Supporting Information

Copper-catalyzed trifluoromethylation of vinyl azides with $BrCF_2CO_2K$: synthesis of α-trifluoromethyl ketones without external fluoride sources

Qinhong Wen, Tianhao Zhang, Xinyu Jia, Yu Wang, Yue Zhao, Taichen Liu, Kai Wei, Zhenghui Kang* and Jiuling Li*

School of Medical Sciences, Pingdingshan University, Pingdingshan 467000, P. R. China
School of Chinese Materia Medica, Nanjing University of Chinese Medicine, Nanjing 210023, China
Zhongshan Institute for Drug Discovery, Shanghai Institute of Materia Medica, Chinese Academy of Sciences. Zhongshan 528400, P. R. China
School of Chemistry and Pharmaceutical Sciences, Guangxi Normal University. Guilin 541004, P. R. China

E-mail: orgchem90@163.com
kangzhenghui@simm.ac.cn

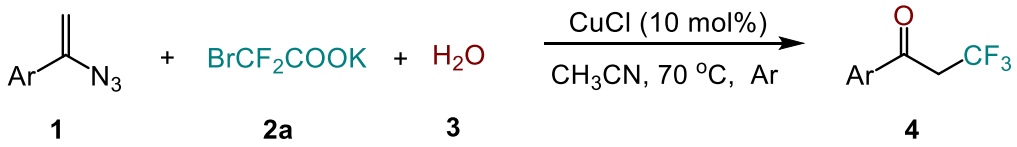
1. General information & materials

General: All ^{1}H NMR (400 MHz, 500 MHz, 600 MHz) and ^{13}C NMR (100 MHz, 125 MHz, 150 MHz) and ^{19}F NMR (376 MHz, 470 MHz, 564 MHz) spectra were recorded on 400 MHz or 500 MHz spectrometers in $CDCl_3$ and DMSO. Chemical shifts were reported in ppm with the solvent signal as reference, and coupling constants (*J*) were given in Hertz. The peak information was described as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. High-resolution mass spectrometry (HRMS) was recorded on a commercial apparatus (ESI Source).

Materials: Precoated silica gel plates GF-254 were used for analytical thin-layer chromatography. Column chromatography was performed on silica gel (300-400 mesh). Materials were prepared according to the known procedure and had physical and spectral properties identical to those earlier reported. Unless otherwise noted, all reagents were obtained commercially and used without further purification. Starting materials (alkenyl azide **1**) were prepared according to literature procedures[1].

2. Experimental procedures

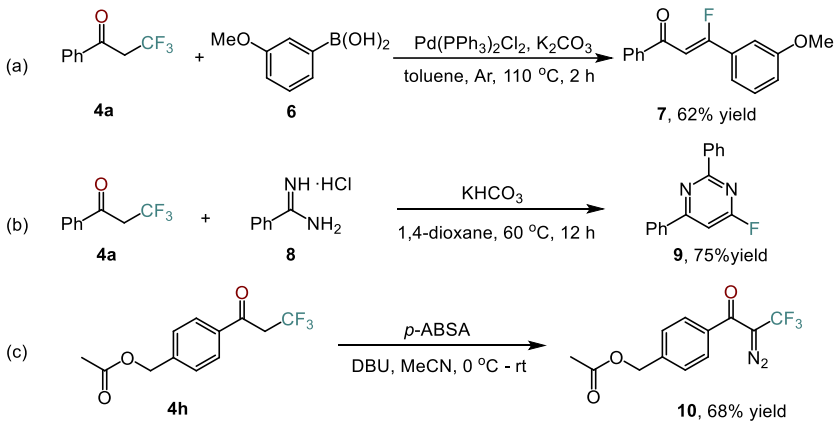
General procedure for α-trifluoromethyl ketone



1 2a 3 4

To an oven-dried 15 mL Schlenk tube equipped with a stir bar was added CuCl (2.0mg, 0.02mmol, 10.0 mol%), $BrCF_2COOK$ **2a** (85mg, 0.4 mmol, 2.0 equiv), 4.0 μL H_2O and vinyl azides **1** (0.2mmol, 1.0 equiv), and suspended in anhydrous CH_3CN (2.0 mL) under dry argon atmosphere. The resulting mixture was stirred at 70℃ for 6 hours. The progress of the reaction was monitored by TLC. After the reaction was complete, the reaction was cooled to room temperature and concentrated under reduced pressure. The residue was purified by flash column chromatography (eluent: EA:PE = 1/40~1/20) to give the pure product **4**.

3. Synthetic application and control experiments.

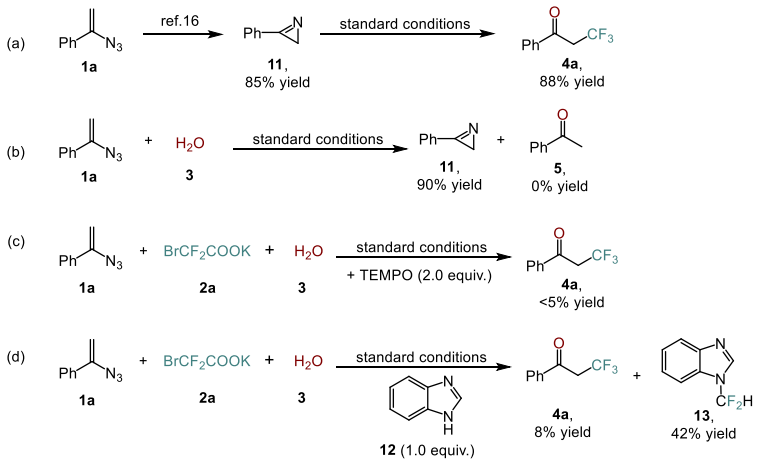


Synthetic application (a): To an oven-dried 15 mL Schlenk tube equipped with a stir bar was added $Pd(PPh_3)Cl_2$ (5 mol%), K_2CO_3 (0.6 mmol, 3.0 equiv), α-trifluoromethyl ketone **4a** (0.28 mmol, 1.4 equiv), and *m*-methoxyphenylboronic acid **6** (0.2 mmol, 1.0 equiv), and suspended in toluene (2 mL). The resulting mixture was stirred at 110℃ for 2 hours. The progress of the reaction was monitored by TLC. After the reaction was complete, the reaction was cooled to room temperature and concentrated under reduced pressure. The residue was purified by flash column

chromatography (eluent: EA:PE = 1/20~1/10) to give the pure product **7** (62% yield).

***Synthetic application (b)*:** To an oven-dried 15 mL Schlenk tube equipped with a stir bar was added $KHCO_3$ (0.6 mmol, 3.0 equiv), α-trifluoromethyl ketone **4a** (0.2 mmol, 1.0 equiv), and benzamidine hydrochloride **8** (0.22 mmol, 1.1 equiv), and suspended in 1,4-dioxane (2 mL). The resulting mixture was stirred at 60 ℃ for 12 hours. The progress of the reaction was monitored by TLC. After the reaction was complete, the reaction was cooled to room temperature and concentrated under reduced pressure. The residue was purified by flash column chromatography (eluent: EA:PE = 1/40~1/20) to give the pure product **9** (75% yield).

***Synthetic application (c)*:** To a 25 mL reaction flask equipped with a stir bar was added α-trifluoromethyl ketone **4h** (0.2 mmol, 1.0 equiv) and *p*-ABSA (4-acetamidobenzenesulfonyl azide, 0.24 mmol, 1.2 equiv), and suspended in acetonitrile (5 mL). The resulting mixture was stirred at 0 ℃, and added DBU (1,8-diazabicyclo [5.4.0] undec-7-ene, 0.22 mmol, 1.1 equiv) dropwise. After the reaction was complete, the reaction was warmed to room temperature and concentrated under reduced pressure. The residue was purified by flash column chromatography (eluent: EA:PE = 1/40~1/20) to give the pure product **10** (68% yield).



***Control experiment (a)*:** 2*H*-Azirine **11** was prepared according to our previous work[1]. The (1-azidovinyl)benzene **1a** (0.5 mmol) was stirred in toluene (3 mL) at 100 ℃, and the progress of the reaction was monitored by TLC. After the reaction was complete, the mixture was purified by flash column chromatography (petroleum ether/ethyl acetate 30:1) to give the pure product **11** in 85% yield. Then, to an oven-dried 15 mL Schlenk tube equipped with a stir bar was added CuCl (2.0 mg, 0.02 mmol, 10.0 mol%), $BrCF_2COOK$ **2a** (85 mg, 0.4 mmol, 2.0 equiv), 4.0 μL H_2O and 2*H*-azirine

11 (0.2 mmol, 1.0 equiv), and suspended in anhydrous CH_3CN (2.0 mL) under dry argon atmosphere. The resulting mixture was stirred at 70℃ for 6 hours. The progress of the reaction was monitored by TLC. After the reaction was complete, the reaction was cooled to room temperature and concentrated under reduced pressure. The residue was purified by flash column chromatography (eluent: EA:PE = 1/40~1/20) to give the pure product **4a** (88% yield).

***Control experiment (b)*:** To an oven-dried 15 mL Schlenk tube equipped with a stir bar was added CuCl (2.0 mg, 0.02 mmol, 10.0 mol%), 4.0 μL H_2O and vinyl azide **1a** (0.2 mmol, 1.0 equiv), and suspended in anhydrous CH_3CN (2.0 mL) under dry argon atmosphere. The resulting mixture was stirred at 70℃ for 6 hours. The progress of the reaction was monitored by TLC. After the reaction was complete, the reaction was cooled to room temperature and concentrated under reduced pressure. The residue was purified by flash column chromatography (eluent: EA:PE = 1/40~1/20) to give the pure 2*H*-azirine **11** (90% yield).

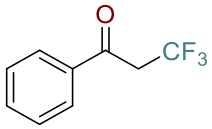
***Control experiment (c)*:** To an oven-dried 15 mL Schlenk tube equipped with a stir bar was added CuCl (2.0 mg, 0.02 mmol, 10.0 mol%), $BrCF_2COOK$ **2a** (85 mg, 0.4 mmol, 2.0 equiv), 4.0 μL H_2O, vinyl azide **1a** (29 mg, 0.2 mmol, 1.0 equiv), and TEMPO (0.4 mml, 2.0 equiv) and suspended in anhydrous CH_3CN (2.0 mL) under dry argon atmosphere. The resulting mixture was stirred at 70℃ for 6 hours. The progress of the reaction was monitored by TLC, and only trace amounts of product **4a** were detected.

***Control experiment (d)*:** To an oven-dried 15 mL Schlenk tube equipped with a stir bar was added CuCl (2.0 mg, 0.02 mmol, 10.0 mol%), $BrCF_2COOK$ **2a** (85 mg, 0.4 mmol, 2.0 equiv), 4.0 μL H_2O, vinyl azide **1a** (29 mg, 0.2 mmol, 1.0 equiv), and benzimidazole **12** (0.2 mml, 1.0 equiv) and suspended in anhydrous CH_3CN (2.0 mL) under dry argon atmosphere. The resulting mixture was stirred at 70℃ for 6 hours. The progress of the reaction was monitored by TLC. After the reaction was complete, the reaction was cooled to room temperature and concentrated under reduced pressure. The residue was purified by flash column chromatography (eluent: EA:PE = 1/40~1/10) to give the pure product **4a** (8% yield) and difluoromethylated benzimidazole product **13** (42% yield).

4 Reference

[1] J. Li, X. Jia, J. Qiu, M. Wang, J. Chen, M. Jing, Y. Xu, X. Zheng, H. Dai. Brønsted Acid-Catalyzed Synthesis of 1,2,5-Trisubstituted Imidazoles via a Multicomponent Reaction of Vinyl Azides with Aromatic Aldehydes and Aromatic Amines. *J. Org. Chem.* **2022**, *87*, 13945−13954.

5. Analytical data of products



3,3,3-trifluoro-1-phenylpropan-1-one

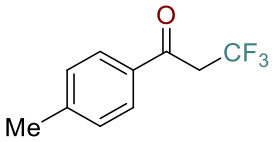
4a: 31 mg, white solid, 83% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.89 (m, 2H), 7.68 – 7.61 (m, 1H), 7.51 (t, J = 7.8 Hz, 2H), 3.80 (q, J = 10.0 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 189.7 (q, J_{CF} = 2.5 Hz), 135.8 (q, J_{CF} = 1.8 Hz), 134.2, 129.0, 128.4, 124.0 (q, J_{CF} = 276.9 Hz), 42.1 (q, J_{CF} = 28.2 Hz).

^{19}F NMR (470 MHz, $CDCl_3$) δ -62.04.

HRMS-ESI: calcd. For $C_9H_7F_3O$ $[M+H]^+$: 189.0522; found: 189.0521.



3,3,3-trifluoro-1-(p-tolyl)propan-1-one

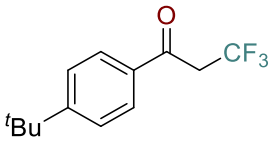
4b: 32 mg, white solid, 79% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 7.9 Hz, 2H), 3.77 (q, J = 10.0 Hz, 2H), 2.43 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 189.4 (q, J_{CF} = 3.0 Hz), 145.4, 133.4 (q, J_{CF} = 1.9 Hz), 129.6, 128.5, 124.1 (q, J_{CF} = 277.8 Hz), 42.0 (q, J_{CF} = 28.0 Hz), 21.7.

^{19}F NMR (471 MHz, $CDCl_3$) δ -61.99.

HRMS-ESI: calcd. For $C_{10}H_9F_3O$ $[M+H]^+$: 203.0678; found: 203.0679.



1-(4-(tert-butyl)phenyl)-3,3,3-trifluoropropan-1-one

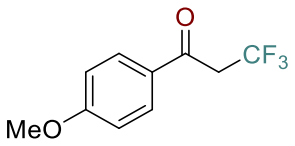
4c: 40 mg, white solid, 82% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.4 Hz, 2H), 7.51 (d, J = 8.2 Hz, 2H), 3.77 (q, J = 10.0 Hz, 2H), 1.34 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 189.3 (q, J_{CF} = 2.5 Hz), 158.2, 133.3 (q, J_{CF} = 2.1 Hz), 128.4, 125.9, 124.1 (q, J_{CF} = 275.8 Hz), 42.0 (q, J_{CF} = 27.3 Hz), 35.3, 31.0.

^{19}F NMR (470 MHz, $CDCl_3$) δ -61.96.

HRMS-ESI: calcd. For $C_{13}H_{15}F_3O$ $[M+H]^+$: 245.1148; found: 245.1150.



3,3,3-trifluoro-1-(4-methoxyphenyl)propan-1-one

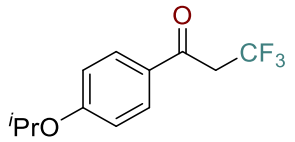
4d: 34 mg, white solid, 78% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 9.0 Hz, 2H), 6.97 (d, J = 9.0 Hz, 2H), 3.89 (s, 3H), 3.74 (q, J = 10.1 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 188.2 (q, J_{CF} = 3.1 Hz), 164.4, 130.8, 129.0 (q, J_{CF} = 2.2 Hz), 124.1 (q, J_{CF} = 2.7 Hz), 55.6, 41.8 (q, J_{CF} = 28.3 Hz).

^{19}F NMR (470 MHz, $CDCl_3$) δ -61.94.

HRMS-ESI: calcd. For $C_{10}H_9F_3O_2$ $[M+H]^+$: 219.0627; found: 219.0627.



3,3,3-trifluoro-1-(4-isopropoxyphenyl)propan-1-one

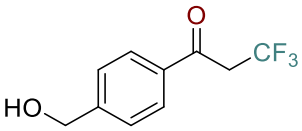
4e: 39 mg, white solid, 79% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.9 Hz, 2H), 6.92 (d, J = 8.9 Hz, 2H), 4.69 – 4.63 (m, 1H), 3.72 (q, J = 10.1 Hz, 2H), 1.37 (s, 3H), 1.35 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 188.1 (q, J_{CF} = 3.0 Hz), 162.9, 130.9, 128.4 (q, J_{CF} = 1.7 Hz), 124.2 (q, J_{CF} = 277.8 Hz), 115.4, 70.4, 41.7 (q, J_{CF} = 28.2 Hz), 21.9, 21.8.

^{19}F NMR (470 MHz, $CDCl_3$) δ -61.93.

HRMS-ESI: calcd. For $C_{12}H_{13}F_3O_2$ $[M+H]^+$: 247.0940; found: 247.0943.



3,3,3-trifluoro-1-(4-(hydroxymethyl)phenyl)propan-1-one

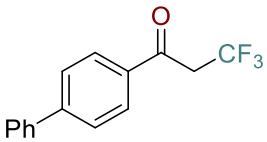
4f: 33 mg, white solid, 75% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.95 (d, J = 8.3 Hz, 2H), 7.51 (d, J = 8.2 Hz, 2H), 5.28 (s, 2H), 3.80 (q, J = 9.9 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 189.2 (q, J_{CF} = 2.5 Hz), 141.6, 135.6 (q, J_{CF} = 1.8 Hz), 128.7, 128.2, 123.9 (q, J_{CF} = 276.3 Hz), 64.6, 42.2 (q, J_{CF} = 28.2 Hz).

^{19}F NMR (470 MHz, $CDCl_3$) δ -61.93.

HRMS-ESI: calcd. For $C_{10}H_9F_3O_2$ $[M+H]^+$: 219.0627; found: 219.0625.



1-([1,1'-biphenyl]-4-yl)-3,3,3-trifluoropropan-1-one

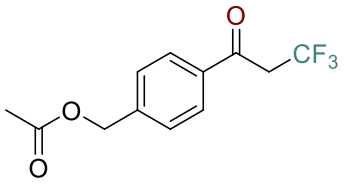
4g: 42 mg, white solid, 79% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.97 (m, 2H), 7.76 – 7.71 (m, 2H), 7.67 – 7.62 (m, 2H), 7.53 – 7.47 (m, 2H), 7.46 – 7.40 (m, 1H), 3.84 (q, J = 10.0 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 189.3 (q, J_{CF} = 2.7 Hz), 146.9, 139.4, 134.5 (q, J_{CF} = 1.6 Hz), 129.1, 129.0, 128.6, 127.6, 127.3, 124.1 (q, J_{CF} = 275.2 Hz), 42.2 (q, J_{CF} = 28.1 Hz).

^{19}F NMR (470 MHz, $CDCl_3$) δ -61.93.

HRMS-ESI: calcd. For $C_{15}H_{11}F_3O$ $[M+H]^+$: 265.0835; found: 265.0837.



4-(3,3,3-trifluoropropanoyl)benzyl acetate

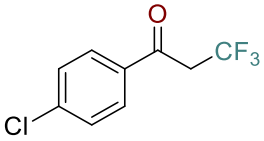
4h: 46 mg, white solid, 89% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.1 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H), 5.17 (s, 2H), 3.79 (q, J = 10.0 Hz, 2H), 2.14 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 189.2 (q, J_{CF} = 3.0 Hz), 170.7, 142.5, 135.4 (q, J_{CF} = 2.1 Hz), 128.7, 128.1, 123.9 (q, J_{CF} = 275.0Hz), 65.2, 42.2 (q, J_{CF} = 28.0 Hz), 20.9.

^{19}F NMR (470 MHz, $CDCl_3$) δ -61.98.

HRMS-ESI: calcd. For $C_{12}H_{11}F_3O_3$ $[M+H]^+$: 261.0733; found: 261.0731.



1-(4-chlorophenyl)-3,3,3-trifluoropropan-1-one

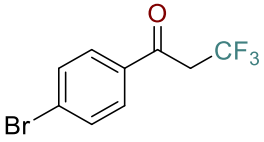
4i: 36 mg, white solid, 80% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.83 (m, 2H), 7.53 – 7.45 (m, 2H), 3.77 (q, J = 9.9 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 188.6 (q, J_{CF} = 3.0 Hz), 140.9, 134.1 (q, J_{CF} = 2.0 Hz), 129.8, 129.3, 123.9 (q, J_{CF} = 275.0 Hz), 42.2 (q, J_{CF} = 28.0 Hz).

19F NMR (470 MHz, $CDCl_3$) δ -61.98.

HRMS-ESI: calcd. For $C_9H_6ClF_3O$ $[M+H]^+$: 223.0132; found: 223.0130.



1-(4-bromophenyl)-3,3,3-trifluoropropan-1-one

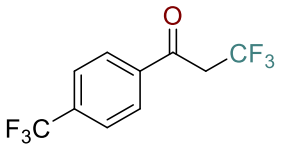
4j: 44 mg, white solid, 82% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.5 Hz, 2H), 7.65 (d, J = 8.5 Hz, 2H), 3.77 (q, J = 9.9 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 188.8 (q, J_{CF} = 3.0 Hz), 134.5 (q, J_{CF} = 1.8 Hz), 132.3, 129.8, 129.7, 123.8 (q, J_{CF} = 277.7 Hz), 42.1 (q, J_{CF} = 28.3 Hz).

^{19}F NMR (470 MHz, $CDCl_3$) δ -61.98.

HRMS-ESI: calcd. For $C_9H_6BrF_3O$ $[M+H]^+$: 266.9627; found: 266.9628.



3,3,3-trifluoro-1-(4-(trifluoromethyl)phenyl)propan-1-one

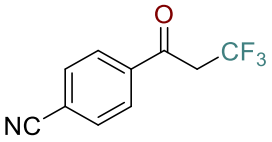
4k: 38 mg, white solid, 75% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.1 Hz, 2H), 7.79 (d, J = 8.0 Hz, 2H), 3.83 (q, J = 9.8 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 188.9 (q, J_{CF} = 2.7 Hz), 138.3, 135.5 (q, J_{CF} = 32.3 Hz), 128.8, 126.1 (q, J_{CF} = 4.0 Hz), 123.7 (q, J_{CF} = 278.7 Hz), 123.3 (q, J_{CF} = 273.7 Hz), 42.5 (q, J_{CF} = 29.3 Hz).

^{19}F NMR (470 MHz, $CDCl_3$) δ -61.97, -63.31.

HRMS-ESI: calcd. For $C_{10}H_6F_6O$ $[M+H]^+$: 257.0396; found: 257.0395.



4-(3,3,3-trifluoropropanoyl)benzonitrile

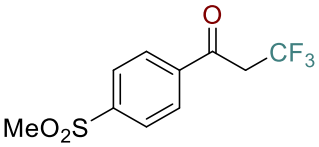
4l: 35 mg, white solid, 81% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.8 Hz, 2H), 7.83 (d, J = 7.5 Hz, 2H), 3.83 (q, J = 9.7 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 188.6 (q, J_{CF} = 3.3 Hz), 138.5 (q, J_{CF} = 1.9 Hz), 132.8, 129.4, 128.8, 123.6 (q, J_{CF} = 275.3 Hz), 117.5, 42.5 (q, J_{CF} = 29.1 Hz).

^{19}F NMR (470 MHz, $CDCl_3$) δ -61.94.

HRMS-ESI: calcd. For $C_{10}H_6F_3NO$ $[M+H]^+$: 214.0474; found: 214.0470.



3,3,3-trifluoro-1-(4-(methylsulfonyl)phenyl)propan-1-one

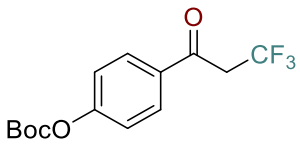
4m: 44 mg, white solid, 83% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 8.1 Hz, 2H), 8.08 (d, J = 8.7 Hz, 2H), 3.85 (q, J = 9.8 Hz, 2H), 3.09 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 188.7 (q, J_{CF} = 3.1 Hz), 145.2, 139.5, 139.5 (q, J_{CF} = 1.7 Hz), 129.3, 128.2, 123.6 (q, J_{CF} = 277.8 Hz), 44.3, 42.6 (q, J_{CF} = 28.3 Hz).

^{19}F NMR (470 MHz, $CDCl_3$) δ -61.92.

HRMS-ESI: calcd. For $C_{10}H_9F_3O_3S$ $[M+H]^+$: 267.0297; found: 267.0298.



tert-butyl (4-(3,3,3-trifluoropropanoyl)phenyl) carbonate

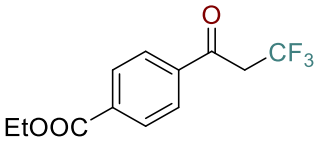
4n: 49 mg, white solid, 81% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.6 Hz, 2H), 7.32 (d, *J* = 8.8 Hz, 2H), 3.77 (q, *J* = 9.9 Hz, 2H), 1.57 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 188.5 (q, J_{CF} = 2.7 Hz), 155.5, 150.8, 133.1 (q, J_{CF} = 2.1 Hz), 130.1, 123.9 (q, J_{CF} = 278.8 Hz), 121.7, 84.5, 42.1 (q, J_{CF} = 28.0 Hz), 27.7.

^{19}F NMR (470 MHz, $CDCl_3$) δ -61.99.

HRMS-ESI: calcd. For $C_{14}H_{15}F_3O_4$ $[M+H]^+$: 305.0995; found: 305.0997.



ethyl 4-(3,3,3-trifluoropropanoyl)benzoate

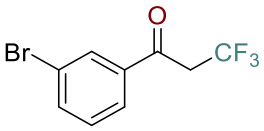
4o: 41 mg, white solid, 79% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.4 Hz, 2H), 7.99 (d, *J* = 8.1 Hz, 2H), 4.42 (q, *J* = 7.1 Hz, 2H), 3.84 (q, *J* = 9.8 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 189.3 (q, J_{CF} = 3.2 Hz), 165.4, 138.7 (q, J_{CF} = 1.7 Hz), 135.3, 130.1, 128.3, 123.8 (q, J_{CF} = 278.7 Hz), 61.7, 42.5 (q, J_{CF} = 29.3 Hz), 14.3.

^{19}F NMR (470 MHz, $CDCl_3$) δ -62.01.

HRMS-ESI: calcd. For $C_{12}H_{11}F_3O_3$ $[M+H]^+$: 261.0733; found: 261.0730.



1-(3-bromophenyl)-3,3,3-trifluoropropan-1-one

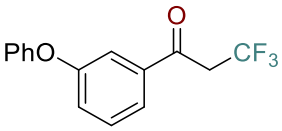
4p: 43 mg, white solid, 80% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.85 (dt, *J* = 7.9, 1.4 Hz, 1H), 7.77 (ddd, *J* = 8.0, 2.0, 1.0 Hz, 1H), 7.40 (t, *J* = 7.9 Hz, 1H), 3.78 (q, *J* = 9.8 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 188.5 (q, J_{CF} = 3.0 Hz), 137.4 (q, J_{CF} = 2.0 Hz), 137.1, 131.4, 130.5, 126.9, 123.3, 123.8 (q, J_{CF} = 278.8 Hz), 42.2 (q, J_{CF} = 28.3 Hz).

^{19}F NMR (470 MHz, $CDCl_3$) δ -62.01.

HRMS-ESI: calcd. For $C_9H_6BrF_3O$ $[M+H]^+$: 266.9627; found: 266.9626.



3,3,3-trifluoro-1-(3-phenoxyphenyl)propan-1-one

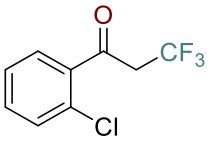
4q: 42 mg, white solid, 75% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 7.7 Hz, 1H), 7.55 (t, J = 2.1 Hz, 1H), 7.47 (t, J = 8.0 Hz, 1H), 7.38 (t, J = 8.0 Hz, 2H), 7.29 – 7.25 (m, 1H), 7.18 (t, J = 7.4 Hz, 1H), 7.03 (d, J = 7.8 Hz, 2H), 3.76 (q, J = 9.9 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 189.2 (q, J_{CF} = 3.1 Hz), 158.2, 156.2, 137.4 (q, J_{CF} = 1.3 Hz), 130.4, 130.1, 123.9 (q, J_{CF} = 276.1 Hz), 124.3, 124.2, 122.9, 119.4, 117.5, 42.3 (q, J_{CF} = 28.3 Hz).

^{19}F NMR (470 MHz, $CDCl_3$) δ -61.94.

HRMS-ESI: calcd. For $C_{15}H_{11}F_3O_2$ $[M+H]^+$: 281.0784; found: 281.0786.



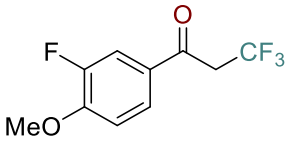
1-(2-chlorophenyl)-3,3,3-trifluoropropan-1-one

4r: 3.1 mg, light yellow oil, 7% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, J = 7.5, 1.6 Hz, 1H), 7.45 (d, J = 1.9 Hz, 1H), 7.42 – 7.39 (m, 1H), 7.37 (dd, J = 4.9, 3.2 Hz, 1H), 3.86 (q, J = 10.0 Hz, 2H).

^{19}F NMR (470 MHz, $CDCl_3$) δ -62.19.

HRMS-ESI: calcd. For $C_9H_6ClF_3O$ $[M+H]^+$: 223.0132; found: 223.0130.



3,3,3-trifluoro-1-(3-fluoro-4-methoxyphenyl)propan-1-one

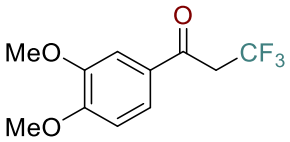
4s: 36 mg, white solid, 76% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.59 (m, 2H), 7.02 (t, J = 8.3 Hz, 1H), 3.96 (s, 3H), 3.73 (q, J = 10.0 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 187.5 (dq, J_{CF} = 2.0, 2.2 Hz), 152.1 (d, J_{CF} = 250.5 Hz), 152.9 (d, J_{CF} = 11.1 Hz), 129.0 (d, J_{CF} = 4.1, 2.1 Hz), 126.0 (d, J_{CF} = 3.4 Hz), 123.9 (q, J_{CF} = 277.7 Hz), 115.9 (d, J_{CF} = 19.2 Hz), 112.5, 56.3, 41.8 (q, J_{CF} = 28.3 Hz).

^{19}F NMR (470 MHz, $CDCl_3$) δ -61.96, -133.18.

HRMS-ESI: calcd. For $C_{10}H_8F_4O$ $[M+H]^+$: 237.0533; found: 237.0534.



1-(3,4-dimethoxyphenyl)-3,3,3-trifluoropropan-1-one

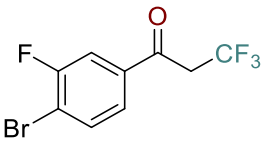
4t: 37 mg, white solid, 74% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.45 (m, 2H), 6.91 (d, J = 8.2 Hz, 1H), 3.96 (s, 3H), 3.93 (s, 3H), 3.75 (q, J = 10.1 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.2 (q, J_{CF} = 2.2 Hz), 154.3, 149.4, 129.1 (q, J_{CF} = 1.3 Hz), 124.1 (q, J_{CF} = 275.1 Hz), 123.5, 110.1, 110.0, 56.2, 56.0, 41.7 (q, J_{CF} = 28.2 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ -61.93.

HRMS-ESI: calcd. For $C_{11}H_{11}F_3O_3$ $[M+H]^+$: 249.0733; found: 249.0735.



1-(4-bromo-3-fluorophenyl)-3,3,3-trifluoropropan-1-one

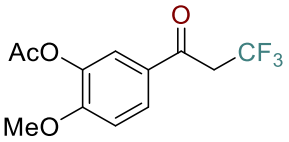
4u: 45 mg, white solid, 79% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.71 (m, 1H), 7.68 (dd, J = 8.9, 2.0 Hz, 1H), 7.58 (dd, J = 8.3, 2.0 Hz, 1H), 3.76 (q, J = 9.8 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 187.8 (dq, J_{CF} = 2.0, 2.0 Hz), 159.4 (q, J_{CF} = 251.5 Hz), 136.6 (dq, J_{CF} = 6.0, 2.0 Hz), 134.4, 124.9 (d, J_{CF} = 4.0 Hz), 123.6 (q, J_{CF} = 275.0 Hz), 116.6 (d, J_{CF} = 22.0 Hz), 116.0 (d, J_{CF} = 23.0 Hz), 42.3 (q, J_{CF} = 29.0 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ -61.98, -104.47.

HRMS-ESI: calcd. For $C_9H_5BrF_4O$ $[M+H]^+$: 284.9533; found: 284.9530.



2-methoxy-5-(3,3,3-trifluoropropanoyl)phenyl acetate

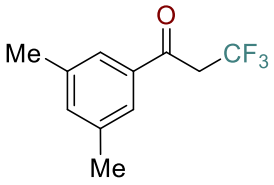
4v: 39 mg, white solid, 70% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 2.0 Hz, 1H), 7.47 (dd, J = 8.2, 2.0 Hz, 1H), 7.16 (d, J = 8.2 Hz, 1H), 3.89 (s, 3H), 3.78 (q, J = 9.9 Hz, 2H), 2.34 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.6 (q, J_{CF} = 2.3 Hz), 168.4, 151.8, 144.8, 134.5 (q, J_{CF} = 1.2 Hz), 123.9 (q, J_{CF} = 275.0 Hz), 123.1, 121.8, 111.6, 56.1, 42.1 (q, J_{CF} = 29.1 Hz), 20.7.

^{19}F NMR (471 MHz, $CDCl_3$) δ -62.01.

HRMS-ESI: calcd. For $C_{12}H_{11}F_3O_4$ $[M+H]^+$: 277.0682; found: 277.0680.



1-(3,5-dimethylphenyl)-3,3,3-trifluoropropan-1-one

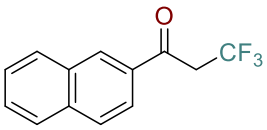
4w: 32 mg, white solid, 73% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (s, 2H), 7.26 (s, 1H), 3.77 (q, J = 10.0 Hz, 2H), 2.38 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.1 (q, J_{CF} = 2.0 Hz), 138.7, 135.9, 126.7, 126.1, 124.1 (q, J_{CF} = 277.8 Hz), 42.1 (q, J_{CF} = 28.0 Hz), 21.2.

^{19}F NMR (471 MHz, $CDCl_3$) δ -62.05.

HRMS-ESI: calcd. For $C_{11}H_{11}F_3O$ $[M+H]^+$: 217.0835; found: 217.0833.



3,3,3-trifluoro-1-(naphthalen-2-yl)propan-1-one

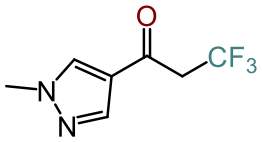
4x: 39 mg, white solid, 82% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, J = 1.8 Hz, 1H), 8.02 – 7.95 (m, 2H), 7.90 (dd, J = 10.3, 8.2 Hz, 2H), 7.65 (ddd, J = 8.2, 6.9, 1.4 Hz, 1H), 7.59 (ddd, J = 8.1, 6.8, 1.4 Hz, 1H), 3.93 (q, J = 10.0 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 189.7 (q, J_{CF} = 3.0 Hz), 136.0, 133.2 (q, J_{CF} = 2.0 Hz), 132.3, 130.6, 129.7, 129.3, 129.0, 127.9, 127.2, 123.5, 124.1 (q, J_{CF} = 277.8 Hz), 42.2 (q, J_{CF} = 28.3 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ -61.89.

HRMS-ESI: calcd. For $C_{13}H_9F_3O$ $[M+H]^+$: 239.0678; found: 239.0680.



3,3,3-trifluoro-1-(1-methyl-1H-pyrazol-4-yl)propan-1-one

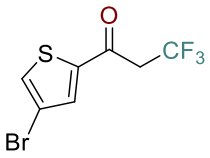
4y: 28 mg, white solid, 73% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.90 (s, 1H), 3.96 (s, 3H), 3.52 (q, J = 10.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 183.1 (q, J_{CF} = 3.3 Hz), 140.6, 133.2, 123.8 (q, J_{CF} = 277.8 Hz), 123.5 (q, J_{CF} = 2.1 Hz), 44.2 (q, J_{CF} = 28.1 Hz), 39.5.

^{19}F NMR (471 MHz, $CDCl_3$) δ -61.93.

HRMS-ESI: calcd. For $C_7H_7F_3N_2O$ $[M+H]^+$:193.0583; found: 193.0585.



1-(4-bromothiophen-2-yl)-3,3,3-trifluoropropan-1-one

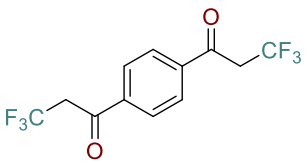
4z: 43 mg, white solid, 77% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.62 (s, 1H), 3.69 (q, J = 9.9 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 181.3 (q, J_{CF} = 3.0 Hz), 143.3 (q, J_{CF} = 2.3 Hz), 135.4, 132.9, 123.4 (q, J_{CF} = 276.1 Hz), 111.3, 42.9 (q, J_{CF} = 29.3 Hz).

^{19}F NMR (470 MHz, $CDCl_3$) δ -61.88.

HRMS-ESI: calcd. For $C_7H_4BrF_3OS$ $[M+H]^+$: 272.9191; found: 272.9193.



1,1'-(1,4-phenylene)bis(3,3,3-trifluoropropan-1-one)

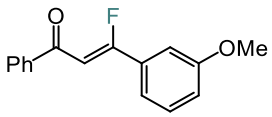
4A: 43 mg, white solid, 72% yield.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.14 (s, 4H), 4.51 (q, J = 10.7 Hz, 4H).

^{13}C NMR (100 MHz, DMSO) δ 191.5 (q, J_{CF} = 3.3 Hz), 139.6 (q, J_{CF} = 1.5 Hz), 129.1, 125.4 (q, J_{CF} = 276.7 Hz), 42.5 (q, J_{CF} = 27.3 Hz).

^{19}F NMR (470 MHz, $CDCl_3$) δ -56.32.

HRMS-ESI: calcd. For $C_{12}H_8F_6O_2$ $[M+H]^+$: 299.0501; found: 299.0504.



(Z)-3-fluoro-3-(3-methoxyphenyl)-1-phenylprop-2-en-1-one

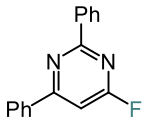
7: 32 mg, white solid, 62% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, J = 7.2, 1.8 Hz, 2H), 7.61 – 7.55 (m, 1H), 7.49 (dd, J = 8.3, 6.9 Hz, 2H), 7.42 – 7.31 (m, 2H), 7.25 (t, J = 2.0 Hz, 1H), 7.05 (ddd, J = 7.9, 2.6, 1.4 Hz, 1H), 6.78 (d, J = 34.1 Hz, 1H), 3.86 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 188.92, 165.1 (d, J_{CF} = 248.0 Hz), 159.9 (d, J_{CF} = 2.0 Hz), 138.60, 132.94, 132.2 (d, J_{CF} = 26.0 Hz), 130.04, 128.60, 128.37, 118.3 (d, J_{CF} = 8.0 Hz), 117.37, 111.2 (d, J_{CF} = 8.0 Hz), 102.1 (d, J_{CF} = 7.0 Hz), 55.50.

^{13}F NMR (470 MHz, $CDCl_3$) δ -96.08.

HRMS-ESI: calcd. For $C_{16}H_{14}FO_2$ $[M+H]^+$: 257.0972; found: 257.0968.



4-fluoro-2,6-diphenylpyrimidine

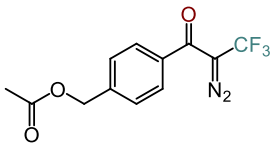
9: 38 mg, white solid, 75% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 – 8.53 (m, 2H), 8.21 (dd, J = 6.7, 3.0 Hz, 2H), 7.56 (dd, J = 5.0, 1.9 Hz, 3H), 7.53 (dd, J = 5.2, 2.0 Hz, 3H), 7.22 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9 (d, J_{CF} = 248.0 Hz), 168.7 (d, J_{CF} = 8.0 Hz), 165.4 (d, J_{CF} = 13.0 Hz), 136.43, 136.1 (d, J_{CF} = 5.0 Hz), 131.5 (d, J_{CF} = 2.0 Hz), 129.05, 128.65, 128.62, 127.41, 126.32, 99.6 (d, J_{CF} = 31.0 Hz).

^{13}F NMR (470 MHz, $CDCl_3$) δ -61.19.

HRMS-ESI: calcd. For $C_{16}H_{12}FN_2$ $[M+H]^+$: 251.0979; found: 251.0982.



4-(2-diazo-3,3,3-trifluoropropanoyl)benzyl acetate

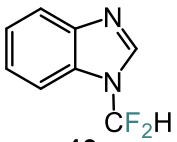
10: 39 mg, light yellow oil, 68% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.1 Hz, 2H), 7.45 (d, J = 8.1 Hz, 2H), 5.16 (s, 2H), 2.13 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 183.9, 170.7, 141.1, 135.8, 128.1, 127.6, 123.0 (q, J_{CF} = 272.7 Hz), 65.3, 20.9.

^{13}F NMR (470 MHz, $CDCl_3$) δ -56.01.

HRMS-ESI: calcd. For $C_{12}H_9F_3N_2O_3$ $[M+H]^+$: 287.0638; found: 287.0635.



13

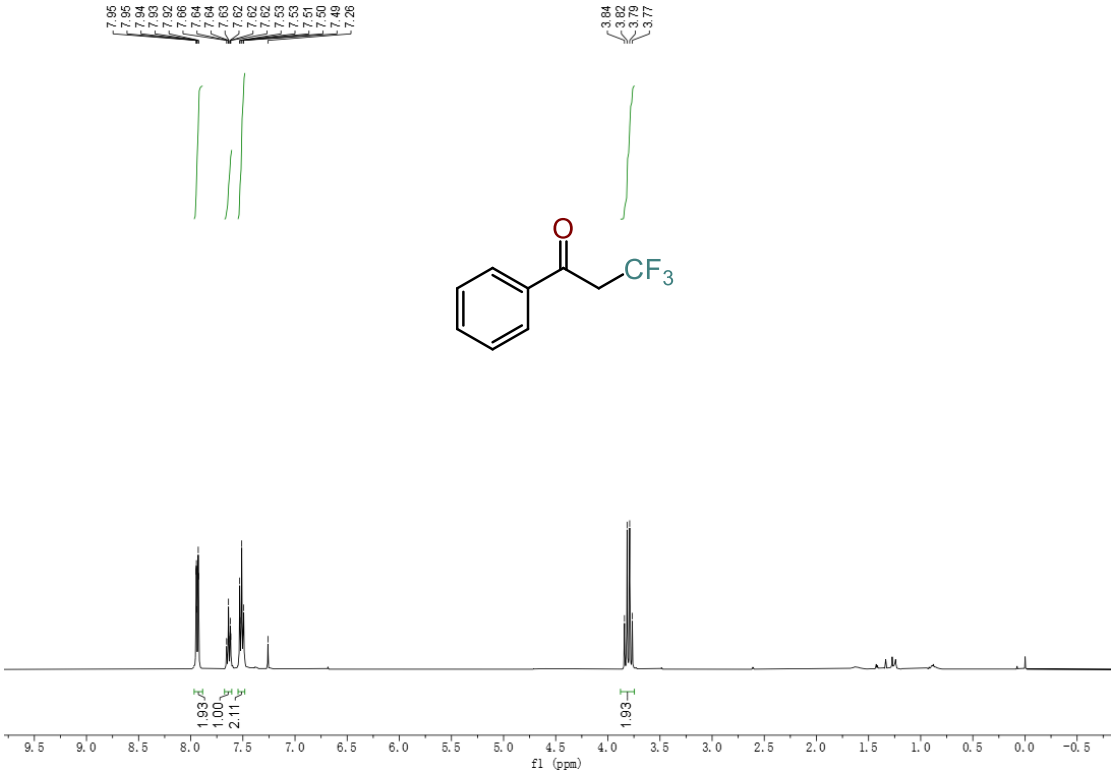
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.85 (dd, J = 6.0, 3.5 Hz, 1H), 7.68 – 7.54 (m, 1H), 7.39 (dt, J = 7.6, 5.0 Hz, 2H), 7.33 (t, J = 60.0 Hz, 1H).

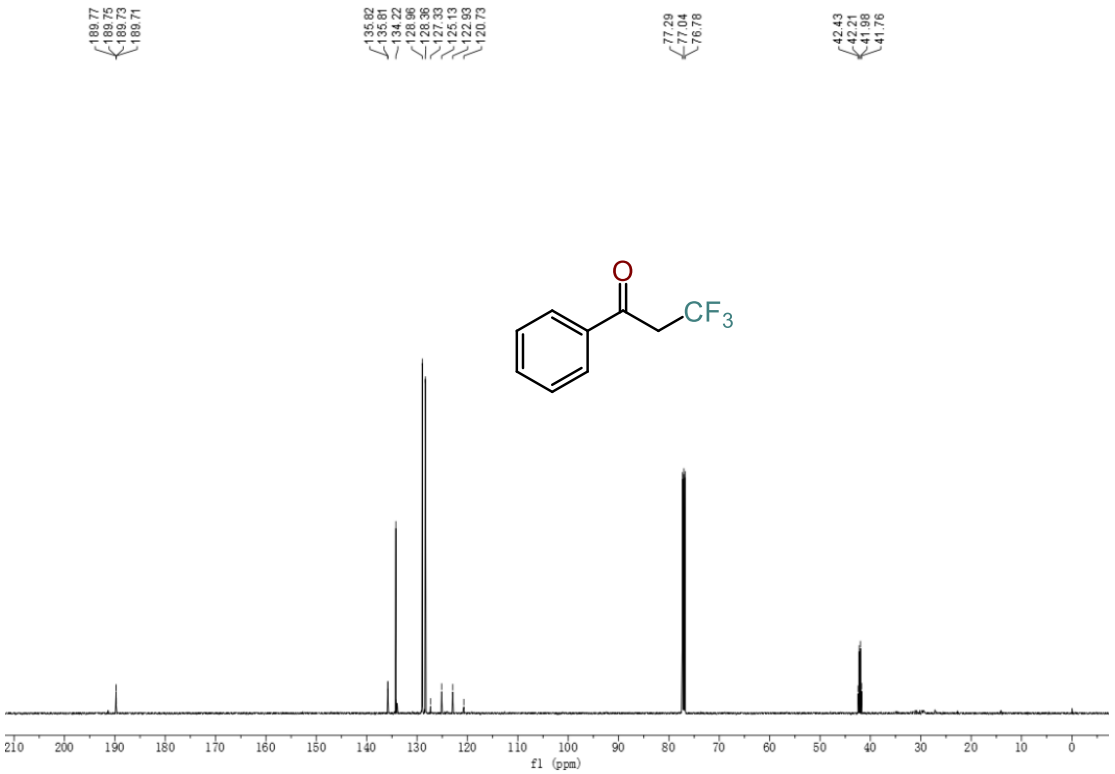
^{13}C NMR (150 MHz, $CDCl_3$) δ 143.9, 139.1, 130.6, 124.8, 124.2, 121.0, 111.1, 109.0 (t, J_{CF} = 249.9 Hz).

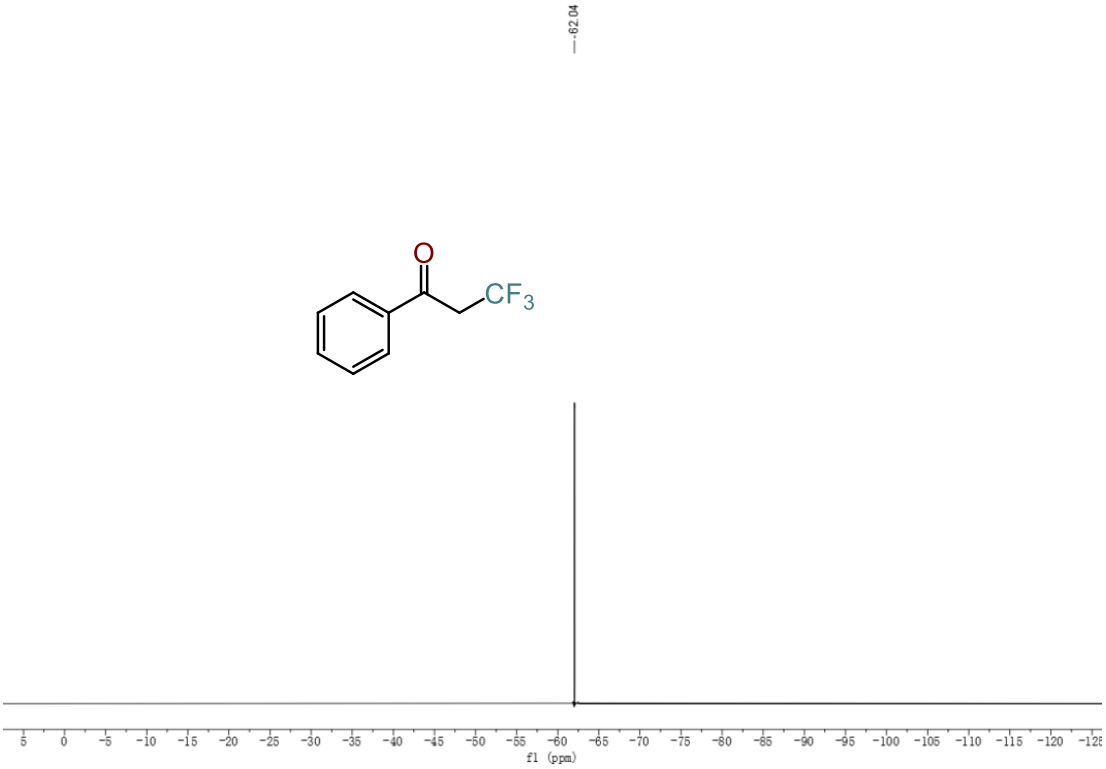
^{19}F NMR (564 MHz, $CDCl_3$) δ -93.67, -93.77.

6. NMR spectra of products

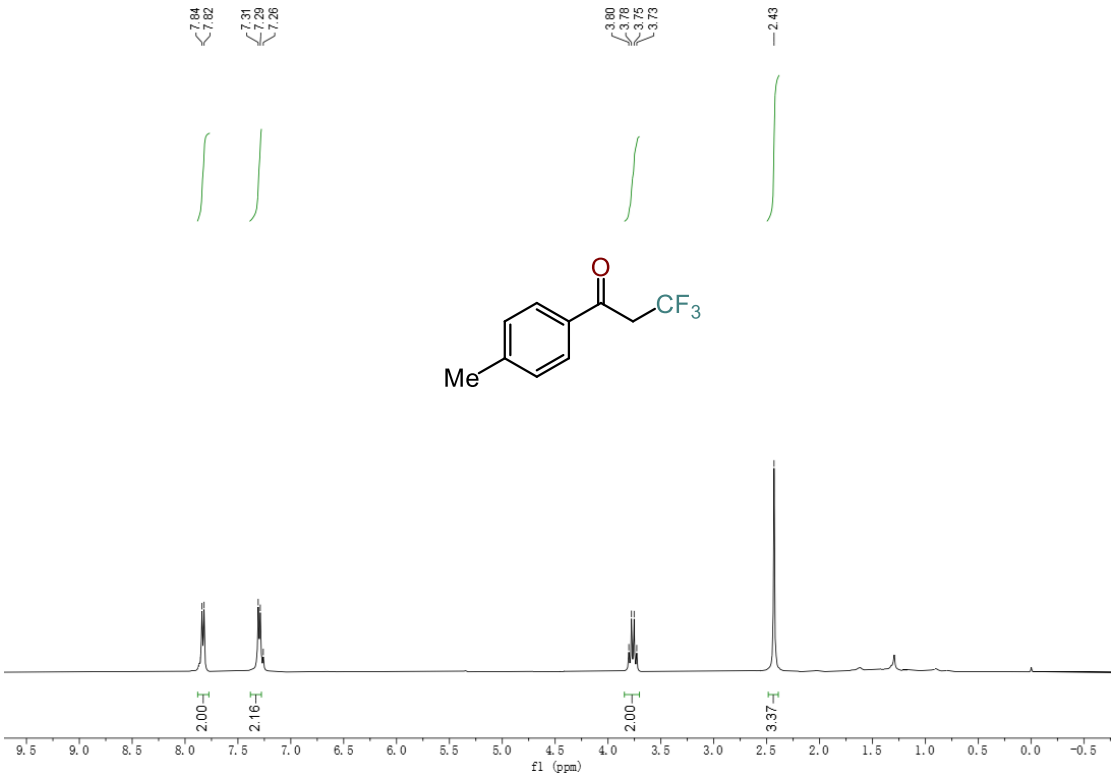
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (125 MHz, $CDCl_3$) and ^{19}F NMR (470 MHz, $CDCl_3$) spectra for 4a

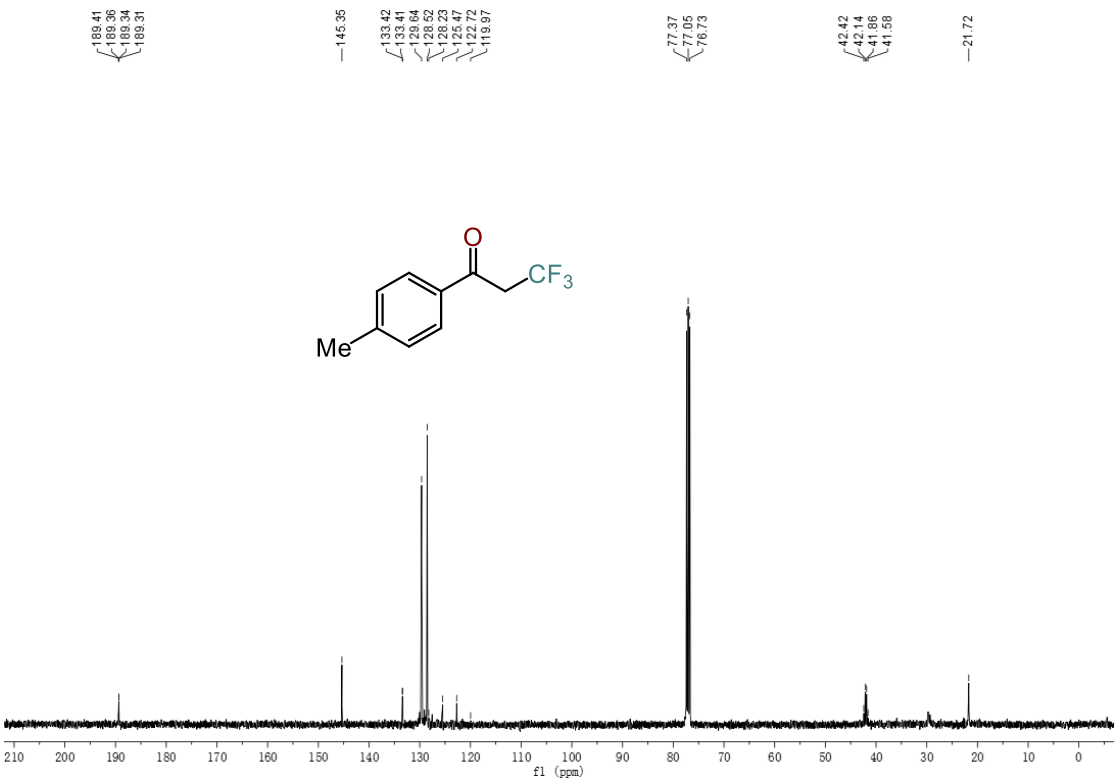


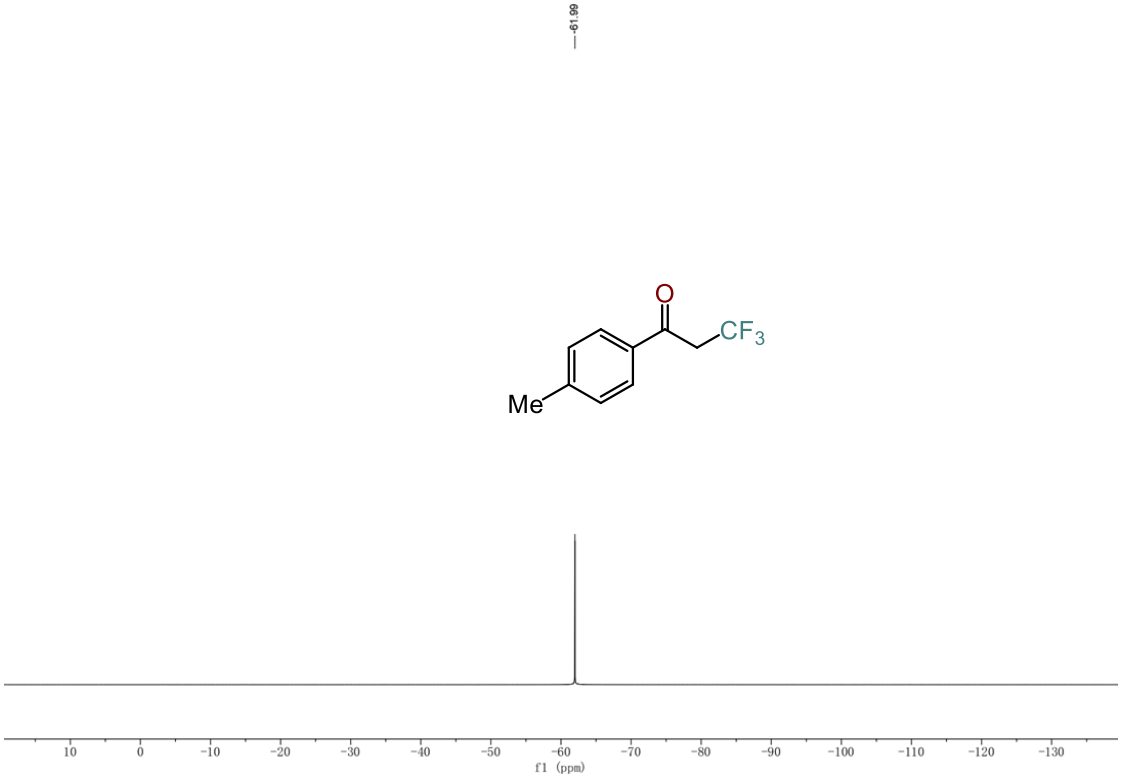




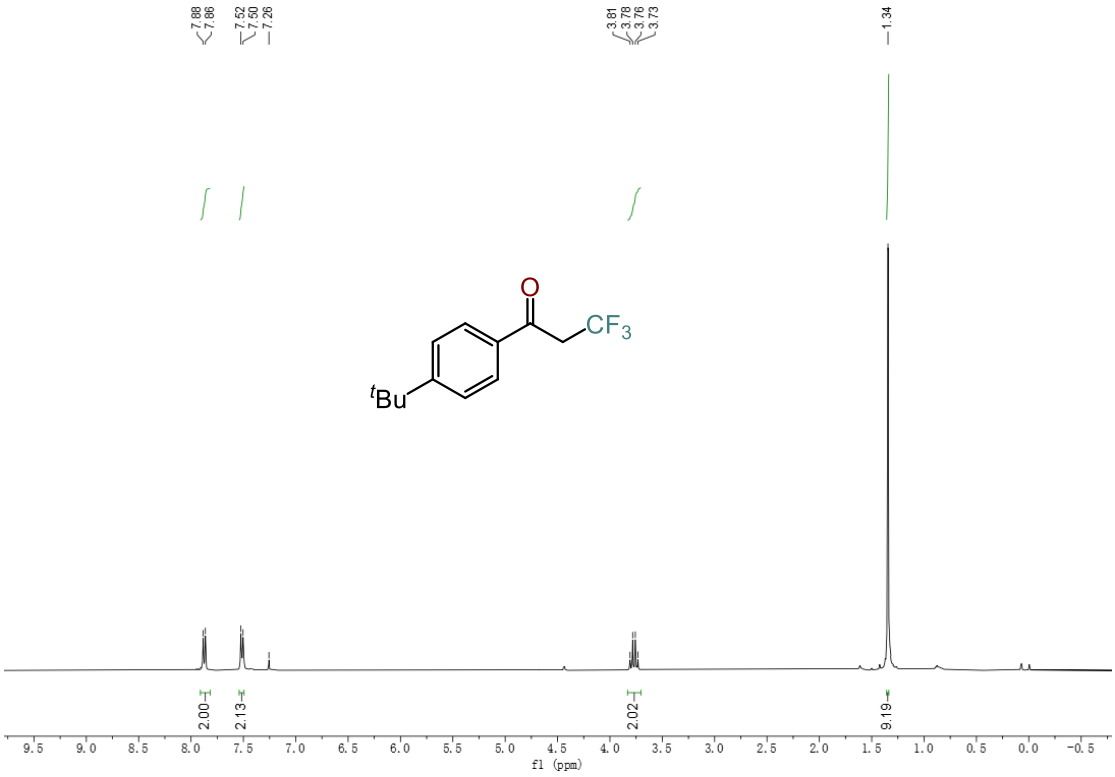
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (470 MHz, $CDCl_3$) spectra for 4b

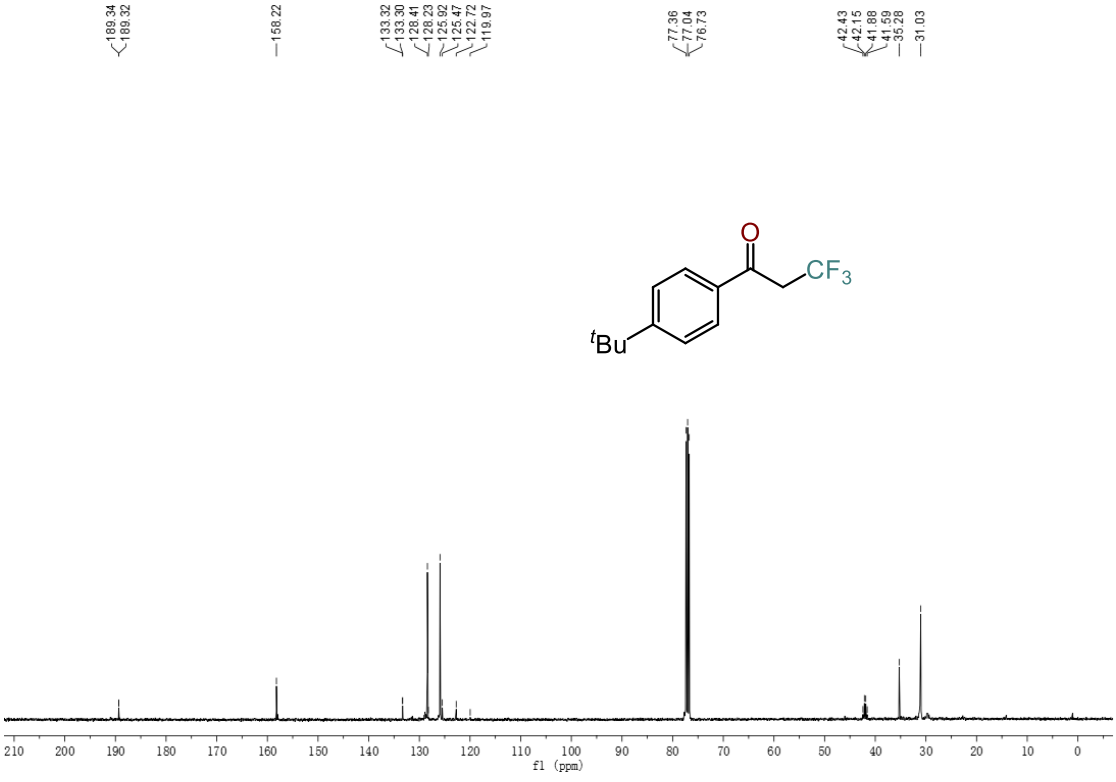


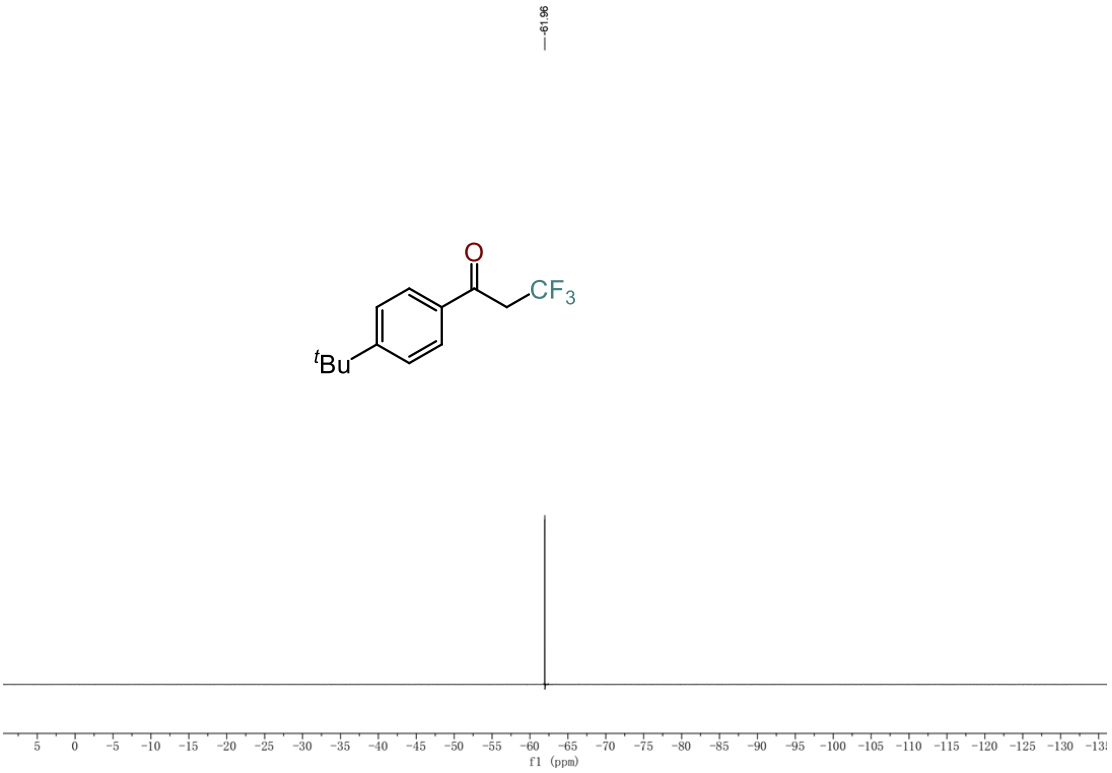

189.41
189.36
189.34
189.31
145.35
133.42
133.41
129.64
128.52
128.23
125.47
122.72
119.97
77.37
77.05
76.73
42.42
42.14
41.86
41.58
21.72
O
CF3
Me
f1 (ppm)


-61.99
O
CF3
Me
f1 (ppm)

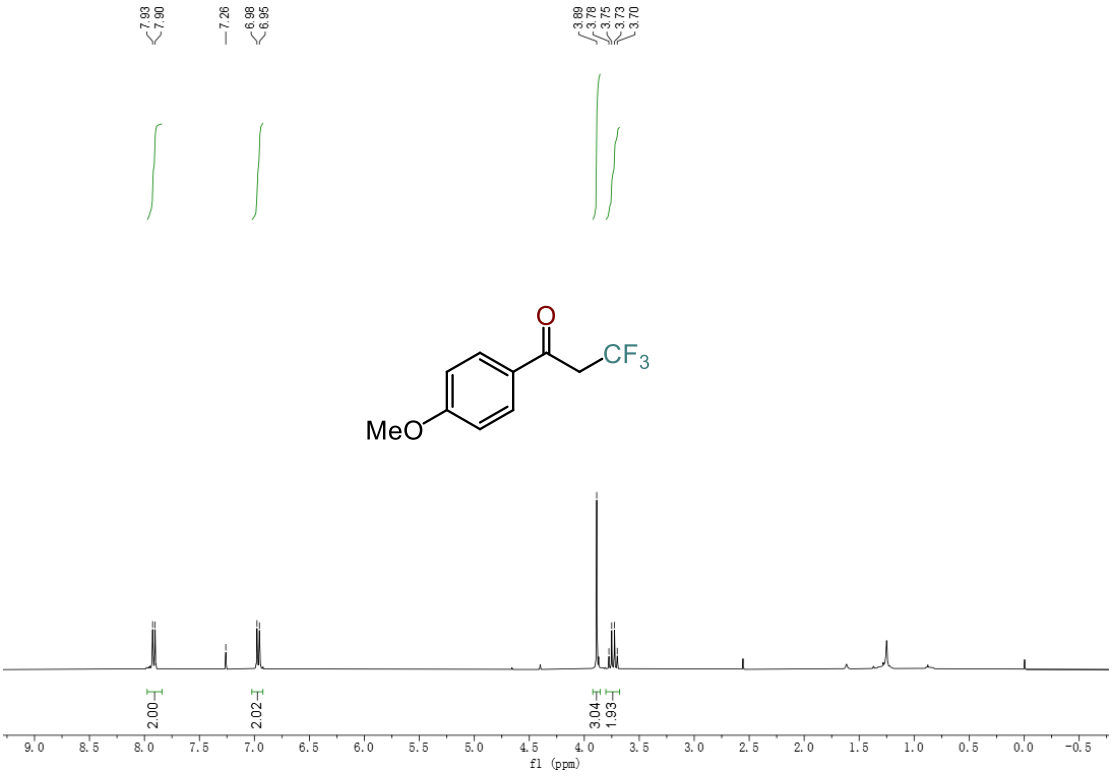
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (470 MHz, $CDCl_3$) spectra for 4c

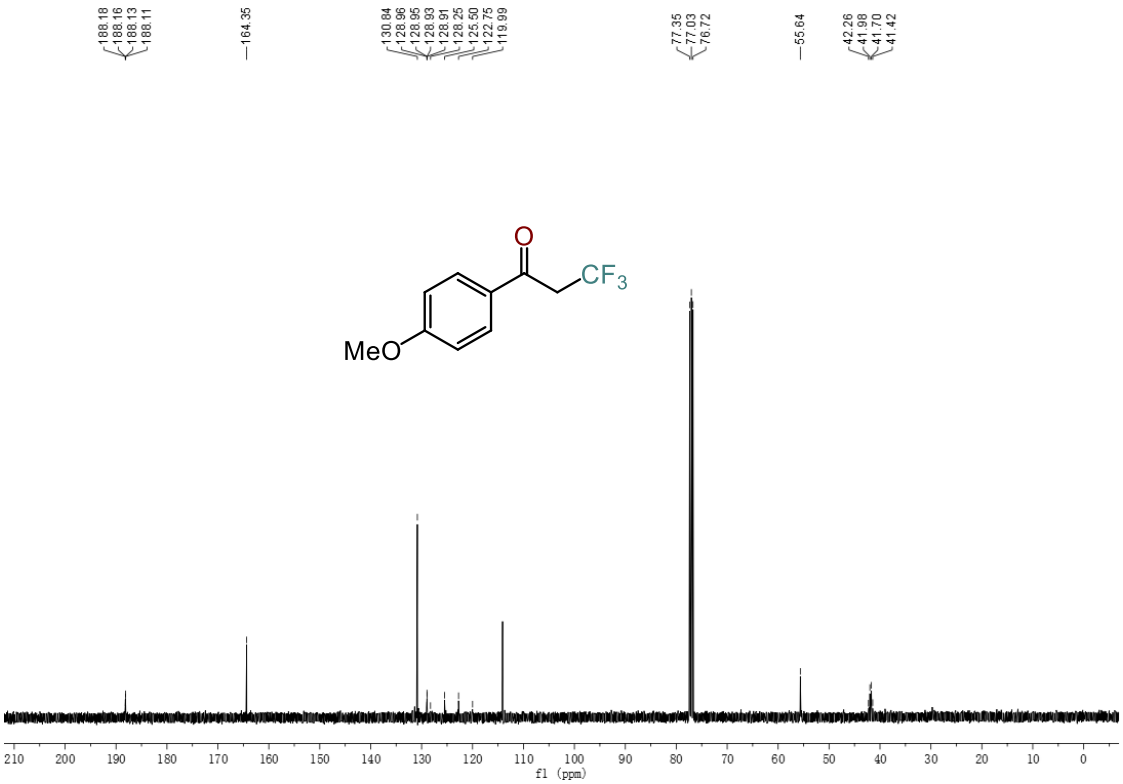


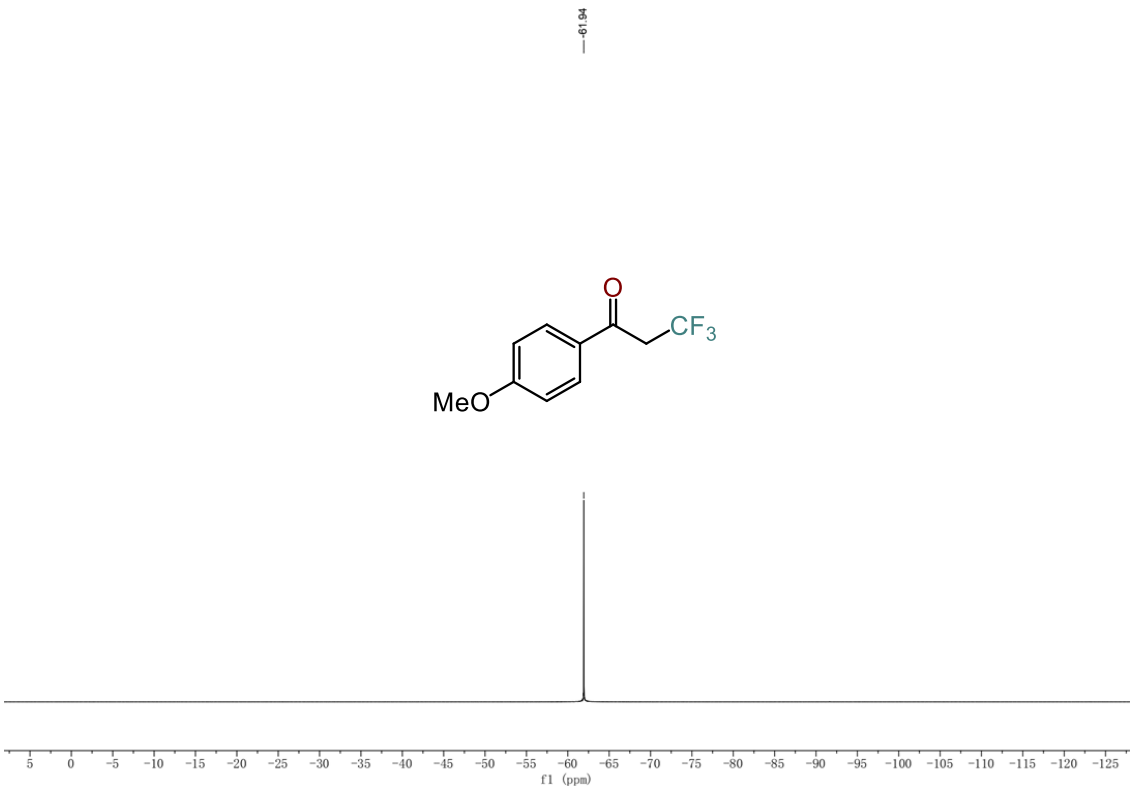




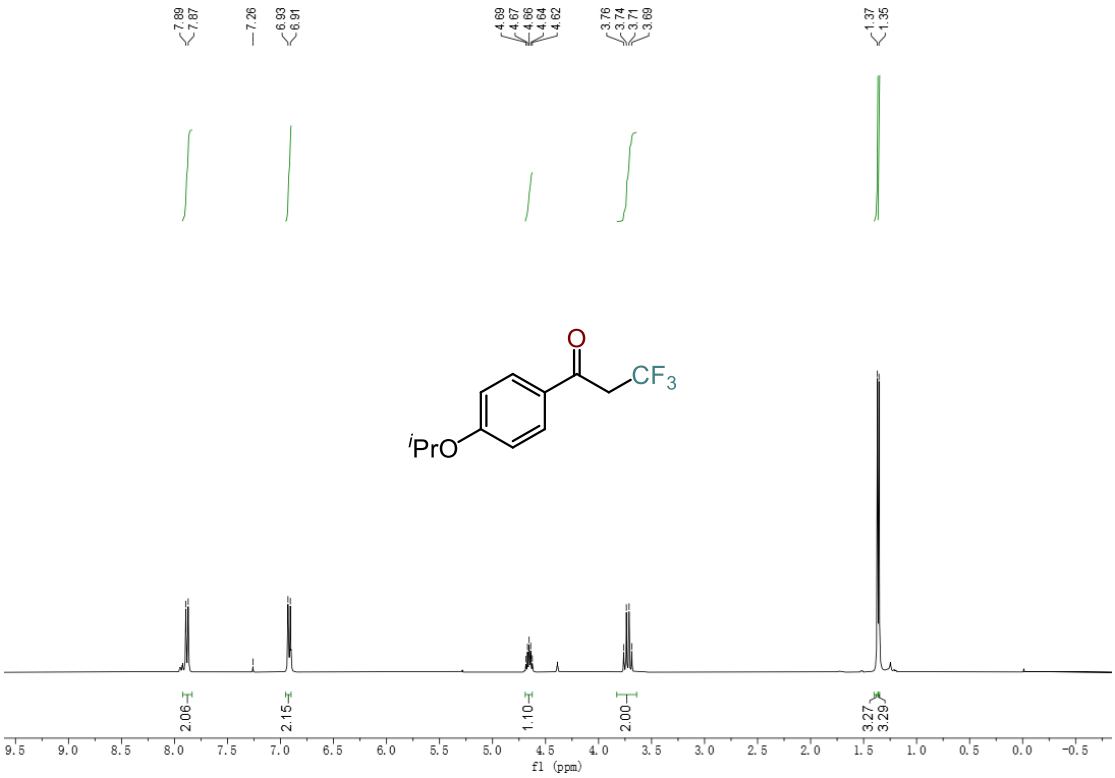
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (470 MHz, $CDCl_3$) spectra for 4d

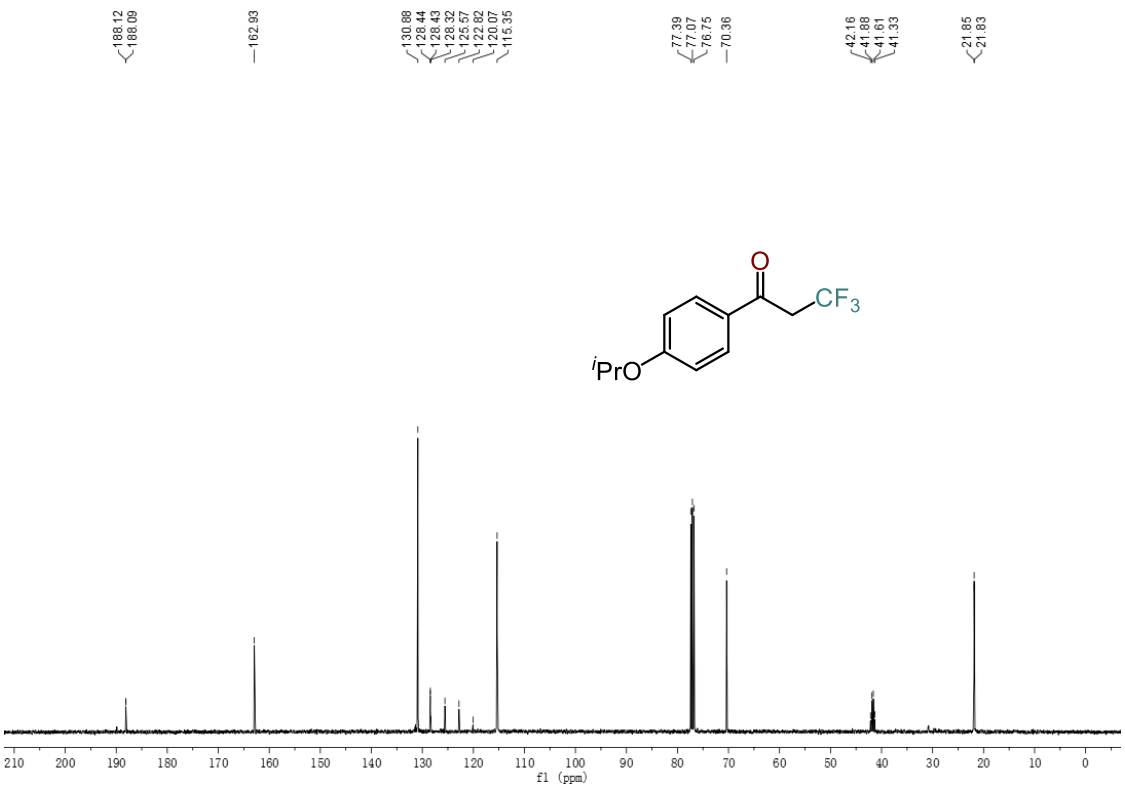


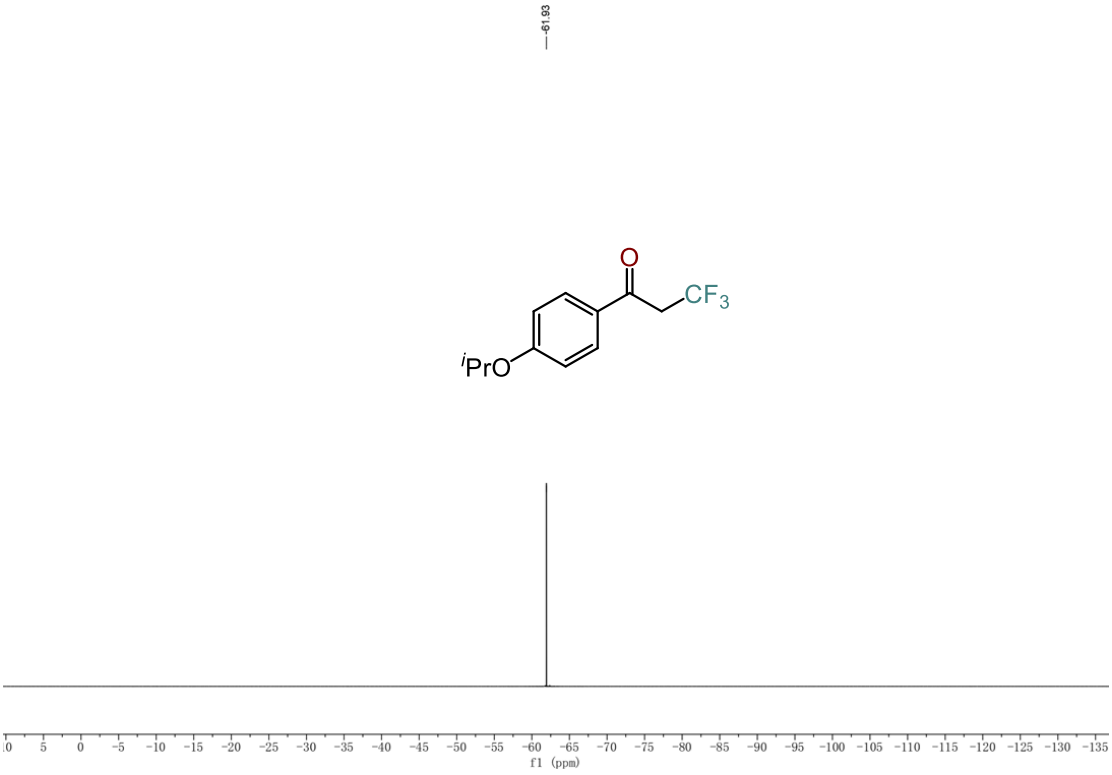

188.18
188.16
188.13
188.11
164.35
130.84
128.96
128.95
128.93
128.91
128.25
125.50
122.75
119.99
77.35
77.03
76.72
55.64
42.26
41.98
41.70
41.42
O
CF3
MeO
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-61.94
O
CF3
MeO
5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125
f1 (ppm)

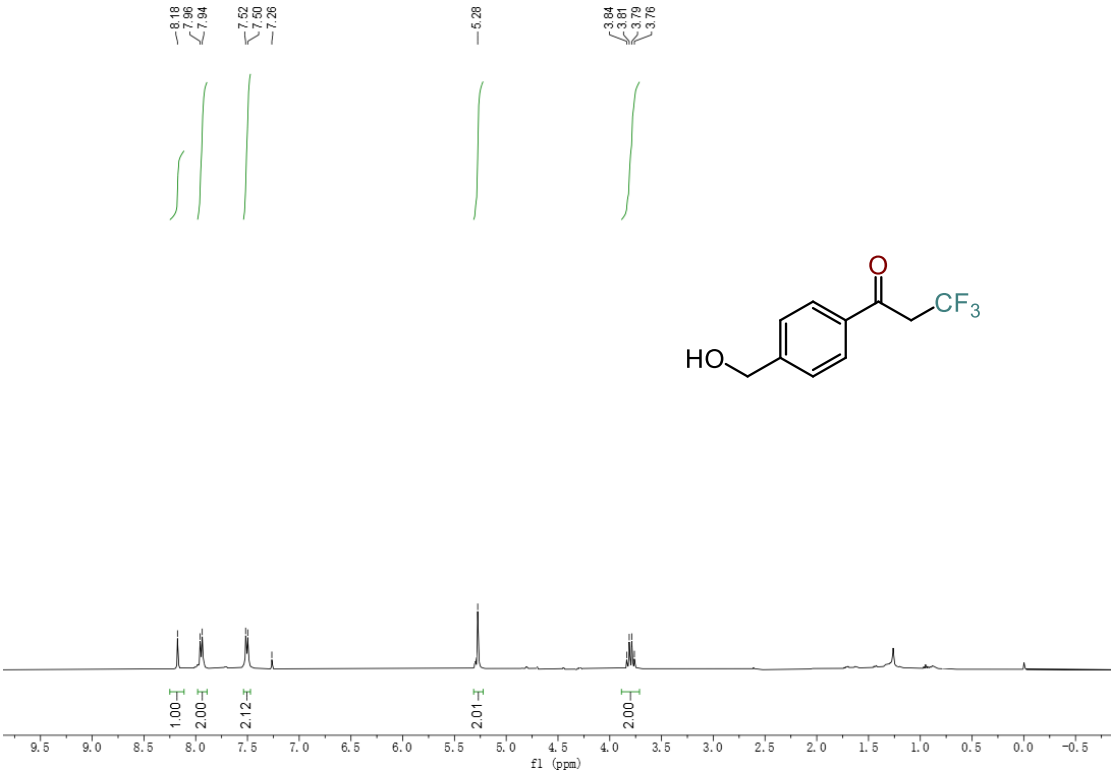
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (470 MHz, $CDCl_3$) spectra for 4e

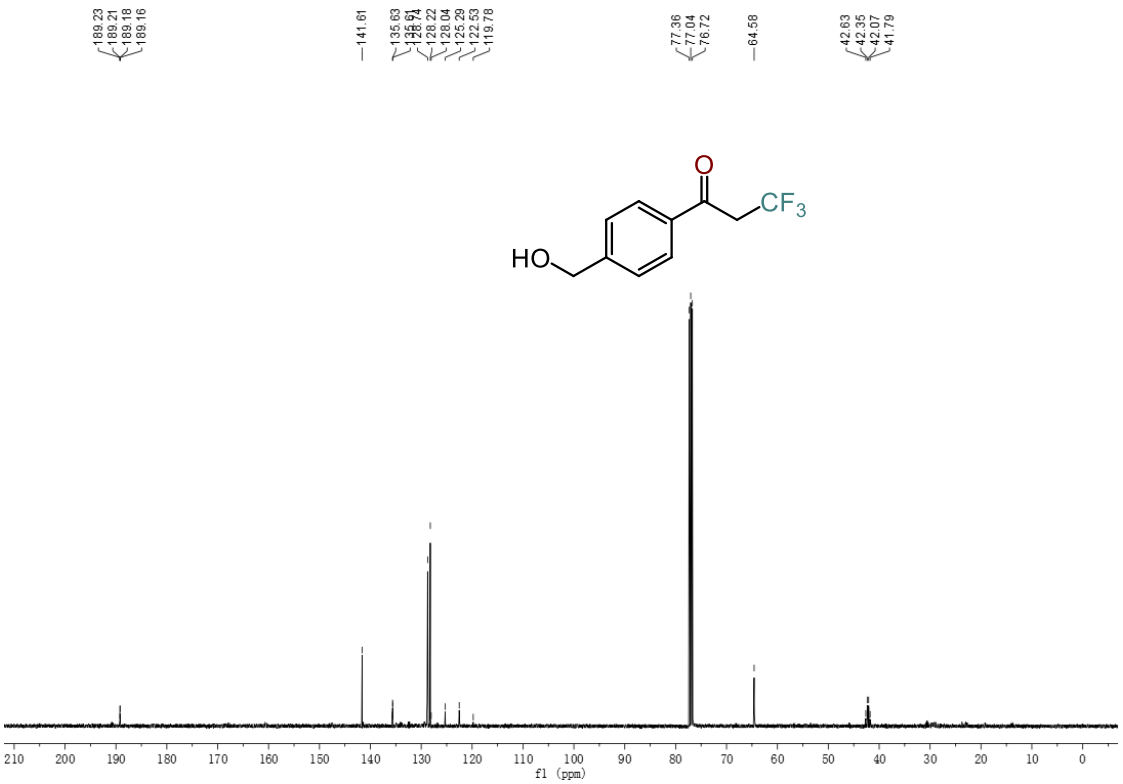


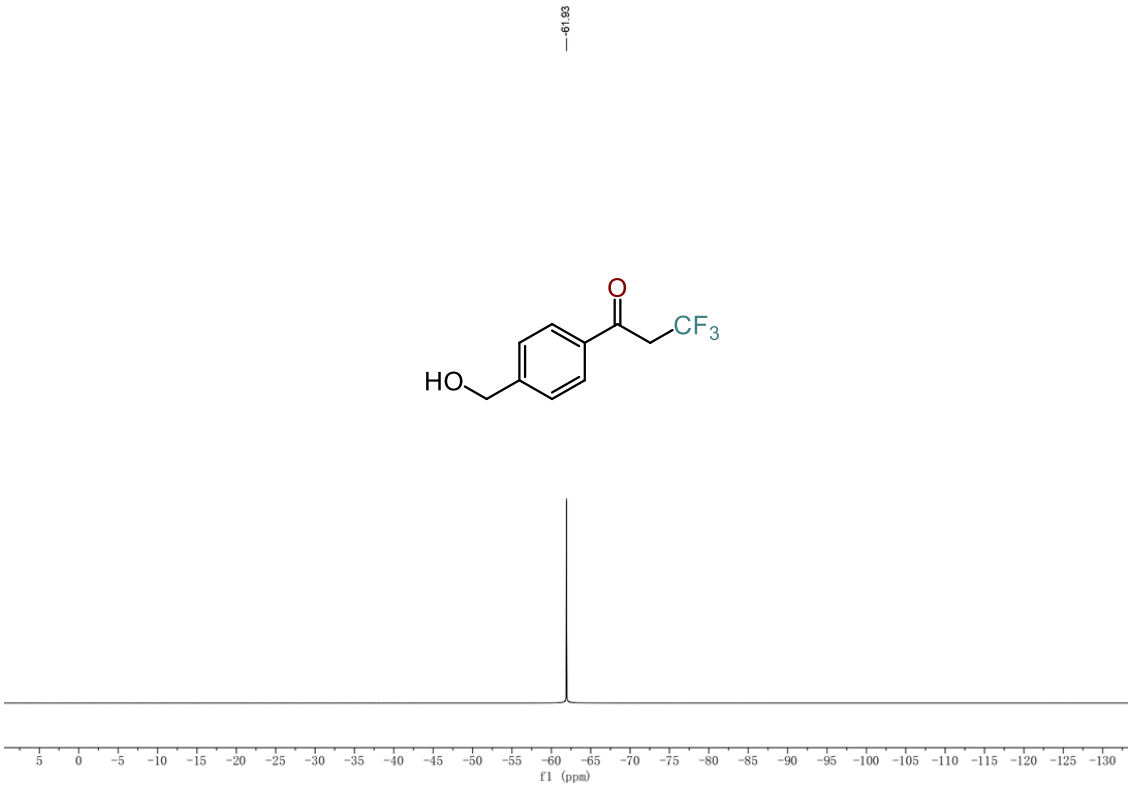




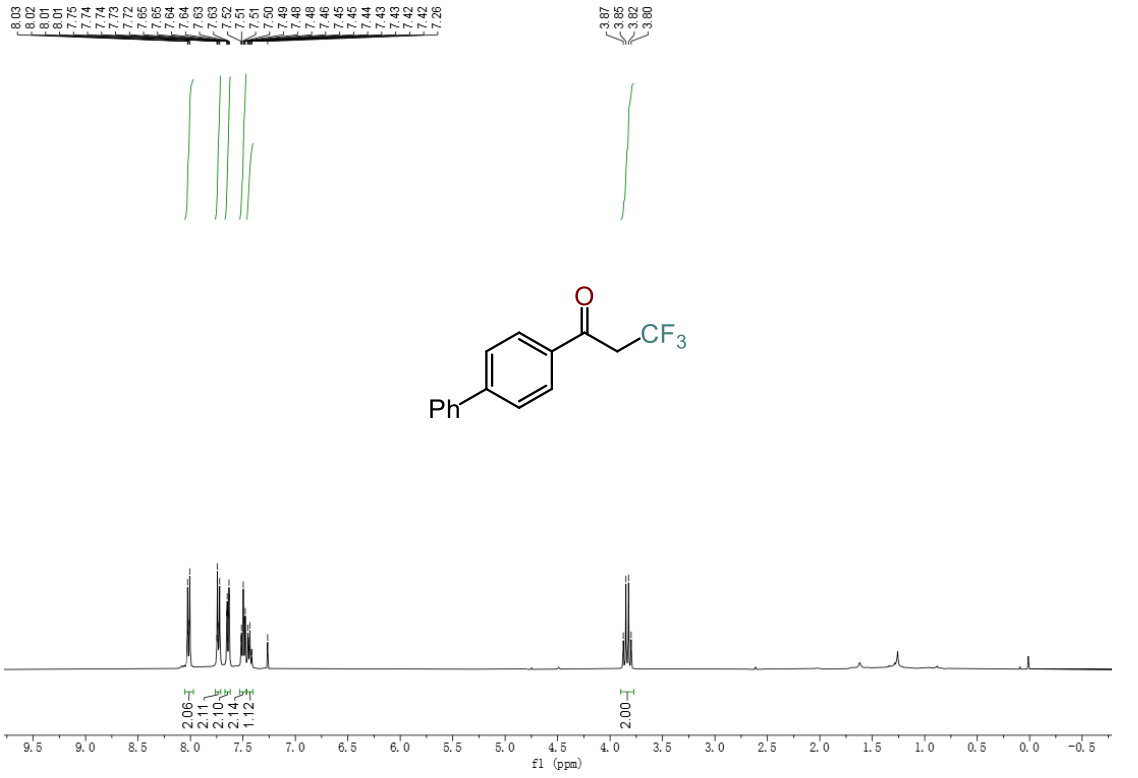
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (470 MHz, $CDCl_3$) spectra for 4f

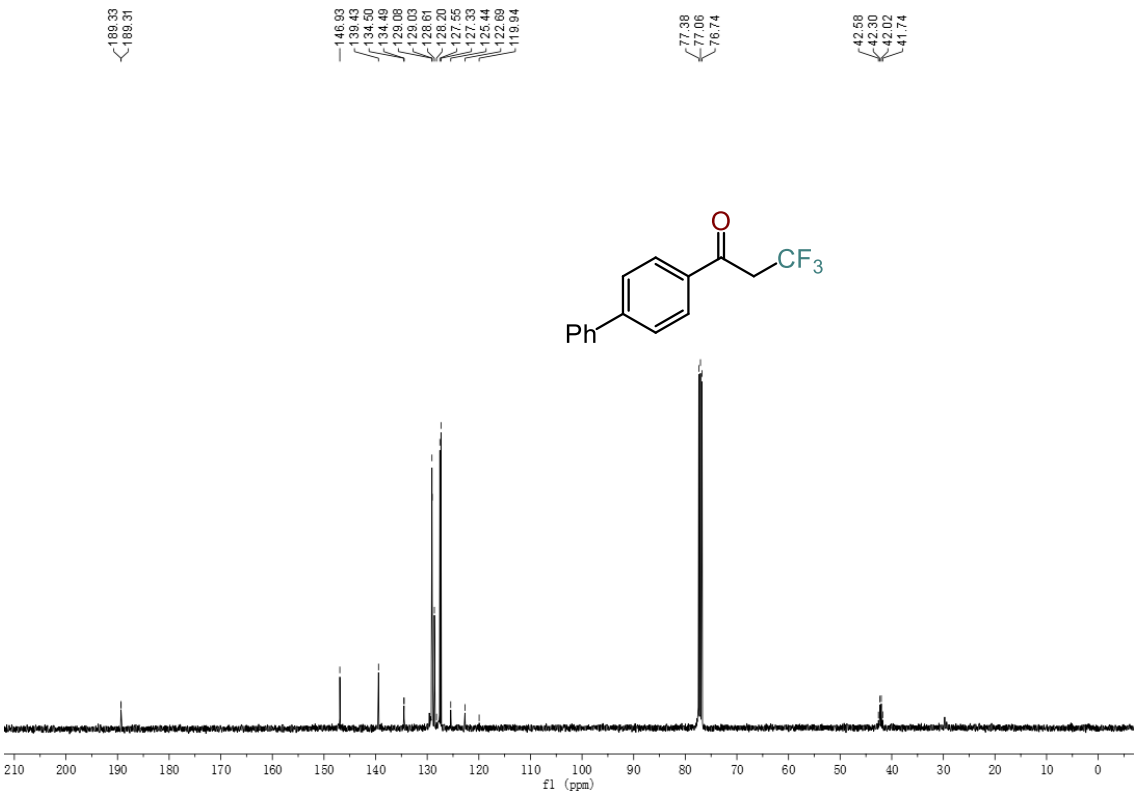


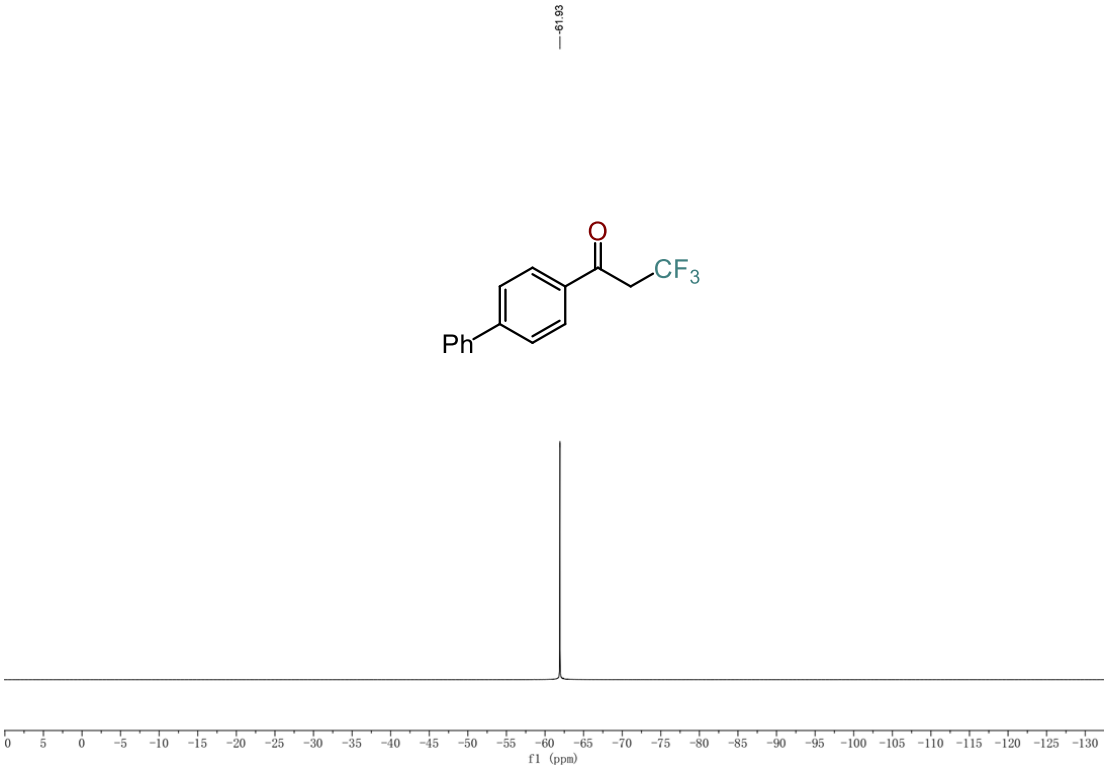

189.23
189.21
189.18
189.16
141.61
135.63
128.22
128.04
125.29
122.53
119.78
77.36
77.04
76.72
64.58
42.63
42.35
42.07
41.79
O
CF3
HO
f1 (ppm)


-61.93
O
CF3
HO
f1 (ppm)

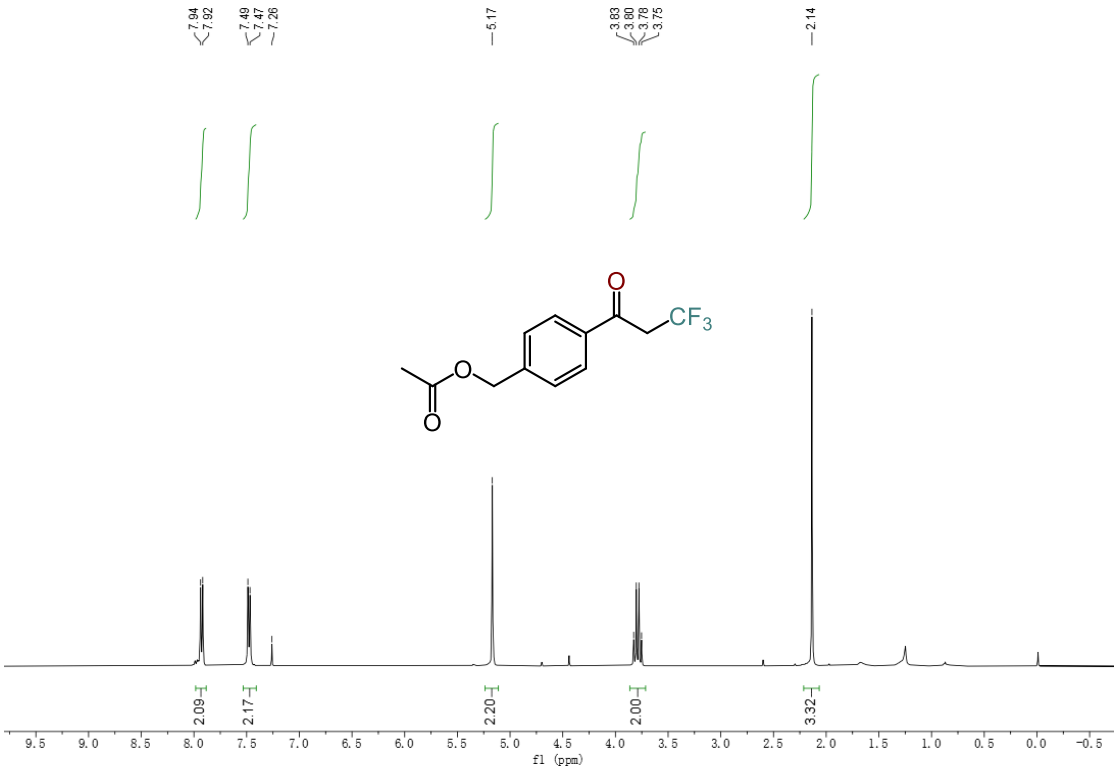
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (470 MHz, $CDCl_3$) spectra for 4g

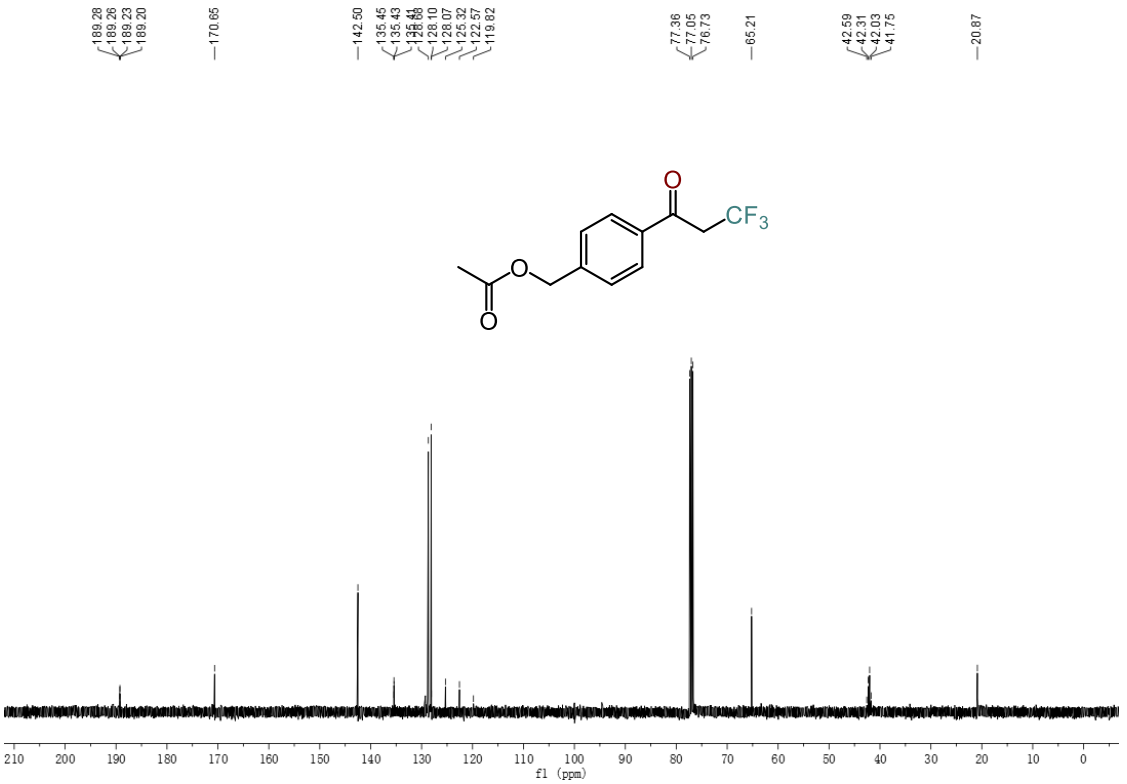


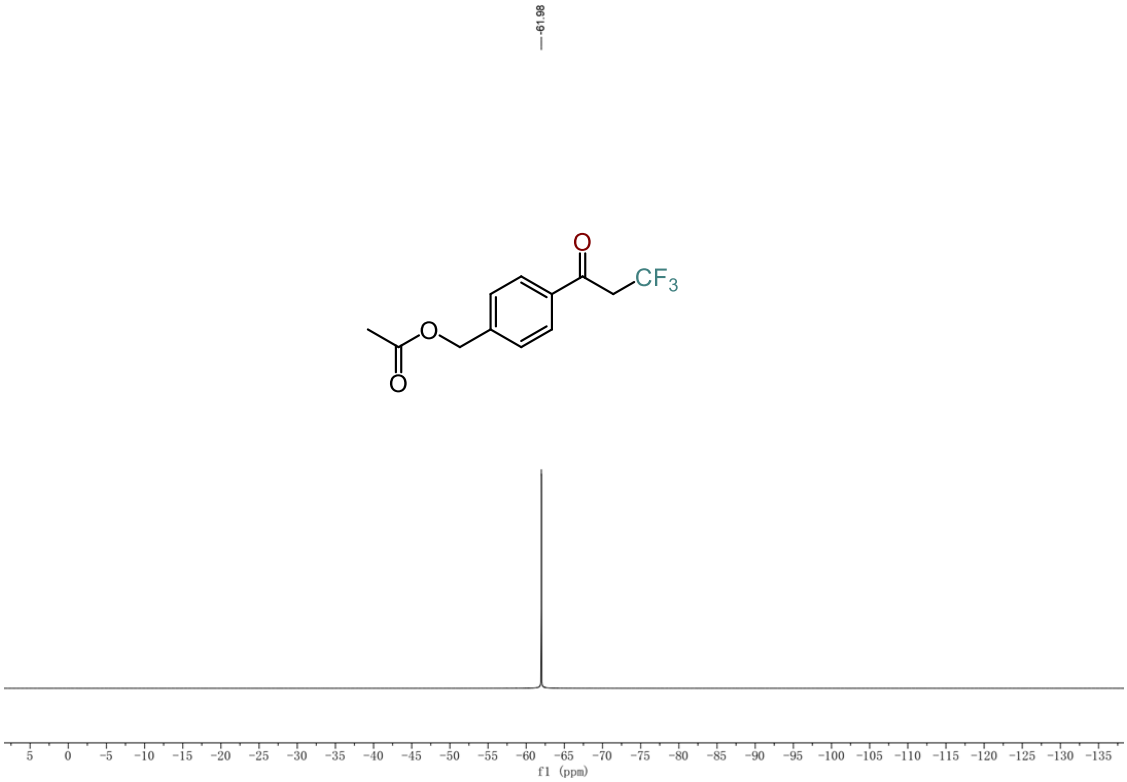




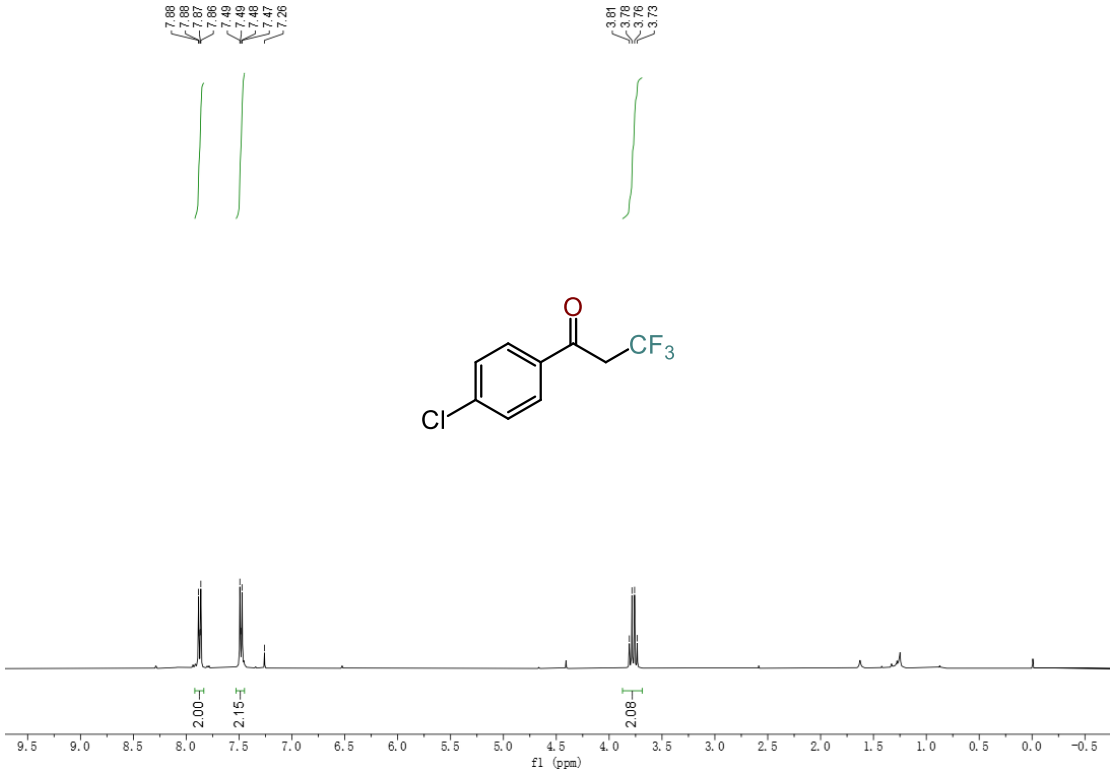
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (470 MHz, $CDCl_3$) spectra for 4h

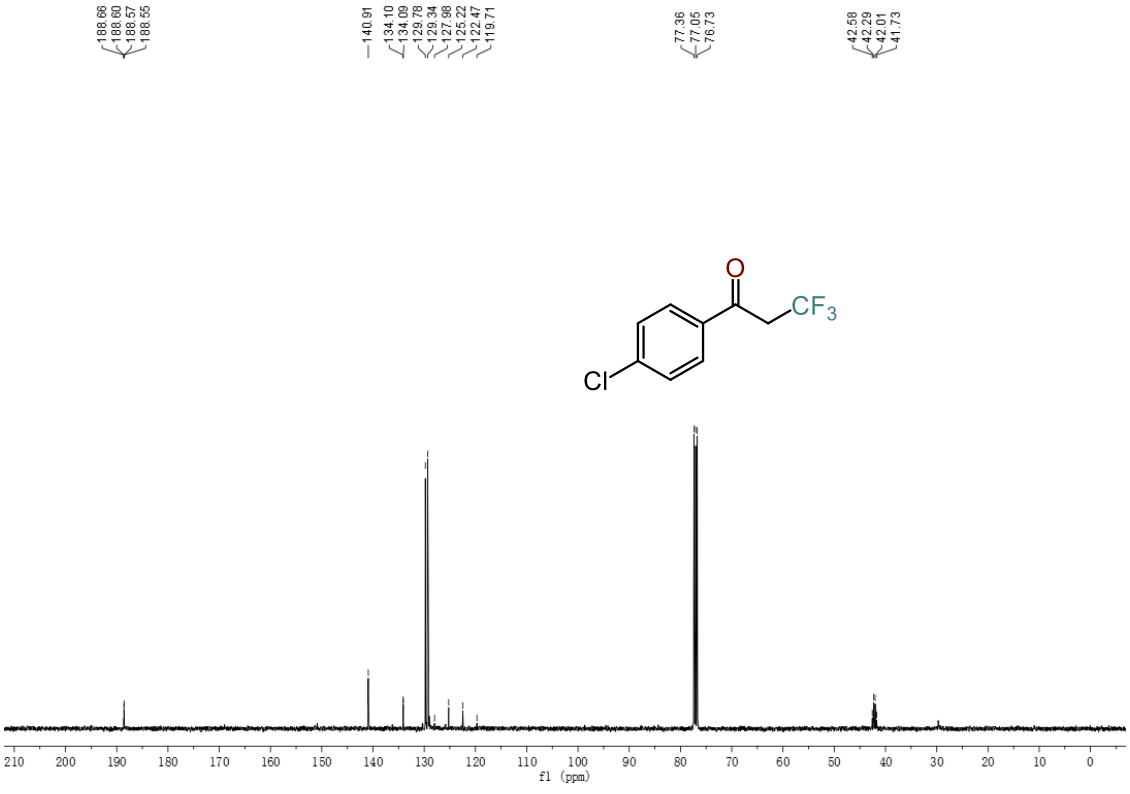


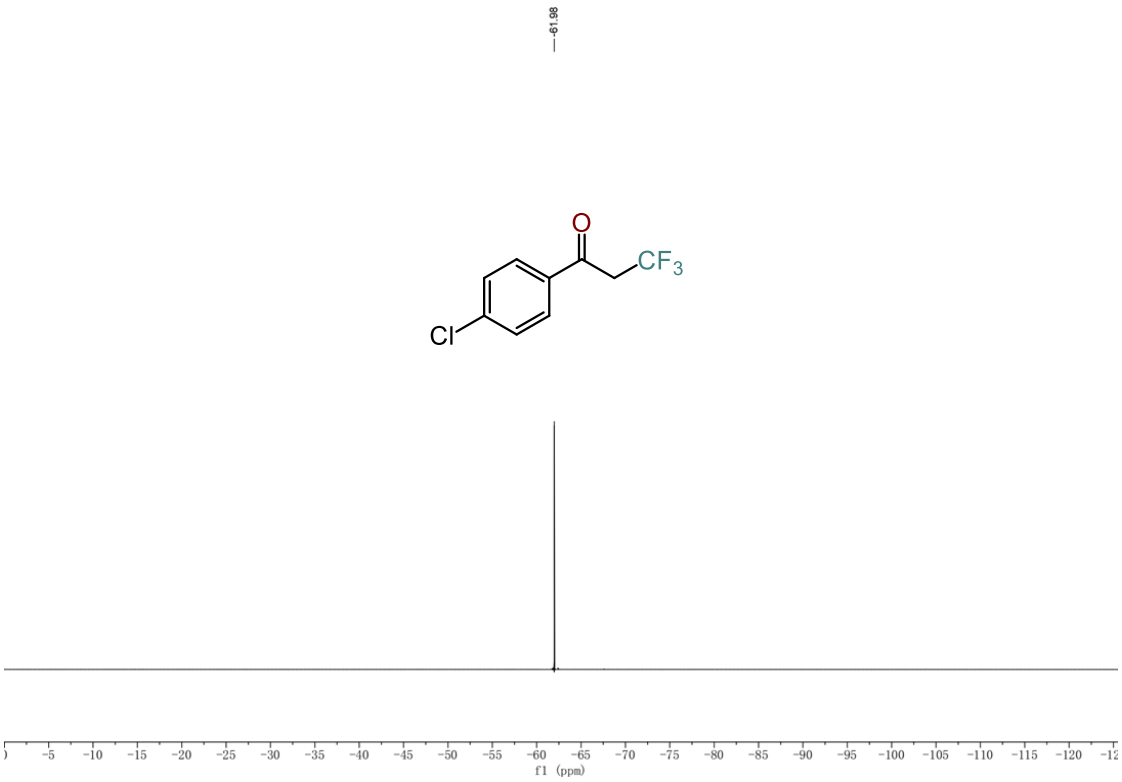

189.28
189.26
189.23
189.20
170.65
142.50
135.45
135.43
128.10
128.07
125.32
122.57
116.82
77.36
77.05
76.73
65.21
42.59
42.31
42.03
41.75
20.87
O
CF3
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-61.98
O
CF3
O
O
5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135
f1 (ppm)

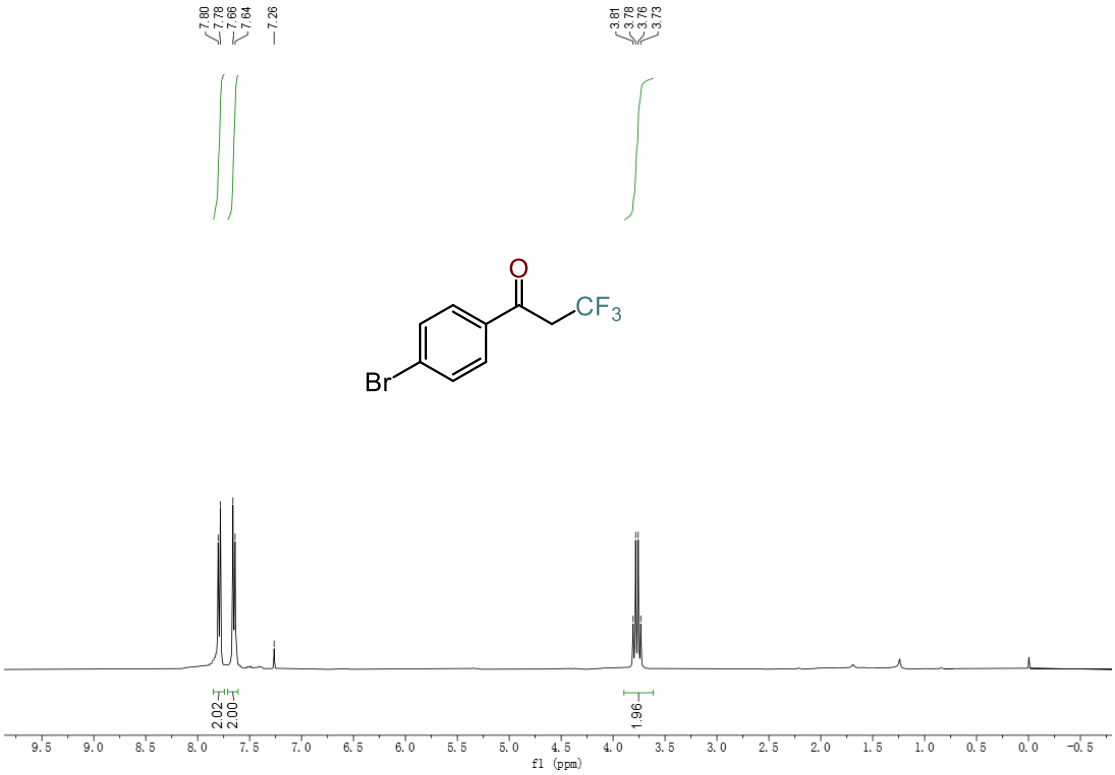
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (470 MHz, $CDCl_3$) spectra for 4i

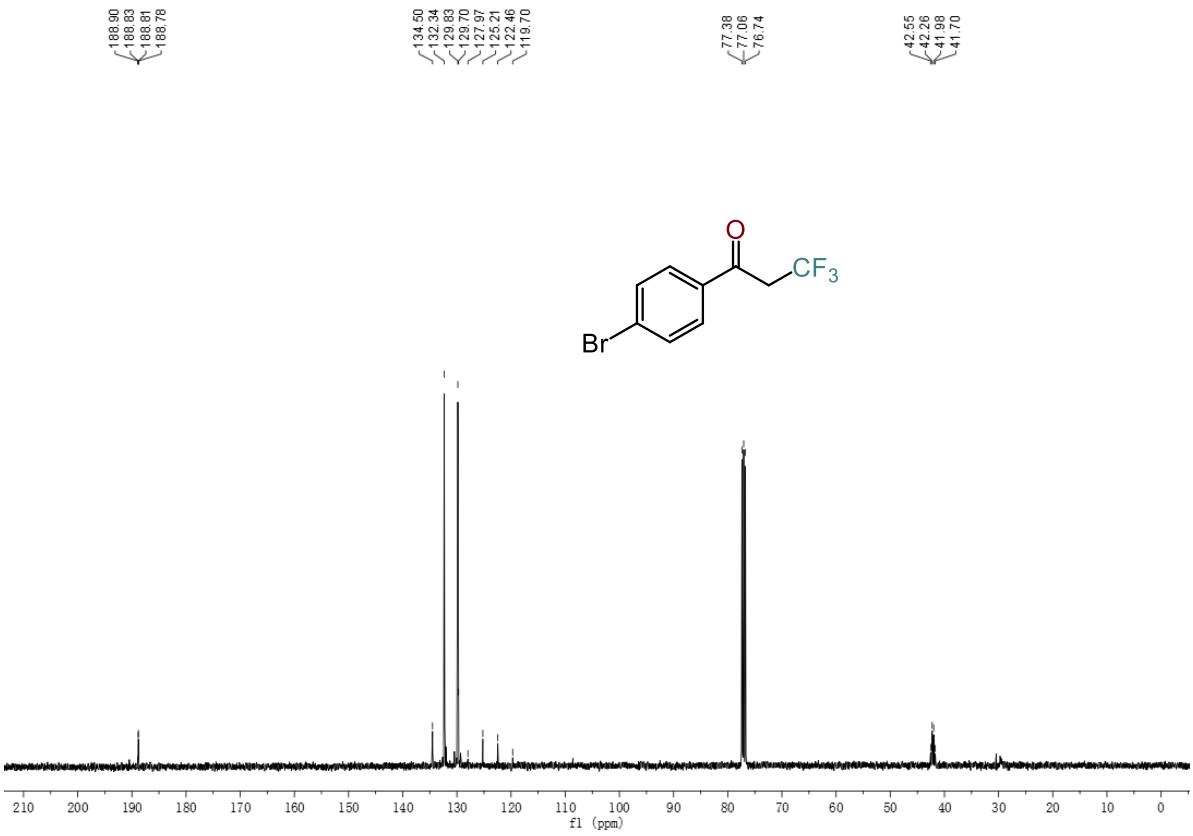


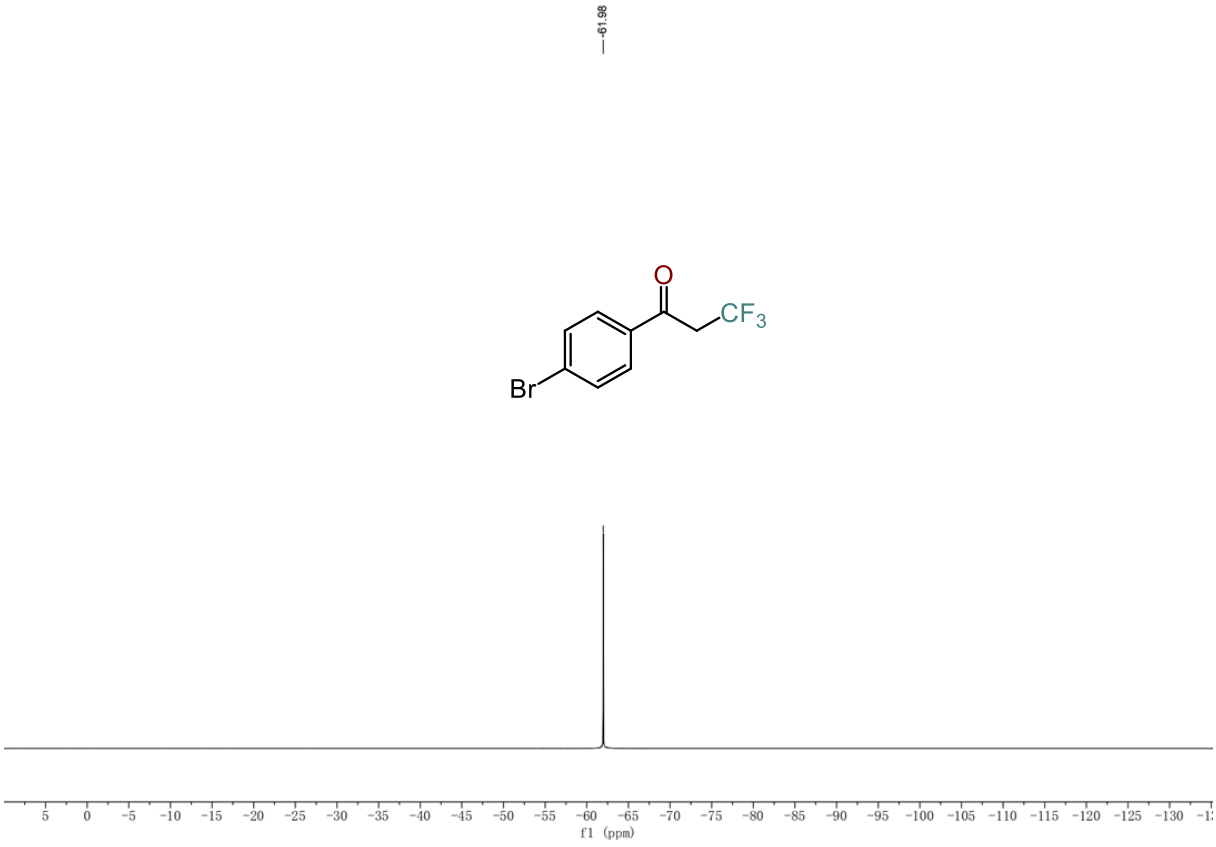




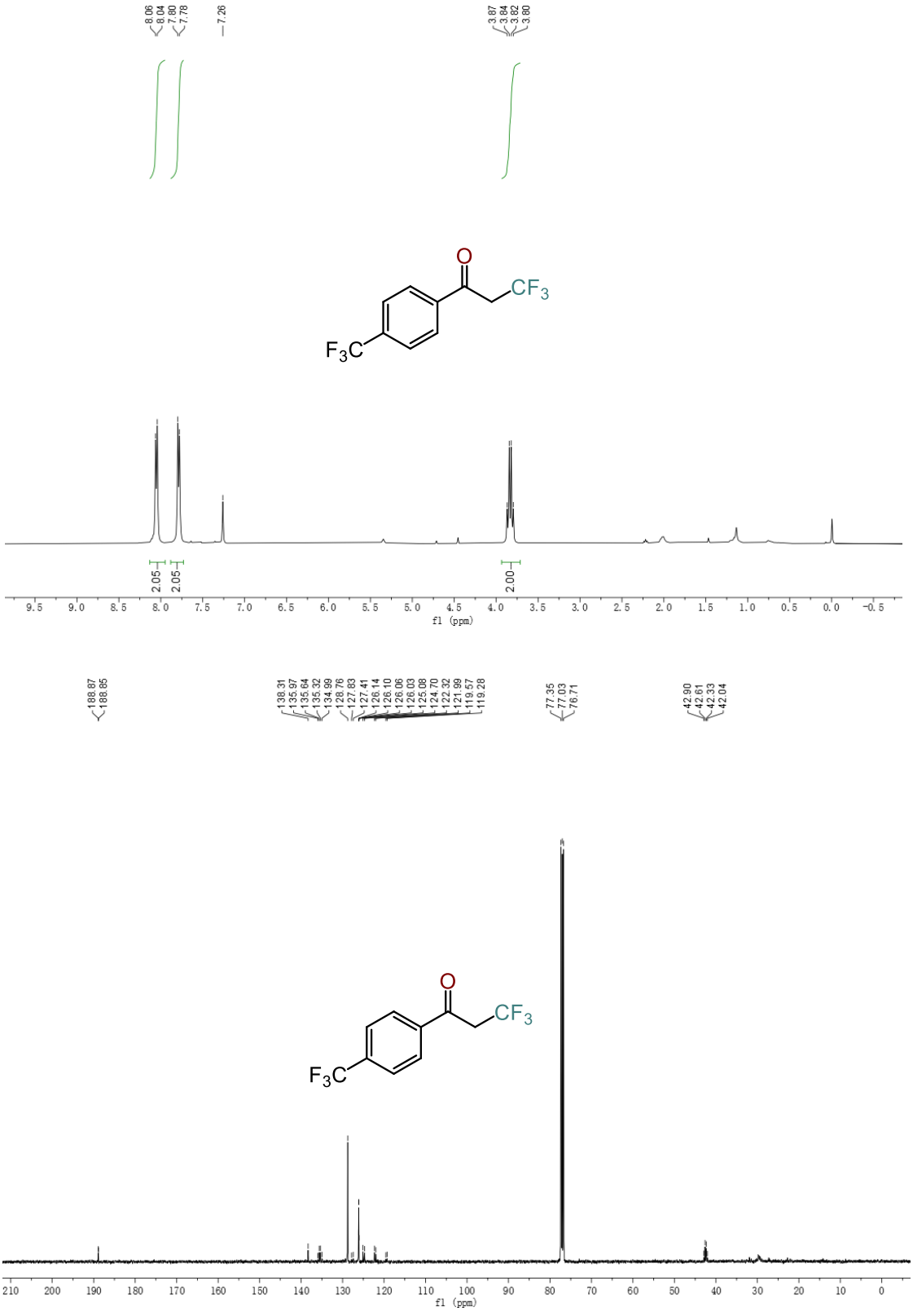
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (470 MHz, $CDCl_3$) spectra for 4j

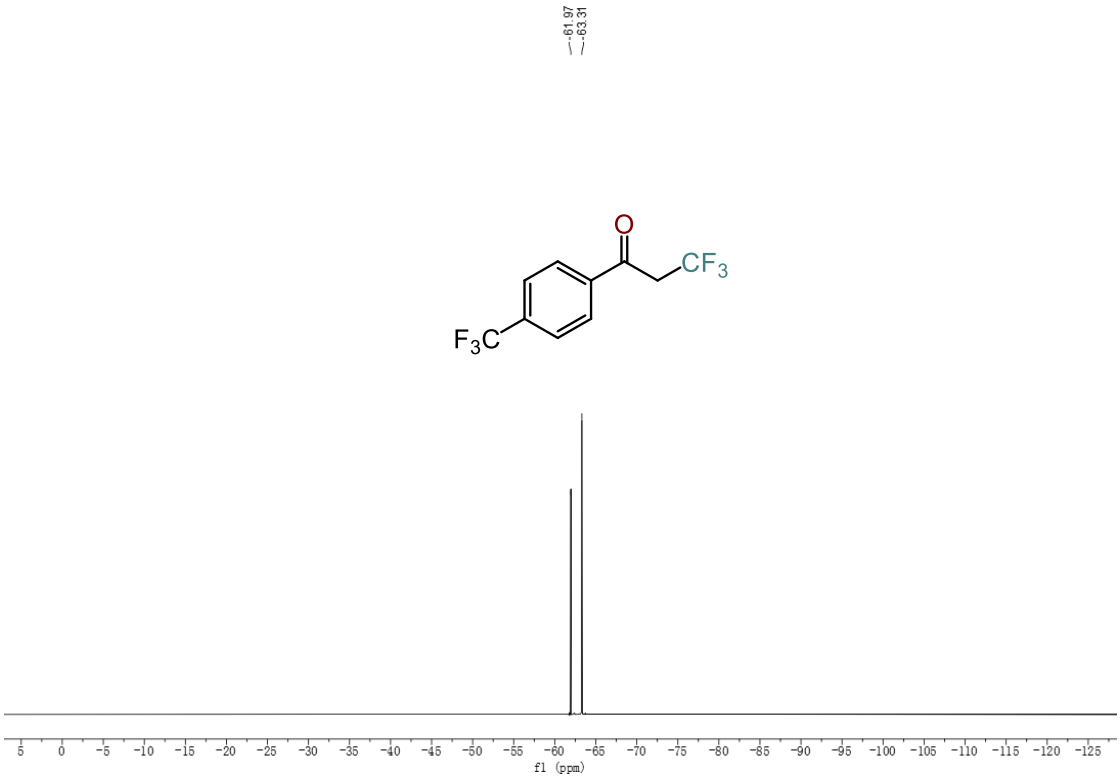



188.90
188.83
188.81
188.78
134.50
132.34
129.83
129.70
127.97
125.21
122.46
119.70
77.38
77.06
76.74
42.55
42.26
41.98
41.70
O
CF3
Br
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

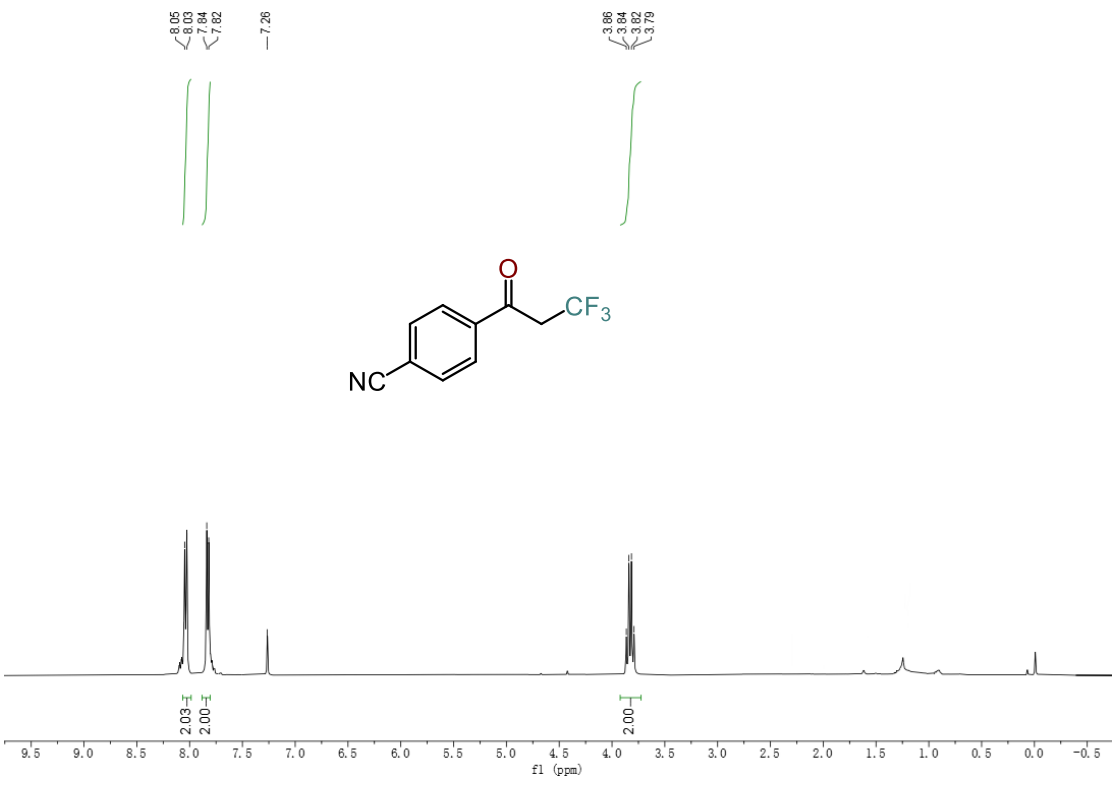

-61.98
O
CF3
Br
5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130
f1 (ppm)

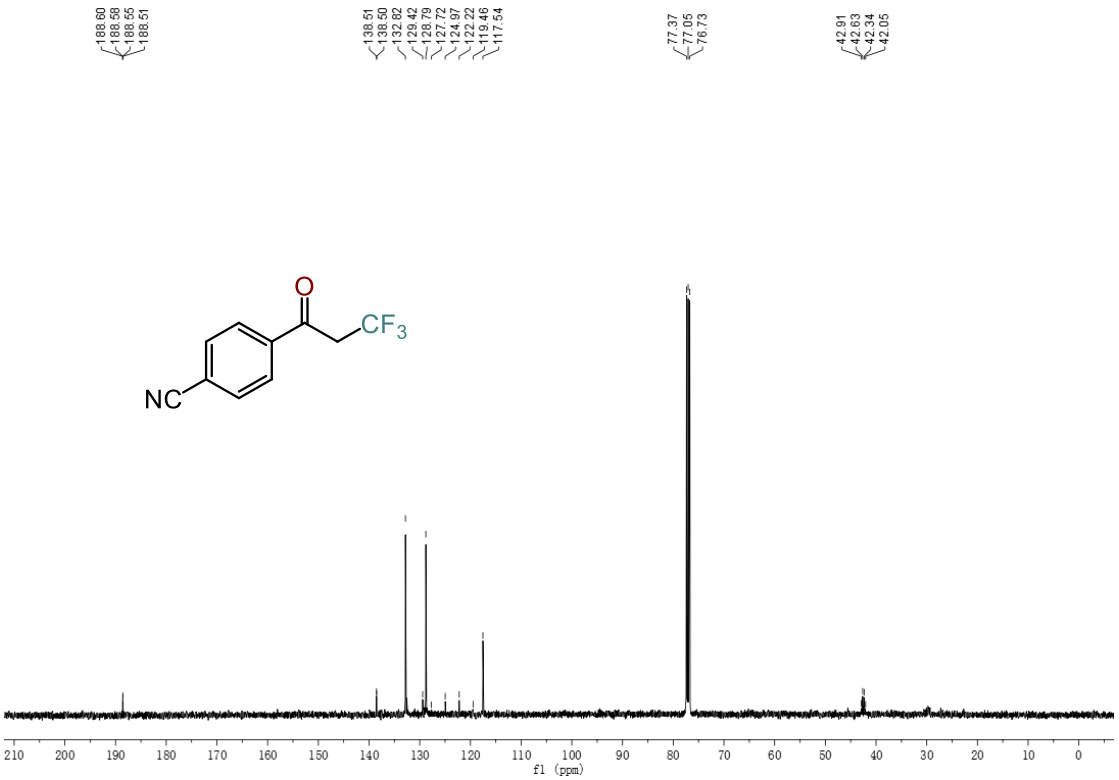
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (470 MHz, $CDCl_3$) spectra for 4k

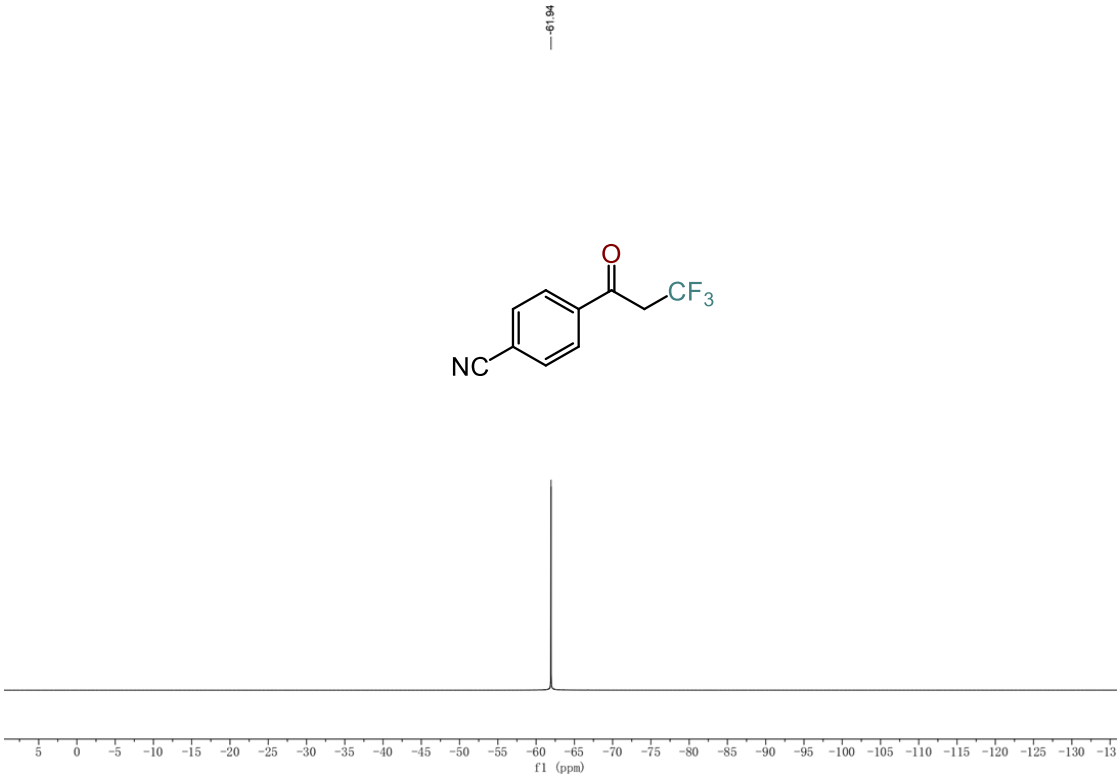




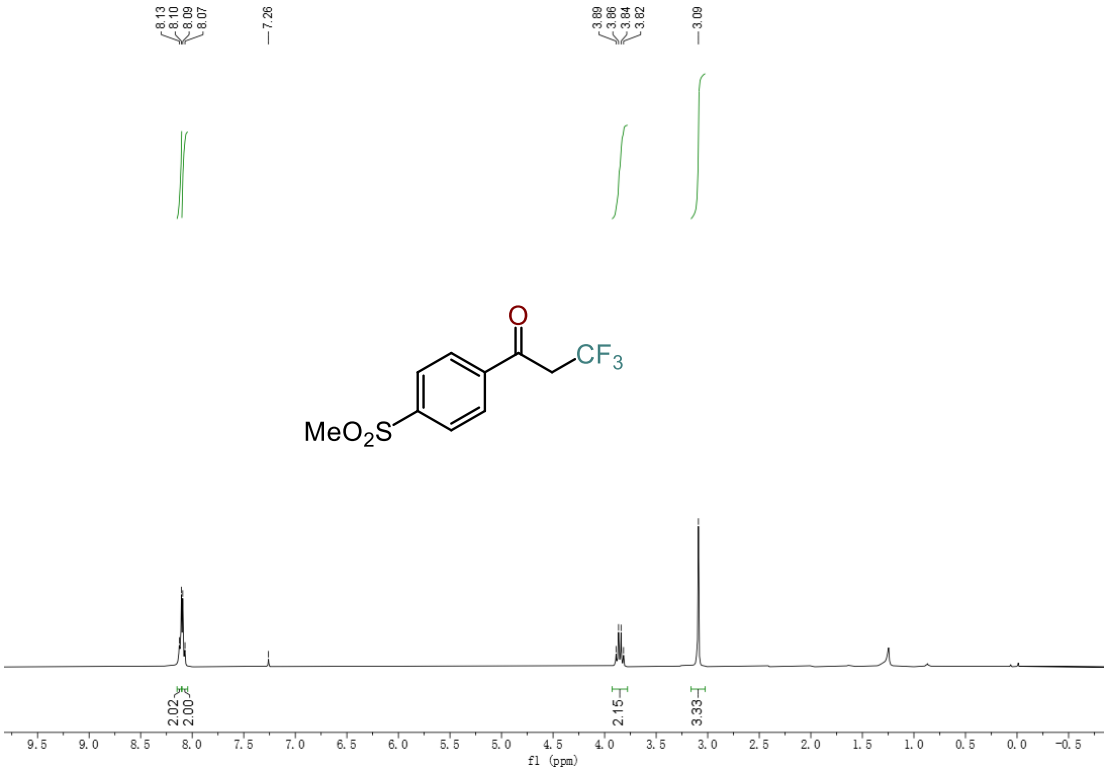
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (470 MHz, $CDCl_3$) spectra for 4l

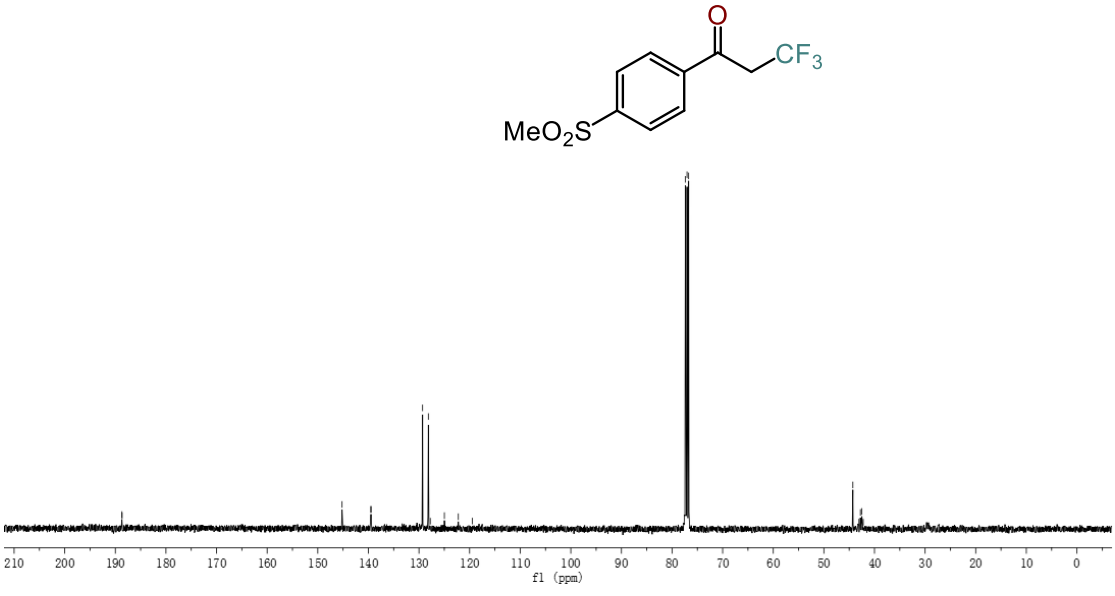


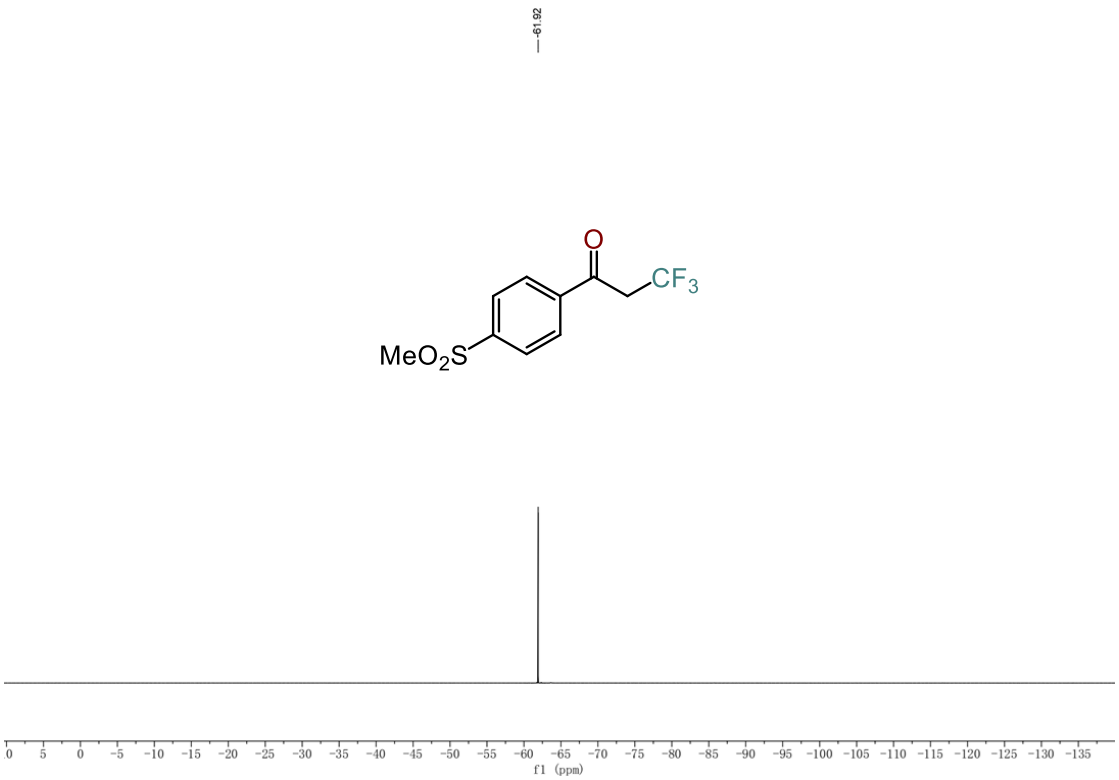

188.60
188.58
188.55
188.51
138.51
138.50
132.82
129.42
128.79
127.72
124.97
122.22
119.46
117.54
77.37
77.05
76.73
42.91
42.63
42.34
42.05
O
CF3
NC
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-61.94
O
CF3
NC
5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -13
f1 (ppm)

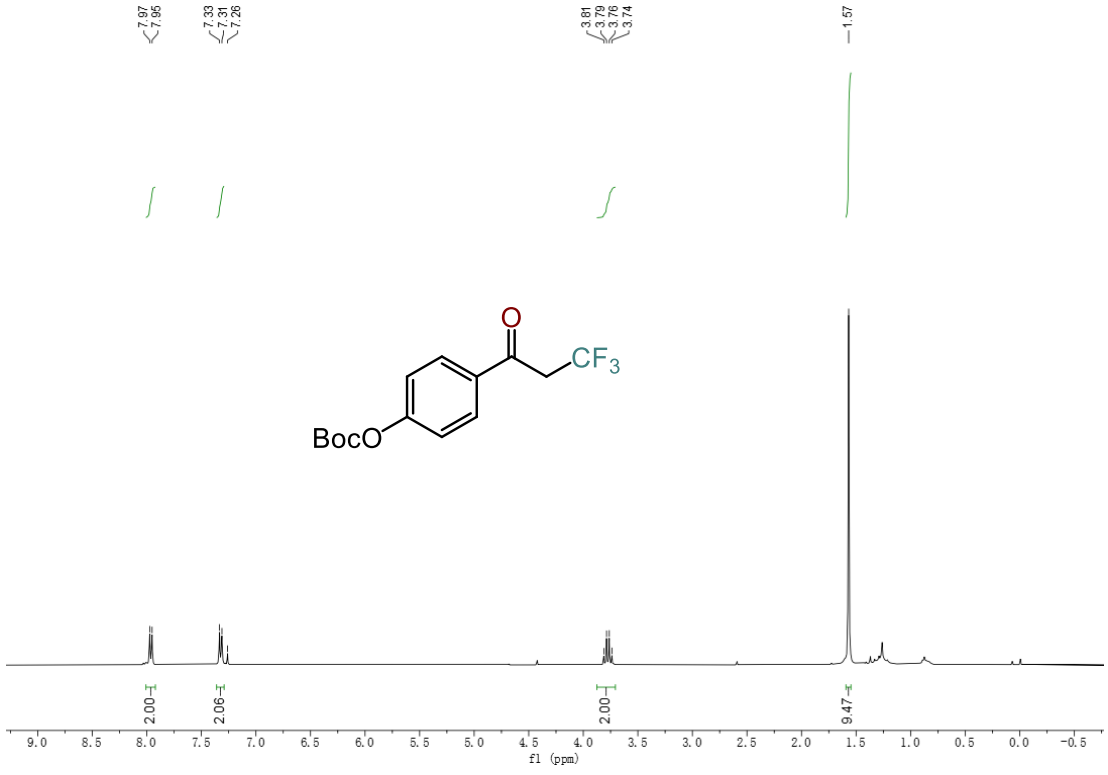
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (470 MHz, $CDCl_3$) spectra for 4m

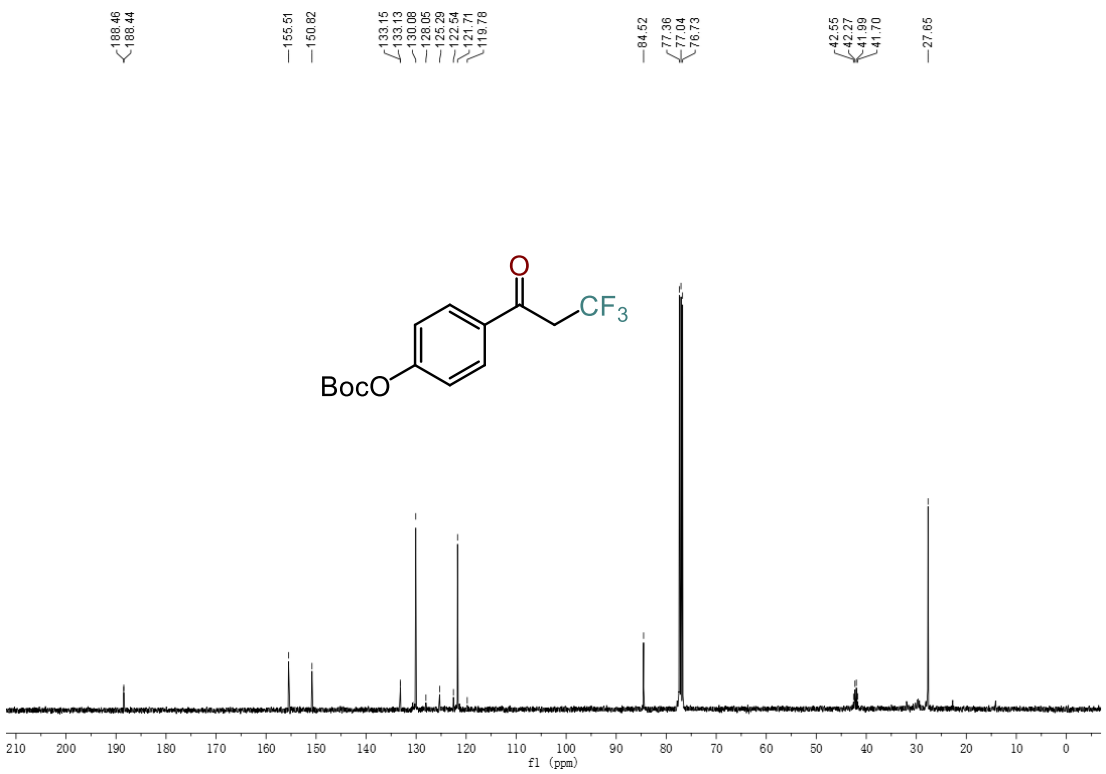


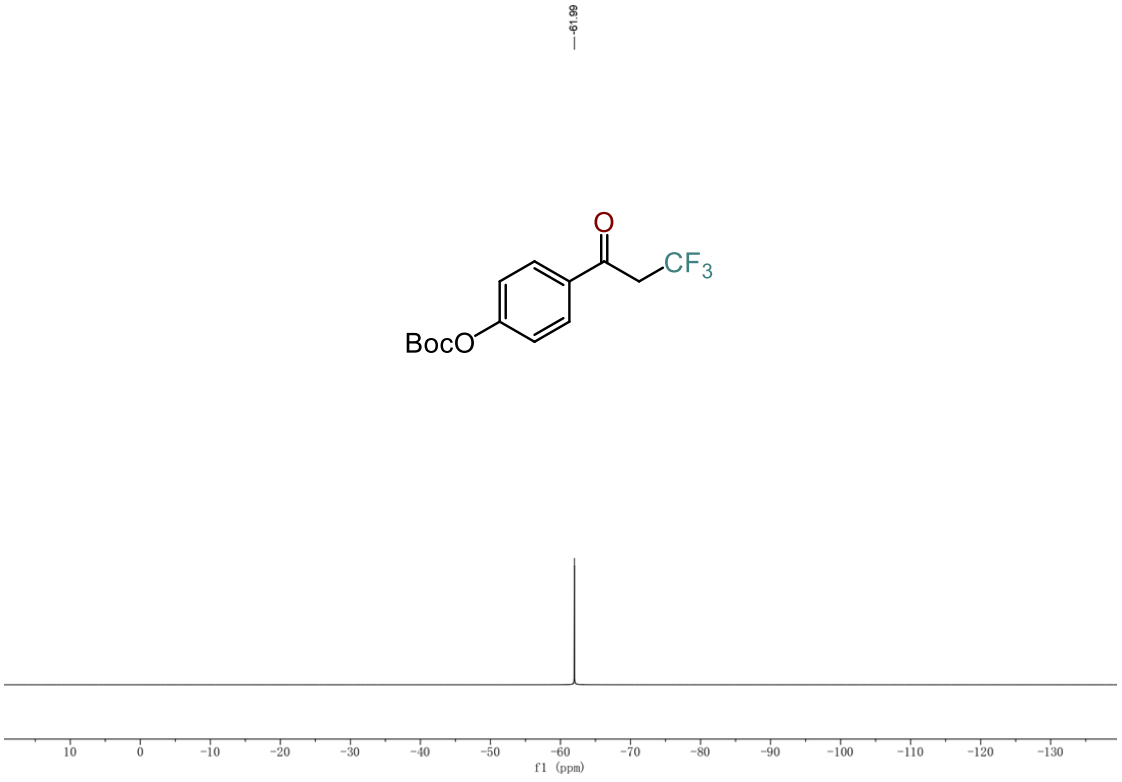




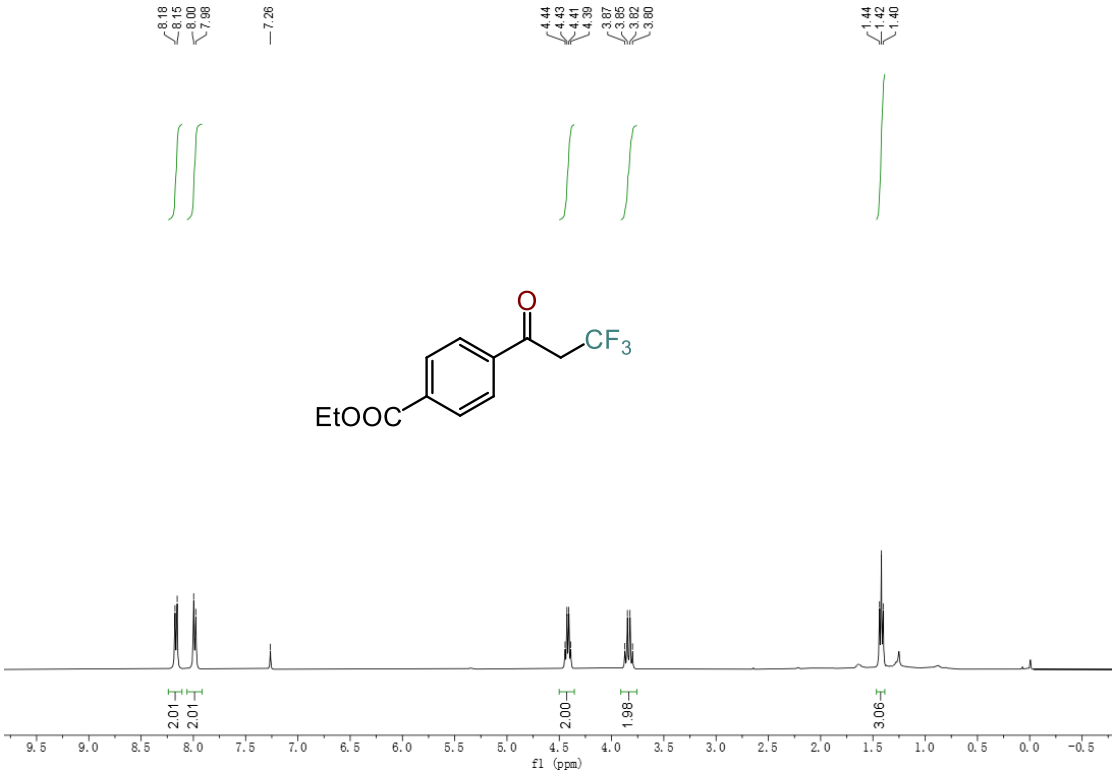
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (470 MHz, $CDCl_3$) spectra for 4n

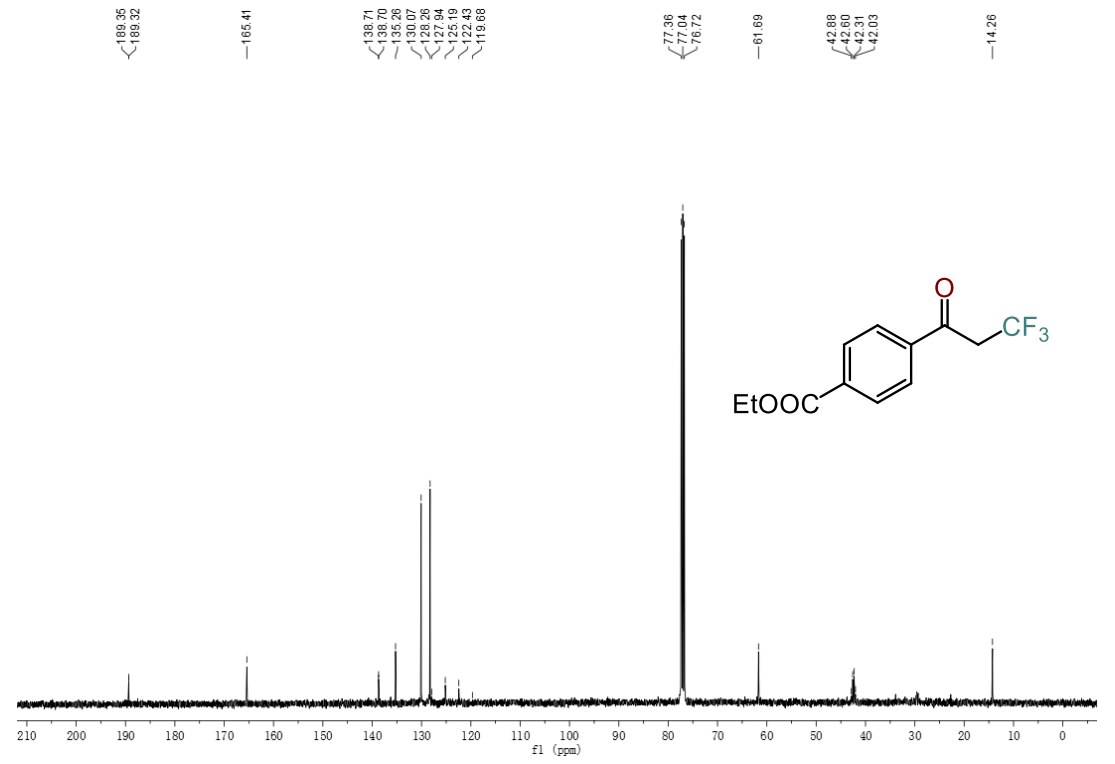


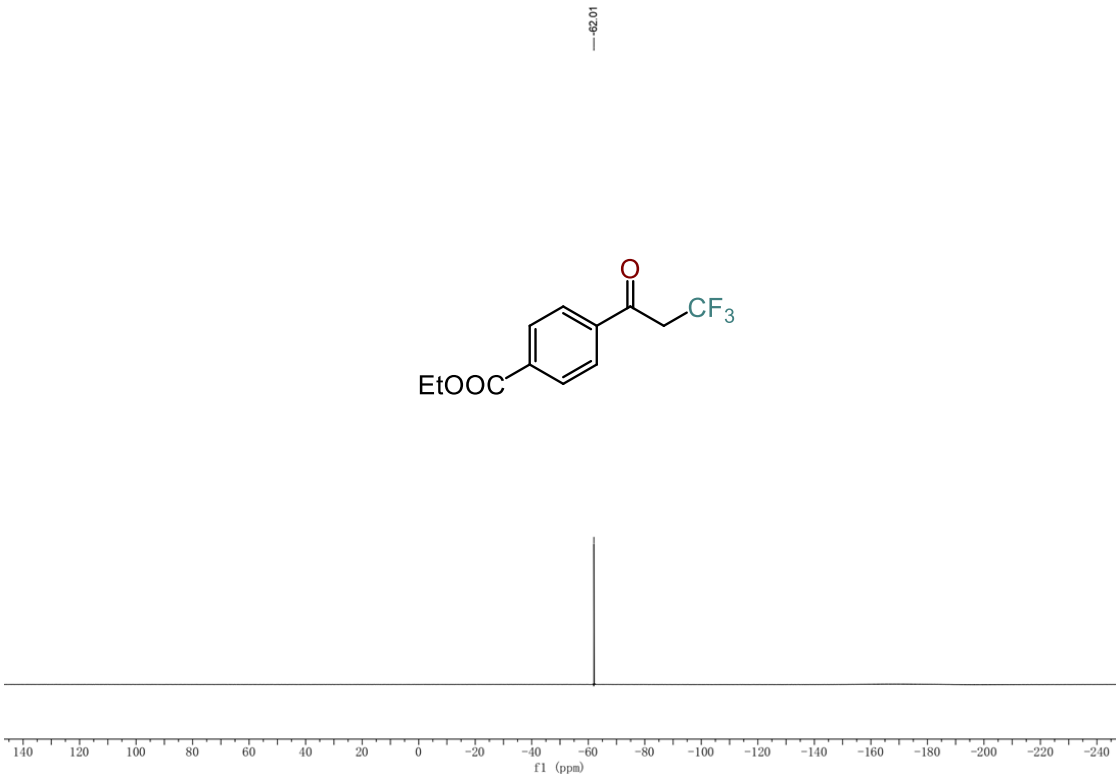

188.46
188.44
155.51
150.82
133.15
133.13
130.08
128.05
125.29
122.54
121.71
119.78
84.52
77.36
77.04
76.73
42.55
42.27
41.99
41.70
27.65
O
CF3
BocO
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-61.99
O
CF3
BocO
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130
f1 (ppm)

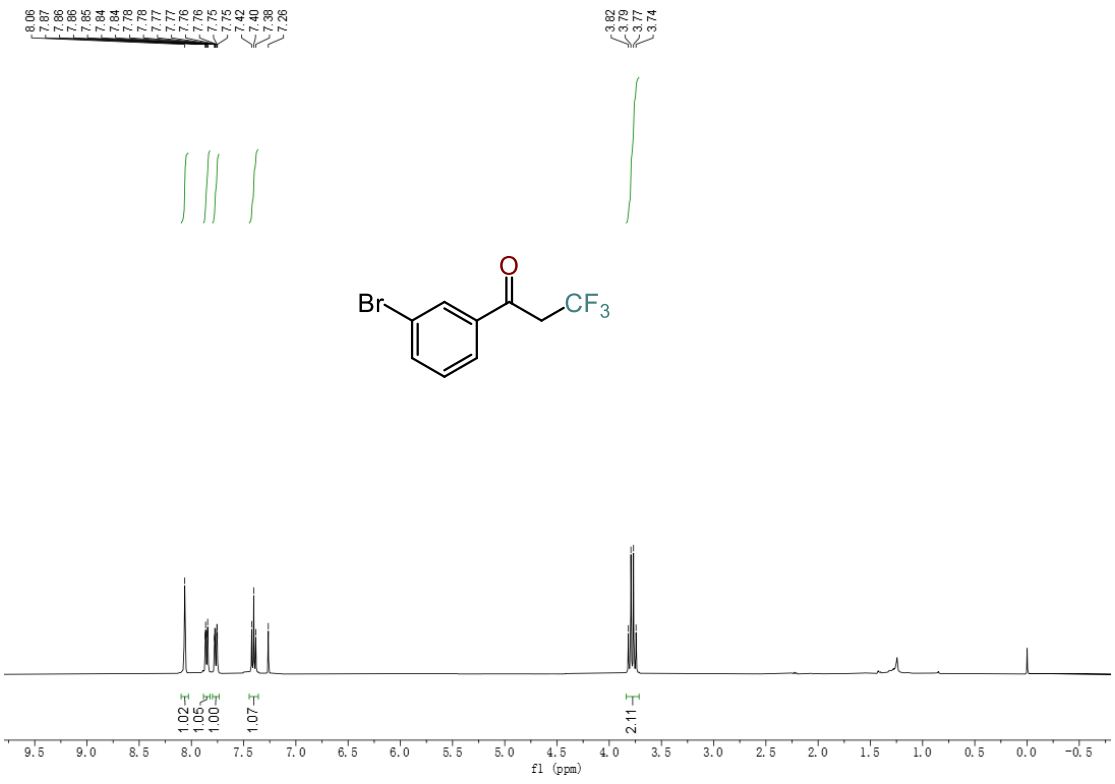
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (470 MHz, $CDCl_3$) spectra for 4o

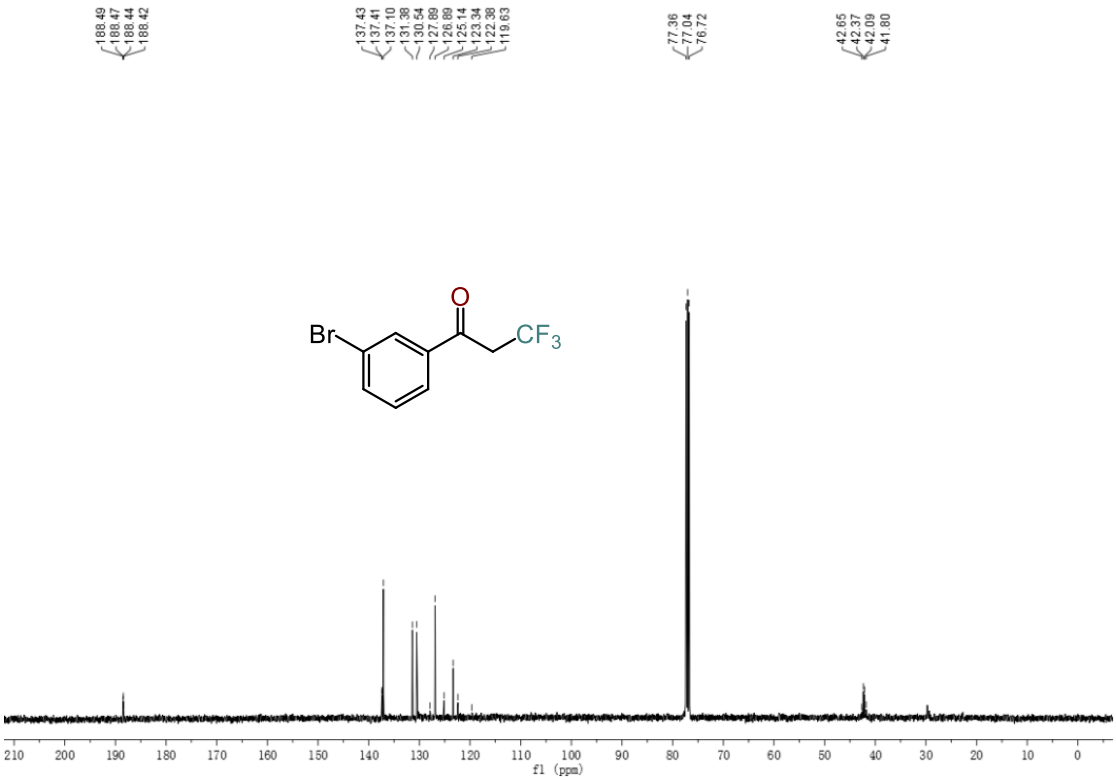






^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (470 MHz, $CDCl_3$) spectra for 4p

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188.47
188.44
188.42
137.43
137.41
137.10
131.38
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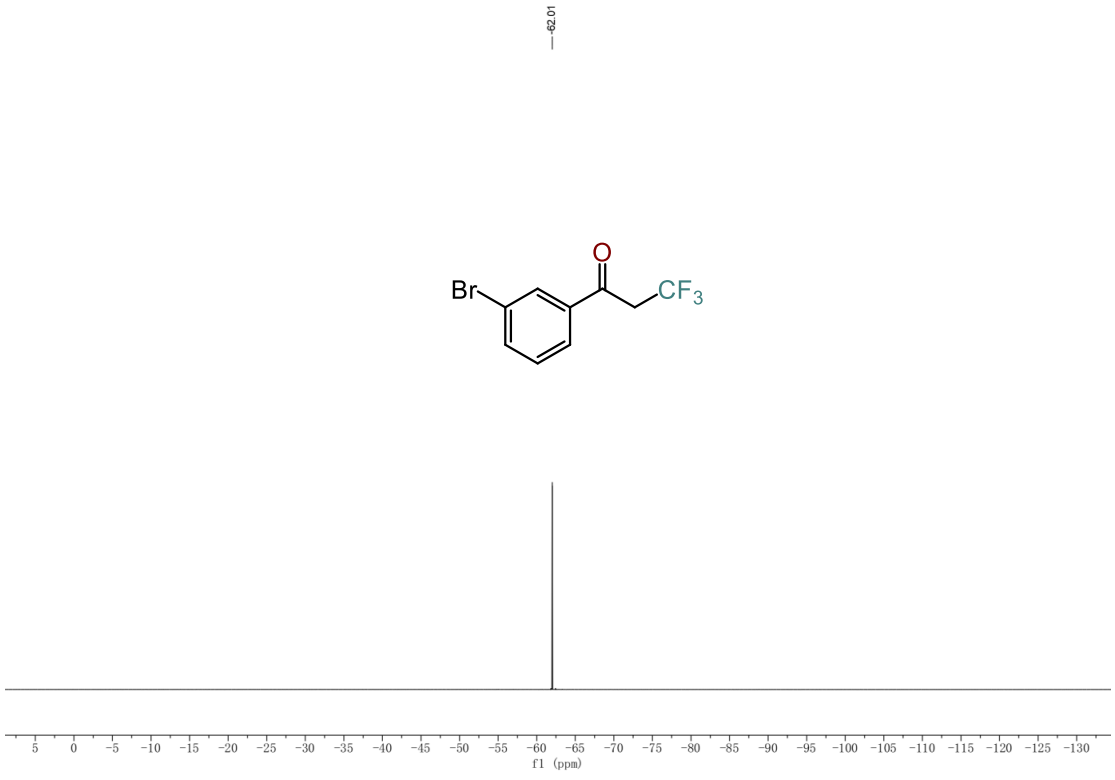
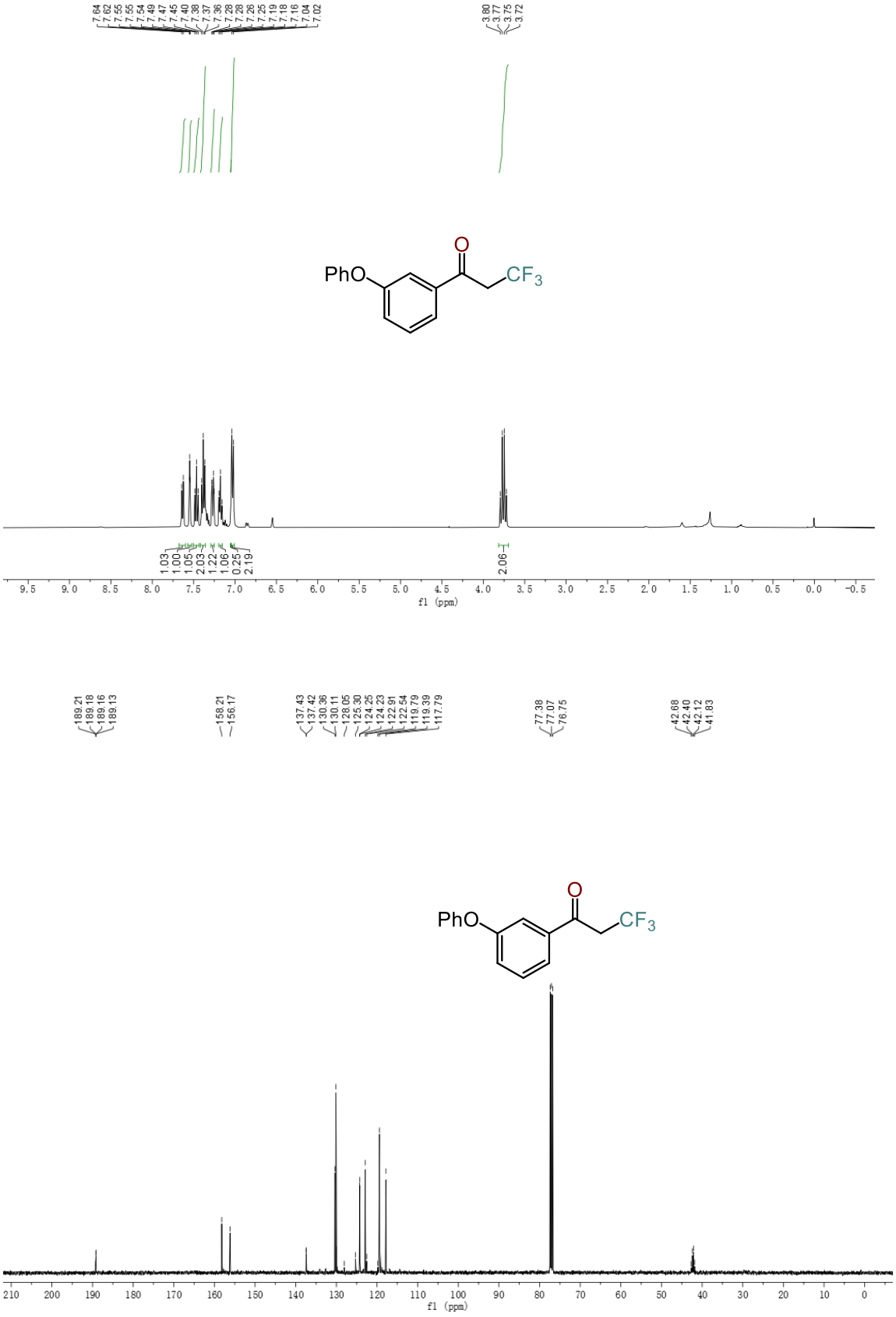
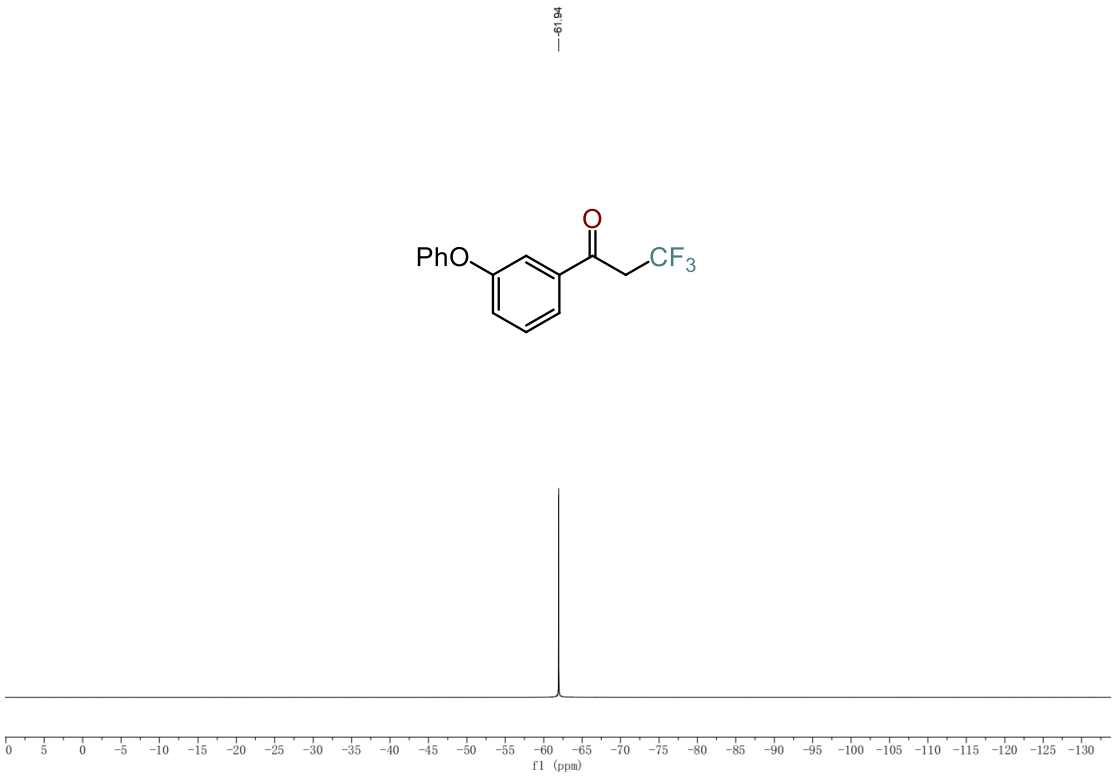
127.89
126.89
125.14
123.34
122.38
119.63
77.36
77.04
76.72
42.65
42.37
42.09
41.80
Br
O
CF3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

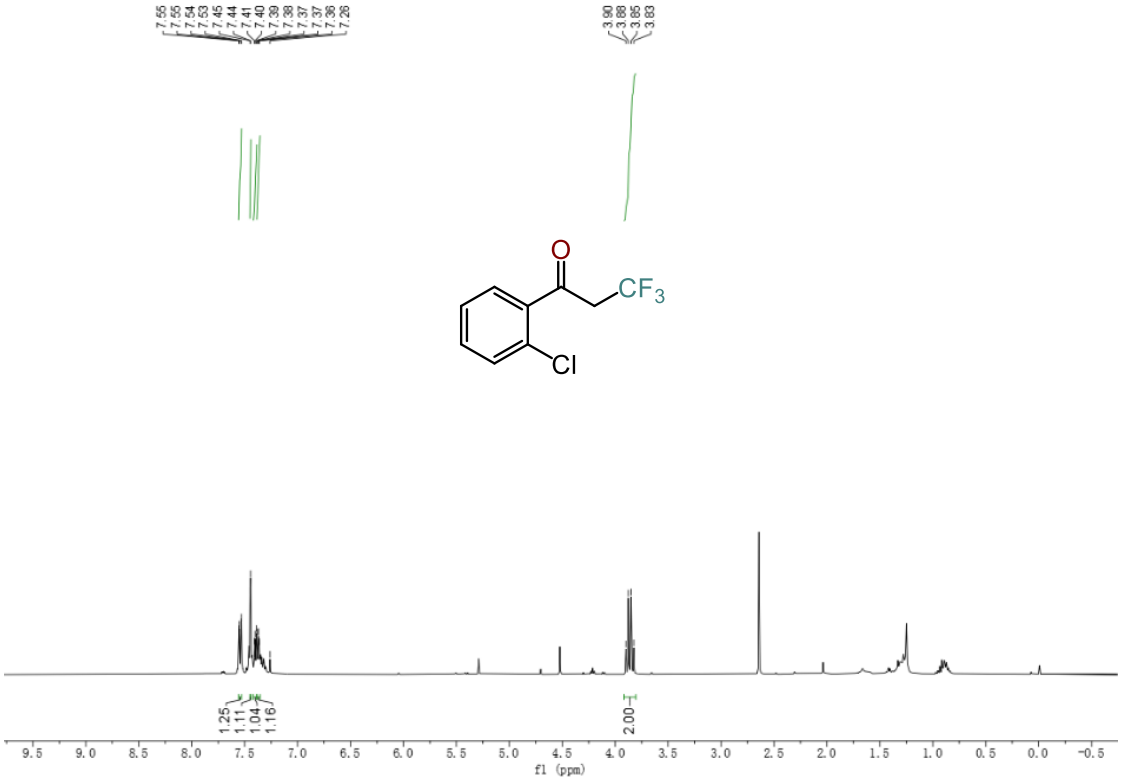

-62.01
Br
O
CF3
5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130
f1 (ppm)

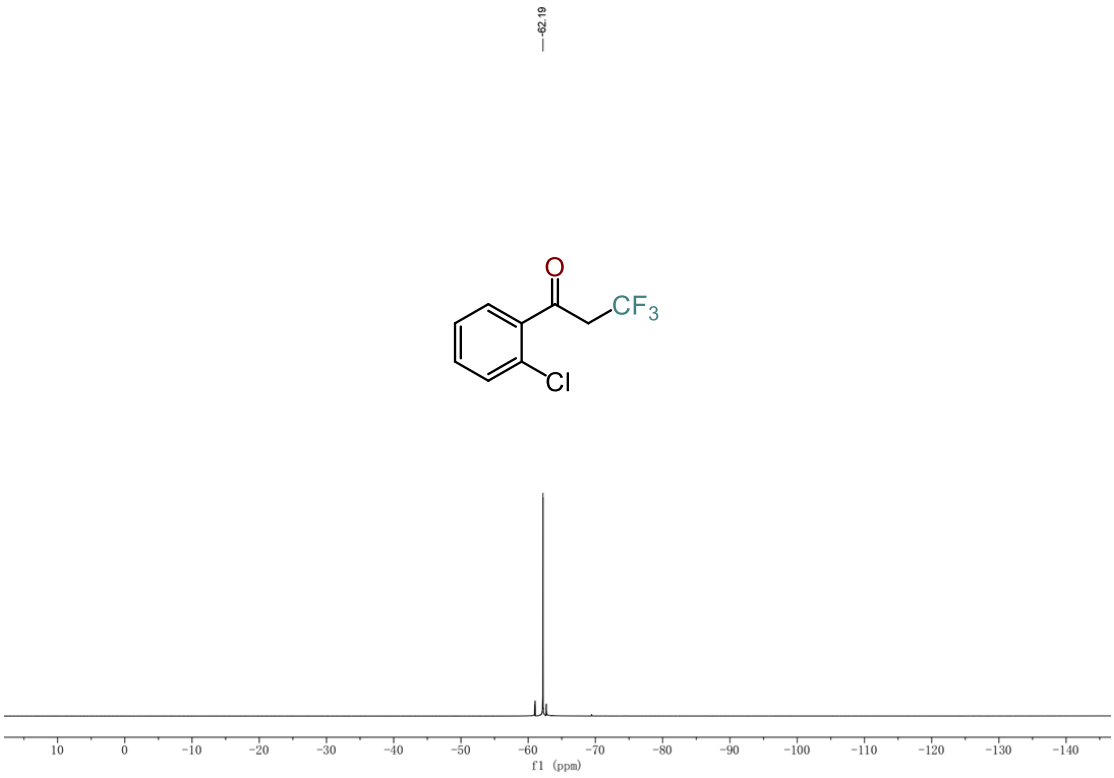
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (470 MHz, $CDCl_3$) spectra for 4q



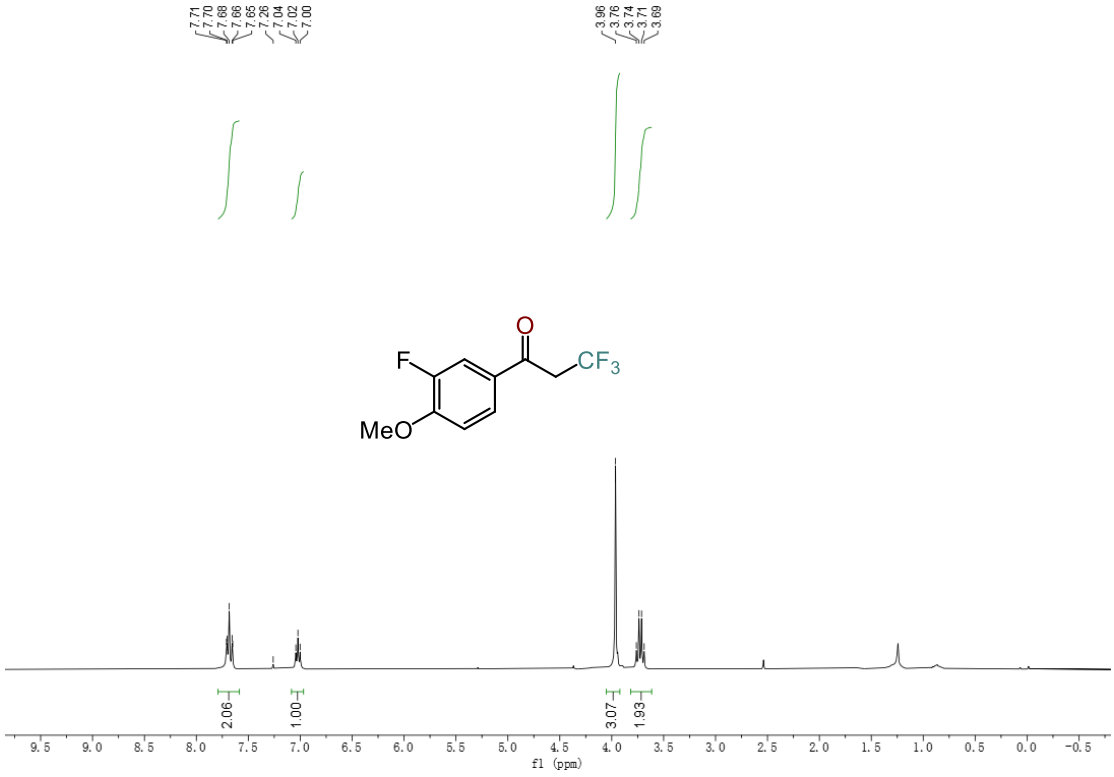


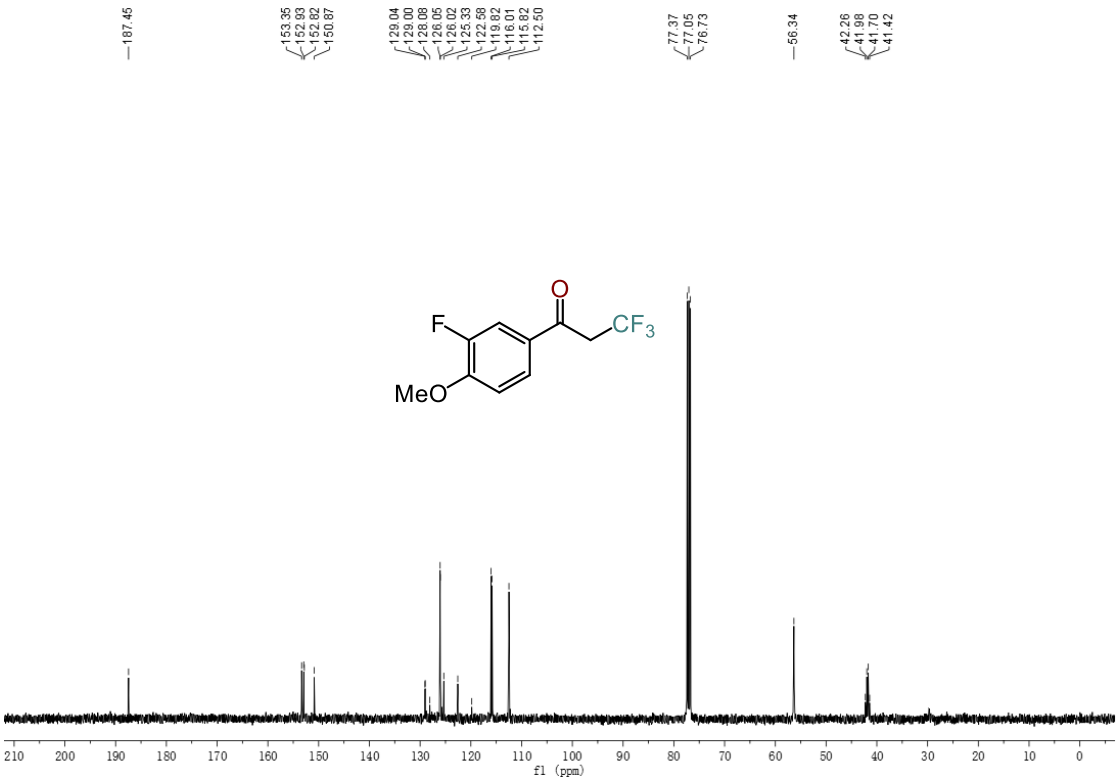
^{1}H NMR (400 MHz, $CDCl_3$) and ^{19}F NMR (470 MHz, $CDCl_3$) spectra for 4r

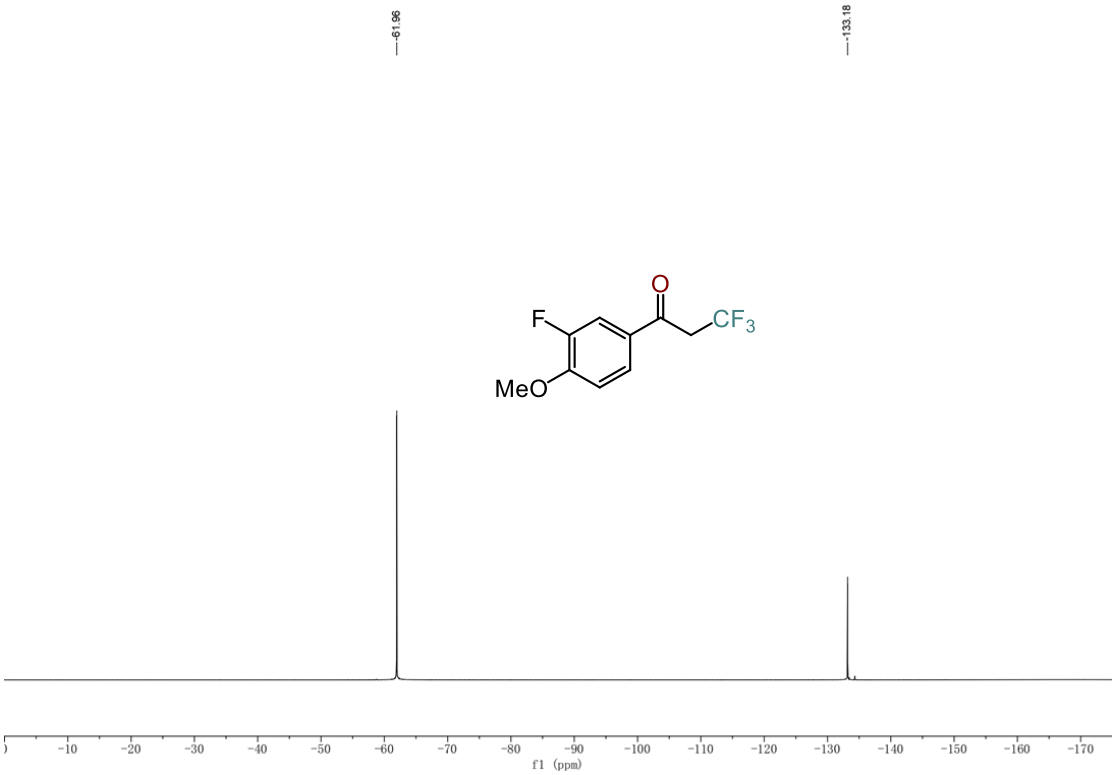




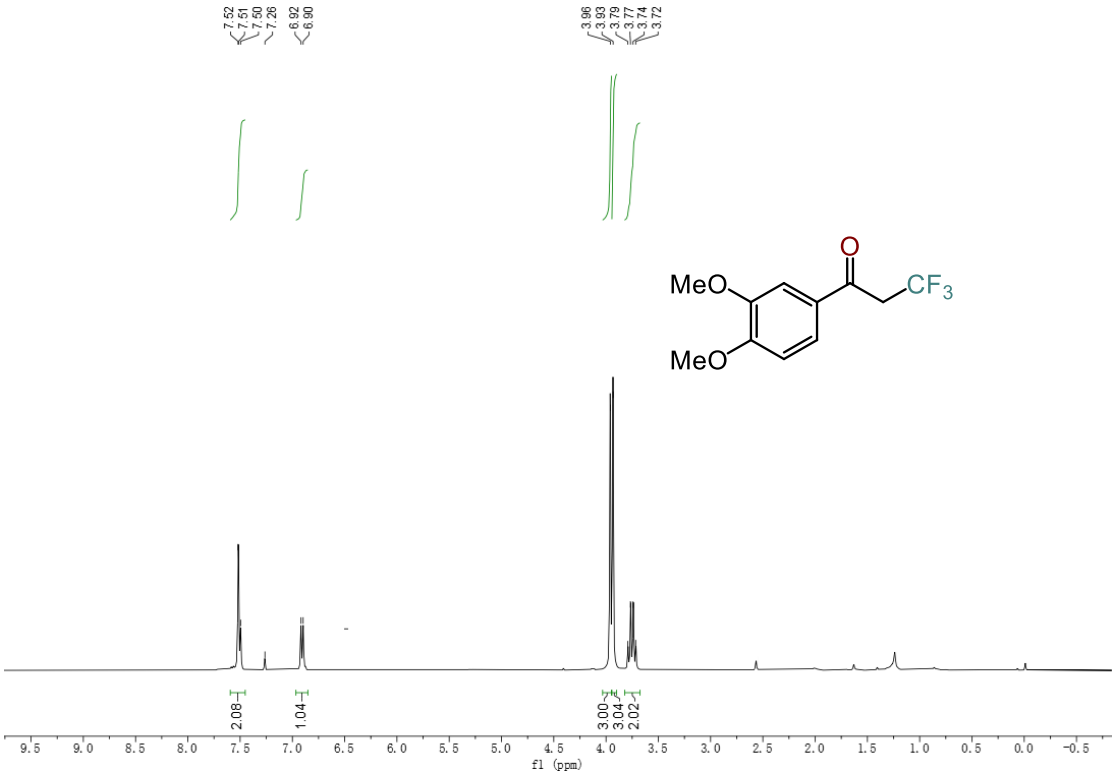
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (470 MHz, $CDCl_3$) spectra for 4s

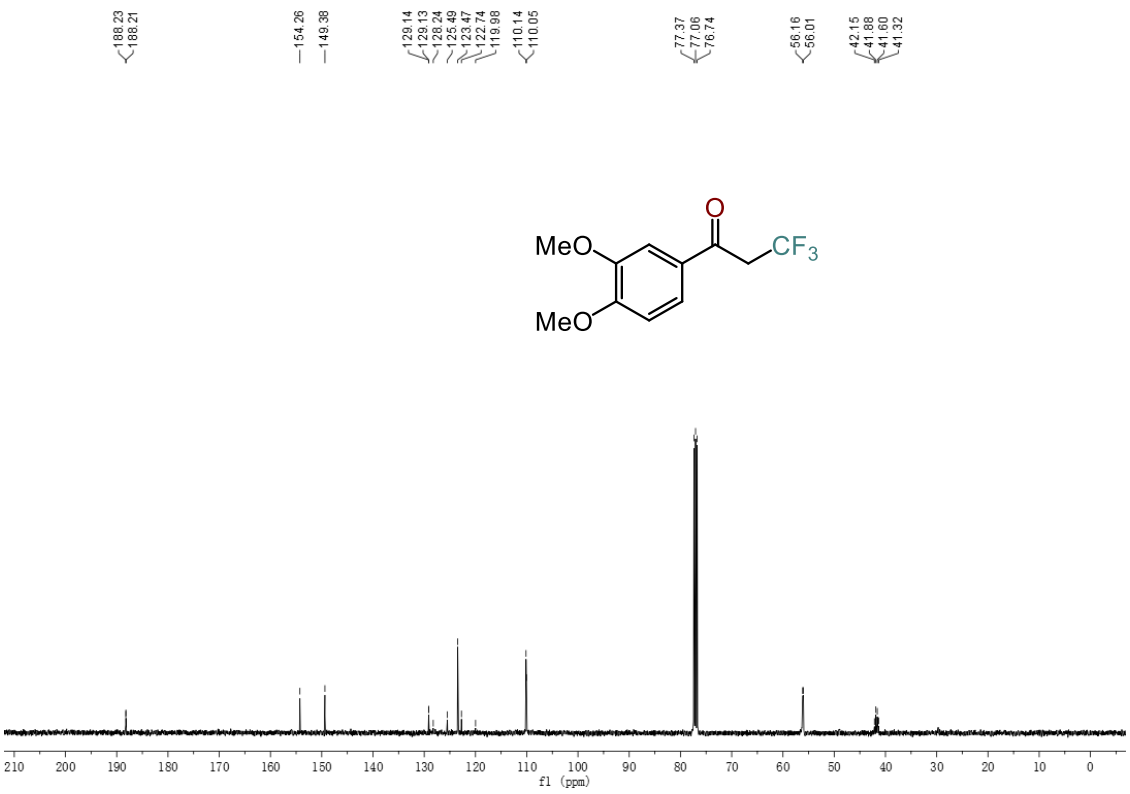


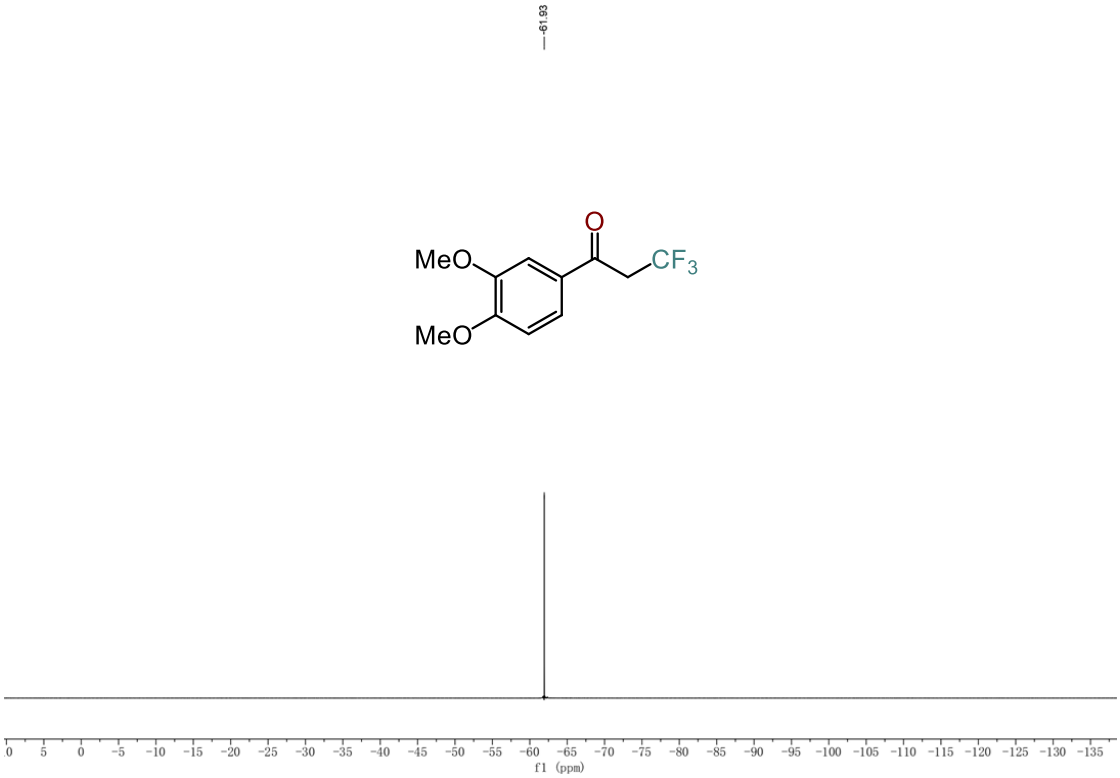

187.45
153.35
152.93
152.82
150.87
129.04
129.00
128.08
126.05
126.02
125.33
122.58
119.82
116.01
115.82
112.50
77.37
77.05
76.73
56.34
42.26
41.98
41.70
41.42
O
F
CF3
MeO
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-61.96
-133.18
O
F
CF3
MeO
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170
f1 (ppm)

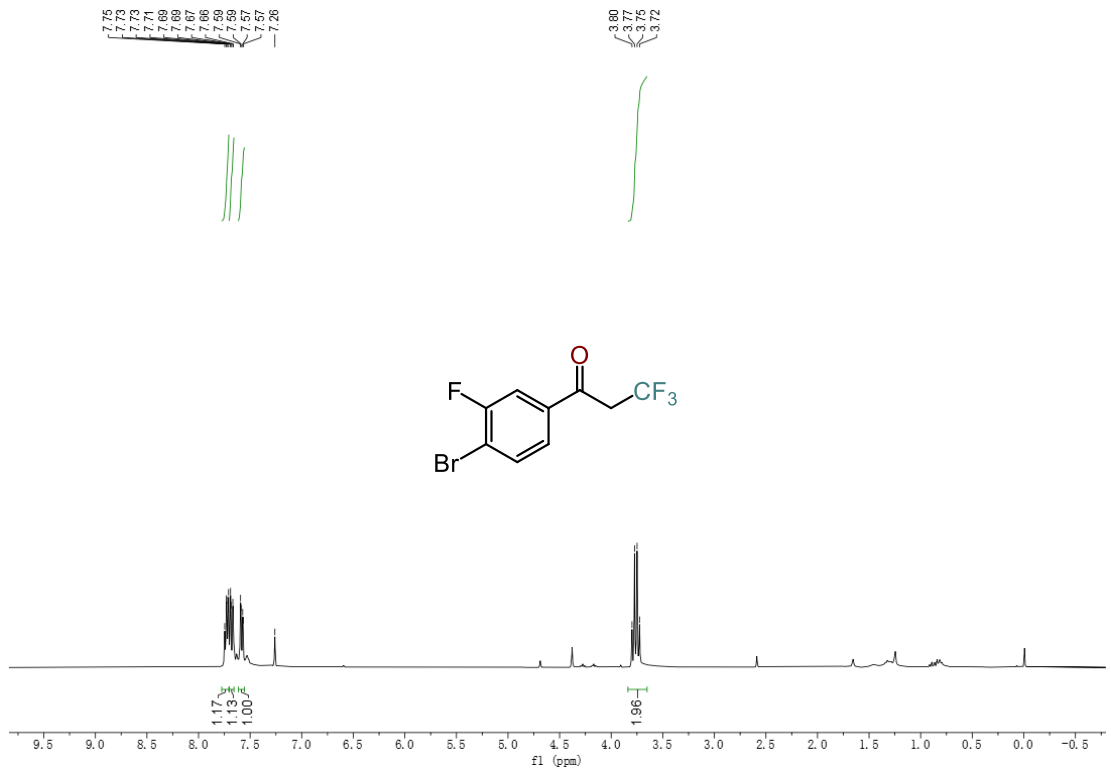
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (470 MHz, $CDCl_3$) spectra for 4t

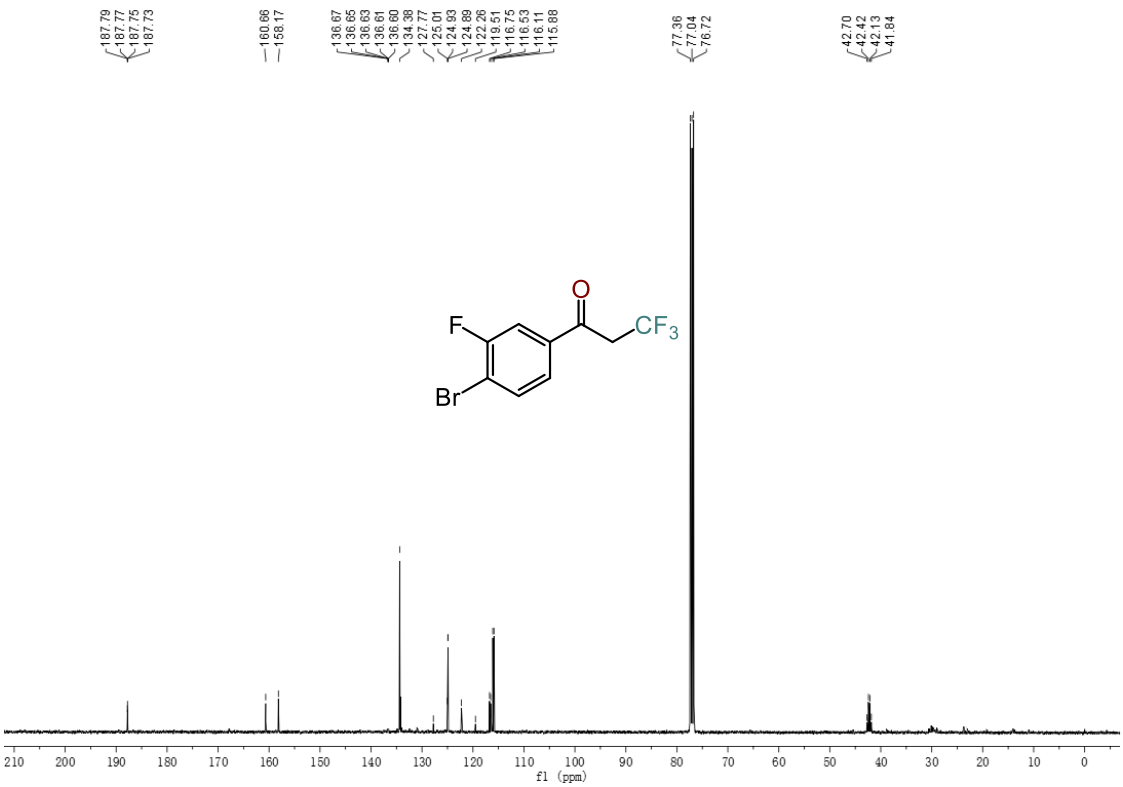






^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (470 MHz, $CDCl_3$) spectra for 4u

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187.77
187.75
187.73
160.06
158.17
136.67
136.65
136.63
136.61
136.60
134.38
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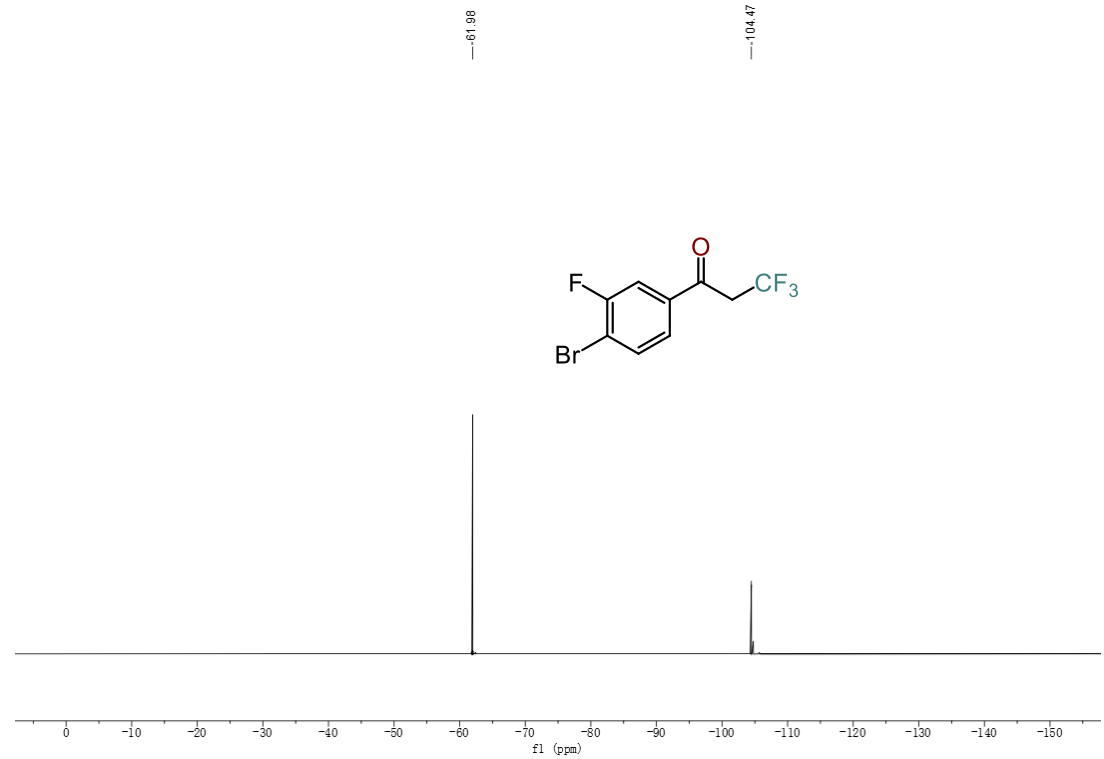
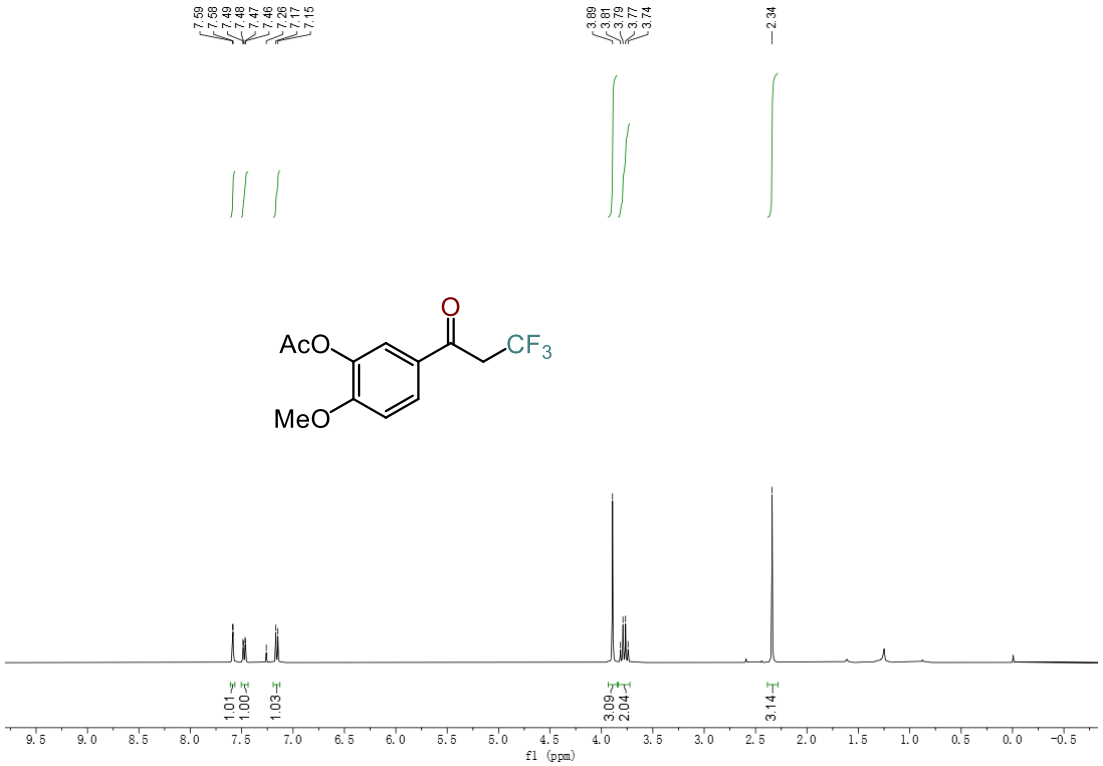
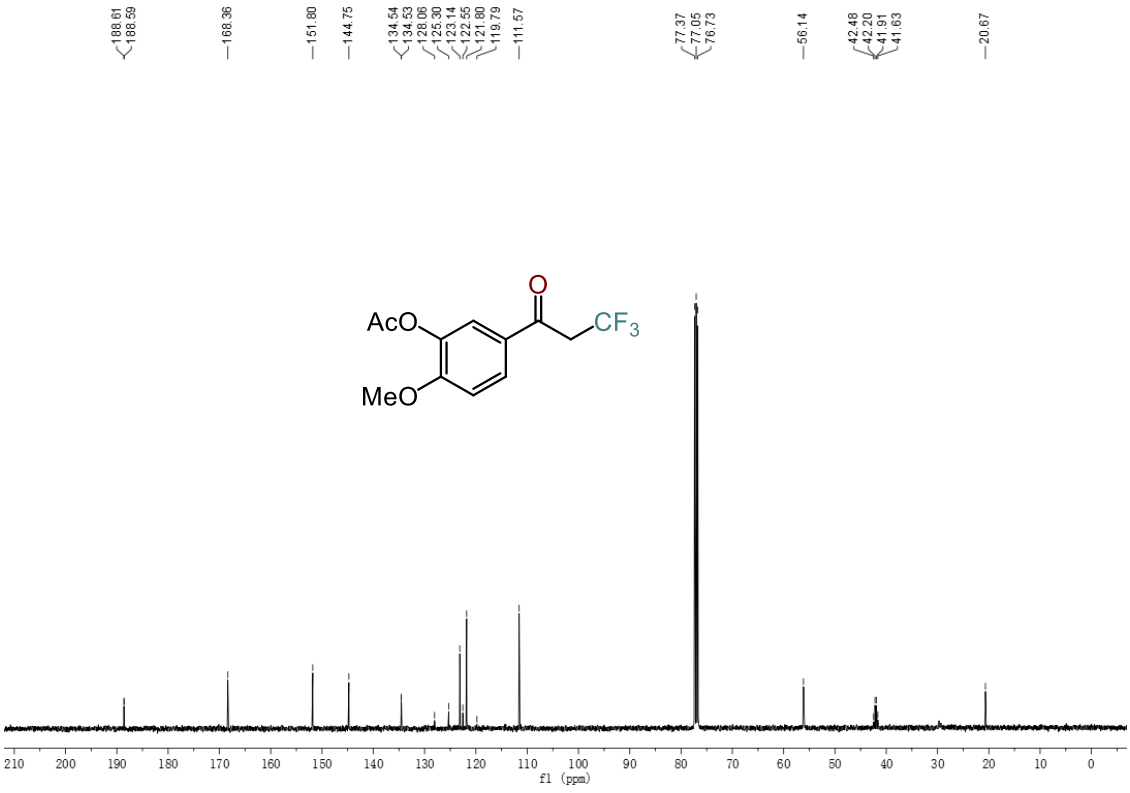
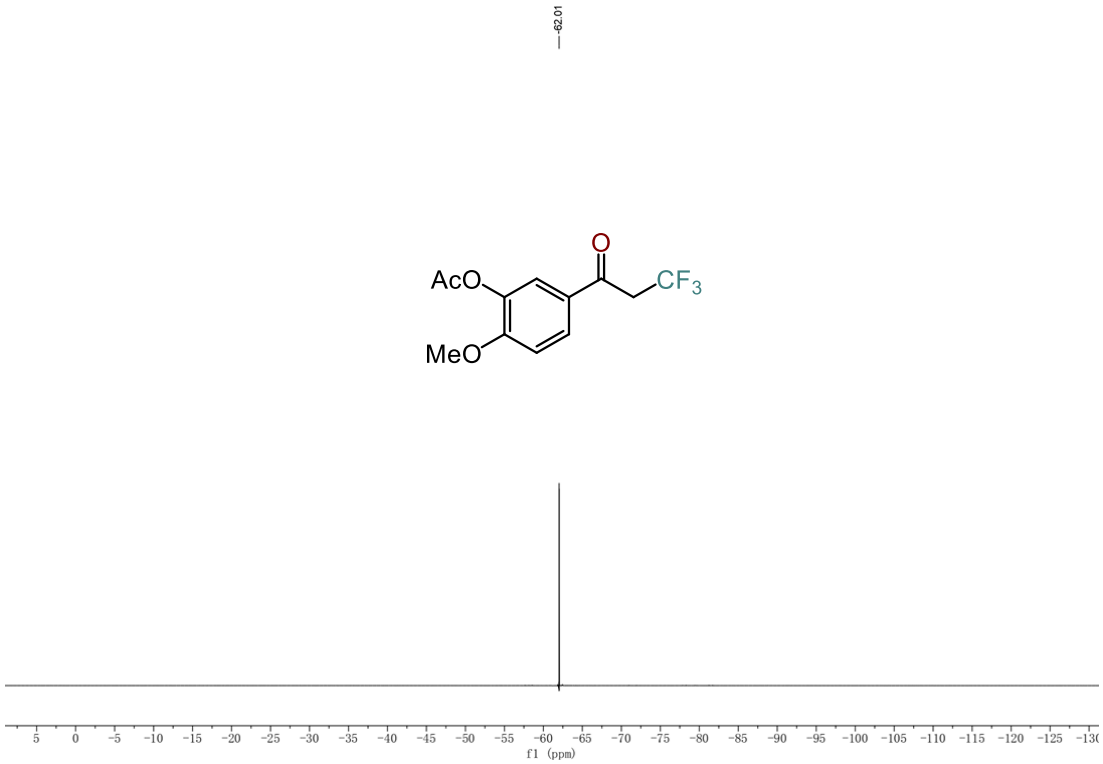
125.01
124.93
124.89
122.26
119.51
116.75
116.53
116.11
115.88
77.36
77.04
76.72
42.70
42.42
42.13
41.84
O
F
Br
CF3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-61.98
-104.47
O
F
Br
CF3
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150
f1 (ppm)

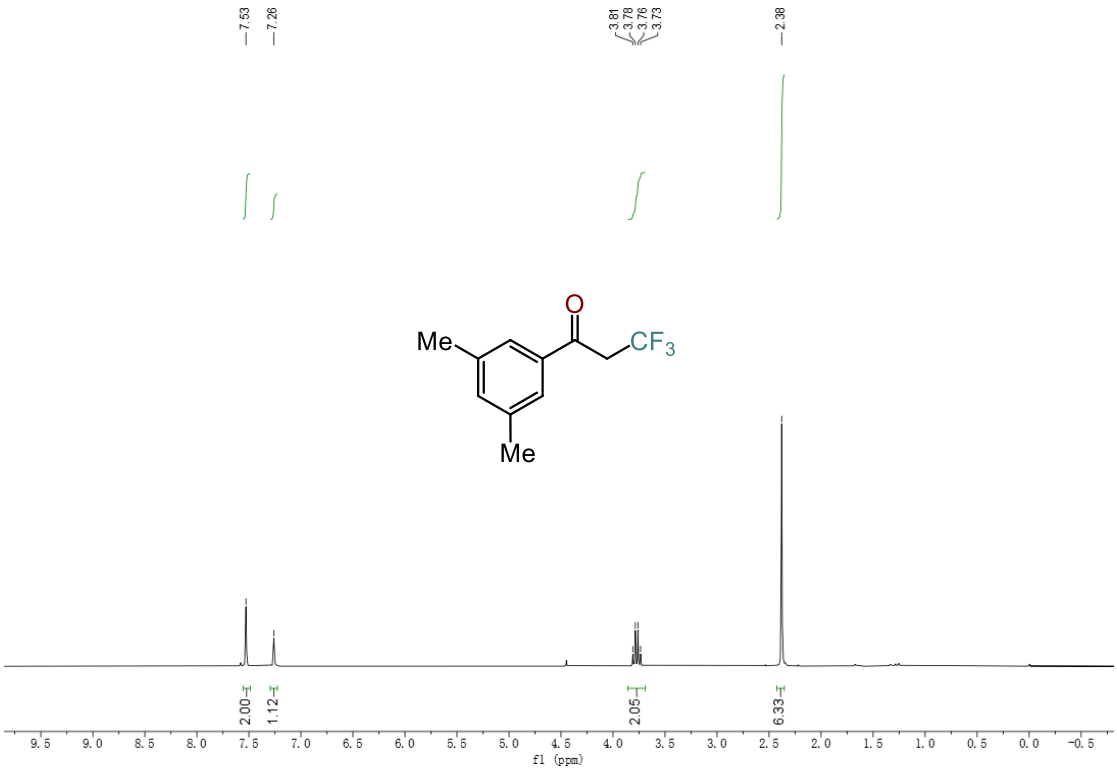
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (470 MHz, $CDCl_3$) spectra for 4v

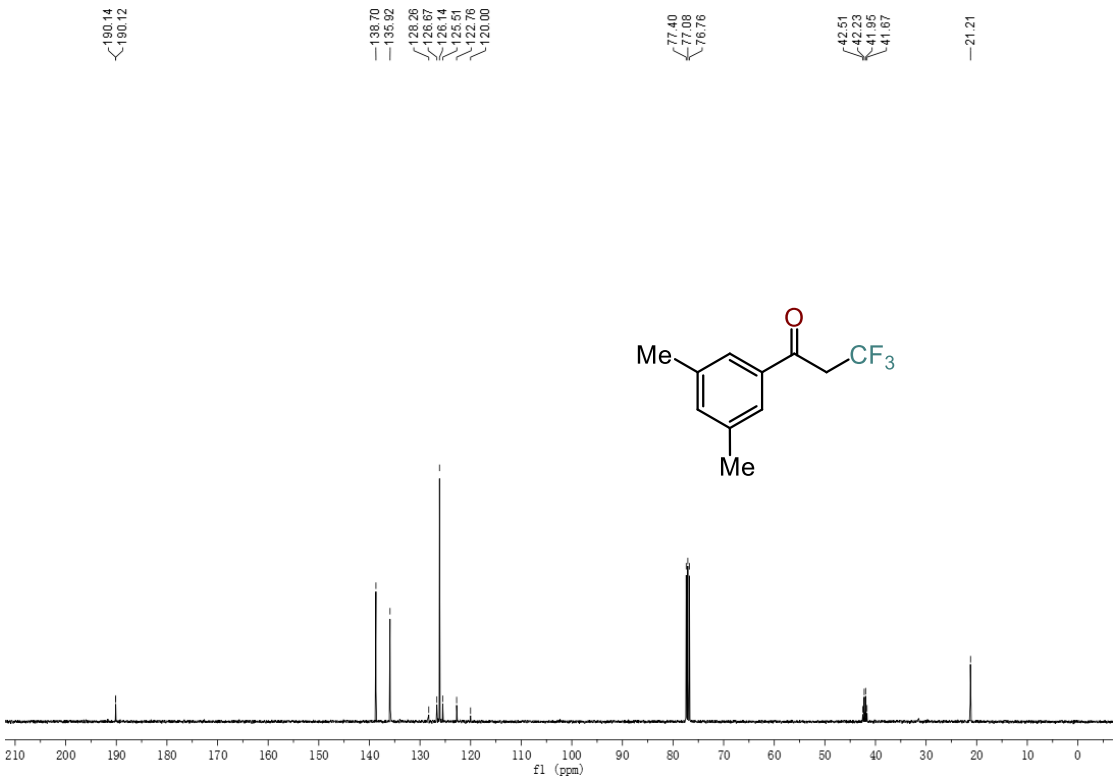


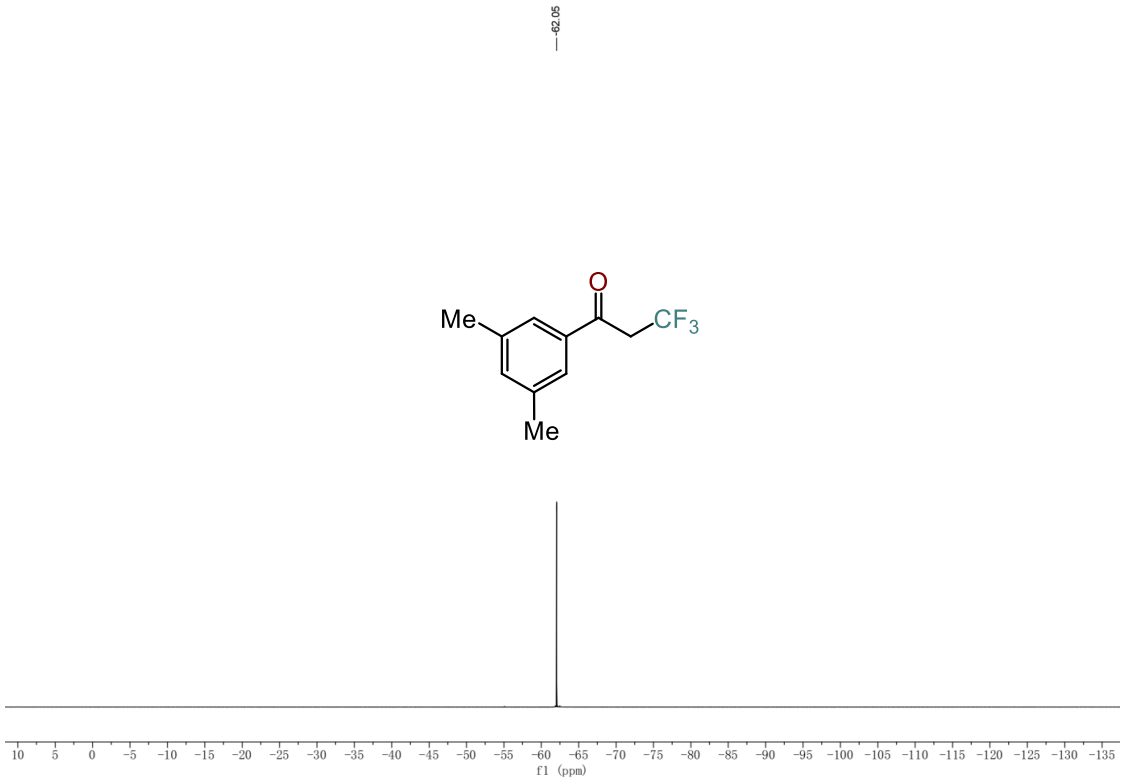




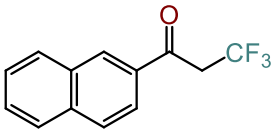
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (470 MHz, $CDCl_3$) spectra for 4w

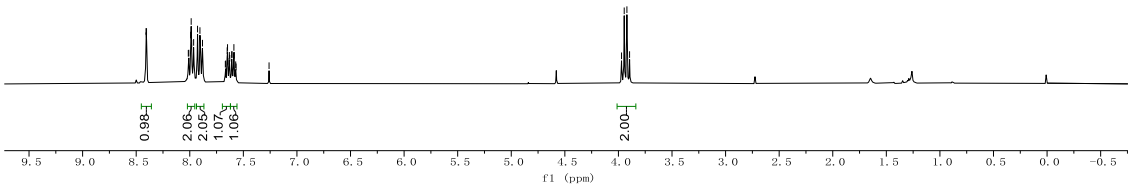


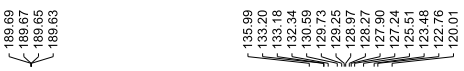

190.14
190.12
138.70
135.92
128.26
126.67
126.14
125.51
122.76
120.00
77.40
77.08
76.76
42.51
42.23
41.95
41.67
21.21
O
Me
CF3
Me
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

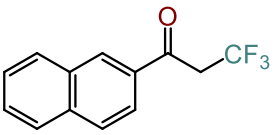

-62.05
O
Me
CF3
Me
10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135
f1 (ppm)

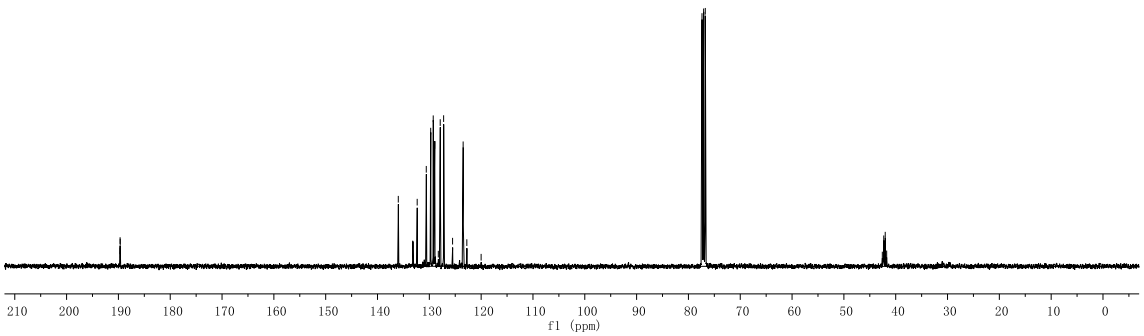
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (470 MHz, $CDCl_3$) spectra for 4x

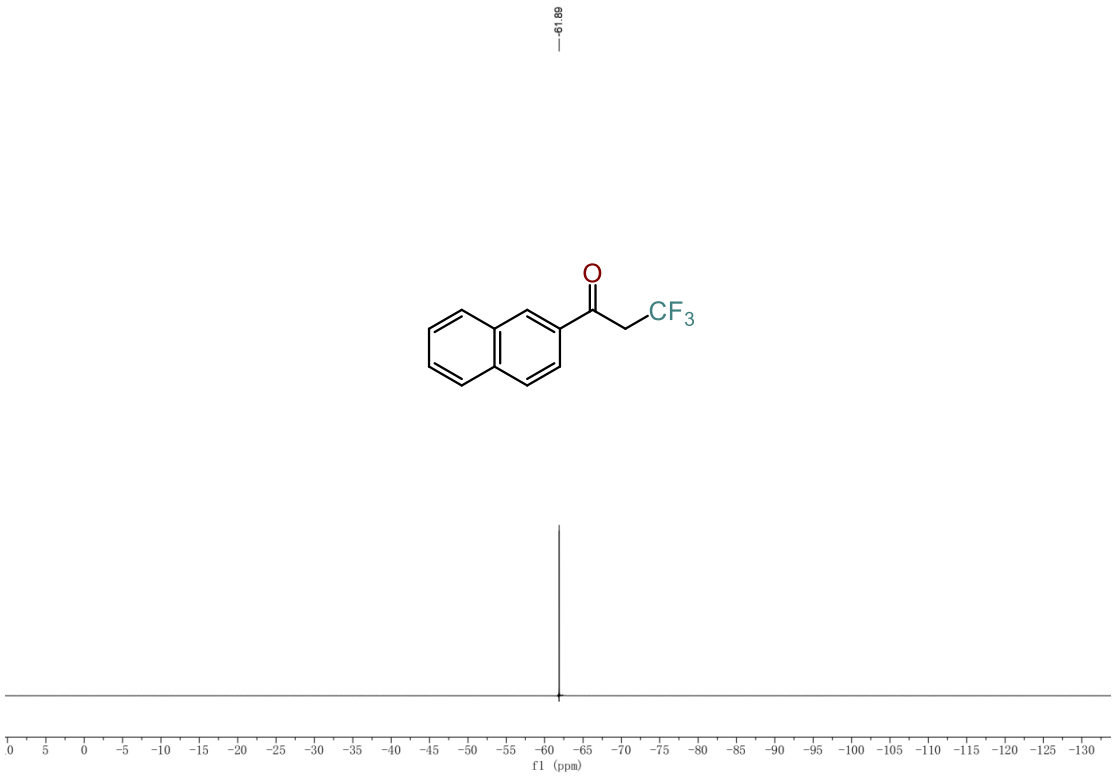




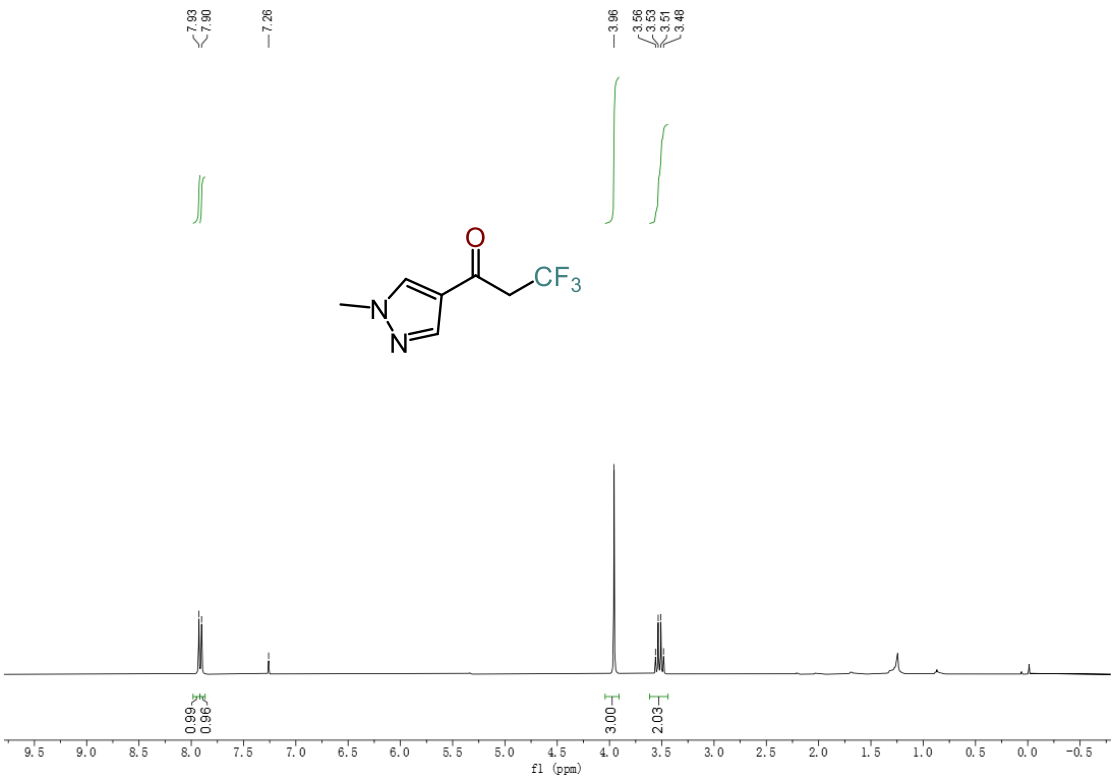


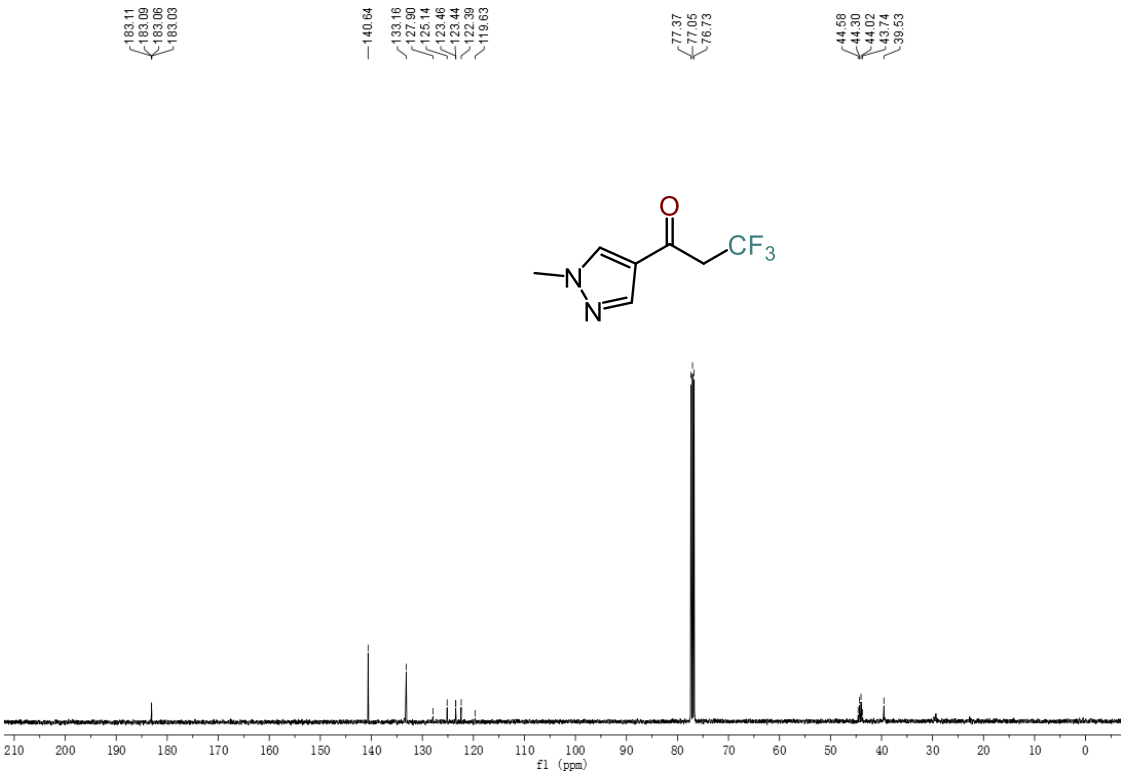


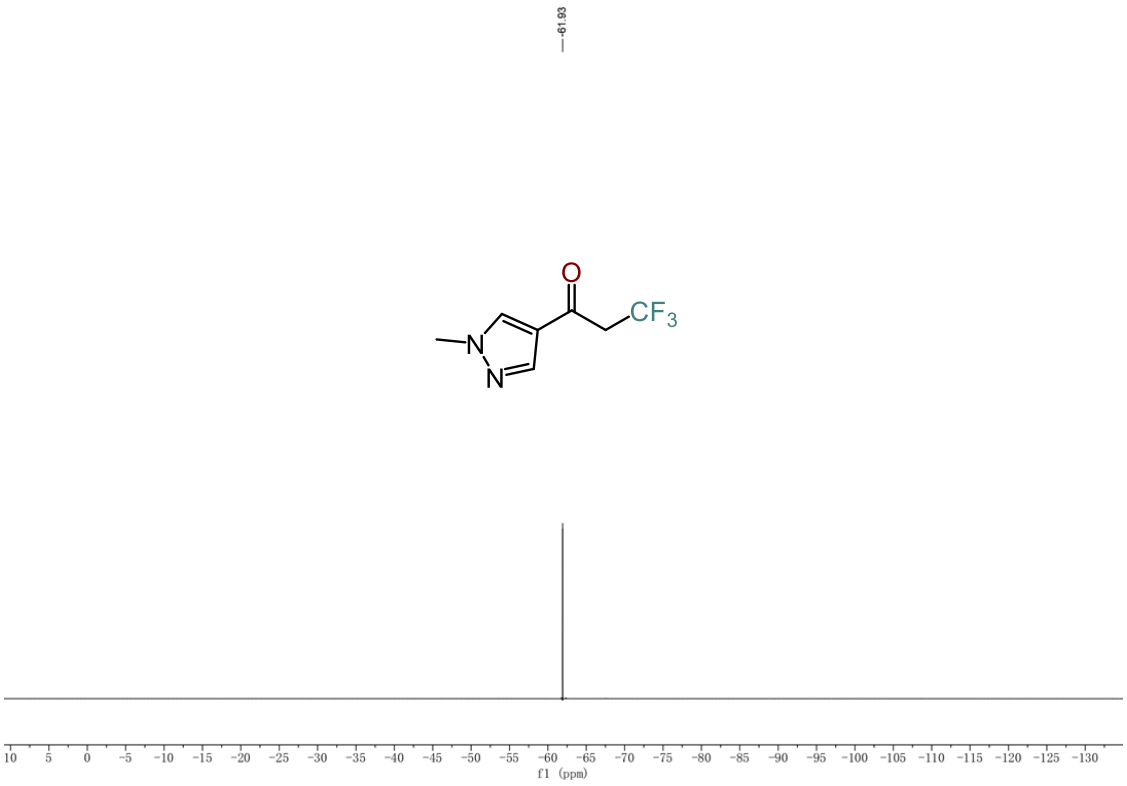




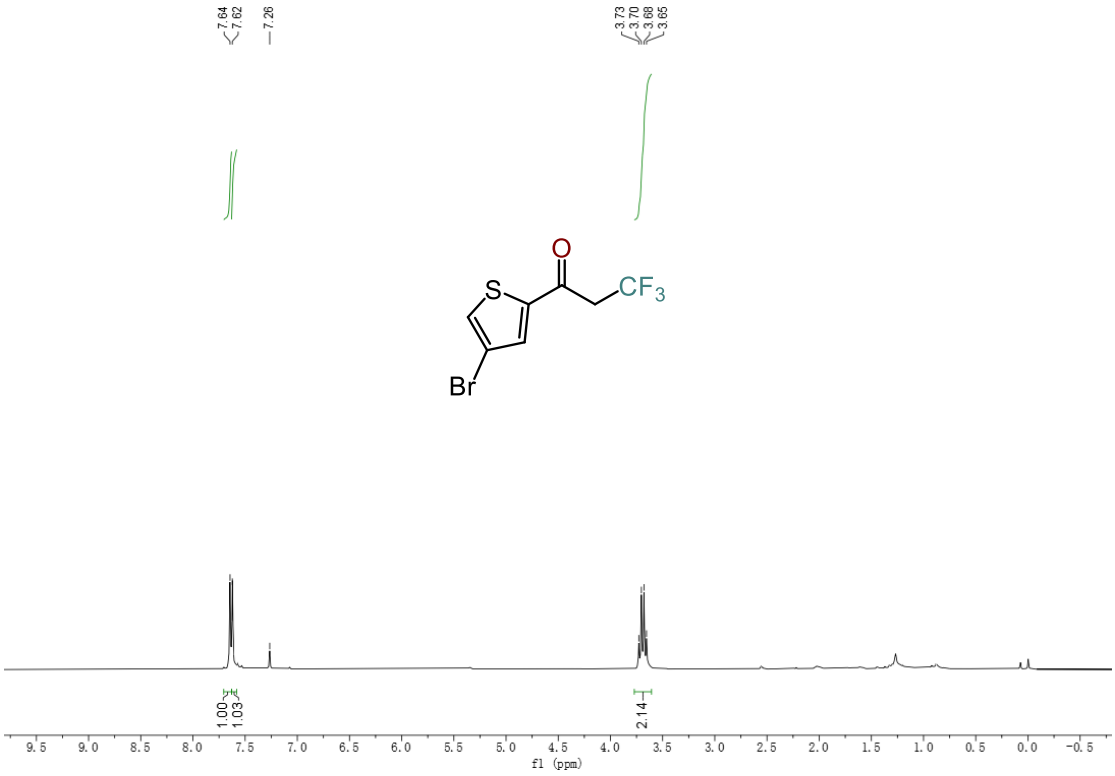
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (470 MHz, $CDCl_3$) spectra for 4y

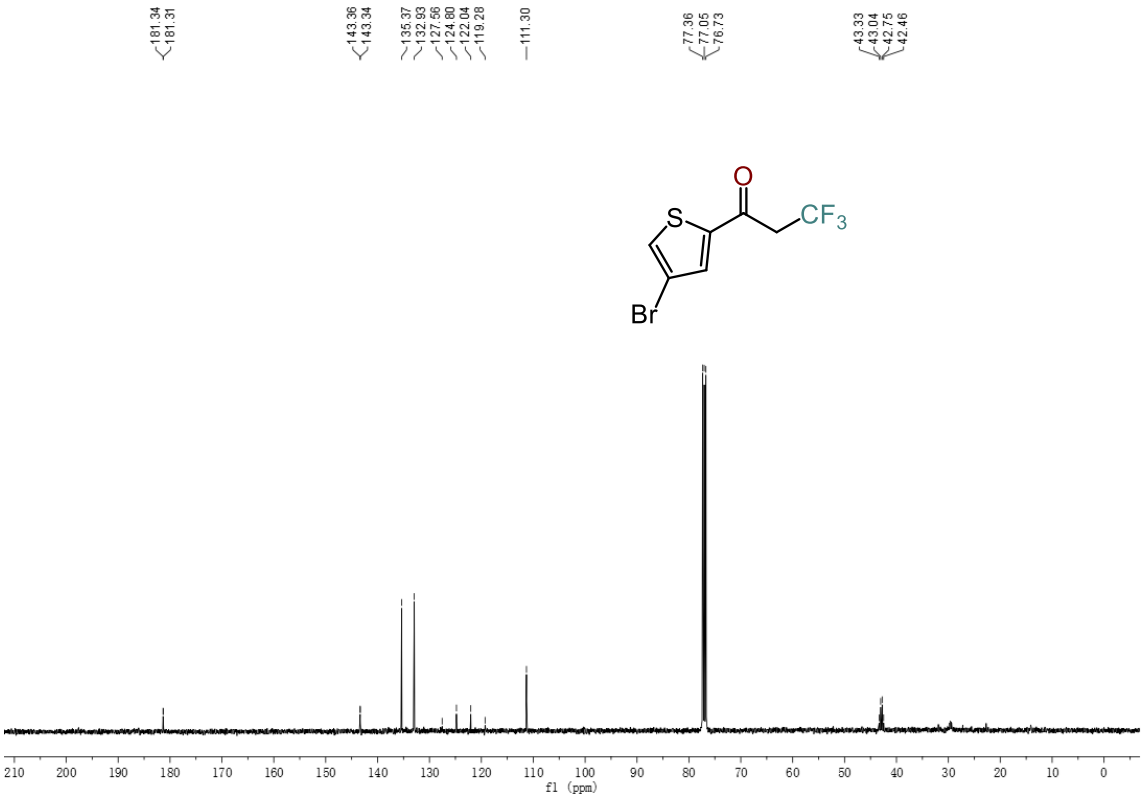


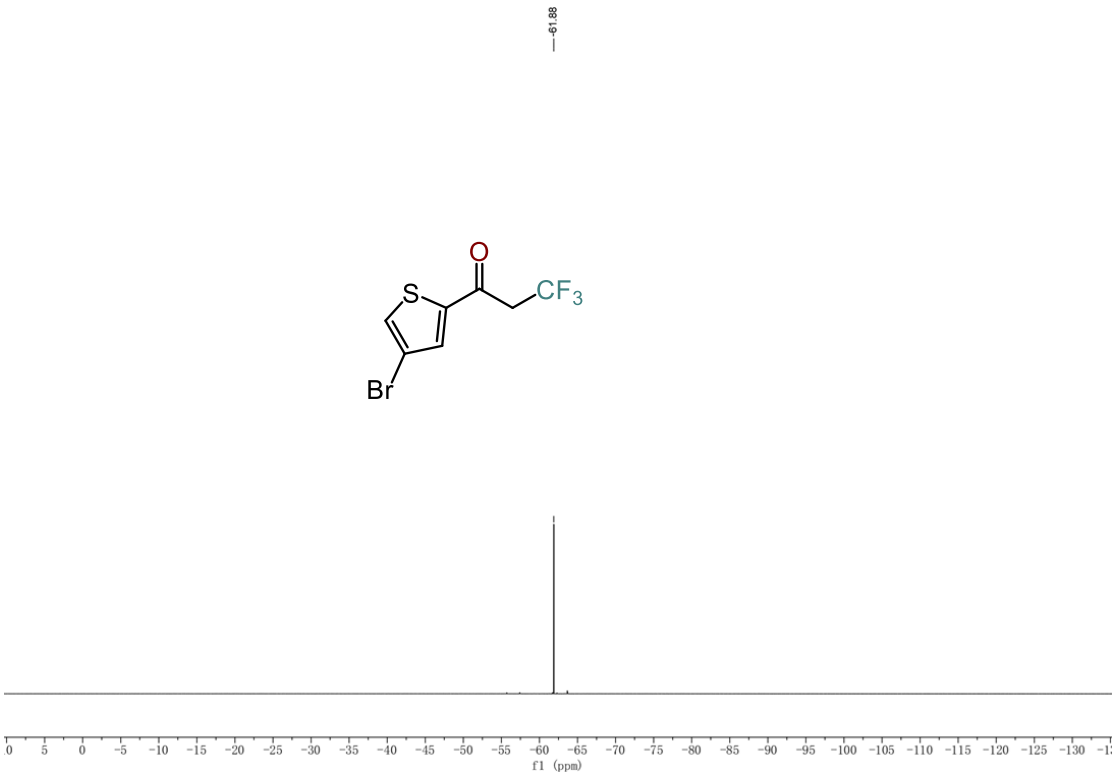

183.11
183.09
183.06
183.03
140.64
133.16
127.90
125.14
123.46
123.44
122.39
119.63
77.37
77.05
76.73
44.58
44.30
44.02
43.74
39.53
O
CF3
N
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-61.93
O
CF3
N
N
10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130
f1 (ppm)

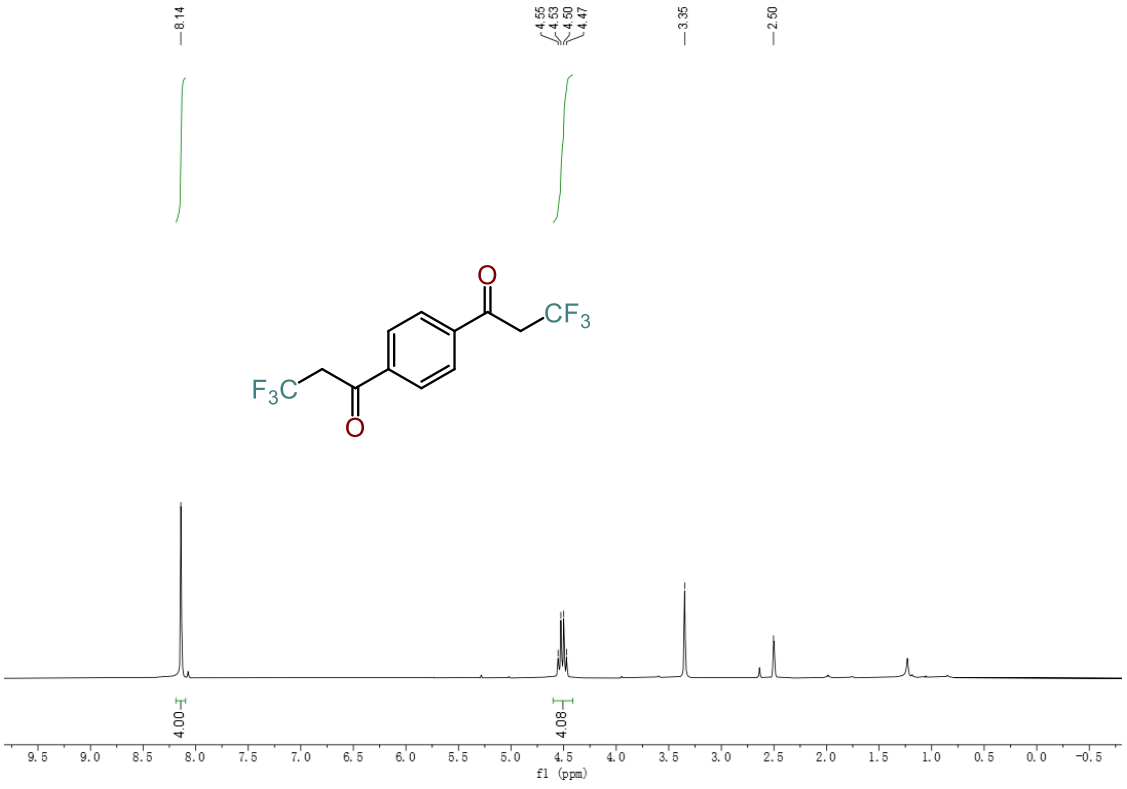
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (470 MHz, $CDCl_3$) spectra for 4z

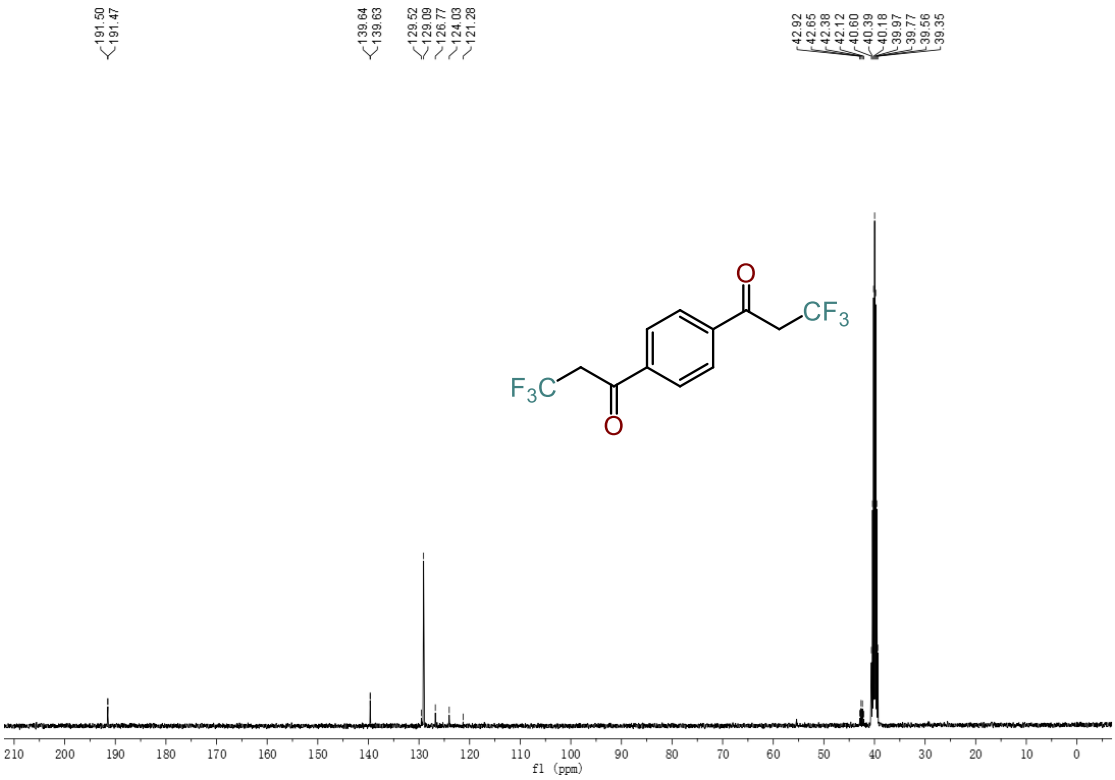






^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (470 MHz, $CDCl_3$) spectra for 4A

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129.09
126.77
124.03
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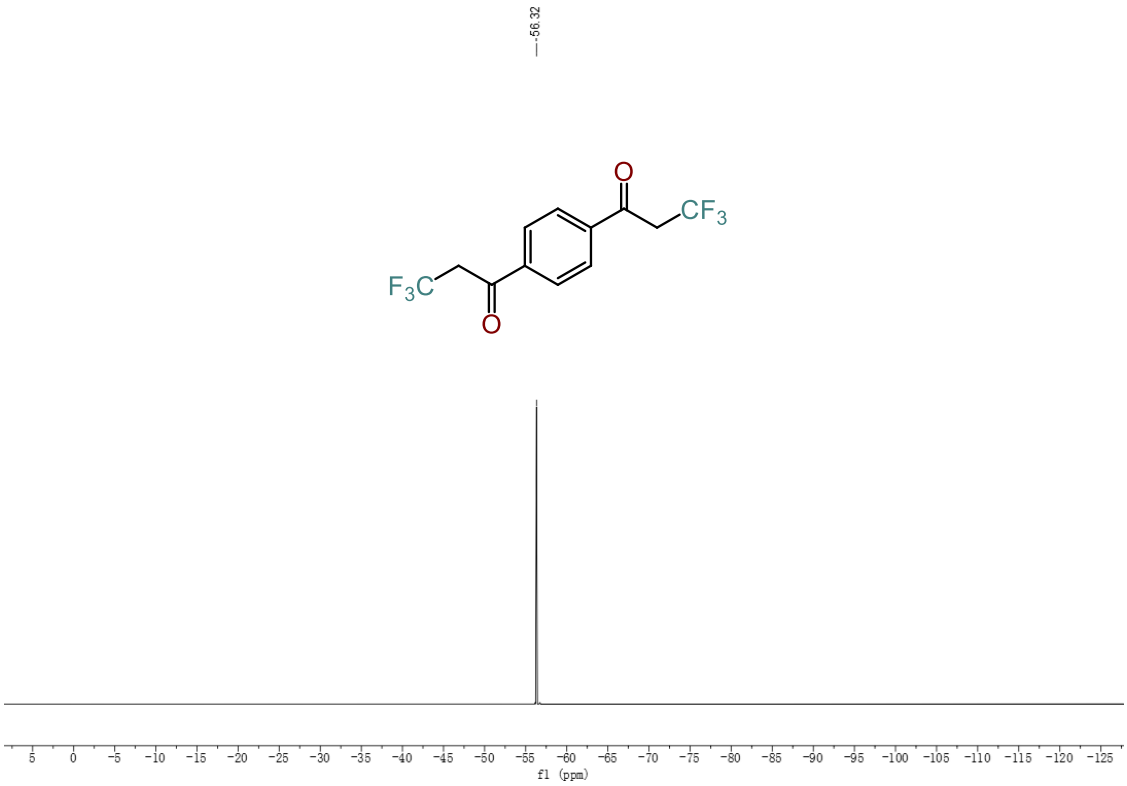
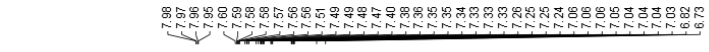
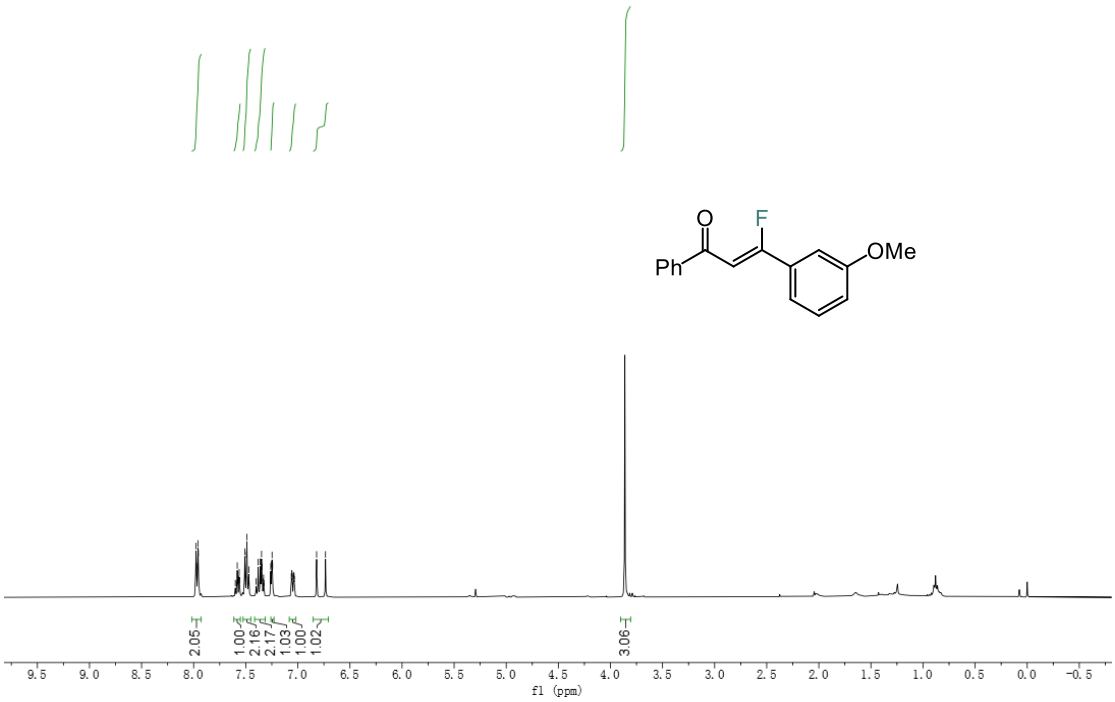
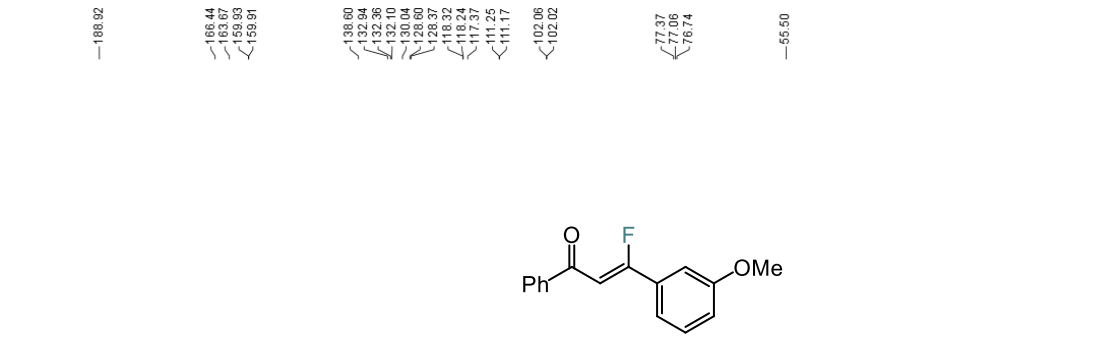
42.65
42.38
42.12
40.60
40.39
40.18
39.97
39.77
39.56
39.35
O
CF3
F3C
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

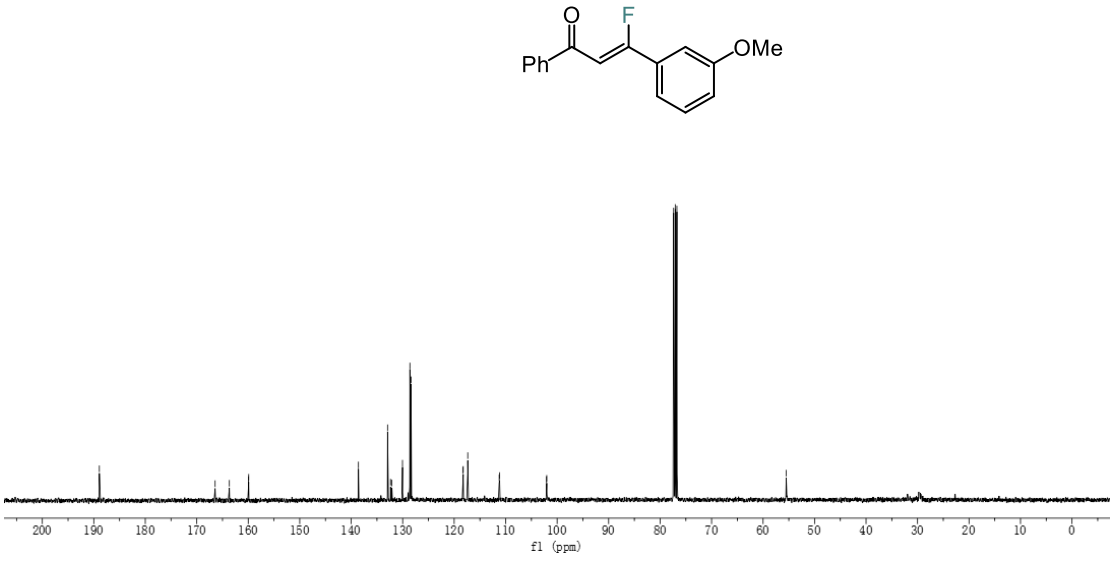

-56.32
O
CF3
F3C
O
5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125
f1 (ppm)

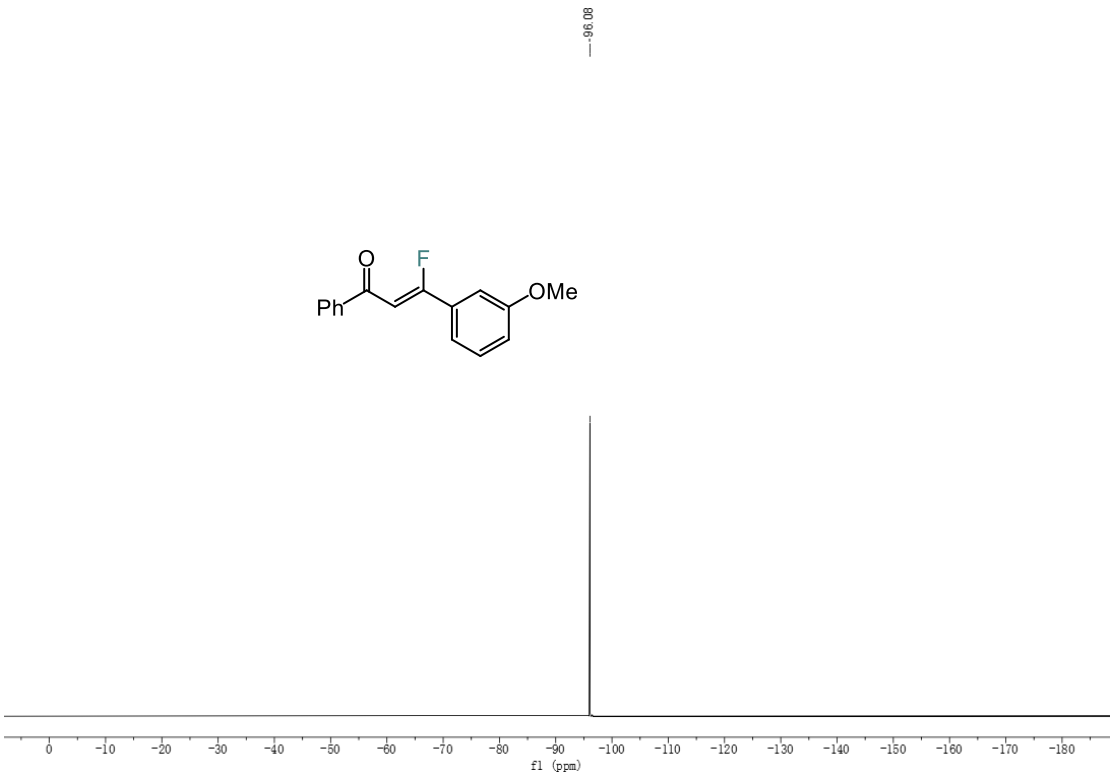
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (470 MHz, $CDCl_3$) spectra for 7



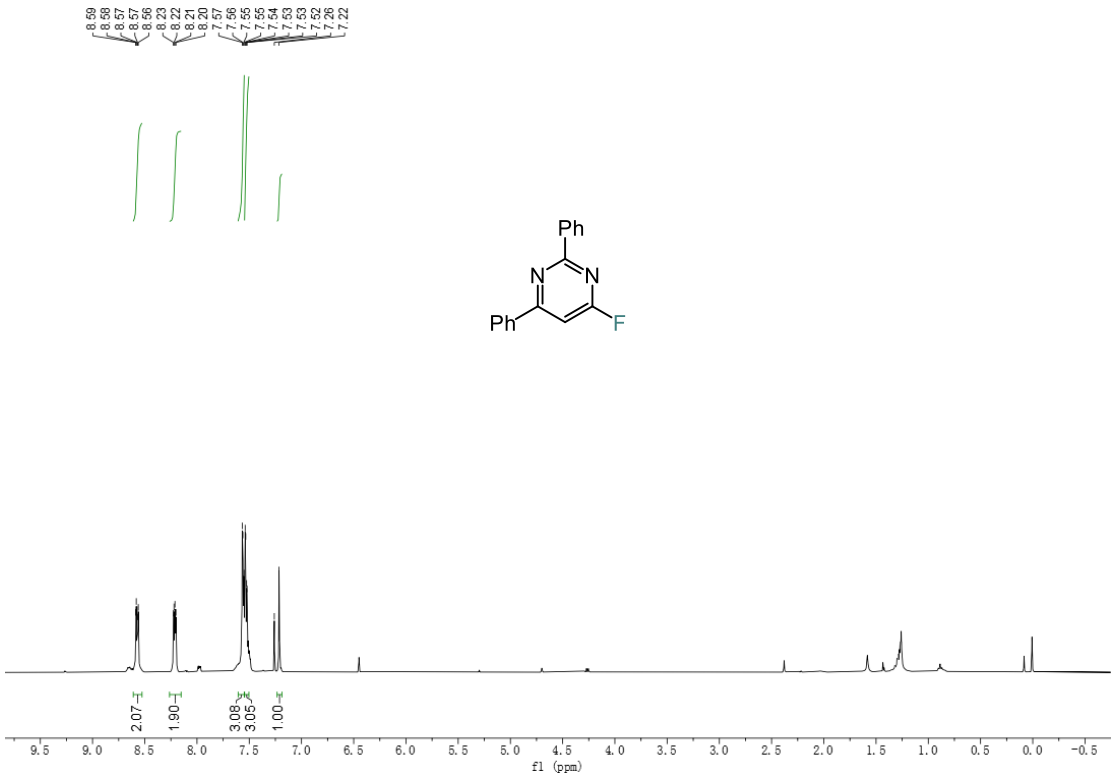


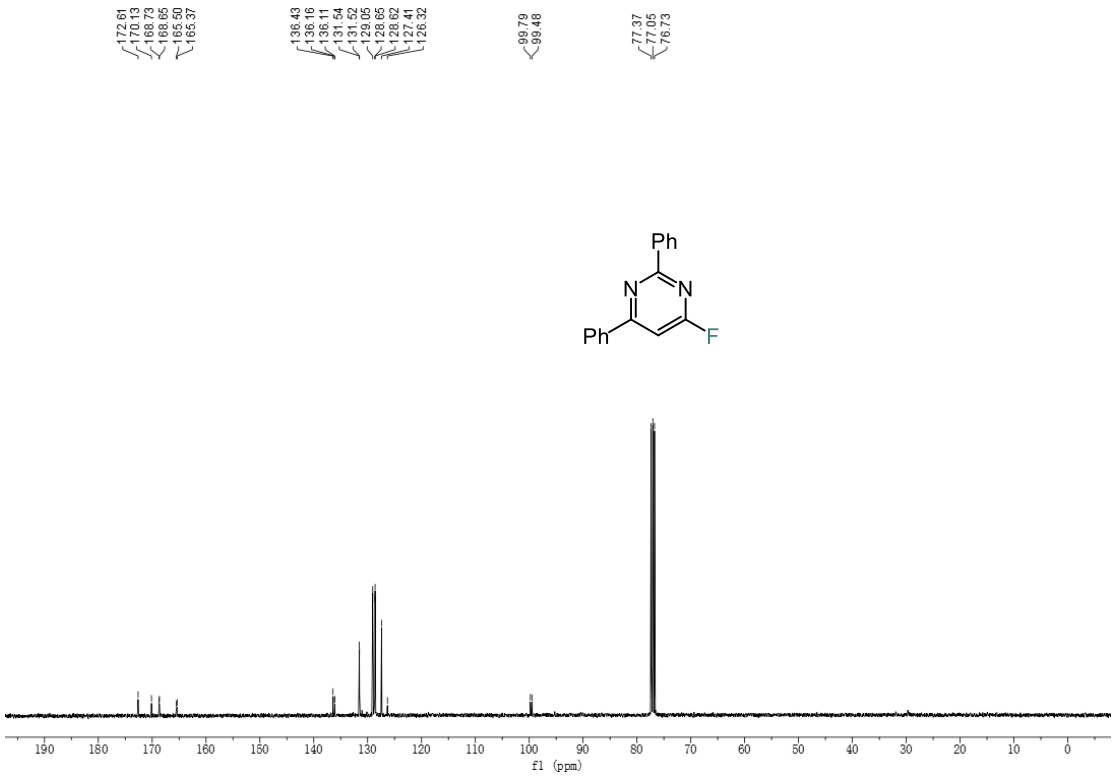






^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (470 MHz, $CDCl_3$) spectra for 9




172.61
170.13
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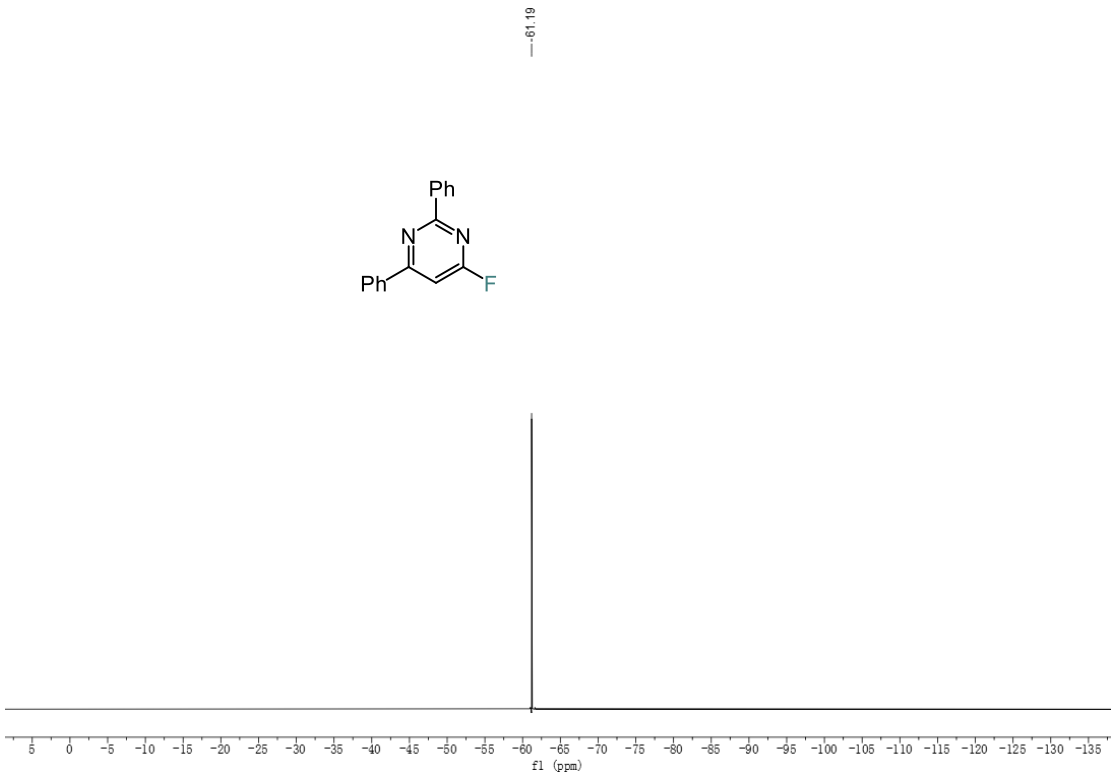
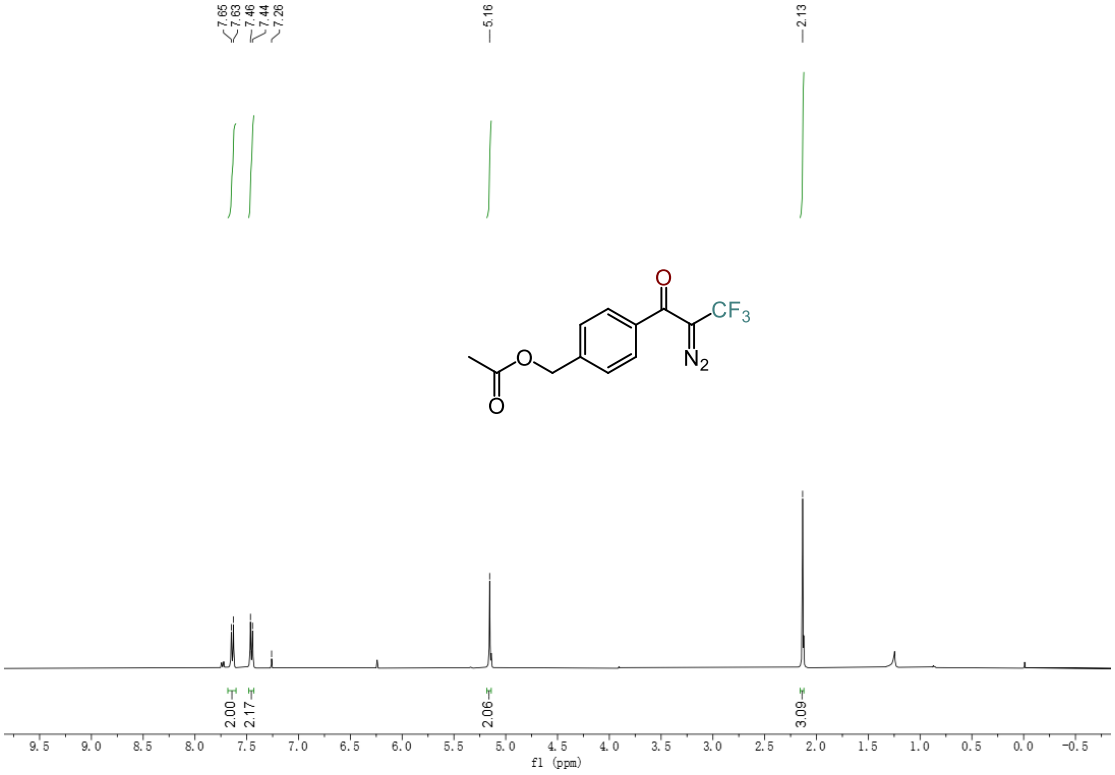
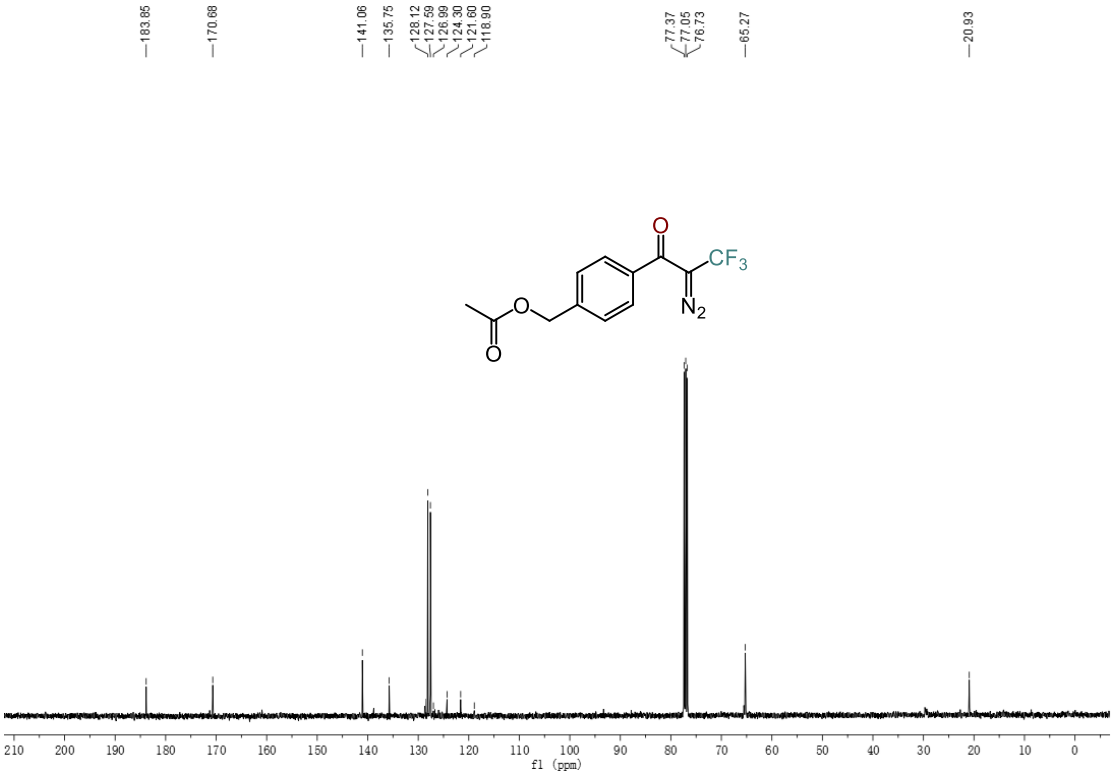
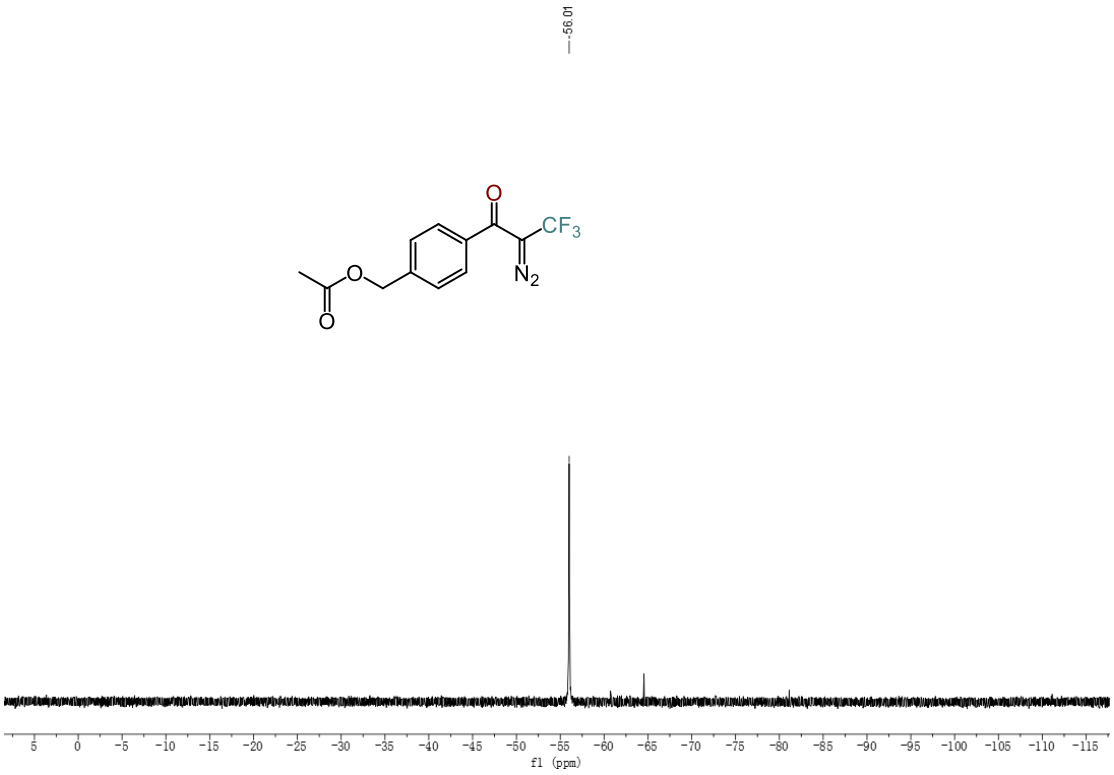
165.50
165.37
136.43
136.16
136.11
131.54
131.52
129.05
128.65
128.62
127.41
126.32
99.79
99.48
77.37
77.05
76.73
Ph
N
N
Ph
F
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-61.19
Ph
N
N
Ph
F
5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135
f1 (ppm)

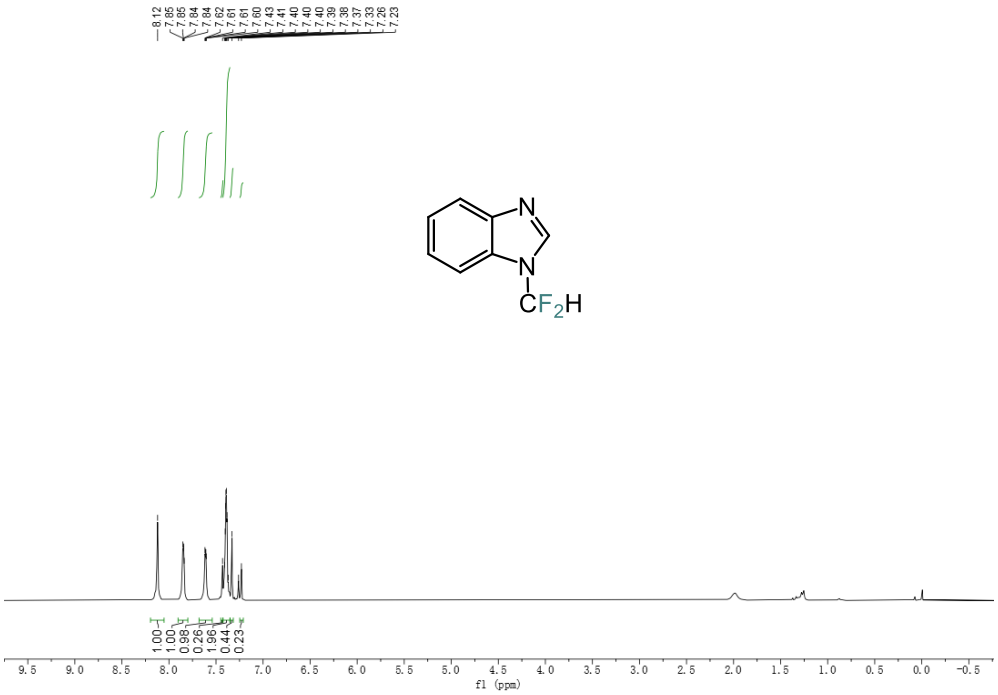
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (470 MHz, $CDCl_3$) spectra for 10

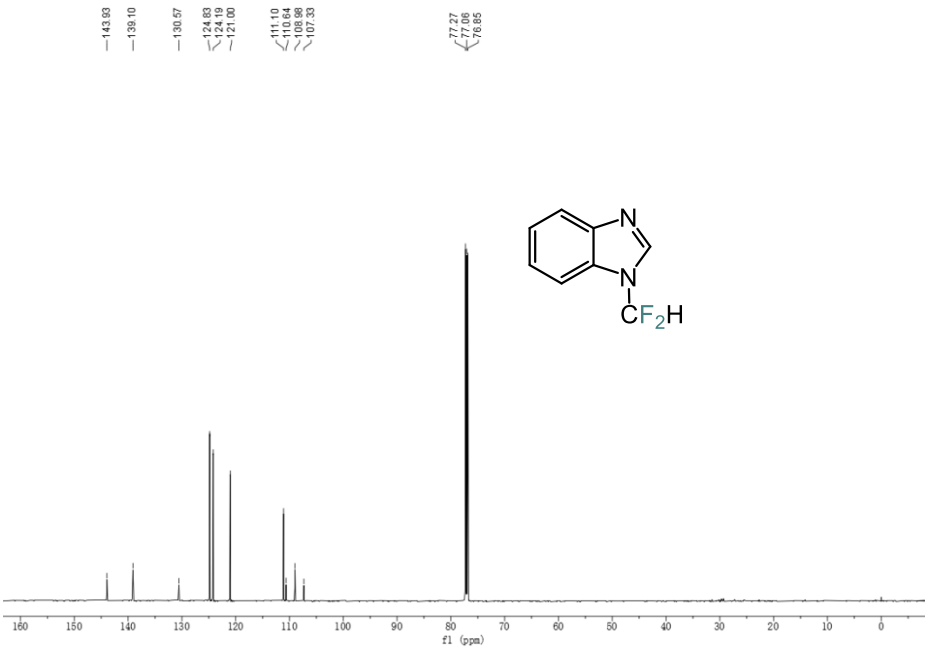


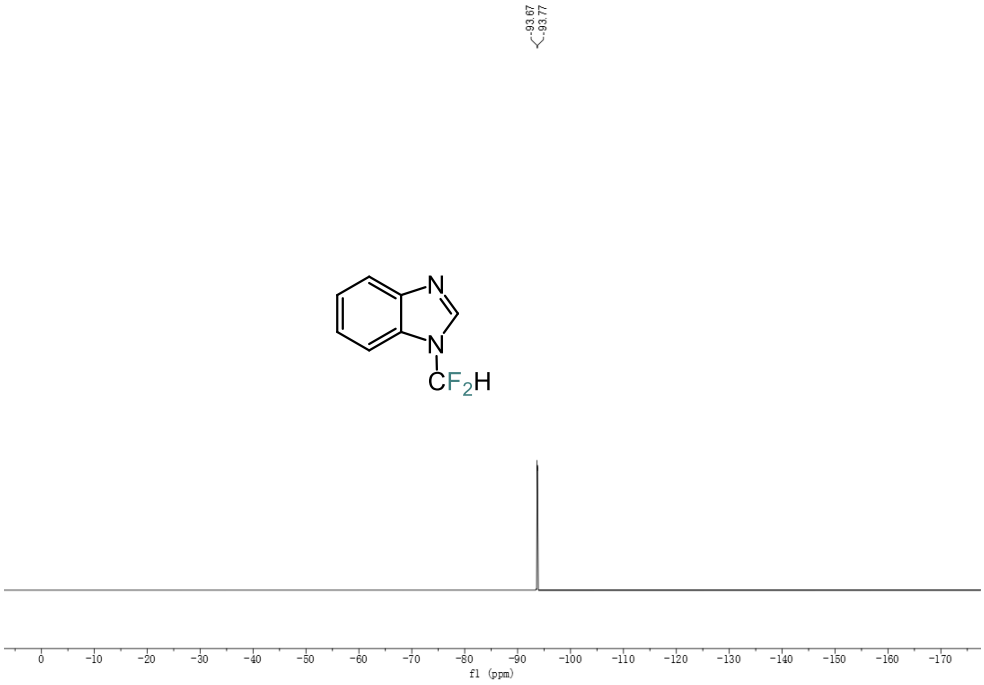




^{1}H NMR (600 MHz, $CDCl_3$), ^{13}C NMR (150 MHz, $CDCl_3$) and ^{19}F NMR (564 MHz, $CDCl_3$) spectra for 13




143.93
139.10
130.57
124.83
124.19
121.00
111.10
110.64
109.98
107.33
77.27
77.06
76.85
N
N
CF2H
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-93.67
-93.77
N
N
CF2H
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)