

Visible-light-triggered direct keto-difluoroacetylation of styrenes with (florosulfonyl)difluoroacetate and DMSO lead to α -difluoroacetated ketones

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1. General Comments

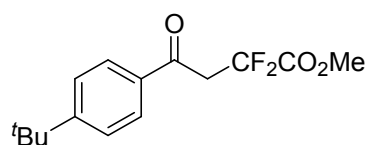
All the reactions were carried out in oven-dried sealed tube with Teflon-lined septum under N₂ atmosphere. Unless indicated, all materials were obtained from commercial sources and used as received. Superdry dimethyl sulfoxide with molecular sieves in it was use in the reaction. ¹H NMR and ¹³C NMR spectra were recorded on 400 MHz at ambient temperature with CDCl₃ as the solvent. ¹⁹F NMR spectra were recorded on 600 MHz at ambient temperature with CDCl₃ as the solvent. Chemical shifts (δ) were given in ppm, referenced to the residual proton resonance of CDCl₃ (7.26), to the carbon resonance of CDCl₃ (77.16). Coupling constants (*J*) were given in Hertz (Hz). The term m, q, t, d, s referred to multiplet, quartet, triplet, doublet, singlet. The reaction progress was monitored by GC-MS if applicable. Column chromatography was performed with silica gel (200-300 meshes). Thin layer chromatography (TLC) was visualized using UV light.

1-Methyl-4-vinylbenzene **1b**,¹ 1-methyl-2-vinylbenzene **1h**,¹ 1-methoxy-2-vinylbenzene **1i**,¹ 1,2-dimethyl-4-vinylbenzene **1j**,¹ 2-vinylnaphthalene **1l**,¹ 1,2-di-p-tolylene **1n**,² 1,2-bis(4-fluorophenyl)ethene **1o**,² 1-methoxy-4-(prop-1-en-1-yl)benzene **1q**,³ 1-fluoro-4-(prop-1-en-1-yl)benzene **1r**,³ pent-1-en-1-ylbenzene **1s**⁴ and (1-cyclohexylvinyl)benzene **1y**⁵ were synthesized according to literature procedures

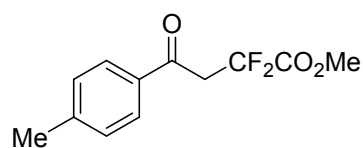
2. Experimental Section

General procedure for the keto-difluoromethylation of alkenes

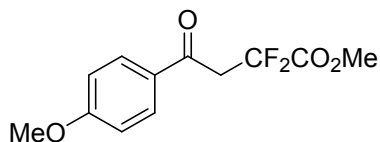
An oven-dried Schleck tube equipped with a stirrer bar was charged with 4.58 mg *fac*-Ir(ppy)₃ (3.5 mol%), which was degassed and refilled with N₂ for 3 times. The alkenes **1a-1x** (0.2 mmol, 1.0 equiv.), Chen reagent FSO₂CF₂COOMe (134.4 mg, 0.7 mmol, 3.5 equiv.) and dry DMSO (4 mL) were added under N₂. The resulting mixture was irradiated for 6 h under room temperature by 3 W blue LEDs. Quenching the reaction with sat. aq. NaHCO₃ and dichloromethane (DCM) was added. The aqueous layer was extracted with DCM twice. The combined organic layer dried by Na₂SO₄, and concentrated in *vacuo* and the residue was purified by chromatography on silica gel to give product **3a-3x**, which were identified by ¹H, ¹³C, and ¹⁹F NMR.



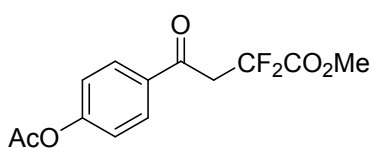
Methyl 4-(4-(*tert*-butyl)phenyl)-2,2-difluoro-4-oxobutanoate (3a)⁶: white solid, 44.9 mg (79% yield); mp: 66.7-68.1 °C; ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.89 – 7.83 (m, 2H), 7.53 – 7.49 (m, 2H), 3.95 – 3.87 (m, 5H), 1.34 (s, 9H); ¹³C NMR (101 MHz, CHLOROFORM-D) δ 192.7 (t, *J* = 5.8 Hz), 164.0 (t, *J* = 31.4 Hz), 158.4, 133.1, 128.3, 126.0, 114.6 (t, *J* = 249.9 Hz), 53.7, 43.9 (t, *J* = 24.5 Hz), 35.4, 31.1; ¹⁹F NMR (565 MHz, CHLOROFORM-D) δ -104.18 (t, *J* = 13.1 Hz). GC-MS *m/z* [M]⁺ 284.



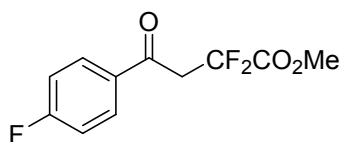
Methyl 2,2-difluoro-4-oxo-4-(*p*-tolyl)butanoate (3b)⁶: white solid, 36.3 mg (75% yield); ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.81 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 3.94 – 3.85 (m, 5H), 2.43 (s, 3H); ¹³C NMR (101 MHz, CHLOROFORM-D) δ 192.7 (t, *J* = 5.9 Hz), 164.0 (t, *J* = 31.6 Hz), 145.5, 133.2, 129.7, 128.4, 114.6 (t, *J* = 249.9 Hz), 53.7, 43.9 (t, *J* = 24.5 Hz), 21.9; ¹⁹F NMR (565 MHz, CHLOROFORM-D) δ -104.30 (t, *J* = 13.4 Hz). GC-MS *m/z* [M]⁺ 242.



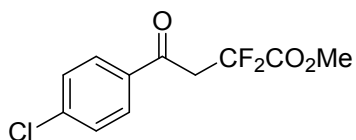
Methyl 2,2-difluoro-4-(4-methoxyphenyl)-4-oxobutanoate (3c)⁷: colorless oil liquid, 10.3 mg (20% yield); ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.89 (d, J = 9.0 Hz, 2H), 6.96 (d, J = 8.9 Hz, 2H), 3.93 – 3.82 (m, 8H); ¹³C NMR (101 MHz, CHLOROFORM-D) δ 191.5 (t, J = 5.9 Hz), 164.4 (t, J = 36.6 Hz), 131.4, 130.7, 128.8, 114.2, (t, J = 39.7 Hz), 114.2, 55.7, 53.7, 43.7 (t, J = 24.4 Hz); ¹⁹F NMR (565 MHz, CHLOROFORM-D) δ -104.46 (t, J = 13.4 Hz). GC-MS m/z [M]⁺ 258.



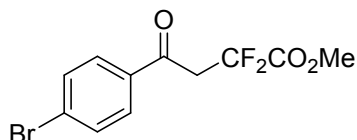
Methyl 4-(4-acetoxyphenyl)-2,2-difluoro-4-oxobutanoate (3d)⁶: white solid, 42.3 mg (74% yield); ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.95 (d, J = 8.6 Hz, 2H), 7.23 (d, J = 8.6 Hz, 2H), 3.95 – 3.85 (m, 5H), 2.33 (s, 3H); ¹³C NMR (101 MHz, CHLOROFORM-D) δ 191.8 (t, J = 5.9 Hz), 168.8, 163.8 (t, J = 31.5 Hz), 155.3, 133.1, 130.0, 122.3, 114.4 (t, J = 250.0 Hz), 53.7, 43.9 (t, J = 24.6 Hz), 21.2; ¹⁹F NMR (565 MHz, CHLOROFORM-D) δ -104.19 (t, J = 13.4 Hz). GC-MS m/z [M]⁺ 286.



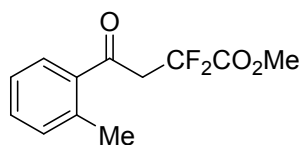
Methyl 2,2-difluoro-4-(4-fluorophenyl)-4-oxobutanoate (3e)⁶: white solid, 32.5 mg (66% yield); ¹H NMR (400 MHz, CHLOROFORM-D) δ 8.00 – 7.91 (m, 2H), 7.17 (dd, J = 11.0, 4.3 Hz, 2H), 3.95 – 3.85 (m, 5H); ¹³C NMR (101 MHz, CHLOROFORM-D) δ 191.5 (t, J = 6.1 Hz), 166.5 (d, J = 256.9 Hz), 163.9 (t, J = 31.5 Hz), 132.1, 131.1 (d, J = 9.6 Hz), 116.3 (d, J = 22.1 Hz), 114.4 (t, J = 250.2 Hz), 53.7 43.9 (t, J = 24.6 Hz); ¹⁹F NMR (565 MHz, CHLOROFORM-D) δ -102.65 (qd, J = 8.2, 5.2 Hz, 1F), -104.20 (t, J = 13.2 Hz, 2F). GC-MS m/z [M]⁺ 246.



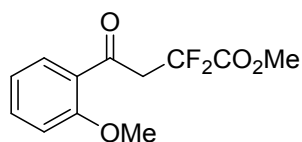
Methyl 4-(4-chlorophenyl)-2,2-difluoro-4-oxobutanoate (3f)⁶: white solid, 25.2 mg (48% yield); ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.86 (d, $J = 8.3$ Hz, 2H), 7.47 (d, $J = 8.4$ Hz, 2H), 3.94 – 3.85 (m, 5H); ¹³C NMR (101 MHz, CHLOROFORM-D) δ 191.9 (t, $J = 5.9$ Hz), 163.8 (t, $J = 31.4$ Hz), 141.0, 133.9, 129.7, 129.4, 114.3 (t, $J = 250.2$ Hz), 53.7, 43.9 (t, $J = 24.7$ Hz); ¹⁹F NMR (565 MHz, CHLOROFORM-D) δ -104.18 (t, $J = 13.2$ Hz). GC-MS m/z [M]⁺ 262.



Methyl 4-(4-bromophenyl)-2,2-difluoro-4-oxobutanoate (3g)⁶: white solid, 41.2 mg (67% yield); ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.80 – 7.76 (m, 2H), 7.66 – 7.62 (m, 2H), 3.93 – 3.84 (m, 5H); ¹³C NMR (101 MHz, CHLOROFORM-D) δ 192.1 (t, $J = 6.0$ Hz), 163.8 (t, $J = 31.4$ Hz), 134.3, 132.4, 129.7, 114.3 (t, $J = 250.3$ Hz), 53.7, 43.9 (t, $J = 24.6$ Hz); ¹⁹F NMR (565 MHz, CHLOROFORM-D) δ -104.14 (t, $J = 13.1$ Hz). GC-MS m/z [M]⁺ 307.

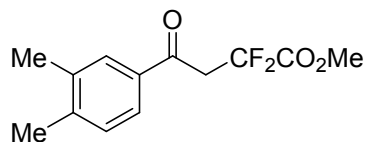


Methyl 2,2-difluoro-4-oxo-4-(o-tolyl)butanoate(3h)⁷: colorless oil liquid, 35.3 mg (73% yield); ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.67 (d, $J = 7.7$ Hz, 1H), 7.44 (t, $J = 7.2$ Hz, 1H), 7.29 (dd, $J = 15.9, 8.0$ Hz, 2H), 3.94 – 3.82 (m, 5H), 2.52 (s, 3H); ¹³C NMR (101 MHz, CHLOROFORM-D) δ 195.9 (t, $J = 5.8$ Hz), 164.0 (t, $J = 31.5$ Hz), 139.8, 135.4, 132.8, 132.6, 129.3, 126.1, 114.5 (t, $J = 249.8$ Hz), 53.6, 46.2 (t, $J = 24.2$ Hz), 21.8; ¹⁹F NMR (565 MHz, CHLOROFORM-D) δ -104.39 (t, $J = 13.4$ Hz). GC-MS m/z [M]⁺ 242.

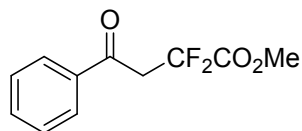


Methyl 2,2-difluoro-4-(2-methoxyphenyl)-4-oxobutanoate (3i)⁷: white solid, 41.3 mg (80% yield); ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.83 (dd, $J = 7.8, 1.8$ Hz, 1H), 7.53 (ddd, $J = 8.9, 7.5, 1.8$ Hz, 1H), 7.04 – 6.98 (m, 2H), 4.01 – 3.94 (m, 5H), 3.91

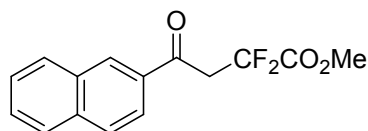
(s, 3H); ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 193.9 (t, $J = 6.7$ Hz), 164.3 (t, $J = 31.6$ Hz), 159.6, 135.4, 131.0, 125.7, 121.0, 114.5 (t, $J = 248.6$ Hz), 111.8, 55.7, 53.5, 49.4 (t, $J = 24.6$ Hz); ^{19}F NMR (565 MHz, CHLOROFORM-D) δ -104.86 (td, $J = 13.7$, 2.6 Hz). GC-MS m/z $[\text{M}]^+$ 258.



Methyl 4-(3,4-dimethylphenyl)-2,2-difluoro-4-oxobutanoate (3j): yellow solid, 32.7 mg (64% yield); mp: 44.0-45.2 °C; ^1H NMR (400 MHz, CHLOROFORM-D) δ 7.67 (s, 1H), 7.63 (dd, $J = 7.9$, 1.7 Hz, 1H), 7.23 (d, $J = 7.9$ Hz, 1H), 3.92 – 3.84 (m, 5H), 2.32 (d, $J = 4.7$ Hz, 6H); ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 192.9 (t, $J = 5.8$ Hz), 164.0 (t, $J = 31.6$ Hz), 144.2, 137.5, 133.6, 130.2, 129.3, 126.1, 114.6 (t, $J = 249.8$ Hz), 53.6, 43.9 (t, $J = 24.4$ Hz), 20.3, 19.9; ^{19}F NMR (565 MHz, CHLOROFORM-D) δ -104.30 (t, $J = 13.5$ Hz). GC-MS m/z $[\text{M}]^+$ 256.

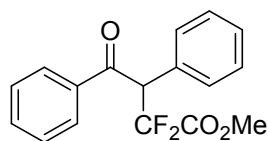


Methyl 2,2-difluoro-4-oxo-4-phenylbutanoate (3k)⁶: colorless oil liquid, 33.8 mg (74% yield); ^1H NMR (400 MHz, CHLOROFORM-D) δ 7.92 (dd, $J = 8.3$, 1.1 Hz, 2H), 7.65 – 7.59 (m, 1H), 7.49 (dd, $J = 10.8$, 4.8 Hz, 2H), 3.96 – 3.88 (m, 5H); ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 193.1 (t, $J = 5.9$ Hz), 163.9 (t, $J = 31.6$ Hz), 135.6, 134.4, 129.0, 128.3, 114.5 (t, $J = 250.0$ Hz), 53.6, 44.0 (t, $J = 24.5$ Hz); ^{19}F NMR (565 MHz, CHLOROFORM-D) δ -104.25 (t, $J = 13.2$ Hz). GC-MS m/z $[\text{M}]^+$ 228.

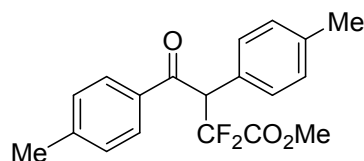


Methyl 2,2-difluoro-4-(naphthalen-2-yl)-4-oxobutanoate (3l)⁶: colorless oil liquid, 22.3 mg (40% yield); ^1H NMR (400 MHz, CHLOROFORM-D) δ 8.41 (s, 1H), 7.96 (dd, $J = 8.7$, 1.8 Hz, 2H), 7.93 – 7.86 (m, 2H), 7.67 – 7.55 (m, 2H), 4.06 (t, $J = 13.3$ Hz, 2H), 3.94 (s, 3H); ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 193.0 (t, $J = 5.9$ Hz), 164.0 (t, $J = 31.5$ Hz), 136.1, 133.0, 132.4, 130.5, 129.8, 129.3, 129.0, 128.0, 127.3,

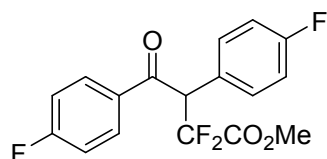
123.4, 114.6 (t, $J = 250.1$ Hz), 53.7, 44.1 (t, $J = 24.6$ Hz); ^{19}F NMR (565 MHz, CHLOROFORM-D) δ -104.14 (t, $J = 13.5$ Hz). GC-MS m/z $[\text{M}]^+$ 278.



Methyl 2,2-difluoro-4-oxo-3,4-diphenylbutanoate (3m): white solid, 37.1 mg (61% yield); mp: 108.9-110.0 °C; ^1H NMR (600 MHz, CHLOROFORM-D) δ 7.84 (d, $J = 7.4$ Hz, 2H), 7.48 (t, $J = 7.4$ Hz, 1H), 7.38 – 7.32 (m, 7H), 5.46 (dd, $J = 19.0, 10.0$ Hz, 1H), 3.87 (s, 3H); ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 194.8 (d, $J = 8.2$ Hz), 164.5 (t, $J = 31.9$ Hz), 135.0, 133.8, 130.6, 130.3, 129.2, 128.9, 128.8, 113.8 (dd, $J = 264.0, 245.2$ Hz), 58.3 (dd, $J = 23.8, 20.2$ Hz), 58.0, 53.7; ^{19}F NMR (565 MHz, CHLOROFORM-D) δ -103.48 (dd, $J = 273.4, 8.7$ Hz, 1F), -112.02 (dd, $J = 274.3, 18.5$ Hz, 1F). GC-MS m/z $[\text{M}]^+$ 304. HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ Calculated for: $\text{C}_{17}\text{H}_{15}\text{F}_2\text{O}_3\text{H}$: 305.0984; Found: 305.0989.

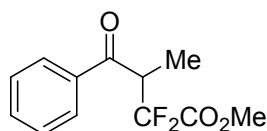


Methyl 2,2-difluoro-4-oxo-3,4-di-p-tolylbutanoate (3n): white solid, 56.4 mg (85% yield); mp: 117.3-118.5 °C; ^1H NMR (400 MHz, CHLOROFORM-D) δ 7.77 – 7.70 (m, 2H), 7.23 (d, $J = 8.0$ Hz, 2H), 7.13 (dd, $J = 8.3, 2.7$ Hz, 4H), 5.40 (dd, $J = 19.0, 10.2$ Hz, 1H), 3.85 (s, 3H), 2.30 (d, $J = 7.7$ Hz, 6H); ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 194.5 (d, $J = 8.3$ Hz), 164.6 (t, $J = 31.9$ Hz), 144.7, 138.7, 132.6, 130.4, 130.0, 129.4, 129.3, 127.5, 113.9 (dd, $J = 263.2, 244.4$ Hz), 58.1, 57.9 (dd, $J = 23.7, 20.2$ Hz), 21.7, 21.2; ^{19}F NMR (565 MHz, CHLOROFORM-D) δ -103.51 (dd, $J = 273.8, 10.0$ Hz, 1F), -112.01 (dd, $J = 273.8, 19.0$ Hz, 1F). GC-MS m/z $[\text{M}]^+$ 332. HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ Calculated for: $\text{C}_{19}\text{H}_{18}\text{F}_2\text{O}_3\text{H}$: 333.1297; Found: 333.1294.

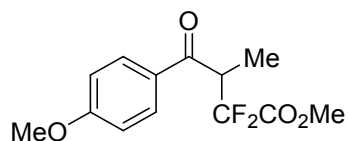


Methyl 2,2-difluoro-3,4-bis(4-fluorophenyl)-4-oxobutanoate (3o): colorless oil liquid, 41.5 mg (61% yield); mp=41.2-42.1 °C; ^1H NMR (400 MHz, CHLOROFORM-

D) δ 7.88 – 7.81 (m, 2H), 7.31 (dd, $J = 8.4, 5.3$ Hz, 2H), 7.07 – 7.00 (m, 4H), 5.39 (dd, $J = 18.7, 9.9$ Hz, 1H), 3.87 (s, 3H); ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 193.1 (d, $J = 8.1$ Hz), 166.1 (d, $J = 257.1$ Hz), 164.3 (t, $J = 31.8$ Hz), 163.2 (d, $J = 248.9$ Hz), 132.3 (d, $J = 8.4$ Hz), 131.9 (d, $J = 9.6$ Hz), 131.3, 126.0, 116.4 (d, $J = 21.7$ Hz), 116.1 (d, $J = 22.1$ Hz), 113.7 (dd, $J = 286.4, 268.3$ Hz), 57.3 (dd, $J = 23.9, 20.4$ Hz), 53.8; ^{19}F NMR (565 MHz, CHLOROFORM-D) δ -102.94 (tt, $J = 7.8, 5.3$ Hz, 1F), -103.57 (dd, $J = 275.7, 9.9$ Hz, 1F), -112.18 (tt, $J = 8.5, 5.1$ Hz, 1F), -112.21 (dd, $J = 275.6, 18.7$ Hz, 1F). GC-MS m/z $[\text{M}]^+$ 340. HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ Calculated for: $\text{C}_{17}\text{H}_{12}\text{F}_4\text{O}_3\text{H}$: 341.0795; Found: 341.0789.

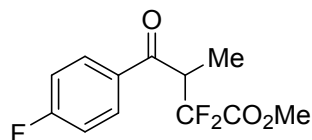


Methyl 2,2-difluoro-3-methyl-4-oxo-4-phenylbutanoate (3p)⁶: colorless oil liquid, 27.1 mg (56% yield); ^1H NMR (400 MHz, CHLOROFORM-D) δ 7.92 (dd, $J = 5.2, 3.4$ Hz, 2H), 7.64 – 7.58 (m, 1H), 7.49 (dd, $J = 10.7, 4.7$ Hz, 2H), 4.37 – 4.25 (m, 1H), 3.85 (s, 3H), 1.48 (d, $J = 7.4$ Hz, 3H); ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 197.8 (d, $J = 5.7$ Hz), 164.2 (t, $J = 32.1$ Hz), 135.3, 134.0, 129.0, 128.7, 115.2 (dd, $J = 259.0, 248.9$ Hz), 53.5, 46.4 (dd, $J = 23.6, 22.0$ Hz), 11.5, 11.5, 11.4; ^{19}F NMR (565 MHz, CHLOROFORM-D) δ -105.46 (dd, $J = 270.0, 11.1$ Hz, 1F), -112.19 (dd, $J = 270.0, 14.9$ Hz, 1F). GC-MS m/z $[\text{M}]^+$ 242.

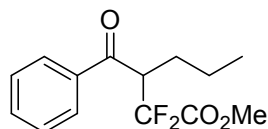


Methyl 2,2-difluoro-4-(4-methoxyphenyl)-3-methyl-4-oxobutanoate (3q)⁷: white solid, 25.2 mg (48% yield); ^1H NMR (400 MHz, CHLOROFORM-D) δ 7.94 – 7.88 (m, 2H), 6.99 – 6.93 (m, 2H), 4.25 (ddt, $J = 14.6, 11.4, 7.3$ Hz, 1H), 3.91 – 3.83 (m, 6H), 1.47 (d, $J = 7.3$ Hz, 3H); ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 196.1 (d, $J = 5.7$ Hz), 164.2 (t, $J = 32.1$ Hz), 131.1, 128.2, 117.9, 115.4 (dd, $J = 258.2, 248.9$ Hz), 55.7, 53.5, 46.1 (dd, $J = 23.6, 21.9$ Hz), 11.8; ^{19}F NMR (565 MHz, CHLOROFORM-D) δ -

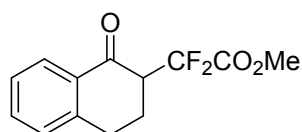
105.39 (dd, $J = 268.5, 11.5$ Hz, 1F), -111.82 (dd, $J = 268.5, 14.5$ Hz, 1F). GC-MS m/z [M]⁺ 272.



Methyl 2,2-difluoro-4-(4-fluorophenyl)-3-methyl-4-oxobutanoate (3r)⁷: colorless oil liquid, 32.2 mg (62% yield); ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.96 (dd, $J = 8.6, 5.4$ Hz, 2H), 7.17 (t, $J = 8.4$ Hz, 2H), 4.32 – 4.20 (m, 1H), 3.86 (s, 3H), 1.47 (d, $J = 7.4$ Hz, 3H); ¹³C NMR (101 MHz, CHLOROFORM-D) δ 196.2 (d, $J = 5.1$ Hz), 166.3 (d, $J = 256.6$ Hz), 164.1 (t, $J = 32.0$ Hz), 131.8, 131.5 (d, $J = 9.5$ Hz), 116.2 (d, $J = 22.0$ Hz), 115.2 (dd, $J = 259.0, 249.4$ Hz), 53.6, 46.3 (dd, $J = 23.7, 21.9$ Hz), 11.5 (t, $J = 4.4$ Hz); ¹⁹F NMR (565 MHz, CHLOROFORM-D) δ -103.43 (tt, $J = 7.9, 5.4$ Hz, 1F), -105.56 (dd, $J = 270.2, 11.3$ Hz, 1F), -111.76 (dd, $J = 270.2, 14.4$ Hz, 1F). GC-MS m/z [M]⁺ 260.

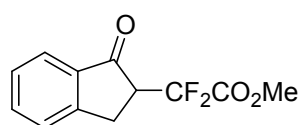


Methyl 3-benzoyl-2,2-difluorohexanoate (3s): colorless oil liquid, 32.9 mg (61% yield); ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.95 (d, $J = 8.1$ Hz, 2H), 7.65 – 7.57 (m, 1H), 7.50 (t, $J = 7.6$ Hz, 2H), 4.34 – 4.23 (m, 1H), 3.82 (s, 3H), 1.99 (dq, $J = 16.2, 8.0$ Hz, 1H), 1.90 – 1.80 (m, 1H), 1.40 – 1.30 (m, 2H), 0.90 (t, $J = 7.3$ Hz, 3H); ¹³C NMR (101 MHz, CHLOROFORM-D) δ 197.5 (dd, $J = 4.5, 2.4$ Hz), 164.0 (t, $J = 32.3$ Hz), 136.9, 134.0, 129.0, 128.6, 115.5 (dd, $J = 258.5, 252.8$ Hz), 53.5, 50.6 (t, $J = 21.7$ Hz), 29.2, 21.0, 14.2; ¹⁹F NMR (565 MHz, CHLOROFORM-D) δ -103.97 (dd, $J = 265.6, 13.1$ Hz, 1F), -107.73 (dd, $J = 265.6, 13.3$ Hz, 1F). GC-MS m/z [M]⁺ 270. HRMS (ESI): m/z [M+H]⁺ Calculated for: C₁₄H₁₆F₂O₃H: 271.1140; Found: 271.1145.



Methyl 2,2-difluoro-2-(1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)acetate (3t)⁶: colorless oil liquid, 30.00 mg (63% yield); ¹H NMR (600 MHz, CHLOROFORM-D) δ

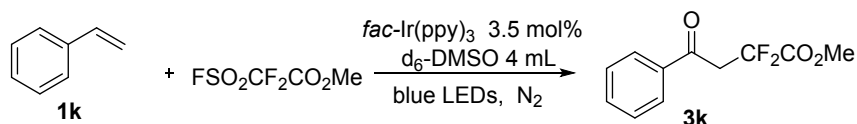
7.98 (d, $J = 8.1$ Hz, 1H), 7.51 (td, $J = 7.6, 1.1$ Hz, 1H), 7.32 (t, $J = 7.6$ Hz, 1H), 7.27 (d, $J = 7.7$ Hz, 1H), 3.95 (s, 3H), 3.60 (ddt, $J = 23.9, 13.7, 4.3$ Hz, 1H), 3.10 (dd, $J = 8.4, 3.4$ Hz, 2H), 2.50 (ddd, $J = 12.8, 7.8, 3.9$ Hz, 1H), 2.28 – 2.21 (m, 1H); ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 193.6 (d, $J = 9.5$ Hz), 164.5 (dd, $J = 32.4, 30.7$ Hz), 164.2, 143.9, 134.5, 131.6 (d, $J = 3.5$ Hz), 129.0, 127.7, 127.2, 114.9 (dd, $J = 258.6, 244.5$ Hz), 53.6, 52.4 (t, $J = 24.3$ Hz), 28.4, 21.8 (t, $J = 3.1$ Hz); ^{19}F NMR (565 MHz, CHLOROFORM-D) δ -109.42 (dd, $J = 270.1, 4.3$ Hz, 1F), -119.04 (dd, $J = 270.1, 24.1$ Hz, 1F). GC-MS m/z $[\text{M}]^+$ 254.

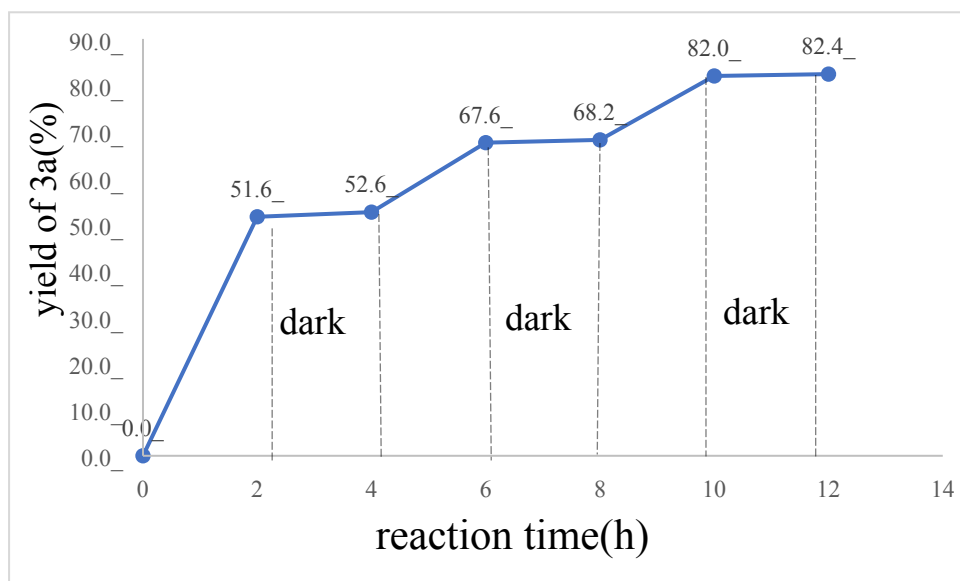


Methyl 2,2-difluoro-2-(1-oxo-2,3-dihydro-1H-inden-2-yl)acetate (3u): colorless oil liquid, 31.76 mg (33% yield); ^1H NMR (400 MHz, CHLOROFORM-D) δ 7.74 (d, $J = 7.7$ Hz, 1H), 7.63 (t, $J = 7.4$ Hz, 1H), 7.51 (d, $J = 7.7$ Hz, 1H), 7.39 (t, $J = 7.5$ Hz, 1H), 3.95 (s, 3H), 3.65 (ddd, $J = 25.2, 13.9, 6.9$ Hz, 1H), 3.38 (d, $J = 6.6$ Hz, 2H); ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 199.5 (d, $J = 8.1$ Hz), 163.6 (t, $J = 31.7$ Hz), 153.0, 136.0, 135.8, 128.1, 126.7, 124.5, 115.1 (dd, $J = 255.4, 250.8$ Hz), 53.8, 51.2 (t, $J = 23.5$ Hz), 26.8; ^{19}F NMR (565 MHz, CHLOROFORM-D) δ -103.70 (dd, $J = 266.4, 7.5$ Hz, 1F), -115.73 (dd, $J = 266.3, 25.3$ Hz, 1F). GC-MS m/z $[\text{M}]^+$ 240. HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ Calculated for: $\text{C}_{12}\text{H}_{10}\text{F}_2\text{O}_3\text{H}$: 241.0671; Found: 241.0668.

Control experiments for insight on reaction mechanism

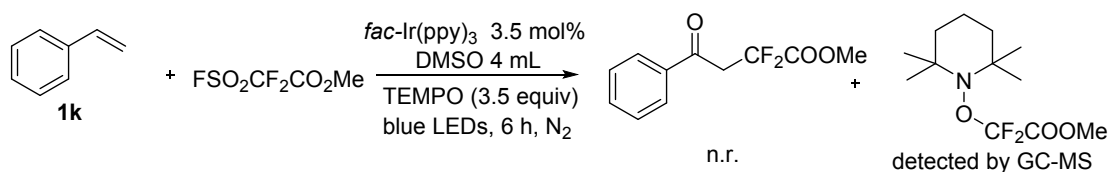
a) The experiment of turn on and off the light





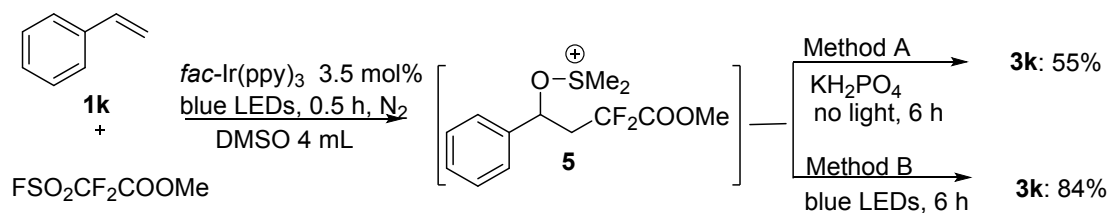
An NMR tube was charged with 0.6 mg *fac*-Ir(ppy)₃ (3.5 mol%) which was degassed and refilled with N₂ for 3 times. Styrene **1k** (2.6 mg, 0.025 mmol, 1.0 equiv), Chen reagent FSO₂CF₂CO₂Me (16.8 mg, 0.0875 mmol, 3.5 equiv.) and dry d₆-DMSO (0.5 mL) were added under N₂. The resulting mixture was alternately irradiated with 3 W blue LEDs and set in dark totally for 12 h. The yield of **3k** was confirmed by ¹H NMR analysis of the crude sample using dibromomethane as internal standard.

b) Control experiment with TEMPO



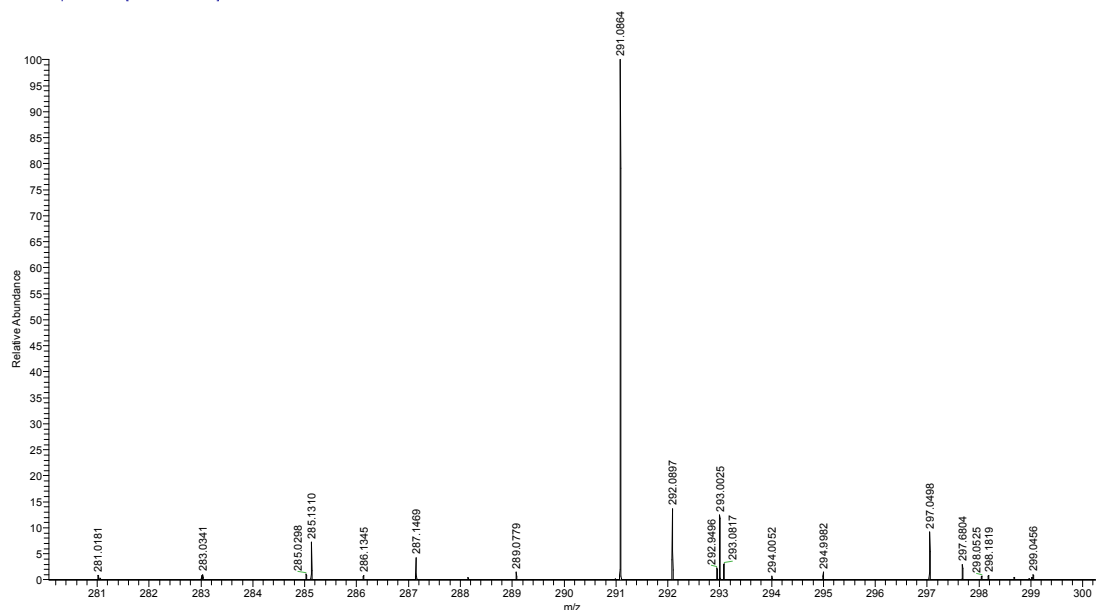
An oven-dried Schleck tube equipped with a stirrer bar was charged with 4.58 mg *fac*-Ir(ppy)₃ (3.5 mol%) and TEMPO (109.2 mg, 0.7 mmol, 3.5 equiv.), which was degassed and refilled with N₂ for 5 times. The alkenes **1k** (0.2 mmol, 1.0 equiv.), Chen's reagent FSO₂CF₂CO₂Me (134.4 mg, 0.7 mmol, 3.5 equiv.) and dry DMSO (4 mL) were added under N₂. The resulting mixture was irradiated for 6 h under room temperature by 3 W blue LEDs. Upon completion of the reaction, detect the reaction mixture with GC-MS.

c) The detection and transformation of alkoxyulfonium ion intermediate **5**.

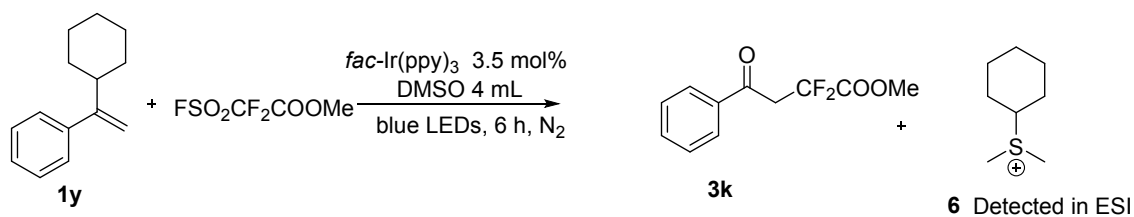


Oven-dried Schleck tube equipped with a stirrer bar was charged with 4.58 mg *fac*-Ir(ppy)₃ (3.5 mol%) which was degassed and refilled with N₂ for 3 times. The styrene **1k** (0.2 mmol, 1.0 equiv.), Chen reagent FSO₂CF₂CO₂Me (134.4 mg, 0.7 mmol, 3.5 equiv.) and dry DMSO (4 mL) were added under N₂. The mixture was irradiated for 0.5 h under room temperature by 3 W blue LEDs. Detect the reaction mixture by NMR and ESI. HRMS Calculated for cation **5** C₁₃H₁₇F₂O₃S⁺ 291.0861, observed 291.0864, in the case the **3k** was observed by NMR in 32% yield. Add KH₂PO₄ (54.4 mg, 0.4 mmol, 2.0 equiv.) to the first tube. The other one was irradiated for 6 h under room temperature by 3 W blue LEDs. They give the product **3k** in 55% and 84% yields, respectively.

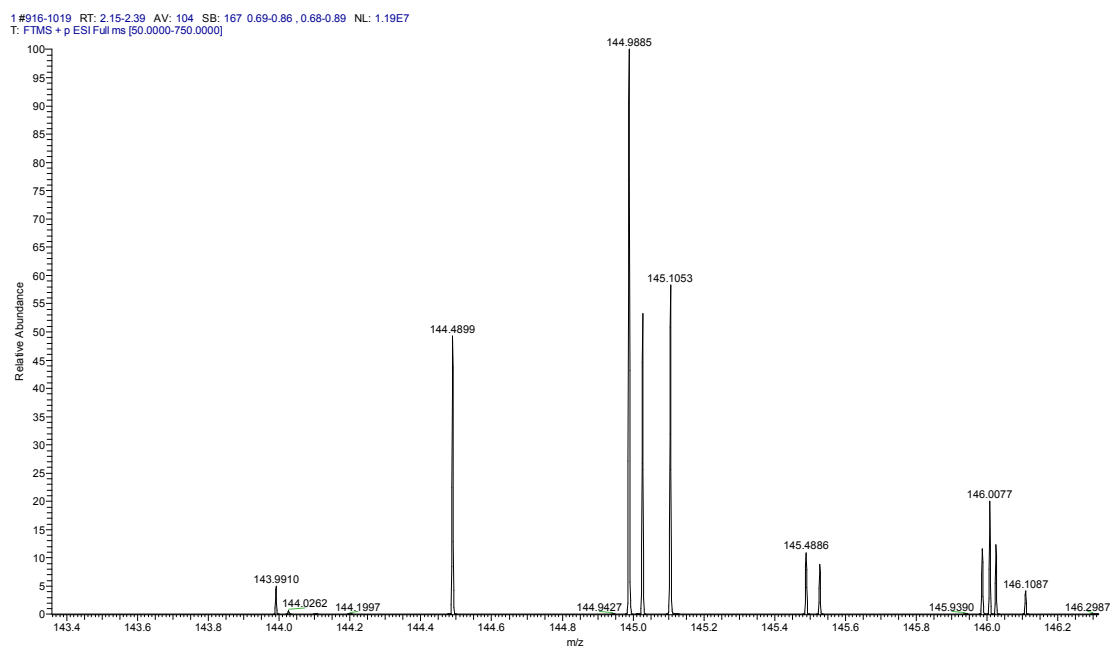
1#1180-1265 RT: 2.75-2.95 AV: 86 SB: 137 0.19-0.33, 0.21-0.38 NL: 4.22E7
T: FTMS + p ESI Full ms [50.0000-750.0000]



d) The reaction of (1-cyclohexylvinyl)benzene with Chen reagent under the photocatalytic reaction condition



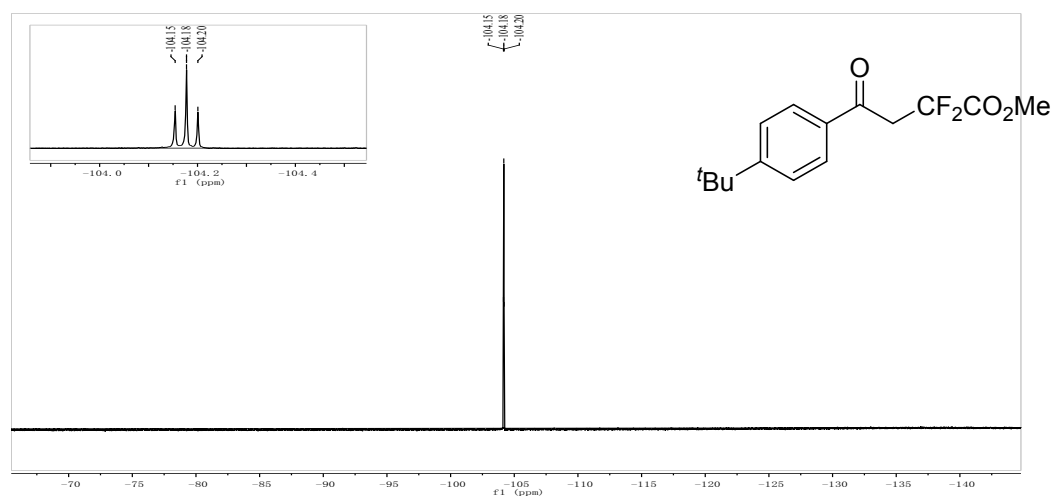
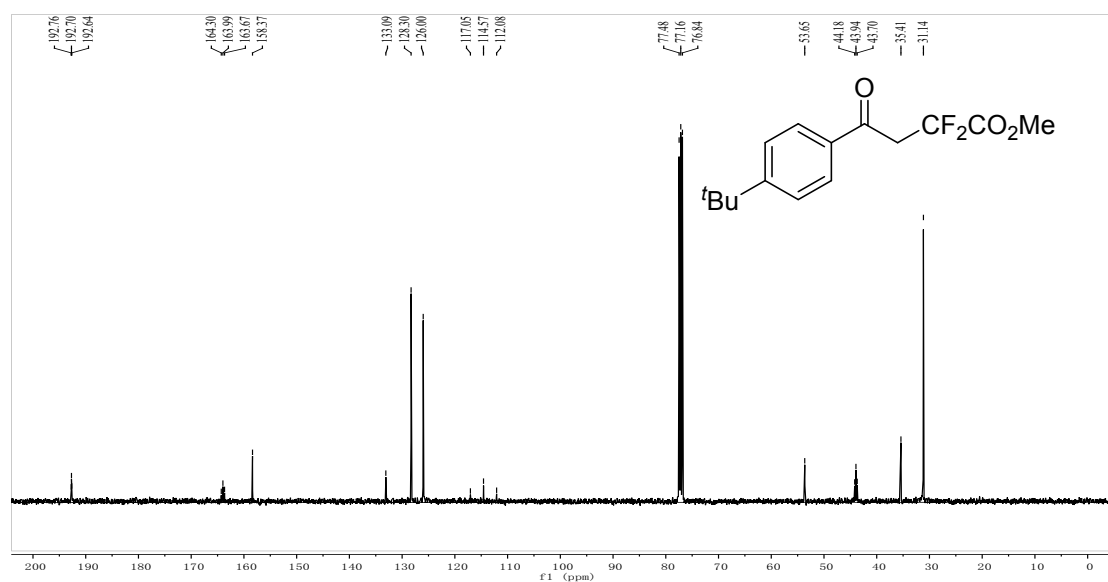
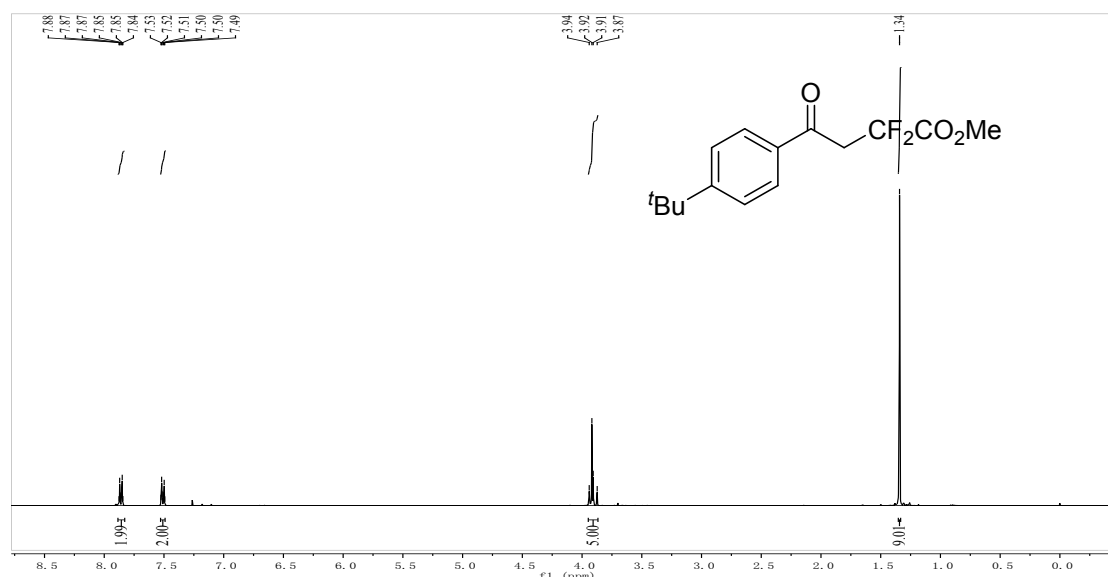
An oven-dried Schleck tube equipped with a stirrer bar was charged with 4.58 mg *fac*-Ir(ppy)₃ (3.5 mol%) which was degassed and refilled with N₂ for 3 times. The (1-cyclohexylvinyl)benzene **1y** (37.2 mg, 0.2 mmol, 1.0 equiv.), Chen reagent FSO₂CF₂CO₂Me (134.4 mg, 0.7 mmol, 3.5 equiv.) and dry DMSO (4 mL) were added under N₂. The resulting mixture was irradiated for 6 h under room temperature by 3 W blue LEDs. Upon completion of the reaction, detect the reaction mixture by NMR and ESI. Quenching the reaction with sat. aq. NaHCO₃ and dichloromethane (DCM) was added. The aqueous layer was extracted with DCM twice. The combined organic layer dried by Na₂SO₄, and concentrated in *vacuo* and the residue was purified by chromatography on silica gel. Product **3k** was obtained. HRMS Calculated for cation **6** C₈H₁₇S⁺ 145.1048, observed 145.1053.



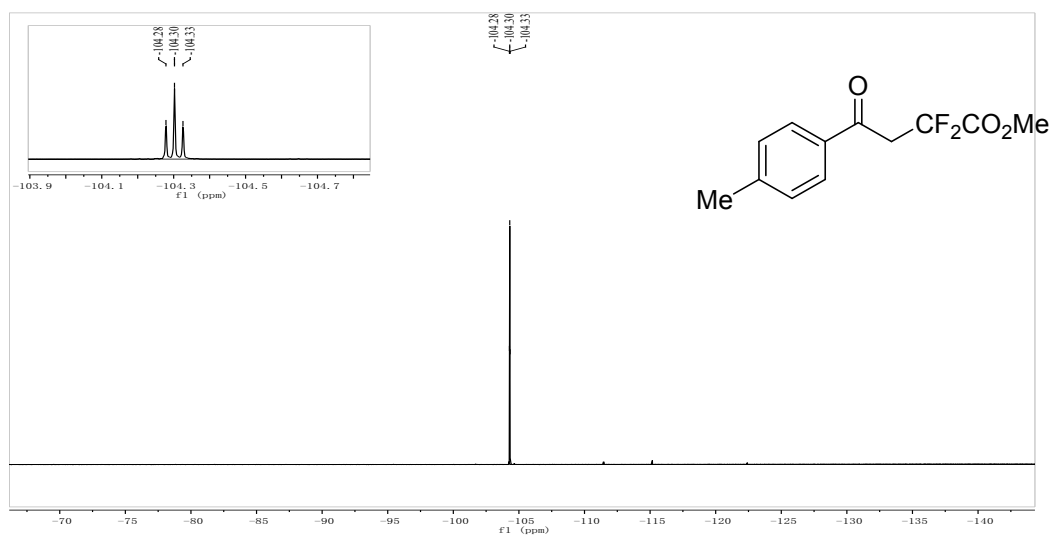
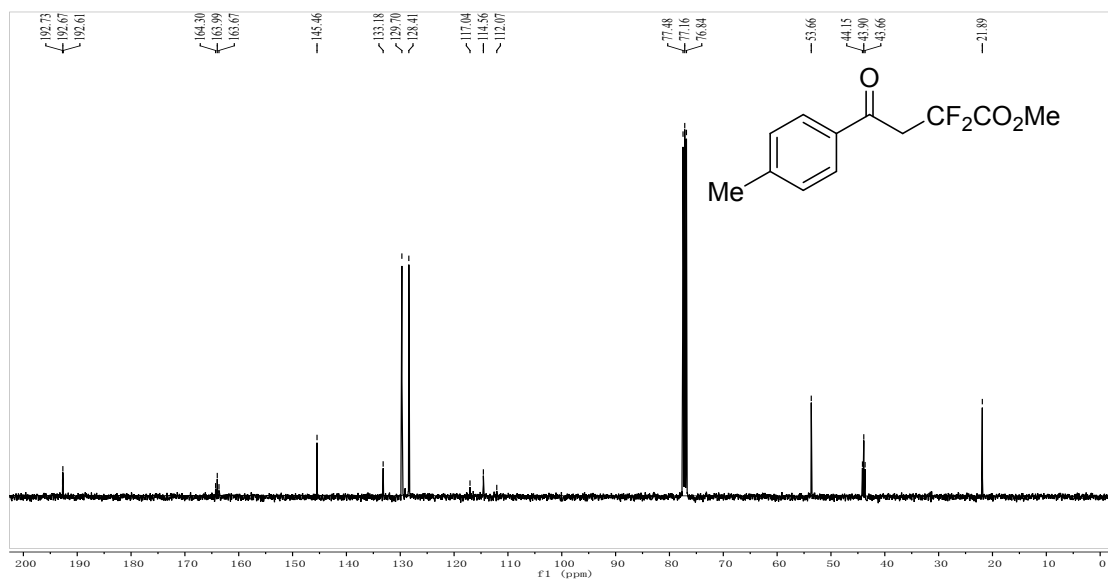
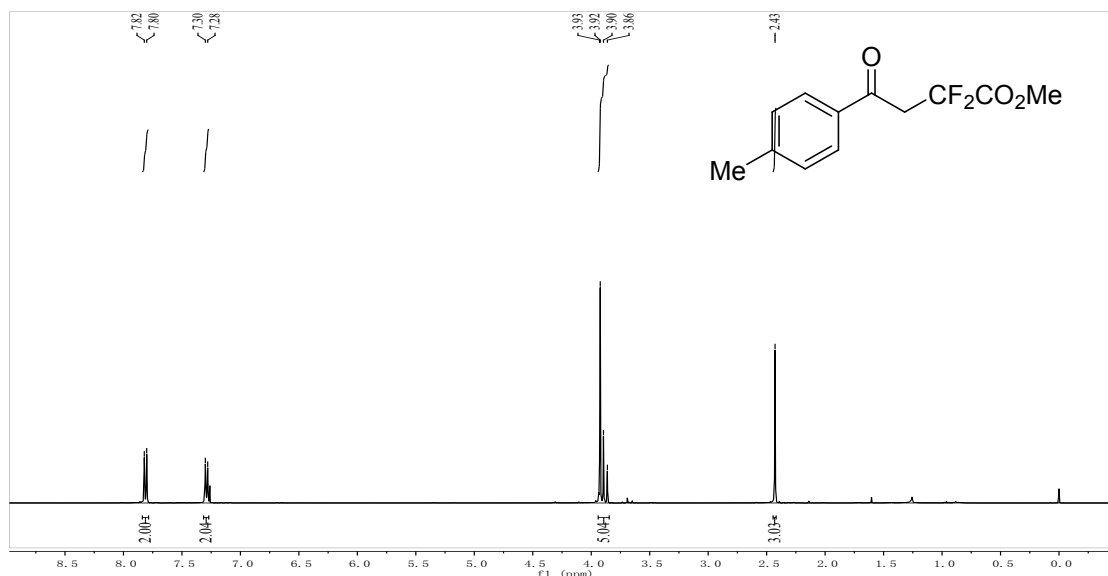
3. Reference

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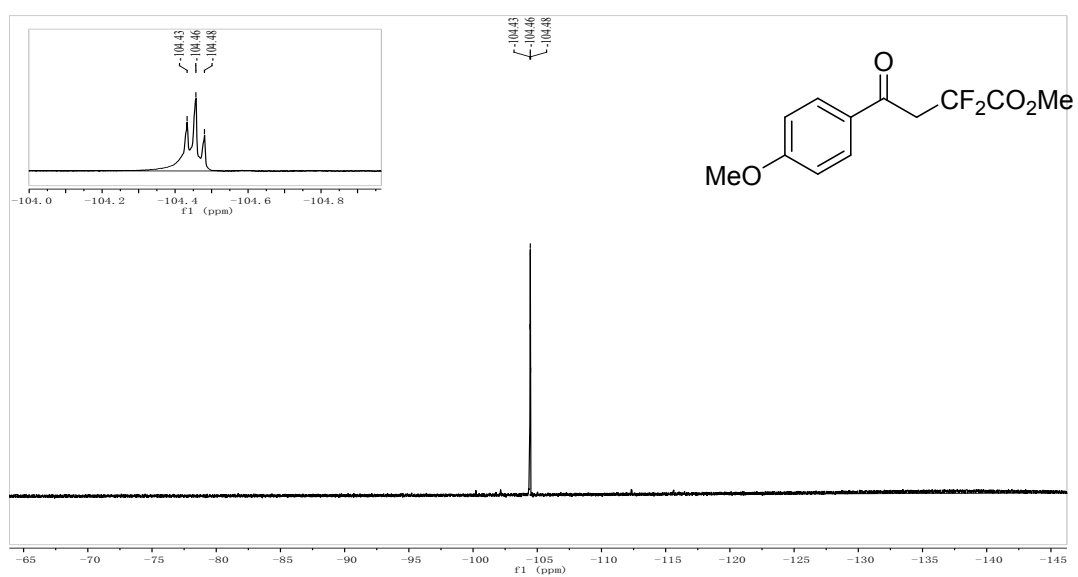
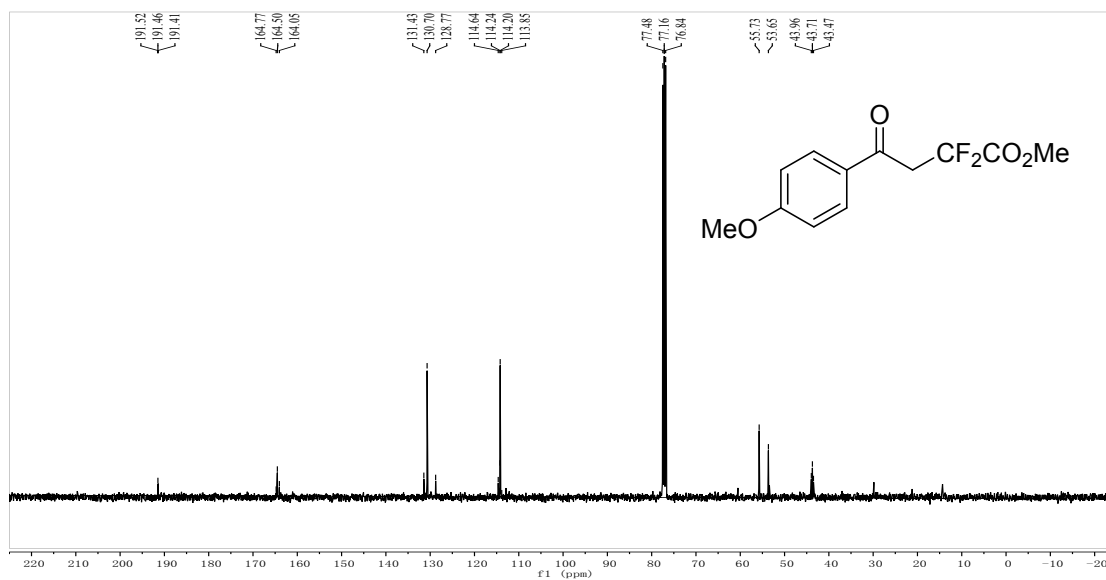
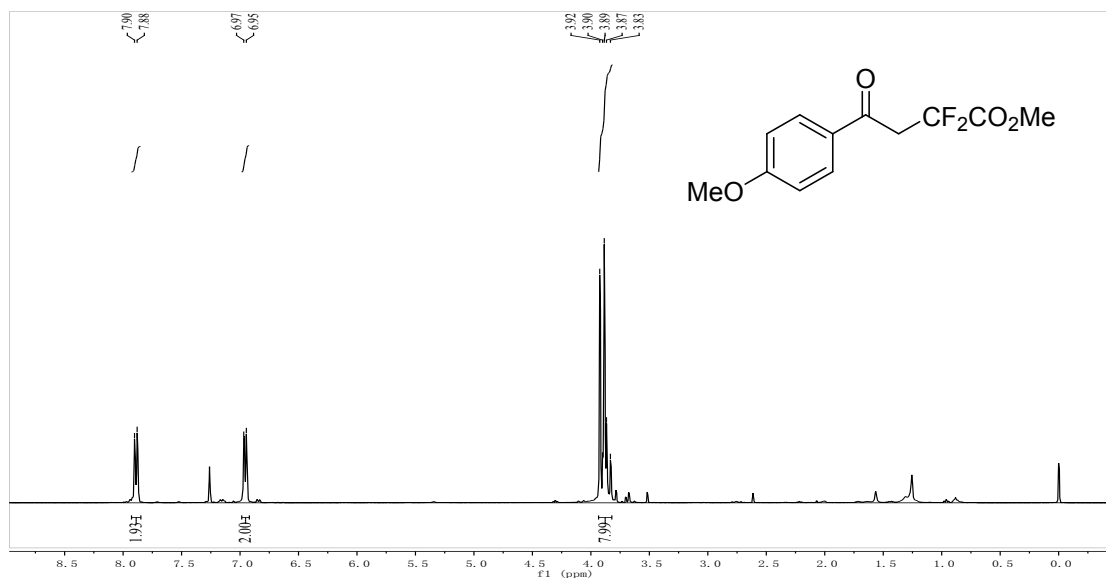
4. Copies of ^1H , ^{13}C NMR, and ^{19}F NMR Spectra



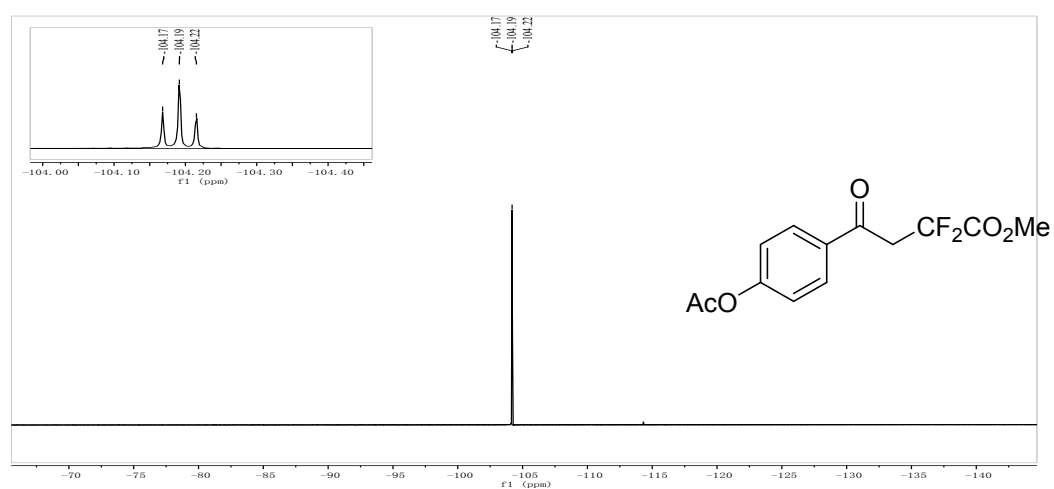
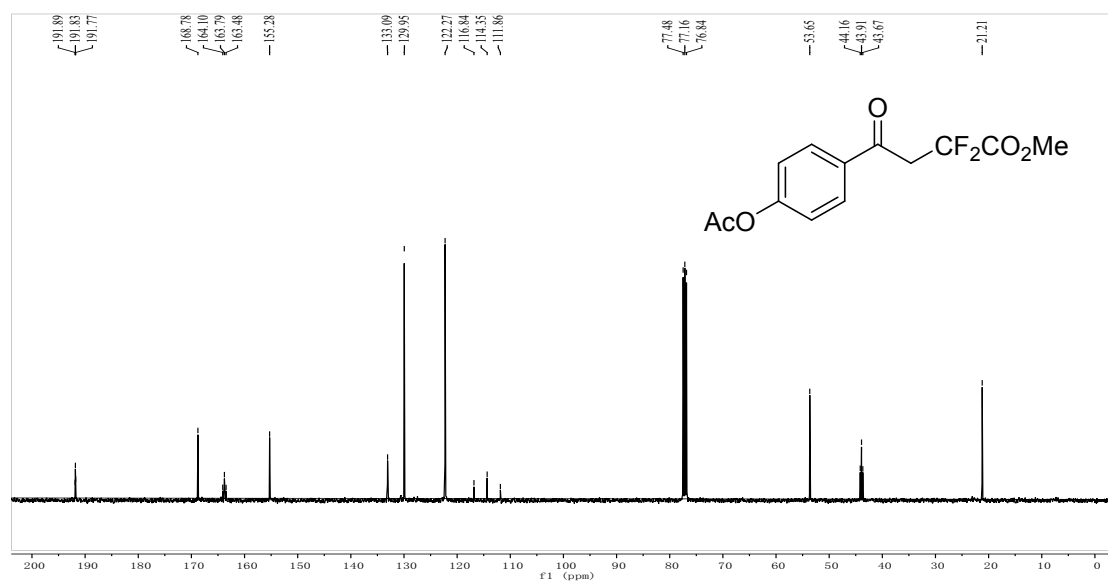
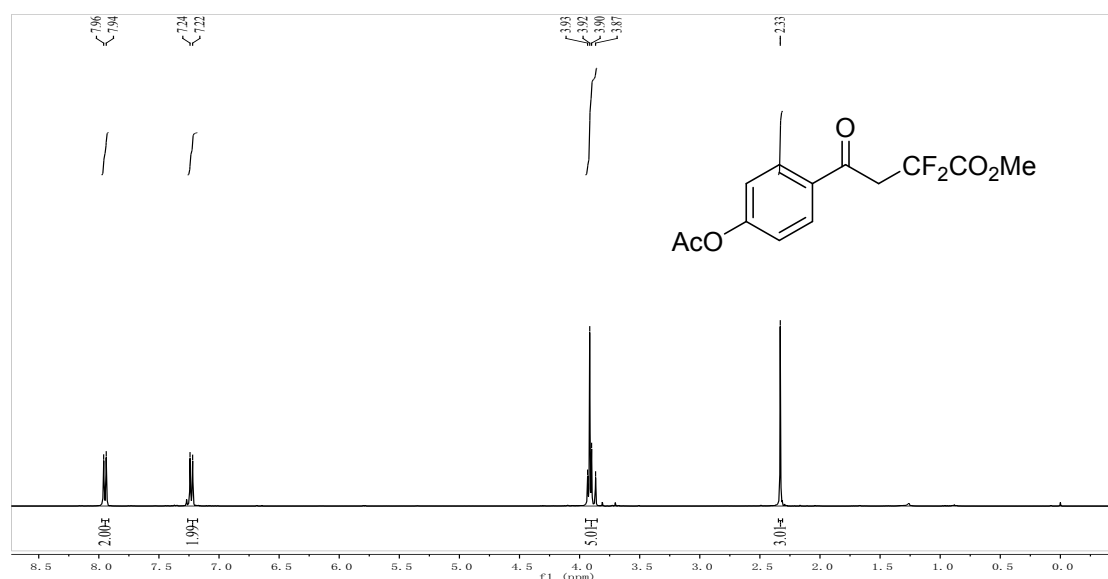
^1H NMR, $^{13}\text{C}\{^1\text{H}\}$ NMR, and ^{19}F NMR of **3a**



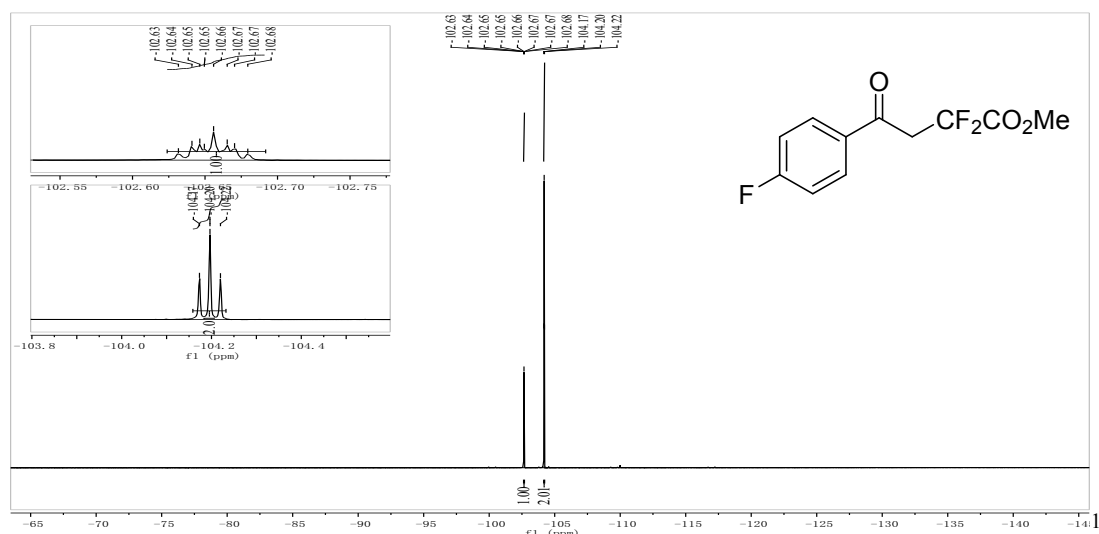
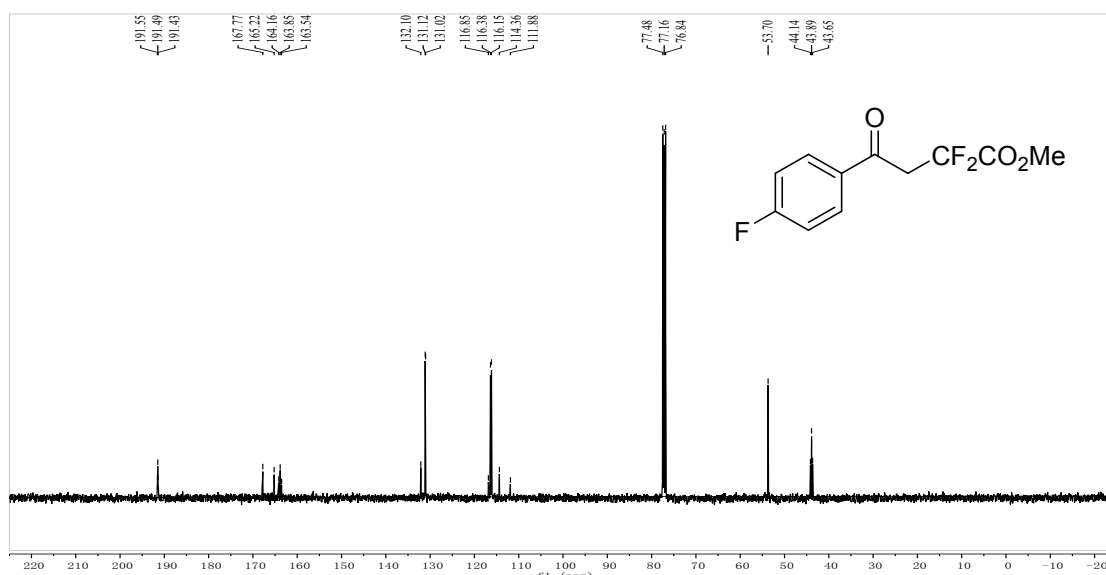
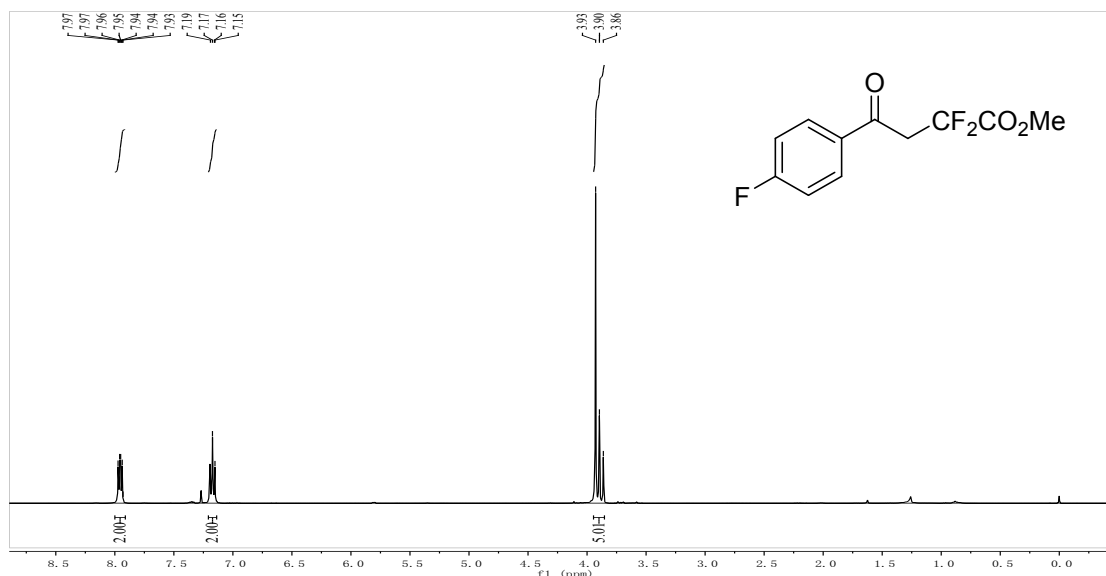
¹H NMR, ¹³C{¹H} NMR, and ¹⁹F NMR of 3b



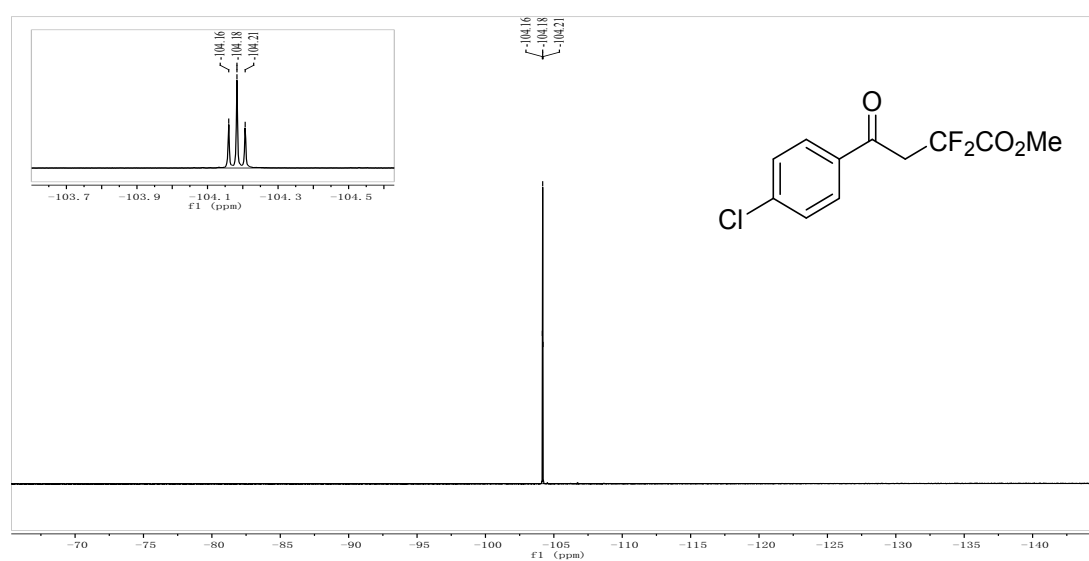
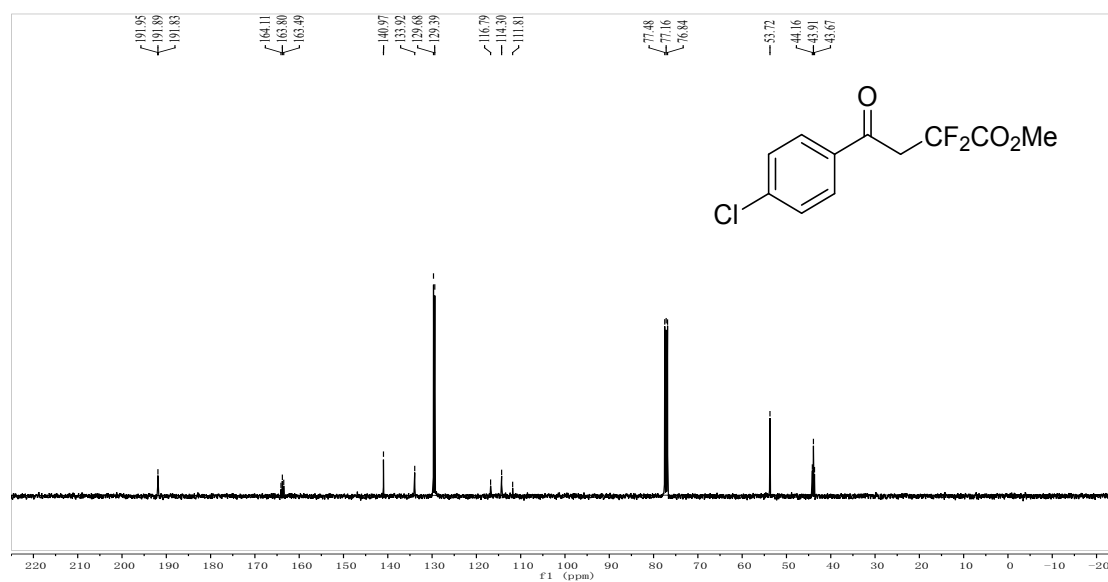
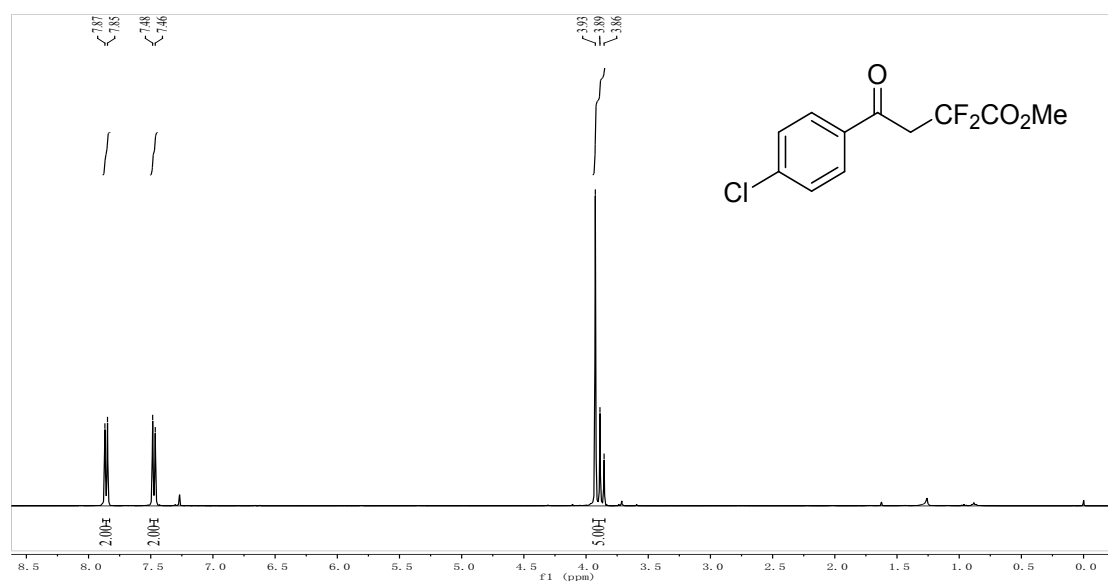
¹H NMR, ¹³C{¹H} NMR, and ¹⁹F NMR of 3c



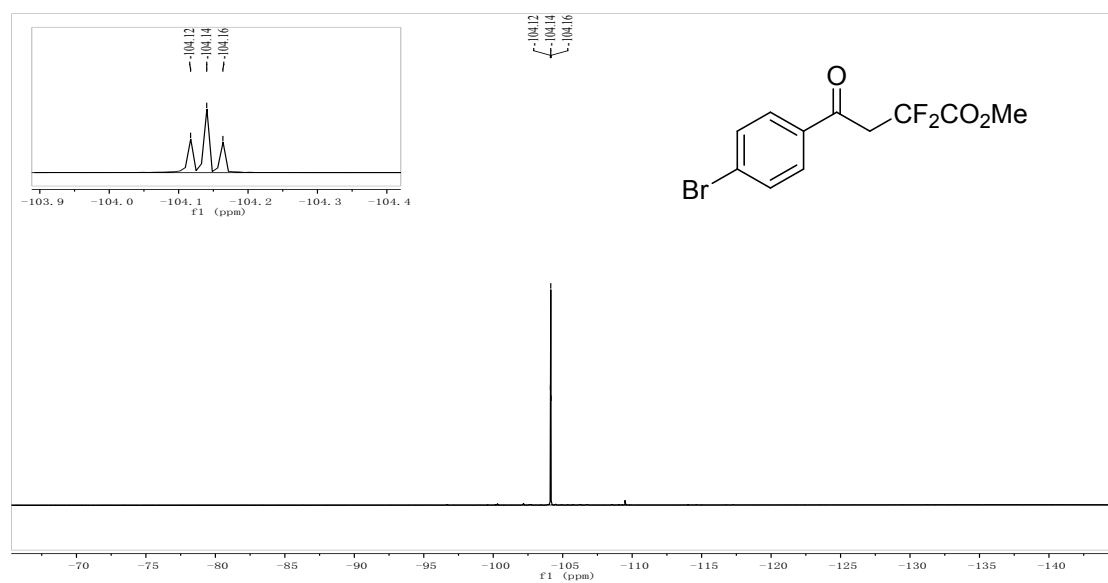
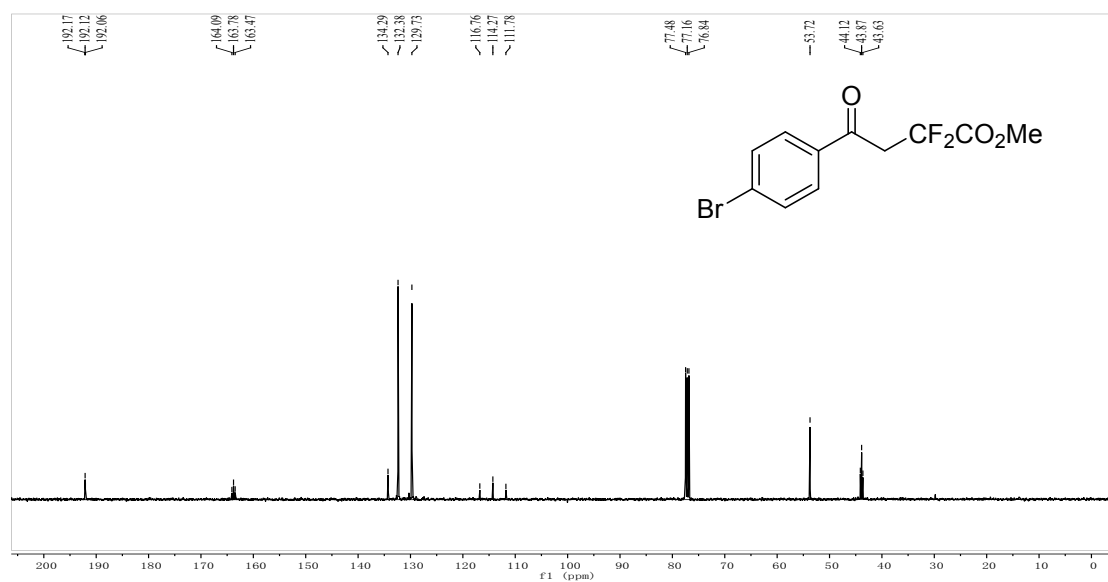
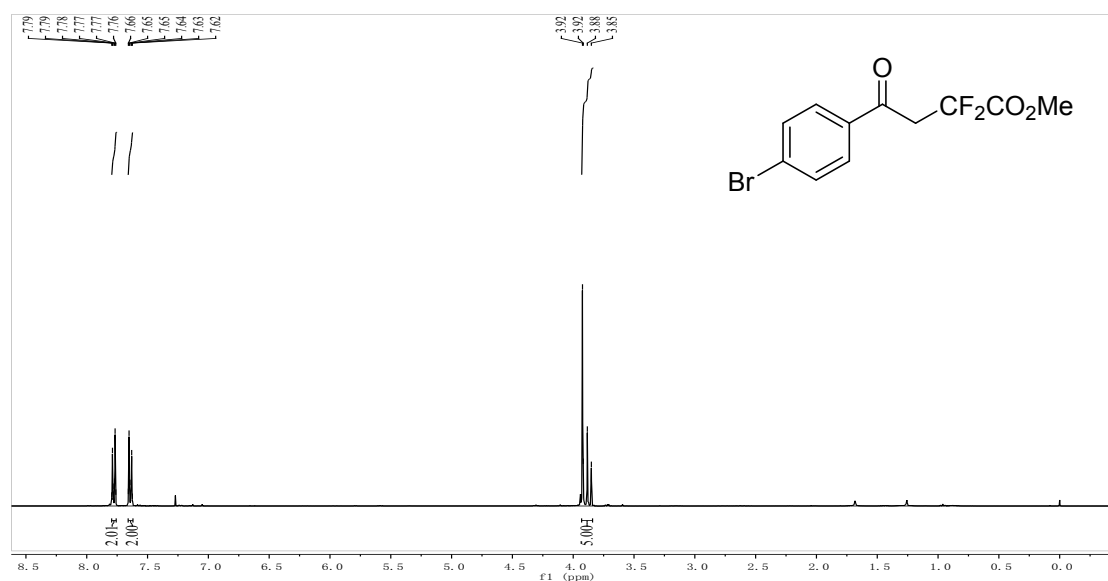
¹H NMR, ¹³C{¹H} NMR, and ¹⁹F NMR of 3d



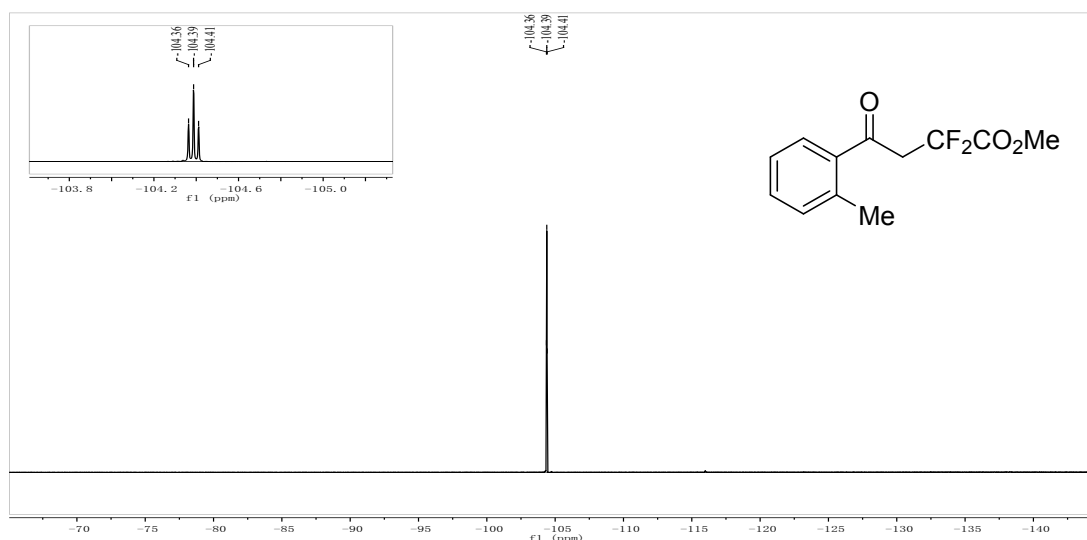
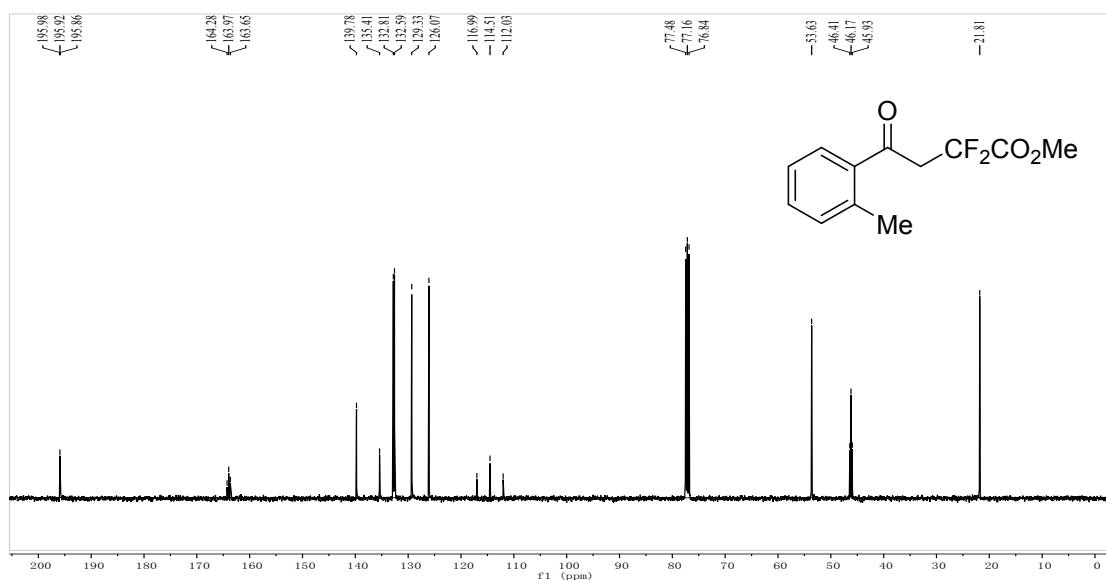
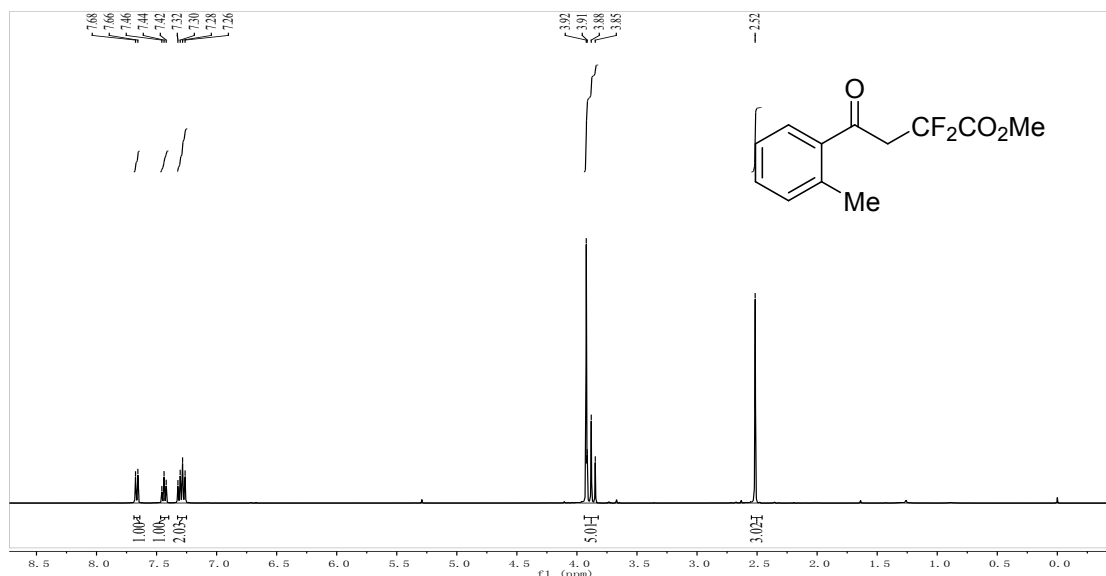
H NMR, ¹³C{¹H} NMR, and ¹⁹F NMR of 3e



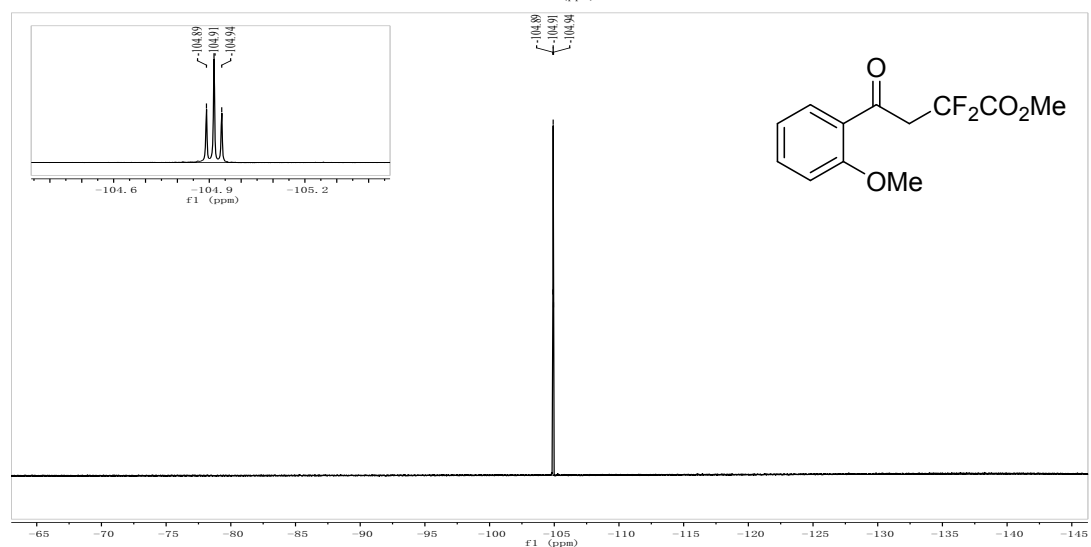
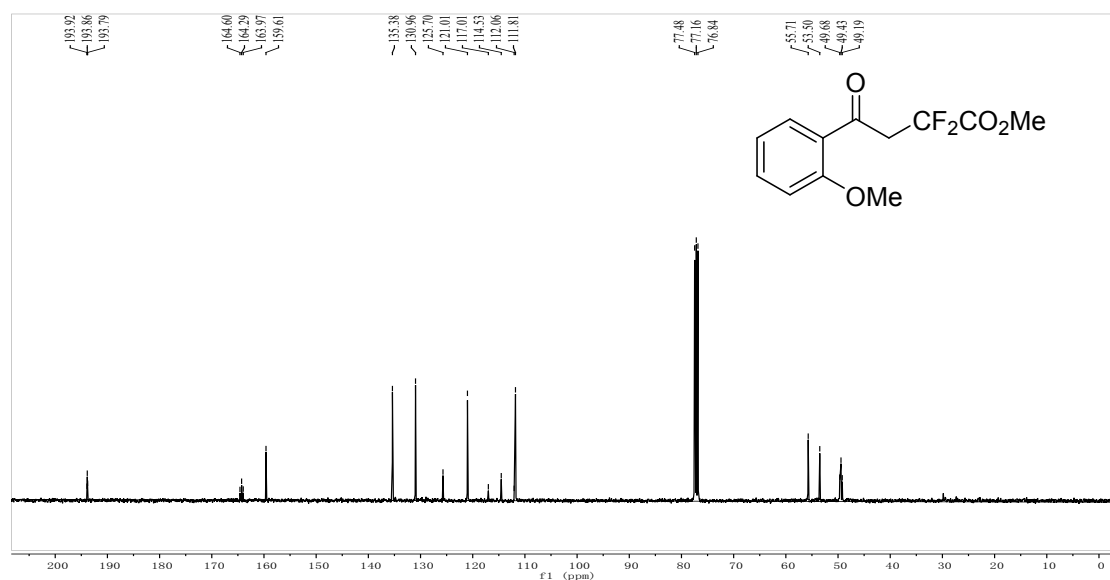
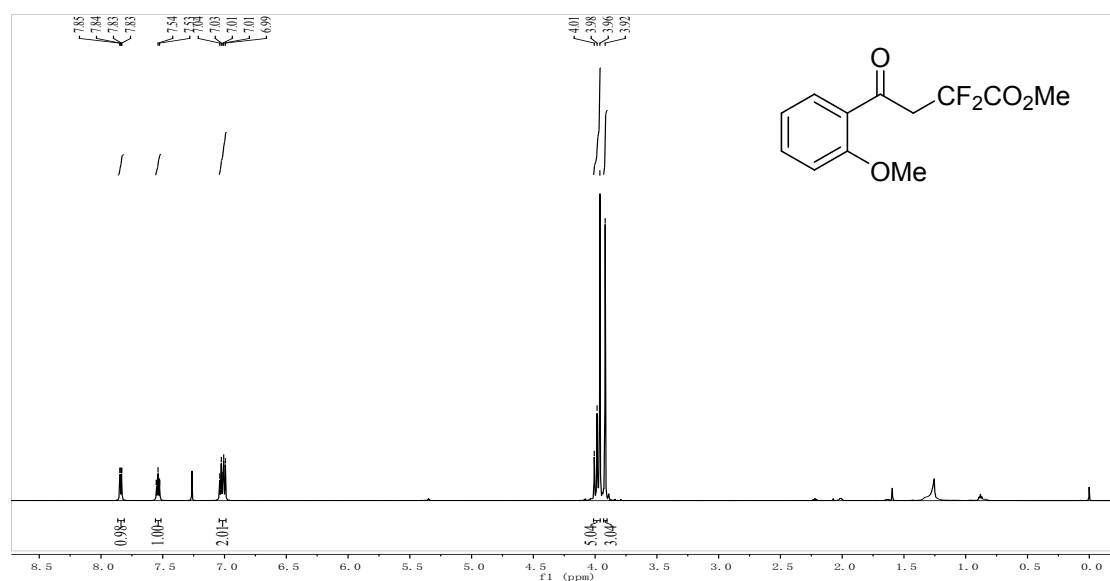
¹H NMR, ¹³C{¹H} NMR, and ¹⁹F NMR of **3f**



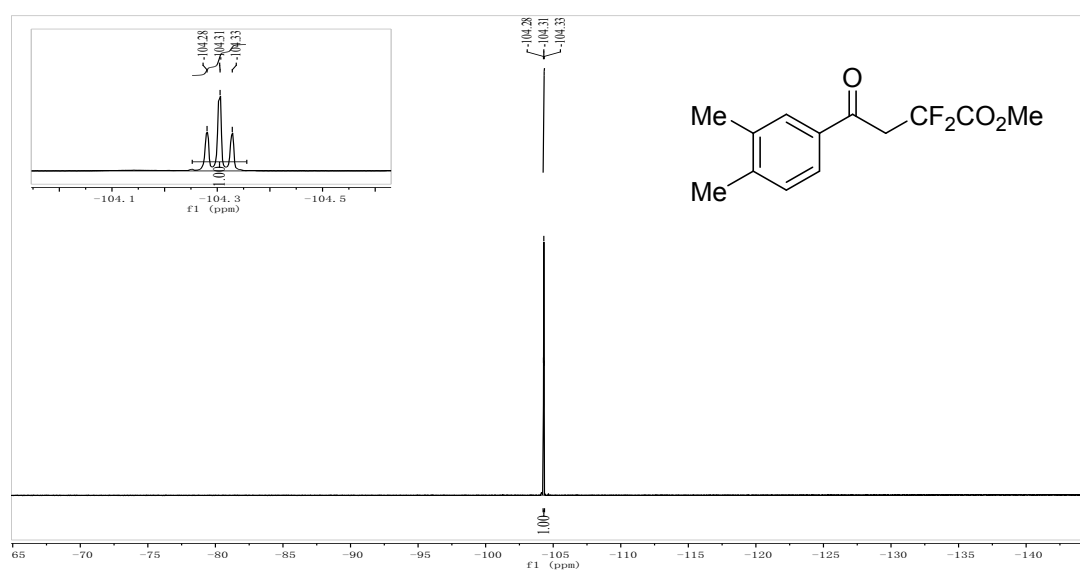
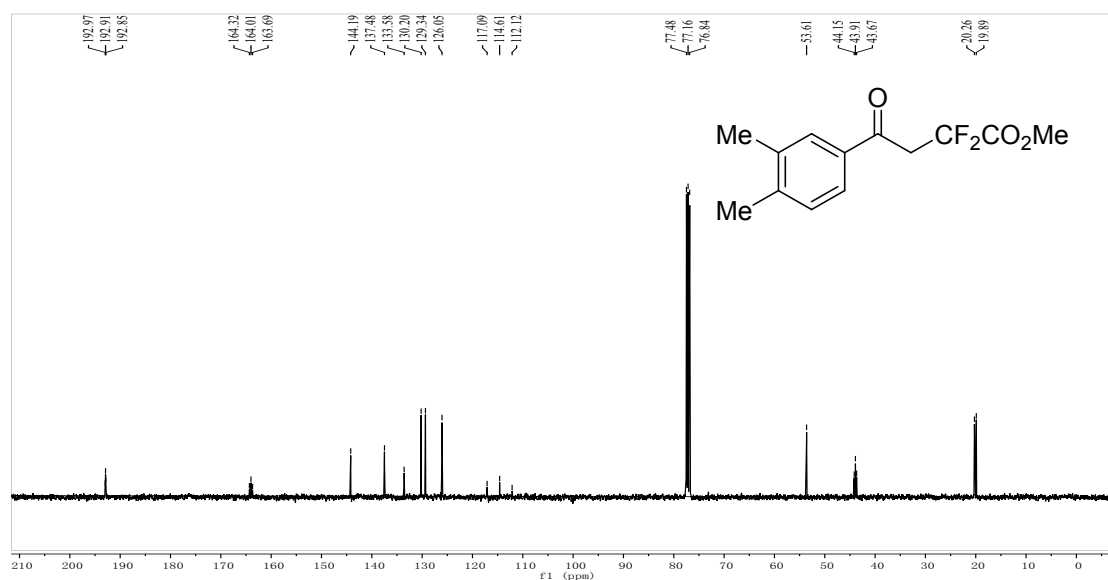
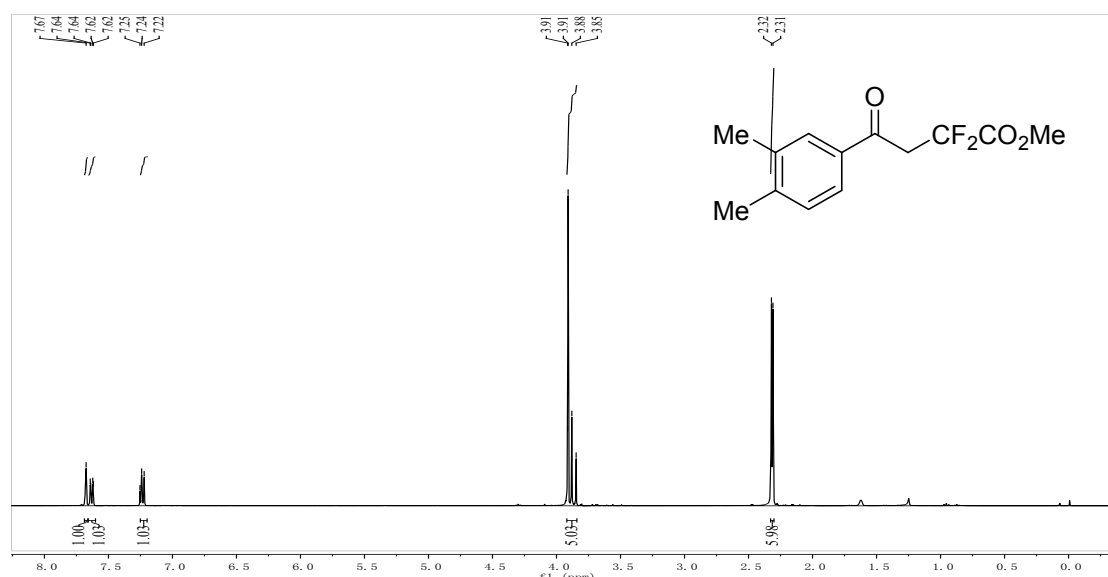
¹H NMR, ¹³C{¹H} NMR, and ¹⁹F NMR of **3g**



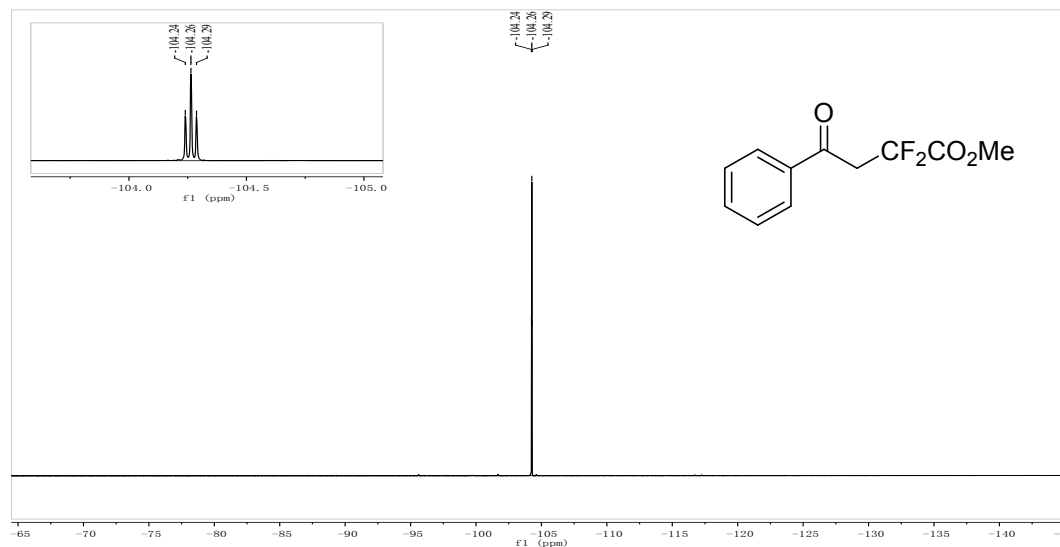
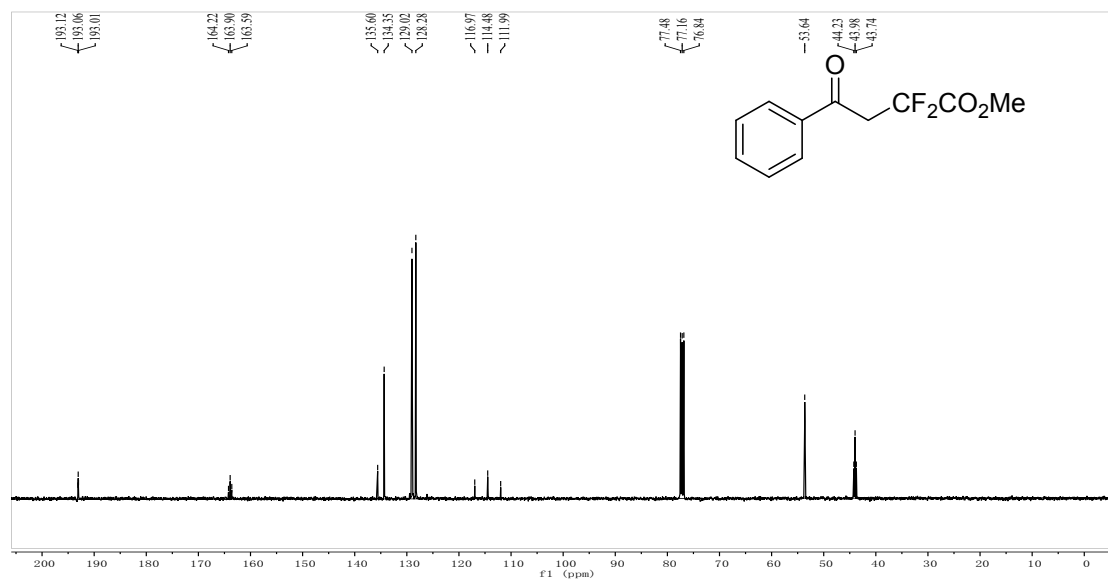
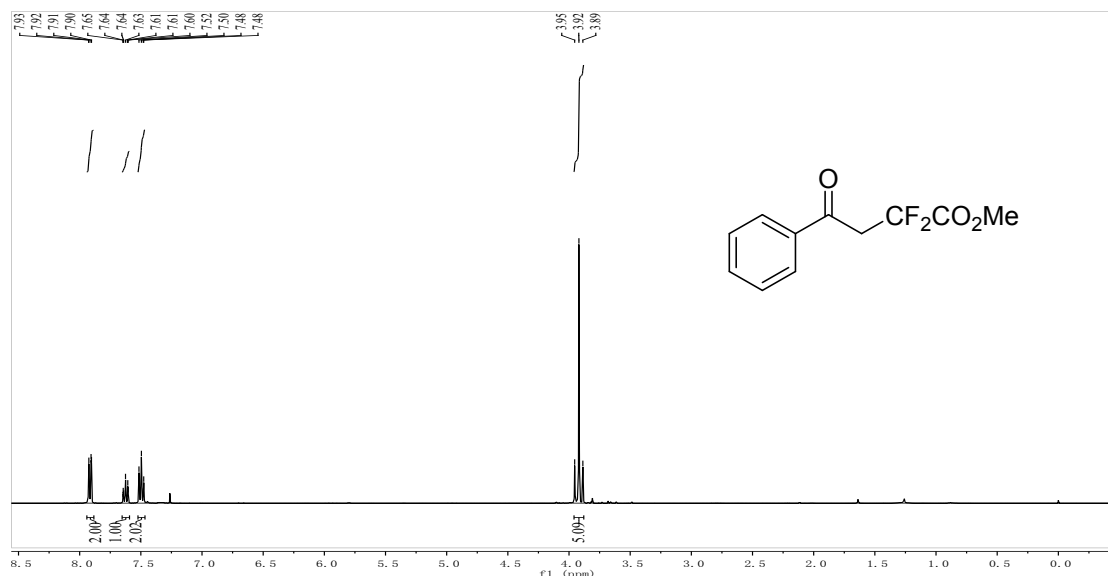
¹H NMR, ¹³C{¹H} NMR, and ¹⁹F NMR of **3h**



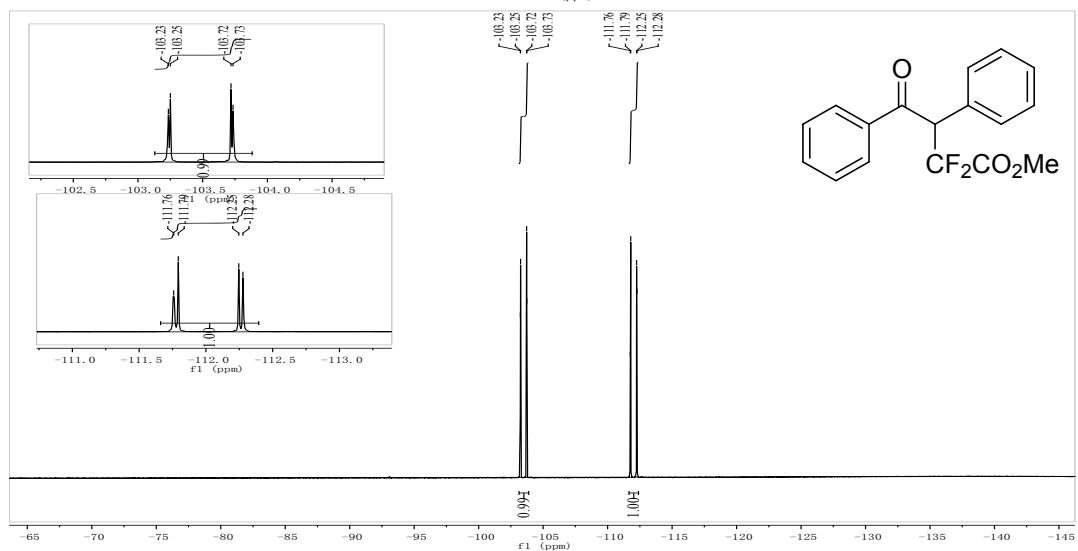
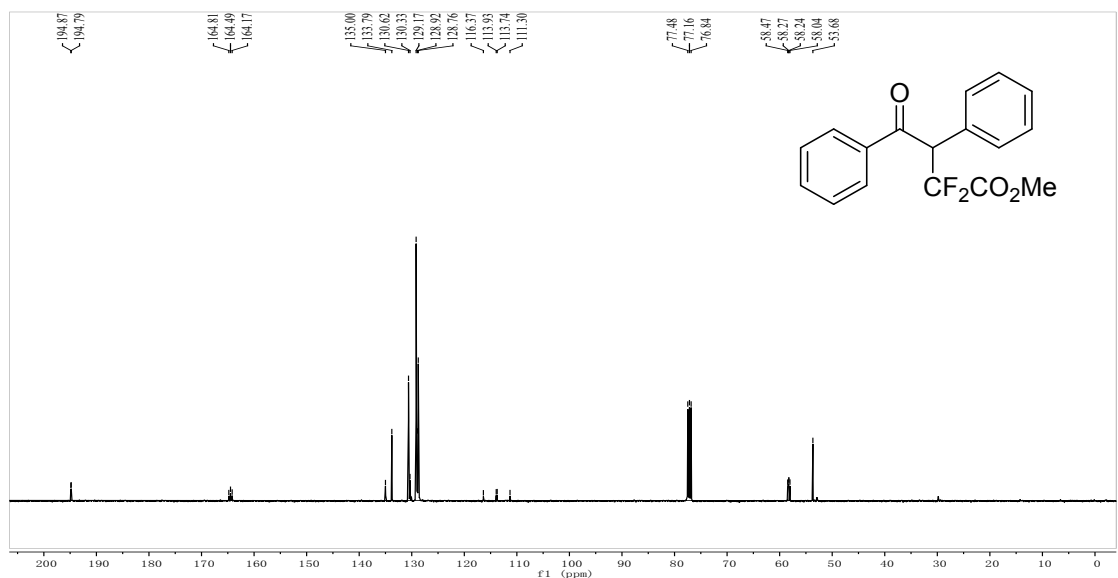
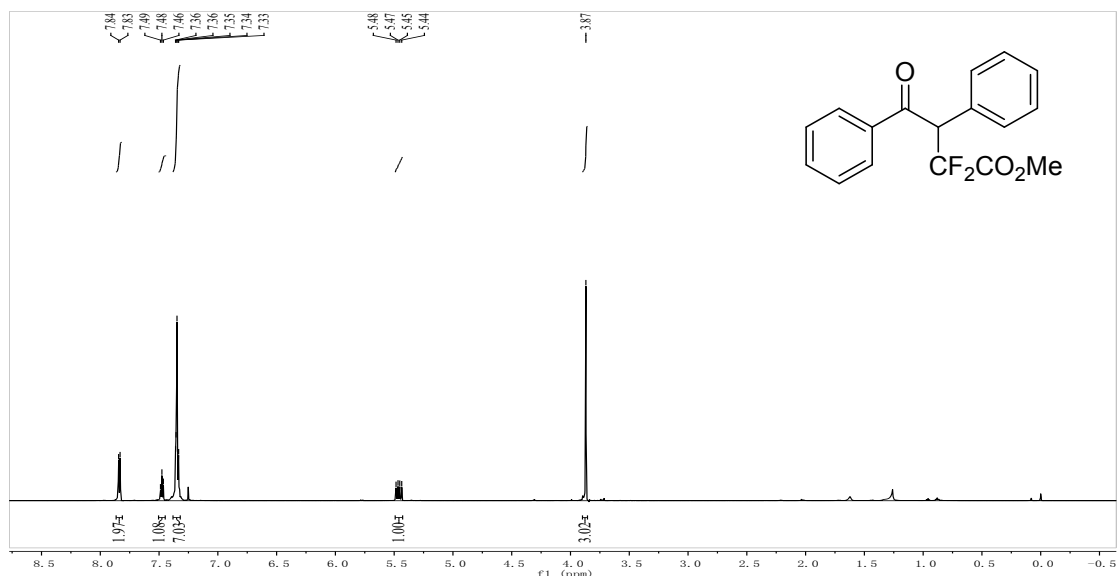
¹H NMR, ¹³C{¹H} NMR, and ¹⁹F NMR of **3i**



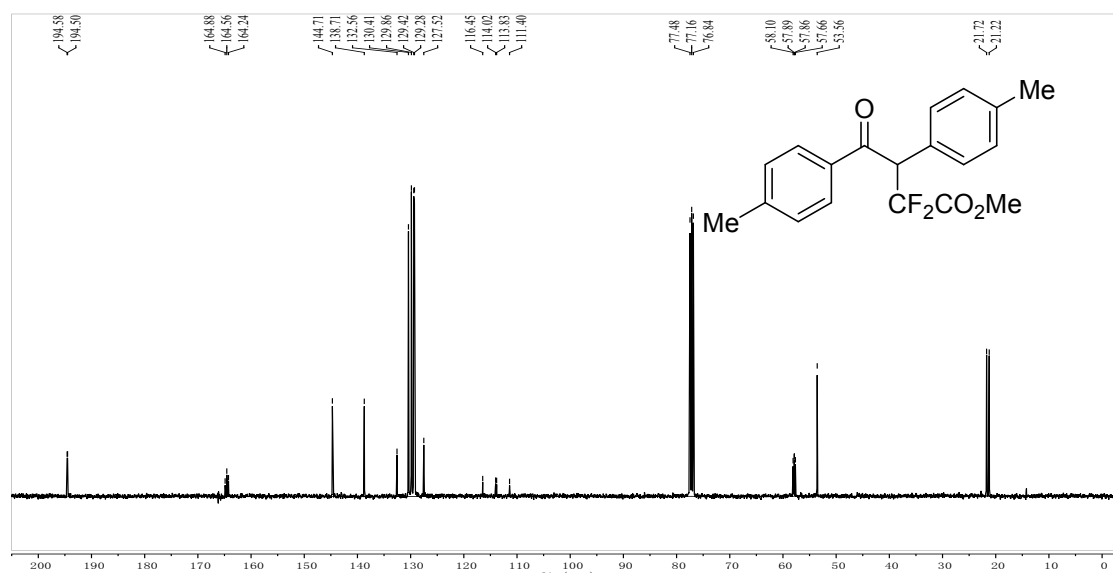
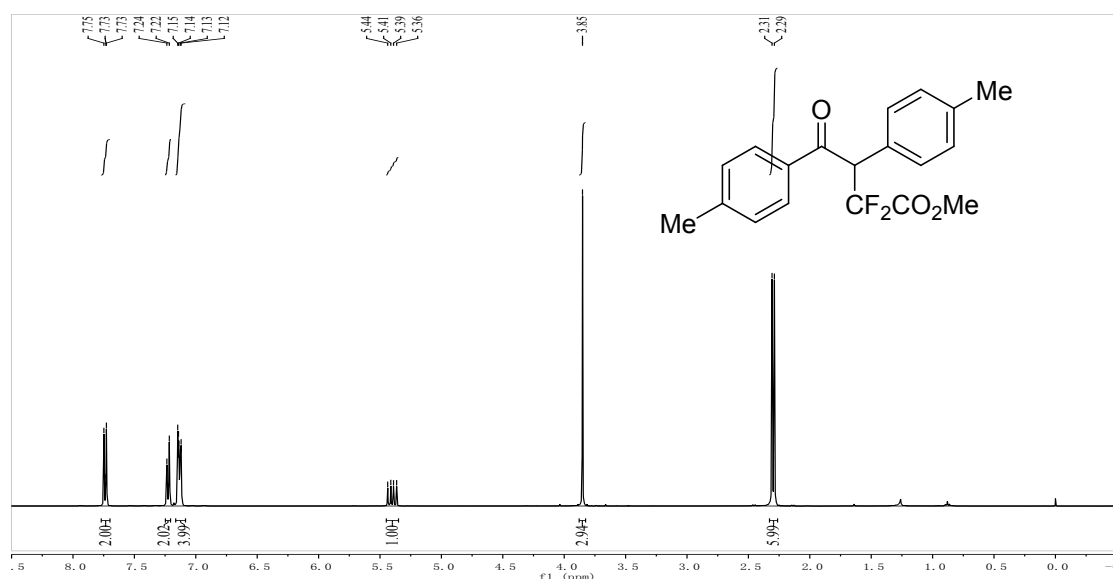
^1H NMR, $^{13}\text{C}\{^1\text{H}\}$ NMR, and ^{19}F NMR of **3j**



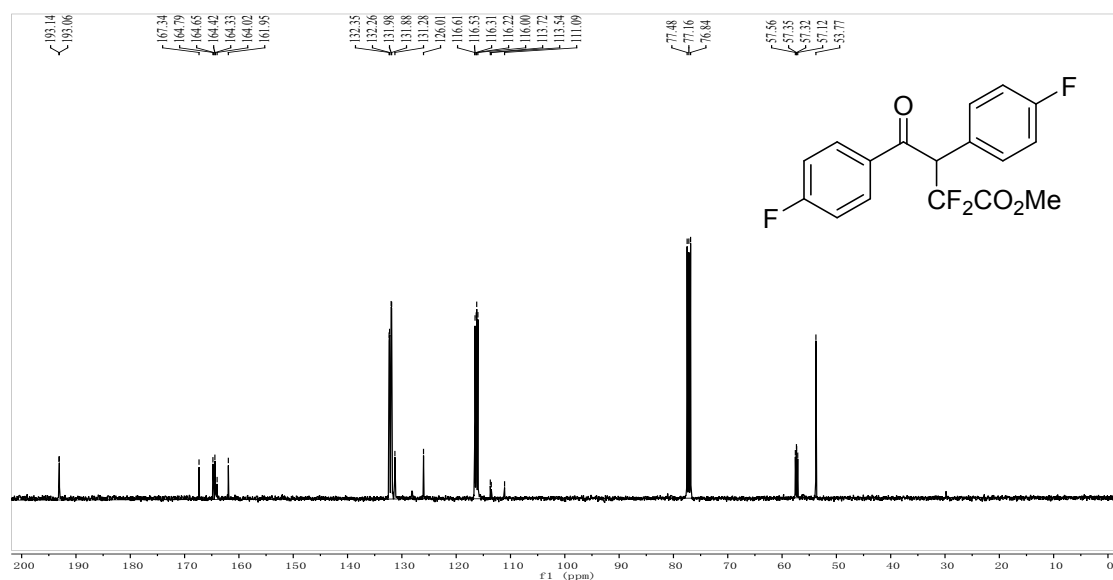
¹H NMR, ¹³C{¹H} NMR, and ¹⁹F NMR of **3k**



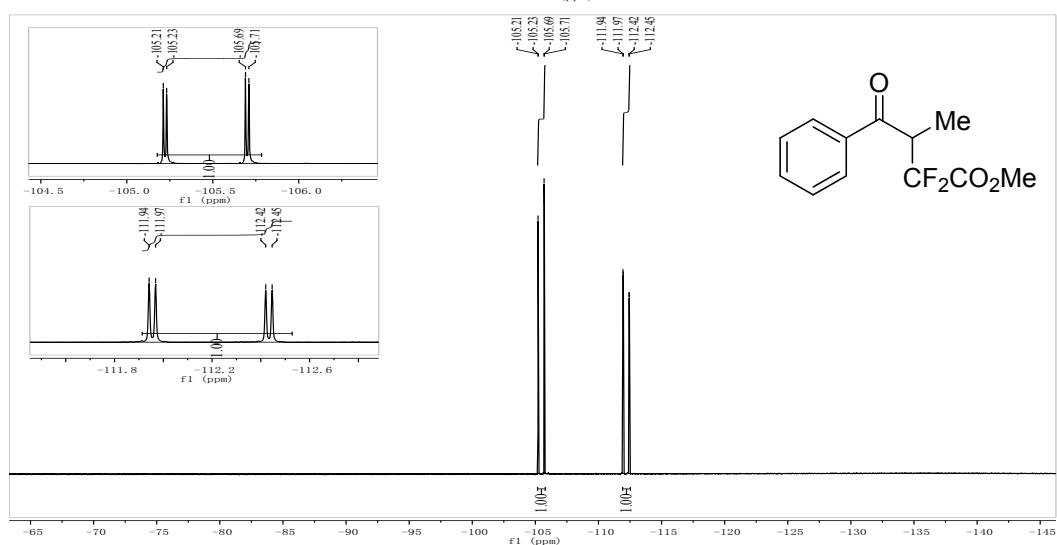
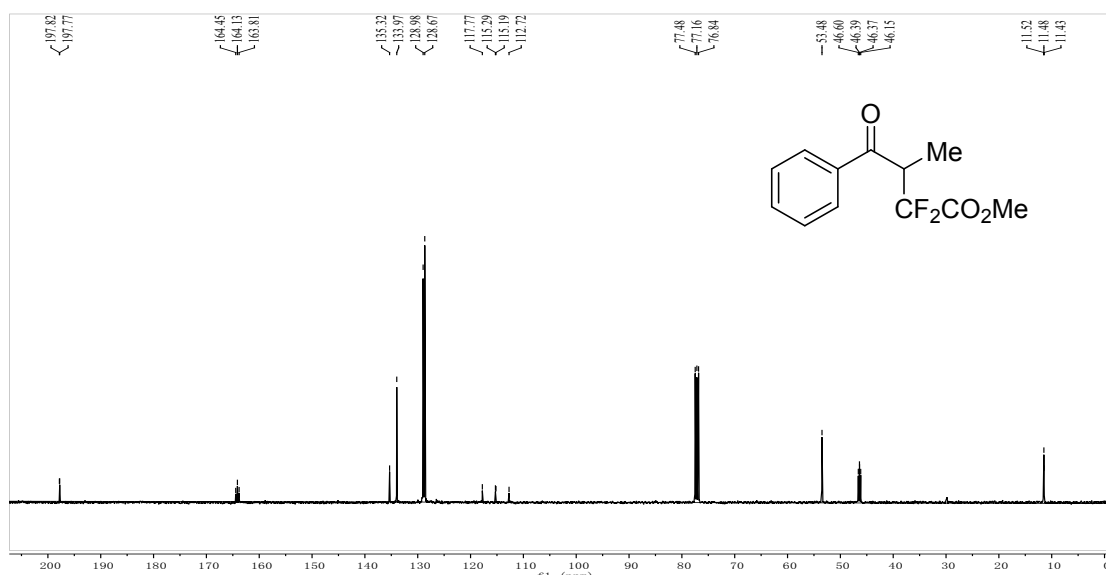
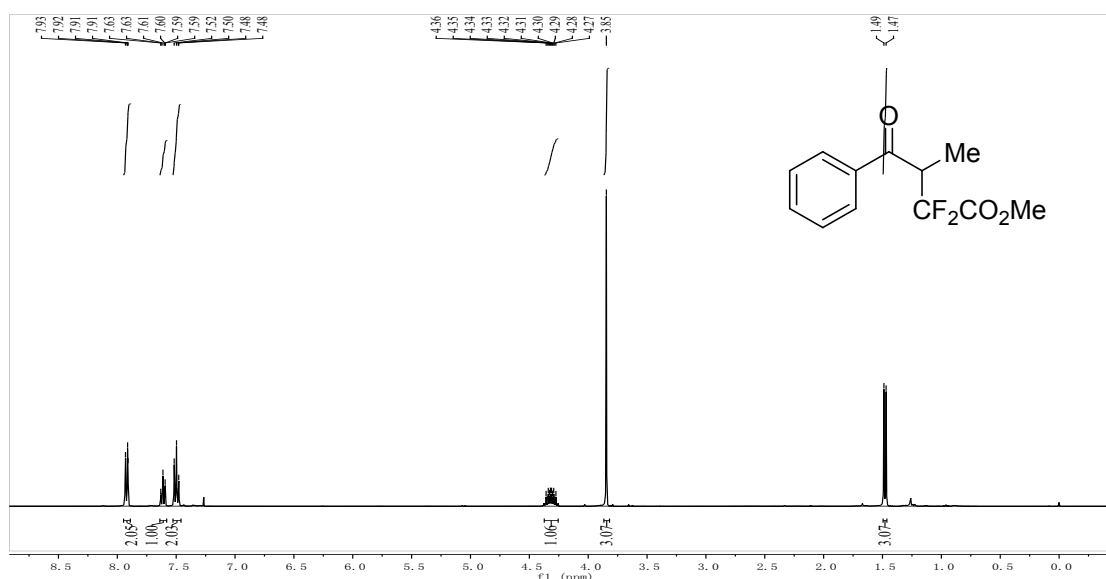
¹H NMR, ¹³C{¹H} NMR, and ¹⁹F NMR of **3m**



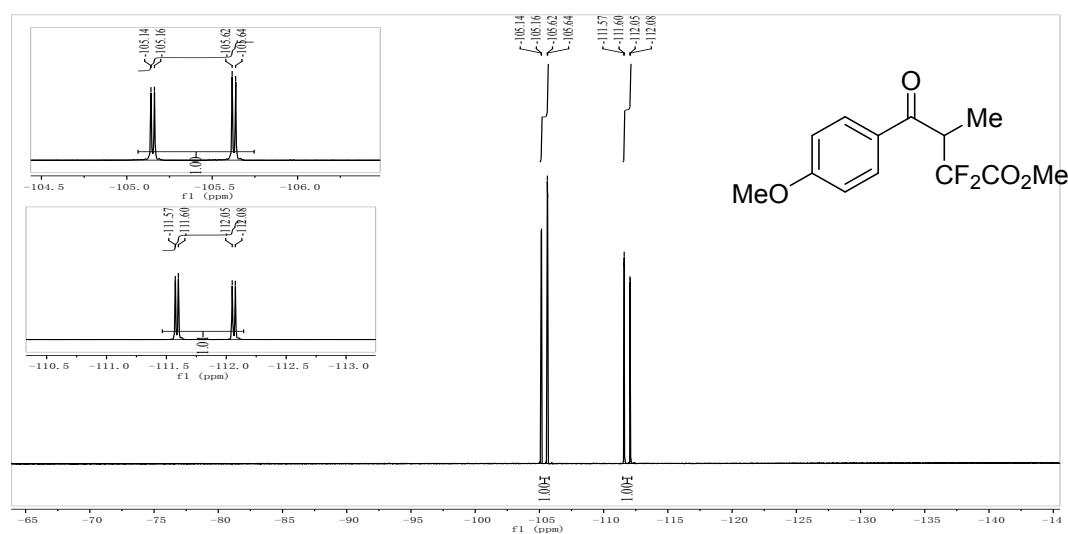
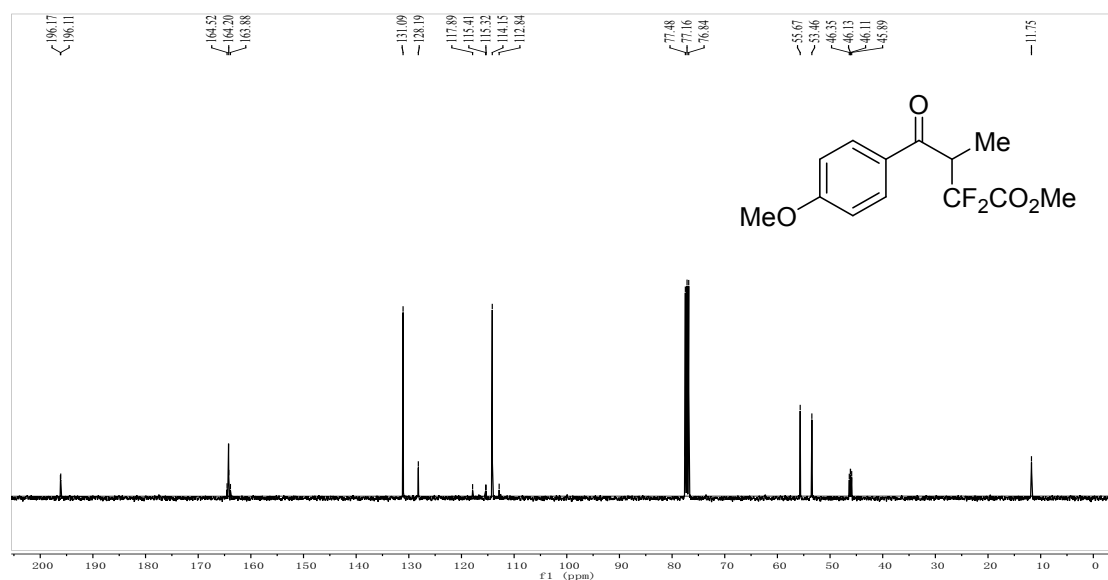
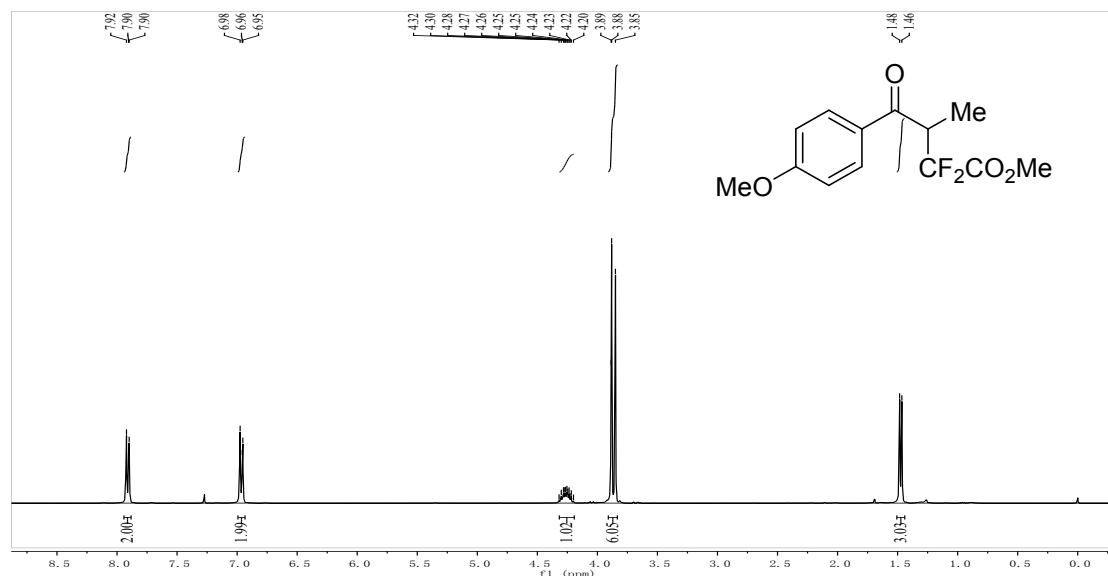
¹H NMR, ¹³C{¹H} NMR, and ¹⁹F NMR of 3n



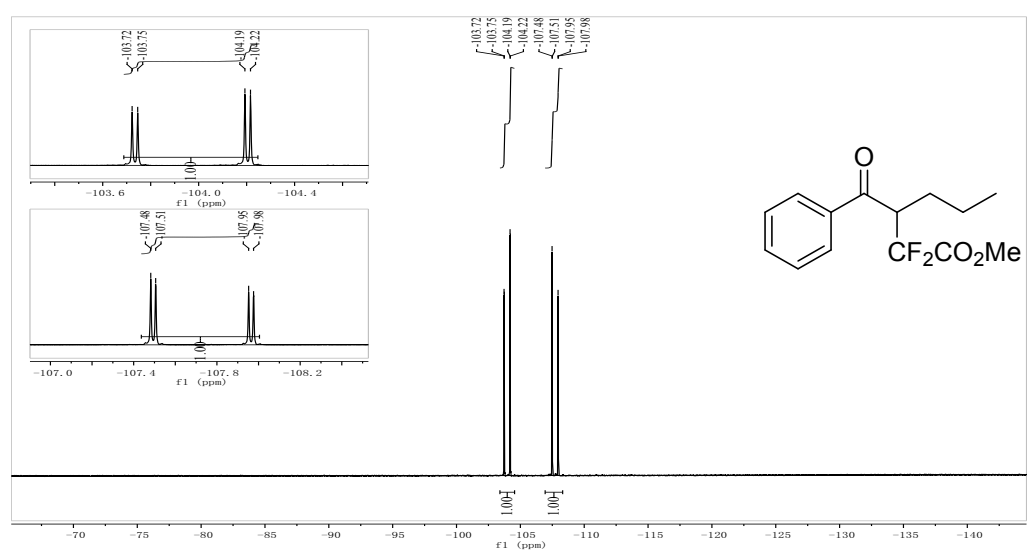
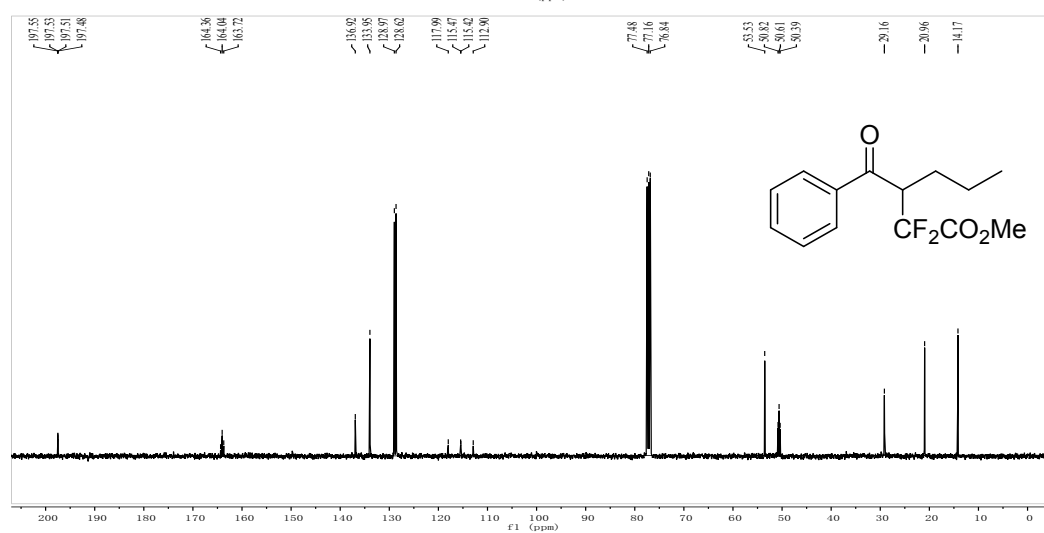
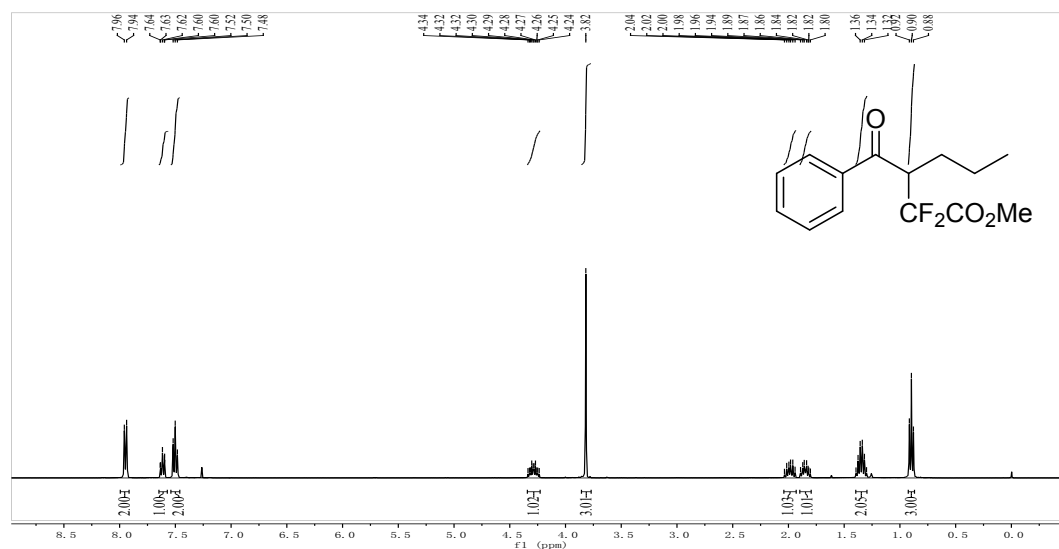
¹H NMR, ¹³C {¹H} NMR, and ¹⁹F NMR of 30



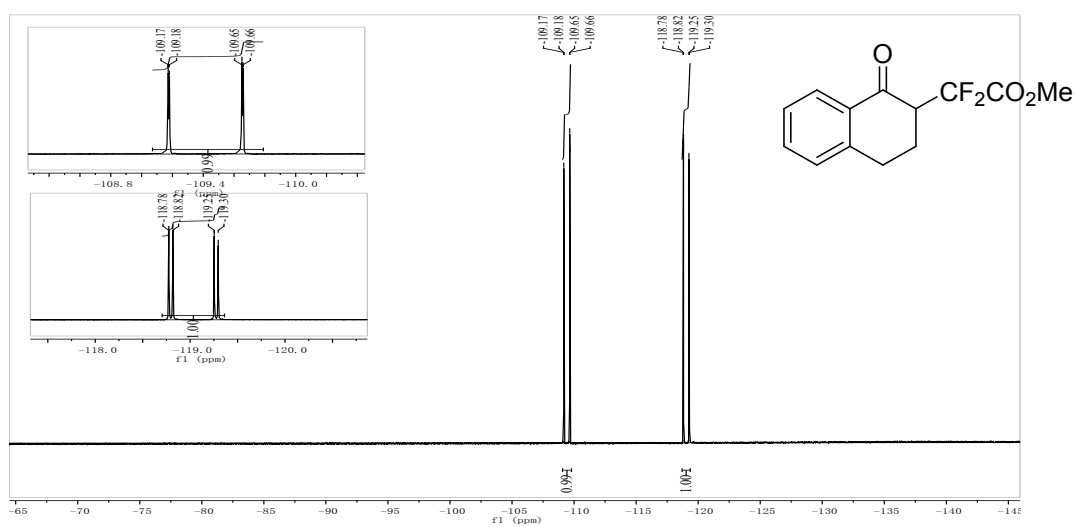
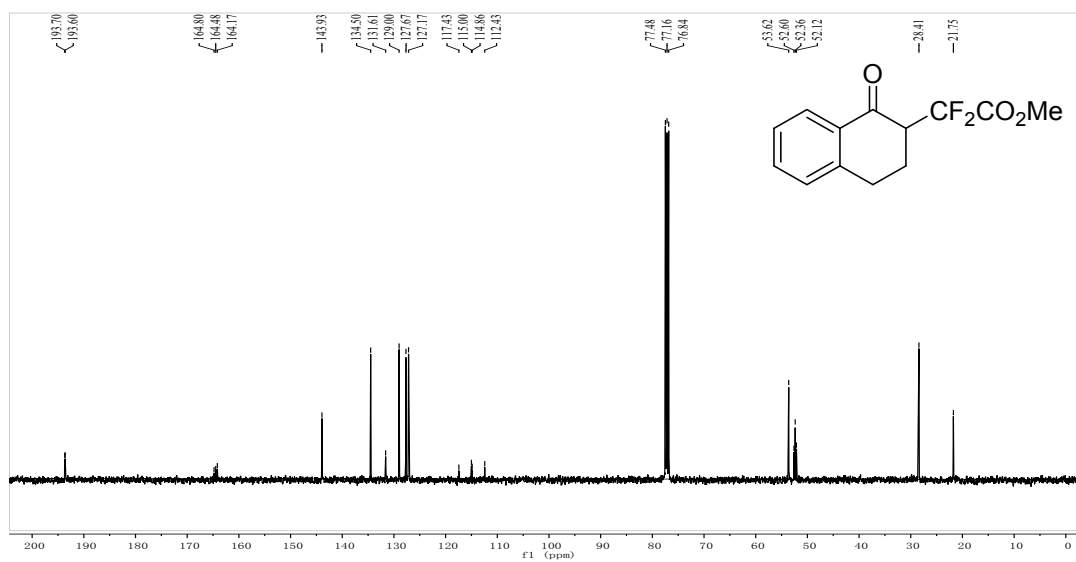
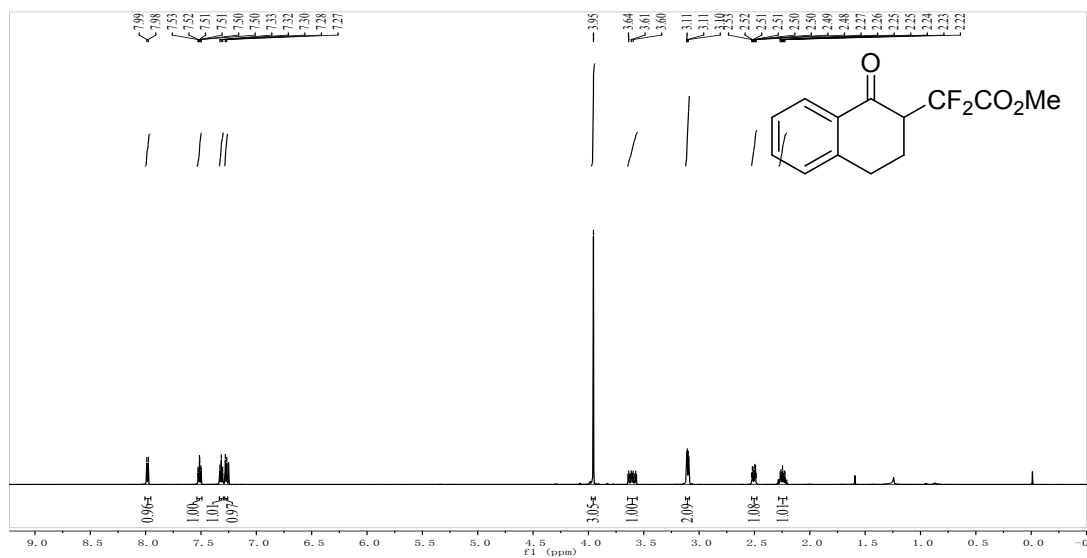
¹H NMR, ¹³C{¹H} NMR, and ¹⁹F NMR of 3p



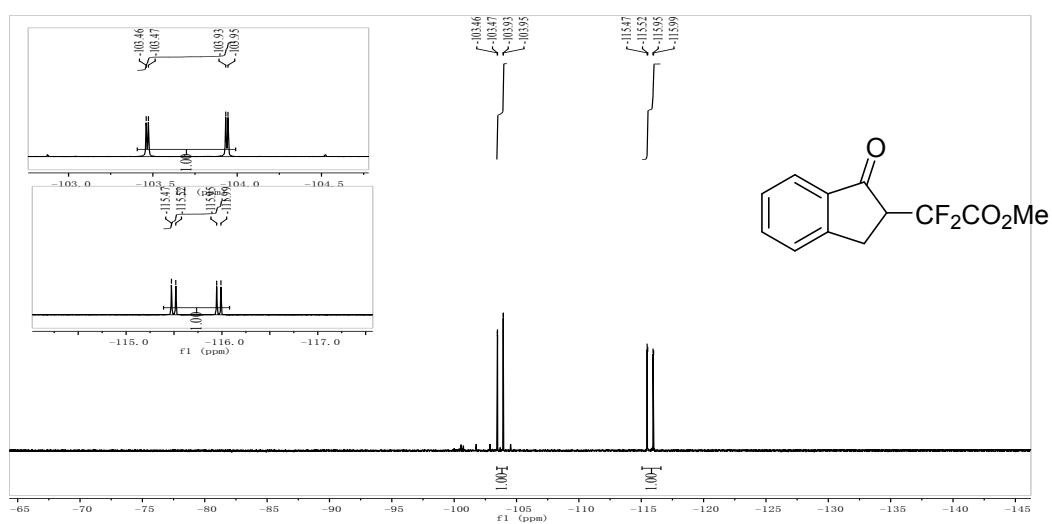
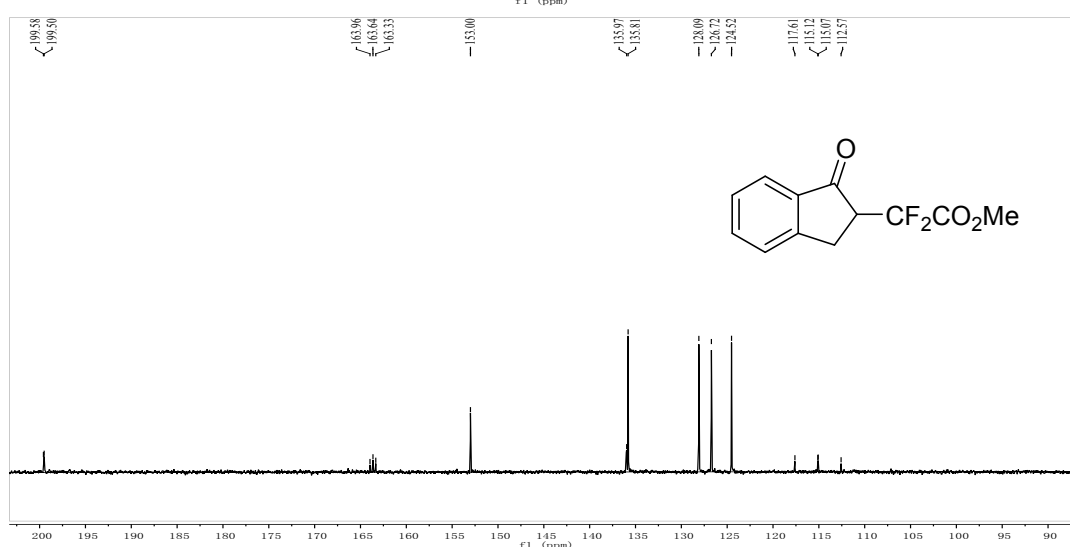
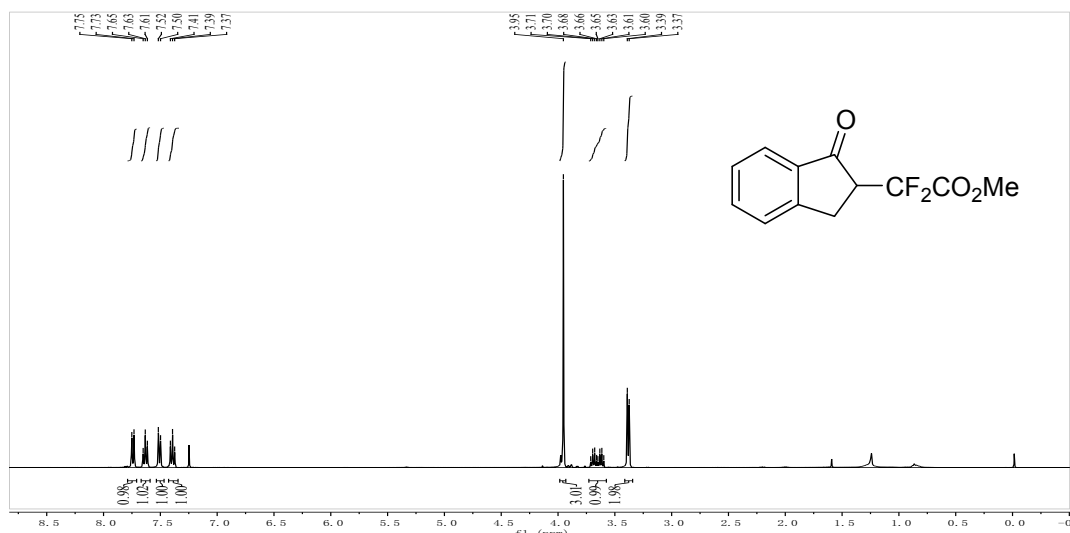
¹H NMR, ¹³C{¹H} NMR, and ¹⁹F NMR of **3q**



¹H NMR, ¹³C {¹H} NMR, and ¹⁹F NMR of 3s



¹H NMR, ¹³C{¹H} NMR, and ¹⁹F NMR of 3t



¹H NMR, ¹³C{¹H} NMR, and ¹⁹F NMR of **3u**