Supporting Information

Synthesis of Fused 3-Trifluoromethyl-1,2,4-Triazoles *via* Base-Promoted [3+2] Cycloaddition of Nitrile Imines and 1*H*-Benzo[*d*]imidazole-2-thiols

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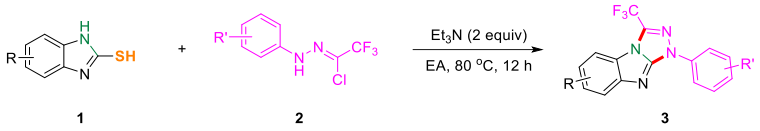
1. General Information

Unless otherwise noted, all experiments were carried out under nitrogen atmosphere. Reactions were monitored by thin-layer chromatography (TLC). TLC was performed using Huanghai 8±0.2 μm precoated glass plates (0.25 mm) and visualized by UV fluorescence quenching and $KMnO_4$. Huanghai silica gel (particle size 200 – 300 mesh) was used for chromatography. ^1H NMR spectra were recorded at room temperature on a Bruker ADVANCE III 500 MHz spectrometer and were reported relative to residual $CDCl_3$ (δ 7.26 ppm). ^{13}C NMR spectra were recorded on a Bruker ADVANCE III 500 MHz spectrometer (125 MHz) and were reported relative to $CDCl_3$ (δ 77.16 ppm). ^{19}F NMR spectra were recorded on a Bruker ADVANCE III 500 MHz spectrometer (471 MHz). Data for ^1H NMR were reported as chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration) using standard abbreviations for multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Data for ^{13}C NMR and ^{19}F NMR were reported in terms of chemical shifts (δ ppm). High resolution mass spectra (HRMS) were obtained by use of a Bruker Compact TOF mass spectrometer in electrospray ionization mode (ESI^+).

Unless otherwise noted, all reagents were purchased commercially from Adamas, Innochem, Alfa, Energy Chemical, Sigma-Aldrich and used without further purification. Petroleum ether (PE) (60 ~ 90 ^oC), ethyl acetate (EA) and dichloromethane (DCM) were used as eluent for silica gel chromatography. Dry solvents were purchased commercially. Nitrile imines derivatives were synthesized smoothly according to literature.[1-2]

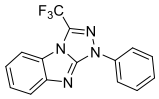
2. General Procedure for Synthesis of Fused 3-Trifluoromethyl-1,2,4-Triazoles via Base-Promoted [3+2] Cycloaddition of Nitrile Imines and 1*H*-Benzo[d]imidazole-2-thiols



1 2 3

A mixture of 1*H*-benzo[*d*]imidazole-2-thiol **1** (15.3 mg, 0.1 mmol, 1 equiv.), nitrile imines **2** (0.15 mmol, 1.5 equiv.), Et_3N (2 equiv.), and EA (1 mL) was added to a 10 mL Schlenk-tube, and the mixture was stirred at 80 °C for 12 hours. After the reaction was completed, the mixture was diluted with EA (20 mL) and filtered. The filtrates were concentrated under reduced pressure to give a crude residue which was purified by flash column chromatography to provide the desired product **3a** in 96% yield as a pale solid. R_f = 0.4 (PE : EA = 20 : 1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.0 Hz, 2H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.55 (t, *J* = 7.8 Hz, 2H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.35 – 7.28 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.7, 149.9, 137.0, 129.8 (q, *J* = 43.8 Hz), 129.7, 126.7, 126.2, 124.5, 121.5, 120.0, 117.94 (q, *J* = 267.5 Hz), 117.90, 112.1. ^{19}F NMR (471 MHz, $CDCl_3$) δ -64.79. HRMS (ESI^+) *m/z* calc'd for $C_{15}H_{10}F_3N_4^+$ $[M+H]^+$: 303.0852, found 303.0855

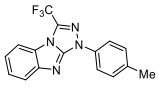
3. Spectra Data of 3a-3x



1-Phenyl-3-(trifluoromethyl)-1*H*-benzo[4,5]imidazo[2,1-*c*][1,2,4]triazole (3a)

Following the general procedure, the desired product **3a** (29.0 mg) was obtained in 96% yield as a pale solid. R_f = 0.4 (PE : EA = 20 : 1).

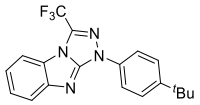
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.0 Hz, 2H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.55 (t, *J* = 7.8 Hz, 2H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.35 – 7.28 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.7, 149.9, 137.0, 129.75 (q, *J* = 43.8 Hz), 129.71, 126.7, 126.2, 124.5, 121.5, 120.0, 117.94 (q, *J* = 267.5 Hz), 117.90, 112.1. ^{19}F NMR (471 MHz, $CDCl_3$) δ -64.79. HRMS (ESI^+) *m/z* calc'd for $C_{15}H_{10}F_3N_4^+$ $[M+H]^+$: 303.0852, found 303.0855.



1-(*p*-Tolyl)-3-(trifluoromethyl)-1*H*-benzo[4,5]imidazo[2,1-*c*][1,2,4]triazole (3b)

Following the general procedure, the desired product **3b** (29.1 mg) was obtained in 92% yield as a pale solid. R_f = 0.4 (PE : EA = 20 : 1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.4 Hz, 2H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.36 – 7.27 (m, 3H), 2.39 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.7, 150.0, 136.6, 134.7, 130.2, 129.5 (q, *J* = 43.8 Hz), 126.1, 124.6, 121.3, 120.0, 118.0 (q, *J* = 268.8 Hz), 117.8, 112.1, 21.2. ^{19}F NMR (471 MHz, $CDCl_3$) δ -64.74. HRMS (ESI^+): calc'd for $C_{16}H_{12}F_3N_4^+$ $[M+H]^+$: 317.1009, found 317.1009.

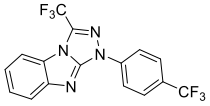


1-(4-(*tert*-Butyl)phenyl)-3-(trifluoromethyl)-1*H*-benzo[4,5]imidazo[2,1-*c*][1,2,4]triazole (3c)

Following the general procedure, the desired product **3c** (32.2 mg) was obtained in 90% yield as a pale solid. R_f = 0.4 (PE : EA = 20 : 1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.6 Hz, 2H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.57 (d, *J* = 8.6 Hz, 2H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.31 (t, *J* = 7.8

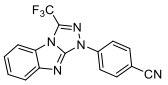
Hz, 1H), 1.37 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.9, 150.0, 134.6, 129.6 (q, *J* = 43.8 Hz), 126.6, 126.2, 124.7, 121.3, 120.0, 119.1, 118.0 (q, *J* = 268.8 Hz), 116.9, 112.1, 34.8, 31.5. ^{19}F NMR (471 MHz, $CDCl_3$) δ -64.73. HRMS (ESI^+): calc'd for $C_{19}H_{18}F_3N_4^+$ $[M+H]^+$: 359.1478, found 359.1476.



3-(Trifluoromethyl)-1-(4-(trifluoromethyl)phenyl)-1*H*-benzo[4,5]imidazo[2,1-*c*][1,2,4]triazole (3d)

Following the general procedure, the desired product **3d** (26.6 mg) was obtained in 72% yield as a colorless oil. R_f = 0.4 (PE : EA = 20 : 1).

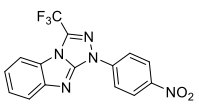
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (d, *J* = 8.6 Hz, 2H), 7.81 (t, *J* = 8.0 Hz, 3H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.5, 149.8, 139.6, 130.6 (q, *J* = 43.8 Hz), 128.5 (q, *J* = 32.5 Hz), 127.0 (q, *J* = 3.8 Hz), 126.5, 124.6, 123.9 (q, *J* = 271.9 Hz), 122.0, 120.2, 117.79 (q, *J* = 268.8 Hz), 117.77, 112.2. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.29, -64.94. HRMS (ESI^+) *m/z* calc'd for $C_{16}H_9F_6N_4^+$ $[M+H]^+$: 371.0726, found 371.0725.



4-(3-(Trifluoromethyl)-1*H*-benzo[4,5]imidazo[2,1-*c*][1,2,4]triazol-1-yl)benzonitrile (3e)

Following the general procedure, the desired product **3e** (20.9 mg) was obtained in 64% yield as a pale solid. R_f = 0.3 (PE : EA = 10 : 1).

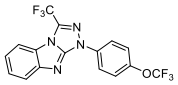
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 (d, *J* = 8.6 Hz, 2H), 7.87 – 7.80 (m, 3H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 1H), 7.35 (t, *J* = 7.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.3, 149.7, 140.1, 133.9, 131.1 (q, *J* = 45.0 Hz), 126.6, 124.6, 122.3, 120.3, 118.4, 118.0, 117.7 (q, *J* = 268.8 Hz), 112.2, 109.9. ^{19}F NMR (471 MHz, $CDCl_3$) δ -64.98. HRMS (ESI^+): calc'd for $C_{16}H_9F_3N_5^+$ $[M+H]^+$: 328.0805, found, 328.0802.



1-(4-Nitrophenyl)-3-(trifluoromethyl)-1*H*-benzo[4,5]imidazo[2,1-*c*][1,2,4]triazole (3f)

Following the general procedure, the desired product **3f** (22.9 mg) was obtained in 66% yield as a pale solid. R_f = 0.2 (PE : EA = 10 : 1).

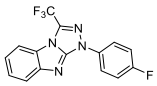
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 – 8.43 (m, 2H), 8.42 – 8.37 (m, 2H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.2, 149.6, 145.4, 141.5, 131.3 (q, *J* = 43.8 Hz), 126.6, 125.6, 124.7, 122.4, 120.4, 117.8, 117.6 (q, *J* = 270.0 Hz), 112.2. ^{19}F NMR (471 MHz, $CDCl_3$) δ -65.17. HRMS (ESI^+): calc'd for $C_{15}H_9F_3N_5O_2^+$ $[M+H]^+$: 348.0703, found 348.0698.



1-(4-(Trifluoromethoxy)phenyl)-3-(trifluoromethyl)-1*H*-benzo[4,5]imidazo[2,1-*c*][1,2,4]triazole (3g)

Following the general procedure, the desired product **3g** (29.7 mg) was obtained in 77% yield as a colorless oil. R_f = 0.3 (PE : EA = 15 : 1).

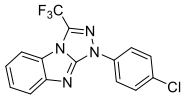
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 – 8.28 (m, 2H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.52 – 7.47 (m, 1H), 7.41 (d, *J* = 8.6 Hz, 2H), 7.33 (t, *J* = 7.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.5, 149.9, 147.2, 135.5, 130.2 (q, *J* = 45.0 Hz), 126.4, 124.7, 122.5, 121.8, 120.6 (q, *J* = 256.3 Hz), 120.1, 119.2, 117.8 (q, *J* = 268.8 Hz), 112.2. ^{19}F NMR (471 MHz, $CDCl_3$) δ -58.05, -64.86. HRMS (ESI^+): calc'd for $C_{16}H_9F_6N_4O^+$ $[M+H]^+$: 387.0675, found 387.0672.



1-(4-Fluorophenyl)-3-(trifluoromethyl)-1*H*-benzo[4,5]imidazo[2,1-*c*][1,2,4]triazole (3h)

Following the general procedure, the desired product **3h** (26.9 mg) was obtained in 84% yield as a colorless oil. R_f = 0.4 (PE : EA = 20 : 1).

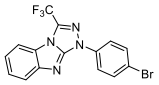
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 – 8.18 (m, 2H), 7.86 – 7.72 (m, 2H), 7.55 – 7.45 (m, 1H), 7.36 – 7.20 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.0 (d, *J* = 245.0 Hz), 151.6, 149.9, 133.2, 129.8 (q, *J* = 45.0 Hz), 126.3, 124.7, 121.6, 120.0, 119.7 (d, *J* = 7.5 Hz), 117.9 (q, *J* = 268.8 Hz), 116.6 (d, *J* = 23.8 Hz), 112.2. ^{19}F NMR (471 MHz, $CDCl_3$) δ -64.79, -114.92. HRMS (ESI^+): calc'd for $C_{15}H_9F_4N_4^+$ $[M+H]^+$: 321.0758, found 321.0755.



1-(4-Chlorophenyl)-3-(trifluoromethyl)-1*H*-benzo[4,5]imidazo[2,1-*c*][1,2,4]triazole (3i)

Following the general procedure, the desired product **3i** (27.9 mg) was obtained in 83% yield as a colorless oil. R_f = 0.4 (PE : EA = 20 : 1).

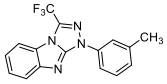
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.7 Hz, 2H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.54 – 7.45 (m, 3H), 7.32 (t, *J* = 7.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.5, 149.9, 135.6, 132.1, 129.8, 129.4 (q, *J* = 45.0 Hz), 126.4, 124.7, 121.7, 120.1, 119.1, 117.9 (q, *J* = 268.8 Hz), 112.2. ^{19}F NMR (471 MHz, $CDCl_3$) δ -64.83. HRMS (ESI^+): calc'd for $C_{15}H_9ClF_3N_4^+$ $[M+H]^+$: 337.0462, found 337.0462.



1-(4-Bromophenyl)-3-(trifluoromethyl)-1*H*-benzo[4,5]imidazo[2,1-*c*][1,2,4]triazole (3j)

Following the general procedure, the desired product **3j** (25.8 mg) was obtained in 68% yield as a pale solid. R_f = 0.4 (PE : EA = 20 : 1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 – 8.15 (m, 2H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.69 – 7.64 (m, 2H), 7.52 – 7.47 (m, 1H), 7.36 – 7.30 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.6, 149.9, 136.1, 132.7, 129.2 (q, *J* = 267.5 Hz), 126.5, 124.7, 121.8, 120.2, 119.9, 119.4, 117.9 (q, *J* = 267.5 Hz), 112.2. ^{19}F NMR (471 MHz, $CDCl_3$) δ -64.86. HRMS (ESI^+): calc'd for $C_{15}H_9BrF_3N_4^+$ $[M+H]^+$: 380.9957, found 380.9957.

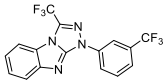


1-(*m*-Tolyl)-3-(trifluoromethyl)-1*H*-benzo[4,5]imidazo[2,1-c][1,2,4]triazole (3k)

Following the general procedure, the desired product **3k** (28.8 mg) was obtained in 91% yield as a pale solid. R_f = 0.4 (PE : EA = 20 : 1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 – 8.03 (m, 2H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 1H), 7.30 (t, *J* = 8.2 Hz, 1H), 7.13 (d, *J* = 7.5 Hz, 1H), 2.48 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.7, 149.9, 139.9, 137.0, 129.6 (q, *J* = 43.8 Hz), 129.5, 127.5, 126.1, 124.6, 121.4, 120.0, 118.4, 118.0 (q, *J* = 268.8 Hz), 115.1, 112.1, 21.8. ^{19}F NMR (471 MHz, $CDCl_3$) δ

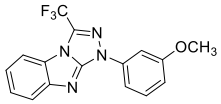
-64.75. HRMS (ESI$^+$): calc'd for $C_{16}H_{12}F_3N_4^+$ [M+H]$^+$: 317.1009, found 317.1010.



3-(Trifluoromethyl)-1-(3-(trifluoromethyl)phenyl)-1*H*-benzo[4,5]imidazo[2,1-*c*][1,2,4]triazole (3l)

Following the general procedure, the desired product **3l** (27.0 mg) was obtained in 73% yield as a colorless oil. R_f = 0.4 (PE : EA = 20 : 1).

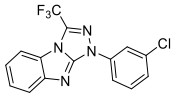
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (d, *J* = 8.2 Hz, 1H), 8.48 (s, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.69 (t, *J* = 7.8 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.5, 149.8, 137.5, 132.4 (q, *J* = 32.5 Hz), 130.46 (q, *J* = 45.0 Hz), 130.45, 126.4, 124.7, 123.7 (q, *J* = 271.3 Hz), 123.1 (q, *J* = 3.8 Hz), 121.9, 120.8, 120.3, 117.8 (q, *J* = 268.8 Hz), 114.8 (q, *J* = 3.8 Hz), 112.2. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.70, -64.88. HRMS (ESI$^+$): calc'd for $C_{16}H_9F_6N_4^+$ [M+H]$^+$: 371.0726, found 371.0726.



1-(3-Methoxyphenyl)-3-(trifluoromethyl)-1*H*-benzo[4,5]imidazo[2,1-*c*][1,2,4]triazole (3m)

Following the general procedure, the desired product **3m** (25.6 mg) was obtained in 77% yield as a colorless oil. R_f = 0.4 (PE : EA = 20 : 1).

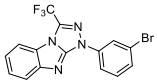
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.8 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.78 – 7.73 (m, 2H), 7.51 – 7.41 (m, 2H), 7.30 (t, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 3.92 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.7, 151.7, 149.9, 138.1, 130.6, 129.7 (q, *J* = 43.8 Hz), 126.2, 124.6, 121.5, 120.1, 117.9 (q, *J* = 268.8 Hz), 112.7, 112.1, 110.1, 103.6, 55.7. ^{19}F NMR (471 MHz, $CDCl_3$) δ -64.77. HRMS (ESI$^+$): calc'd for $C_{16}H_{12}F_3N_4O^+$ [M+H]$^+$: 333.0958, found 333.0959.



1-(3-Chlorophenyl)-3-(trifluoromethyl)-1*H*-benzo[4,5]imidazo[2,1-*c*][1,2,4]triazole (3n)

Following the general procedure, the desired product **3n** (23.5 mg) was obtained in 70% yield as a colorless oil. R_f = 0.3 (PE : EA = 20 : 1).

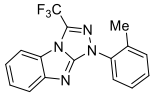
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 – 8.24 (m, 1H), 8.22 (d, *J* = 8.2 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.34 – 7.28 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.5, 149.8, 137.9, 135.7, 130.8, 130.2 (q, *J* = 43.8 Hz), 126.7, 126.3, 124.6, 121.8, 120.2, 118.0, 117.84 (q, *J* = 268.8 Hz), 115.9, 112.1. ^{19}F NMR (471 MHz, $CDCl_3$) δ -64.95. HRMS (ESI^+): calc'd for $C_{15}H_9ClF_3N_4^+$ $[M+H]^+$: 337.0462, found 337.0462.



1-(3-Bromophenyl)-3-(trifluoromethyl)-1*H*-benzo[4,5]imidazo[2,1-*c*][1,2,4]triazole (3o)

Following the general procedure, the desired product **3o** (24.7 mg) was obtained in 65% yield as a pale solid. R_f = 0.4 (PE : EA = 20 : 1).

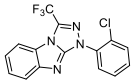
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 (s, 1H), 8.30 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.54 – 7.41 (m, 3H), 7.34 (t, *J* = 7.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.5, 149.9, 138.0, 131.1, 130.3 (q, *J* = 45.0 Hz), 129.7, 126.4, 124.7, 123.5, 121.8, 120.9, 120.2, 117.8 (q, *J* = 268.8 Hz), 116.4, 112.2. ^{19}F NMR (471 MHz, $CDCl_3$) δ -64.86. HRMS (ESI^+): calc'd for $C_{15}H_9BrF_3N_4^+$ $[M+H]^+$: 380.9957, found 380.9956.



1-(*o*-Tolyl)-3-(trifluoromethyl)-1*H*-benzo[4,5]imidazo[2,1-*c*][1,2,4]triazole (3p)

Following the general procedure, the desired product **3p** (16.1 mg) was obtained in 51% yield as a pale solid. R_f = 0.4 (PE : EA = 20 : 1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.2 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.62 (d, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.44 – 7.36 (m, 3H), 7.31 (t, *J* = 7.8 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.4, 150.1, 134.8, 134.5, 132.1, 130.0 (q, *J* = 43.8 Hz), 129.8, 127.3, 126.14, 126.11, 125.3, 121.1, 119.9, 118.0 (q, *J* = 268.8 Hz), 112.2, 18.6. ^{19}F NMR (471 MHz, $CDCl_3$) δ -64.81. HRMS (ESI^+): calc'd for $C_{16}H_{12}F_3N_4^+$ $[M+H]^+$: 317.1009, found 317.1009.

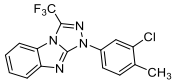


1-(2-Chlorophenyl)-3-(trifluoromethyl)-1*H*-benzo[4,5]imidazo[2,1-*c*][1,2,4]triazol

e (3q)

Following the general procedure, the desired product **3q** (17.5 mg) was obtained in 52% yield as a colorless oil. R_f = 0.4 (PE : EA = 20 : 1).

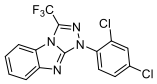
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.2 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.72 – 7.68 (m, 1H), 7.65 – 7.61 (m, 1H), 7.52 – 7.44 (m, 3H), 7.32 (t, *J* = 7.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.2, 150.0, 133.3, 131.4, 131.3, 130.3 (q, *J* = 43.8 Hz), 128.6, 128.2, 126.2, 125.4, 121.4, 120.0, 117.8 (q, *J* = 268.8 Hz), 112.2. ^{19}F NMR (471 MHz, $CDCl_3$) δ -64.94. HRMS (ESI^+): calc'd for $C_{15}H_9ClF_3N_4^+$ $[M+H]^+$: 337.0462, found 337.0461.



1-(3-Chloro-4-methylphenyl)-3-(trifluoromethyl)-1*H*-benzo[4,5]imidazo[2,1-*c*][1,2,4]triazole (3r)

Following the general procedure, the desired product **3r** (30.5 mg) was obtained in 87% yield as a pale solid. R_f = 0.3 (PE : EA = 20 : 1).

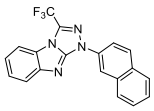
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, *J* = 2.1 Hz, 1H), 8.11 – 8.09 (m, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 1H), 7.40 (d, *J* = 8.2 Hz, 1H), 7.33 (t, *J* = 7.8 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.5, 149.9, 135.7, 135.5, 134.6, 131.8, 130.0 (q, *J* = 43.8 Hz), 126.3, 124.7, 121.7, 120.1, 118.5, 117.9 (q, *J* = 267.5 Hz), 116.0, 112.1, 23.2. ^{19}F NMR (471 MHz, $CDCl_3$) δ -64.79. HRMS (ESI^+): calc'd for $C_{16}H_{11}ClF_3N_4^+$ $[M+H]^+$: 351.0619, found 351.0618.



1-(2,4-Dichlorophenyl)-3-(trifluoromethyl)-1*H*-benzo[4,5]imidazo[2,1-*c*][1,2,4]triazole (3s)

Following the general procedure, the desired product **3s** (21.1 mg) was obtained in 57% yield as a colorless oil. R_f = 0.3 (PE : EA = 20 : 1).

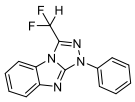
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 – 7.74 (m, 2H), 7.65 – 7.63 (m, 2H), 7.51 – 7.44 (m, 2H), 7.33 (t, *J* = 7.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.0, 149.9, 136.7, 132.2, 132.0, 131.2, 131.0 (q, *J* = 45.0 Hz), 129.2, 128.5, 126.3, 125.4, 121.6, 120.1, 117.8 (q, *J* = 268.8 Hz), 112.2. ^{19}F NMR (471 MHz, $CDCl_3$) δ -65.00. HRMS (ESI^+): calc'd for $C_{15}H_8Cl_2F_3N_4^+$ $[M+H]^+$: 371.0073, found 371.0073.



1-(Naphthalen-2-yl)-3-(trifluoromethyl)-1*H*-benzo[4,5]imidazo[2,1-*c*][1,2,4]triazole (3t)

Following the general procedure, the desired product **3t** (17.6 mg) was obtained in 50% yield as a pale solid. R_f = 0.4 (PE : EA = 20 : 1).

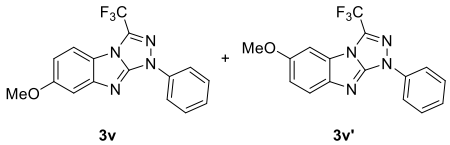
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.63 (d, *J* = 1.5 Hz, 1H), 8.28 (dd, *J* = 8.9, 2.1 Hz, 1H), 7.94 – 7.88 (m, 2H), 7.78 (t, *J* = 8.6 Hz, 2H), 7.70 (d, *J* = 8.2 Hz, 1H), 7.48 – 7.38 (m, 3H), 7.24 (t, *J* = 7.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.7, 150.0, 134.5, 133.5, 131.7, 129.9, 129.8 (q, *J* = 45.0 Hz), 128.3, 127.9, 127.3, 126.3, 126.2, 124.6, 121.5, 120.1, 118.0 (q, *J* = 268.8 Hz), 116.8, 115.4, 112.1. ^{19}F NMR (471 MHz, $CDCl_3$) δ -64.70. HRMS (ESI$^+$): calc'd for $C_{19}H_{12}F_3N_4^+$ $[M+H]^+$: 353.1009, found 353.1009.



3-(Difluoromethyl)-1-phenyl-1*H*-benzo[4,5]imidazo[2,1-*c*][1,2,4]triazole (3u)

Following the general procedure, the desired product **3u** (26.1 mg) was obtained in 92% yield as a pale solid. R_f = 0.4 (PE : EA = 20 : 1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 – 8.20 (m, 2H), 7.83 (dd, *J* = 16.8, 8.2 Hz, 2H), 7.58 – 7.52 (m, 2H), 7.49 – 7.44 (m, 1H), 7.36 –7.27 (m, 2H), 7.01 (t, *J* = 52.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.8, 150.0, 137.3, 133.8 (t, *J* = 31.3 Hz), 129.7, 126.3, 125.9, 124.9, 121.2, 119.7, 117.7, 112.8, 108.1 (t, *J* = 235.0 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -116.67 (d, *J* = 52.0 Hz). HRMS (ESI$^+$) m/z calc'd for $C_{15}H_{11}F_2N_4^+$ $[M+H]^+$: 285.0946, found 285.0945.



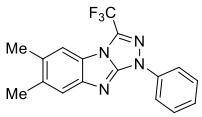
7-Methoxy-1-phenyl-3-(trifluoromethyl)-1*H*-benzo[4,5]imidazo[2,1-*c*][1,2,4]triazole (3v) and

6-Methoxy-1-phenyl-3-(trifluoromethyl)-1*H*-benzo[4,5]imidazo[2,1-*c*][1,2,4]triaz

ole (3v')

Following the general procedure, a mixture of **3v** and **3v'** (29.4 mg) was obtained in 88% yield as a pale solid with approximately a ratio of 1:1.1. R_f = 0.3 (PE : EA = 20 : 1).

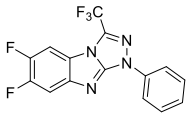
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41 – 8.19 (m, 3.6H), 7.74 (d, *J* = 8.8 Hz, 0.85H), 7.65 (d, *J* = 8.8 Hz, 1.09H), 7.62 – 7.49 (t, *J* = 7.2 Hz, 3.69H), 7.40 – 7.30 (m, 3.28H), 7.26 (s, 0.77H), 7.14 (d, *J* = 8.8 Hz, 0.74H), 6.93 (d, *J* = 8.8 Hz, 1H), 3.925 (s, 2.91H), 3.920 (s, 2.62H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.6, 155.2, 152.1, 151.2, 144.0, 137.1, 137.0, 129.7, 129.3 (q, *J* = 43.8 Hz), 126.6, 126.4, 124.7, 120.4, 119.0, 118.0 (q, *J* = 267.5 Hz), 117.9, 117.7, 114.7, 112.5, 110.7, 102.4, 96.4, 56.2, 55.8. ^{19}F NMR (471 MHz, $CDCl_3$) δ -64.48, -64.74. HRMS (ESI^+) m/z calc'd for $C_{16}H_{12}F_3N_4O^+$ $[M+H]^+$: 333.0958, found 333.0958.



6,7-Dimethyl-1-phenyl-3-(trifluoromethyl)-1*H*-benzo[4,5]imidazo[2,1-*c*][1,2,4]tri azole (3w)

Following the general procedure, the desired product **3w** (31.2 mg) was obtained in 95% yield as a pale solid. R_f = 0.4 (PE : EA = 20 : 1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 7.9 Hz, 2H), 7.58 – 7.50 (m, 3H), 7.47 (s, 1H), 7.31 (t, *J* = 7.4 Hz, 1H), 2.39 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.4, 148.3, 137.2, 135.3, 130.6, 129.7, 129.5 (q, *J* = 41.3 Hz), 126.4, 122.9, 120.1, 118.0 (q, *J* = 268.8 Hz), 117.8, 112.1, 20.7, 20.5. ^{19}F NMR (471 MHz, $CDCl_3$) δ -64.76. HRMS (ESI^+) m/z calc'd for $C_{17}H_{14}F_3N_4^+$ $[M+H]^+$: 331.1165, found 331.1163.

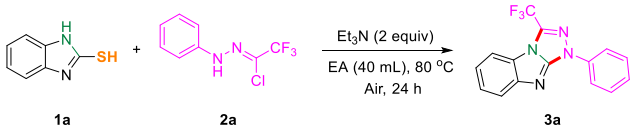


6,7-Difluoro-1-phenyl-3-(trifluoromethyl)-1*H*-benzo[4,5]imidazo[2,1-*c*][1,2,4]tria zole (3x)

Following the general procedure, the desired product **3x** (27.7 mg) was obtained in 82% yield as a pale solid. R_f = 0.4 (PE : EA = 20 : 1).

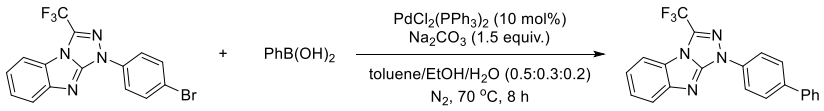
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 7.8 Hz, 2H), 7.64 – 7.51 (m, 4H), 7.37 – 7.31 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.5, 149.9 (d, *J* = 245.0, 13.8 Hz), 146.5 (dd, *J* = 242.5, 15.0 Hz), 145.6 (dd, *J* = 11.3, 1.3 Hz), 136.7, 129.8, 129.3 (q, *J* = 43.8 Hz), 127.0, 119.5 (dd, *J* = 10.0, 1.2 Hz), 117.9, 117.8 (q, *J* = 268.8 Hz), 107.8 (d, *J* = 20.0 Hz), 100.9 (d, *J* = 23.8 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -64.49, -137.17, -142.13. HRMS (ESI^+) m/z calc'd for $C_{15}H_8F_5N_4^+[M+H]^+$: 339.0664, found 339.0664.

4. Gram-scale Reaction and Derivatizations of 3j



1a 0.6 g, 4 mmol | **2a** 1.33 g, 6 mmol | **3a** 1.11 g, 92%

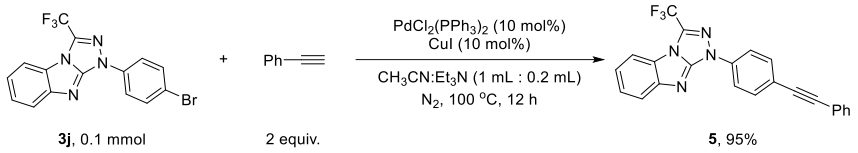
A mixture of 1*H*-benzo[*d*]imidazole-2-thiol **1** (0.61 g, 4 mmol, 1 equiv.), nitrile imines **2a** (1.33 g, 6 mmol, 1.5 equiv.), Et_3N (1.11 mL, 8 mmol, 2 equiv.), and EA (40 mL) was added to a 100 mL round-bottom flask, and the mixture was stirred at 80 °C for 24 hours. After the reaction was completed, the mixture was diluted with EA and filtered. The filtrates were concentrated under reduced pressure to give a crude residue which was purified by flash column chromatography to provide 1.11 g of **3a** in 92% yield as a pale solid.



3j, 0.1 mmol | 2.2 equiv. | **4**, 92%

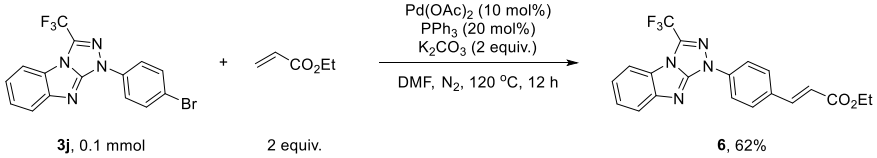
According to literature,[3] under N_2 atmosphere, a mixture of **3j** (37.9 mg, 0.1 mmol, 1 equiv.), $PhB(OH)_2$ (26.8 mg, 0.22 mmol, 2.2 equiv.), $PdCl_2(PPh_3)_2$ (7.2 mg, 0.01 mmol, 0.1 equiv.), Na_2CO_3 (17.0 mg, 0.15 mmol, 1.5 equiv.), and toluene:EtOH:H_2O (degassed)(0.5 mL: 0.3 mL: 0.2 mL) were added to a 10 mL-Schlenk tube, subsequently, the sealed tube was stirred at 70 °C for 8 h. After the reaction was finished, the solution was evaporated under reduced pressure to give the crude product which was purified by flash column chromatography to provide compound **4** as a colorless oil in 92% yield. R_f = 0.3 (PE : EA = 20 : 1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.6 Hz, 2H), 7.85 (d, *J* = 8.2 Hz, 1H), 7.81 – 7.74 (m, 3H), 7.63

(d, *J* = 7.2 Hz, 2H), 7.54 – 7.44 (m, 3H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.33 (t, *J* = 7.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.7, 150.0, 140.1, 139.6, 136.2, 129.9 (q, *J* = 43.8 Hz), 129.1, 128.3, 127.8, 127.2, 126.3, 124.7, 121.5, 120.1, 118.3, 118.0 (q, *J* = 268.8 Hz), 112.2. ^{19}F NMR (471 MHz, $CDCl_3$) δ -64.74. HRMS (ESI^+): calc'd for $C_{21}H_{14}F_3N_4^+$ $[M+H]^+$: 379.1165, found 379.1164.



3j, 0.1 mmol 2 equiv. **5**, 95%

According to literature,[4] under N_2 atmosphere, a mixture of **3j** (38.1 mg, 0.1 mmol, 1 equiv.), phenylacetylene (22 μL, 0.2 mmol, 2 equiv.), $PdCl_2(PPh_3)_2$ (7.0 mg, 0.01 mmol, 0.1 equiv.), CuI (2.1 mg, 0.01 mmol, 0.1 equiv.), and CH_3CN:Et_3N (1 mL: 0.2 mL) were added to a 10 mL-Schlenk tube, subsequently, the sealed tube was stirred at 100 °C for 12 h. After the reaction was finished, the solution was evaporated under reduced pressure to give the crude product which was purified by flash column chromatography to provide compound **5** as a colorless oil in 95% yield. R_f = 0.4 (PE : EA = 20 : 1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.6 Hz, 2H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.70 (d, *J* = 8.6 Hz, 2H), 7.58 – 7.52 (m, 2H), 7.50 (t, *J* = 7.8 Hz, 1H), 7.40 – 7.29 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.5, 149.9, 136.5, 133.0, 131.8, 130.1 (q, *J* = 45.0 Hz), 128.6, 128.5, 126.3, 124.6 123.1, 121.7, 121.6, 120.1, 117.9 (q, *J* = 268.8 Hz), 117.7, 112.1, 90.5, 88.7. ^{19}F NMR (471 MHz, $CDCl_3$) δ -64.80. HRMS (ESI^+): calc'd for $C_{23}H_{14}F_3N_4^+$ $[M+H]^+$: 403.1165, found 403.1166.

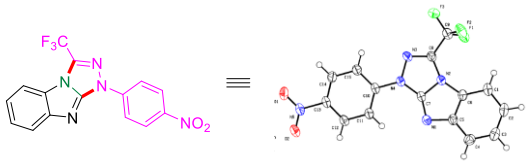


3j, 0.1 mmol 2 equiv. **6**, 62%

Following the literature,[5] under N_2 atmosphere, a mixture of **3j** (38.0 mg, 0.1 mmol, 1 equiv.), ethyl acrylate (22 μL, 0.2 mmol, 2 equiv.), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol, 0.1 equiv.), PPh_3 (5.3 mg, 0.02 mmol, 0.2 equiv.), K_2CO_3 (28.0 mg, 0.2 mmol, 2 equiv.), and DMF (1 mL) were added to a 10 mL-Schlenk tube, subsequently, the sealed tube was stirred at 120 °C for 12 h. After the reaction was finished, the solution was added

water (15 mL) and extracted by EA (15 mL x 3). The combined organic phase was dried by anhydrous Na_2SO_4 and filtered. The filtrates were evaporated under reduced pressure to give the crude product which was purified by flash column chromatography to provide compound **6** as a colorless oil in 62% yield. R_f = 0.2 (PE : EA = 10 : 1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.6 Hz, 2H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.72 – 7.68 (m, 3H), 7.51 (t, *J* = 7.8 Hz, 1H), 7.34 (t, *J* = 7.8 Hz, 1H), 6.48 (d, *J* = 16.0 Hz, 1H), 4.29 (q, *J* = 7.2 Hz, 2H), 1.36 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.0, 151.6, 149.9, 143.3, 138.2, 132.8, 130.3 (q, *J* = 45.0 Hz), 129.5, 126.4, 124.7, 121.9, 120.2, 118.9, 118.1, 117.9 (q, *J* = 268.8 Hz), 112.2, 60.8, 14.5. ^{19}F NMR (471 MHz, $CDCl_3$) δ -64.85. HRMS (ESI^+): calc'd for $C_{20}H_{16}F_3N_4O_2^+$ $[M+H]^+$: 401.1220, found 401.1221.

5. X-ray Crystallography Data of 3f



3f

CCDC: 2289201

Table S1 Crystal data and structure refinement for 3f.	
Identification code	2289201
Empirical formula	$C_{15}H_8F_3N_5O_2$
Formula weight	347.26
Temperature/K	170.00
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	5.0516(6)
b/Å	25.263(3)
c/Å	11.1686(13)
α/°	90
β/°	101.502(4)
γ/°	90
Volume/Å^3	1396.7(3)
Z	4
ρ_{calc}g/cm^3	1.651
μ/mm^{-1}	0.142
F(000)	704.0
Crystal size/mm^3	0.42 × 0.16 × 0.15
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.056 to 55.176
Index ranges	$-6 \le h \le 6$, $-32 \le k \le 29$, $-14 \le l \le 14$
Reflections collected	13208
Independent reflections	3219 [R_{int} = 0.0475, R_{sigma} = 0.0404]
Data/restraints/parameters	3219/0/226
Goodness-of-fit on F^2	1.162
Final R indexes [I>=2σ (I)]	R_1 = 0.0663, wR_2 = 0.1271
Final R indexes [all data]	R_1 = 0.0938, wR_2 = 0.1430
Largest diff. peak/hole / e Å^{-3}	0.26/-0.28

6. References

1. D. Wang, X. Wan, Y. Zhou, J. Liu, J. Cai and G.-J. Deng, *Asian J. Org. Chem.*, 2023, **12**, e202200674.

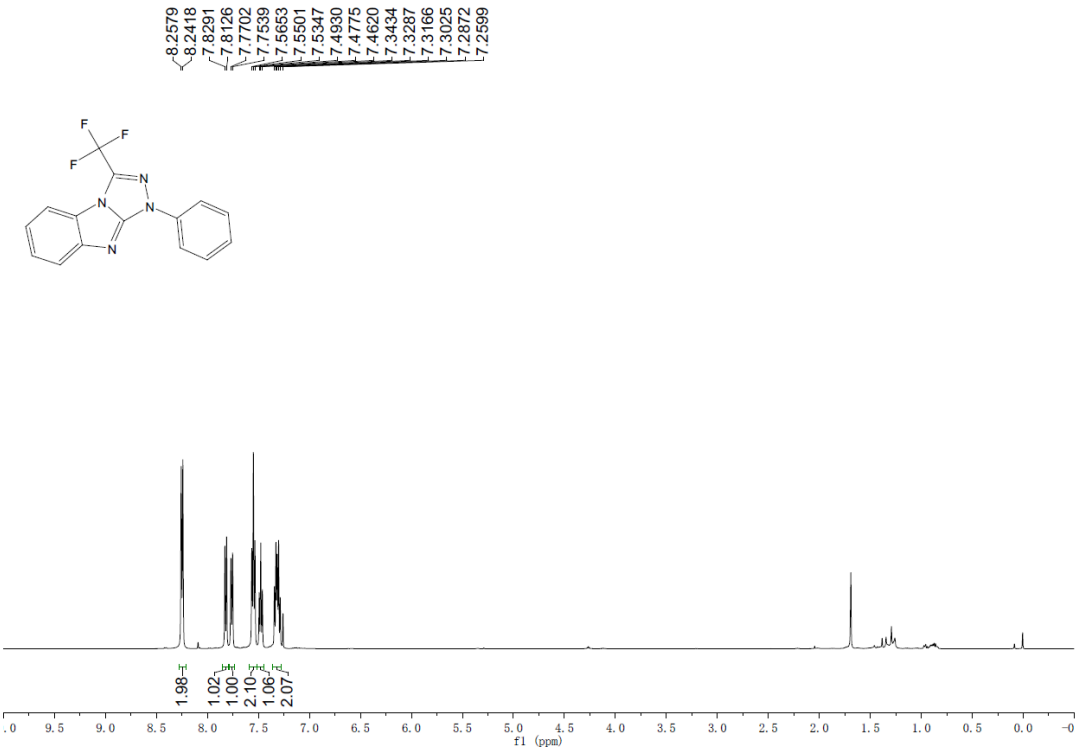
2. (a) Y. Zhang, J.-L. Zeng, Z. Chen and R. Wang, *J. Org. Chem.*, 2022, **87**, 14514–14522; (b) Y. Zhou, C.-F. Gao, H. Ma, J. Nie, J.-A. Ma and F.-G. Zhang, *Chem.−Asian J.*, 2022, **17**, e202200436.

3. N. Miyaura, T. Yanagi and A. Suzuki, *Synth. Commun.*, 1981, **11**, 513−519.

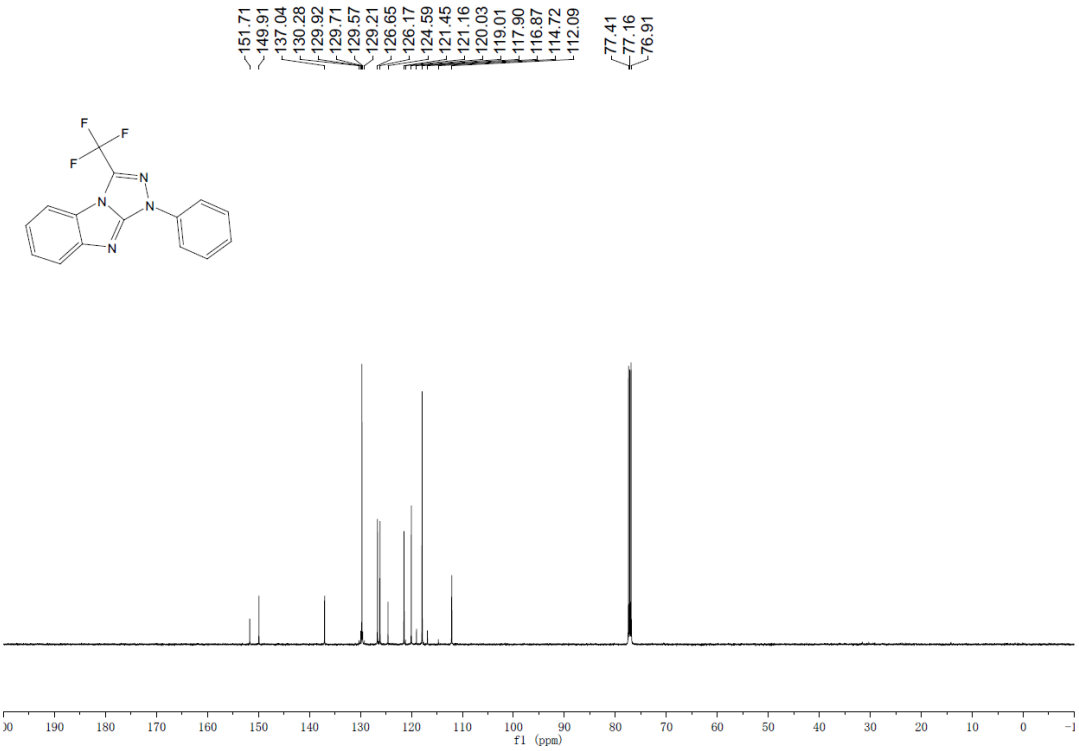
4. D. Wang, F. Zhang, F. Xiao and G.-J. Deng, *Org. Biomol. Chem.*, 2019, **17**, 9163−9168.

5. J. Wang, P.-B. Bai and S.-D. Yang, *Chin. Chem. Lett.*, 2022, **33**, 2397−2401.

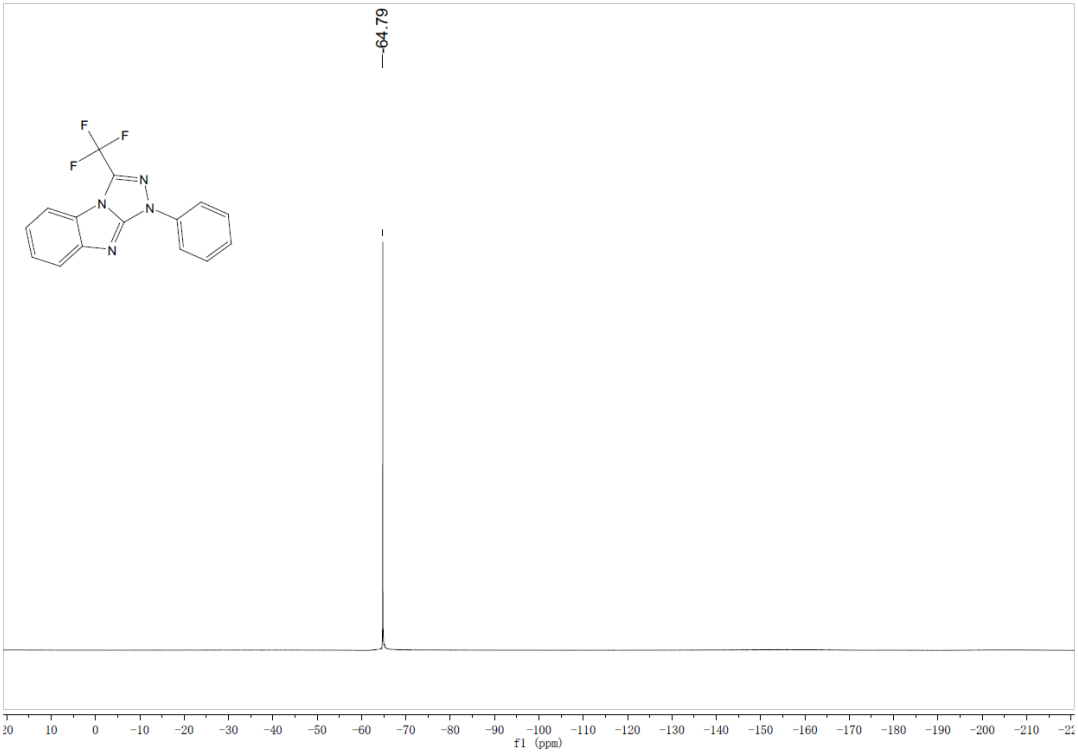
7. NMR Spectra



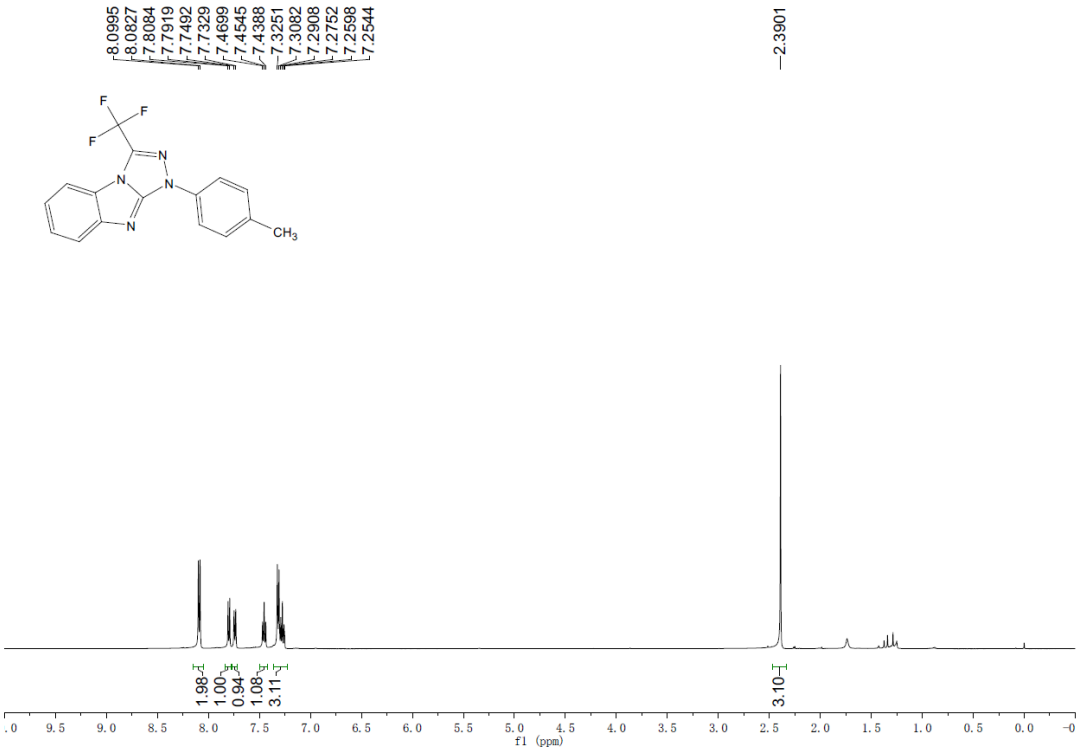
^{1}H NMR (500 MHz, $CDCl_3$) of **3a**.



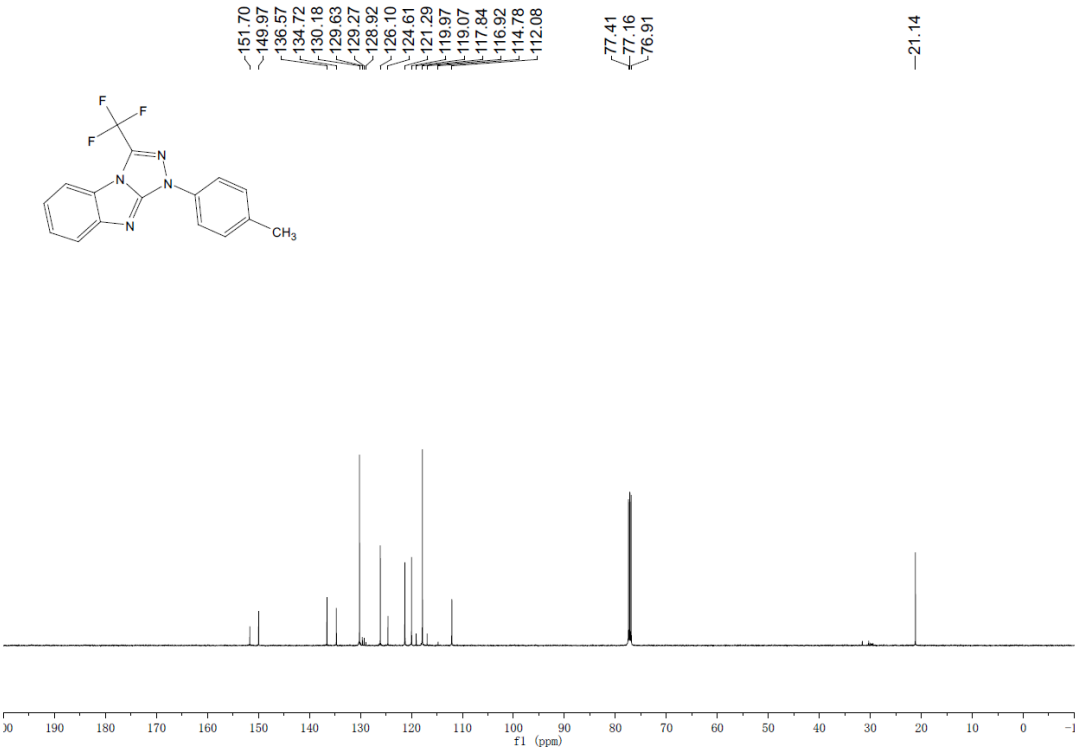
^{13}C NMR (125 MHz, $CDCl_3$) of **3a**.



^{19}F NMR (471 MHz, $CDCl_3$) of **3a**.

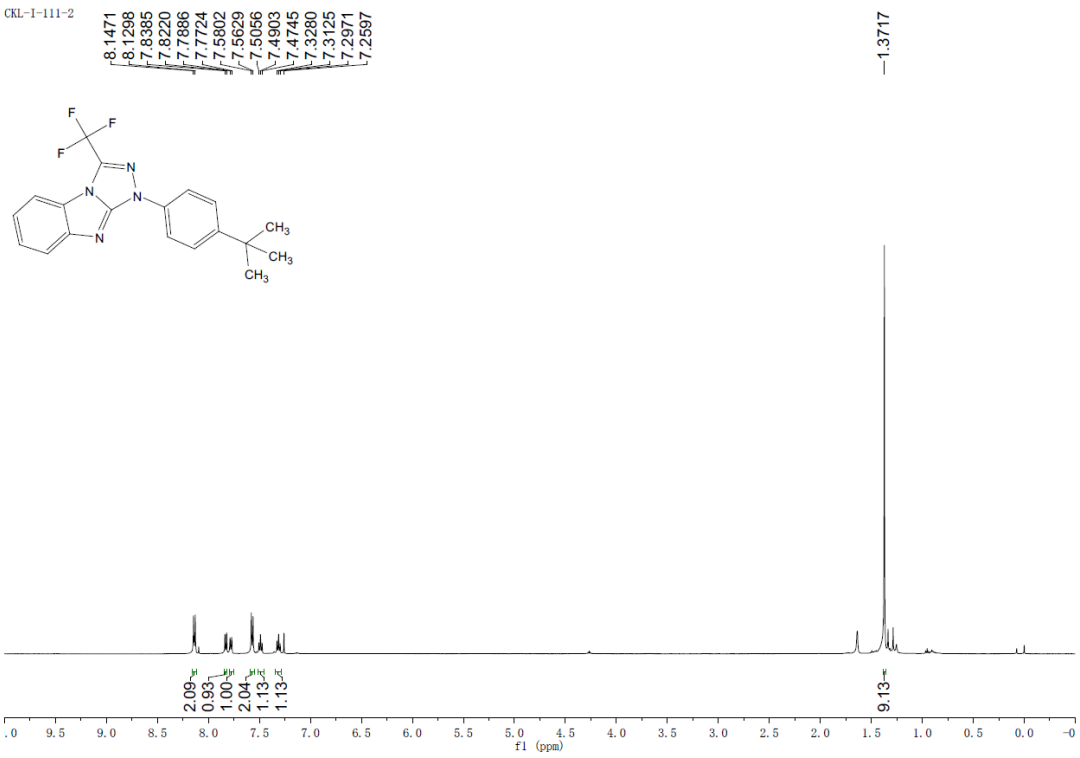


^{1}H NMR (500 MHz, $CDCl_3$) of **3b**.

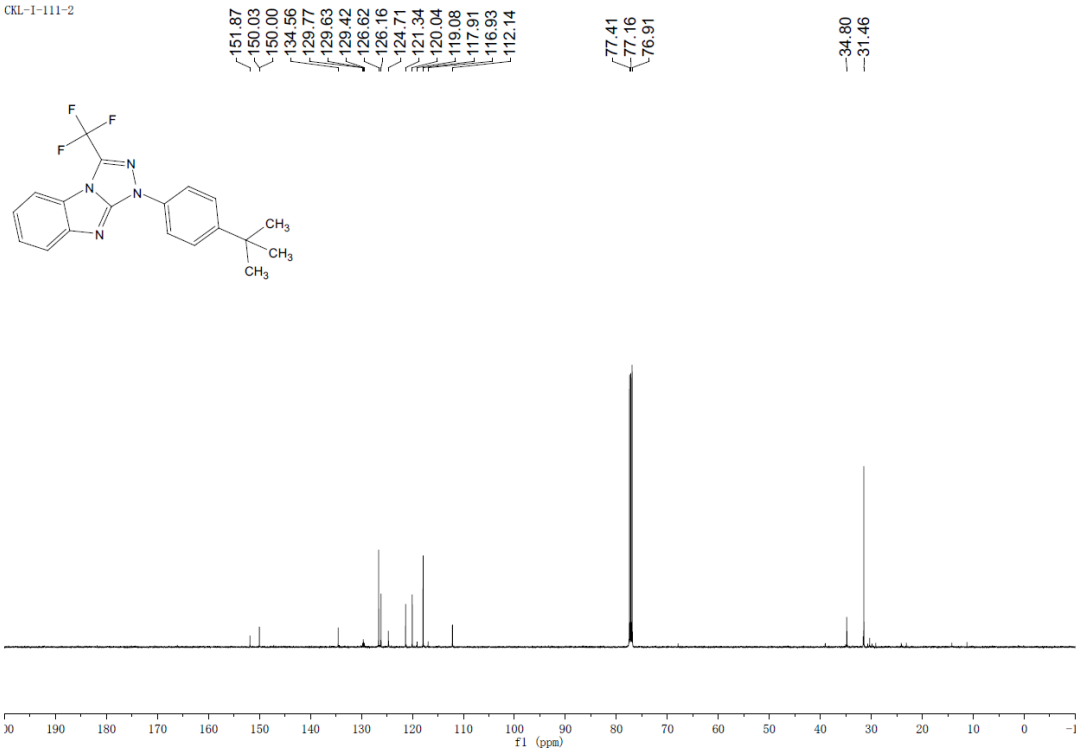


^{13}C NMR (125 MHz, $CDCl_3$) of **3b**.

^{19}F NMR (471 MHz, $CDCl_3$) of **3b**.

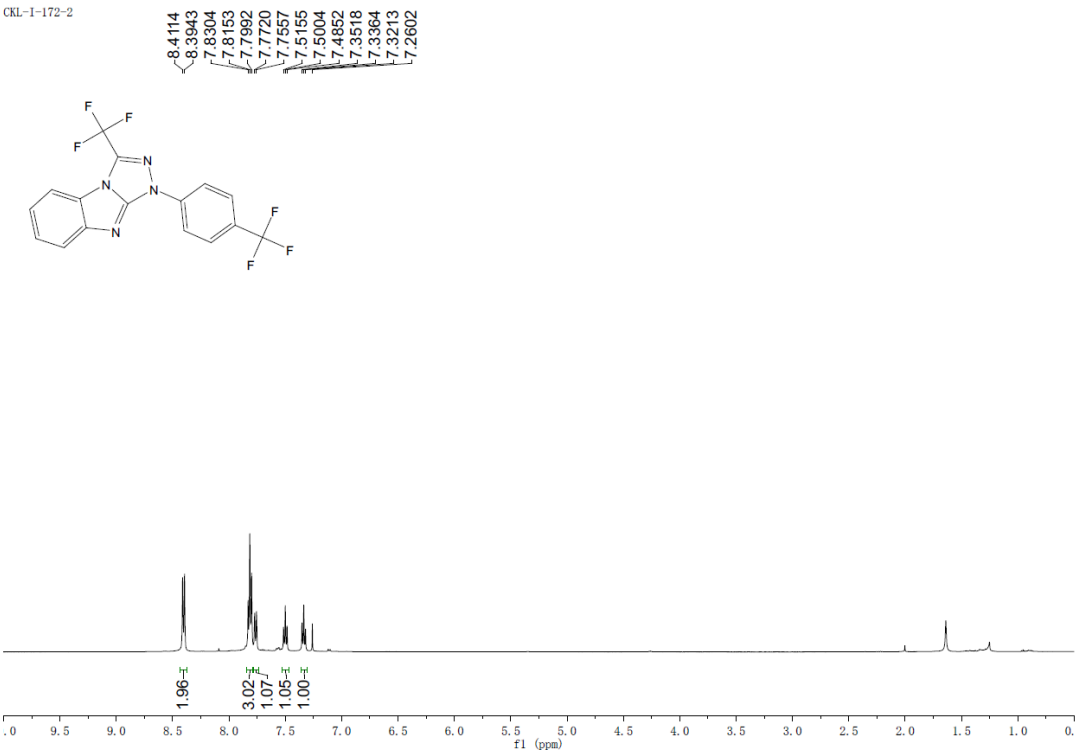


^{1}H NMR (500 MHz, $CDCl_3$) of **3c**.

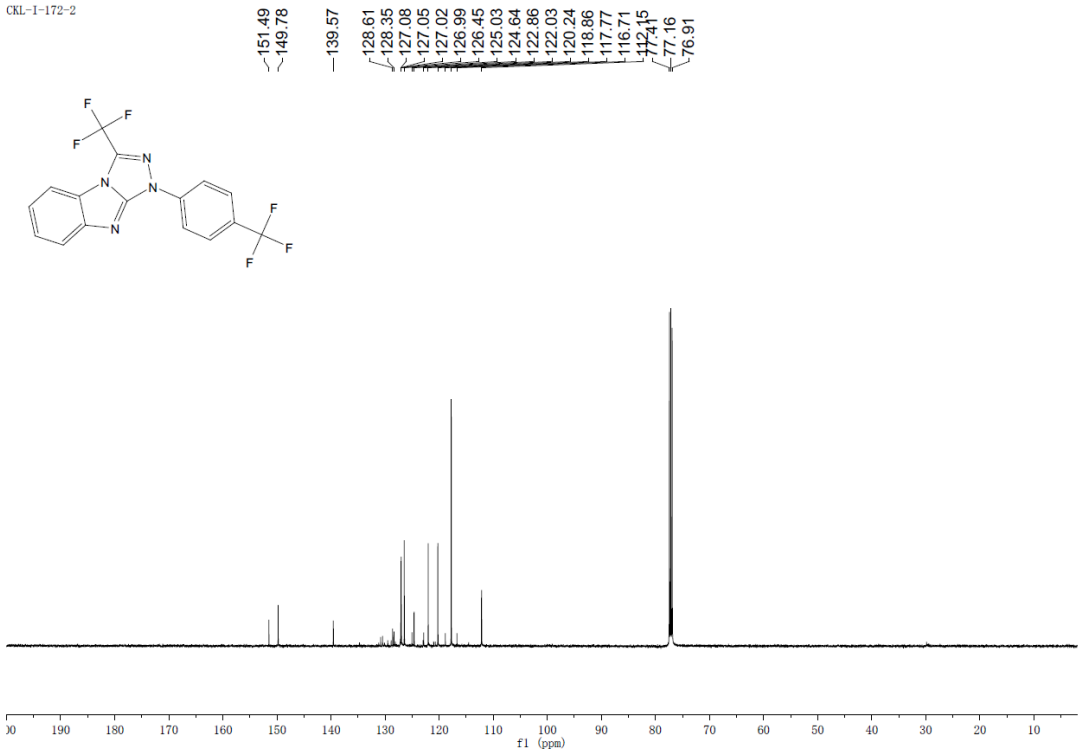


^{13}C NMR (125 MHz, $CDCl_3$) of **3c**.

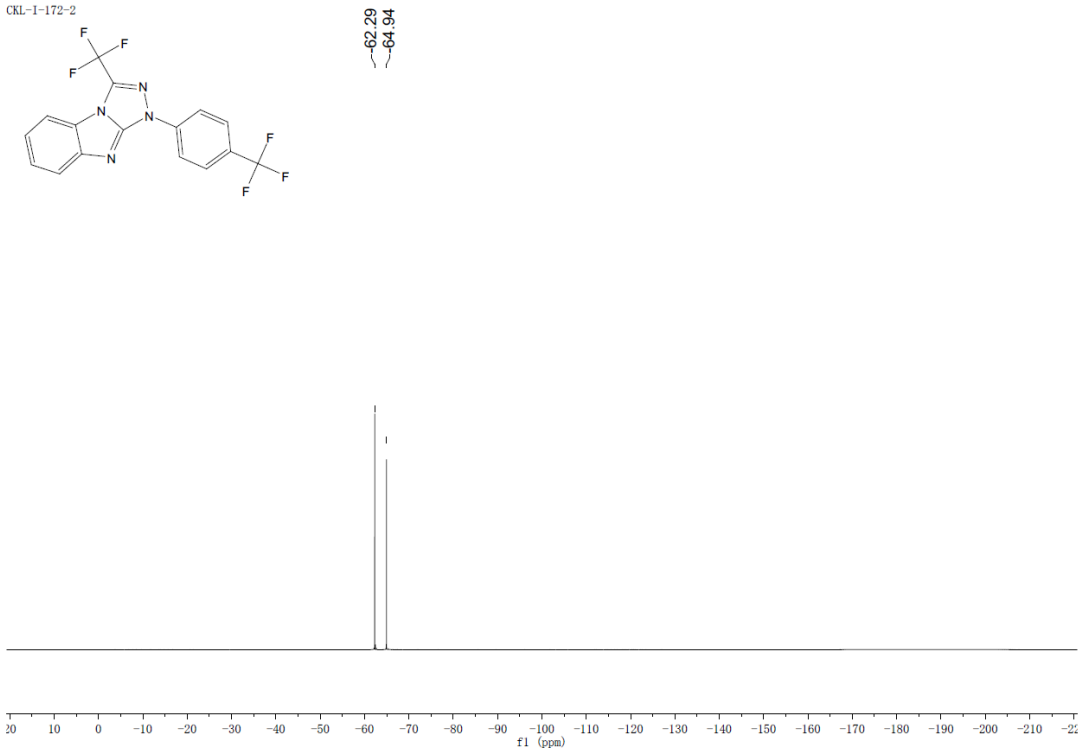
^{19}F NMR (471 MHz, $CDCl_3$) of **3c**.



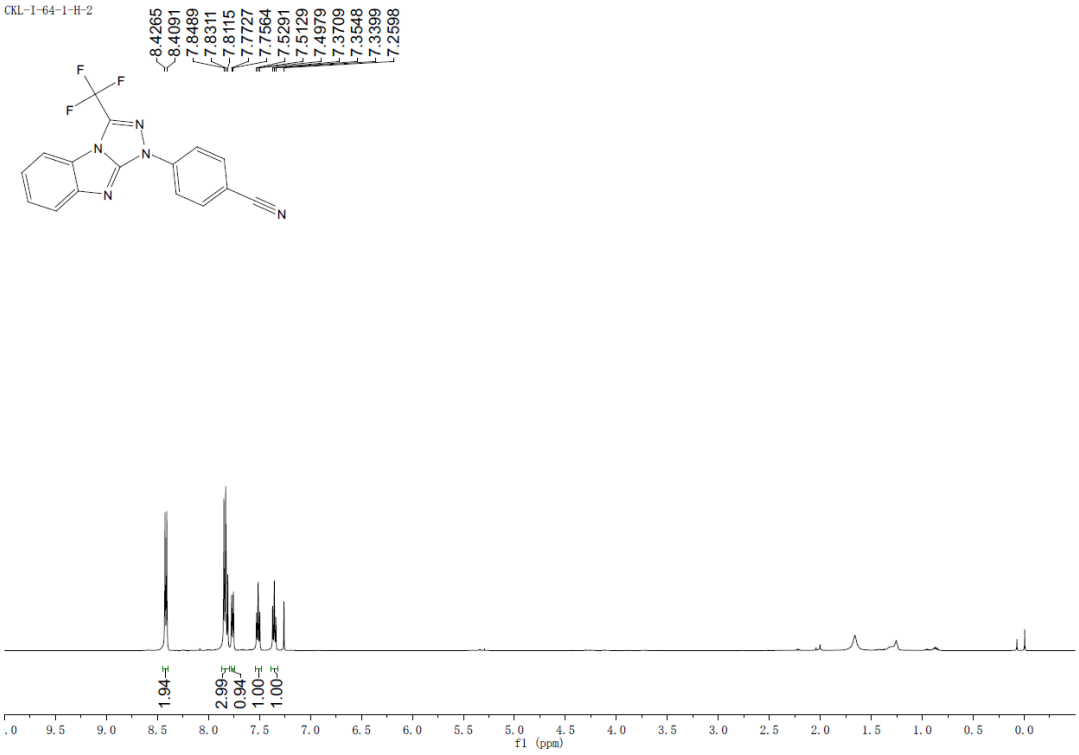
^{1}H NMR (500 MHz, $CDCl_3$) of **3d**.



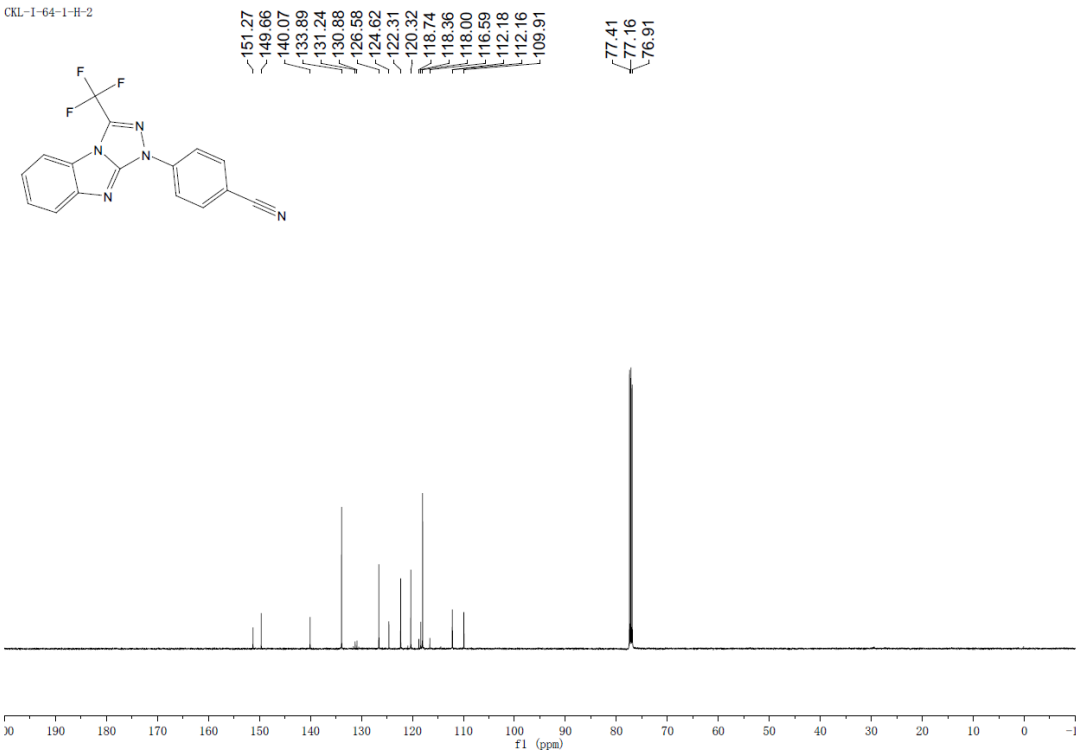
^{13}C NMR (125 MHz, $CDCl_3$) of **3d**.



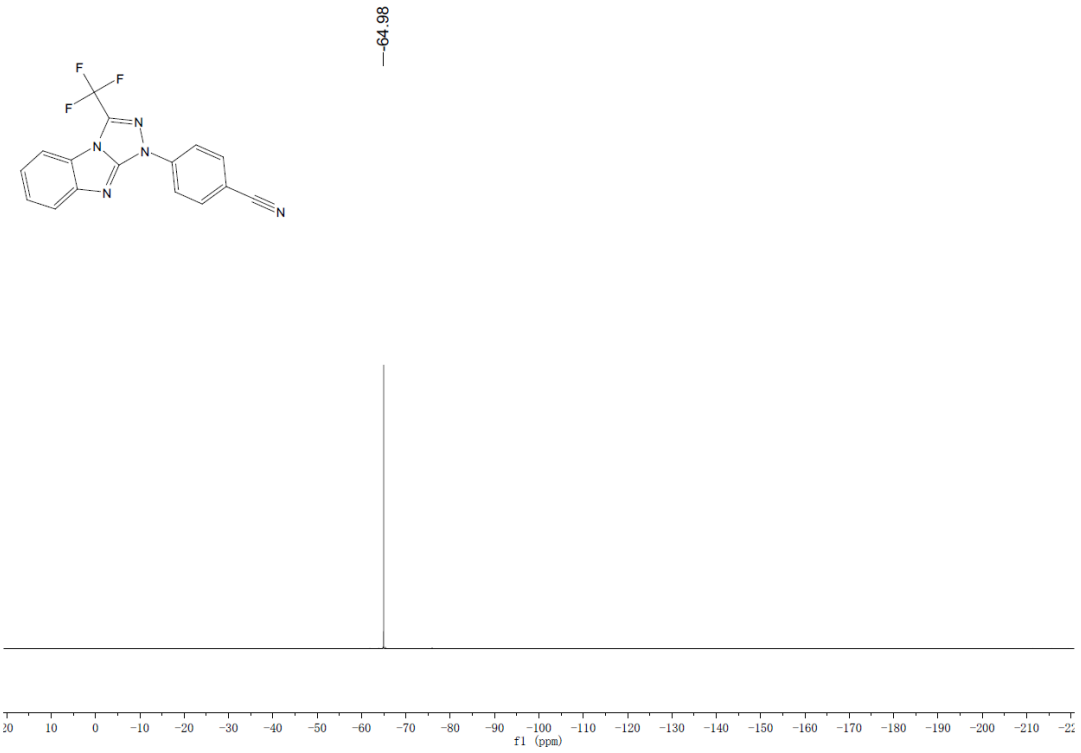
^{19}F NMR (471 MHz, $CDCl_3$) of **3d**.



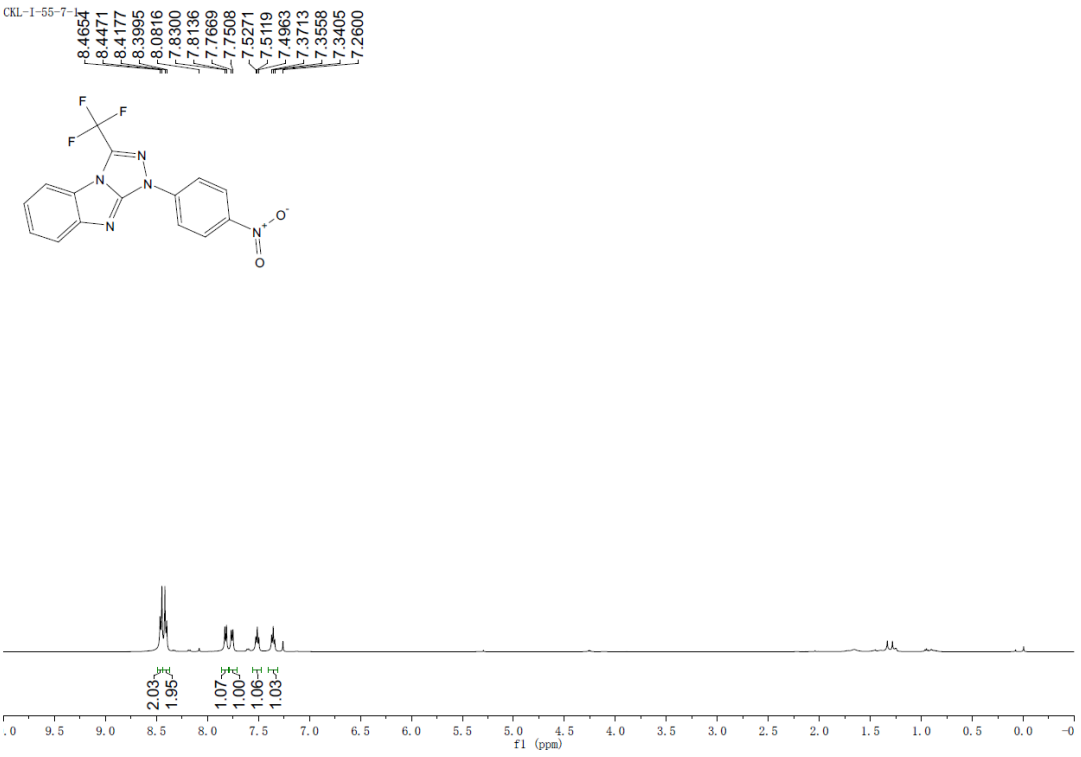
^{1}H NMR (500 MHz, $CDCl_3$) of **3e**.



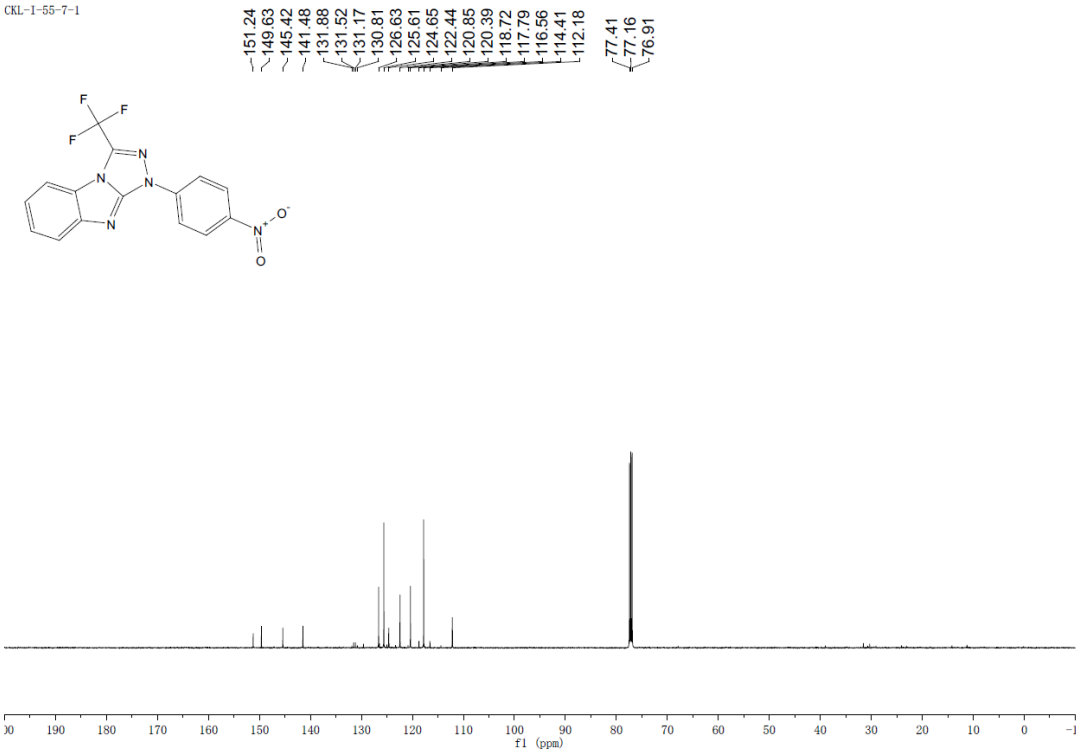
^{13}C NMR (125 MHz, $CDCl_3$) of **3e**.



^{19}F NMR (471 MHz, $CDCl_3$) of **3e**.

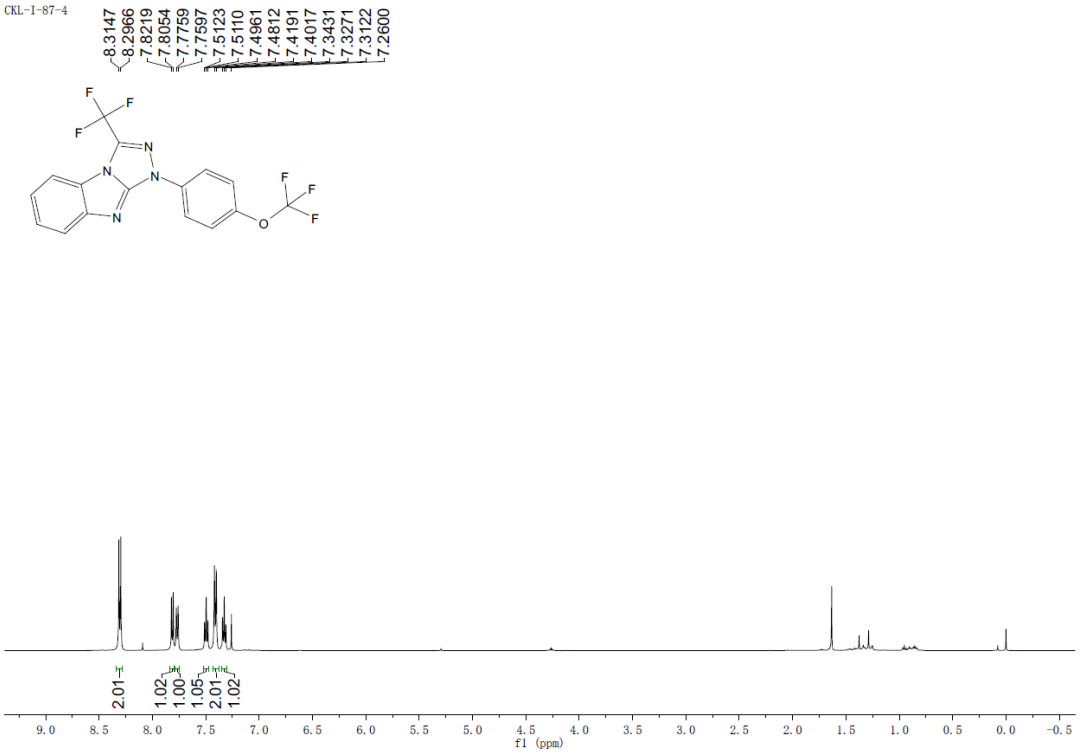


^{1}H NMR (500 MHz, $CDCl_3$) of **3f**.

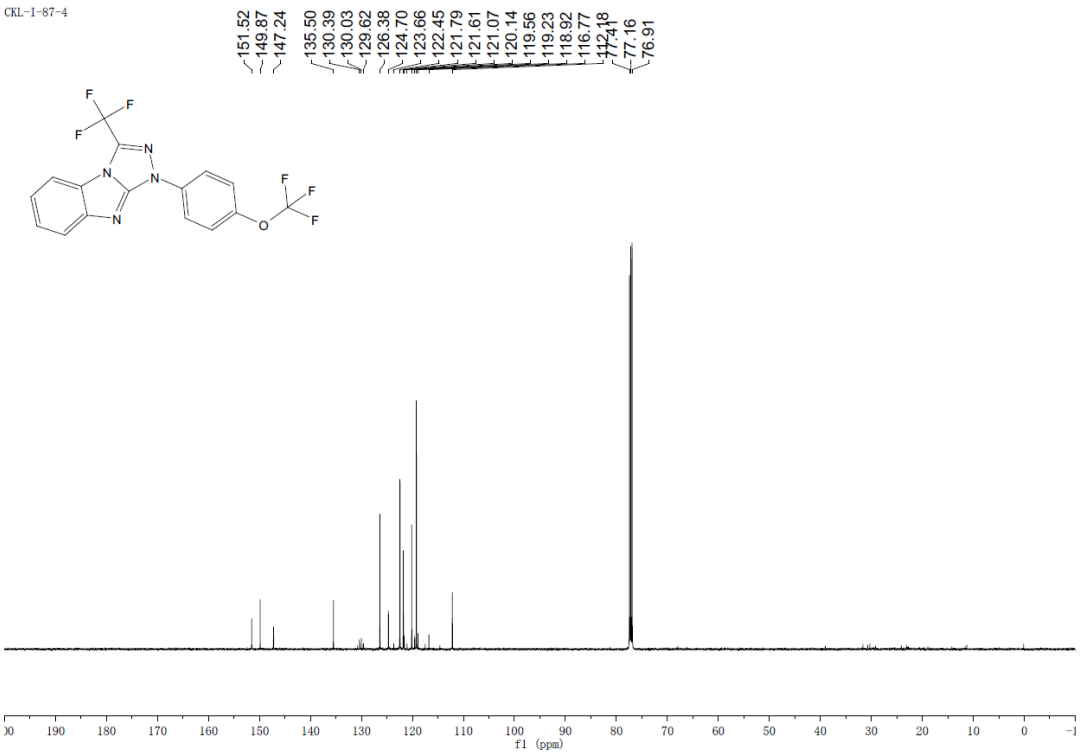


^{13}C NMR (125 MHz, $CDCl_3$) of **3f**.

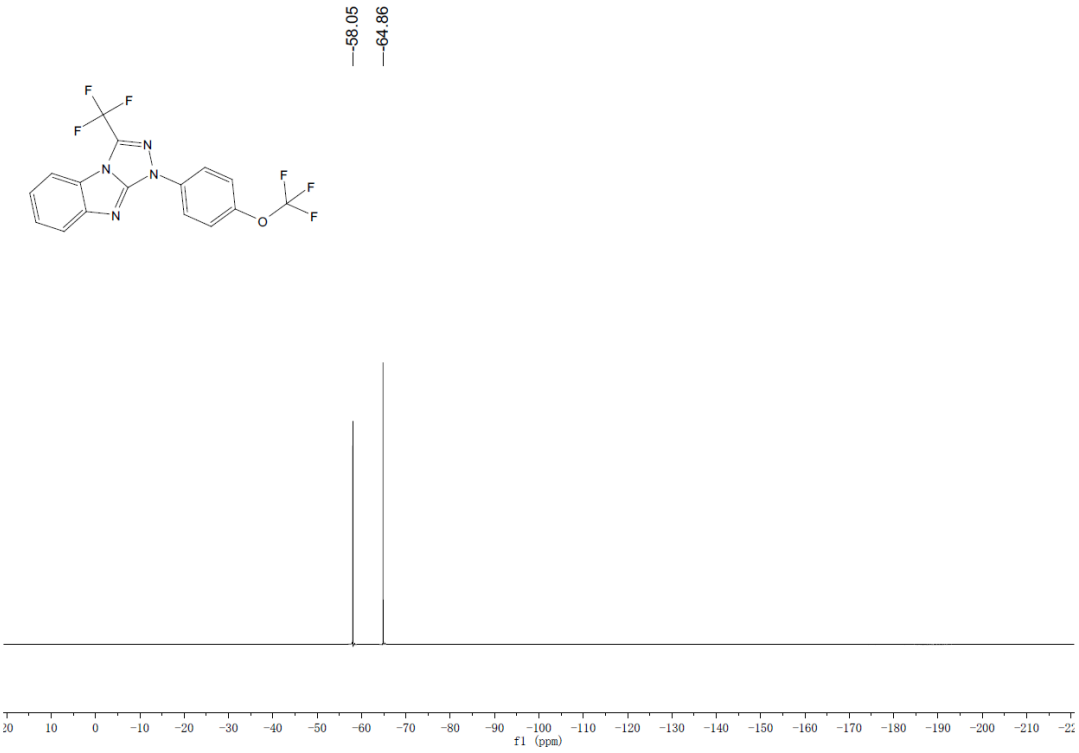
^{19}F NMR (471 MHz, $CDCl_3$) of **3f**.



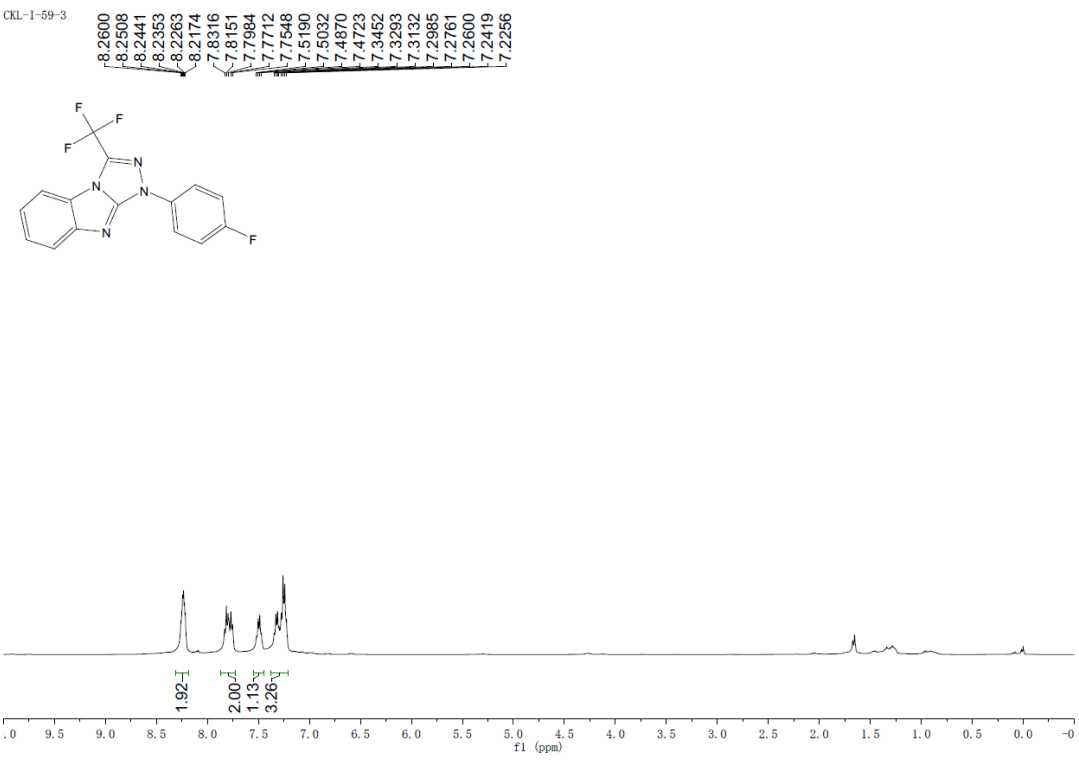
^{1}H NMR (500 MHz, $CDCl_3$) of **3g**.



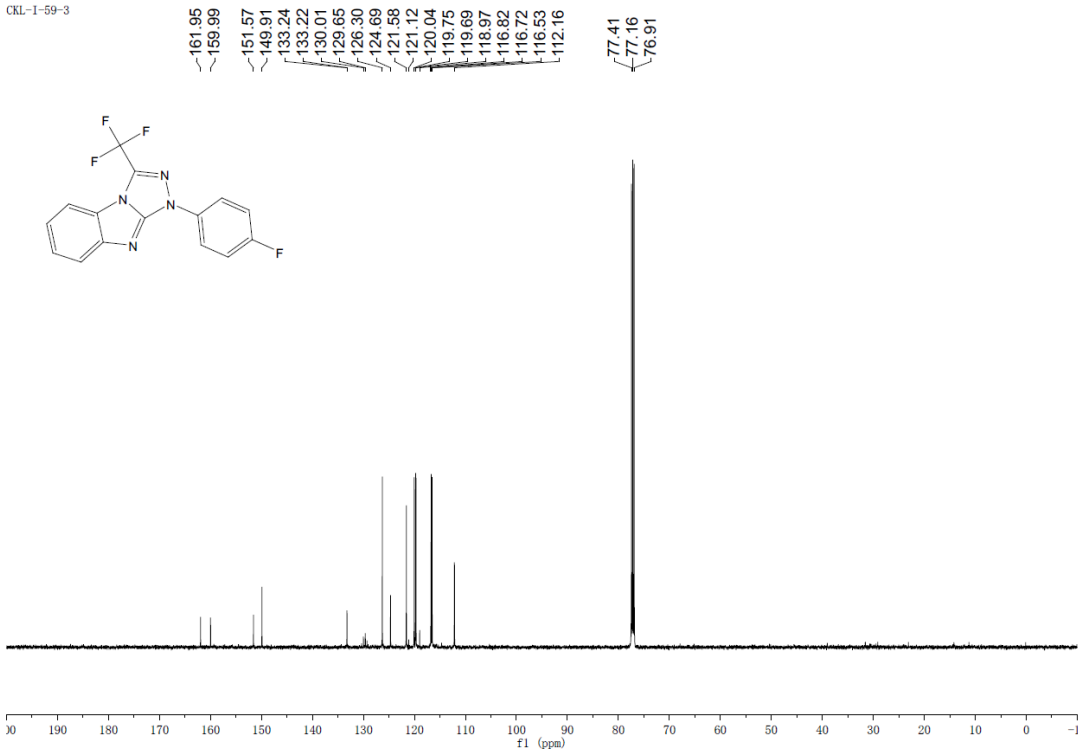
^{13}C NMR (125 MHz, $CDCl_3$) of **3g**.



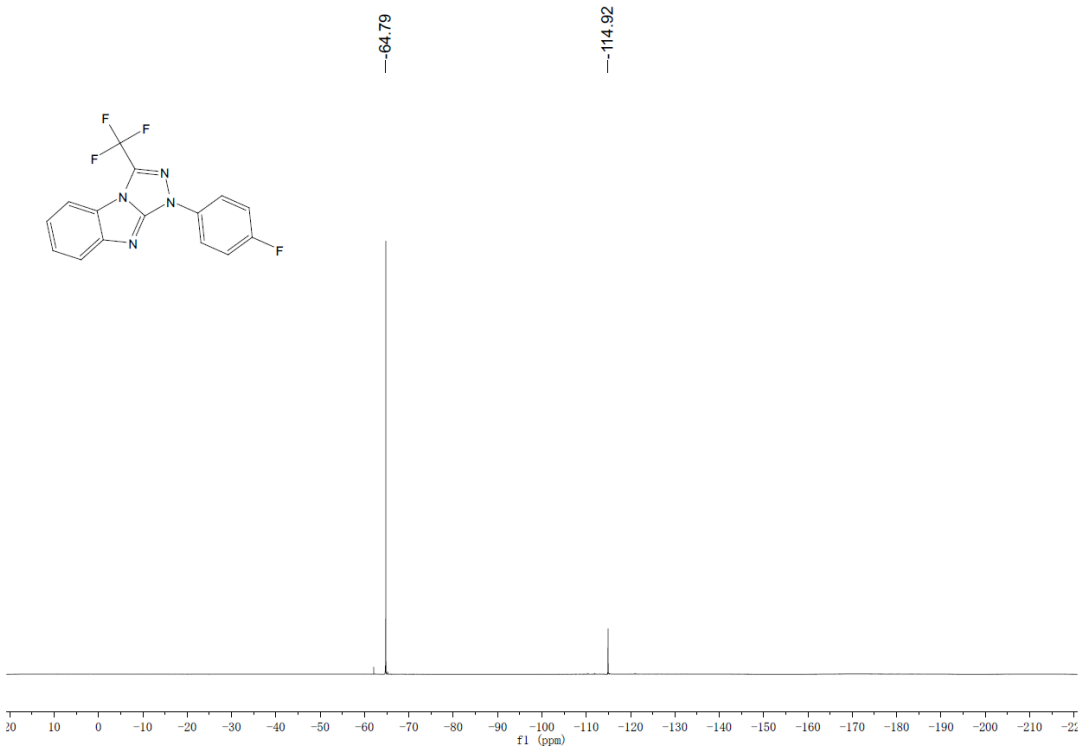
^{19}F NMR (471 MHz, $CDCl_3$) of **3g**.



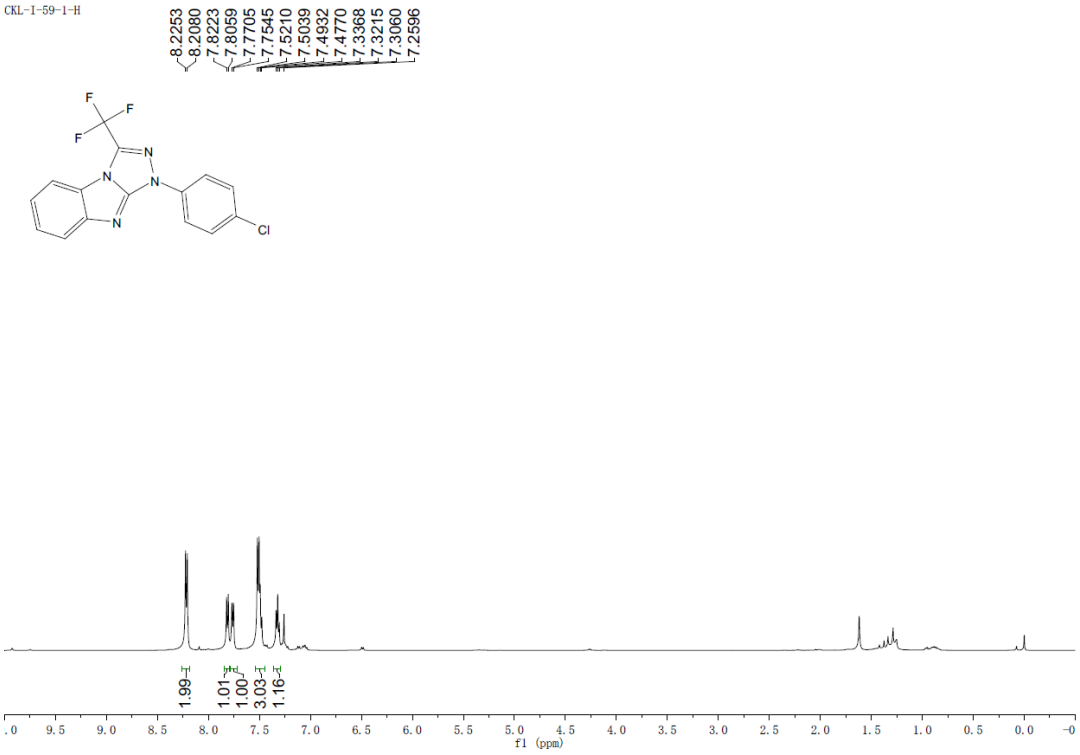
^{1}H NMR (500 MHz, $CDCl_3$) of **3h**.



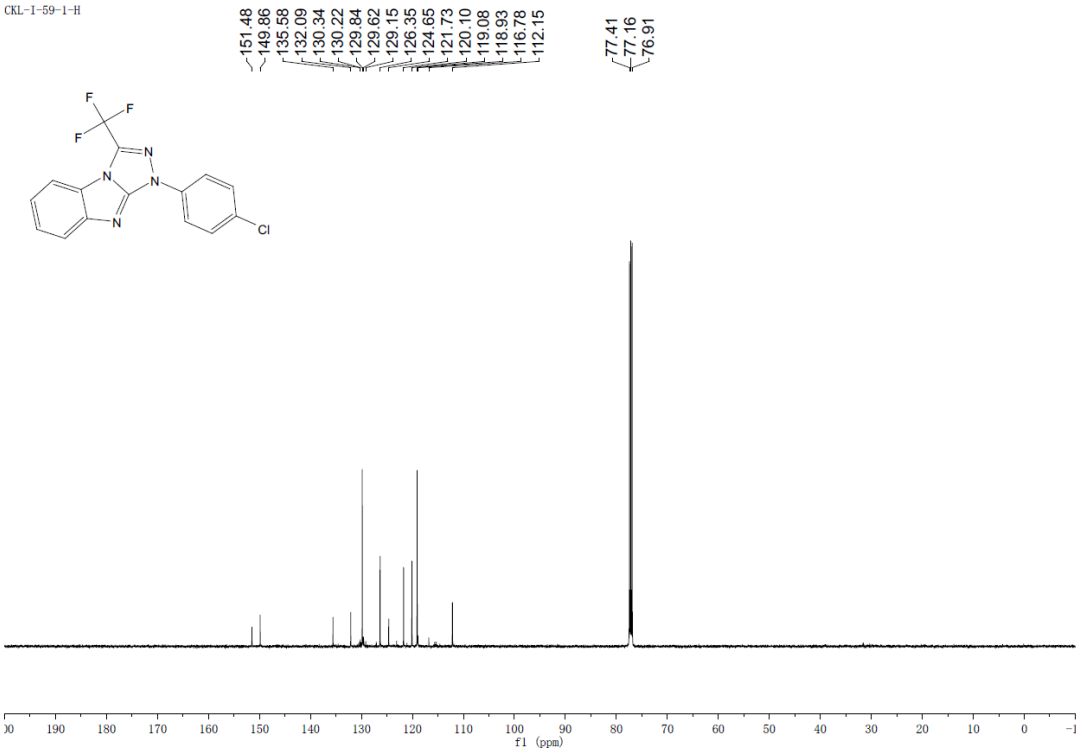
^{13}C NMR (125 MHz, $CDCl_3$) of **3h**.



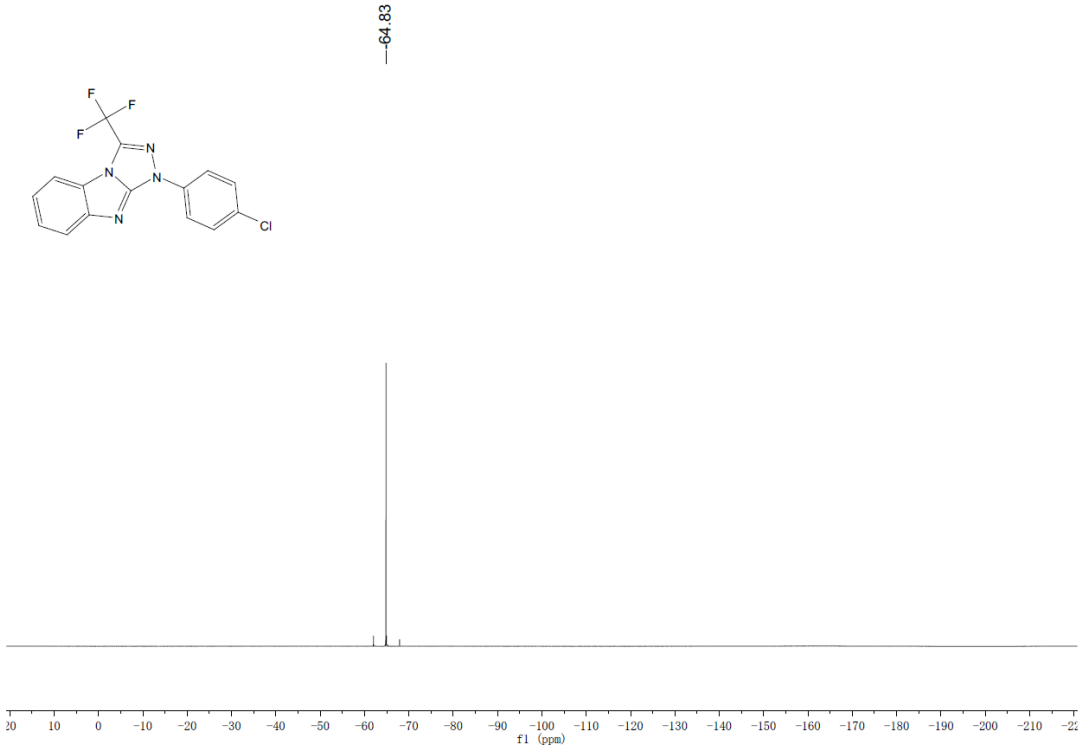
^{19}F NMR (471 MHz, $CDCl_3$) of **3h**.



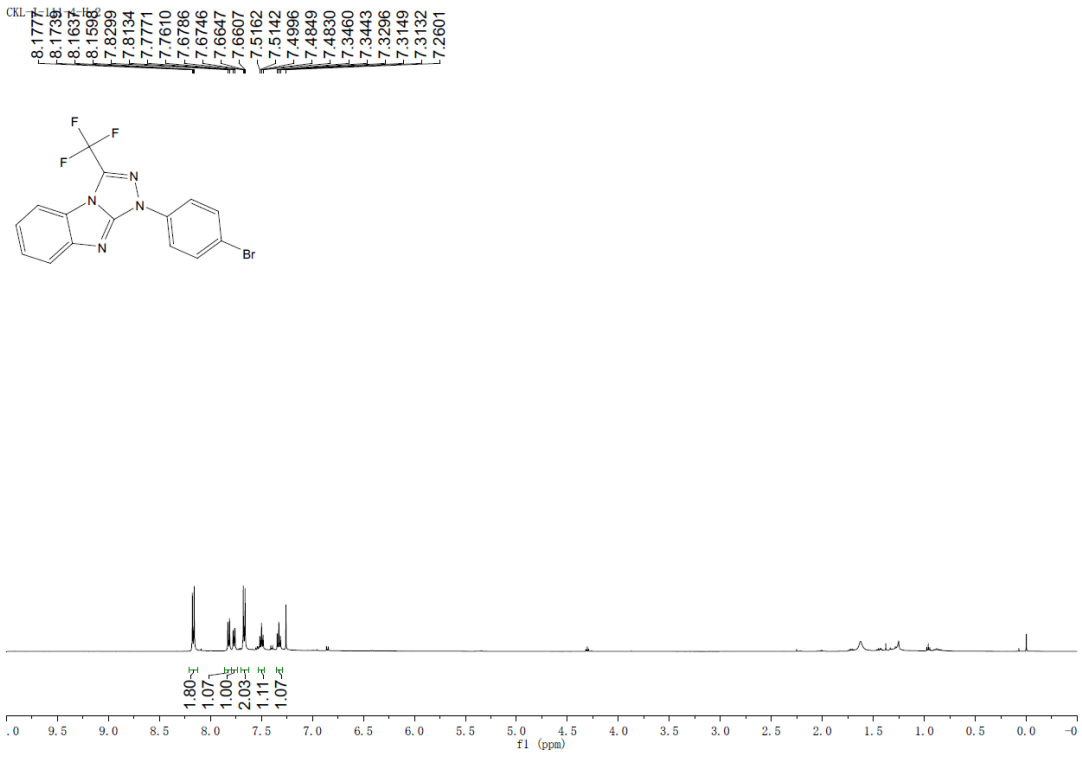
^{1}H NMR (500 MHz, $CDCl_3$) of **3i**.



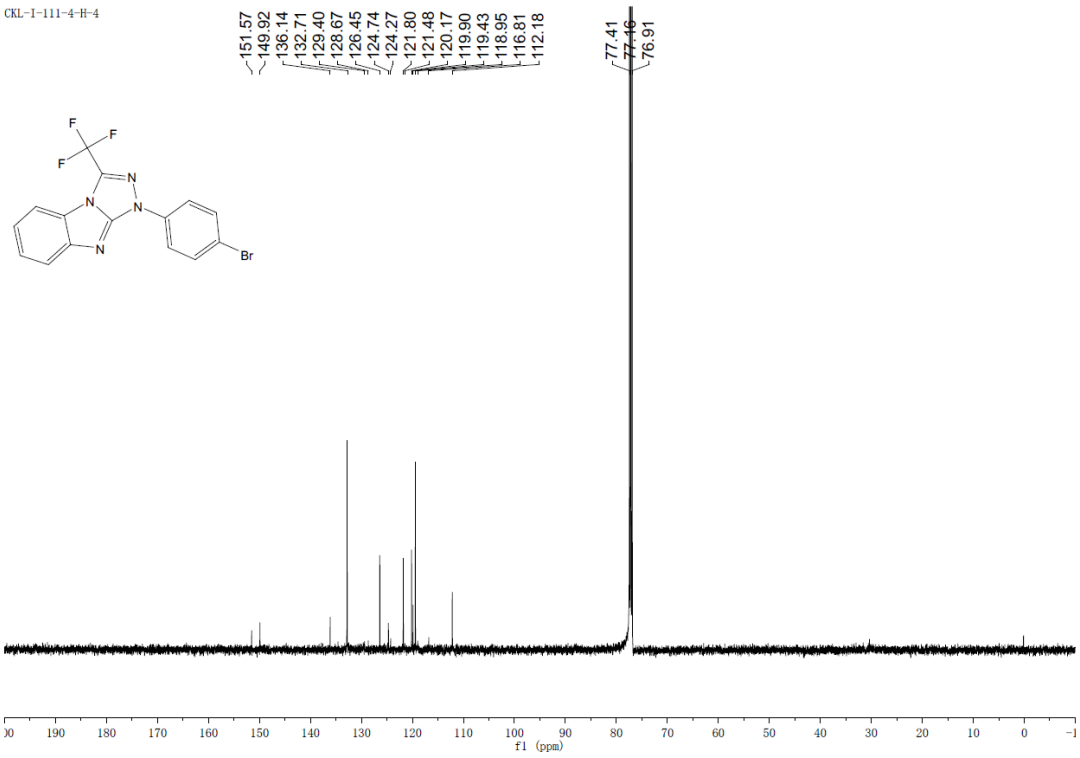
^{13}C NMR (125 MHz, $CDCl_3$) of **3i**.



^{19}F NMR (471 MHz, $CDCl_3$) of **3i**.

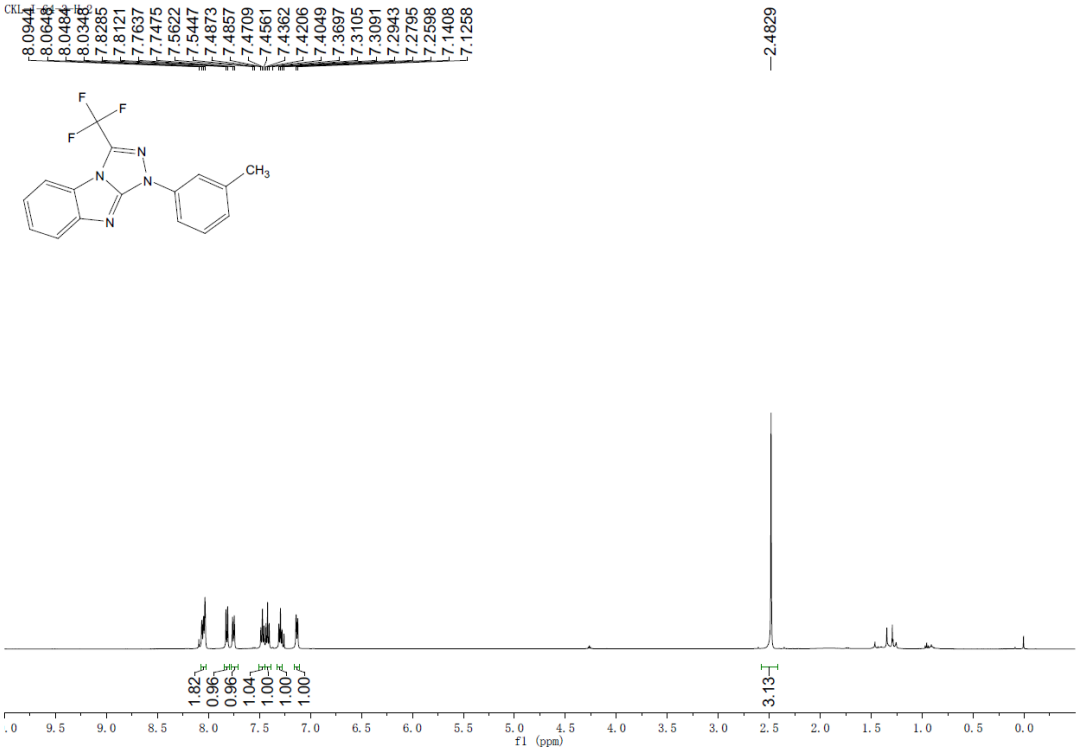


^{1}H NMR (500 MHz, $CDCl_3$) of **3j**.

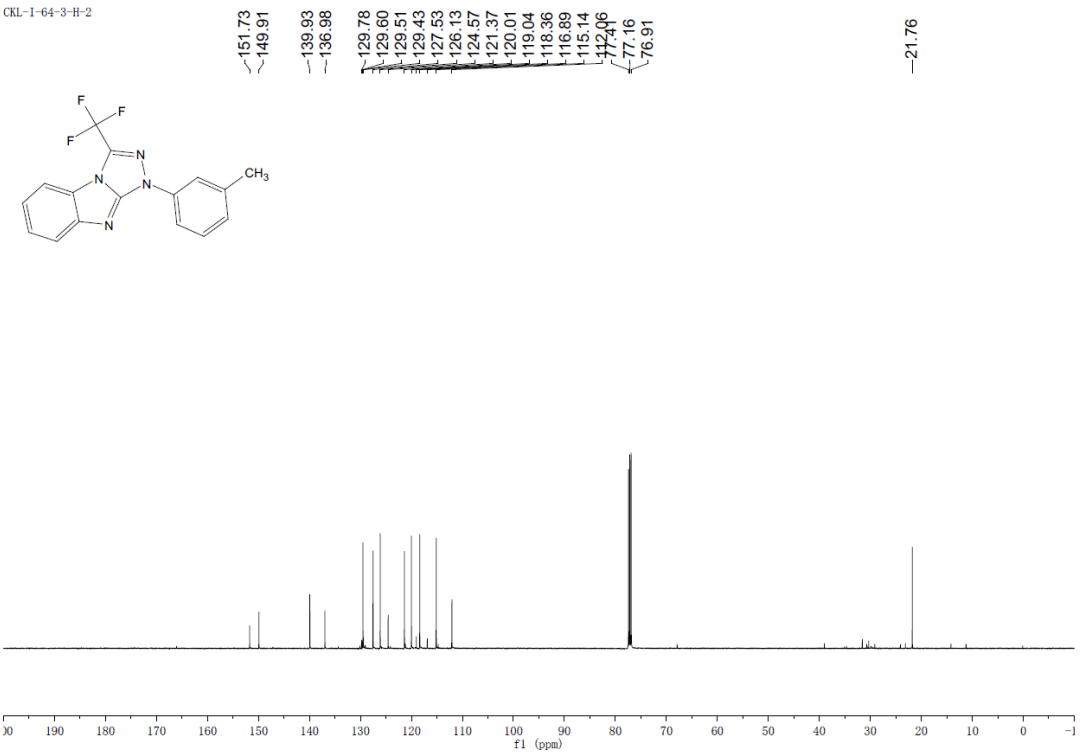


^{13}C NMR (125 MHz, $CDCl_3$) of **3j**.

^{19}F NMR (471 MHz, $CDCl_3$) of **3j**.

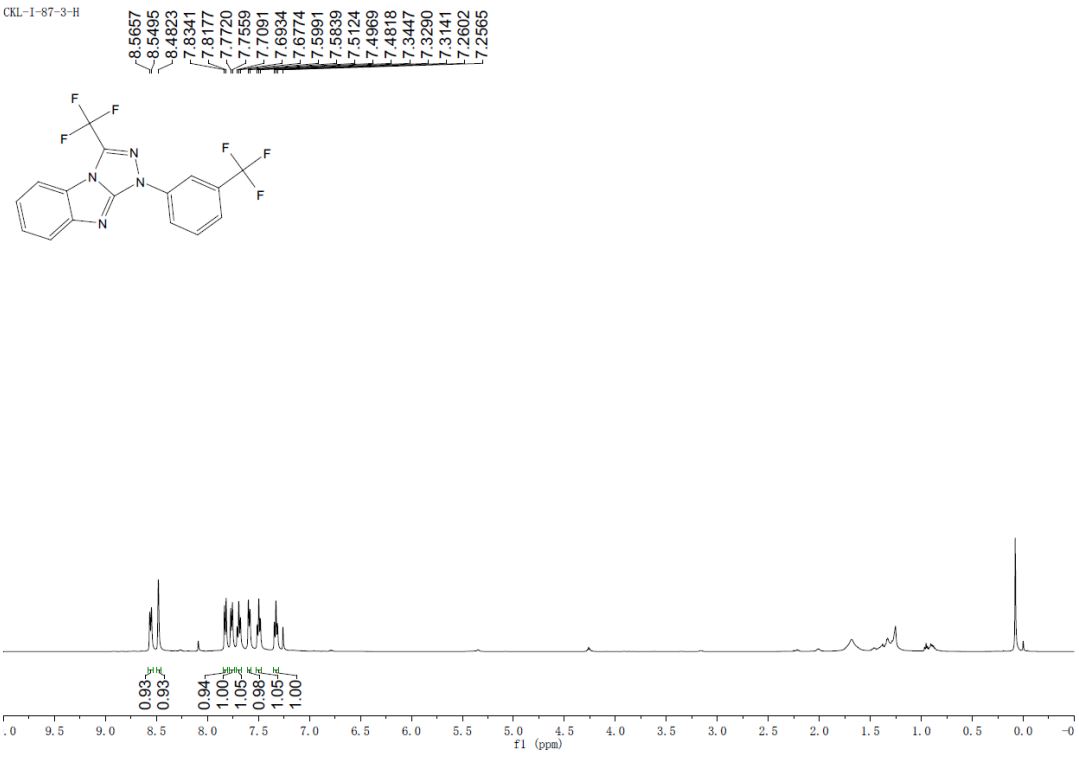


^{1}H NMR (500 MHz, $CDCl_3$) of **3k**.

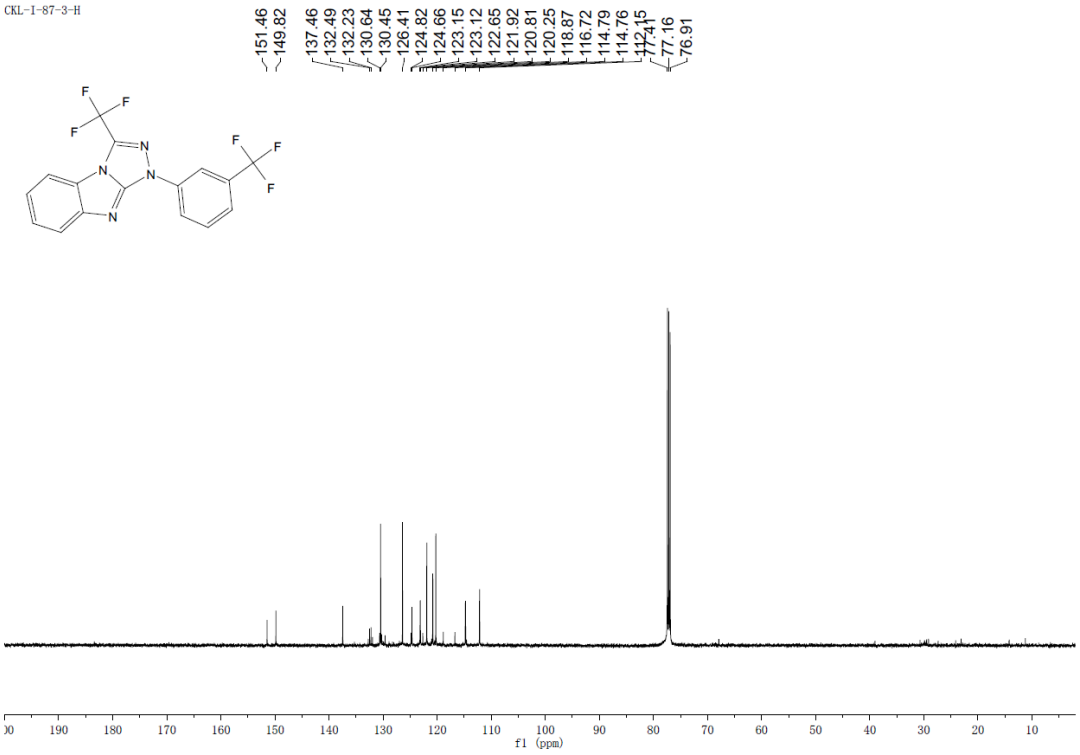


^{13}C NMR (125 MHz, $CDCl_3$) of **3k**.

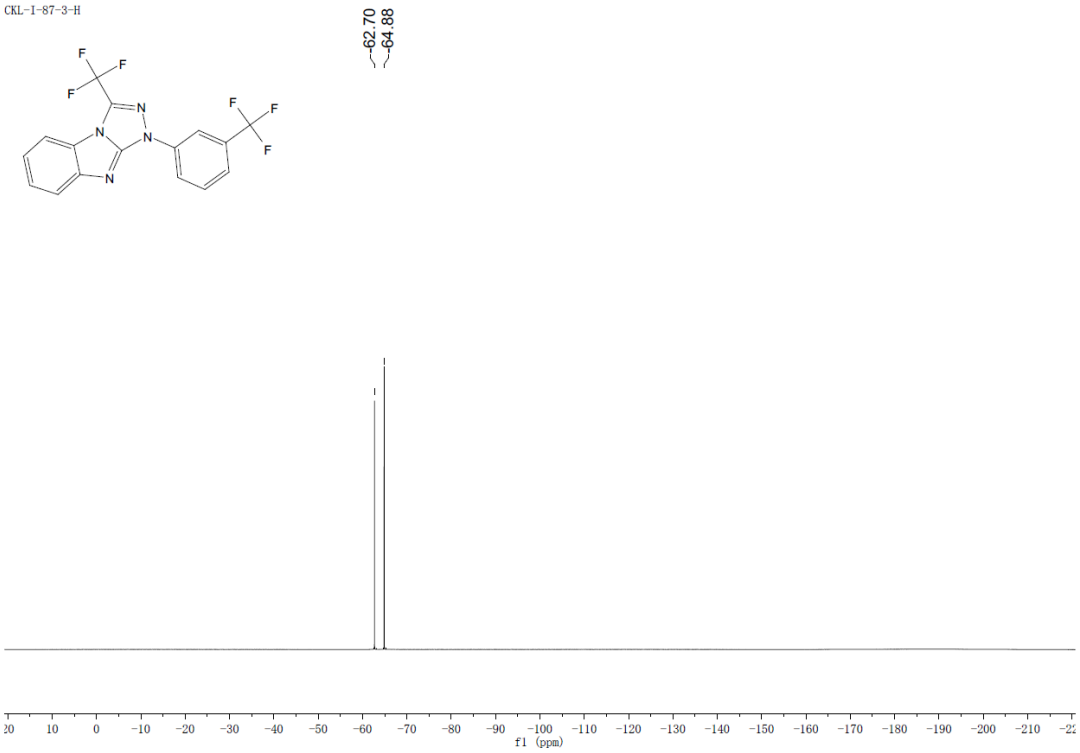
^{19}F NMR (471 MHz, $CDCl_3$) of **3k**.



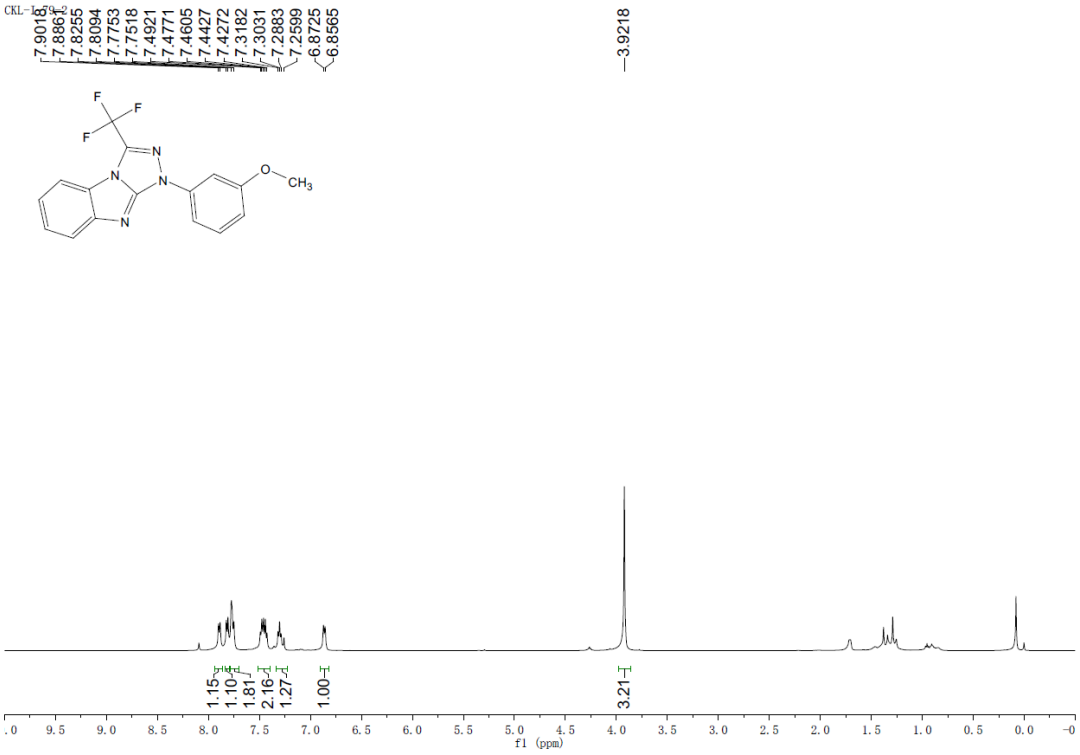
^{1}H NMR (500 MHz, $CDCl_3$) of **3l**.



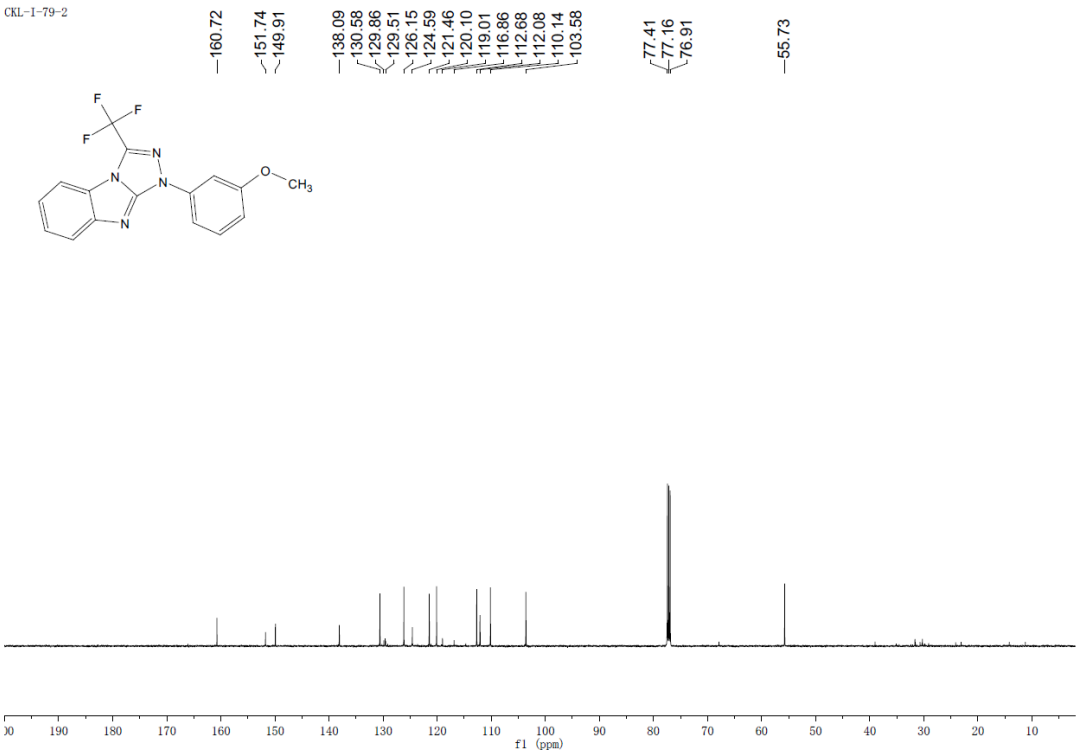
^{13}C NMR (125 MHz, $CDCl_3$) of **3l**.



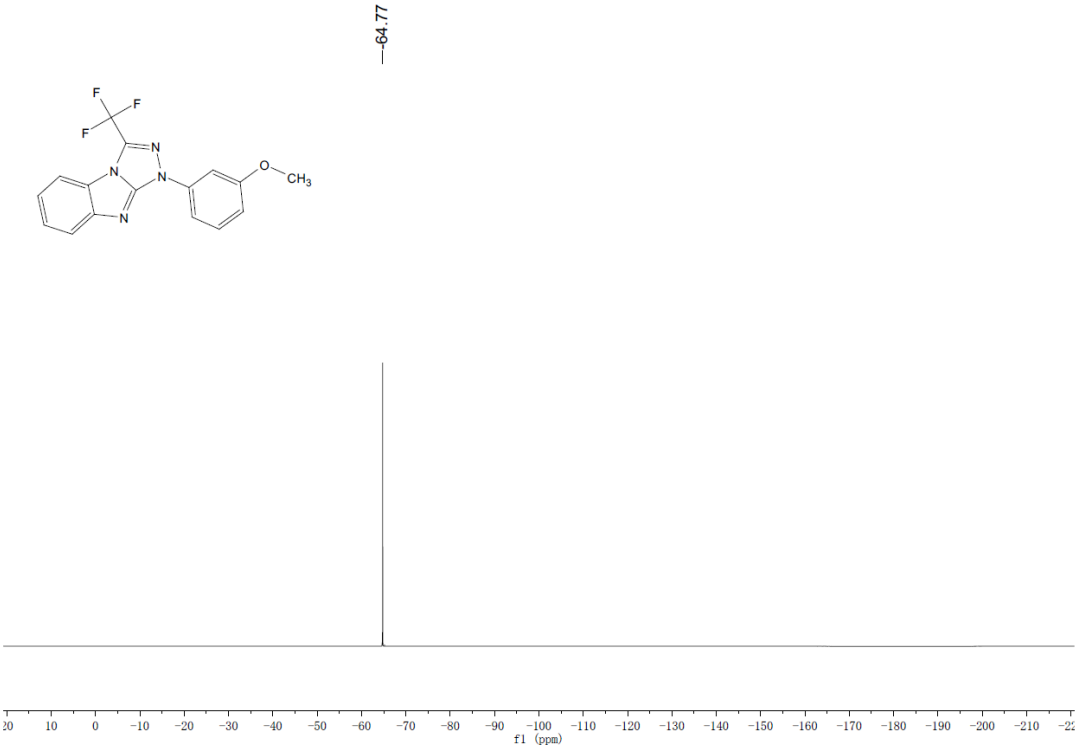
^{19}F NMR (471 MHz, $CDCl_3$) of **3l**.



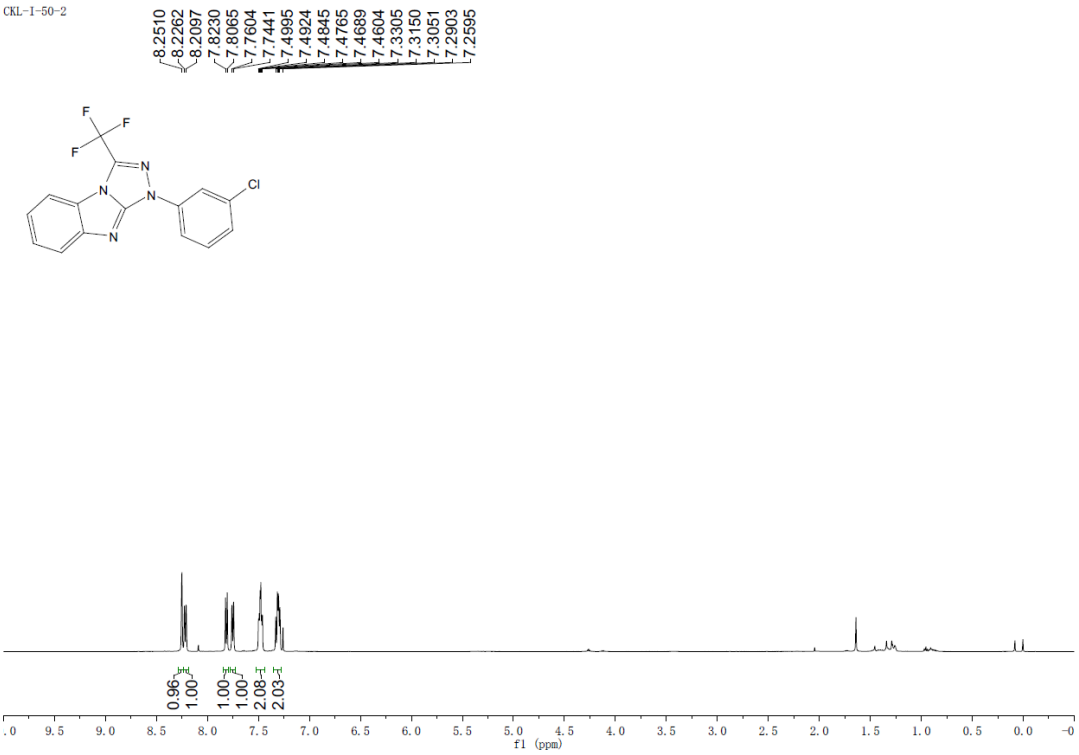
^{1}H NMR (500 MHz, $CDCl_3$) of **3m**.



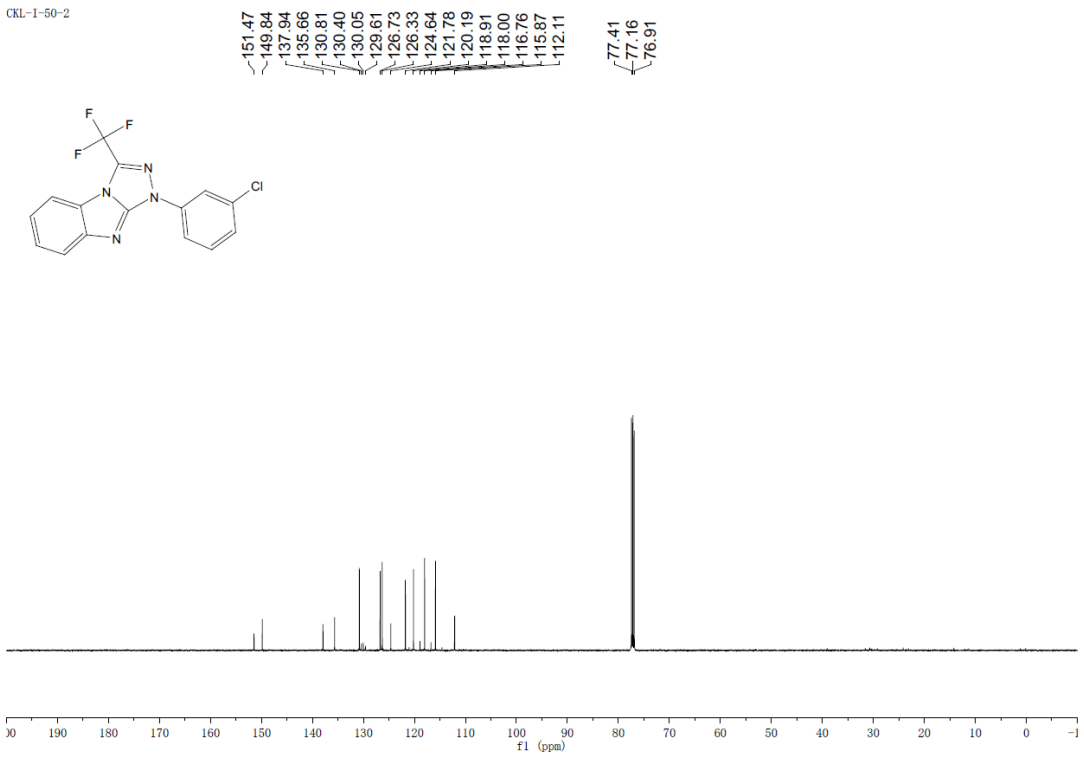
^{13}C NMR (125 MHz, $CDCl_3$) of **3m**.



^{19}F NMR (471 MHz, $CDCl_3$) of **3m**.

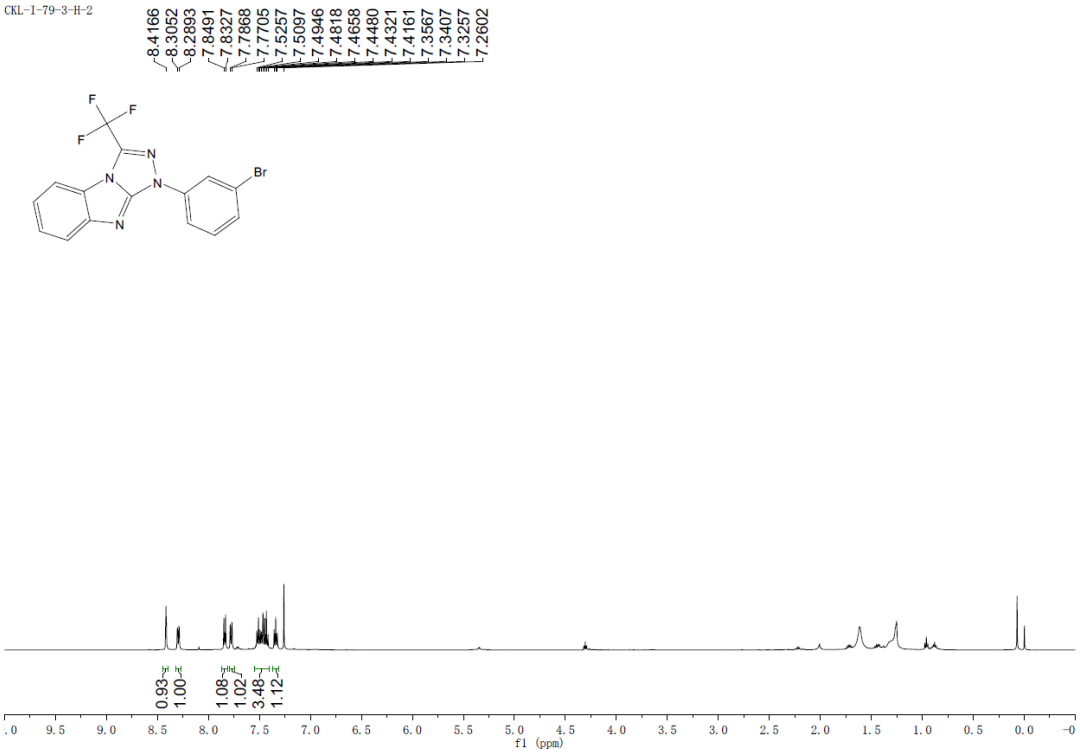


^{1}H NMR (500 MHz, $CDCl_3$) of **3n**.

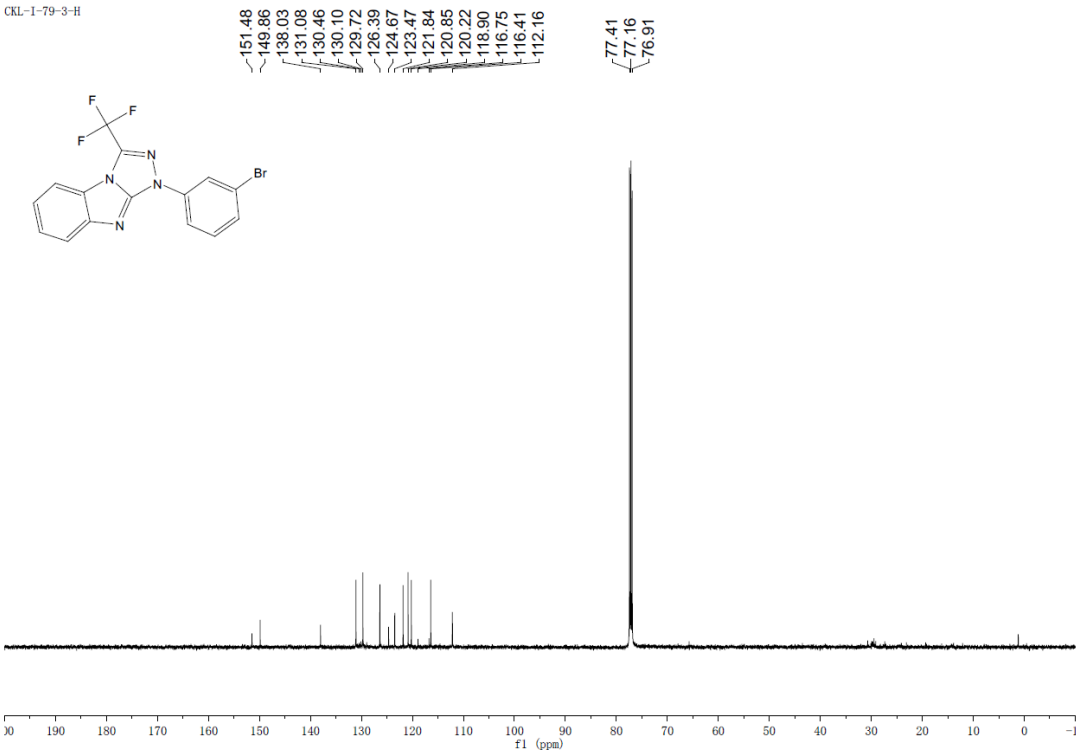


^{13}C NMR (125 MHz, $CDCl_3$) of **3n**.

^{19}F NMR (471 MHz, $CDCl_3$) of **3n**.

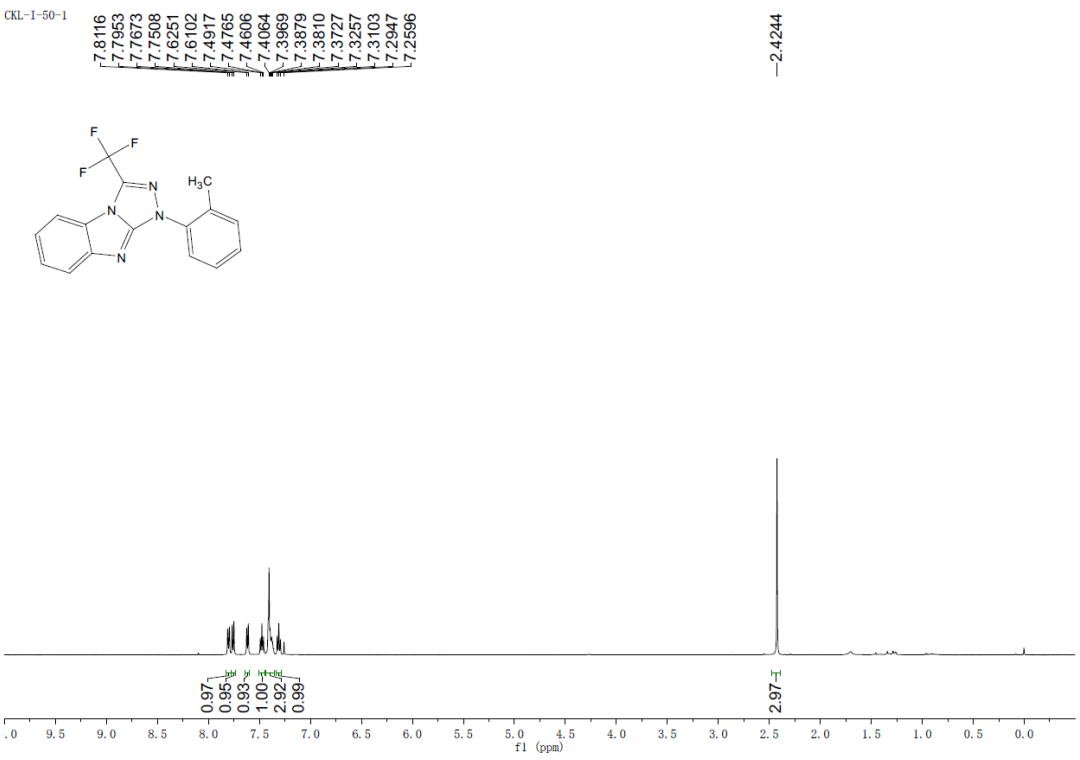


^{1}H NMR (500 MHz, $CDCl_3$) of **3o**.

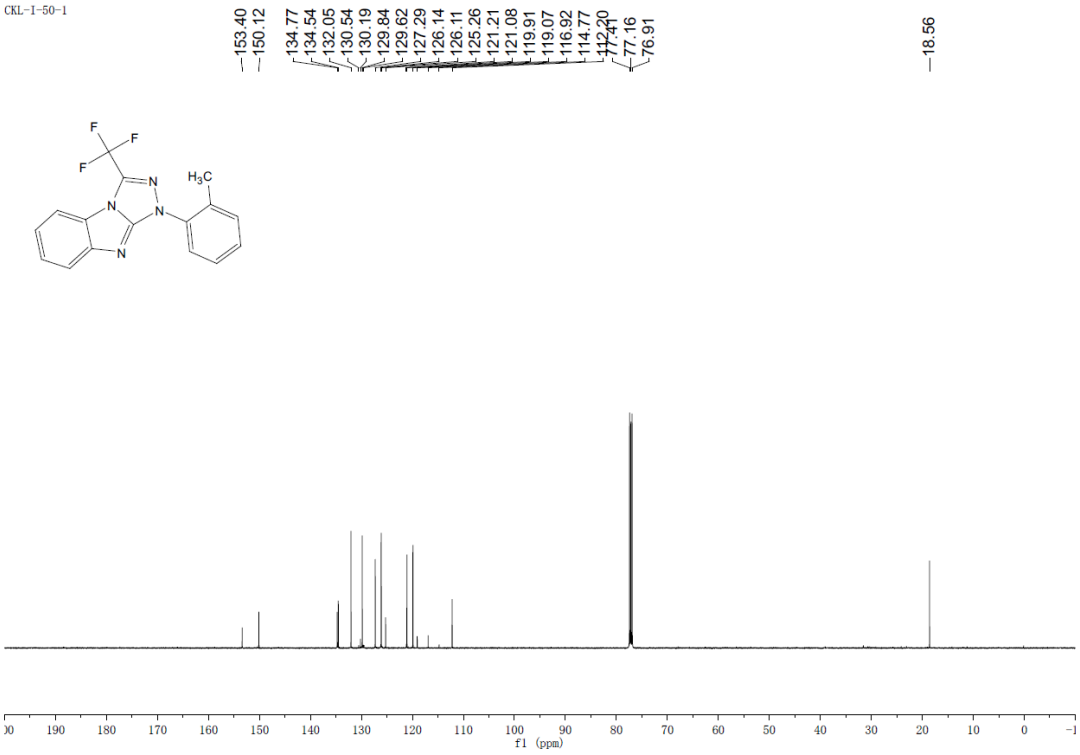


^{13}C NMR (125 MHz, $CDCl_3$) of **3o**.

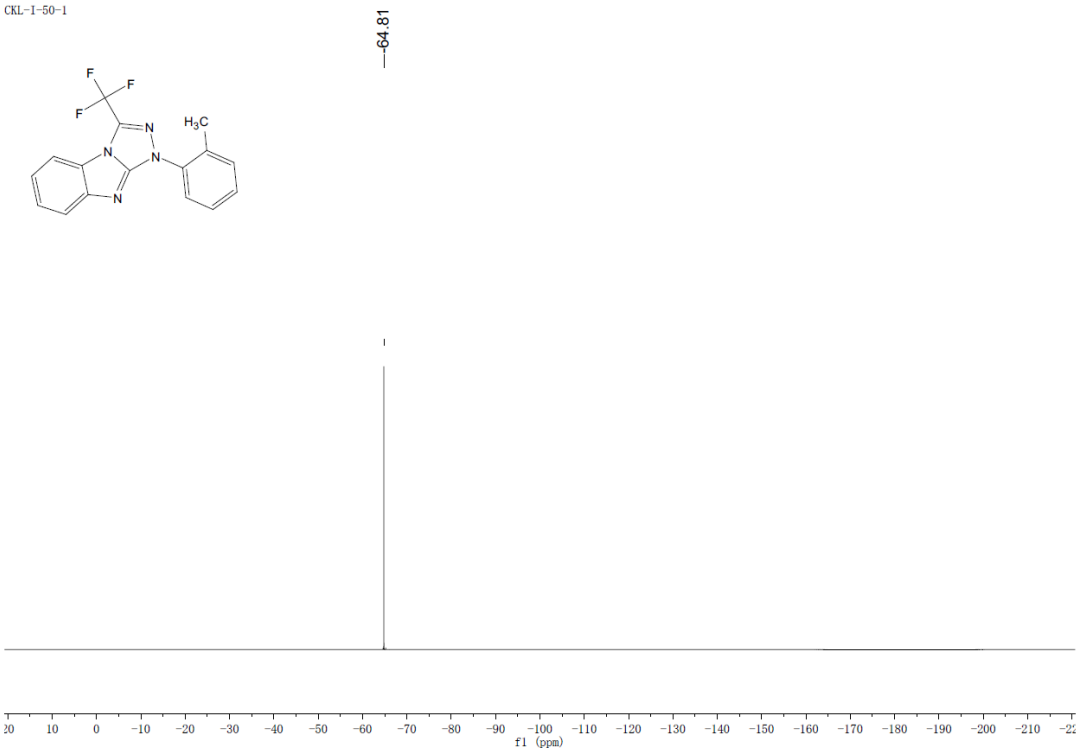
^{19}F NMR (471 MHz, $CDCl_3$) of **3o**.



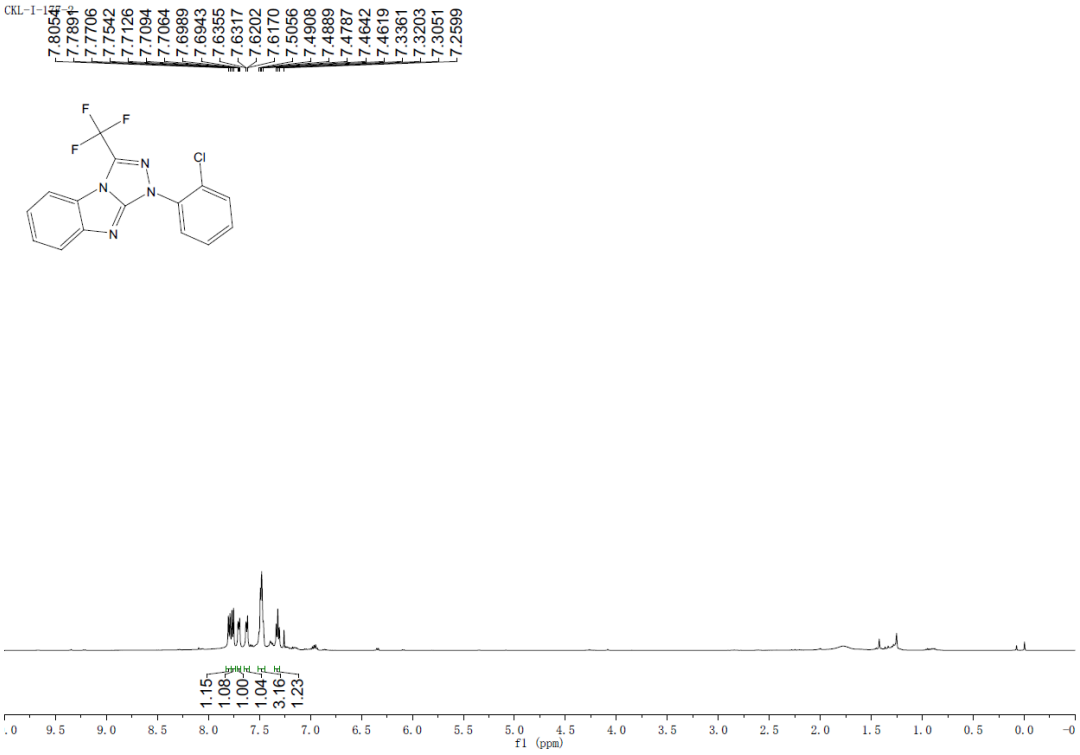
^{1}H NMR (500 MHz, $CDCl_3$) of **3p**.



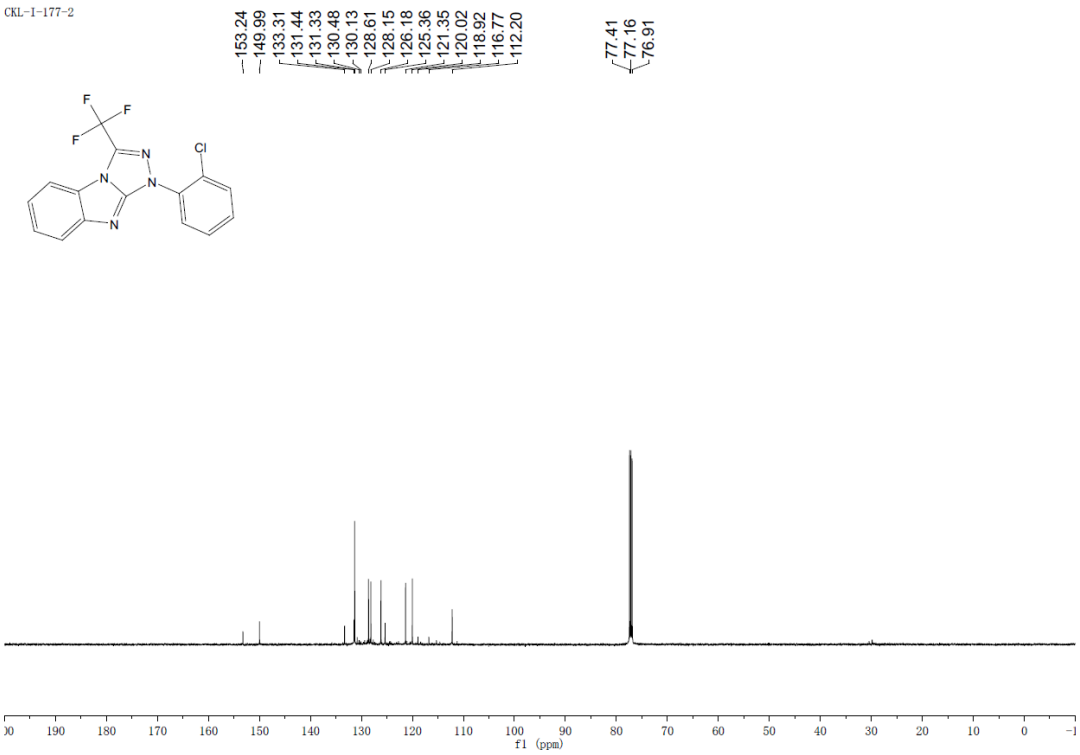
^{13}C NMR (125 MHz, $CDCl_3$) of **3p**.



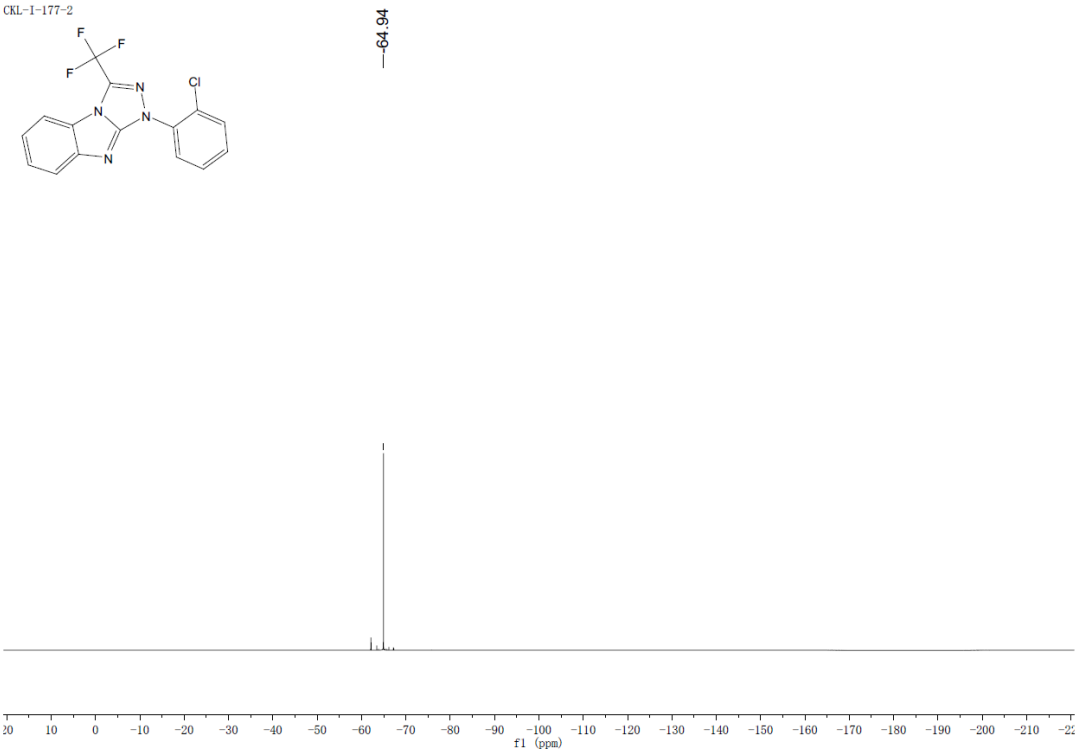
^{19}F NMR (471 MHz, $CDCl_3$) of **3p**.



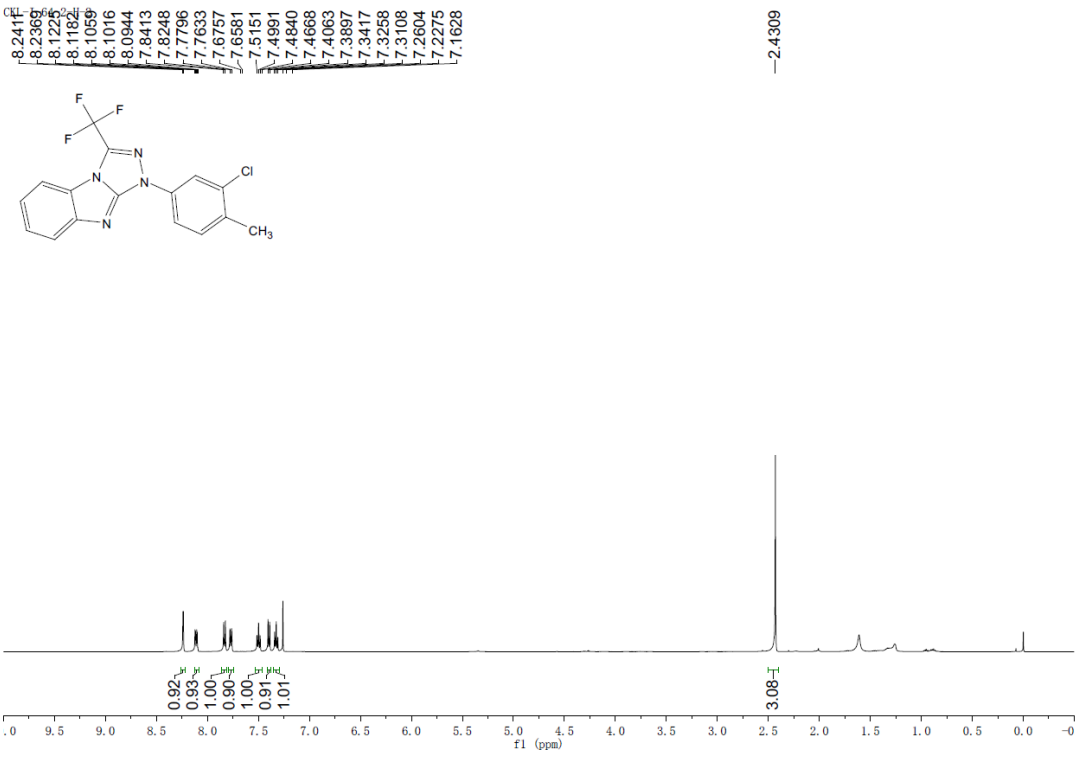
^{1}H NMR (500 MHz, $CDCl_3$) of **3q**.



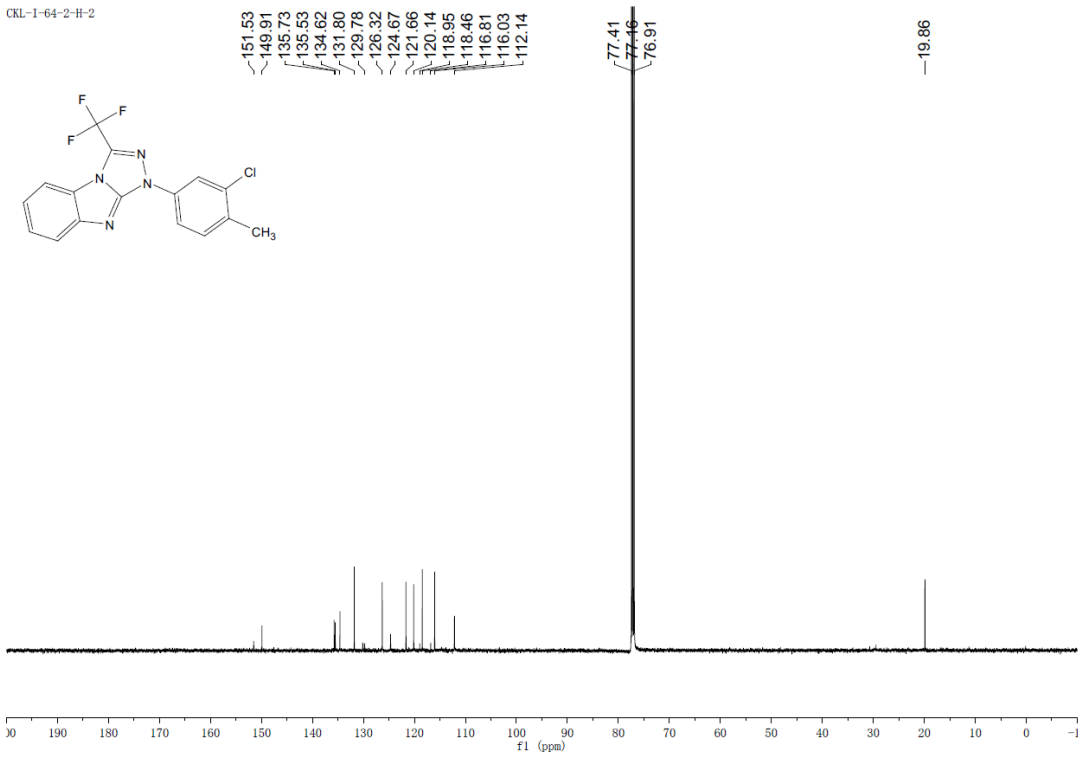
^{13}C NMR (125 MHz, $CDCl_3$) of **3q**.



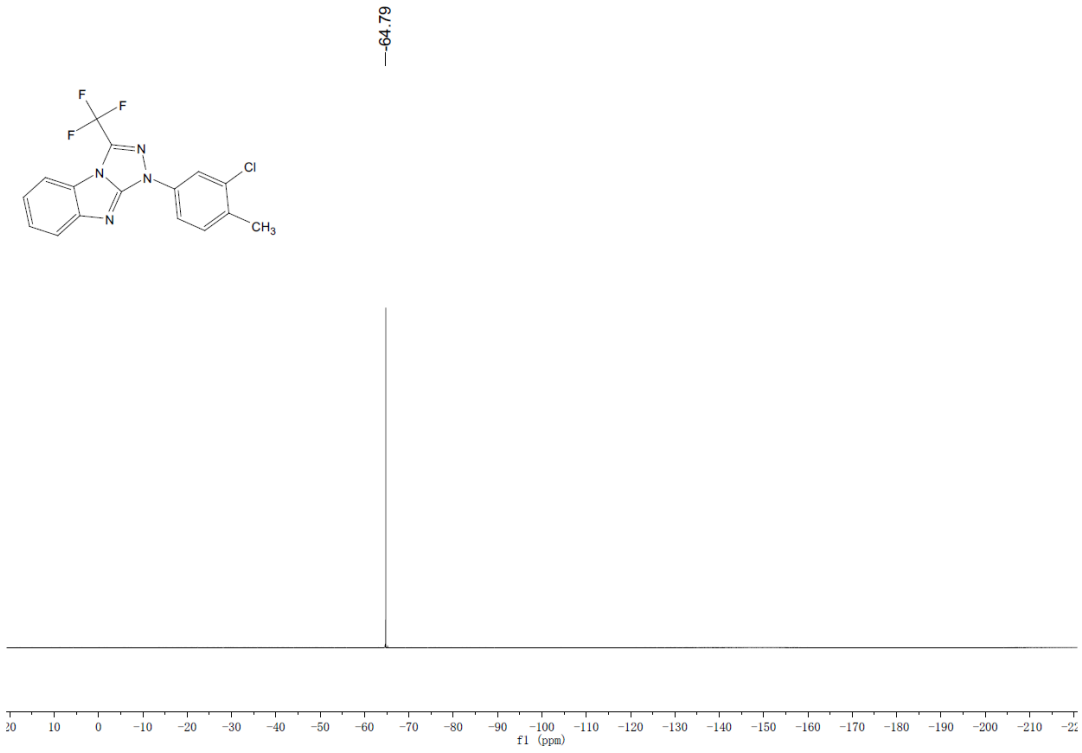
^{19}F NMR (471 MHz, $CDCl_3$) of **3q**.



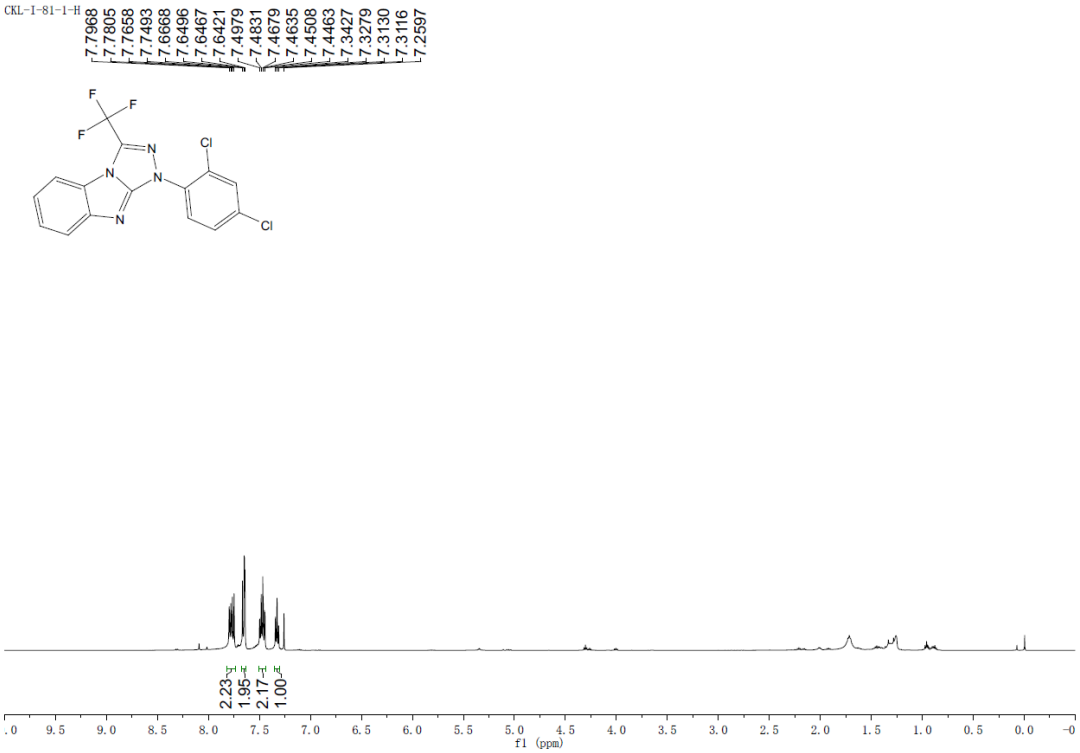
^{1}H NMR (500 MHz, $CDCl_3$) of **3r**.



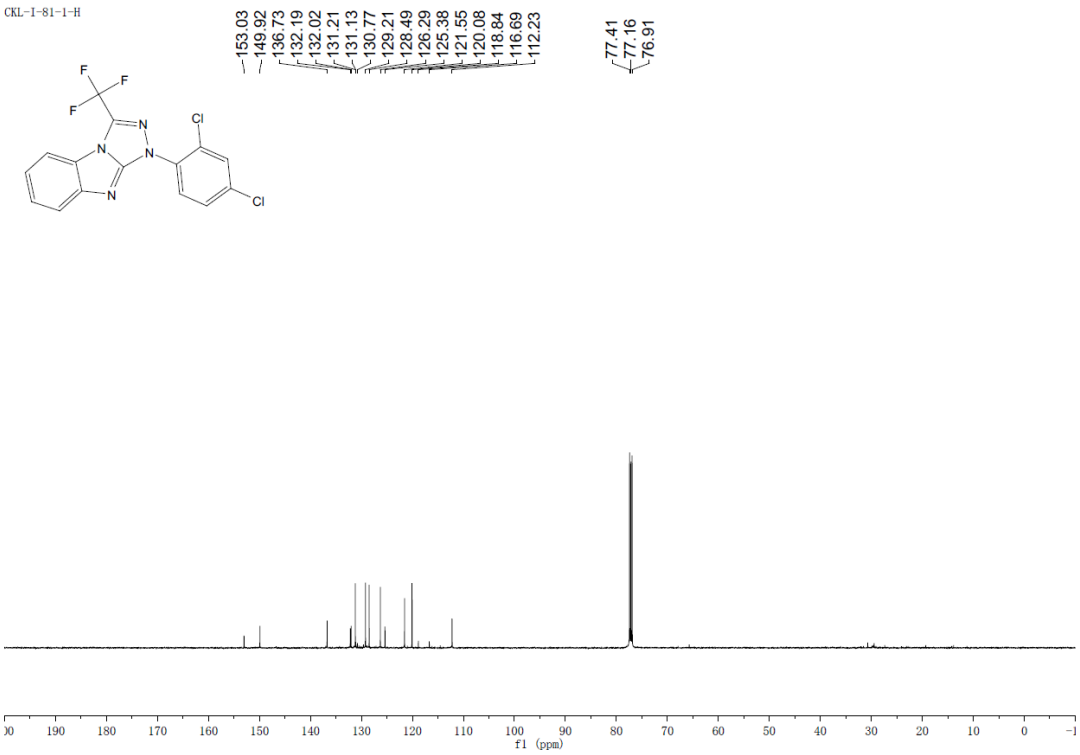
^{13}C NMR (125 MHz, $CDCl_3$) of **3r**.



^{19}F NMR (471 MHz, $CDCl_3$) of **3r**.

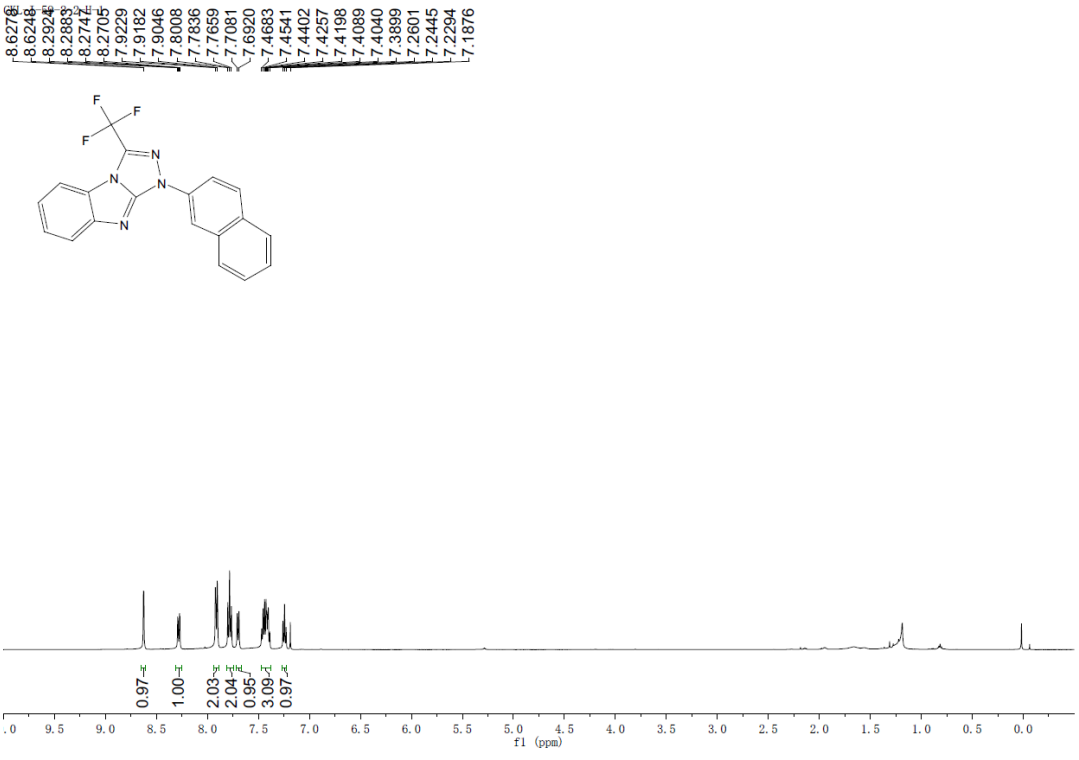


^{1}H NMR (500 MHz, $CDCl_3$) of **3s**.

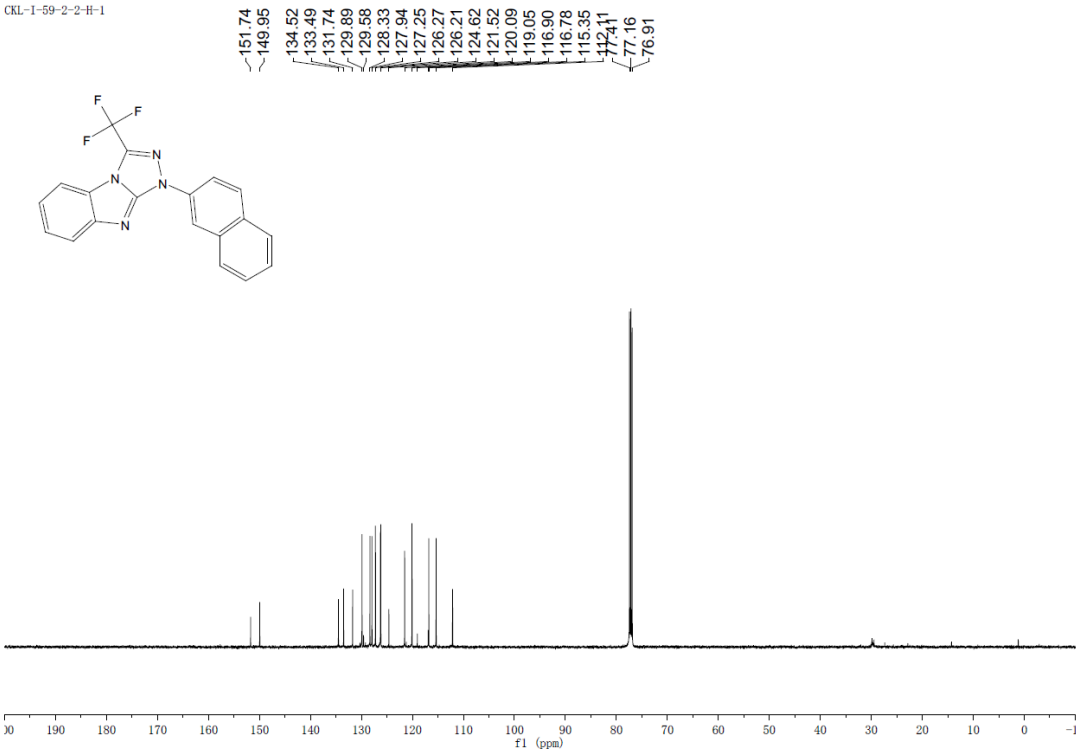


^{13}C NMR (125 MHz, $CDCl_3$) of **3s**.

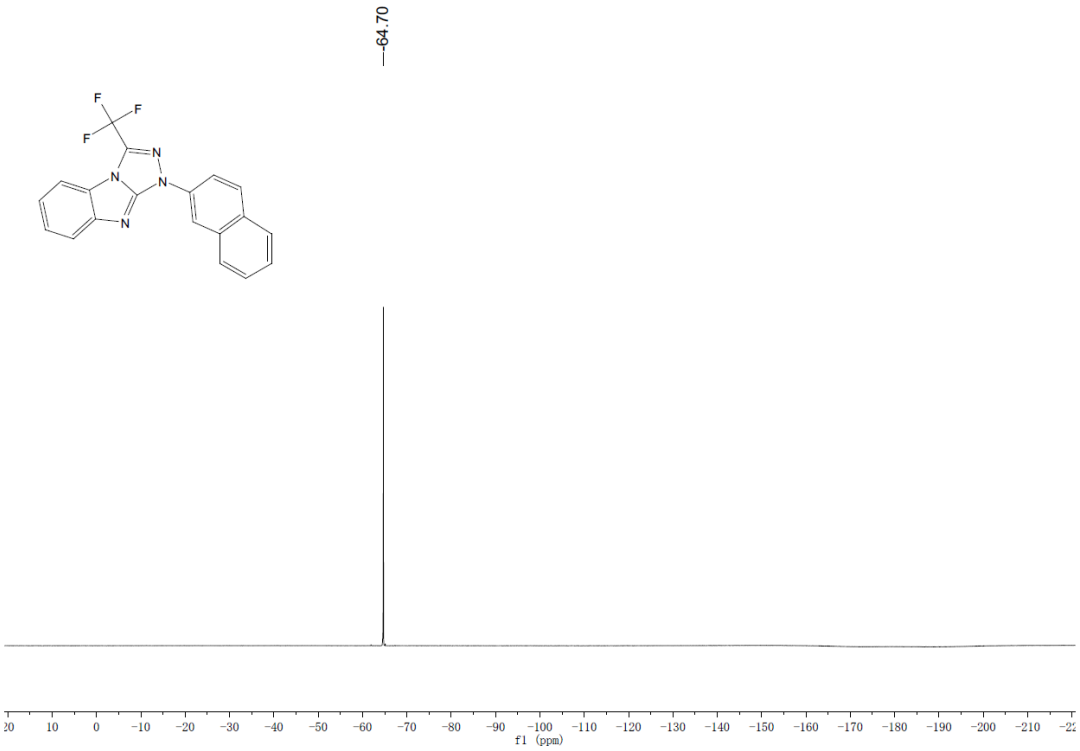
^{19}F NMR (471 MHz, $CDCl_3$) of **3s**.



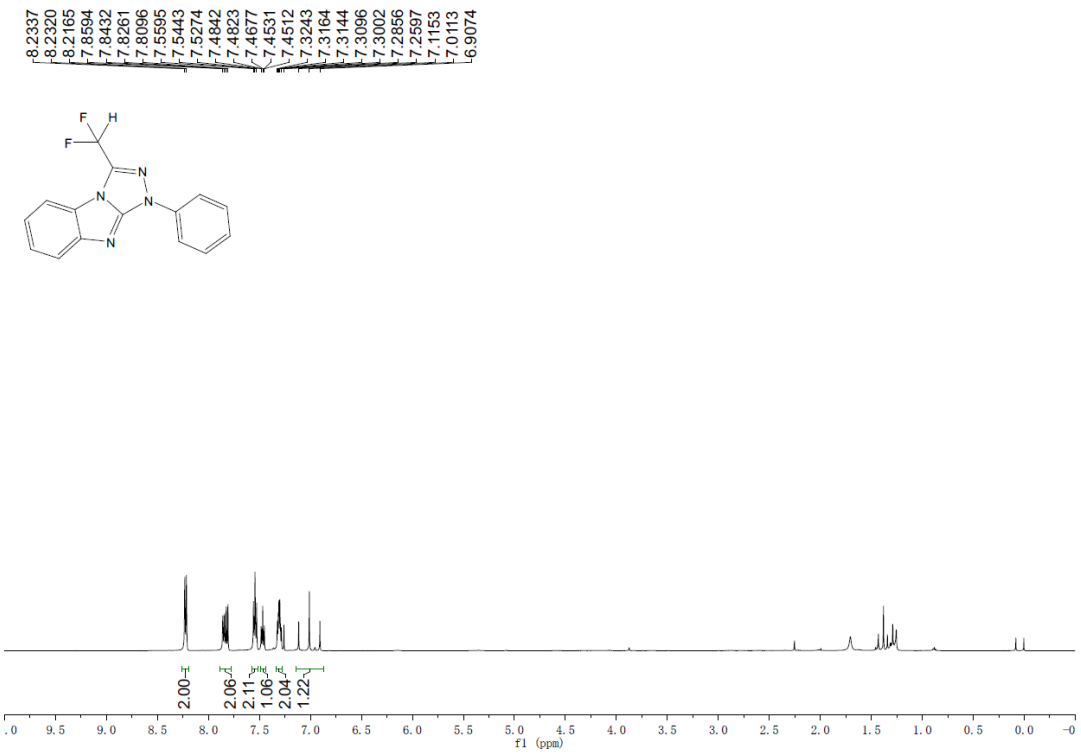
^{1}H NMR (500 MHz, $CDCl_3$) of **3t**.



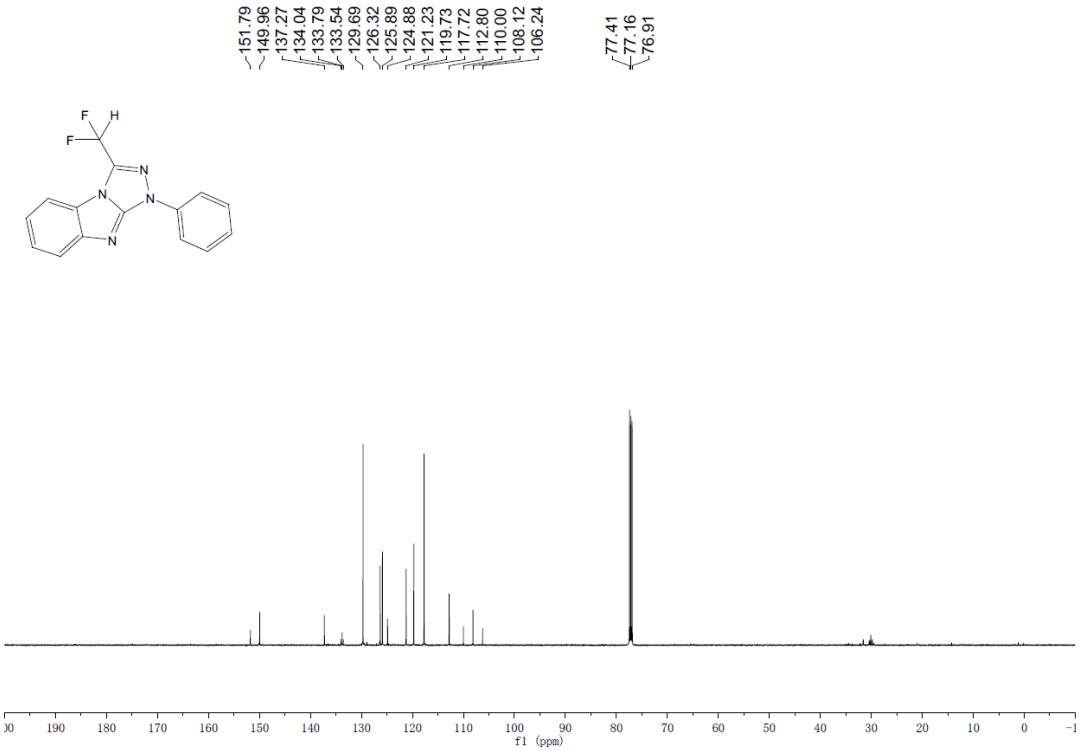
^{13}C NMR (125 MHz, $CDCl_3$) of **3t**.



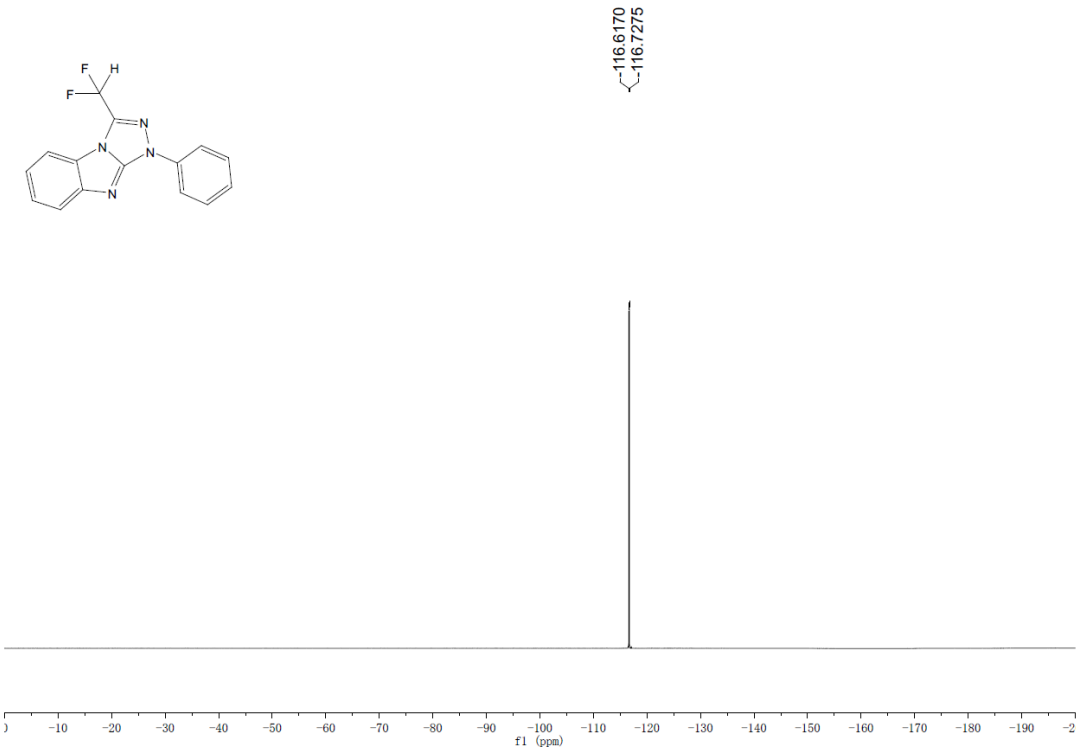
^{19}F NMR (471 MHz, $CDCl_3$) of **3t**.



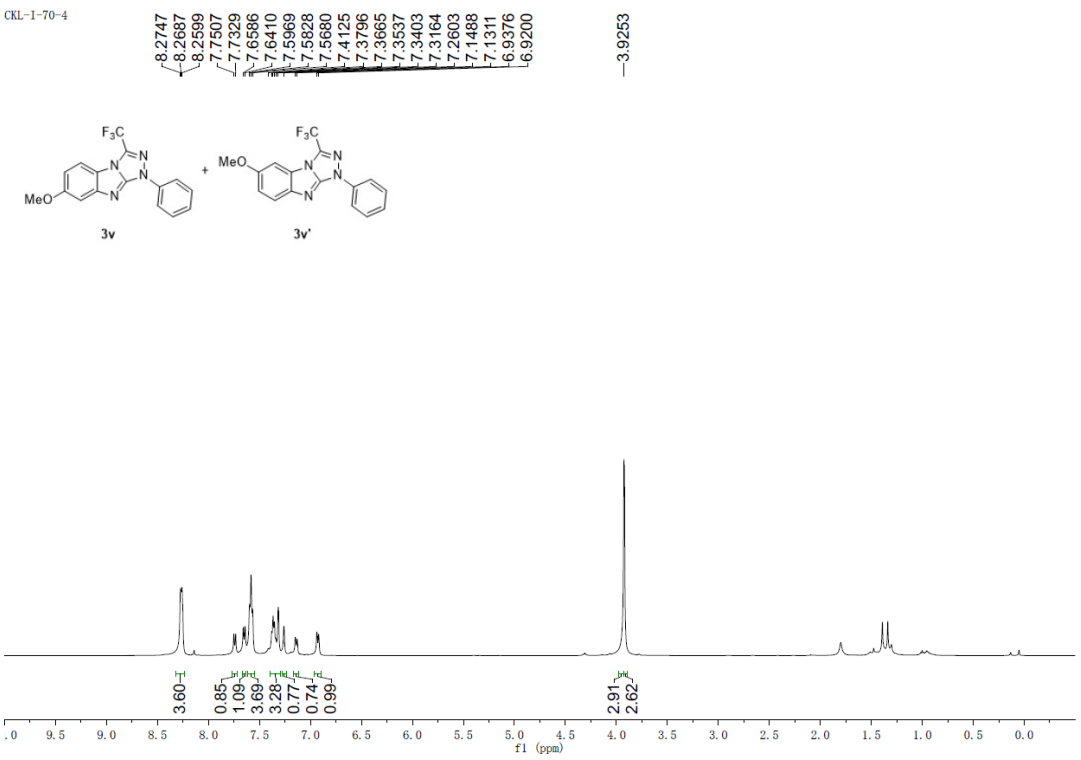
^{1}H NMR (500 MHz, $CDCl_3$) of **3u**.



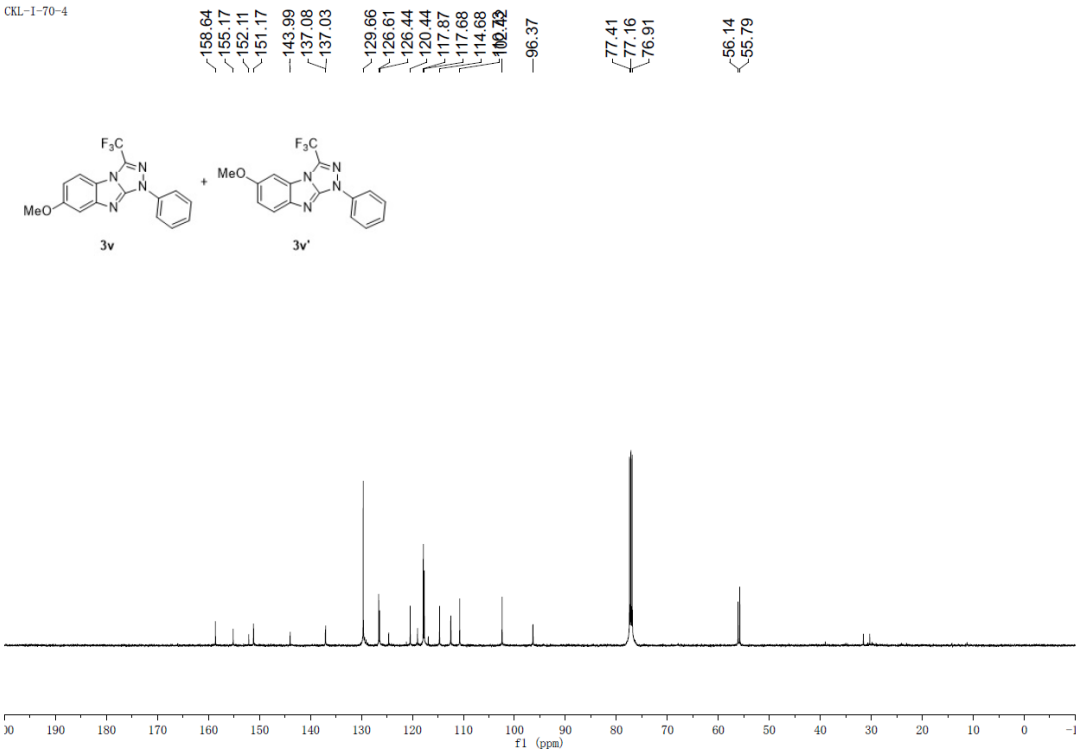
^{13}C NMR (125 MHz, $CDCl_3$) of **3u**.



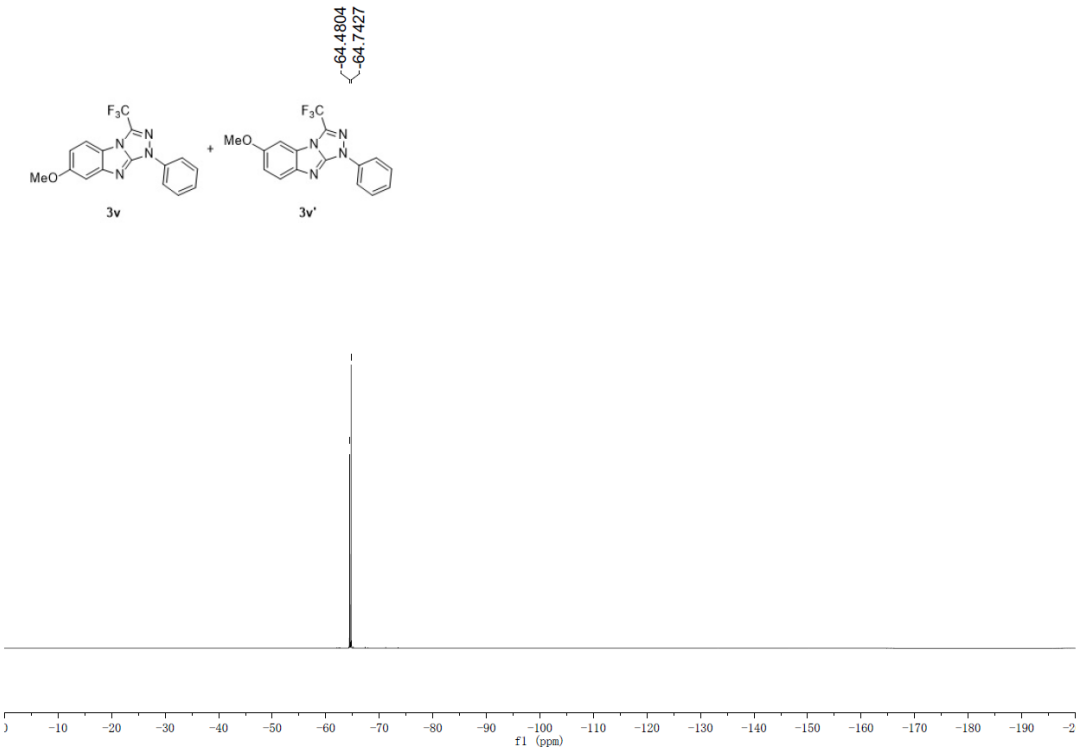
^{19}F NMR (471 MHz, $CDCl_3$) of **3u**.



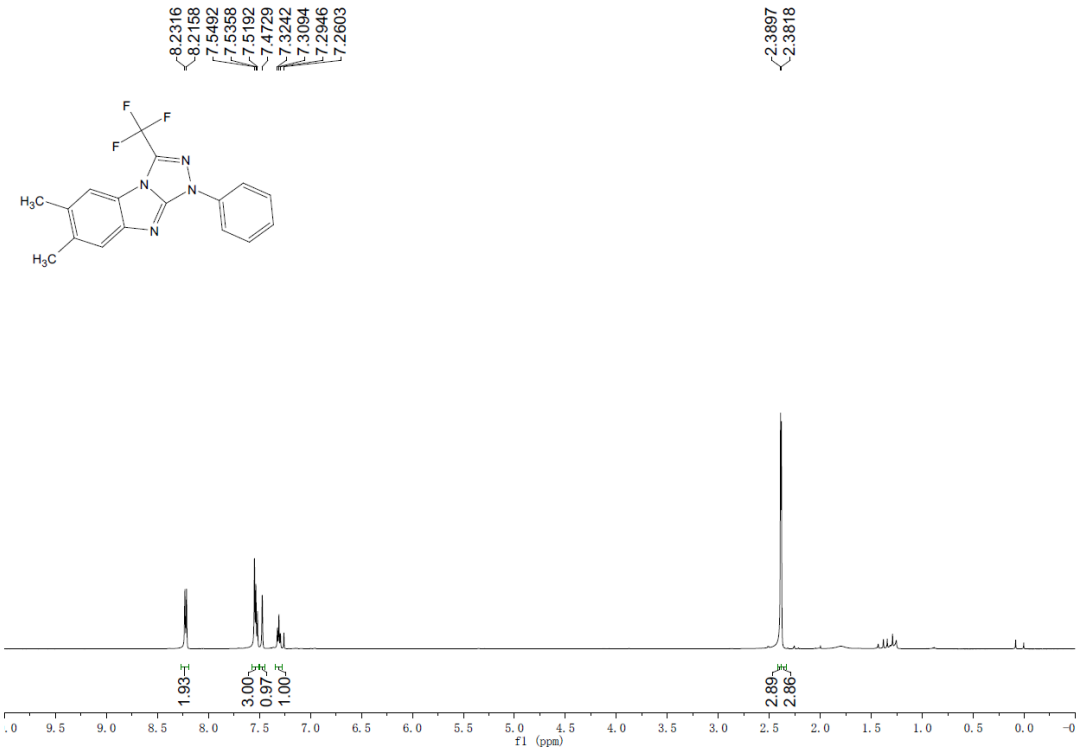
^{1}H NMR (500 MHz, $CDCl_3$) of **3v** and **3v'**.



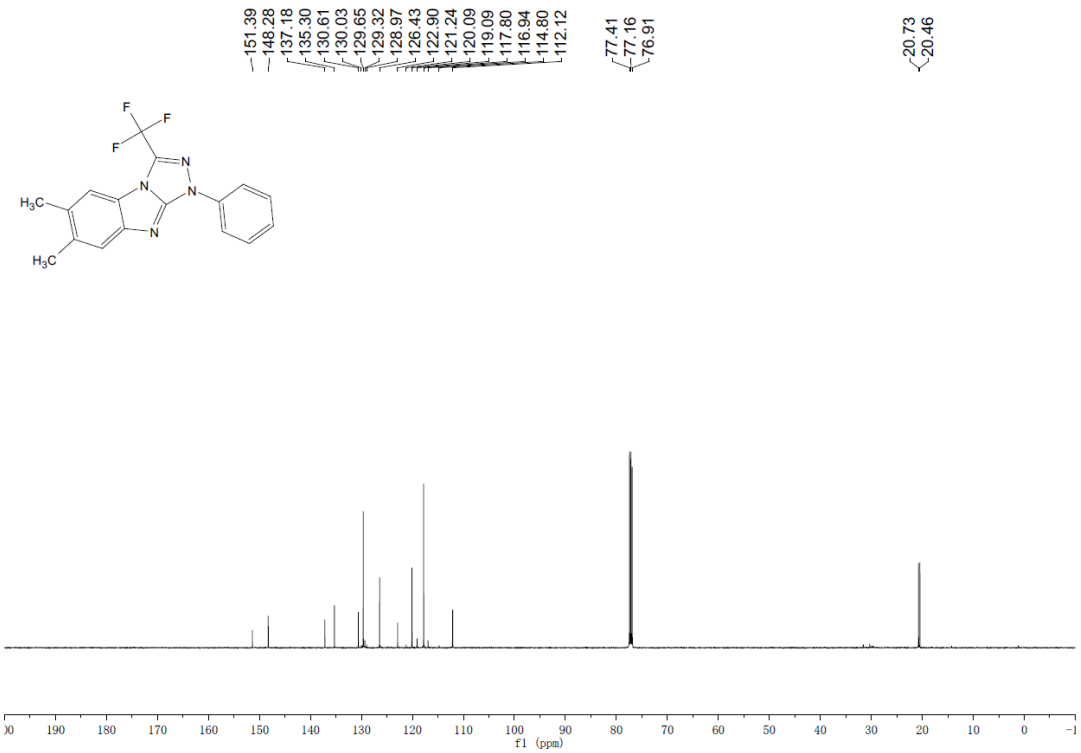
^{13}C NMR (125 MHz, $CDCl_3$) of **3v** and **3v'**.



^{19}F NMR (471 MHz, $CDCl_3$) of **3v** and **3v'**.

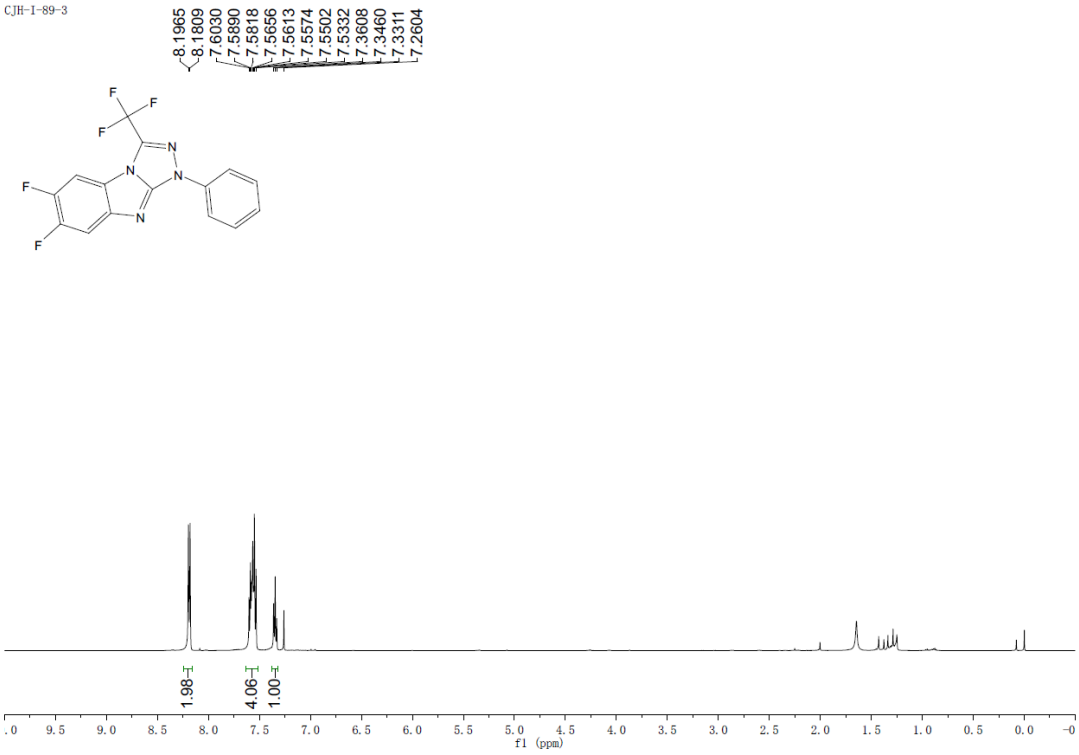


^{1}H NMR (500 MHz, $CDCl_3$) of **3w**.

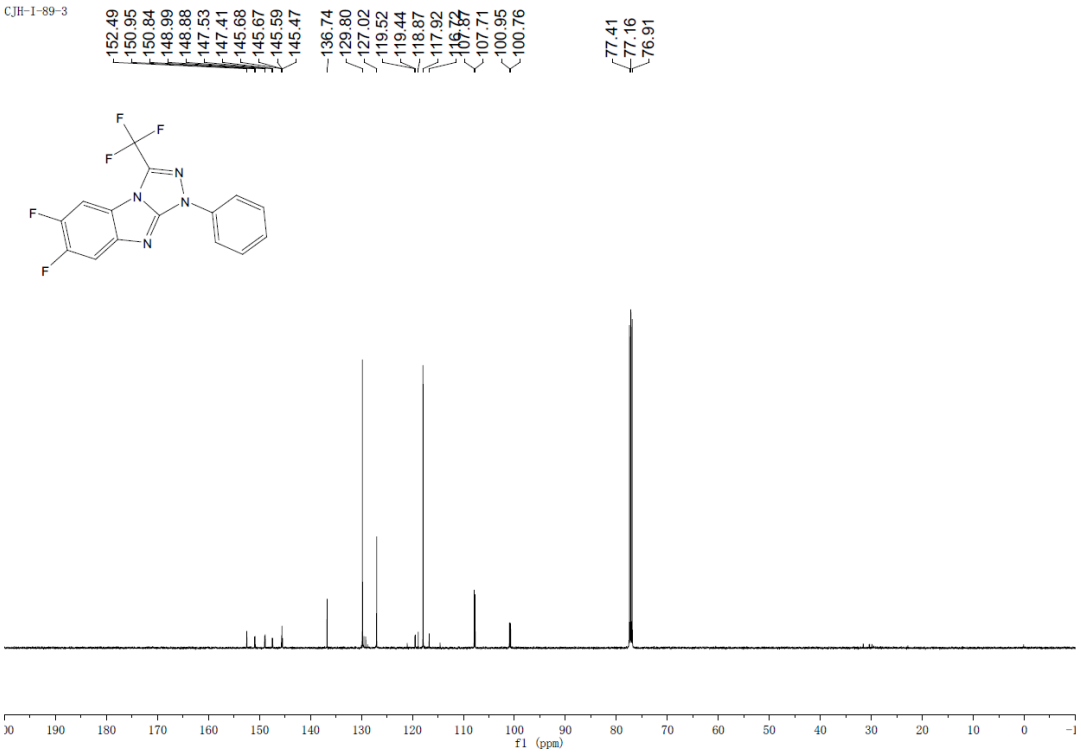


^{13}C NMR (125 MHz, $CDCl_3$) of **3w**.

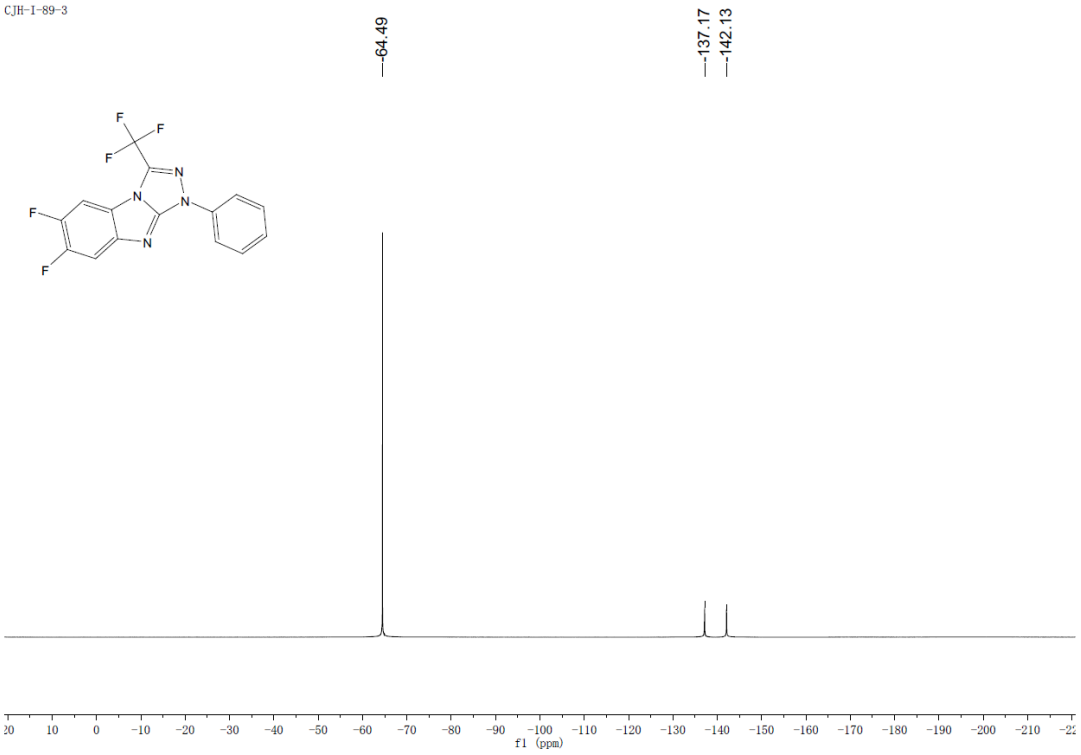
^{19}F NMR (471 MHz, $CDCl_3$) of **3w**.



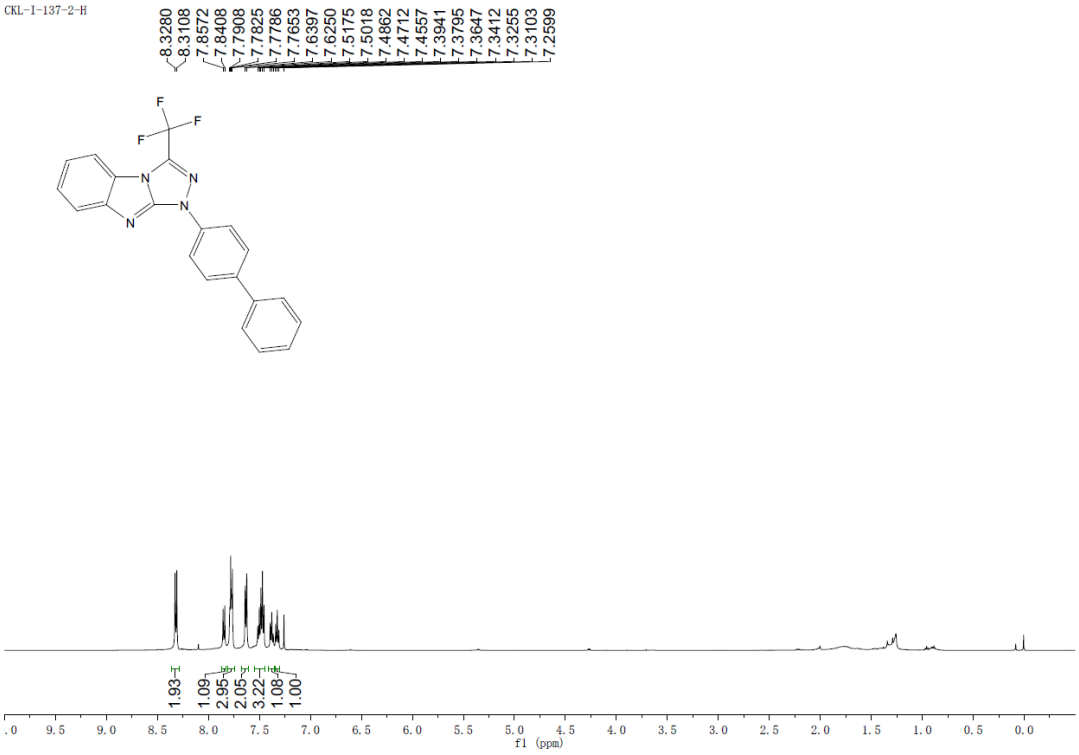
^{1}H NMR (500 MHz, $CDCl_3$) of **3x**.



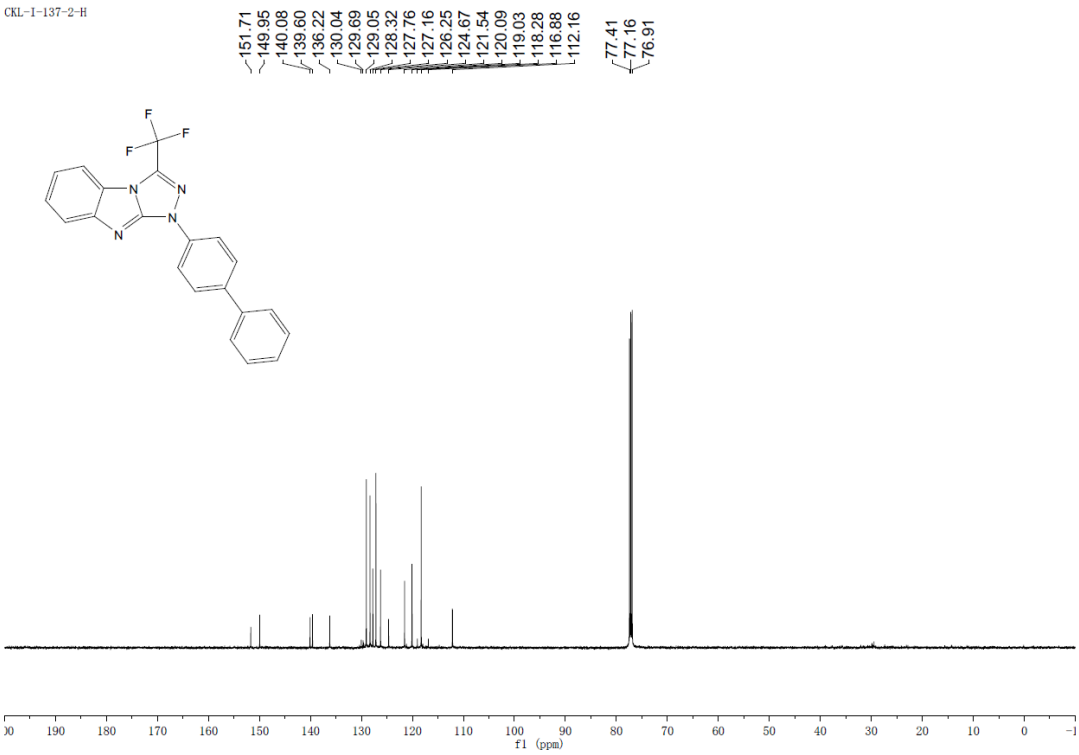
^{13}C NMR (125 MHz, $CDCl_3$) of **3x**.



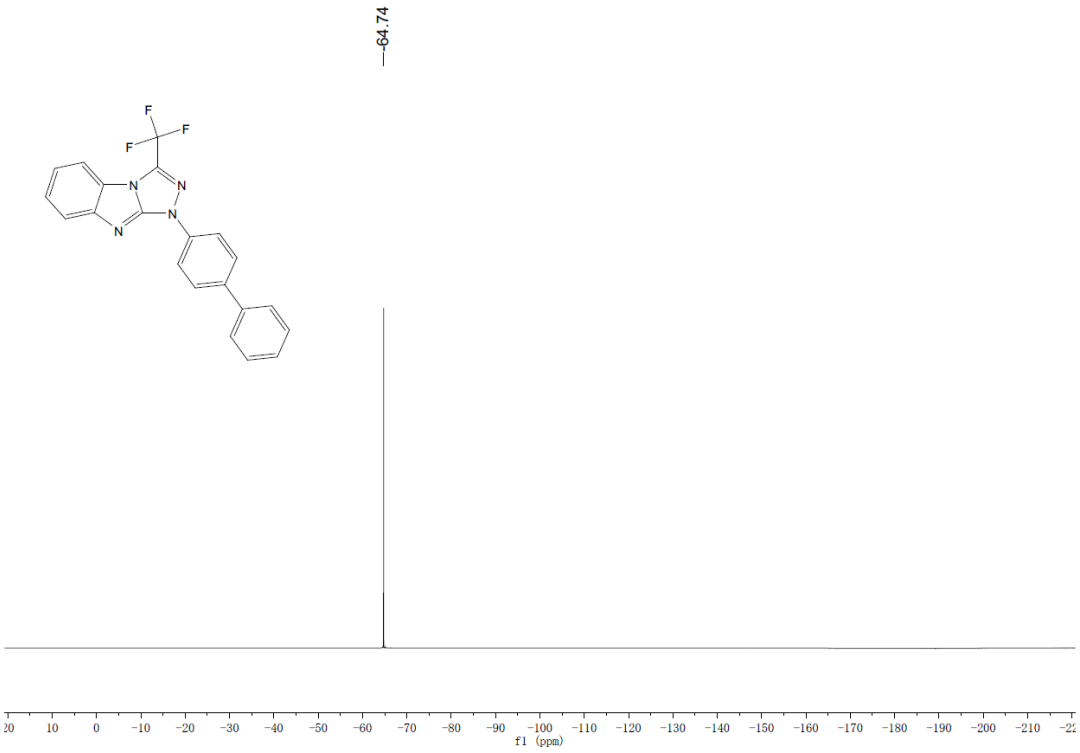
^{19}F NMR (471 MHz, $CDCl_3$) of **3x**.



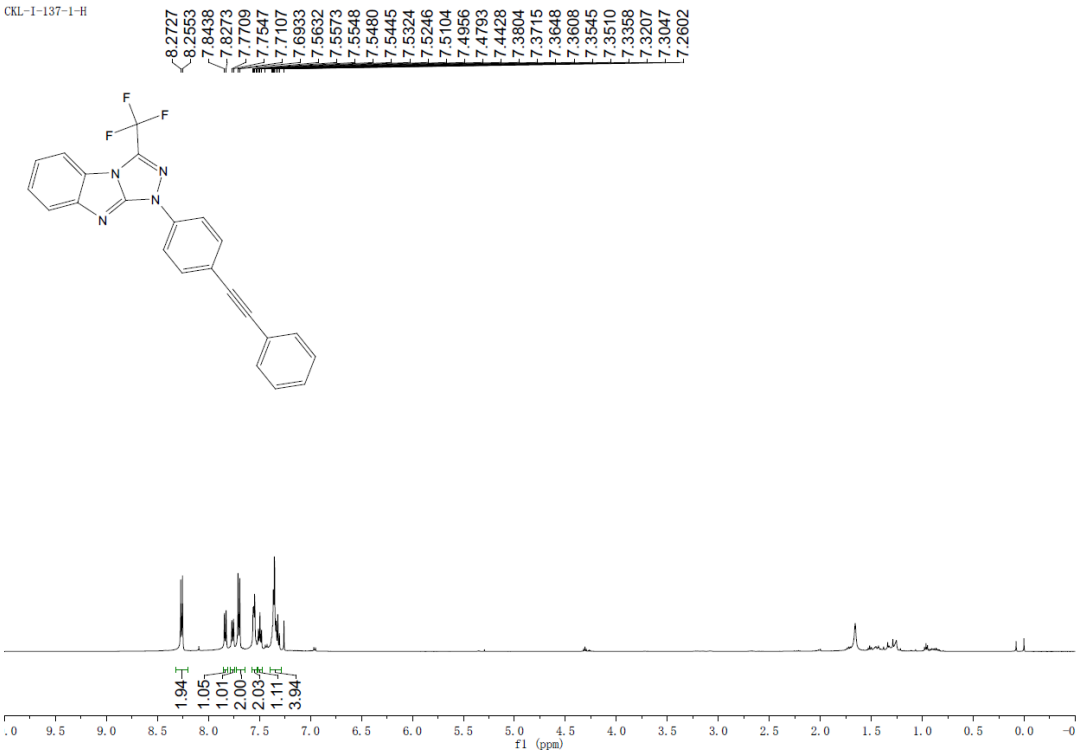
^{1}H NMR (500 MHz, $CDCl_3$) of **4**.



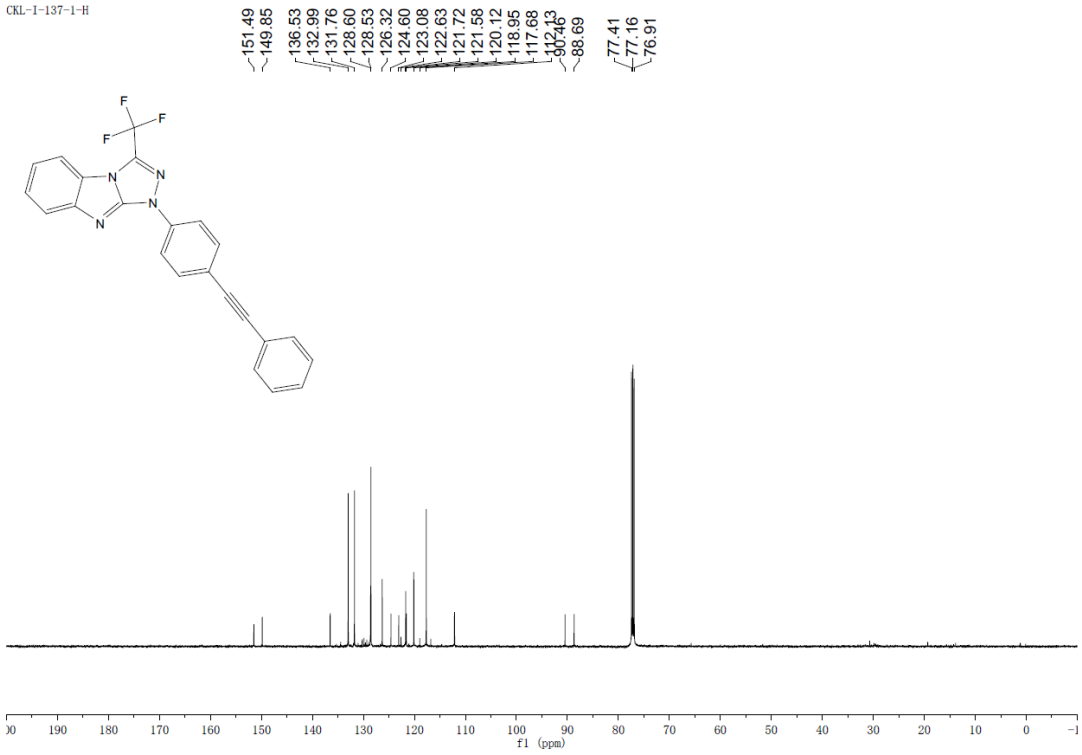
^{13}C NMR (125 MHz, $CDCl_3$) of **4**.



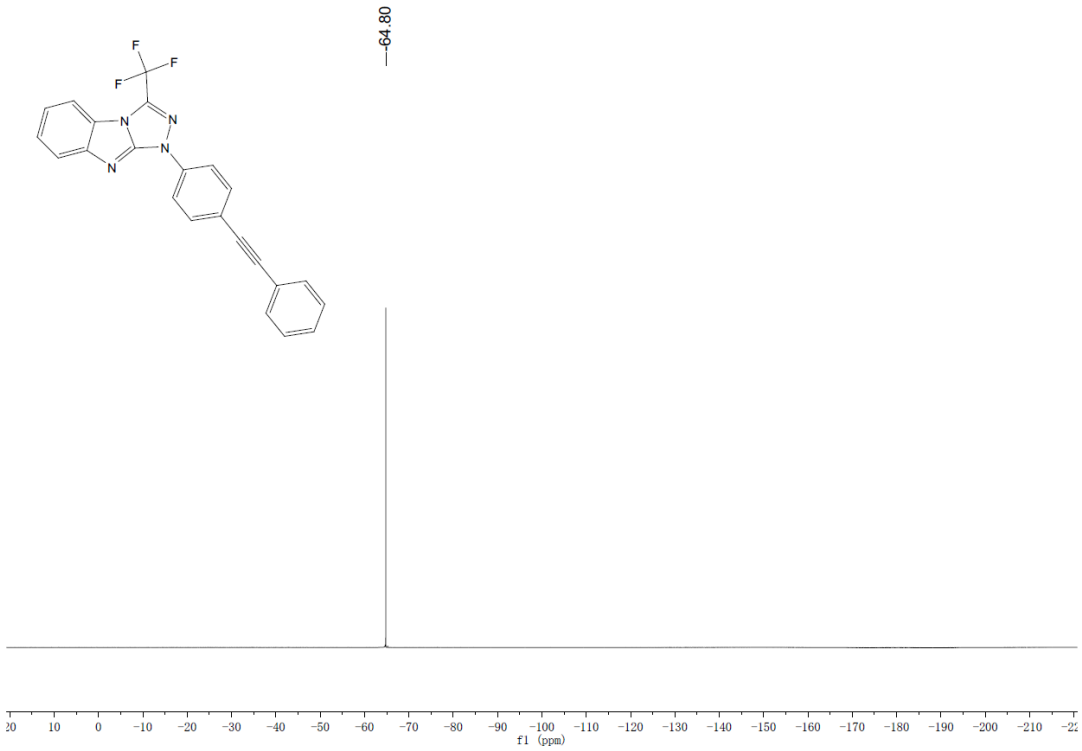
^{19}F NMR (471 MHz, $CDCl_3$) of **4**.



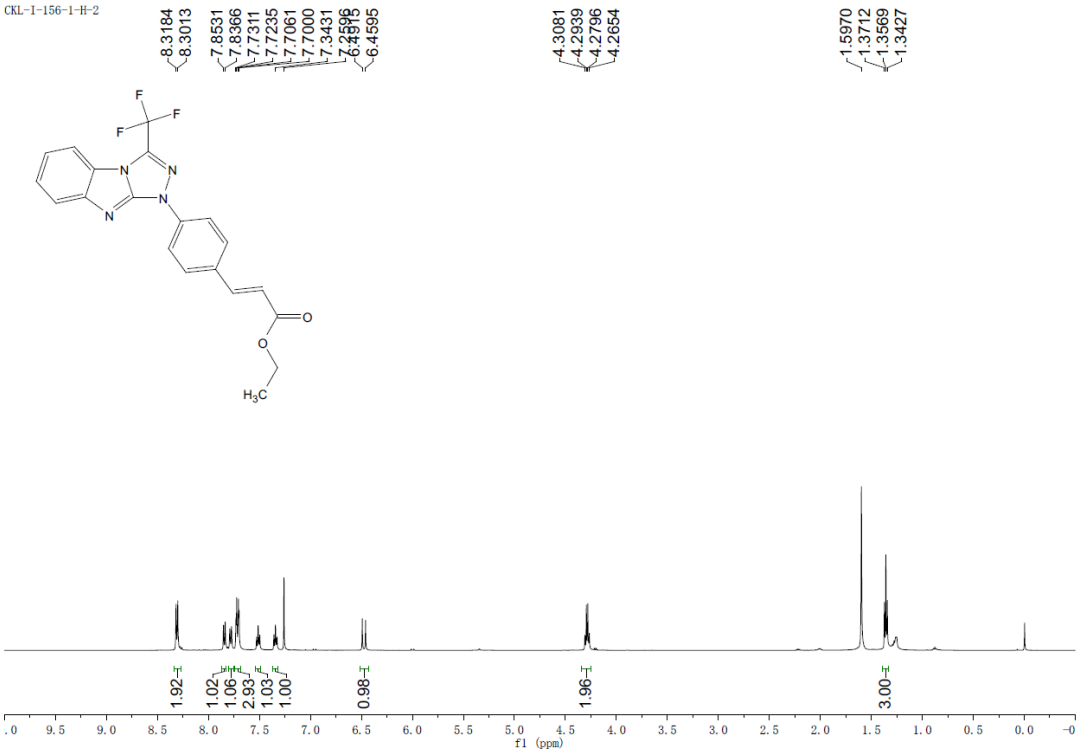
^{1}H NMR (500 MHz, $CDCl_3$) of **5**.



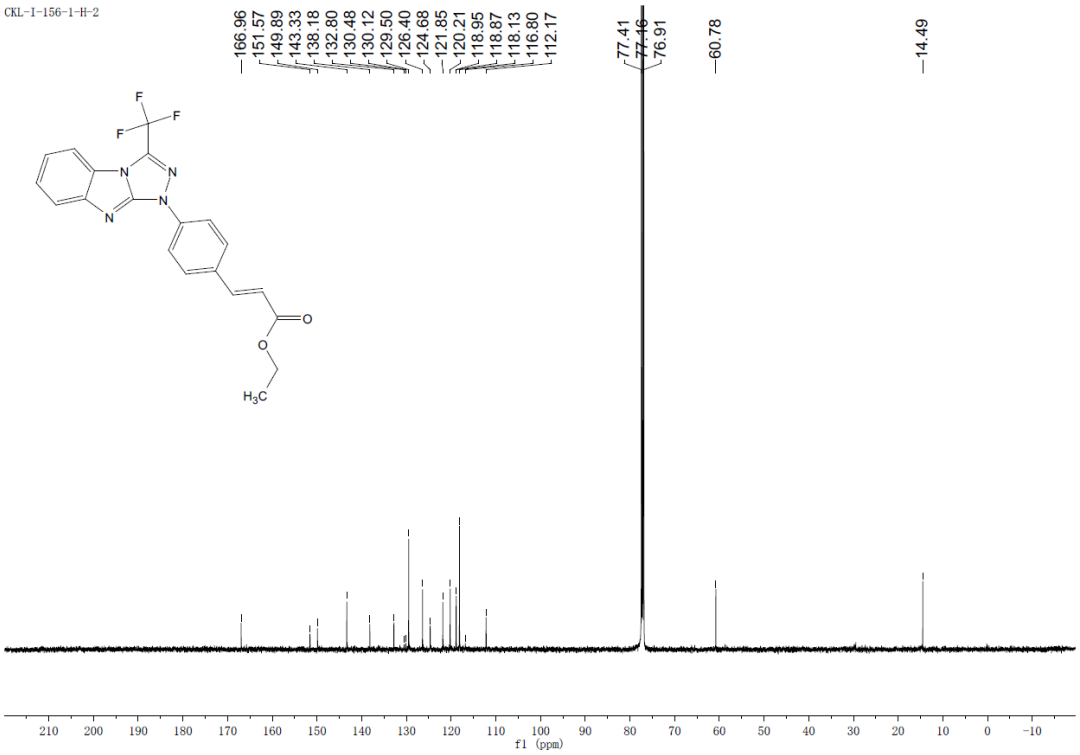
^{13}C NMR (125 MHz, $CDCl_3$) of **5**.



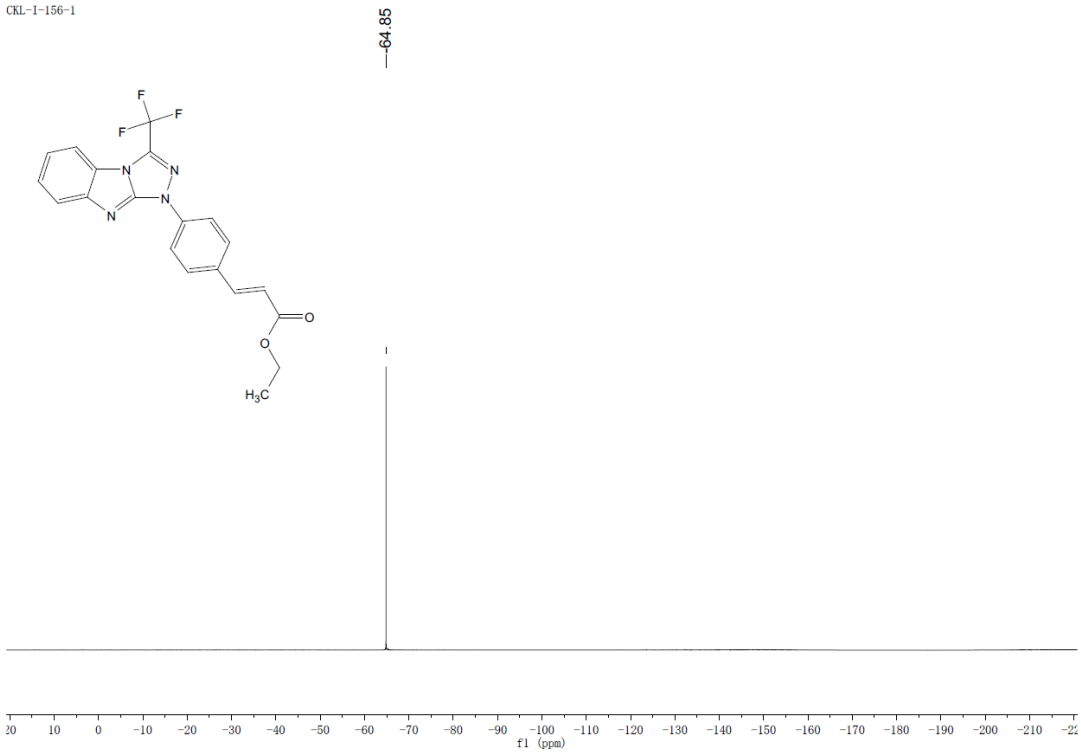
^{19}F NMR (471 MHz, $CDCl_3$) of **5**.



^{1}H NMR (500 MHz, $CDCl_3$) of **6**.



^{13}C NMR (125 MHz, $CDCl_3$) of **6**.



^{19}F NMR (471 MHz, $CDCl_3$) of **6**.