

Regioselective C(*sp*³)-H Fluorination of Ketones: From Methyl to Monofluoromethyl Group

Qiu-Zi Wu, Yang-Jie Mao, Kun Zhou, Hong-Yan Hao, Lei Chen, Shuang Wang, Zhen-Yuan Xu, Shao-Jie Lou,* and Dan-Qian Xu*

Catalytic Hydrogenation Research Center, State Key Laboratory Breeding Base of Green Chemistry-Synthesis Technology, Key Laboratory of Green Pesticides and Cleaner Production Technology of Zhejiang Province, Zhejiang University of Technology, Hangzhou 310014, P. R. China.

Table of Contents

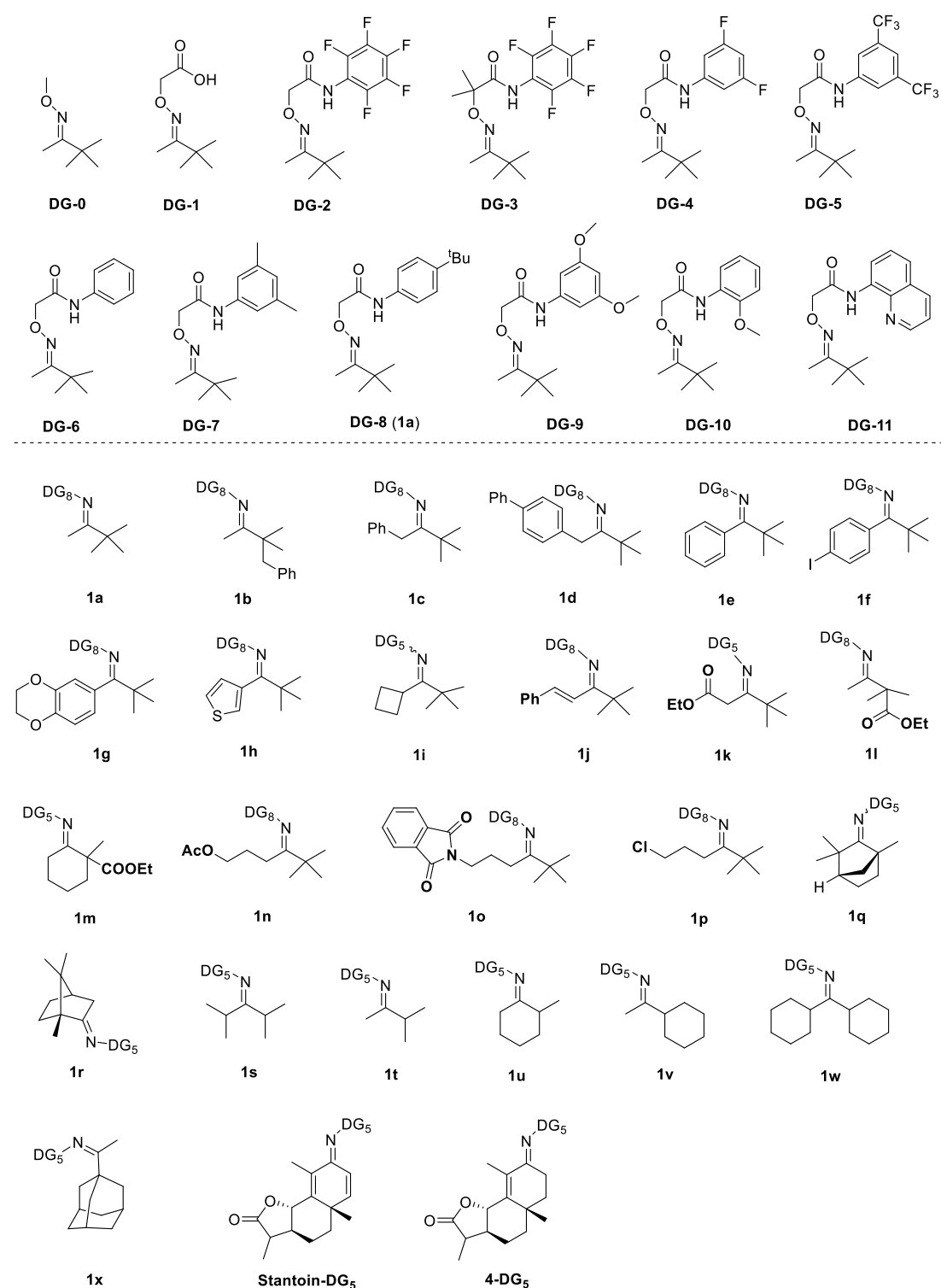
I.	General.....	S2
II.	Preparation and characterization of the starting materials	S3
III.	Screening of the fluorination conditions.....	S17
IV.	Removal of auxiliary and large-scale synthesis.....	S20
V.	Characterization of fluorination products.....	S21
VI.	X-Ray data for 4-CH₂F	S33
VII.	References.....	S34
VIII.	NMR Spectra.....	S35

I. General

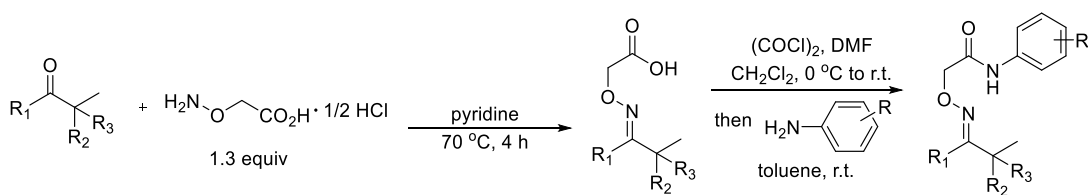
Unless otherwise stated, all experiments were carried out under air atmosphere. The reagents and solvents were purchased from commercial suppliers and used without further purification unless noted. ^1H NMR and ^{13}C NMR spectra were obtained on a Bruker AVANCE III 500 instrument in CDCl_3 using TMS as an internal standard, operating at 500 MHz and 126 MHz, respectively. Chemical shifts (δ) are expressed in ppm and coupling constants J are given in Hz. For CDCl_3 solutions, the chemical shifts are reported as parts per million (ppm) to residual protium or carbon of the solvents; CHCl_3 δH (7.26 ppm) and CDCl_3 δC (77.03 ppm); ^{19}F NMR spectra were recorded on a Bruker AVANCE III or Ascend400. Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, ddd = doublet of doublet of doublets, m = multiplet. GC experiments were carried out using Agilent 7890B GC. GC-MS experiments that used dodecane as an internal standard were performed with a Thermo DSQ II, Trace GC Ultra. High resolution mass spectra (HRMS (ESI-TOF)) were obtained on an Agilent 6545 Q-TOF LCMS spectrometer equipped with an ESI source.

II. Preparation and characterization of the starting materials

Substrates used in this paper:



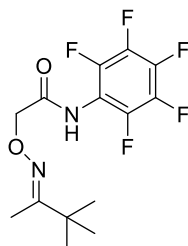
Ketones for substrates **1a**, **1q**, **1r**, **1s**, **1t**, **1u**, **1v**, **1w**, **1x** and **Stantoin-DG₅** are commercially available. Ketones for substrates **1b**, **1c**, **1d**, **1e**, **1f**, **1g**, **1h**, **1i**, **1j**, **1k**, **1l** and **1m** were synthesized following the literature procedures.¹ Ketones for substrates **1n**, **1o** and **1p** were synthesized following the literature procedures.² Ketone for substrate **4-DG₅** was synthesized following the literature procedure.³



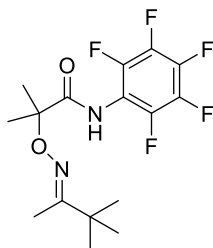
Scheme S1. Synthetic route for the oxime substrates

Step 1: The alkanone-3-iminoxy-2-acetic acids were prepared according to the literature.¹ Ketone (3.0 mmol, 1.0 equiv.) and aminooxyacetic acid hemihydrochloride (0.50 g, 3.9 mmol, 1.3 equiv.) were weighed into an oven dried 50 mL round bottom flask. Then pyridine (5 mL) was added and the mixture was stirred at 70 °C for 4 h. Upon completion, most pyridine was evaporated under vacuum. The resulting mixture was diluted with EtOAc (50 mL) and washed successively with water (30 mL) for three times and diluted HCl aqueous solution (50 mL, ca. 0.03 M). The organic phase was dried with anhydrous MgSO₄ and the solvent was removed under vacuum. The pure compounds were obtained in good yields for all cases without chromatography and used for next step directly. (Ketones for substrates **1m**, **1q**, **1r**, **1u**, **Stantoin-DG₅** and **4-DG₅** were stirred at 100 °C for 8 h)

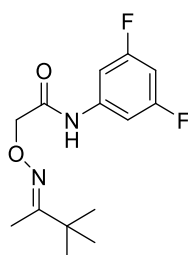
Step 2: The amidation process was proceeded according to the literature.⁴ Alkanone-3-iminoxy-2-acetic acid obtained in the previous step was dissolved in CH₂Cl₂ (20 mL) under stirring at 0 °C, oxalyl chloride (0.46 g, 3 mmol, 1.2 equiv.) was added dropwise followed by two drops of DMF. The mixture was allowed to warm to room temperature and stirred for 3 h. Upon completion, the solvent and excess oxalyl chloride were removed under reduced pressure. The residue was dissolved in toluene (20 mL) and amine (3 mmol, 1.0 equiv.) was then added. Then the mixture was stirred under the room temperature for 2 h. After cooled down to room temperature, the mixture was concentrated in *vacuo* and purified by flash column chromatography on silica gel to afford the final oxime ether product (Substrates of **DG-2** and **DG-3** were stirred and refluxed for 3 h after the toluene was added.)



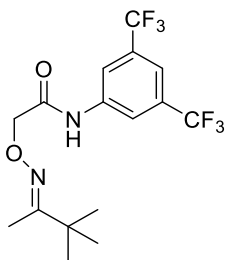
(E)-N-(3,5-bis(trifluoromethyl)phenyl)-2-(((1-cyclobutyl-3-fluoro-2,2-dimethylpropylidene)amino)oxy)acetamide (DG-2**):** Colorless solid; $R_f = 0.57$ (petroleum ether-EtOAc = 5:1); ¹H NMR (500 MHz, CDCl₃) δ 7.79 (s, 1H), 4.68 (s, 2H), 1.94 (s, 3H), 1.16 (s, 9H); ¹³C NMR (126 MHz, CDCl₃) δ 169.3, 167.9, 143.9-143.5 (m), 142.0-141.5 (m), 140.3-139.8 (m), 139.1-138.7 (m), 136.9-136.6 (m), 112.5-111.3 (m), 72.3, 37.5, 27.5, 11.0; **HRMS** (ESI-TOF) m/z : [M+Na]⁺ Calcd. for C₁₄H₁₅F₅N₂O₂Na 361.0951, found: 361.0952.



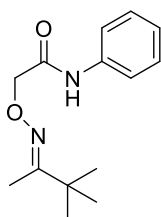
(E)-N-(3,5-bis(trifluoromethyl)phenyl)-2-(((1-cyclobutyl-3-fluoro-2,2-dimethylpropylidene)amino)oxy)acetamide (DG-3): Colorless solid; $R_f = 0.73$ (petroleum ether-EtOAc = 5:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.95 (s, 1H), 1.92 (s, 3H), 1.57 (s, 6H), 1.15 (s, 9H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 174.4, 166.7, 143.9-143.5 (m), 142.0-141.5 (m), 141.8-141.6 (m), 139.1-138.5 (m), 137.0-136.5 (m), 112.5-112.0 (m), 82.7, 37.8, 27.5, 24.4, 10.8; **HRMS** (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{16}\text{H}_{19}\text{F}_5\text{N}_2\text{O}_2\text{Na}$ 389.1264, found: 389.1268.



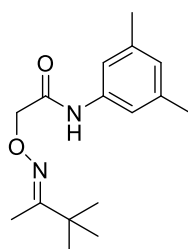
(E)-N-(3,5-bis(trifluoromethyl)phenyl)-2-(((1-cyclobutyl-3-fluoro-2,2-dimethylpropylidene)amino)oxy)acetamide (DG-4): Colorless solid; $R_f = 0.54$ (petroleum ether-EtOAc = 5:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.24 (s, 1H), 7.18-7.09 (m, 2H), 6.57 (tt, $J = 8.9, 2.3$ Hz, 1H), 4.59 (s, 2H), 1.95 (s, 3H), 1.16 (s, 9H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 169.0, 167.7, 163.2 (dd, $J = 246.5, 14.6$ Hz), 139.5 (t, $J = 13.3$ Hz), 103.0-102.5 (m), 99.6 (t, $J = 25.6$ Hz), 72.6, 37.5, 27.6, 11.0; **HRMS** (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{14}\text{H}_{18}\text{F}_2\text{N}_2\text{O}_2\text{Na}$ 307.1234, found: 307.1235.



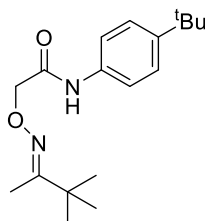
(E)-N-(3,5-bis(trifluoromethyl)phenyl)-2-(((1-cyclobutyl-3-fluoro-2,2-dimethylpropylidene)amino)oxy)acetamide (DG-5): Colorless solid; $R_f = 0.58$ (petroleum ether-EtOAc = 5:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.47 (s, 1H), 8.03 (s, 2H), 7.63 (s, 1H), 4.64 (s, 2H), 1.98 (s, 3H), 1.17 (s, 9H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 169.3, 168.0, 138.8, 132.5 (q, $J = 33.6$ Hz), 123.1 (q, $J = 272.7$ Hz), 119.5-119.4 (m), 117.7-117.6 (m), 72.6, 37.6, 27.6, 11.1; **HRMS** (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{16}\text{H}_{18}\text{F}_6\text{N}_2\text{O}_2\text{Na}$ 407.1170, found: 407.1168.



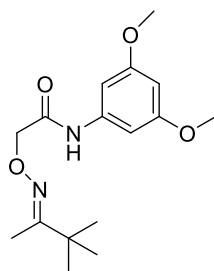
(E)-N-(3,5-bis(trifluoromethyl)phenyl)-2-(((1-cyclobutyl-3-fluoro-2,2-dimethylpropylidene)amino)oxy)acetamide (DG-6): Colorless solid; $R_f = 0.47$ (petroleum ether-EtOAc = 5:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.10 (s, 1H), 7.53 (d, $J = 7.6$ Hz, 2H), 7.35 (t, $J = 8.0$ Hz, 2H), 7.14 (t, $J = 7.4$ Hz, 1H), 4.62 (s, 2H), 1.96 (s, 3H), 1.16 (s, 9H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 168.6, 167.0, 137.3, 129.0, 124.4, 119.8, 72.8, 37.4, 27.6, 10.9; **HRMS** (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{14}\text{H}_{20}\text{N}_2\text{O}_2\text{Na}$ 271.1422, found: 271.1423.



(E)-N-(3,5-bis(trifluoromethyl)phenyl)-2-(((1-cyclobutyl-3-fluoro-2,2-dimethylpropylidene)amino)oxy)acetamide (DG-7): Colorless solid; $R_f = 0.51$ (petroleum ether-EtOAc = 5:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.97 (s, 1H), 7.16 (s, 2H), 6.78 (s, 1H), 4.61 (s, 2H), 2.32 (s, 6H), 1.96 (s, 3H), 1.16 (s, 9H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 168.5, 166.8, 138.7, 137.1, 126.2, 117.6, 72.8, 37.4, 27.6, 21.3, 10.9; **HRMS** (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{16}\text{H}_{24}\text{N}_2\text{O}_2\text{Na}$ 299.1735, found: 299.1737.

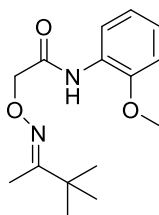


(E)-N-(4-(tert-butyl)phenyl)-2-(((3,3-dimethylbutan-2-ylidene)amino)oxy)acetamide (DG-8): Colorless solid; $R_f = 0.60$ (petroleum ether-EtOAc = 5:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.05 (s, 1H), 7.45 (d, $J = 8.7$ Hz, 2H), 7.37 (d, $J = 8.7$ Hz, 2H), 4.62 (s, 2H), 1.96 (s, 3H), 1.32 (s, 9H), 1.16 (s, 9H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 168.6, 166.8, 147.4, 134.6, 125.8, 119.7, 72.8, 37.4, 34.4, 31.3, 27.6, 10.9; **HRMS** (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{18}\text{H}_{28}\text{N}_2\text{O}_2\text{Na}$ 327.2048, found: 327.2052.

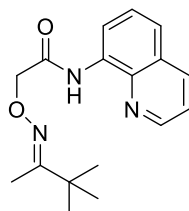


(E)-N-(3,5-bis(trifluoromethyl)phenyl)-2-(((1-cyclobutyl-3-fluoro-2,2-dimethylpropylidene)amino)oxy)acetamide (DG-9):

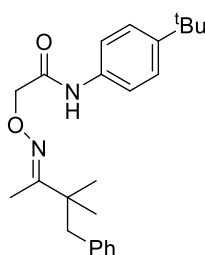
oxy)acetamide (DG-9): Colorless solid; $R_f = 0.32$ (petroleum ether-EtOAc = 5:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.06 (s, 1H), 6.76 (s, 2H), 6.26 (s, 1H), 4.60 (s, 2H), 3.79 (s, 6H), 1.95 (s, 3H), 1.15 (s, 9H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 168.8, 167.1, 161.1, 139.0, 98.1, 96.7, 72.8, 55.4, 37.4, 27.6, 10.9; **HRMS** (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{16}\text{H}_{24}\text{N}_2\text{O}_4\text{Na}$ 331.1634, found: 331.1636.



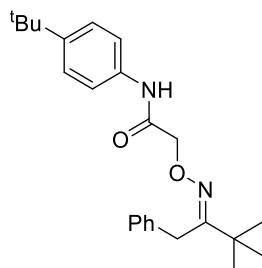
(E)-N-(3,5-bis(trifluoromethyl)phenyl)-2-(((1-cyclobutyl-3-fluoro-2,2-dimethylpropylidene)amino)oxy)acetamide (DG-10): Colorless solid; $R_f = 0.51$ (petroleum ether-EtOAc = 5:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.69 (s, 1H), 8.46 (dd, $J = 8.0, 1.6$ Hz, 1H), 7.06 (td, $J = 7.9, 1.6$ Hz, 1H), 6.98 (td, $J = 7.7, 1.1$ Hz, 1H), 6.89 (dd, $J = 8.1, 1.2$ Hz, 1H), 4.65 (s, 2H), 3.85 (s, 3H), 1.99 (s, 3H), 1.15 (s, 9H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 168.5, 166.2, 147.9, 127.2, 123.7, 121.1, 119.5, 110.0, 73.0, 55.6, 37.3, 27.4, 10.7; **HRMS** (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{15}\text{H}_{22}\text{N}_2\text{O}_3\text{Na}$ 301.1528, found: 301.1529.



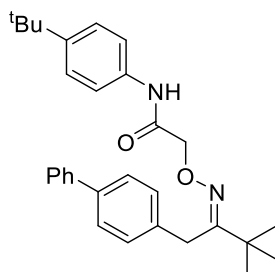
(E)-N-(3,5-bis(trifluoromethyl)phenyl)-2-(((1-cyclobutyl-3-fluoro-2,2-dimethylpropylidene)amino)oxy)acetamide (DG-11): Colorless solid; $R_f = 0.49$ (petroleum ether-EtOAc = 5:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 10.60 (s, 1H), 8.86-8.81 (m, 1H), 8.74 (dd, $J = 4.2, 1.6$ Hz, 1H), 8.15 (d, $J = 9.8$ Hz, 1H), 7.57-7.49 (m, 2H), 7.44 (dd, $J = 8.3, 4.2$ Hz, 1H), 4.79 (s, 2H), 2.17 (s, 3H), 1.14 (s, 9H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 169.4, 166.5, 148.0, 138.7, 136.2, 134.1, 128.0, 127.3, 121.7, 121.5, 116.4, 73.2, 37.4, 27.4, 11.0; **HRMS** (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{17}\text{H}_{21}\text{N}_3\text{O}_2\text{Na}$ 322.1531, found: 322.1534.



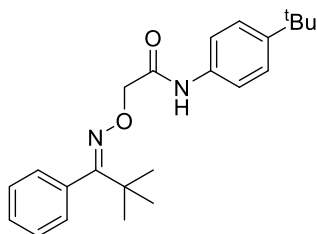
(E)-N-(4-(tert-butyl)phenyl)-2-(((3,3-dimethyl-4-phenylbutan-2-ylidene)amino)oxy)acetamide (1b): Colorless solid; $R_f = 0.46$ (petroleum ether-EtOAc = 5:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.91 (s, 1H), 7.35 (d, $J = 8.8$ Hz, 2H), 7.31 (d, $J = 8.8$ Hz, 2H), 7.23 (t, $J = 7.3$ Hz, 2H), 7.16 (t, $J = 7.3$ Hz, 1H), 7.09 (d, $J = 6.9$ Hz, 2H), 4.57 (s, 2H), 2.79 (s, 1H), 2.03 (s, 3H), 1.33 (s, 9H), 1.15 (s, 6H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 168.6, 165.6, 147.5, 137.8, 134.5, 130.2, 127.9, 126.4, 125.8, 119.9, 72.8, 46.2, 41.7, 34.4, 31.4, 25.4, 11.8; **HRMS** (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{24}\text{H}_{32}\text{N}_2\text{O}_2\text{Na}$ 403.2361, found: 403.2365.



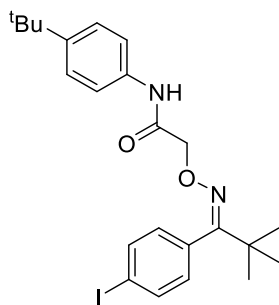
(E)-N-(4-(tert-butyl)phenyl)-2-(((3,3-dimethyl-1-phenylbutan-2-ylidene)amino)oxy)acetamide (1c): Colorless solid; $R_f = 0.59$ (petroleum ether-EtOAc = 5:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.54 (s, 1H), 7.35 (t, $J = 7.5$ Hz, 2H), 7.33-7.30 (m, 2H), 7.27-7.23 (m, 3H), 7.20 (d, $J = 8.7$ Hz, 2H), 4.63 (s, 2H), 3.84 (s, 2H), 1.32 (s, 9H), 1.21 (s, 9H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 167.9, 167.0, 147.4, 137.1, 134.4, 128.8, 127.9, 126.4, 125.6, 119.9, 73.0, 37.8, 34.4, 32.1, 31.4, 28.1; **HRMS** (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{24}\text{H}_{32}\text{N}_2\text{O}_2\text{Na}$ 403.2361, found: 403.2369.



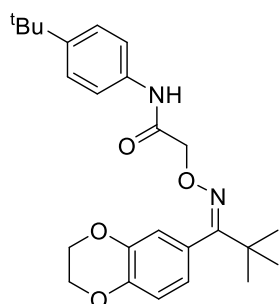
(E)-N-(4-(tert-butyl)phenyl)-2-(((3,3-dimethyl-1-(naphthalen-2-yl)butan-2-ylidene)amino)oxy)acetamide (1d): Colorless solid; $R_f = 0.61$ (petroleum ether-EtOAc = 5:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.61-7.54 (m, 4H), 7.49-7.42 (m, 3H), 7.40-7.35 (m, 1H), 7.33 (d, $J = 8.3$ Hz, 2H), 7.20-7.15 (m, 2H), 7.12-7.05 (m, 2H), 4.67 (s, 2H), 3.87 (s, 2H), 1.26 (s, 9H), 1.26 (s, 9H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 167.8, 166.6, 147.3, 140.4, 139.3, 136.2, 134.2, 128.7, 128.4, 127.5, 127.3, 127.0, 125.6, 119.9, 73.2, 37.8, 34.3, 31.8, 31.3, 28.0; **HRMS** (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{28}\text{H}_{34}\text{N}_2\text{O}_2\text{Na}$ 497.2674, found: 497.2674.



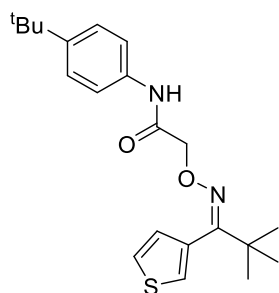
(E)-N-(4-(tert-butyl)phenyl)-2-(((2,2-dimethyl-1-phenylpropylidene)amino)oxy)acetamide (1e): Colorless solid; $R_f = 0.59$ (petroleum ether-EtOAc = 5:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.66 (s, 1H), 7.54-7.49 (m, 2H), 7.49-7.43 (m, 1H), 7.37 (s, 4H), 7.18-7.12 (m, 2H), 4.61 (s, 2H), 1.34 (s, 9H), 1.22 (s, 9H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 169.0, 167.7, 147.3, 134.6, 134.1, 128.3, 128.1, 127.0, 125.8, 119.3, 72.9, 37.5, 34.3, 31.3, 28.1; **HRMS** (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{23}\text{H}_{30}\text{N}_2\text{O}_2\text{Na}$ 389.2205, found: 389.2205.



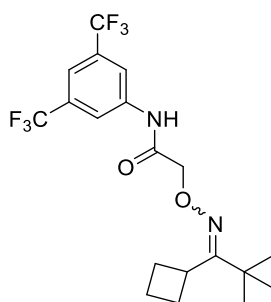
(E)-N-(4-(tert-butyl)phenyl)-2-(((1-(4-iodophenyl)-2,2-dimethylpropylidene)amino)oxy)acetamide (1f): Colorless solid; $R_f = 0.70$ (petroleum ether-EtOAc = 5:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.85 (d, $J = 8.3$ Hz, 2H), 7.58 (s, 1H), 7.41-7.32 (m, 4H), 6.90 (d, $J = 8.3$ Hz, 2H), 4.58 (s, 2H), 1.33 (s, 9H), 1.20 (s, 9H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 168.2, 167.4, 147.5, 137.5, 134.5, 133.4, 128.9, 125.9, 119.4, 94.1, 72.9, 37.5, 34.4, 31.4, 28.1; **HRMS** (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{23}\text{H}_{29}\text{IN}_2\text{O}_2\text{Na}$ 515.1171, found: 515.1175.



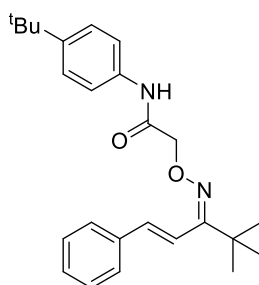
(E)-N-(4-(tert-butyl)phenyl)-2-(((1-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-2,2-dimethylpropylidene)amino)oxy)acetamide (1g): Colorless solid; $R_f = 0.43$ (petroleum ether-EtOAc = 5:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.75 (s, 1H), 7.42 (d, $J = 8.7$ Hz, 2H), 7.37 (d, $J = 8.8$ Hz, 2H), 6.99 (d, $J = 8.2$ Hz, 1H), 6.67 (d, $J = 1.9$ Hz, 1H), 6.60 (dd, $J = 8.2, 2.0$ Hz, 1H), 4.61 (s, 2H), 4.33 (s, 4H), 1.33 (s, 9H), 1.19 (s, 9H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 168.5, 167.9, 147.3, 143.5, 134.7, 126.9, 125.8, 120.1, 119.3, 117.3, 116.1, 72.9, 64.4, 37.7, 34.4, 31.4, 28.2; **HRMS** (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{25}\text{H}_{32}\text{N}_2\text{O}_4\text{Na}$ 447.2260, found: 447.2260.



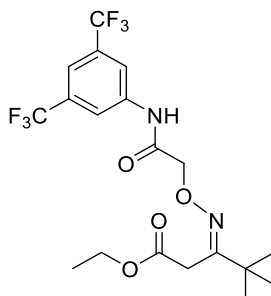
(E)-N-(4-(tert-butyl)phenyl)-2-(((2,2-dimethyl-1-(thiophen-3-yl)propylidene)amino)oxy)acetamide (1h): Colorless solid; $R_f = 0.68$ (petroleum ether-EtOAc = 5:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.68 (s, 1H), 7.49 (dd, $J = 4.9, 2.9$ Hz, 1H), 7.37 (s, 4H), 7.18 (dd, $J = 2.9, 1.2$ Hz, 1H), 7.00 (dd, $J = 4.9, 1.2$ Hz, 1H), 4.62 (s, 2H), 1.33 (s, 9H), 1.21 (s, 9H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 167.6, 165.4, 147.4, 134.5, 132.8, 127.4, 125.8, 125.6, 122.4, 119.4, 72.8, 37.6, 34.3, 31.3, 28.1; **HRMS** (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{21}\text{H}_{28}\text{N}_2\text{O}_2\text{SNa}$ 395.1769, found: 395.1769.



N-(3,5-bis(trifluoromethyl)phenyl)-2-(((1-cyclobutyl-2,2-dimethylpropylidene)amino)oxy)acetamide (1i): Colorless solid; $R_f = 0.71$ (petroleum ether-EtOAc = 5:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) (major isomer) δ 8.55 (d, $J = 10.1$ Hz, 1H), 8.02 (s, 2H), 7.62 (s, 1H), 4.64 (s, 2H), 3.45 (p, $J = 9.2$ Hz, 1H), 2.72 (pd, $J = 9.5, 2.3$ Hz, 2H), 2.28-2.20 (m, 2H), 2.11-1.95 (m, 2H), 1.16 (s, 9H); $^1\text{H NMR}$ (500 MHz, CDCl_3) (minor isomer) δ 8.55 (d, $J = 10.1$ Hz, 1H), 8.02 (s, 2H), 7.62 (s, 1H), 4.65 (s, 2H), 3.26 (p, $J = 8.4$ Hz, 1H), 2.72 (pd, $J = 9.5, 2.3$ Hz, 2H), 2.28-2.20 (m, 2H), 2.11-1.95 (m, 2H), 1.32 (s, 9H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) (major isomer) δ 170.9, 169.4, 138.9, 132.5 (q, $J = 33.5$ Hz), 123.1 (q, $J = 272.8$ Hz), 119.4-119.2 (m), 117.7-117.5 (m), 72.8, 38.3, 35.2, 27.8, 27.4, 19.1; $^{13}\text{C NMR}$ (126 MHz, CDCl_3) (minor isomer) δ 170.9, 170.1, 138.9, 132.5 (q, $J = 33.5$ Hz), 123.1 (q, $J = 272.8$ Hz), 119.3, 117.7-117.5 (m), 72.9, 38.8, 37.7, 28.0, 27.4, 18.0; **HRMS** (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{19}\text{H}_{22}\text{F}_6\text{N}_2\text{O}_2\text{Na}$ 447.1483, found: 447.1484.



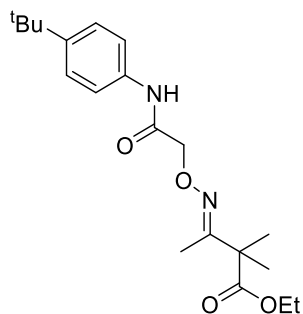
N-(4-(tert-butyl)phenyl)-2-(((1E,3E)-4,4-dimethyl-1-phenylpent-1-en-3-ylidene)amino)oxy)acetamide (1j): Colorless solid; $R_f = 0.57$ (petroleum ether-EtOAc = 5:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.03 (s, 1H), 7.53 (d, $J = 8.5$ Hz, 2H), 7.47-7.41 (m, 2H), 7.41-7.35 (m, 4H), 7.35-7.32 (m, 2H), 6.71 (d, $J = 16.8$ Hz, 1H), 4.71 (s, 2H), 1.31 (s, 9H), 1.28 (s, 9H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 168.2, 163.8, 147.5, 139.7, 136.3, 134.6, 129.1, 128.9, 127.0, 125.9, 119.6, 116.6, 73.3, 37.8, 34.4, 31.4, 28.8; **HRMS** (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{25}\text{H}_{32}\text{N}_2\text{O}_2\text{Na}$ 415.2361, found: 415.2367.



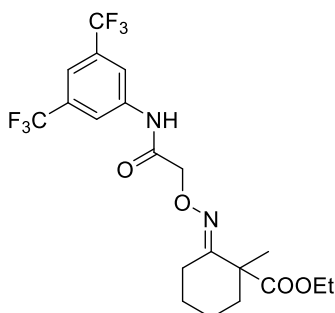
ethyl

(E)-3-((2-(((3,5-bis(trifluoromethyl)phenyl)amino)-2-oxoethoxy)imino)-4,4-dimethylpentanoate (1k): Colorless solid; $R_f = 0.47$ (petroleum ether-EtOAc = 5:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 9.56 (s, 1H), 8.41 (s, 2H), 7.59 (s, 1H), 4.71 (s, 2H), 4.27 (q, $J = 7.2$ Hz, 2H), 3.51 (s, 2H), 1.34 (t, $J = 7.1$ Hz, 3H),

1.13 (s, 9H); ^{13}C NMR (126 MHz, CDCl_3) δ 170.5, 169.7, 161.7, 139.9, 132.1 (q, $J = 33.1$ Hz), 123.3 (q, $J = 272.7$ Hz), 119.6-119.4 (m), 117.1-116.9 (m), 73.2, 62.2, 37.4, 31.4, 27.1, 14.0; HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{19}\text{H}_{22}\text{F}_6\text{N}_2\text{O}_4\text{Na}$ 479.1381, found: 479.1381.

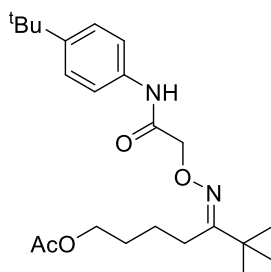


ethyl (E)-3-((2-((4-tert-butylphenyl)amino)-2-oxoethoxy)imino)-2,2-dimethylbutanoate (1l): Colorless solid; $R_f = 0.50$ (petroleum ether-EtOAc = 5:1); ^1H NMR (500 MHz, CDCl_3) δ 7.93 (s, 1H), 7.46 (d, $J = 8.6$ Hz, 2H), 7.36 (d, $J = 8.6$ Hz, 2H), 4.66 (s, 2H), 4.18 (q, $J = 7.1$ Hz, 2H), 1.95 (s, 3H), 1.41 (s, 6H), 1.32 (s, 9H), 1.25 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 174.6, 168.2, 161.7, 147.5, 134.6, 125.8, 119.8, 73.0, 61.2, 49.1, 34.4, 31.3, 23.1, 14.1, 12.6; HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{20}\text{H}_{30}\text{N}_2\text{O}_4\text{Na}$ 385.2103, found: 385.2106.



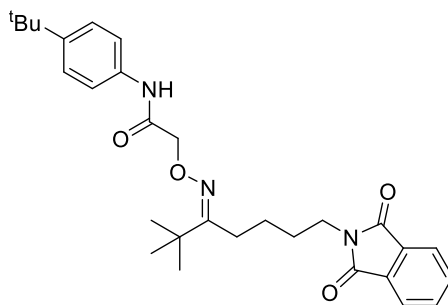
ethyl

(E)-2-((2-((3,5-bis(trifluoromethyl)phenyl)amino)-2-oxoethoxy)imino)-1-methylcyclohexane-1-carboxylate (1m): Colorless solid; $R_f = 0.50$ (petroleum ether-EtOAc = 5:1); ^1H NMR (500 MHz, CDCl_3) δ 8.39 (s, 1H), 8.21 (s, 2H), 7.61 (s, 1H), 4.77-4.62 (m, 2H), 4.22 (q, $J = 7.1$ Hz, 2H), 3.34-3.22 (m, 1H), 2.51-2.37 (m, 1H), 2.01-1.99 (m, 1H), 1.82-1.84 (m, 1H), 1.53-1.41 (m, 3H), 1.38 (s, 3H), 1.27 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 174.9, 169.5, 164.2, 139.0, 132.3 (q, $J = 33.4$ Hz), 123.2 (q, $J = 272.7$ Hz), 119.9-119.7 (m), 117.6-117.3 (m), 72.7, 61.5, 50.1, 37.2, 25.1, 24.1, 22.8, 22.7, 14.1; HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{20}\text{H}_{22}\text{F}_6\text{N}_2\text{O}_4\text{Na}$ 491.1381, found: 491.1390.

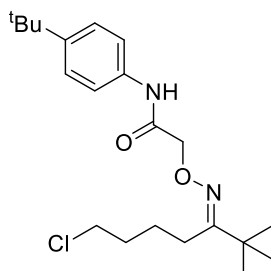


(E)-5-((2-((4-tert-butylphenyl)amino)-2-oxoethoxy)imino)-6,6-dimethylheptyl acetate (1n): Yellow oil; $R_f = 0.29$ (petroleum ether-EtOAc = 5:1); ^1H NMR (500 MHz, CDCl_3) δ 8.02 (s, 1H), 7.43 (d, $J = 8.7$ Hz, 2H), 7.36 (d, $J = 8.7$ Hz, 2H), 4.60 (s, 2H), 4.13 (t, $J = 6.4$ Hz, 2H), 2.42-2.34 (m, 2H), 2.02 (s, 3H), 1.75 (p, $J = 6.9, 6.3$ Hz, 2H), 1.71-1.63 (m, 2H), 1.31 (s, 9H), 1.16 (s, 9H); ^{13}C NMR (126 MHz,

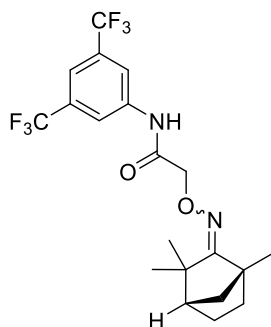
CDCl₃) δ 171.1, 169.6, 168.5, 147.5, 134.6, 125.9, 119.6, 72.9, 63.7, 37.7, 34.3, 31.3, 29.2, 27.7, 26.1, 23.4, 20.9; **HRMS** (ESI-TOF) m/z : [M+Na]⁺ Calcd. for C₂₃H₃₆N₂O₄Na 427.2573, found: 427.2577.



(E)-N-(4-(tert-butyl)phenyl)-2-(((7-(1,3-dioxoisindolin-2-yl)-2,2-dimethylheptan-3-ylidene)amino)oxy)acetamide (1o): Colorless solid; R_f = 0.29 (petroleum ether-EtOAc = 5:1); **¹H NMR** (500 MHz, CDCl₃) δ 8.03 (s, 1H), 7.79 (dd, J = 5.4, 3.1 Hz, 2H), 7.68 (dd, J = 5.5, 3.0 Hz, 2H), 7.46 (d, J = 8.7 Hz, 2H), 7.36 (d, J = 8.7 Hz, 2H), 4.50 (s, 2H), 3.75 (t, J = 7.1 Hz, 2H), 2.47-2.35 (m, 2H), 1.83 (p, J = 7.3 Hz, 2H), 1.69-1.59 (m, 2H), 1.31 (s, 9H), 1.13 (s, 9H); **¹³C NMR** (126 MHz, CDCl₃) δ 169.3, 168.5, 168.4, 147.3, 134.7, 133.9, 131.9, 125.8, 123.1, 119.6, 72.8, 37.6, 37.2, 34.3, 31.3, 28.9, 27.7, 26.1, 23.8; **HRMS** (ESI-TOF) m/z : [M+Na]⁺ Calcd. for C₂₉H₃₇N₃O₄Na 514.2682, found: 514.2681.

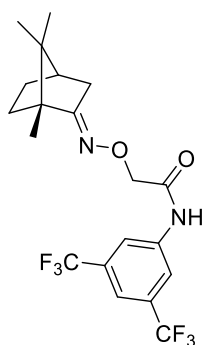


(E)-N-(4-(tert-butyl)phenyl)-2-(((7-chloro-2,2-dimethylheptan-3-ylidene)amino)oxy)acetamide (1p): Colorless solid; R_f = 0.53 (petroleum ether-EtOAc = 5:1); **¹H NMR** (500 MHz, CDCl₃) δ 8.01 (s, 1H), 7.45 (d, J = 8.7 Hz, 2H), 7.37 (d, J = 8.7 Hz, 2H), 4.61 (s, 2H), 3.61 (t, J = 6.4 Hz, 2H), 2.41-2.35 (m, 2H), 1.90 (p, J = 6.7 Hz, 2H), 1.83-1.73 (m, 2H), 1.32 (s, 9H), 1.17 (s, 9H); **¹³C NMR** (126 MHz, CDCl₃) δ 169.5, 168.5, 147.5, 134.6, 125.9, 119.7, 72.9, 44.4, 37.7, 34.4, 32.9, 31.4, 27.8, 25.7, 24.2; **HRMS** (ESI-TOF) m/z : [M+Na]⁺ Calcd. for C₂₁H₃₃ClN₂O₂Na 403.2128, found: 403.2131.

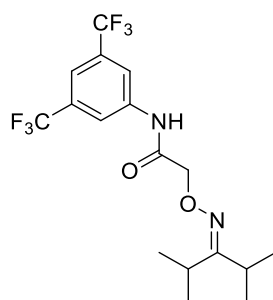


N-(3,5-bis(trifluoromethyl)phenyl)-2-(((1R,4S)-1,3,3-trimethylbicyclo[2.2.1]heptan-2-ylidene)amino)oxy)acetamide (1q): Colorless solid; R_f = 0.64 (petroleum ether-EtOAc = 5:1); **¹H NMR** (500 MHz, CDCl₃) (major isomer) δ 8.50 (s, 1H), 8.01 (s, 2H), 7.63 (s, 1H), 4.58 (s, 2H), 1.92 (s, 1H), 1.87-1.83 (m, 1H), 1.78 (dd, J = 10.3, 1.9 Hz, 1H), 1.68-1.63 (m, 2H), 1.47-1.41 (m, 2H), 1.40 (s, 3H), 1.37 (s, 3H), 1.24 (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) (major isomer) δ 176.8, 169.5, 138.9, 132.5 (q, J = 33.6 Hz), 123.1 (q, J = 272.7 Hz), 119.3-119.1 (m), 117.8-117.6 (m), 72.8, 50.8, 48.6, 45.1, 43.4, 34.4, 25.2, 23.6,

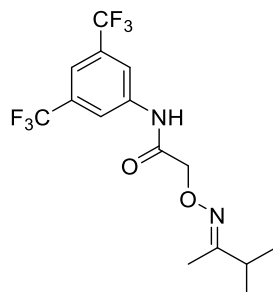
22.9, 17.0; **HRMS** (ESI-TOF) m/z : $[M+Na]^+$ Calcd. for $C_{20}H_{22}F_6N_2O_2Na$ 459.1483, found: 459.1488.



N-(3,5-bis(trifluoromethyl)phenyl)-2-(((1R,4R,E)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ylidene)amino)oxyacetamide (1r): Colorless solid; $R_f = 0.50$ (petroleum ether-EtOAc = 5:1); 1H NMR (500 MHz, $CDCl_3$) δ 8.42 (s, 1H), 8.02 (s, 2H), 7.63 (s, 1H), 4.62 (d, $J = 3.9$ Hz, 2H), 2.64 (dt, $J = 18.1, 3.8$ Hz, 1H), 2.14 (d, $J = 18.1$ Hz, 1H), 2.01 (t, $J = 4.4$ Hz, 1H), 1.96-1.88 (m, 1H), 1.80 (td, $J = 12.3, 4.1$ Hz, 1H), 1.50-1.45 (m, 1H), 1.33-1.28 (m, 1H), 1.03 (s, 3H), 0.97 (s, 3H), 0.86 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.5, 169.3, 138.8, 132.5 (q, $J = 33.5$ Hz), 123.1 (q, $J = 272.7$ Hz), 119.4-119.3 (m), 117.8-117.6 (m), 72.6, 52.6, 48.4, 43.7, 34.2, 32.8, 27.2, 19.4, 18.4, 11.1; **HRMS** (ESI-TOF) m/z : $[M+Na]^+$ Calcd. for $C_{20}H_{22}F_6N_2O_2Na$ 459.1483, found: 459.1486.

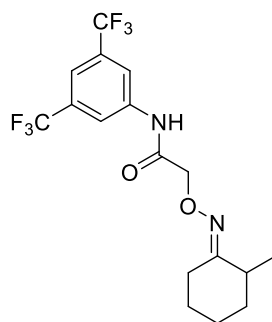


N-(3,5-bis(trifluoromethyl)phenyl)-2-(((2,4-dimethylpentan-3-ylidene)amino)oxy)acetamide (1s): Colorless solid; $R_f = 0.64$ (petroleum ether-EtOAc = 5:1); 1H NMR (500 MHz, $CDCl_3$) δ 8.42 (s, 1H), 8.01 (s, 2H), 7.63 (s, 1H), 4.61 (s, 2H), 3.22-3.14 (m, 1H), 2.67-2.58 (m, 1H), 1.25 (d, $J = 7.1$ Hz, 6H), 1.16 (d, $J = 6.8$ Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.1, 169.4, 138.8, 132.5 (q, $J = 33.5$ Hz), 123.0 (q, $J = 272.8$ Hz), 119.3-119.2 (m), 117.8-117.6 (m), 72.7, 31.3, 28.7, 21.2, 19.1; **HRMS** (ESI-TOF) m/z : $[M+Na]^+$ Calcd. for $C_{17}H_{20}F_6N_2O_2Na$ 421.1327, found: 421.1328.



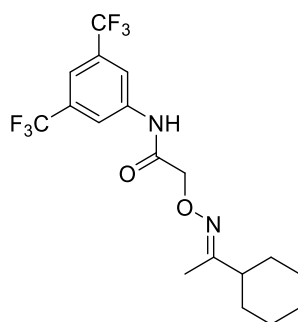
(E)-N-(3,5-bis(trifluoromethyl)phenyl)-2-(((3-methylbutan-2-ylidene)amino)oxy)acetamide (1t): Colorless solid; $R_f = 0.53$ (petroleum ether-EtOAc = 5:1); 1H NMR (500 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.96 (s, 2H), 7.55 (s, 1H), 4.54 (s, 2H), 2.53-2.44 (m, 1H), 1.88 (s, 3H), 1.06 (d, $J = 6.9$ Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.2, 166.3, 138.7, 133.5 (q, $J = 34.4$ Hz), 123.1 (q, $J = 274.2$ Hz),

119.5-119.4 (m), 117.8-117.7 (m), 72.5, 34.5, 19.7, 12.1; **HRMS** (ESI-TOF) m/z : $[M+Na]^+$ Calcd. for $C_{15}H_{16}F_6N_2O_2Na$ 393.1014, found: 393.1019.



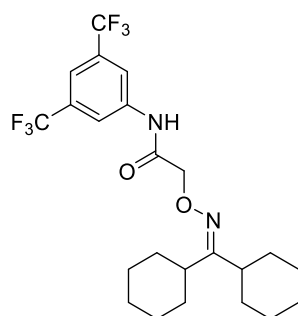
(E)-N-(3,5-bis(trifluoromethyl)phenyl)-2-(((2-methylcyclohexylidene)amino)oxy)acetamide (1u):

Colorless solid; $R_f = 0.57$ (petroleum ether-EtOAc = 5:1); 1H NMR (500 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.05 (s, 2H), 7.63 (s, 1H), 4.62 (s, 2H), 3.12-3.00 (m, 1H), 2.43-2.36 (m, 1H), 2.13-2.07 (m, 1H), 1.98-1.89 (m, 1H), 1.88-1.79 (m, 2H), 1.62-1.48 (m, 2H), 1.43-1.31 (m, 1H), 1.13 (d, $J = 6.7$ Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.4, 167.3, 138.8, 132.5 (q, $J = 33.5$ Hz), 123.1 (q, $J = 272.6$ Hz), 119.5-119.4 (m), 118.0-117.3 (m), 72.5, 37.2, 35.6, 26.3, 24.9, 24.2, 16.9; **HRMS** (ESI-TOF) m/z : $[M+Na]^+$ Calcd. for $C_{17}H_{18}F_6N_2O_2Na$ 419.1170, found: 419.1173.



(E)-N-(3,5-bis(trifluoromethyl)phenyl)-2-(((1-cyclohexylethylidene)amino)oxy)acetamide (1v):

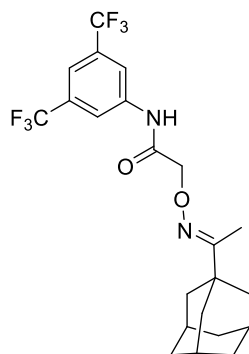
Colorless solid; $R_f = 0.56$ (petroleum ether-EtOAc = 5:1); 1H NMR (500 MHz, $CDCl_3$) δ 8.41 (s, 1H), 8.04 (s, 2H), 7.63 (s, 1H), 4.62 (s, 2H), 2.26-2.19 (m, 1H), 1.96 (s, 3H), 1.84-1.77 (m, 4H), 1.40-1.26 (m, 5H), 1.26-1.16 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.2, 165.7, 138.8, 132.43 (q, $J = 33.5$ Hz), 123.7 (q, $J = 272.8$ Hz), 119.5-119.4 (m), 117.7-117.6 (m), 72.5, 44.5, 30.1, 25.9, 12.8; **HRMS** (ESI-TOF) m/z : $[M+Na]^+$ Calcd. for $C_{18}H_{20}F_6N_2O_2Na$ 433.1327, found: 433.1327.



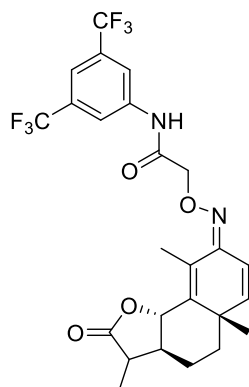
N-(3,5-bis(trifluoromethyl)phenyl)-2-(((dicyclohexylmethylene)amino)oxy)acetamide (1w):

Colorless solid; $R_f = 0.67$ (petroleum ether-EtOAc = 5:1); 1H NMR (500 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.01 (s, 2H), 7.62 (s, 1H), 4.59 (s, 2H), 2.96 (tt, $J = 12.1, 3.4$ Hz, 1H), 2.26 (tt, $J = 11.5, 2.9$ Hz, 1H), 1.87-1.77 (m, 6H), 1.71 (d, $J = 12.7$ Hz, 3H), 1.65-1.60 (m, 2H), 1.57 (dd, $J = 12.5, 3.3$ Hz, 1H), 1.41-1.16 (m, 8H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.8, 169.5, 138.9, 132.5 (q, $J = 33.5$ Hz), 123.1 (q,

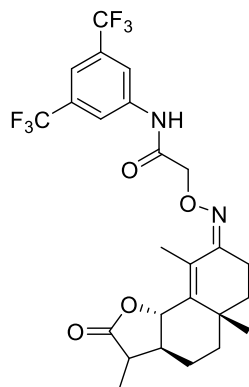
$J = 272.8$ Hz), 119.3-119.2 (m), 117.7-117.5 (m), 72.6, 41.2, 39.3, 31.9, 28.9, 26.3, 26.2, 25.9, 25.9;
HRMS (ESI-TOF) m/z : $[M+Na]^+$ Calcd. for $C_{23}H_{28}F_6N_2O_2Na$ 501.1953, found: 501.1956.



2-(((E)-1-((3r,5r,7r)-adamantan-1-yl)ethylidene)amino)oxy)-N-(3,5-bis(trifluoromethyl)phenyl)acetamide (1x): Colorless solid; $R_f = 0.61$ (petroleum ether-EtOAc = 5:1); 1H NMR (500 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.04 (s, 2H), 7.63 (s, 1H), 4.63 (s, 2H), 2.07 (s, 3H), 1.93 (s, 3H), 1.80 (d, $J = 2.7$ Hz, 7H), 1.77 (s, 2H), 1.70 (d, $J = 12.0$ Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.4, 168.1, 138.8, 132.5 (q, $J = 33.5$ Hz), 123.1 (q, $J = 272.7$ Hz), 119.5-119.3 (m), 117.7-117.5 (m), 72.6, 39.6, 39.5, 36.6, 28.1, 10.1; **HRMS** (ESI-TOF) m/z : $[M+Na]^+$ Calcd. for $C_{22}H_{24}F_6N_2O_2Na$ 485.1640, found: 485.1640.



N-(3,5-bis(trifluoromethyl)phenyl)-2-(((3aS,5aS,9bS,Z)-3,5a,9-trimethyl-2-oxo-2,3,3a,5,5a,9b-hexahydronaphtho[1,2-b]furan-8(4H)-ylidene)amino)oxy)acetamide (Stantoin-DG₅): Colorless solid; $R_f = 0.41$ (petroleum ether-EtOAc = 2:1); 1H NMR (500 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.05 (s, 2H), 7.63 (s, 1H), 6.95 (d, $J = 10.1$ Hz, 1H), 6.22 (d, $J = 10.1$ Hz, 1H), 4.82 (d, $J = 11.0$ Hz, 1H), 4.73 (s, 2H), 2.43-2.34 (m, 1H), 2.16 (s, 3H), 2.08-1.96 (m, 1H), 1.87-1.80 (m, 2H), 1.71 (td, $J = 12.6, 3.7$ Hz, 1H), 1.54 (td, $J = 13.2, 4.4$ Hz, 1H), 1.31 (s, 3H), 1.28 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.8, 168.9, 153.0, 147.9, 141.2, 138.7, 132.4 (q, $J = 33.8$ Hz), 125.2 (q, $J = 273.8$ Hz), 122.2, 119.6-119.5 (m), 117.9-117.5 (m), 112.3, 82.1, 73.2, 53.5, 41.2, 41.0, 38.2, 25.7, 23.6, 12.4, 12.1; **HRMS** (ESI-TOF) m/z : $[M+Na]^+$ Calcd. for $C_{25}H_{24}F_6N_2O_4Na$ 553.1538, found: 553.1547.

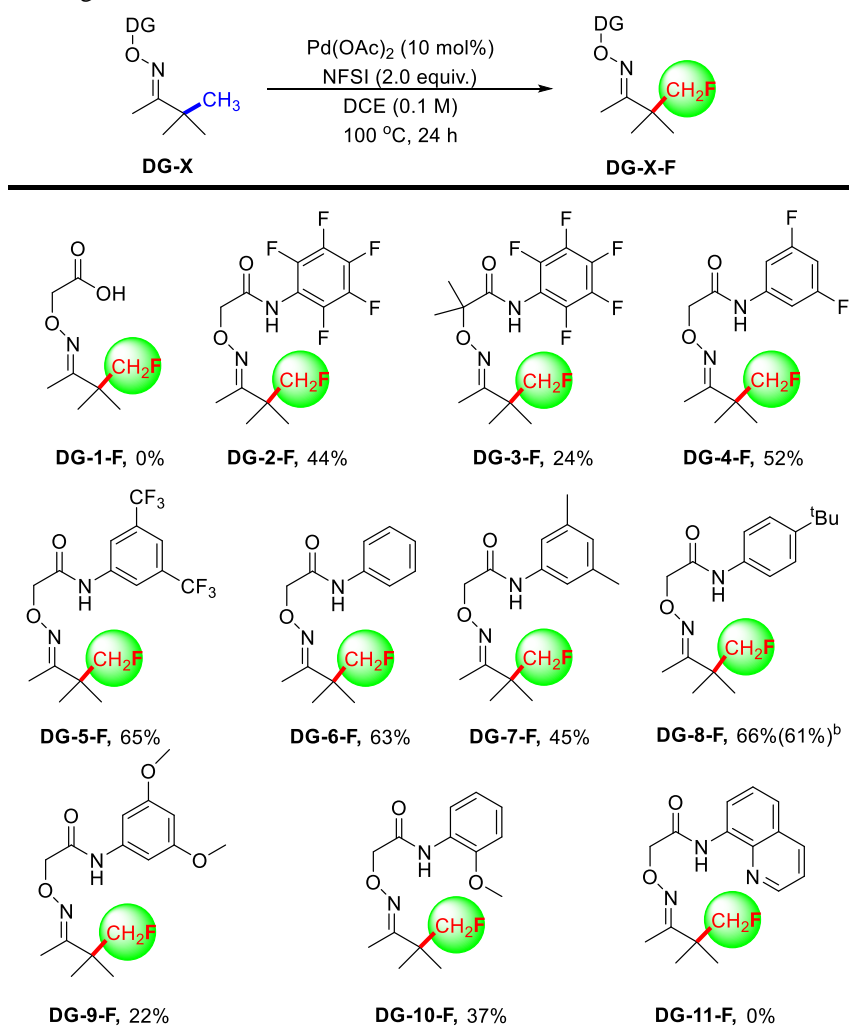


N-(3,5-bis(trifluoromethyl)phenyl)-2-(((3a*S*,5a*S*,9b*S*,*Z*)-3,5a,9-trimethyl-2-oxo-2,3,3a,5,5a,9b-hexahydronaphtho[1,2-*b*]furan-8(4*H*)-ylidene)amino)oxy)acetamide (4-DG₃): Colorless solid; $R_f = 0.39$ (petroleum ether-EtOAc = 2:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.40 (s, 1H), 8.05 (s, 2H), 7.64 (s, 1H), 4.71 (s, 2H), 4.71-4.67 (m, 1H), 3.12 (dt, $J = 17.3, 4.0$ Hz, 1H), 2.42-2.30 (m, 2H), 2.10 (d, $J = 1.2$ Hz, 3H), 2.03-1.96 (m, 1H), 1.94-1.86 (m, 1H), 1.77-1.70 (m, 2H), 1.70-1.63 (m, 2H), 1.50 (td, $J = 13.3, 4.3$ Hz, 1H), 1.28 (d, $J = 6.9$ Hz, 3H), 1.26 (s, 3H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 178.0, 168.8, 160.2, 143.1, 138.7, 132.5 (q, $J = 33.5$ Hz), 123.4, 123.1 (q, $J = 272.7$ Hz), 119.6-119.5 (m), 117.9-117.7 (m), 82.6, 73.1, 52.9, 41.5, 41.1, 37.4, 37.2, 24.6, 24.5, 19.6, 12.8, 12.4; **HRMS** (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{25}\text{H}_{26}\text{F}_6\text{N}_2\text{O}_4\text{Na}$ 555.1694, found: 555.1685.

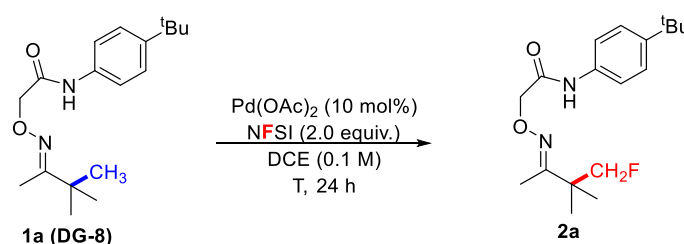
III. Screening of the fluorination conditions

A. C(sp³)-H fluorination of ketone oximes

Table S1. Screening of auxiliaries^a

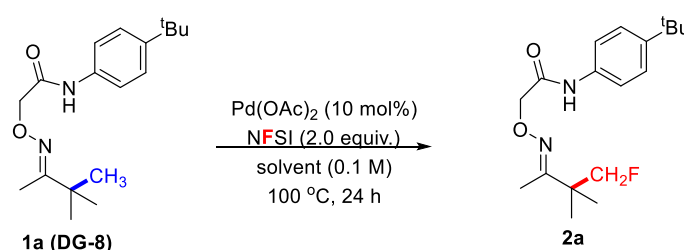


^a Reaction conditions: DG-X (0.05 mmol), Pd(OAc)₂ (10 mol%), NFSI = N-fluorobenzenesulfonimide (0.1 mmol) and DCE = 1, 2-dichloroethane (0.5 mL) were added to a test tube, the mixture was stirred at 100 °C for 24 h. ^b 3 h. Yields were determined by GC-MS analysis using dodecane as an internal standard.

Table S2. Screening of reaction temperature^a


Entry	T (°C)	Yield of 2a (%) ^b
1	50	35
2	75	58
3	100	66
4	120	42

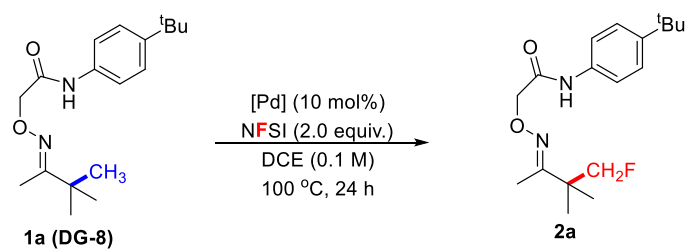
^aReaction conditions: **1a** (0.05 mmol), Pd(OAc)₂ (10 mol%), NFSI = N-fluorobenzenesulfonimide (0.1 mmol) and DCE (0.5 mL) were added to a test tube, the mixture was stirred at indicated temperature for 24 h. Yields were determined by GC-MS analysis using dodecane as an internal standard.

Table S3. Screening of solvents^a


Entry	Solvent	Yield of 2a (%) ^b
1	DCE	66
2	CHCl ₃	55
3	HFIP	-
4	Toluene	57
5	PhCl	59
6	PhCF ₃	53
7	THF	19
8	1,4-dioxane	36
9	EtOAc	47
10	CH ₃ NO ₂	56
11	CH ₃ CN	4
12	DMF	0
13	Acetone	12

^aReaction conditions: **1a** (0.05 mmol), Pd(OAc)₂ (10 mol%), NFSI = N-fluorobenzenesulfonimide (0.1 mmol) and solvent (0.5 mL) were added to a test tube, the mixture was stirred at 100 °C for 24 h. Yields were determined by GC-MS analysis using dodecane as an internal standard.

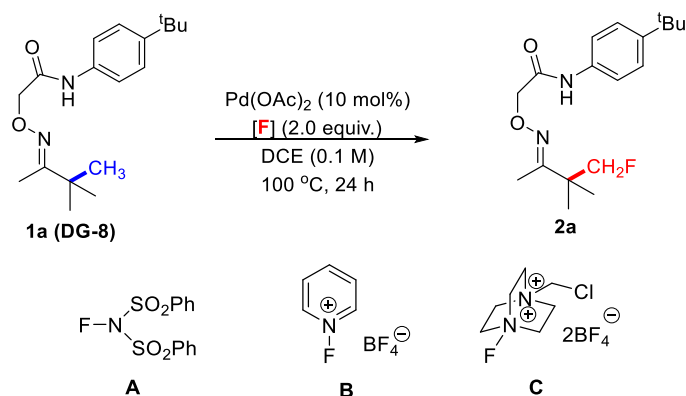
Table S4. Screening of Pd catalysts^a



Entry	[Pd]	Yield of 2a (%) ^b
1	-	5
2	Pd(OAc)₂	66+13^c (61)^d
3	PdCl ₂	54
4	Pd(dba) ₂	32
5	Pd(TFA) ₂	45
6	Pd(PPh ₃) ₄	40
7	[PdCl(C ₃ H ₅) ₂]	66+3 ^c (64) ^d
8	PdCl ₂ (cod)	61+2 ^c (62) ^d
9	Pd(CN)Cl ₂	55+2 ^c (60) ^d
10	PdCl ₂ (C ₆ H ₅ CN) ₂	54 (59) ^d
11	PdCl ₂ (dppf) ₂	51
12	PdCl ₂ [P(Cy) ₃] ₂	11

^aReaction conditions: **1a** (0.05 mmol), [Pd] (10 mol%), NFSI = N-fluorobenzenesulfonimide (0.1 mmol) and DCE = 1, 2-dichloroethane (0.5 mL) were added to a test tube, the mixture was stirred at 100 °C for 24 h. ^cDi-fluorination products. ^d3 h. Yields were determined by GC-MS analysis using dodecane as an internal standard.

Table S5. Screening of fluorinating reagents^a



Entry	Fluorination agent	Yield of 4a (%) ^b
1	A	66 (61)^c
2	B	11
3	C	36

^aReaction conditions: **1a** (0.05 mmol), Pd(OAc)₂ (10 mol%), Fluorination agent (0.1 mmol), and DCE = 1, 2-dichloroethane (1.0 mL) were added to a test tube, the mixture was stirred at 100 °C for 24 h. ^c3 h. Yields were determined by GC-MS analysis using dodecane as an

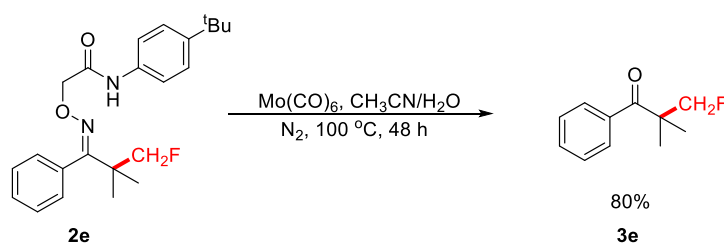
internal standard.

B. General conditions for the substrate scope research

In a 10 mL test tube equipped with a stir bar, substrate (0.2 mmol), Pd(OAc)₂ (4.5 mg, 0.02 mmol), NFSI (126.0 mg, 0.4 mmol), and DCE (2.0 mL) were added successively. Then the tube was sealed and stirred at the appropriate temperature for specific time. Upon completion, the resulting mixture was cooled to room temperature, diluted with DCM and concentrated under reduced pressure. Then the residue was purified by silica gel chromatography to afford the desired fluorinated products.

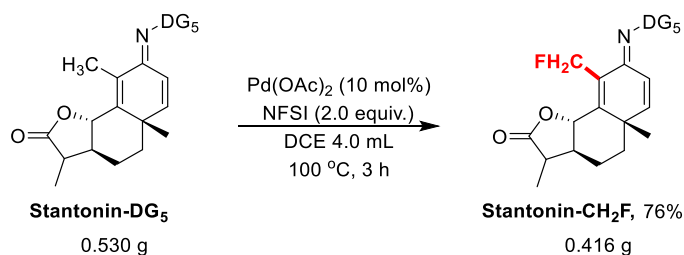
IV. Removal of auxiliary and a scale-up reaction

A. Removing the directing group from ketones



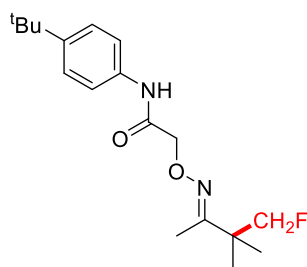
Following the literature procedure⁴. A 25 mL Schlenk tube was charged with (E)-N-(4-(tert-butyl)phenyl)-2-(((3-fluoro-2,2-dimethyl-1-phenylpropylidene)amino)oxy)acetamide (**2e**) (19.25 mg, 0.05 mmol, 1.0 equiv.), Mo(CO)₆ (26.4 mg, 0.1 mmol, 2.0 equiv.), CH₃CN (0.5 mL), H₂O (0.1 mL). The tube was sealed with a Teflon-lined screw cap, refrigerated with liquid nitrogen, evacuated the air and filled with nitrogen by the Schlenk line for 3 times. Then the tube was heated at 100 °C for 48 h under stirring. Then the tube was allowed to cool to room temperature. The solvent was then removed in *vacuo* and the residue was purified through flash column chromatography on silica gel (eluent: petroleum ether/EtOAc = 10:1) to give the corresponding product **3e** as a colorless oil (7.2 mg, 80% yield).

B. Scale-up synthesis of Stantonin-CH₂F



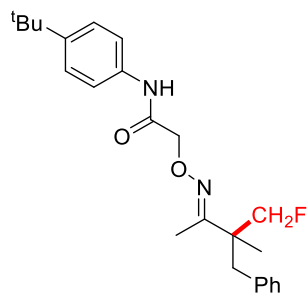
In a 25 mL test tube equipped with a stir bar, **Stantonin-DG₅** (0.530 g, 1.0 mmol), Pd(OAc)₂ (22 mg, 0.1 mmol), NFSI (0.630 g, 2.0 mmol), and DCE (4.0 mL) were added successively. Then the tube was sealed and stirred at the appropriate temperature for 3 h. Upon completion, the resulting mixture was cooled to room temperature, diluted with DCM and concentrated under reduced pressure. Then the residue was purified by silica gel chromatography (eluent: petroleum ether/EtOAc = 3:1) to afford the desired fluorinated product **Stantonin-CH₂F** as a colorless solid (0.416 g, 76% yield).

V. Characterization of fluorination products



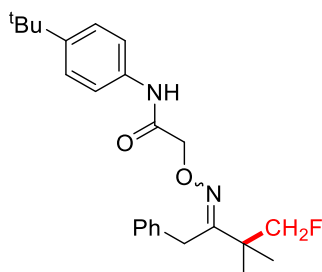
(E)-N-(4-(tert-butyl)phenyl)-2-(((4-fluoro-3,3-dimethylbutan-2-ylidene)amino)oxy)acetamide (**2a**):

Following the general condition, stirred at 100 °C for 3 h, obtained the **2a** as a colorless solid (35.4 mg, 55%); $R_f = 0.29$ (petroleum ether-EtOAc = 5:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.96 (s, 1H), 7.46-7.44 (m, 2H), 7.39-7.33 (m, 2H), 4.63 (s, 2H), 4.39 (d, $J = 47.6$ Hz, 2H), 1.99 (s, 3H), 1.32 (s, 9H), 1.19 (d, $J = 1.7$ Hz, 6H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 168.2, 163.2 (d, $J = 2.0$ Hz), 147.5, 134.6, 125.8, 119.7, 88.7 (d, $J = 174.8$ Hz), 72.9, 41.7 (d, $J = 17.9$ Hz), 34.3, 31.3, 21.8 (d, $J = 5.1$ Hz), 11.0; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -222.15 (s, 1F); **HRMS** (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{18}\text{H}_{27}\text{FN}_2\text{O}_2\text{Na}$ 345.1954, found: 345.1954.



(E)-2-(((3-benzyl-4-fluoro-3-methylbutan-2-ylidene)amino)oxy)-N-(4-(tert-butyl)phenyl)acetamide (**2b**):

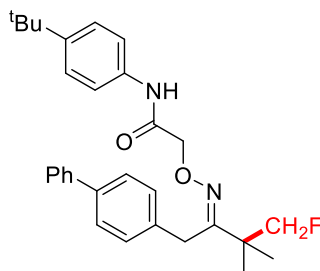
Following the general condition, stirred at 100 °C for 3 h, obtained the **2b** as a colorless solid (38.2 mg, 48%); $R_f = 0.24$ (petroleum ether-EtOAc = 5:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.76 (s, 1H), 7.35 (d, $J = 8.6$ Hz, 2H), 7.32 (d, $J = 9.3$ Hz, 2H), 7.25 (t, $J = 7.4$ Hz, 2H), 7.18 (t, $J = 7.4$ Hz, 1H), 7.11 (d, $J = 7.2$ Hz, 2H), 4.55 (s, 2H), 4.39 (d, $J = 47.5$ Hz, 2H), 2.94-2.85 (m, 2H), 2.05 (s, 3H), 1.33 (s, 9H), 1.21 (s, 3H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 147.6, 144.9, 136.4, 134.4, 133.2, 130.2, 128.2, 126.8, 125.8, 120.0, 86.2 (d, $J = 173.4$ Hz), 73.0, 45.9 (d, $J = 18.0$ Hz), 40.4 (d, $J = 3.8$ Hz), 34.4, 31.4, 20.1 (d, $J = 4.6$ Hz), 11.9; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -225.63 (s, 1F); **HRMS** (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{24}\text{H}_{31}\text{FN}_2\text{O}_2\text{Na}$ 421.2267, found: 421.2268.



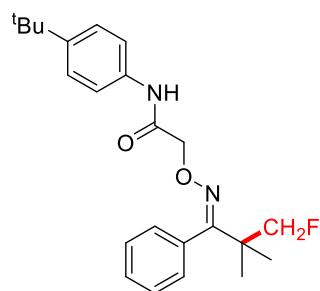
N-(4-(tert-butyl)phenyl)-2-(((4-fluoro-3,3-dimethyl-1-phenylbutan-2-ylidene)amino)oxy)acetamide (**2c**):

Following the general condition, using the $[\text{PdCl}(\text{C}_3\text{H}_5)]_2$ as the catalyst, stirred at 100 °C for 3 h, obtained the **2c** as a colorless solid (38.2 mg, 48%); $R_f = 0.29$ (petroleum ether-EtOAc = 5:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) (major isomer) δ 7.53 (s, 1H), 7.38-7.33 (m, 2H), 7.33-7.30 (m, 2H), 7.28-2.24 (m,

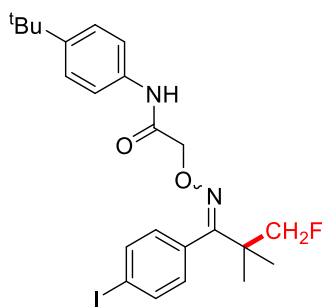
4H), 7.24-7.21 (m, 1H), 4.65 (s, 2H), 4.42 (d, $J = 47.6$ Hz, 2H), 3.86 (s, 2H), 1.27 (s, 9H), 1.23 (s, 3H), 1.22 (s, 3H); $^1\text{H NMR}$ (500 MHz, CDCl_3) (minor isomer) δ 7.57 (s, 1H), 7.38-7.33 (m, 2H), 7.33-7.30 (m, 2H), 7.28-2.24 (m, 4H), 7.24-7.21 (m, 1H), 4.67 (s, 2H), 4.42 (d, $J = 47.6$ Hz, 2H), 3.68 (s, 2H), 1.27 (s, 9H), 1.23 (s, 3H), 1.22 (s, 3H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) (major isomer) δ 167.7, 163.7, 147.5, 136.3, 134.4, 128.9, 127.9, 126.6, 125.7, 119.9, 88.9 (d, $J = 175.3$ Hz), 73.2, 42.8, 42.1 (d, $J = 18.0$ Hz), 34.4, 31.4, 24.4, 22.4; $^{13}\text{C NMR}$ (126 MHz, CDCl_3) (minor isomer) δ 167.7, 163.7, 147.5, 136.2, 134.4, 128.9, 128.0, 126.7, 125.7, 119.9, 88.9 (d, $J = 175.3$ Hz), 73.2, 53.1, 42.8, 42.1 (d, $J = 18.0$ Hz), 32.2, 31.4, 22.4; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -221.74 (s, 1F); **HRMS** (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{24}\text{H}_{31}\text{FN}_2\text{O}_2\text{Na}$ 421.2267, found: 421.2271.



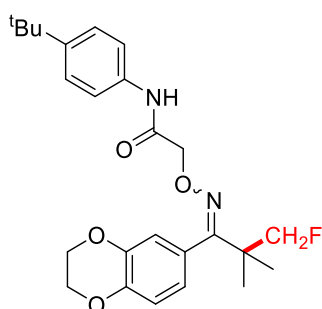
(E)-N-(4-(tert-butyl)phenyl)-2-(((4-fluoro-3,3-dimethyl-1-(naphthalen-2-yl)butan-2-ylidene)amino)oxy)acetamide (2d): Following the general condition, stirred at 100 °C for 3 h, obtained the **2d** as a colorless solid (47.4 mg, 50%); $R_f = 0.49$ (petroleum ether-EtOAc = 5:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.61-7.50 (m, 4H), 7.47-7.41 (m, 3H), 7.39-7.36 (m, 1H), 7.33 (d, $J = 8.3$ Hz, 2H), 7.20-7.16 (m, 2H), 7.14-7.09 (m, 2H), 4.69 (s, 2H), 4.47 (d, $J = 47.6$ Hz, 2H), 3.89 (s, 2H), 1.28 (d, $J = 1.7$ Hz, 6H), 1.26 (s, 9H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 167.5, 163.4, 147.4, 140.4, 139.6, 135.5, 134.2, 128.8, 128.4, 127.6, 127.4, 127.0, 125.7, 120.0, 88.9 (d, $J = 175.4$ Hz), 73.4, 42.1 (d, $J = 18.0$ Hz), 34.3, 31.9, 31.3, 22.4 (d, $J = 5.1$ Hz); $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -221.67 (s, 1F); **HRMS** (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{28}\text{H}_{33}\text{FN}_2\text{O}_2\text{Na}$ 497.2580, found: 497.2579.



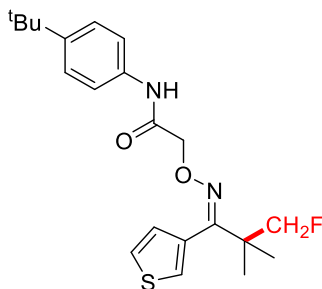
(E)-N-(4-(tert-butyl)phenyl)-2-(((3-fluoro-2,2-dimethyl-1-phenylpropylidene)amino)oxy)acetamide (2e): Following the general condition, stirred at 100 °C for 3 h, obtained the **2e** as a colorless solid (46.1 mg, 60%); $R_f = 0.35$ (petroleum ether-EtOAc = 5:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.63 (s, 1H), 7.55-7.50 (m, 2H), 7.50-7.44 (m, 1H), 7.37 (s, 4H), 7.19 (d, $J = 6.8$ Hz, 2H), 4.62 (s, 2H), 4.35 (d, $J = 47.4$ Hz, 2H), 1.33 (s, 9H), 1.24 (d, $J = 1.7$ Hz, 6H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 167.5, 165.4, 147.4, 134.5, 132.9, 128.6, 128.6, 127.0, 125.8, 119.4, 88.3 (d, $J = 175.5$ Hz), 73.1, 42.0 (d, $J = 18.3$ Hz), 34.4, 31.3, 22.2 (d, $J = 5.0$ Hz); $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -220.06 (s, 1F); **HRMS** (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{23}\text{H}_{29}\text{FN}_2\text{O}_2\text{Na}$ 407.2111, found: 407.2113.



N-(4-(tert-butyl)phenyl)-2-(((3-fluoro-1-(4-iodophenyl)-2,2-dimethylpropylidene)amino)oxy)acetamide (2f): Following the general condition, stirred at 100 °C for 3 h, obtained the **2f** as a colorless solid (54.2 mg, 53%); $R_f = 0.58$ (petroleum ether-EtOAc = 5:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) (major isomer) δ 7.86 (d, $J = 8.3$ Hz, 2H), 7.55 (s, 1H), 7.42-7.30 (m, 4H), 6.93 (d, $J = 8.3$ Hz, 2H), 4.60 (s, 2H), 4.32 (d, $J = 47.3$ Hz, 2H), 1.33 (s, 9H), 1.22 (d, $J = 1.7$ Hz, 6H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 167.2, 164.5, 147.5, 137.8, 134.4, 132.2, 128.9, 125.9, 119.5, 94.6, 88.2 (d, $J = 175.8$ Hz), 73.1, 42.0 (d, $J = 18.4$ Hz), 34.4, 31.3, 22.2 (d, $J = 5.0$ Hz); $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -219.63 (s, 1F); **HRMS** (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{23}\text{H}_{28}\text{FIN}_2\text{O}_2\text{Na}$ 533.1077, found: 533.1077.

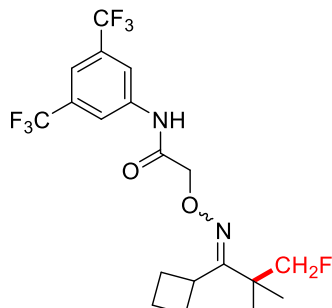


N-(4-(tert-butyl)phenyl)-2-(((1-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-3-fluoro-2,2-dimethylpropylidene)amino)oxy)acetamide (2g): Following the general condition, stirred at 100 °C for 3 h, obtained the **2g** as a colorless solid (43.0 mg, 51%); $R_f = 0.35$ (petroleum ether-EtOAc = 5:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) (major isomer) δ 7.72 (s, 1H), 7.44-7.40 (m, 2H), 7.39-7.34 (m, 2H), 7.00 (d, $J = 8.2$ Hz, 1H), 6.71 (d, $J = 1.9$ Hz, 1H), 6.65 (dd, $J = 8.2, 1.9$ Hz, 1H), 4.62 (s, 2H), 4.34 (d, $J = 47.4$ Hz, 2H), 4.33 (s, 4H), 1.33 (s, 9H), 1.21 (d, $J = 1.6$ Hz, 6H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 167.7, 164.8, 147.4, 143.8 (d, $J = 16.9$ Hz), 134.6, 125.8, 125.6, 120.1, 119.4, 116.1, 88.4 (d, $J = 175.3$ Hz), 73.1, 64.4, 42.2 (d, $J = 18.3$ Hz), 34.4, 31.4, 22.3 (d, $J = 5.0$ Hz); $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -220.15 (s, 1F); **HRMS** (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{25}\text{H}_{31}\text{FN}_2\text{O}_4\text{Na}$ 465.2166, found: 465.2170.

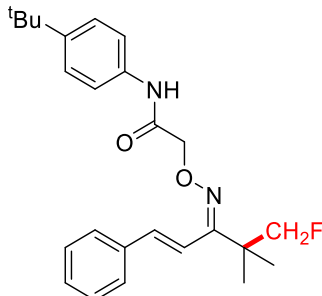


(E)-N-(4-(tert-butyl)phenyl)-2-(((3-fluoro-2,2-dimethyl-1-(thiophen-3-yl)propylidene)amino)oxy)acetamide (2h): Following the general condition, stirred at 100 °C for 3 h, obtained the **2h** as a colorless solid (39.8 mg, 52%); $R_f = 0.49$ (petroleum ether-EtOAc = 5:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.68 (s,

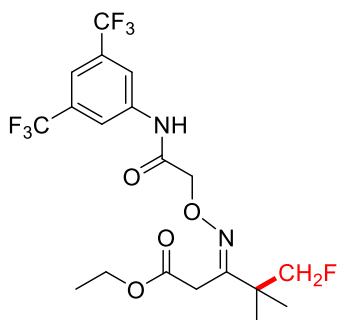
1H), 7.50 (dd, $J = 4.9, 2.9$ Hz, 1H), 7.42-7.32 (m, 4H), 7.27-7.23 (m, 1H), 7.04 (d, $J = 5.8$ Hz, 1H), 4.64 (s, 2H), 4.35 (d, $J = 47.4$ Hz, 2H), 1.33 (s, 9H), 1.24 (s, 6H); ^{13}C NMR (126 MHz, CDCl_3) δ 167.4, 161.7, 147.4, 134.5, 131.7, 127.2, 126.0, 125.8, 123.1, 119.5, 88.5 (d, $J = 175.3$ Hz), 73.0, 42.1 (d, $J = 18.2$ Hz), 34.3, 31.3, 22.2.; ^{19}F NMR (376 MHz, CDCl_3) δ -220.47 (s, 1F); HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{21}\text{H}_{27}\text{FN}_2\text{O}_2\text{SNa}$ 413.1675, found: 413.1673.



N-(3,5-bis(trifluoromethyl)phenyl)-2-(((1-cyclobutyl-3-fluoro-2,2-dimethylpropylidene)amino)oxy)acetamide (2i): Following the general condition, stirred at 100 °C for 3 h, obtained the **2i** as a colorless solid (35.4 mg, 40%); $R_f = 0.32$ (petroleum ether-EtOAc = 5:1); ^1H NMR (500 MHz, CDCl_3) (major isomer) δ 8.56 (s, 1H), 8.06 (s, 2H), 7.62 (s, 1H), 4.66 (s, 2H), 4.40 (d, $J = 47.4$ Hz, 2H), 3.40 (p, $J = 9.2$ Hz, 1H), 2.76-2.67 (m, 2H), 2.28-2.21 (m, 2H), 2.03-1.98 (m, 1H), 1.20 (d, $J = 1.8$ Hz, 6H); ^{13}C NMR (126 MHz, CDCl_3) (major isomer) δ 169.3, 166.8, 139.0, 132.4 (q, $J = 33.5$ Hz), 123.1 (q, $J = 272.6$ Hz), 119.5-119.4 (m), 117.7-117.5 (m), 88.8 (d, $J = 174.3$ Hz), 73.1, 42.5 (d, $J = 17.5$ Hz), 35.1, 27.2, 21.9 (d, $J = 5.2$ Hz), 19.2; ^{19}F NMR (376 MHz, CDCl_3) δ -63.31 (s, 6F), -220.00 (s, 1F); HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{19}\text{H}_{21}\text{F}_7\text{N}_2\text{O}_2\text{Na}$ 465.1389, found: 465.1392.

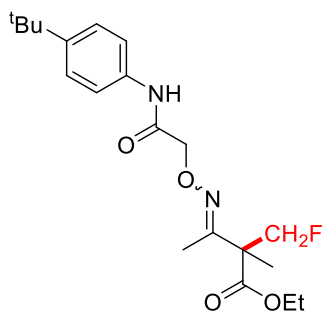


N-(4-(tert-butyl)phenyl)-2-(((1E,3E)-5-fluoro-4,4-dimethyl-1-phenylpent-1-en-3-ylidene)amino)oxy)acetamide (2j): Following the general condition, using the $[\text{PdCl}(\text{C}_3\text{H}_5)]_2$ as the catalyst, stirred at 100 °C for 4 h, obtained the **2j** as a colorless solid (49.2 mg, 60%); $R_f = 0.32$ (petroleum ether-EtOAc = 5:1); ^1H NMR (500 MHz, CDCl_3) δ 7.98 (s, 1H), 7.53 (d, $J = 7.1$ Hz, 2H), 7.48 (d, $J = 16.8$ Hz, 1H), 7.44-7.39 (m, 5H), 7.36-7.33 (m, 2H), 6.68 (d, $J = 16.8$ Hz, 1H), 4.73 (s, 2H), 4.47 (d, $J = 47.6$ Hz, 2H), 1.32 (d, $J = 1.7$ Hz, 6H), 1.31 (s, 9H); ^{13}C NMR (126 MHz, CDCl_3) δ 167.9, 160.3, 147.5, 140.4, 136.1, 134.6, 129.3, 128.9, 127.1, 125.8, 119.7, 115.9, 89.2 (d, $J = 175.2$ Hz), 73.6, 42.0 (d, $J = 18.1$ Hz), 34.4, 31.4, 23.0 (d, $J = 5.1$ Hz); ^{19}F NMR (376 MHz, CDCl_3) δ -221.46 (s, 1F); HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{25}\text{H}_{31}\text{FN}_2\text{O}_2\text{Na}$ 433.2267, found: 433.2269.

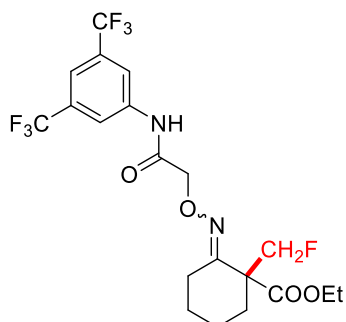


ethyl

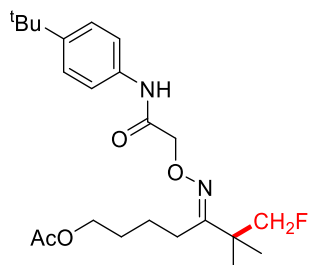
(E)-3-((2-((3,5-bis(trifluoromethyl)phenyl)amino)-2-oxoethoxy)imino)-5-fluoro-4,4-dimethylpentanoate (2k): Following the general condition, but Pd(OAc)₂ (9.0 mg, 0.04 mmol), NFSI (189.0 mg, 0.6 mmol) was added and the reaction time was 48 h. **2k** was obtained as a colorless solid (26.5 mg, 28%); *R_f* = 0.25 (petroleum ether-EtOAc = 5:1); ¹H NMR (500 MHz, CDCl₃) δ 9.51 (s, 1H), 8.40 (s, 2H), 7.60 (s, 1H), 4.74 (s, 2H), 4.34 (d, *J* = 47.6 Hz, 2H), 4.32-4.24 (dd, *J* = 7.2 Hz, 2H), 3.57 (s, 2H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.19 (d, *J* = 1.6 Hz, 6H); ¹³C NMR (126 MHz, CDCl₃) δ 170.1, 169.3, 158.7, 139.8, 132.1 (q, *J* = 33.3 Hz), 123.3 (q, *J* = 275.0 Hz), 119.6-119.5 (m), 117.2-117.1 (m), 88.9 (d, *J* = 176.1 Hz), 73.4, 62.3, 41.7 (d, *J* = 17.9 Hz), 31.9, 21.5, 14.0; ¹⁹F NMR (376 MHz, CDCl₃) δ -63.04 (s, 6F), -224.10 (s, 1F); **HRMS** (ESI-TOF) *m/z*: [M+Na]⁺ Calcd. for C₁₉H₂₁F₇N₂O₄Na 497.1287, found: 497.1281.



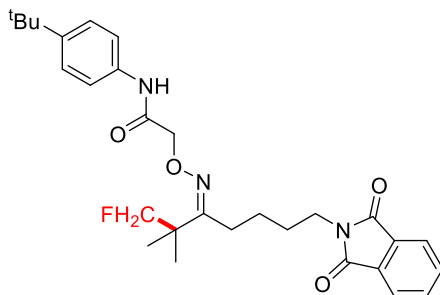
ethyl 3-((2-((4-(tert-butyl)phenyl)amino)-2-oxoethoxy)imino)-2-(fluoromethyl)-2-methylbutanoate (2l): Following the general condition, stirred at 100 °C for 3 h, obtained the **2l** as a colorless solid (38.8 mg, 51%); *R_f* = 0.29 (petroleum ether-EtOAc = 5:1); ¹H NMR (500 MHz, CDCl₃) (major isomer) δ 7.82 (s, 1H), 7.46 (d, *J* = 8.7 Hz, 2H), 7.36 (d, *J* = 8.7 Hz, 2H), 4.85-4.63 (m, 2H), 4.67 (s, 2H), 4.28-4.21 (m, 2H), 1.99 (s, 3H), 1.50 (d, *J* = 1.3 Hz, 3H), 1.32 (s, 9H), 1.27 (t, *J* = 7.1 Hz, 3H); ¹H NMR (500 MHz, CDCl₃) (minor isomer) δ 7.80 (s, 1H), 7.46 (d, *J* = 8.7 Hz, 2H), 7.36 (d, *J* = 8.7 Hz, 2H), 4.67 (s, 2H), 4.08-3.78 (m, 2H), 1.98 (s, 3H), 1.53 (s, 3H), 1.32 (s, 9H), 1.27 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) (major isomer) δ 171.2 (d, *J* = 5.2 Hz), 158.6, 167.8, 147.7, 134.5, 125.9, 119.8, 85.6 (d, *J* = 174.5 Hz), 73.2, 61.8, 53.7 (d, *J* = 19.9 Hz), 48.1, 34.4, 31.3, 18.0, 14.1; ¹³C NMR (126 MHz, CDCl₃) (minor isomer) δ 171.3, 167.8, 158.9, 147.7, 134.5, 125.9, 119.8, 85.6 (d, *J* = 174.5 Hz), 73.2, 62.0, 54.4, 48.1, 34.4, 31.3, 19.2, 12.6; ¹⁹F NMR (376 MHz, CDCl₃) (major isomer) δ -226.66 (s, 1F); **HRMS** (ESI-TOF) *m/z*: [M+Na]⁺ Calcd. for C₂₀H₂₉FN₂O₄Na 403.2009, found: 403.2016.



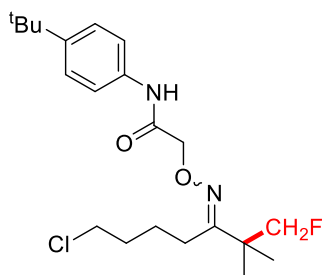
ethyl-((2-((3,5-bis(trifluoromethyl)phenyl)amino)-2-oxoethoxy)imino)-1-(fluoromethyl)cyclohexane-1-carboxylate (2m): Following the general condition, stirred at 100 °C for 3 h, obtained the **2m** as a colorless solid (48.6 mg, 50%); $R_f = 0.28$ (petroleum ether-EtOAc = 5:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) (major isomer) δ 8.51 (s, 1H), 8.16 (s, 2H), 7.61 (s, 1H), 4.86-4.54 (m, 2H), 4.70 (d, $J = 24.5$ Hz, 2H), 4.32-4.23 (m, 2H), 3.36-3.25 (m, 1H), 2.52-2.46 (m, 1H), 2.10-1.99 (m, 1H), 1.96-1.79 (m, 2H), 1.52-1.41 (m, 1H), 1.29 (q, $J = 7.2$ Hz, 2H), 1.29 (t, $J = 7.2$ Hz, 3H); $^1\text{H NMR}$ (500 MHz, CDCl_3) (minor isomer) δ 8.33 (s, 1H), 8.18 (s, 2H), 7.61 (s, 1H), 4.70 (d, $J = 24.5$ Hz, 2H), 4.32-4.23 (m, 2H), 3.89 (dd, $J = 102.0, 11.1$ Hz, 2H), 3.36-3.25 (m, 1H), 2.58-2.52 (m, 1H), 2.10-1.99 (m, 1H), 1.96-1.79 (m, 2H), 1.59-1.58 (m, 2H), 1.52-1.41 (m, 1H), 1.29 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) (major isomer) δ 171.2 (d, $J = 4.1$ Hz), 169.1, 161.0, 139.0, 132.4 (q, $J = 5.1$ Hz), 123.2 (q, $J = 273.2$ Hz), 119.7-119.6 (m), 117.6-117.4 (m), 85.1 (d, $J = 177.0$ Hz), 73.0, 62.2, 54.6 (d, $J = 18.6$ Hz), 31.4 (d, $J = 4.3$ Hz), 24.7, 24.0, 22.0, 14.1; $^{13}\text{C NMR}$ (126 MHz, CDCl_3) (minor isomer) δ 171.1 (d, $J = 2.7$ Hz), 169.0, 161.0, 139.0, 132.4 (q, $J = 4.1$ Hz), 123.2 (q, $J = 273.2$ Hz), 119.9-119.8 (m), 117.6-117.4 (m), 85.1 (d, $J = 177.0$ Hz), 73.0, 62.2, 55.1, 33.5, 24.9, 24.2, 22.2, 14.1; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -63.08 (s, 6F), -222.27 (s, 1F); **HRMS** (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{20}\text{H}_{21}\text{F}_7\text{N}_2\text{O}_4\text{Na}$ 509.1287, found: 509.1289.



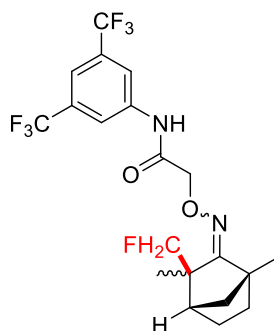
(E)-5-((2-((4-(tert-butyl)phenyl)amino)-2-oxoethoxy)imino)-7-fluoro-6,6-dimethylheptyl acetate (2n): Following the general condition, stirred at 100 °C for 3 h, obtained the **2n** as a yellow oil (53.2 mg, 63%); $R_f = 0.41$ (petroleum ether-EtOAc = 3:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.93 (s, 1H), 7.44 (d, $J = 8.7$ Hz, 2H), 7.36 (d, $J = 8.7$ Hz, 2H), 4.62 (s, 2H), 4.37 (d, $J = 5.1$ Hz, 2H), 4.13 (t, $J = 6.3$ Hz, 2H), 2.45-2.35 (m, 2H), 2.02 (s, 3H), 1.75 (p, $J = 6.3$ Hz, 2H), 1.72-1.64 (m, 2H), 1.31 (s, 9H), 1.20 (d, $J = 1.7$ Hz, 6H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 171.1, 168.2, 166.1, 147.5, 134.6, 125.8, 119.7, 88.7 (d, $J = 174.9$ Hz), 73.1, 63.6, 42.0 (d, $J = 17.9$ Hz), 34.4, 31.3, 29.1, 26.0, 23.0, 22.0 (d, $J = 5.1$ Hz), 20.9; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -221.08 (s, 1F); **HRMS** (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{23}\text{H}_{35}\text{FN}_2\text{O}_4\text{Na}$ 445.2479, found: 445.2482.



(E)-N-(4-(tert-butyl)phenyl)-2-(((7-(1,3-dioxoisindolin-2-yl)-1-fluoro-2,2-dimethylheptan-3-ylidene)amino)oxy)acetamide (2o): Following the general condition, stirred at 100 °C for 3 h, obtained the **2o** as a colorless solid (79.5 mg, 78%); $R_f = 0.27$ (petroleum ether-EtOAc = 3:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.96 (s, 1H), 7.80 (dd, $J = 5.4, 3.0$ Hz, 2H), 7.70 (dd, $J = 5.4, 3.0$ Hz, 2H), 7.47 (d, $J = 8.7$ Hz, 2H), 7.36 (d, $J = 8.7$ Hz, 2H), 4.54 (s, 2H), 4.36 (d, $J = 47.6$ Hz, 2H), 3.76 (t, $J = 7.0$ Hz, 2H), 2.47-2.40 (m, 2H), 1.83 (p, $J = 7.2$ Hz, 2H), 1.71-1.60 (m, 2H), 1.32 (s, 9H), 1.18 (s, 6H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 168.4, 168.2, 165.9, 147.4, 134.7, 134.0, 132.0, 125.8, 123.2, 119.7, 88.7 (d, $J = 175.0$ Hz), 73.1, 42.0 (d, $J = 18.1$ Hz), 37.1, 34.4, 31.4, 28.8, 26.0, 23.4, 22.0 (d, $J = 4.9$ Hz); $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -220.00 (s, 1F); **HRMS** (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{29}\text{H}_{36}\text{FN}_3\text{O}_4\text{Na}$ 532.2588, found: 532.2591.

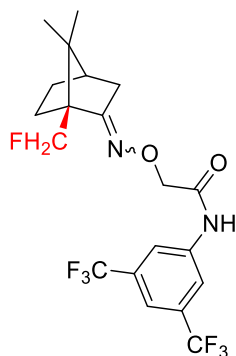


N-(4-(tert-butyl)phenyl)-2-(((7-chloro-1-fluoro-2,2-dimethylheptan-3-ylidene)amino)oxy)acetamide (2p): Following the general condition, stirred at 100 °C for 3 h, obtained the **2p** as a colorless solid (43.0 mg, 54%); $R_f = 0.28$ (petroleum ether-EtOAc = 5:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) (major isomer) δ 7.92 (s, 1H), 7.45 (d, $J = 8.7$ Hz, 2H), 7.37 (d, $J = 8.7$ Hz, 2H), 4.63 (s, 2H), 4.38 (d, $J = 47.6$ Hz, 2H), 3.61 (t, $J = 6.5$ Hz, 2H), 2.46-2.35 (m, 2H), 1.89 (q, $J = 6.7$ Hz, 2H), 1.83-1.71 (m, 2H), 1.32 (s, 9H), 1.21 (d, $J = 1.7$ Hz, 6H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) (major isomer) δ 168.2, 166.0, 147.5, 134.6, 125.9, 119.7, 88.8 (d, $J = 175.1$ Hz), 73.1, 44.3, 42.0 (d, $J = 18.0$ Hz), 34.4, 32.8, 31.4, 25.6, 23.8, 22.0; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -221.12 (s, 1F); **HRMS** (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{21}\text{H}_{32}\text{ClFN}_2\text{O}_2\text{Na}$ 421.2034, found: 421.2038.

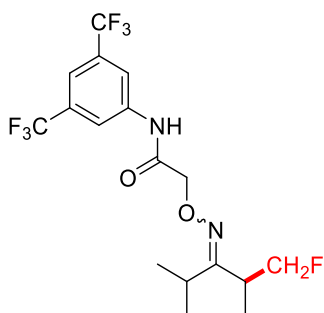


N-(3,5-bis(trifluoromethyl)phenyl)-2-(((1R,4S)-3-(fluoromethyl)-1,3-dimethylbicyclo[2.2.1]heptan-3-ylidene)amino)oxy)acetamide (2q):

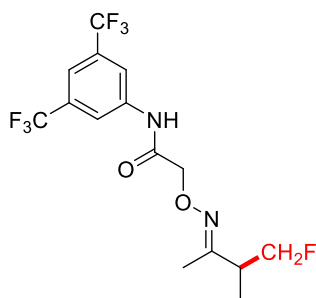
n-2-ylidene)amino)oxy)acetamide (2q): Following the general condition, stirred at 100 °C for 12 h, obtained the **2q** as a colorless solid (41.8 mg, 46%); Other fluorination regioisomers have also been determined by GC-MS (13% and 5%, respectively); $R_f = 0.21$ (petroleum ether-EtOAc = 5:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) (major isomer) δ 8.58 (s, 1H), 8.05 (s, 2H), 7.62 (s, 1H), 4.85-4.49 (m, 2H), 4.59 (s, 2H), 2.07-1.98 (m, 2H), 1.94-1.85 (m, 2H), 1.75-1.66 (m, 1H), 1.57-1.54 (m, 1H), 1.46-1.42 (m, 1H), 1.40 (s, 3H), 1.37 (s, 3H); $^1\text{H NMR}$ (500 MHz, CDCl_3) (minor isomer) δ 8.40 (s, 1H), 8.06 (s, 2H), 7.62 (s, 1H), 4.59 (s, 2H), 3.80 (dd, $J = 118.5, 11.4$ Hz, 2H), 2.07-1.98 (m, 2H), 1.84-1.77 (m, 2H), 1.75-1.66 (m, 1H), 1.60-1.57 (m, 1H), 1.51-1.46 (m, 1H), 1.41 (s, 3H), 1.38 (s, 3H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) (major isomer) δ 173.2, 169.3, 138.9, 132.4 (q, $J = 33.5$ Hz), 123.1 (q, $J = 4.2$ Hz), 119.4-119.3 (m), 117.8-117.5 (m), 82.8 (d, $J = 167.3$ Hz), 73.0, 48.3, 48.0, 45.4 (d, $J = 28.8$ Hz), 38.8 (d, $J = 1.5$ Hz), 31.0, 24.2, 23.2, 22.6; $^{13}\text{C NMR}$ (126 MHz, CDCl_3) (minor isomer) δ 172.9, 169.3, 138.8, 132.4 (q, $J = 33.5$ Hz), 123.1 (q, $J = 4.2$ Hz), 119.6-119.5 (m), 117.8-117.5 (m), 82.8 (d, $J = 167.3$ Hz), 73.0, 55.9, 55.0 (d, $J = 19.5$ Hz), 44.9, 39.8, 28.7 (d, $J = 4.3$ Hz), 25.1, 23.1, 22.7. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -63.07 (s, 6F), -223.37 (s, 1F); **HRMS** (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{20}\text{H}_{21}\text{F}_7\text{N}_2\text{O}_2\text{Na}$ 477.1389, found: 477.1394.



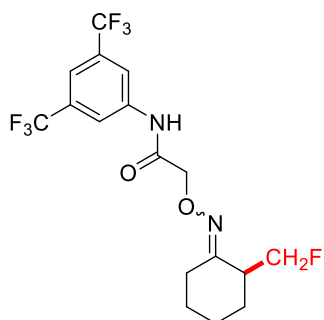
N-(3,5-bis(trifluoromethyl)phenyl)-2-(((1S,4R)-1-(fluoromethyl)-7,7-dimethylbicyclo[2.2.1]hepta n-2-ylidene)amino)oxy)acetamide (2r): Following the general condition, stirred at 100 °C for 18 h, obtained the **2r** as a colorless solid (51.8 mg, 57%); $R_f = 0.28$ (petroleum ether-EtOAc = 5:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) (major isomer) δ 8.60 (s, 1H), 8.05 (s, 2H), 7.61 (s, 1H), 4.80-4.56 (m, 2H), 4.64 (d, $J = 20.0$ Hz, 2H), 2.72 (dt, $J = 18.2, 3.3$ Hz, 1H), 2.18 (d, $J = 18.2$ Hz, 1H), 2.05-1.93 (m, 3H), 1.51-1.42 (m, 1H), 1.41-1.35 (m, 1H), 1.11 (s, 3H), 1.02 (s, 3H); $^1\text{H NMR}$ (500 MHz, CDCl_3) (minor isomer) δ 8.67 (s, 1H), 8.08 (s, 2H), 7.61 (s, 1H), 4.80-4.56 (m, 2H), 4.68 (d, $J = 20.0$ Hz, 2H), 2.72 (dt, $J = 18.2, 3.3$ Hz, 1H), 2.18 (d, $J = 18.2$ Hz, 1H), 2.05-1.93 (m, 3H), 1.51-1.42 (m, 1H), 1.41-1.35 (m, 1H), 1.27 (s, 3H), 0.99 (s, 3H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 169.7, 169.1, 138.9, 132.41 (q, $J = 33.6$ Hz), 123.1 (q, $J = 272.7$ Hz), 119.4-119.3 (m), 117.7-117.4 (m), 81.0 (d, $J = 168.4$ Hz), 72.9, 56.0 (d, $J = 18.5$ Hz), 48.7, 44.6, 34.1, 27.6 (d, $J = 5.1$ Hz), 26.8, 20.4, 19.2; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -63.08 (s, 6F), -228.84 (s, 1F); **HRMS** (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{20}\text{H}_{21}\text{F}_7\text{N}_2\text{O}_2\text{Na}$ 477.1389, found: 477.1389.



N-(3,5-bis(trifluoromethyl)phenyl)-2-(((1-fluoro-2,4-dimethylpentan-3-ylidene)amino)oxy)acetamide (2s): Following the general condition, stirred at 100 °C for 2 h, obtained the **2s** as a colorless solid (54.1 mg, 65%); $R_f = 0.49$ (petroleum ether-EtOAc = 5:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) (major isomer) δ 8.30 (s, 1H), 8.04 (s, 2H), 7.62 (s, 1H), 4.64 (d, $J = 3.3$ Hz, 2H), 4.70-4.34 (m, 2H), 3.40-3.27 (m, $J = 7.0$ Hz, 1H), 2.99-2.87 (m, 1H), 1.22 (dd, $J = 7.0, 3.7$ Hz, 6H), 1.18 (dd, $J = 7.0, 1.4$ Hz, 3H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) (major isomer) δ 169.2, 169.0 (d, $J = 2.6$ Hz), 138.8, 132.4 (q, $J = 33.5$ Hz), 123.1 (q, $J = 272.7$ Hz), 119.5-119.4 (m), 117.8-117.6 (m), 85.6 (d, $J = 170.6$ Hz), 72.8, 36.1 (d, $J = 19.4$ Hz), 28.2, 18.8 (d, $J = 18.0$ Hz), 15.6 (d, $J = 7.3$ Hz); $^{19}\text{F NMR}$ (376 MHz, CDCl_3) (major isomer) δ -63.10 (s, 6F), -216.67 (s, 1F); $^{19}\text{F NMR}$ (376 MHz, CDCl_3) (minor isomer) δ -63.10 (s, 6F), -211.90 (s, 1F); **HRMS** (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{17}\text{H}_{19}\text{F}_7\text{N}_2\text{O}_2\text{Na}$ 439.1227, found: 439.1232.

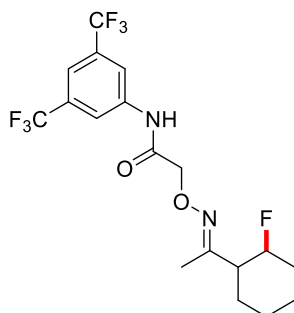


(E)-N-(3,5-bis(trifluoromethyl)phenyl)-2-(((4-fluoro-3-methylbutan-2-ylidene)amino)oxy)acetamide (2t): Following the general condition, stirred at 100 °C for 3 h, obtained the **2t** as a colorless solid (41.1 mg, 53%); $R_f = 0.28$ (petroleum ether-EtOAc = 5:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.33 (s, 1H), 8.06 (d, $J = 1.5$ Hz, 2H), 7.63 (s, 1H), 4.67 (s, 2H), 4.62-4.53 (m, 2H), 2.90-2.80 (m, 1H), 2.03 (s, 3H), 1.18 (dd, $J = 7.2, 1.2$ Hz, 3H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 169.0, 161.9 (d, $J = 2.8$ Hz), 138.8, 132.4 (q, $J = 34.2$ Hz), 122.0 (q, $J = 272.4$ Hz), 119.6-119.5 (m), 117.8-117.6 (m), 84.6 (d, $J = 169.2$ Hz), 72.8, 40.5 (d, $J = 18.8$ Hz), 13.3 (d, $J = 7.4$ Hz), 12.8; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -63.05 (s, 6F), -219.30 (s, 1F); **HRMS** (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{15}\text{H}_{15}\text{F}_7\text{N}_2\text{O}_2\text{Na}$ 411.0914, found: 411.0920.

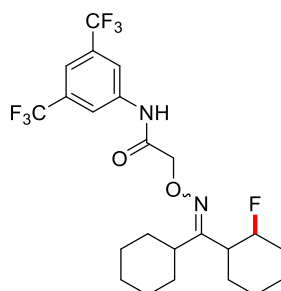


N-(3,5-bis(trifluoromethyl)phenyl)-2-(((2-(fluoromethyl)cyclohexylidene)amino)oxy)acetamide

(2u): Following the general condition, stirred at 100 °C for 5 h, using the HFIP as the solvent, obtained the **2u** as a colorless solid (48.0 mg, 58%); $R_f = 0.25$ (petroleum ether-EtOAc = 5:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.56 (s, 1H), 8.07 (s, 2H), 7.62 (s, 1H), 4.79-4.46 (m, 2H), 4.63 (s, 2H), 3.14-3.09 (m, 1H), 2.76-2.60 (m, 1H), 2.19-2.03 (m, 2H), 1.95-1.82 (m, 2H), 1.62-1.54 (m, 2H), 1.54-1.47 (m, 1H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) (major isomer) δ 169.1, 162.8 (d, $J = 3.3$ Hz), 138.9, 132.5 (q, $J = 18.8$ Hz), 123.0 (q, $J = 272.4$ Hz), 119.6-119.5 (m), 117.7-117.6 (m), 83.4 (d, $J = 167.5$ Hz), 72.8, 42.7 (d, $J = 20.1$ Hz), 29.3 (d, $J = 5.5$ Hz), 26.3, 25.8, 24.1; $^{13}\text{C NMR}$ (126 MHz, CDCl_3) (minor isomer) 169.3, 161.3, 139.1, 132.2 (q, $J = 18.8$ Hz), 123.5 (q, $J = 270.0$ Hz), 119.4-119.3 (m), 117.5-117.4 (m), 85.0 (d, $J = 167.3$ Hz), 72.7, 34.2 (d, $J = 17.3$ Hz), 28.5, 25.9 (d, $J = 11.1$ Hz), 25.0, 21.6; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) (major isomer) δ -63.04 (s, 6F), -222.96 (s, 1F); $^{19}\text{F NMR}$ (376 MHz, CDCl_3) (minor isomer) δ -63.04 (s, 6F), -216.00 (s, 1F); **HRMS** (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{17}\text{H}_{17}\text{F}_7\text{N}_2\text{O}_2\text{Na}$ 437.1076, found: 437.1078.

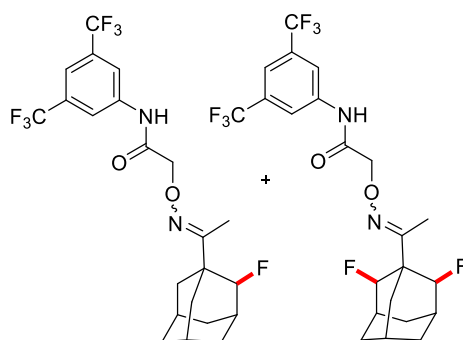


N-(3,5-bis(trifluoromethyl)phenyl)-2-(((E)-1-((2S)-2-fluorocyclohexyl)ethylidene)amino)oxy)acetamide (2v): Following the general condition, stirred at 100 °C for 24 h, obtained the **2v** as a colorless solid (47.1 mg, 55%); $R_f = 0.28$ (petroleum ether-EtOAc = 5:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.38 (s, 1H), 8.08 (s, 2H), 7.61 (s, 1H), 4.67 (d, $J = 1.8$ Hz, 2H), 4.70-4.53 (m, 1H), 2.52-2.42 (m, 1H), 2.27-2.20 (m, 1H), 2.03 (s, 3H), 1.92-1.84 (m, 2H), 1.79-1.72 (m, 1H), 1.57-1.47 (m, 1H), 1.45-1.30 (m, 3H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 169.3, 162.0, 138.9, 132.3 (q, $J = 33.4$ Hz), 123.1 (q, $J = 272.5$ Hz), 119.6-119.5 (m), 117.7-117.5 (m), 92.4 (d, $J = 175.7$ Hz), 72.7, 50.2 (d, $J = 17.3$ Hz), 32.1 (d, $J = 18.0$ Hz), 29.0 (d, $J = 7.3$ Hz), 24.7 (d, $J = 2.0$ Hz), 23.9 (d, $J = 11.5$ Hz), 13.0; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -163.06 (s, 6F), -171.35 (s, 1F); **HRMS** (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{18}\text{H}_{19}\text{F}_7\text{N}_2\text{O}_2\text{Na}$ 451.1232, found: 451.1233.



N-(3,5-bis(trifluoromethyl)phenyl)-2-((cyclohexyl((2S)-2-fluorocyclohexyl)methylene)amino)oxy)acetamide (2w): Following the general condition, stirred at 100 °C for 3 h, obtained the **2w** as a colorless solid (59.5 mg, 60%); $R_f = 0.35$ (petroleum ether-EtOAc = 5:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) (major isomer) δ 8.31 (s, 1H), 8.07 (s, 2H), 7.61 (s, 1H), 4.65 (s, 2H), 4.80-4.57 (m, 2H), 3.13-3.05 (m, 1H), 2.53-2.45 (m, 1H), 2.23-2.15 (m, 1H), 2.03-1.92 (m, 1H), 1.89-1.80 (m, 3H), 1.78-1.68 (m, 4H), 1.58-1.44 (m, 3H), 1.40-1.26 (m, 6H); $^1\text{H NMR}$ (500 MHz, CDCl_3) (minor isomer) δ 8.85 (s, 1H), 8.11

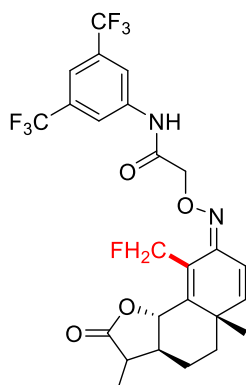
(s, 2H), 7.60 (s, 1H), 5.07-4.89 (m, 1H), 4.64 (s, 2H), 4.80-4.57 (m, 1H), 3.02-2.91 (m, 1H), 2.60-2.53 (m, 1H), 2.23-2.15 (m, 1H), 1.89-1.80 (m, 3H), 1.78-1.68 (m, 4H), 1.58-1.44 (m, 3H), 1.40-1.26 (m, 5H); ^{13}C NMR (126 MHz, CDCl_3) (major isomer) δ 169.6, 168.3, 138.9, 132.4 (q, $J = 33.5$ Hz), 123.1 (q, $J = 271.8$ Hz), 119.5-119.4 (m), 117.7 -117.5 (m), 93.9 (d, $J = 173.6$ Hz), 72.7, 46.2 (d, $J = 17.8$ Hz), 38.5, 32.4 (d, $J = 18.0$ Hz), 31.7 (d, $J = 7.1$ Hz), 28.5 (d, $J = 10.0$ Hz), 26.0 (d, $J = 6.2$ Hz), 25.8, 25.1 (d, $J = 1.9$ Hz), 24.0 (d, $J = 11.5$ Hz); ^{13}C NMR (126 MHz, CDCl_3) (minor isomer) δ 169.7, 167.0, 139.2, 132.4 (q, $J = 33.7$ Hz), 123.2 (q, $J = 272.7$ Hz), 119.5-119.4 (m), 117.4 -117.3 (m), 89.3 (d, $J = 175.1$ Hz), 72.9, 44.1 (d, $J = 19.0$ Hz), 39.5, 31.0 (d, $J = 23.3$ Hz), 29.7, 28.7 (d, $J = 22.6$ Hz), 26.2 (d, $J = 10.2$ Hz), 26.0, 24.5 (d, $J = 1.1$ Hz), 19.7 (d, $J = 2.5$ Hz); ^{19}F NMR (376 MHz, CDCl_3) δ -63.09 (s, 6F), -170.80 (s, 1F); HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{23}\text{H}_{27}\text{F}_7\text{N}_2\text{O}_2\text{Na}$ 519.1858, found: 519.1864.



N-(3,5-bis(trifluoromethyl)phenyl)-2-((1-((1S,2S,3R,5R,7S)-2-fluoroadamantan-1-yl)ethylidene)amino)oxy)acetamide (2x-1): Following the general condition, stirred at 100 °C for 2 h, obtained the mixture of **2x-1** and **2x-2** as a colorless solid (75.6 mg, 77%); $R_f = 0.35$ (petroleum ether-EtOAc = 5:1); ^1H NMR (500 MHz, CDCl_3) δ 8.58 (s, 1H), 8.10 (s, 2H), 7.61 (s, 1H), 4.90 (dd, $J = 49.9, 3.7$ Hz, 1H), 4.67 (s, 2H), 2.36-2.11 (m, 3H), 2.09 (s, 3H), 2.08-1.98 (m, 3H), 1.96-1.87 (m, 1H), 1.80-1.67 (m, 4H), 1.64-1.57 (m, 2H); ^{13}C NMR (126 MHz, CDCl_3) (major isomer) δ 169.5, 164.6, 139.0, 132.3 (q, $J = 33.2$ Hz), 123.1 (q, $J = 272.7$ Hz), 112.0-119.1 (m), 117.9-117.1 (m), 94.9 (d, $J = 182.9$ Hz), 72.8, 39.1 (d, $J = 5.6$ Hz), 36.2, 33.5, 32.7 (d, $J = 18.1$ Hz), 30.5, 27.1, 10.2; ^{13}C NMR (126 MHz, CDCl_3) (minor isomer) δ 169.5, 164.6, 139.0, 132.3 (q, $J = 33.2$ Hz), 123.1 (q, $J = 272.7$ Hz), 112.0-119.1 (m), 117.9-117.1 (m), 94.9 (d, $J = 182.9$ Hz), 72.8, 39.1 (d, $J = 5.6$ Hz), 36.2, 33.1 (d, $J = 4.7$ Hz), 32.7 (d, $J = 18.1$ Hz), 30.2, 27.1, 10.2; ^{19}F NMR (376 MHz, CDCl_3) (major isomer) δ -63.07 (s, 6F), -179.41 (s, 1F); ^{19}F NMR (376 MHz, CDCl_3) (minor isomer) δ -63.07 (s, 6F), -179.89 (s, 1F); HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{22}\text{H}_{23}\text{F}_7\text{N}_2\text{O}_2\text{Na}$ 503.1545, found: 503.1546.

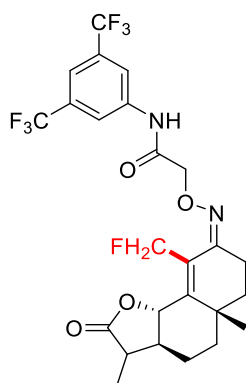
N-(3,5-bis(trifluoromethyl)phenyl)-2-((1-((1r,2R,3R,5r,7S,8S)-2,8-difluoroadamantan-1-yl)ethylidene)amino)oxy)acetamide (2x-2): Following the general condition, stirred at 100 °C for 2 h, obtained the mixture of **2x-1** and **2x-2** as a colorless solid (75.6 mg, 77%); $R_f = 0.35$ (petroleum ether-EtOAc = 5:1); ^1H NMR (500 MHz, CDCl_3) δ 8.56 (s, 2H), 8.10 (s, 2H), 7.61 (s, 1H), 5.34 (dd, $J = 48.7, 3.9$ Hz, 1H), 4.83-4.72 (m, 1H), 4.70 (d, $J = 4.0$ Hz, 2H), 2.36-2.11 (m, 2H), 2.08-1.98 (m, 2H), 1.98 (s, 3H), 1.96-1.87 (m, 1H), 1.80-1.67 (m, 4H), 1.64-1.57 (m, 2H); ^{13}C NMR (126 MHz, CDCl_3) (major isomer) δ 169.3, 161.9, 139.0, 132.3 (q, $J = 33.2$ Hz), 123.1 (q, $J = 272.7$ Hz), 112.0-119.1 (m), 117.9 -117.1 (m), 91.0 (d, $J = 181.2$ Hz), 73.0, 43.6 (d, $J = 17.6$ Hz), 35.3 (d, $J = 9.1$ Hz), 32.1 (d, $J = 18.8$ Hz), 29.1-29.0 (m), 27.2 (d, $J = 1.2$ Hz), 26.3, 11.4 (d, $J = 3.1$ Hz), 27.08 , 26.32 – 26.13 (m), 10.18 ; ^{13}C NMR (126 MHz, CDCl_3) (minor isomer) δ 169.3, 161.9, 139.0, 132.3 (q, $J = 33.2$ Hz), 123.1 (q, $J = 272.7$ Hz), 112.0-119.1 (m), 117.9 -117.1 (m), 91.0 (d, $J = 181.2$ Hz), 73.0, 43.6 (d, $J = 17.6$ Hz), 34.8 (d, $J = 8.8$ Hz), 32.3 (d, $J = 17.7$ Hz), 29.1-29.0 (m), 27.2 (d, $J = 1.2$ Hz), 26.3, 11.4 (d,

$J = 3.1$ Hz); ^{19}F NMR (376 MHz, CDCl_3) (minor isomer) δ -63.07 (s, 6F), -187.35 (s, 2F); ^{19}F NMR (376 MHz, CDCl_3) (major isomer) δ -63.07 (s, 6F), -187.10 (s, 2F); HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{22}\text{H}_{22}\text{F}_8\text{N}_2\text{O}_2\text{Na}$ 521.1451, found: 521.1460.



N-(3,5-bis(trifluoromethyl)phenyl)-2-((((3a*S*,5a*S*,9b*S*,*Z*)-9-(fluoromethyl)-3,5a-dimethyl-2-oxo-2,3,3a,5,5a,9b-hexahydronaphtho[1,2-*b*]furan-8(4*H*)-ylidene)amino)oxy)acetamide

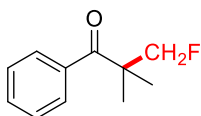
(Stantonin- CH_2F): Following the general condition, stirred at 100 °C for 3 h, obtained the Stantonin- CH_2F as a colorless solid (82.2 mg, 75%); $R_f = 0.27$ (petroleum ether-EtOAc = 2:1); ^1H NMR (500 MHz, CDCl_3) δ 8.82 (s, 1H), 8.09 (s, 2H), 7.58 (s, 1H), 6.94 (d, $J = 10.2$ Hz, 1H), 6.19 (d, $J = 10.2$ Hz, 2H), 5.70 (dd, $J = 15.8, 9.7$ Hz, 1H), 5.61 (dd, $J = 15.8, 9.7$ Hz, 1H), 4.87 (dd, $J = 11.4, 6.3$ Hz, 1H), 4.74 (s, 2H), 2.47-2.38 (m, 1H), 2.06 (d, $J = 15.4$ Hz, 1H), 1.89 (ddd, $J = 23.1, 11.7, 3.2$ Hz, 2H), 1.73 (qd, $J = 12.7, 3.6$ Hz, 1H), 1.62 (td, $J = 13.1, 4.3$ Hz, 1H), 1.35 (s, 3H), 1.28 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 177.0, 168.8, 150.4, 147.9 (d, $J = 6.9$ Hz), 147.3, 138.9, 132.2 (q, $J = 33.4$ Hz), 123.1 (q, $J = 273.5$ Hz), 121.3 (d, $J = 14.3$ Hz), 119.8-119.7 (m), 117.6-117.4 (m), 112.5, 81.4 (d, $J = 2.6$ Hz), 75.4 (d, $J = 159.7$ Hz), 73.4, 53.6, 41.6 (d, $J = 1.9$ Hz), 40.9, 38.3, 25.9, 23.4, 12.4; ^{19}F NMR (376 MHz, CDCl_3) δ -62.98 (s, 6F), -208.74 (s, 1F); HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{25}\text{H}_{23}\text{F}_7\text{N}_2\text{O}_4\text{Na}$ 571.1444, found: 571.1446.



N-(3,5-bis(trifluoromethyl)phenyl)-2-((((3a*S*,5a*S*,9b*S*,*Z*)-9-(fluoromethyl)-3,5a-dimethyl-2-oxo-2,3,3a,5,5a,6,7,9b-octahydronaphtho[1,2-*b*]furan-8(4*H*)-ylidene)amino)oxy)acetamide (4- CH_2F):

Following the general condition, stirred at 75 °C for 3 h, obtained the 4- CH_2F as a colorless solid (85.8 mg, 78%); $R_f = 0.34$ (petroleum ether-EtOAc = 2:1); ^1H NMR (500 MHz, CDCl_3) δ 8.80 (s, 1H), 8.09 (s, 2H), 7.59 (s, 1H), 5.73-5.50 (m, 2H), 4.76 (dd, $J = 11.6, 6.4$ Hz, 1H), 4.72 (s, 2H), 3.12 (dt, $J = 17.3, 3.8$ Hz, 1H), 2.43-2.33 (m, 2H), 2.04-1.99 (m, 1H), 1.94 (qd, $J = 11.8, 3.2$ Hz, 1H), 1.83-1.72 (m, 2H), 1.72-1.63 (m, 2H), 1.56 (td, $J = 13.3, 4.0$ Hz, 1H), 1.30 (s, 3H), 1.28 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 177.2, 168.9, 157.6, 149.8 (d, $J = 6.7$ Hz), 139.0, 132.2 (q, $J = 33.4$ Hz), 123.1 (q, $J =$

272.5 Hz), 122.8 (d, $J = 14.7$ Hz), 119.8-119.7 (m), 117.5 (dt, $J = 7.6, 3.7$ Hz), 81.9 (d, $J = 2.2$ Hz), 76.0 (d, $J = 159.1$ Hz), 73.4, 52.8, 41.1, 41.0, 37.8, 36.7, 24.9 (d, $J = 2.8$ Hz), 24.4, 19.2, 12.3; ^{19}F NMR (376 MHz, CDCl_3) δ -75.65 (s, 6F), -220.00 (s, 1F); HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{25}\text{H}_{25}\text{F}_7\text{N}_2\text{O}_4\text{Na}$ 573.1600, found: 573.1597.



3-fluoro-2,2-dimethyl-1-phenylpropan-1-one (3e): Colorless oil (7.2 mg, 80%); $R_f = 0.53$ (petroleum ether-EtOAc = 10:1); ^1H NMR (500 MHz, CDCl_3) δ 7.71-7.65 (m, 2H), 7.52-7.48 (m, 1H), 7.46-7.41 (m, 2H), 4.56 (d, $J = 47.3$ Hz, 2H), 1.40 (d, $J = 1.7$ Hz, 6H); ^{13}C NMR (126 MHz, CDCl_3) δ 138.3, 131.2, 128.2, 127.5, 88.9 (d, $J = 174.4$ Hz), 48.6 (d, $J = 18.6$ Hz), 22.1 (d, $J = 5.4$ Hz); ^{19}F NMR (376 MHz, CDCl_3) δ -221.88 (s, 1F).

VI. X-Ray data for 4- CH_2F

X-ray for 4- CH_2F

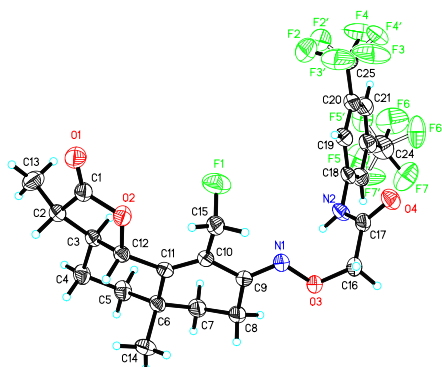


Table S6. Crystal data and structure refinement for mo_dd19398_0m.

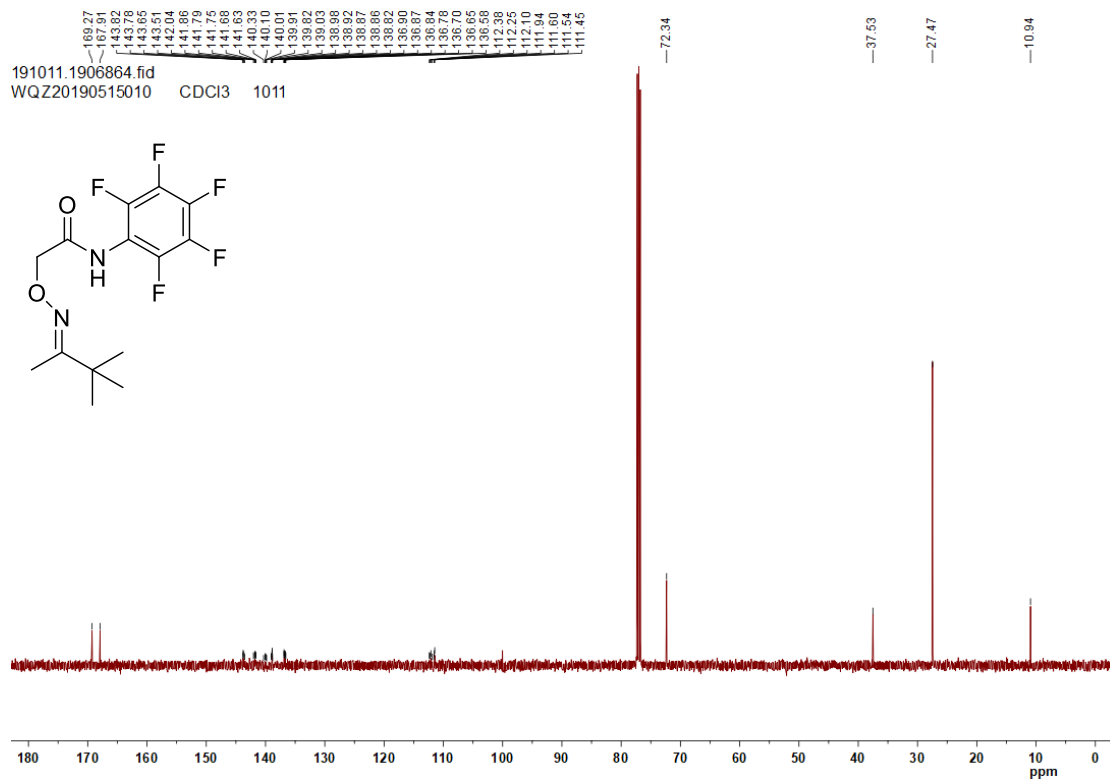
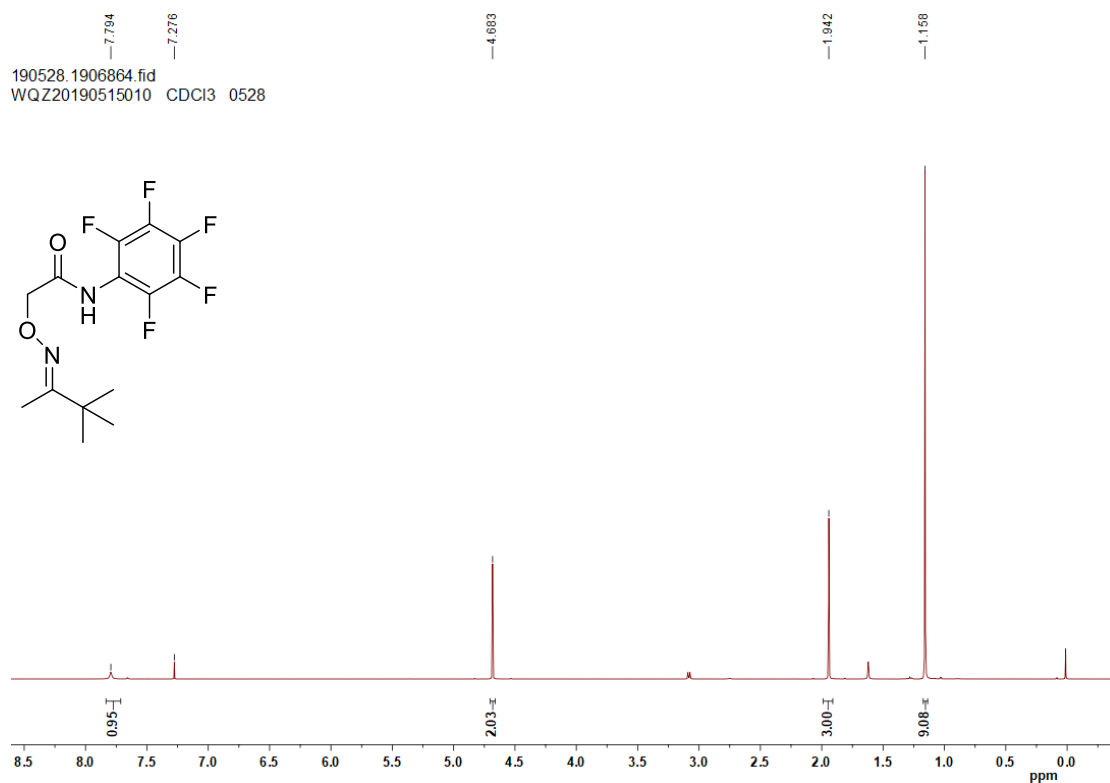
Identification code	mo_dd19398_0m	
Empirical formula	$\text{C}_{25}\text{H}_{25}\text{F}_7\text{N}_2\text{O}_4$	
Formula weight	550.47	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	$a = 8.7568(3)$ Å	$\alpha = 90^\circ$
	$b = 16.7646(6)$ Å	$\beta = 90^\circ$
	$c = 17.6194(6)$ Å	$\gamma = 90^\circ$
Volume	$2586.60(16)$ Å ³	
Z	4	
Density (calculated)	1.414 Mg/m ³	
Absorption coefficient	0.129 mm ⁻¹	

F(000)	1136
Crystal size	0.200 x 0.150 x 0.120 mm ³
Theta range for data collection	2.430 to 25.992 °
Index ranges	-10<=h<=10, -17<=k<=20, -21<=l<=21
Reflections collected	13082
Independent reflections	5052 [R(int) = 0.0332]
Completeness to theta = 25.242 °	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6695
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	5052 / 24 / 400
Goodness-of-fit on F ²	1.058
Final R indices [I>2sigma(I)]	R1 = 0.0530, wR2 = 0.1205
R indices (all data)	R1 = 0.0798, wR2 = 0.1419
Absolute structure parameter	0.0(4)
Extinction coefficient	0.025(4)
Largest diff. peak and hole	0.394 and -0.180 e.Å ⁻³

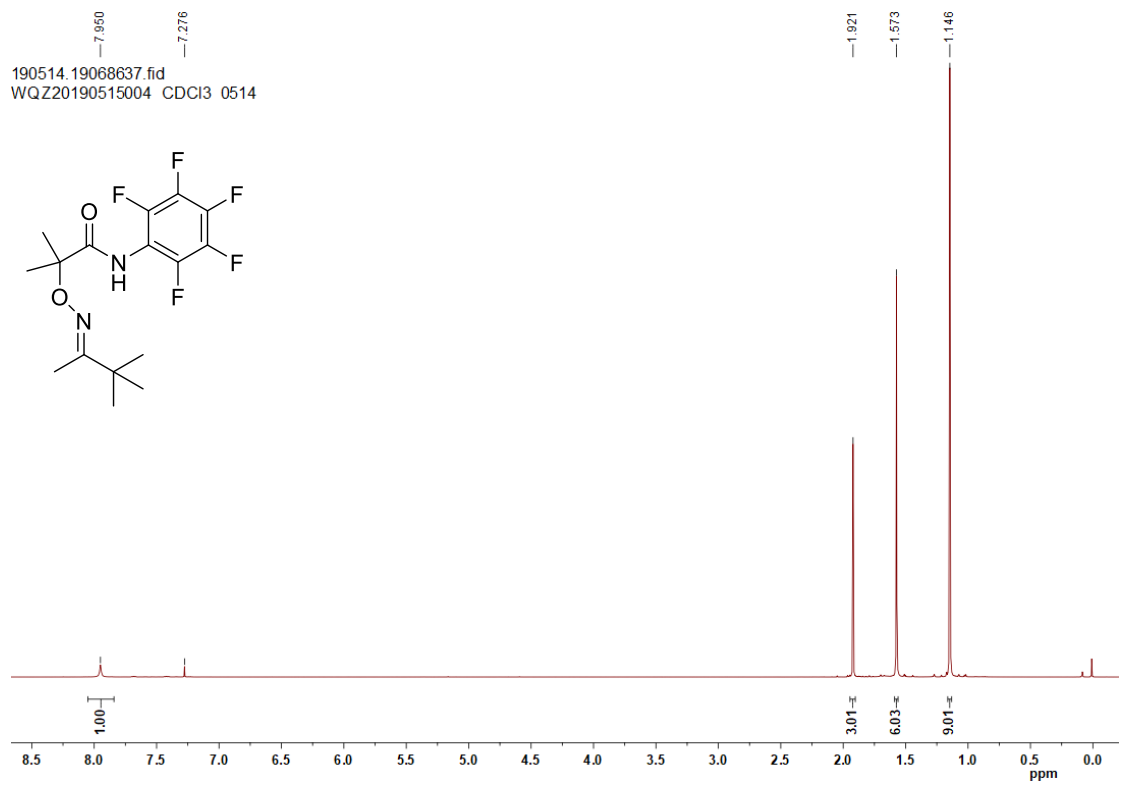
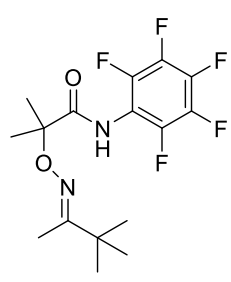
VII. References

1. R.-Y. Zhu, L.-Y. Liu, and J.-Q. Yu, Highly versatile β -C(sp³)-H iodination of ketones using a practical auxiliary. *J. Am. Chem. Soc.* **2017**, *139*, 12394-12397.
2. Q.-L. Yang, Y.-Q. Li, C. Ma, P. Fang, X.-J. Zhang, and T.-S. Mei, Palladium-catalyzed C(sp³)-H oxygenation via electrochemical oxidation. *J. Am. Chem. Soc.* **2017**, *139*, 3293-3298.
3. T. Kang, Y. Kim, D. Lee, Z. Wang, and S. Chang, Iridium-catalyzed intermolecular amidation of sp³ C-H bonds: late-stage functionalization of an unactivated methyl group. *J. Am. Chem. Soc.* **2014**, *136*, 4141-4144.
4. Y.-J. Mao, S.-J. Lou, H.-Y. Hao, and D.-Q. Xu, Selective C(sp³)-H and C(sp²)-H fluorination of alcohols using. *Angew. Chem. Int. Ed.* **2018**, *57*, 14085-14089.

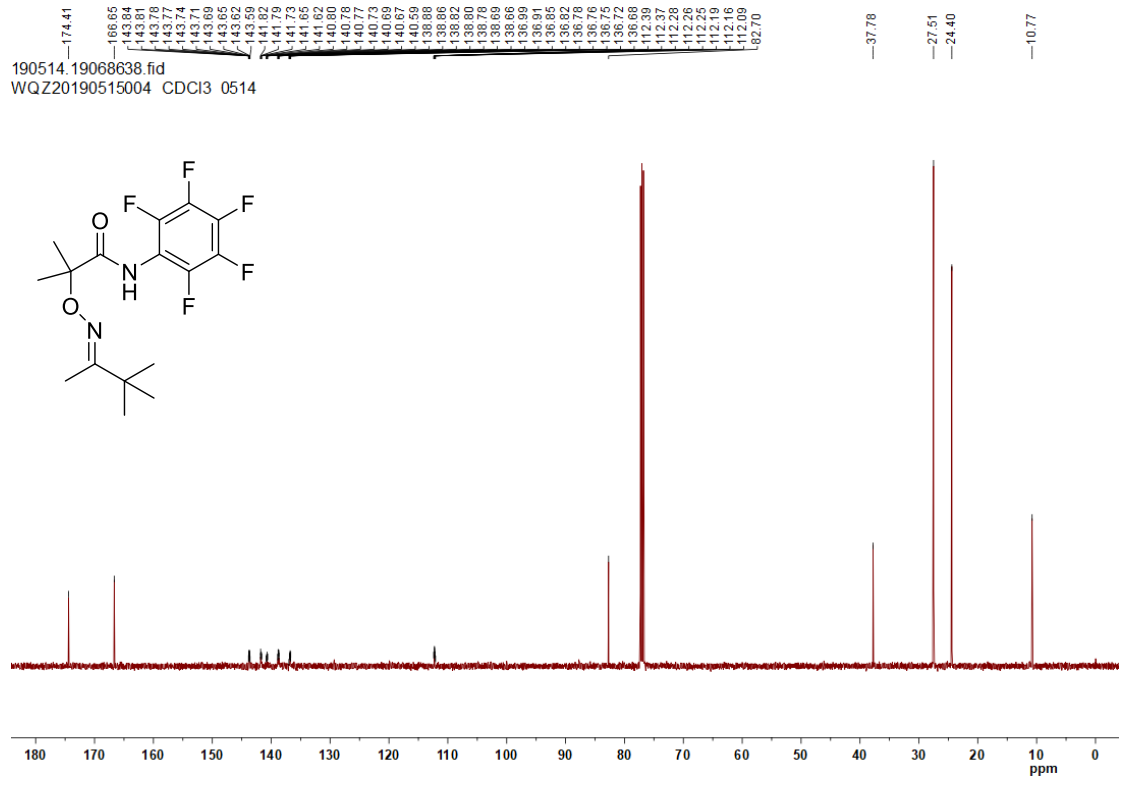
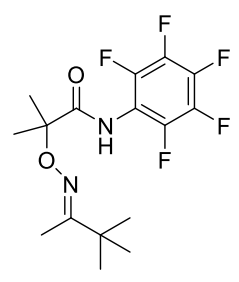
VIII. NMR Spectra

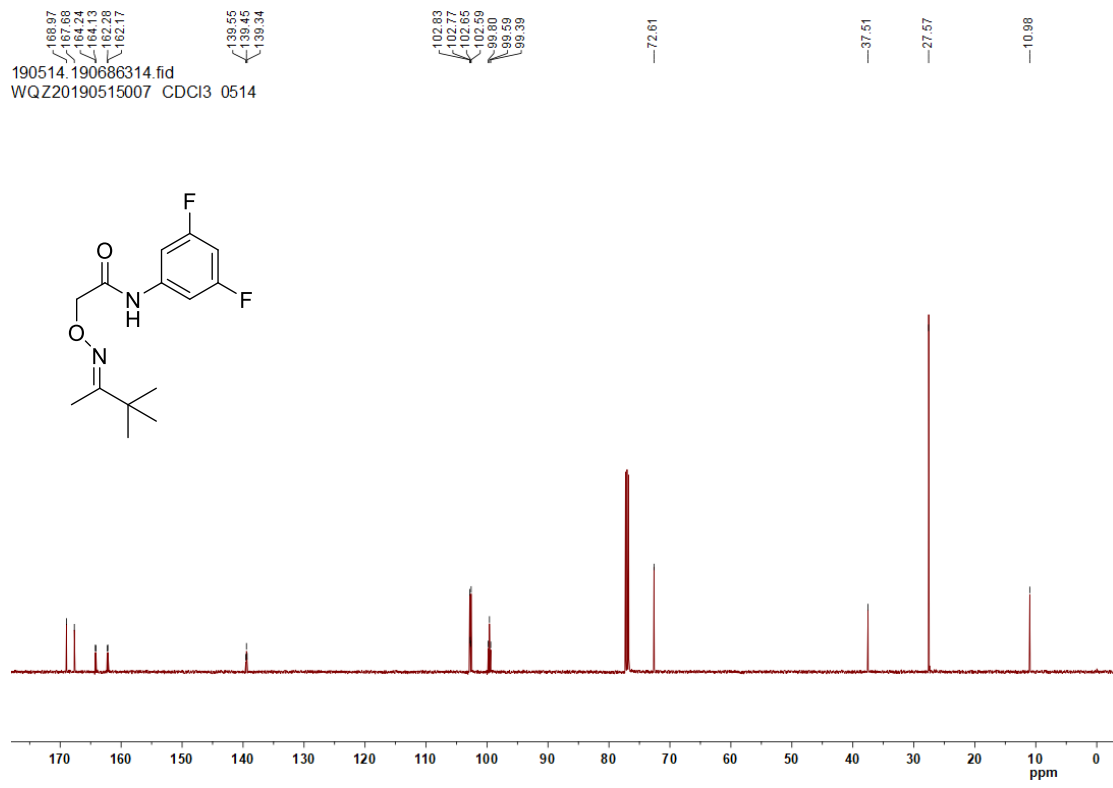
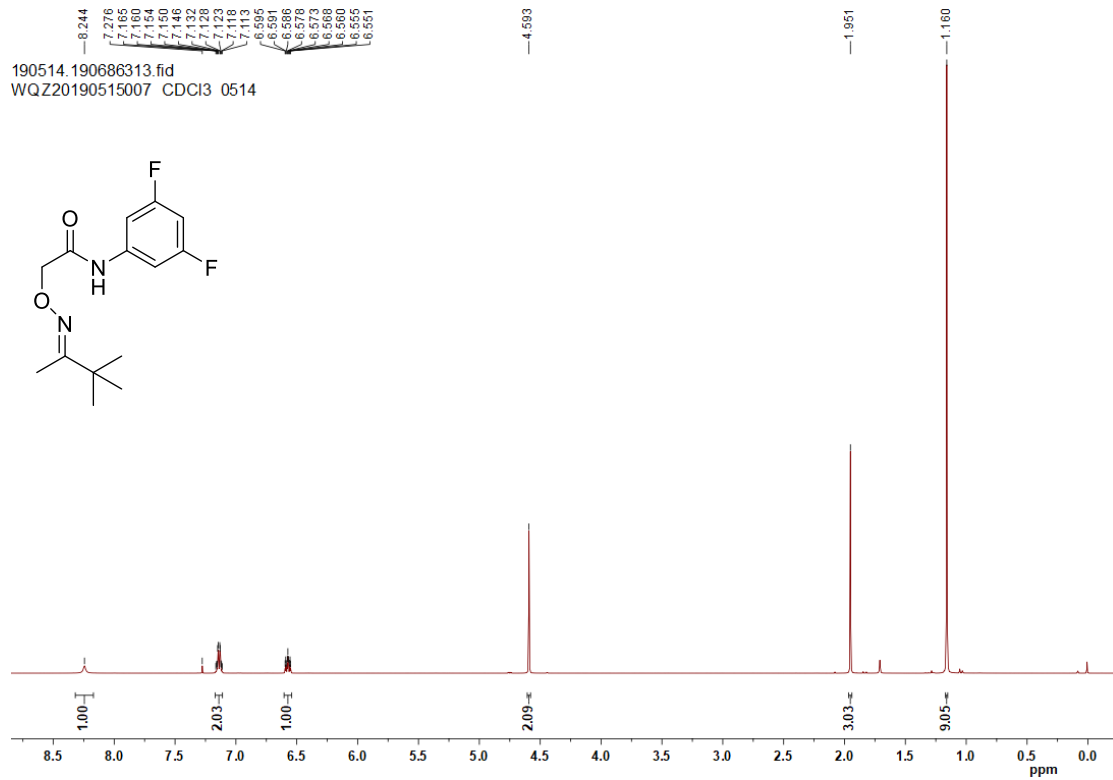


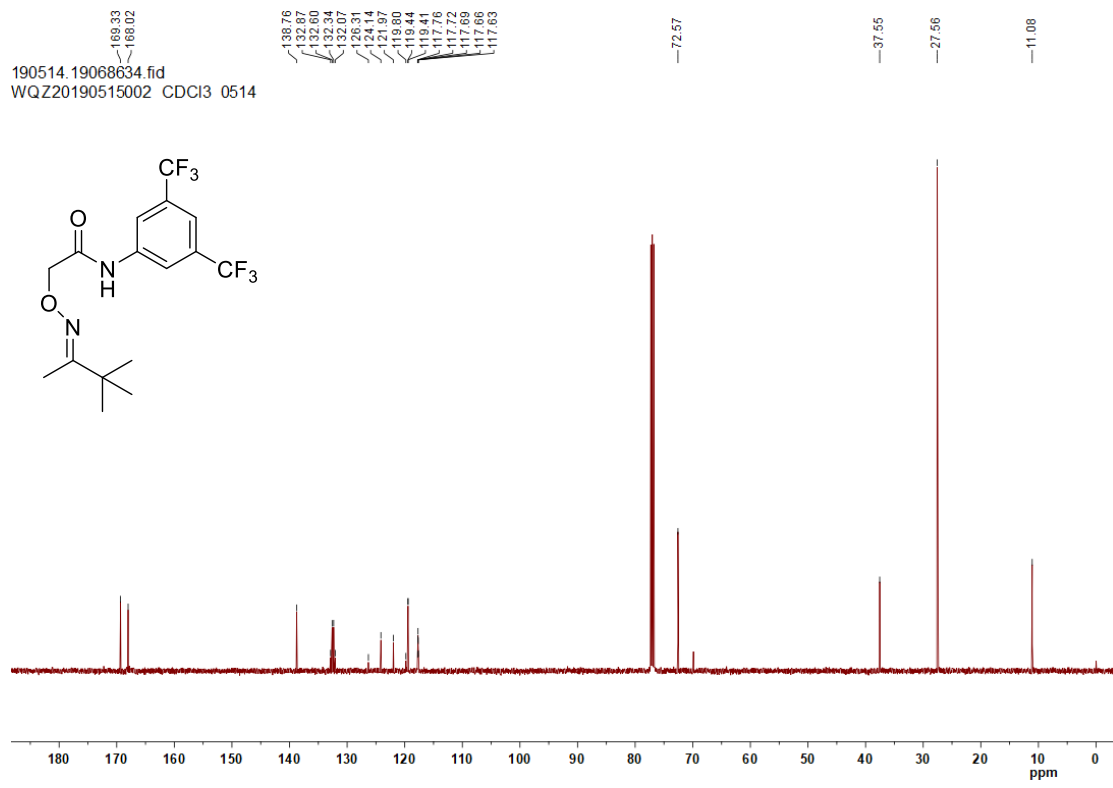
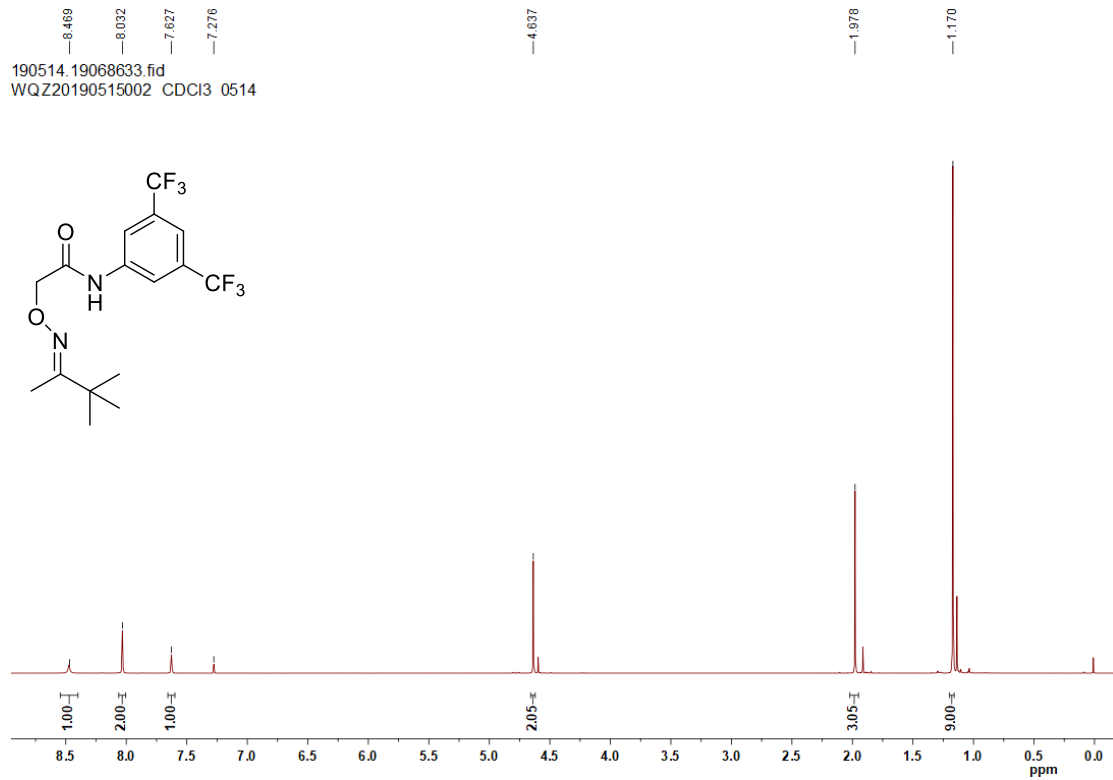
190514.19068637.fid
 WQZ20190515004 CDCl3 0514



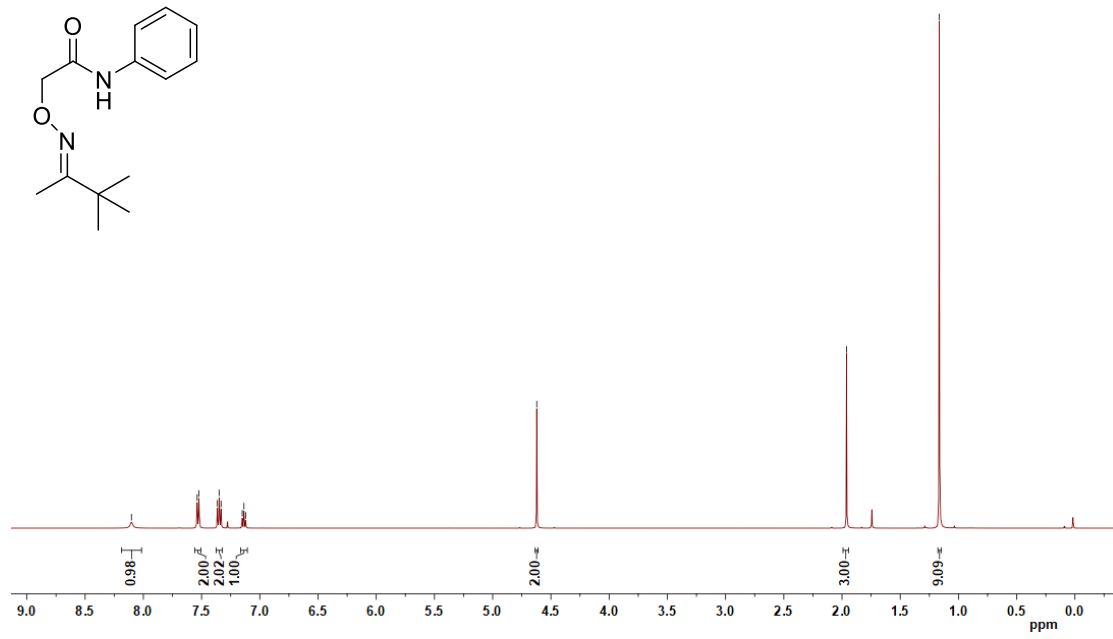
190514.19068638.fid
 WQZ20190515004 CDCl3 0514



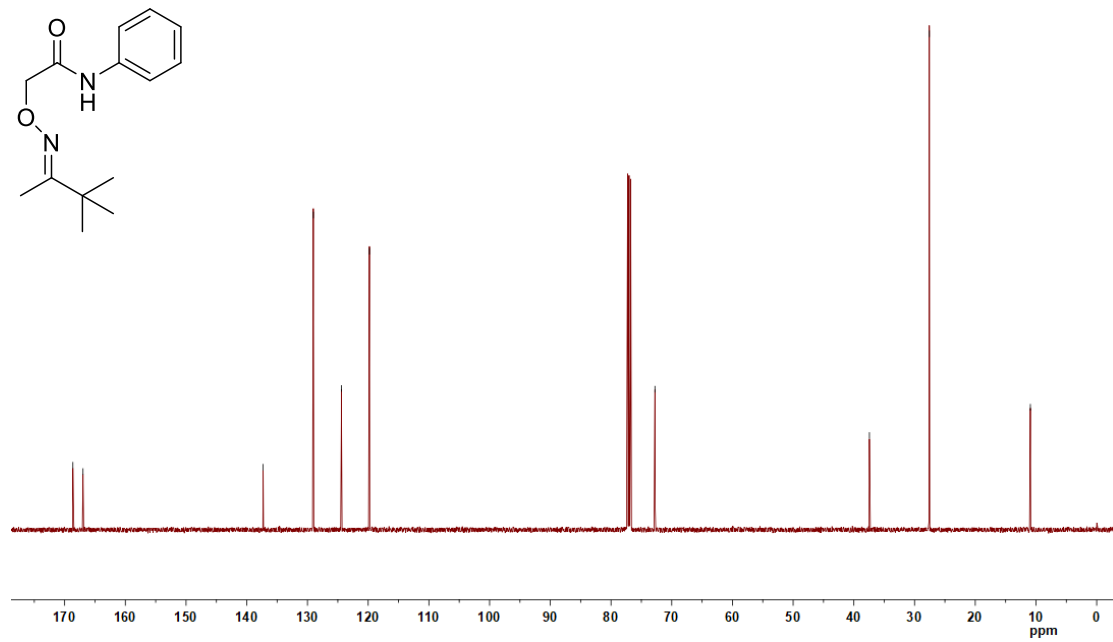




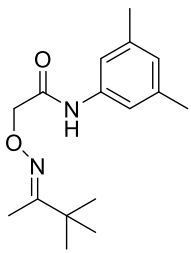
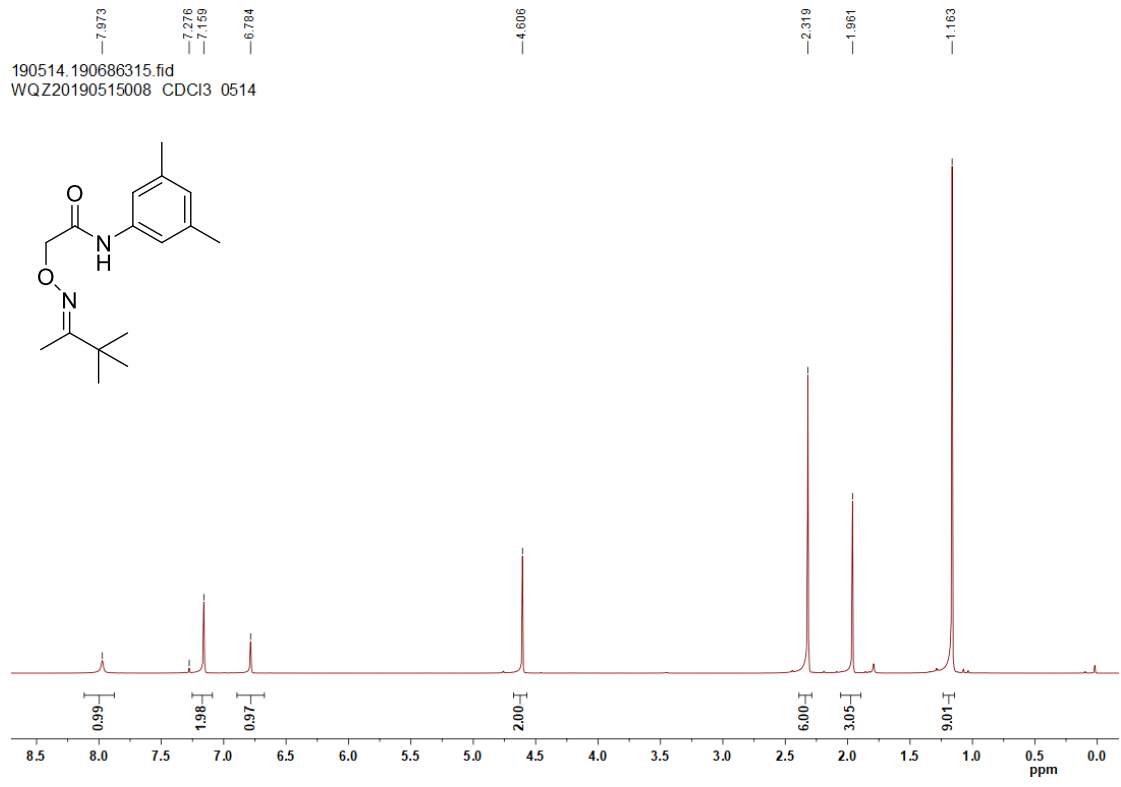
190514.19068635.fid
 WQZ20190515003 CDCI3 0514



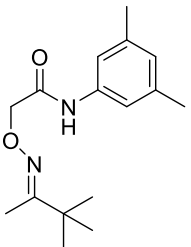
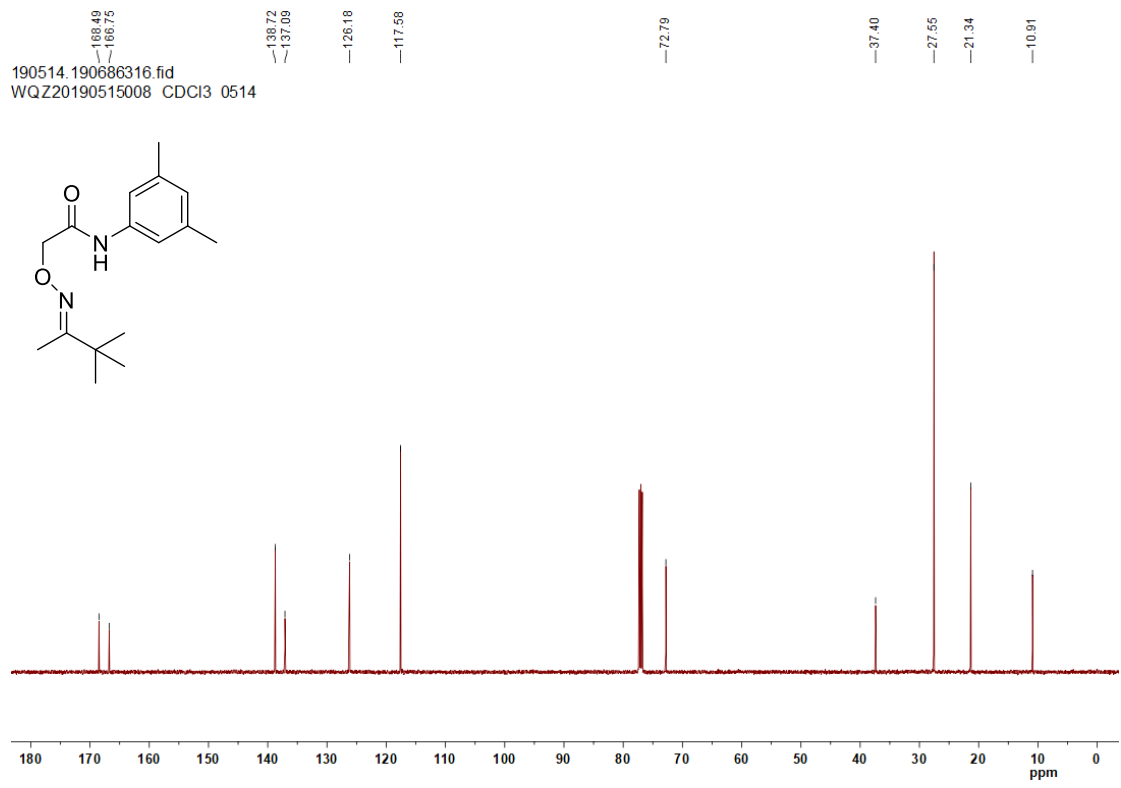
190514.19068636.fid
 WQZ20190515003 CDCI3 0514



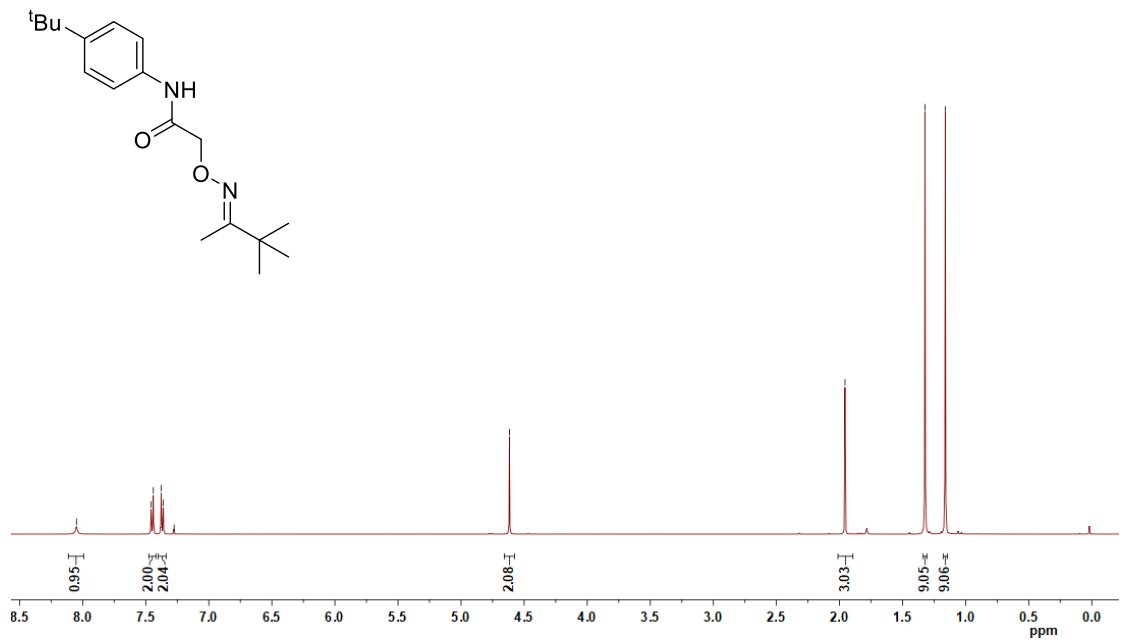
190514.190686315.fid
 WQZ20190515008 CDCl3 0514



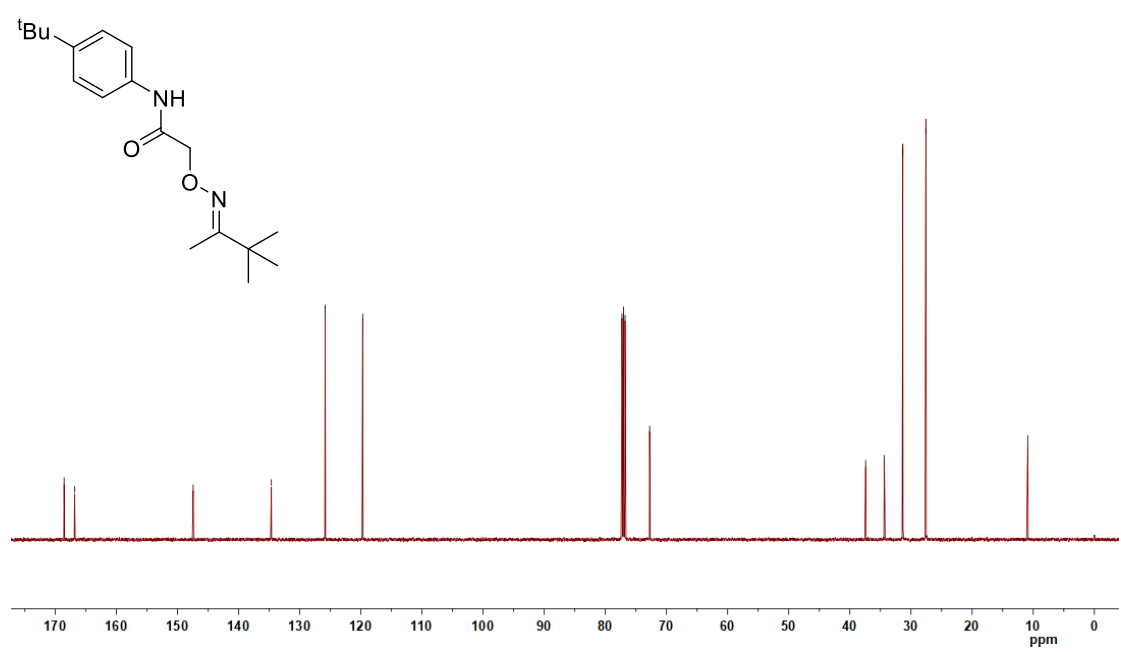
190514.190686316.fid
 WQZ20190515008 CDCl3 0514

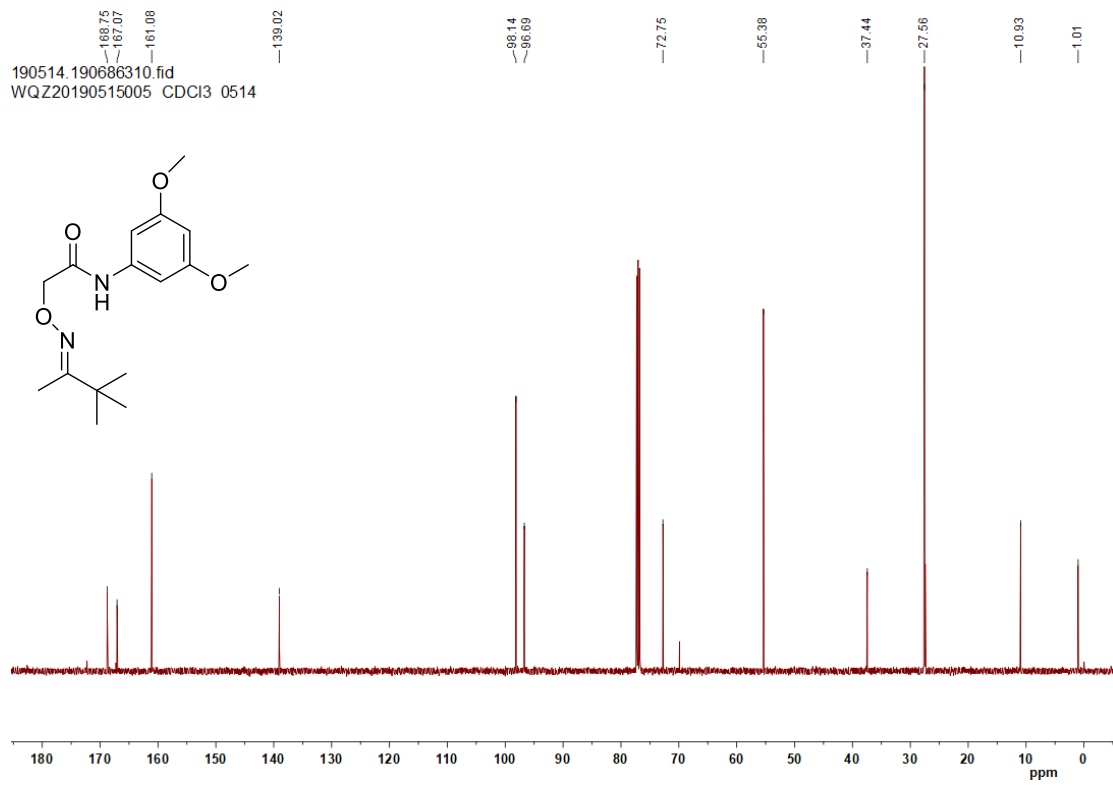
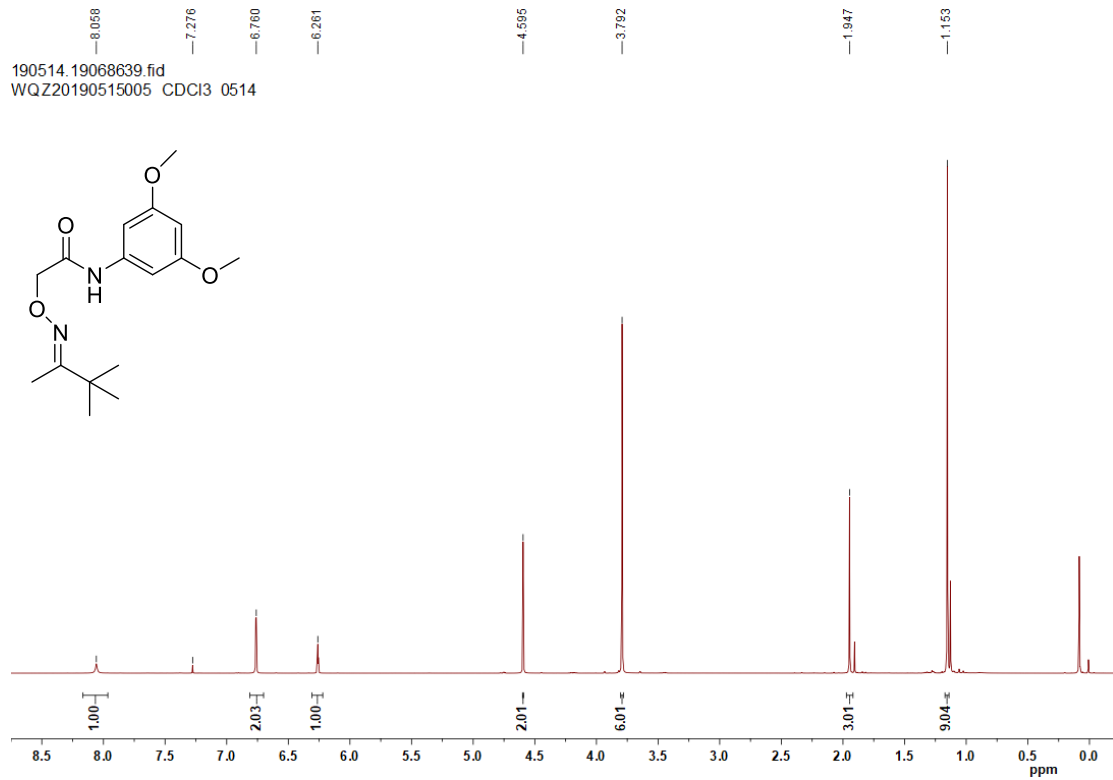


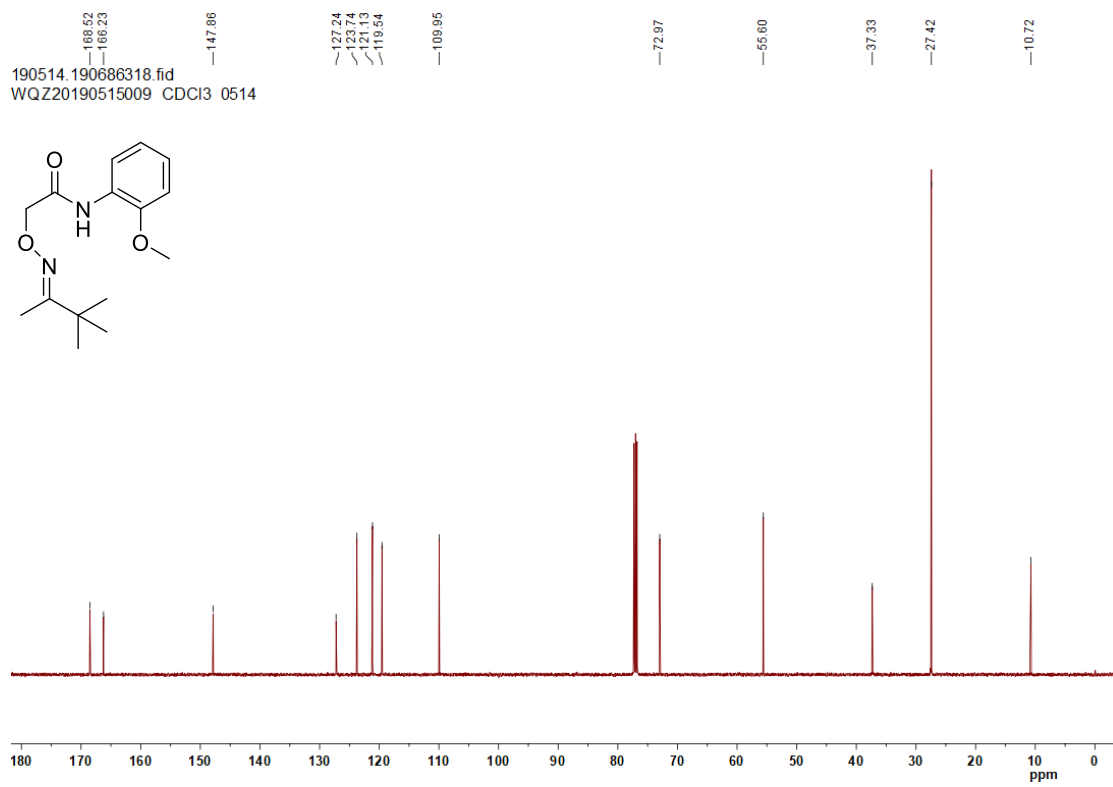
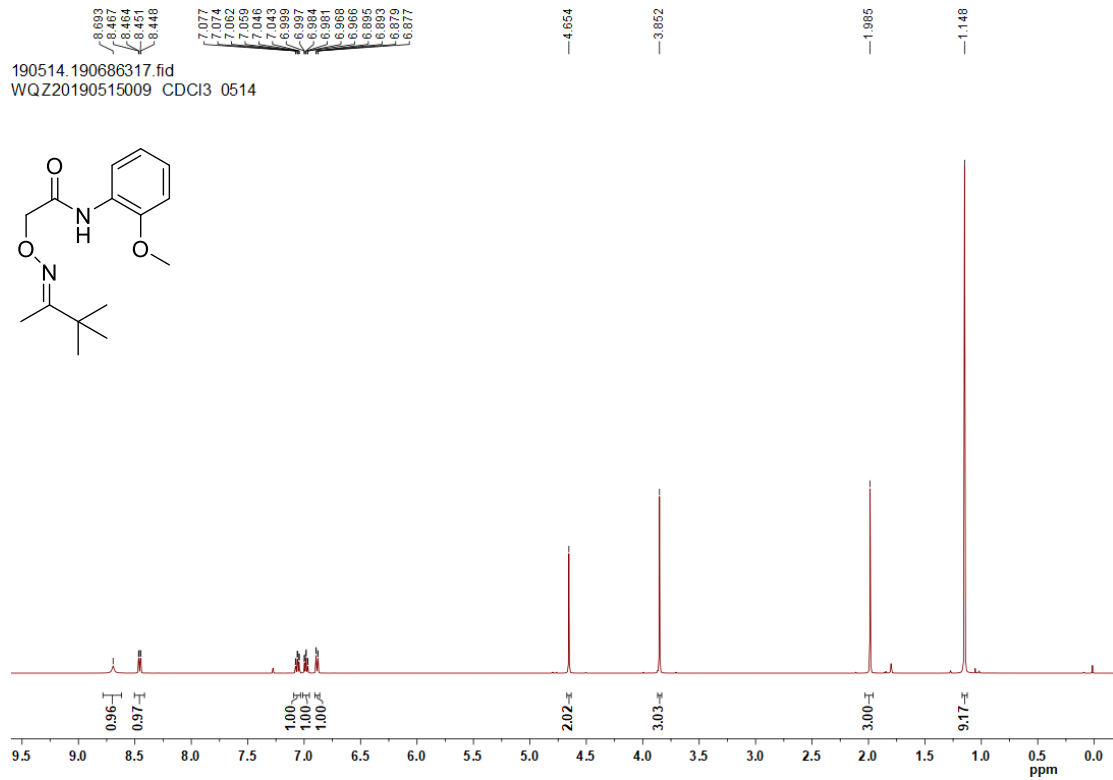
190514.190686311.fid
WQZ20190515006 CDCl3 0514

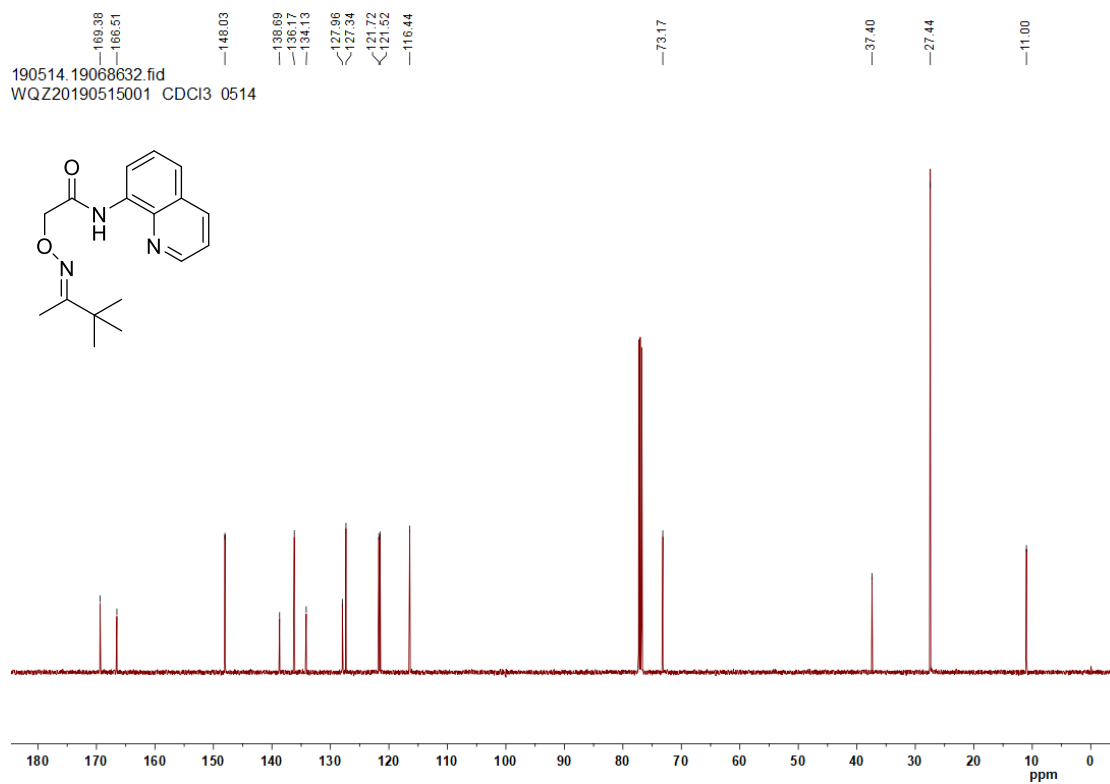
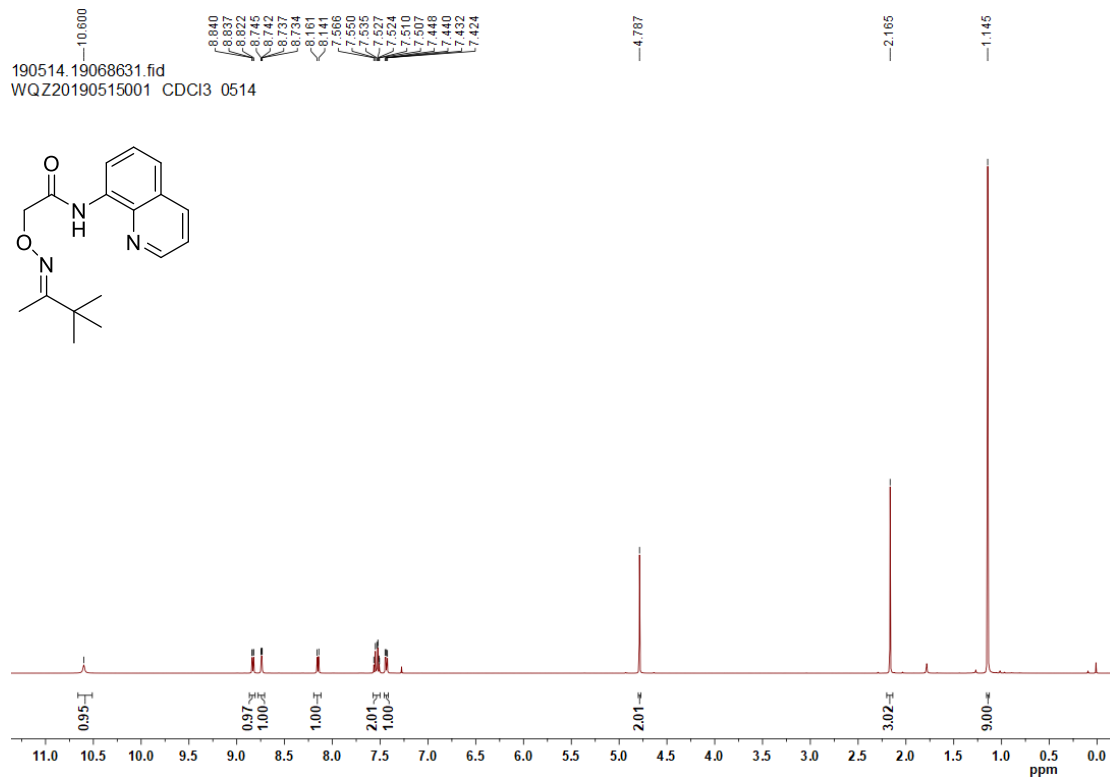


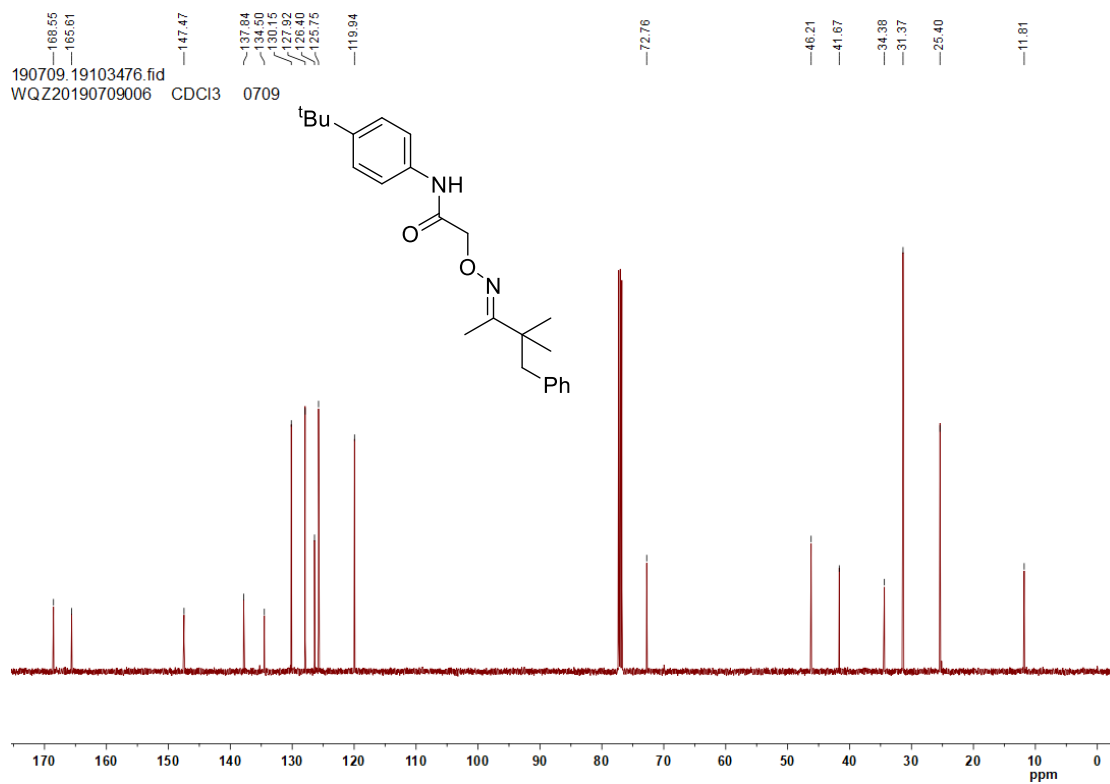
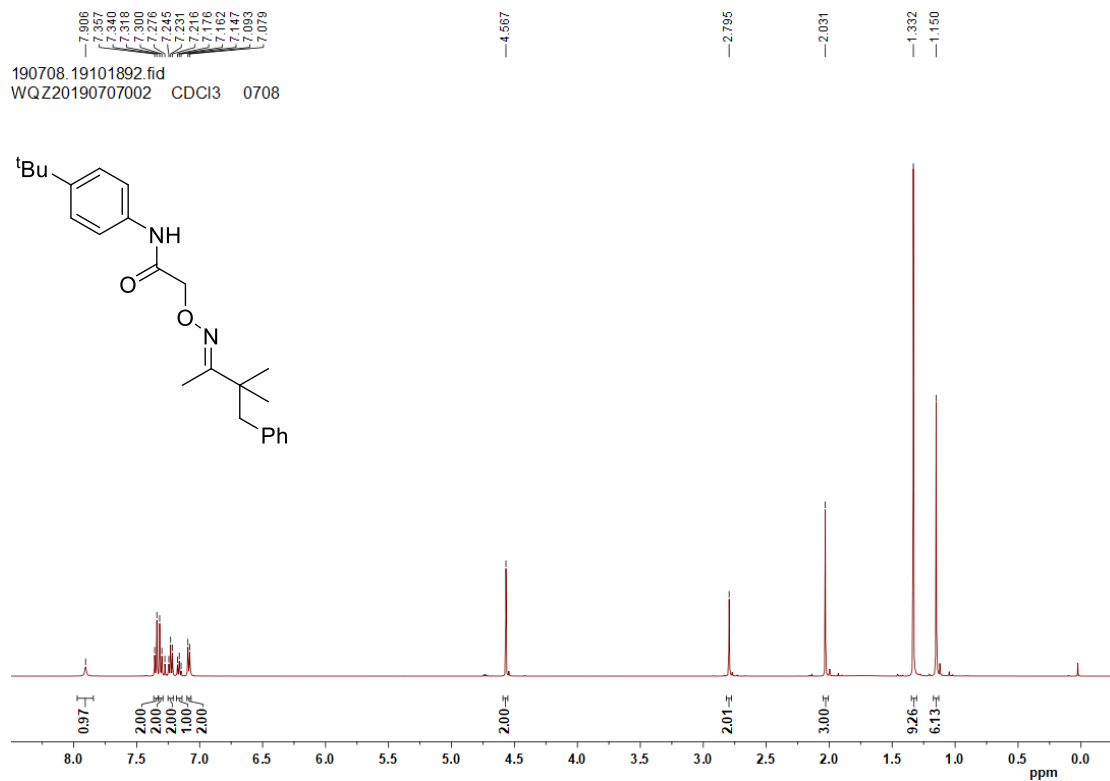
190514.190686312.fid
WQZ20190515006 CDCl3 0514

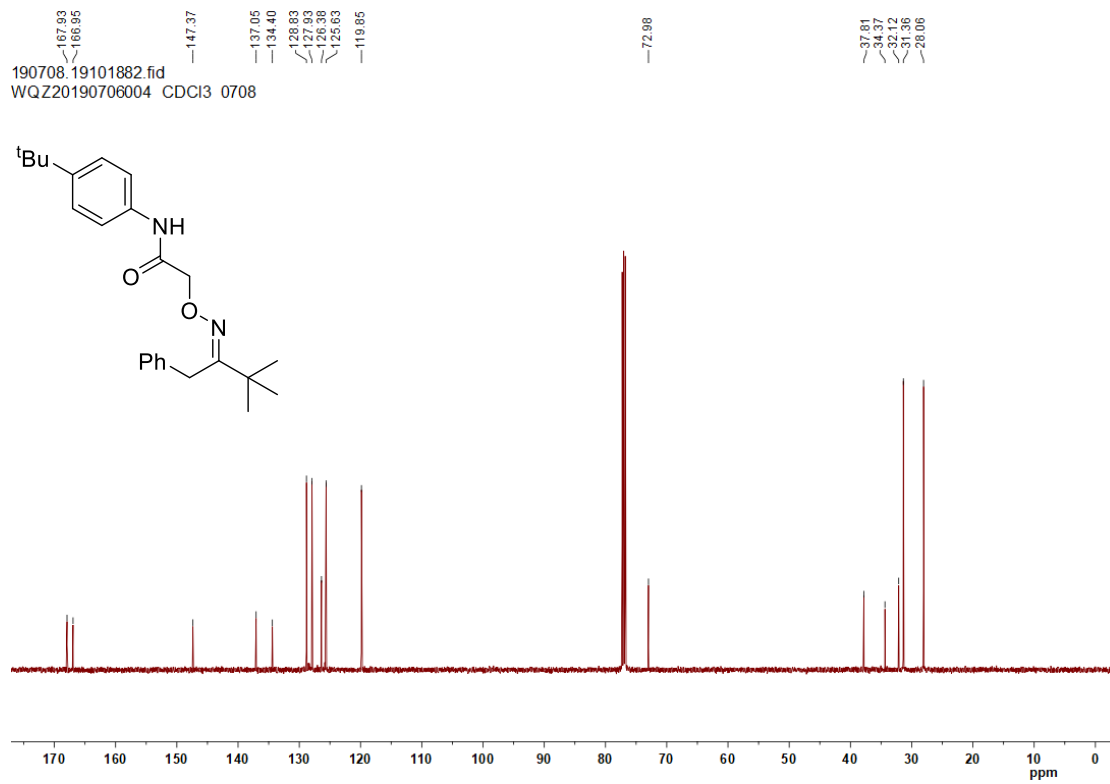
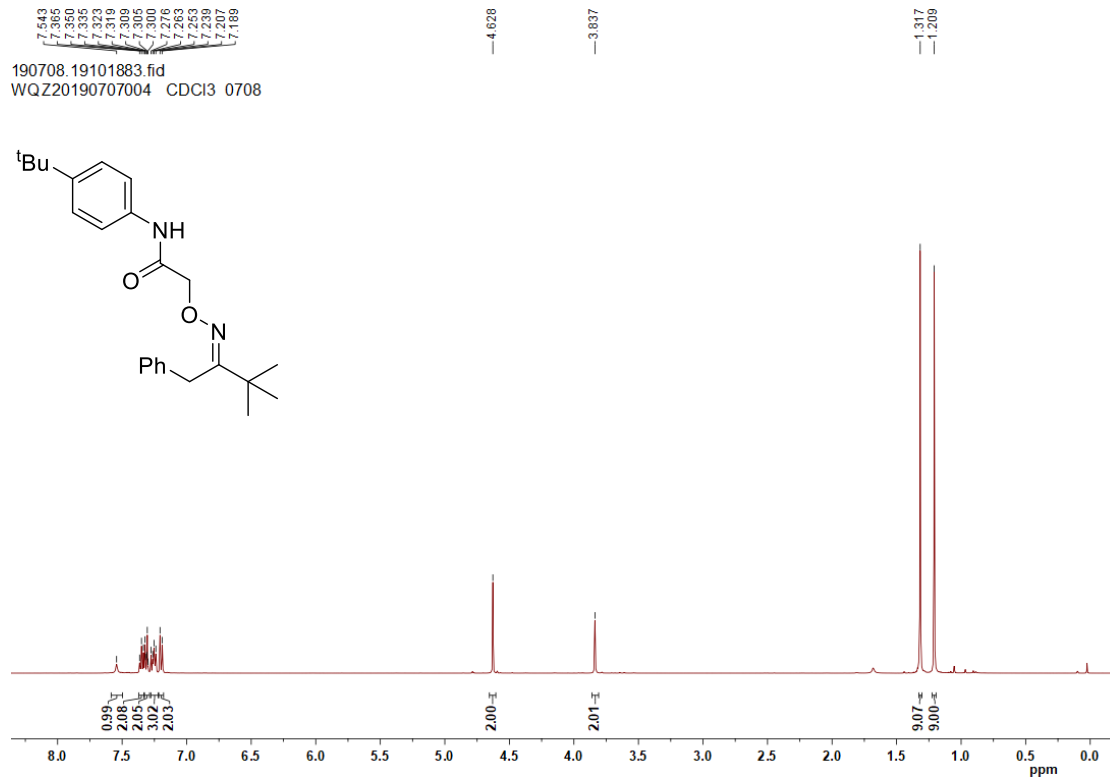










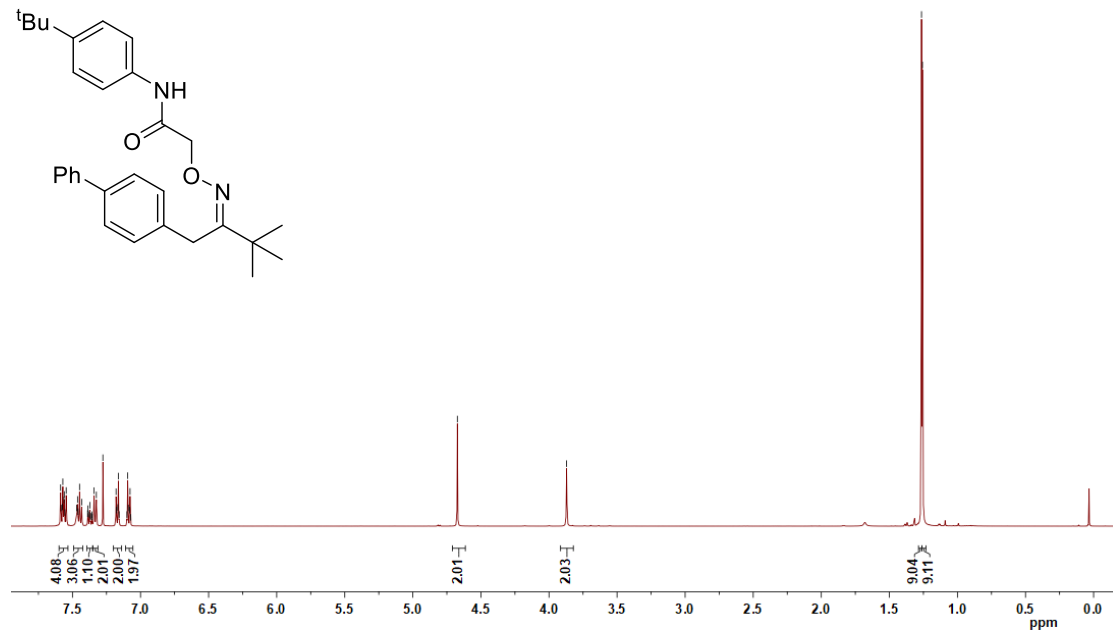


7.587
7.593
7.574
7.563
7.560
7.546
7.469
7.448
7.432
7.389
7.386
7.384
7.375
7.362
7.359
7.357
7.354
7.341
7.325
7.307
7.287
7.176
7.166
7.162
7.157
7.099
7.094
7.080
7.080
7.077
7.072
4.673

3.871

1.264
1.257

200530.20025951.fid
WQZ20200530001 CDCl3 0530

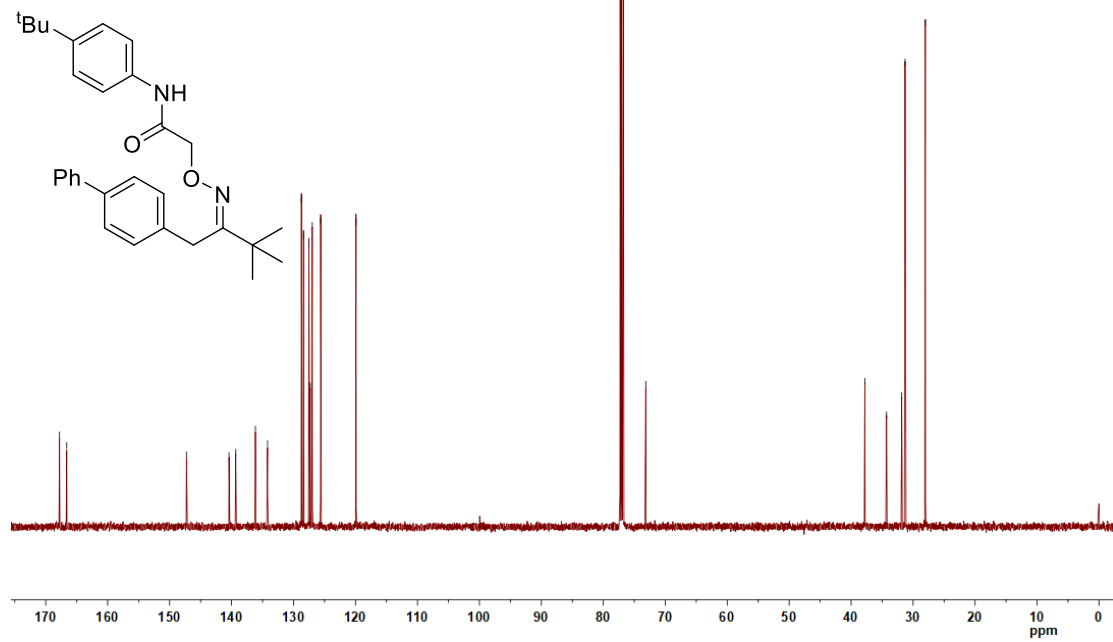


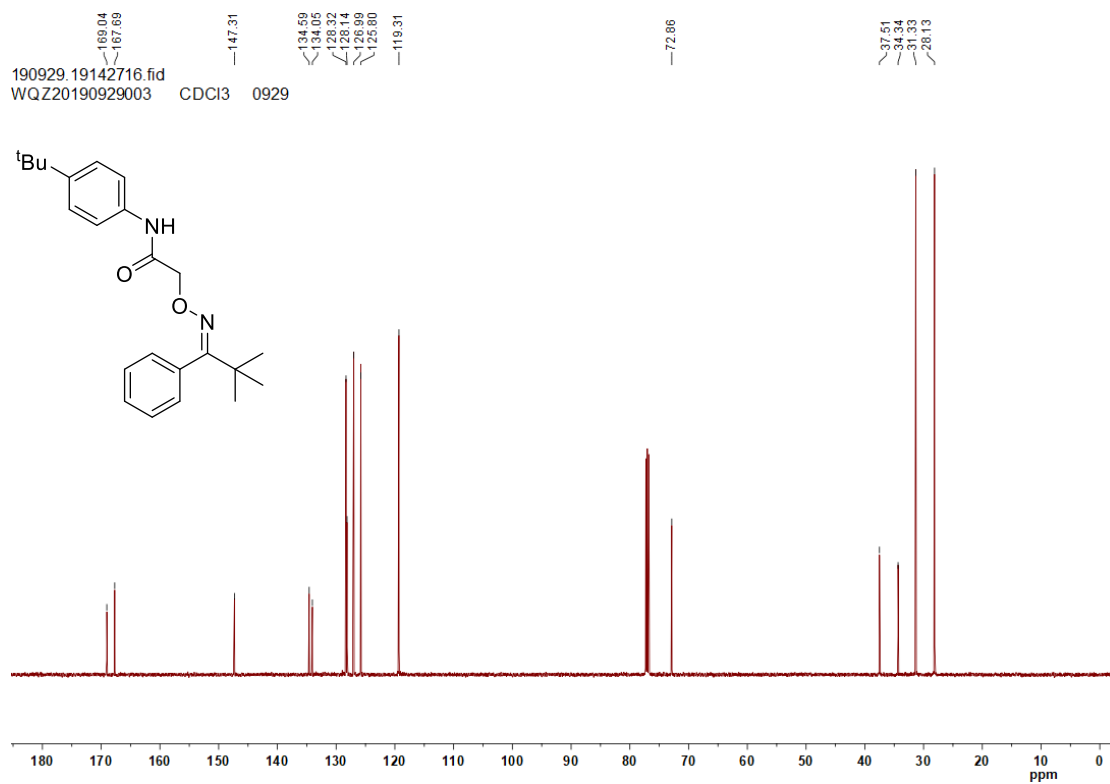
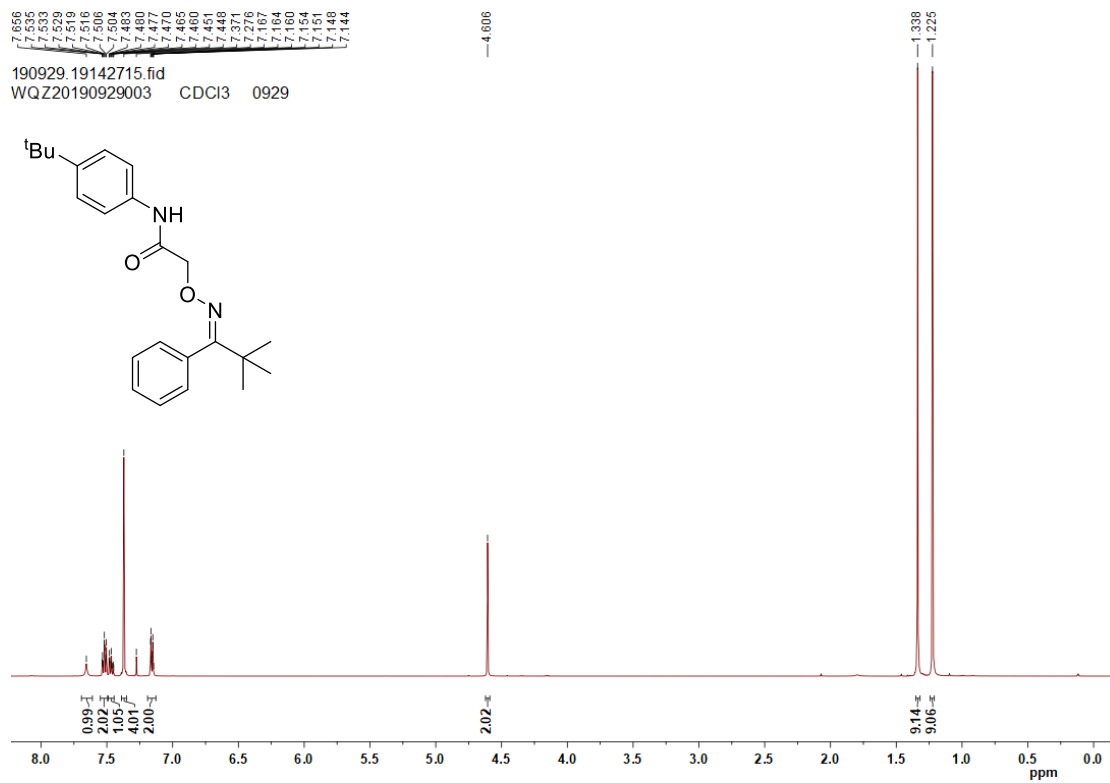
167.77
166.61
147.26
140.41
139.33
136.16
134.20
128.73
127.50
127.51
127.31
126.98
125.62
119.92

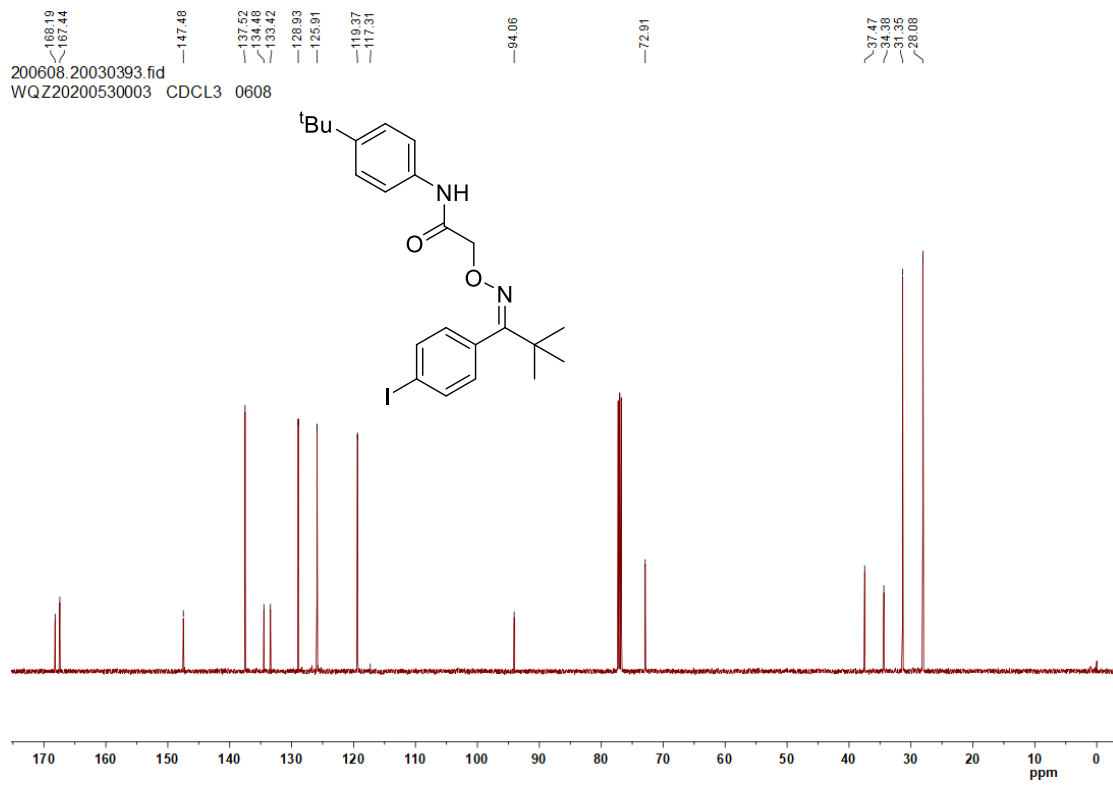
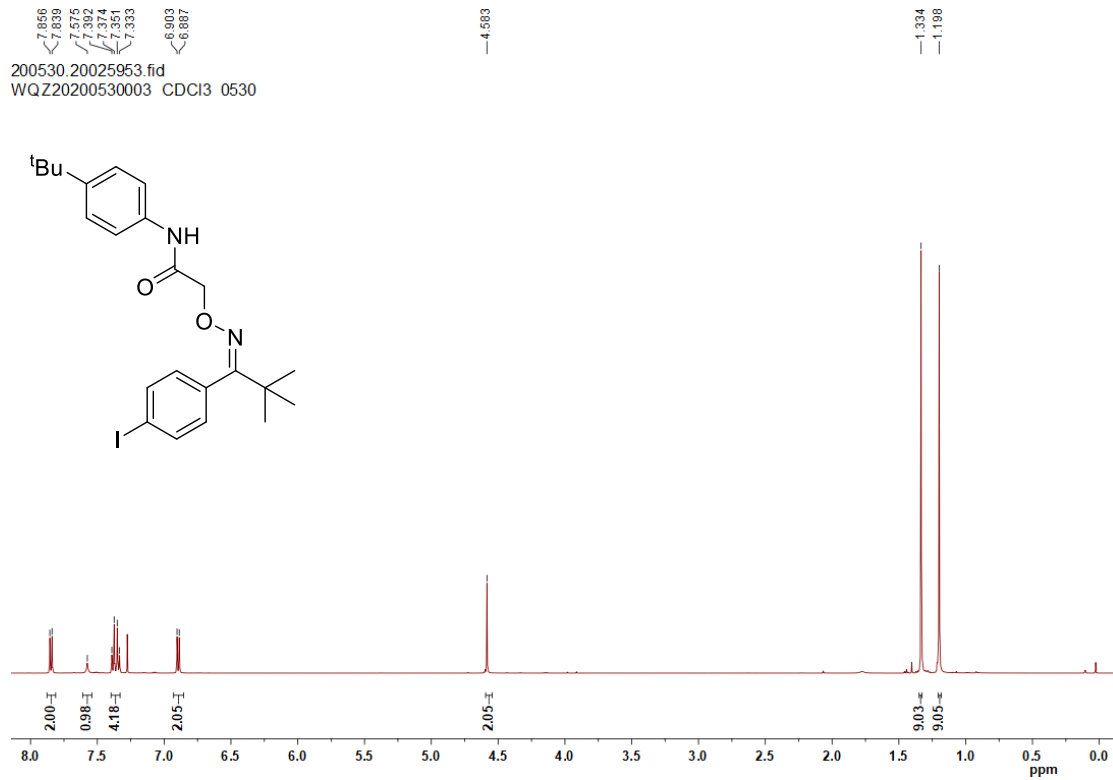
73.15

37.70
34.29
31.84
31.29
28.03

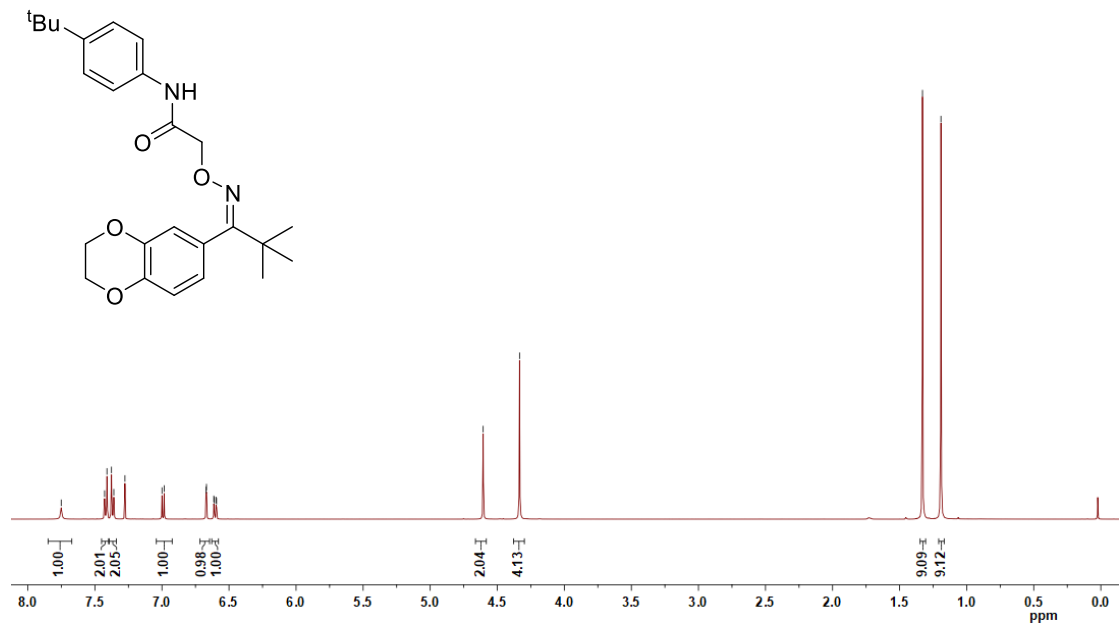
200606.20030391.fid
WQZ20200530001 CDCl3 0606



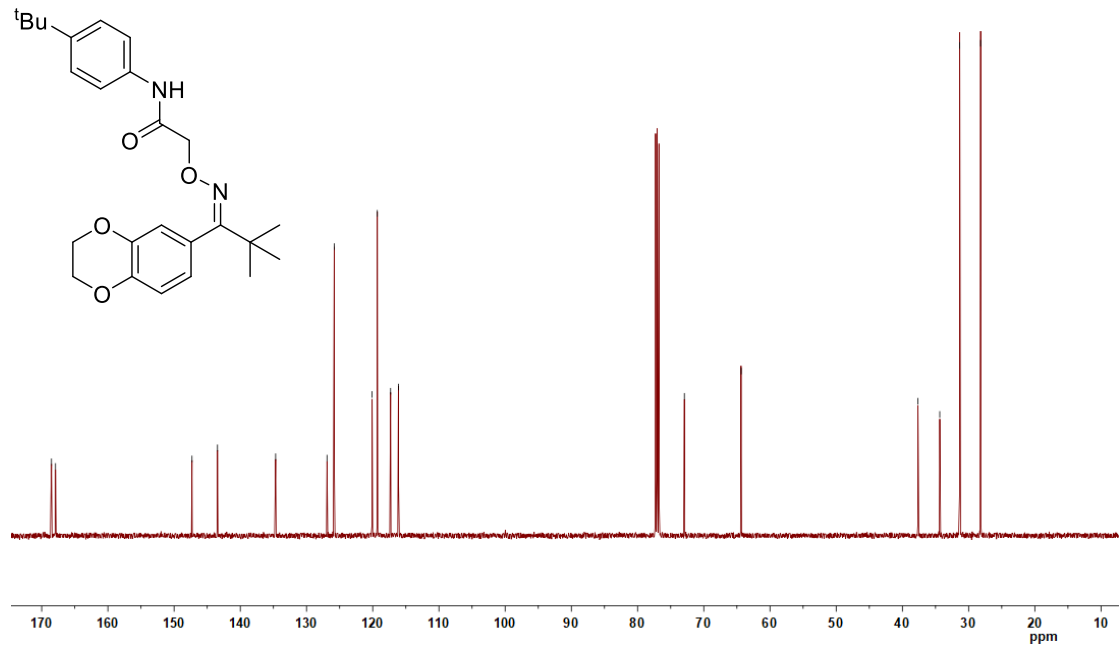




191128.19179051.fid
 WQZ20191128001 CDCl₃ 1128

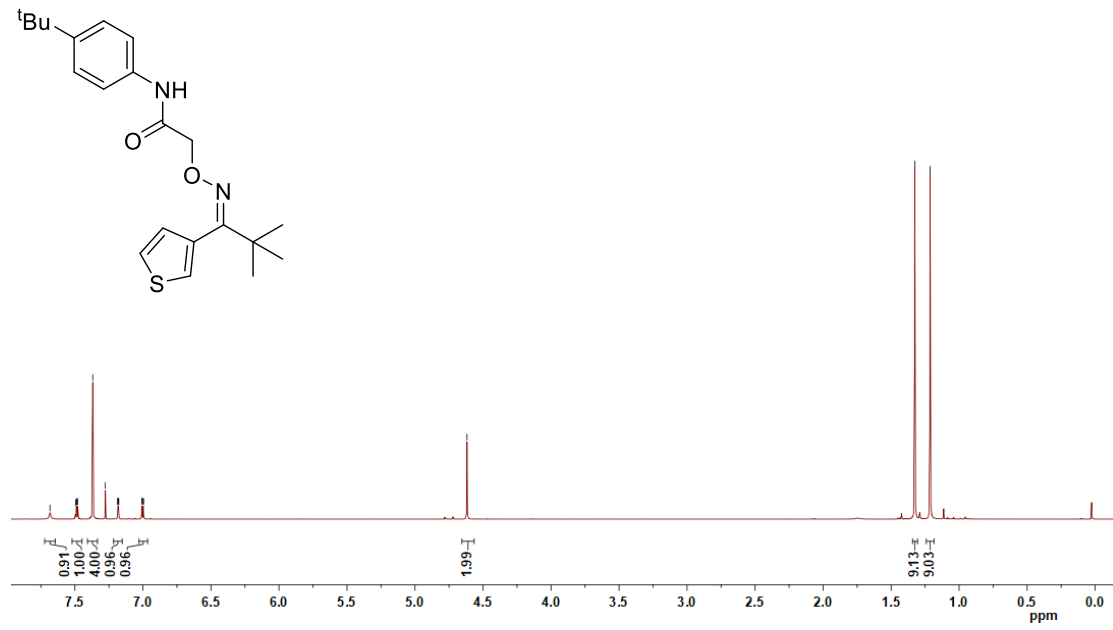


191130.1918007.fid
 WQZ20191130003 CDCl₃ 1130



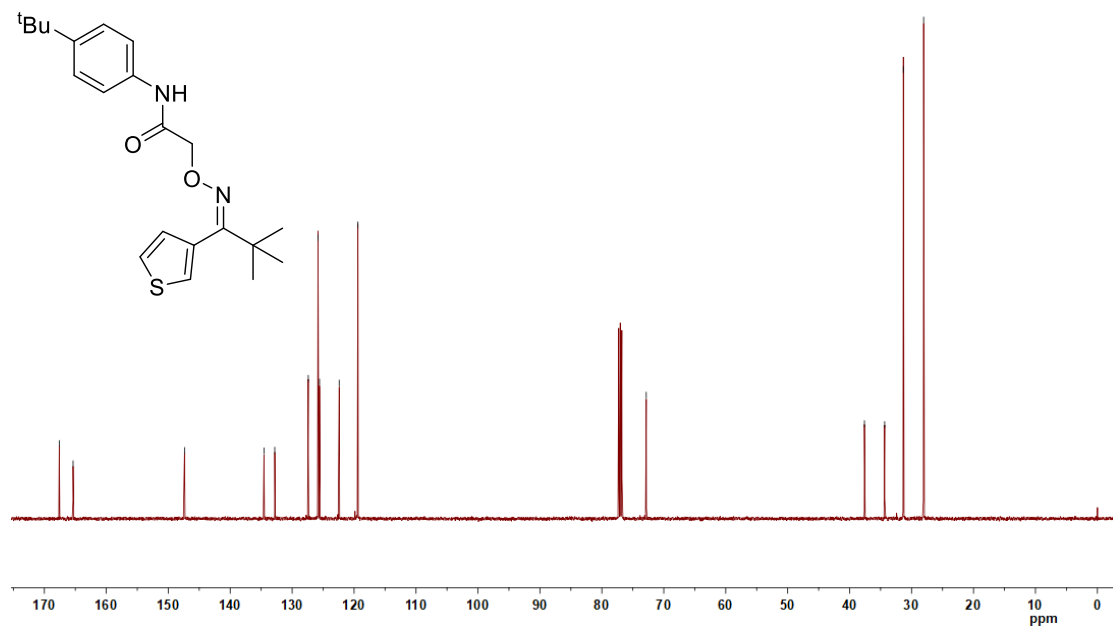
7.683
7.495
7.490
7.485
7.480
7.369
7.276
7.186
7.183
7.180
7.178
7.006
6.998
6.996

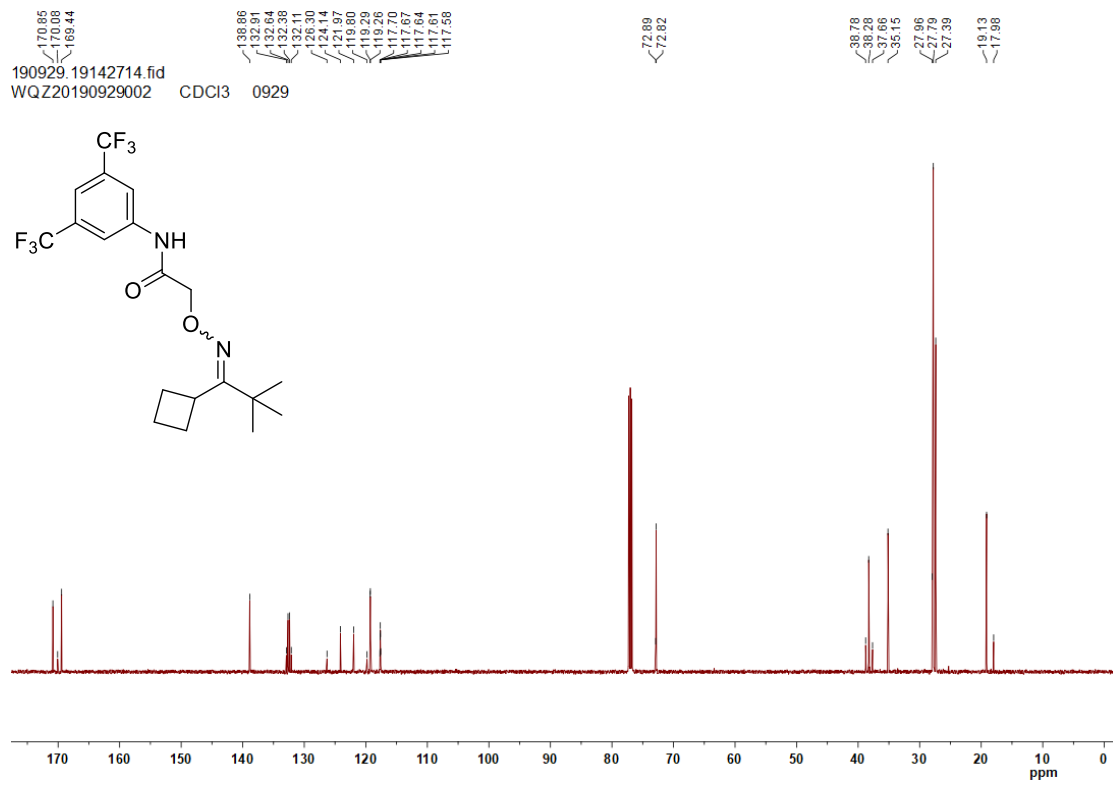
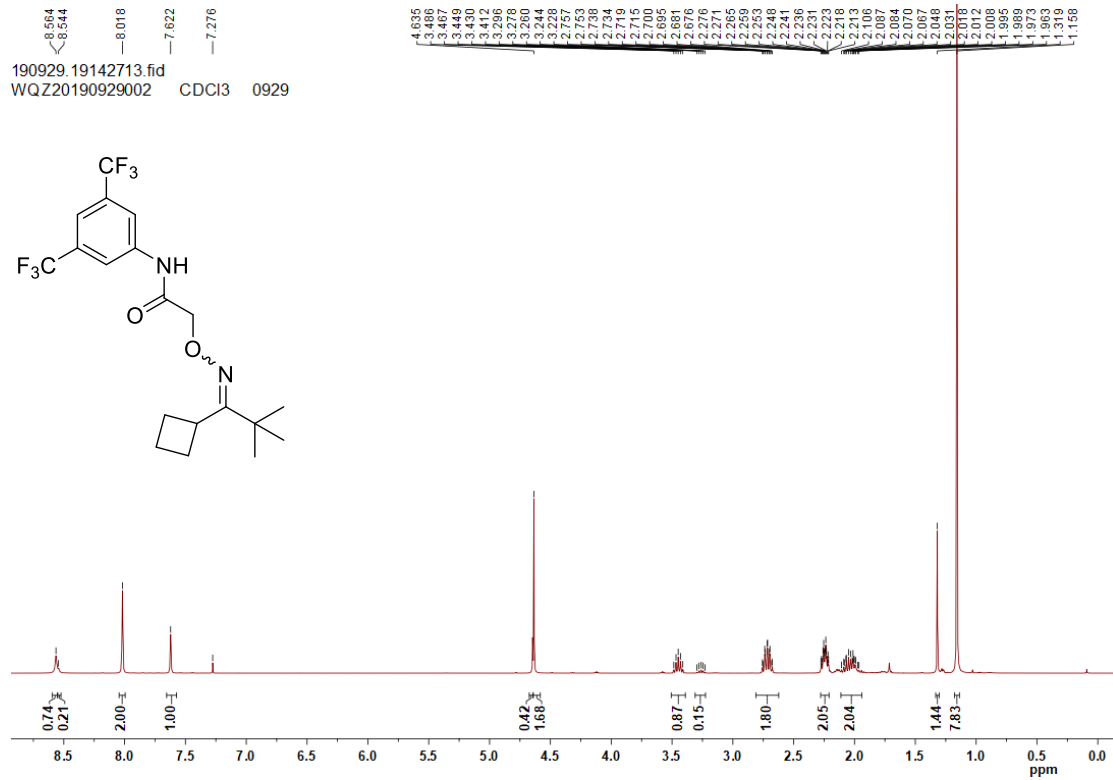
200530.20025952.fid
WQZ20200530002 CDCl3 0530

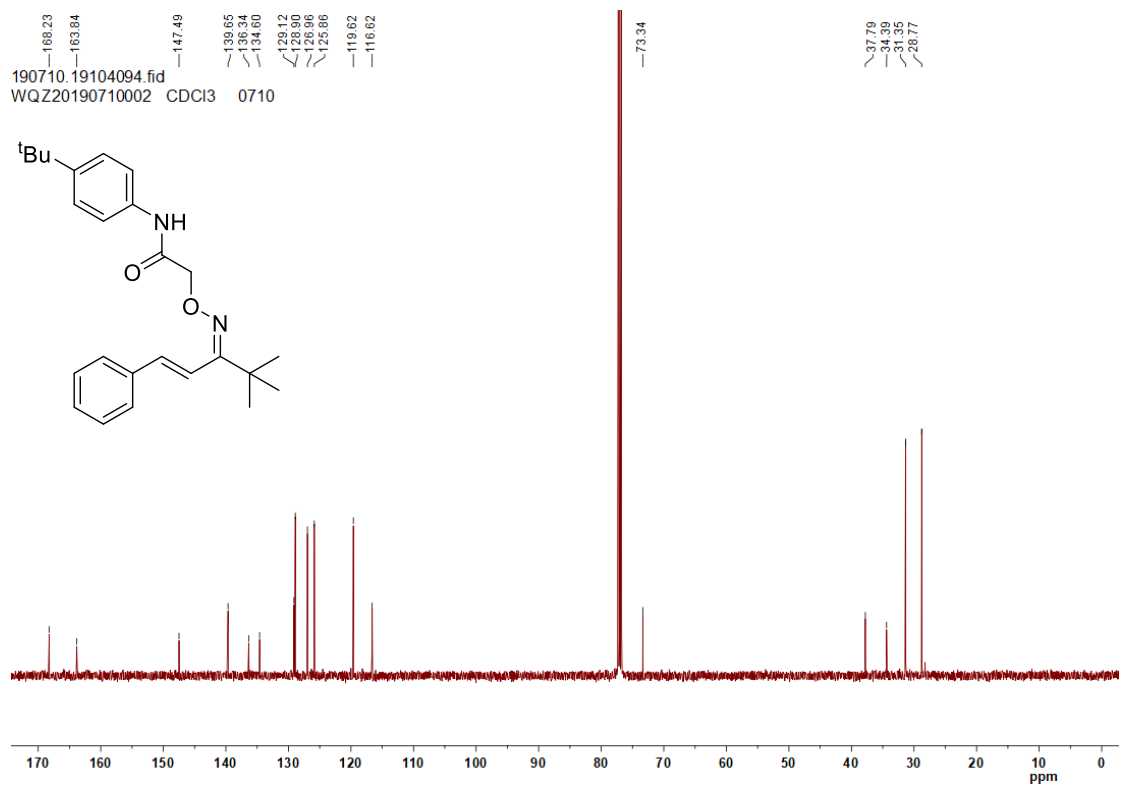
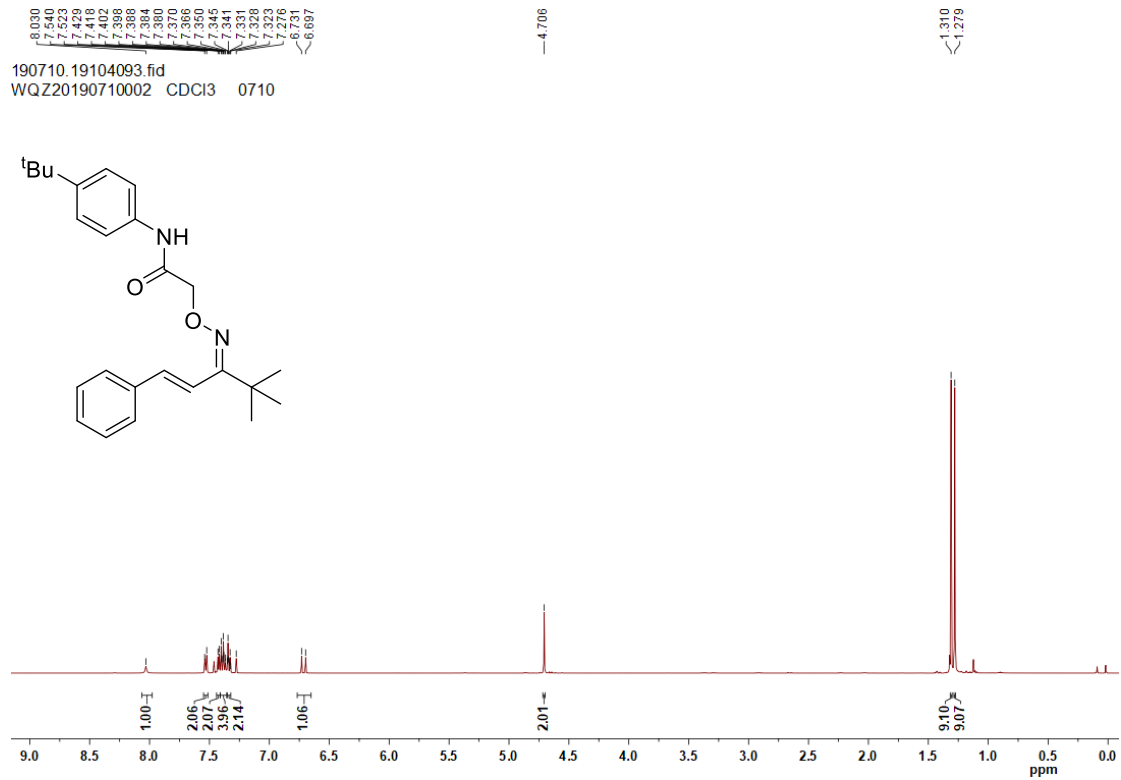


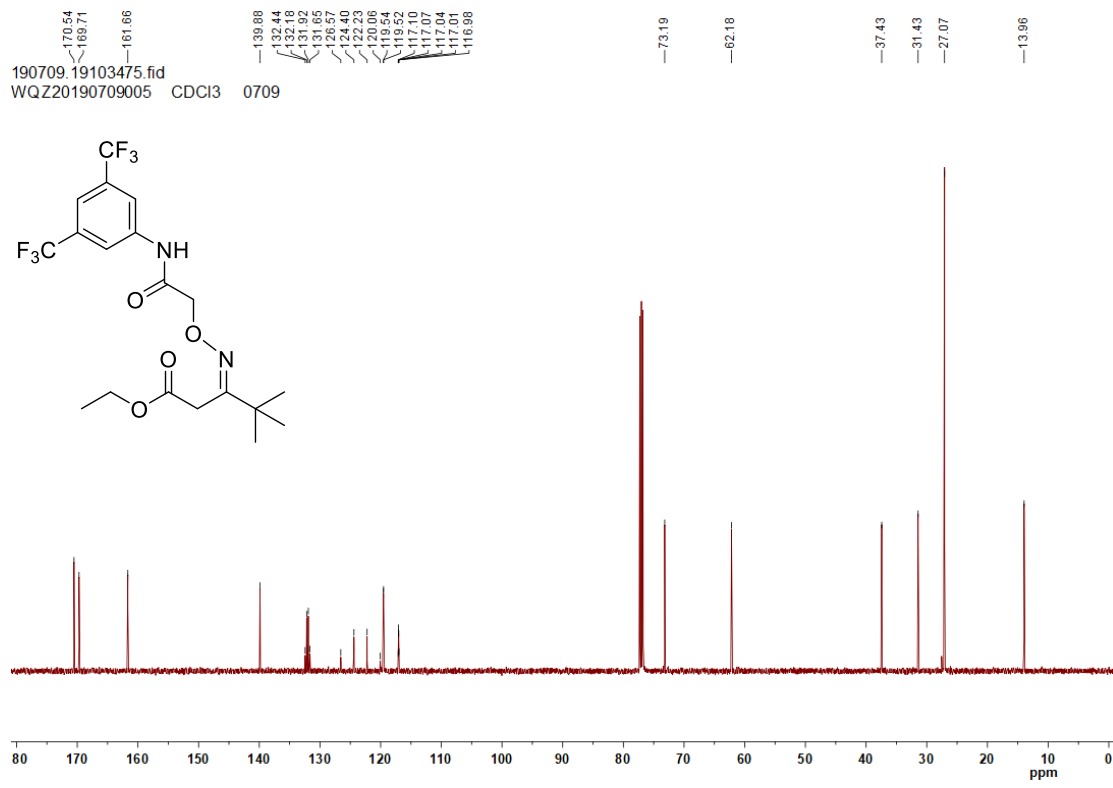
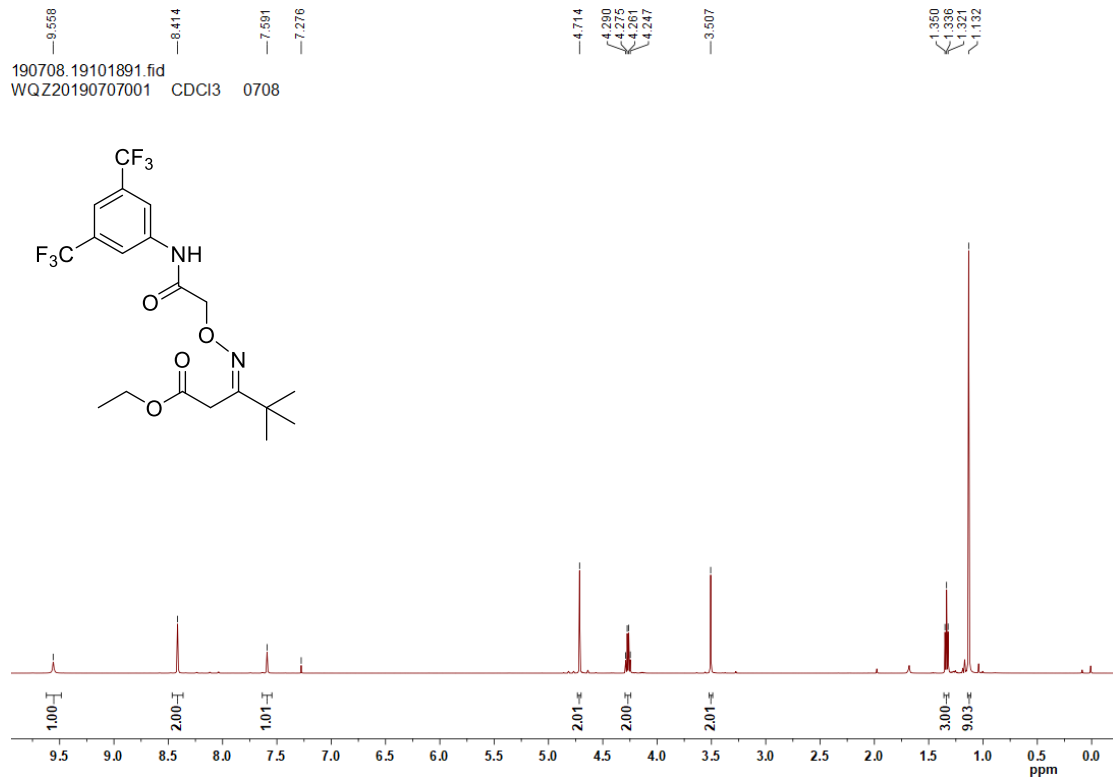
167.59
165.38
147.37
134.54
132.80
127.40
125.82
125.58
122.40
119.38

200606.20030392.fid
WQZ20200530002 CDCl3 0606

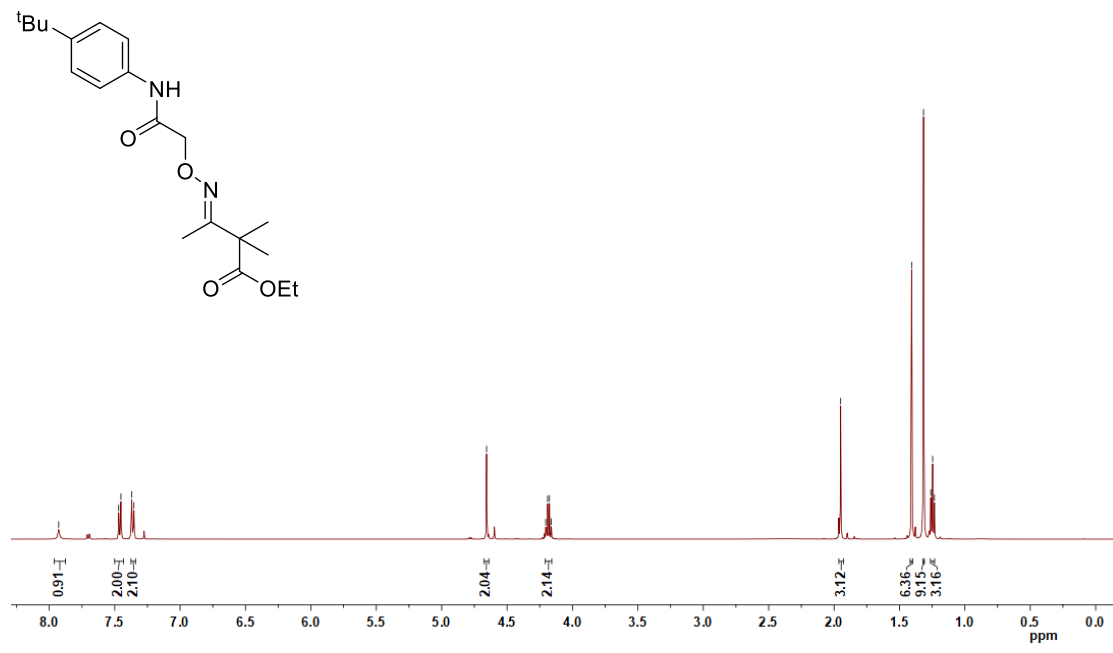




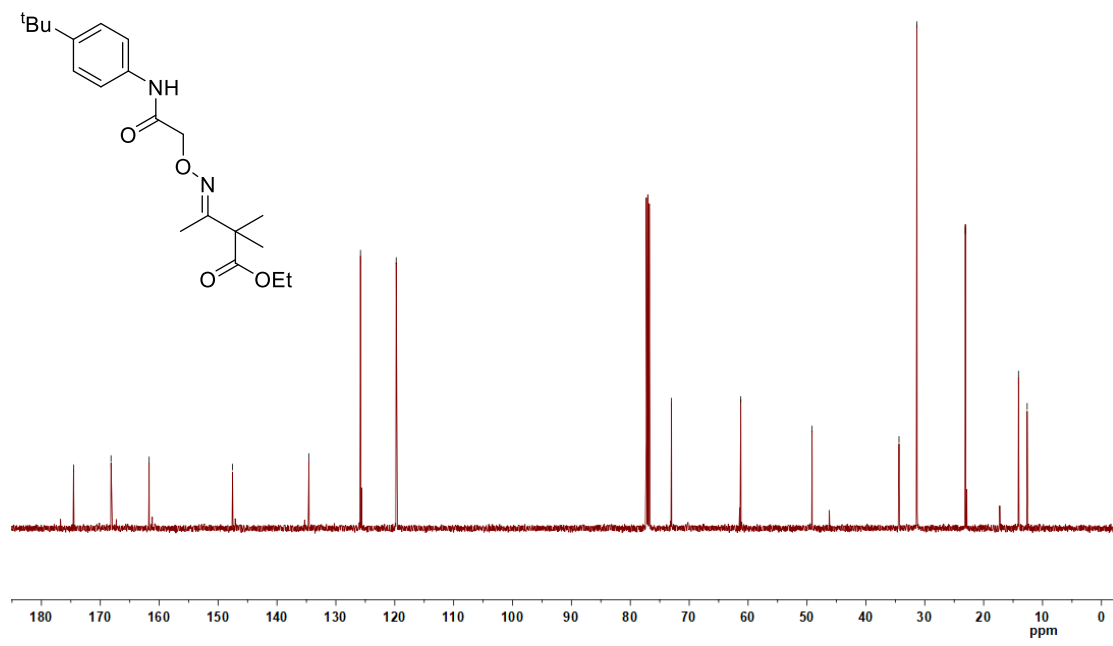


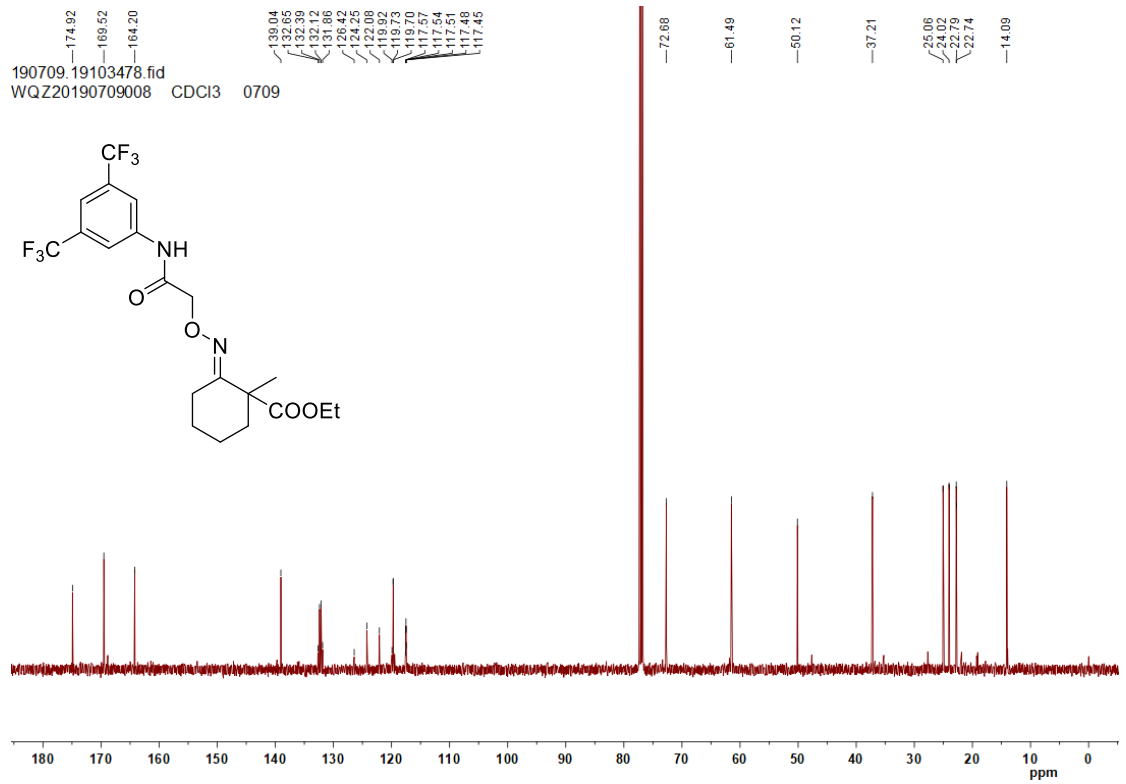
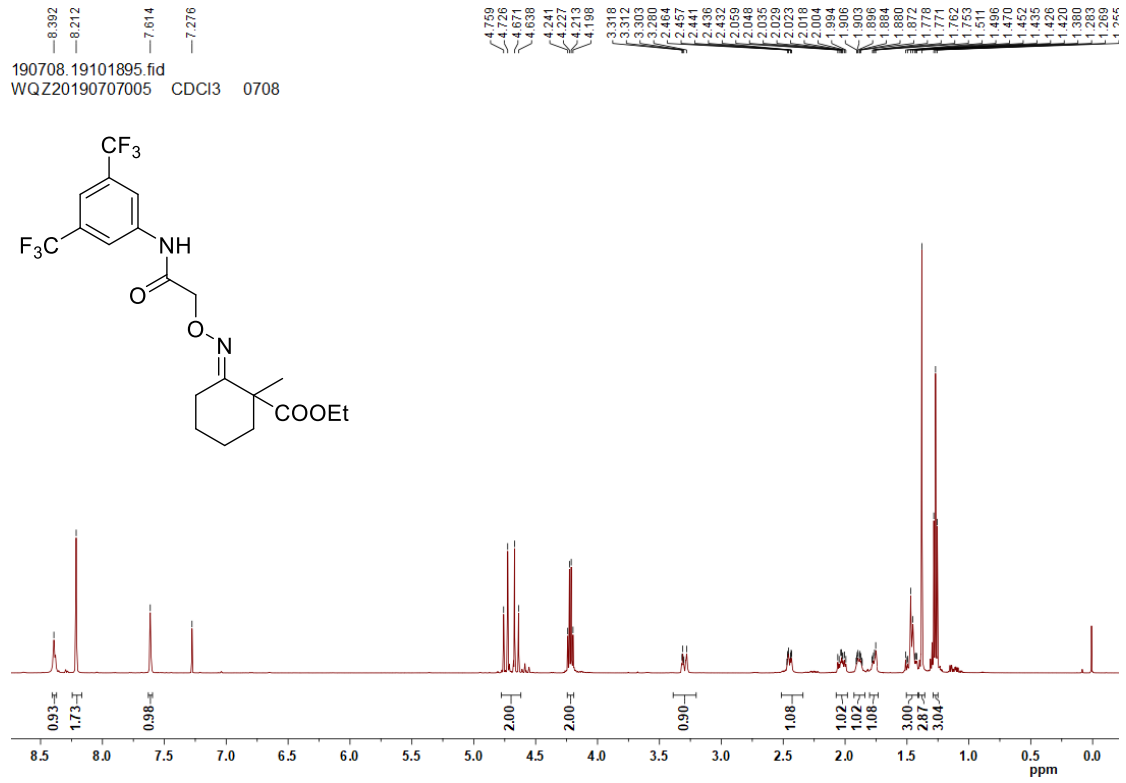


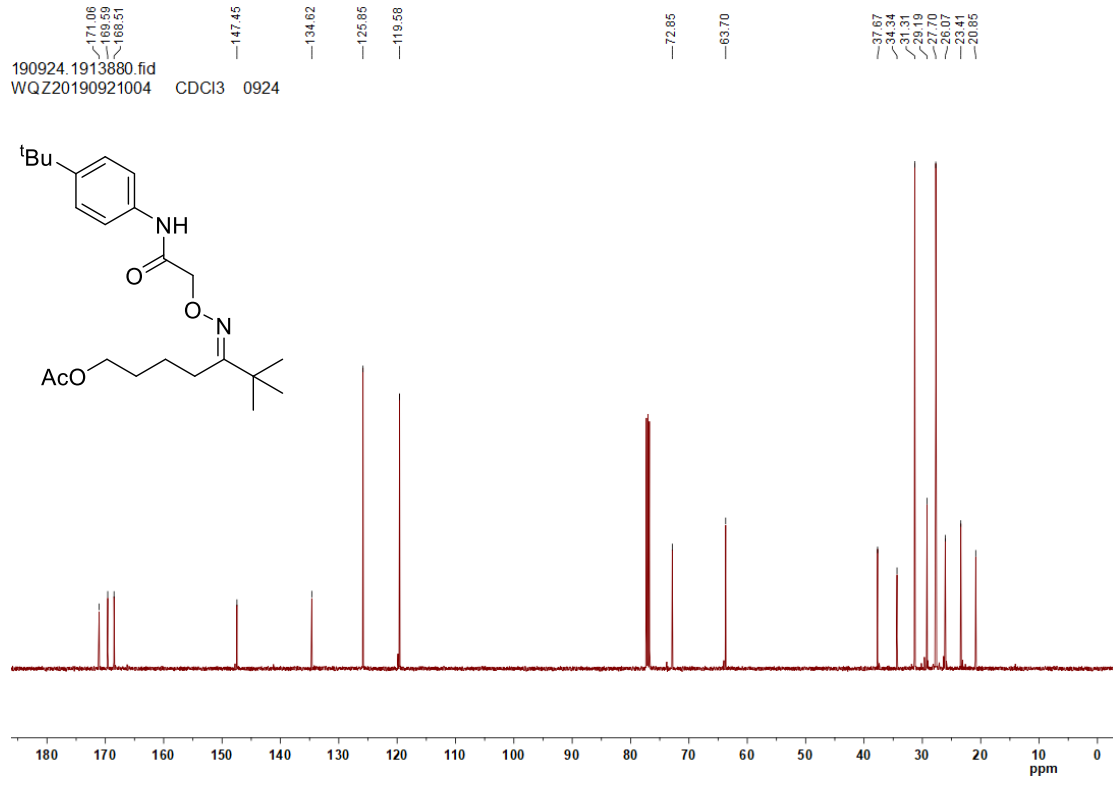
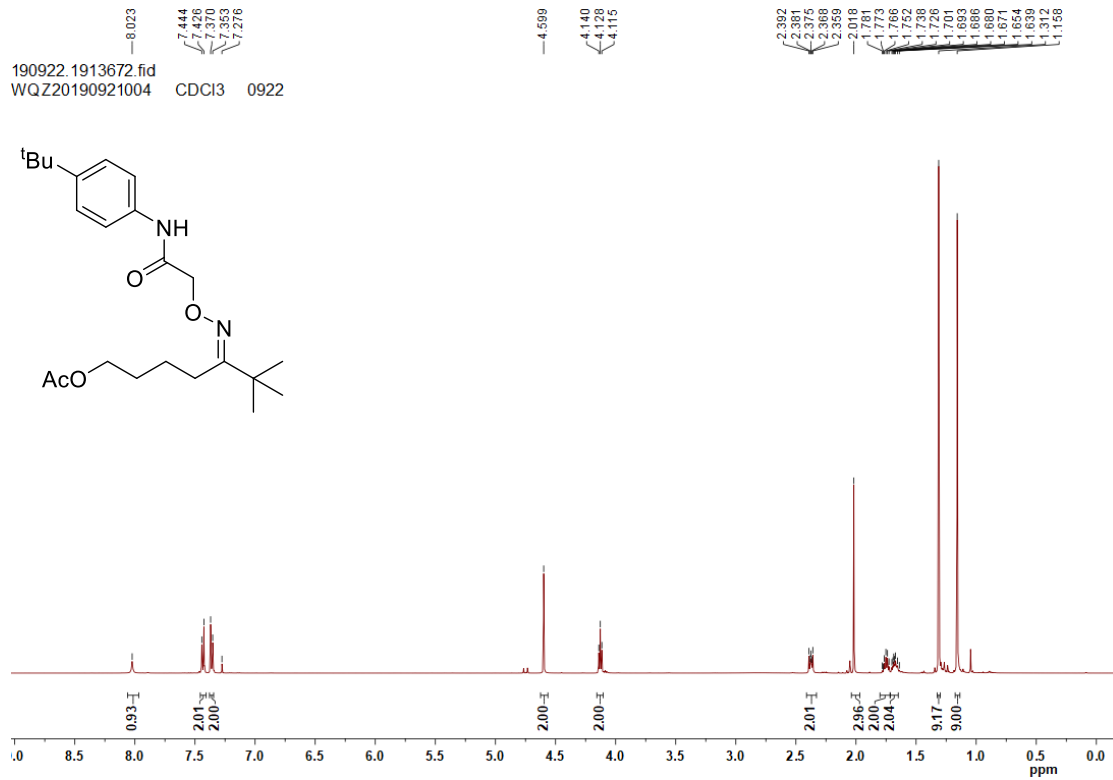
190816_19119041.fid
WQZ20190816003 CDCI3 0816

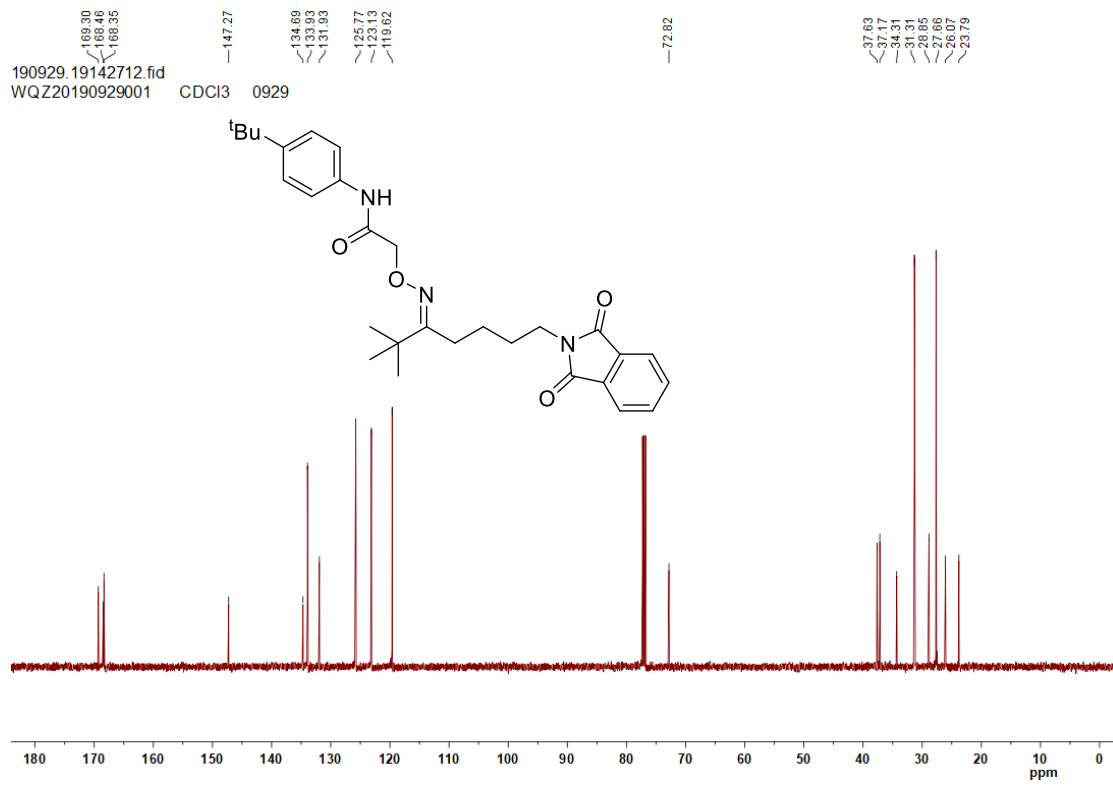
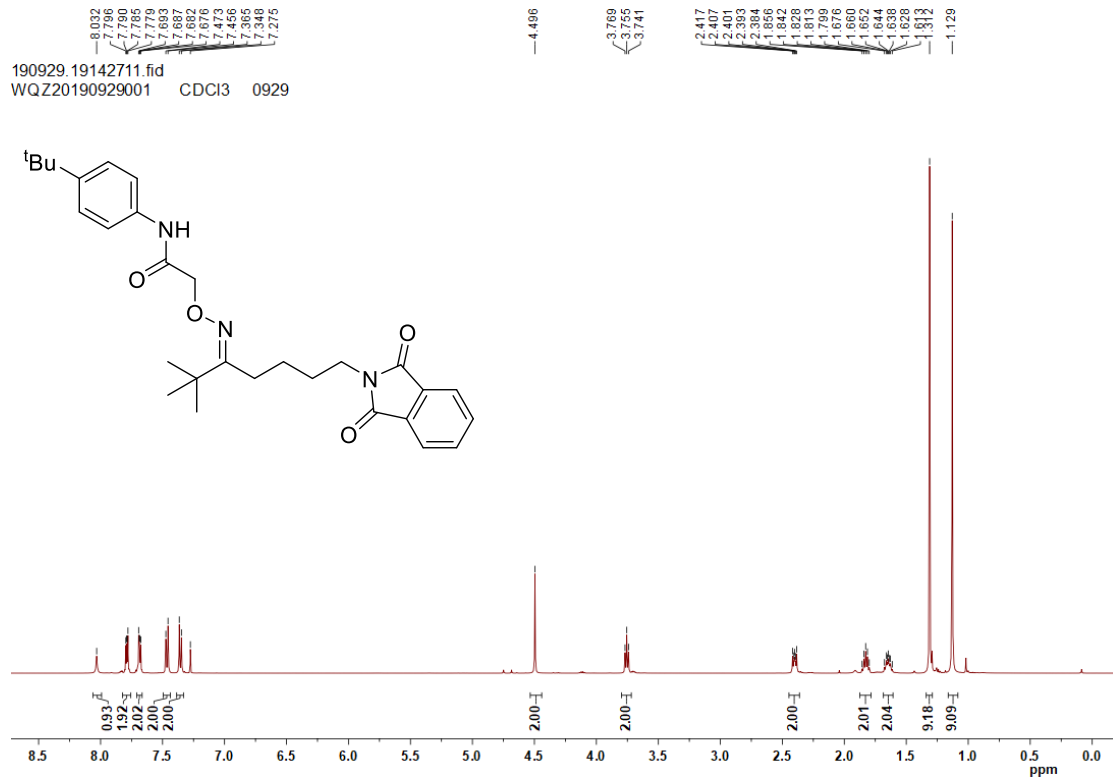


190816_19119042.fid
WQZ20190816003 CDCI3 0816

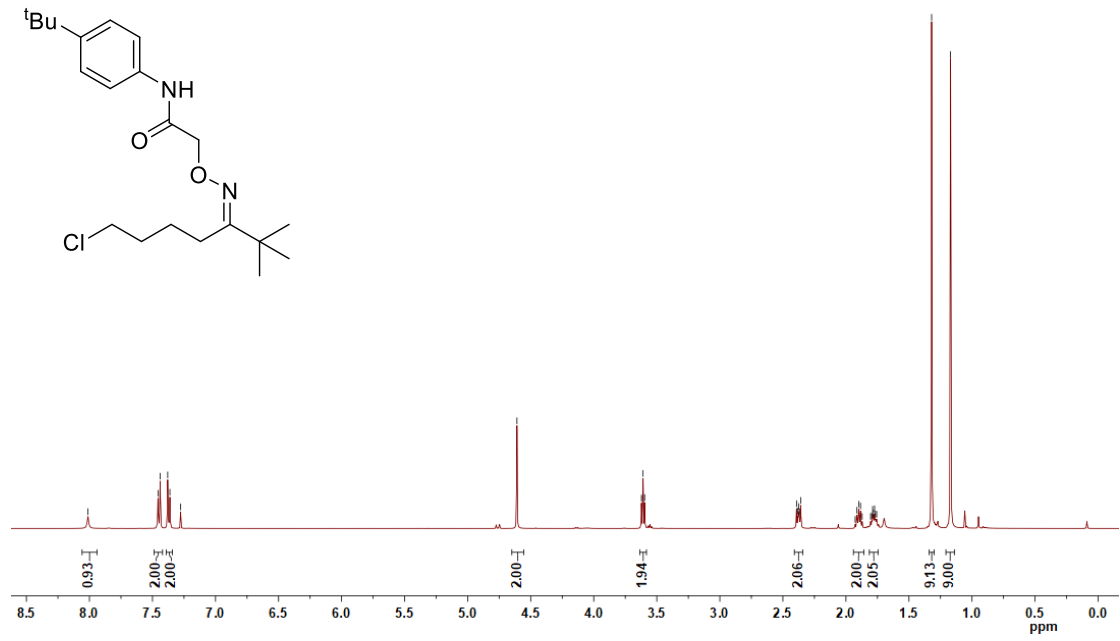




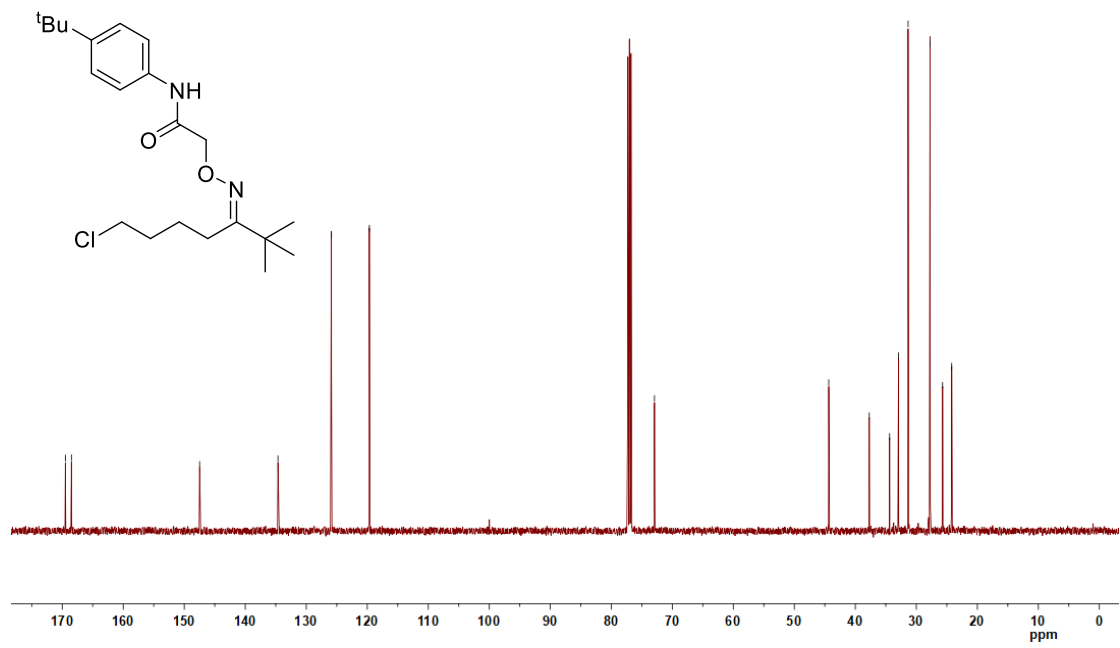


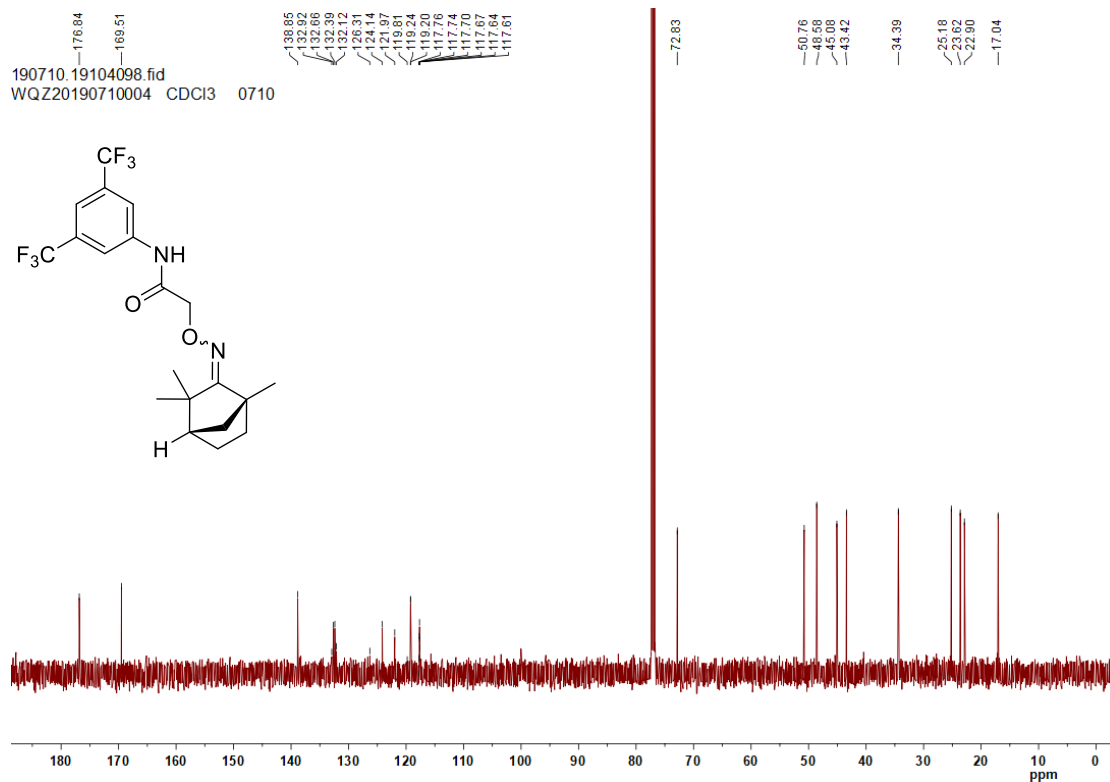
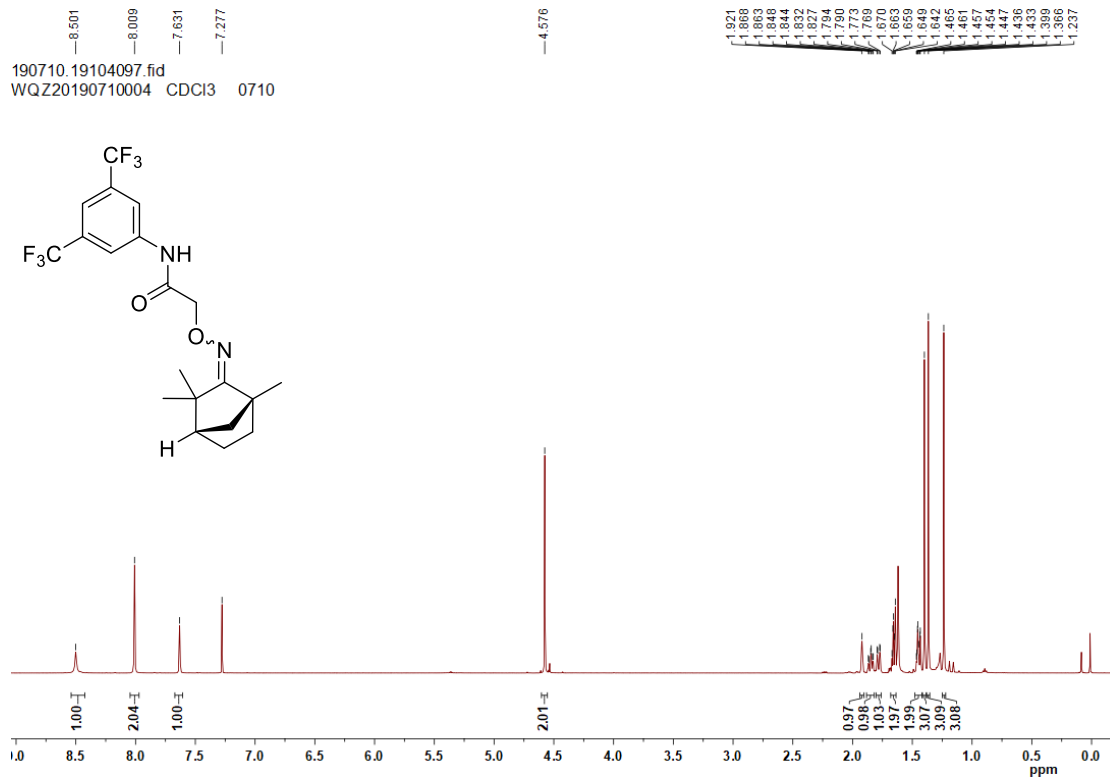


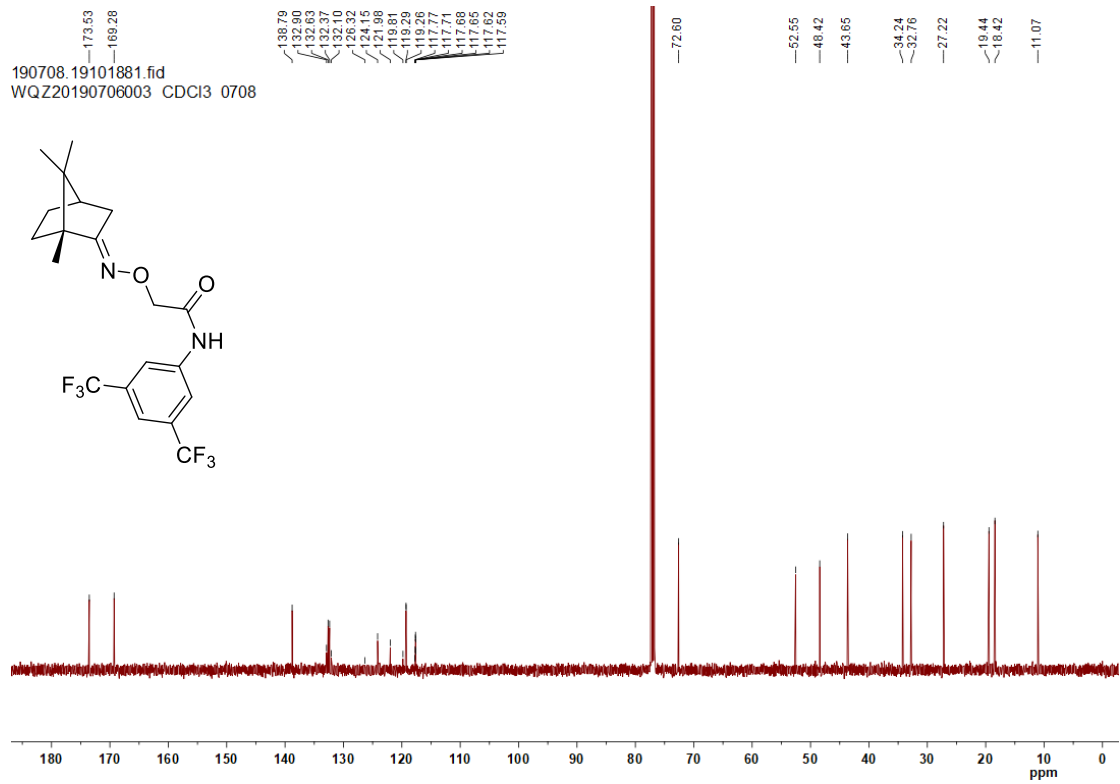
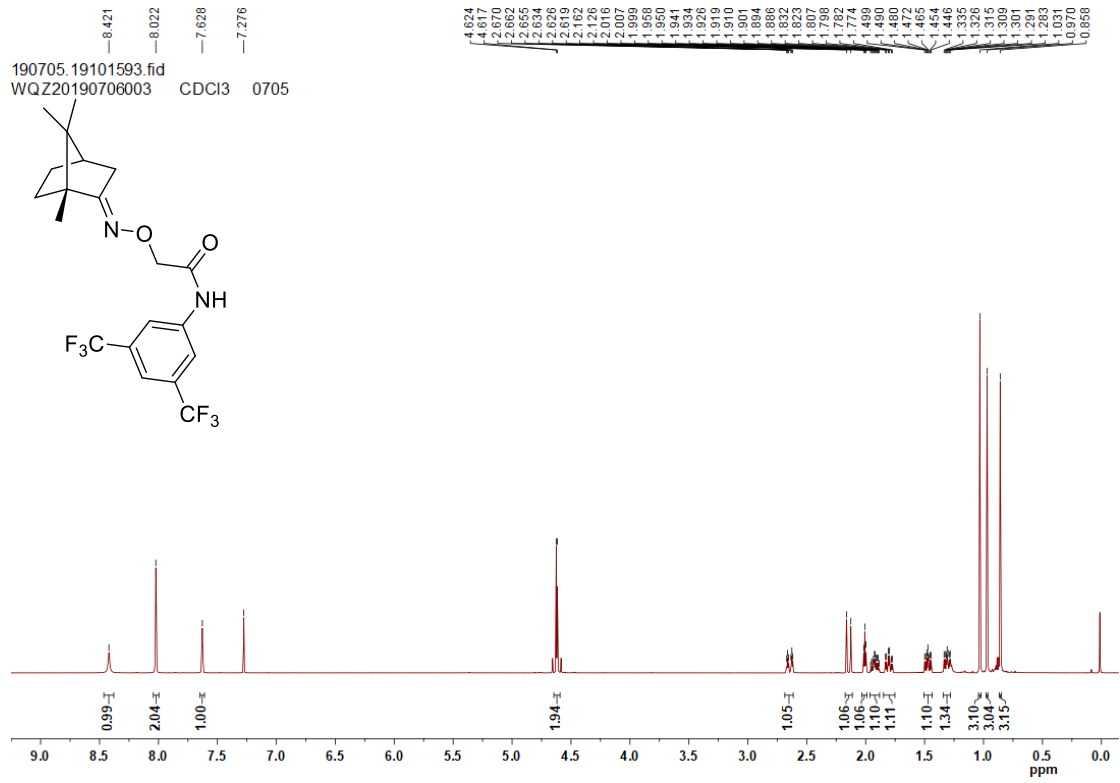
190830.1912430.fid
 WQZ20190830001 CDCI3 0830

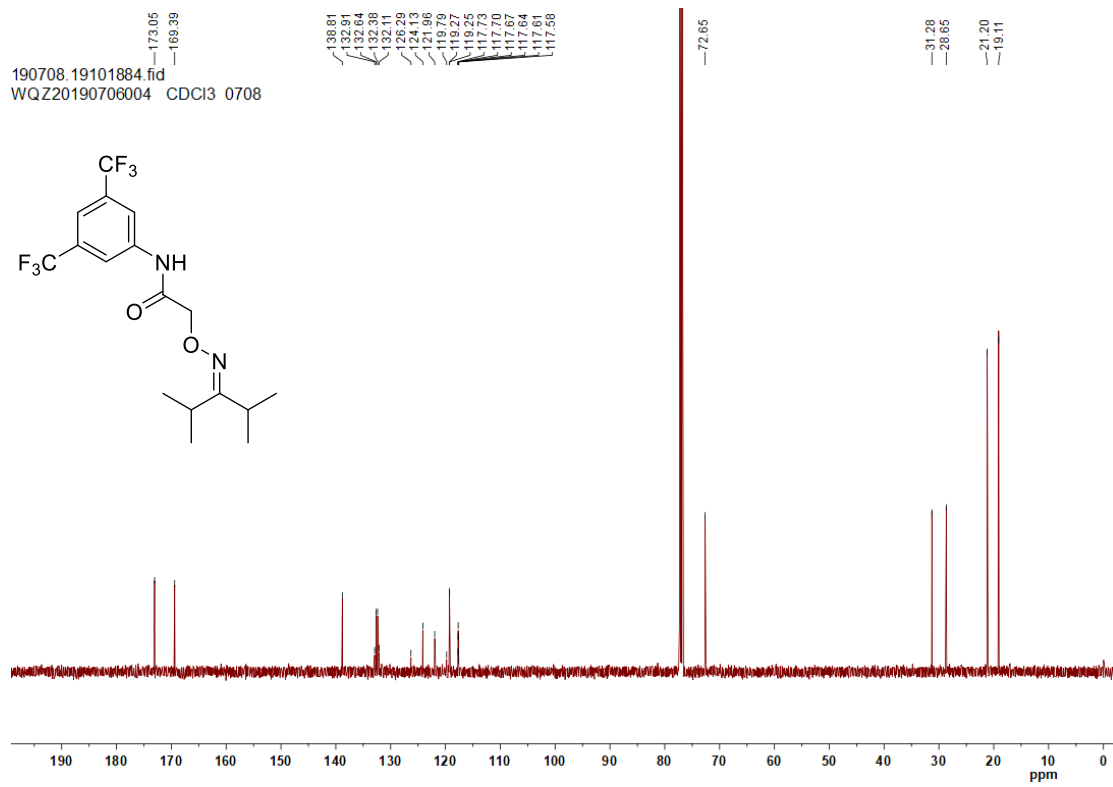
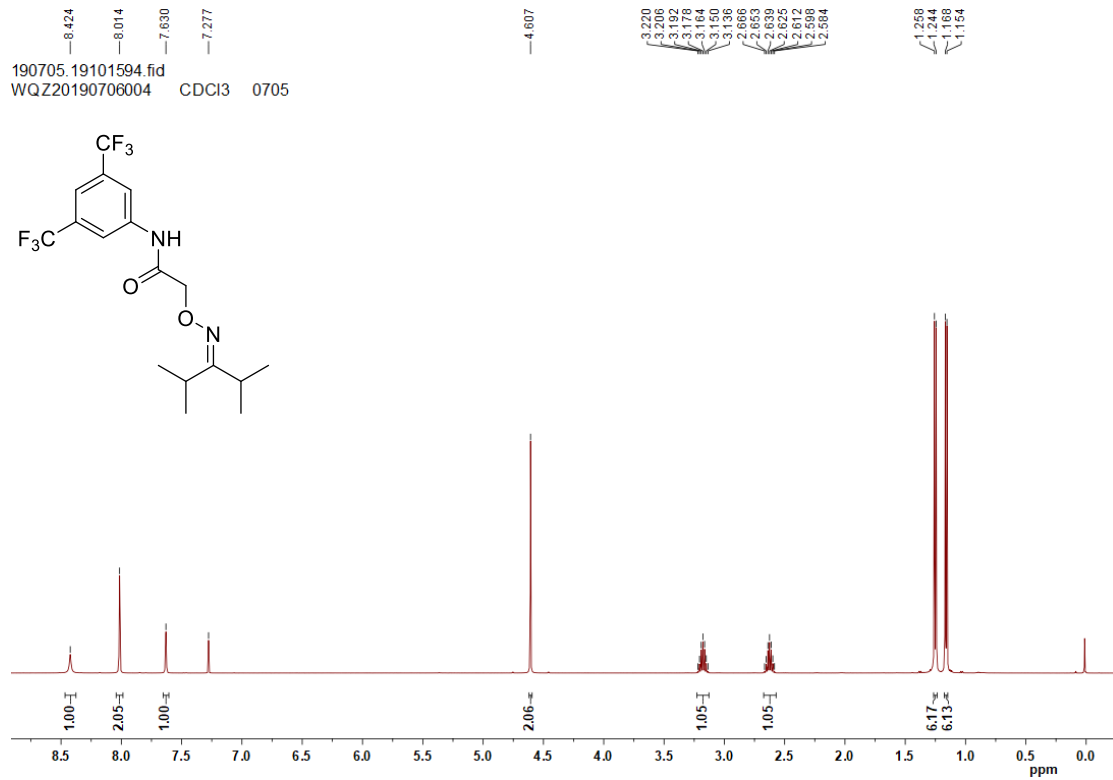


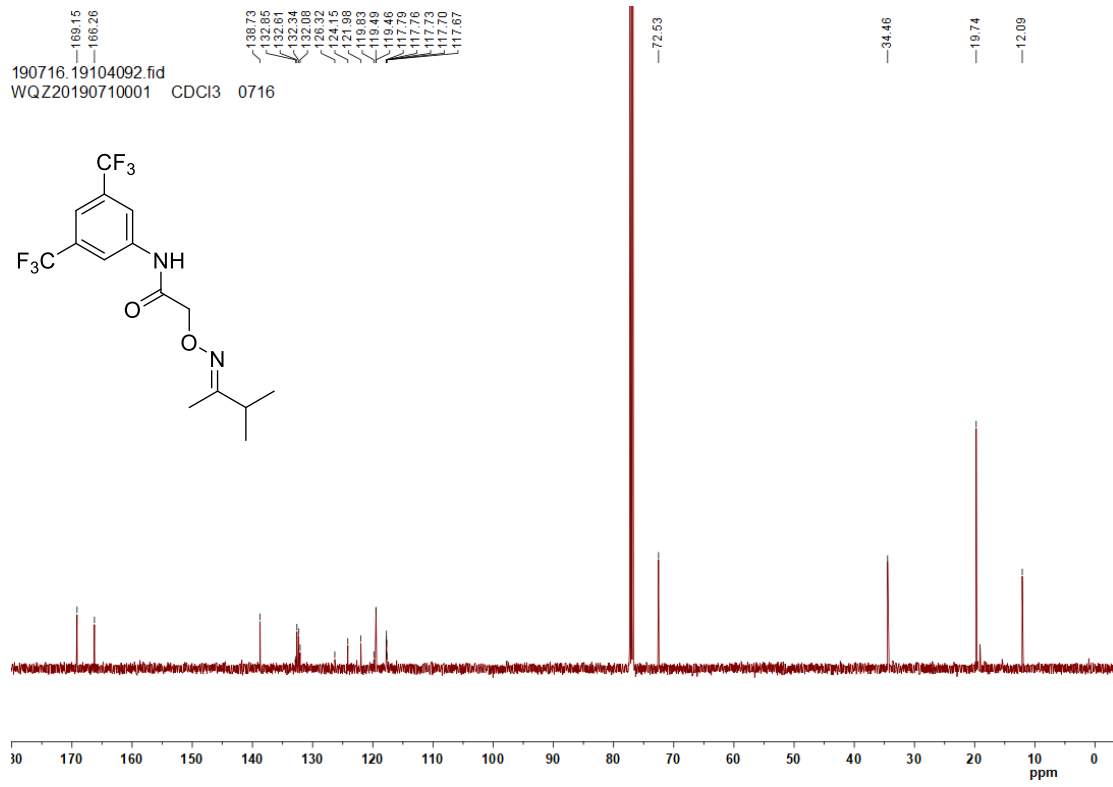
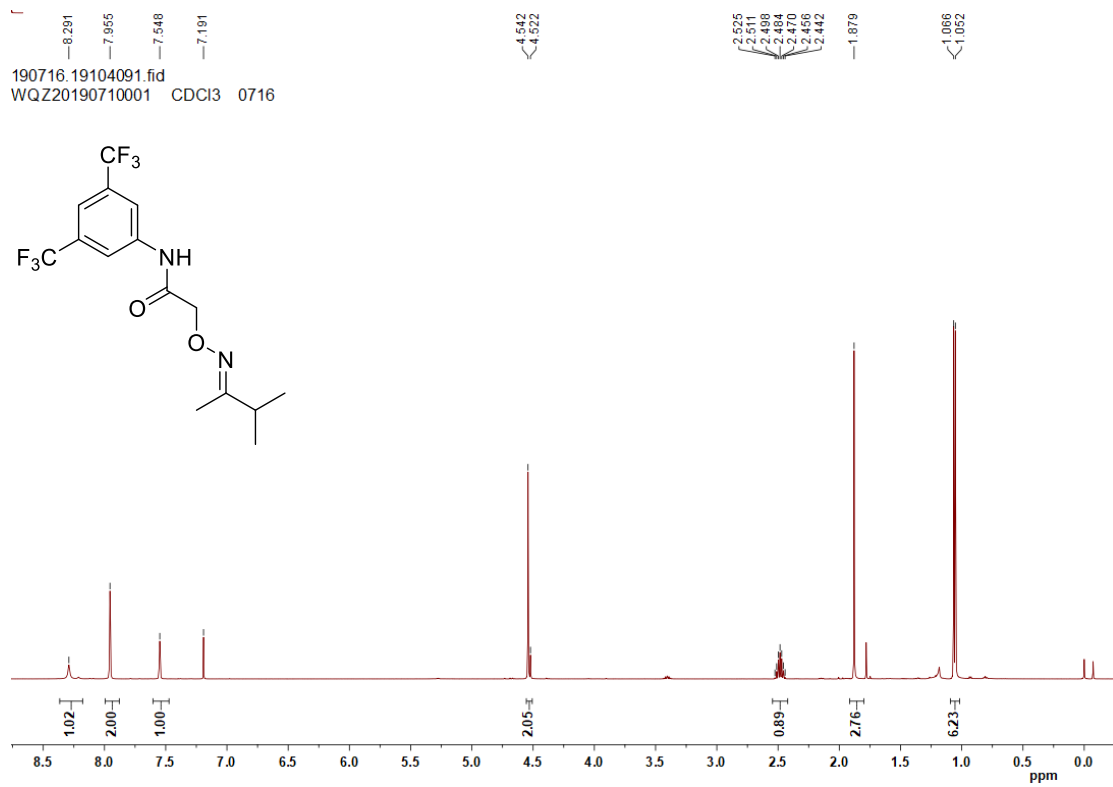
190902.1912581.fid
 WQZ20190830001 CDCI3 0902

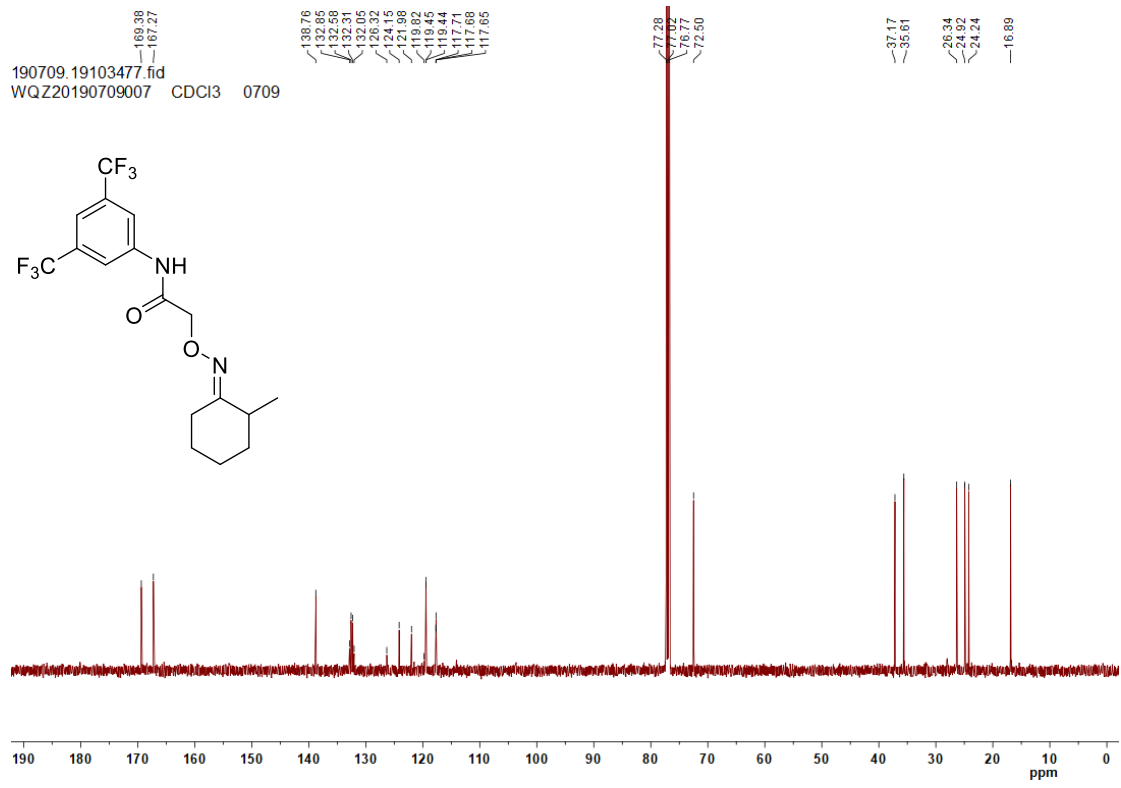
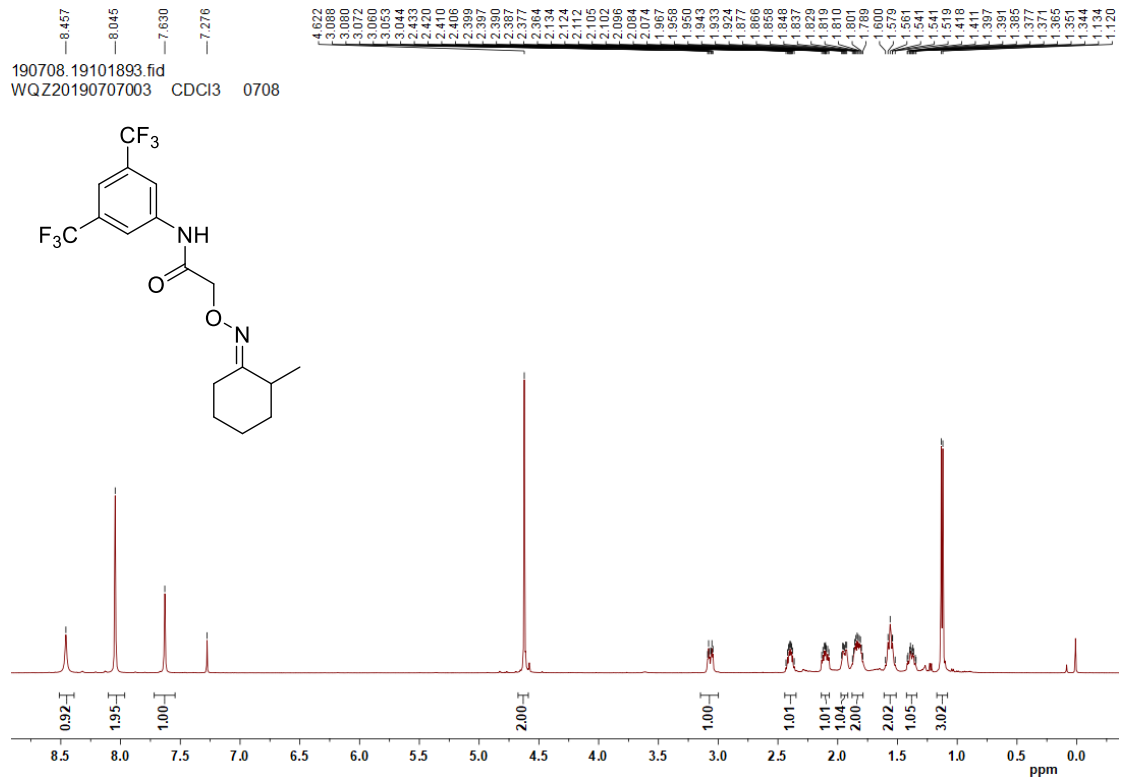


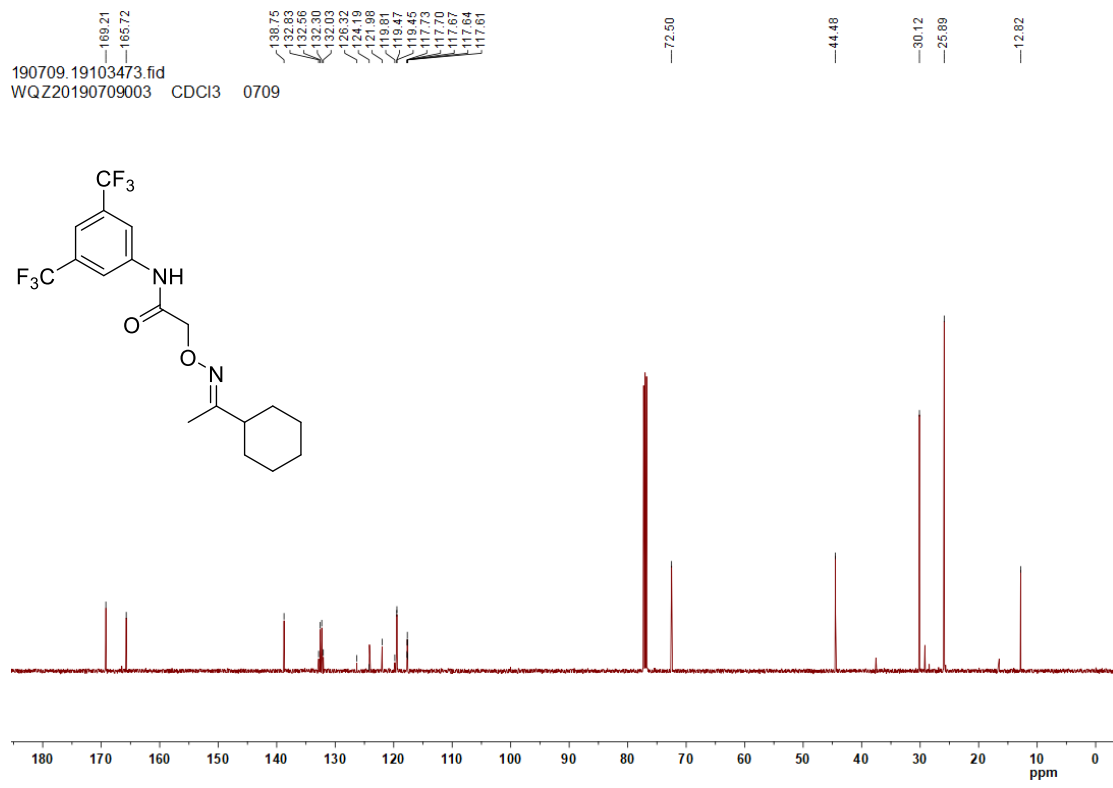
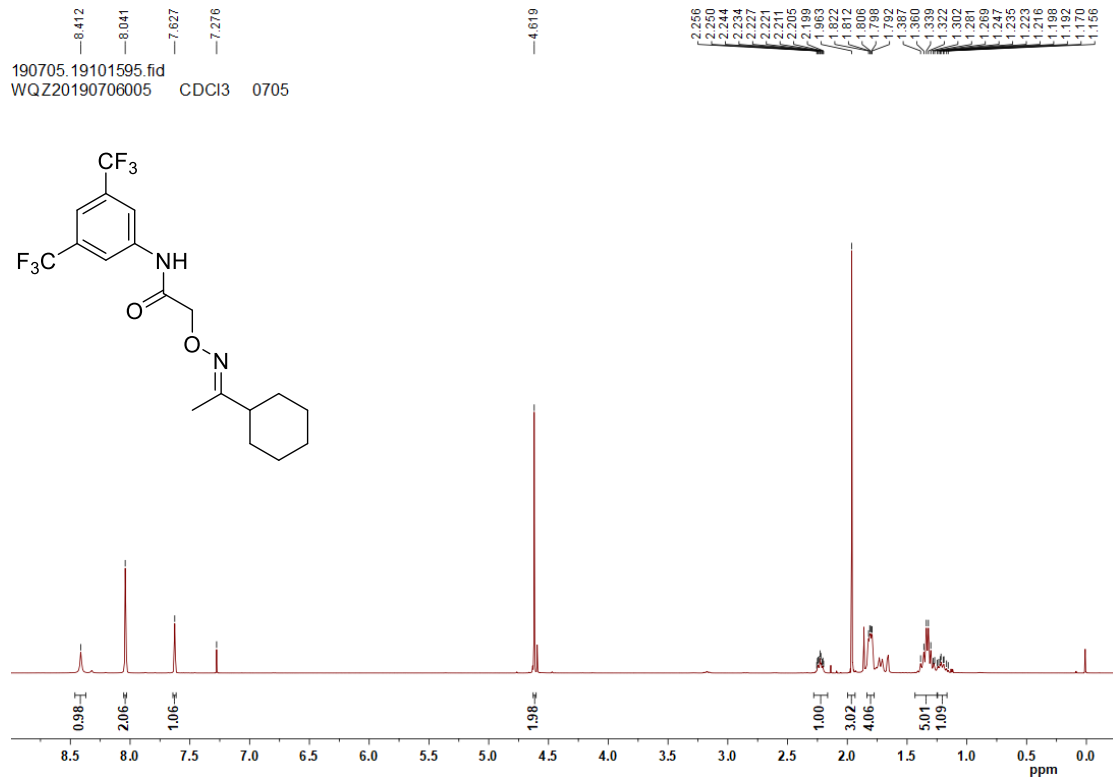


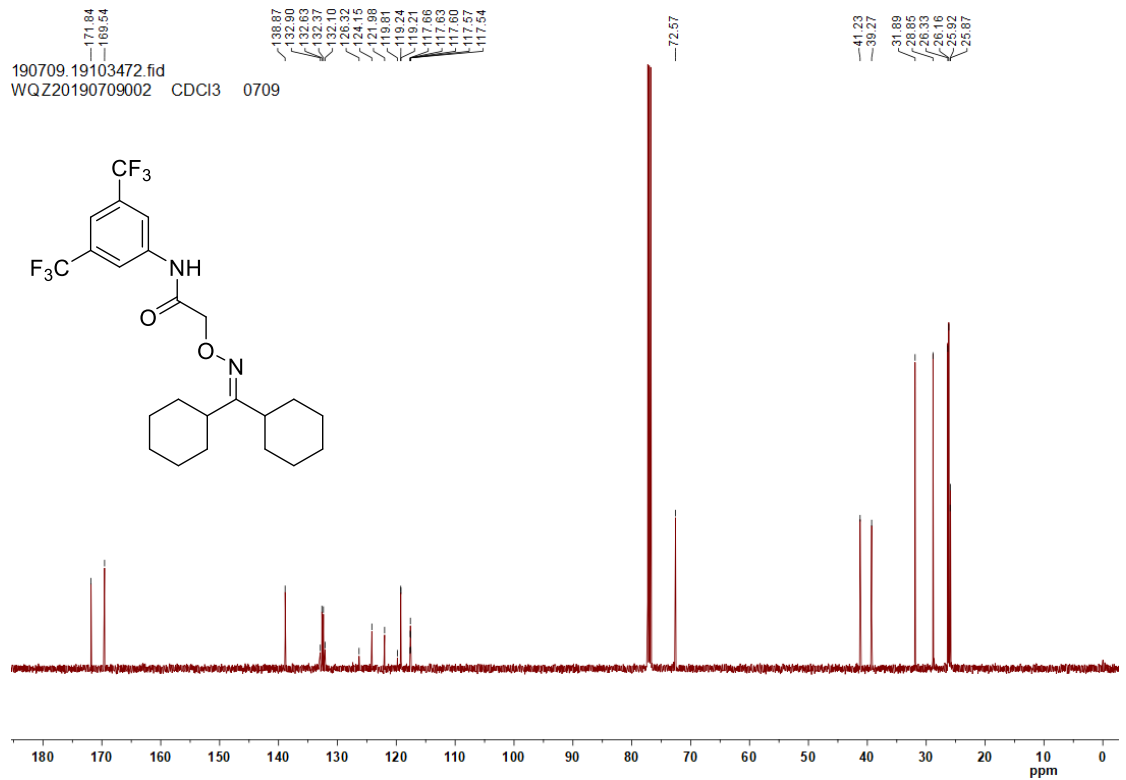
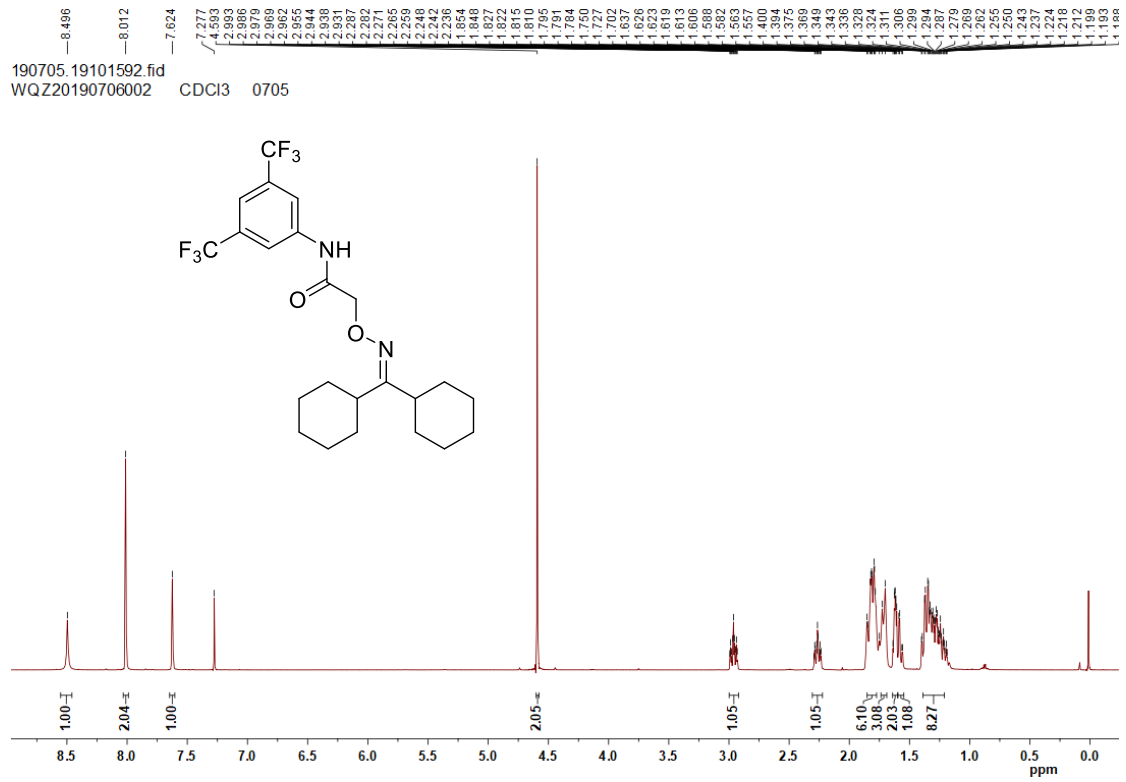


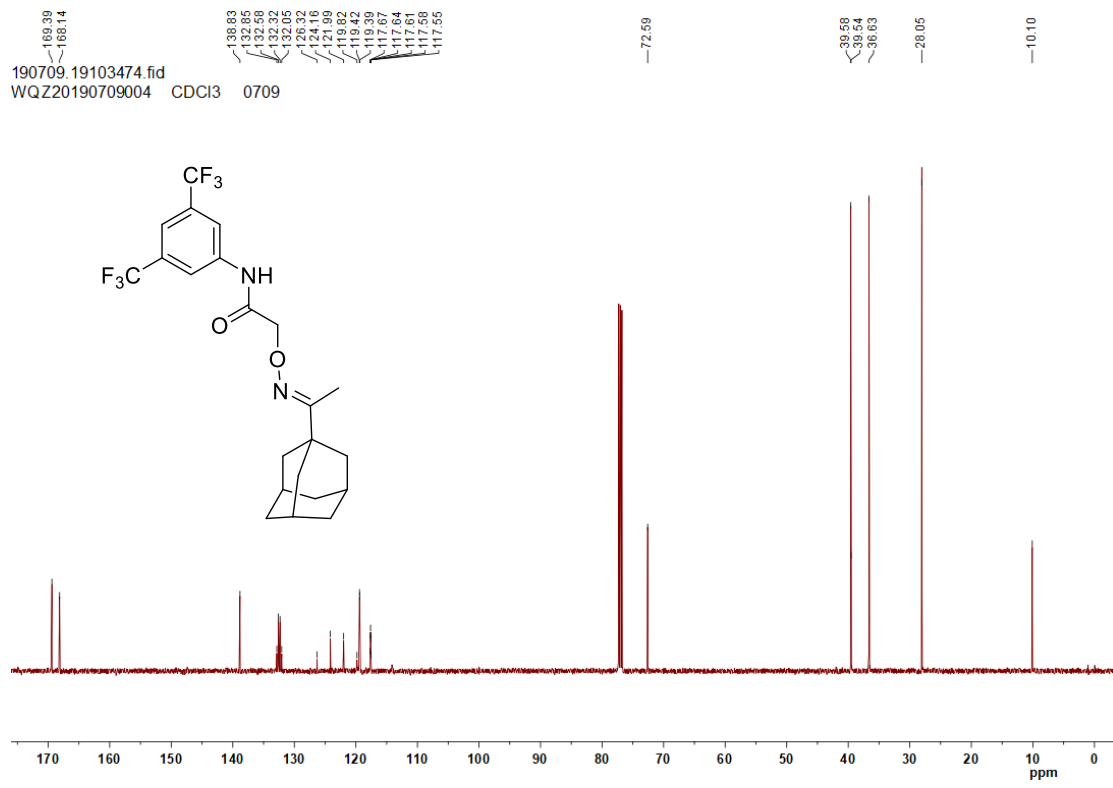
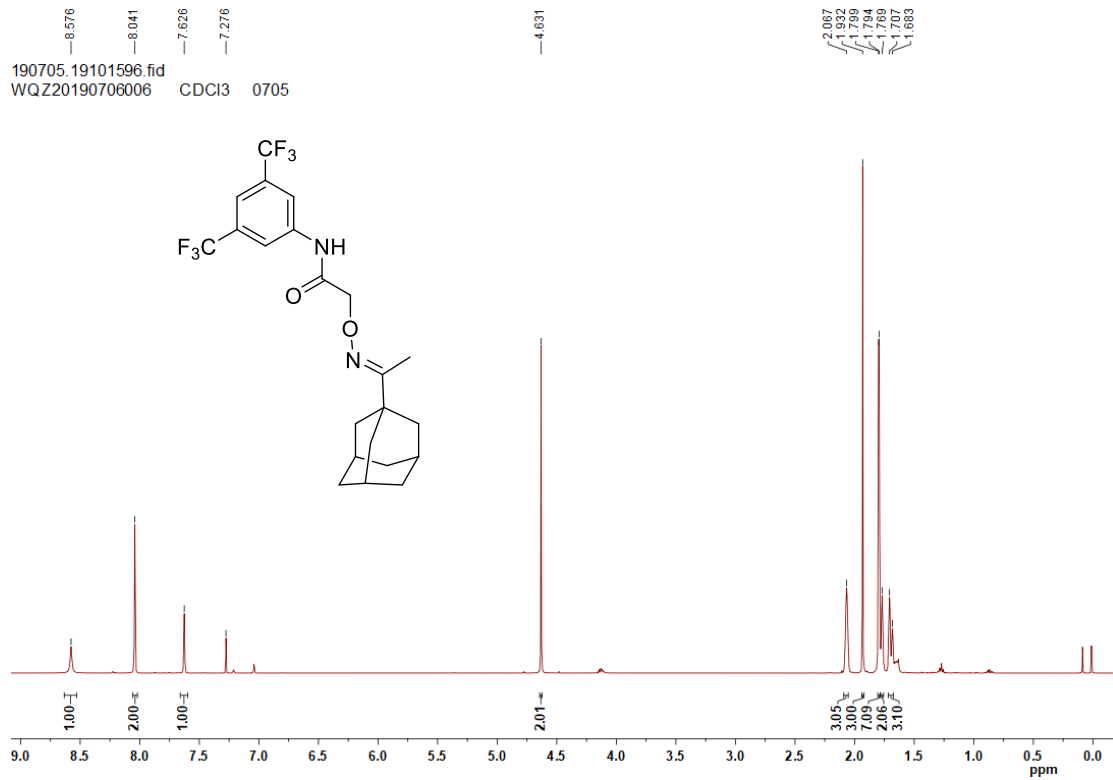


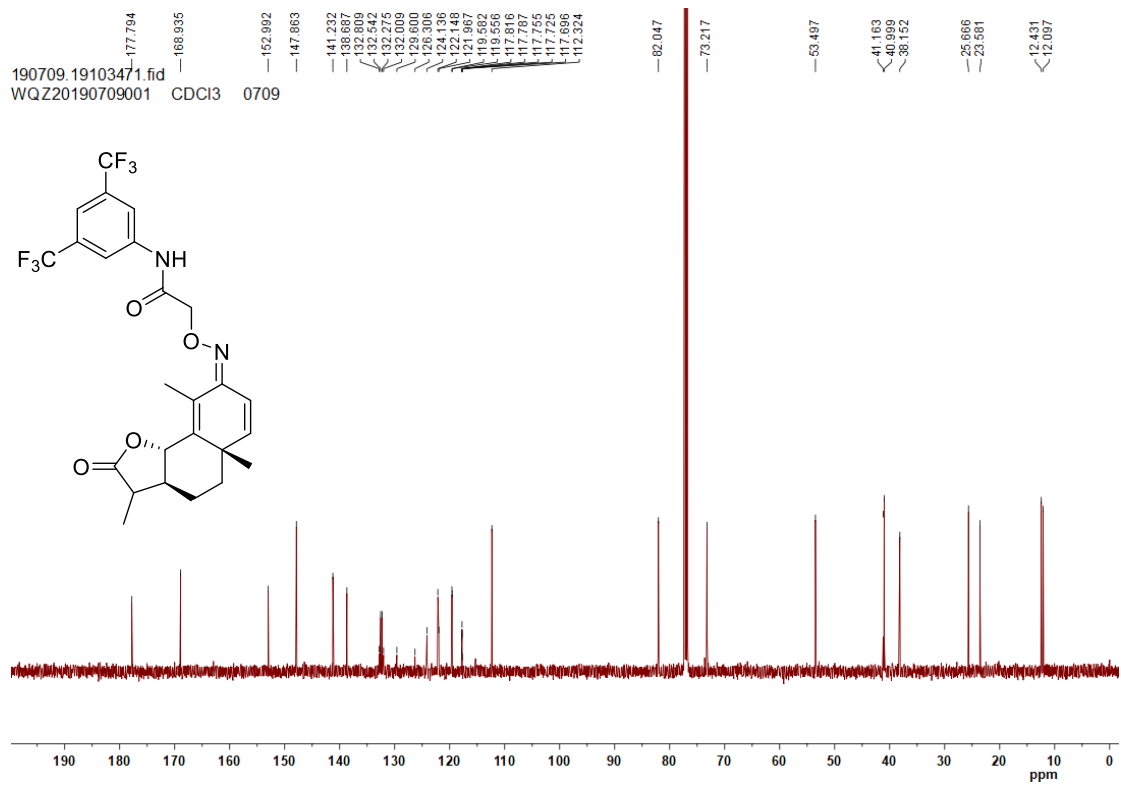
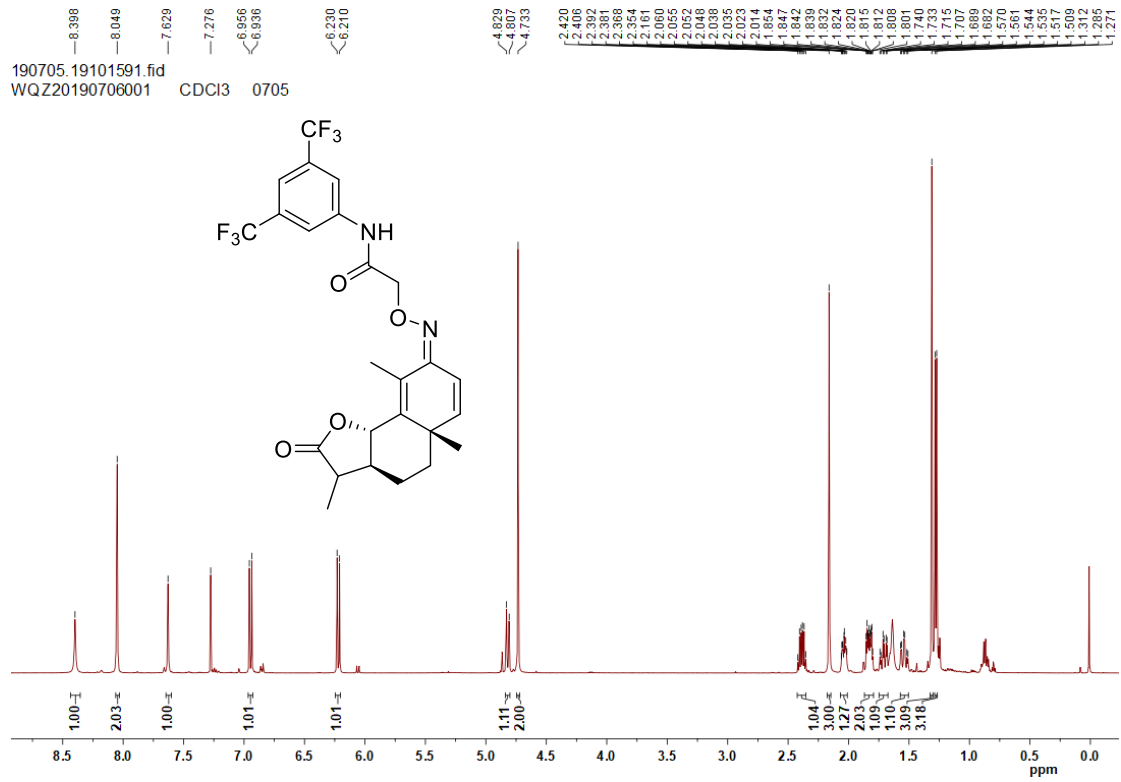


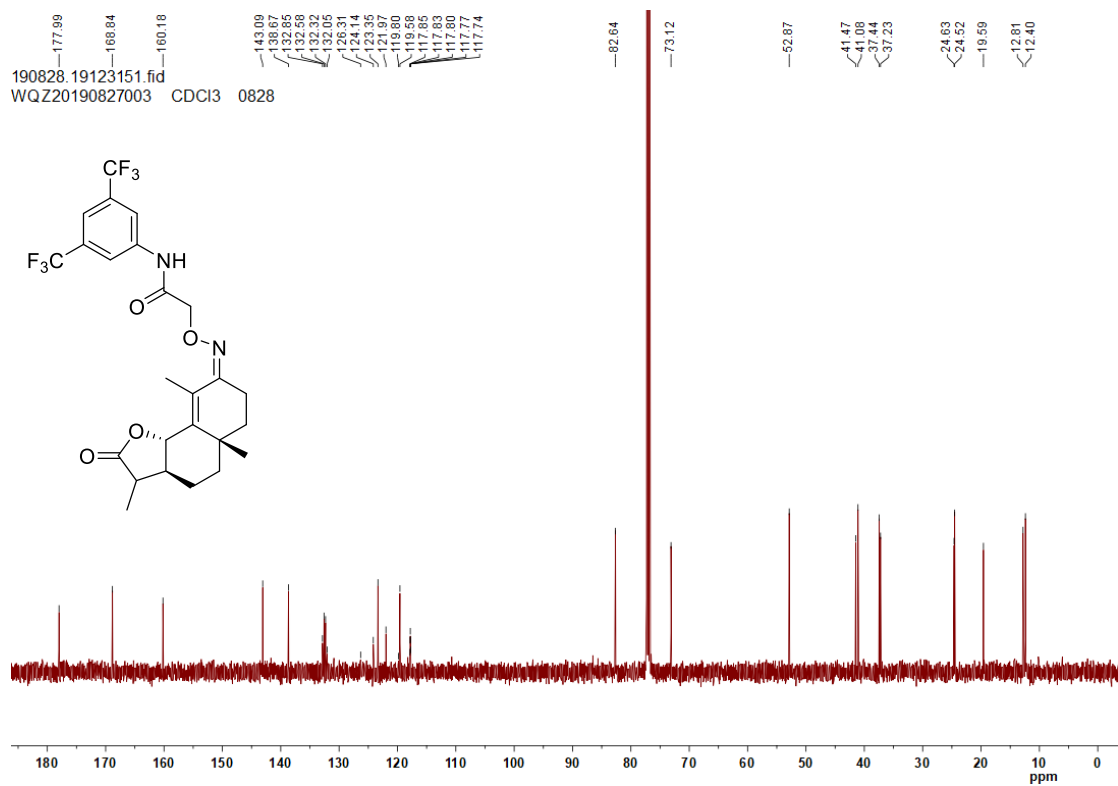
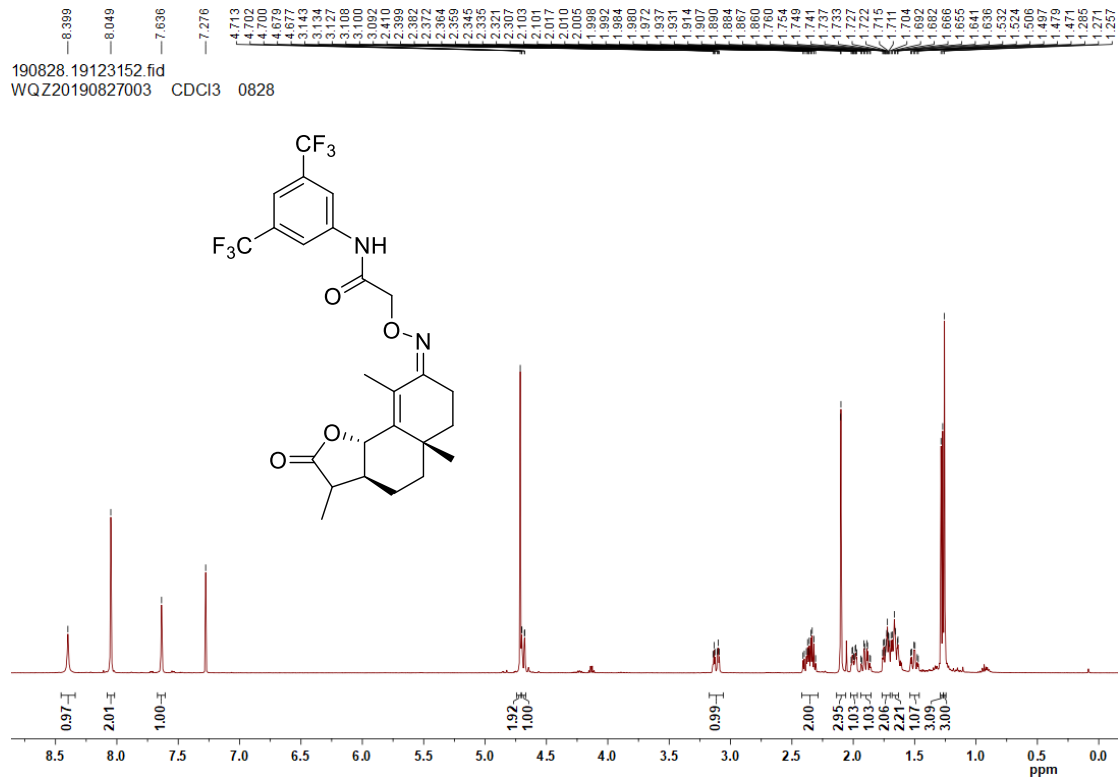


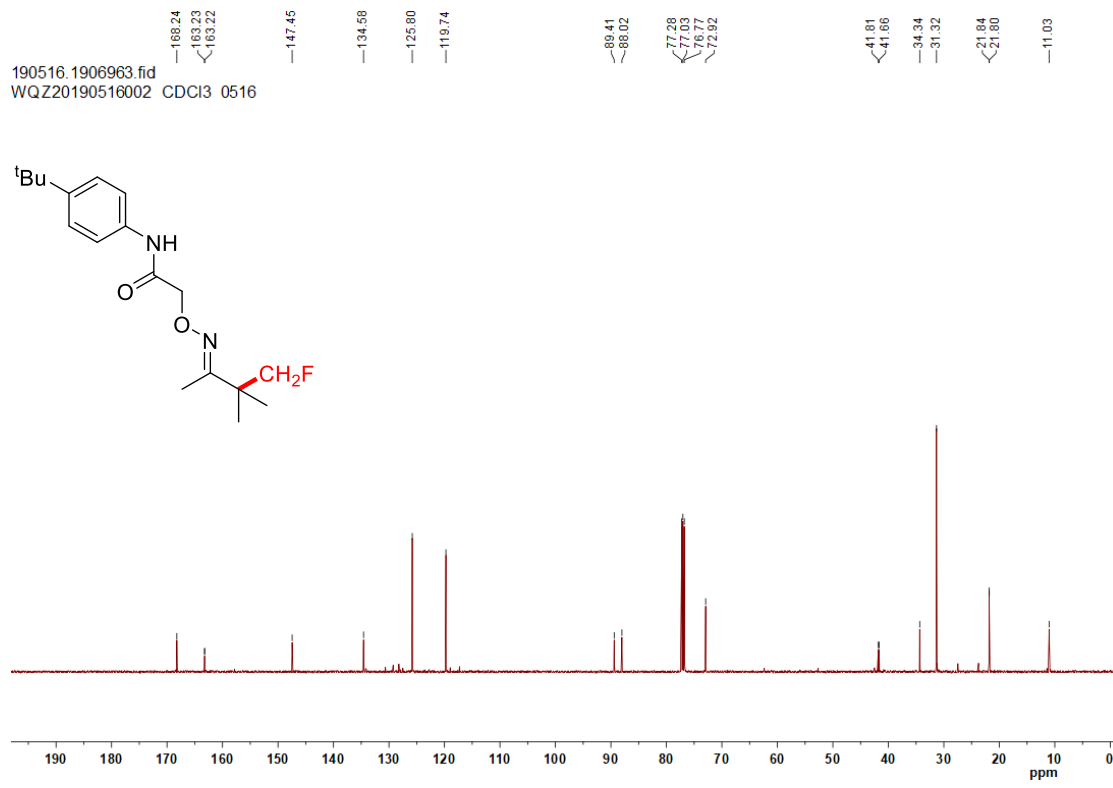
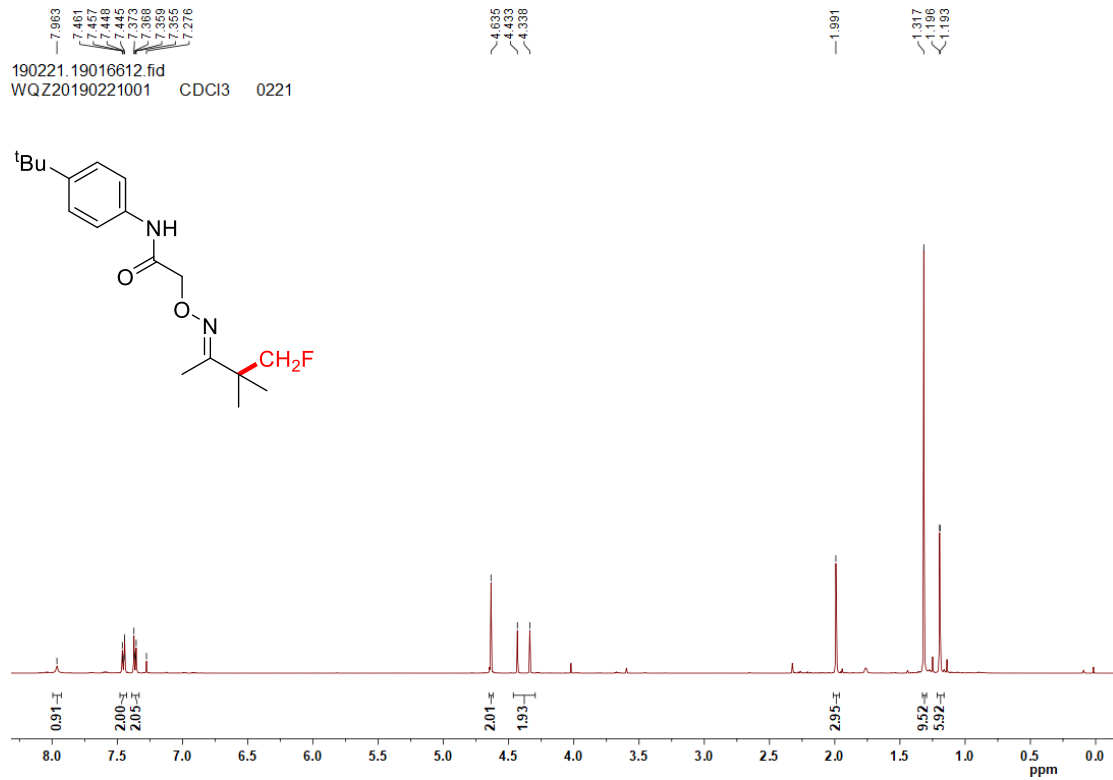






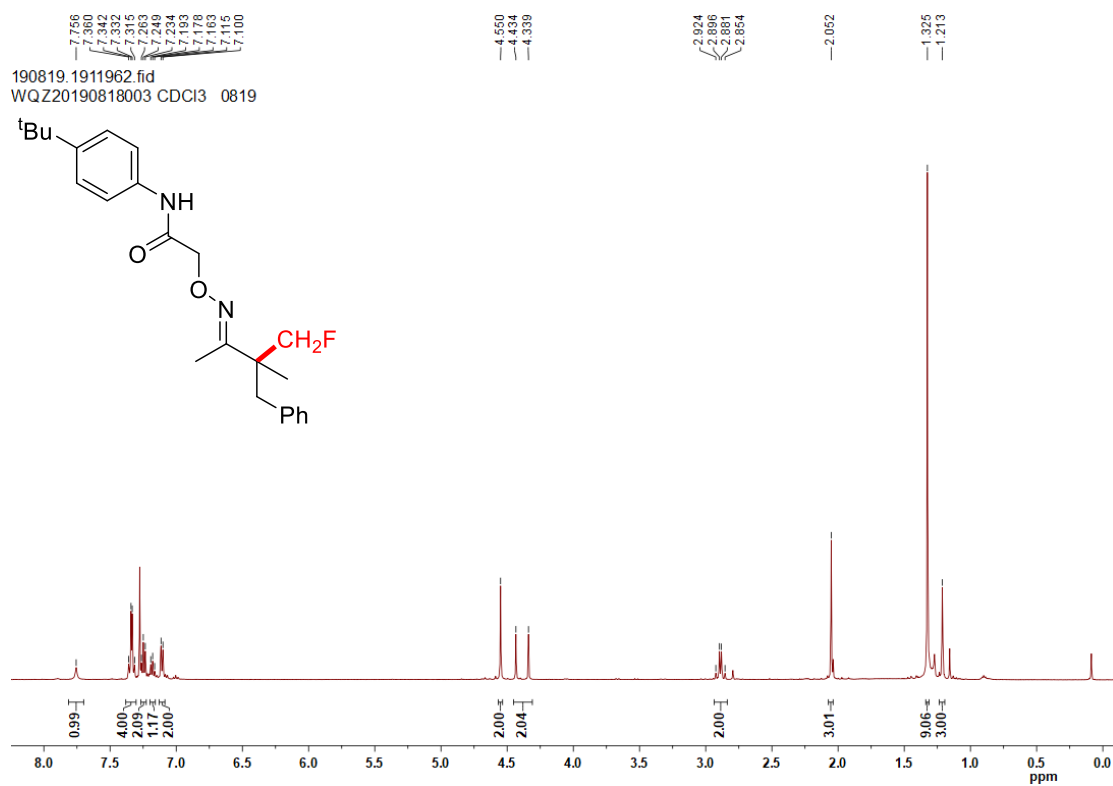
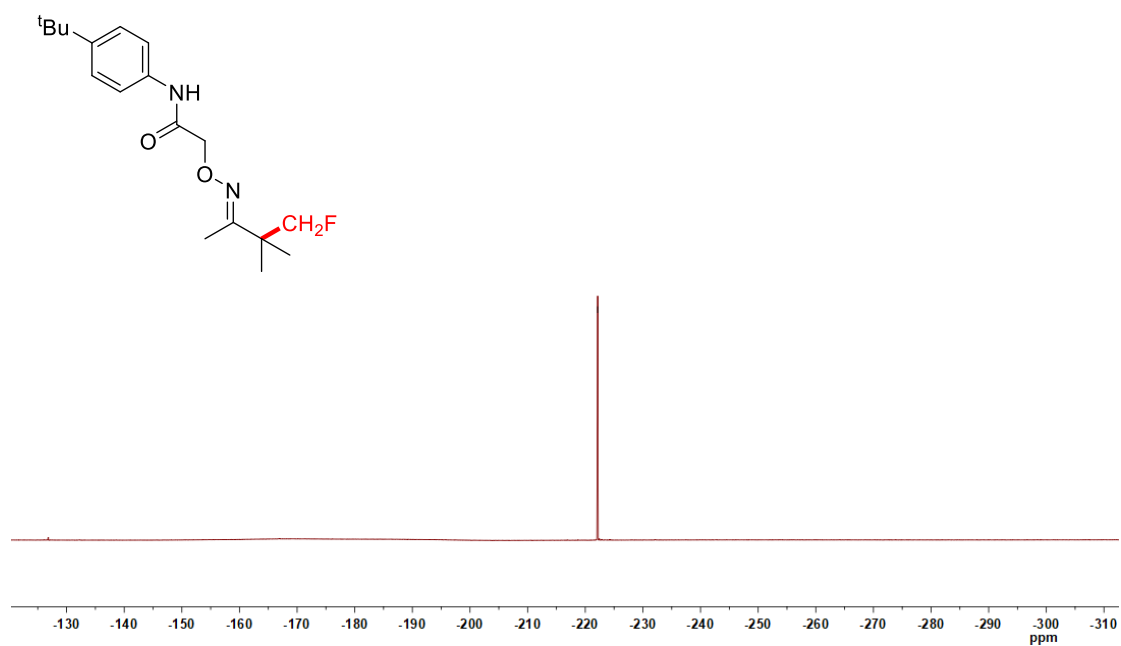


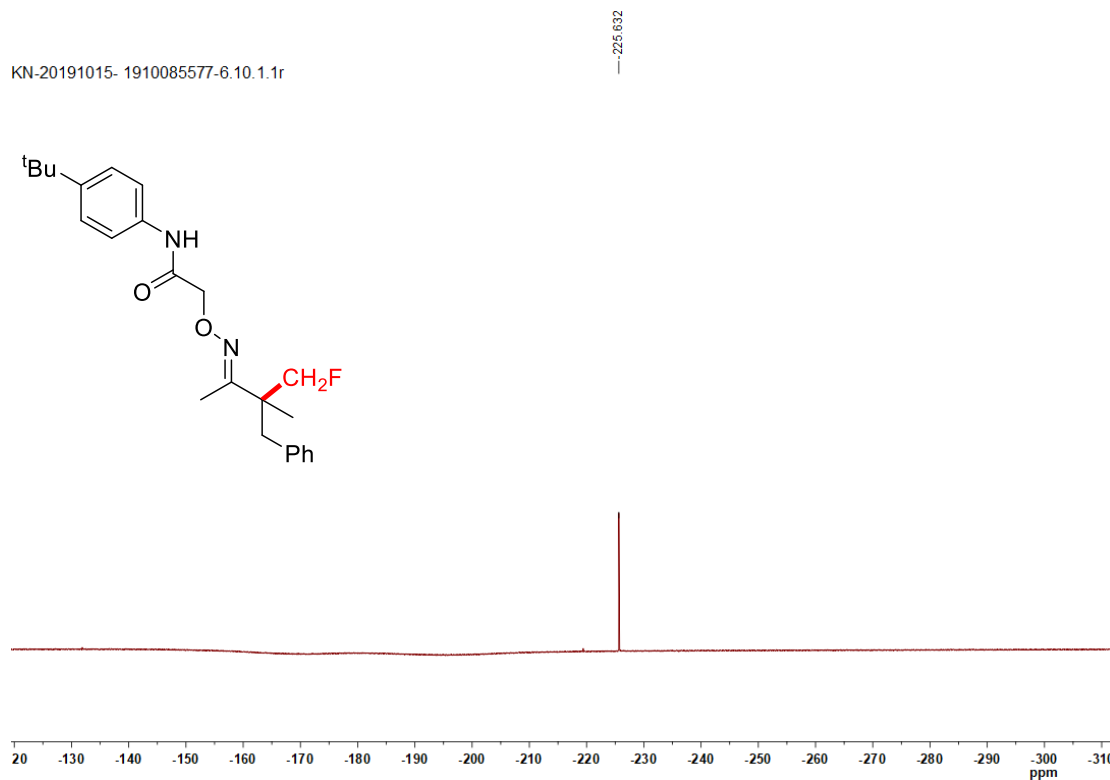
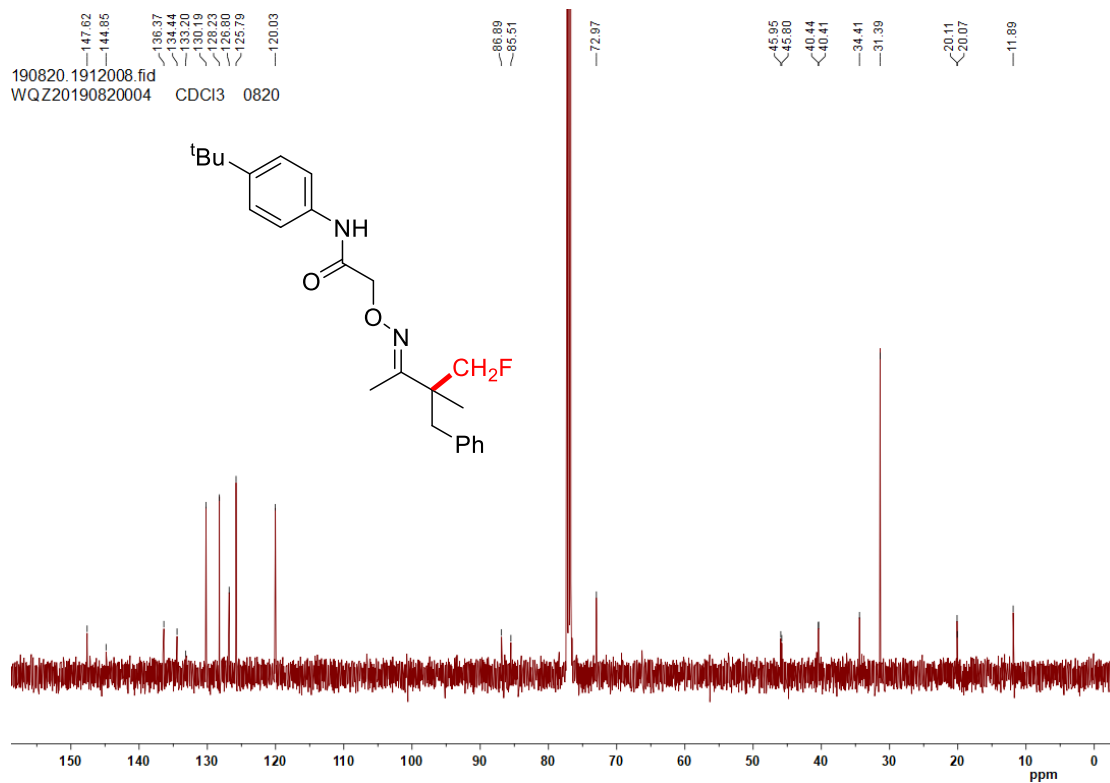


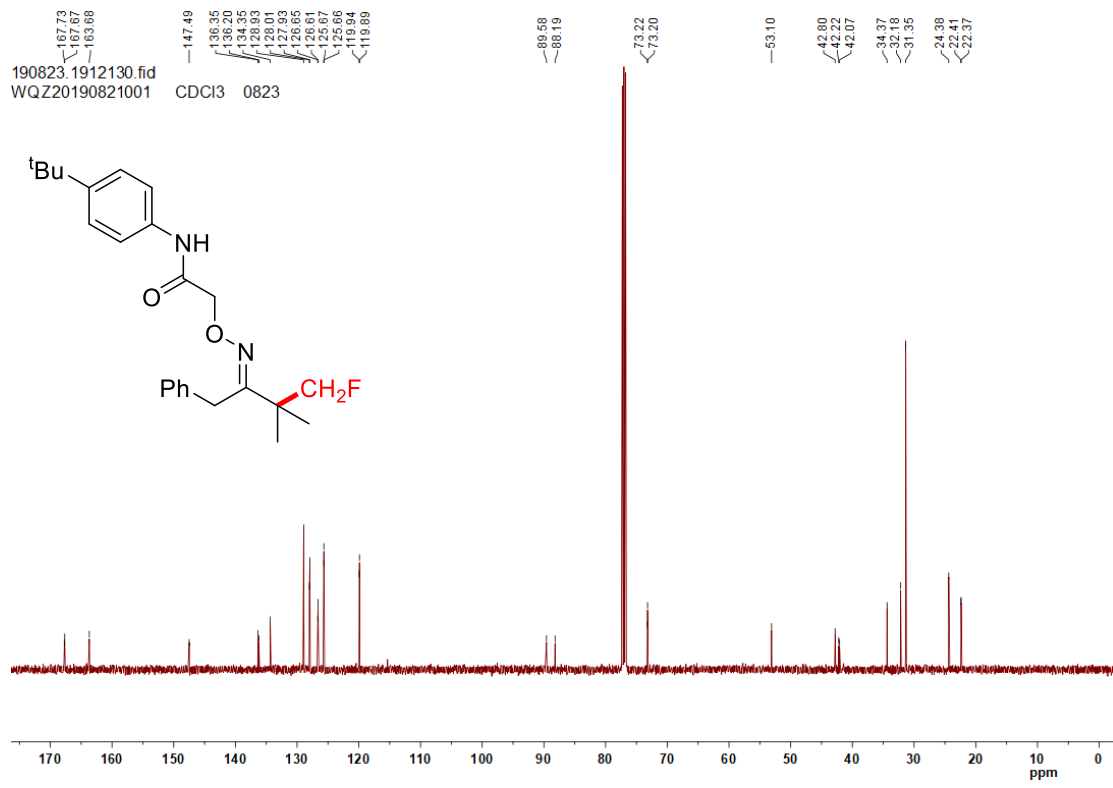
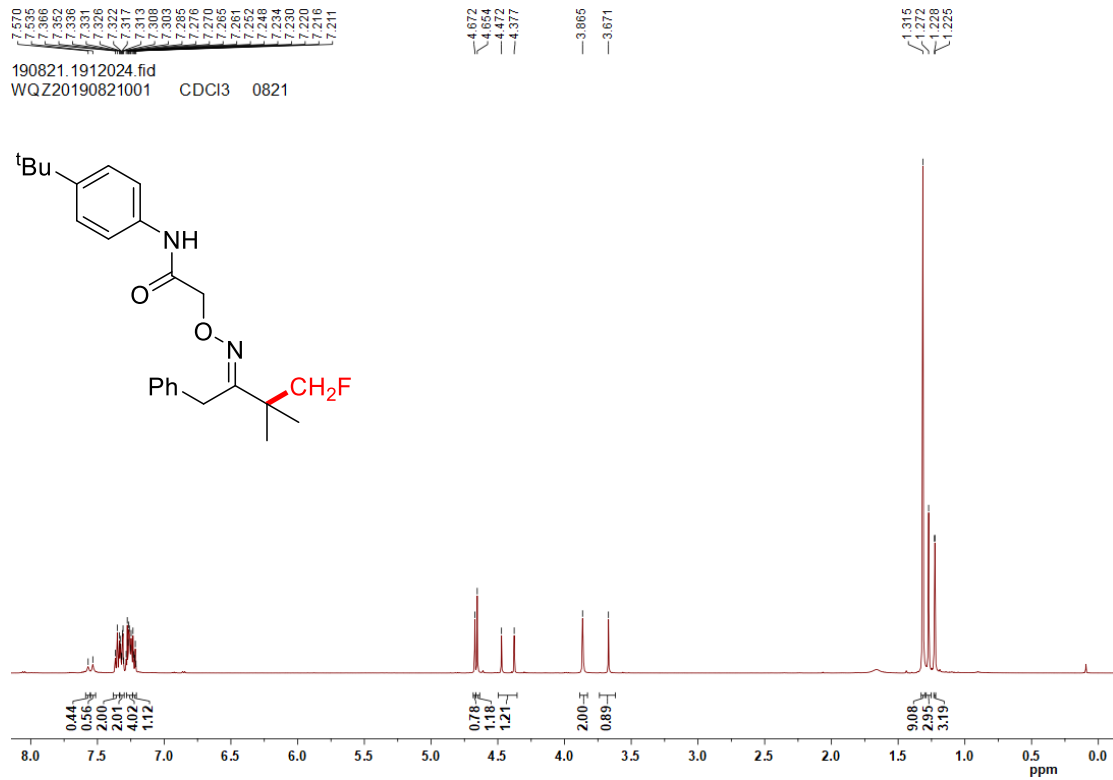


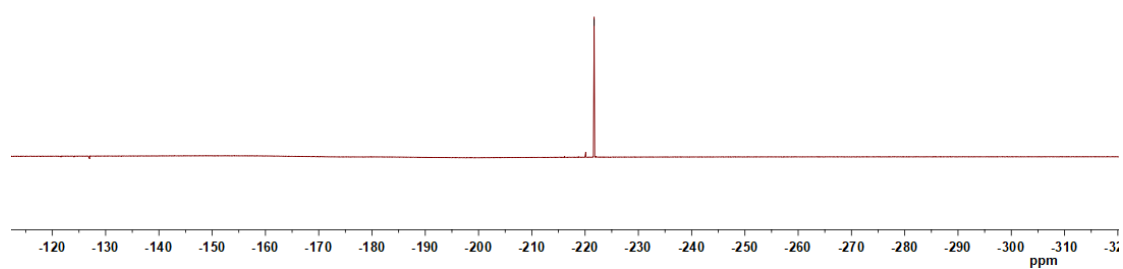
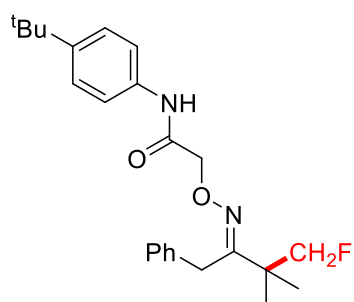
KN-20191015- 1910085577-1.10.1.1r

—222.152









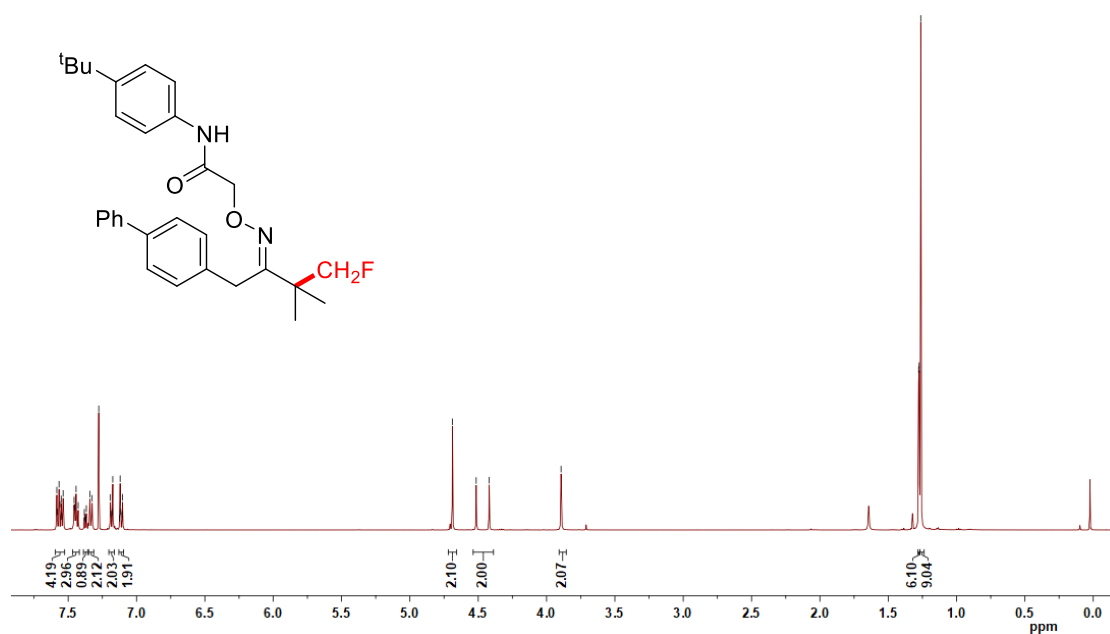
7.583
7.580
7.567
7.564
7.551
7.547
7.537
7.457
7.453
7.442
7.442
7.382
7.379
7.371
7.367
7.342
7.335
7.325
7.191
7.187
7.178
7.174
7.125
7.120
7.106
7.106
7.102

4.686
4.596
4.420

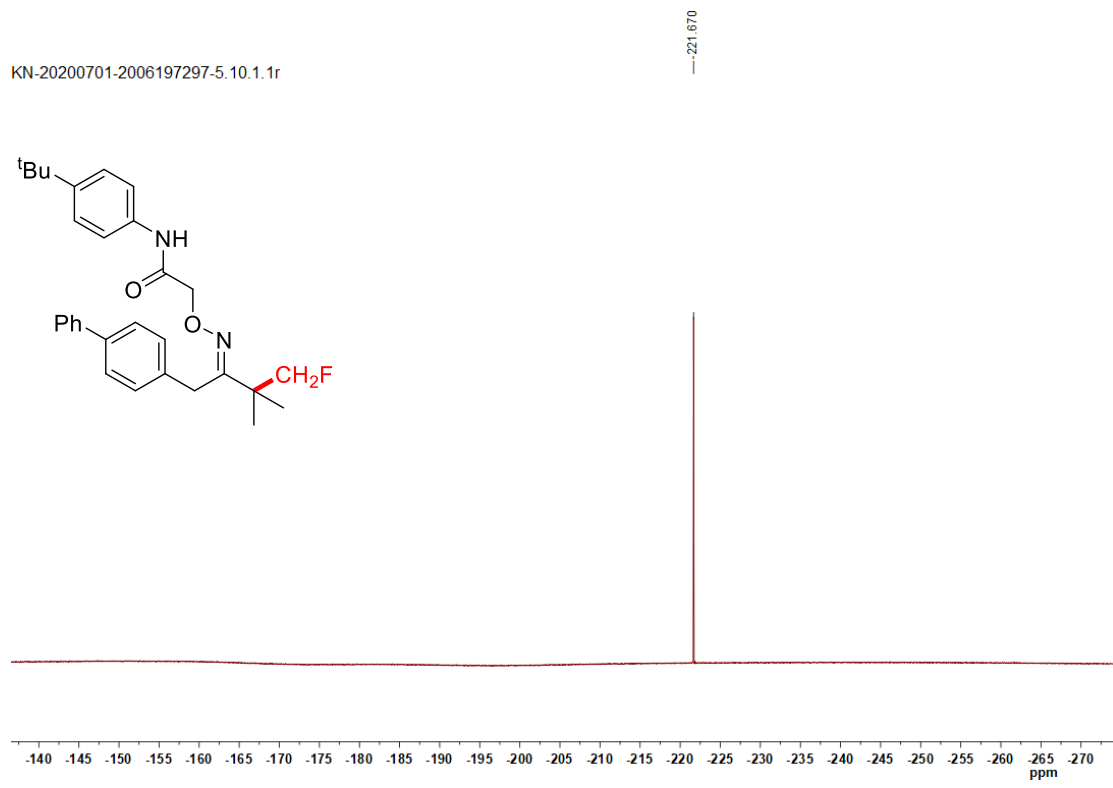
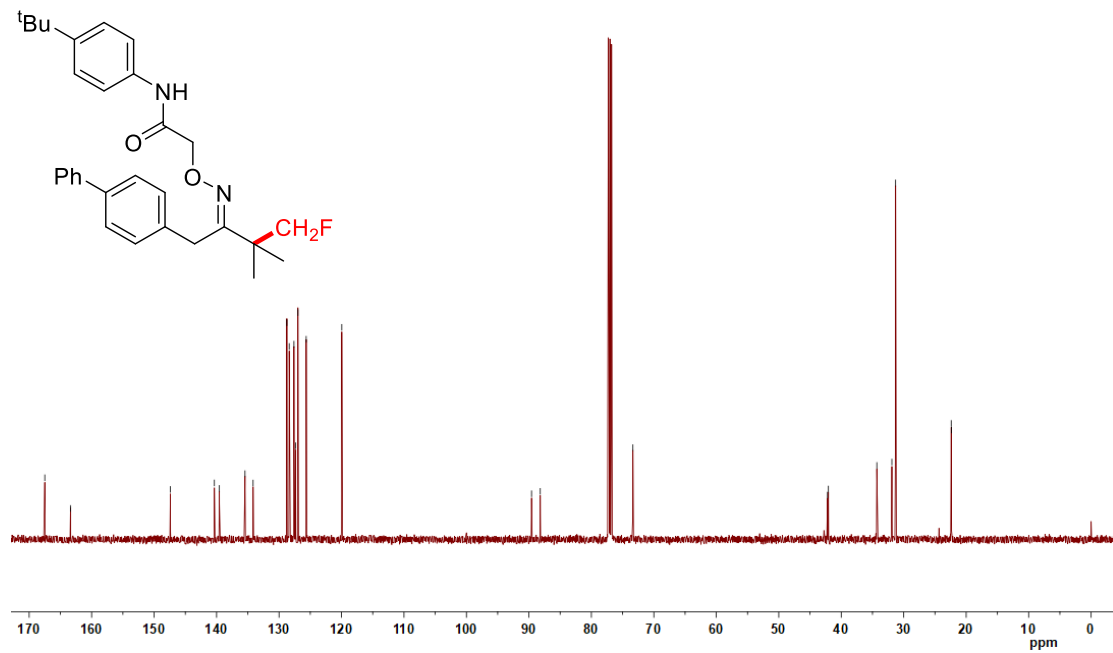
-3.884

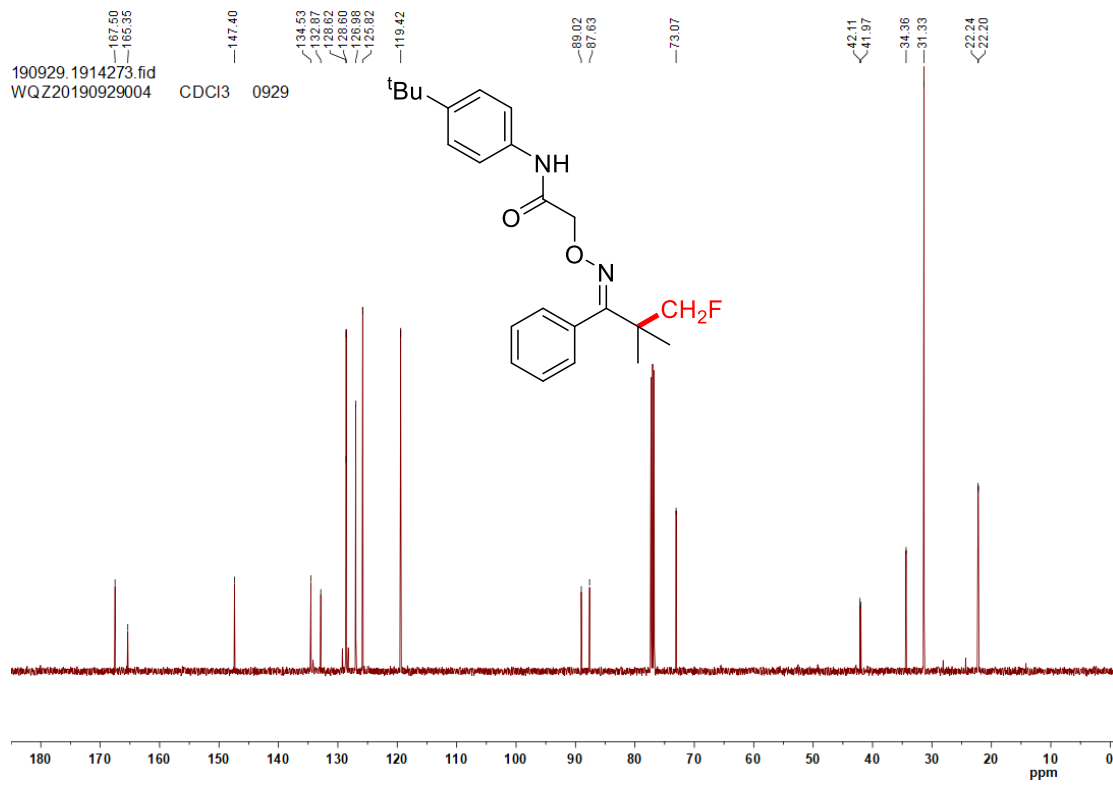
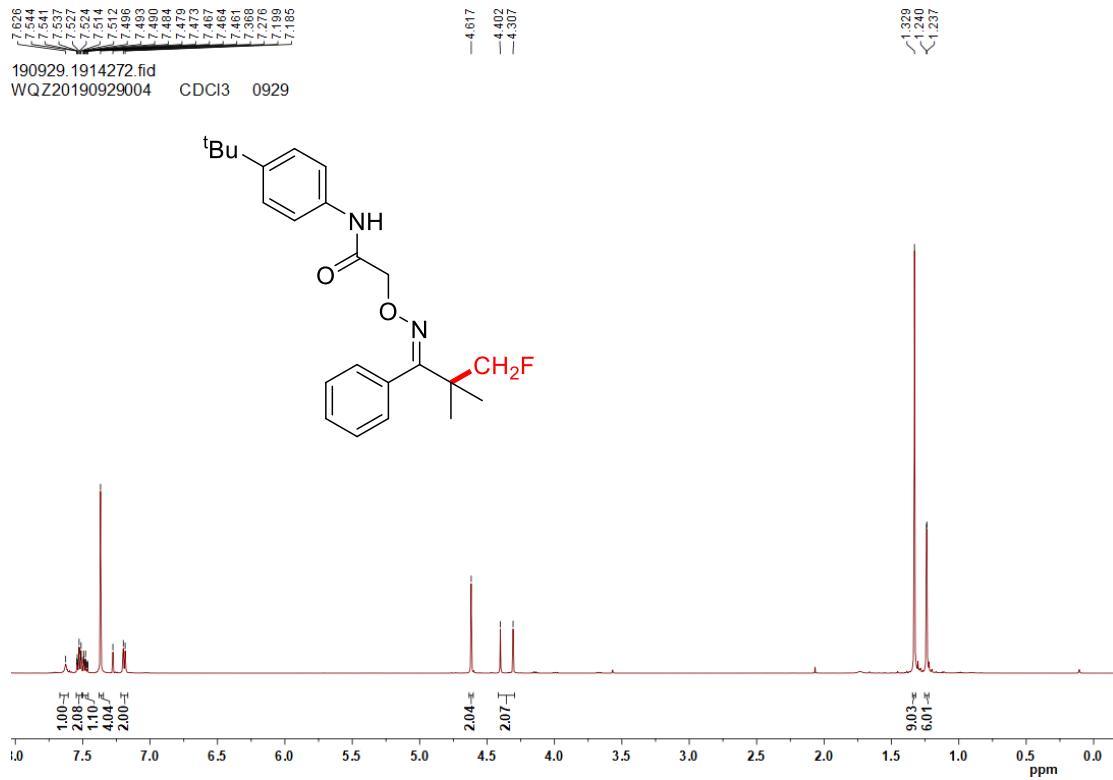
1.277
1.274
1.262

200530.2002598.fid
WQZ20200530006 CDCl3 0530



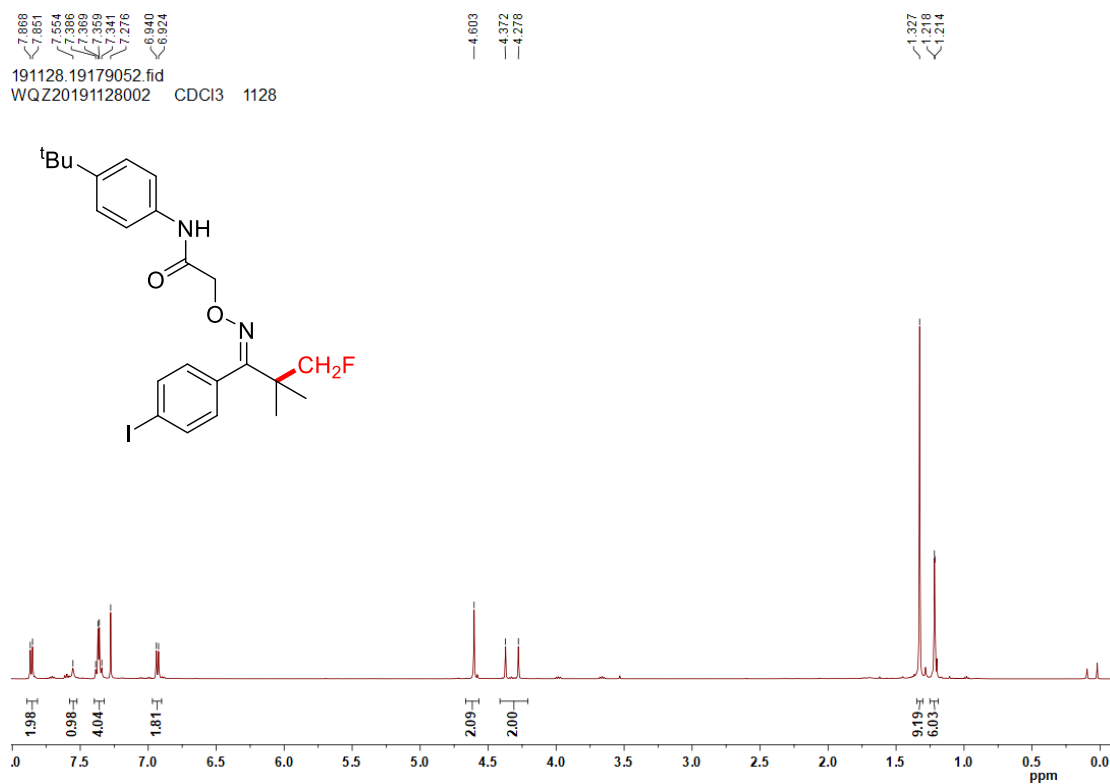
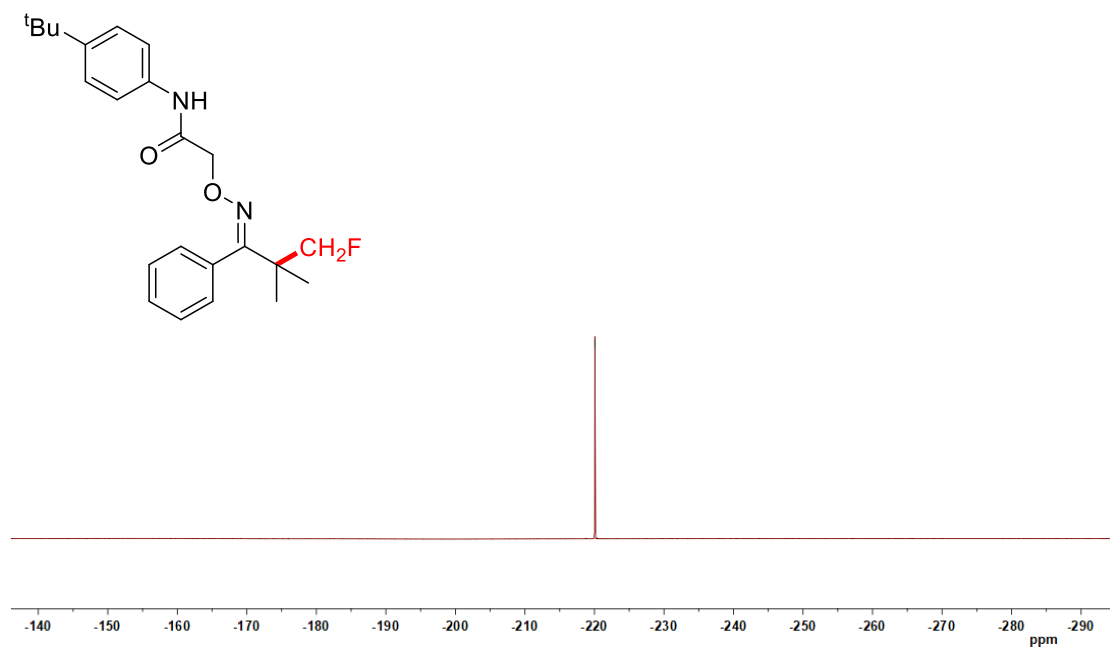
200606.20030394.fid
WQZ20200530006 CDCL3 0606



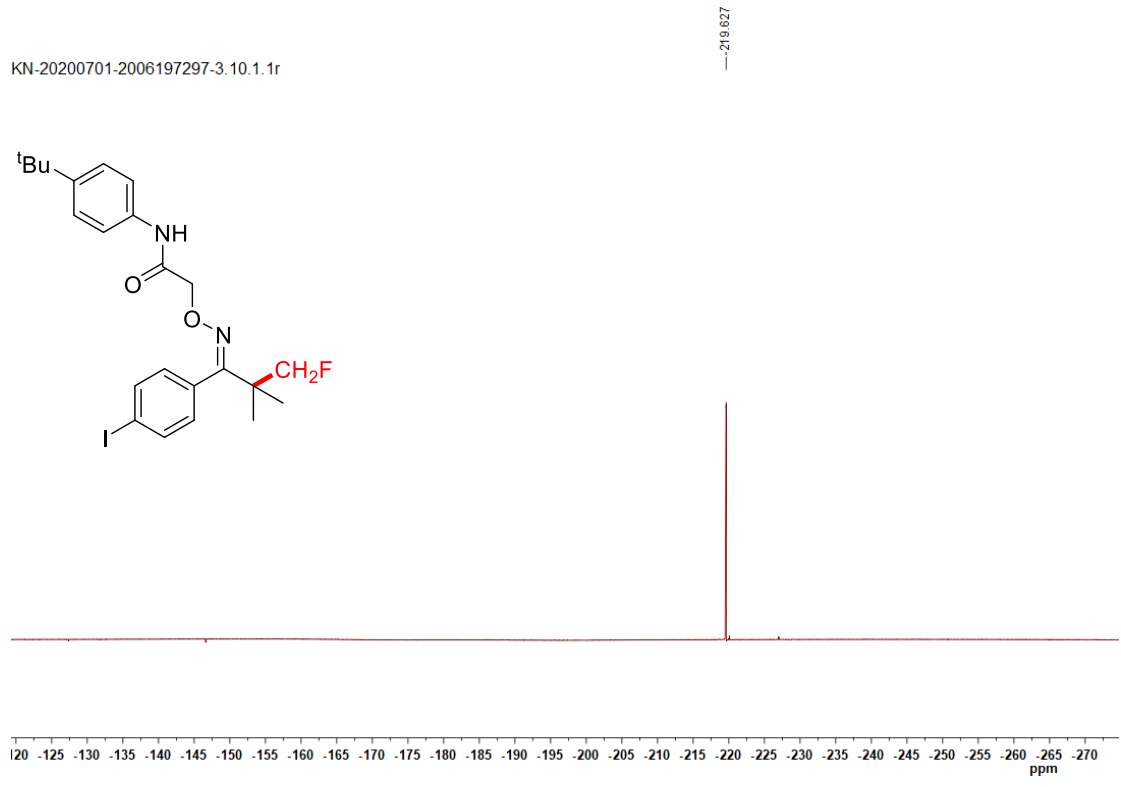
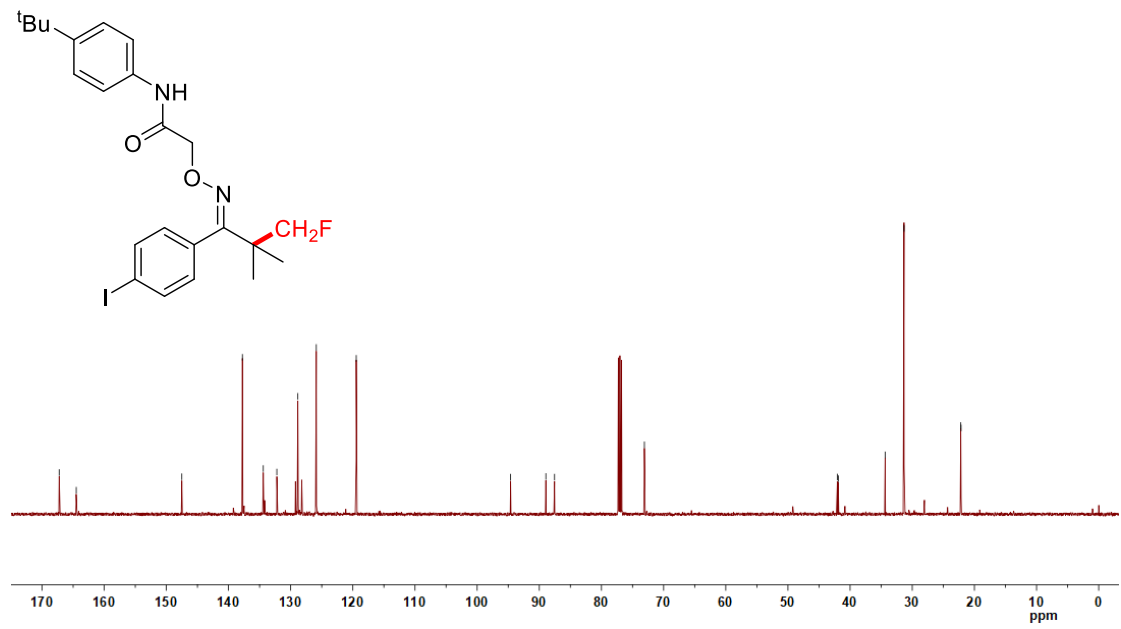


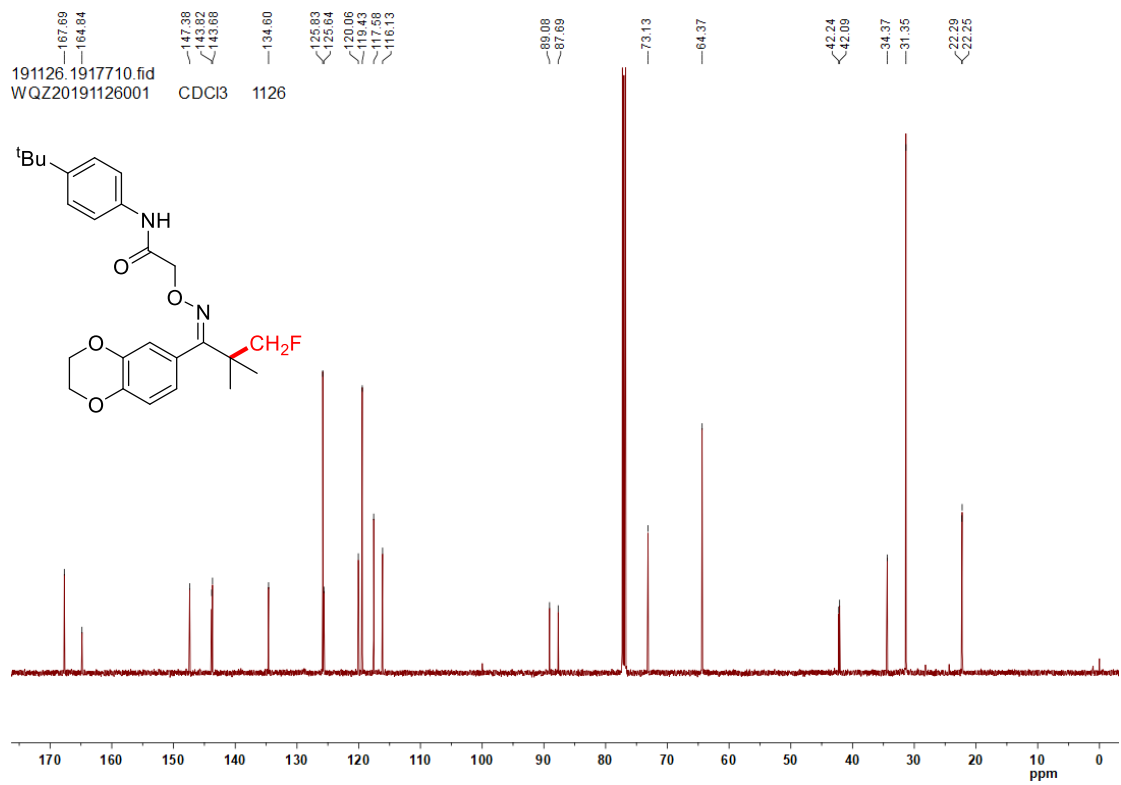
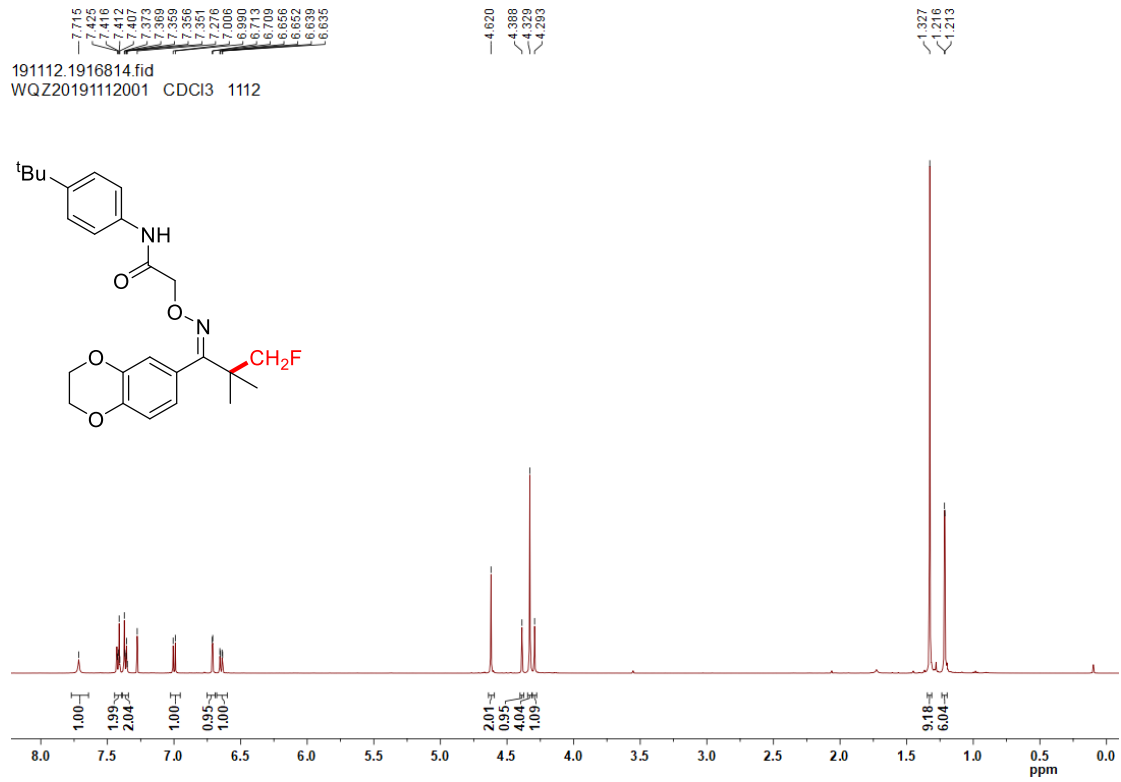
KN-20191015- 1910085577-19.10.1.1r

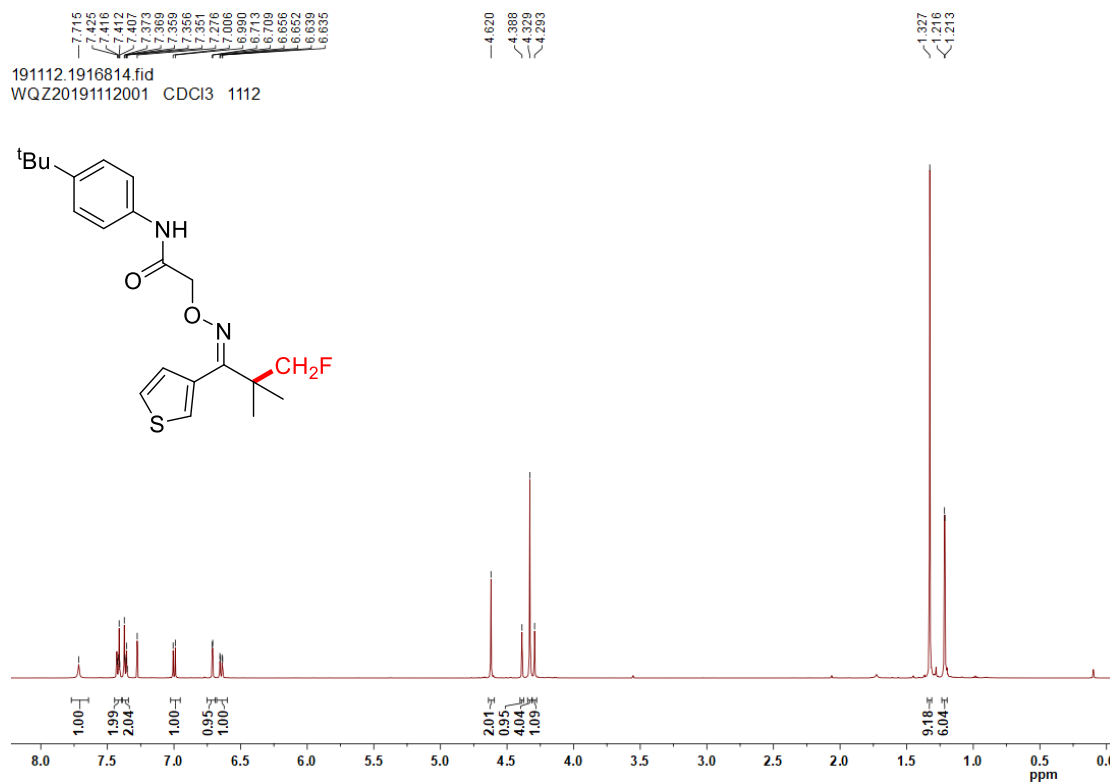
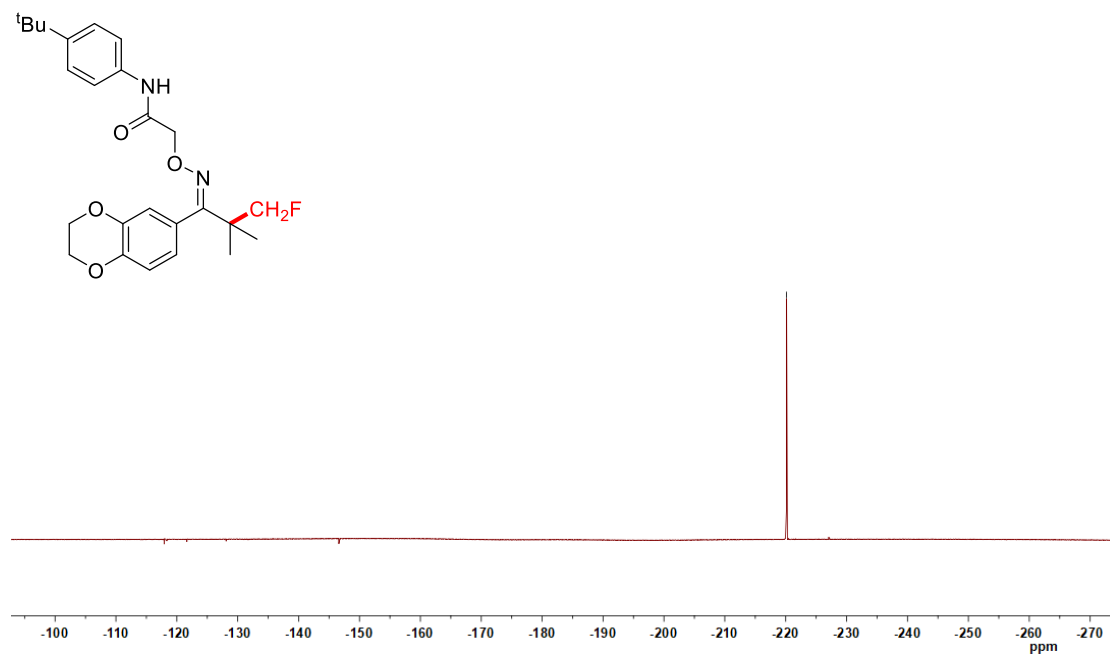
—220.061



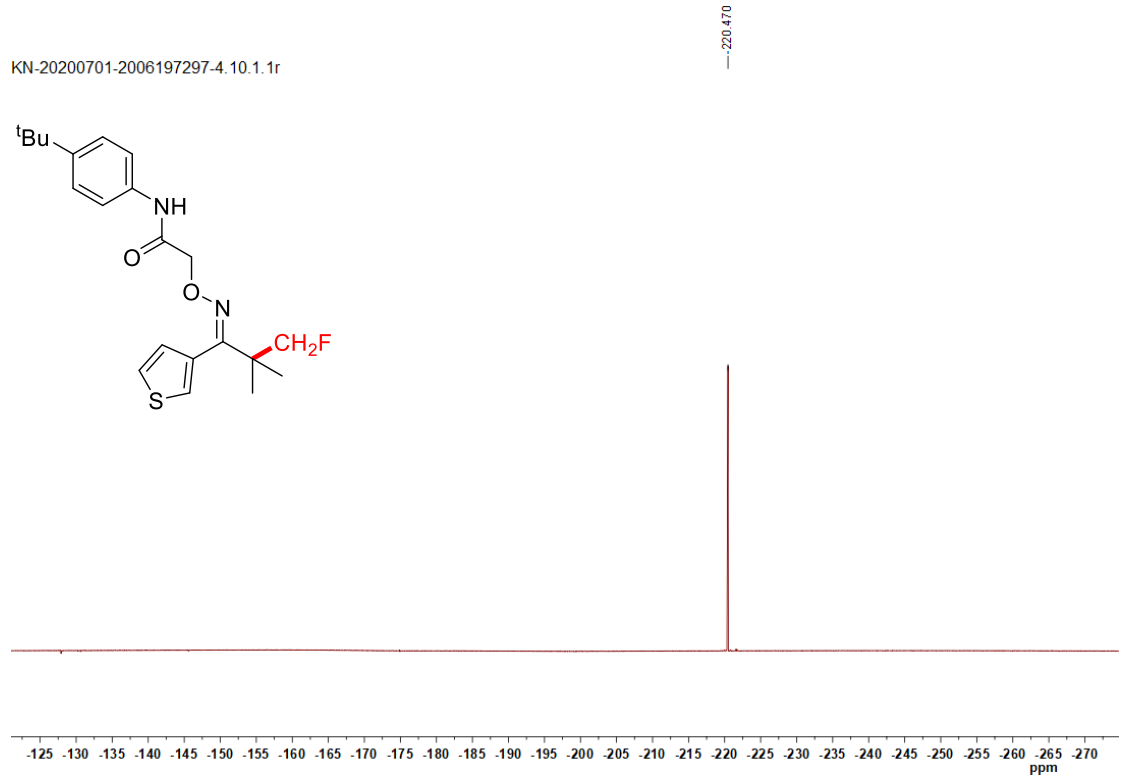
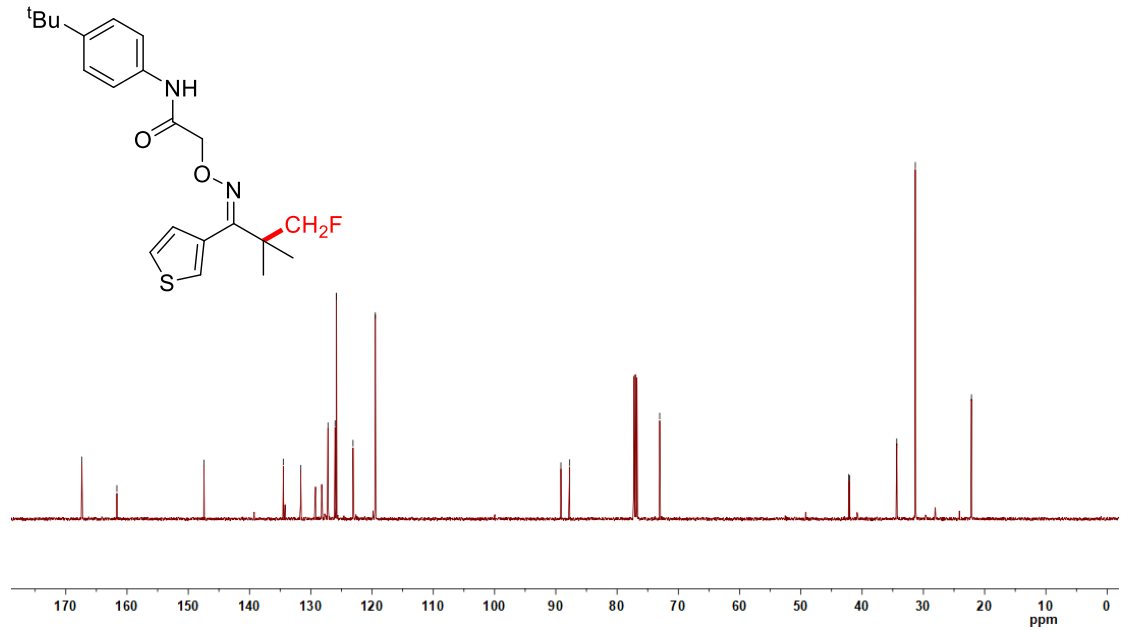
200530.2002596.fid
 WQZ-20200530004 CDCL3 0530

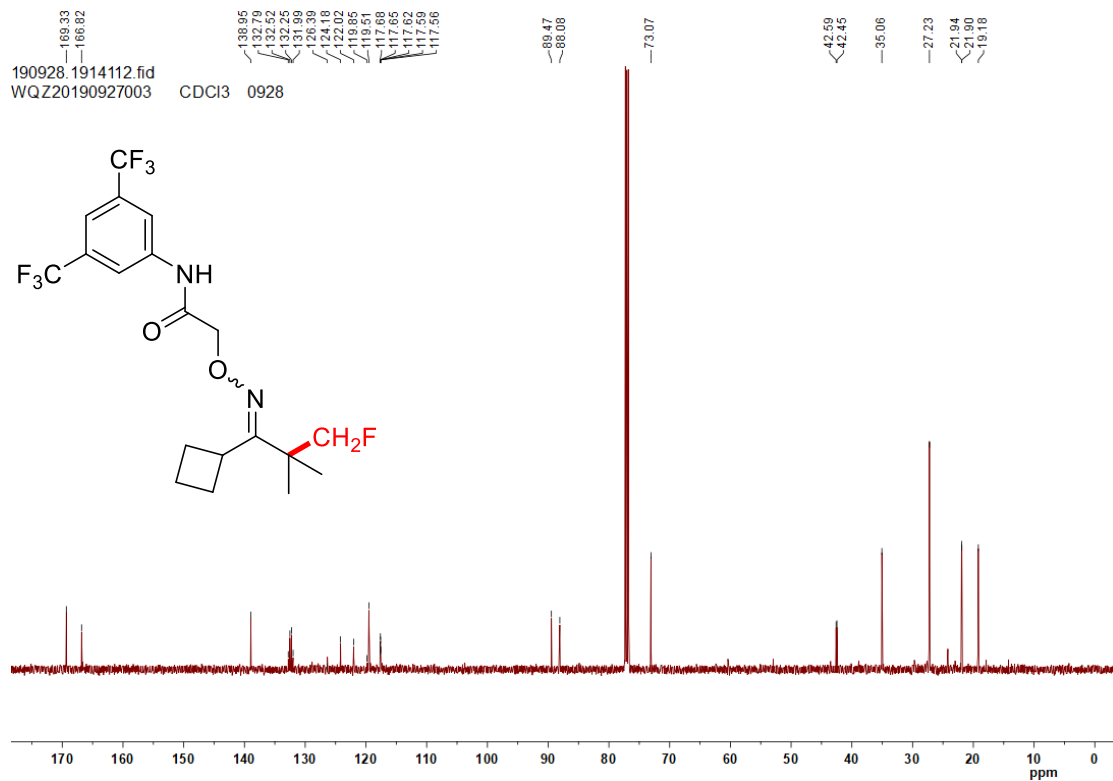
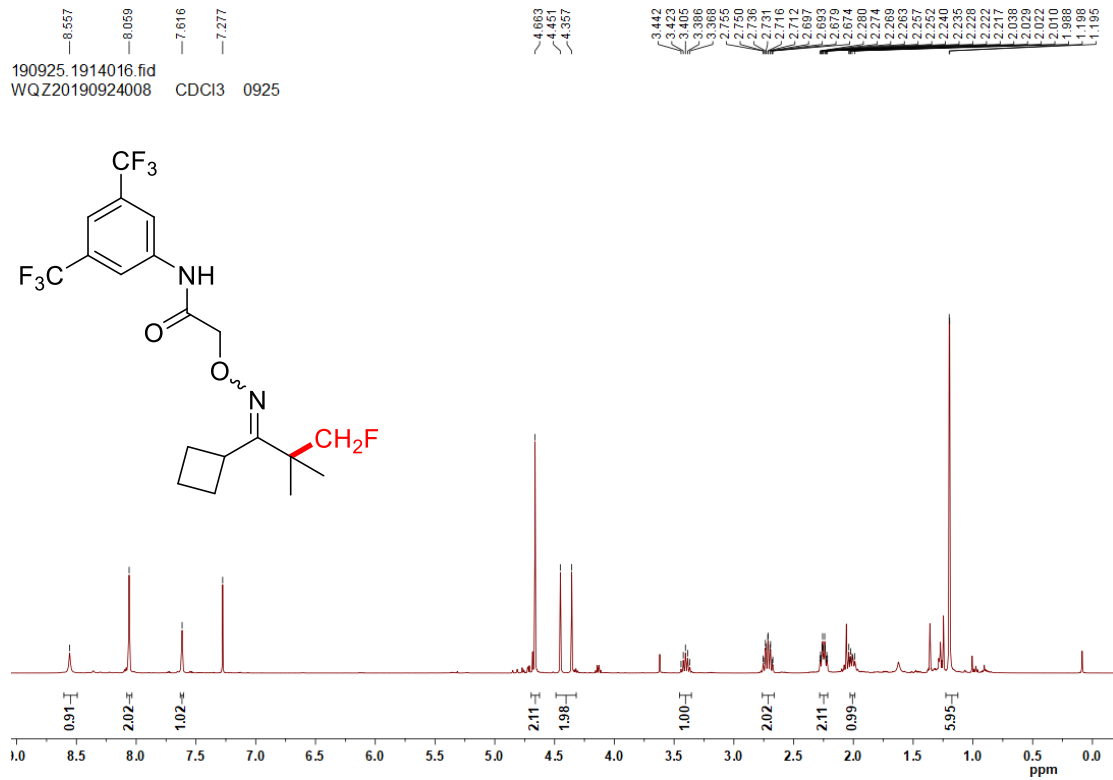






200530.20025971.fid
wqz20200530005 CDCL3 0530

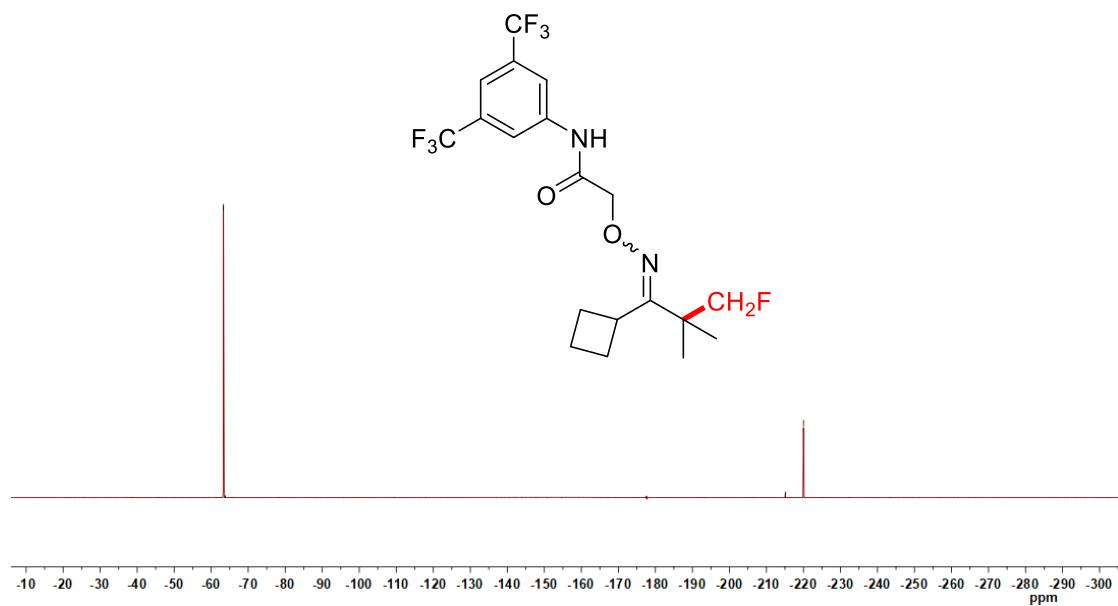




KN-20191015-1910085577-22.10.1.1r

63.314

-219.998

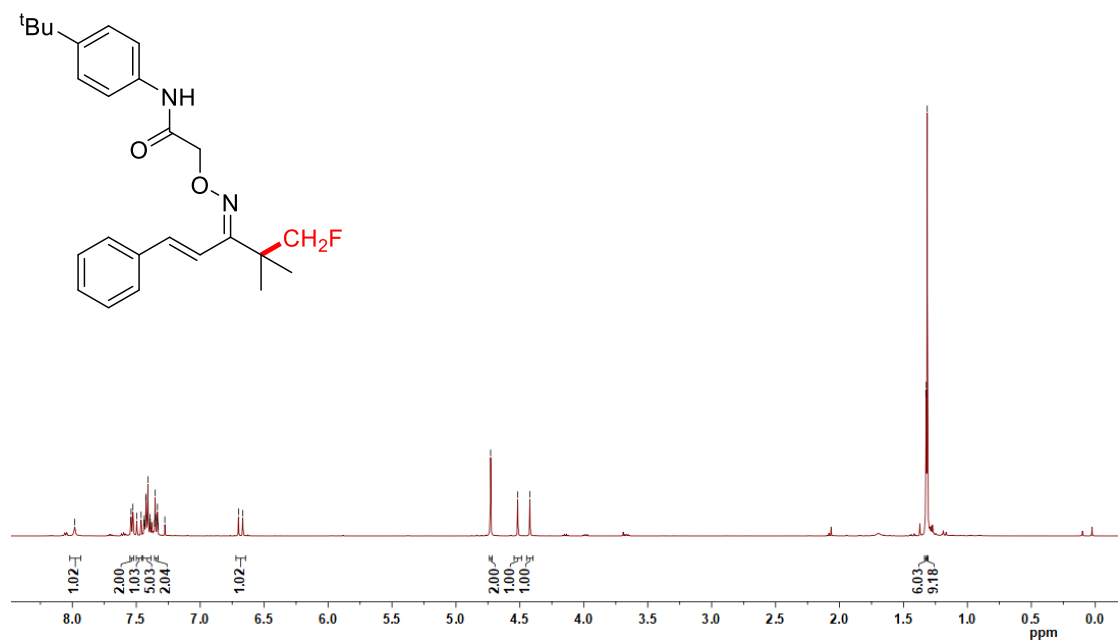


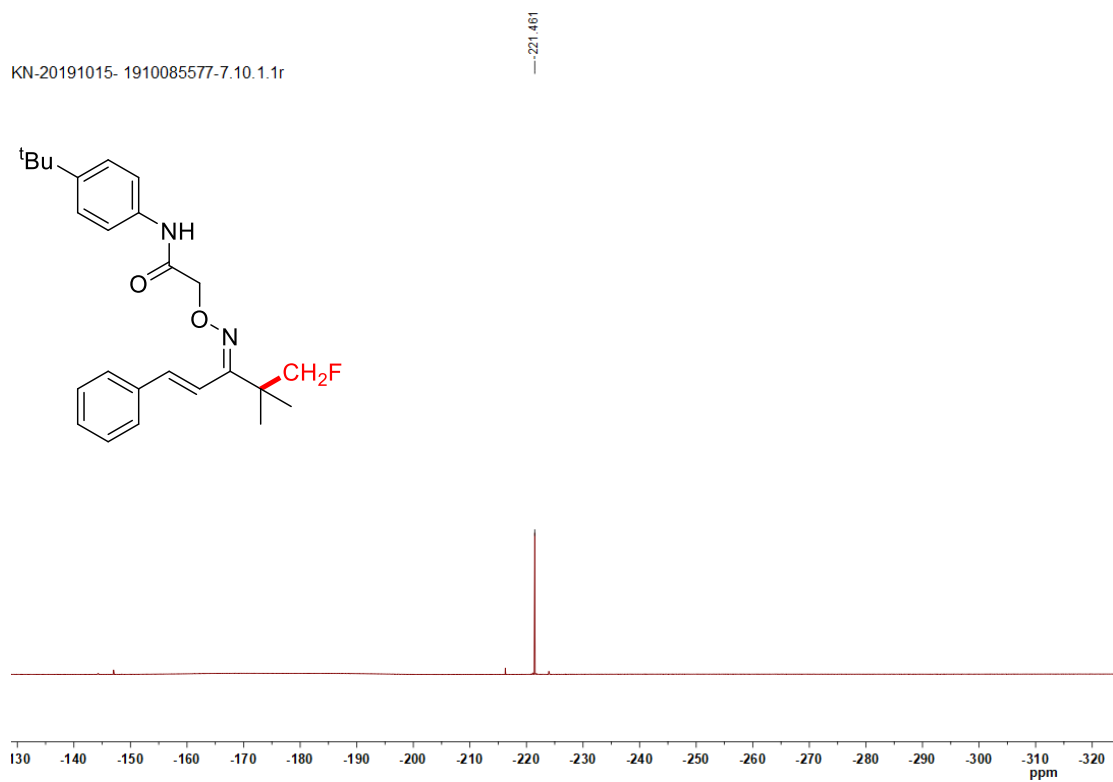
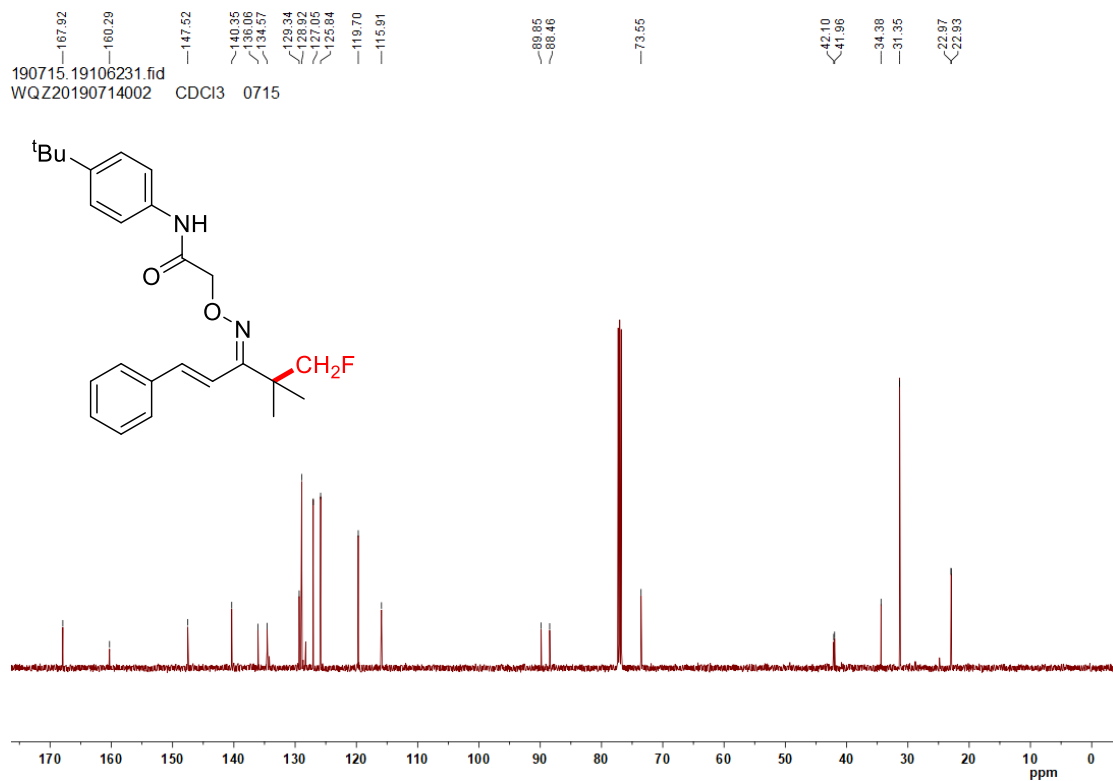
7.992
7.541
7.526
7.496
7.462
7.440
7.437
7.426
7.423
7.409
7.395
7.393
7.390
7.367
7.352
7.348
7.338
7.334
7.330
7.276
6.867

4.729
4.517
4.422

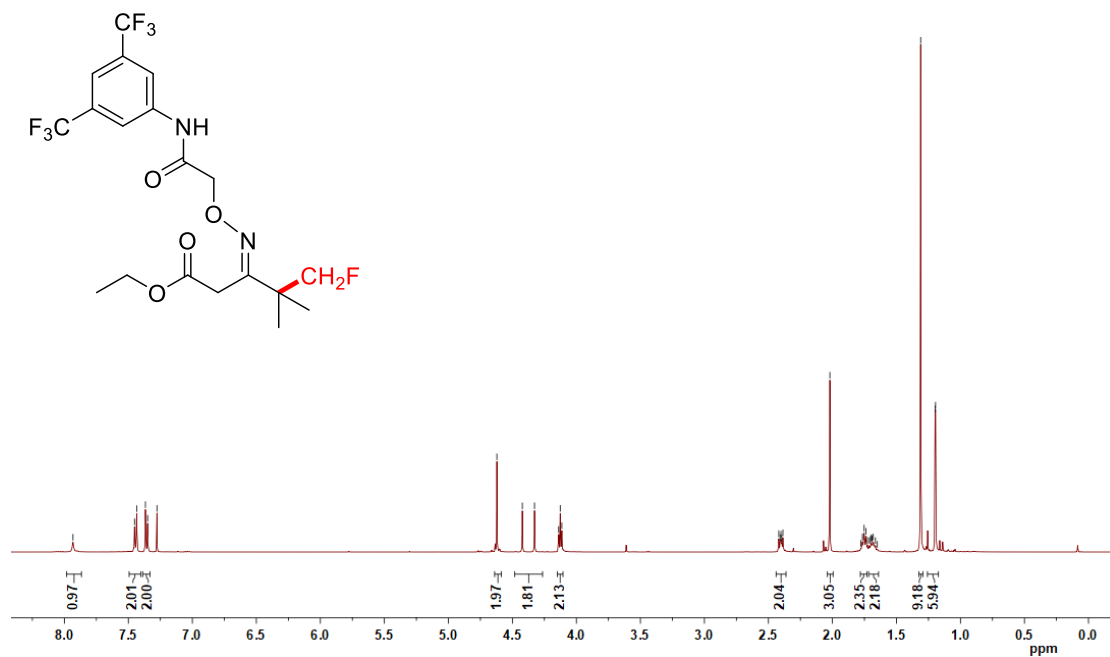
1.325
1.321
1.314

190613_19087344.fid
WQZ20190613004 CDCl3 0613

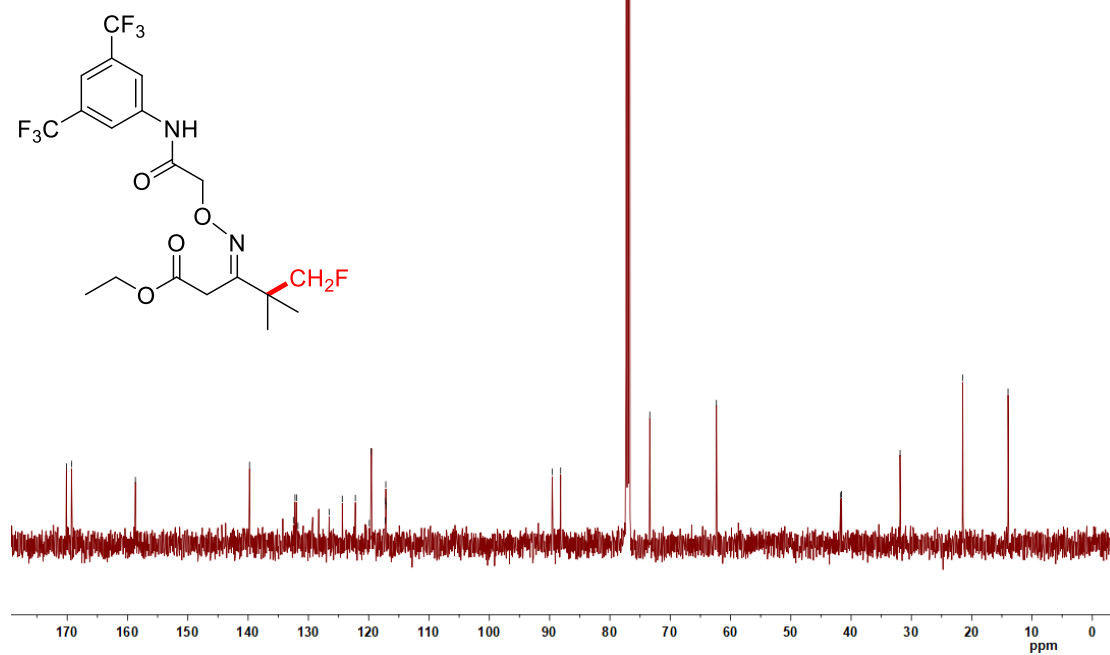




190920.1913600.fid
WQZ20190920001 CDCl3 0920

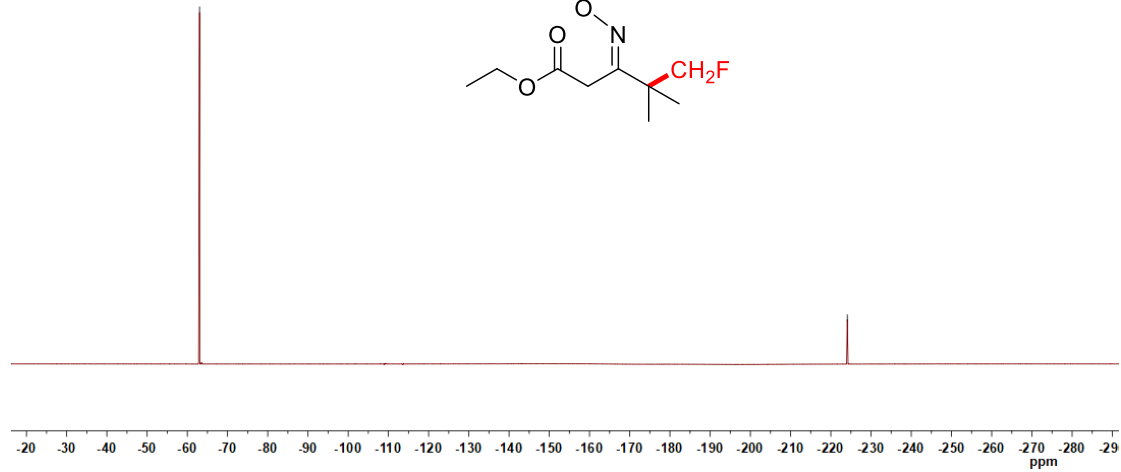
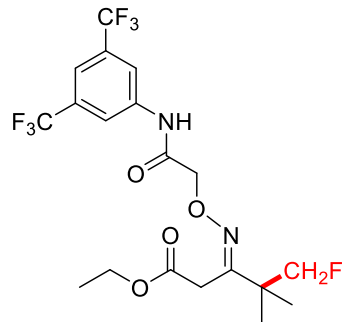


190819.19119612.fid
WQZ20190816002 CDCl3 0819



KN-20191015-1910085577-5.10.1.1r
-63.035

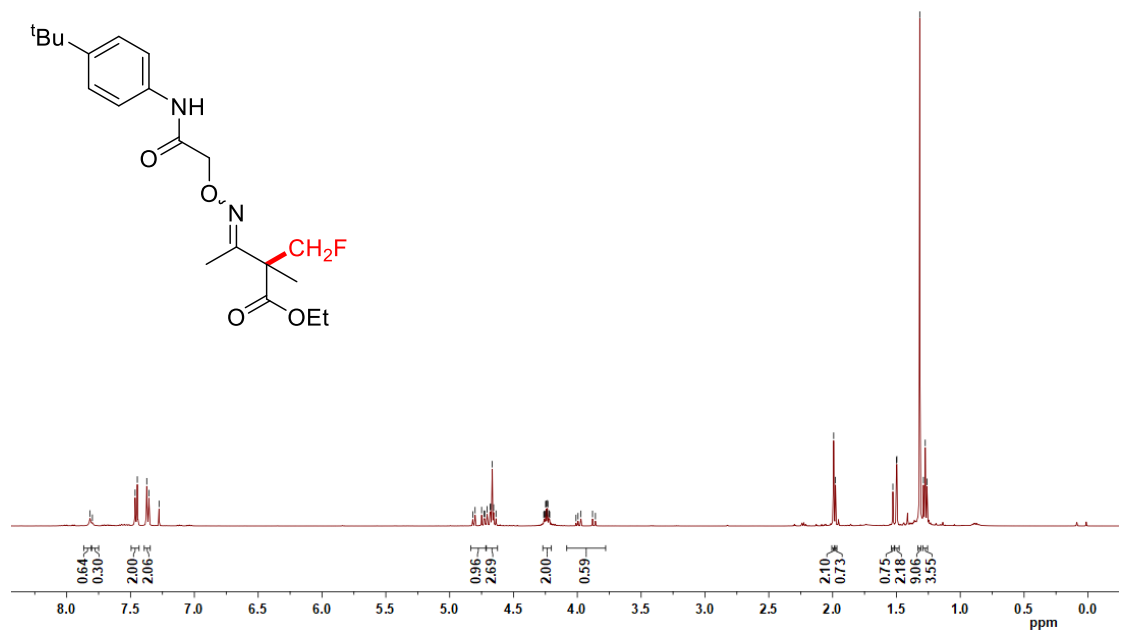
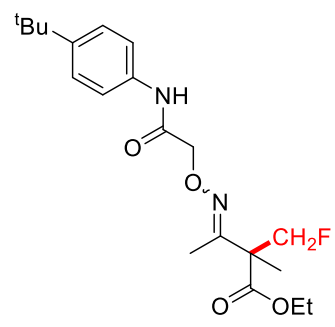
-224.095

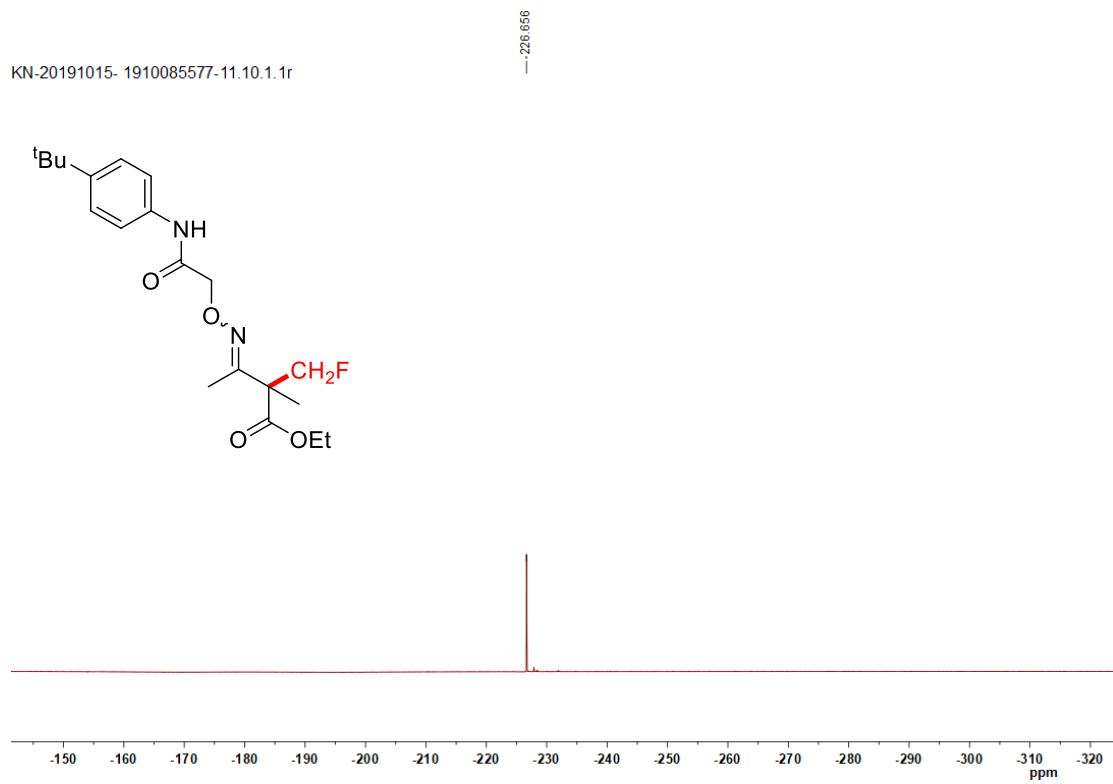
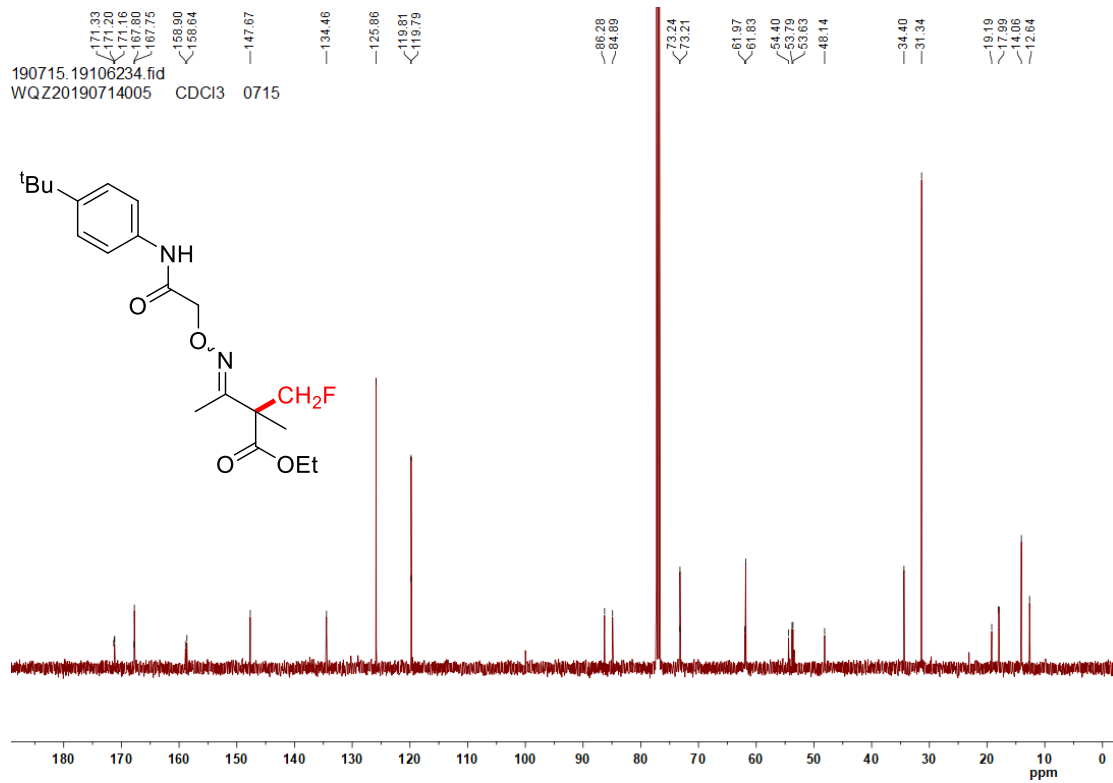


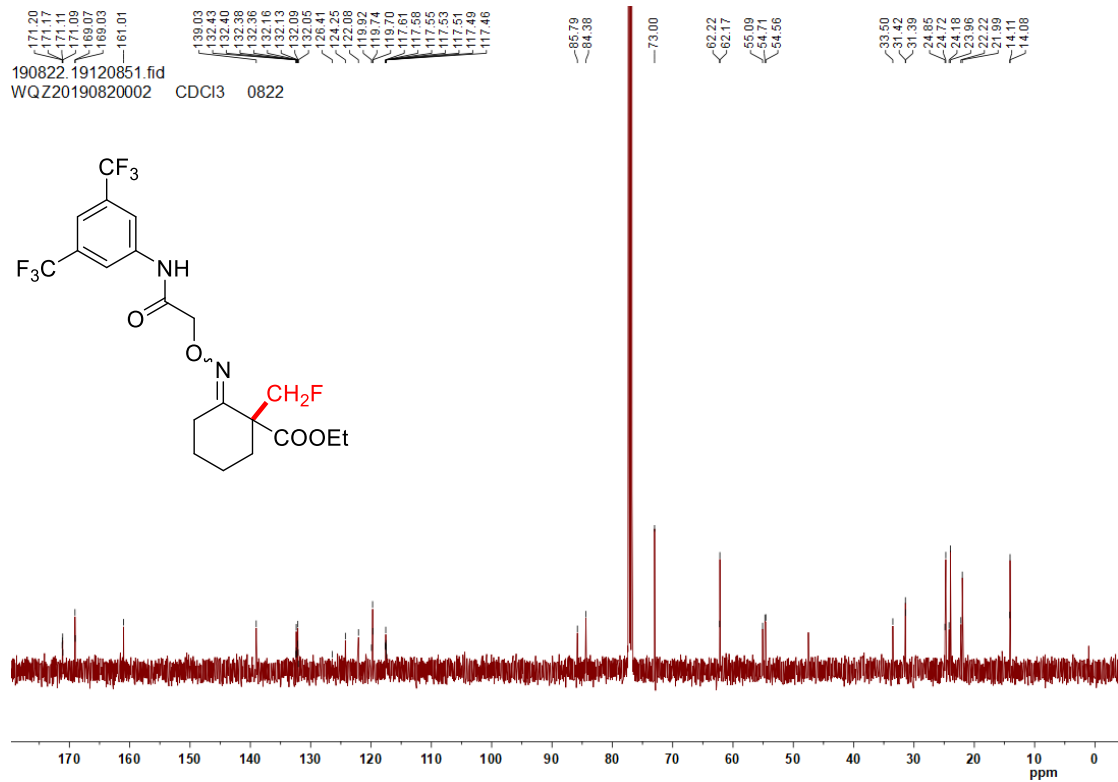
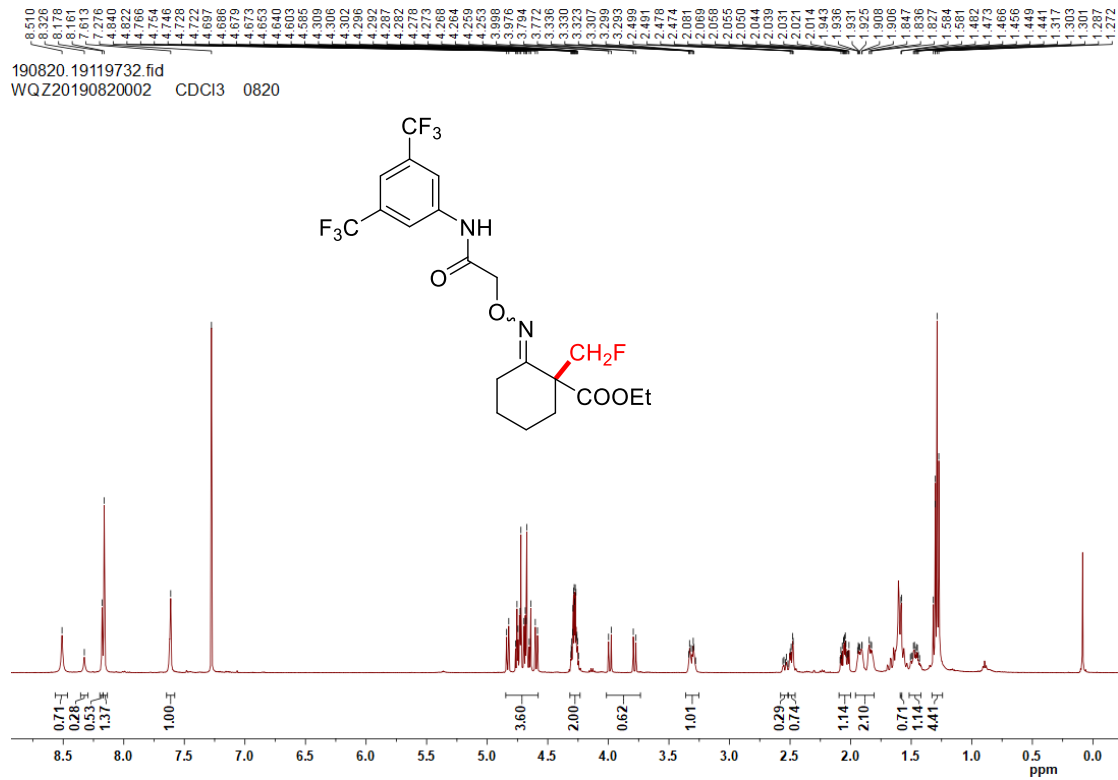
190319.1903281.fid
WQZ20180318001 CDCL3 0319

4.819
4.801
4.750
4.731
4.725
4.706
4.684
4.666
4.655
4.637
4.263
4.259
4.253
4.246
4.245
4.239
4.234
4.230
4.222
4.220
4.216
4.211
3.994
3.972
3.881
3.858

1.992
1.977
1.528
1.499
1.487
1.317
1.289
1.274
1.260

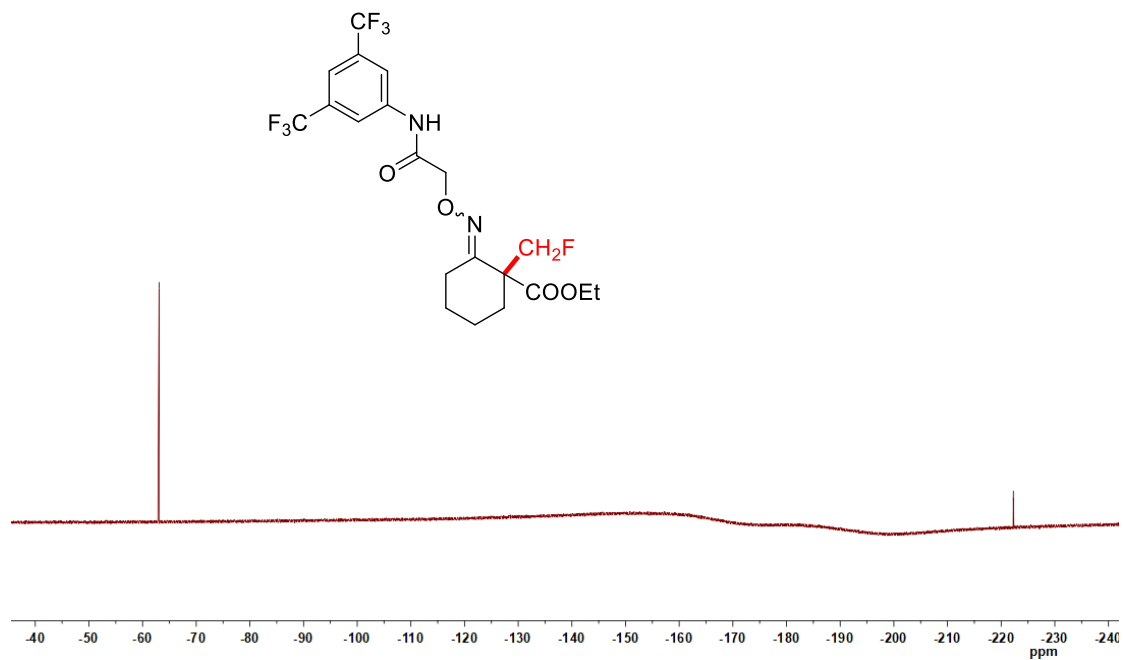




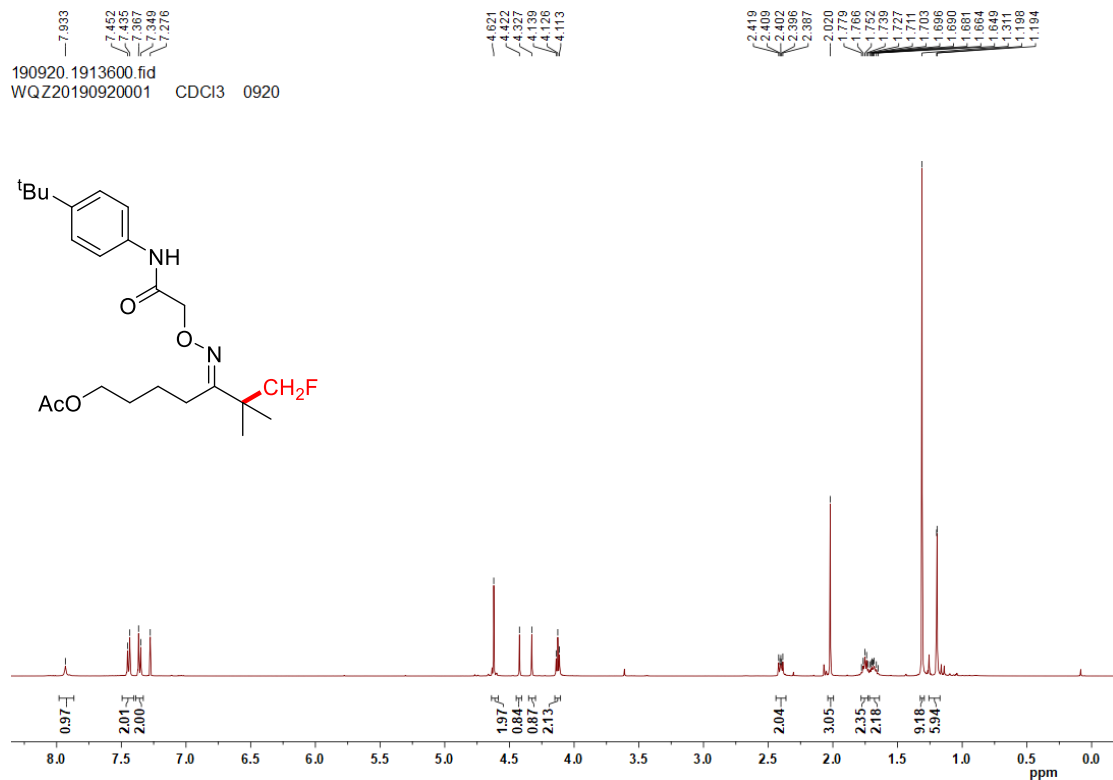


KN-20191015-1910085577-12.10.1.1r
-63.078

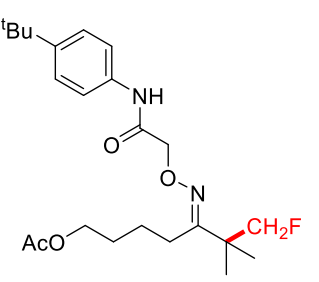
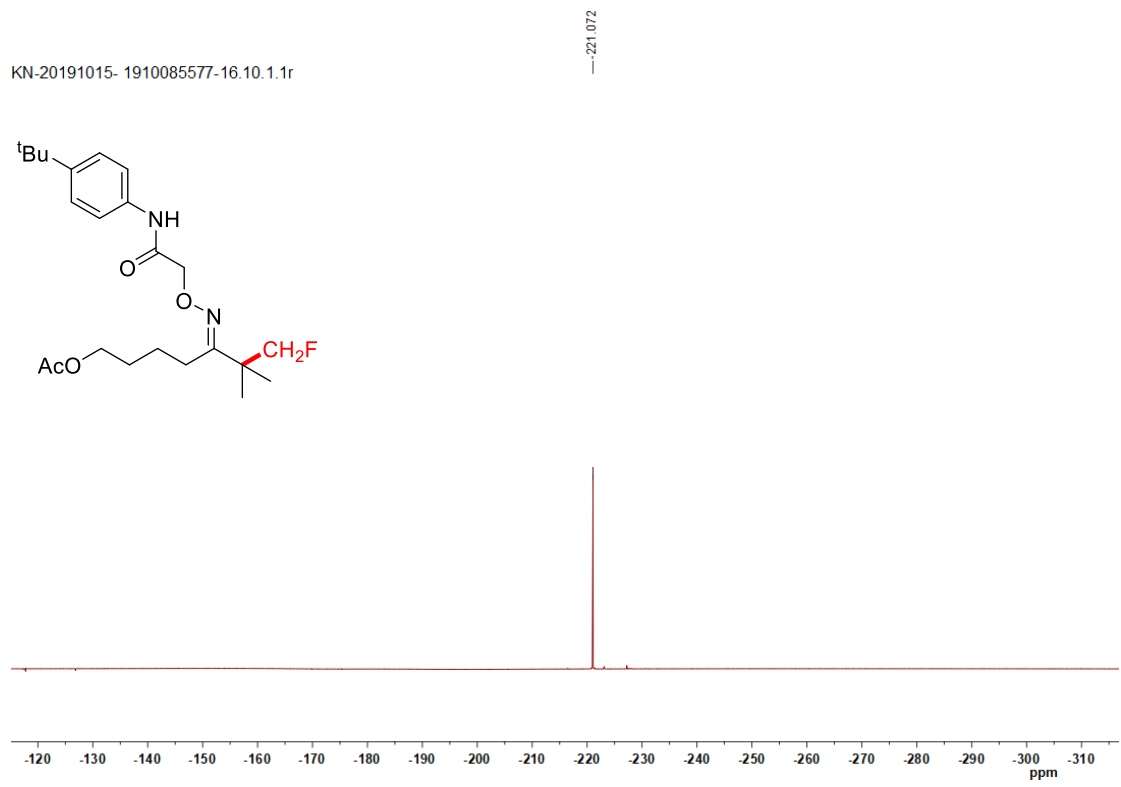
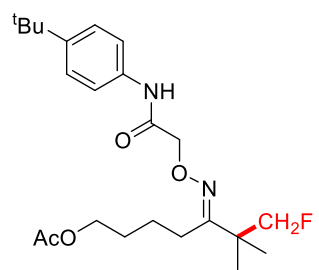
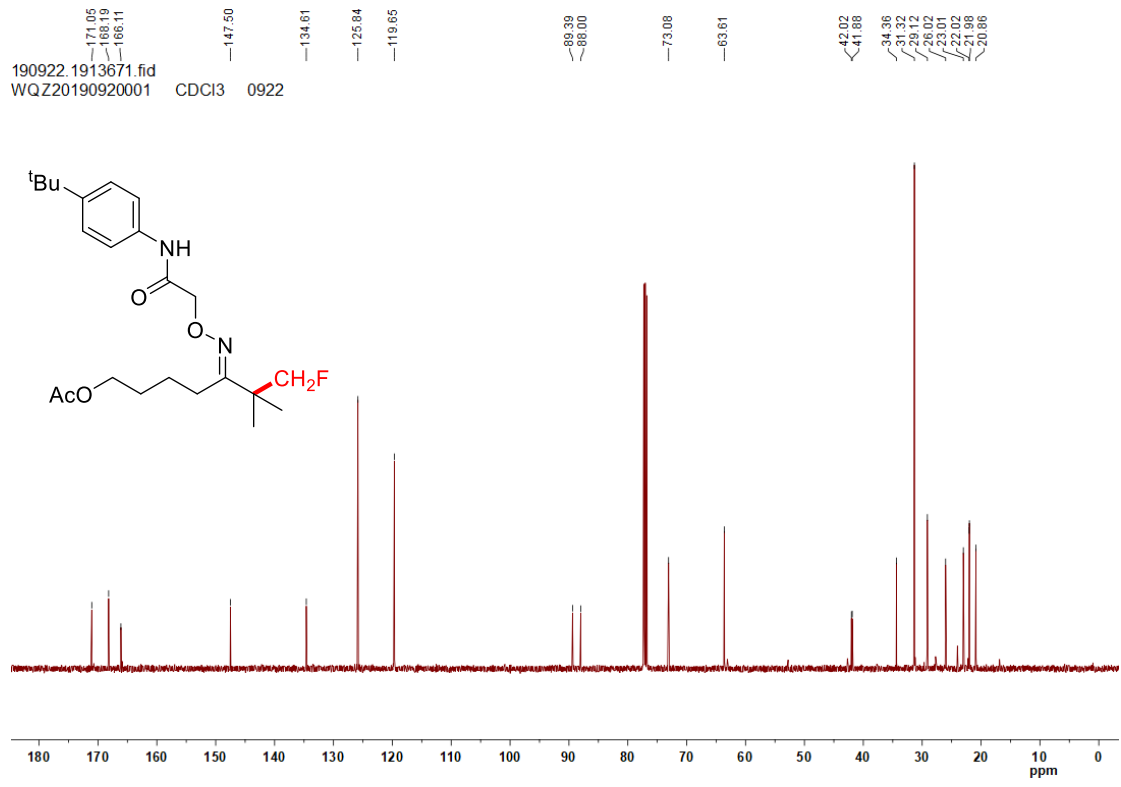
-222.273

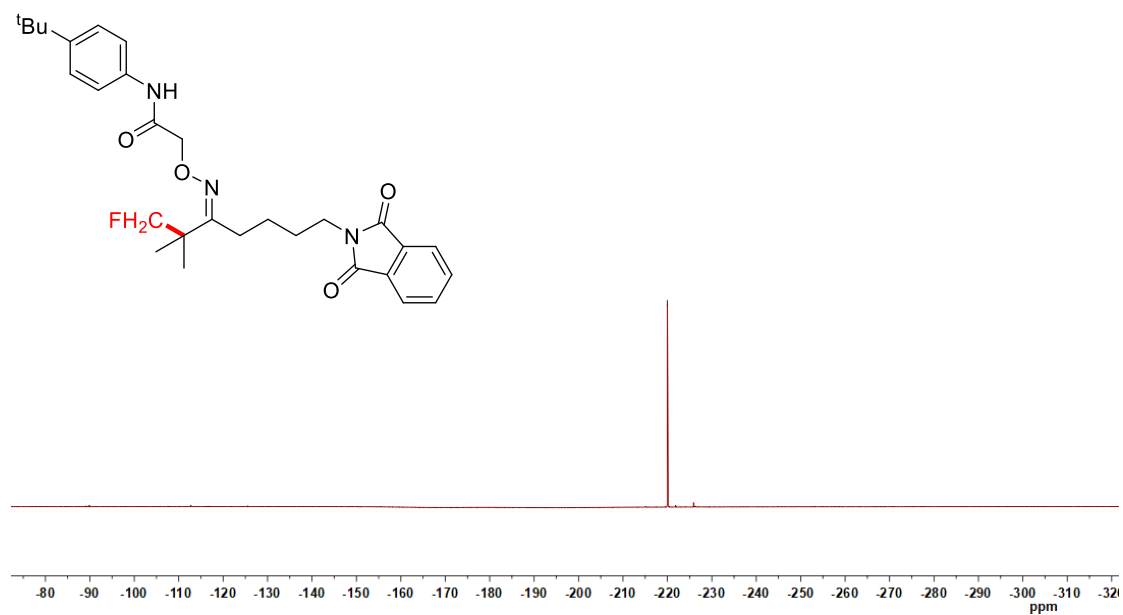


190920.1913600.fid
WQZ20190920001 CDCl3 0920

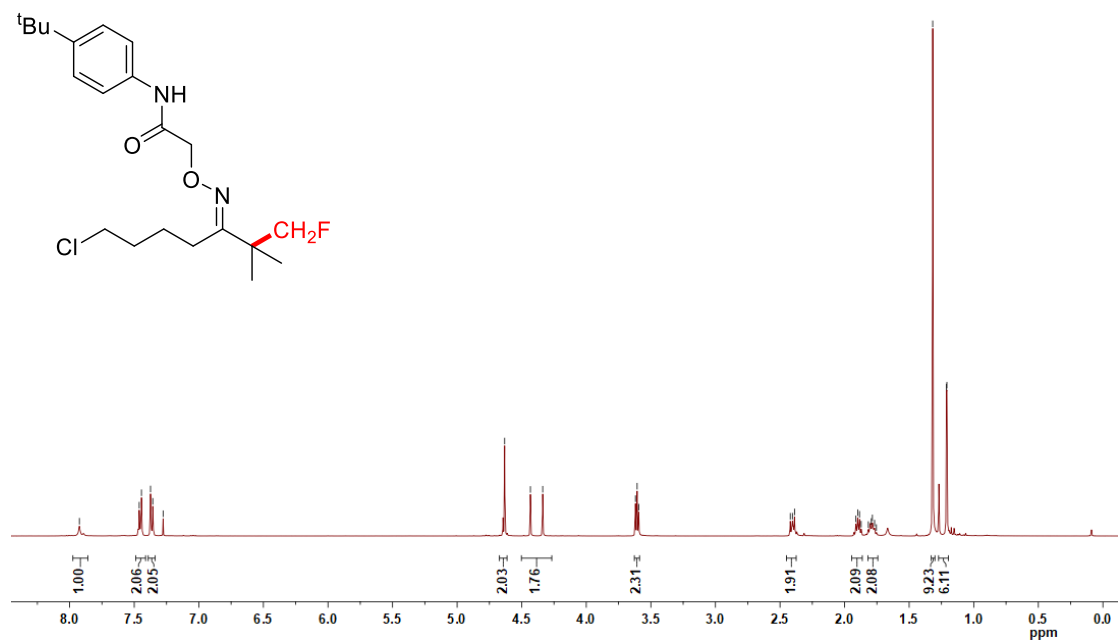


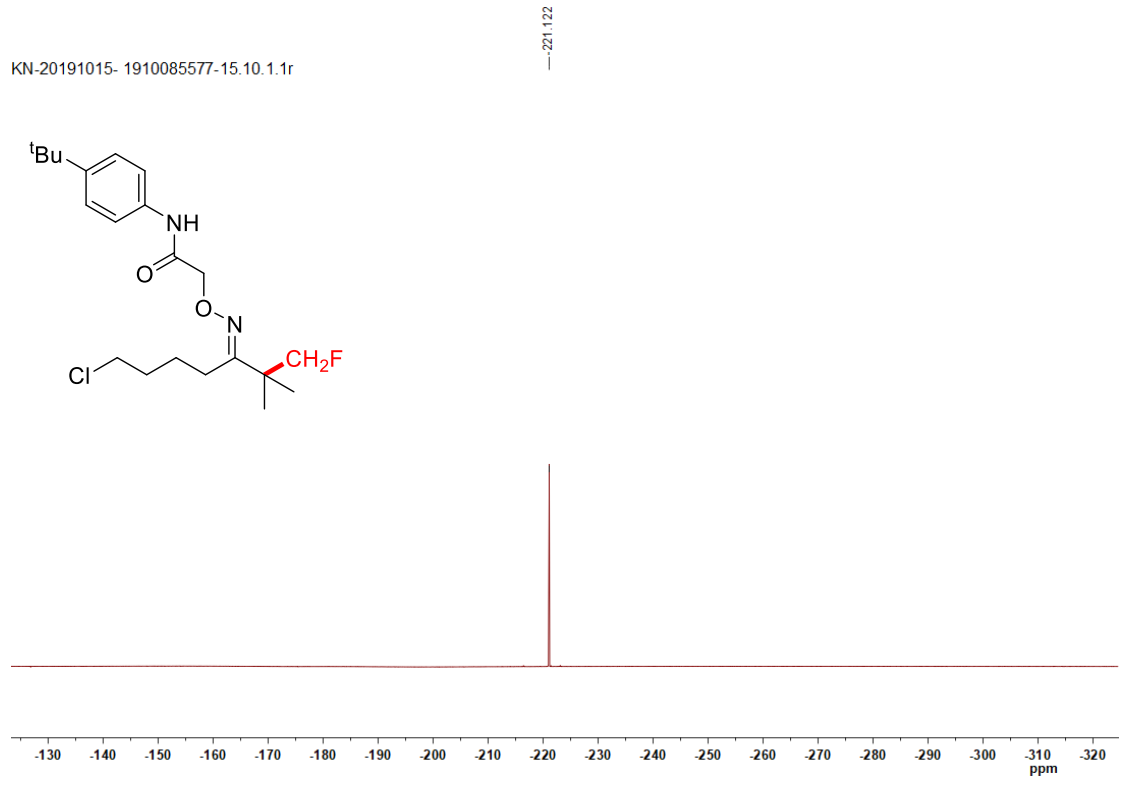
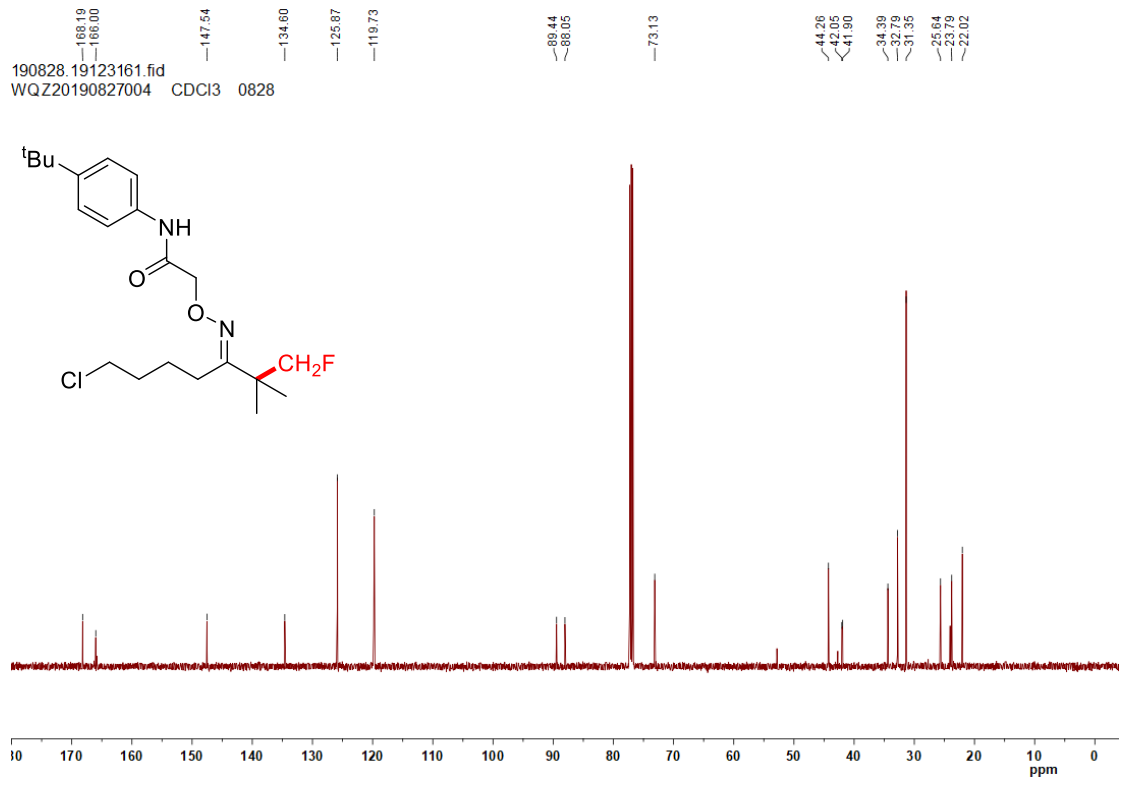
190922 1913671.fid
 WQZ20190920001 CDCl3 0922

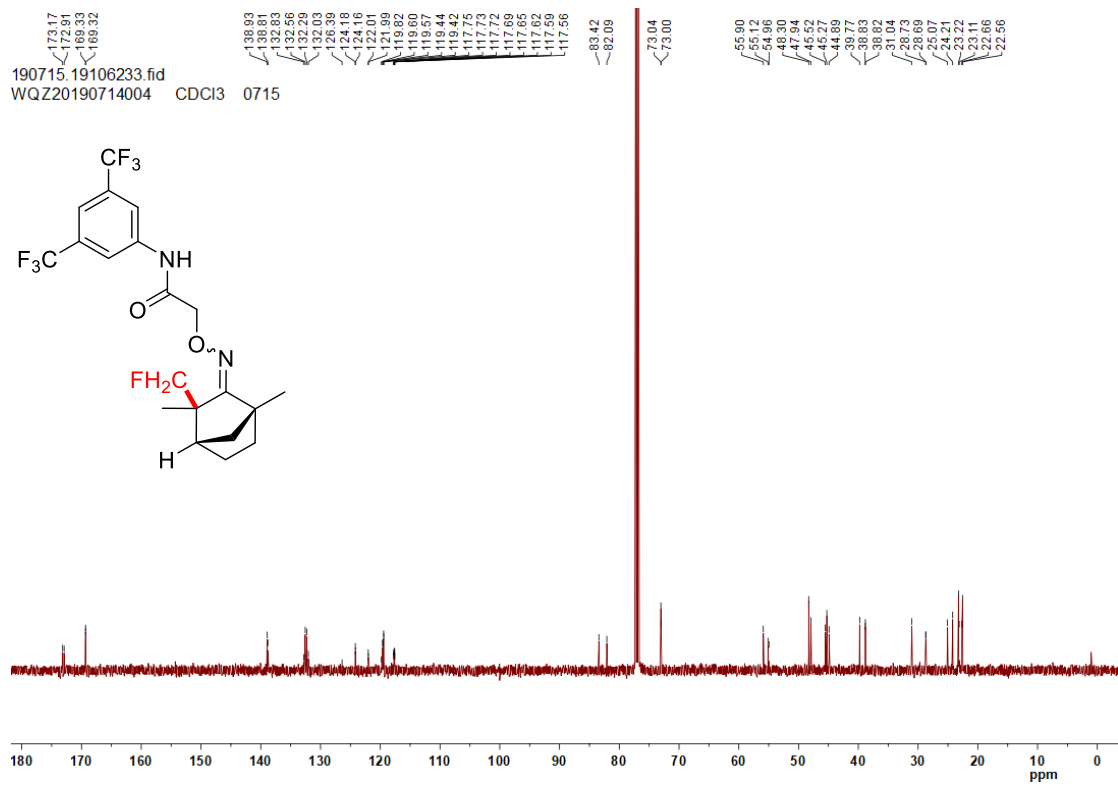
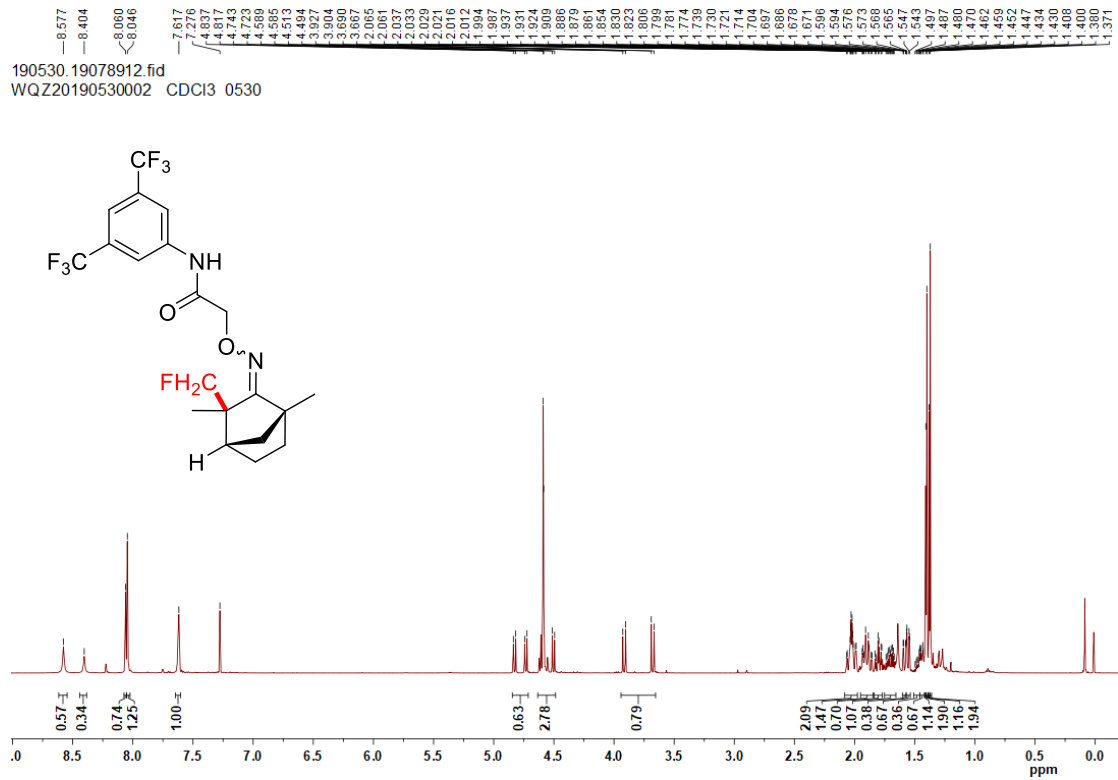




190826 19122361.fid
WQZ20190826001 CDCI3 0826



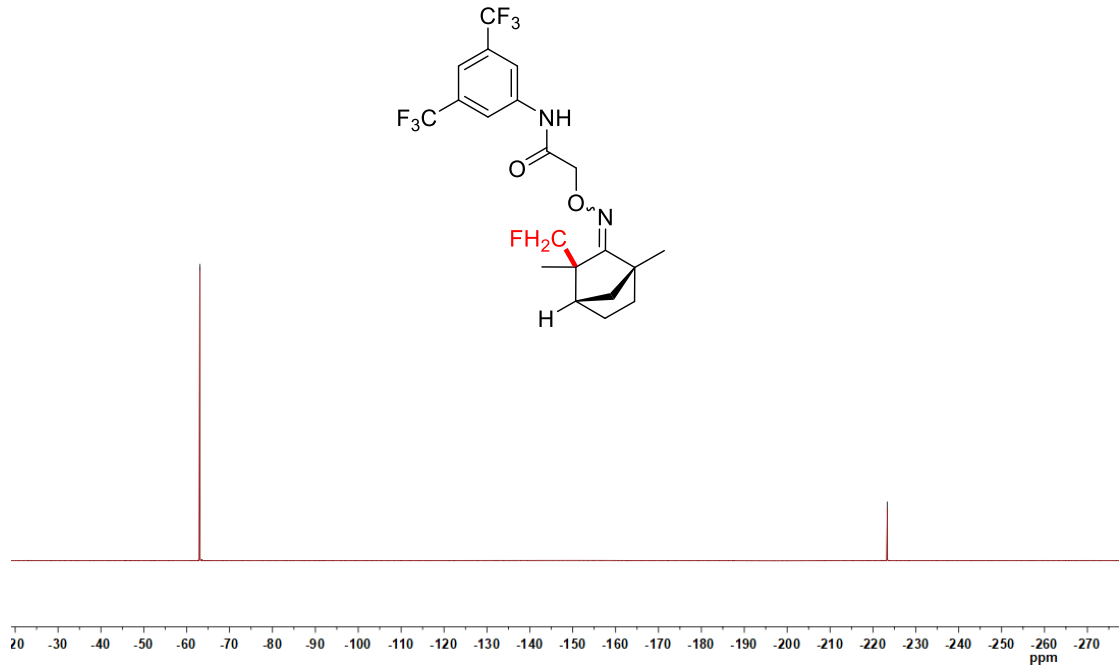




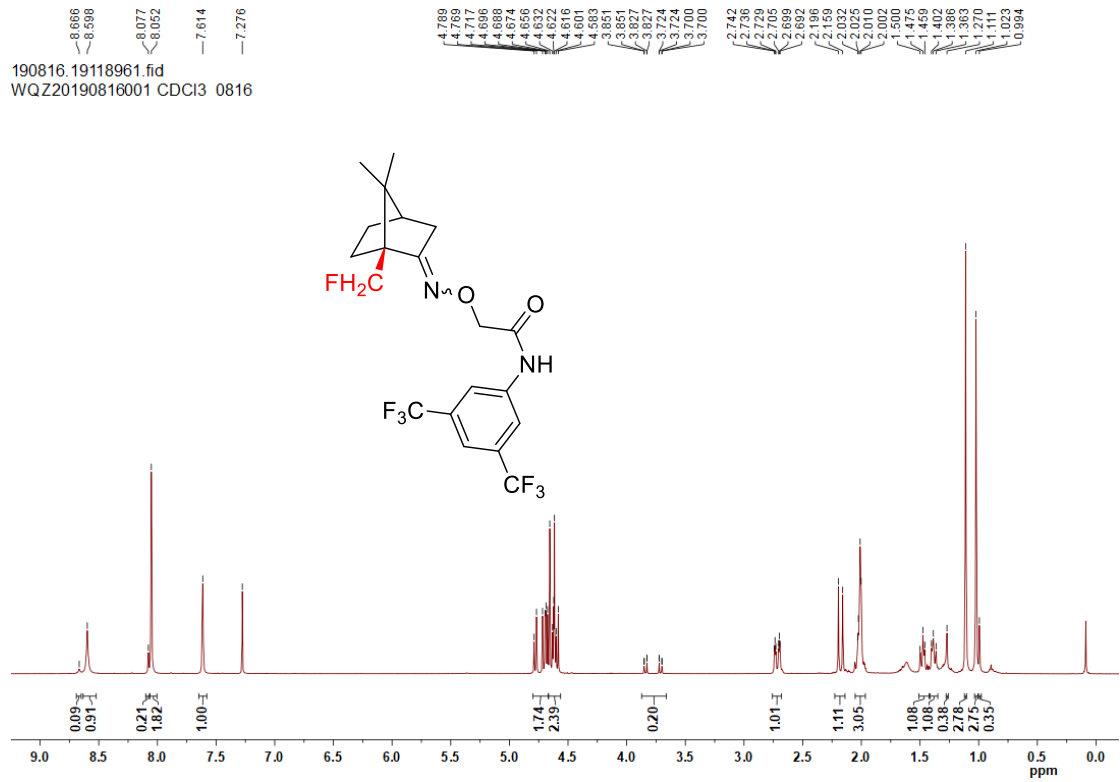
KN-20191015- 1910085577-14.10.1.1r

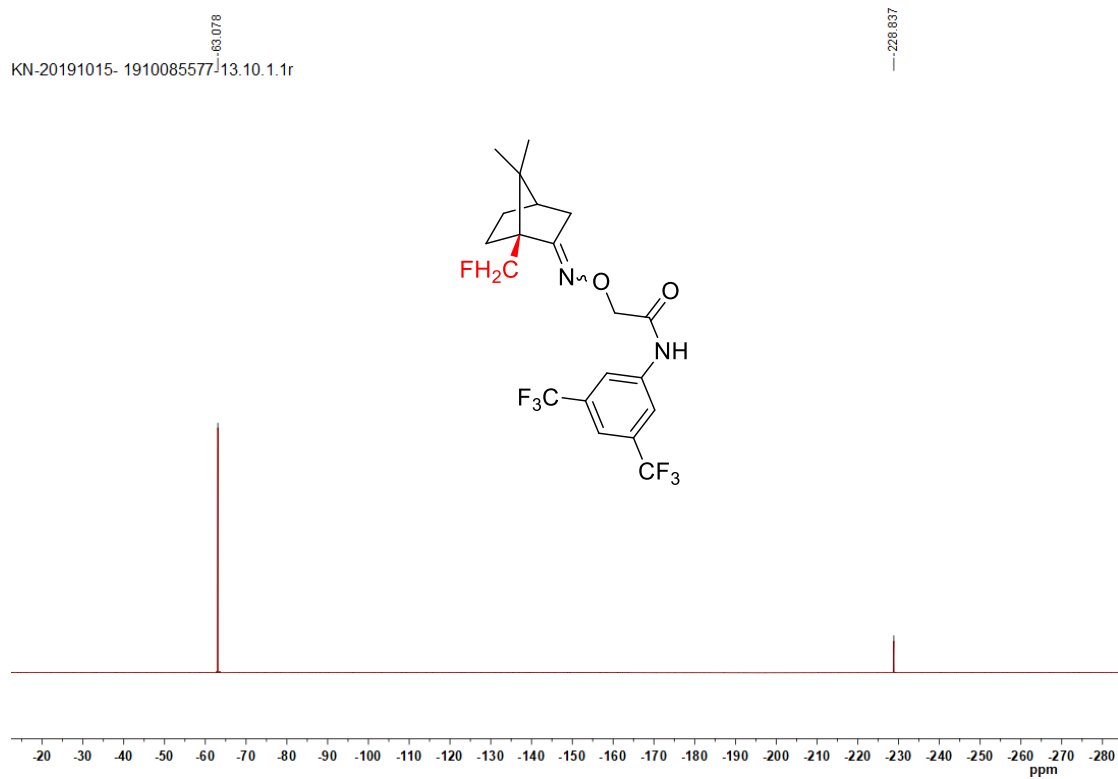
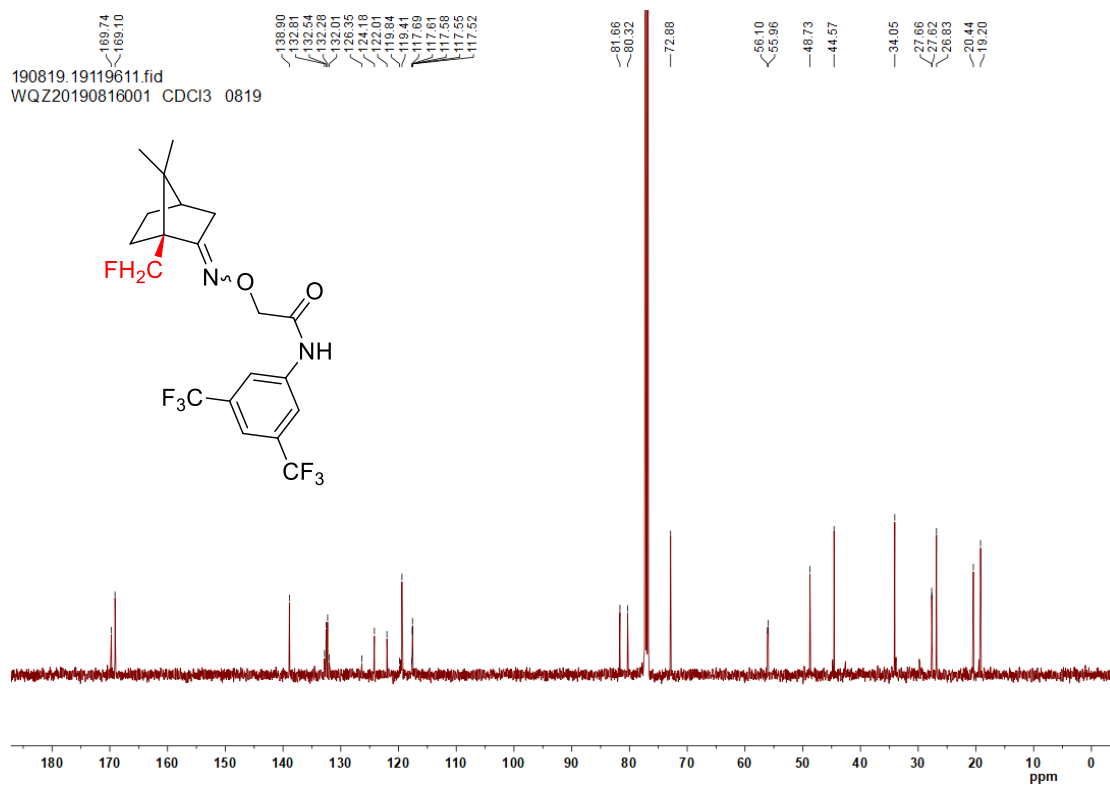
-63.067

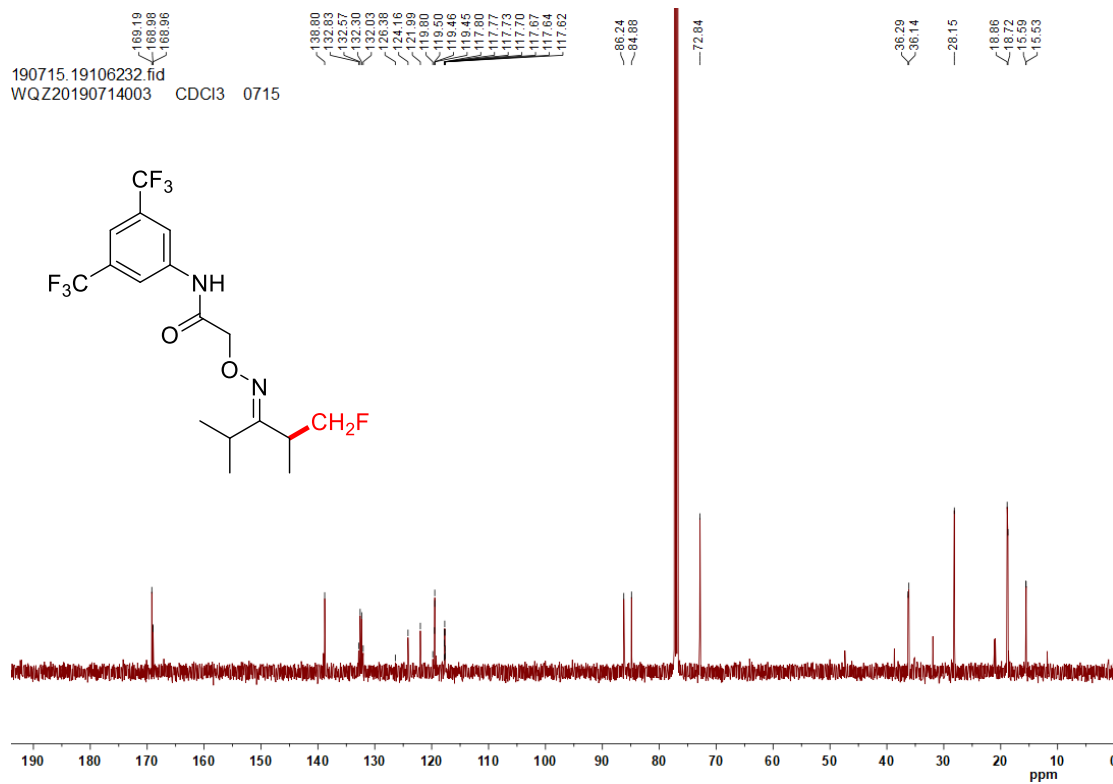
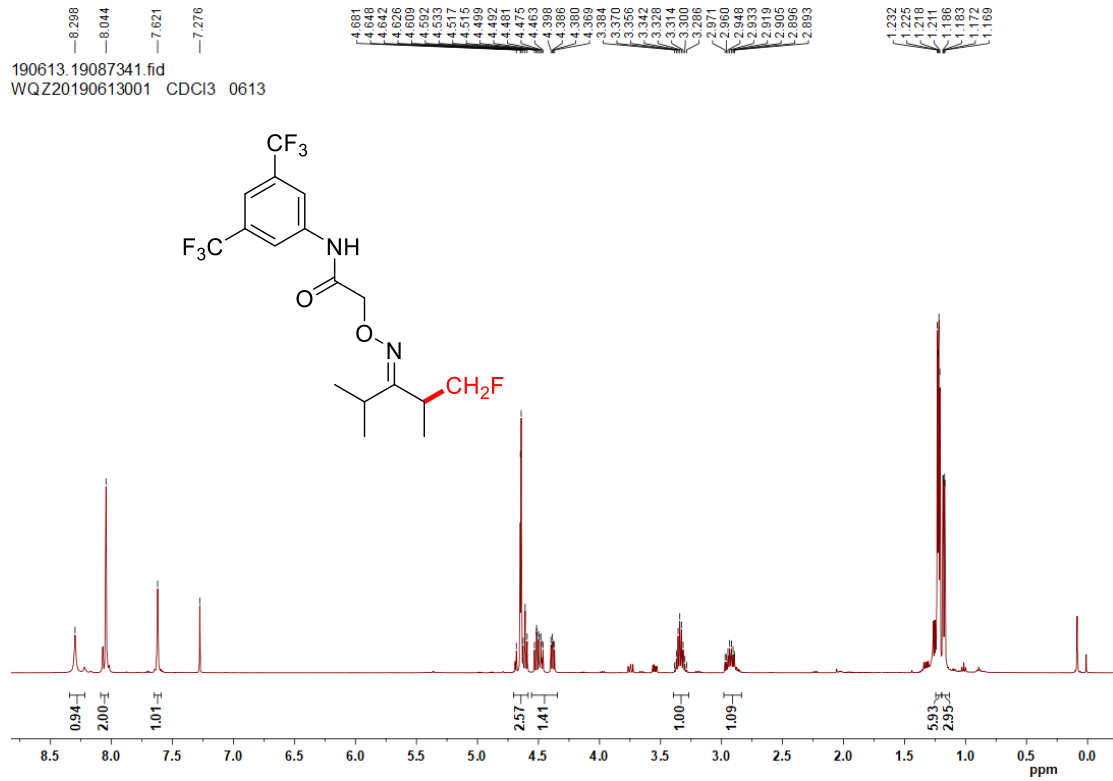
-223.372

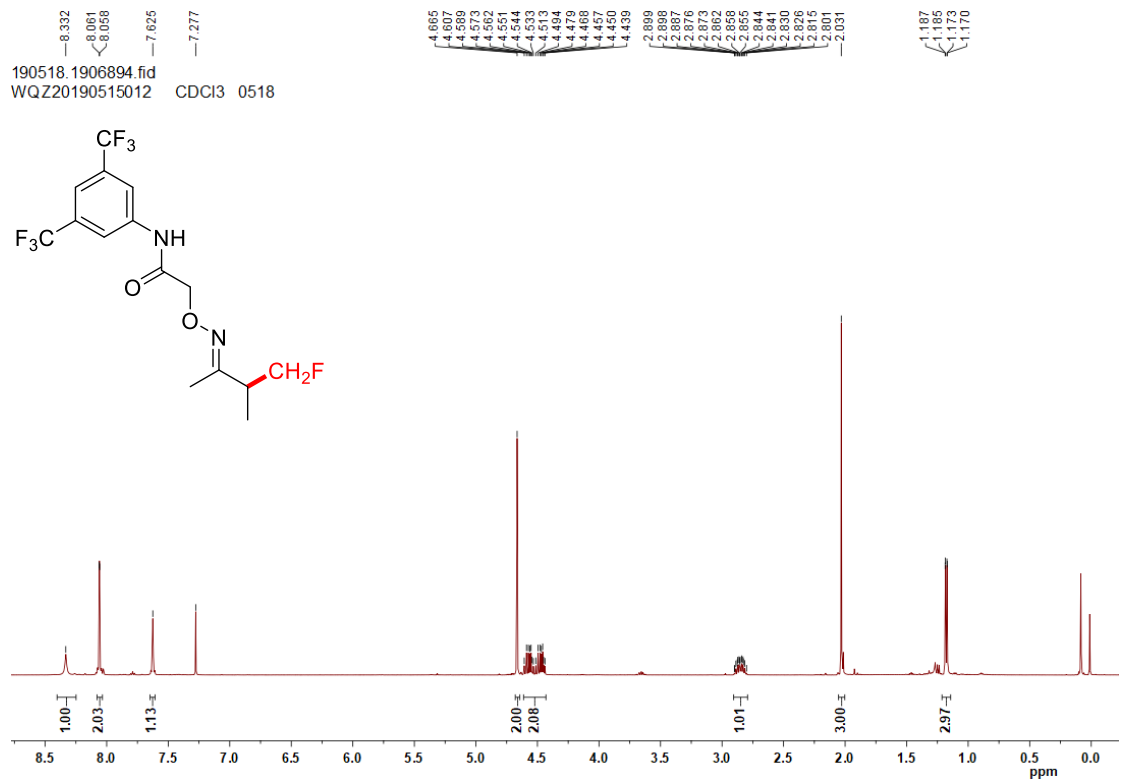
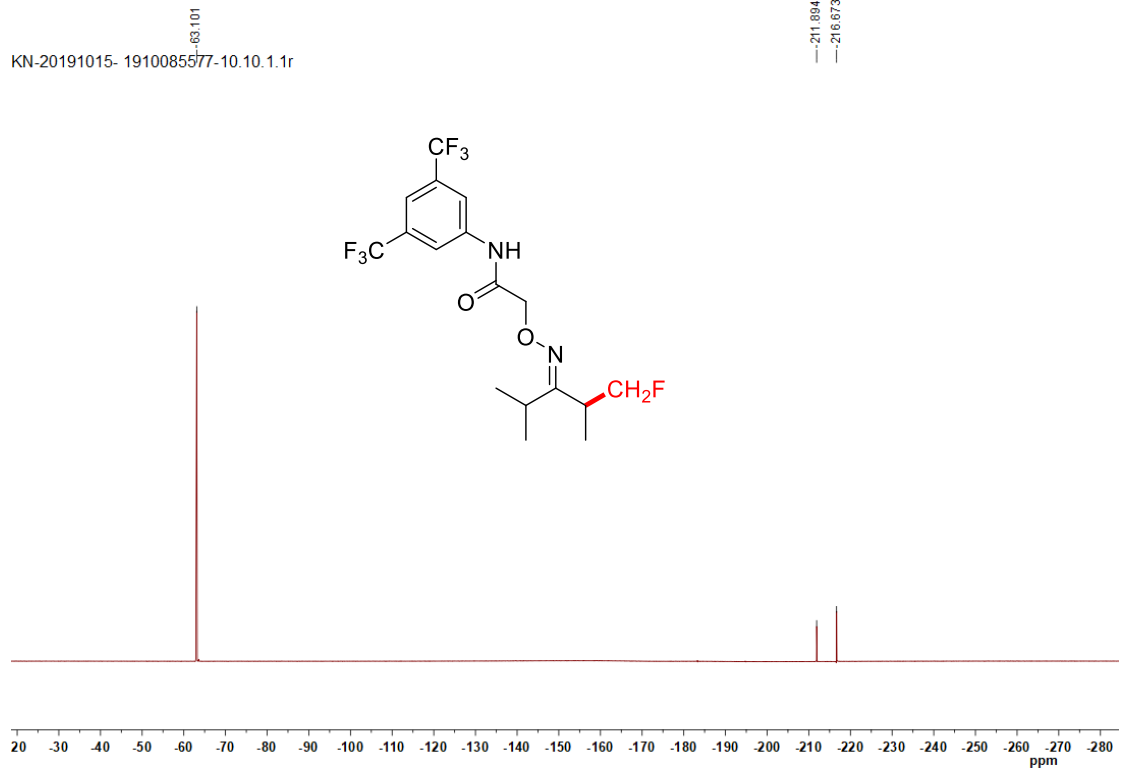


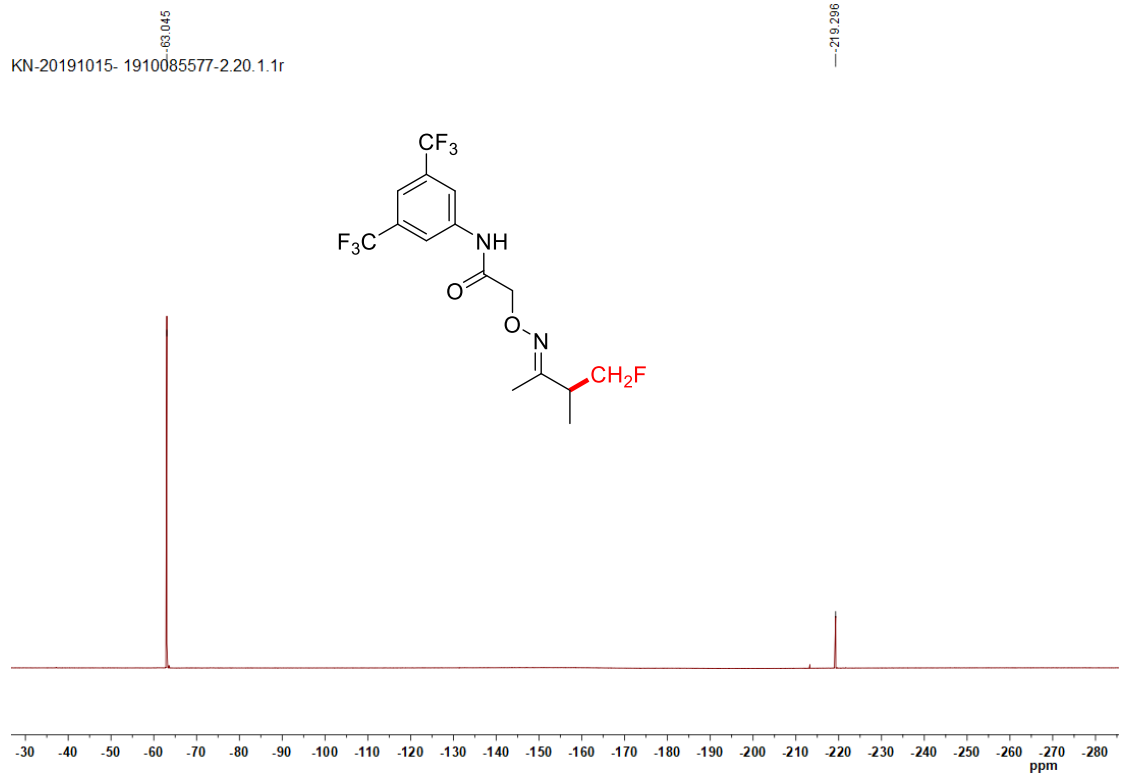
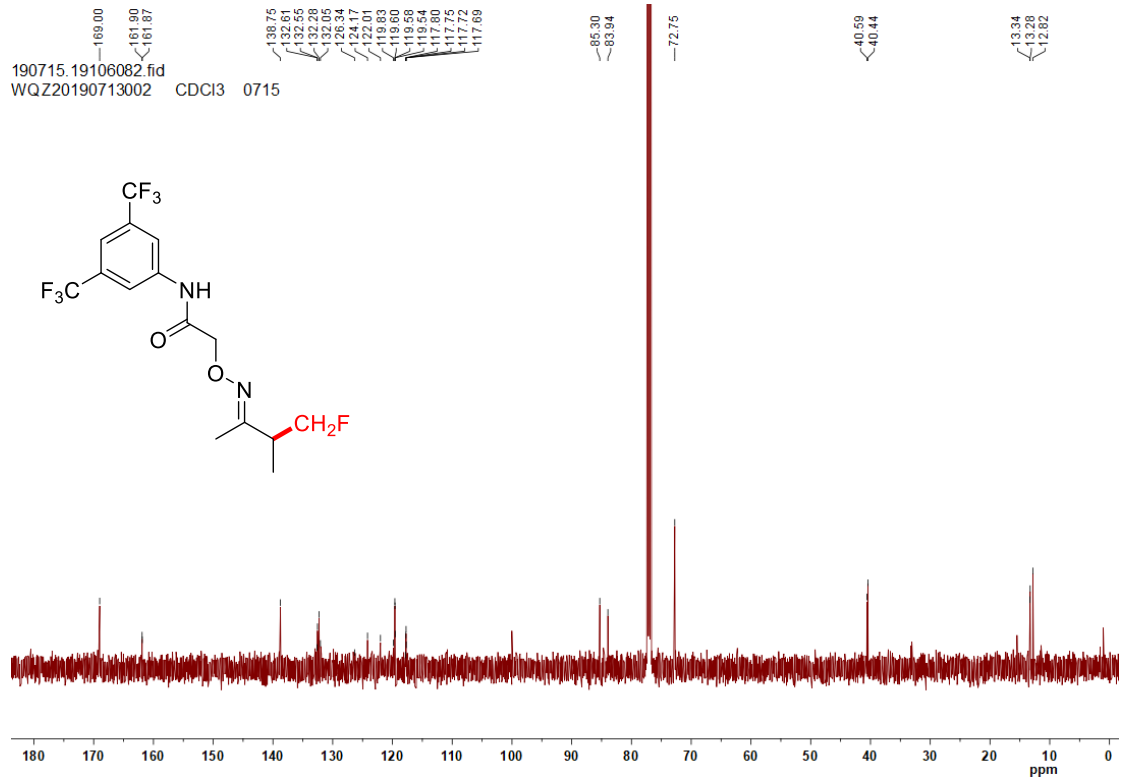
190816.19118961.fid
WQZ20190816001 CDCl₃ 0816

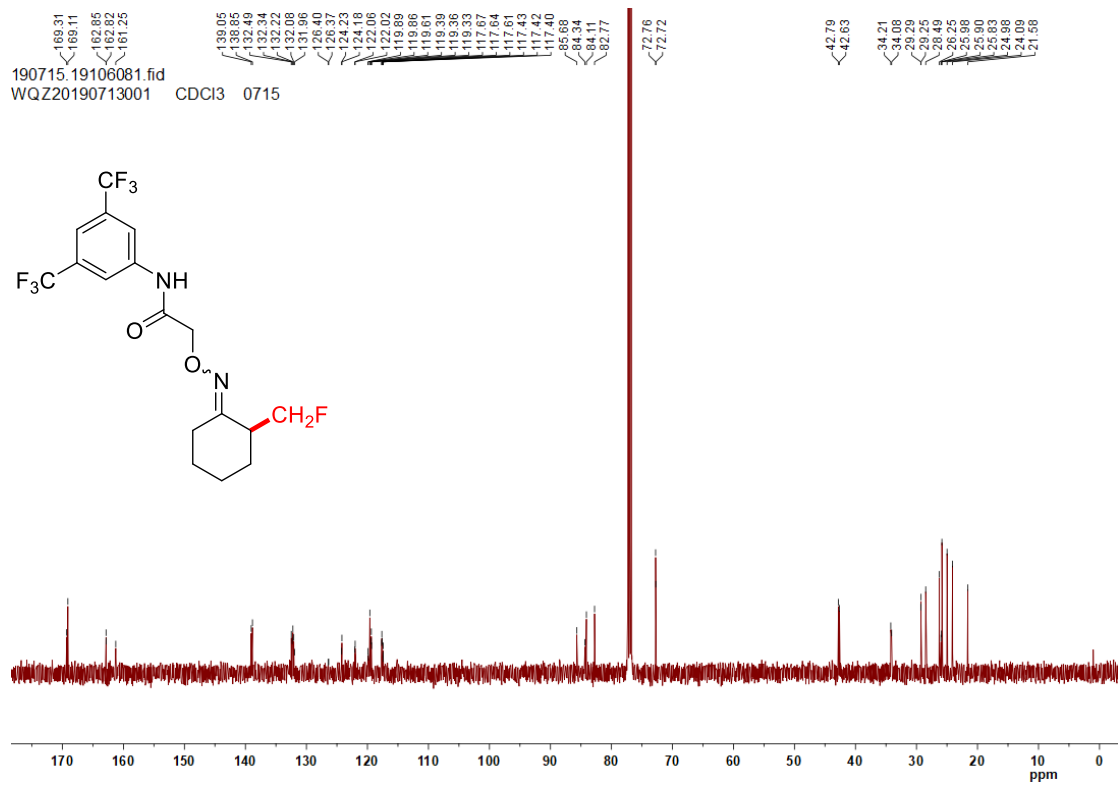
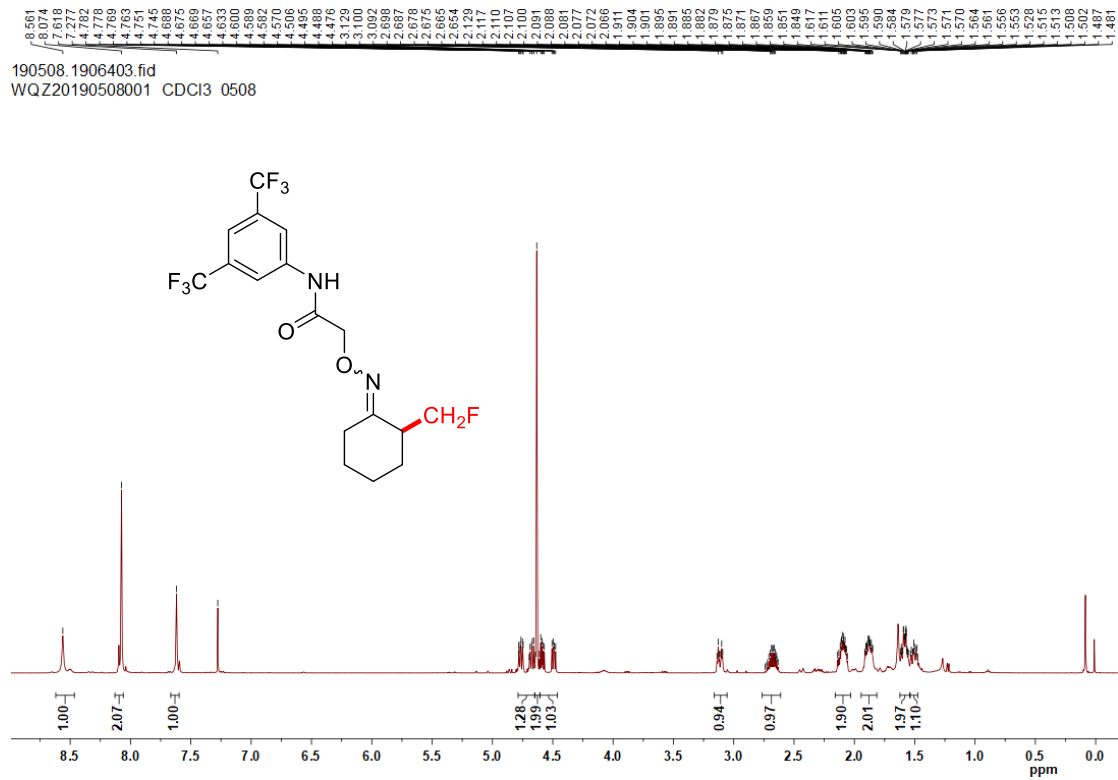








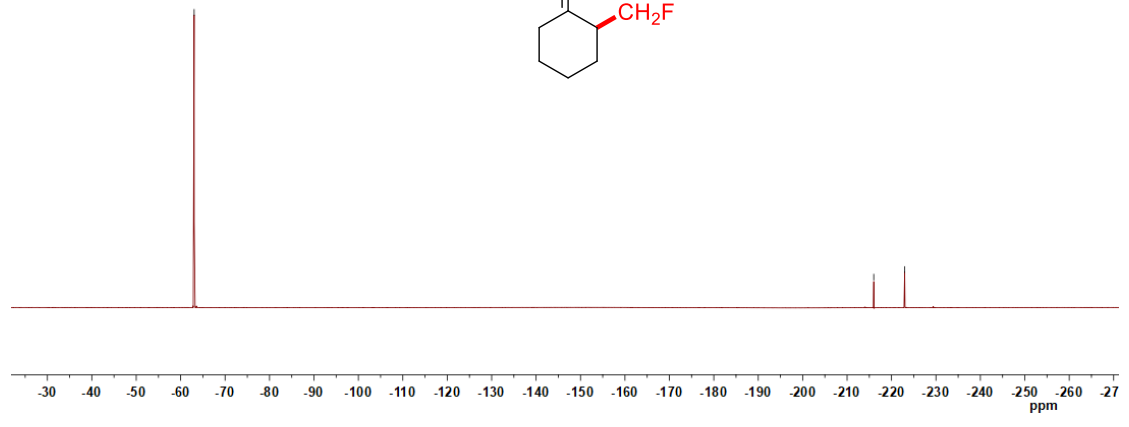
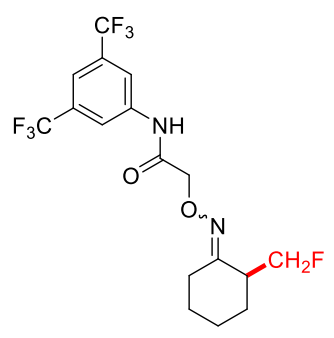




KN-20191015-1910085577-3.10.1.1r

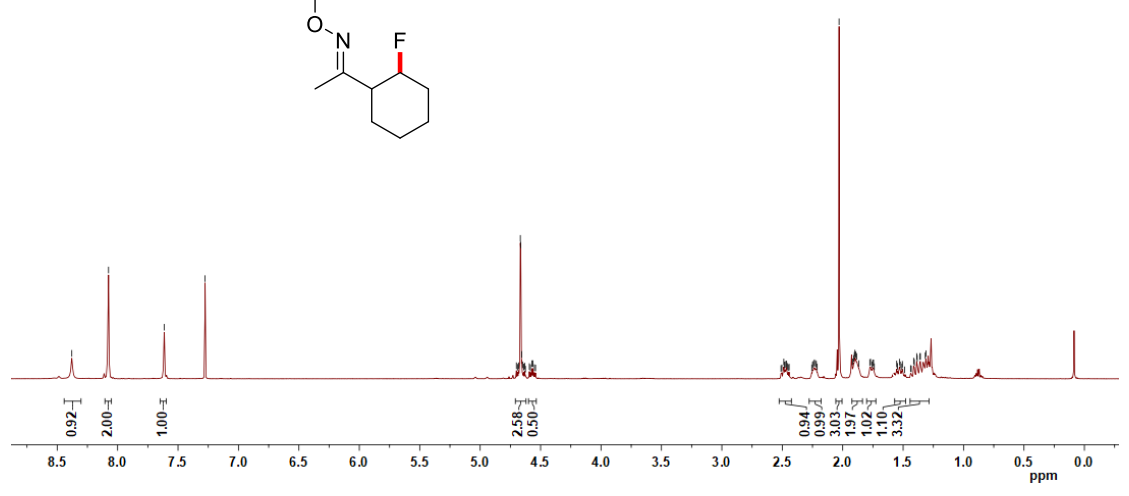
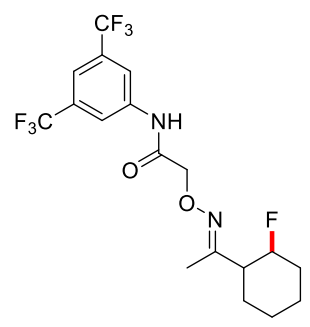
63.035

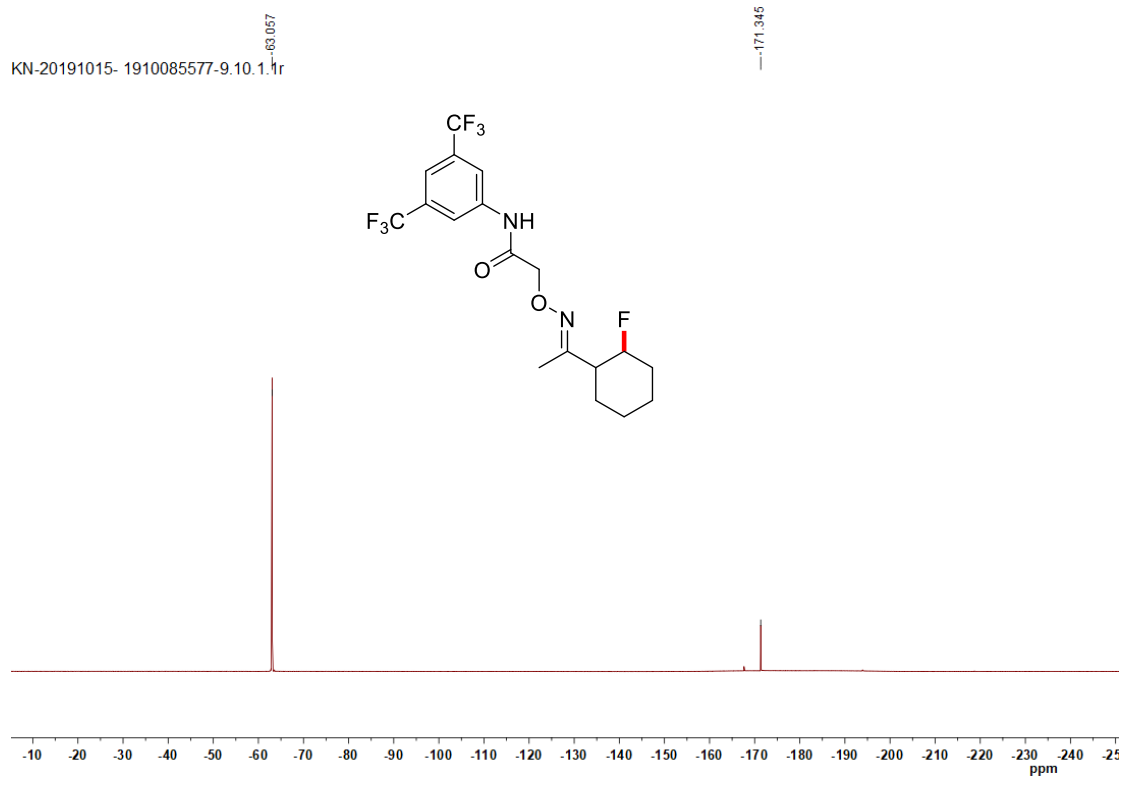
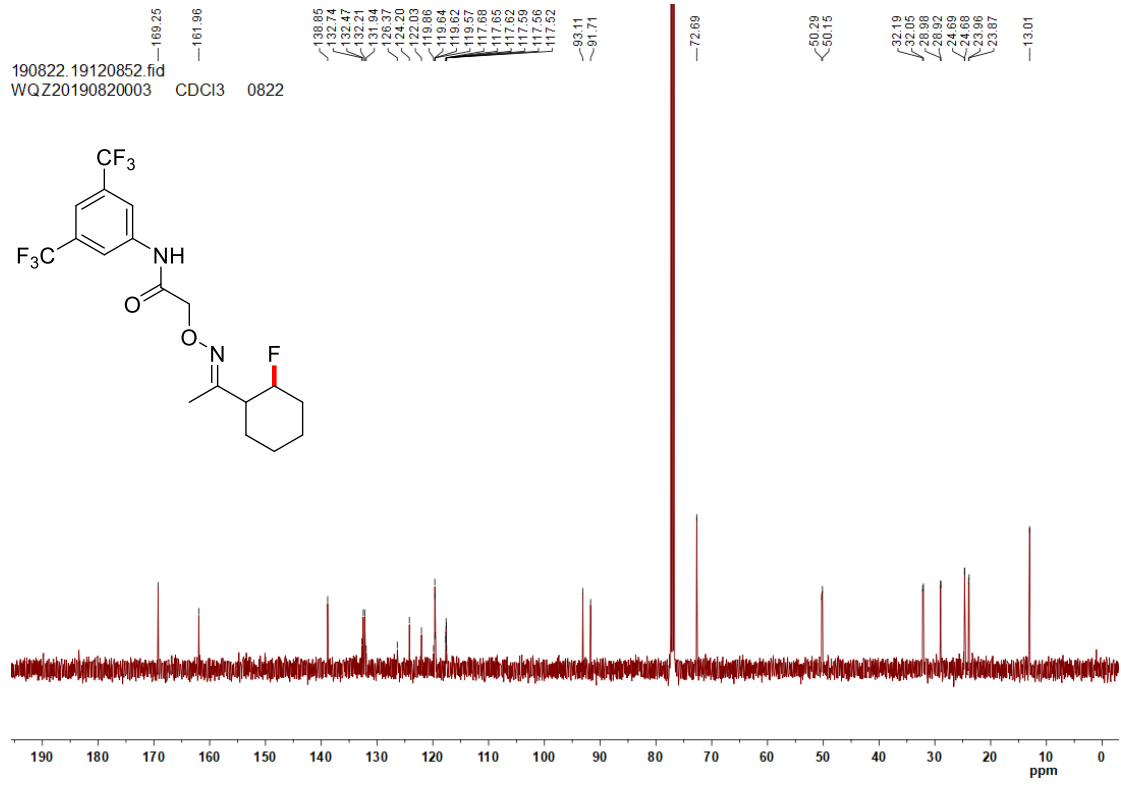
-216.002
-222.962

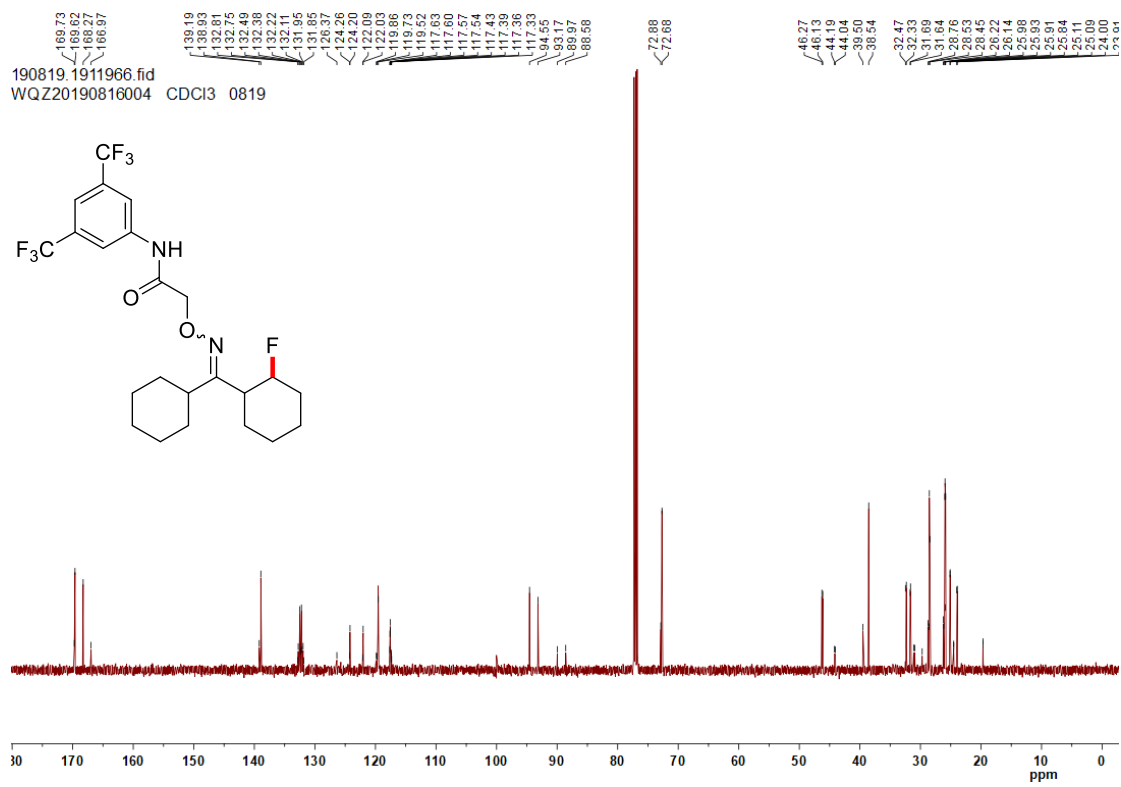
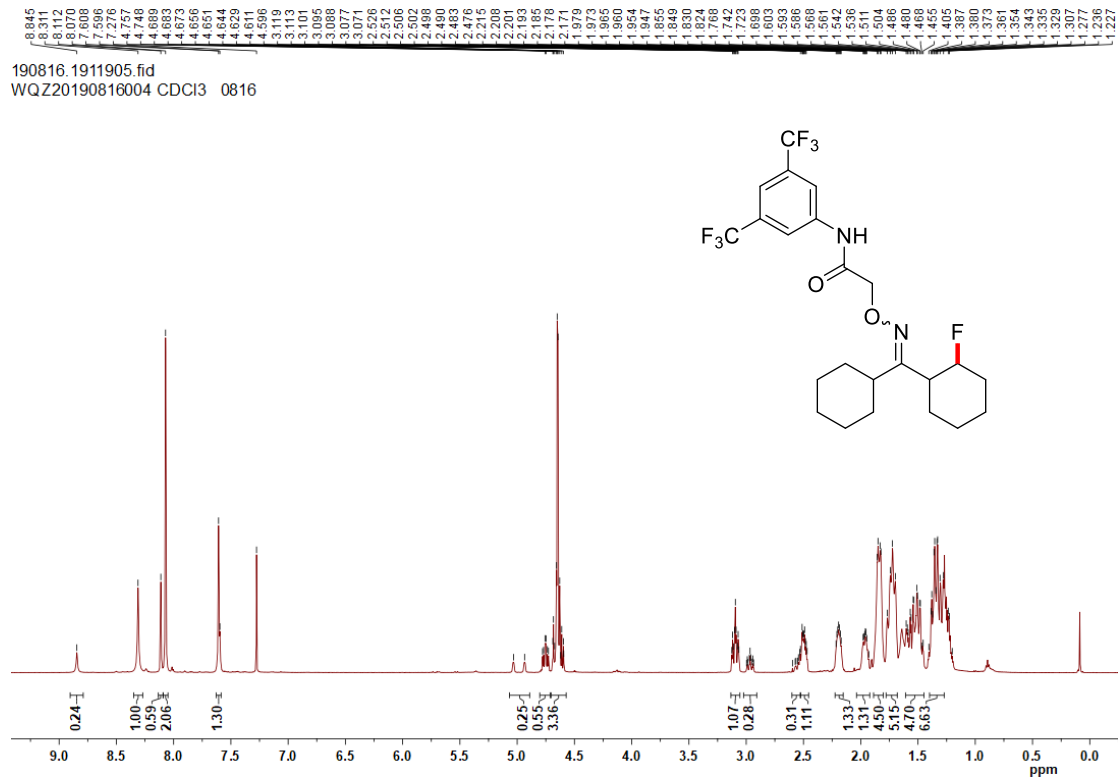


190820.19119733.fid
WQZ20190820003 CDCl3 0820

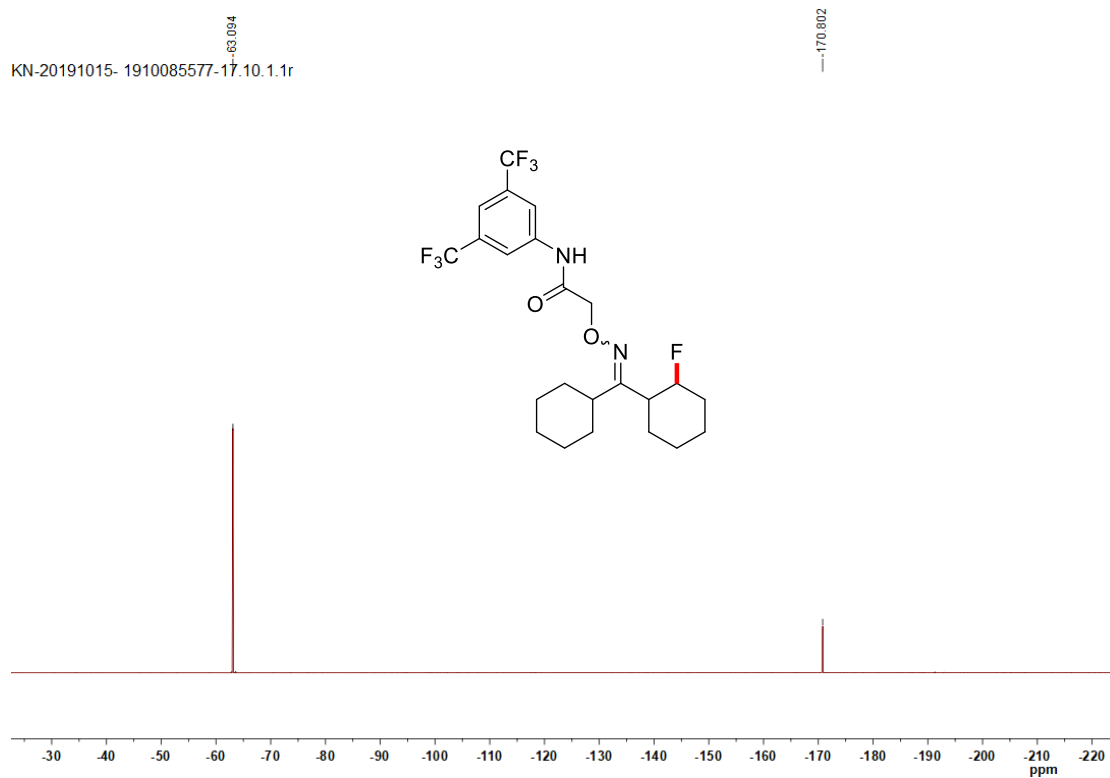
8.379 8.075 7.614 7.276
4.700 4.691 4.682 4.668 4.664 4.656 4.649 4.640 4.631 4.625 4.593 4.584 4.572 4.563 4.551 4.541 4.532 4.511 2.503 2.487 2.483 2.471 2.464 2.454 2.451 2.443 2.256 2.249 2.242 2.234 2.224 2.218 2.211 2.030 1.916 1.916 1.908 1.903 1.893 1.889 1.885 1.866 1.776 1.770 1.770 1.757 1.747 1.746 1.739 1.553 1.546 1.531 1.524 1.524 1.506 1.489 1.438 1.433 1.433 1.407 1.407 1.383 1.360 1.357 1.316 1.311



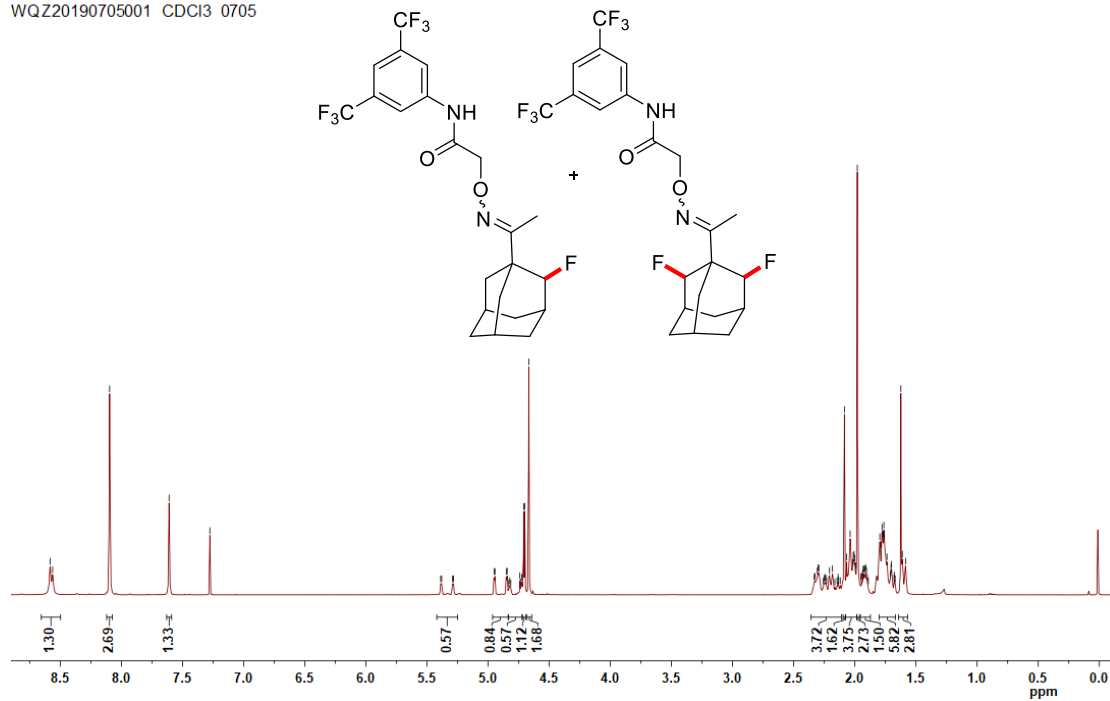


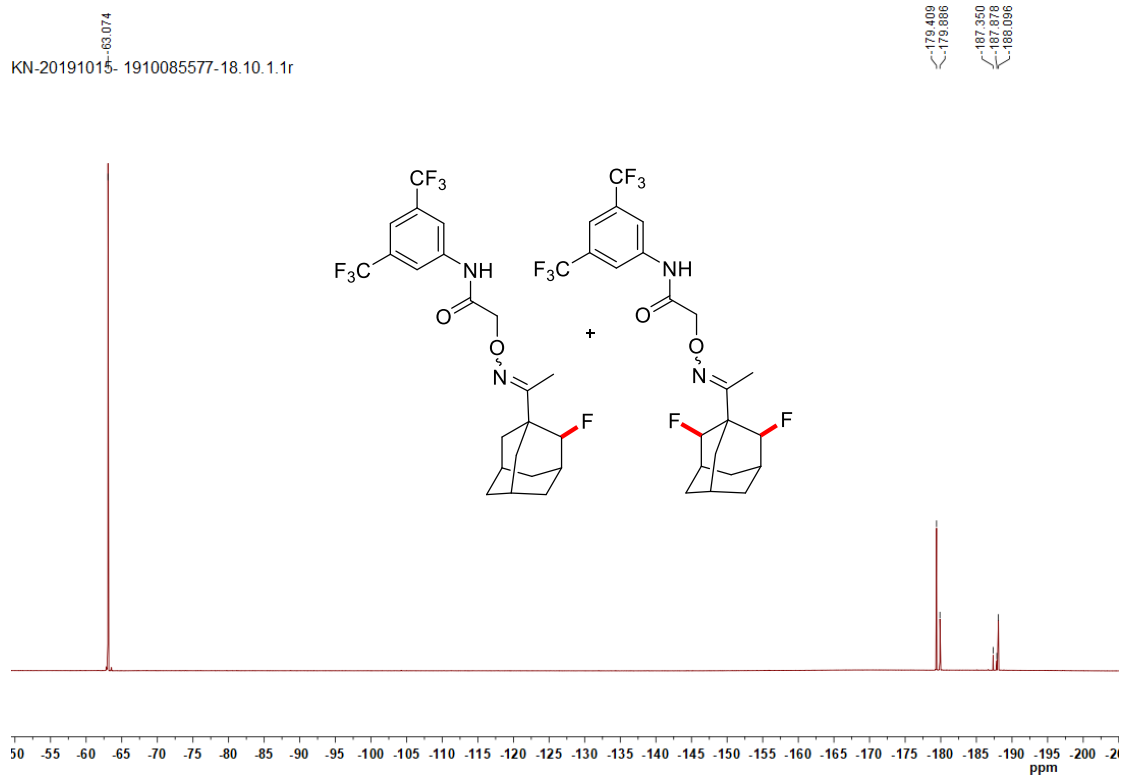
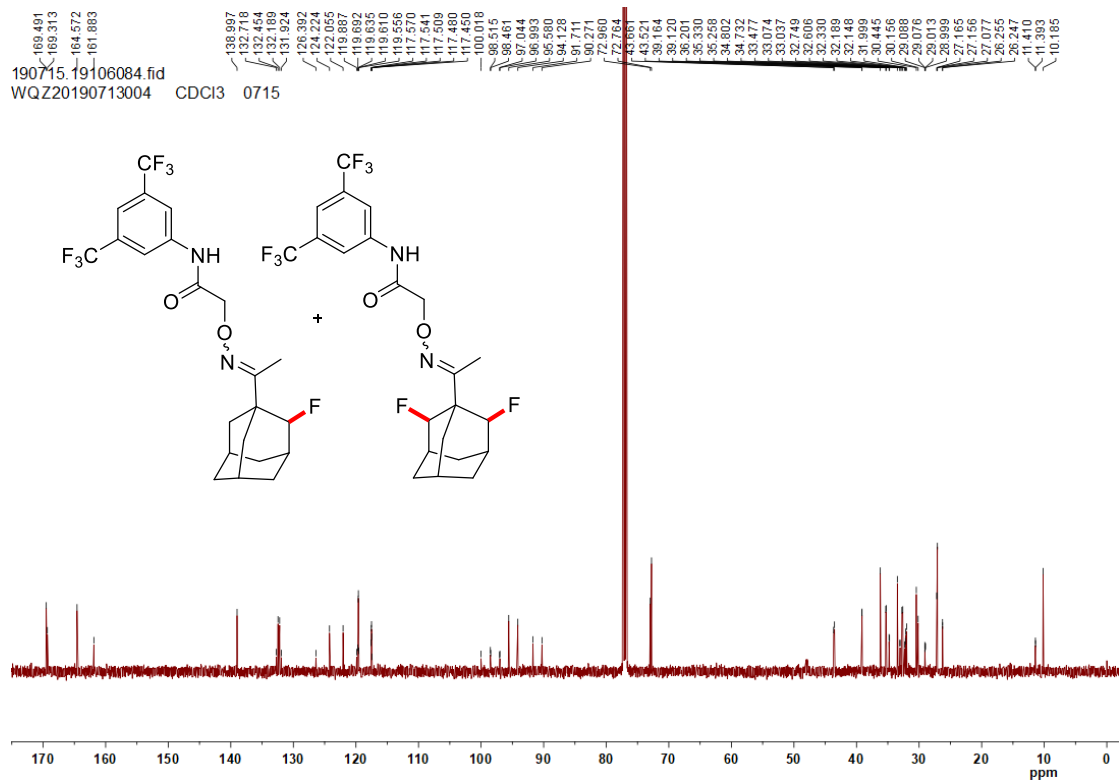


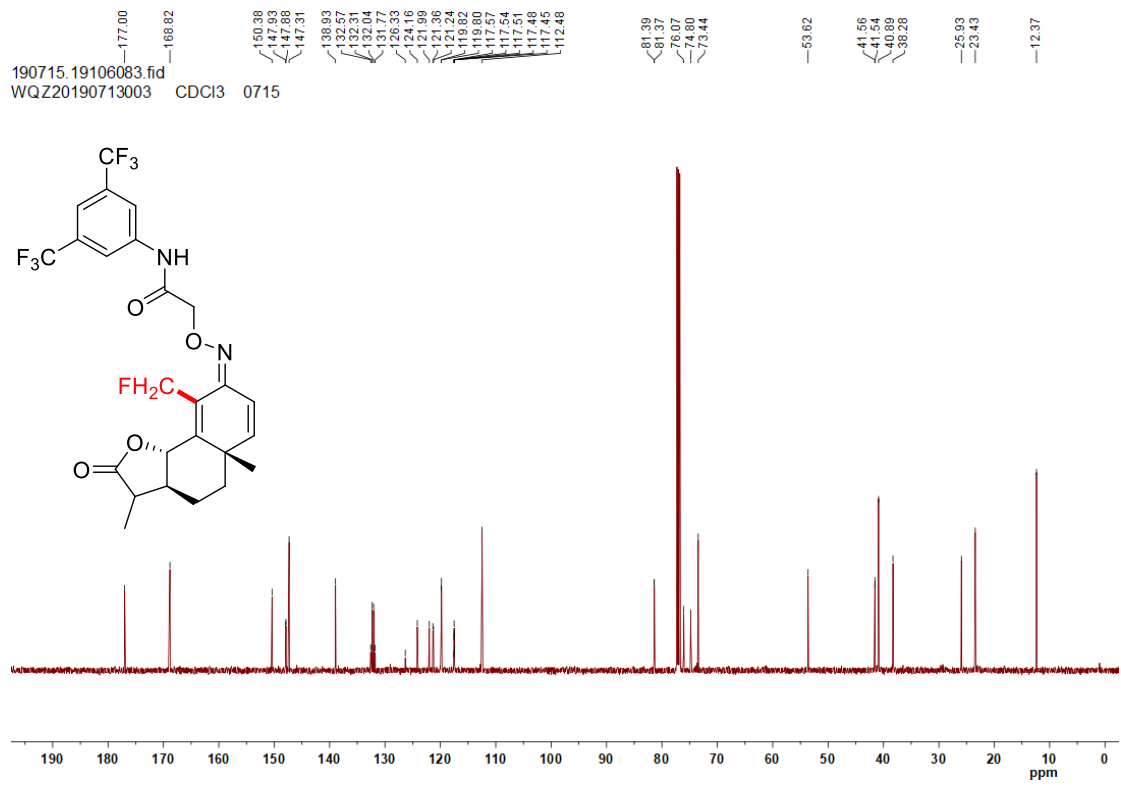
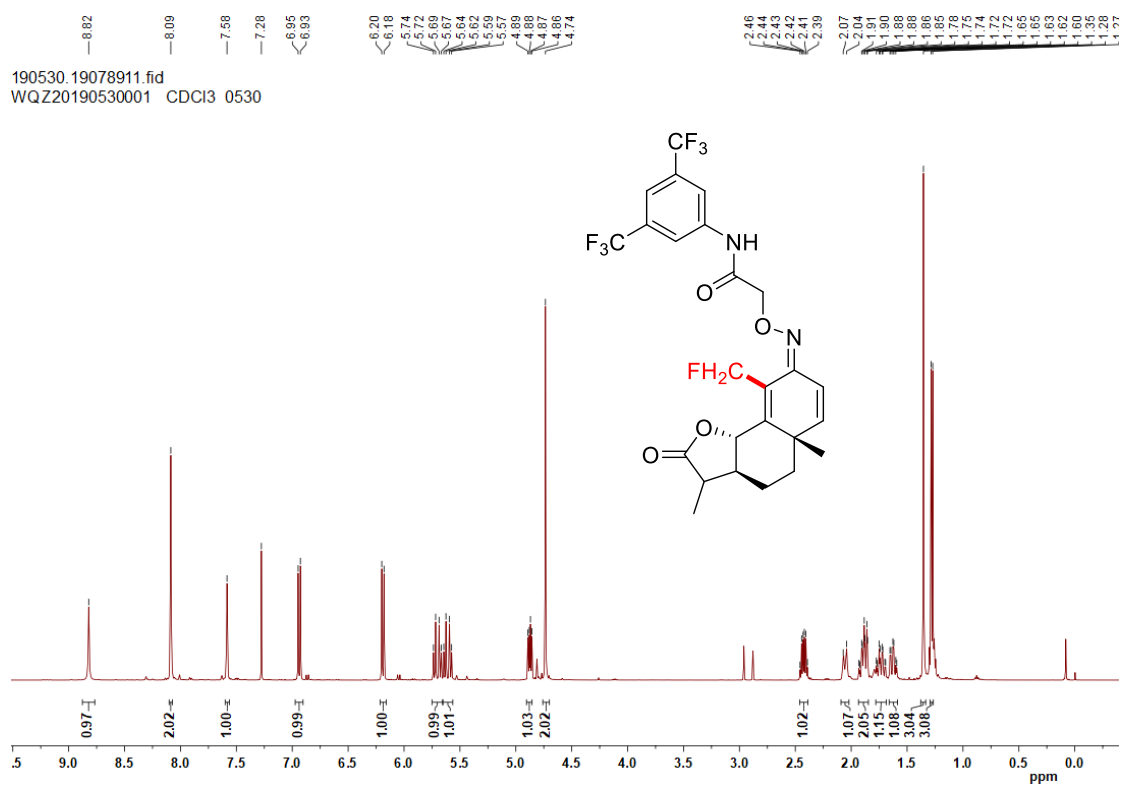
KN-20191015- 1910085577-17.10.1.1r



190705.1910150.fid
WQZ20190705001 CDCl3 0705

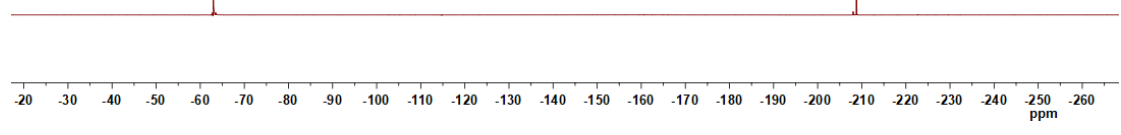
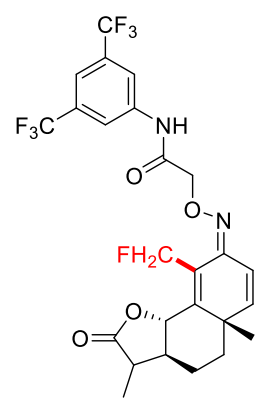






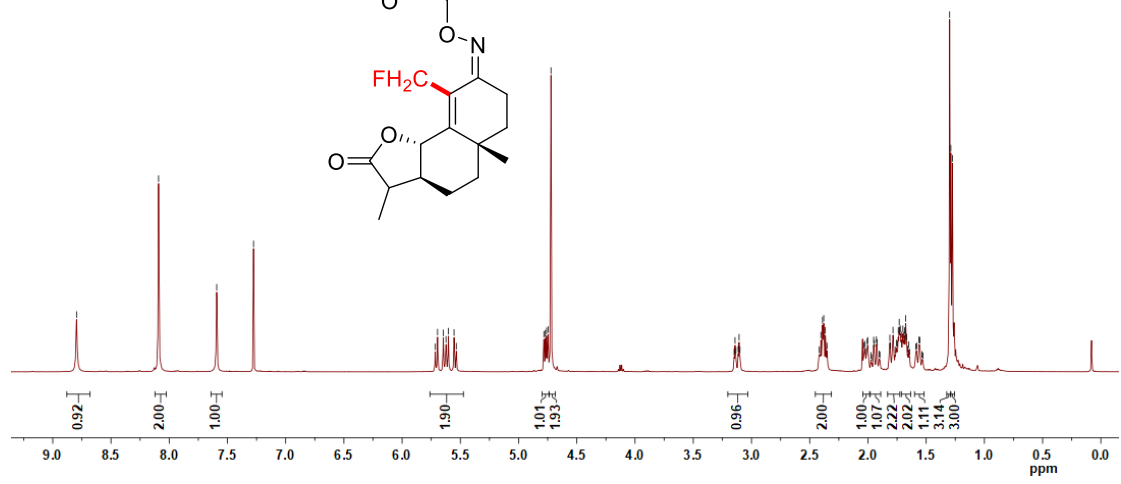
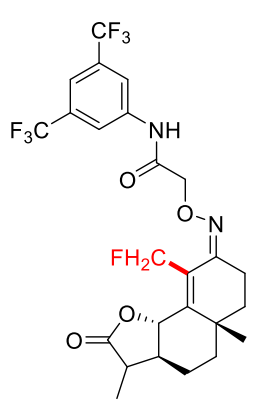
KN-20191015-1910085577-4.10.1.1r

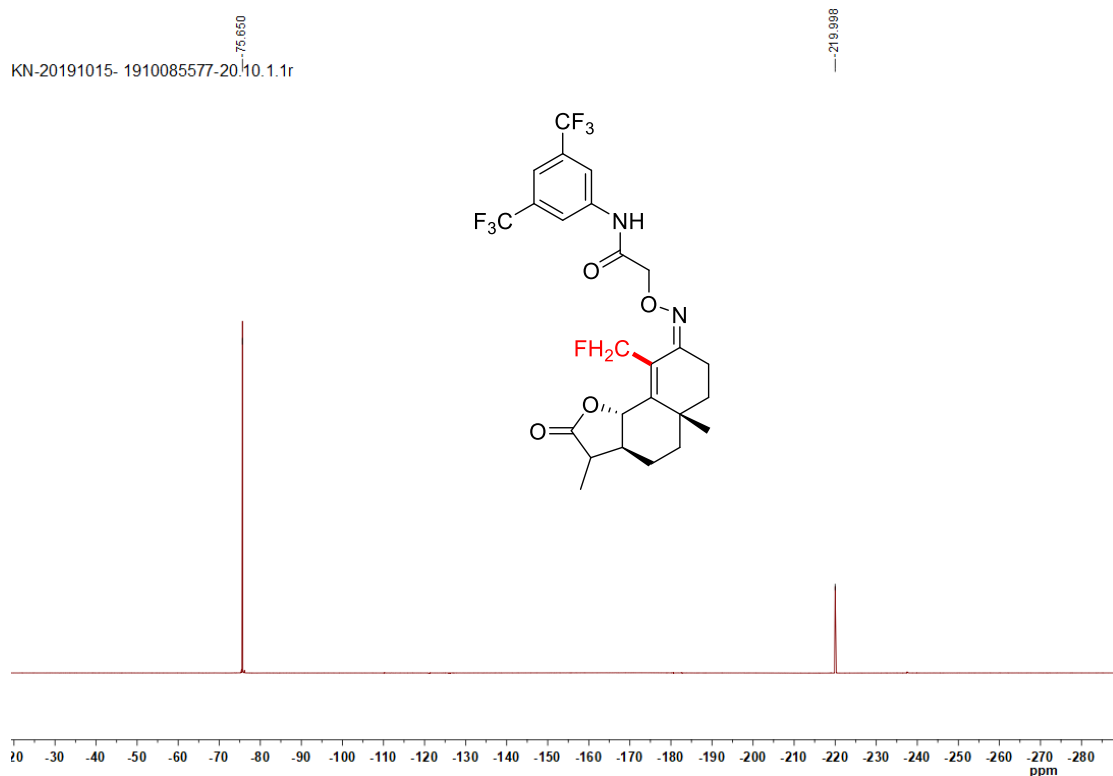
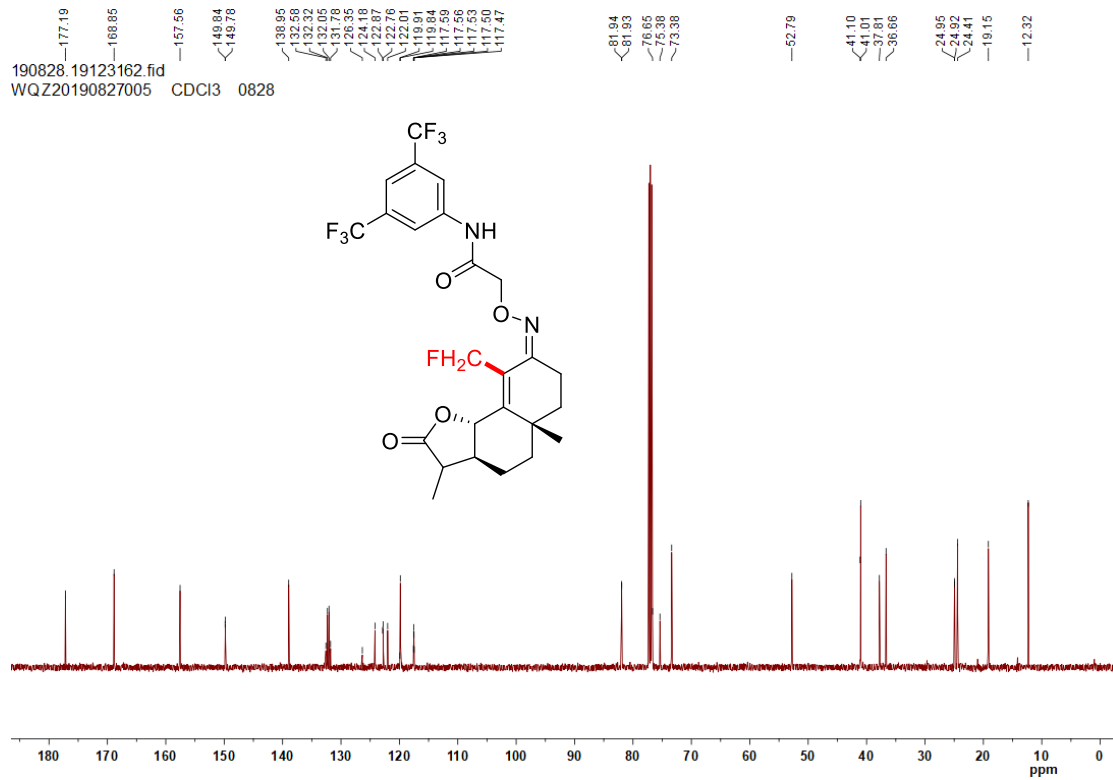
-208.744



190826_19122362.fid
WQZ20190826002 CDCI3 0826

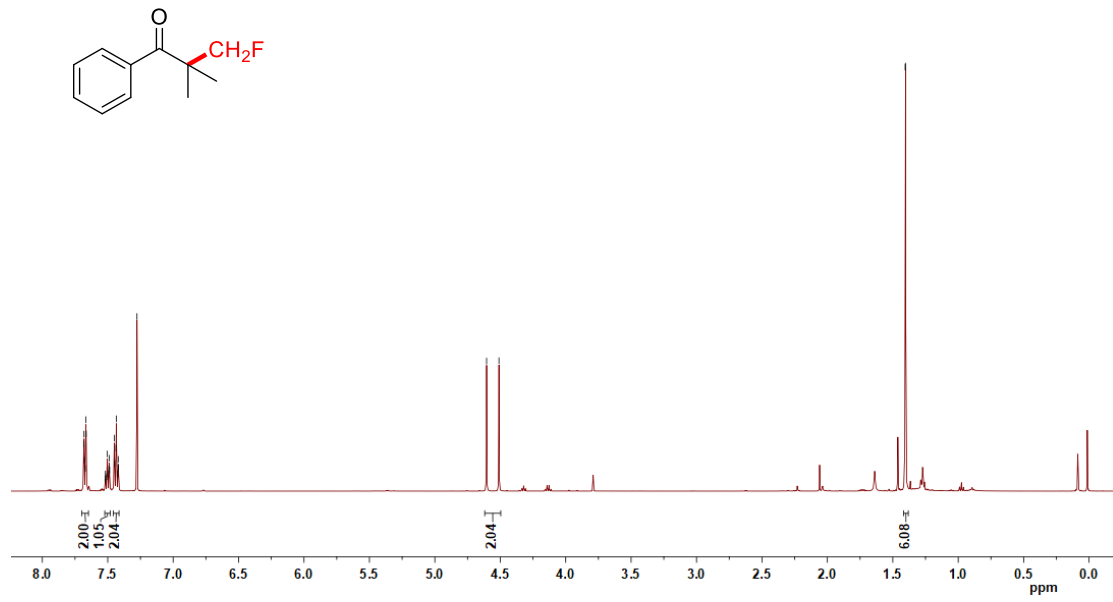
8.796
8.091
7.592
7.276
5.715
5.696
5.646
5.623
5.603
5.596
5.536
4.783
4.770
4.760
4.747
4.722
4.722
3.149
3.141
3.134
3.114
3.107
3.099
2.418
2.390
2.380
2.366
2.352
2.032
2.028
2.021
2.021
2.002
1.974
1.968
1.951
1.945
1.927
1.904
1.897
1.812
1.807
1.785
1.766
1.746
1.740
1.739
1.731
1.722
1.713
1.700
1.682
1.682
1.675
1.668
1.659
1.649
1.643
1.589
1.589
1.562
1.564
1.556
1.527
1.298
1.298
1.274





7.684
7.682
7.679
7.666
7.665
7.520
7.518
7.515
7.507
7.503
7.493
7.491
7.488
7.486
7.449
7.447
7.434
7.434
7.423
7.420
7.418
7.277

191227.1918898.fid
WQZ20191216001 CDCl3 1227



138.29
131.19
127.43
127.40

89.61
88.22

48.68
48.53

22.16
22.12

191230.1919376.fid
WQZ20191230001 CDCl3 1230

