Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Iron-catalyzed *ortho* trifluoromethylation of anilines *via* picolinamide assisted photoinduced C-H functionalization

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General Information

All commercial reagents were used as received. All products were isolated by short chromatography on a silica gel (200-300 mesh) column using petroleum ether (60-90°C) and ethyl acetate. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker Advance DRX-400 and DRX-500 spectrometers at ambient temperature with $CDCl_3$ as solvent and tetramethylsilane (TMS) as the internal standard. All chemical shift values are quoted in ppm and coupling constants quoted in Hz. Compounds for HRMS were analyzed by positive mode electrospray ionization (ESI) using Agilent 6530 QTOF mass spectrometer.

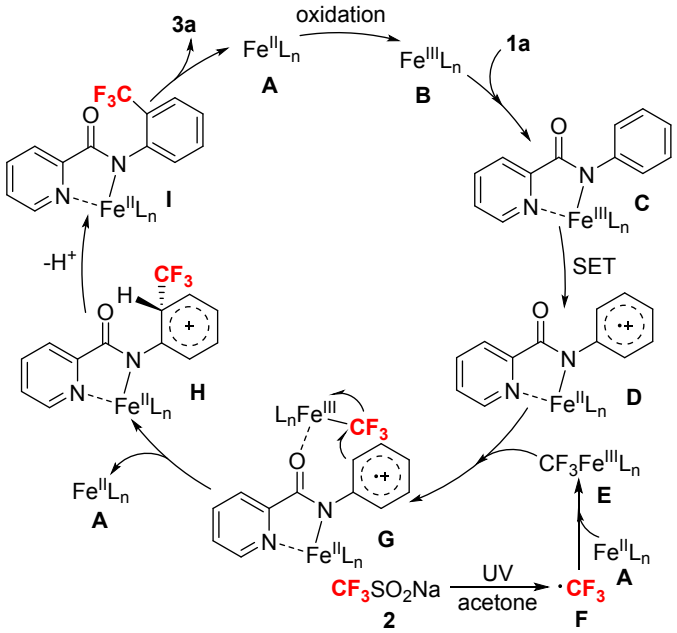
General procedures for the preparation of picolinamide substrates

A mixture of anilines (10 mmol), pyridine-2-carbonyl chloride hydrochloride (1.05 equiv), NEt_3 (3.0 equiv) in anhydrous CH_2Cl_2 (20 mL) was stirred at room temperature overnight. Water was added and the mixture was extracted with CH_2Cl_2. The combined organic layer was washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The resulting residue was purified by silica gel flash chromatography to give the desired amide products.

General experimental procedure for synthesis of product 3

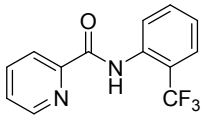
Amide **1** (0.2 mmol), Langlois' reagent **2** (0.4 mmol), ferrocene (15 mol %) and acetone (2.0 mL) were combined in a 25 mL. The mixture was then stirred under UV irradiation (λ = 254 nm, intensity of 4.0 mW cm^{-2}) for 36 hours at room temperature. After the conversion was completed as indicated by TLC, the mixture was evaporated under reduced pressure. The residue was purified directly by flash column chromatography (EA/PE, 1:200) to give the product **3**.

According to the experiment results and previous work,[1] a possible mechanism was suggested as follow:



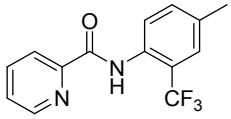
Characterization of the products

***N*-(2-(trifluoromethyl)phenyl)picolinamide (3a)**[1]



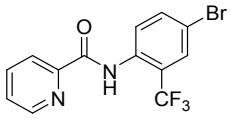
White solid, 72% yield. M.p. 65-66 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.58 (s, 1H), 8.58 (d, *J* = 4.7 Hz, 1H), 8.51 (d, *J* = 8.3 Hz, 1H), 8.22 (d, *J* = 7.8 Hz, 1H), 7.85 – 7.81 (m, 1H), 7.59 (d, *J* = 7.7 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 1H), 7.44 – 7.41 (m, 1H), 7.16 (d, *J* = 7.7 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.40, 148.31, 147.31, 136.64, 134.50 (q, *J* = 2.5 Hz), 131.91, 125.71, 125.14 (q, *J* = 5.0 Hz), 123.12 (q, *J* = 273.4 Hz), 123.00, 121.97, 121.47, 118.83 (q, *J* = 30.3 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -60.92. HRMS (ESI) calculated for $C_{13}H_9F_3N_2O^+$: 267.0740 $[M+H]^+$, found: 267.0742.

***N*-(4-methyl-2-(trifluoromethyl)phenyl)picolinamide (3b)**[1]



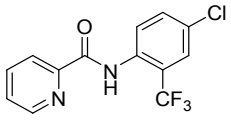
White solid, 67% yield. M.p. 67-68 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.55 (s, 1H), 8.66 (d, *J* = 4.4 Hz, 1H), 8.41 (d, *J* = 8.4 Hz, 1H), 8.29 (d, *J* = 7.8 Hz, 1H), 7.94 – 7.90 (m, 1H), 7.51 – 7.48 (m, 1H), 7.46 (s, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.32, 148.42, 147.25, 136.62, 133.05, 132.37 (q, *J* = 1.3 Hz), 131.85 (q, *J* = 1.3 Hz), 125.60, 125.50 (q, *J* = 5.0 Hz), 123.39 (q, *J* = 273.4 Hz), 122.26, 121.44, 118.96 (q, *J* = 30.3 Hz), 19.83. ^{19}F NMR (471 MHz, $CDCl_3$) δ -60.82. HRMS (ESI) calculated for $C_{14}H_{11}F_3N_2O^+$: 281.0896 $[M+H]^+$, found: 281.0898.

***N*-(4-bromo-2-(trifluoromethyl)phenyl)picolinamide (3c)**[1]



White solid, 57% yield. M.p. 110-111 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.67 (s, 1H), 8.65 (d, *J* = 4.2 Hz, 1H), 8.55 (d, *J* = 8.9 Hz, 1H), 8.27 (d, *J* = 7.8 Hz, 1H), 7.91 (td, *J* = 7.7, 1.6 Hz, 1H), 7.77 (d, *J* = 1.9 Hz, 1H), 7.71 (d, *J* = 8.9 Hz, 1H), 7.53 – 7.49 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.35, 149.05, 148.35, 137.72, 135.87, 134.75 (q, *J* = 1.0 Hz), 129.14 (q, *J* = 5.0 Hz), 126.87, 124.34, 123.18 (q, *J* = 274.2 Hz), 122.53, 121.22 (q, *J* = 31.3 Hz), 116.54. ^{19}F NMR (471 MHz, $CDCl_3$) δ -61.27. HRMS (ESI) calculated for $C_{13}H_8BrF_3N_2O^+$: 344.9845 $[M+H]^+$, found: 344.9852.

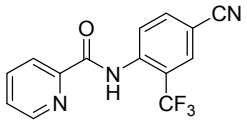
***N*-(4-chloro-2-(trifluoromethyl)phenyl)picolinamide (3d)**[1]



White solid, 51% yield. M.p. 115-116 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.66 (s, 1H), 8.65 (d, *J* = 4.7 Hz, 1H), 8.60 (d, *J* = 8.9 Hz, 1H), 8.28 (d, *J* = 7.8 Hz, 1H), 7.94 – 7.89 (m, 1H), 7.63 (d, *J* = 2.2 Hz, 1H), 7.56 (d, *J* = 8.9 Hz, 1H), 7.50 (dd, *J* = 7.1, 5.2 Hz, 1H). ^{13}C NMR

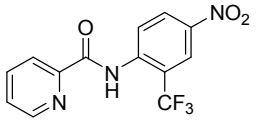
(101 MHz, $CDCl_3$) δ 162.37, 149.06, 148.34, 137.71, 134.24 (q, *J* = 1.0 Hz), 132.87, 129.29, 126.86, 126.30 (q, *J* = 5.0 Hz), 124.19, 123.30 (q, *J* = 273.7 Hz), 122.52, 121.06 (q, *J* = 30.3 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -61.33. HRMS (ESI) calculated for $C_{13}H_8ClF_3N_2O^+$: 301.0350 $[M+H]^+$, found: 301.0355.

***N*-(4-cyano-2-(trifluoromethyl)phenyl)picolinamide (3e)**



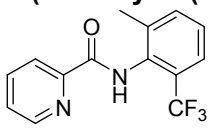
White solid, 25% yield. M.p. 145-146 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 11.00 (s, 1H), 8.94 (d, *J* = 8.7 Hz, 1H), 8.68 (d, *J* = 4.2 Hz, 1H), 8.30 (d, *J* = 7.8 Hz, 1H), 7.96 (dd, *J* = 7.8, 1.7 Hz, 2H), 7.88 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.58 – 7.55 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.59, 148.48, 139.63, 137.96, 136.74, 130.39 (q, *J* = 5.0 Hz), 127.35, 123.01 (q, *J* = 274.7 Hz), 122.76, 122.33, 122.23, 119.67 (q, *J* = 31.5 Hz), 117.61, 107.14. ^{19}F NMR (470 MHz, $CDCl_3$) δ -61.69. HRMS (ESI) calculated for $C_{14}H_8F_3N_3O^+$: 292.0692 $[M+H]^+$, found: 292.0698.

***N*-(4-nitro-2-(trifluoromethyl)phenyl)picolinamide (3f)**



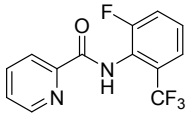
White solid, 18% yield. M.p. 152-153 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 11.11 (s, 1H), 9.02 (d, *J* = 9.2 Hz, 1H), 8.69 (d, *J* = 4.2 Hz, 1H), 8.57 (d, *J* = 2.6 Hz, 1H), 8.48 (dd, *J* = 9.2, 2.6 Hz, 1H), 8.31 (d, *J* = 7.8 Hz, 1H), 7.99 – 7.95 (m, 1H), 7.57 (ddd, *J* = 7.6, 4.8, 1.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.62, 147.49, 147.35, 141.57, 140.26, 136.99, 127.40, 126.43, 121.93 (q, *J* = 274.7 Hz), 121.82, 121.52 (q, *J* = 5.0 Hz), 120.93, 118.23 (q, *J* = 31.5 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -61.64. HRMS (ESI) calculated for $C_{13}H_8F_3N_3O_3^+$: 312.0591 $[M+H]^+$, found: 312.0586.

***N*-(2-methyl-6-(trifluoromethyl)phenyl)picolinamide (3g)**[1]



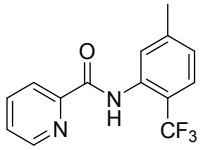
White solid, 60% yield. M.p. 55-56 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 9.81 (s, 1H), 8.65 (d, *J* = 4.2 Hz, 1H), 8.28 (d, *J* = 7.8 Hz, 1H), 7.90 (t, *J* = 7.7 Hz, 1H), 7.56 (d, *J* = 7.7 Hz, 1H), 7.51 (d, *J* = 7.1 Hz, 2H), 7.34 (t, *J* = 7.7 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.77, 149.21, 148.34, 138.79, 137.49, 134.66, 133.18 (q, *J* = 1.0 Hz), 127.42, 127.11, 126.61, 123.98 (q, *J* = 5.0 Hz), 123.79 (q, *J* = 273.7 Hz), 122.63, 18.47. ^{19}F NMR (471 MHz, $CDCl_3$) δ -61.67. HRMS (ESI) calculated for $C_{14}H_{11}F_3N_2O^+$: 281.0896 $[M+H]^+$, found: 281.0909.

***N*-(2-fluoro-6-(trifluoromethyl)phenyl)picolinamide (3h)**[1]



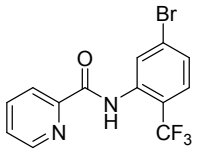
White solid, 49% yield. M.p. 80-81 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.73 (s, 1H), 8.65 (d, *J* = 4.7 Hz, 1H), 8.28 (d, *J* = 7.8 Hz, 1H), 7.93 – 7.89 (m, 1H), 7.54 – 7.50 (m, 2H), 7.41 (dd, *J* = 7.9, 3.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.70, 158.50 (d, *J* = 255.5), 148.74, 148.37, 137.55, 128.49 (q, *J* = 1.0 Hz), 128.20 (d, *J* = 9.1 Hz), 126.83, 124.36 (q, *J* = 273.7 Hz), 122.75, 121.83 (q, *J* = 30.3 Hz), 121.74 (q, *J* = 5.0 Hz), 120.48 (d, *J* = 21.2 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -61.34, -114.22. HRMS (ESI) calculated for $C_{13}H_8F_4N_2O^+$: 285.0646 $[M+H]^+$, found: 285.0637.

***N*-(5-methyl-2-(trifluoromethyl)phenyl)picolinamide (3i)**[1]



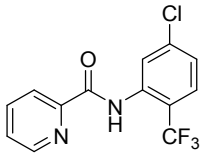
White solid, 69% yield. M.p. 57-58 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.60 (s, 1H), 8.63 (d, *J* = 4.1 Hz, 1H), 8.40 (s, 1H), 8.27 (d, *J* = 7.8 Hz, 1H), 7.91 – 7.86 (m, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.47 (dd, *J* = 6.8, 5.1 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.37, 149.42, 148.29, 143.61, 137.60, 135.31 (q, *J* = 1.0 Hz), 126.64, 126.04 (q, *J* = 5.0 Hz), 124.79, 124.37 (q, *J* = 273.7 Hz), 123.51, 122.41, 117.22 (q, *J* = 30.3 Hz), 21.63. ^{19}F NMR (471 MHz, $CDCl_3$) δ -60.42. HRMS (ESI) calculated for $C_{14}H_{11}F_3N_2O^+$: 281.0896 $[M+H]^+$, found: 281.0895.

***N*-(5-bromo-2-(trifluoromethyl)phenyl)picolinamide (3j)**[1]



White solid, 58% yield. M.p. 102-103 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.71 (s, 1H), 8.89 (s, 1H), 8.65 (d, *J* = 4.2 Hz, 1H), 8.28 (d, *J* = 7.8 Hz, 1H), 7.92 (td, *J* = 7.7, 1.6 Hz, 1H), 7.51 (t, *J* = 7.4 Hz, 2H), 7.36 (dd, *J* = 8.4, 0.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.36, 148.94, 148.36, 137.76, 136.69, 127.44, 127.36 (q, *J* = 5.0 Hz), 126.97, 126.94, 125.51, 123.93 (q, *J* = 273.7 Hz), 122.57, 118.28 (q, *J* = 30.3 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -60.97. HRMS (ESI) calculated for $C_{13}H_8BrF_3N_2O^+$: 344.9845 $[M+H]^+$, found: 344.9845.

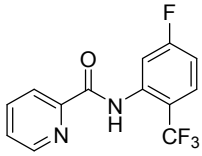
***N*-(5-chloro-2-(trifluoromethyl)phenyl)picolinamide (3k)**[1]



White solid, 50% yield. M.p. 82-83 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.72 (s, 1H), 8.74 (s, 1H), 8.64 (d, *J* = 4.5 Hz, 1H), 8.27 (d, *J* = 7.8 Hz, 1H), 7.92 (td, *J* = 7.7, 1.3 Hz, 1H), 7.56 (d, *J* = 8.5 Hz, 1H), 7.53 – 7.49 (m, 1H), 7.19 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.36, 148.93, 148.35, 139.20, 137.75, 136.70, 127.24 (q, *J* = 5.0 Hz), 126.94, 123.93, 123.85 (q, *J* = 273.7 Hz), 122.56, 122.49, 117.74 (q, *J* = 30.3 Hz). ^{19}F NMR (471

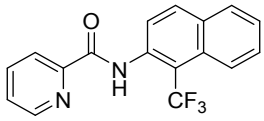
MHz, $CDCl_3$) δ -60.87. HRMS (ESI) calculated for $C_{13}H_8ClF_3N_2O^+$: 301.0350 $[M+H]^+$, found: 301.0355.

***N*-(5-fluoro-2-(trifluoromethyl)phenyl)picolinamide (3l)**[1]



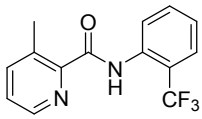
White solid, 42% yield. M.p. 66-67 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 10.79 (s, 1H), 8.66 (d, *J* = 4.7 Hz, 1H), 8.51 (dd, *J* = 11.2, 2.1 Hz, 1H), 8.29 (d, *J* = 7.8 Hz, 1H), 7.93 (td, *J* = 7.7, 1.6 Hz, 1H), 7.64 (dd, *J* = 8.7, 6.1 Hz, 1H), 7.52 (ddd, *J* = 7.6, 4.8, 1.1 Hz, 1H), 6.95 – 6.88 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.40 (d, *J* = 251.5 Hz), 163.85, 148.97, 148.37, 137.76, 137.67, 128.07 (q, *J* = 5.0 Hz), 126.95, 123.91 (q, *J* = 273.7 Hz), 122.57, 115.30 (q, *J* = 30.3 Hz), 110.68 (d, *J* = 23.2 Hz), 109.83 (d, *J* = 28.2 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -60.30, -104.57. HRMS (ESI) calculated for $C_{13}H_8F_4N_2O^+$: 285.0646 $[M+H]^+$, found: 285.0651.

***N*-(1-(trifluoromethyl)naphthalen-2-yl)picolinamide (3m)**[1]



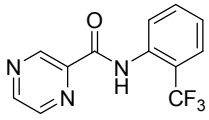
White solid, 43% yield. M.p. 135-136 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 11.02 (s, 1H), 8.68 (d, *J* = 4.7 Hz, 1H), 8.53 (d, *J* = 9.1 Hz, 1H), 8.33 (d, *J* = 7.8 Hz, 1H), 8.23 (d, *J* = 9.5 Hz, 1H), 8.03 (d, *J* = 9.1 Hz, 1H), 7.95 – 7.91 (m, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.60 (ddd, *J* = 8.6, 6.9, 1.4 Hz, 1H), 7.54 – 7.50 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.59, 149.54, 148.29, 137.69, 135.17 (q, *J* = 2.0 Hz), 133.18, 131.24, 130.23, 128.62, 127.91, 126.78, 125.69, 124.57 (q, *J* = 5.0 Hz), 124.30 (q, *J* = 277.8 Hz), 122.64, 122.30, 113.74 (q, *J* = 28.3 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.20. HRMS (ESI) calculated for $C_{17}H_{11}F_3N_2O^+$: 317.0896 $[M+H]^+$, found: 317.0903.

3-methyl-*N*-(2-(trifluoromethyl)phenyl)picolinamide (3n)[1]



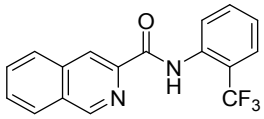
White solid, 68% yield. M.p. 75-76 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 10.91 (s, 1H), 8.54 (d, *J* = 8.3 Hz, 1H), 8.48 (d, *J* = 4.3 Hz, 1H), 7.66 – 7.62 (m, 2H), 7.59 (t, *J* = 7.9 Hz, 1H), 7.37 (dd, *J* = 7.7, 4.6 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 2.81 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.85, 146.23, 145.62, 141.24, 136.38, 135.90 (q, *J* = 1.0 Hz), 132.75, 126.24, 126.11 (q, *J* = 5.0 Hz), 124.20 (q, *J* = 273.7 Hz), 123.70, 122.97, 119.94 (q, *J* = 30.3 Hz), 20.70. ^{19}F NMR (471 MHz, $CDCl_3$) δ -61.07. HRMS (ESI) calculated for $C_{14}H_{11}F_3N_2O^+$: 281.0896 $[M+H]^+$, found: 281.0904.

***N*-(2-(trifluoromethyl)phenyl)pyrazine-2-carboxamide (3o)**[1]



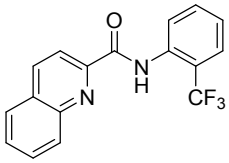
White solid, 57% yield. M.p. 120-121 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.25 (s, 1H), 9.51 (d, *J* = 0.9 Hz, 1H), 8.83 (d, *J* = 2.3 Hz, 1H), 8.64 (s, 1H), 8.54 (d, *J* = 8.3 Hz, 1H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.63 (t, *J* = 7.9 Hz, 1H), 7.29 (d, *J* = 7.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.07, 147.81, 144.76, 144.05, 142.65, 134.93 (q, *J* = 2.0 Hz), 133.03, 126.26 (q, *J* = 5.0 Hz), 124.59, 124.06 (q, *J* = 273.7 Hz), 123.26, 120.09 (q, *J* = 30.3 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -60.79. HRMS (ESI) calculated for $C_{12}H_8F_3N_3O^+$: 268.0692 $[M+H]^+$, found: 268.0693.

***N*-(2-(trifluoromethyl)phenyl)isoquinoline-3-carboxamide (3p)**[1]



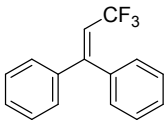
White solid, 70% yield. M.p. 142-143 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.89 (s, 1H), 9.26 (s, 1H), 8.71 (s, 1H), 8.66 (d, *J* = 8.3 Hz, 1H), 8.08 (d, *J* = 8.0 Hz, 1H), 8.03 (d, *J* = 8.1 Hz, 1H), 7.82 – 7.77 (m, 1H), 7.76 – 7.71 (m, 1H), 7.68 (d, *J* = 7.9 Hz, 1H), 7.63 (t, *J* = 7.9 Hz, 1H), 7.26 – 7.22 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.01, 151.34, 143.14, 136.06, 135.81 (q, *J* = 2.0 Hz), 132.92, 131.25, 129.96, 129.24, 128.21, 127.82, 126.15 (q, *J* = 5.0 Hz), 124.23 (q, *J* = 273.7 Hz), 123.90, 123.12, 120.97, 119.84 (q, *J* = 30.3 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -60.89. HRMS (ESI) calculated for $C_{17}H_{11}F_3N_2O^+$: 317.0896 $[M+H]^+$, found: 317.0905.

***N*-(2-(trifluoromethyl)phenyl)quinoline-2-carboxamide (3q)**



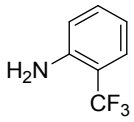
White solid, 42% yield. M.p. 145-146 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.99 (s, 1H), 8.67 (d, *J* = 8.3 Hz, 1H), 8.36 (s, 2H), 8.18 (d, *J* = 8.5 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.80 (t, *J* = 7.7 Hz, 1H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.64 (dd, *J* = 15.0, 7.7 Hz, 2H), 7.27 – 7.24 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.50, 148.99, 146.25, 137.93, 135.68, 133.02, 130.41, 130.06, 129.53, 128.42, 127.67, 126.23 (q, *J* = 5.0 Hz), 124.28 (q, *J* = 273.4 Hz), 123.92, 122.63, 119.65 (q, *J* = 30.3 Hz), 118.58. ^{19}F NMR (471 MHz, $CDCl_3$) δ -60.80. HRMS (ESI) calculated for $C_{17}H_{11}F_3N_2O^+$: 317.0896 $[M+H]^+$, found: 317.0906.

(3,3,3-trifluoroprop-1-ene-1,1-diyl)dibenzene (3aa)[2]



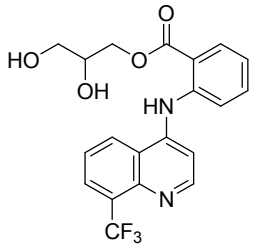
Colourless oil, 21% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 6.3, 2.8 Hz, 3H), 7.34 – 7.31 (m, 3H), 7.26 – 7.22 (m, 4H), 6.12 (q, *J* = 8.3 Hz, 1H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -55.59.

2-(trifluoromethyl)aniline (4a)[1]



Colourless oil, 90% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.9 Hz, 1H), 7.30 (dd, *J* = 11.4, 4.0 Hz, 1H), 6.79 (t, *J* = 7.6 Hz, 1H), 6.74 (d, *J* = 8.2 Hz, 1H), 4.04 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.45 (q, *J* = 1.3 Hz), 131.82 (q, *J* = 1.3 Hz), 125.50 (q, *J* = 5.0 Hz), 124.02 (q, *J* = 272.2 Hz), 116.58, 116.08, 112.80 (q, *J* = 30.3 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -60.92.

2,3-dihydroxypropyl 2-((8-(trifluoromethyl)quinolin-4-yl)amino)benzoate (5a)[3]



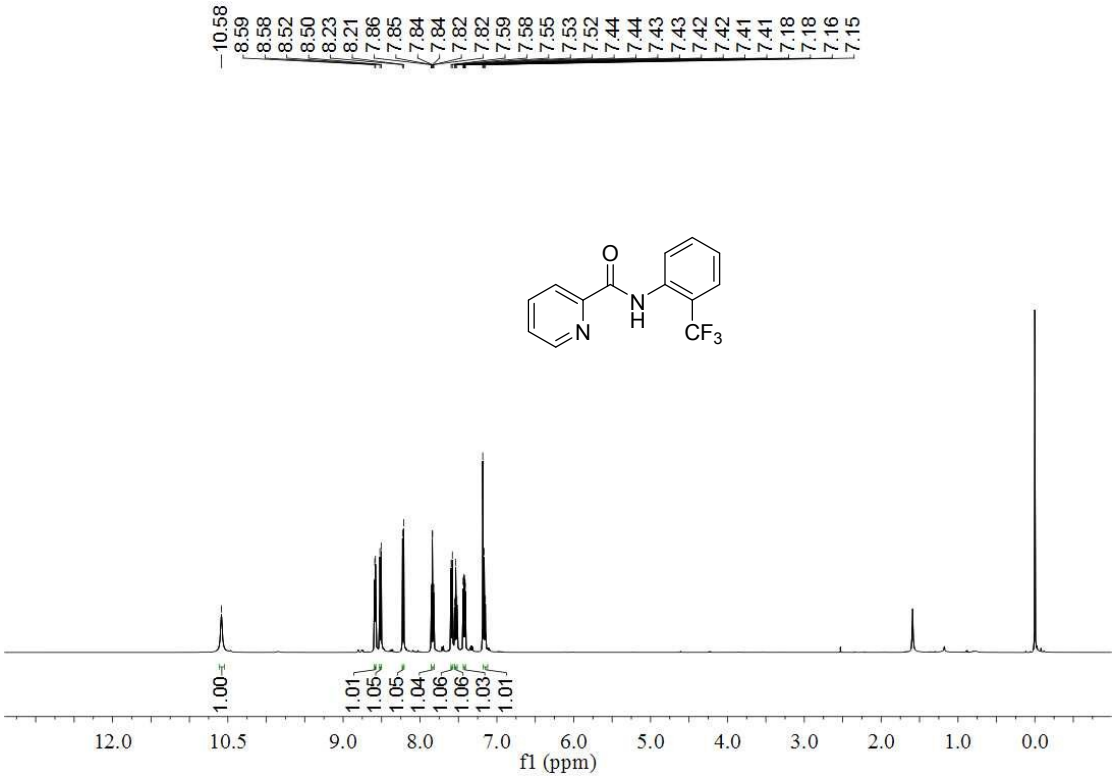
White solid, 45% yield. M.p. 179-180 ^{o}C. ^{1}H NMR (400 MHz, MeOD) δ 8.69 (d, *J* = 5.3 Hz, 1H), 8.42 (d, *J* = 8.4 Hz, 1H), 8.12 (d, *J* = 7.0 Hz, 1H), 8.11 – 8.08 (m, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.68 – 7.65 (m, 1H), 7.59 – 7.56 (m, 1H), 7.52 (d, *J* = 5.3 Hz, 1H), 7.11 – 7.07 (m, 1H), 3.69 (dd, *J* = 10.4, 5.2 Hz, 1H), 3.62 (dd, *J* = 11.3, 4.7 Hz, 2H), 3.56 (dd, *J* = 11.3, 6.0 Hz, 2H); ^{13}C NMR (101 MHz, MeOD) δ 169.87, 152.19, 147.12, 146.43, 144.22, 135.09, 132.79, 129.21 (q, *J* = 5.0 Hz), 128.24 (q, *J* = 28.3 Hz), 126.52, 125.52, 125.20 (q, *J* = 234.4 Hz), 123.07, 122.52, 119.17, 117.52, 106.05, 73.36, 64.19; ^{19}F NMR (471 MHz, MeOD) δ -61.02. HRMS (ESI) calculated for $C_{20}H_{17}F_3N_2O_4^+$: 407.1213 $[M+H]^+$, found: 407.1208.

References:

1. J. Xu, L. Qiao, J. Shen, K. Chai, C. Shen, P. Zhang, *Org. Lett.*, 2017, **19**, 5661.
2. C. Shen, J. Xu, B. Ying, P. Zhang, *ChemCatChem*, 2016, **8**, 3560.
3. G. Mouzin, H. Cousse, J. M. Autin, *Synthesis*, 1980, 55.

Copies of NMR Spectra

3a ^{1}H NMR



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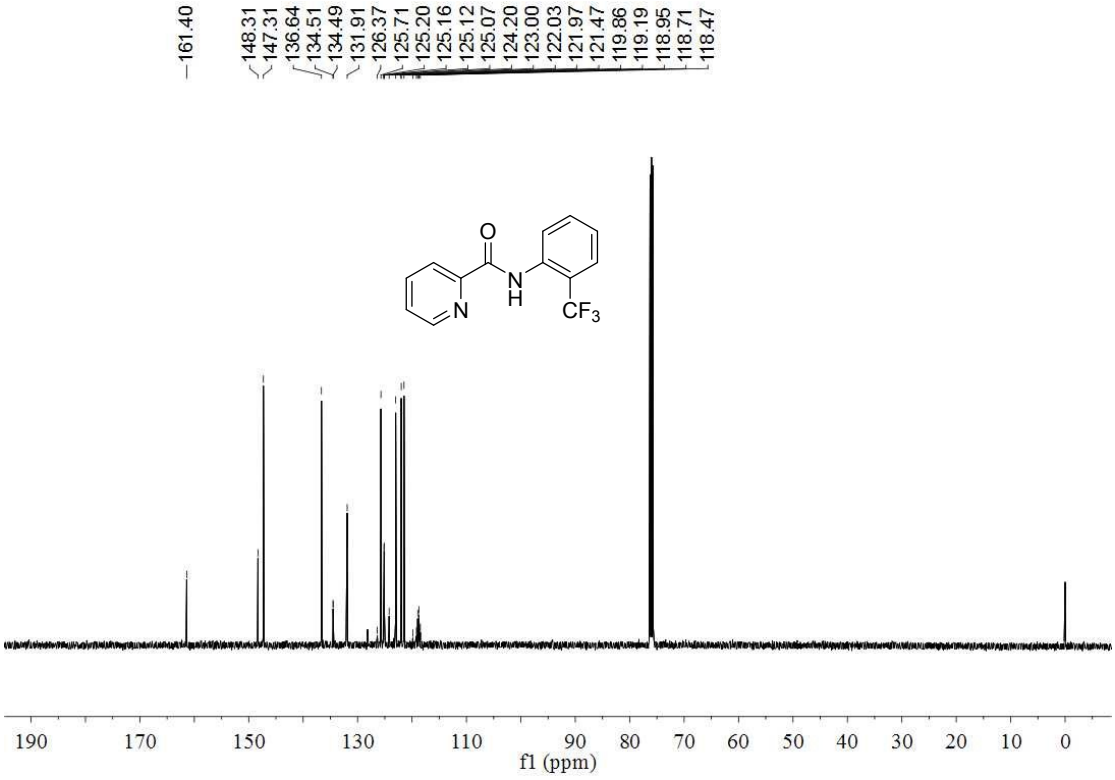

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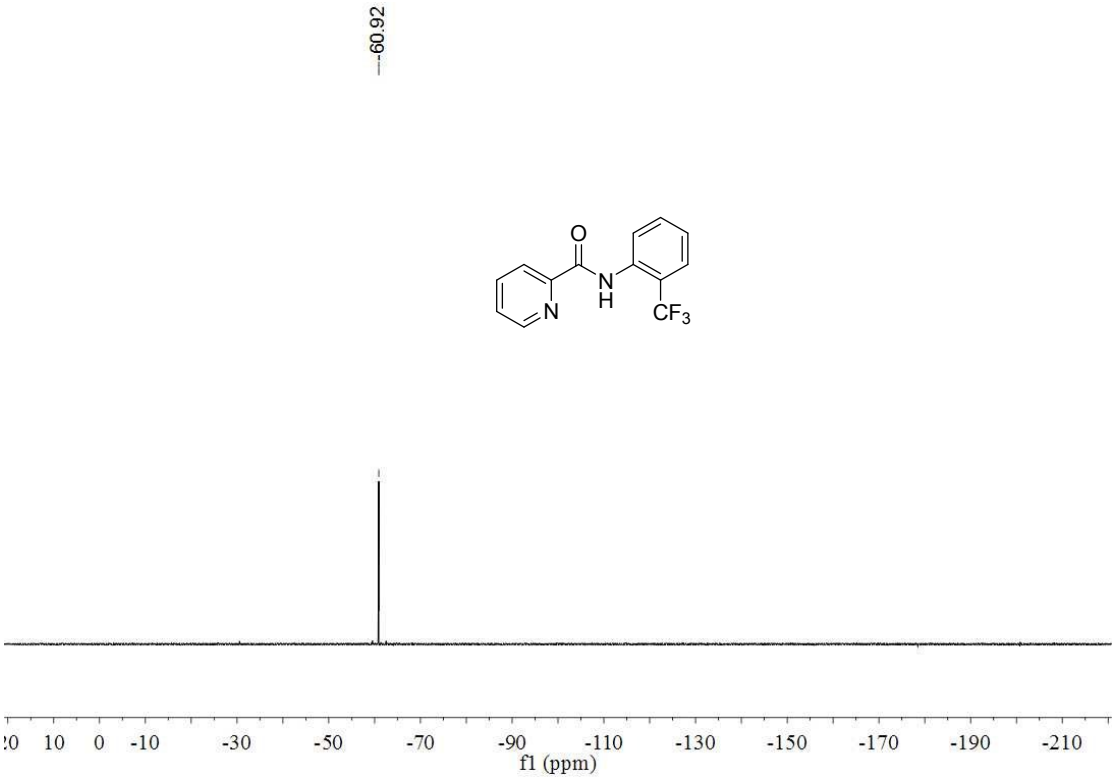

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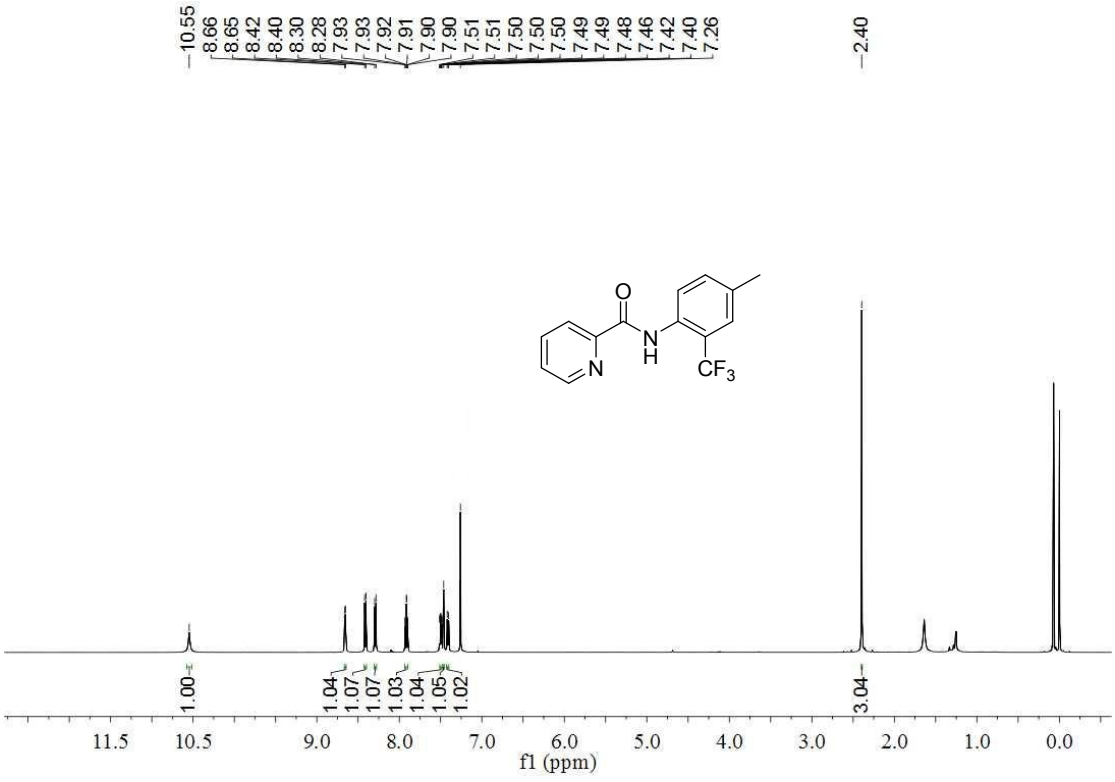

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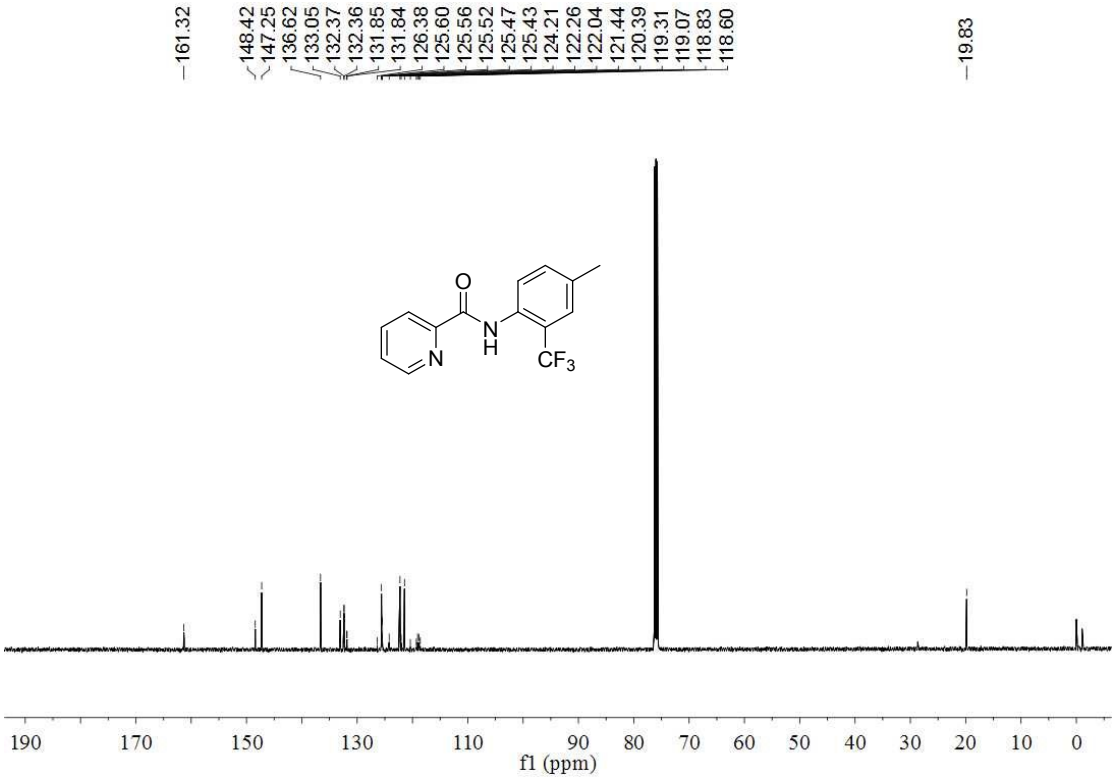

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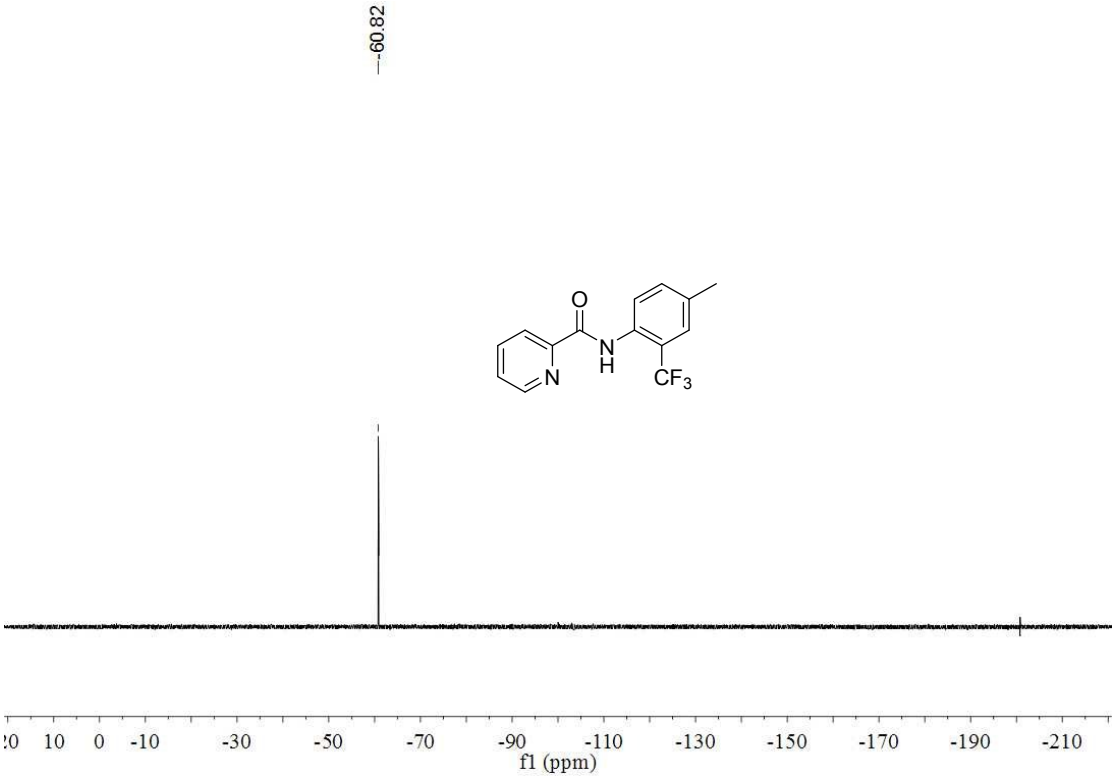

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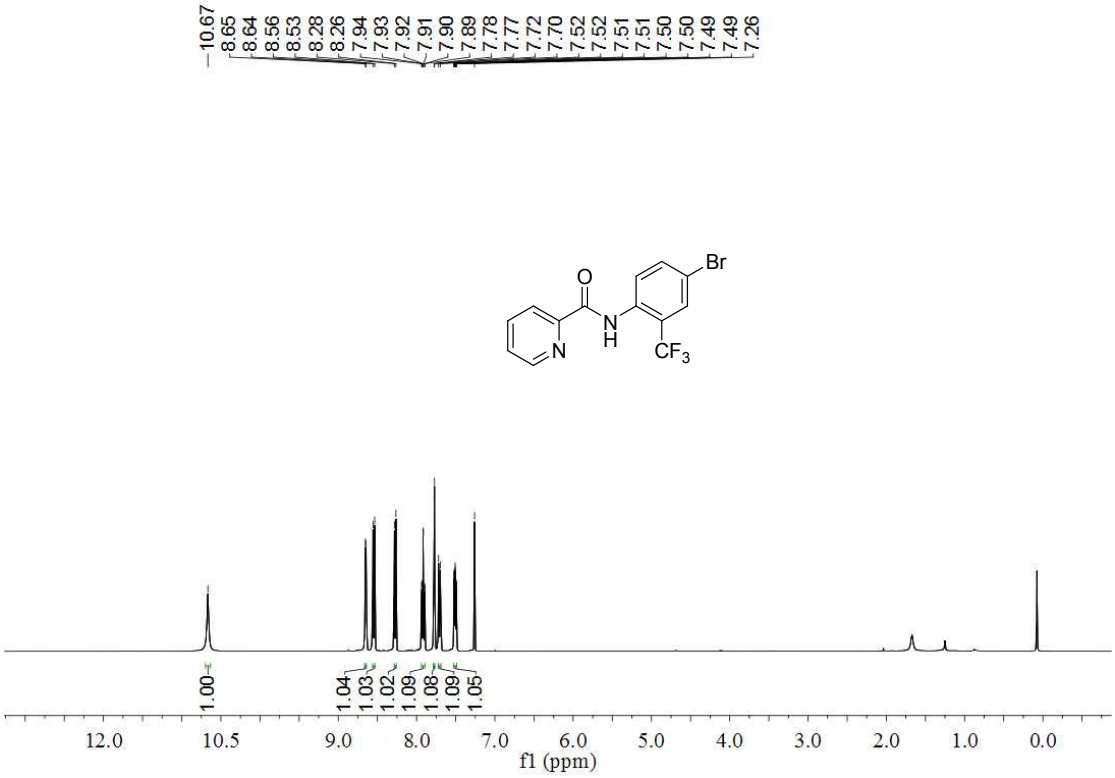

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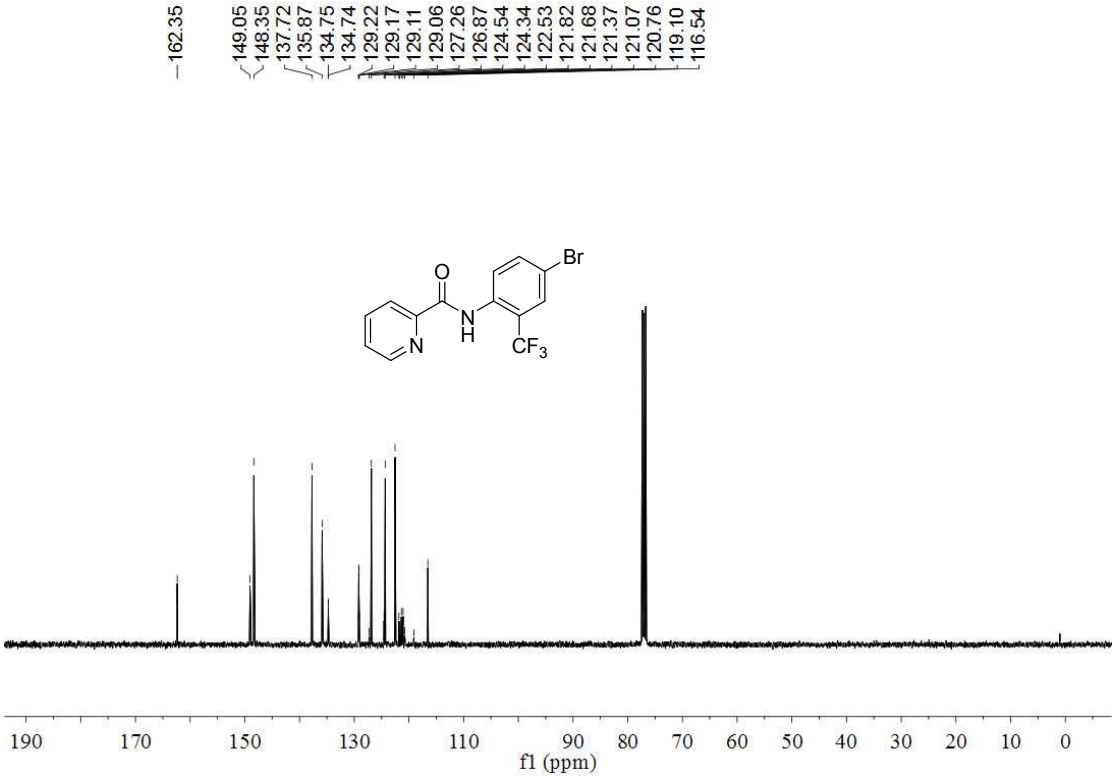

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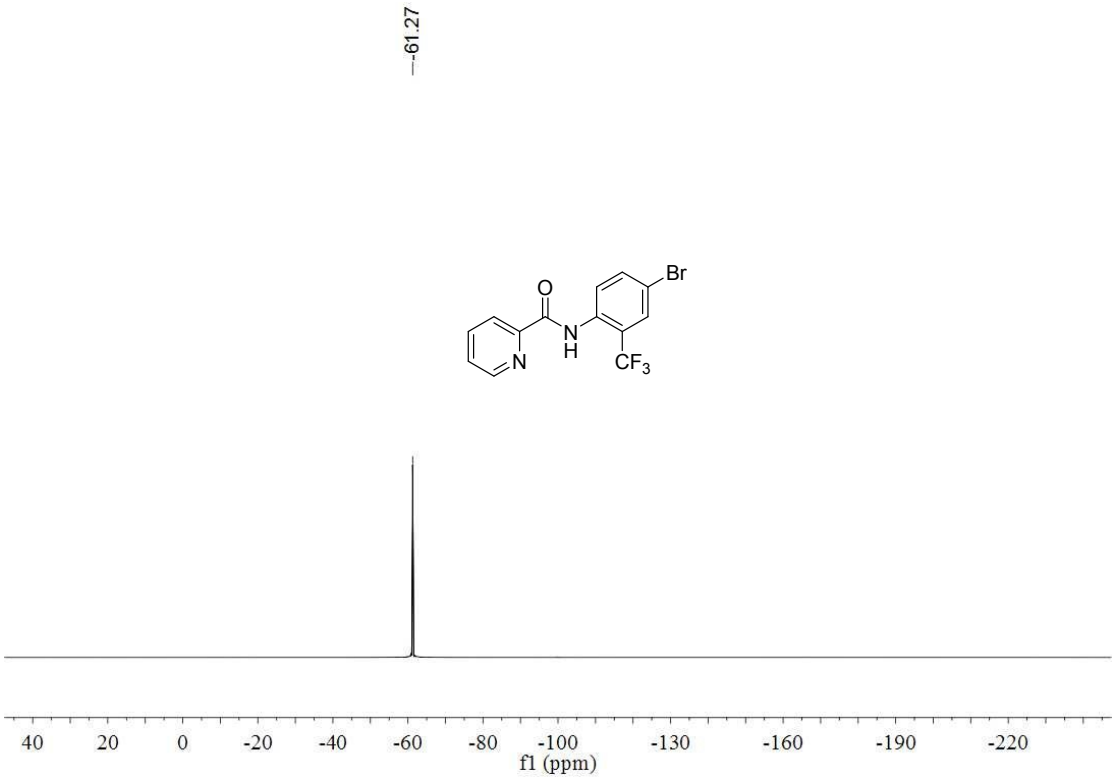

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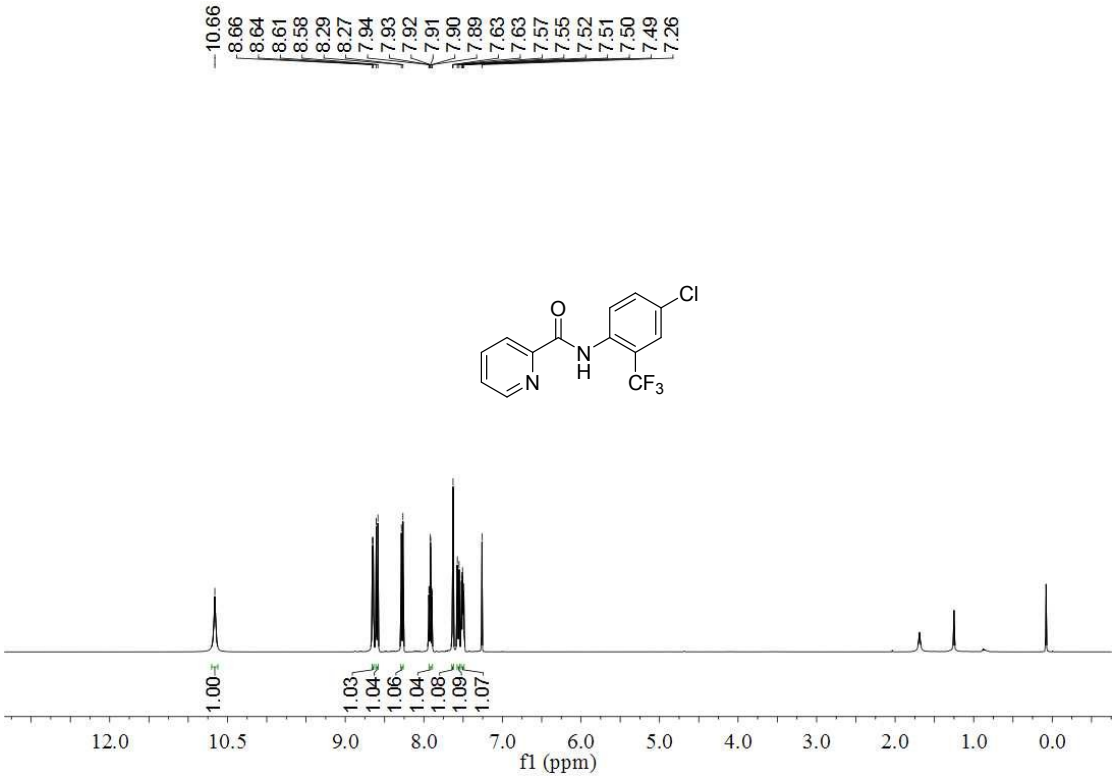

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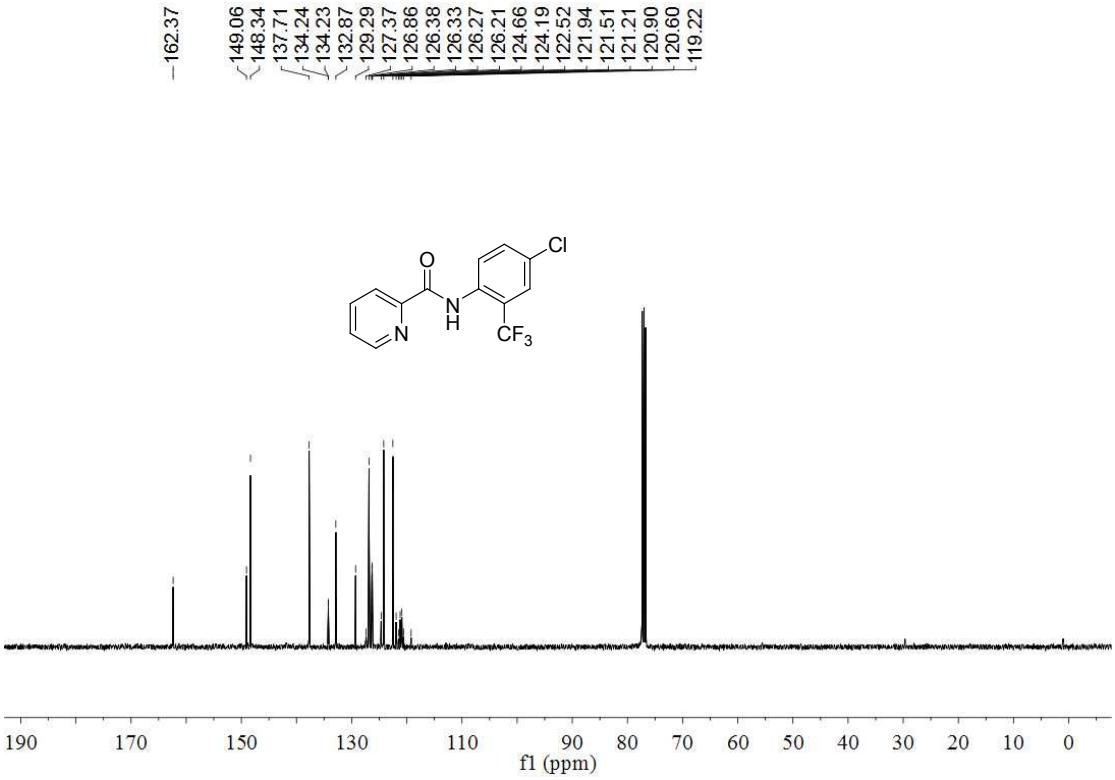

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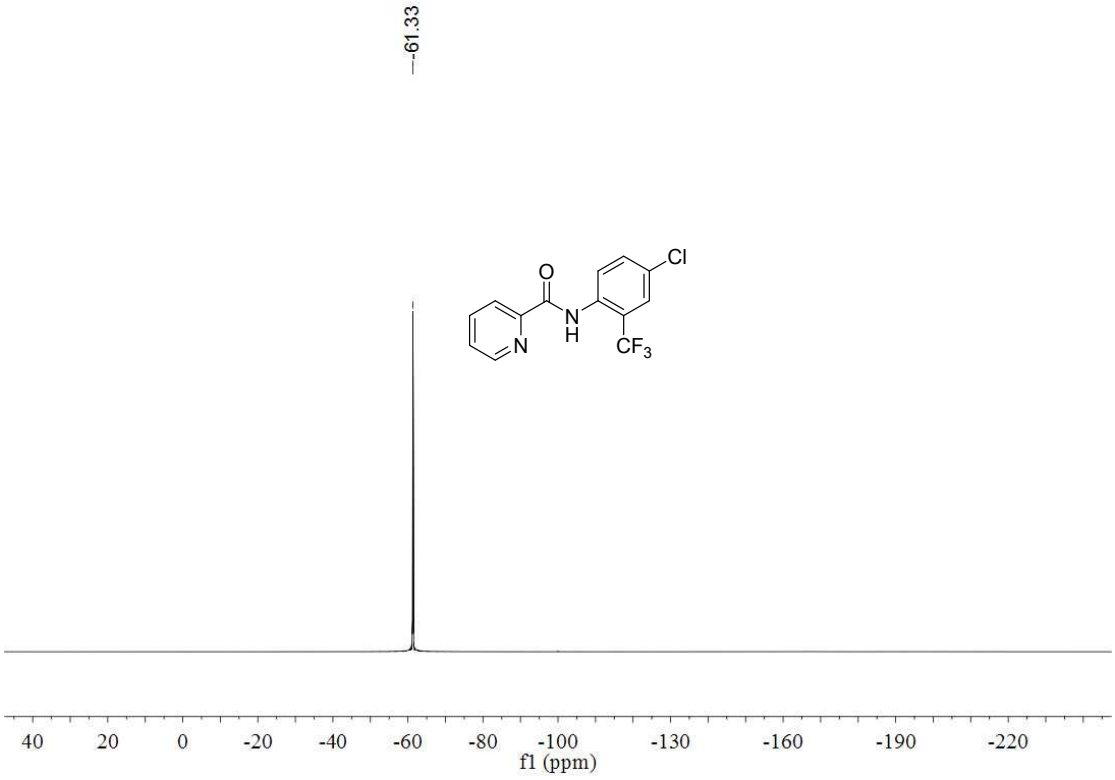

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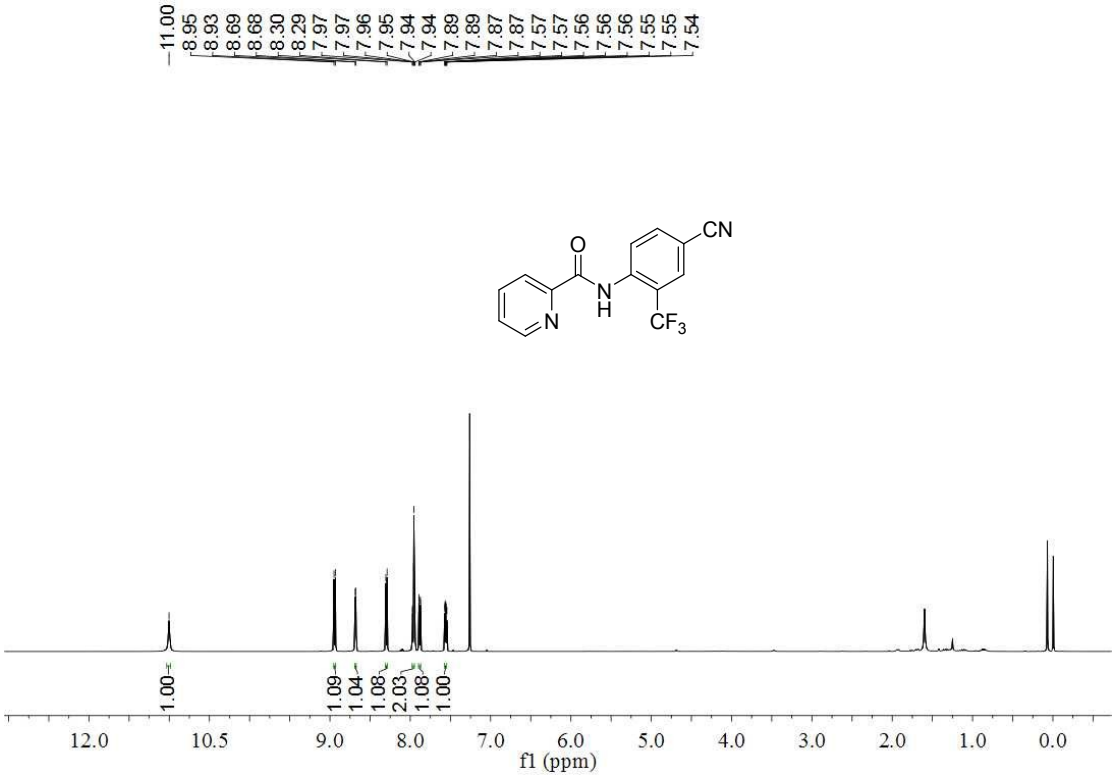

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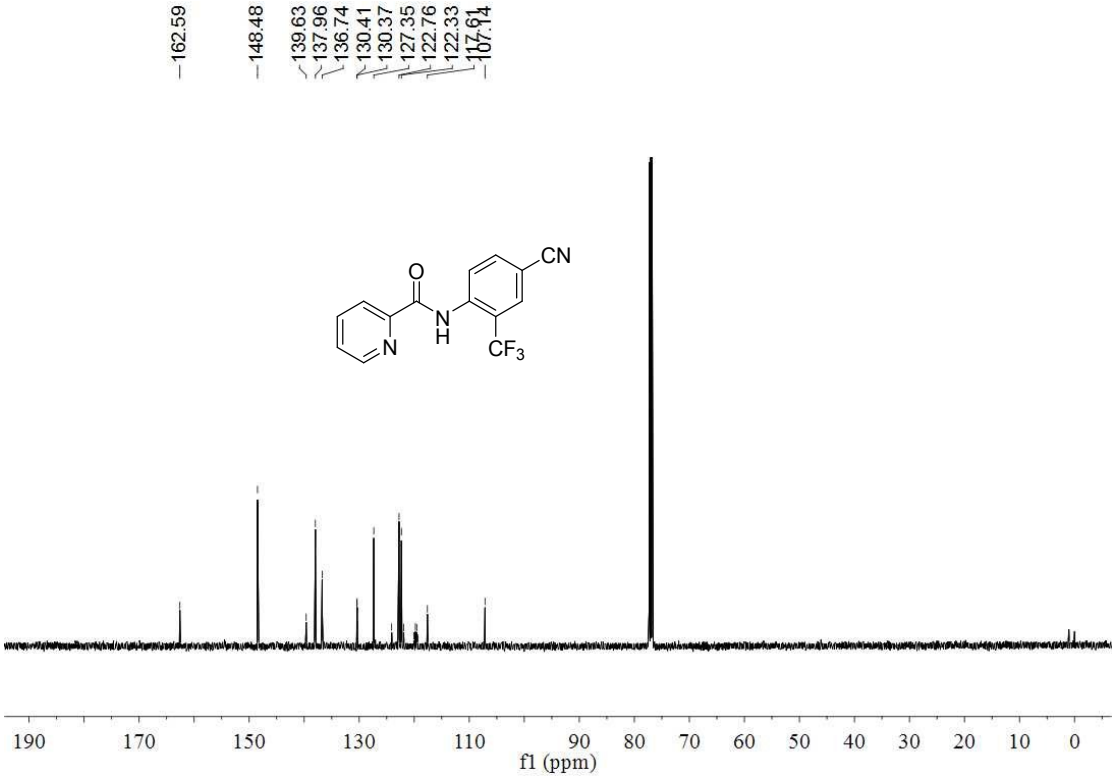

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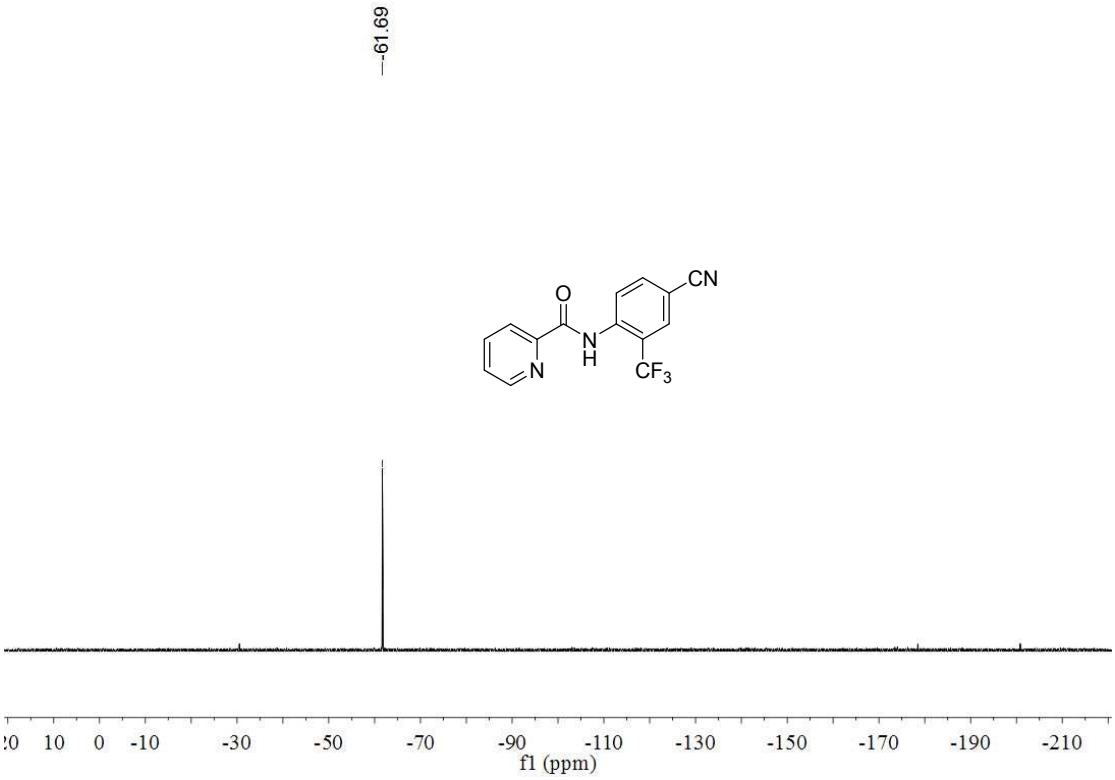

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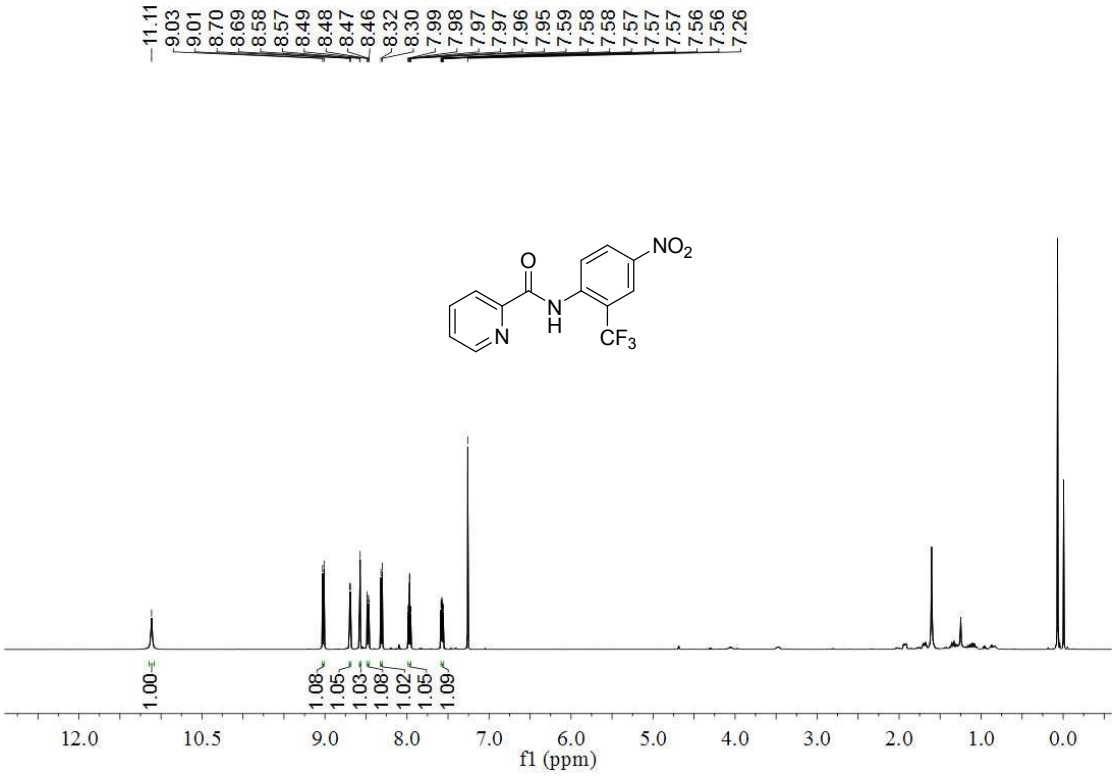

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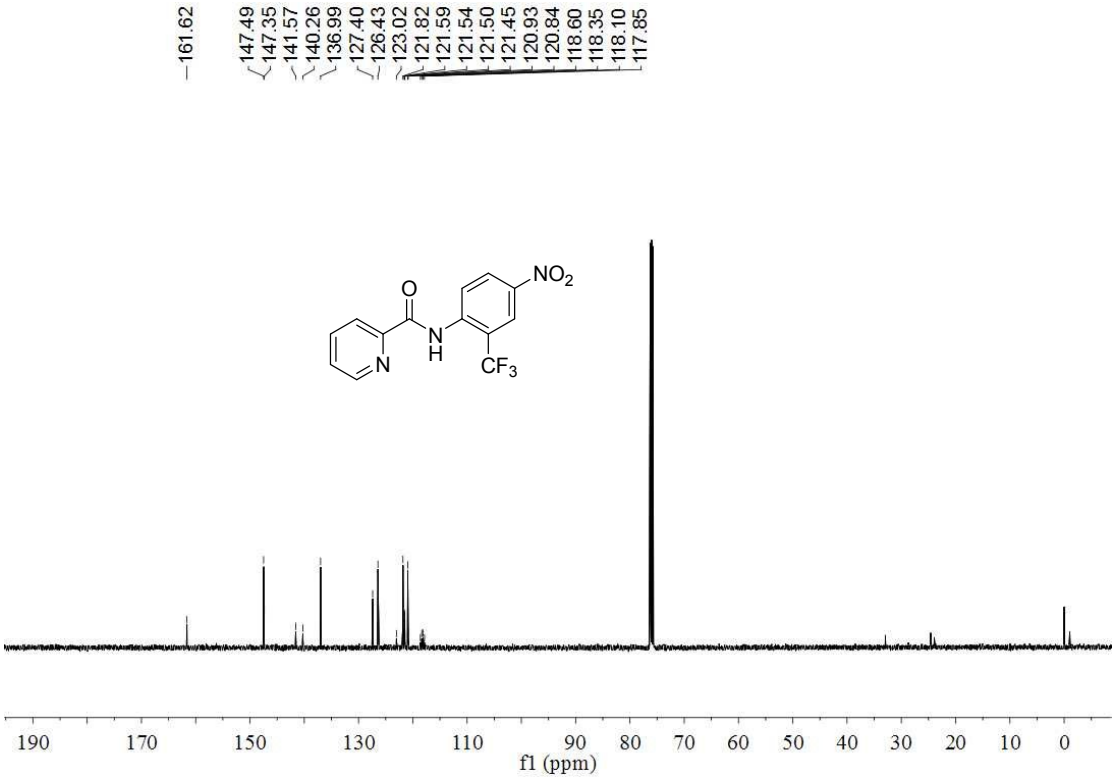

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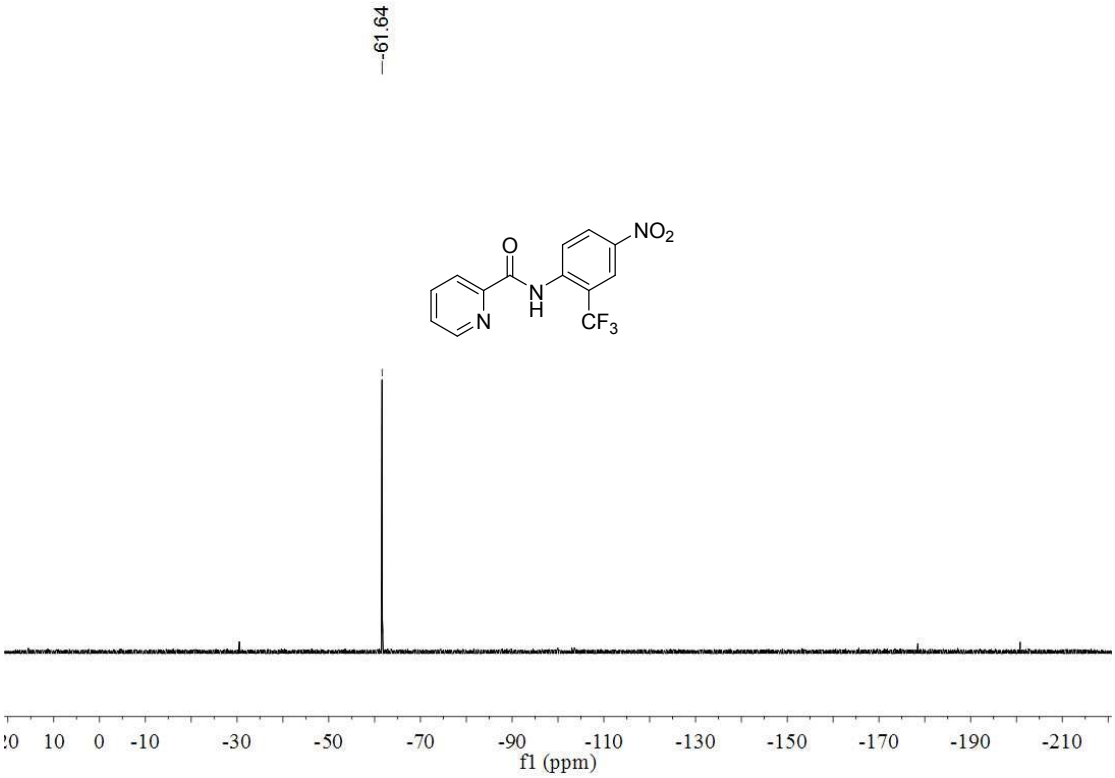

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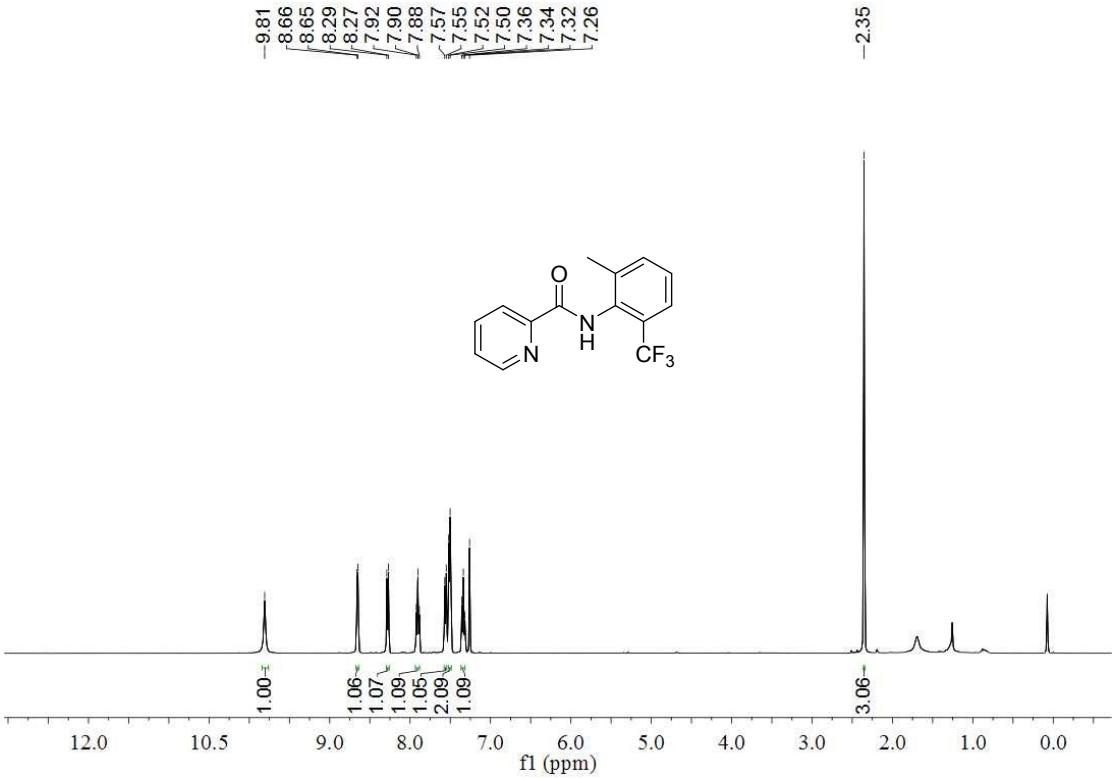

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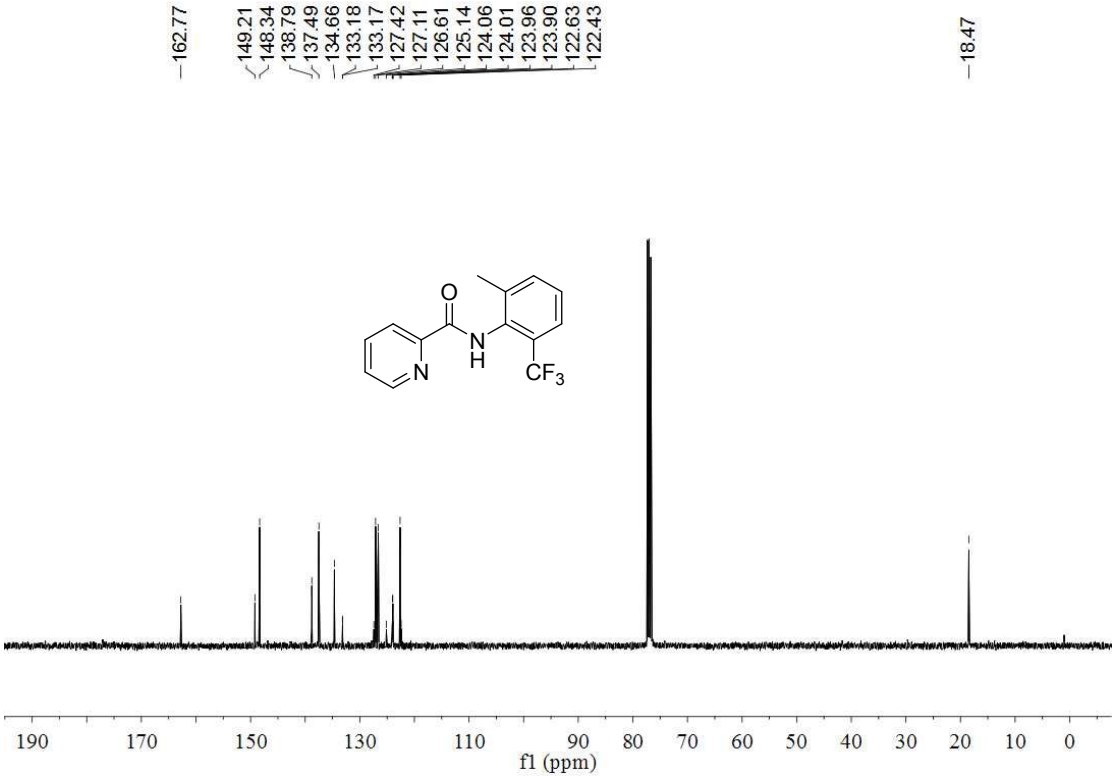

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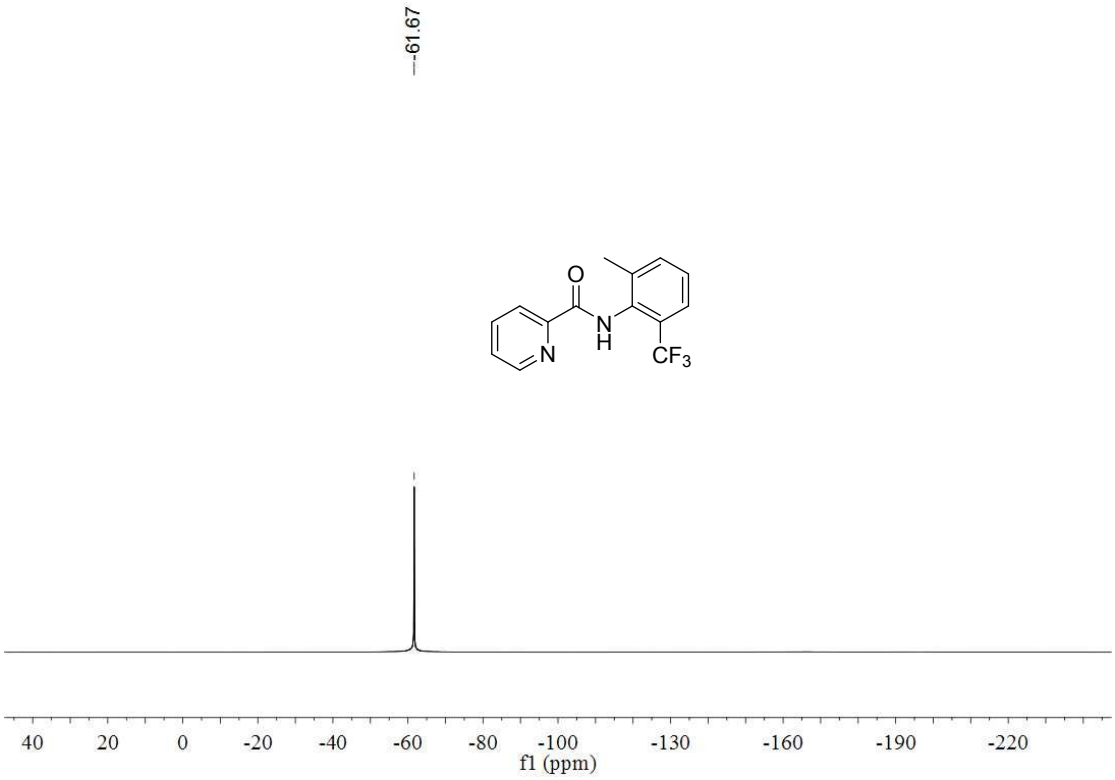

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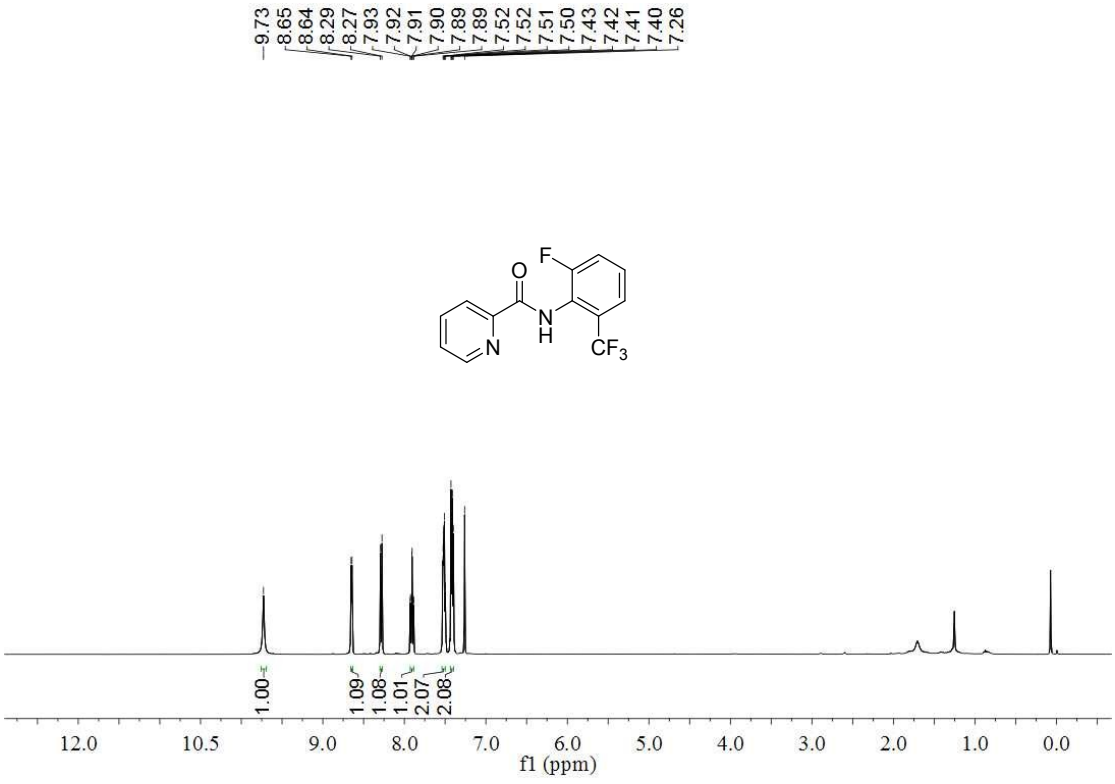

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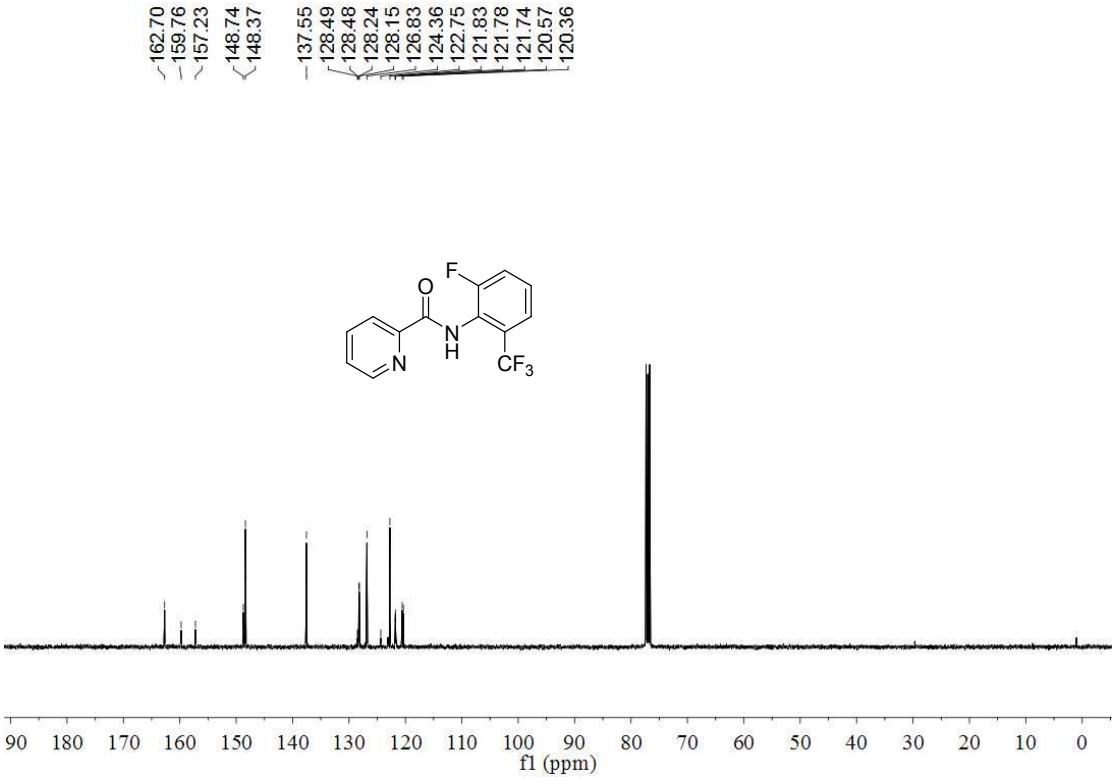

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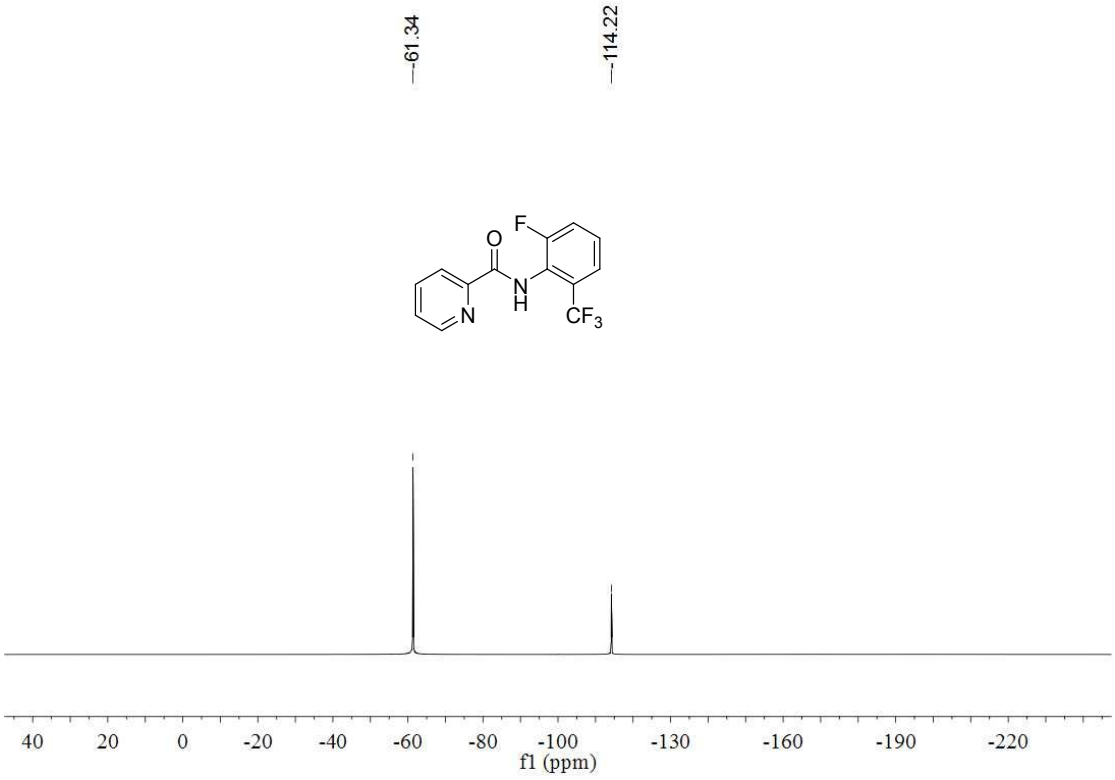

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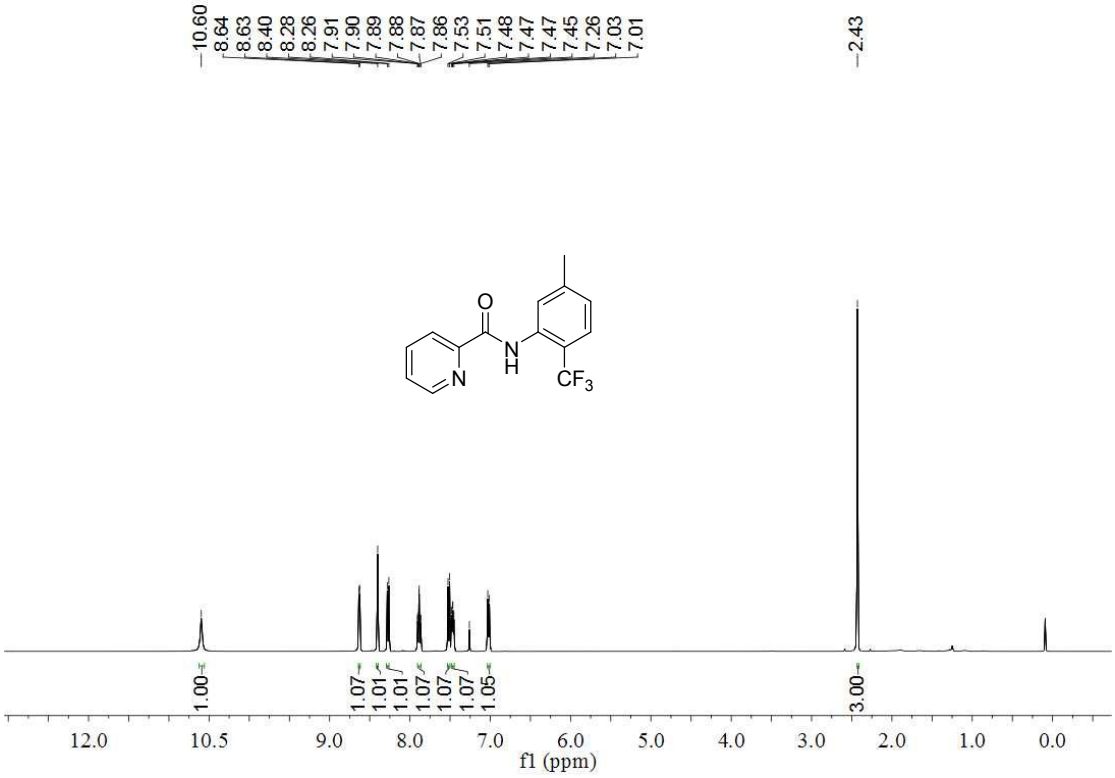

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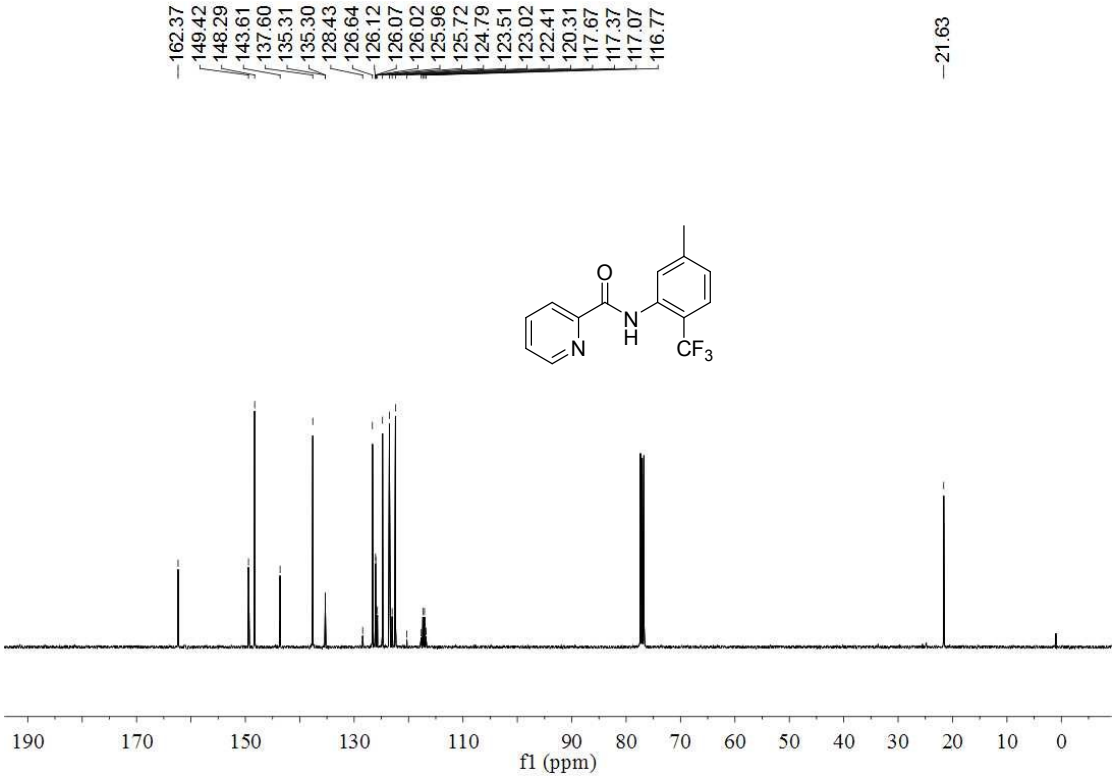

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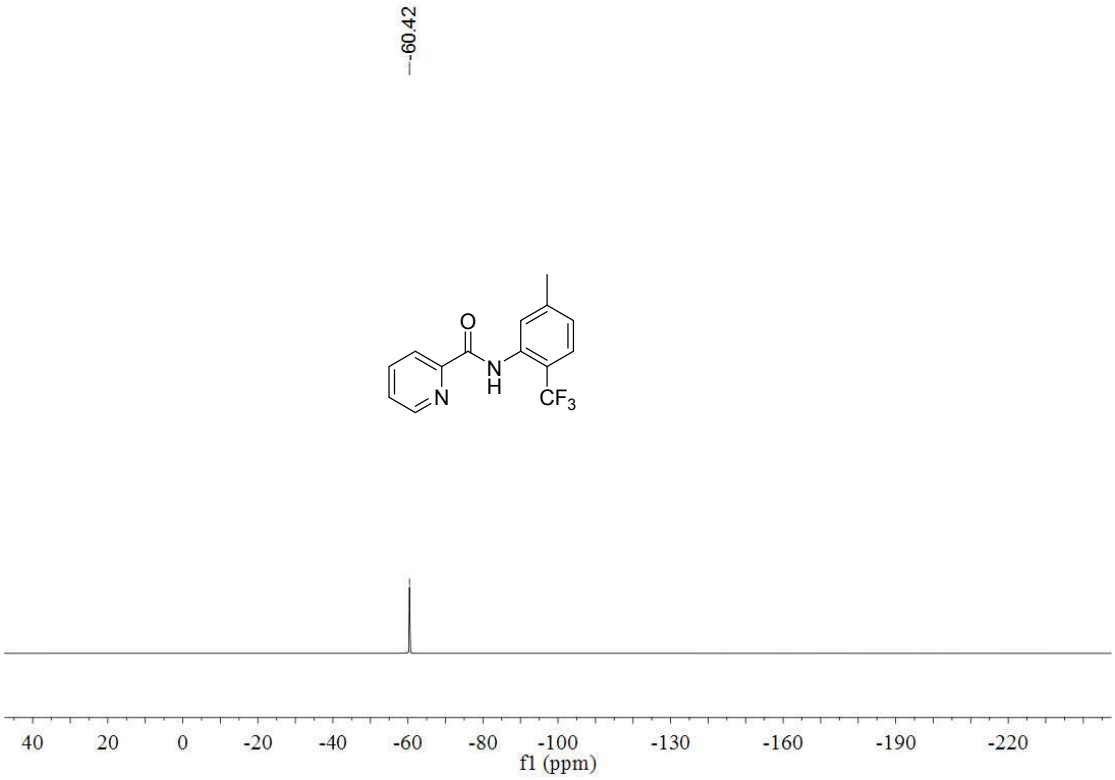

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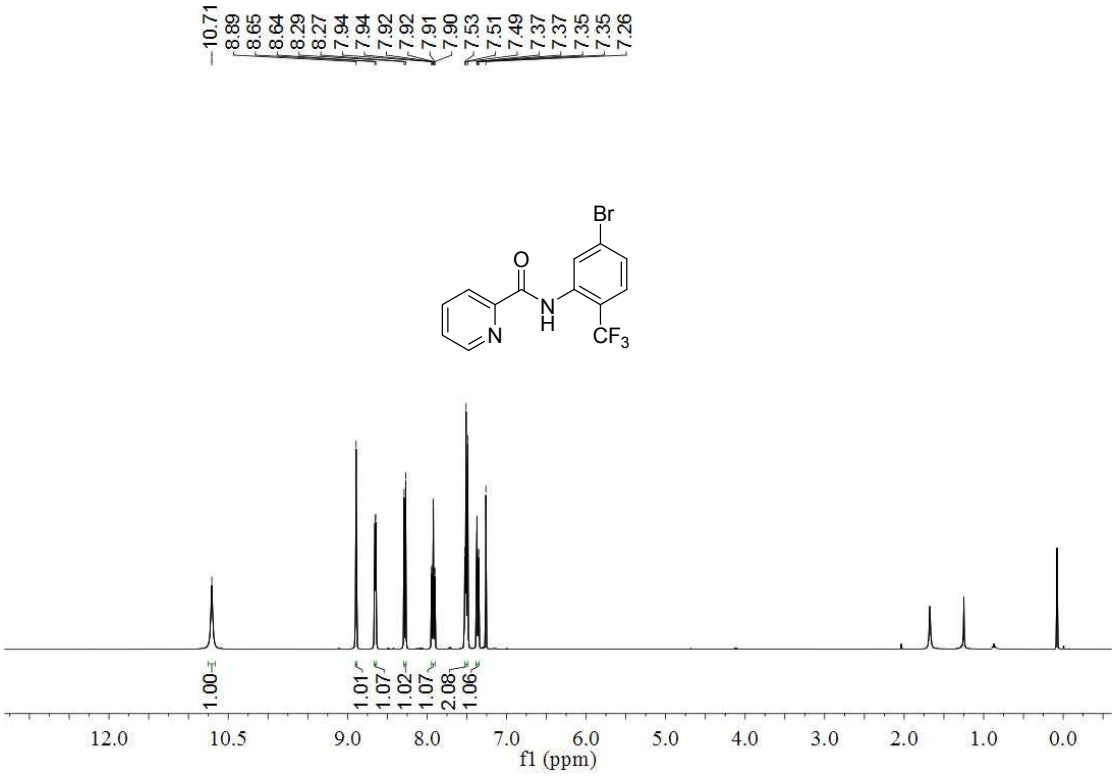

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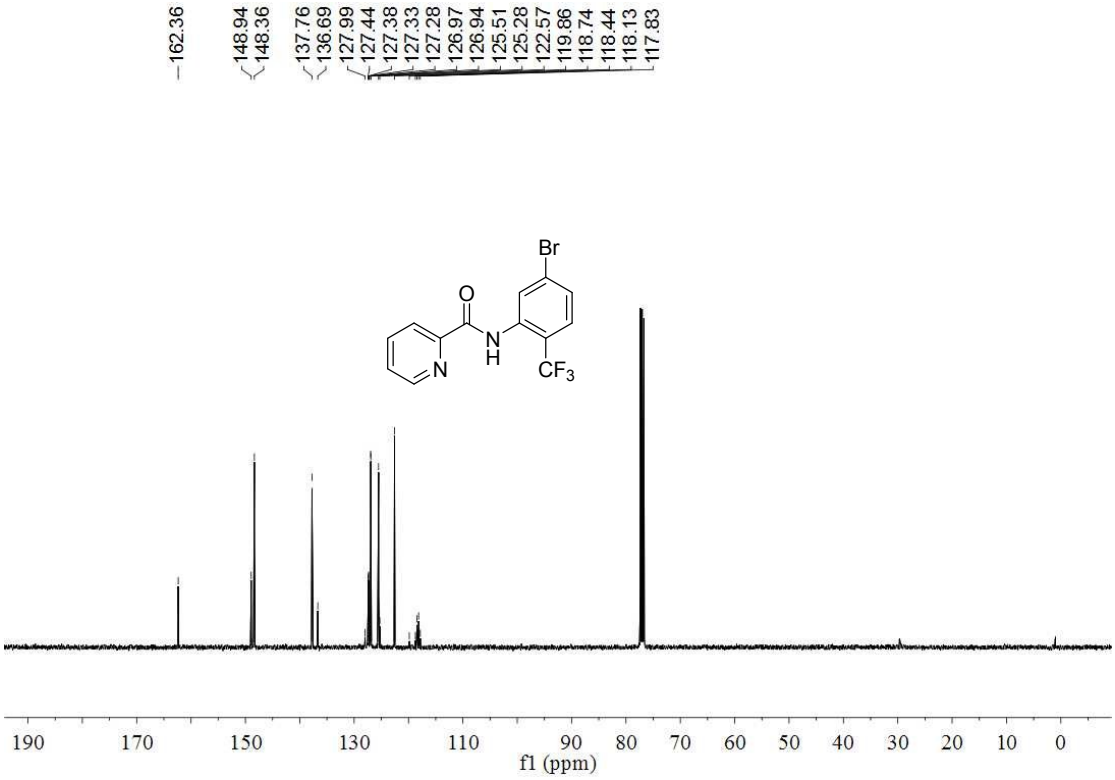

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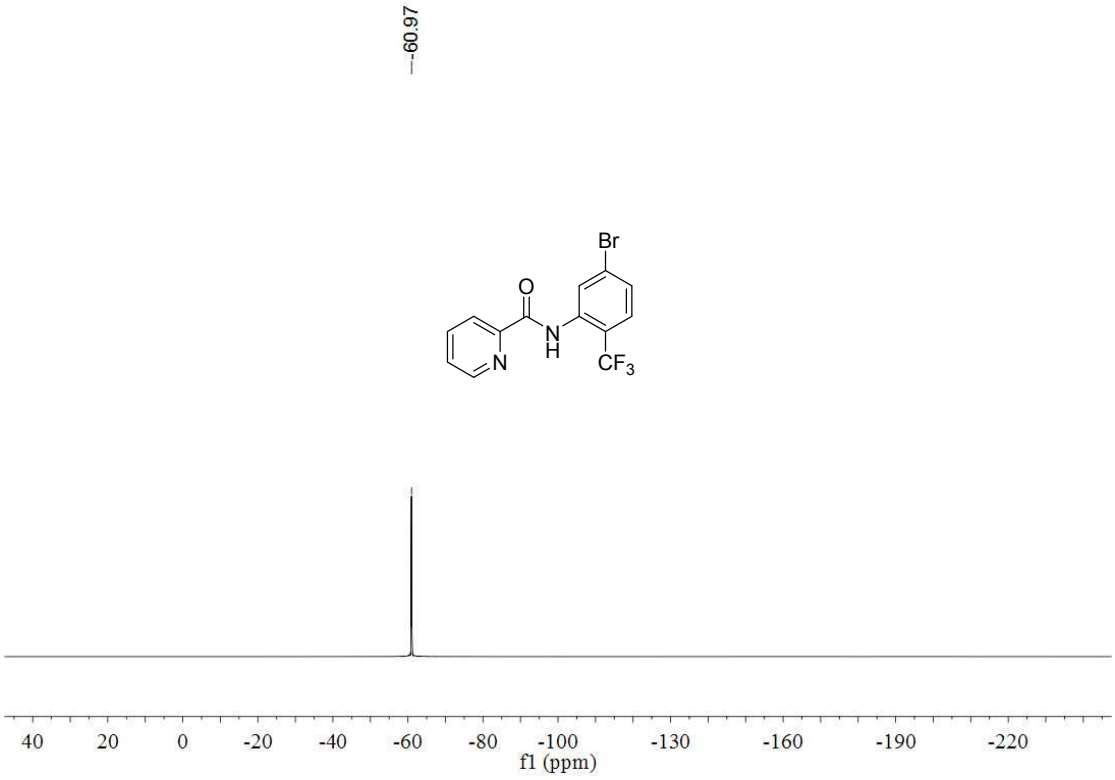

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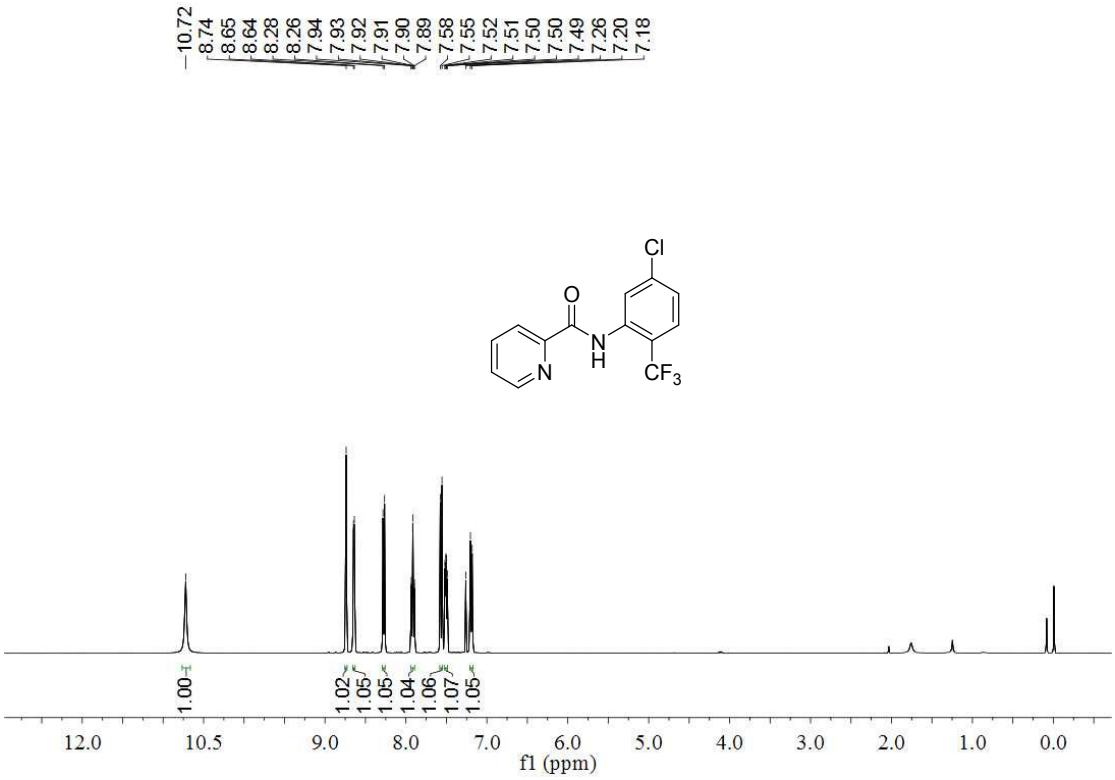

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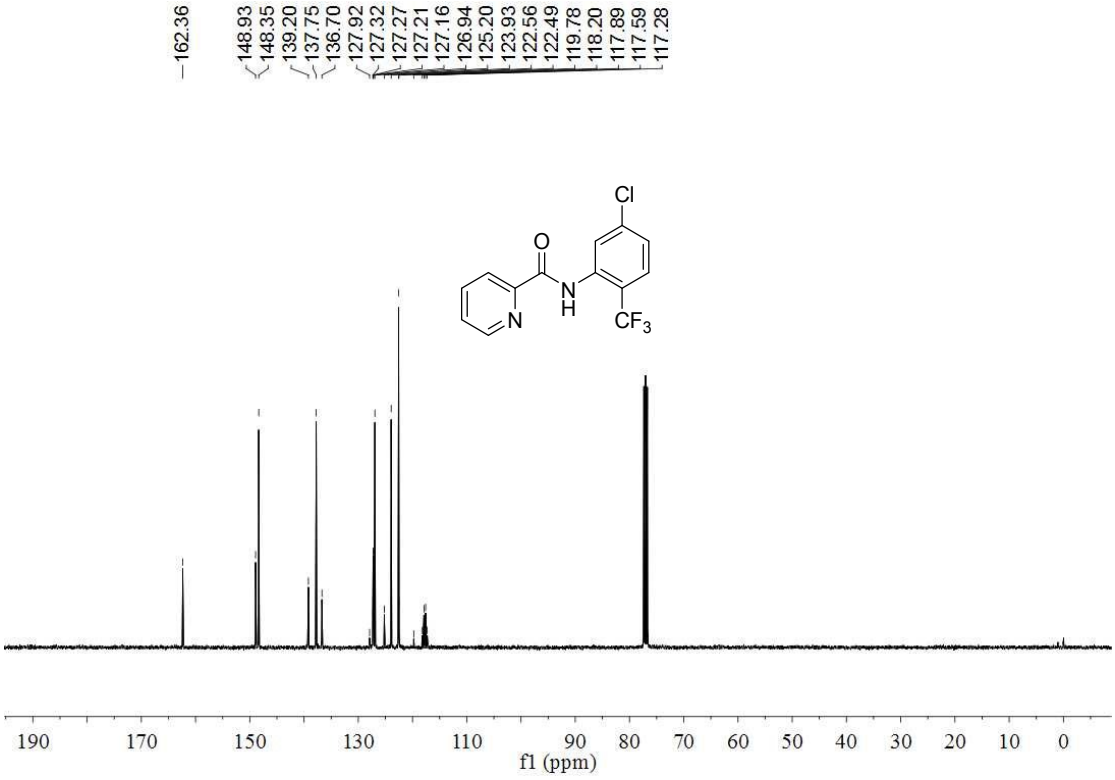

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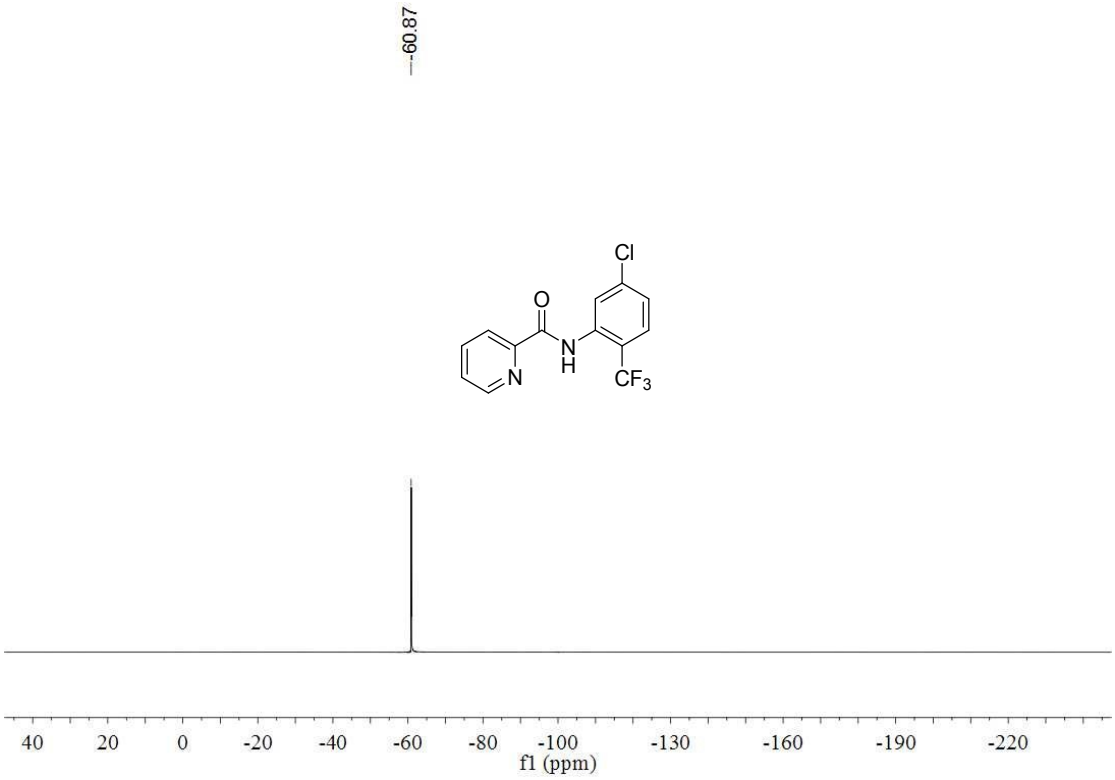

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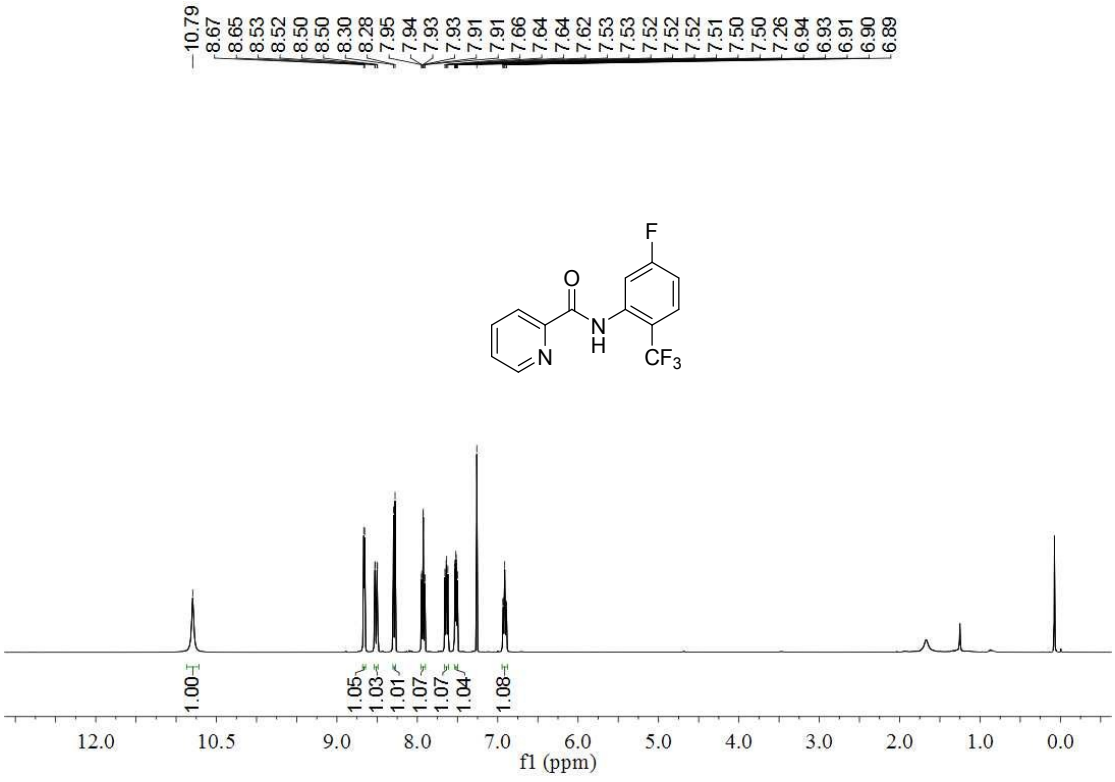

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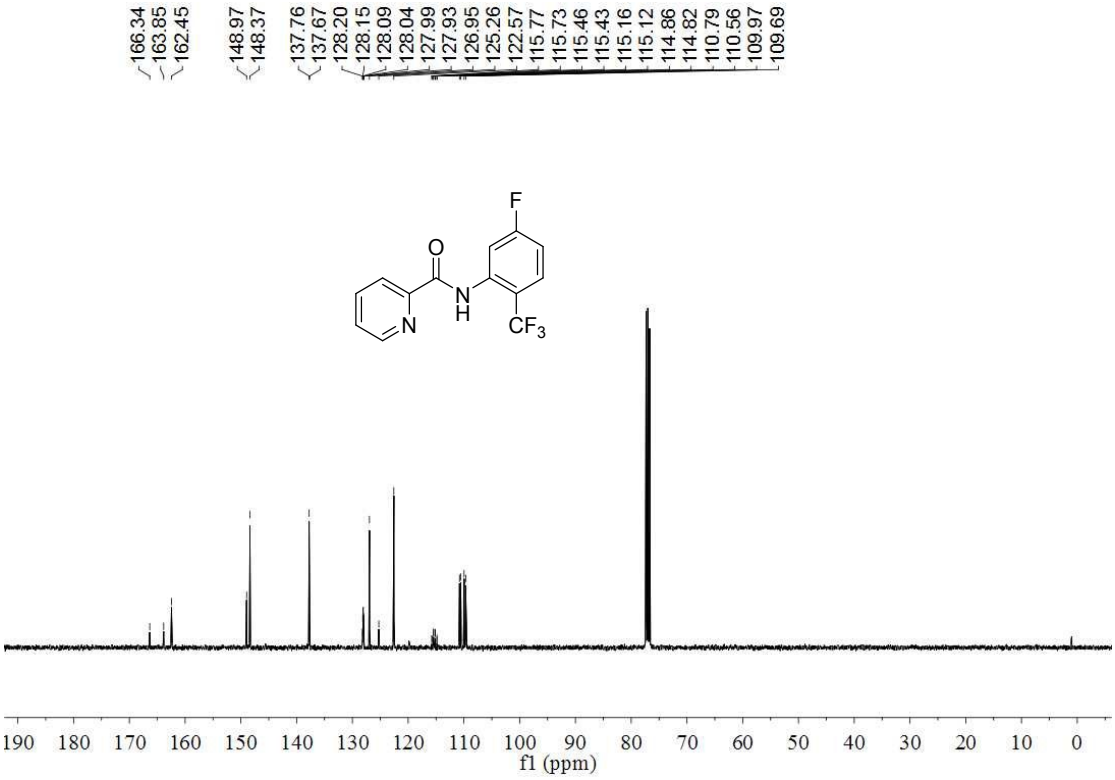

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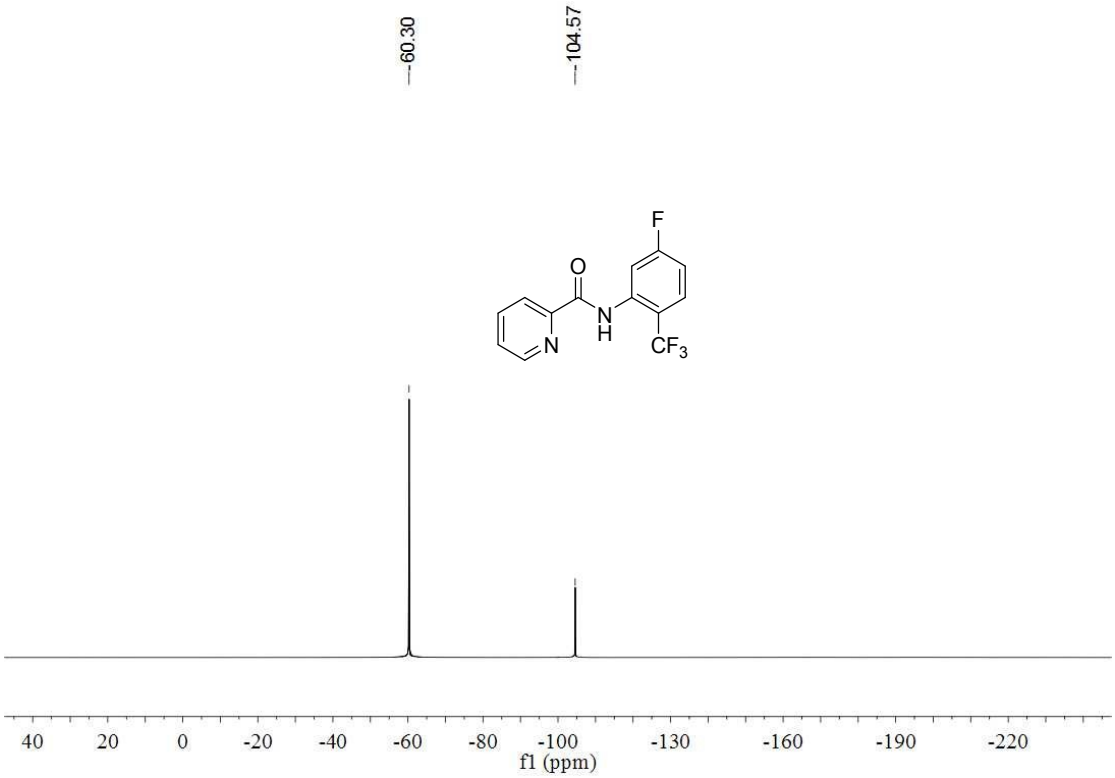

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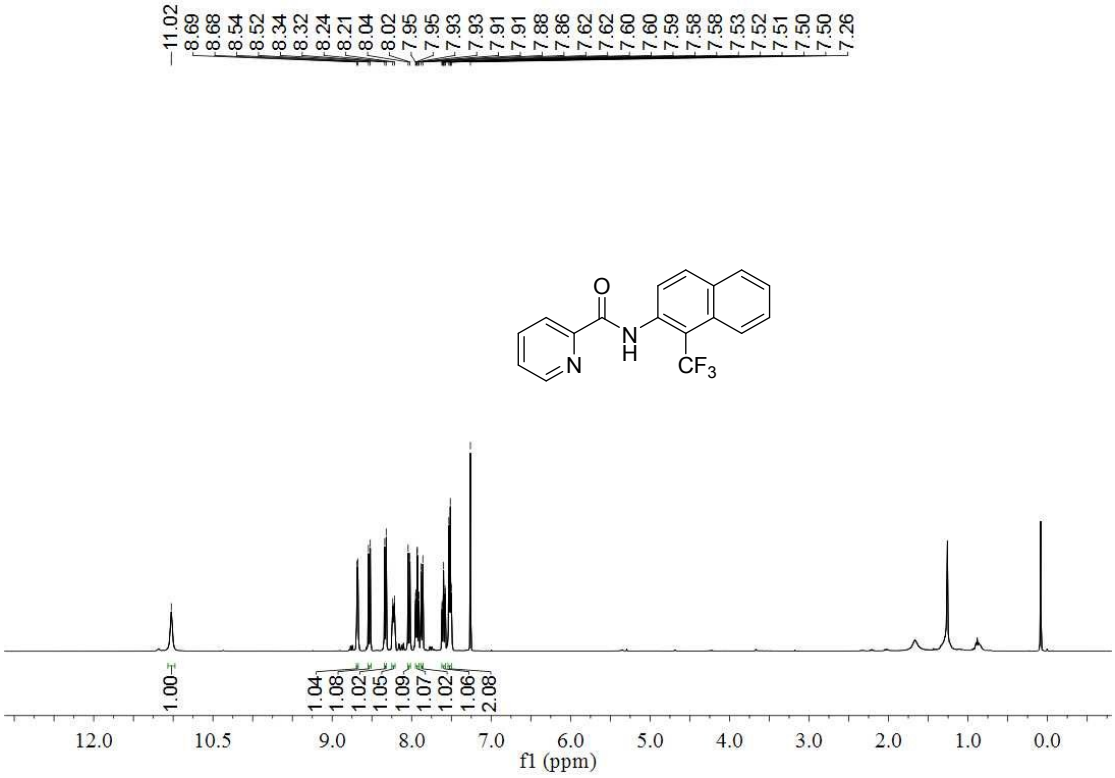
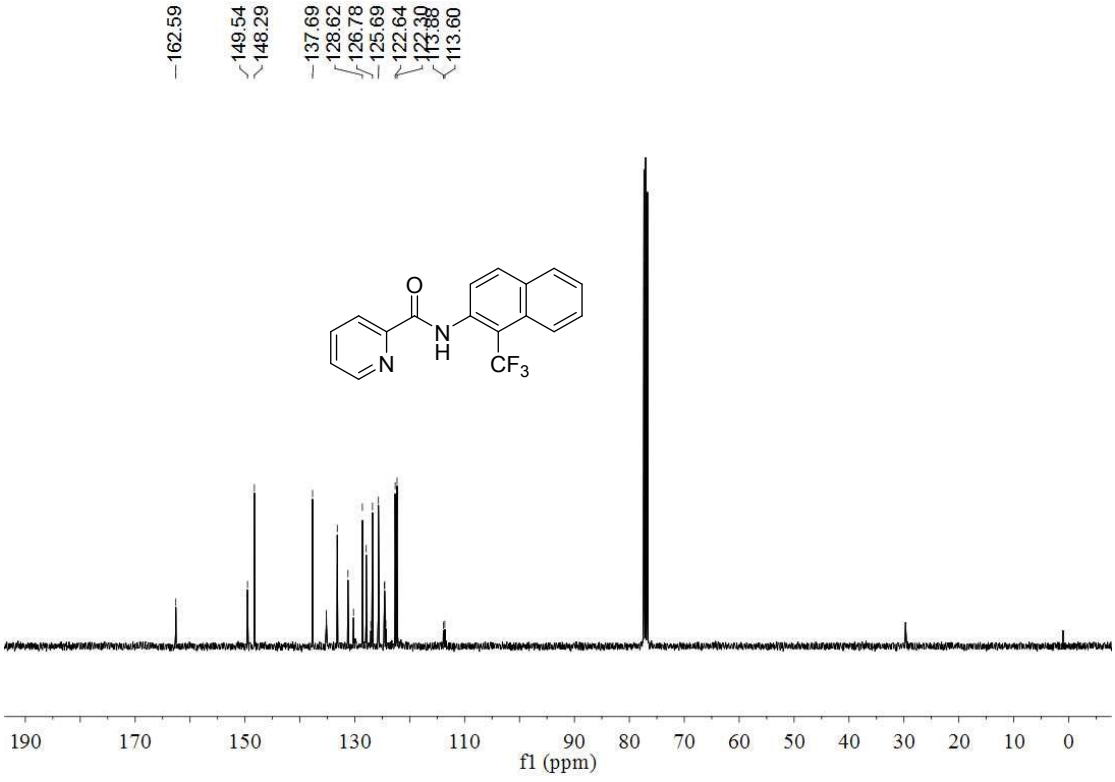
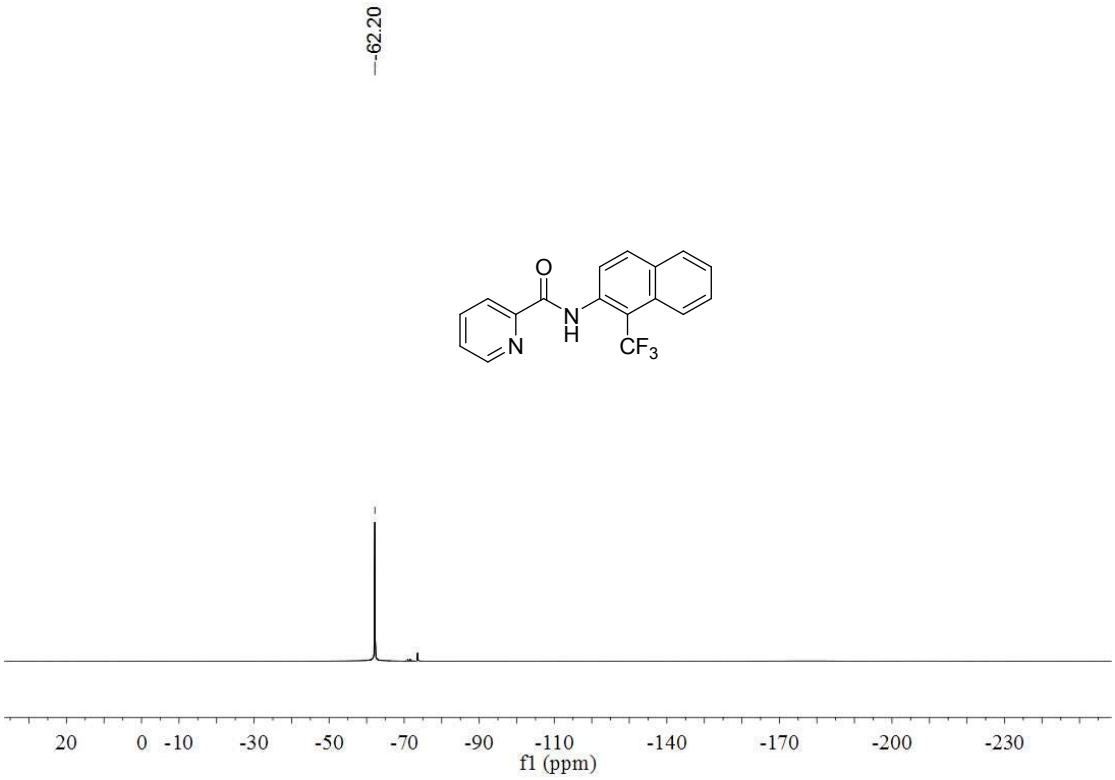


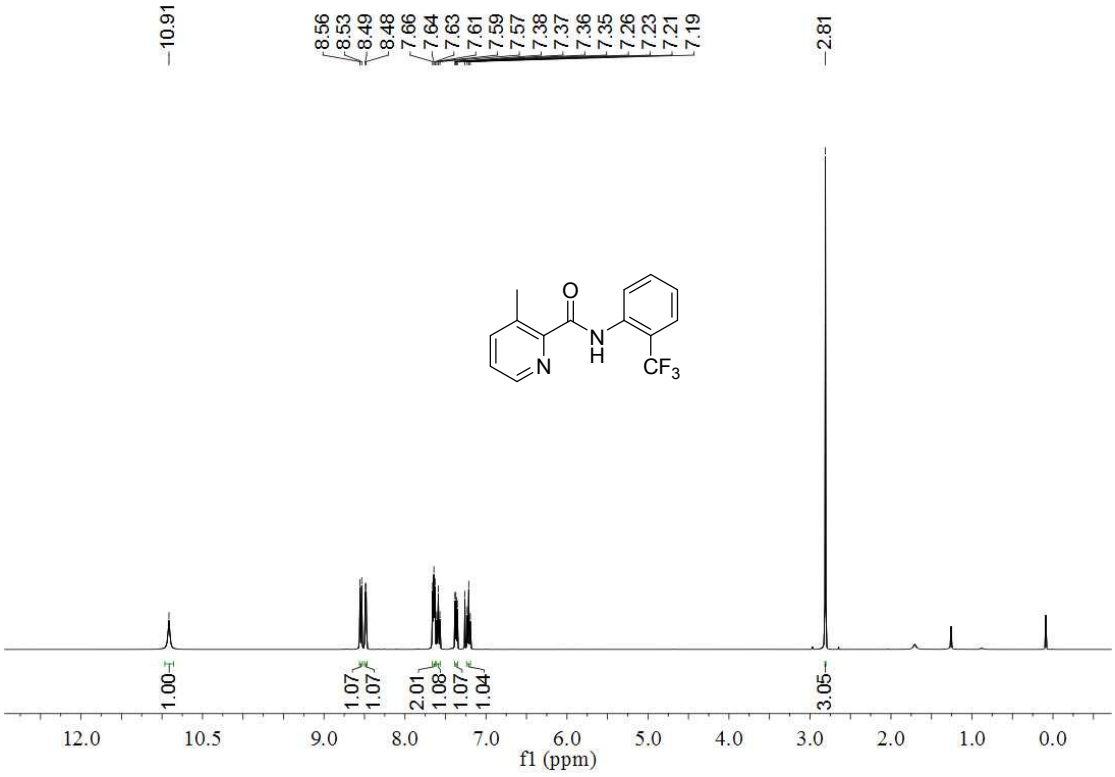
3m ^{13}C NMR



3m ^{19}F NMR



3n ^{1}H NMR



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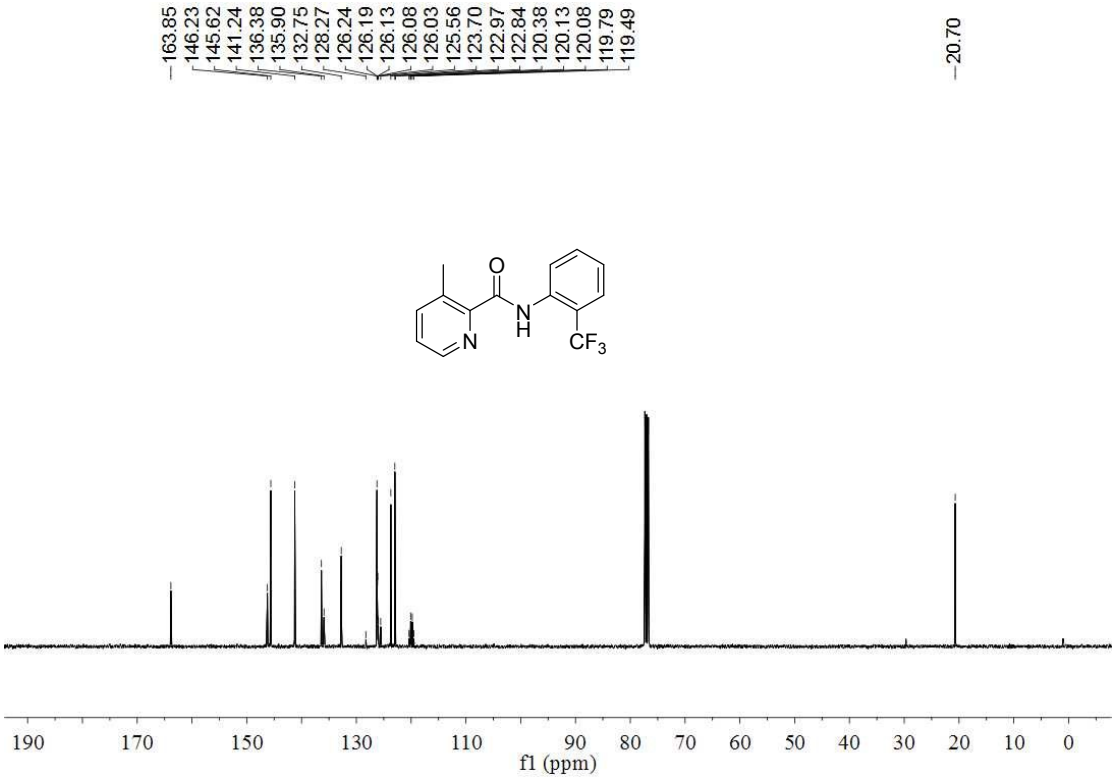
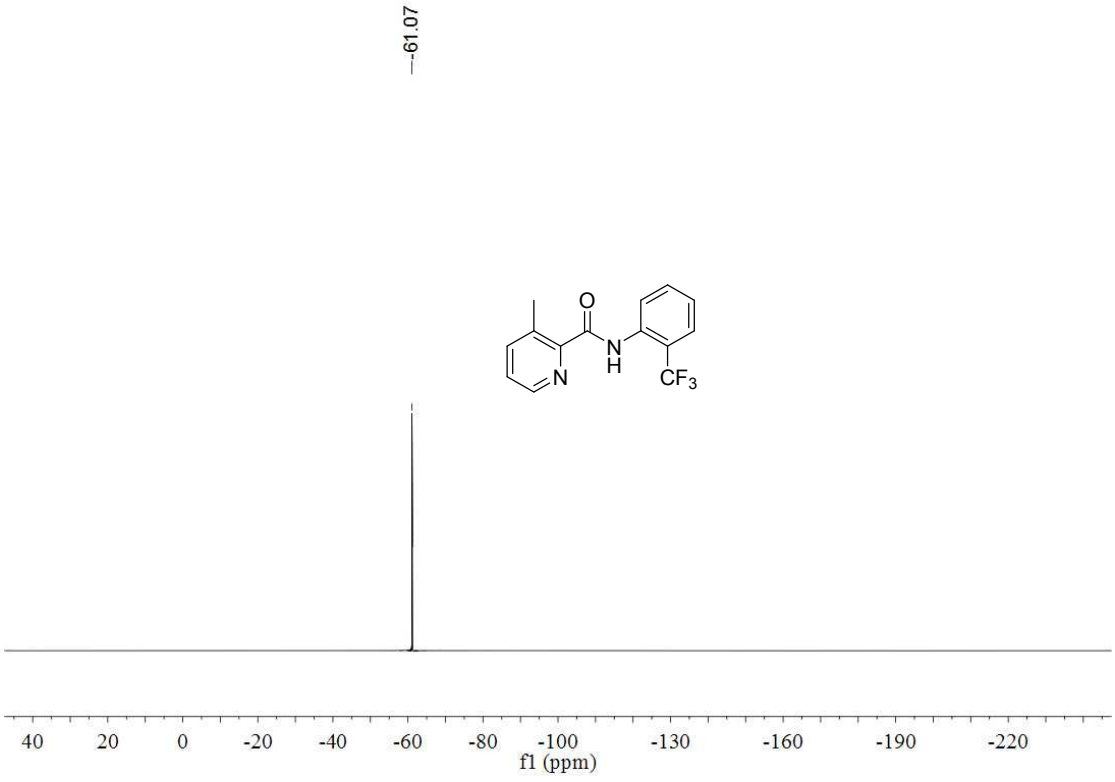
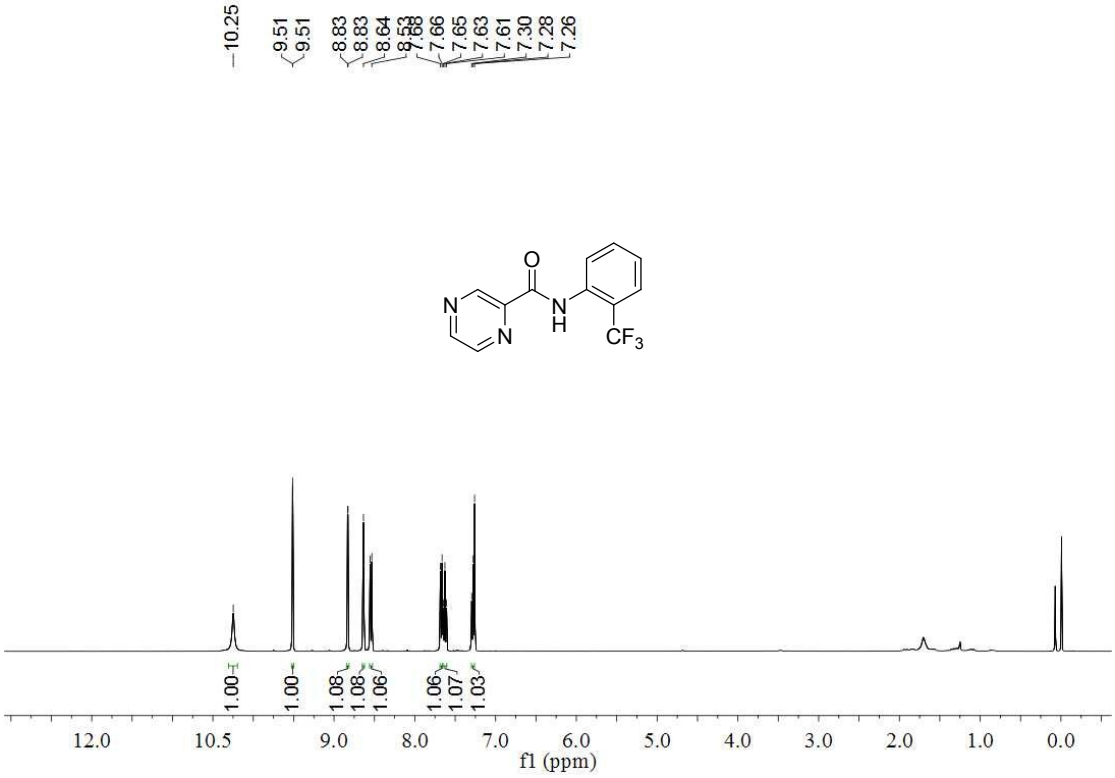


3n ^{19}F NMR



3o ^{1}H NMR



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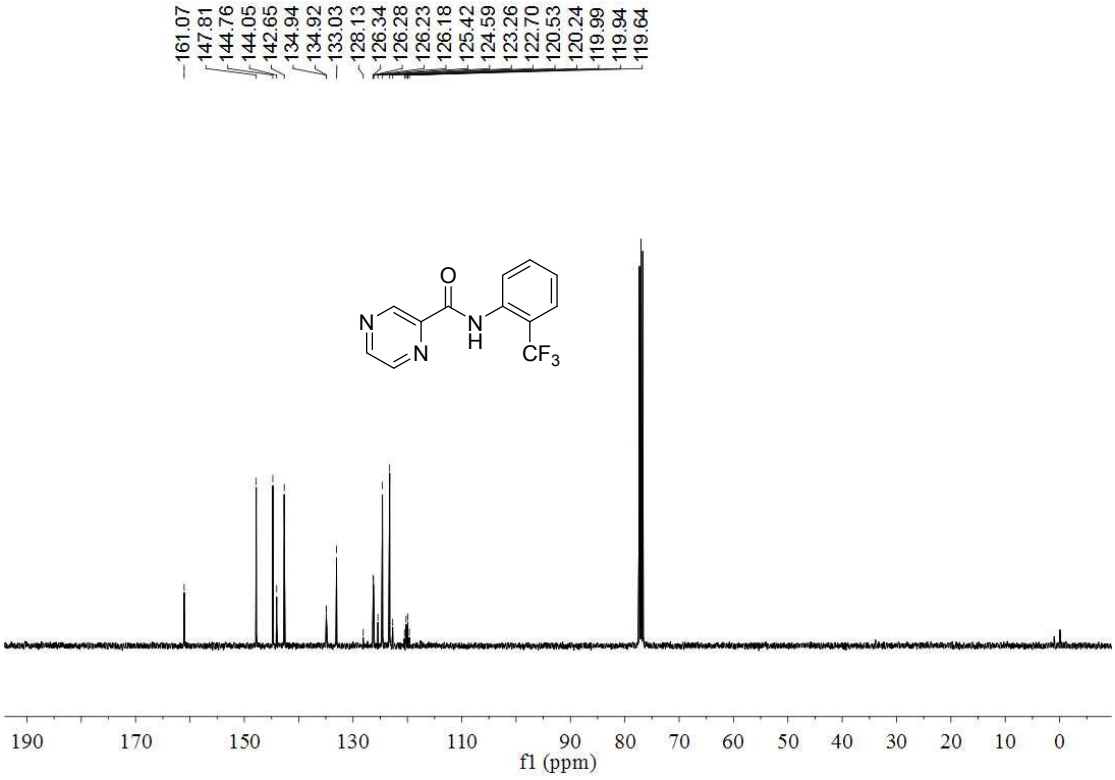
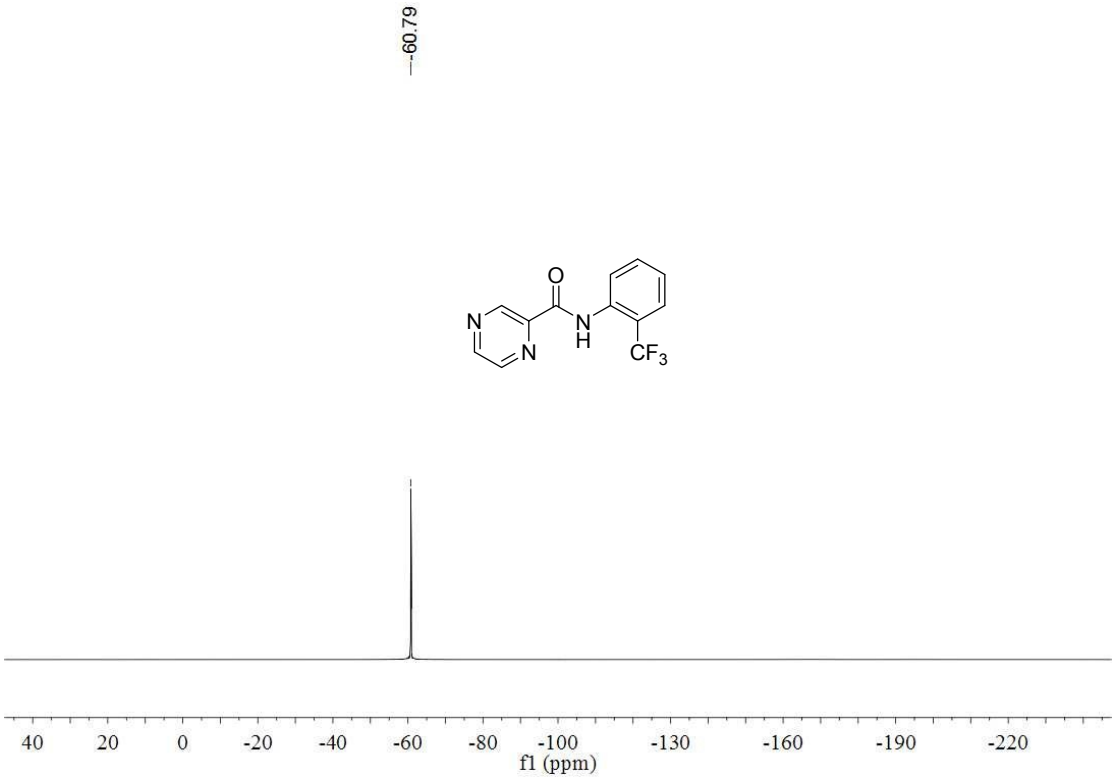
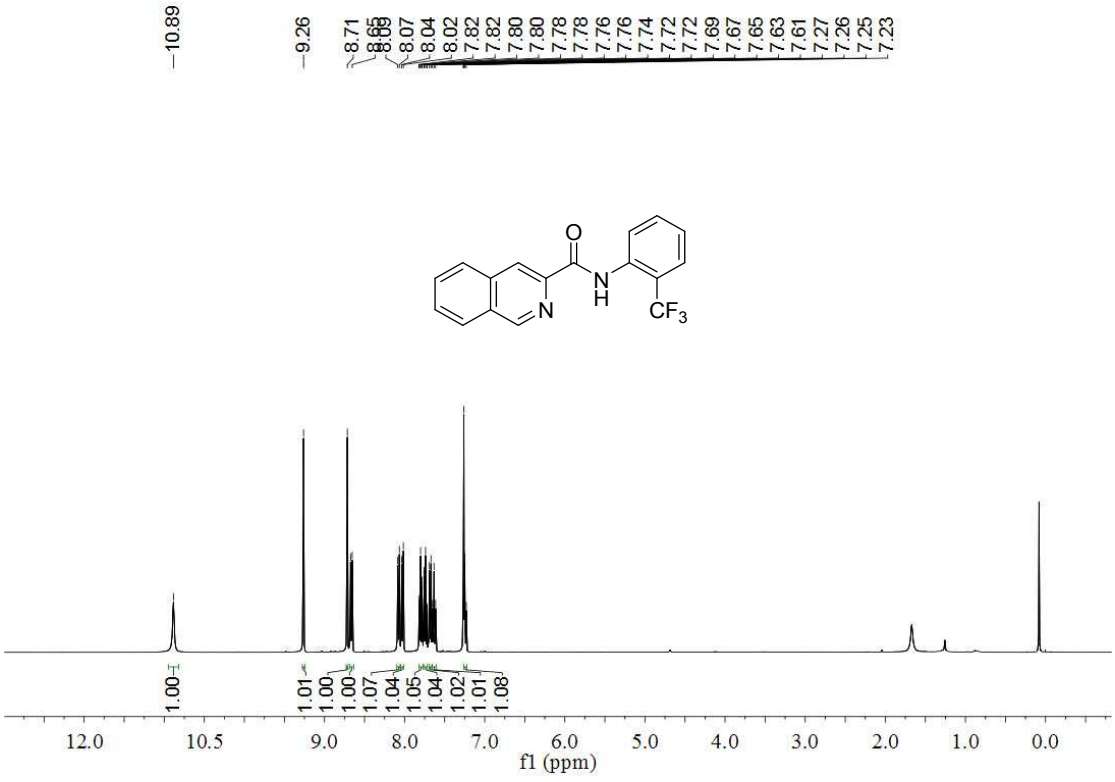


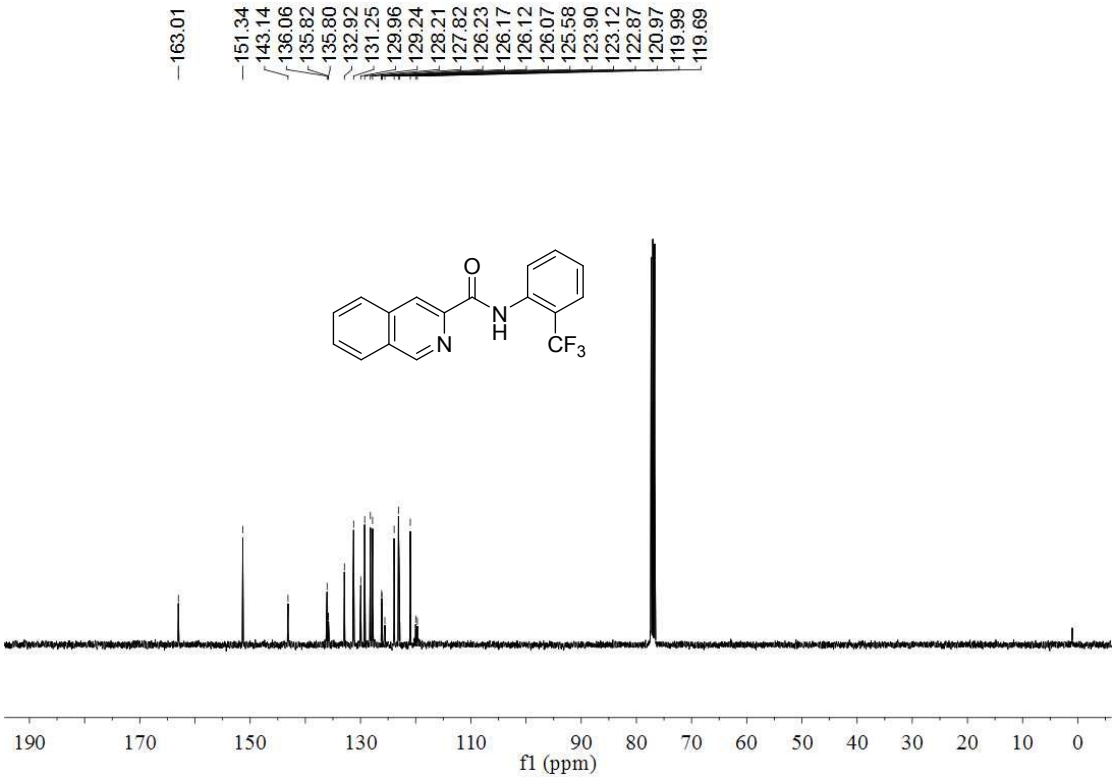
3o ^{19}F NMR



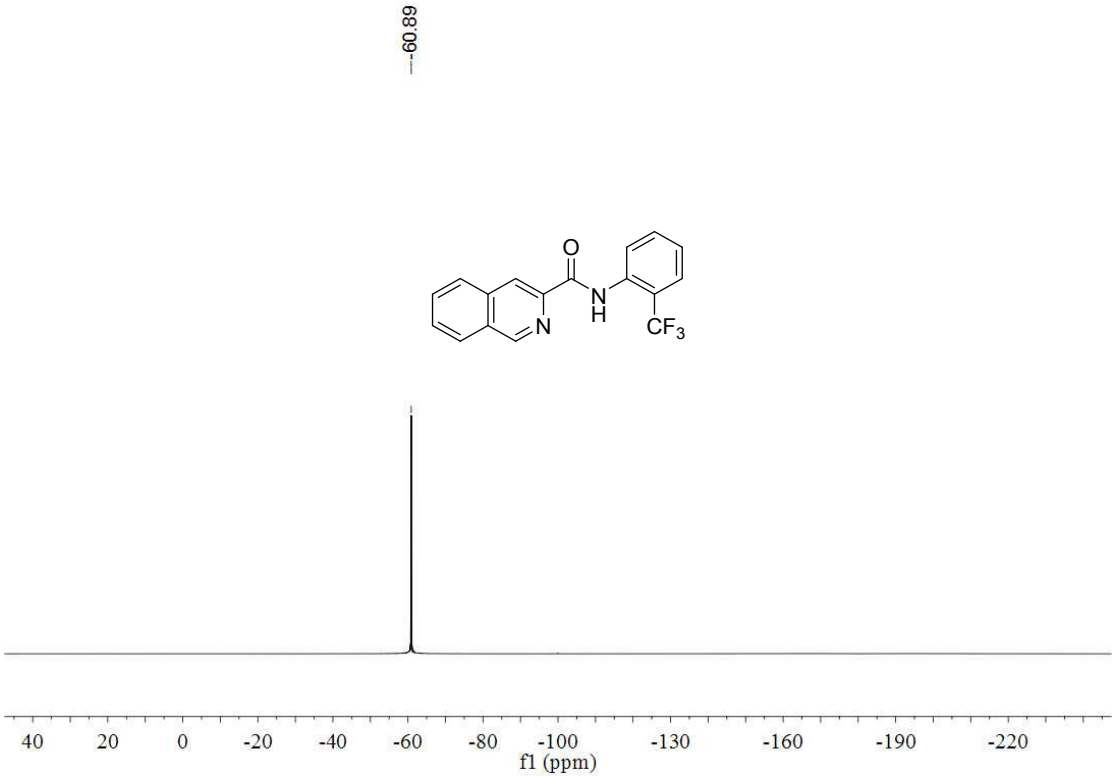
3p ^{1}H NMR



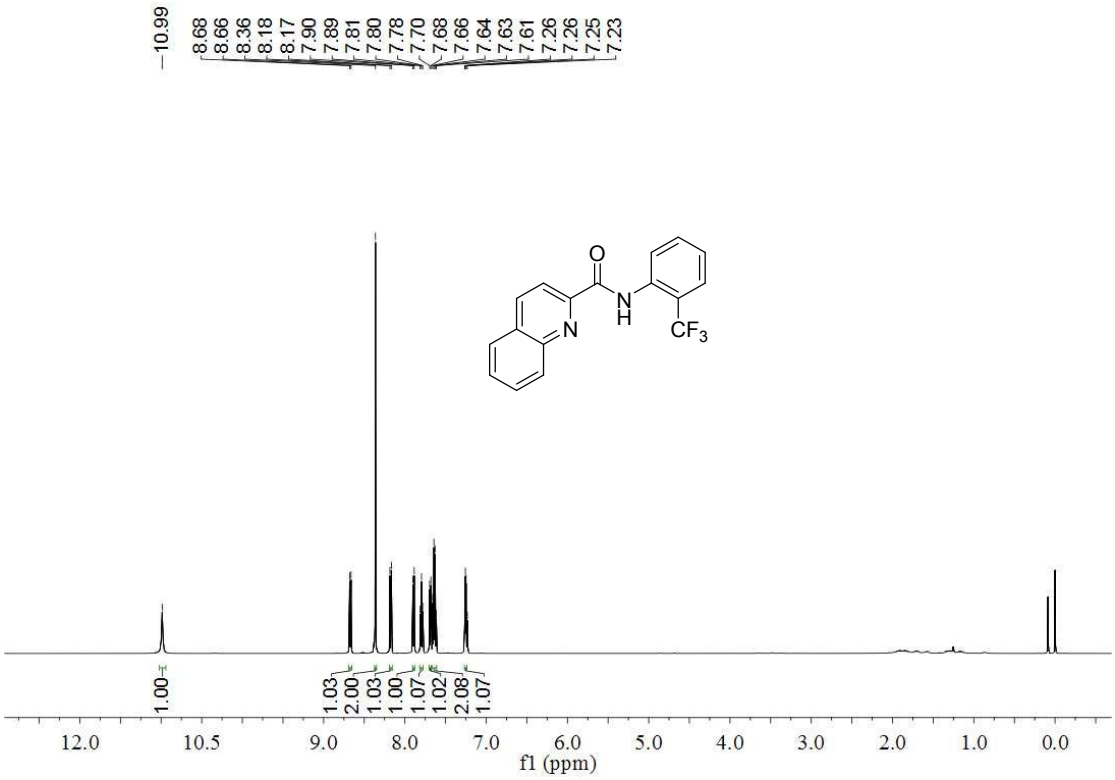
3p ^{13}C NMR



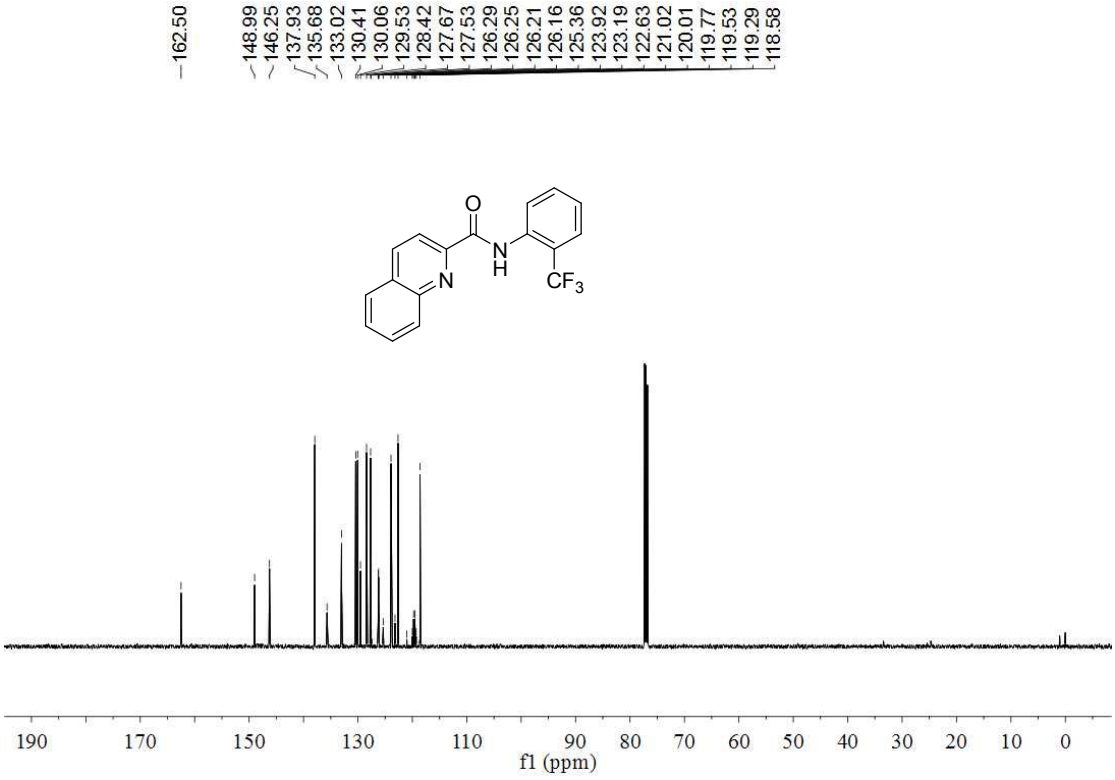
3p ^{19}F NMR



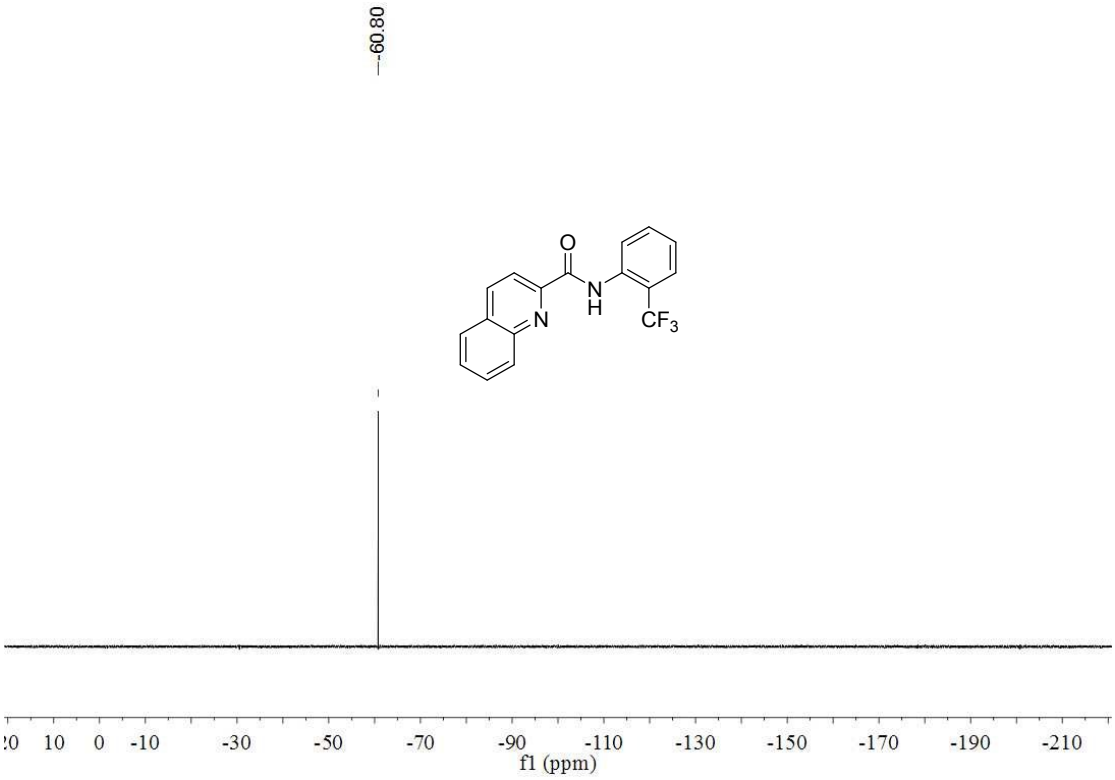
3q ^{1}H NMR



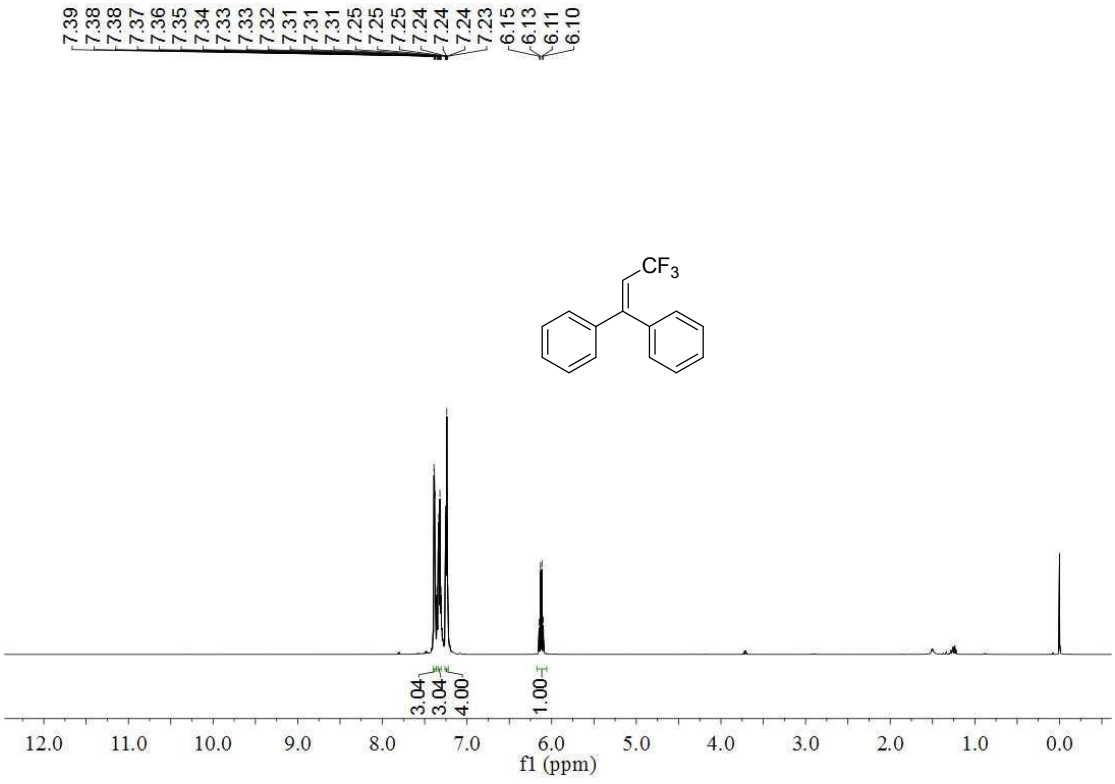
3q ^{13}C NMR



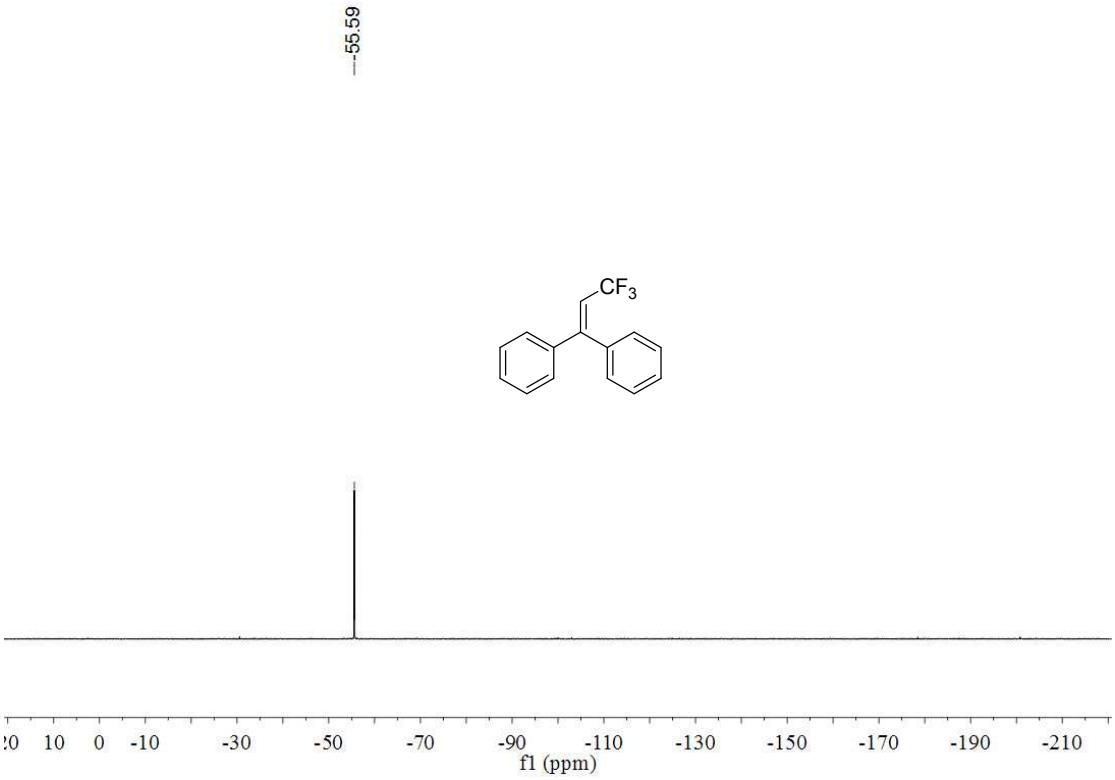
3q ^{19}F NMR



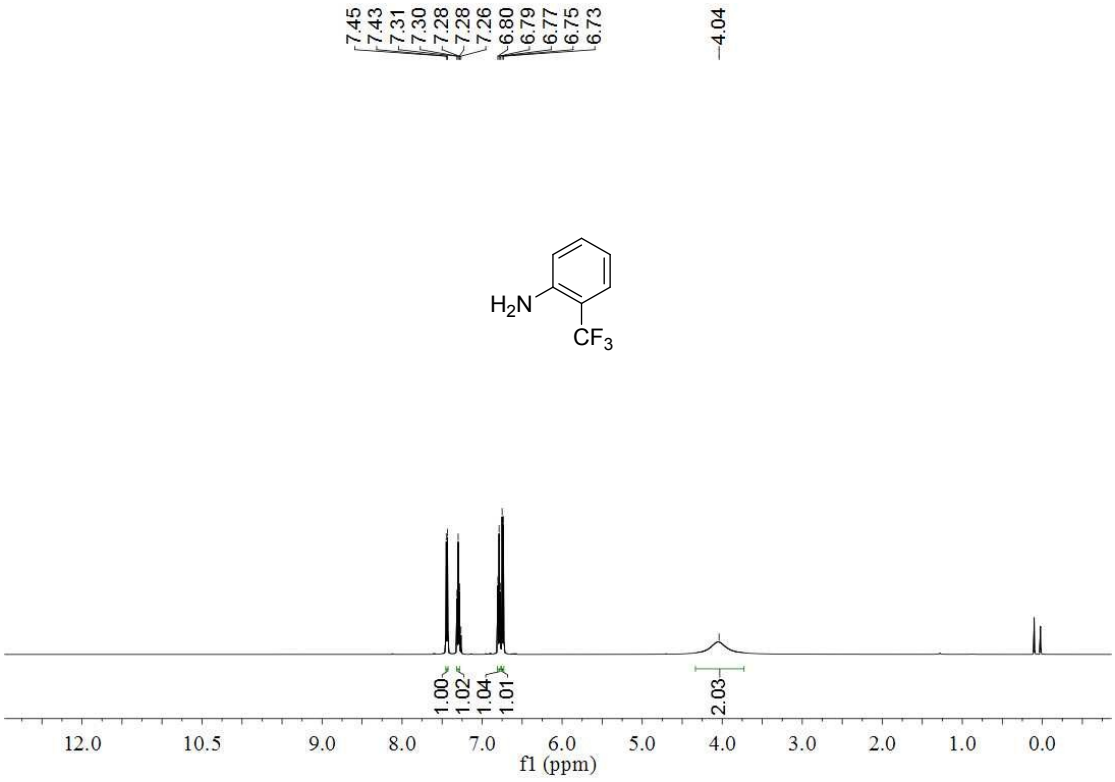
3aa ^{1}H NMR



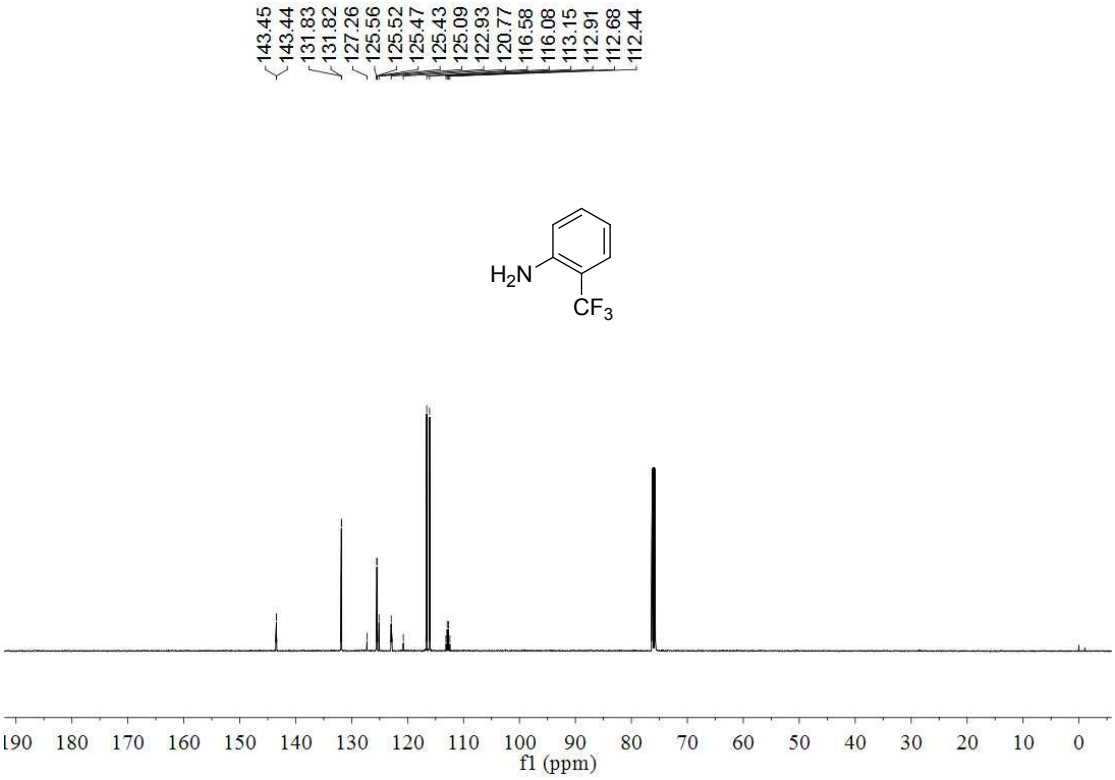
3aa ^{19}F NMR



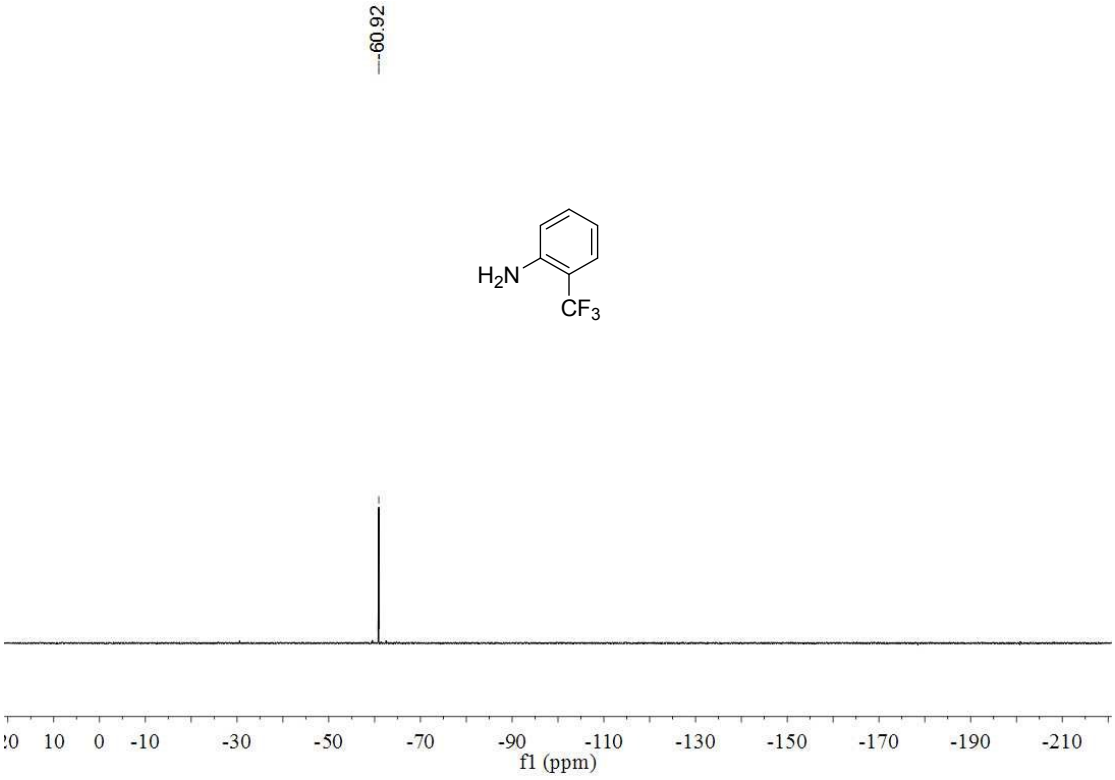
4a ^{1}H NMR



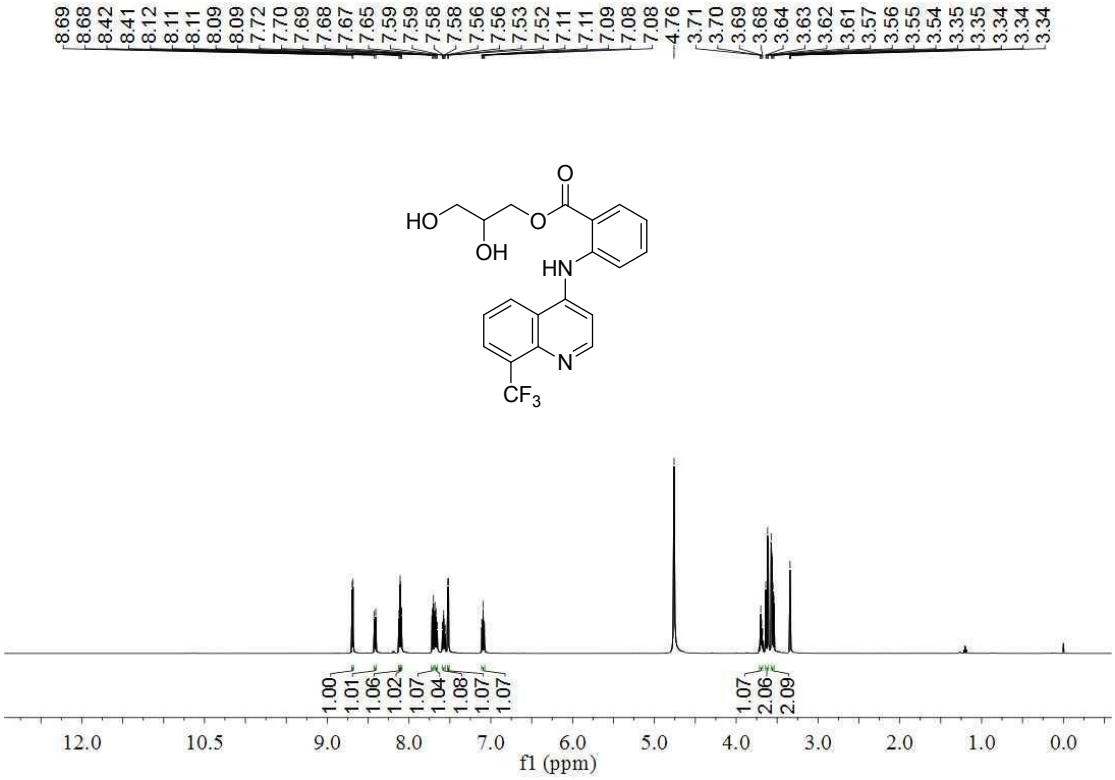
4a ^{13}C NMR



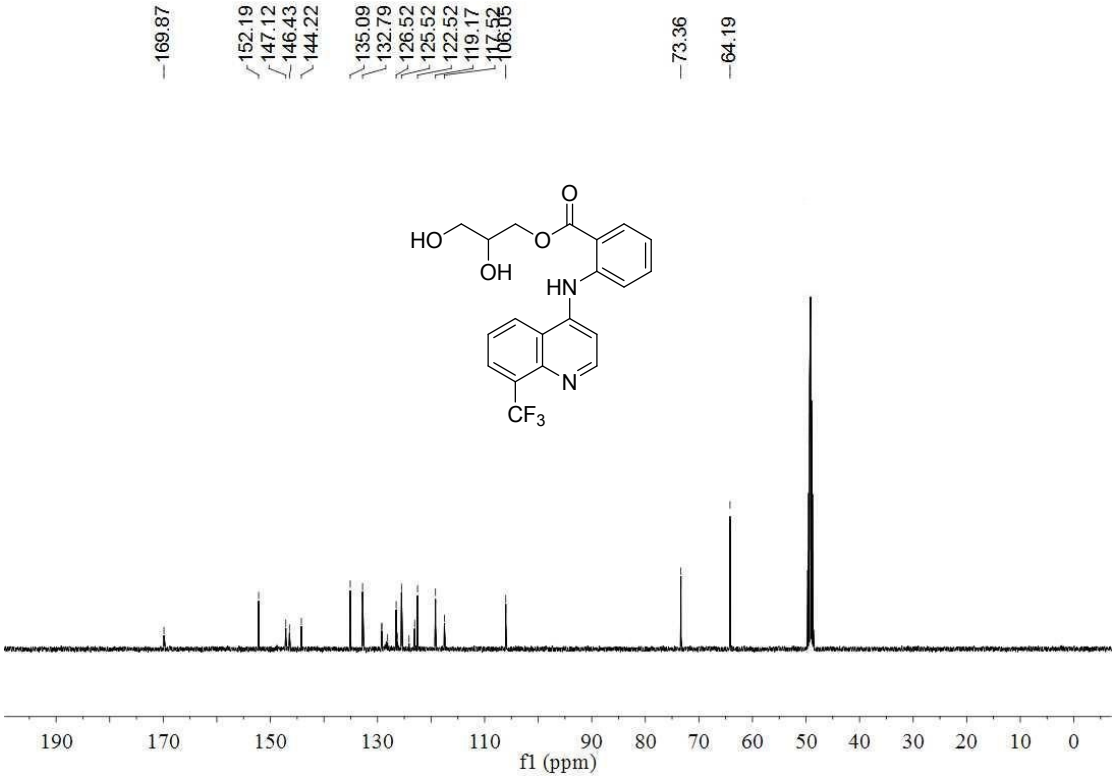
4a ^{19}F NMR



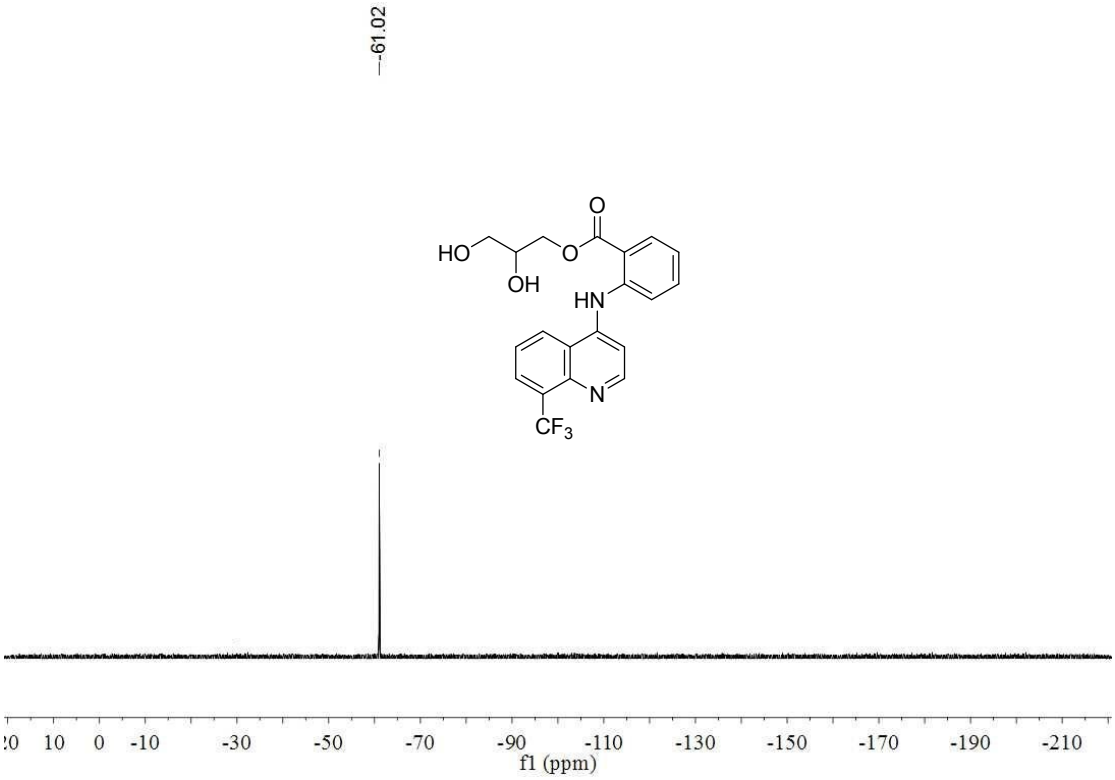
5a ^{1}H NMR



5a ^{13}C NMR



5a ^{19}F NMR


-61.02
HO
OH
O
O
HN
N
CF3
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)