Supporting Information

Transition-Metal-Free Synthesis of *β*-Trifluoromethylated Enamines with Trifluoromethanesulfinate

Huanfeng Jiang*, Wei Huang, Yue Yu, Songjian Yi, Jiawei Li, Wanqing Wu*

Key Laboratory of Functional Molecular Engineering of Guangdong Province, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, P. R. China

E-mail: cewuwq@scut.edu.cn, jianghf@scut.edu.cn

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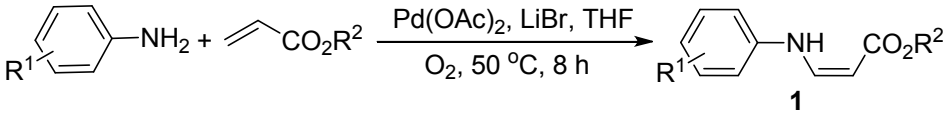
A. General Methods

All the commercial reagents were used without further purification. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker DRX-400 spectrometer using $CDCl_3$ as solvent with TMS as the internal standard. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively. Mass spectra were recorded on a Thermo Scientific ISQ gas chromatograph-mass spectrometer. The data of HRMS was carried out on a high-resolution mass spectrometer (LCMS-IT-TOF). IR spectra were obtained either as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Bruker TENSOR 27 spectrometer. Melting points were determined with a Büchi Melting Point B-545 instrument. TLC was performed using commercially available 100-400 mesh silica gel plates (GF_{254}). X-ray structural analyses were conducted on an x-ray analysis instrument.

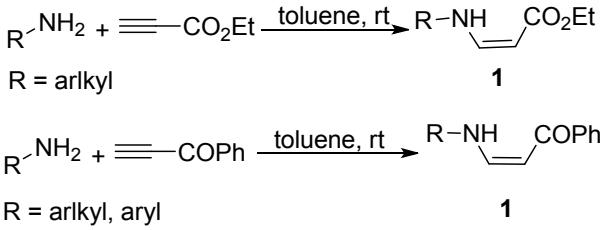
B. General Procedure for the Preparation of 1 and 3

General Procedure for the Preparation of 1a-1x, 1a'-1g' [1]



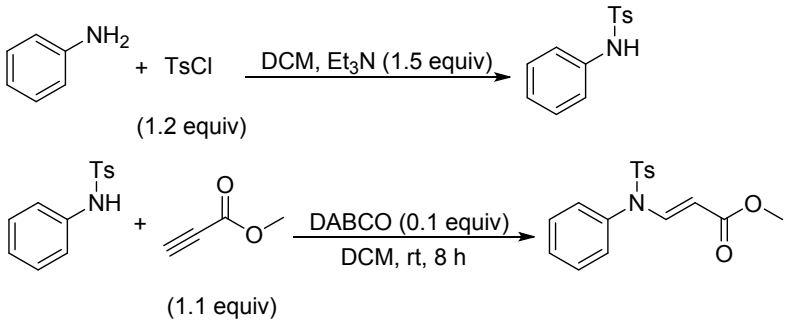
To a 25 mL round bottom flask, a solution of $Pd(OAc)_2$ (0.15 mmol), LiBr (10 mmol), amine (5 mmol), and alkene (6 mmol) in THF (10 mL) with an O_2 balloon, and the mixture was heated at 50 °C under magnetic stirring for 8 h. After completion, the reaction mixture was quenched with water (10 mL) and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over $MgSO_4$, and the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc/Et_3N) to afford the corresponding products **1a-1x, 1a'-1g'** in 60-90% yields.

General Procedure for the Preparation of 1y-1z, 1h'-1i' [2]



To a 25 mL round bottom flask, a solution of amine (5.5 mmol) in toluene, was added ethyl propiolate or ynone (5 mmol). The mixture was stirred at room temperature for about 4 h and monitored by TLC. After the completion of the reaction, the reaction mixture was then concentrated under reduced pressure and residue was purified by silica gel column chromatography using EtOAc/petroleum ether to afford the corresponding products **1y-1z, 1h'-1i'** in 80-90% yields.

General Procedure for the Preparation of 3 [3]



To a stirred solution of aniline (10 mmol) and Et_3N (15 mmol) in dry DCM at 0 °C was added *p*-toluenesulfonyl chloride (TsCl) (12 mmol) portion wise and reaction mixture was stirred at room temperature for 1 h. Then the reaction mixture was acidified by the addition of dilute HCl and the aqueous layer was extracted with DCM. The combined organic layer was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to afford N-Ts aniline in quantitative yield. Then to a stirred solution of N-Ts aniline (5 mmol) in dry CH_2Cl_2, was added DABCO (0.1 equiv) and ethyl propiolate (1.1 equiv.) at room temperature and stirred for 8 h (TLC). The reaction mixture was then concentrated under reduced pressure and residue was purified by silica gel column chromatography using EtOAc/petroleum ether to yield the vinylogous carbamate in about 85% yield.

General Procedure for the Preparation of 2

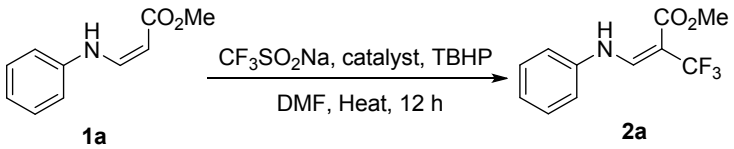
To a test tube, a mixture of enamine **1** (0.5 mmol), CF_3SO_2Na (2 mmol), DMF (2 mL) was added TBHP (4 equiv, 274 μL, 70% solution in water) slowly under a vigorous stirring. Then the mixture was stirred under the atmosphere of air at 50 °C for 12 h. After the reaction was completed (monitored by TLC), water (10 mL) was added to the reaction mixture, and the resulting mixture was extracted with ethyl acetate. The combined organic layers were then dried over $MgSO_4$, filtered, and then concentrated in vacuo. Purification of the residue on a preparative TLC afforded the desired products **2**.

Reference

[1] X. Ji, H. Huang, W. Wu, X. Li and H. Jiang, *J. Org. Chem*., **2013**, *78*, 11155.
[2] J. Yang, C. Wang, X. Xie, H. Li and Y. Li, *Eur. J. Org. Chem*., **2010**, 4189.
[3] S. J. Gharpure, V. Prasath and V. Kumar, *Chem. Commun*., **2015**, *51*, 13623.

C. Optimization of the Reaction Conditions

Table S1. Screening reaction conditions for trifluoromethylation of enamines[a]



1a **2a**

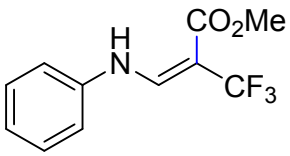
Entry	Catalyst	T/°C	Yield of **2a**[b] (%)

1	-	rt	56
2	-	80	60
3	CuCl	50	63
4	CuBr	50	63
5	CuI	50	68
6	$CuCl_2{\cdot}2H_2O$	50	64
7	$Cu(OAc)_2$	50	66
8	$Cu(OTf)_2$	50	67
9	$CuSO_4{\cdot}5H_2O$	50	64
10	$Cu(acac)_2$	50	69
11[c]	-	50	51
12[d]	-	50	69
13[c]	$Cu(OAc)_2$	50	61
14[d]	$Cu(OAc)_2$	50	43
15[e]	-	50	59
16[f]	-	50	12

[a] Reaction conditions: All reactions were performed with **1a** (0.1 mmol), CF_3SO_2Na (4 equiv), catalyst (10 mol%), TBHP (2 equiv), DMF (1 mL) for 12 h unless otherwise noted. [b] Determined by ^{19}F NMR spectroscopy using fluorobenzene as an internal standard. [c] The reaction proceeded with an O_2 balloon. [d] Under N_2 atmosphere. [e] With CF_3SO_2Na (2 equiv). [f] With CF_3SO_2Na (1 equiv).

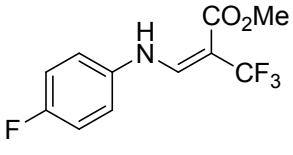
D. Analytical Data

***(E)*-Methyl 3-(Phenylamino)-2-(trifluoromethyl)acrylate (2a)**



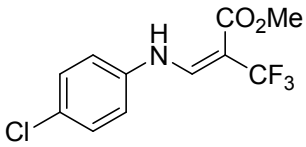
Yellow solid (104.1 mg, 85%), mp 59.2-60.7 °C; IR (KBr): 3240, 1685, 1638, 1235, 1113 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 10.47 (d, J = 12.4 Hz, 1H), 7.84 (d, J = 13.3 Hz, 1H), 7.36 (t, J = 7.9 Hz, 2H), 7.14 (t, J = 7.4 Hz, 1H), 7.06 (d, J = 8.0 Hz, 2H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 145.3 (q, J = 6.3 Hz), 139.3, 129.8, 124.6, 124.5 (q, J = 266.6 Hz), 116.8, 91.4 (q, J = 32.3 Hz), 51.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.79 (s, 3F). HRMS ESI (m/z): calcd for $C_{11}H_{10}F_3NNaO_2$ $[M + Na]^+$: 268.0561, found: 268.0556.

***(E)*-Methyl 3-((4-Fluorophenyl)amino)-2-(trifluoromethyl)acrylate (2b)**



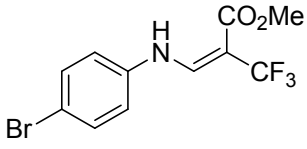
White solid (94.7 mg, 72%), mp 64.3-66.1 °C; IR (KBr): 3297, 1685, 1630, 1223, 1093 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 10.46 (d, J = 12.7 Hz, 1H), 7.75 (dd, J = 13.2, 0.9 Hz, 1H), 7.10-7.03 (m, 4H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 159.8 (d, J = 242.9 Hz), 145.8 (q, J = 6.3 Hz), 135.7 (d, J = 2.8 Hz), 124.5 (q, J = 266.5 Hz), 118.5 (d, J = 8.2 Hz), 116.6 (d, J = 23 Hz), 91.5 (q, J = 32.5 Hz), 51.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.86 (s, 3F), -117.89--117.96 (m, 1F). HRMS ESI (m/z): calcd for $C_{11}H_9F_4NNaO_2$ $[M + Na]^+$: 286.0467, found: 286.0462.

***(E)*-Methyl 3-((4-Chlorophenyl)amino)-2-(trifluoromethyl)acrylate (2c)**



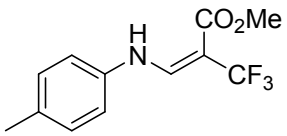
Light yellow solid (93.5 mg, 67%), mp 100.4-101.7 °C; IR (KBr): 3282, 1686, 1626, 1231, 1092 cm^{-1}; 1H NMR (400 MHz, $CDCl_3$) δ 10.46 (d, J = 12.7 Hz, 1H), 7.76 (d, J = 13.1 Hz, 1H), 7.32 (d, J = 8.8 Hz, 2H), 6.99 (d, J = 8.8 Hz, 2H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 145.0 (q, J = 6.3 Hz), 138.0, 129.9, 129.8, 124.3 (q, J = 266.6 Hz), 118.0, 92.1 (q, J = 32.7 Hz), 51.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.98 (s, 3F). HRMS ESI (m/z): calcd for $C_{11}H_9ClF_3NNaO_2$ [M + Na]$^+$: 302.0172, found: 302.0166.

***(E)*-Methyl 3-((4-Bromophenyl)amino)-2-(trifluoromethyl)acrylate (2d)**



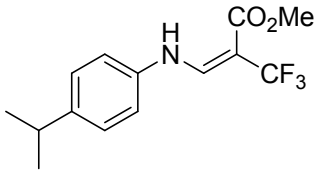
Light yellow solid (106.6 mg, 66%), mp 59.2-60.7 °C; IR (KBr): 3250, 2931, 2328, 1626, 1231, 1097cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 10.46 (d, J = 12.7 Hz, 1H), 7.76 (dd, J = 13.2, 0.8 Hz, 1H), 7.46 (d, J = 8.8 Hz, 2H), 6.94 (d, J = 8.8 Hz, 2H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 144.9 (q, J = 6.4 Hz), 138.5, 132.8, 124.3 (q, J = 265.6 Hz), 118.3, 117.3, 92.2 (q, J = 33.2 Hz), 51.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.01 (s, 3F). HRMS ESI (m/z): calcd for $C_{11}H_9BrF_3NNaO_2$ [M + Na]$^+$: 345.9666, found: 345.9661.

***(E)*-Methyl 3-(p-Tolylamino)-2-(trifluoromethyl)acrylate (2e)**



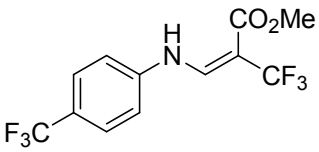
Light yellow solid (104.9 mg, 81%), mp 75.2-76.5 °C; IR (KBr): 2923, 1635, 1242, 1111 1026 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 10.43 (d, J = 12.9 Hz, 1H), 7.80 (d, J = 12.6 Hz, 1H), 7.16 (d, J = 8.2 Hz, 2H), 6.96 (d, J = 8.4 Hz, 2H), 3.83 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 145.6 (q, J = 6.2 Hz), 136.9, 134.5, 130.3, 124.7 (q, J = 266.5 Hz), 116.8, 90.7 (q, J = 32.5 Hz), 51.3, 20.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.64 (s, 3F). HRMS ESI (m/z): calcd for $C_{12}H_{12}F_3NNaO_2$ [M + Na]$^+$: 282.0718, found: 282.0712.

***(E)*-Methyl 3-((4-Isopropylphenyl)amino)-2-(trifluoromethyl)acrylate (2f)**



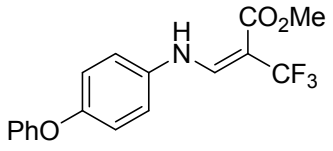
Yellow oil (101.9 mg, 71%); IR (KBr): 2961, 1684, 1630, 1233, 1113 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 10.47 (d, J = 13.1 Hz, 1H), 7.85 (dd, J = 13.4, 0.8 Hz, 1H), 7.25 (d, J = 8.5 Hz, 2H), 7.03 (d, J = 8.5 Hz, 2H), 3.86 (s, 3H), 2.93 (m, 1H), 1.28 (d, J = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 145.7 (q, J = 6.2 Hz), 137.2, 127.7, 124.7 (q, J = 266.4 Hz), 117.0, 90.8 (q, J = 32.4 Hz), 51.3, 33.5, 23.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.64 (s, 3F). HRMS ESI (m/z): calcd for $C_{14}H_{16}F_3NNaO_2$ [M + Na]$^+$: 310.1031, found: 310.1025.

***(E)*-Methyl 2-(Trifluoromethyl)-3-((4-(trifluoromethyl)phenyl)amino)acrylate (2g)**



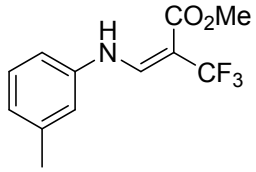
White solid (115.8 mg, 74%), mp 99.3-100.7 °C; IR (KBr): 3241, 1678, 1622, 1315, 1118 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 10.60 (d, J = 12.7 Hz, 1H), 7.86 (dd, J = 13.0, 0.9 Hz, 1H), 7.61 (d, J = 8.5 Hz, 2H), 7.14 (d, J = 8.5 Hz, 2H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 144.3 (q, J = 6.4 Hz), 142.2, 127.2 (q, J = 3.7 Hz), 126.4 (q, J = 32,9 Hz), 124.0 (dd, J = 266.9, 16.5 Hz), 124.0 (dd, J = 801.0, 13.8 Hz), 116.4, 93.5 (q, J = 32.6 Hz), 51.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.35 (s, 3F), -62.24 (s, 3F). HRMS ESI (m/z): calcd for $C_{12}H_9F_6NNaO_2$ [M + Na]$^+$: 336.0435, found: 336.0430.

***(E)*-Methyl 3-((4-Phenoxyphenyl)amino)-2-(trifluoromethyl)acrylate (2h)**



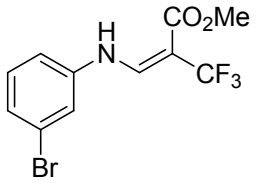
Deep yellow oil (109.5 mg, 65%); IR (KBr): 2954, 1684, 1636, 1225, 1114 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 10.48 (d, J = 13.2 Hz, 1H), 7.78 (dd, J = 13.3, 0.8 Hz, 1H), 7.38-7.32 (m, 2H), 7.12 (t, J = 7.4 Hz, 1H), 7.06-6.97 (m, 6H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 157.2, 154.2, 145.8 (q, J = 6.2 Hz), 135.0, 129.8, 124.6 (q, J = 266.6 Hz), 123.4, 120.3, 118.6, 118.5, 91.0 (q, J = 32.6 Hz), 51.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.68 (s, 3F). HRMS ESI (m/z): calcd for $C_{17}H_{14}F_3NNaO_3$ [M + Na]+: 360.0823, found: 360.0818.

***(E)*-Methyl 3-(m-Tolylamino)-2-(trifluoromethyl)acrylate (2i)**



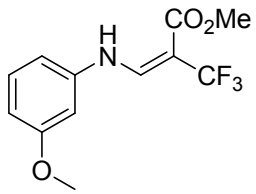
White oil (95.8 mg, 74%); IR (KBr): 2947, 1683, 1632, 1227, 1114 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 10.43 (d, J = 12.6 Hz, 1H), 7.84 (dd, J = 13.3, 0.7 Hz, 1H), 7.24 (t, J = 8.0 Hz, 1H), 6.95 (d, J = 7.6 Hz, 1H), 6.87 (d, J = 7.5 Hz, 2H), 3.84 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 145.4 (q, J = 6.3 Hz), 140.0, 139.3, 129.7, 125.5, 124.6 (q, J = 266.4 Hz), 117.5, 113.9, 91.2 (q, J = 32.4 Hz), 51.4, 21.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.72 (s, 3F). HRMS ESI (m/z): calcd for $C_{12}H_{12}F_3NNaO_2$ [M + Na]$^+$: 282.0718, found: 282.0712.

***(E)*-Methyl 3-((3-Bromophenyl)amino)-2-(trifluoromethyl)acrylate (2j)**



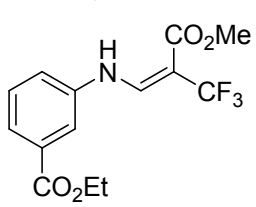
White solid (145.4 mg, 90%), mp 73.8-75.5 ^oC; IR (KBr): 2955, 1684, 1634, 1588, 1231, 1110 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 10.44 (d, J = 12.6 Hz, 1H), 7.76 (d, J = 13.1 Hz, 1H), 7.27-7.17 (m, 3H), 6.97 (d, J = 8.0 Hz, 1H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 144.7 (q, J = 6.4 Hz), 140.7, 131.1, 127.5, 124.2 (q, J = 267.0 Hz), 123.6, 119.8, 115.4, 92.7 (q, J = 32.6 Hz), 51. 6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.08 (s, 3F). HRMS ESI (m/z): calcd for $C_{11}H_9BrF_3NNaO_2$ [M + Na]$^+$: 345.9666, found: 345.9661.

***(E)*-Methyl 3-((3-Methoxyphenyl)amino)-2-(trifluoromethyl)acrylate (2k)**



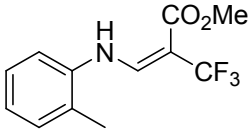
yellow oil (101.8 mg, 74%); IR (KBr): 2949, 1684, 1601, 1223, 1110 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 10.43 (d, J = 12.7 Hz, 1H), 7.82 (d, J = 13.3 Hz, 1H), 7.26 (t, J = 8 Hz, 1H), 6.69-6.65 (m, 2H), 6.58 (t, J = 2.2 Hz, 1H), 3.84 (s, 3H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 160.9, 145.3 (q, J = 6.1 Hz), 140.6, 130.7, 124.5 (q, J = 266.5 Hz), 109.9, 109.0, 103.1, 91.5 (q, J = 32.5 Hz), 55.4, 51.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.84 (s, 3F). HRMS ESI (m/z): calcd for $C_{12}H_{12}F_3NNaO_3$ [M + Na]$^+$: 298.0667, found: 298.0661.

***(E)*-Ethyl 3-((3,3,3-Trifluoro-2-(methoxycarbonyl)prop-1-en-1-yl)amino)benzoate (2l)**



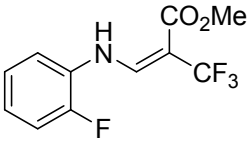
Light yellow solid (120.5 mg, 76%), mp 97.2-98.6 ^oC; IR (KBr): 2990, 1695, 1622, 1291, 1231, 1104 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 10.55 (d, J = 13.0 Hz, 1H), 7.86 (d, J = 13.2 Hz, 1H), 7.79 (d, J = 7.8 Hz, 1H), 7.73 (s, 1H), 7.42 (t, J = 7.9 Hz, 1H), 7.23 (dd, J = 8.4, 2.0 Hz, 1H), 4.39 (q, J = 7.1 Hz, 2H), 3.84 (s, 3H), 1.40 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 165.7, 145.0 (q, J = 6.2 Hz), 139.5, 132.3, 129.9, 125.5, 124.3 (q, J = 266.3 Hz), 120.8, 117.5, 92.3 (q, J = 32.7 Hz), 61.4, 51.6, 14.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.99 (s,3F). HRMS ESI (m/z): calcd for $C_{14}H_{14}F_3NNaO_4$ [M + Na]$^+$: 340.0773, found: 340.0767.

***(E)*-Methyl 3-(*o*-Tolylamino)-2-(trifluoromethyl)acrylate (2m)**



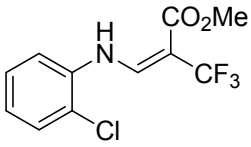
Light yellow solid (89.4 mg, 69%), mp 64.7-65.7 °C; IR (KBr): 2938, 1666, 1599, 1244, 1107 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 10.59 (d, J = 12.1 Hz, 1H), 7.87 (d, J = 13.1 Hz, 1H), 7.27-7.20 (m, 2H), 7.12 (d, J = 7.9 Hz, 1H), 7.07 (t, J = 7.4 Hz, 1H), 3.86 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 145.8 (q, J = 6.2 Hz), 138.0, 131.2, 127.4, 127.0, 124.6 (q, J = 266.4 Hz), 124.6, 114.9, 91.5 (q, J = 32.5 Hz), 51.5 (d, J = 3.1 Hz), 17.3 (d, J = 2.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.75 (s, 3F). HRMS ESI (m/z): calcd for $C_{12}H_{12}F_3NNaO_2$ $[M + Na]^+$: 282.0718, found: 282.0712.

***(E)*-Methyl 3-((2-Fluorophenyl)amino)-2-(trifluoromethyl)acrylate (2n)**



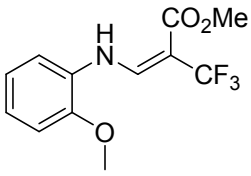
Light yellow solid (110.5 mg, 84%), mp 78.3-80.0 °C; IR (KBr): 2854, 1678, 1622, 1315, 1118 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 10.59 (d, J = 12.2 Hz, 1H), 7.83 (d, J = 13.1 Hz, 1H), 7.20-7.04 (m, 4H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 152.7 (d, J = 244.4 Hz), 144.6 (q, J = 6.3 Hz), 127.9 (d, J = 10.7 Hz), 125.0 (d, J = 3.7 Hz), 124.8 (d, J = 7.3.0 Hz), 124.3 (q, J = 266.8 Hz), 116.3 (d, J = 18.8 Hz), 116.0 (d, J = 0.7 Hz), 93.0 (q, J = 32.4 Hz), 51.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.18 (s, 3F), -130.99--131.05 (m, 1F). HRMS ESI (m/z): calcd for $C_{11}H_9F_4NNaO_2$ $[M + Na]^+$: 286.0467, found: 286.0462.

***(E)*-Methyl 3-((2-Chlorophenyl)amino)-2-(trifluoromethyl)acrylate (2o)**



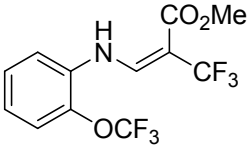
White solid (118.6 mg, 85%), mp 98.2-99.8 °C; IR (KBr): 2941, 1684, 1627, 1236, 1098 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 10.89 (d, J = 12.6 Hz, 1H), 7.84 (d, J = 13.0 Hz, 1H), 7.40 (dd, J = 8.0, 1.3 Hz, 1H), 7.31-7.26 (m, 1H), 7.18 (d, J = 7.3 Hz, 1H), 7.05 (td, J = 7.9, 1.4 Hz, 1H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 143.8 (q, J = 6.4 Hz), 136.3, 130.2, 128.1, 124.7, 124.3 (q, J = 266.8 Hz), 123.3, 114.9, 93.3 (q, J = 32.3 Hz), 51.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.20 (s, 3F). HRMS ESI (m/z): calcd for $C_{11}H_9ClF_3NNaO_2$ $[M + Na]^+$: 302.0172, found: 302.0166.

***(E)*-Methyl 3-((2-Methoxyphenyl)amino)-2-(trifluoromethyl)acrylate (2p)**



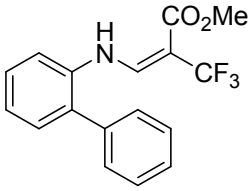
Light yellow solid (97.6 mg, 71%), mp 81.5-83.2 °C; IR (KBr): 2957, 1689, 1624, 1212, 1099 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 10.70 (d, J = 13.2 Hz, 1H), 7.86 (d, J = 13.6 Hz, 1H), 7.12 (dd, J = 7.9, 1.2 Hz, 1H), 7.08 (td, J = 7.8, 1.5 Hz, 1H), 7.00-6.91 (m, 2H), 3.93 (s, 3H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 148.7, 144.1 (q, J = 6.3 Hz), 128.8, 124.7 (q, J = 266.5 Hz), 124.5, 121.1, 113.8, 111.2, 91.5 (q, J = 32.5 Hz), 55.9, 51.39. ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.71 (s, 3F). HRMS ESI (m/z): calcd for $C_{12}H_{12}F_3NNaO_3$ $[M + Na]^+$: 298.0667, found: 298.0661.

***(E)*-Methyl 3-((2-(Trifluoromethoxy)phenyl)amino)-2-(trifluoromethyl)acrylate (2q)**



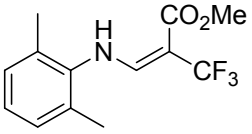
White oil (151.3 mg, 92%); IR (KBr): 2955, 1687, 1638, 1254, 1198 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 10.76 (d, J = 12.4 Hz, 1H), 7.82 (d, J = 13.0 Hz, 1H), 7.34-7.28 (m, 2H), 7.24 (d, J = 8.4 Hz, 1H), 7.12 (t, J = 7.8 Hz, 1H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 143.9 (q, J = 6.4 Hz), 138.5, 132.5, 128.0, 124.4, 124.2 (q, J = 266.9 Hz), 122.0 (d, J = 1.1 Hz), 120.6 (q, J = 257.9 Hz), 115.6, 93.8 (q, J = 32.5 Hz), 51.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.05 (s), -60.40 (s, 3F). HRMS ESI (m/z): calcd for $C_{12}H_9F_6NNaO_3$ $[M + Na]^+$: 352.0384, found: 352.0379.

***(E)*-Methyl 3-([1,1'-Biphenyl]-2-ylamino)-2-(trifluoromethyl)acrylate (2r)**



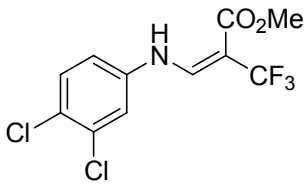
White solid (96.3 mg, 60%), mp 77.6-79.1 °C; IR (KBr): 2954, 1688, 1633, 1306, 1232, 1117 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 10.31 (d, J = 12.8 Hz, 1H), 7.80 (d, J = 13.2 Hz, 1H), 7.52-7.48 (m, 2H), 7.44-7.41 (m, 1H), 7.39-7.35 (m, 3H), 7.31-7.28 (m, 1H), 7.23-7.17 (m, 2H), 3.65 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 144.9 (q, J = 6.1 Hz), 137.3, 136.9, 132.5, 131.2, 129.2, 129.1, 128.9, 128.1, 125.9, 124.6 (q, J = 266.8 Hz), 124.5, 115.5, 91.5 (q, J = 32.0 Hz), 51.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.85 (s, 3F). HRMS ESI (m/z): calcd for $C_{17}H_{14}F_3NNaO_2$ $[M + Na]^+$: 344.0874, found: 344.0869.

***(E)*-Methyl 3-((2,6-Dimethylphenyl)amino)-2-(trifluoromethyl)acrylate (2s)**



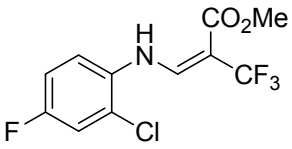
White solid (101.0 mg, 74%), mp 70.1-72.6 °C; IR (KBr): 2925, 1686, 1630, 1229, 1112 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.93 (d, J = 12.9 Hz, 1H), 7.37 (dd, J = 13.6, 0.9 Hz, 1H), 7.11 (s, 3H), 3.84 (s, 3H), 2.31 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 152.1 (q, J = 6.2 Hz), 137.8, 132.8, 128.9, 126.9, 124.8 (q, J = 266.2 Hz), 89.3 (q, J = 32.4 Hz), 51.2, 18.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.53 (s, 3F). HRMS ESI (m/z): calcd for $C_{13}H_{14}F_3NNaO_2$ $[M + Na]^+$: 296.0874, found: 296.0869.

***(E)*-Methyl 3-((3,4-Dichlorophenyl)amino)-2-(trifluoromethyl)acrylate (2t)**



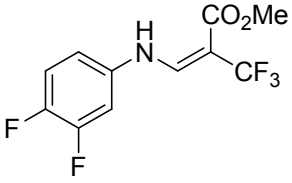
Light yellow solid (104.8 mg, 67%), mp 82.3-83.9 °C; IR (KBr): 2956, 1684, 1640, 1233, 1122 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 10.47 (d, J = 12.7 Hz, 1H), 7.72 (dd, J = 13.0, 1.0 Hz, 1H), 7.40 (d, J = 8.7 Hz, 1H), 7.16 (d, J = 2.7 Hz, 1H), 6.90 (dd, J = 8.7, 2.7 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 144.5 (q, J = 6.3 Hz), 138.9, 133.9, 131.4, 128.0, 124.1 (q, J = 267.0 Hz), 118.4, 116.0, 93.1 (q, J = 32.6 Hz), 51.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.23 (s, 3F). HRMS ESI (m/z): calcd for $C_{11}H_8Cl_2F_3NNaO_2$ $[M + Na]^+$: 335.9782, found: 335.9776.

***(E)*-Methyl 3-((2-Chloro-4-fluorophenyl)amino)-2-(trifluoromethyl)acrylate (2u)**



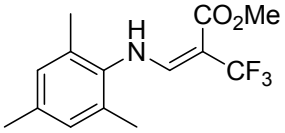
White solid (95.0 mg, 64%), mp 91.3-92.5 °C; IR (KBr): 3217, 1687, 1628, 1219, 1097 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 10.82 (d, J = 12.6 Hz, 1H), 7.76 (d, J = 12.9 Hz, 1H), 7.22-7.14 (m, 2H), 7.07-7.01 (m, 1H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 158.7 (d, J = 246.0 Hz), 144.3 (q, J = 6.3 Hz), 133.2 (d, J = 3.3 Hz), 124.2 (q, J = 266.8 Hz) 124.1 (d, J = 10.3 Hz), 117.6 (d, J = 36 Hz), 116.3 (d, J = 8.7 Hz), 115.3 (d, J = 22.6 Hz), 93.4 (q, J = 32.6 Hz), 51.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.25 (s, 3F), -116.52 (s, 1F). HRMS ESI (m/z): calcd for $C_{11}H_8ClF_4NNaO_2$ $[M + Na]^+$: 320.0077, found: 320.0072.

***(E)*-Methyl 3-((3,4-Difluorophenyl)amino)-2-(trifluoromethyl)acrylate (2v)**



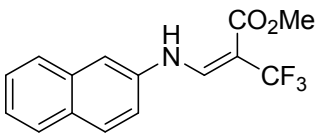
White solid (98.4 mg, 70%), mp 86.5-87.5 °C; IR (KBr): 3234, 1691, 1629, 1218, 1102 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 10.45 (d, J = 12.3 Hz, 1H), 7.69 (dd, J = 13.0, 0.8 Hz, 1H), 7.16 (dd, J = 18.3, 8.8 Hz, 1H), 6.94-6.88 (m, 1H), 6.82-6.76 (m, 1H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 150.9 (dd, J = 248.6, 13.7 Hz), 147.4(dd, J = 244.9, 12.6 Hz), 145.2 (q, J = 6.3 Hz), 136.2 (dd, J = 7.9, 3.1 Hz), 124.2 (q, J = 266.9 Hz), 118.5 (d, J = 18.6 Hz), 112.7 (dd, J = 6.2, 3.6 Hz), 106.5 (d, J = 20.8 Hz), 92.6 (q, J = 32.8 Hz), 51.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.16 (s, 3F), -134.12 (d, 1F), -142.44 (d, 1F). HRMS ESI (m/z): calcd for $C_{11}H_8F_5NNaO_2$ $[M + Na]^+$: 304.0373, found: 304.0367.

***(E)*-Methyl 3-(Mesitylamino)-2-(trifluoromethyl)acrylate (2w)**



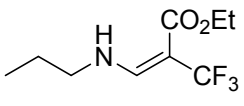
White solid (107.6 mg, 75%), mp 93.3-94.5 °C; IR (KBr): 3297, 1683, 1632, 1220, 1110 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.83 (d, J = 13.1 Hz, 1H), 7.32 (dd, J = 13.6, 0.9 Hz, 1H), 6.92 (s, 2H), 3.84 (s, 3H), 2.29 (s, 3H), 2.25 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 152.5 (q, J = 6.2 Hz), 136.8, 135.3, 132.8, 129.5, 124.9 (q, J = 266.3 Hz), 89.0 (q, J = 32.6 Hz), 51.2, 20.8, 18.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.81 (s, 3F). HRMS ESI (m/z): calcd for $C_{14}H_{16}F_3NNaO_2$ $[M + Na]^+$: 310.1031, found: 310.1025.

***(E)*-Methyl 3-(Naphthalen-2-ylamino)-2-(trifluoromethyl)acrylate (2x)**



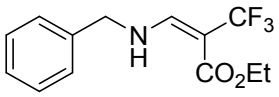
Light yellow solid (106.2 mg, 72%), mp 77.3-79.1 °C; IR (KBr): 2939, 1678, 1624, 1223, 1107 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 10.65 (d, J = 12.9 Hz, 1H), 7.99 (dd, J = 13.2, 0.7 Hz, 1H), 7.85 (d, J = 8.8 Hz, 1H), 7.79 (dd, J = 11.8, 8.2 Hz, 2H), 7.53-7.48 (m, 1H), 7.47-7.39 (m, 2H), 7.24 (dd, J = 8.8, 2.3 Hz, 1H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 145.3 (q, J = 6.2 Hz), 136.8, 133.9, 130.8, 130.1, 127.8, 127.3, 127.2, 125.3, 124.5 (q, J = 266.8 Hz), 117.1, 112.8, 91.6 (q, J = 32.6 Hz), 51.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.76 (s, 3F). HRMS ESI (m/z): calcd for $C_{15}H_{12}F_3NNaO_2$ $[M + Na]^+$: 318.0718, found: 318.0712.

***(E)*-Ethyl 3-(Propylamino)-2-(trifluoromethyl)acrylate (2y)**



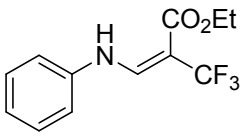
Light yellow oil (47.2 mg, 42%); IR (KBr): 3795, 2939, 1623, 1458, 1108 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 7.27 (d, J = 14.3 Hz, 1H), 4.24 (q, J = 7.1 Hz, 2H), 3.24 (q, J = 6.7 Hz, 2H), 1.63 (dt, J = 14.4, 7.2 Hz, 2H), 1.32 (t, J = 7.1 Hz, 3H), 0.98 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 152.9 (q, J = 5.9 Hz), 125.2 (q, J = 265.7 Hz), 87.1 (q, J = 32.1 Hz), 59.7, 51.1, 24.1, 14.3, 10.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.97 (s, 3F). HRMS ESI (m/z): calcd for $C_9H_{14}F_3NNaO_2$ $[M + Na]^+$: 248.0874, found: 248.0869.

***(E)*-Ethyl 3-(Benzylamino)-2-(trifluoromethyl)acrylate (2z)**



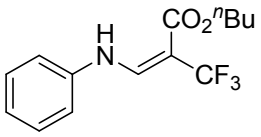
Light yellow solid (61.4 mg, 45%), mp 55.0-55.9 °C; IR (KBr): 2936, 1685, 1623, 1392, 1224, 1108 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.85 (d, J = 7.6 Hz, 1H), 7.39-7.29 (m, 4H), 7.26-7.22 (m, 2H), 4.43 (d, J = 6.0 Hz, 2H), 4.21 (q, J = 7.1 Hz, 2H), 1.29 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 152.7 (q, J = 6.1 Hz), 136.9, 129.0, 128.1, 127.2, 125.0 (q, J =266.0 Hz), 88.3 (q, J = 32.3 Hz), 59.9, 52.9, 14.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.15 (s, 3F). HRMS ESI (m/z): calcd for $C_{13}H_{14}F_3NNaO_2$ $[M + Na]^+$: 296.0874, found: 296.0869.

***(E)*-Ethyl 3-(Phenylamino)-2-(trifluoromethyl)acrylate (2a')**



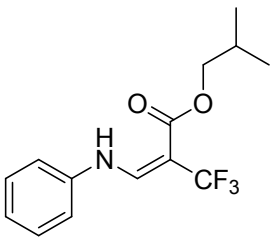
Yellow oil (107.5 mg, 83%); IR (KBr): 2986, 1677, 1634, 1225, 1111 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 10.49 (d, J = 12.5 Hz, 1H), 7.84 (dd, J = 13.3, 0.8 Hz, 1H), 7.36 (m, 2H), 7.13 (t, J = 7.4 Hz, 1H), 7.06 (d, J = 7.7 Hz, 2H), 4.30 (q, J = 7.1 Hz, 2H), 1.35 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 145.2 (q, J = 6.3 Hz), 139.4, 129.8, 124.6 (q, J = 266.7 Hz), 124.5, 116.7, 91.8 (q, J = 32.3 Hz), 60.4, 14.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.80 (s, 3F). HRMS ESI (m/z): calcd for $C_{12}H_{12}F_3NNaO_2$ $[M + Na]^+$: 282.0718, found: 282.0712.

***(E)*-Butyl 3-(Phenylamino)-2-(trifluoromethyl)acrylate (2b')**



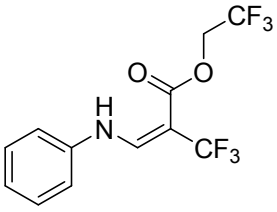
Light yellow oil (93.3 mg, 65%); IR (KBr): 2956, 1679, 1636, 1228, 1116 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 10.49 (d, J = 12.9 Hz, 1H), 7.84 (dd, J = 13.3, 0.9 Hz, 1H), 7.38-7.34 (m, 2H), 7.13 (t, J = 7.4 Hz, 1H), 7.06 (d, J = 7.7 Hz, 2H), 4.25 (t, J = 6.5 Hz, 2H), 1.74-1.67 (m, 2H), 1.50-1.41 (m, 2H), 0.97 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 145.1 (q, J = 6.3 Hz), 139.4, 129.8, 124.6 (q, J = 266.7 Hz), 124.5, 116.7, 91.8 (q, J = 32.2 Hz), 64.2, 30.7, 19.1, 13.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.84 (s, 3F). HRMS ESI (m/z): calcd for $C_{14}H_{16}F_3NNaO_2$ $[M + Na]^+$: 310.1031, found: 310.1025.

***(E)*-Isobutyl 3-(Phenylamino)-2-(trifluoromethyl)acrylate (2c')**



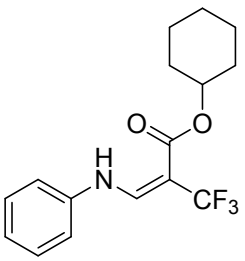
White oil (97.6 mg, 68%); IR (KBr): 2961, 1679, 1636, 1227, 1114 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 10.49 (d, J = 12.8 Hz, 1H), 7.84 (dd, J = 13.3, 0.9 Hz, 1H), 7.39-7.32 (m, 2H), 7.16-7.11 (m, 1H), 7.06 (d, J = 7.7 Hz, 2H), 4.03 (d, J = 6.4 Hz, 2H), 2.03 (m, 1H), 1.00 (d, J = 6.7 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 145.2 (q, J= 6.2 Hz), 139.4, 129.8, 124.6 (q, J= 266.7 Hz), 124.5, 116.7, 91.8 (q, J= 32.4 Hz), 70.4, 27.8, 18.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.47 (s, 3F). HRMS ESI (m/z): calcd for $C_{14}H_{16}F_3NNaO_2$ $[M + Na]^+$: 310.1031, found: 310.1025.

***(E)*-2,2,2-Trifluoroethyl 3-(Phenylamino)-2-(trifluoromethyl)acrylate (2d')**



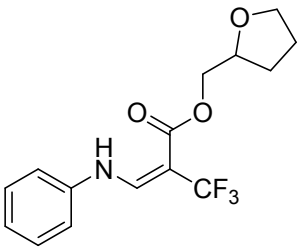
White solid (136.1 mg, 87%), mp 64.1-65.6 °C; IR (KBr): 3298, 1684, 1619, 1317, 1226 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 10.32 (d, J = 12.7 Hz, 1H), 7.92 (dd, J = 13.6, 0.6 Hz, 1H), 7.39 (m, 2H), 7.19 (t, J = 7.4 Hz, 1H), 7.10 (d, J = 7.7 Hz, 2H), 4.63 (q, J = 8.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 146.9 (q, J = 6.1 Hz), 138.9, 130.0, 125.3, 123.6 (q, J = 275.9 Hz), 123.5 (q, J = 266.8 Hz), 117.2, 92.1 (q, J = 33.3 Hz), 59.8 (q, J = 36.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.78 (s, 3F), -73.86--73.94 (t, J = 8.27 Hz, 3F). HRMS ESI (m/z): calcd for $C_{12}H_9F_6NNaO_2$ $[M + Na]^+$: 336.0435, found: 336.0430.

***(E)*-Cyclohexyl 3-(Phenylamino)-2-(trifluoromethyl)acrylate (2e')**



Yellow oil (109.5 mg, 70%); IR (KBr): 2938, 1677, 1638, 1232, 1119 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 10.51 (d, J = 13.0 Hz, 1H), 7.83 (dd, J = 13.2, 0.8 Hz, 1H), 7.37-7.33 (m, 2H), 7.12 (t, J = 7.4 Hz, 1H), 7.05 (d, J = 7.7 Hz, 2H), 5.04- 4.96 (m, 1H), 1.88-1.39 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 144.9 (q, J = 6.3 Hz), 139.5, 129.8, 124.6 (q, J = 266.7 Hz), 124.4, 116.6, 92.2 (q, J = 32.0 Hz), 72.4, 31.3, 25.4, 23.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.86 (s, 3F). HRMS ESI (m/z): calcd for $C_{16}H_{18}F_3NNaO_2$ $[M + Na]^+$: 336.1187, found: 336.1182.

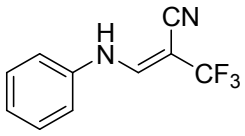
***(E)*-(Tetrahydrofuran-2-yl)methyl 3-(Phenylamino)-2-(trifluoromethyl)acrylate (2f')**



White oil (110.2 mg, 70%); IR (KBr): 2965, 1682, 1642, 1227, 1113 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 10.39 (d, J = 16 Hz, 1H), 7.84 (dd, J = 13.4, 0.7 Hz, 1H), 7.35 (m, 2H), 7.13 (t, J = 7.4 Hz, 1H), 7.06 (d, J = 7.7 Hz, 2H), 4.34-4.29 (m, 1H), 4.24-4.17 (m, 2H), 3.93-3.78 (m, 1H), 3.83-3.78 (m, 1H), 2.05-1.77 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 145.2 (q, J = 6.0 Hz), 139.3, 129.8, 124.6, 124.5 (q, J = 266.7 Hz), 116.8, 91.5 (q, J = 32.2 Hz), 76.3, 68.6, 65.9,

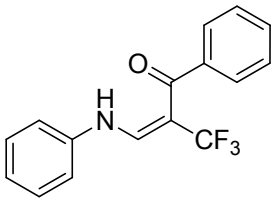
27.8, 25.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.69 (s, 3F). HRMS ESI (m/z): calcd for $C_{15}H_{16}F_3NNaO_3$ [M + Na]$^+$: 338.0980, found: 338.0974.

***(E)*-3-(Phenylamino)-2-(Trifluoromethyl)acrylonitrile (2g')**



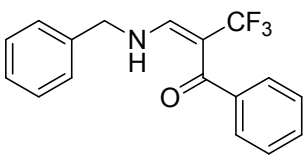
Yellow solid (63.6 mg, 60%), mp 143.8-145.4 °C; IR (KBr): 3249, 2218, 1663, 1297, 1108 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 13.9 Hz, 1H), 7.78 (d, J = 14.8 Hz, 1H), 7.42-7.35 (m, 2H), 7.19 (t, J = 7.5 Hz, 1H), 7.09 (d, J = 8.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.6 (q, J = 4.3 Hz), 138.8, 130.0, 125.2, 123.3 (q, J = 267.3 Hz), 117.1, 113.7, 74.2 (q, J = 38.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.69 (s, 3F). HRMS ESI (m/z): calcd for $C_{10}H_7F_3N_2Na$ [M + Na]$^+$: 235.0459, found: 235.0454.

***(E)*-1-Phenyl-3-(Phenylamino)-2-(trifluoromethyl)prop-2-en-1-one (2h')**



Yellow solid (80.0 mg, 55%), mp 64.3-65.4 °C; IR (KBr): 3060, 2927, 1653, 1320, 1107 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.50 (d, J = 11.5 Hz, 1H), 8.01 (d, J = 12.9 Hz, 1H), 7.53 (d, J = 7.0 Hz, 2H), 7.48- 7.32 (m, 5H), 7.25- 7.12 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 147.7 (q, J = 6.1 Hz), 141.0, 138.9, 130.2, 129.9, 127.9, 126.5 (d, J = 1.6 Hz), 125.7, 125.6 (q, J = 267.8 Hz), 117.7, 101.6 (q, J = 31.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -52.95 (s). HRMS ESI (m/z): calcd for $C_{16}H_{12}F_3NNaO$ [M + Na]$^+$: 314.0769, found: 314.0763.

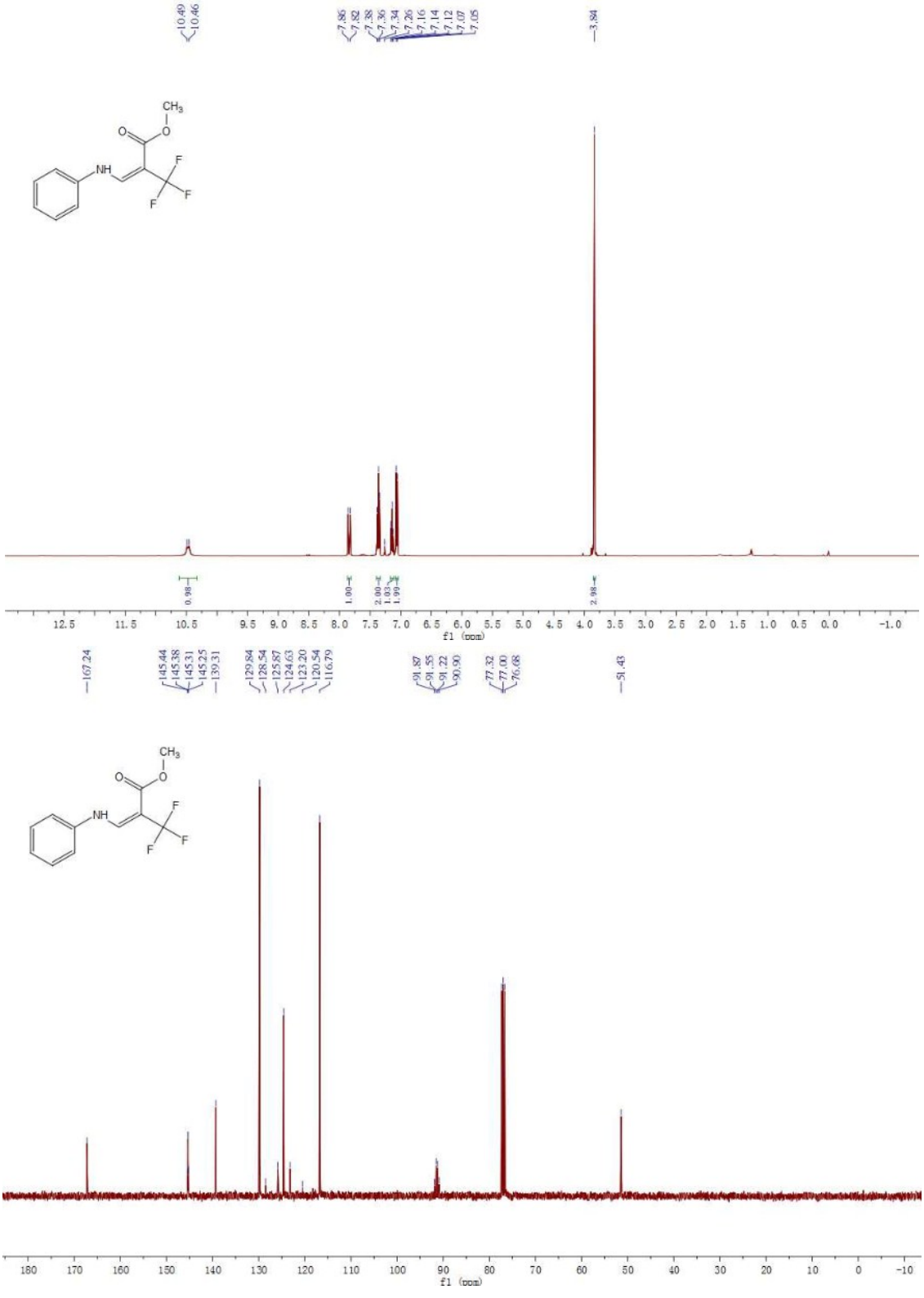
***(E)*-3-(Benzylamino)-1-Phenyl-2-(trifluoromethyl)prop-2-en-1-one (2i')**

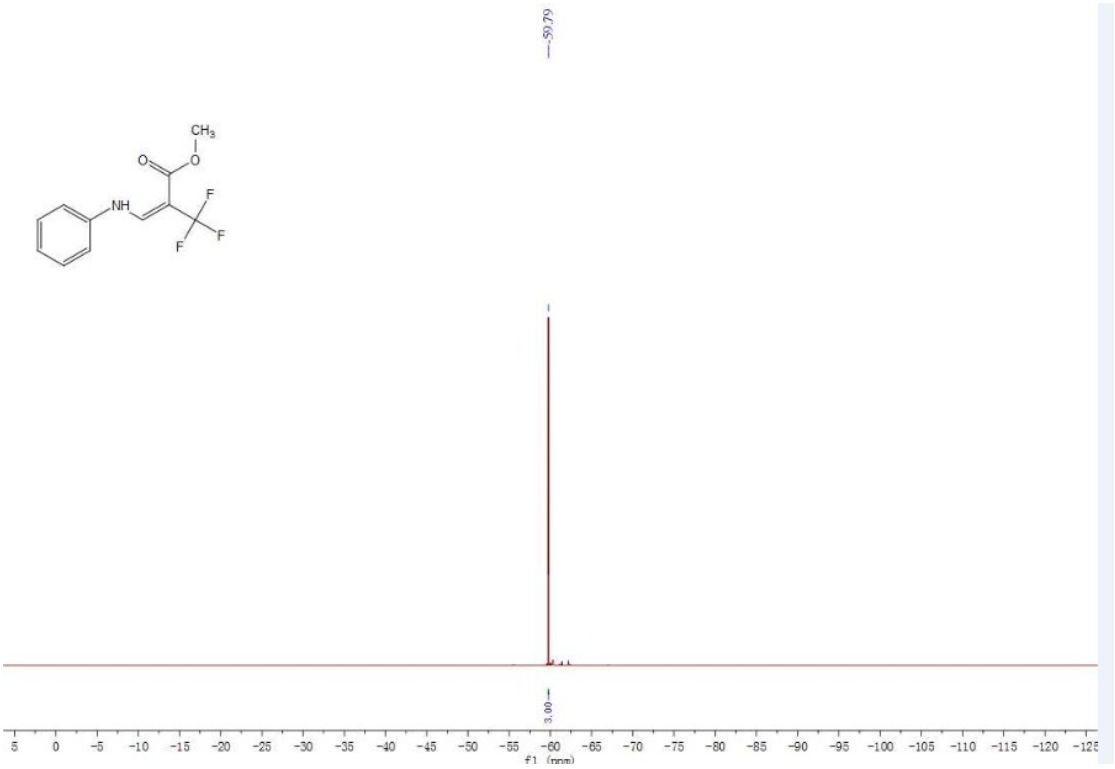


Light yellow solid (76.3 mg, 50%), mp 96.4-97.6 °C; IR (KBr): 3187, 2934, 1648, 1564, 1105 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.05 (s, 1H), 7.56 (d, J = 13.2 Hz, 1H), 7.47 (d, J = 6.8 Hz, 2H), 7.42- 7.32 (m, 6H), 7.28 (d, J = 6.8 Hz, 2H), 4.52 (d, J = 6.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.8, 155.2 (q, J = 6.0 Hz), 141.4, 136.1, 129.8, 129.1, 128.4, 127.8, 127.4, 126.4 (d, J = 1.5 Hz), 126.0 (q, J = 267.3 Hz), 99.3 (q, J = 31.4 Hz), 53.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -52.39 (s, 3F). HRMS ESI (m/z): calcd for $C_{17}H_{14}F_3NNaO$ [M + Na]$^+$: 328.0925, found: 328.0920.

E. NMR Spectra

2a

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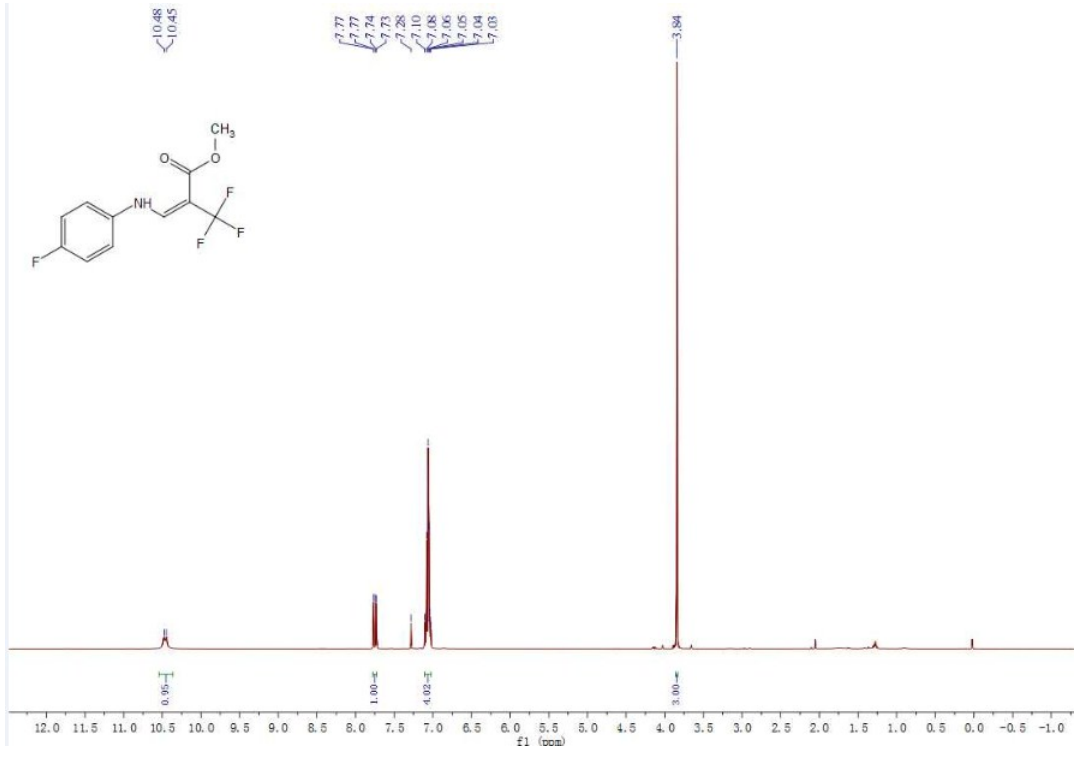
O
O
NH
F
F
F
3.00
f1 (ppm)

2b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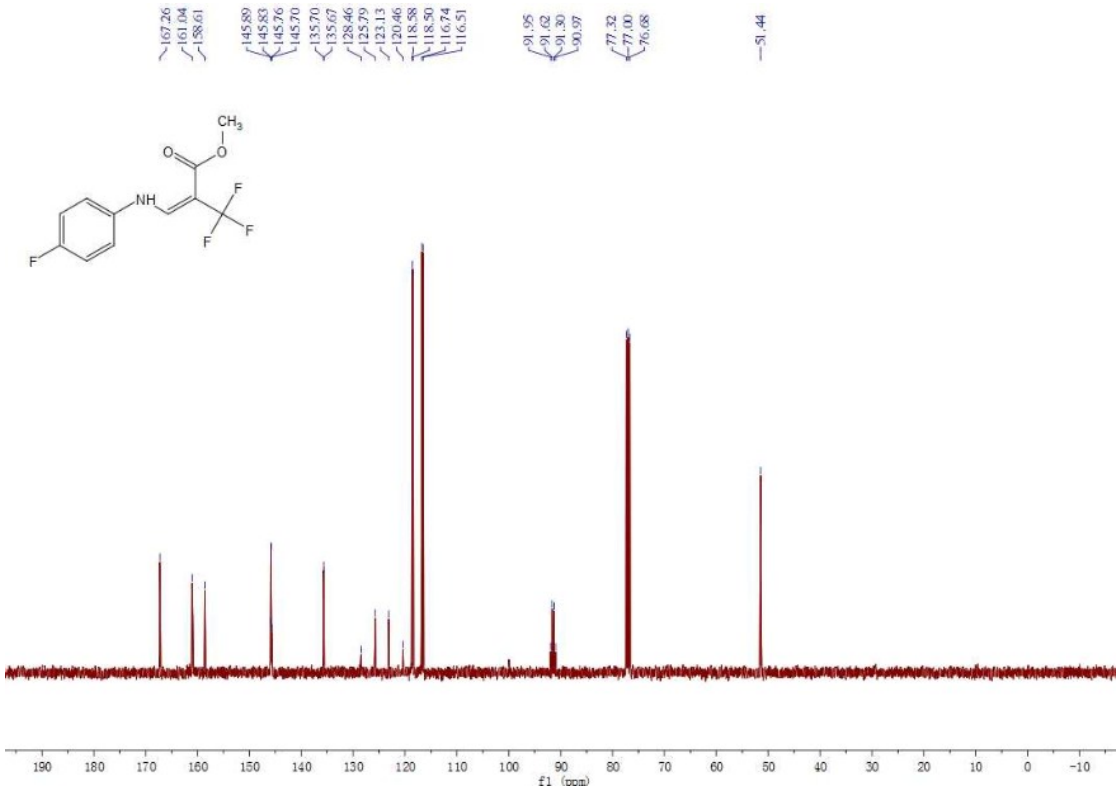
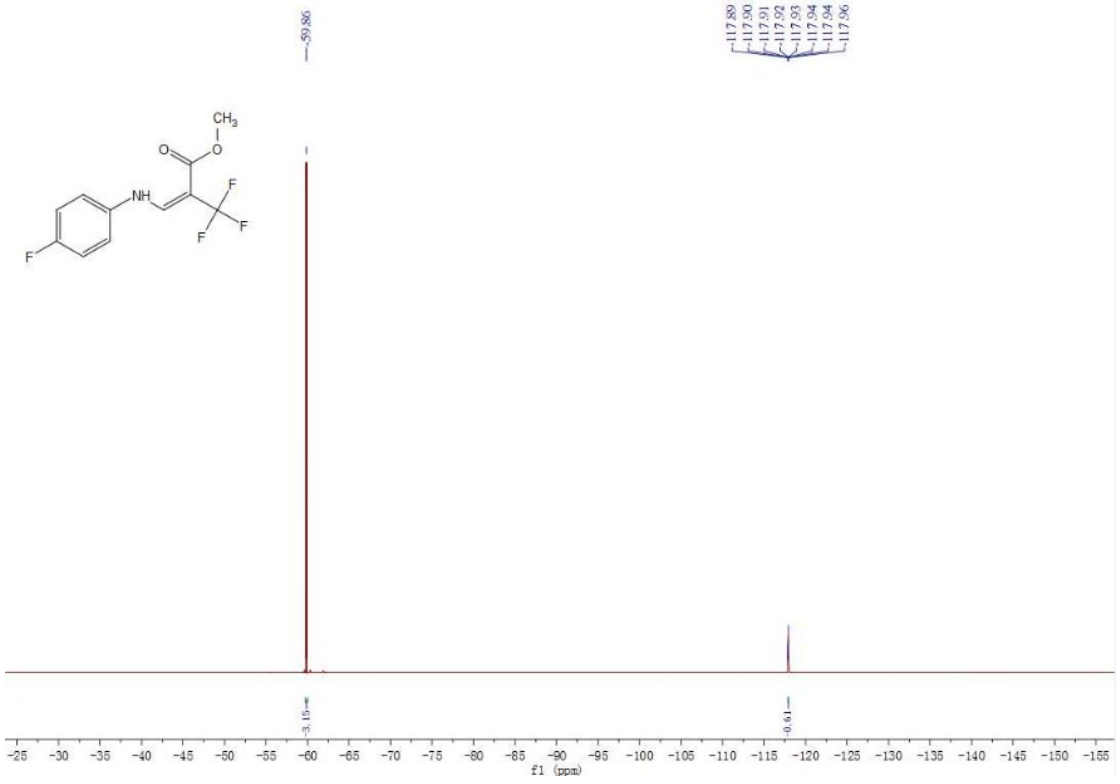
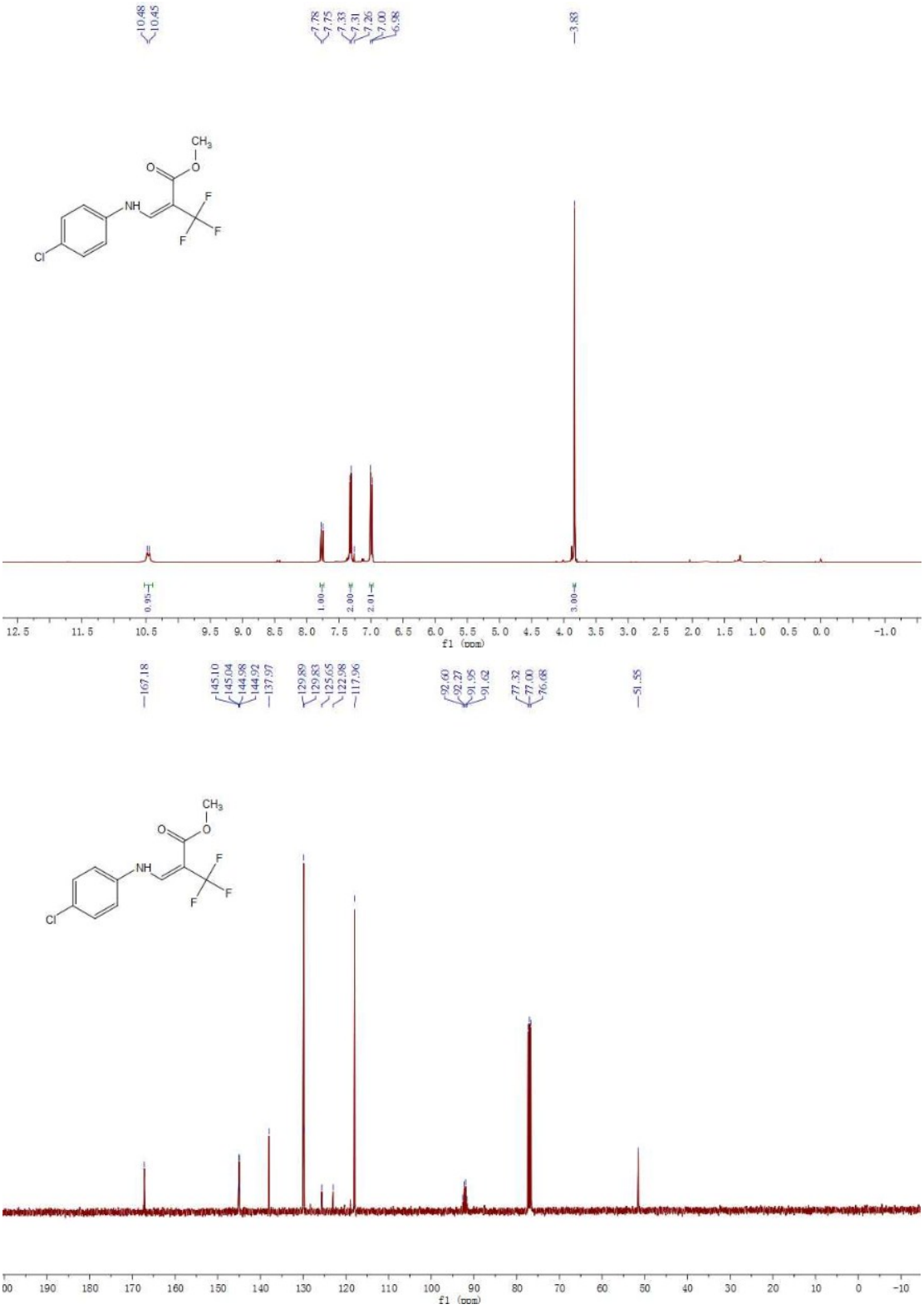
10.45
7.77
7.77
7.74
7.73
7.28
7.10
7.08
7.06
7.05
7.04
7.03
3.84
CH3
O
O
NH
F
F
F
F
0.95
1.00
4.02
3.00
f1 (ppm)


167.26
161.04
158.61
145.89
145.83
145.76
145.70
135.70
135.67
128.46
125.79
123.13
120.46
118.58
118.50
116.74
116.51
91.95
91.62
91.30
90.97
77.32
77.00
76.68
51.44
CH3
O
O
NH
F
F
F
F
f1 (ppm)


59.86
117.89
117.90
117.91
117.92
117.93
117.94
117.94
117.96
CH3
O
O
NH
F
F
F
F
-59.86
-117.92
f1 (ppm)

2c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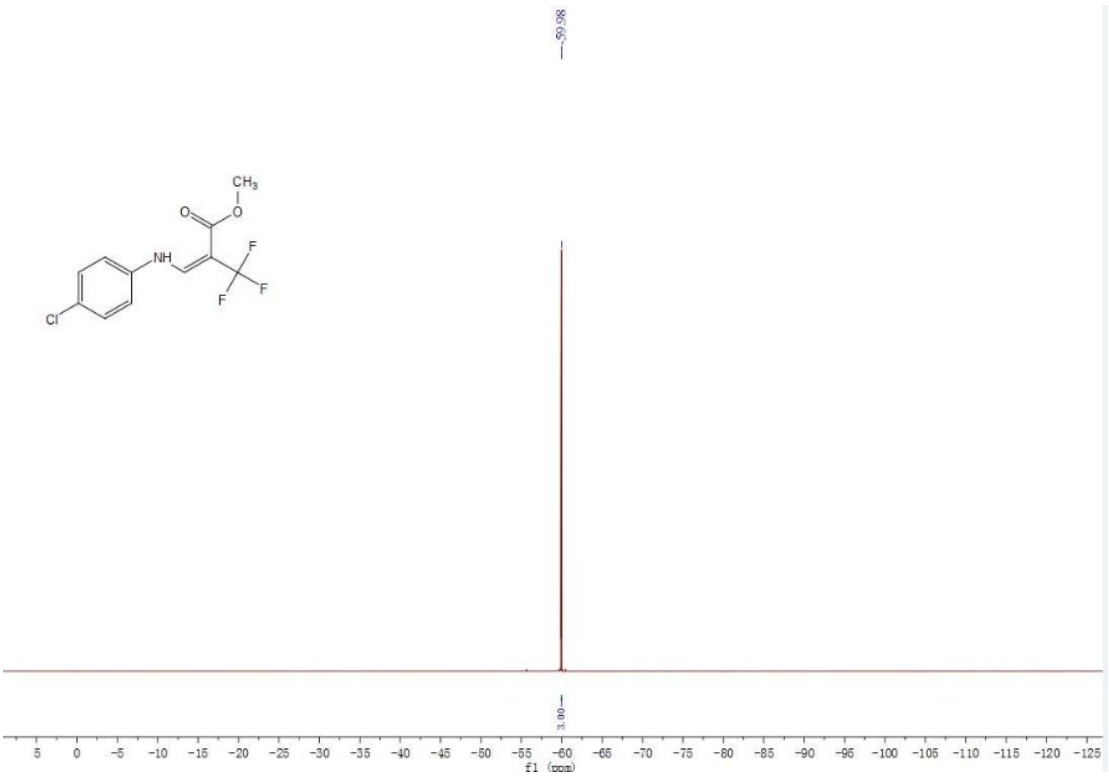
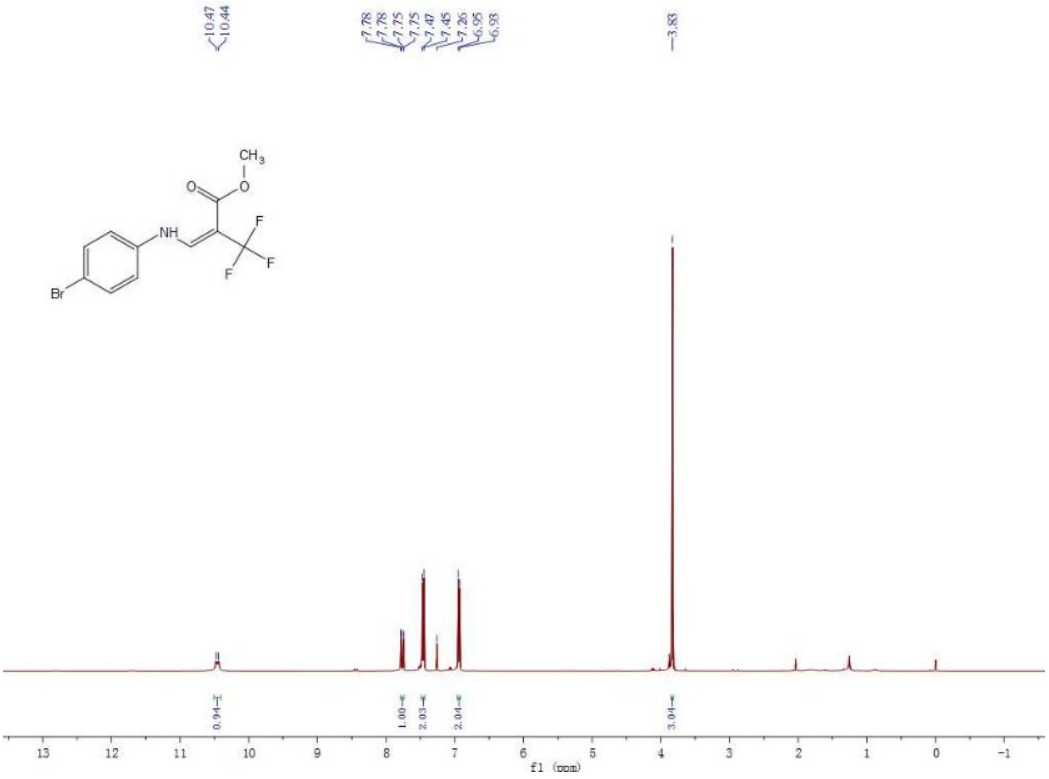
10.45
7.78
7.75
7.33
7.31
7.26
7.00
6.98
3.83
CH3
O
O
NH
F
F
F
Cl
0.95
1.00
2.00
2.01
3.00
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)
167.18
145.10
145.04
144.58
144.52
137.97
129.89
129.83
125.65
122.98
117.96
92.60
92.27
91.95
91.62
77.32
77.00
76.68
51.55
CH3
O
O
NH
F
F
F
Cl
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


-59.98
CH3
O
O
NH
F
F
F
Cl
3.00
f1 (ppm)

2d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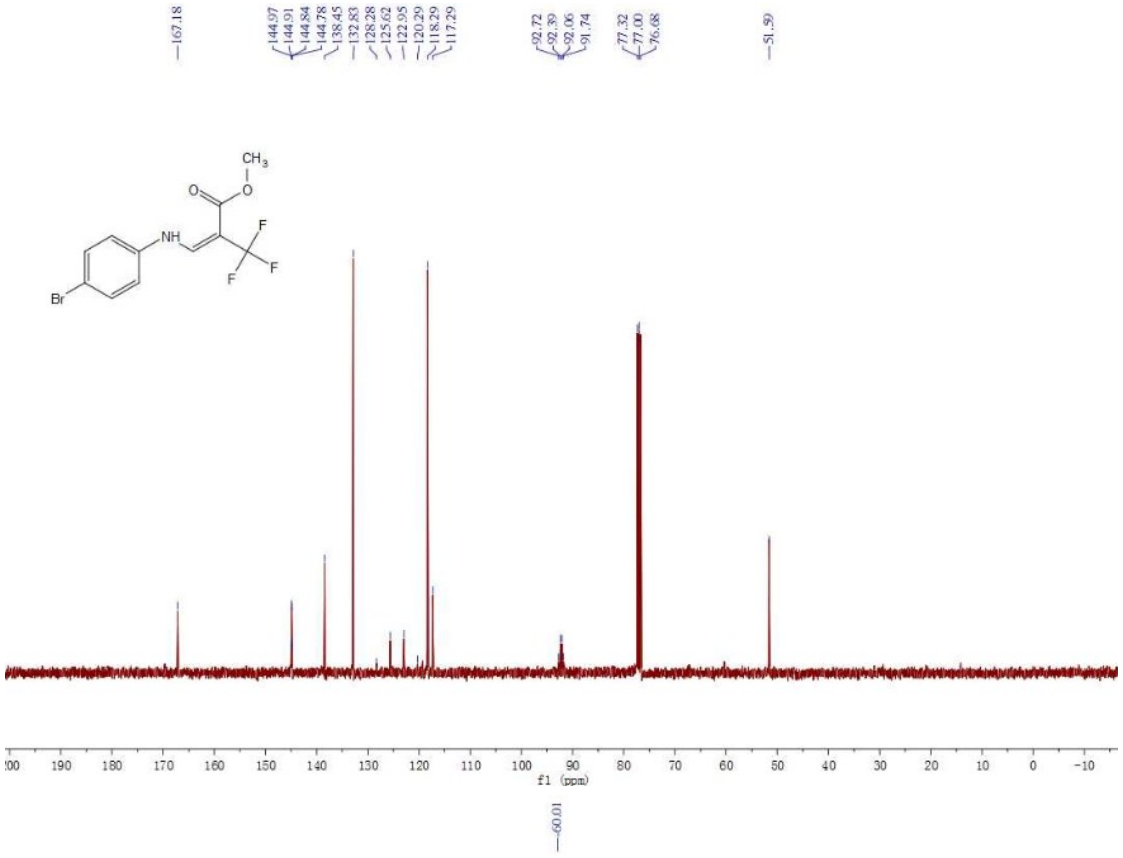
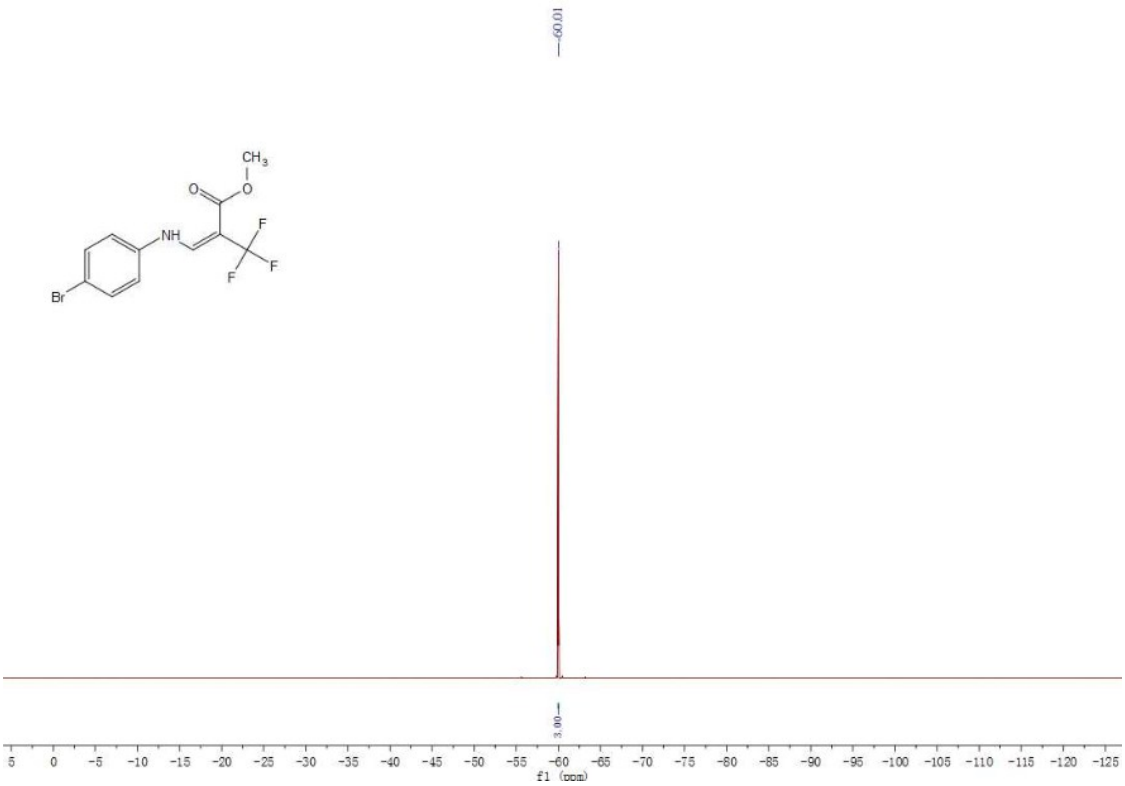
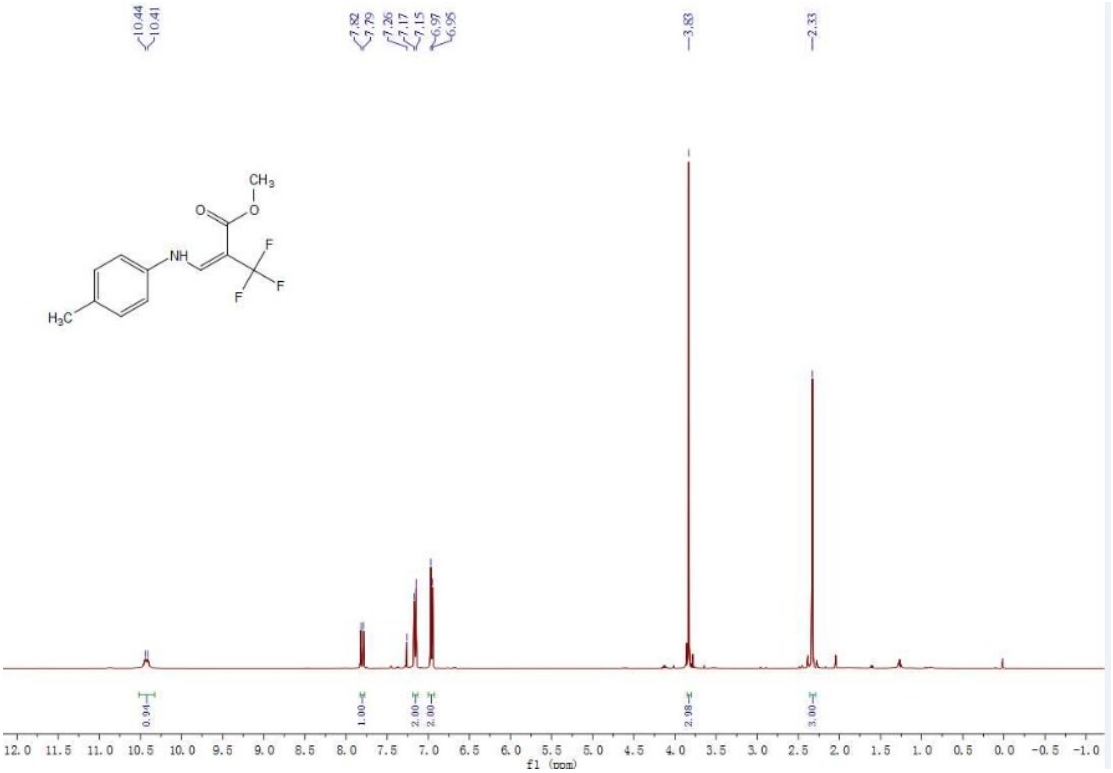
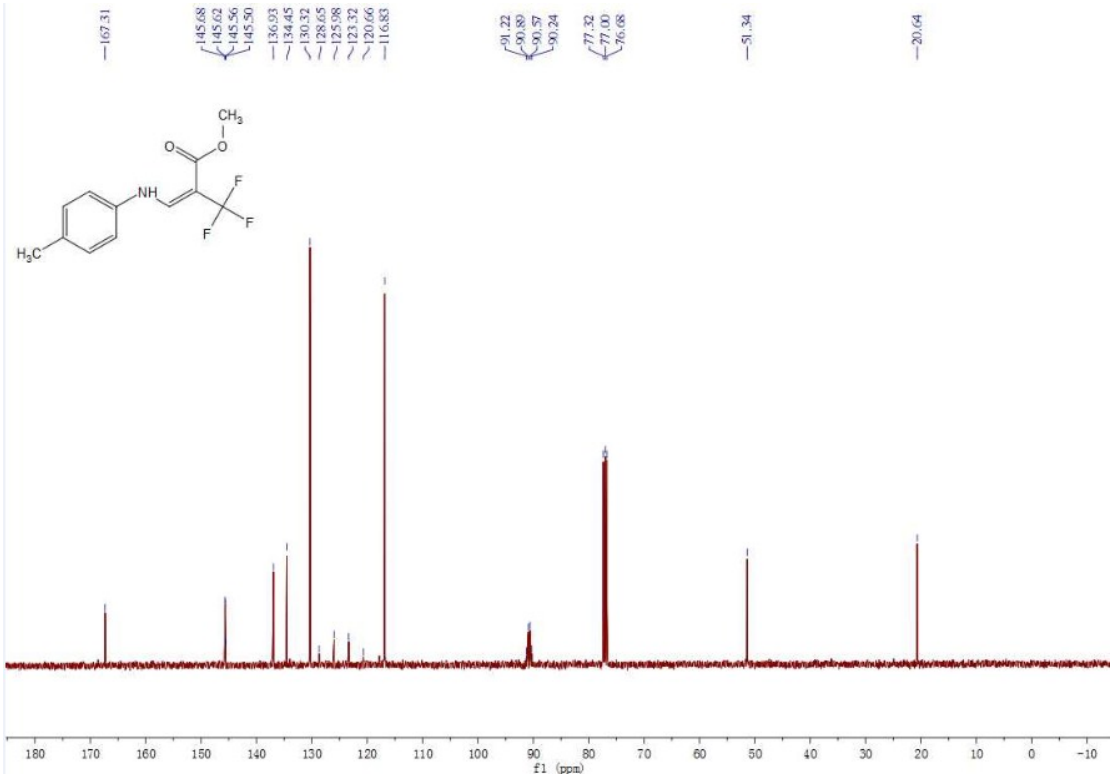
10.44
7.78
7.78
7.75
7.75
7.47
7.45
7.26
6.95
6.93
3.83
CH3
O
O
NH
F
F
F
Br
0.94
1.00
2.03
2.04
3.04
f1 (ppm)


167.18
144.97
144.91
144.84
144.78
138.45
132.83
128.28
125.62
122.95
120.29
118.29
117.29
92.72
92.39
92.06
91.74
77.32
77.00
76.68
51.59
CH3
O
O
NH
F
F
F
Br
f1 (ppm)


-60.01
CH3
O
O
NH
F
F
F
Br
3.00
f1 (ppm)

2e


10.44
10.41
7.82
7.79
7.26
7.17
7.15
6.97
6.95
3.83
2.33
CH3
O
O
NH
F
F
F
H3C
0.94
1.00
2.00
2.00
2.98
3.00
f1 (ppm)


167.31
145.68
145.62
145.56
145.50
136.93
134.45
130.32
128.65
125.98
123.32
120.66
116.83
91.22
90.80
90.57
90.24
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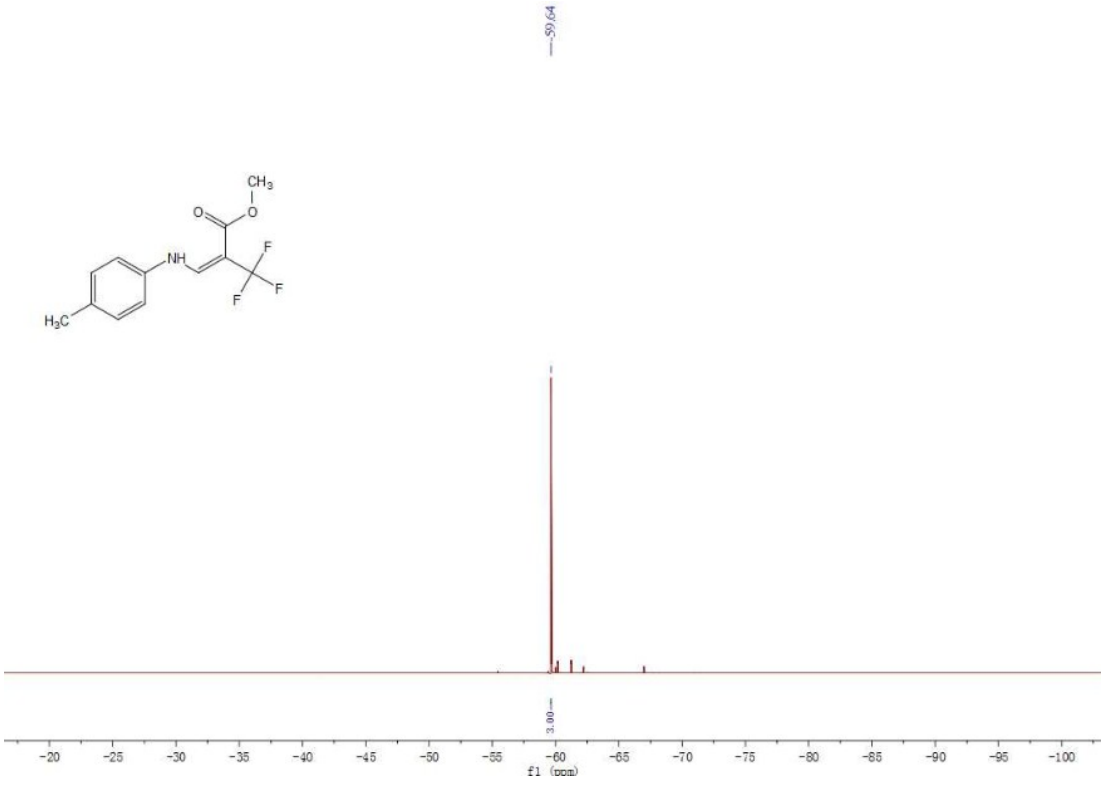
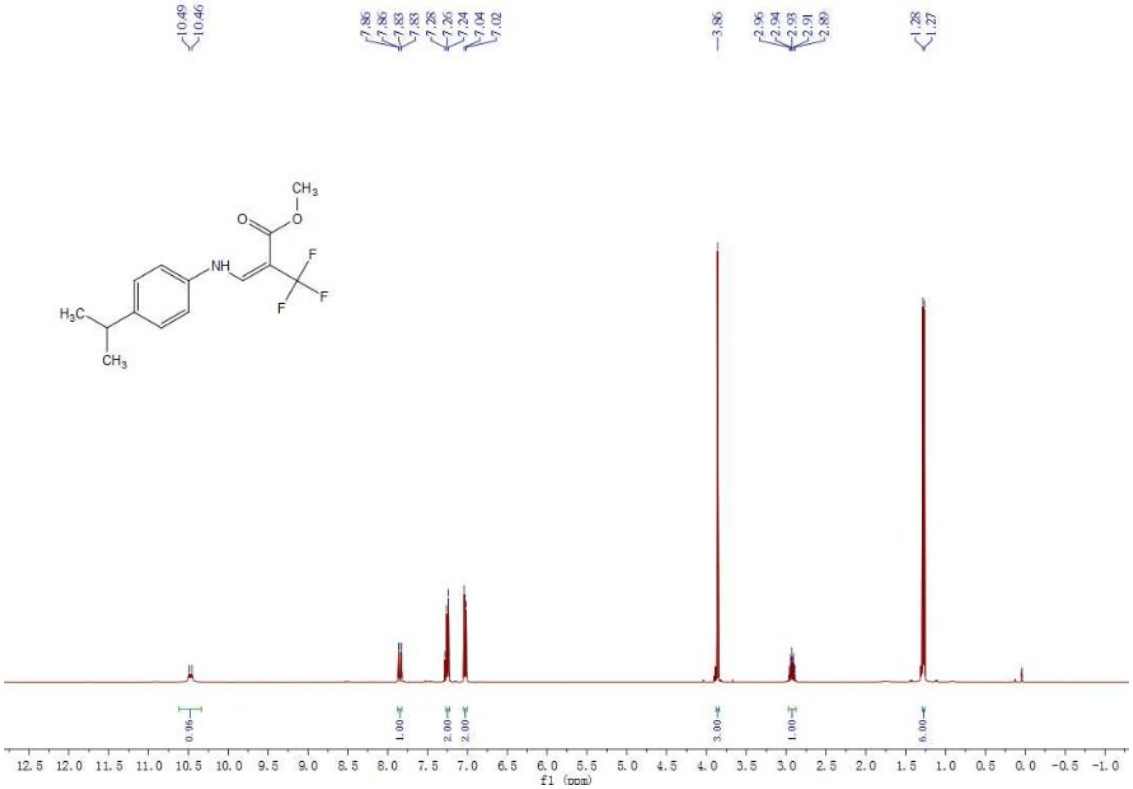
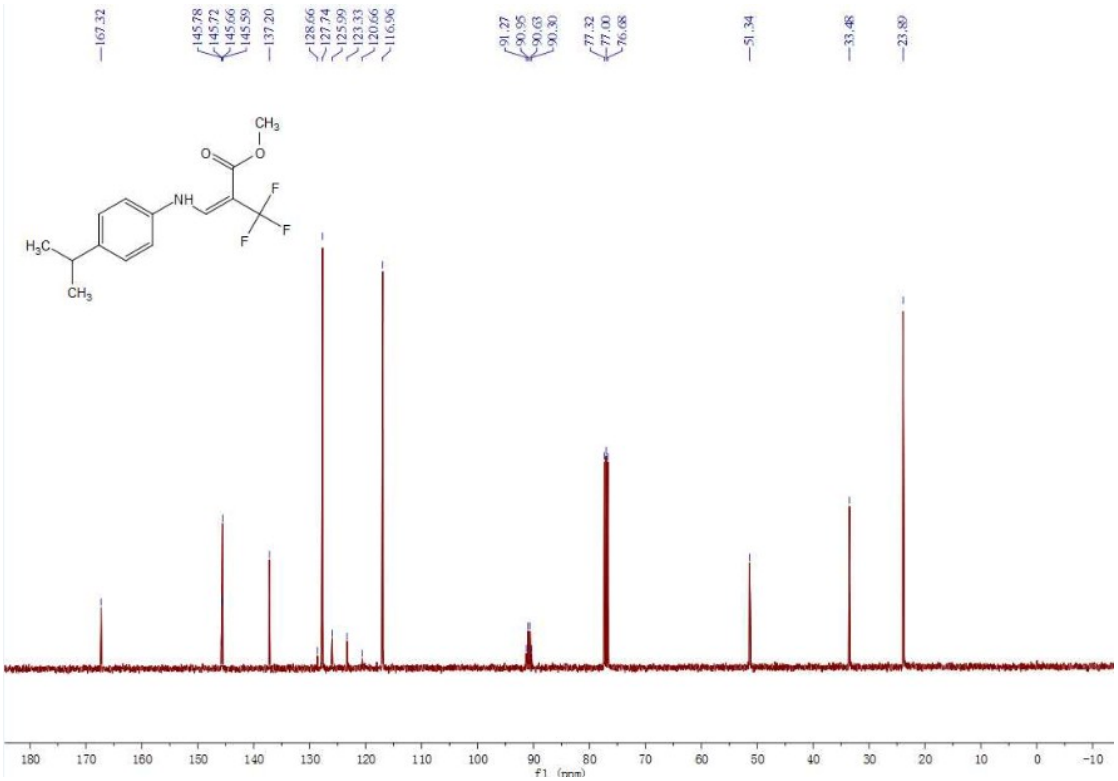
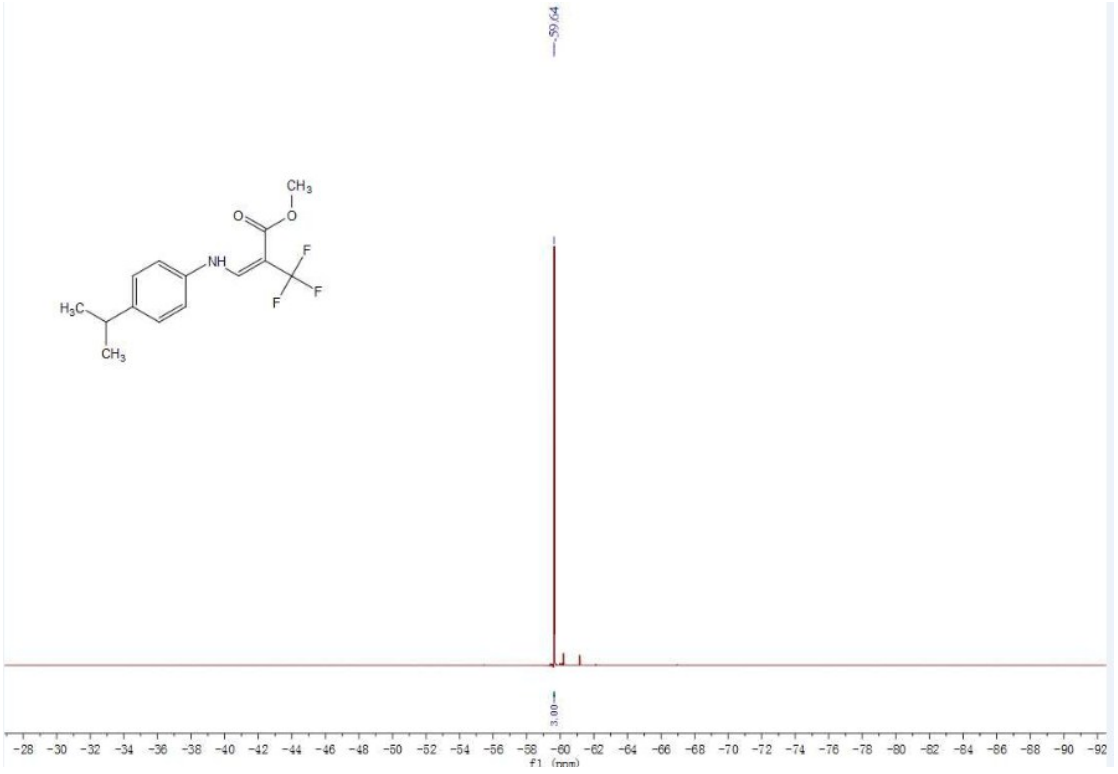
O
O
NH
F
F
F
H3C
f1 (ppm)


-59.64
CH3
O
O
NH
F
F
F
H3C
3.00
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
f1 (ppm)

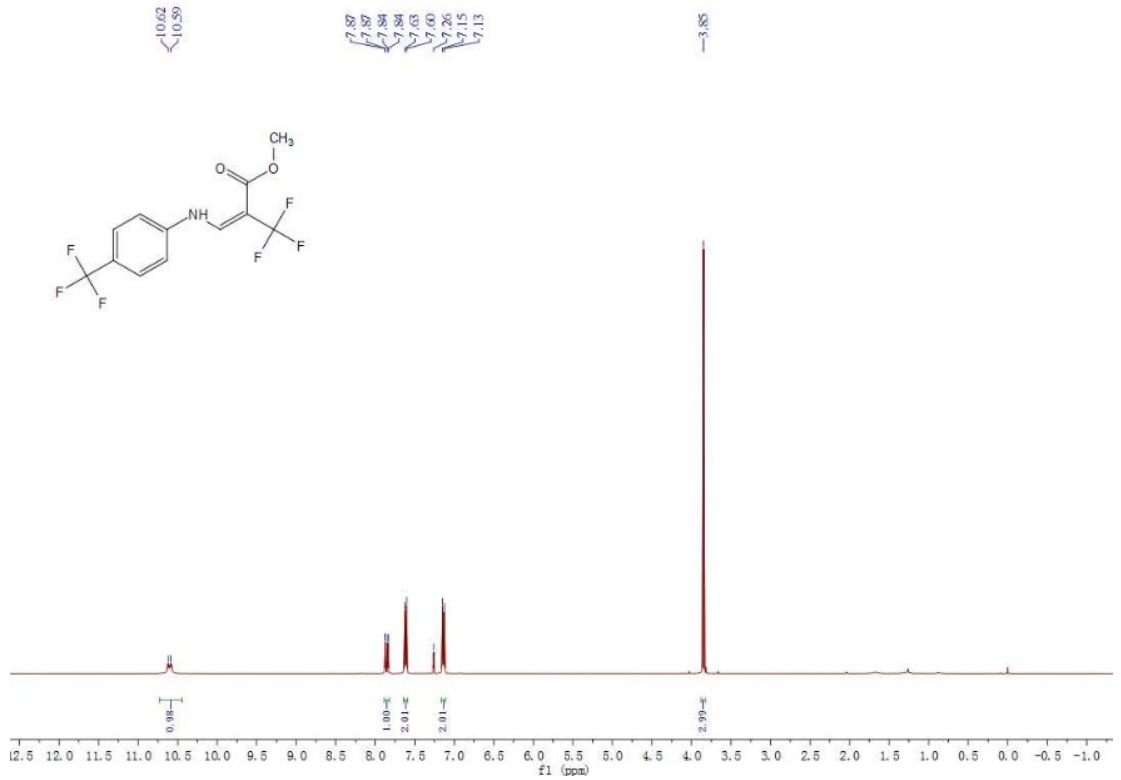
2f

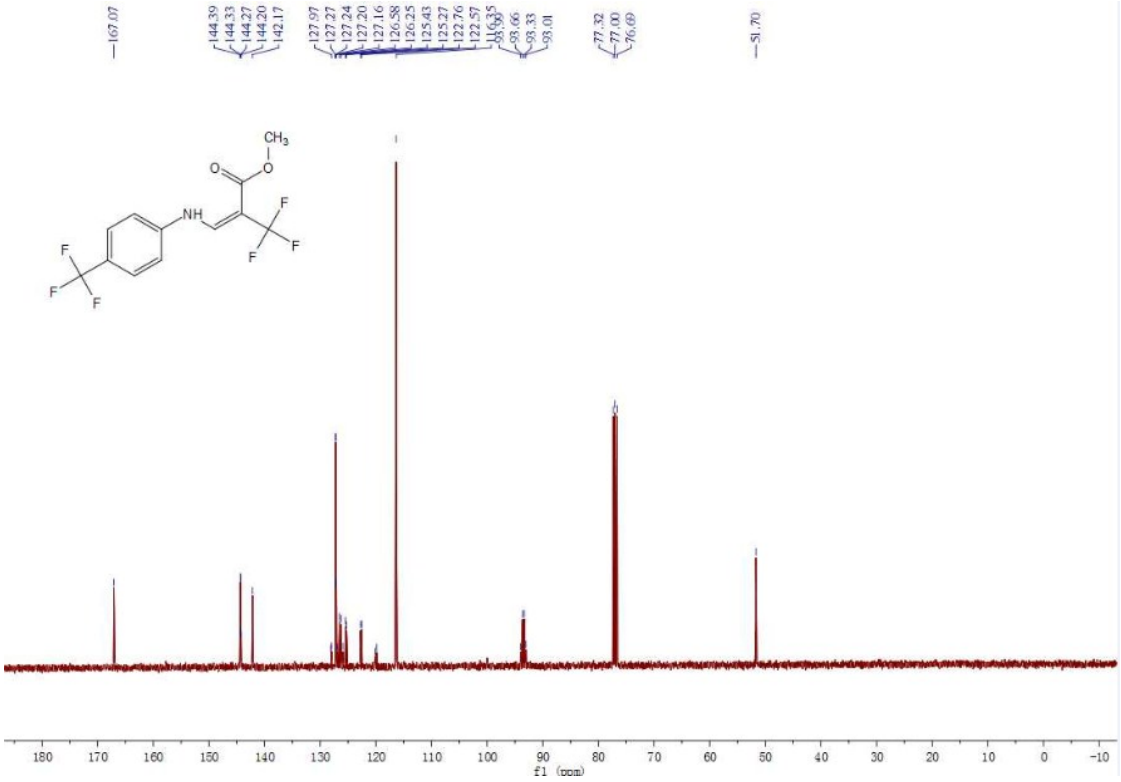

10.49
10.46
7.86
7.86
7.83
7.83
7.28
7.26
7.24
7.04
7.02
3.86
2.96
2.94
2.93
2.91
2.89
1.28
1.27
CH3
O
O
NH
F
F
F
H3C
CH3
0.98
1.00
2.00
2.00
3.00
1.00
6.00
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

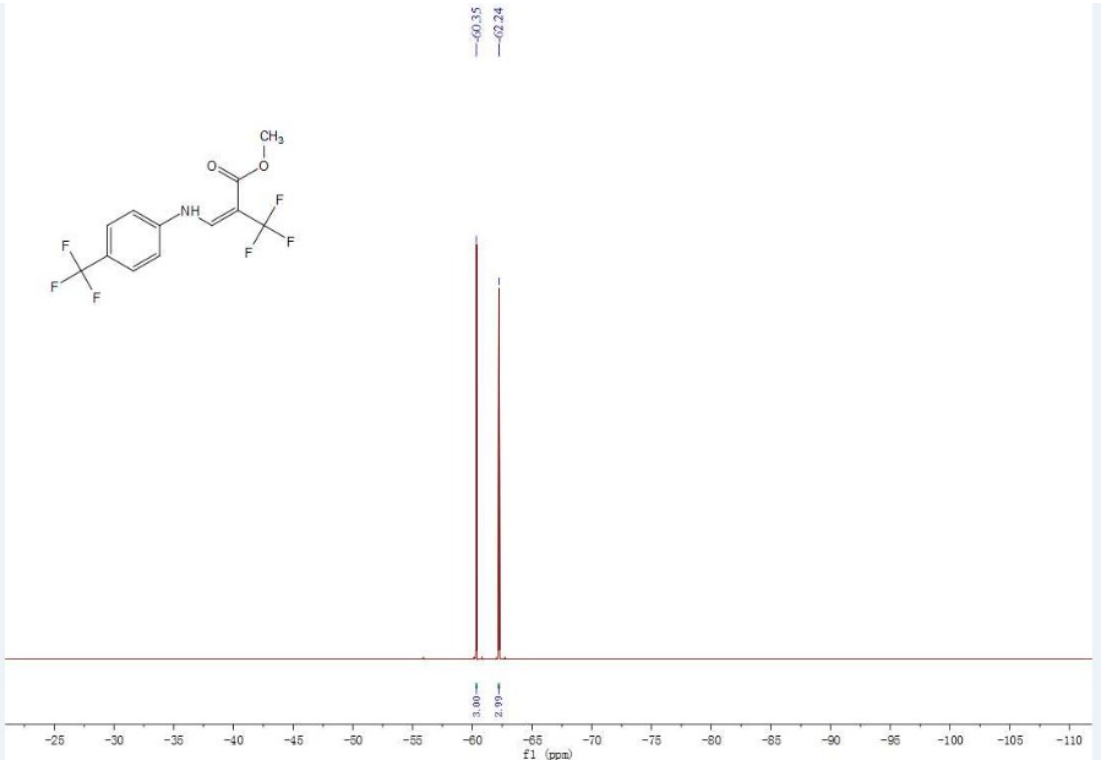

167.32
145.78
145.72
145.66
145.59
137.20
128.66
127.74
125.99
123.33
120.66
116.96
91.27
90.95
90.63
90.30
77.32
77.00
76.68
51.34
33.48
23.80
CH3
O
O
NH
F
F
F
H3C
CH3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-59.64
CH3
O
O
NH
F
F
F
H3C
CH3
3.00
-28 -30 -32 -34 -36 -38 -40 -42 -44 -46 -48 -50 -52 -54 -56 -58 -60 -62 -64 -66 -68 -70 -72 -74 -76 -78 -80 -82 -84 -86 -88 -90 -92
f1 (ppm)

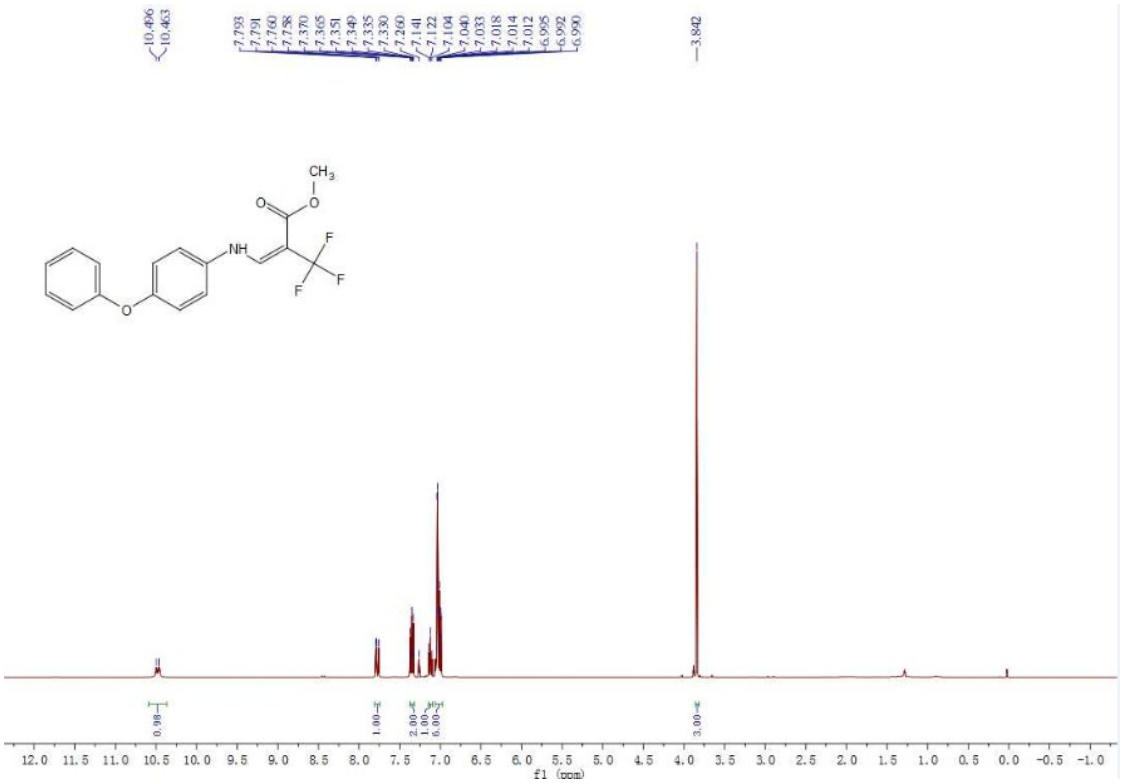
2g

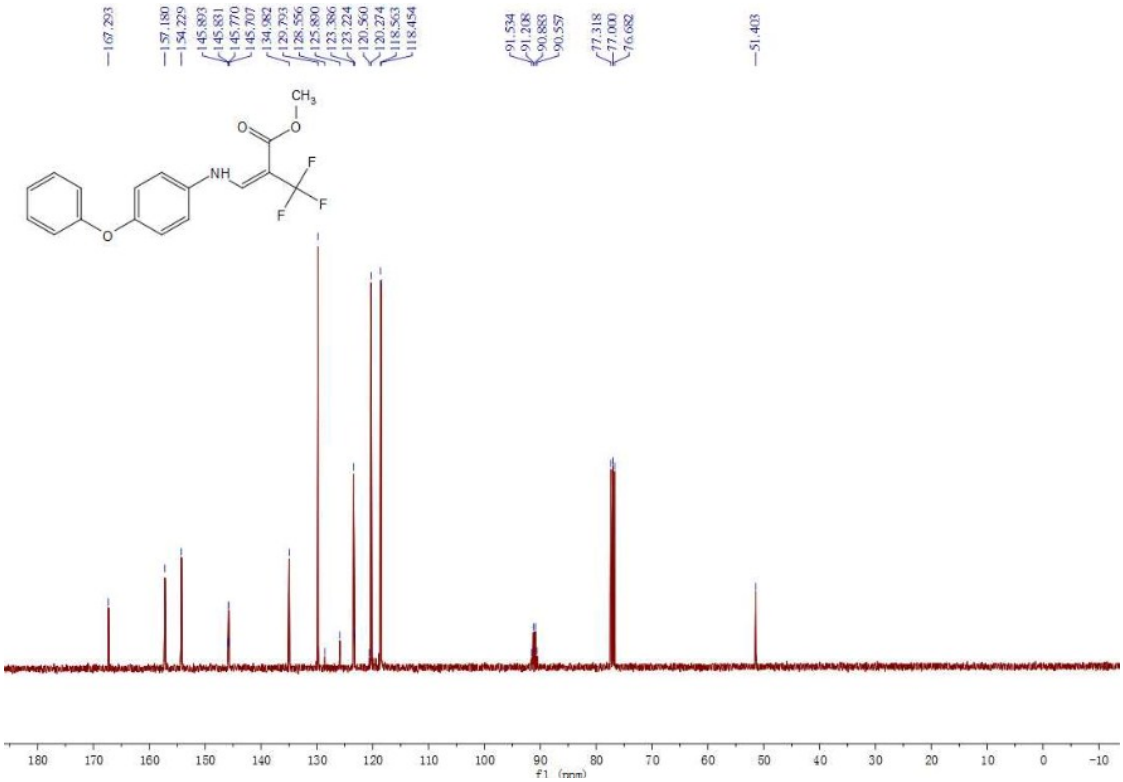

10.62
10.59
7.89
7.87
7.84
7.84
7.63
7.60
7.26
7.15
7.13
3.85
CH3
O
O
NH
F
F
F
F
F
F
0.98
1.00
2.01
2.01
2.99
f1 (ppm)

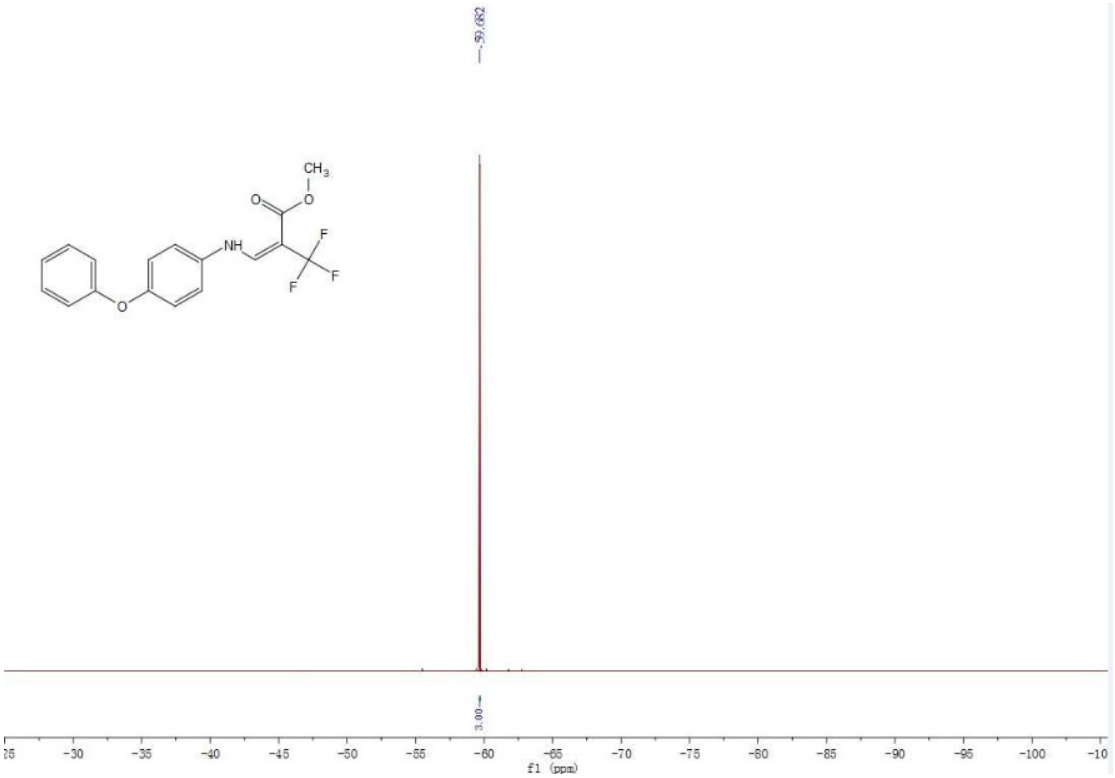

167.07
144.39
144.33
144.27
144.20
142.17
127.97
127.27
127.24
127.20
127.16
126.58
126.25
125.43
125.27
122.76
122.57
116.35
93.66
93.33
93.01
77.32
77.00
76.69
51.70
CH3
O
O
NH
F
F
F
F
F
F
f1 (ppm)


-60.35
-62.24
CH3
O
O
NH
F
F
F
F
F
3.00
2.99
-25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110
f1 (ppm)

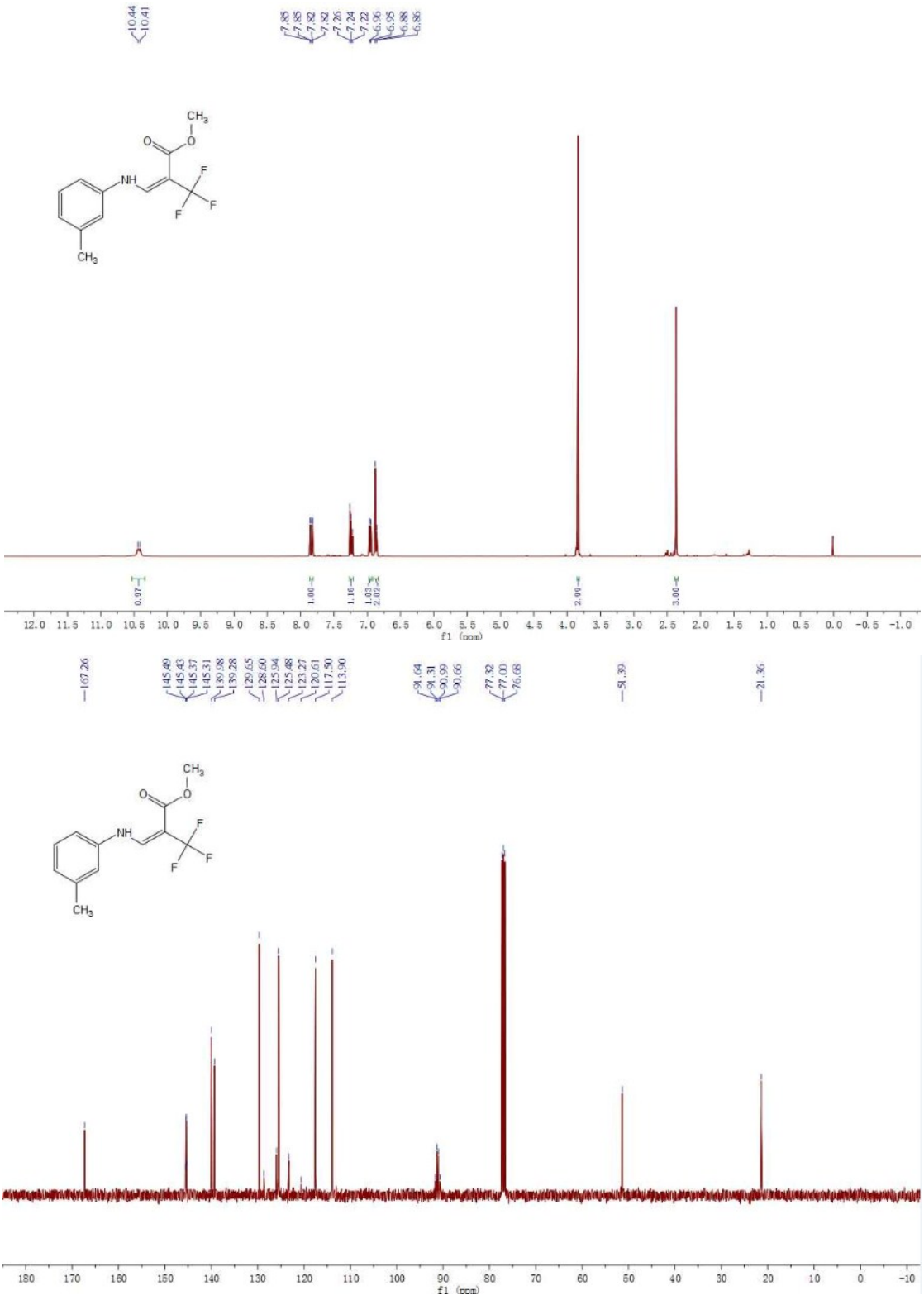
2h

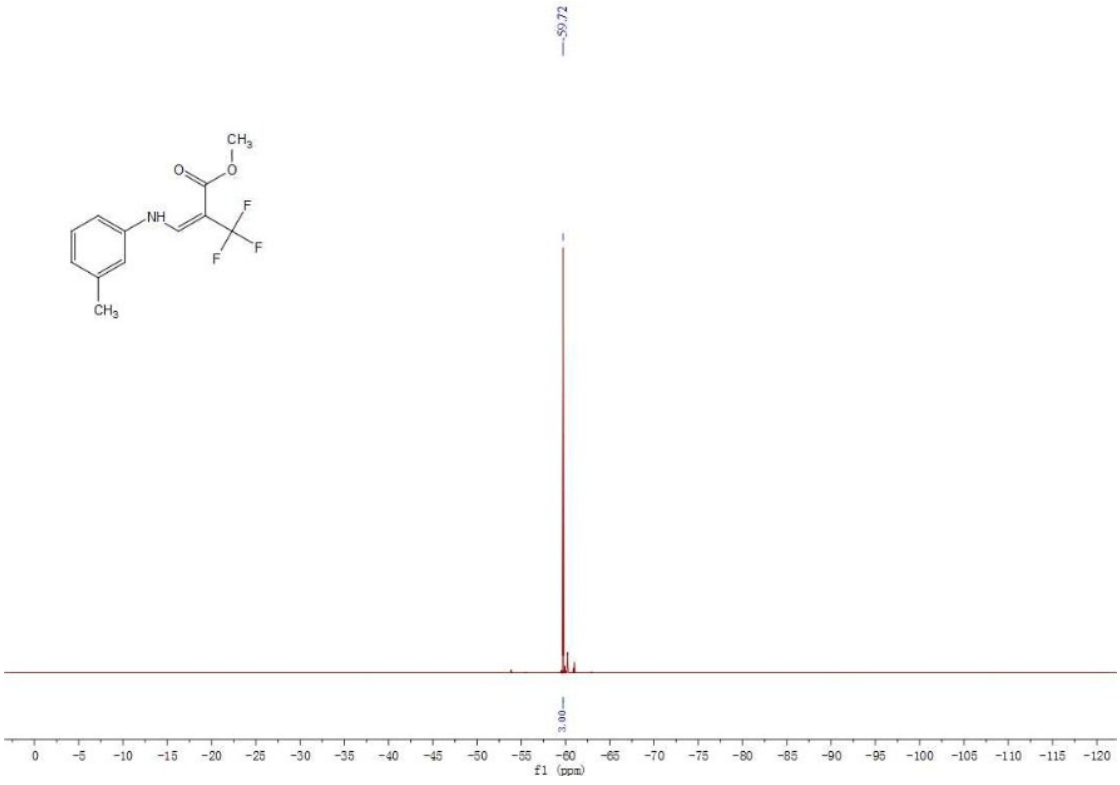

10.496
10.463
7.793
7.791
7.760
7.758
7.370
7.365
7.351
7.340
7.335
7.330
7.260
7.141
7.122
7.104
7.040
7.033
7.018
7.014
7.012
6.995
6.992
6.990
3.842
CH3
O
O
NH
F
F
F
O
0.98
1.00
2.00
1.00
6.00
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


167.293
157.180
154.229
145.893
145.831
145.770
145.707
134.082
129.793
128.556
125.890
123.386
123.224
120.560
120.274
118.563
118.454
91.534
91.208
90.883
90.557
77.318
77.000
76.682
51.403
CH3
O
O
NH
F
F
F
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

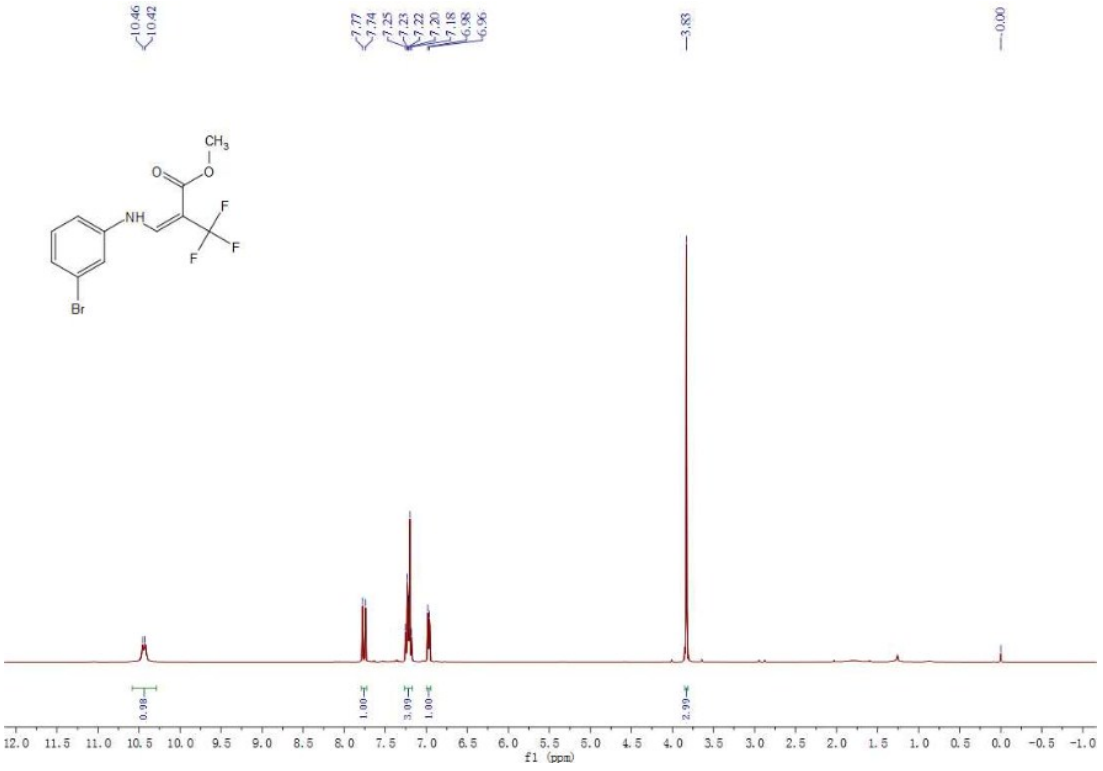

-59.662
CH3
O
O
NH
F
F
F
O
3.00
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-10
f1 (ppm)

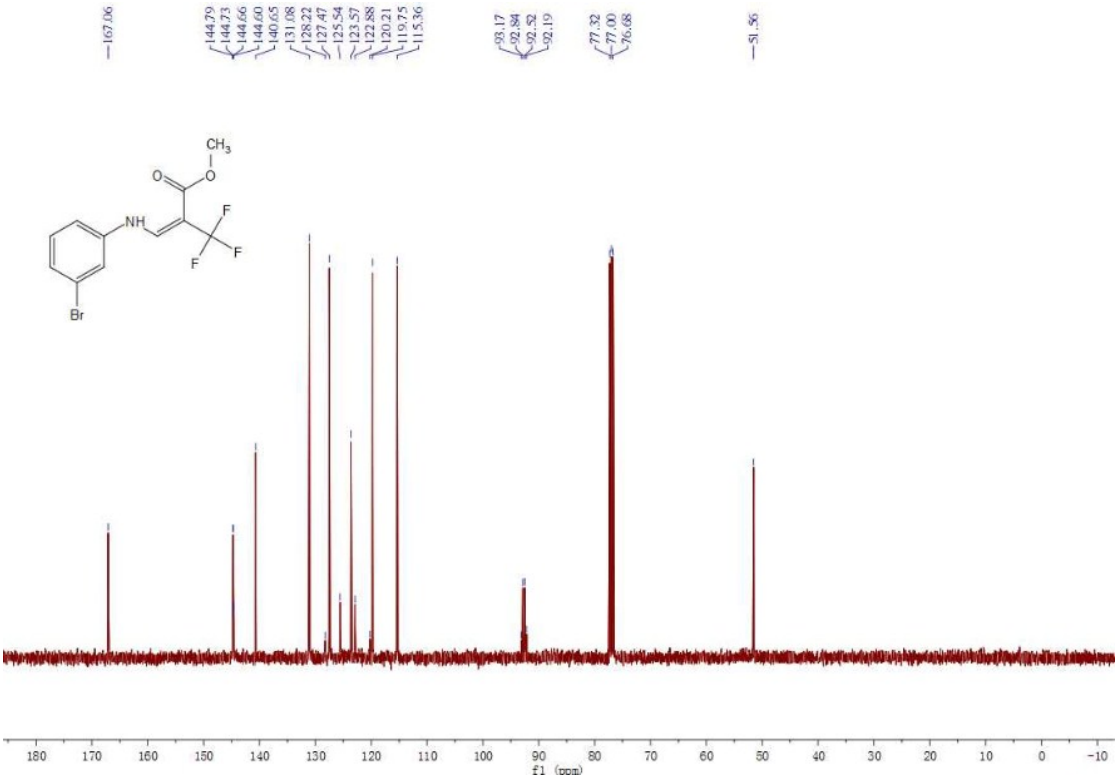
2i

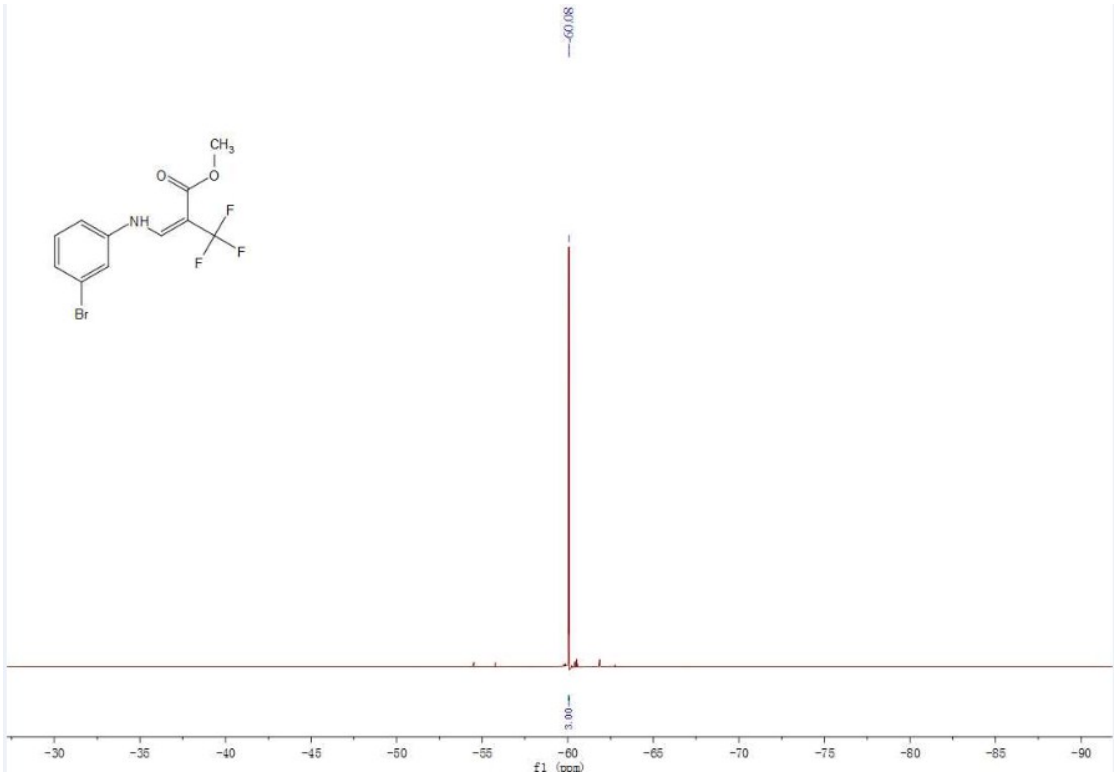

10.44
10.41
7.85
7.85
7.82
7.82
7.26
7.24
7.22
6.96
6.95
6.88
6.86
CH3
O
O
NH
F
F
F
CH3
0.97
1.00
1.16
1.03
2.02
2.99
3.00
f1 (ppm)
167.26
145.49
145.43
145.37
145.31
139.98
139.28
129.65
128.60
125.94
125.48
123.27
120.61
117.50
113.90
91.64
91.31
90.99
90.66
77.32
77.00
76.68
51.39
21.36
f1 (ppm)


-59.72
CH3
O
O
NH
F
F
F
CH3
3.00
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
f1 (ppm)

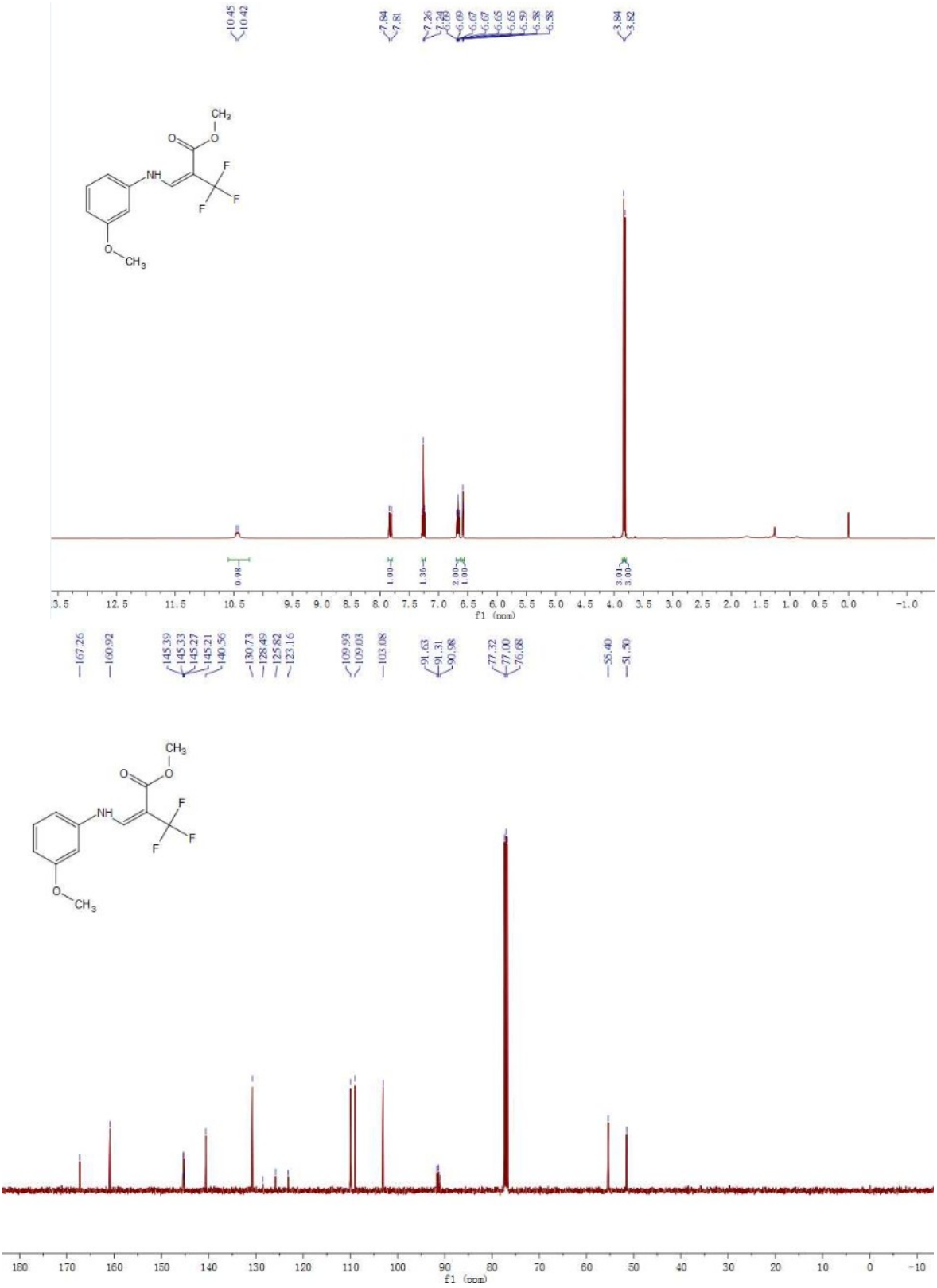
2j

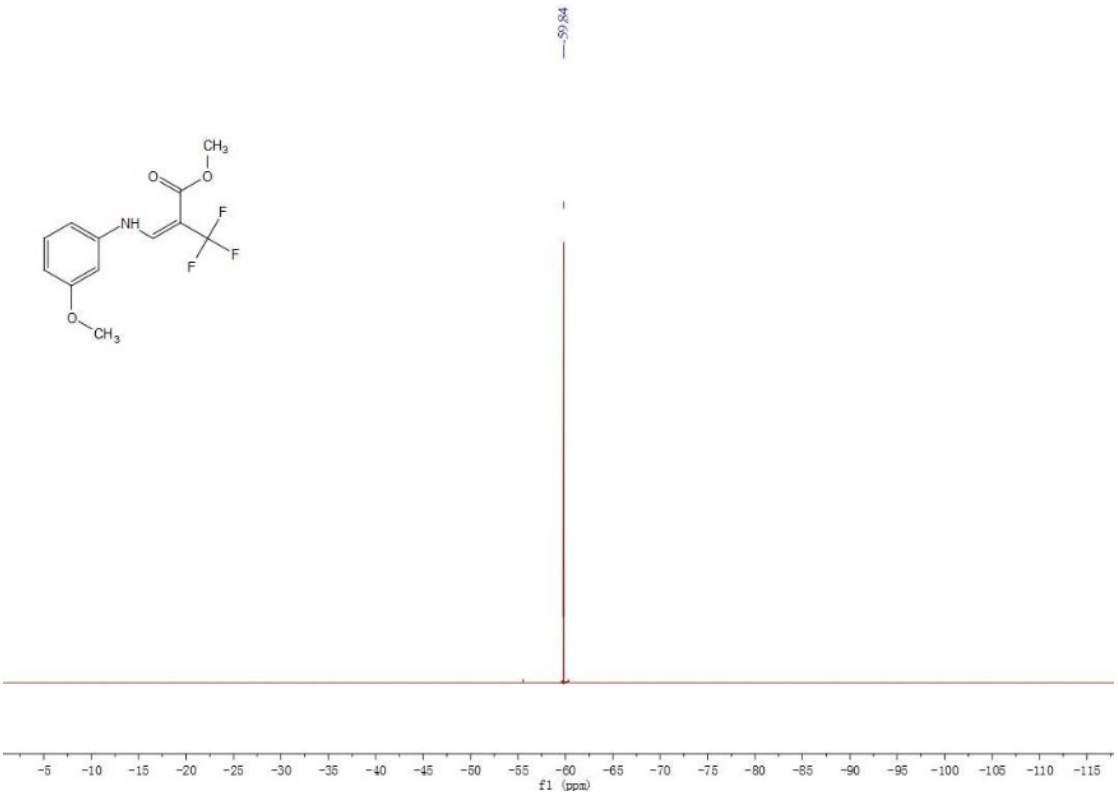

10.46
10.42
7.77
7.74
7.25
7.23
7.22
7.20
7.18
6.98
6.96
3.83
0.00
CH3
O
O
NH
F
F
F
Br
0.98
1.00
3.09
1.00
2.99
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


167.06
144.79
144.73
144.66
144.60
140.65
131.08
128.22
127.47
125.54
123.57
122.88
120.21
119.75
115.36
93.17
92.84
92.52
92.19
77.32
77.00
76.68
51.56
CH3
O
O
NH
F
F
F
Br
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

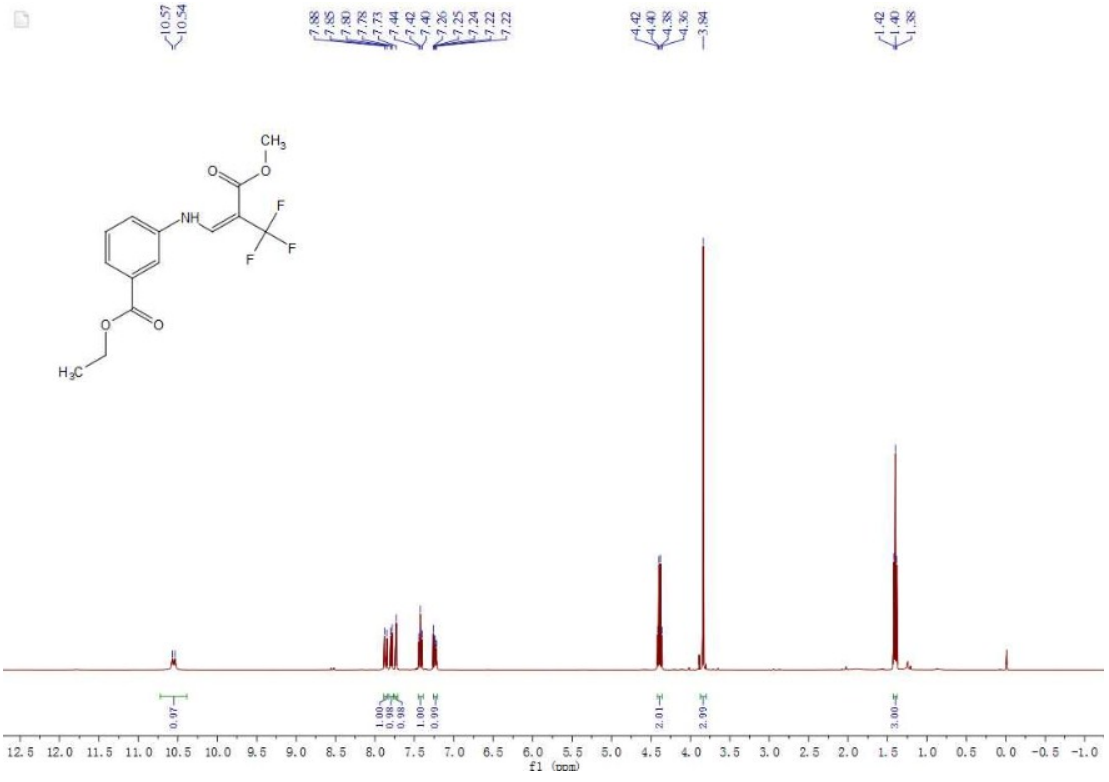

-60.08
CH3
O
O
NH
F
F
F
Br
3.00
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
f1 (ppm)

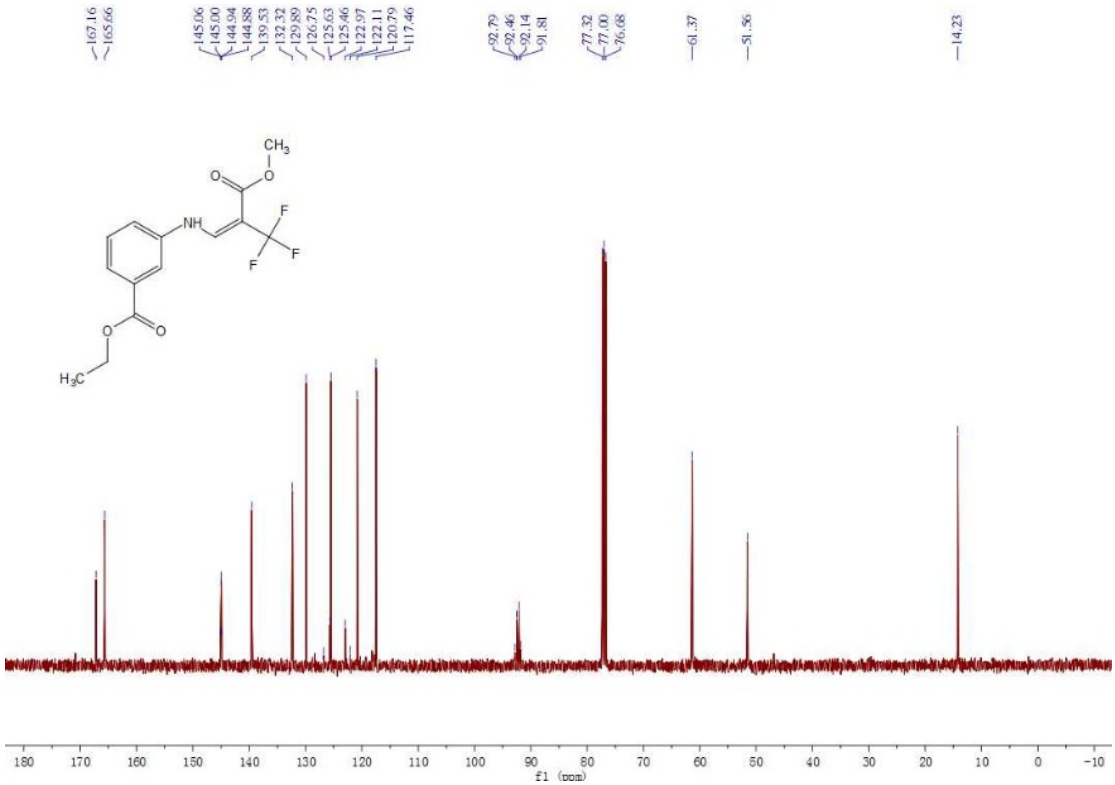
2k

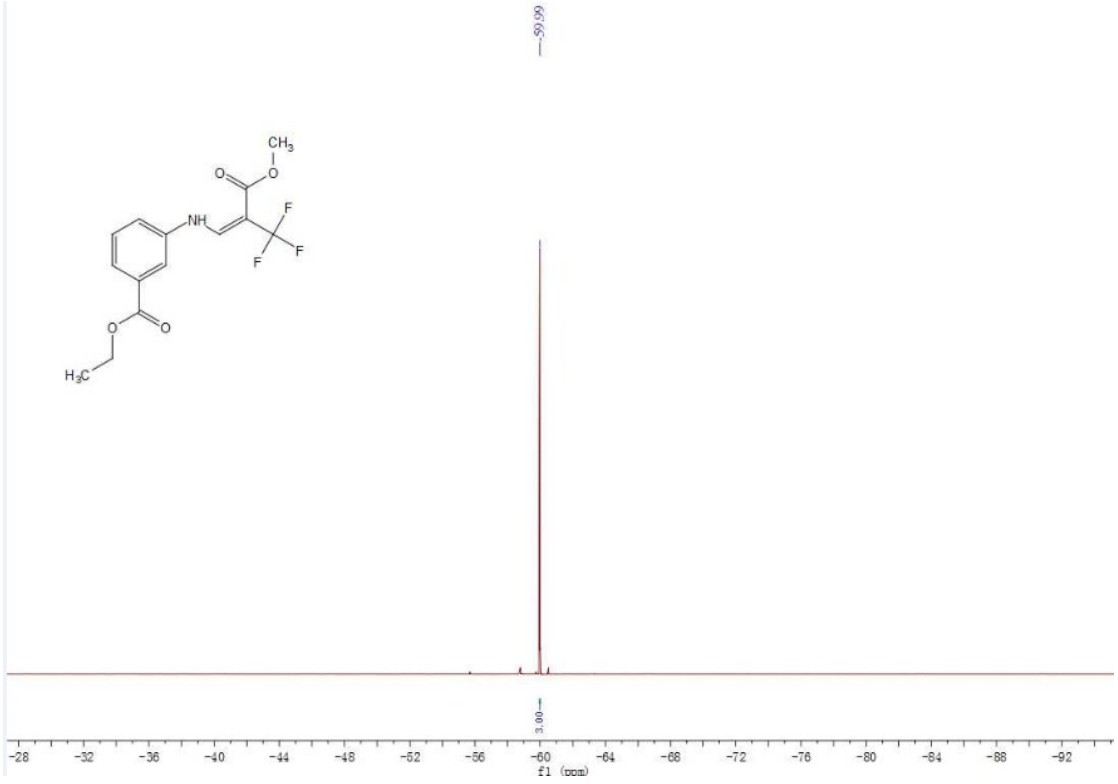

10.45
10.42
7.84
7.81
7.26
6.69
6.67
6.65
6.59
6.58
6.58
3.84
3.82
CH3
O
O
NH
F
F
F
O
CH3
0.98
1.00
1.36
2.00
1.00
3.01
3.00
f1 (ppm)
167.26
160.92
145.39
145.33
145.27
145.21
140.56
130.73
128.49
125.82
123.16
109.93
109.03
103.08
91.63
91.31
90.98
77.32
77.00
76.68
55.40
51.50
f1 (ppm)


-59.884
CH3
O
O
NH
F
F
F
O
CH3
-5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115
f1 (ppm)

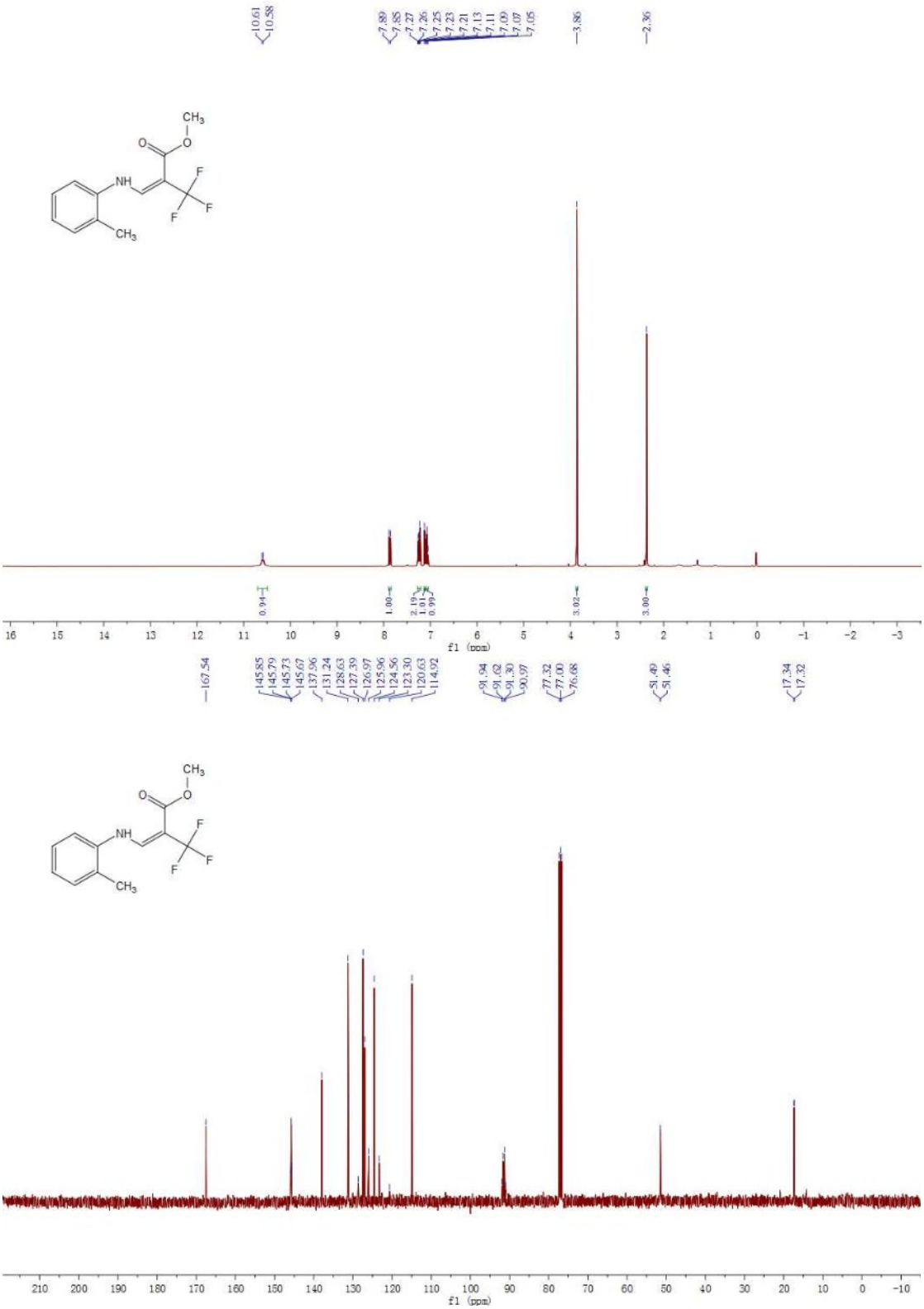
2l

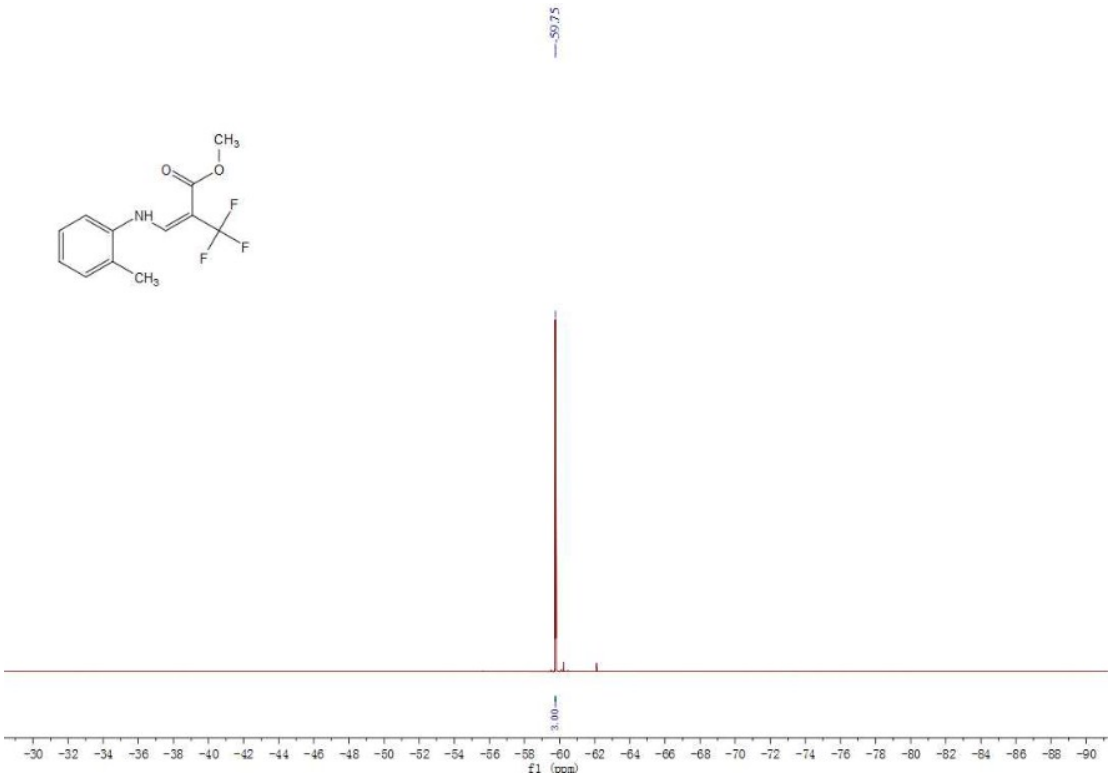

10.57
10.54
7.88
7.85
7.80
7.78
7.73
7.44
7.42
7.40
7.26
7.25
7.24
7.22
7.22
4.42
4.40
4.38
4.36
3.94
1.42
1.40
1.38
CH3
O
O
NH
F
F
F
O
O
H3C
0.97
1.00
0.98
0.98
1.00
0.99
2.01
2.99
3.00
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


167.16
165.66
145.06
145.00
144.94
144.88
139.53
132.32
129.89
126.75
125.63
125.46
122.97
122.11
120.79
117.46
92.79
92.46
92.14
91.81
77.32
77.00
76.68
61.37
51.56
14.23
CH3
O
O
NH
F
F
F
O
O
H3C
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

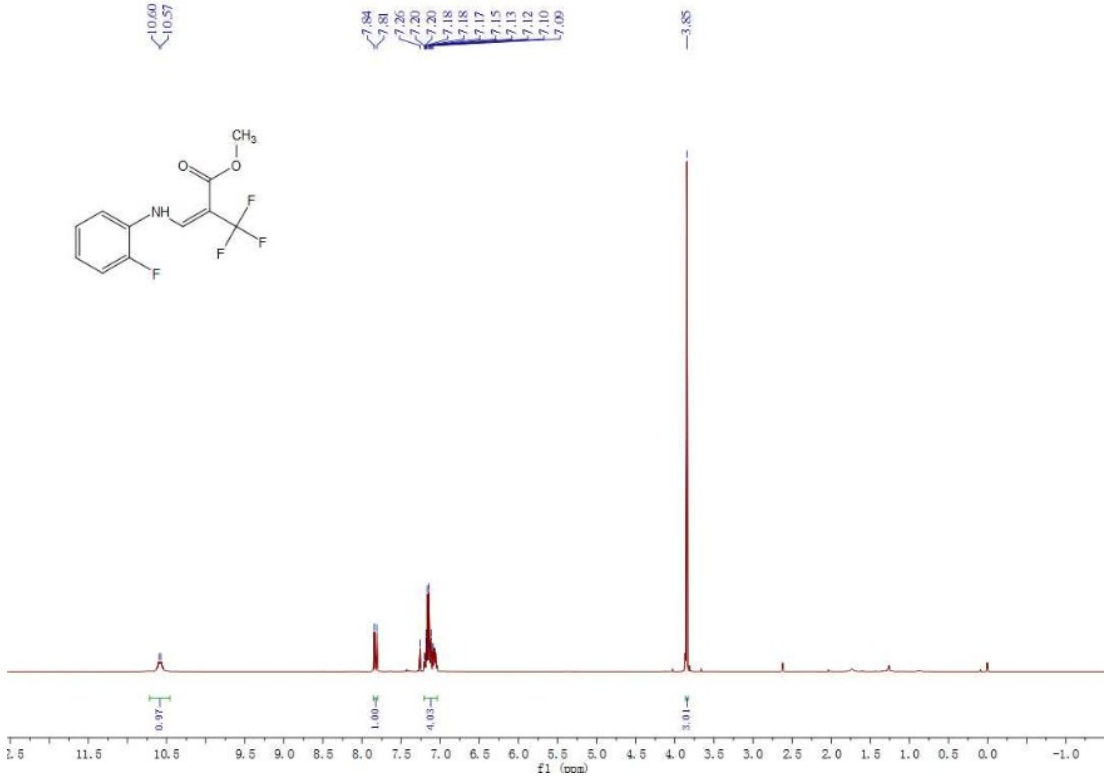

-59.99
CH3
O
O
NH
F
F
F
O
O
H3C
3.00
-28
-32
-36
-40
-44
-48
-52
-56
-60
-64
-68
-72
-76
-80
-84
-88
-92
f1 (ppm)

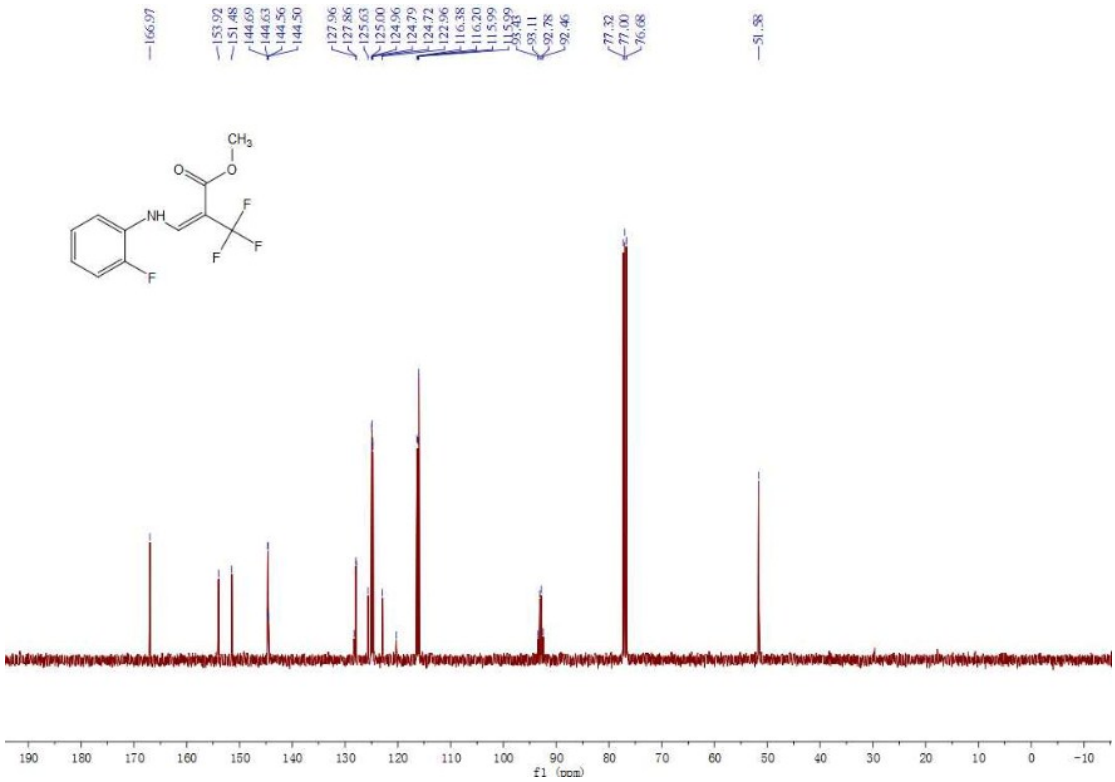
2m

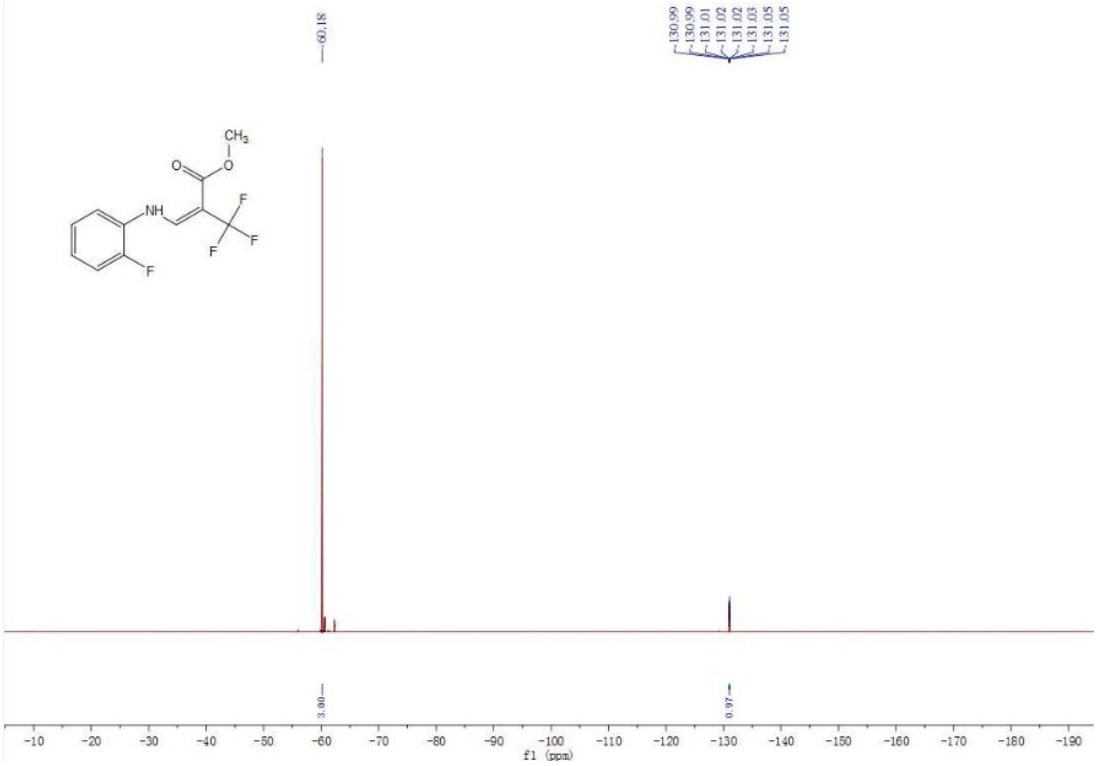



-59.75
CH3
O
O
NH
F
F
F
CH3
3.00
-30 -32 -34 -36 -38 -40 -42 -44 -46 -48 -50 -52 -54 -56 -58 -60 -62 -64 -66 -68 -70 -72 -74 -76 -78 -80 -82 -84 -86 -88 -90
f1 (ppm)

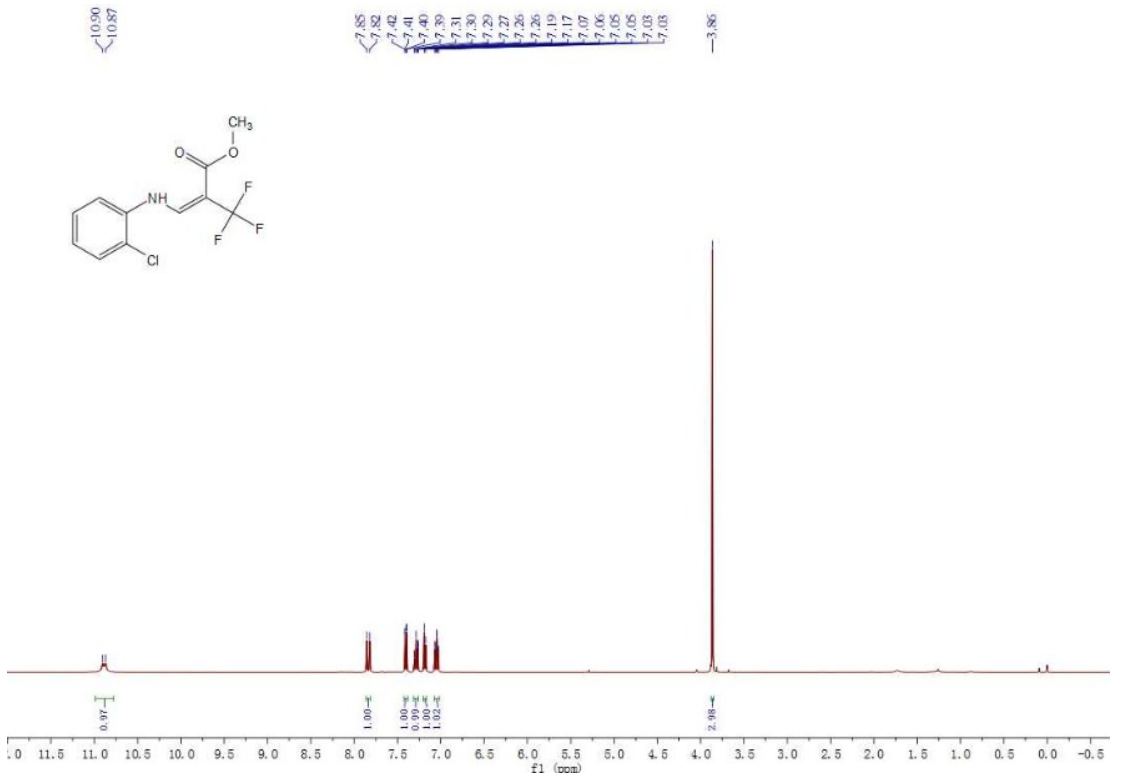
2n

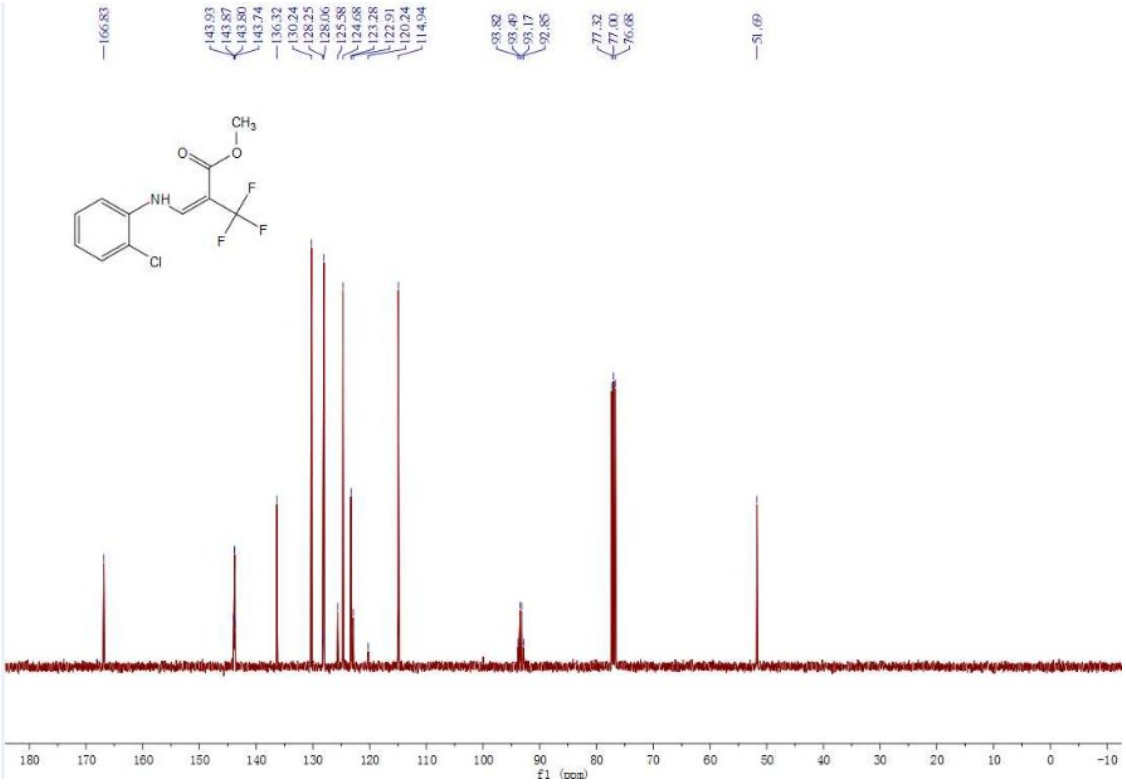

10.60
10.57
7.84
7.81
7.26
7.20
7.20
7.18
7.18
7.17
7.15
7.13
7.12
7.10
7.09
3.85
CH3
O
O
NH
F
F
F
F
0.97
1.00
4.03
3.01
2.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -1.0
f1 (ppm)

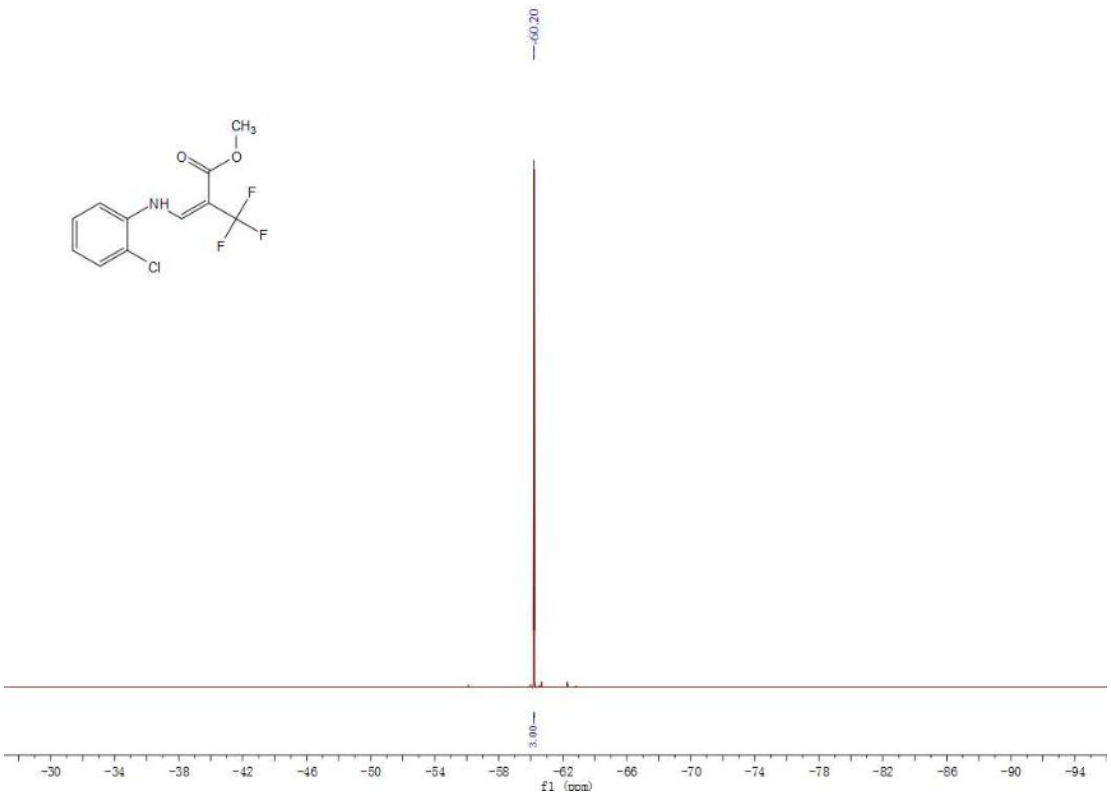

166.97
153.92
151.48
144.69
144.63
144.56
144.50
127.96
127.86
125.63
125.00
124.96
124.79
124.72
122.96
116.38
116.20
115.99
115.79
93.48
93.11
92.78
92.46
77.32
77.00
76.68
51.58
CH3
O
O
NH
F
F
F
F
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


60.18
130.99
130.99
131.01
131.02
131.02
131.03
131.05
131.05
CH3
O
O
NH
F
F
F
F
3.00
0.97
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

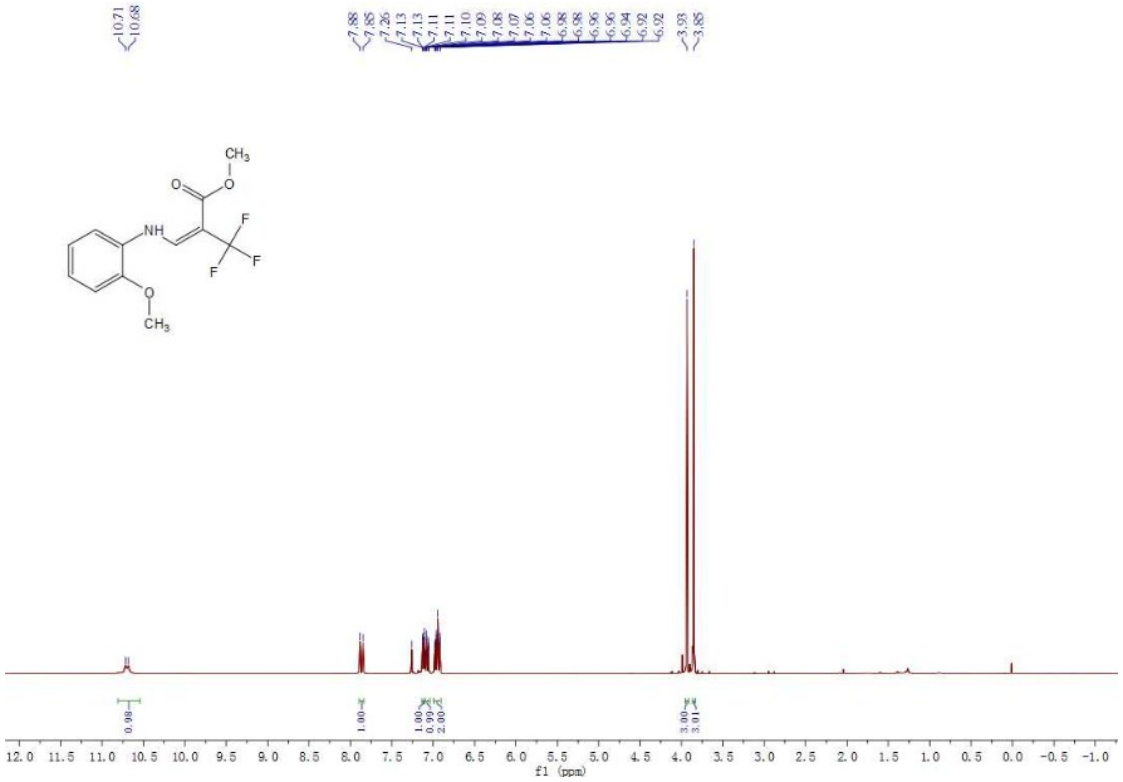
2o

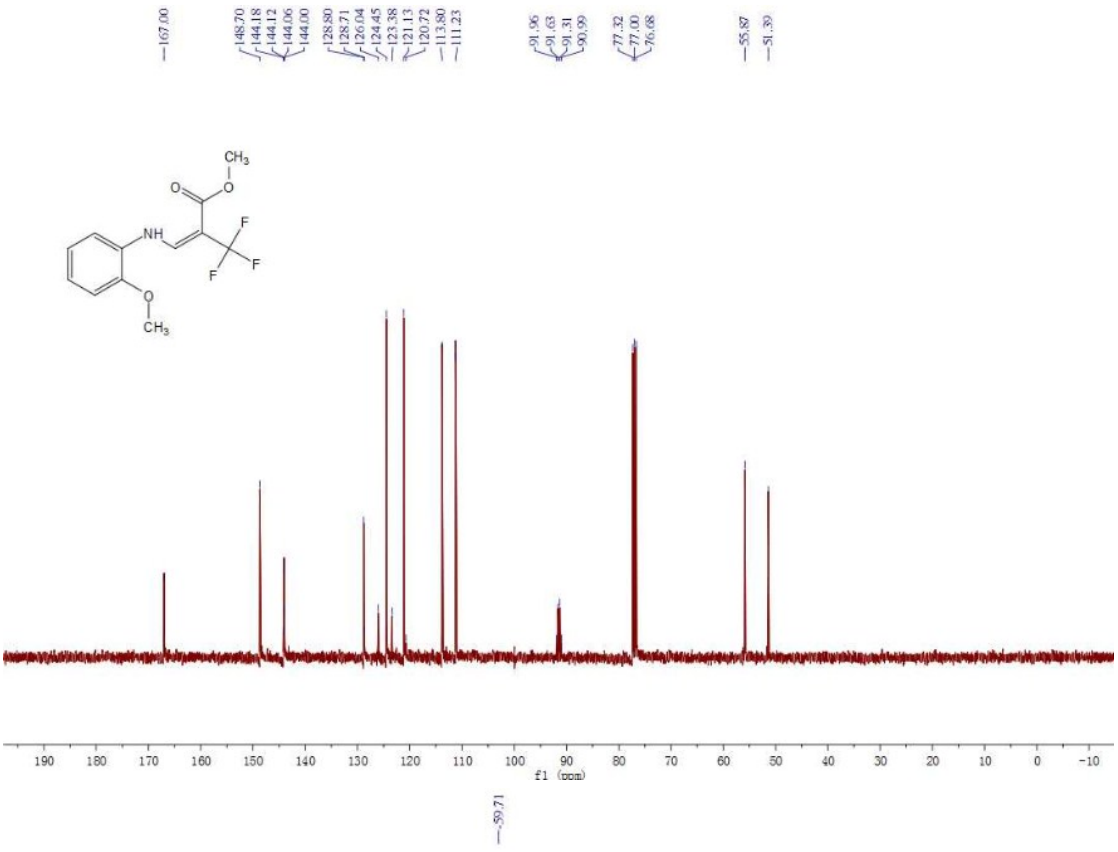

10.90
10.87
7.85
7.82
7.42
7.41
7.40
7.39
7.31
7.30
7.29
7.27
7.26
7.19
7.17
7.07
7.06
7.05
7.05
7.03
7.03
3.86
CH3
O
O
NH
F
F
F
Cl
0.97
1.00
1.00
0.99
1.00
1.02
2.98
f1 (ppm)

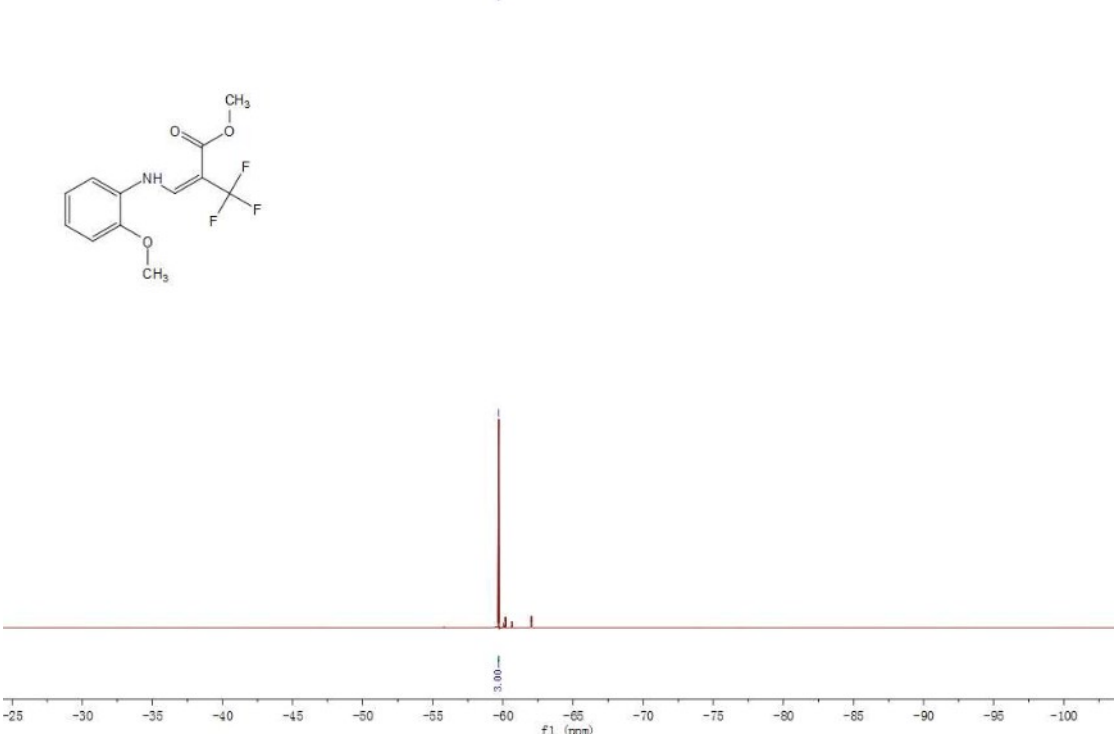

166.83
143.93
143.87
143.80
143.74
136.32
130.24
128.25
128.06
125.58
124.68
123.28
122.91
120.24
114.94
93.82
93.49
93.17
92.85
77.32
77.00
76.68
51.69
CH3
O
O
NH
F
F
F
Cl
f1 (ppm)


-60.20
CH3
O
O
NH
F
F
F
Cl
3.00
-30
-34
-38
-42
-46
-50
-54
-58
-62
-66
-70
-74
-78
-82
-86
-90
-94
f1 (ppm)

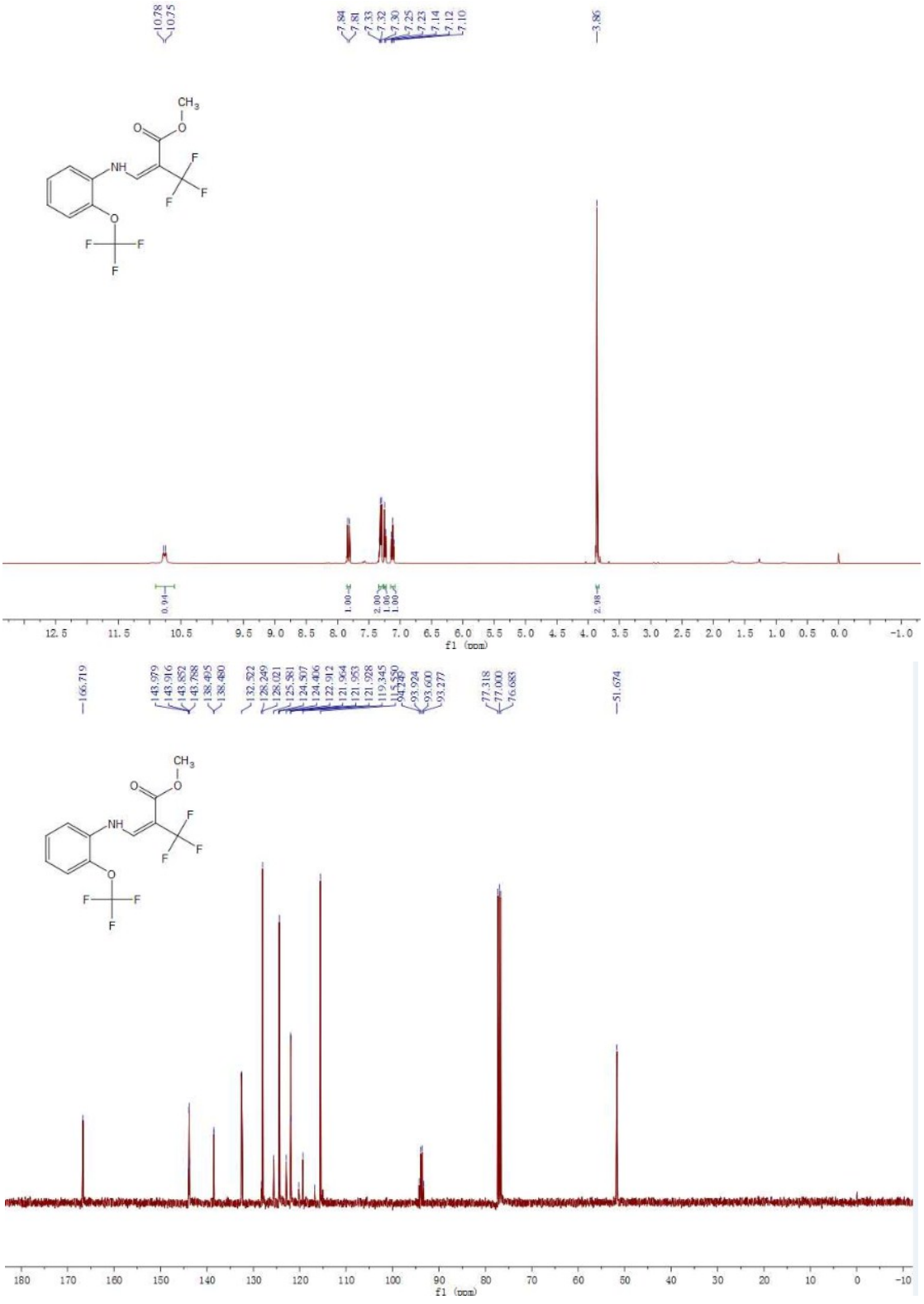
2p

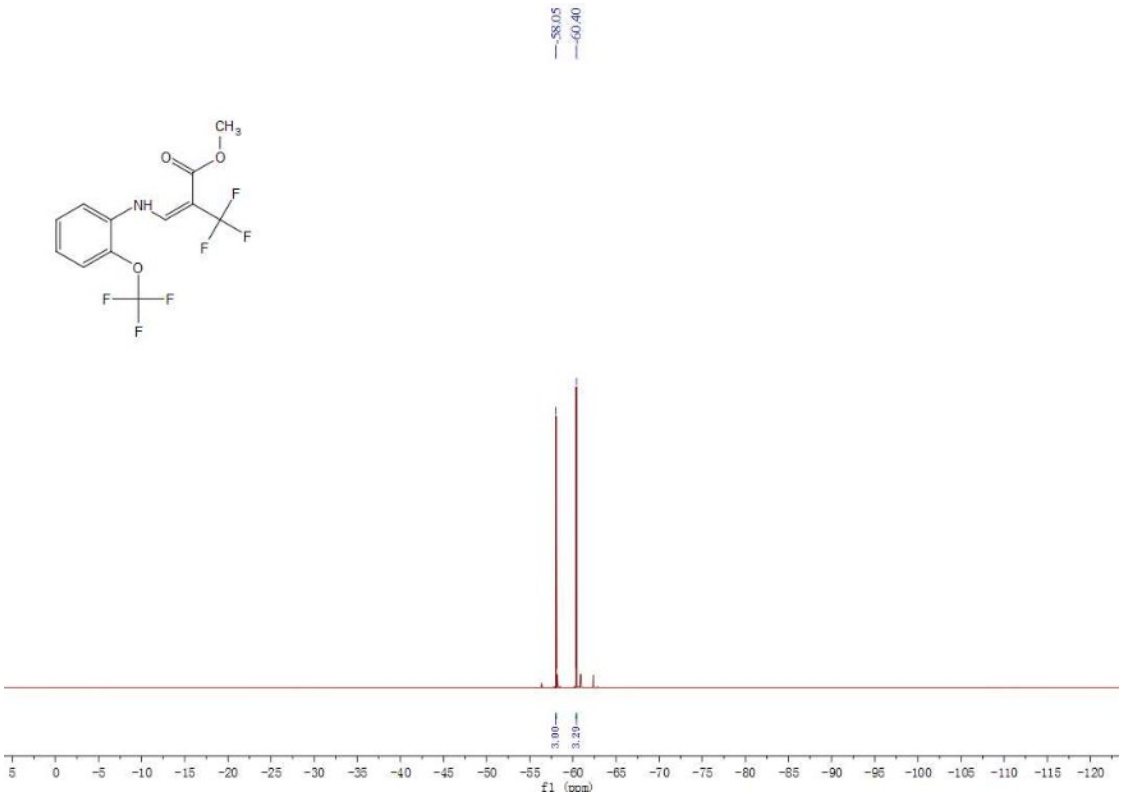

10.71
10.68
7.88
7.85
7.26
7.13
7.11
7.11
7.10
7.09
7.08
7.07
7.06
7.06
6.98
6.96
6.96
6.94
6.92
6.92
3.93
3.85
CH3
O
O
NH
F
F
F
O
CH3
0.98
1.00
1.00
0.99
2.00
3.00
3.01
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


167.00
148.70
144.18
144.12
144.06
144.00
128.80
128.71
126.04
124.45
123.38
121.13
120.72
113.80
111.23
91.96
91.63
91.31
90.99
77.32
77.00
76.68
55.87
51.39
CH3
O
O
NH
F
F
F
O
CH3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

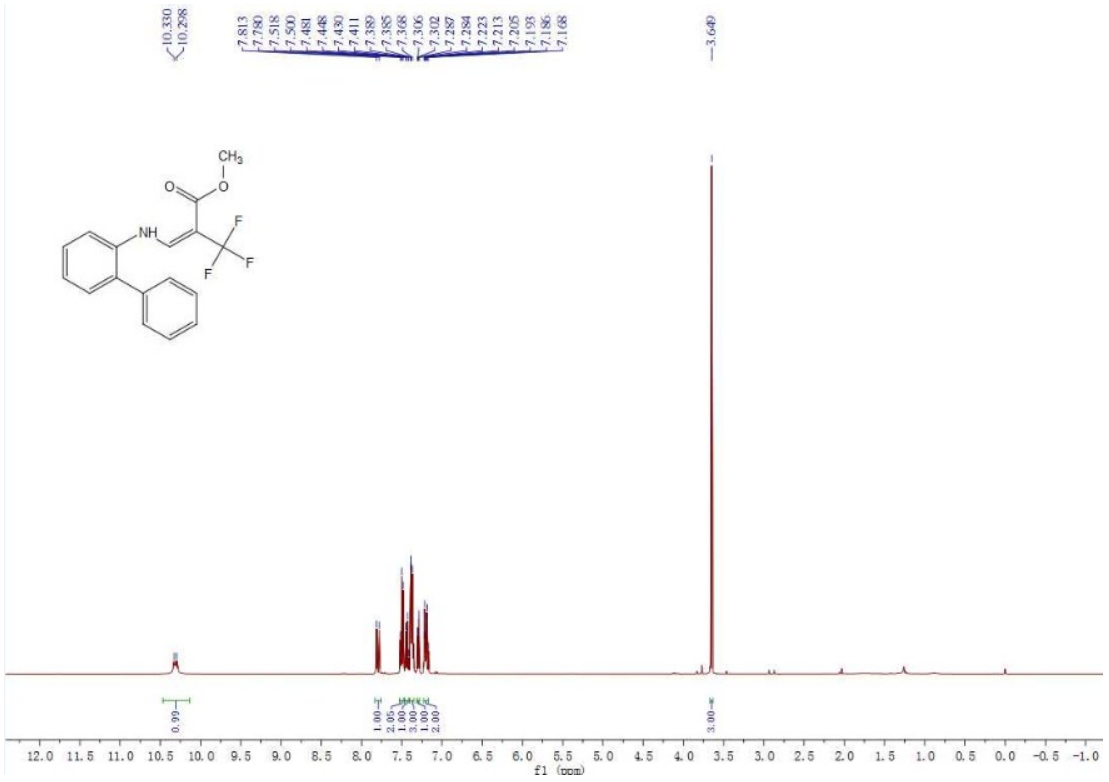

-59.71
CH3
O
O
NH
F
F
F
O
CH3
3.00
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
f1 (ppm)

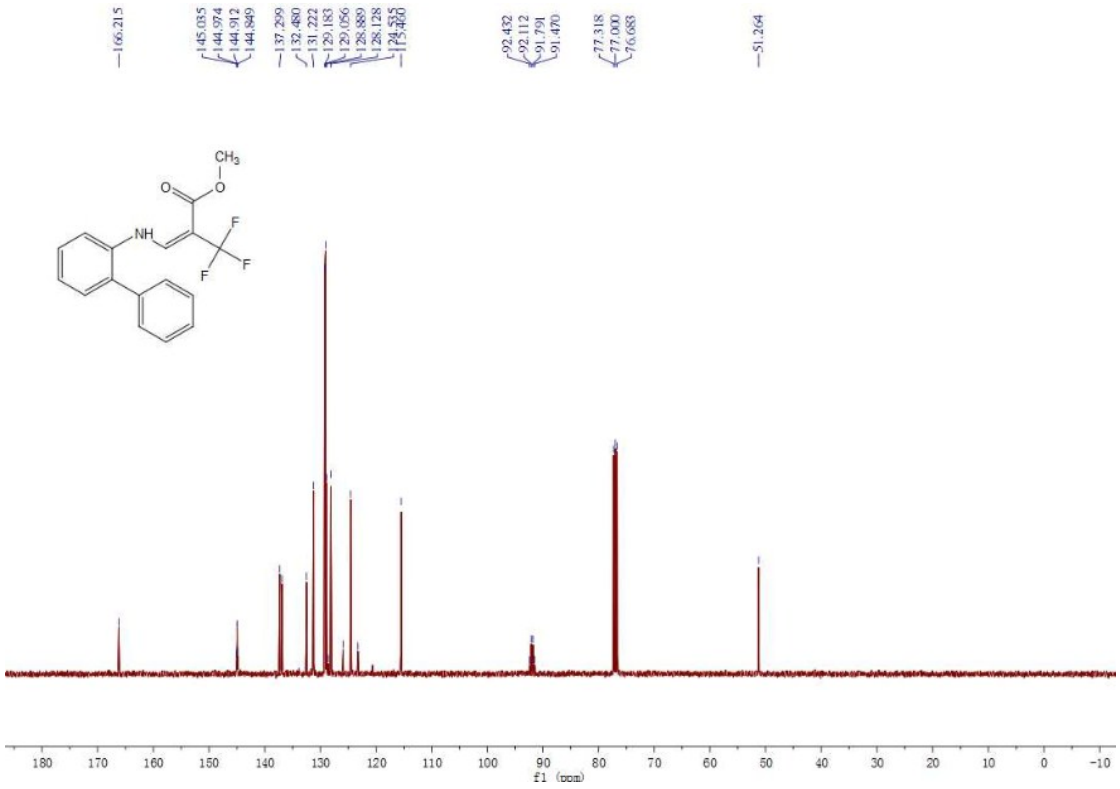
2q

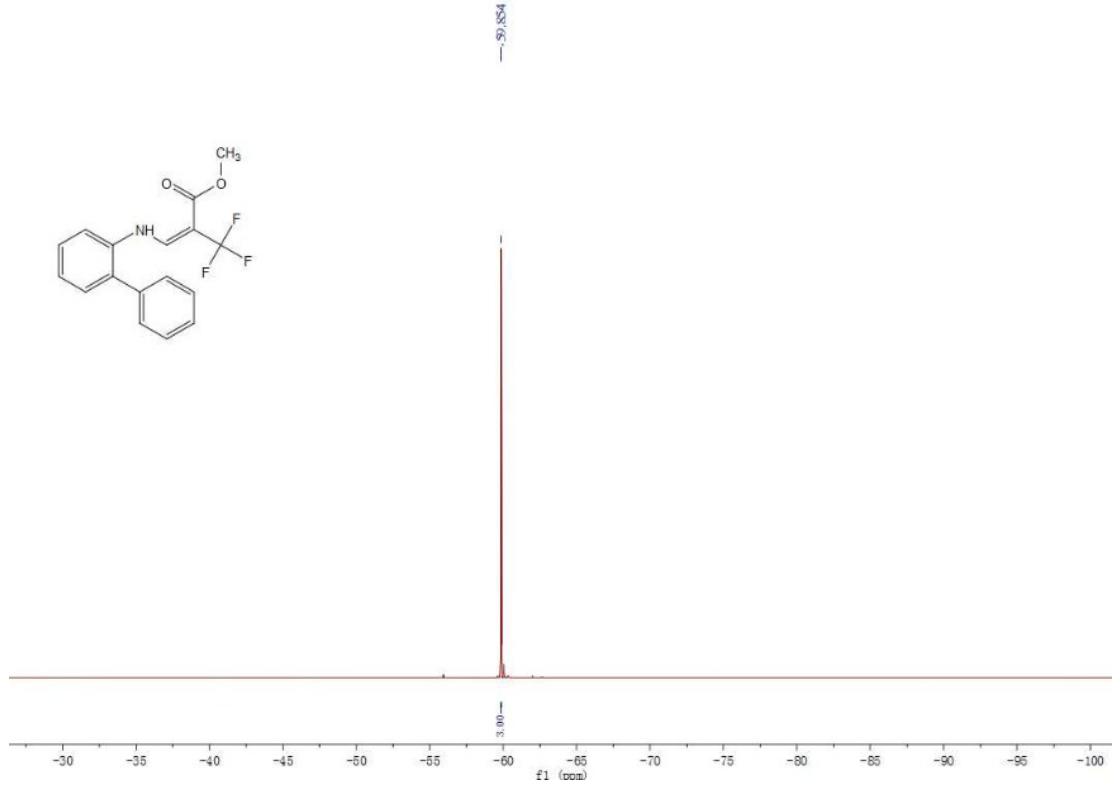

10.78
10.75
7.84
7.81
7.33
7.32
7.30
7.25
7.23
7.14
7.12
7.10
3.86
CH3
O
O
NH
F
F
F
O
F
F
F
0.94
1.00
2.00
1.06
1.00
2.98
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)
166.719
143.979
143.916
143.852
143.788
138.495
138.480
132.522
128.249
128.021
125.581
124.507
124.406
122.912
121.964
121.953
121.928
119.345
94.250
93.924
93.600
93.277
77.318
77.000
76.683
51.674
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


-58.05
-60.40
CH3
O
O
NH
F
F
F
O
F
F
F
3.00
3.29
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
f1 (ppm)

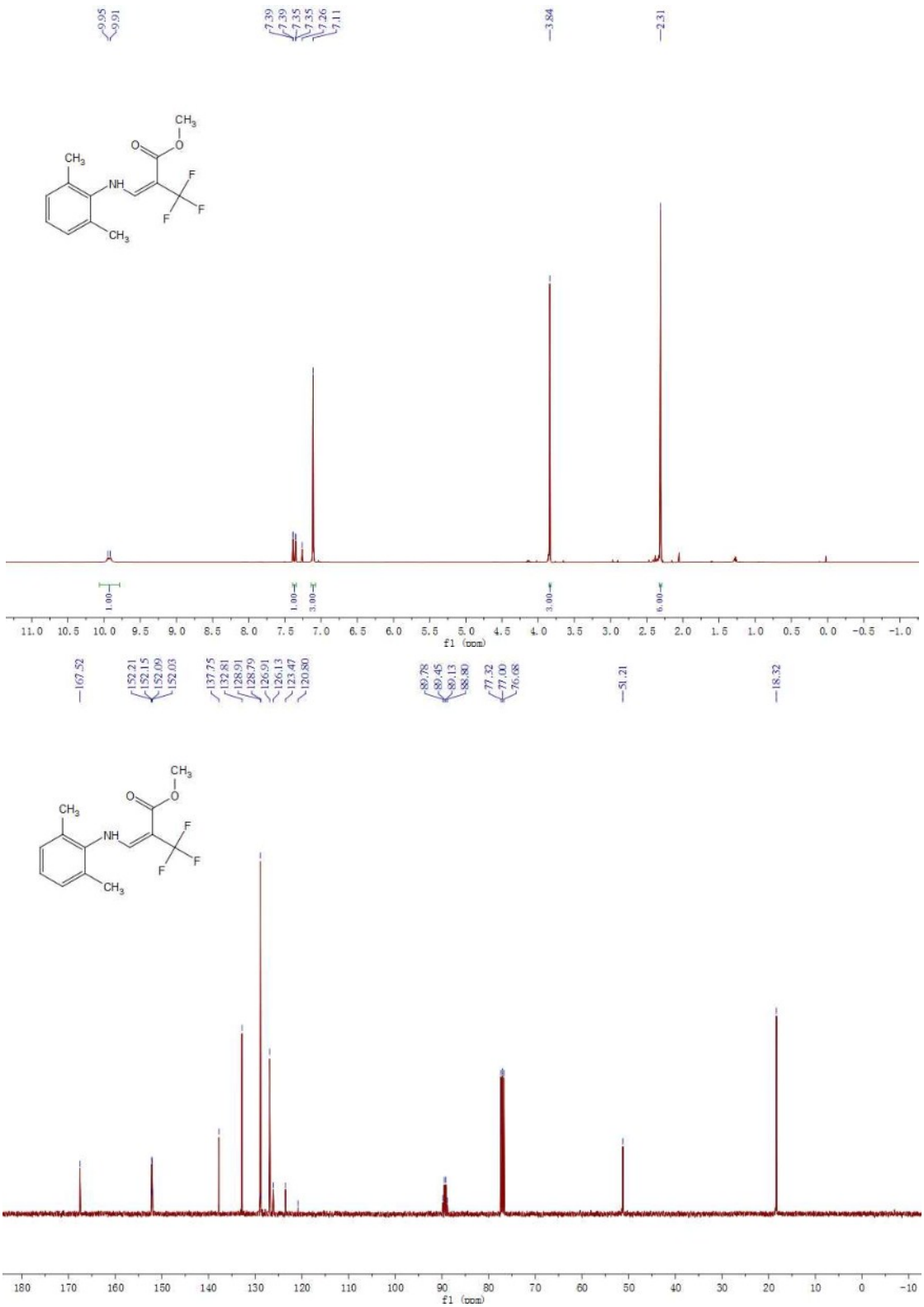
2r

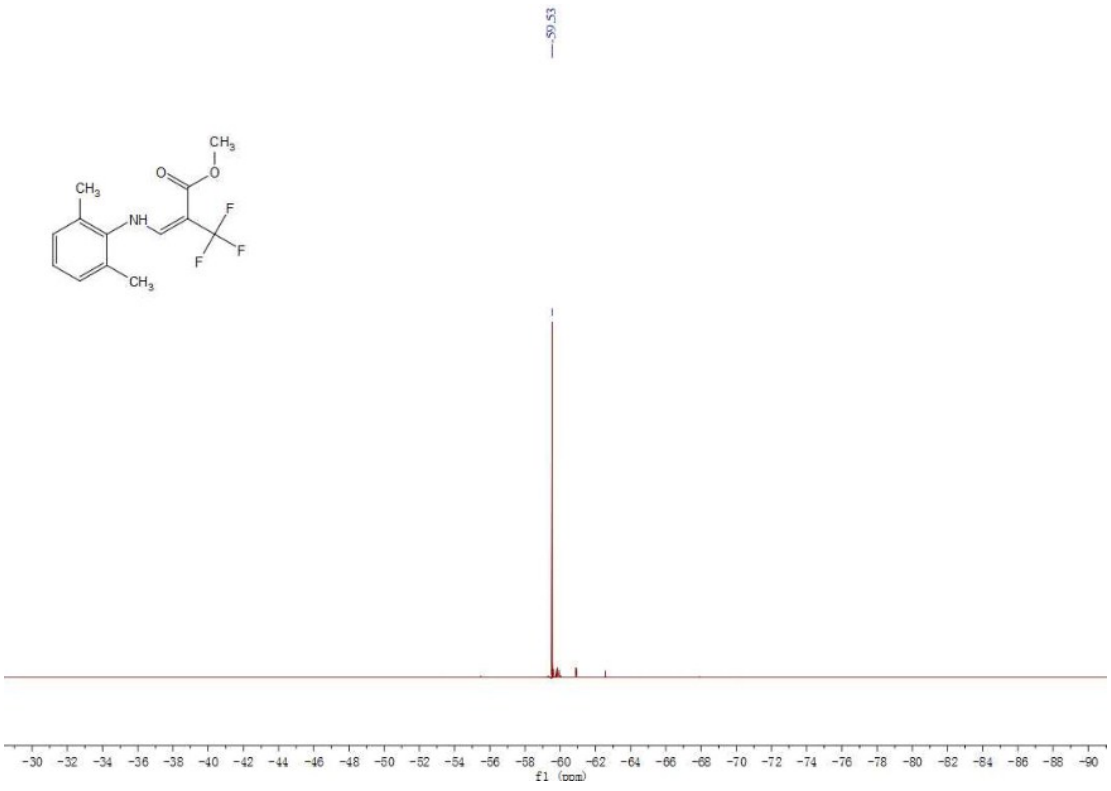

10.330
10.298
7.813
7.780
7.518
7.500
7.481
7.448
7.430
7.411
7.389
7.385
7.368
7.306
7.302
7.287
7.284
7.223
7.213
7.205
7.193
7.186
7.168
3.649
CH3
O
O
NH
F
F
F
0.99
1.00
2.05
1.00
1.00
2.00
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


166.215
145.035
144.974
144.912
144.849
137.299
132.480
131.222
129.183
129.056
128.889
128.128
124.535
123.460
92.432
92.112
91.791
91.470
77.318
77.000
76.683
51.264
CH3
O
O
NH
F
F
F
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

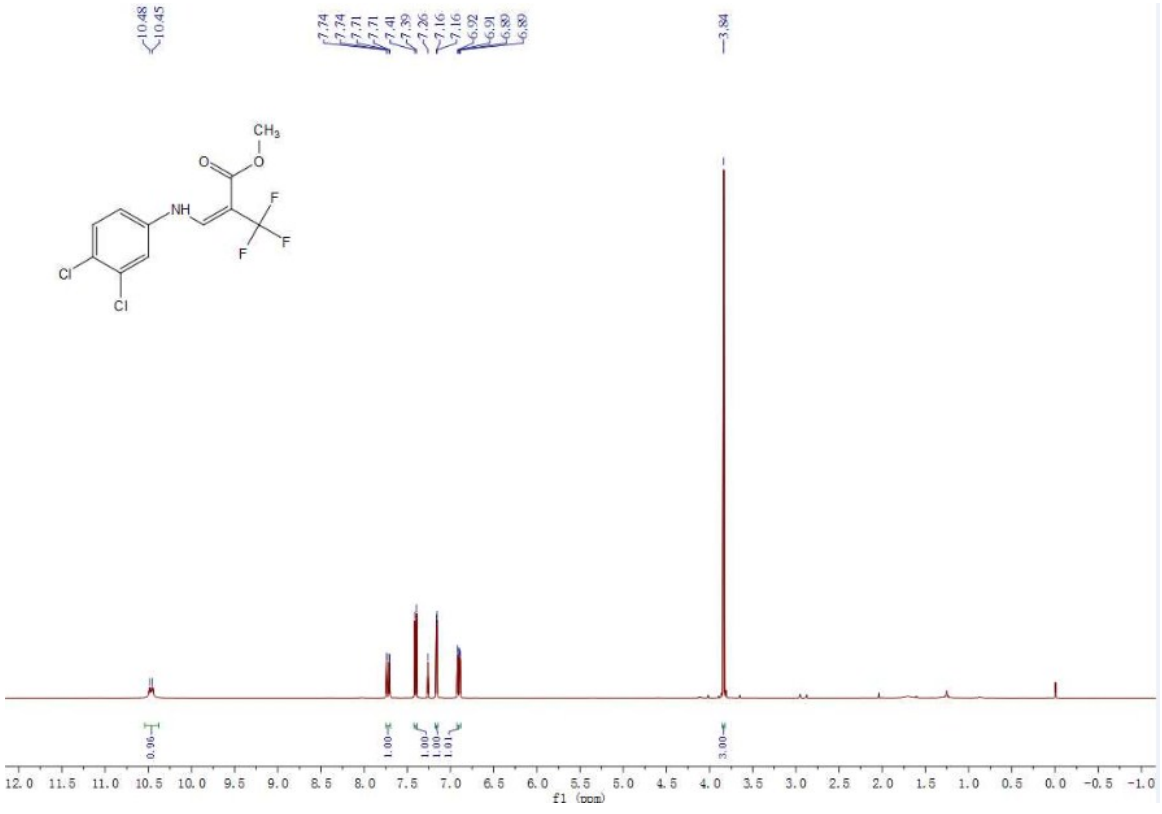

-59.854
CH3
O
O
NH
F
F
F
3.00
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
f1 (ppm)

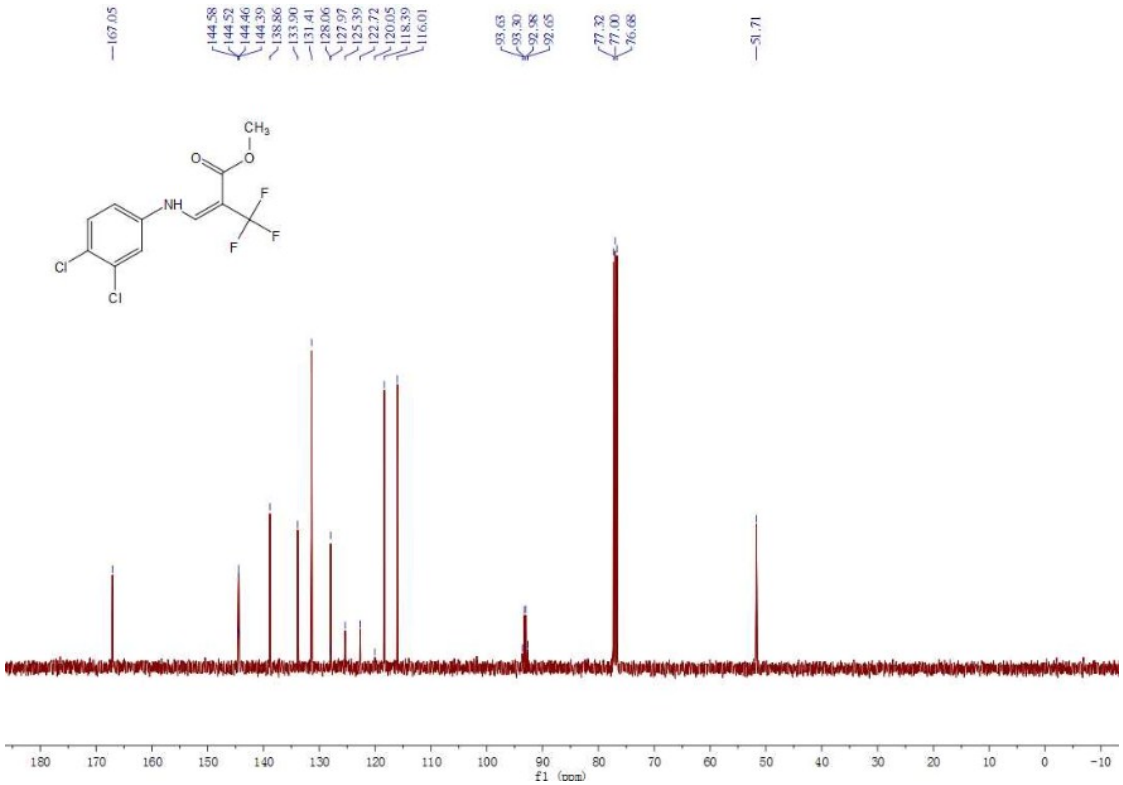
2s

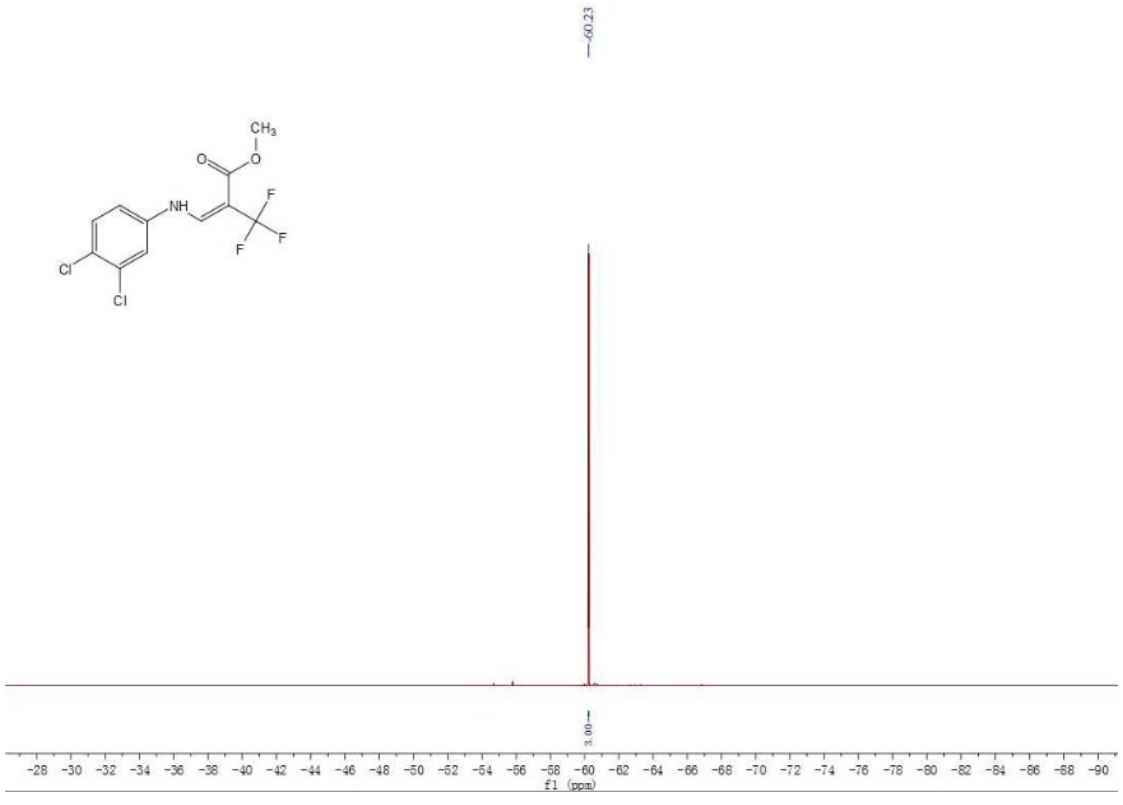

9.95
9.91
7.39
7.39
7.35
7.35
7.26
7.11
3.84
2.31
CH3
O
O
CH3
NH
F
F
F
CH3
1.00
1.00
3.00
3.00
6.00
f1 (ppm)
167.52
152.21
152.15
152.09
152.03
137.75
132.81
128.91
128.79
126.91
126.13
123.47
120.80
89.78
89.45
89.13
88.80
77.32
77.00
76.68
51.21
18.32
f1 (ppm)


-59.53
CH3
O
O
CH3
NH
F
F
F
CH3
-30 -32 -34 -36 -38 -40 -42 -44 -46 -48 -50 -52 -54 -56 -58 -60 -62 -64 -66 -68 -70 -72 -74 -76 -78 -80 -82 -84 -86 -88 -90
f1 (ppm)

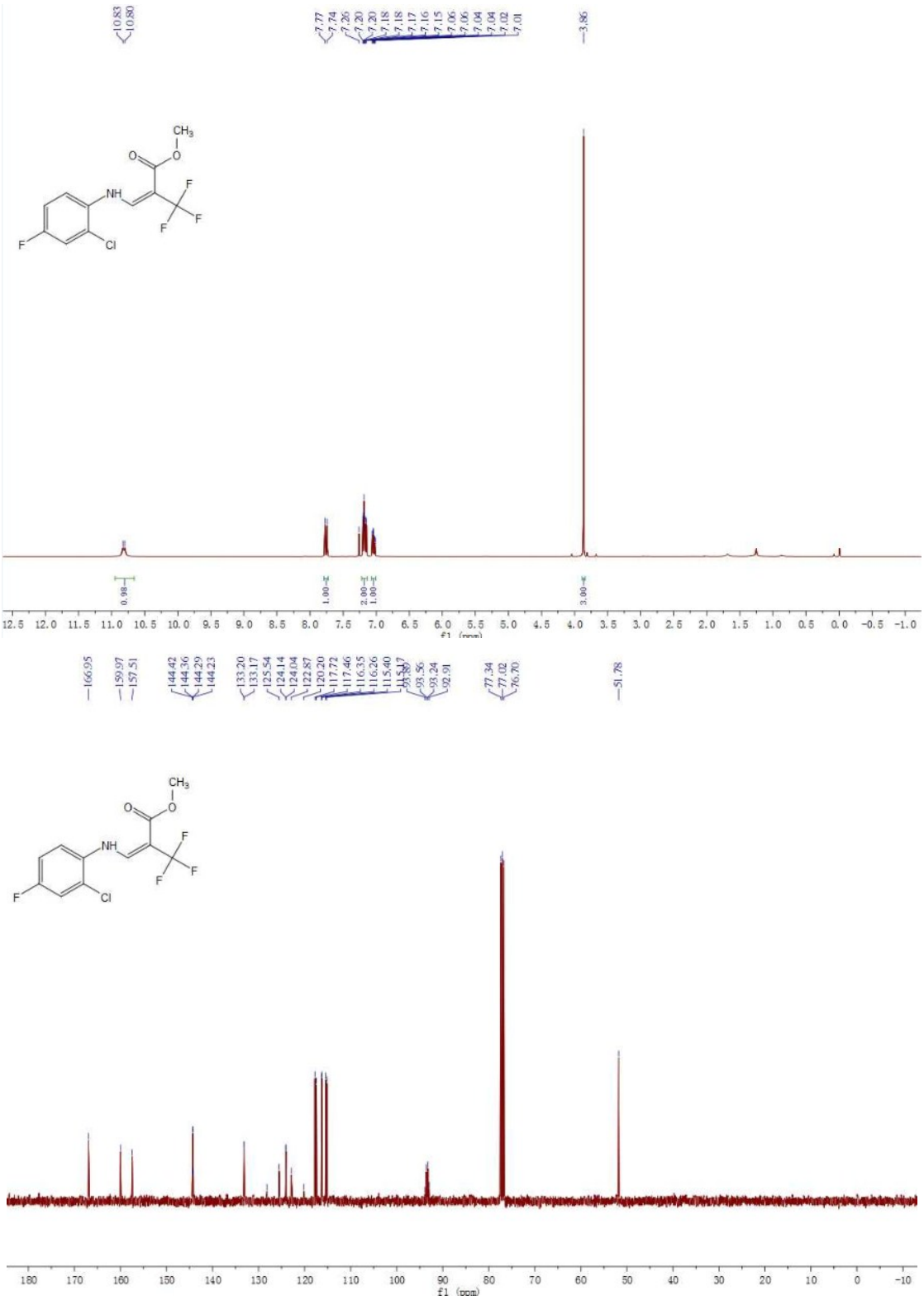
2t

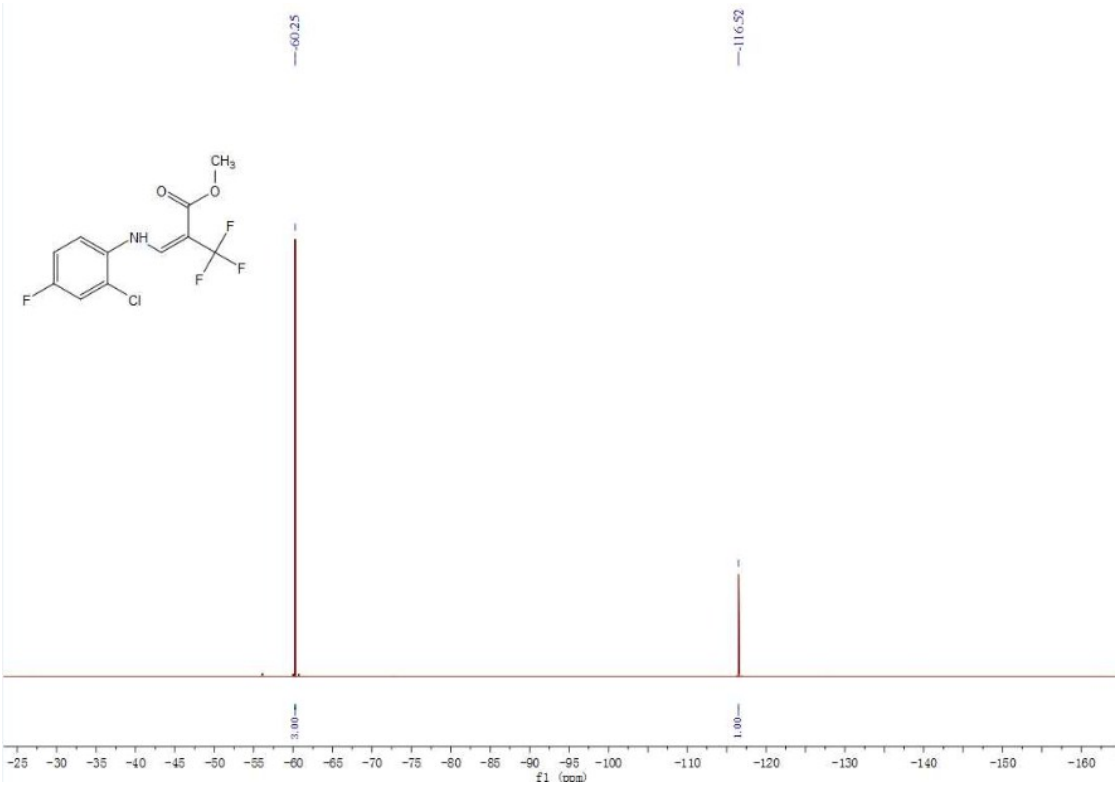

10.48
10.45
7.74
7.74
7.71
7.71
7.41
7.39
7.26
7.16
7.16
6.92
6.91
6.89
6.89
3.84
CH3
O
O
NH
F
F
F
Cl
Cl
0.96
1.00
1.00
1.00
1.01
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


167.05
144.58
144.52
144.46
144.39
138.86
133.90
131.41
128.06
127.97
125.39
122.72
120.05
118.39
116.01
93.63
93.30
92.98
92.65
77.32
77.00
76.68
51.71
CH3
O
O
NH
F
F
F
Cl
Cl
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

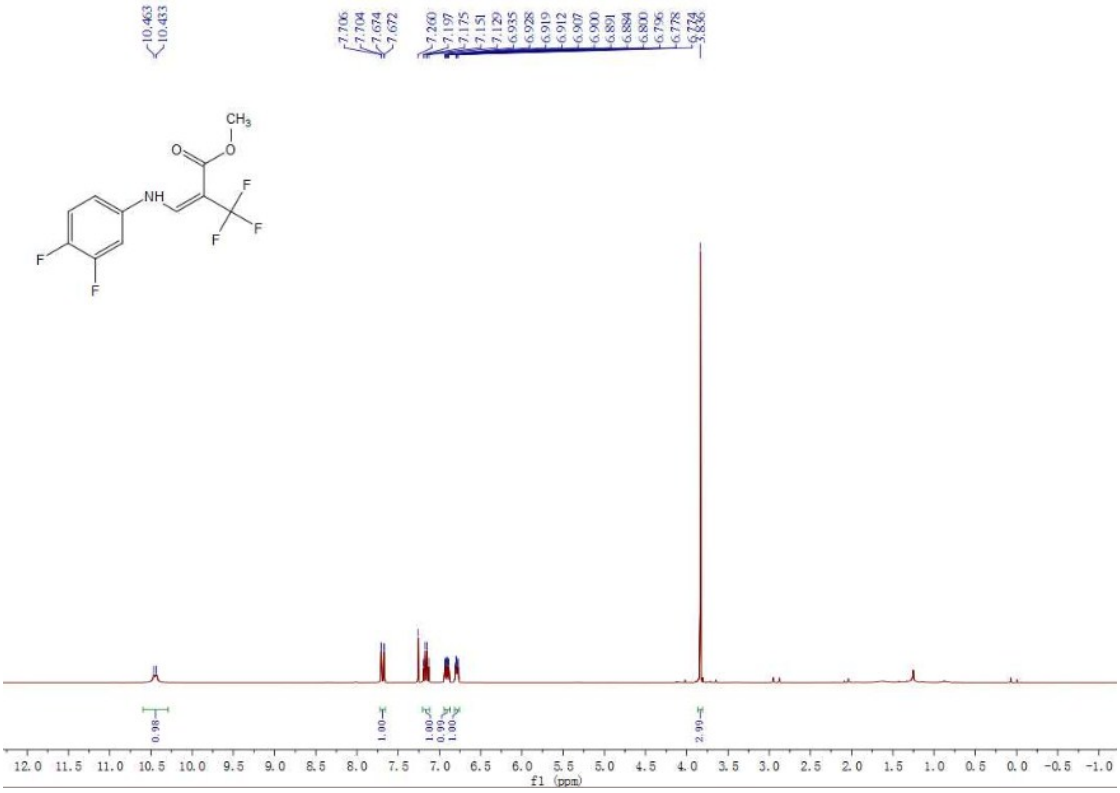

-60.23
CH3
O
O
NH
F
F
F
Cl
Cl
3.00
-28 -30 -32 -34 -36 -38 -40 -42 -44 -46 -48 -50 -52 -54 -56 -58 -60 -62 -64 -66 -68 -70 -72 -74 -76 -78 -80 -82 -84 -86 -88 -90
f1 (ppm)

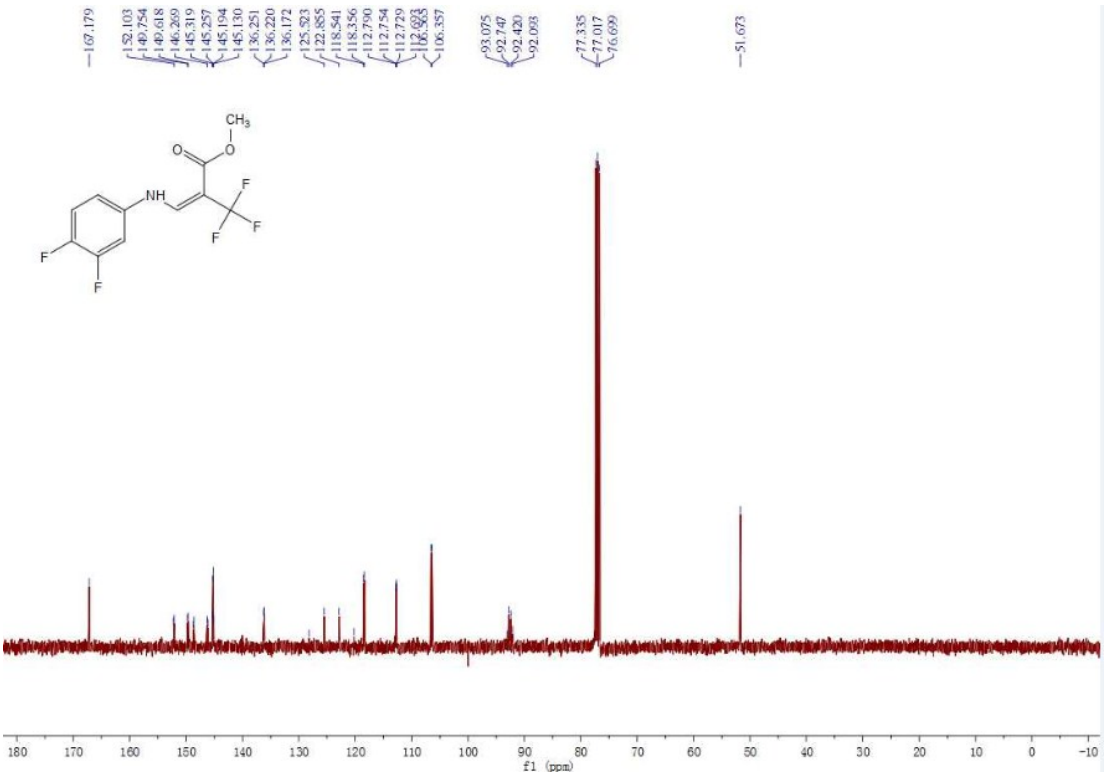
2u

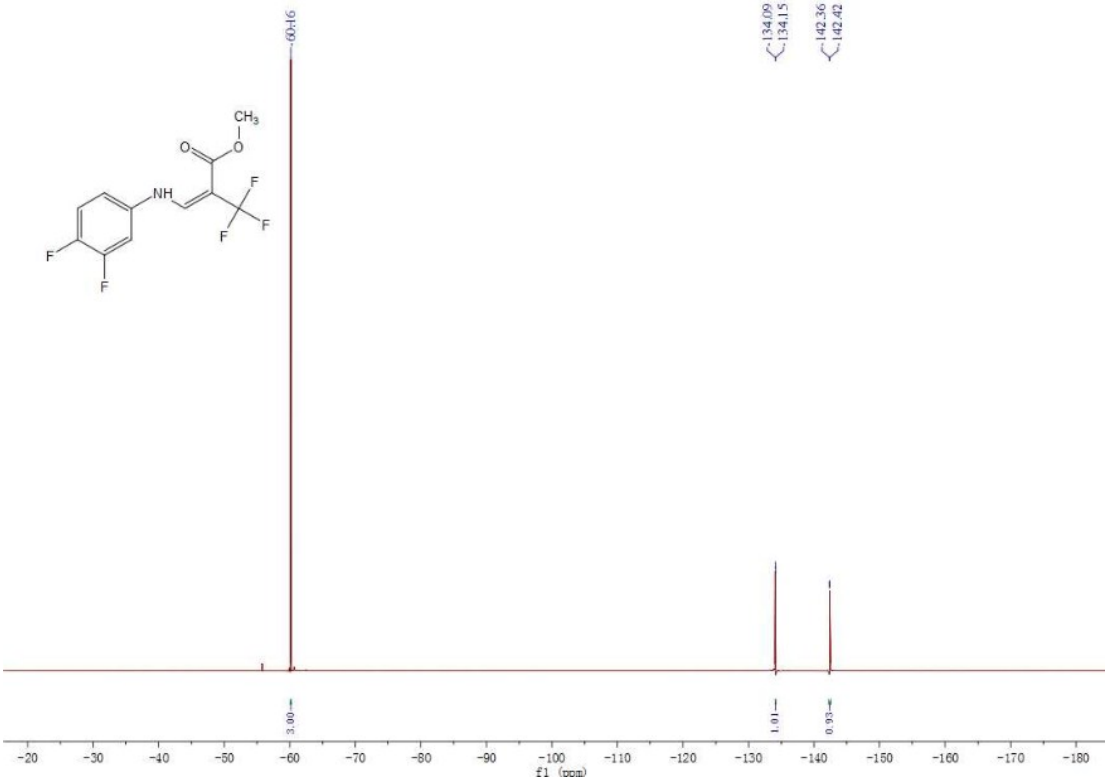

10.83
10.80
7.77
7.74
7.26
7.20
7.20
7.18
7.18
7.17
7.16
7.15
7.06
7.06
7.04
7.04
7.02
7.01
3.86
CH3
O
O
NH
F
F
F
F
Cl
0.98
1.00
2.00
1.00
3.00
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
166.95
159.97
157.51
144.42
144.36
144.29
144.23
133.20
133.17
125.54
124.14
124.04
122.87
120.20
117.72
117.46
116.35
116.26
115.40
93.56
93.24
92.91
77.34
77.02
76.70
51.78
CH3
O
O
NH
F
F
F
F
Cl
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-60.25
-116.52
CH3
O
O
NH
F
F
F
F
Cl
3.00
1.00
-25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)

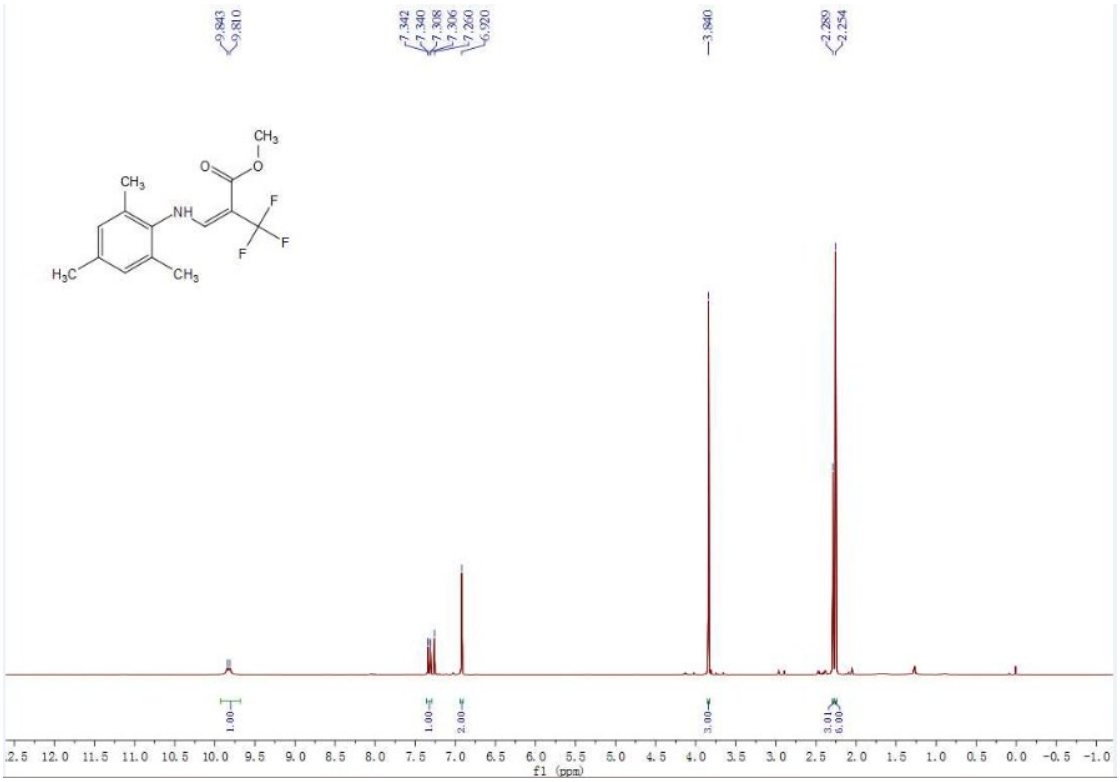
2v

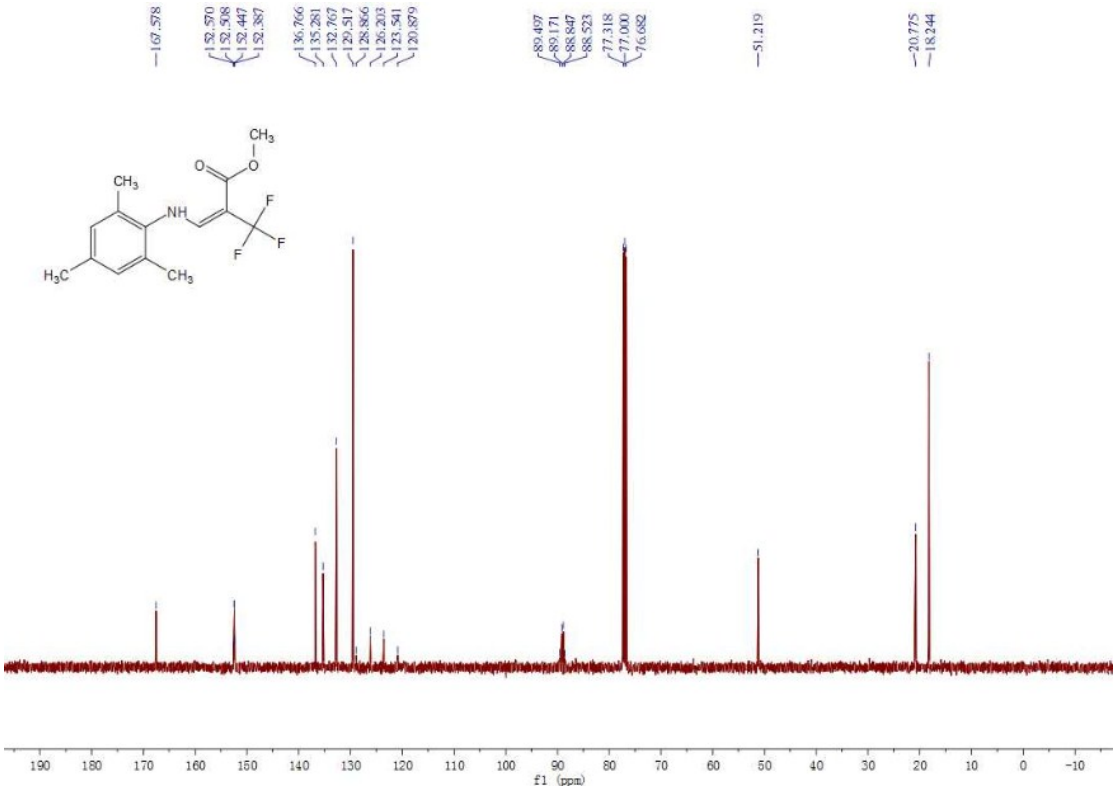

10.463
10.433
7.706
7.704
7.674
7.672
7.260
7.197
7.175
7.151
7.129
6.935
6.928
6.919
6.912
6.907
6.900
6.891
6.884
6.800
6.796
6.778
6.774
3.836
CH3
O
O
NH
F
F
F
F
F
0.98
1.00
1.00
0.99
1.00
2.99
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

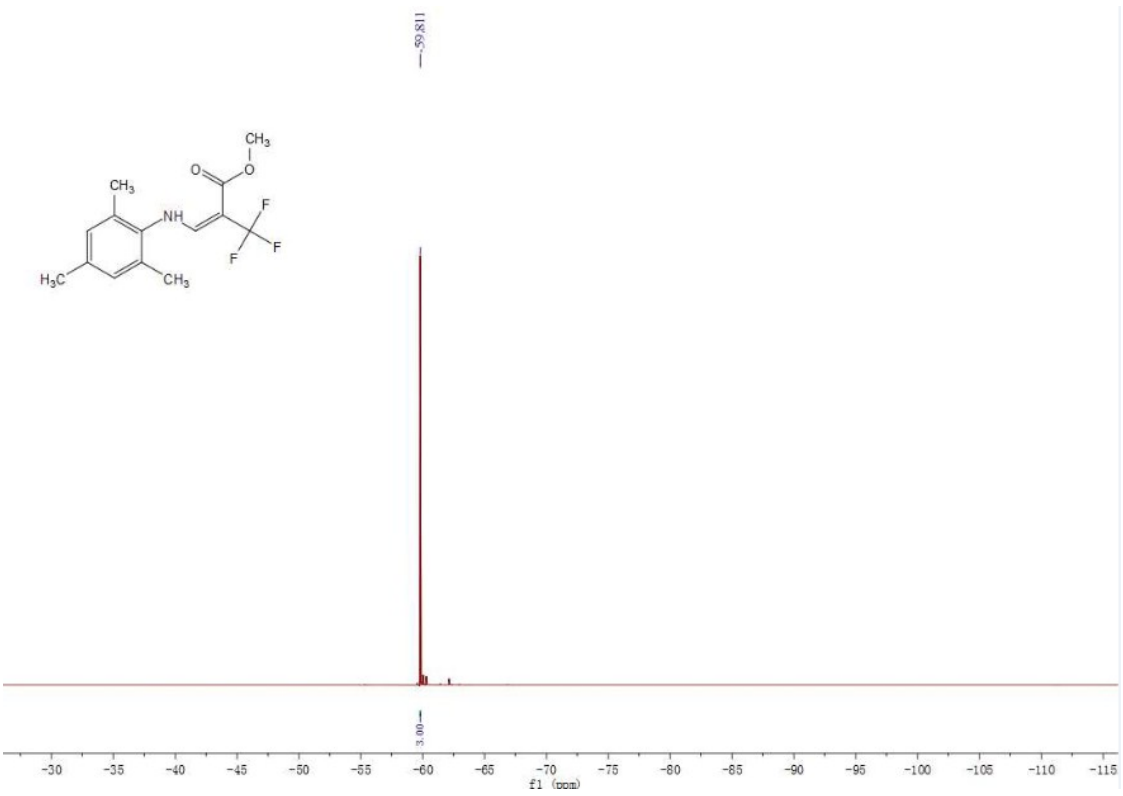

167.179
152.103
149.754
149.618
146.269
145.319
145.257
145.194
145.130
136.251
136.220
136.172
125.523
122.885
118.541
118.356
112.790
112.754
112.729
106.357
93.075
92.747
92.420
92.093
77.335
77.017
76.699
51.673
CH3
O
O
NH
F
F
F
F
F
f1 (ppm)


60.16
134.09
134.15
142.36
142.42
CH3
O
O
NH
F
F
F
F
F
3.00
1.01
0.93
f1 (ppm)

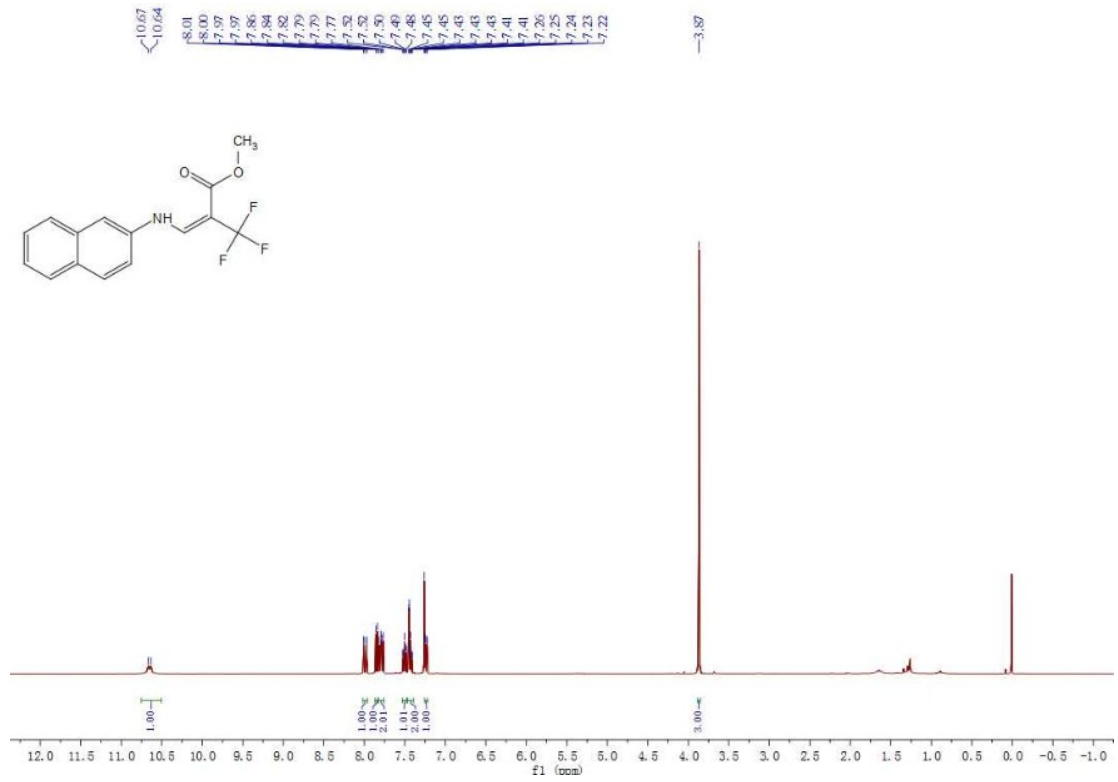
2w

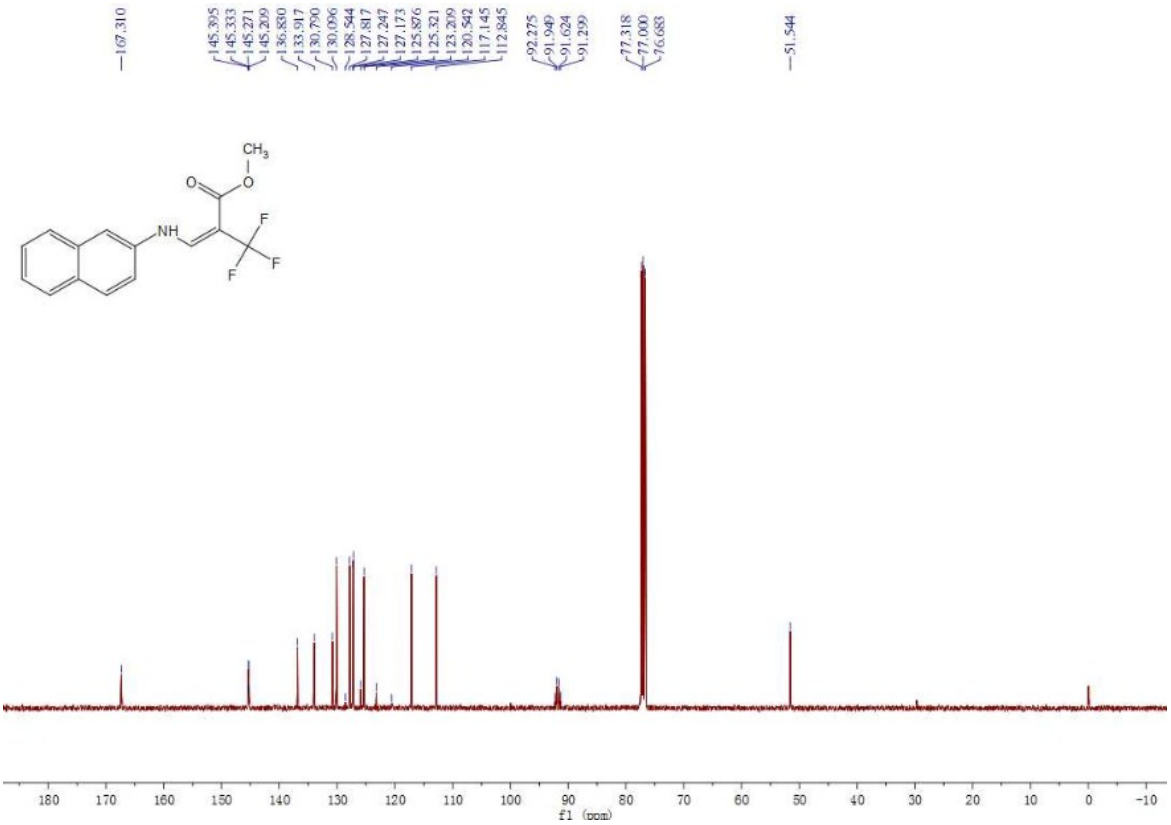

9.843
9.810
7.342
7.340
7.308
7.306
7.260
6.920
3.840
2.289
2.254
f1 (ppm)

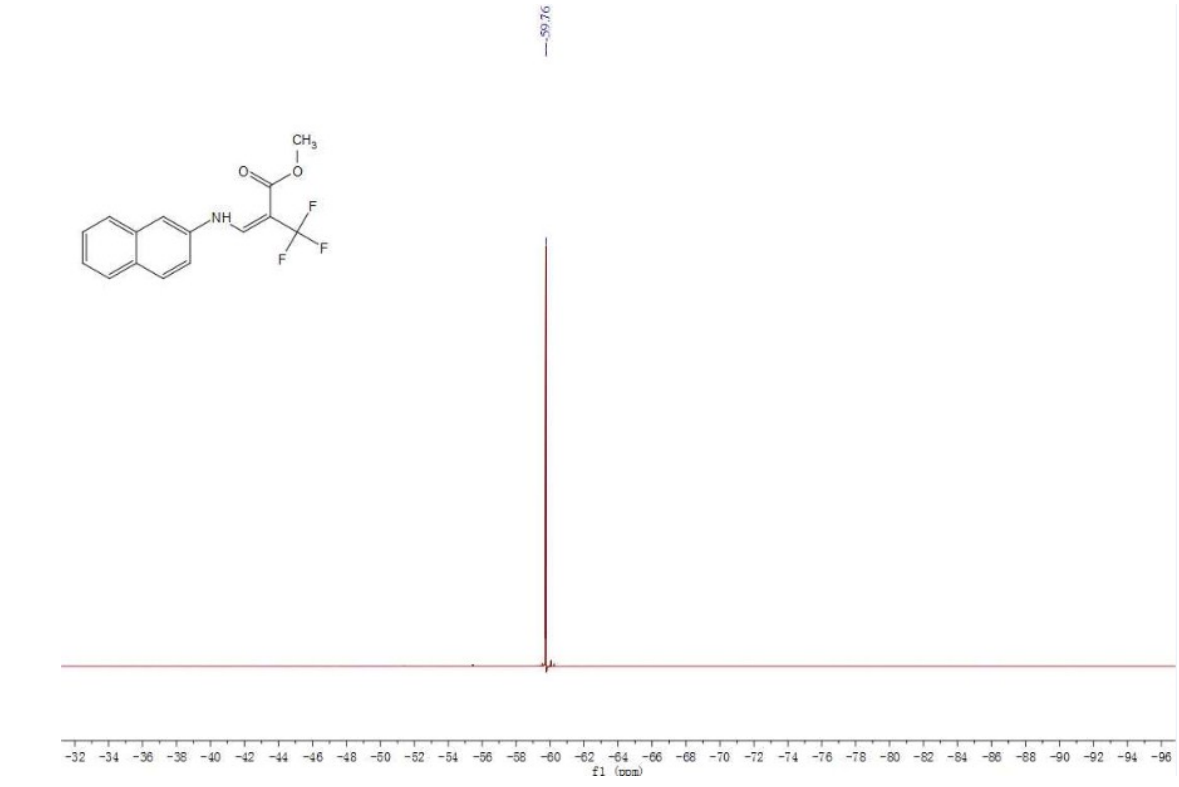

167.578
152.570
152.508
152.447
152.387
136.766
135.281
132.767
129.517
128.866
126.203
123.541
120.879
89.497
89.171
88.847
88.523
77.318
77.000
76.682
51.219
20.775
18.244
f1 (ppm)


-59.811
CH3
O
O
CH3
NH
F
F
F
H3C
CH3
3.00
-30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115
f1 (ppm)

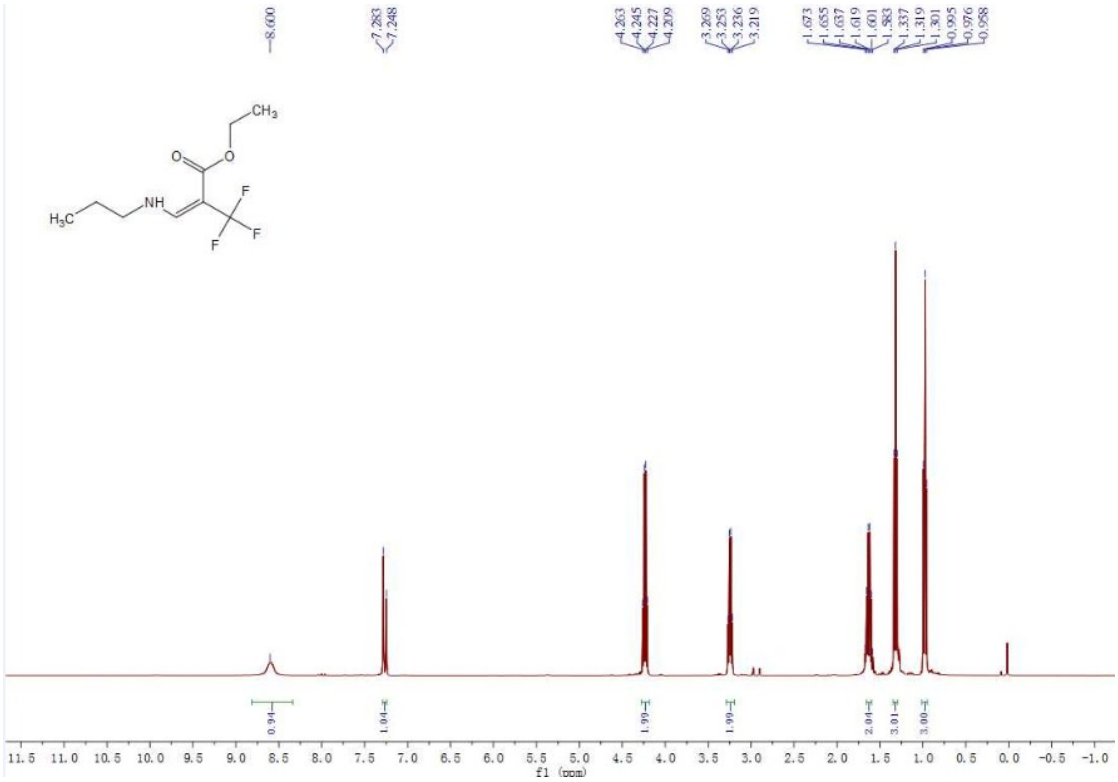
2x

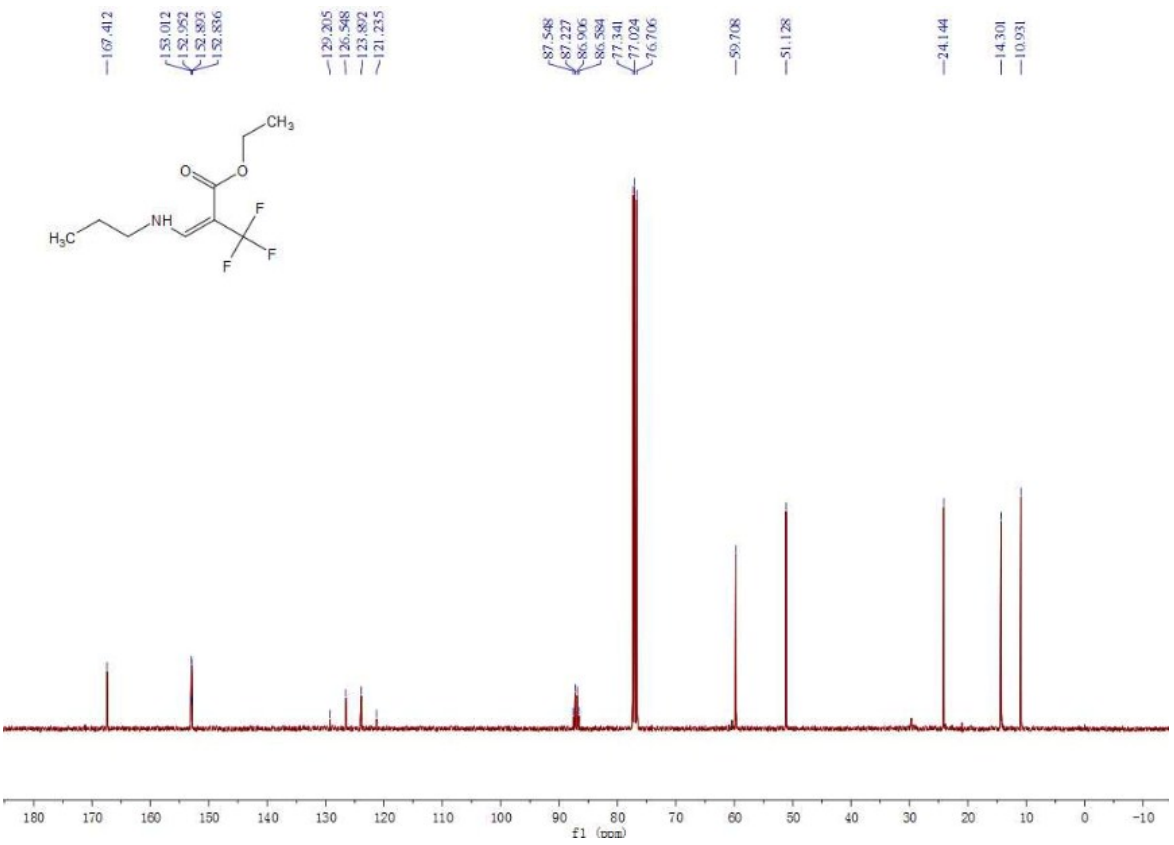

10.67
10.64
8.01
8.00
7.97
7.86
7.84
7.82
7.79
7.79
7.77
7.52
7.52
7.50
7.49
7.48
7.45
7.45
7.43
7.43
7.43
7.41
7.41
7.26
7.25
7.24
7.23
7.22
3.87
CH3
O
O
NH
F
F
F
1.00
1.00
1.00
2.01
1.01
2.00
1.00
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

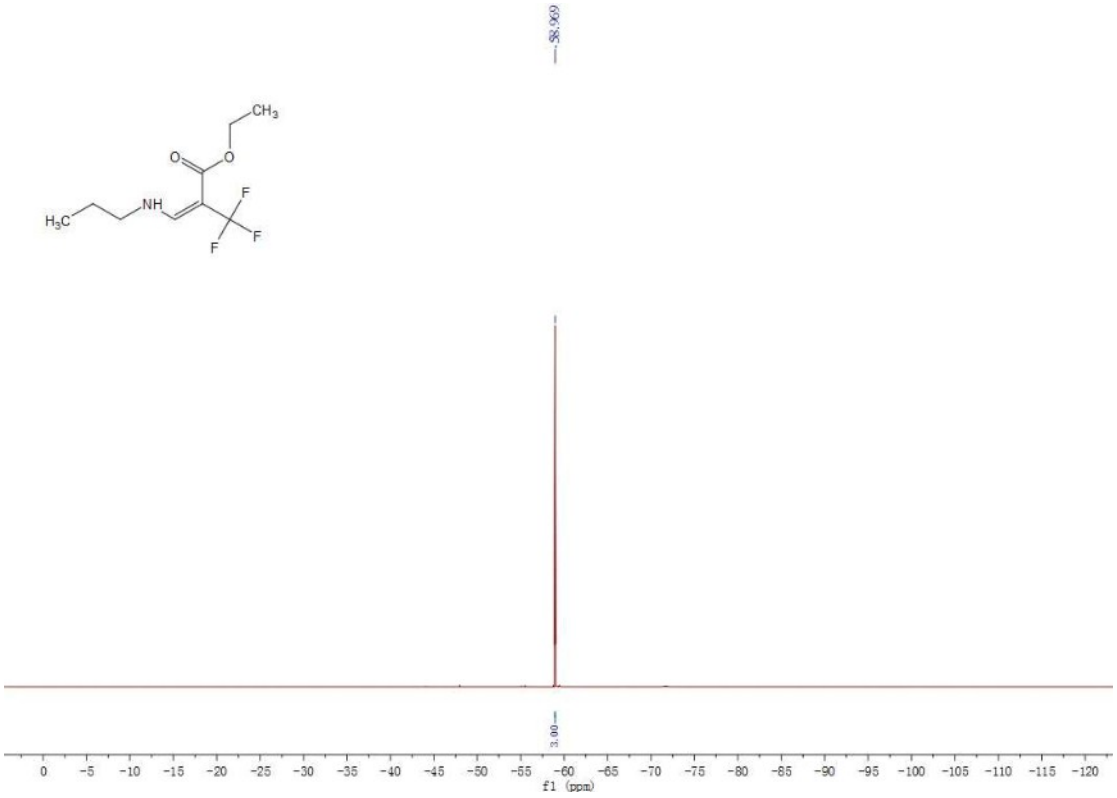

167.310
145.395
145.333
145.271
145.209
136.880
133.917
130.790
130.096
128.544
127.817
127.247
127.173
125.876
125.321
123.209
120.542
117.145
112.845
92.275
91.949
91.624
91.299
77.318
77.000
76.683
51.544
CH3
O
O
NH
F
F
F
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


59.76
CH3
O
O
NH
F
F
F
-32 -34 -36 -38 -40 -42 -44 -46 -48 -50 -52 -54 -56 -58 -60 -62 -64 -66 -68 -70 -72 -74 -76 -78 -80 -82 -84 -86 -88 -90 -92 -94 -96
f1 (ppm)

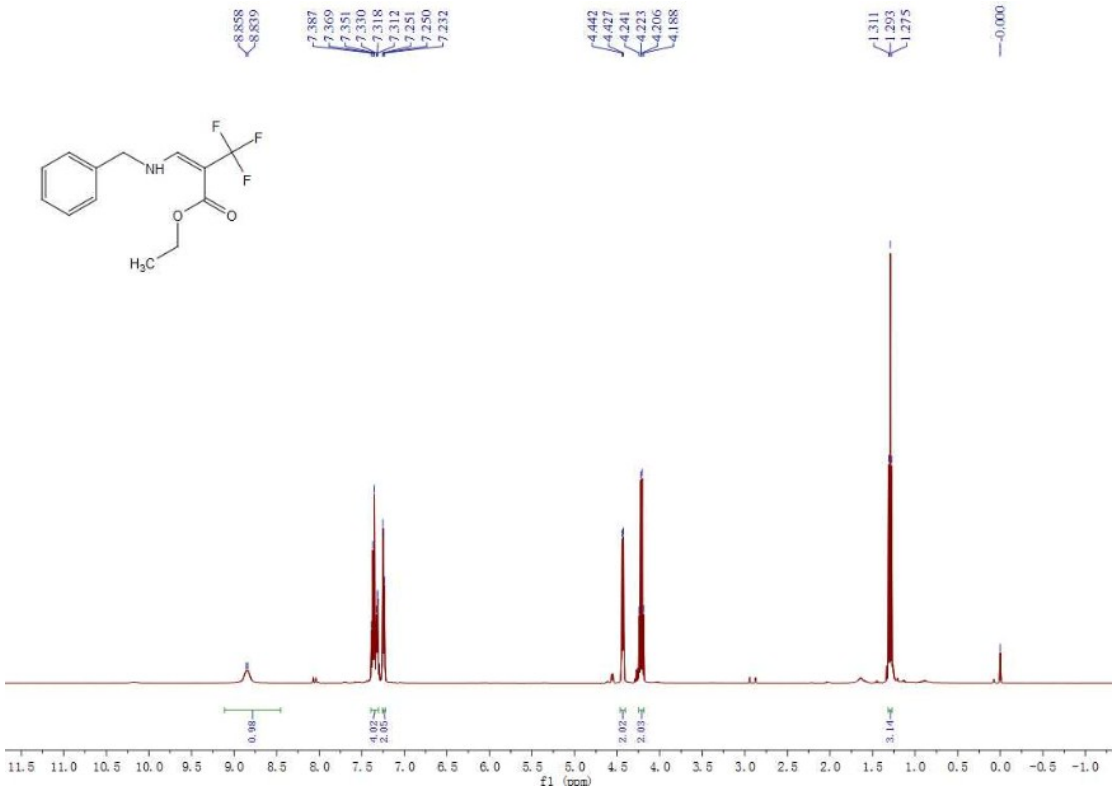
2y

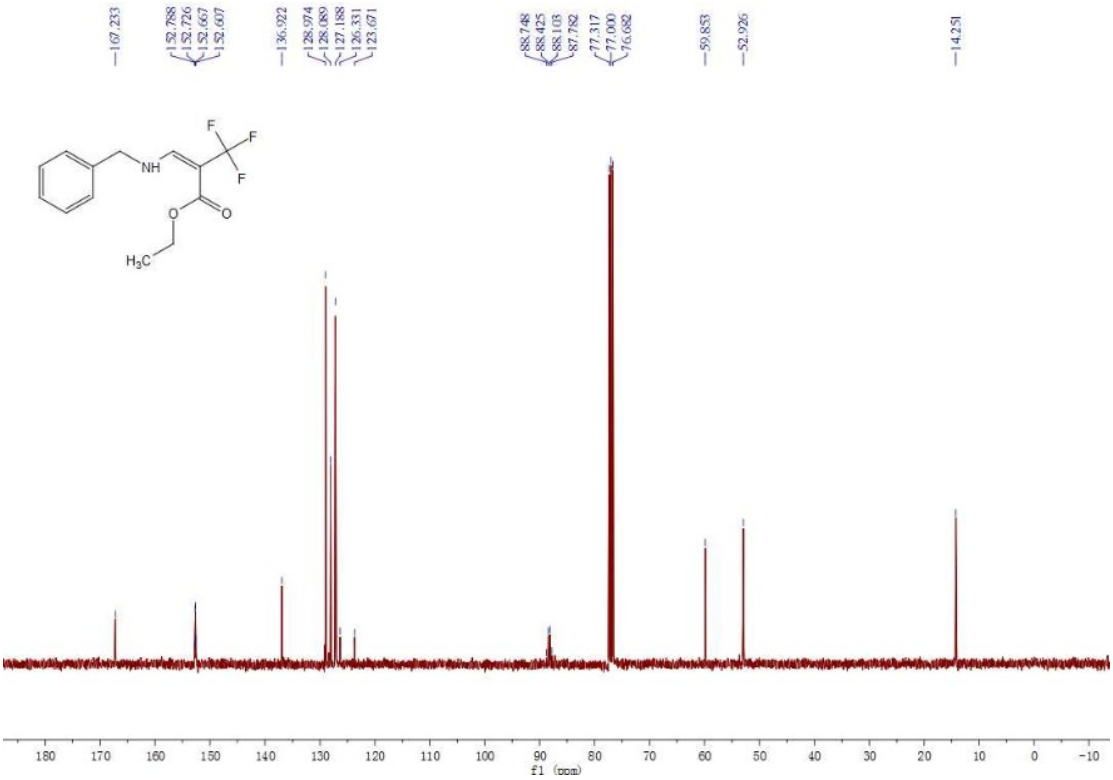

8.600
7.283
7.248
4.263
4.245
4.227
4.209
3.269
3.253
3.236
3.219
1.673
1.655
1.637
1.619
1.601
1.583
1.337
1.319
1.301
0.995
0.976
0.958
0.94
1.04
1.99
1.99
2.04
3.01
3.00
f1 (ppm)

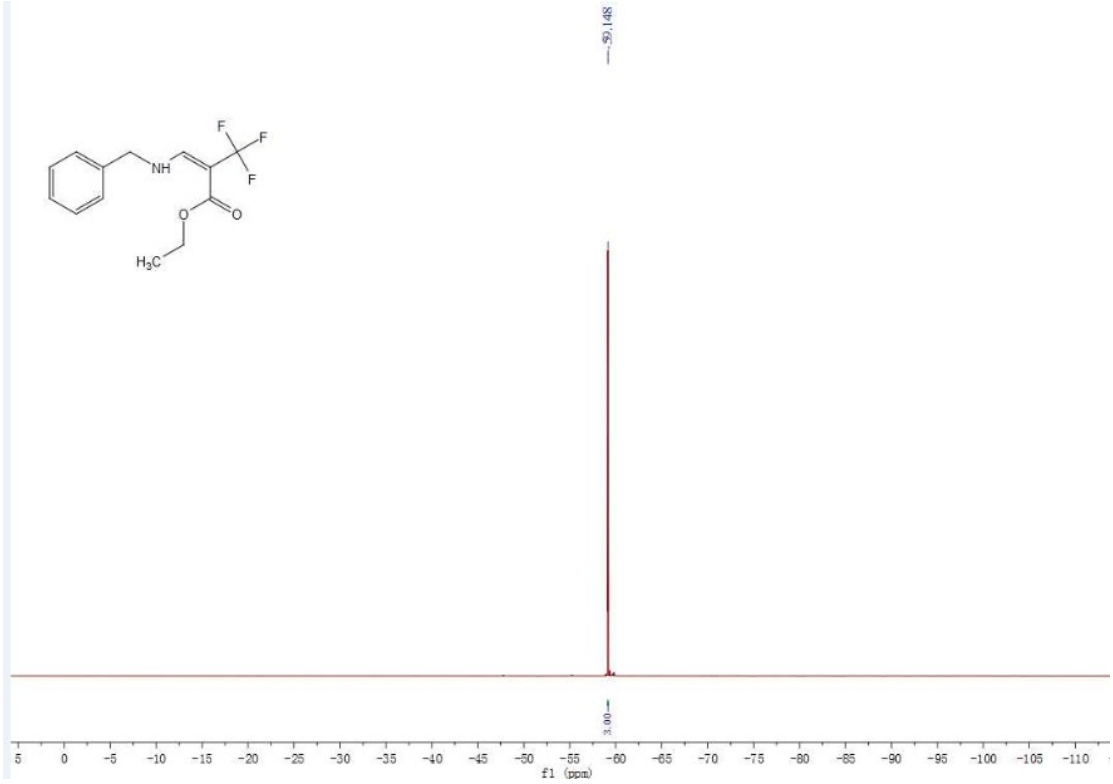

167.412
153.012
152.952
152.893
152.836
129.205
126.548
123.892
121.235
87.548
87.227
86.906
86.584
77.341
77.024
76.706
59.708
51.128
24.144
14.301
10.931
f1 (ppm)


-58.969
CH3
O
O
NH
H3C
F
F
F
3.00
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
f1 (ppm)

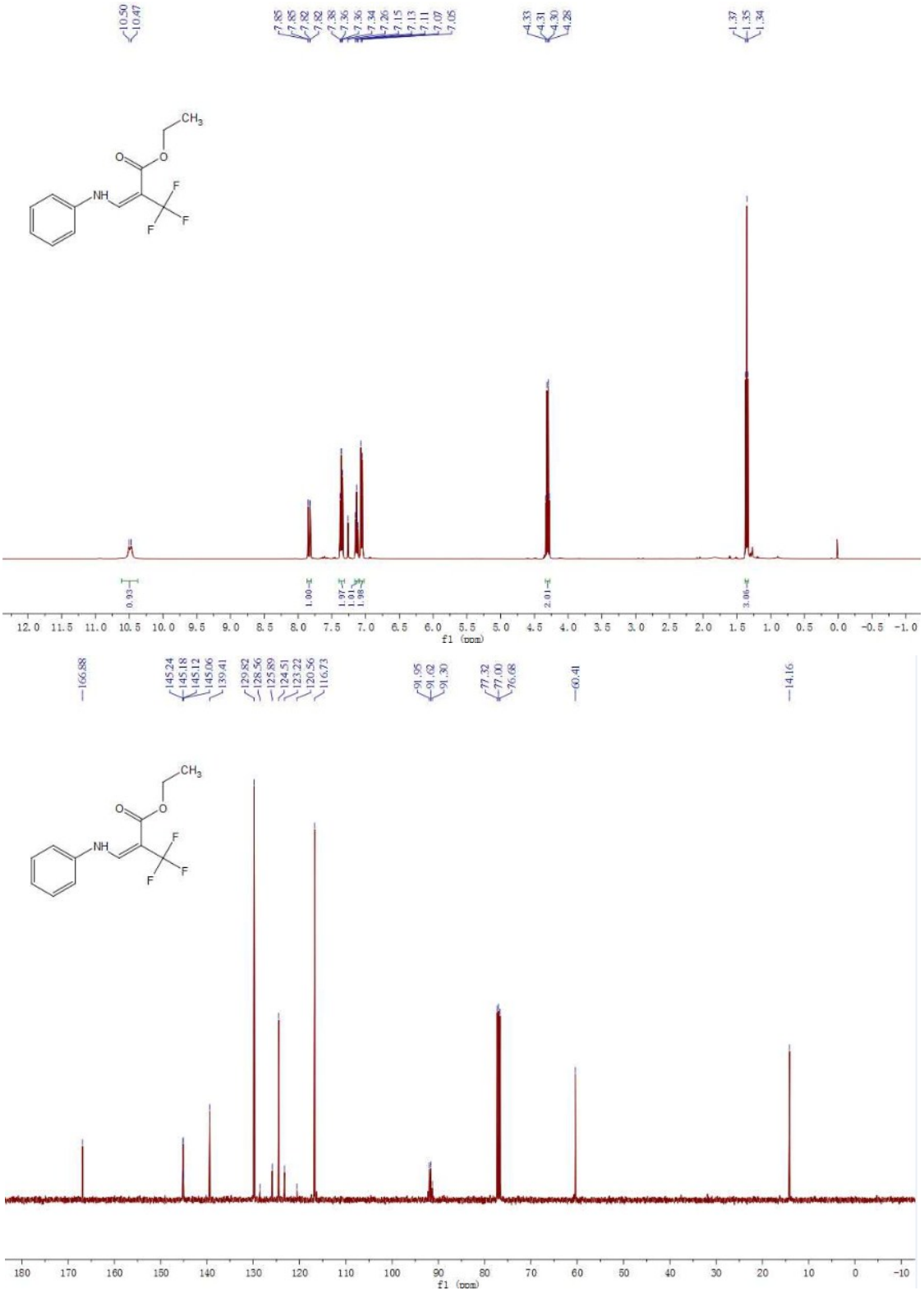
2z

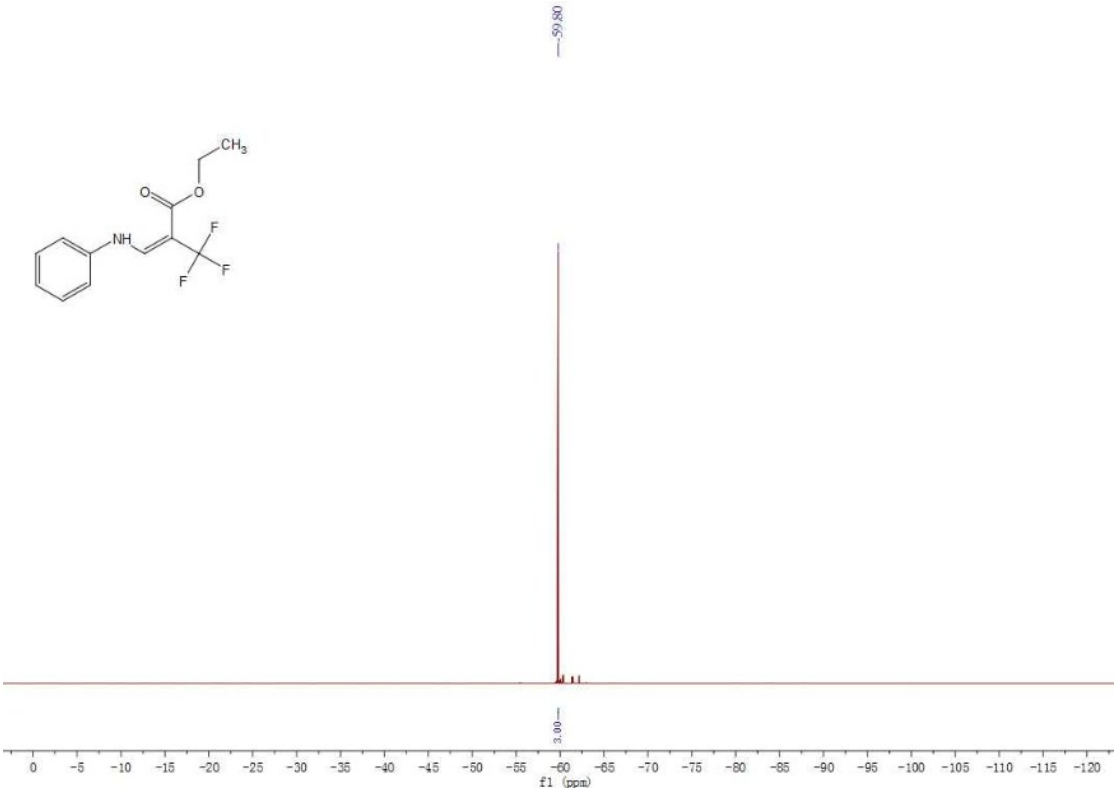

8.858
8.839
7.387
7.369
7.351
7.330
7.318
7.312
7.251
7.250
7.232
4.442
4.427
4.241
4.223
4.206
4.188
1.311
1.293
1.275
0.000
F
F
F
NH
O
O
H3C
0.98
4.02
2.05
2.02
2.03
3.14
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


167.233
152.788
152.726
152.667
152.607
136.922
128.974
128.689
127.188
126.331
123.671
88.748
88.425
88.103
87.782
77.317
77.000
76.682
59.853
52.926
14.251
F
F
F
NH
O
O
H3C
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

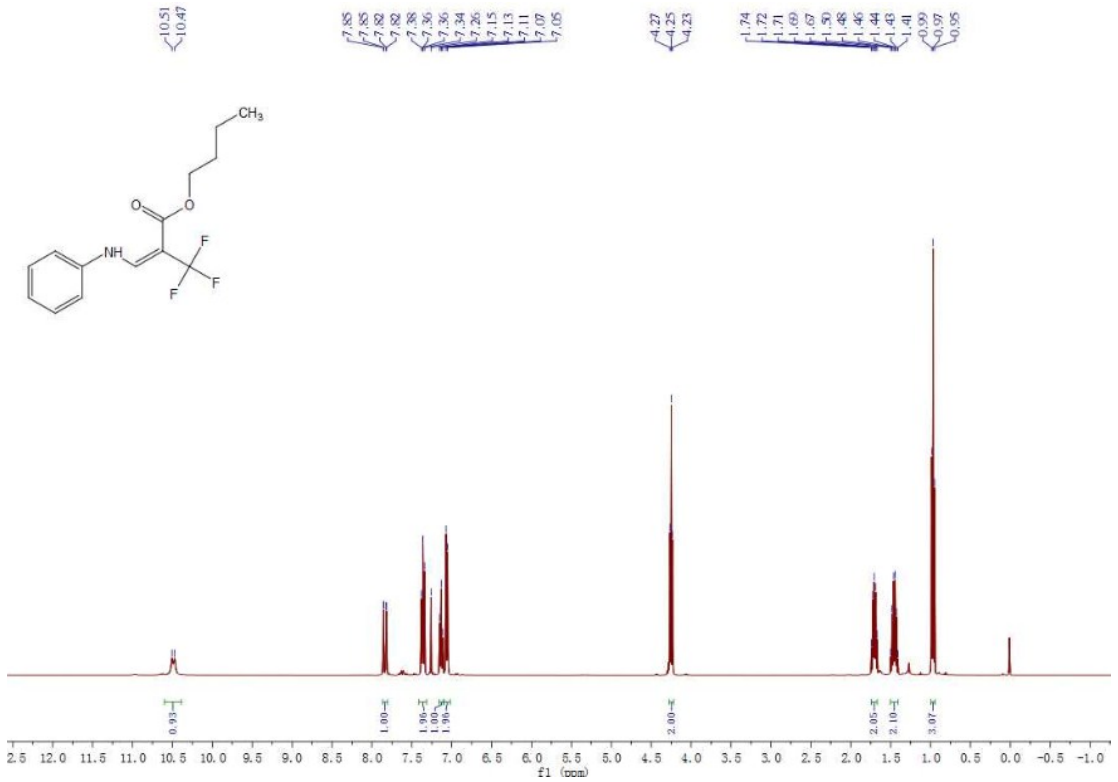

-59.148
F
F
F
NH
O
O
H3C
3.00
5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110
f1 (ppm)

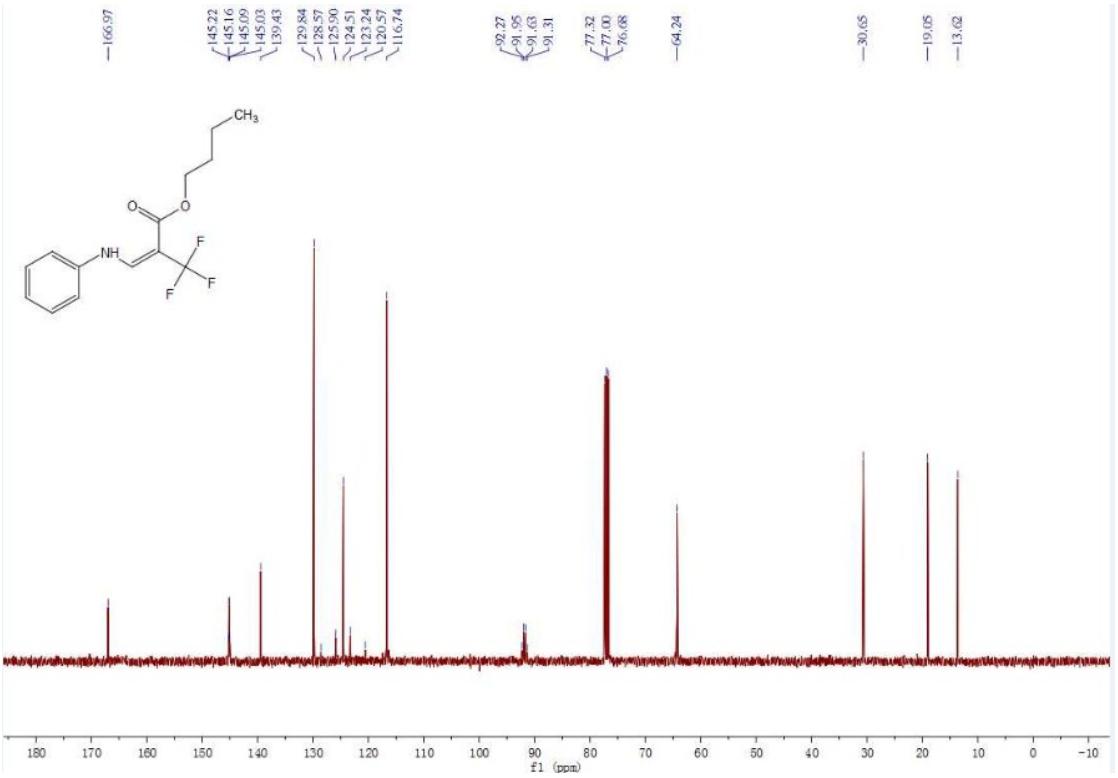
2a’

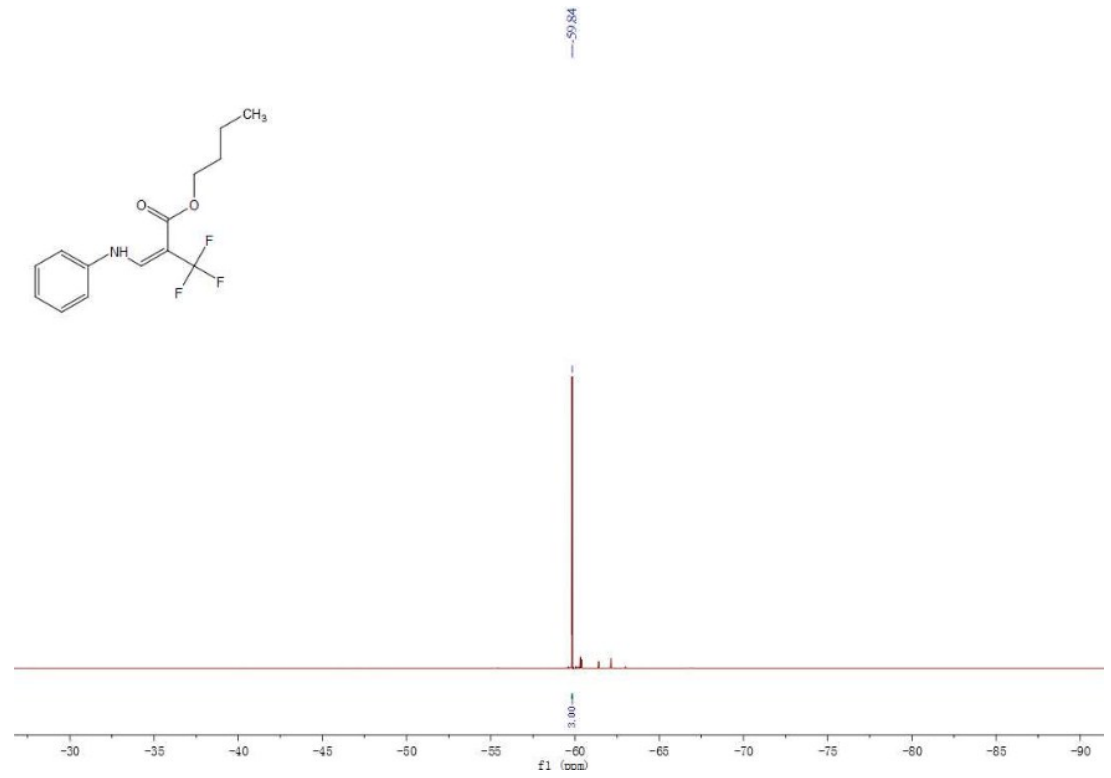

10.50
10.47
7.85
7.85
7.82
7.82
7.38
7.36
7.36
7.34
7.26
7.15
7.13
7.11
7.07
7.05
4.33
4.31
4.30
4.28
1.37
1.35
1.34
CH3
O
O
NH
F
F
F
0.93
1.00
1.97
1.01
1.98
2.01
3.06
f1 (ppm)
166.88
145.24
145.18
145.12
145.06
139.41
129.82
128.56
125.89
124.51
123.22
120.56
116.73
91.95
91.62
91.30
77.32
77.00
76.68
60.41
14.16
f1 (ppm)


-59.80
CH3
O
O
NH
F
F
F
3.00
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
f1 (ppm)

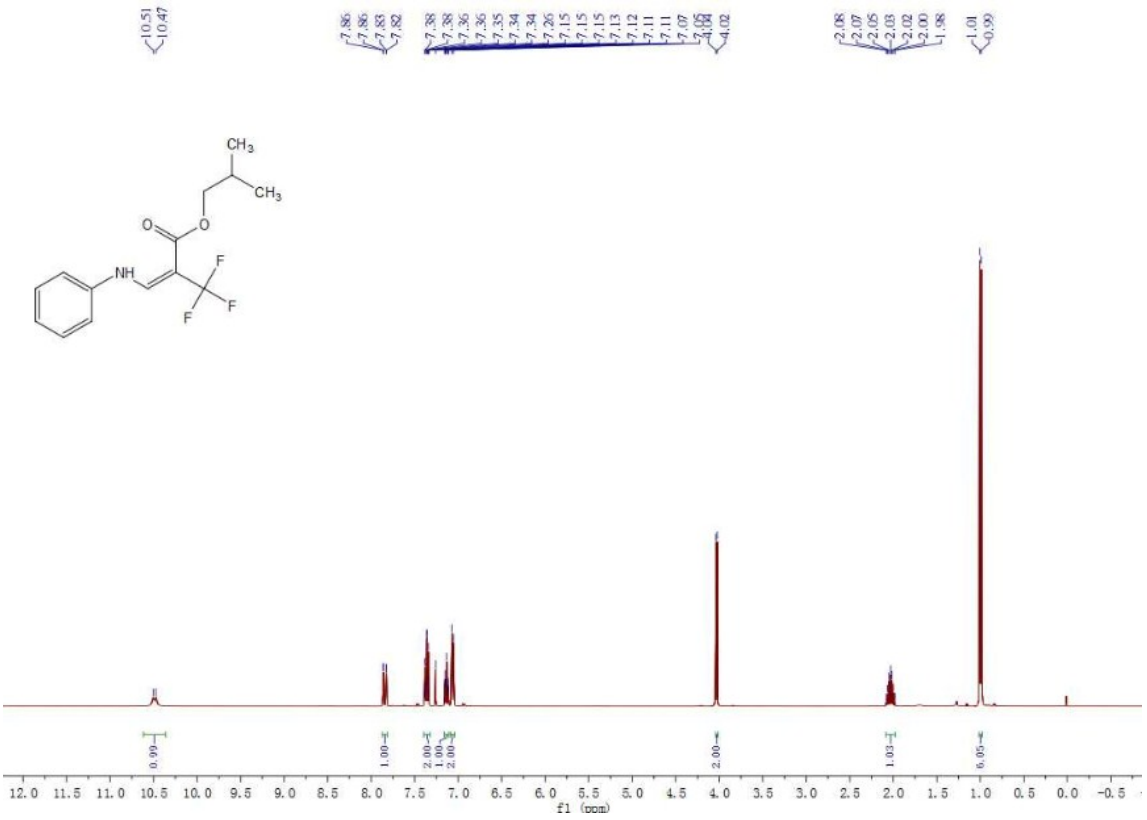
2b’

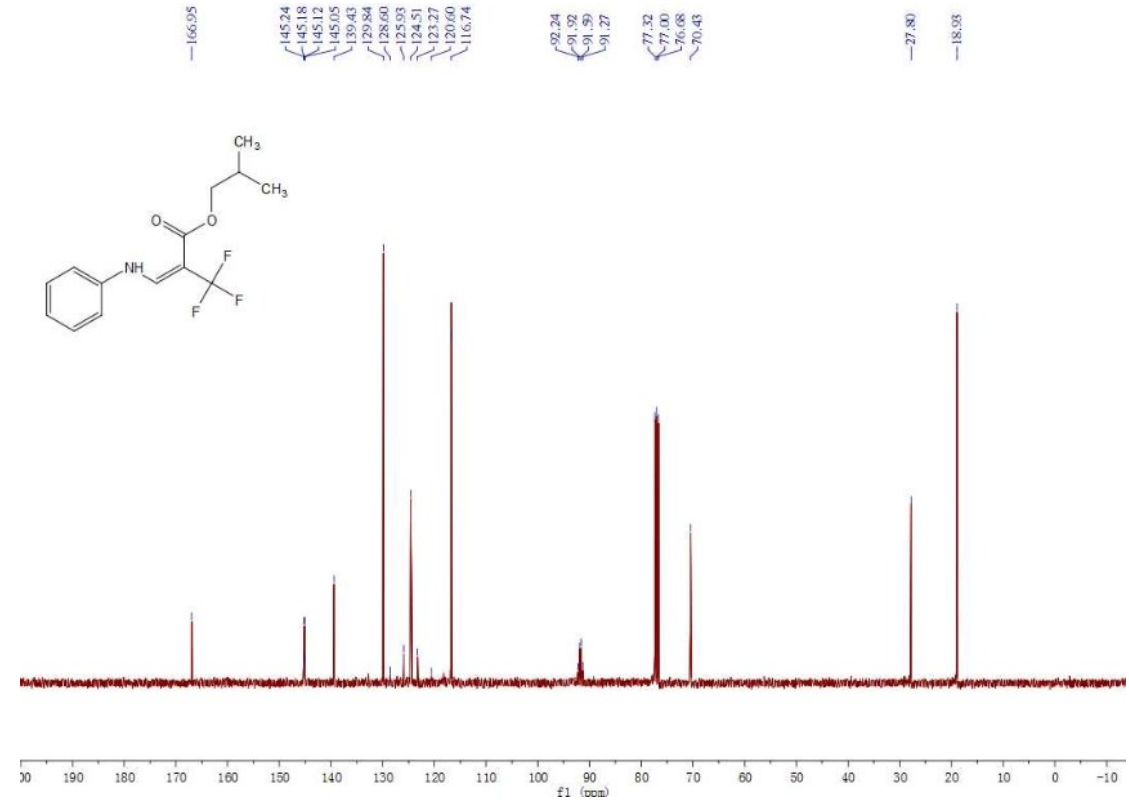

10.51
10.47
7.85
7.85
7.82
7.82
7.38
7.36
7.36
7.34
7.26
7.15
7.13
7.11
7.07
7.05
4.27
4.25
4.23
1.74
1.72
1.71
1.69
1.67
1.50
1.48
1.46
1.44
1.43
1.41
0.99
0.97
0.95
CH3
O
O
NH
F
F
F
0.93
1.00
1.96
1.00
1.96
2.00
2.05
2.10
3.07
2.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

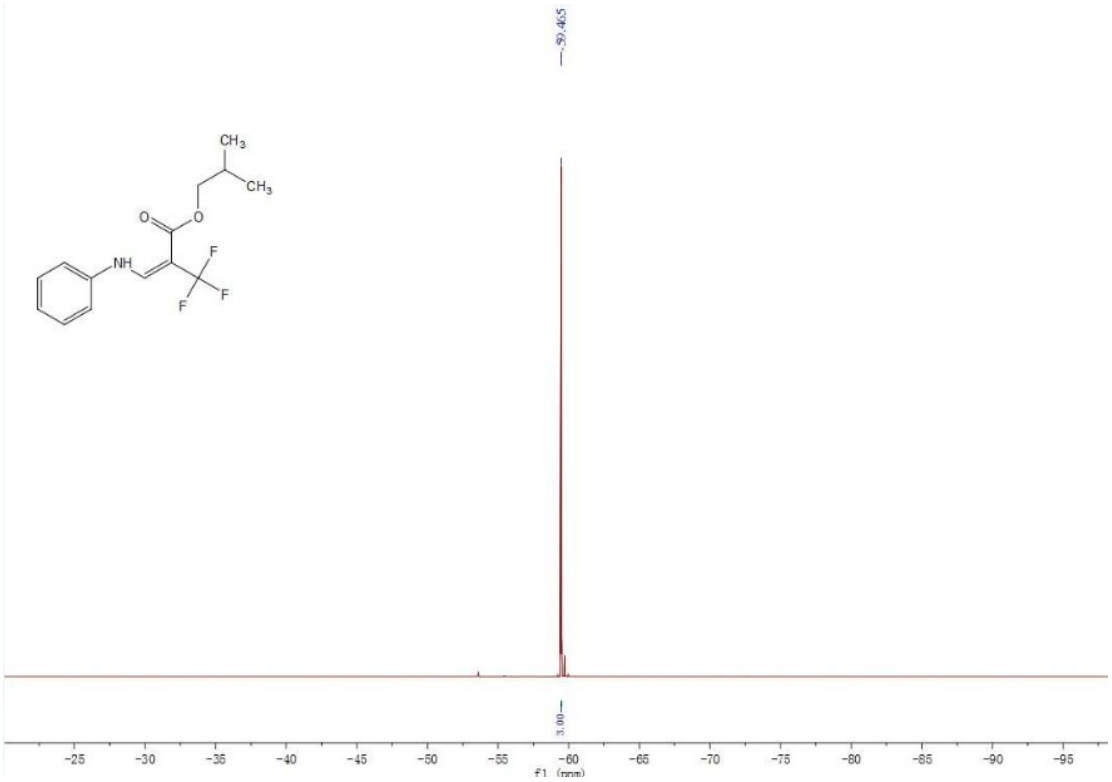

166.97
145.22
145.16
145.09
145.03
139.43
129.84
128.57
125.90
124.51
123.24
120.57
116.74
92.27
91.95
91.63
91.31
77.32
77.00
76.68
64.24
30.65
19.05
13.62
CH3
O
O
NH
F
F
F
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-59.84
CH3
O
O
NH
F
F
F
3.00
-30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90
f1 (ppm)

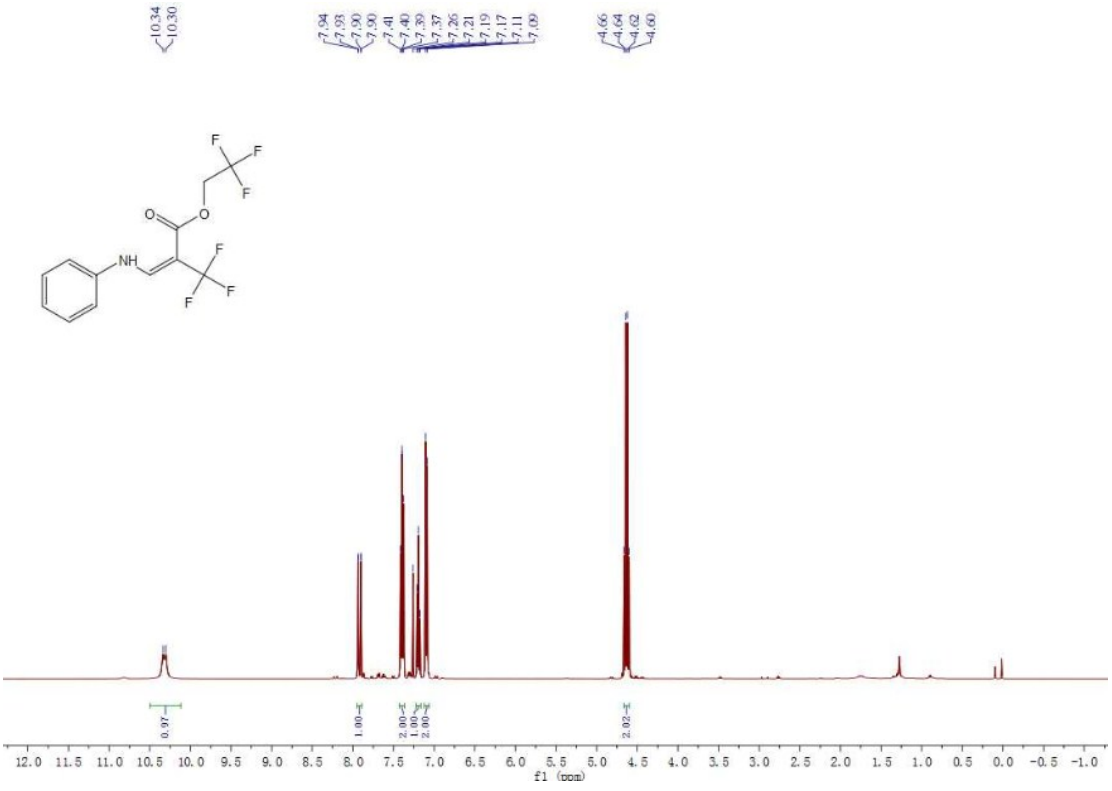
2c’

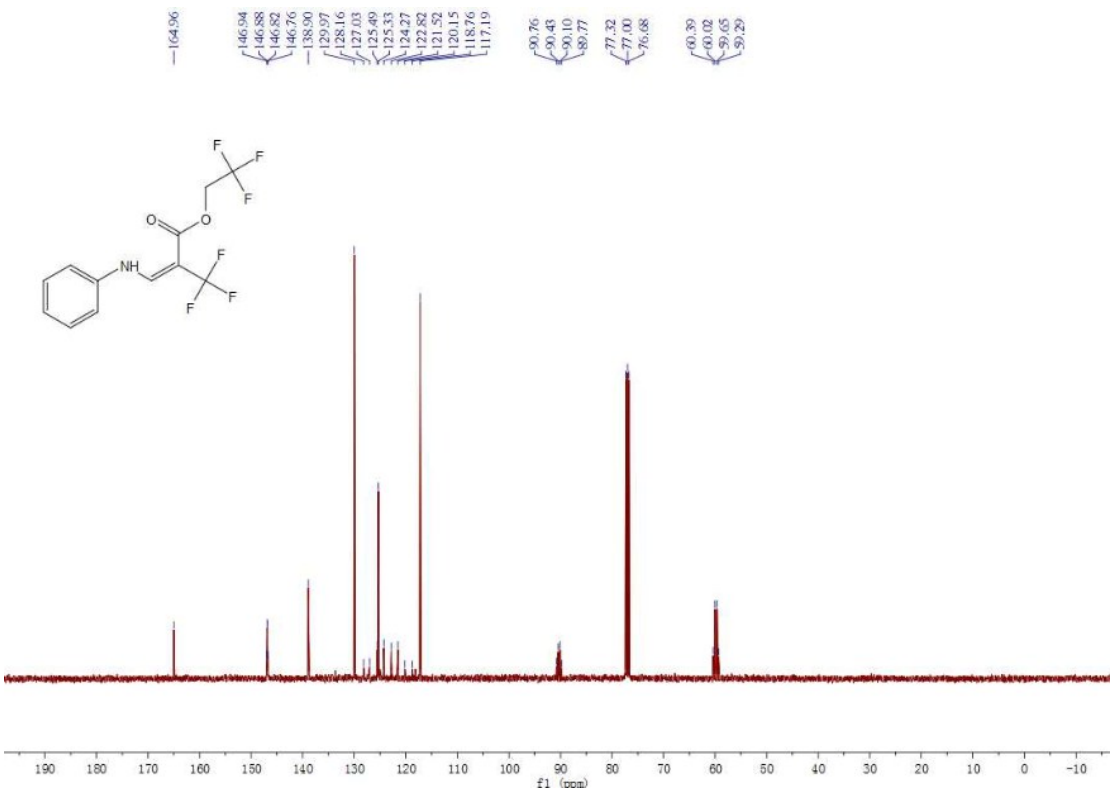

10.51
10.47
7.86
7.86
7.83
7.82
7.38
7.38
7.36
7.36
7.35
7.34
7.34
7.26
7.15
7.15
7.13
7.12
7.11
7.07
4.02
2.08
2.07
2.05
2.03
2.02
2.00
1.98
1.01
0.99
CH3
CH3
O
O
NH
F
F
F
0.99
1.00
2.00
1.00
2.00
2.00
1.03
6.05
f1 (ppm)

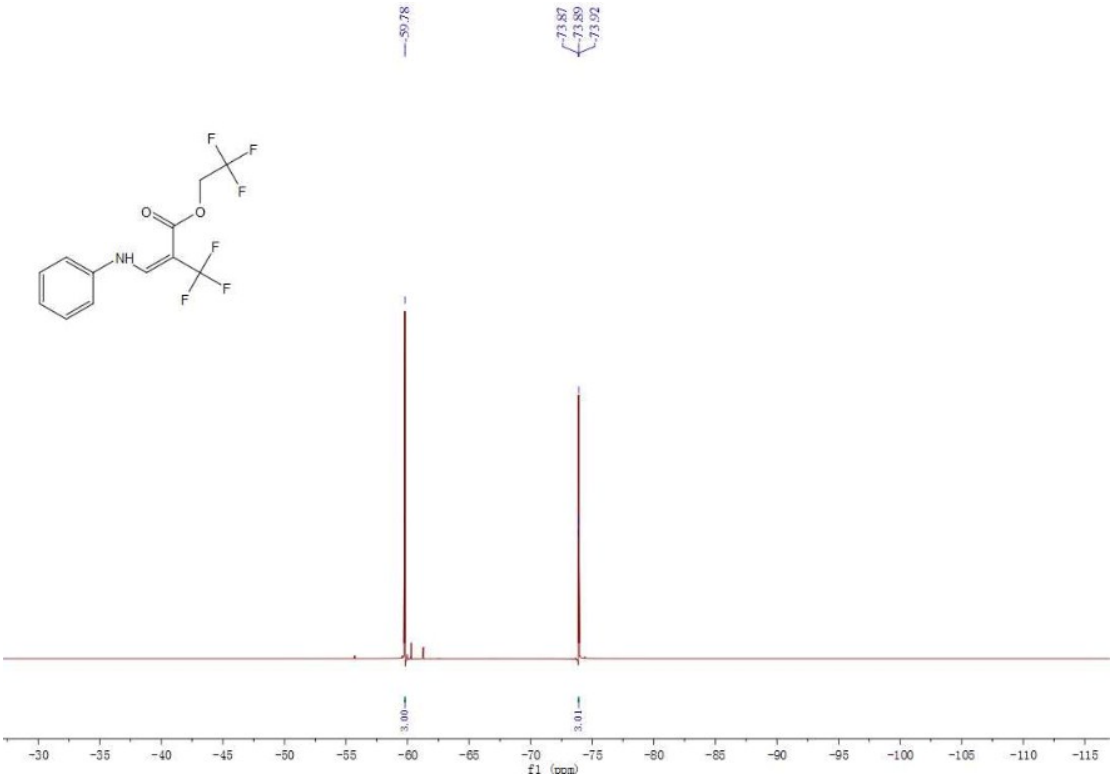

166.95
145.24
145.18
145.12
145.05
139.43
129.84
128.60
125.93
124.51
123.27
120.60
116.74
92.24
91.92
91.59
91.27
77.32
77.00
76.68
70.43
27.80
18.93
CH3
CH3
O
O
NH
F
F
F
f1 (ppm)


-59.465
CH3
CH3
O
O
NH
F
F
F
3.00
-25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95
f1 (ppm)

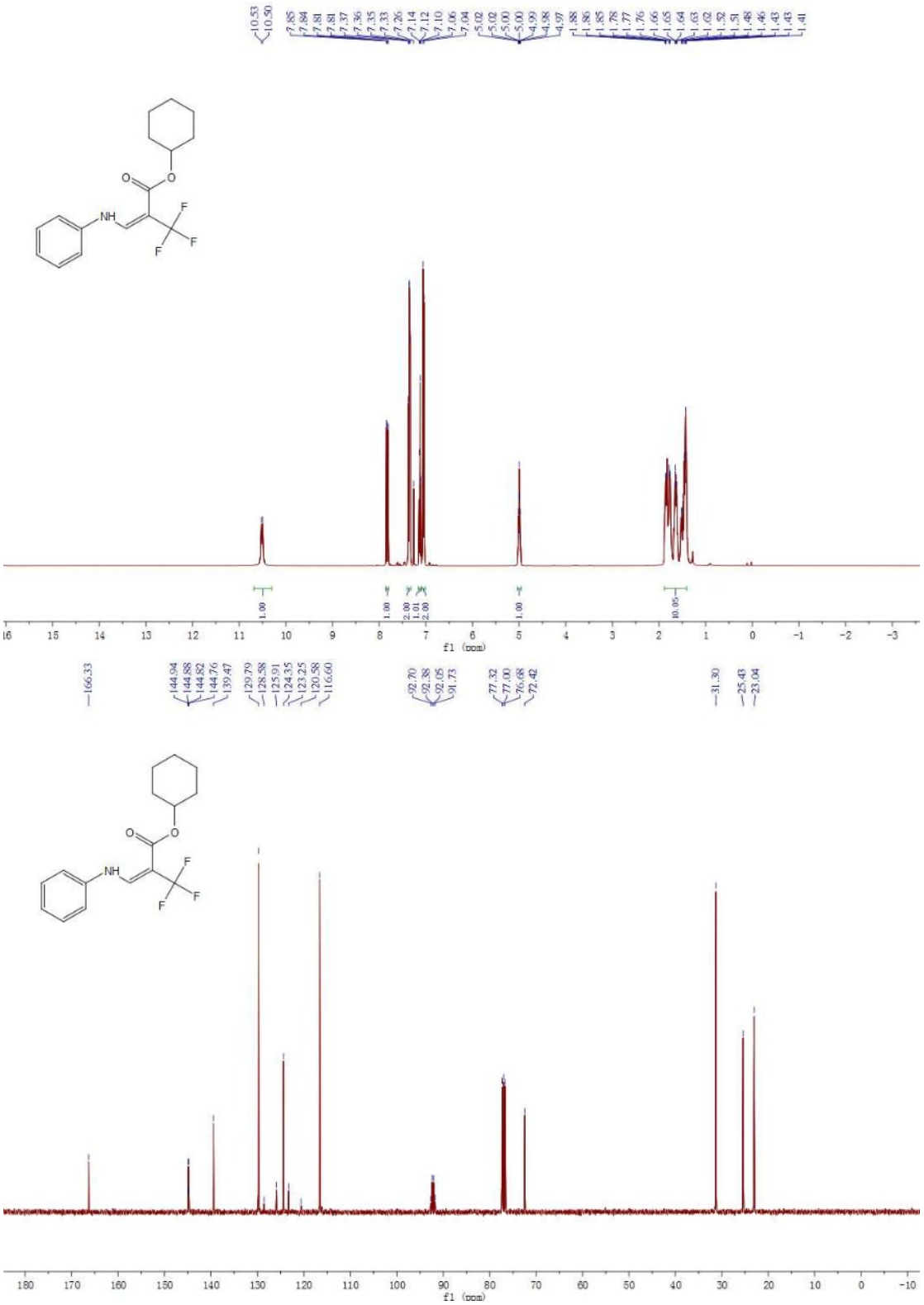
2d’

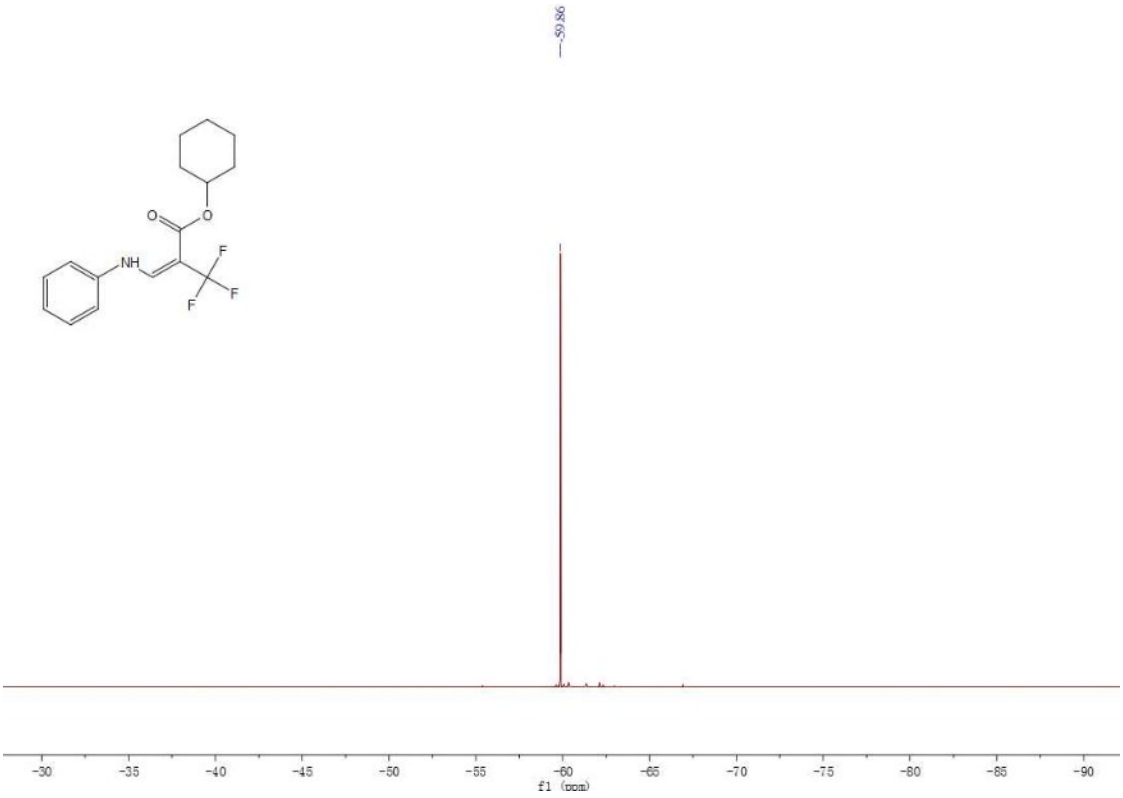

10.34
10.30
7.94
7.93
7.90
7.90
7.41
7.40
7.39
7.37
7.26
7.21
7.19
7.17
7.11
7.09
4.66
4.64
4.62
4.60
F
F
F
O
O
NH
F
F
F
0.97
1.00
2.00
1.00
2.00
2.02
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


164.96
146.94
146.88
146.82
146.76
138.90
129.97
128.16
127.03
125.49
125.33
124.27
122.82
121.52
120.15
118.76
117.19
90.76
90.43
90.10
89.77
77.32
77.00
76.68
60.39
60.02
59.65
59.29
f1 (ppm)

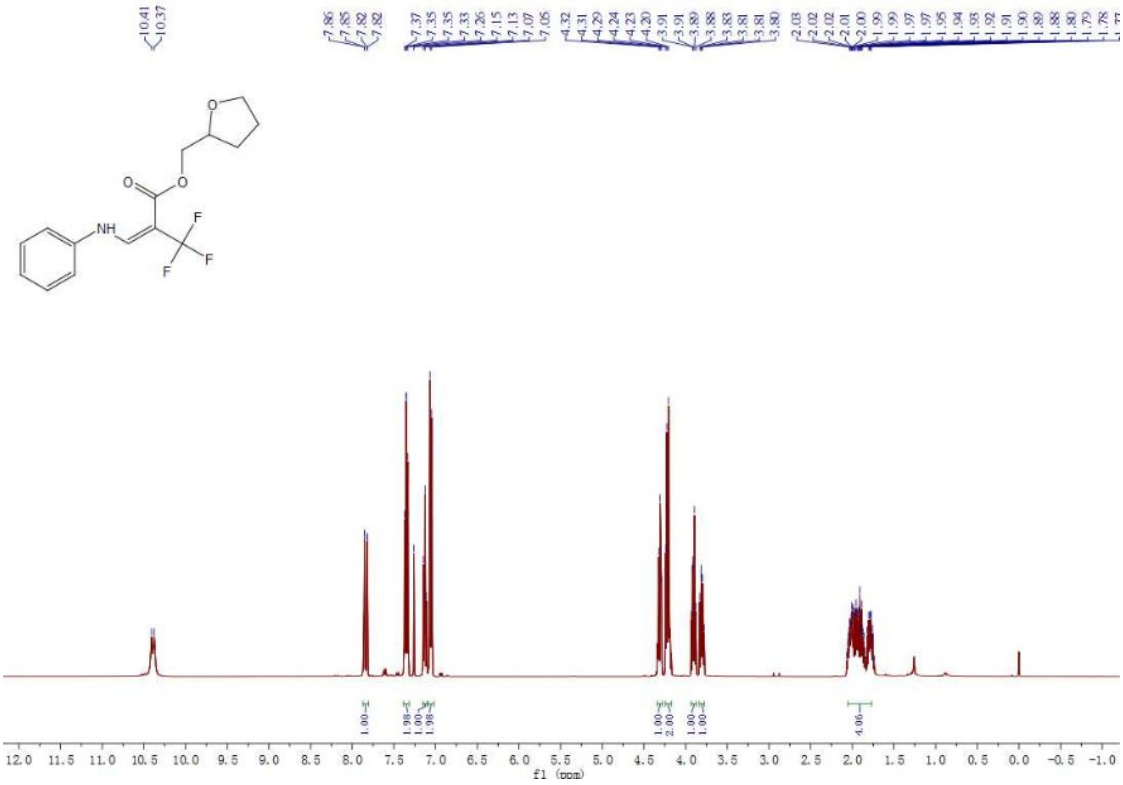

59.78
73.87
73.89
73.92
3.00
3.01
f1 (ppm)

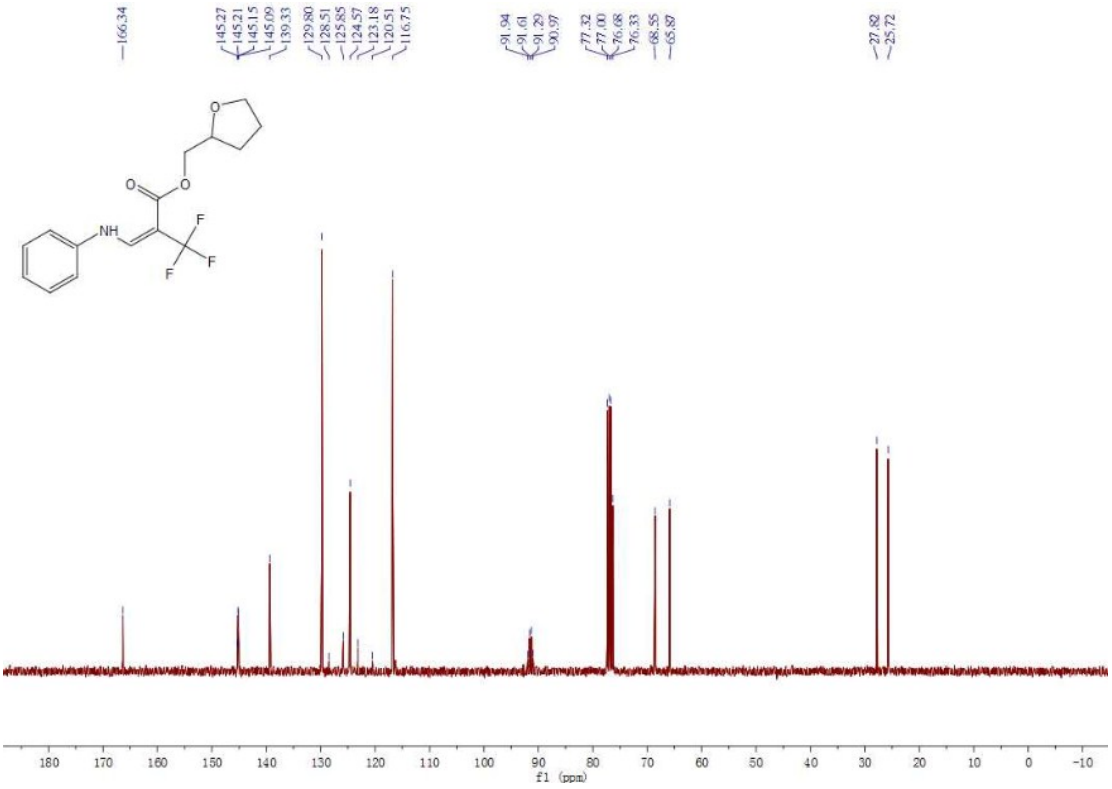
2e’

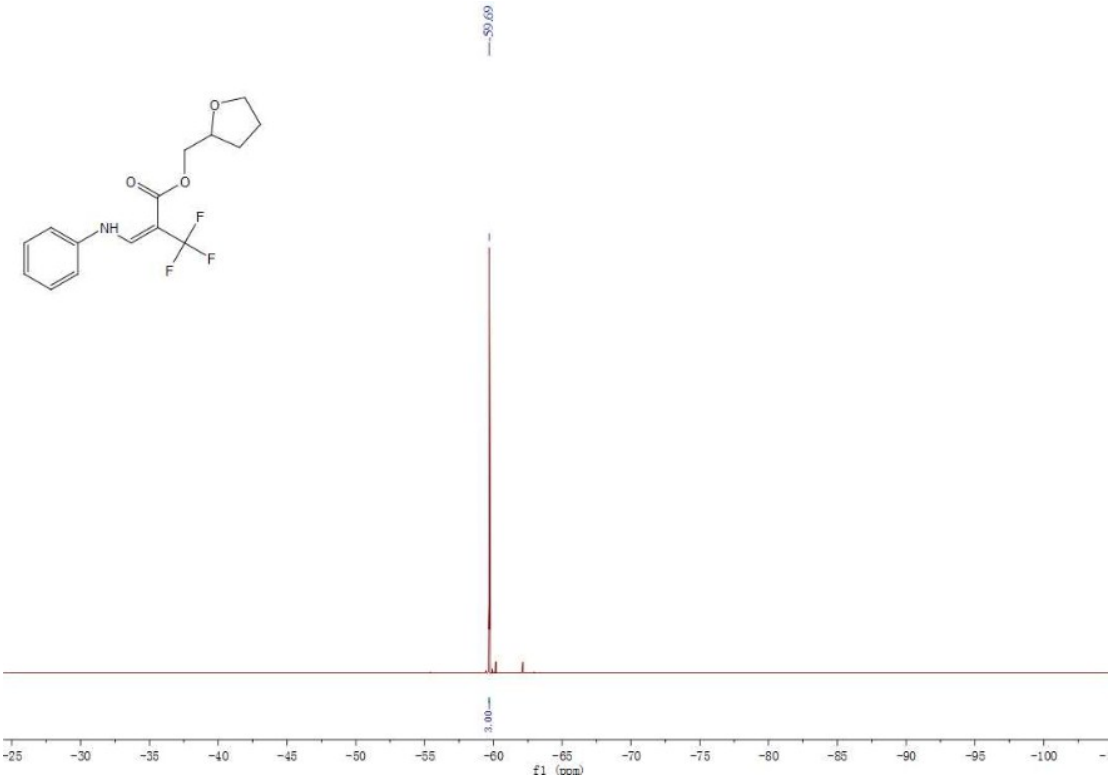



-59.86
O
O
NH
F
F
F
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
f1 (ppm)

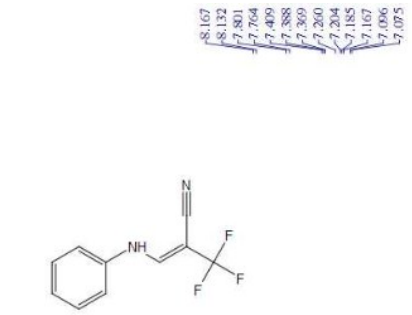
2f'

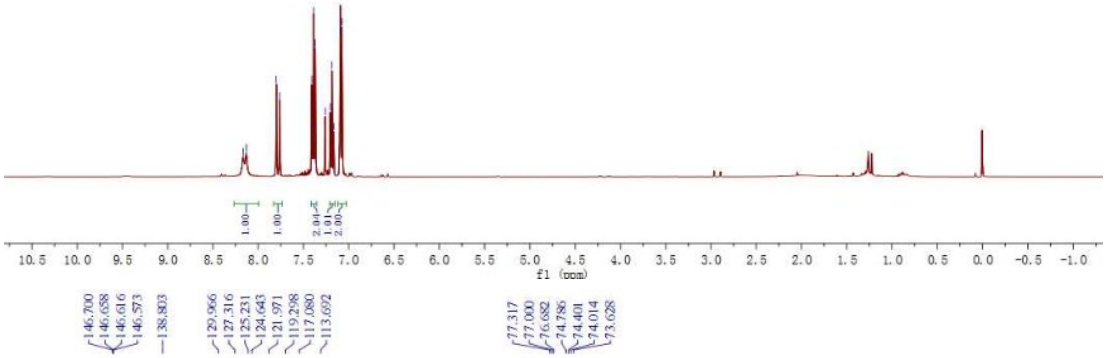

10.41
10.37
7.86
7.85
7.82
7.82
7.37
7.35
7.33
7.26
7.15
7.13
7.07
7.05
4.32
4.31
4.29
4.24
4.23
4.20
3.91
3.89
3.88
3.83
3.81
3.80
2.03
2.02
2.02
2.01
2.00
1.99
1.99
1.97
1.97
1.95
1.94
1.93
1.92
1.91
1.90
1.89
1.88
1.80
1.79
1.78
O
O
NH
F
F
F
1.00
1.98
1.00
1.98
1.00
2.00
1.00
1.00
4.06
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


166.34
145.27
145.21
145.15
145.09
139.33
129.80
128.51
125.85
124.57
123.18
120.51
116.75
91.94
91.61
91.29
90.97
77.32
77.00
76.68
76.33
68.55
65.87
27.82
25.72
O
O
O
NH
F
F
F
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

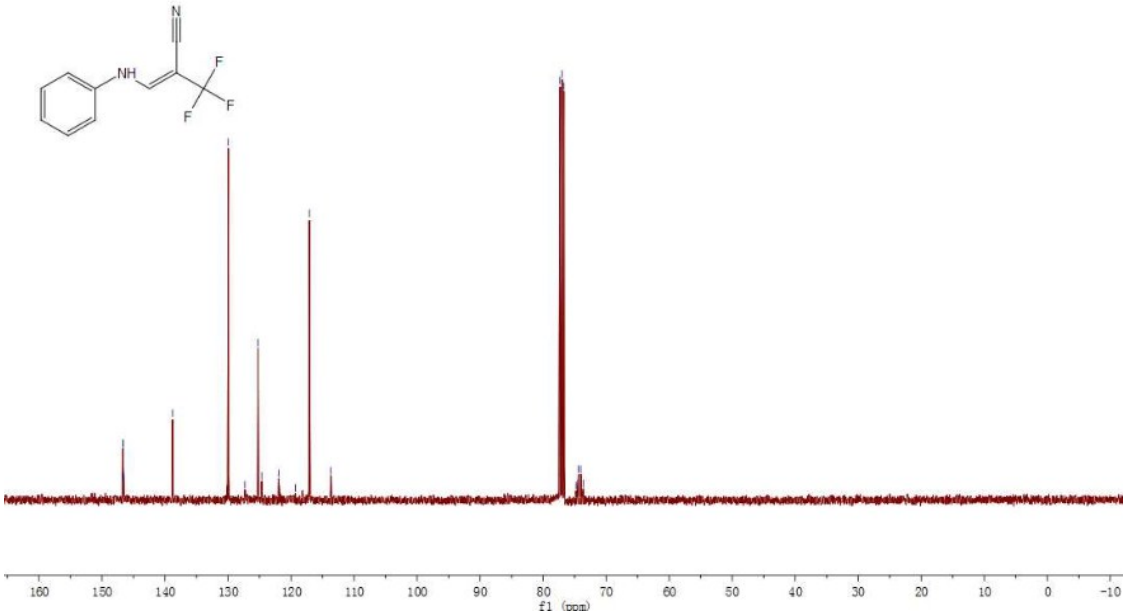

-59.69
O
O
O
NH
F
F
F
3.00
-25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100
f1 (ppm)

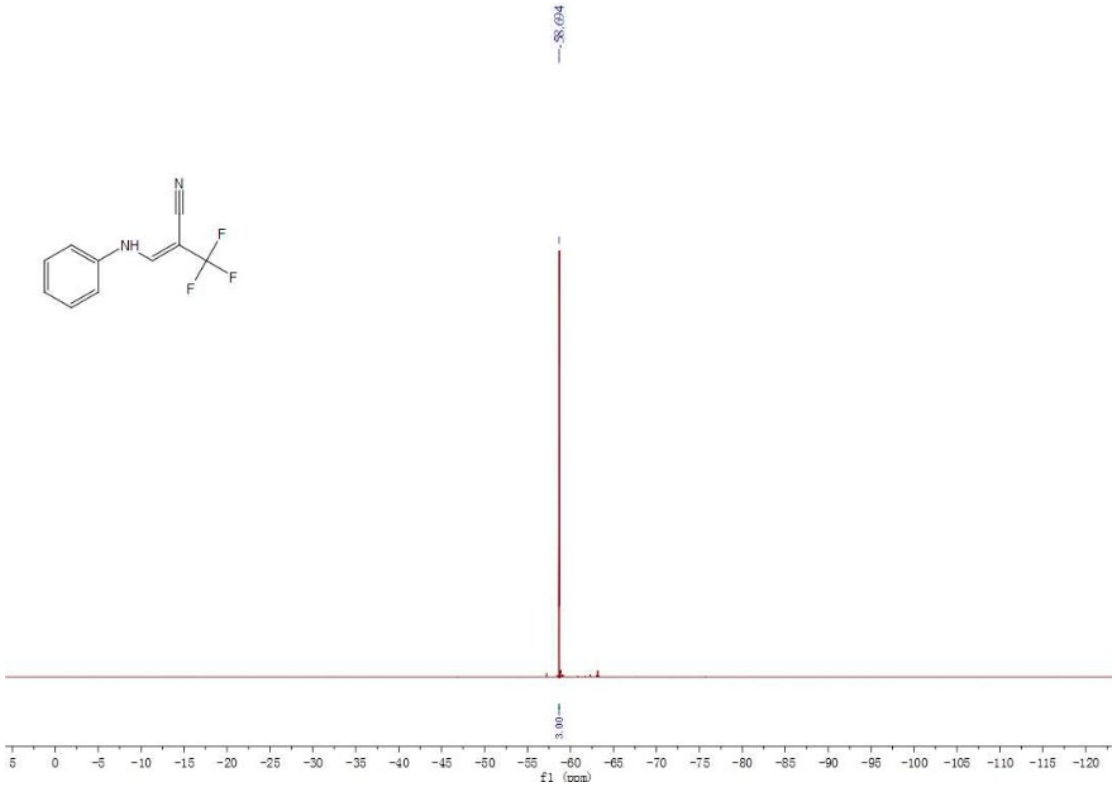
2g’


8.167
8.132
7.801
7.764
7.409
7.388
7.369
7.260
7.204
7.185
7.167
7.006
7.075
N
NH
F
F
F

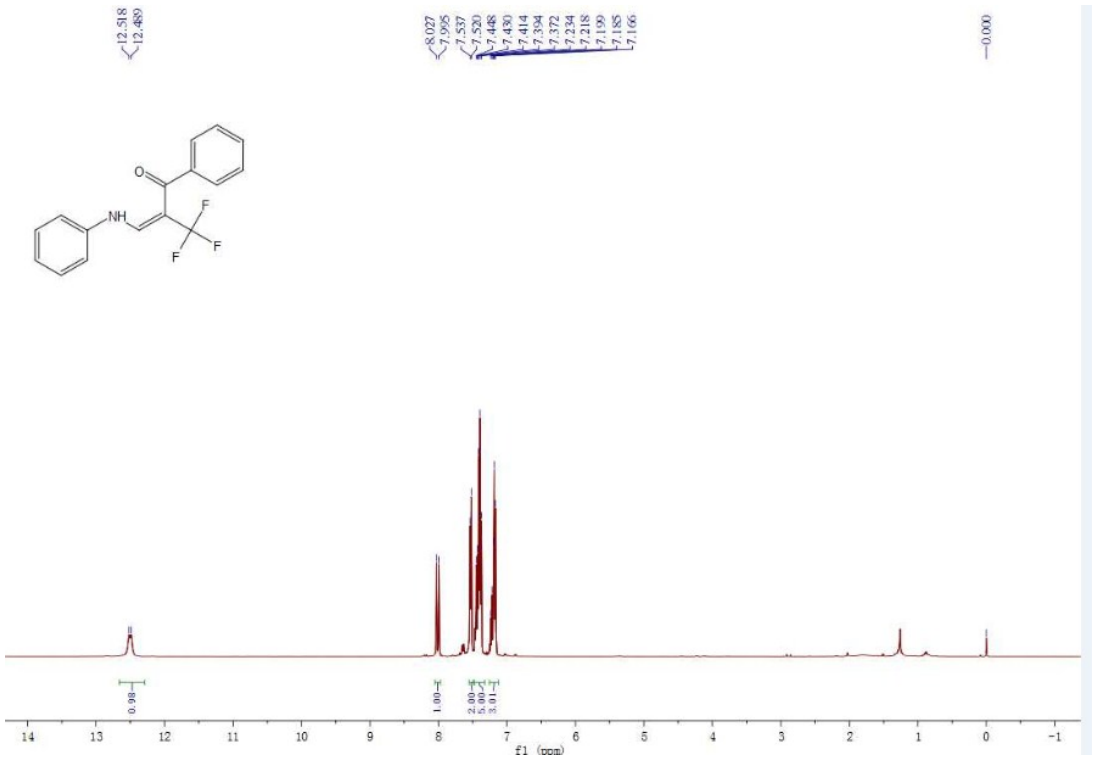

1.00
1.00
2.04
1.01
2.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

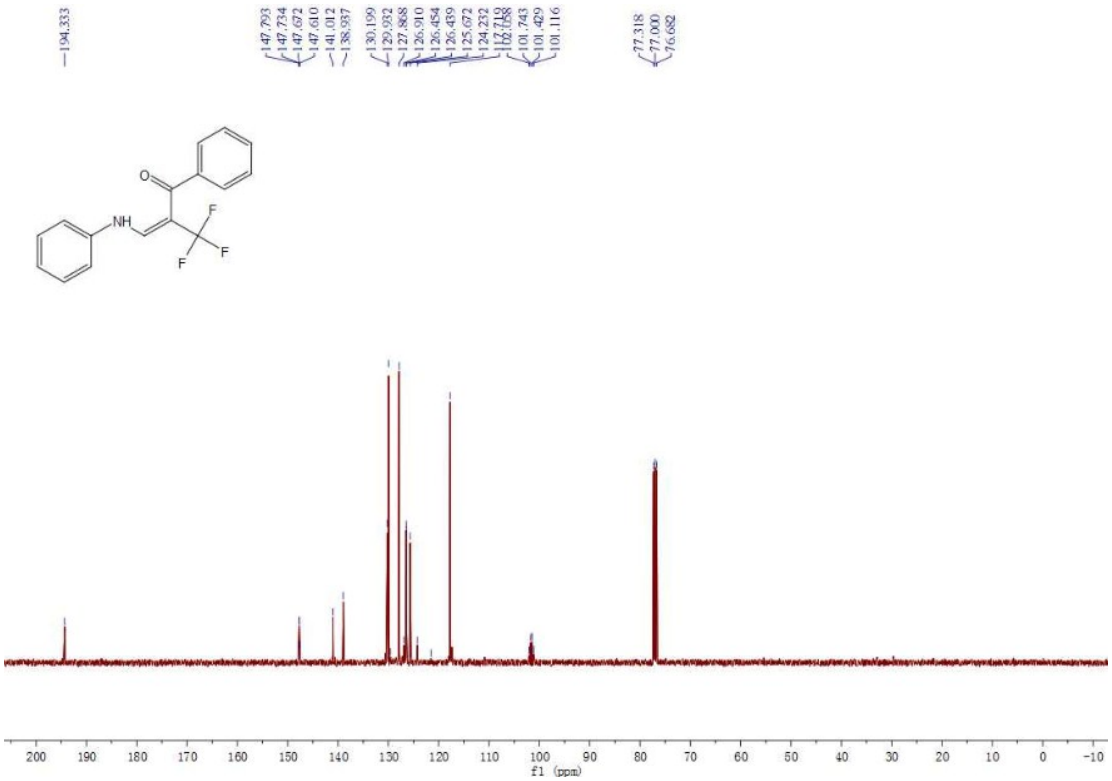
146.700
146.658
146.616
146.573
138.803
129.966
127.316
125.231
124.643
121.991
119.298
117.080
113.692
77.317
77.000
76.682
74.786
74.401
74.014
73.628

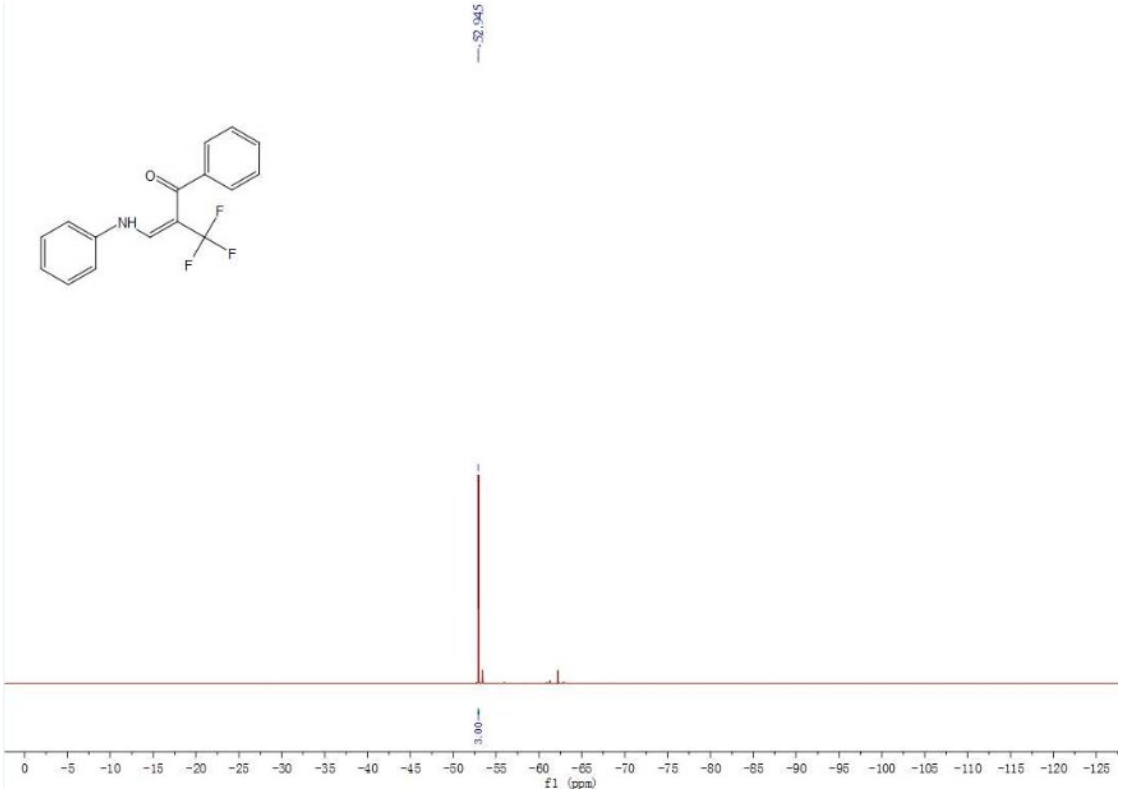

N
NH
F
F
F
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-58.694
N
NH
F
F
F
3.00
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
f1 (ppm)

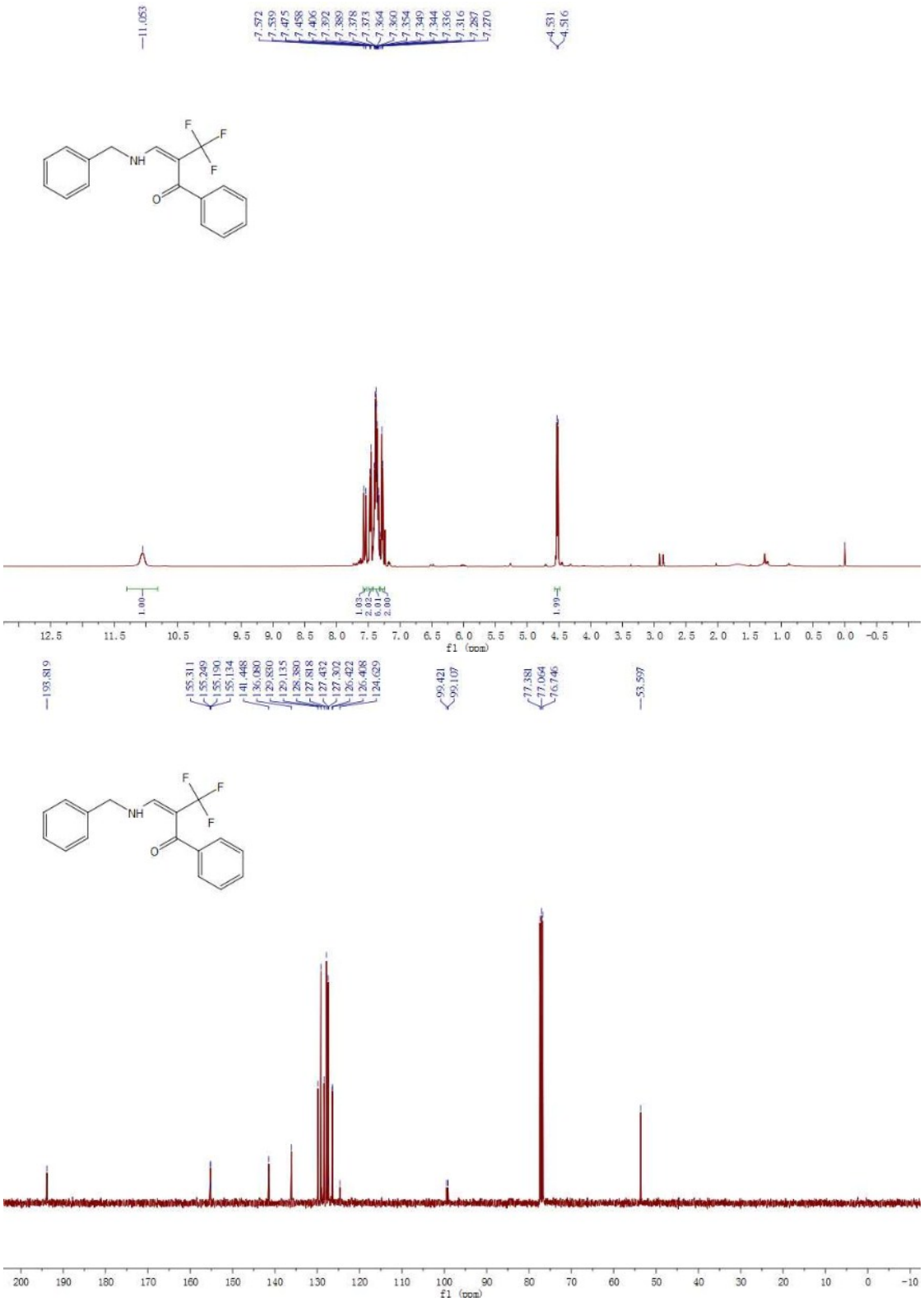
2h’

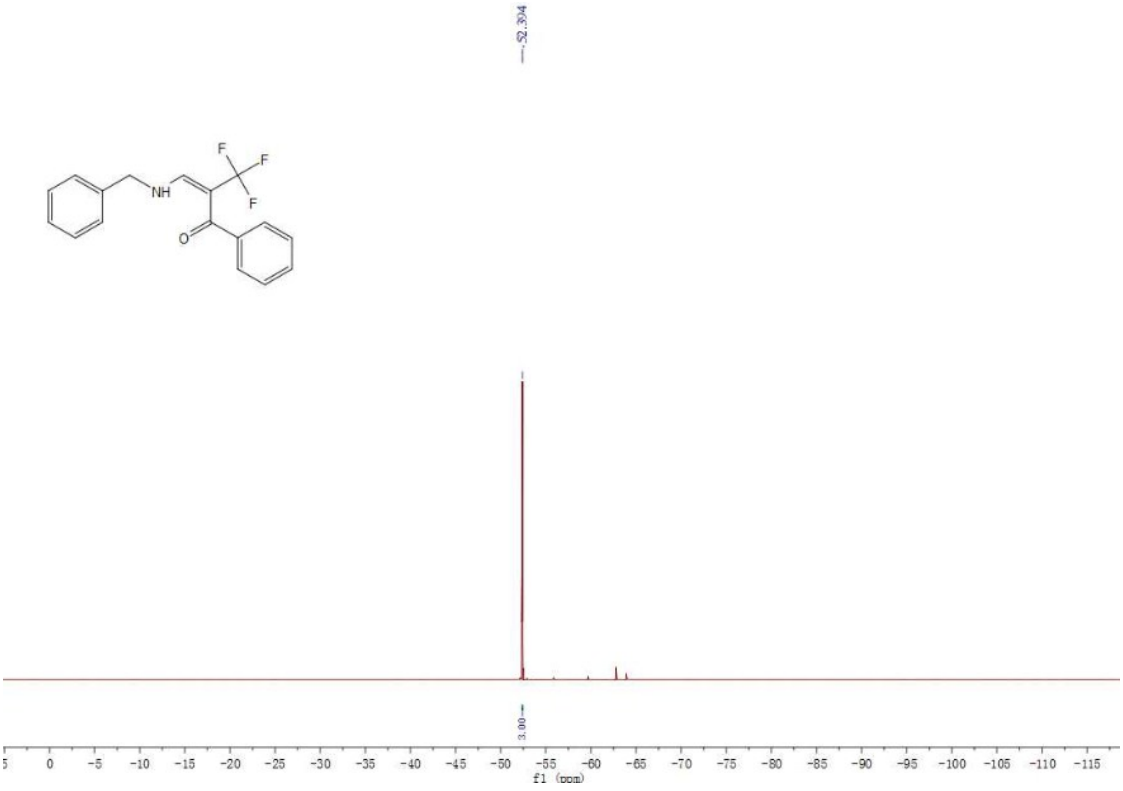

12.518
12.489
8.027
7.995
7.537
7.520
7.448
7.430
7.414
7.394
7.372
7.234
7.218
7.199
7.185
7.166
0.000
O
NH
F
F
F
0.98
1.00
2.00
5.90
3.91
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)


194.333
147.793
147.734
147.672
147.610
141.012
138.937
130.199
129.932
127.888
126.910
126.454
126.439
125.672
124.232
117.719
117.668
101.743
101.429
101.116
77.318
77.000
76.682
O
NH
F
F
F
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-52.945
O
NH
F
F
F
3.00
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)

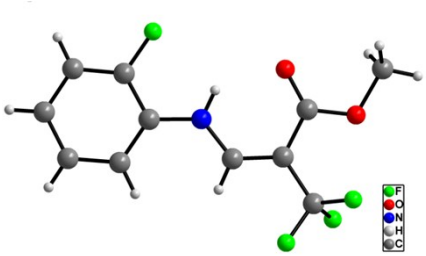
2i’


11.053
7.572
7.539
7.475
7.458
7.406
7.392
7.389
7.378
7.373
7.364
7.360
7.354
7.349
7.344
7.336
7.316
7.287
7.270
4.531
4.516
NH
F
F
F
O
1.00
1.03
2.02
6.01
2.00
1.99
f1 (ppm)
193.819
155.311
155.249
155.190
155.134
141.448
136.080
129.830
129.135
128.380
127.818
127.432
127.302
126.422
126.408
124.029
99.421
99.107
77.381
77.064
76.746
53.597
f1 (ppm)


-52.304
F
F
F
NH
O
3.00
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
f1 (ppm)

F. X-ray Crystallographic Data

The X-ray crystallographic structures for **2n**. Crystal data have been deposited to CCDC, number 1542511.



Empirical formula	$C_{11}H_9F_4NO_2$
Formula weight	263.19
Temperature	150.00 (10) K
Wavelength	1.54184 Å
Crystal system, space group	monoclinic, P_12_1/c_1
Unit cell dimensions	a = 9.57475(17) Å alpha = 90.00 deg. b = 13.6182(2) Å beta = 98.8820(17) deg. c = 8.60542(16) Å gamma = 90.00 deg.
Volume	1108.61(3) $Å^3$
Z, Calculated density	4, 1.577 Mg/m^3
Absorption coefficient	1.359 mm^{-1}
F(000)	536
Crystal size	0.60×0.40×0.08 mm
Theta range for data collection	4.67 to 74.38 deg.
Limiting indices	$-8 \leq h \leq 11$, $-13 \leq k \leq 16$, $-10 \leq l \leq 9$
Reflections collected / unique	4161 / 2186, [R(int) = 0.0222]
Completeness to theta = 74.38	99.90%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2186 / 0 / 164
Goodness-of-fit on F^2	1.061

Final R indices [I>2sigma(I)]	R1 = 0.0377, wR2 = 0.1036
R indices (all data)	R1 = 0.0404, wR2 = 0.1065