Supporting Information

Silver-Catalyzed Geminal Aminofluorination of Diazoketones with Anilines and *N*-Fluorobenzenesulphonimide

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General: All reactions were performed under an argon atmosphere in a 10 mL microwave tube. 1,2-Dichloroethane was dried over CaH_2 before use. For chromatography, 200-300 mesh silica gel (Qingdao, China) was used. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were measured recorded on Brucker ARX 400 spectrometer in $CDCl_3$ or DMSO-d_6 solution. MS and HRMS were performed on Thermo MAT95XP. Chemical shifts (δ) were given in ppm, referenced to the residual proton resonance of $CDCl_3$ (7.26) and DMSO-d_6 (2.50), to the carbon resonance of $CDCl_3$ (77.16) and DMSO-d_6 (39.52). Coupling constants (J) were given in Hertz (Hz). The term m, q, t, d, s referred to multiplet, quartet, triplet, doublet, singlet. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

General procedure for $AgNO_3$-catalyzed gem-aminofluorination of diazoketones with anilines and NFSI:

A 10 mL snap microwave tube under argon atmosphere was charged with $AgNO_3$ (6.8 mg, 20 mol %), aniline (0.2 mmol), diazoketone (0.4 mmol), NFSI (0.4 mmol), and K_2CO_3 (0.4 mmol). Then 2 mL of DCE were added via syringe. The resulting solution was stirred at room temperature for 12 h. After the reaction was completed, the mixture was filtered through a short path of silica gel, eluting with ethyl acetate. The volatile compounds were removed in *vacuo* and the residue was purified by column chromatography (SiO_2).

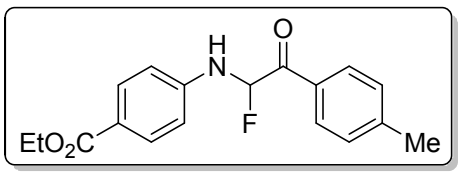
Table S1. Optimization of reaction conditions using various silver (I) salts, bases and solvents.[a]

Entry	Catalyst (20 mol %)	Base (2 equiv.)	Solvent (2 mL)	Yield (%) [b]	
				3a	**4a**
1	$AgNO_3$	K_2CO_3	DCE	70	12
2	AgOAc	K_2CO_3	DCE	64	12
3	AgOTf	K_2CO_3	DCE	58	14
4	Ag_2O	K_2CO_3	DCE	56	13
5	AgF	K_2CO_3	DCE	60	13
6	$AgNO_3$	Na_2CO_3	DCE	56	11
7	$AgNO_3$	Cs_2CO_3	DCE	<5	35
8	$AgNO_3$	Li_2CO_3	DCE	<5	37
9	$AgNO_3$	$KHCO_3$	DCE	36	10
10	$AgNO_3$	K_3PO_4	DCE	24	22
11	$AgNO_3$	KOH	DCE	0	30
12	$AgNO_3$	K_2CO_3	Tolune	30	7
13	$AgNO_3$	K_2CO_3	THF	40	8
14	$AgNO_3$	K_2CO_3	MeCN	8	10

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (2 equiv.), NFSI (2 equiv.), silver catalyst (20 mol %), base (2 equiv.), solvent (2 mL) under argon at room temperature for 12 h. [b] Yields were determined by ^{1}H NMR using methyl sulfone as the internal standard.

Characterization data

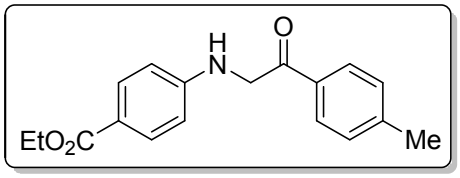
ethyl 4-((1-fluoro-2-oxo-2-(p-tolyl)ethyl)amino)benzoate (3a)



Pale yellow solid (64%, 40 mg, eluent: petroleum ether/ethyl acetate = 10/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 8.03 (d, J = 8.6 Hz, 2H), 7.68 (d, J = 8.6 Hz, 2H), 7.38 (d, J = 7.7 Hz, 2H), 7.23 (d, J = 7.8 Hz, 2H), 5.87 (d, $J_{H\text{-}F}$ = 48.5 Hz, 1H), 4.36 (q, J = 7.1 Hz, 2H), 2.36 (s, 3H), 1.39 (t, J =

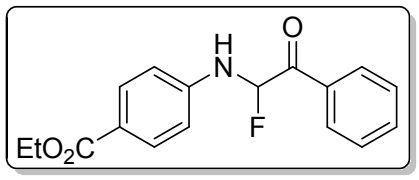
7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1 (d, $J_{C\text{-}F}$ = 21.4 Hz), 166.1, 140.8, 140.0 (d, $J_{C\text{-}F}$ = 2.4 Hz), 131.3 (d, $J_{C\text{-}F}$ = 19.2 Hz), 131.0, 129.7, 126.9 (d, $J_{C\text{-}F}$ = 6.3 Hz), 119.3, 92.0 (d, $J_{C\text{-}F}$ = 189.1 Hz), 61.1, 21.4, 14.5; ^{19}F NMR (377 MHz, $CDCl_3$) δ -173.75 (dd, $J_{H\text{-}F}$ = 49.3 Hz, $J_{C\text{-}F}$ = 6.3 Hz); EI-MS (*m/z*, relative intensity): 315 (M^+, 11), 192 (26), 164 (21), 149 (51), 123 (100), 91 (27), 77 (34); HRMS (EI) calcd. for $C_{18}H_{18}O_3NF$ $[M]^+$ 315.1265, found: 315.1262.

ethyl 4-((2-oxo-2-(p-tolyl)ethyl)amino)benzoate (4a)



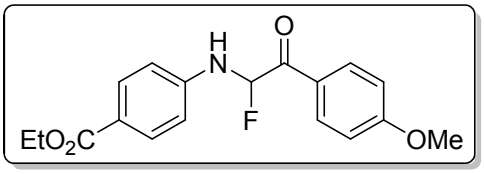
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.1 Hz, 2H), 7.50 (d, J = 8.3 Hz, 2H), 7.42 (s, 1H), 7.24 – 7.15 (m), 4.34 (q, J = 7.0 Hz, 2H), 3.71 (s, 2H), 2.36 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 166.2, 141.9, 137.7, 131.0, 130.8, 130.1, 129.5, 126.1, 118.9, 61.0, 44.6, 21.2, 14.4; EI-MS (*m/z*, relative intensity): 297 (M^+, 20), 252 (7), 192 (3), 165 (32), 132 (74), 105 (100), 91 (17), 77 (20); HRMS (EI) calcd. for $C_{18}H_{19}O_3N$ $[M]^+$ 297.1359, found: 297.1362.

ethyl 4-((1-fluoro-2-oxo-2-phenylethyl)amino)benzoate (3b)



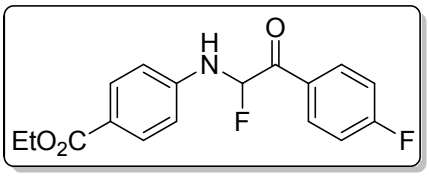
Pale yellow solid (68%, 41 mg, eluent: petroleum ether/ethyl acetate = 10/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 8.03 (d, J = 8.7 Hz, 2H), 7.68 (d, J = 8.7 Hz, 2H), 7.55 – 7.47 (m, 2H), 7.46 – 7.38 (m, 3H), 5.91 (d, $J_{H\text{-}F}$ = 48.4 Hz, 1H), 4.36 (q, J = 7.1 Hz, 2H), 1.39 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8 (d, $J_{C\text{-}F}$ = 21.1 Hz), 166.1, 140.8, 134.2 (d, $J_{C\text{-}F}$ = 19.3 Hz), 131.0, 129.9 (d, $J_{C\text{-}F}$ = 2.1 Hz), 129.0, 127.0, 126.7 (d, $J_{C\text{-}F}$ = 6.6 Hz), 119.4, 92.0 (d, $J_{C\text{-}F}$ = 189.8 Hz), 61.1, 14.4; ^{19}F NMR (377 MHz, $CDCl_3$) δ -176.02 (dd, $J_{H\text{-}F}$ = 48.4 Hz, $J_{C\text{-}F}$ = 6.3 Hz); EI-MS (*m/z*, relative intensity): 301 (M^+, 19), 256 (6), 192 (57), 164 (32), 149 (39), 109 (100), 91 (33), 77 (14); HRMS (EI) calcd. for $C_{17}H_{16}O_3NF$ $[M]^+$ 301.1109, found: 301.1107.

ethyl 4-((1-fluoro-2-(4-methoxyphenyl)-2-oxoethyl)amino)benzoate (3c)



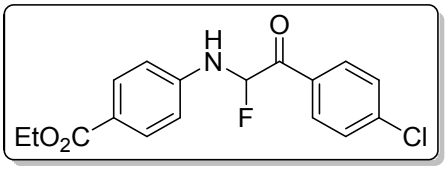
Pale yellow solid (44%, 29 mg, eluent: petroleum ether/ethyl acetate = 10/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, J = 5.6 Hz, 1H), 8.04 (d, J = 8.6 Hz, 2H), 7.69 (d, J = 8.6 Hz, 2H), 7.41 (d, J = 7.8 Hz, 2H), 6.94 (d, J = 8.4 Hz, 2H), 5.85 (d, $J_{H\text{-}F}$ = 48.7 Hz, 1H), 4.36 (q, J = 7.1 Hz, 2H), 3.81 (s, 3H), 1.39 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1 (d, $J_{C\text{-}F}$ = 21.7 Hz), 166.1, 161.0 (d, $J_{C\text{-}F}$ = 2.5 Hz), 140.8, 131.0, 128.8 (d, $J_{C\text{-}F}$ = 5.8 Hz), 127.0, 126.4 (d, $J_{C\text{-}F}$ = 19.7 Hz), 119.3, 114.5, 92.0 (d, $J_{C\text{-}F}$ = 188.5 Hz), 61.1, 55.5, 14.5; ^{19}F NMR (377 MHz, $CDCl_3$) δ -170.11 (dd, $J_{H\text{-}F}$ = 49.1 Hz, $J_{C\text{-}F}$ = 7.7 Hz); EI-MS (*m/z*, relative intensity): 331 (M^+, 3), 286 (1), 192 (4), 164 (5), 149 (5), 139 (100), 91 (18), 77 (16); HRMS (EI) calcd. for $C_{18}H_{18}O_4NF$ $[M]^+$ 331.1214, found: 331.1217.

ethyl 4-((1-fluoro-2-(4-fluorophenyl)-2-oxoethyl)amino)benzoate (3d)



Pale yellow solid (60%, 38 mg, eluent: petroleum ether/ethyl acetate = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, J = 4.9 Hz, 1H), 8.06 (d, J = 8.6 Hz, 2H), 7.71 (d, J = 8.6 Hz, 2H), 7.55 – 7.47 (m, 2H), 7.13 (t, J = 8.5 Hz, 2H), 5.91 (d, $J_{H\text{-}F}$ = 48.3 Hz, 1H), 4.39 (q, J = 7.1 Hz, 2H), 1.41 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6 (d, $J_{C\text{-}F}$ = 21.1 Hz), 166.1, 140.7, 131.0, 128.9, 128.9 (d, $J_{C\text{-}F}$ = 1.9 Hz), 128.8, 127.1, 119.4, 116.1 (d, $J_{C\text{-}F}$ = 22.0 Hz), 91.3 (d, J = 190.1 Hz), 61.1, 14.4; ^{19}F NMR (377 MHz, $CDCl_3$) δ -111.05 – -111.17 (m), -174.67 (d, $J_{H\text{-}F}$ = 48.3 Hz); EI-MS (*m/z*, relative intensity): 319 (M^+, 4), 274 (1), 192 (16), 164 (10), 149 (8), 139 (19), 91 (25), 77 (100); HRMS (EI) calcd. for $C_{17}H_{15}O_3NF_2$ $[M]^+$ 319.1015, found: 319.1012.

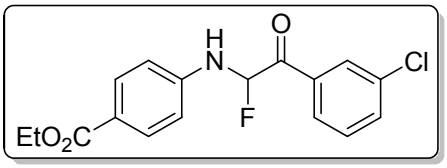
ethyl 4-((2-(4-chlorophenyl)-1-fluoro-2-oxoethyl)amino)benzoate (3e)



Pale yellow solid (65%, 43 mg, eluent: petroleum ether/ethyl acetate = 5/1); ^{1}H NMR

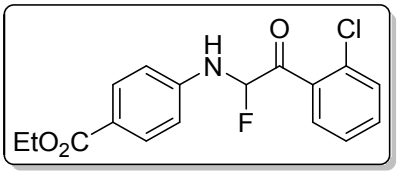
(400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 8.03 (d, J = 8.5 Hz, 2H), 7.67 (d, J = 8.5 Hz, 2H), 7.42 (dd, J = 23.6, 8.3 Hz, 4H), 5.88 (d, J = 48.2 Hz, 1H), 4.36 (q, J = 7.1 Hz, 2H), 1.38 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4 (d, $J_{C\text{-}F}$ = 20.7 Hz), 166.1, 140.6, 135.9 (d, $J_{C\text{-}F}$ = 2.5 Hz), 132.7 (d, $J_{C\text{-}F}$ = 19.7 Hz), 131.0, 129.2, 128.0 (d, $J_{C\text{-}F}$ = 6.8 Hz), 127.1, 119.4, 91.2 (d, $J_{C\text{-}F}$ = 190.8 Hz), 61.1, 14.4; ^{19}F NMR (377 MHz, $CDCl_3$) δ -177.43 (dd, $J_{H\text{-}F}$ = 49.0 Hz, $J_{C\text{-}F}$ = 6.4 Hz); EI-MS (*m/z*, relative intensity): 335 (M^+, 15), 242 (9), 192 (100), 164 (52), 149 (36), 143 (81), 91 (29), 76 (13); HRMS (EI) calcd. for $C_{17}H_{15}O_3NClF$ $[M]^+$ 335.0719, found: 335.0717.

ethyl 4-((2-(3-chlorophenyl)-1-fluoro-2-oxoethyl)amino)benzoate (3f)



Pale yellow solid (53%, 35 mg, eluent: petroleum ether/ethyl acetate = 10/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, J = 4.9 Hz, 1H), 8.04 (d, J = 8.4 Hz, 2H), 7.67 (d, J = 8.5 Hz, 2H), 7.51 (s, 1H), 7.44 – 7.32 (m, 3H), 5.88 (d, $J_{H\text{-}F}$ = 48.1 Hz, 1H), 4.36 (q, J = 7.1 Hz, 2H), 1.39 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 166.1, 140.6, 136.0 (d, $J_{C\text{-}F}$ = 19.7 Hz), 135.0, 131.0, 130.0 (d, $J_{C\text{-}F}$ = 1.3 Hz), 127.1, 126.5 (d, $J_{C\text{-}F}$ = 7.6 Hz), 124.7 (d, $J_{C\text{-}F}$ = 6.9 Hz), 119.4, 91.0 (d, $J_{C\text{-}F}$ = 191.8 Hz), 61.2, 14.5; ^{19}F NMR (377 MHz, $CDCl_3$) δ -179.05 (dd, $J_{H\text{-}F}$ = 48.4 Hz, $J_{C\text{-}F}$ = 7.0 Hz); EI-MS (*m/z*, relative intensity): 335 (M^+, 18), 242 (6), 192 (100), 164 (29), 149 (9), 143 (28), 91 (6), 76 (4); HRMS (EI) calcd. for $C_{17}H_{15}O_3NClF$ $[M]^+$ 335.0719, found: 335.0720.

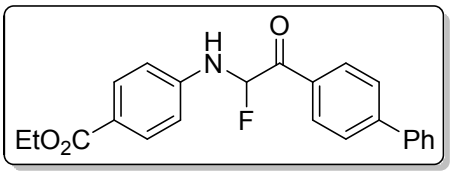
ethyl 4-((2-(2-chlorophenyl)-1-fluoro-2-oxoethyl)amino)benzoate (3g)



Pale yellow solid (56%, 37 mg, eluent: petroleum ether/ethyl acetate = 10/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, J = 5.1 Hz, 1H), 8.05 (d, J = 8.5 Hz, 2H), 7.70 (d, J = 8.5 Hz, 2H), 7.45 (t, J = 7.2 Hz, 2H), 7.40 – 7.28 (m, 2H), 6.29 (d, $J_{H\text{-}F}$ = 47.5 Hz, 1H), 4.37 (q, J = 7.1 Hz, 2H), 1.39 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 166.1, 140.7, 134.7 (d, $J_{C\text{-}F}$ = 4.1 Hz), 132.3 (d, $J_{C\text{-}F}$ =

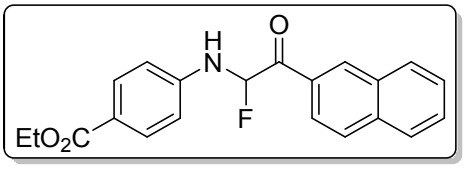
18.5 Hz), 131.5 (d, $J_{C\text{-}F}$ = 2.8 Hz), 131.0, 130.4, 129.7 (d, $J_{C\text{-}F}$ = 5.4 Hz), 127.5, 127.0, 119.3, 89.2 (d, $J_{C\text{-}F}$ = 189.5 Hz), 61.1, 14.5; ^{19}F NMR (377 MHz, $CDCl_3$) δ -174.06 (dd, $J_{H\text{-}F}$ = 47.9 Hz, $J_{C\text{-}F}$ = 7.2 Hz); EI-MS (*m/z*, relative intensity): 335 (M^+, 18), 242 (9), 192 (100), 164 (49), 149 (12), 143 (46), 91 (10), 76 (6); HRMS (EI) calcd. for $C_{17}H_{15}O_3NClF$ $[M]^+$ 335.0719, found: 335.0721.

ethyl 4-((2-([1,1'-biphenyl]-4-yl)-1-fluoro-2-oxoethyl)amino)benzoate (3h)



Pale yellow solid (58%, 44 mg, eluent: petroleum ether/ethyl acetate = 10/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, J = 5.7 Hz, 1H), 8.05 (d, J = 8.6 Hz, 2H), 7.72 (d, J = 8.6 Hz, 2H), 7.64 (d, J = 8.1 Hz, 2H), 7.58 (d, J = 8.5 Hz, 4H), 7.45 (t, J = 7.4 Hz, 2H), 7.37 (t, J = 7.3 Hz, 1H), 5.96 (d, $J_{H\text{-}F}$ = 48.4 Hz, 1H), 4.37 (q, J = 7.1 Hz, 2H), 1.39 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8 (d, $J_{C\text{-}F}$ = 21.2 Hz), 166.1, 142.9 (d, $J_{C\text{-}F}$ = 2.2 Hz), 140.8, 140.3, 133.1 (d, $J_{C\text{-}F}$ = 19.3 Hz), 131.0, 129.0, 127.9, 127.7, 127.3, 127.2 (d, $J_{C\text{-}F}$ = 6.4 Hz), 127.0, 119.3, 91.8 (d, $J_{C\text{-}F}$ = 189.9 Hz), 61.1, 14.4; ^{19}F NMR (377 MHz, $CDCl_3$) δ -175.73 (dd, $J_{H\text{-}F}$ = 48.7 Hz, $J_{C\text{-}F}$ = 7.4 Hz); EI-MS (*m/z*, relative intensity): 377 (M^+, 6), 284 (5), 192 (10), 185 (100), 165 (38), 119 (17), 91 (13), 76 (4); HRMS (EI) calcd. for $C_{23}H_{20}O_3NF$ $[M]^+$ 377.1422, found: 377.1424.

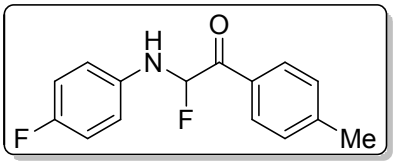
ethyl 4-((1-fluoro-2-(naphthalen-2-yl)-2-oxoethyl)amino)benzoate (3i)



Pale yellow solid (64%, 45 mg, eluent: petroleum ether/ethyl acetate = 10/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.06 – 7.96 (m, 3H), 7.91 – 7.82 (m, 3H), 7.70 (d, J = 8.6 Hz, 2H), 7.61 – 7.48 (m, 3H), 6.07 (d, $J_{H\text{-}F}$ = 48.3 Hz, 1H), 4.37 (q, J = 7.1 Hz, 2H), 1.39 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8 (d, $J_{C\text{-}F}$ = 21.1 Hz), 166.1, 140.8, 133.8, 133.0, 131.5 (d, $J_{C\text{-}F}$ = 19.1 Hz), 130.9, 129.0, 128.4, 127.9, 127.1, 126.9, 126.8, 126.8, 126.7, 123.4 (d, $J_{C\text{-}F}$ = 5.4 Hz), 119.4, 92.2 (d, $J_{C\text{-}F}$ = 190.0 Hz), 61.1, 14.4; ^{19}F NMR (377 MHz, $CDCl_3$) δ

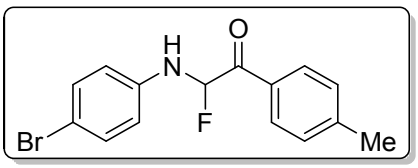
-175.76 (dd, $J_{H\text{-}F}$ = 49.1 Hz, $J_{C\text{-}F}$ = 6.0 Hz); EI-MS (*m/z*, relative intensity): 351 (M^+, 7), 258 (6), 192 (9), 168 (7), 159 (100), 119 (19), 91 (16), 77 (11); HRMS (EI) calcd. for $C_{21}H_{18}O_3NF$ $[M]^+$ 351.1265, found: 351.1267.

2-fluoro-2-((4-fluorophenyl)amino)-1-(p-tolyl)ethan-1-one (3j)



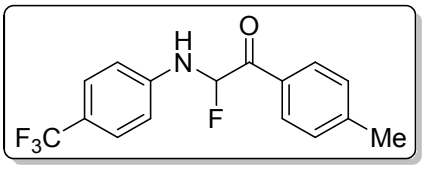
Pale yellow solid (63%, 33 mg, eluent: petroleum ether/ethyl acetate = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.62 – 7.50 (m, 2H), 7.38 (d, J = 7.3 Hz, 2H), 7.23 (d, J = 7.8 Hz, 2H), 7.04 (t, J = 8.6 Hz, 2H), 5.85 (d, $J_{H\text{-}F}$ = 48.6 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8 (d, $J_{C\text{-}F}$ = 21.1 Hz), 159.9 (d, $J_{C\text{-}F}$ = 244.4 Hz), 140.0 (d, $J_{C\text{-}F}$ = 2.7 Hz), 132.8 (d, $J_{C\text{-}F}$ = 2.7 Hz), 131.6 (d, $J_{C\text{-}F}$ = 19.3 Hz), 129.7, 126.9 (d, $J_{C\text{-}F}$ = 6.2 Hz), 122.0 (d, $J_{C\text{-}F}$ = 8.0 Hz), 115.9 (d, $J_{C\text{-}F}$ = 22.6 Hz), 92.0 (d, $J_{C\text{-}F}$ = 188.7 Hz), 21.4; ^{19}F NMR (377 MHz, $CDCl_3$) δ -116.90 –- 117.00 (m), -173.42 (dd, $J_{H\text{-}F}$ = 48.7 Hz, $J_{C\text{-}F}$ = 4.7 Hz); EI-MS (*m/z*, relative intensity): 261 (M^+, 16), 213 (20), 149 (8), 123 (100), 109 (43), 91 (13), 77 (35); HRMS (EI) calcd. for $C_{15}H_{13}ONF_2$ $[M]^+$ 261.0960, found: 261.0958.

2-((4-bromophenyl)amino)-2-fluoro-1-(p-tolyl)ethan-1-one (3k)



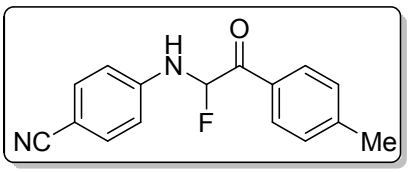
Pale yellow solid (56%, 36 mg, eluent: petroleum ether/ethyl acetate = 25/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.50 (d, J = 8.9 Hz, 2H), 7.45 (d, J = 8.9 Hz, 2H), 7.37 (d, J = 7.4 Hz, 2H), 7.22 (d, J = 7.8 Hz, 2H), 5.84 (d, $J_{H\text{-}F}$ = 48.6 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8 (d, $J_{C\text{-}F}$ = 21.3 Hz), 140.0 (d, $J_{C\text{-}F}$ = 2.6 Hz), 135.9, 132.2, 131.4 (d, $J_{C\text{-}F}$ = 19.2 Hz), 129.7, 126.9 (d, $J_{C\text{-}F}$ = 6.2 Hz), 121.7, 117.8, 92.0 (d, $J_{C\text{-}F}$ = 188.7 Hz), 21.4; ^{19}F NMR (377 MHz, $CDCl_3$) δ -173.55 (dd, $J_{H\text{-}F}$ = 49.1 Hz, $J_{C\text{-}F}$ = 6.8 Hz); EI-MS (*m/z*, relative intensity): 321 (M^+, 5), 275 (7), 149 (18), 123 (100), 109 (26), 91 (30), 77 (29); HRMS (EI) calcd. for $C_{15}H_{13}ONBrF$ $[M]^+$ 321.0159, found: 321.0161.

2-fluoro-1-(p-tolyl)-2-((4-(trifluoromethyl)phenyl)amino)ethan-1-one (3l)



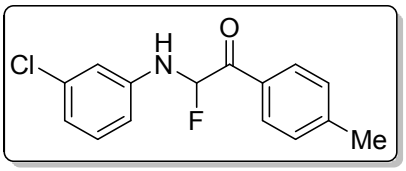
Pale yellow solid (73%, 45 mg, eluent: petroleum ether/ethyl acetate = 20/1); ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.70 (s, 1H), 7.92 (d, J = 8.4 Hz, 2H), 7.69 (d, J = 8.5 Hz, 2H), 7.45 (d, J = 7.5 Hz, 2H), 7.25 (d, J = 7.7 Hz, 2H), 6.05 (d, $J_{H\text{-}F}$ = 47.5 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.4 (d, $J_{C\text{-}F}$ = 24.8 Hz), 141.7, 139.2 (d, $J_{C\text{-}F}$ = 2.6 Hz), 132.3 (d, $J_{C\text{-}F}$ = 20.0 Hz), 129.3, 127.2 (d, $J_{C\text{-}F}$ = 5.3 Hz), 126.0 (q, $J_{C\text{-}F}$ = 3.5 Hz), 124.3 (q, $J_{C\text{-}F}$ = 271.5 Hz), 124.2 (q, $J_{C\text{-}F}$ = 32.1 Hz), 120.0, 90.5 (d, $J_{C\text{-}F}$ = 183.4 Hz), 20.8; ^{19}F NMR (377 MHz, DMSO-d_6) δ -60.54 (s, 3F), -172.37 (d, $J_{H\text{-}F}$ = 47.5 Hz, 1F); EI-MS (*m/z*, relative intensity): 311 (M^+, 8), 188 (10), 149 (37), 123 (100), 109 (27), 91 (11), 77 (24); HRMS (EI) calcd. for $C_{16}H_{13}ONF_4$ $[M]^+$ 311.0928, found: 311.0925.

4-((1-fluoro-2-oxo-2-(p-tolyl)ethyl)amino)benzonitrile (3m)



Pale yellow solid (67%, 36 mg, eluent: petroleum ether/ethyl acetate = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, J = 4.0 Hz, 1H), 7.74 (d, J = 8.7 Hz, 2H), 7.61 (d, J = 8.7 Hz, 2H), 7.36 (d, J = 7.5 Hz, 2H), 7.22 (d, J = 7.9 Hz, 2H), 5.86 (d, $J_{H\text{-}F}$ = 48.4 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3 (d, $J_{C\text{-}F}$ = 21.8 Hz), 140.9, 140.2 (d, $J_{C\text{-}F}$ = 2.5 Hz), 133.4, 131.1 (d, $J_{C\text{-}F}$ = 19.4 Hz), 129.7, 126.8 (d, $J_{C\text{-}F}$ = 6.2 Hz), 120.1, 118.7, 108.1, 91.9 (d, $J_{C\text{-}F}$ = 189.0 Hz), 21.4; ^{19}F NMR (377 MHz, $CDCl_3$) δ -173.99 (d, $J_{H\text{-}F}$ = 47.1 Hz); EI-MS (*m/z*, relative intensity): 268 (M^+, 9), 220 (3), 145 (8), 123 (100), 117 (13), 90 (14), 77 (24); HRMS (EI) calcd. for $C_{16}H_{13}ON_2F$ $[M]^+$ 268.1006, found: 268.1005.

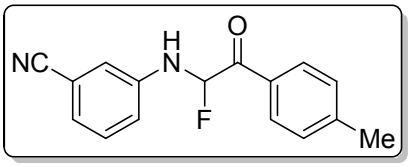
2-((3-chlorophenyl)amino)-2-fluoro-1-(p-tolyl)ethan-1-one (3n)



Pale yellow solid (76%, 42 mg, eluent: petroleum ether/ethyl acetate = 20/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.73 (s, 1H), 7.47 – 7.34 (m,

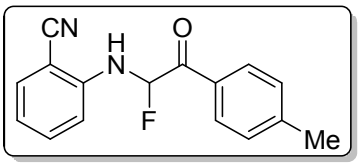
3H), 7.30 – 7.20 (m, 3H), 7.14 (d, J = 8.0 Hz, 1H), 5.85 (d, $J_{H\text{-}F}$ = 48.6 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9 (d, $J_{C\text{-}F}$ = 21.4 Hz), 140.0 (d, $J_{C\text{-}F}$ = 2.5 Hz), 137.9, 134.9, 131.4(d, $J_{C\text{-}F}$ = 19.3 Hz), 130.2, 129.6, 126.9 (d, $J_{C\text{-}F}$ = 6.1 Hz), 125.2, 120.3, 118.1, 92.0 (d, $J_{C\text{-}F}$ = 188.8 Hz), 21.4; ^{19}F NMR (377 MHz, $CDCl_3$) δ -173.64 (dd, $J_{H\text{-}F}$ = 49.3 Hz, $J_{C\text{-}F}$ = 7.2 Hz); EI-MS (*m/z*, relative intensity): 277 (M^+, 12), 222 (1), 154 (15), 123 (100), 109 (35), 91 (12), 77 (31); HRMS (EI) calcd. for $C_{15}H_{13}ONClF$ $[M]^+$ 277.0664, found: 277.0662.

3-((1-fluoro-2-oxo-2-(p-tolyl)ethyl)amino)benzonitrile (3o)



Pale yellow solid (62%, 33 mg, eluent: petroleum ether/ethyl acetate = 10/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, J = 4.2 Hz, 1H), 8.02 (s, 1H), 7.83 – 7.74 (m, 1H), 7.46 – 7.41 (m, 2H), 7.37 (d, J = 7.8 Hz, 2H), 7.23 (d, J = 7.7 Hz, 2H), 5.87 (d, $J_{H\text{-}F}$ = 48.4 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3 (d, $J_{C\text{-}F}$ = 21.8 Hz), 140.1 (d, $J_{C\text{-}F}$ = 2.6 Hz), 137.7, 131.1 (d, $J_{C\text{-}F}$ = 19.4 Hz), 130.1, 129.7, 128.5, 126.8 (d, $J_{C\text{-}F}$ = 6.1 Hz), 124.3, 123.3, 118.4, 113.3, 91.9 (d, $J_{C\text{-}F}$ = 188.9 Hz), 21.4; ^{19}F NMR (377 MHz, $CDCl_3$) δ -174.21 (dd, $J_{H\text{-}F}$ = 49.1 Hz, $J_{C\text{-}F}$ = 7.2 Hz); EI-MS (*m/z*, relative intensity): 268 (M^+, 9), 220 (2), 145 (7), 123 (100), 117 (11), 90 (10), 77 (22); HRMS (EI) calcd. for $C_{16}H_{13}ON_2F$ $[M]^+$ 268.1006, found: 268.1004.

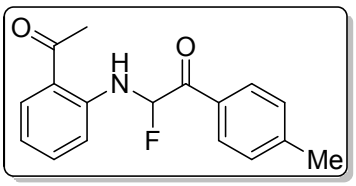
2-((1-fluoro-2-oxo-2-(p-tolyl)ethyl)amino)benzonitrile (3p)



Pale yellow solid (60%, 32 mg, eluent: petroleum ether/ethyl acetate = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 8.36 (d, J = 8.4 Hz, 1H), 7.64 – 7.52 (m, 2H), 7.38 (d, J = 7.7 Hz, 2H), 7.25 – 7.15 (m, 3H), 5.87 (d, $J_{H\text{-}F}$ = 48.1 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4 (d, $J_{C\text{-}F}$ = 22.1 Hz), 140.1 (d, $J_{C\text{-}F}$ = 2.3 Hz), 139.3, 134.3, 132.5, 131.1 (d, $J_{C\text{-}F}$ = 19.7 Hz), 129.7, 126.7 (d, $J_{C\text{-}F}$ = 6.4 Hz), 125.1, 121.5, 115.9, 103.1, 91.9 (d, $J_{C\text{-}F}$ = 189.7 Hz), 21.4; ^{19}F NMR (377 MHz, $CDCl_3$) δ -175.33 (dd, $J_{H\text{-}F}$ = 48.7 Hz, $J_{C\text{-}F}$ = 8.4 Hz); EI-MS (*m/z*, relative intensity):

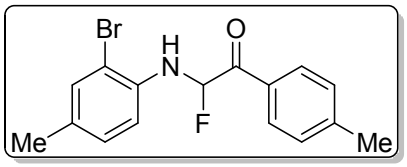
268 (M^+, 9), 220 (1), 145 (11), 123 (100), 117 (10), 90 (15), 77 (22); HRMS (EI) calcd. for $C_{16}H_{13}ON_2F$ $[M]^+$ 268.1006, found: 268.1008.

2-((2-acetylphenyl)amino)-2-fluoro-1-(p-tolyl)ethan-1-one (3q)



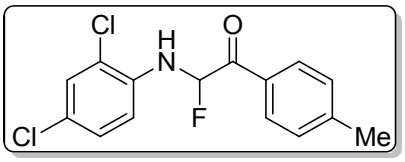
Pale yellow solid (59%, 34 mg, eluent: petroleum ether/ethyl acetate = 20/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.61 (s, 1H), 8.75 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 7.9 Hz, 1H), 7.55 (t, J = 7.8 Hz, 1H), 7.44 (d, J = 7.7 Hz, 2H), 7.25 – 7.14 (m, 3H), 5.84 (d, $J_{H\text{-}F}$ = 48.1 Hz, 1H), 2.69 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.7, 168.4 (d, $J_{C\text{-}F}$ = 22.0 Hz), 139.9, 139.5 (d, $J_{C\text{-}F}$ = 2.2 Hz), 135.2, 132.1 (d, $J_{C\text{-}F}$ = 20.2 Hz), 131.8, 129.5, 126.7 (d, $J_{C\text{-}F}$ = 6.4 Hz), 123.4, 122.6, 121.0, 91.9 (d, $J_{C\text{-}F}$ = 191.0 Hz), 28.6, 21.4; ^{19}F NMR (377 MHz, $CDCl_3$) δ -176.91 (d, $J_{H\text{-}F}$ = 48.2 Hz); EI-MS (*m/z*, relative intensity): 285 (M^+, 2), 222 (2), 162 (100), 144 (56), 116 (46), 91 (9), 77 (19); HRMS (EI) calcd. for $C_{17}H_{16}O_2NF$ $[M]^+$ 285.1160, found: 285.1157.

2-((2-bromo-4-methylphenyl)amino)-2-fluoro-1-(p-tolyl)ethanone (3r)



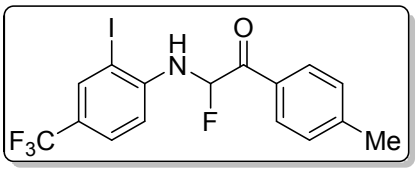
Pale yellow solid (64%, 43 mg, eluent: petroleum ether/ethyl acetate = 100/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 8.23 (s, 1H), 7.48 – 7.40 (m, 3H), 7.27 (d, J = 7.7 Hz, 2H), 6.87 (d, J = 8.1 Hz, 1H), 5.90 (d, $J_{H\text{-}F}$ = 48.4 Hz, 1H), 2.40 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9 (d, $J_{C\text{-}F}$ = 21.4 Hz), 139.9 (d, $J_{C\text{-}F}$ = 2.4 Hz), 138.9, 134.4, 132.0, 131.6 (d, $J_{C\text{-}F}$ = 19.5 Hz), 129.6, 126.9, 126.8, 122.5, 110.7, 92.1 (d, $J_{C\text{-}F}$ = 189.6 Hz), 21.4, 21.4; ^{19}F NMR (377 MHz, $CDCl_3$) δ -174.39 (dd, $J_{H\text{-}F}$ = 49.1 Hz, $J_{C\text{-}F}$ = 7.4 Hz); EI-MS (*m/z*, relative intensity): 335 (M^+, 7), 256 (40), 236 (40), 184 (21), 123 (100), 109 (31), 90 (12), 77 (59); HRMS (EI) calcd. for $C_{16}H_{15}ONBrF$ $[M]^+$ 335.0316, found: 335.0318.

2-((2,4-dichlorophenyl)amino)-2-fluoro-1-(p-tolyl)ethan-1-one (3s)



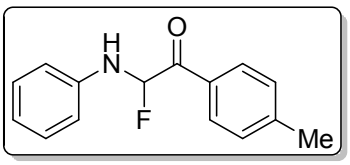
Pale yellow solid (61%, 38 mg, eluent: petroleum ether/ethyl acetate = 20/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (s, 1H), 8.38 (d, J = 8.7 Hz, 1H), 7.50 – 7.38 (m, 3H), 7.27 (d, J = 6.1 Hz, 3H), 5.91 (d, $J_{H\text{-}F}$ = 48.3 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9 (d, $J_{C\text{-}F}$ = 21.6 Hz), 140.1 (d, $J_{C\text{-}F}$ = 2.5 Hz), 132.5, 131.3 (d, $J_{C\text{-}F}$ = 19.5 Hz), 130.1, 129.7, 129.0, 128.1, 126.8 (d, $J_{C\text{-}F}$ = 6.2 Hz), 124.1, 122.4, 92.1 (d, $J_{C\text{-}F}$ = 189.4 Hz), 21.4; ^{19}F NMR (377 MHz, $CDCl_3$) δ -174.55 (dd, $J_{H\text{-}F}$ = 48.9 Hz, $J_{C\text{-}F}$ = 7.8 Hz); EI-MS (*m/z*, relative intensity): 311 (M^+, 8), 256 (1), 221 (2), 160 (14), 123 (100), 103 (22), 91 (7), 77 (25); HRMS (EI) calcd. for $C_{15}H_{12}ONCl_2F$ $[M]^+$ 311.0274, found: 311.0273.

2-fluoro-2-((2-iodo-4-(trifluoromethyl)phenyl)amino)-1-(p-tolyl)ethan-1-one (3t)



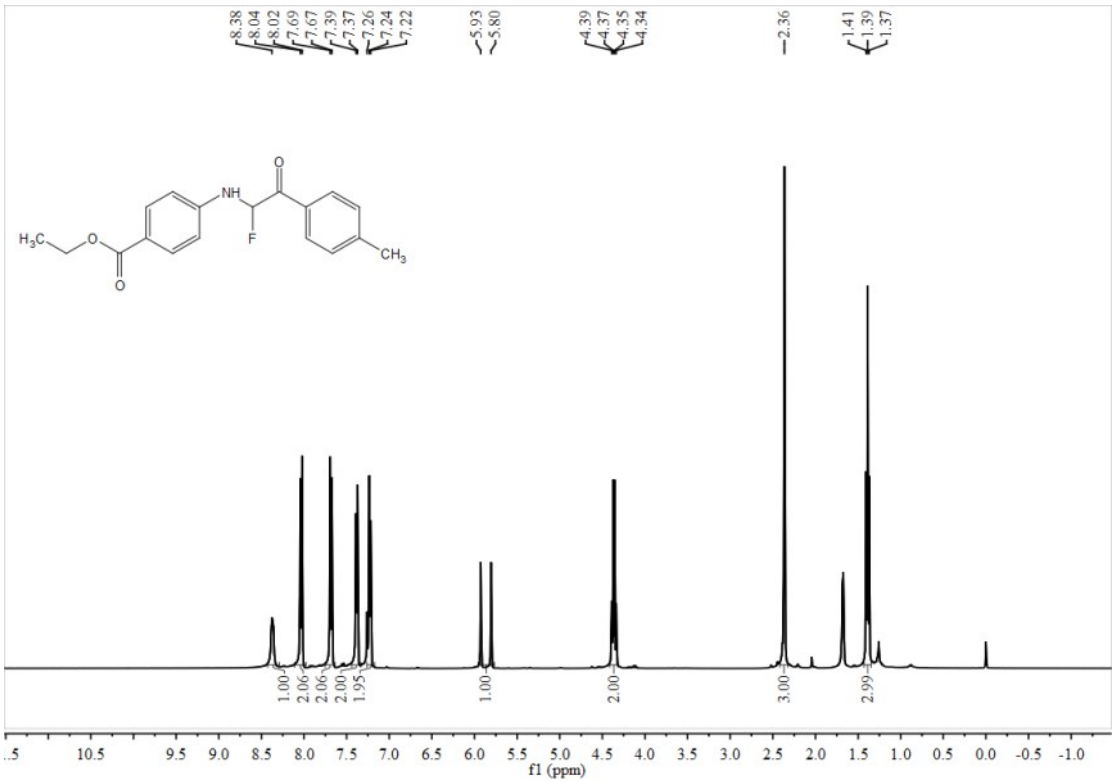
Pale yellow solid (69%, 60 mg, eluent: petroleum ether/ethyl acetate = 200/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, J = 5.2 Hz, 1H), 8.45 (d, J = 8.6 Hz, 1H), 8.06 (s, 1H), 7.61 (d, J = 8.6 Hz, 1H), 7.42 (d, J = 7.7 Hz, 2H), 7.25 (d, J = 7.5 Hz, 2H), 5.91 (d, $J_{H\text{-}F}$ = 48.2 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3 (d, $J_{C\text{-}F}$ = 21.9 Hz), 140.4, 140.2 (d, $J_{C\text{-}F}$ = 2.6 Hz), 136.0 (q, $J_{C\text{-}F}$ = 3.8 Hz), 131.1 (d, $J_{C\text{-}F}$ = 19.6 Hz), 129.8, 128.2 (q, $J_{C\text{-}F}$ = 33.3 Hz), 126.8 (d, $J_{C\text{-}F}$ = 6.2 Hz), 126.7 (q, $J_{C\text{-}F}$ =3.2 Hz), 122.9 (q, $J_{C\text{-}F}$ = 272.4 Hz), 121.0, 92.1 (d, $J_{C\text{-}F}$ = 189.7 Hz), 89.0, 21.4; ^{19}F NMR (377 MHz, DMSO-d_6) δ -62.33 (s, 3F), -174.63 (dd, $J_{H\text{-}F}$ = 48.8 Hz, $J_{C\text{-}F}$ = 8.1 Hz, 1F); EI-MS (*m/z*, relative intensity): 437 (M^+, 3), 370 (2), 187 (16), 144 (5), 123 (100), 103 (16), 91 (7), 77 (18); HRMS (EI) calcd. for $C_{16}H_{12}ONFI$ $[M]^+$ 436.9894, found: 436.9890.

2-fluoro-2-(phenylamino)-1-(p-tolyl)ethan-1-one (3u)

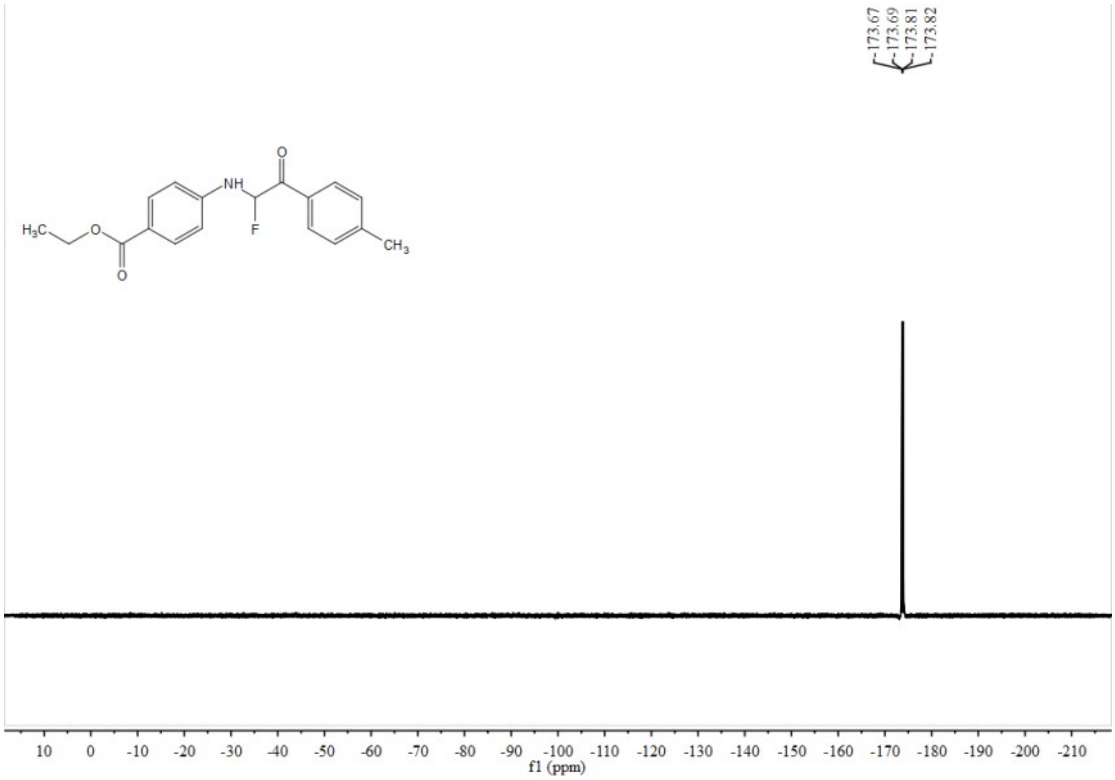


Pale yellow solid (41%, 20 mg, eluent: petroleum ether/ethyl acetate = 20/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.60 (d, J = 7.9 Hz, 2H), 7.43 – 7.32 (m,

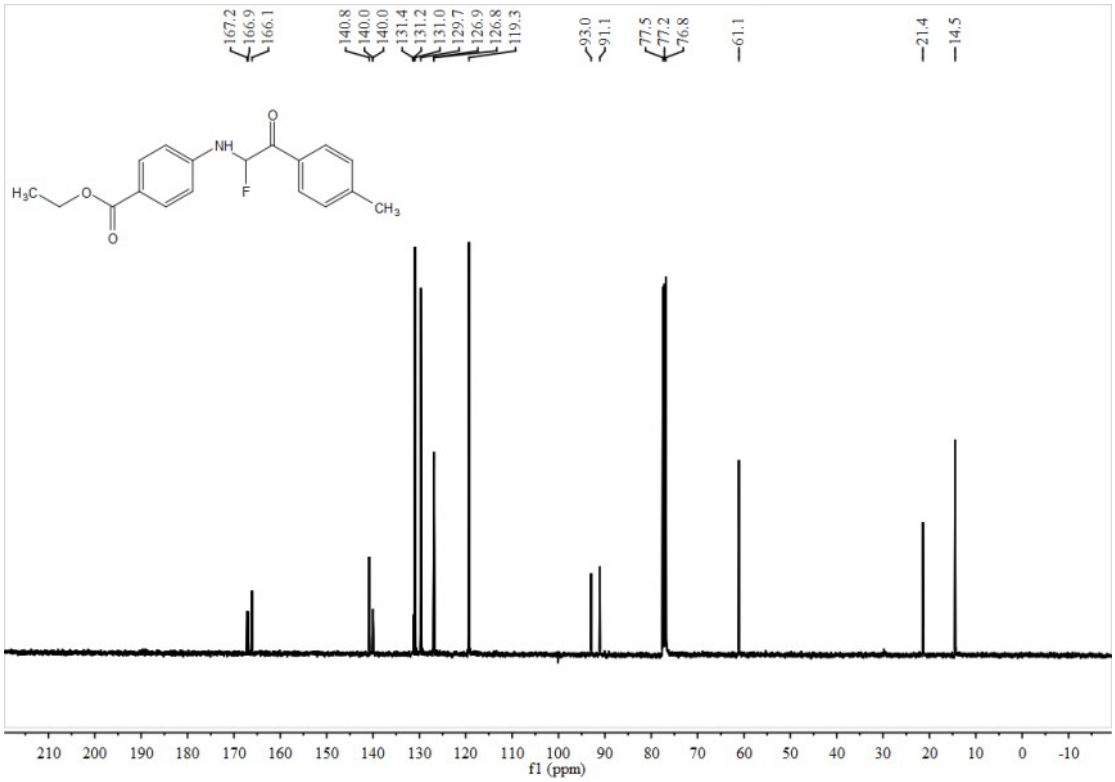
4H), 7.23 (d, J = 7.8 Hz, 2H), 7.16 (t, J = 7.4 Hz, 1H), 5.86 (d, $J_{H\text{-}F}$ = 48.7 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8 (d, $J_{C\text{-}F}$ = 21.0 Hz), 139.9 (d, $J_{C\text{-}F}$ = 2.7 Hz), 136.8, 131.7 (d, $J_{C\text{-}F}$ = 19.3 Hz), 129.6, 129.3, 127.0 (d, $J_{C\text{-}F}$ = 6.2 Hz), 125.2, 120.2, 92.1 (d, $J_{C\text{-}F}$ = 188.8 Hz), 21.4; ^{19}F NMR (377 MHz, $CDCl_3$) δ -172.97 (dd, $J_{H\text{-}F}$ = 48.6 Hz, $J_{C\text{-}F}$ = 5.7 Hz); EI-MS (*m/z*, relative intensity): 243 (M^+, 25), 195 (7), 149 (44), 123 (100), 109 (49), 92 (52), 77 (93); HRMS (EI) calcd. for $C_{15}H_{14}ONF$ $[M]^+$ 243.1054, found: 243.1056.



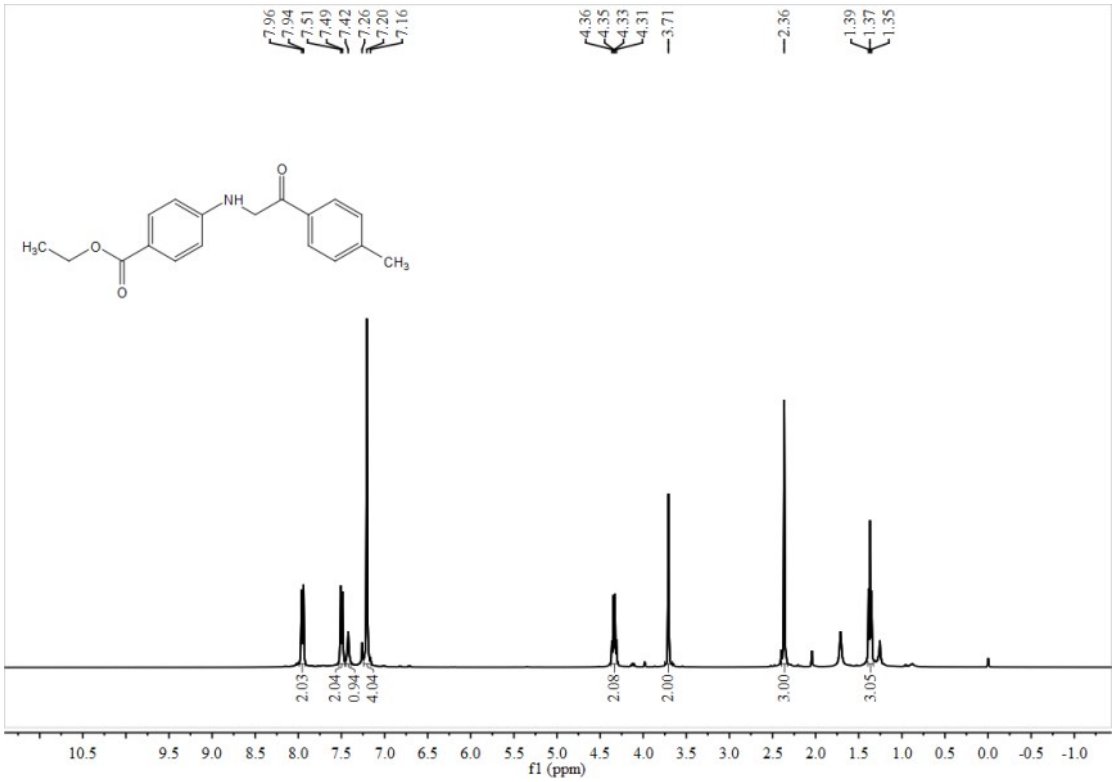
^{1}H NMR of **3a**



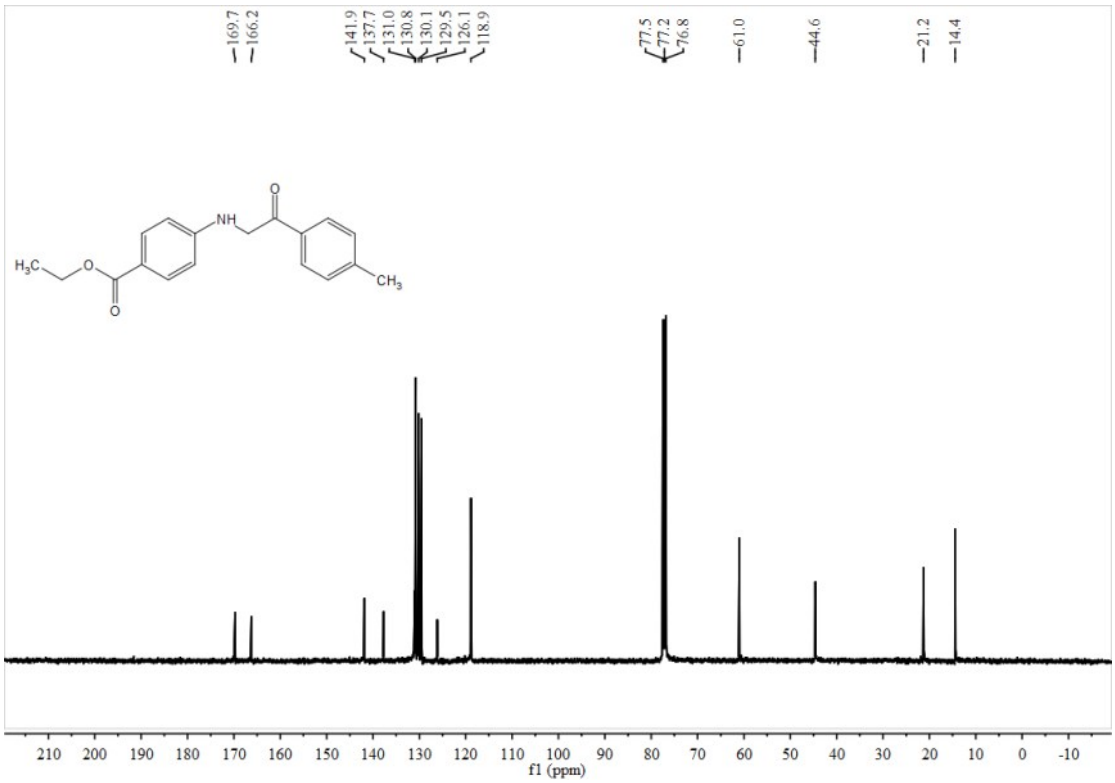
^{19}F NMR of **3a**



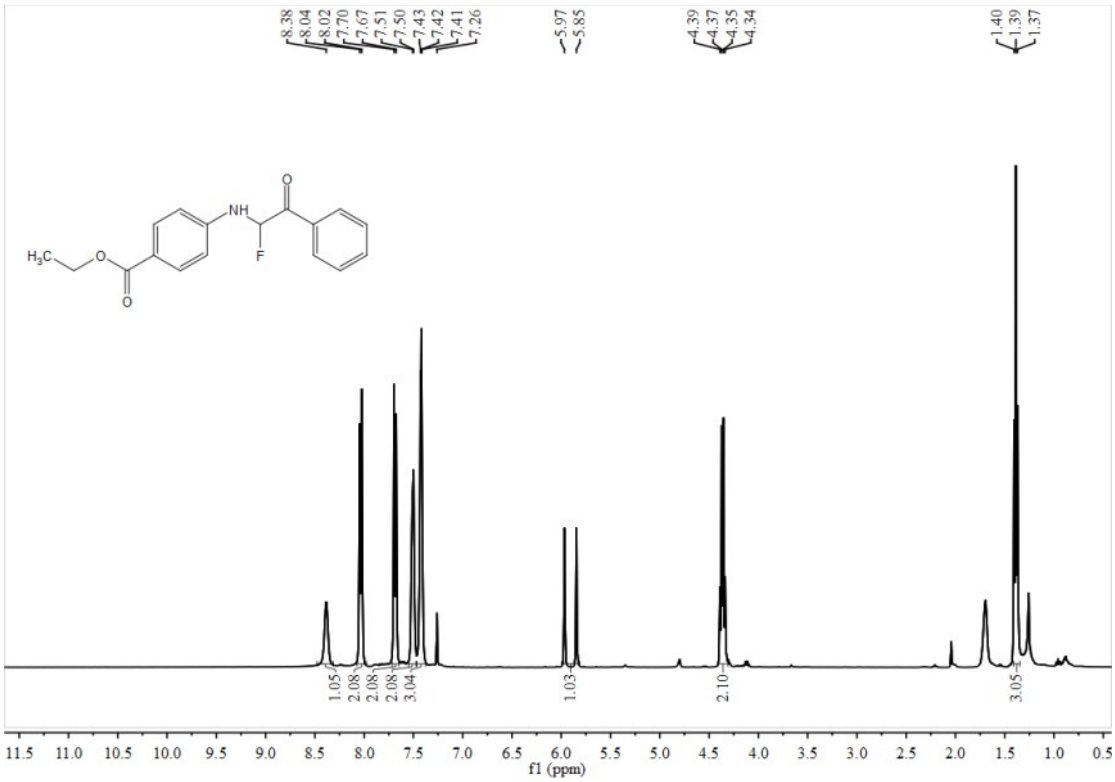
^{13}C NMR of **3a**



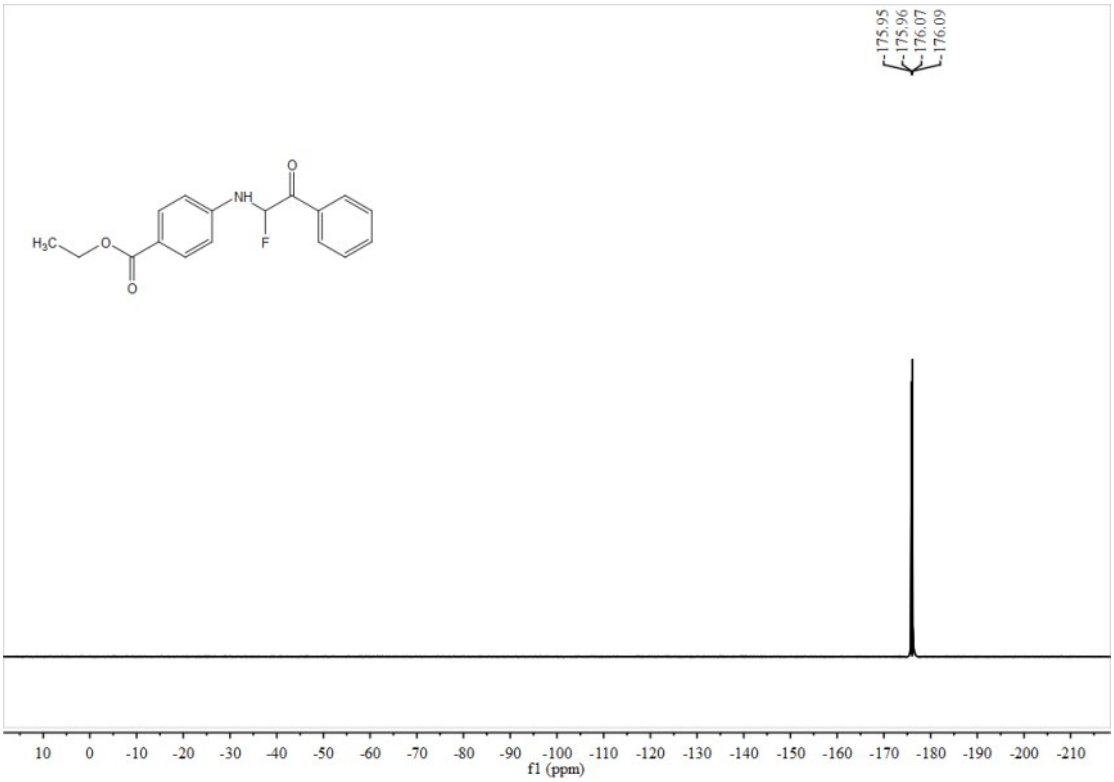
^{1}H NMR of **4a**



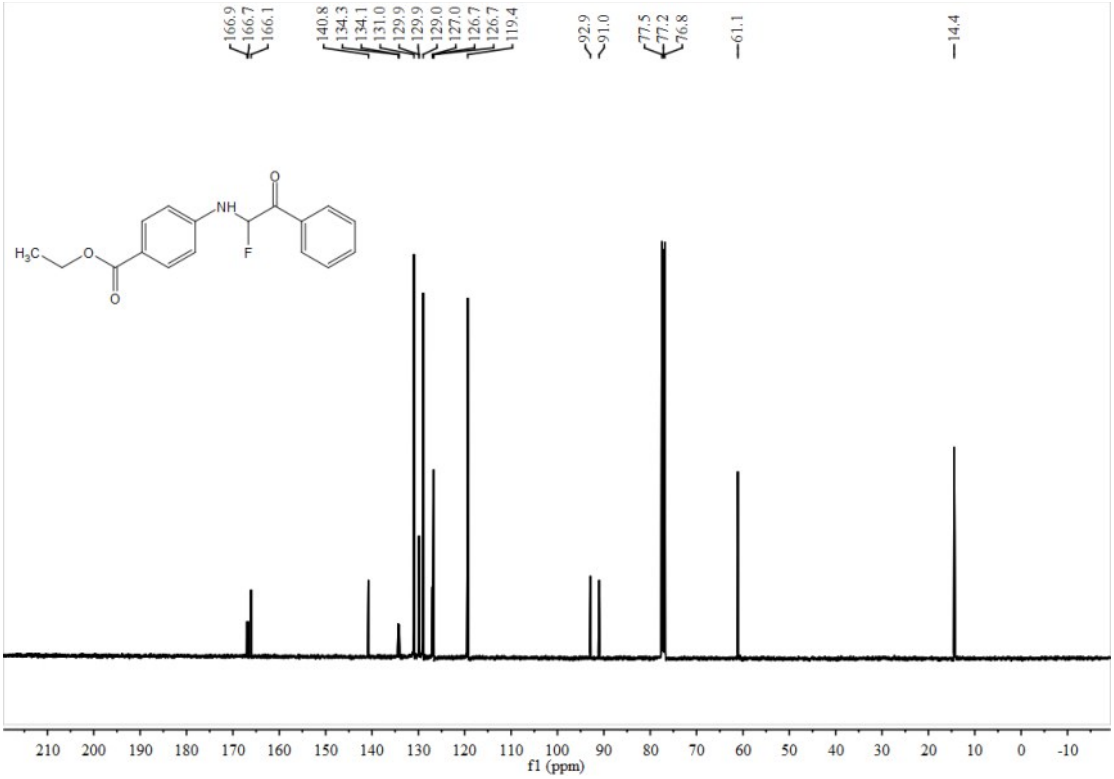
^{13}C NMR of **4a**



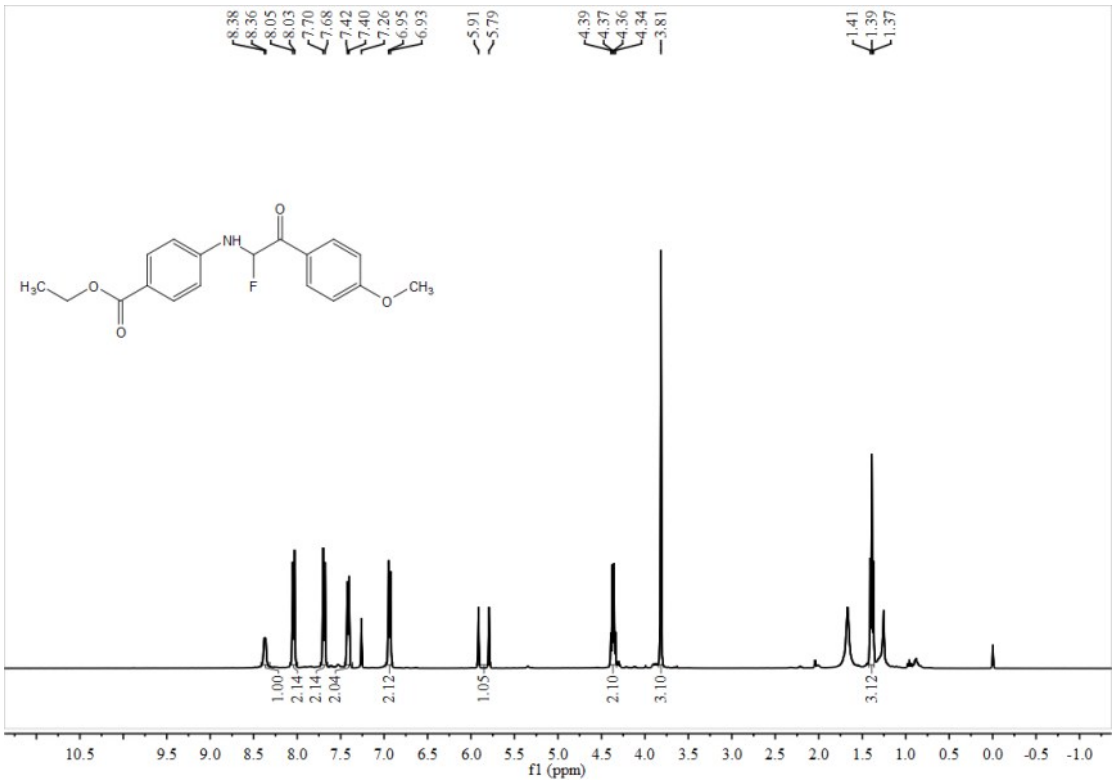
^{1}H NMR of **3b**



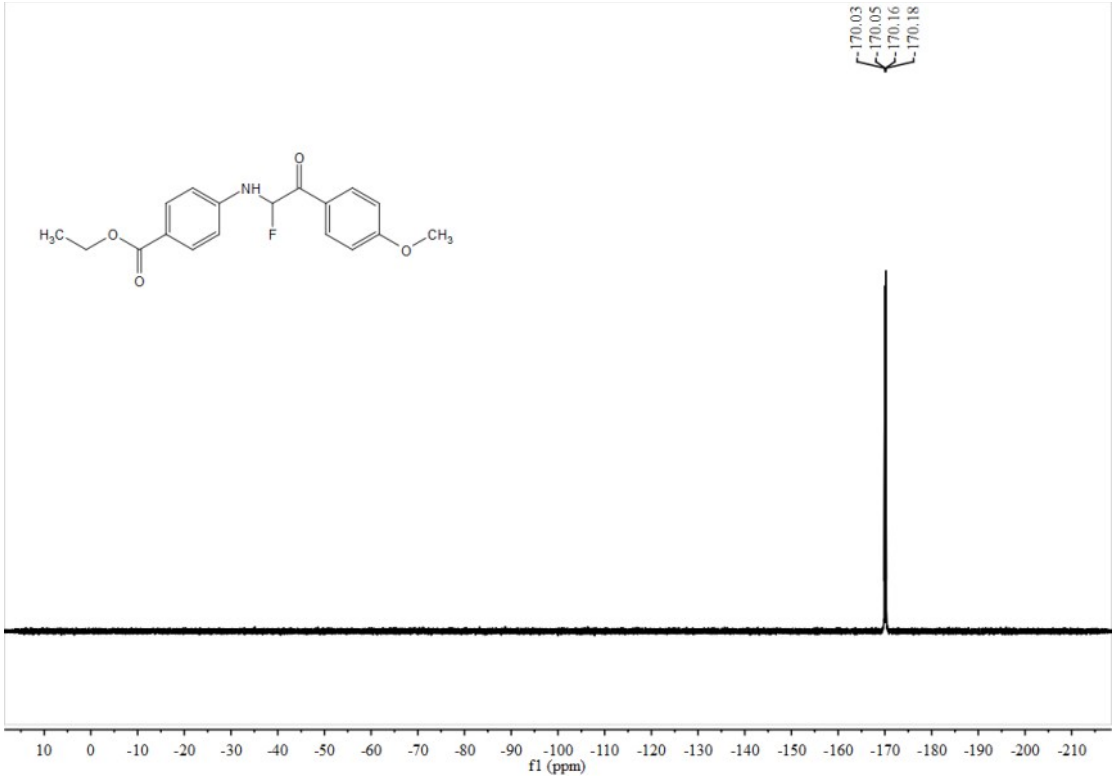
^{19}F NMR of **3b**



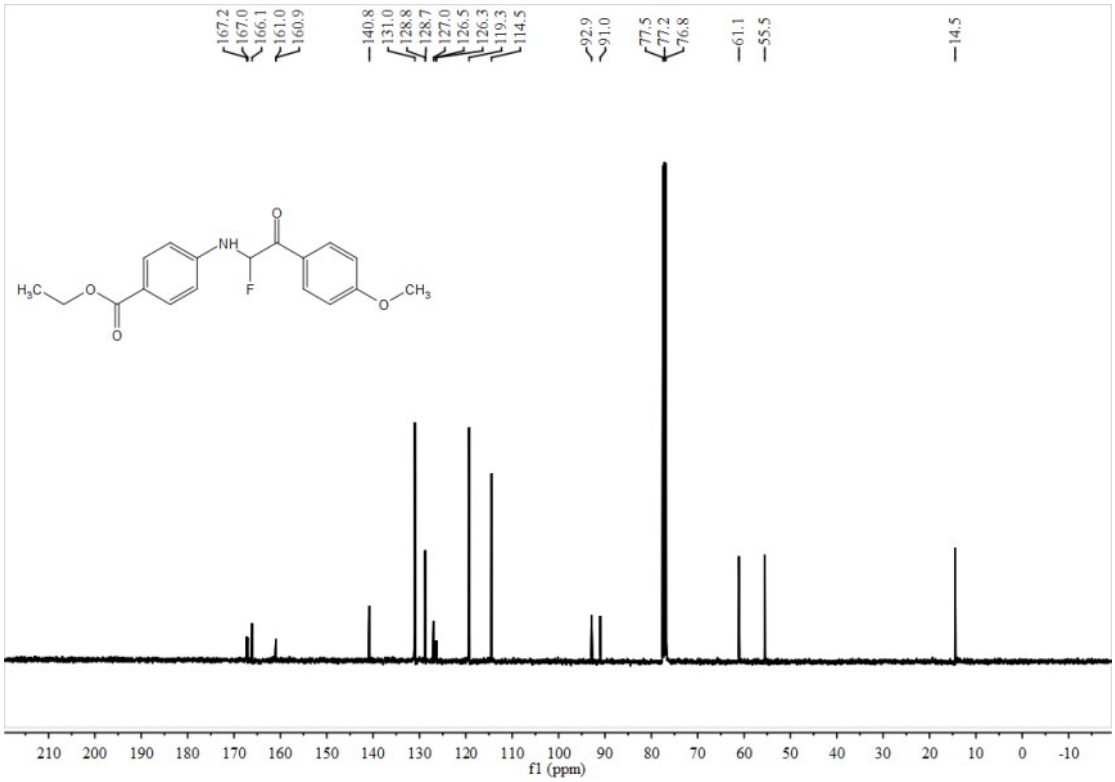
^{13}C NMR of **3b**



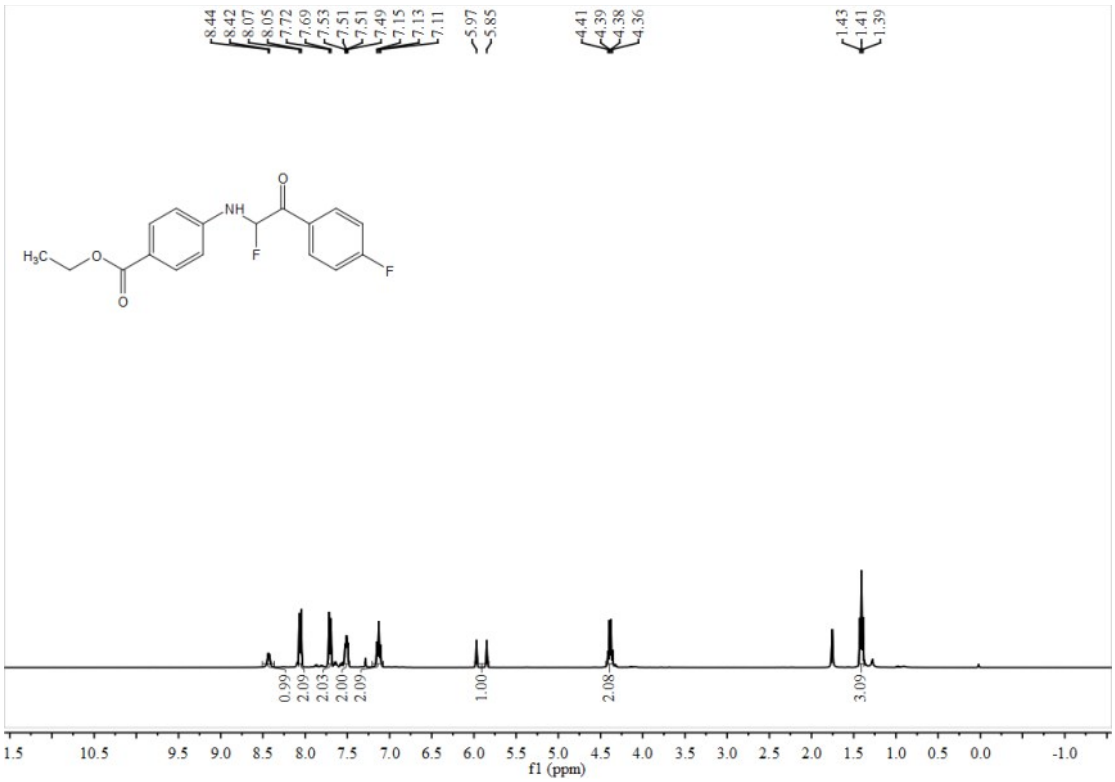
^{1}H NMR of **3c**



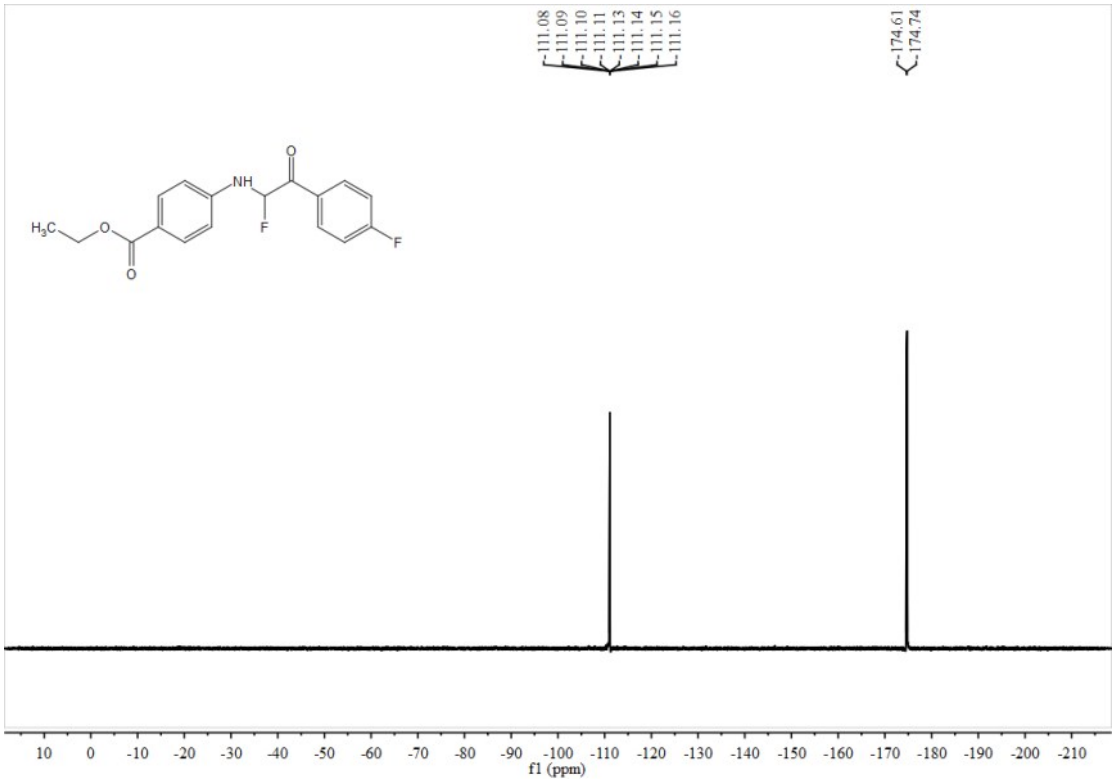
^{19}F NMR of **3c**



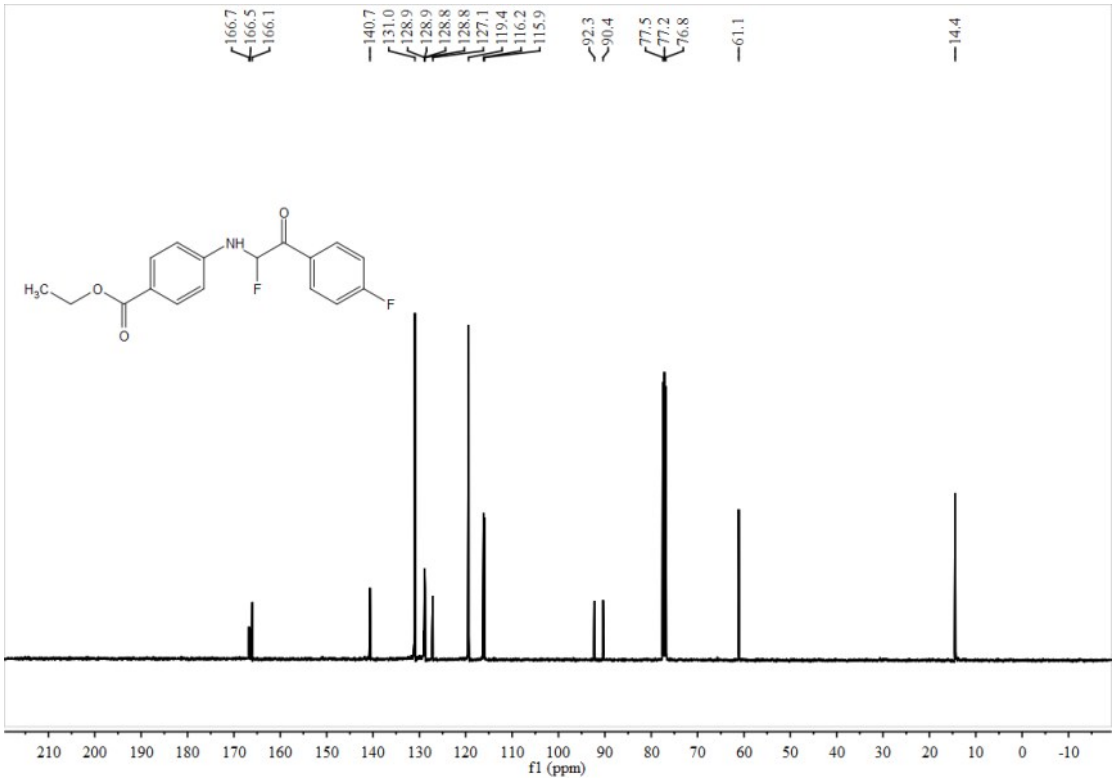
^{13}C NMR of **3c**



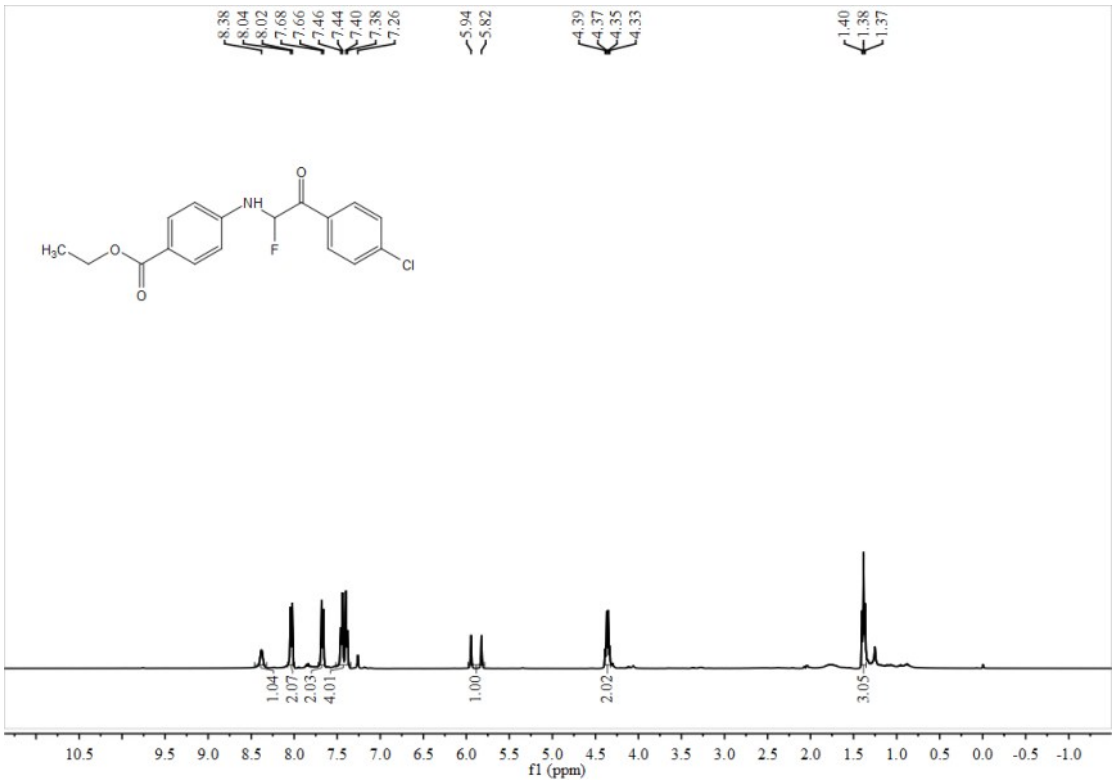
^{1}H NMR of **3d**



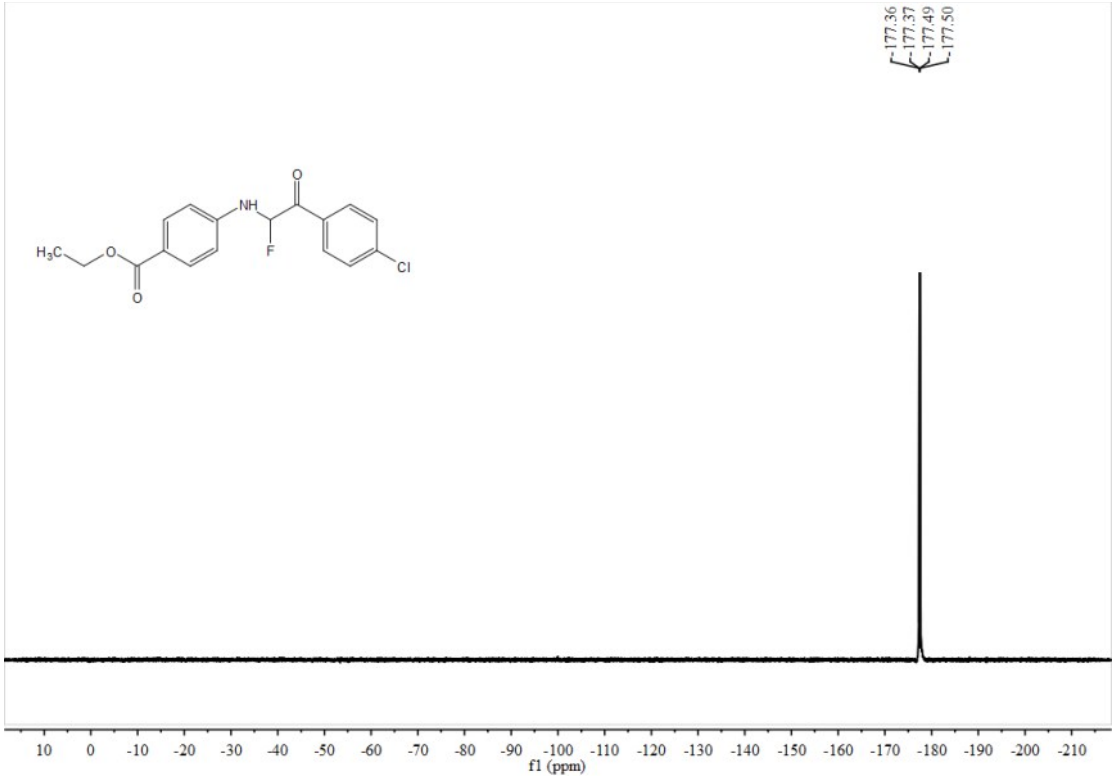
^{19}F NMR of **3d**



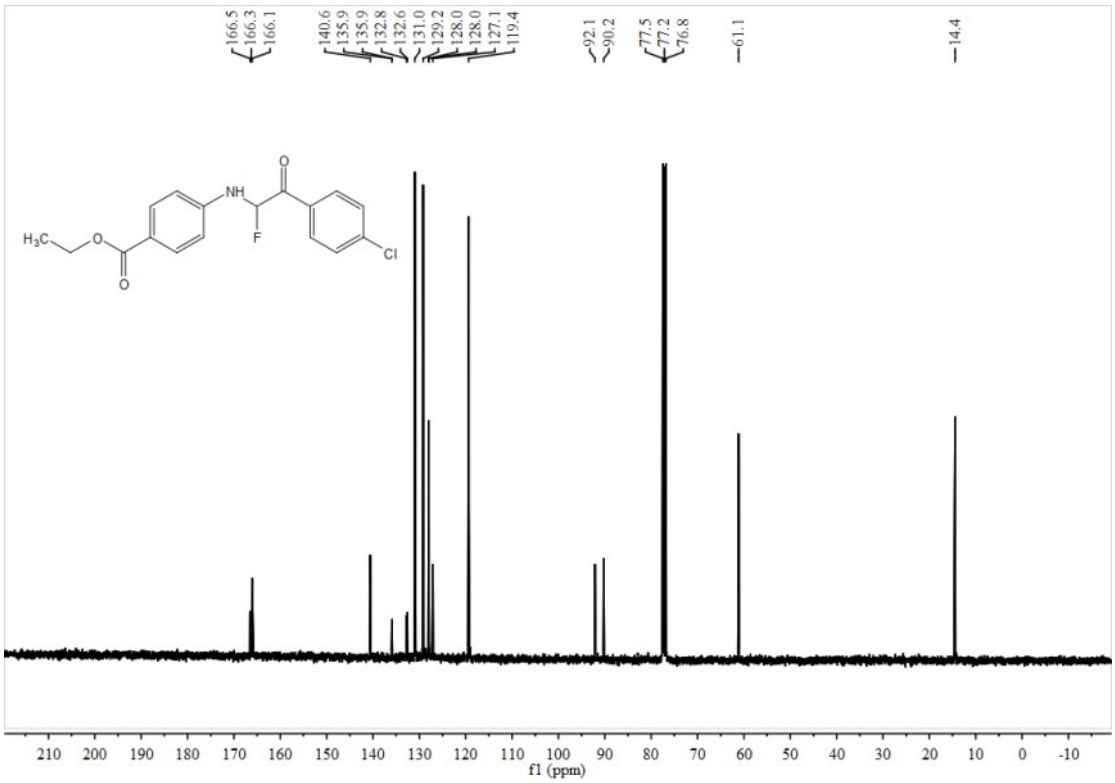
^{13}C NMR of **3d**



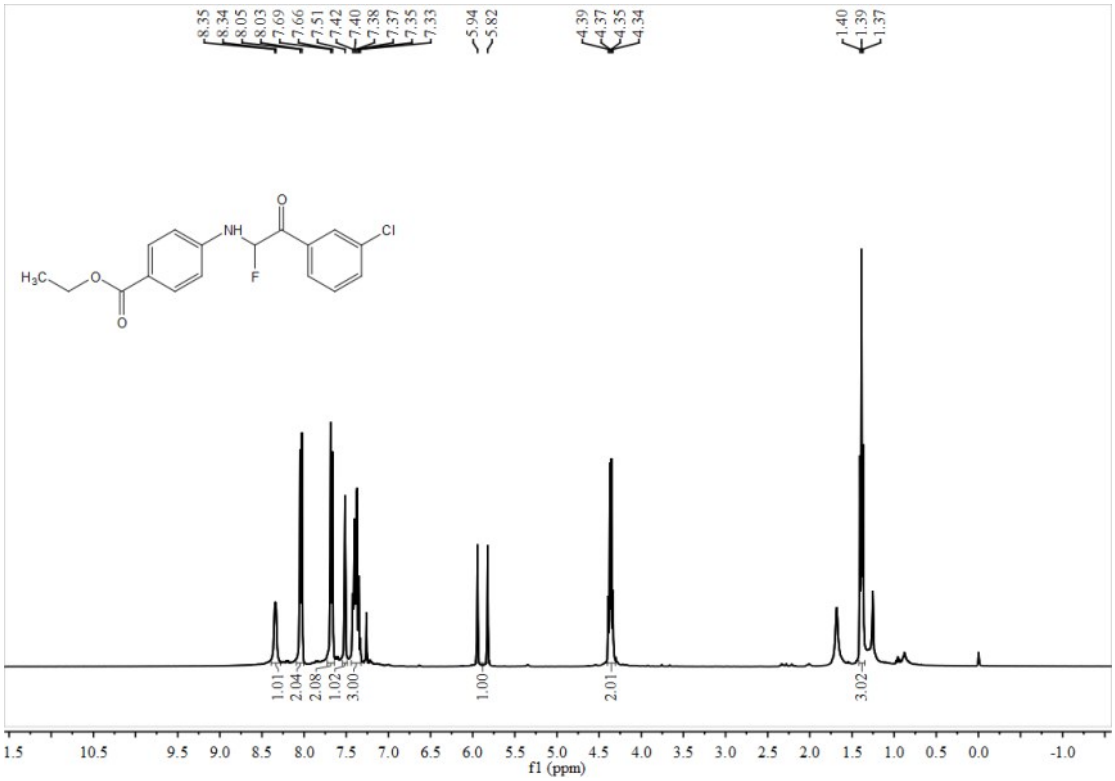
^{1}H NMR of **3e**



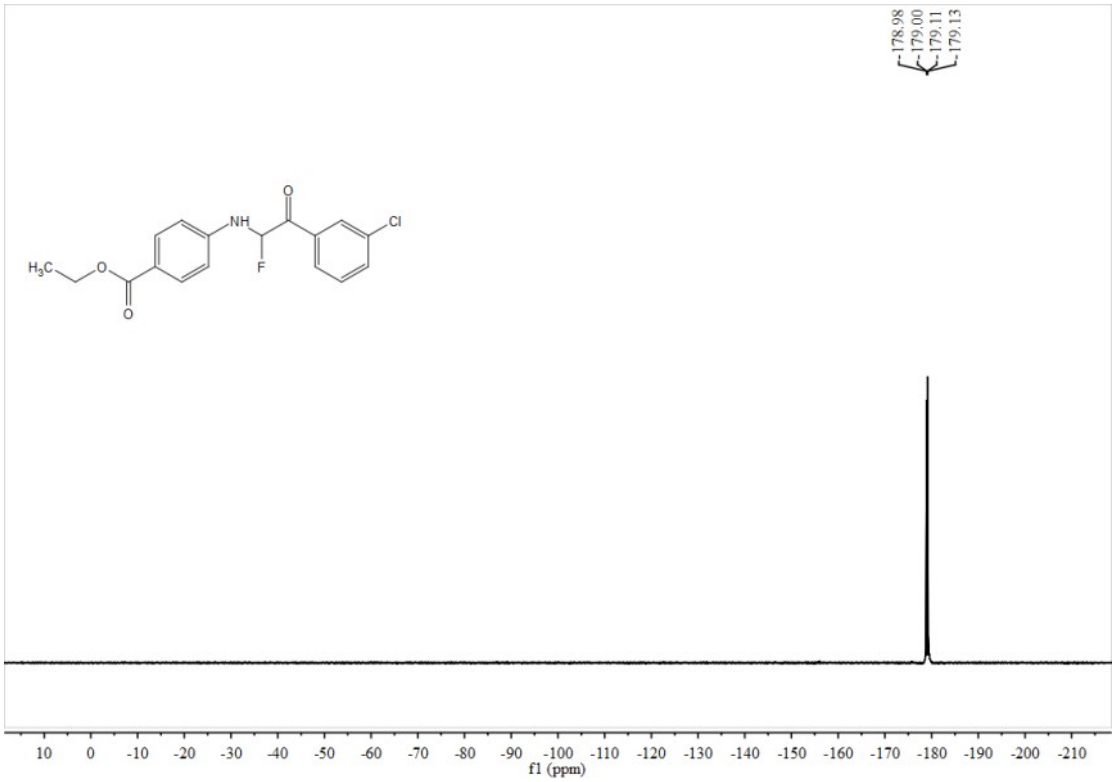
^{19}F NMR of **3e**



^{13}C NMR of **3e**



^{1}H NMR of **3f**



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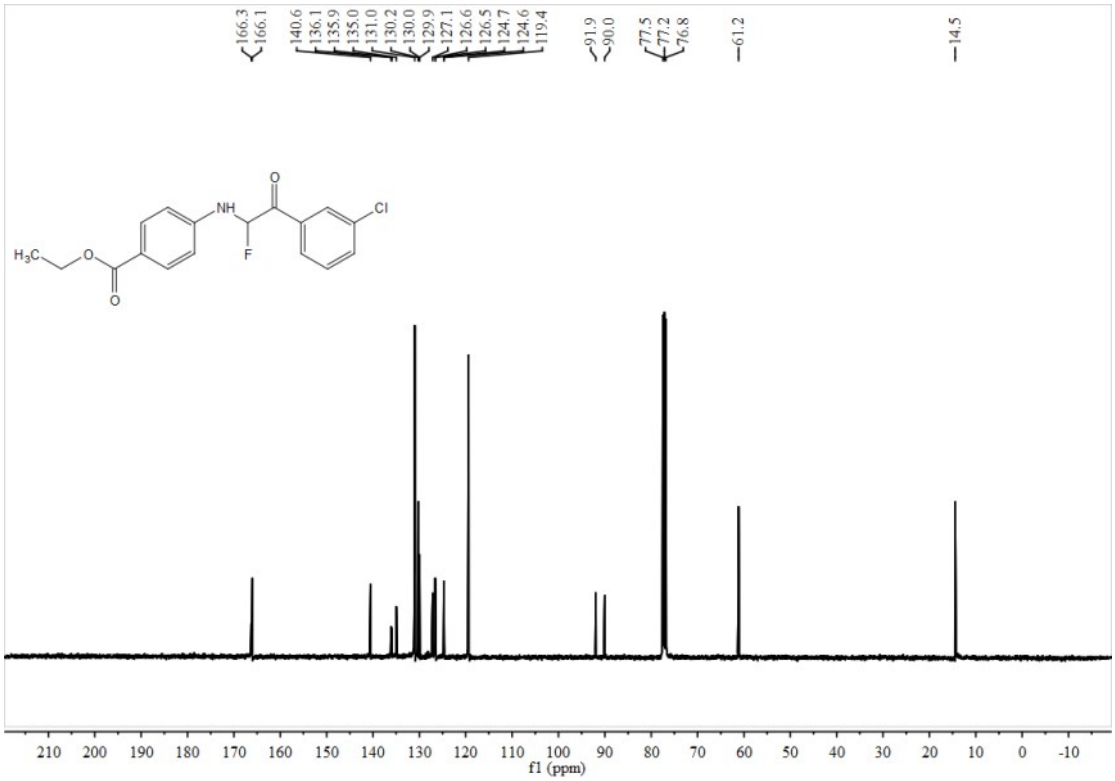

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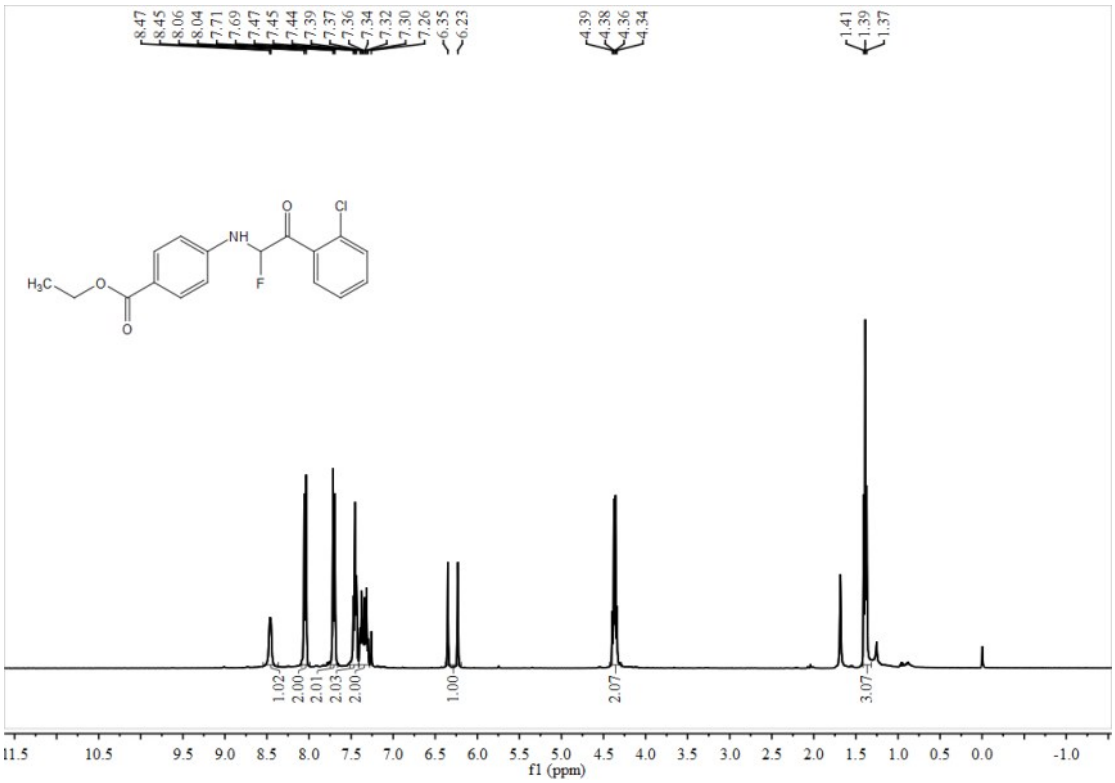
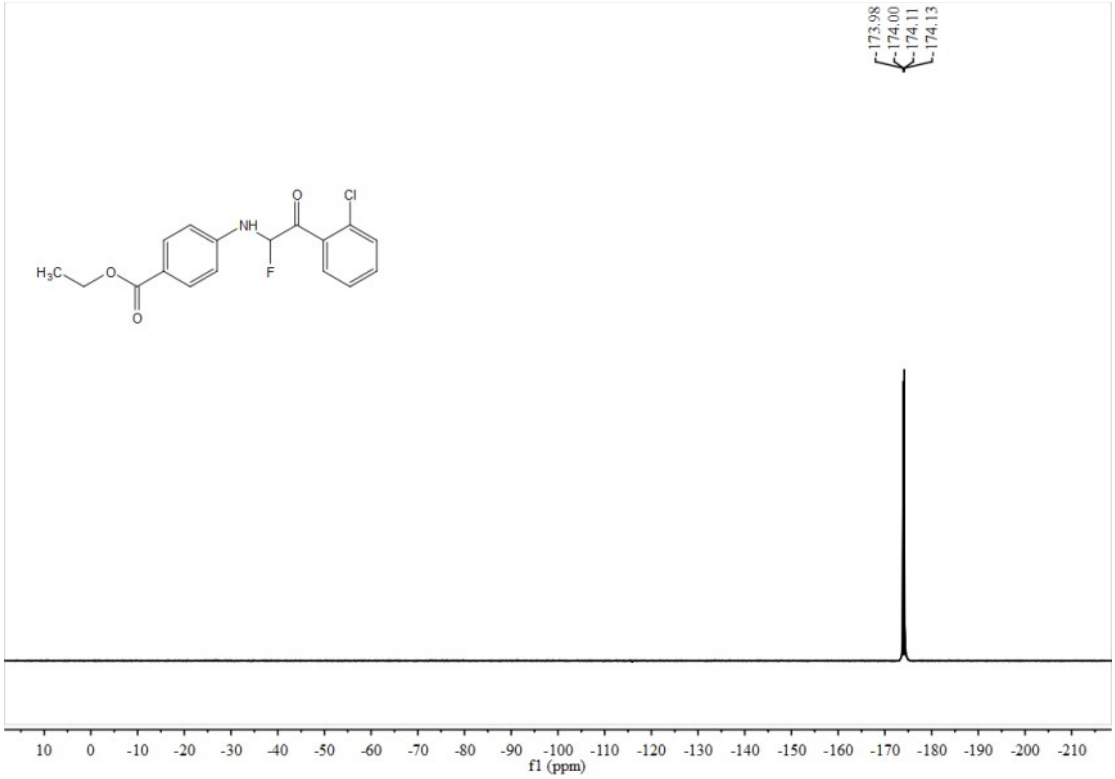
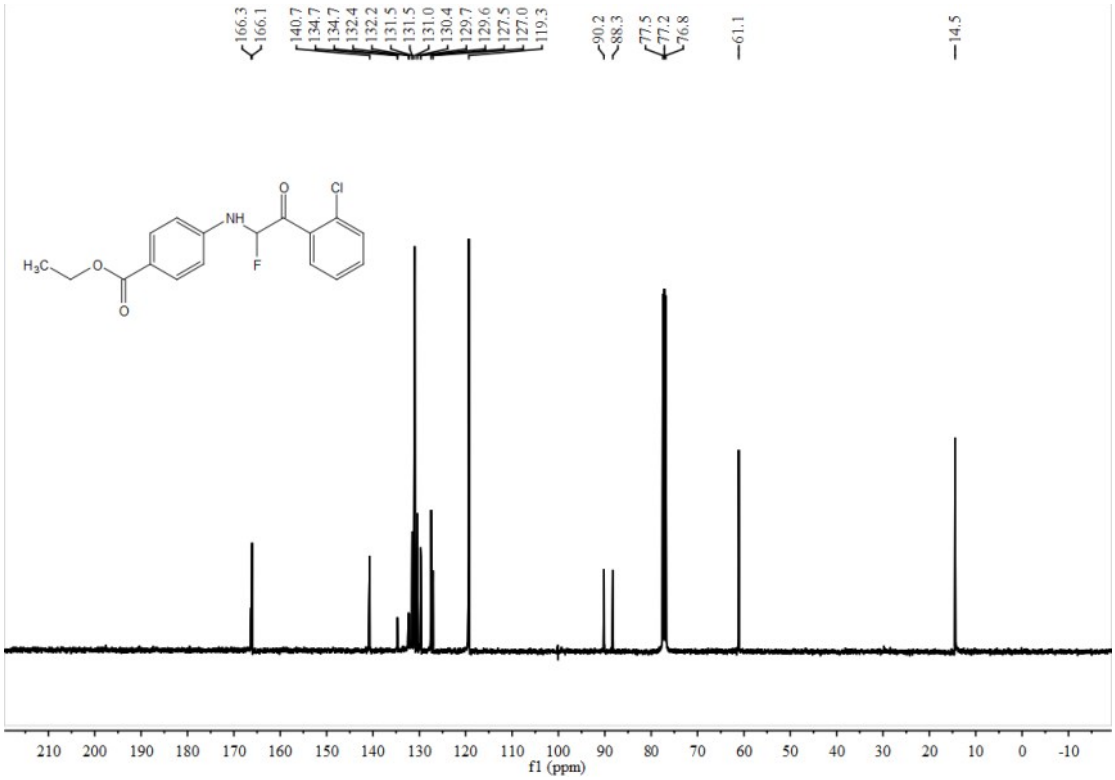


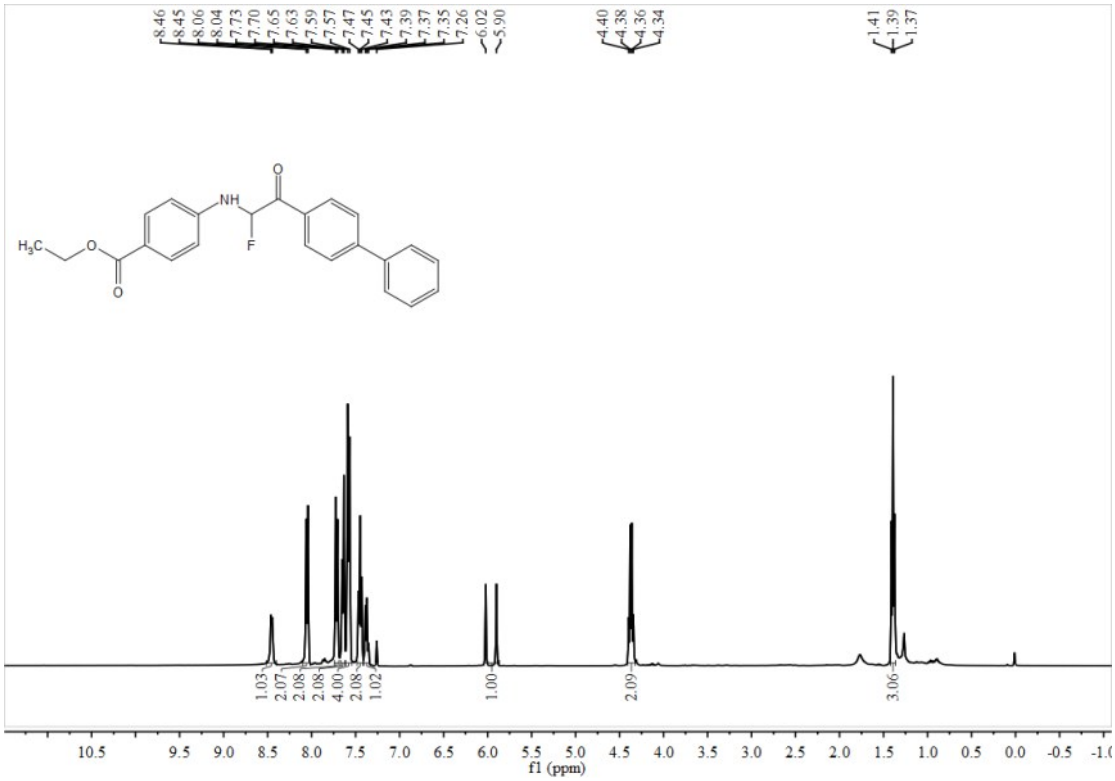
^{1}H NMR of **3g**



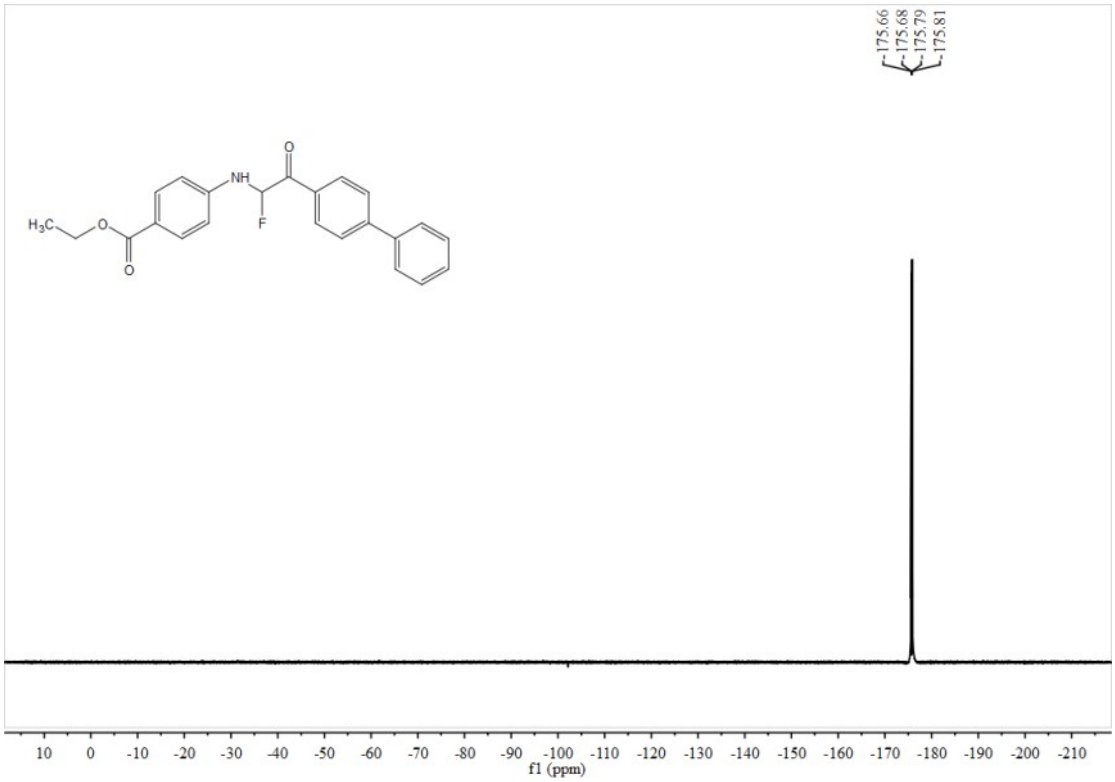
^{19}F NMR of **3g**



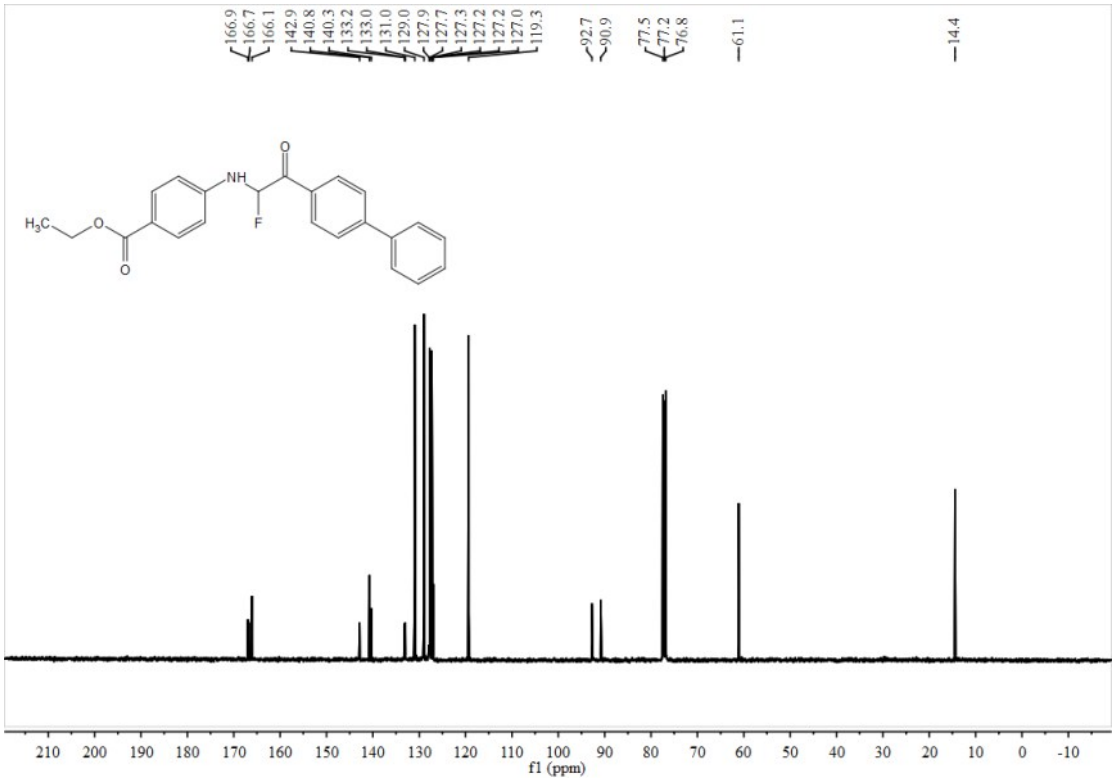
^{13}C NMR of **3g**



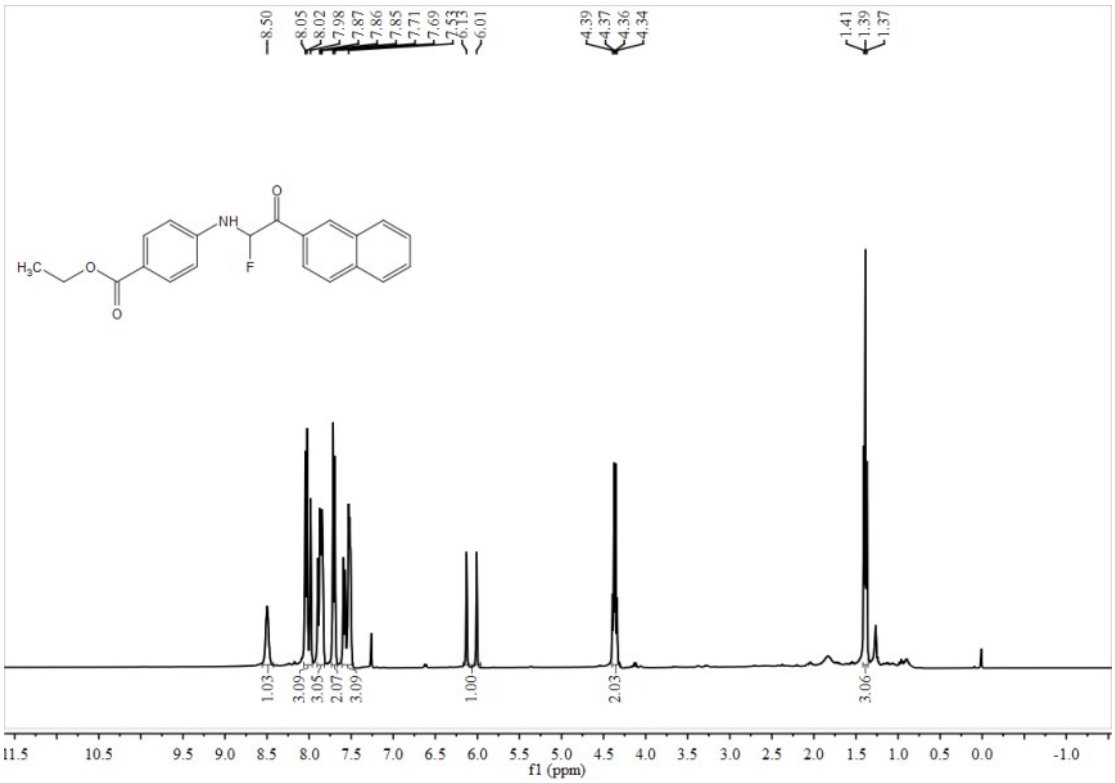
^{1}H NMR of **3h**



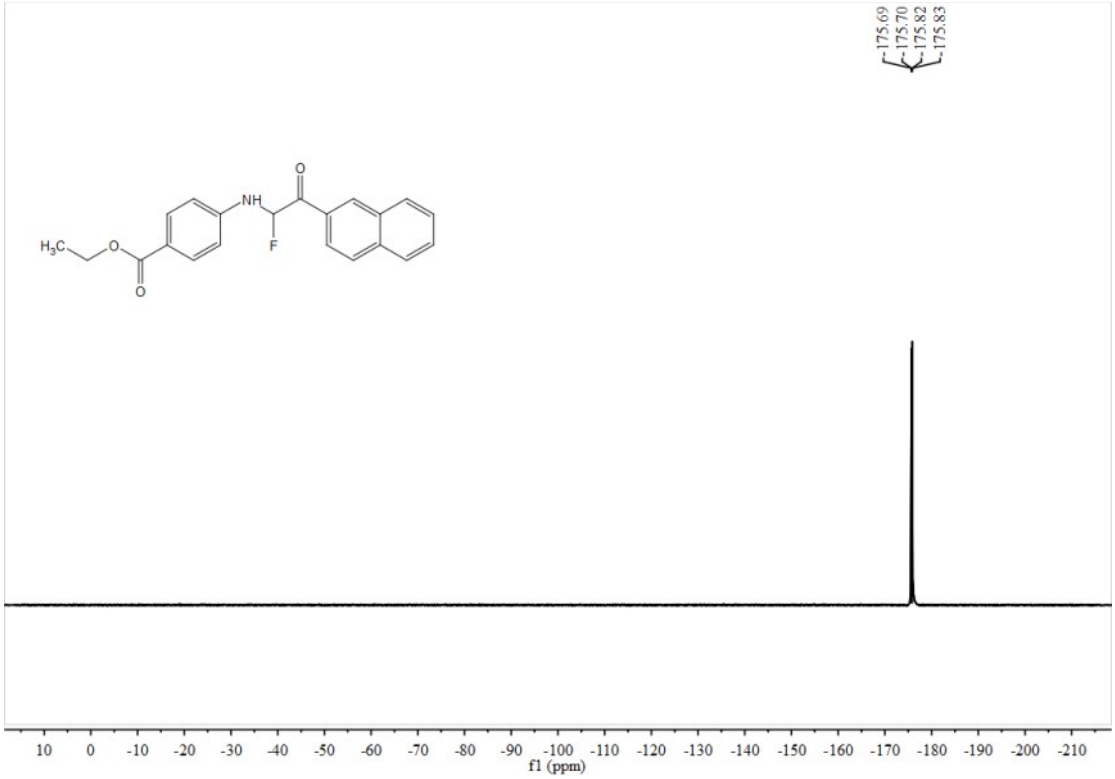
^{19}F NMR of **3h**



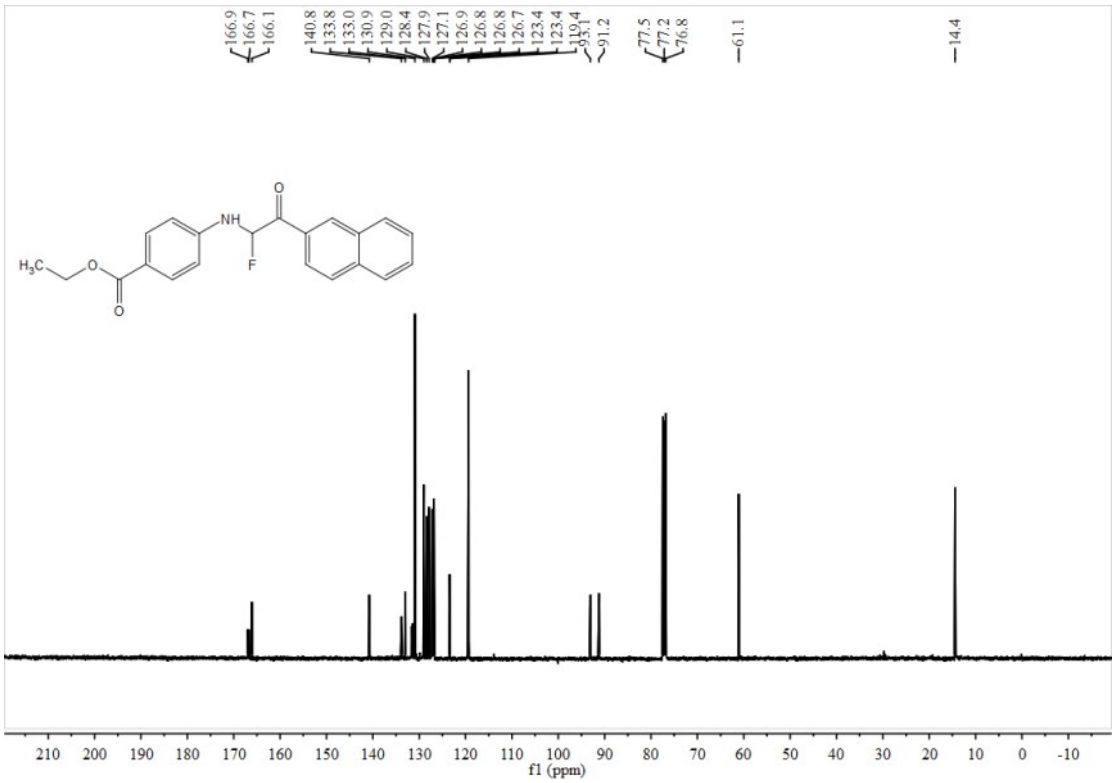
^{13}C NMR of **3h**



^{1}H NMR of **3i**



^{19}F NMR of **3i**



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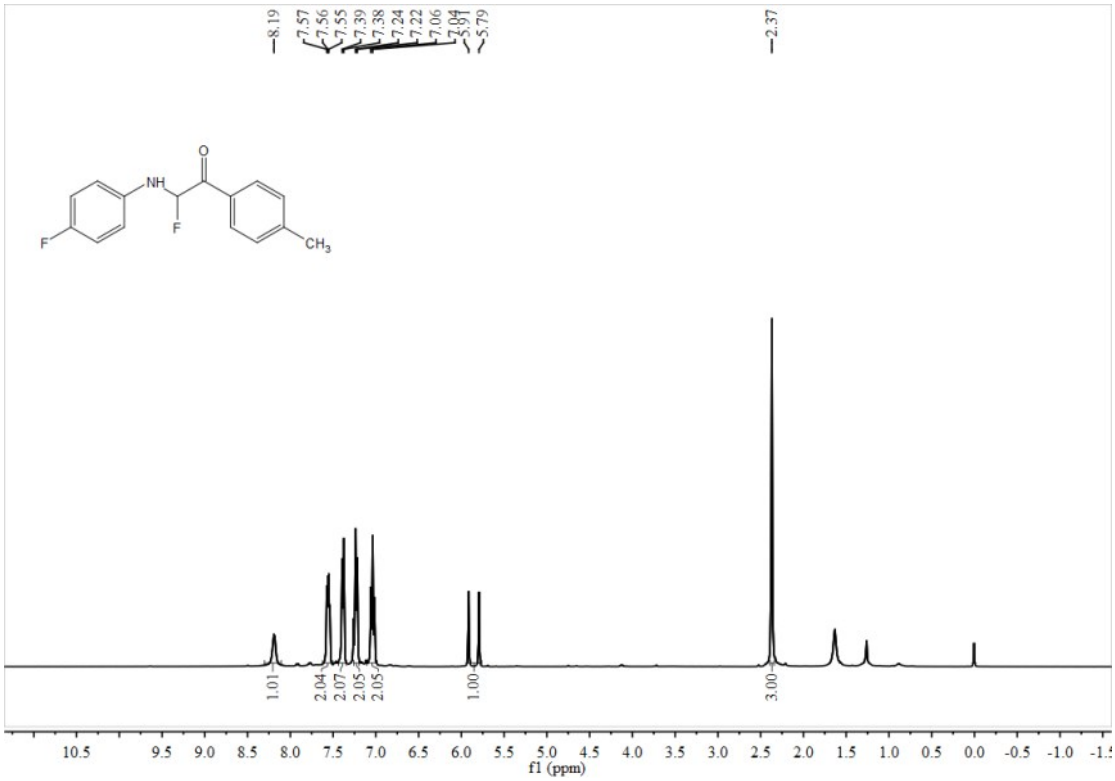

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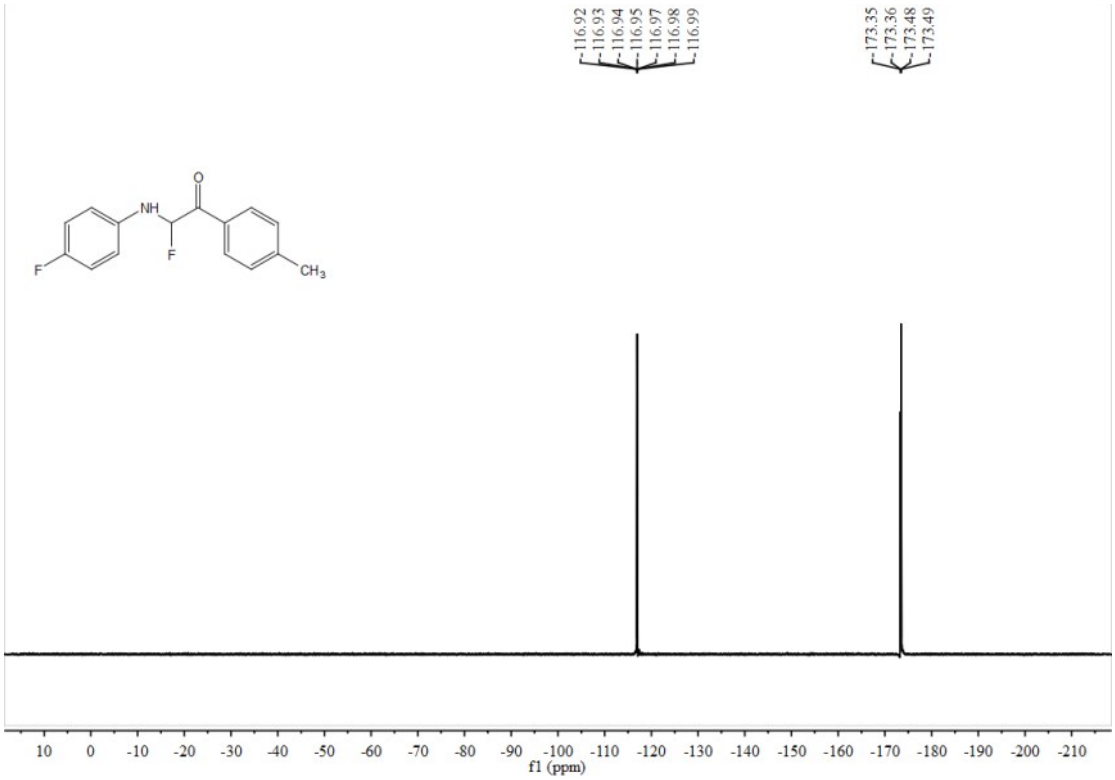

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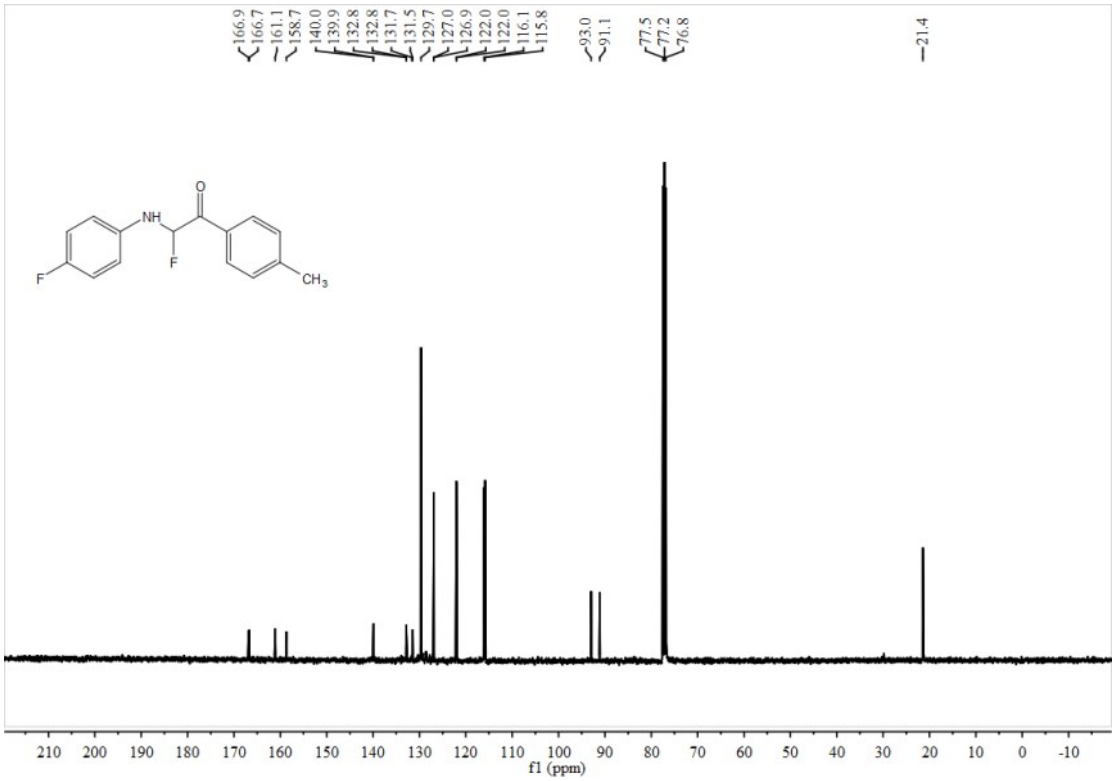

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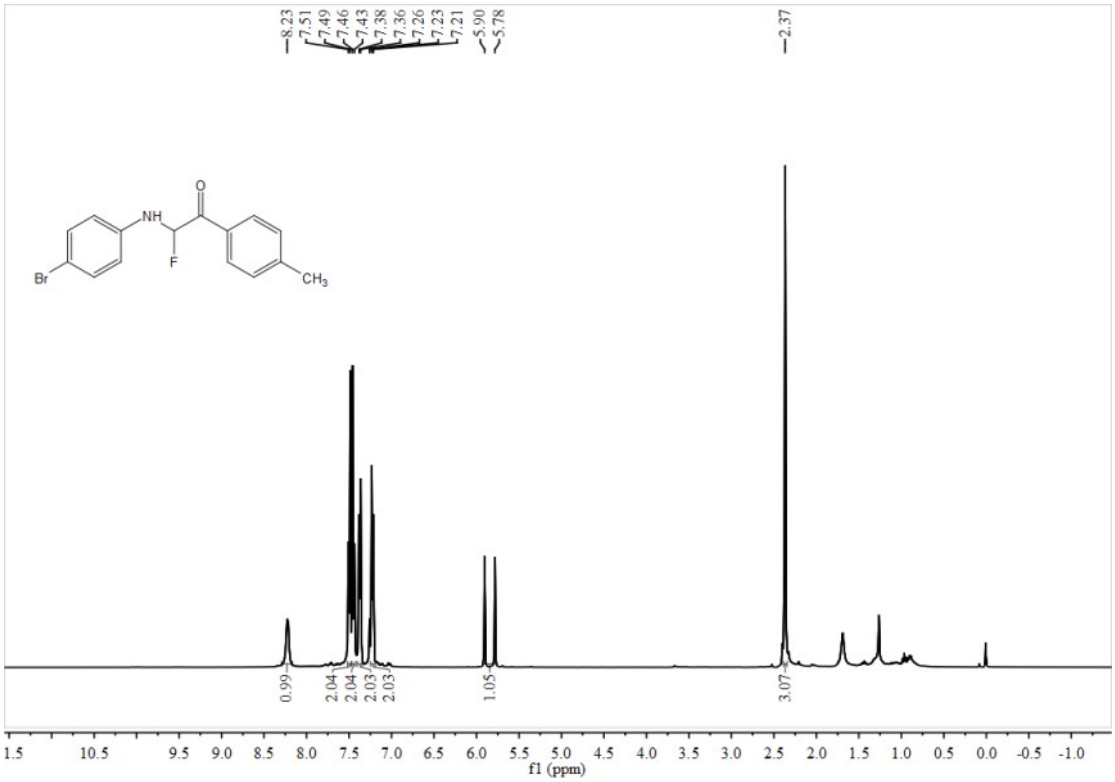

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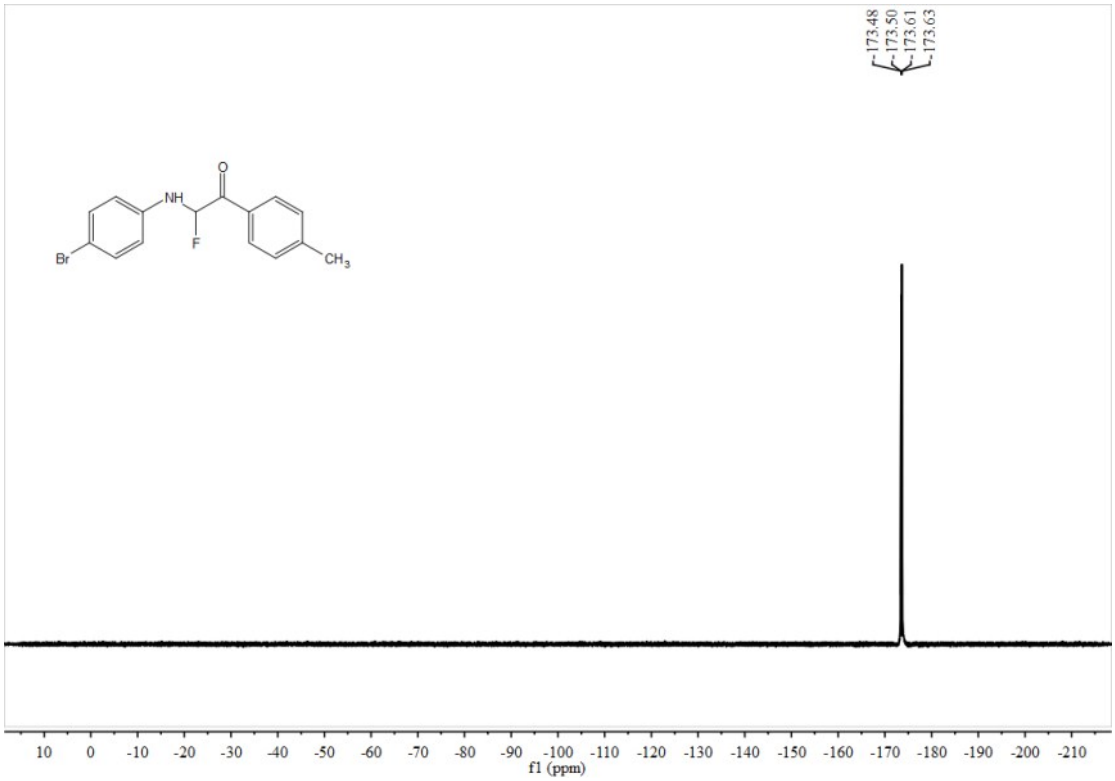

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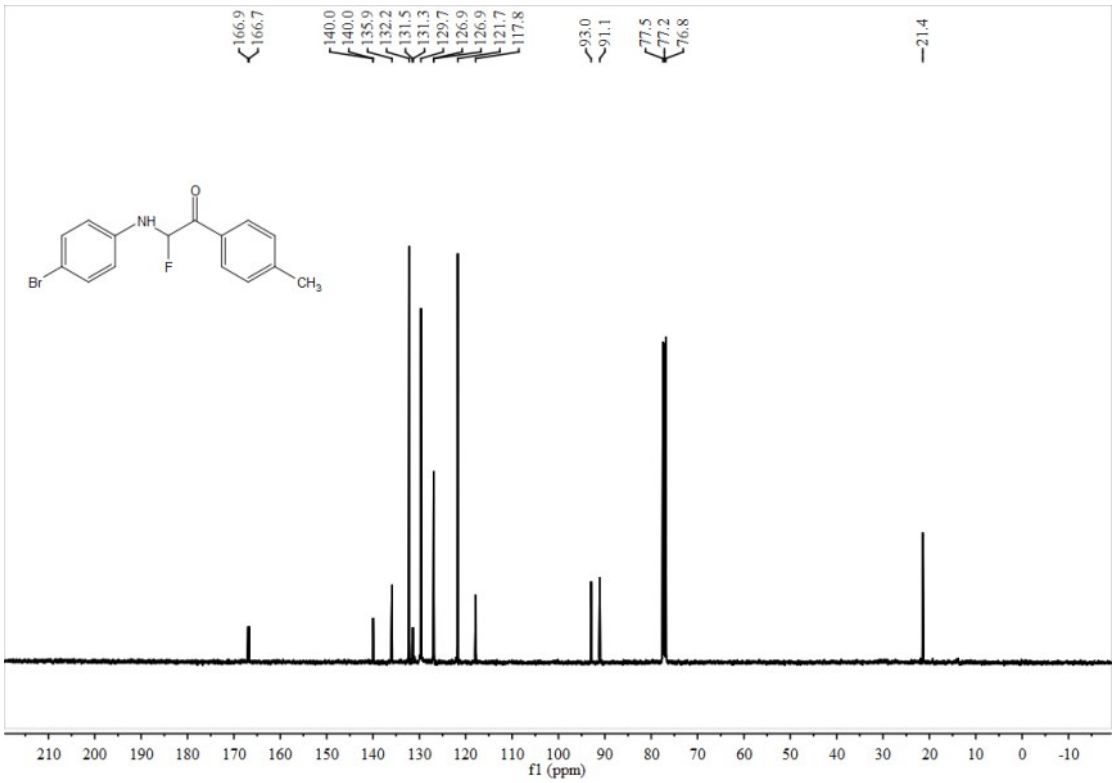

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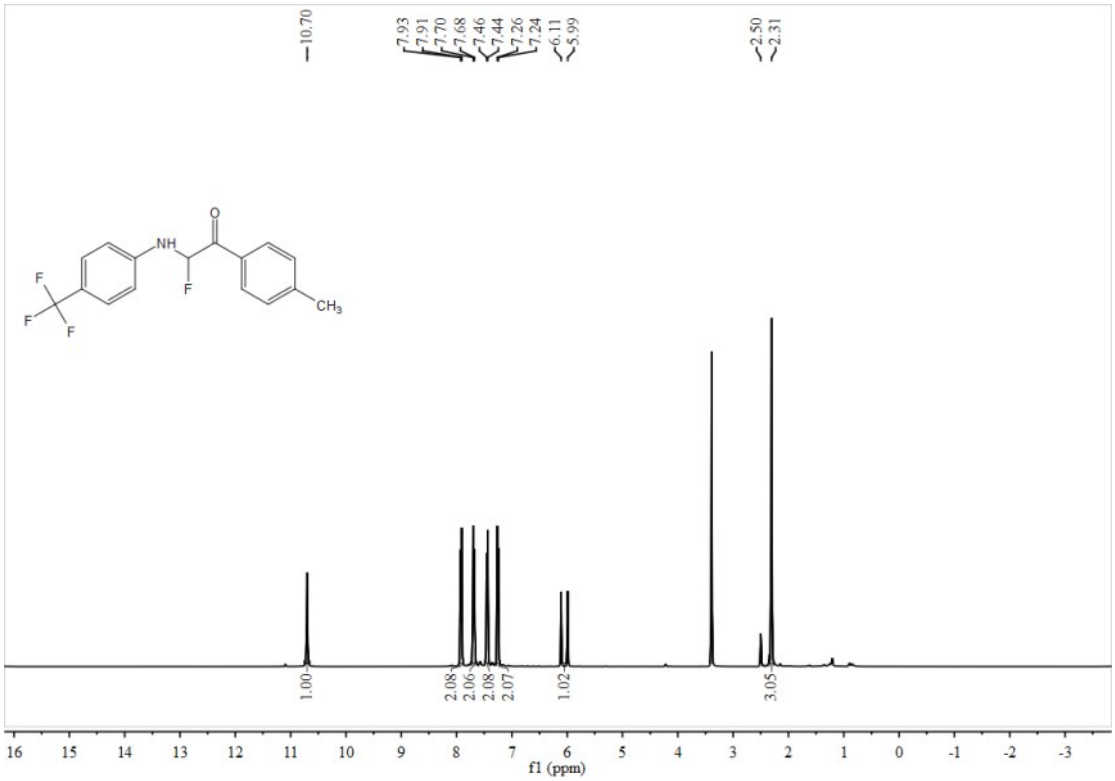

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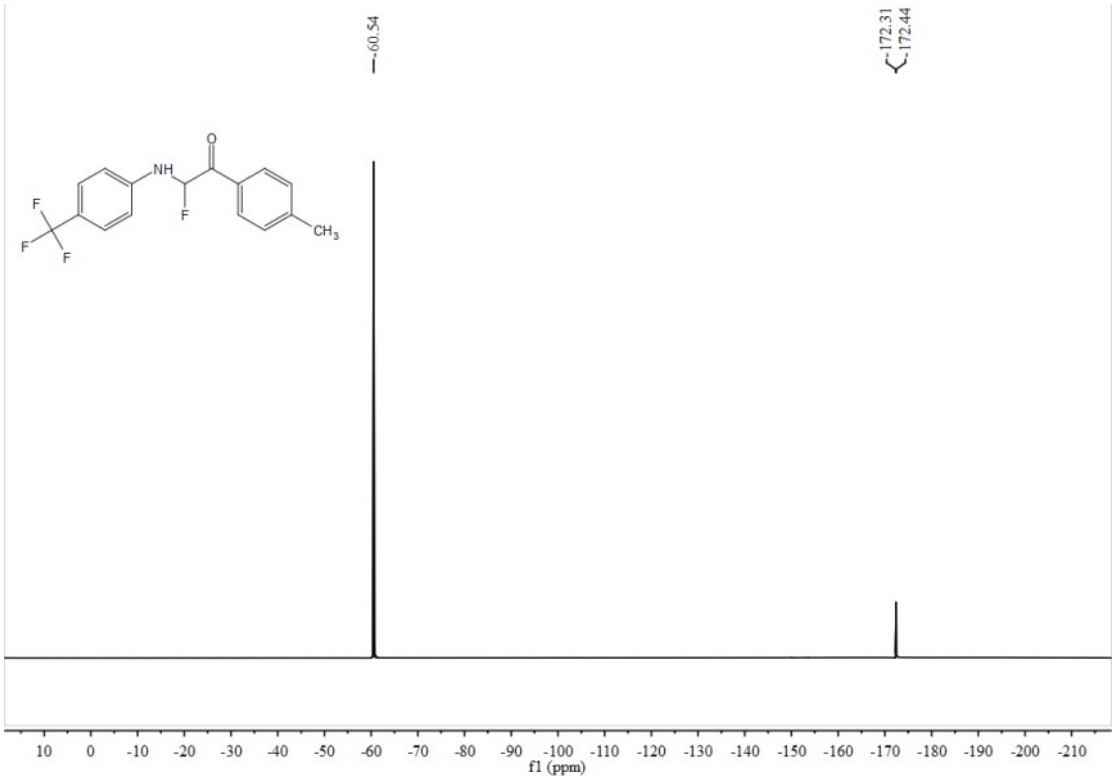

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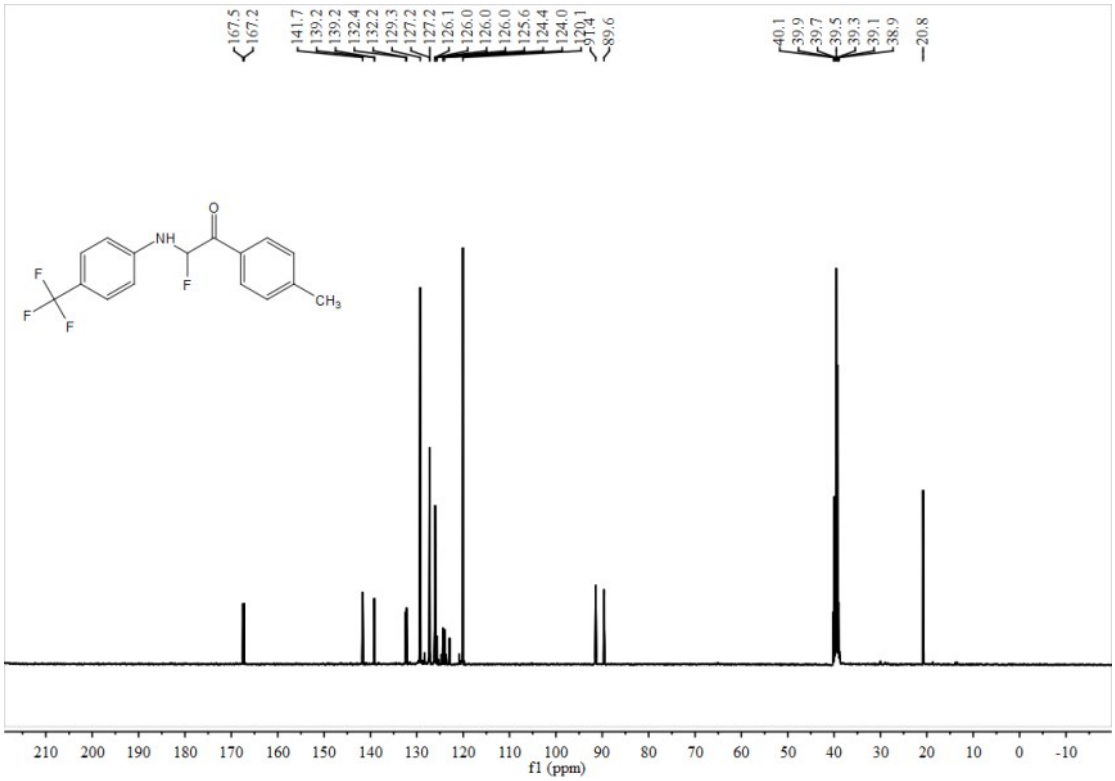

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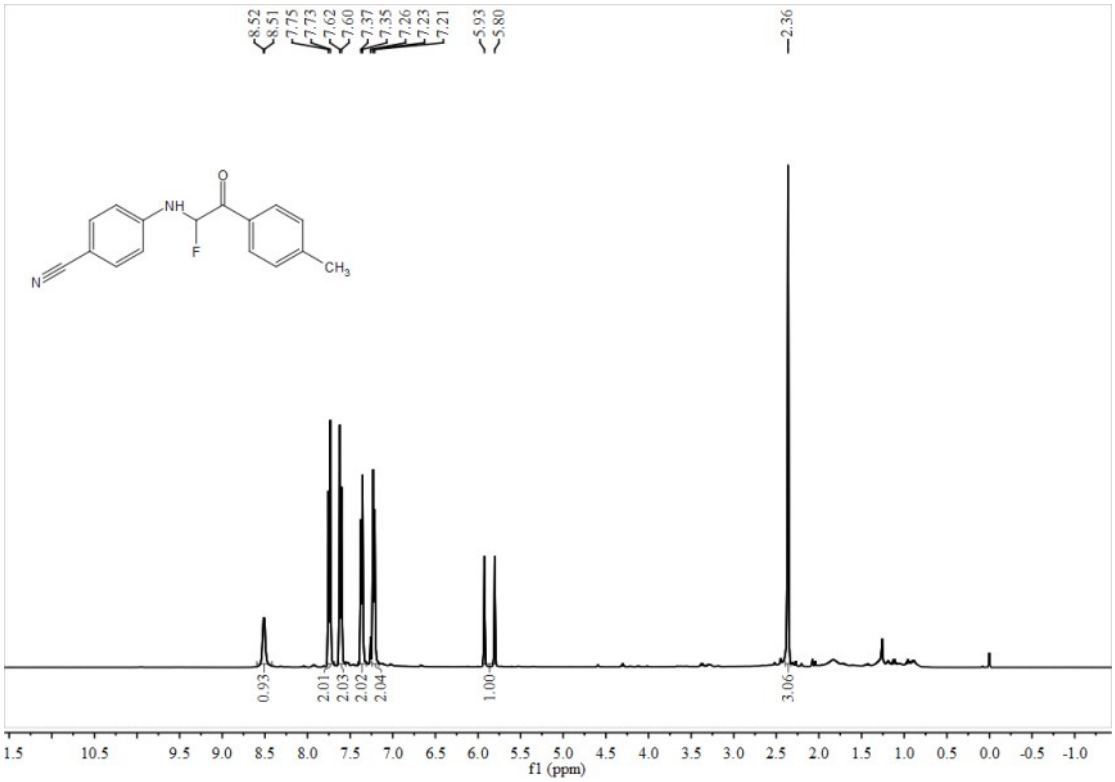

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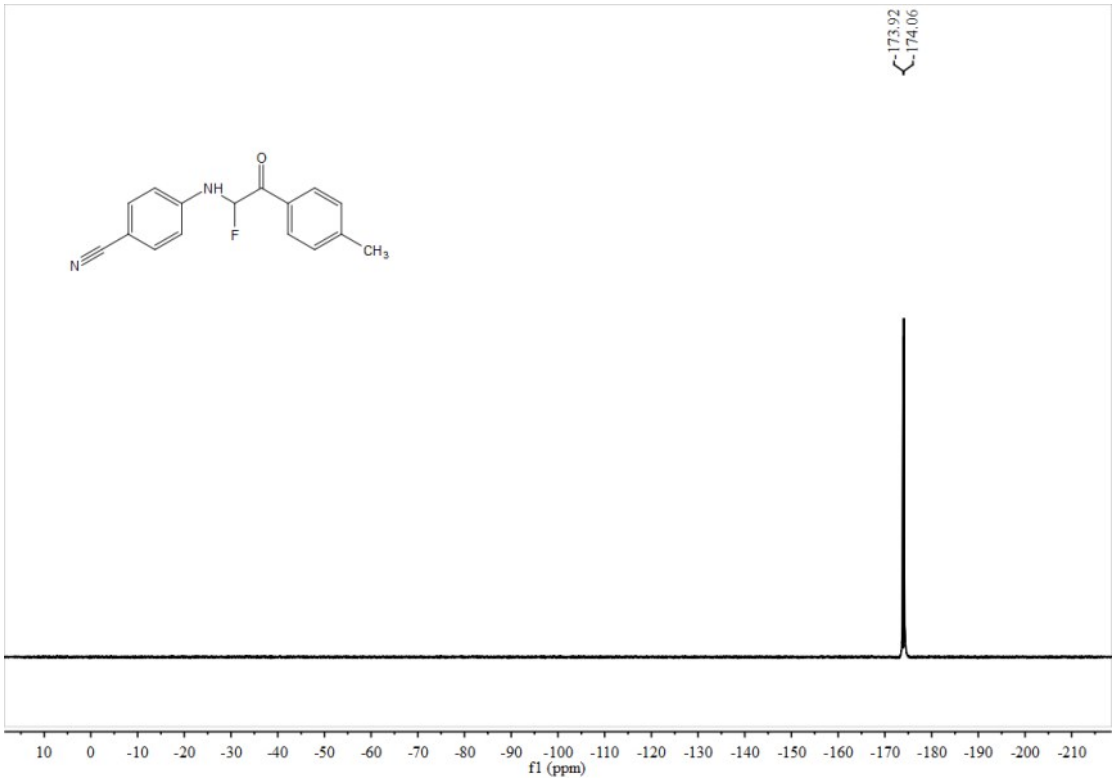
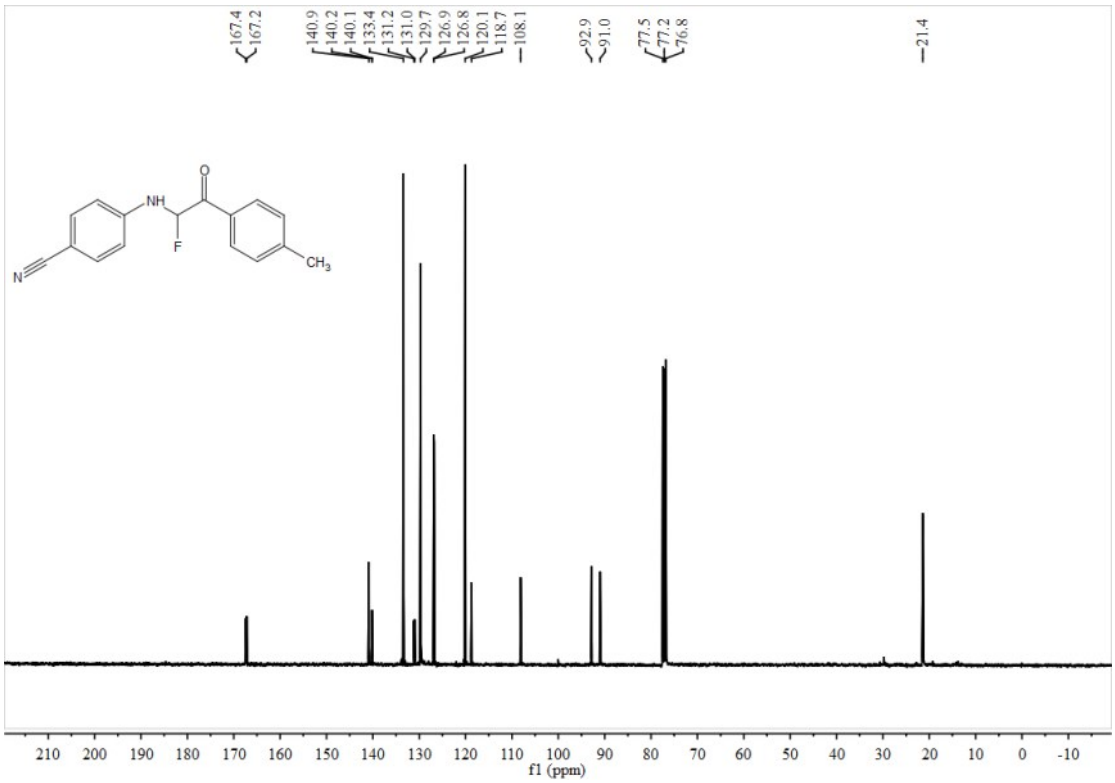


^{19}F NMR of **3m**



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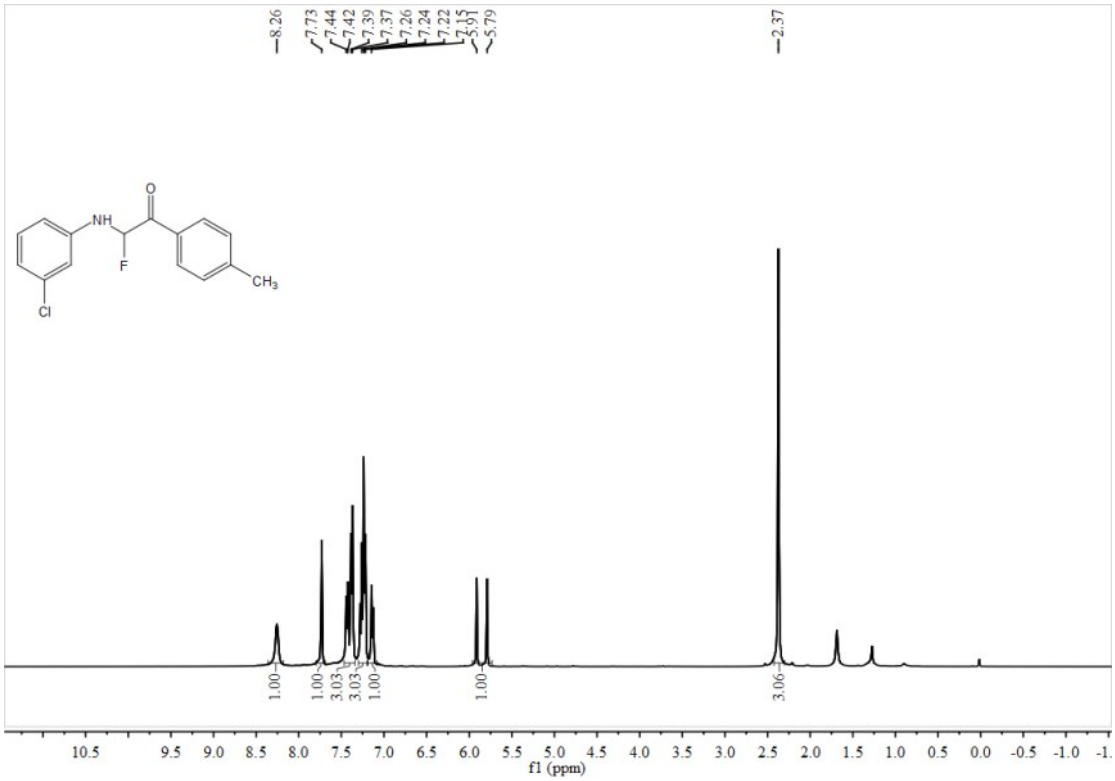
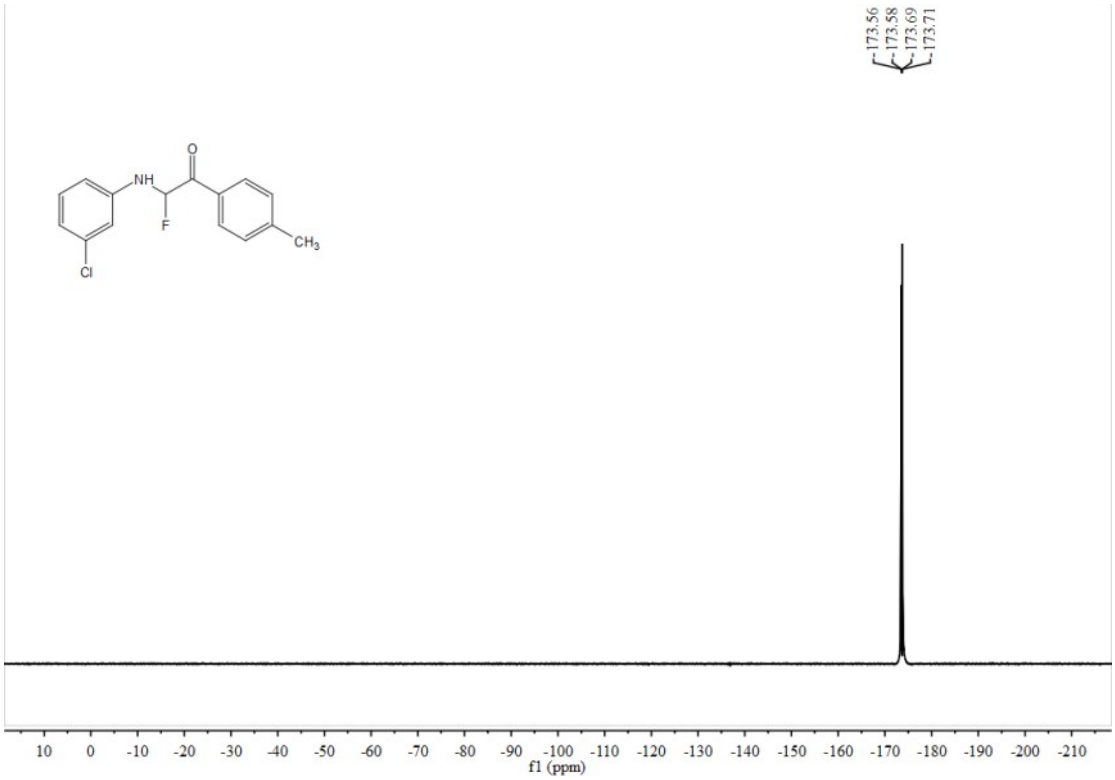


^{1}H NMR of **3n**



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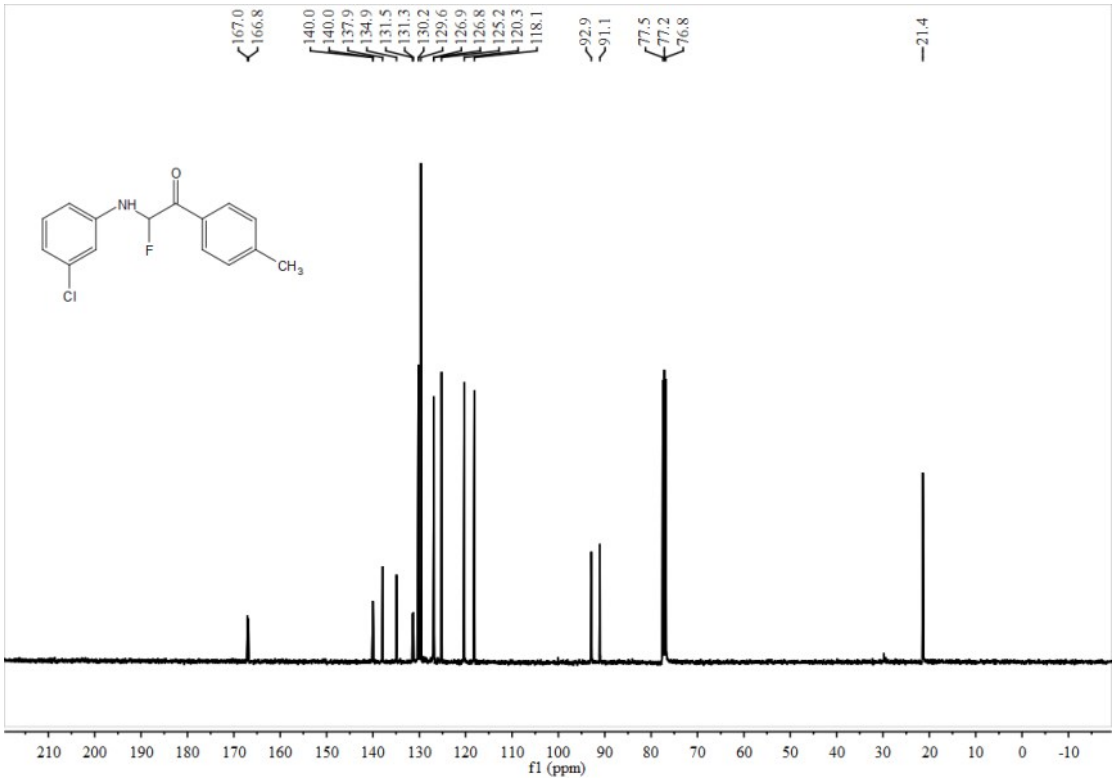

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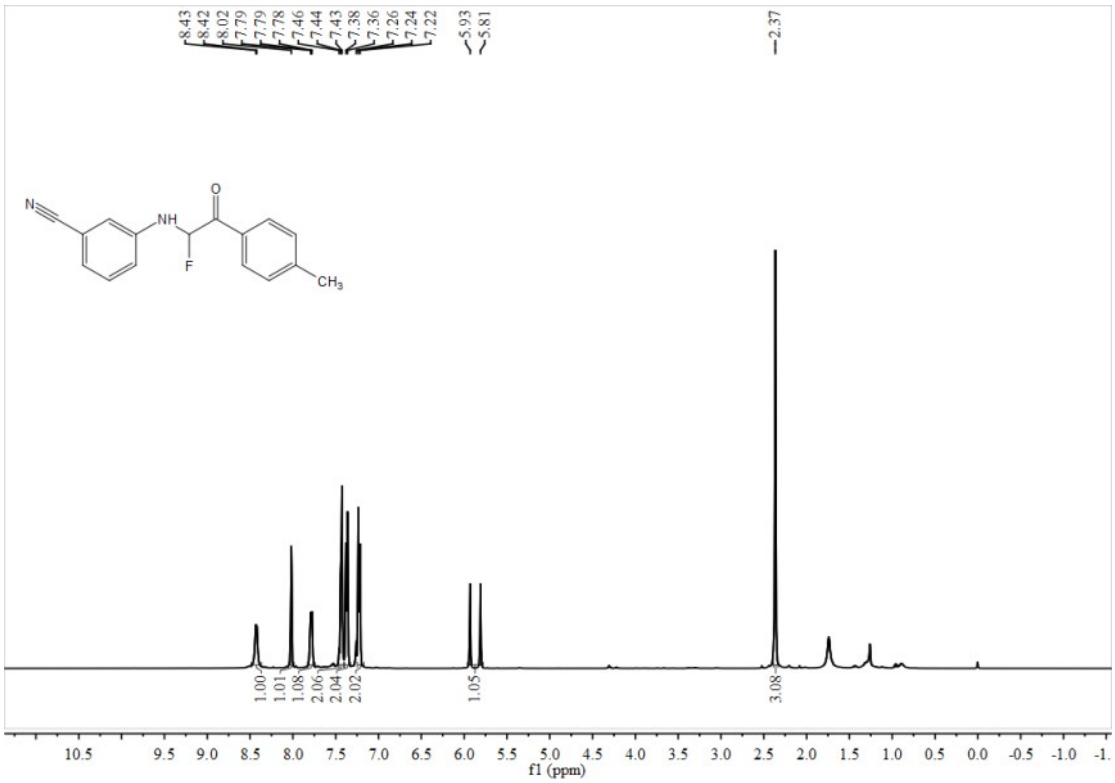
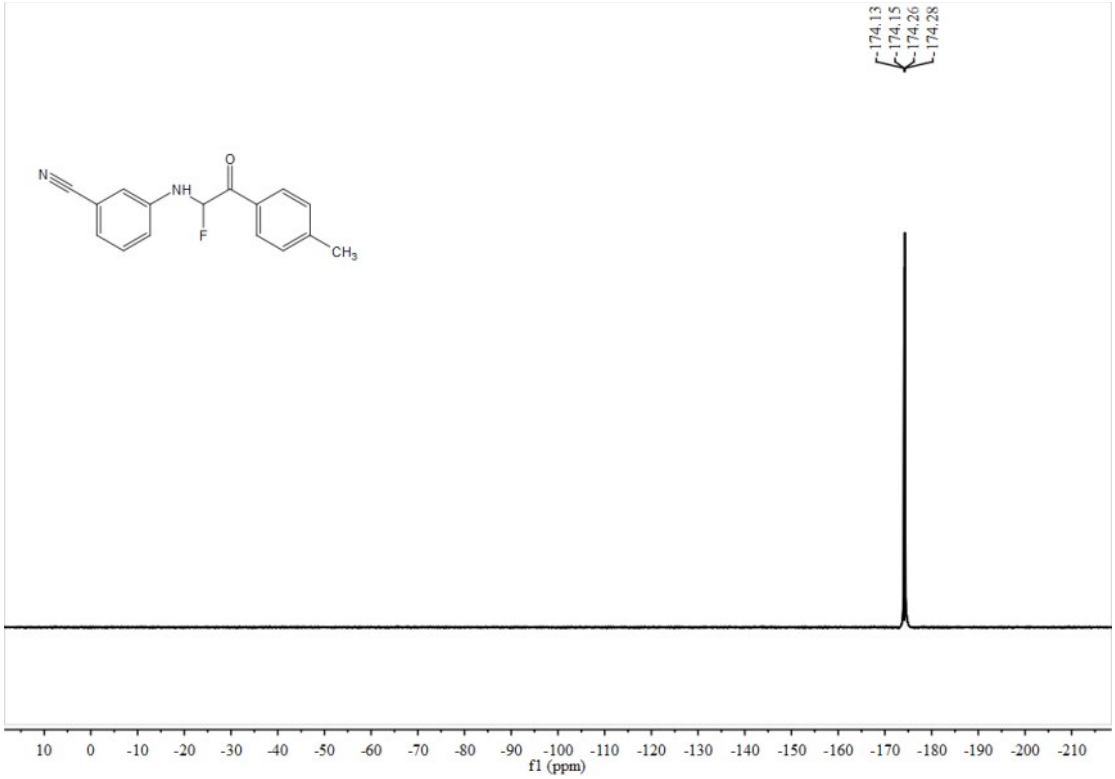


^{1}H NMR of **3o**



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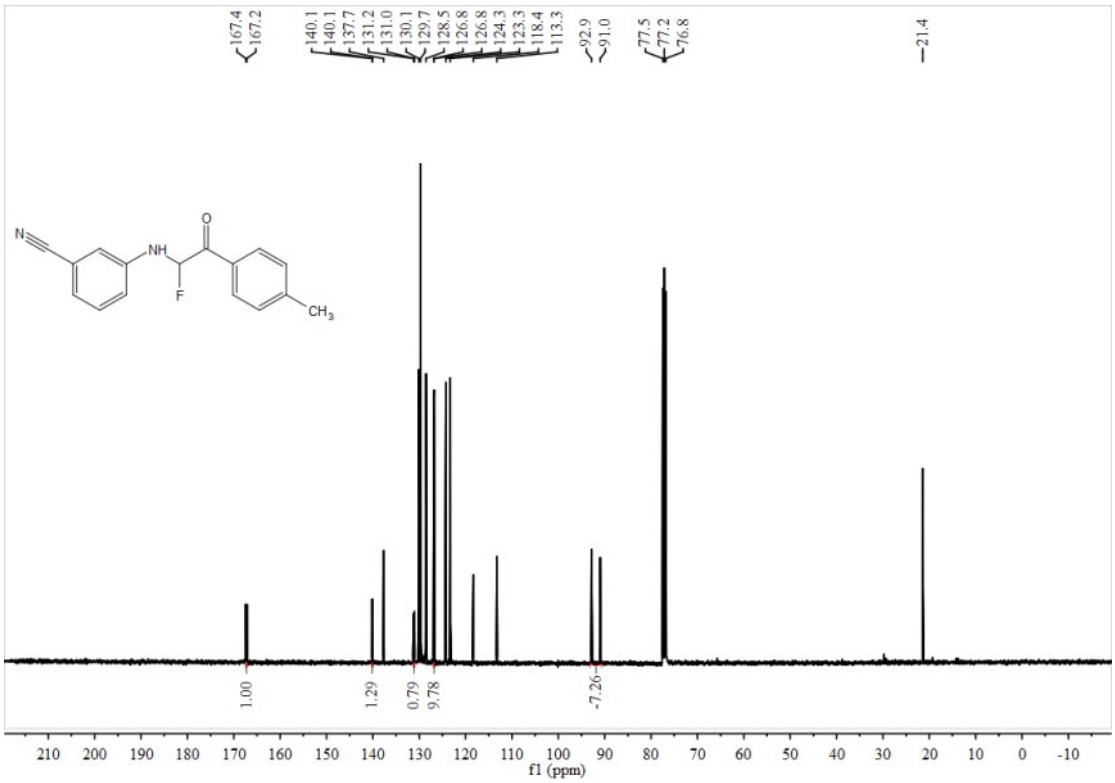

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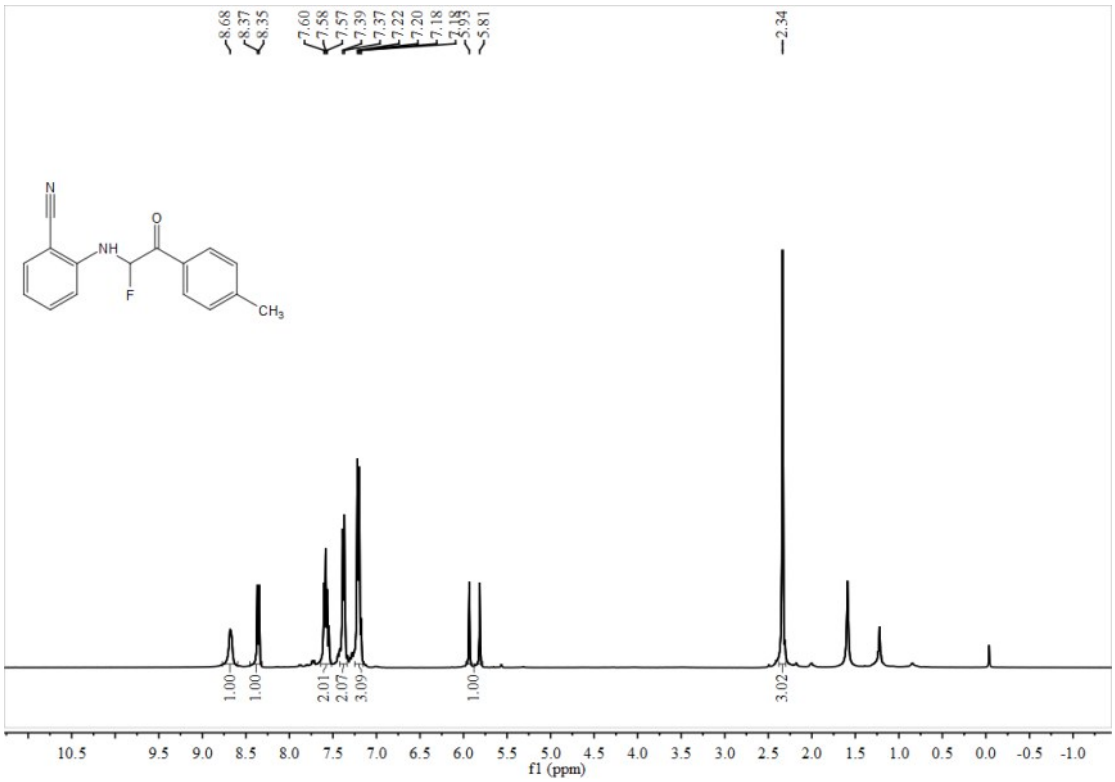
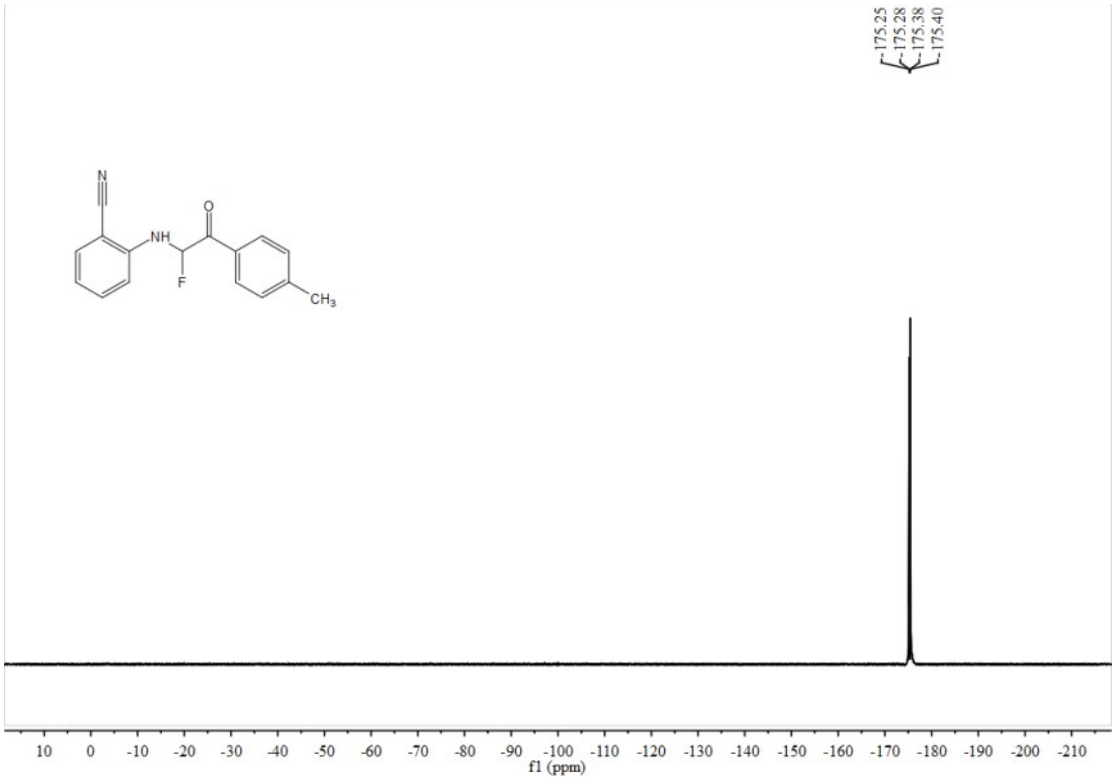
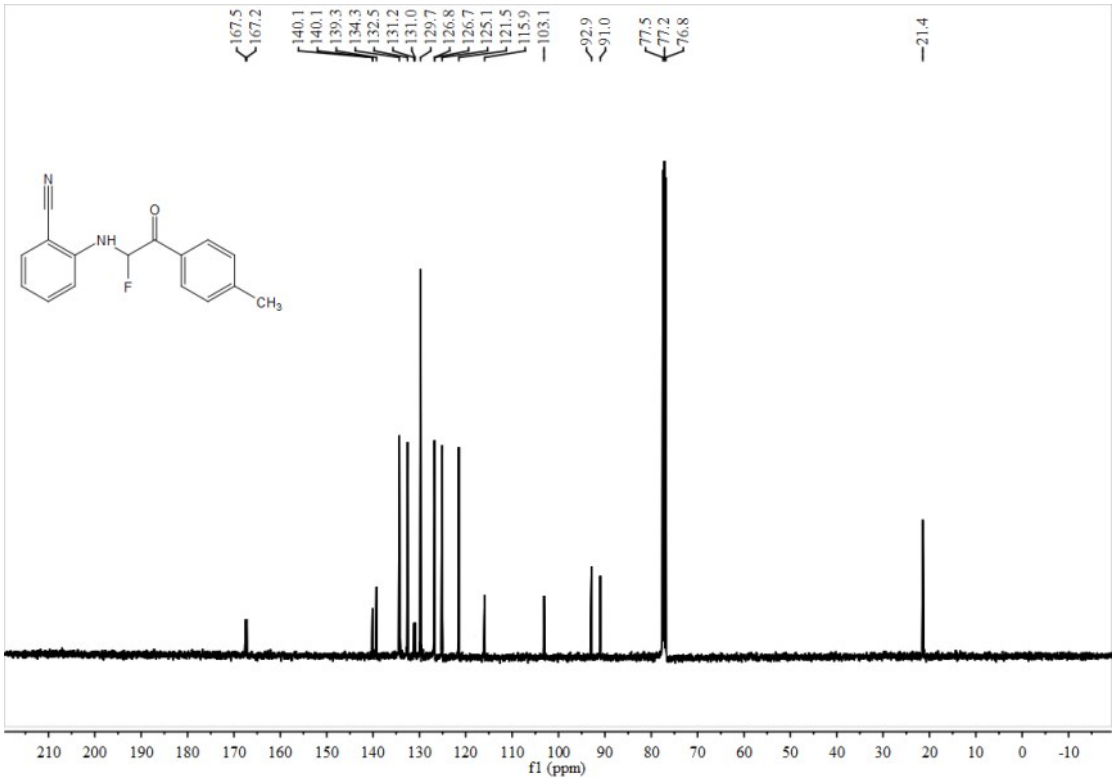


^{1}H NMR of **3p**



^{19}F NMR of **3p**



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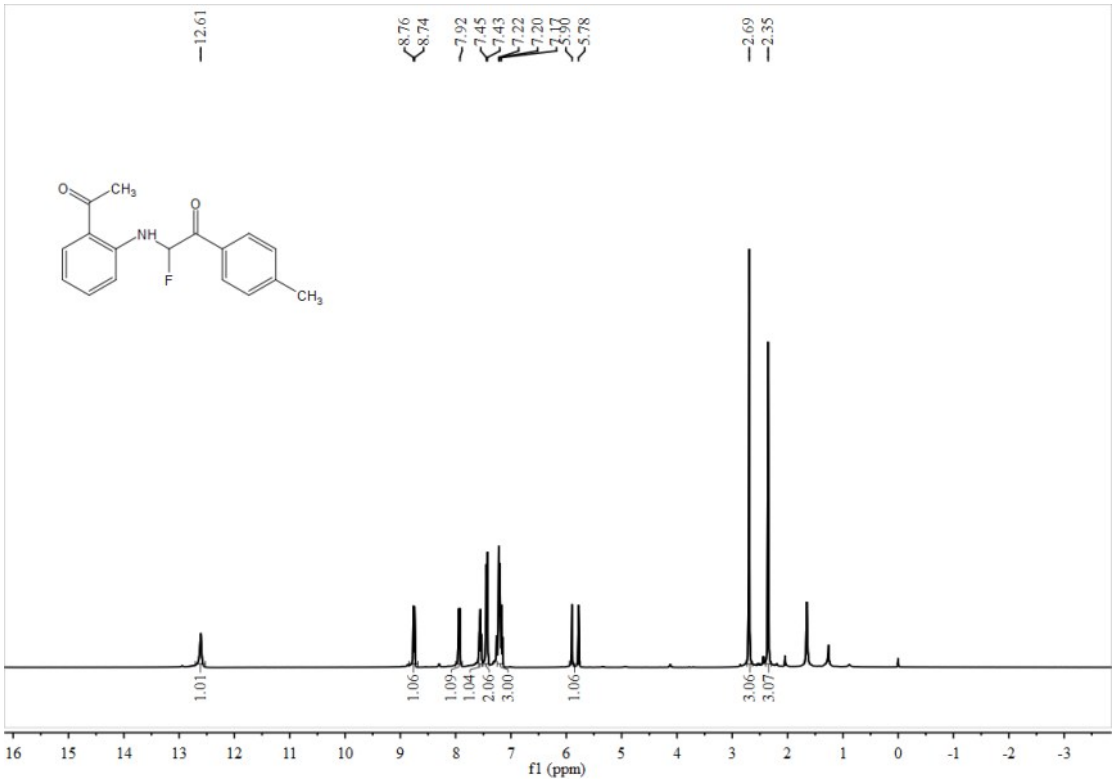

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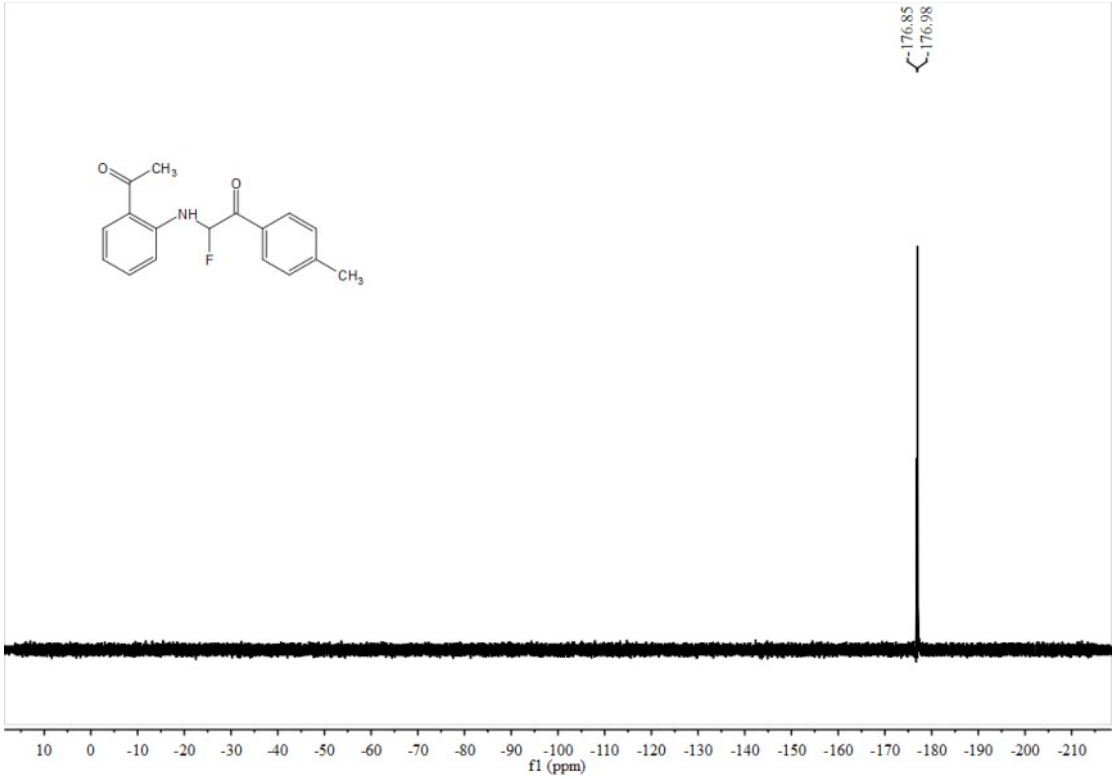
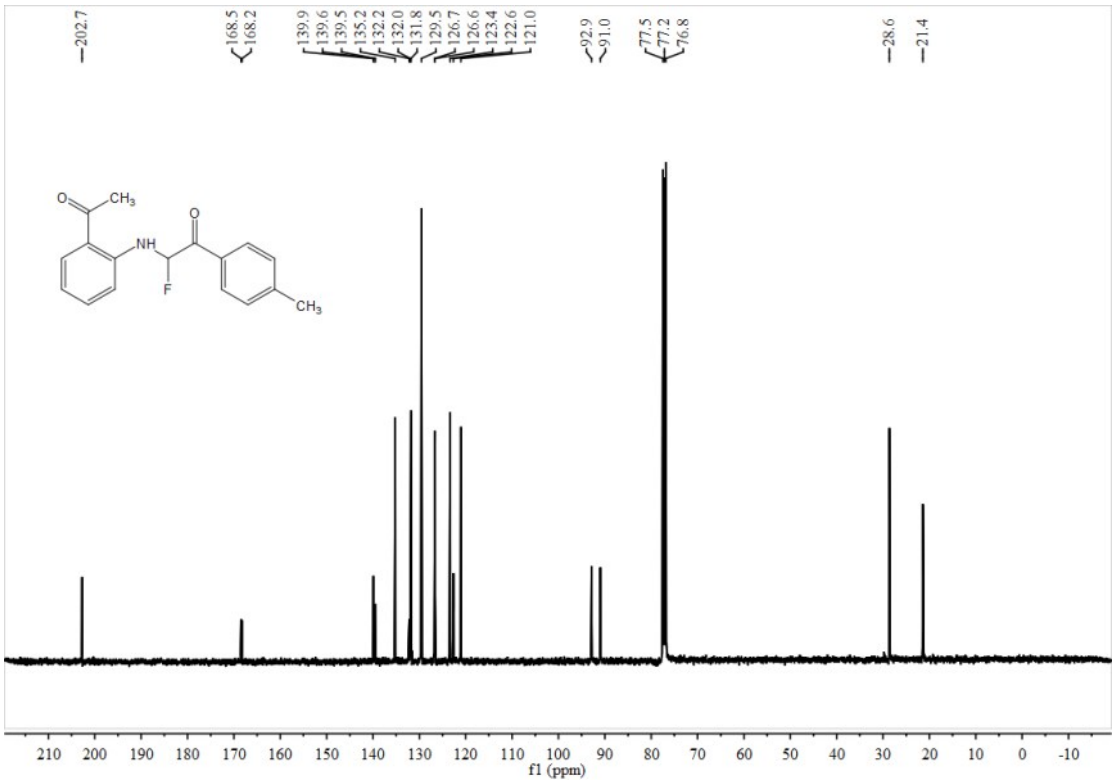
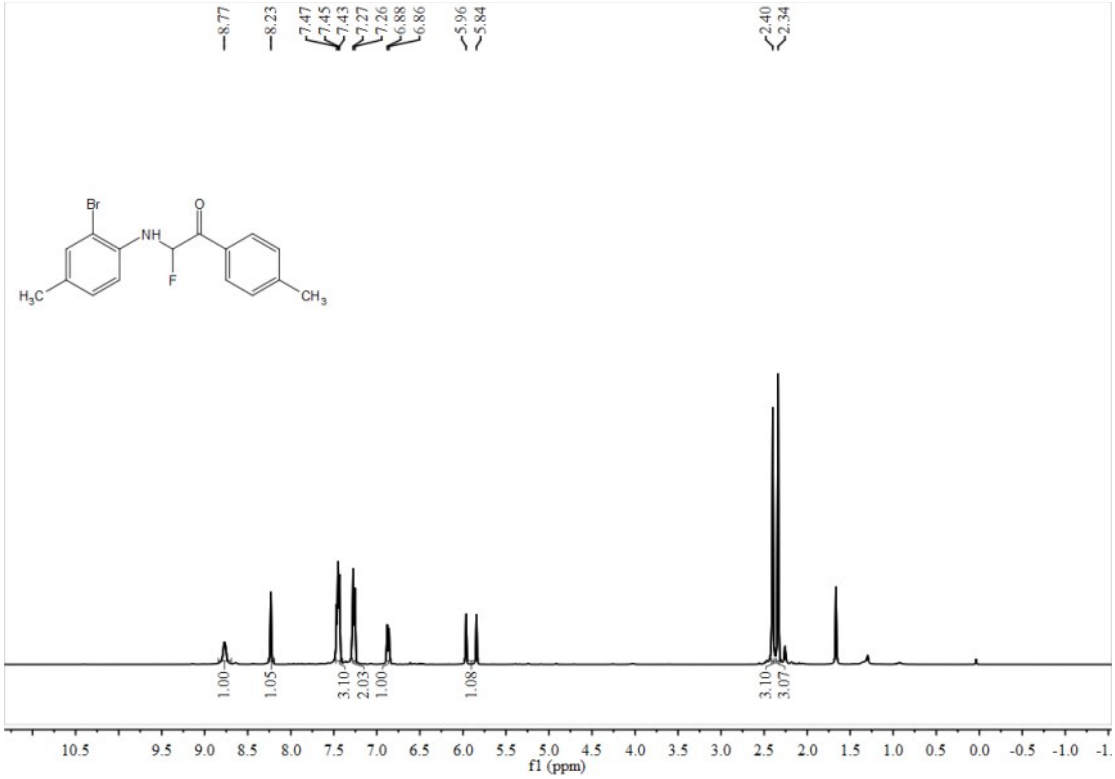


^{19}F NMR of **3q**



^{13}C NMR of **3q**



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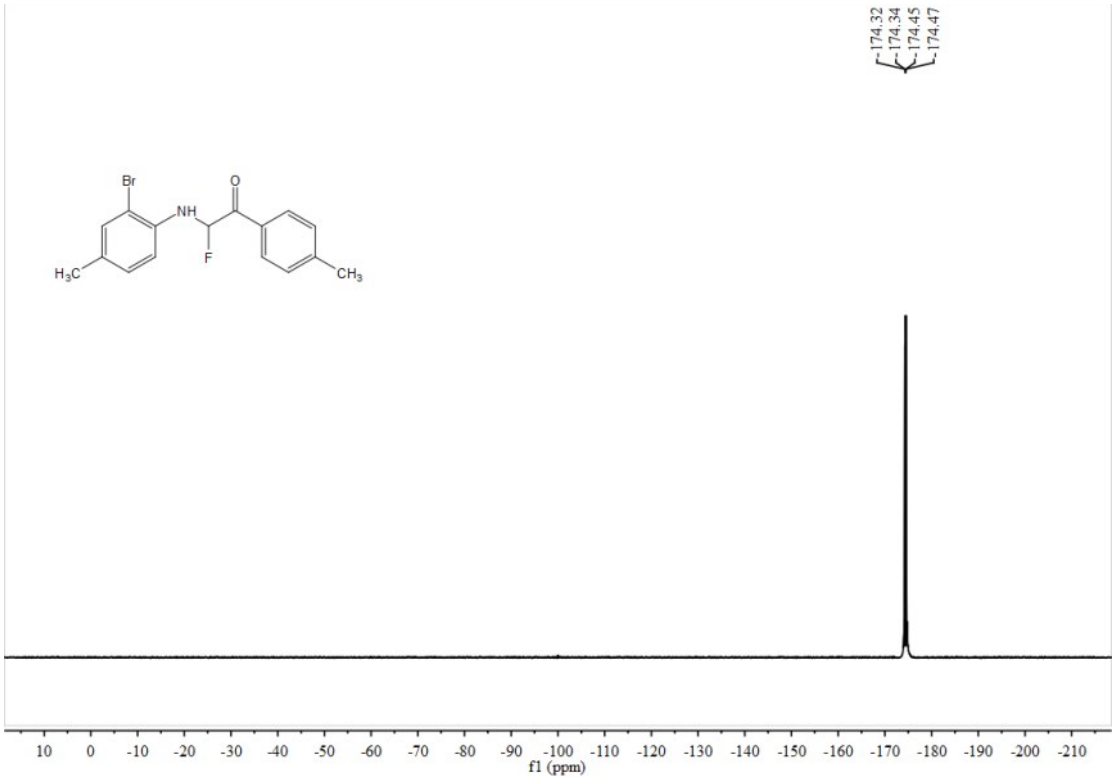

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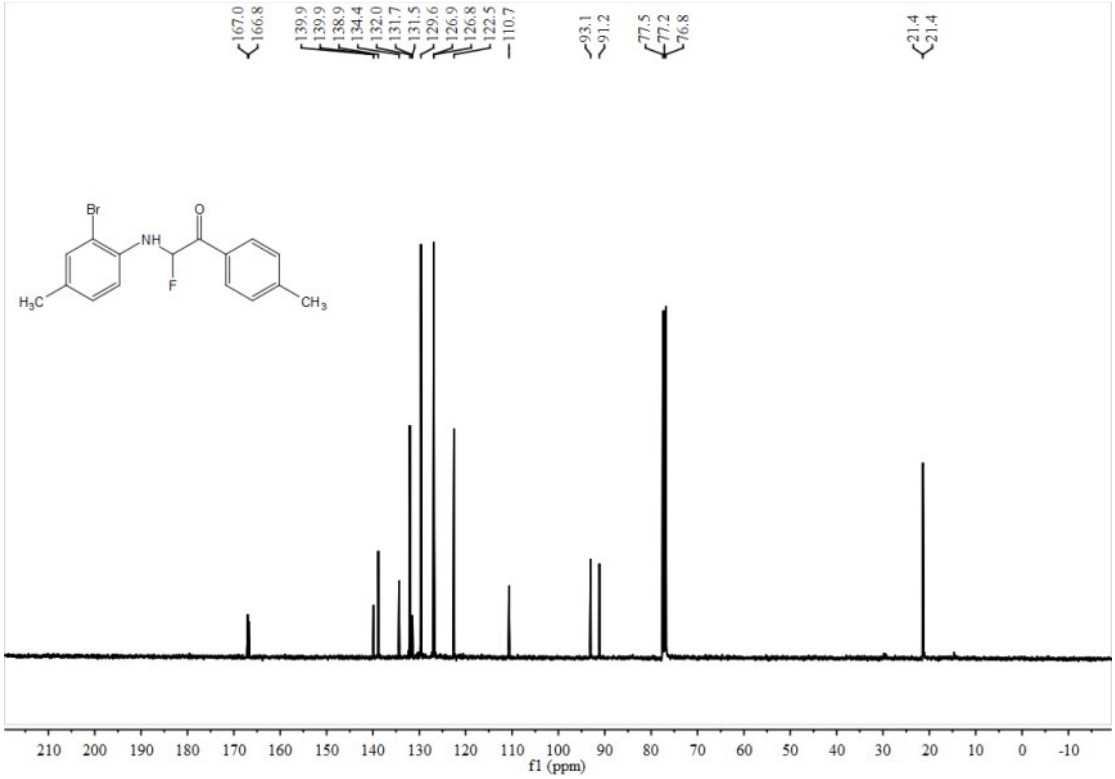

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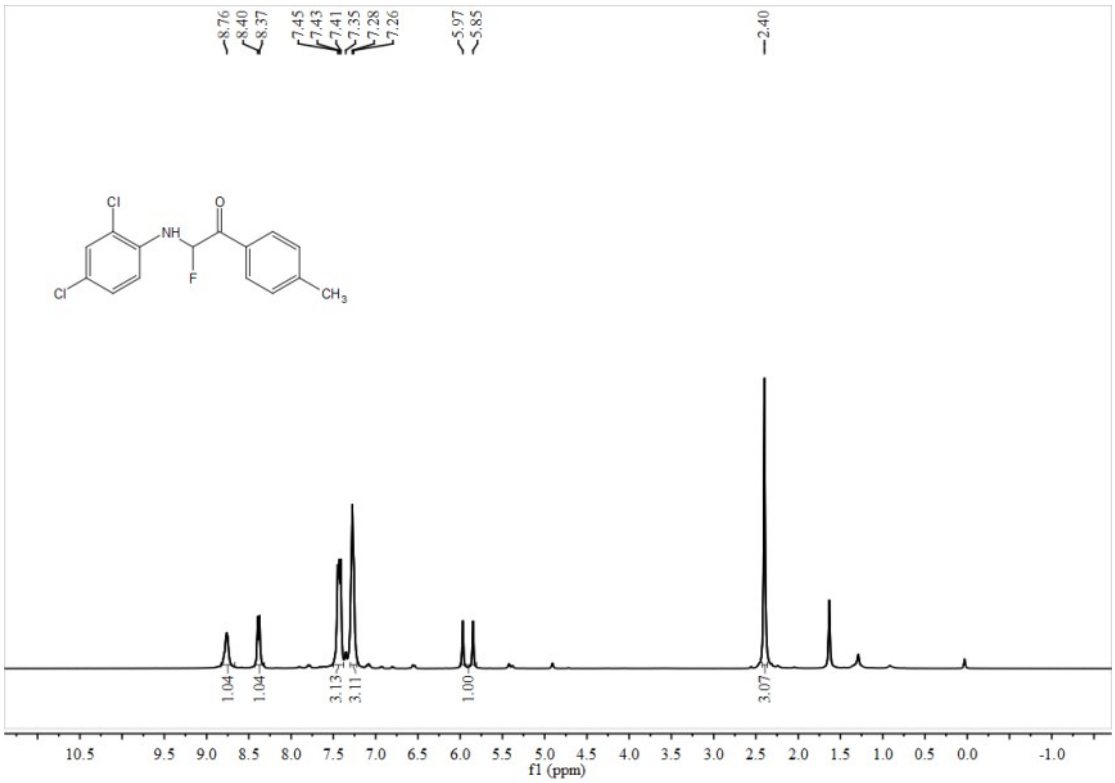

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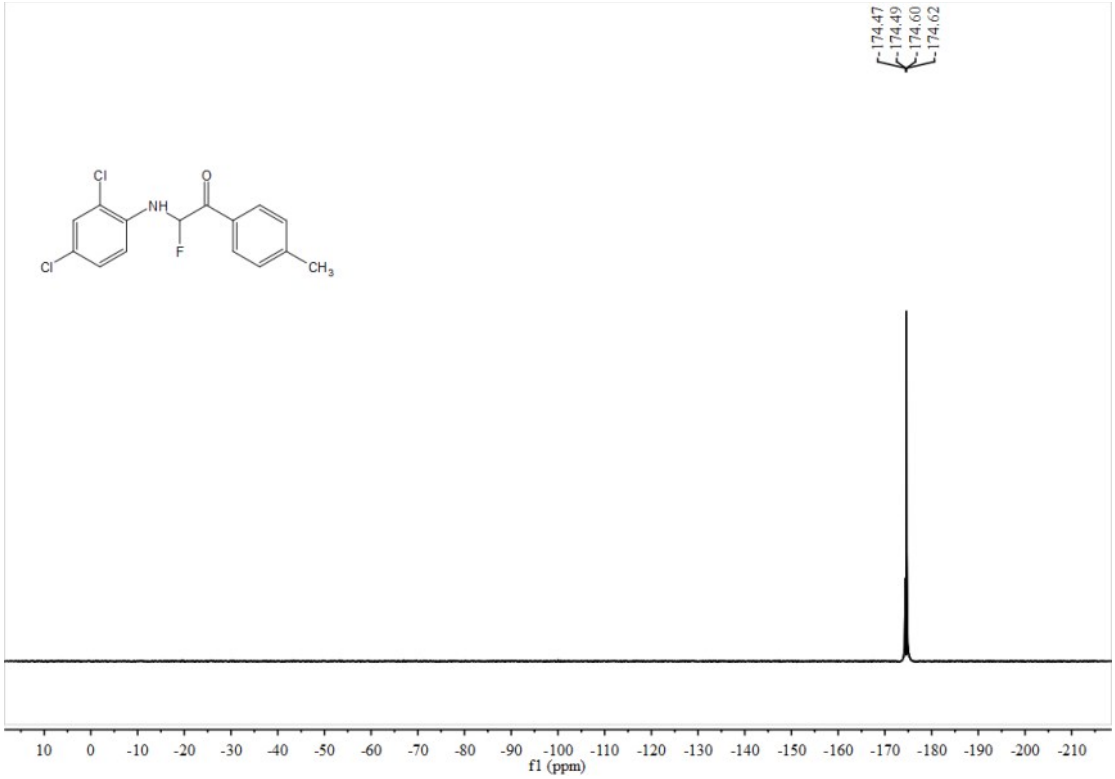

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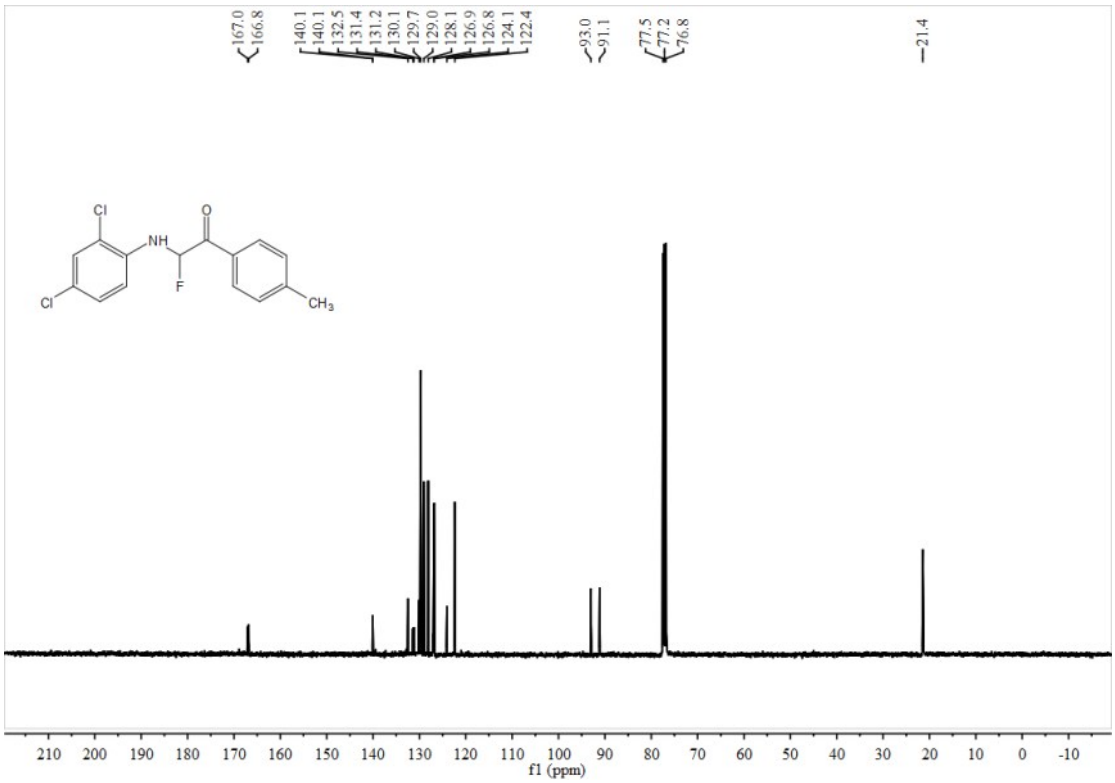

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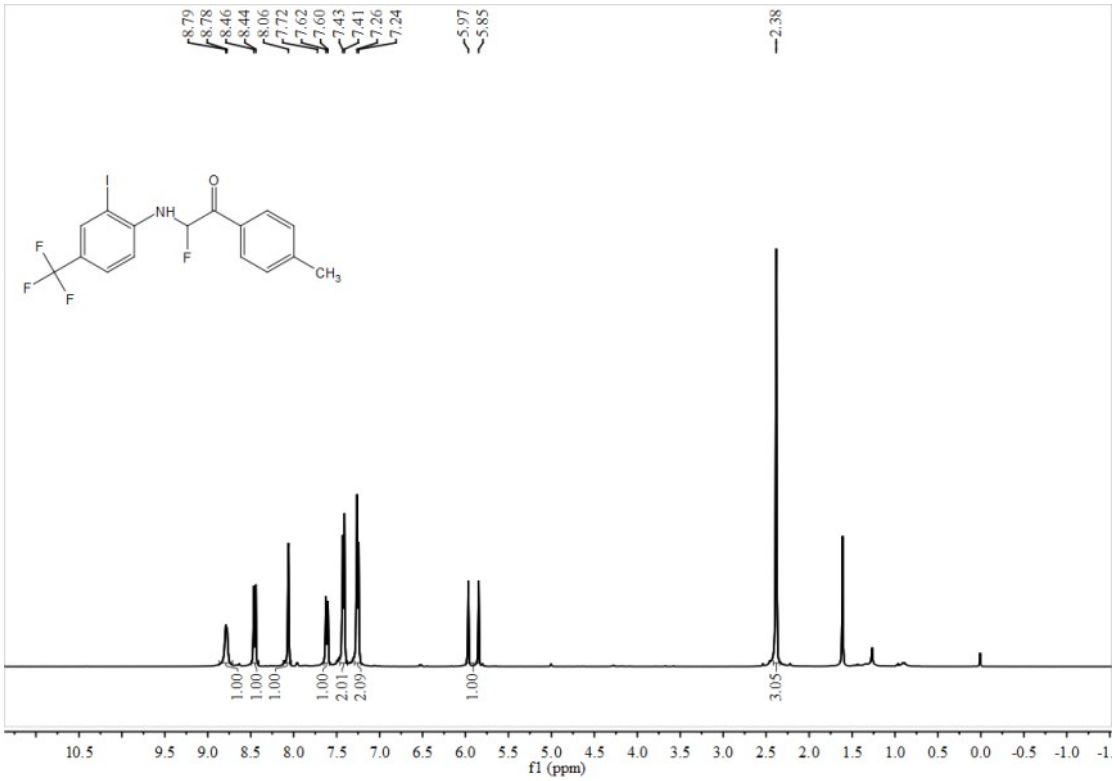
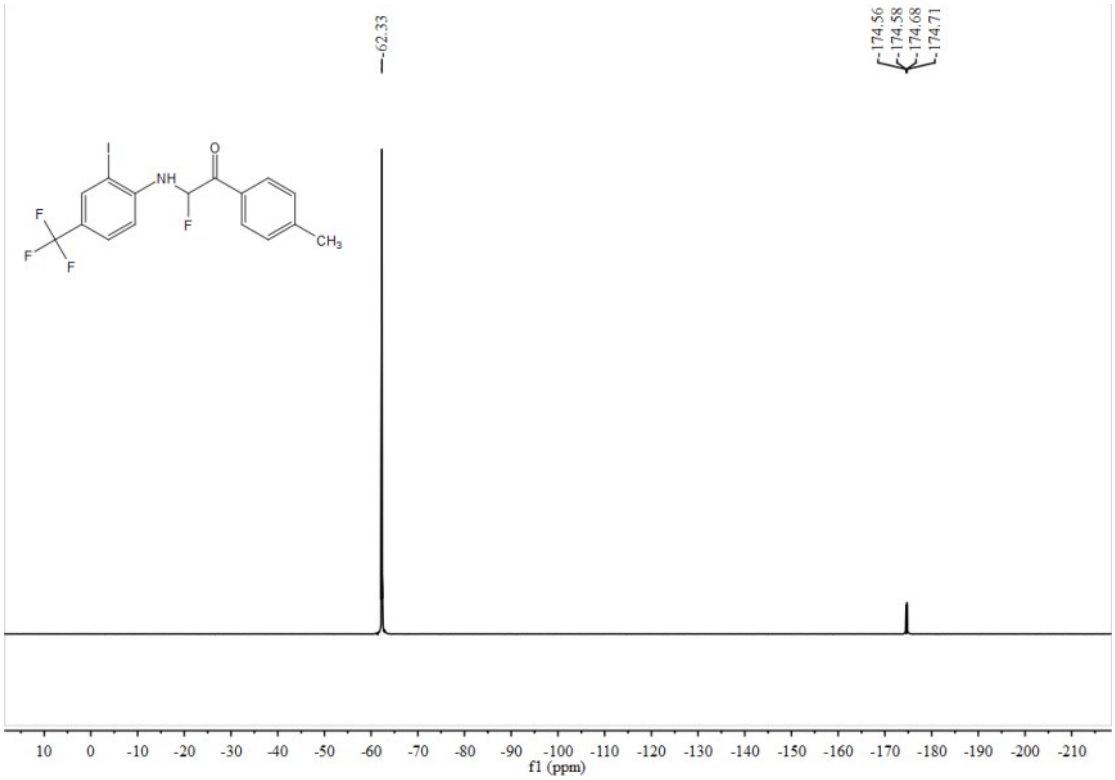
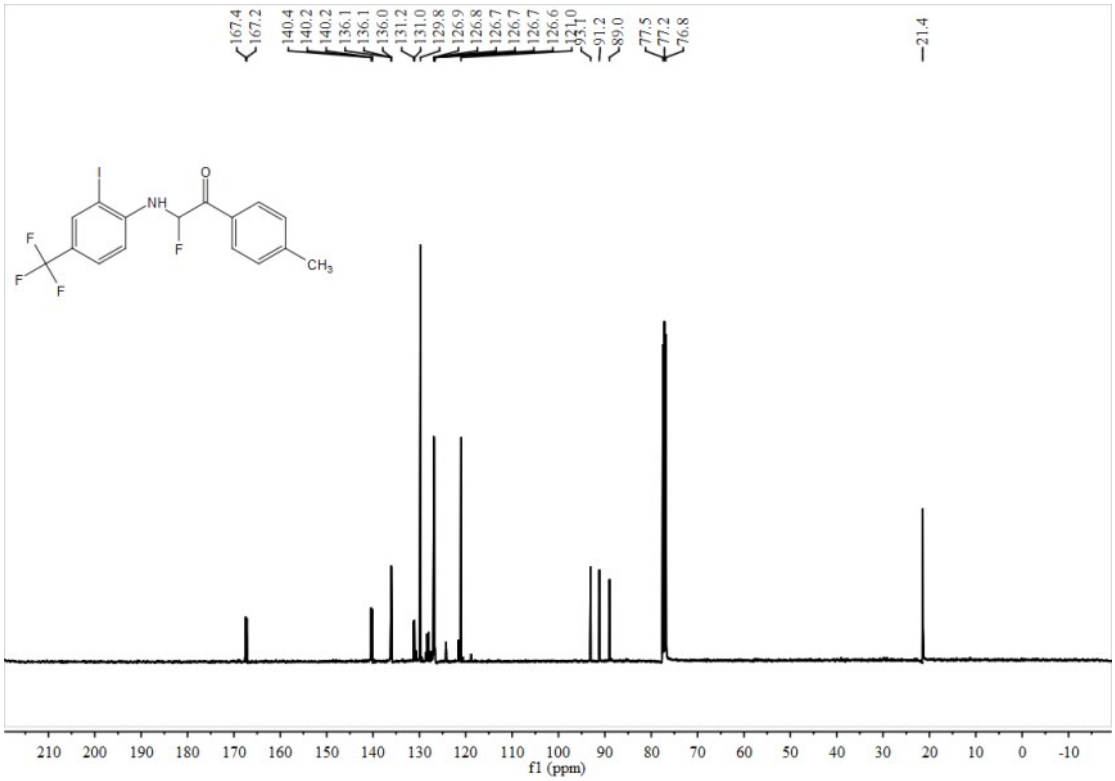


^{1}H NMR of **3t**



^{19}F NMR of **3t**



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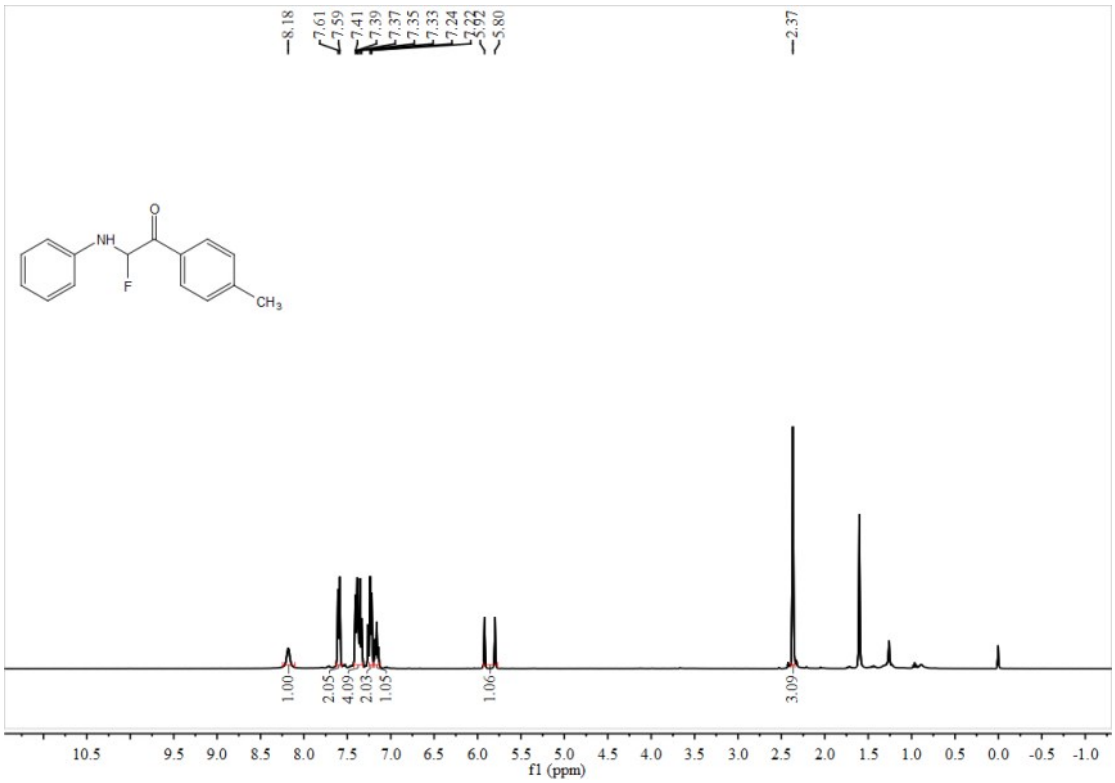
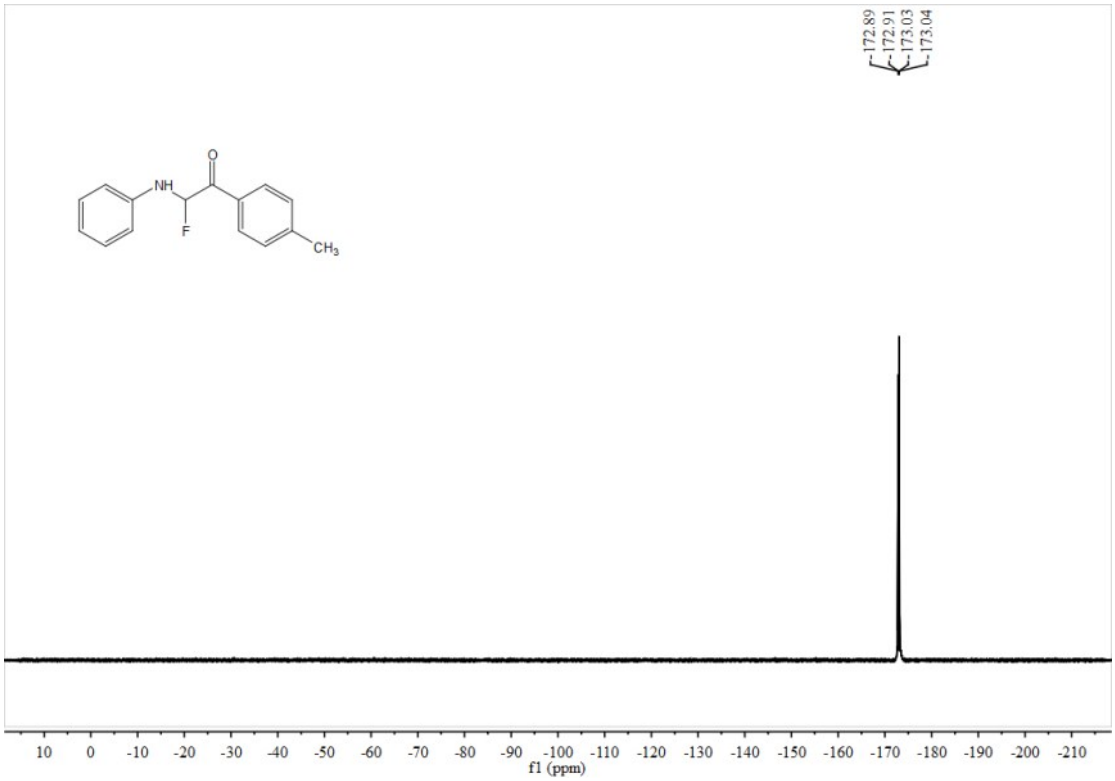
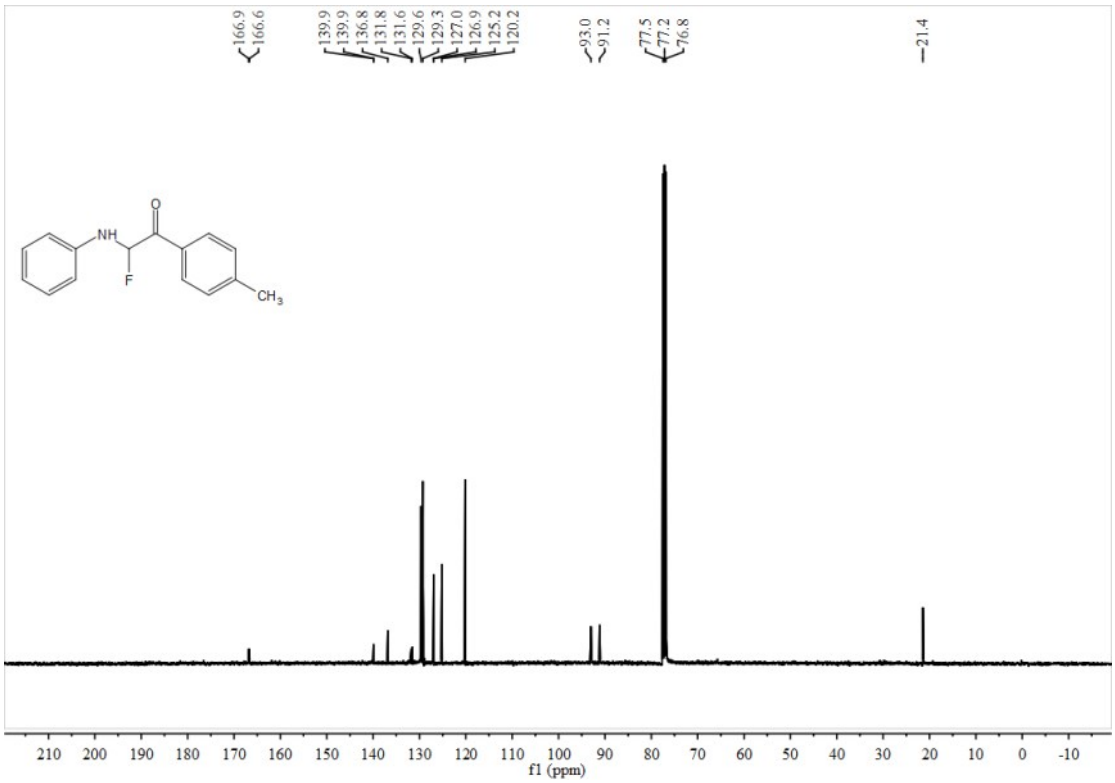


^{1}H NMR of **3u**



^{19}F NMR of **3u**


166.9
166.6
139.9
139.9
136.8
131.8
131.6
129.6
129.3
127.0
126.9
125.2
120.2
93.0
91.2
77.5
77.2
76.8
21.4
NH
F
O
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

^{13}C NMR of **3u**