

Supporting Information

Direct Access to α,α -chlorofluoro Arylketones via Mild Electrophilic Heterohalogenation of Arylalkynes

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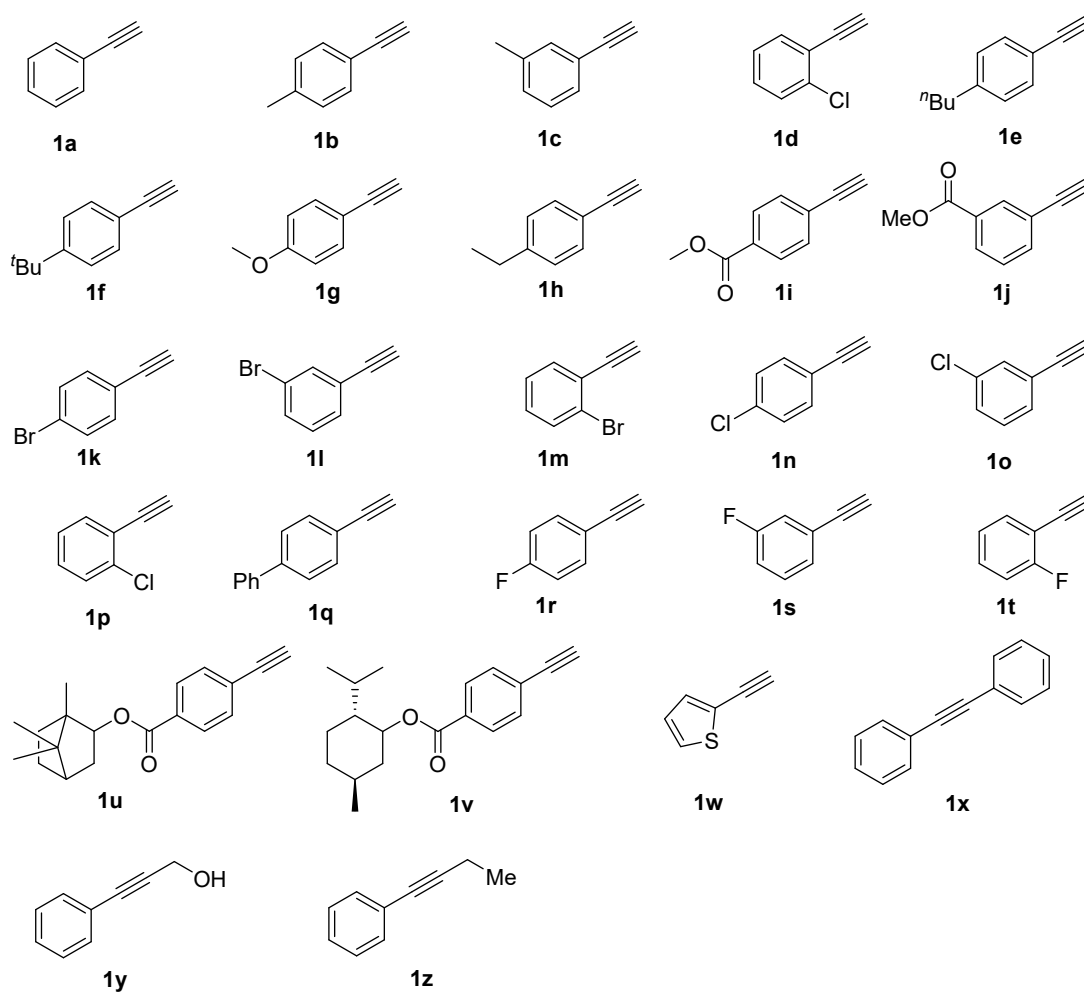
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General information

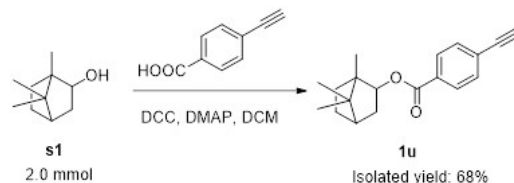
Chemicals and solvents were purchased from commercial sources (Energy Chemical, J&KChemic, TCI, Fluka, Acros, SCRC) and used without further purification and used as received unless noted. All products were purified by flash chromatography on silica gel. The chemical yields referred are isolated products. ^1H , ^{13}C and ^{19}F Nuclear Magnetic Resonance (^1H , ^{13}C and ^{19}F NMR) spectra were recorded on Bruker 500 MHz NMR spectrometer using Deuterated chloroform (CDCl_3) as solvent and tetramethylsilane (TMS) as an internal standard. ^1H NMR and ^{13}C NMR spectra were recorded on 500MHz MHz Bruker spectrometers. Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane. The used abbreviations are as follows: s (singlet), d (doublet), t (triplet), quart. (quartet), quint (quintet), m (multiplet). Multiplets which arise from accidental equality of coupling constants of magnetically non-equivalent protons are marked as virtual (virt.). High resolution mass spectra (HRMS) data were measured by ESI-microTOF II. Melting points were measured by SGW® X-4B and are not corrected. Reactions were monitored by TLC analysis using silica gel 60 Å F-254 thin layer plates and compounds were visualized with a UV light at 254 nm or 365 nm. Moreover, Aromatic Alkynes are named as **1**, the final products α,α -chlorofluoroketones are named **2** respectively.



Scheme S1. Substrates employed for the reaction

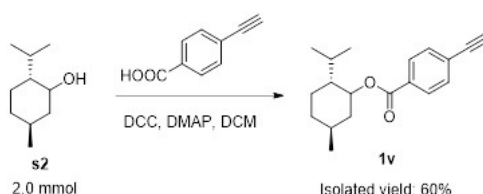
Substrate preparation

Synthesis of compound 1u: In a 25 mL round-bottom flask, L(-)-Borneol **s1** (2.0 mmol), 4-ethynyl-benzoic acid (2.4 mmol), DMAP (0.2 mmol), CH₂Cl₂ (10 mL) and dicyclohexylcarbodiimide (4.0 mmol) were successively added. The mixture was stirred at room temperature overnight. The reaction was quenched with aqueous NH₄Cl, extracted with EtOAc (3 × 30 mL). The combined ethyl acetate layer was washed with brine (10 mL) and dried over anhydrous Na₂SO₄. The solvent was removed under vacuum. The crude product was purified by flash column chromatography (eluting with petroleum ether/ethyl acetate = 10/1) on silica gel to afford product **1u** (384.1 mg, 68% yield) as a white solid.



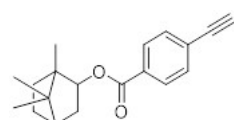
Scheme S2. The general procedure synthesis experiment of **1u**

Synthesis of compound 1v: In a 25 mL round-bottom flask, L-Menthol **s2** (2.0 mmol), 4-ethynyl-benzoic acid (2.4 mmol), DMAP (0.2 mmol), CH₂Cl₂ (10 mL) and dicyclohexylcarbodiimide (4.0 mmol) were successively added. The mixture was stirred at room temperature overnight. The reaction was quenched with aqueous NH₄Cl, extracted with EtOAc (3 × 30 mL). The combined ethyl acetate layer was washed with brine (10 mL) and dried over anhydrous Na₂SO₄. The solvent was removed under vacuum. The crude product was purified by flash column chromatography (eluting with petroleum ether/ethyl acetate = 10/1) on silica gel to afford product **1v** (341.3 mg, 60% yield) with light yellow liquid.



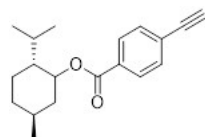
Scheme S3. The general procedure synthesis experiment of **1v**

(1) 1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 4-ethynylbenzoate (**1u**)



White solid (192.0 mg, 68%). MP: 83-85 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.01 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 2H), 5.11 (ddd, *J* = 10.0, 3.5, 2.2 Hz, 1H), 3.23 (s, 1H), 2.53 – 2.43 (m, 1H), 2.11 (ddd, *J* = 12.9, 9.5, 4.5 Hz, 1H), 1.81 (ttd, *J* = 12.1, 4.4, 3.2 Hz, 1H), 1.74 (t, *J* = 4.5 Hz, 1H), 1.45 – 1.37 (m, 1H), 1.31 (ddd, *J* = 12.1, 9.4, 4.4 Hz, 1H), 1.11 (dd, *J* = 13.9, 3.5 Hz, 1H), 0.96 (s, 3H), 0.91 (d, *J* = 3.5 Hz, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 166.1, 132.0, 130.8, 129.4, 126.5, 82.9, 80.8, 79.9, 49.1, 47.9, 44.9, 36.9, 28.1, 27.4, 19.7, 18.9, 13.6.

(2) (2R,5S)-2-isopropyl-5-methylcyclohexyl 4-ethynylbenzoate (**1v**)

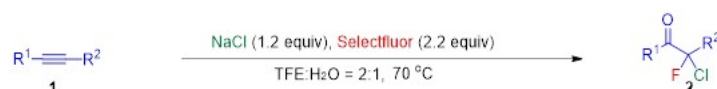


Light yellow oil (170.6 mg, 60%). ¹H NMR (500 MHz, CDCl₃) δ 7.99 (d, *J* = 8.5 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 4.93 (td, *J* = 10.8, 4.4 Hz, 1H), 3.22 (s, 1H), 2.12 (dtd, *J* = 12.0, 4.0, 1.7 Hz, 1H), 1.94 (ddt, *J* = 14.0, 7.0, 3.5 Hz, 1H),

1.77 – 1.68 (m, 2H), 1.55 (dddd, $J = 13.8, 12.4, 6.5, 3.3$ Hz, 2H), 1.17 – 1.05 (m, 2H), 0.92 (t, $J = 6.5$ Hz, 7H), 0.79 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 165.4, 132.0, 130.8, 129.40, 126.5, 82.7, 79.9, 75.1, 47.2, 40.9, 34.3, 31.4, 26.5, 23.6, 22.0, 20.7, 16.5.

Typical procedure for the synthesis of 2

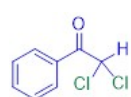
Synthesis of compound 2: A solution of alkynes **1** (1.0 mmol), Selectfluor (2.2 mmol, 2.2 equiv), NaCl (1.2 mmol, 1.2 equiv), in $\text{CF}_3\text{CH}_2\text{OH}/\text{H}_2\text{O}$ (2/1, 3.0 ml) were stirred under air atmosphere at 70 °C (heating mantle) for 3-4 h. After completion of the reaction, the solvent was removed under reduced pressure by rotary evaporation. Then, the product **2** was obtained by flash column chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 10:1).



Scheme S4. The general procedure synthesis experiment of α,α -chlorofluoro ketones

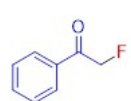
Control experiments

(1) 2,2-dichloro-1-phenylethan-1-one (**4a'**)

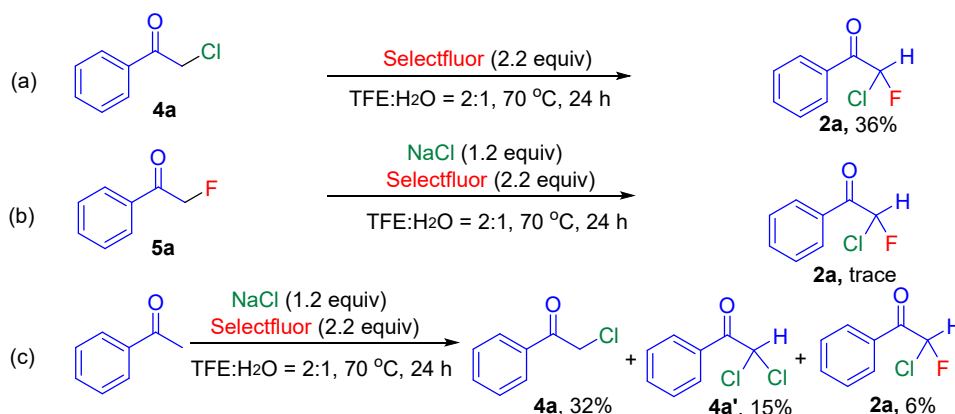


Light yellow liquid. ^1H NMR (500 MHz, CDCl_3) δ 8.08 (dd, $J = 8.4, 1.1$ Hz, 2H), 7.65 (t, $J = 7.4$ Hz, 1H), 7.52 (t, $J = 7.9$ Hz, 2H), 6.71 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 185.8, 134.5, 131.2, 129.7, 128.9, 67.7.

(2) 2-fluoro-1-phenylethan-1-one (**5a**)



Light yellow liquid. ^1H NMR (500 MHz, CDCl_3) δ 7.90 (d, $J = 8.0$ Hz, 2H), 7.64 (t, $J = 7.4$ Hz, 1H), 7.51 (t, $J = 7.8$ Hz, 2H), 5.56 (d, $J = 46.9$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 193.5 (d, $J_{\text{C-F}} = 7.5$ Hz), 134.2, 133.7, 129.0, 127.8 (d, $J_{\text{C-F}} = 1.3$ Hz), 83.6 (d, $J_{\text{C-F}} = 90.6$ Hz).



Scheme S5. Control experiments

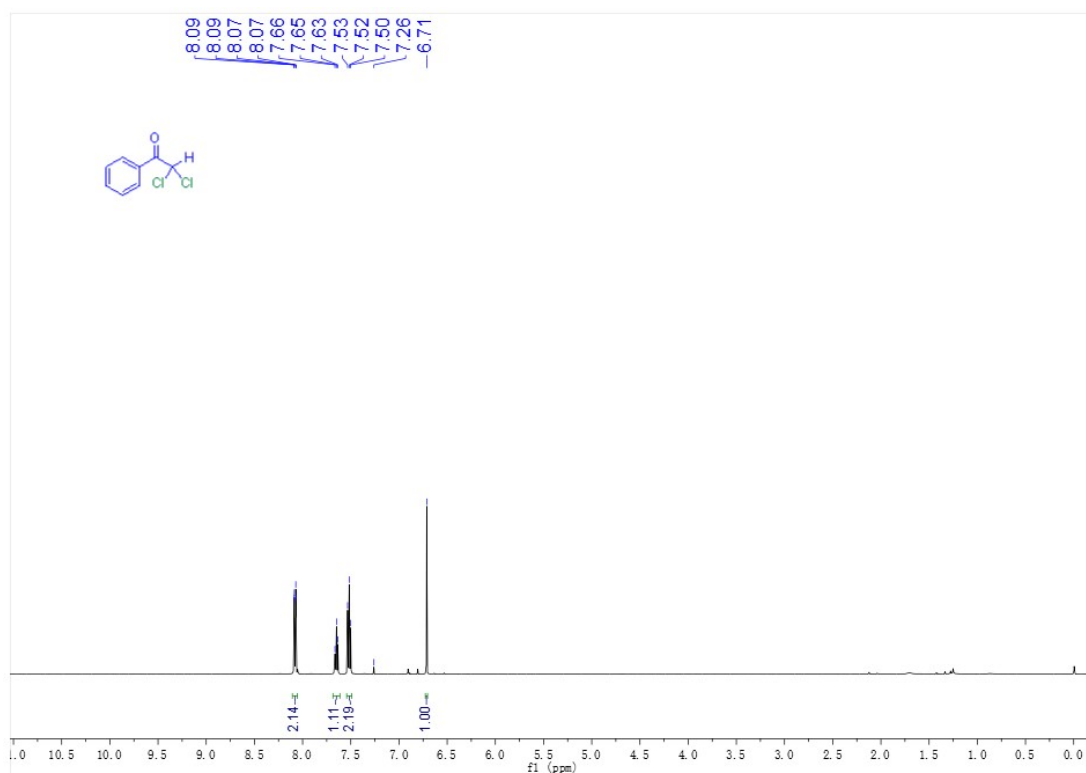


Figure S1. $^1\text{H-NMR}$ spectrum of 4a'

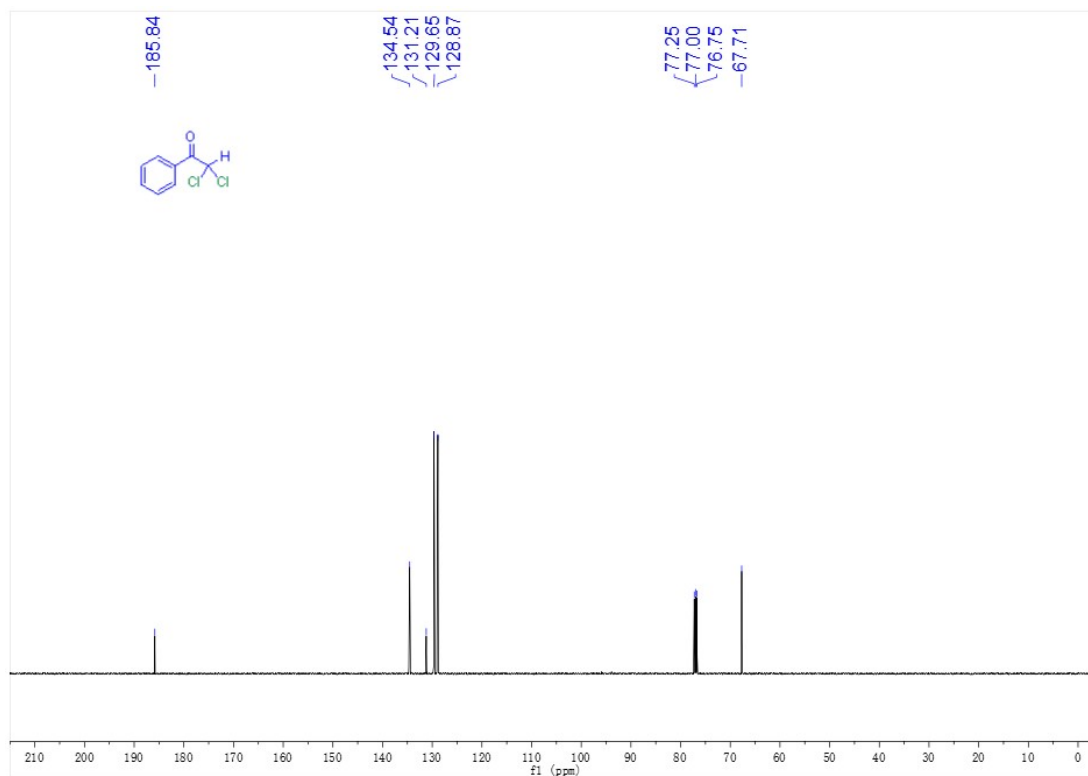


Figure S2. $^{13}\text{C-NMR}$ spectrum of 4a'

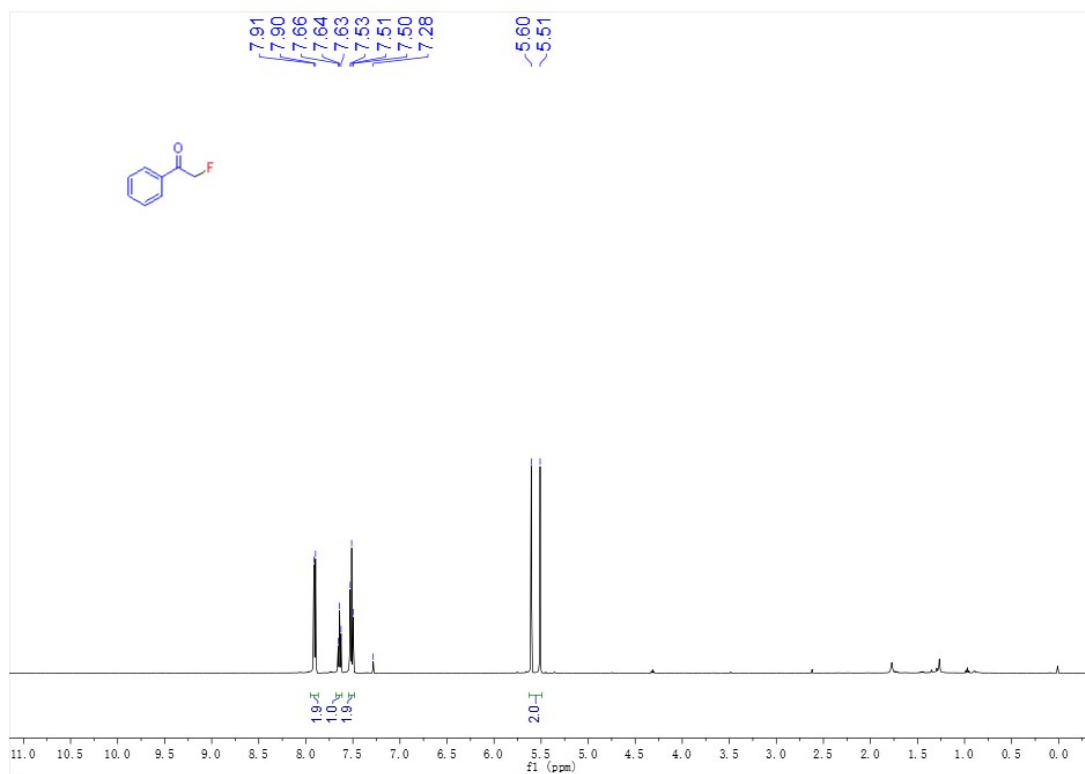


Figure S3. ¹H-NMR spectrum of 5a

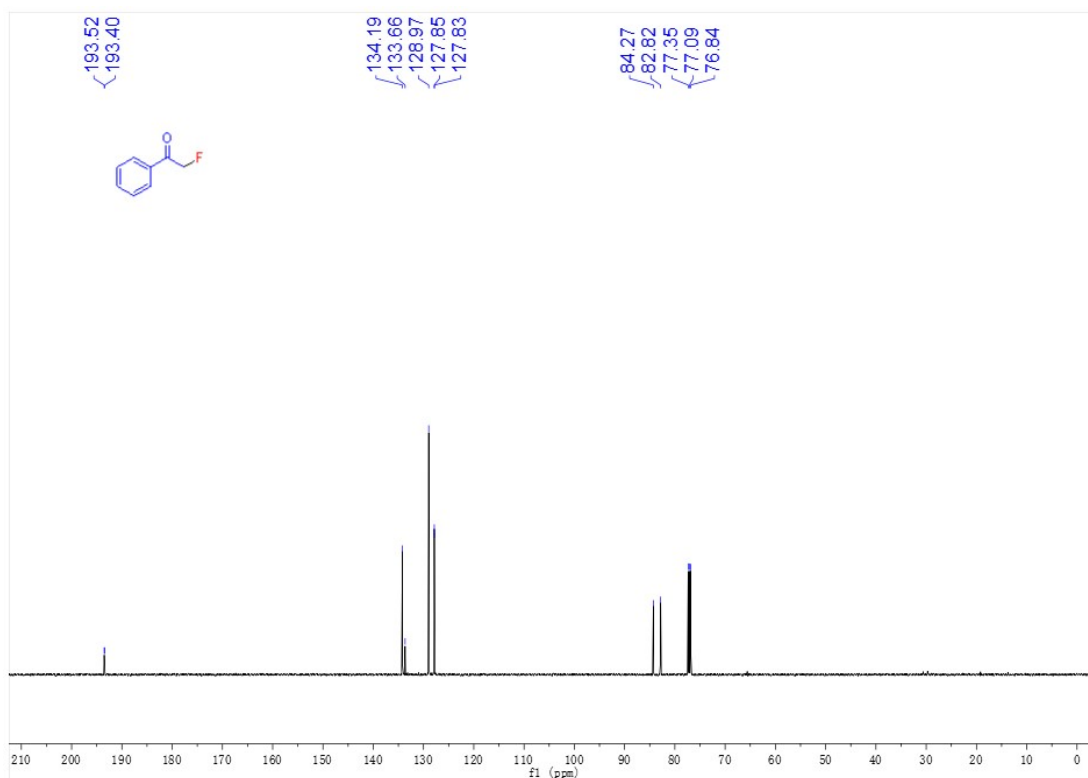


Figure S4. ¹³C-NMR spectrum of 5a

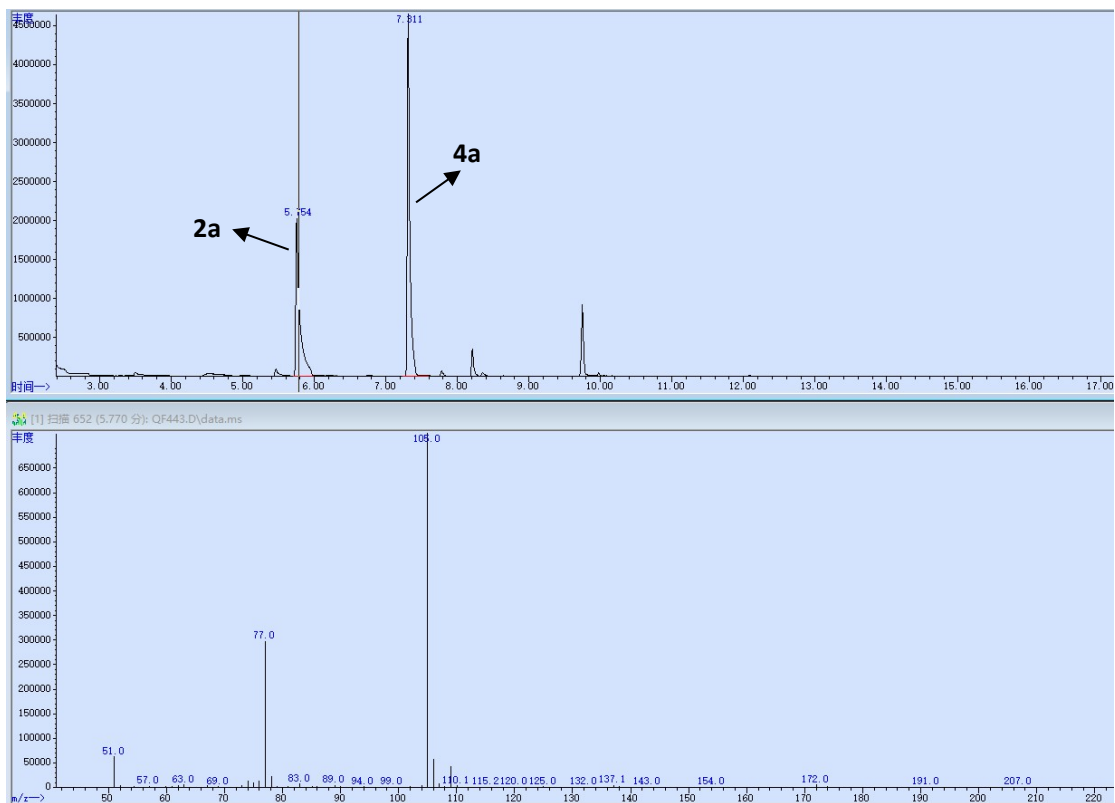


Figure S5. GC-MS analysis of control experiment (a)

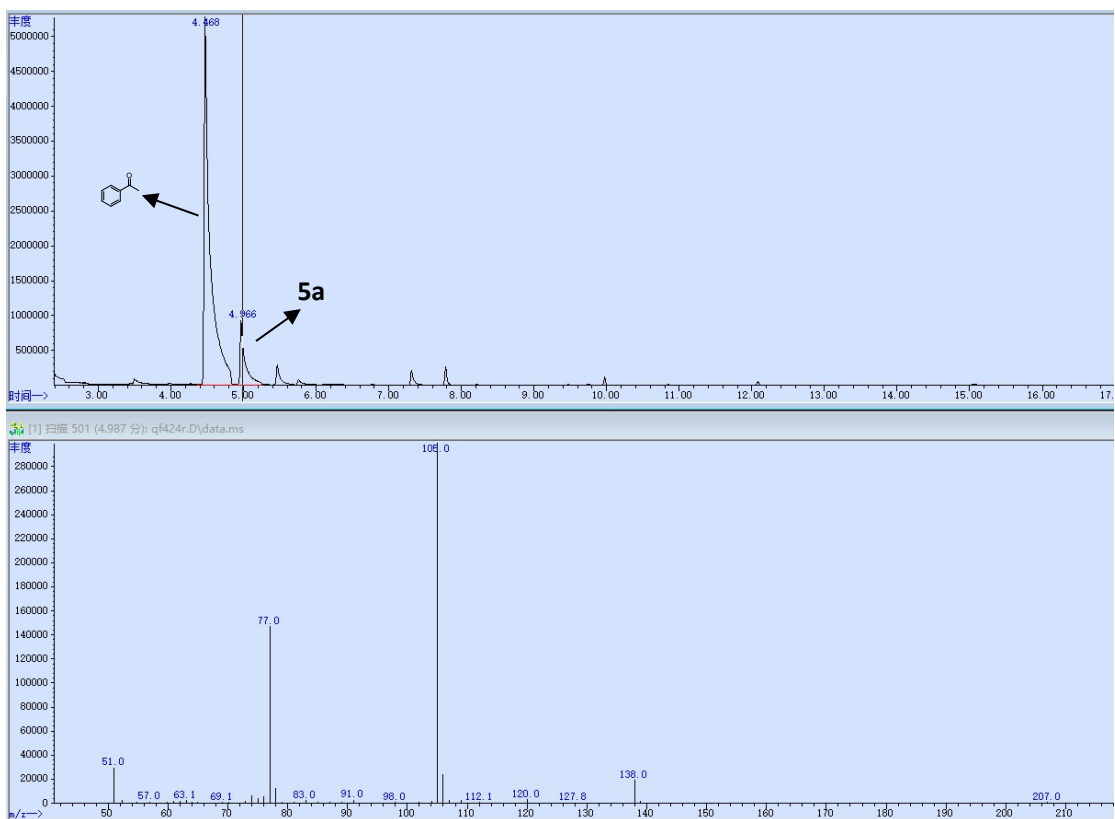


Figure S6. GC-MS analysis of control experiment (d)

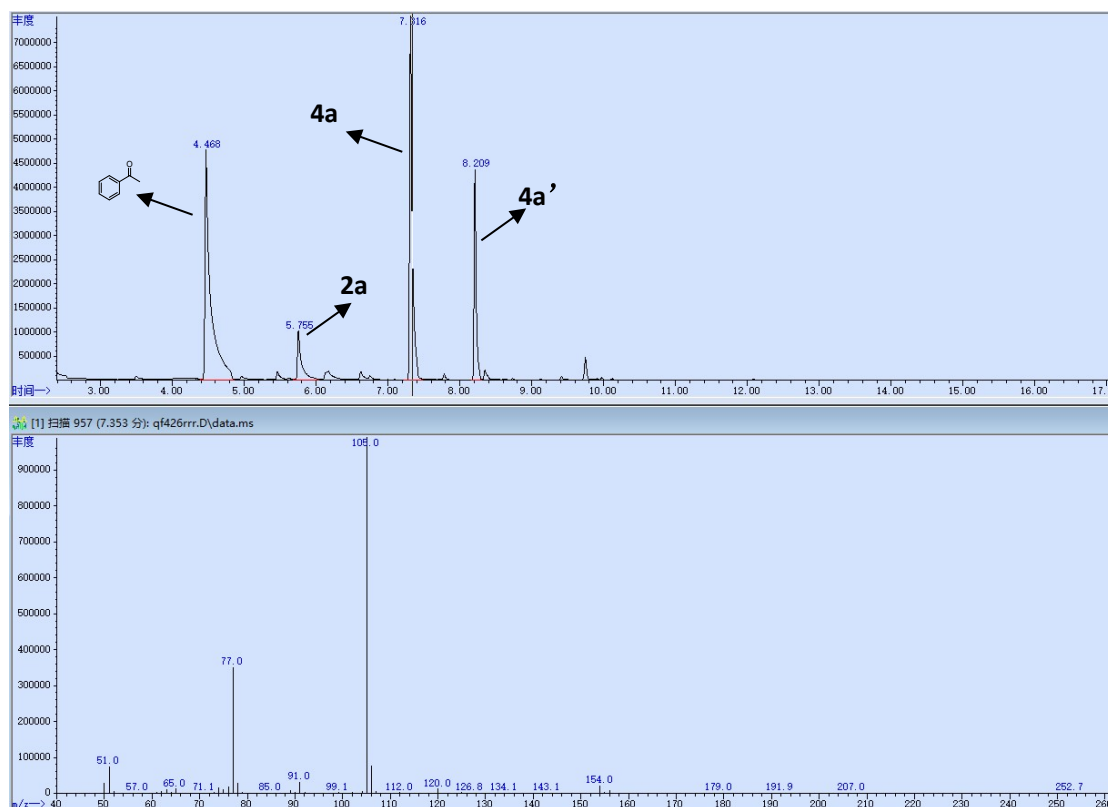
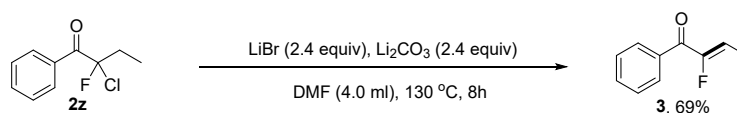


Figure S7. GC-MS analysis of control experiment (e)

The transformation of products

General procedure for compound 3



Scheme S6. The general procedure synthesis experiment of 3

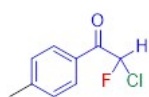
(Z)-2-fluoro-1-phenylbut-2-en-1-one: A solution of **2z** (1.0 mmol), LiBr (2.4 mmol, 2.4 equiv), Li₂CO₃ (2.4 mmol, 2.4 equiv), in DMF (4.0 mL) was stirred under air atmosphere at 130 °C (heating mantle) for 8 h in Fig. 5. After completion of the reaction, the solvent was removed under reduced pressure by rotary evaporation. Then, the compound **3** was obtained (113.3 mg, 69% yield) by flash column chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 5:1).

Analytic data of the obtained compounds

(1) 2-chloro-2-fluoro-1-phenylethan-1-one (**2a**)

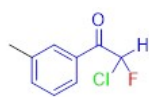
Light yellow oil (139.8 mg, 81%, purity > 99.5%). ¹H NMR (500 MHz, CDCl₃) δ 8.07 (d, *J* = 8.2 Hz, 2H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 7.9 Hz, 2H), 6.84 (d, *J* = 50.8 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 187.3 (d, *J*_{C-F} = 22.5 Hz), 134.7, 131.1, 129.6 (d, *J*_{C-F} = 2.5 Hz), 128.9, 95.1 (d, *J*_{C-F} = 256.2 Hz); ¹⁹F NMR (471 MHz, CDCl₃) δ -146.6 (d, *J* = 51.8 Hz, 1F). HRMS (ESI-TOF): calcd. for C₈H₇FCIO [M+H]⁺: 173.0164; found: 173.0160.

(2) 2-chloro-2-fluoro-1-(p-tolyl)ethan-1-one (**2b**)



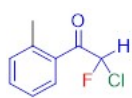
Light yellow oil (128.8 mg, 69%, purity = 99%). ^1H NMR (500 MHz, CDCl_3) δ 7.96 (d, $J = 8.2$ Hz, 2H), 7.31 (d, $J = 8.1$ Hz, 2H), 6.82 (d, $J = 50.8$ Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 186.9 (d, $J_{\text{C-F}} = 22.5$ Hz), 146.0, 129.7 (d, $J_{\text{C-F}} = 2.5$ Hz), 129.6, 128.6, 95.1 (d, $J_{\text{C-F}} = 256.3$ Hz), 21.8; ^{19}F NMR (471 MHz, CDCl_3) δ -146.4 (d, $J = 51.81$ Hz, 1F). HRMS (ESI-TOF): calcd. for $\text{C}_9\text{H}_9\text{FClO}$ [$\text{M}+\text{K}$] $^+$: 224.9879; found: 224.9890.

(3) 2-chloro-2-fluoro-1-(m-tolyl)ethan-1-one (**2c**)



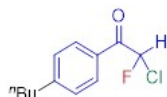
Light yellow oil (126.9 mg, 68%, purity = 99%). ^1H NMR (500 MHz, CDCl_3) δ 7.85 (d, $J = 8.2$ Hz, 2H), 7.47 (d, $J = 7.8$ Hz, 1H), 7.40 (t, $J = 7.6$ Hz, 1H), 6.85 (d, $J = 50.8$ Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 187.4 (d, $J_{\text{C-F}} = 22.5$ Hz), 138.9, 135.6, 131.1, 130.0 (d, $J_{\text{C-F}} = 2.5$ Hz), 128.7, 126.8 (d, $J_{\text{C-F}} = 2.5$ Hz), 94.9 (d, $J_{\text{C-F}} = 255.0$ Hz), 21.3; ^{19}F NMR (471 MHz, CDCl_3) δ -146.7 (d, $J = 51.8$ Hz, 1F). HRMS (ESI-TOF): calcd. for $\text{C}_9\text{H}_8\text{FClO}$ [$\text{M} + \text{K}$] $^+$: 224.9879; found: 224.9878.

(4) 2-chloro-2-fluoro-1-(o-tolyl)ethan-1-one (**2d**)



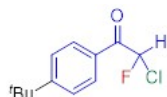
Light yellow oil (121.3 mg, 65%, purity > 99.5%). ^1H NMR (500 MHz, CDCl_3) δ 7.78 (d, $J = 7.8$ Hz, 1H), 7.48 (t, $J = 7.1$ Hz, 1H), 7.36 – 7.28 (m, 2H), 6.82 (d, $J = 51.0$ Hz, 1H), 2.55 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 189.7 (d, $J_{\text{C-F}} = 21.3$ Hz), 141.0, 133.1, 132.5, 131.3, 129.2 (d, $J_{\text{C-F}} = 3.8$ Hz), 125.7, 94.9 (d, $J_{\text{C-F}} = 256.3$ Hz), 21.4; ^{19}F NMR (471 MHz, CDCl_3) δ -145.2 (d, $J = 47.1$ Hz, 1F). HRMS (ESI-TOF): calcd. for $\text{C}_9\text{H}_8\text{FClO}$ [$\text{M}+\text{Na}$] $^+$: 209.0140; found: 209.0134.

(5) 1-(4-butylphenyl)-2-chloro-2-fluoroethan-1-one (**2e**)



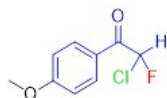
Light yellow oil (162.4 mg, 71%, purity > 99.5%). ^1H NMR (500 MHz, CDCl_3) δ 7.98 (d, $J = 8.2$ Hz, 2H), 7.32 (d, $J = 8.3$ Hz, 2H), 6.83 (d, $J = 50.8$ Hz, 1H), 2.69 (t, $J = 10.0$ Hz, 2H), 1.63 (m, 2H), 1.37 (m, 2H), 0.94 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 187.0 (d, $J_{\text{C-F}} = 21.3$ Hz), 150.9, 129.8 (d, $J_{\text{C-F}} = 2.5$ Hz), 129.0, 128.8, 95.2 (d, $J_{\text{C-F}} = 256.3$ Hz), 35.8, 33.0, 22.3, 13.8; ^{19}F NMR (471 MHz, CDCl_3) δ -146.3 (d, $J = 51.81$ Hz, 1F). HRMS (ESI-TOF): calcd. for $\text{C}_{12}\text{H}_{14}\text{FClO}$ [$\text{M}+\text{Na}$] $^+$: 251.0609; found: 251.0606.

(6) 1-(4-(tert-butyl)phenyl)-2-chloro-2-fluoroethan-1-one (**2f**)



Light yellow oil (148.6 mg, 65%, purity = 98%). ^1H NMR (500 MHz, CDCl_3) δ 8.01 (d, $J = 8.3$ Hz, 2H), 7.53 (d, $J = 8.7$ Hz, 2H), 6.83 (d, $J = 50.8$ Hz, 1H), 1.35 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 186.9 (d, $J_{\text{C-F}} = 22.5$ Hz), 158.9, 129.6 (d, $J_{\text{C-F}} = 2.5$ Hz), 128.5, 125.9, 95.2 (d, $J_{\text{C-F}} = 256.2$ Hz), 35.3, 30.9; ^{19}F NMR (471 MHz, CDCl_3) δ -146.4 (d, $J = 51.8$ Hz, 1F). HRMS (ESI-TOF): calcd. for $\text{C}_{12}\text{H}_{15}\text{FClO}$ [$\text{M}+\text{H}$] $^+$: 229.0790; found: 229.0792.

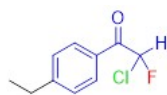
(7) 2-chloro-2-fluoro-1-(4-methoxyphenyl)ethan-1-one (**2g**)



Yellow oil (156.0 mg, 77%, purity > 99.5%). ^1H NMR (500 MHz, CDCl_3) δ 8.05 (d, $J = 8.5$ Hz, 2H), 7.00 – 6.95 (m, 2H), 6.79 (d, $J = 50.9$ Hz, 1H), 3.90 (s,

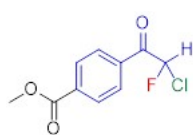
3H); ^{13}C NMR (125 MHz, CDCl_3) δ 185.9 (d, $J_{\text{C-F}} = 22.5$ Hz), 164.7, 132.1 (d, $J_{\text{C-F}} = 2.5$ Hz), 123.9, 114.2, 95.4 (d, $J_{\text{C-F}} = 255.0$ Hz), 55.6; ^{19}F NMR (471 MHz, CDCl_3) δ -145.5 (d, $J = 51.8$ Hz, 1F). HRMS (ESI-TOF): calcd. for $\text{C}_9\text{H}_9\text{FCIO}_2$ $[\text{M}+\text{H}]^+$: 203.0270; found : 203.0270.

(8) 2-chloro-1-(4-ethylphenyl)-2-fluoroethan-1-one (**2h**)



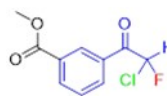
Light yellow oil (132.4 mg, 66%, purity = 99%). ^1H NMR(500 MHz, CDCl_3) δ 7.99 (d, $J = 8.2$ Hz, 2H), 7.34 (d, $J = 8.3$ Hz, 2H), 6.82 (d, $J = 55.0$ Hz, 1H), 2.74 (q, $J = 7.6$ Hz, 2H), 1.27 (t, $J = 7.6$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 188.0 (d, $J_{\text{C-F}} = 21.2$ Hz), 152.1, 129.8 (d, $J_{\text{C-F}} = 2.5$ Hz), 128.8, 128.4, 95.1 (d, $J_{\text{C-F}} = 255.0$ Hz), 29.1, 15.0; ^{19}F NMR (471 MHz, CDCl_3) δ -146.4 (d, $J = 51.8$ Hz, 1F). HRMS (ESI-TOF): calcd. for $\text{C}_{10}\text{H}_{11}\text{FCIO}$ $[\text{M}+\text{H}]^+$: 201.0477; found : 201.0479.

(9) methyl 4-(2-chloro-2-fluoroacetyl)benzoate (**2i**)



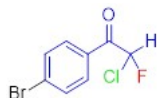
White solid (168.4 mg, 73%, purity>99.5%); MP: 77-80 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.20 – 8.08 (m, 4H), 6.82 (d, $J = 50.7$ Hz, 1H), 3.96 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 186.92(d, $J_{\text{C-F}} = 23.8$ Hz), 165.8, 135.2, 134.3 (d, $J_{\text{C-F}} = 2.5$ Hz), 129.9, 129.6 (d, $J_{\text{C-F}} = 2.5$ Hz), 95.3 (d, $J_{\text{C-F}} = 256.3$ Hz), 52.6; ^{19}F NMR (471 MHz, CDCl_3) δ -146.6 (d, $J = 47.1$ Hz, 1F). HRMS (ESI-TOF): calcd. for $\text{C}_{10}\text{H}_9\text{FCIO}_3$ $[\text{M}+\text{H}]^+$: 231.0218; found : 231.0211.

(10) methyl 3-(2-chloro-2-fluoroacetyl)benzoate (**2j**)



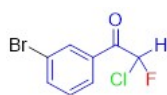
Light yellow oil (173.0 mg, 75%, purity>99.5%). ^1H NMR (500 MHz, CDCl_3) δ 8.67 (s, 1H), 8.30 (d, $J = 8.9$ Hz, 1H), 8.25 (d, $J = 8.6$ Hz, 1H), 7.61 (t, $J = 7.8$ Hz, 1H), 6.87 (d, $J = 50.6$ Hz, 1H), 3.95 (d, $J = 0.8$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 186.6 (d, $J_{\text{C-F}} = 22.5$ Hz), 165.7, 135.4, 133.7 (d, $J_{\text{C-F}} = 2.5$ Hz), 131.4, 131.0, 130.6 (d, $J_{\text{C-F}} = 2.5$ Hz), 129.2, 95.1 (d, $J_{\text{C-F}} = 256.2$ Hz), 52.6; ^{19}F NMR (471 MHz, CDCl_3) δ -146.9 (d, $J = 51.8$ Hz, 1F). HRMS (ESI-TOF): calcd. for $\text{C}_{10}\text{H}_9\text{FCIO}_3$ $[\text{M}+\text{H}]^+$: 231.0219; found : 231.0219.

(11) 1-(4-bromophenyl)-2-chloro-2-fluoroethan-1-one (**2k**)



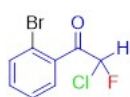
Light yellow oil (201.2 mg, 80%, purity>99.5%). ^1H NMR (500 MHz, CDCl_3) δ 7.94 (d, $J = 8.2$ Hz, 2H), 7.70 – 7.65 (m, 2H), 6.76 (d, $J = 50.8$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 186.6 (d, $J_{\text{C-F}} = 23.7$ Hz), 132.3, 131.1 (d, $J_{\text{C-F}} = 2.5$ Hz), 130.3, 129.7, 95.4 (d, $J_{\text{C-F}} = 256.2$ Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -146.0 (d, $J = 51.8$ Hz, 1F). HRMS (ESI-TOF): calcd. for $\text{C}_8\text{H}_6\text{FCIBrO}$ $[\text{M}+\text{H}]^+$: 250.9269; found : 250.9274.

(12) 1-(3-bromophenyl)-2-chloro-2-fluoroethan-1-one (**2l**)



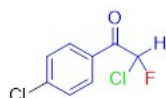
Light yellow oil (181.1 mg, 72%, purity>99.5%). ^1H NMR (500 MHz, CDCl_3) δ 8.19 (s, 1H), 8.03 – 7.97 (m, 1H), 7.78 (ddd, $J = 8.0, 1.9, 1.0$ Hz, 1H), 7.41 (t, $J = 7.9$ Hz, 1H), 6.78 (d, $J = 50.7$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 186.2 (d, $J_{\text{C-F}} = 23.7$ Hz), 137.6, 132.7 (d, $J_{\text{C-F}} = 2.5$ Hz), 132.5 (d, $J_{\text{C-F}} = 2.5$ Hz), 130.4, 128.2 (d, $J_{\text{C-F}} = 2.5$ Hz), 123.1, 95.2 (d, $J_{\text{C-F}} = 256.2$ Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -145.4 (d, $J = 51.8$ Hz, 1F). HRMS (ESI-TOF): calcd. for $\text{C}_8\text{H}_6\text{FCIBrO}$ $[\text{M}+\text{H}]^+$: 250.9269; found : 250.9275.

(13) 1-(2-bromophenyl)-2-chloro-2-fluoroethan-1-one (**2m**)



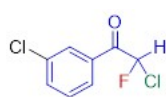
Light yellow oil (188.6 mg, 75%, purity = 98%). ^1H NMR (500 MHz, CDCl_3) δ 7.67 (dd, $J = 7.7, 1.3$ Hz, 1H), 7.58 (dd, $J = 7.5, 1.9$ Hz, 1H), 7.47 – 7.38 (m, 2H), 6.96 (d, $J = 50.5$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 190.7 (d, $J_{\text{C-F}} = 23.7$ Hz), 135.4, 133.9, 133.2, 130.3 (d, $J_{\text{C-F}} = 2.5$ Hz), 127.5, 119.8, 94.6 (d, $J_{\text{C-F}} = 256.2$ Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -145.7 (d, $J = 51.8$ Hz, 1F). HRMS (ESI-TOF): calcd. for $\text{C}_8\text{H}_6\text{FClBrO}$ $[\text{M}+\text{H}]^+$: 250.0469; found : 250.0475.

(14) 2-chloro-1-(4-chlorophenyl)-2-fluoroethan-1-one (**2n**)



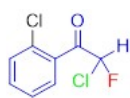
Light yellow oil (157.3 mg, 76%, purity = 98%). ^1H NMR (500 MHz, CDCl_3) δ 8.02 (d, $J = 8.2$ Hz, 2H), 7.54 – 7.45 (m, 2H), 6.77 (d, $J = 50.8$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 186.3 (d, $J_{\text{C-F}} = 22.5$ Hz), 141.4, 131.1, 131.1, 129.3, 95.4 (d, $J_{\text{C-F}} = 256.2$ Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -145.9 (d, $J = 51.8$ Hz, 1F). HRMS (ESI-TOF): calcd. for $\text{C}_8\text{H}_6\text{FCl}_2\text{O}$ $[\text{M}+\text{H}]^+$: 206.9774; found : 206.9773.

(15) 2-chloro-1-(3-chlorophenyl)-2-fluoroethan-1-one (**2o**)



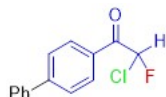
Light yellow oil (128.4 mg, 62%, purity > 99.5%). ^1H NMR (500 MHz, CDCl_3) δ 8.04 (s, 1H), 7.96 (d, $J = 7.7$ Hz, 1H), 7.63 (d, $J = 7.6$ Hz, 1H), 7.47 (t, $J = 7.9$ Hz, 1H), 6.78 (d, $J = 50.7$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 186.3 (d, $J_{\text{C-F}} = 23.8$ Hz), 135.3, 134.6, 132.6, 130.2, 129.6 (d, $J_{\text{C-F}} = 2.5$ Hz), 127.7 (d, $J_{\text{C-F}} = 2.5$ Hz), 96.3 (d, $J_{\text{C-F}} = 256.3$ Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -146.3 (d, $J = 51.81$ Hz, 1F). HRMS (ESI-TOF): calcd. for $\text{C}_8\text{H}_6\text{FCl}_2\text{O}$ $[\text{M}+\text{Na}]^+$: 228.9594; found : 228.9588.

(16) 2-chloro-1-(2-chlorophenyl)-2-fluoroethan-1-one (**2p**)



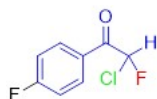
Light yellow oil (128.4 mg, 62%, purity > 99.5%). ^1H NMR (500 MHz, CDCl_3) δ 7.68 – 7.64 (m, 1H), 7.53 – 7.45 (m, 2H), 7.40 (td, $J = 7.7, 1.6$ Hz, 1H), 7.00 (d, $J = 50.5$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 190.0 (d, $J_{\text{C-F}} = 23.7$ Hz), 133.4, 133.3, 131.9, 130.7, 130.6 (d, $J_{\text{C-F}} = 2.5$ Hz), 127.1, 95.1 (d, $J_{\text{C-F}} = 255.0$ Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -145.9 (d, $J = 51.8$ Hz, 1F). HRMS (ESI-TOF): calcd. for $\text{C}_8\text{H}_5\text{FCl}_2\text{O}$ $\text{Na}[\text{M} + \text{Na}]^+$: 228.9594; found : 228.9596.

(17) 1-([1,1'-biphenyl]-4-yl)-2-chloro-2-fluoroethan-1-one (**2q**)



White solid (184.0 mg, 74%, purity = 99%); MP: 77-80 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.15 (d, $J = 8.2$ Hz, 2H), 7.76 – 7.72 (m, 2H), 7.64 (dt, $J = 8.3, 1.8$ Hz, 2H), 7.52 – 7.47 (m, 2H), 7.46 – 7.41 (m, 1H), 6.86 (d, $J = 50.8$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 186.9 (d, $J_{\text{C-F}} = 22.5$ Hz), 147.4, 139.3, 130.3 (d, $J_{\text{C-F}} = 2.5$ Hz), 129.7, 129.1, 128.7, 127.5, 127.3, 95.3 (d, $J_{\text{C-F}} = 255.0$ Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -146.3 (d, $J = 47.1$ Hz, 1F). HRMS (ESI-TOF): calcd. for $\text{C}_{14}\text{H}_{11}\text{FClO}$ $[\text{M}+\text{H}]^+$: 249.0477; found : 249.0476.

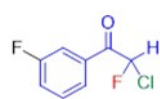
(18) 2-chloro-2-fluoro-1-(4-fluorophenyl)ethan-1-one (**2r**)



Light yellow oil (135.3 mg, 71%, purity > 99.5%). ^1H NMR (500 MHz, CDCl_3) δ 8.16 – 8.10 (m, 2H), 7.23 – 7.17 (m, 2H), 6.76 (d, $J = 50.8$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 186.0 (d, $J_{\text{C-F}} = 23.7$ Hz), 166.6 (d, $J_{\text{C-F}} = 256.2$ Hz), 132.6 (dd, $J_{\text{C-F}} = 8.7$ Hz, 2.5 Hz), 127.4, 116.3 (d, $J_{\text{C-F}} = 22.5$ Hz), 96.5 (d, $J_{\text{C-F}} = 256.2$ Hz); ^{19}F NMR

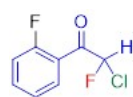
(471 MHz, CDCl₃) δ -101.30 – -101.25 (m, 1F), -145.5 (d, J = 51.8 Hz, 1F). HRMS (ESI-TOF): calcd. for C₈H₆F₂ClO [M+H]⁺ : 191.0069; found : 191.0067.

(19) 2-chloro-2-fluoro-1-(3-fluorophenyl)ethan-1-one (**2s**)



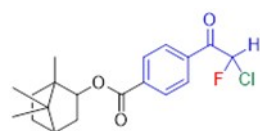
Light yellow oil (114.3 mg, 60%, purity>99.5%). ¹H NMR (500 MHz, CDCl₃) δ 7.87 (d, J = 7.9 Hz, 1H), 7.76 (d, J = 9.2 Hz, 1H), 7.51 (td, J = 8.0, 5.5 Hz, 1H), 7.37 (tdd, J = 8.2, 2.6, 0.9 Hz, 1H), 6.78 (d, J = 50.7 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 186.3 (dd, J_{C-F} = 23.8, 2.5 Hz), 162.7 (d, J_{C-F} = 247.5 Hz), 133.0 (dd, J_{C-F} = 6.3, 1.3 Hz), 130.6 (d, J_{C-F} = 7.5 Hz), 125.5 (t, J_{C-F} = 2.5 Hz), 121.9 (d, J_{C-F} = 21.3 Hz), 116.5 (dd, J_{C-F} = 23.8, 2.5 Hz), 95.3 (d, J_{C-F} = 256.3 Hz); ¹⁹F NMR (471 MHz, CDCl₃) δ -110.5 – -110.6 (m, 1F), -146.3 (d, J = 51.8 Hz, 1F). HRMS (ESI-TOF): calcd. for C₈H₅F₂ClOK [M+K]⁺ : 228.9629; found : 228.9634.

(20) 2-chloro-2-fluoro-1-(2-fluorophenyl)ethan-1-one (**2t**)



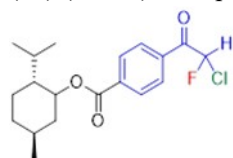
Light yellow oil (114.3 mg, 60%, purity>99.5%). ¹H NMR (500 MHz, CDCl₃) δ 8.00 (t, J = 6.7 Hz, 1H), 7.69 – 7.58 (m, 1H), 7.32 (t, J = 7.5 Hz, 1H), 7.19 (dd, J = 10.9, 8.7 Hz, 1H), 6.98 (d, J = 50.9 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 185.6 (dd, J_{C-F} = 22.5, 5.0 Hz), 161.5 (d, J_{C-F} = 253.8 Hz), 136.5 (d, J_{C-F} = 8.8 Hz), 131.7, 125.1 (d, J_{C-F} = 2.5 Hz), 120.6 (d, J_{C-F} = 12.5 Hz), 116.7 (d, J_{C-F} = 22.5 Hz), 95.2 (dd, J_{C-F} = 250.0, 12.5 Hz); ¹⁹F NMR (471 MHz, CDCl₃) δ -107.5 – -107.6 (m, 1F), -148.4 (dd, J = 51.8, 9.4 Hz, 1F). HRMS (ESI-TOF): calcd. for C₈H₅F₂ClOK[M+K]⁺ : 228.9628; found : 228.9630.

(21) 1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 4-(2-chloro-2-fluoroacetyl)benzoate (**2u**)



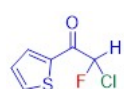
Light yellow oil (264.6 mg, 75%, purity = 98%). ¹H NMR (500 MHz, CDCl₃) δ 8.19 (d, J = 8.7 Hz, 2H), 8.14 (d, J = 8.4 Hz, 2H), 6.82 (d, J = 50.7 Hz, 1H), 5.14 (ddd, J = 10.0, 3.5, 2.2 Hz, 1H), 2.55 – 2.45 (m, 1H), 2.10 (ddd, J = 13.5, 9.5, 4.4 Hz, 1H), 1.82 (ttd, J = 12.2, 4.5, 3.2 Hz, 1H), 1.76 (t, J = 4.5 Hz, 1H), 1.43 (dddd, J = 13.0, 12.0, 4.5, 2.2 Hz, 1H), 1.31 (ddd, J = 12.2, 9.5, 4.7 Hz, 1H), 1.13 (dd, J = 13.9, 3.5 Hz, 1H), 0.97 (s, 3H), 0.92 (d, J = 2.2 Hz, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 187.0 (d, J_{C-F} = 22.5 Hz), 165.5, 136.0, 134.2 (d, J_{C-F} = 1.2 Hz), 129.8, 129.6 (d, J_{C-F} = 2.5 Hz), 95.3 (d, J_{C-F} = 255 Hz), 81.5, 49.1, 47.9, 44.9, 36.8, 28.1, 27.4, 19.7, 18.9, 13.6; ¹⁹F NMR (471 MHz, CDCl₃) δ -146.5 (dd, J = 51.8, 9.4 Hz, 1F). HRMS (ESI-TOF): calcd. for C₁₉H₂₃FClO₃[M+H]⁺ : 353.1314 ; found : 353.1310.

(22) (2R,5S)-2-isopropyl-5-methylcyclohexyl 4-(2-chloro-2-fluoroacetyl)benzoate (**2v**)



Light yellow oil (170.4 mg, 48%, purity = 97%). ¹H NMR (500 MHz, CDCl₃) δ 8.17 (d, J = 8.6 Hz, 2H), 8.13 (d, J = 8.5 Hz, 2H), 6.82 (dd, J = 50.7, 1.4 Hz, 1H), 4.96 (td, J = 10.9, 4.4 Hz, 1H), 2.13 (dtd, J = 12.0, 4.4, 3.9, 1.8 Hz, 1H), 1.93 (ddq, J = 10.0, 7.0, 3.6, 2.8 Hz, 1H), 1.78 – 1.71 (m, 2H), 1.56 (dq, J = 12.0, 3.4 Hz, 2H), 1.18 – 1.08 (m, 2H), 0.93 (t, J = 7.3 Hz, 7H), 0.79 (d, J = 6.9 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 187.00 (dd, J_{C-F} = 23.8, 1.2 Hz), 164.8, 136.0, 134.1 (d, J_{C-F} = 1.2 Hz), 129.9, 129.6 (d, J_{C-F} = 2.5 Hz), 95.3 (dd, J_{C-F} = 256.3, 5.0 Hz), 75.8, 47.2, 40.8, 34.2, 31.4, 26.5, 23.6, 22.0, 20.7, 16.5; ¹⁹F NMR (471 MHz, CDCl₃) δ -146.6 (dd, J = 51.8, 23.6 Hz, 1F). HRMS (ESI-TOF): calcd. for C₁₉H₂₅FClO₃[M+H]⁺ : 355.1470; found : 355.1469.

(23) 2-chloro-2-fluoro-1-(thiophen-2-yl)ethan-1-one (**2w**)



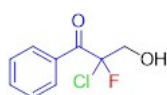
Light yellow oil (78.6 mg, 44%, purity>99.5%). ^1H NMR (500 MHz, CDCl_3) δ 8.05 – 8.00 (m, 1H), 7.83 (d, $J = 4.9$ Hz, 1H), 7.22 (t, $J = 5.0$ Hz, 1H), 6.66 (d, $J = 50.8$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 181.2 (d, $J_{\text{C-F}} = 23.7$ Hz), 137.0 (d, $J_{\text{C-F}} = 2.5$ Hz), 136.5, 135.2 (d, $J_{\text{C-F}} = 5.0$ Hz), 128.7, 95.8 (d, $J_{\text{C-F}} = 256.2$ Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -143.6 (d, $J = 51.8$ Hz, 1F). HRMS (ESI-TOF): calcd. for $\text{C}_6\text{H}_5\text{FCISO}[\text{M}+\text{H}]^+$: 178.9728; found : 178.9727.

(24) 2-chloro-2-fluoro-1,2-diphenylethan-1-one (**2x**)



Light yellow oil (74.6 mg, 30%, purity>99.5%). ^1H NMR (500 MHz, CDCl_3) δ 8.01 (d, $J = 8.4$ Hz, 2H), 7.69 – 7.63 (m, 2H), 7.57 (t, $J = 7.4$ Hz, 1H), 7.50 – 7.39 (m, 5H); ^{13}C NMR (125 MHz, CDCl_3) δ 188.7 (d, $J_{\text{C-F}} = 33.7$ Hz), 136.3 (d, $J_{\text{C-F}} = 22.5$ Hz), 133.8, 132.0 (d, $J_{\text{C-F}} = 2.5$ Hz), 130.6 (d, $J_{\text{C-F}} = 2.5$ Hz), 130.3, 128.7, 128.4, 125.7 (d, $J_{\text{C-F}} = 62.5$ Hz), 109.8 (d, $J_{\text{C-F}} = 255.0$ Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -106.5 (s, 1F). HRMS (ESI-TOF): calcd. for $\text{C}_{14}\text{H}_{10}\text{FCIONa}[\text{M}+\text{Na}]^+$: 271.0296 ; found : 271.0296.

(25) 2-chloro-2-fluoro-3-hydroxy-1-phenylpropan-1-one (**2y**)



Light yellow oil (113.5 mg, 56%, purity>99.5%). ^1H NMR (500 MHz, CDCl_3) δ 8.16 (d, $J = 8.3$ Hz, 2H), 7.63 (t, $J = 7.4$ Hz, 1H), 7.49 (t, $J = 7.9$ Hz, 2H), 4.39 (dd, $J = 23.6, 12.9$ Hz, 1H), 4.17 (t, $J = 12.7$ Hz, 1H), 3.16 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 189.9 (d, $J_{\text{C-F}} = 28.7$ Hz), 134.5, 131.5 (d, $J_{\text{C-F}} = 2.5$ Hz), 130.5 (d, $J_{\text{C-F}} = 5.0$ Hz), 128.5, 106.6 (d, $J_{\text{C-F}} = 261.2$ Hz), 66.6 (d, $J_{\text{C-F}} = 25.0$ Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -126.3 (dd, $J = 14.1, 23.5$ Hz, 1F). HRMS (ESI-TOF): calcd. for $\text{C}_9\text{H}_9\text{FCIO}_2[\text{M}+\text{H}]^+$: 203.0270 ; found : 203.0271.

(26) 2-chloro-2-fluoro-1-phenylbutan-1-one (**2z**)



Light yellow oil (86.3 mg, 43%, purity>99.5%). ^1H NMR (500 MHz, CDCl_3) δ 8.16 (d, $J = 8.4$ Hz, 2H), 7.61 (t, $J = 7.4$ Hz, 1H), 7.49 (t, $J = 7.8$ Hz, 2H), 2.56 – 2.37 (m, 2H), 1.16 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 189.8 (d, $J_{\text{C-F}} = 28.7$ Hz), 133.8, 132.0 (d, $J_{\text{C-F}} = 2.5$ Hz), 130.5 (d, $J_{\text{C-F}} = 5.0$ Hz), 128.4, 110.8 (d, $J_{\text{C-F}} = 258.7$ Hz), 32.8 (d, $J_{\text{C-F}} = 22.5$ Hz), 7.4 (d, $J_{\text{C-F}} = 3.7$ Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -116.9 (d, $J = 18.8$ Hz, 1F). HRMS (ESI-TOF): calcd. for $\text{C}_{10}\text{H}_{11}\text{FCIO}[\text{M}+\text{H}]^+$: 201.0477 ; found : 201.0480.

Crystal data of **2q**

Crystallographic data of compound **2q**

White block-like single crystals of **2q** were grown by layering DCM at ambient temperature. An ORTEP representation of the structure is shown below.

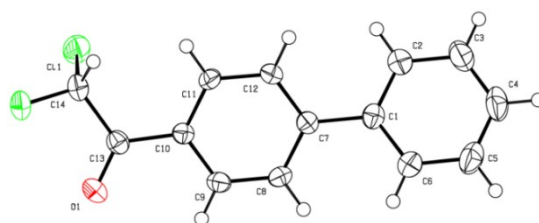
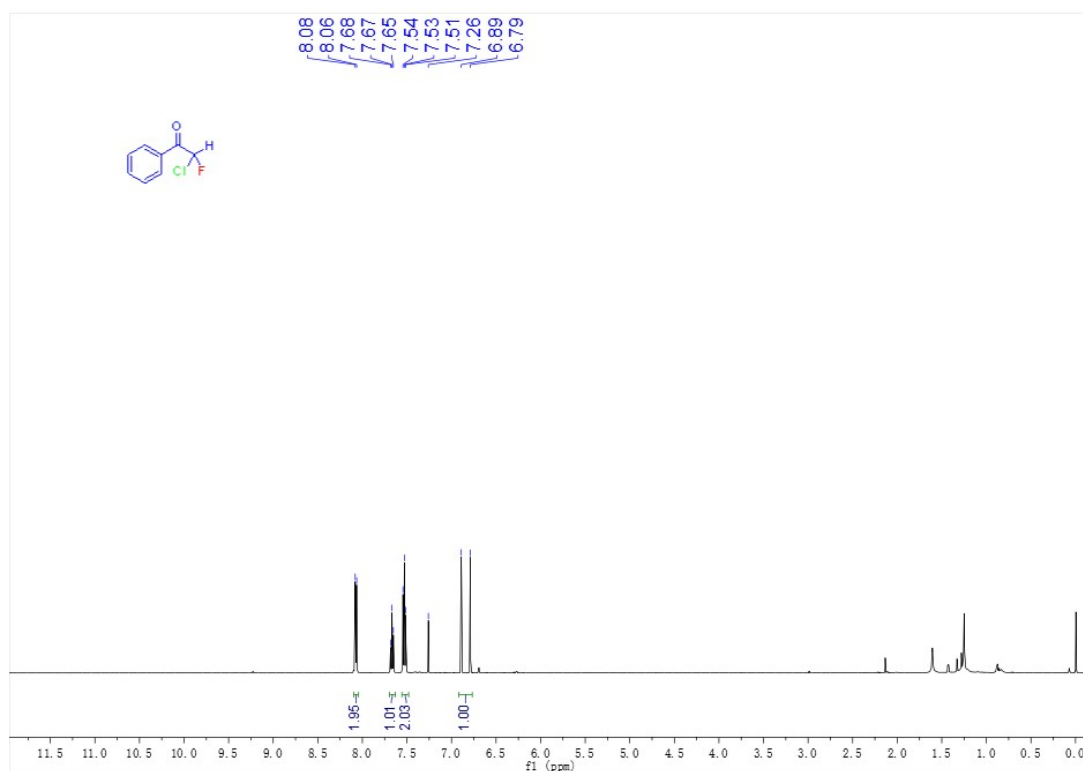


Figure S8. Molecular structure of **2q** (CCDC:2105099)

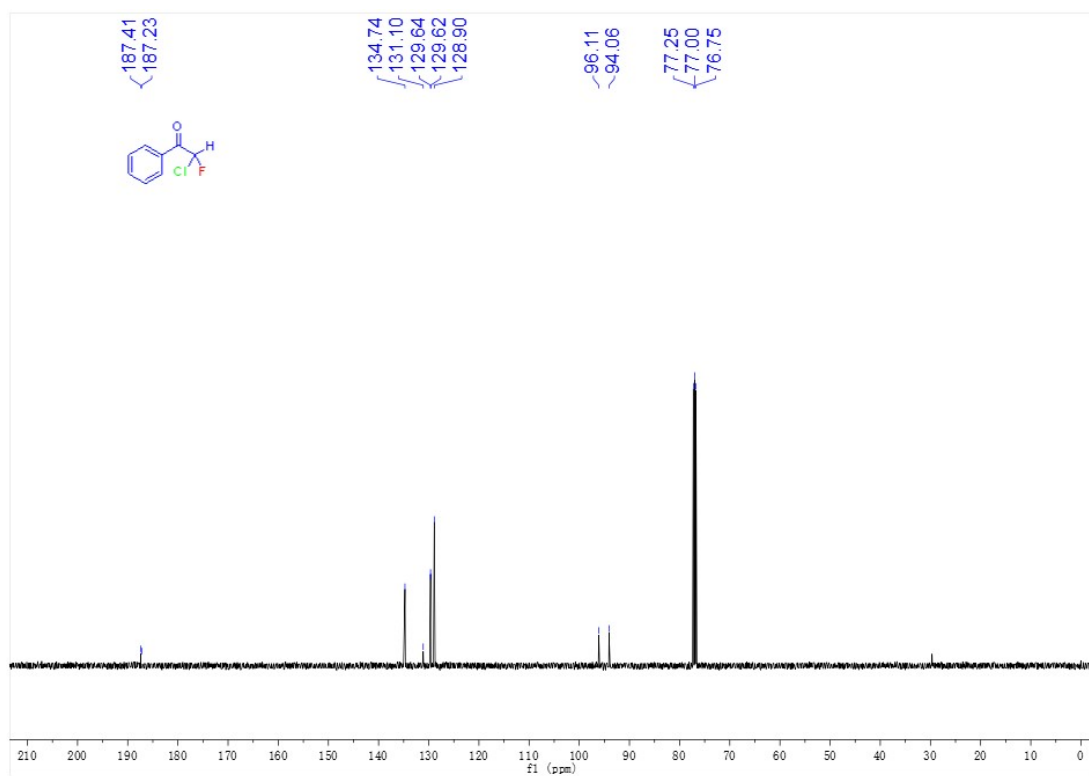
Table S1 Crystal data and structure refinement for 2q

Identification code	2q
Empirical formula	C ₁₄ H ₁₀ ClFO
Formula weight	248.67
Temperature/K	149.99(10)
Crystal system	monoclinic
Space group	P2 ₁
a/Å	5.1673(5)
b/Å	10.7029(11)
c/Å	10.6241(9)
α/°	90
β/°	102.439(9)
γ/°	90
Volume/Å ³	573.78(9)
Z	2
ρ _{calc} /cm ³	1.439
μ/mm ⁻¹	0.324
F(000)	256.0
Crystal size/mm ³	0.14 × 0.13 × 0.12
Radiation	Mo Kα (λ = 0.71073)
2θ range for data collection/°	5.468 to 59.024
Index ranges	-7 ≤ h ≤ 4, -14 ≤ k ≤ 11, -11 ≤ l ≤ 13
Reflections collected	2900
Independent reflections	2014 [R _{int} = 0.0226, R _{sigma} = 0.0429]
Data/restraints/parameters	2014/1/155
Goodness-of-fit on F ²	1.044
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0364, wR ₂ = 0.0806
Final R indexes [all data]	R ₁ = 0.0420, wR ₂ = 0.0848
Largest diff. peak/hole / e Å ⁻³	0.18/-0.24
Flack parameter	0.11(9)

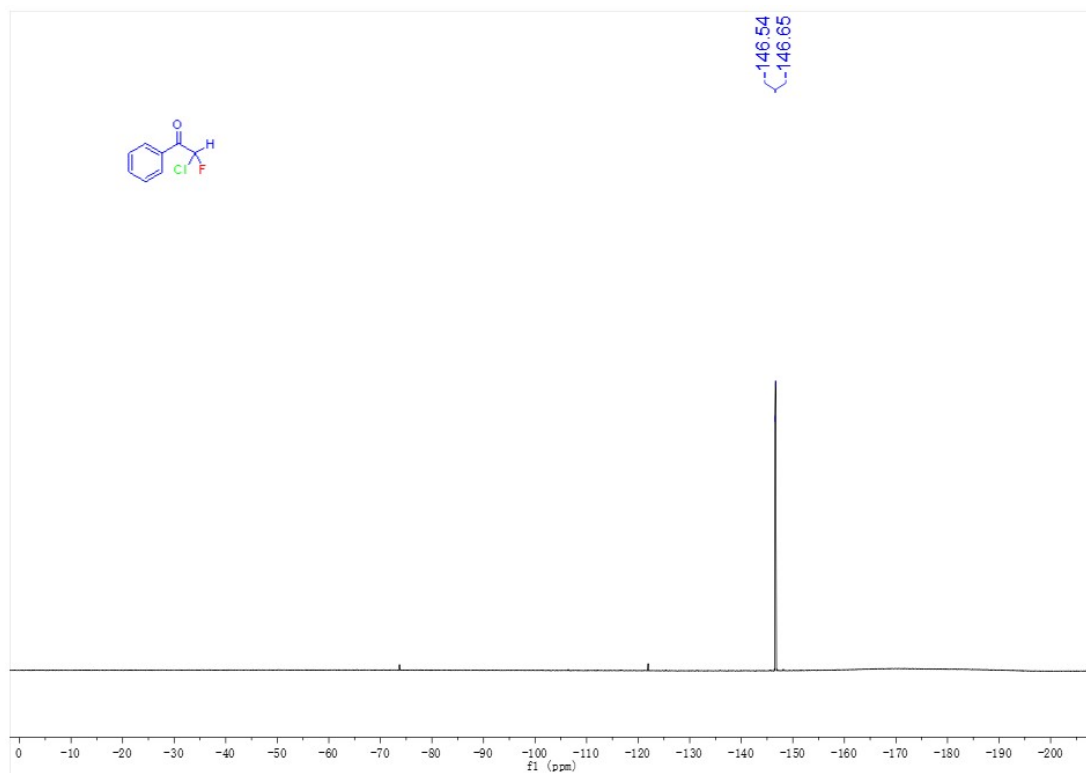
NMR spectra of the obtained compounds**¹H NMR spectrum for 2a**



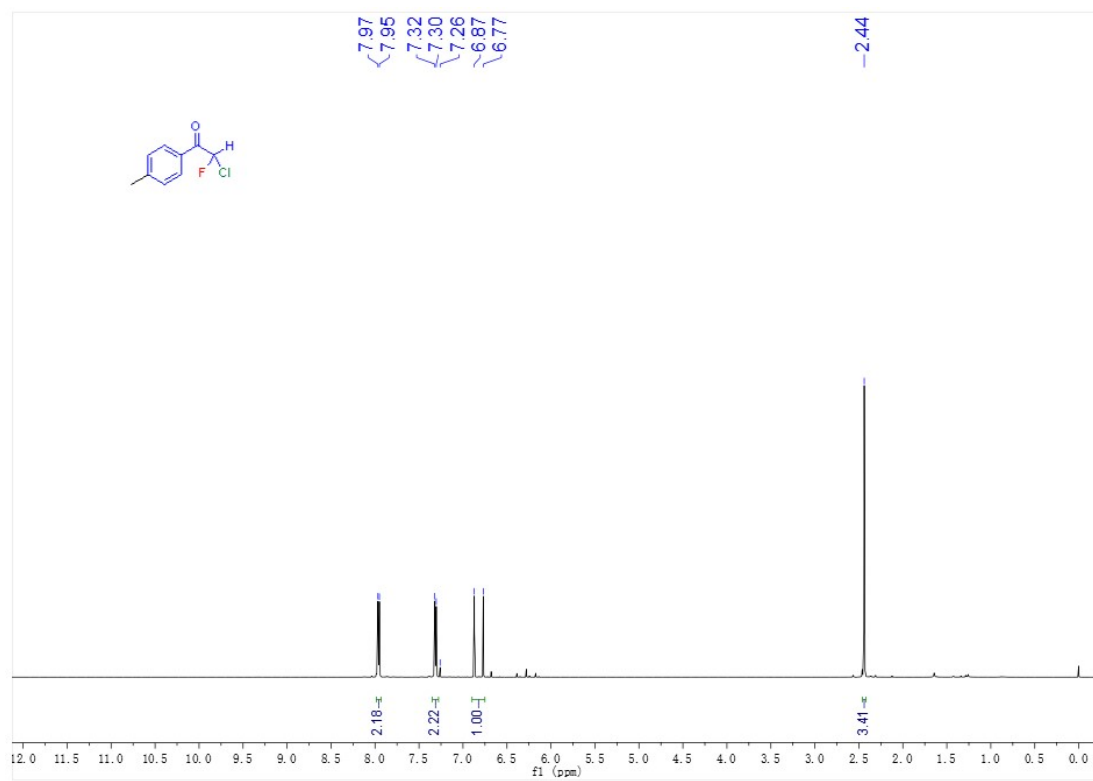
¹³C NMR spectrum for 2a



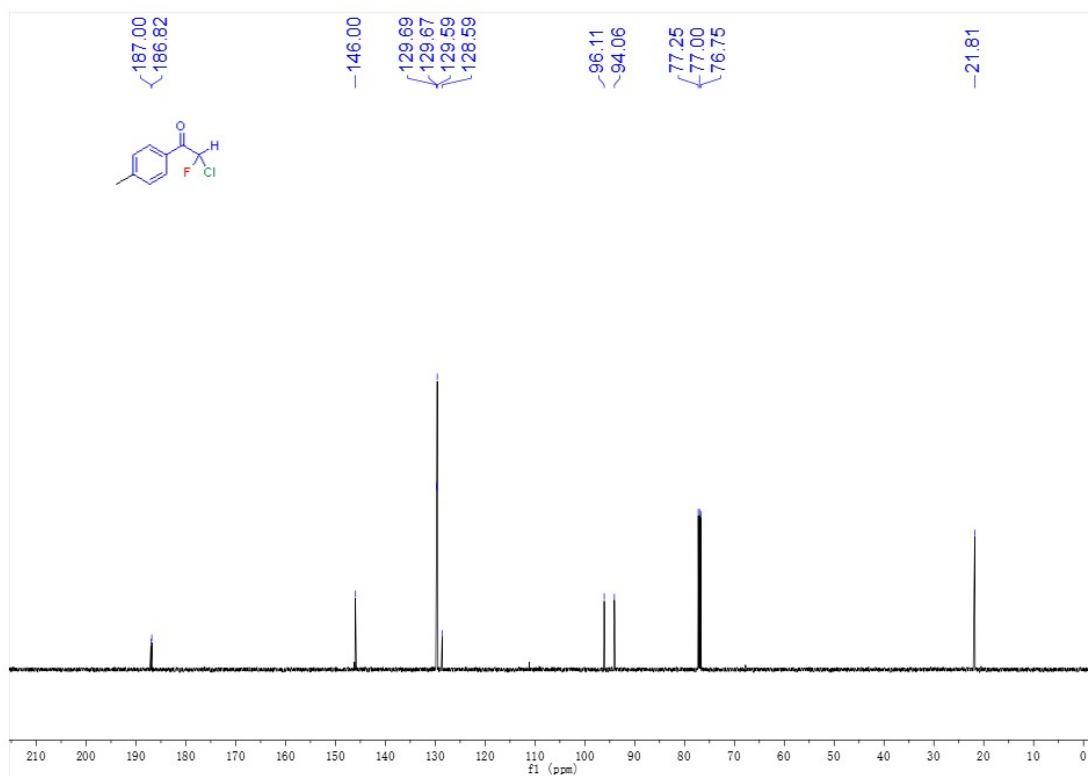
¹⁹F NMR spectrum for 2a



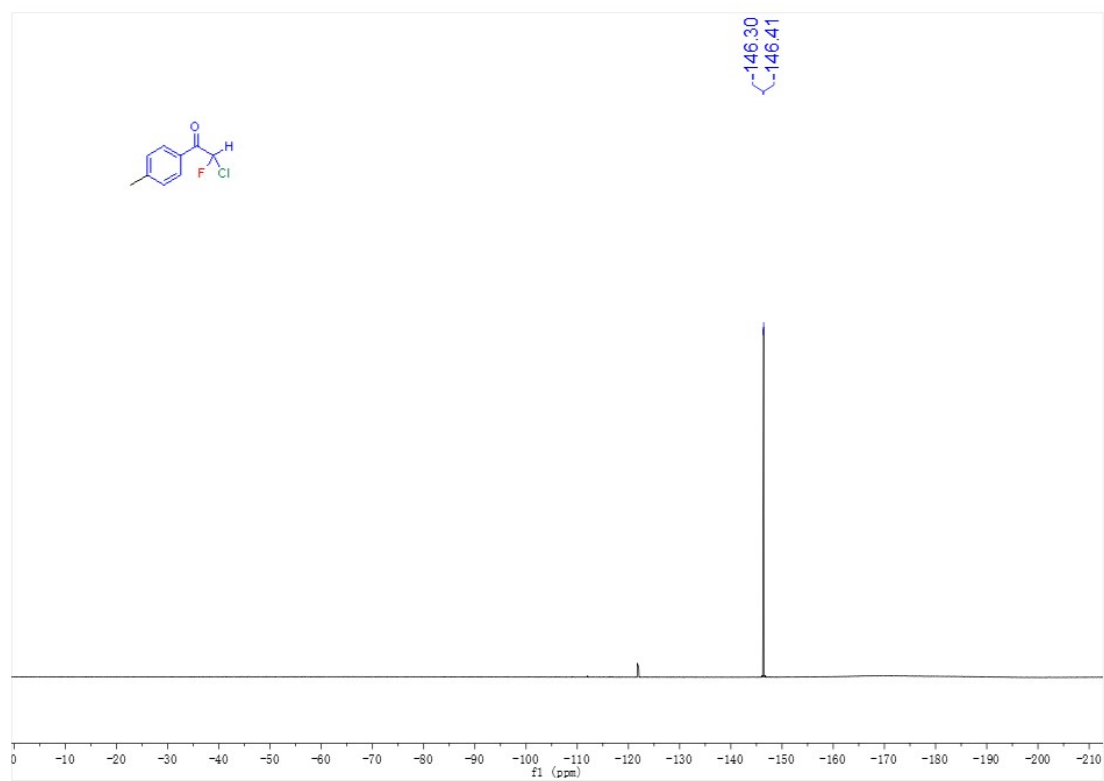
¹H NMR spectrum for 2b



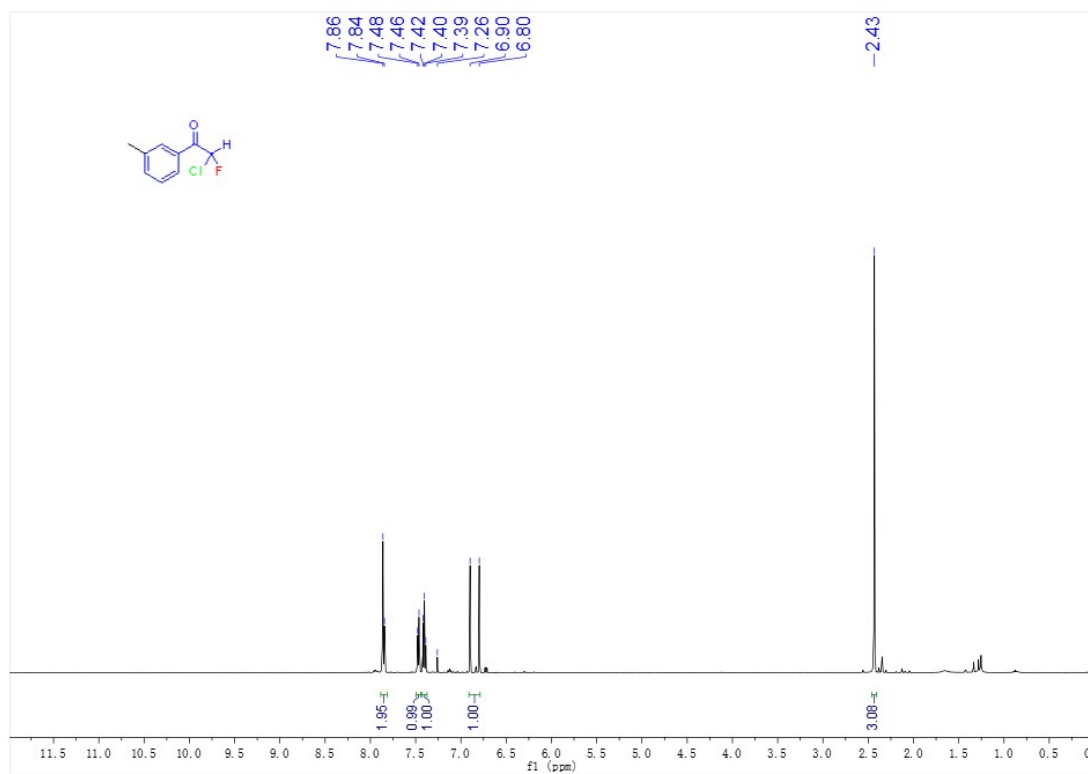
¹³C NMR spectrum for 2b



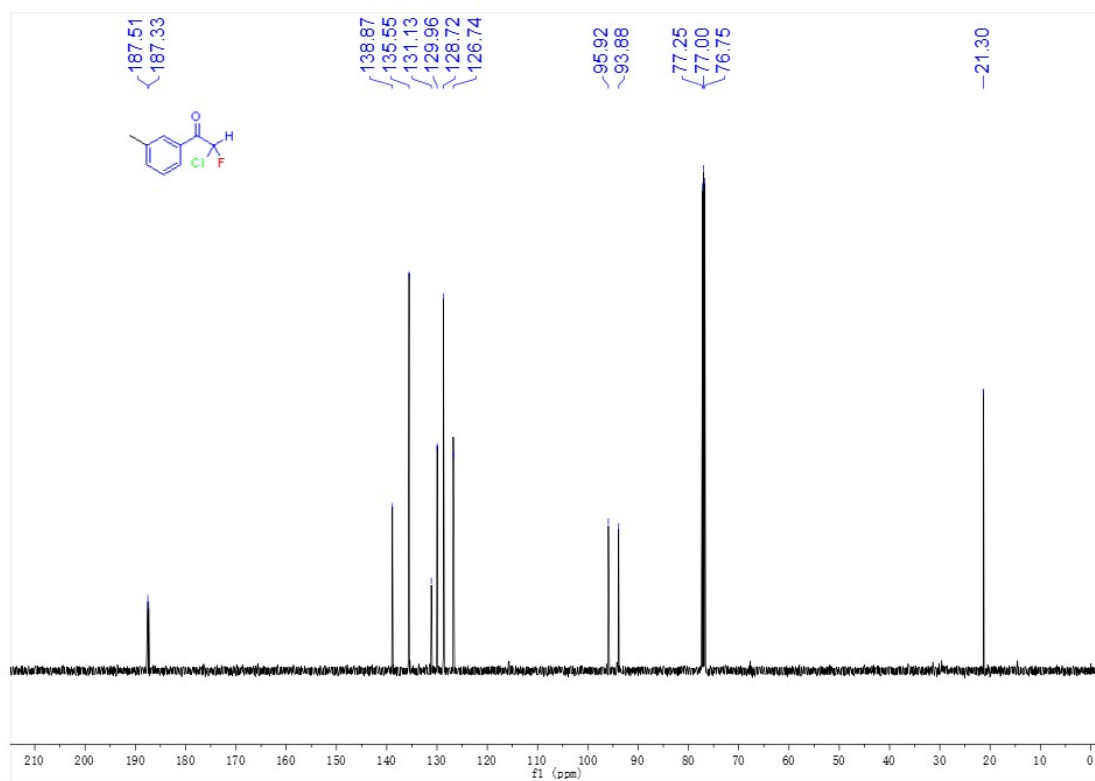
¹⁹F NMR spectrum for 2b



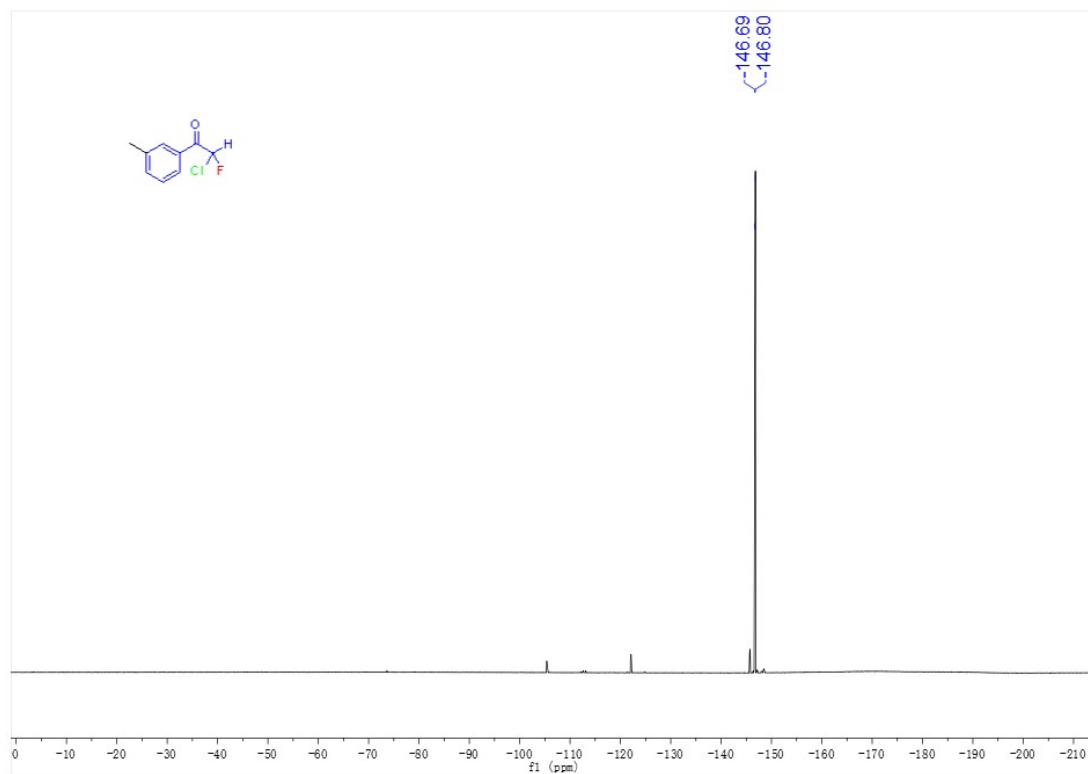
¹H NMR spectrum for 2c



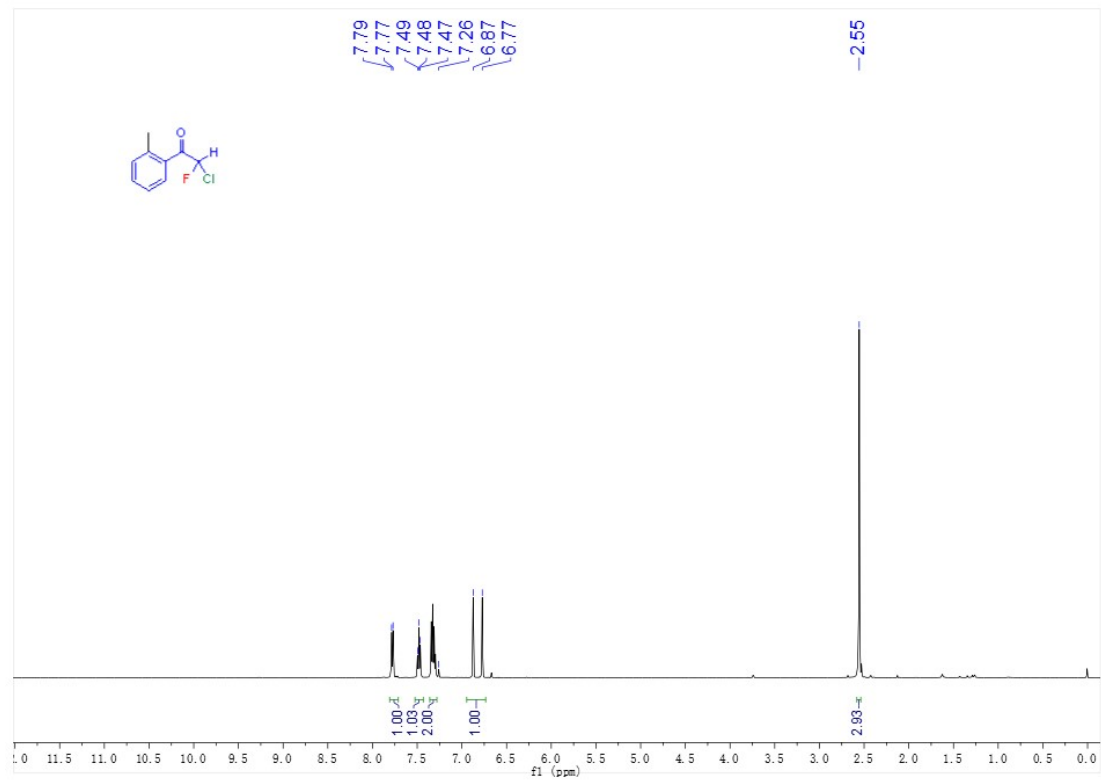
¹³C NMR spectrum for 2c



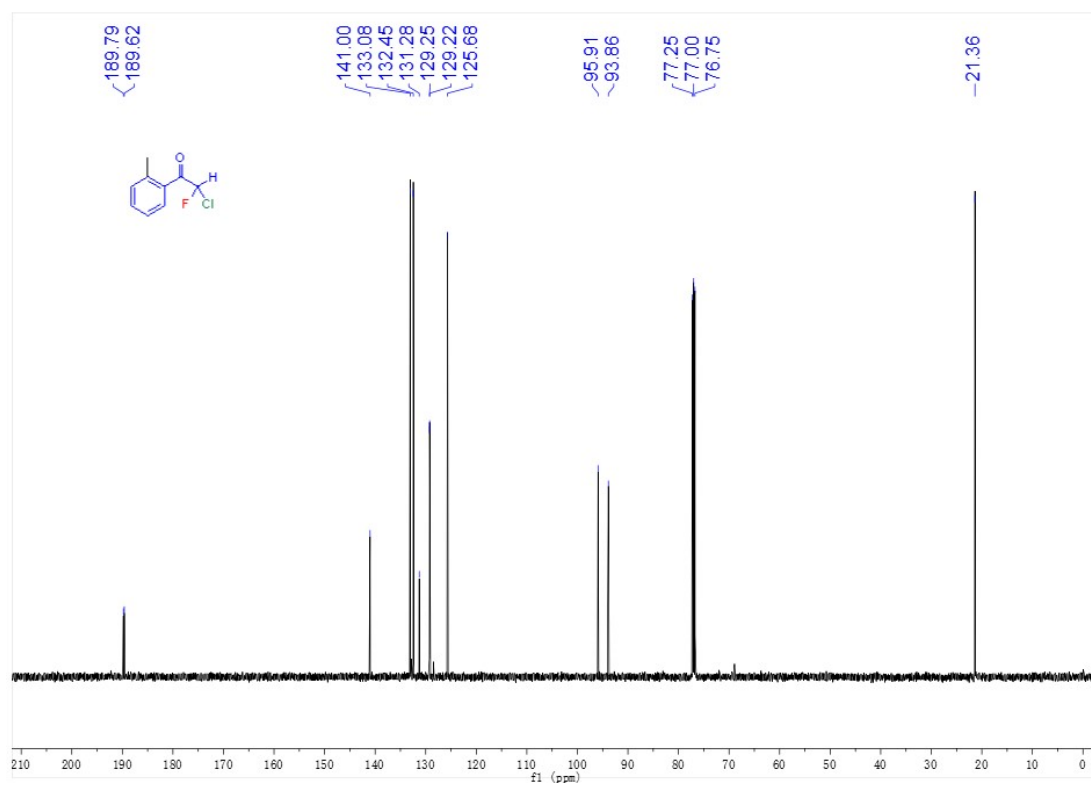
¹⁹F NMR spectrum for 2c



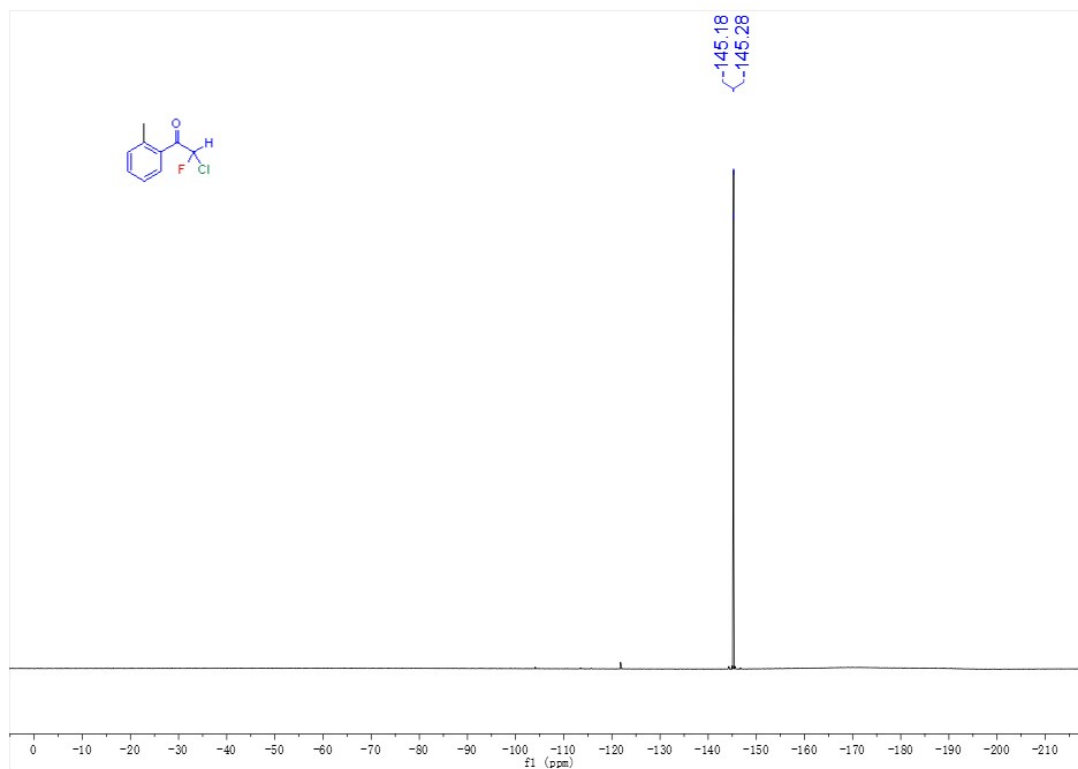
¹H NMR spectrum for 2d



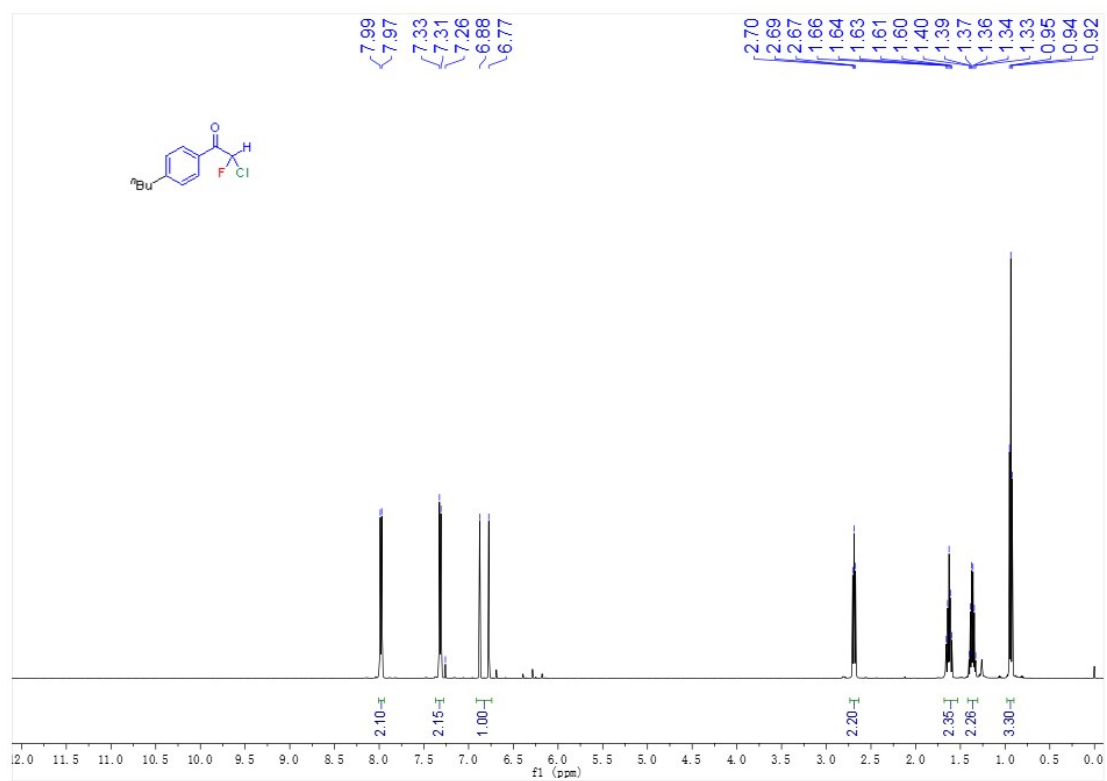
¹³C NMR spectrum for 2d



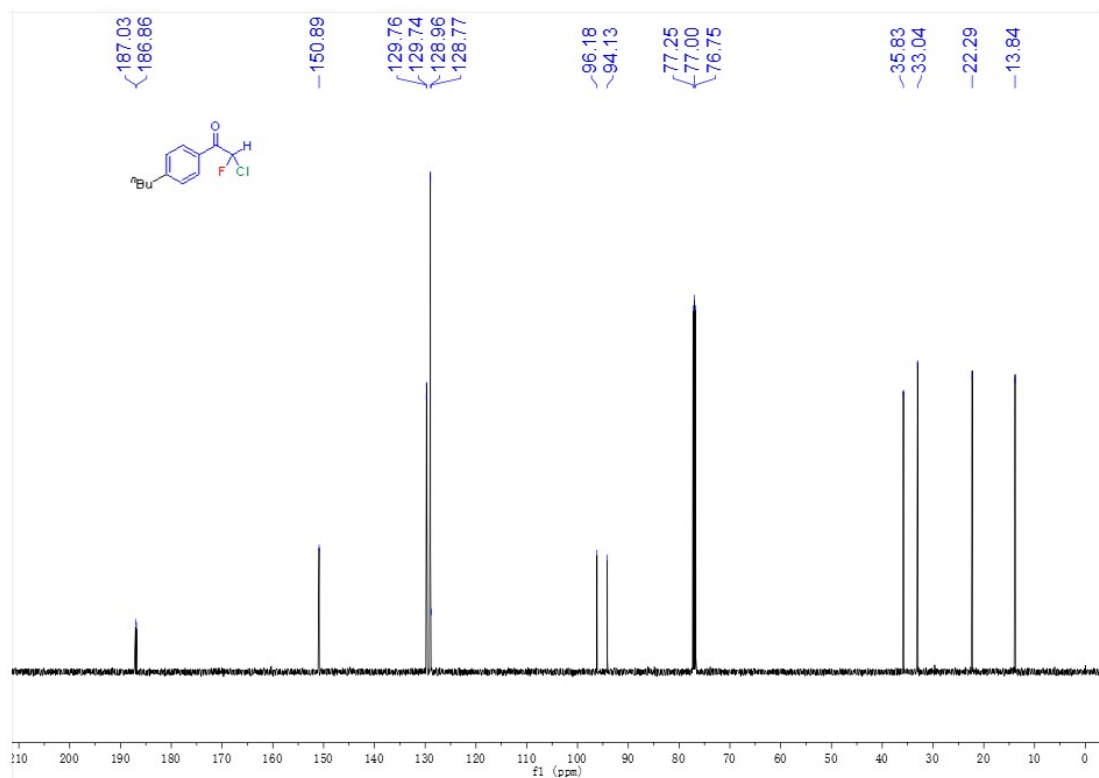
¹⁹F NMR spectrum for 2d



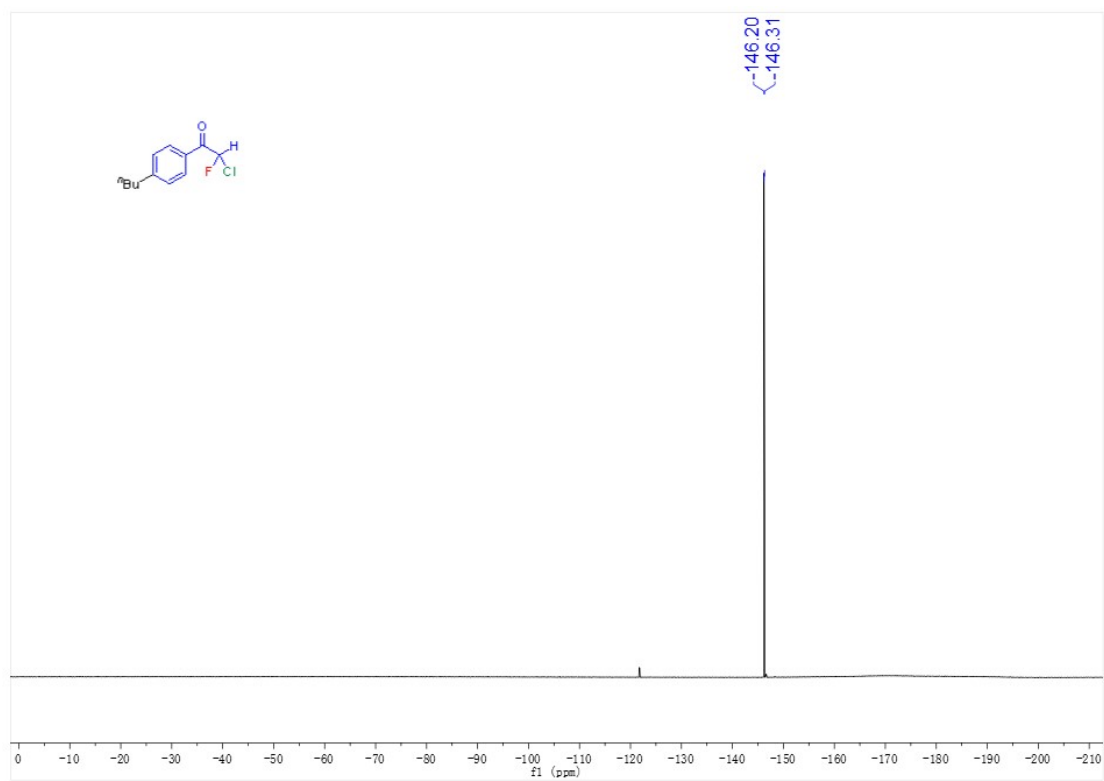
¹H NMR spectrum for 2e



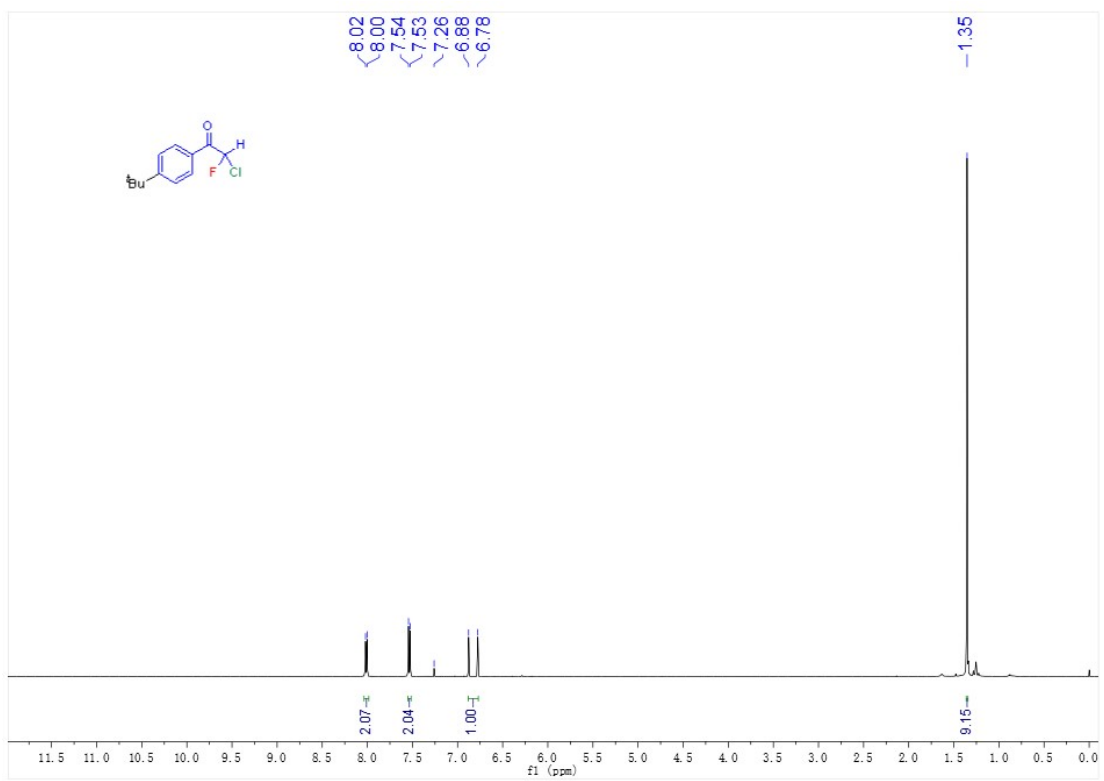
¹³C NMR spectrum for 2e



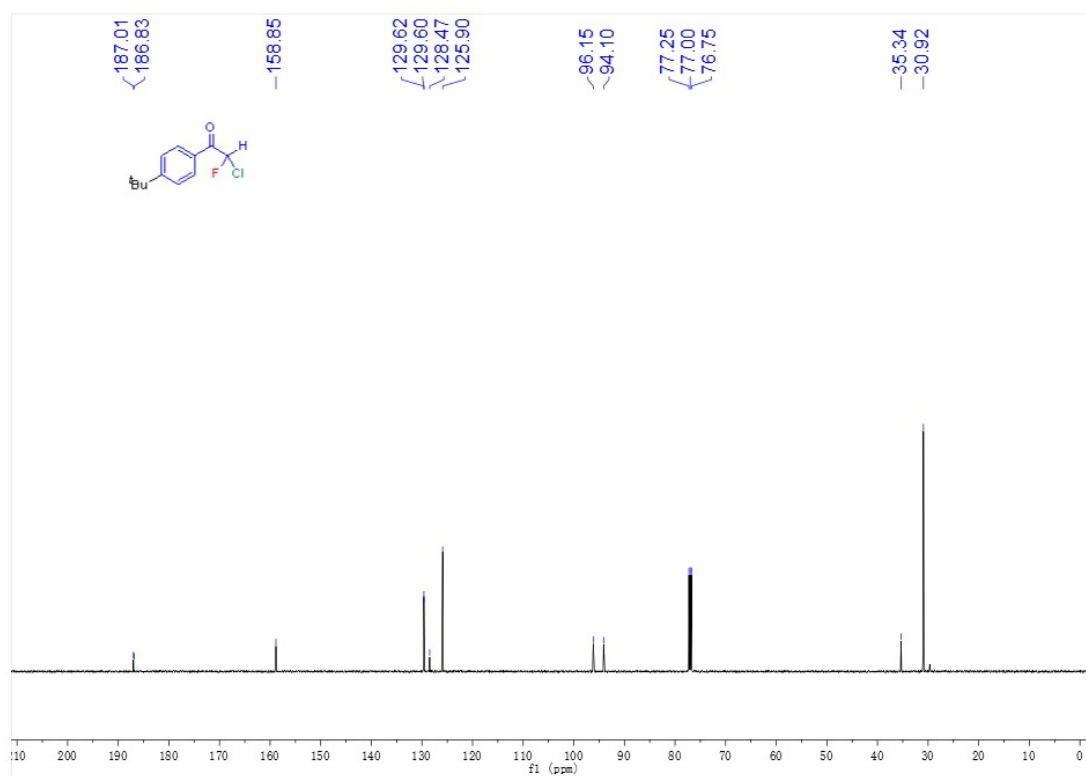
¹⁹F NMR spectrum for 2e



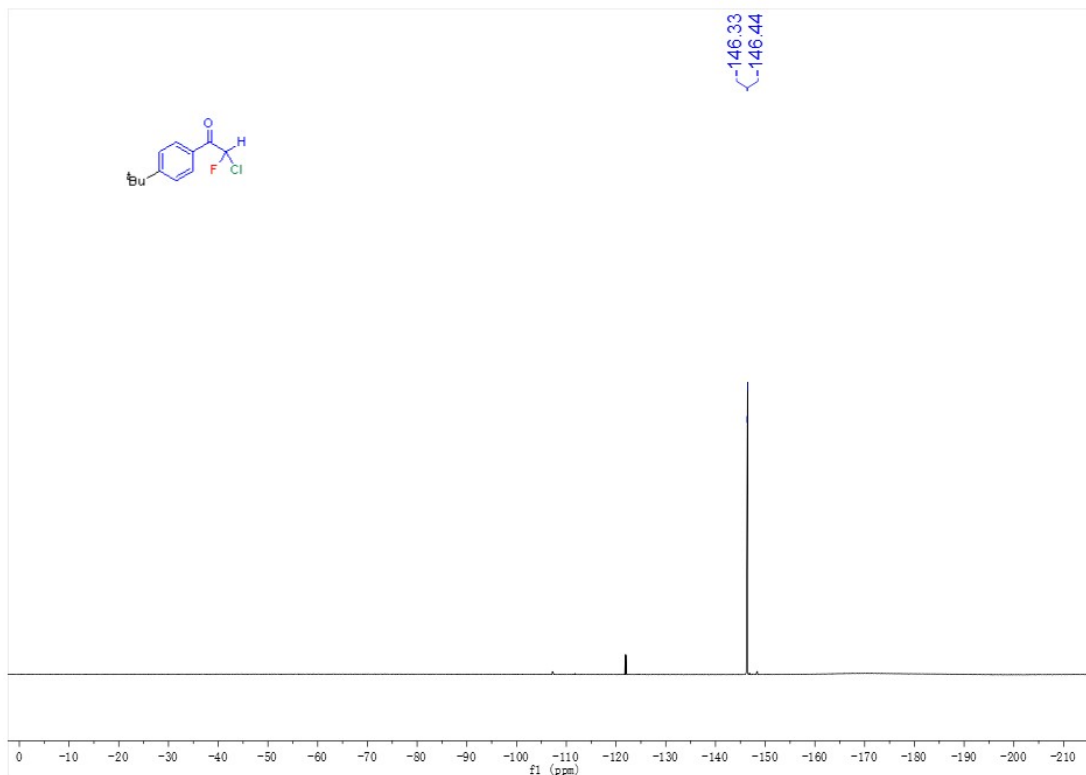
¹H NMR spectrum for 2f



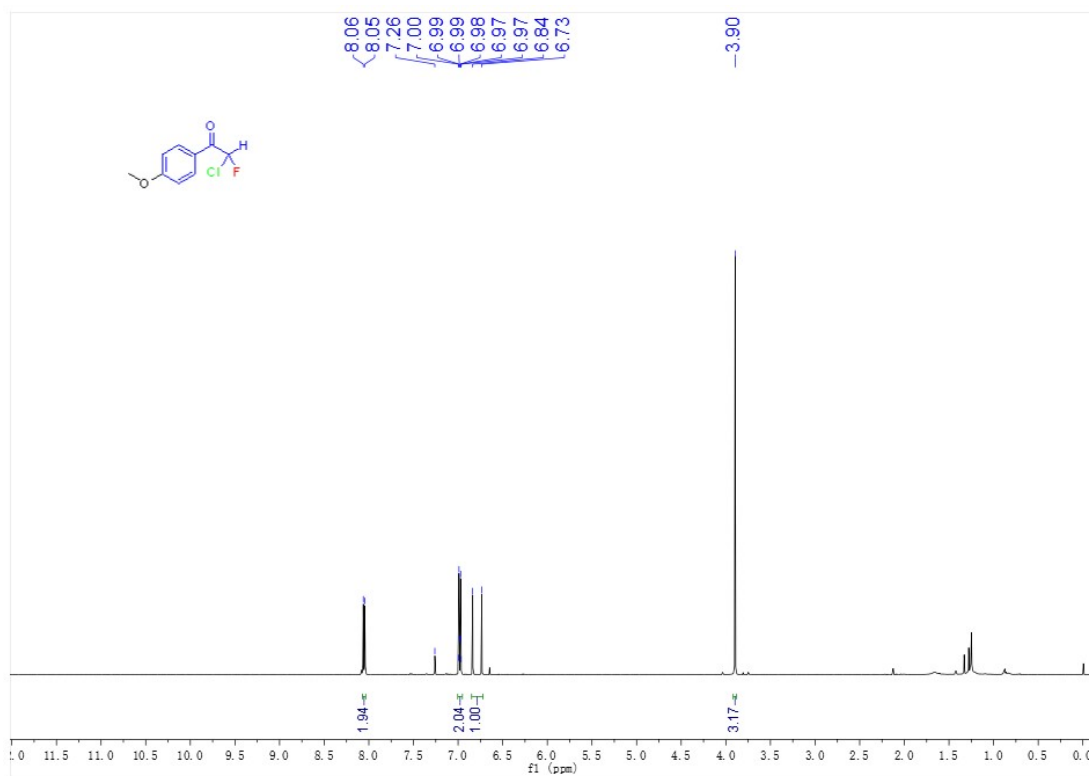
¹³C NMR spectrum for 2f



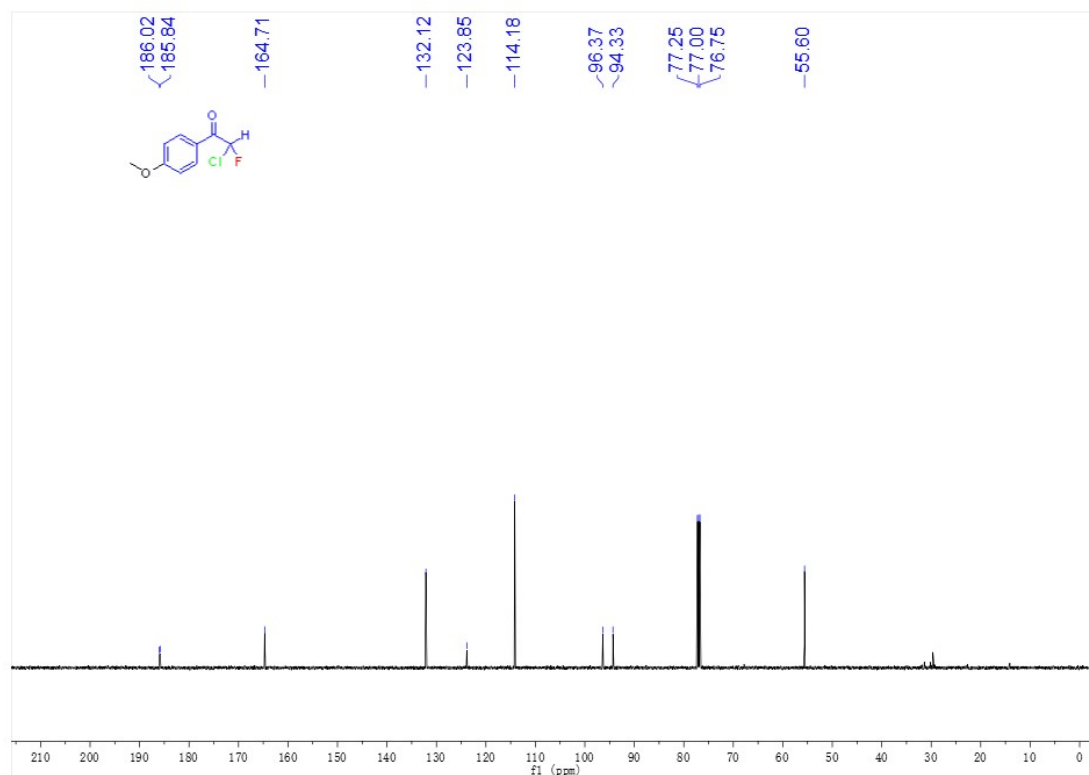
¹⁹F NMR spectrum for 2f



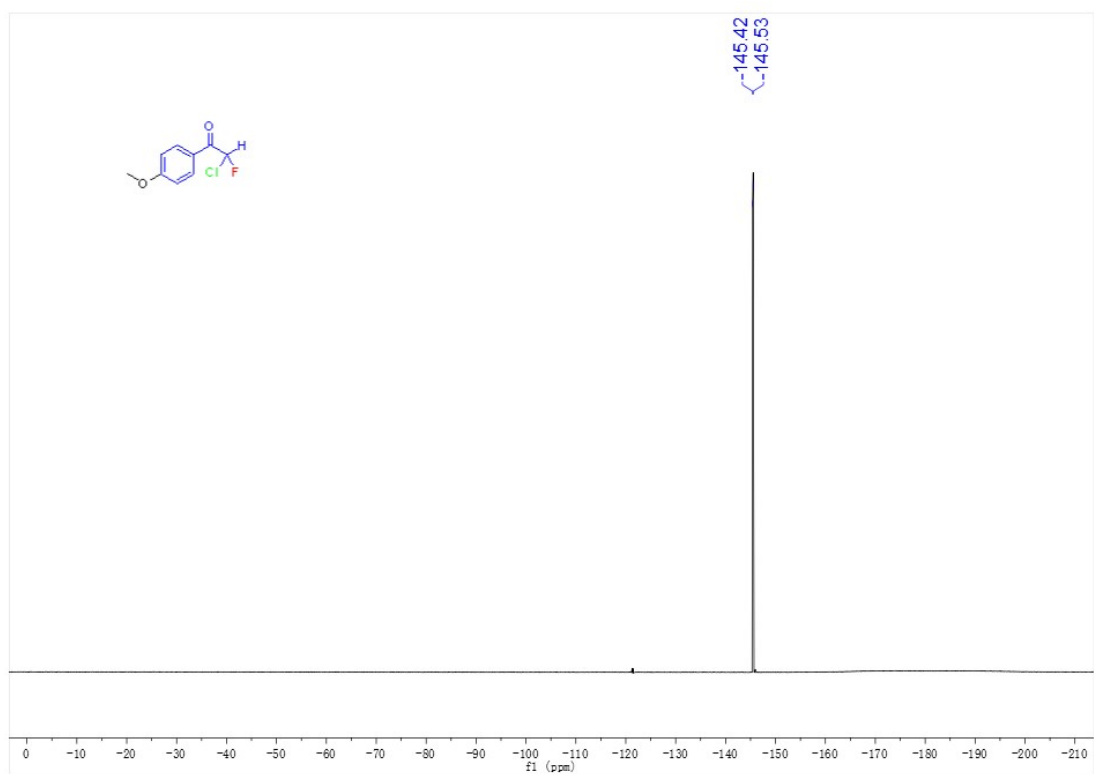
¹H NMR spectrum for 2g



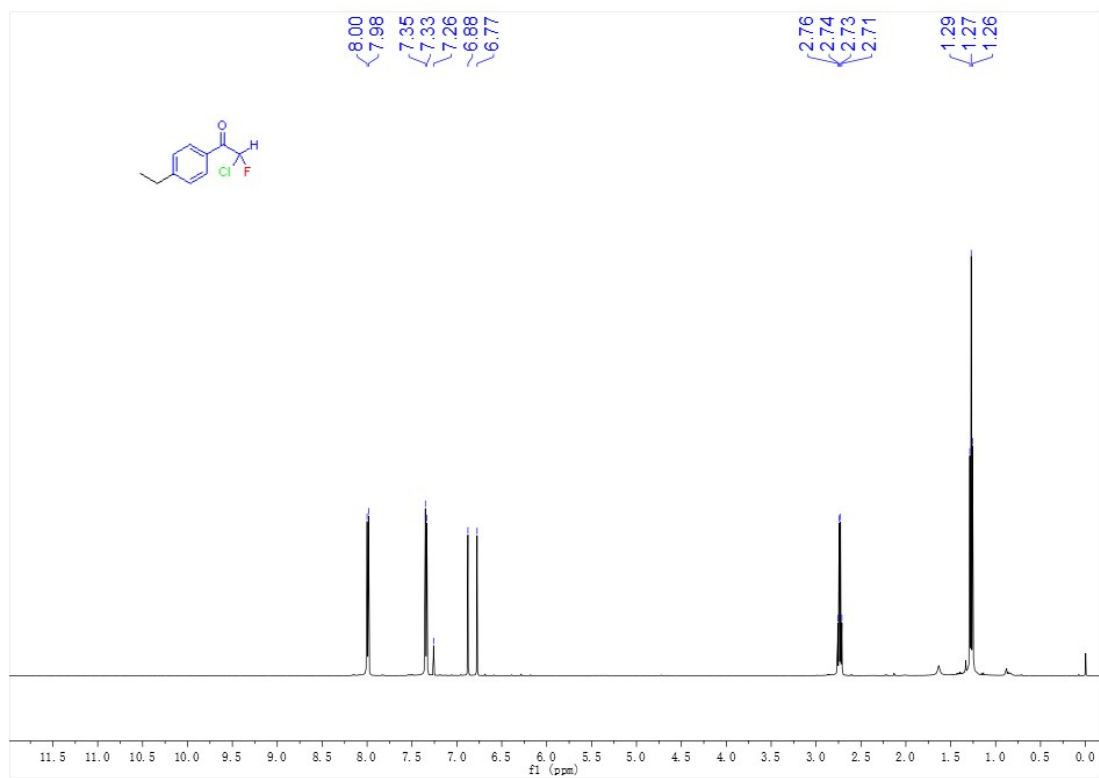
¹³C NMR spectrum for 2g



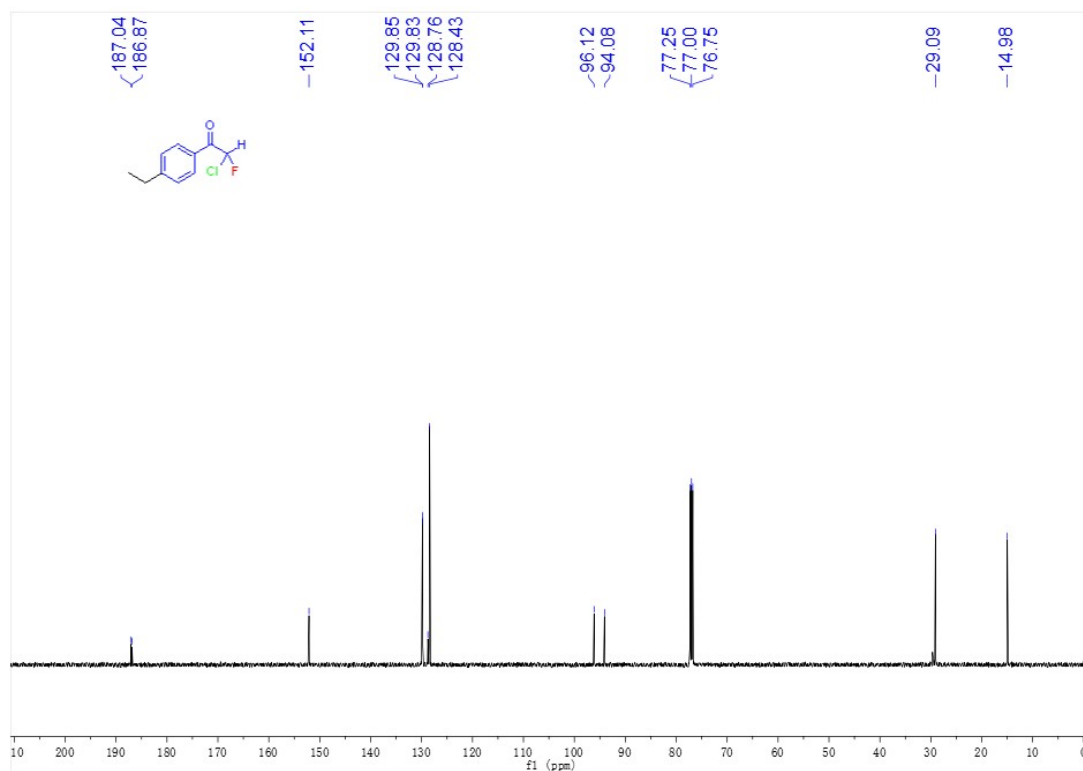
¹⁹F NMR spectrum for 2g



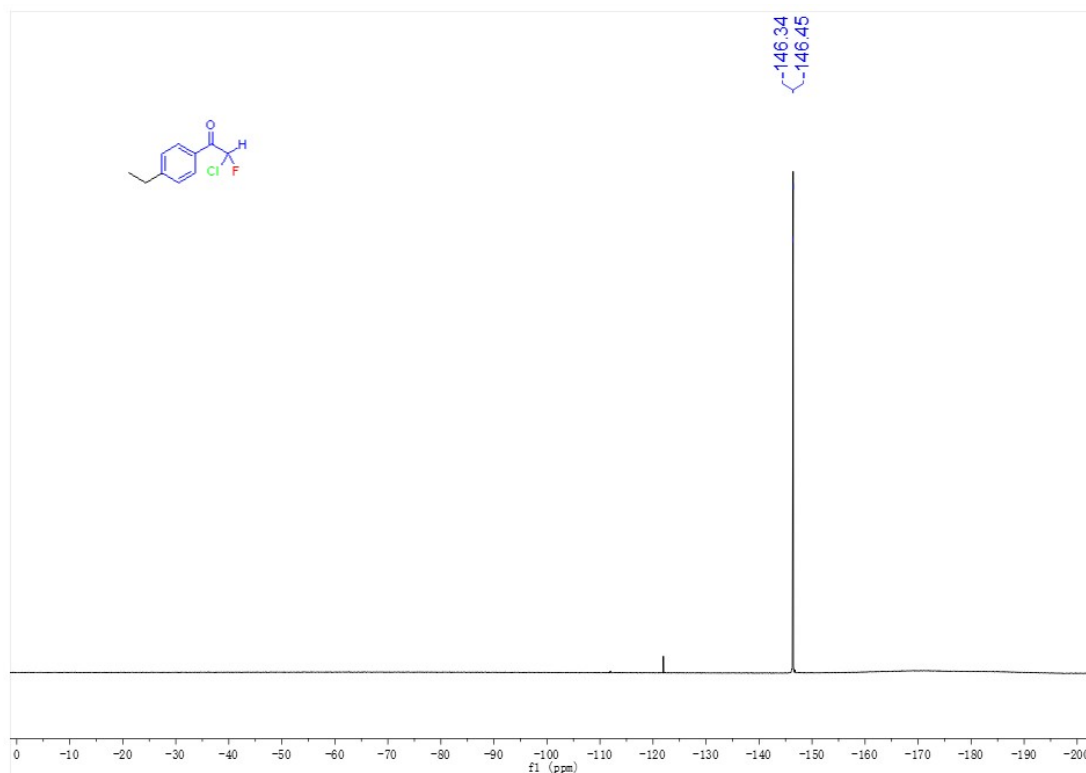
¹H NMR spectrum for 2h



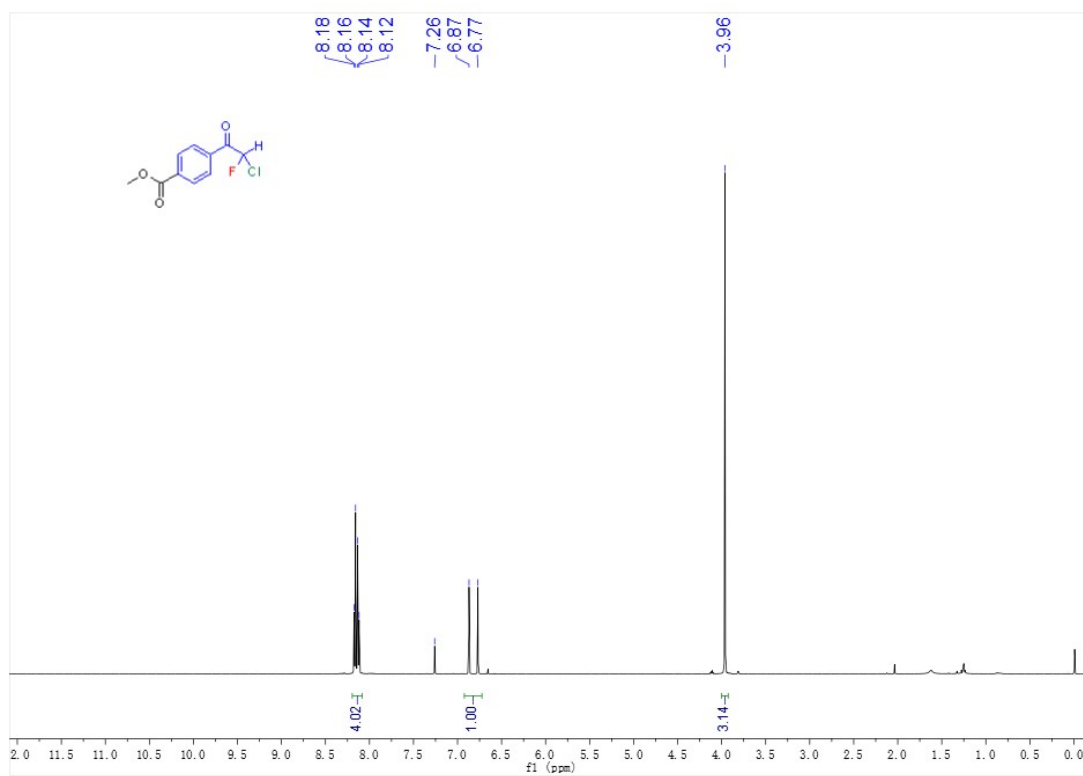
¹³C NMR spectrum for 2h



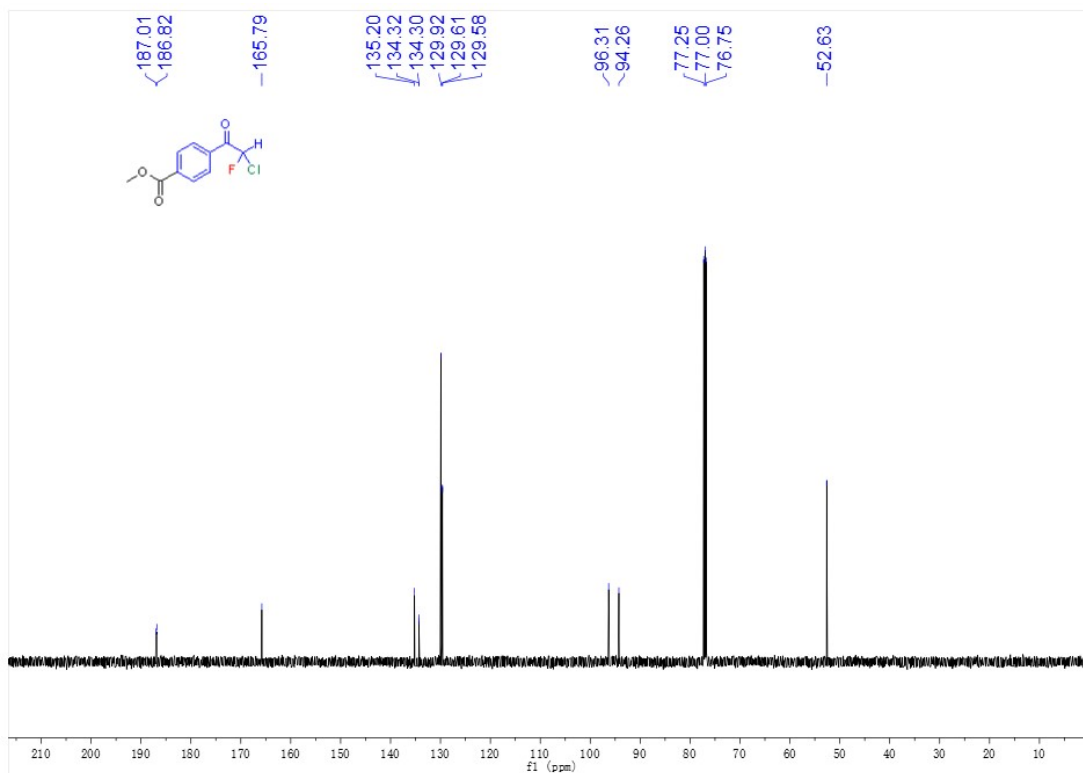
¹⁹F NMR spectrum for 2h



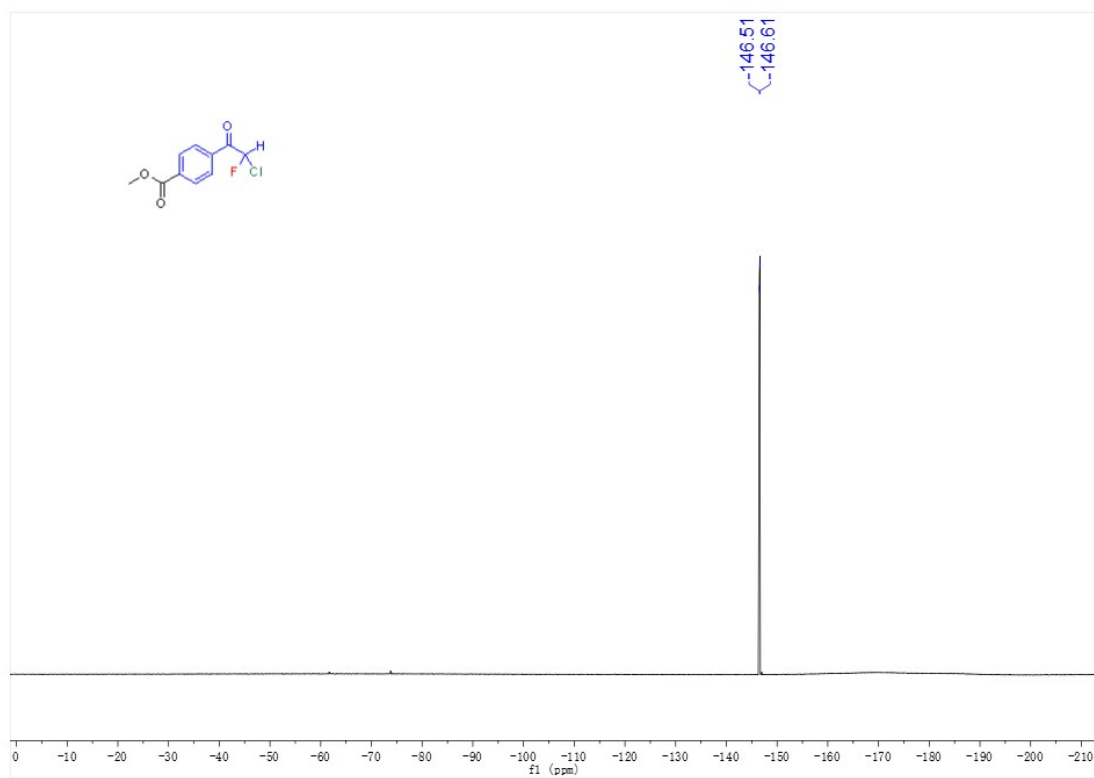
¹H NMR spectrum for 2i



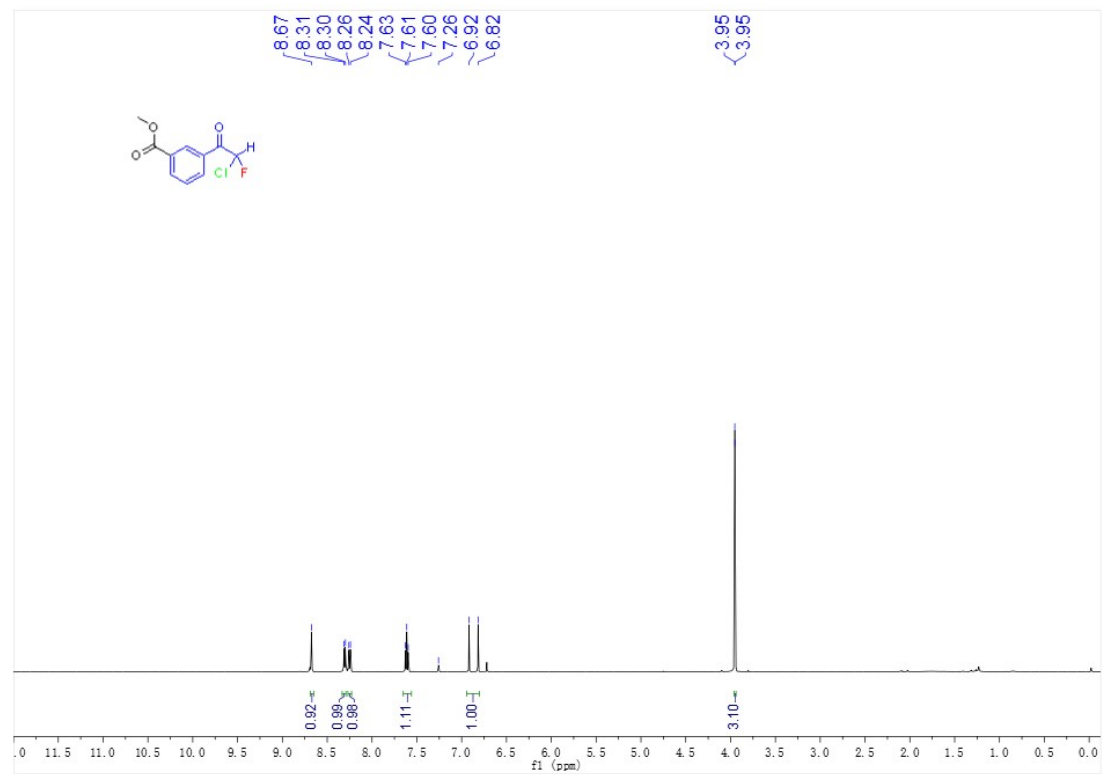
¹³C NMR spectrum for 2i



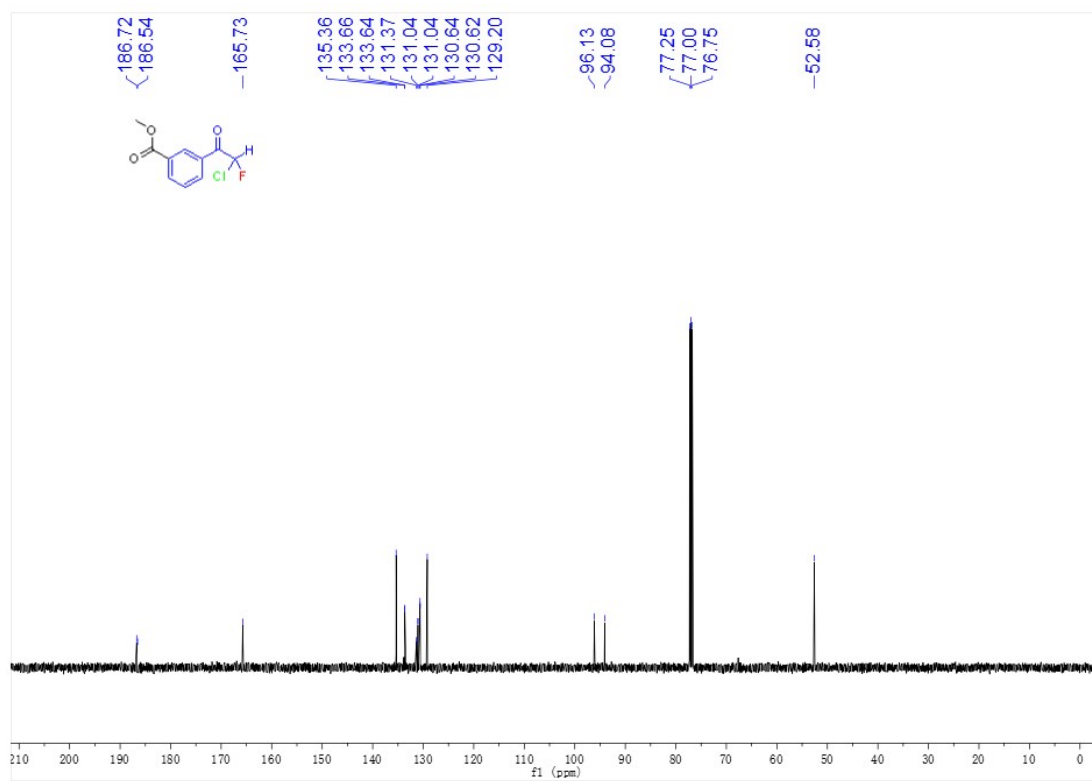
¹⁹F NMR spectrum for 2i



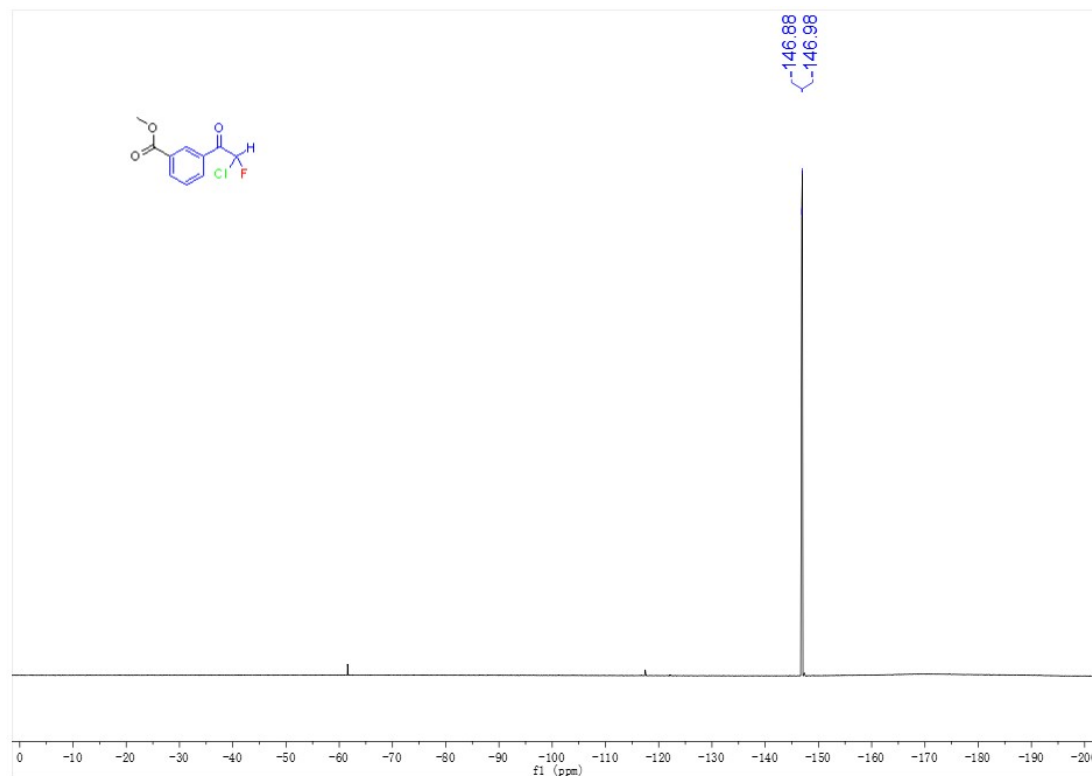
¹H NMR spectrum for 2j



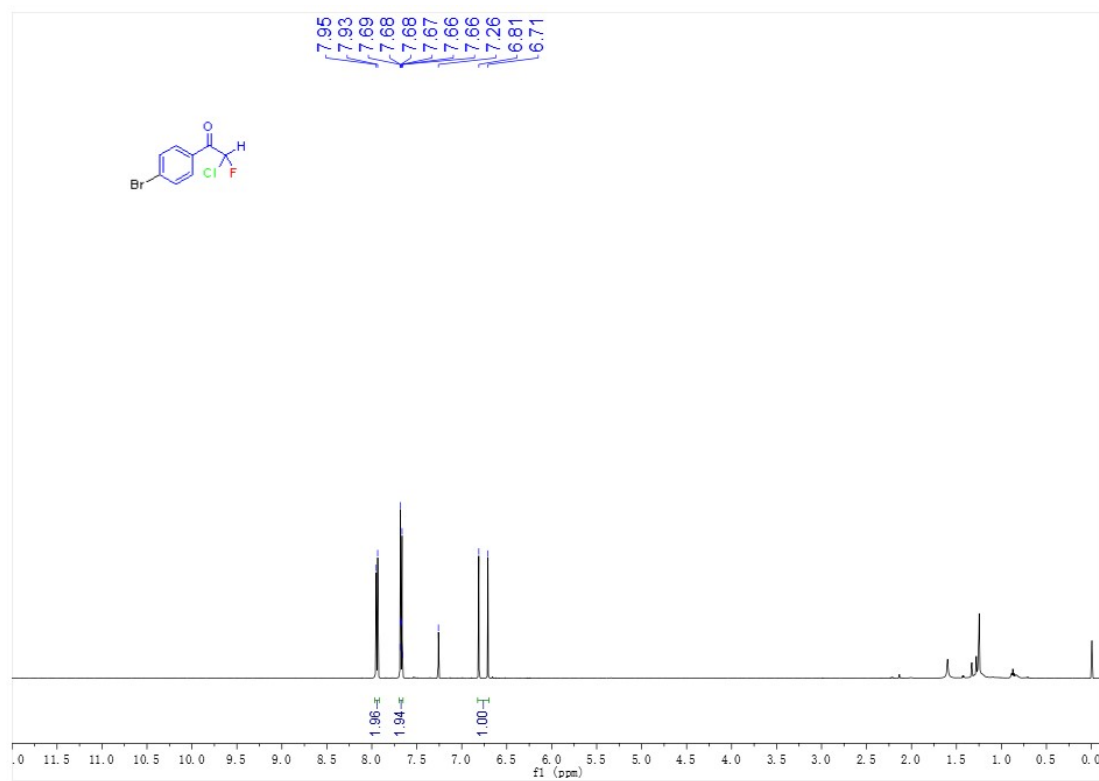
¹³C NMR spectrum for 2j



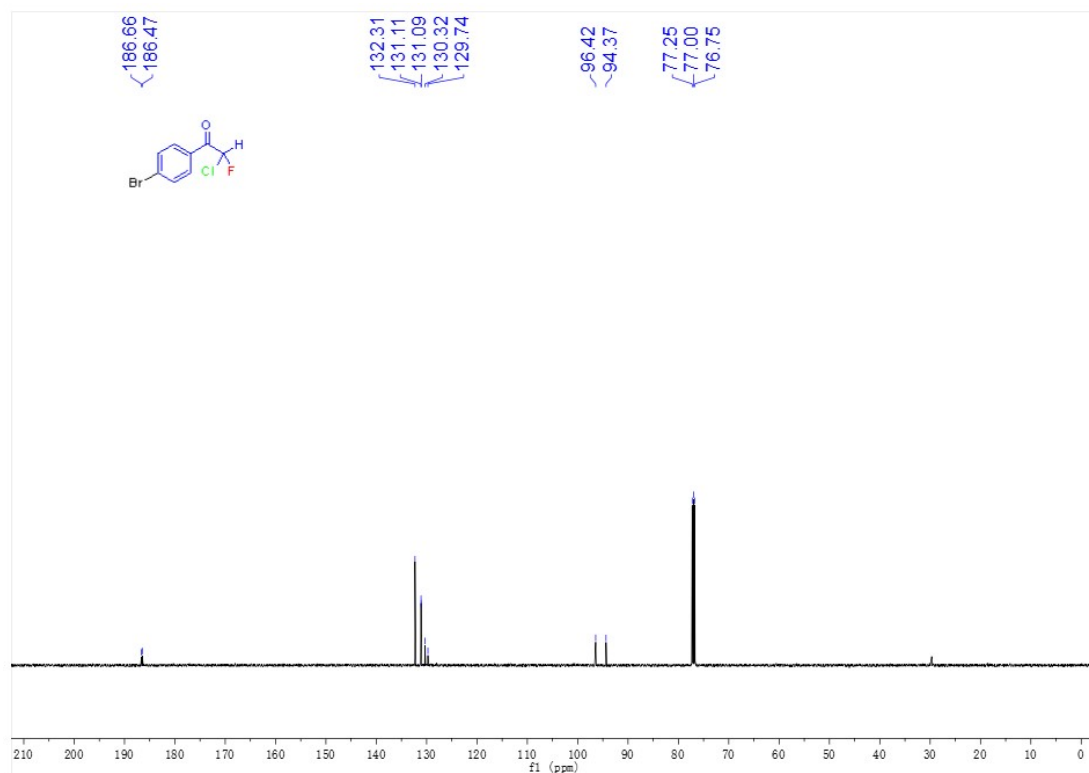
¹⁹F NMR spectrum for 2j



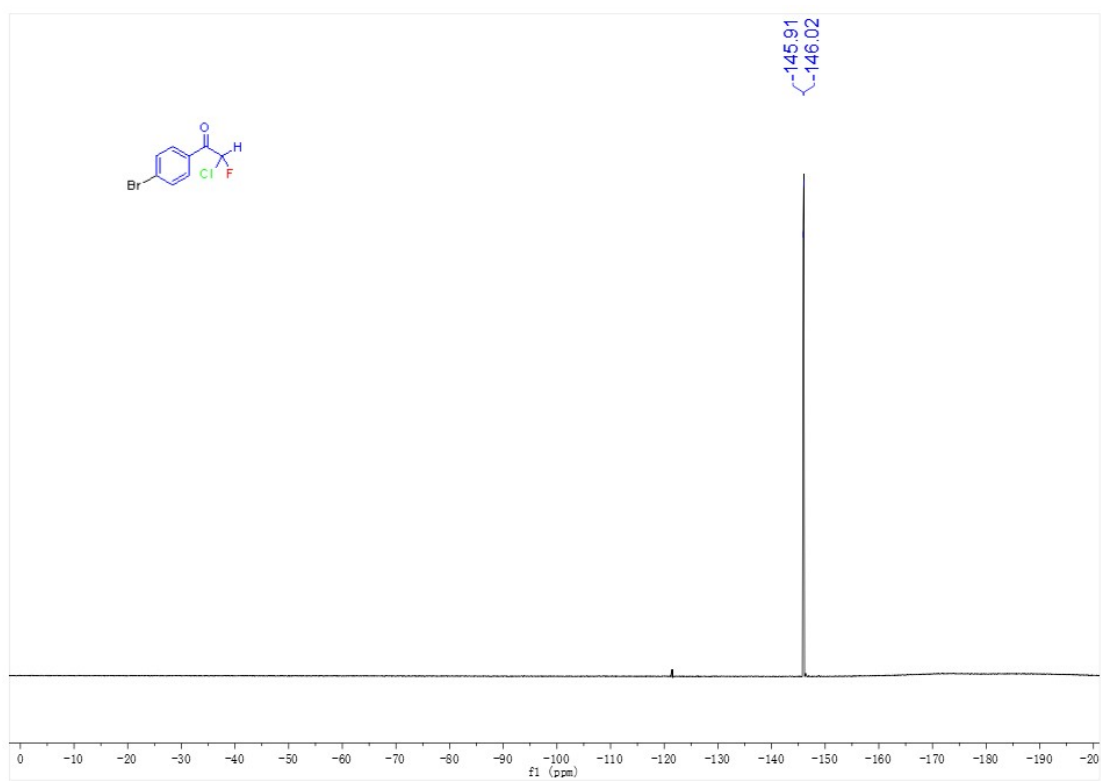
¹H NMR spectrum for 2k



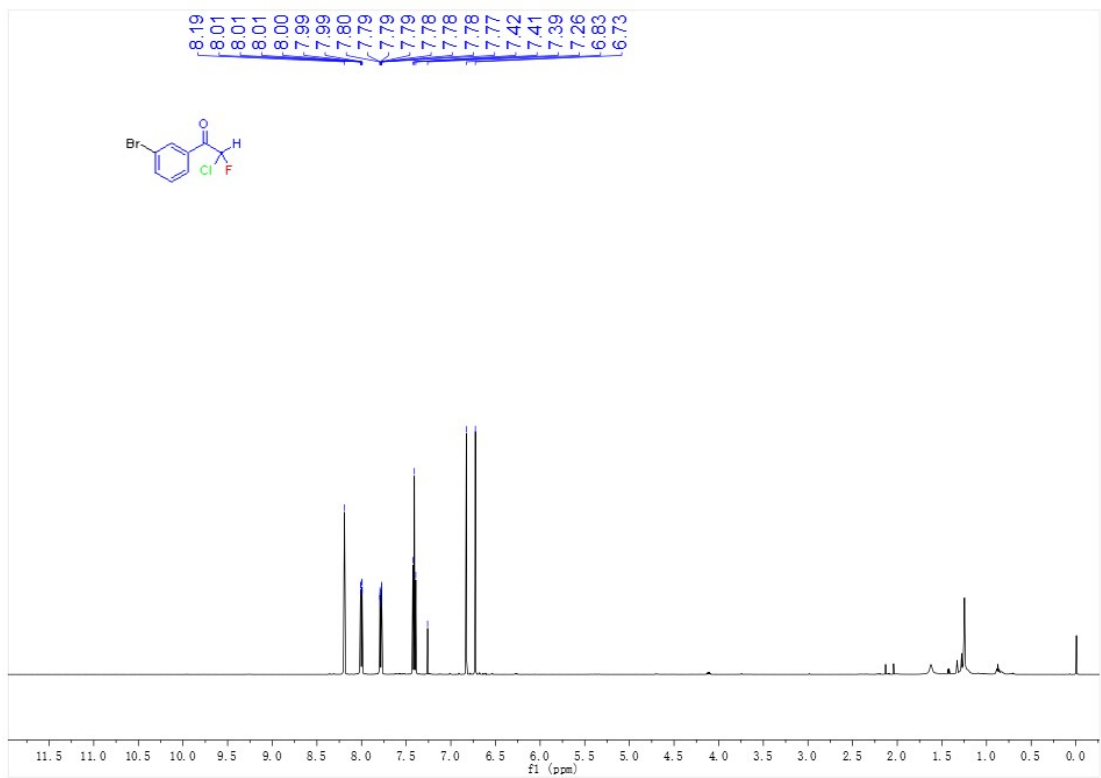
¹³C NMR spectrum for 2k



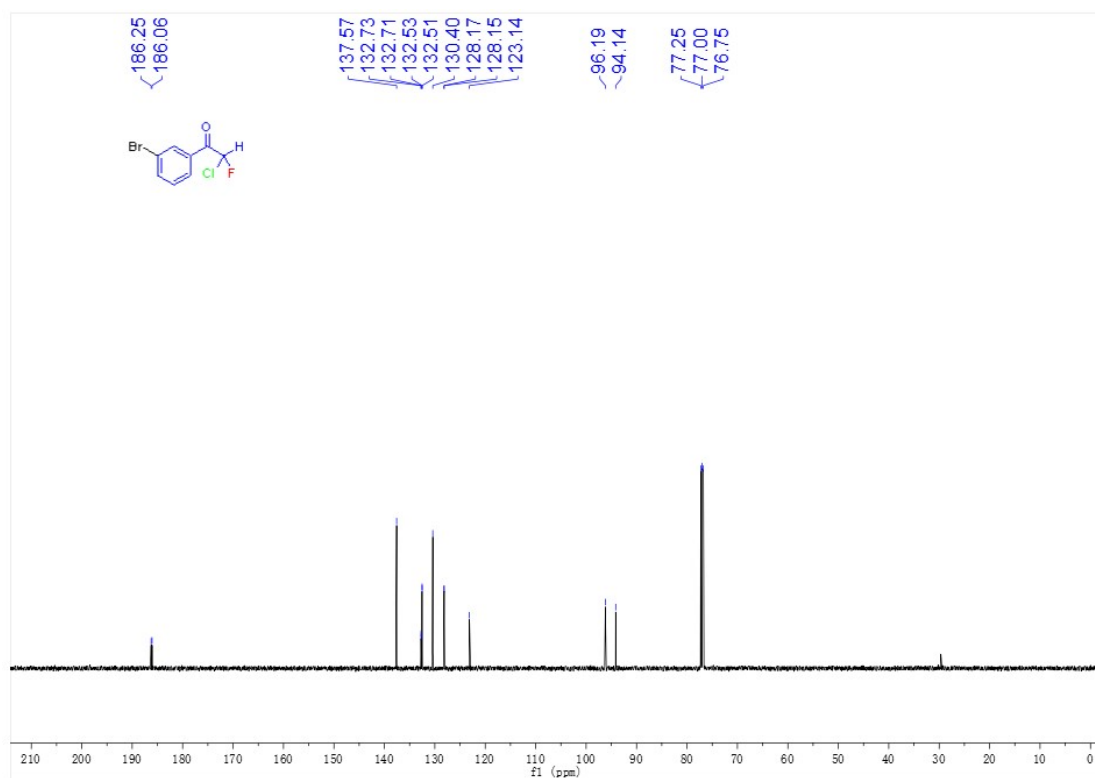
¹⁹F NMR spectrum for 2k



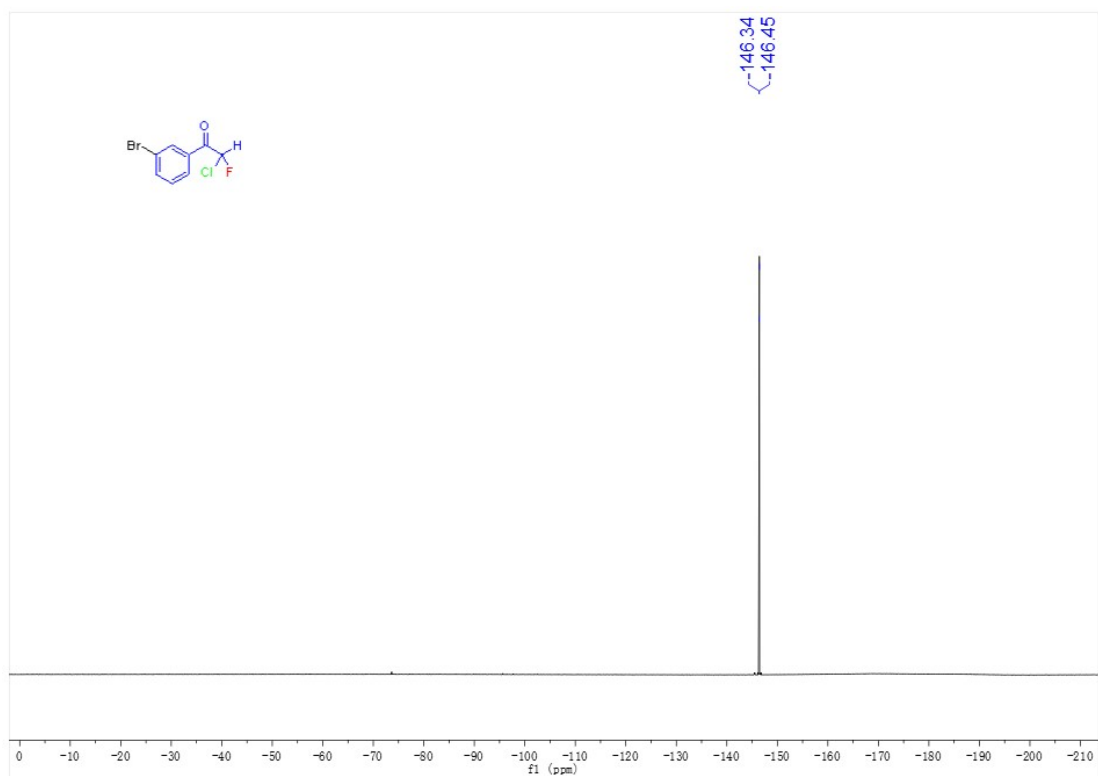
¹H NMR spectrum for 2l



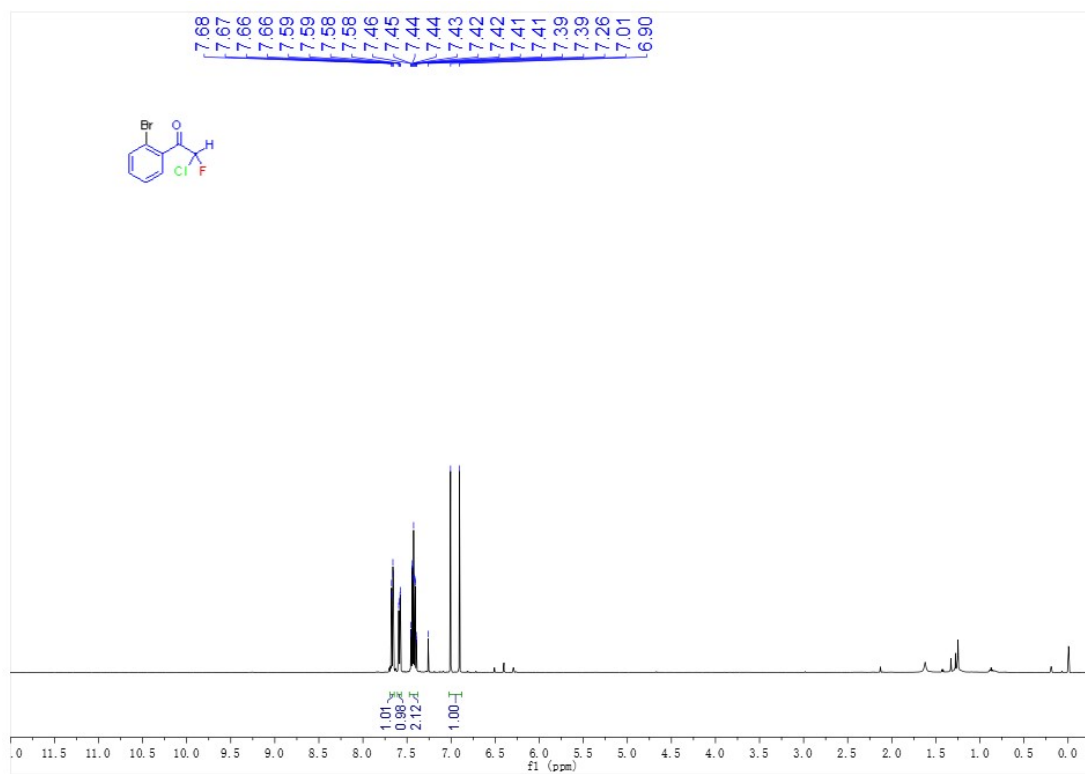
¹³C NMR spectrum for 2l



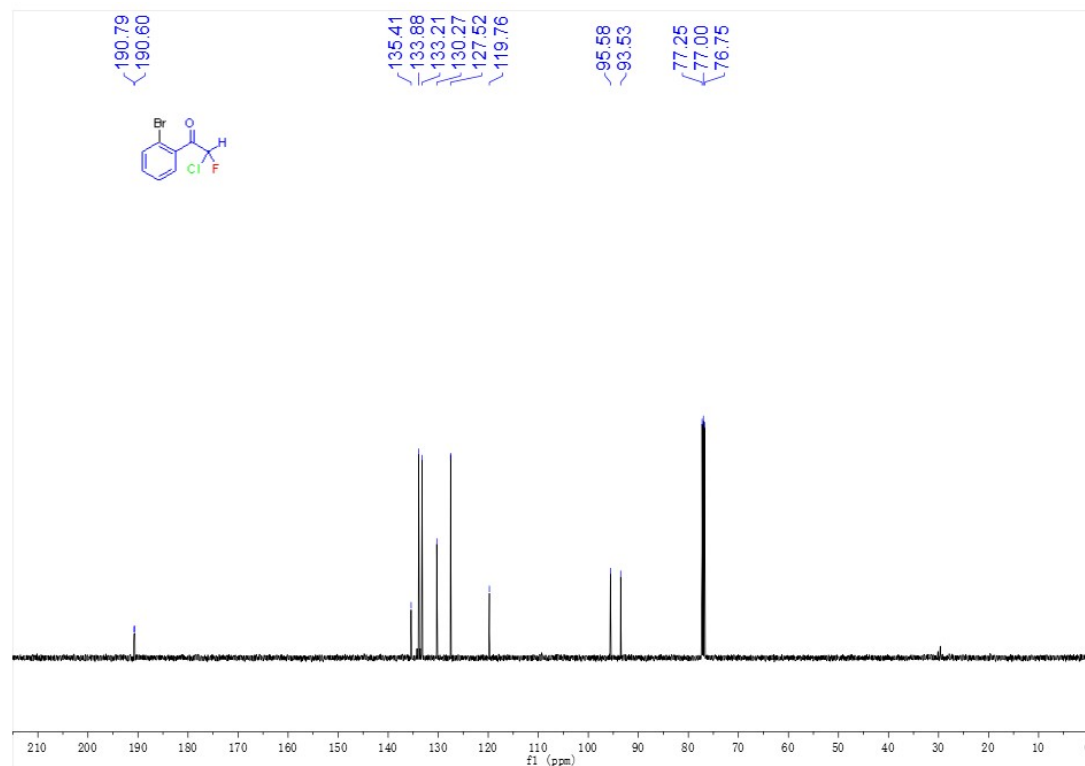
¹⁹F NMR spectrum for 2l



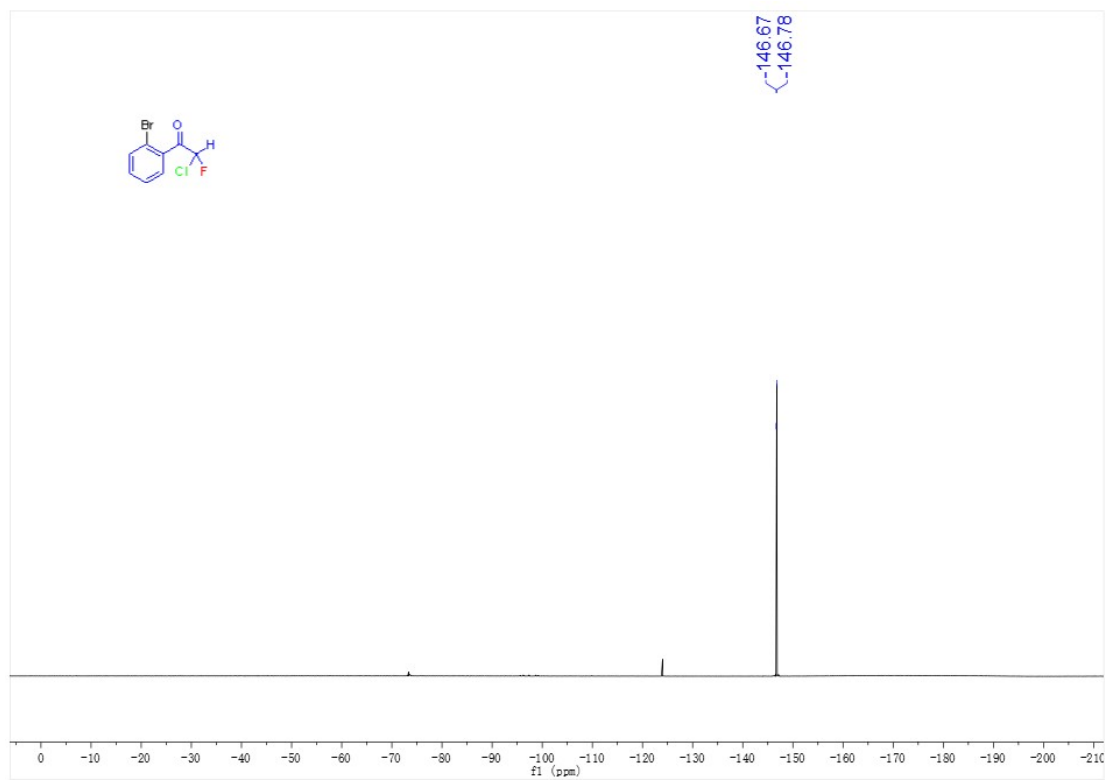
¹H NMR spectrum for 2m



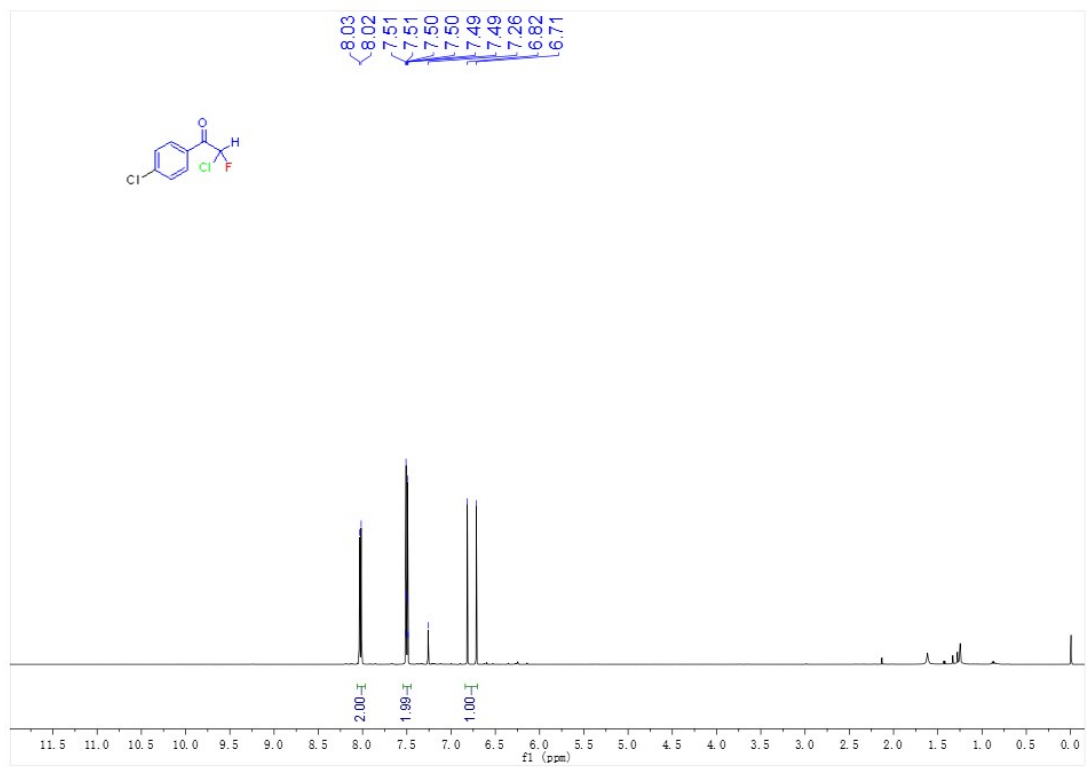
¹³C NMR spectrum for 2m



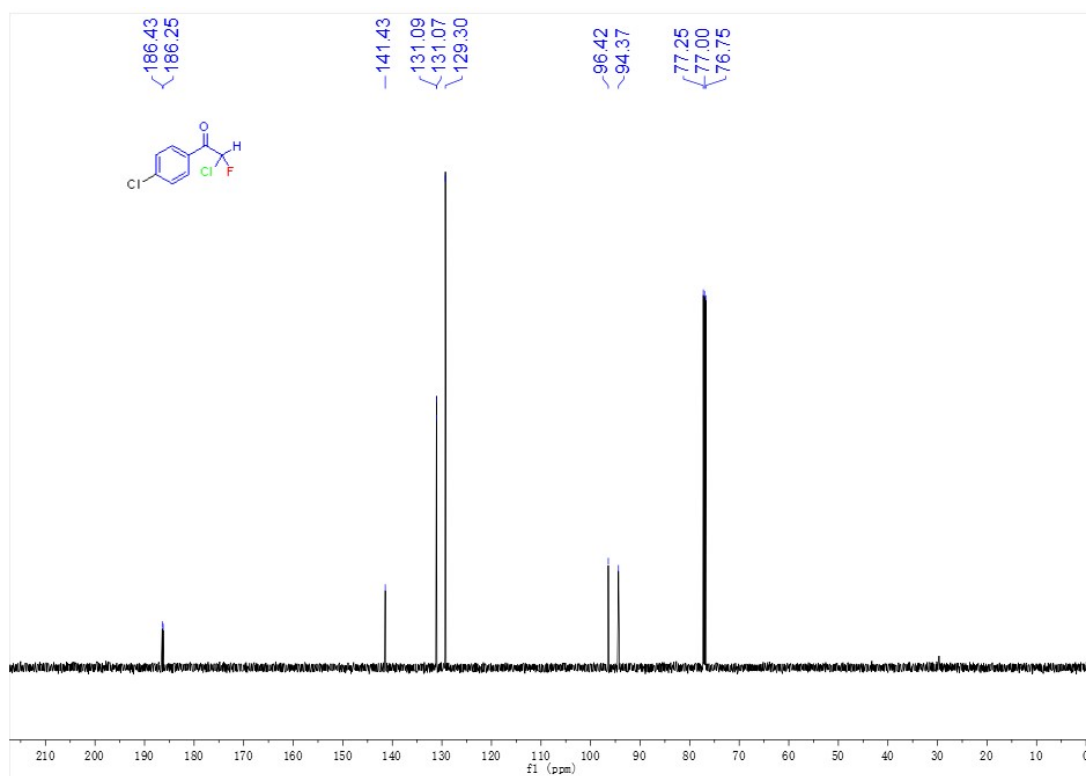
¹⁹F NMR spectrum for 2m



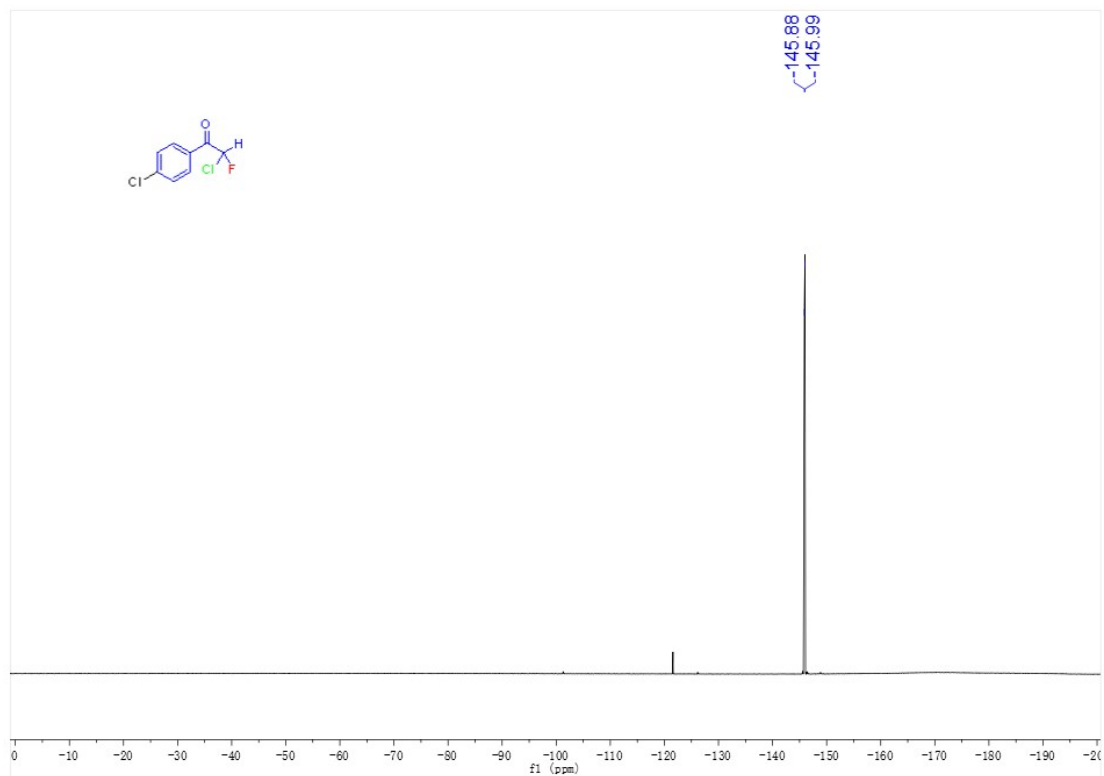
¹H NMR spectrum for 2n



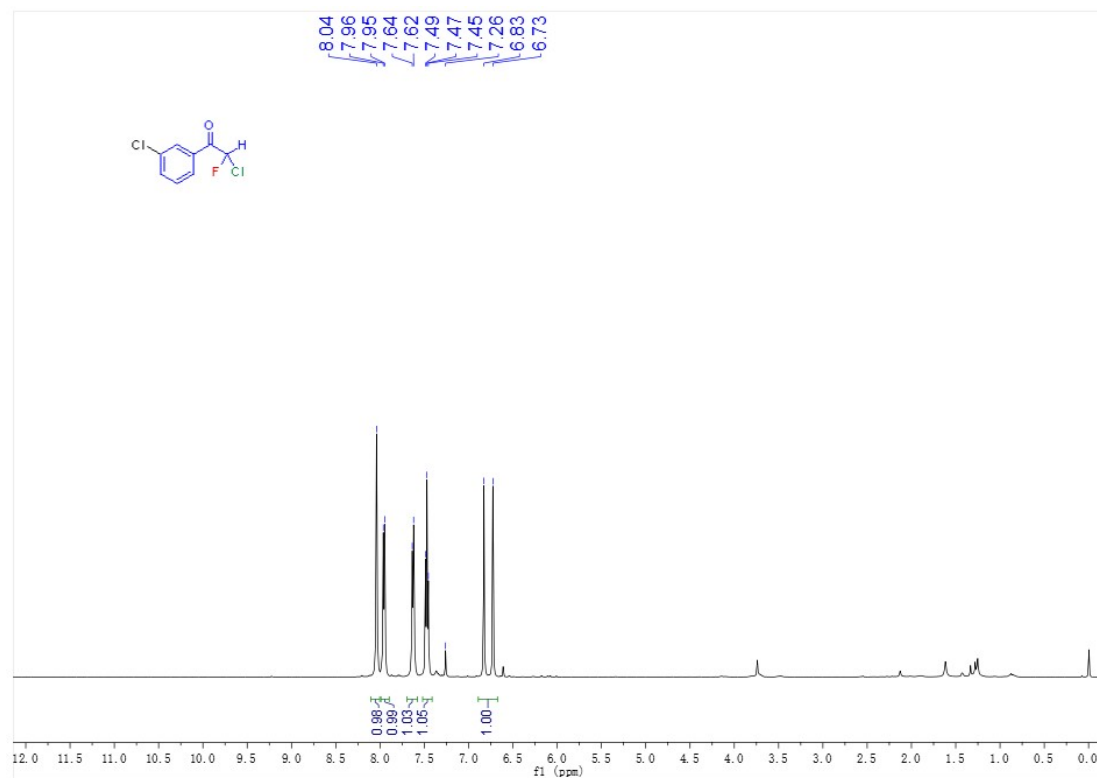
¹³C NMR spectrum for 2n



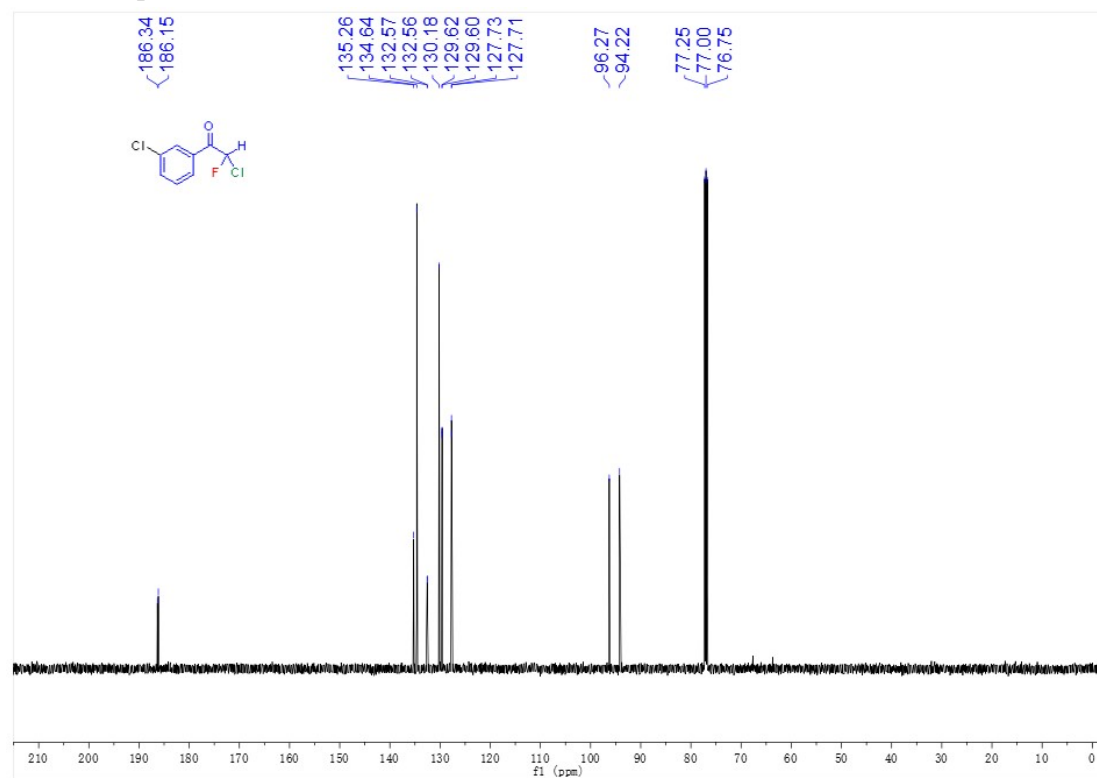
¹⁹F NMR spectrum for 2n



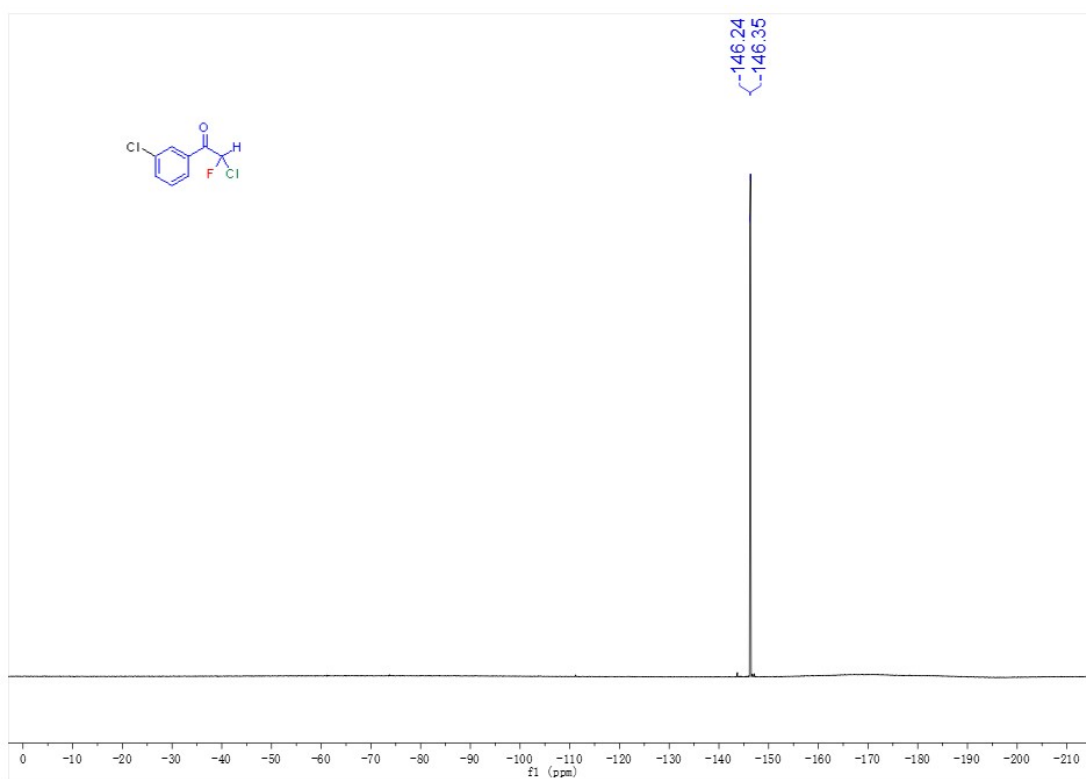
¹H NMR spectrum for 2o



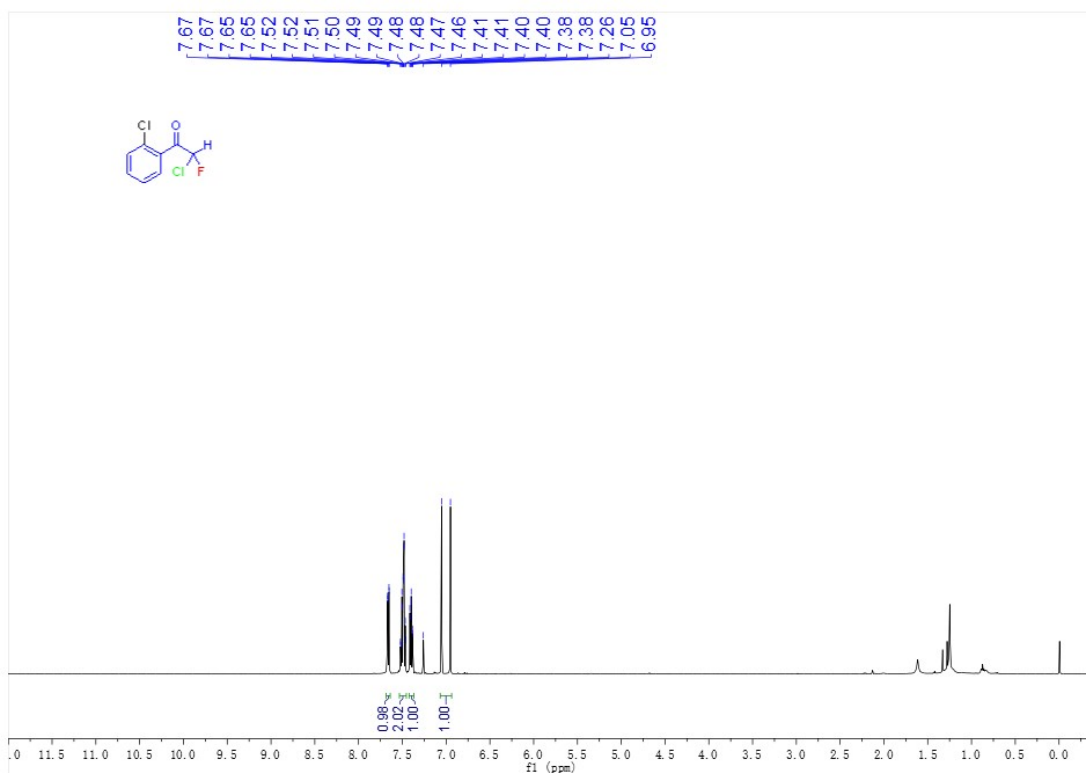
¹³C NMR spectrum for 2o



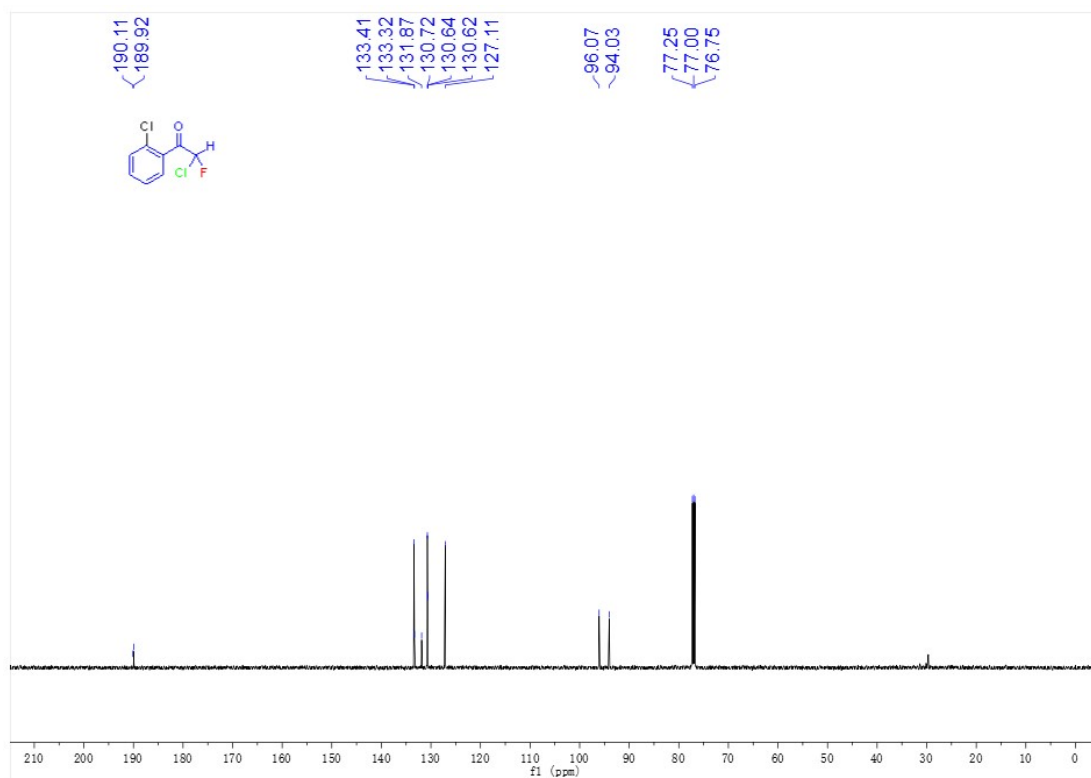
¹⁹F NMR spectrum for 2o



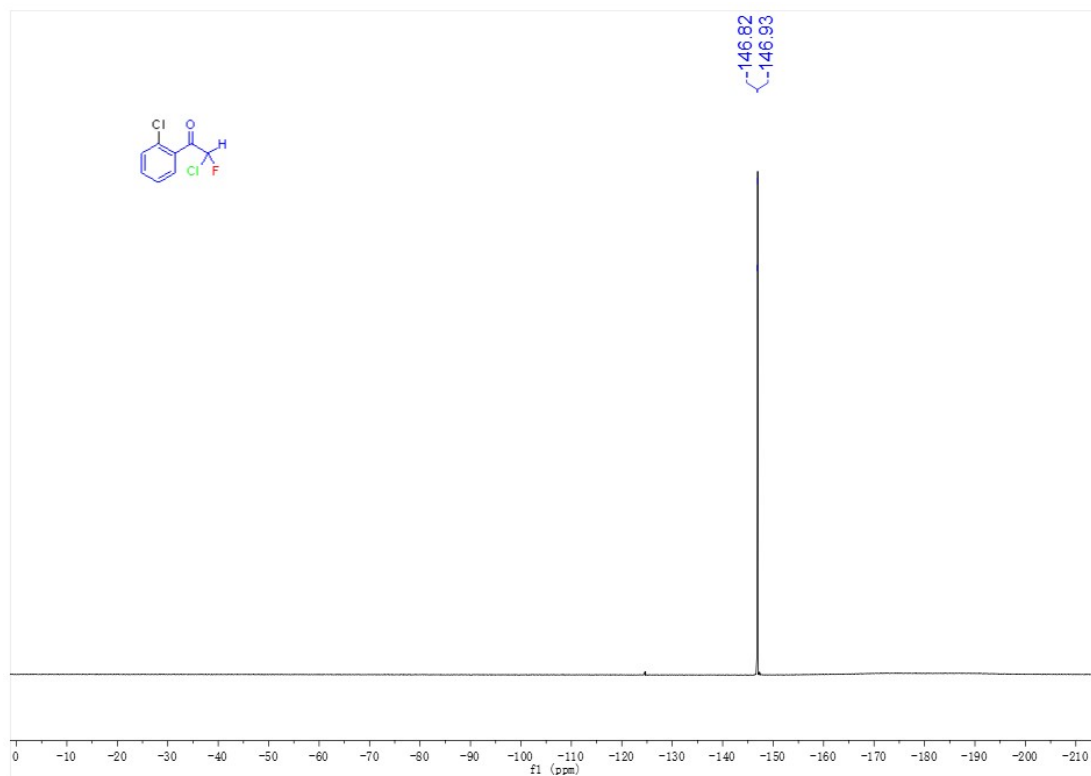
¹H NMR spectrum for 2p



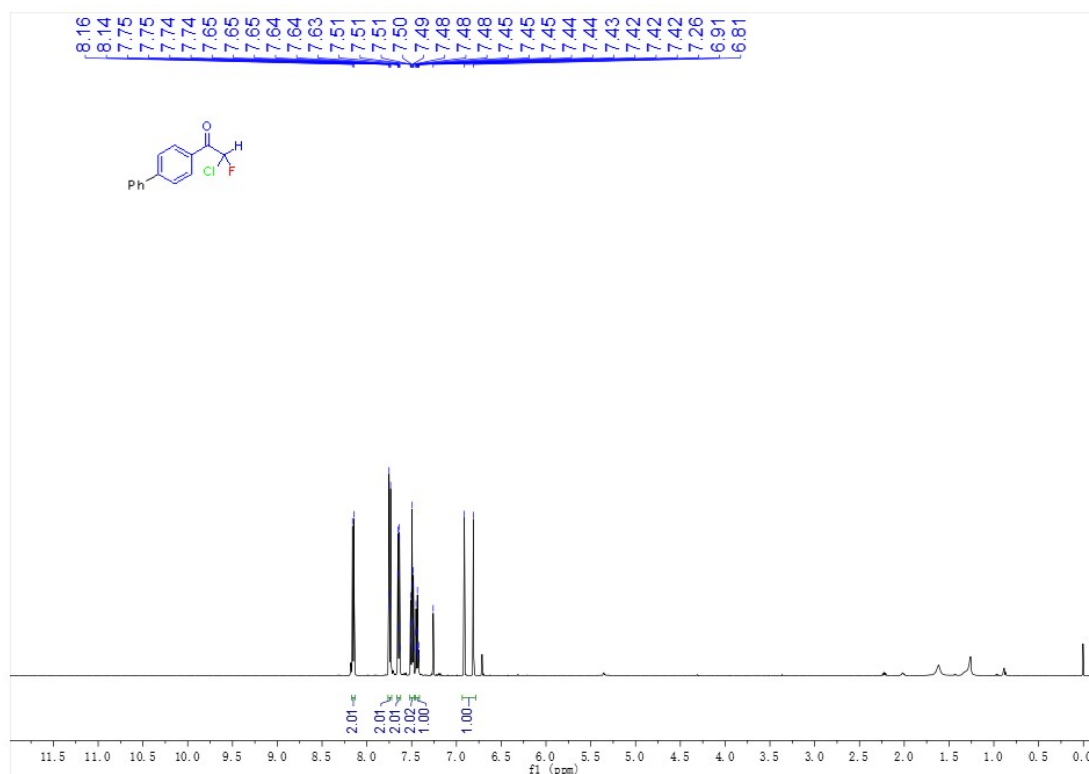
¹³C NMR spectrum for 2p



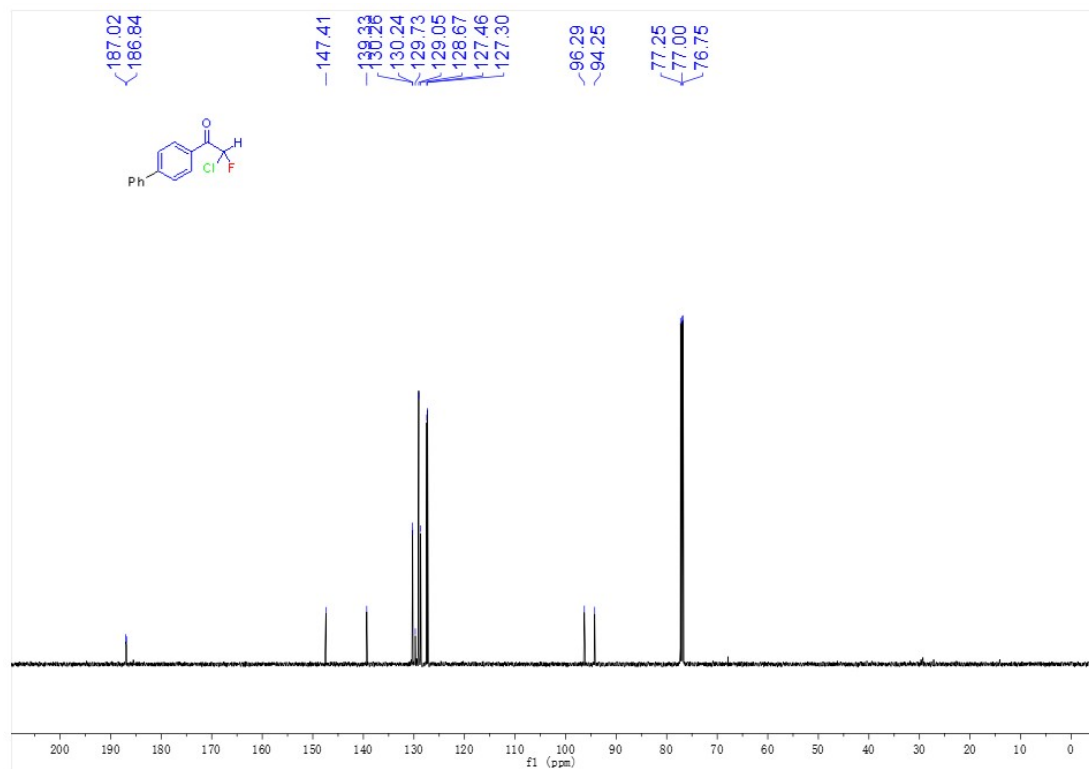
¹⁹F NMR spectrum for 2p



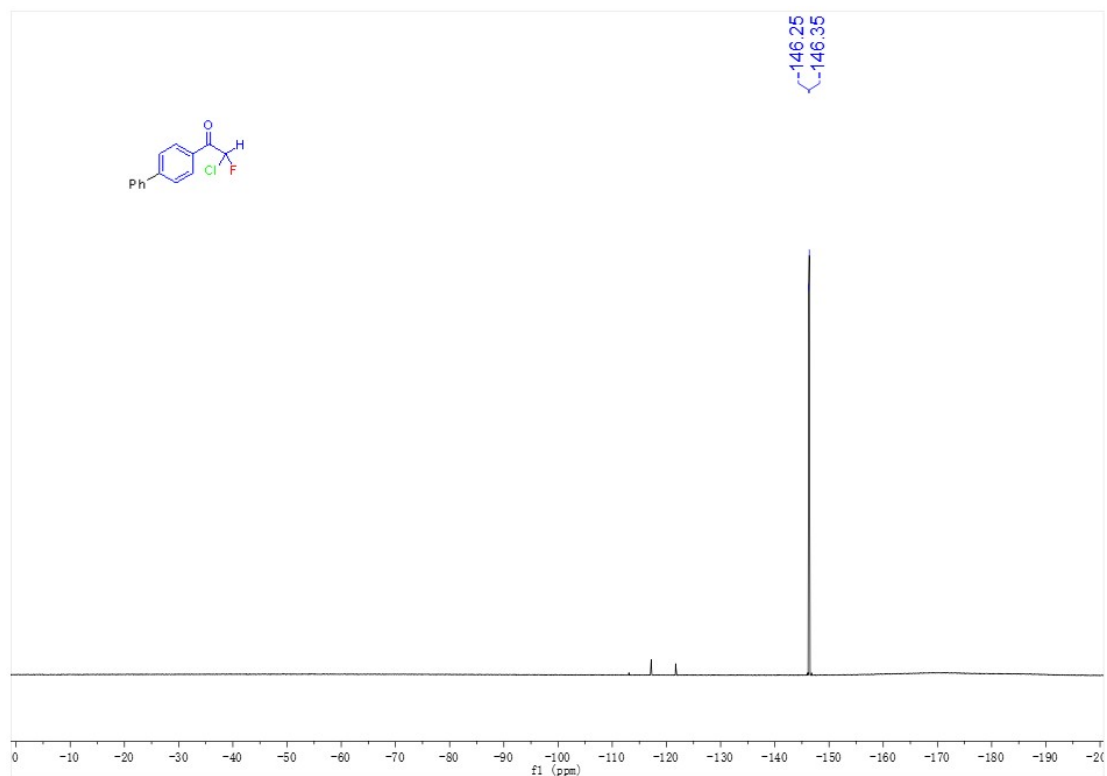
¹H NMR spectrum for 2q



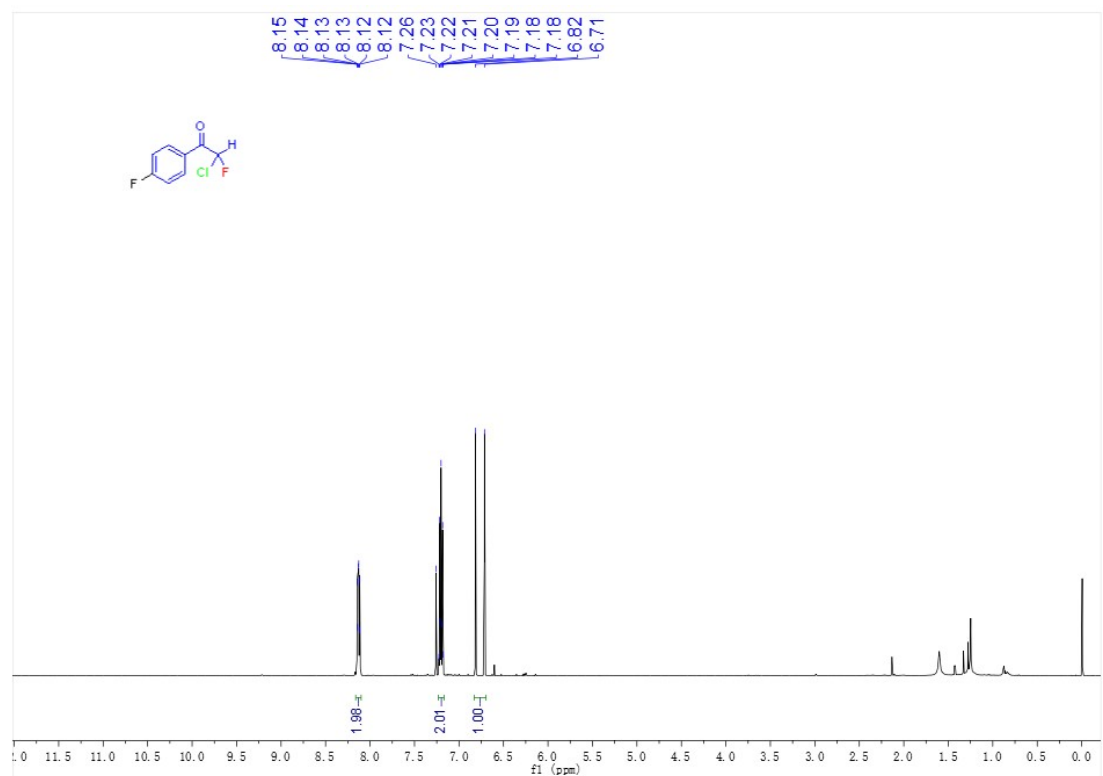
¹³C NMR spectrum for 2q



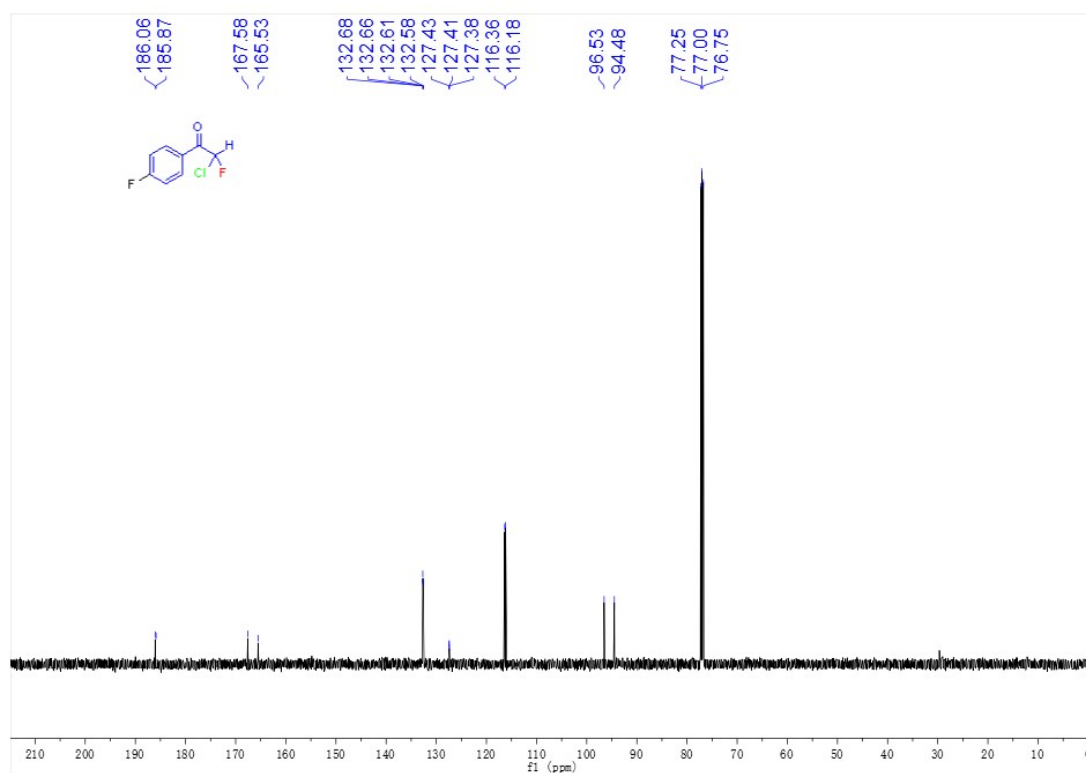
¹⁹F NMR spectrum for 2q



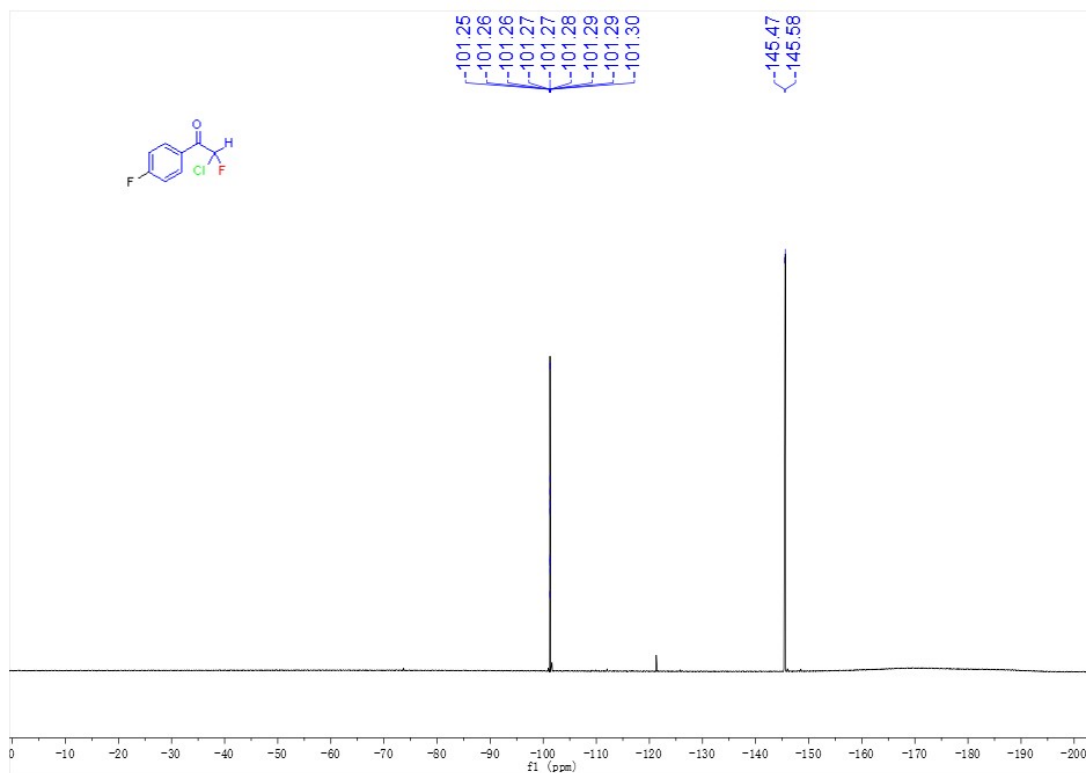
¹H NMR spectrum for 2r



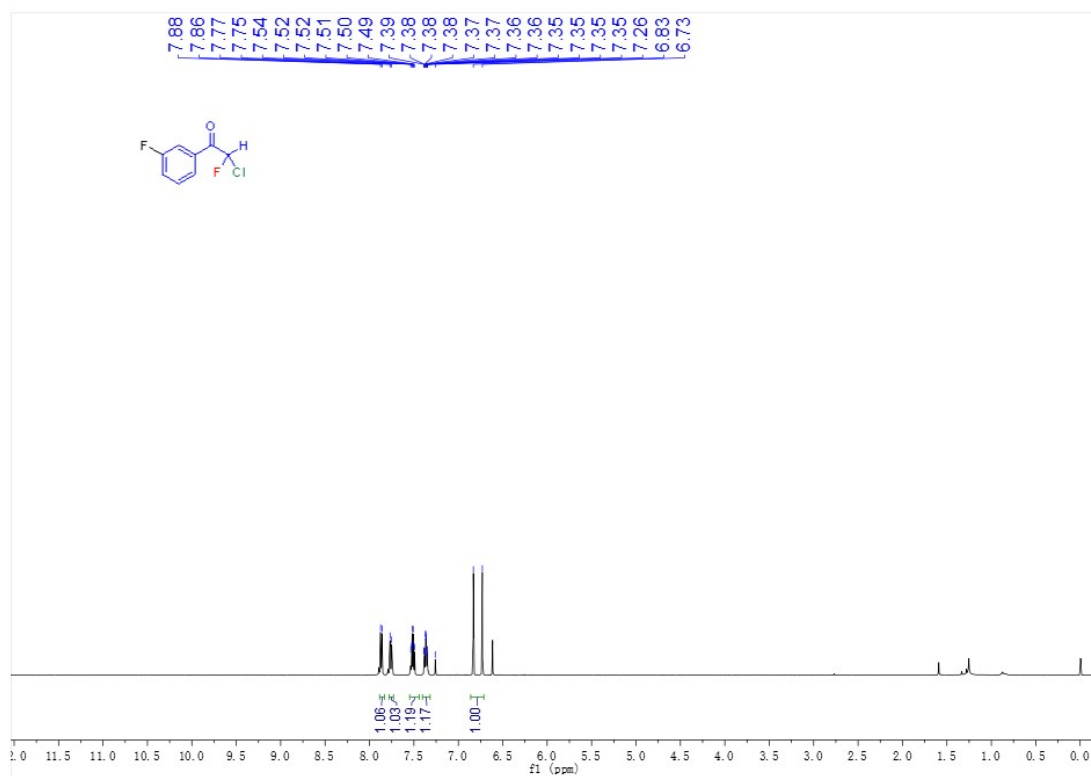
¹³C NMR spectrum for 2r



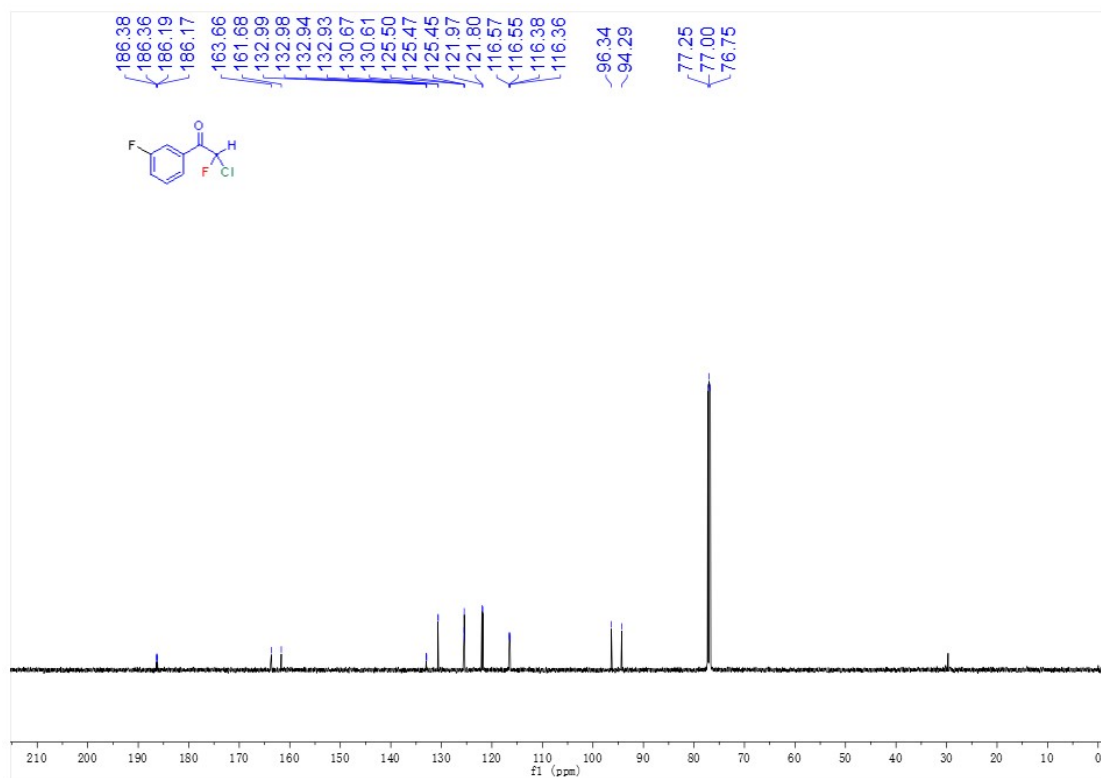
¹⁹F NMR spectrum for 2r



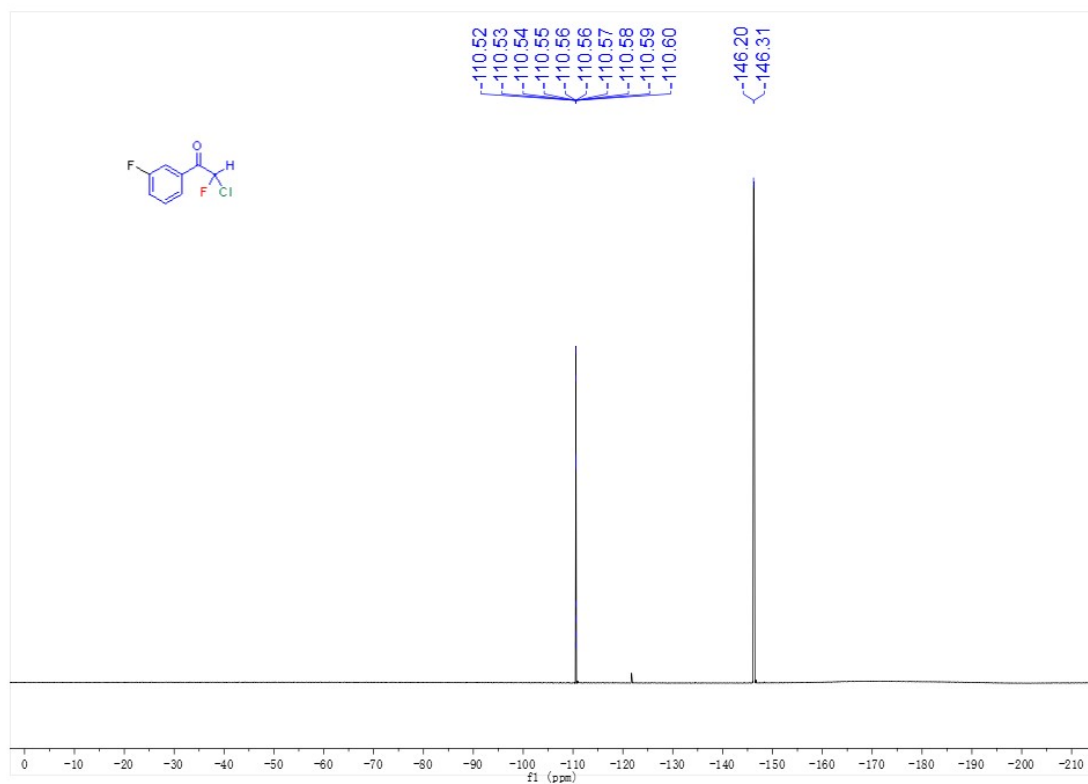
¹H NMR spectrum for 2s



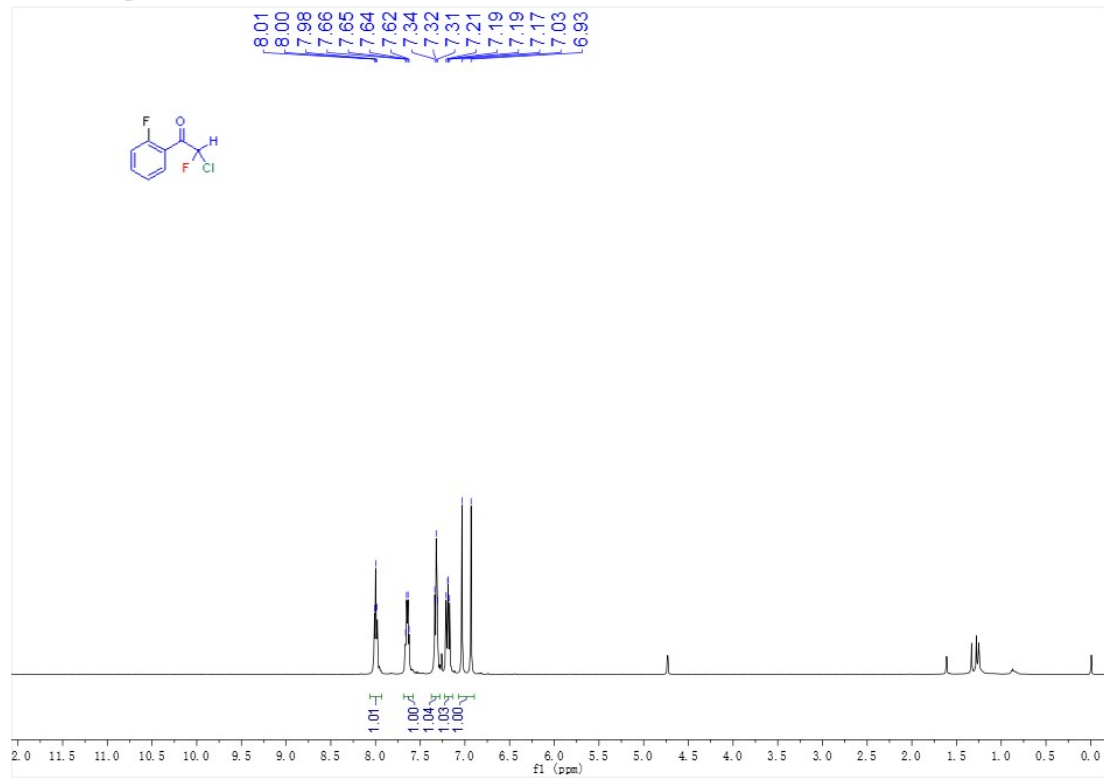
¹³C NMR spectrum for 2s



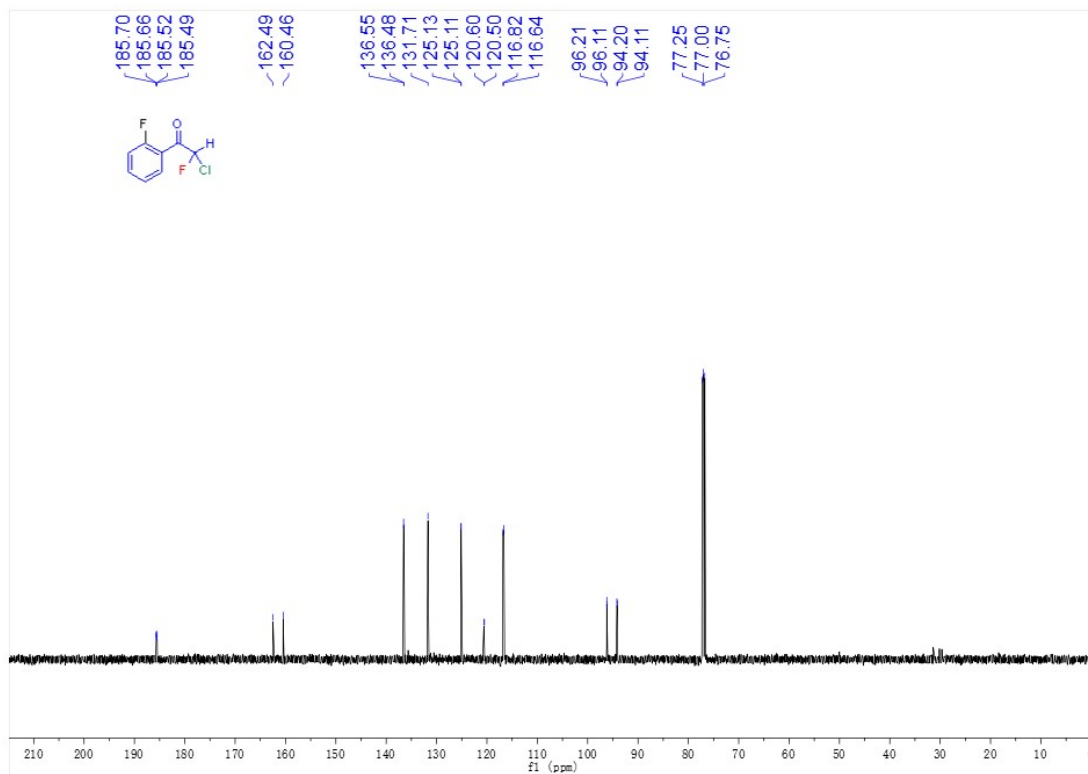
¹⁹F NMR spectrum for 2s



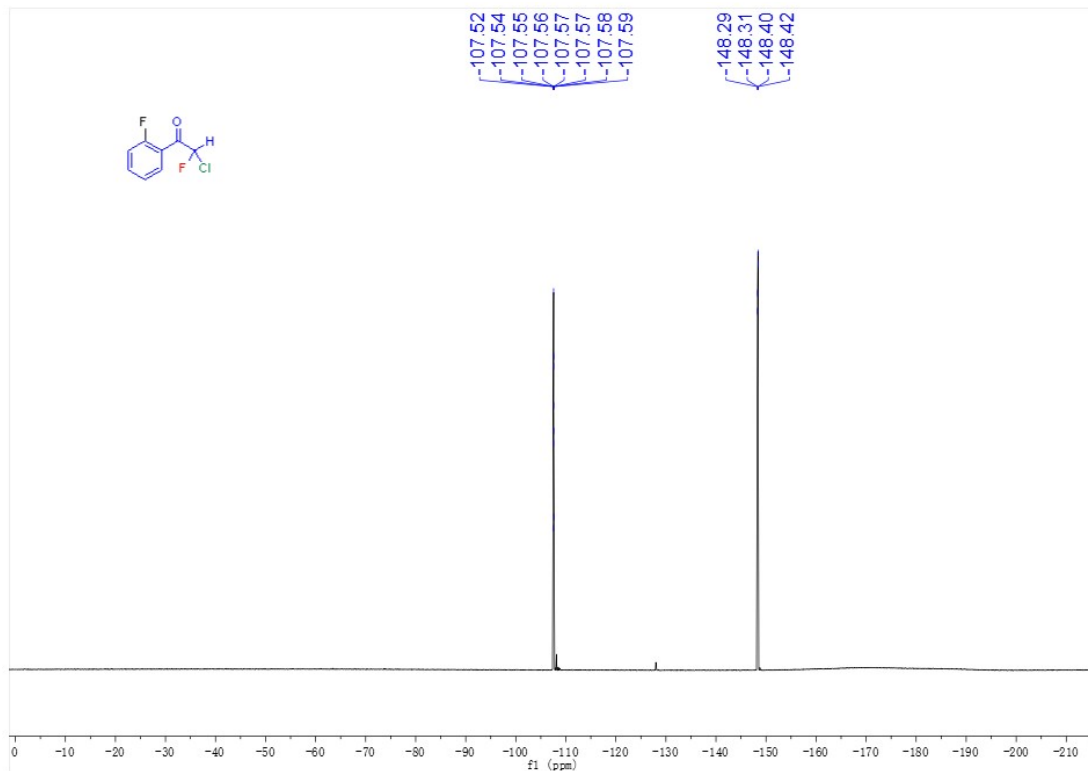
¹H NMR spectrum for 2t



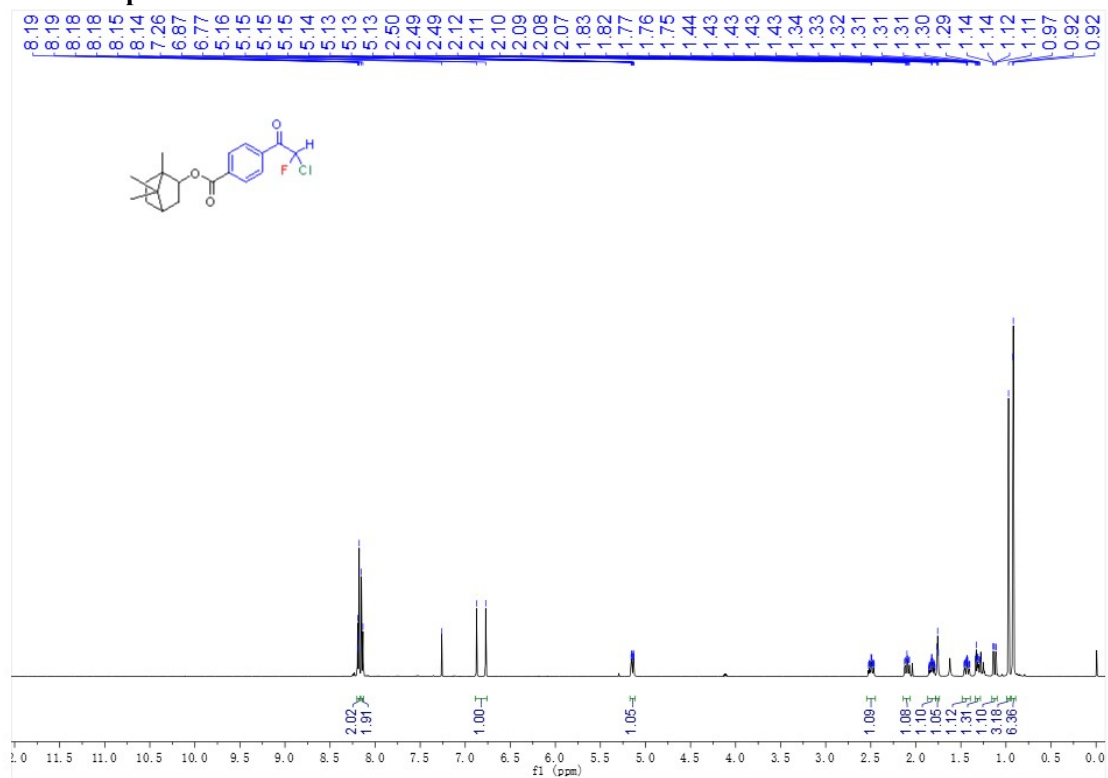
¹³C NMR spectrum for 2t



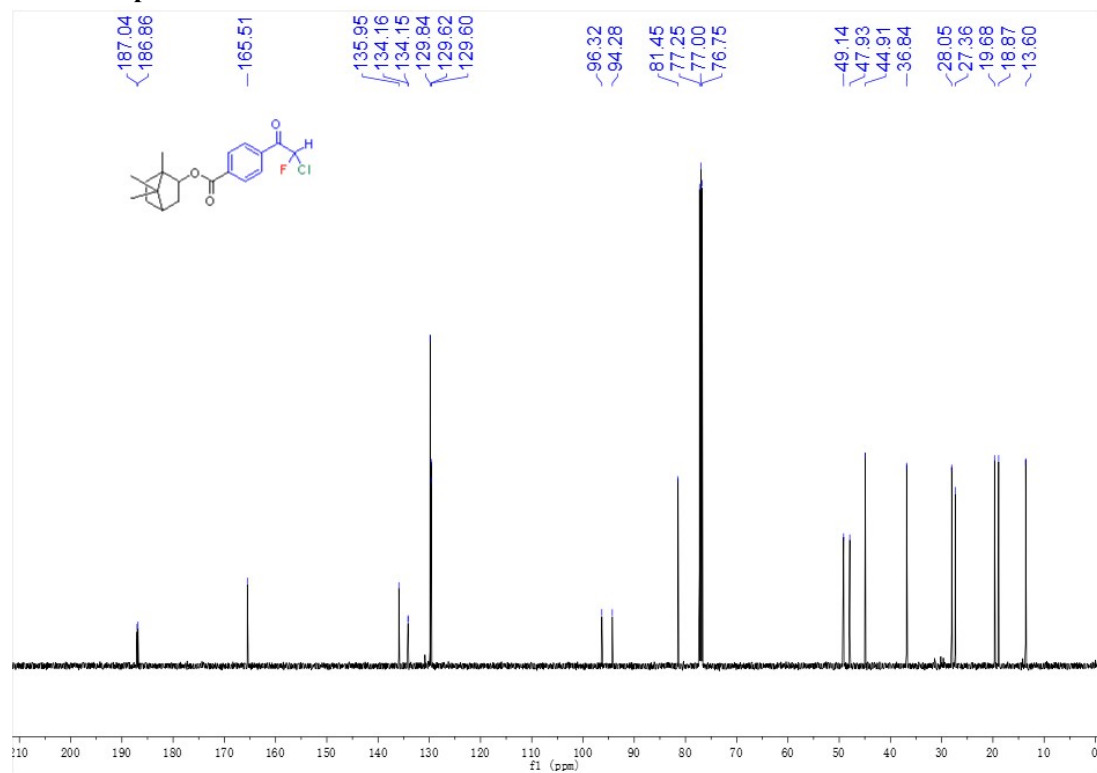
¹⁹F NMR spectrum for 2t



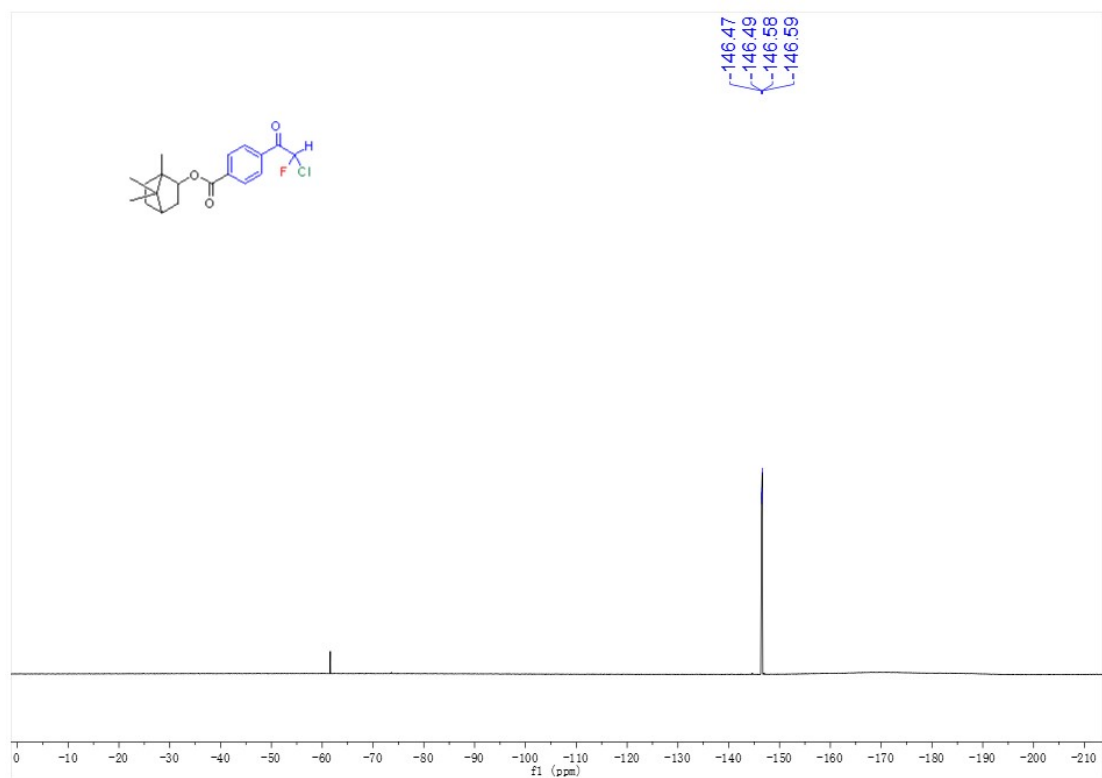
¹H NMR spectrum for 2u



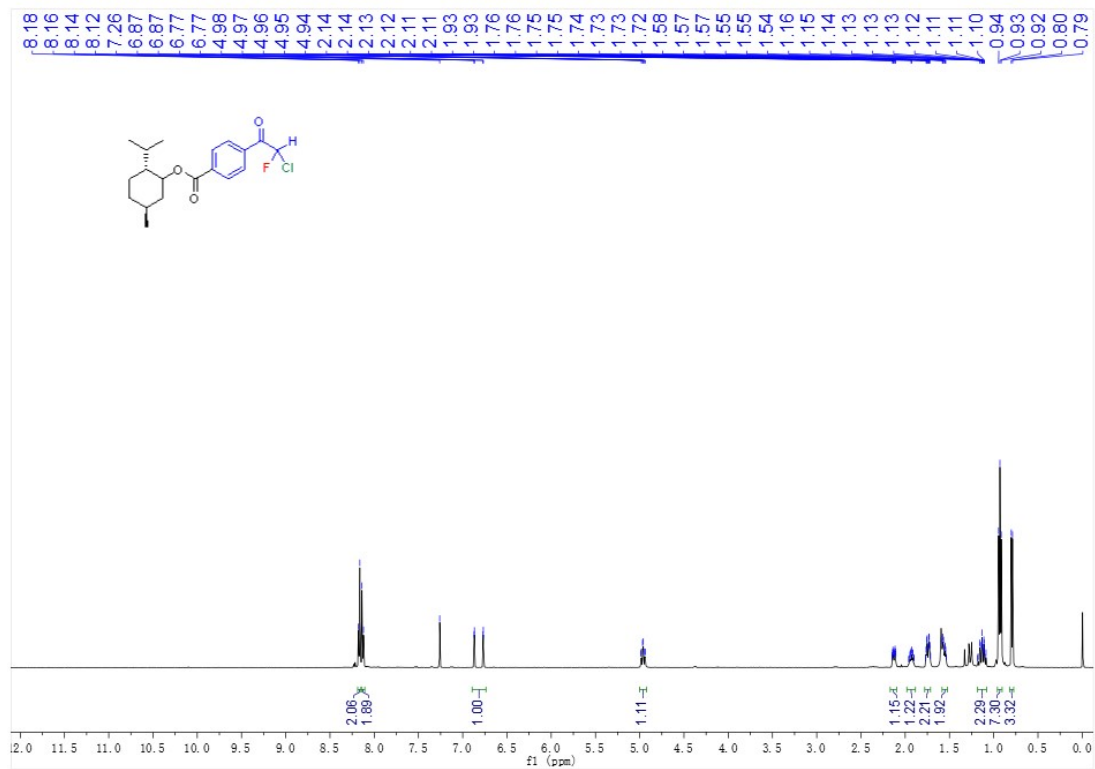
¹³C NMR spectrum for 2u



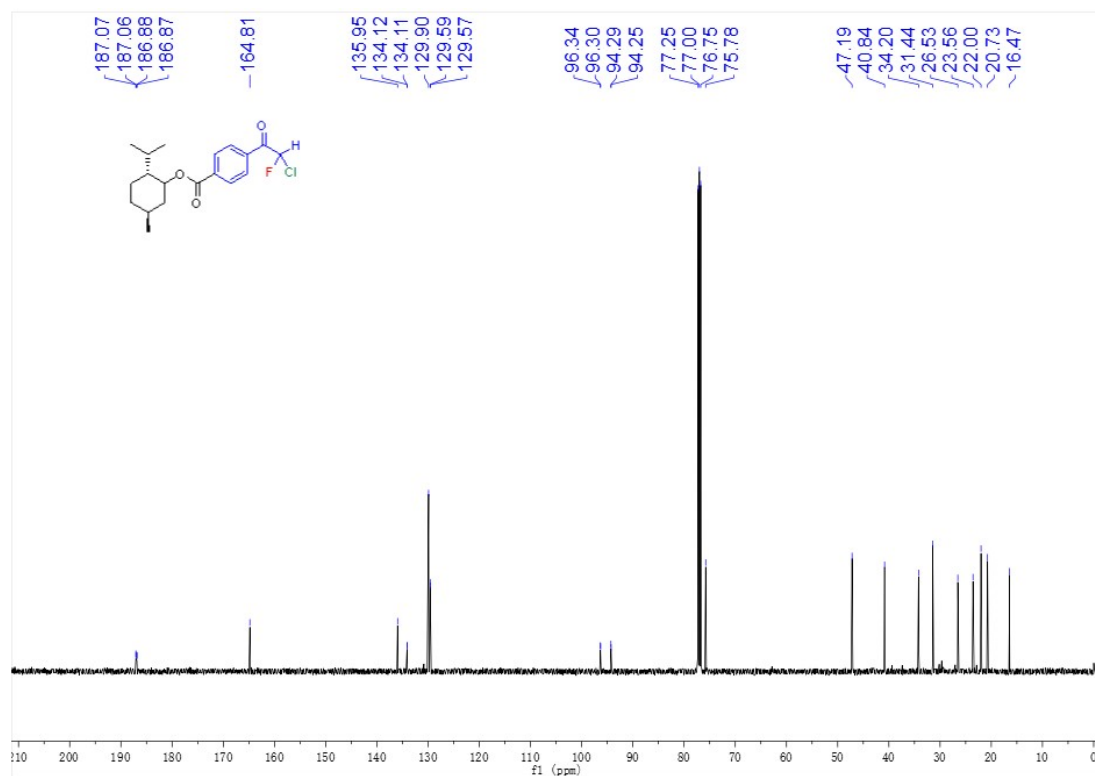
¹⁹F NMR spectrum for 2u



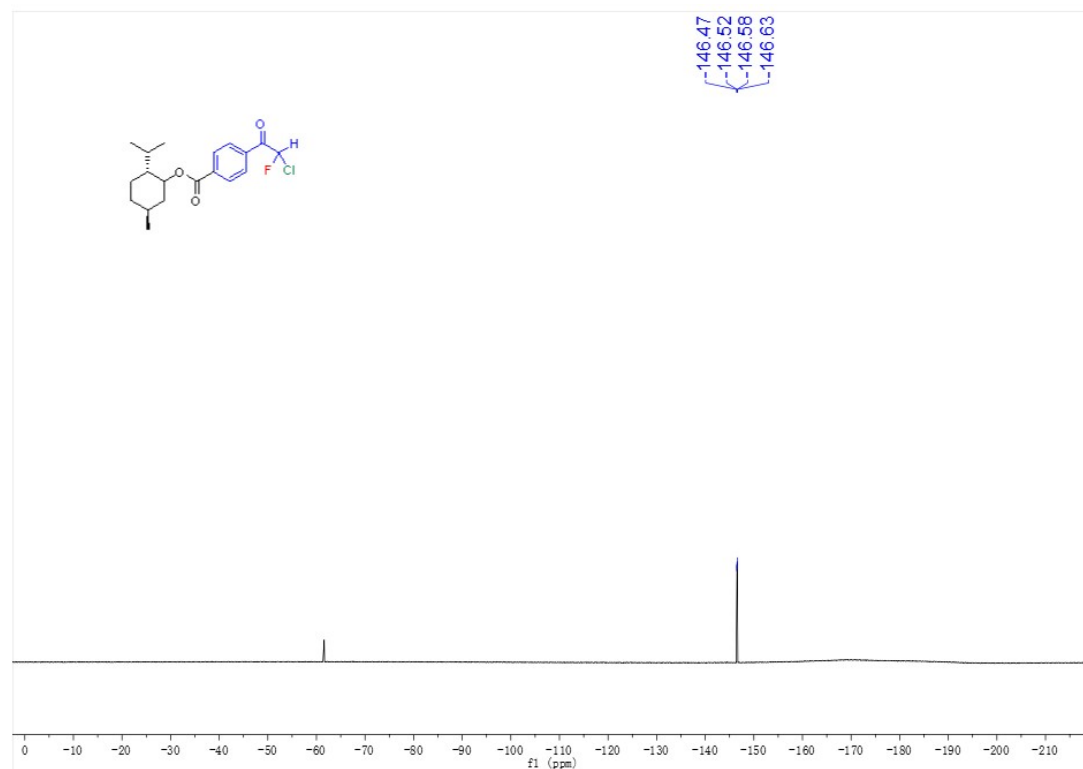
¹H NMR spectrum for 2v



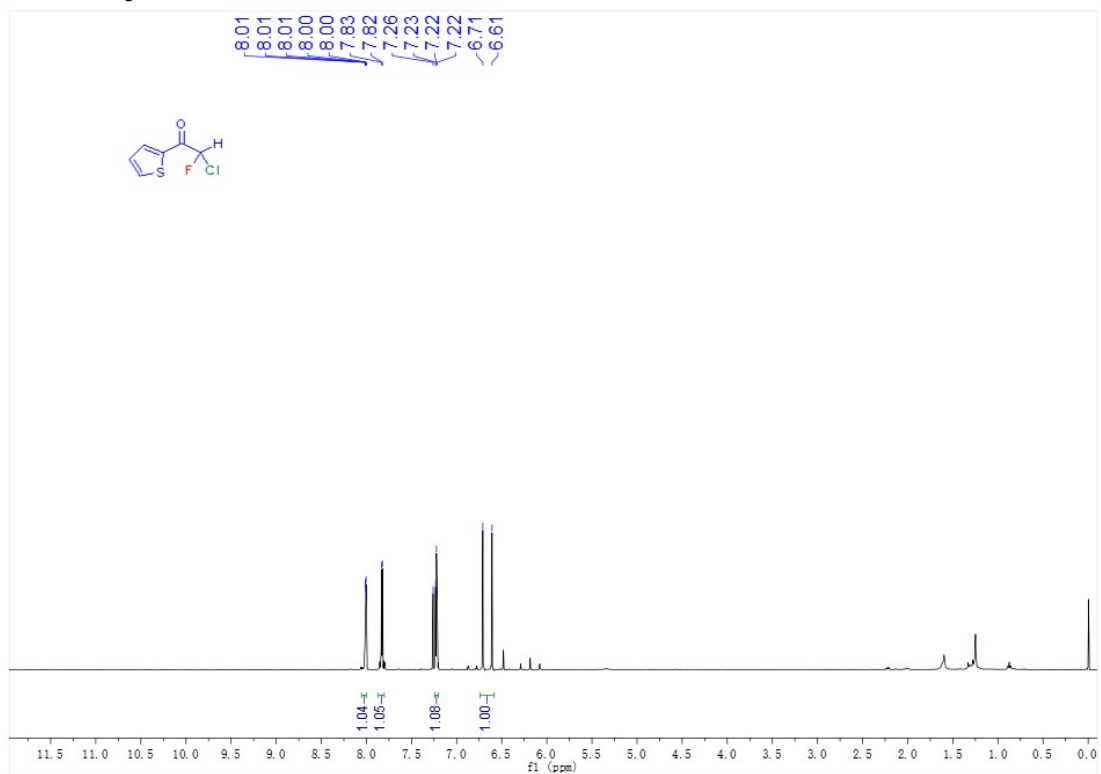
¹³C NMR spectrum for 2v



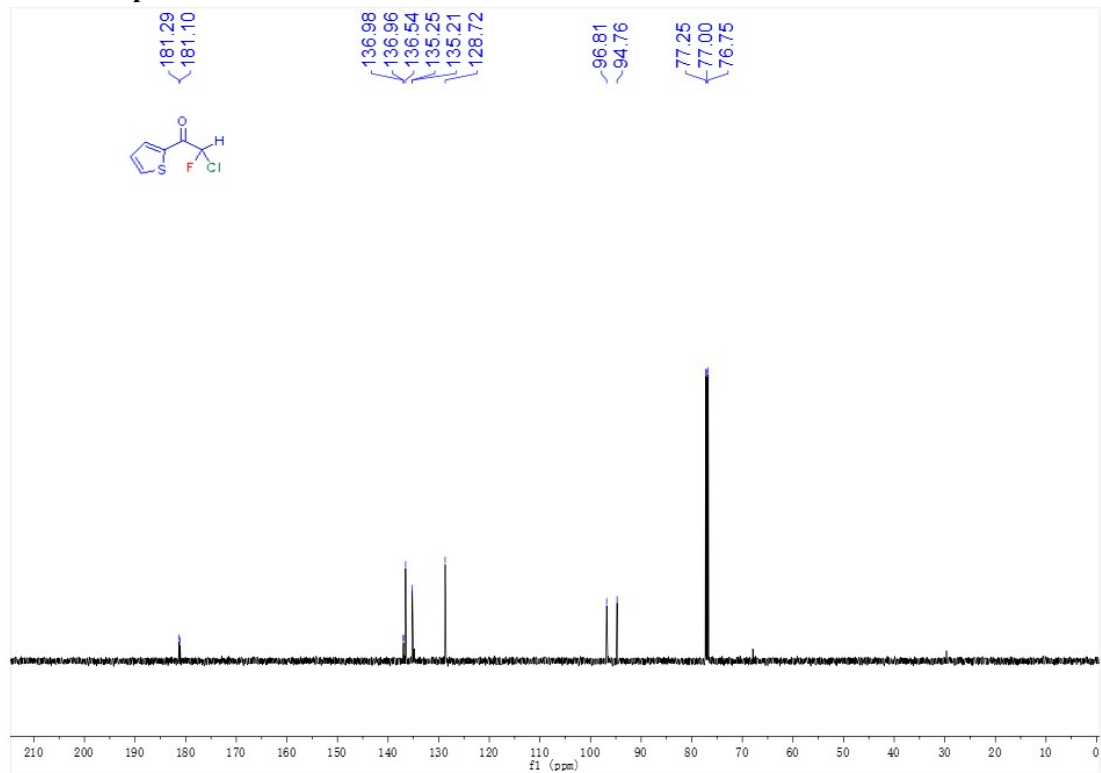
¹⁹F NMR spectrum for 2v



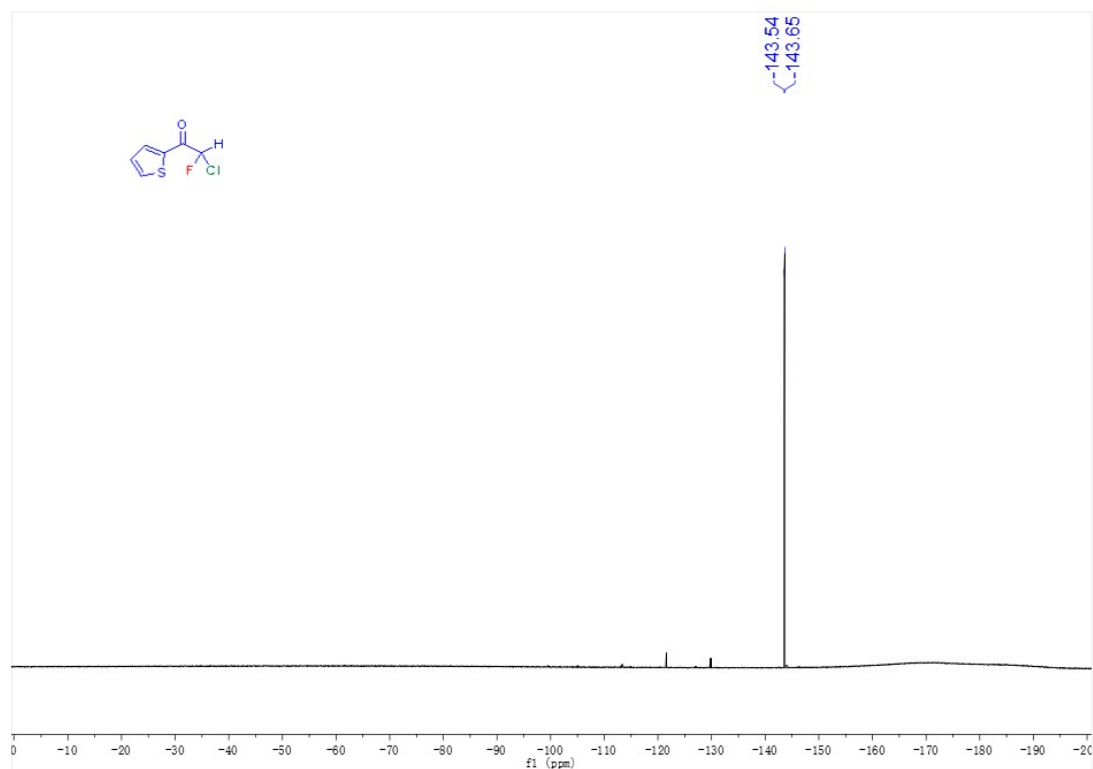
¹H NMR spectrum for 2w



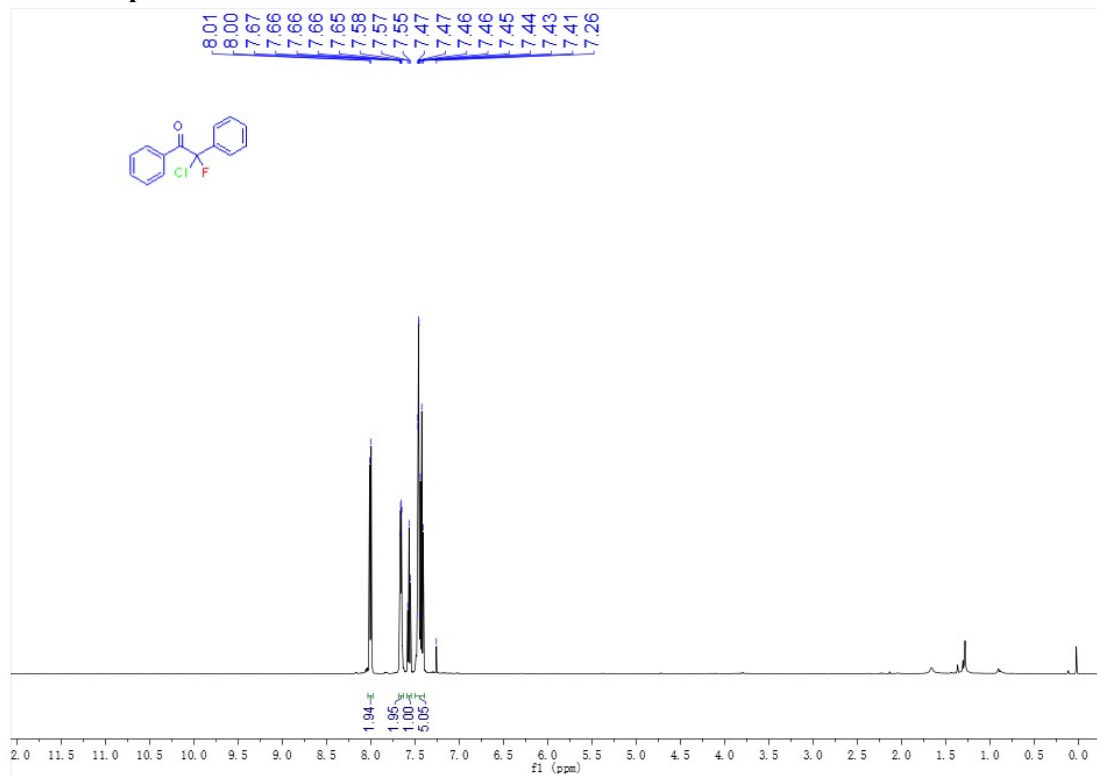
¹³C NMR spectrum for 2w



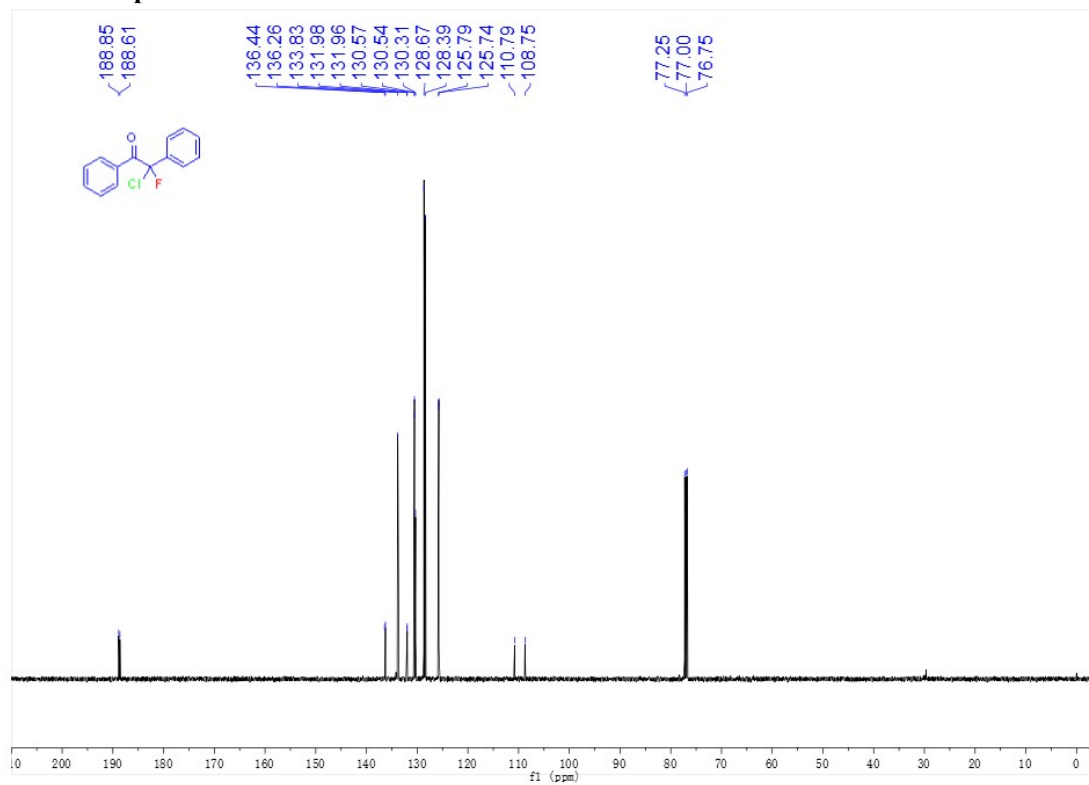
¹⁹F NMR spectrum for 2w



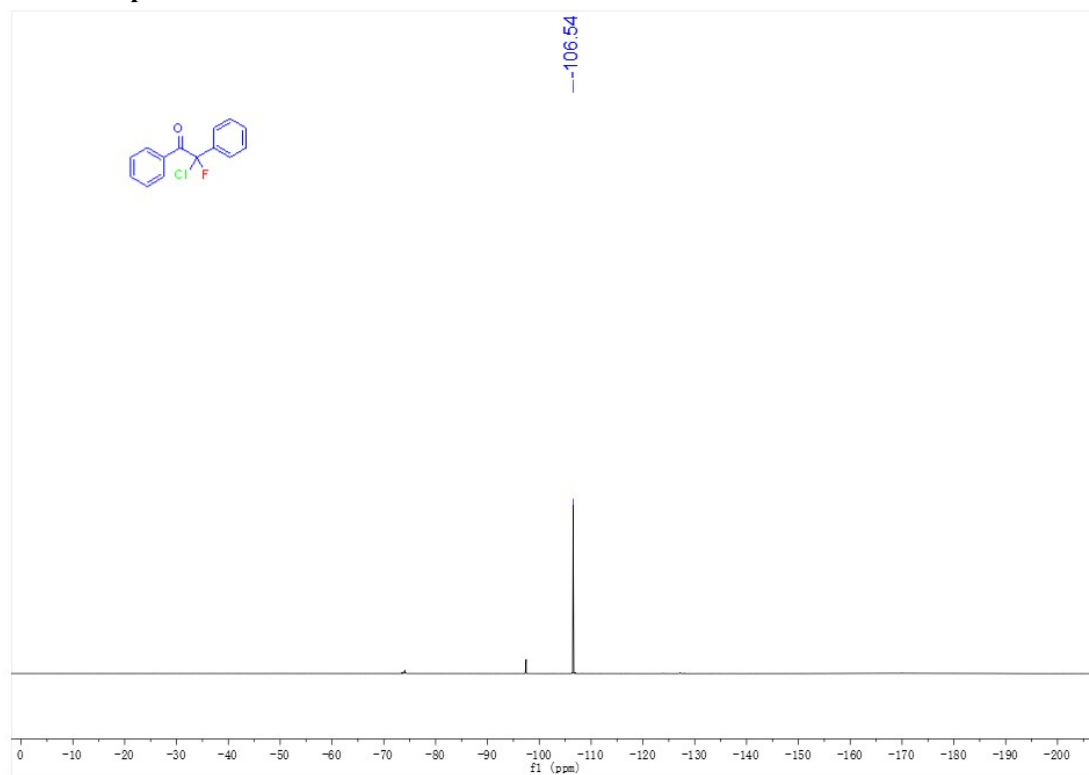
¹H NMR spectrum for 2x



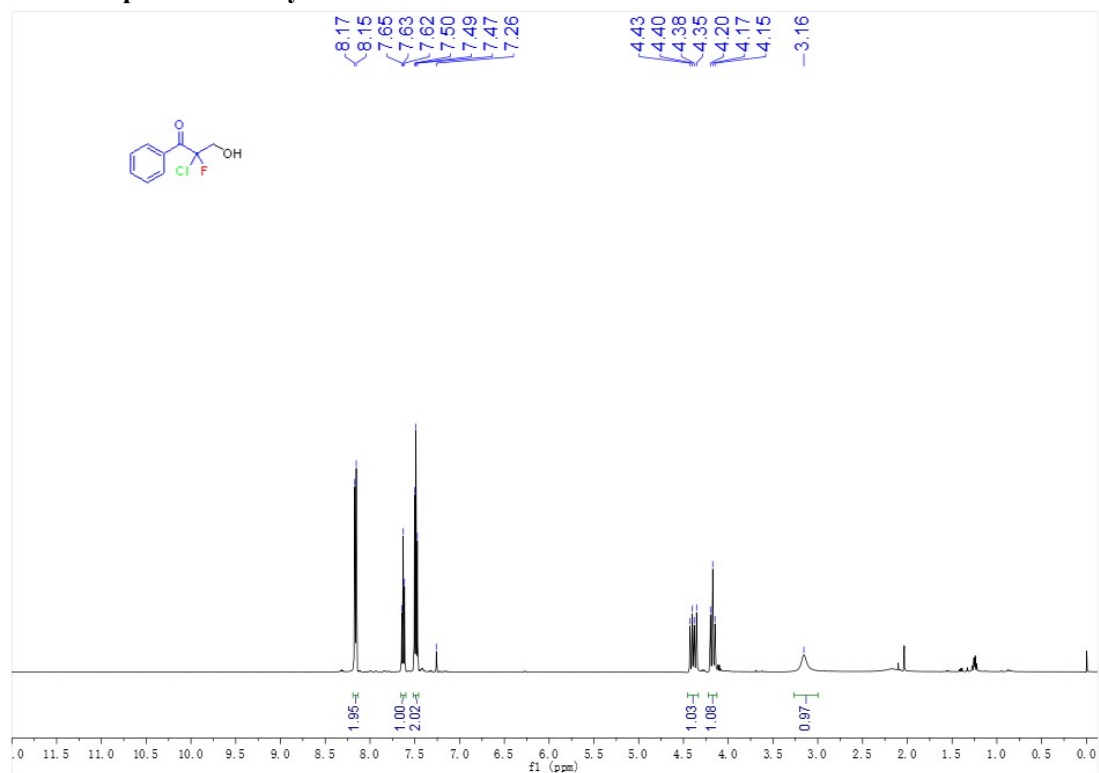
¹³C NMR spectrum for 2x



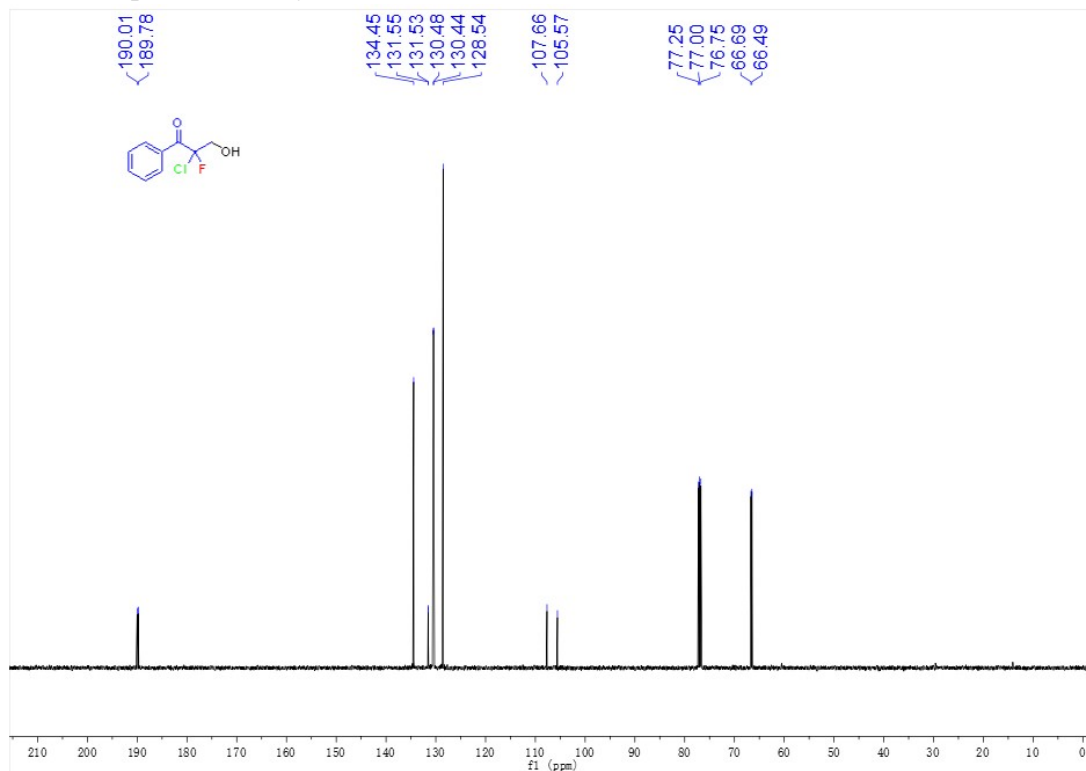
¹⁹F NMR spectrum for 2x



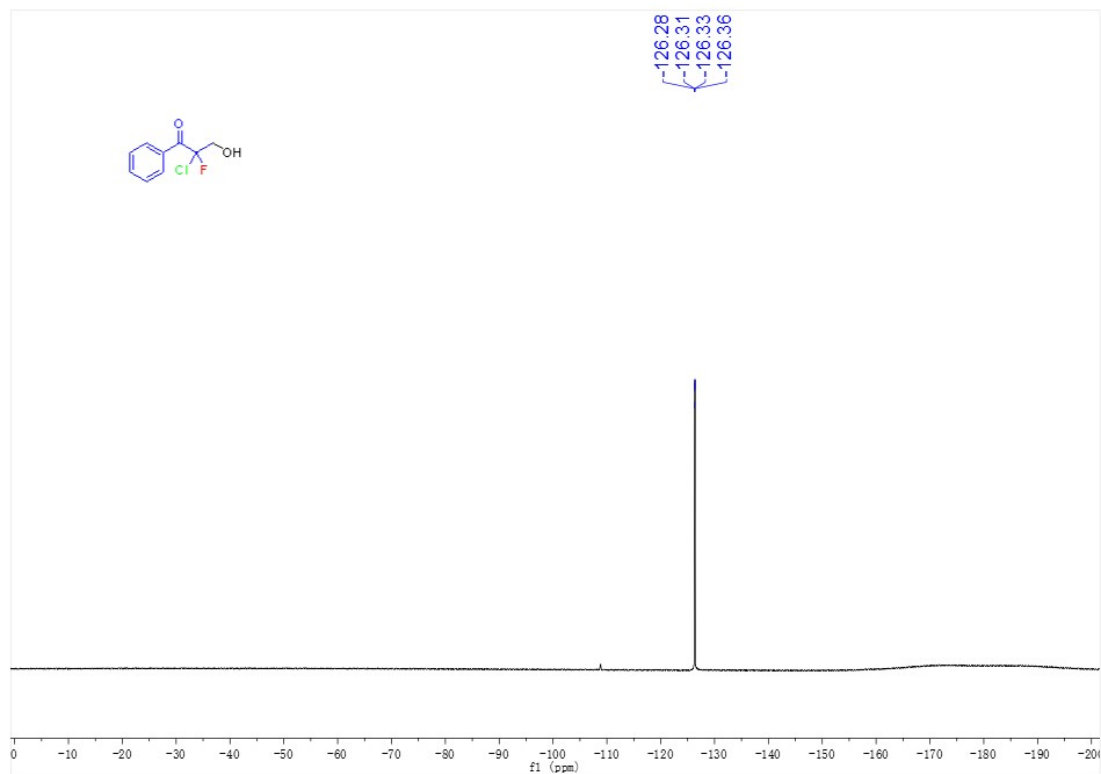
¹H NMR spectrum for 2y



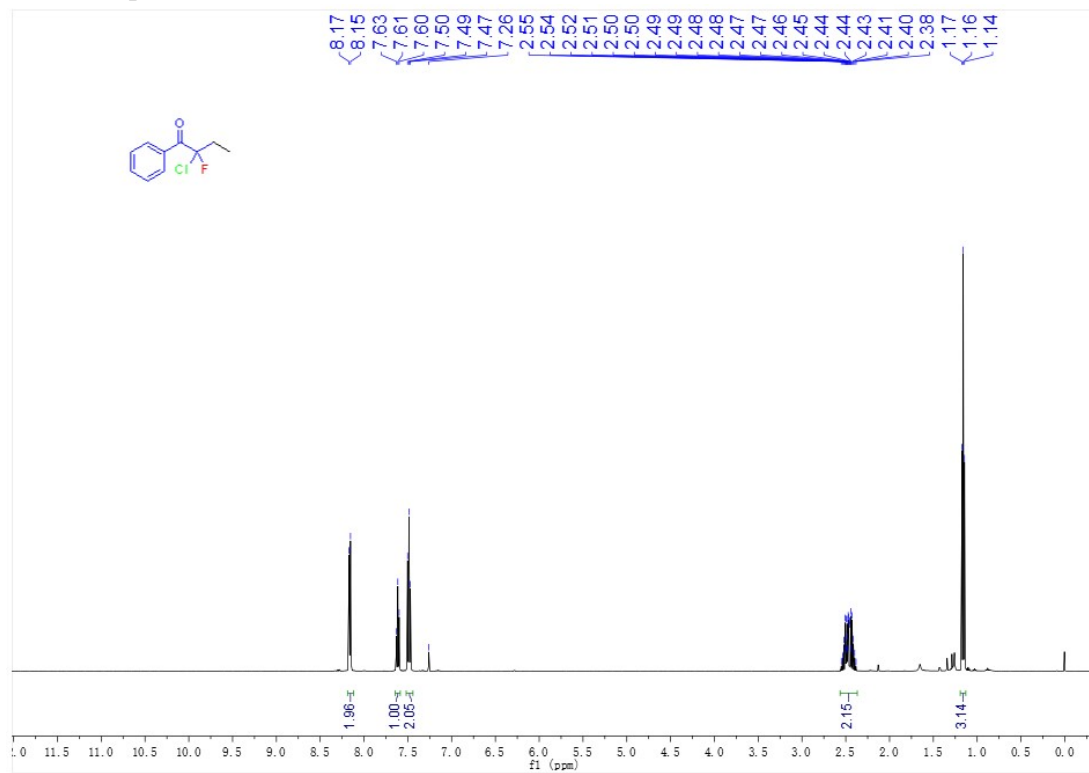
¹³C NMR spectrum for 2y



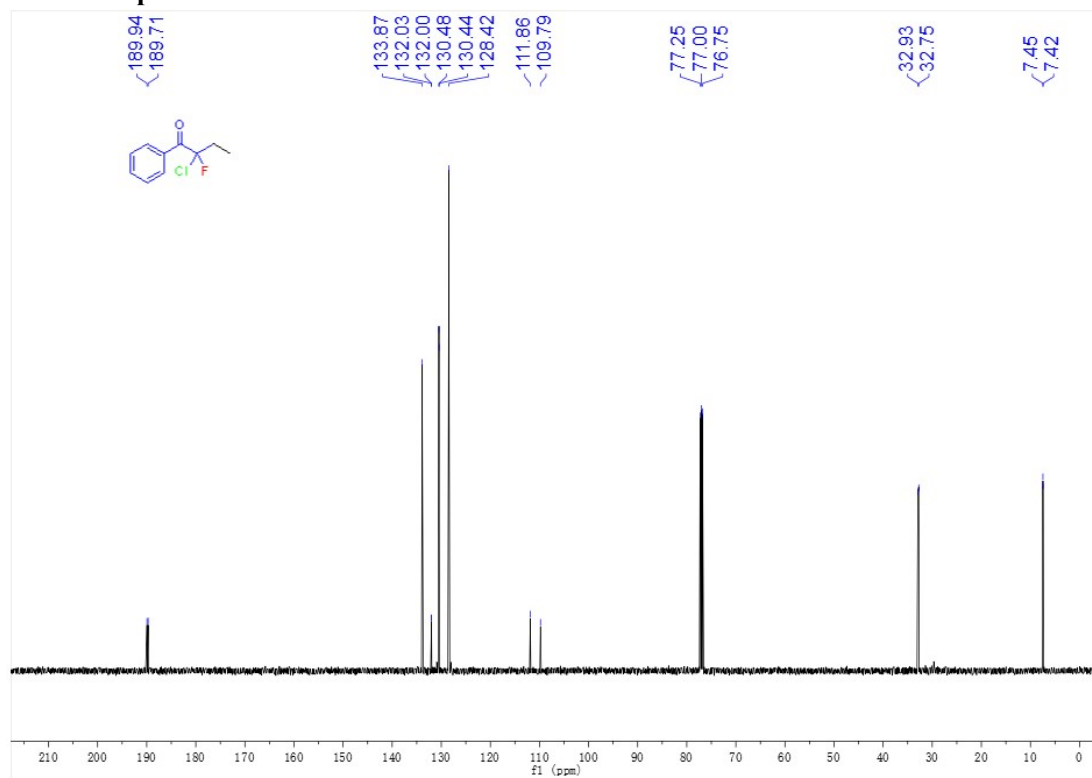
¹⁹F NMR spectrum for 2y



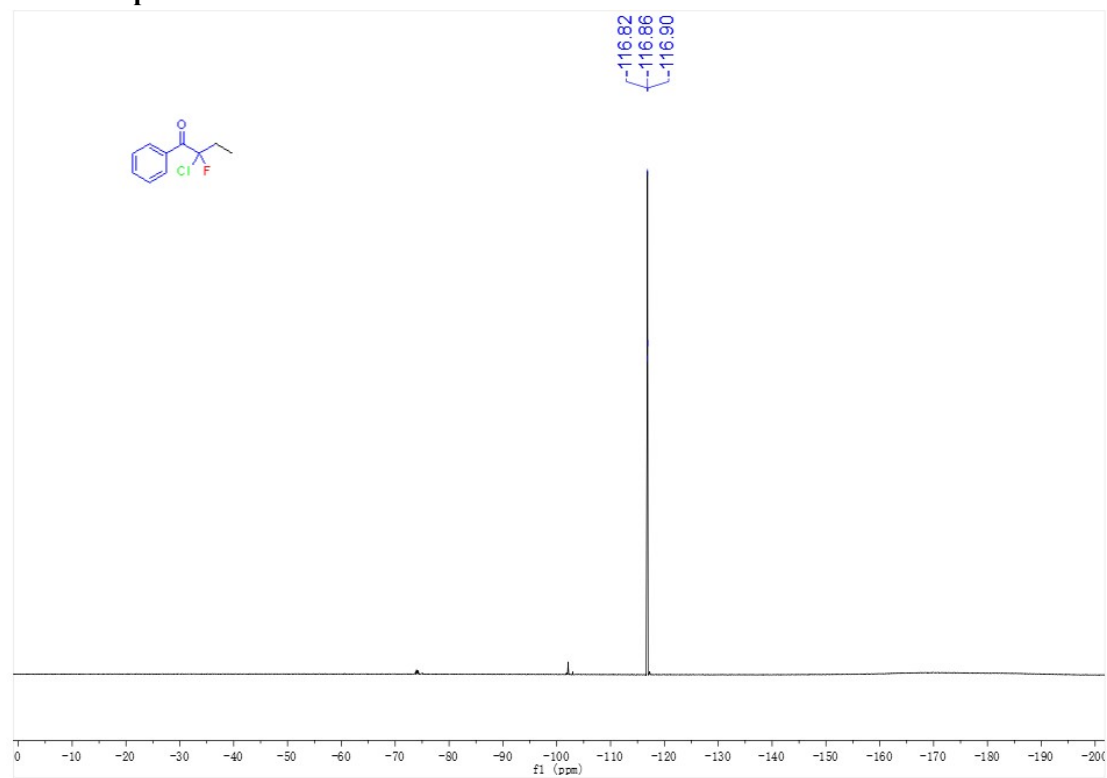
¹H NMR spectrum for 2z



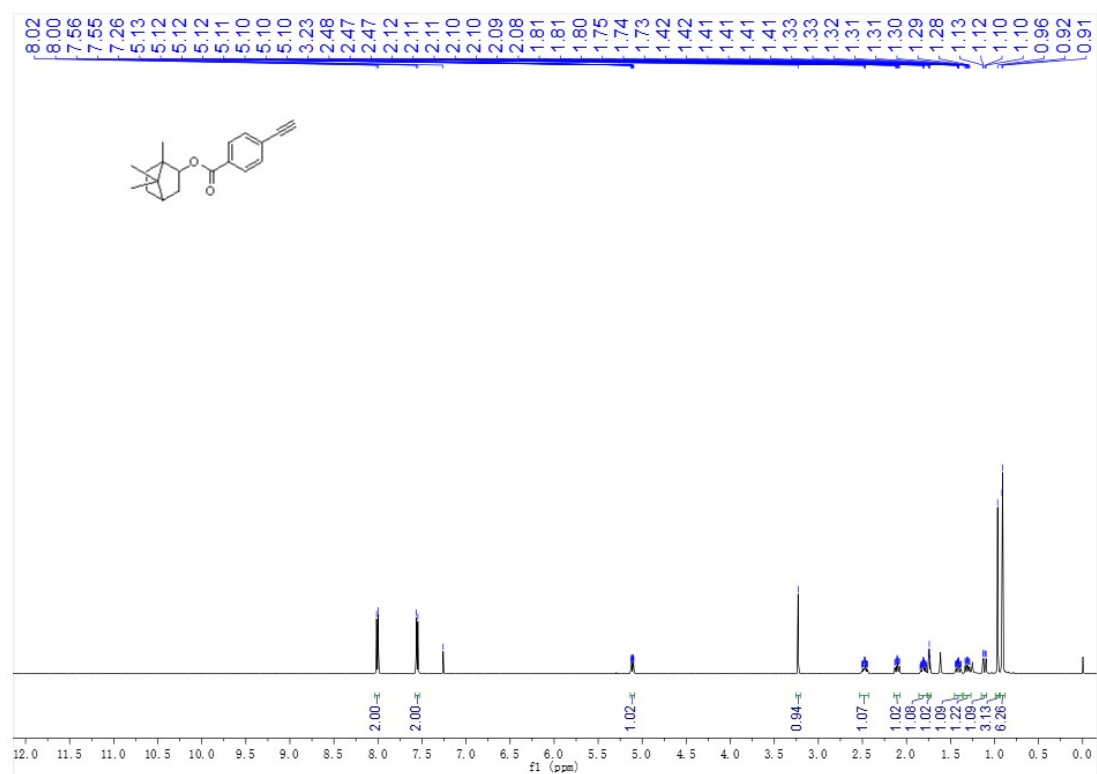
¹³C NMR spectrum for 2z



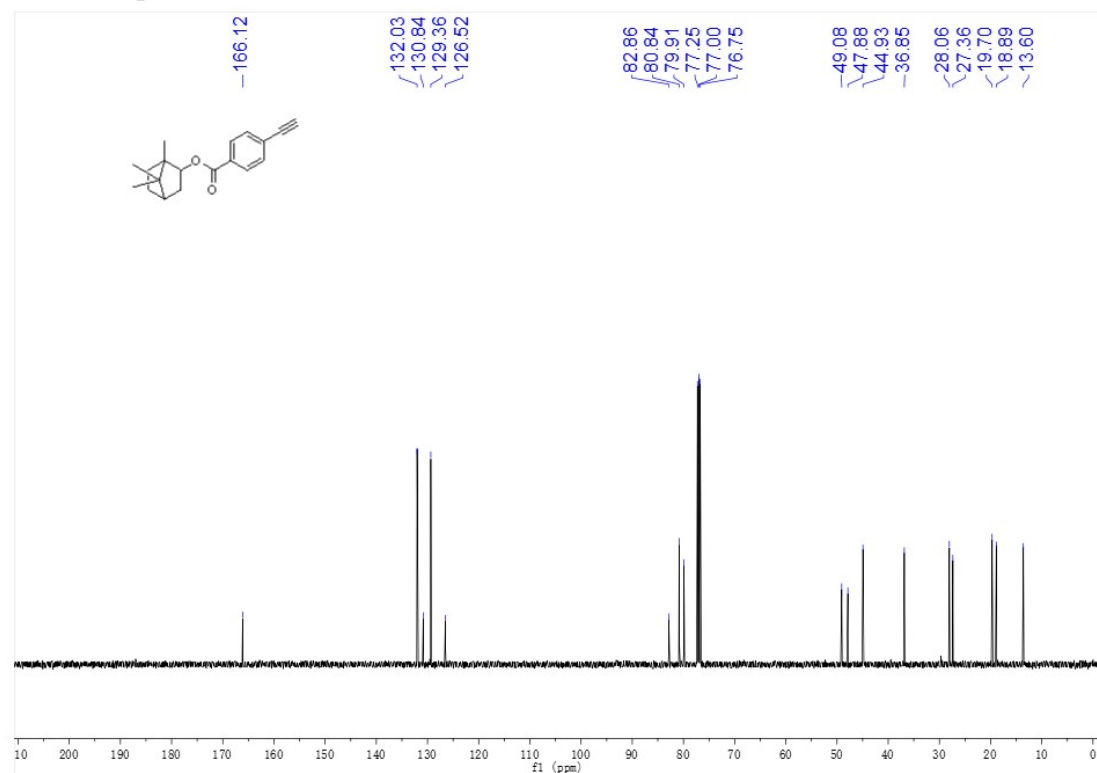
¹⁹F NMR spectrum for 2z



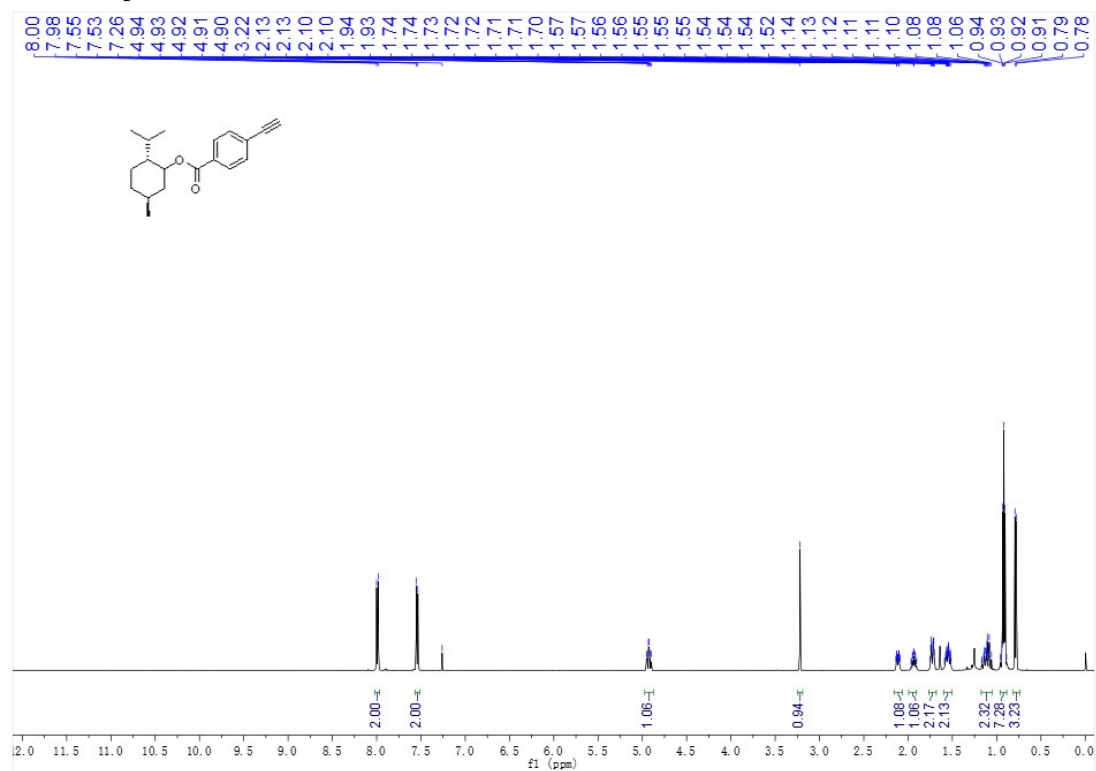
¹H NMR spectrum for 1u



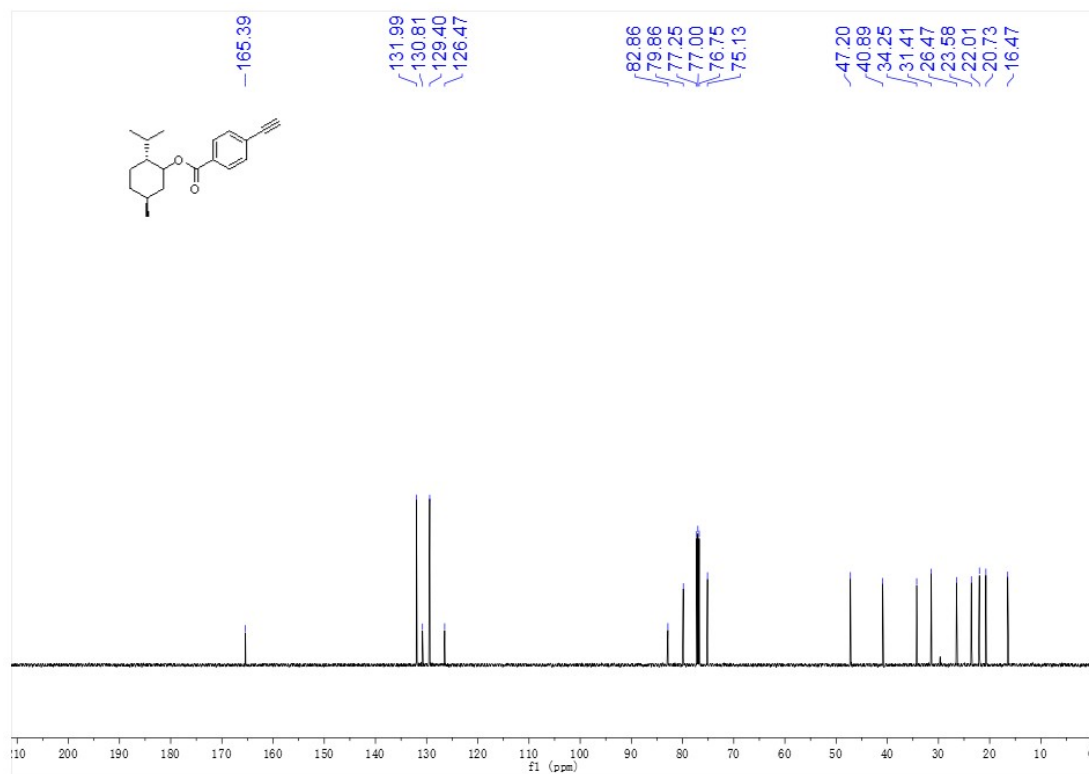
¹³C NMR spectrum for 1u



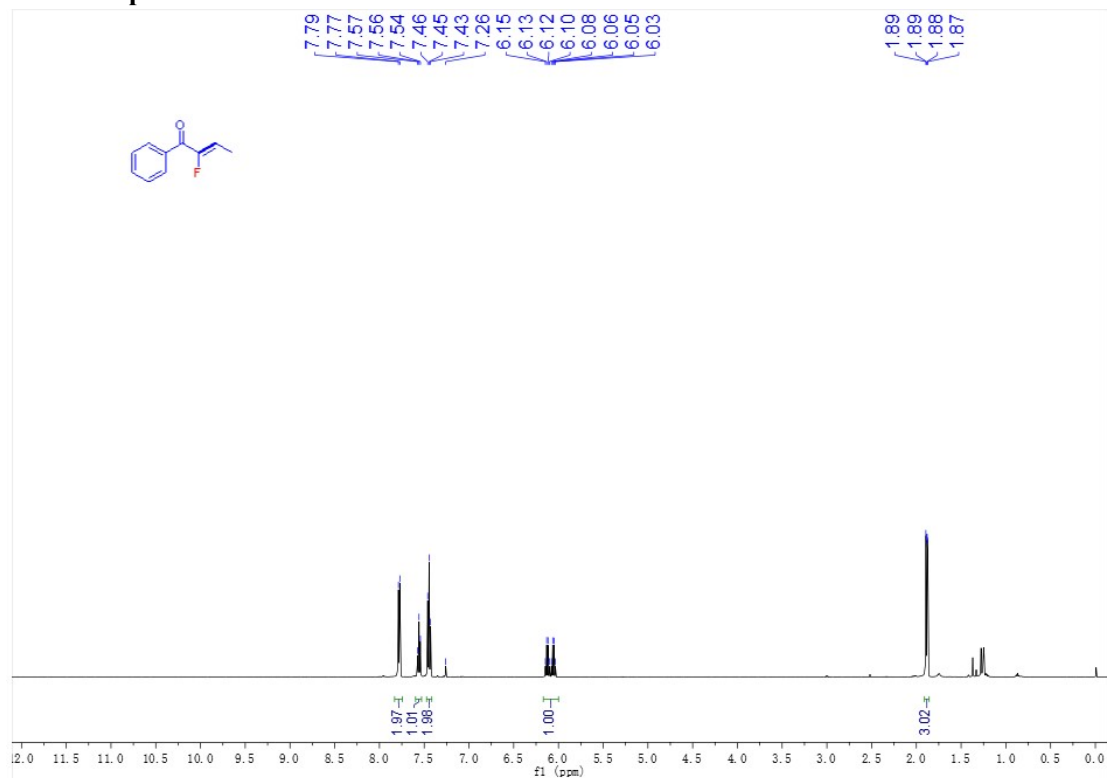
¹H NMR spectrum for 1v



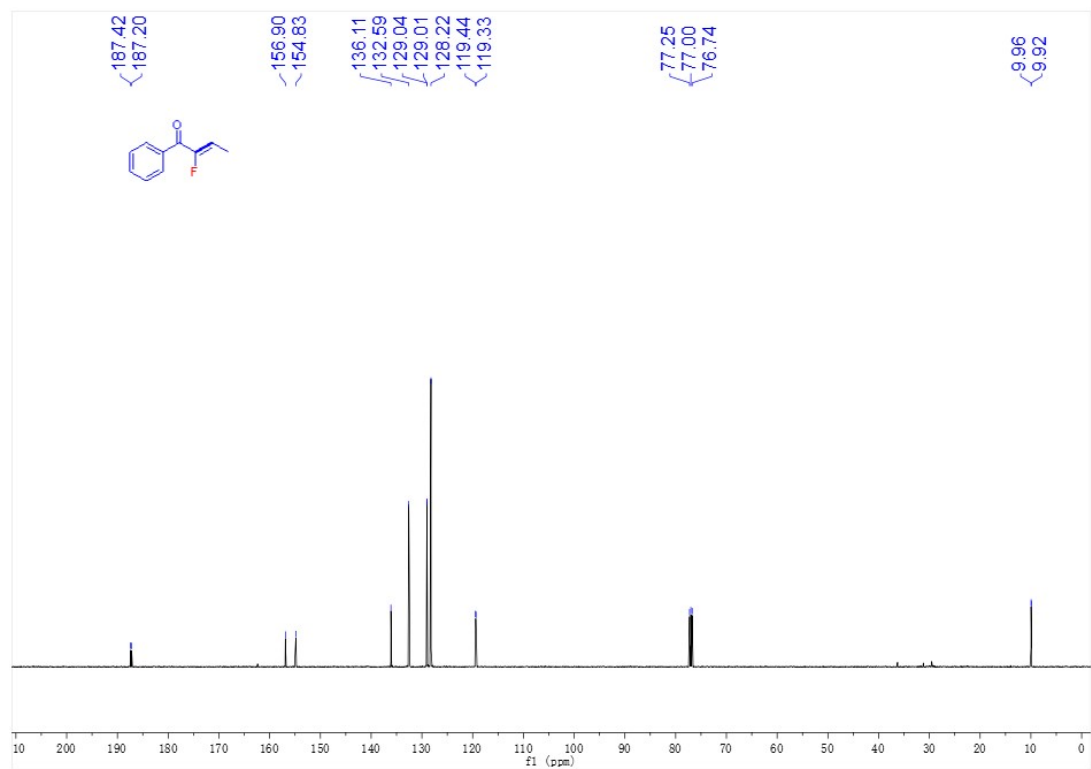
¹³C NMR spectrum for 1v



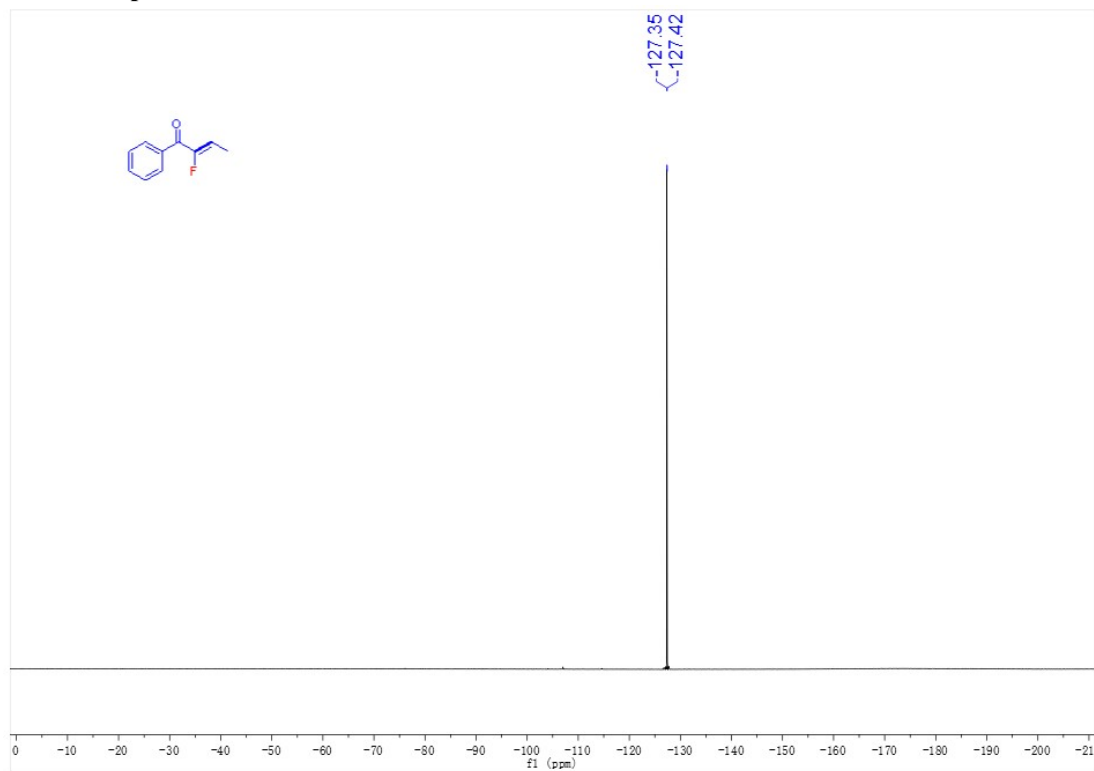
¹H NMR spectrum for 3



¹³C NMR spectrum for 3



¹⁹F NMR spectrum for 3



Theoretical calculations

General information

Density functional theory (DFT) calculations were carried out using Gaussian 09 program [1]. Geometrical optimization calculations were carried out at the PBE0-D3(BJ) [2, 3]/def2-TZVPD [4, 5] level with the SMD continuum solvent model [6] for CF₃CH₂OH without any symmetry assumptions unless otherwise stated. Harmonic vibration frequency calculations were performed at the same level for verifying the resulting geometries as local minima (with all the frequencies real) or saddle points (with only one imaginary frequency). The assignment of the saddle points was performed using the intrinsic reaction coordinate (IRC) calculations. Free energy of **1a**, Cl⁻, F⁻ and H₂O are set as 0 kcal mol⁻¹. Free energy of H⁺ was calculated in H₅O₂⁺ form.

Energies of Stationary Points

Supplementary Table 1. Electronic energies (*E*), zero-point energy corrected energies (*E* + *ZPE*), electronic and thermal enthalpies (*H*), Gibbs free energies (*G*) of the stationary points calculated at the PBE0-D3(BJ)/def2-TZVPD level of theory with the SMD continuum solvent model for CF₃CH₂OH.

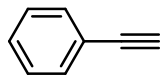
Table S2

	<i>E</i> (Hartree)	<i>E</i> + <i>ZPE</i> (Hartree)	<i>H</i> (Hartree)	<i>G</i> (Hartree)
1a	-308.145566	-308.035683	-308.028339	-308.066095
Selectfluor	-943.834859	-943.610345	-943.600049	-943.644864
2a	-943.255352	-943.133098	-943.122757	-943.169445
4a	-844.072998	-843.943010	-843.933415	-843.977988
4a'	-1303.531756	-1303.411057	-1303.400373	-1303.448211
TS-A	-1404.046970	-1403.824877	-1403.812409	-1403.863591
B	-559.773545	-559.771679	-559.768302	-559.792988
C	-768.013556	-767.900672	-767.891938	-767.934296
D	-844.452655	-844.310068	-844.300282	-844.344445
E	-844.058501	-843.928826	-843.919077	-843.964204
TS-F	-1787.874990	-1787.521946	-1787.501286	-1787.572515
G	-943.664972	-943.529935	-943.519535	-943.565673
TS-H	-1403.838584	-1403.706355	-1403.693399	-1403.747983
I	-1303.941435	-1303.807685	-1303.797020	-1303.844106
J	-844.285895	-844.067130	-844.057595	-844.100814
H ₂ O	-76.390849	-76.369615	-76.365835	-76.387263
H ₅ O ₂ ⁺	-153.221074	-153.163412	-153.158076	-153.187721
Cl ⁻	-460.232561	-460.232561	-460.230200	-460.247583

F⁻ -99.931714 -99.931714 -99.929354 -99.945873

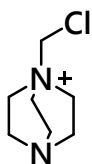
Cartesian coordinates of the optimized geometries

1a



C	-2.19841300	-0.00003700	-0.00007000
C	-1.50322900	1.20231200	-0.00004500
C	-0.11852600	1.20752500	0.00000500
C	0.58657200	0.00002600	0.00003300
C	-0.11847200	-1.20750400	0.00000700
C	-1.50317400	-1.20235400	-0.00004300
C	2.01124300	0.00006100	0.00009700
C	3.21547300	0.00007400	0.00010000
H	-3.28274700	-0.00006200	-0.00011000
H	-2.04301100	2.14264100	-0.00006500
H	0.42792200	2.14349700	0.00002600
H	0.42801900	-2.14345200	0.00002900
H	-2.04291400	-2.14270800	-0.00006100
H	4.28388800	-0.00053100	-0.00032500

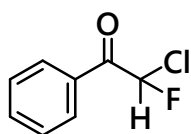
Selectfluor



C	0.07711300	-0.39570100	1.26500700
C	0.02425900	-0.54488600	-1.17271200
C	0.71650500	1.52310700	-0.09186000
C	2.14655600	1.00528300	0.11988000
N	-0.22485300	0.35255400	0.00247400
C	1.46831300	-1.02960400	1.11905600
C	1.53266300	-0.83085300	-1.24064900
C	-1.59744700	0.90940700	0.00135000
Cl	-2.84543000	-0.33540100	-0.00023600
H	0.02740400	0.33328300	2.07381800
H	-0.70153700	-1.14304100	1.40432000
H	-0.55832700	-1.44941700	-1.00925500
H	-0.34683700	-0.03007000	-2.05857100
H	0.56669000	1.95678000	-1.08043000
H	0.41673400	2.24315100	0.66856200
H	2.50837900	1.28296500	1.11050800

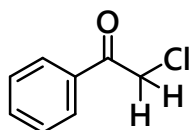
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H	1.38059100	-2.10335900	0.94939700
H	1.98807200	-0.27684600	-2.06222400
H	1.68772300	-1.89490100	-1.42093500
H	-1.71561800	1.51457500	0.89737400
H	-1.71334200	1.51221900	-0.89679000
N	2.19485300	-0.44495900	-0.00099800

2a



C	-3.52627700	-0.33744300	-0.00957300
C	-3.08964400	0.95492900	0.26030300
C	-1.74039300	1.24921200	0.21815500
C	-0.81244100	0.24947600	-0.08384600
C	-1.25650100	-1.04732200	-0.34923600
C	-2.61098200	-1.33430800	-0.31724900
C	0.61292700	0.62418000	-0.13307900
C	1.62913200	-0.53182700	-0.17474200
O	0.99011200	1.77208200	-0.15126500
F	1.41500400	-1.35242200	0.89807000
Cl	3.28682000	0.05350500	-0.12166300
H	-4.58564900	-0.56731800	0.02027300
H	-3.80561400	1.73165600	0.50313000
H	-1.38669600	2.25234000	0.42542600
H	-0.55733400	-1.83693100	-0.59446700
H	-2.95262000	-2.34014300	-0.53224800
H	1.52111300	-1.11544100	-1.09075500

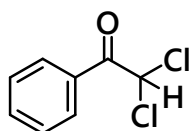
4a



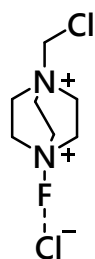
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C	-2.93169100	0.96601700	-0.00004100
C	-1.57041300	1.20836200	-0.00000600
C	-0.66530400	0.14565300	0.00002800
C	-1.14615300	-1.16439000	0.00002600
C	-2.51088800	-1.40400300	-0.00000900

C	0.78418300	0.45919800	0.00006500
C	1.72836900	-0.71989800	0.00002900
Cl	3.43043900	-0.24156500	-0.00002300
O	1.18868200	1.60261900	0.00001400
H	-4.47145600	-0.53171400	-0.00007000
H	-3.62901100	1.79619600	-0.00006700
H	-1.19155600	2.22358000	-0.00000500
H	-0.46528800	-2.00707500	0.00005200
H	-2.87805400	-2.42389200	-0.00000900
H	1.55122400	-1.33427700	0.88412600
H	1.55116900	-1.33427300	-0.88405900

4a'



C	3.67843100	-0.35720300	-0.19876500
C	3.29646500	0.84219900	0.39148800
C	1.95908400	1.18260200	0.45707600
C	0.98711100	0.32475800	-0.06401900
C	1.37752800	-0.87989000	-0.65115800
C	2.71957400	-1.21482600	-0.71921800
C	-0.42201000	0.75574100	0.02863000
C	-1.50390200	-0.26410200	-0.35914600
O	-0.74405200	1.85491000	0.41321900
Cl	-3.05045600	0.51385600	-0.65841800
Cl	-1.62252200	-1.43375300	0.97736600
H	4.72821300	-0.62387400	-0.25209700
H	4.04540400	1.51028500	0.80105100
H	1.64853500	2.11369200	0.91577900
H	0.64964700	-1.56625600	-1.06479100
H	3.01709800	-2.14916700	-1.18080800
H	-1.24955100	-0.82138600	-1.25631700

TS-A

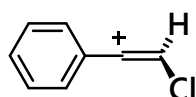
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C	1.06778200	-0.28239100	-1.27004800
C	1.08459500	-0.45661100	1.17079700
C	0.82371200	1.71931100	0.10109300
C	-0.68133200	1.51151000	-0.13390100
N	1.50908900	0.38134500	0.00055400
C	-0.41874400	-0.64867500	-1.12978900
C	-0.45140700	-0.42286500	1.25554200
C	2.97015700	0.65194700	0.00553700
Cl	3.93776100	-0.81641400	-0.00020300
F	-2.81201800	-0.12453400	-0.00245500
H	1.24679900	0.43184200	-2.07255600
H	1.67930000	-1.16885400	-1.42296800
H	1.45500100	-1.46464900	0.99816100
H	1.54828400	-0.03974500	2.06331100
H	1.03818000	2.10235700	1.09748000
H	1.25989000	2.37471100	-0.65094600
H	-0.97637000	1.83254400	-1.13132400
H	-1.25387100	2.06100100	0.61141800
H	-0.95853000	-0.37197500	-2.03399600
H	-0.55097600	-1.71227000	-0.93846200
H	-0.79206500	0.22960900	2.05766800
H	-0.83867100	-1.42772100	1.41438100
H	3.20412100	1.22671600	-0.88775900
H	3.19887700	1.21467300	0.90764000
Cl	-4.77322100	-0.35551900	0.00226200

B

Cl-F

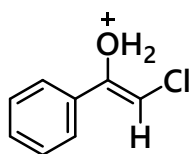
F	0.00000000	0.00000000	-1.06096200
Cl	0.00000000	0.00000000	0.56168600

C

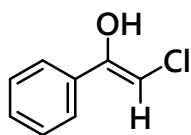


C	-3.14729800	-0.00025900	-0.27850400
C	-2.48637100	-1.22640600	-0.14681500
C	-1.14558900	-1.24237200	0.11817400
C	-0.45081800	0.00023000	0.25394200
C	-1.14597100	1.24256900	0.11802600
C	-2.48674800	1.22611700	-0.14691700
C	0.86849900	0.00043900	0.50275900
C	2.13028300	-0.00003800	0.75620300
Cl	3.30360800	-0.00005000	-0.48807400
H	-4.21105300	-0.00044500	-0.49049300
H	-3.03747000	-2.15162800	-0.25597300
H	-0.59147000	-2.16615600	0.22824700
H	-0.59215200	2.16654300	0.22804000
H	-3.03813700	2.15115700	-0.25613500
H	2.49303400	-0.00029600	1.78236100

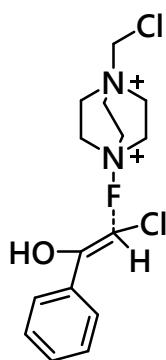
D



C	-3.42080700	-0.28626000	-0.08956800
C	-2.86758500	0.96284300	-0.33554000
C	-1.49610100	1.14293600	-0.27356900
C	-0.66821500	0.06324100	0.03984500
C	-1.22782800	-1.18789100	0.30452300
C	-2.59873800	-1.35926300	0.22983300
C	0.77704200	0.22109100	0.06955000
C	1.69852200	-0.66764800	-0.27247800
Cl	3.37810100	-0.38699600	-0.14984000
H	-4.49507200	-0.42327200	-0.14035300
H	-3.50653500	1.80235500	-0.58437800
H	-1.06688100	2.11548900	-0.48391100
H	-0.58835300	-2.01783500	0.58217500
H	-3.02883400	-2.33255600	0.43647400
H	1.41202400	-1.63137600	-0.66936400
H	0.92153300	1.79834500	1.36081400
H	2.15984900	1.69274400	0.34405300
O	1.19835100	1.53009300	0.45827300

E

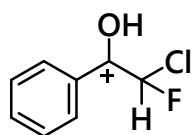
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C	-1.50664100	1.17179000	0.00012800
C	-0.64298700	0.07541200	-0.00002100
C	-1.19242600	-1.21000500	-0.00014300
C	-2.56383100	-1.38820900	-0.00010400
C	0.81075500	0.30218700	-0.00005100
C	1.71664700	-0.68357400	0.00012400
Cl	3.40628500	-0.33775300	0.00006000
O	1.15201200	1.60887800	-0.00025900
H	-4.49177600	-0.43459700	0.00006600
H	-3.53599200	1.85286700	0.00027400
H	-1.10093700	2.17517000	0.00022400
H	-0.55204600	-2.08361800	-0.00028300
H	-2.97071300	-2.39337600	-0.00020500
H	1.47672100	-1.73383200	0.00031900
H	2.11610300	1.69821800	-0.00017600

TS-F

N	0.85409500	-0.75379600	-0.23749000
C	2.46058900	0.95482700	-0.72514600
C	2.99851400	-1.39538000	-1.08835500
C	2.77393300	-0.53991600	1.18377800
C	1.35311500	-1.12164000	1.07564800
N	3.25241300	-0.20622600	-0.19989100
C	0.97026200	0.67280000	-0.47789000
C	1.48061900	-1.53265900	-1.29049800
C	4.71666500	0.05997700	-0.24463100

Cl	5.20282200	1.35163500	0.84183600
F	-0.83705500	-1.09095600	-0.26553200
C	-3.08833800	0.86422500	0.09415000
C	-2.66294300	1.31095800	-1.16263800
C	-2.65383100	2.66232400	-1.45115000
C	-3.06498700	3.58471100	-0.49642100
C	-3.48500200	3.14954600	0.75360700
C	-3.49519700	1.79927900	1.05206200
H	2.77393200	1.85349200	-0.19875200
H	2.69548400	1.04248100	-1.78440100
H	3.50404900	-1.22251500	-2.03637900
H	3.42760300	-2.26137500	-0.58769400
H	3.46169100	-1.26431300	1.61610900
H	2.78411800	0.37906200	1.76428600
H	0.70845300	-0.68685200	1.83745000
H	1.35000600	-2.20724700	1.15411100
H	0.59433000	1.20159000	0.39588500
H	0.38417600	0.93866400	-1.35625200
H	1.17968000	-2.57434000	-1.19425000
H	1.15986200	-1.13452300	-2.25083800
H	5.22686700	-0.85472700	0.04931500
H	4.97089300	0.34545200	-1.26329700
H	-2.33046800	0.60783200	-1.91524200
H	-2.32085100	2.99964200	-2.42587300
H	-3.05728200	4.64397300	-0.72760400
H	-3.80831400	3.86622500	1.49966200
H	-3.82599600	1.46207200	2.02601500
C	-3.09778300	-0.54830600	0.43431200
C	-2.81009400	-1.54251000	-0.48124800
H	-2.80059400	-1.36552100	-1.54403600
O	-3.34065200	-0.82218500	1.69961600
H	-3.38972600	-1.78123800	1.84993500
Cl	-2.94093200	-3.18345900	-0.02460600

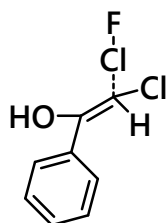
G



C	-3.53004100	-0.32243900	-0.03789500
C	-3.09313300	0.98371900	0.17840800
C	-1.74901500	1.26504800	0.16152000
C	-0.82232200	0.22594800	-0.06857800
C	-1.27509800	-1.09062300	-0.28752900

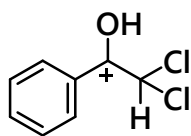
C	-2.62579700	-1.35361700	-0.27236300
C	0.55823400	0.52712900	-0.07621600
C	1.59963200	-0.58590100	-0.17428800
F	1.44926600	-1.40192800	0.89608400
Cl	3.24268500	0.05119400	-0.19484000
H	-4.59264600	-0.53797400	-0.02456900
H	-3.81097300	1.77371000	0.36079100
H	-1.39381900	2.27293100	0.33460700
H	-0.57851900	-1.89593500	-0.48177500
H	-2.98233500	-2.36135100	-0.44469400
H	1.45778600	-1.15100600	-1.09760200
O	0.93115700	1.73864600	0.00517100
H	1.90745900	1.84191100	0.02104500

TS-H



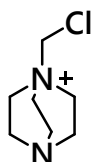
F	0.42815100	3.72019400	0.16796300
Cl	0.22601500	2.09926000	0.08443000
C	-1.77266700	-0.49350800	-0.65414600
C	-0.91538600	-0.95757000	0.26433800
Cl	-3.46951400	-0.47069200	-0.36447400
O	-1.28764500	-1.40903600	1.47773200
C	0.53992400	-0.98053800	0.04423500
C	1.08098600	-0.99813000	-1.24436000
C	2.45223500	-0.97376000	-1.42655000
C	3.30471000	-0.94670700	-0.32953100
C	2.77527300	-0.95086400	0.95303900
C	1.40276700	-0.96957900	1.14246900
H	-1.46928600	-0.10222600	-1.61188600
H	-2.24316000	-1.30557300	1.59743200
H	0.42665200	-1.04648300	-2.10694400
H	2.85860400	-0.98804800	-2.43164700
H	4.37899200	-0.93199000	-0.47589600
H	3.43438200	-0.93603700	1.81394700
H	0.99405600	-0.96083000	2.14525800

I



C	-3.68603900	0.34824100	-0.20966800
C	-3.30099400	-0.88219100	0.31938000
C	-1.96751000	-1.20116500	0.40593400
C	-0.99865100	-0.28154200	-0.04820300
C	-1.40010300	0.95698600	-0.58534100
C	-2.73942800	1.26383300	-0.65872000
C	0.37073200	-0.62721200	0.05582500
C	1.47323400	0.31782300	-0.37106000
Cl	2.95022400	-0.55181000	-0.77316800
Cl	1.71962900	1.43174400	0.98351000
H	-4.73978600	0.59583300	-0.27309100
H	-4.05006700	-1.58454300	0.66327100
H	-1.65459800	-2.15196900	0.81769700
H	-0.67609700	1.67884500	-0.93989800
H	-3.05369000	2.21605400	-1.06706700
H	1.18933900	0.89537100	-1.24581900
O	0.68067700	-1.75581500	0.55692400
H	1.64454100	-1.93057500	0.56482100

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C	0.07711300	-0.39570100	1.26500700
C	0.02425900	-0.54488600	-1.17271200
C	0.71650500	1.52310700	-0.09186000
C	2.14655600	1.00528300	0.11988000
N	-0.22485300	0.35255400	0.00247400
C	1.46831300	-1.02960400	1.11905600
C	1.53266300	-0.83085300	-1.24064900
C	-1.59744700	0.90940700	0.00135000
Cl	-2.84543000	-0.33540100	-0.00023600
H	0.02740400	0.33328300	2.07381800
H	-0.70153700	-1.14304100	1.40432000
H	-0.55832700	-1.44941700	-1.00925500
H	-0.34683700	-0.03007000	-2.05857100
H	0.56669000	1.95678000	-1.08043000
H	0.41673400	2.24315100	0.66856200

H	2.50837900	1.28296500	1.11050800
H	2.80398000	1.45806700	-0.62296500
H	2.03063300	-0.87528200	2.04043000
H	1.38059100	-2.10335900	0.94939700
H	1.98807200	-0.27684600	-2.06222400
H	1.68772300	-1.89490100	-1.42093500
H	-1.71561800	1.51457500	0.89737400
H	-1.71334200	1.51221900	-0.89679000
N	2.19485300	-0.44495900	-0.00099800
H ₂ O			
O	0.00000000	0.00000000	0.11804000
H	0.00000000	0.76117400	-0.47215800
H	0.00000000	-0.76117400	-0.47215800
H ₅ O ₂ ⁺			
O	1.19500500	-0.03909500	-0.09547100
O	-1.19539100	-0.03919000	0.09545100
H	0.00532600	-0.00008800	-0.00049400
H	1.58038700	0.84901400	-0.06448100
H	1.57513400	-0.53603600	0.64430100
H	-1.58152300	0.84840900	0.06528700
H	-1.57623900	-0.53501200	-0.64445200

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