

Supporting information

A Ligand assisted Manganese-enabled Direct C-H Difluoromethylation of Arenes

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1. Reagents

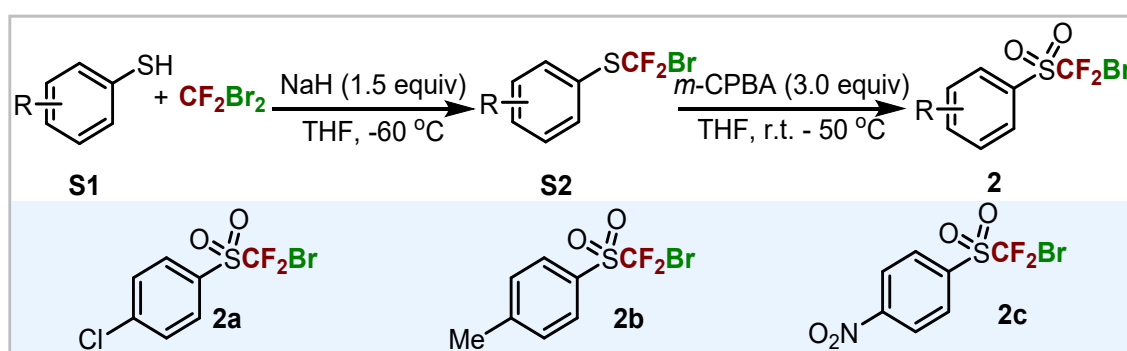
Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. Column chromatography purifications were performed using 200–300 mesh silica gel.

2. Instruments

NMR spectra were recorded on Varian Inova–400 MHz, Inova–300 MHz, Bruker DRX–400 or Bruker DRX–500 instruments and calibrated using residual solvent peaks as internal reference. Multiplicities are recorded as: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, t = triplet, m = multiplet. HRMS analysis were carried out using a Bruker microTOF–Q instrument or a TOF–MS instrument.

3. Preparation of starting materials

3.1 Synthesis of bromofluoromethyl reagents



2a, **2b** and **2c** was prepared according to reported methods.¹

Step 1: Thiophenol (**S1**, 20 mmol, 1.0 equiv.) diluted in THF (10 mL) was slowly added to a suspension of 60% NaH (30 mmol, 1.5 equiv.) in anhydrous THF (40 mL) at $0\text{ }^\circ\text{C}$ over a period of 30 minutes under nitrogen atmosphere. The mixture was cooled to $-60\text{ }^\circ\text{C}$ for 1 h, then CF_2Br_2 (60 mmol, 3.0 equiv.) diluted in THF (10 mL) was added portionwise, and stirred for 3 h at $-60\text{ }^\circ\text{C}$. Then the reaction mixture was slowly warmed to room temperature and stirred overnight. The reaction was cooled in an ice-water bath and the excess of NaH was quenched by dropwise addition of water. The aqueous phase was extracted with EtOAc (3 x 60 mL), the combined organic layers washed with water (3 x 60 mL), brine (100 mL), and dried over Na_2SO_4 . After the removal of the solvent under reduced pressure, the crude product was purified by flash column chromatography to give a colorless liquid of intermediate **S2**.

Step 2: To a solution of intermediate **S2** in DCM (40 mL) was slowly added *m*-CPBA (3.0 equiv.) at $0\text{ }^\circ\text{C}$, and the reaction was stirred at $50\text{ }^\circ\text{C}$ for 4 h. Then the reaction mixture was concentrated, dissolved in EtOAc (100 mL) and washed with 10 % NaOH (100 mL), saturated NaCl (100 mL) and dried over Na_2SO_4 . The solvent was removed in vacuo and the residue was by flash column chromatography to give target product **2**.

3.2 Synthesis of 2-((bromodifluoromethyl)sulfonyl)benzo[d]thiazole

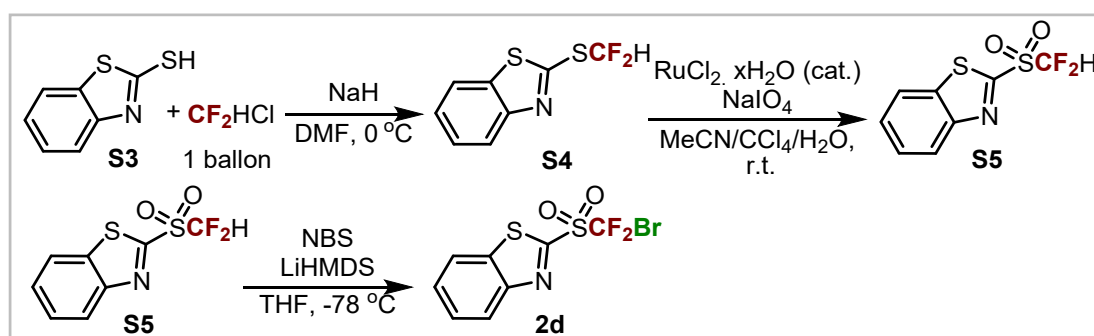
2d was prepared according to reported methods.²

Step 1: A dry flask was evacuated and backfilled with N_2 for 3 times. NaH (33 mol) followed by DMF (80 mL) was added at $0\text{ }^\circ\text{C}$. Then **S3** (30 mol, 1.0 equiv.) in DMF (20 mL) was added dropwise with

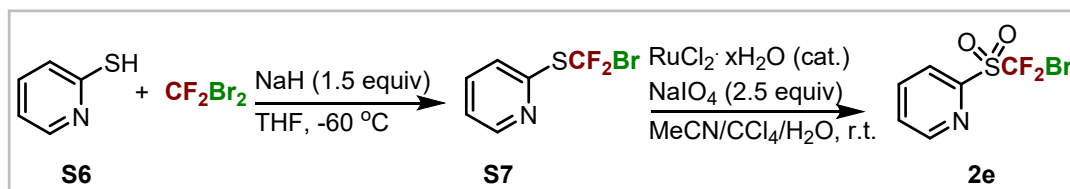
syringe at 0°C, and then the mixture was stirred at r. t. for 0.5 h. CHClF₂ gas was bubbled to the system for 1 h. The mixture was stirred at r. t for 12 h. After the reaction was complete, the mixture was quenched dropwise by H₂O at 0°C. The mixture was extracted with Et₂O for 3 times. Then the organic phase was combined and dried over anhydrous Na₂SO₄. The solvent was removed under vacuum and the residue was purified by flash column chromatography on silica gel to provide **S4**.

Step 2: To a flask add **S4** (20 mmol, 1.0 equiv.), MeCN (20 mL), CCl₄ (20 mL), H₂O (40 mL), and RuCl₃·xH₂O (5 mol%) were added. Then NaIO₄ (50 mol, 2.5 equiv.) was added. The mixture was stirred at r. t for 12 h. After the reaction was complete, the mixture was neutralized by saturated aq. NaHCO₃. After filtration, the filter residue was washed with EtOAc. The filtrate mixture was extracted with EtOAc for 3 times. Then the organic phase was combined and dried over anhydrous Na₂SO₄. The solvent was removed under vacuum and the residue was purified by flash column chromatography on silica gel to provide **S5**.

Step 3: Sulfone **S5** (5 mmol, 1.0 equiv.) and NBS (15 mmol, 3.0 equiv.) were added to a dry Schlenk tube. The flask was evacuated and backfilled with pure N₂ for 3 times. Then THF (20 mL) was added with syringe under N₂ atmosphere. The mixture was cooled to -78 °C, LiHMDS (1.0 M in THF, 15 mmol, 15 mL, 3.0 equiv.) was added with syringe under N₂ atmosphere in 15 min. The mixture was stirred at -78 °C for 3 h. After the reaction was complete, the mixture was quenched by saturated aq. NH₄Cl (10 mL). After the mixture was warmed to r. t., the aqueous layer was extracted with Et₂O for 3 times. Then the organic phase was combined and dried over anhydrous Na₂SO₄. The solvent was removed under vacuum and the residue was purified by flash column chromatography on silica gel to provide the 2-((bromodifluoromethyl)sulfonyl)benzo[*d*]thiazole **2d**.



3.3 Synthesis of difluoromethyl-2-pyridyl sulfone



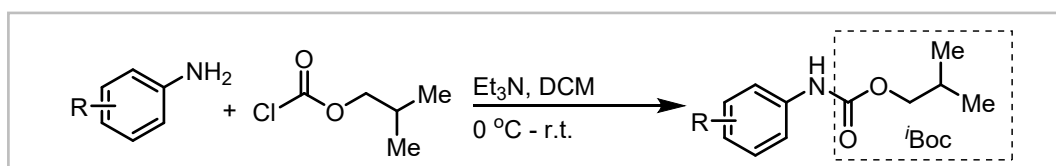
2e was prepared according to reported methods.^{1,2}

Step 1: Thiophenol (**S6**, 20 mmol, 1.0 equiv.) diluted in THF (10 mL) was slowly added to a suspension of 60% NaH (30 mmol, 1.5 equiv.) in anhydrous THF (40 mL) at 0 °C over a period of 30 minutes under nitrogen atmosphere. The mixture was cooled to -60 °C for 1 h, then CF₂Br₂ (60 mmol, 3.0 equiv.) diluted in THF (10 mL) was added portionwise, and stirred for 3 h at -60 °C. Then the reaction mixture was slowly warmed to room temperature and stirred overnight. The reaction was cooled in an ice water bath and the excess of NaH was quenched by dropwise addition of water. The aqueous phase was extracted with EtOAc (3 x 60 mL), the combined organic layers washed with water (3 x 60 mL), brine (100 mL),

and dried over Na₂SO₄. After the removal of the solvent under reduced pressure, the crude product was purified by flash column chromatography to give a colorless liquid of intermediate **S7**.

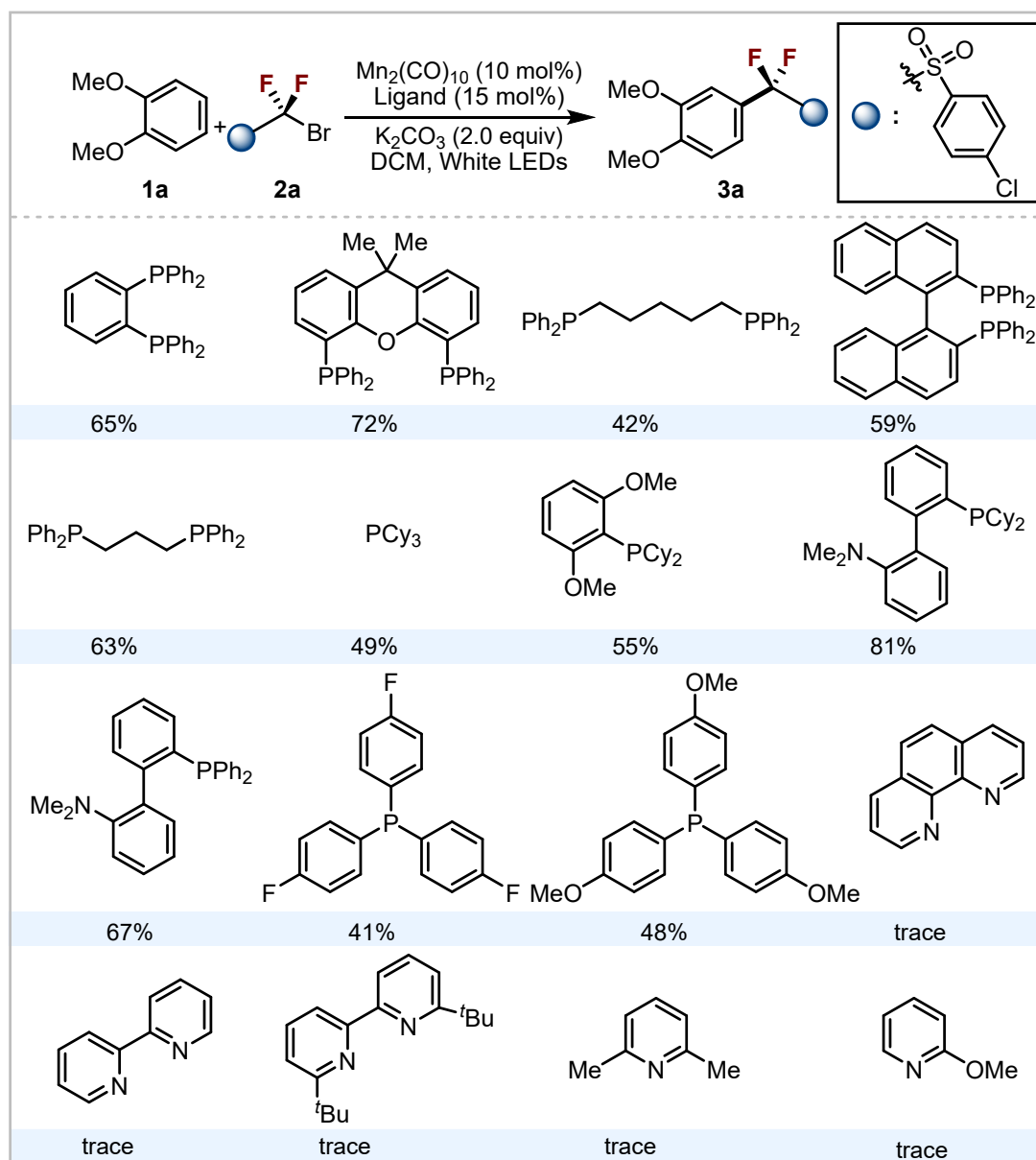
Step 2: To a flask **S7** (20 mmol, 1.0 equiv.), MeCN (20 mL), CCl₄ (20 mL), H₂O (40 mL), and RuCl₃·xH₂O (5 mol%) were added. Then NaIO₄ (50 mol, 2.5 equiv.) was added. The mixture was stirred at r. t for 12 h. After the reaction was complete, the mixture was neutralized by saturated aq. NaHCO₃. After filtration, the filter residue was washed with EtOAc. The filtrate mixture was extracted with EtOAc for 3 times. Then the organic phase was combined and dried over anhydrous Na₂SO₄. The solvent was removed under vacuum and the residue was purified by flash column chromatography on silica gel to provide target product.

3.4 Synthesis of *t*-Boc-protected anilines³



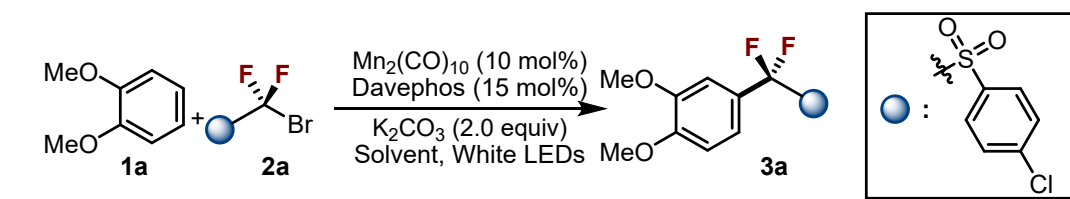
A solution of isobutyl chloroformate (2.2 mL, 1.7 equiv.) in 20 mL of DCM was cooled to 0 °C, and a solution of aniline (10 mmol) and triethylamine (1.8 mL, 1.3 equiv.) in 10 mL of DCM was added dropwise. The mixture was warmed to room temperature and stirred overnight. The mixture was extracted with EA (20 mL x 3), dried over anhydrous Na₂SO₄ and concentrated in vacuo. The residue was purified by column chromatography on silica gel to give the corresponding product as a white solid with >90% yield.

4. Screening of Ligand



^a Standard condition: **1a** (0.2 mmol), **2a** (0.6 mmol), $\text{Mn}_2(\text{CO})_{10}$ (10 mmol%), K_2CO_3 (2 equiv), Ligand (15 mmol%), DCE (2 mL), 40 °C, 36 h. ^b Yield were based on GC analysis using tridecane as an internal standard. **2a**: *p*-ClPhSO₂CF₂Br.

5. Screening of Solvent

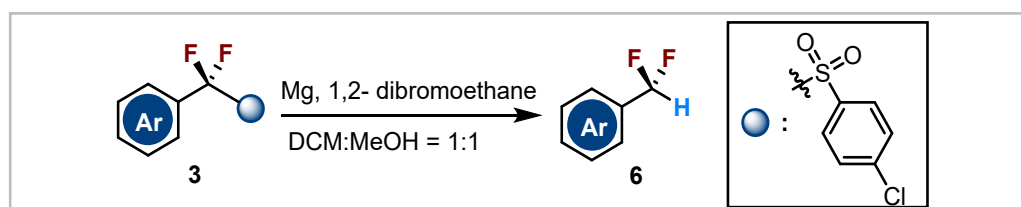


Entry	Solvent	Yield (%)
1	DCE	72
2	DCM	81
3	CCl_4	-
4	CHCl_3	65
5	MeCN	48
6	DMF	54
7	1,4-Dioxane	45
8	MeOH	51
9	MTBE	45

^a Standard condition: **1a** (0.2 mmol), **2a** (0.6 mmol), $\text{Mn}_2(\text{CO})_{10}$ (10 mmol%), K_2CO_3 (2 equiv), DavePhos (15 mmol%), Solvent (2 mL), 40 °C, 36 h. ^b Yield were based on GC analysis using tridecane as an internal standard. **2a**: $p\text{-ClPhSO}_2\text{CF}_2\text{Br}$.

6. Synthetic Application

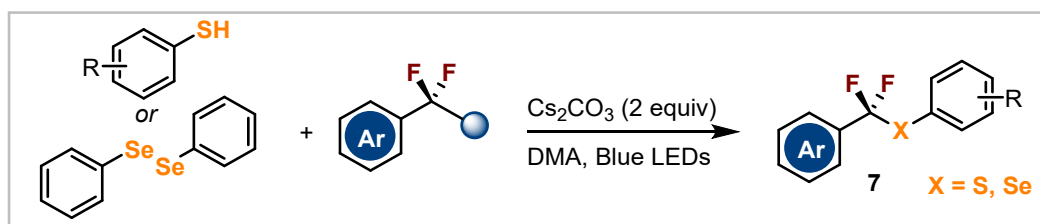
6.1 Reductive desulfonylation reaction ¹



A suspension of magnesium turnings (120 mg, 5 mmol) in MeOH (3 mL) was treated with dibromoethane (10 μL) in MeOH (3 mL), and the mixture was stirred for a few minutes until evolution of H_2 started. And then, the solution of **3** (0.2 mmol) in DCM (5 mL) was added dropwise, and the mixture was stirred for 3 h at r. t. The solvent was evaporated, and the residue was treated with saturated aqueous NH_4Cl , extracted with EA (10 mL) for 3 times. The organic layers was dried by anhydrous Na_2SO_4 . The solvent

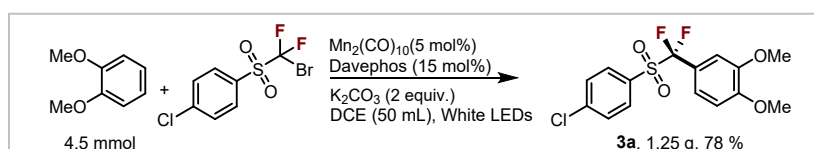
was evaporated, and the residue was purified by flash column chromatography to afford the corresponding product **6**.

6.2 Synthesis of aryldifluoromethyl ether ⁴

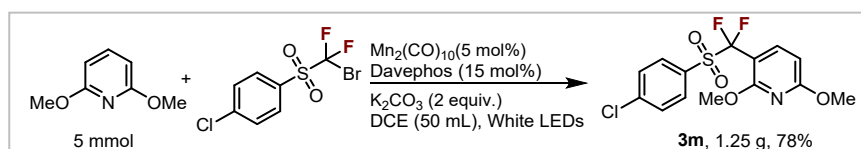


A mixture of **3** (0.24 mmol, 1.2 equiv), arylthiols or diphenyl diselenide (0.2 mmol), Cs_2CO_3 (2 equiv), DMA (2 mL) in a 15 mL glass vial sealed at r. t under Blue LEDs irradiation for 24 h. The reaction mixture cooled to room temperature and concentrated in vacuo. The resulting residue was purified by column chromatography on silica gel to give the product **7**.

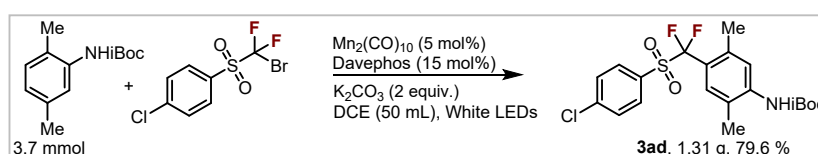
7. Gram-scale synthesis



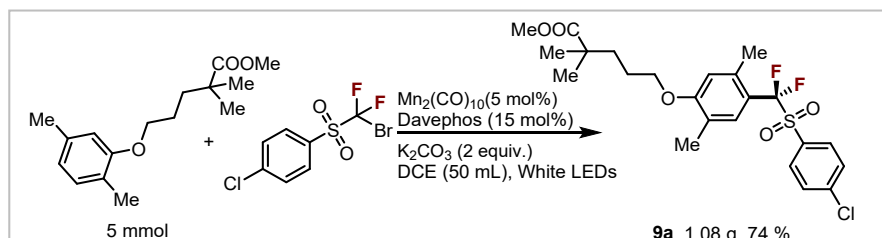
To an oven-dried 100 mL sealed flask, $\text{Mn}_2(\text{CO})_{10}$ (5 mol%), DavePhos (15 mol%), K_2CO_3 (2 equiv.), 1,2-dimethoxybenzene (5 mmol), 1-(bromodifluoromethyl)sulfonyl-4-chlorobenzene (3 equiv.), DCE (50 mL) were added and the flask was backfilled with nitrogen. The resulting reaction mixture was vigorously stirred under the irradiation of white LEDs (distance app. 4.0 cm from the bulb) at 40 °C for 48 h. After the reaction finished, the solvent was removed under vacuum, and the resulting residue was purified by flash column chromatography to afford the corresponding product in 1.25 g, 78% yield.



To an oven-dried 100 mL sealed flask, $\text{Mn}_2(\text{CO})_{10}$ (5 mol%), DavePhos (15 mol%), K_2CO_3 (2 equiv.), 2,6-dimethoxypyridine (5 mmol), 1-(bromodifluoromethyl)sulfonyl-4-chlorobenzene (3 equiv.), DCE (50 mL) were added and the flask was backfilled with nitrogen. The resulting reaction mixture was vigorously stirred under the irradiation of white LEDs (distance app. 4.0 cm from the bulb) at 40 °C for 48 h. After the reaction finished, the solvent was removed under vacuum, and the resulting residue was purified by flash column chromatography to afford the corresponding product in 1.25 g, 78% yield.

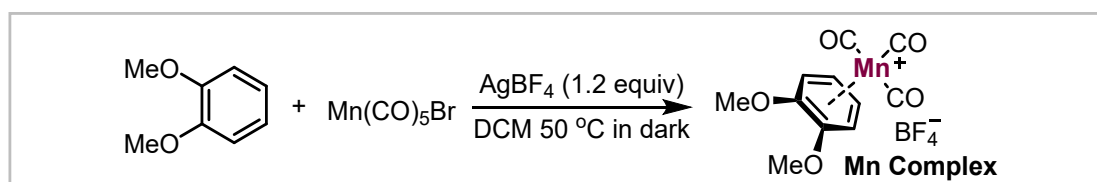


To an oven-dried 100 mL sealed flask, $\text{Mn}_2(\text{CO})_{10}$ (5 mol%), DavePhos (15 mol%), K_2CO_3 (2 equiv.), isobutyl (2,5-dimethylphenyl) carbamate (5 mmol), 1-((bromodifluoromethyl)sulfonyl)-4-chlorobenzene (3 equiv.), DCE (50 mL) were added and the flask was backfilled with nitrogen. The resulting reaction mixture was vigorously stirred under the irradiation of white LEDs (distance app. 4.0 cm from the bulb) at 40 °C for 48 h. After the reaction finished, the solvent was removed under vacuum, and the resulting residue was purified by flash column chromatography to afford the corresponding product in 1.31 g, 79.6 % yield.

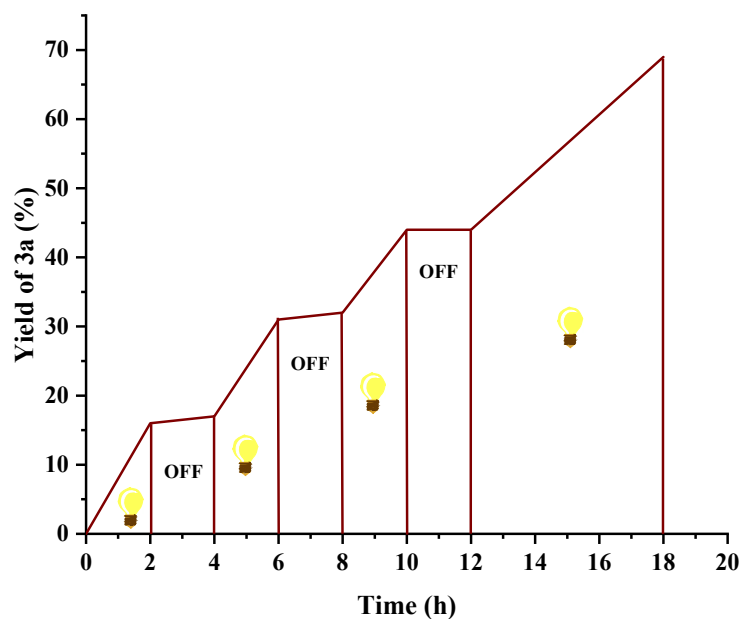


To an oven-dried 100 mL sealed flask, $\text{Mn}_2(\text{CO})_{10}$ (5 mol%), DavePhos (15 mol%), K_2CO_3 (2 equiv.), Gemfibrozil-ester (5 mmol), 1-((bromodifluoromethyl)sulfonyl)-4-chlorobenzene (3 equiv.), DCE (50 mL) were added and the flask was backfilled with nitrogen. The resulting reaction mixture was vigorously stirred under the irradiation of white LEDs (distance app. 4.0 cm from the bulb) at 40 °C for 48 h. After the reaction finished, the solvent was removed under vacuum, and the resulting residue was purified by flash column chromatography to afford the corresponding product in 1.08 g, 74 % yield.

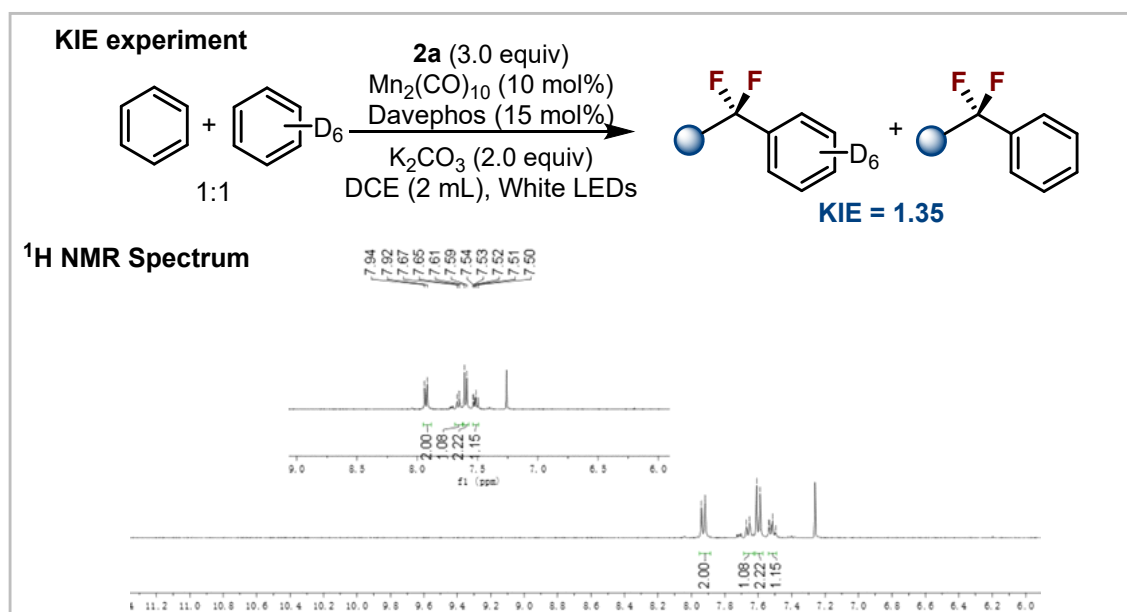
8. Synthesis of Mn complex ⁵



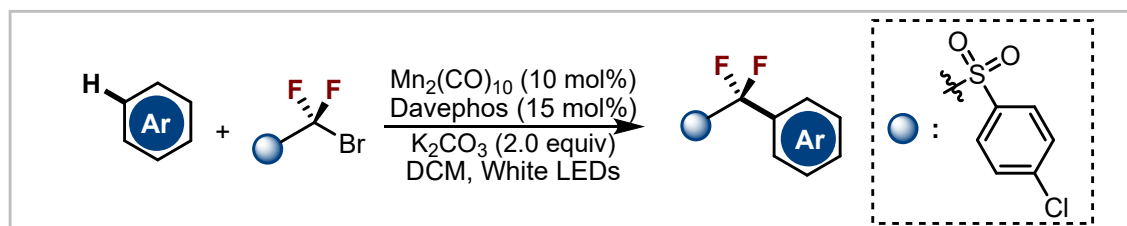
$[\text{Mn}(\text{CO})_3(1,2\text{-dimethoxybenzene})]\text{BF}_4$ was prepared by a modified procedure.⁵ $\text{Mn}(\text{CO})_5\text{Br}$ (1.0 g) and AgBF_4 (1.1 equiv) were dissolved in 50 mL of CH_2Cl_2 and refluxed for 2 h under N_2 in the dark. The 1,2-dimethoxybenzene (2 equiv) in 10 mL of CH_2Cl_2 was then added and the reaction mixture refluxed overnight. After it was cooled to room temperature, the solution was filtered through Celite and concentrated to ca. 20 mL in vacuo and the product precipitated with diethyl ether. The Yellow $[\text{Mn}(\text{CO})_3(1,2\text{-dimethoxybenzene})]\text{BF}_4$ salts were washed repeatedly with ether and dried in vacuo. Yellow solid.



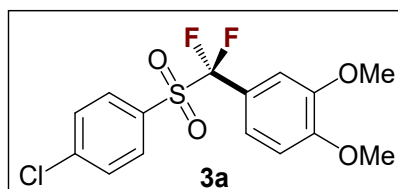
11. KIE experiments



12. General Procedure for difluoromethylation of arenes



A mixture of Arenes (**1**, 0.2 mmol), bromofluoromethyl reagent (**2**, 0.2 mmol), $\text{Mn}_2(\text{CO})_{10}$ (10 mol%), K_2CO_3 (0.4 mol, 2 equiv), DavePhos (15 mol%) and DCM (2 mL) in a 15 mL glass vial sealed was heated at 40 °C under white LEDs irradiation for 36 hours. The reaction mixture cooled to room temperature and concentrated in vacuo. The resulting residue was purified by column chromatography on silica gel to give the product.



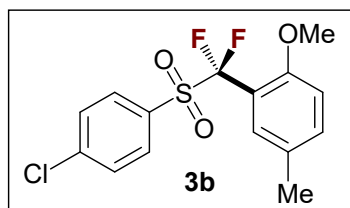
4-(((4-chlorophenyl)sulfonyl)difluoromethyl)-1,2-dimethoxybenzene, (3a), Yield: 81%

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.88 (d, $J = 8.5$ Hz, 2H), 7.54 (d, $J = 8.6$ Hz, 2H), 7.20 (dd, $J = 8.5, 1.8$ Hz, 1H), 7.06 (d, $J = 1.9$ Hz, 1H), 6.92 (d, $J = 8.5$ Hz, 1H), 3.87 (d, $J = 4.4$ Hz, 6H).

$^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -100.7.

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 152.5, 149.0, 142.2, 132.2, 131.4, 129.7, 122.0 (t, $J_{\text{C-F}} = 287.3$ Hz), 121.4 (t, $J_{\text{C-F}} = 6.5$ Hz), 117.9 (t, $J_{\text{C-F}} = 22.8$ Hz), 110.8, 110.2 (t, $J_{\text{C-F}} = 5.9$ Hz), 56.1, 56.0.

HRMS Calcd for $\text{C}_{15}\text{H}_{13}\text{ClF}_2\text{O}_4\text{S}$ [$\text{M}+\text{Na}^+$]: 385.0083; Found: 385.0075.



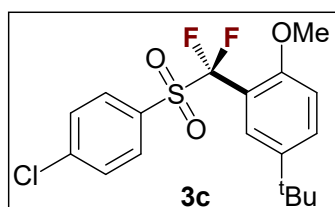
2-(((4-chlorophenyl)sulfonyl)difluoromethyl)-1-methoxy-4-methylbenzene, (3b), Yield: 59%

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.87 (d, $J = 8.6$ Hz, 2H), 7.55 (d, $J = 8.7$ Hz, 2H), 7.30 (d, $J = 7.9$ Hz, 2H), 6.85 (d, $J = 8.2$ Hz, 1H), 3.70 (s, 3H), 2.32 (s, 3H).

$^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -97.0.

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 156.7, 143.3, 142.0, 132.4, 132.3, 131.2, 129.4, 127.0 (t, $J_{\text{C-F}} = 7.8$ Hz), 122.7 (t, $J_{\text{C-F}} = 289.2$ Hz), 114.2 (t, $J_{\text{C-F}} = 20.1$ Hz), 112.4, 56.2, 34.3, 31.4.

HRMS Calcd for $\text{C}_{15}\text{H}_{13}\text{ClF}_2\text{O}_3\text{S}$ [$\text{M}+\text{Na}^+$]: 369.0134; Found: 369.0141.



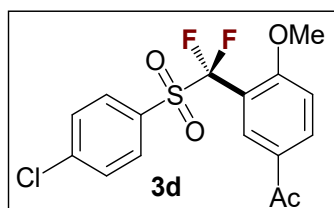
4-(tert-butyl)-2-(((4-chlorophenyl)sulfonyl)difluoromethyl)-1-methoxybenzene, (3c), Yield: 63%

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.85 (d, $J = 8.5$ Hz, 2H), 7.58 – 7.48 (m, 3H), 7.41 (d, $J = 2.5$ Hz, 1H), 6.90 (d, $J = 8.8$ Hz, 1H), 3.74 (s, 3H), 1.28 (s, 9H).

$^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -97.2.

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 156.7, 143.3, 142.0, 132.4, 132.3, 131.2, 129.5, 127.0 (t, $J_{\text{C-F}} = 7.8$ Hz), 122.7 (t, $J_{\text{C-F}} = 289.2$ Hz), 114.2 (t, $J_{\text{C-F}} = 20.1$ Hz), 112.4, 56.2, 34.3, 31.4.

HRMS Calcd for C₁₈H₁₉ClF₂O₃S [M+Na⁺]: 411.0604; Found: 411.0597.



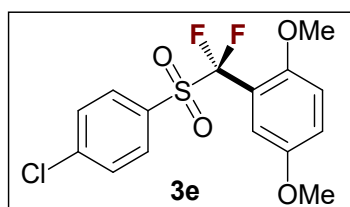
1-(3-(((4-chlorophenyl)sulfonyl)difluoromethyl)-4-methoxyphenyl)ethan-1-one, (3d), Yield: 48%

¹H NMR (400 MHz, CDCl₃) δ 8.15 (dd, *J* = 8.8, 2.2 Hz, 1H), 8.11 (d, *J* = 2.2 Hz, 1H), 7.90 (d, *J* = 8.6 Hz, 2H), 7.58 (d, *J* = 8.7 Hz, 2H), 7.04 (d, *J* = 8.8 Hz, 1H), 3.86 (s, 3H), 2.58 (s, 3H).

¹⁹F NMR (377 MHz, CDCl₃) δ -97.3.

¹³C NMR (101 MHz, CDCl₃) δ 195.6, 162.4, 142.4, 134.7, 132.3, 132.0, 131.3 (t, *J*_{C-F} = 7.9 Hz), 130.0, 129.7, 122.1 (t, *J*_{C-F} = 289.8 Hz), 115.1 (t, *J*_{C-F} = 21.1 Hz), 112.4, 56.5, 26.4.

HRMS Calcd for C₁₆H₁₃ClF₂O₄S [M+Na⁺]: 397.0083; Found: 397.0091.



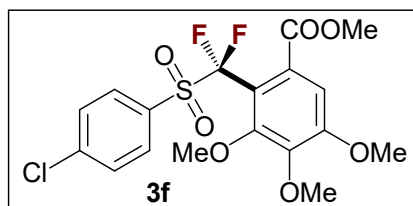
2-(((4-chlorophenyl)sulfonyl)difluoromethyl)-1,4-dimethoxybenzene, (3e), Yield: 51%

¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, *J* = 8.6 Hz, 2H), 7.55 (d, *J* = 8.7 Hz, 2H), 7.05 (dt, *J* = 5.0, 3.0 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 1H), 3.78 (s, 3H), 3.69 (s, 3H).

¹⁹F NMR (377 MHz, CDCl₃) δ -97.2.

¹³C NMR (101 MHz, CDCl₃) δ 153.3, 153.0 (t, *J*_{C-F} = 2.3 Hz), 142.1, 132.3, 132.3, 129.5, 122.3 (t, *J*_{C-F} = 290.5 Hz), 120.0, 115.5 (t, *J*_{C-F} = 20.6 Hz), 114.9 (t, *J*_{C-F} = 8.2 Hz), 114.3, 56.8, 56.0.

HRMS Calcd for C₁₅H₁₃ClF₂O₄S [M+Na⁺]: 385.0083; Found: 385.0085.



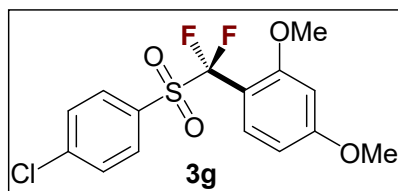
methyl 2-(((4-chlorophenyl)sulfonyl)difluoromethyl)-3,4,5-trimethoxybenzoate, (3f), Yield: 44%

¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, *J* = 8.6 Hz, 2H), 7.56 (d, *J* = 8.6 Hz, 2H), 6.77 (s, 1H), 3.91 (s, 3H), 3.90 (s, 3H), 3.86 (s, 3H), 3.85 (s, 3H).

¹⁹F NMR (377 MHz, CDCl₃) δ -87.0.

¹³C NMR (101 MHz, CDCl₃) δ 168.3, 156.6, 153.9 (t, *J*_{C-F} = 3.5 Hz), 143.9, 141.9, 133.5, 132.1, 130.1 (t, *J*_{C-F} = 4.0 Hz), 129.5, 122.9 (t, *J*_{C-F} = 292.2 Hz), 112.4 (t, *J*_{C-F} = 20.5 Hz), 107.5, 62.0, 61.0, 56.4, 53.0.

HRMS Calcd for C₁₈H₁₇ClF₂O₇S [M+Na⁺]: 473.0244; Found: 473.0252.



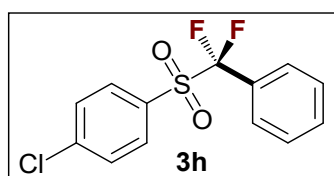
1-(((4-chlorophenyl)sulfonyl)difluoromethyl)-2,4-dimethoxybenzene, (3g), Yield: 70%

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.86 (d, $J = 8.5$ Hz, 2H), 7.54 (d, $J = 8.6$ Hz, 2H), 7.42 (d, $J = 8.8$ Hz, 1H), 6.55 (d, $J = 8.6$ Hz, 1H), 6.45 (s, 1H), 3.83 (s, 3H), 3.70 (s, 3H).

$^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -96.6.

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 164.6, 160.3, 141.9, 132.3, 131.6 (t, $J_{\text{C-F}} = 7.9$ Hz), 129.4, 122.8 (t, $J_{\text{C-F}} = 288.7$ Hz), 107.1 (t, $J_{\text{C-F}} = 21.3$ Hz), 105.1, 99.5, 56.0, 55.7.

HRMS Calcd for $\text{C}_{15}\text{H}_{13}\text{ClF}_2\text{O}_4\text{S}$ [$\text{M}+\text{Na}^+$]: 385.0083; Found: 385.0079.



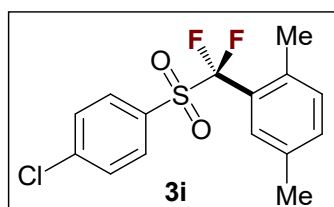
1-chloro-4-((difluoro(phenyl)methyl)sulfonyl)benzene, (3h), Yield: 43%

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.93 (d, $J = 8.7$ Hz, 2H), 7.66 (d, $J = 7.6$ Hz, 2H), 7.60 (d, $J = 8.7$ Hz, 3H), 7.51 (t, $J = 7.6$ Hz, 2H).

$^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -101.8.

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 142.5, 132.6, 132.3, 132.1, 131.2, 130.1, 130.0, 128.6, 127.8 (t, $J_{\text{C-F}} = 6.1$ Hz), 126.3 (t, $J_{\text{C-F}} = 22.0$ Hz), 121.8 (t, $J_{\text{C-F}} = 286.3$ Hz).

HRMS Calcd for $\text{C}_{13}\text{H}_9\text{ClF}_2\text{O}_2\text{S}$ [$\text{M}+\text{Na}^+$]: 324.9872; Found: 324.9879.



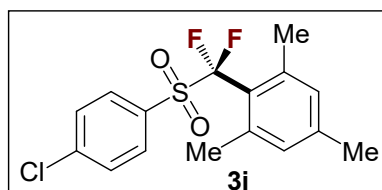
2-(((4-chlorophenyl)sulfonyl)difluoromethyl)-1,4-dimethylbenzene, (3i), Yield: 48%

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.97 (d, $J = 8.6$ Hz, 2H), 7.63 (d, $J = 8.6$ Hz, 2H), 7.35 (s, 1H), 7.28 (d, $J = 7.8$ Hz, 1H), 7.20 (d, $J = 7.8$ Hz, 1H), 2.56 (t, $J = 3.4$ Hz, 3H), 2.38 (s, 3H).

$^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -95.8.

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 156.9, 156.2, 156.2, 153.5, 153.1, 123.6, 117.1, 117.1, 113.9, 113.9, 56.7, 56.1.

HRMS Calcd for $\text{C}_{15}\text{H}_{13}\text{ClF}_2\text{O}_2\text{S}$ [$\text{M}+\text{Na}^+$]: 353.0185; Found: 353.0190.



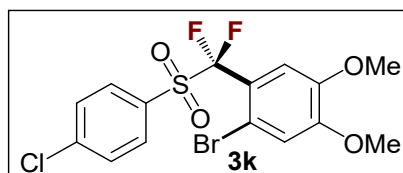
2-(((4-chlorophenyl)sulfonyl)difluoromethyl)-1,3,5-trimethylbenzene, (3j), Yield: 46%

¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, *J* = 8.6 Hz, 2H), 7.53 (d, *J* = 8.7 Hz, 2H), 6.87 (s, 2H), 2.48 (t, *J* = 5.0 Hz, 6H), 2.22 (s, 3H).

¹⁹F NMR (377 MHz, CDCl₃) δ -87.4.

¹³C NMR (101 MHz, CDCl₃) δ 142.3, 142.2, 140.8 (t, *J*_{C-F} = 3.1 Hz), 132.3, 131.9, 129.8, 125.3 (t, *J*_{C-F} = 290.1 Hz), 120.5 (t, *J*_{C-F} = 18.5 Hz), 22.5 (t, *J*_{C-F} = 6.6 Hz), 21.1.

HRMS Calcd for C₁₆H₁₅ClF₂O₂S [M+Na⁺]: 367.0342; Found: 367.0331 .



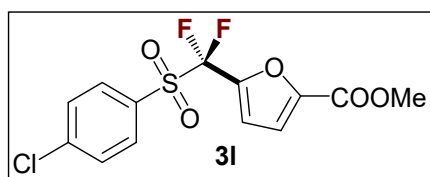
1-Bromo-2-(((4-chlorophenyl)sulfonyl)difluoromethyl)-4,5-dimethoxybenzene, (3k), Yield: 55%.

¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, *J* = 8.6 Hz, 2H), 7.62 (d, *J* = 8.6 Hz, 2H), 7.14 (s, 1H), 7.08 (s, 1H), 3.95 (s, 3H), 3.92 (s, 3H).

¹⁹F NMR (377 MHz, CDCl₃) δ -96.1.

¹³C NMR (101 MHz, CDCl₃) δ 152.4, 148.2, 142.6, 132.5, 131.5, 129.9, 121.6 (t, *J* = 288.5 Hz), 118.0, 117.5 (t, *J* = 21.4 Hz), 113.3 (t, *J* = 7.6 Hz), 56.5, 56.4.

HRMS Calcd for C₁₅H₁₂ClBrF₂O₄S [M+Na⁺]: 462.9194; Found: 462.9201.



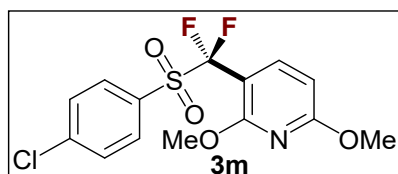
methyl 5-(((4-chlorophenyl)sulfonyl)difluoromethyl)furan-2-carboxylate, (3l), Yield: 86%

¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, *J* = 8.7 Hz, 2H), 7.67 – 7.48 (m, 2H), 7.26 – 7.14 (m, 1H), 7.00 (d, *J* = 3.7 Hz, 1H), 3.86 (s, 3H).

¹⁹F NMR (377 MHz, CDCl₃) δ -102.5.

¹³C NMR (101 MHz, CDCl₃) δ 158.1, 148.0, 143.2, 142.4 (t, *J* = 31.5 Hz), 132.4, 130.7, 130.1, 118.4, 117.2, 116.6 (t, *J*_{C-F} = 287.1 Hz), 52.6.

HRMS Calcd for C₁₄H₁₂F₂O₅S [M+Na⁺]: 353.0266; Found: 353.0270.



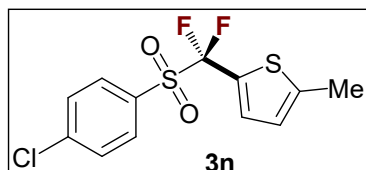
3-(((4-chlorophenyl)sulfonyl)difluoromethyl)-2,6-dimethoxypyridine, (3m), Yield: 85%

¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, *J* = 8.7 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.57 (d, *J* = 8.7 Hz, 2H), 6.39 (d, *J* = 8.4 Hz, 1H), 3.95 (s, 3H), 3.87 (s, 3H).

¹⁹F NMR (377 MHz, CDCl₃) δ -98.2.

^{13}C NMR (101 MHz, CDCl_3) δ 166.0, 161.6, 142.2, 141.9 (t, $J_{\text{C-F}} = 6.7$ Hz), 132.3, 132.1, 129.6, 122.2 (t, $J_{\text{C-F}} = 288.0$ Hz), 102.1, 99.9 (t, $J_{\text{C-F}} = 23.3$ Hz), 54.1, 54.0.

HRMS Calcd for $\text{C}_{14}\text{H}_{12}\text{ClF}_2\text{NO}_4\text{S}$ [$\text{M}+\text{Na}^+$]: 386.0036; Found: 386.0044.



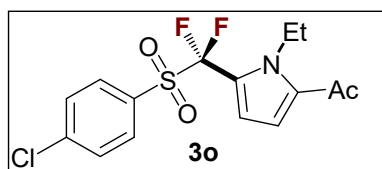
2-(((4-chlorophenyl)sulfonyl)difluoromethyl)-5-methylthiophene, (3n), Yield: 64%

^1H NMR (400 MHz, CDCl_3) δ 7.96 (d, $J = 8.6$ Hz, 2H), 7.62 (d, $J = 8.6$ Hz, 2H), 7.36 (d, $J = 3.7$ Hz, 1H), 6.85 (dd, $J = 2.3, 1.1$ Hz, 1H), 2.57 (d, $J = 0.9$ Hz, 3H).

^{19}F NMR (377 MHz, CDCl_3) δ -92.5.

^{13}C NMR (101 MHz, CDCl_3) δ 147.5, 142.5, 132.6 (t, $J_{\text{C-F}} = 5.4$ Hz), 132.4, 129.9, 120.7 (t, $J_{\text{C-F}} = 286.1$ Hz), 126.4, 123.6 (t, $J_{\text{C-F}} = 27.3$ Hz), 15.6.

HRMS Calcd for $\text{C}_{12}\text{H}_9\text{ClF}_2\text{O}_2\text{S}_2$ [$\text{M}+\text{Na}^+$]: 344.9593; Found: 344.9587.



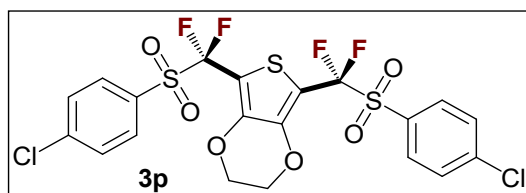
1-(5-(((4-Chlorophenyl)sulfonyl)difluoromethyl)-1-ethyl-1H-pyrrol-2-yl)ethan-1-one, (3o), Yield: 71%.

^1H NMR (400 MHz, CDCl_3) δ 7.88 (d, $J = 8.5$ Hz, 2H), 7.69 – 7.51 (m, 2H), 6.92 (d, $J = 4.2$ Hz, 1H), 6.51 (d, $J = 4.3$ Hz, 1H), 4.14 (s, 3H), 3.83 (s, 3H).

^{19}F NMR (377 MHz, CDCl_3) δ -96.4.

^{13}C NMR (101 MHz, CDCl_3) δ 161.1, 142.7, 132.2, 131.2, 129.9, 128.3, 123.3 (t, $J_{\text{C-F}} = 28.5$ Hz), 119.4 (t, $J_{\text{C-F}} = 286.4$ Hz), 116.9, 115.1 (t, $J_{\text{C-F}} = 5.2$ Hz), 51.7, 34.8.

HRMS (ESI) Calcd for $\text{C}_{15}\text{H}_{14}\text{ClF}_2\text{NO}_3\text{S}$ [$\text{M}+\text{Na}^+$]: 384.0249; Found: 384.0255.



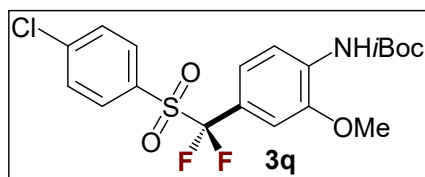
5,7-bis(((4-chlorophenyl)sulfonyl)difluoromethyl)-2,3-dihydrothieno[3,4-b][1,4]dioxine, (3p), Yield: 74%.

^1H NMR (400 MHz, CDCl_3) δ 8.00 – 7.88 (m, 4H), 7.69 – 7.54 (m, 4H), 4.28 (s, 4H).

^{19}F NMR (377 MHz, CDCl_3) δ -94.9.

^{13}C NMR (101 MHz, CDCl_3) δ 143.7, 142.9, 132.5, 131.0 (t, $J_{\text{C-F}} = 118.52$ Hz), 130.0, 120.1 (t, $J_{\text{C-F}} = 288.5$ Hz), 106.0 (t, $J_{\text{C-F}} = 29.8$ Hz), 64.7.

HRMS Calcd for $\text{C}_{20}\text{H}_{12}\text{Cl}_2\text{F}_4\text{O}_6\text{S}_3$ [$\text{M}+\text{Na}^+$]: 612.9001; Found: 612.9013.



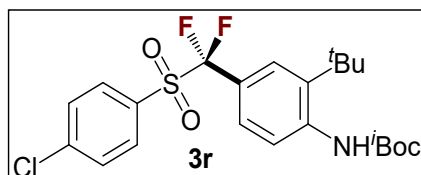
isobutyl 4-(((4-chlorophenyl)sulfonyl)difluoromethyl)-2-methoxyphenyl)carbamate, (3q), Yield: 75%

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.26 (d, $J = 8.4$ Hz, 1H), 7.91 (d, $J = 8.6$ Hz, 2H), 7.59 (d, $J = 8.7$ Hz, 2H), 7.40 (s, 1H), 7.22 (dd, $J = 8.6, 1.6$ Hz, 1H), 7.10 (d, $J = 1.7$ Hz, 1H), 3.98 (d, $J = 6.7$ Hz, 2H), 3.93 (s, 3H), 0.98 (d, $J = 6.7$ Hz, 6H).

$^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -101.0.

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 153.3, 147.1, 142.3, 132.2, 132.0, 131.4, 129.7, 121.5 (t, $J_{\text{C-F}} = 6.4$ Hz), 121.4 (t, $J_{\text{C-F}} = 287.4$ Hz), 119.5 (t, $J_{\text{C-F}} = 22.83$ Hz), 117.3, 109.0 (t, $J_{\text{C-F}} = 6.1$ Hz), 71.7, 56.0, 27.9, 19.1.

HRMS Calcd for $\text{C}_{19}\text{H}_{20}\text{ClF}_2\text{NO}_5\text{S}$ [$\text{M}+\text{Na}^+$]: 470.0611; Found: 470.0615.



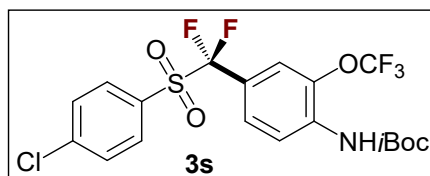
isobutyl (2-(tert-butyl)-4-(((4-chlorophenyl)sulfonyl)difluoromethyl)phenyl)carbamate, (3r), Yield: 64%

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.97 (dd, $J = 14.5, 8.4$ Hz, 1H), 7.90 (d, $J = 8.5$ Hz, 2H), 7.57 (d, $J = 8.6$ Hz, 2H), 7.52 (d, $J = 9.1$ Hz, 2H), 6.83 (s, 1H), 3.98 (d, $J = 6.7$ Hz, 2H), 2.07 – 1.93 (m, 1H), 1.43 (s, 9H), 0.96 (d, $J = 6.7$ Hz, 6H).

$^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -101.4.

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 153.7, 142.4, 140.1, 132.4, 131.6, 129.8, 126.8 (t, $J_{\text{C-F}} = 6.0$ Hz), 126.2 (t, $J_{\text{C-F}} = 6.1$ Hz), 122.1 (t, $J_{\text{C-F}} = 287.34$ Hz), 121.6 (t, $J_{\text{C-F}} = 22.1$ Hz), 71.9, 34.6, 30.5, 28.1, 19.1.

HRMS Calcd for $\text{C}_{22}\text{H}_{26}\text{ClF}_2\text{NO}_4\text{S}$ [$\text{M}+\text{Na}^+$]: 496.1131; Found: 496.1139.



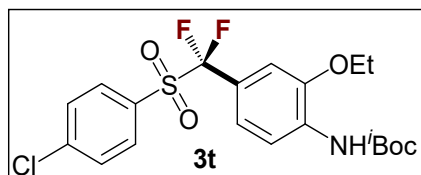
Isobutyl 4-(((4-chlorophenyl)sulfonyl)difluoromethyl)-2-(trifluoromethoxy)phenyl)carbamate, (3s), Yield: 67%

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.45 (d, $J = 8.8$ Hz, 1H), 7.92 (d, $J = 8.6$ Hz, 2H), 7.66 – 7.56 (m, 3H), 7.51 (s, 1H), 7.12 (s, 1H), 4.01 (d, $J = 6.7$ Hz, 2H), 2.02 (dp, $J = 13.4, 6.7$ Hz, 1H), 0.99 (d, $J = 6.7$ Hz, 6H).

$^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -57.7, -101.6.

^{13}C NMR (101 MHz, CDCl_3) δ 152.9, 142.8, 137.0, 135.1, 132.4, 131.1, 130.0, 127.6 (t, $J_{\text{C-F}} = 6.0$ Hz), 120.6 (t, $J_{\text{C-F}} = 23.6$ Hz), 120.3 (t, $J_{\text{C-F}} = 5.6$ Hz), 119.8, 72.4, 28.0, 19.1.

HRMS Calcd for $\text{C}_{19}\text{H}_{17}\text{ClF}_5\text{NO}_5\text{S}$ [$\text{M}+\text{Na}^+$]: 524.0328; Found: 524.0340.



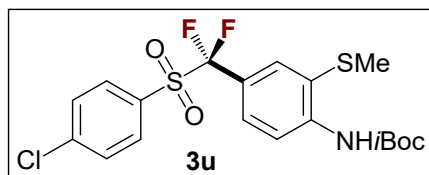
Isobutyl (4-(((4-chlorophenyl)sulfonyl)difluoromethyl)-2-ethoxyphenyl)carbamate, (3t), Yield: 48%.

^1H NMR (400 MHz, CDCl_3) δ 8.24 (s, 1H), 7.90 (d, $J = 7.0$ Hz, 2H), 7.58 (d, $J = 7.2$ Hz, 2H), 7.39 (s, 1H), 7.20 (d, $J = 7.5$ Hz, 1H), 7.08 (s, 1H), 4.16 (d, $J = 6.1$ Hz, 2H), 3.98 (d, $J = 5.2$ Hz, 2H), 2.02 (d, $J = 8.7$ Hz, 1H), 1.48 (s, 3H), 0.98 (d, $J = 5.5$ Hz, 6H).

^{19}F NMR (377 MHz, CDCl_3) δ -101.1.

^{13}C NMR (101 MHz, CDCl_3) δ 153.4, 146.5, 142.4, 132.3, 132.1, 131.5, 129.8, 121.3 (t, $J_{\text{C-F}} = 6.4$ Hz), 119.6 (t, $J_{\text{C-F}} = 22.7$ Hz), 117.4, 110.0 (t, $J_{\text{C-F}} = 6.1$ Hz), 71.8, 64.8, 28.1, 19.2, 14.7.

HRMS (ESI) Calcd for $\text{C}_{20}\text{H}_{22}\text{ClF}_2\text{NO}_5\text{S}$ [$\text{M}+\text{Na}^+$]: 484.0773; Found: 484.0781.



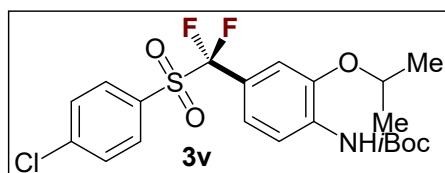
isobutyl (4-(((4-chlorophenyl)sulfonyl)difluoromethyl)-2-(methylthio)phenyl)carbamate, (3u), Yield: 43%.

^1H NMR (400 MHz, CDCl_3) δ 8.33 (d, $J = 8.7$ Hz, 1H), 7.93 (d, $J = 8.6$ Hz, 3H), 7.75 (d, $J = 1.9$ Hz, 1H), 7.60 (d, $J = 8.6$ Hz, 2H), 7.56 (dd, $J = 8.8, 1.9$ Hz, 1H), 4.00 (d, $J = 6.7$ Hz, 2H), 2.41 (s, 3H), 2.07-1.97 (m, $J = 13.4, 6.7$ Hz, 1H), 0.99 (d, $J = 6.7$ Hz, 6H).

^{19}F NMR (377 MHz, CDCl_3) δ -101.5.

^{13}C NMR (101 MHz, CDCl_3) δ 153.4, 142.7, 142.6, 132.8 (t, $J_{\text{C-F}} = 6.0$ Hz), 132.4, 131.4, 129.9, 128.9 (t, $J_{\text{C-F}} = 5.9$ Hz), 124.8, 121.6 (t, $J_{\text{C-F}} = 287.7$ Hz), 120.5 (t, $J_{\text{C-F}} = 23.0$ Hz), 118.2, 72.0, 28.1, 19.2, 19.1.

HRMS Calcd for $\text{C}_{19}\text{H}_{20}\text{ClF}_2\text{NO}_4\text{S}_2$ [$\text{M}+\text{Na}^+$]: 486.0383; Found: 486.0393.

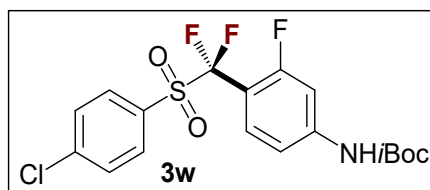


isobutyl (4-(((4-chlorophenyl)sulfonyl)difluoromethyl)-2-isopropoxyphenyl)carbamate, (3v), Yield: 61%.

^1H NMR (400 MHz, CDCl_3) δ 8.25 (d, $J = 8.2$ Hz, 1H), 7.90 (d, $J = 8.5$ Hz, 2H), 7.58 (d, $J = 8.6$ Hz, 2H), 7.38 (s, 1H), 7.18 (d, $J = 8.6$ Hz, 1H), 7.10 (d, $J = 1.5$ Hz, 1H), 4.66 (dt, $J = 12.1, 6.1$ Hz, 1H), 3.98 (d, $J = 6.7$ Hz, 2H), 2.01 (dp, $J = 13.4, 6.7$ Hz, 1H), 1.40 (d, $J = 6.1$ Hz, 6H), 0.98 (d, $J = 6.7$ Hz, 6H).

^{19}F NMR (377 MHz, CDCl_3) δ -101.2.

^{13}C NMR (101 MHz, CDCl_3) δ 153.4, 145.3, 142.4, 132.3, 131.5, 129.8, 122.0 (t, $J_{\text{C-F}} = 287.5$ Hz), 121.1 (t, $J_{\text{C-F}} = 6.4$ Hz), 119.5 (t, $J_{\text{C-F}} = 22.7$ Hz), 117.6, 111.5 (t, $J_{\text{C-F}} = 6.0$ Hz), 71.9, 71.8, 28.1, 22.0, 19.2.
HRMS Calcd for $\text{C}_{21}\text{H}_{24}\text{ClF}_2\text{NO}_5\text{S}$ [$\text{M}+\text{Na}^+$]: 498.0924; Found: 498.0933.



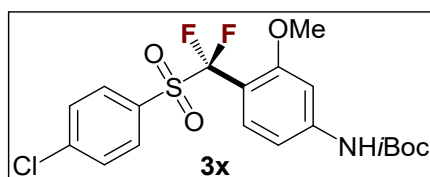
isobutyl 4-(((4-chlorophenyl)sulfonyl)difluoromethyl)-3-fluorophenylcarbamate, (**3w**), Yield: 49%

^1H NMR (400 MHz, CDCl_3) δ 7.94 (d, $J = 8.6$ Hz, 2H), 7.60 (d, $J = 8.6$ Hz, 2H), 7.48 (dd, $J = 19.8, 11.3$ Hz, 2H), 7.15 (d, $J = 8.6$ Hz, 1H), 7.08 (s, 1H), 3.98 (d, $J = 6.6$ Hz, 2H), 1.94 - 2.01 (m, 1H), 0.96 (d, $J = 6.7$ Hz, 6H).

^{19}F NMR (377 MHz, CDCl_3) δ -99.0 (d, $J_{\text{C-F}} = 22.7$ Hz), -108.6 (d, $J_{\text{C-F}} = -6.11$ Hz).

^{13}C NMR (101 MHz, CDCl_3) δ 161.5 (d, $J_{\text{C-F}} = 257.2$ Hz), 153.1, 144.4 (d, $J_{\text{C-F}} = 11.6$ Hz), 142.7, 132.4, 131.2, 130.7 (t, $J_{\text{C-F}} = 6.8$ Hz), 129.9, 121.4 (t, $J_{\text{C-F}} = 289.9$ Hz), 113.5 (d, $J_{\text{C-F}} = 2.8$ Hz), 106.6 (d, $J_{\text{C-F}} = 27.2$ Hz), 72.1, 28.0, 19.1.

HRMS Calcd for $\text{C}_{18}\text{H}_{17}\text{ClF}_3\text{NO}_4\text{S}$ [$\text{M}+\text{Na}^+$]: 458.0411; Found: 458.0420.



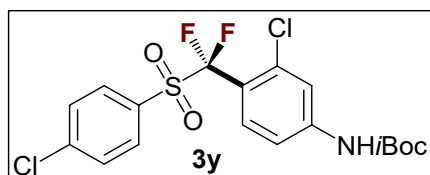
isobutyl 4-(((4-chlorophenyl)sulfonyl)difluoromethyl)-3-methoxyphenylcarbamate, (**3x**), Yield: 65%

^1H NMR (400 MHz, CDCl_3) δ 7.87 (d, $J = 8.6$ Hz, 2H), 7.55 (d, $J = 8.7$ Hz, 2H), 7.39 (d, $J = 8.5$ Hz, 2H), 7.00 (s, 1H), 6.81 (dd, $J = 8.6, 1.8$ Hz, 1H), 3.96 (d, $J = 6.7$ Hz, 2H), 3.70 (s, 3H), 2.06 - 1.84 (m, 1H), 0.96 (d, $J = 6.7$ Hz, 6H).

^{19}F NMR (377 MHz, CDCl_3) δ -97.0.

^{13}C NMR (101 MHz, CDCl_3) δ 159.9, 153.4, 143.9, 142.1, 132.4, 132.3, 130.9 (t, $J_{\text{C-F}} = 7.9$ Hz), 129.5, 122.6 (t, $J_{\text{C-F}} = 288.7$ Hz), 109.8, 108.8 (t, $J_{\text{C-F}} = 21.3$ Hz), 102.1, 71.9, 56.0, 28.0, 19.1.

HRMS Calcd for $\text{C}_{19}\text{H}_{20}\text{ClF}_2\text{NO}_5\text{S}$ [$\text{M}+\text{Na}^+$]: 470.0611; Found: 470.0613.



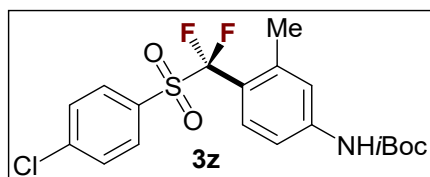
isobutyl 3-chloro-4-(((4-chlorophenyl)sulfonyl)difluoromethyl)phenylcarbamate, (**3y**), Yield: 44%

^1H NMR (400 MHz, CDCl_3) δ 7.93 (d, $J = 8.6$ Hz, 2H), 7.69 - 7.53 (m, 4H), 7.39 (d, $J = 8.8$ Hz, 1H), 6.92 (s, 1H), 3.98 (d, $J = 6.6$ Hz, 2H), 2.05 - 1.92 (m, 1H), 0.97 (d, $J = 6.7$ Hz, 6H).

^{19}F NMR (377 MHz, CDCl_3) δ -96.5.

^{13}C NMR (101 MHz, CDCl_3) δ 153.0, 142.8, 142.6, 135.0, 132.3, 131.9 (t, $J_{\text{C-F}} = 7.7$ Hz), 131.4, 129.8, 121.6 (t, $J_{\text{C-F}} = 290.3$ Hz), 120.8, 118.1 (t, $J_{\text{C-F}} = 21.5$ Hz), 115.9, 72.0, 27.9, 19.0.

HRMS Calcd for C₁₈H₁₇Cl₂F₂NO₄S [M+Na⁺]: 474.0116; Found: 474.0129.



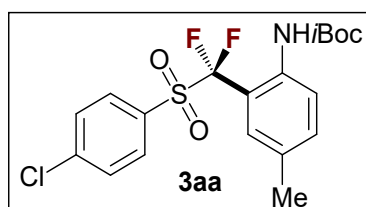
Isobutyl (4-(((4-chlorophenyl)sulfonyl)difluoromethyl)-3-methylphenyl)carbamate, (3z), Yield: 44%.

¹H NMR (400 MHz, CDCl₃) δ 7.93 (d, *J* = 8.6 Hz, 2H), 7.63 – 7.54 (m, 2H), 7.43 (d, *J* = 9.0 Hz, 1H), 7.33 (d, *J* = 7.9 Hz, 2H), 6.90 (s, 1H), 3.97 (d, *J* = 6.6 Hz, 2H), 2.54 (t, *J* = 3.2 Hz, 3H), 1.98 (m, 1.93-2.03, 1H), 0.96 (d, *J* = 6.7 Hz, 6H).

¹⁹F NMR (377 MHz, CDCl₃) δ -95.5.

¹³C NMR (101 MHz, CDCl₃) δ 153.4, 142.4, 141.9, 140.7, 132.3, 131.7, 130.9 (t, *J*_{C-F} = 8.3 Hz), 129.8, 123.5 (t, *J*_{C-F} = 291.6 Hz), 121.5, 118.6 (t, *J*_{C-F} = 20.7 Hz), 115.4, 71.8, 28.0, 21.0, 19.1.

HRMS Calcd for C₁₉H₂₀ClF₂NO₄S [M+Na⁺]: 454.0662; Found: 454.0671.



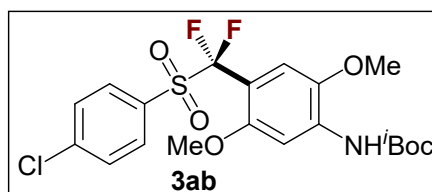
isobutyl (2-(((4-chlorophenyl)sulfonyl)difluoromethyl)-4-methylphenyl)carbamate, (3aa), Yield: 58%.

¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, *J* = 8.5 Hz, 2H), 7.85 (dd, *J* = 7.7, 4.6 Hz, 1H), 7.65 (s, 1H), 7.61 (d, *J* = 8.7 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 1H), 3.96 (d, *J* = 6.7 Hz, 2H), 2.33 (s, 3H), 2.07 – 1.92 (m, 1H), 0.97 (d, *J* = 6.7 Hz, 6H).

¹⁹F NMR (377 MHz, CDCl₃) δ -99.1.

¹³C NMR (101 MHz, CDCl₃) δ 154.3, 143.0, 135.0, 134.4, 134.3, 132.3, 130.8, 130.0, 129.5 (t, *J*_{C-F} = 8.2 Hz), 122.5 (t, *J*_{C-F} = 288.3 Hz), 71.7, 28.1, 20.8, 19.1.

HRMS Calcd for C₁₉H₂₀ClF₂NO₄S [M+Na⁺]: 454.0662; Found: 454.0650.



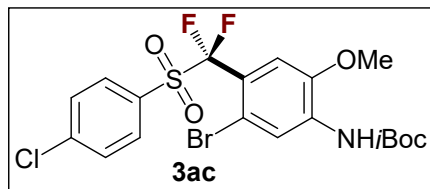
Isobutyl (4-(((4-chlorophenyl)sulfonyl)difluoromethyl)-2,5-dimethoxyphenyl)carbamate, (3ab), Yield: 80%.

¹H NMR (400 MHz, CDCl₃) δ 7.92 (s, 1H), 7.83 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 8.6 Hz, 2H), 7.42 (s, 1H), 6.91 (s, 1H), 3.95 (d, *J* = 6.7 Hz, 2H), 3.84 (s, 3H), 3.65 (s, 3H), 2.11 – 1.87 (m, 1H), 0.96 (d, *J* = 6.8 Hz, 6H).

¹⁹F NMR (377 MHz, CDCl₃) δ -96.9.

^{13}C NMR (101 MHz, CDCl_3) δ 153.9, 153.4, 141.9, 140.9, 133.2, 132.4, 132.3, 129.4, 122.5 (t, $J_{\text{C-F}} = 288.9$ Hz), 110.8 (t, $J_{\text{C-F}} = 8.1$ Hz), 106.8 (t, $J_{\text{C-F}} = 21.3$ Hz), 102.9, 71.8, 56.5, 56.4, 28.0, 19.1.

HRMS (ESI) Calcd for $\text{C}_{20}\text{H}_{22}\text{ClF}_2\text{NO}_6\text{S}$ [$\text{M}+\text{Na}^+$]: 500.0722; Found: 500.0709.



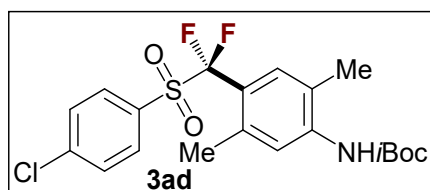
isobutyl (5-bromo-4-(((4-chlorophenyl)sulfonyl)difluoromethyl)-2-methoxyphenyl)carbamate, (3ac), Yield: 48%.

^1H NMR (400 MHz, CDCl_3) δ 8.50 (s, 1H), 7.91 (d, $J = 8.5$ Hz, 2H), 7.59 (d, $J = 8.6$ Hz, 2H), 7.34 (s, 1H), 7.07 (s, 1H), 3.99 (d, $J = 6.7$ Hz, 2H), 3.92 (s, 3H), 2.09 – 1.90 (m, 1H), 0.98 (d, $J = 6.7$ Hz, 6H).

^{19}F NMR (377 MHz, CDCl_3) δ -96.3.

^{13}C NMR (101 MHz, CDCl_3) δ 153.1, 146.1, 142.7, 132.5, 131.5, 129.9, 123.8, 118.8 (t, $J_{\text{C-F}} = 21.4$ Hz), 113.8 (t, $J_{\text{C-F}} = 2.4$ Hz), 112.1 (t, $J_{\text{C-F}} = 8.0$ Hz), 72.1, 56.3, 28.0, 19.2.

HRMS Calcd for $\text{C}_{19}\text{H}_{19}\text{BrClF}_2\text{NO}_5\text{S}$ [$\text{M}+\text{Na}^+$]: 547.9716 ; Found: 547.9717.



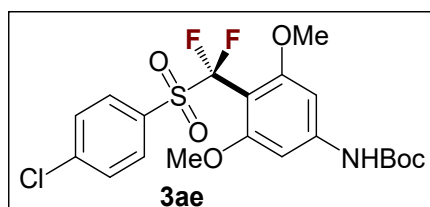
isobutyl (4-(((4-chlorophenyl)sulfonyl)difluoromethyl)-2,5-dimethylphenyl)carbamate, (3ad), Yield: 73%.

^1H NMR (400 MHz, CDCl_3) δ 7.95 (s, 1H), 7.93 (d, $J = 8.6$ Hz, 2H), 7.58 (d, $J = 8.6$ Hz, 2H), 7.30 (s, 1H), 6.58 (s, 1H), 3.97 (d, $J = 6.7$ Hz, 3H), 2.52 (t, $J = 3.2$ Hz, 4H), 2.23 (s, 4H), 2.11 – 1.89 (m, 2H), 0.97 (d, $J = 6.7$ Hz, 9H).

^{19}F NMR (377 MHz, CDCl_3) δ -95.4.

^{13}C NMR (101 MHz, CDCl_3) δ 153.5, 142.3, 140.0, 138.6, 132.3, 131.8, 131.5 (t, $J_{\text{C-F}} = 8.2$ Hz), 129.7, 123.5 (t, $J_{\text{C-F}} = 288.9$ Hz), 123.3, 122.9, 118.6 (t, $J_{\text{C-F}} = 20.4$ Hz), 71.9, 28.0, 20.8 (t, $J_{\text{C-F}} = 4.3$ Hz), 19.2, 17.2.

HRMS Calcd for $\text{C}_{20}\text{H}_{22}\text{ClF}_2\text{NO}_4\text{S}$ [$\text{M}+\text{Na}^+$]: 468.0818; Found: 468.0820.



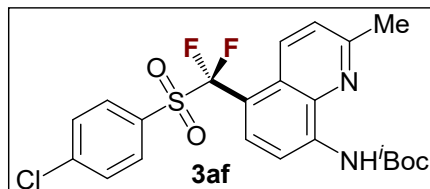
isobutyl (4-(((4-chlorophenyl)sulfonyl)difluoromethyl)-3,5-dimethoxyphenyl)carbamate, (3ae), Yield: 61%.

^1H NMR (400 MHz, CDCl_3) δ 7.83 (d, $J = 8.5$ Hz, 2H), 7.58 (s, 1H), 7.53 (d, $J = 8.6$ Hz, 2H), 7.26 (s, 1H), 6.10 (d, $J = 1.4$ Hz, 1H), 3.83 (s, 3H), 3.50 (s, 3H), 1.52 (s, 9H).

^{19}F NMR (377 MHz, CDCl_3) δ -93.4.

^{13}C NMR (101 MHz, CDCl_3) δ 164.0, 161.1, 153.0, 142.4, 141.5, 132.4, 131.7, 129.5, 100.8, 95.6, 81.0, 56.1, 55.7, 28.4.

HRMS Calcd for $\text{C}_{20}\text{H}_{22}\text{ClF}_2\text{NO}_6\text{S}$ [$\text{M}+\text{Na}^+$]: 500.0717; Found: 500.0726.



Isobutyl (5-(((4-chlorophenyl)sulfonyl)difluoromethyl)-2-methylquinolin-8-yl)carbamate, (3af),

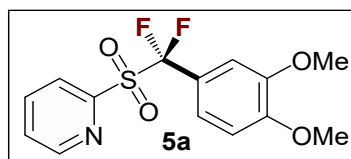
Yield: 51%

^1H NMR (400 MHz, CDCl_3) δ 9.52 (s, 1H), 8.61 (d, $J = 8.8$ Hz, 1H), 8.45 (d, $J = 8.0$ Hz, 1H), 7.94 (d, $J = 8.4$ Hz, 2H), 7.70 (d, $J = 8.4$ Hz, 1H), 7.60 (d, $J = 8.5$ Hz, 2H), 7.45 (d, $J = 8.9$ Hz, 1H), 4.06 (d, $J = 6.7$ Hz, 2H), 2.76 (s, 3H), 2.16 – 1.99 (m, 2H), 1.03 (d, $J = 6.7$ Hz, 6H).

^{19}F NMR (377 MHz, CDCl_3) δ -94.5.

^{13}C NMR (101 MHz, CDCl_3) δ 166.8, 159.5, 156.6 (d, $J_{\text{C-F}} = 2.1$ Hz), 153.8, 143.7, 143.7, 134.3, 129.7, 129.7, 129.2, 129.2, 127.8, 127.7, 117.4, 63.8, 33.3, 28.7 (t, $J_{\text{C-F}} = 2.3$ Hz), 19.1, 19.1.

HRMS Calcd for $\text{C}_{22}\text{H}_{21}\text{ClF}_2\text{N}_2\text{O}_4\text{S}$ [$\text{M}+\text{Na}^+$]: 505.0771; Found: 505.0785.



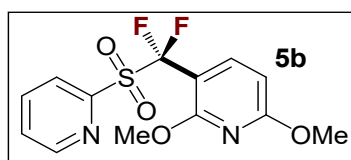
2-(((3,4-dimethoxyphenyl)difluoromethyl)sulfonyl)pyridine, (5a), Yield: 72%.

^1H NMR (400 MHz, CDCl_3) δ 8.88 (dd, $J = 4.6, 0.7$ Hz, 1H), 8.17 (d, $J = 7.8$ Hz, 1H), 8.01 (td, $J = 7.8, 1.7$ Hz, 1H), 7.65 (ddd, $J = 7.6, 4.7, 1.0$ Hz, 1H), 7.29 (dd, $J = 8.5, 1.9$ Hz, 1H), 7.16 (d, $J = 1.9$ Hz, 1H), 6.96 (d, $J = 8.5$ Hz, 1H), 3.92 (s, 3H), 3.90 (s, 3H).

^{19}F NMR (377 MHz, CDCl_3) δ -99.7.

^{13}C NMR (101 MHz, CDCl_3) δ 152.8, 152.7, 151.0, 149.1, 138.3, 128.6, 126.7, 122.8 (t, $J_{\text{C-F}} = 286.8$), 121.6 (t, $J_{\text{C-F}} = 6.4$ Hz), 118.0 (t, $J_{\text{C-F}} = 22.7$ Hz), 110.9, 110.4, 56.2, 56.2.

HRMS Calcd for $\text{C}_{14}\text{H}_{13}\text{F}_2\text{NO}_4\text{S}$ [$\text{M}+\text{Na}^+$]: 352.0426; Found: 352.0433.



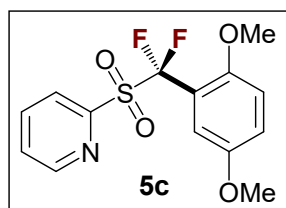
3-(difluoro(pyridin-2-ylsulfonyl)methyl)-2,6-dimethoxy pyridine, (5b), Yield: 65%

^1H NMR (400 MHz, CDCl_3) δ 8.89 – 8.81 (m, 1H), 8.18 (d, $J = 7.9$ Hz, 1H), 8.01 (td, $J = 7.8, 1.7$ Hz, 1H), 7.74 (d, $J = 8.4$ Hz, 1H), 7.64 (ddd, $J = 7.6, 4.7, 1.0$ Hz, 1H), 6.40 (d, $J = 8.4$ Hz, 1H), 3.96 (s, 3H), 3.89 (s, 3H).

^{19}F NMR (377 MHz, CDCl_3) δ -97.0.

^{13}C NMR (101 MHz, CDCl_3) δ 166.1, 161.7, 153.4, 150.9, 141.9 (t, $J_{\text{C-F}} = 6.7$ Hz), 138.2, 128.5, 126.7, 122.9 (t, $J_{\text{C-F}} = 289.4$ Hz), 102.2, 100.1 (t, $J_{\text{C-F}} = 23.0$ Hz), 54.1, 54.1.

HRMS Calcd for C₁₃H₁₂F₂N₂O₄S [M+Na⁺]: 353.0378; Found: 353.0390.



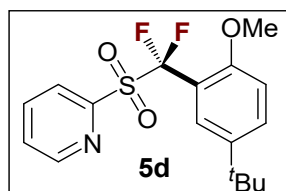
2-(((2,5-dimethoxyphenyl)difluoromethyl)sulfonyl)pyridine, (**5c**), Yield: 53%.

¹H NMR (400 MHz, CDCl₃) δ 8.85 (d, *J* = 3.9 Hz, 1H), 8.16 (d, *J* = 7.9 Hz, 1H), 8.00 (td, *J* = 7.8, 1.7 Hz, 1H), 7.63 (ddd, *J* = 7.6, 4.7, 0.9 Hz, 1H), 7.07 (dd, *J* = 12.5, 3.0 Hz, 2H), 6.92 (d, *J* = 8.7 Hz, 1H), 3.78 (s, 3H), 3.74 (s, 3H).

¹⁹F NMR (377 MHz, CDCl₃) δ -95.8.

¹³C NMR (101 MHz, CDCl₃) δ 153.5, 153.3, 153.1 (t, *J*_{C-F} = 2.6 Hz), 150.8, 138.1, 128.4, 126.6, 123.0 (t, *J*_{C-F} = 291.8 Hz), 120.2, 115.7 (t, *J*_{C-F} = 20.5 Hz), 114.7 (t, *J*_{C-F} = 8.3 Hz), 114.3, 56.9, 56.0.

HRMS Calcd for C₁₄H₁₃F₂NO₄S [M+Na⁺]: 352.0426; Found: 352.0433.



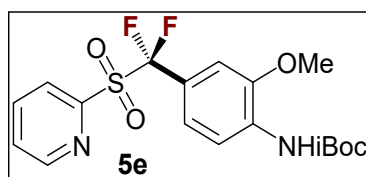
2-(((5-(tert-butyl)-2-methoxyphenyl)difluoromethyl)sulfonyl)pyridine, (**5d**), Yield: 49%

¹H NMR (400 MHz, CDCl₃) δ 8.84 (dd, *J* = 4.7, 0.8 Hz, 1H), 8.14 (d, *J* = 7.9 Hz, 1H), 7.99 (td, *J* = 7.8, 1.7 Hz, 1H), 7.62 (ddd, *J* = 7.6, 4.7, 1.0 Hz, 1H), 7.57 – 7.46 (m, 2H), 6.92 (d, *J* = 8.6 Hz, 1H), 3.79 (s, 3H), 1.29 (s, 9H).

¹⁹F NMR (377 MHz, CDCl₃) δ -95.6.

¹³C NMR (101 MHz, CDCl₃) δ 156.9, 153.6, 150.8, 143.3, 138.1, 131.3, 128.3, 126.9 (t, *J*_{C-F} = 8.0 Hz), 126.6, 123.5 (t, *J*_{C-F} = 290.5 Hz), 114.3 (t, *J*_{C-F} = 20.0 Hz), 112.4, 56.3, 34.3, 31.4.

HRMS Calcd for C₁₇H₁₉F₂NO₃S [M+Na⁺]: 378.0946; Found: 378.0945.



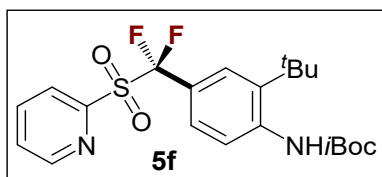
Isobutyl 4-(difluoro(pyridin-2-ylsulfonyl)methyl)-2-methoxyphenylcarbamate, (**5e**), Yield: 61%

¹H NMR (400 MHz, CDCl₃) δ 8.89 (d, *J* = 4.0 Hz, 1H), 8.27 (d, *J* = 8.3 Hz, 1H), 8.18 (d, *J* = 7.8 Hz, 1H), 8.03 (td, *J* = 7.8, 1.5 Hz, 1H), 7.67 (dd, *J* = 7.5, 4.7 Hz, 1H), 7.41 (s, 1H), 7.33 – 7.23 (m, 1H), 7.19 (s, 1H), 3.98 (d, *J* = 6.7 Hz, 2H), 3.94 (s, 3H), 2.12 – 1.84 (m, 1H), 0.98 (d, *J* = 6.7 Hz, 6H).

¹⁹F NMR (377 MHz, CDCl₃) δ -100.0.

¹³C NMR (101 MHz, CDCl₃) δ 153.4, 152.7, 151.0, 147.2, 138.3, 132.1, 128.7, 126.7, 122.7 (t, *J*_{C-F} = 289.0 Hz), 121.5 (t, *J*_{C-F} = 6.4 Hz), 119.5 (t, *J*_{C-F} = 22.6 Hz), 117.4, 109.2 (t, *J*_{C-F} = 6.1 Hz), 71.8, 56.1, 28.0, 19.1.

HRMS Calcd for C₁₈H₂₀F₂N₂O₅S [M+Na⁺]: 437.0953; Found: 437.0960.



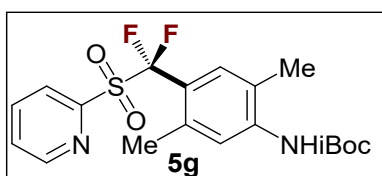
Isobutyl (2-(tert-butyl)-4-(difluoro(pyridin-2-ylsulfonyl)methyl)phenyl)carbamate, (5f), Yield: 58%

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.88 (d, $J = 3.8$ Hz, 1H), 8.16 (d, $J = 7.8$ Hz, 1H), 8.01 (td, $J = 7.8, 1.6$ Hz, 2H), 7.66 (t, $J = 5.6$ Hz, 2H), 7.56 (dd, $J = 8.5, 1.7$ Hz, 1H), 6.82 (s, 1H), 3.98 (d, $J = 6.7$ Hz, 2H), 2.06 – 1.92 (m, 1H), 1.44 (s, 9H), 0.96 (d, $J = 6.7$ Hz, 6H).

$^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -100.1.

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 153.7, 152.8, 151.0, 140.2, 138.3, 128.7, 126.8 (d, $J_{\text{C-F}} = 8.5$ Hz), 126.8, 126.4 (t, $J_{\text{C-F}} = 6.0$ Hz), 71.8, 34.6, 30.5, 28.1, 19.1.

HRMS Calcd for $\text{C}_{21}\text{H}_{26}\text{F}_2\text{N}_2\text{O}_4\text{S}$ [$\text{M}+\text{Na}^+$]: 463.1474; Found: 463.1482.



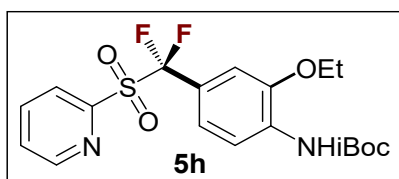
Isobutyl (4-(difluoro(pyridin-2-ylsulfonyl)methyl)-2,5-dimethylphenyl)carbamate, (5g), Yield: 68%

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.92 – 8.83 (m, 1H), 8.18 (d, $J = 7.8$ Hz, 1H), 8.01 (td, $J = 7.8, 1.6$ Hz, 1H), 7.95 (s, 1H), 7.65 (ddd, $J = 7.6, 4.7, 0.9$ Hz, 1H), 7.37 (s, 1H), 6.57 (s, 1H), 3.96 (d, $J = 6.7$ Hz, 2H), 2.56 (t, $J = 3.1$ Hz, 3H), 2.24 (s, 3H), 2.12 – 1.91 (m, 1H), 0.96 (d, $J = 6.7$ Hz, 6H).

$^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -94.3.

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 153.5, 153.1, 151.0, 140.0, 138.7, 138.3, 131.6 (t, $J_{\text{C-F}} = 8.3$ Hz), 128.6, 126.7, 124.3 (t, $J_{\text{C-F}} = 290.6$ Hz), 123.3, 122.9, 118.7 (t, $J_{\text{C-F}} = 20.1$ Hz), 71.9, 28.0, 20.8, 19.1, 17.2.

HRMS Calcd for $\text{C}_{19}\text{H}_{22}\text{F}_2\text{N}_2\text{O}_4\text{S}$ [$\text{M}+\text{Na}^+$]: 435.1166; Found: 435.1171.



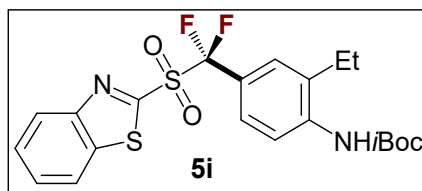
Isobutyl (4-(difluoro(pyridin-2-ylsulfonyl)methyl)-2-ethoxyphenyl)carbamate, (5h), Yield: 56%.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.86 (dd, $J = 4.6, 0.8$ Hz, 1H), 8.24 (d, $J = 8.3$ Hz, 1H), 8.15 (d, $J = 7.8$ Hz, 1H), 8.00 (td, $J = 7.8, 1.7$ Hz, 1H), 7.64 (ddd, $J = 7.6, 4.7, 1.0$ Hz, 1H), 7.37 (s, 1H), 7.24 (dd, $J = 8.6, 1.4$ Hz, 1H), 7.16 (d, $J = 1.6$ Hz, 1H), 4.16 (q, $J = 7.0$ Hz, 2H), 3.97 (d, $J = 6.7$ Hz, 2H), 2.00 (tq, $J = 13.4, 6.7$ Hz, 1H), 1.47 (t, $J = 7.0$ Hz, 3H), 0.97 (d, $J = 6.7$ Hz, 6H).

$^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -100.0.

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 153.4, 152.8, 151.0, 146.5, 138.3, 132.1, 128.6, 126.7, 122.7 (t, $J_{\text{C-F}} = 288.9$ Hz), 121.3 (t, $J_{\text{C-F}} = 6.4$ Hz), 119.5 (t, $J_{\text{C-F}} = 22.4$ Hz), 117.4, 110.1 (t, $J_{\text{C-F}} = 6.0$ Hz), 71.8, 64.8, 28.0, 19.2, 14.7.

HRMS (ESI) Calcd for $\text{C}_{19}\text{H}_{22}\text{F}_2\text{N}_2\text{O}_5\text{S}$ [$\text{M}+\text{Na}^+$]: 451.1115; Found: 451.1123.



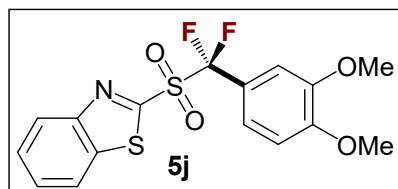
Isobutyl (4-((benzo[d]thiazol-2-ylsulfonyl)difluoromethyl)-2-ethylphenyl)carbamate, (5i), Yield: 34%.

¹H NMR (400 MHz, CDCl₃) δ 8.41 – 8.30 (m, 1H), 8.18 (d, *J* = 8.6 Hz, 1H), 8.10 – 8.00 (m, 1H), 7.65 (dddd, *J* = 17.6, 10.7, 7.9, 1.7 Hz, 3H), 7.53 (d, *J* = 1.8 Hz, 1H), 6.68 (s, 1H), 3.99 (d, *J* = 6.7 Hz, 2H), 2.63 (q, *J* = 7.5 Hz, 2H), 2.10 – 1.92 (m, 1H), 1.26 (t, *J* = 7.5 Hz, 3H), 0.98 (d, *J* = 6.7 Hz, 6H).

¹⁹F NMR (377 MHz, CDCl₃) δ -99.1.

¹³C NMR (101 MHz, CDCl₃) δ 159.7, 153.6, 153.1, 140.3, 138.4, 132.0, 128.8, 128.0 (t, *J*_{C-F} = 5.9 Hz), 127.2 (t, *J*_{C-F} = 6.0 Hz), 126.4, 122.4, 119.9 (t, *J*_{C-F} = 11.0 Hz), 72.0, 28.0, 24.1, 19.2, 13.2.

HRMS Calcd for C₂₁H₂₂F₂N₂O₄S₂ [M+Na⁺]: 491.0881; Found: 491.0890.



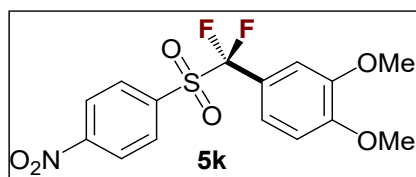
2-(((3,4-dimethoxyphenyl)difluoromethyl)sulfonyl)benzo[d]thiazole, (5j), Yield: 41%

¹H NMR (400 MHz, CDCl₃) δ 8.42 – 8.30 (m, 1H), 8.11 – 8.02 (m, 1H), 7.76 – 7.63 (m, 2H), 7.40 – 7.32 (m, 1H), 7.17 (d, *J* = 2.0 Hz, 1H), 6.99 (d, *J* = 8.5 Hz, 1H), 3.95 (s, 3H), 3.89 (s, 3H).

¹⁹F NMR (377 MHz, CDCl₃) δ -98.7.

¹³C NMR (101 MHz, CDCl₃) δ 159.7, 153.2, 153.1, 149.4, 138.4, 128.9, 128.1, 126.4, 122.4, 122.0 (t, *J*_{C-F} = 6.5 Hz), 111.1, 110.4 (t, *J*_{C-F} = 5.8 Hz), 56.3, 56.2.

HRMS Calcd for C₁₆H₁₃F₂NO₄S₂ [M+Na⁺]: 408.0146; Found: 408.0158.



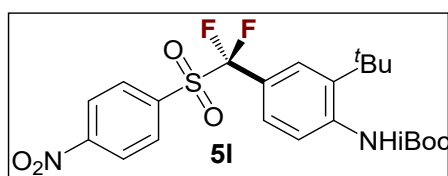
4-(Difluoro((4-nitrophenyl)sulfonyl)methyl)-1,2-dimethoxybenzene, (5k), Yield: 55%

¹H NMR (400 MHz, CDCl₃) δ 8.46 (d, *J* = 8.9 Hz, 2H), 8.23 (d, *J* = 8.8 Hz, 2H), 7.26 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.14 (d, *J* = 2.0 Hz, 1H), 6.98 (d, *J* = 8.5 Hz, 1H), 3.95 (s, 3H), 3.94 (s, 3H).

¹⁹F NMR (377 MHz, CDCl₃) δ -99.8.

¹³C NMR (101 MHz, CDCl₃) δ 153.0, 151.9, 149.3, 139.2, 132.4, 124.4, 122.4 (t, *J*_{C-F} = 288 Hz), 121.8 (t, *J*_{C-F} = 6.5 Hz), 117.2 (t, *J*_{C-F} = 22.6 Hz), 111.0, 110.4 (t, *J*_{C-F} = 5.9 Hz), 56.3, 56.2.

HRMS Calcd for C₁₅H₁₃F₂NO₆S [M+Na⁺]: 396.0324; Found: 396.0330.



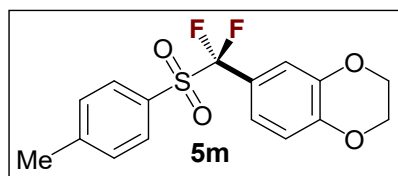
Isobutyl 2-(tert-butyl)-4-(difluoro((4-nitrophenyl)sulfonyl)methyl)phenyl)carbamate, (5l), Yield: 47%.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.53 – 8.40 (m, 2H), 8.22 (d, $J = 8.8$ Hz, 2H), 8.05 (d, $J = 8.5$ Hz, 1H), 7.61 (d, $J = 1.8$ Hz, 1H), 7.55 (dd, $J = 8.6, 2.0$ Hz, 1H), 6.86 (s, 1H), 4.00 (d, $J = 6.7$ Hz, 2H), 2.08 – 1.89 (m, 1H), 1.46 (s, 8H), 0.98 (d, $J = 6.7$ Hz, 6H).

$^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -100.3.

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 153.6, 151.9, 140.5, 139.2, 132.5, 127.0 (t, $J_{\text{C-F}} = 6.0$ Hz), 126.3 (t, $J_{\text{C-F}} = 6.2$ Hz), 124.4, 71.9, 34.6, 30.5, 28.1, 19.1.

HRMS Calcd for $\text{C}_{22}\text{H}_{26}\text{F}_2\text{N}_2\text{O}_6\text{S}$ [$\text{M}+\text{Na}^+$]: 507.1372; Found: 507.1384.



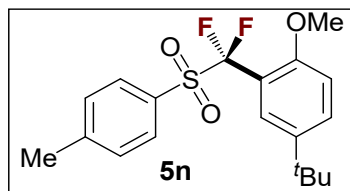
6-(Difluoro(tosyl)methyl)-2,3-dihydrobenzo[b][1,4]dioxine, (5m), Yield: 53%.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.88 (d, $J = 8.2$ Hz, 2H), 7.40 (d, $J = 8.1$ Hz, 2H), 7.20 (d, $J = 2.0$ Hz, 1H), 7.13 (dd, $J = 8.5, 2.1$ Hz, 1H), 6.95 (d, $J = 8.5$ Hz, 1H), 4.30 (td, $J = 5.3, 2.1$ Hz, 4H), 2.49 (s, 3H).

$^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -101.0.

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 147.3, 146.7, 143.7, 131.0, 130.1, 130.0, 121.4 (t, $J_{\text{C-F}} = 6.3$ Hz), 117.7, 117.5 (t, $J_{\text{C-F}} = 6.3$ Hz), 64.7, 64.3, 22.0.

HRMS Calcd for $\text{C}_{16}\text{H}_{14}\text{F}_2\text{O}_4\text{S}$ [$\text{M}+\text{Na}^+$]: 363.0473; Found: 363.0465.



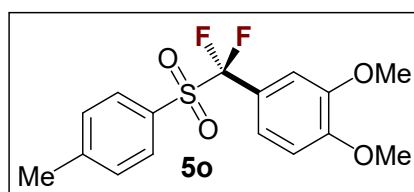
4-(tert-butyl)-2-(difluoro(tosyl)methyl)-1-methoxybenzene, (5n), Yield: 51%

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.79 (d, $J = 8.2$ Hz, 2H), 7.50 (dd, $J = 8.7, 2.5$ Hz, 1H), 7.37 (d, $J = 2.5$ Hz, 1H), 7.34 (d, $J = 8.1$ Hz, 2H), 6.90 (d, $J = 8.8$ Hz, 1H), 3.74 (s, 3H), 2.45 (s, 3H), 1.27 (s, 9H).

$^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -97.6.

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 156.8 (t, $J_{\text{C-F}} = 2.1$ Hz), 146.2, 143.1, 130.9, 130.9 (t, $J_{\text{C-F}} = 9.7$ Hz), 129.7, 127.0 (t, $J_{\text{C-F}} = 7.8$ Hz), 122.7 (t, $J_{\text{C-F}} = 288.8$ Hz), 114.7 (t, $J_{\text{C-F}} = 20.1$ Hz), 112.4, 56.2, 34.2, 31.4, 21.8.

HRMS Calcd for $\text{C}_{19}\text{H}_{22}\text{F}_2\text{O}_3\text{S}$ [$\text{M}+\text{Na}^+$]: 391.1155; Found: 391.1149.



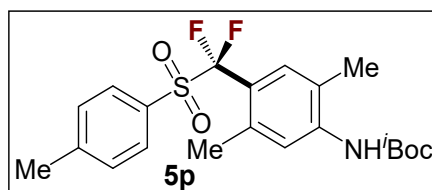
4-(difluoro(tosyl)methyl)-1,2-dimethoxybenzene, (5o), Yield: 63%

¹H NMR (400 MHz, CDCl₃) δ 7.85 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.24 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.08 (d, *J* = 1.9 Hz, 1H), 6.94 (d, *J* = 8.5 Hz, 1H), 3.92 (s, 3H), 3.90 (s, 3H), 2.48 (s, 3H).

¹⁹F NMR (377 MHz, CDCl₃) δ -101.2.

¹³C NMR (101 MHz, CDCl₃) δ 152.4, 149.0, 146.7, 131.0, 130.0, 130.0, 122.0 (t, *J*_{C-F} = 287.0 Hz), 121.5 (t, *J*_{C-F} = 6.5 Hz), 118.7 (t, *J*_{C-F} = 22.9 Hz), 110.8, 110.4 (t, *J*_{C-F} = 5.9 Hz), 56.2, 56.2, 21.9.

HRMS Calcd for C₁₆H₁₆F₂O₄S [M+Na⁺]: 391.1150; Found: 391.1161.



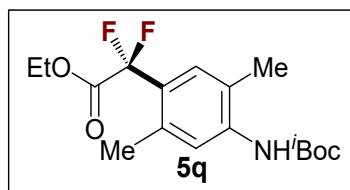
Isobutyl (4-(difluoro(tosyl)methyl)-2,5-dimethylphenyl)carbamate, (5p), Yield: 71%

¹H NMR (400 MHz, CDCl₃) δ 7.93 (s, 1H), 7.86 (d, *J* = 8.2 Hz, 2H), 7.40 (d, *J* = 8.1 Hz, 2H), 7.31 (s, 1H), 6.55 (s, 1H), 3.98 (d, *J* = 6.7 Hz, 2H), 2.51 (t, *J* = 3.2 Hz, 3H), 2.48 (s, 3H), 2.23 (s, 3H), 2.11 – 1.90 (m, 1H), 0.98 (d, *J* = 6.7 Hz, 6H).

¹⁹F NMR (377 MHz, CDCl₃) δ -95.8.

¹³C NMR (101 MHz, CDCl₃) δ 153.5, 146.6, 139.7, 138.5, 131.5 (t, *J*_{C-F} = 8.2 Hz), 130.9, 130.2, 130.0, 123.4 (t, *J*_{C-F} = 288.6 Hz), 123.2, 122.8, 119.2 (t, *J*_{C-F} = 20.7 Hz), 71.8, 28.0, 21.9, 20.8, 19.2, 17.2.

HRMS Calcd for C₂₁H₂₅F₂NO₄S [M+Na⁺]: 448.1370; Found: 448.1361.



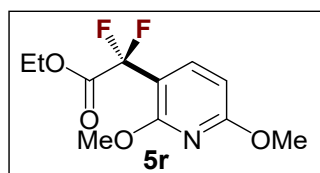
Ethyl 2,2-difluoro-2-(4-((isobutoxycarbonyl)amino)-2,5-dimethylphenyl)acetate, (5q), Yield: 84%

¹H NMR (400 MHz, CDCl₃) δ 7.81 (s, 1H), 7.34 (s, 1H), 6.47 (s, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 3.97 (d, *J* = 6.7 Hz, 2H), 2.37 (s, 3H), 2.25 (s, 3H), 1.99 (dp, *J* = 13.4, 6.7 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H), 0.97 (d, *J* = 6.7 Hz, 6H).

¹⁹F NMR (377 MHz, CDCl₃) δ -100.8.

¹³C NMR (101 MHz, CDCl₃) δ 163.3 (t, *J*_{C-F} = 35.7 Hz), 152.7, 137.1, 134.3 (t, *J*_{C-F} = 2.9 Hz), 127.1 (t, *J*_{C-F} = 8.8 Hz), 121.9, 113.1 (t, *J*_{C-F} = 251.7 Hz), 70.6, 62.0, 27.0, 18.5, 18.0, 16.1, 12.9.

HRMS Calcd for C₁₇H₂₃F₂NO₄ [M+Na⁺]: 366.1487; Found: 366.1493.



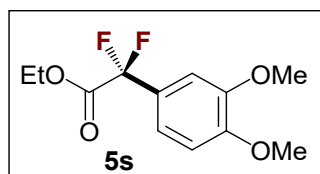
Ethyl 2-(2,6-dimethoxy-pyridin-3-yl)-2,2-difluoroacetate, (5r), Yield: 95%

¹H NMR (400 MHz, CDCl₃) δ 7.80 (d, *J* = 8.3 Hz, 1H), 6.37 (d, *J* = 8.3 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 3.93 (d, *J* = 1.9 Hz, 6H), 1.31 (t, *J* = 7.1 Hz, 3H).

¹⁹F NMR (377 MHz, CDCl₃) δ -101.7.

^{13}C NMR (101 MHz, CDCl_3) δ 165.0, 164.0 (t, $J_{\text{C-F}} = 34.5$ Hz), 159.9 (t, $J_{\text{C-F}} = 5.1$ Hz), 138.5 (t, $J_{\text{C-F}} = 6.2$ Hz), 112.4 (t, $J_{\text{C-F}} = 248.0$ Hz), 107.4 (t, $J_{\text{C-F}} = 26.2$ Hz), 101.5, 62.9, 53.9, 53.7, 14.1.

HRMS Calcd for $\text{C}_{11}\text{H}_{13}\text{F}_2\text{NO}_4$ [$\text{M}+\text{Na}^+$]: 284.0705; Found: 284.0710.



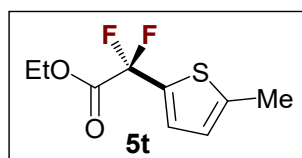
Ethyl 2-(3,4-dimethoxyphenyl)-2,2-difluoroacetate, (5s), Yield: 51%

^1H NMR (400 MHz, CDCl_3) δ 7.17 (dd, $J = 8.5, 1.5$ Hz, 1H), 7.09 (d, $J = 1.9$ Hz, 1H), 6.90 (d, $J = 8.4$ Hz, 1H), 4.30 (q, $J = 7.1$ Hz, 2H), 3.90 (s, 6H), 1.30 (t, $J = 7.1$ Hz, 3H).

^{19}F NMR (377 MHz, CDCl_3) δ -102.6.

^{13}C NMR (101 MHz, CDCl_3) δ 164.5 (t, $J_{\text{C-F}} = 36.0$ Hz), 151.2, 149.1, 125.2 (t, $J_{\text{C-F}} = 26.2$ Hz), 118.6 (t, $J_{\text{C-F}} = 6.6$ Hz), 113.5 (t, $J_{\text{C-F}} = 252.0$ Hz), 110.9, 108.4 (t, $J_{\text{C-F}} = 6.1$ Hz), 63.2, 56.1, 56.1, 14.0.

HRMS Calcd for $\text{C}_{12}\text{H}_{14}\text{F}_2\text{O}_4$ [$\text{M}+\text{Na}^+$]: 283.0752; Found: 283.0760.



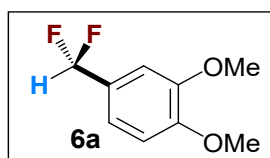
Ethyl 2,2-difluoro-2-(5-methylthiophen-2-yl)acetate, (5t), Yield: 93%.

^1H NMR (400 MHz, CDCl_3) δ 7.20 – 7.15 (m, 1H), 6.75 – 6.66 (m, 1H), 4.35 (q, $J = 7.1$ Hz, 2H), 2.50 (d, $J = 1.1$ Hz, 3H), 1.35 (t, $J = 7.1$ Hz, 4H).

^{19}F NMR (377 MHz, CDCl_3) δ -92.8.

^{13}C NMR (101 MHz, CDCl_3) δ 163.6 (t, $J_{\text{C-F}} = 35.4$ Hz), 144.3, 131.3 (t, $J_{\text{C-F}} = 30.3$ Hz), 128.7 (t, $J_{\text{C-F}} = 5.8$ Hz), 125.5, 111.8 (t, $J_{\text{C-F}} = 249.9$ Hz), 63.5, 15.4, 14.0.

HRMS Calcd for $\text{C}_9\text{H}_{10}\text{F}_2\text{O}_2\text{S}$ [$\text{M}+\text{Na}^+$]: 243.0262; Found: 243.0266.



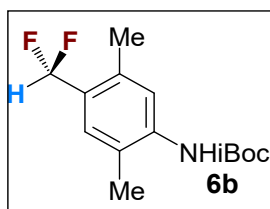
4-(difluoromethyl)-1,2-dimethoxybenzene, (6a), Yield: 71%.

^1H NMR (400 MHz, CDCl_3) δ 7.08 – 6.99 (m, 2H), 6.88 (d, $J = 8.1$ Hz, 1H), 6.57 (t, $J = 56.7$ Hz, 1H), 3.89 (s, 3H), 3.89 (s, 3H).

^{19}F NMR (377 MHz, CDCl_3) δ -108.2.

^{13}C NMR (101 MHz, CDCl_3) δ 151.0, 149.3, 127.0 (t, $J_{\text{C-F}} = 22.6$ Hz), 118.8 (t, $J_{\text{C-F}} = 7.0$ Hz), 115.0 (t, $J_{\text{C-F}} = 237.7$ Hz), 110.8, 108.1 (t, $J_{\text{C-F}} = 5.3$ Hz), 56.0, 56.0.

HRMS Calcd for $\text{C}_9\text{H}_{10}\text{F}_2\text{O}_2$ [$\text{M}+\text{H}^+$]: 189.0722; Found: 189.0727.



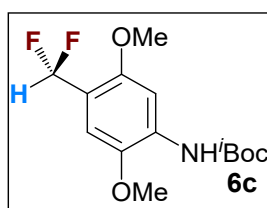
Isobutyl (4-(difluoromethyl)-2,5-dimethylphenyl)carbamate, (6b), Yield: 78%.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.80 (s, 1H), 7.28 (s, 1H), 6.70 (t, $J = 55.7$ Hz, 1H), 6.44 (s, 1H), 3.97 (d, $J = 6.7$ Hz, 2H), 2.39 (s, 3H), 2.25 (s, 3H), 2.10 – 1.92 (m, 1H), 0.98 (d, $J = 6.7$ Hz, 6H).

$^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -112.0.

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 153.9, 138.0, 135.3 (t, $J_{\text{C-F}} = 4.7$ Hz), 128.0 (t, $J_{\text{C-F}} = 7.3$ Hz), 127.5 (t, $J_{\text{C-F}} = 21.0$ Hz), 122.4, 114.4 (t, $J_{\text{C-F}} = 237.0$ Hz), 71.8, 28.1, 19.2, 18.4, 17.3.

HRMS Calcd for $\text{C}_{14}\text{H}_{19}\text{F}_2\text{NO}_2$ [$\text{M}+\text{Na}^+$]: 294.1276; Found: 294.1281.



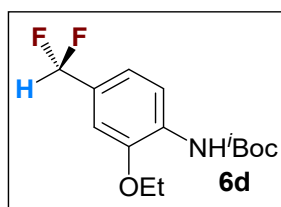
Isobutyl (4-(difluoromethyl)-2,5-dimethoxyphenyl)carbamate, (6c), Yield: 66%.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.93 (s, 1H), 7.36 (s, 1H), 7.04 (s, 1H), 6.94 (t, $J = 14.1$ Hz, 1H), 3.97 (d, $J = 6.7$ Hz, 2H), 3.88 (s, 3H), 3.85 (s, 3H), 1.99 (td, $J = 13.5, 6.8$ Hz, 1H), 0.98 (d, $J = 6.7$ Hz, 6H).

$^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -113.4.

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 153.7, 152.1 (t, $J_{\text{C-F}} = 6.4$ Hz), 141.4, 131.0, 115.6 (t, $J_{\text{C-F}} = 22.3$ Hz), 114.0, 111.6, 109.3, 107.8 (t, $J_{\text{C-F}} = 5.6$ Hz), 102.2, 71.7, 60.5, 56.4, 56.4, 28.1, 19.2.

HRMS (ESI) Calcd for $\text{C}_{14}\text{H}_{19}\text{F}_2\text{NO}_4$ [$\text{M}+\text{Na}^+$]: 326.1180; Found: 326.1186.



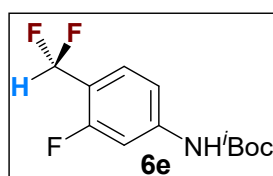
tert-butyl (4-(difluoromethyl)-2-ethoxyphenyl)carbamate, (6d), Yield: 69%.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.17 (d, $J = 7.4$ Hz, 1H), 7.30 (s, 1H), 7.06 (d, $J = 8.3$ Hz, 1H), 7.00 (s, 1H), 6.58 (t, $J = 56.7$ Hz, 1H), 4.14 (q, $J = 7.0$ Hz, 2H), 3.97 (d, $J = 6.7$ Hz, 2H), 2.01 (dp, $J = 13.4, 6.7$ Hz, 1H), 1.48 (t, $J = 7.0$ Hz, 3H), 0.98 (d, $J = 6.7$ Hz, 6H).

$^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -108.8.

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 153.6, 146.9, 130.2, 128.6 (t, $J_{\text{C-F}} = 22.5$ Hz), 119.0 (t, $J_{\text{C-F}} = 6.8$ Hz), 117.7, 115.0 (t, $J_{\text{C-F}} = 238.0$ Hz), 107.6 (t, $J_{\text{C-F}} = 5.5$ Hz), 71.7, 64.6, 28.1, 19.2, 14.9.

HRMS Calcd for $\text{C}_{14}\text{H}_{19}\text{F}_2\text{NO}_3$ [$\text{M}+\text{Na}^+$]: 310.1225; Found: 310.1230.



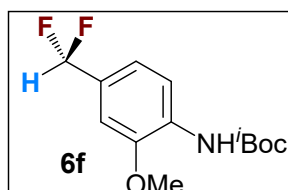
isobutyl (4-(difluoromethyl)-3-fluorophenyl)carbamate, (6e), Yield: 45%.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.48 (dd, $J = 14.2, 6.1$ Hz, 1H), 7.07 (dd, $J = 8.5, 1.6$ Hz, 1H), 6.81 (s, 1H), 3.97 (d, $J = 6.6$ Hz, 1H), 1.97 (td, $J = 13.4, 6.7$ Hz, 1H), 0.97 (d, $J = 6.7$ Hz, 3H).

$^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -112.9, -117.8.

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 153.3, 142.2 (d, $J_{\text{C-F}} = 10.9$ Hz), 130.0 (d, $J_{\text{C-F}} = 208.6$ Hz), 127.5 (d, $J_{\text{C-F}} = 20.0$ Hz), 127.5 (d, $J_{\text{C-F}} = 4.6$ Hz), 113.8, 110.8 (t, $J_{\text{C-F}} = 237.4$ Hz), 110.7 (t, $J_{\text{C-F}} = 237.2$ Hz), 105.9 (d, $J_{\text{C-F}} = 26.4$ Hz), 72.0, 28.1, 19.2.

HRMS Calcd for $\text{C}_{12}\text{H}_{14}\text{F}_3\text{NO}_2$ [$\text{M}+\text{Na}^+$]: 284.0869; Found: 284.0873.



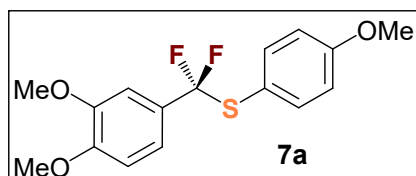
tert-butyl (4-(difluoromethyl)-2-methoxyphenyl)carbamate, (6f), Yield: 74%

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.18 (d, $J = 7.9$ Hz, 1H), 7.31 (s, 1H), 7.07 (d, $J = 8.3$ Hz, 1H), 7.01 (s, 1H), 6.59 (t, $J = 56.7$ Hz, 1H), 3.97 (d, $J = 6.7$ Hz, 2H), 3.92 (s, 3H), 2.10 – 1.89 (m, 1H), 0.98 (d, $J = 6.7$ Hz, 6H).

$^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -108.8.

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 153.6, 147.7, 130.2, 128.6 (t, $J_{\text{C-F}} = 22.5$ Hz), 119.1 (t, $J_{\text{C-F}} = 6.9$ Hz), 117.7, 114.9 (t, $J_{\text{C-F}} = 238.0$ Hz), 106.8 (t, $J_{\text{C-F}} = 5.5$ Hz), 71.7, 56.0, 28.1, 19.2.

HRMS Calcd for $\text{C}_{13}\text{H}_{17}\text{F}_2\text{NO}_3$ [$\text{M}+\text{Na}^+$]: 296.1069; Found: 296.1078.



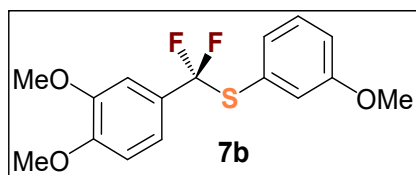
((3,4-dimethoxyphenyl)difluoromethyl)(4-methoxyphenyl)sulfane, (7a), Yield: 66%

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.53 (d, $J = 8.7$ Hz, 2H), 7.13 (d, $J = 8.4$ Hz, 1H), 7.02 (d, $J = 1.8$ Hz, 1H), 6.94 – 6.82 (m, 3H), 3.91 (s, 3H), 3.90 (s, 3H), 3.83 (s, 3H).

$^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -71.1.

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 161.3, 150.8, 148.8, 138.3, 118.5 (t, $J_{\text{C-F}} = 4.1$ Hz), 114.7, 110.6, 108.7 (t, $J_{\text{C-F}} = 4.6$ Hz), 56.1, 55.5.

HRMS Calcd for $\text{C}_{16}\text{H}_{16}\text{F}_2\text{O}_3\text{S}$ [$\text{M}+\text{Na}^+$]: 349.0686; Found: 349.0693.



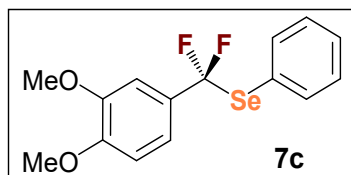
((3,4-dimethoxyphenyl)difluoromethyl)(3-methoxyphenyl)sulfane, (7b), Yield: 58%.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.29 (d, $J = 7.8$ Hz, 1H), 7.23 – 7.12 (m, 3H), 7.04 (d, $J = 1.9$ Hz, 1H), 6.96 (dd, $J = 7.8, 2.1$ Hz, 1H), 6.87 (d, $J = 8.4$ Hz, 1H), 3.91 (s, 3H), 3.90 (s, 3H), 3.81 (s, 3H).

^{19}F NMR (377 MHz, CDCl_3) δ -69.9.

^{13}C NMR (101 MHz, CDCl_3) δ 159.8, 150.9, 148.8, 129.8, 128.9, 128.5, 128.5, 127.8, 121.1, 118.6 (t, $J_{\text{C-F}} = 5.0$ Hz), 116.2, 110.6, 108.6 (t, $J_{\text{C-F}} = 4.4$ Hz), 56.2, 55.5.

HRMS Calcd for $\text{C}_{16}\text{H}_{16}\text{F}_2\text{O}_3\text{S}$ [$\text{M}+\text{Na}^+$]: 349.0680; Found: 349.0690.



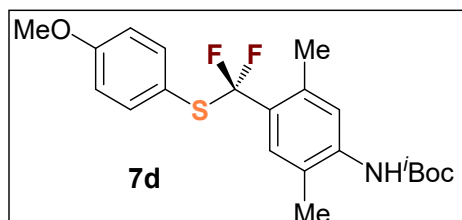
((3,4-dimethoxyphenyl)difluoromethyl)(phenyl)selane, (7c), Yield: 31%.

^1H NMR (400 MHz, CDCl_3) δ 7.65 (d, $J = 7.1$ Hz, 1H), 7.40 (t, $J = 7.4$ Hz, 1H), 7.32 (t, $J = 7.4$ Hz, 3H), 7.07 (d, $J = 7.4$ Hz, 1H), 6.92 (s, 1H), 6.84 (d, $J = 8.4$ Hz, 1H), 3.90 (s, 3H), 3.85 (s, 3H).

^{19}F NMR (377 MHz, CDCl_3) δ -68.1.

^{13}C NMR (101 MHz, CDCl_3) δ 148.7, 137.2, 129.5, 129.2, 118.1, 110.6, 108.3, 56.1, 56.1, 29.9.

HRMS Calcd for $\text{C}_{15}\text{H}_{14}\text{F}_2\text{O}_2\text{Se}$ [$\text{M}+\text{Na}^+$]: 367.0019; Found: 367.0032.



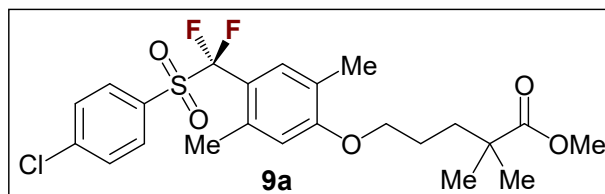
Isobutyl 4-(difluoro((4-methoxyphenyl)thio)methyl)-2,5-dimethylphenyl)carbamate, (7d), Yield: 56%.

^1H NMR (400 MHz, CDCl_3) δ 7.81 (s, 1H), 7.53 (d, $J = 8.8$ Hz, 2H), 7.23 (s, 1H), 6.89 (d, $J = 8.8$ Hz, 2H), 6.44 (s, 1H), 3.97 (d, $J = 6.7$ Hz, 2H), 3.83 (s, 3H), 2.57 (s, 3H), 2.21 (s, 3H), 1.99 (td, $J = 13.4, 6.7$ Hz, 1H), 0.98 (d, $J = 6.7$ Hz, 6H).

^{19}F NMR (377 MHz, CDCl_3) δ -70.1.

^{13}C NMR (101 MHz, CDCl_3) δ 161.3, 153.8, 138.4, 137.9, 135.4, 128.3 (t, $J_{\text{C-F}} = 7.0$ Hz), 127.9, 123.1, 118.4, 114.6, 71.8, 55.5, 28.1, 19.2, 17.2.

HRMS Calcd for $\text{C}_{21}\text{H}_{25}\text{F}_2\text{NO}_3\text{S}$ [$\text{M}+\text{Na}^+$]: 432.1415; Found: 432.1421.



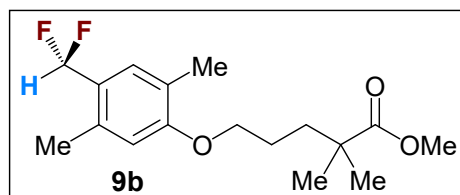
Methyl 5-(4-(((4-chlorophenyl)sulfonyl)difluoromethyl)-2,5-dimethylphenoxy)-2,2-dimethylpentanoate, (9a), Yield: 81%.

^1H NMR (400 MHz, CDCl_3) δ 7.84 (d, $J = 8.5$ Hz, 2H), 7.48 (d, $J = 8.5$ Hz, 2H), 7.17 (s, 1H), 6.56 (s, 1H), 3.88 (t, $J = 5.6$ Hz, 2H), 3.58 (s, 3H), 2.44 (t, $J = 2.9$ Hz, 3H), 2.10 (s, 3H), 1.80 – 1.52 (m, 4H), 1.14 (s, 6H).

^{19}F NMR (377 MHz, CDCl_3) δ -94.8.

^{13}C NMR (101 MHz, CDCl_3) δ 178.2, 160.0, 142.1, 138.7, 132.2, 132.0, 131.6 (t, $J_{\text{C-F}} = 8.0$ Hz), 129.6, 124.5, 123.8 (t, $J_{\text{C-F}} = 288.7$ Hz), 115.2 (t, $J_{\text{C-F}} = 20.5$ Hz), 114.4, 68.1, 51.8, 42.1, 37.0, 25.2, 25.0, 20.9, 15.7.

HRMS Calcd for $\text{C}_{23}\text{H}_{27}\text{ClF}_2\text{O}_5\text{S}$ [$\text{M}+\text{Na}^+$]: 511.1128; Found: 511.1111.



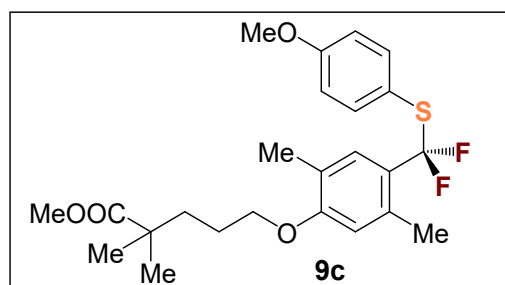
Methyl 5-(4-(difluoromethyl)-2,5-dimethylphenoxy)-2,2-dimethylpentanoate, (9b), Yield: 67%.

^1H NMR (400 MHz, CDCl_3) δ 7.24 (s, 1H), 6.68 (t, $J = 14.1$ Hz, 1H), 6.60 (s, 1H), 3.94 (t, $J = 5.7$ Hz, 2H), 3.67 (s, 3H), 2.38 (s, 3H), 2.20 (s, 3H), 1.82 – 1.67 (m, 4H), 1.22 (s, 6H).

^{19}F NMR (377 MHz, CDCl_3) δ -110.3.

^{13}C NMR (101 MHz, CDCl_3) δ 178.4, 158.6, 135.2 (t, $J_{\text{C-F}} = 4.6$ Hz), 128.4 (t, $J_{\text{C-F}} = 7.0$ Hz), 124.3, 124.0 (t, $J_{\text{C-F}} = 21.1$ Hz), 114.9 (t, $J_{\text{C-F}} = 237.1$ Hz), 113.4, 68.2, 51.9, 42.2, 37.1, 25.3, 25.2, 18.6, 15.8.

HRMS Calcd for $\text{C}_{17}\text{H}_{24}\text{F}_2\text{O}_3$ [$\text{M}+\text{Na}^+$]: 337.1586; Found: 337.1591.



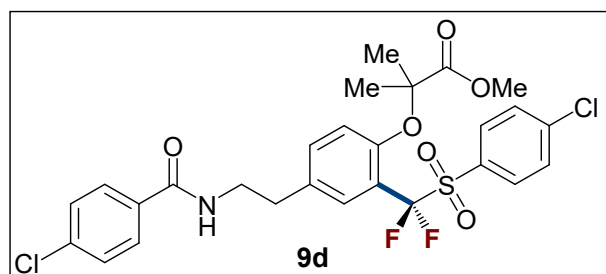
Methyl 5-(4-(difluoro((4-methoxyphenyl)thio)methyl)-2,5-dimethylphenoxy)-2,2-dimethylpentanoate, (9c), Yield: 49%.

^1H NMR (400 MHz, CDCl_3) δ 7.59 – 7.50 (m, 2H), 7.23 (s, 1H), 6.90 (d, $J = 8.8$ Hz, 2H), 6.60 (s, 1H), 3.95 (t, $J = 5.6$ Hz, 2H), 3.83 (s, 3H), 3.67 (s, 3H), 2.55 (s, 3H), 2.16 (s, 3H), 1.59 (s, 2H), 1.22 (s, 6H).

^{19}F NMR (377 MHz, CDCl_3) δ -69.0.

^{13}C NMR (101 MHz, CDCl_3) δ 178.4, 161.2, 158.5, 138.3, 135.3, 128.6 (t, $J_{\text{C-F}} = 6.6$ Hz), 123.9, 118.7, 114.6, 114.1, 68.2, 55.5, 51.9, 42.2, 37.2, 25.3, 25.2, 15.8.

HRMS Calcd for $\text{C}_{24}\text{H}_{30}\text{F}_2\text{O}_4\text{S}$ [$\text{M}+\text{Na}^+$]: 475.1725; Found: 475.1734.



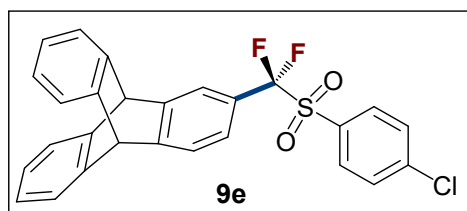
Methyl 2-(4-(2-(4-chlorobenzamido)ethyl)-2-(((4-chlorophenyl)sulfonyl)difluoromethyl)phenoxy)-2-methylpropanoate, (9d), Yield: 44%.

¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, *J* = 8.6 Hz, 2H), 7.67 (d, *J* = 8.5 Hz, 2H), 7.56 (d, *J* = 8.6 Hz, 2H), 7.40 – 7.31 (m, 3H), 7.31 – 7.22 (m, 1H), 6.63 (d, *J* = 8.6 Hz, 1H), 6.42 (s, 1H), 3.76 (s, 3H), 3.63 (q, *J* = 6.6 Hz, 2H), 2.87 (t, *J* = 6.8 Hz, 2H), 1.61 (s, 6H).

¹⁹F NMR (377 MHz, CDCl₃) δ -96.4.

¹³C NMR (101 MHz, CDCl₃) δ 174.7, 166.7, 153.9, 142.3, 137.8, 133.9, 132.9, 132.2, 132.0, 131.9, 130.8 (t, *J*_{C-F} = 7.7 Hz), 129.8, 128.9, 128.6, 122.4 (t, *J*_{C-F} = 289.4 Hz), 117.7, 116.7 (t, *J*_{C-F} = 20.0 Hz), 80.0, 52.8, 41.1, 34.6, 24.9.

HRMS Calcd for C₂₇H₂₅Cl₂F₂NO₆S [M+Na⁺]: 622.0640; Found: 622.0653.



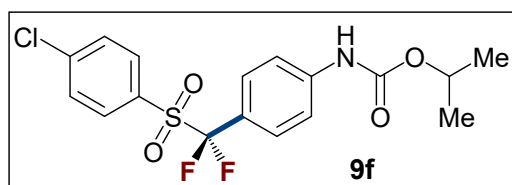
(9r,10r)-2-(((4-chlorophenyl)sulfonyl)difluoromethyl)-9,10-dihydro-9,10-[1,2]benzenoanthracene, (9e), Yield: 32%.

¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, *J* = 8.6 Hz, 2H), 7.60 (d, *J* = 1.3 Hz, 1H), 7.57 – 7.46 (m, 3H), 7.46 – 7.38 (m, 4H), 7.36 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.11 – 6.95 (m, 4H), 5.52 (s, 1H), 5.48 (s, 1H).

¹⁹F NMR (377 MHz, CDCl₃) δ -100.8.

¹³C NMR (101 MHz, CDCl₃) δ 150.3, 146.2, 144.5, 144.3, 142.4, 132.3, 131.4, 125.6 (t, *J*_{C-F} = 6.36 Hz), 129.7, 125.7, 125.7, 124.1, 124.0, 123.9, 122.8 (t, *J*_{C-F} = 5.8 Hz), 54.1, 53.9.

HRMS Calcd for C₂₇H₁₇ClF₂O₂S [M+Na⁺]: 501.0498; Found: 501.0509.



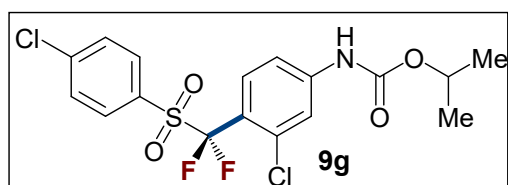
Isopropyl (4-(((4-chlorophenyl)sulfonyl)difluoromethyl)phenyl)carbamate, (9f), Yield: 35%.

¹H NMR (400 MHz, CDCl₃) δ 7.92 (d, *J* = 8.6 Hz, 2H), 7.67 – 7.45 (m, 6H), 6.80 (s, 1H), 5.04 (dt, *J* = 12.5, 6.3 Hz, 1H), 1.31 (d, *J* = 6.3 Hz, 6H).

¹⁹F NMR (377 MHz, CDCl₃) δ -101.3.

¹³C NMR (101 MHz, CDCl₃) δ 152.9, 142.5, 142.4, 132.4, 131.5, 129.8, 129.1 (t, *J*_{C-F} = 6.0 Hz), 120.3 (t, *J*_{C-F} = 22.8 Hz), 118.0, 69.6, 22.2.

HRMS Calcd for C₁₇H₁₆ClF₂NO₄S [M+Na⁺]: 426.0349; Found: 426.0358.



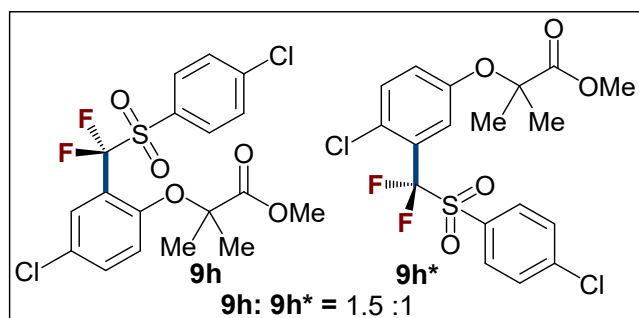
Isopropyl (3-chloro-4-(((4-chlorophenyl)sulfonyl)difluoromethyl)phenyl)carbamate, (9g), Yield: 31%.

¹H NMR (400 MHz, CDCl₃) δ 7.93 (d, *J* = 8.6 Hz, 2H), 7.71 – 7.50 (m, 4H), 7.37 (d, *J* = 9.5 Hz, 1H), 6.85 (s, 1H), 5.03 (dt, *J* = 12.5, 6.3 Hz, 1H), 1.31 (d, *J* = 6.3 Hz, 6H).

¹⁹F NMR (377 MHz, CDCl₃) δ -96.5.

¹³C NMR (101 MHz, CDCl₃) δ 152.6, 143.0, 142.7, 135.1 (t, *J*_{C-F} = 2.3 Hz), 132.4, 132.0 (t, *J*_{C-F} = 7.7 Hz), 131.5, 129.9, 121.8 (t, *J*_{C-F} = 290.4 Hz), 120.9, 118.1 (t, *J*_{C-F} = 21.6 Hz), 116.0, 70.0, 22.1.

HRMS Calcd for C₁₇H₁₅Cl₂F₂NO₄S [M+Na⁺]: 459.9965; Found: 459.9971.

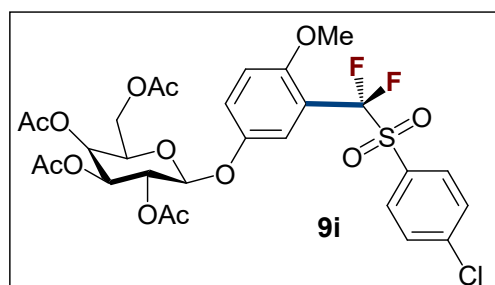


methyl 2-(4-chloro-2-(((4-chlorophenyl)sulfonyl)difluoromethyl)phenoxy)-2-methylpropanoate (**9h**);
methyl 2-(4-chloro-3-(((4-chlorophenyl)sulfonyl)difluoromethyl)phenoxy)-2-methylpropanoate (**9h***);
a mixture of **9h** and **9h*** in a ratio of 1.5:1.

9h **¹⁹F NMR** (377 MHz, CDCl₃) δ -96.6

9h* **¹⁹F NMR** (377 MHz, CDCl₃) δ -97.3

HRMS Calcd for C₁₈H₁₆Cl₂F₂O₅S [M+Na⁺]: 474.9956; Found: 474.9949.



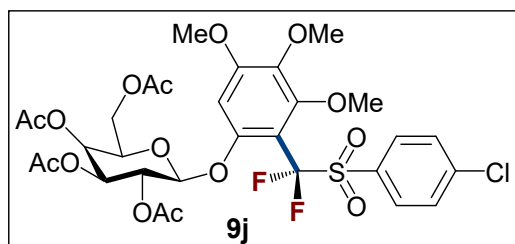
(2R,4S,5R,6S)-2-(acetoxymethyl)-6-(3-(((4-chlorophenyl)sulfonyl)difluoromethyl)-4-methoxyphenoxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate, (9i), Yield: 52%

¹H NMR (400 MHz, CDCl₃) δ 9.07 (dd, *J* = 8.8, 2.1 Hz, 1H), 9.01 (d, *J* = 2.2 Hz, 1H), 8.97 (s, 1H), 8.27 (s, 1H), 7.90 (d, *J* = 8.6 Hz, 2H), 7.61 – 7.49 (m, 2H), 7.13 (d, *J* = 8.9 Hz, 1H), 6.29 (d, *J* = 5.5 Hz, 1H), 6.00 (t, *J* = 5.5 Hz, 1H), 5.75 – 5.63 (m, 1H), 4.57 – 4.28 (m, 3H), 3.85 (s, 3H), 2.16 (s, 3H), 2.14 (s, 3H), 2.08 (s, 3H).

¹⁹F NMR (377 MHz, CDCl₃) δ -97.3.

¹³C NMR (101 MHz, CDCl₃) δ 170.5, 169.8, 169.5, 160.9, 152.7 (t, *J*_{C-F} = 58.5 Hz), 142.7, 142.1, 136.0, 132.4, 132.2, 132.1 (t, *J*_{C-F} = 8.2 Hz), 131.3, 129.5, 128.1, 122.4 (t, *J*_{C-F} = 289.7 Hz), 115.5 (t, *J*_{C-F} = 20.9 Hz), 112.5, 86.4, 80.5, 73.1, 70.8, 63.2, 56.3, 20.9, 20.7, 20.5.

HRMS Calcd for C₂₈H₂₉ClF₂O₁₃S [M+Na⁺]: 701.0878; Found: 701.0900.



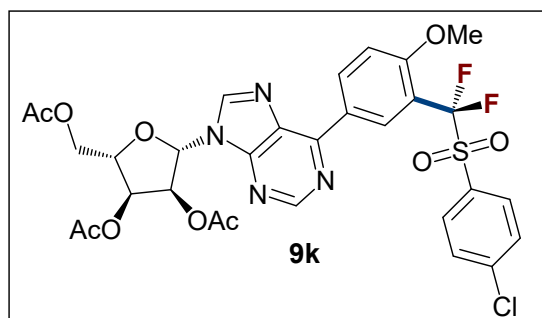
(2R,4S,5R,6S)-2-(acetoxymethyl)-6-(2-(((4-chlorophenyl)sulfonyl)difluoromethyl)-3,4,5-trimethoxyphenoxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate, (9j), Yield: 43%

¹H NMR (400 MHz, CDCl₃) δ 8.91 (s, 1H), 8.20 (s, 1H), 7.84 (d, *J* = 8.7 Hz, 2H), 7.46 (d, *J* = 8.7 Hz, 2H), 6.69 (s, 1H), 6.24 (d, *J* = 4.7 Hz, 1H), 6.04 – 5.90 (m, 1H), 5.69 (t, *J* = 5.3 Hz, 1H), 4.52 – 4.43 (m, 2H), 4.37 (dd, *J* = 12.9, 5.1 Hz, 1H), 3.96 (s, 3H), 3.88 (s, 3H), 3.85 (s, 3H), 2.14 (s, 3H), 2.10 (s, 3H), 2.08 (s, 3H).

¹⁹F NMR (377 MHz, CDCl₃) δ -84.9.

¹³C NMR (101 MHz, CDCl₃) δ 170.4, 169.7, 169.5, 158.4, 156.2, 154.5 (t, *J* = 3.6 Hz), 151.9, 150.9, 143.3, 143.2, 141.5, 133.6, 132.1, 131.0, 129.2, 123.5 (t, *J* = 292.6 Hz), 113.5 (t, *J* = 20.0 Hz), 110.4, 86.9, 80.3, 73.3, 70.4, 62.9, 62.0, 60.9, 56.3, 20.8, 20.6, 20.5.

HRMS Calcd for C₃₀H₃₃ClF₂O₁₅S [M+Na⁺]: 761.1089; Found: 761.1103.



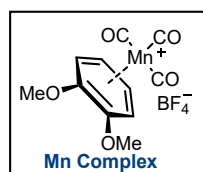
(2S,3S,4S,5S)-2-(acetoxymethyl)-5-(6-(3-(((4-chlorophenyl)sulfonyl)difluoromethyl)-4-methoxyphenyl)-9H-purin-9-yl)tetrahydrofuran-3,4-diyl diacetate, (9k), Yield: 76%

¹H NMR (400 MHz, CDCl₃) δ 9.07 (dd, *J* = 8.8, 2.1 Hz, 1H), 9.01 (d, *J* = 2.2 Hz, 1H), 8.97 (s, 1H), 8.27 (s, 1H), 7.90 (d, *J* = 8.6 Hz, 2H), 7.56 – 7.49 (m, 2H), 7.13 (d, *J* = 8.9 Hz, 1H), 6.29 (d, *J* = 5.5 Hz, 1H), 6.00 (t, *J* = 5.5 Hz, 1H), 5.76 – 5.57 (m, 1H), 4.55 – 4.32 (m, 3H), 3.85 (s, 3H), 2.15 (d, *J* = 6.9 Hz, 6H), 2.08 (s, 3H).

¹⁹F NMR (377 MHz, CDCl₃) δ -97.3.

¹³C NMR (101 MHz, CDCl₃) δ 170.5, 169.7, 169.5, 160.9, 152.71 (t, *J*_{C-F} = 58.5 Hz), 142.7, 142.4 (d, *J*_{C-F} = 52.0 Hz), 136.0, 132.4, 132.2, 131.3, 132.1 (t, *J*_{C-F} = 8.2 Hz), 129.5, 128.1, 122.4 (t, *J*_{C-F} = 289.7 Hz), 115.5 (t, *J* = 20.9 Hz), 112.5, 86.4, 80.5, 73.1, 70.8, 63.2, 56.3, 20.9, 20.7, 20.5.

HRMS Calcd for C₃₀H₂₇ClF₂N₄O₁₀S [M+Na⁺]: 731.0997; Found: 731.0974.

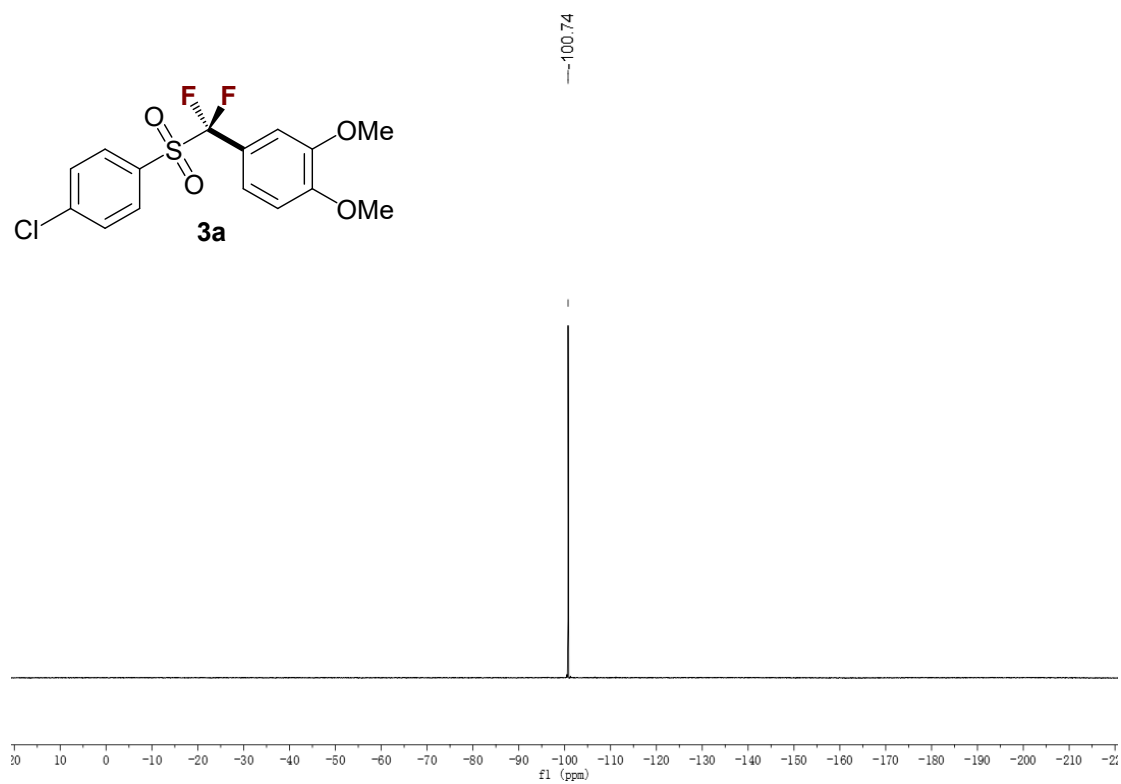
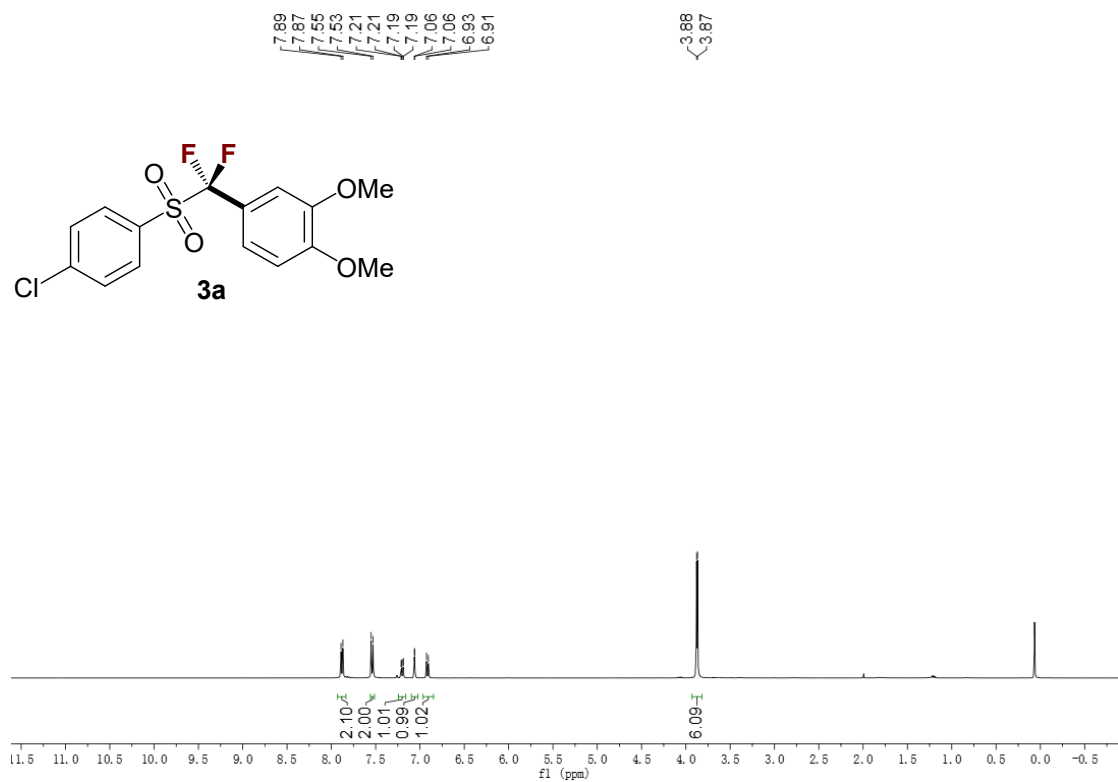


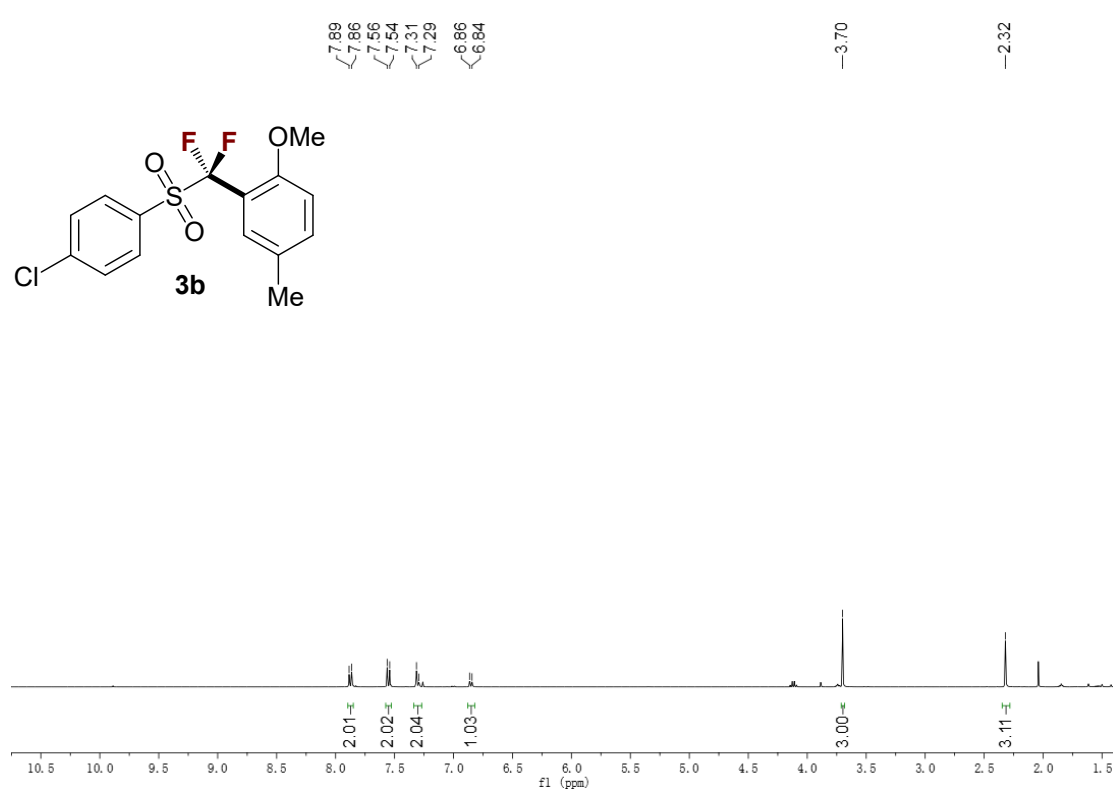
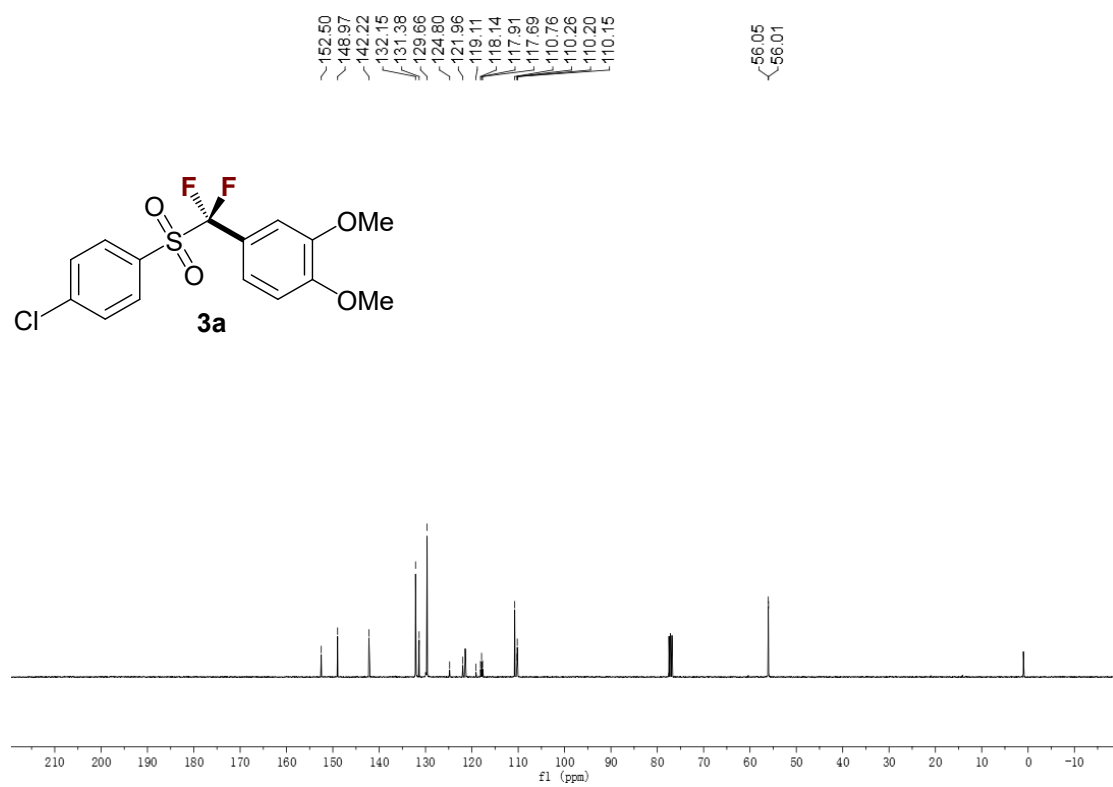
¹H NMR (400 MHz, Acetone) δ 6.83 (s, 2H), 6.48 (s, 2H), 4.19 (s, 6H).

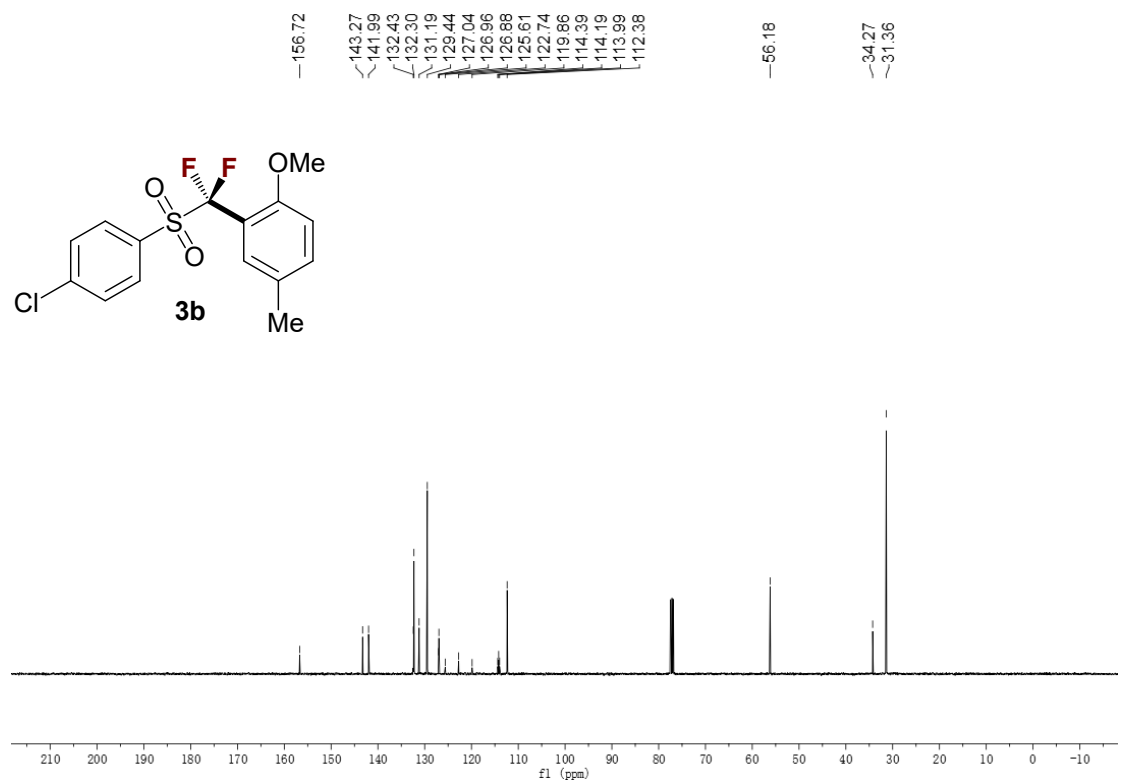
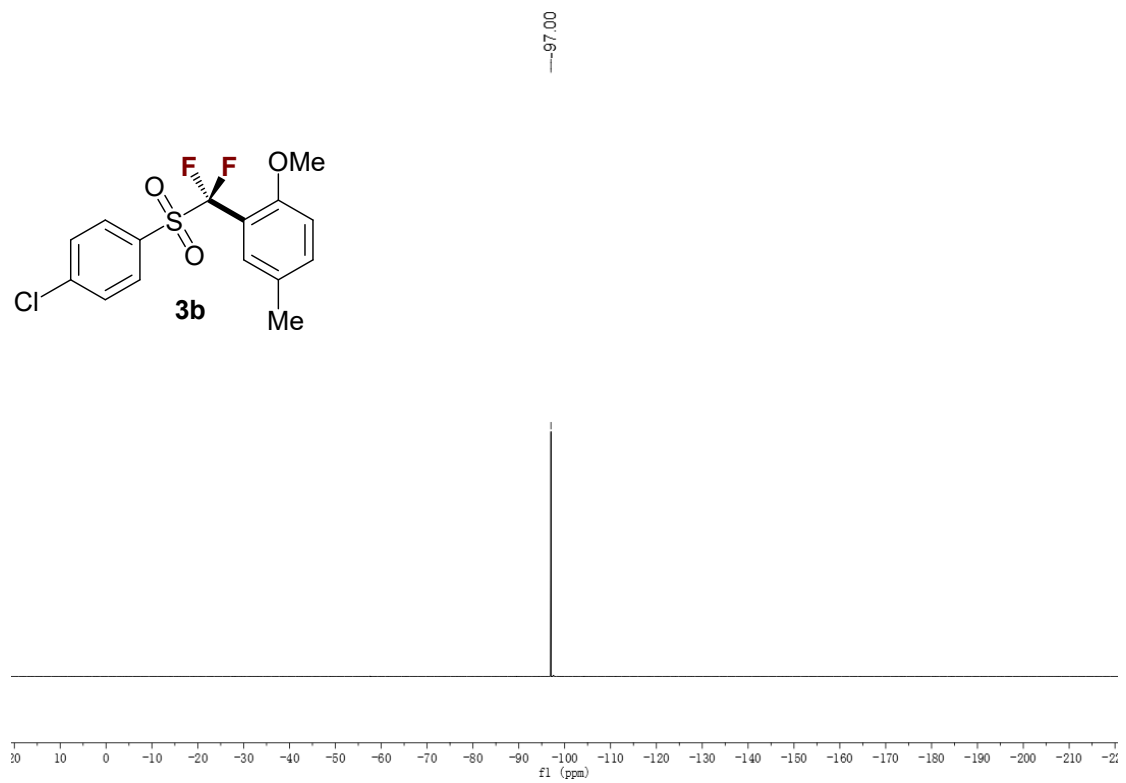
13. Reference

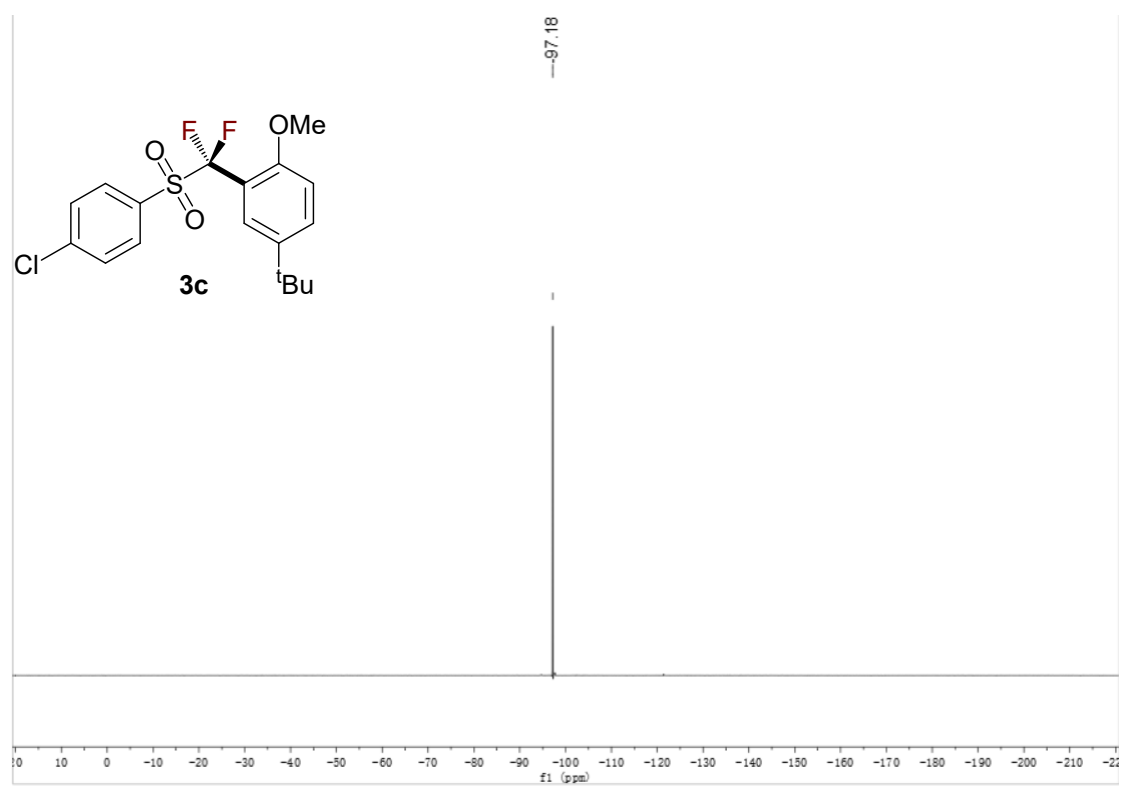
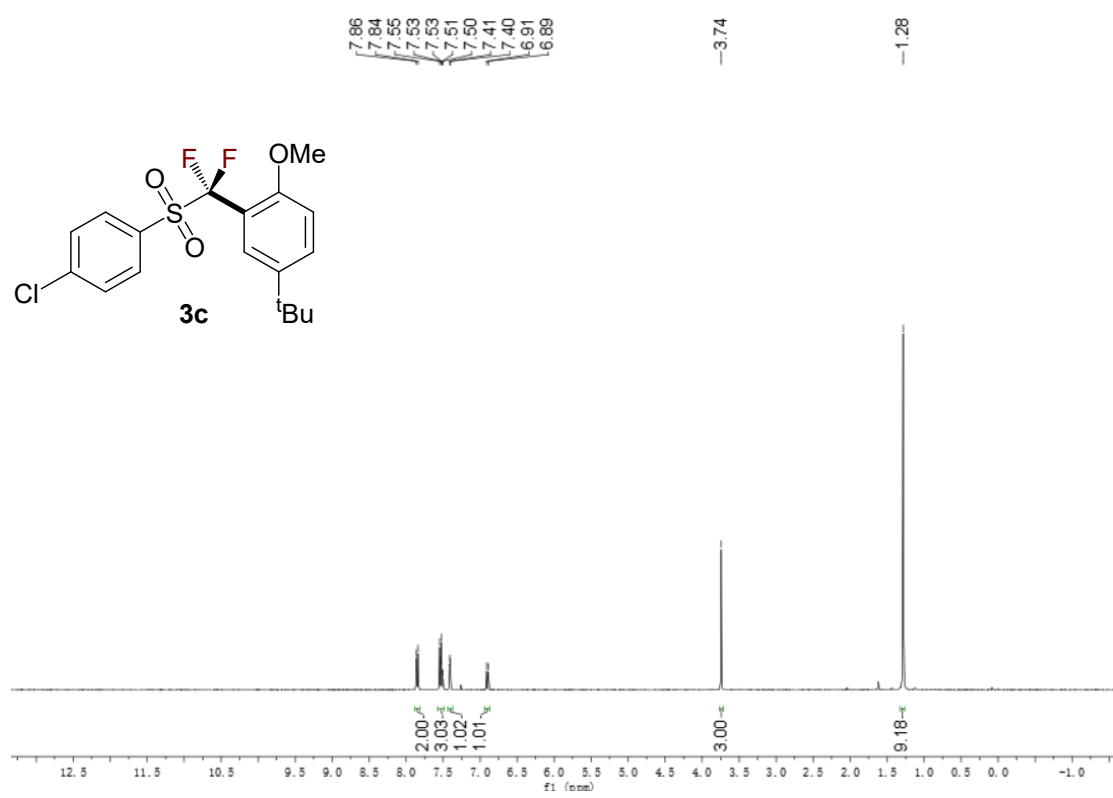
- 1) J. Han, J. Han, S. Chem, T. Zhong, Y. J. He, X. L. Yang, G. Q. Wang, C. J. Zhu, J. Xie. *Nat. Synth.* **2022**, *1*, 475-486.
- 2) J. J. Yu, X. Zhang, X. X. Wu, T. Liu, Z. Q. Zhang, J. Wu, C. Zhu. *Chem.* **2023**, *9*, 472-482.
- 3) X. P. Jiang, Y. Q. Q. Jiang, Q. Q. Liu, B. Li, D. Q. Shi, Y. S. Zhao. *J. Org. Chem.* **2022**, *87*, 3546-3554.
- 4) Z. Q. Wei, Z. Z. Lou, C. F. Ni, W. Zhang, J. B. Hu. *Chem. Commun.* **2022**, *58*, 10024-10027.
- 5) a) K. Li, W. Q. Wu, Y. Z. Lin, H. Shi. *Nat. Commun.* **2023**, *14*, 2170; b) S.H. Sun, L. K. Yeung, D. A. Sweigart. *Organometallics.* **1995**, *14*, 2613-2615.

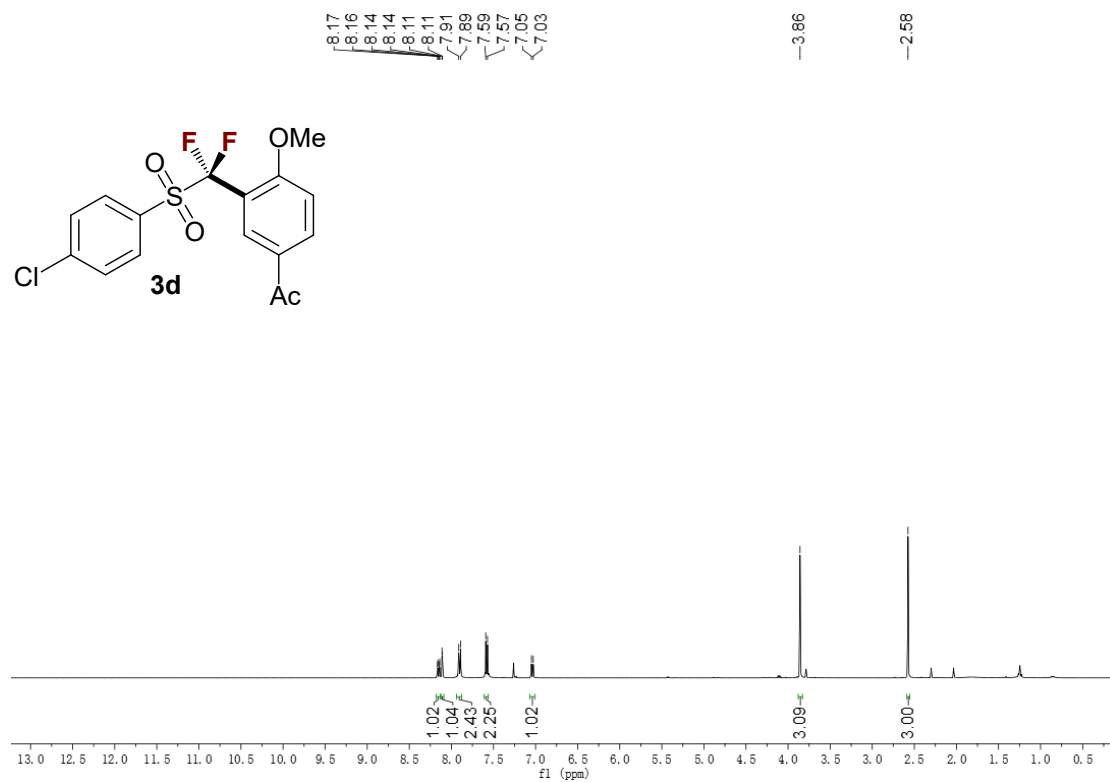
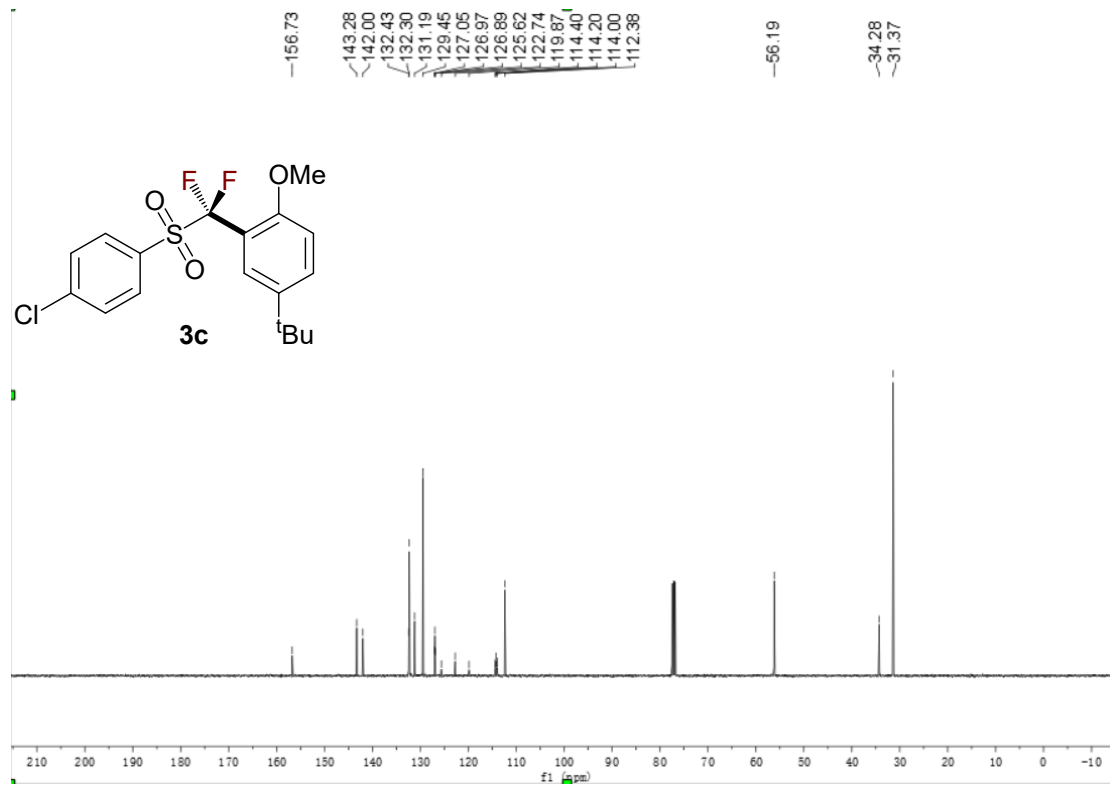
14. Copies of NMR spectra

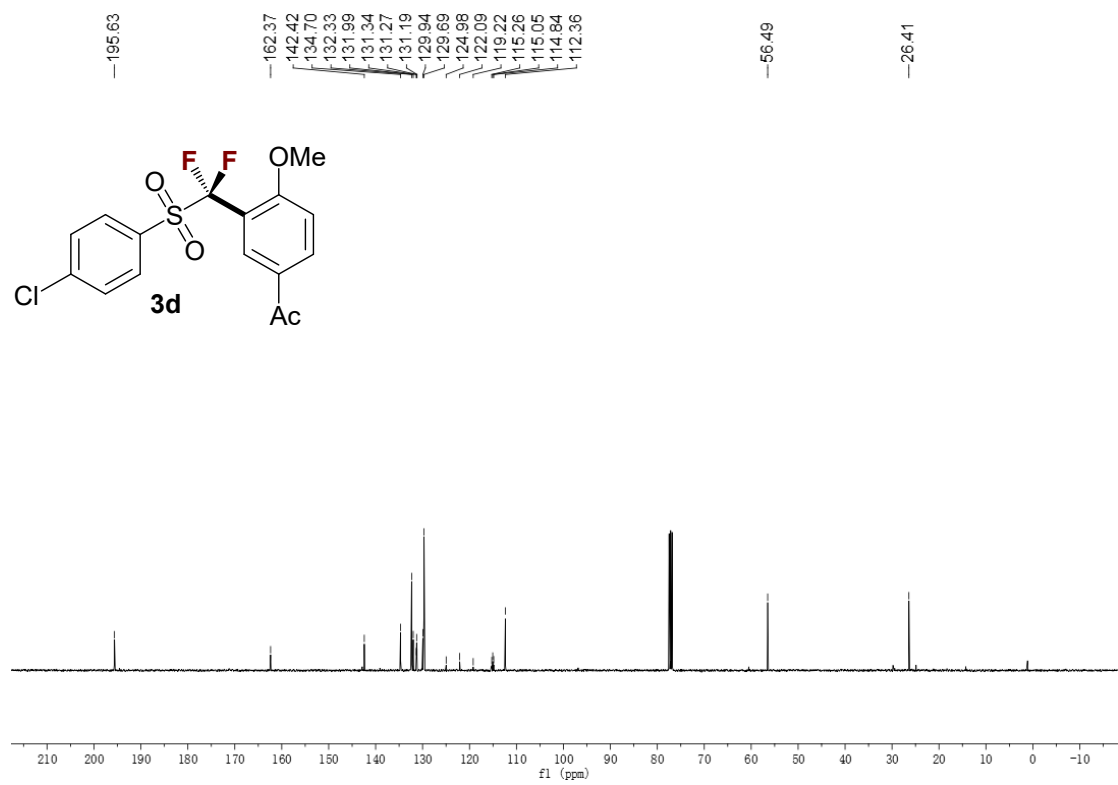
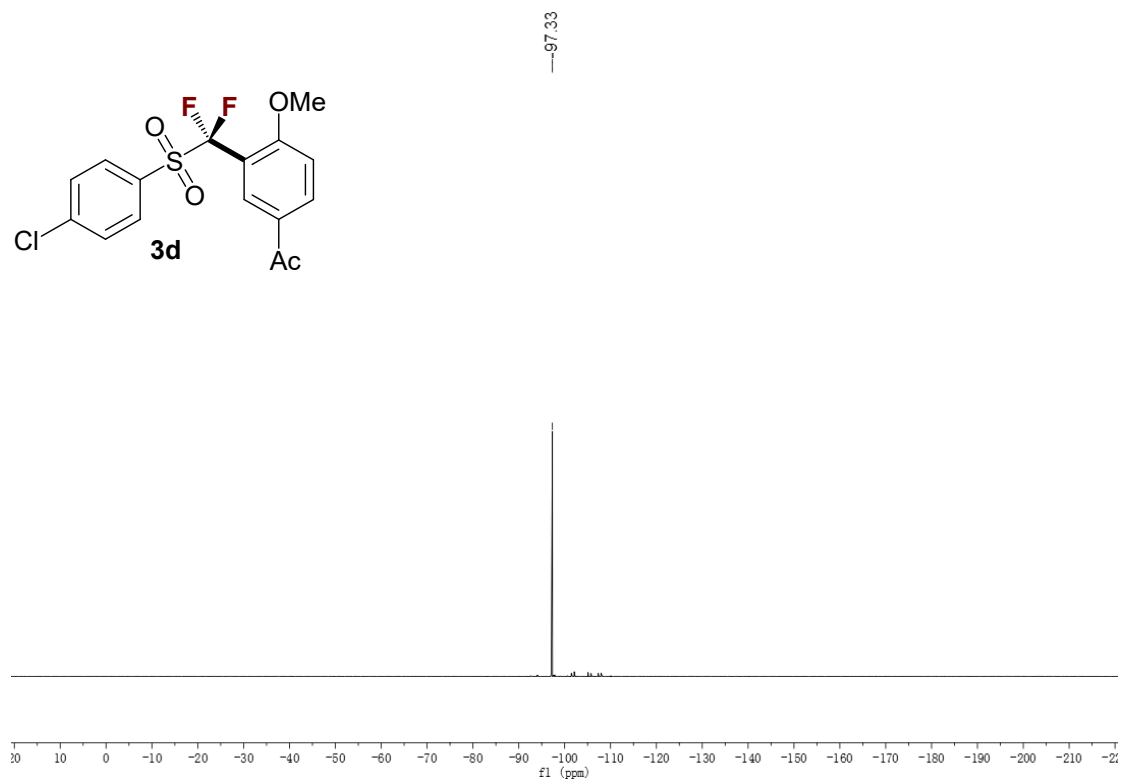


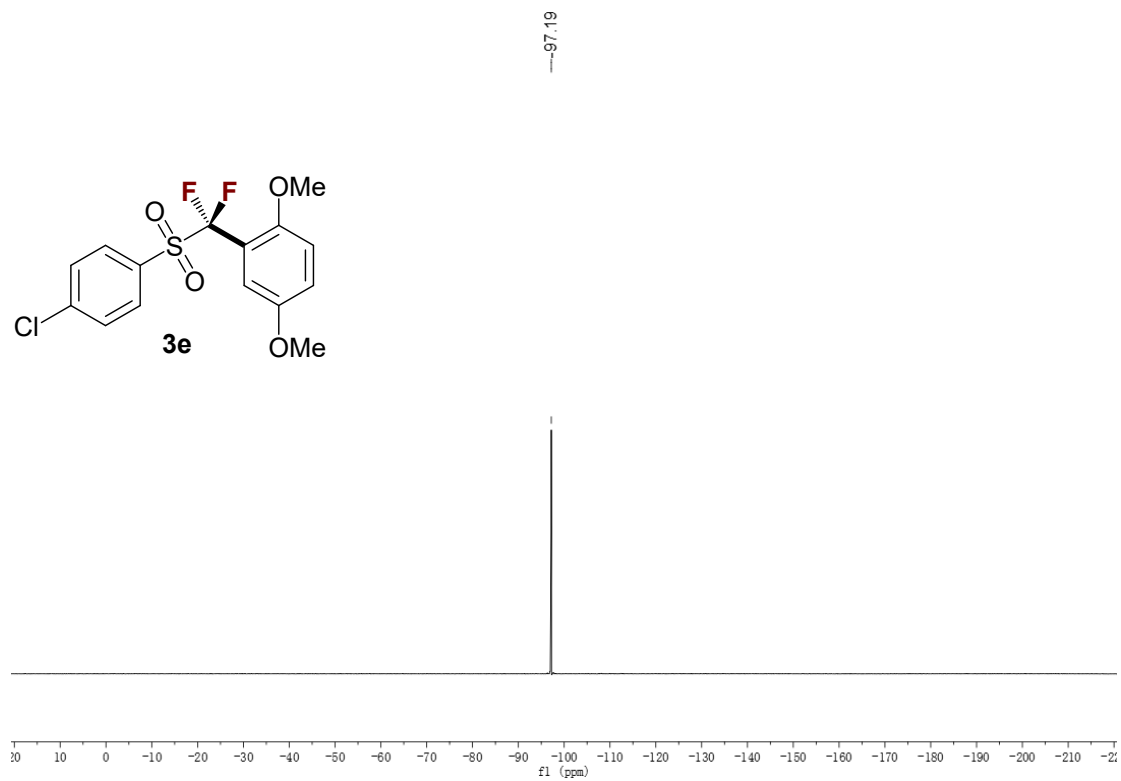
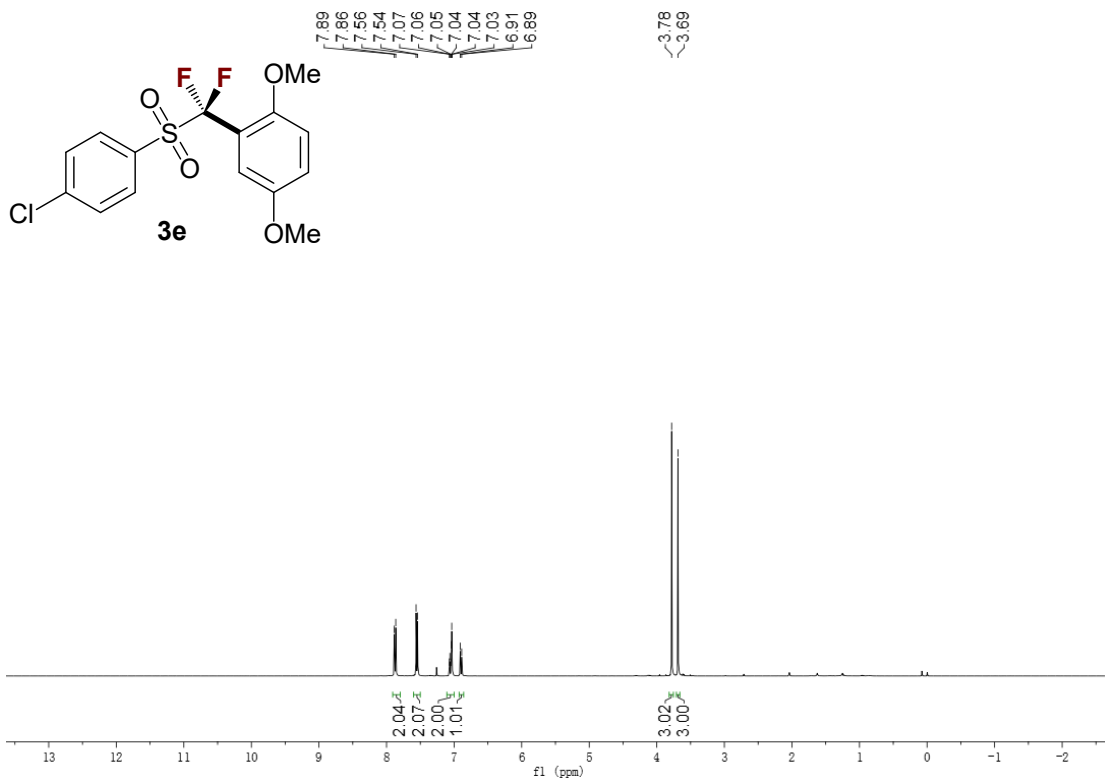


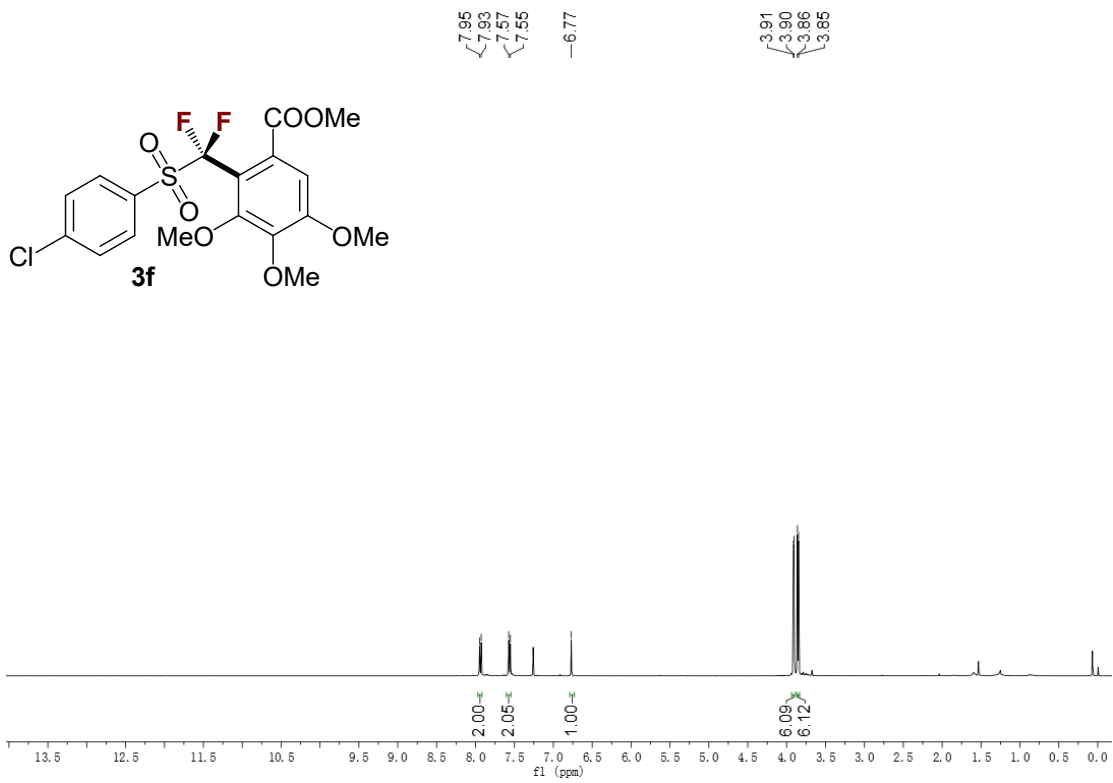
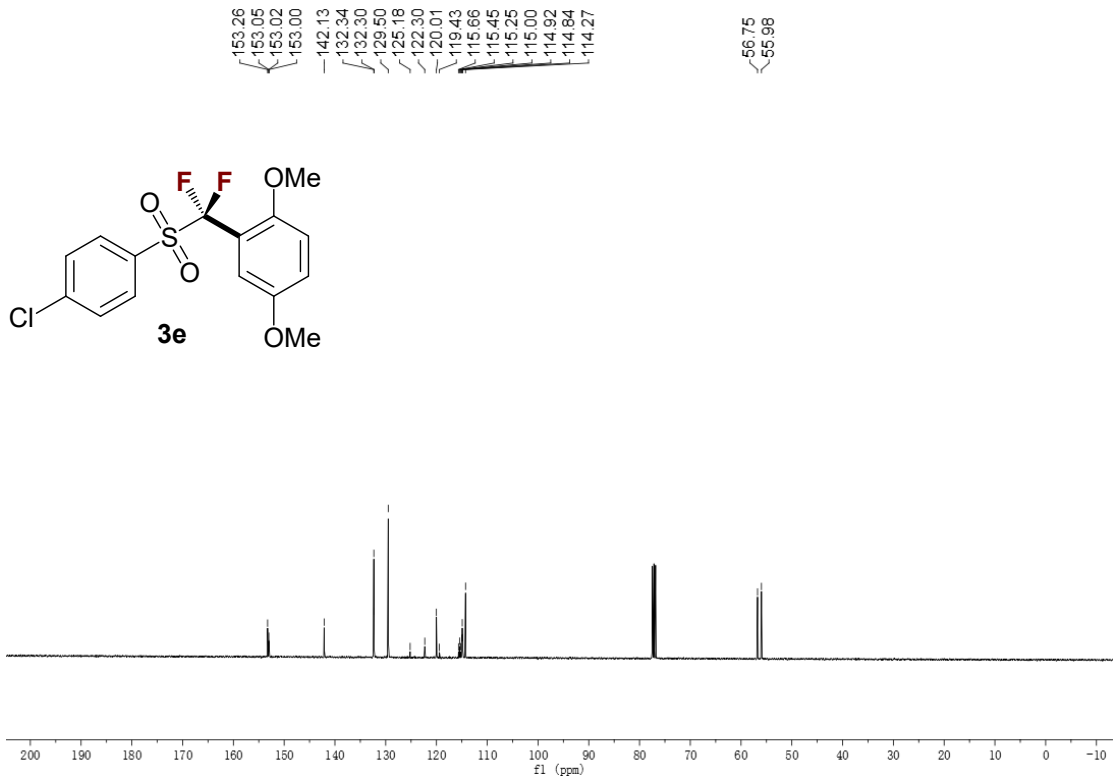


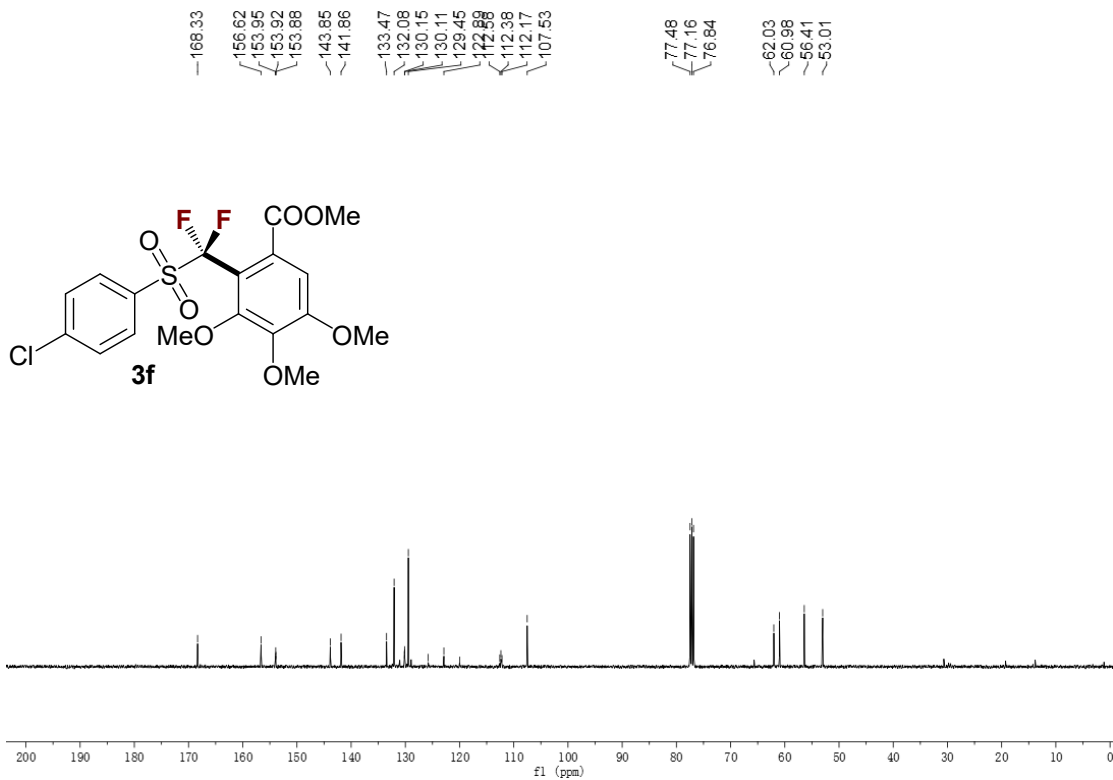
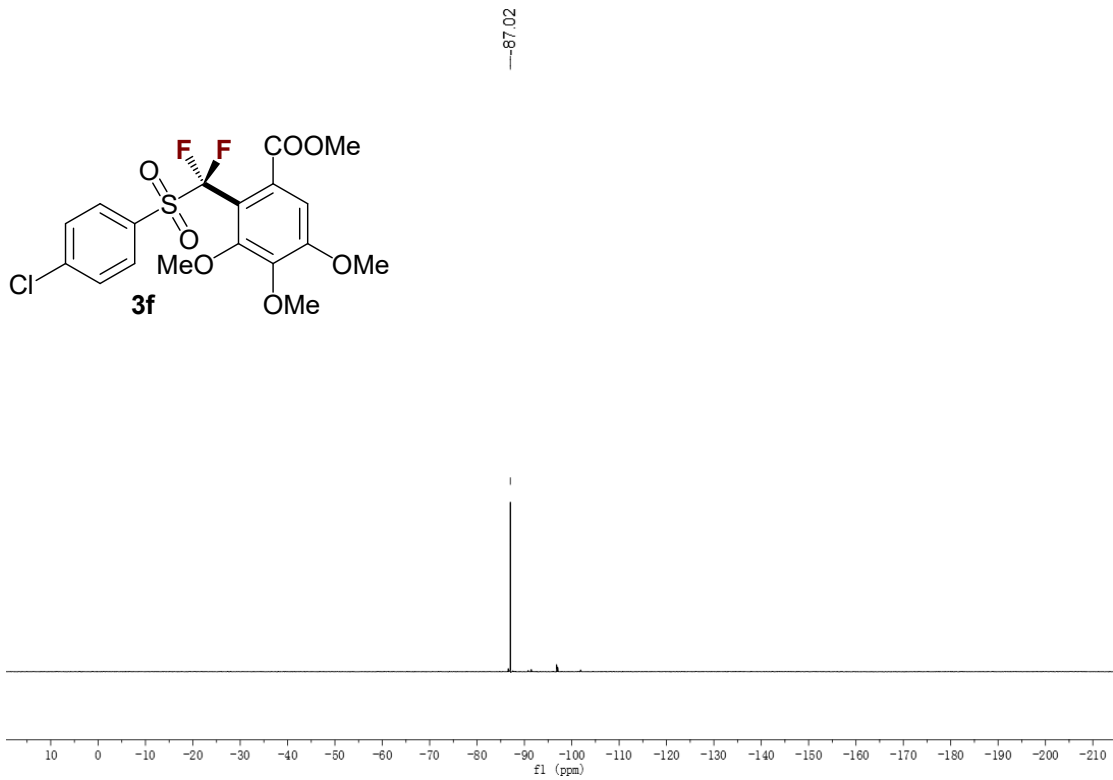


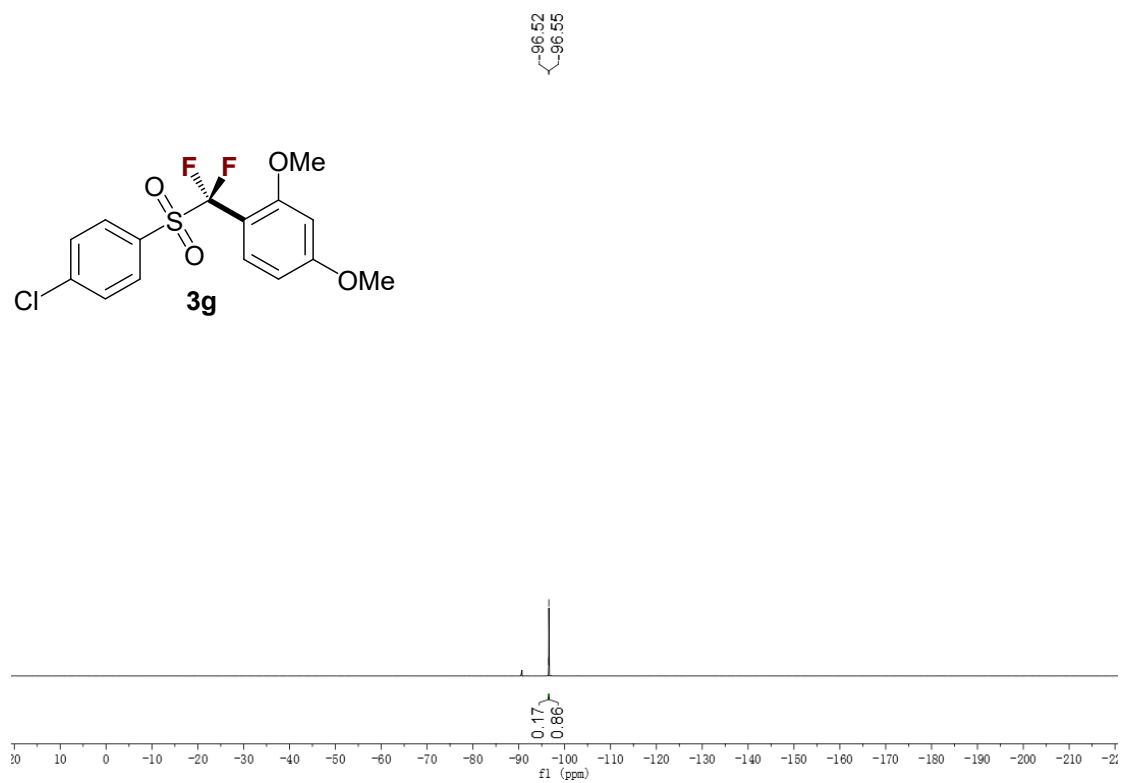
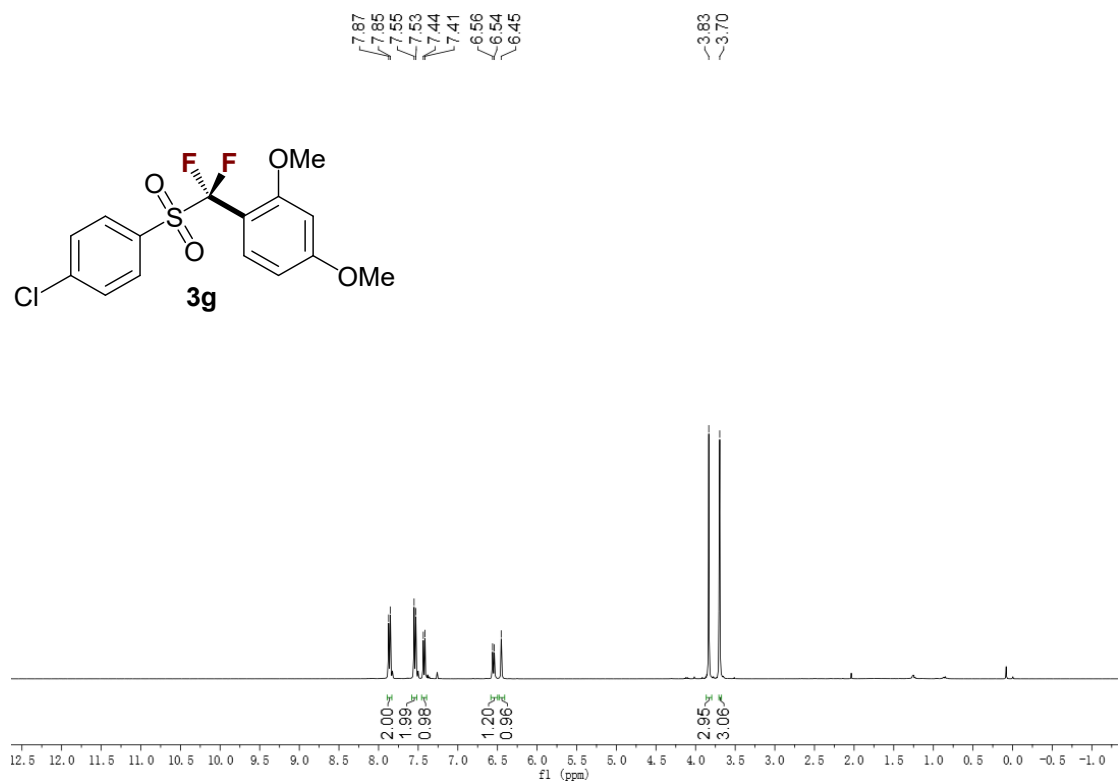




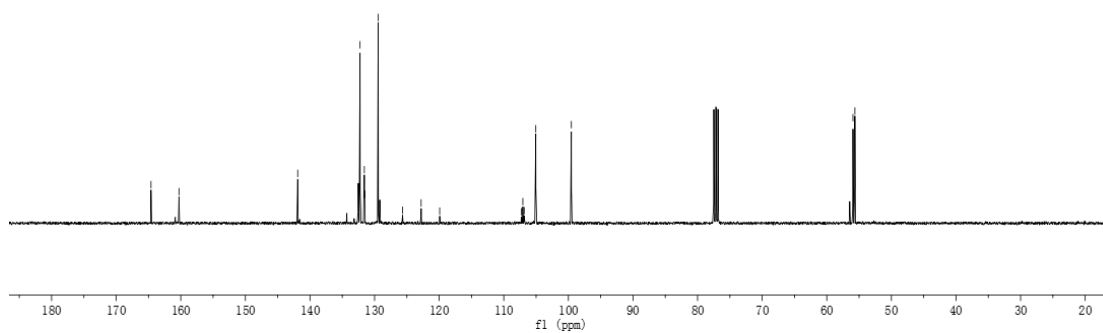
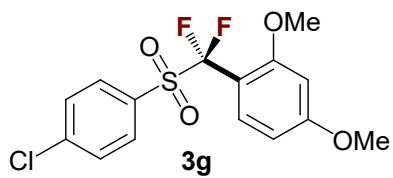




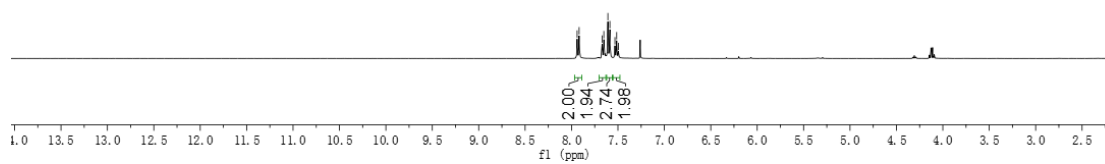
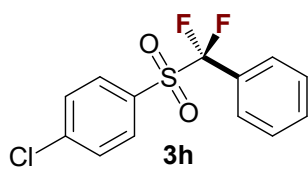


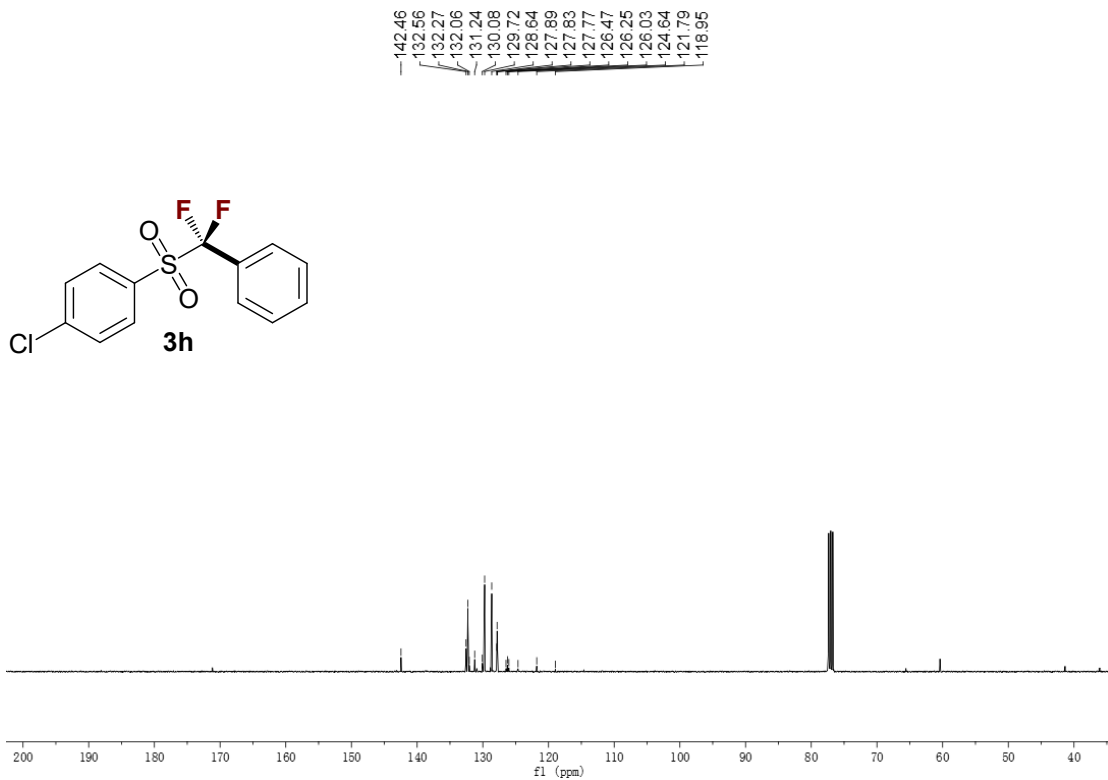
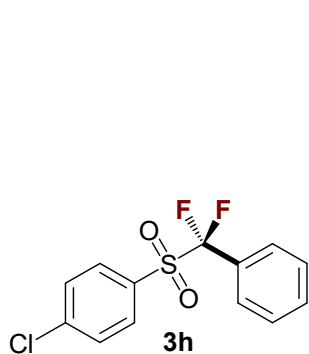
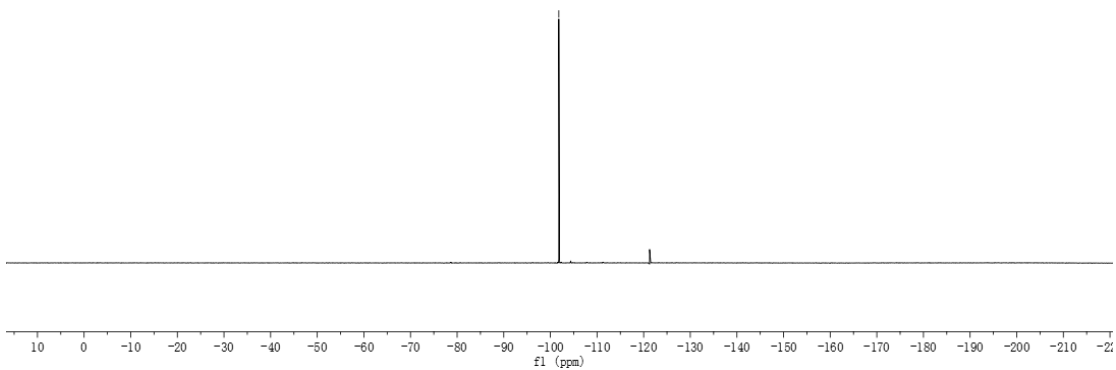
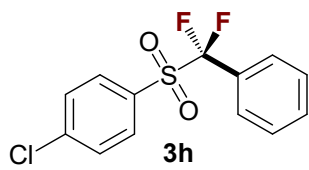


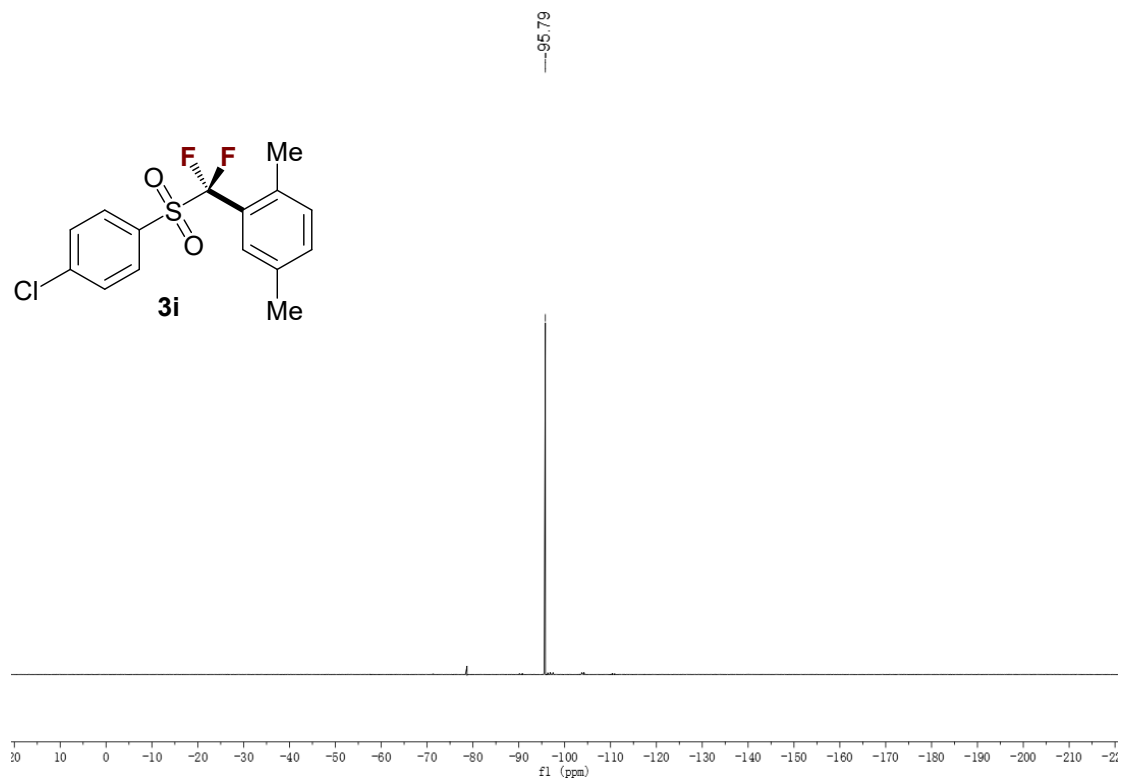
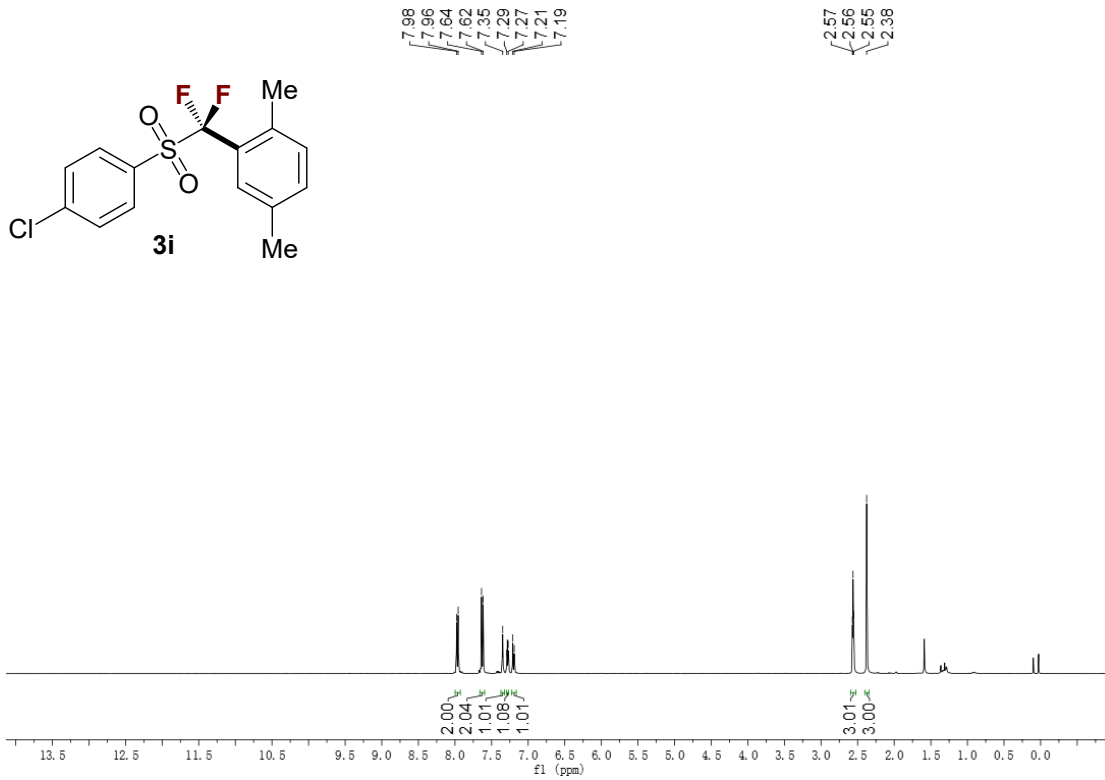
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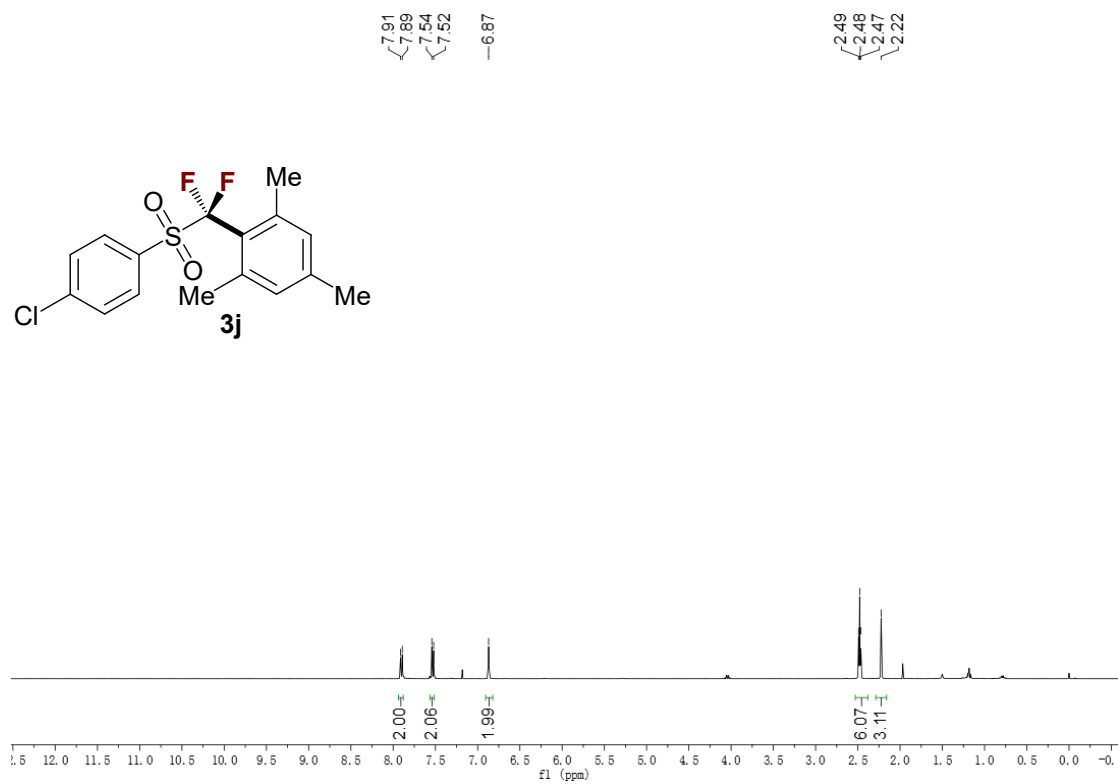
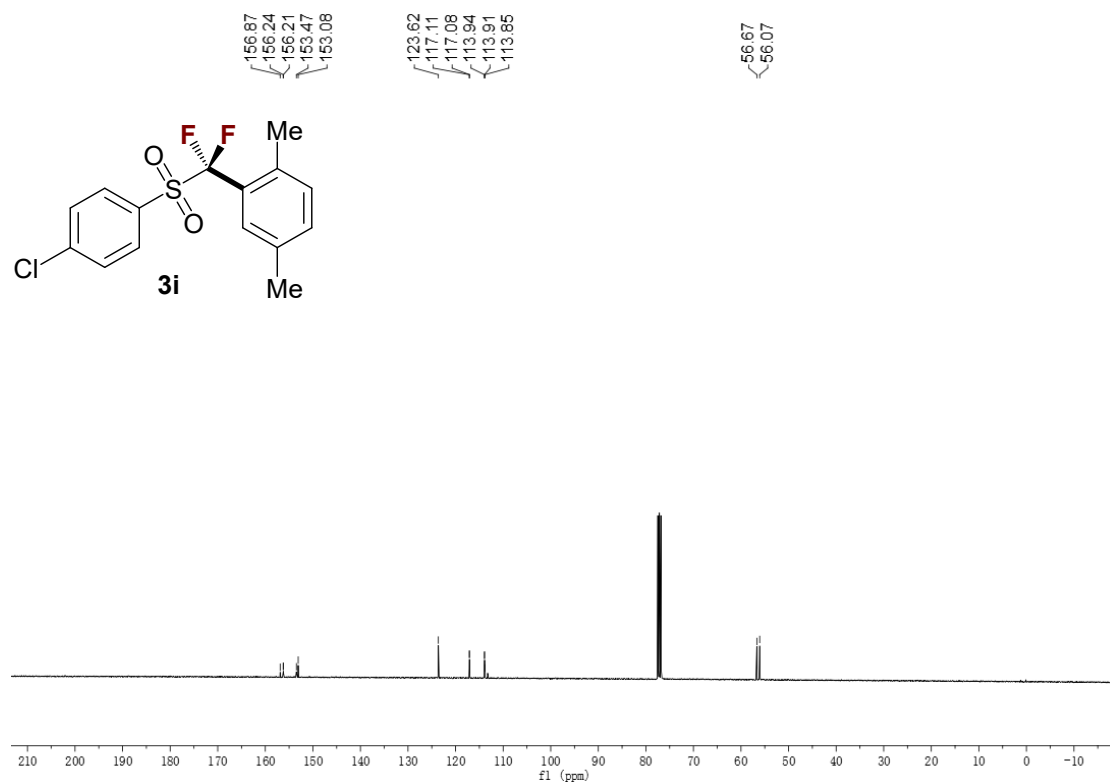


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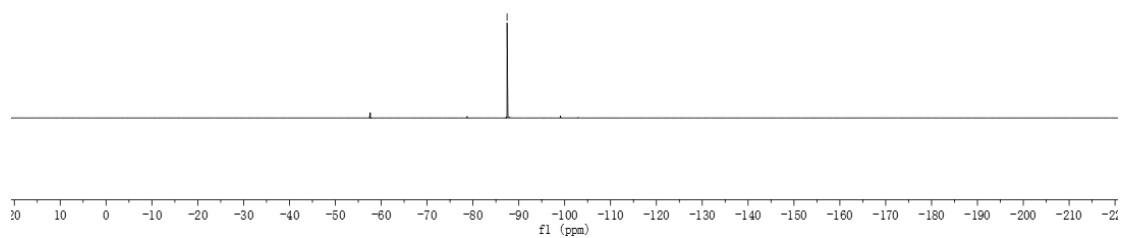
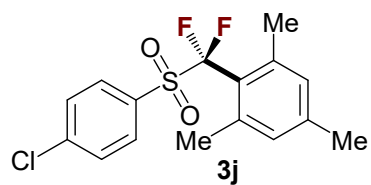






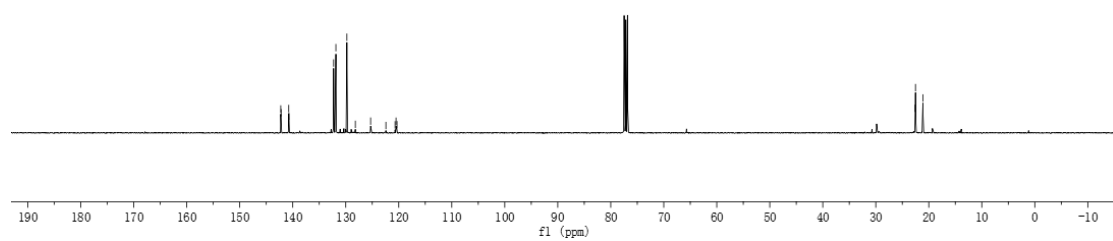
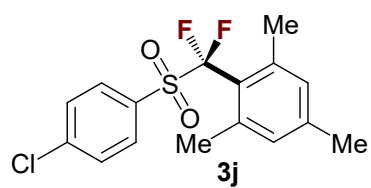


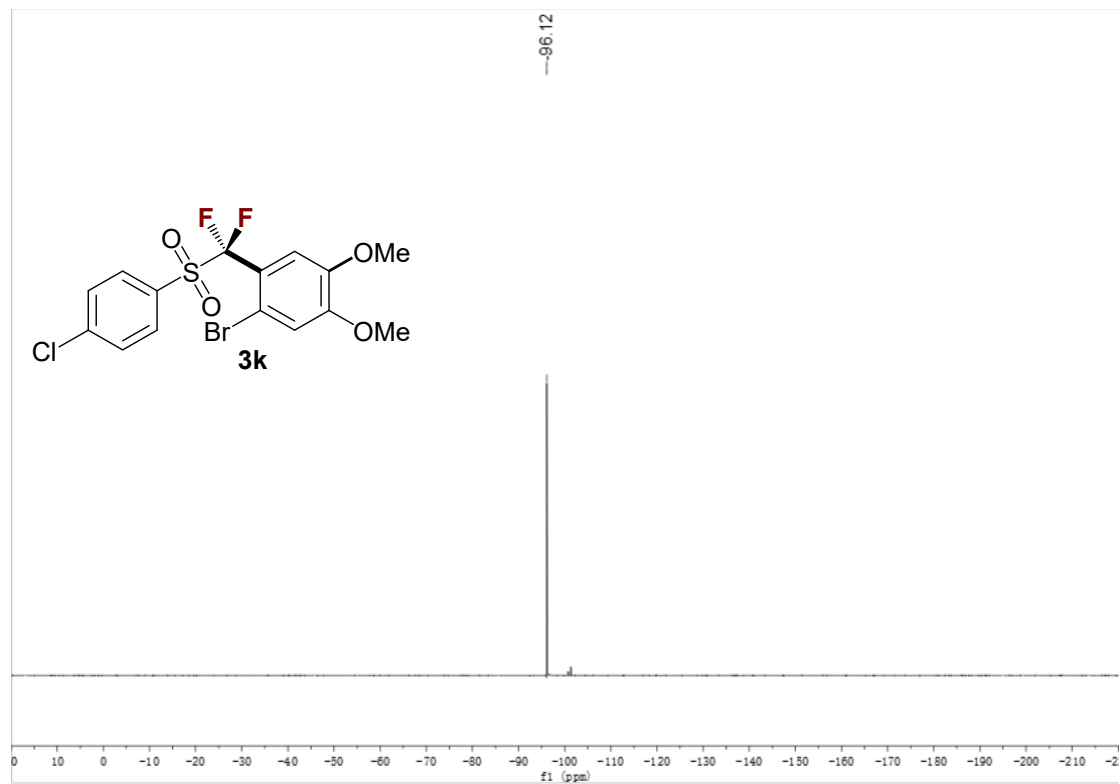
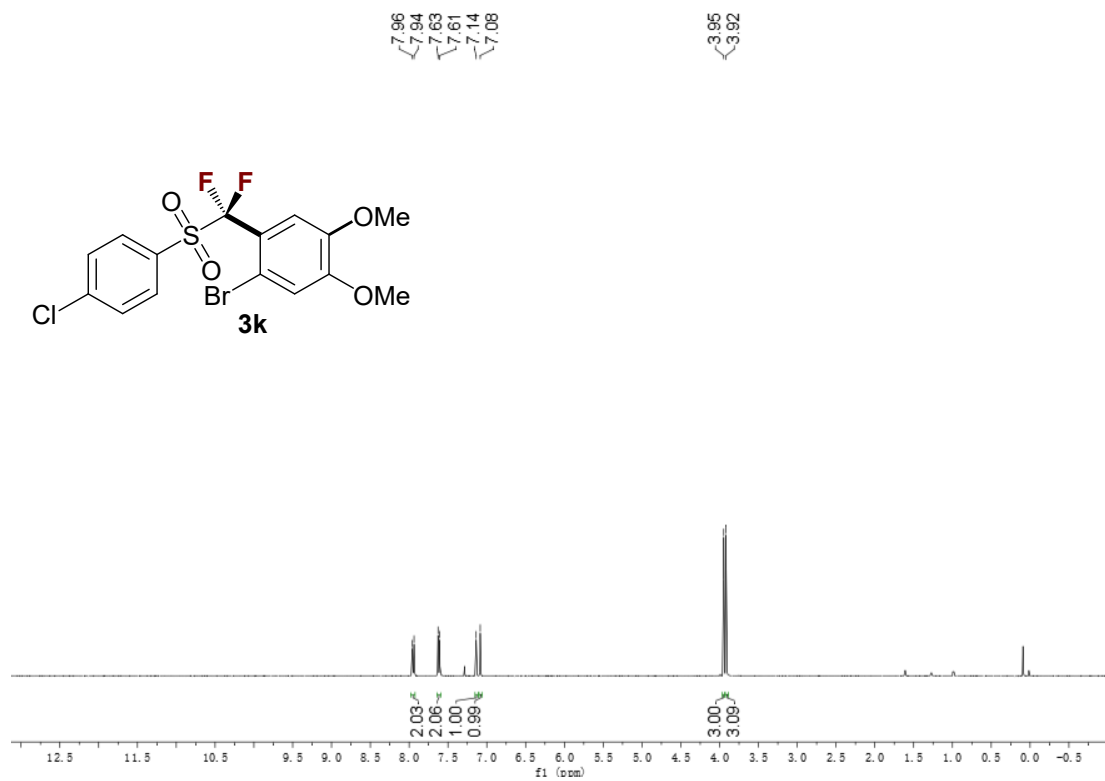
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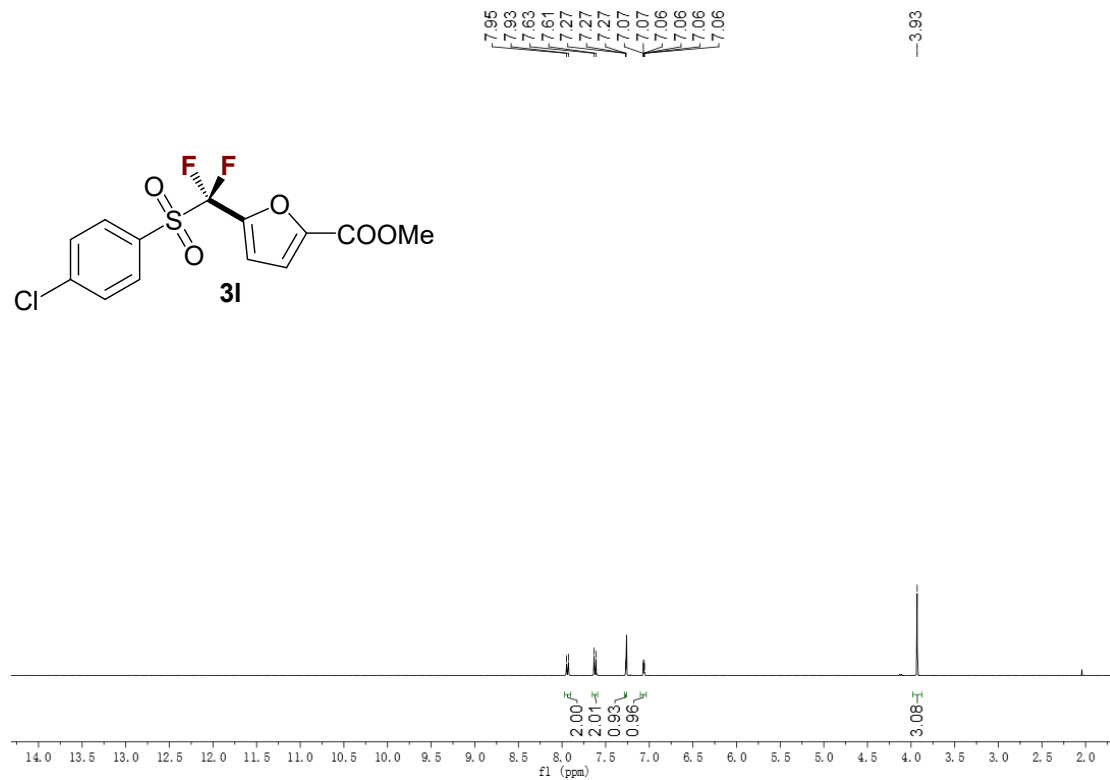
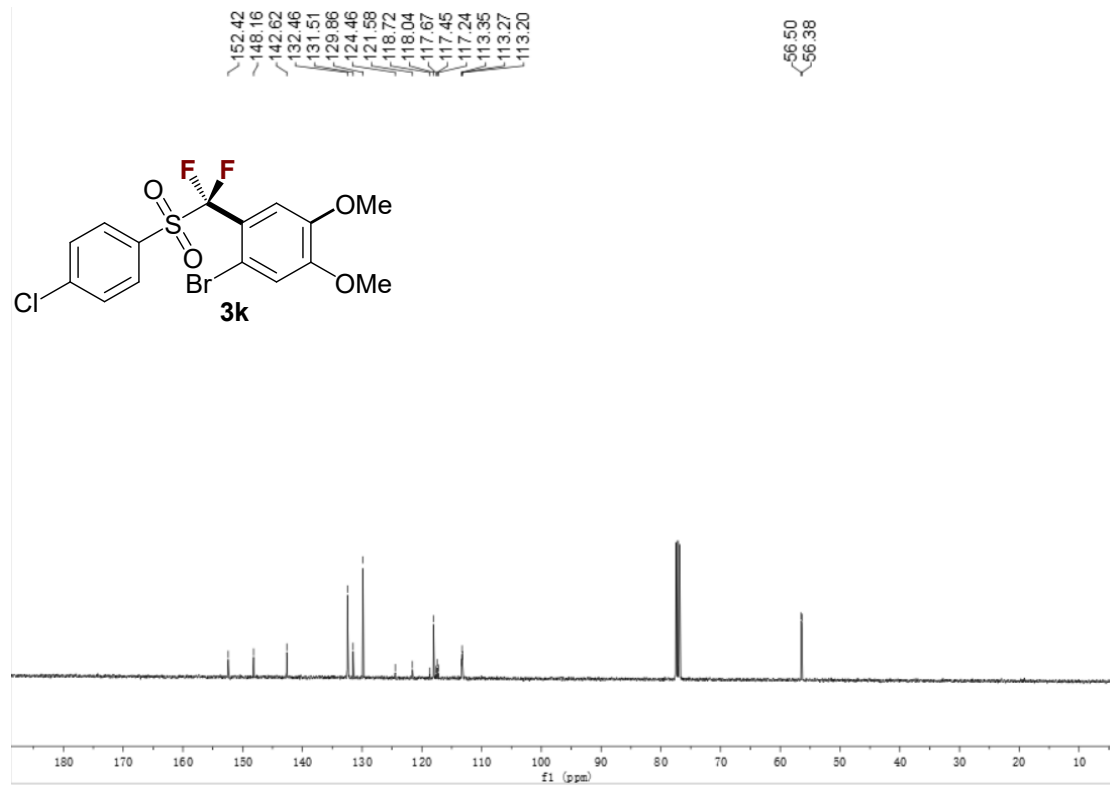


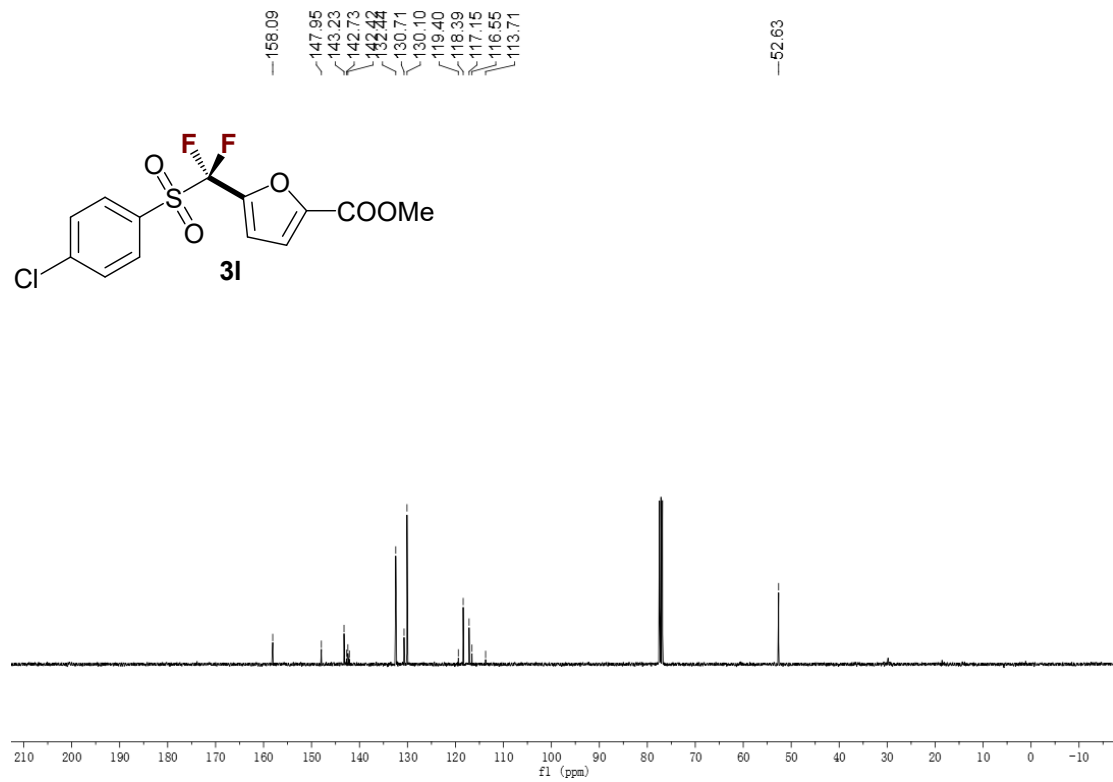
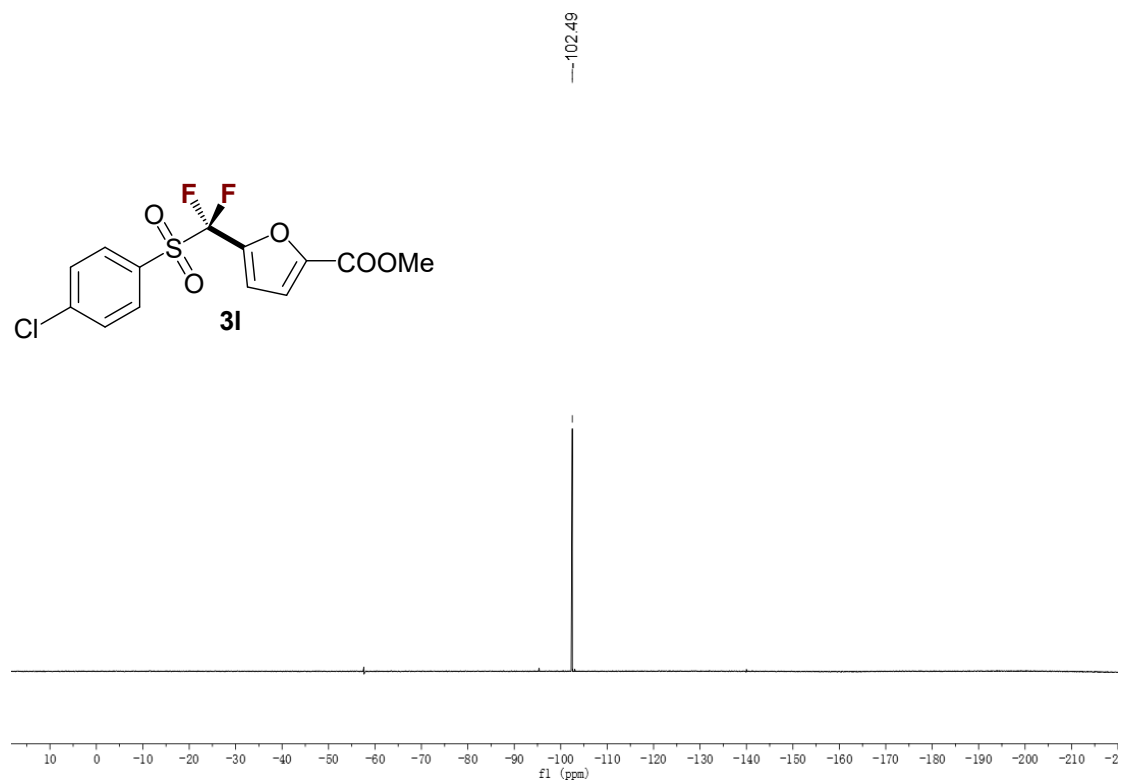
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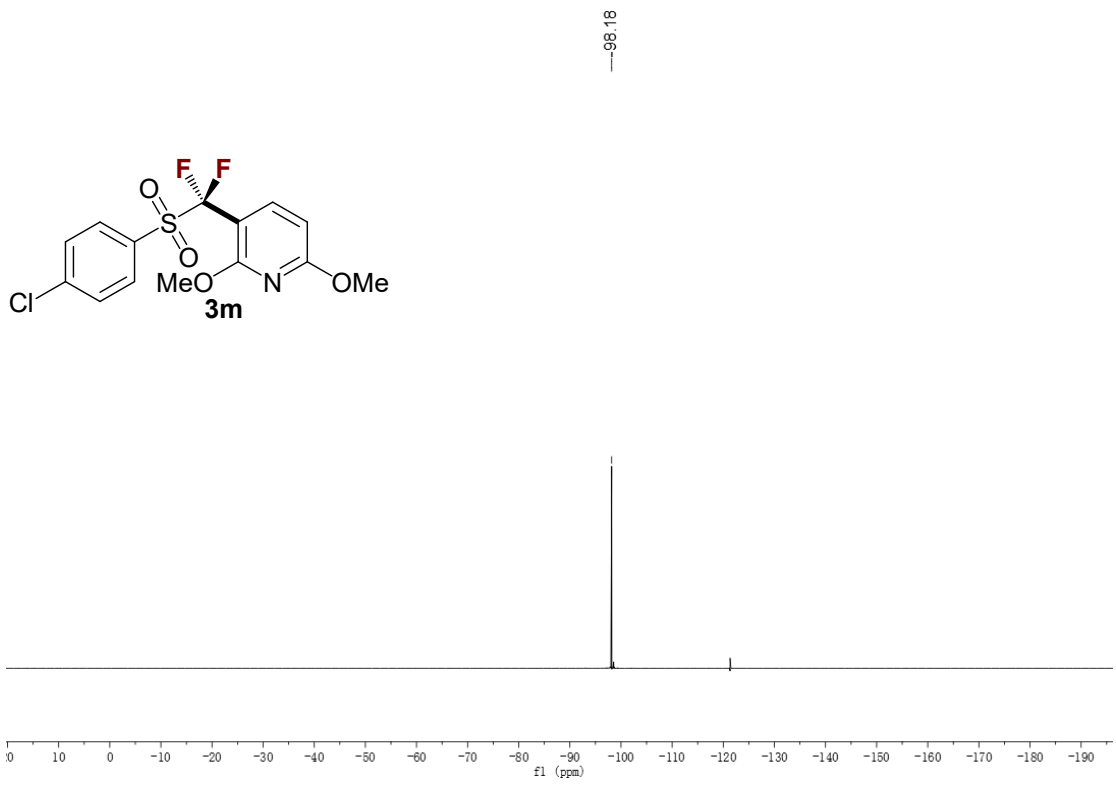
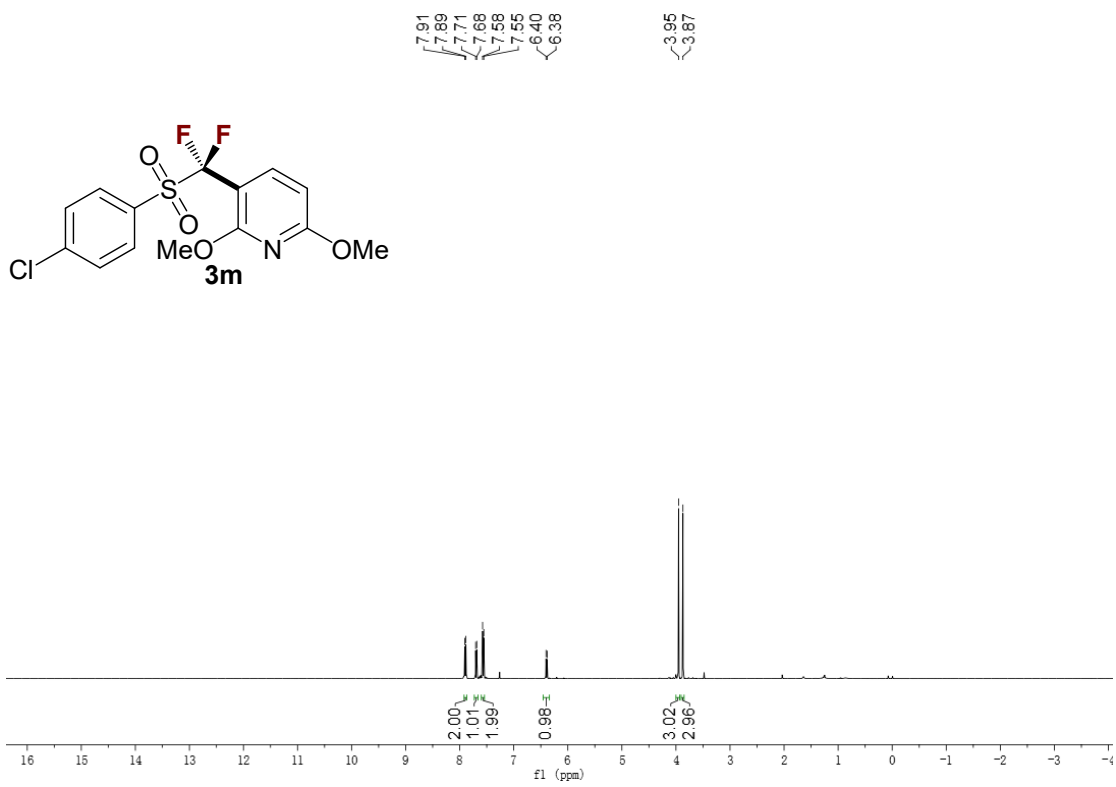
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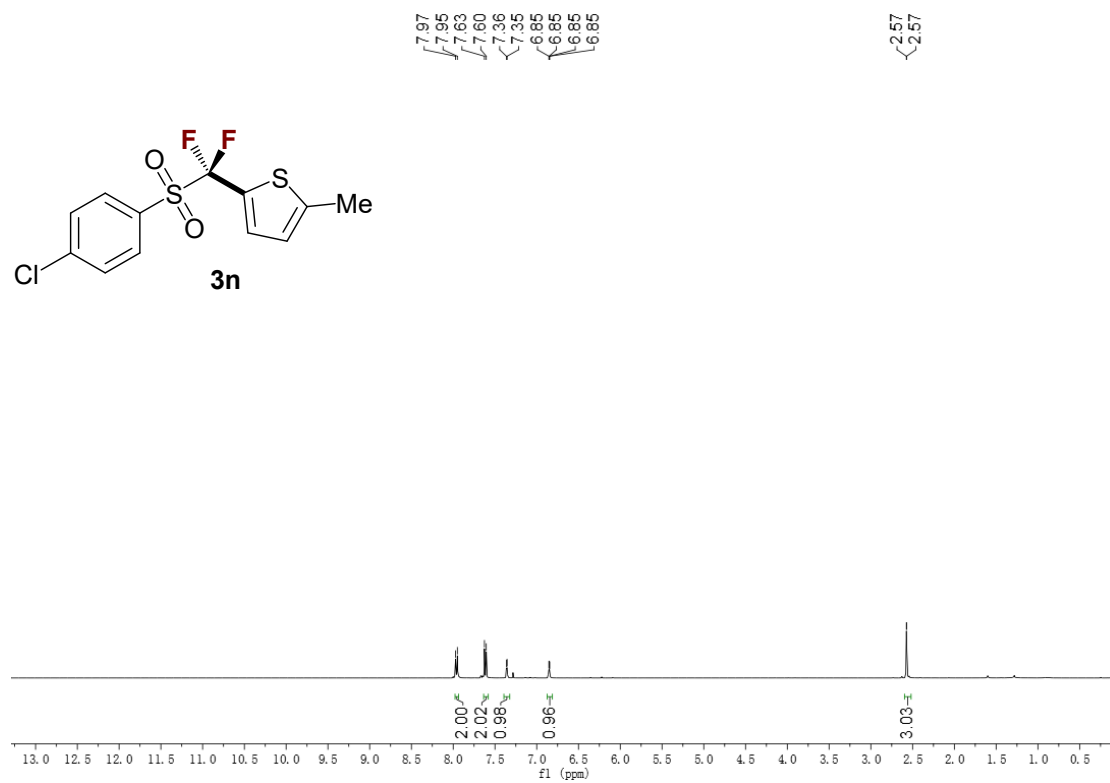
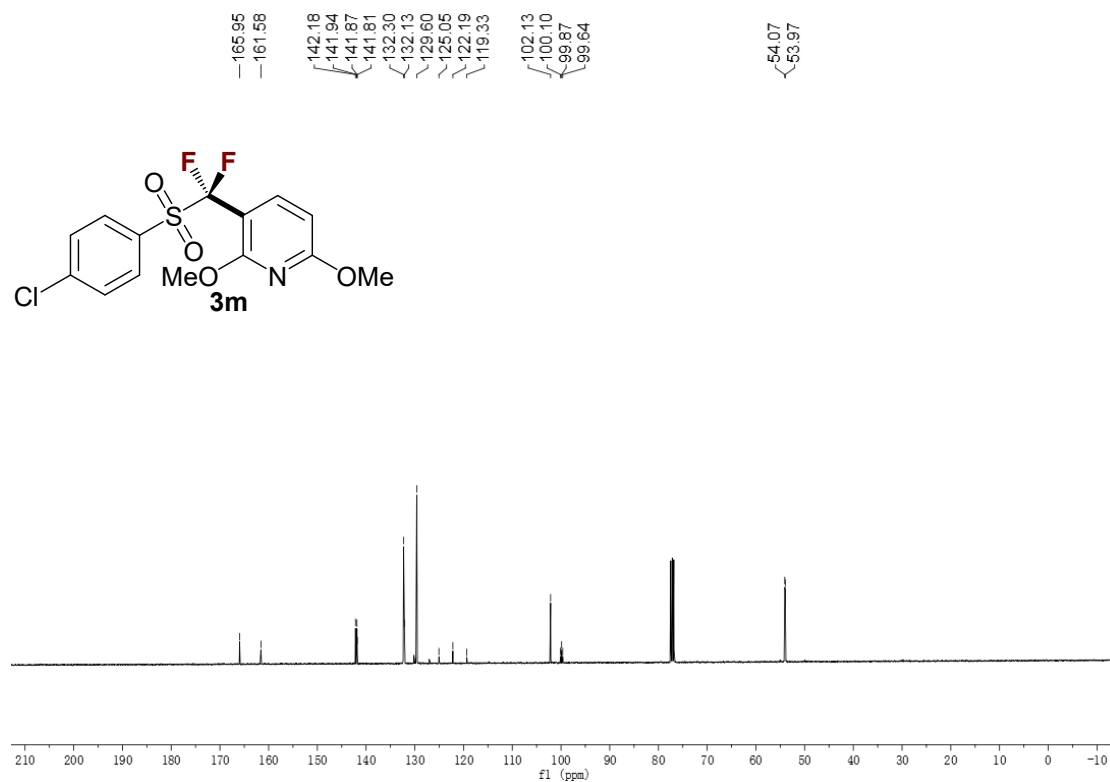


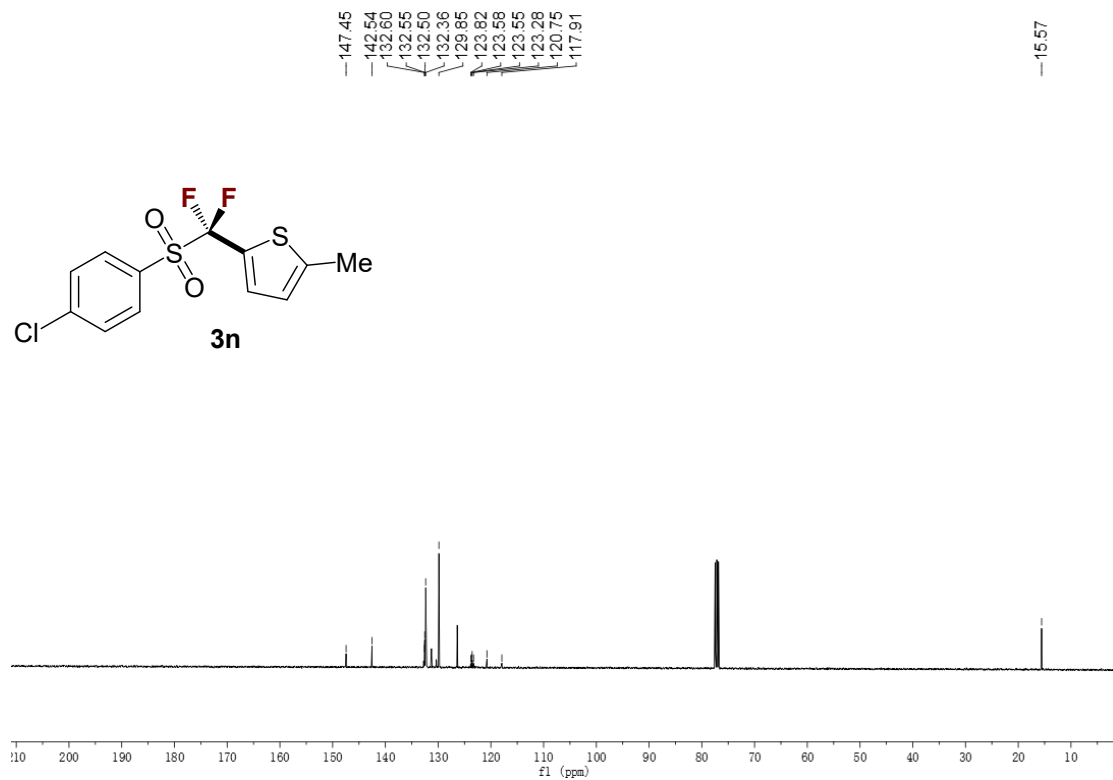
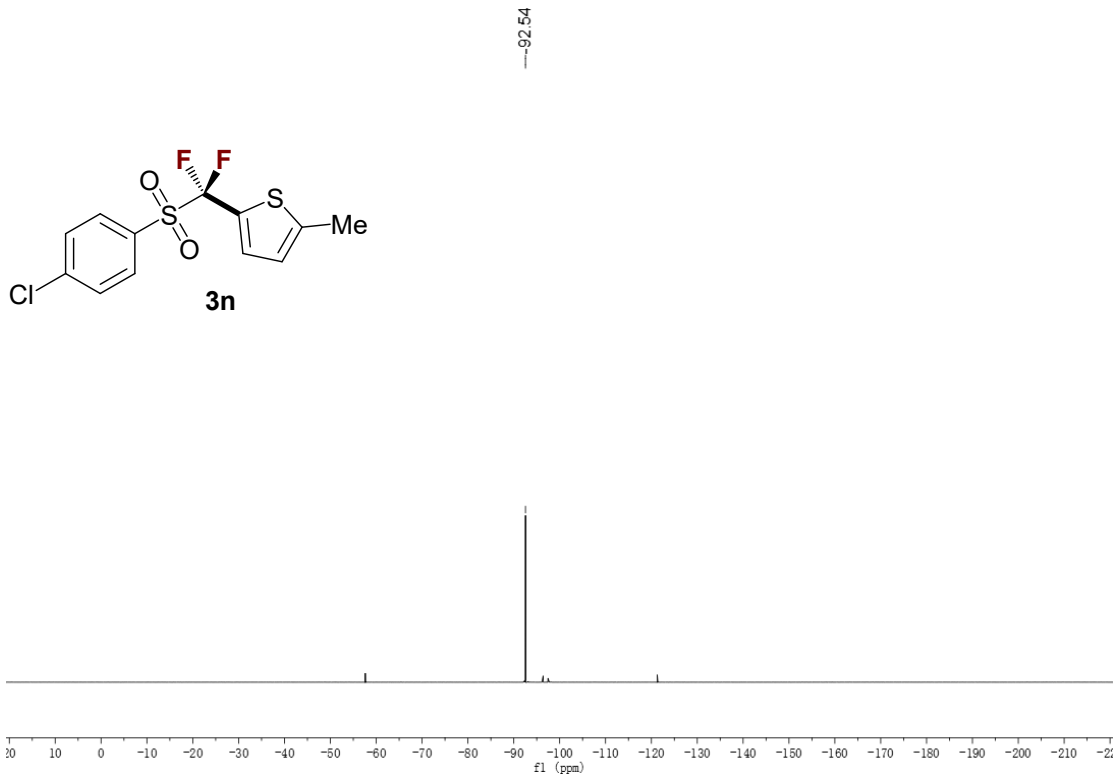


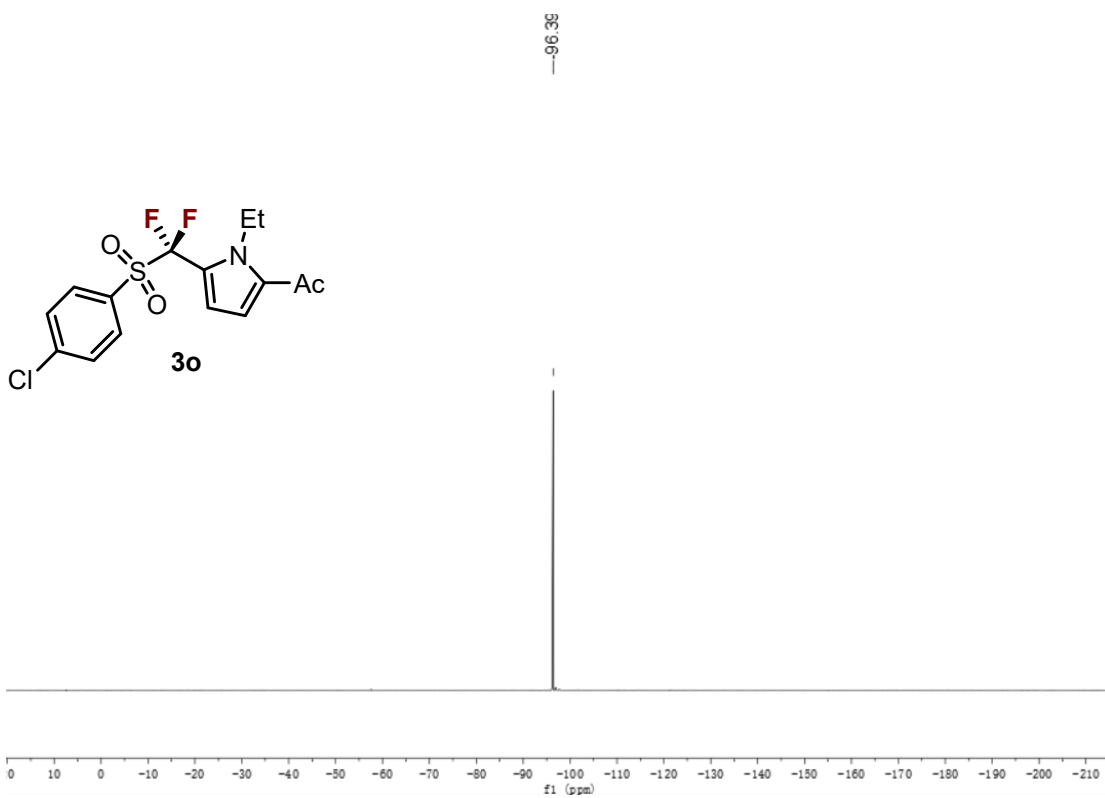
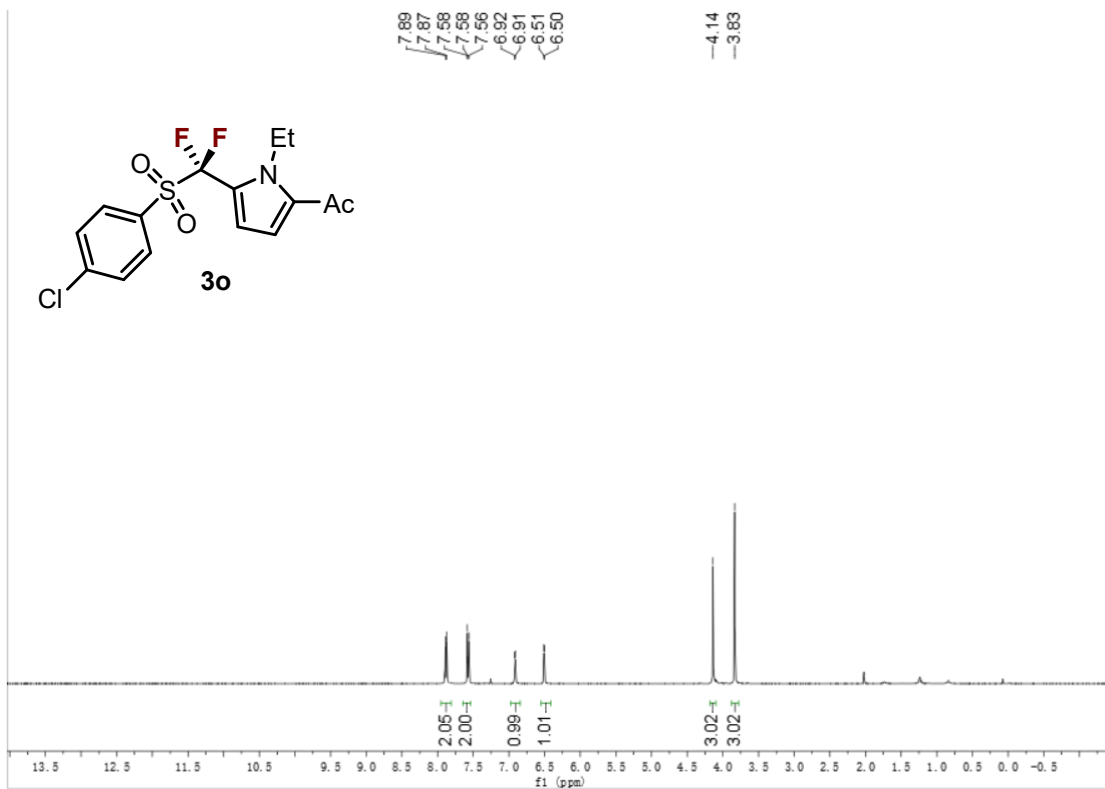


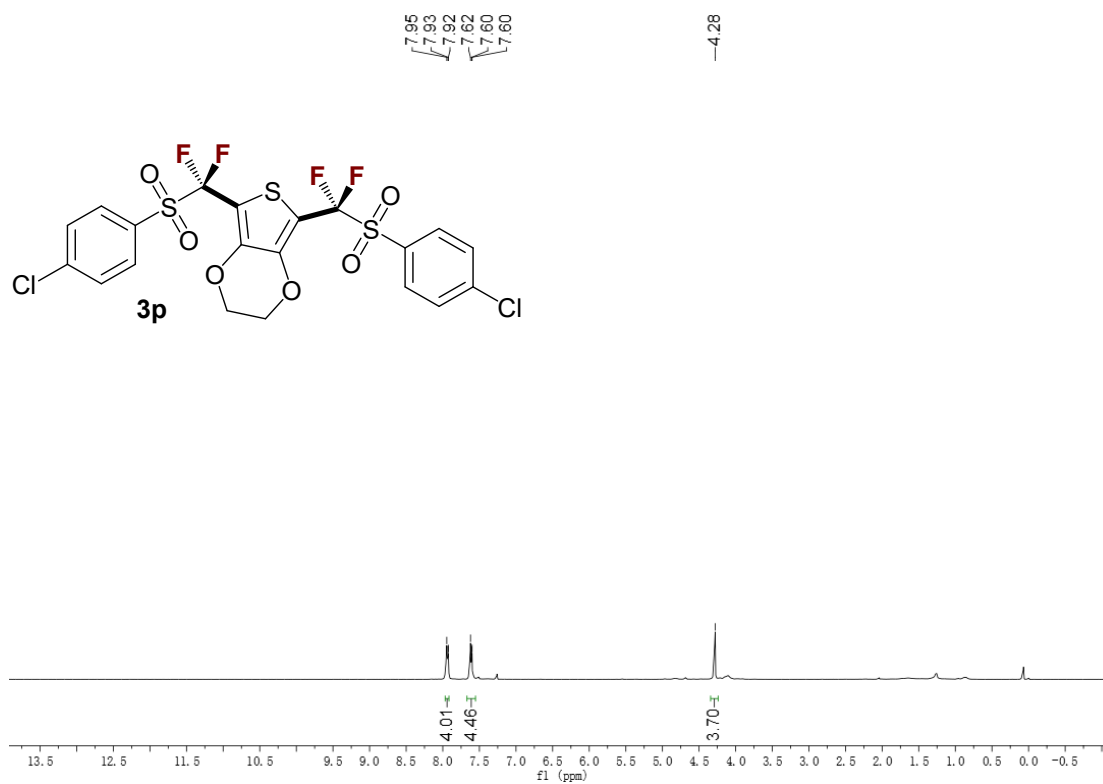
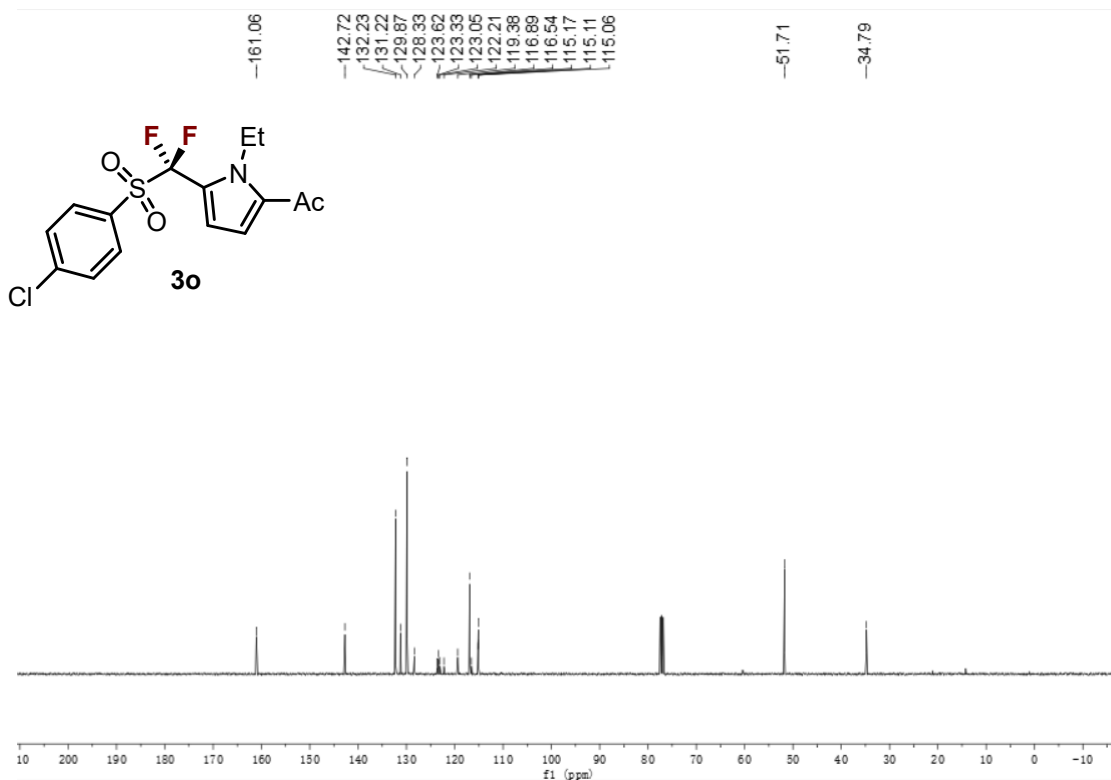


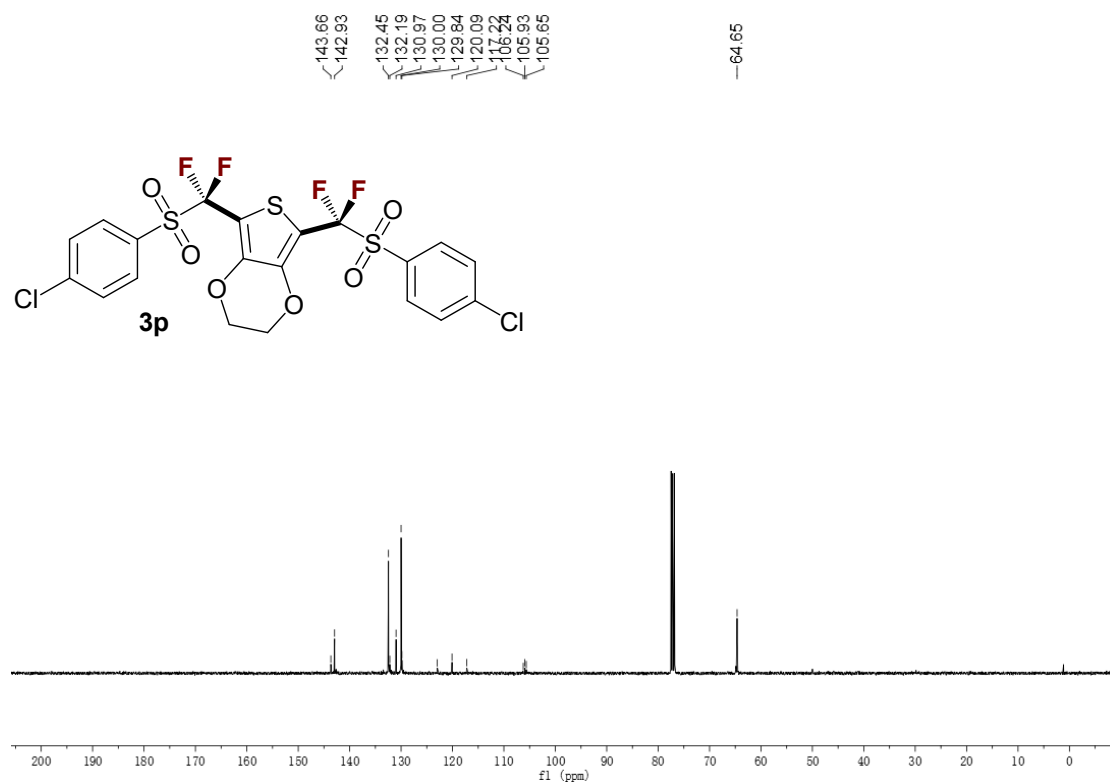
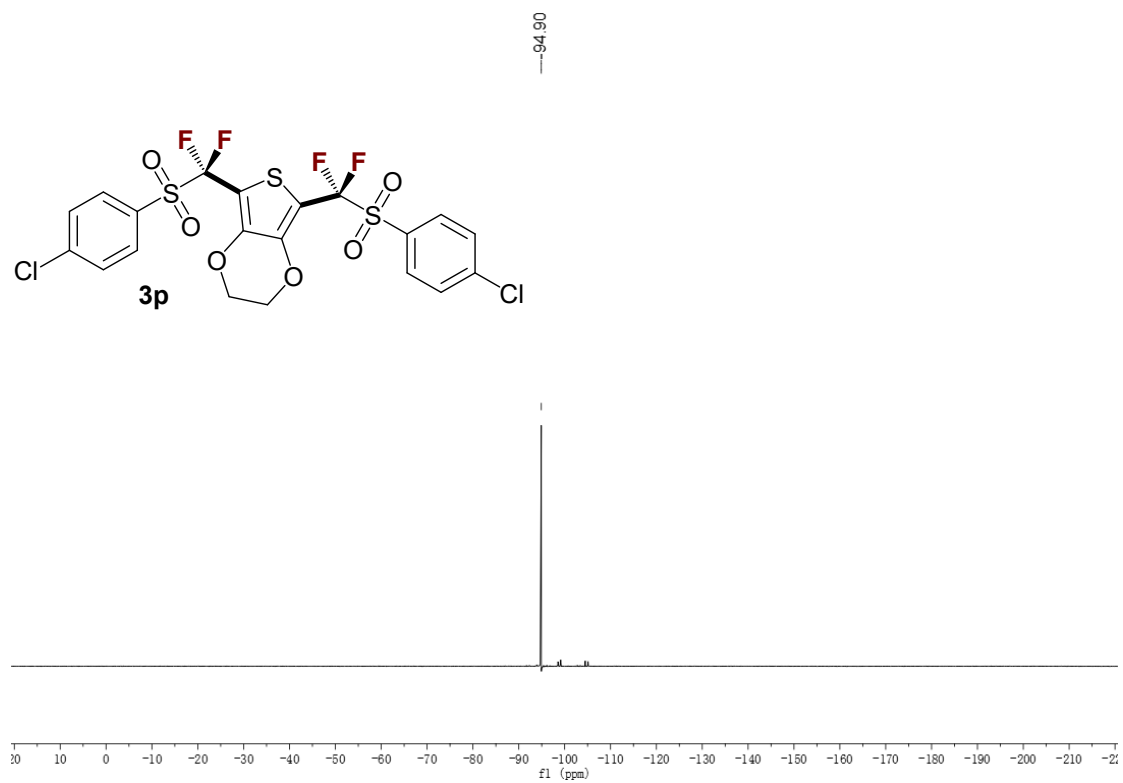


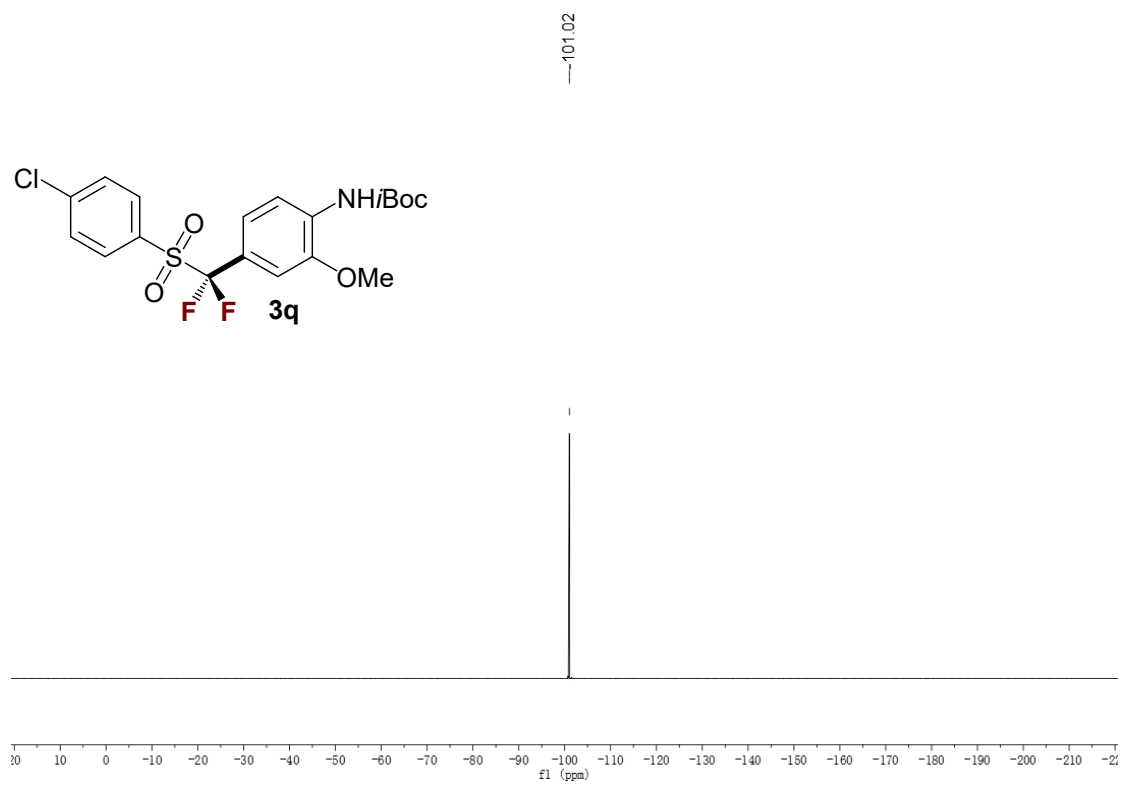
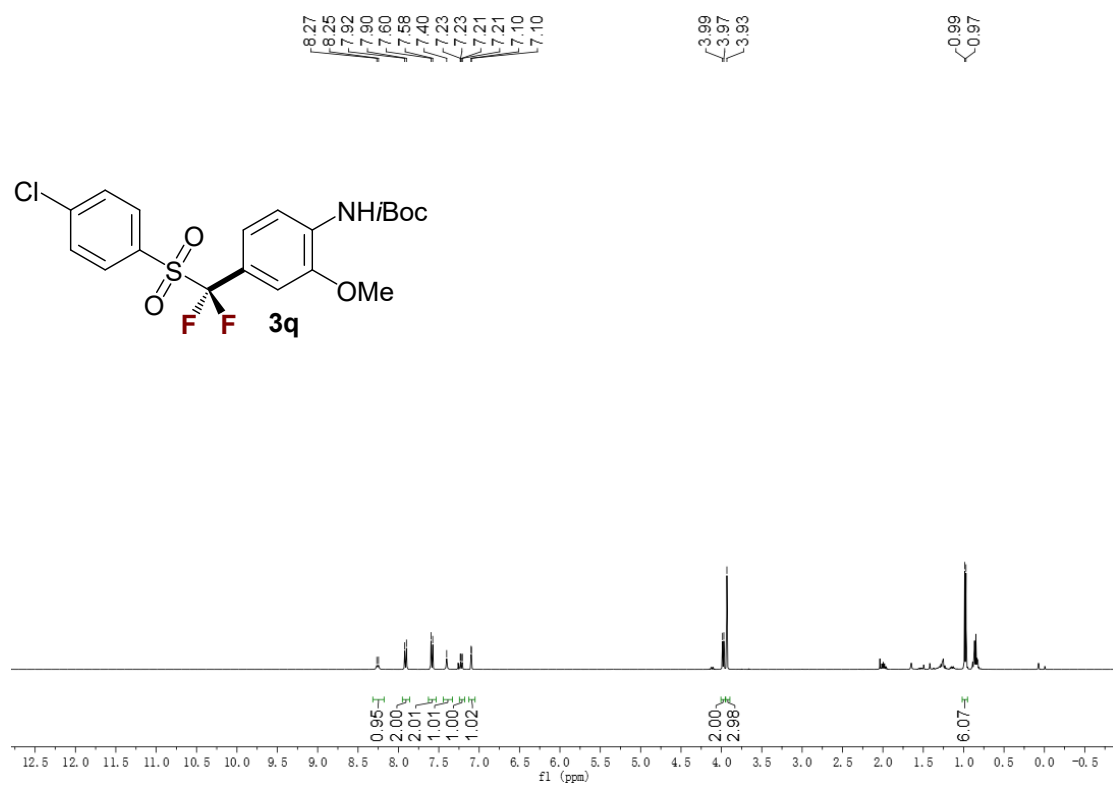


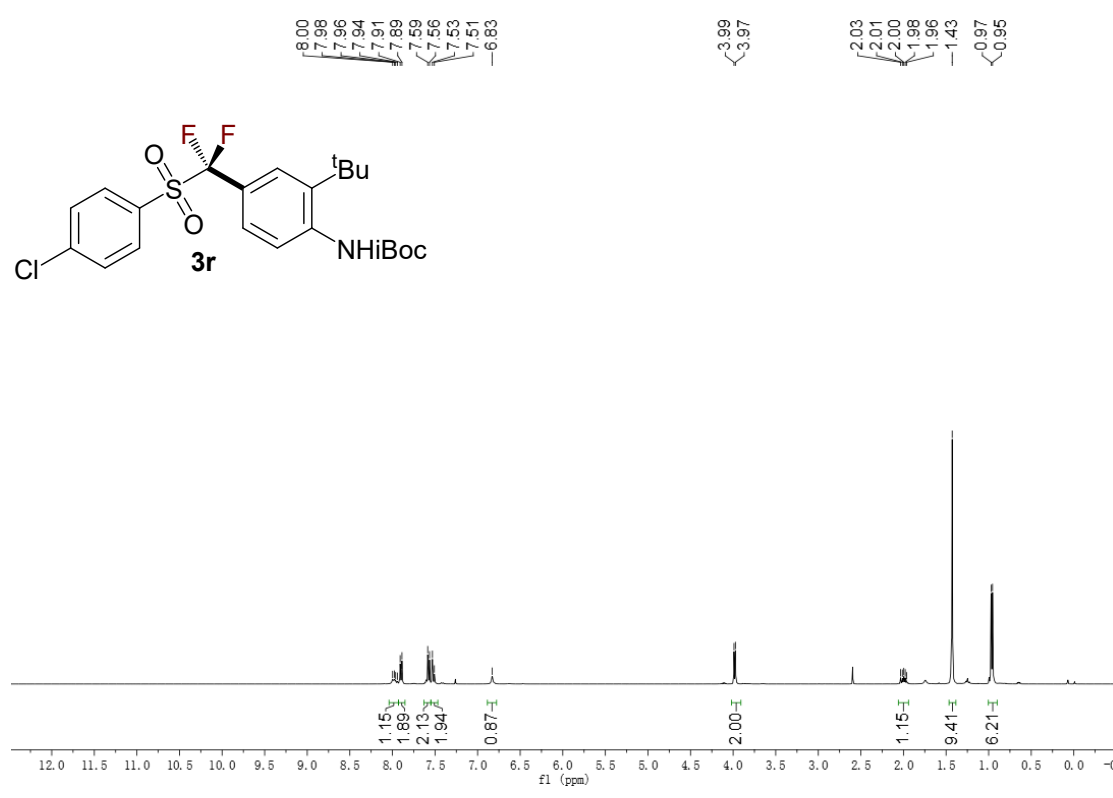
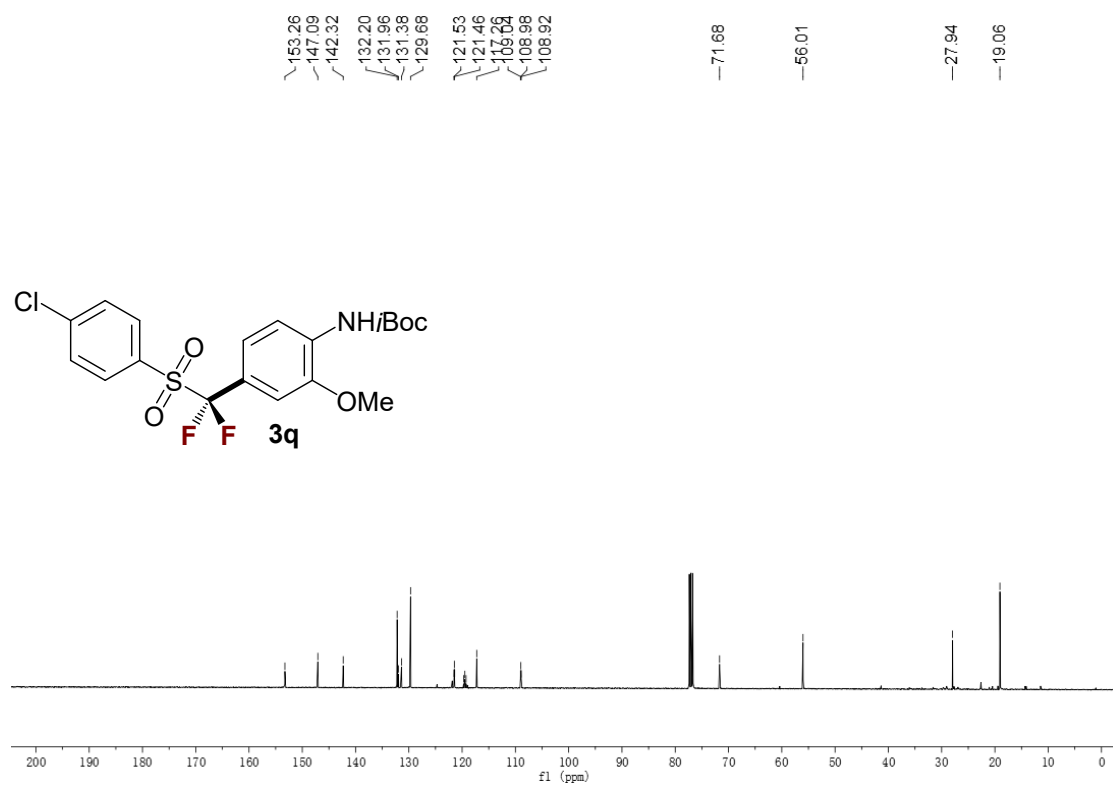




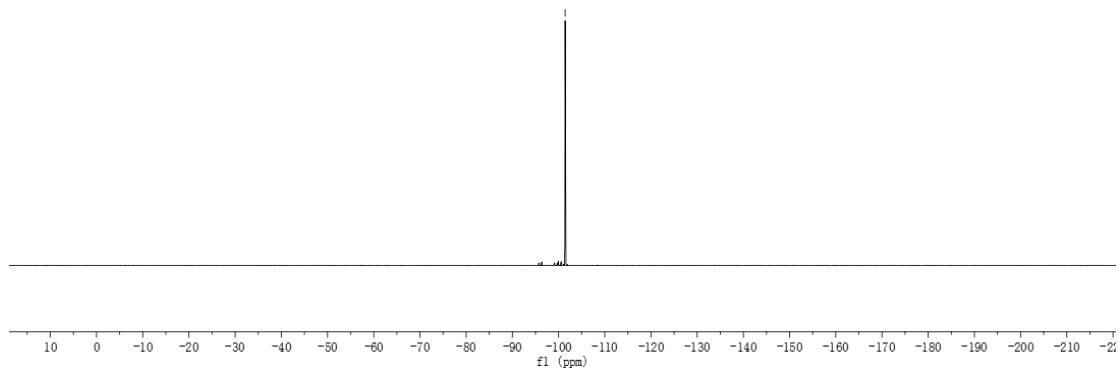
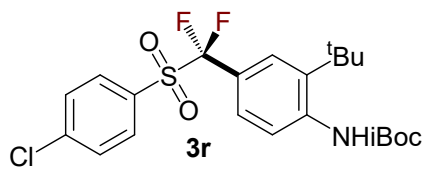




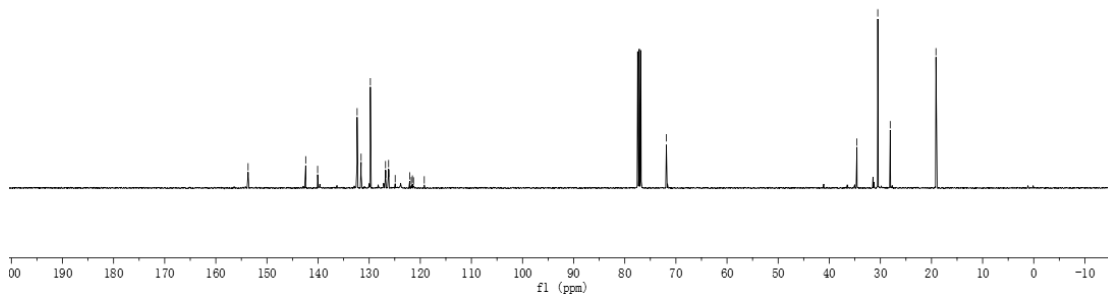
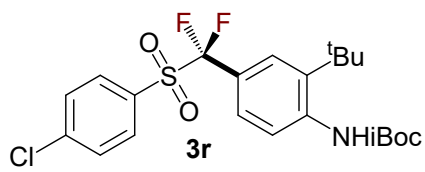


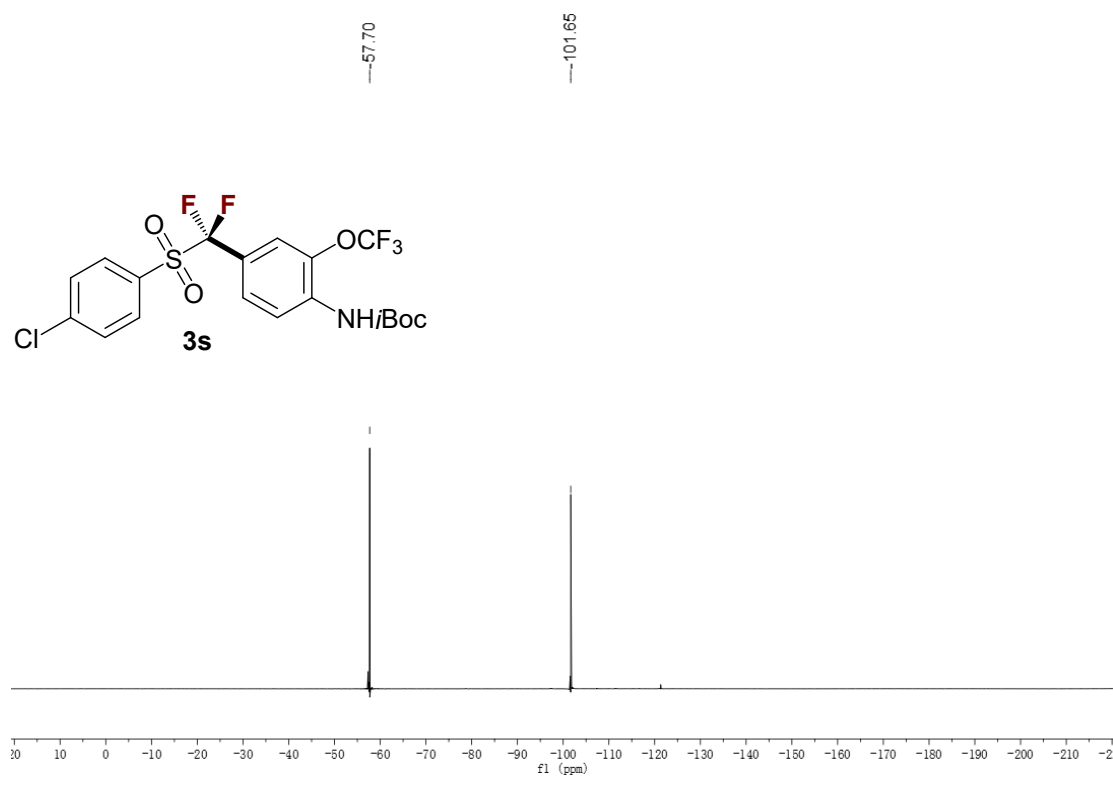
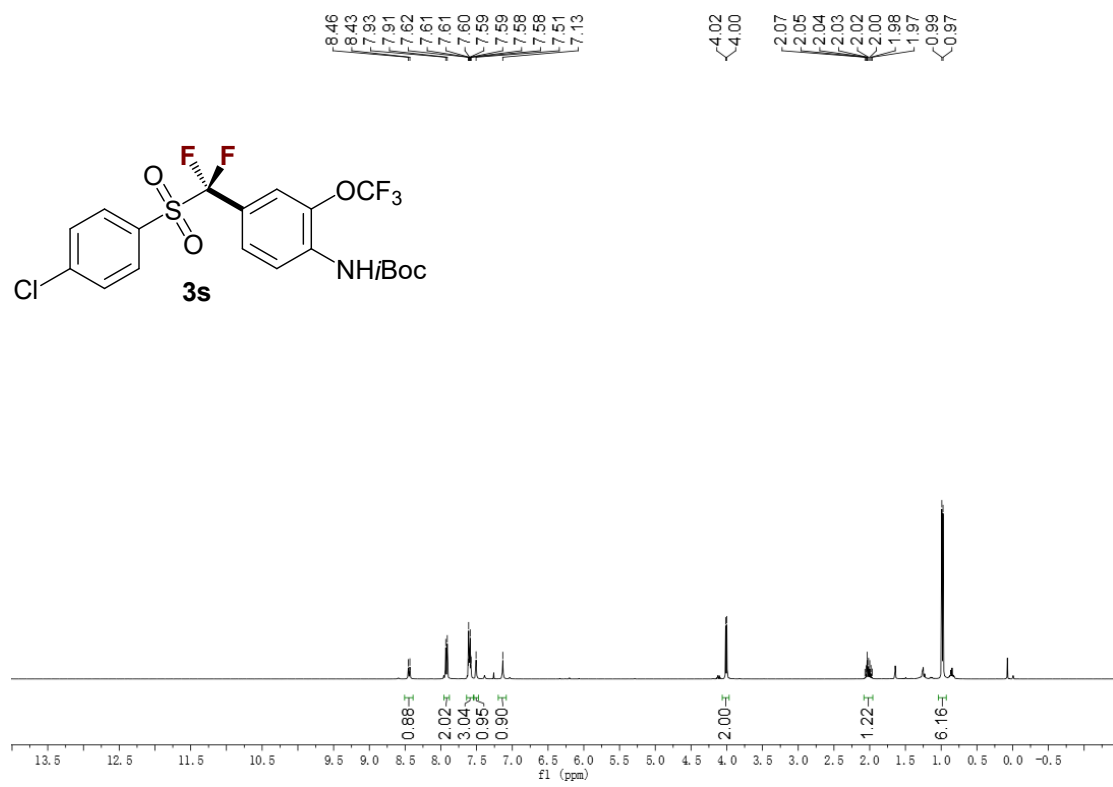


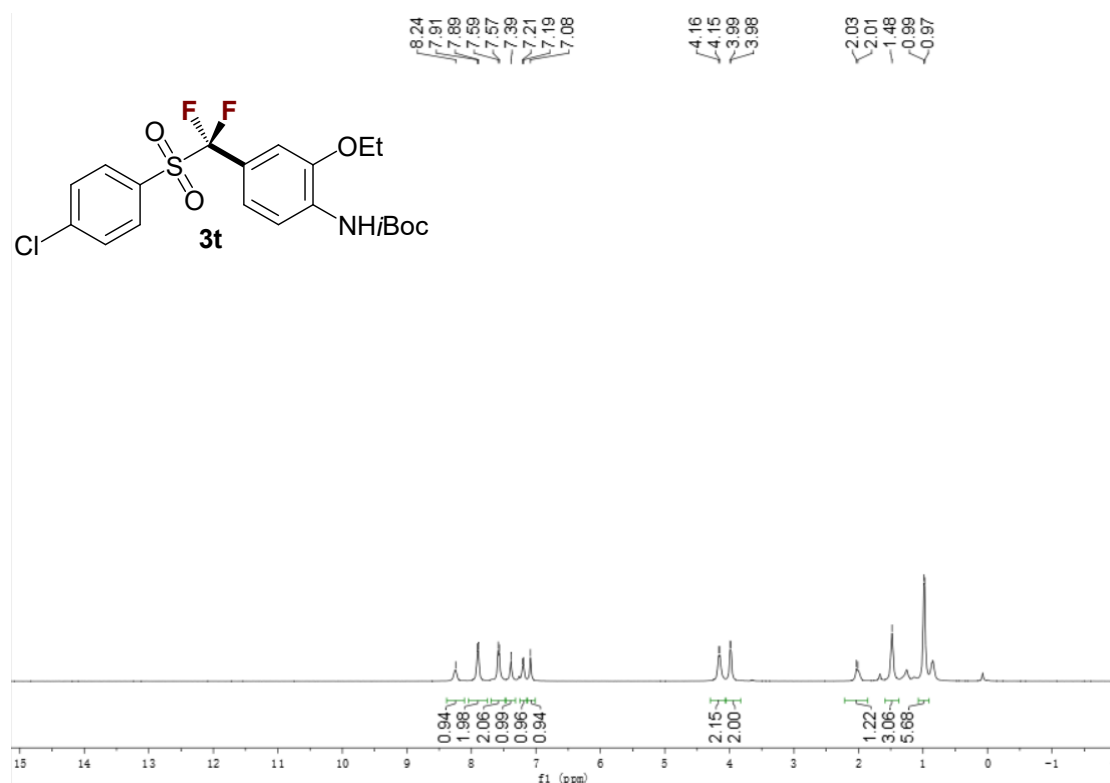
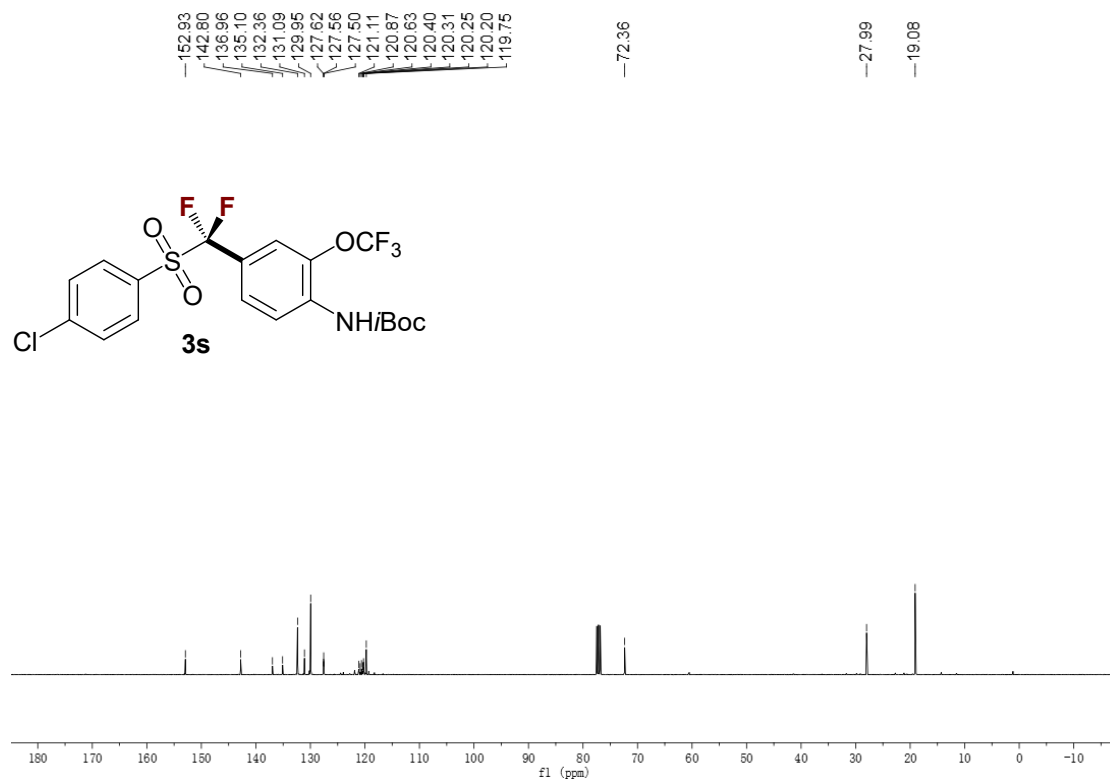
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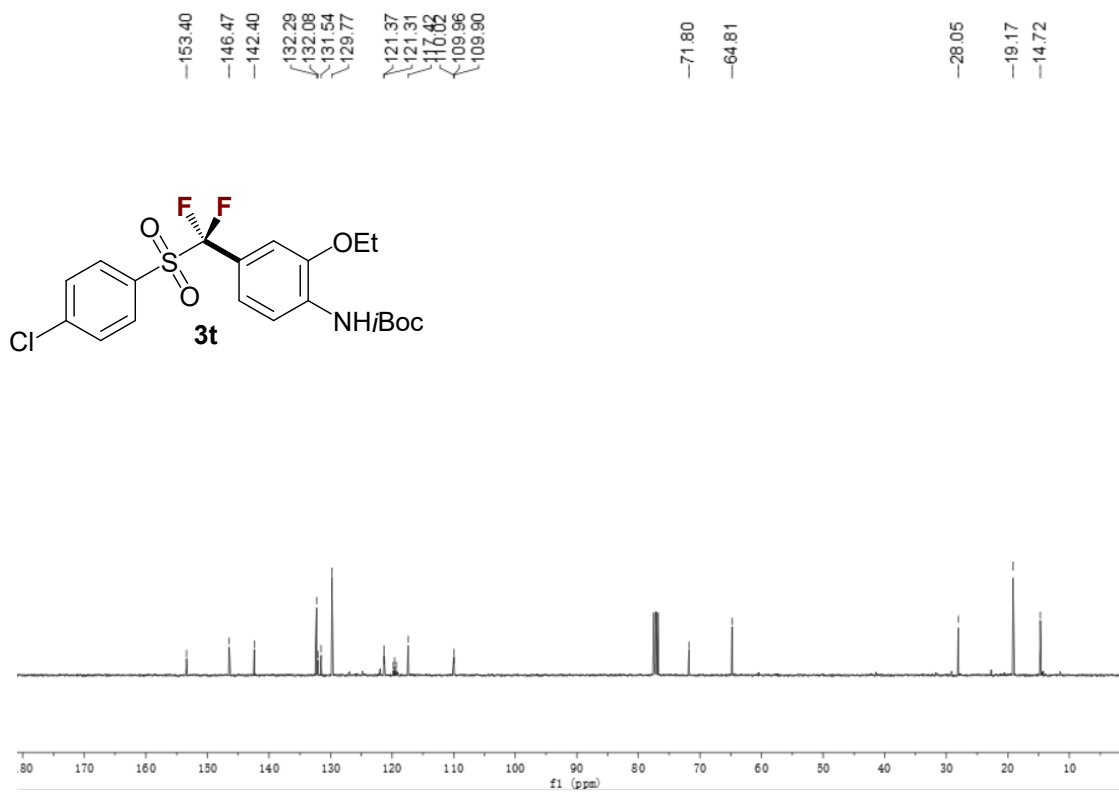
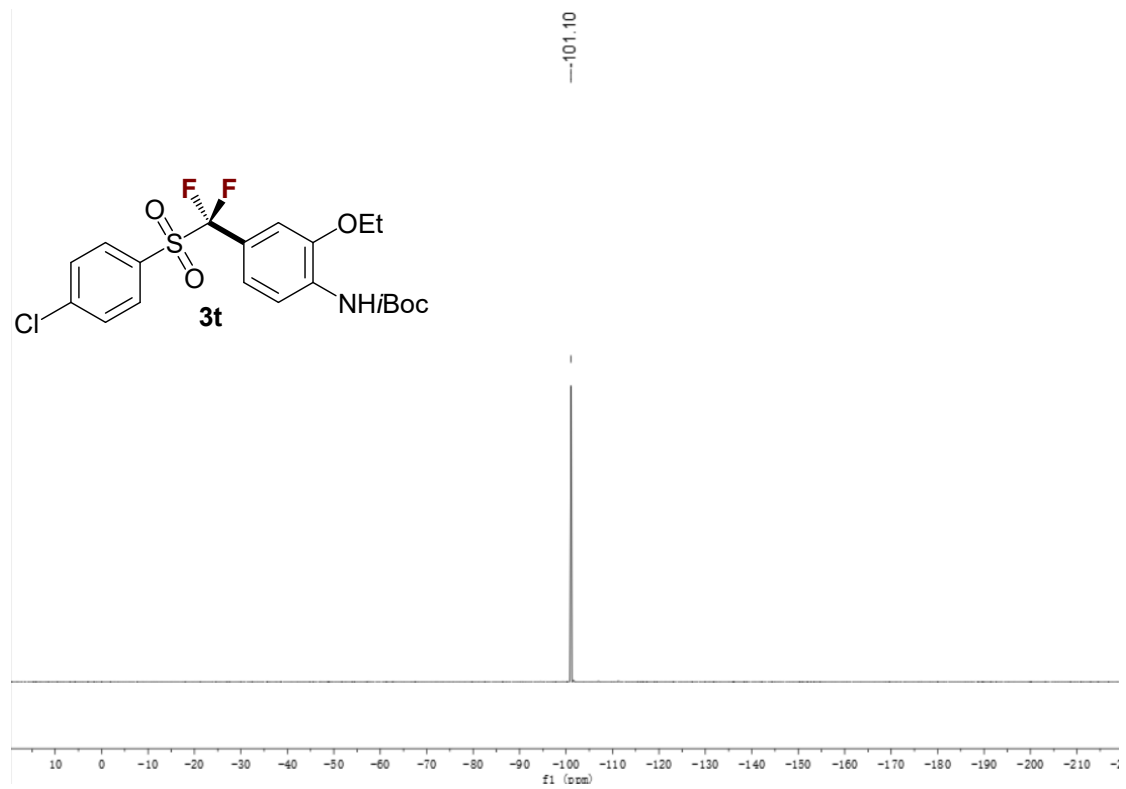


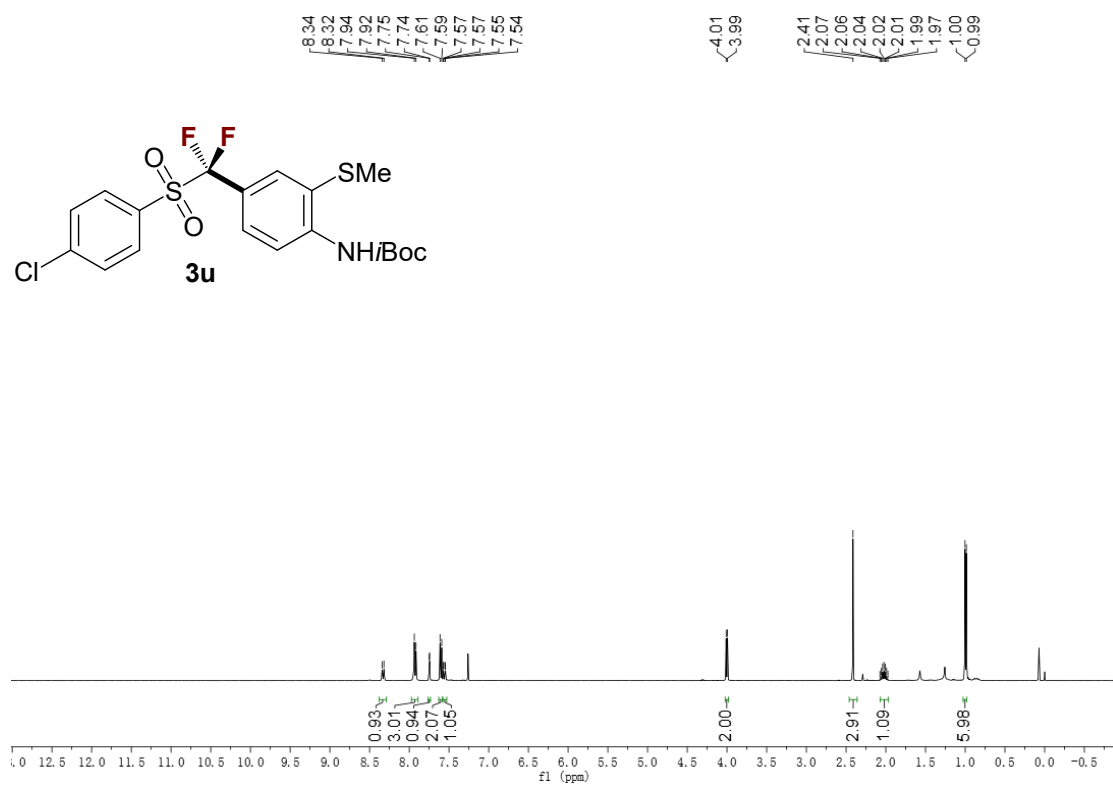
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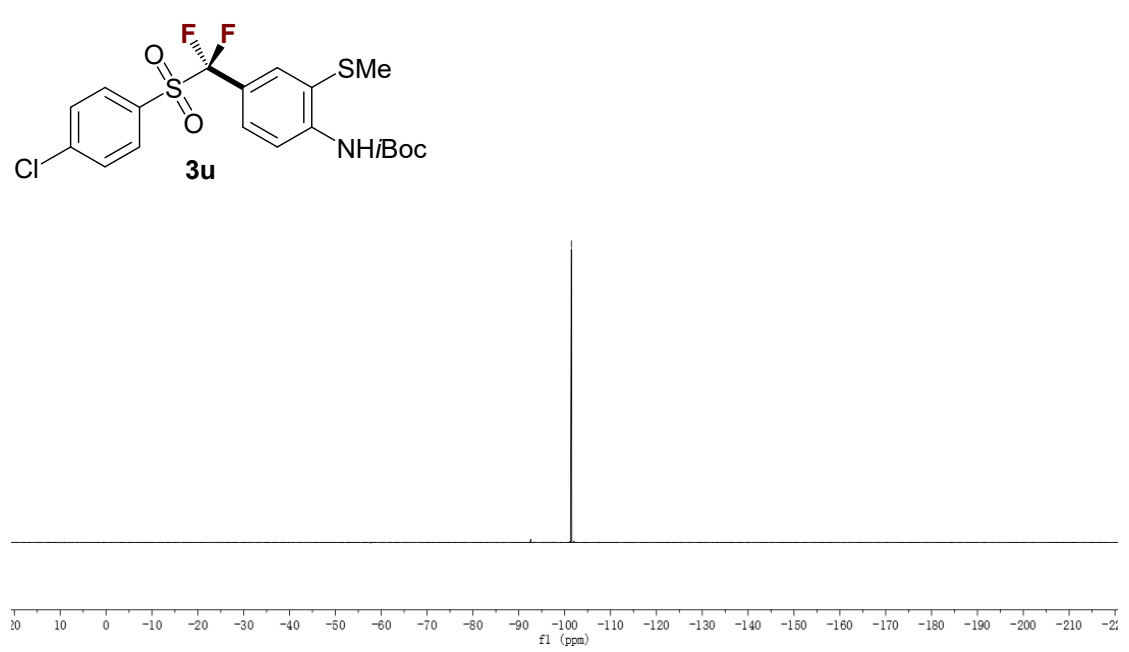


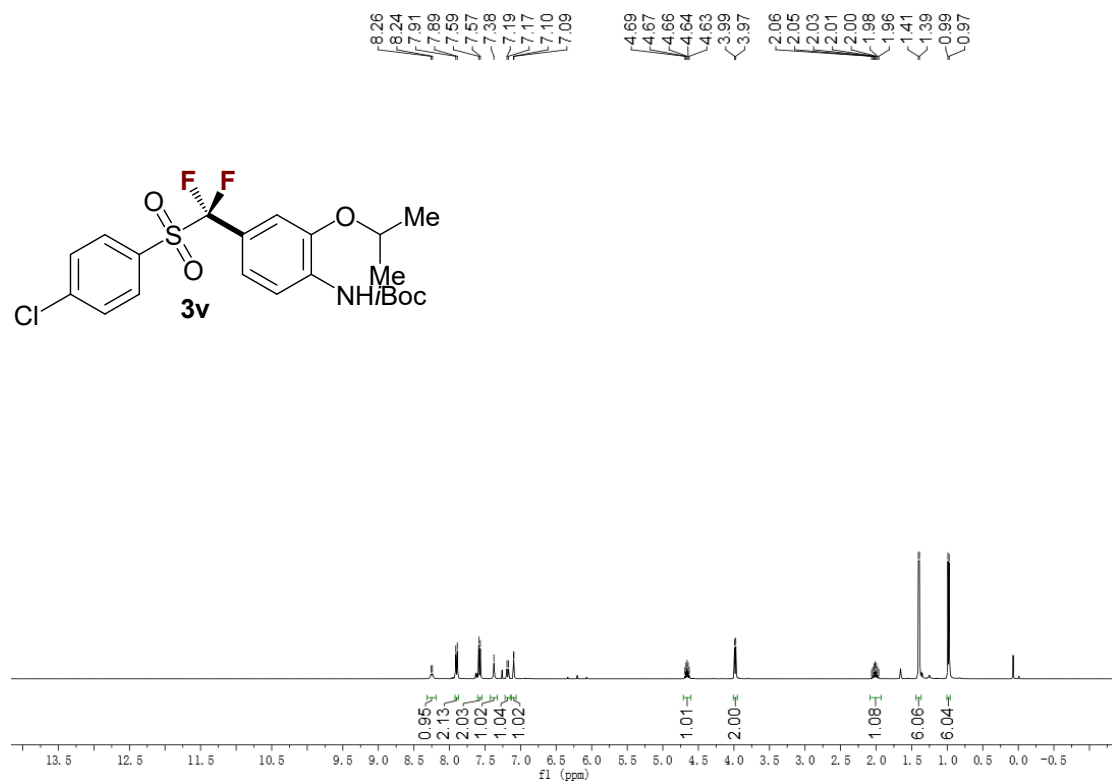
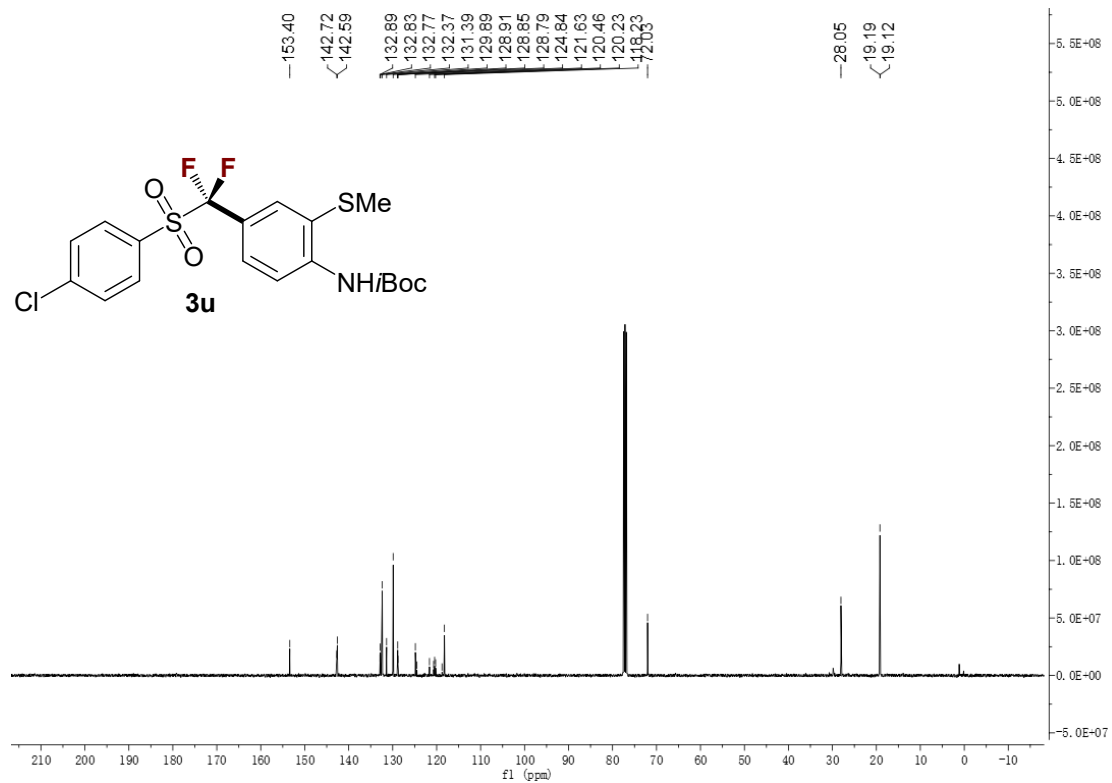




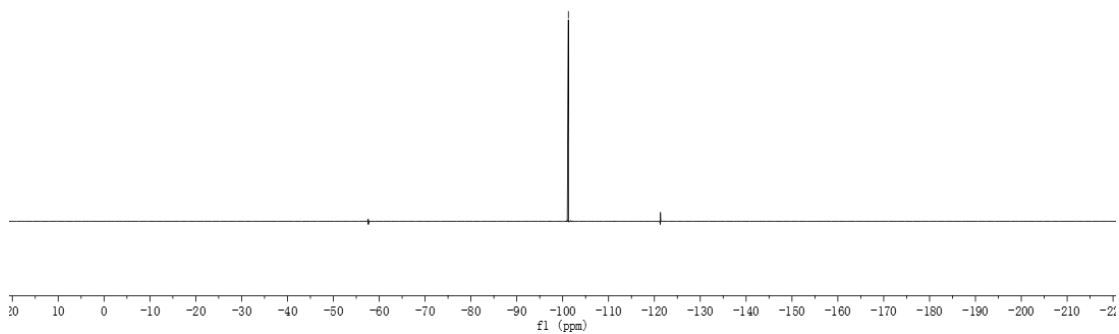
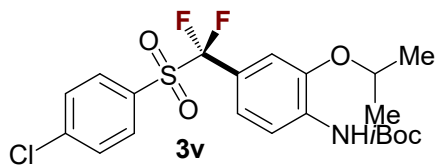


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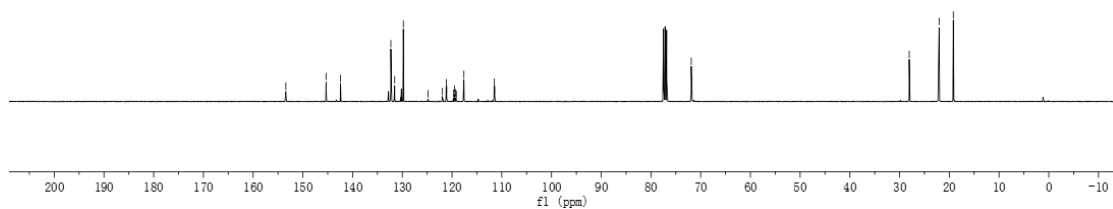
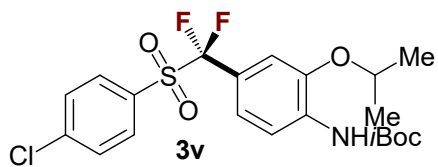


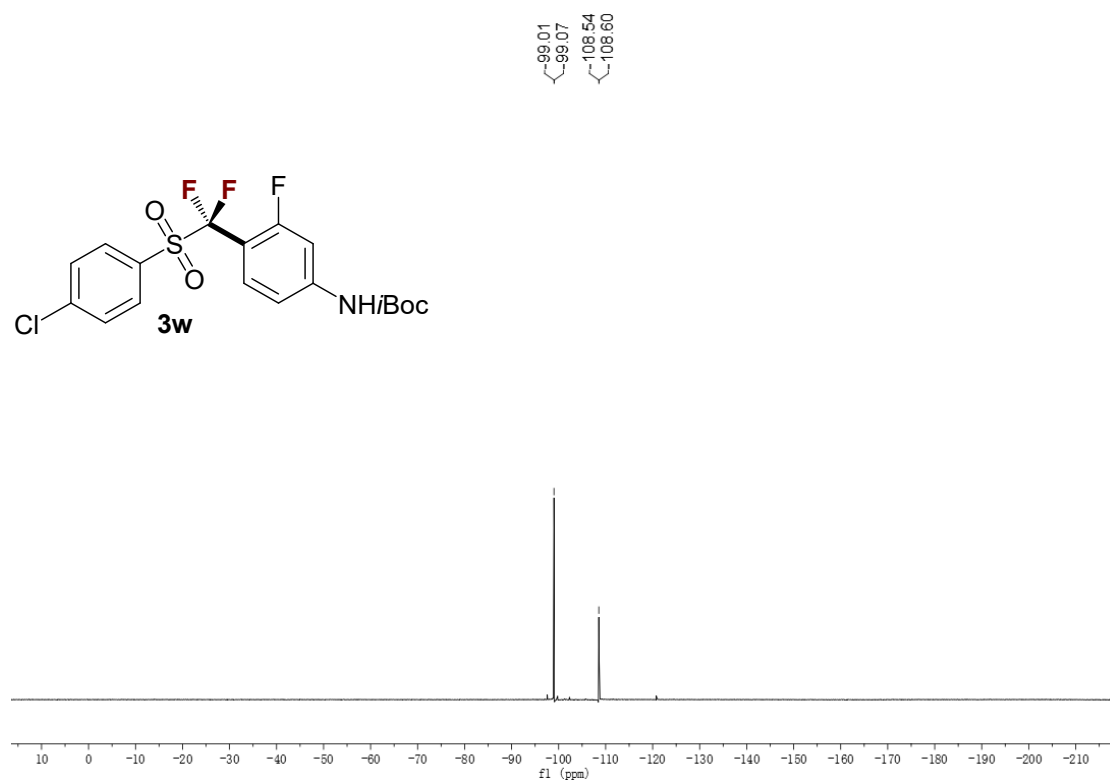
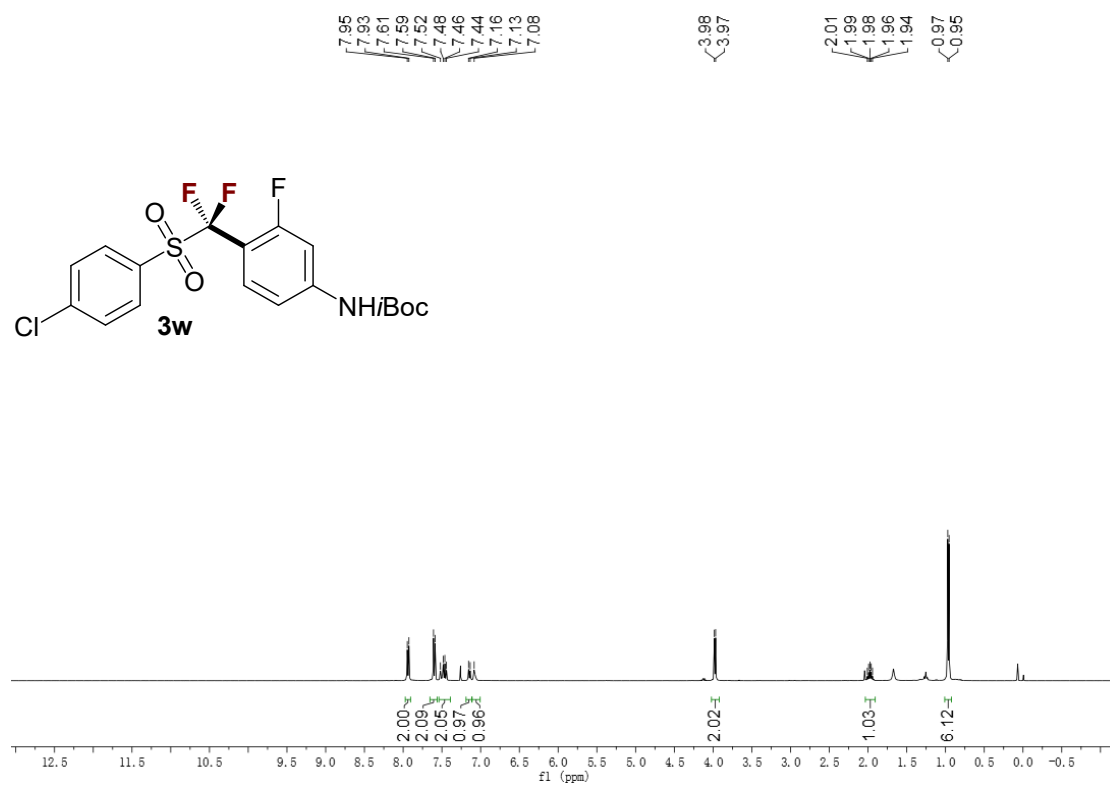
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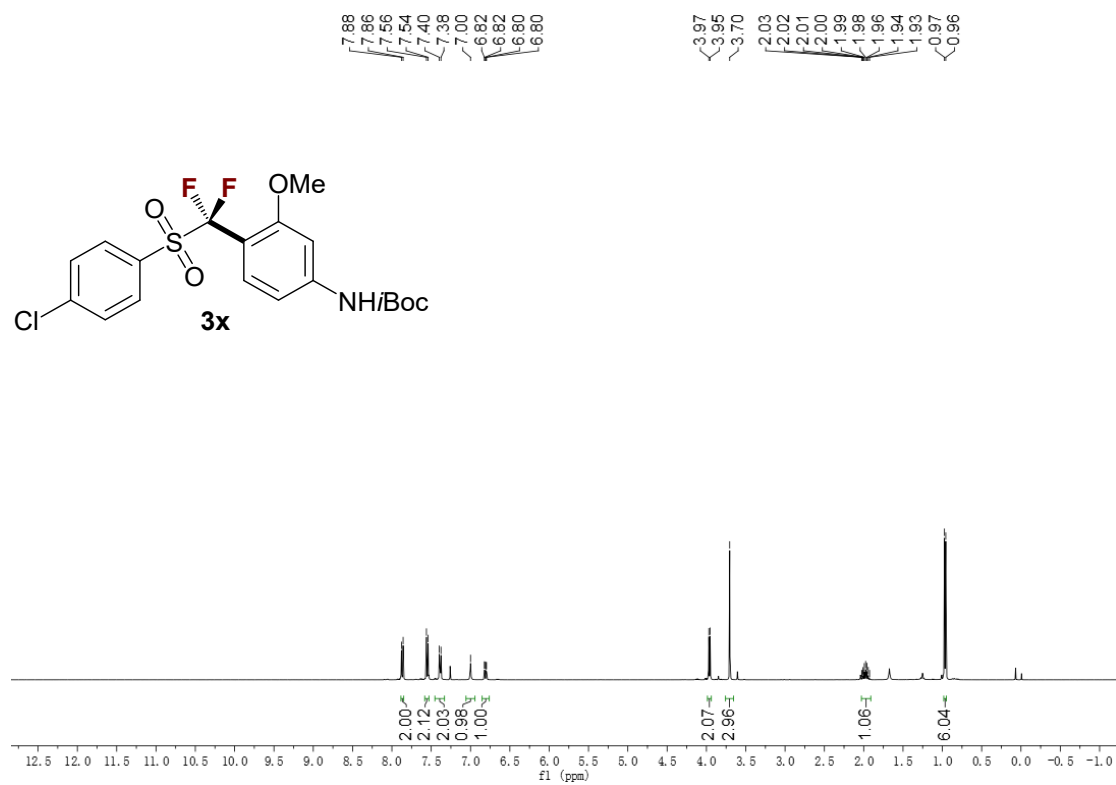
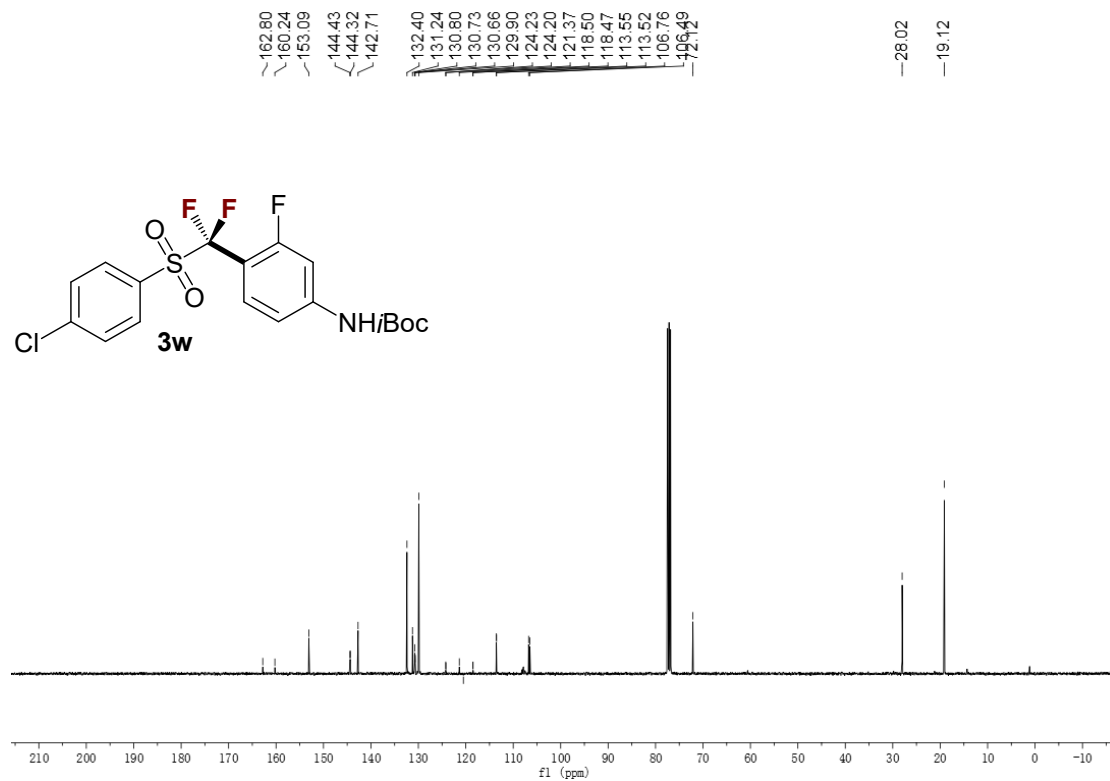


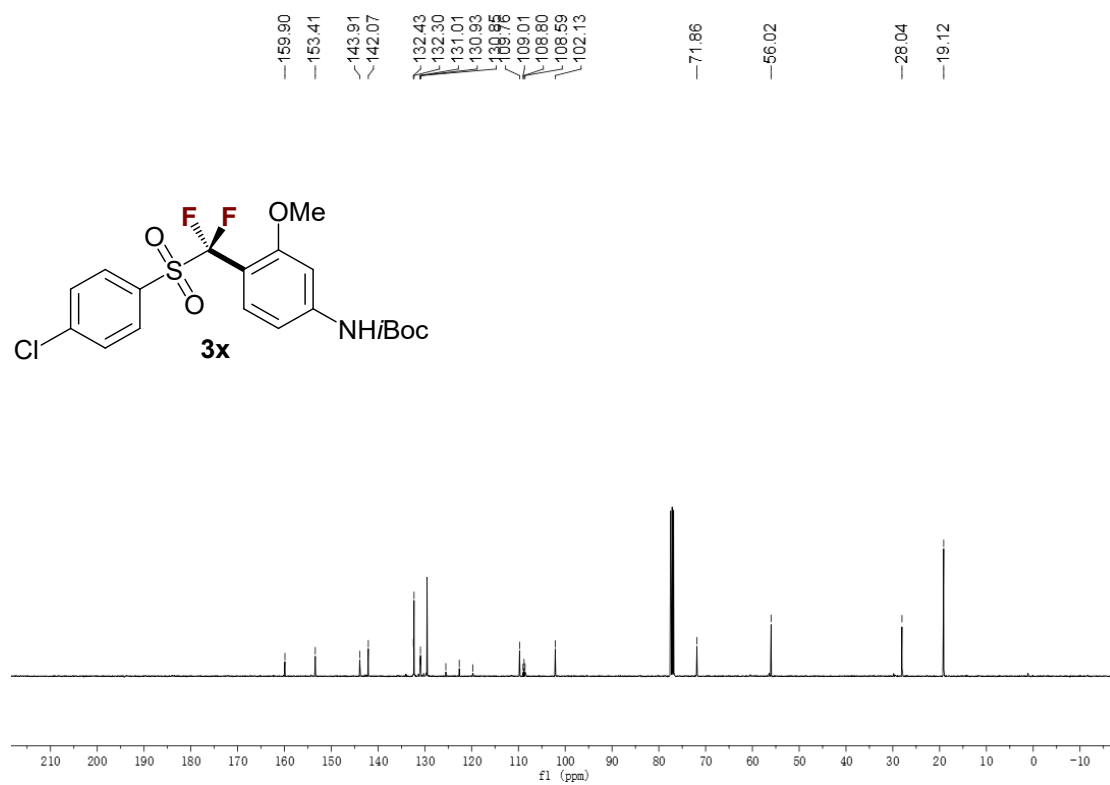
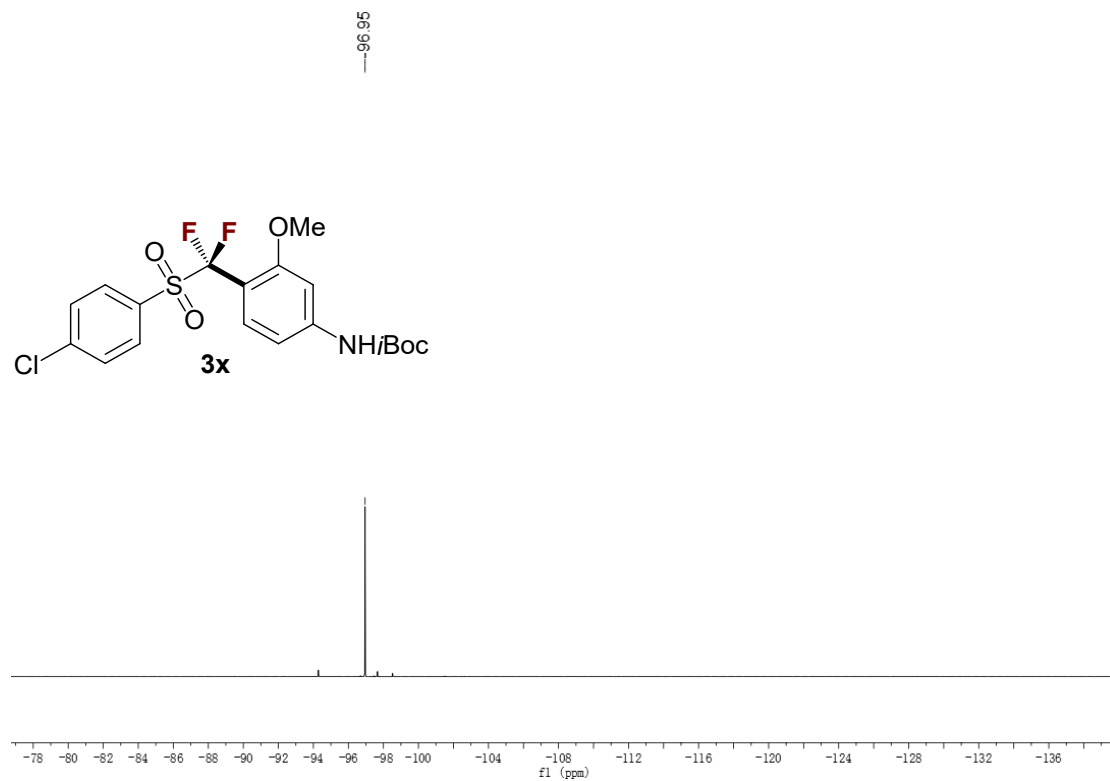
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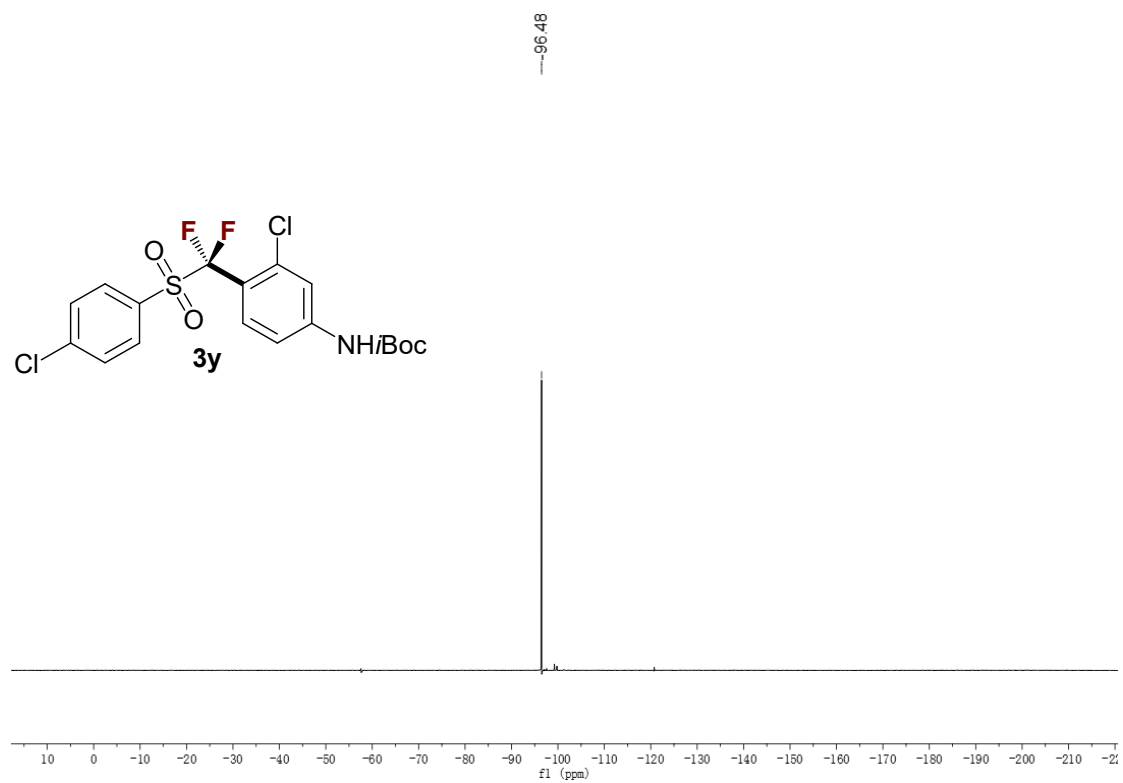
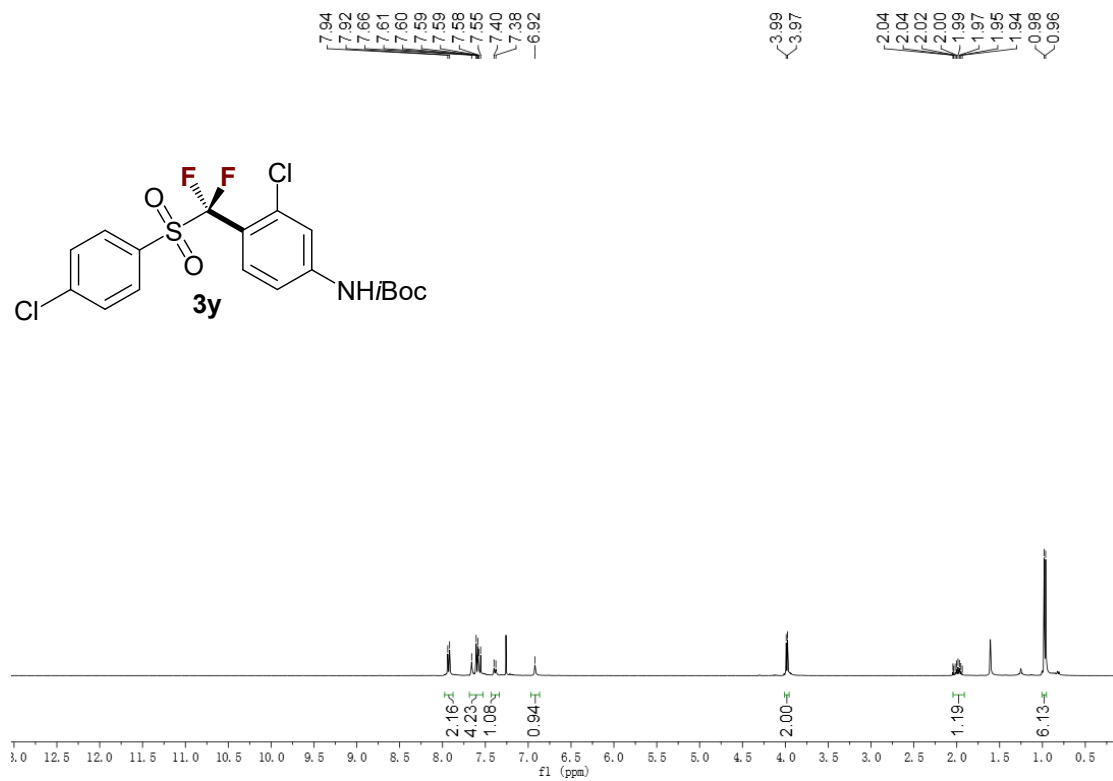
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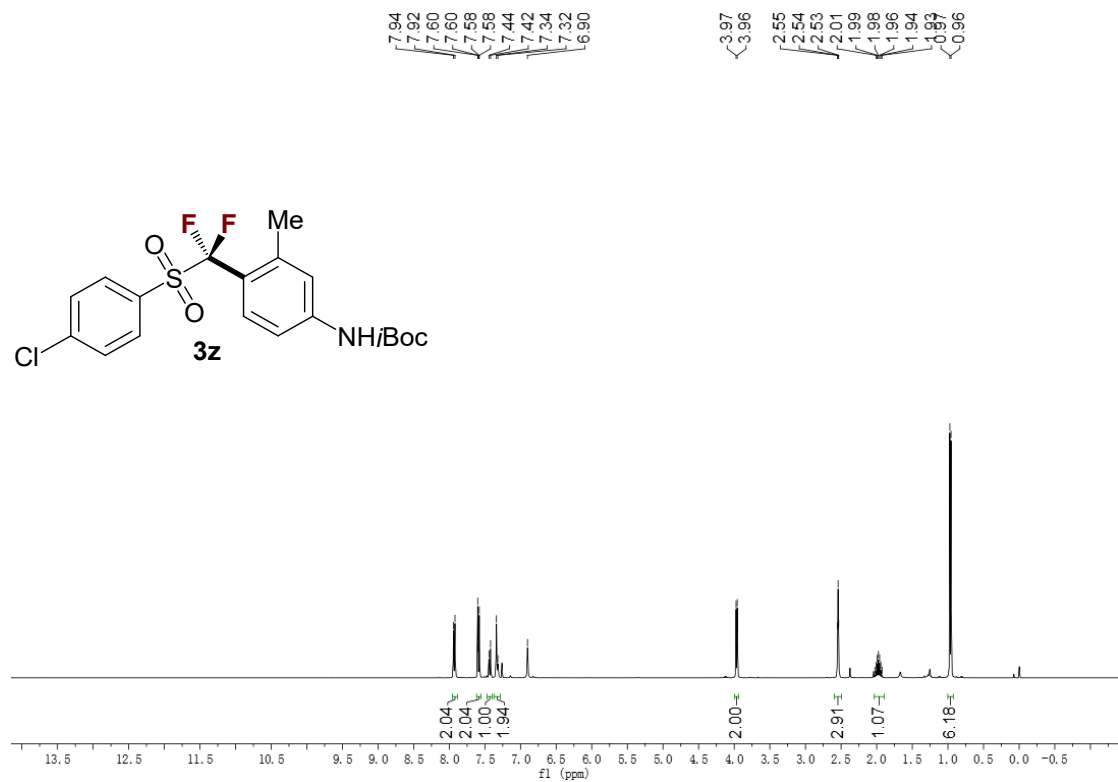
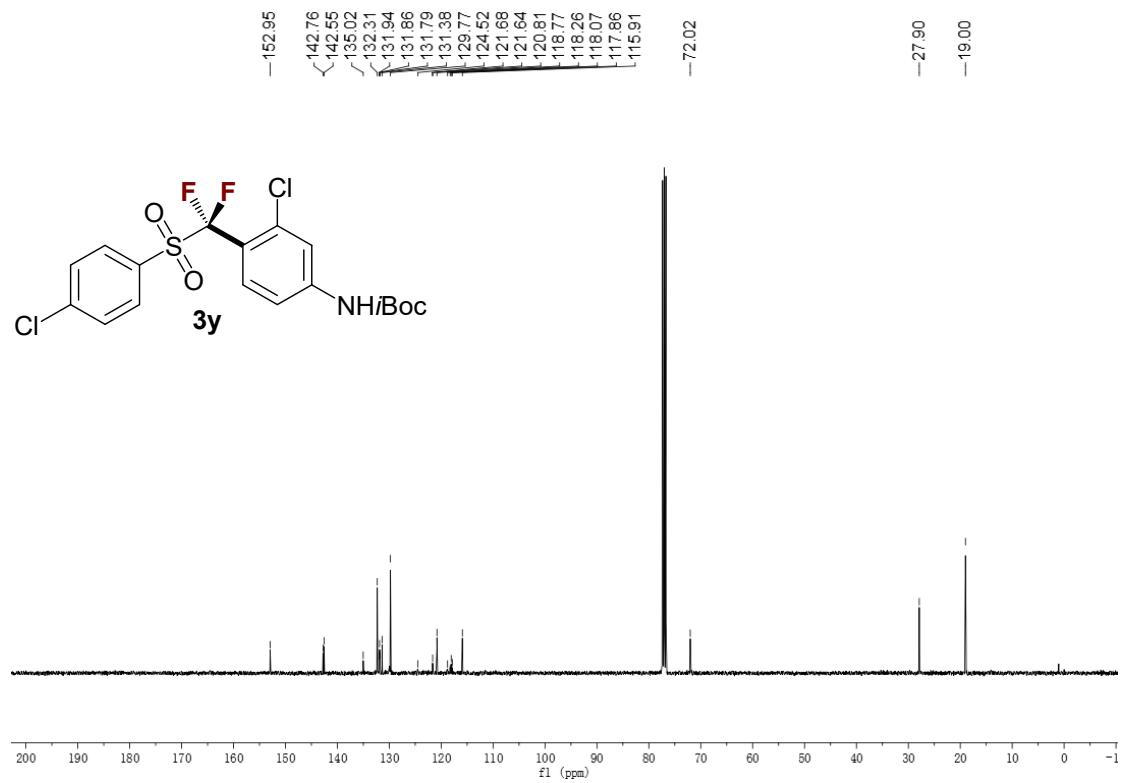


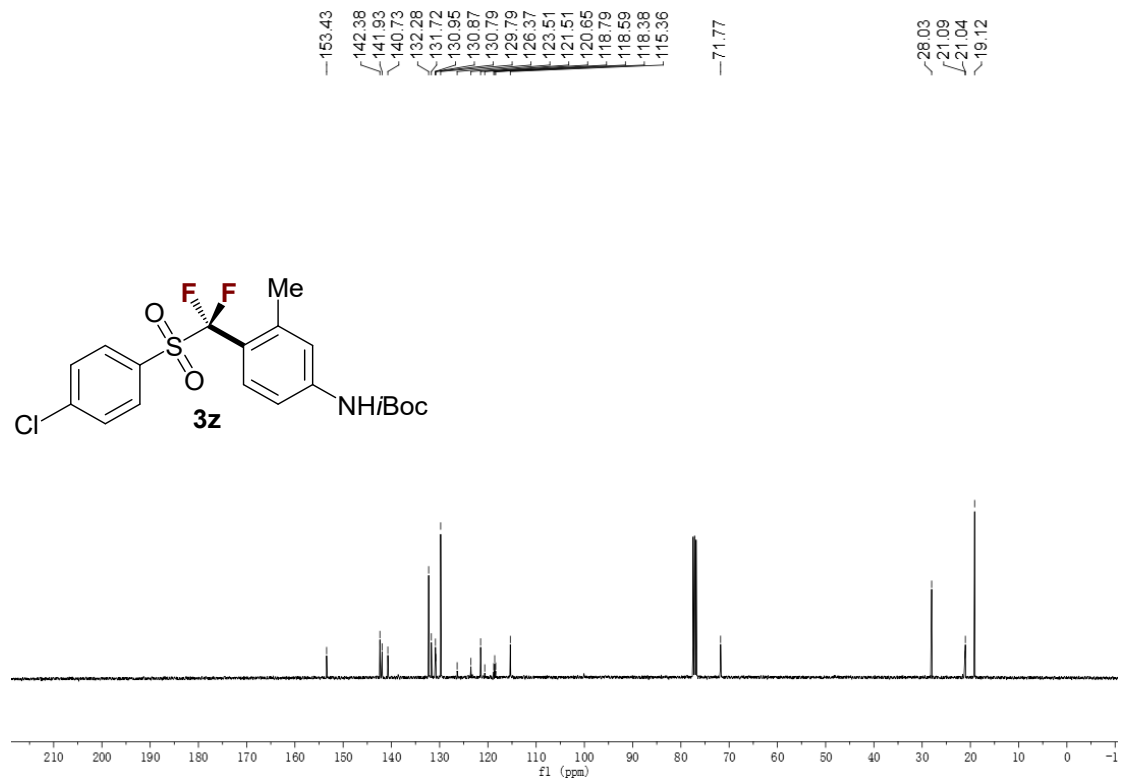
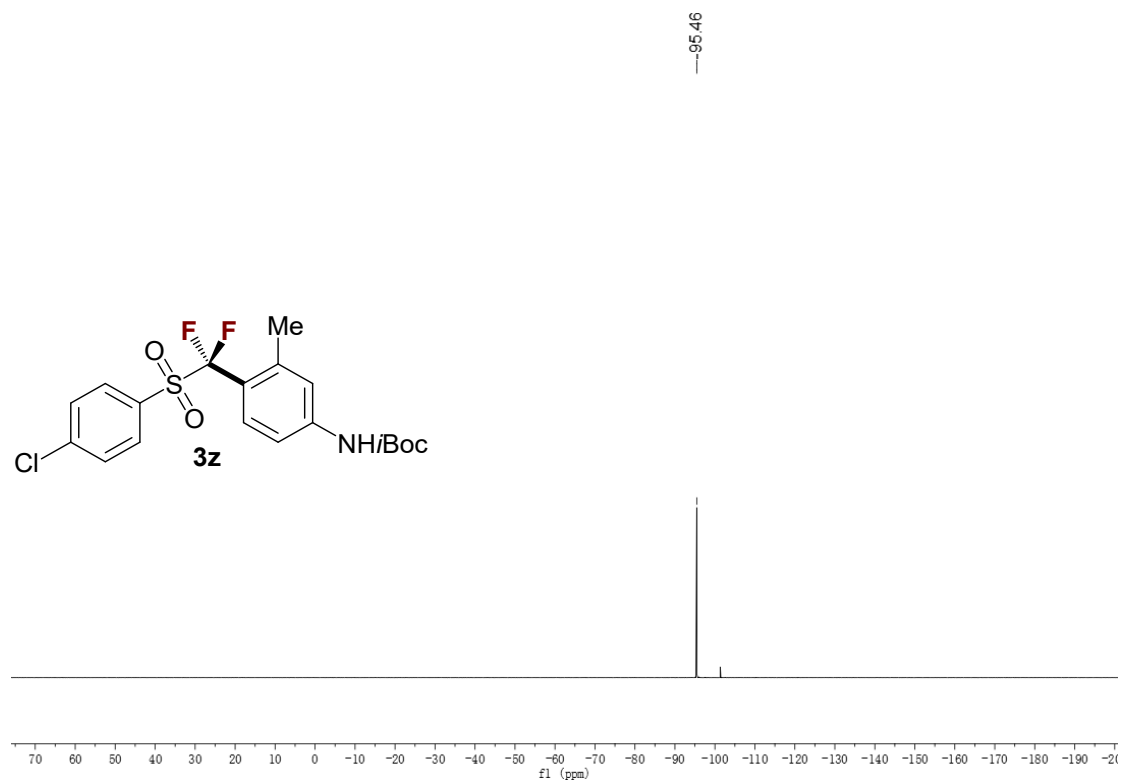


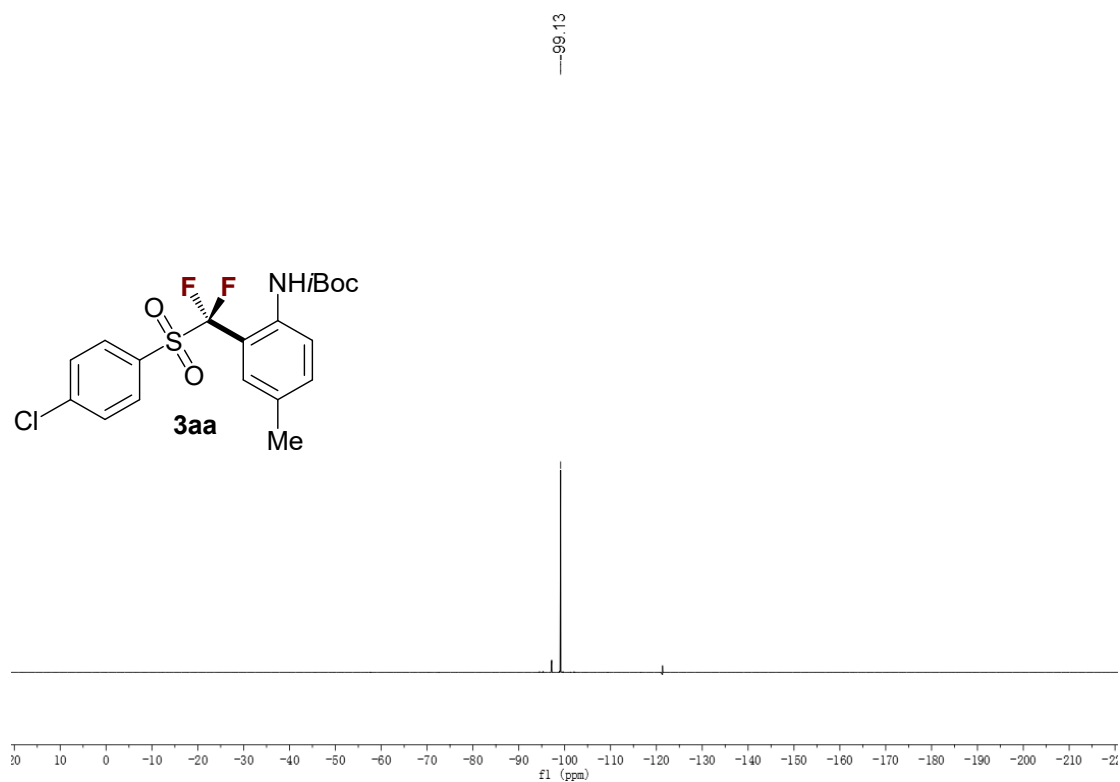
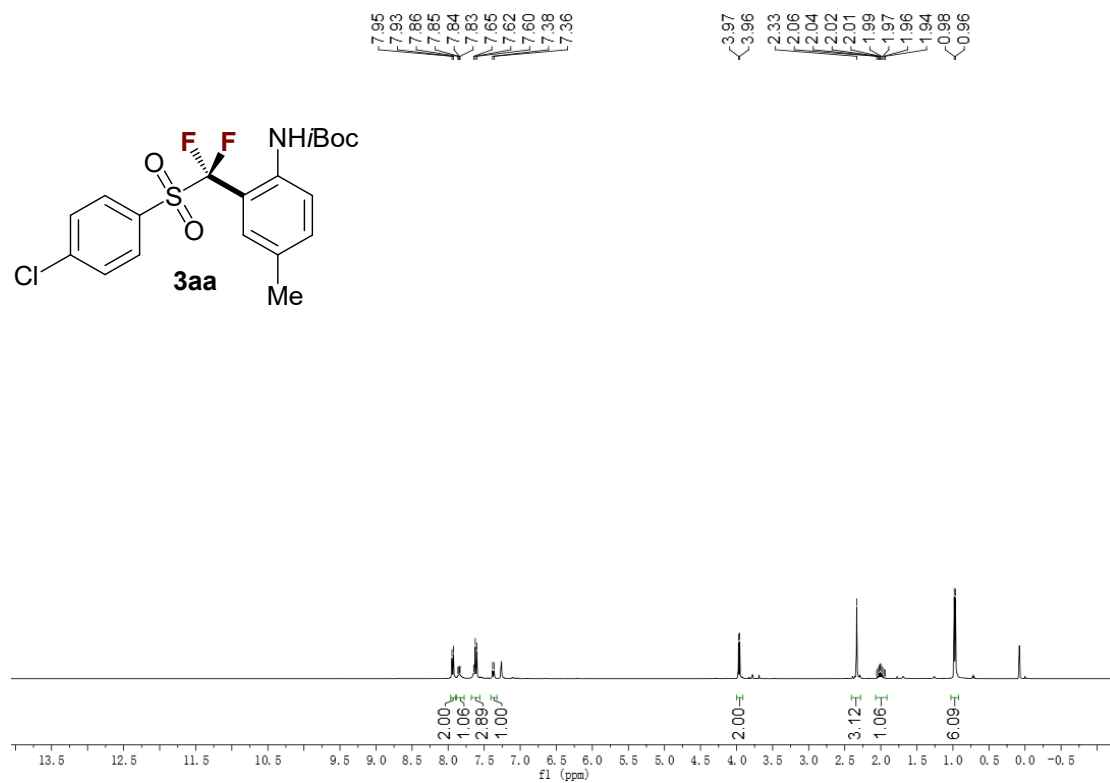


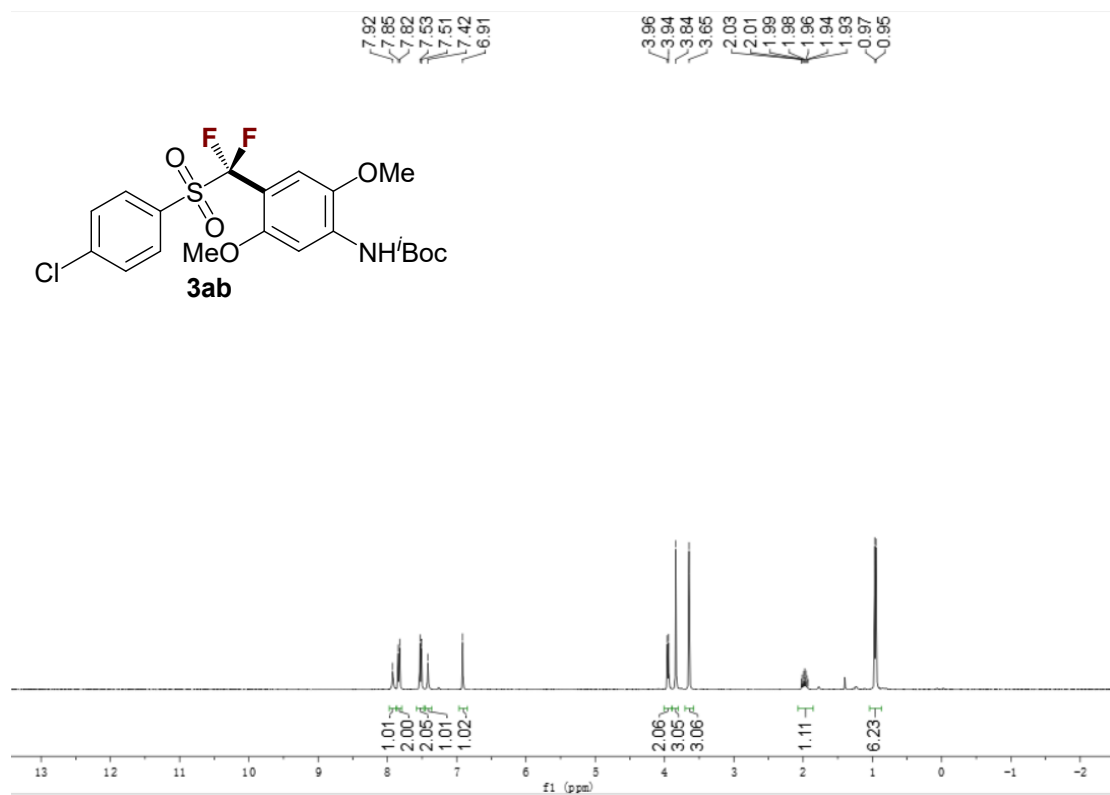
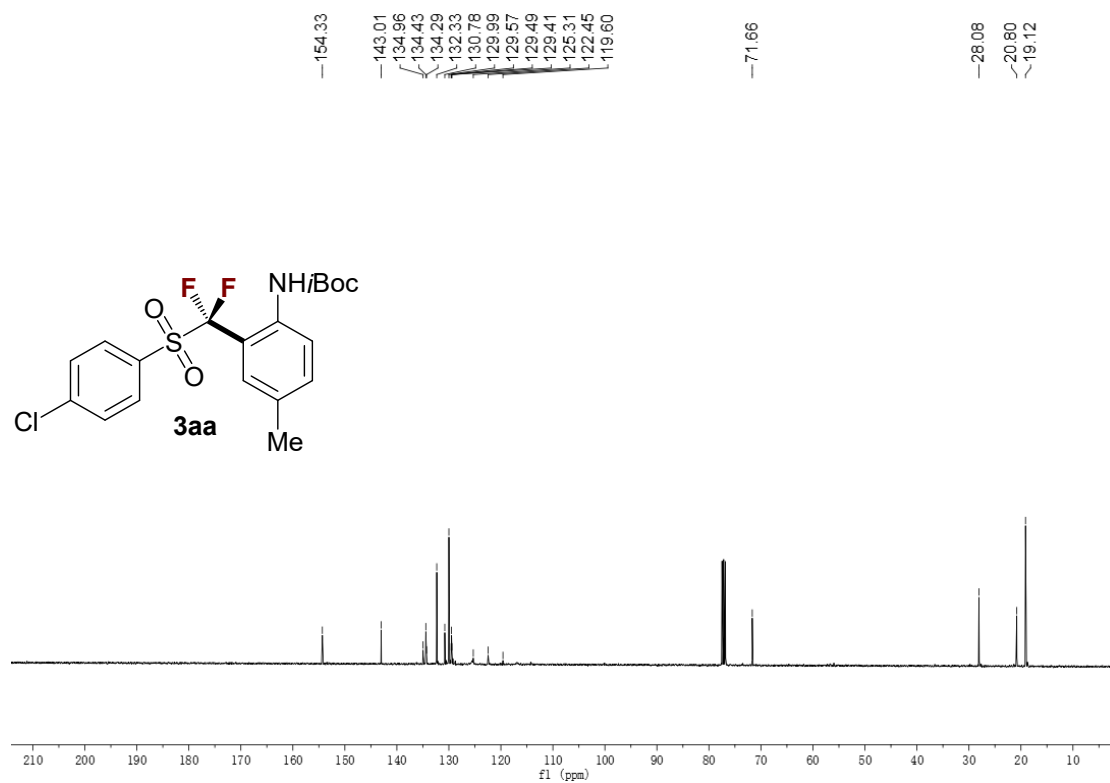


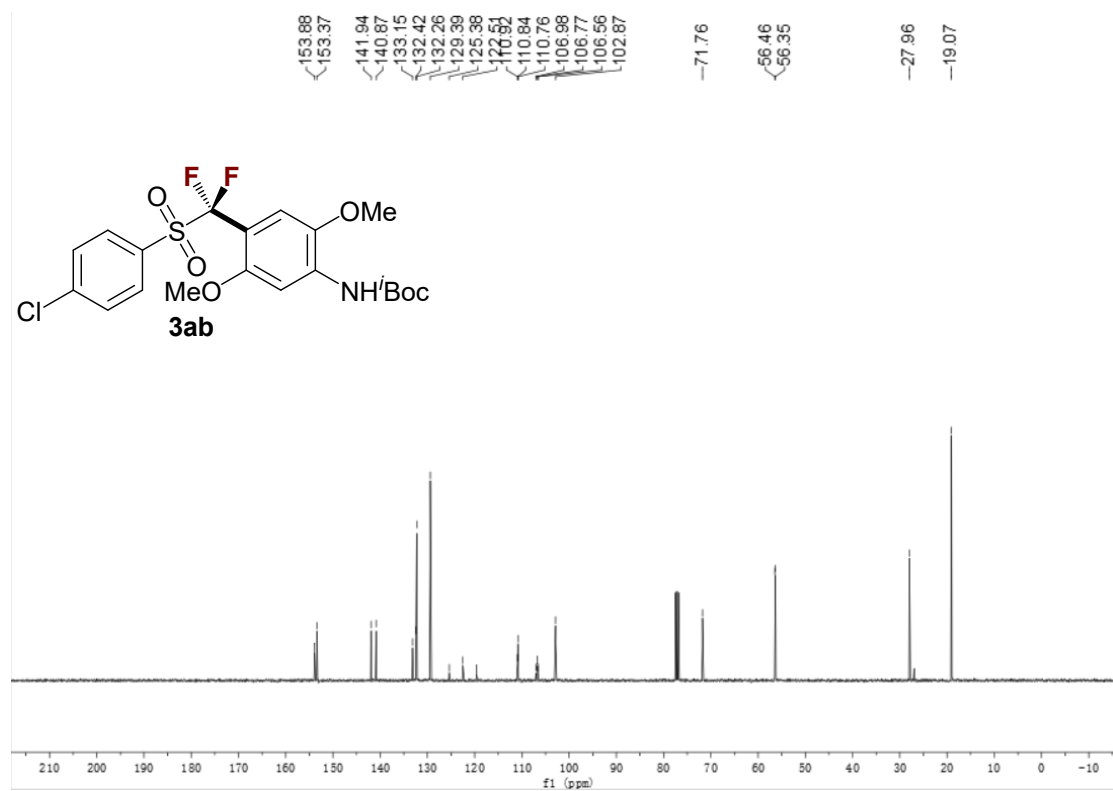
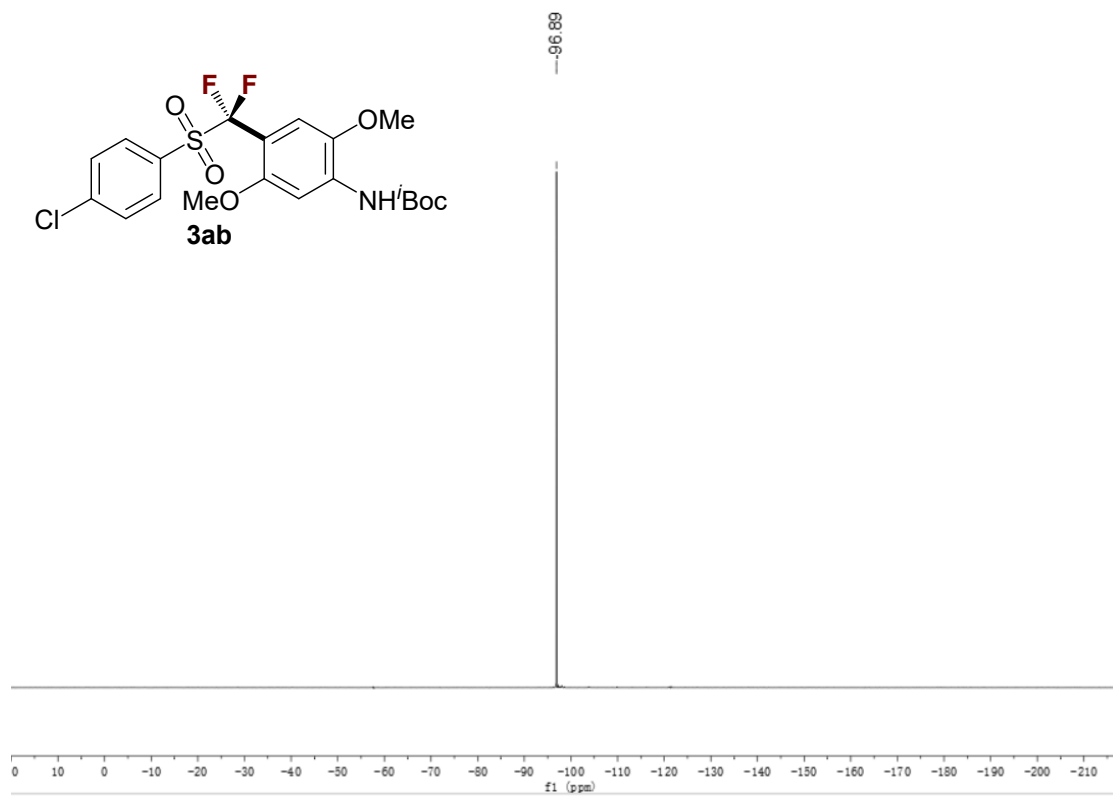


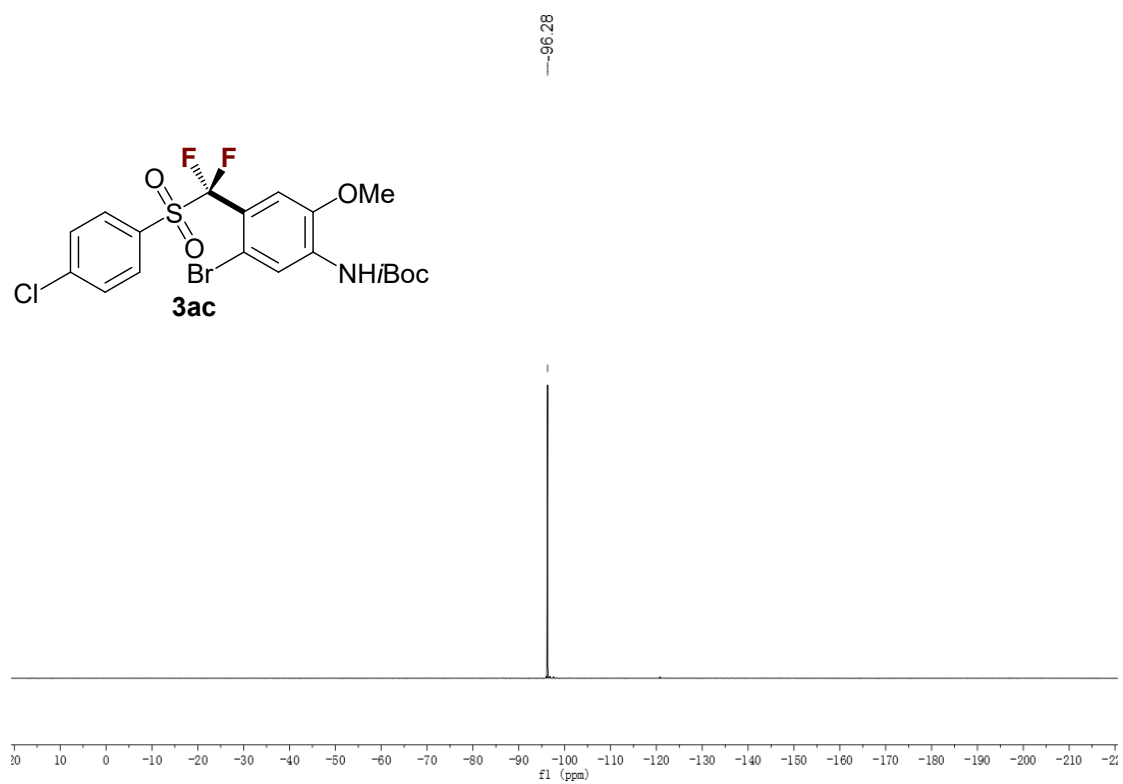
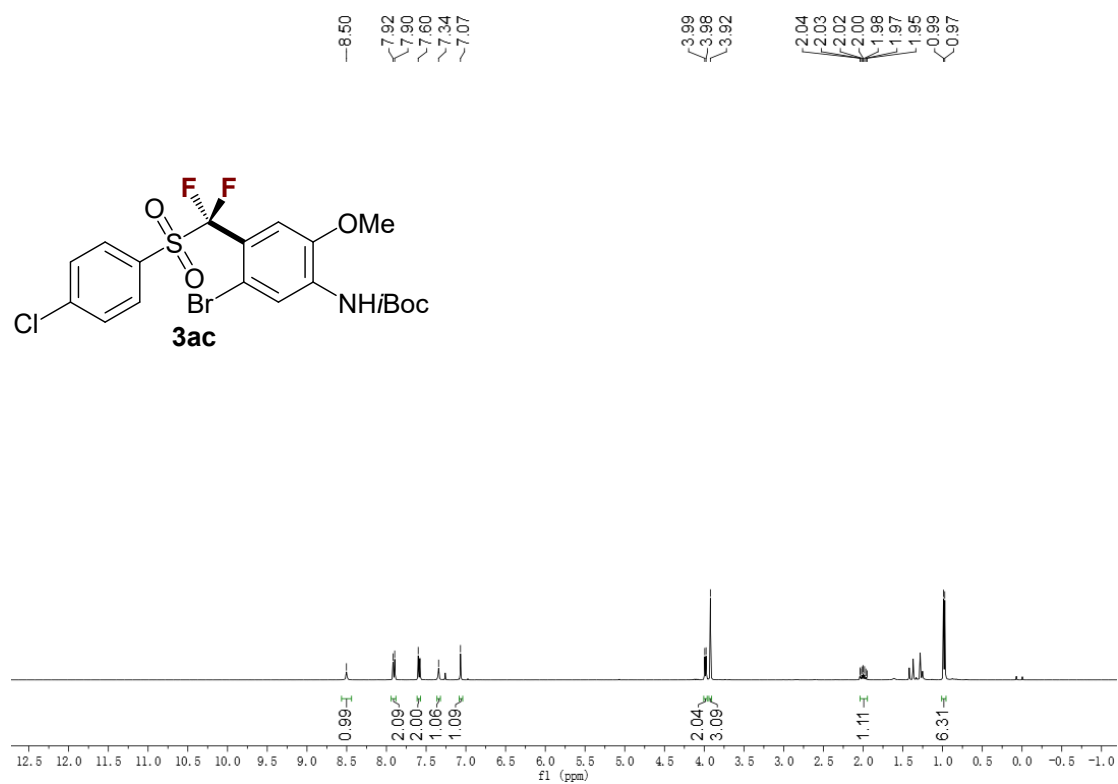


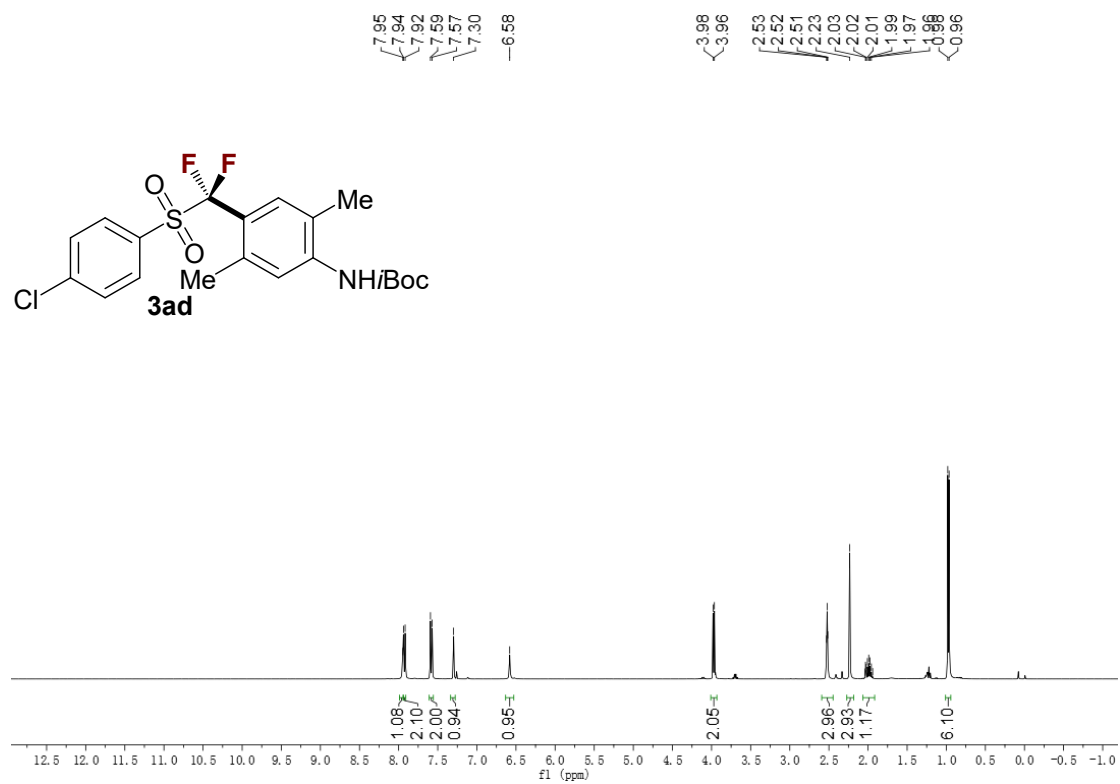
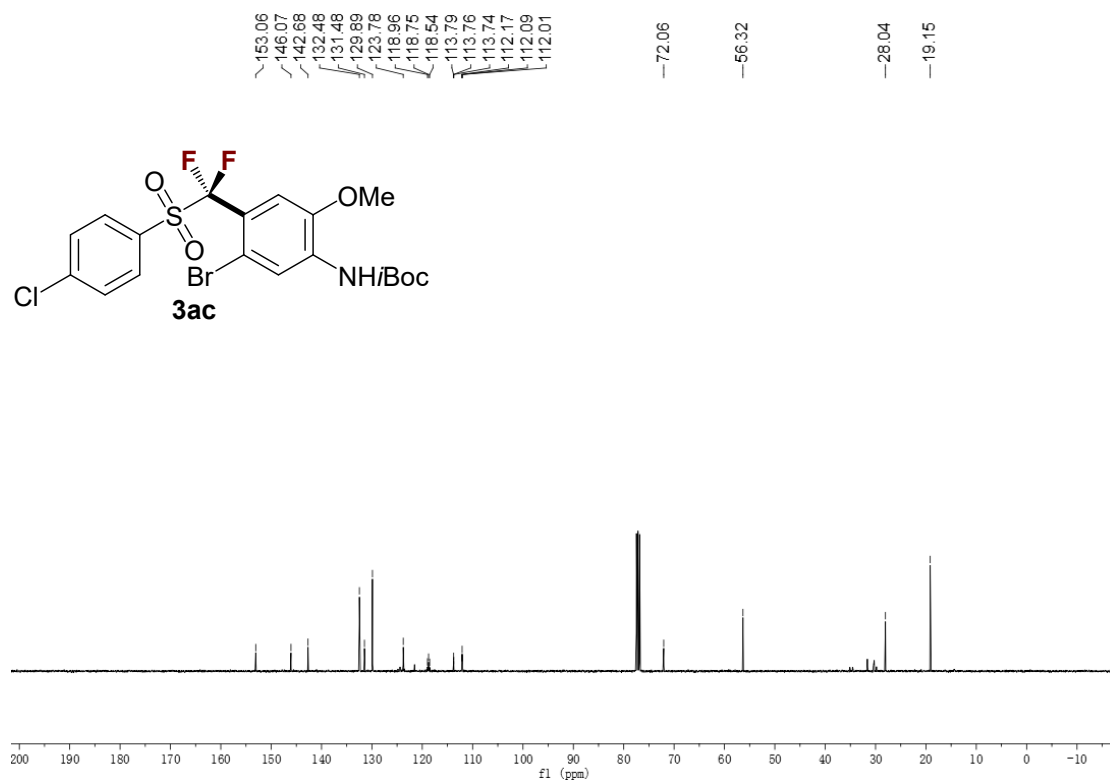


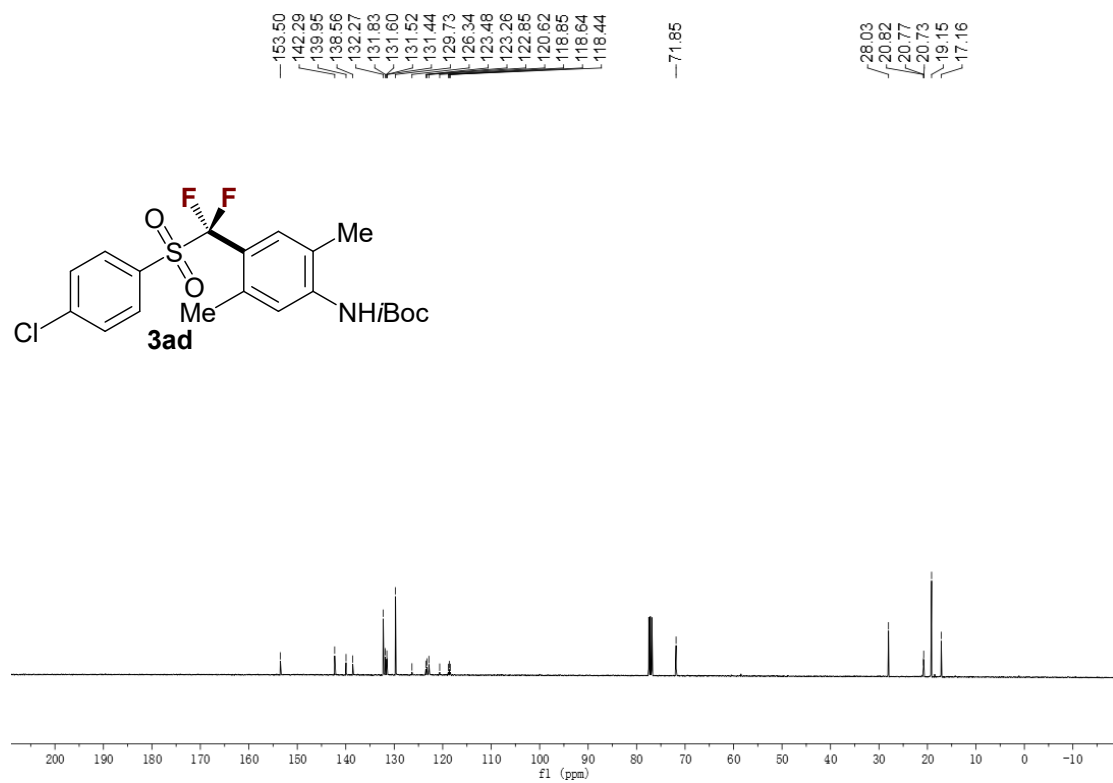
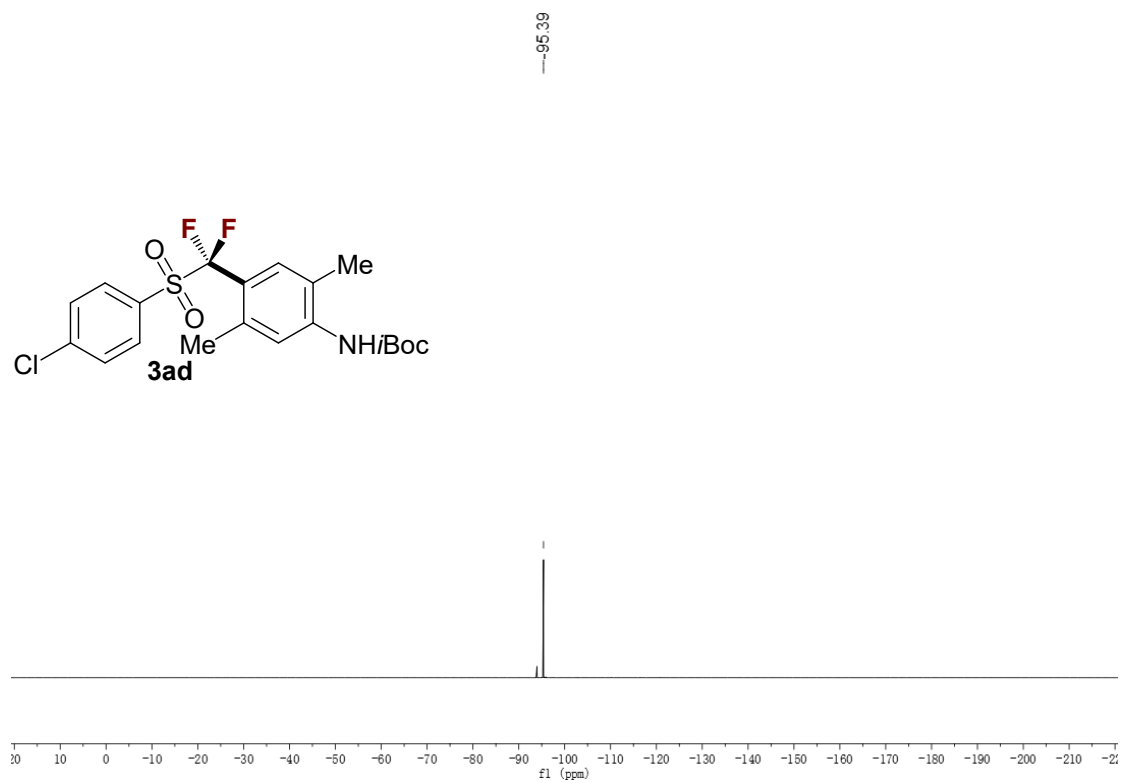


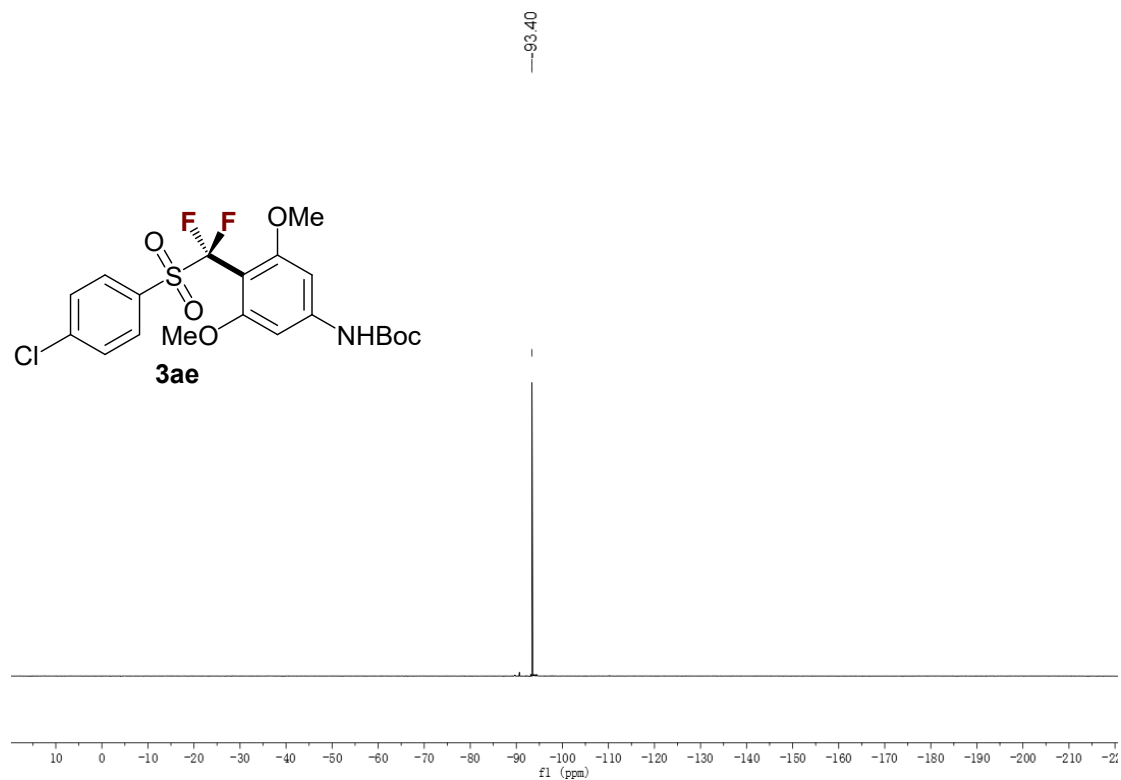
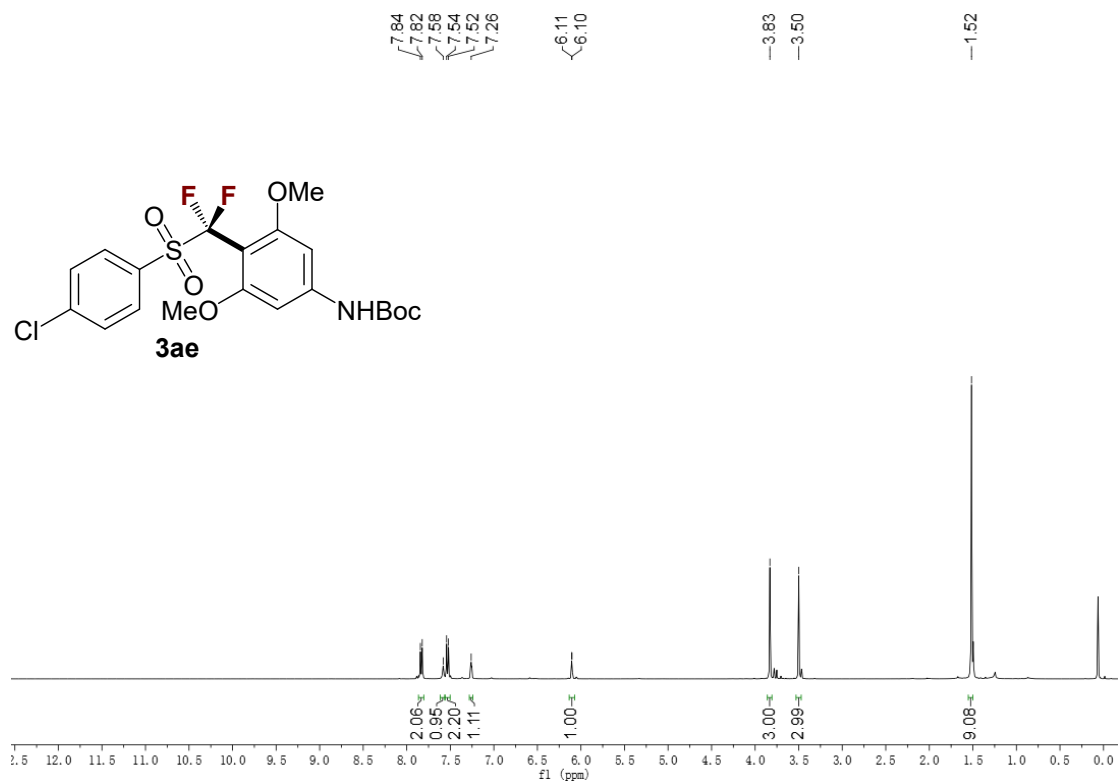


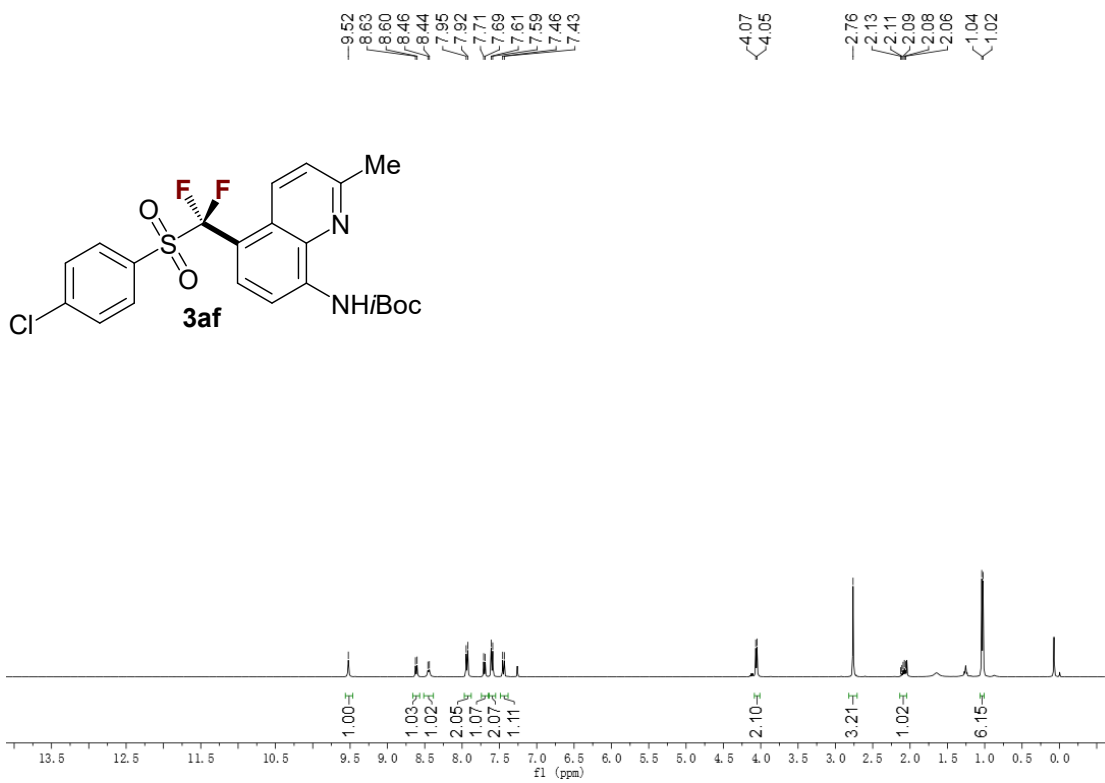
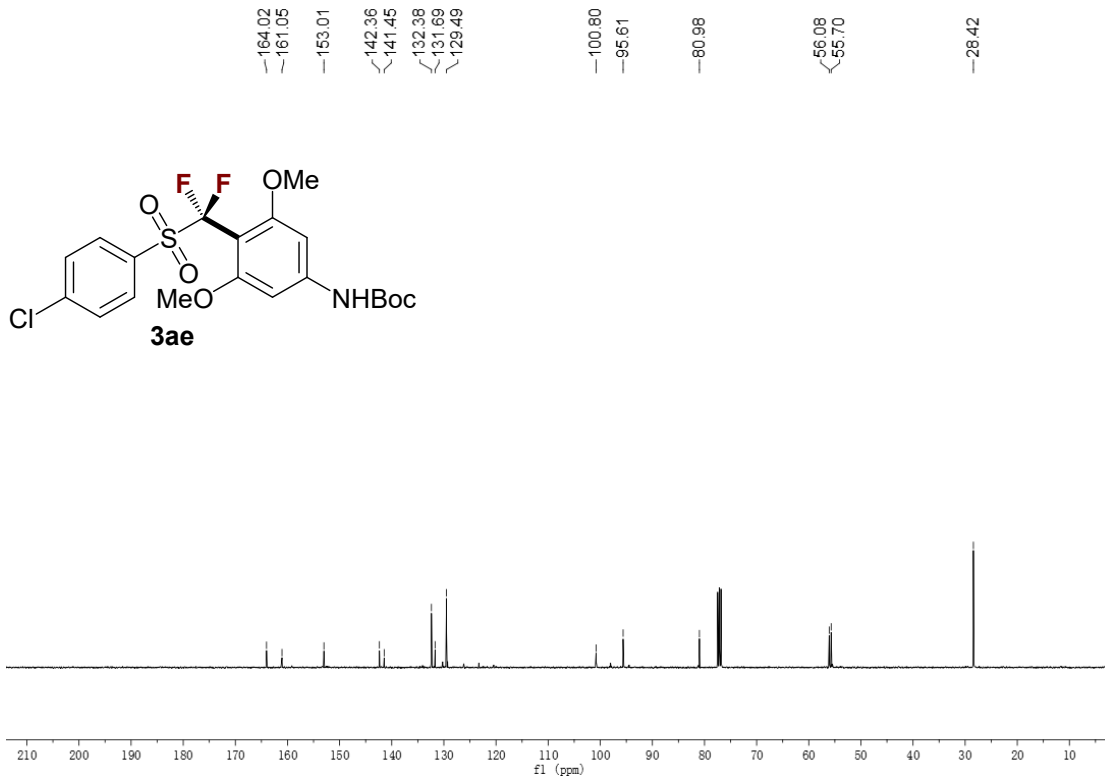


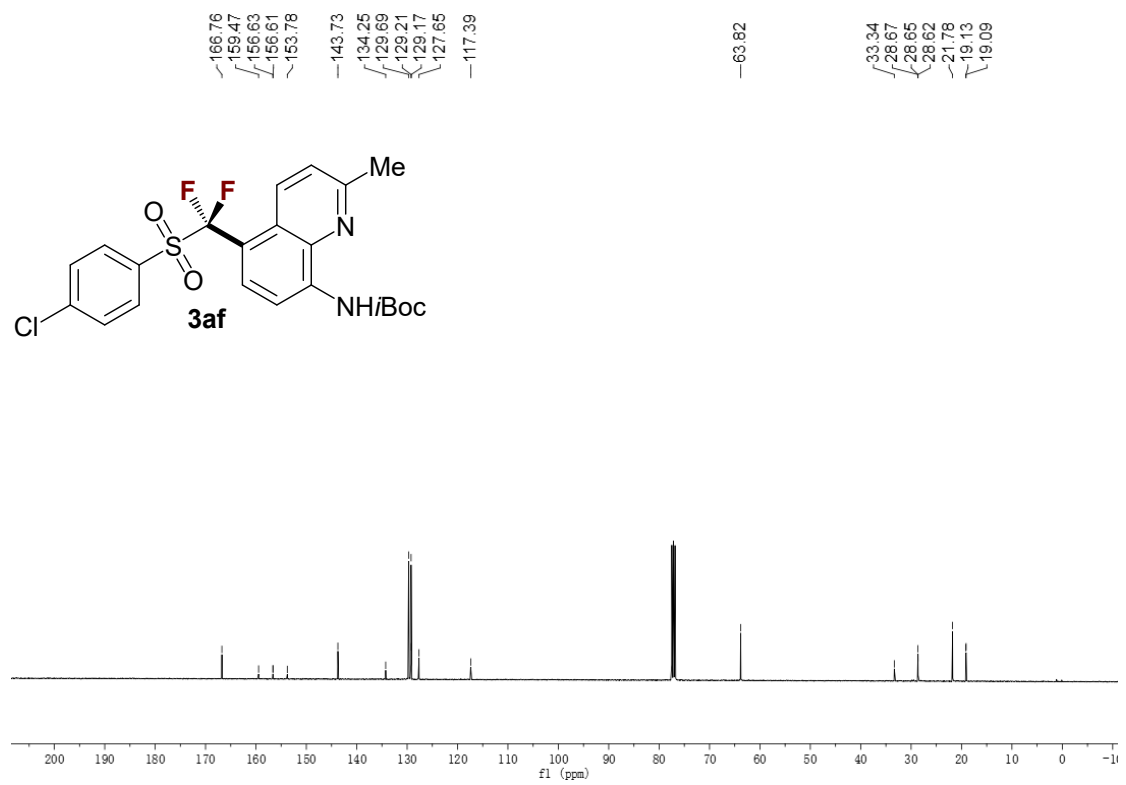
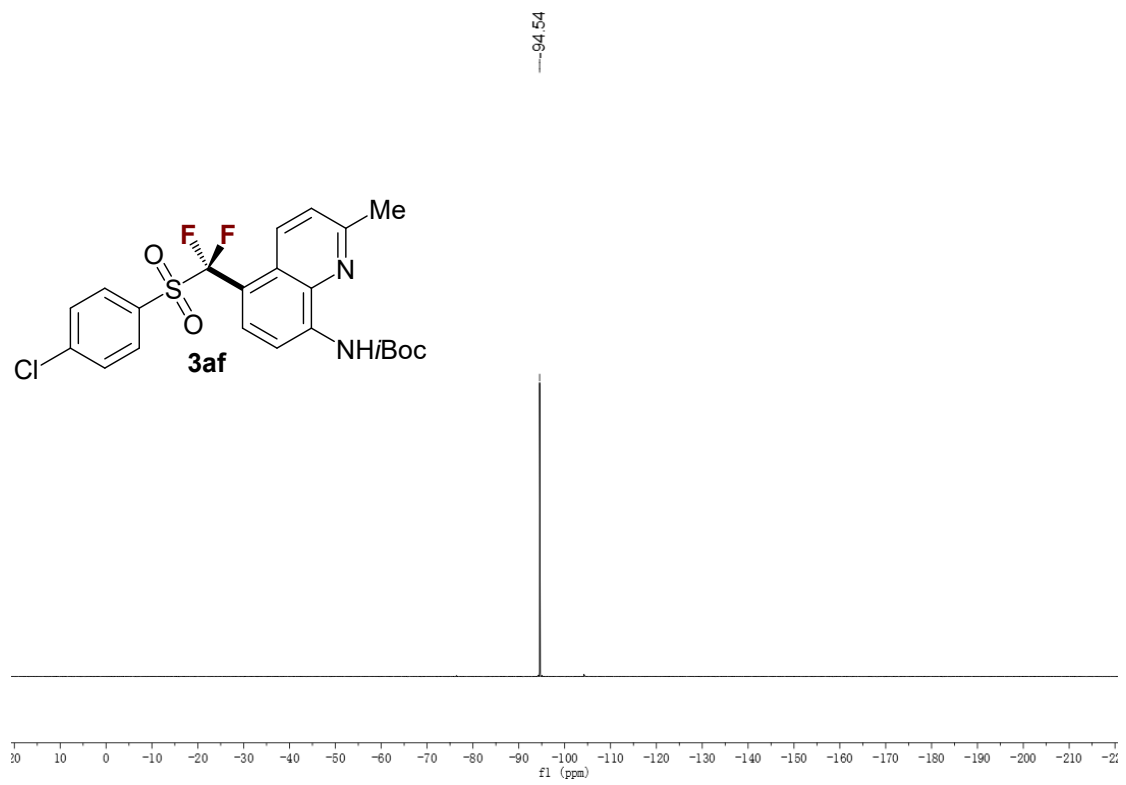


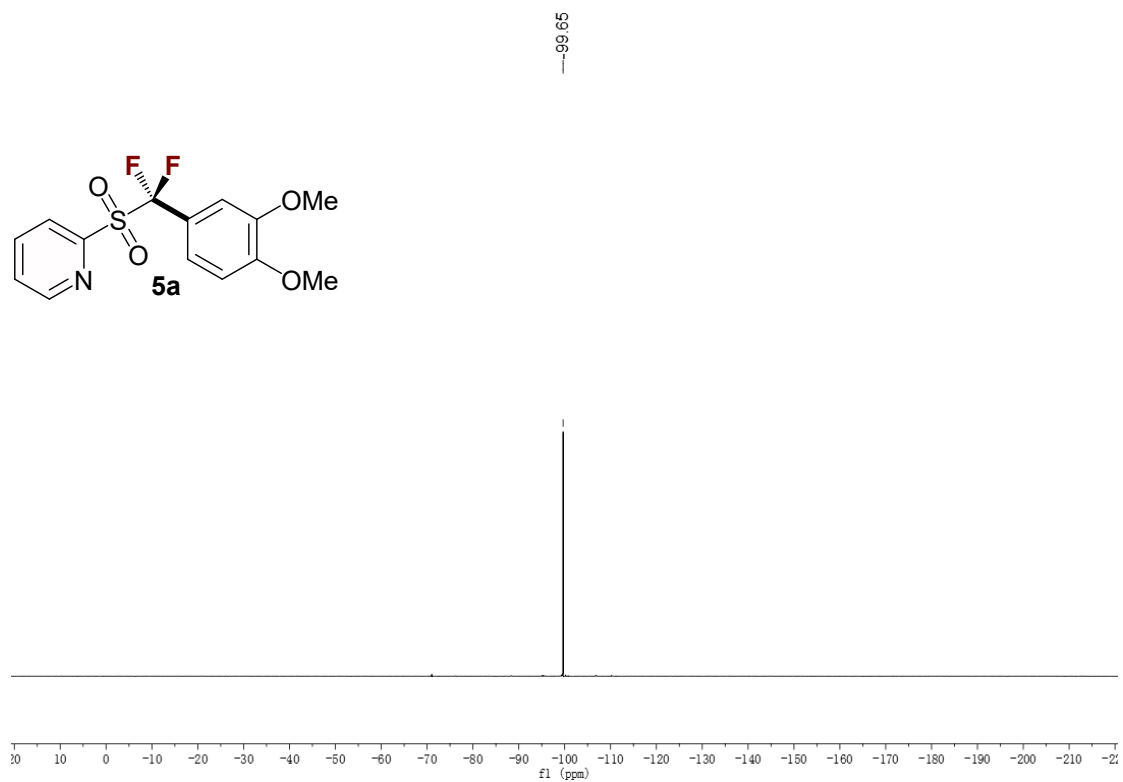
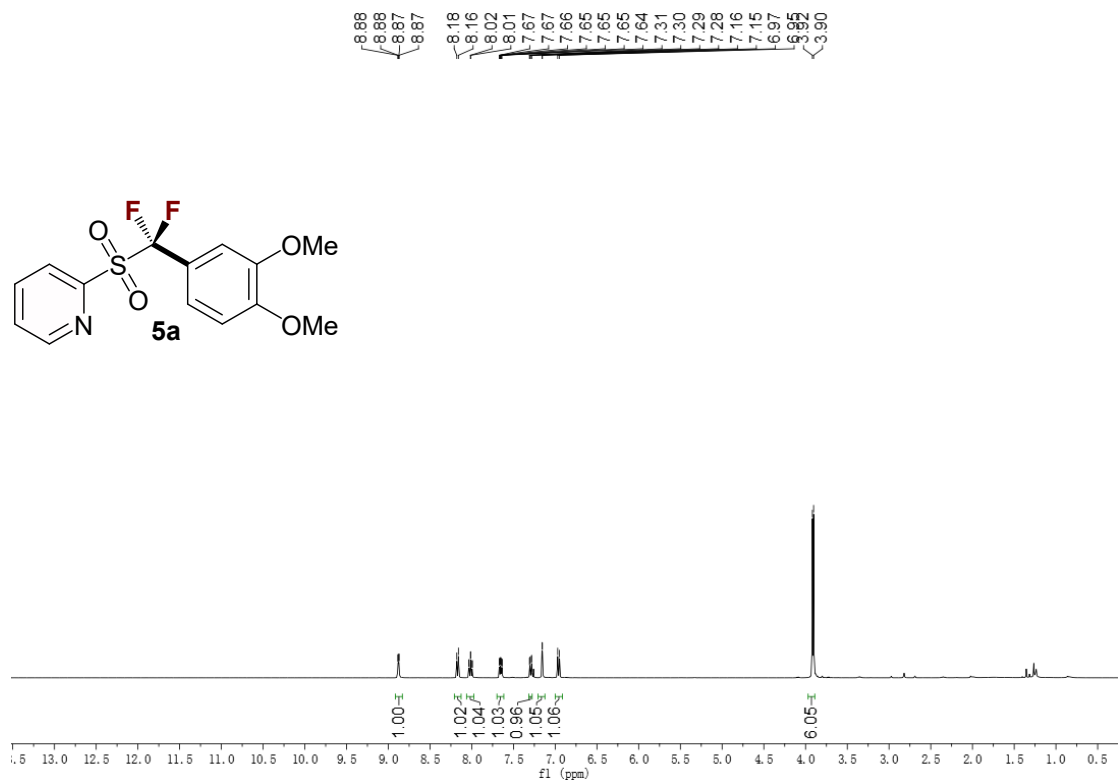


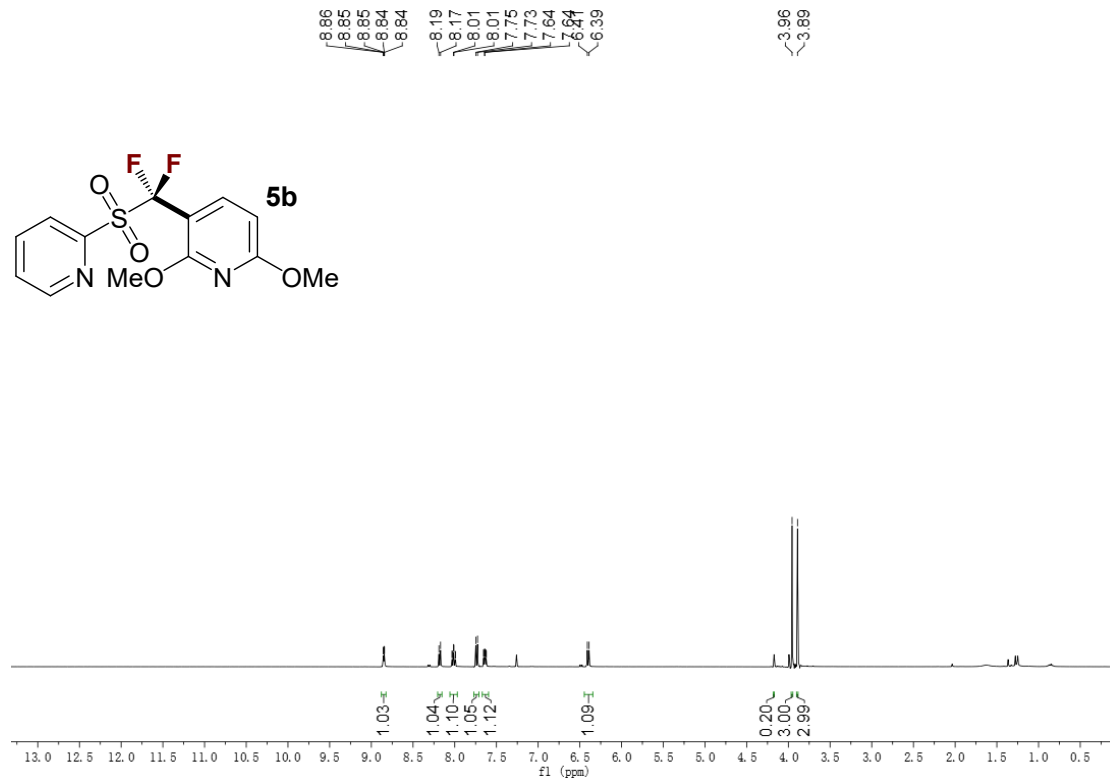
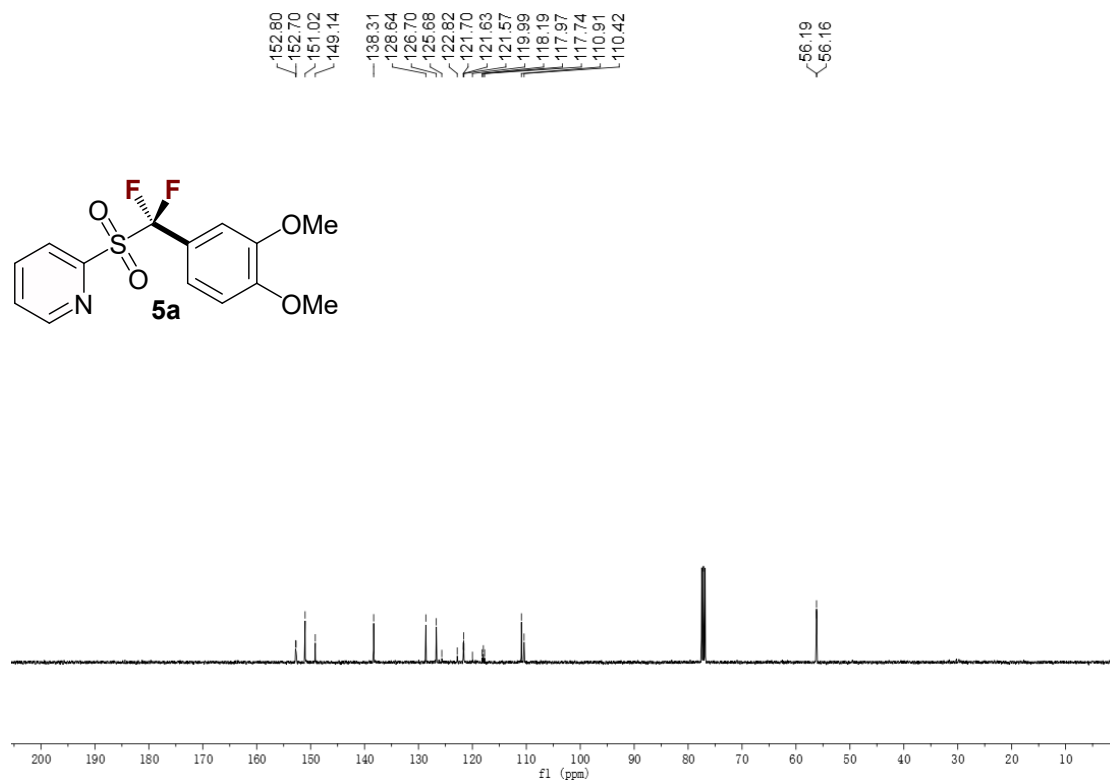


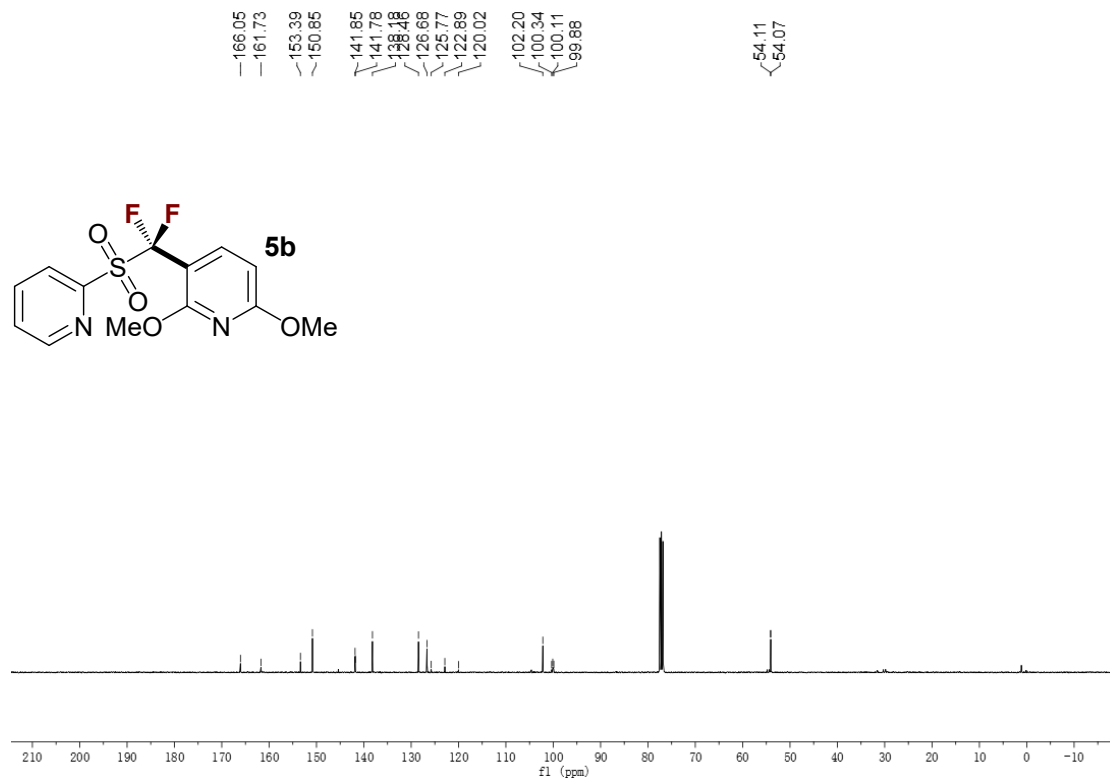
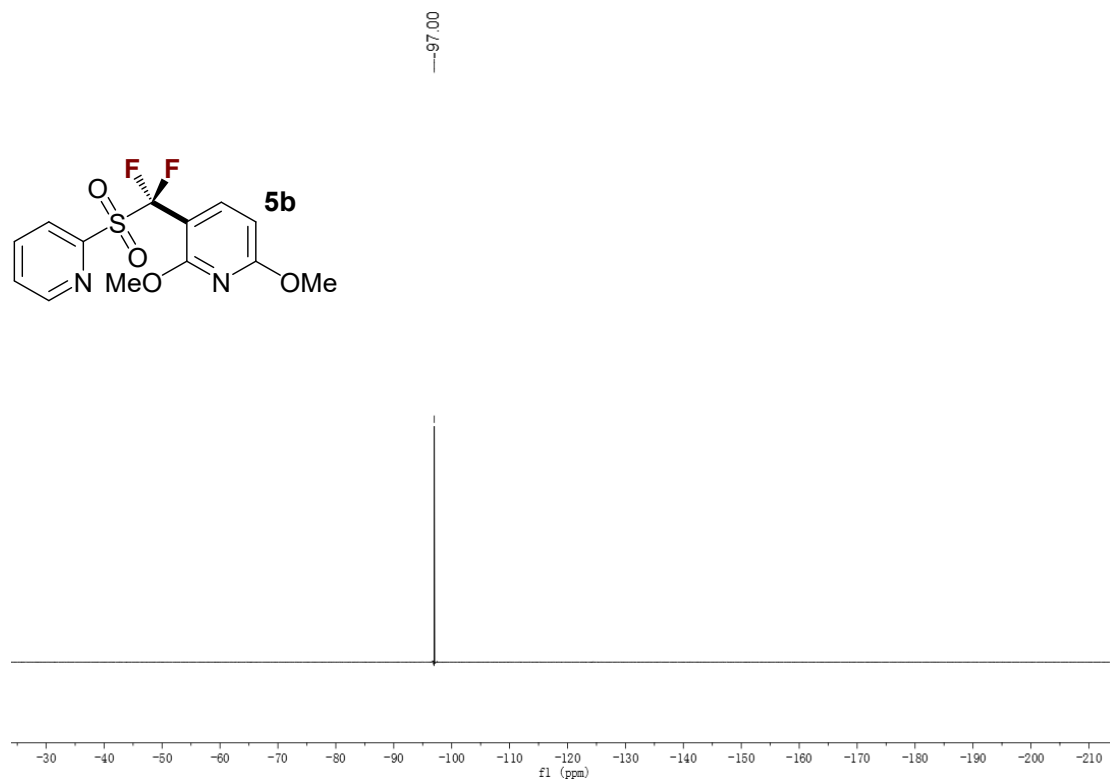




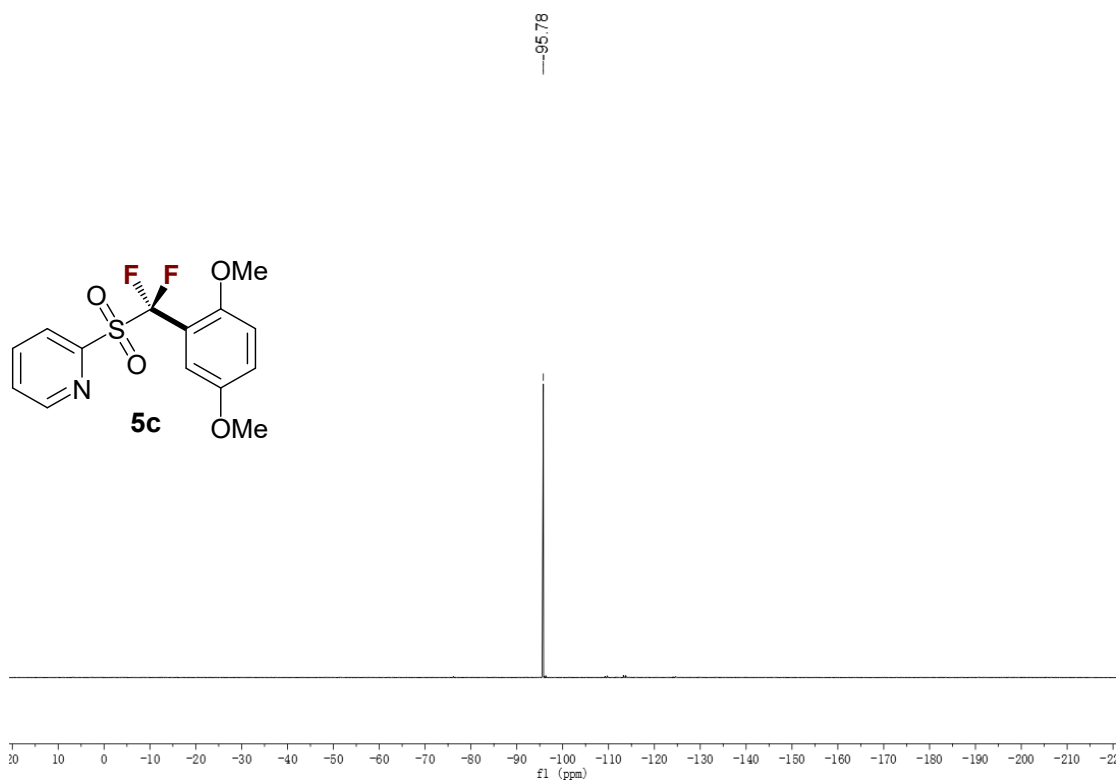
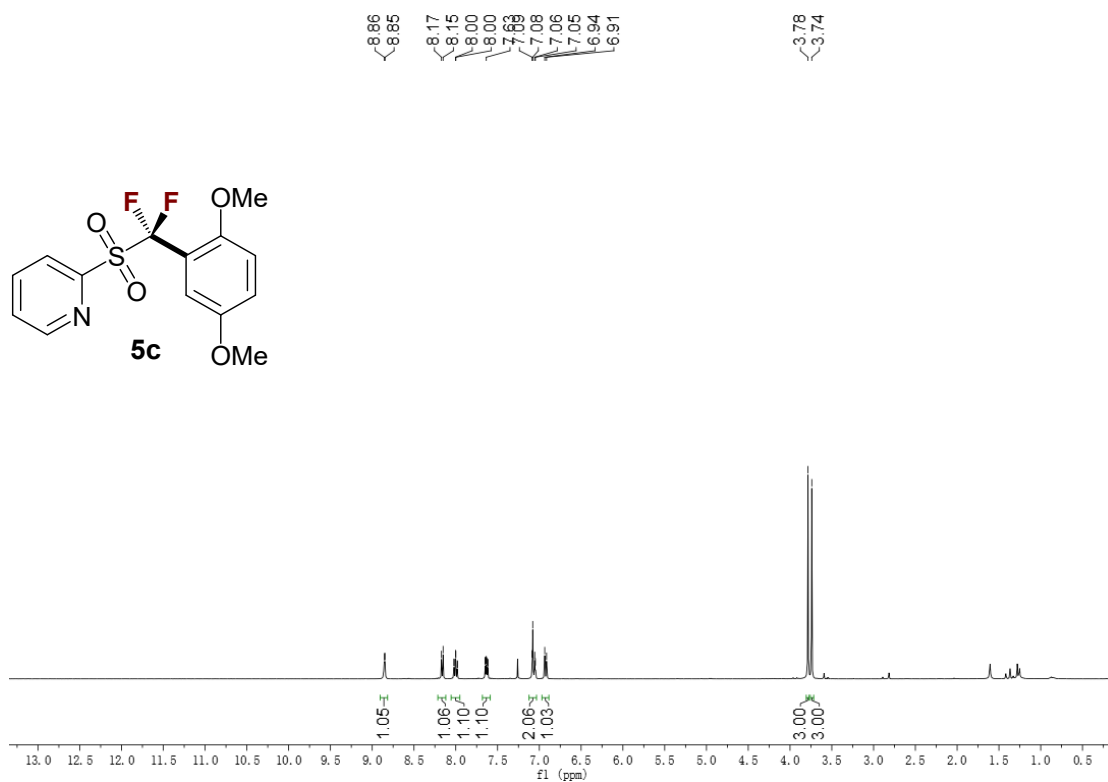


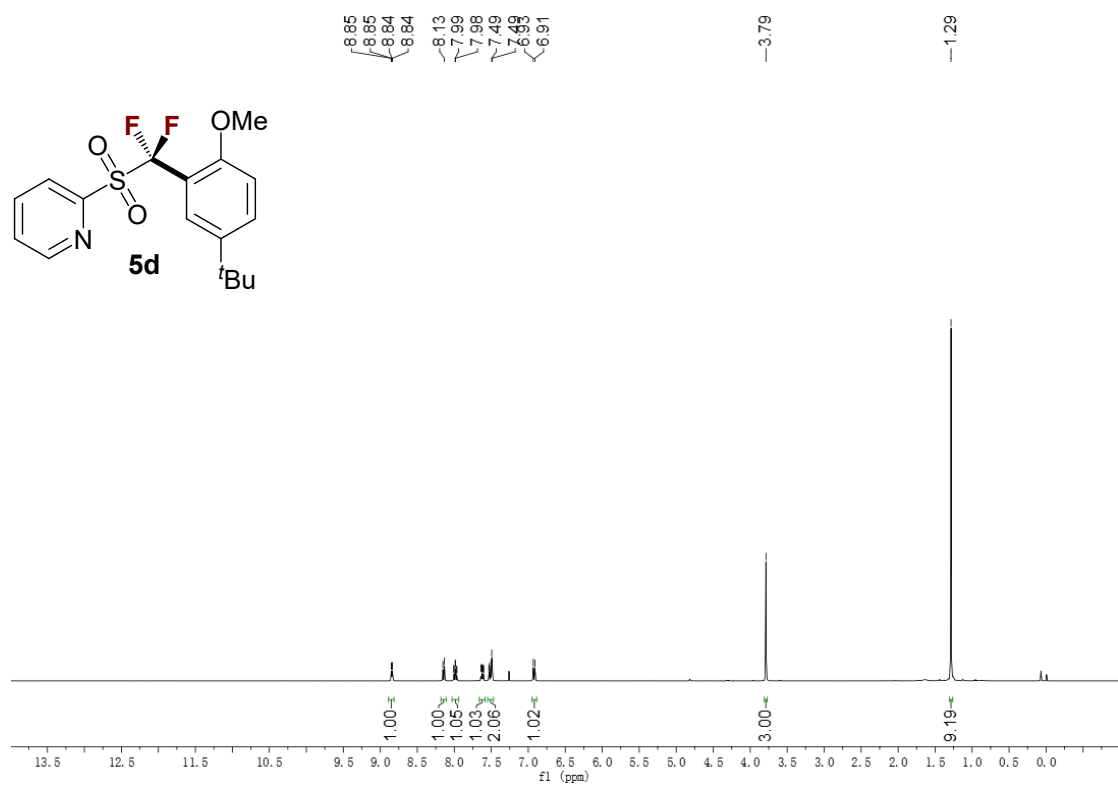
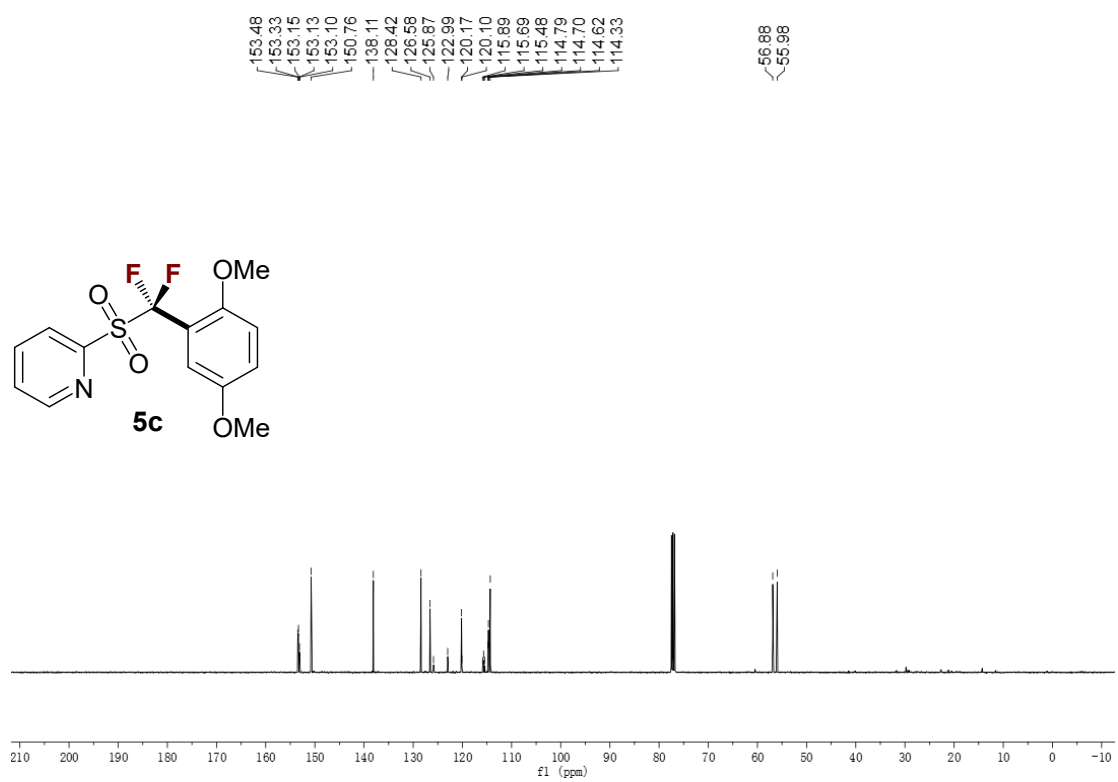


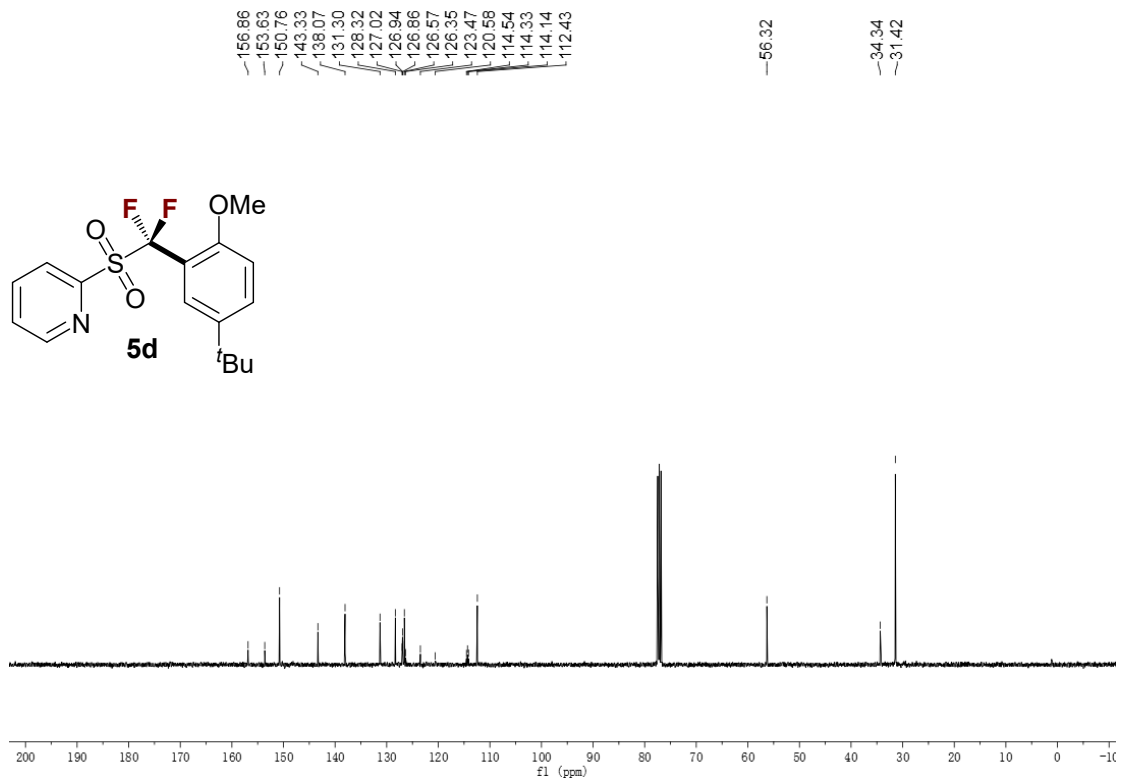
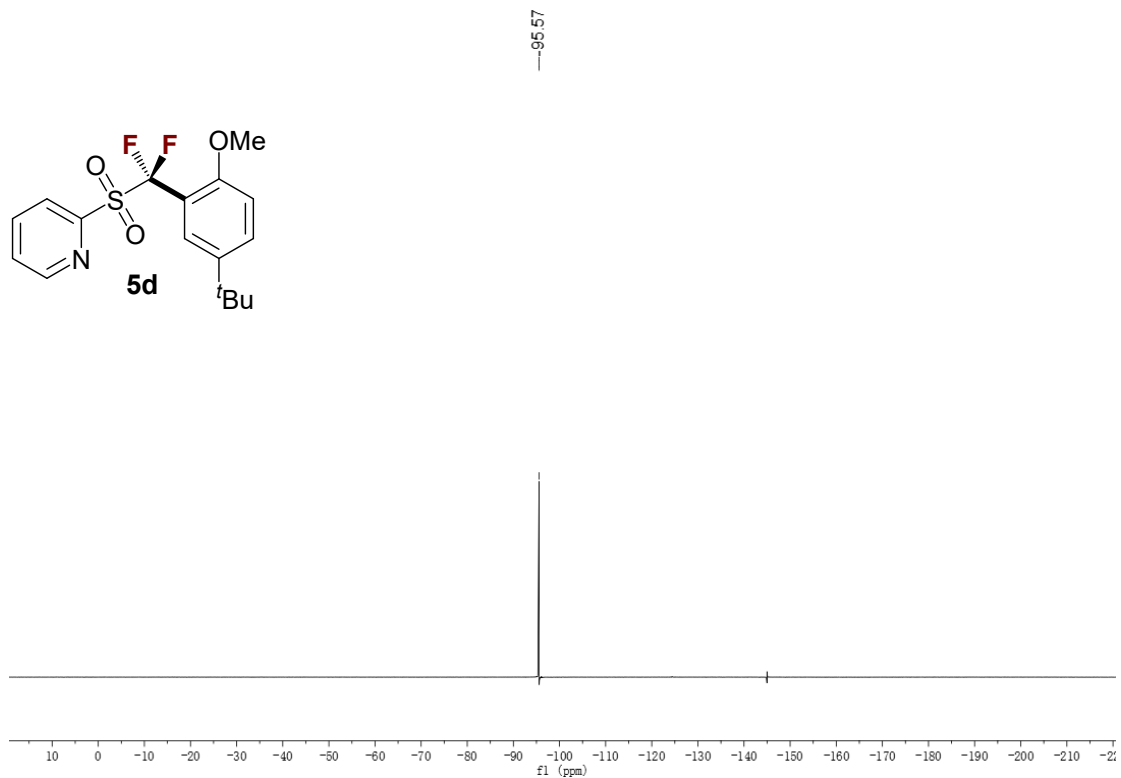
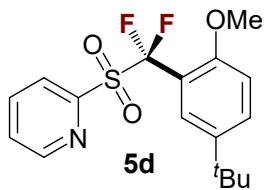


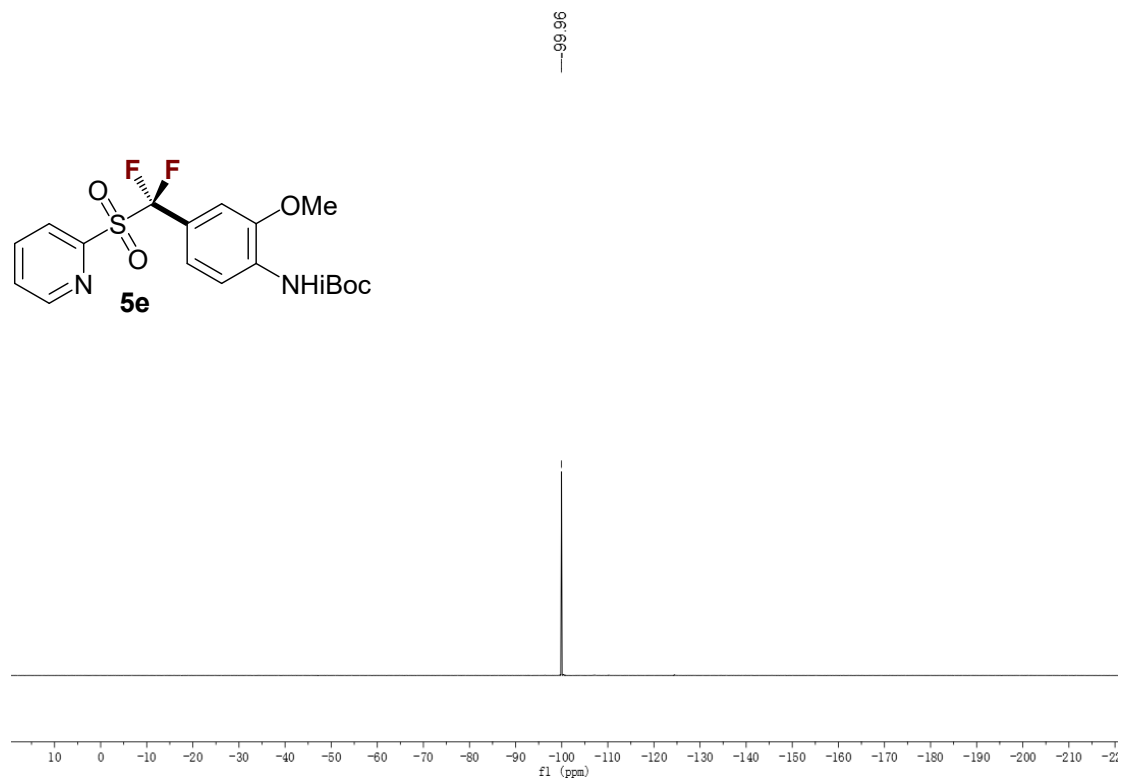
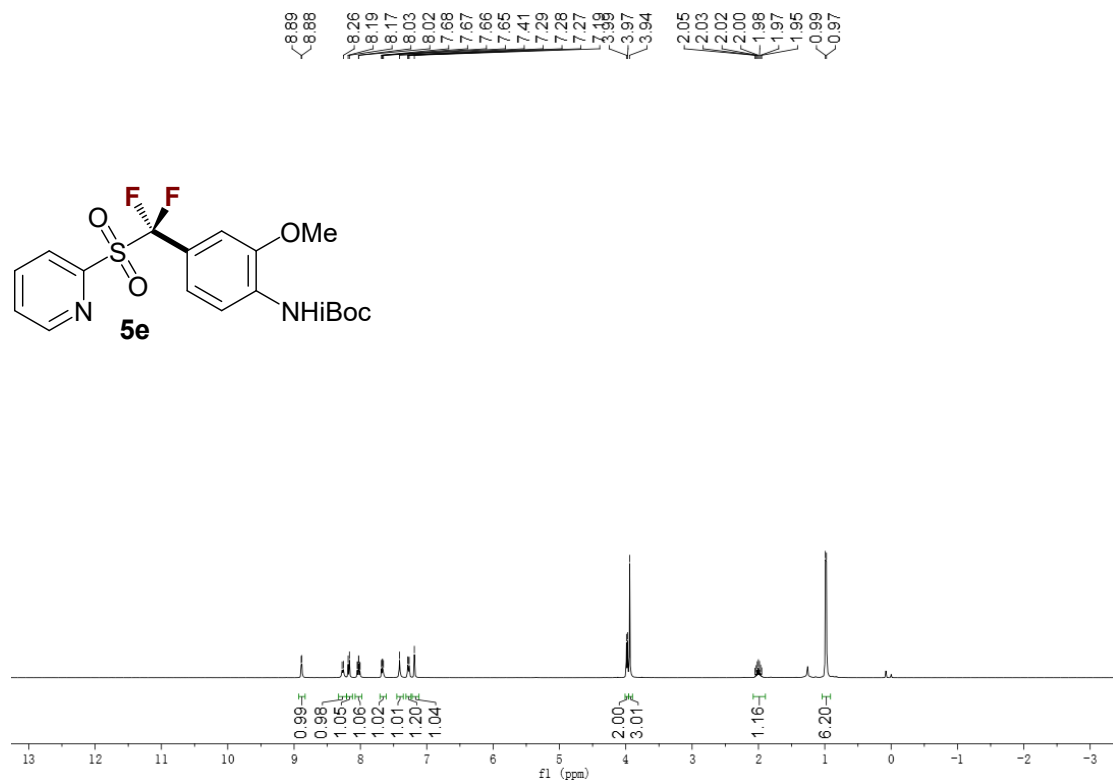


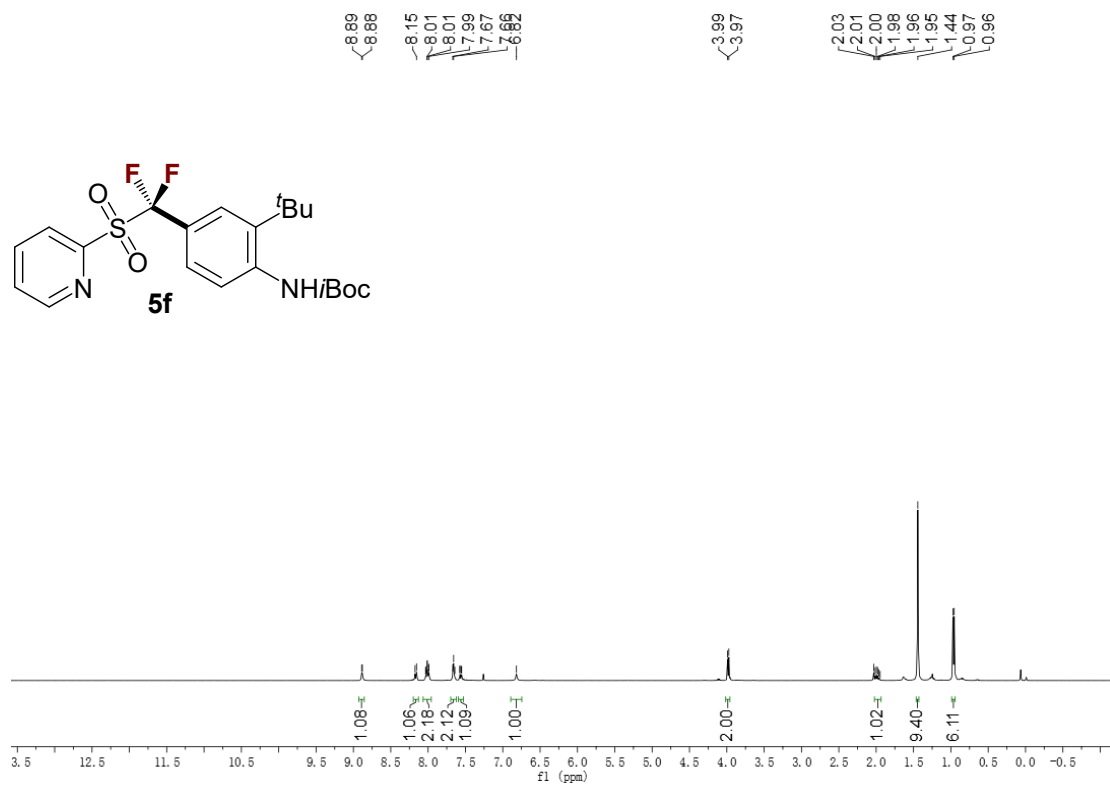
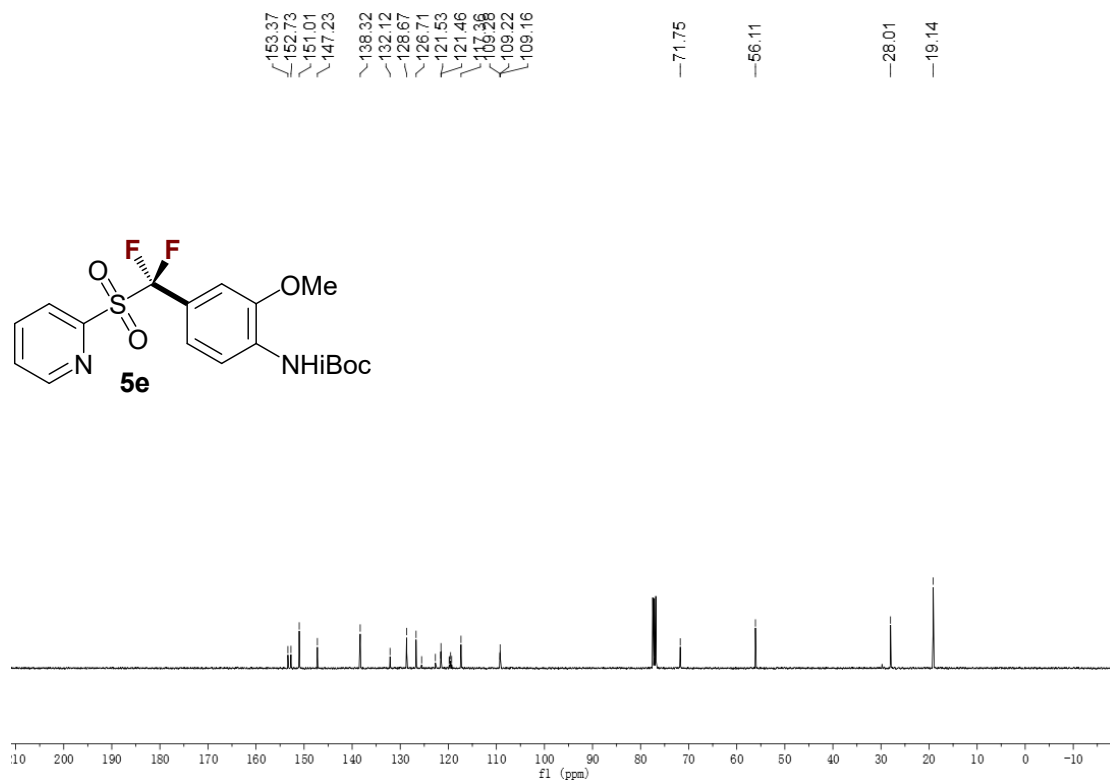
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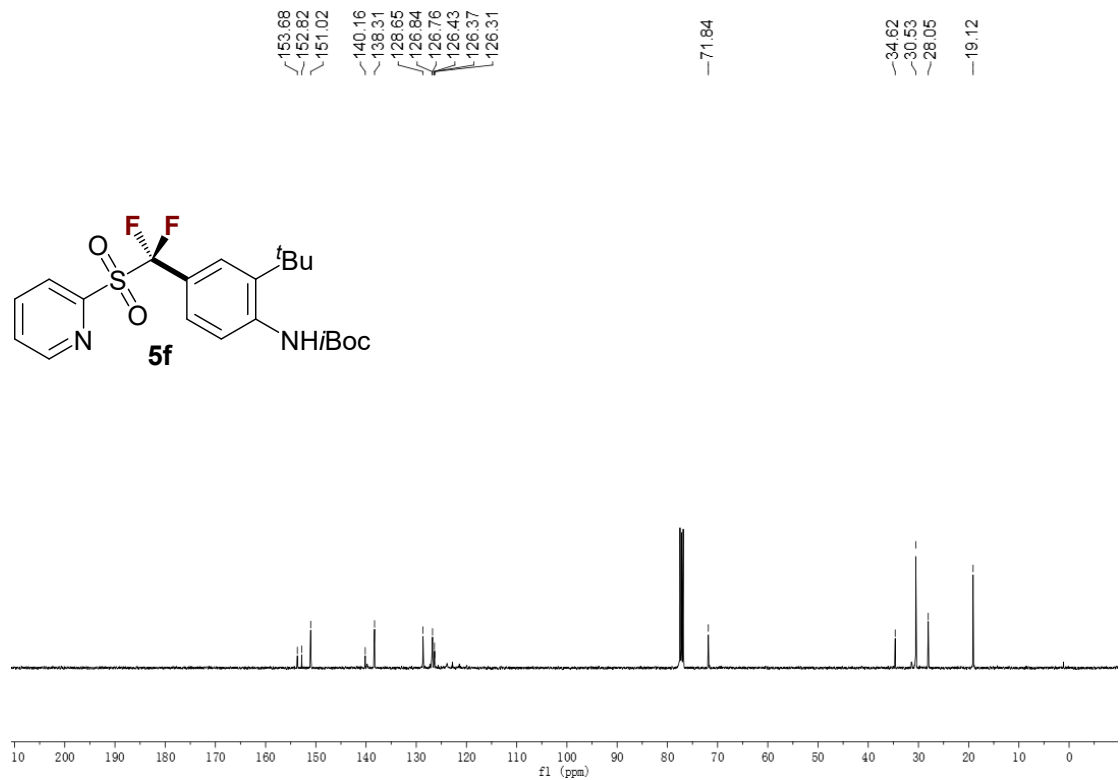
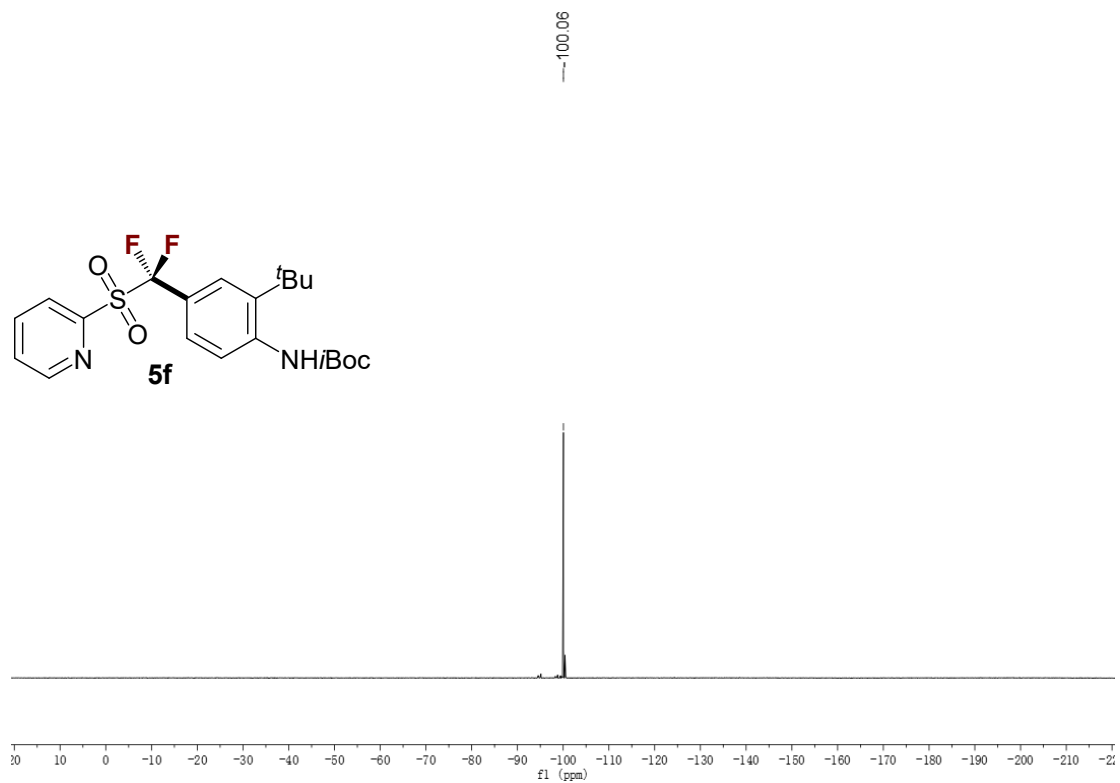


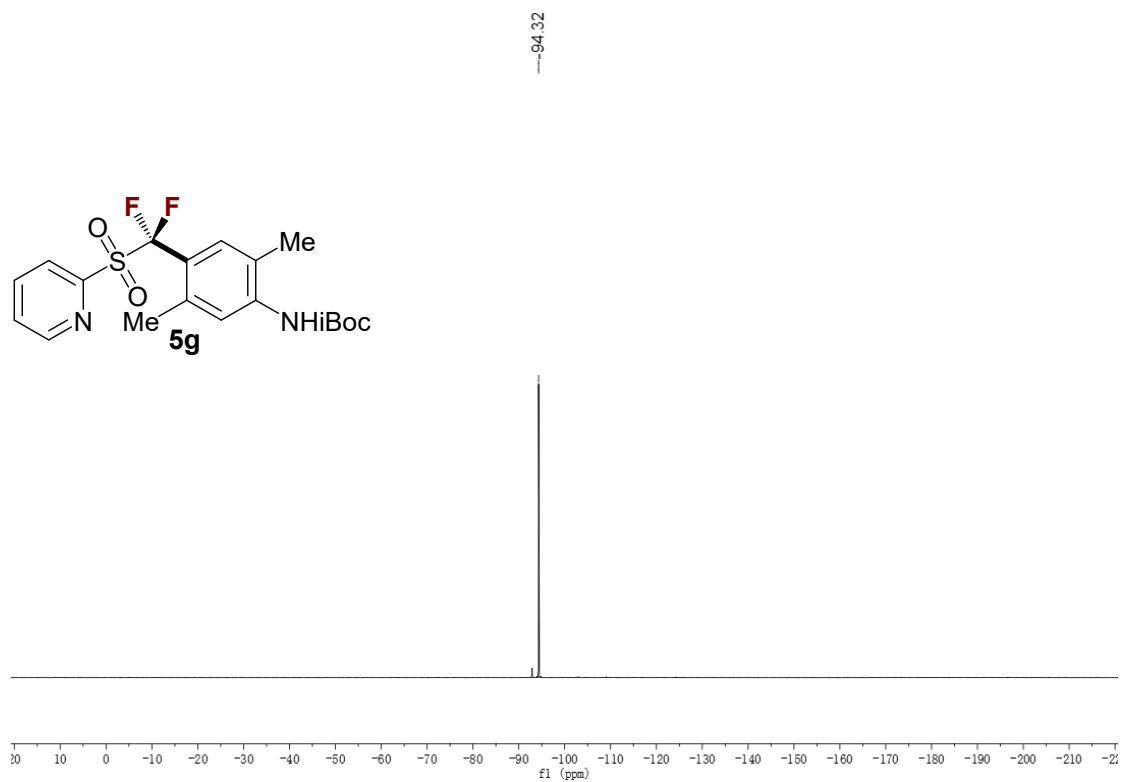
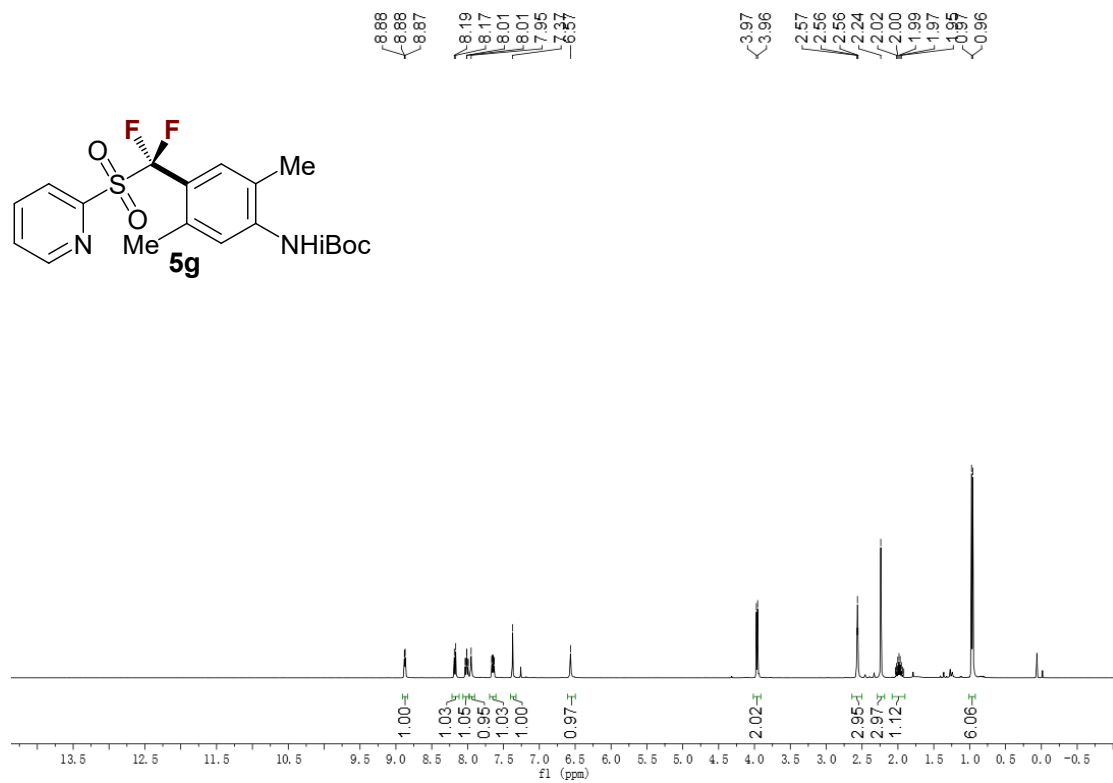


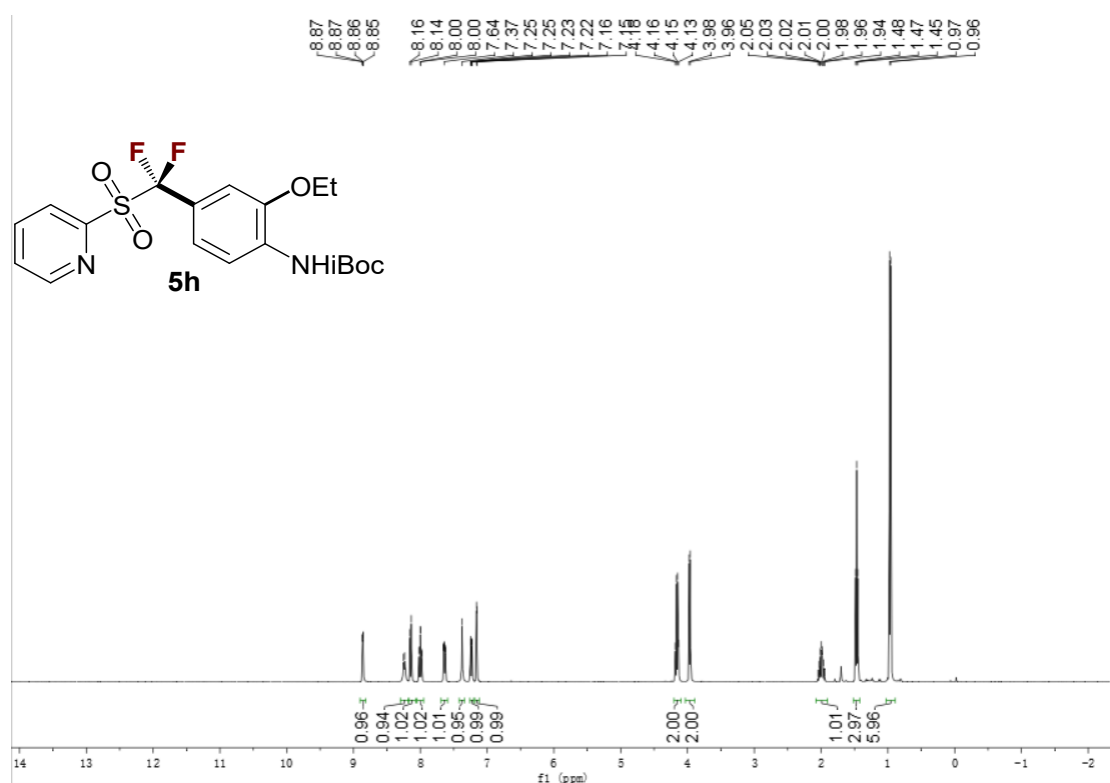
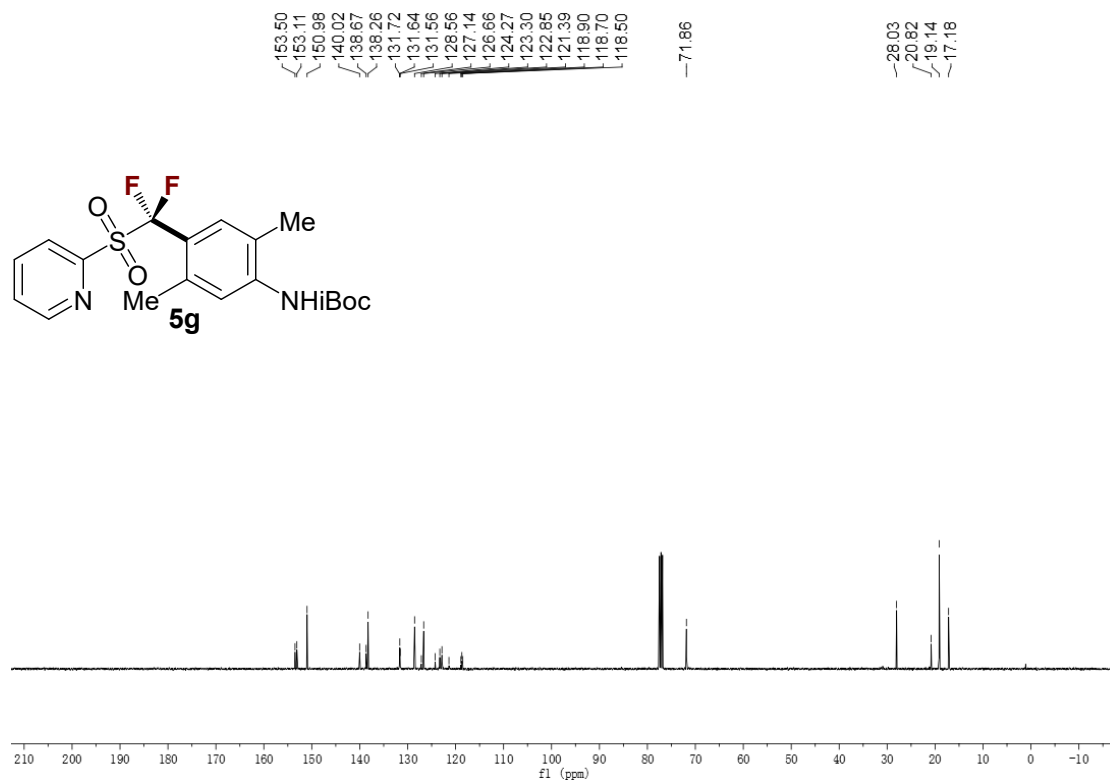


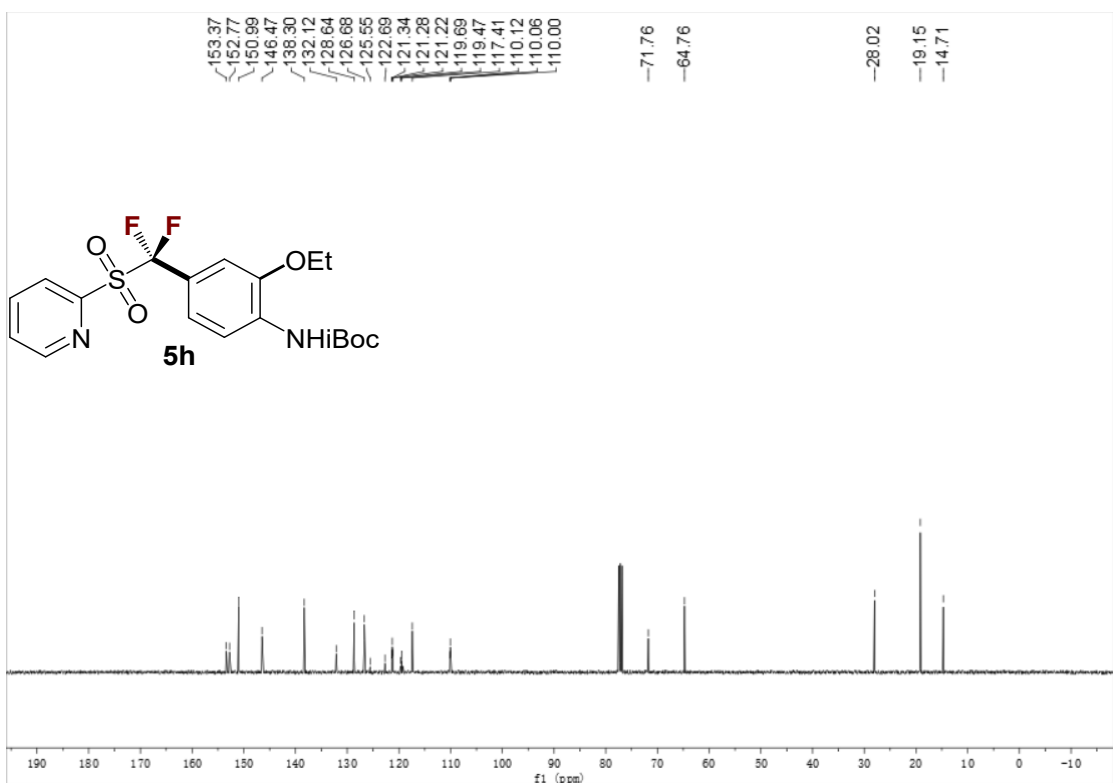
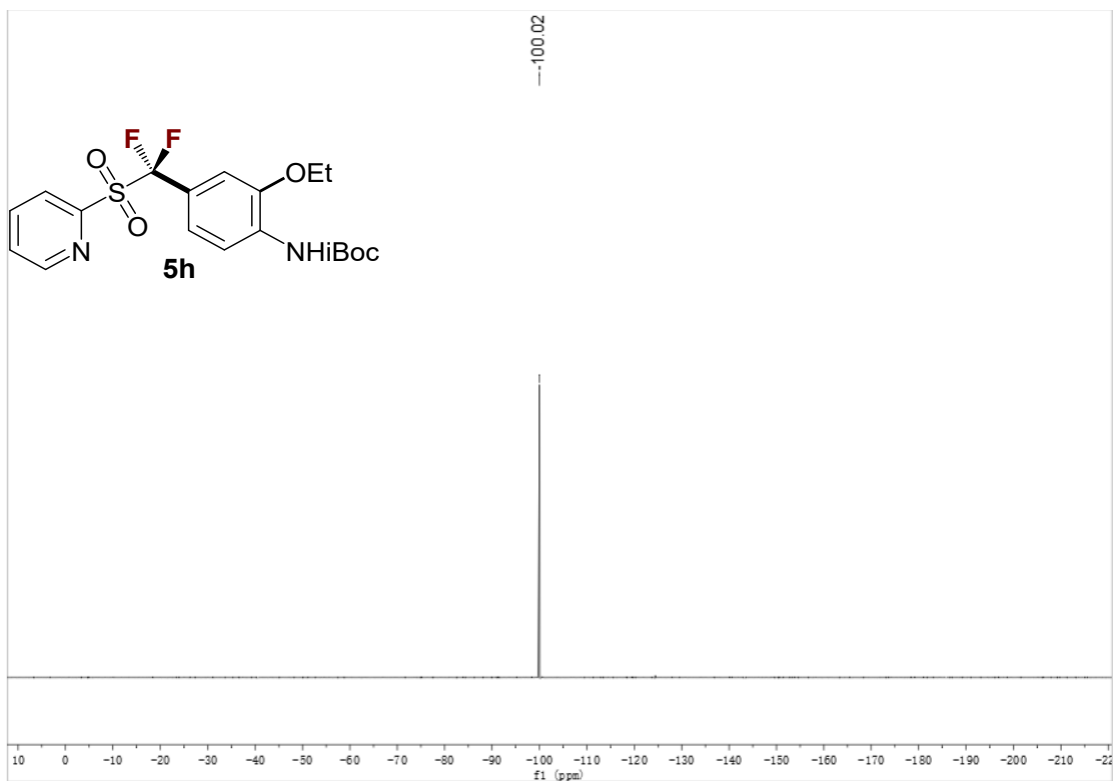


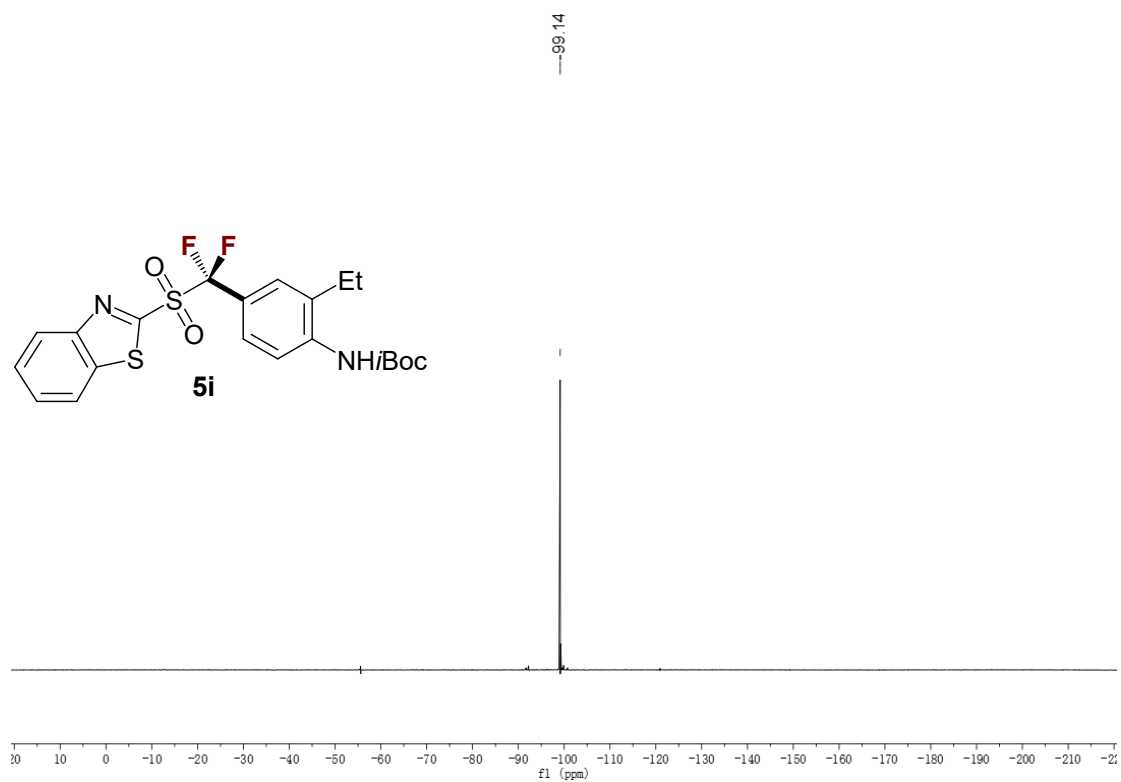
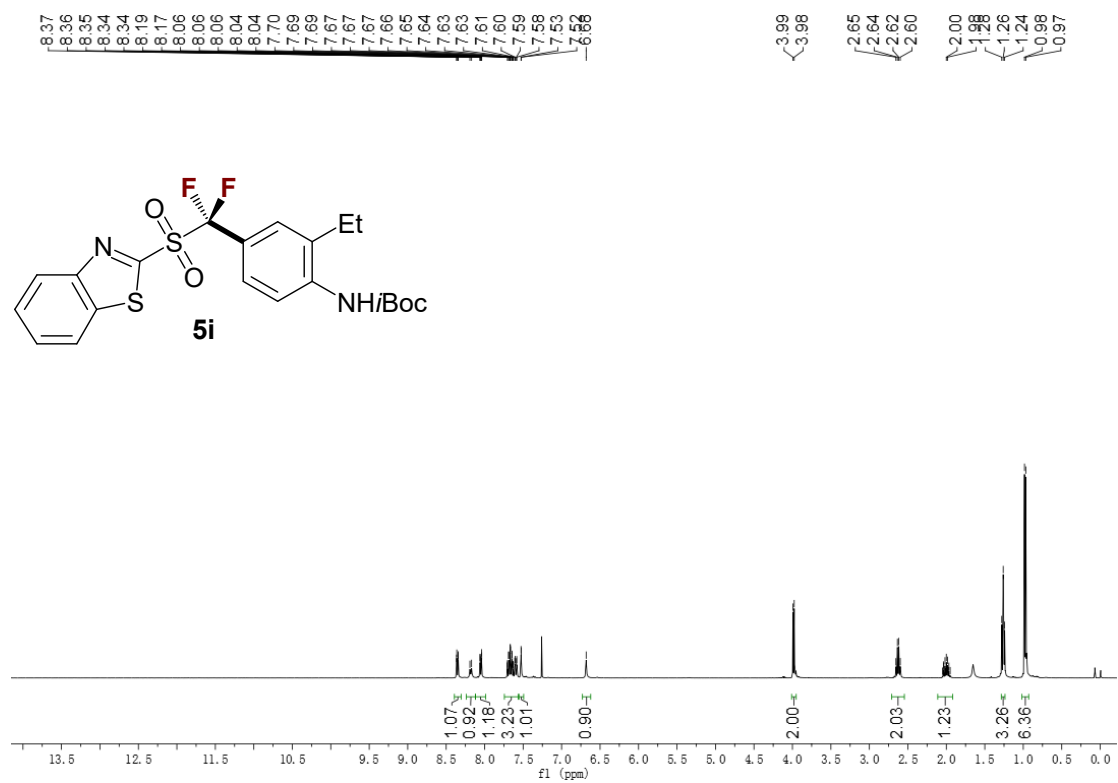


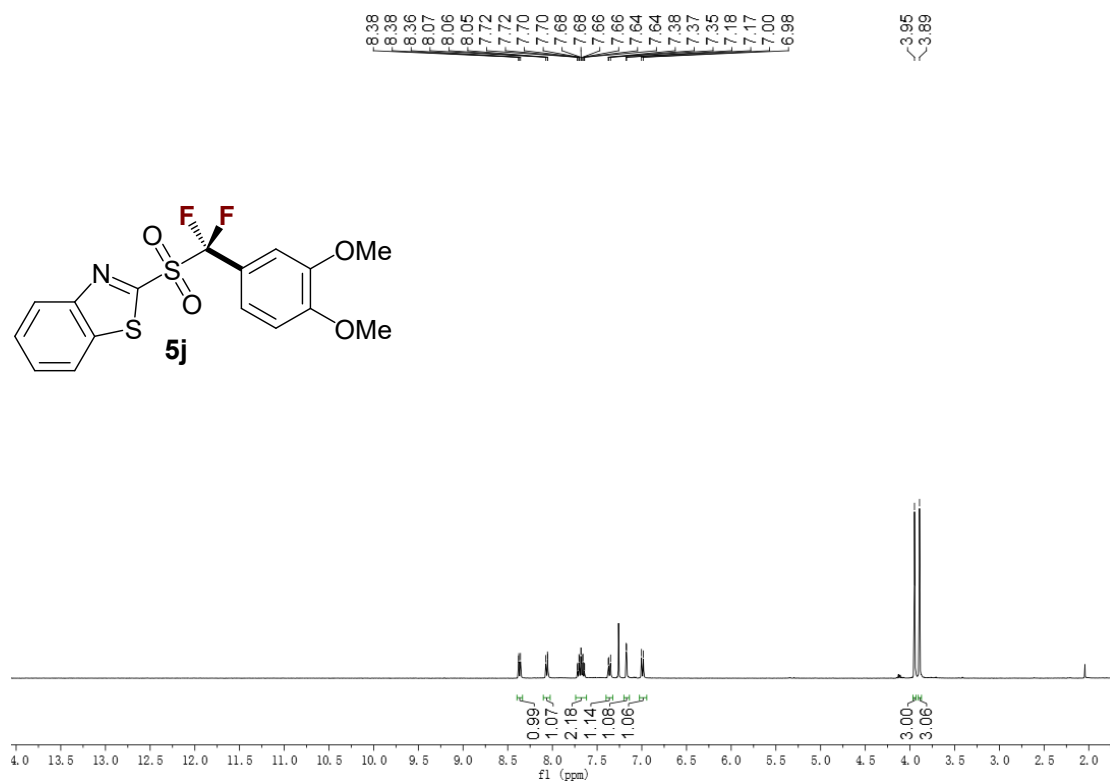
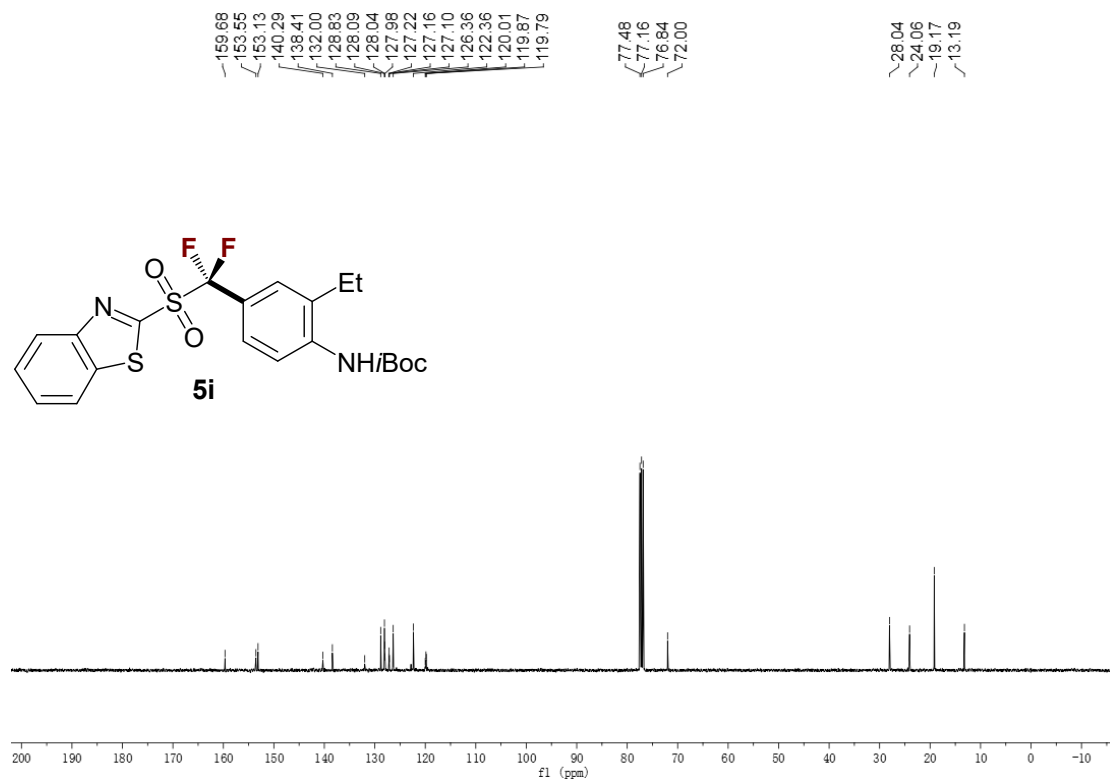


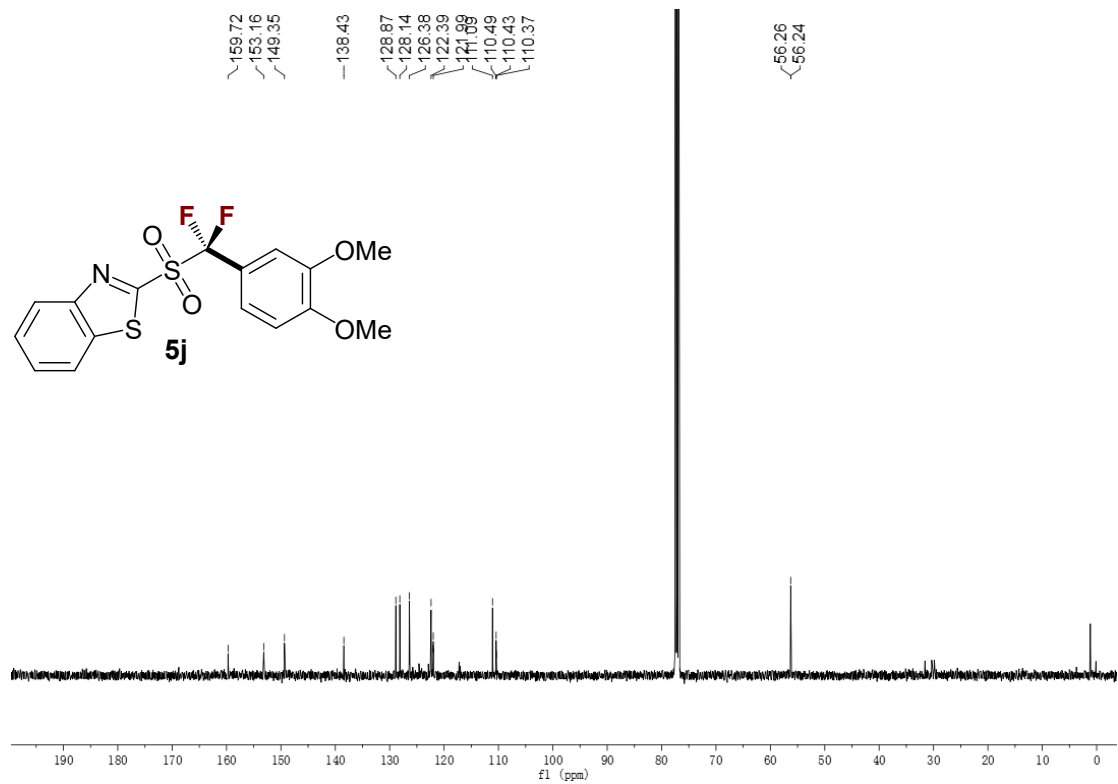
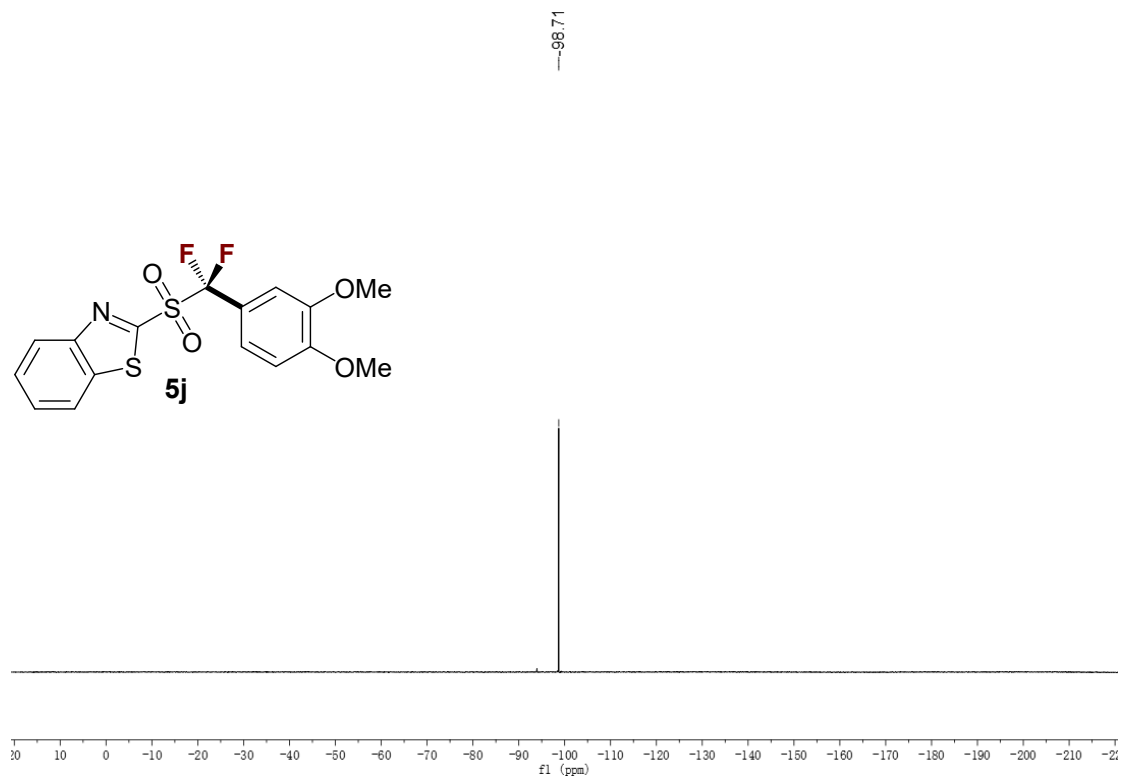


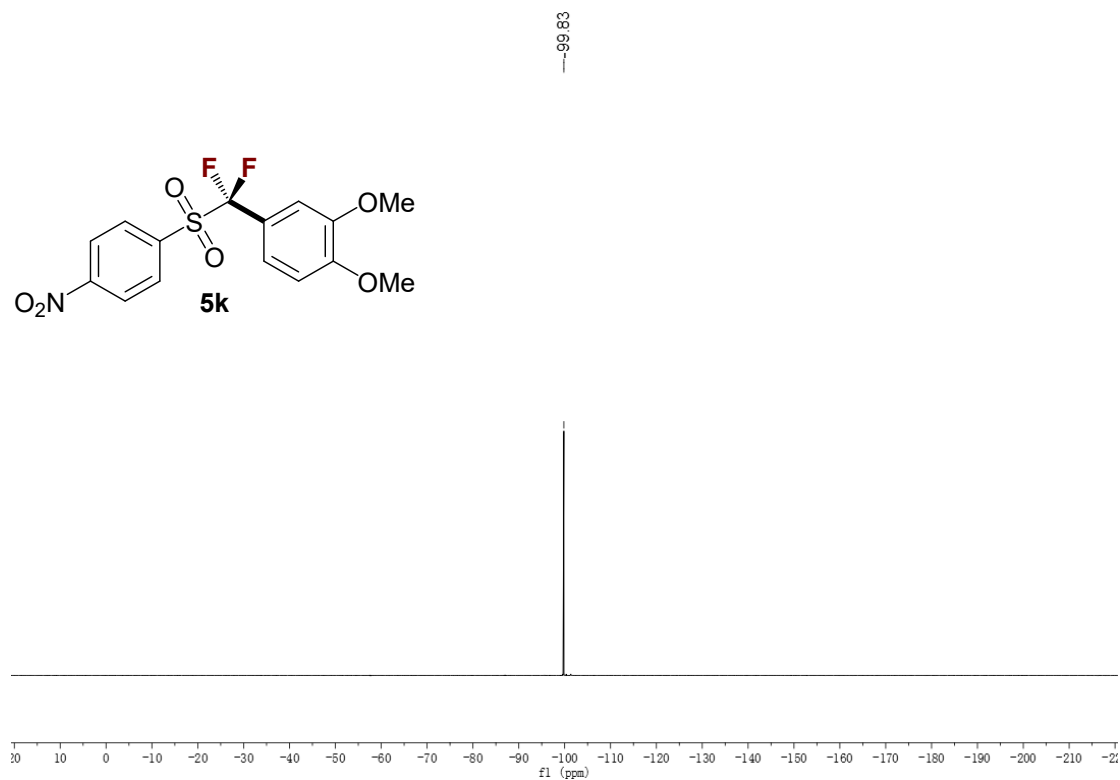
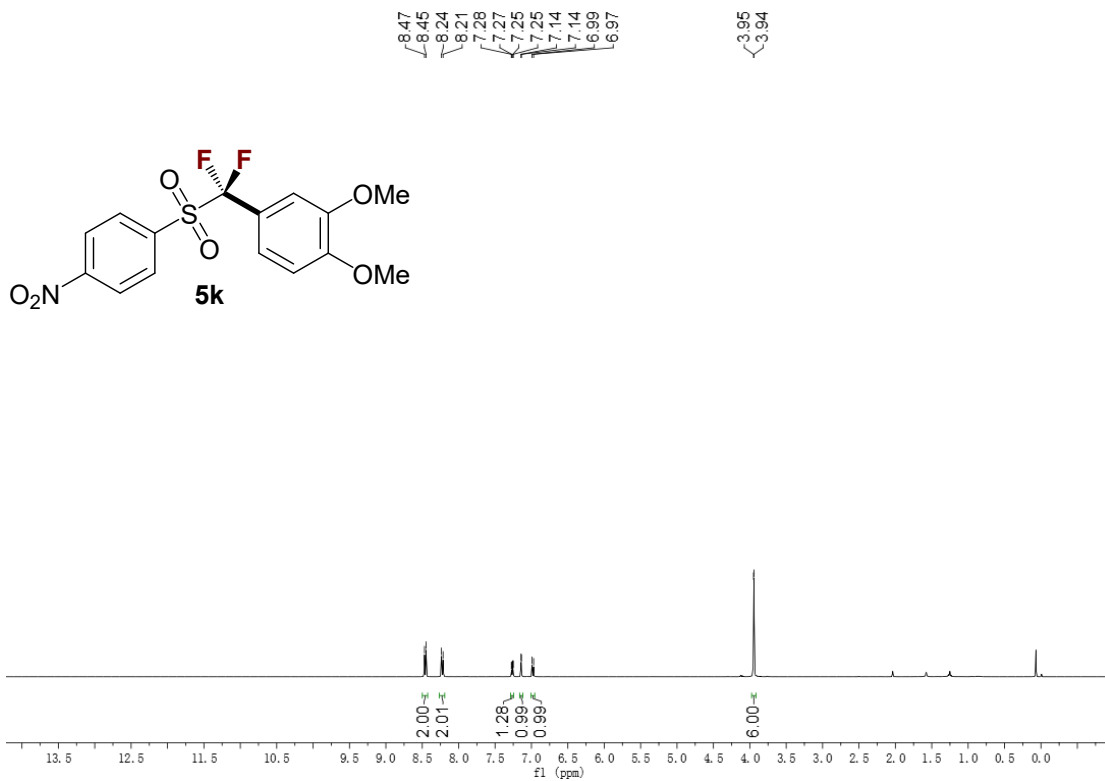


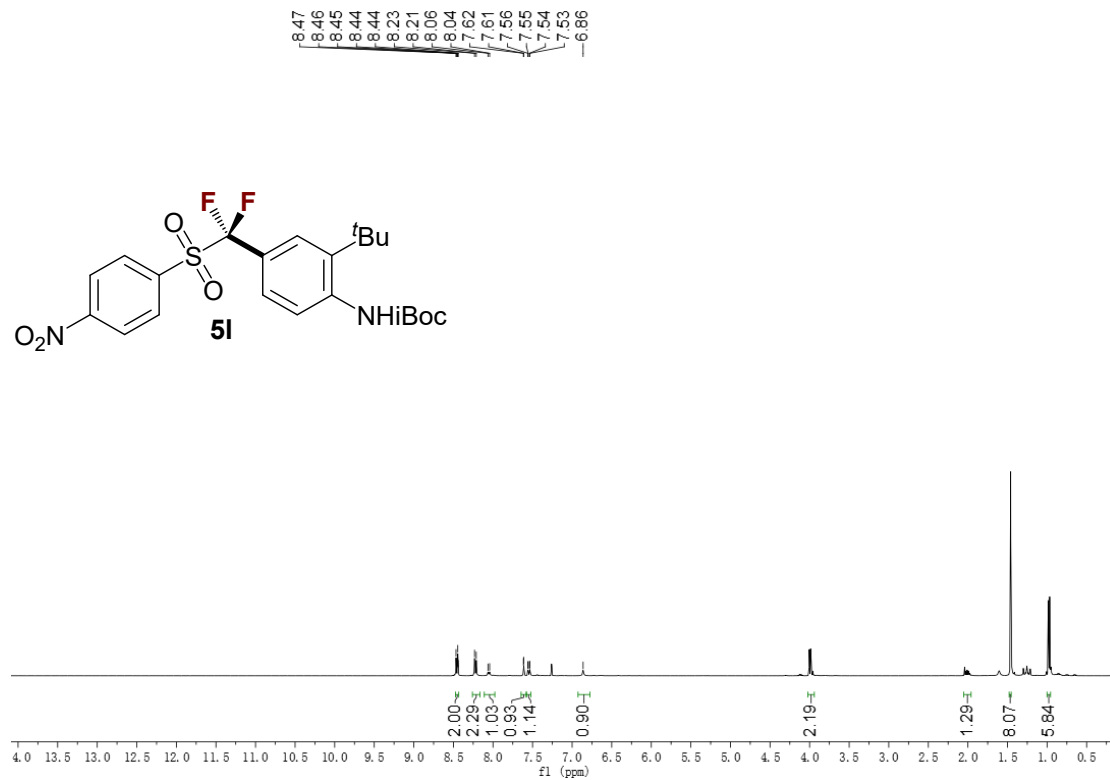
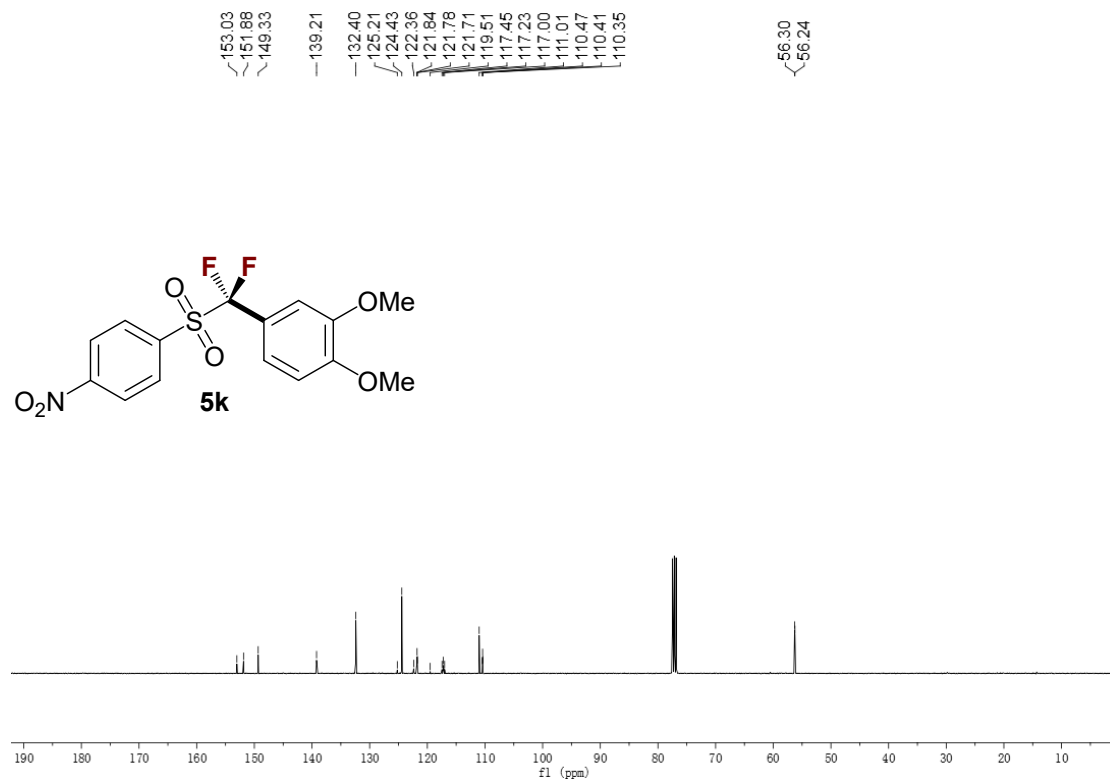


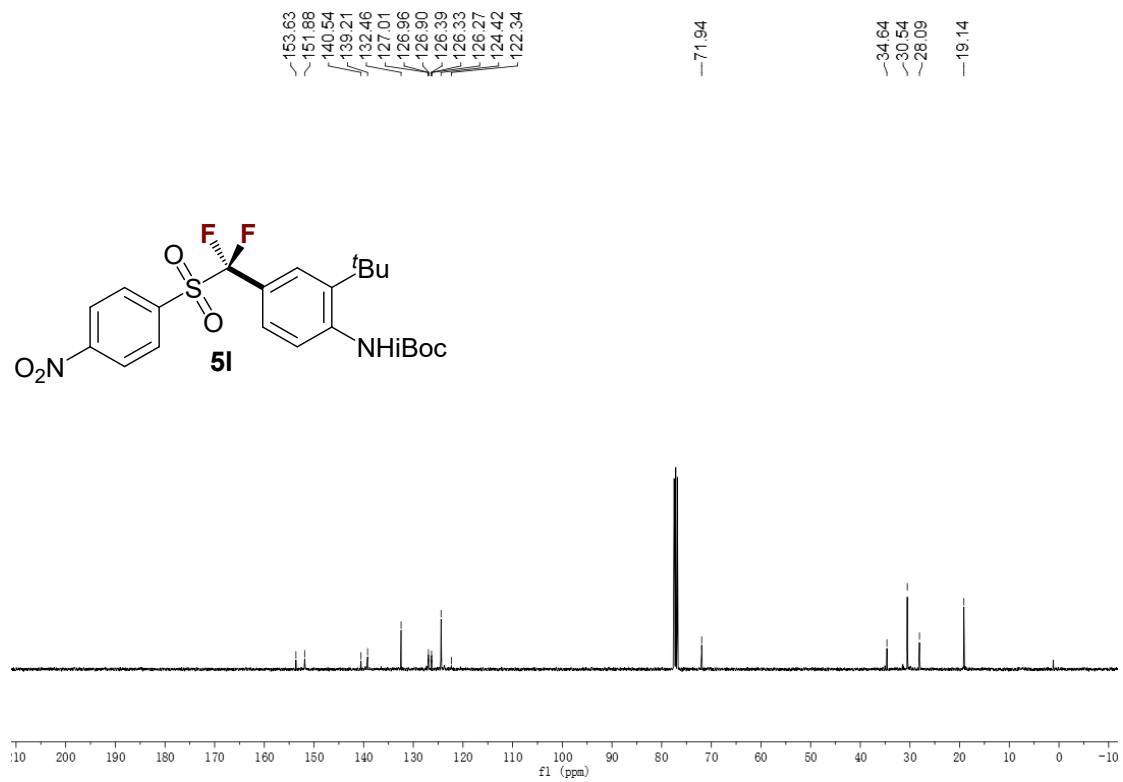
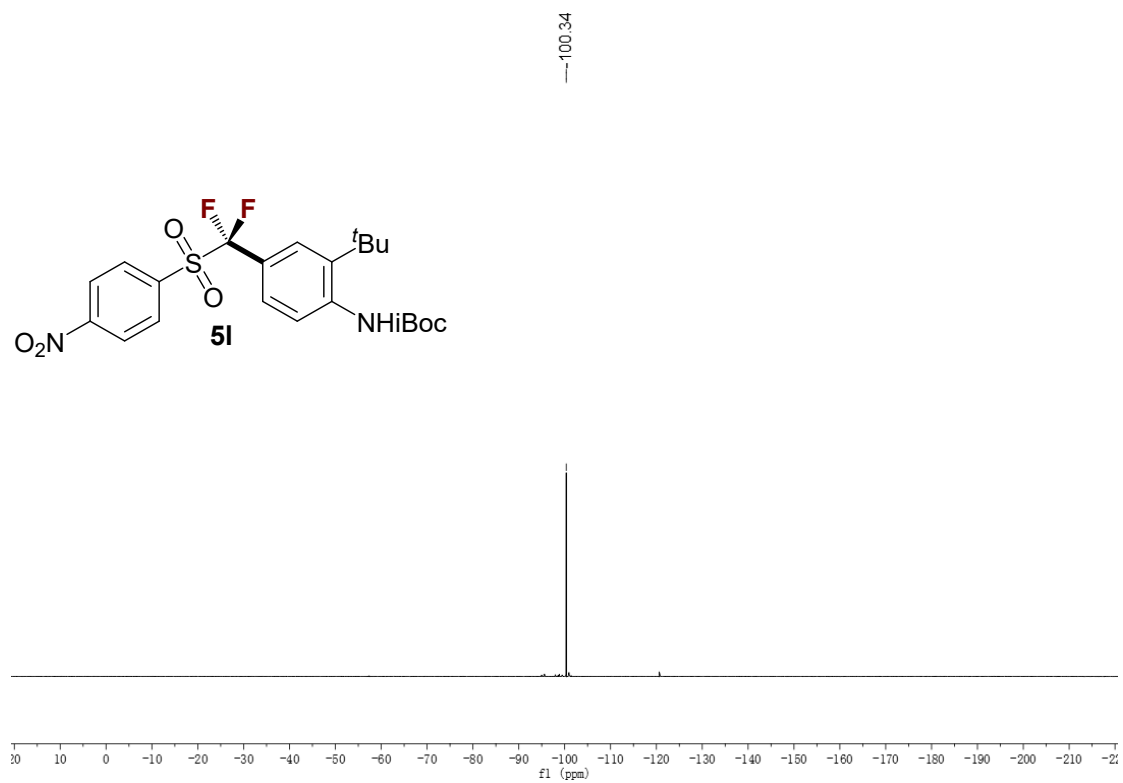


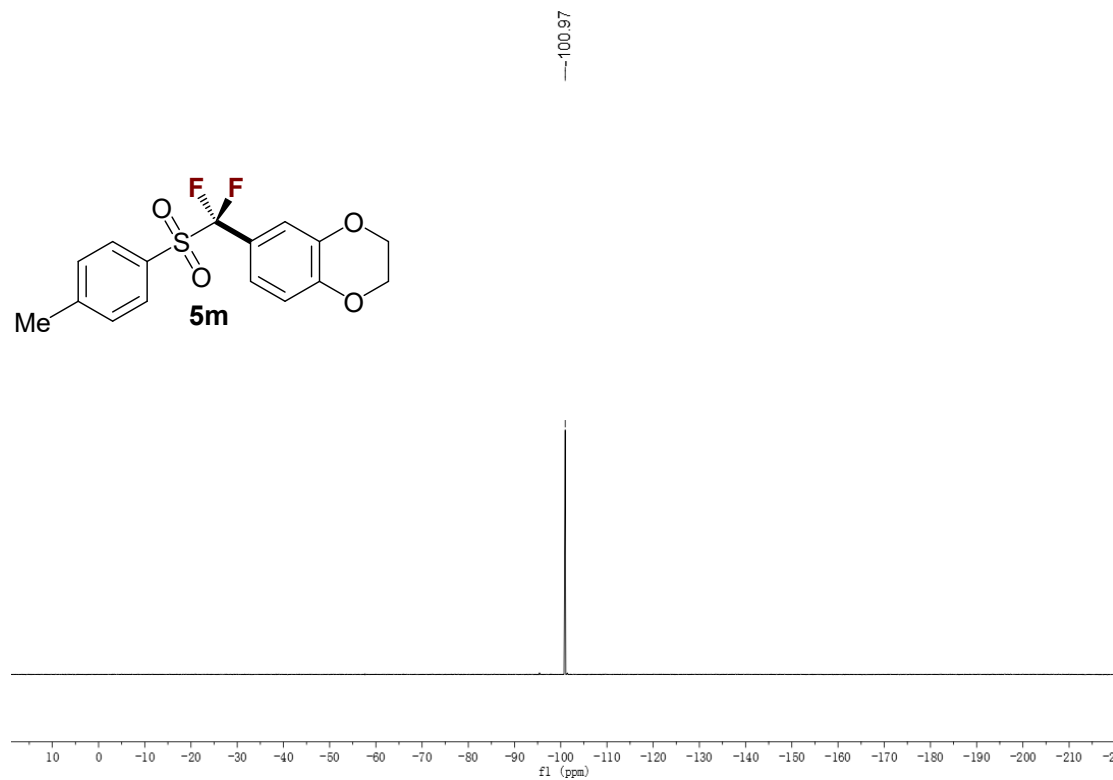
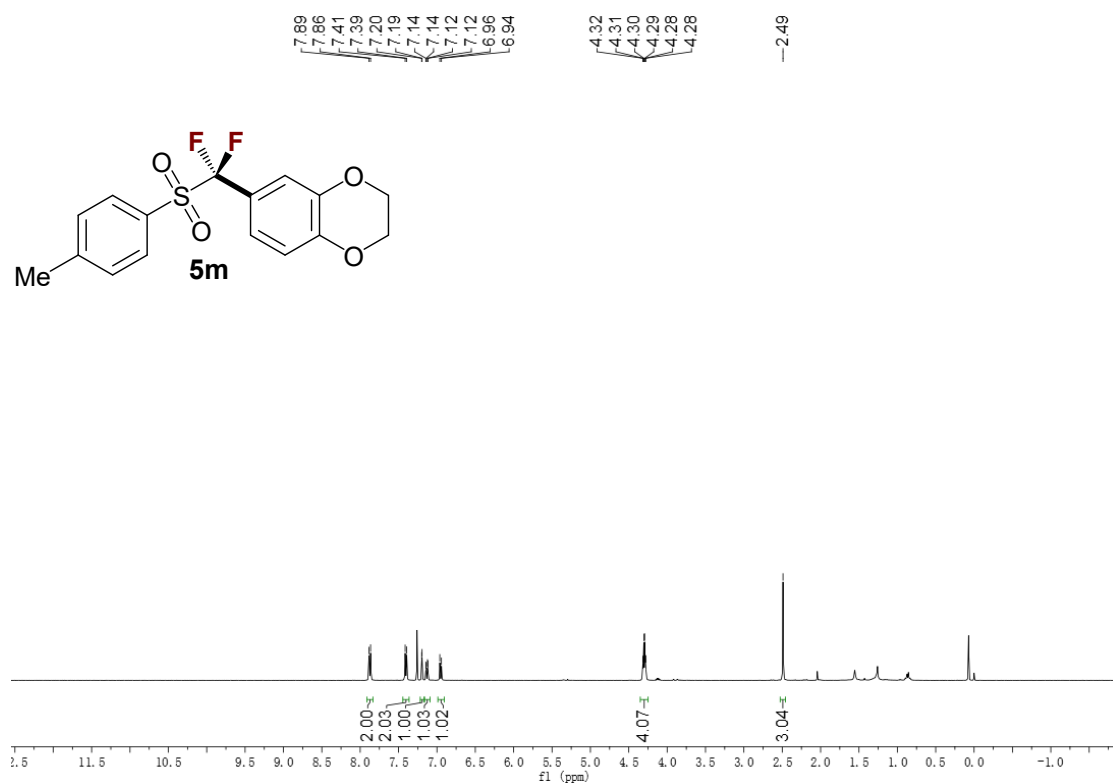


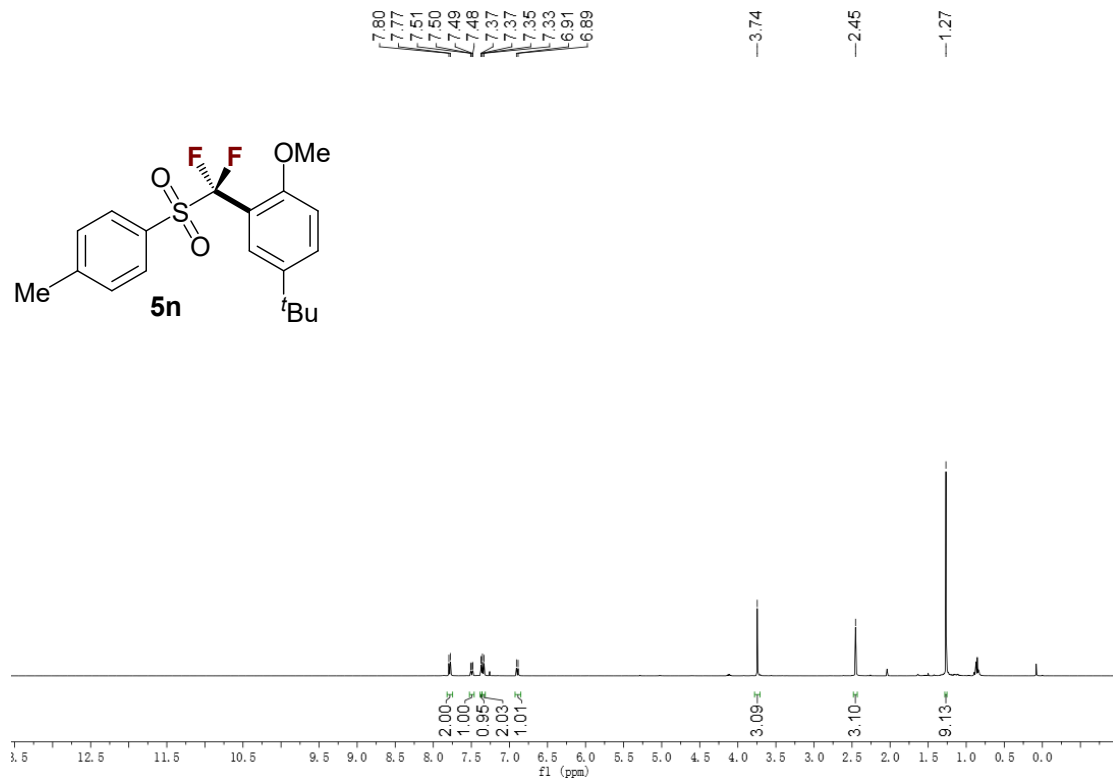
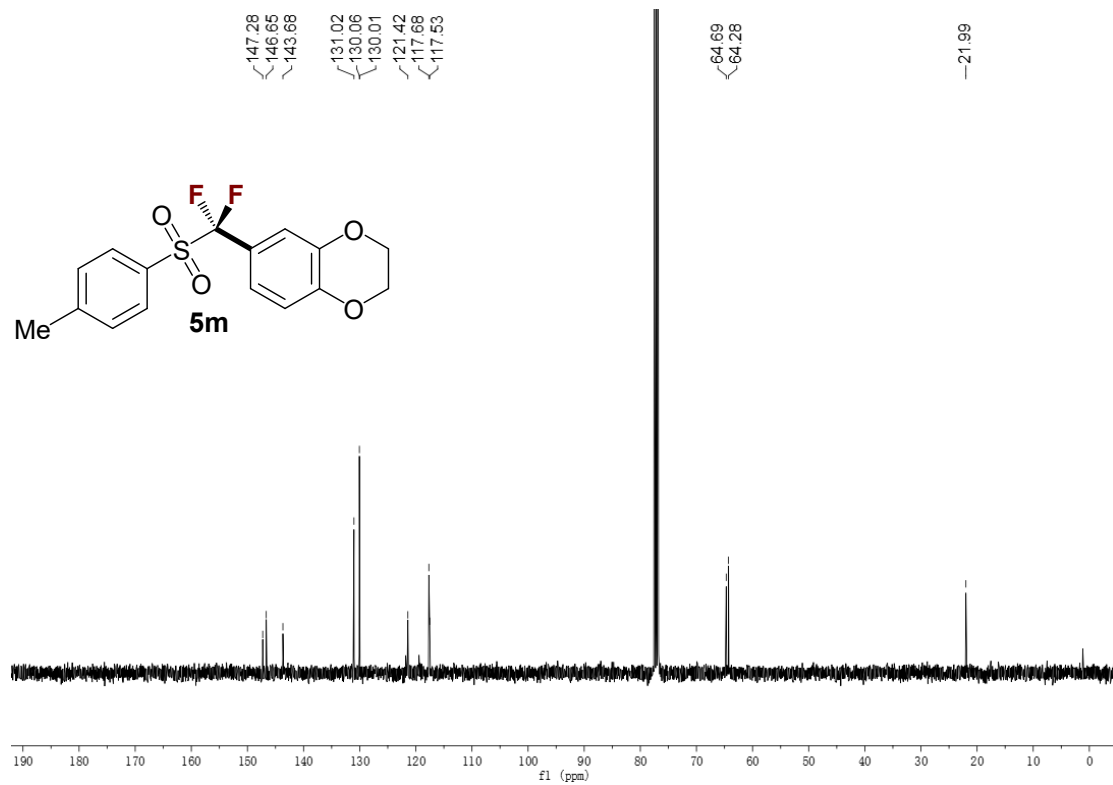


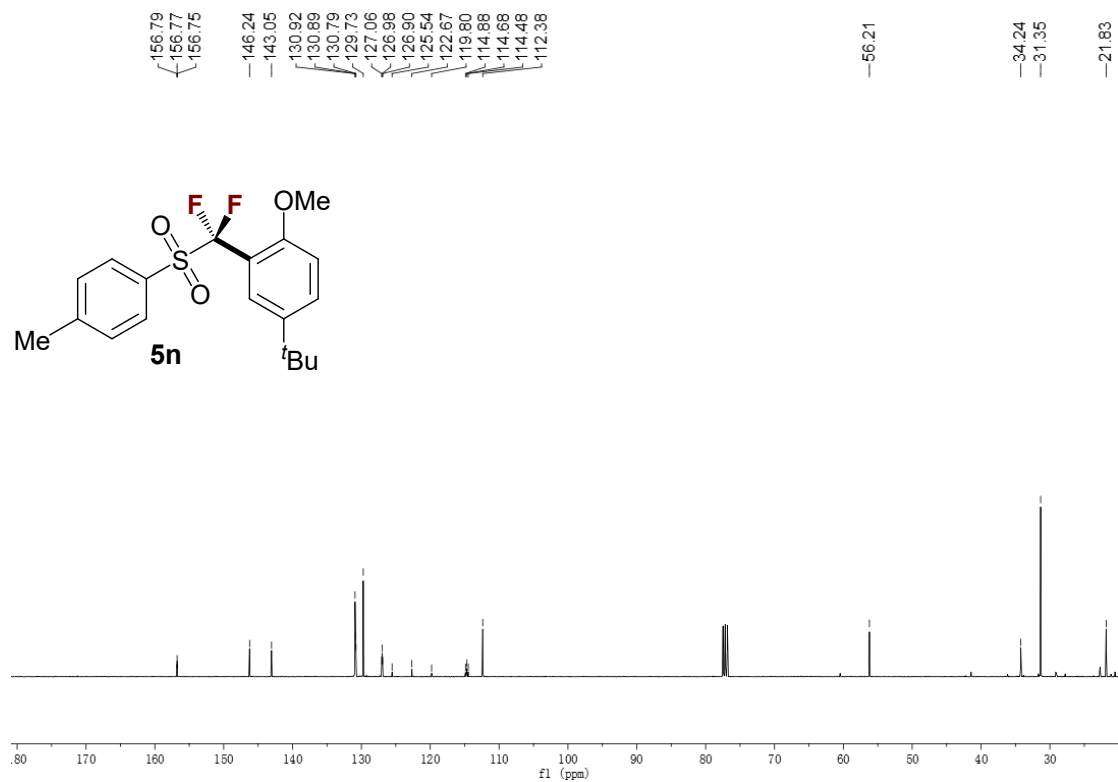
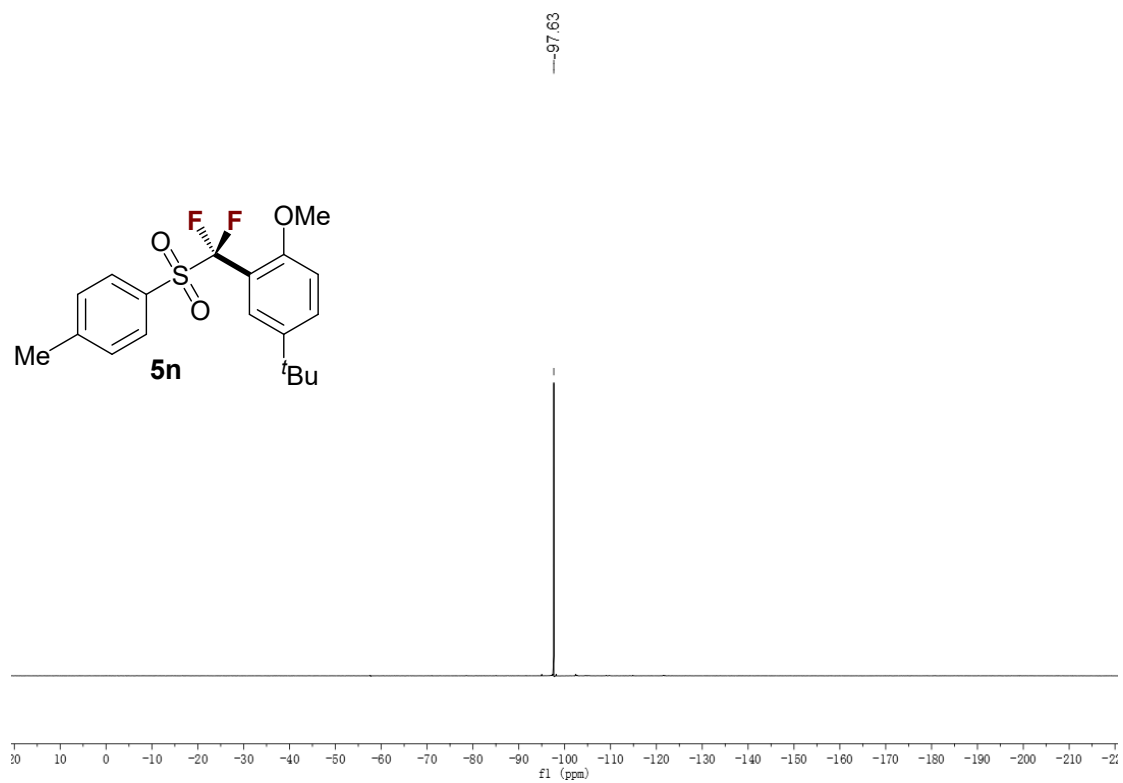


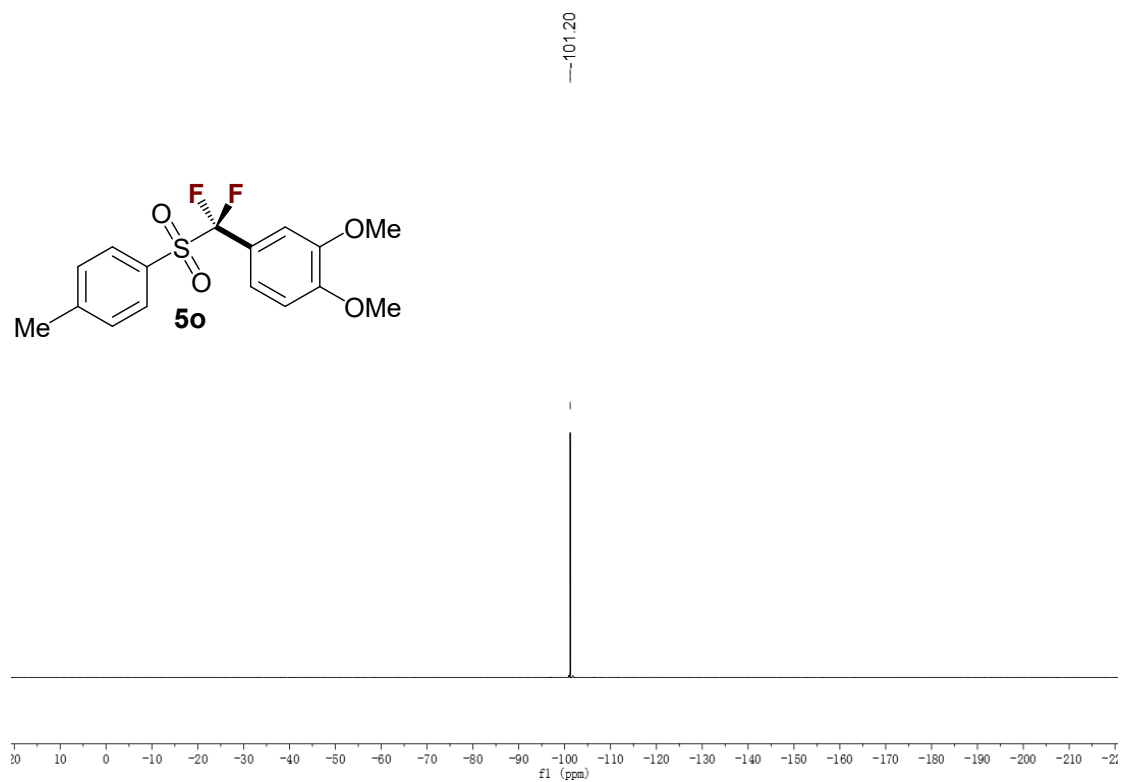
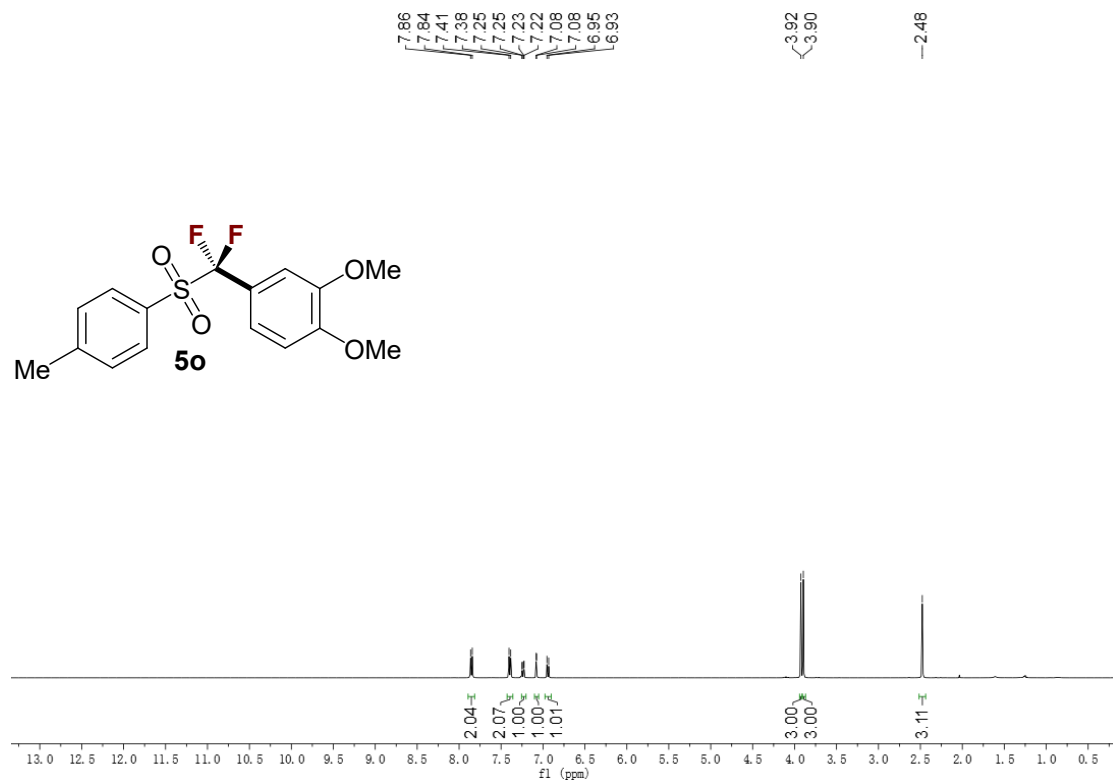


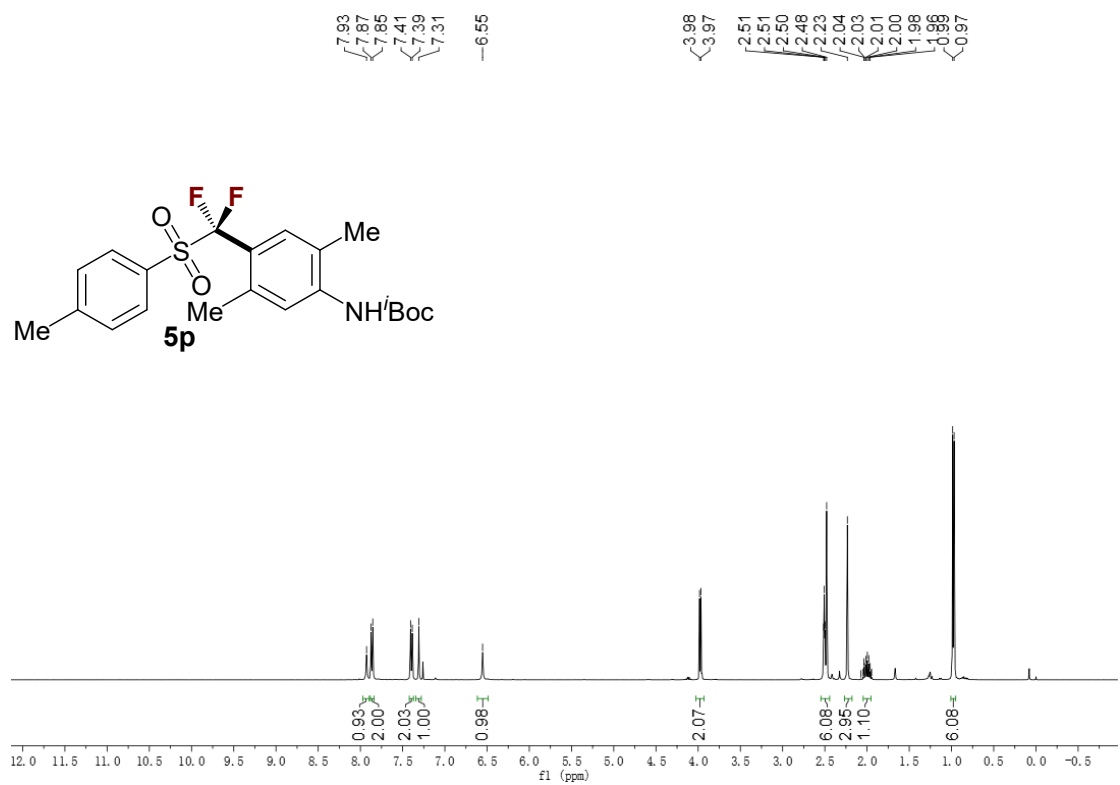
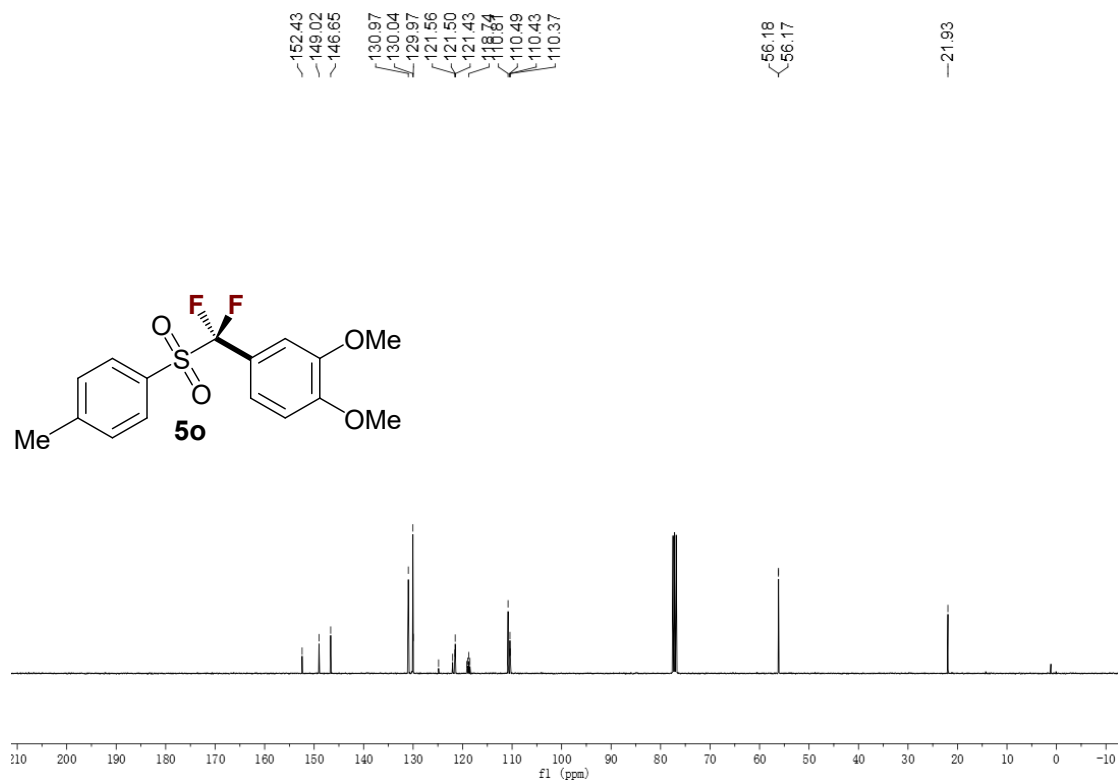


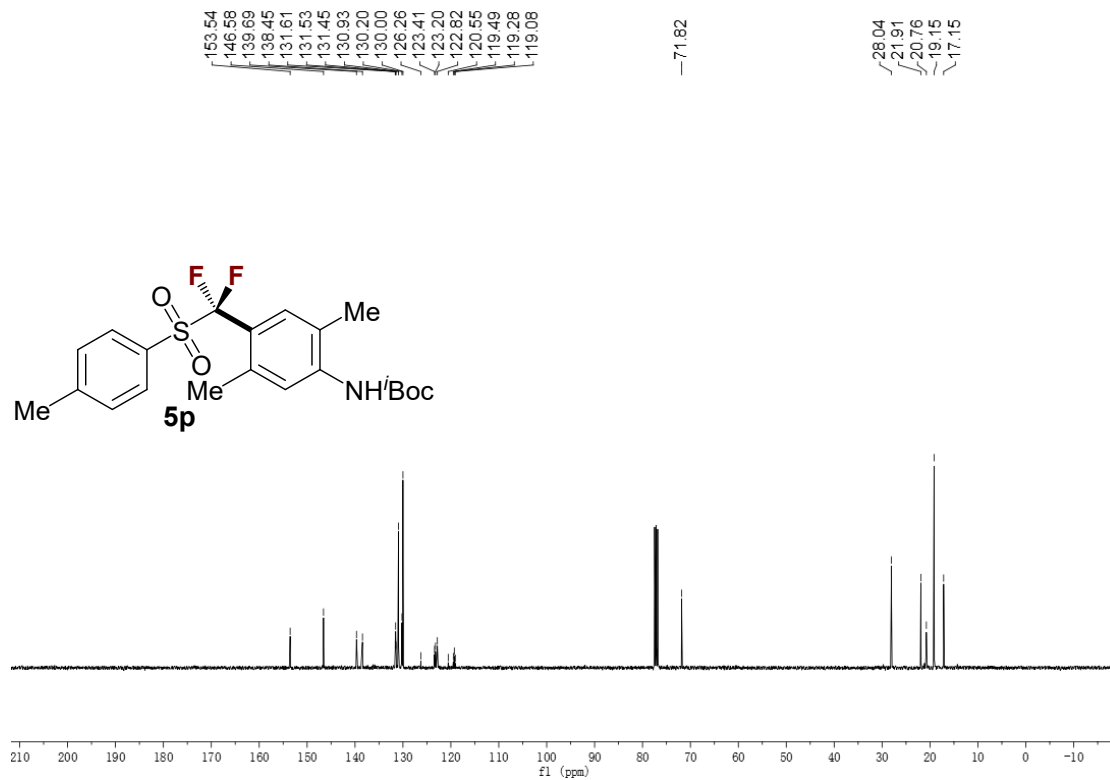
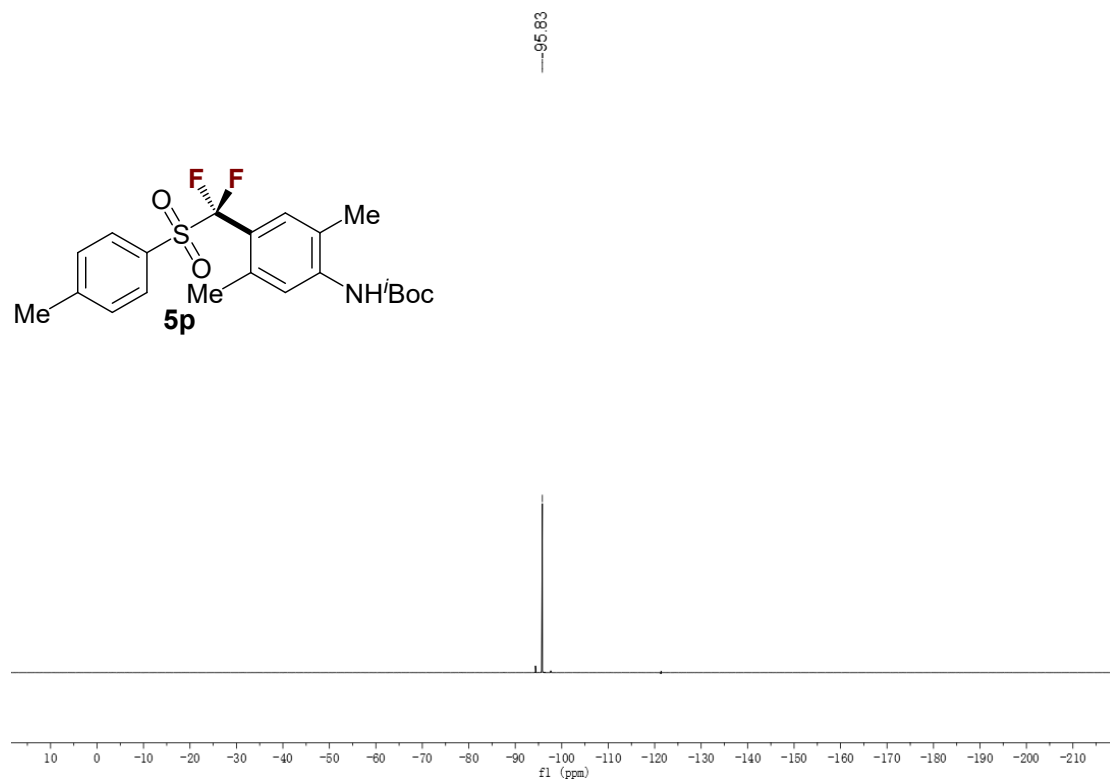


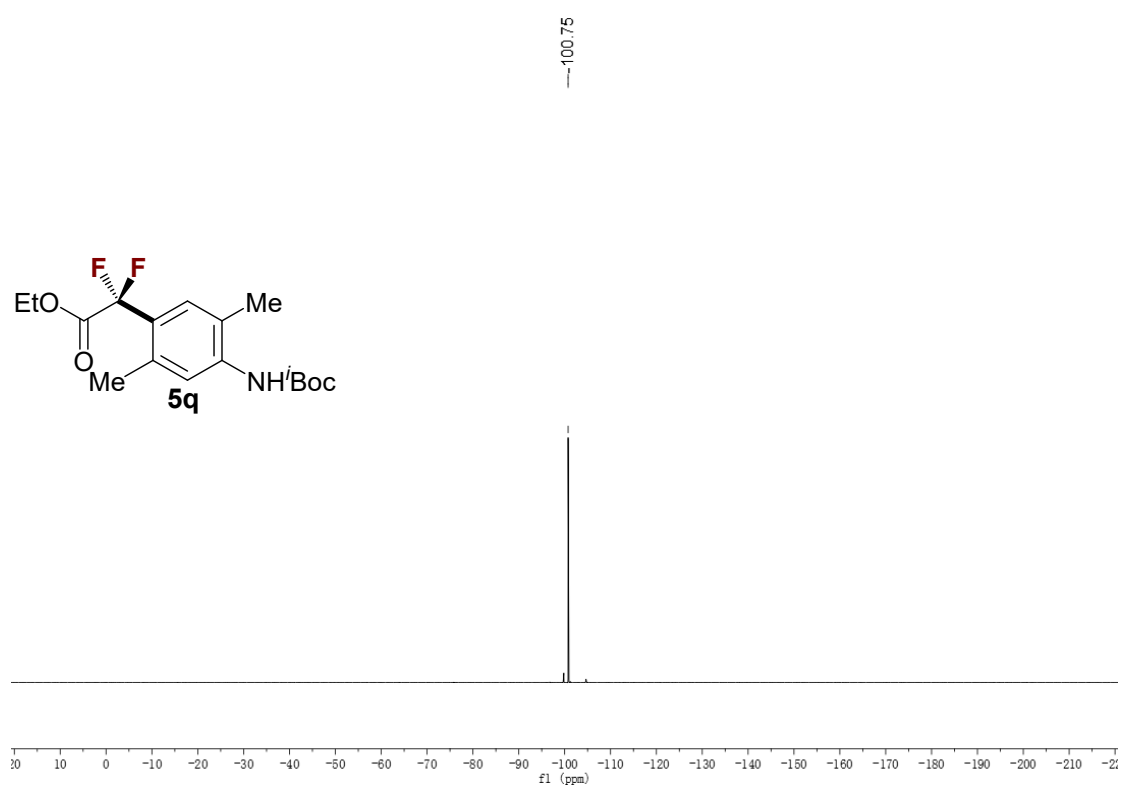
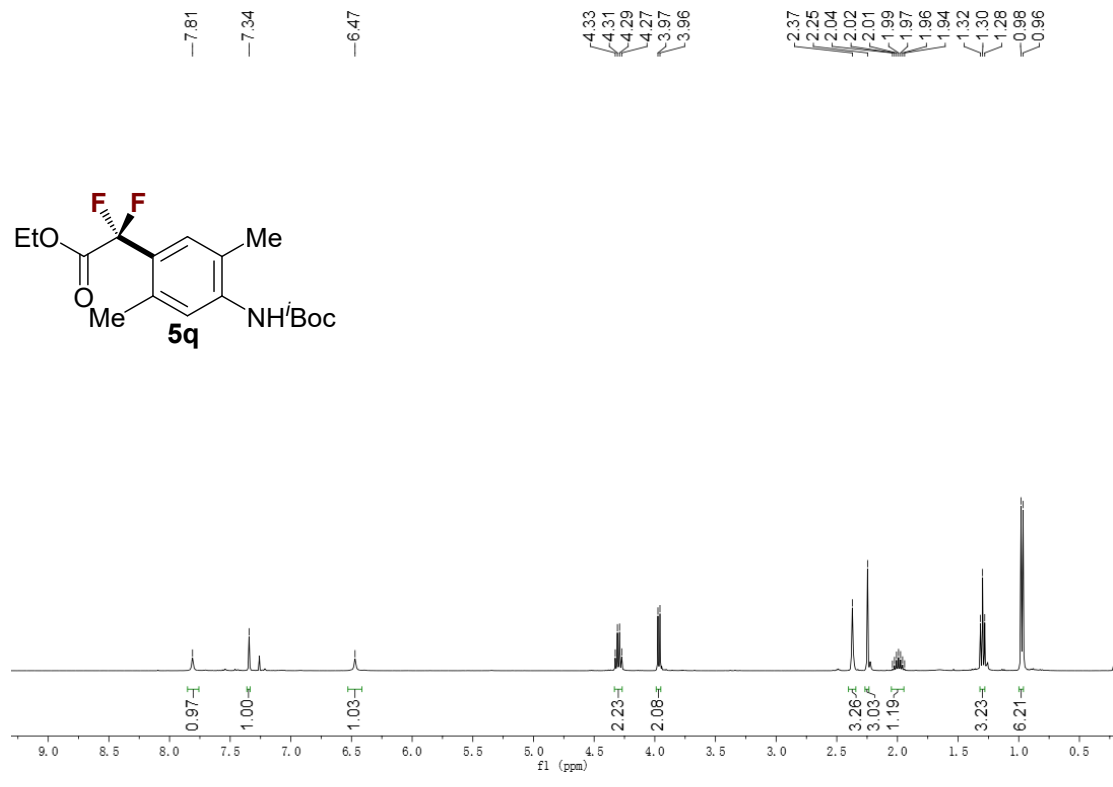


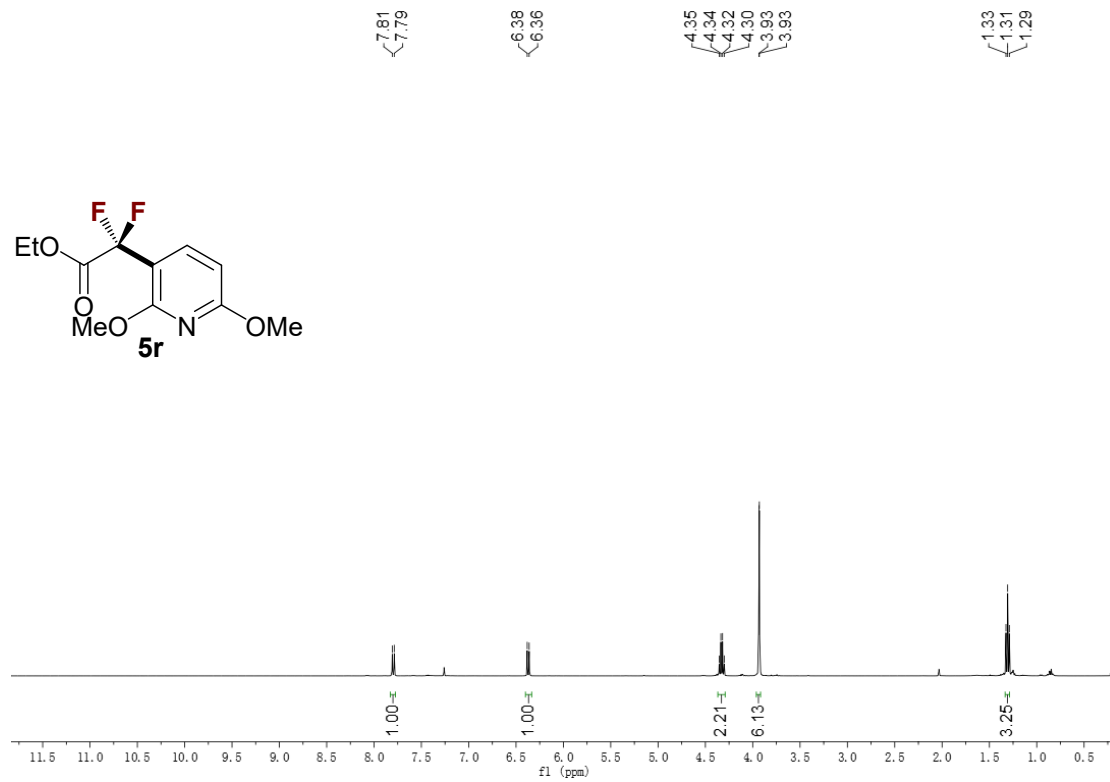
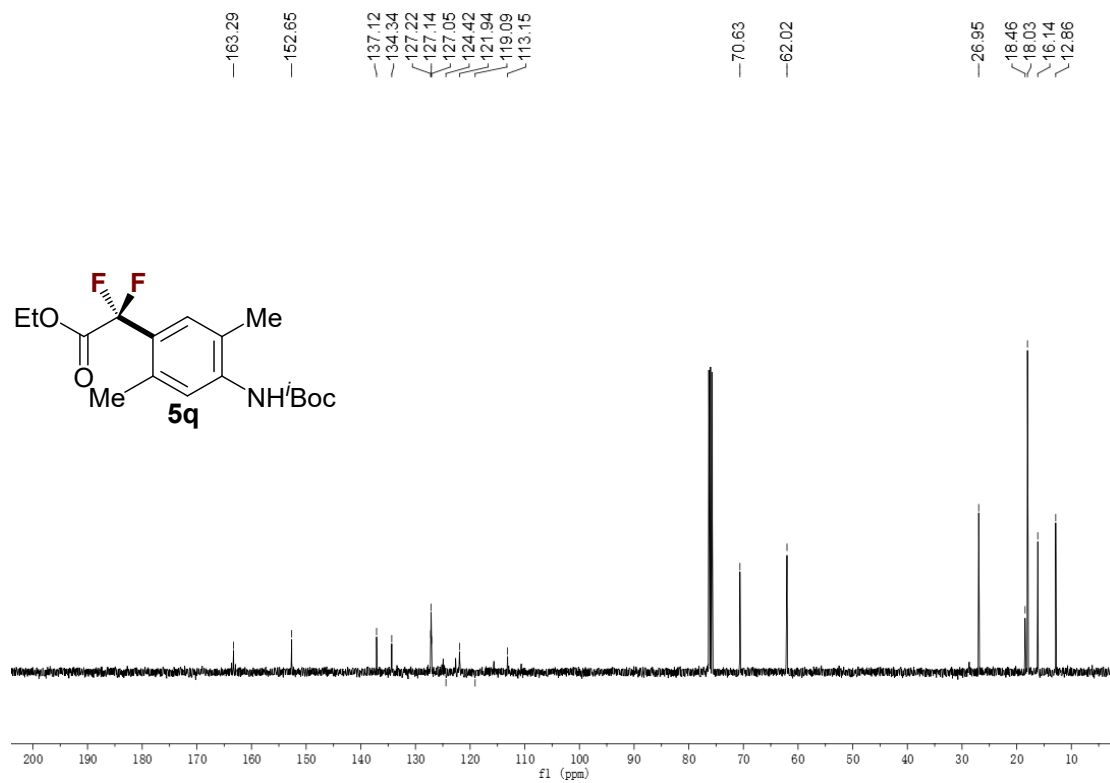


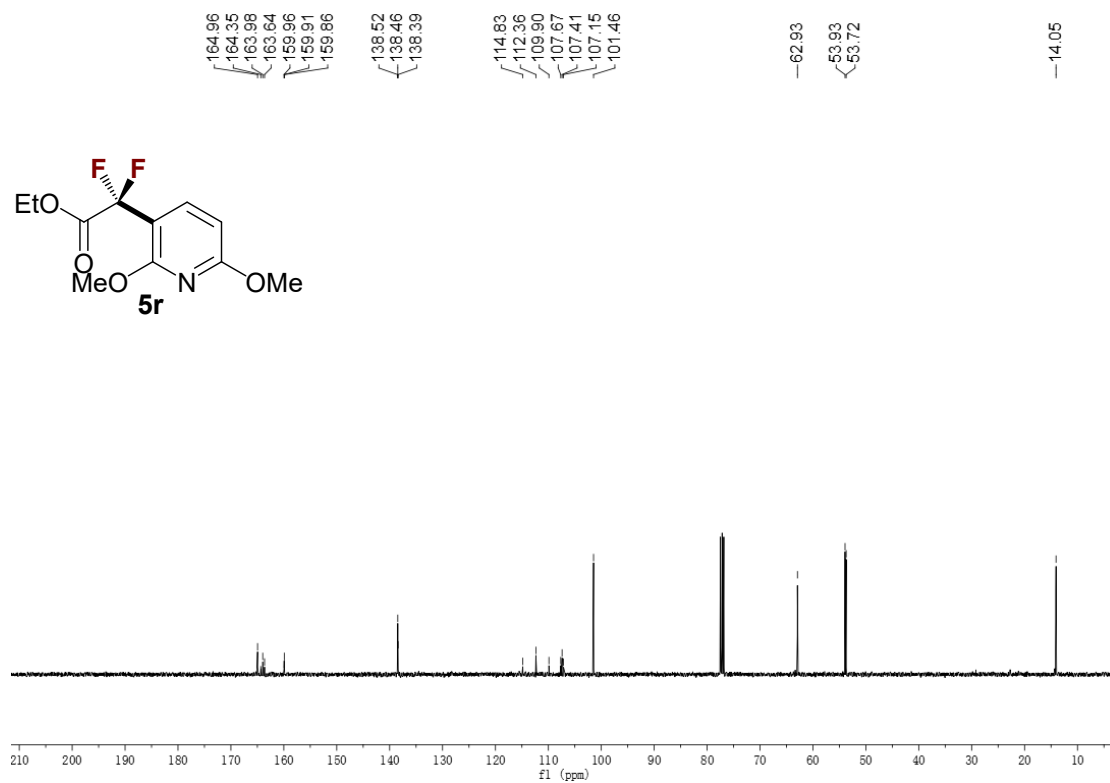
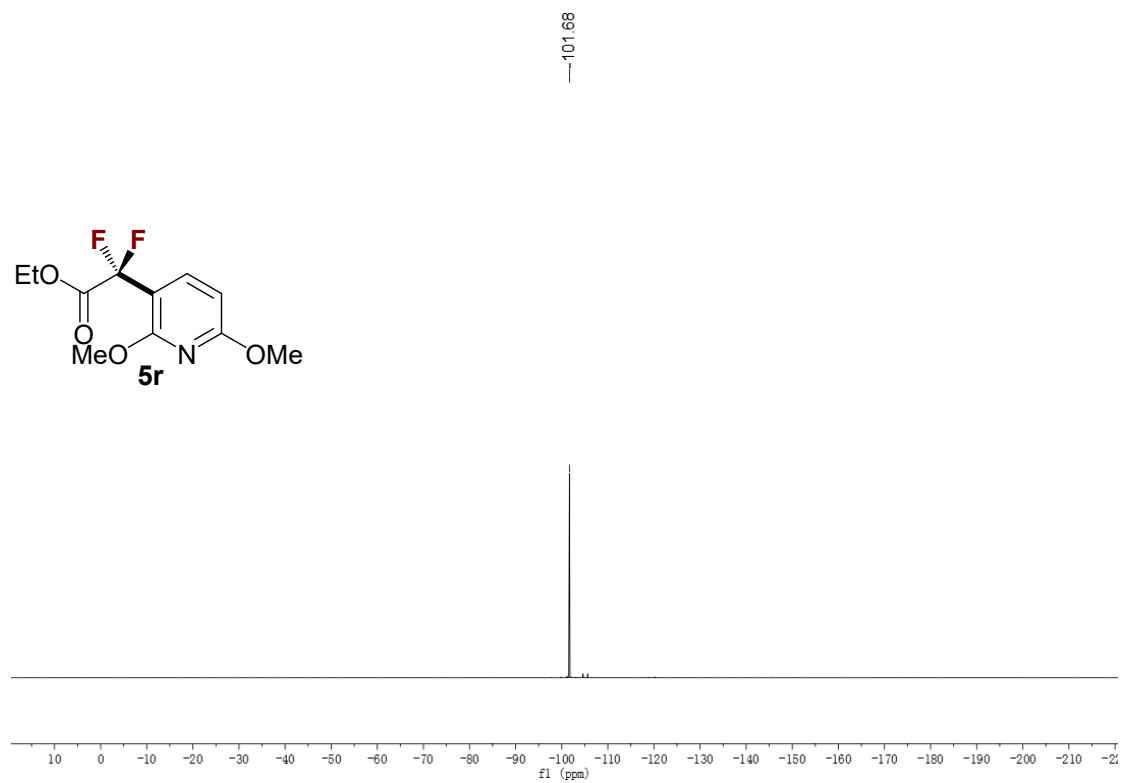


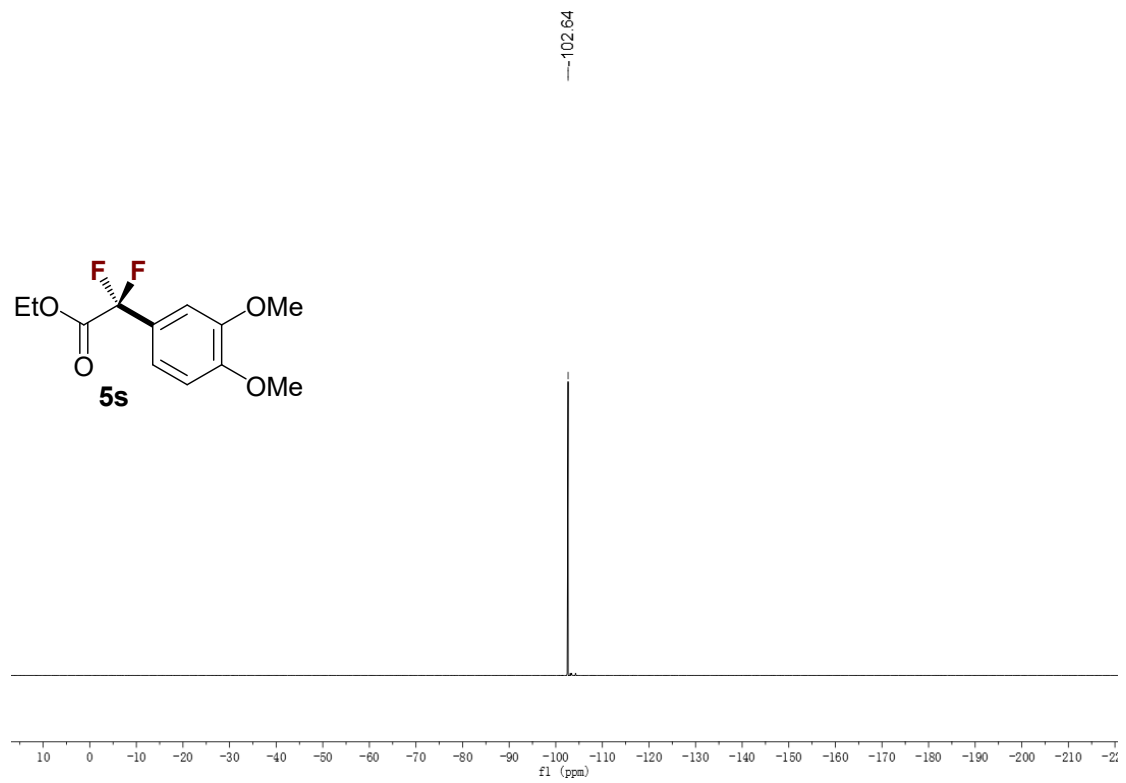
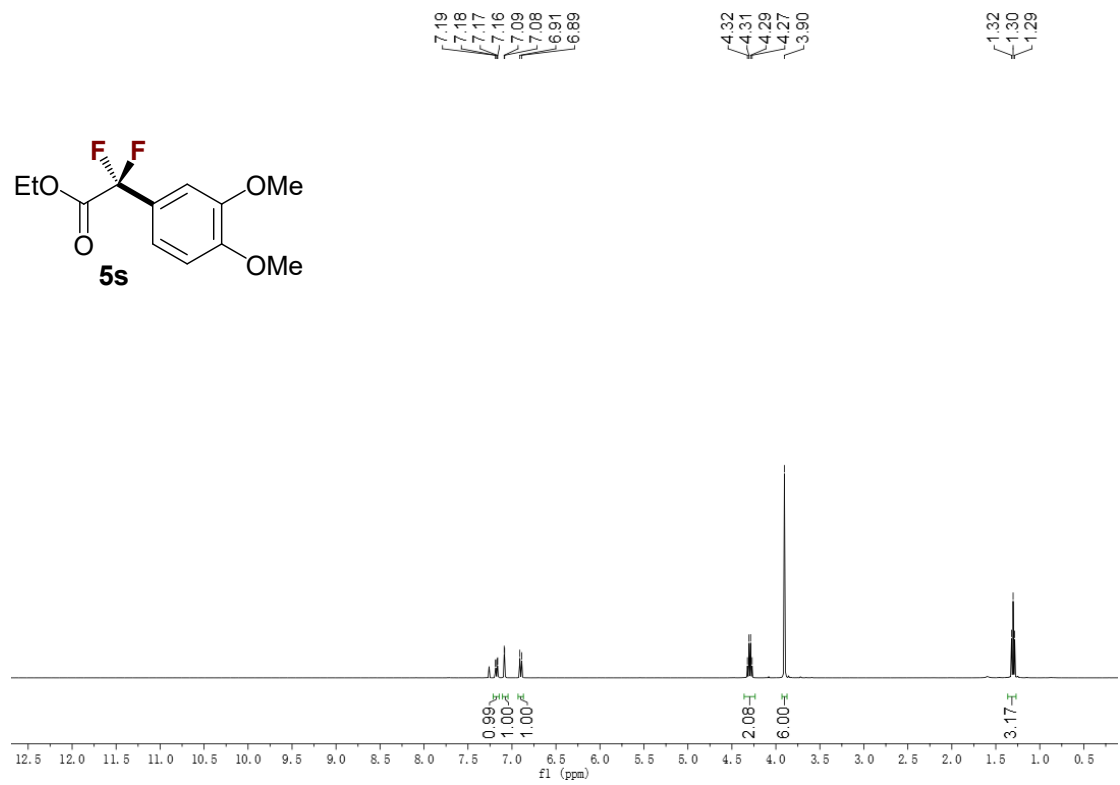


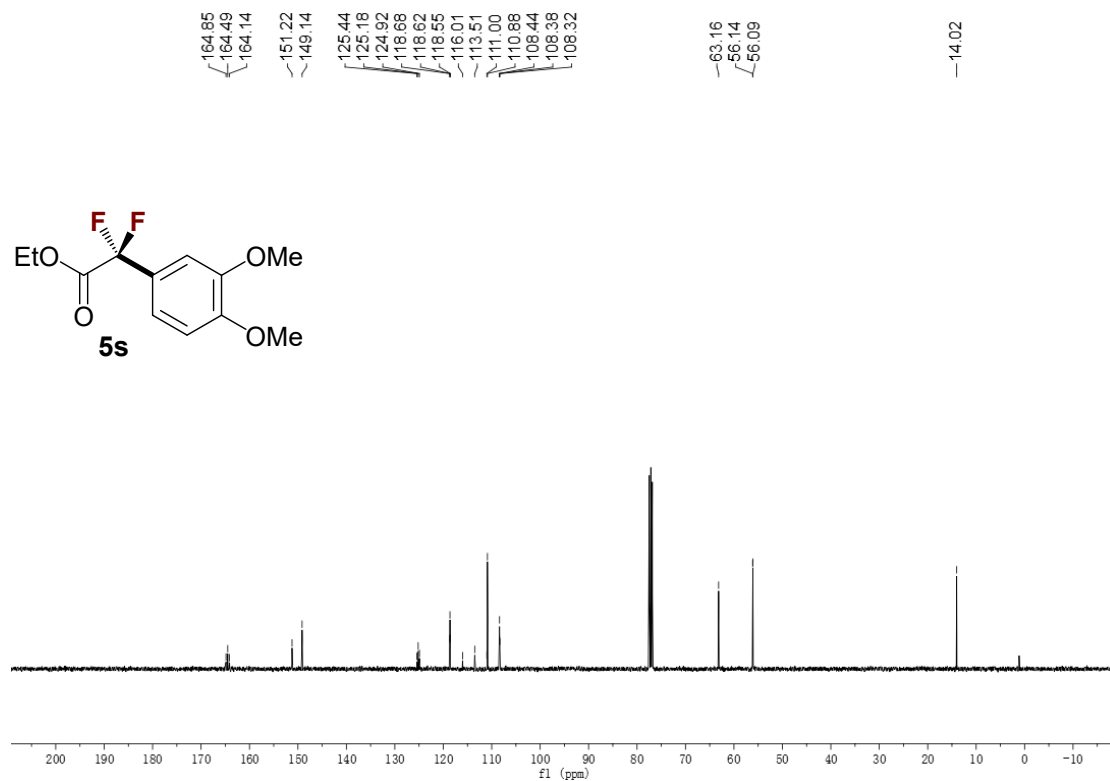


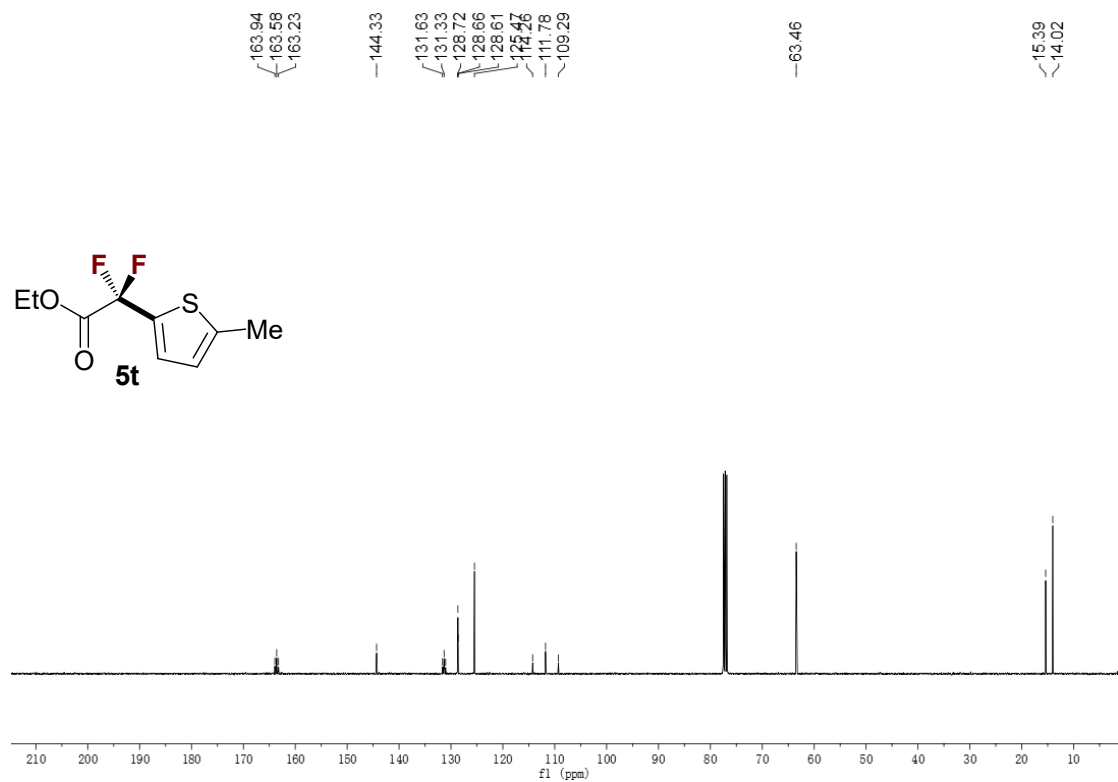


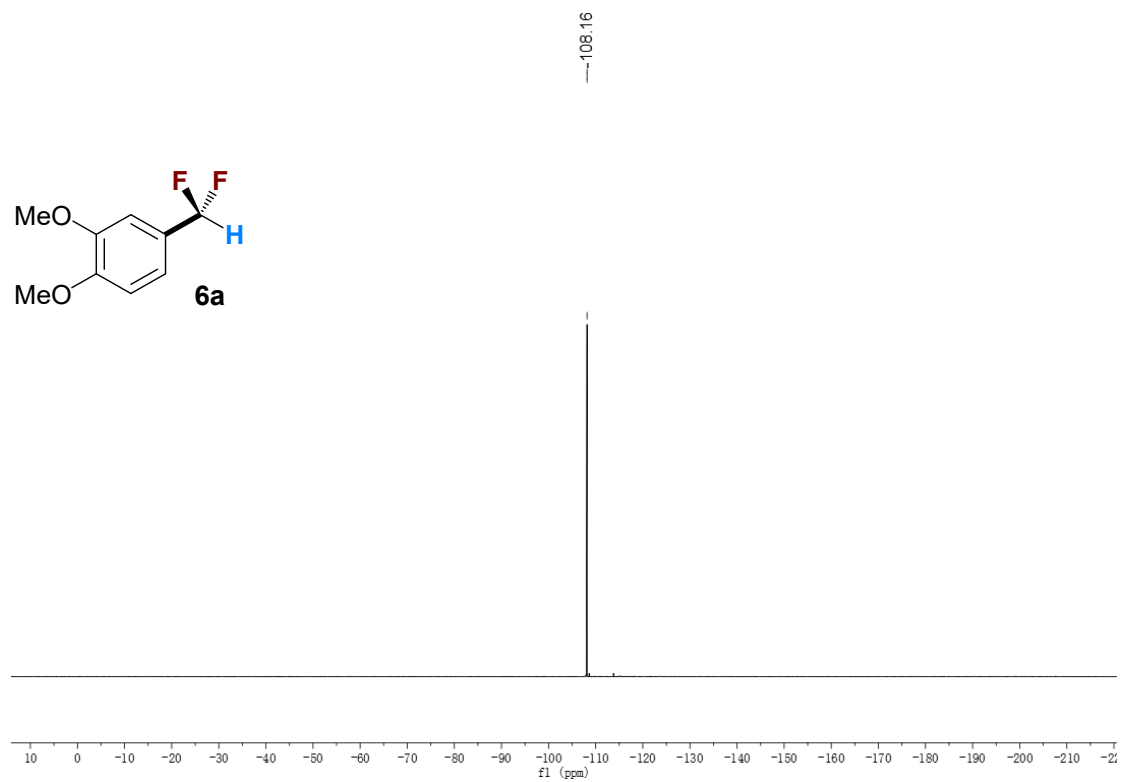
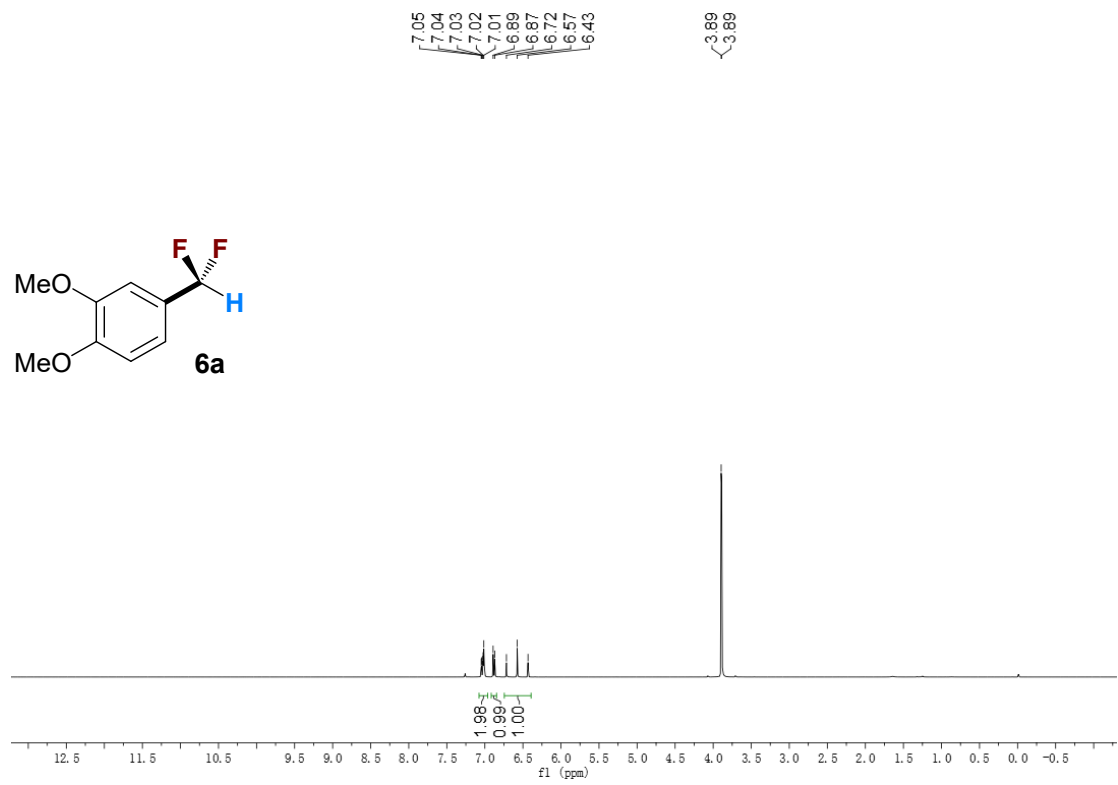


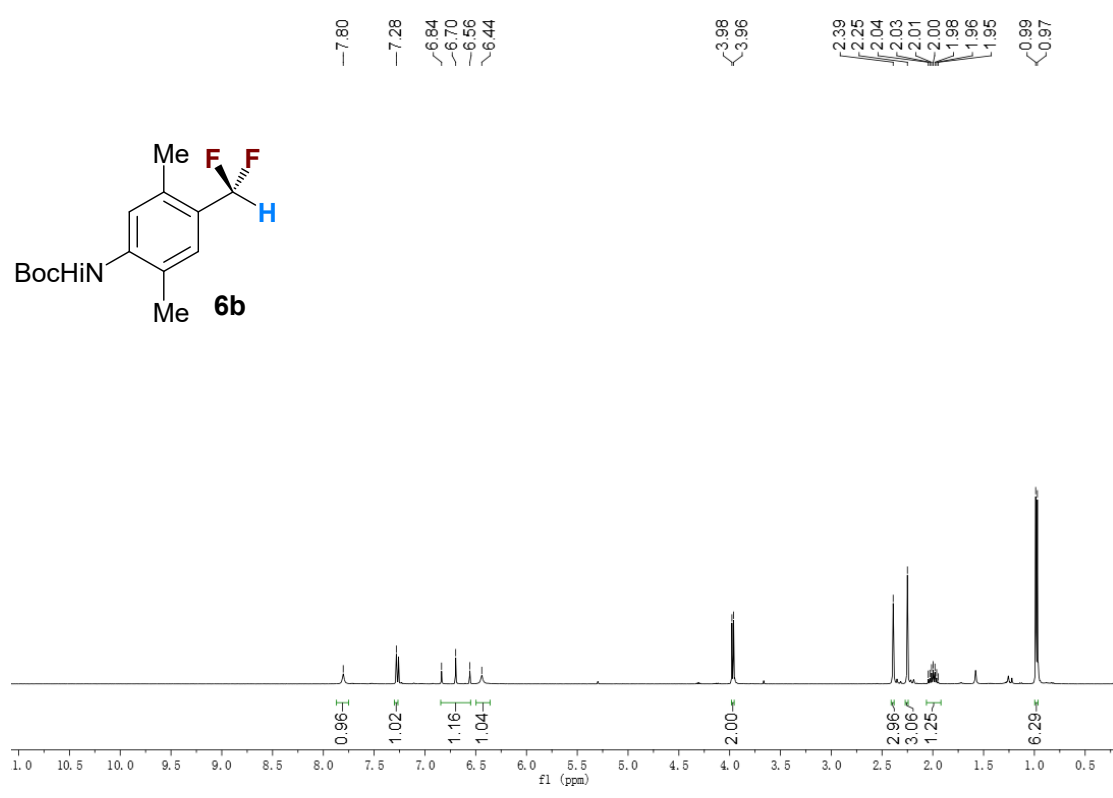
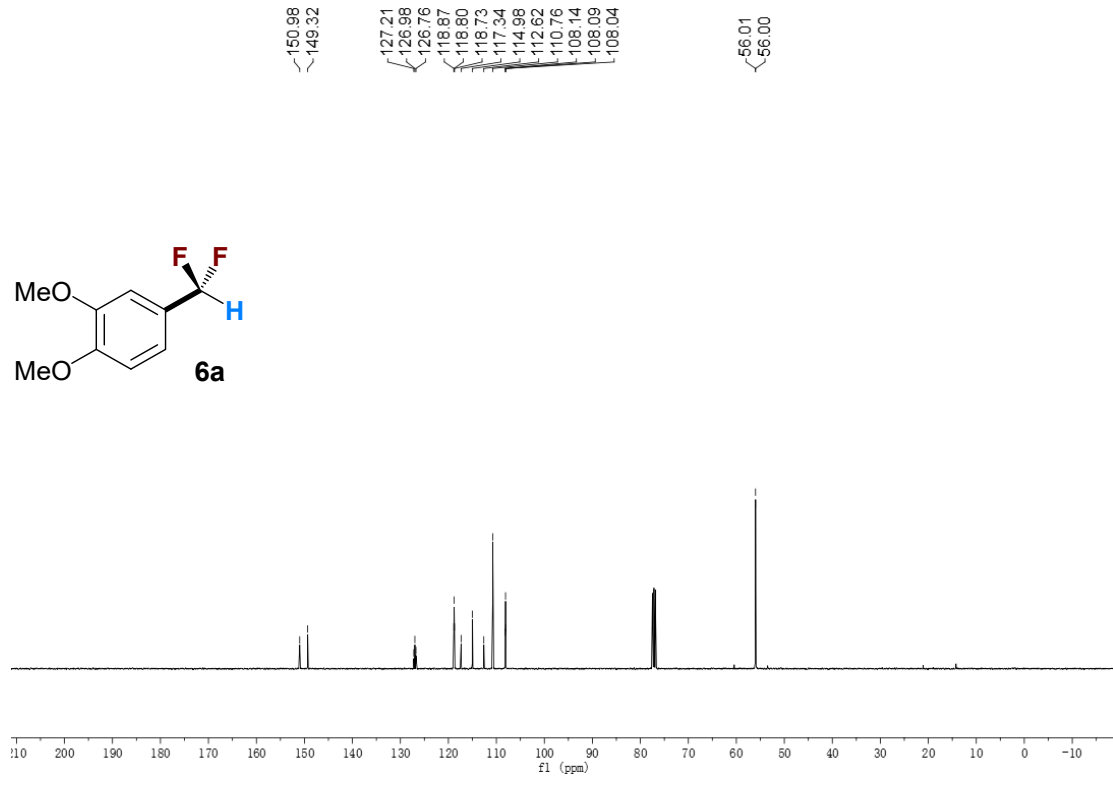


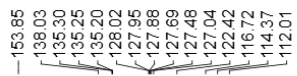
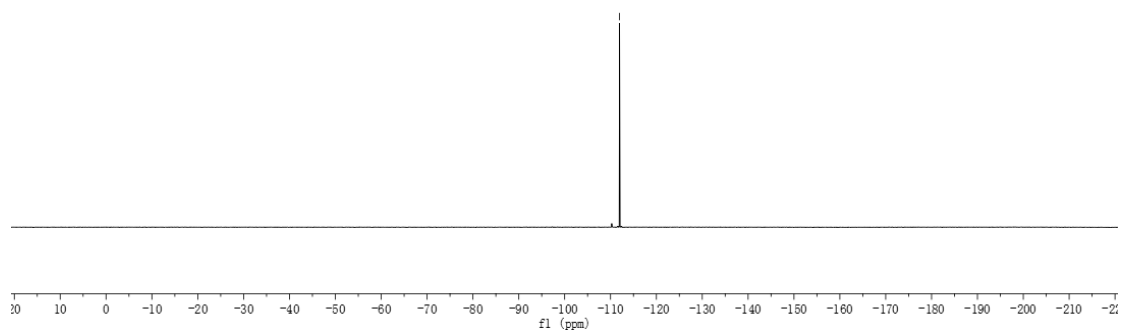
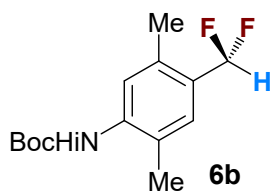












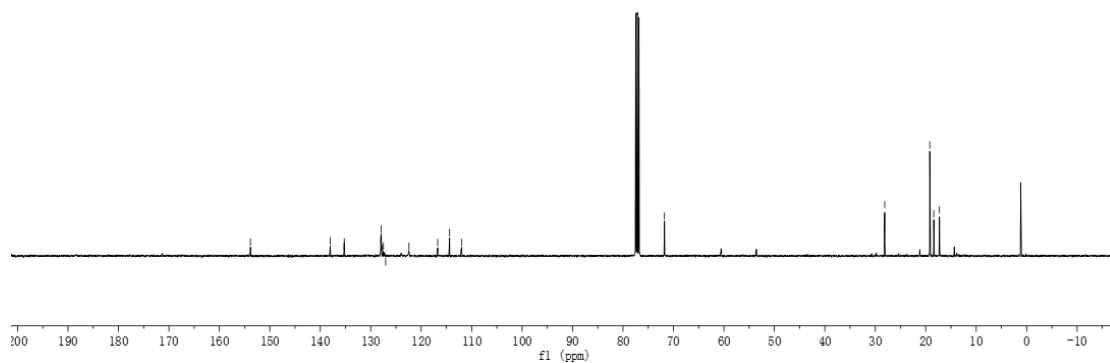
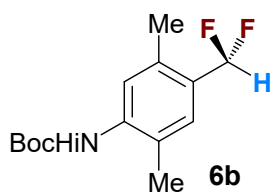
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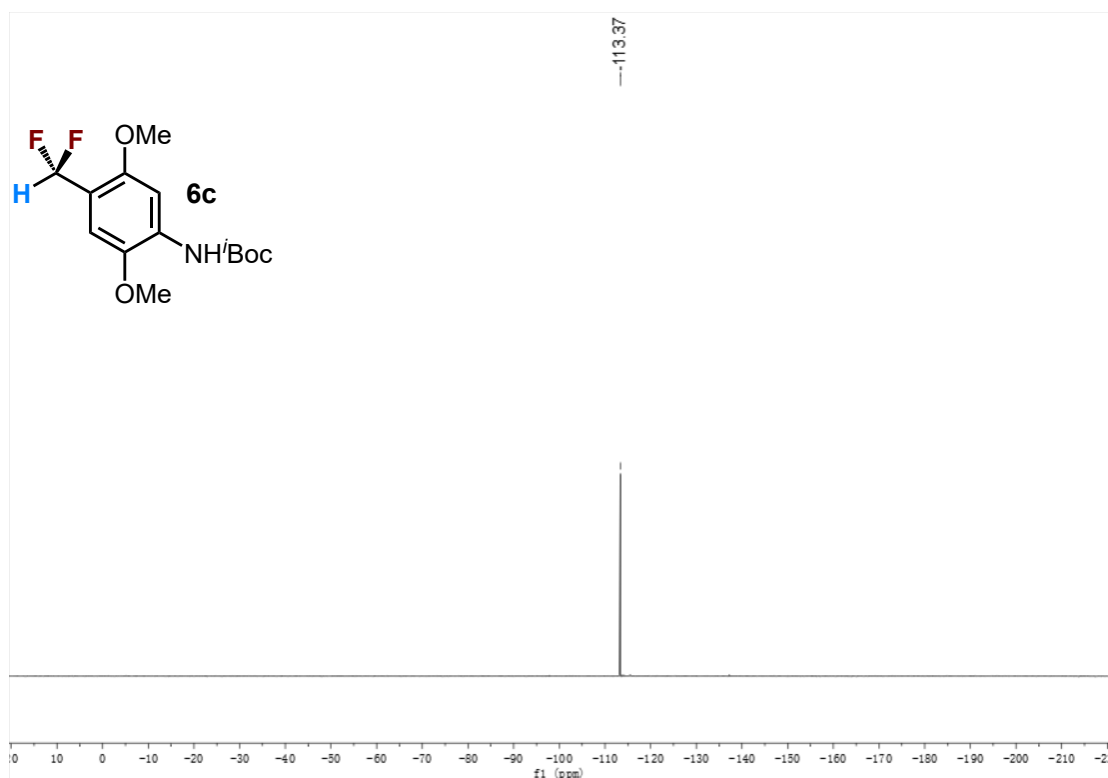
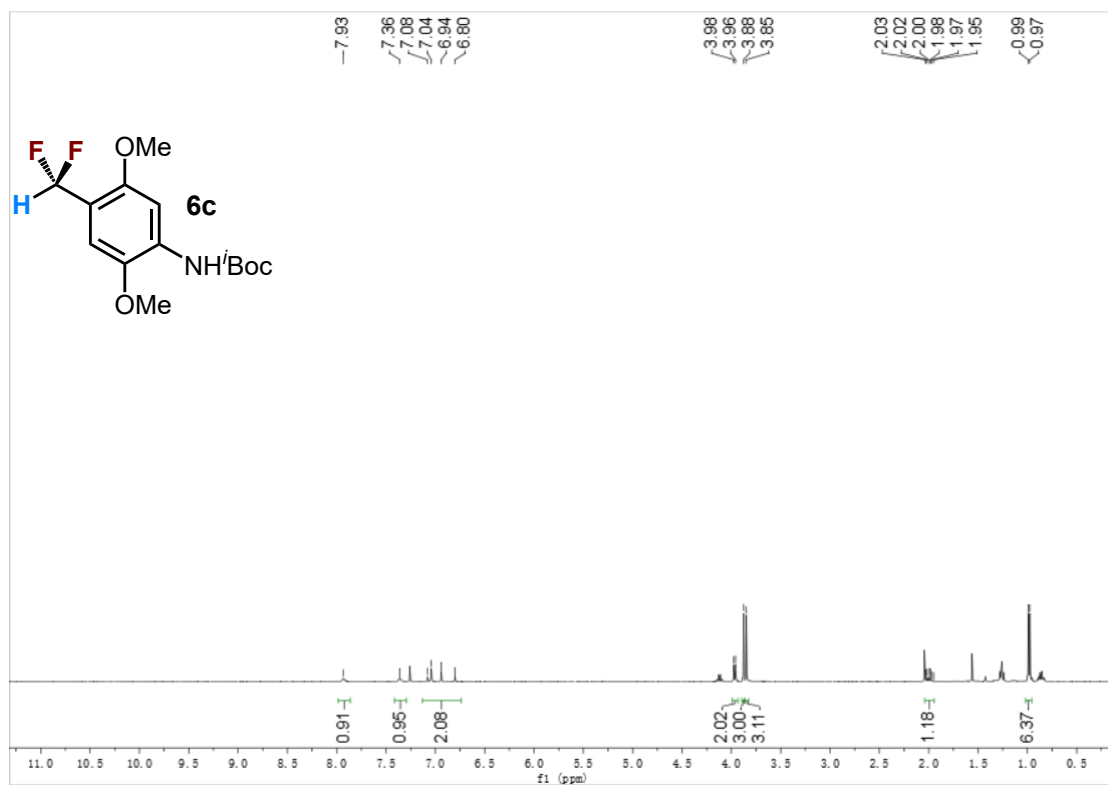
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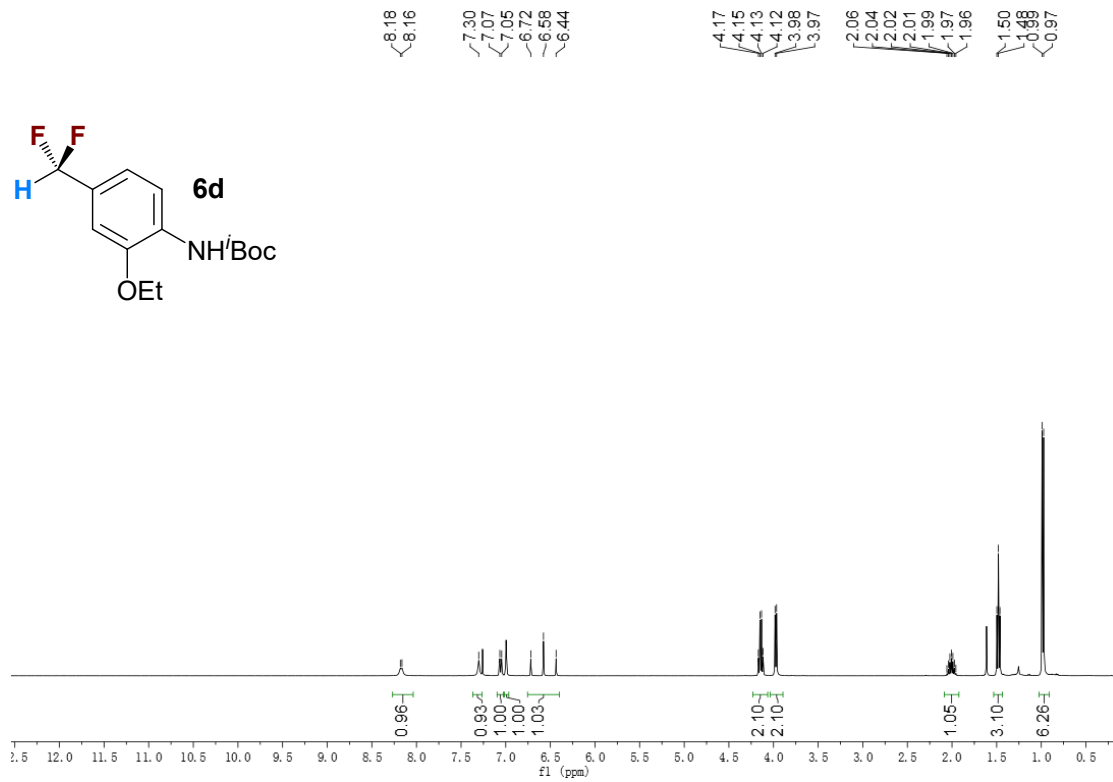
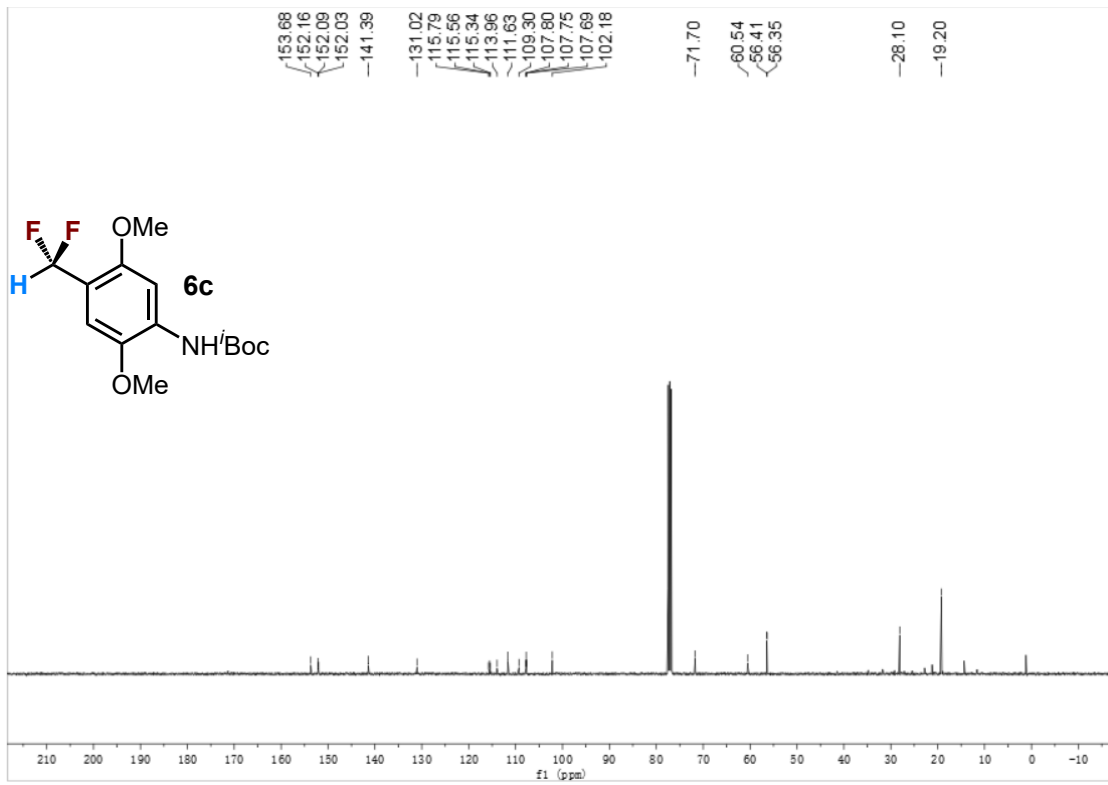
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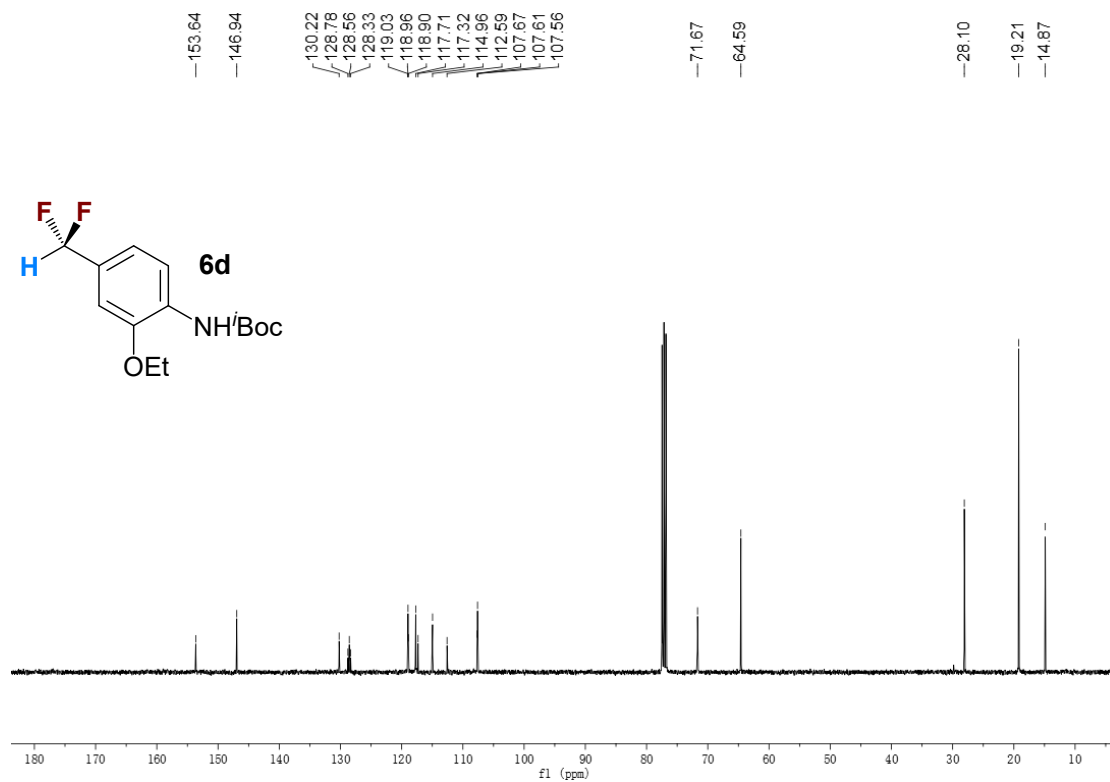
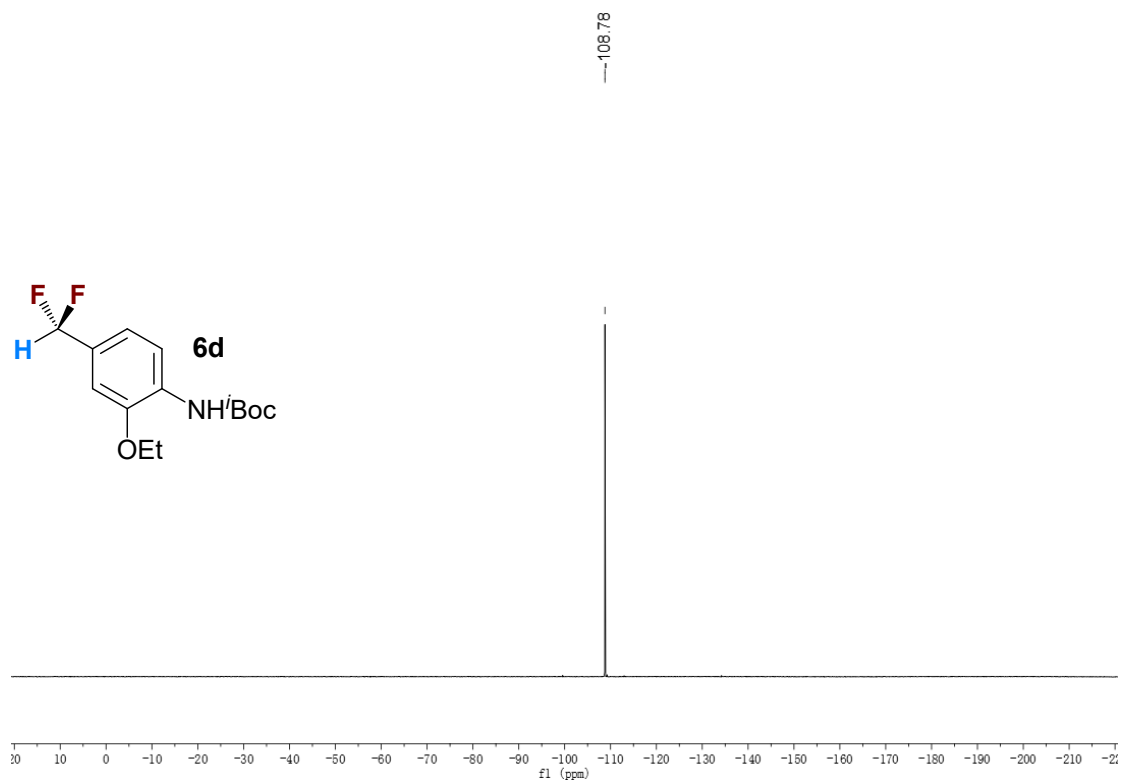
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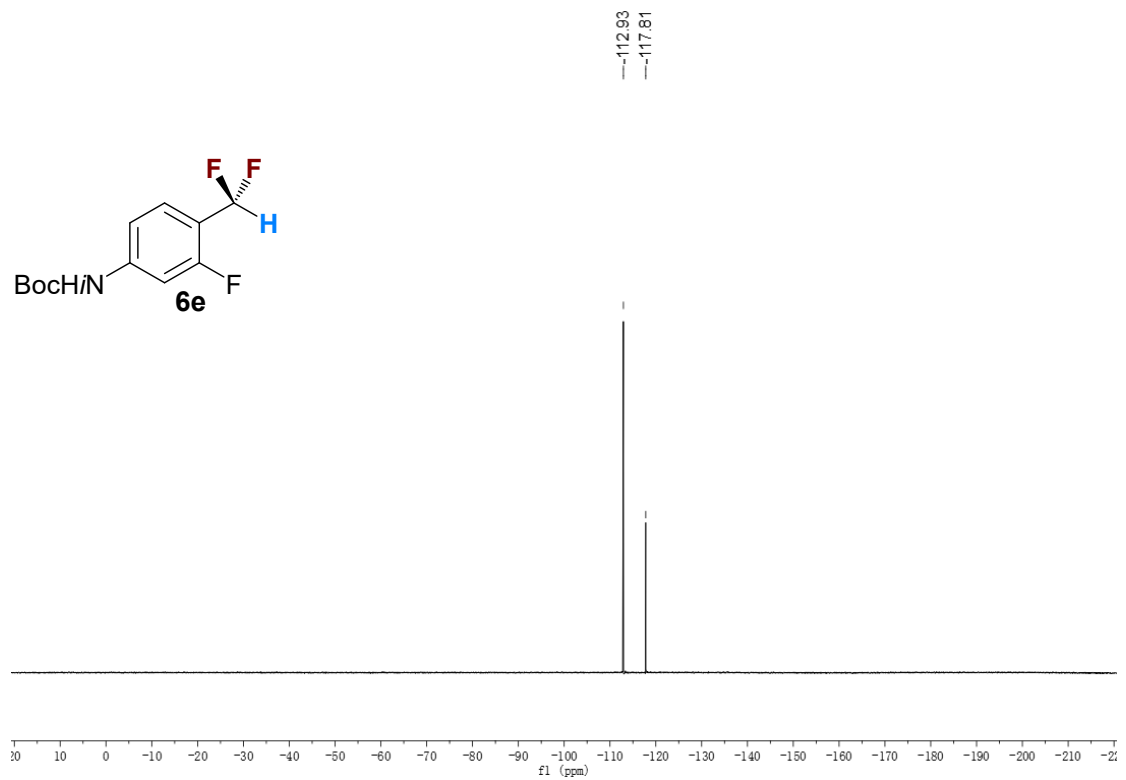
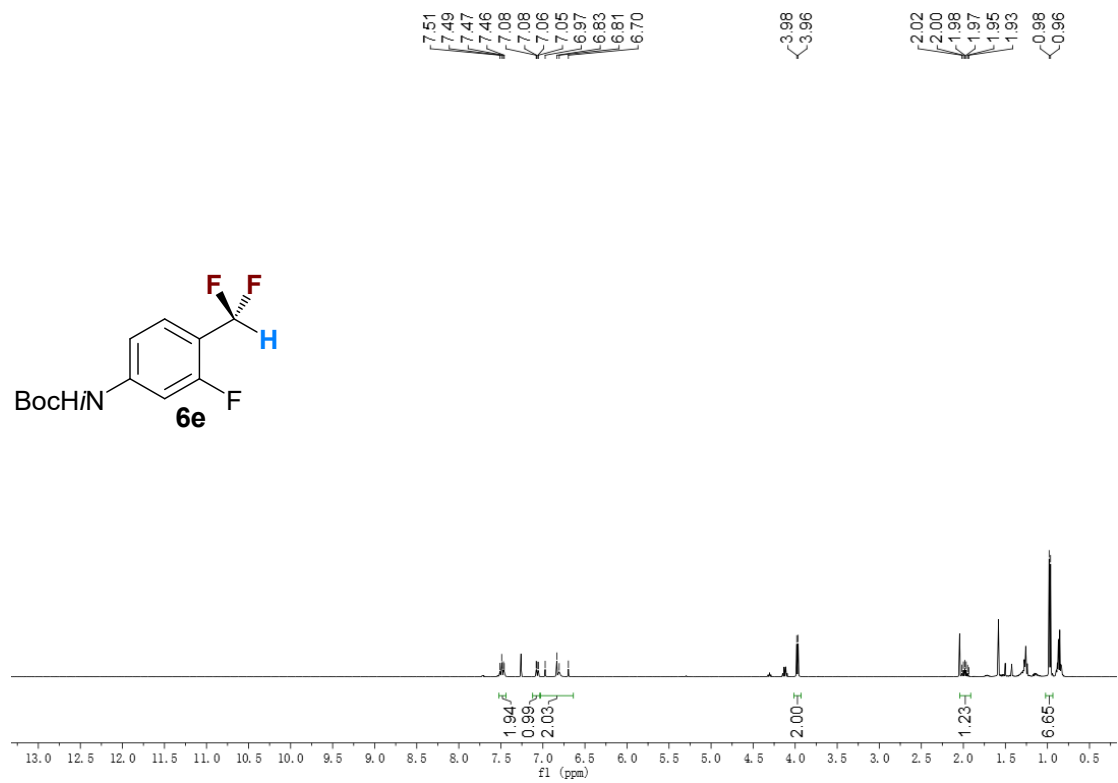
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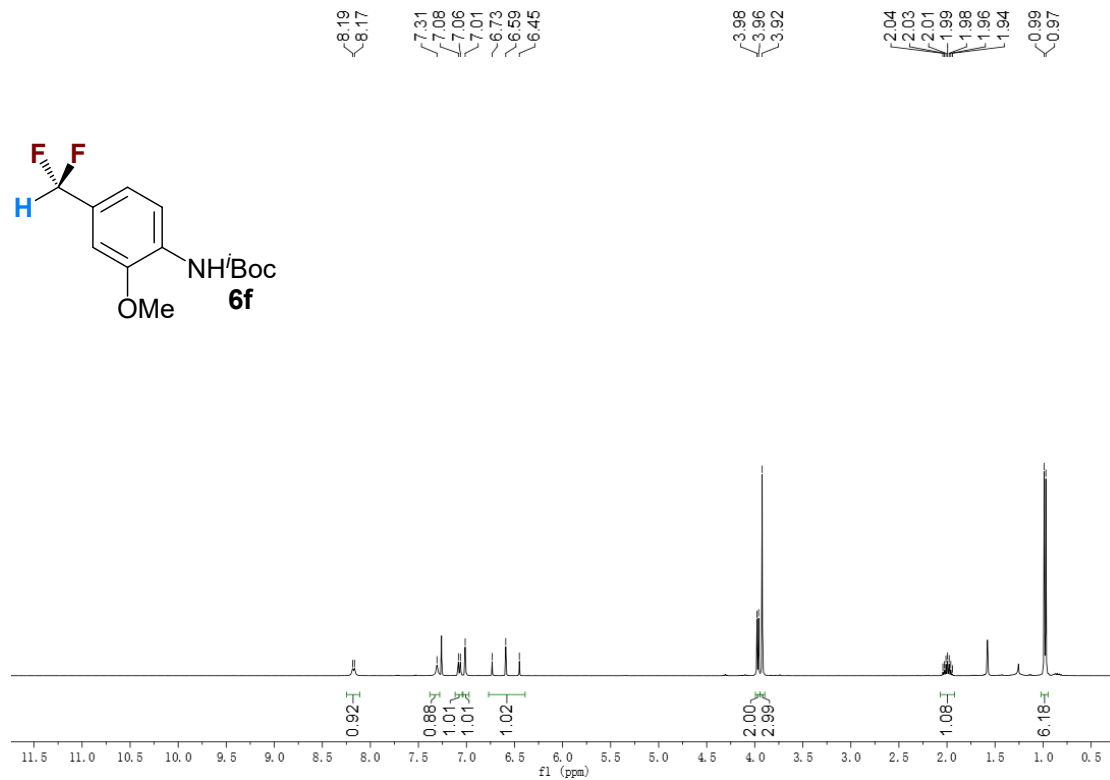
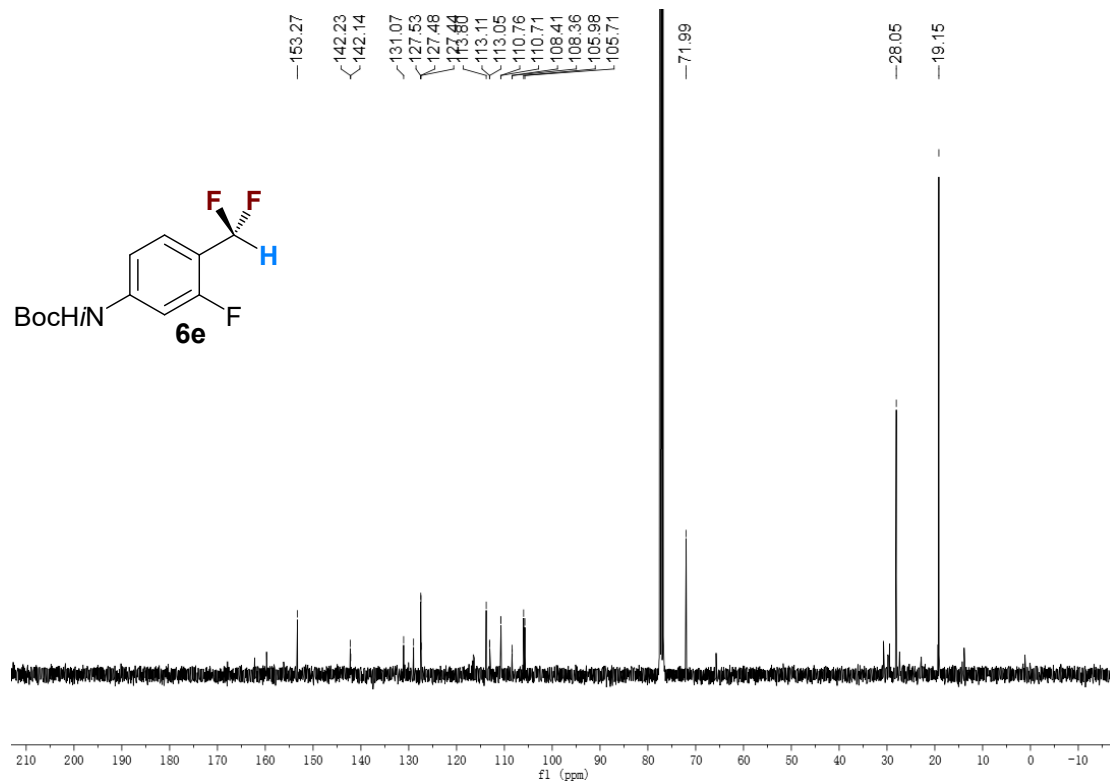


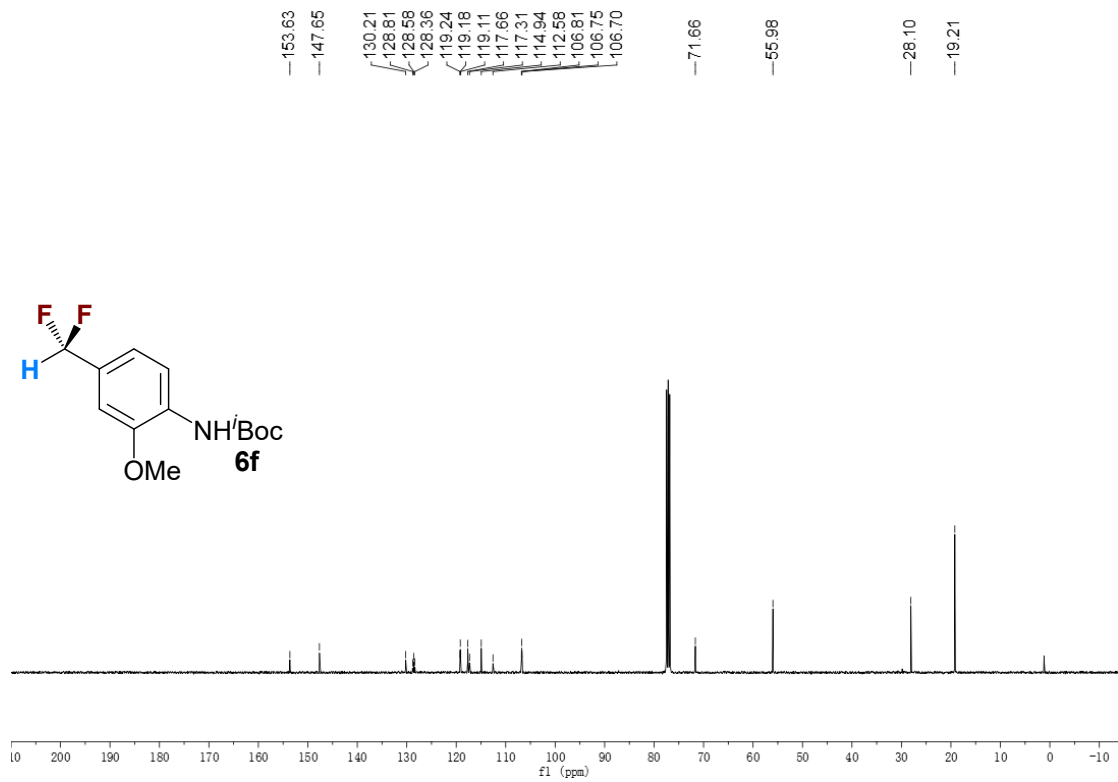
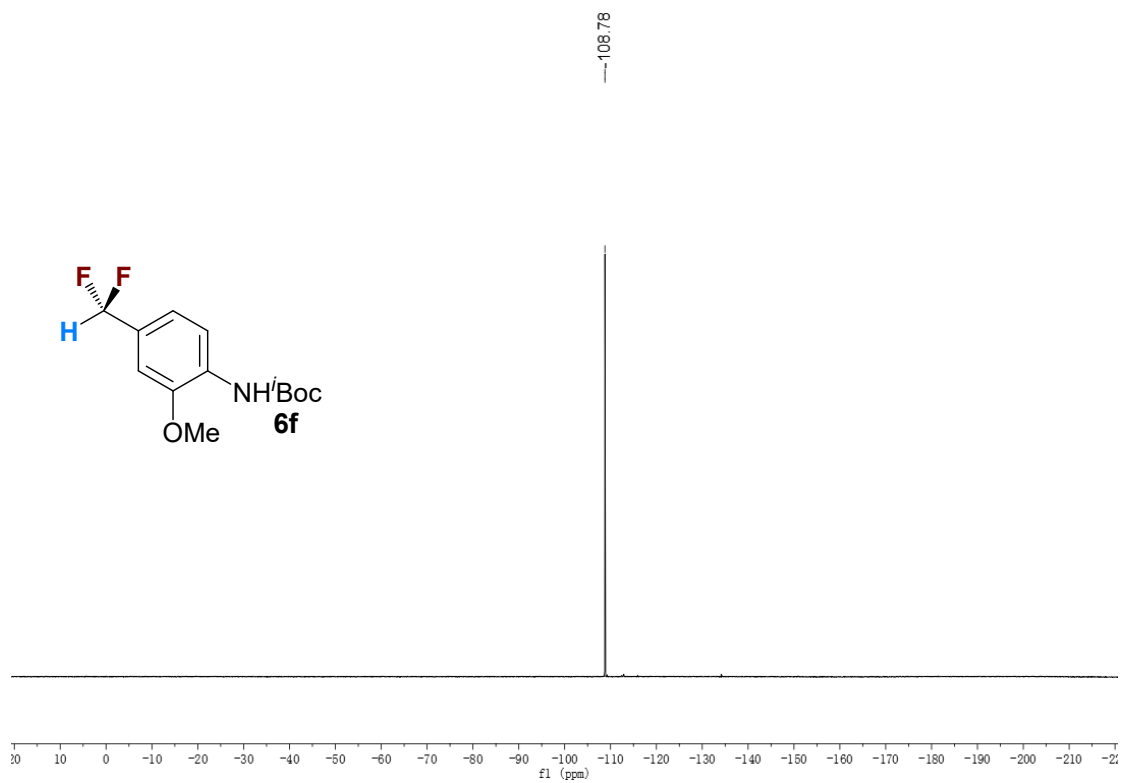


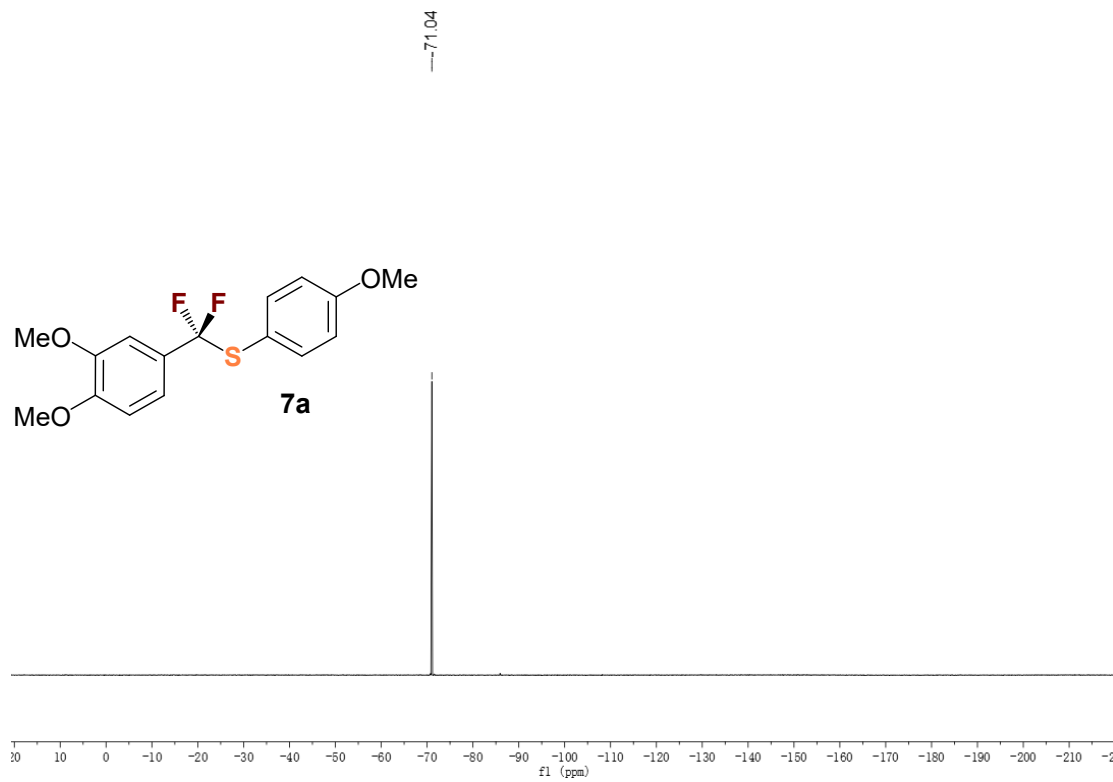
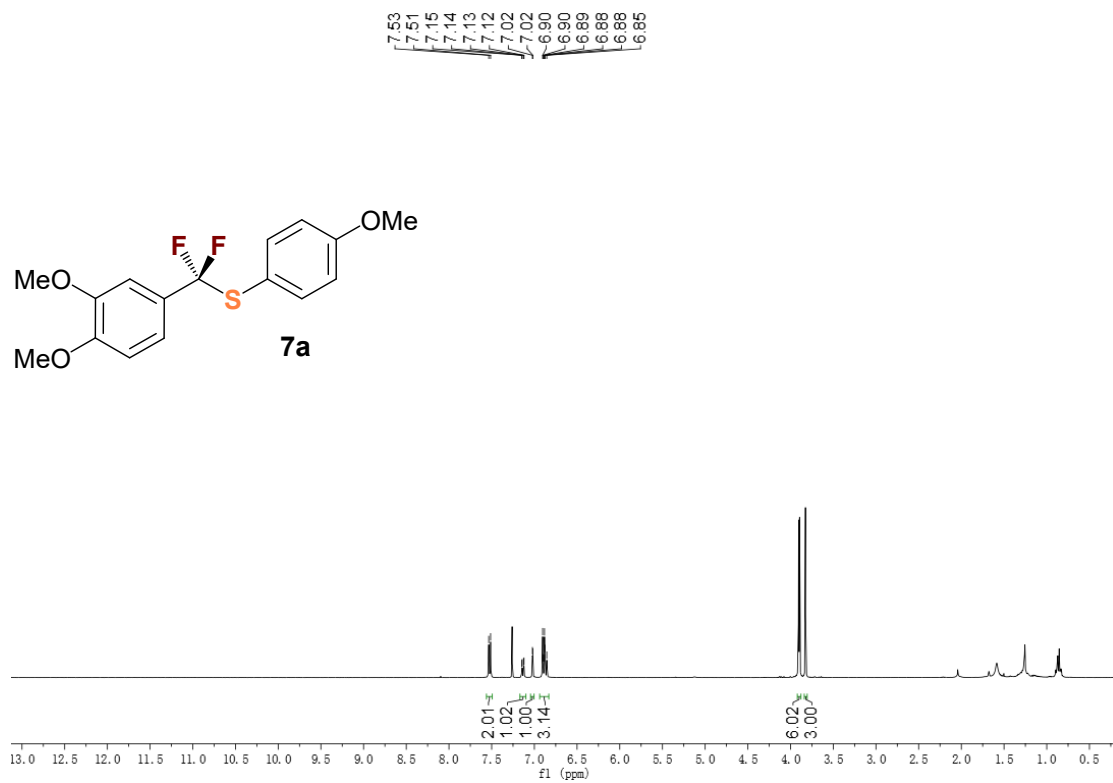


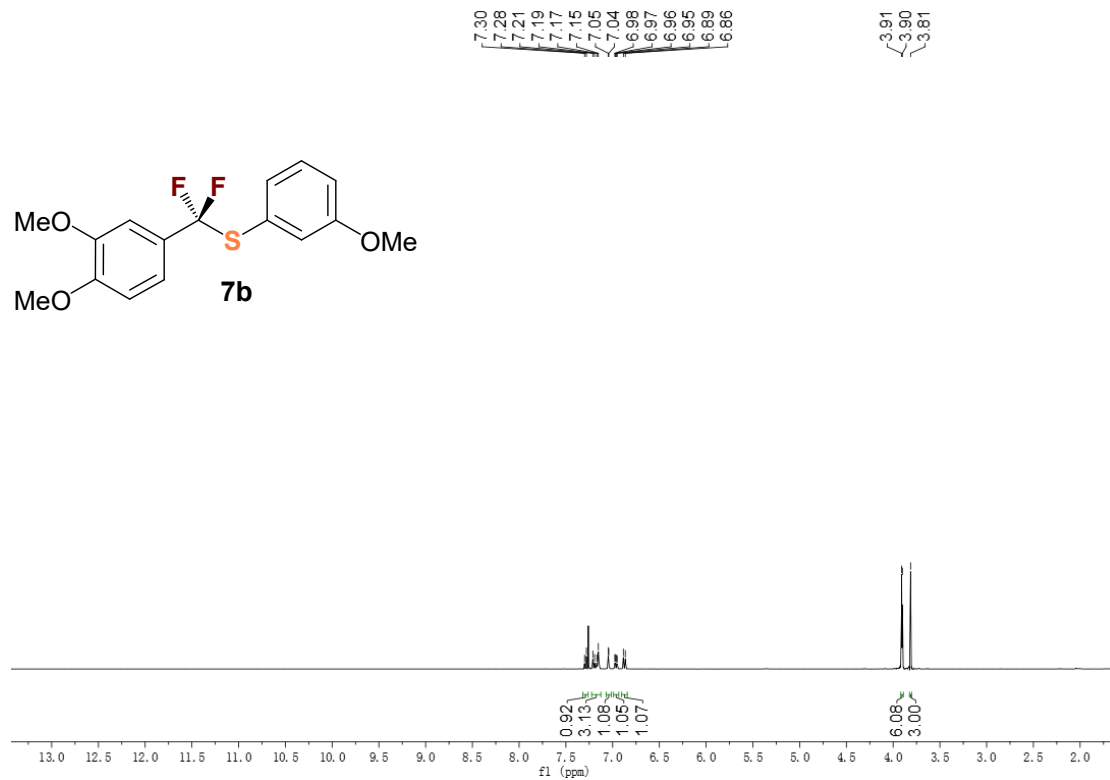
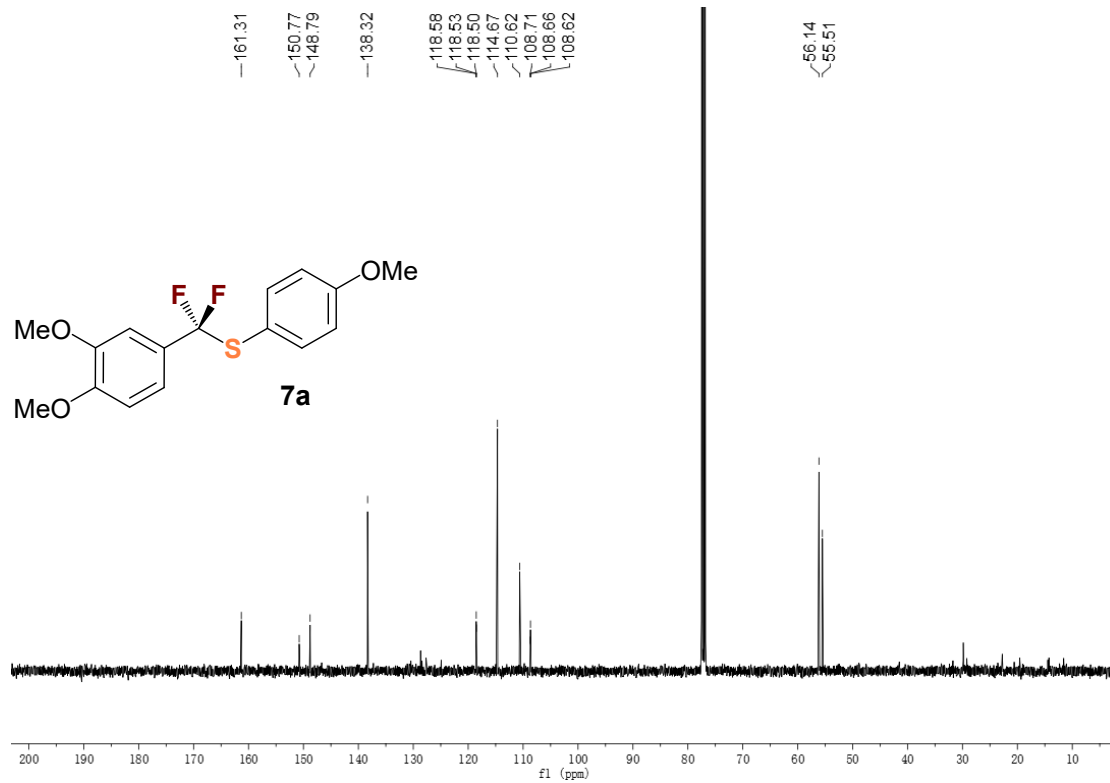


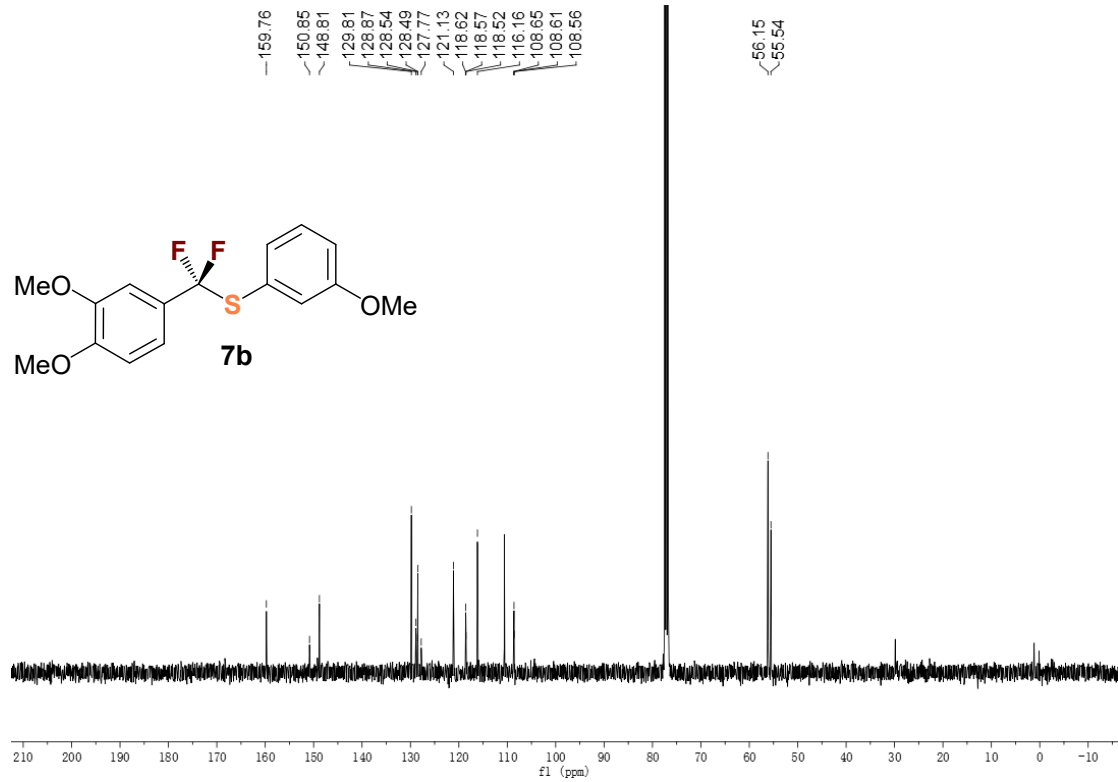
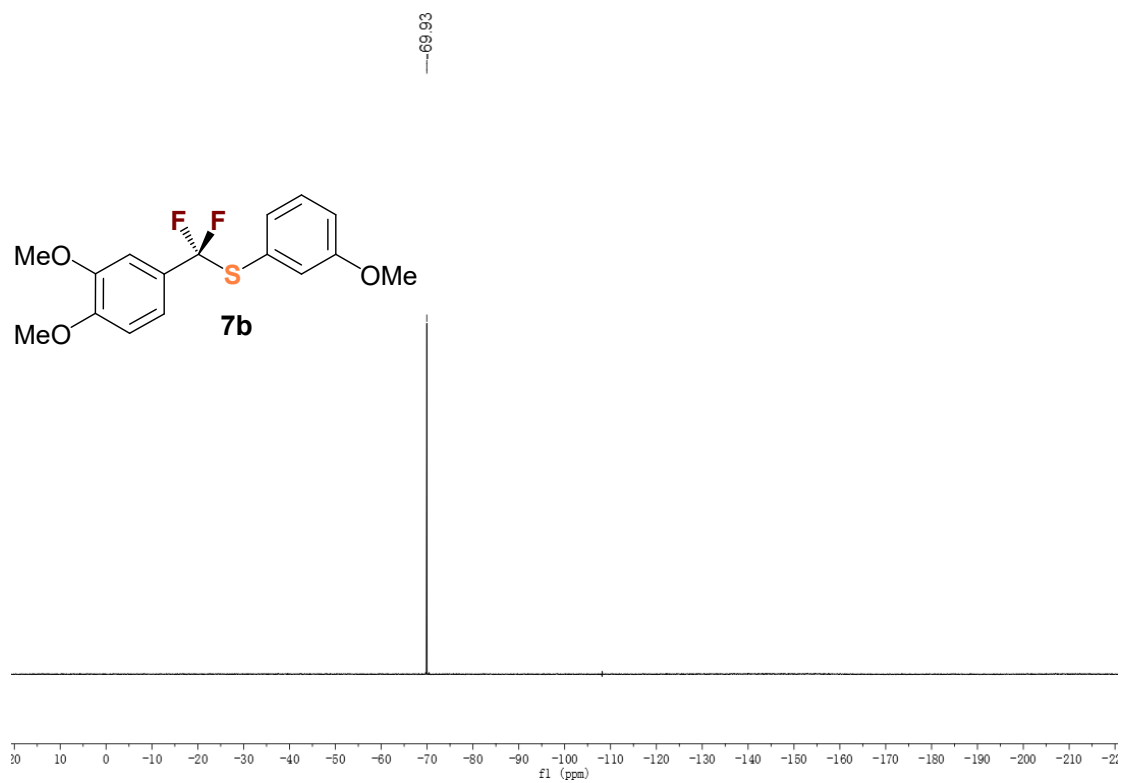


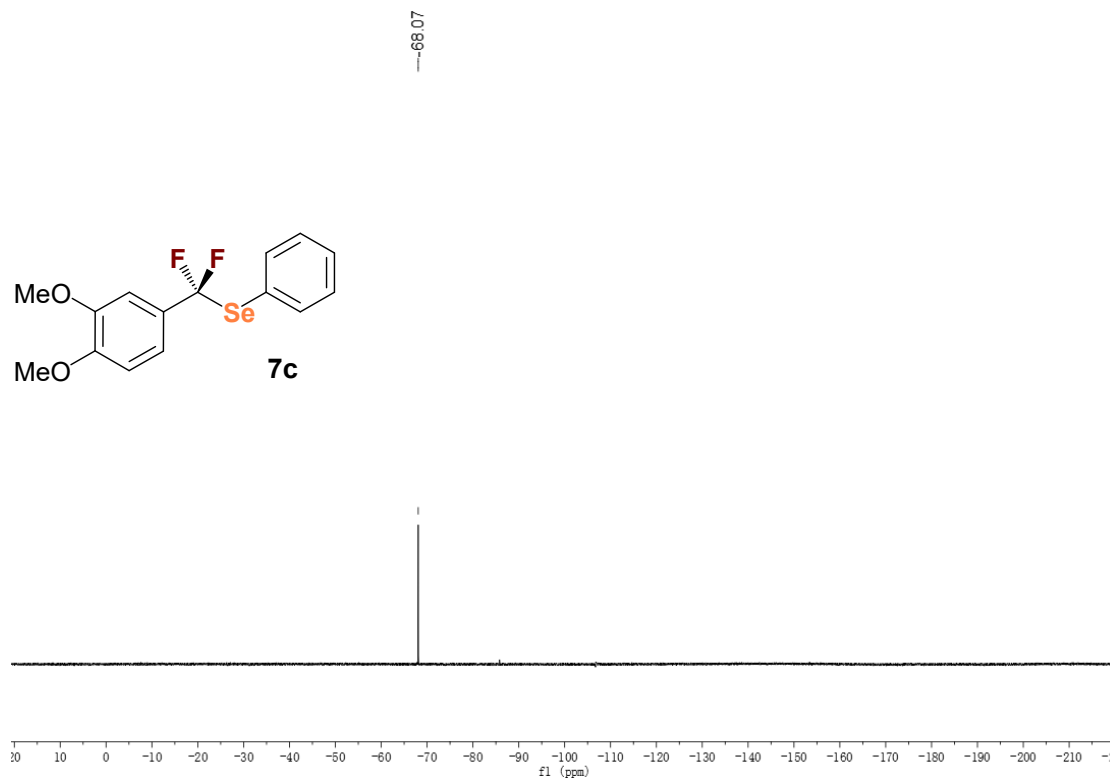
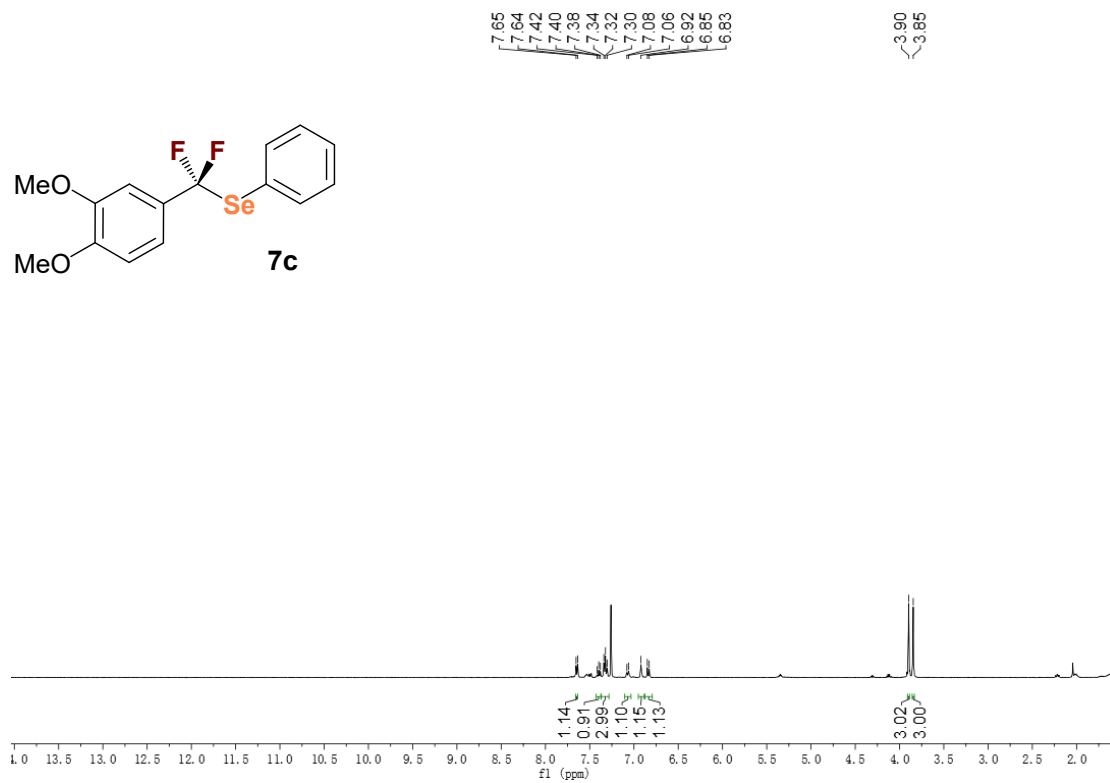
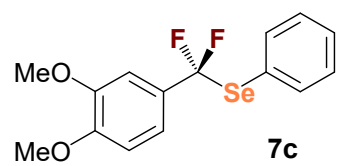


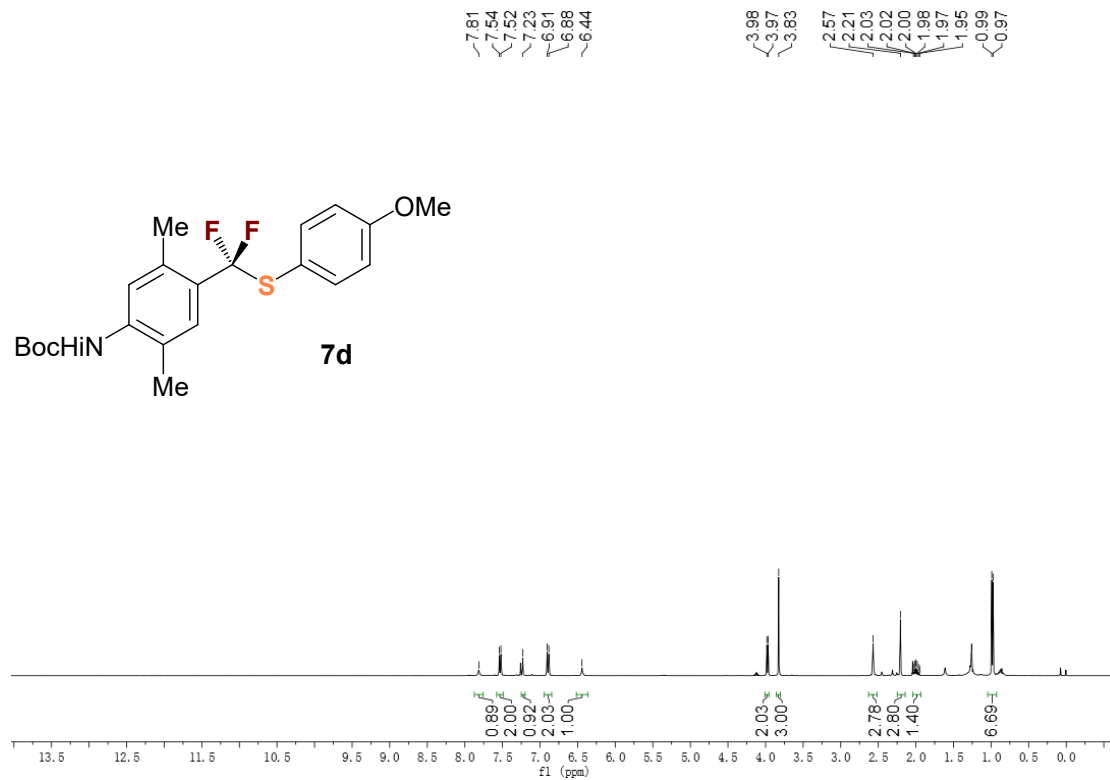
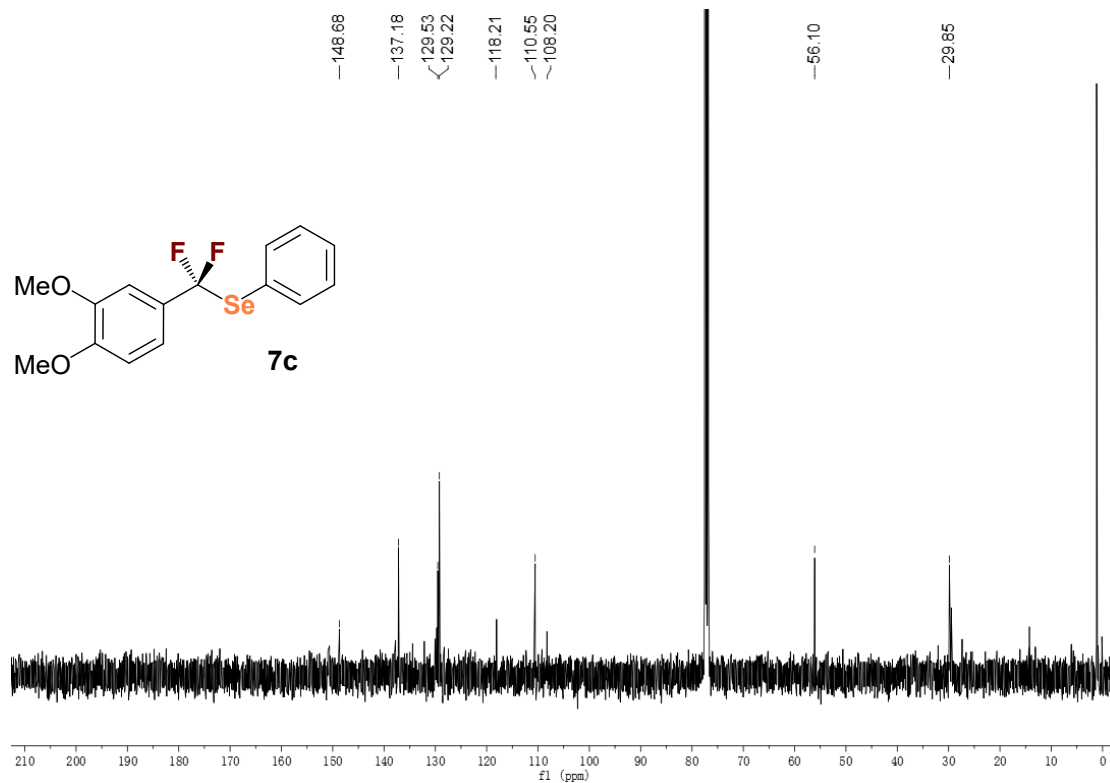


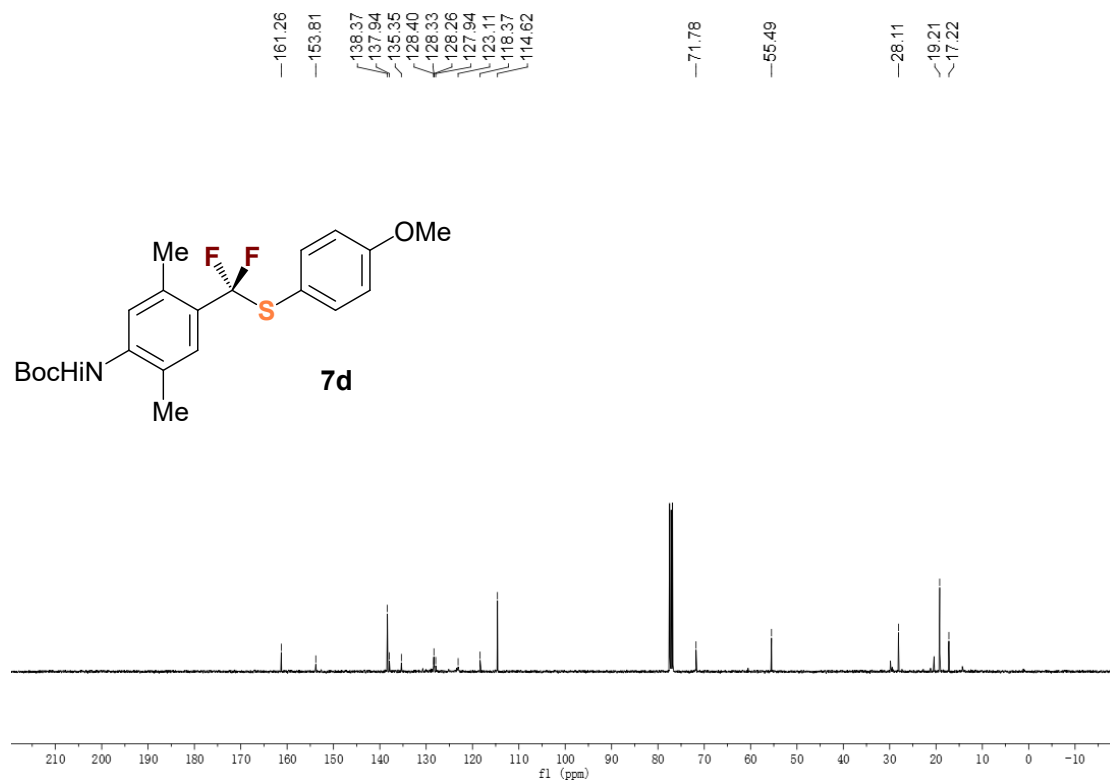
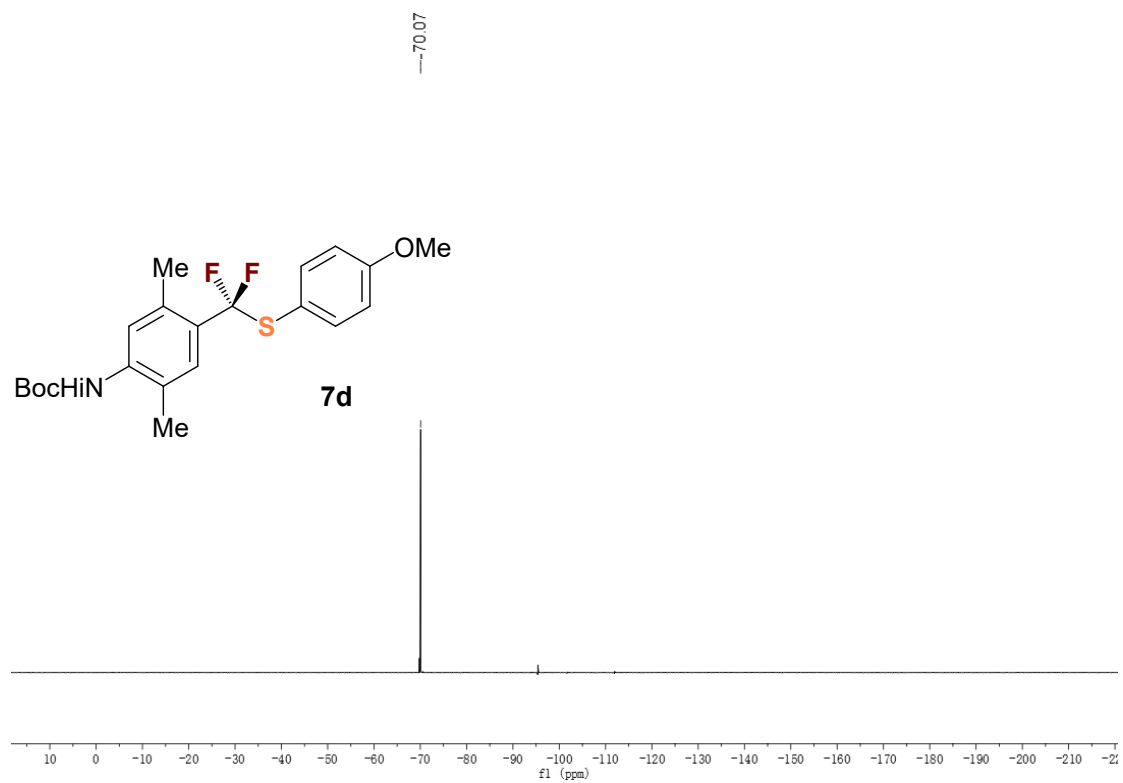


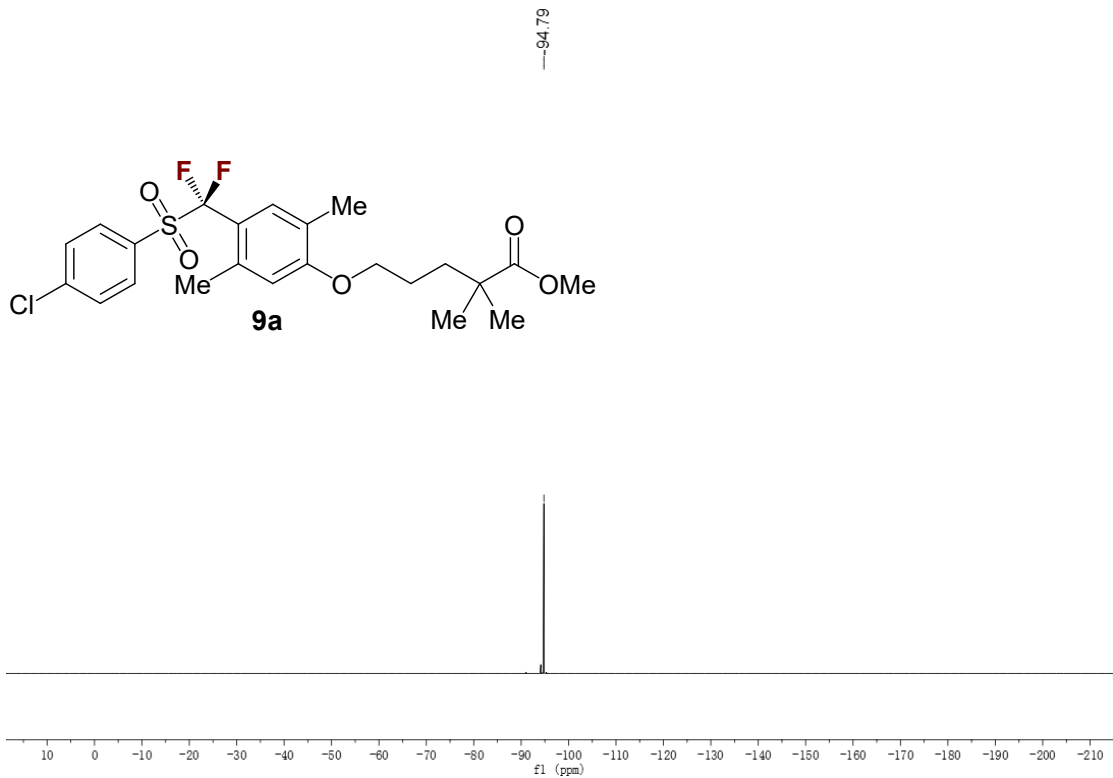
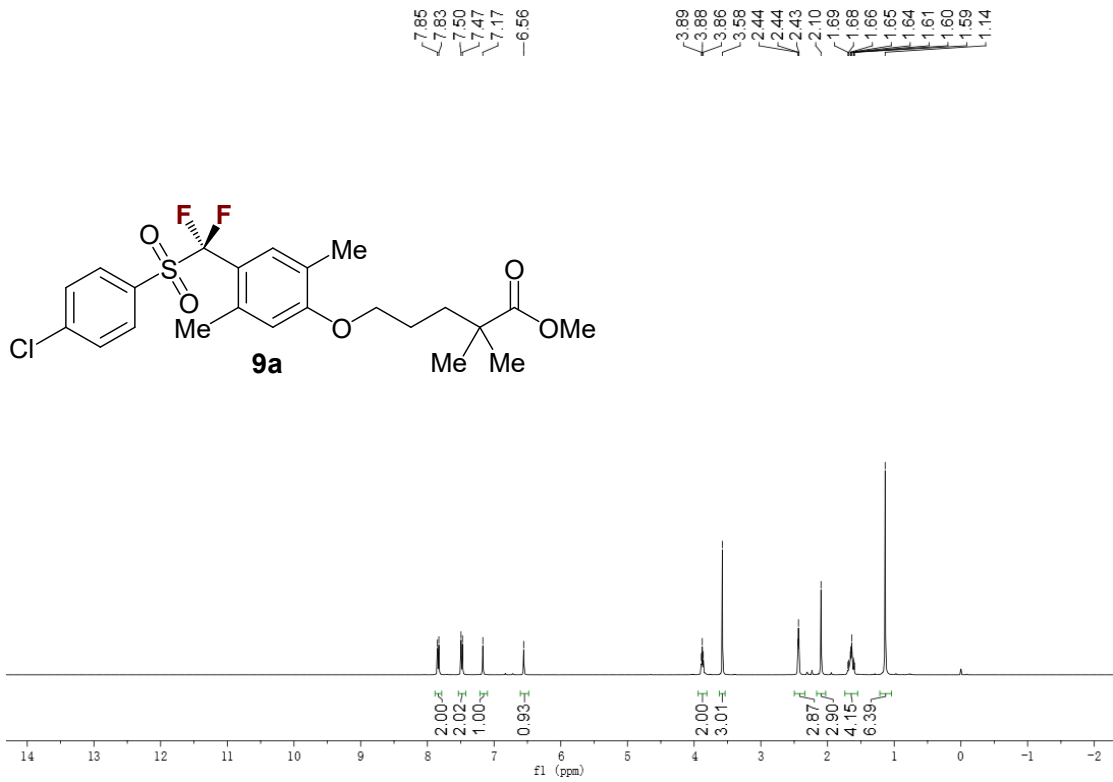


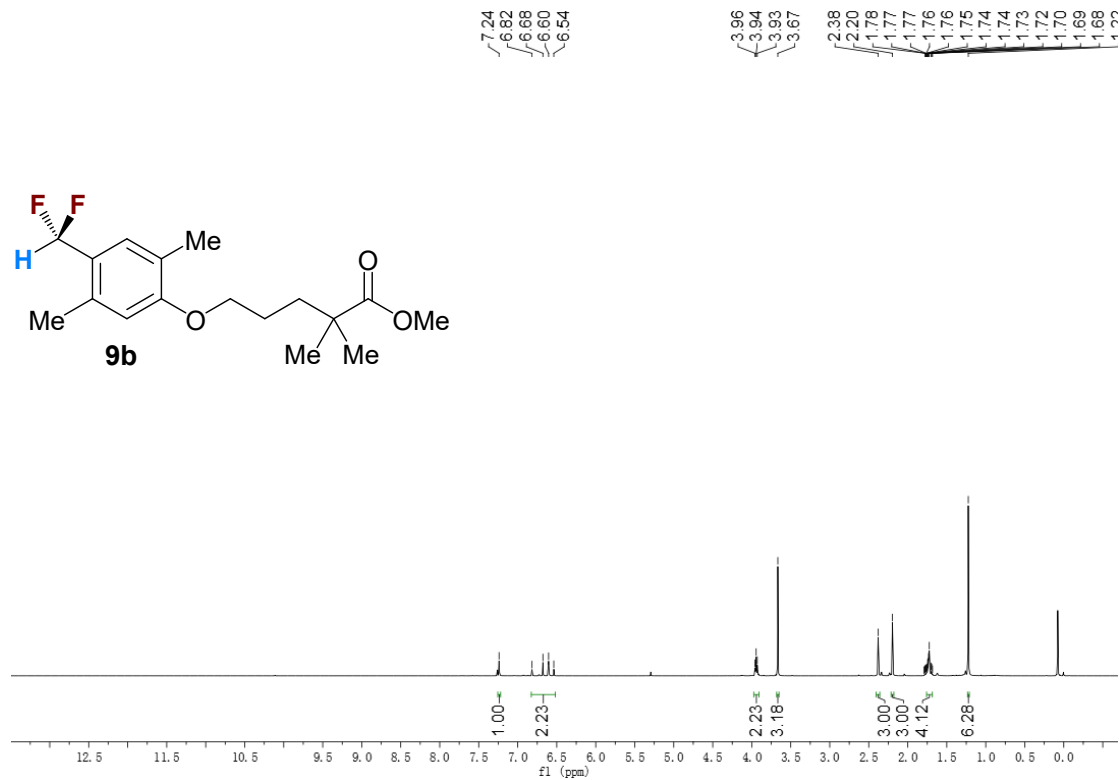
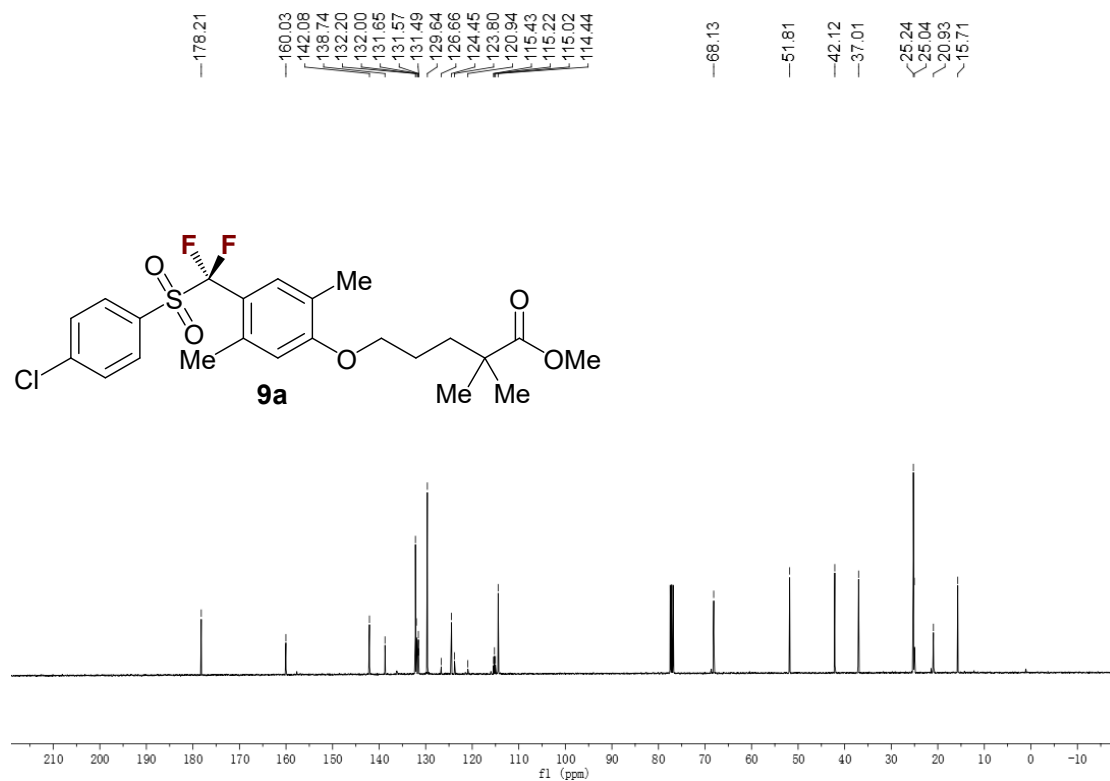


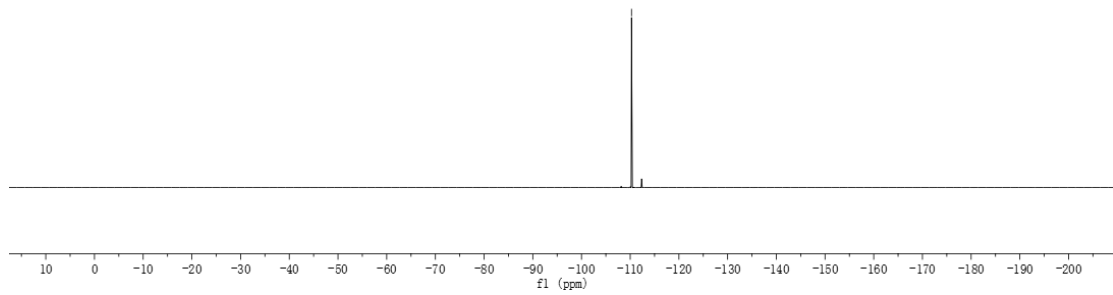
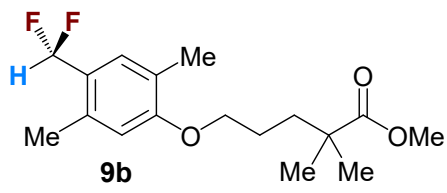




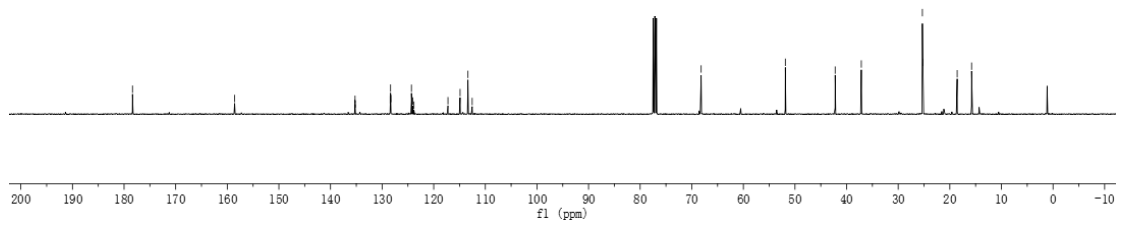
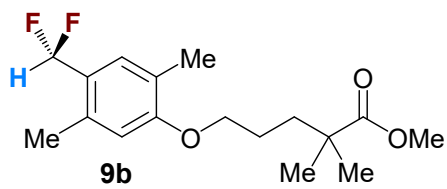


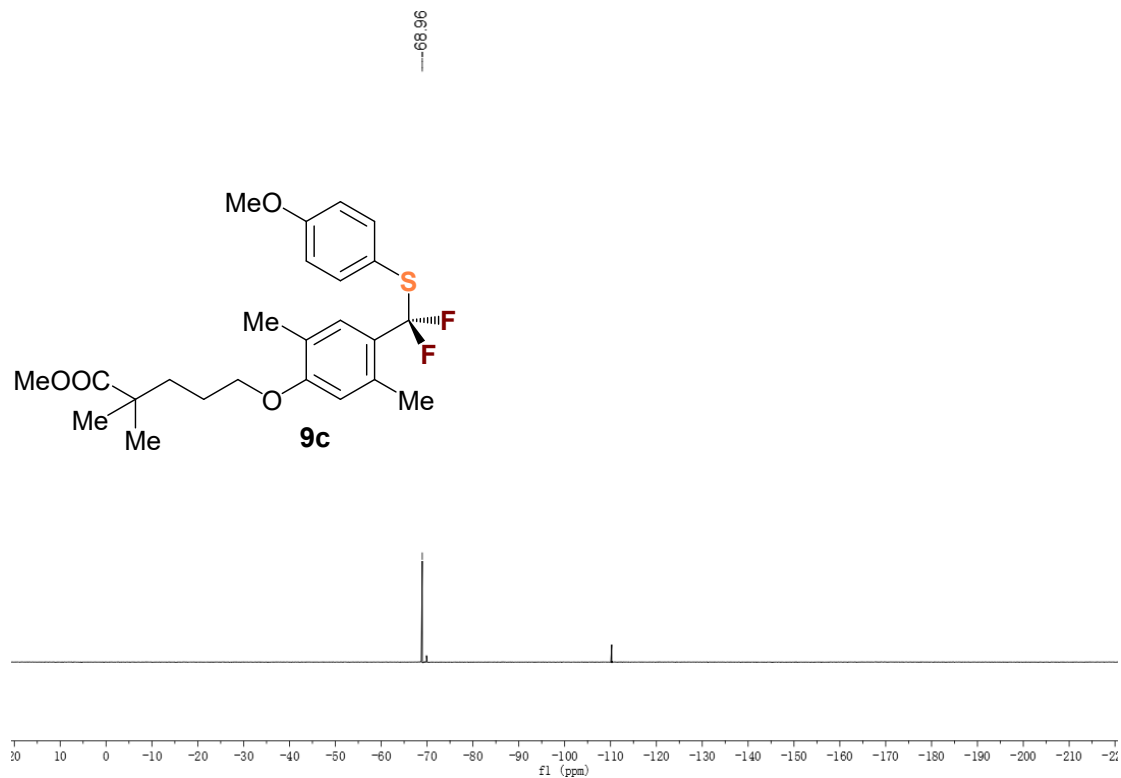
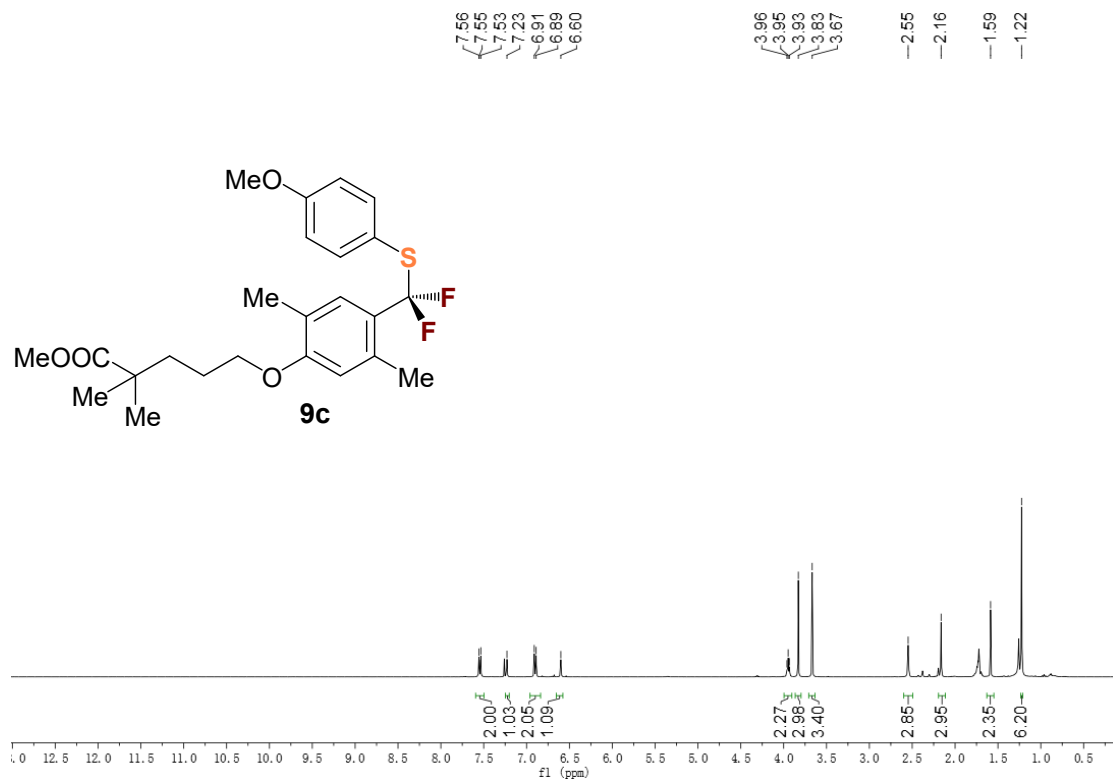


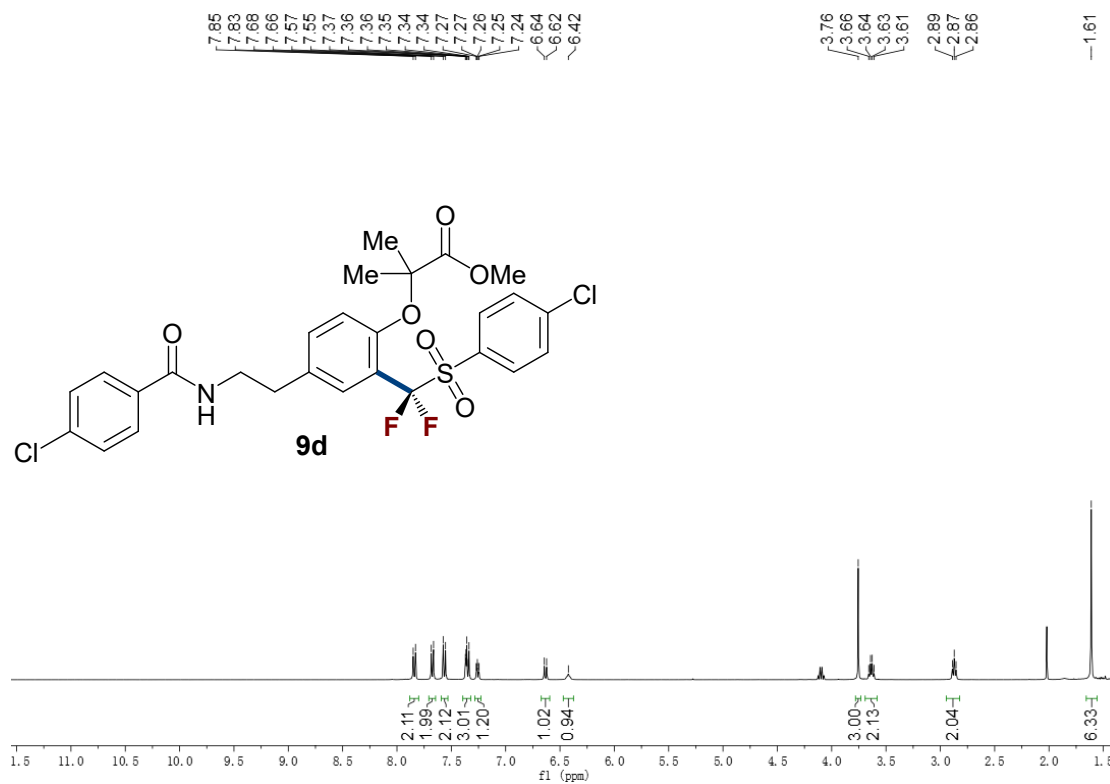
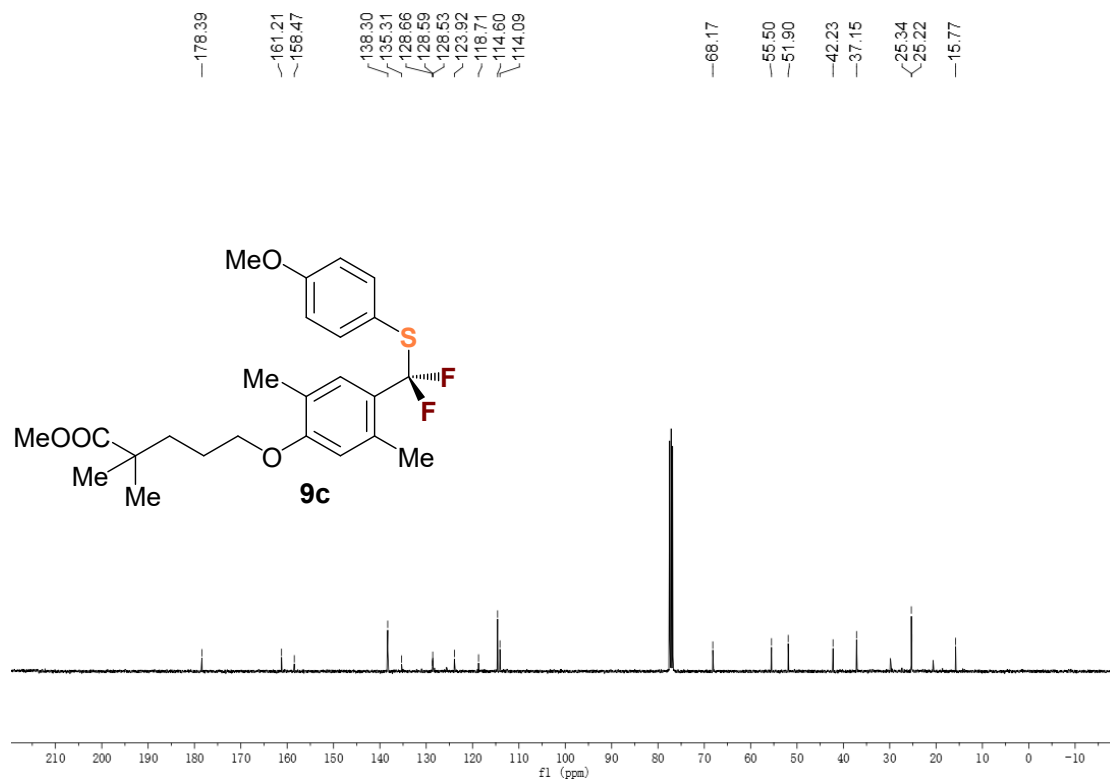


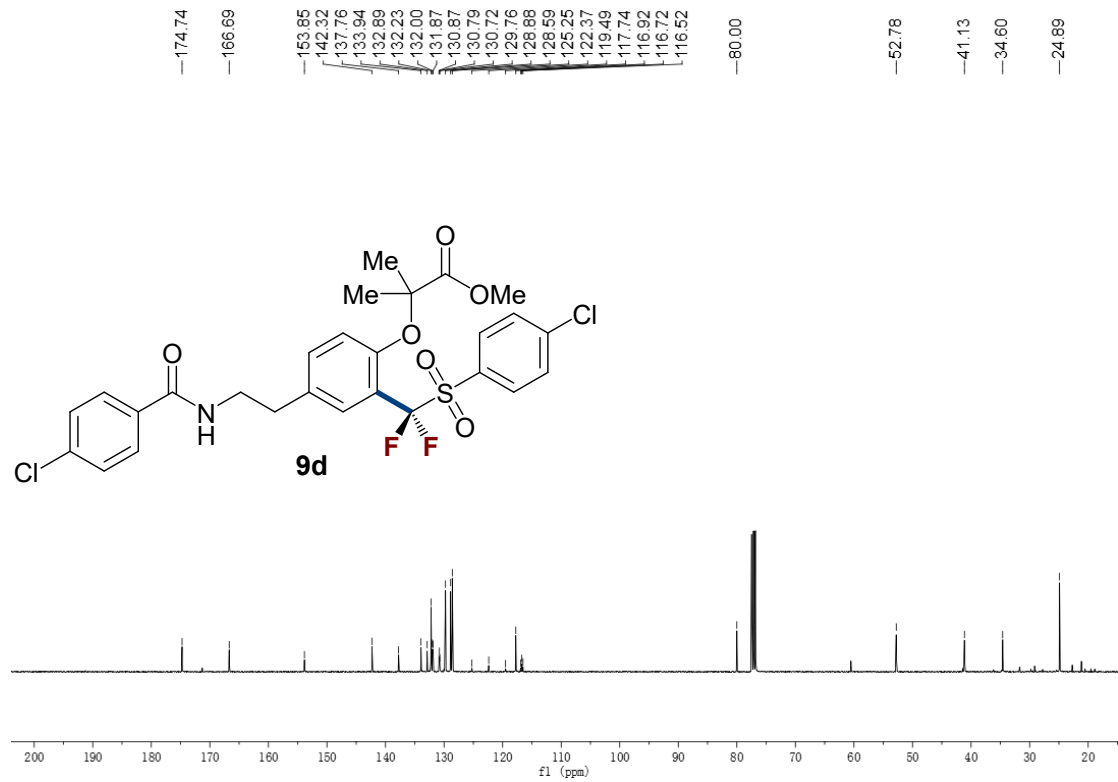
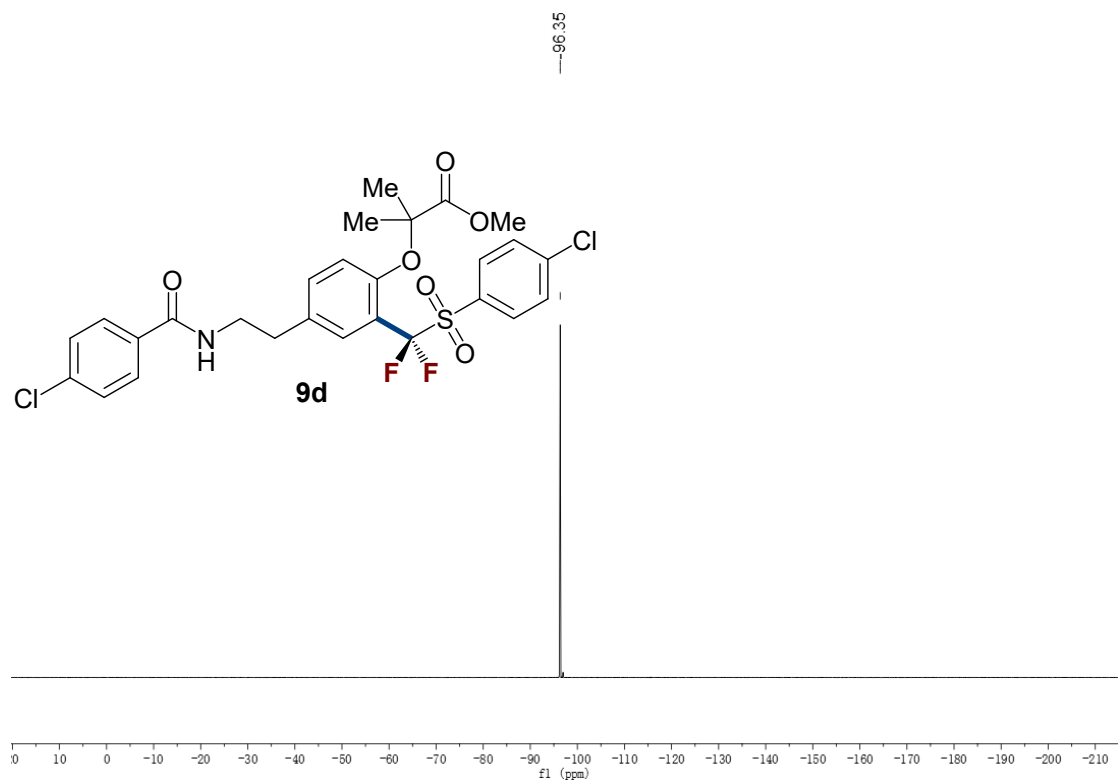


- 178.37
- 158.57
- 135.29
- 135.24
- 135.19
- 128.43
- 128.36
- 128.29
- 124.32
- 124.25
- 124.04
- 123.83
- 117.24
- 114.89
- 113.37
- 112.54
- 68.18
- 51.87
- 42.21
- 37.14
- 25.31
- 25.20
- 18.57
- 15.78

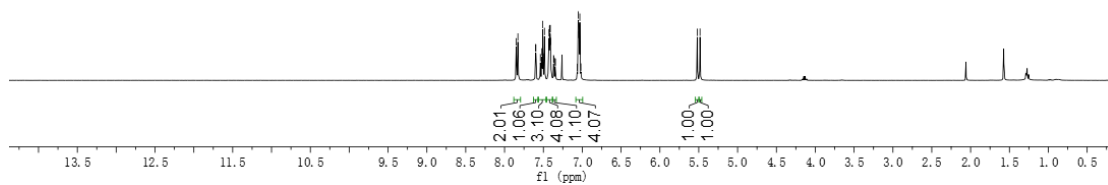
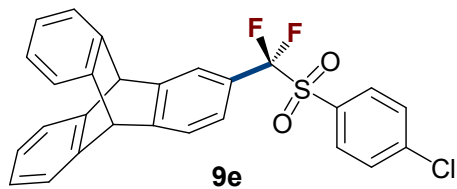




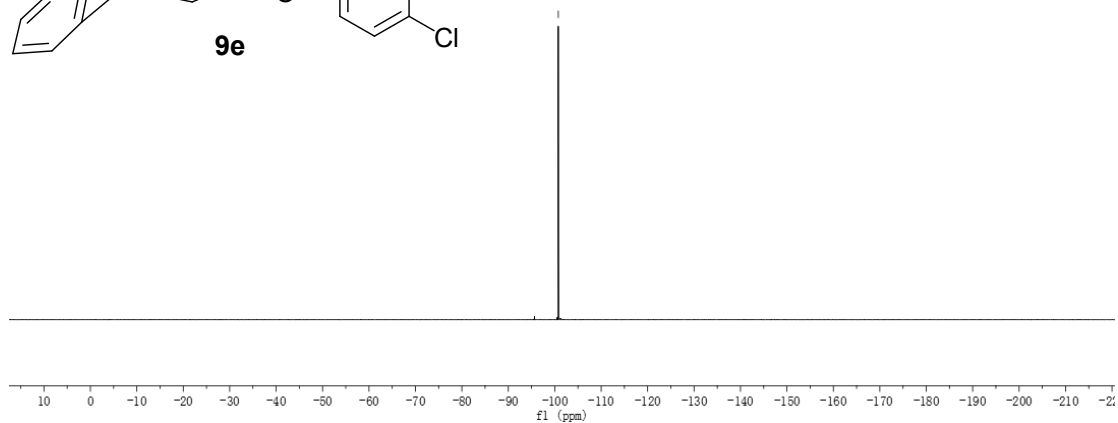
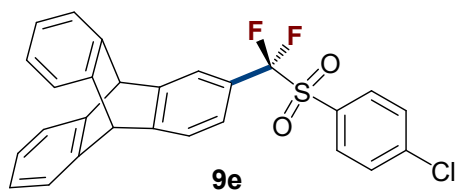


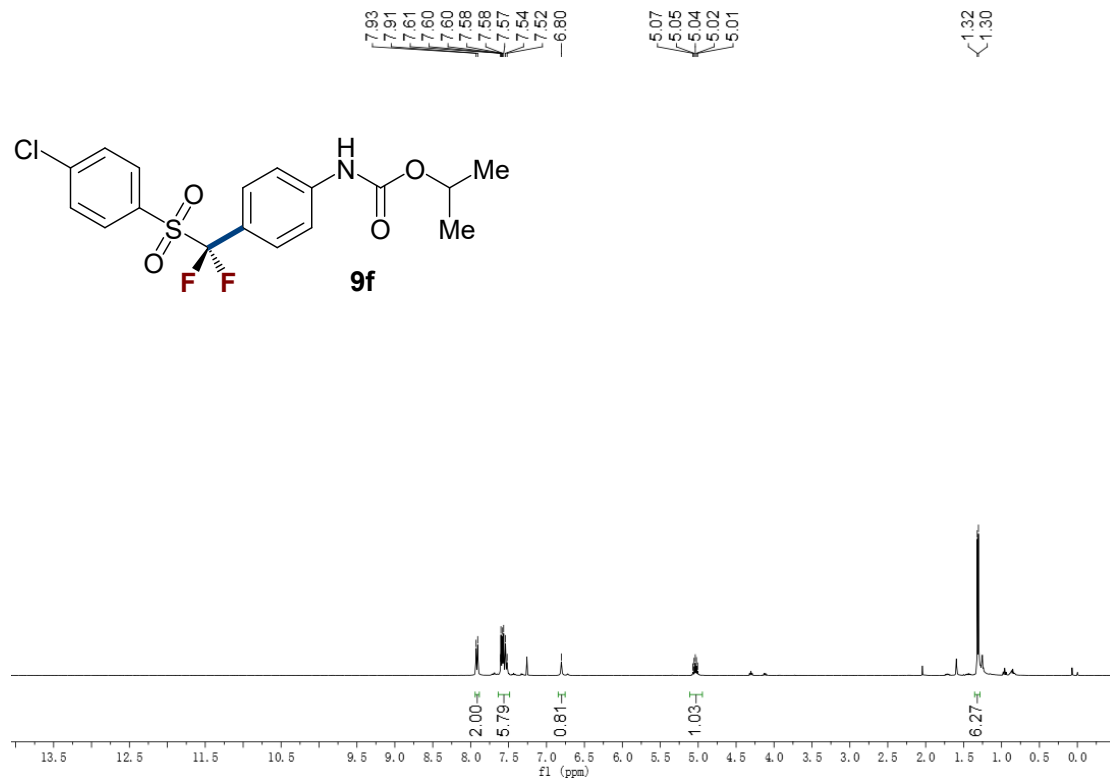
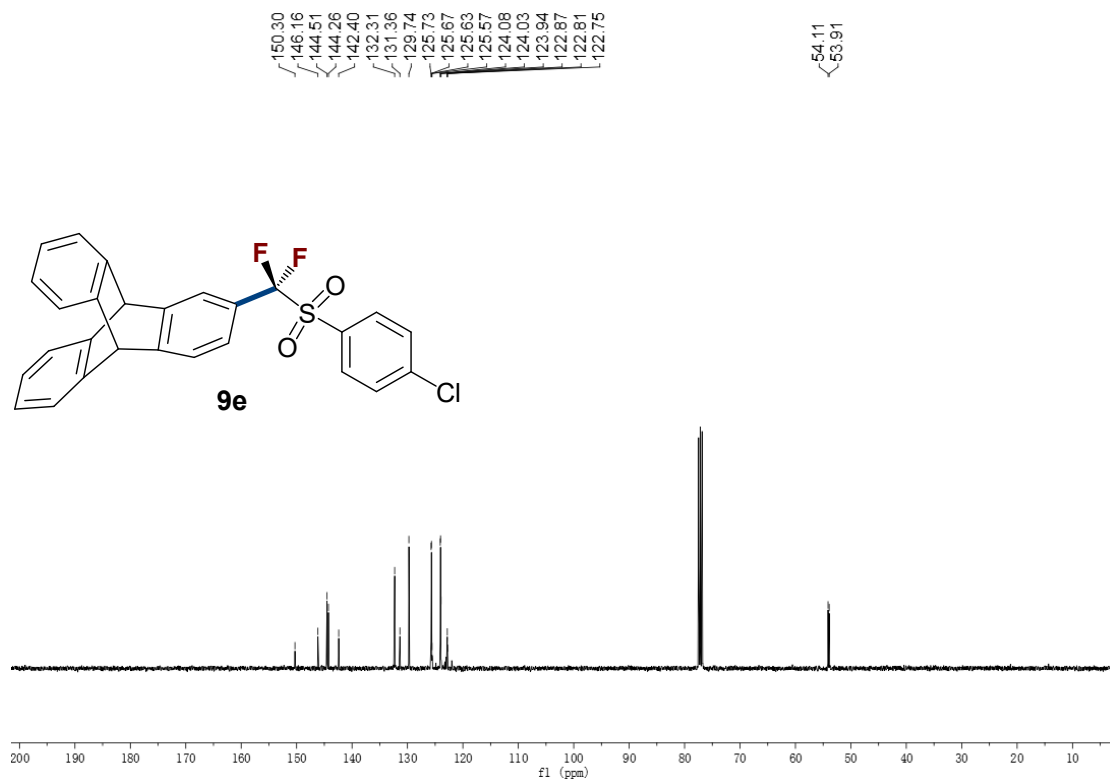


7.85
7.83
7.60
7.60
7.54
7.52
7.51
7.50
7.49
7.49
7.43
7.43
7.42
7.42
7.41
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7.07
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7.04
7.04
7.03
7.02
5.52
5.48

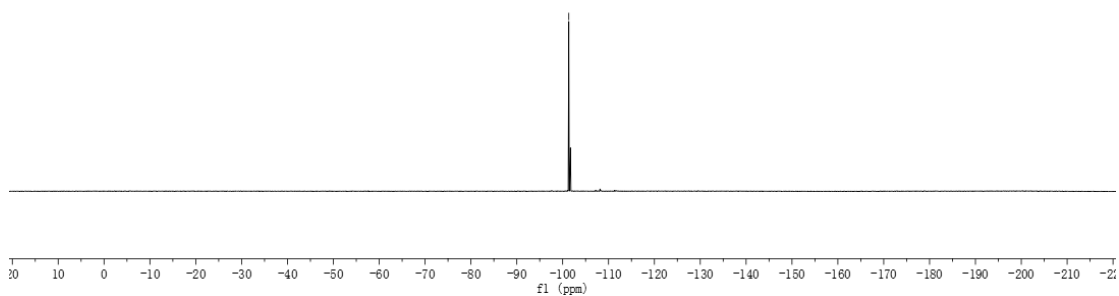
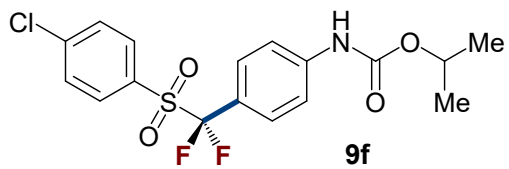


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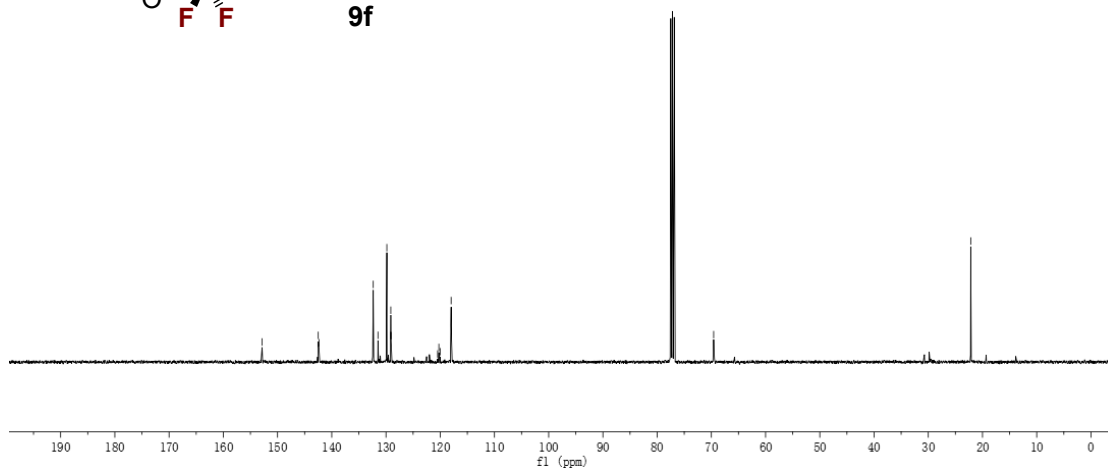
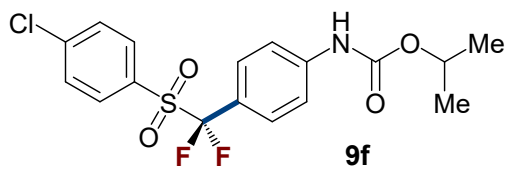


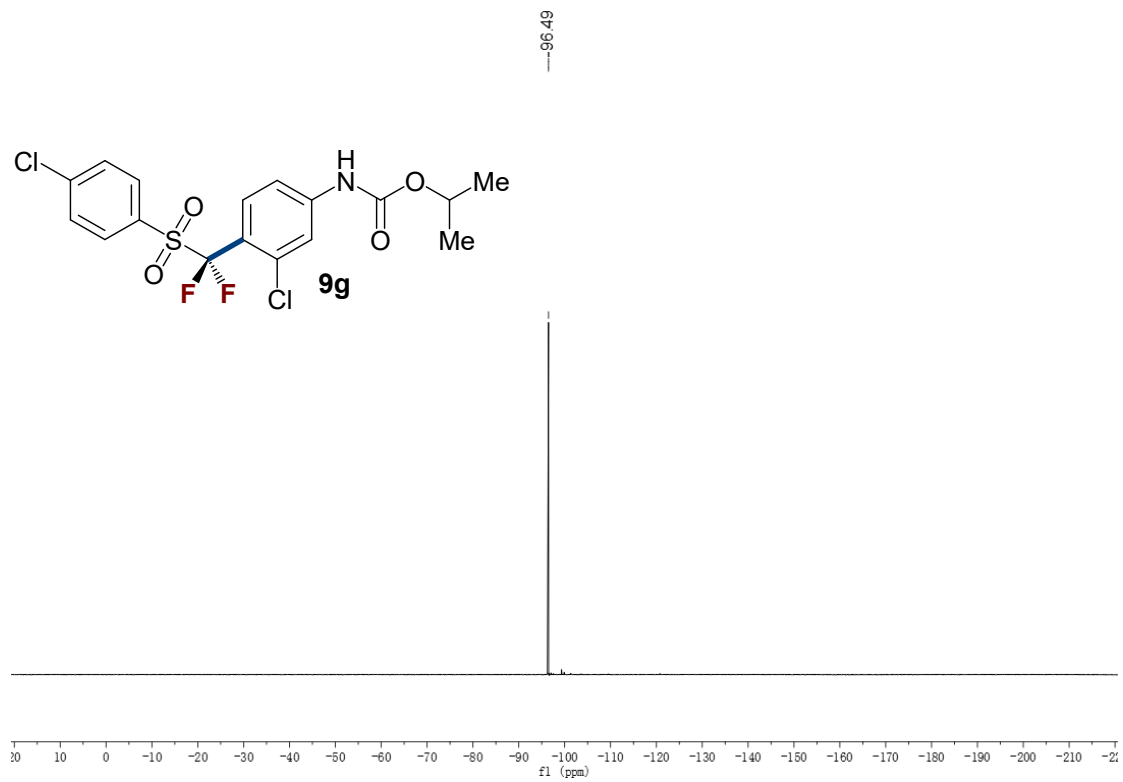
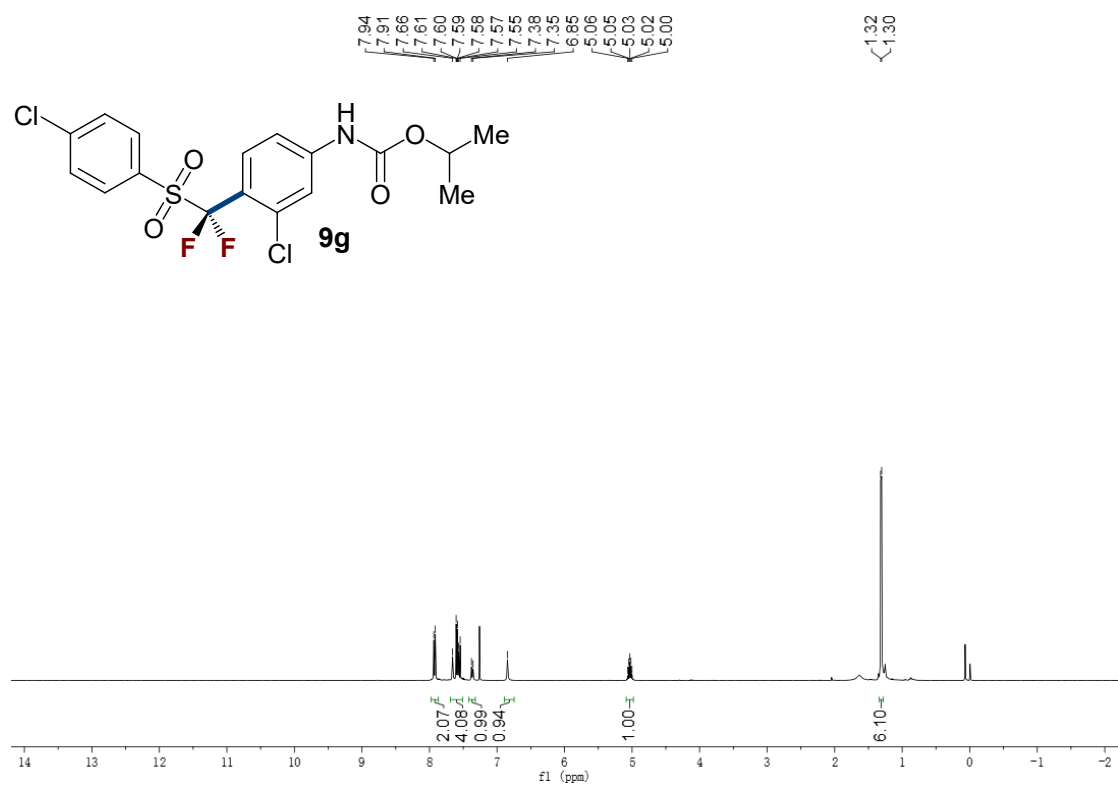


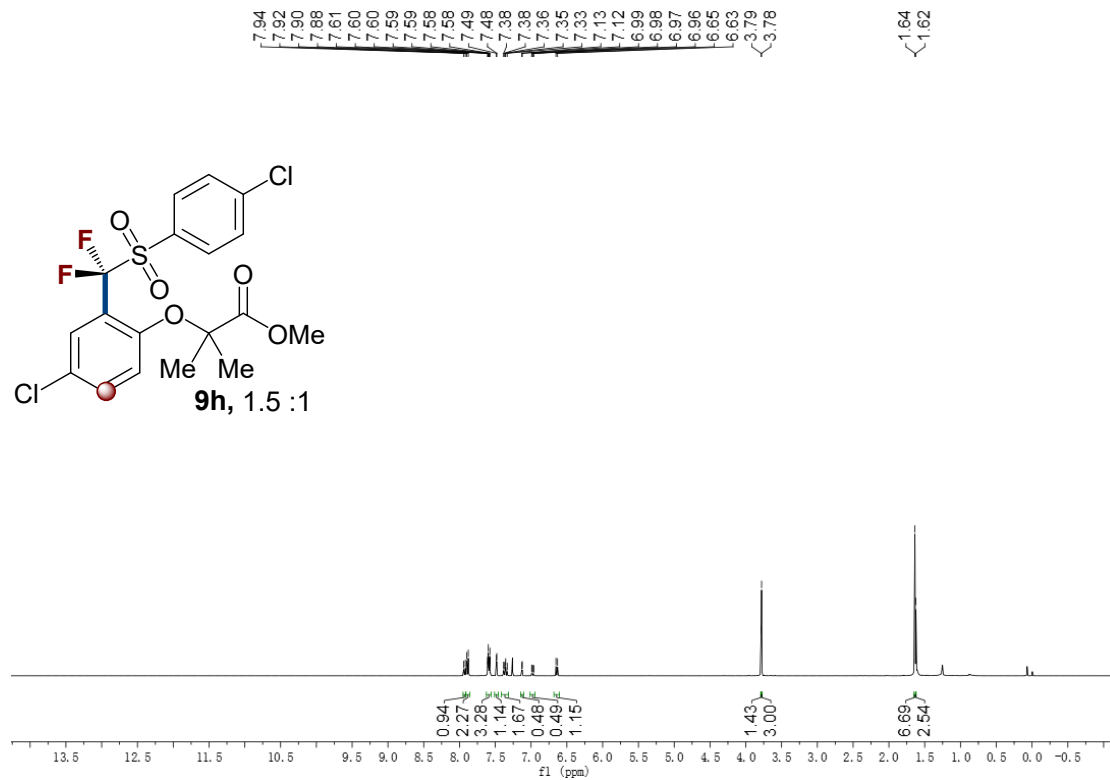
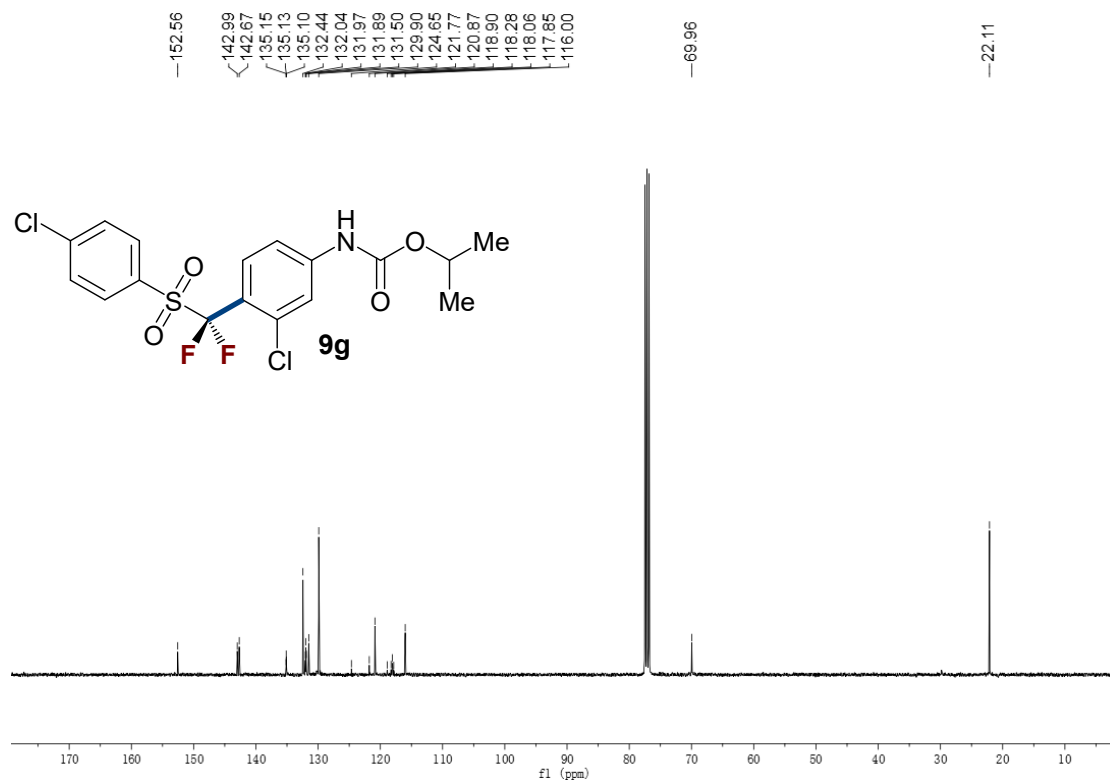
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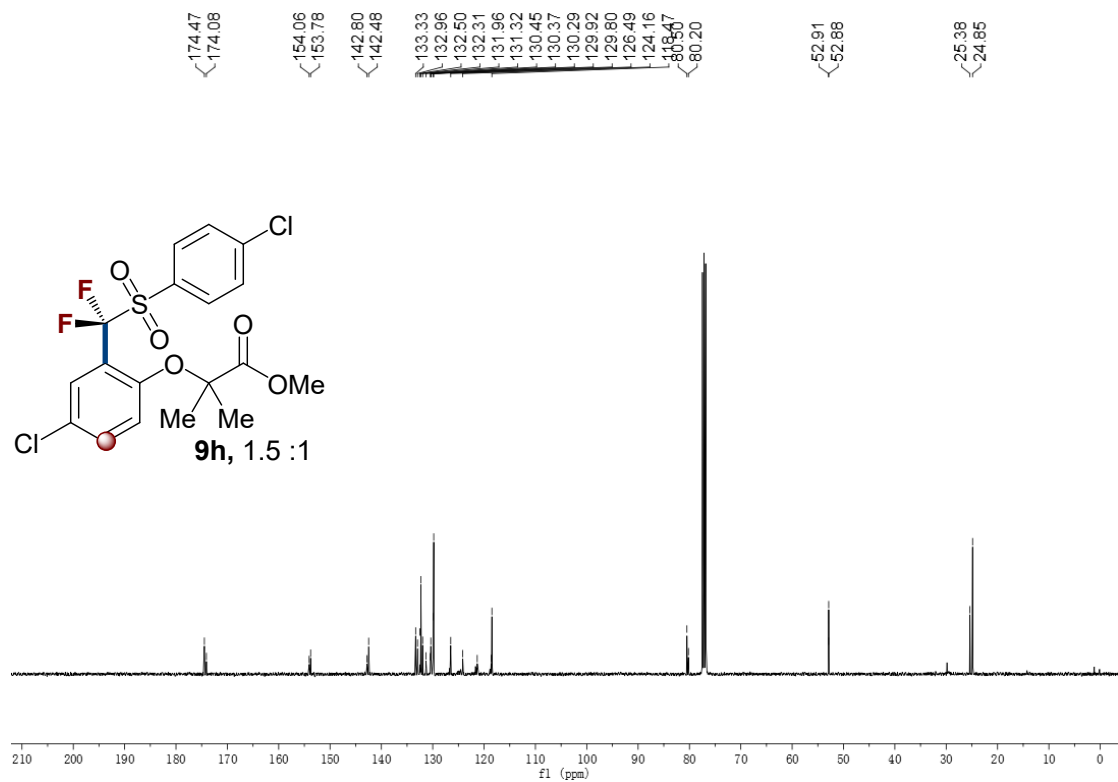
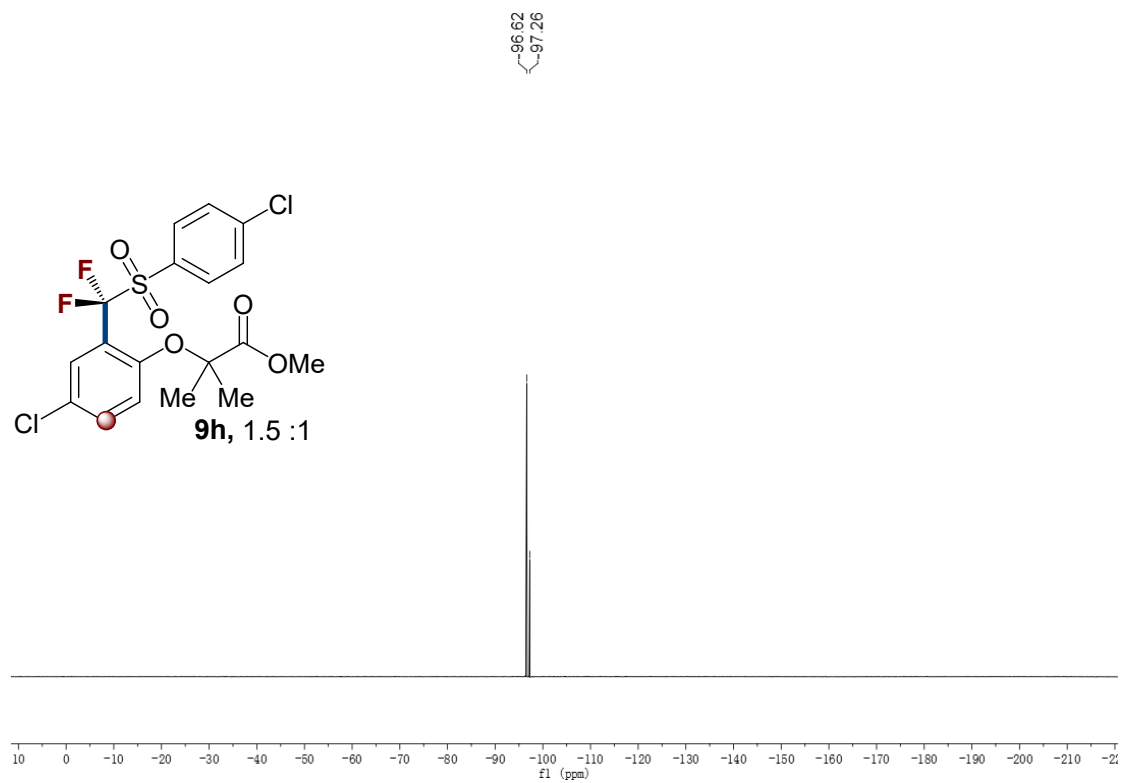


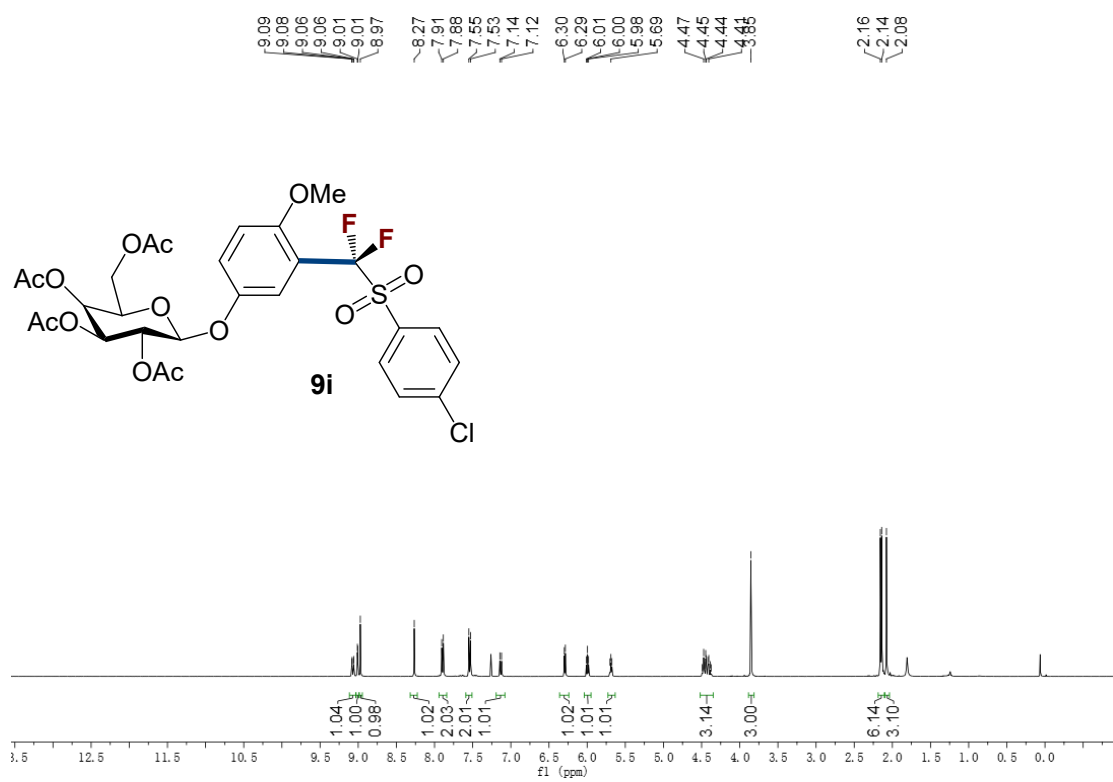
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117.99
69.58
22.17



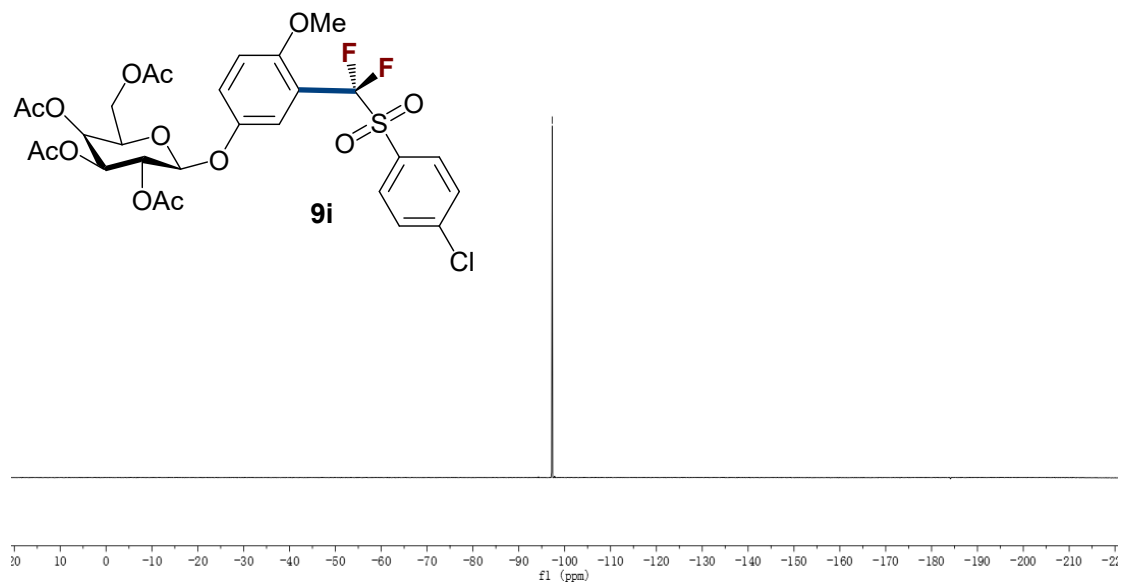


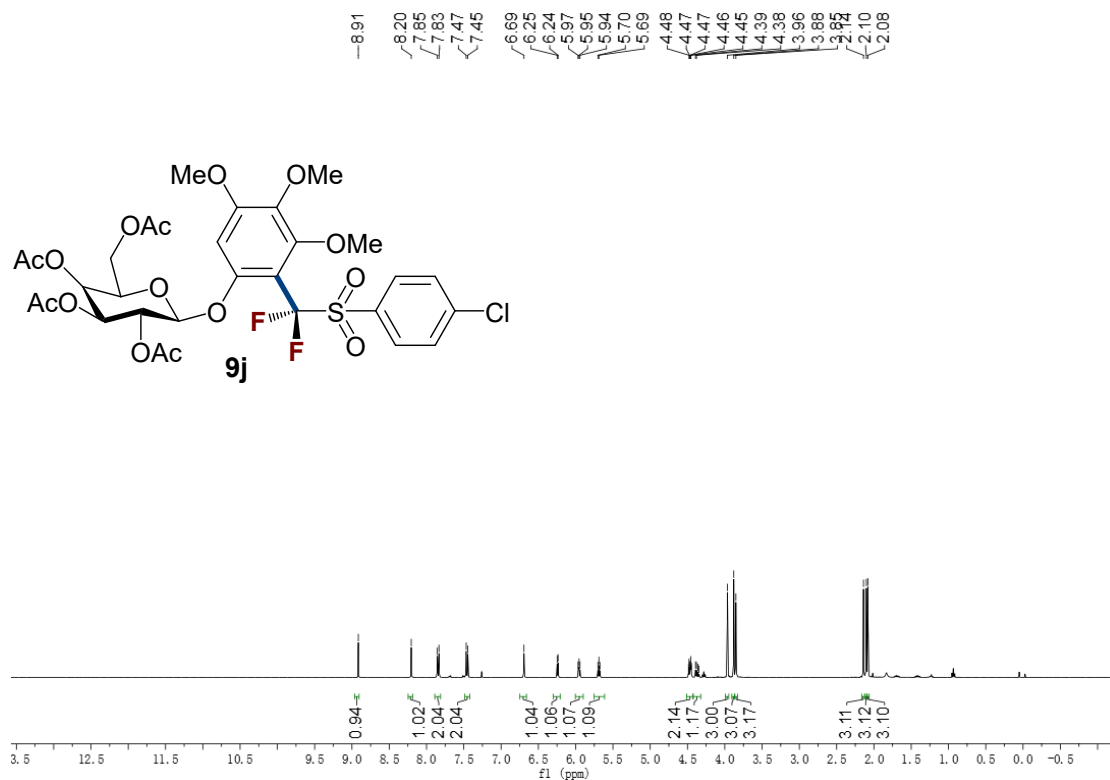
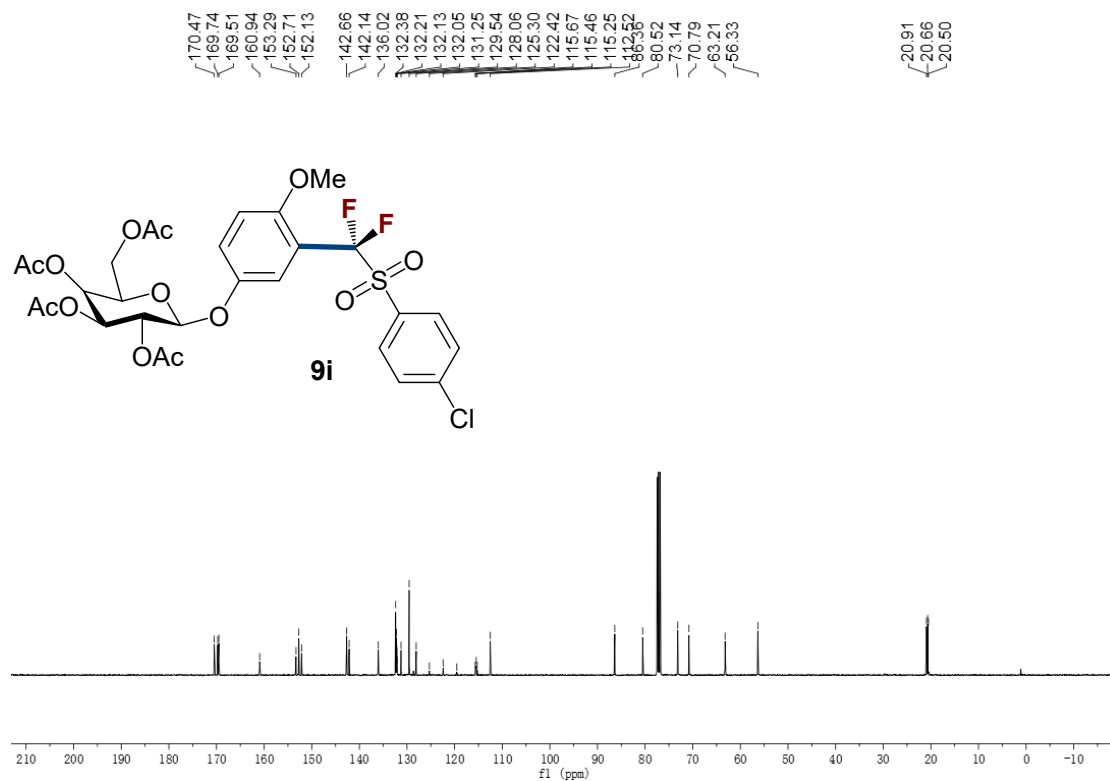




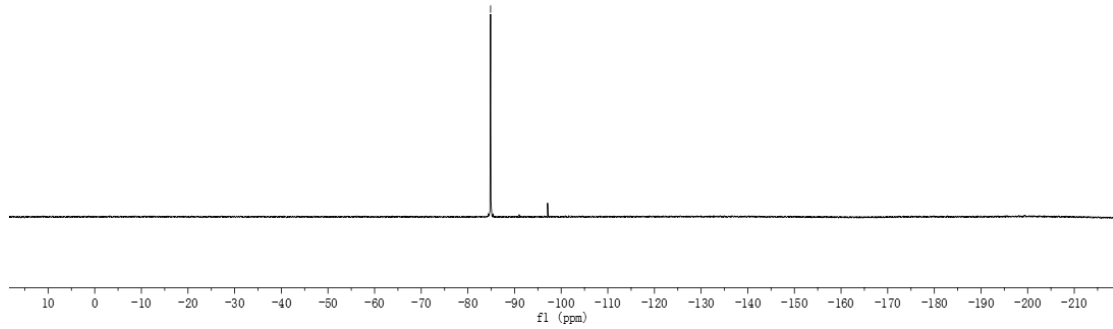
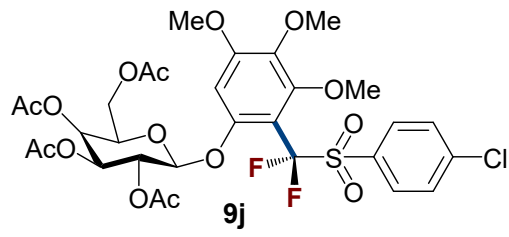


--97.29





---84.87



170.37, 166.68, 169.54, 156.15, 151.90, 150.89, 143.31, 143.20, 141.47, 132.09, 126.36, 123.45, 120.54, 113.68, 113.48, 113.28, 110.42, 86.90, 80.31, 73.29, 70.43, 62.91, 62.04, 60.91, 56.29, 20.81, 20.59, 20.53

