Electronic Supplementary Information

Copper-Catalyzed Four-Component Radical Cascade Cyclization of Enynes to Assemble Trifluoromethyl- and Carbamoyloxyl-substituted Pyrrolo[1,2-*a*]benzimidazoles

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Content

1. General Information

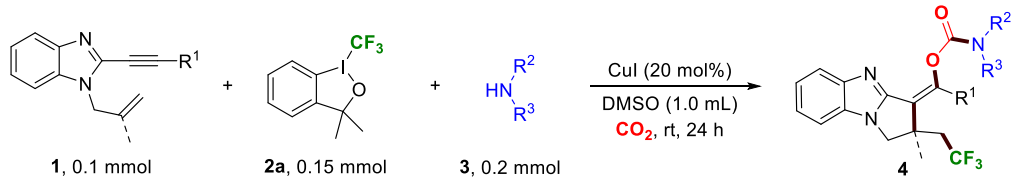
All reactions were carried out in Schlenk tubes under CO_2 atmosphere, unless otherwise noted. Commercial reagents were purchased from commercial suppliers (Energy Chemical, Alfa Aesar, Bidepharm, Tansoole and Aladdin) or prepared according to standard procedures. Solvents were purified and dried according to standard operation procedure. Analytical thin layer chromatography (TLC) was performed on 0.20 mm silica gel HSGF254 plates (Nuotai, China), and visualized under 254nm UV light. Column chromatography was performed on 200–300 mesh silica gel (Haiyang, China). The reactions were monitored by GC, GC-MS or TLC. GC analysis was performed on GC 2014 plus, and GC-MS results were recorded on GC-MS QP2010.

^1H, ^{13}C, and ^{19}F NMR spectra were recorded on a Zhongke-Niujin QUANTUM-I nuclear magnetic resonance spectrometer at 400 MHz, 101 MHz, and 372 MHz respectively. Chemical shifts (δ) were reported in ppm relative to the residual solvent signal ($CDCl_3$: δ = 7.256 ppm for ^1H NMR and δ = 77.00 ppm for $^{13}C\{^1H\}$ NMR). Chemical shifts (ppm) were recorded with tetramethyl silane (TMS) as the internal reference standard. Data for ^1H NMR are recorded as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz), integration. Data for ^{13}C, and ^{19}F NMR are reported as follows: chemical shift (δ ppm), multiplicity (d = doublet, q = quartet), coupling constant (Hz).

The high resolution mass spectra (HRMS) were measured on a Waters Xevo G2-XS using electrospray ionization time-of-flight (ESI-TOF). Melting points were determined with a digital melting point measuring instrument (WRS-1C, Shanghai INESA Physico-Optical Instrument Co., Ltd.). The single-crystal X-ray diffraction was recorded at a temperature of 293(2) K on Rigaku XtaLAB diffractometer.

The 1,6-enynes 1-allyl-2-ethynyl-benzoimidazoles **1** were synthesized according to the reported literature.[1] Togni's reagents **2** and amines **3** were purchased from commercial suppliers, and used without further purification.

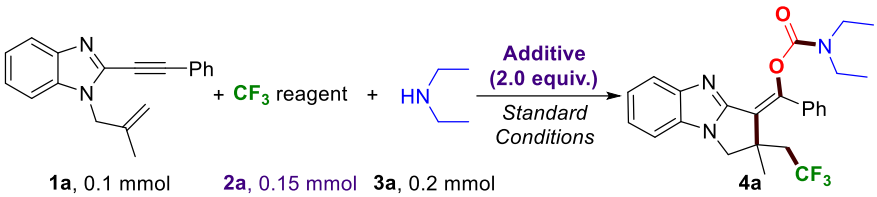
2. General experimental procedure for the synthesis of target products 4



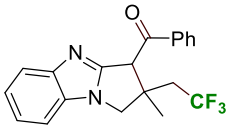
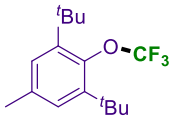
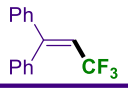
1, 0.1 mmol **2a**, 0.15 mmol **3**, 0.2 mmol **4**

An oven-dried 25-mL Schlenk tube, equipped with a magnetic stir bar and charged with 1-allyl-2-ethynyl-benzoimidazoles **1** (0.1 mmol), Togni's reagent **2a** (50 mg, 0.15 mmol), and CuI (3.8 mg, 20 mol%) and dry DMSO (1.0 mL). Then, the mixture was evacuated for a while and CO_2 (1 atm) was introduced into the reaction tube. The mixture was stirred for 24 h at room temperature. Upon completion, the reaction mixture was diluted with EtOAc and washed with H_2O. The organic layer was dried with anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography over silica gel using petroleum ether/ethyl acetate (3:1) to afford the target products **4**.

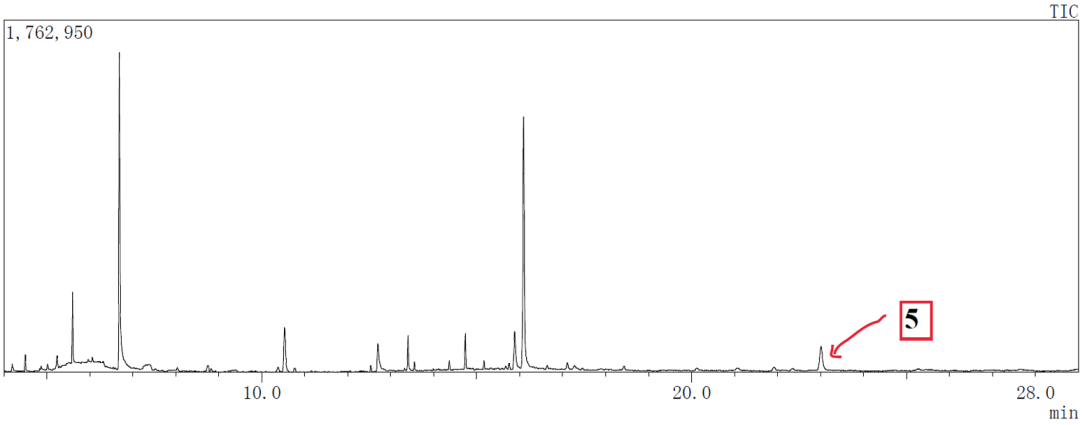
3. GC-MS analysis of the control experiments

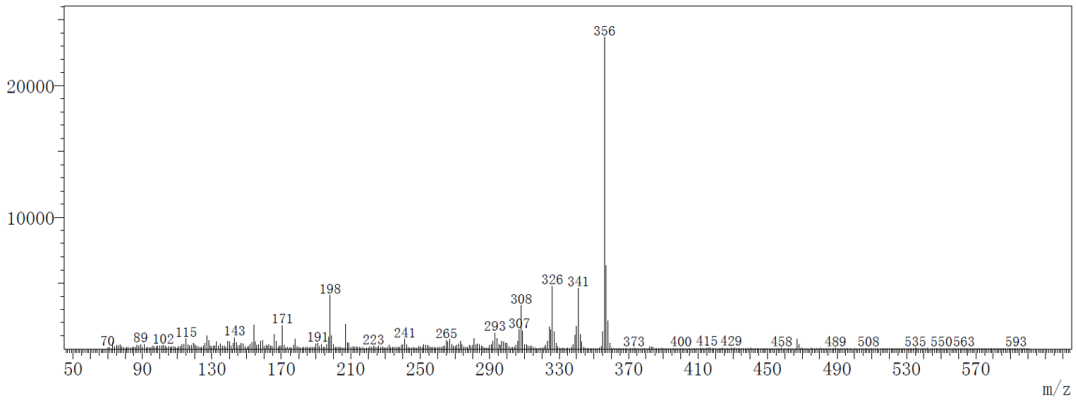


1a, 0.1 mmol **2a**, 0.15 mmol **3a**, 0.2 mmol **4a**

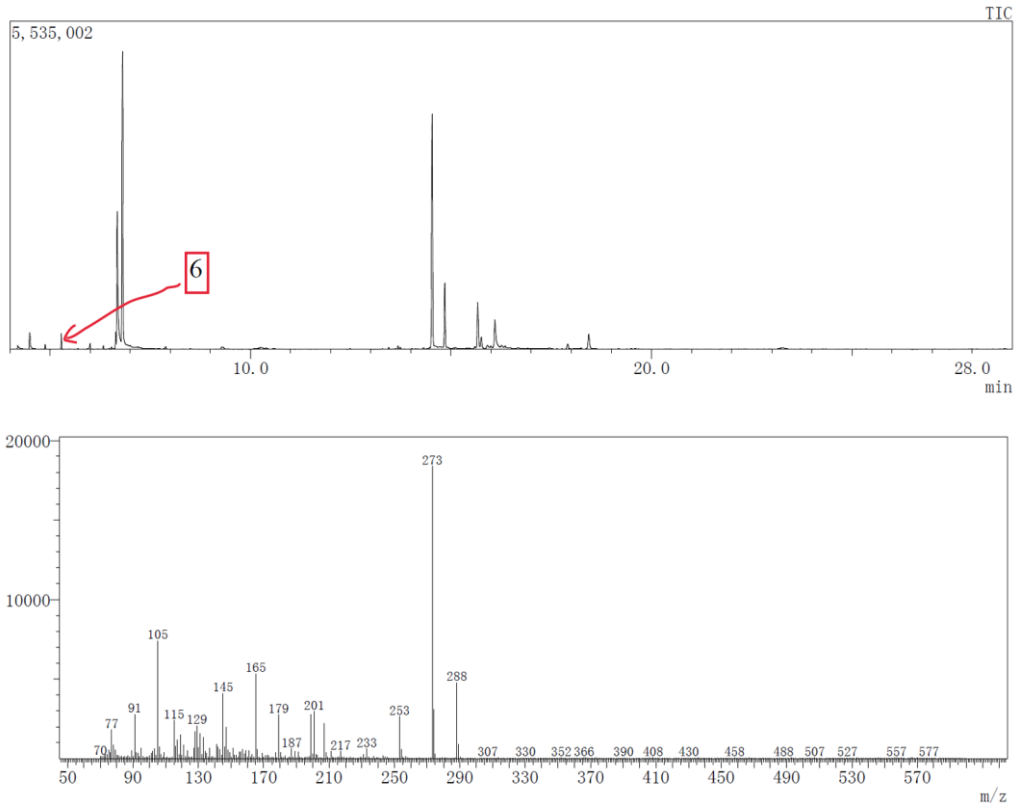
eq	Additive	4a	Capture product	
a)	TEMPO	not detected		**5**, m/z=358 $[M]^+$ detected by GC-MS
b)	BHT	not detected		**6**, m/z=288 $[M]^+$ detected by GC-MS
c)	1,1-diphenylethylene	not detected		**7**, m/z=248 $[M]^+$ detected by GC-MS

a) The GC-MS spectrum of product 5

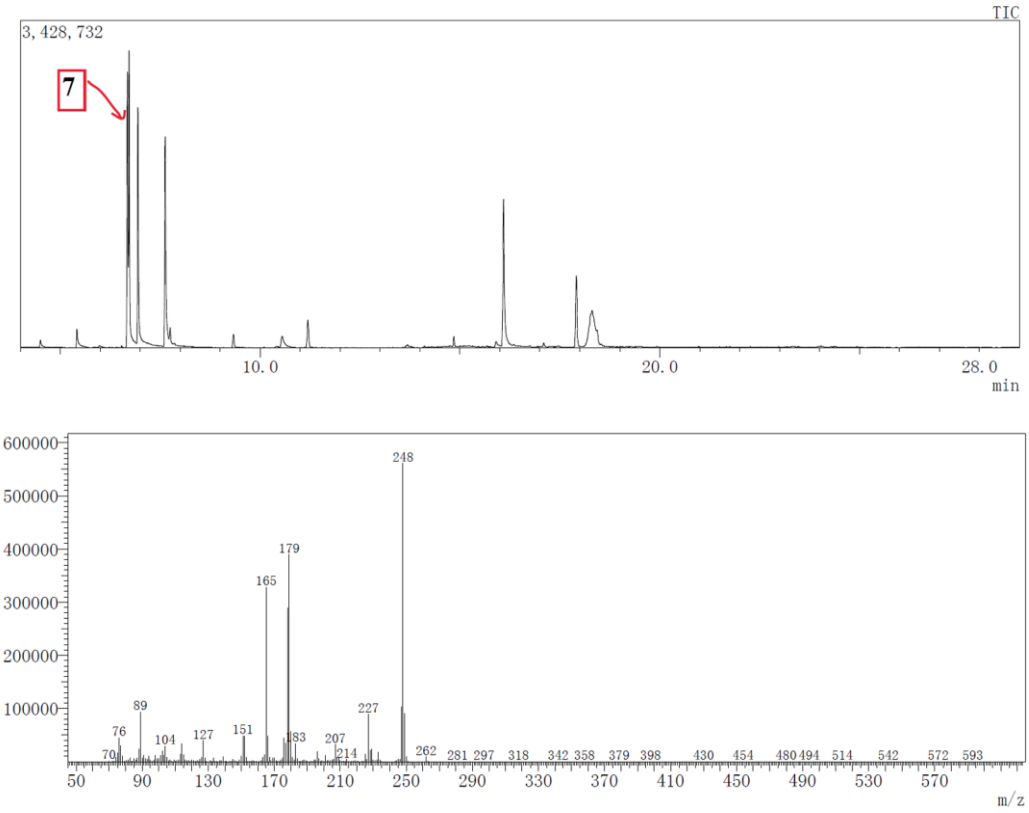




b) The GC-MS spectrum of product 6

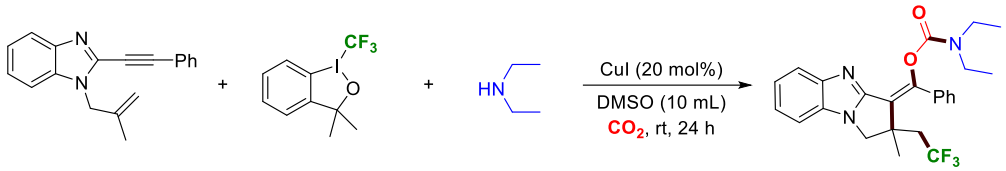


c) The GC-MS spectrum of product 7



4. Synthetic Applications

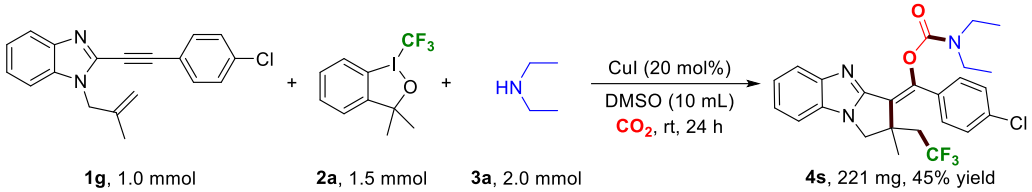
a) Preparation of 4a at 1 mmol Gram-Scales



1a, 1.0 mmol **2a**, 1.5 mmol **3a**, 2.0 mmol **4a**, 215 mg, 47% yield

An oven-dried 100-mL Schlenk tube, equipped with a magnetic stir bar and charged with 1-(2-methylallyl)-2-(phenylethynyl)-1*H*-benzo[*d*]imidazole **1a** (272 mg, 1.0 mmol), Togni's reagent **2a** (495 mg, 1.5 mmol), and CuI (38 mg, 20 mol%) and dry DMSO (10 mL). Then, the mixture was evacuated for a while and CO_2 (1 atm) was introduced into the reaction tube. Diethylamine **3a** (0.21mL, 2.0 mmol) was subsequently added via a syringe under stirring. The mixture was stirred for 24 h at room temperature. Upon completion, the reaction mixture was diluted with EtOAc and washed with H_2O. The organic layer was dried with anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography over silica gel using petroleum ether/ethyl acetate (7:1) to afford the pale yellow solid **4a** in 47% yield (215 mg).

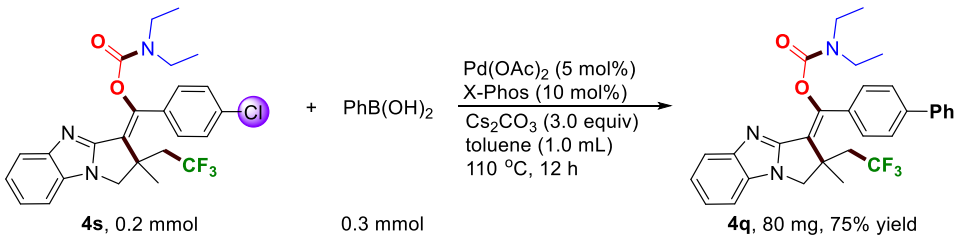
b) Preparation of 4s at 1 mmol Gram-Scales



1g, 1.0 mmol **2a**, 1.5 mmol **3a**, 2.0 mmol **4s**, 221 mg, 45% yield

An oven-dried 100-mL Schlenk tube, equipped with a magnetic stir bar and charged with 2-((4-chlorophenyl)ethynyl)-1-(2-methylallyl)-1*H*-benzo[*d*]imidazole **1g** (306 mg, 1.0 mmol), Togni's reagent **2a** (495 mg, 1.5 mmol), and CuI (38 mg, 20 mol%) and dry DMSO (10 mL). Then, the mixture was evacuated for a while and CO_2 (1 atm) was introduced into the reaction tube. Diethylamine **3a** (0.21mL, 2.0 mmol) was subsequently added via a syringe under stirring. The mixture was stirred for 24 h at room temperature. Upon completion, the reaction mixture was diluted with EtOAc and washed with H_2O. The organic layer was dried with anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography over silica gel using petroleum ether/ethyl acetate (7:1) to afford the pale yellow solid **4a** in 45% yield (221 mg).

c) Procedure for the synthesis of compound 4q[2]

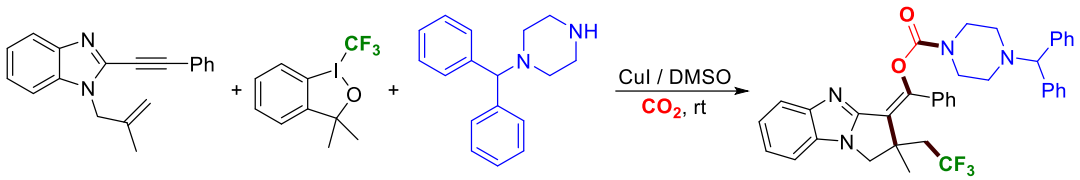


4s, 0.2 mmol 0.3 mmol **4q**, 80 mg, 75% yield

To an oven-dried 10-mL Schlenk tube with a magnetic stir bar was added **4s** (98.2 mg, 0.2 mmol), $Pd(OAc)_2$ (2.4 mg, 5 mol%), X-Phos (9.6 mg, 10 mol%), Cs_2CO_3 (196 mg, 0.90 mmol, 3.0 equiv), and toluene (1.0 mL) under a N_2 atmosphere, and the resultant solution was stirred at room temperature for

10 mins. Then, phenylboronic acid (36.6 mg, 0.3 mmol, 1.5 equiv, in 1 mL toluene) was added to the reaction mixture and stirred at 110 °C for 12 h under an N_2 atmosphere. Upon completion, the mixture was cooled to room temperature, diluted with EtOAc and washed with H_2O. The organic layer was dried with anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography over silica gel using petroleum ether/ethyl acetate (7:1) to afford the pale yellow solid **4q** in 75% yield (80 mg).

d) Procedure for the synthesis of compound 4y



1a, 0.2 mmol **2a**, 0.3 mmol **3n**, 0.4 mmol **4y**, 42 mg, 33% yield

core precursor of drug cinnarizine

An oven-dried 25-mL Schlenk tube, equipped with a magnetic stir bar and charged with 1-(2-methylallyl)-2-(phenylethynyl)-1H-benzo[d]imidazole **1a** (54.4 mg, 0.2 mmol), Togni's reagent **2a** (99 mg, 0.3 mmol), 1-benzhydrylpiperazine **3n** (100 mg, 0.4 mmol), and CuI (7.6 mg, 20 mol%) and dry DMSO (2.0 mL). Then, the mixture was evacuated for a while and CO_2 (1 atm) was introduced into the reaction tube. The mixture was stirred for 24 h at room temperature. Upon completion, the reaction mixture was diluted with EtOAc and washed with H_2O. The organic layer was dried with anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography over silica gel using petroleum ether/ethyl acetate (5:1) to afford the colourless solid **4y** in 33% yield (42 mg).

5. X-ray crystal structure and data for compound 4s

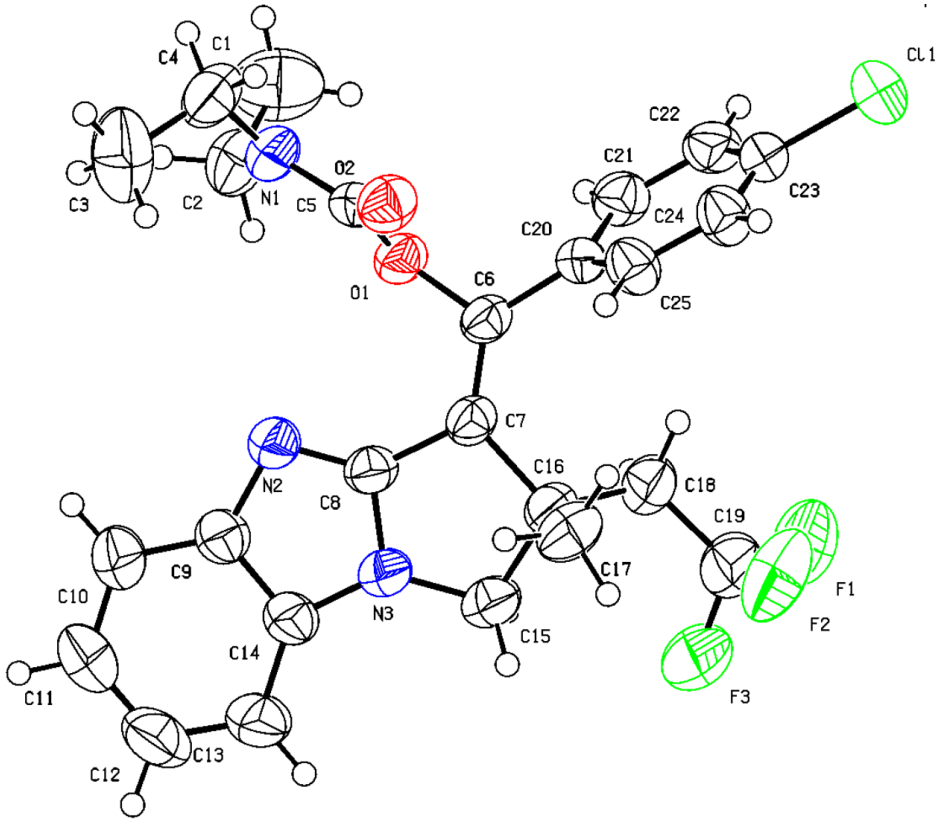


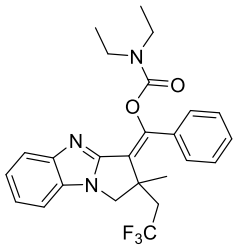
Table S1. Crystal data and structure refinements for 4s (CCDC number: 2488803)

Identification code	**4s**
Empirical formula	$C_{25}H_{25}ClF_3N_3O_2$
Formula weight	491.93
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	7.1709(5)
b/Å	8.8883(7)
c/Å	19.2532(15)
α/°	97.350(6)
β/°	96.784(6)
γ/°	91.666(6)
Volume/Å^3	1207.32(16)
Z	2
ρ_{calc} g/cm^3	1.353
μ/mm^{-1}	0.209
F(000)	512.0
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.836 to 65.234
Index ranges	$-10 \le h \le 10$, $-13 \le k \le 12$, $-26 \le l \le 29$
Reflections collected	16574
Independent reflections	8106 [R_{int} = 0.0652, R_{sigma} = 0.1440]

Data/restraints/parameters	8106/0/310
Goodness-of-fit on F^2	0.948
Final R indexes [I>=2σ (I)]	$R_1 = 0.0704$, $wR_2 = 0.1213$
Final R indexes [all data]	$R_1 = 0.2524$, $wR_2 = 0.1764$
Largest diff. peak/hole / e $Å^{-3}$	0.19/-0.22

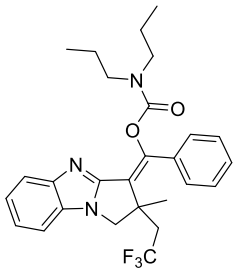
6. ^1H, ^{13}C and ^{19}F NMR spectra data of the products

(*Z*)-(2-methyl-2-(2,2,2-trifluoroethyl)-1,2-dihydro-3*H*-benzo[*d*]pyrrolo[1,2-a]imidazol-3-ylidene)(phenyl)methyl diethylcarbamate (4a)



Following general procedure, the crude product was purified by column chromatography on silica gel (petroleum/ethyl acetate = 7:1, v/v) to afford a pale yellow solid; yield: 31.1 mg, 68%; mp:168.4−169.7 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.70–7.68 (m, 1H), 7.58–7.56 (m, 2H), 7.46–7.44 (m, 3H), 7.31–7.29 (m, 1H), 7.25–7.20 (m, 2H), 4.30 (d, J = 10.6 Hz, 1H), 3.98 (d, J = 10.6 Hz, 1H), 3.59 (q, J = 7.1 Hz, 2H), 3.34 (q, J = 7.1 Hz, 2H), 2.50–2.37 (m, 1H), 2.32–2.20 (m, 1H), 1.49 (s, 3H), 1.31 (t, J = 7.2 Hz, 3H), 1.16 (t, J = 7.1 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$): δ 154.7, 153.6, 149.3, 147.2, 134.9, 131.9, 129.67, 129.61, 128.4, 126.1 (q, J = 278.5 Hz), 125.1, 122.5, 122.1, 120.4, 109.4, 54.2 (d, J = 2.2 Hz), 45.6, 41.8, 41.7, 41.6 (q, $J_{C\text{-}F}$ = 26.9Hz), 26,4, 13.8, 12.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.01. HRMS (ESI-TOF) m/z calcd. for $C_{25}H_{26}F_3N_3O_2H^+$ ($[M+H]^+$) 458.2055, found 458.2074.

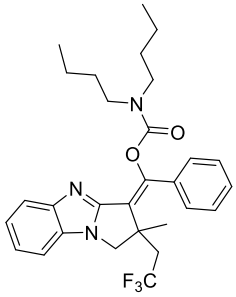
(*Z*)-(2-methyl-2-(2,2,2-trifluoroethyl)-1,2-dihydro-3*H*-benzo[*d*]pyrrolo[1,2-a]imidazol-3-ylidene)(phenyl)methyl dipropylcarbamate (4b)



Following general procedure, the crude product was purified by column chromatography on silica gel (petroleum/ethyl acetate = 7:1, v/v) to afford a pale yellow solid; yield: 31.5 mg, 65%; mp:137.5−139.0 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.65–7.59 (m, 1H), 7.50–7.46 (m, 2H), 7.39–7.36 (m, 3H), 7.23–7.21 (m, 1H), 7.18–7.14 (m, 2H), 4.22 (d, J = 10.6 Hz, 1H), 3.90 (d, J = 10.6 Hz, 1H), 3.41 (t, J = 7.6 Hz, 2H), 3.16 (t, J = 7.4 Hz, 2H), 2.42–2.30 (m, 1H),

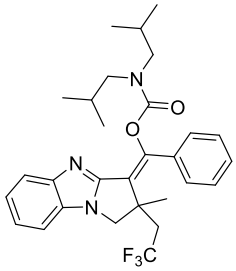
2.24–2.12 (m, 1H), 1.66–1.51 (m, 4H), 1.41 (s, 3H), 0.84–0.78 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.7, 154.0, 149.4, 147.1, 135.0, 131.9, 129.6, 129.5, 128.4, 126.1 (q, J = 280.2 Hz), 125.3, 122.5, 122.1, 120.5, 109.4, 54.2 (d, J = 3.0 Hz), 49.4, 49.2, 45.7, 41.8 (q, J = 27.2 Hz), 26.5, 21.6, 20.8, 11.3, 11.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.01. HRMS (ESI-TOF) m/z calcd. for $C_{27}H_{30}F_3N_3O_2H^+$ ([M+H]$^+$) 486.2368, found 486.2383.

(*Z*)-(2-methyl-2-(2,2,2-trifluoroethyl)-1,2-dihydro-3*H*-benzo[*d*]pyrrolo[1,2-a]imidazol-3-ylidene)(phenyl)methyl dibutylcarbamate (4c)



Following general procedure, the crude product was purified by column chromatography on silica gel (petroleum/ethyl acetate = 7:1, v/v) to afford a pale yellow solid; yield: 26.2 mg, 51%; mp:121.0−122.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70–7.68 (m, 1H), 7.57–7.52 (m, 2H), 7.47–7.44 (m, 3H), 7.31–7.28 (m, 1H), 7.25–7.20 (m, 2H), 4.35 (d, J = 10.8 Hz, 1H), 4.03 (d, J = 10.6 Hz, 1H), 3.56 (t, J = 7.6 Hz, 2H), 3.31 (t, J = 7.5 Hz, 2H), 2.51–2.38 (m, 1H), 2.33–2.20 (m, 1H), 1.67–1.55 (m, 4H), 1.49 (s, 3H), 1.34–1.27 (m, 4H), 0.90–0.87 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.7, 154.0, 149.4, 147.1, 135.0, 131.9, 129.6, 129.5, 128.4, 126.1 (q, J = 280.2 Hz), 125.3, 122.5, 122.1, 120.5, 109.4, 54.2, 47.4, 47.1, 45.6, 41.7 (q, J = 26.2 Hz), 30.6, 29.7, 26.5, 20.4, 19.9, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.02. HRMS (ESI-TOF) m/z calcd. for $C_{29}H_{34}F_3N_3O_2H^+$ ([M+H]$^+$) 514.2681, found 514.2697.

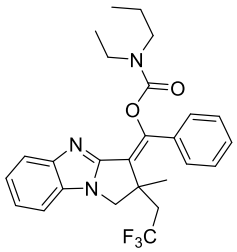
(*Z*)-(2-methyl-2-(2,2,2-trifluoroethyl)-1,2-dihydro-3*H*-benzo[*d*]pyrrolo[1,2-a]imidazol-3-ylidene)(phenyl)methyl diisobutylcarbamate (4d)



Following general procedure, the crude product was purified by column chromatography on silica gel (petroleum/ethyl acetate = 7:1, v/v) to afford a pale yellow solid; yield: 16.4 mg, 32%; mp:120.1−121.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66–7.61 (m, 1H), 7.48–7.45 (m, 2H), 7.38–7.36 (m, 3H), 7.24–7.22 (m, 1H), 7.18–7.14 (m, 2H), 4.23 (d, J = 10.6 Hz, 1H), 3.92 (d, J = 10.8 Hz, 1H), 3.30 (d, J = 7.7 Hz, 2H), 3.02 (d, J = 9.2 Hz, 2H), 2.44–2.31 (m,

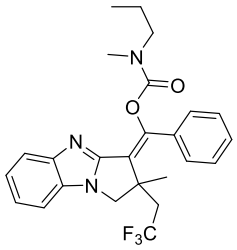
1H), 2.25–2.13 (m, 1H), 2.05–1.90 (m, 2H), 1.42 (s, 3H), 0.89 (t, J = 6.8 Hz, 6H), 0.76 (dd, J = 6.6, 4.3 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.6, 154.1, 149.4, 147.0, 134.8, 131.9, 129.6, 129.5, 128.4, 126.0 (q, J = 279.8 Hz), 125.5, 122.5, 122.1, 120.5, 109.4, 55.6, 55.2, 54.2, 45.6, 41.7 (q, J = 26.5 Hz), 27.2, 26.7, 26.5, 20.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.94. HRMS (ESI-TOF) m/z calcd. for $C_{29}H_{34}F_3N_3O_2H^+$ ($[M+H]^+$) 514.2681, found 514.2692.

(*Z*)-(2-methyl-2-(2,2,2-trifluoroethyl)-1,2-dihydro-3*H*-benzo[*d*]pyrrolo[1,2-a]imidazol-3-ylidene)(phenyl)methyl ethyl(propyl)carbamate (4e)



Following general procedure, the crude product was purified by column chromatography on silica gel (petroleum/ethyl acetate = 7:1, v/v) to afford a pale yellow wax; yield: 28.2 mg, 60%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72–7.70 (m, 1H), 7.57–7.56 (m, 2H), 7.46–7.44 (m, 3H), 7.31–7.28 (m, 1H), 7.26–7.22 (m, 2H), 4.30 (d, J = 10.6 Hz, 1H), 3.98 (d, J = 10.8 Hz, 1H), 3.59 (q, J = 7.2 Hz, 1H), 3.49 (t, J = 7.6 Hz, 1H), 3.34 (q, J = 7.8 Hz, 1H), 3.24 (t, J = 7.5 Hz, 1H), 2.50–2.37 (m, 1H), 2.32–2.20 (m, 1H), 1.71 (q, J = 7.5 Hz, 1H), 1.62 (q, J = 7.5 Hz, 1H), 1.49 (s, 3H), 1.28 (t, J = 7.2 Hz, 2H), 1.16 (t, J = 7.1 Hz, 1H), 0.90 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.6, 153.8, 149.2, 147.2, 134.9, 131.8, 129.6, 129.5, 128.4, 126.0 (q, J = 279.8 Hz), 125.1, 122.5, 122.2, 120.4, 109.4, 54.2, 48.8, 48.7, 45.6, 42.4, 42.2, 41.7 (q, J = 27.3 Hz), 26.4, 21.7, 21.0, 13.7, 12.7, 11.3, 11.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.01. HRMS (ESI-TOF) m/z calcd. for $C_{26}H_{28}F_3N_3O_2H^+$ ($[M+H]^+$) 472.2206, found 472.2215.

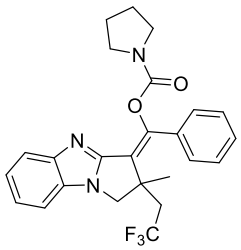
(*Z*)-(2-methyl-2-(2,2,2-trifluoroethyl)-1,2-dihydro-3*H*-benzo[*d*]pyrrolo[1,2-a]imidazol-3-ylidene)(phenyl)methyl methyl(propyl)carbamate (4f)



Following general procedure, the crude product was purified by column chromatography on silica gel (petroleum/ethyl acetate = 7:1, v/v) to afford a pale yellow solid; yield: 18.3 mg, 40%; mp:175.0−176.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67–7.62 (m, 1H), 7.51–7.48 (m, 2H), 7.39–7.38 (m, 3H), 7.24–7.22 (m, 1H), 7.19–7.15 (m, 2H), 4.23 (d, J = 10.8 Hz, 1H), 3.91 (d, J = 10.8 Hz, 1H), 3.42 (t, J = 7.5 Hz, 1H), 3.20 (d, J = 7.3 Hz, 1H), 3.11 (s, 2H), 2.87

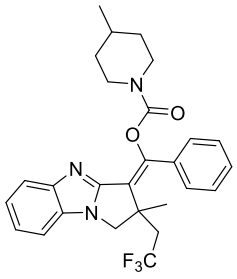
(s, 1H), 2.43–2.29 (m, 1H), 2.24–2.12 (m, 1H), 1.72–1.66 (m, 1H), 1.60–1.51 (m, 1H), 1.42 (s, 3H), 0.87–0.82 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.7, 154.2, 149.4, 147.3, 135.0, 131.9, 129.72, 129.68, 128.4, 126.1 (q, J = 280.0 Hz), 125.2, 122.6, 122.2, 120.5, 109.4, 54.2, 51.2, 45.6, 41.8 (q, J = 27.2 Hz), 34.8, 26.5, 21.0, 20.4, 11.3, 11.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.02. HRMS (ESI-TOF) m/z calcd. for $C_{25}H_{26}F_3N_3O_2H^+$ ([M+H]$^+$) 458.2055, found 458.2075.

(*Z*)-(2-methyl-2-(2,2,2-trifluoroethyl)-1,2-dihydro-3*H*-benzo[*d*]pyrrolo[1,2-a]imidazol-3-ylidene)(phenyl)methyl pyrrolidine-1-carboxylate (4g)



Following general procedure, the crude product was purified by column chromatography on silica gel (petroleum/ethyl acetate = 7:1, v/v) to afford a pale yellow solid; yield: 24.6 mg, 54%; mp:165.5−167.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71-7.69 (m, 1H), 7.61–7.58 (m, 2H), 7.47–7.44 (m, 3H), 7.32–7.30 (m, 1H), 7.27–7.23 (m, 2H), 4.31 (d, J = 10.8 Hz, 1H), 3.99 (d, J = 10.8 Hz, 1H), 3.84–3.76 (m, 2H), 3.46–3.36 (m, 2H), 2.50–2.38 (m, 1H), 2.32–2.20 (m, 1H), 2.04–1.97 (m, 2H), 1.95–1.88 (m, 2H), 1.48 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.5, 152.8, 149.1, 147.5, 134.8, 131.7, 129.7, 129.6, 128.4, 126.0 (q, J = 279.8 Hz), 124.8, 122.7, 122.3, 120.4, 109.5, 54.2, 46.57, 46.51, 45.6, 41.7 (q, J = 27.1 Hz), 26.5, 25.8, 25.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.03. HRMS (ESI-TOF) m/z calcd. for $C_{25}H_{24}F_3N_3O_2H^+$ ([M+H]$^+$) 456.1899, found 456.1897.

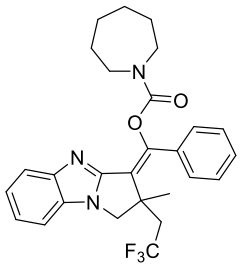
(*Z*)-(2-methyl-2-(2,2,2-trifluoroethyl)-1,2-dihydro-3*H*-benzo[*d*]pyrrolo[1,2-a]imidazol-3-ylidene)(phenyl)methyl 4-methylpiperidine-1-carboxylate (4h)



Following general procedure, the crude product was purified by column chromatography on silica gel (petroleum/ethyl acetate = 7:1, v/v) to afford a pale yellow solid; yield: 23.7 mg, 49%; mp:166.0−168.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73–7.71 (m, 1H), 7.58–7.56 (m, 2H), 7.47–7.45 (m, 3H), 7.32–7.29 (m, 1H), 7.27–7.23 (m, 2H), 4.38–4.29 (m, 2H), 4.13 (d, J = 12.7 Hz, 1H), 3.99 (d, J = 10.8 Hz, 1H), 3.09–3.00 (m, 1H), 2.84–2.76 (m, 1H), 2.49–2.40 (m, 1H), 2.32–2.22 (m, 1H), 1.80–1.71 (m, 2H), 1.67–1.58 (m, 2H), 1.49 (s, 3H), 1.38–1.28

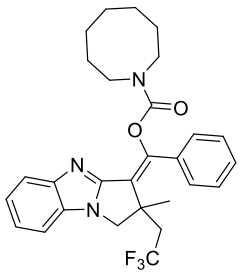
(m, 1H), 1.06 (d, J = 6.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.6, 153.1, 149.3, 147.3, 134.8, 131.8, 129.7, 129.6, 128.4, 127.4, 126.0 (q, J = 279.1 Hz), 125.1, 122.6, 122.2, 120.3, 54.2, 45.6, 45.3, 44.7, 41.6 (q, J = 26.8 Hz), 33.6, 31.0, 26.5, 26.4, 22.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.99. HRMS (ESI-TOF) m/z calcd. for $C_{27}H_{28}F_3N_3O_2H^+$ ($[M+H]^+$) 484.2212, found 484.2218.

(*Z*)-(2-methyl-2-(2,2,2-trifluoroethyl)-1,2-dihydro-3*H*-benzo[*d*]pyrrolo[1,2-a]imidazol-3-ylidene)(phenyl)methyl azepane-1-carboxylate (4i)



Following general procedure, the crude product was purified by column chromatography on silica gel (petroleum/ethyl acetate = 7:1, v/v) to afford a pale yellow solid; yield: 27.1 mg, 56%; mp:181.7−183.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73-7.69 (m, 1H), 7.59–7.56 (m, 2H), 7.46–7.44 (m, 3H), 7.32–7.29 (m, 1H), 7.26–7.22 (m, 2H), 4.30 (d, J = 10.6 Hz, 1H), 3.99 (d, J = 10.8 Hz, 1H), 3.69 (t, J = 6.0 Hz, 2H), 3.45 (t, J = 5.6 Hz, 2H), 2.50–2.37 (m, 1H), 2.32–2.20 (m, 1H), 1.97–1.93 (m, 2H), 1.84–1.80 (m, 2H), 1.75–1.65 (m, 4H), 1.48 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.5, 153.8, 149.2, 147.2, 134.9, 131.8, 129.69, 129.64, 128.4, 126.0 (q, J = 279.7 Hz), 125.2, 122.6, 122.2, 120.3, 109.4, 54.1 (d, J = 2.9 Hz), 47.3, 46.8, 45.6 (d, J = 1.8 Hz), 41.6 (q, J = 27.1 Hz), 28.14, 28.11, 27.28, 27.24, 26.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.99. HRMS (ESI-TOF) m/z calcd. for $C_{27}H_{28}F_3N_3O_2H^+$ ($[M+H]^+$) 484.2212, found 484.2231.

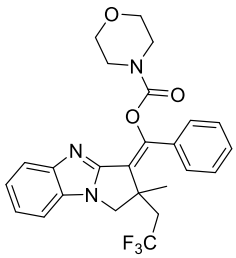
(*Z*)-(2-methyl-2-(2,2,2-trifluoroethyl)-1,2-dihydro-3*H*-benzo[*d*]pyrrolo[1,2-a]imidazol-3-ylidene)(phenyl)methyl azocane-1-carboxylate (4j)



Following general procedure, the crude product was purified by column chromatography on silica gel (petroleum/ethyl acetate = 7:1, v/v) to afford a pale yellow solid; yield: 24.9 mg, 50%; mp:176−178 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66–7.64 (m, 1H), 7.51–7.48 (m, 2H), 7.40–7.37 (m, 3H), 7.25–7.21 (m, 1H), 7.19–7.16 (m, 2H), 4.24 (d, J = 10.8 Hz, 1H), 3.92 (d, J = 10.8 Hz, 1H), 3.55 (t, J = 5.8 Hz, 2H), 3.34 (t, J = 5.8 Hz, 2H), 2.42–2.30 (m, 1H), 2.25–

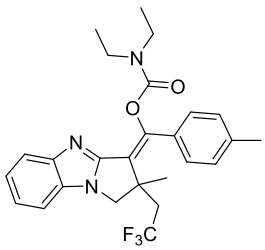
2.12 (m, 1H), 1.84–1.82 (m, 2H), 1.64–1.55 (m, 8H), 1.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.6, 153.6, 149.4, 147.2, 134.9, 131.9, 129.7, 129.6, 128.4, 126.1 (q, J = 279.9 Hz), 125.3, 122.5, 122.2, 120.4, 109.4, 54.1, 48.6, 48.3, 45.6, 41.6 (q, J = 26.7 Hz), 26.9, 26.7, 26.5, 26.1, 25.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.99. HRMS (ESI-TOF) m/z calcd. for $C_{28}H_{30}F_3N_3O_2H^+$ ($[M+H]^+$) 498.2368, found 498.2362.

(*Z*)-(2-methyl-2-(2,2,2-trifluoroethyl)-1,2-dihydro-3*H*-benzo[*d*]pyrrolo[1,2-a]imidazol-3-ylidene)(phenyl)methyl morpholine-4-carboxylate (4k)



Following general procedure, the crude product was purified by column chromatography on silica gel (petroleum/ethyl acetate = 7:1, v/v) to afford a pale yellow solid; yield: 19.3 mg, 41%; mp:155−157 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77–7.73 (m, 1H), 7.59–7.55 (m, 2H), 7.50–7.47 (m, 3H), 7.34–7.32 (m, 1H), 7.28–7.26 (m, 2H), 4.33 (d, J = 10.8 Hz, 1H), 4.02–3.99 (m, 3H), 3.82–3.77 (m, 4H), 3.53 (m, 2H), 2.50–2.38 (m, 1H), 2.33–2.21 (m, 1H), 1.50 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.4, 153.3, 149.2, 146.9, 134.4, 131.8, 129.9, 129.5, 128.6, 125.9 (q, J = 277.5 Hz), 125.2, 122.8, 122.4, 120.3, 109.6, 66.5, 54.2, 45.5 (d, J = 22.0 Hz), 44.4, 41.6 (q, J = 27.2 Hz), 26.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.03. HRMS (ESI-TOF) m/z calcd. for $C_{25}H_{24}F_3N_3O_3H^+$ ($[M+H]^+$) 472.1848, found 472.1855.

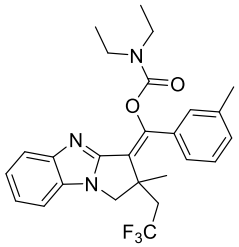
(*Z*)-(2-methyl-2-(2,2,2-trifluoroethyl)-1,2-dihydro-3*H*-benzo[*d*]pyrrolo[1,2-a]imidazol-3-ylidene)(*p*-tolyl)methyl diethylcarbamate (4n)



Following general procedure, the crude product was purified by column chromatography on silica gel (petroleum/ethyl acetate = 7:1, v/v) to afford a colorless solid; yield: 29.2 mg, 62%; mp:182−184 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71–7.67 (m, 1H), 7.46–7.44 (m, 2H), 7.31–7.28 (m, 1H), 7.26–7.21 (m, 4H), 4.29 (d, J = 10.6 Hz, 1H), 3.98 (d, J = 10.6 Hz, 1H), 3.59 (q, J = 7.2 Hz, 2H), 3.34 (q, J = 7.1 Hz, 2H), 2.47–2.37 (m, 4H; including a single peak of CH_3 group), 2.34–2.27 (m, 1H), 1.50 (s, 3H), 1.31 (t, J = 7.2 Hz, 3H), 1.15 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.7, 153.6, 149.2, 147.4, 139.7, 132.0, 131.8, 129.4, 129.1, 126.1 (q, J = 278.5 Hz), 124.8, 122.5, 122.1, 120.3, 109.4, 54.2 (q, J = 2.8 Hz), 45.6 (d, J =

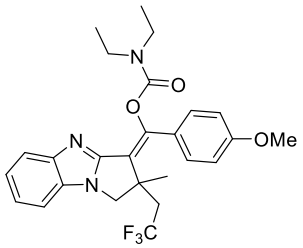
1.9 Hz), 41.77, 41.70, 41.6 (q, J = 26.9 Hz), 26.5, 21.4, 13.9, 12.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.95. HRMS (ESI-TOF) m/z calcd. for $C_{26}H_{28}F_3N_3O_2H^+$ ([M+H]$^+$) 472.2212, found 472.2220.

(*Z*)-(2-methyl-2-(2,2,2-trifluoroethyl)-1,2-dihydro-3*H*-benzo[*d*]pyrrolo[1,2-a]imidazol-3-ylidene)(*m*-tolyl)methyl diethylcarbamate (4o)



Following general procedure, the crude product was purified by column chromatography on silica gel (petroleum/ethyl acetate = 7:1, v/v) to afford a pale yellow solid; yield: 24.0 mg, 51%; mp:141−143 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63–7.61 (m, 1H), 7.30–7.26 (m, 3H), 7.24–7.21 (m, 1H), 7.20–7.14 (m, 3H), 4.22 (d, J = 10.6 Hz, 1H), 3.91 (d, J = 10.6 Hz, 1H), 3.52 (q, J = 7.2 Hz, 2H), 3.27 (q, J = 7.2 Hz, 2H), 2.41–2.29 (m, 4H; including a single peak of CH_3 group), 2.26–2.17 (m, 1H), 1.42 (s, 3H), 1.23 (t, J = 7.3 Hz, 3H), 1.09 (t, J = 7.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.7, 153.6, 149.3, 147.5, 138.2, 134.8, 131.8, 130.4, 130.0, 128.3, 126.6, 126.1 (q, J = 279.1 Hz), 124.8, 122.5, 122.1, 120.4, 109.4, 54.3 (d, J = 2.9 Hz), 45.6, 41.8, 41.7, 41.6 (q, J = 27.1 Hz), 26.5, 21.4, 13.9, 12.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.00. HRMS (ESI-TOF) m/z calcd. for $C_{26}H_{28}F_3N_3O_2H^+$ ([M+H]$^+$) 472.2212, found 472.2218.

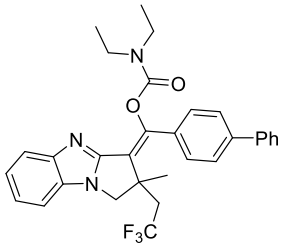
(*Z*)-(4-methoxyphenyl)(2-methyl-2-(2,2,2-trifluoroethyl)-1,2-dihydro-3*H*-benzo[*d*]pyrrolo[1,2-a]imidazol-3-ylidene)methyl diethylcarbamate (4p)



Following general procedure, the crude product was purified by column chromatography on silica gel (petroleum/ethyl acetate = 7:1, v/v) to afford a colorless solid; yield: 30.7 mg, 63%; mp:180−181 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71–7.68 (m, 1H), 7.51–7.47 (m, 2H), 7.31–7.29 (m, 1H), 7.26–7.22 (m, 2H), 6.98–6.95 (m, 2H), 4.30 (d, J = 10.6 Hz, 1H), 3.99 (d, J = 10.6 Hz, 1H), 3.86 (s, 3H), 3.59 (q, J = 7.2 Hz, 2H), 3.34 (q, J = 7.5 Hz, 2H), 2.50–2.41 (m, 1H), 2.38–2.26 (m, 1H), 1.51 (s, 3H), 1.31 (t, J = 7.2 Hz, 3H), 1.15 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.4, 154.7, 153.7, 149.1, 147.4, 131.8, 131.0, 127.2, 126.1 (q, J = 280.0 Hz), 124.8, 122.5, 122.2, 120.3, 113.7, 109.4, 55.2, 54.3 (d, J = 2.9 Hz), 45.7, 41.8, 41.7, 41.6 (q, J = 27.3 Hz), 26.5, 13.9, 13.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.94. HRMS

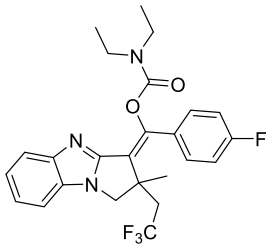
(ESI-TOF) m/z calcd. for $C_{26}H_{28}F_3N_3O_3H^+$ ([M+H]$^+$) 488.2161, found 488.2169.

(*Z*)-[1,1'-biphenyl]-4-yl(2-methyl-2-(2,2,2-trifluoroethyl)-1,2-dihydro-3*H*-benzo[*d*]pyrrolo[1,2-a]imidazol-3-ylidene)methyl diethylcarbamate (4q)



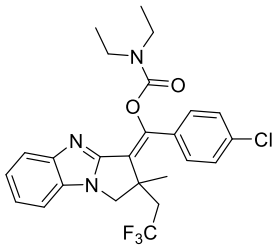
Following general procedure, the crude product was purified by column chromatography on silica gel (petroleum/ethyl acetate = 7:1, v/v) to afford a pale yellow solid; yield: 26.7 mg, 50%; mp:164−166 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64–7.60 (m, 3H), 7.58–7.54 (m, 4H), 7.41–7.36 (m, 2H), 7.32–7.27 (m, 1H), 7.24–7.21 (m, 1H), 7.17–7.14 (m, 2H), 4.24 (d, J = 10.8 Hz, 1H), 3.92 (d, J = 10.6 Hz, 1H), 3.54 (q, J = 7.1 Hz, 2H), 3.28 (q, J = 7.1 Hz, 2H), 2.47–2.34 (m, 1H), 2.32–2.22 (m, 1H), 1.45 (s, 3H), 1.25 (t, J = 7.2 Hz, 3H), 1.09 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.7, 153.6, 149.3, 146.9, 142.2, 139.9, 133.8, 131.8, 130.0, 128.8, 127.7, 127.05, 127.01, 126.0 (q, J = 280.0 Hz), 125.2, 122.5, 122.1, 120.4, 109.4, 54.2 (d, J = 2.9 Hz), 45.7 (d, J = 1.1 Hz), 41.79, 41.75 (q, J = 27.1 Hz), 41.73, 26.5, 13.8, 12.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.91. HRMS (ESI-TOF) m/z calcd. for $C_{31}H_{30}F_3N_3O_2H^+$ ([M+H]$^+$) 534.2368, found 534.2383.

(*Z*)-(4-fluorophenyl)(2-methyl-2-(2,2,2-trifluoroethyl)-1,2-dihydro-3*H*-benzo[*d*]pyrrolo[1,2-a]imidazol-3-ylidene)methyl diethylcarbamate (4r)



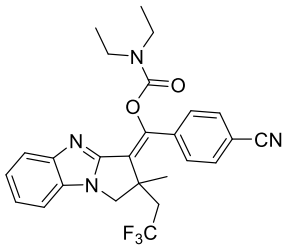
Following general procedure, the crude product was purified by column chromatography on silica gel (petroleum/ethyl acetate = 7:1, v/v) to afford a colorless solid; yield: 28.5 mg, 60%; mp:147−149 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72–7.68 (m, 1H), 7.59–7.54 (m, 2H), 7.32–7.30 (m, 1H), 7.25–7.23 (m, 2H), 7.18–7.13 (m, 2H), 4.32 (d, J = 10.7 Hz, 1H), 3.99 (d, J = 10.7 Hz, 1H), 3.59 (q, J = 7.1 Hz, 2H), 3.34 (q, J = 7.1 Hz, 2H), 2.50–2.38 (m, 1H), 2.32–2.19 (m, 1H), 1.48 (s, 3H), 1.31 (t, J = 7.2 Hz, 3H), 1.16 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.3 (d, J = 250.2 Hz), 154.4, 153.5, 149.2, 146.1, 131.8, 131.7 (d, J = 8.4 Hz), 131.0 (d, J = 3.7 Hz), 125.9 (q, J = 279.8 Hz), 125.5, 122.7, 122.3, 120.4, 115.6 (d, J = 21.6 Hz), 109.5, 54.1 (d, J = 2.9 Hz), 45.6 (d, J = 2.2 Hz), 41.87, 41.83 (q, J = 27.0 Hz), 41.7, 26.5, 13.9, 12.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.00, -110.12. HRMS (ESI-TOF) m/z calcd. for $C_{25}H_{25}F_4N_3O_2H^+$ ([M+H]$^+$) 476.1961, found 476.1985.

(*Z*)-(4-chlorophenyl)(2-methyl-2-(2,2,2-trifluoroethyl)-1,2-dihydro-3*H*-benzo[*d*]pyrrolo[1,2-a]imidazol-3-ylidene)methyl diethylcarbamate (4s)



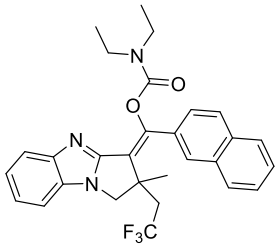
Following general procedure, the crude product was purified by column chromatography on silica gel (petroleum/ethyl acetate = 7:1, v/v) to afford a pale yellow solid; yield: 31.4 mg, 64%; mp:185−186 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73–7.68 (m, 1H), 7.53–7.50 (m, 2H), 7.46–7.43 (m, 2H), 7.33–7.30 (m, 1H), 7.27–7.23 (m, 2H), 4.33 (d, J = 10.7 Hz, 1H), 3.99 (d, J = 10.7 Hz, 1H), 3.59 (q, J = 7.2 Hz, 2H), 3.34 (q, J = 7.1 Hz, 2H), 2.51–2.39 (m, 1H), 2.34–2.22 (m, 1H), 1.48 (s, 3H), 1.30 (t, J = 7.2 Hz, 3H), 1.16 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.4, 153.5, 149.3, 145.8, 135.8, 133.4, 131.8, 131.0, 128.8, 125.9 (q, J = 280.8 Hz), 125.7, 122.7, 122.2, 120.5, 109.5, 54.1 (d, J = 2.5 Hz), 45.6, 41.93 (q, J = 27.2 Hz), 41.91, 41.8, 26.5, 13.9, 12.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.95. HRMS (ESI-TOF) m/z calcd. for $C_{25}H_{25}F_3N_3O_2ClH^+$ ($[M+H]^+$) 492.1666, found 492.1655.

(*Z*)-(4-cyanophenyl)(2-methyl-2-(2,2,2-trifluoroethyl)-1,2-dihydro-3*H*-benzo[*d*]pyrrolo[1,2-a]imidazol-3-ylidene)methyl diethylcarbamate (4t)



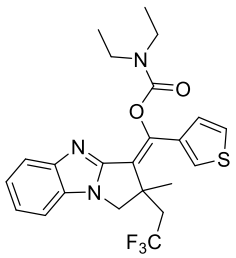
Following general procedure, the crude product was purified by column chromatography on silica gel (petroleum/ethyl acetate = 7:1, v/v) to afford a yellow solid; yield: 28.0 mg, 58%; mp:207−209 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73–7.69 (m, 2H), 7.64–7.62 (m, 3H), 7.26–7.23 (m, 1H), 7.20–7.17 (m, 2H), 4.28 (d, J = 10.8 Hz, 1H), 3.93 (d, J = 10.8 Hz, 1H), 3.53 (q, J = 7.9 Hz, 2H), 3.26 (q, J = 7.1 Hz, 2H), 2.43–2.31 (m, 1H), 2.22–2.21 (m, 1H), 1.39 (s, 3H), 1.24 (t, J = 7.0 Hz, 3H), 1.09 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.0, 153.4, 149.3, 144.6, 139.5, 132.3, 131.8, 130.5, 126.4, 125.7 (q, J = 280.0 Hz), 122.9, 122.4, 120.6, 118.1, 113.5, 109.6, 54.1, 45.6, 42.1 (q, J = 27.5 Hz), 41.9, 41.8, 26.5, 13.9, 12.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.00. HRMS (ESI-TOF) m/z calcd. for $C_{26}H_{25}F_3N_4O_2H^+$ ($[M+H]^+$) 483.2008, found 483.2021.

(*Z*)-(2-methyl-2-(2,2,2-trifluoroethyl)-1,2-dihydro-3*H*-benzo[*d*]pyrrolo[1,2-a]imidazol-3-ylidene)(naphthalen-2-yl)methyl diethylcarbamate (4u)



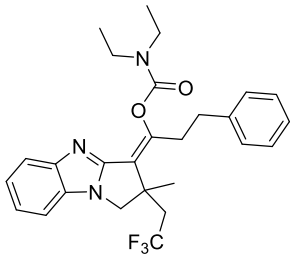
Following general procedure, the crude product was purified by column chromatography on silica gel (petroleum/ethyl acetate = 7:1, v/v) to afford a yellow solid; yield: 23.8 mg, 47%; mp:154−156 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (s, 1H), 7.86–7.80 (m, 3H), 7.66–7.63 (m, 1H), 7.59–7.56 (m, 1H), 7.51–7.47 (m, 2H), 7.25–7.23 (m, 1H), 7.18–7.16 (m, 2H), 4.26 (d, J = 10.8 Hz, 1H), 3.92 (d, J = 10.8 Hz, 1H), 3.53 (q, J = 7.1 Hz, 2H), 3.27 (q, J = 7.2 Hz, 2H), 2.47–2.35 (m, 1H), 2.30–2.18 (m, 1H), 1.44 (s, 3H), 1.22 (t, J = 7.2 Hz, 3H), 1.08 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.7, 153.6, 149.3, 147.2, 133.4, 132.5, 132.3, 131.9, 129.4, 128.5, 128.3, 127.8, 127.2, 126.7, 126.5, 125.9 (q, J = 280.0 Hz), 125.4, 122.6, 122.2, 120.4, 109.4, 54.1, 45.7, 41.9 (q, J = 27.1 Hz), 41.88, 41.80, 26.6, 13.9, 12.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.93. HRMS (ESI-TOF) m/z calcd. for $C_{29}H_{28}F_3N_3O_2H^+$ ($[M+H]^+$) 508.2212, found 508.2207.

(Z)-(2-methyl-2-(2,2,2-trifluoroethyl)-1,2-dihydro-3*H*-benzo[*d*]pyrrolo[1,2-a]imidazol-3-ylidene)(thiophen-3-yl)methyl diethylcarbamate (4v)



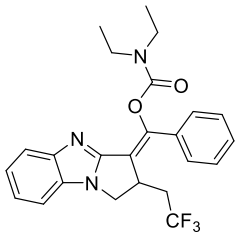
Following general procedure, the crude product was purified by column chromatography on silica gel (petroleum/ethyl acetate = 7:1, v/v) to afford a yellow solid; yield: 22.2 mg, 48%; mp:134−136 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70–7.66 (m, 1H), 7.57–7.56 (m, 1H), 7.42–7.40 (m, 1H), 7.31–7.27 (m, 2H), 7.24–7.21 (m, 2H), 4.31 (d, J = 10.6 Hz, 1H), 4.00 (d, J = 10.8 Hz, 1H), 3.61 (q, J = 7.3 Hz, 2H), 3.35 (q, J = 7.1 Hz, 2H), 2.54–2.45 (m, 1H), 2.42–2.33 (m, 1H), 1.54 (s, 3H), 1.33 (t, J = 7.2 Hz, 3H), 1.17 (t, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.4, 153.6, 149.3, 142.4, 135.2, 131.8, 128.5, 127.2, 126.2, 126.1 (q, J = 279.8 Hz), 126.0, 122.6, 122.2, 120.4, 109.4, 54.4 (d, J = 2.5 Hz), 45.6, 41.8, 41.7, 41.3 (q, J = 27.1 Hz), 26.3, 13.9, 13.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.02. HRMS (ESI-TOF) m/z calcd. for $C_{23}H_{24}F_3N_3O_2SH^+$ ($[M+H]^+$) 464.1620, found 464.1622.

(*Z*)-1-(2-methyl-2-(2,2,2-trifluoroethyl)-1,2-dihydro-3*H*-benzo[*d*]pyrrolo[1,2-a]imidazol-3-ylidene)-3-phenylpropyl diethylcarbamate (4w)



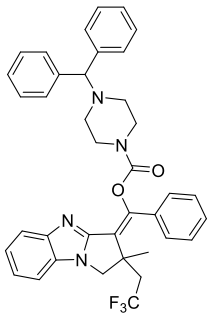
Following general procedure, the crude product was purified by column chromatography on silica gel (petroleum/ethyl acetate = 7:1, v/v) to afford a yellow solid; yield: 19.4 mg, 40%; mp:152−154 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59–7.57 (m, 1H), 7.23 (d, J = 7.3 Hz, 2H), 7.19–7.12 (m, 6H), 4.23 (d, J = 10.9 Hz, 1H), 3.82 (d, J = 10.9 Hz, 1H), 3.70–3.57 (m, 2H), 3.39–3.29 (m, 2H), 2.95–2.87 (m, 2H), 2.83–2.71 (m, 2H), 2.37–2.23 (m, 2H), 1.48 (s, 3H), 1.36 (t, J = 7.2 Hz, 3H), 1.18 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.6, 153.4, 149.3, 149.0, 140.4, 131.6, 128.6, 128.5, 126.4, 125.8 (q, J = 280.2Hz), 124.0, 122.3, 122.0, 120.1, 109.3, 54.4, 44.8 (d, J = 1.9 Hz), 42.0 (q, J = 26.8 Hz), 41.95, 41.90, 34.8, 32.3, 24.7, 14.0, 12.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.10. HRMS (ESI-TOF) m/z calcd. for $C_{27}H_{30}F_3N_3O_2H^+$ ([M+H]$^+$) 486.2368, found 486.2359.

(*Z*)-phenyl(2-(2,2,2-trifluoroethyl)-1,2-dihydro-3*H*-benzo[*d*]pyrrolo[1,2-a]imidazol-3-ylid ene)methyl diethylcarbamate (4x)



Following general procedure, the crude product was purified by column chromatography on silica gel (petroleum/ethyl acetate = 7:1, v/v) to afford a pale yellow wax; yield: 13.3 mg, 30%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63–7.61 (m, 1H), 7.57–7.54 (m, 2H), 7.41–7.34 (m, 3H), 7.25–7.23 (m, 1H), 7.18–7.16 (m, 2H), 4.39–4.32 (m, 2H), 4.12–4.06 (m, 1H), 3.69–3.58 (m, 2H), 3.36–3.25 (m, 2H), 2.30–2.15 (m, 2H), 1.36 (t, J = 7.2 Hz, 3H), 1.13 (t, J = 7.1 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$): δ 154.5, 153.5, 149.3, 146.5, 134.4, 131.7, 129.7, 128.8, 127.4, 126.1 (q, J = 278.5 Hz), 122.9, 122.5, 120.2, 118.1, 109.5, 47.1, 42.0, 41.9, 37.23 (q, J = 27.6 Hz), 37.20 (d, J = 2.0 Hz), 14.1, 13.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.12. HRMS (ESI-TOF) m/z calcd. for $C_{24}H_{24}F_3N_3O_2H^+$ ([M+H]$^+$) 444.1899, found 444.1892.

(*Z*)-(2-methyl-2-(2,2,2-trifluoroethyl)-1,2-dihydro-3*H*-benzo[*d*]pyrrolo[1,2-*a*]imidazol-3-ylidene)(phenyl)methyl 4-benzhydrylpiperazine-1-carboxylate (4y)



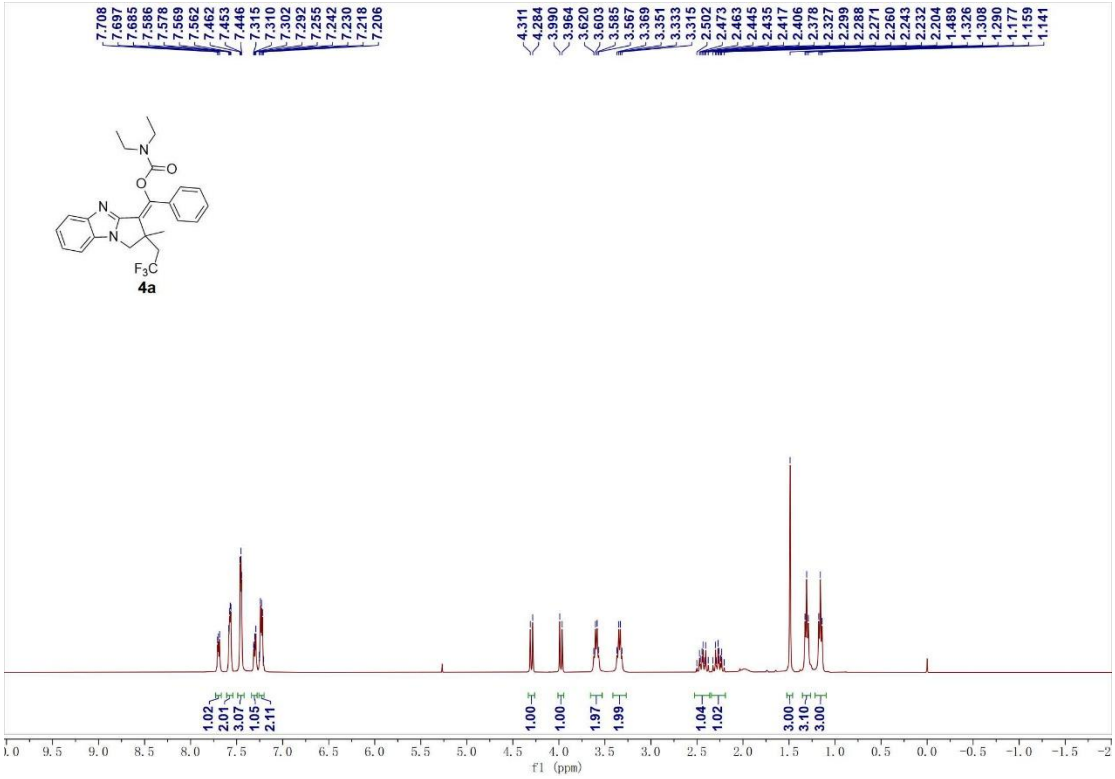
Mp:216−218 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69–7.67 (m, 1H), 7.56–7.54 (m, 2H), 7.47–7.43 (m, 7H), 7.31–7.25 (m, 7H), 7.21–7.17 (m, 2H), 4.39 (s, 1H), 4.28 (d, J = 10.6 Hz, 1H), 3.96 (d, J = 10.6 Hz, 1H), 3.82–3.79 (m, 2H), 3.54 (m, 2H), 2.67–2.64 (m, 2H), 2.48–2.47 (m, 2H), 2.44–2.55 (m, 1H), 2.30–2.18 (m, 1H), 1.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.5, 153.1, 149.3, 147.0, 142.2, 134.6, 131.8, 129.7, 129.5, 128.5, 127.9,127.0, 125.9 (q, J = 280.0 Hz), 125.1, 122.6, 122.2, 120.4, 109.5, 75.9, 54.1 (d, J = 1.8 Hz), 51.3, 51.2, 45.6, 45.0, 44.2, 41.6 (q, J = 27.1 Hz), 26.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.95.

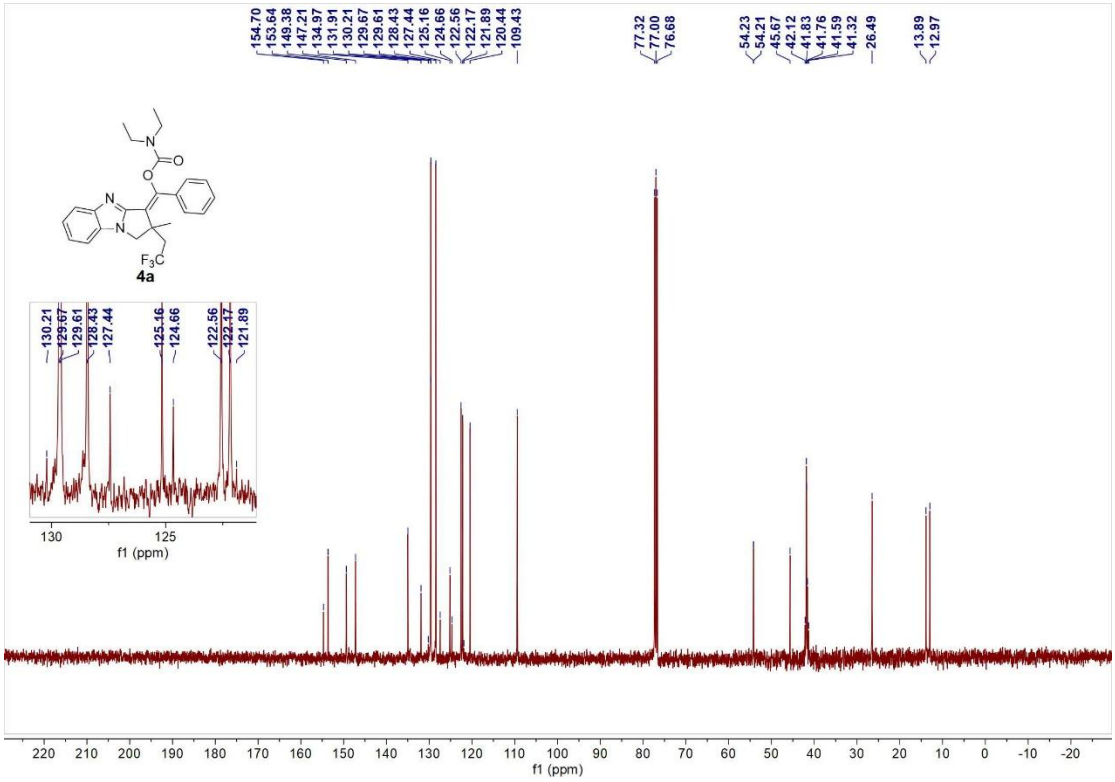
7. References

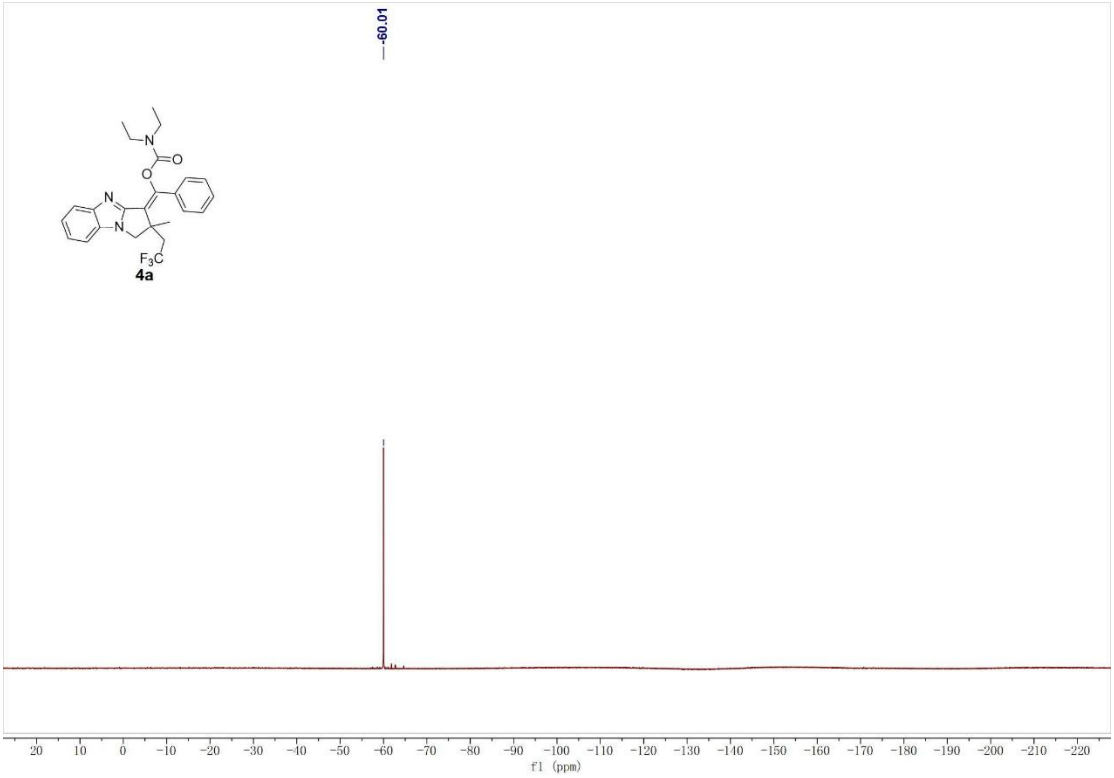
1. Y. Liu, N. Zhang, Y. Xu and Y. Chen, *J. Org. Chem.*, 2021, **86**, 16882−16891.

2. Y. Dong, X. Guo, Y. Yu and G. Liu, *Mol Divers*, 2013, **17**, 1−7.

8. Copies of ^{1}H, ^{13}C and ^{19}F NMR charts of the products



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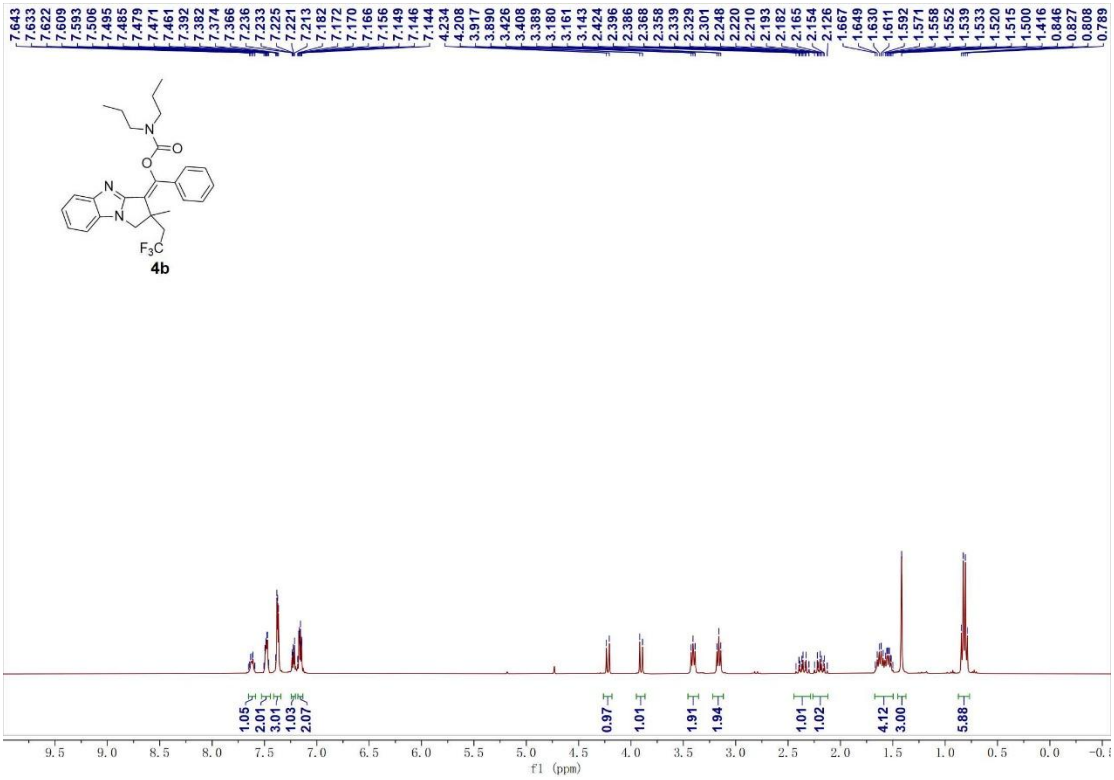
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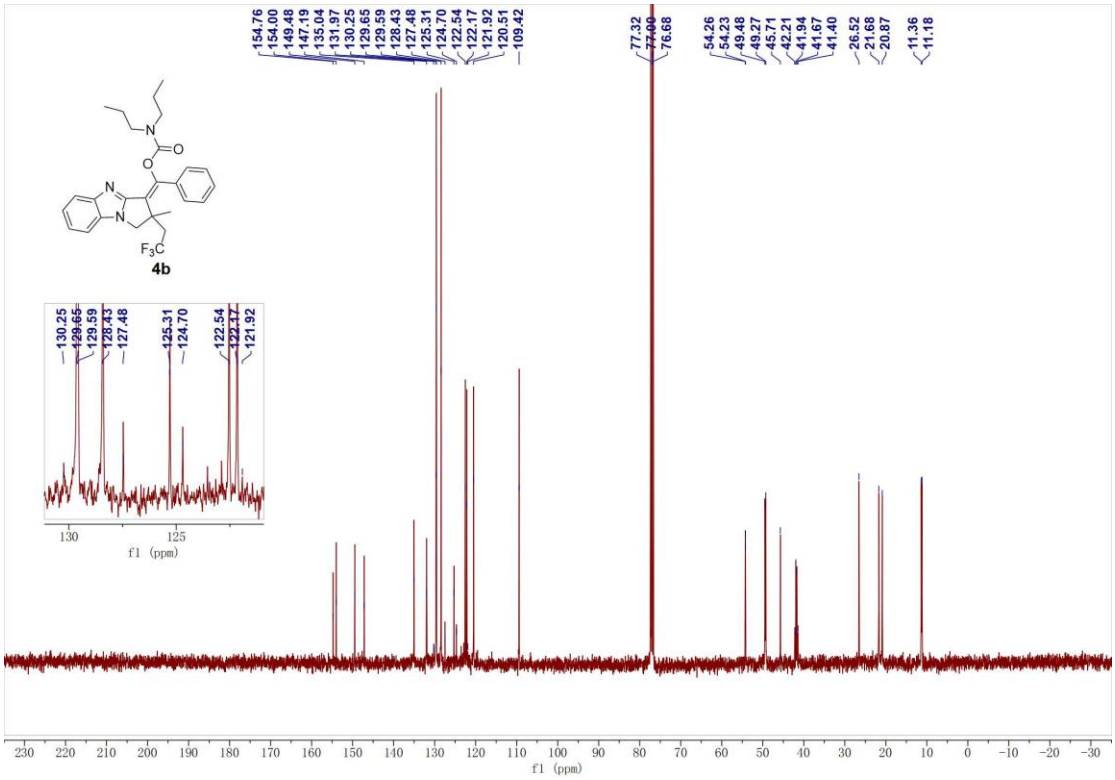
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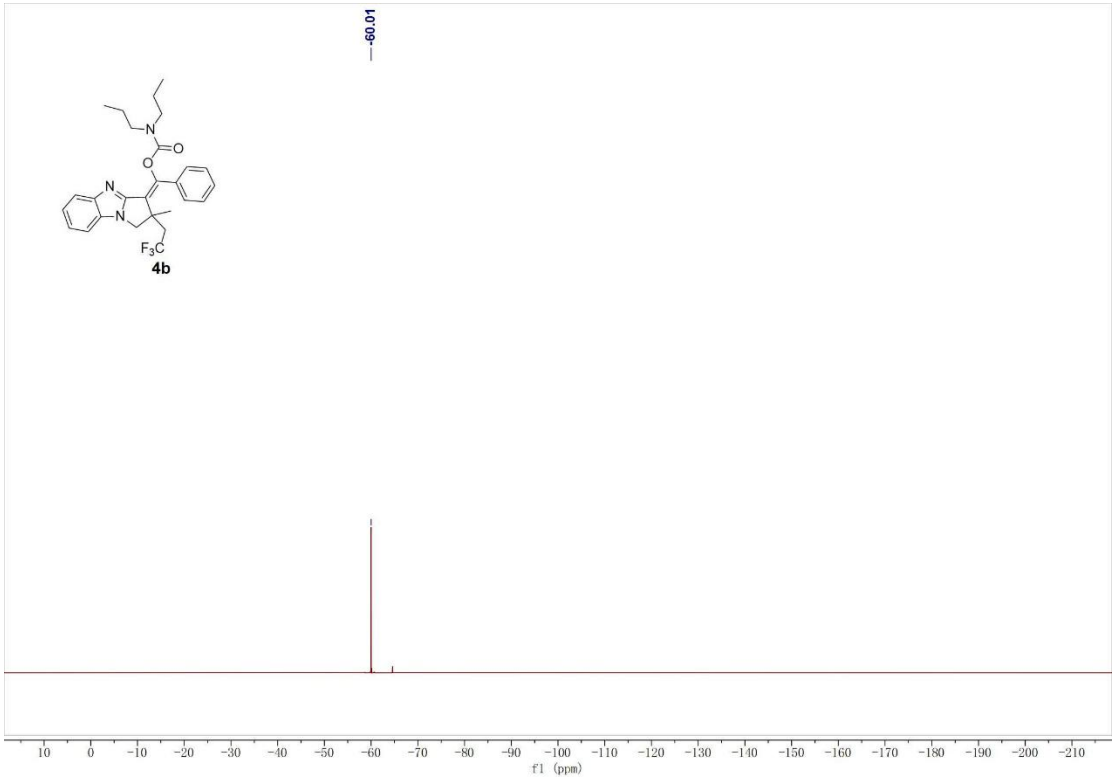
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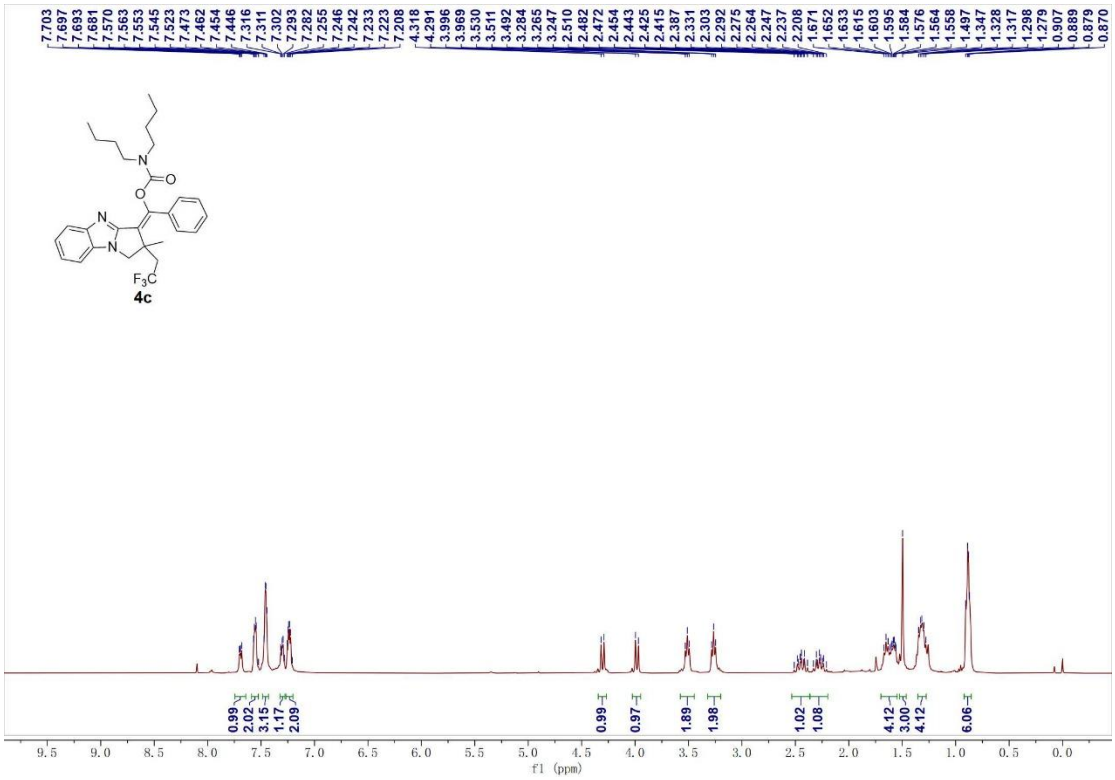
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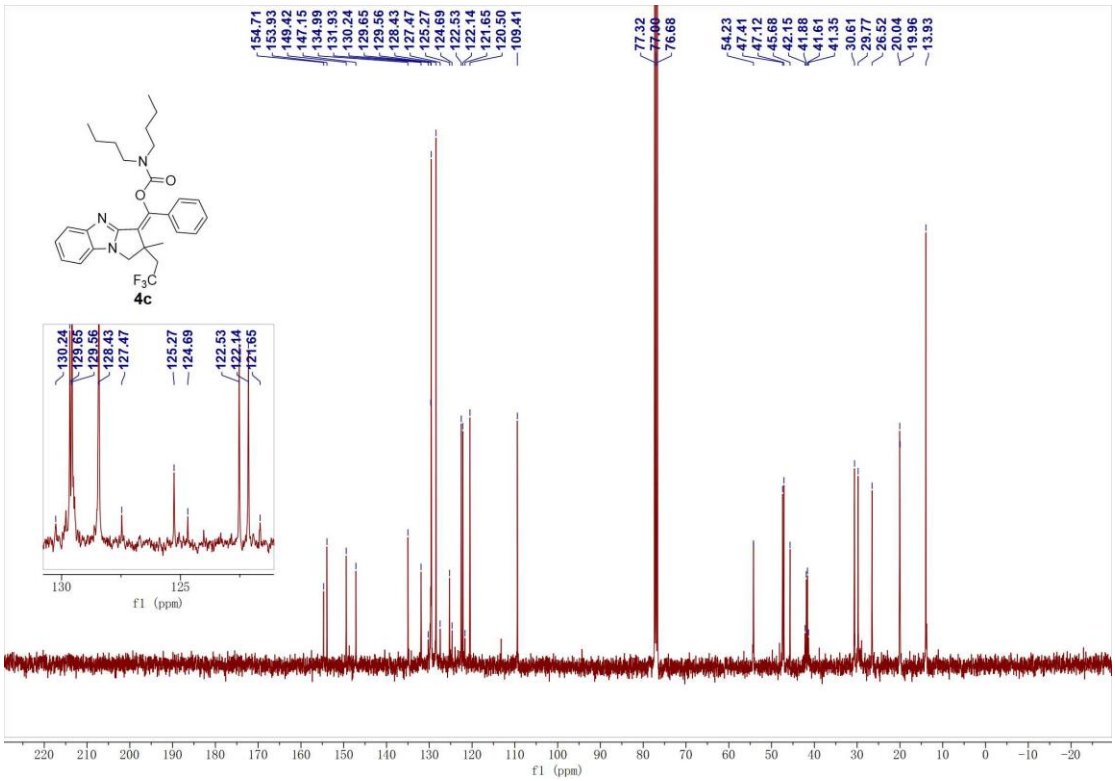
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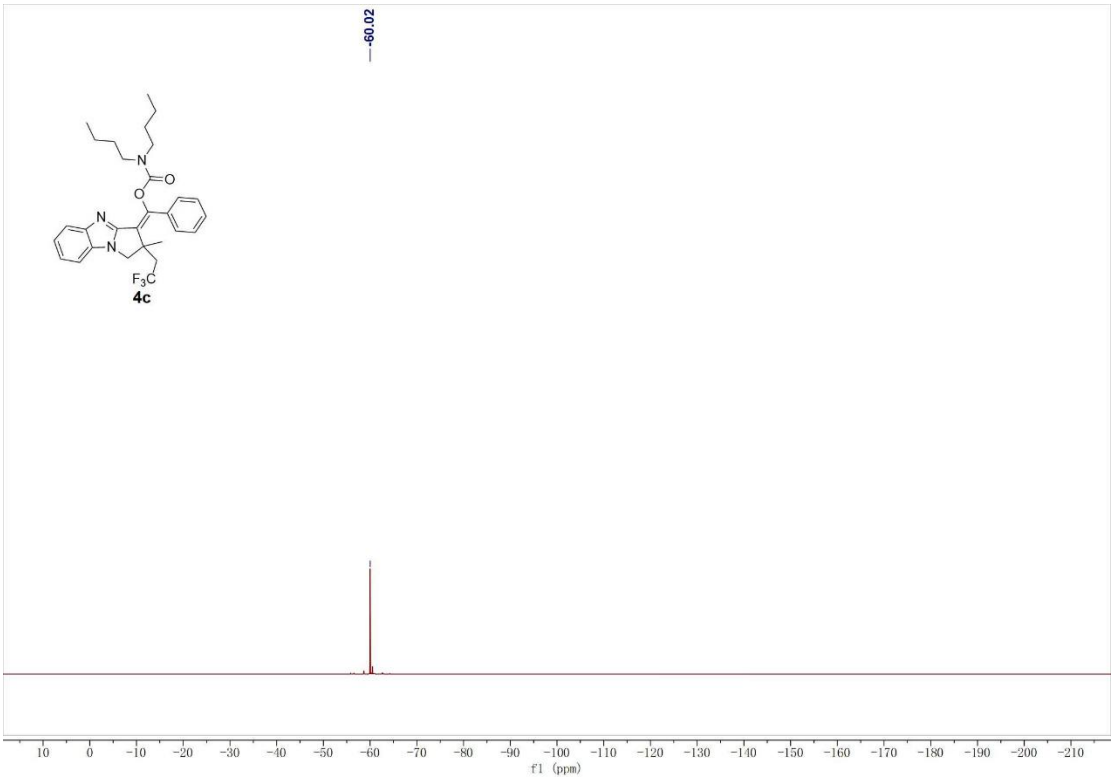
f1 (ppm)
f1 (ppm)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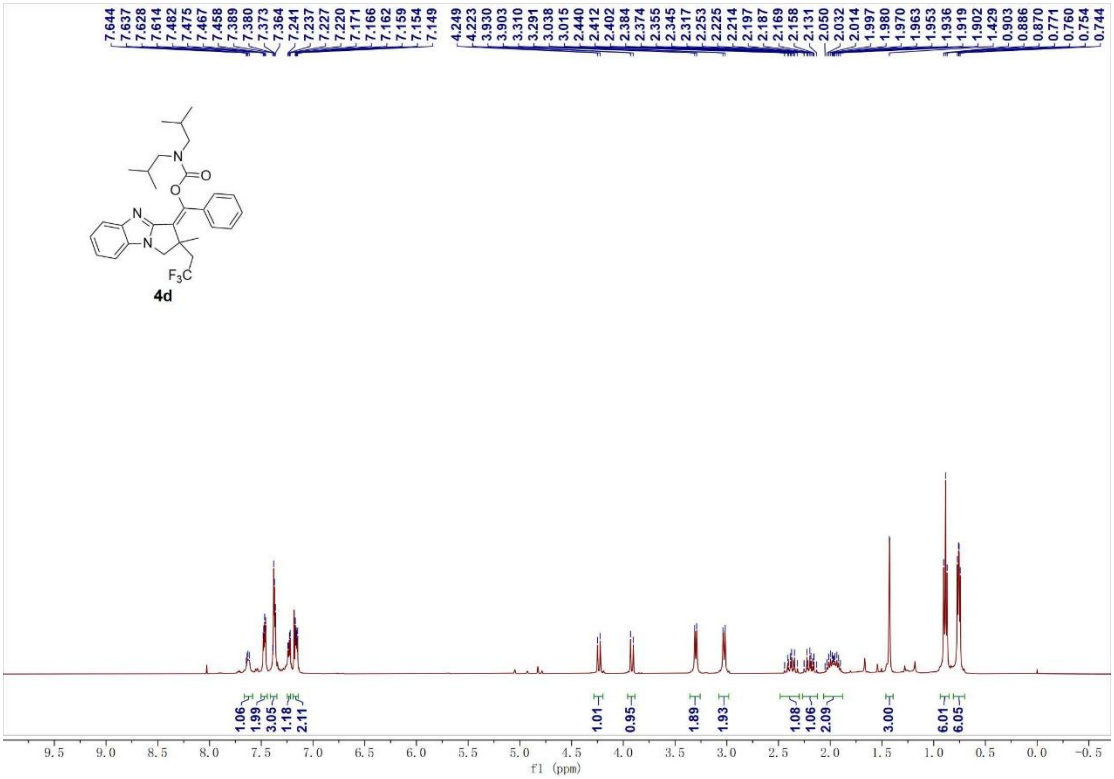
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7.220
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7.166
7.162
7.159
7.154
7.149
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4.223
3.930
3.903
3.310
3.291
3.038
3.015
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2.412
2.402
2.384
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2.225
2.214
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2.187
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2.158
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2.050
2.032
2.014
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1.970
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1.919
1.902
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0.903
0.886
0.870
0.771
0.760
0.754
0.744
4d
1.06
1.99
3.05
1.18
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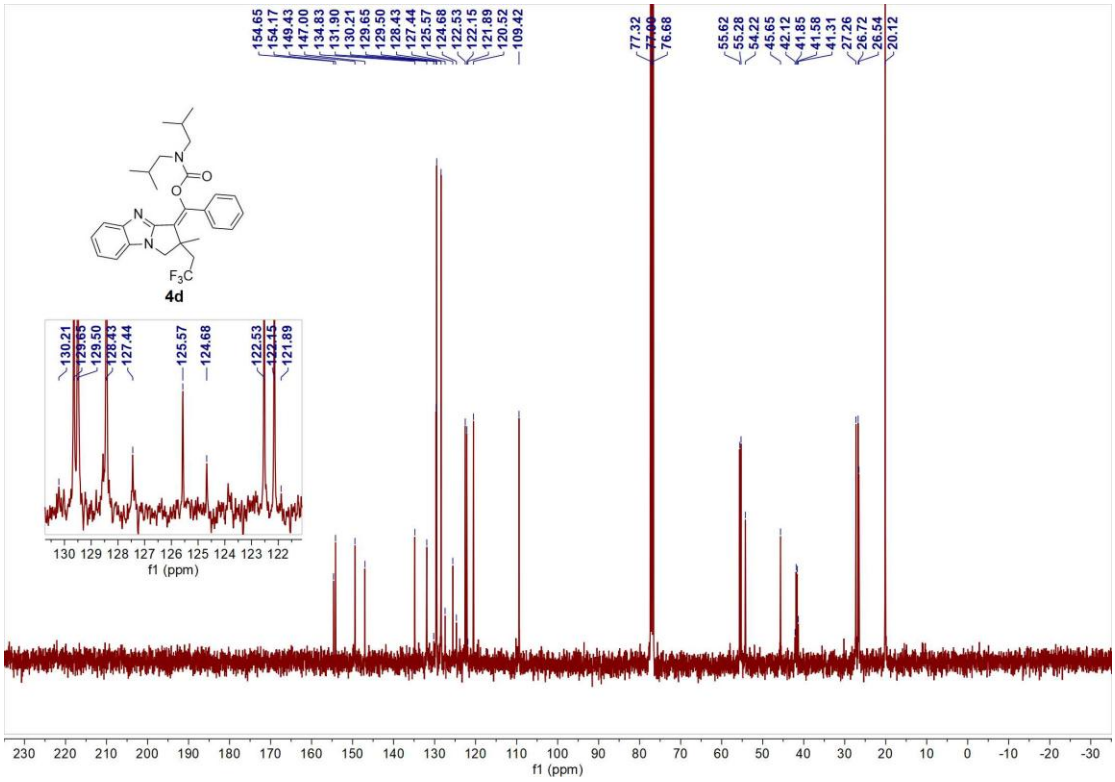
1.08
1.06
2.09
3.00
6.01
6.05
f1 (ppm)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76.68
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55.28
54.22
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42.12
41.85
41.58
41.31
27.26
26.72
26.54
20.12
4d
130.21
129.65
129.50
128.43
127.44
125.57
124.68
122.53
122.15
121.89
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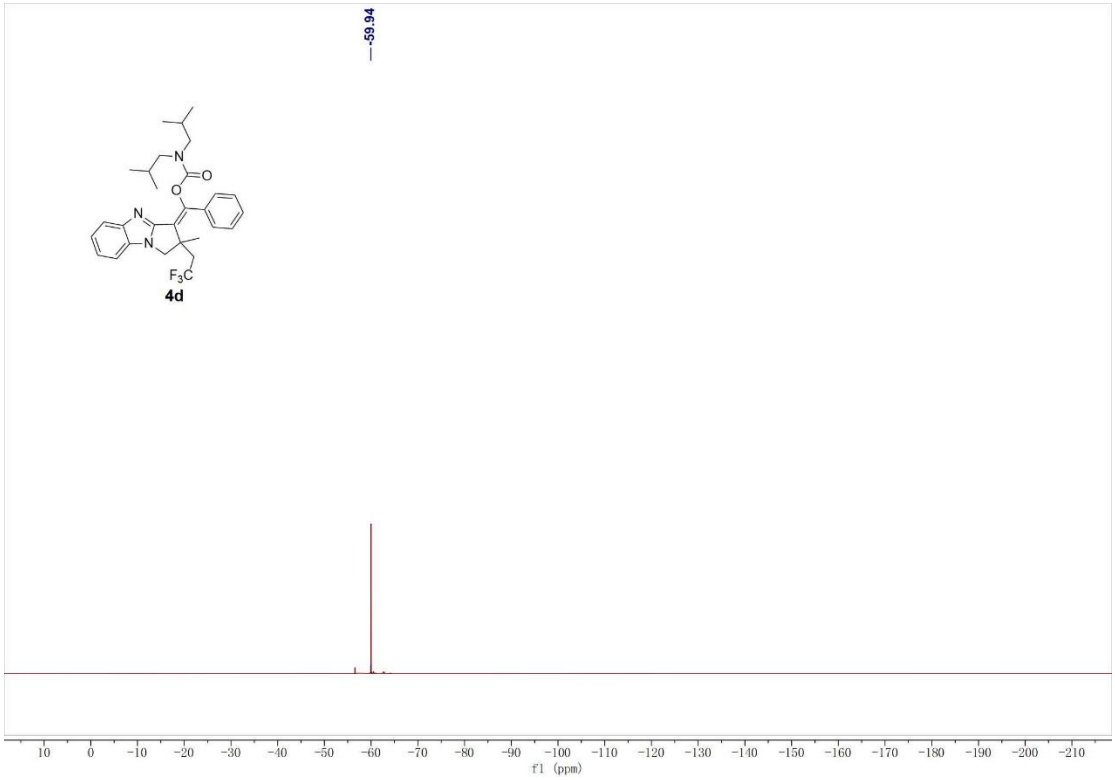
f1 (ppm)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)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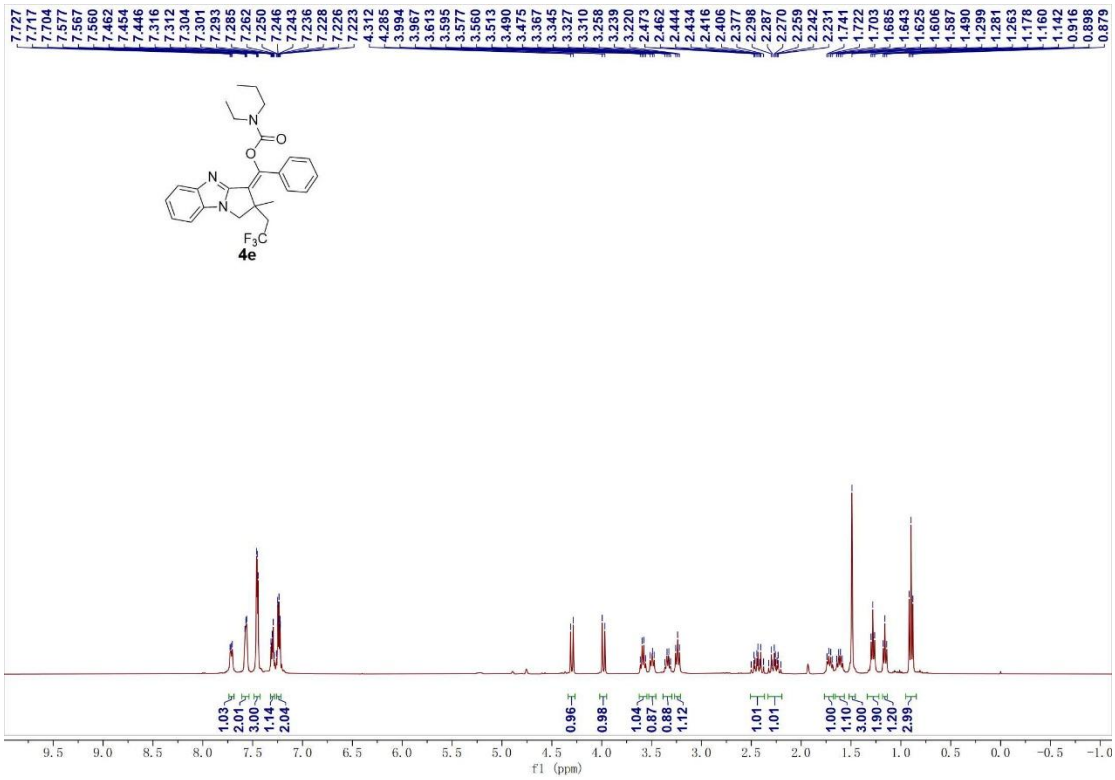
f1 (ppm)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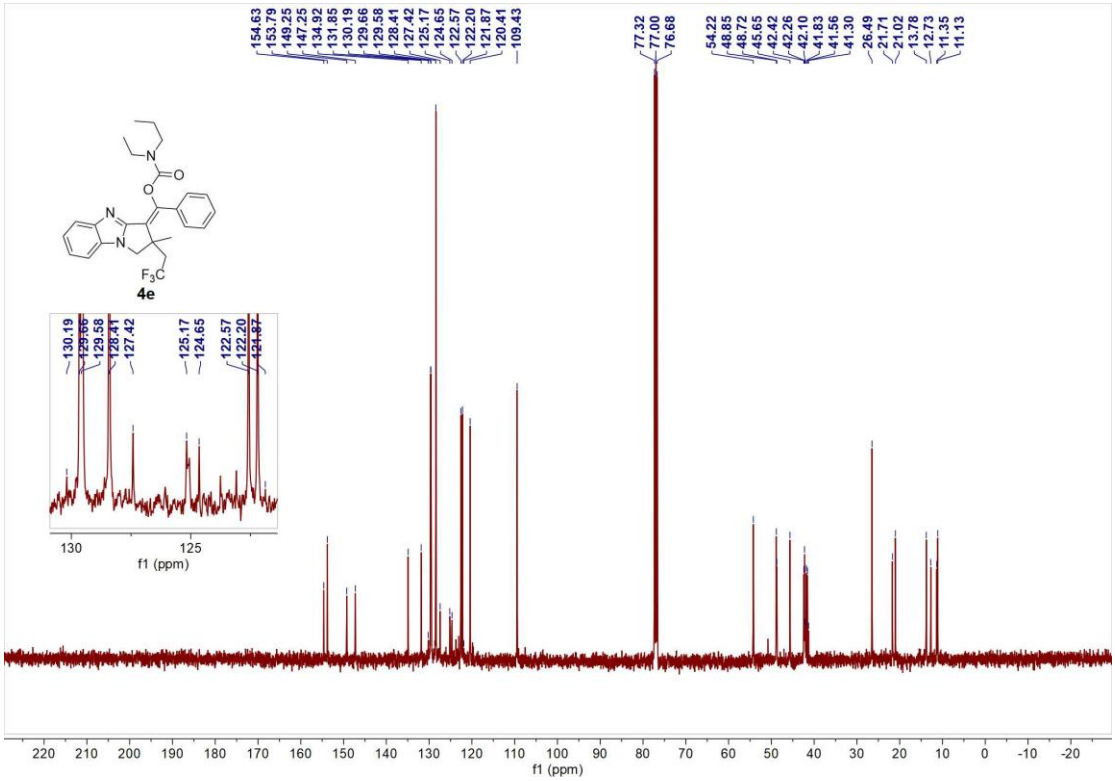
f1 (ppm)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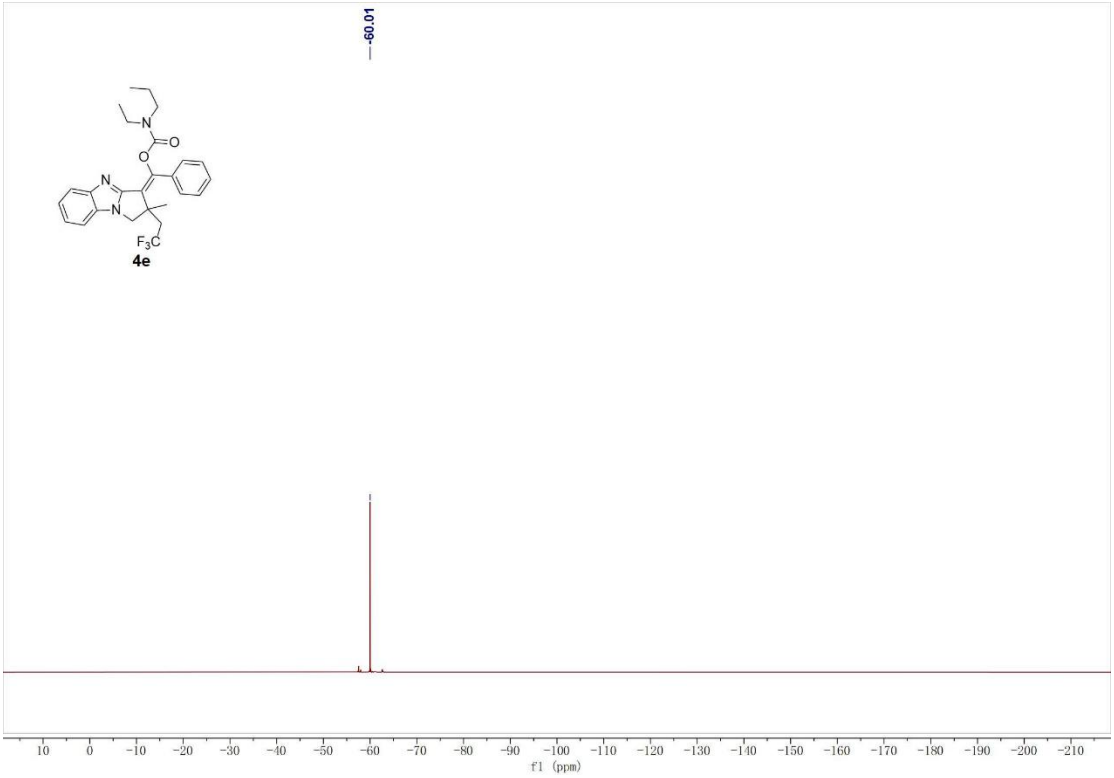
f1 (ppm)
f1 (ppm)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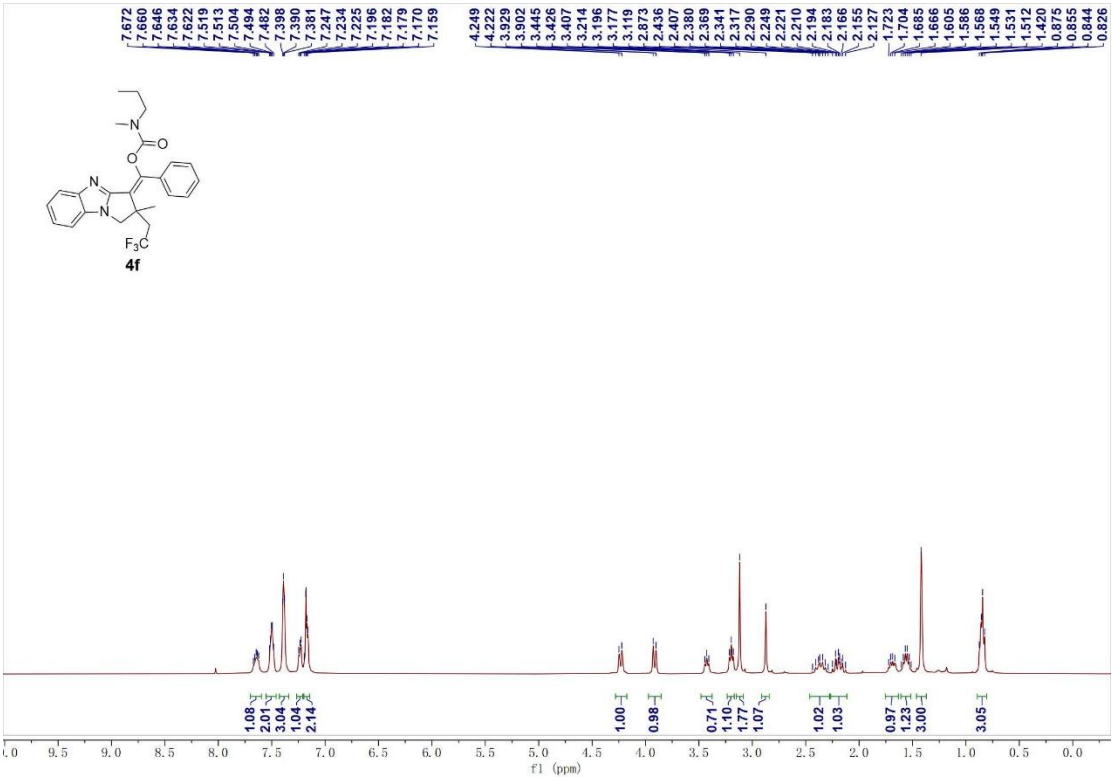
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1.568
1.549
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0.826
4f
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2.01
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2.14
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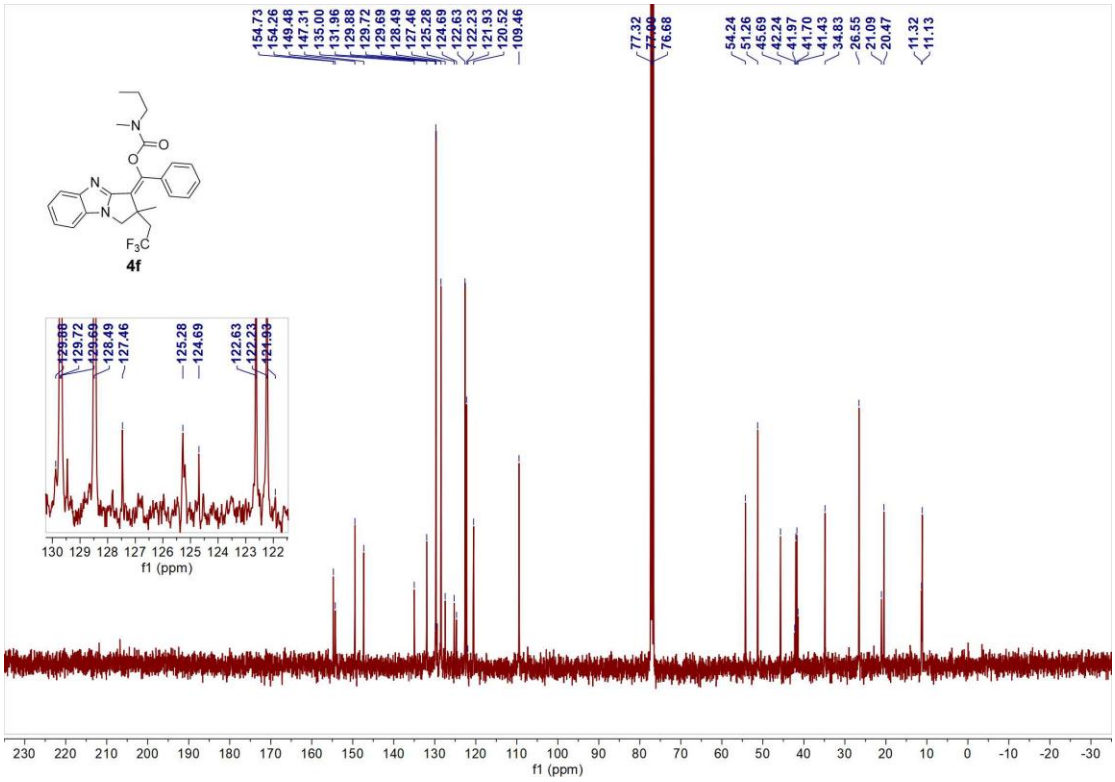
f1 (ppm)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77.32
77.00
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51.26
45.69
42.24
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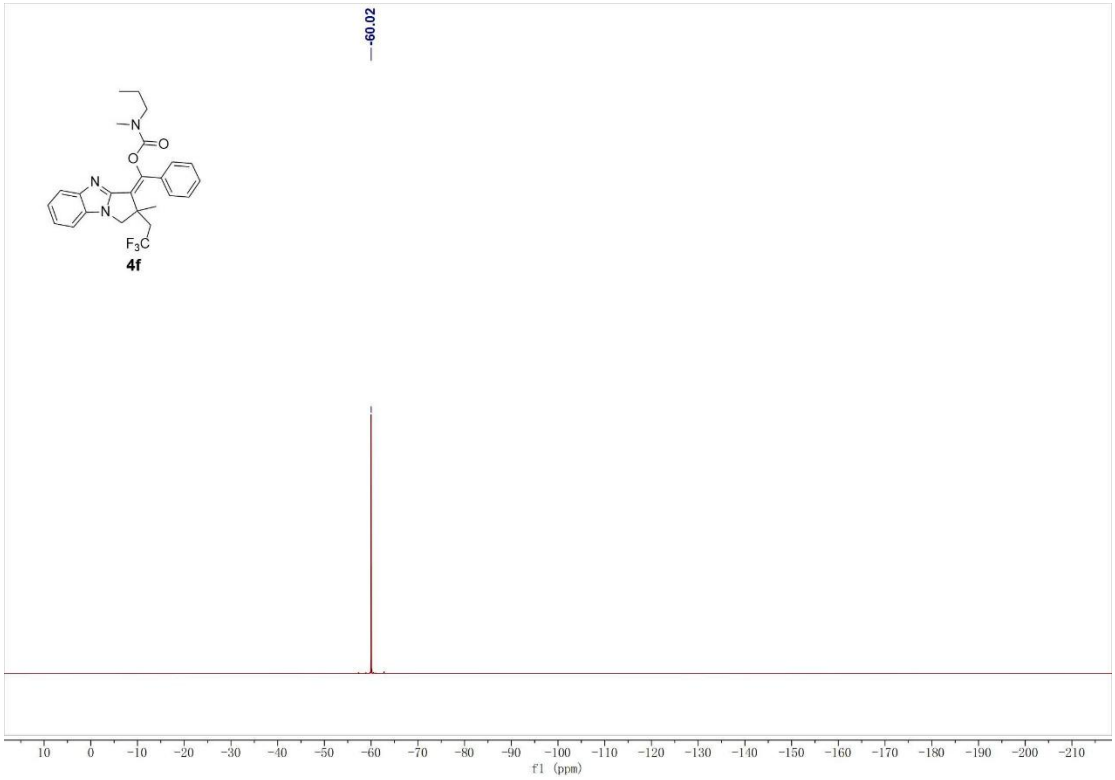
26.55
21.09
20.47
11.32
11.13
4f
f1 (ppm)
f1 (ppm)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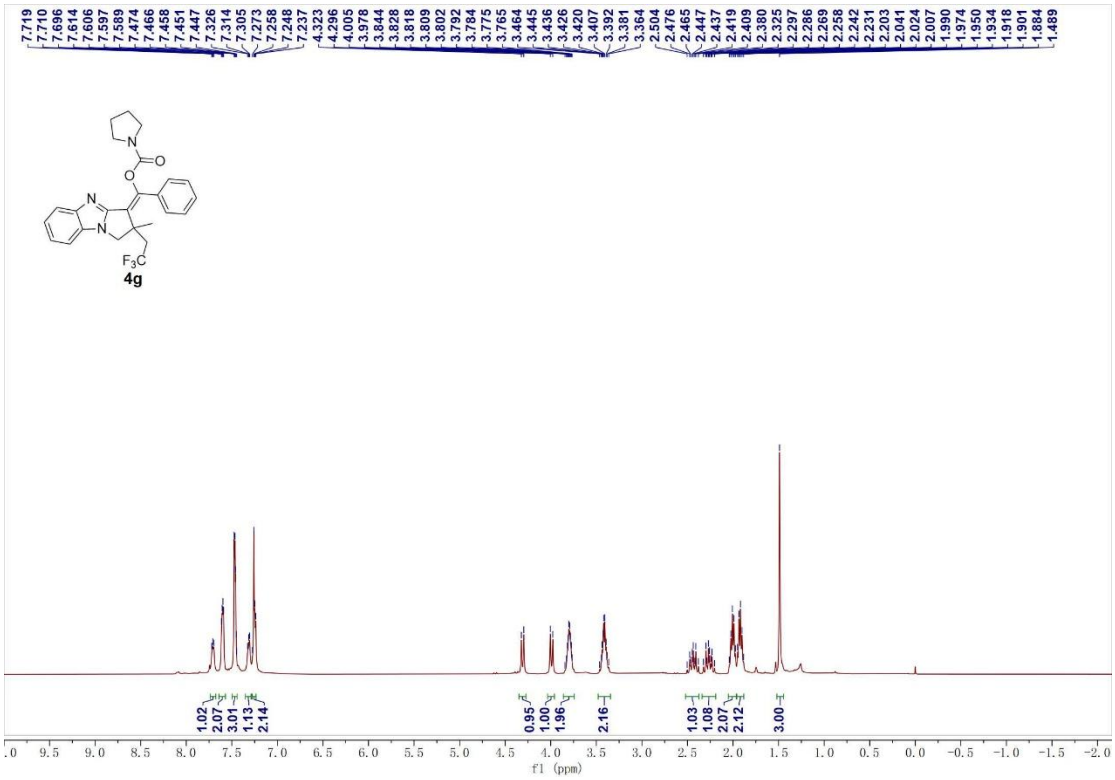
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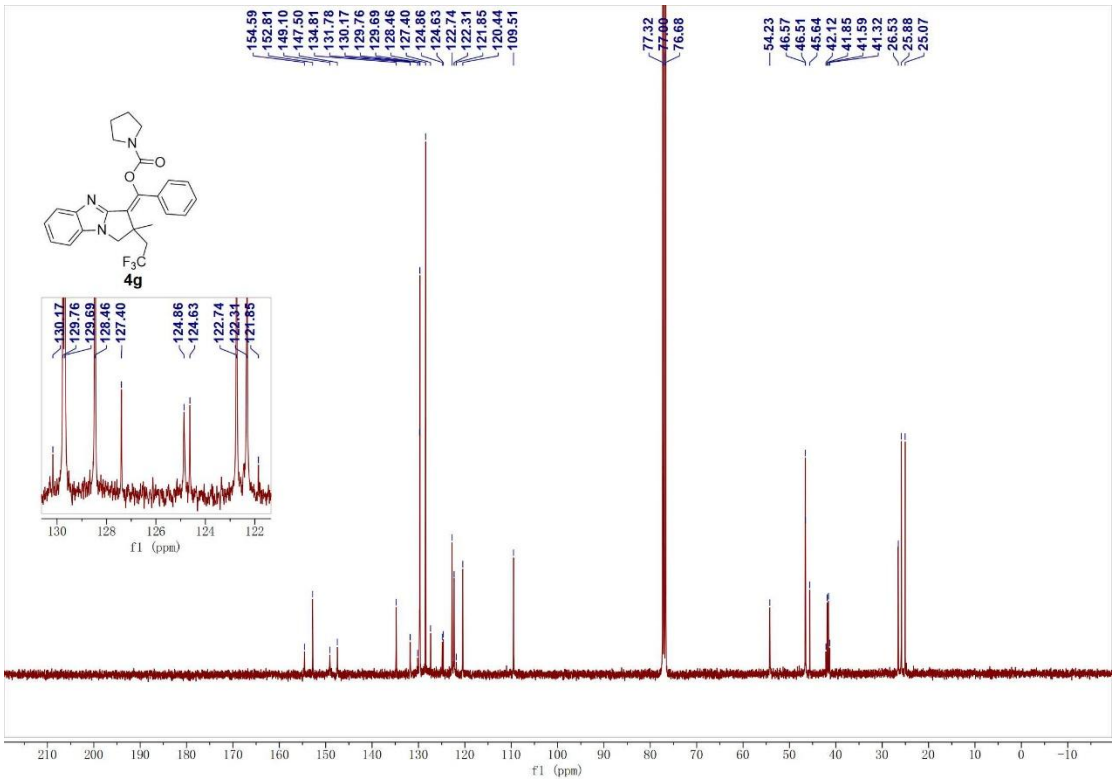
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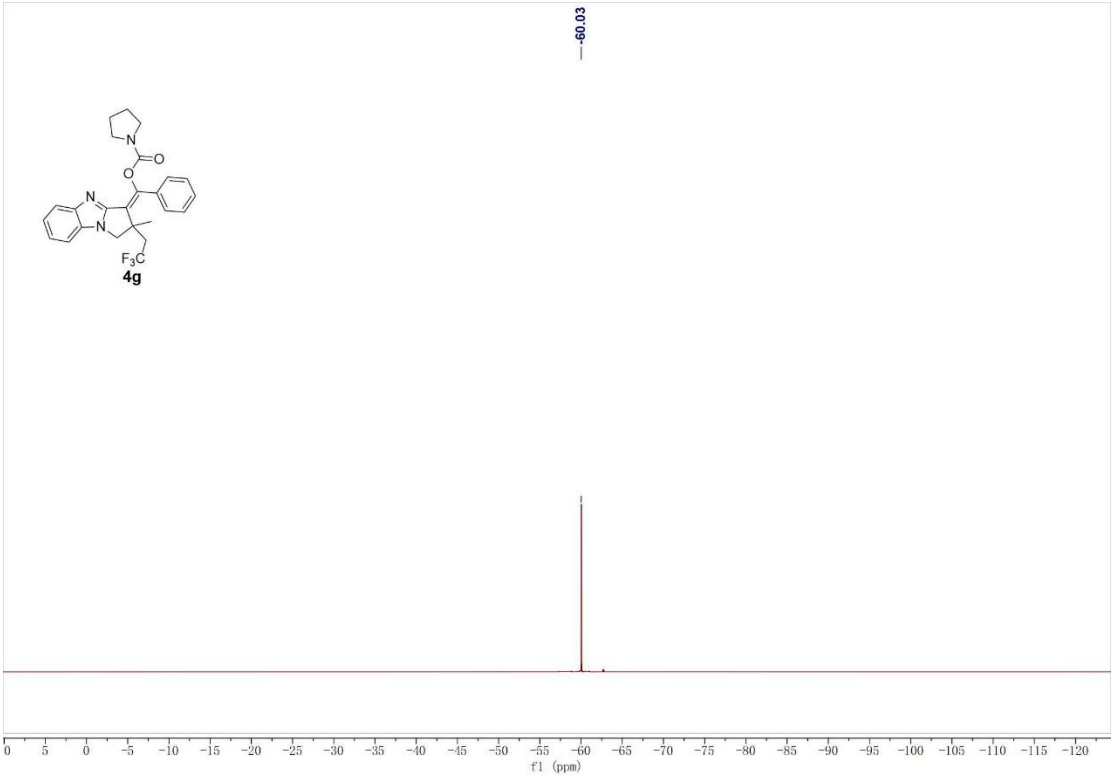
f1 (ppm)
f1 (ppm)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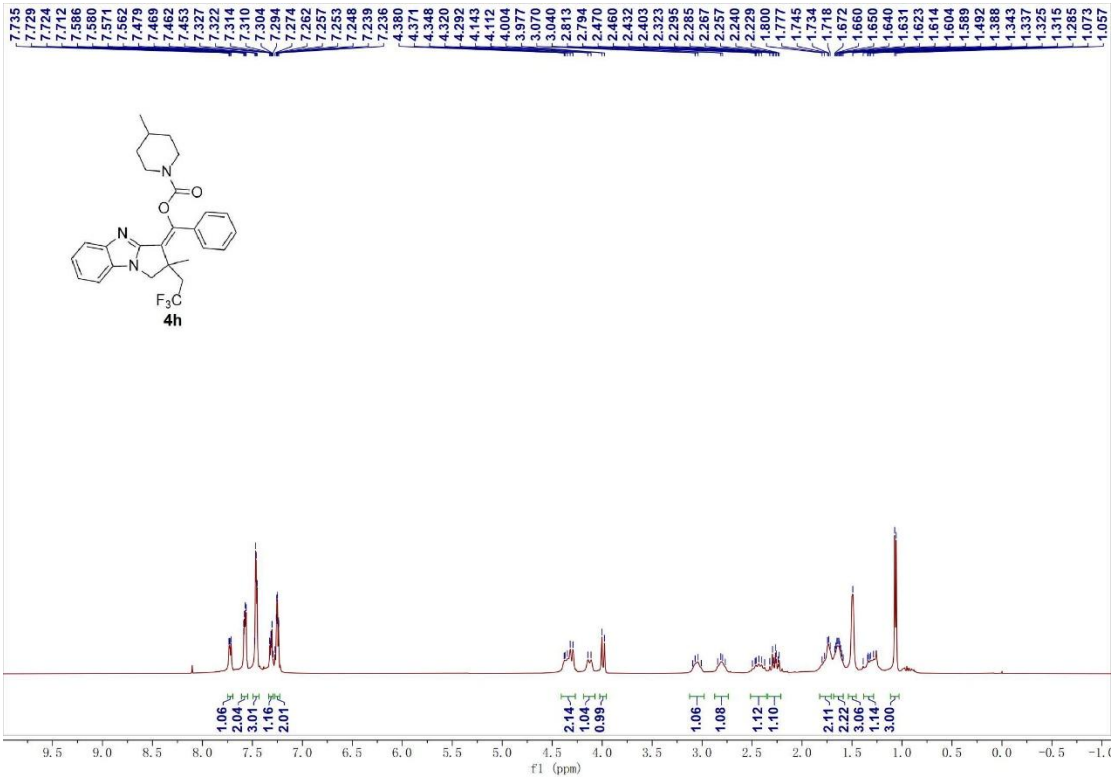
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2.04
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1.16
2.01
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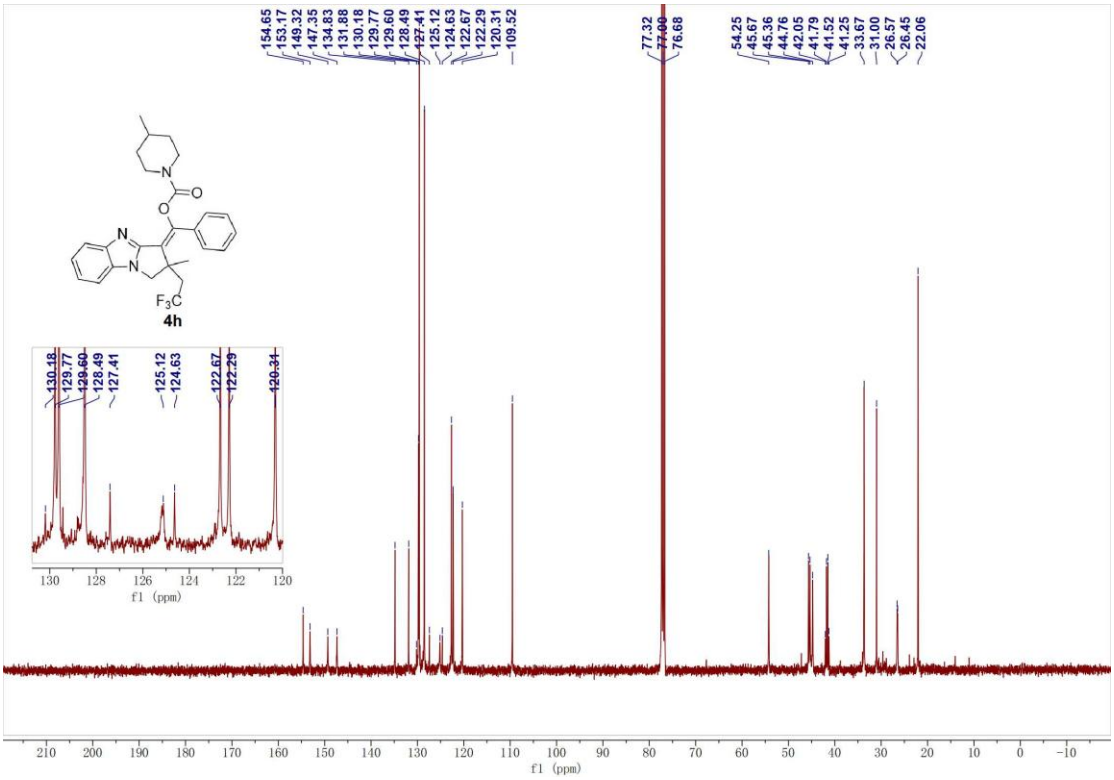
3.00
f1 (ppm)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45.67
45.36
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33.67
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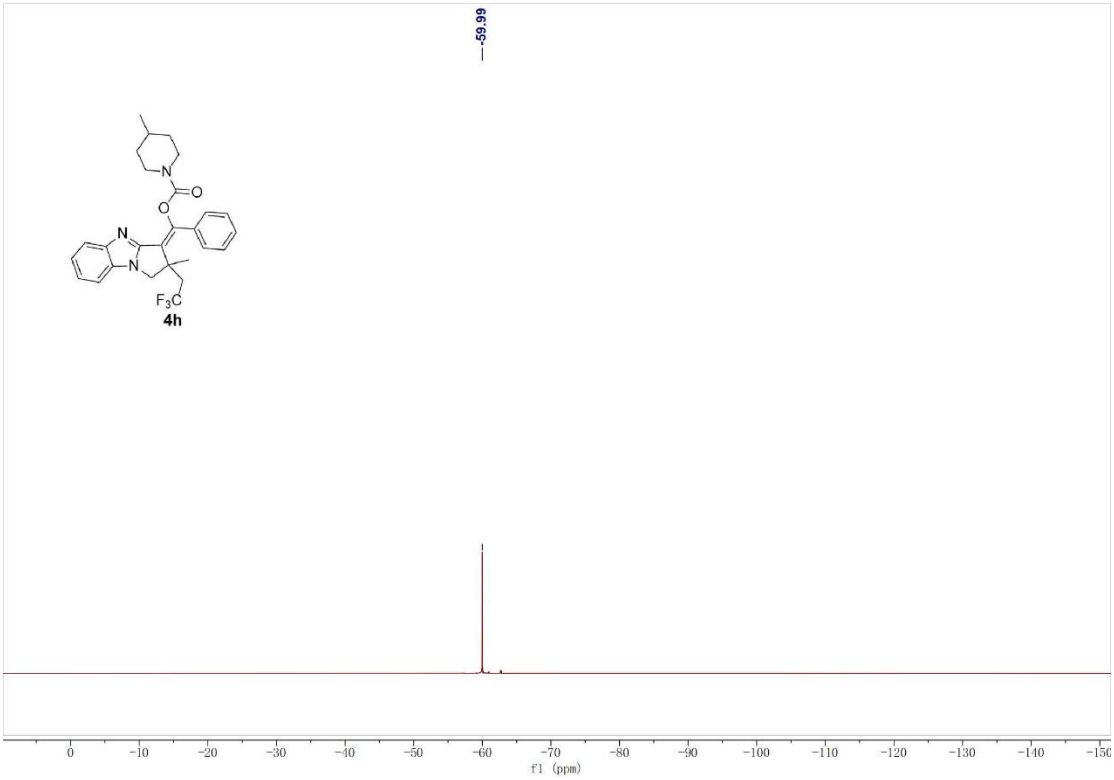
26.45
22.06
4h
f1 (ppm)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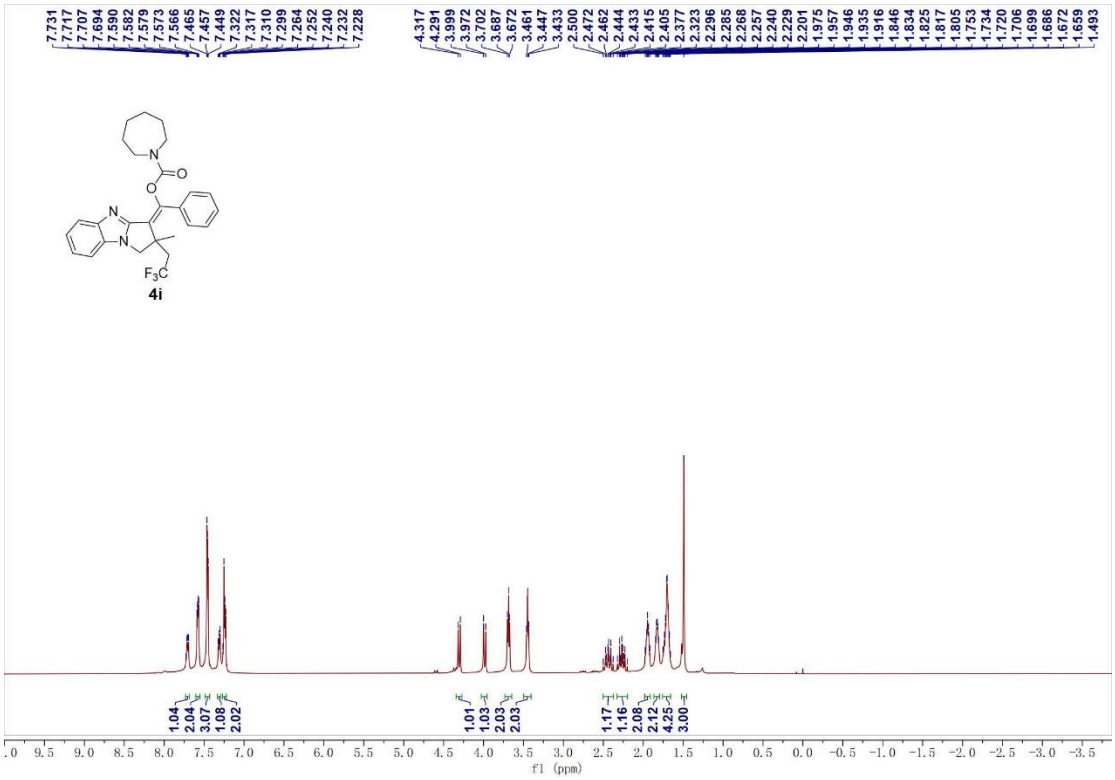
f1 (ppm)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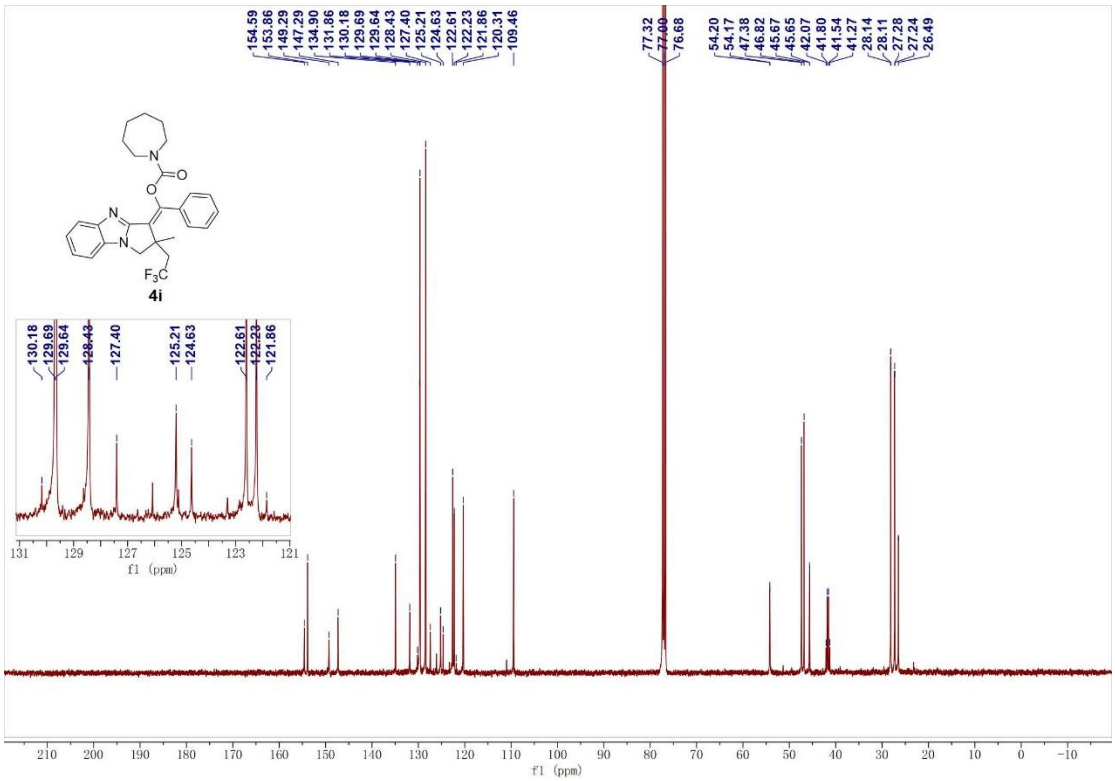
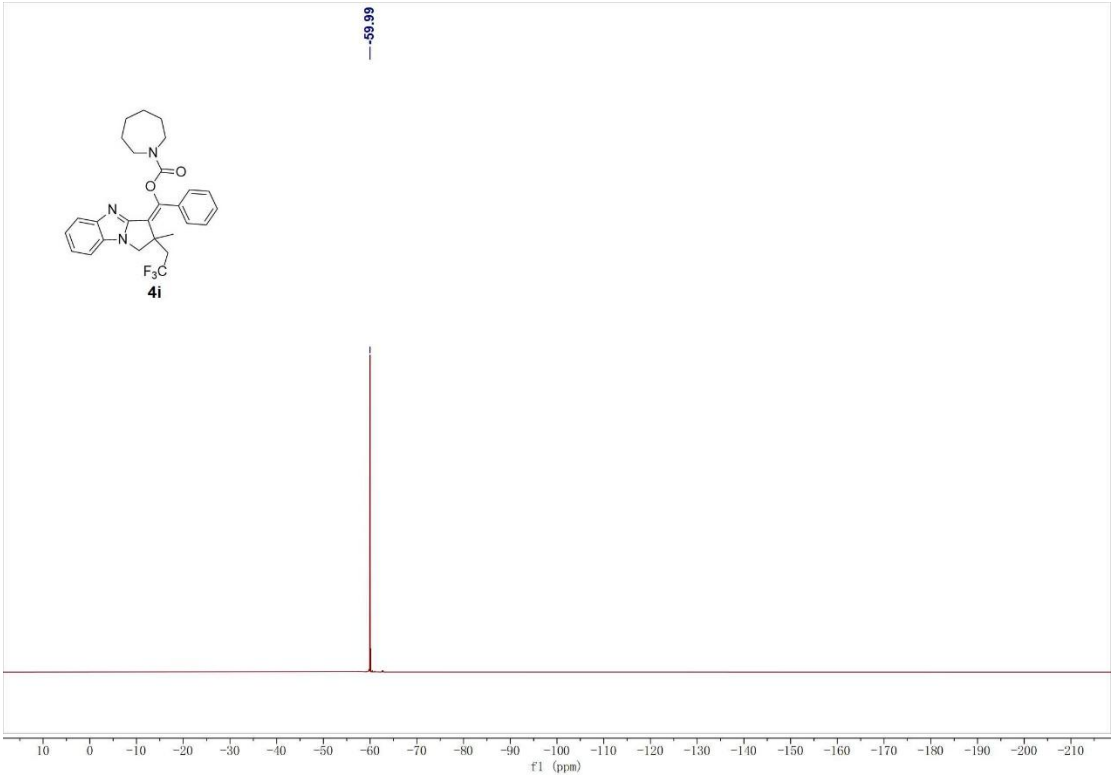
f1 (ppm)


4i
f1 (ppm)
f1 (ppm)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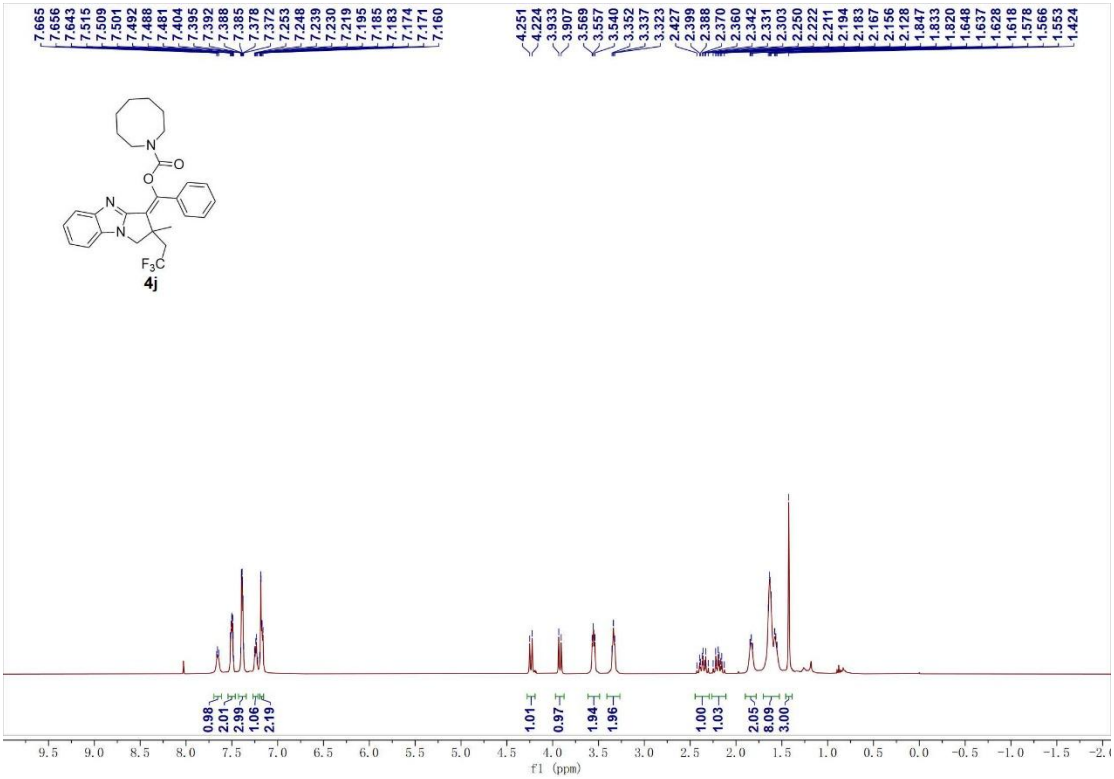
f1 (ppm)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7.230
7.219
7.195
7.185
7.183
7.174
7.171
7.160
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4.224
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1.618
1.578
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1.553
1.424
4j
0.98
2.01
2.99
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2.19
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1.96
1.00
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2.05
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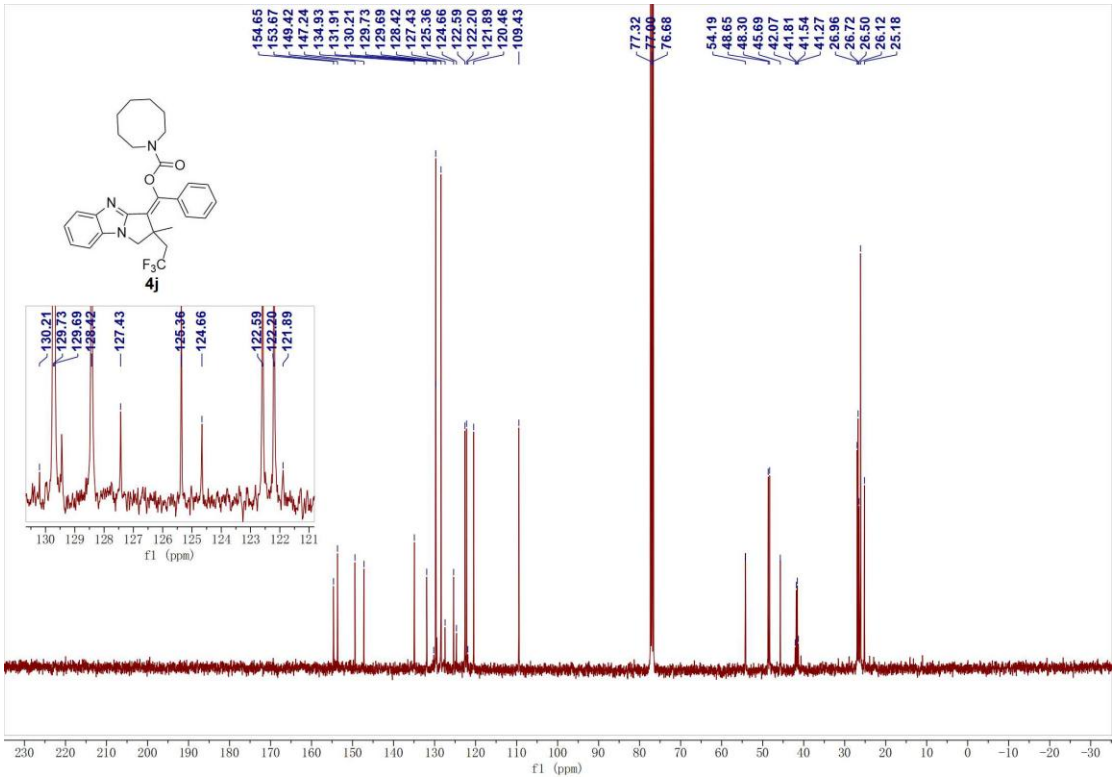
3.00
f1 (ppm)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124.66
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122.20
121.89
120.46
109.43
77.32
77.00
76.68
54.19
48.65
48.30
45.69
42.07
41.81
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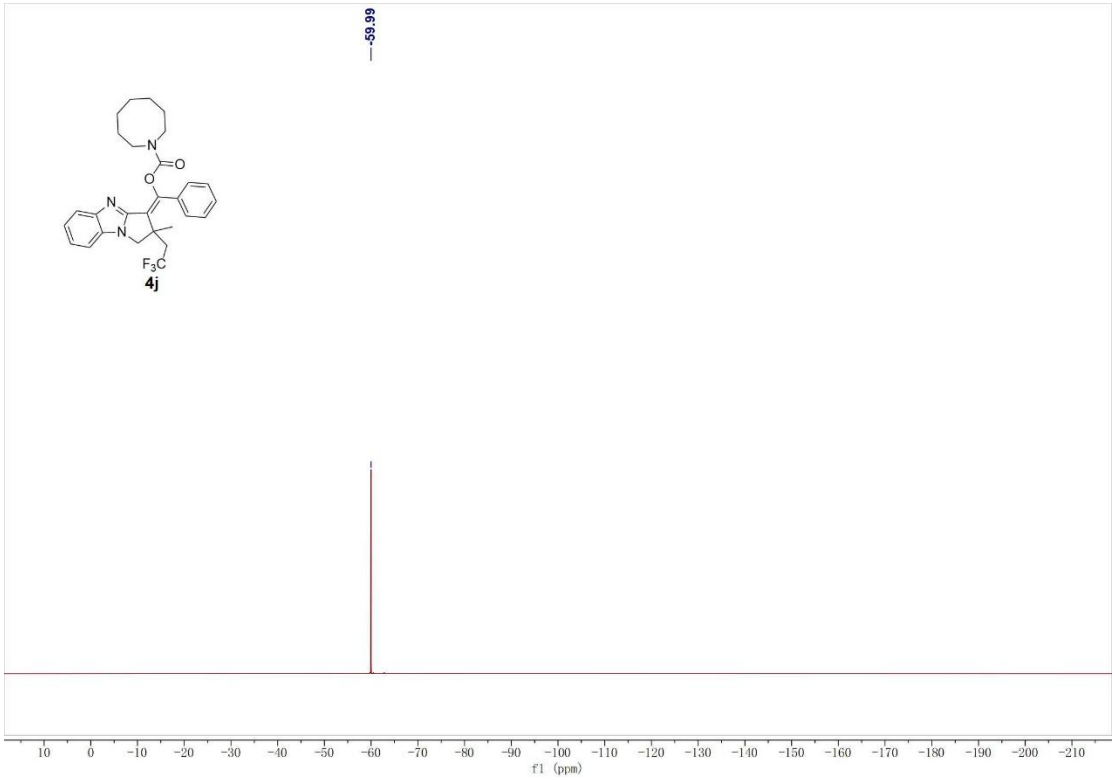
41.27
26.96
26.72
26.50
26.12
25.18
4j
f1 (ppm)
f1 (ppm)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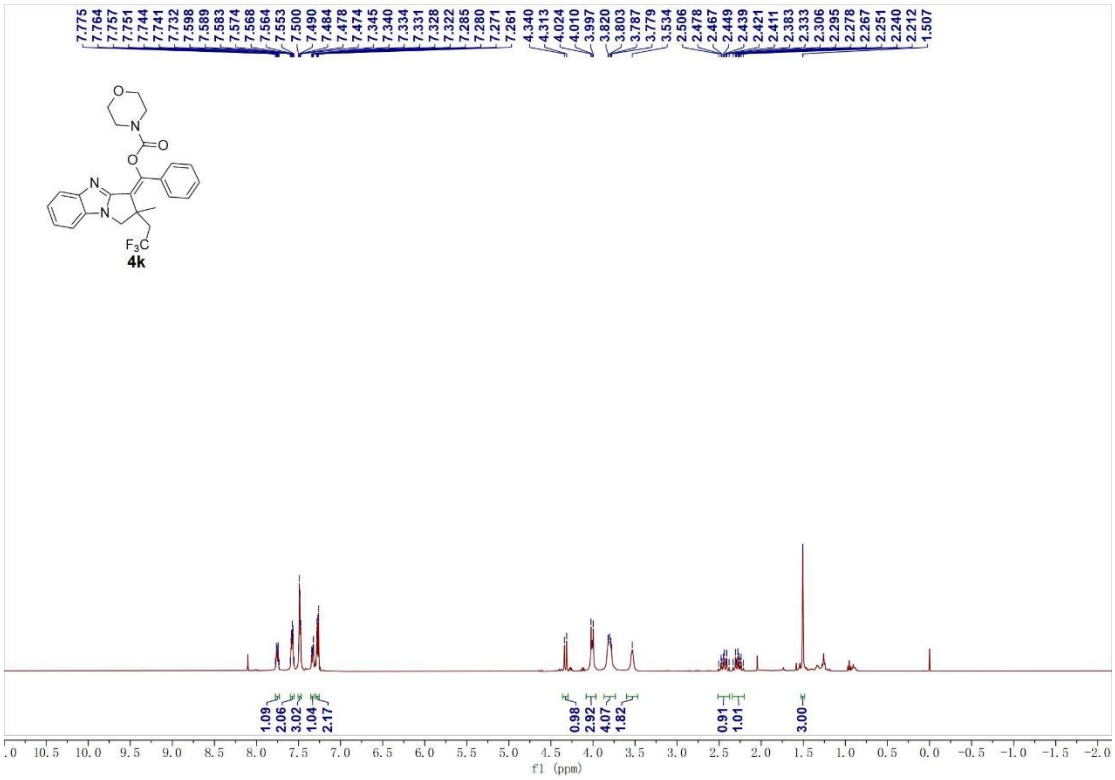
4j
f1 (ppm)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3.803
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2.383
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4k
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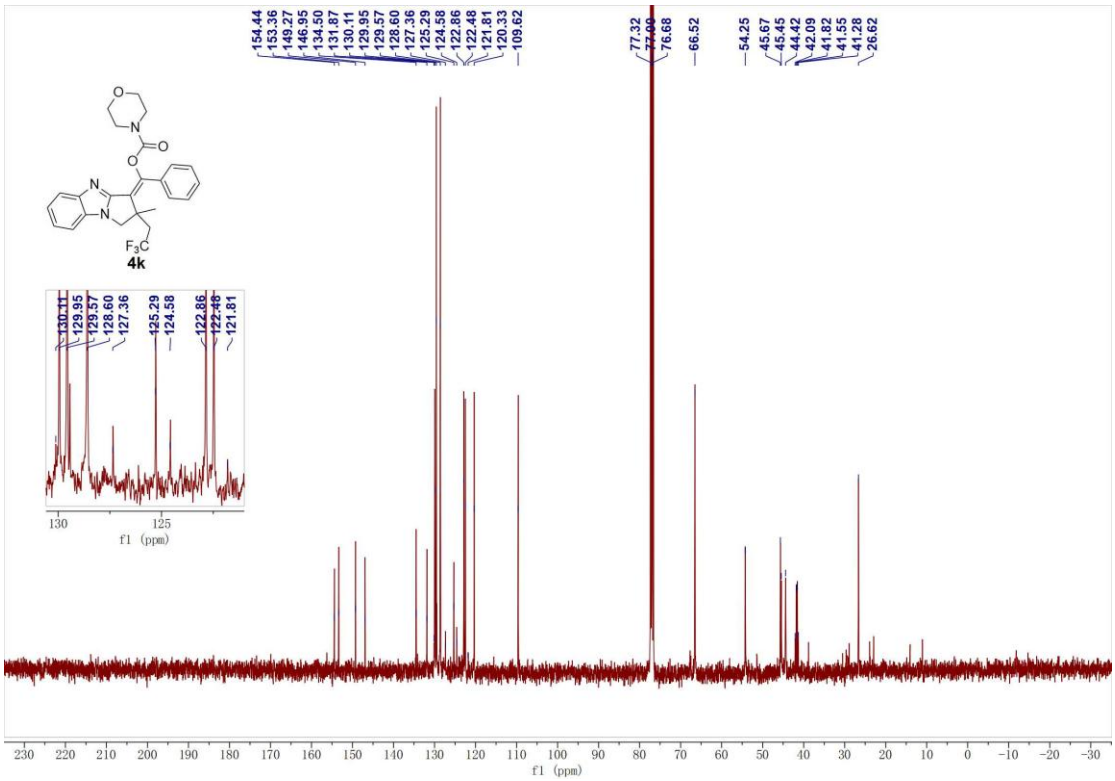
3.00
f1 (ppm)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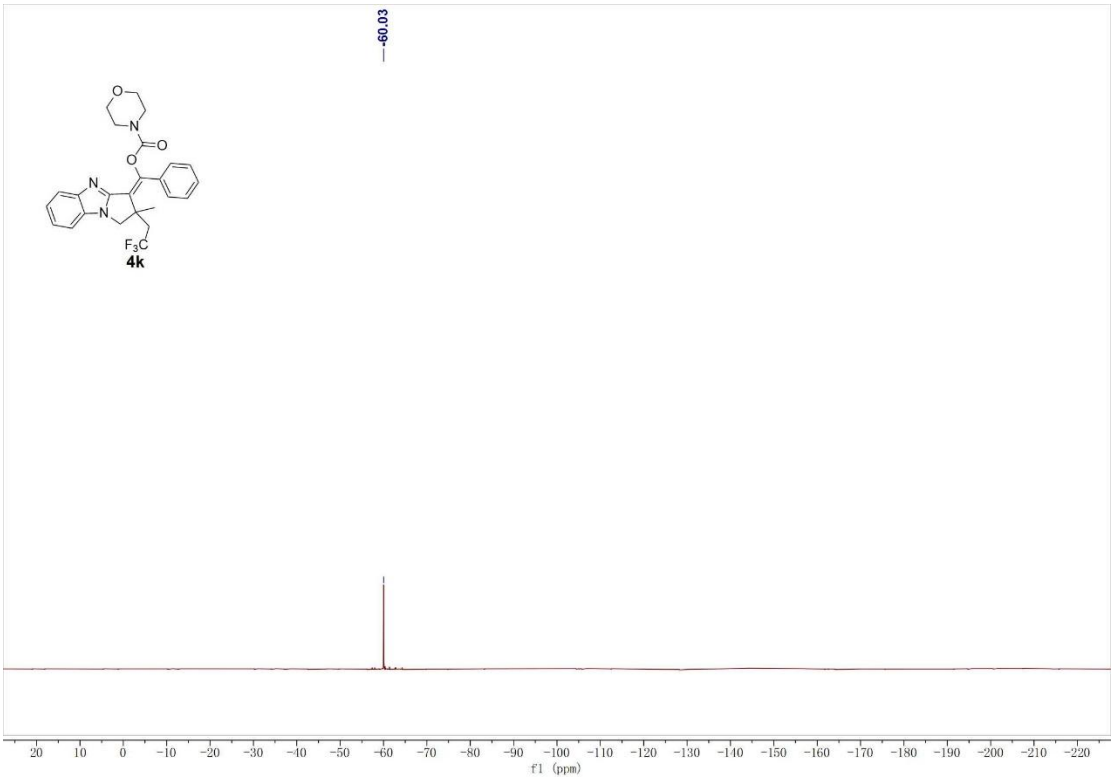
41.55
41.28
26.62
4k
f1 (ppm)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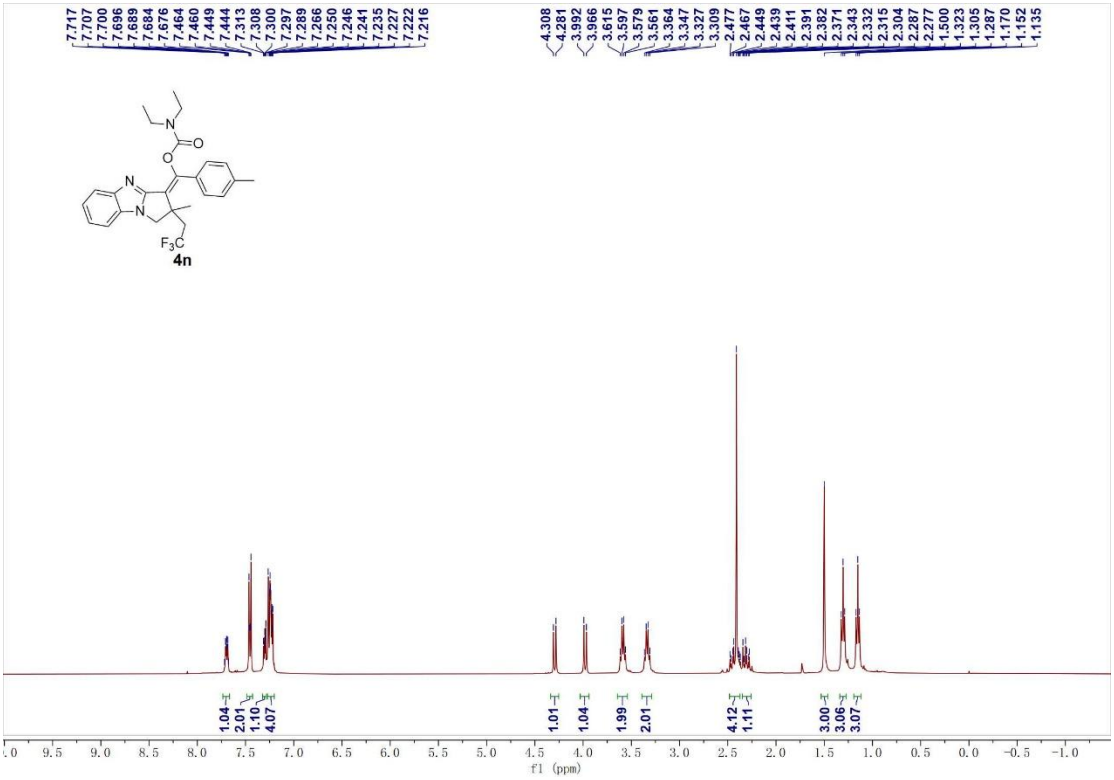
4k
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −220
f1 (ppm)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4.308 4.281 3.992 3.966 3.615 3.597 3.579 3.561 3.364 3.347 3.327 3.309 2.477 2.467 2.449 2.439 2.411 2.391 2.382 2.371 2.343 2.332 2.315 2.304 2.287 2.277 1.500 1.323 1.305 1.287 1.170 1.152 1.135
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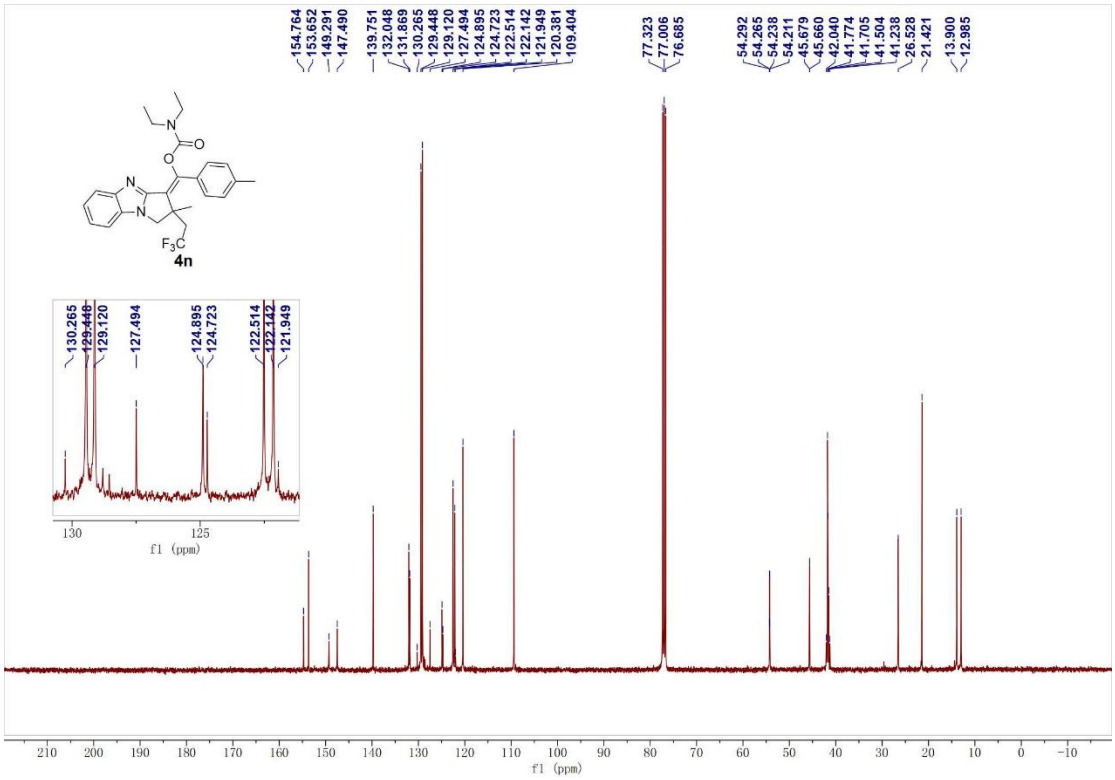
1.04 2.01 1.10 4.07 1.01 1.04 1.99 2.01 4.12 1.11 3.00 3.06 3.07
f1 (ppm)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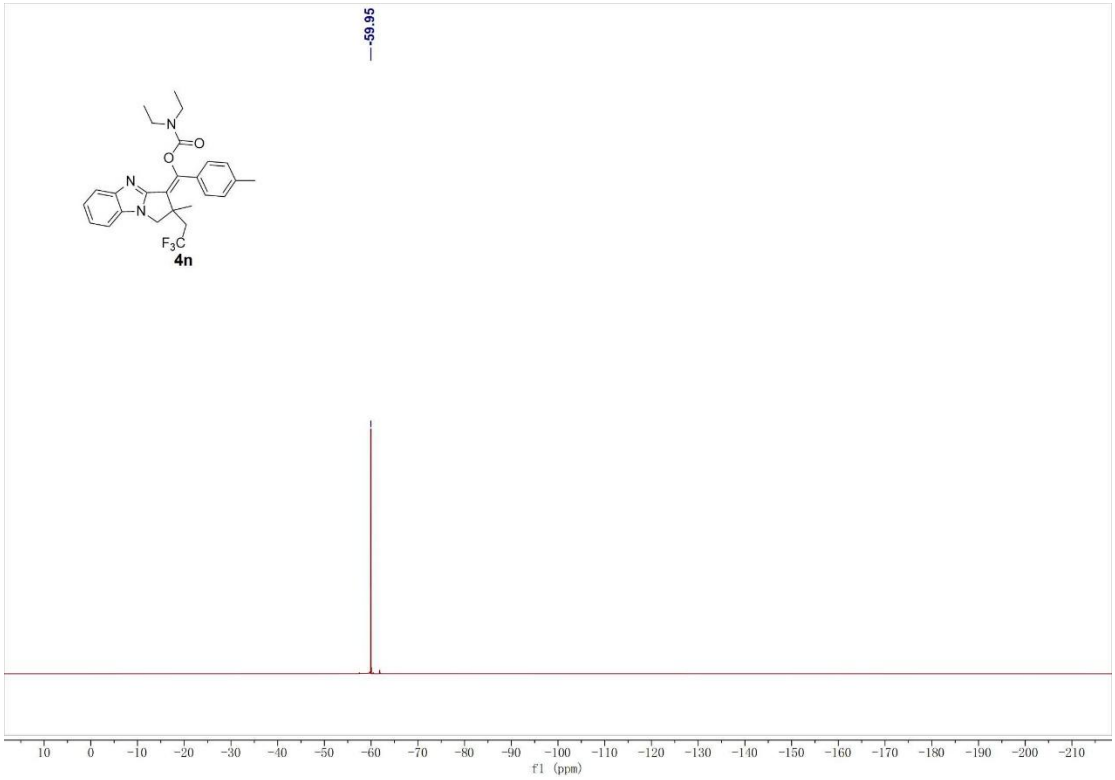
12.985
4n
f1 (ppm)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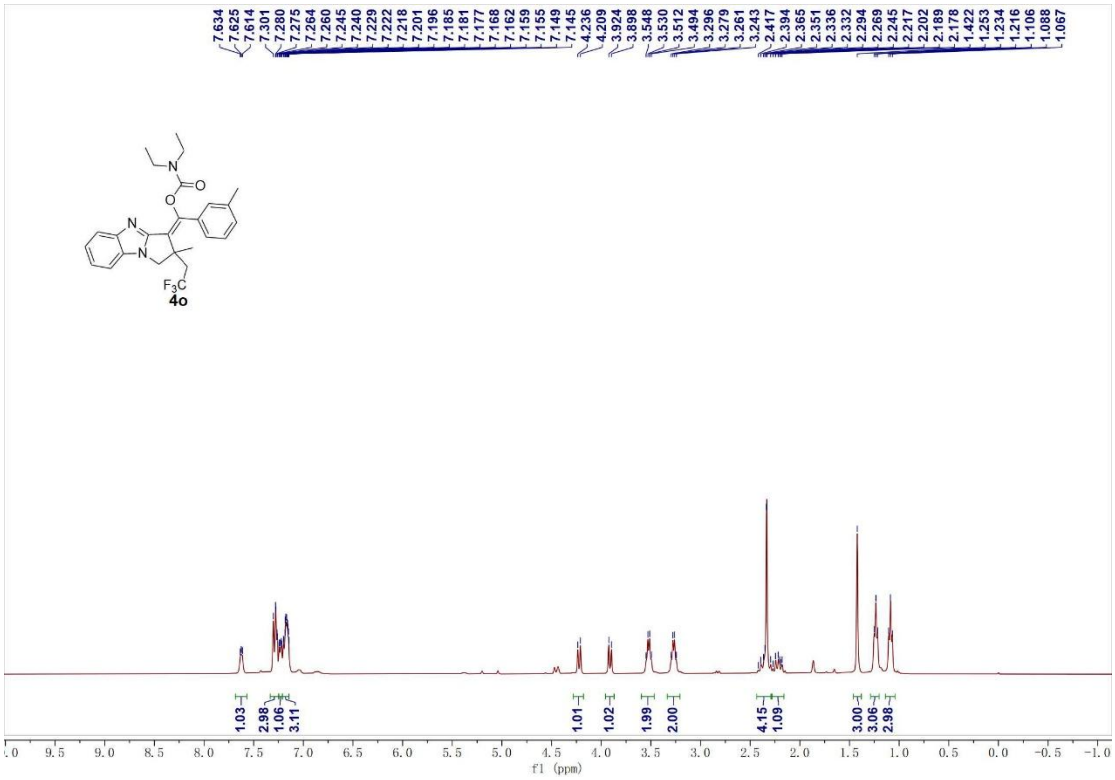
4n
f1 (ppm)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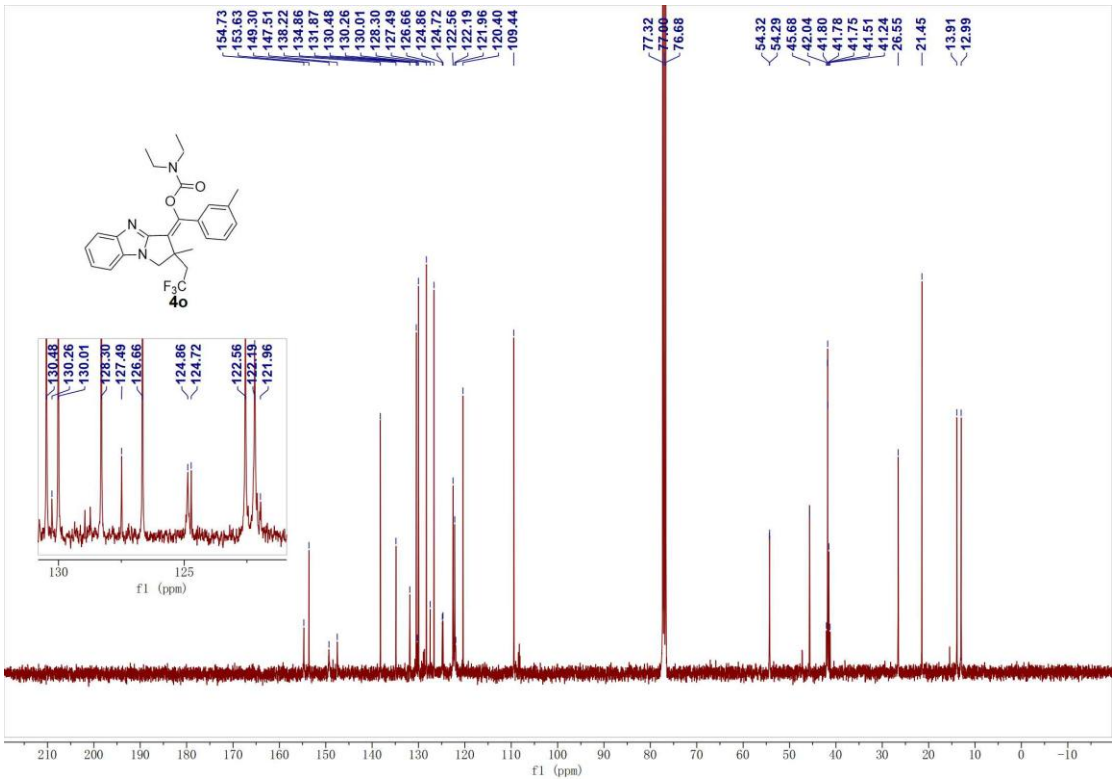
2.98
f1 (ppm)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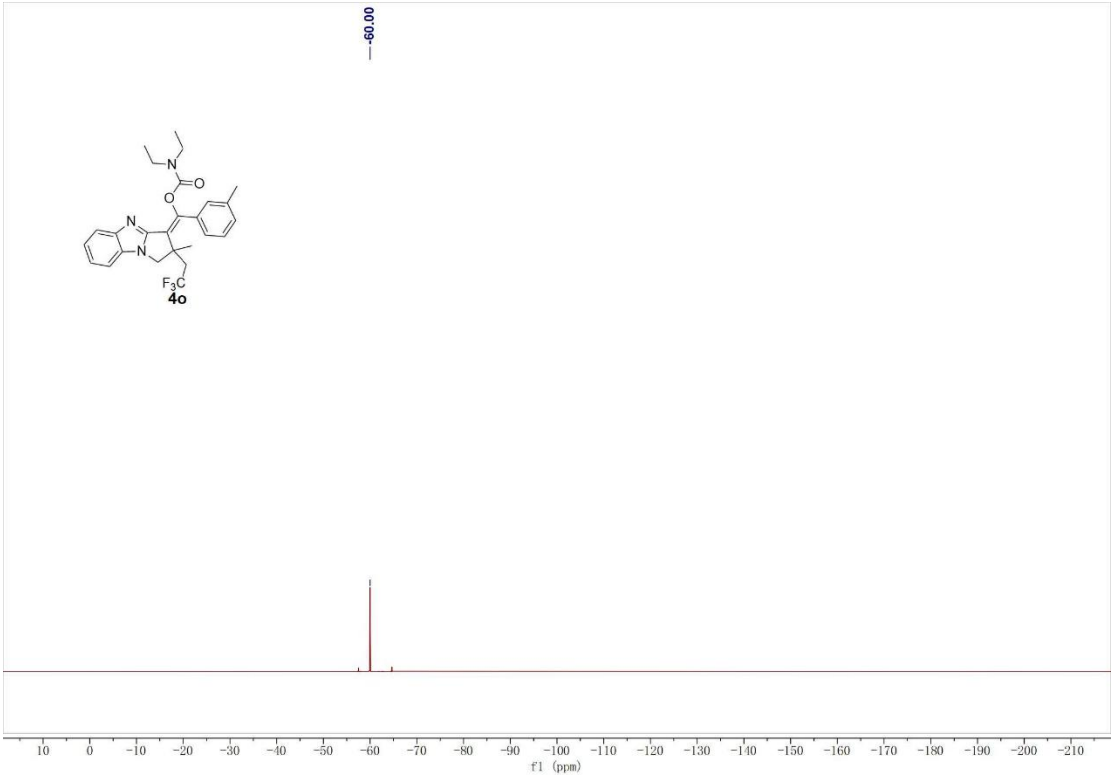
F3C
4o
f1 (ppm)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4o
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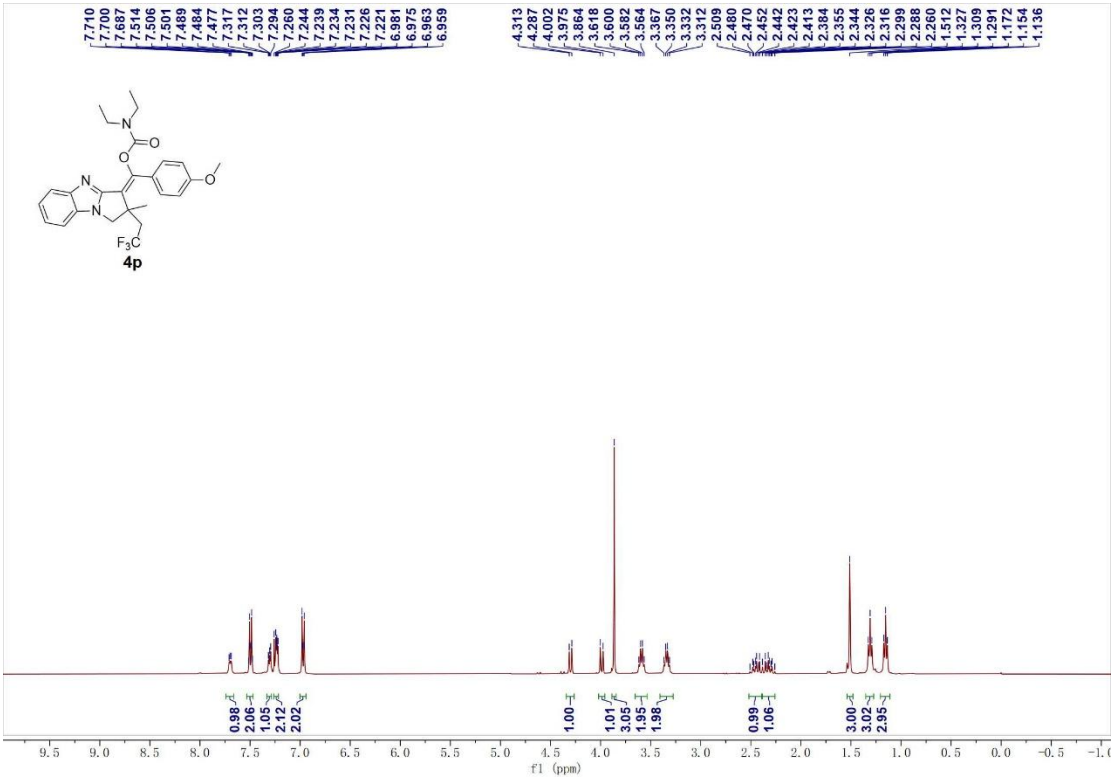
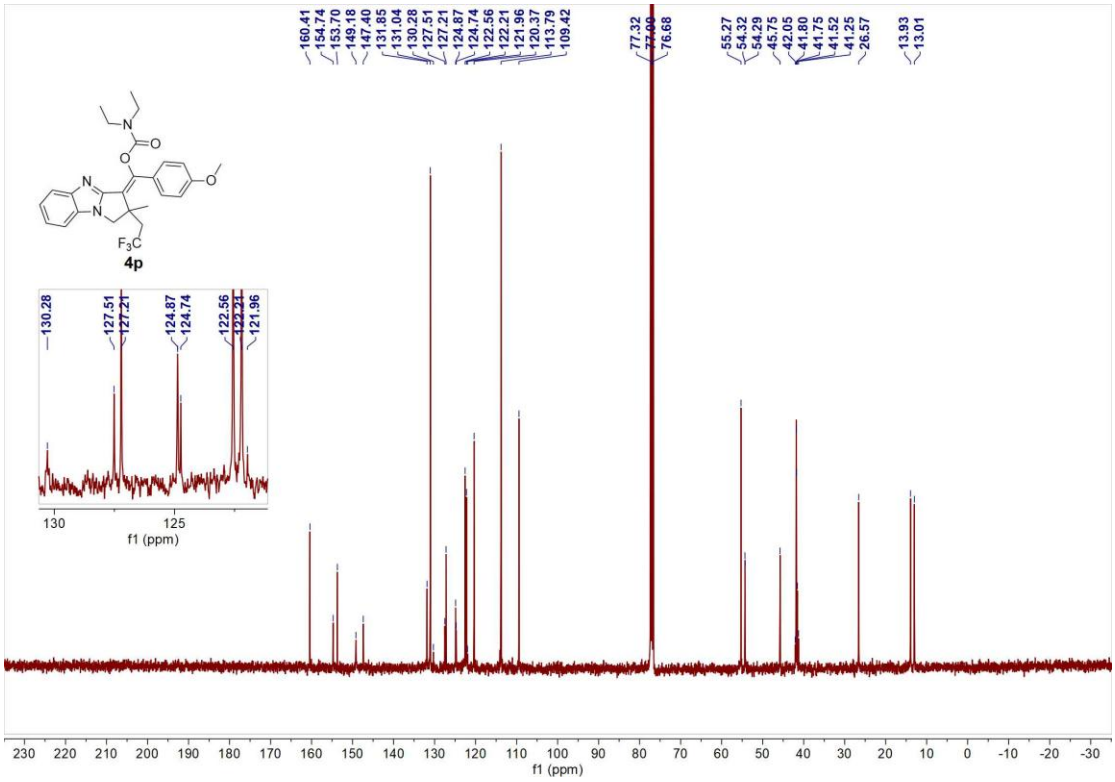
f1 (ppm)


7.710 7.700 7.687 7.514 7.506 7.501 7.489 7.484 7.477 7.317 7.312 7.303 7.294 7.260 7.244 7.239 7.234 7.231 7.226 7.221 6.981 6.975 6.963 6.959
4.313 4.287 4.002 3.975 3.864 3.618 3.600 3.582 3.564 3.367 3.350 3.332 3.312 2.509 2.480 2.470 2.452 2.442 2.423 2.413 2.384 2.355 2.344 2.326 2.316 2.299 2.288 2.260 1.512 1.327 1.309 1.291 1.172 1.154 1.136
4p
0.98 2.06 1.05 2.12 2.02 1.00 1.01 3.05 1.95 1.98 0.99 1.06 3.00 3.02 2.95
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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131.04
130.28
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124.87
124.74
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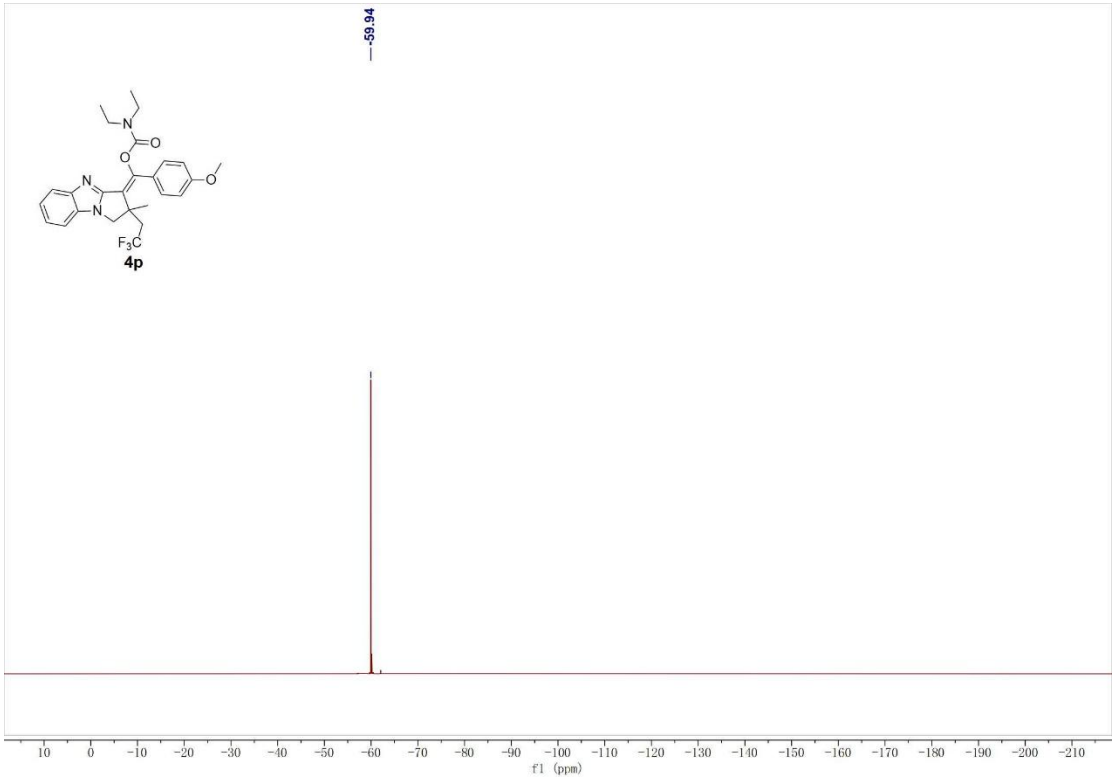
120.37
113.79
109.42
77.32
77.00
76.68
55.27
54.32
54.29
45.75
42.05
41.80
41.75
41.52
41.25
26.57
13.93
13.01
4p
130.28
127.51
127.21
124.87
124.74
122.56
122.21
121.96
130
125
f1 (ppm)
f1 (ppm)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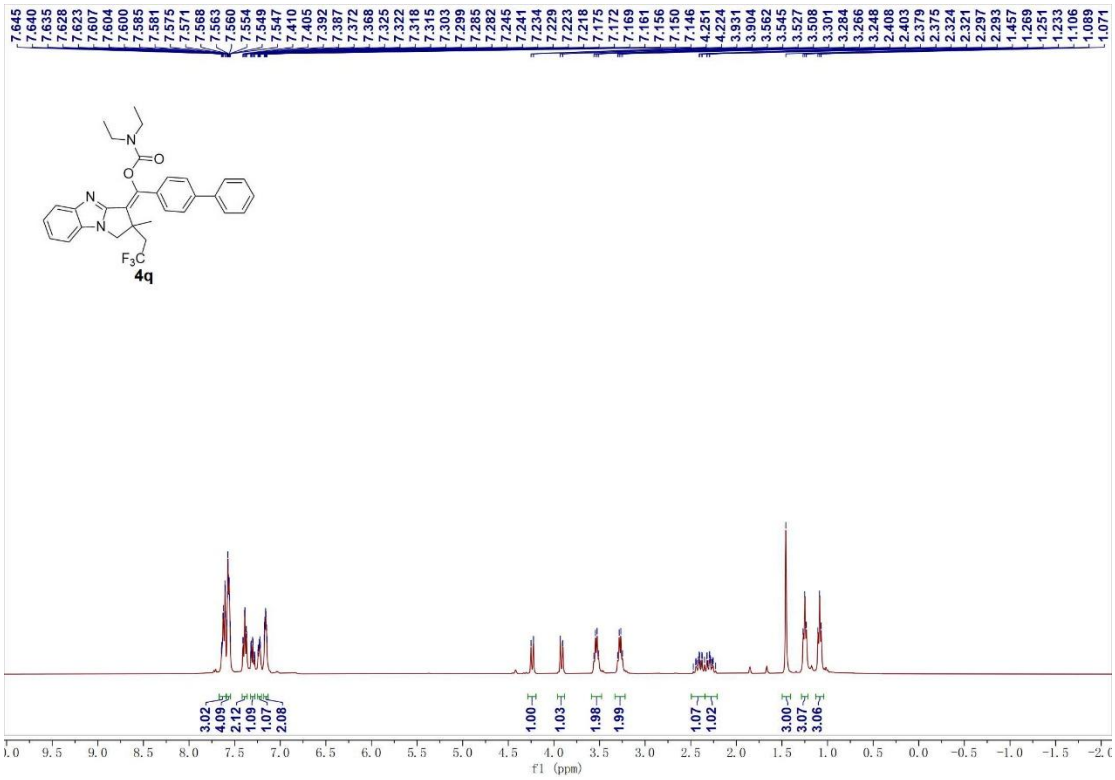
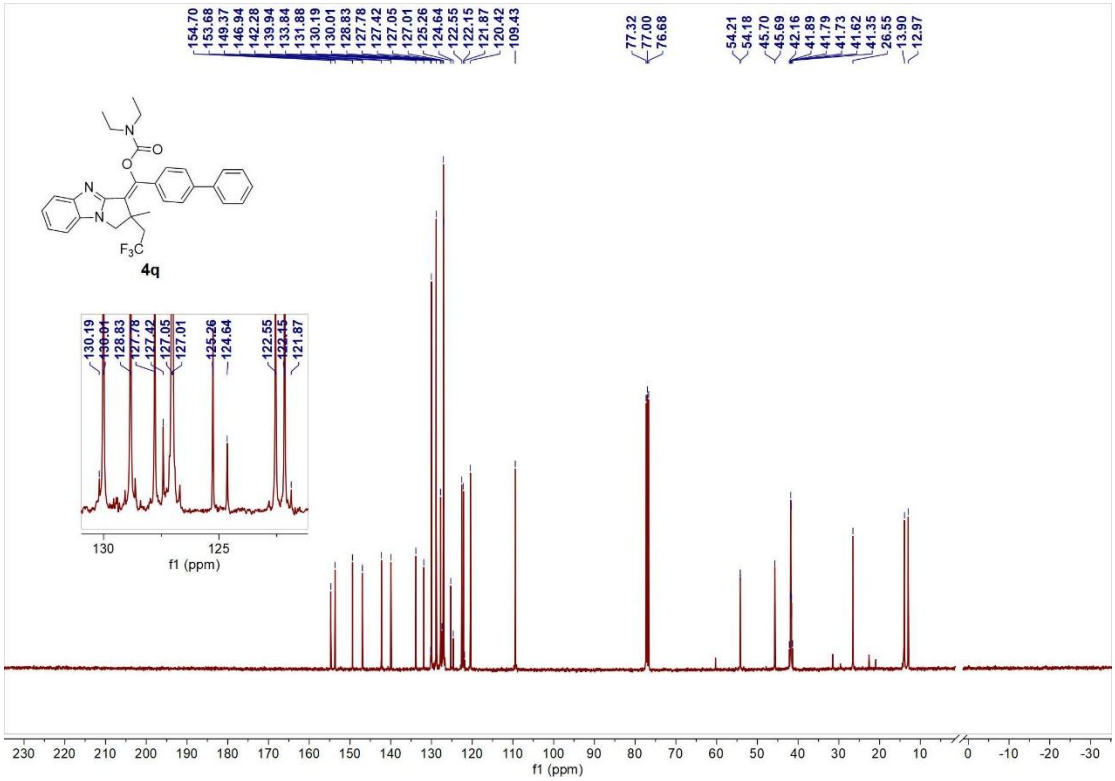
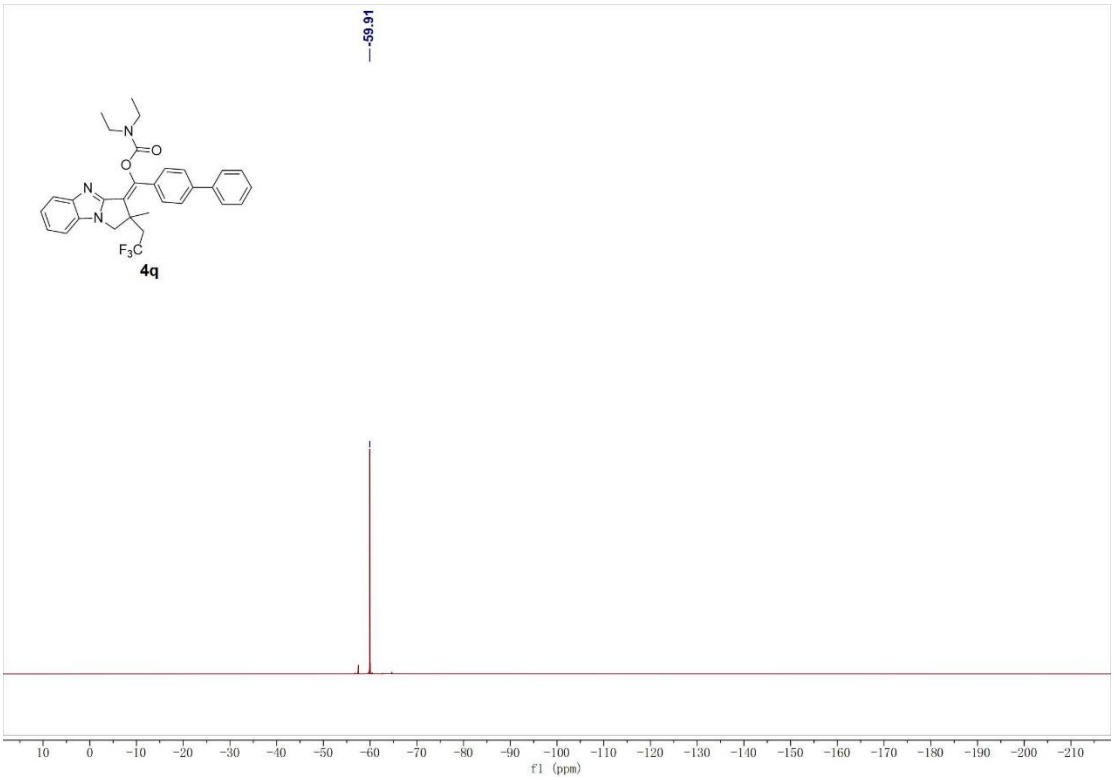

4q
f1 (ppm)


4q
f1 (ppm)
f1 (ppm)


-59.91
4q
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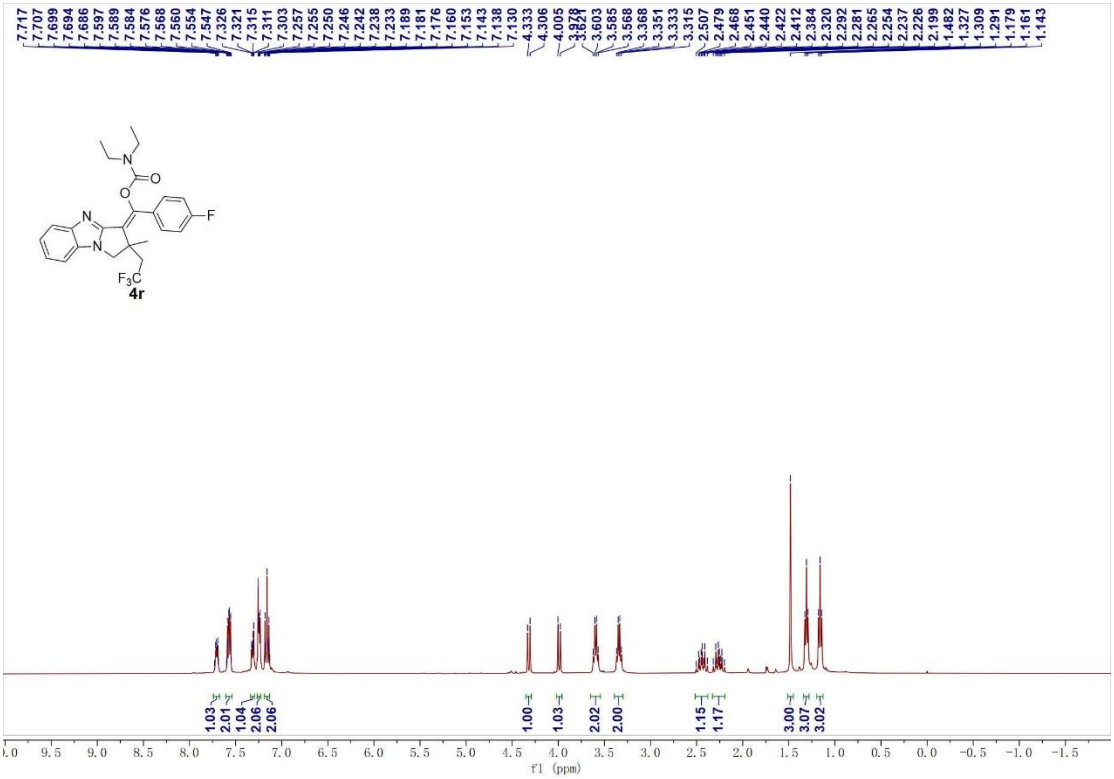
f1 (ppm)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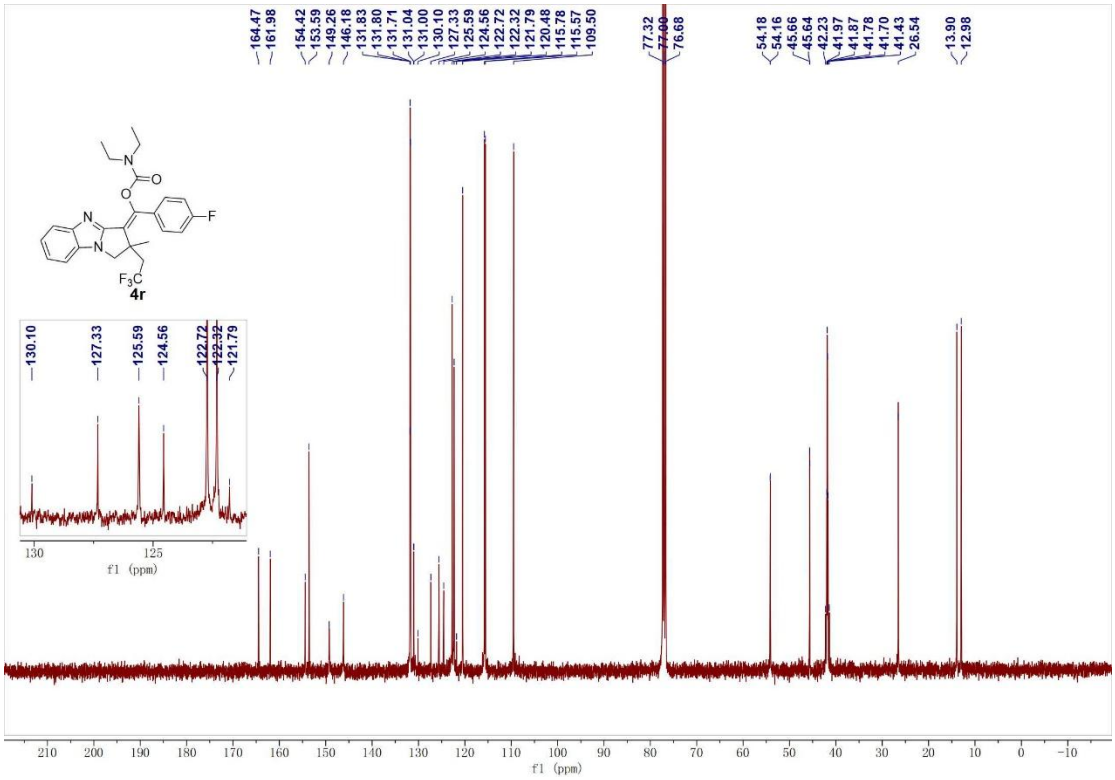
4r
1.03 2.01 1.04 2.06 2.06 1.00 1.03 2.02 2.00 1.15 1.17 3.00 3.07 3.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)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131.83
131.80
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131.04
131.00
130.10
127.33
125.59
124.56
122.72
122.32
121.79
120.48
115.78
115.57
109.50
77.32
77.00
76.68
54.18
54.16
45.66
45.64
42.23
41.97
41.87
41.78
41.70
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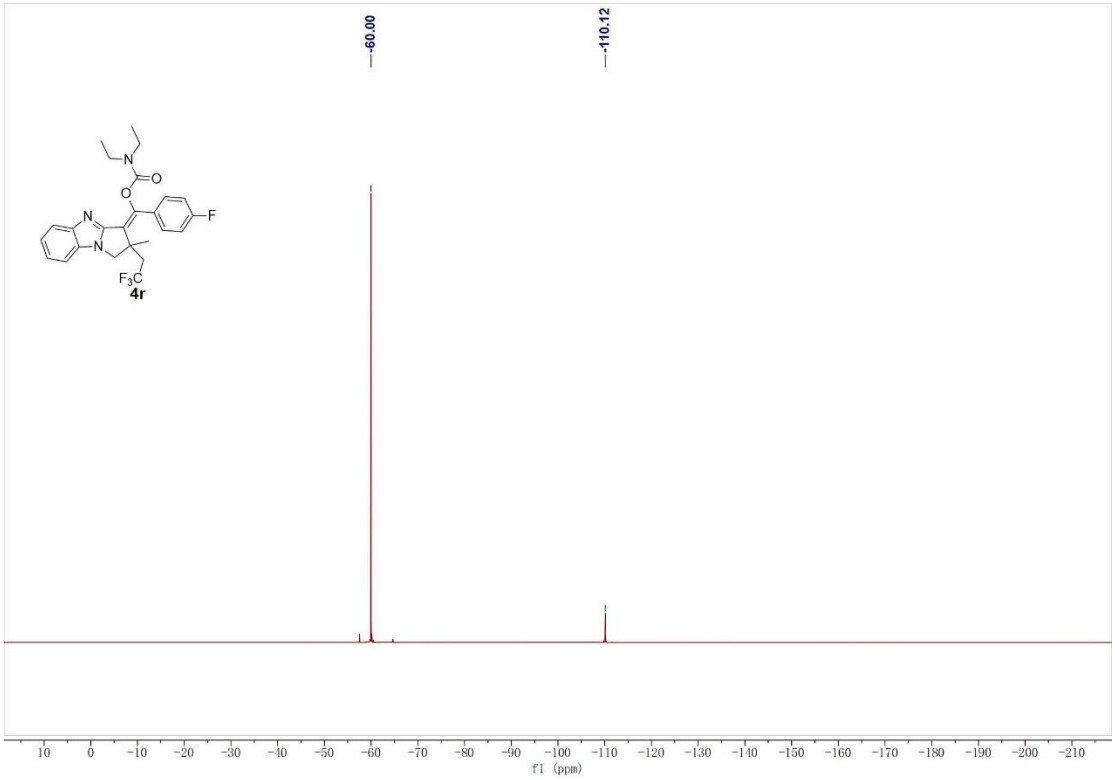
26.54
13.90
12.98
4r
f1 (ppm)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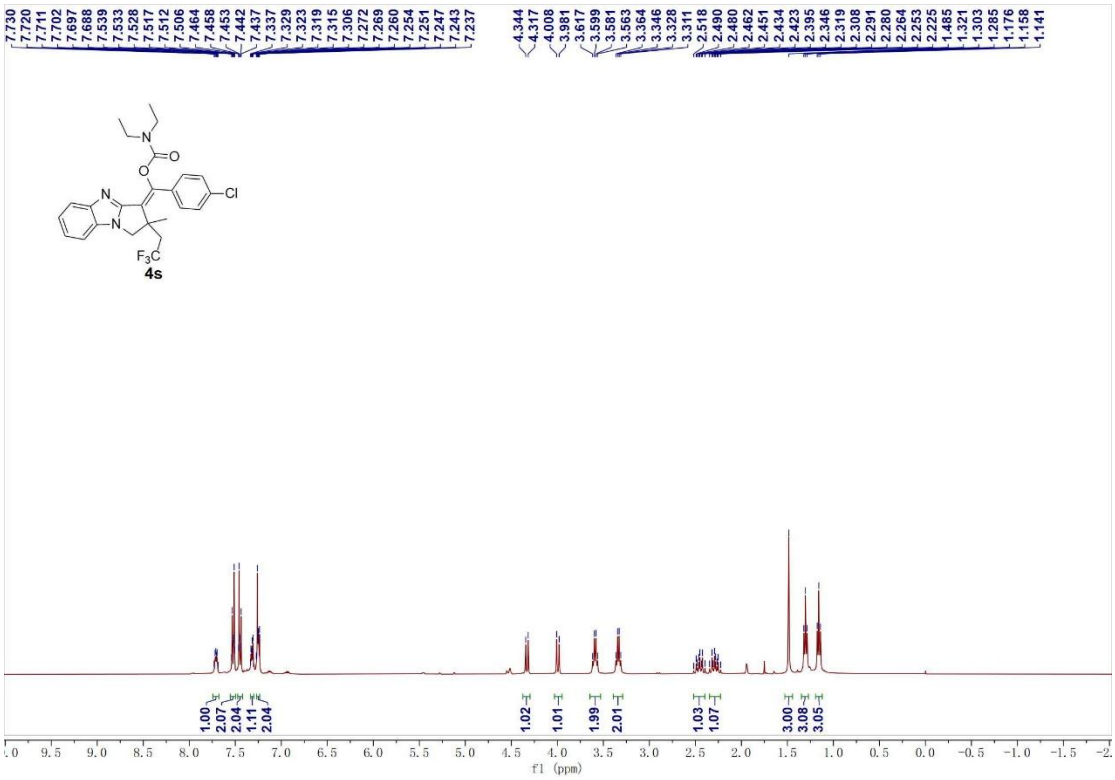
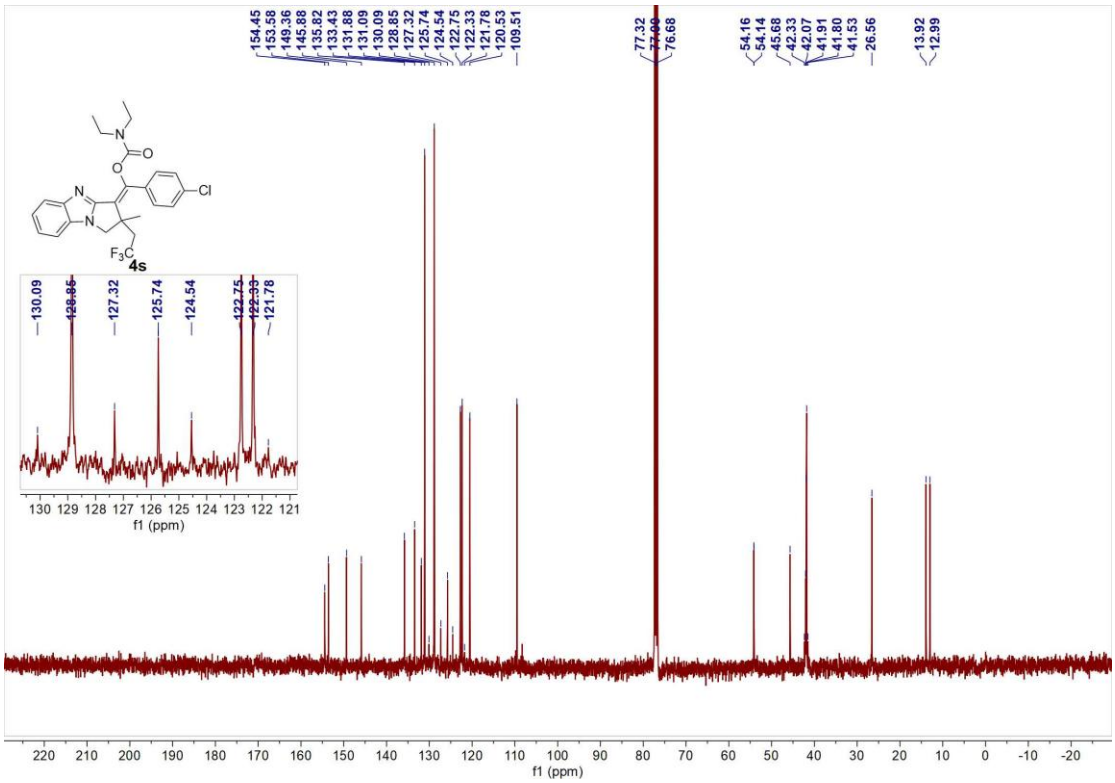
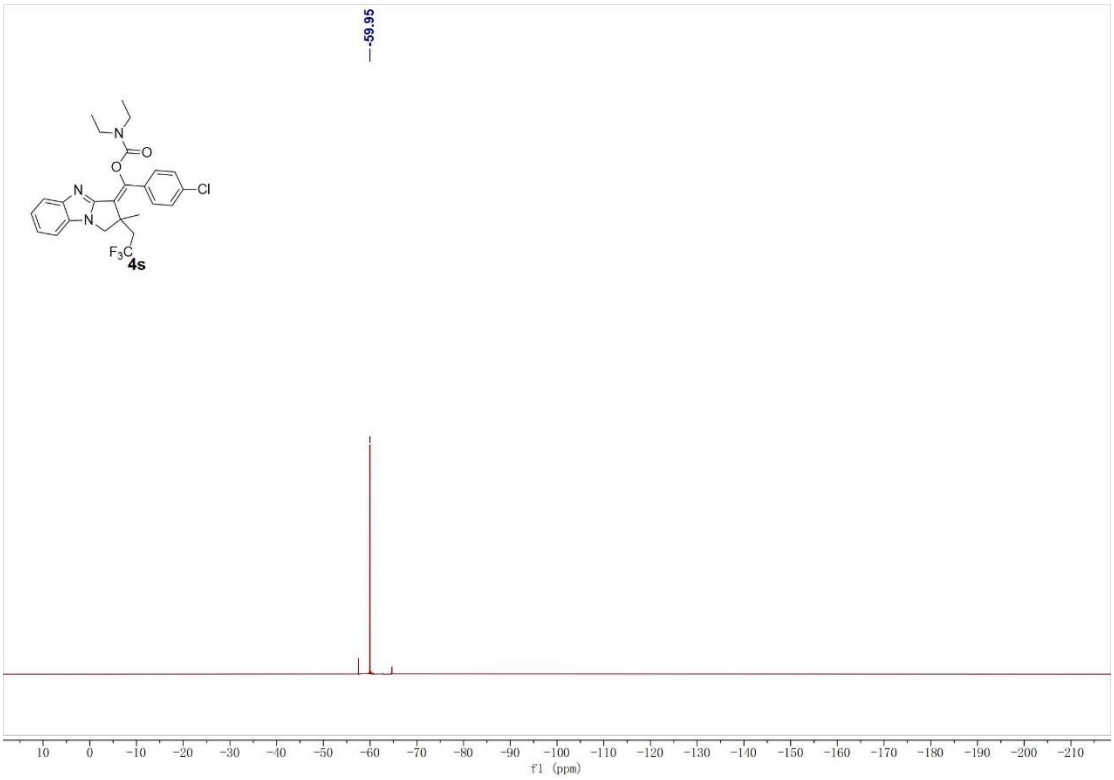
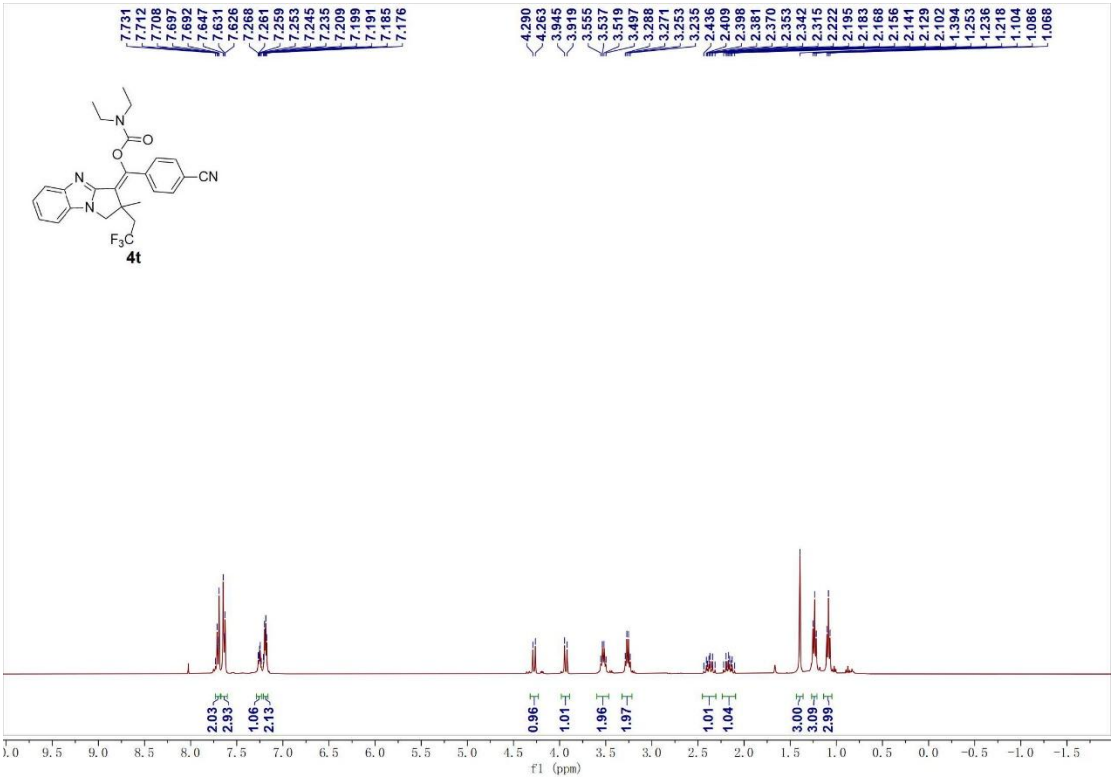
-110.12
4r
f1 (ppm)


4s
f1 (ppm)


4s
f1 (ppm)
f1 (ppm)


-59.95
Cl
F3C
4s
f1 (ppm)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7.261
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7.253
7.245
7.235
7.209
7.199
7.191
7.185
7.176
4.290
4.263
3.945
3.919
3.555
3.537
3.519
3.497
3.288
3.271
3.253
3.235
2.436
2.409
2.398
2.381
2.370
2.353
2.342
2.315
2.222
2.195
2.183
2.168
2.156
2.141
2.129
2.102
1.394
1.253
1.236
1.218
1.104
1.086
1.068
CN
F3C
4t
2.03
2.93
1.06
2.13
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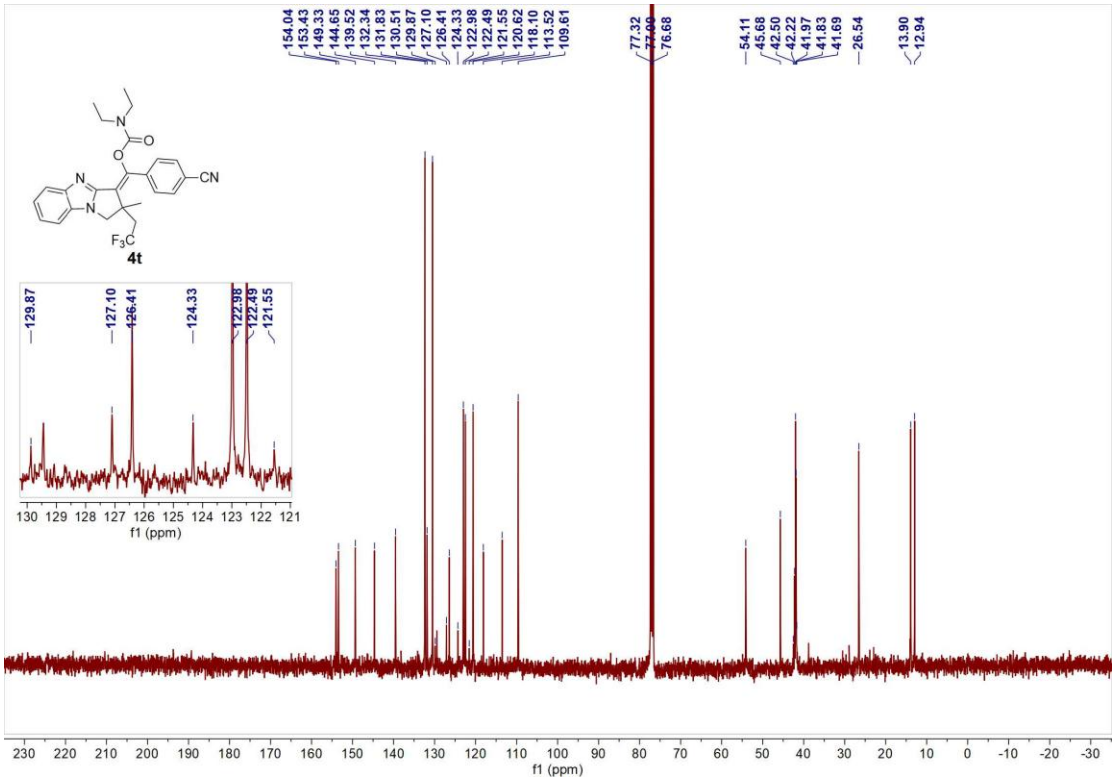
1.01
1.96
1.97
1.01
1.04
3.00
3.09
2.99
f1 (ppm)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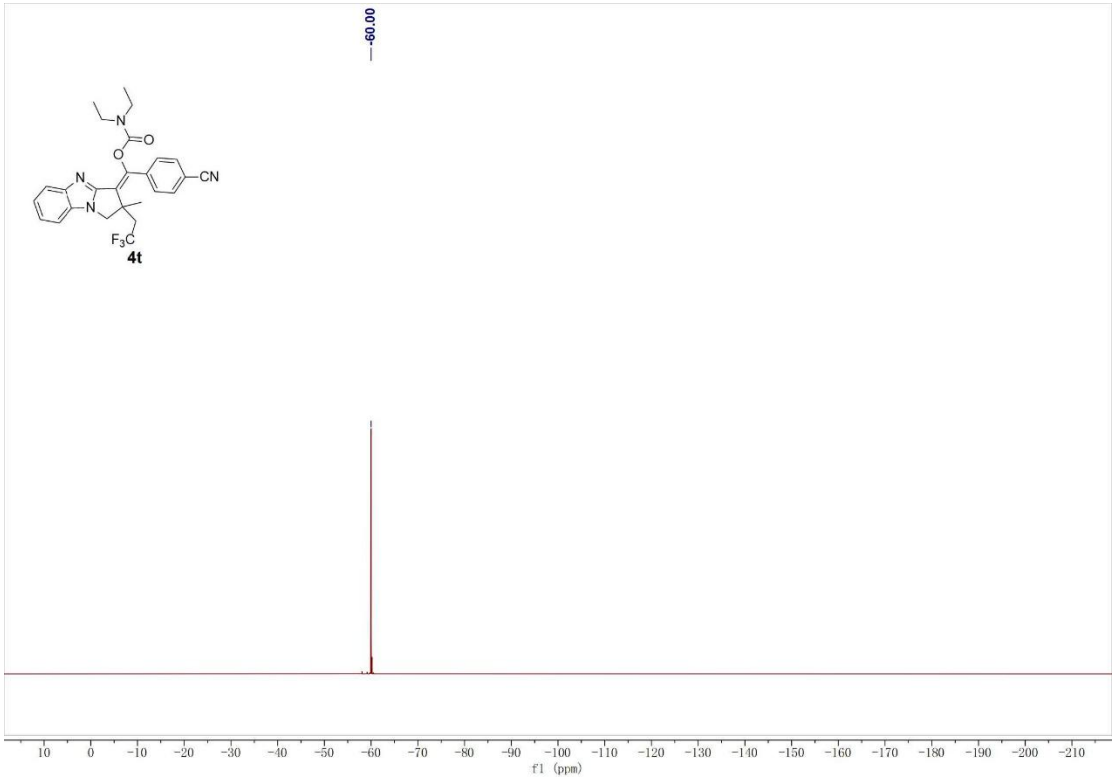
122.98
122.49
121.55
120.62
118.10
113.52
109.61
77.32
77.00
76.68
54.11
45.68
42.50
42.22
41.97
41.83
41.69
26.54
13.90
12.94
CN
F3C
4t
129.87
127.10
126.41
124.33
122.98
122.49
121.55
130 129 128 127 126 125 124 123 122 121
f1 (ppm)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)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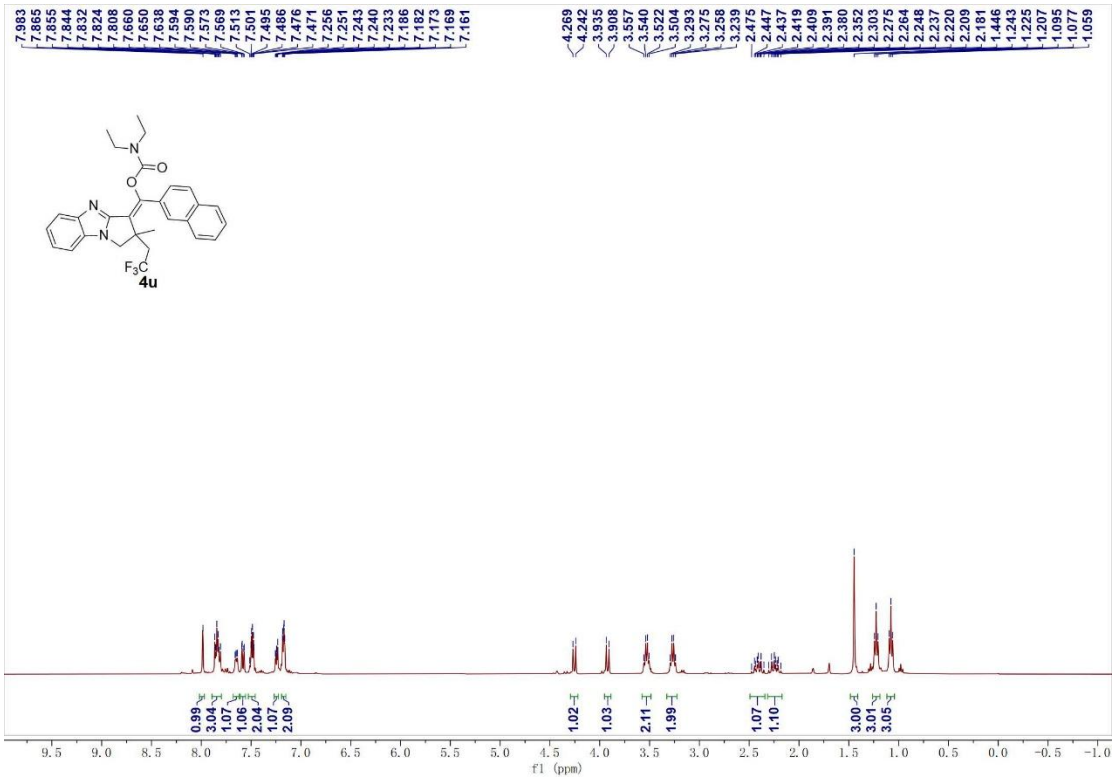
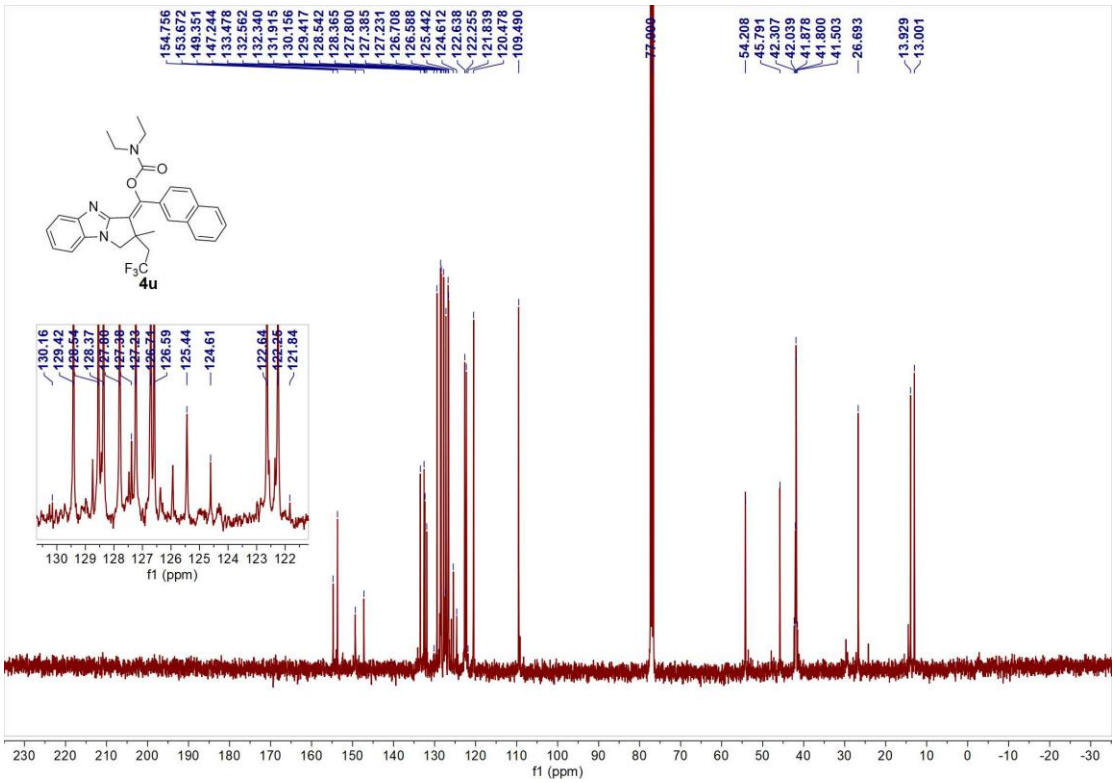
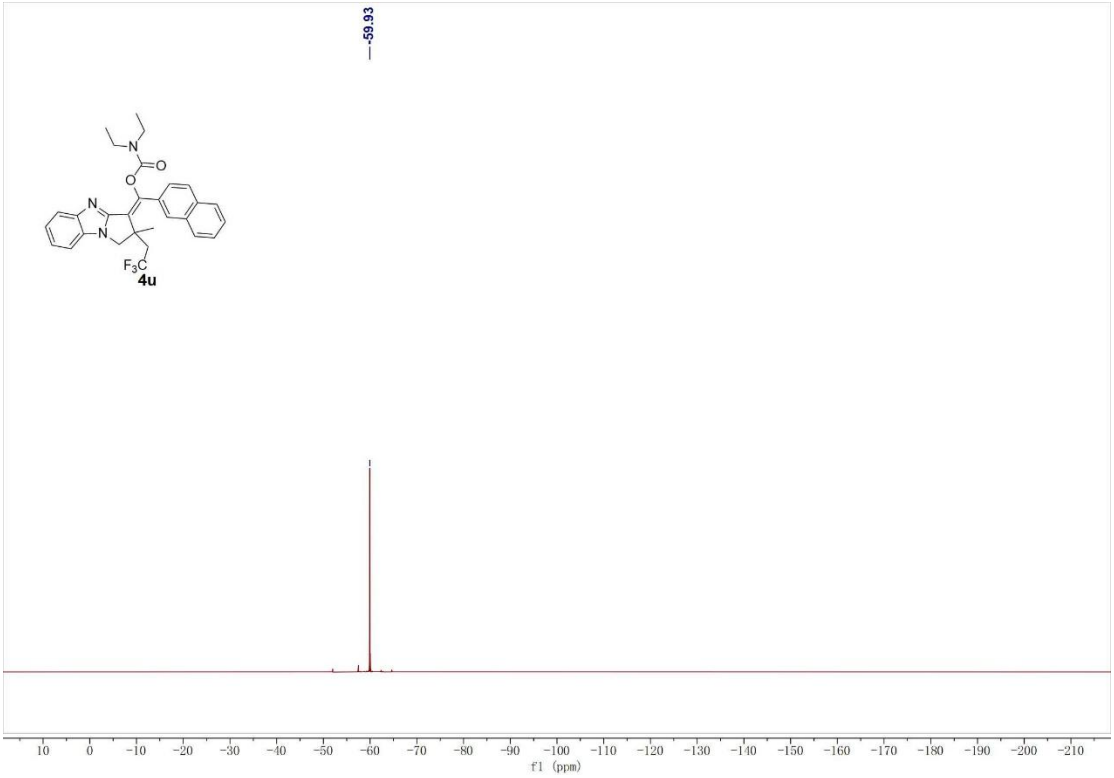
CN
F3C
4t
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


4u
f1 (ppm)


4u
f1 (ppm)
f1 (ppm)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4u
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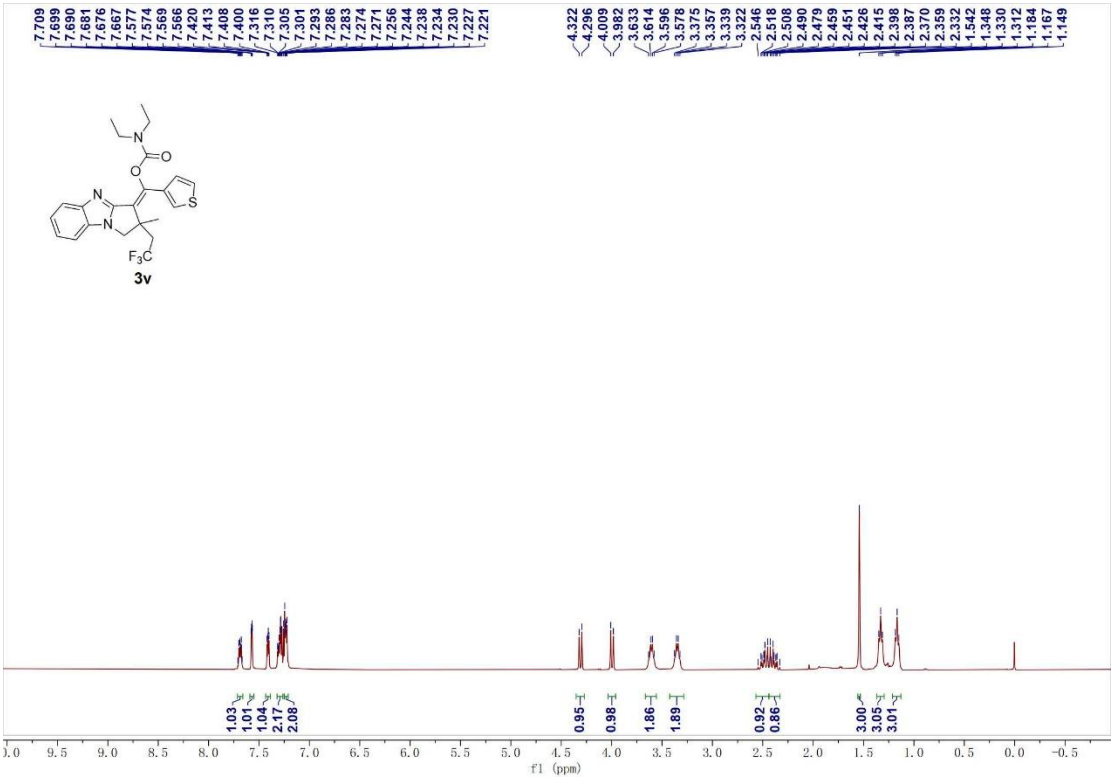
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7.408
7.400
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7.310
7.305
7.301
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7.283
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7.271
7.256
7.244
7.238
7.234
7.230
7.227
7.221
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4.296
4.009
3.982
3.633
3.614
3.596
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3.322
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2.518
2.508
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2.459
2.451
2.426
2.415
2.398
2.387
2.370
2.359
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1.542
1.348
1.330
1.312
1.184
1.167
1.149
3v
1.03
1.01
1.04
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0.86
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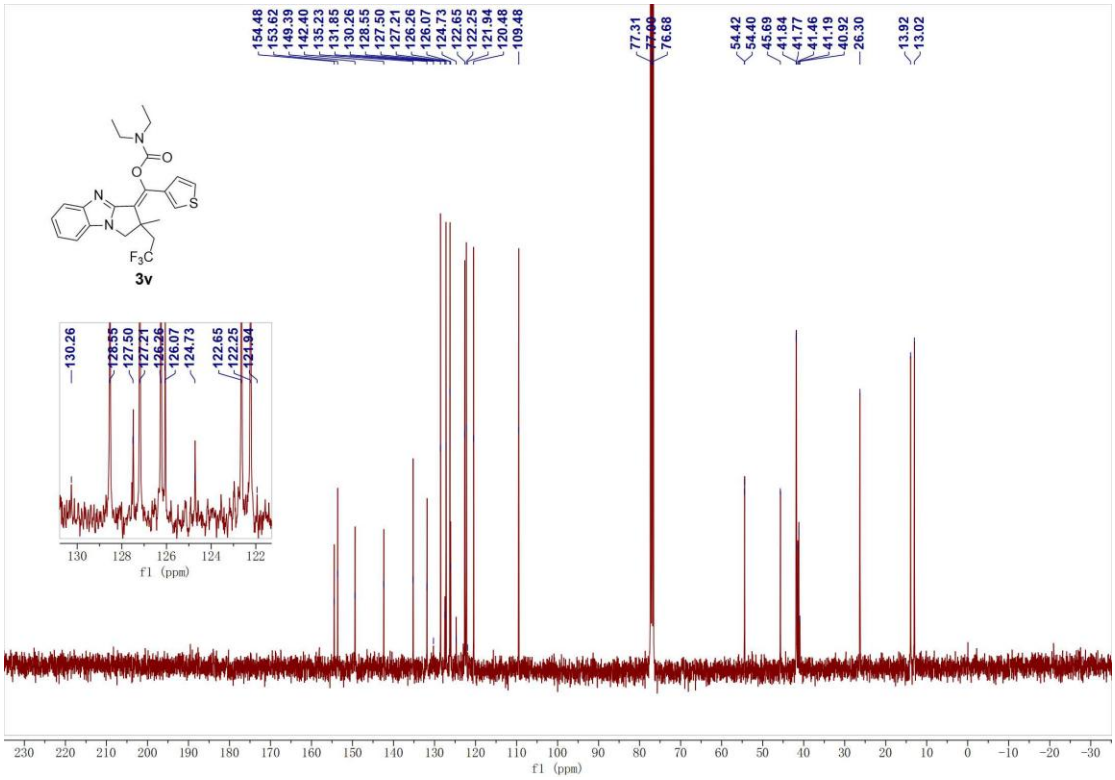
3.01
f1 (ppm)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126.26
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124.73
122.65
122.25
121.94
120.48
109.48
77.31
77.00
76.68
54.42
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45.69
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41.77
41.46
41.19
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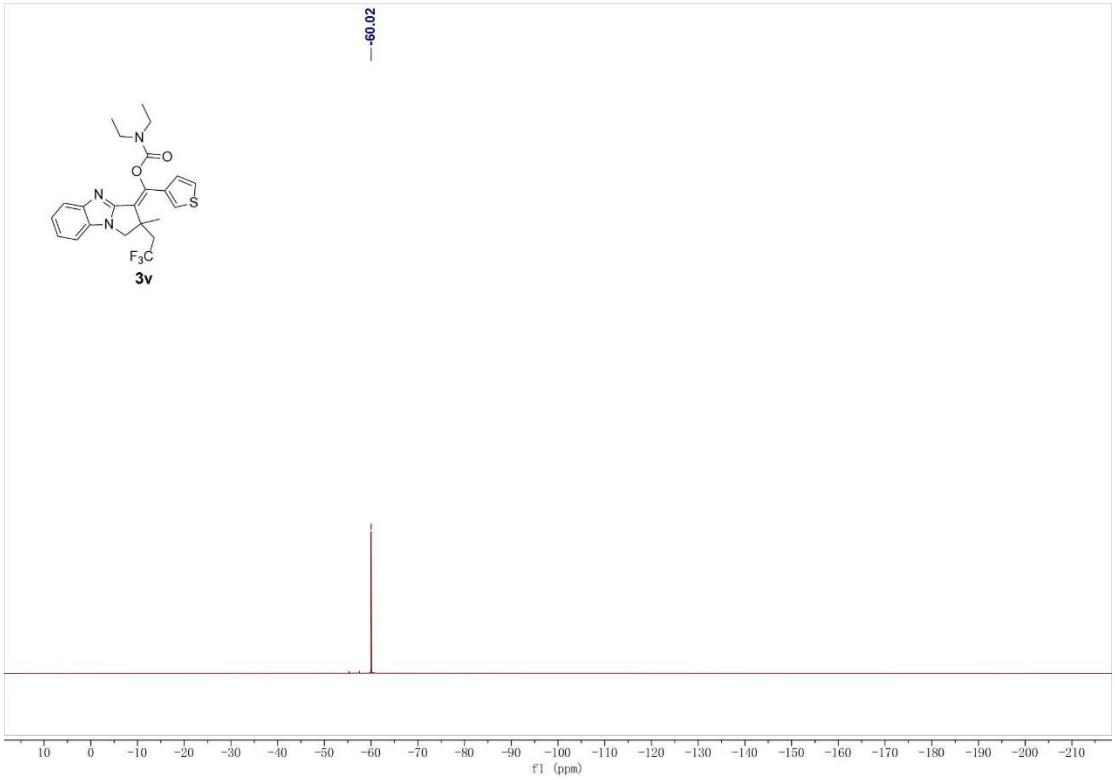
26.30
13.92
13.02
3v
f1 (ppm)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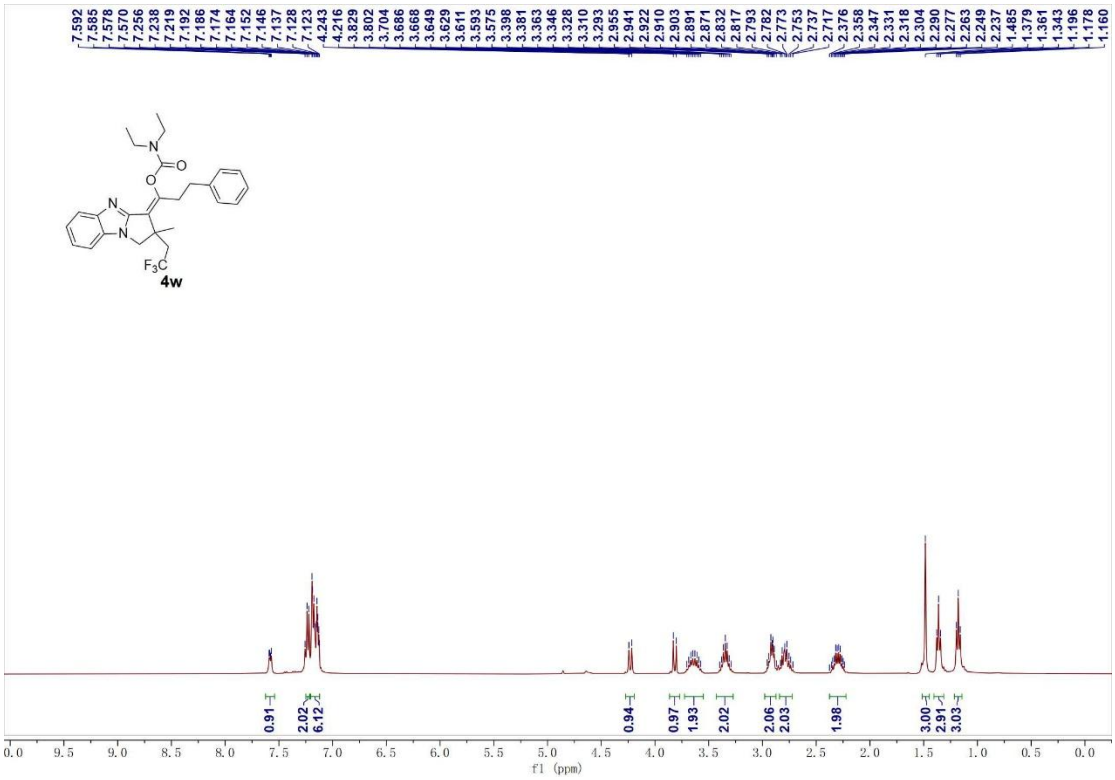
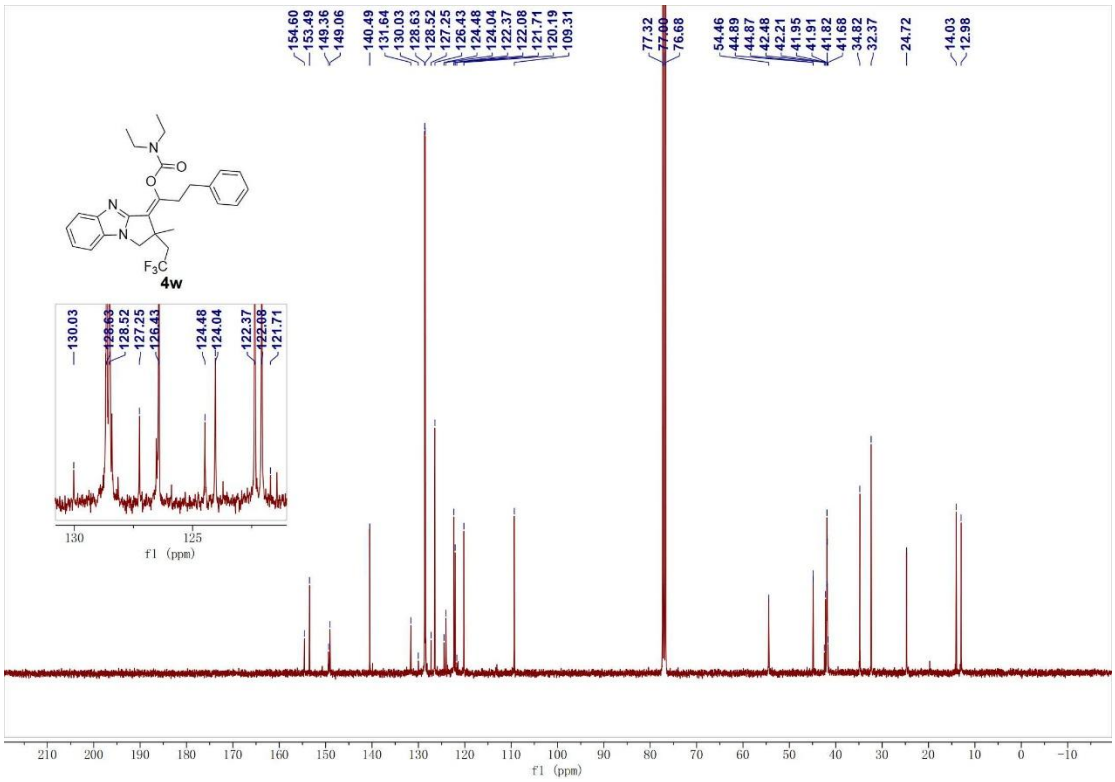
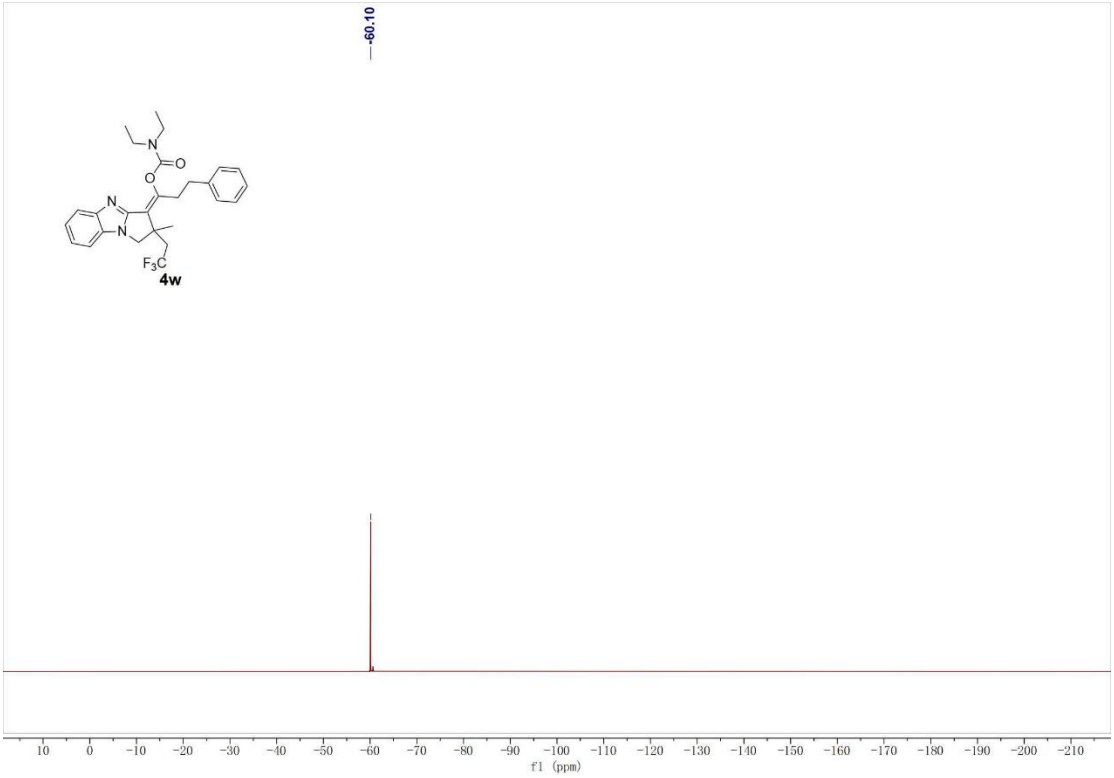

4w
f1 (ppm)


4w
f1 (ppm)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4w
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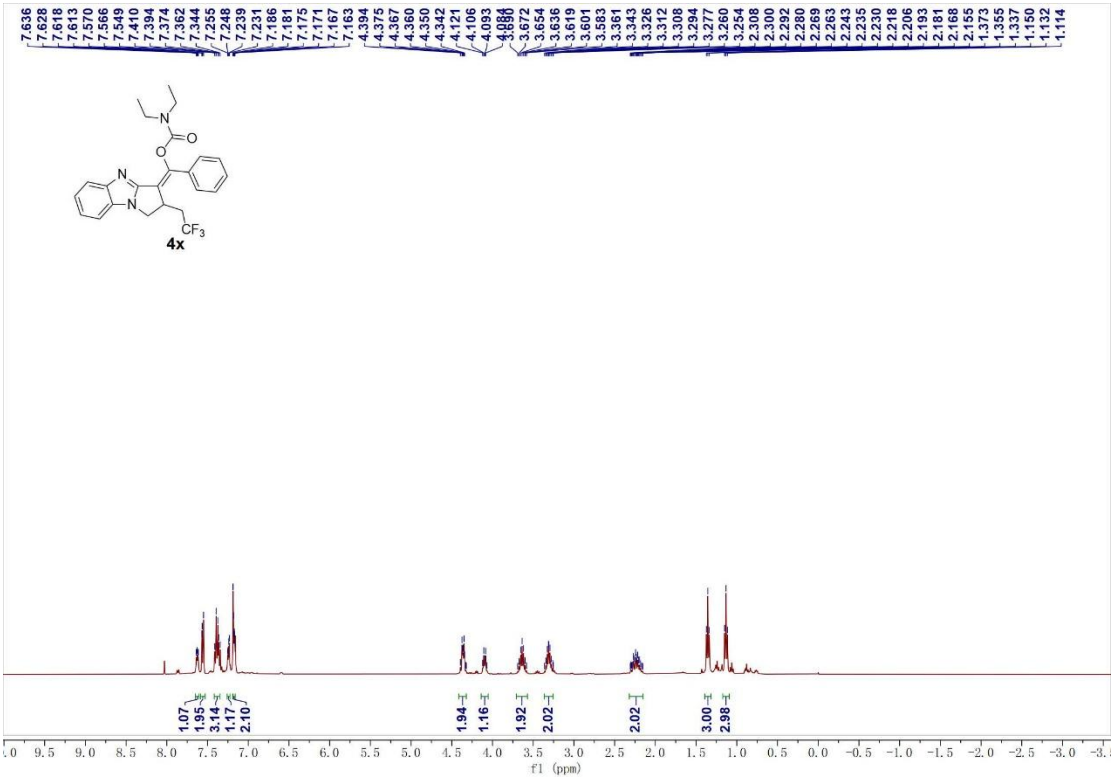
f1 (ppm)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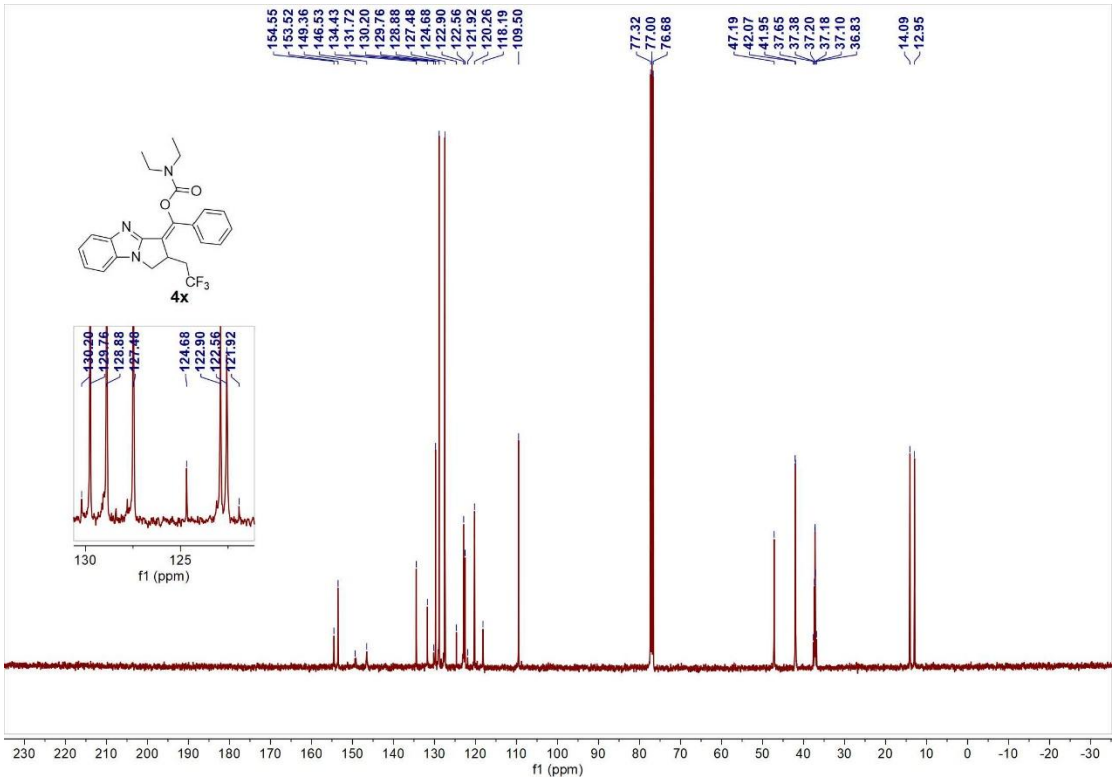
4x
1.07 1.95 3.14 1.17 2.10 1.94 1.16 1.92 2.02 2.02 3.00 2.98
f1 (ppm)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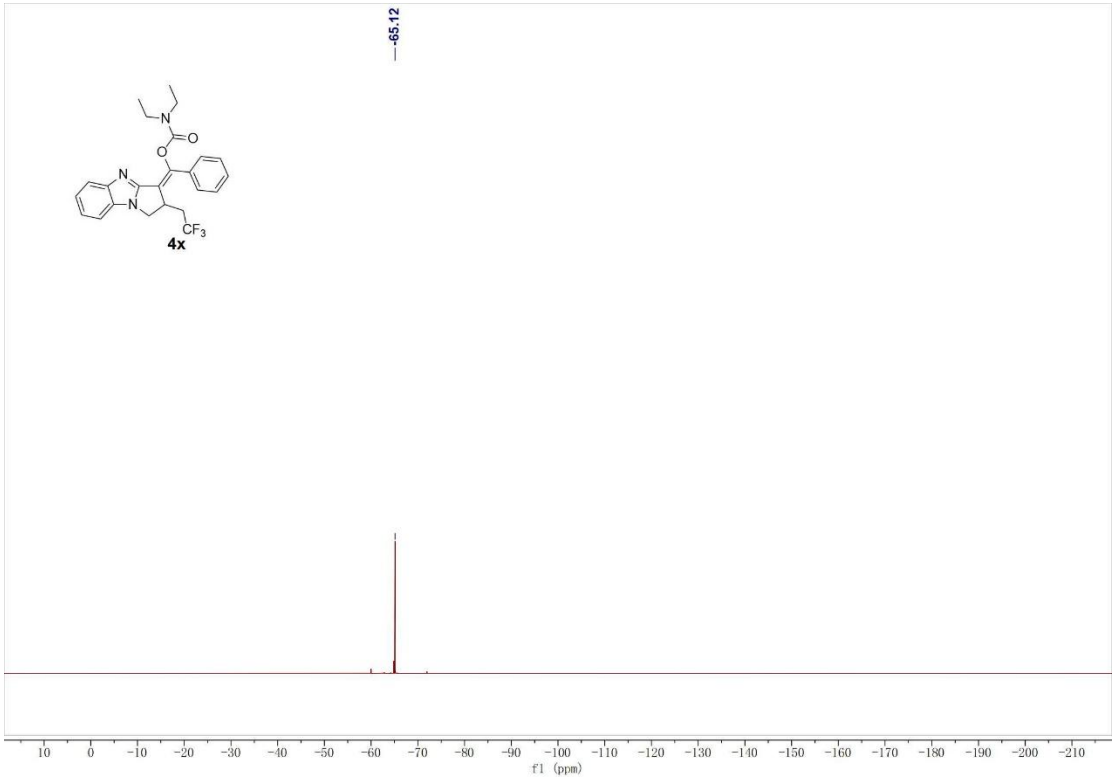
122.56
121.92
120.26
118.19
109.50
77.32
77.00
76.68
47.19
42.07
41.95
37.65
37.38
37.20
37.18
37.10
36.83
14.09
12.95
4x
130.20
129.76
128.88
127.48
124.68
122.90
122.56
121.92
130
125
f1 (ppm)
f1 (ppm)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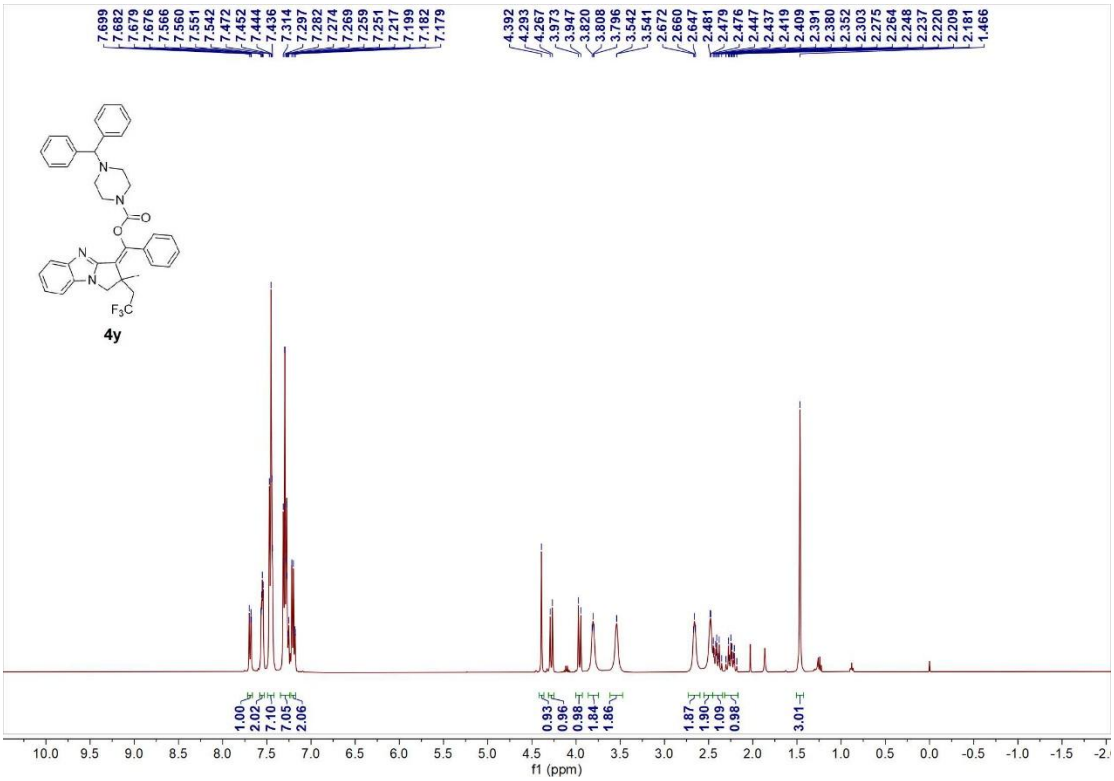
4x
f1 (ppm)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7.217
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7.182
7.179
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4.293
4.267
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3.947
3.820
3.808
3.796
3.542
3.541
2.672
2.660
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2.479
2.476
2.447
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2.419
2.409
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2.380
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2.275
2.264
2.248
2.237
2.220
2.209
2.181
1.466
4y
1.00
2.02
7.10
7.05
2.06
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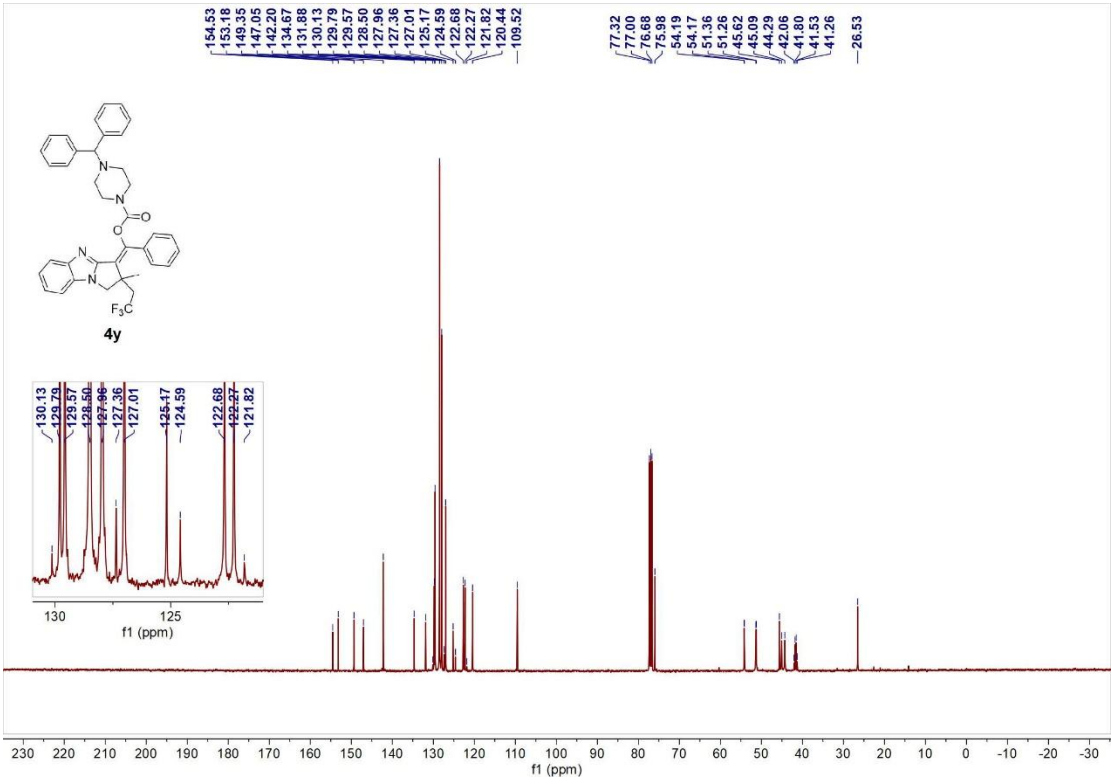
0.98
1.84
1.86
1.87
1.90
1.09
0.98
3.01
f1 (ppm)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127.36
127.01
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124.59
122.68
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77.32
77.00
76.68
75.98
54.19
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51.36
51.26
45.62
45.09
44.29
42.06
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41.26
26.53
4y
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129.79
129.57
128.50
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125.47
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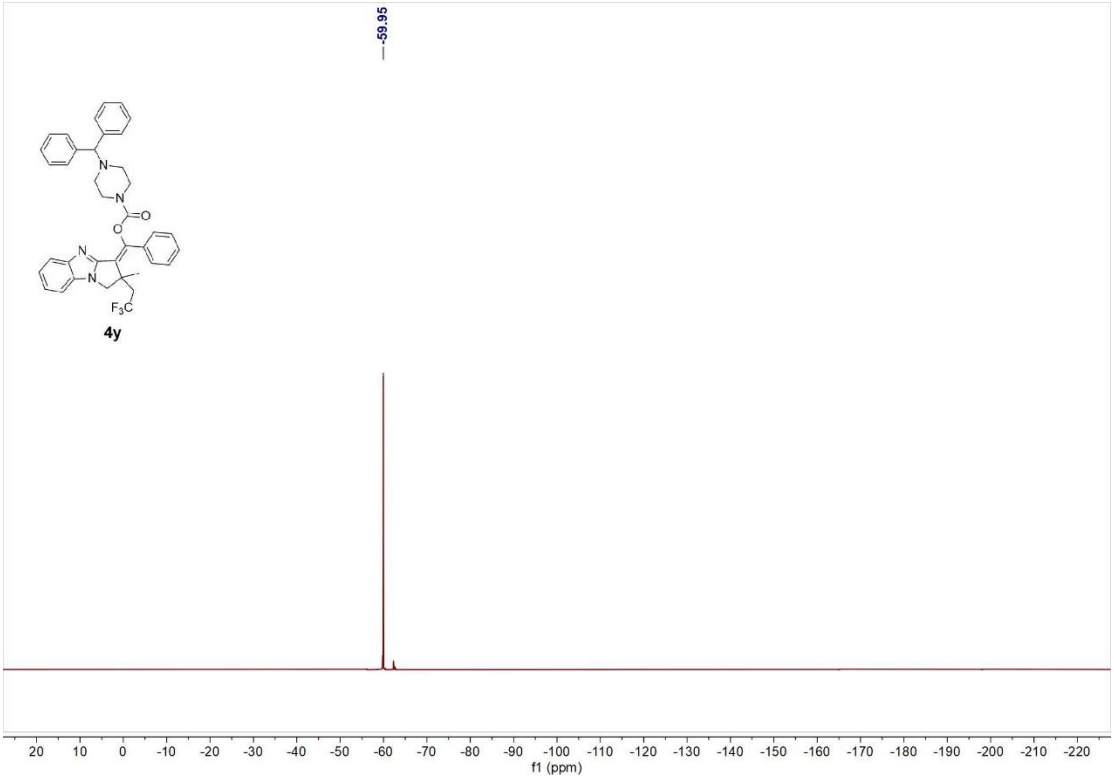
122.68
122.27
121.82
130
125
f1 (ppm)
f1 (ppm)


-59.95
4y
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)