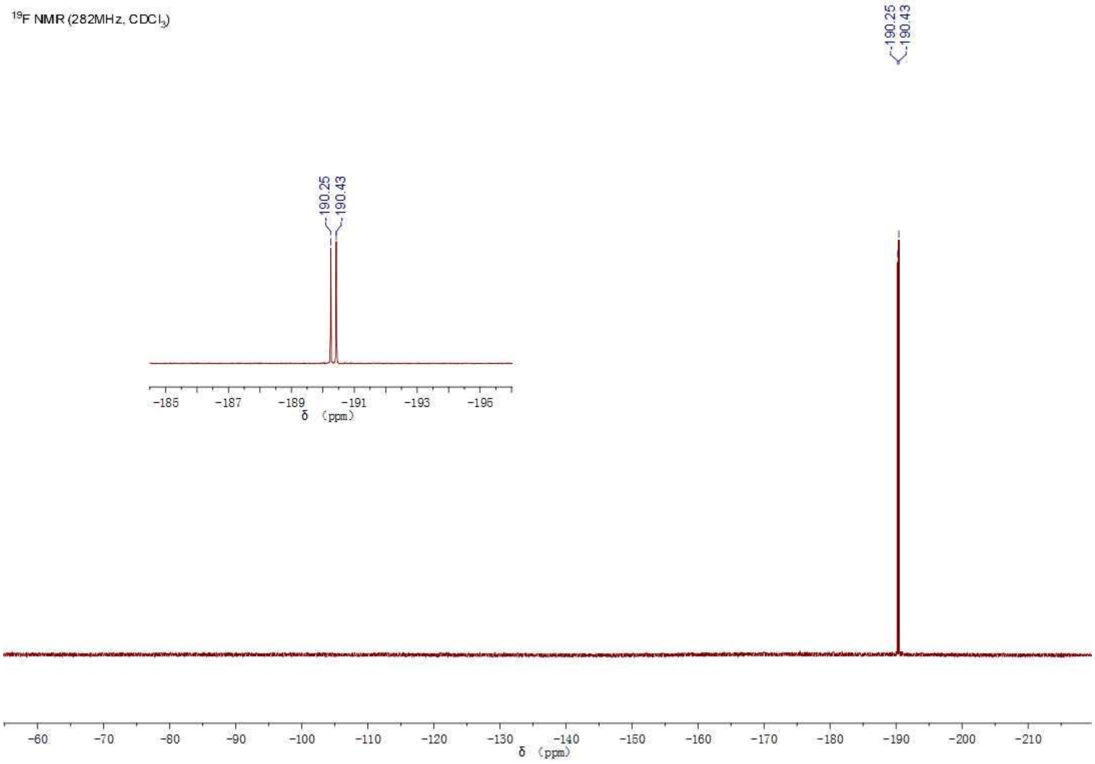

O
COOEt
F

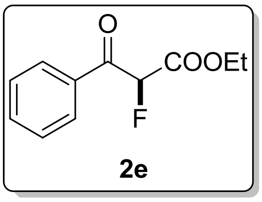
2e


^{1}H NMR (400MHz, CDCl$_3$)
8.05
8.03
7.66
7.64
7.62
7.52
7.50
7.48
7.26
5.93
5.80
4.33
4.32
4.31
4.29
4.29
4.27
4.27
1.27
1.26
1.24
1.88
1.00
1.96
1.07
1.96
3.09
0.5
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
0.0
-0.
δ (ppm)

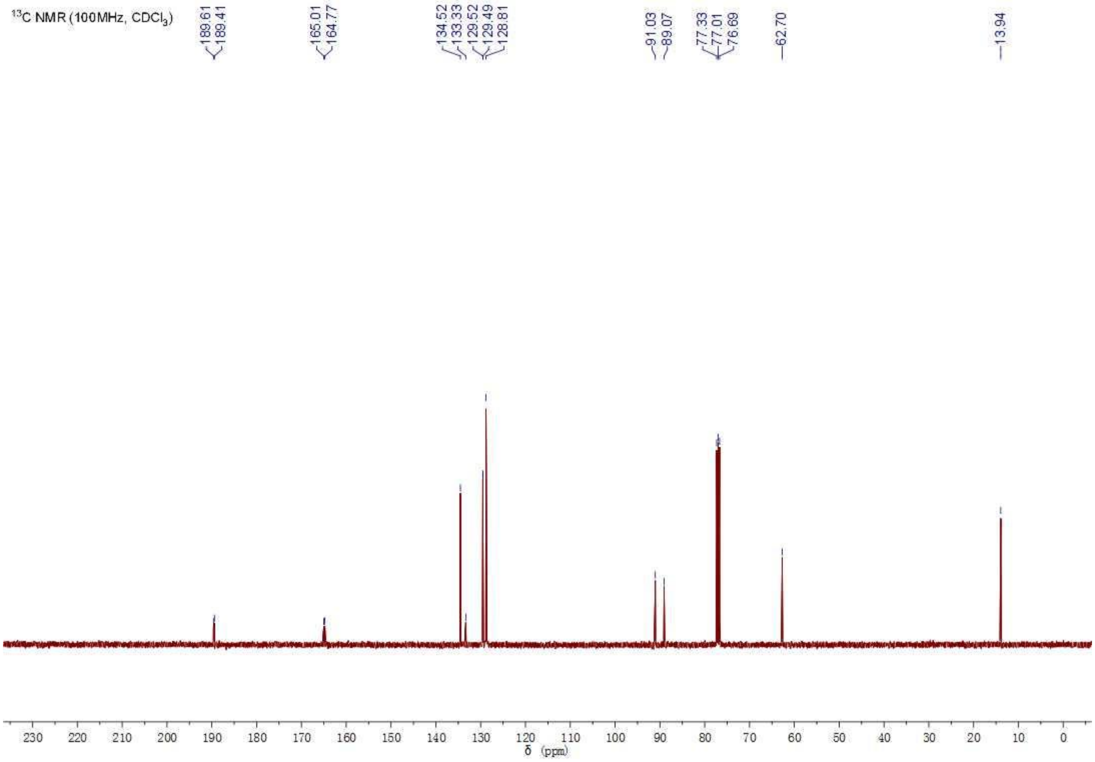

O
COOEt
F

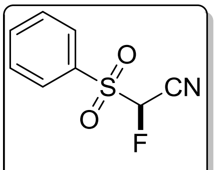
2e


^{19}F NMR (282MHz, CDCl$_3$)
-190.25
-190.43
-190.25
-190.43
-185
-187
-189
-191
-193
-195
δ (ppm)
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
δ (ppm)

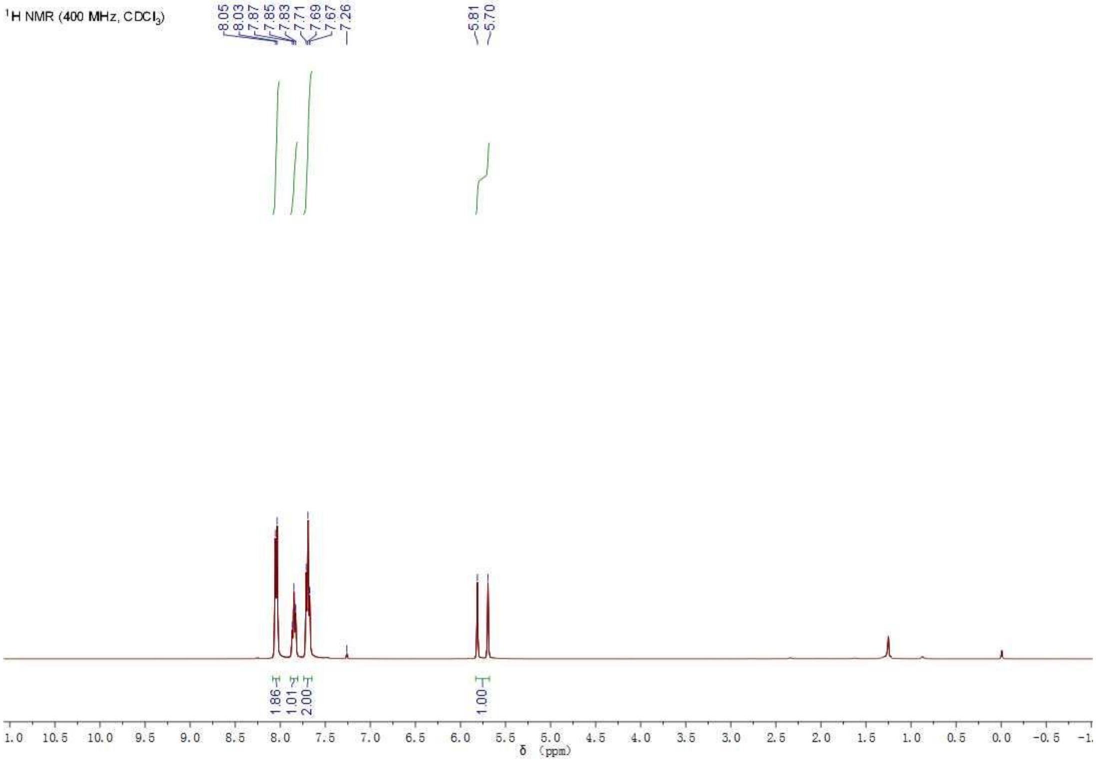

O
COOEt
F

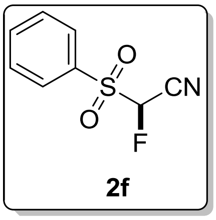
2e


^{13}C NMR (100MHz, CDCl$_3$)
189.61
189.41
165.01
164.77
134.52
133.33
129.52
129.49
128.81
91.03
89.07
77.33
77.01
76.69
62.70
13.94
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

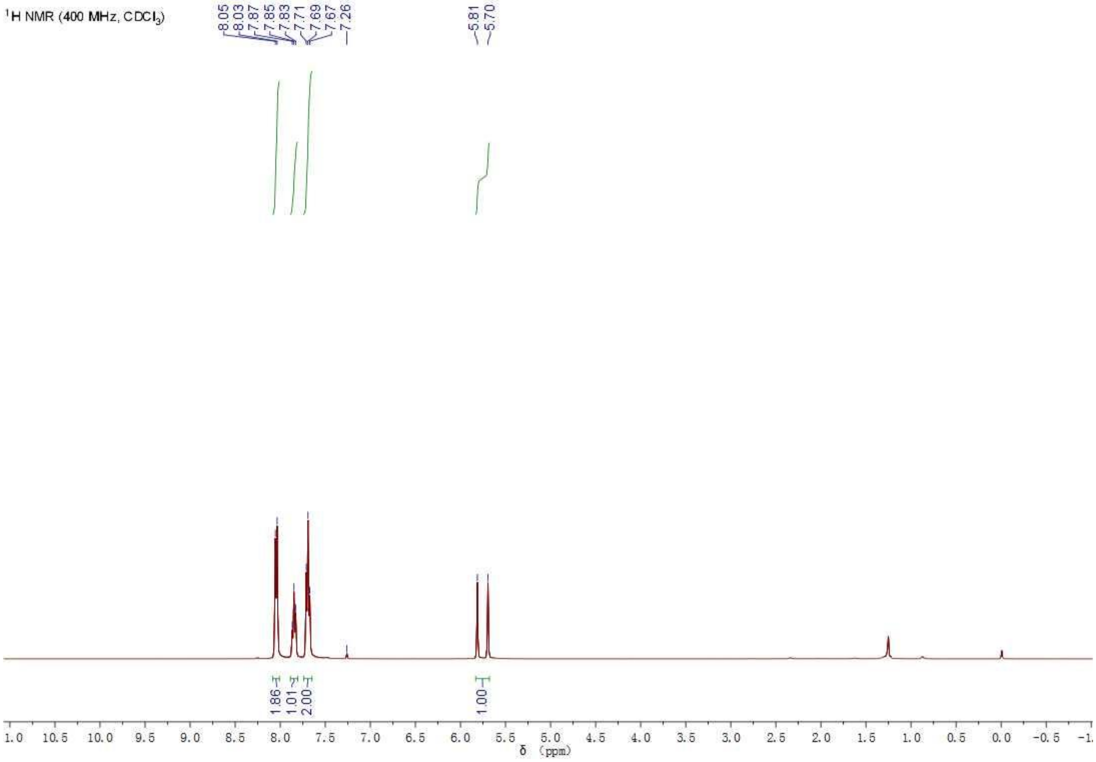

O
S
O
CN
F

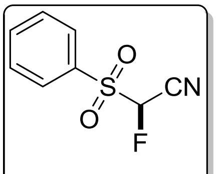
2f


^{1}H NMR (400 MHz, CDCl$_3$)
8.05
8.03
7.87
7.85
7.83
7.71
7.69
7.67
7.26
5.81
5.70
1.86
1.01
2.00
1.00
1.0
10.5
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
0.0
−0.5
−1.
δ (ppm)

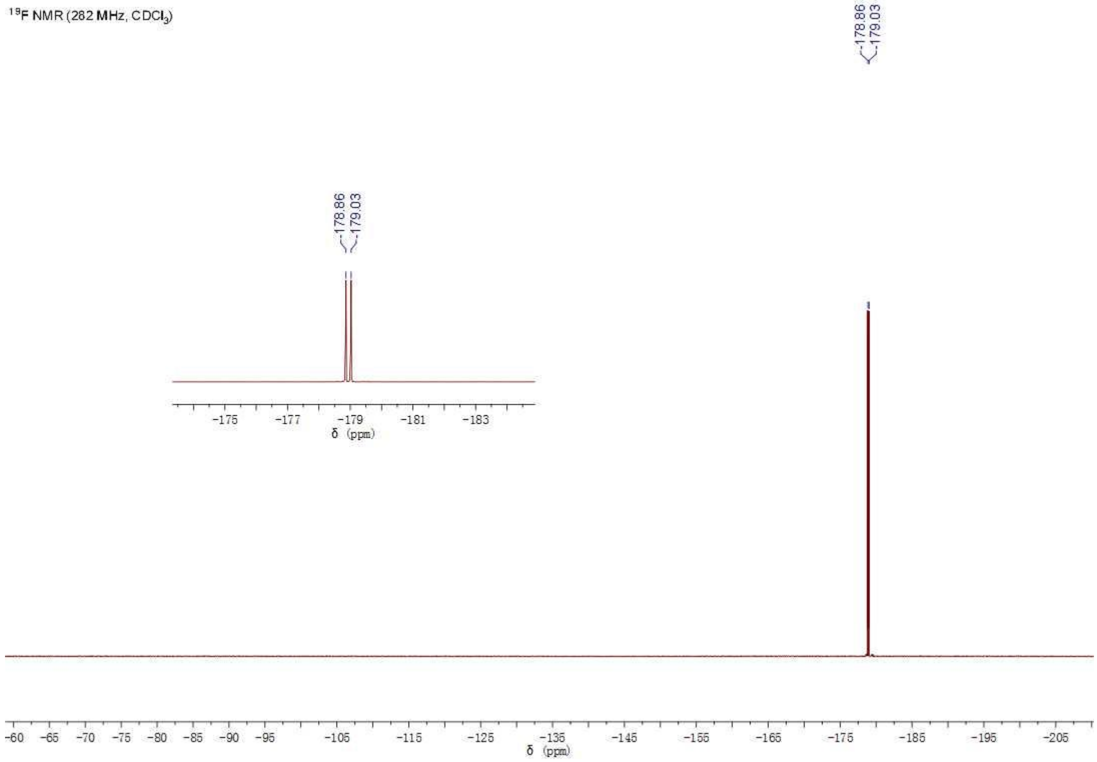

O
S
CN
O
F

2f

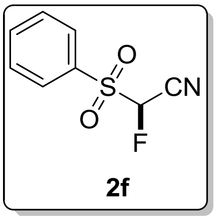

^{1}H NMR (400 MHz, CDCl$_3$)
8.05
8.03
7.87
7.85
7.83
7.71
7.69
7.67
7.26
5.81
5.70
1.86
1.01
2.00
1.00
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.
δ (ppm)



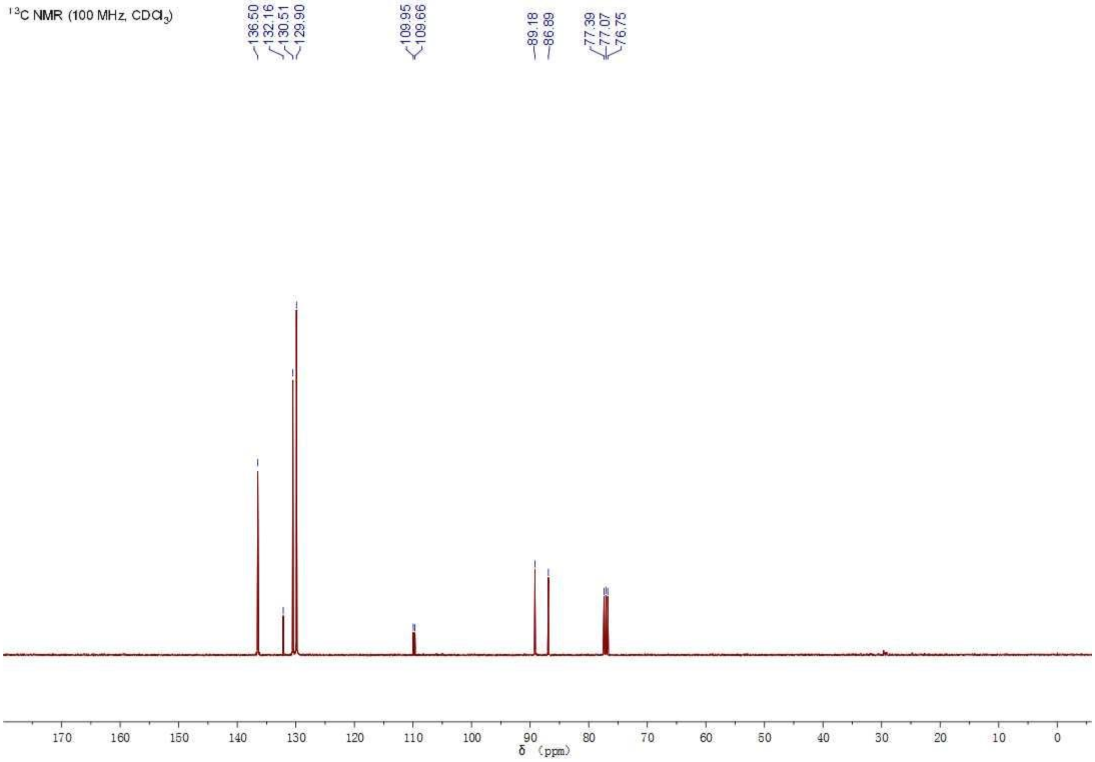
2f



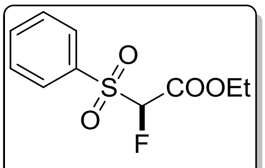
^{19}F NMR (282 MHz, CDCl$_3$)



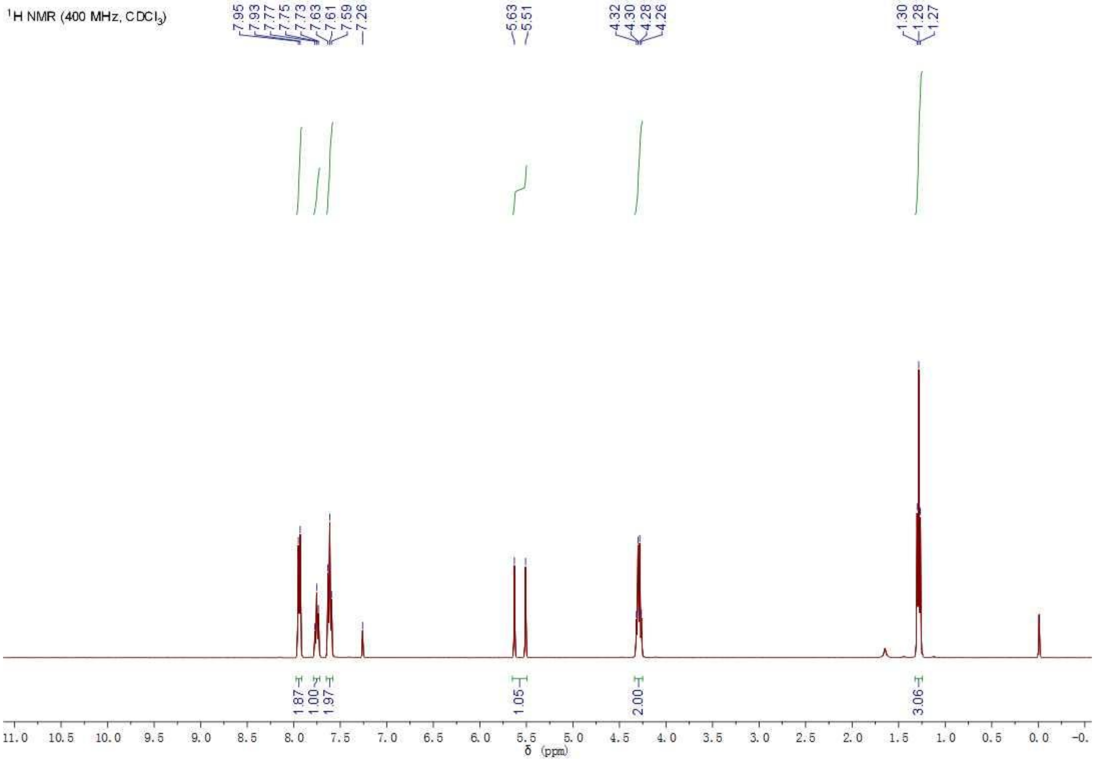
O
S
O
CN
F
2f



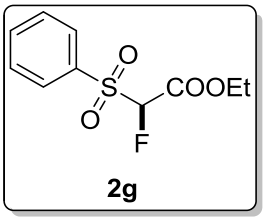
^{13}C NMR (100 MHz, CDCl$_3$)
136.50
132.16
130.51
129.90
109.95
109.66
89.18
86.89
77.39
77.07
76.75
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)



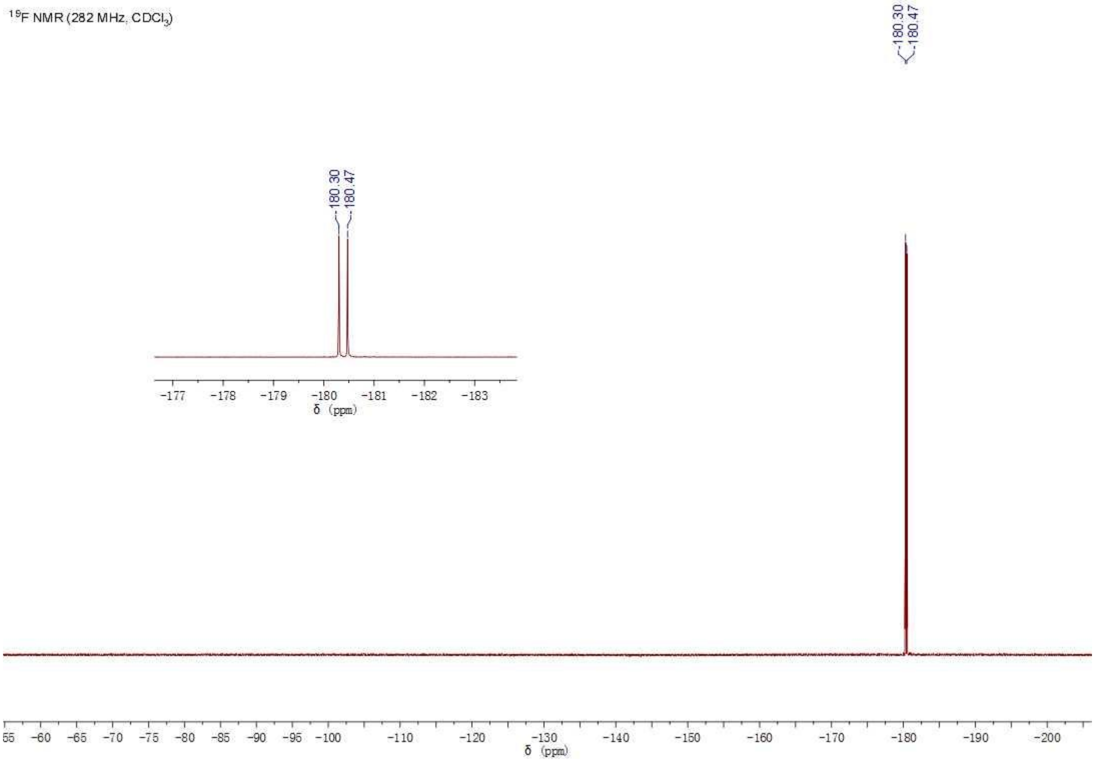
2g

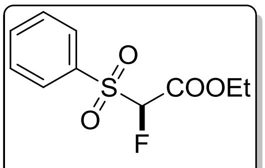


^{1}H NMR (400 MHz, CDCl$_3$)

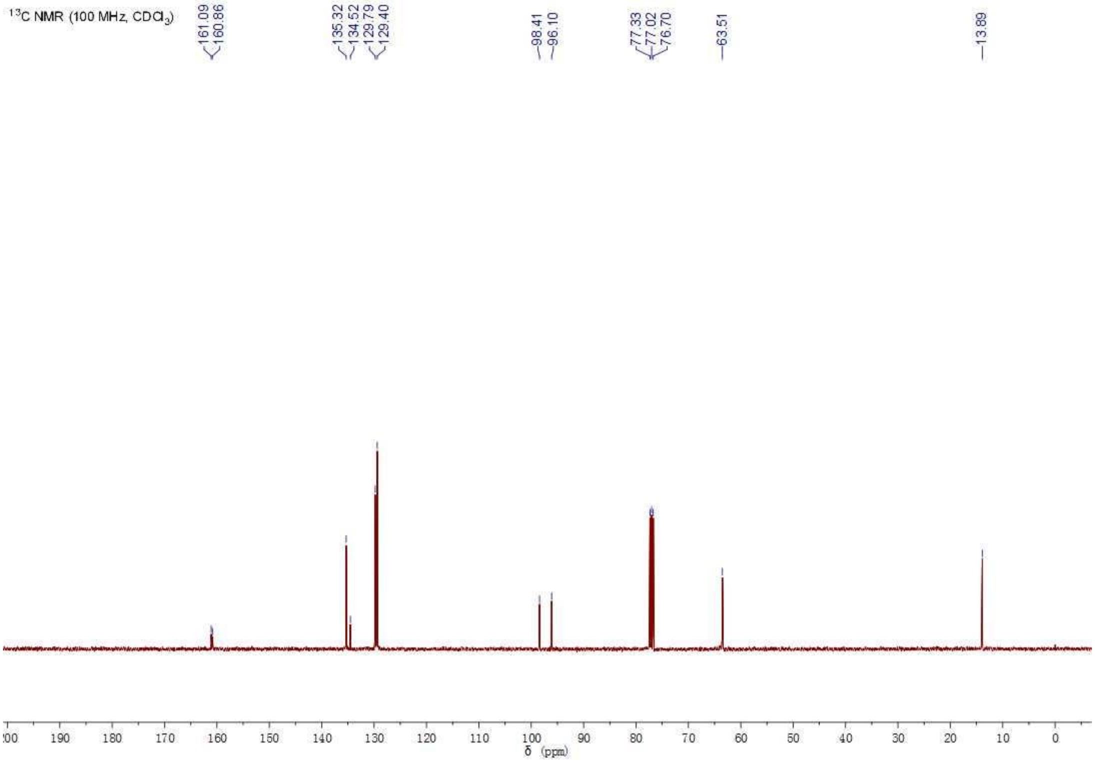

O
S
O
COOEt
F

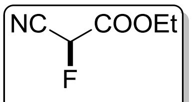
2g


^{19}F NMR (282 MHz, CDCl$_3$)
-180.30
-180.47
-177
-178
-179
-180
-181
-182
-183
δ (ppm)
55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
δ (ppm)

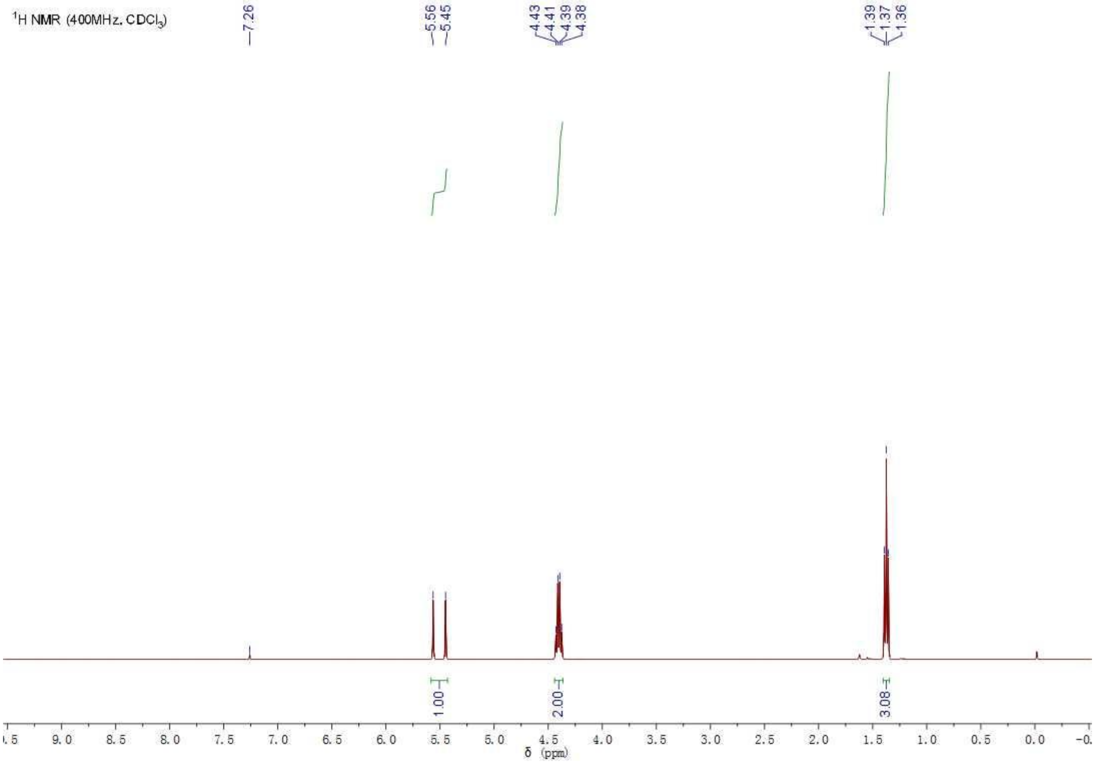

O
S
O
COOEt
F

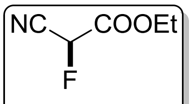
2g


^{13}C NMR (100 MHz, CDCl$_3$)
161.09
160.86
135.32
134.52
129.79
129.40
98.41
96.10
77.33
77.02
76.70
63.51
13.89
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

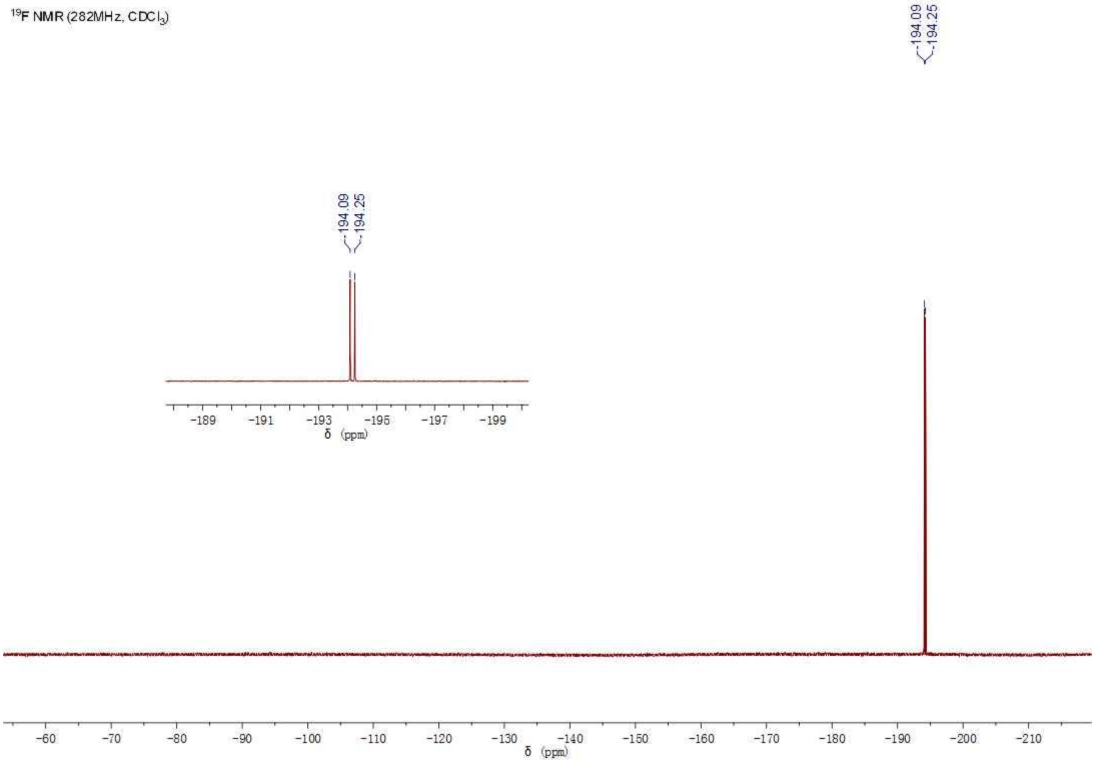

NC
COOEt
F

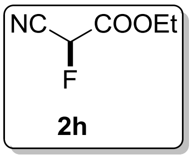
2h


^{1}H NMR (400MHz, CDCl$_3$)
7.26
5.56
5.45
4.43
4.41
4.39
4.38
1.39
1.37
1.36
1.00
2.00
3.08
.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
-0.
δ (ppm)

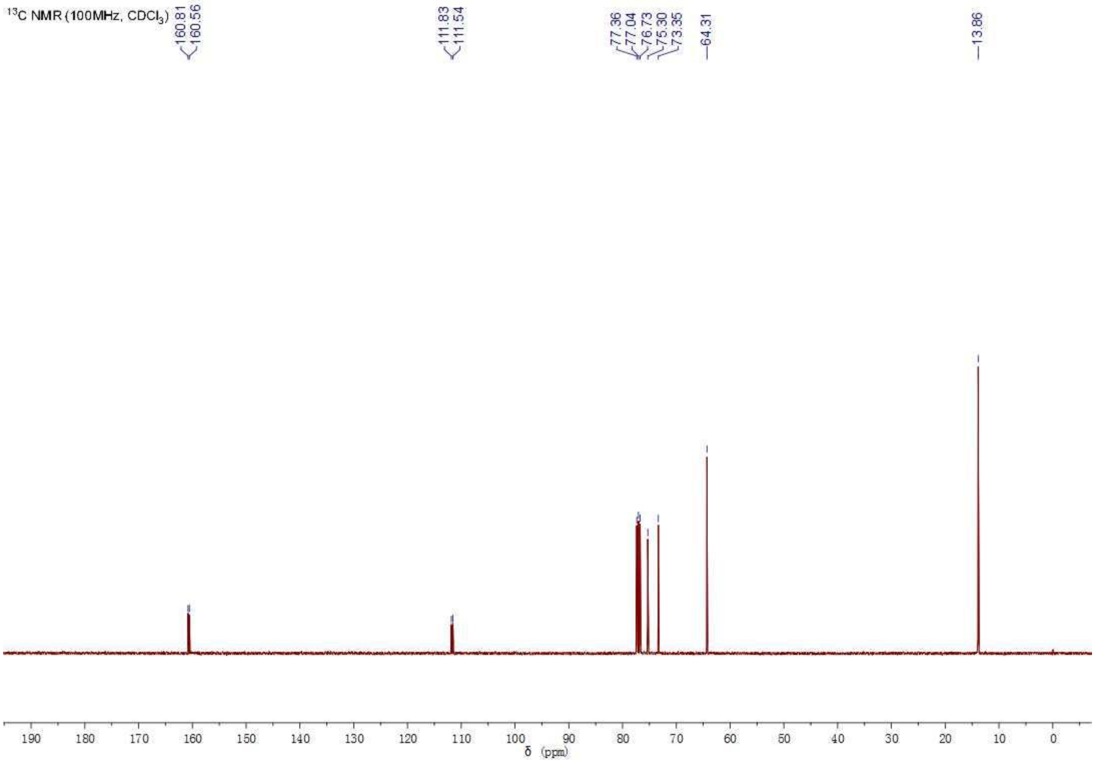

NC
COOEt
F

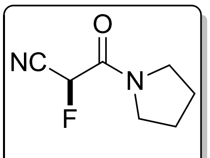
2h


^{19}F NMR (282MHz, CDCl$_3$)
-194.09
-194.25
-194.09
-194.25
-189
-191
-193
-195
-197
-199
δ (ppm)
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
δ (ppm)

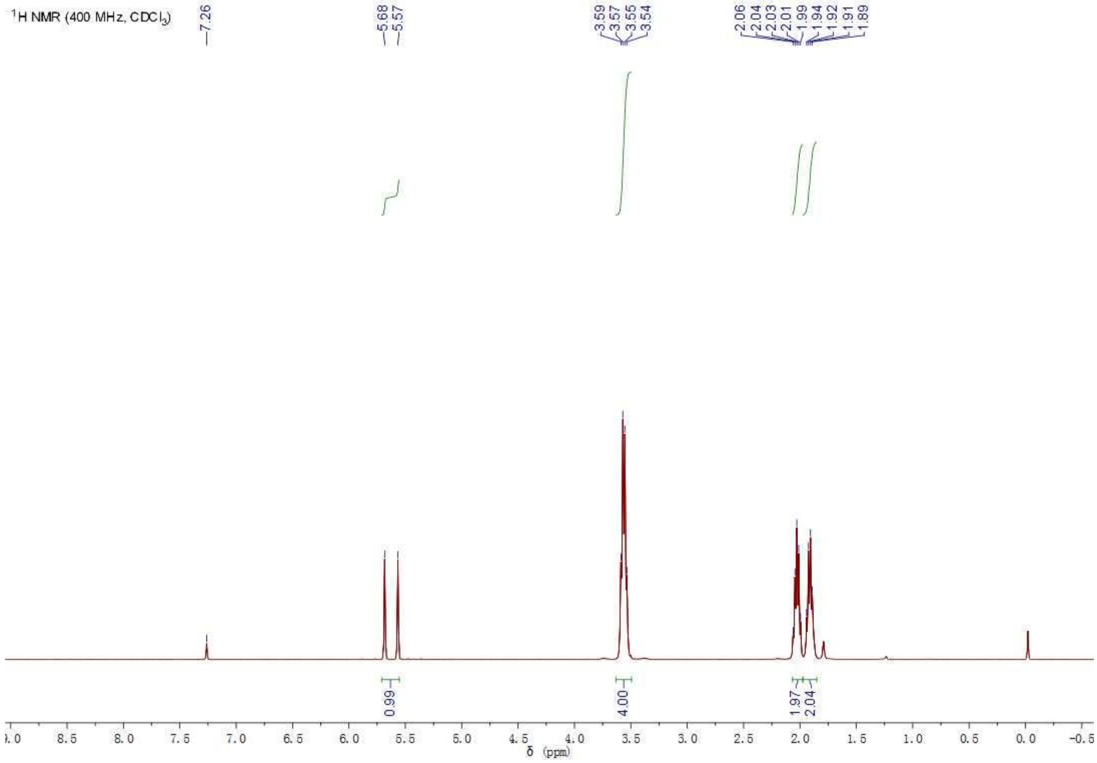

NC
COOEt
F

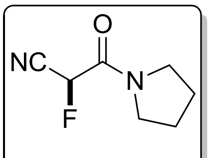
2h


^{13}C NMR (100MHz, CDCl$_3$)
160.81
160.56
111.83
111.54
77.36
77.04
76.73
75.30
73.35
64.31
13.86
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

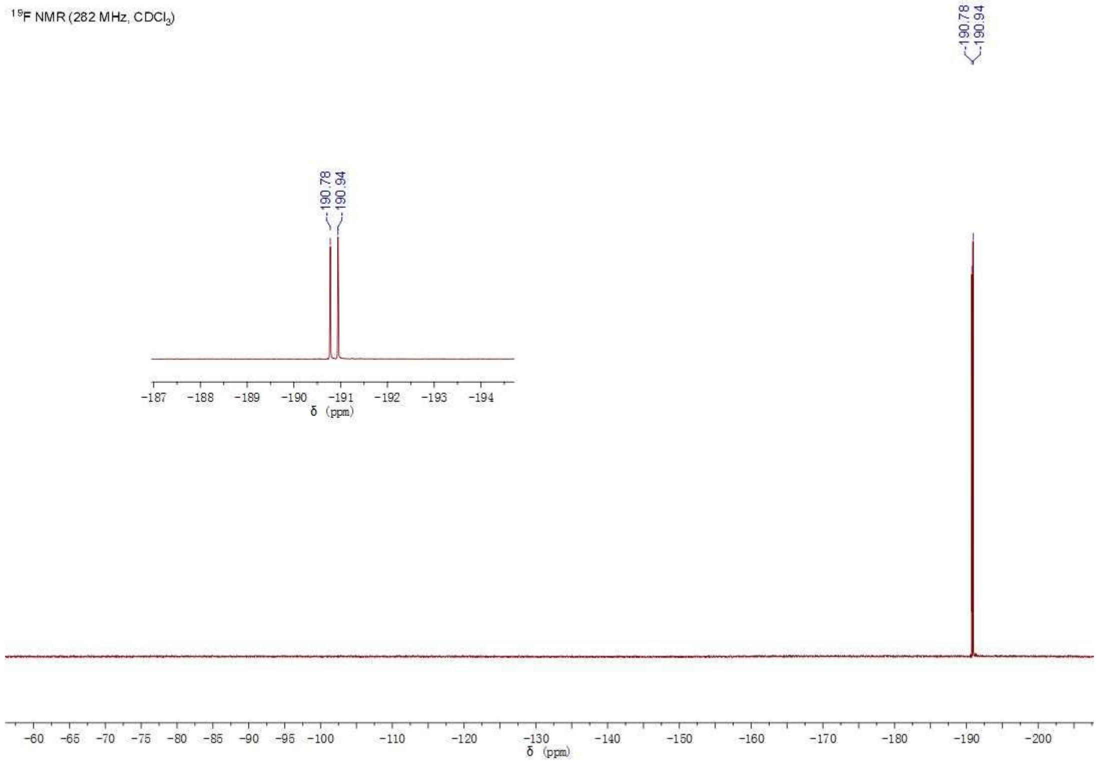

NC
O
N
F

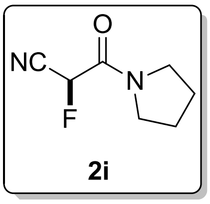
2i


¹H NMR (400 MHz, CDCl3)
7.26
5.68
5.57
3.59
3.57
3.55
3.54
2.06
2.04
2.03
2.01
1.99
1.94
1.92
1.91
1.89
0.99
4.00
1.97
2.04
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
δ (ppm)

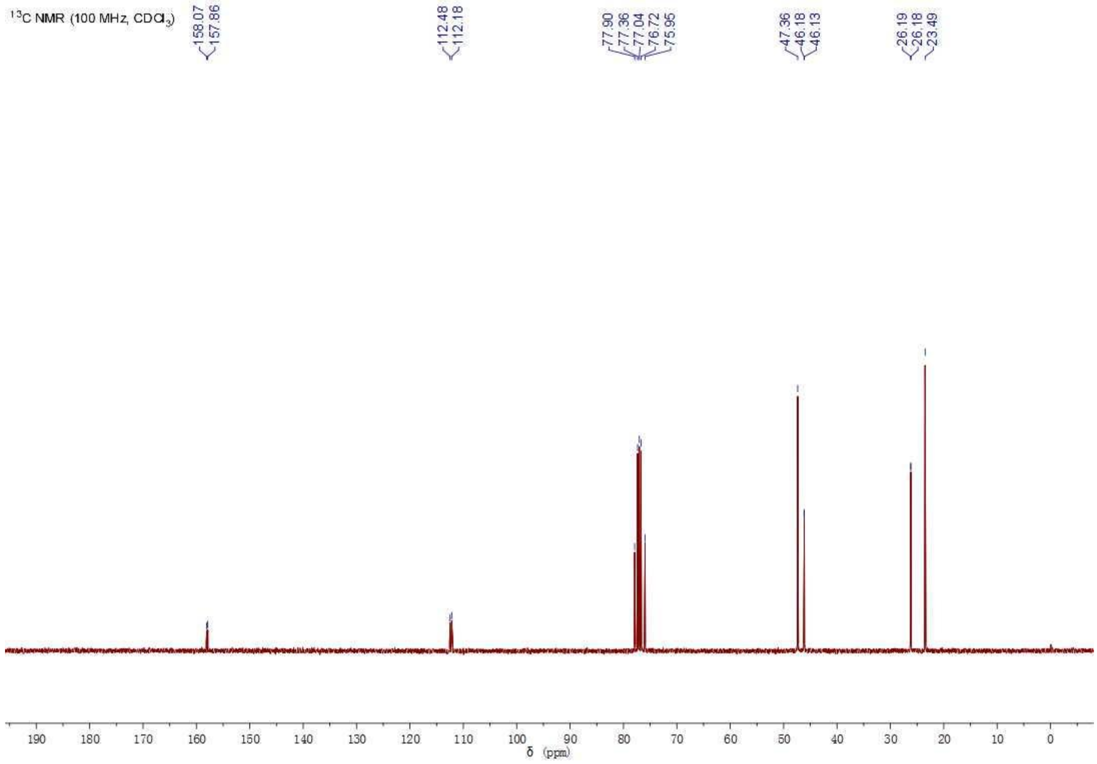


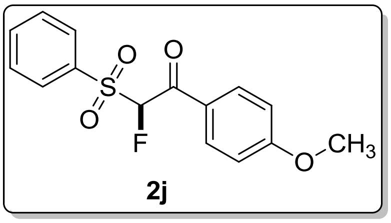
2i


^{19}F NMR (282 MHz, CDCl$_3$)
-190.78
-190.94
-187 -188 -189 -190 -191 -192 -193 -194
δ (ppm)
-60 -65 -70 -75 -80 -85 -90 -95 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
δ (ppm)

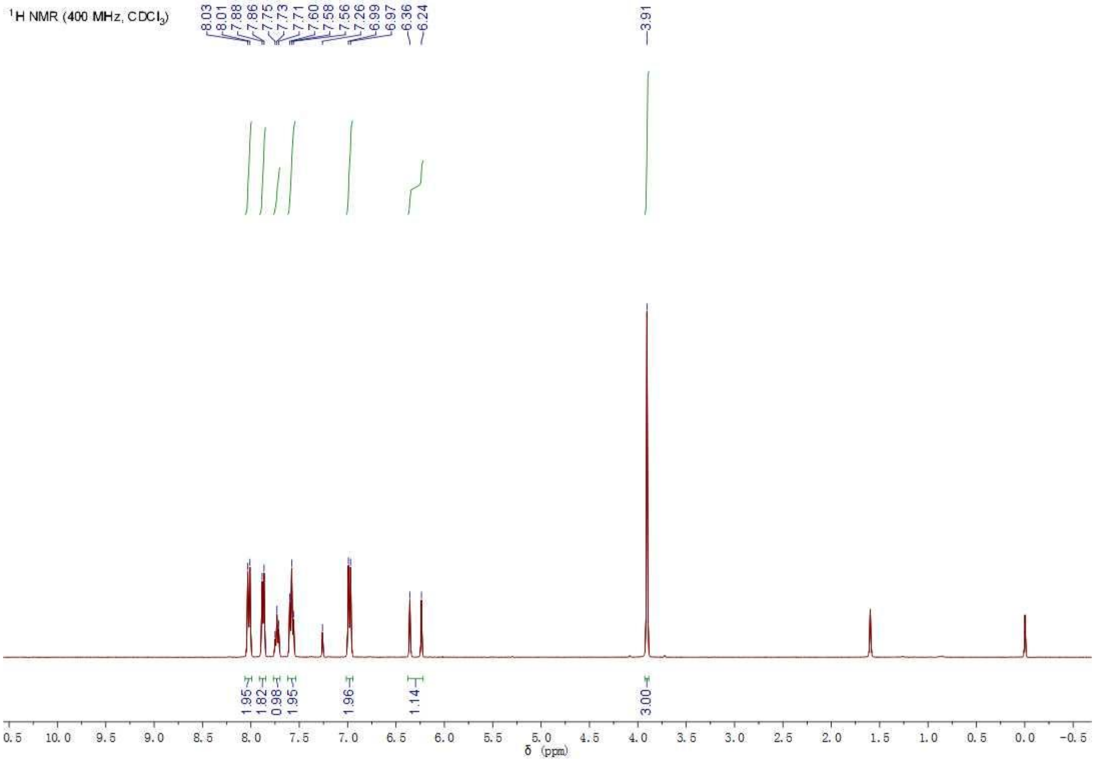

O
NC
N
F

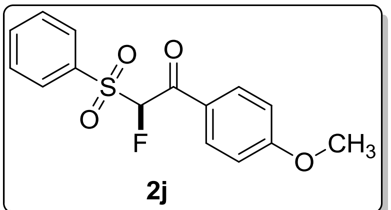
2i


13C NMR (100 MHz, CDCl3)
158.07
157.86
112.48
112.18
77.90
77.36
77.04
76.72
75.95
47.36
46.18
46.13
26.19
26.18
23.49
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

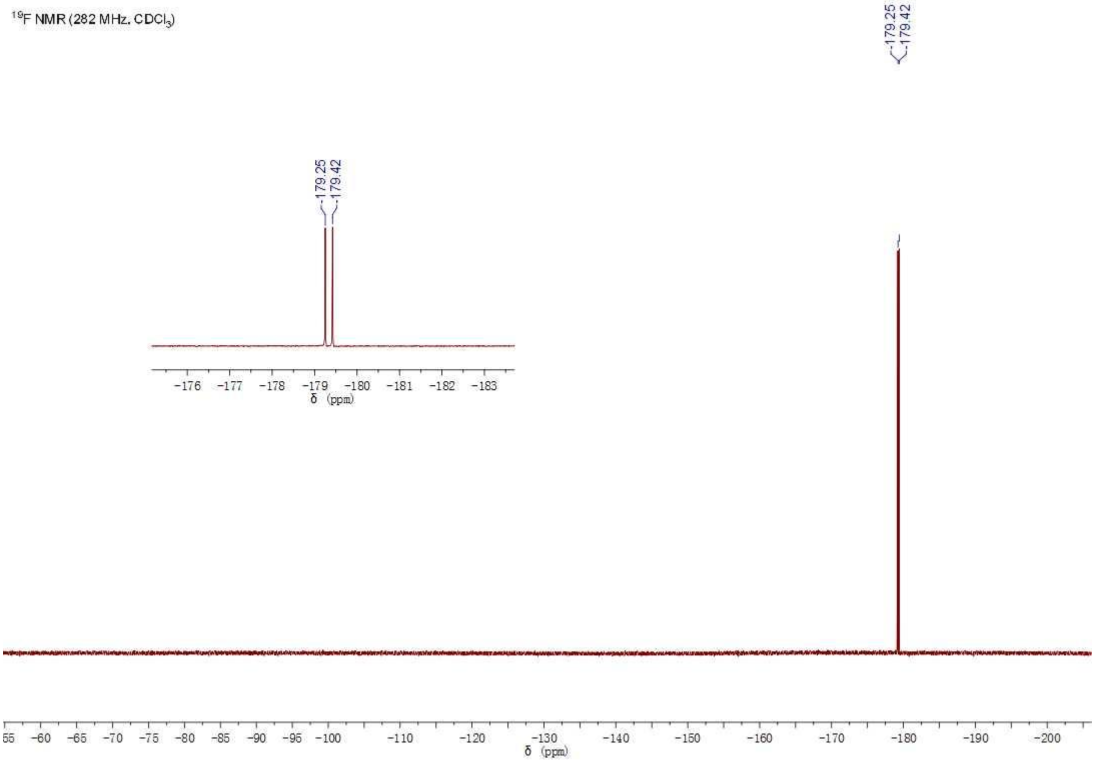

O
O
S
O
F
O
CH3

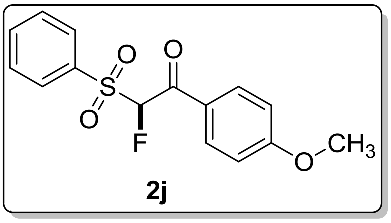
2j


^{1}H NMR (400 MHz, CDCl$_3$)
8.03
8.01
7.88
7.86
7.75
7.73
7.71
7.60
7.58
7.56
7.26
6.99
6.97
6.36
6.24
3.91
1.95
1.82
0.98
1.95
1.96
1.14
3.00
0.5
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
0.0
-0.5
δ (ppm)

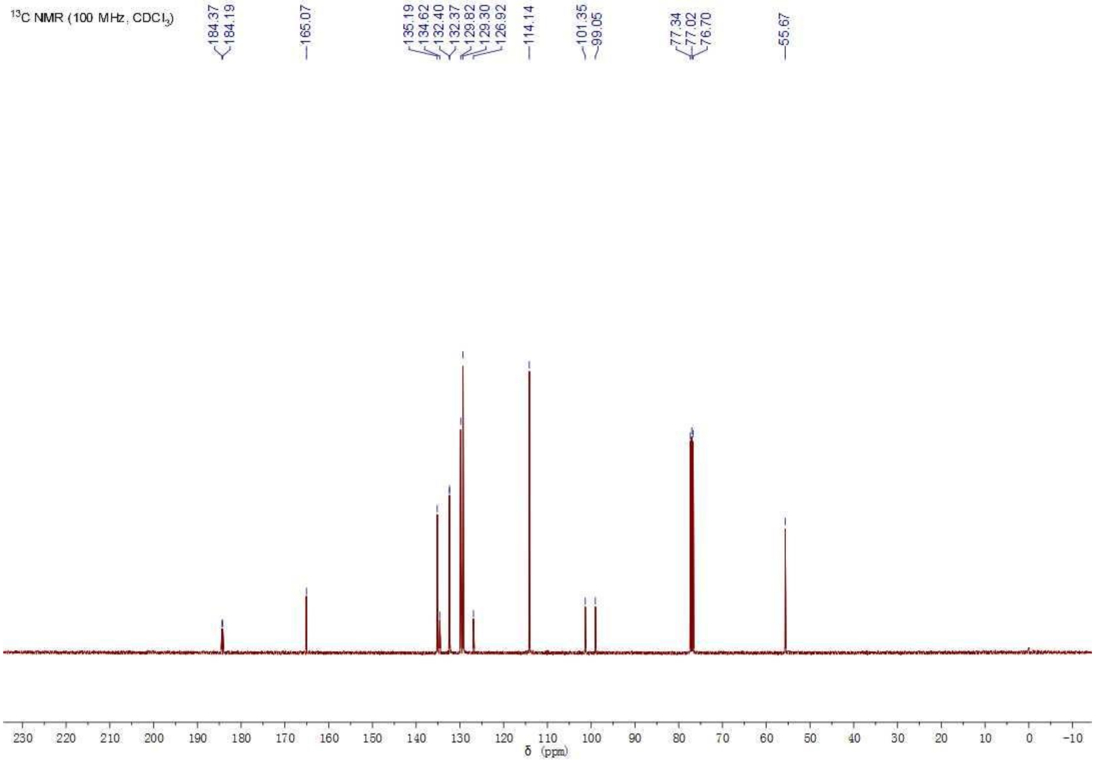


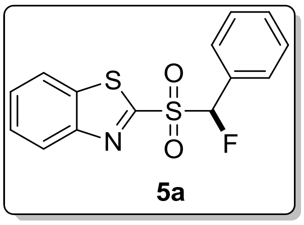
2j


19F NMR (282 MHz, CDCl3)
-179.25
-179.42
-176 -177 -178 -179 -180 -181 -182 -183
δ (ppm)
55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
δ (ppm)

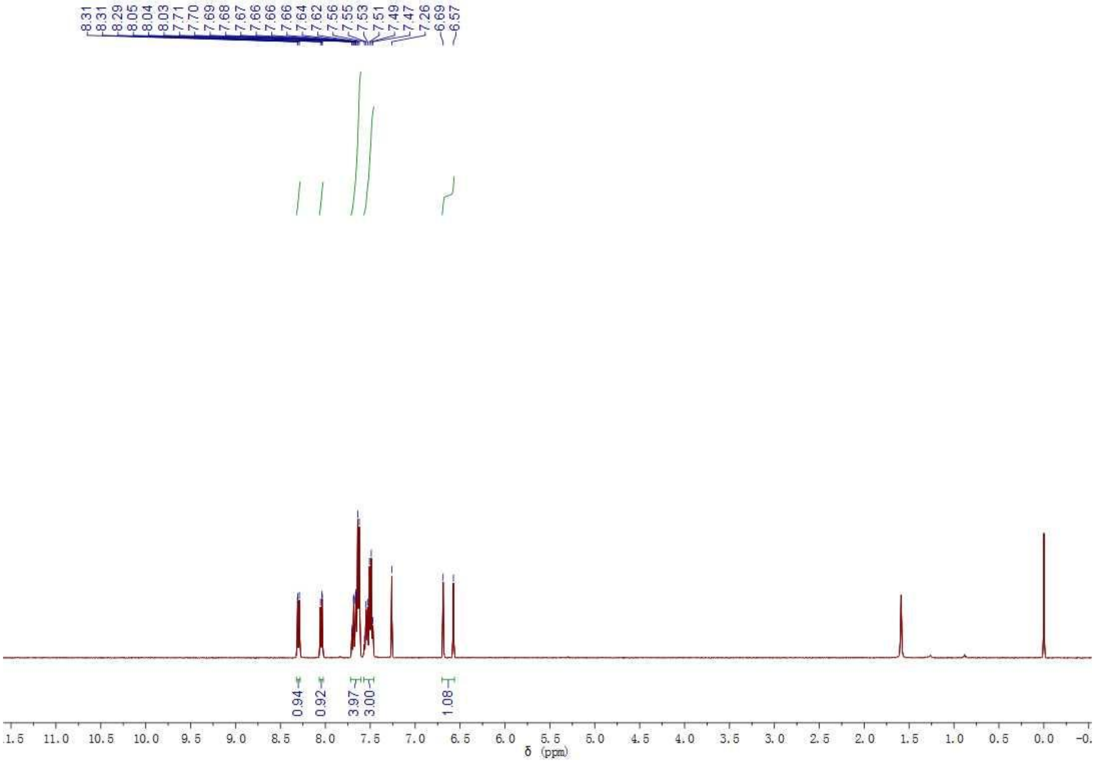

O
O
S
O
F
O
CH3

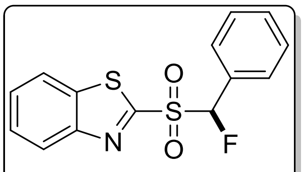
2j


^{13}C NMR (100 MHz, CDCl$_3$)
184.37
184.19
165.07
135.19
134.62
132.40
132.37
129.82
129.30
126.92
114.14
101.35
99.05
77.34
77.02
76.70
55.67
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
δ (ppm)

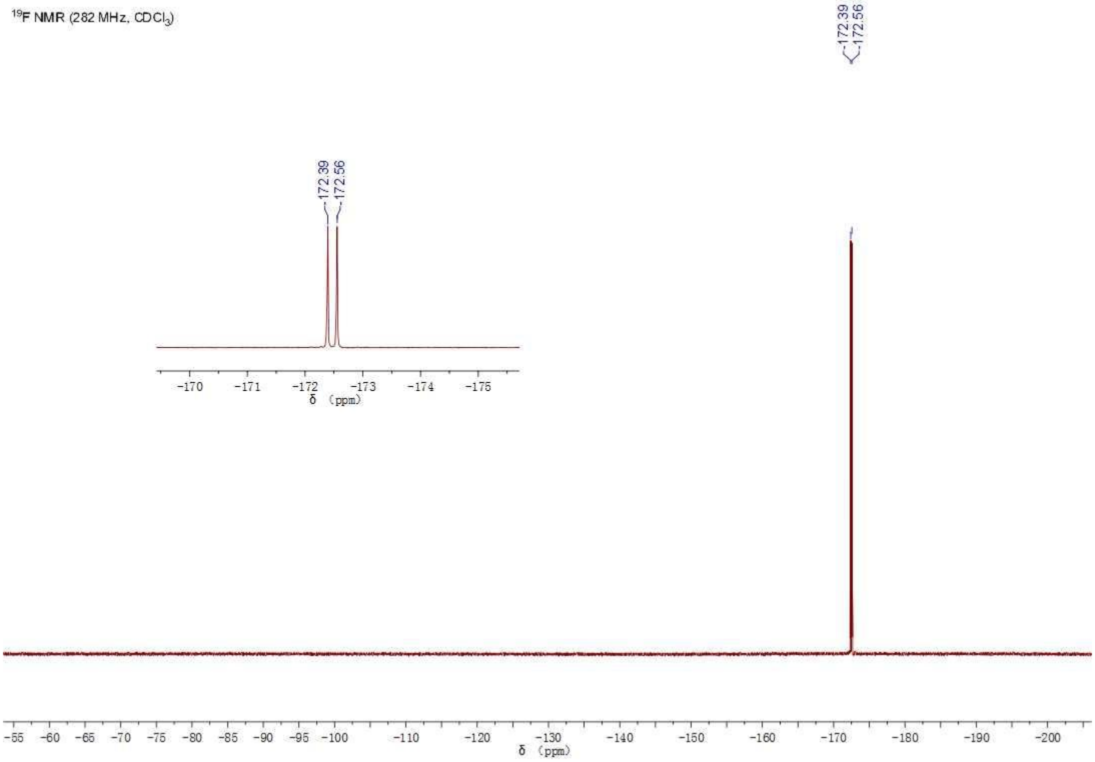

S
N
O
S
O
F

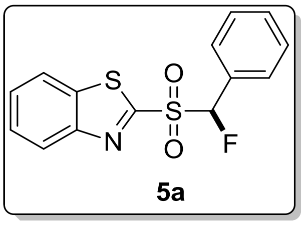
5a


8.31
8.31
8.29
8.05
8.04
8.03
7.71
7.70
7.69
7.68
7.67
7.66
7.66
7.66
7.64
7.62
7.56
7.55
7.53
7.51
7.49
7.47
7.26
6.69
6.57
0.94
0.92
3.97
3.00
1.08
1.5
11.0
10.5
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
0.0
-0.
δ (ppm)

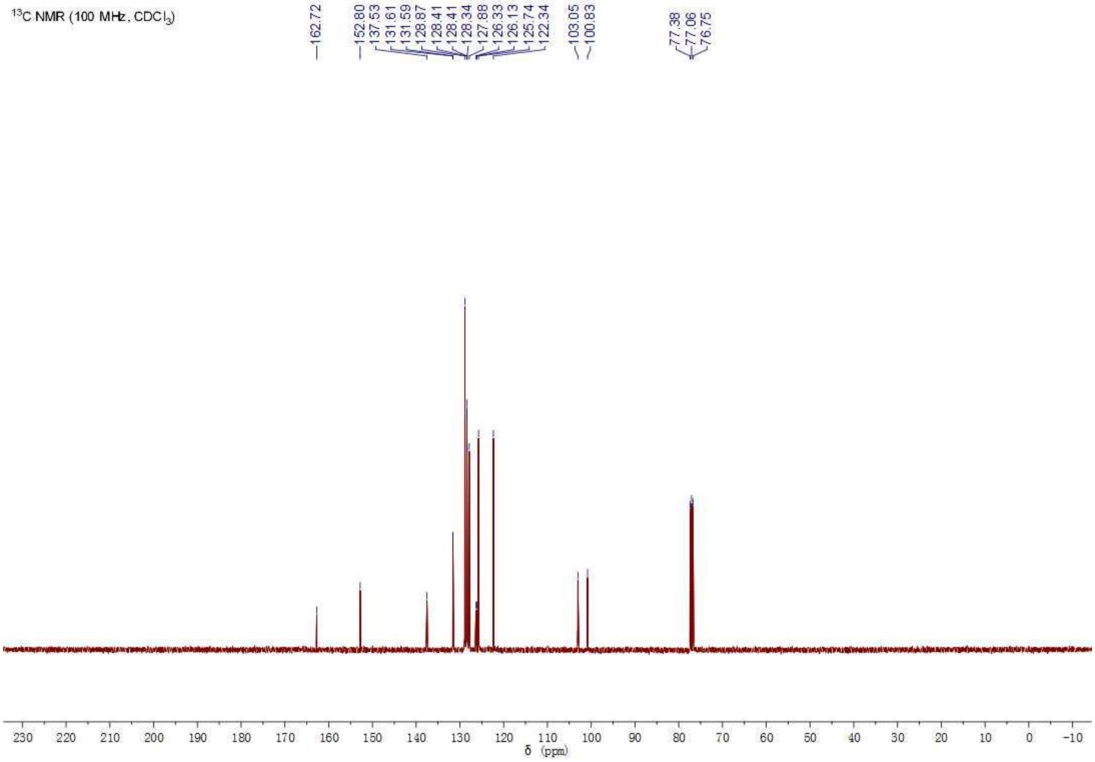

S
N
O
O
S
F

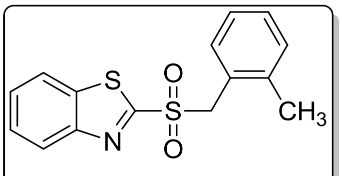
5a


^{19}F NMR (282 MHz, CDCl$_3$)
-172.39
-172.56
-172.39
-172.56
-170
-171
-172
-173
-174
-175
δ (ppm)
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
δ (ppm)

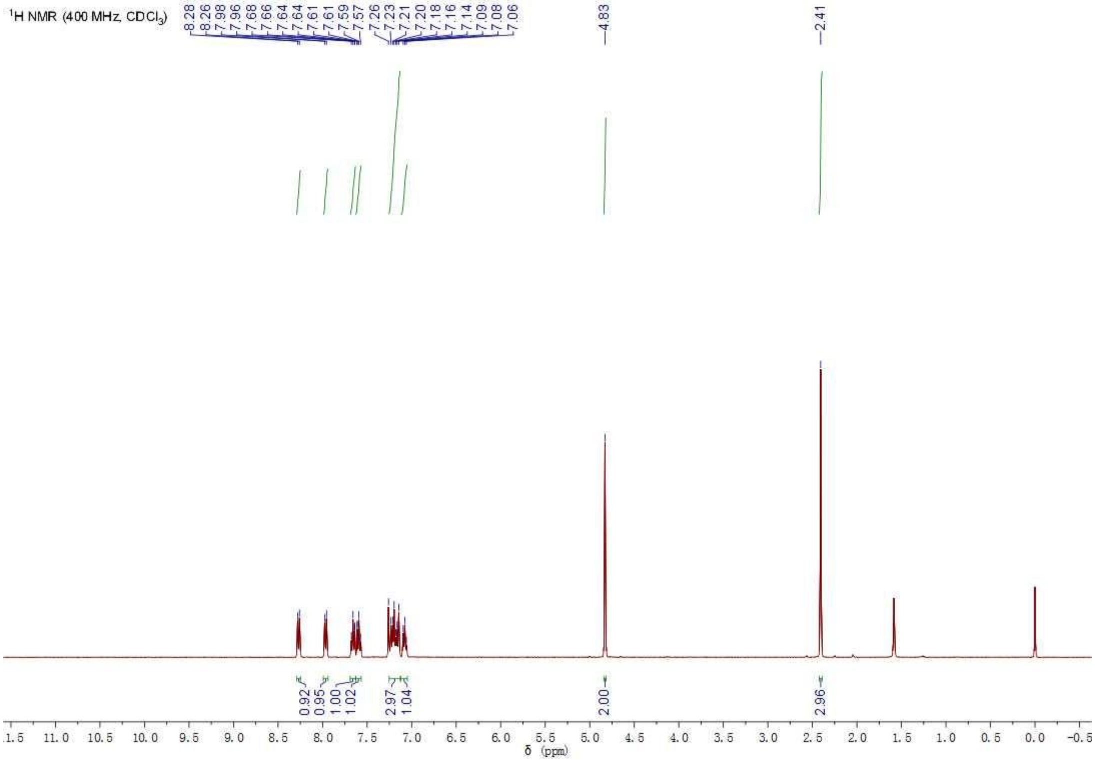

S
N
O
O
S
F

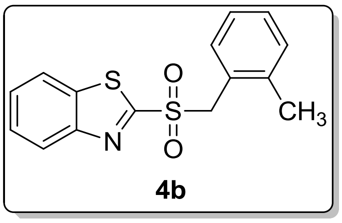
5a


^{13}C NMR (100 MHz, CDCl$_3$)
162.72
152.80
137.53
131.61
131.59
128.87
128.41
128.41
128.34
127.88
126.33
126.13
125.74
122.34
103.05
100.83
77.38
77.06
76.75
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
δ (ppm)

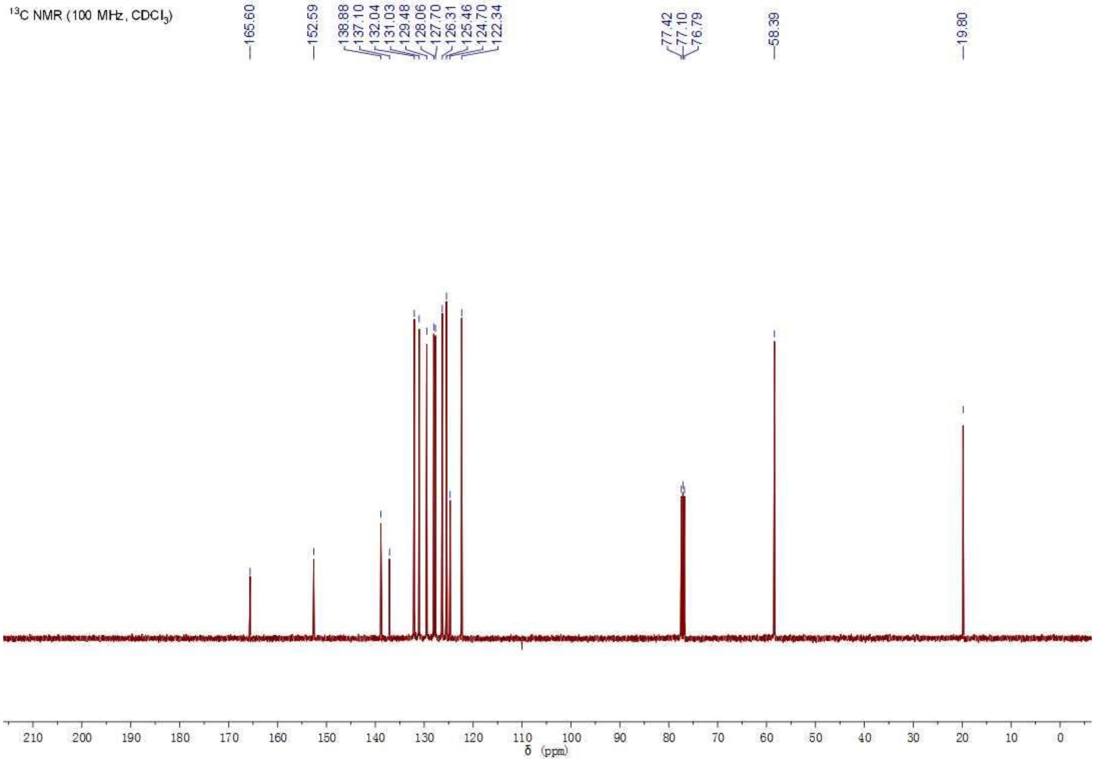

S
N
O
S
O
CH3

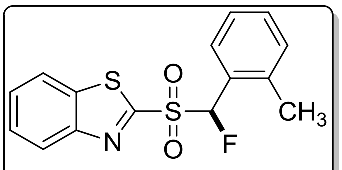
4b


1H NMR (400 MHz, CDCl3)
8.28
8.26
7.98
7.96
7.68
7.66
7.64
7.64
7.61
7.61
7.59
7.57
7.26
7.23
7.21
7.20
7.18
7.16
7.14
7.09
7.08
7.06
4.83
2.41
0.92
0.95
1.00
1.02
2.97
1.04
2.00
2.96
1.5
11.0
10.5
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
0.0
-0.5
δ (ppm)

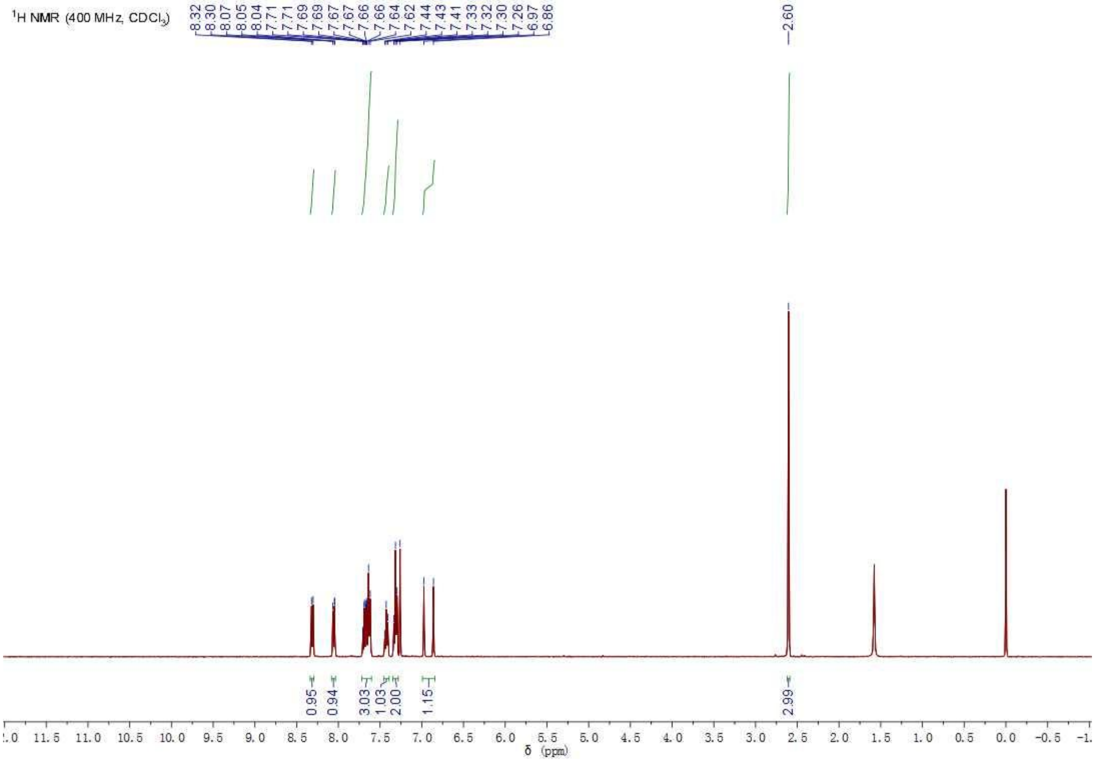

S
N
O
S
O
CH3

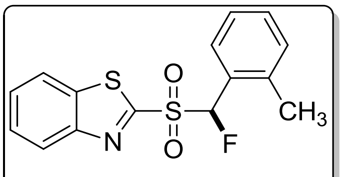
4b


^{13}C NMR (100 MHz, CDCl$_3$)
165.60
152.59
138.88
137.10
132.04
131.03
129.48
128.06
127.70
126.31
125.46
124.70
122.34
77.42
77.10
76.79
58.39
19.80
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

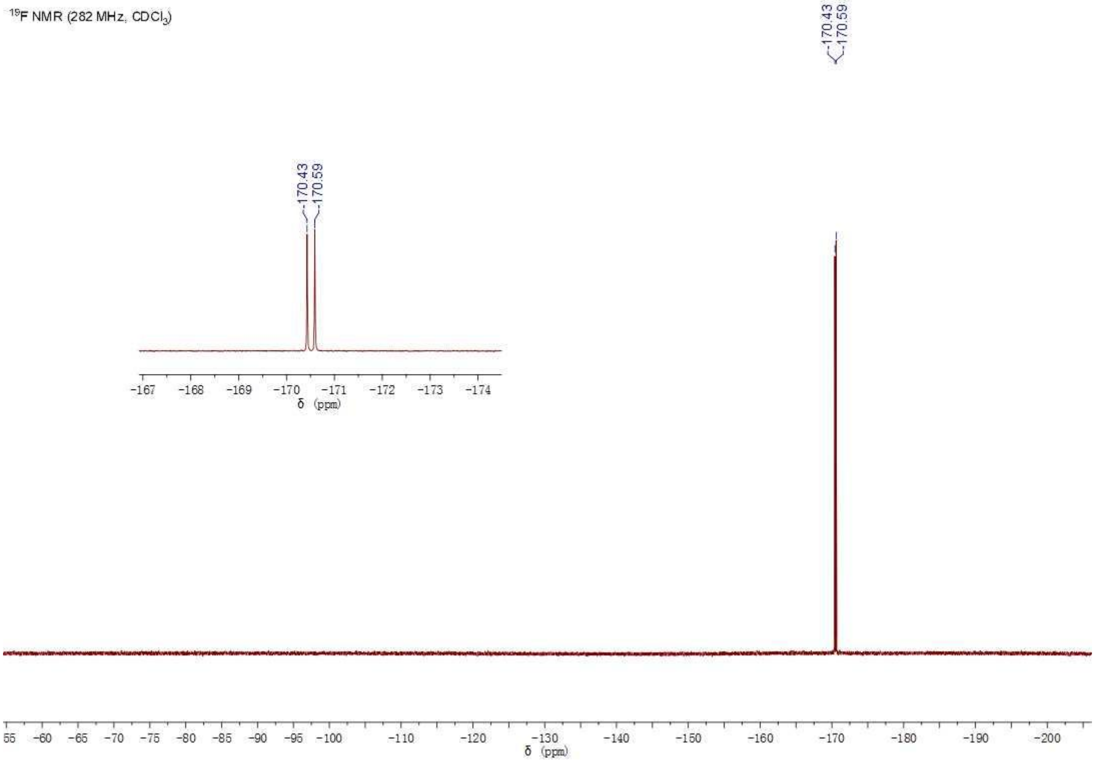

S
N
O
S
O
F
CH3

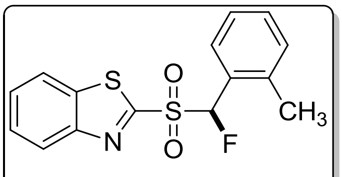
5b


1H NMR (400 MHz, CDCl3)
8.32
8.30
8.07
8.05
8.04
7.71
7.69
7.69
7.67
7.66
7.66
7.64
7.62
7.44
7.43
7.41
7.33
7.32
7.30
7.26
6.97
6.86
2.60
0.95
0.94
3.03
1.03
2.00
1.15
2.99
12.0
11.5
11.0
10.5
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
0.0
-0.5
-1.0
δ (ppm)

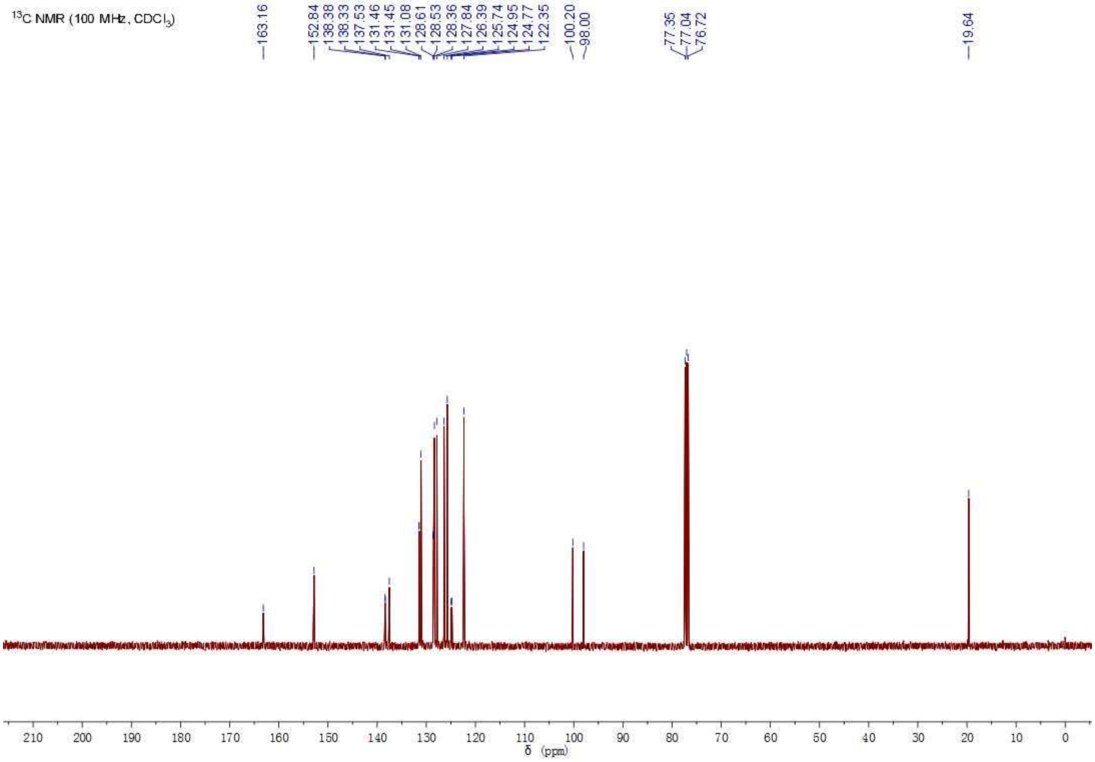

S
O
S
O
N
F
CH$_3$

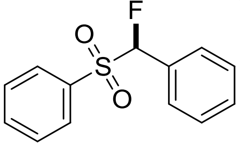
5b


^{19}F NMR (282 MHz, CDCl$_3$)
-170.43
-170.59
-170.43
-170.59
-167
-168
-169
-170
-171
-172
-173
-174
δ (ppm)
55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
δ (ppm)

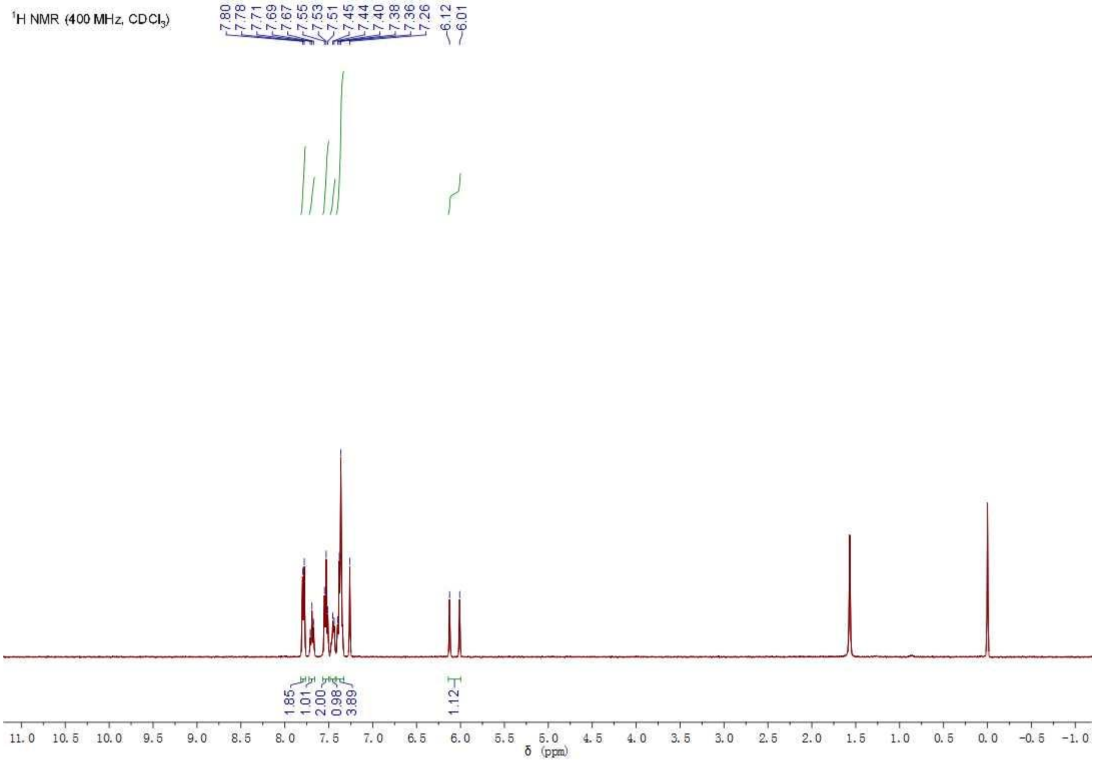

S
O
S
O
N
F
CH3

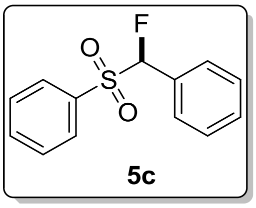
5b


^{13}C NMR (100 MHz, CDCl$_3$)
163.16
152.84
138.38
138.33
137.53
131.46
131.45
131.08
128.61
128.53
128.36
127.84
126.39
125.74
124.95
124.77
122.35
100.20
98.00
77.35
77.04
76.72
19.64
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

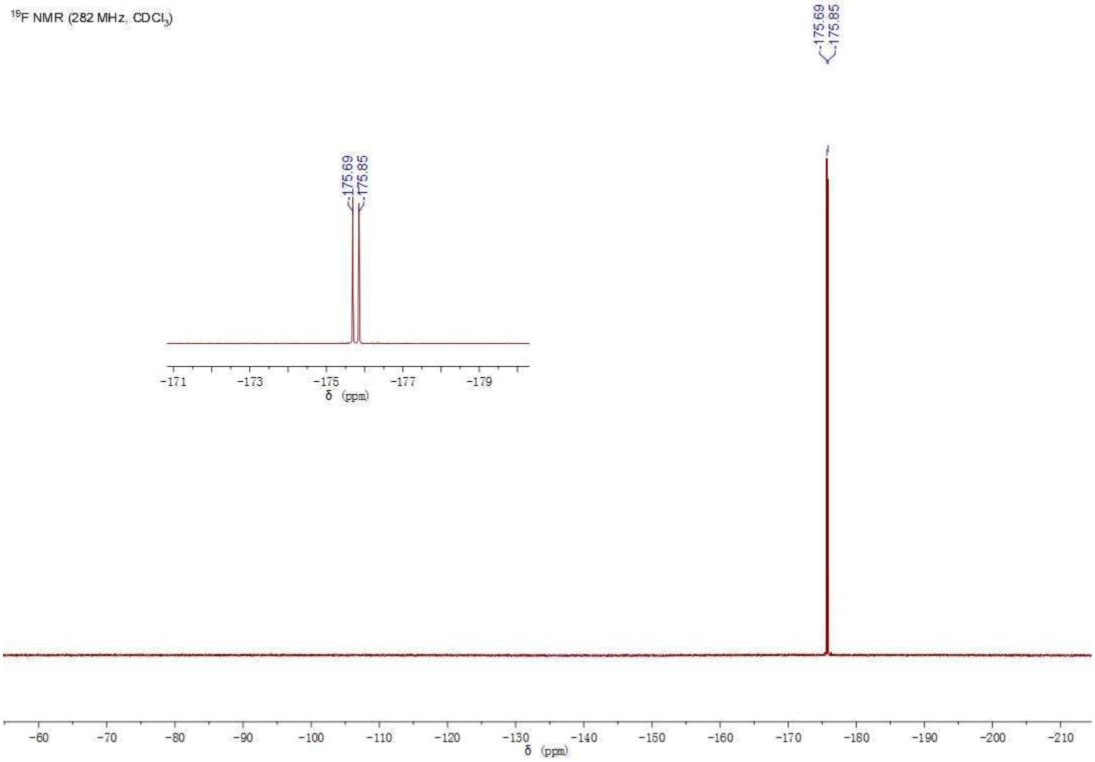

F
O
S
O

5c

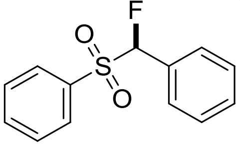

^{1}H NMR (400 MHz, CDCl$_3$)
7.80
7.78
7.71
7.69
7.67
7.55
7.53
7.51
7.45
7.44
7.40
7.38
7.36
7.26
6.12
6.01
1.85
1.01
2.00
0.98
3.89
1.12
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
δ (ppm)



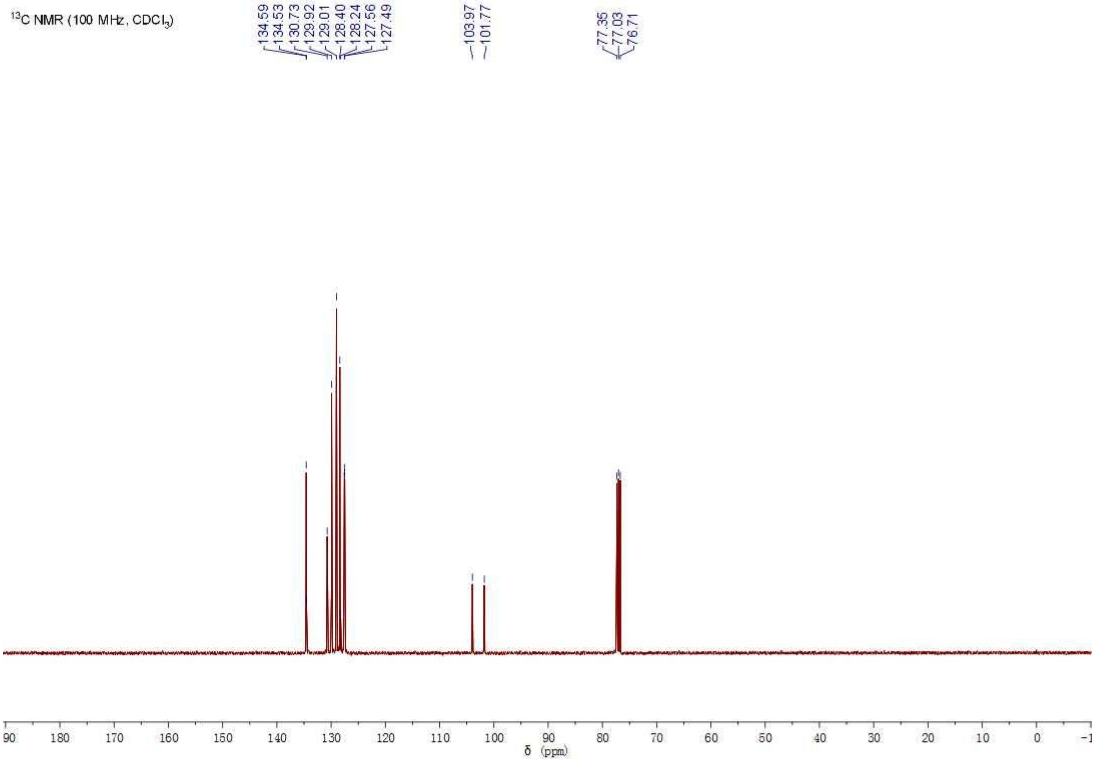
5c

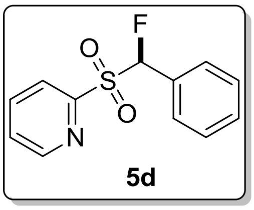


^{19}F NMR (282 MHz, CDCl$_3$)
-175.69
-175.85
-171
-173
-175
-177
-179
δ (ppm)
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
δ (ppm)

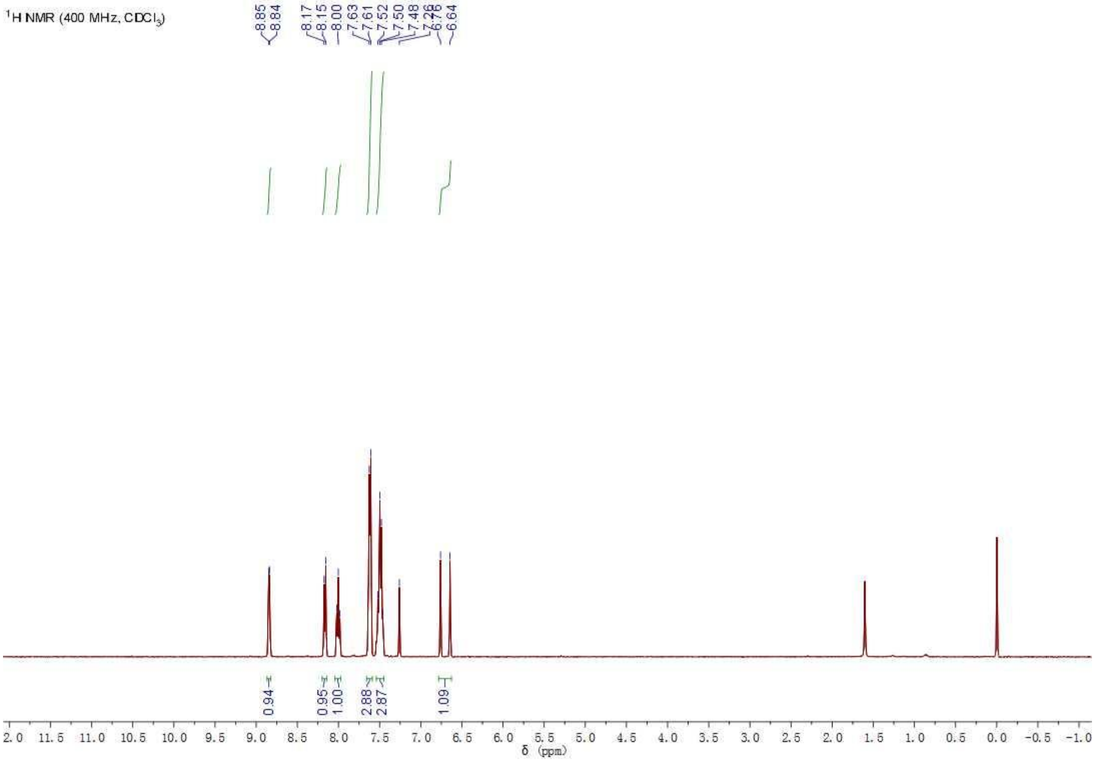

F
O
S
O

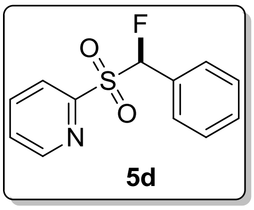
5c

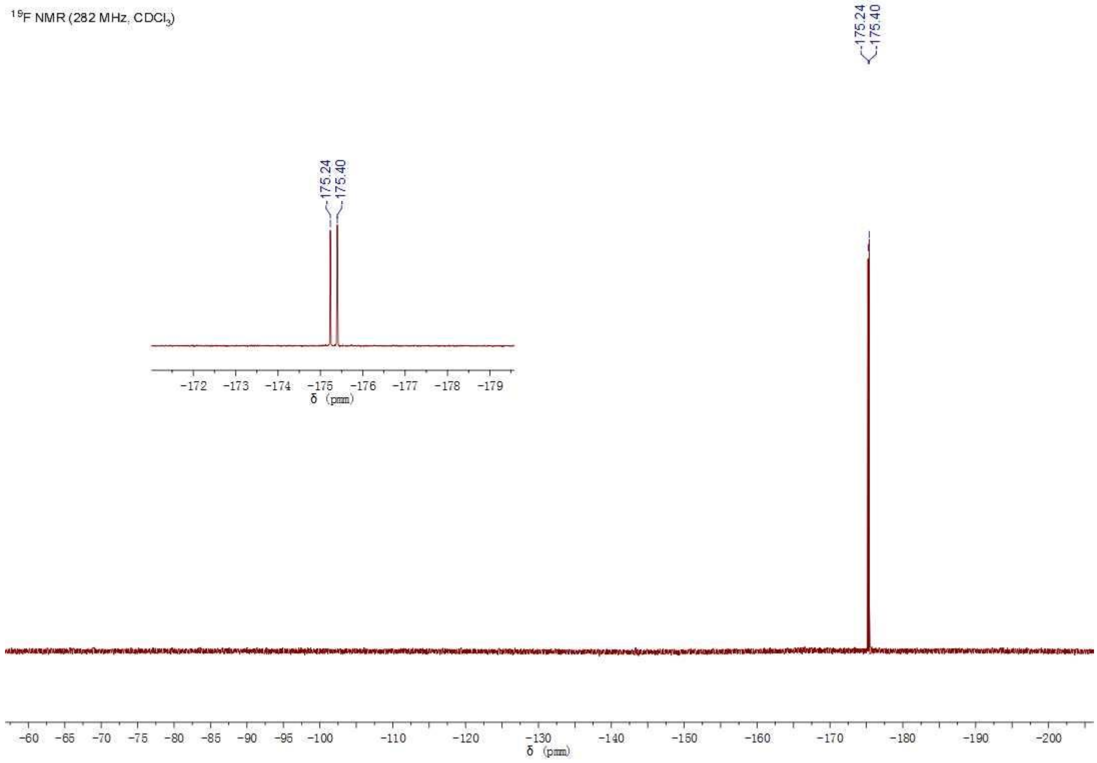

^{13}C NMR (100 MHz, CDCl$_3$)
134.59
134.53
130.73
129.92
129.01
128.40
128.24
127.56
127.49
103.97
101.77
77.35
77.03
76.71
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
δ (ppm)

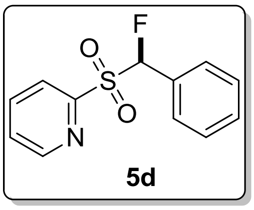

F
O
S
O
N

5d

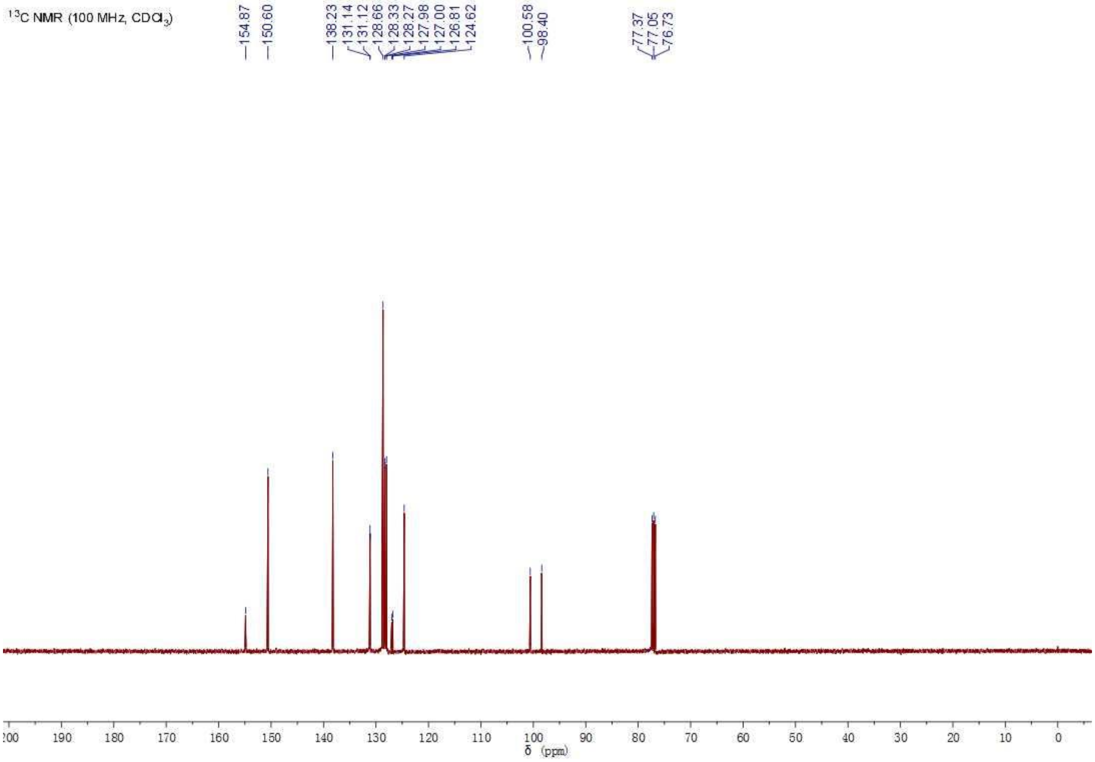

^{1}H NMR (400 MHz, CDCl$_3$)
8.85
8.84
8.17
8.15
8.00
7.63
7.61
7.52
7.50
7.48
7.26
6.76
6.64
0.94
0.95
1.00
2.88
2.87
1.09
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
δ (ppm)

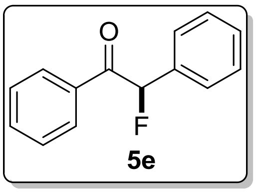

F
O
S
O
N
5d


^{19}F NMR (282 MHz, CDCl$_3$)
-175.24
-175.40
-172 -173 -174 -175 -176 -177 -178 -179
δ (ppm)
-60 -65 -70 -75 -80 -85 -90 -95 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
δ (ppm)

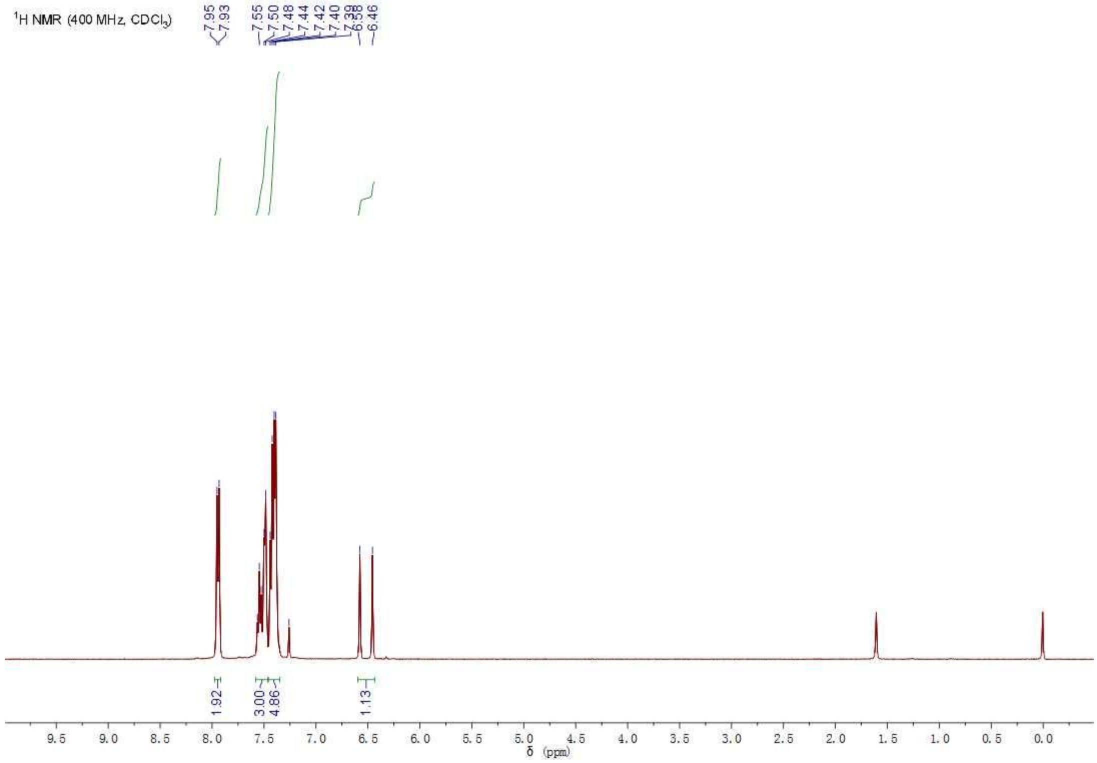

F
O
S
O
N

5d

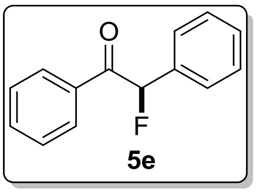

^{13}C NMR (100 MHz, CDCl$_3$)
154.87
150.60
138.23
131.14
131.12
128.66
128.33
128.27
127.98
127.00
126.81
124.62
100.58
98.40
77.37
77.05
76.73
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)



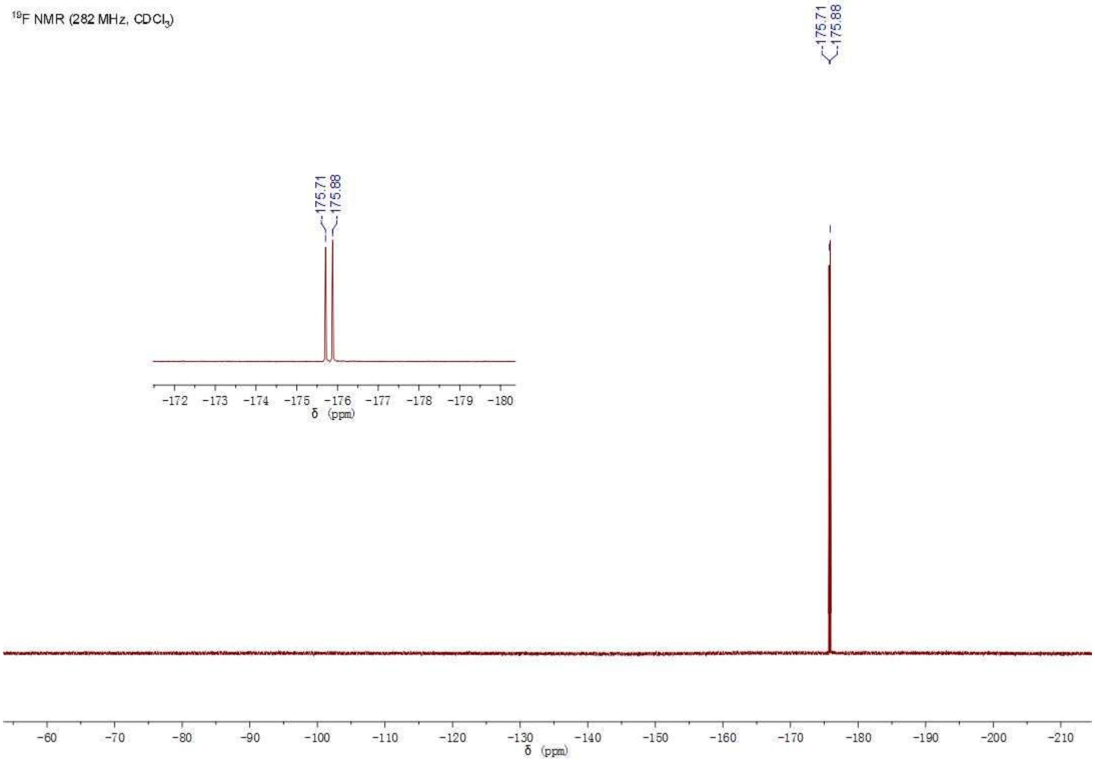
5e

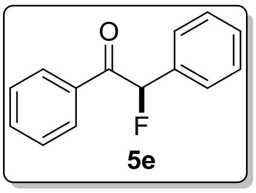


^{1}H NMR (400 MHz, CDCl$_3$)
7.95
7.93
7.55
7.50
7.48
7.44
7.42
7.40
7.39
6.58
6.46
1.92
3.00
4.86
1.13
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)

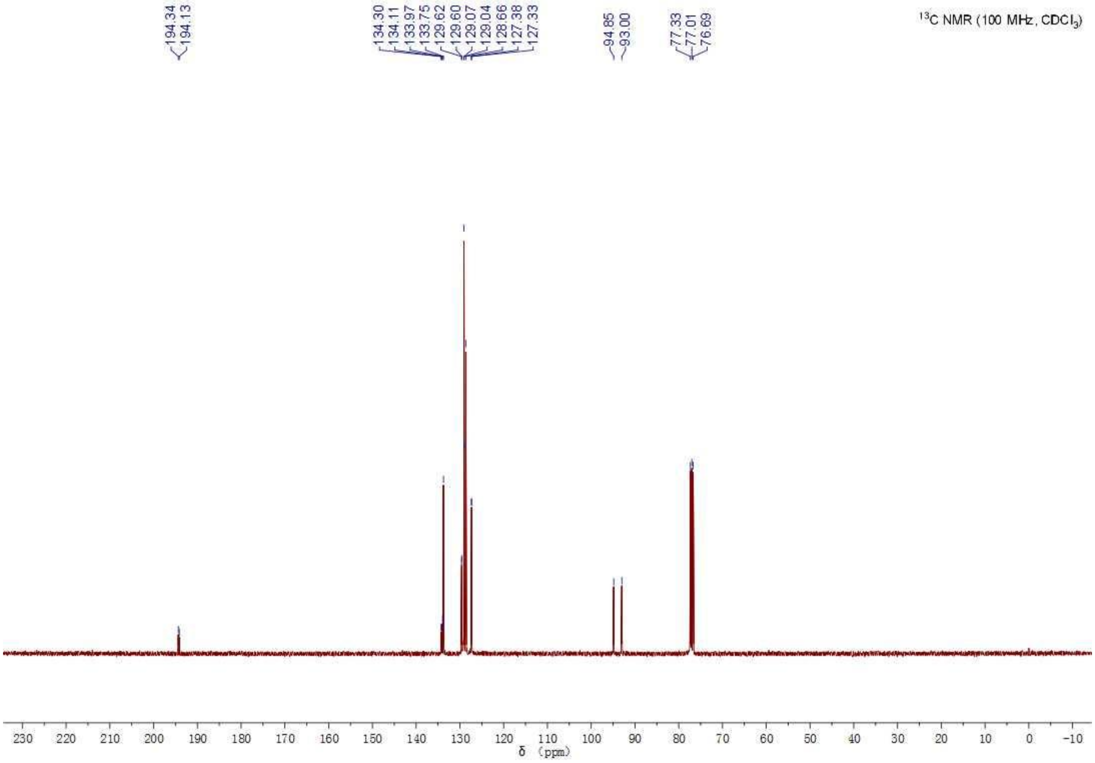

O
F

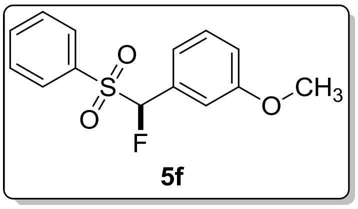
5e


^{19}F NMR (282 MHz, CDCl$_3$)
-175.71
-175.88
-175.71
-175.88
−172
−173
−174
−175
−176
−177
−178
−179
−180
δ (ppm)
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
δ (ppm)

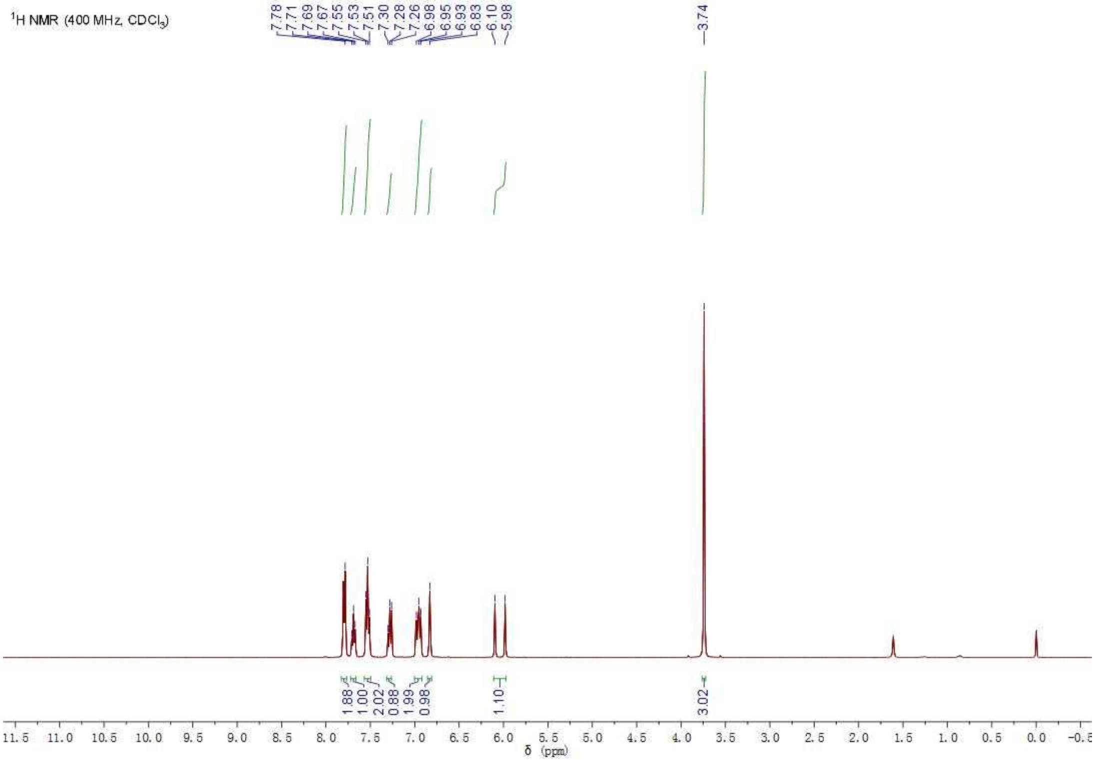


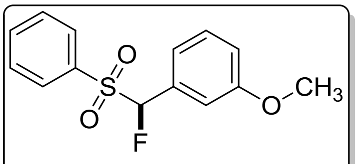
5e


194.34
194.13
134.30
134.11
133.97
133.75
129.62
129.60
129.07
129.04
128.66
127.38
127.33
94.85
93.00
77.33
77.01
76.69
^{13}C NMR (100 MHz, CDCl$_3$)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
δ（ppm）

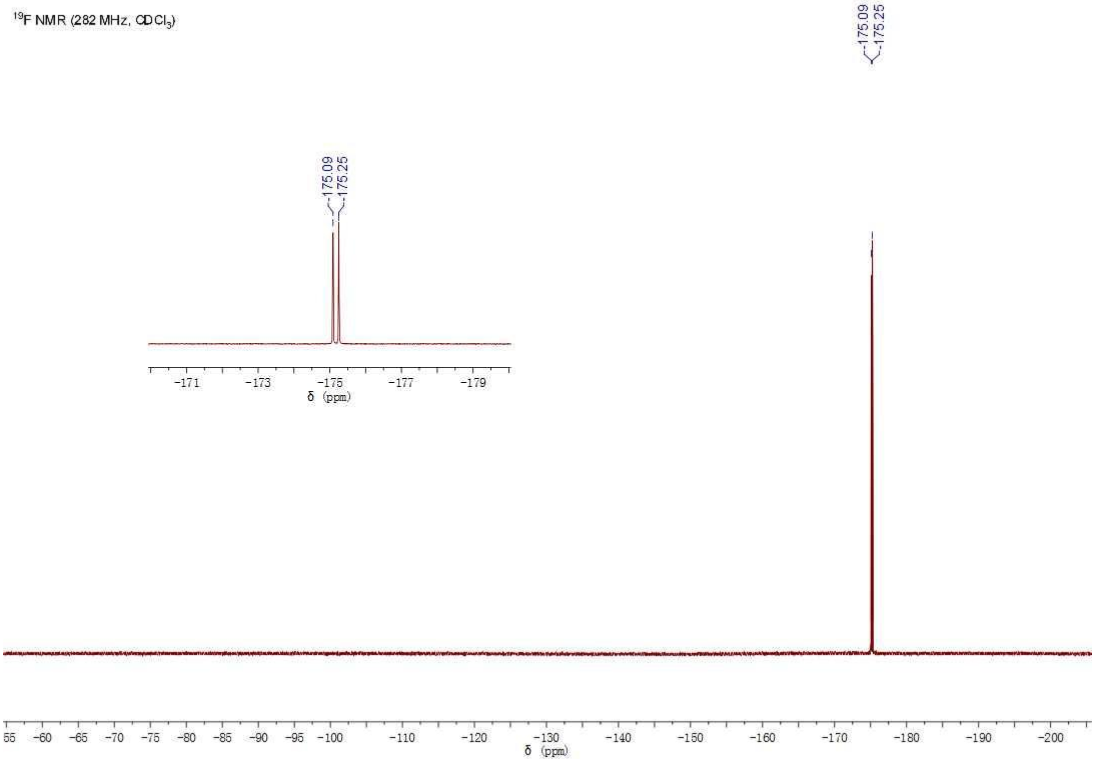

O
S
O
F
O
CH3

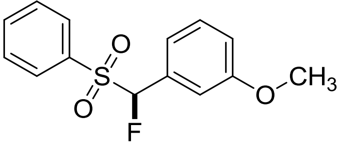
5f


1H NMR (400 MHz, CDCl3)
7.78
7.71
7.69
7.67
7.55
7.53
7.51
7.30
7.28
7.26
6.98
6.95
6.93
6.83
6.10
5.98
3.74
1.88
1.00
2.02
0.88
1.99
0.98
1.10
3.02
11.5
11.0
10.5
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
0.0
-0.5
δ (ppm)

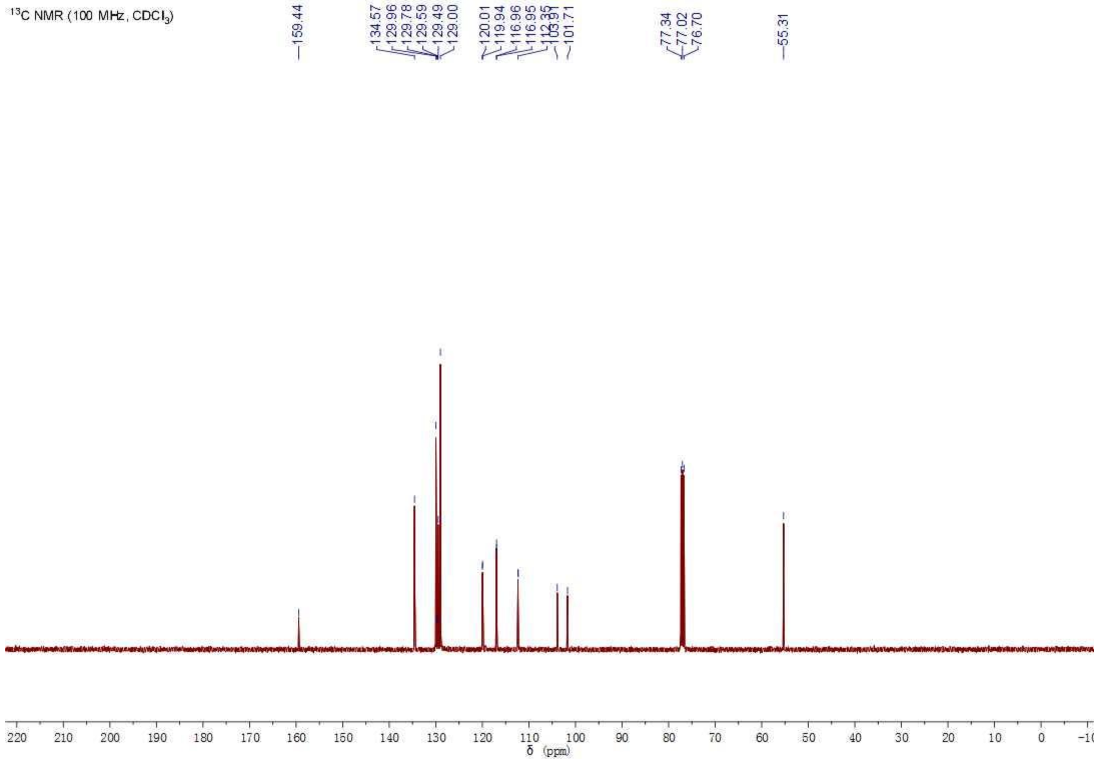

O
S
O
F
O
CH3

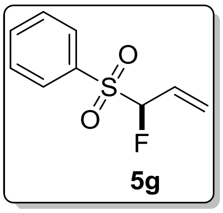
5f


19F NMR (282 MHz, CDCl3)
-175.09
-175.25
-175.09
-175.25
-171
-173
-175
-177
-179
δ (ppm)
55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
δ (ppm)

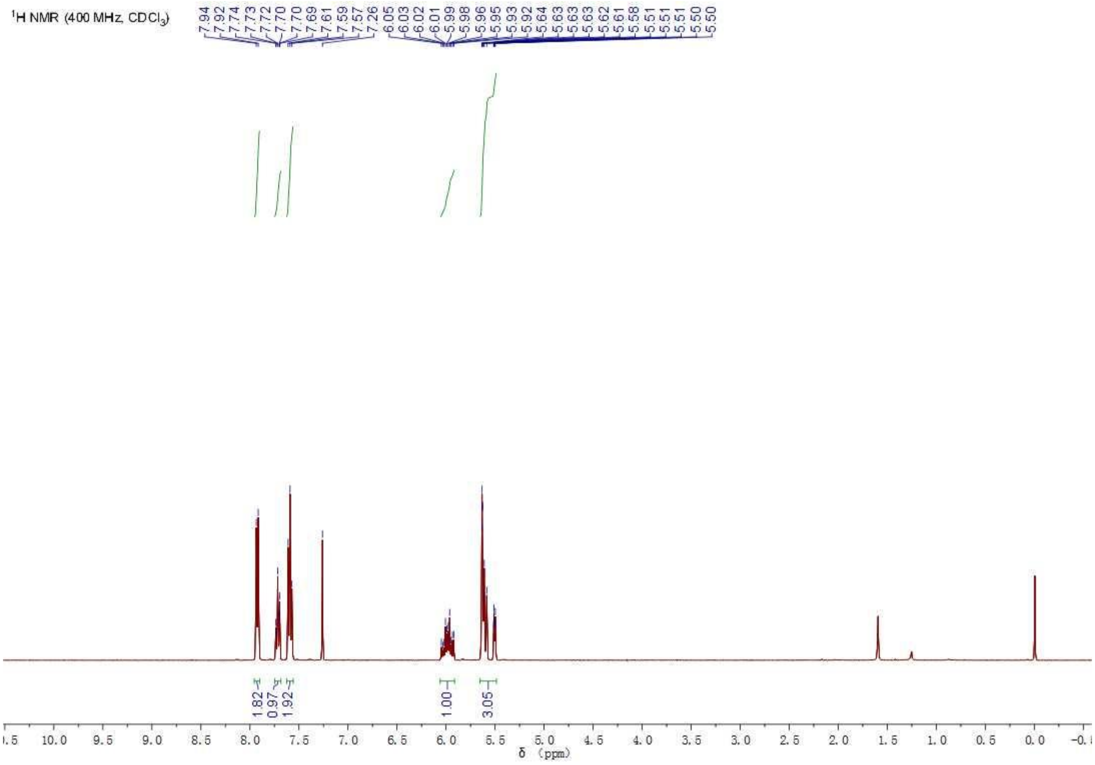

O
S
O
F
O
CH3

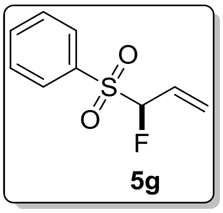
5f


13C NMR (100 MHz, CDCl3)
159.44
134.57
129.96
129.78
129.59
129.49
129.00
120.01
119.94
116.96
116.95
112.35
103.91
101.71
77.34
77.02
76.70
55.31
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)

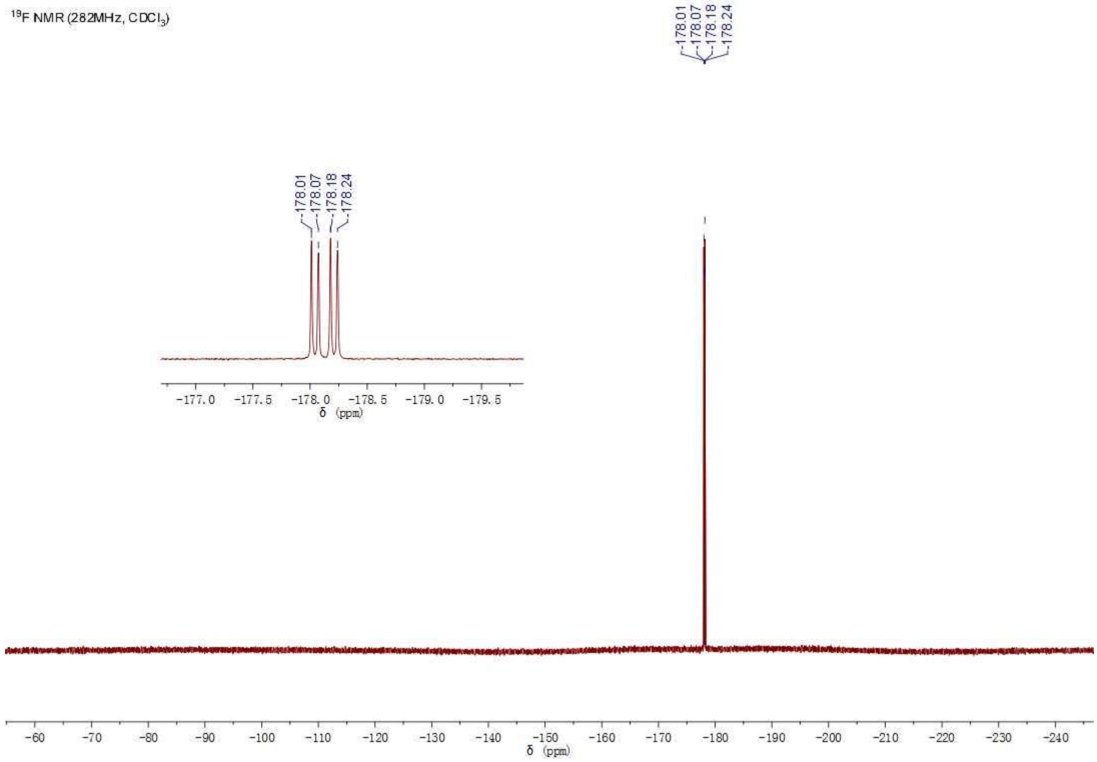

O
S
O
F

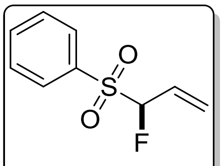
5g


^{1}H NMR (400 MHz, CDCl$_3$)
7.94
7.92
7.74
7.73
7.72
7.70
7.69
7.61
7.59
7.57
7.26
6.05
6.03
6.02
6.01
5.99
5.98
5.96
5.95
5.93
5.92
5.64
5.63
5.63
5.63
5.62
5.61
5.58
5.51
5.51
5.51
5.50
5.50
1.82
0.97
1.92
1.00
3.05
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
0.0
δ (ppm)

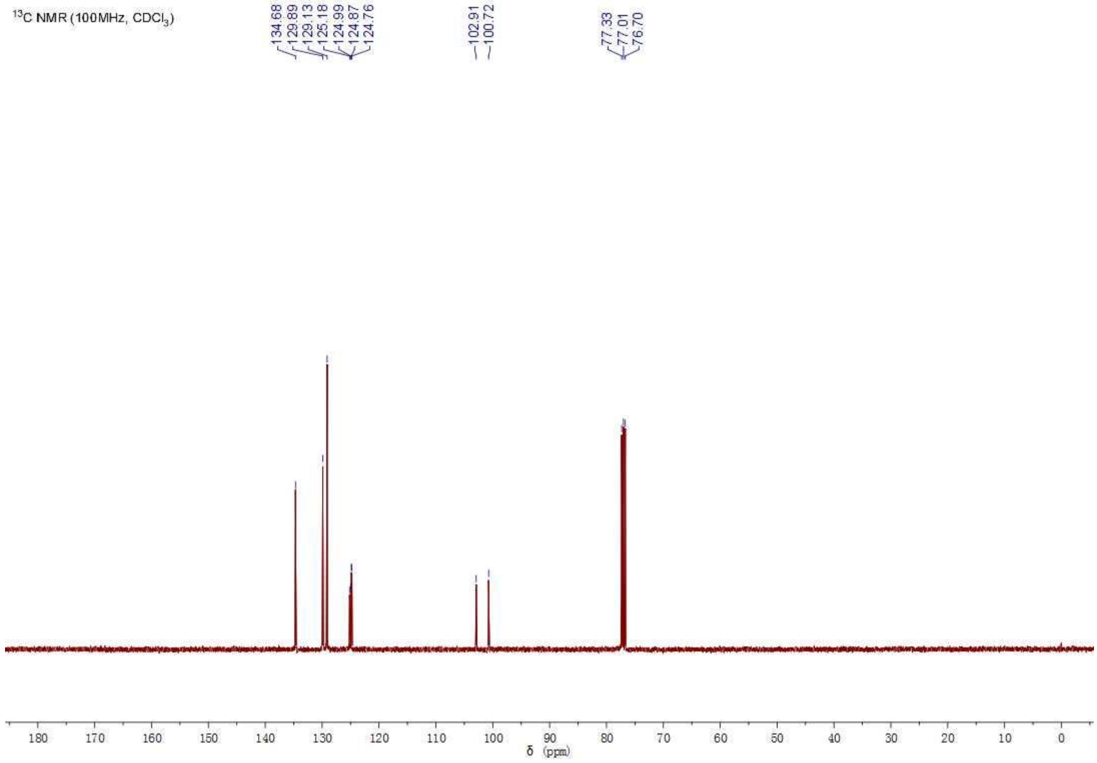

O
S
O
F

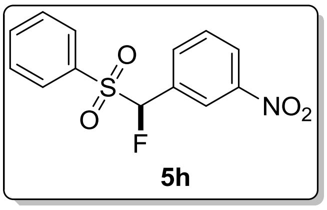
5g


^{19}F NMR (282MHz, CDCl$_3$)
-178.01
-178.07
-178.18
-178.24
-177.0
-177.5
-178.0
-178.5
-179.0
-179.5
δ (ppm)
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
-240
δ (ppm)

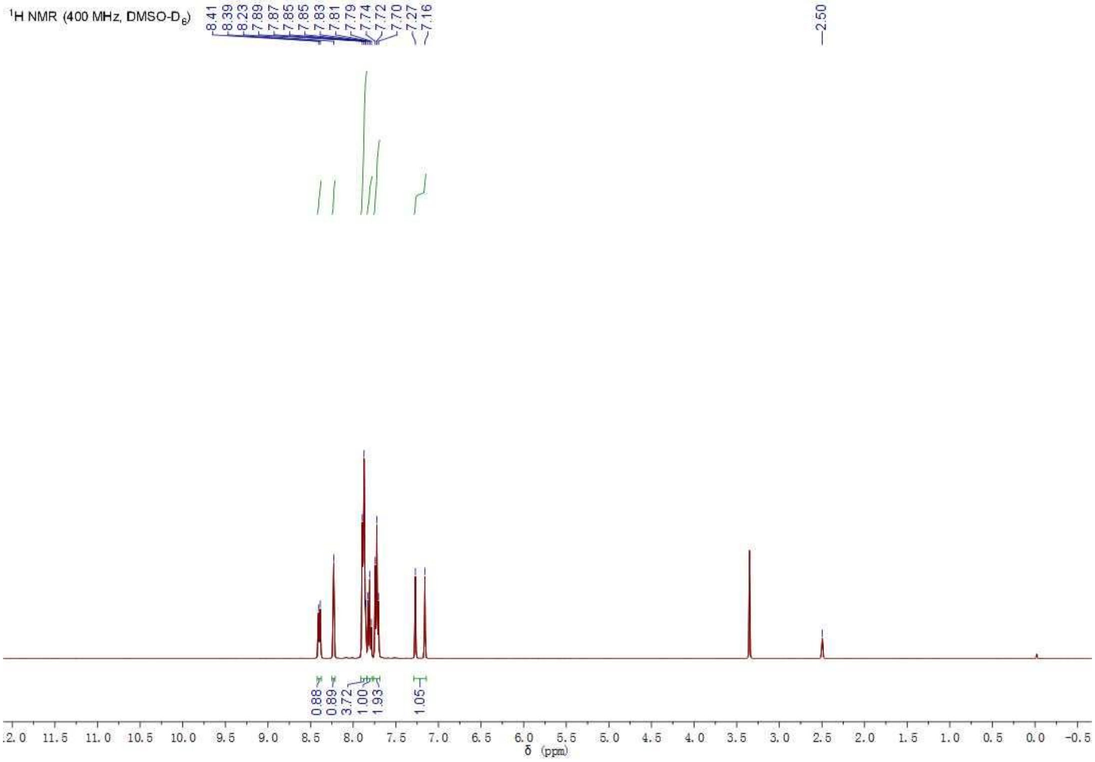

O
S
O
F

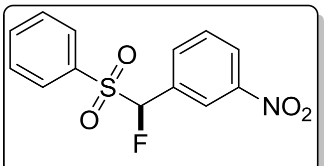
5g


^{13}C NMR (100MHz, CDCl$_3$)
134.68
129.89
129.13
125.18
124.99
124.87
124.76
102.91
100.72
77.33
77.01
76.70
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

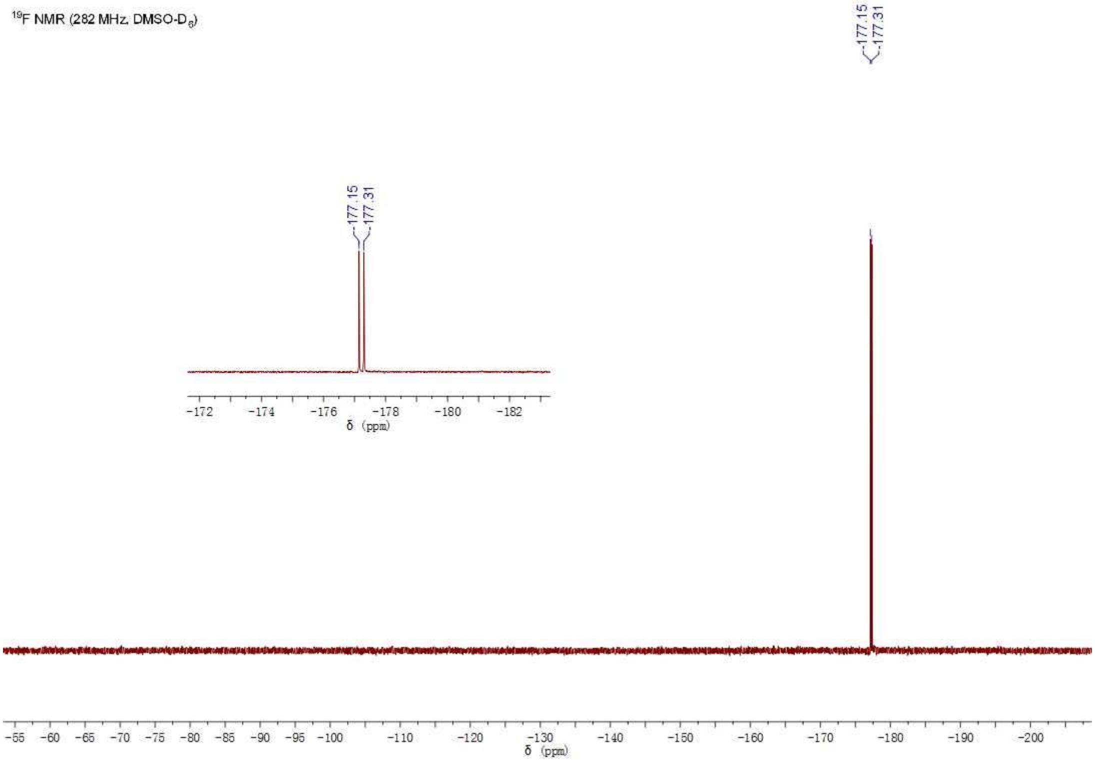

O
S
O
F
NO2

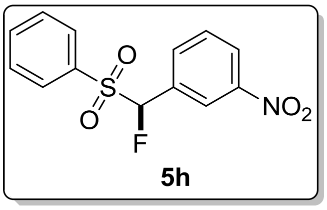
5h


1H NMR (400 MHz, DMSO-D6)
8.41
8.39
8.23
7.89
7.87
7.85
7.83
7.81
7.79
7.74
7.72
7.70
7.27
7.16
2.50
0.88
0.89
3.72
1.00
1.93
1.05
12.0
11.5
11.0
10.5
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
0.0
-0.5
δ (ppm)

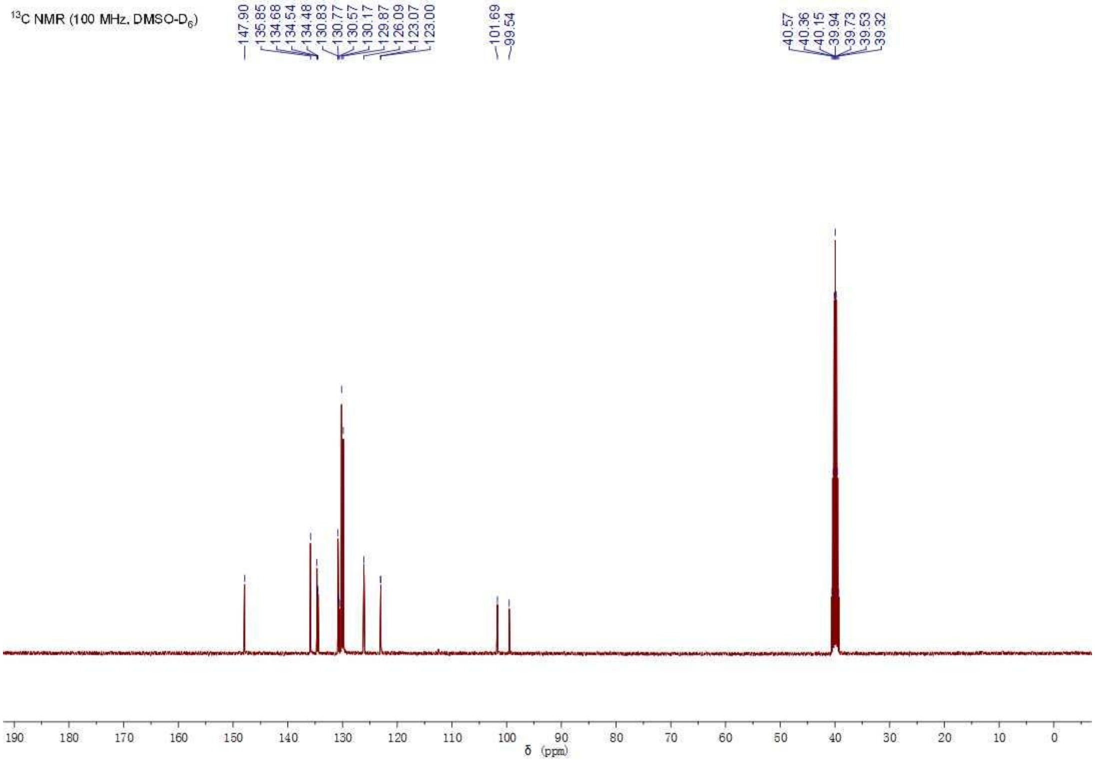

O
S
O
F
NO2

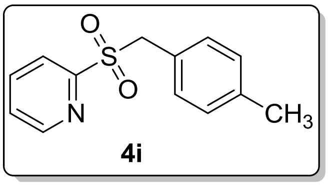
5h


19F NMR (282 MHz, DMSO-D6)
-177.15
-177.31
-177.15
-177.31
-172
-174
-176
-178
-180
-182
δ (ppm)
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
δ (ppm)

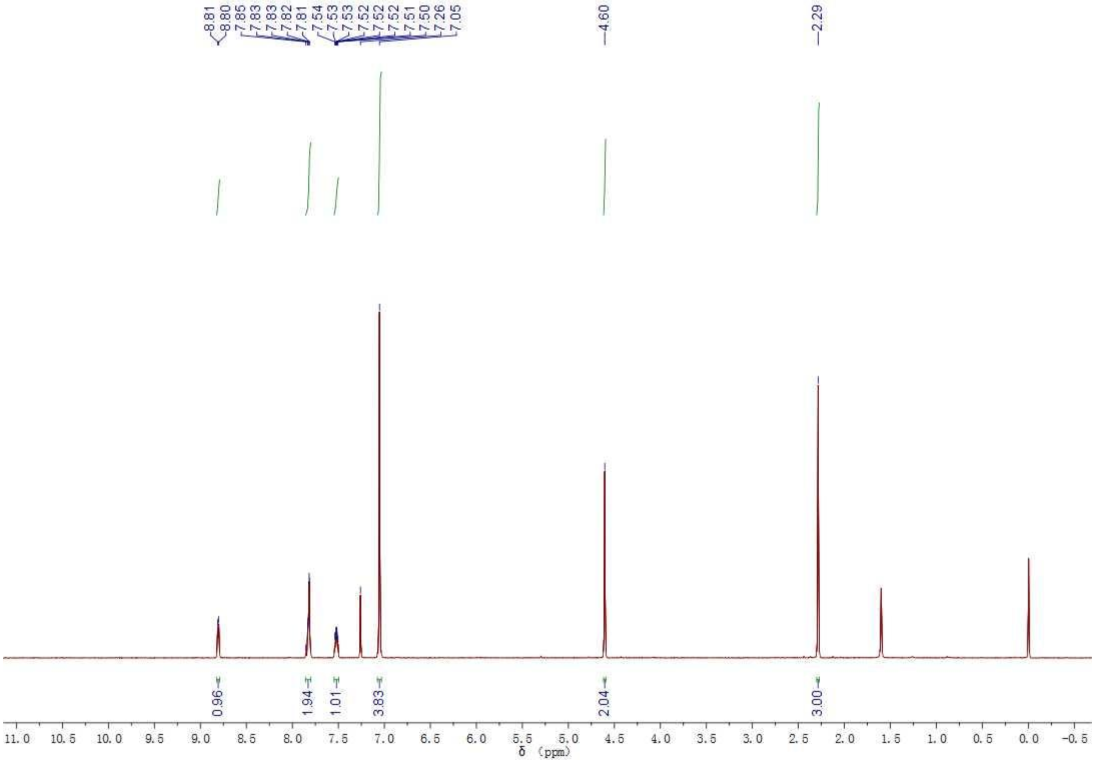

O
S
O
F
NO2

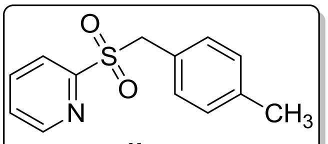
5h


13C NMR (100 MHz, DMSO-D6)
147.90
135.85
134.68
134.54
134.48
130.83
130.77
130.57
130.17
129.87
126.09
123.07
123.00
101.69
99.54
40.57
40.36
40.15
39.94
39.73
39.53
39.32
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

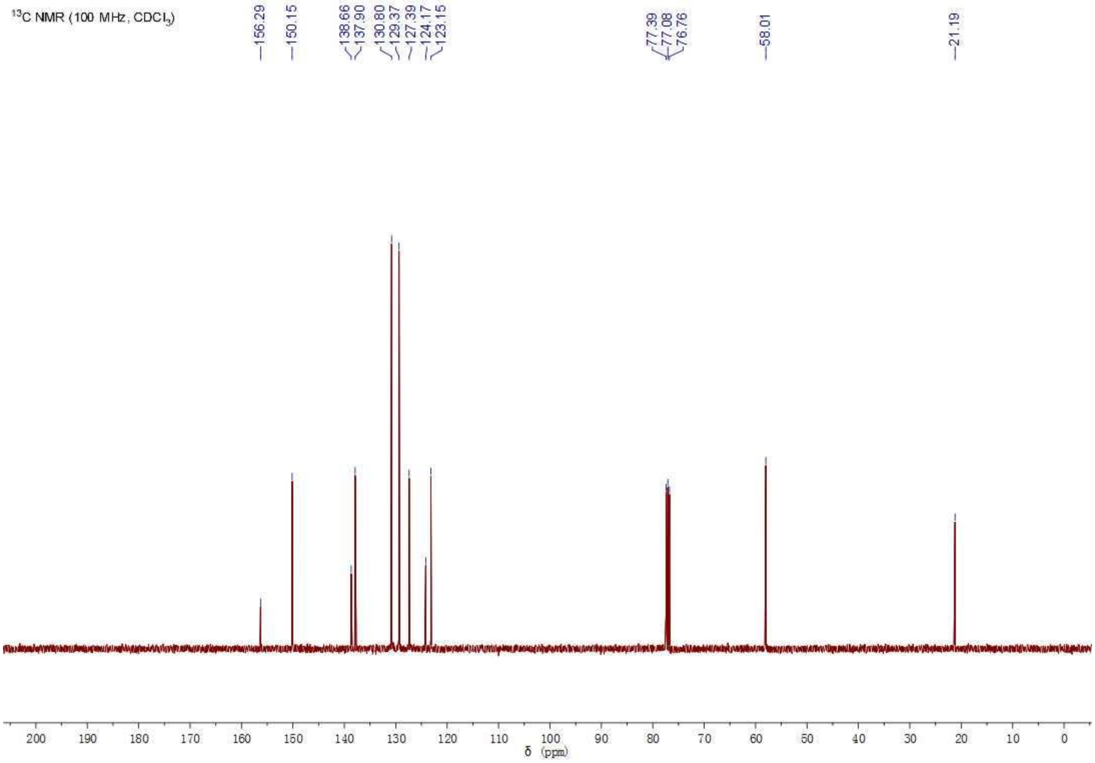

O
S
O
N
CH3

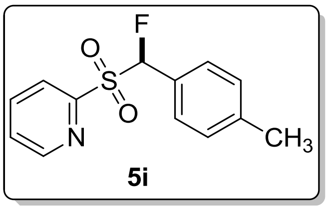
4i


8.81
8.80
7.85
7.83
7.83
7.82
7.81
7.54
7.53
7.53
7.52
7.52
7.52
7.51
7.50
7.26
7.05
4.60
2.29
0.96
1.94
1.01
3.83
2.04
3.00
11.0
10.5
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
0.0
−0.5
δ (ppm)

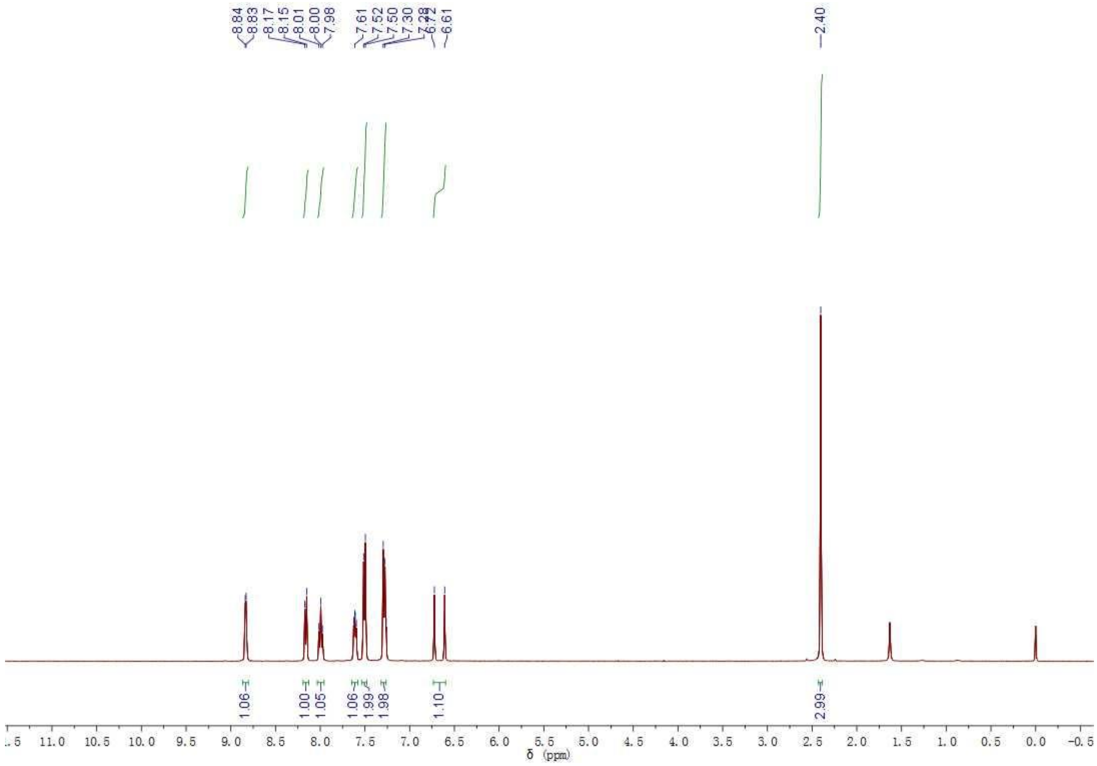

O
S
O
N
CH3

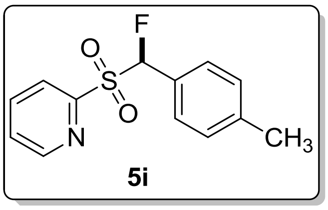
4i


^{13}C NMR (100 MHz, CDCl$_3$)
156.29
150.15
138.66
137.90
130.80
129.37
127.39
124.17
123.15
77.39
77.08
76.76
58.01
21.19
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

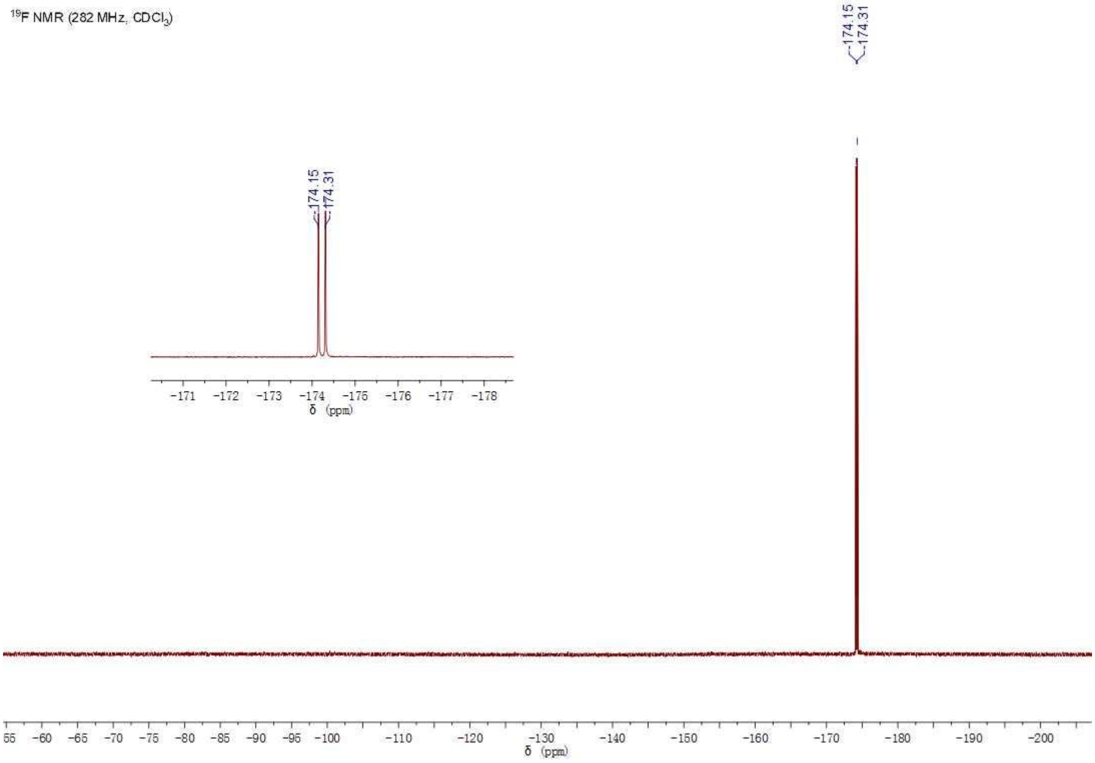

F
O
S
O
N
CH3

5i

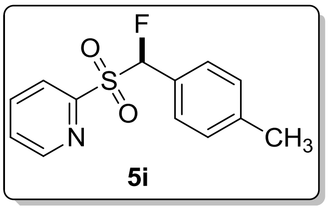

8.84
8.83
8.17
8.15
8.01
8.00
7.98
7.61
7.52
7.50
7.30
7.28
6.72
6.61
2.40
1.06
1.00
1.05
1.06
1.99
1.98
1.10
2.99
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
δ (ppm)



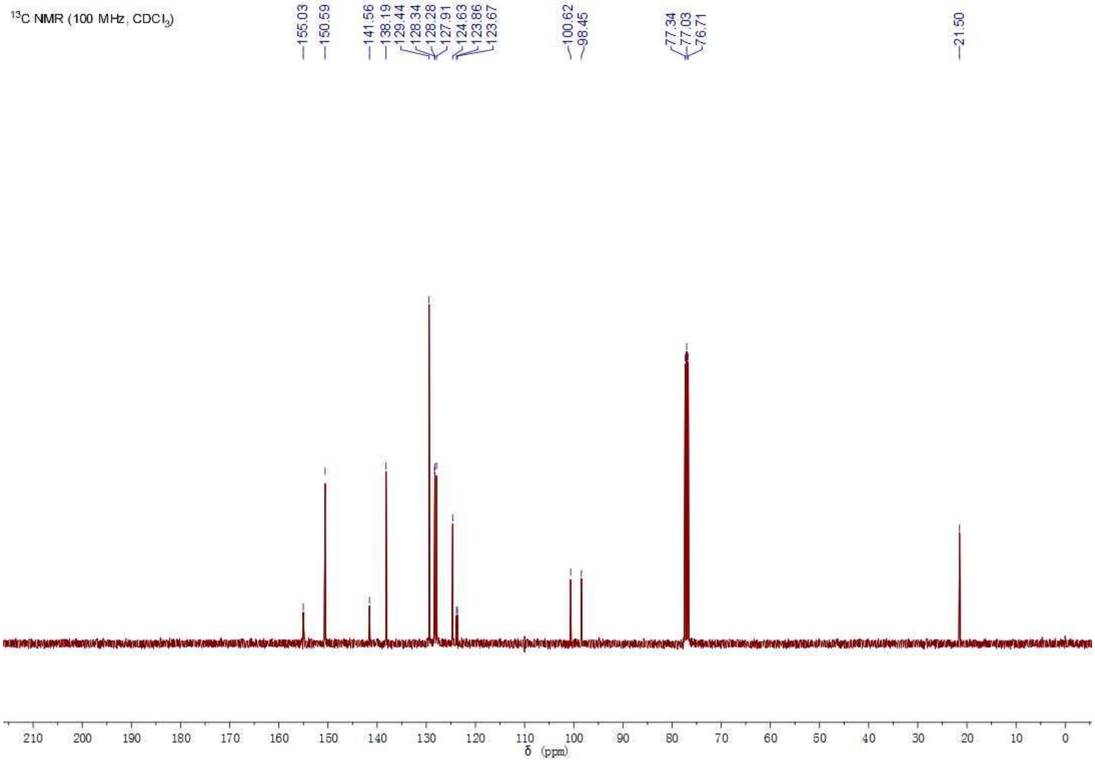
5i

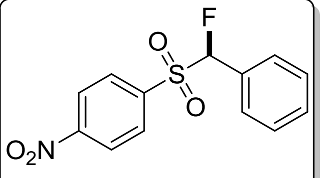


^{19}F NMR (282 MHz, $CDCl_3$)

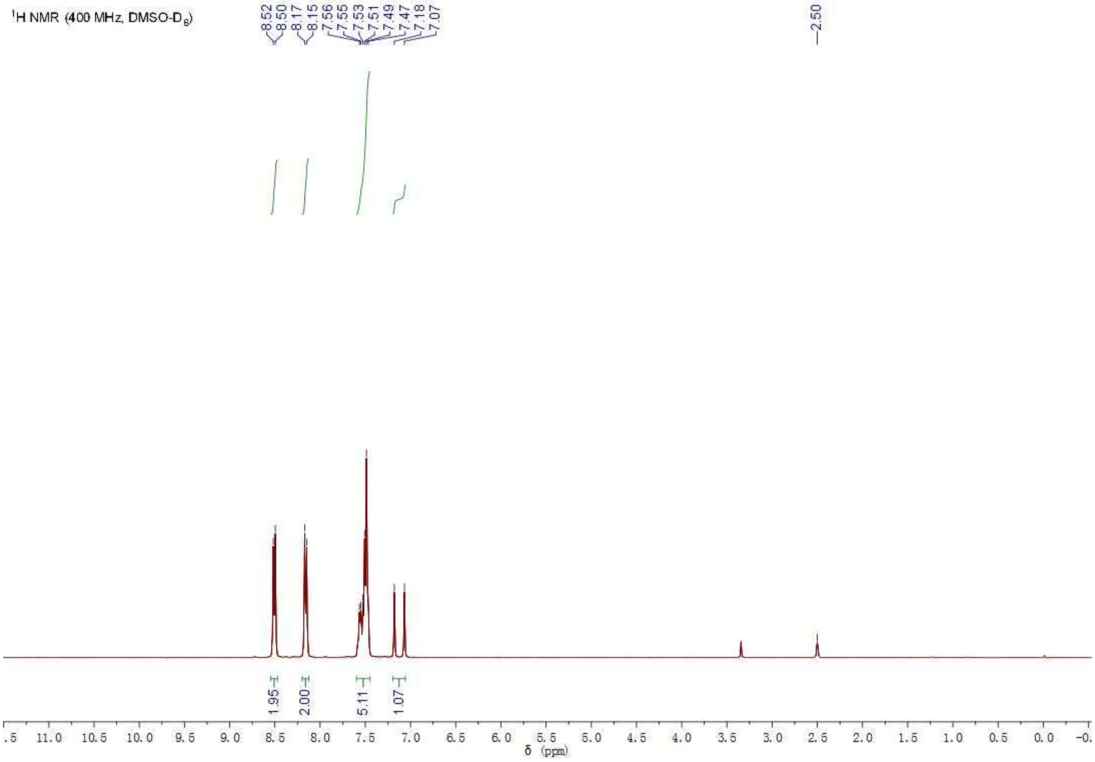

F
O
S
O
N
CH3

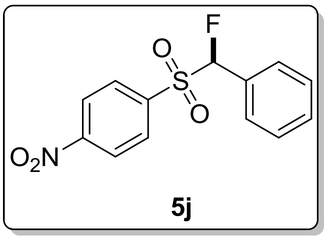
5i


^{13}C NMR (100 MHz, CDCl$_3$)
155.03
150.59
141.56
138.19
129.44
128.34
128.28
127.91
124.63
123.86
123.67
100.62
98.45
77.34
77.03
76.71
21.50
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

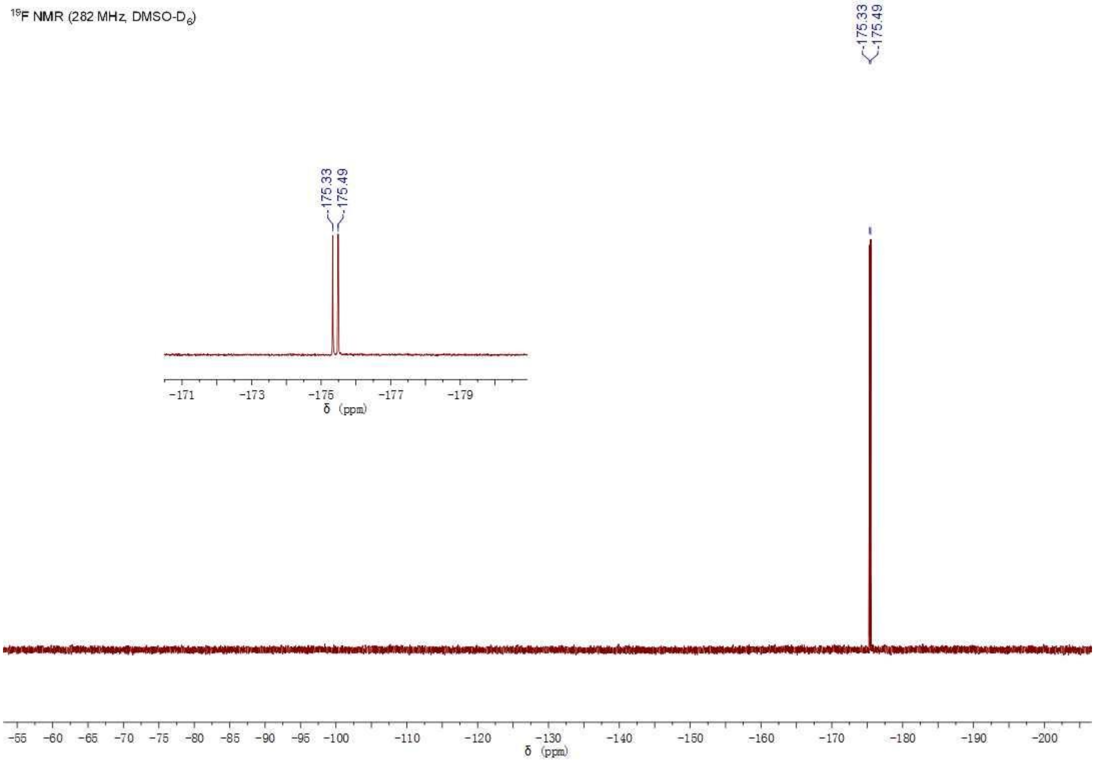

F
O
S
O
O2N

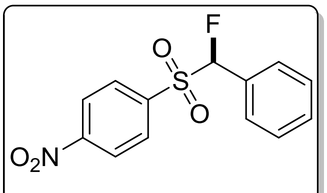
5j


1H NMR (400 MHz, DMSO-D6)
8.52
8.50
8.17
8.15
7.56
7.55
7.53
7.51
7.49
7.47
7.18
7.07
2.50
1.95
2.00
5.11
1.07
.5
11.0
10.5
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
0.0
-0.
δ (ppm)

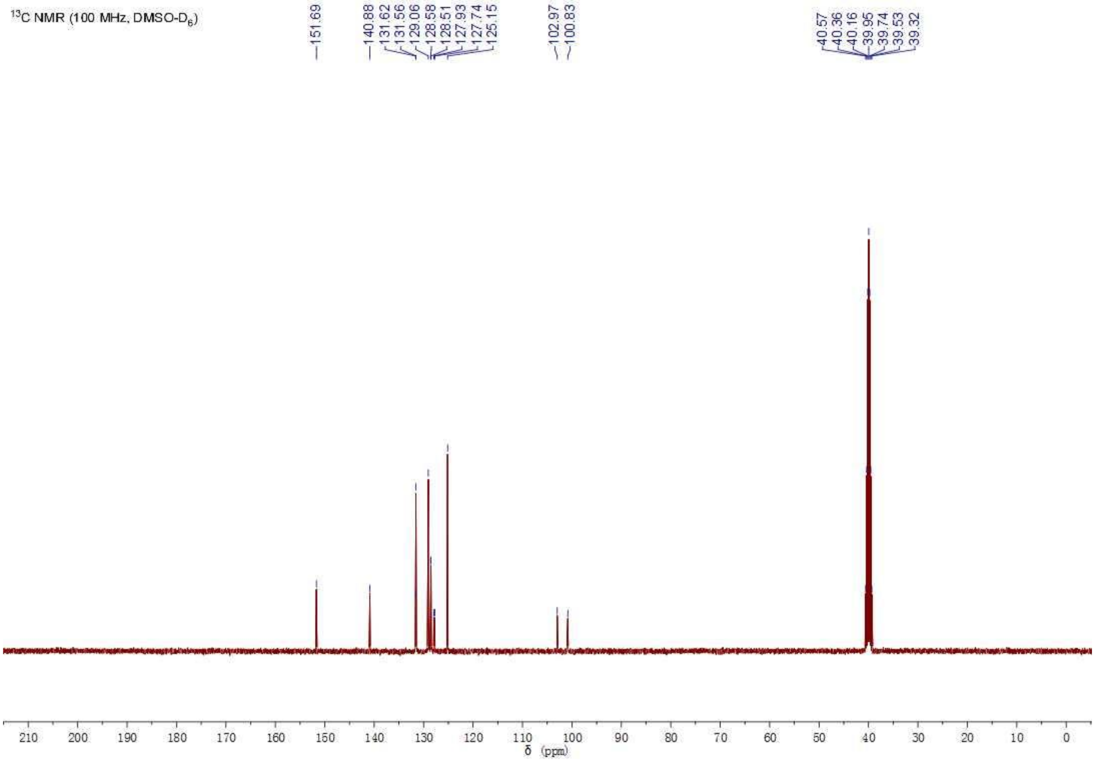


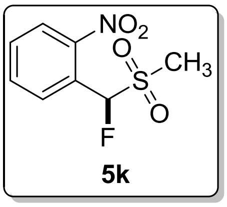
5j


^{19}F NMR (282 MHz, DMSO-D$_6$)
-175.33
-175.49
-171
-173
-175
-177
-179
δ (ppm)
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200

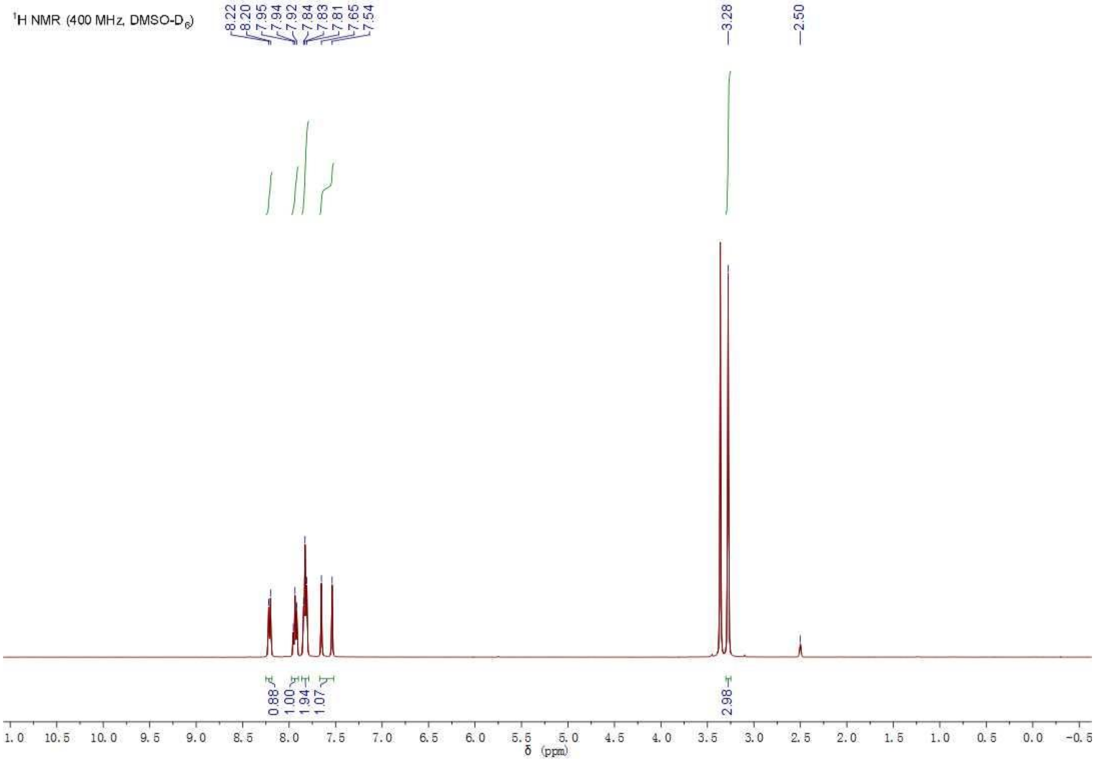

F
O
S
O
O2N

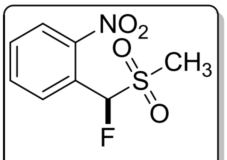
5j


^{13}C NMR (100 MHz, DMSO-D$_6$)
151.69
140.88
131.62
131.56
129.06
128.58
128.51
127.93
127.74
125.15
102.97
100.83
40.57
40.36
40.16
39.95
39.74
39.53
39.32
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

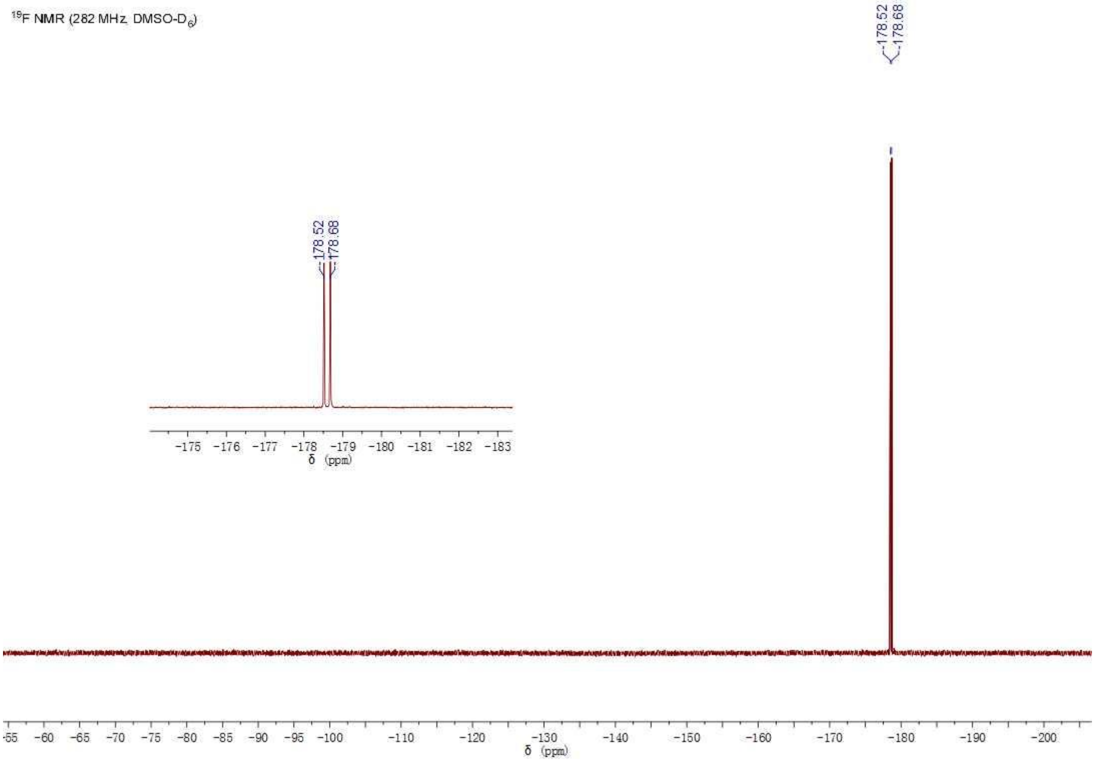

NO2
O
S
CH3
O
F

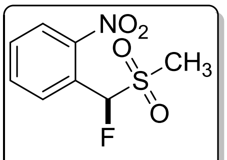
5k


¹H NMR (400 MHz, DMSO-D6)
8.22
8.20
7.95
7.94
7.92
7.84
7.83
7.81
7.65
7.54
3.28
2.50
0.88
1.00
1.94
1.07
2.98
1.0
10.5
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
0.0
-0.5
δ (ppm)

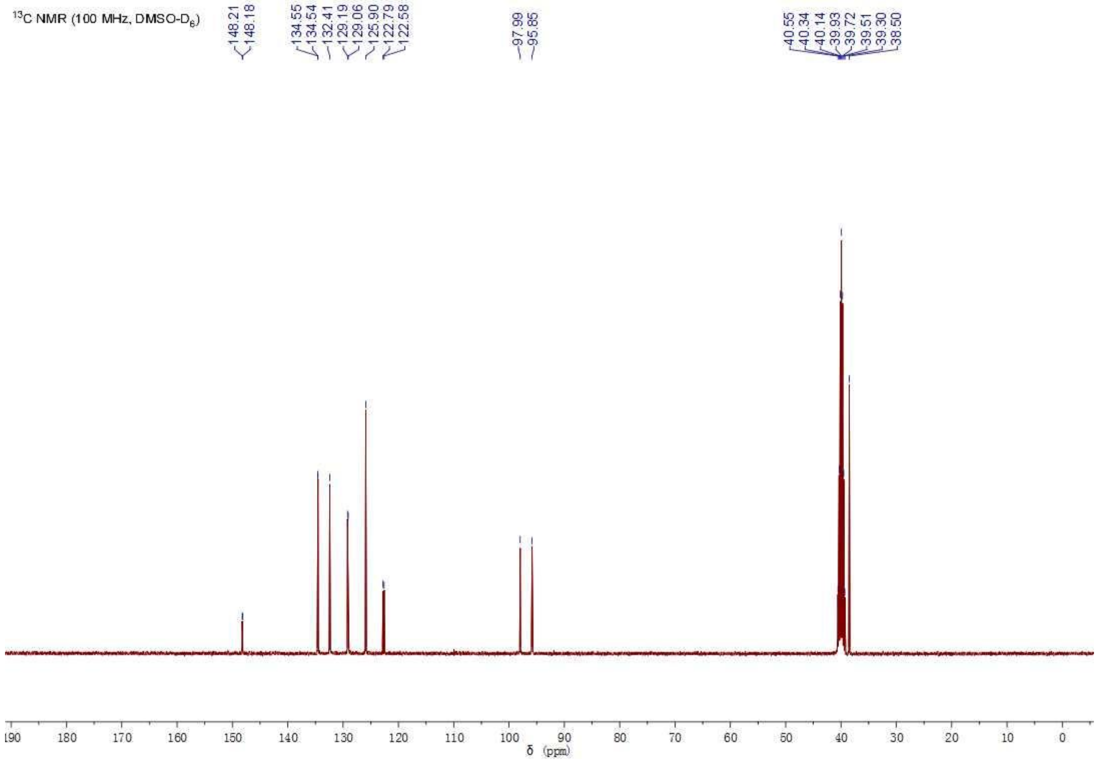

NO2
O
S
CH3
O
F

5k


^{19}F NMR (282 MHz, DMSO-D$_6$)
-178.52
-178.68
-178.52
-178.68
-175 -176 -177 -178 -179 -180 -181 -182 -183
δ (ppm)
55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
δ (ppm)


NO2
O
S
CH3
O
F

5k


13C NMR (100 MHz, DMSO-D6)
148.21
148.18
134.55
134.54
132.41
129.19
129.06
125.90
122.79
122.58
97.99
95.85
40.55
40.34
40.14
39.93
39.72
39.51
39.30
38.50
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)