

SUPPORTING INFORMATION

**Silver-Catalyzed Fragmentation of All-Carbon Quaternary Centers
from sp^3 to sp^2 Carbon via C-C Bond Cleavage**

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1. General information

Commercial reagents were purchased from Energy Chemical, Adamas, or Bide Pharmatech and were used as received unless otherwise noted. Flash chromatography was performed using glass columns with silica gel (200-300 mesh). All new compounds (starting materials and products) were characterized by NMR and high-resolution mass spectrometry. NMR spectra were recorded using a Bruker AV III, Ascend 500 HD, or Bruker AVANCE III HD 400. Data for ^1H are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration, and coupling constant (Hz). Data for ^{13}C NMR and ^{19}F NMR are reported as follows: chemical shift (δ ppm), (multiplicity, coupling constants, if it is available). The high-resolution mass spectra (HRMS) were recorded on Agilent Q-TOF 6545 (ESI Source). Single-crystal X-ray diffraction (XRD) data were collected on a Rigaku SuperNova X-ray single-crystal diffractometer.

Starting materials **1a**, **1b**, **1c**, **1d**, **1f**, **1h**, **1i**, TIPS-**1k**, TIPS-**1n**, **1p**, and **1q** are known compounds,¹ while **1e**, **1g**, **1j**, **1k**, **1l**, **1m**, **1n**, **1o**, **1r**, **1s**, **1t**, and **1u** are new compounds prepared according to our reported procedure (Figure S1).¹

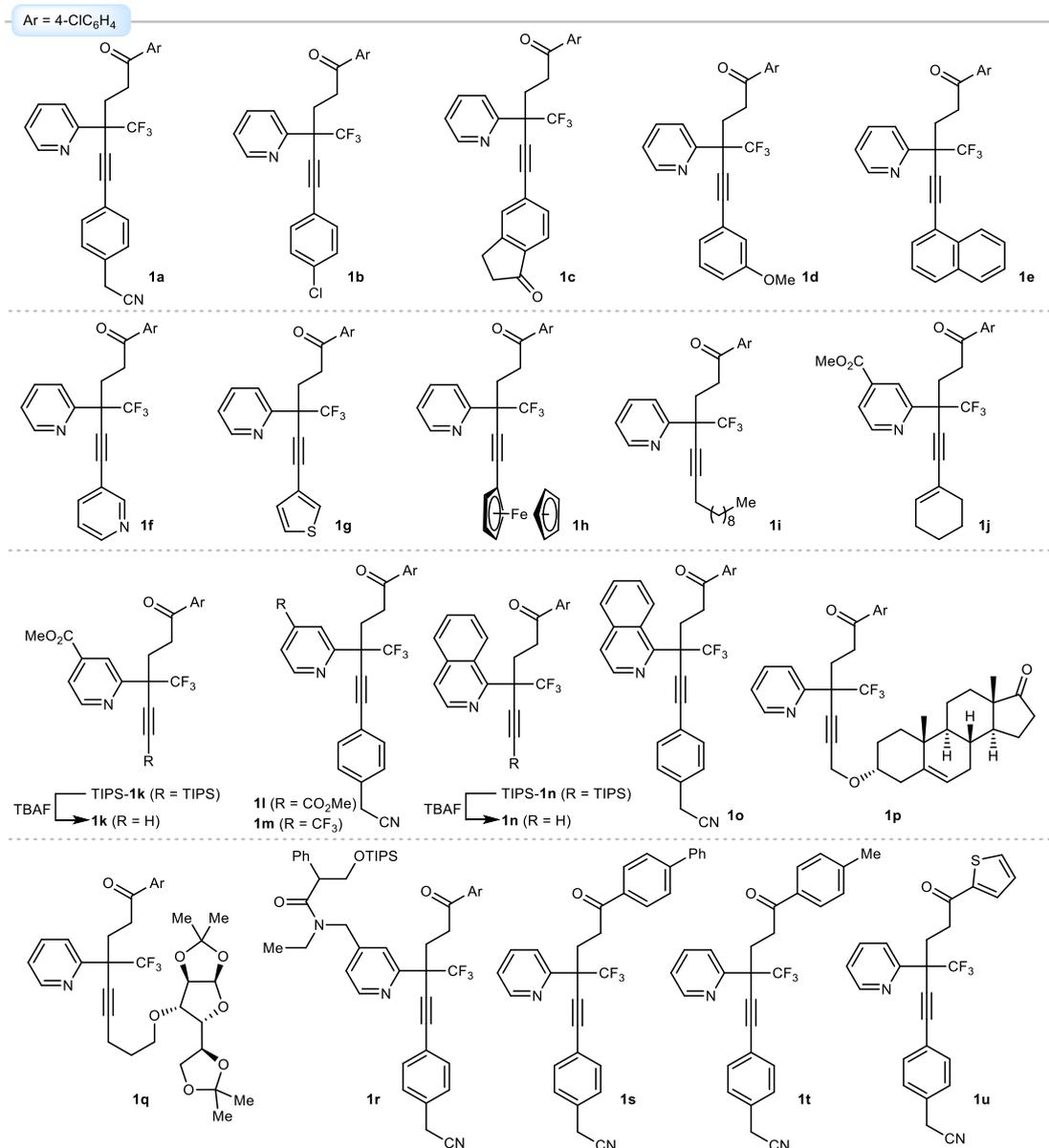
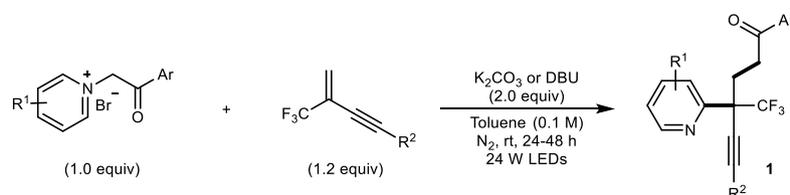


Figure S1 Starting materials

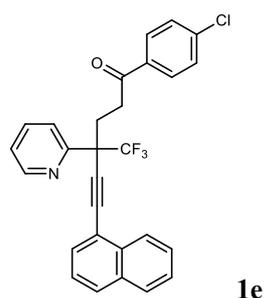
2. General procedure for the preparation of starting materials

General Procedure A:¹



An oven-dried Schlenk tube was charged with *N*-benzoylmethylpyridinium bromide (0.2 mmol, 1.0 equiv), trifluoromethyl alkene (0.24 mmol, 1.2 equiv, when trifluoromethyl alkene is solid), and K₂CO₃ (0.4 mmol, 2.0 equiv, when K₂CO₃ was used). The tube was capped, evacuated, and filled with nitrogen (three cycles). To these solids, degassed toluene (2.0 mL, 0.1 M), trifluoromethyl

alkene (0.24 mmol, 1.2 equiv, when trifluoromethyl alkene is liquid), and DBU (0.4 mmol, 2.0 equiv, when DBU was used) were added sequentially under a nitrogen atmosphere. The mixture was stirred and irradiated with a 24 W white LED bulb (PHILIPS, 5 cm away) at room temperature for 24 h. The reaction mixture was passed through a short pad of silica eluting with petroleum ether-EtOAc (v/v 1/1) to remove the base. The resulting solution was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to afford compound **1**.



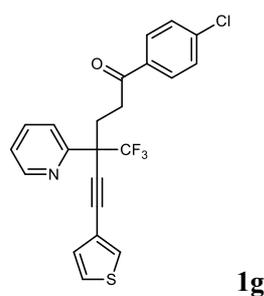
The title compound was prepared according to **General Procedure A** using K₂CO₃ (55.2 mg, 0.4 mmol) as the base. The crude material was purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 95:5, v/v) to afford **1e** as a colorless oil (86 mg, 90%).

¹H NMR (400 MHz, CDCl₃) δ 8.70 (d, *J* = 4.8 Hz, 1H), 8.31 (d, *J* = 8.0 Hz, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 7.91-7.78 (m, 5H), 7.73 (d, *J* = 7.1 Hz, 1H), 7.60-7.51 (m, 2H), 7.47-7.41 (m, 1H), 7.34 (dd, *J* = 8.4, 1.8 Hz, 3H), 3.35-3.23 (m, 2H), 3.08-2.96 (m, 1H), 2.83-2.72 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 197.7, 153.7, 149.3, 139.5, 137.0, 135.0, 133.4, 133.2, 131.0, 129.6, 129.5, 128.8, 128.5, 127.3, 126.6, 125.7, 125.4 (q, *J* = 285.8 Hz), 125.1 (2C), 123.6, 119.4, 89.4, 86.1, 53.5 (q, *J* = 27.0 Hz), 34.5, 27.9.

¹⁹F NMR (376 MHz, CDCl₃) δ -72.3.

HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₂₈H₂₀ClF₃NO 478.1180; Found 478.1185.



The title compound was prepared according to **General Procedure A** using K₂CO₃ (55.2 mg, 0.4

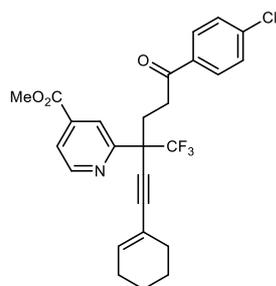
mmol) as the base. The crude material was purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 95:5, v/v) to afford **1g** as a colorless oil (81.5 mg, 94%).

¹H NMR (400 MHz, CDCl₃) δ 8.66 (ddd, *J* = 4.8, 1.9, 0.9 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.87-7.83 (m, 2H), 7.79 (td, *J* = 7.8, 1.9 Hz, 1H), 7.54 (dd, *J* = 3.0, 1.2 Hz, 1H), 7.41-7.35 (m, 2H), 7.35-7.28 (m, 2H), 7.16 (dd, *J* = 5.0, 1.2 Hz, 1H), 3.25-3.08 (m, 2H), 2.97-2.87 (m, 1H), 2.72-2.62 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 197.7, 153.6, 149.2, 139.5, 136.9, 135.0, 130.0, 129.9, 129.5, 128.8, 125.7, 125.2 (q, *J* = 285.8 Hz), 125.0, 123.5, 120.8, 84.2, 82.9, 53.1 (q, *J* = 26.9, 26.5 Hz), 34.3, 27.7.

¹⁹F NMR (376 MHz, CDCl₃) δ -72.5.

HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₂₂H₁₆ClF₃NOS 434.0588; Found 434.0584.



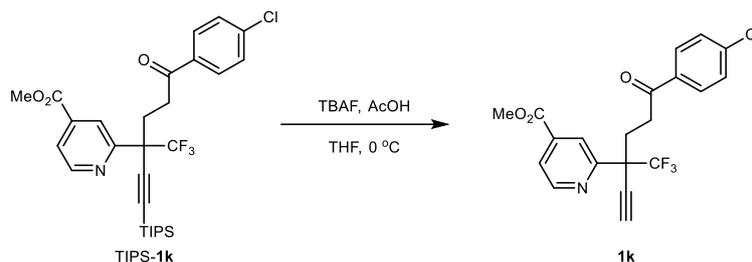
The title compound was prepared according to **General Procedure A** using DBU (60.9 mg, 0.4 mmol) as the base. The crude material was purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 95:5, v/v) to afford **1j** as a pale yellow oil (64.5 mg, 66%).

¹H NMR (400 MHz, CDCl₃) δ 8.78 (dd, *J* = 4.9, 0.9 Hz, 1H), 8.49 (t, *J* = 1.1 Hz, 1H), 7.89-7.81 (m, 3H), 7.43-3.34 (m, 2H), 6.25 (tt, *J* = 3.9, 1.8 Hz, 1H), 3.99 (s, 3H), 3.19-3.03 (m, 2H), 2.86-2.74 (m, 1H), 2.65-2.56 (m, 1H), 2.25-2.17 (m, 2H), 2.17-2.10 (m, 2H), 1.70-1.65 (m, 2H), 1.64-1.59 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 197.6, 165.3, 155.4, 149.8, 139.5, 138.3, 137.0, 135.0, 129.5, 128.8, 125.1 (q, *J* = 285.8 Hz), 124.3, 122.6, 119.5, 90.2, 81.2, 53.0 (q, *J* = 28.1 Hz), 52.9, 34.2, 28.9, 27.8, 25.6, 22.1, 21.3.

¹⁹F NMR (376 MHz, CDCl₃) δ -72.6.

HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₂₆H₂₄ClF₃NO₃ 490.1391; Found 490.1392.



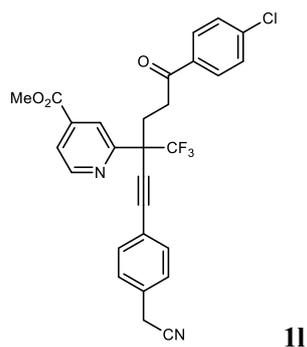
To a solution of TIPS-**1k**¹ (106 mg) in THF (3 mL) was added AcOH (3 μ L), and TBAF (0.21 mmol, 1 M in THF) at 0 °C. After the reaction was complete, as determined by TLC analysis, saturated aq NH_4Cl (5 mL) was added and the reaction mixture was extracted with EtOAc (3x). The combined organic layers were dried over anhydrous Na_2SO_4 , filtered, and concentrated under reduced pressure. The residue was purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 92:8, v/v) to afford **1k** as a pale yellow solid (58.3 mg, 76%).

¹H NMR (500 MHz, CDCl_3) δ 8.80 (dd, J = 4.9, 0.9 Hz, 1H), 8.46 (t, J = 1.2 Hz, 1H), 7.87 (dd, J = 5.0, 1.5 Hz, 1H), 7.86-7.79 (m, 2H), 7.43-7.37 (m, 2H), 4.00 (s, 3H), 3.18-3.09 (m, 2H), 2.82 (q, J = 11.8 Hz, 1H), 2.72 (s, 1H), 2.67-2.56 (m, 1H).

¹³C NMR (101 MHz, CDCl_3) δ 197.3, 165.3, 154.4, 150.1, 139.7, 138.6, 135.0, 129.5, 129.0, 124.0, 123.0, 53.1, 52.7 (q, J = 27.0 Hz), 34.1, 27.5.

¹⁹F NMR (471 MHz, CDCl_3) δ -72.6.

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{16}\text{ClF}_3\text{NO}_3$ 410.0765; Found 410.0762.



The title compound was prepared according to **General Procedure A** using K_2CO_3 (55.2 mg, 0.4 mmol) as the base. The crude material was purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 4:1, v/v) to afford **11** as a brown-yellow solid (89.2 mg, 85%).

mp 163-164 °C

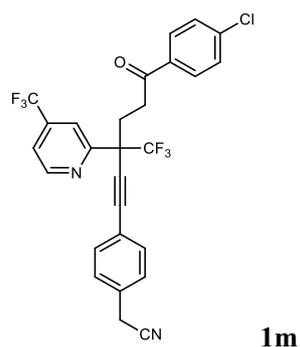
¹H NMR (400 MHz, CDCl_3) δ 8.82 (dd, J = 5.0, 0.8 Hz, 1H), 8.53 (d, J = 1.2 Hz, 1H), 7.89 (dd, J = 4.9, 1.5 Hz, 1H), 7.85-7.81 (m, 2H), 7.57-7.53 (m, 2H), 7.40-7.36 (m, 2H), 7.35-7.33 (m, 2H),

4.00 (s, 3H), 3.79 (s, 2H), 3.26-3.09 (m, 2H), 2.93-2.86 (m, 1H), 2.75-2.65 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 197.4, 165.2, 154.8, 150.1, 139.6, 138.5, 134.9, 132.7, 131.0, 129.5, 128.9, 128.1, 125.1 (q, $J = 281.8$ Hz), 124.2, 122.8, 121.6, 117.3, 87.4, 84.9, 53.3 (q, $J = 27.2$ Hz), 53.0, 34.2, 27.7, 23.6.

^{19}F NMR (376 MHz, CDCl_3) δ -72.3.

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{28}\text{H}_{21}\text{ClF}_3\text{N}_2\text{O}_3$ 525.1187; Found 525.1179.



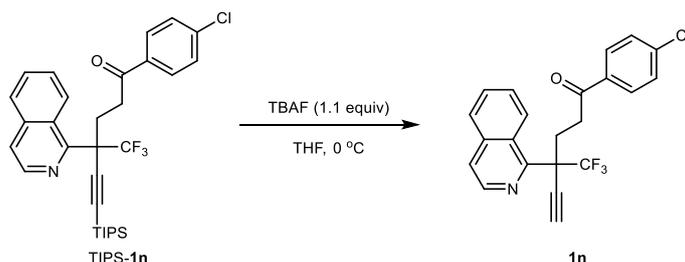
The title compound was prepared according to **General Procedure A** using K_2CO_3 (55.2 mg, 0.4 mmol) as the base. The crude material was purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 94:6 to 88:12, v/v) to afford **1m** as a pale-yellow oil (63.9 mg, 60%).

^1H NMR (500 MHz, CDCl_3) δ 8.86 (d, $J = 5.0$ Hz, 1H), 8.20 (s, 1H), 7.87-7.81 (m, 2H), 7.58 (dd, $J = 5.0, 1.5$ Hz, 1H), 7.53 (d, $J = 8.1$ Hz, 2H), 7.41-7.37 (m, 2H), 7.35 (d, $J = 7.9$ Hz, 2H), 3.79 (s, 2H), 3.27-3.12 (m, 2H), 2.91 (ddd, $J = 16.5, 11.1, 4.4$ Hz, 1H), 2.73 (ddd, $J = 12.8, 11.1, 4.0$ Hz, 1H).

^{13}C NMR (126 MHz, CDCl_3) δ 197.2, 155.3, 150.3, 139.7, 139.4 (q, $J = 34.3$ Hz), 134.9, 132.7, 131.2, 129.5, 128.9, 128.2, 124.9 (q, $J = 284.9$ Hz), 122.6 (q, $J = 273.4$ Hz), 121.3, 120.6 (q, $J = 3.6$ Hz), 119.4 (q, $J = 3.2$ Hz), 117.2, 87.6, 84.5, 53.3 (q, $J = 27.4$ Hz), 34.1, 27.5, 23.6.

^{19}F NMR (471 MHz, CDCl_3) δ -64.7, -72.3.

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{27}\text{H}_{18}\text{ClF}_6\text{N}_2\text{O}$ 535.1006; Found 535.1001.



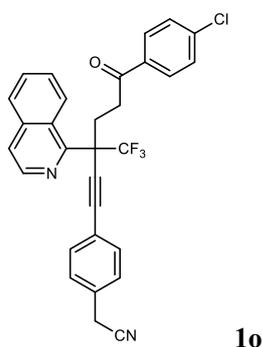
To a solution of TIPS-**1n**¹ (94.7 mg) in THF (3 mL) was added TBAF (1.1 equiv, 1 M in THF) at 0 °C. After the reaction was complete, as determined by TLC analysis, saturated aq NH₄Cl (5 mL) was added and the reaction mixture was extracted with EtOAc (3x). The combined organic layers were dried over anhydrous Na₂SO₄, filtered off, and concentrated under reduced pressure. The residue was purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 95:5, v/v) to afford **1n** as a pale yellow oil (64.8 mg, 95%).

¹H NMR (400 MHz, CDCl₃) δ 9.26-9.19 (m, 1H), 8.54 (d, *J* = 5.5 Hz, 1H), 7.93-7.85 (m, 3H), 7.73-7.68 (m, 2H), 7.64 (ddd, *J* = 8.4, 6.8, 1.5 Hz, 1H), 7.42-7.37 (m, 2H), 3.59-3.52 (m, 1H), 3.27-3.06 (m, 2H), 2.79 (s, 1H), 2.68-2.60 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 198.2, 150.2, 140.7, 139.4, 137.7, 135.2, 129.9, 129.6, 128.8, 128.2, 127.7, 127.4 (q, *J* = 3.0 Hz), 126.8, 125.7 (q, *J* = 286.8 Hz), 122.5, 80.4, 78.0, 52.1 (q, *J* = 27.3 Hz), 34.8, 29.4.

¹⁹F NMR (376 MHz, CDCl₃) δ -70.9.

HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₂₂H₁₆ClF₃NO 402.0867; Found 402.0867.



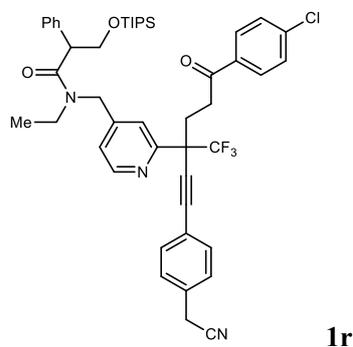
The title compound was prepared according to **General Procedure A** using K₂CO₃ (55.2 mg, 0.4 mmol) as the base. The crude material was purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 4:1, v/v) to afford **1o** as a pale yellow oil (78 mg, 75%).

¹H NMR (400 MHz, CDCl₃) δ 9.29 (d, *J* = 8.7 Hz, 1H), 8.57 (d, *J* = 5.5 Hz, 1H), 7.92-7.85 (m, 3H), 7.74-7.68 (m, 2H), 7.64 (ddd, *J* = 8.5, 6.8, 1.5 Hz, 1H), 7.48-7.43 (m, 2H), 7.39-7.33 (m, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 3.74 (s, 2H), 3.67-3.60 (m, 1H), 3.33-3.24 (m, 1H), 3.18-3.10 (m, 1H), 2.79-2.72 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 198.3, 150.8, 140.8, 139.4, 137.8, 135.2, 132.4, 130.9, 129.9, 129.6, 128.8, 128.3, 128.1, 127.8, 127.2, 126.9, 125.9 (q, *J* = 286.8 Hz), 122.5, 121.8, 117.3, 88.3, 86.8, 52.7 (q, *J* = 27.3 Hz), 34.9, 29.5, 23.6.

^{19}F NMR (376 MHz, CDCl_3) δ -70.6.

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{30}\text{H}_{21}\text{ClF}_3\text{N}_2\text{O}$ 517.1289; Found 517.1281.



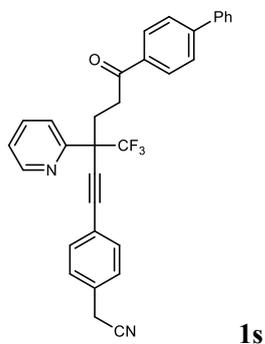
The title compound was prepared according to **General Procedure A** using K_2CO_3 (55.2 mg, 0.4 mmol) as the base. The crude material was purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 85:15, v/v) to afford **1r** as a pale yellow oil (130 mg, 78%).

^1H NMR (400 MHz, CDCl_3) δ 8.56-8.44 (m, 1H), 7.85-7.71 (m, 3H), 7.53 (d, J = 8.0 Hz, 1H), 7.45 (t, J = 8.4 Hz, 1H), 7.41-7.33 (m, 4H), 7.30-6.92 (m, 6H), 4.99-3.69 (m, 7H), 3.58-3.36 (m, 1H), 3.33-3.01 (m, 3H), 2.96-2.85 (m, 1H), 2.69-2.59 (m, 1H), 1.05-0.96 (m, 24H).

^{13}C NMR (101 MHz, CDCl_3) δ 197.8, 197.7, 172.4, 172.3, 153.4, 149.4, 148.7, 148.6, 139.7, 139.6, 136.9, 136.8, 135.0, 132.8, 132.8, 132.7, 129.6, 128.9, 128.9, 128.4, 128.3, 128.1, 128.1, 122.1, 121.8, 117.4, 86.8, 86.8, 85.6, 67.1, 67.0, 52.0, 51.9, 48.4, 48.1, 42.9, 42.8, 34.4, 27.6, 23.7, 18.0, 18.0, 14.3, 14.3, 12.0, 12.0.

^{19}F NMR (471 MHz, CDCl_3) δ -72.2, -72.3, -72.5, -72.5.

HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{47}\text{H}_{53}\text{ClF}_3\text{N}_3\text{NaO}_3\text{Si}$ 850.3389; Found 850.3391.



The title compound was prepared according to **General Procedure A** using K_2CO_3 (55.2 mg, 0.4 mmol) as the base. The crude material was purified by silica gel flash chromatography (petroleum

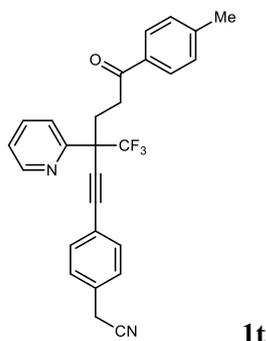
ether/ethyl acetate = 4:1, v/v) to afford **1s** as a yellow oil (72 mg, 71%).

¹H NMR (500 MHz, CDCl₃) δ 8.69 (dd, *J* = 5.1, 1.7 Hz, 1H), 8.02-7.95 (m, 3H), 7.81 (td, *J* = 7.7, 1.9 Hz, 1H), 7.66-7.62 (m, 2H), 7.61-7.57 (m, 2H), 7.55-7.51 (m, 2H), 7.46 (dd, *J* = 8.4, 6.8 Hz, 2H), 7.42-7.37 (m, 1H), 7.36-7.30 (m, 3H), 3.77 (s, 2H), 3.29-3.16 (m, 2H), 3.03-2.96 (m, 1H), 2.76-2.69 (m, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 198.5, 153.5, 149.3, 145.8, 139.8, 136.9, 135.4, 132.7, 130.7, 129.0, 128.7, 128.2, 128.0, 127.2, 127.2, 125.3 (q, *J* = 284.8 Hz), 124.9, 123.5, 121.8, 117.3, 86.8, 85.6, 53.2 (q, *J* = 27.1 Hz), 34.3, 27.9, 23.6.

¹⁹F NMR (471 MHz, CDCl₃) δ -72.4.

HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₃₂H₂₄F₃N₂O 509.1835; Found 509.1828.



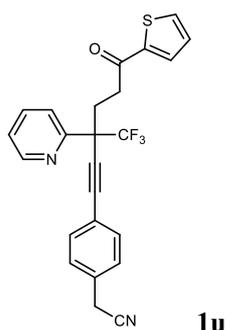
The title compound was prepared according to **General Procedure A** using K₂CO₃ (55.2 mg, 0.4 mmol) as the base. The crude material was purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 4:1, v/v) to afford **1t** as a yellow oil (71.4 mg, 80%).

¹H NMR (400 MHz, CDCl₃) δ 8.67 (ddd, *J* = 4.8, 1.9, 0.9 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.83-7.77 (m, 3H), 7.55-7.48 (m, 2H), 7.34-7.30 (m, 3H), 7.21 (d, *J* = 8.0 Hz, 2H), 3.77 (s, 2H), 3.25-3.09 (m, 2H), 2.98-2.88 (m, 1H), 2.73-2.64 (m, 1H), 2.38 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 198.5, 153.6, 149.2, 143.9, 136.9, 134.3, 132.7, 130.8, 129.2, 128.2, 128.0, 125.3 (q, *J* = 285.8 Hz), 124.8, 123.5, 121.9, 117.3, 86.8, 85.6, 53.3 (q, *J* = 27.0 Hz), 34.2, 27.9, 23.6, 21.6.

¹⁹F NMR (376 MHz, CDCl₃) δ -72.4.

HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₇H₂₁F₃N₂NaO 469.1498; Found 469.1494.



The title compound was prepared according to **General Procedure A** using K_2CO_3 (55.2 mg, 0.4 mmol) as the base. The crude material was purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 4:1, v/v) to afford **1u** as a pale yellow oil (66.5 mg, 76%).

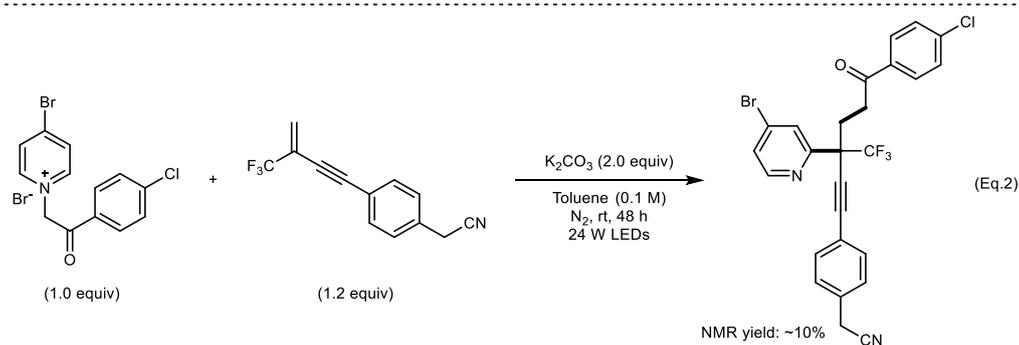
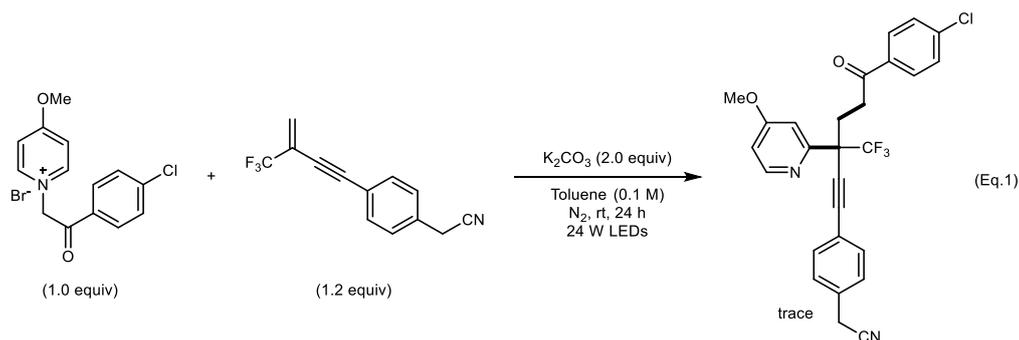
^1H NMR (500 MHz, CDCl_3) δ 8.68 (dt, $J = 4.6, 1.5$ Hz, 1H), 7.98 (d, $J = 7.9$ Hz, 1H), 7.80 (td, $J = 7.7, 1.9$ Hz, 1H), 7.66 (dd, $J = 3.8, 1.2$ Hz, 1H), 7.60 (dd, $J = 5.0, 1.1$ Hz, 1H), 7.56-7.50 (m, 2H), 7.36-7.30 (m, 3H), 7.08 (dd, $J = 4.9, 3.8$ Hz, 1H), 3.78 (s, 2H), 3.24 (ddd, $J = 13.1, 11.0, 5.0$ Hz, 1H), 3.09 (ddd, $J = 15.7, 10.9, 4.8$ Hz, 1H), 2.91 (ddd, $J = 16.0, 11.0, 4.9$ Hz, 1H), 2.70 (ddd, $J = 13.0, 11.0, 4.8$ Hz, 1H).

^{13}C NMR (126 MHz, CDCl_3) δ 191.8, 153.4, 149.2, 144.0, 136.9, 133.7, 132.6, 132.0, 130.8, 128.1, 128.0, 125.2 (q, $J = 284.8$ Hz), 124.9, 123.6, 121.8, 117.3, 86.9, 85.4, 53.2 (q, $J = 27.0$ Hz), 35.0, 28.0, 23.6.

^{19}F NMR (471 MHz, CDCl_3) δ -72.4.

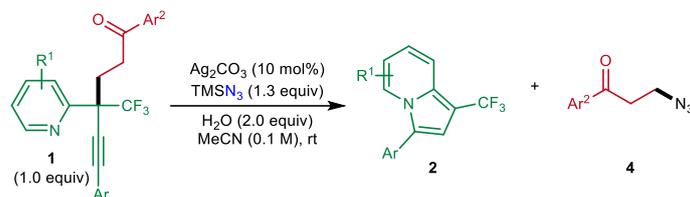
HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{18}\text{F}_3\text{N}_2\text{OS}$ 439.1086; Found 439.1071.

Limitations of the Reaction

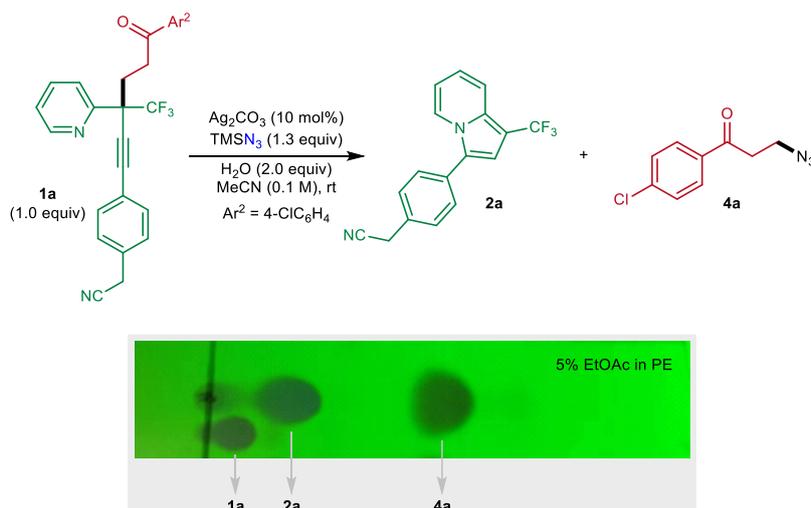


3. General procedure for the synthesis of indolizines and β -azido-ketones

General Procedure B:



To a screw-cap vial equipped with a magnetic stir bar was added Ag_2CO_3 (10 mol%). Then a solution of compound **1** (1.0 equiv) in MeCN (0.1 M), H_2O (2.0 equiv), and TMSN_3 (1.3 equiv) was added in sequence. The tube was capped and stirred at room temperature. After the reaction was complete (monitored by TLC), the reaction mixture was concentrated under reduced pressure, and the residue was purified by flash chromatography (SiO_2) to afford the products **2** and **4**.



Compound **2a** was synthesized according to **General Procedure B** using **1a** (70 mg, 0.15 mmol, 1.0 equiv.) Reaction time: 7 h. The crude was purified by flash column chromatography (AcOH:EtOAc:PE = 1:5:94 to 1:20:79, v/v/v) to afford compound **2a** as a pale yellow solid (91% yield, 41 mg) and compound **4a** as a pale yellow oil (86% yield, 27 mg), respectively.

2-(4-(1-(Trifluoromethyl)indolizin-3-yl)phenyl)acetonitrile (**2a**):

mp 100-101 °C

TLC (SiO_2) $R_f = 0.35$ (hexanes/ethyl acetate = 4:1), [UV light]

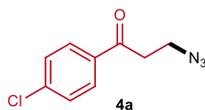
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.21 (dt, $J = 7.2, 1.1$ Hz, 1H), 7.65 (dq, $J = 9.1, 1.1$ Hz, 1H), 7.58-7.53 (m, 2H), 7.49-7.43 (m, 2H), 7.03 (s, 1H), 6.95 (ddd, $J = 9.1, 6.6, 1.0$ Hz, 1H), 6.66 (td, $J = 6.9, 1.3$ Hz, 1H), 3.83 (s, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 131.7 (q, $J = 3.0$ Hz), 131.1, 129.7, 129.2, 128.8, 124.7, 124.7 (q, $J = 267.7$ Hz), 122.7, 120.6, 118.0, 117.6, 112.4 (q, $J = 3.0$ Hz), 112.3, 103.2 (q, $J = 37.4$ Hz), 23.5.

^{19}F NMR (376 MHz, CDCl_3) δ -54.8.

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{17}\text{H}_{12}\text{F}_3\text{N}_2$ 301.0947; Found 301.0947.

3-Azido-1-(4-chlorophenyl)propan-1-one (4a):²

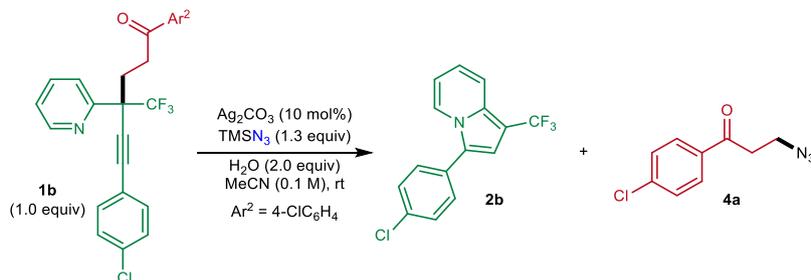


mp 108-109 °C

^1H NMR (400 MHz, CDCl_3) δ 7.93-7.87 (m, 2H), 7.49-7.43 (m, 2H), 3.73 (t, $J = 6.4$ Hz, 2H), 3.21 (t, $J = 6.4$ Hz, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 196.0, 140.0, 134.7, 129.5, 129.1, 46.1, 37.6.

HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_9\text{H}_8\text{ClN}_3\text{NaO}$ 232.0248; Found 232.0249.



Compound **2b** was synthesized according to **General Procedure B** using **1b** (69.3 mg, 0.15 mmol, 1.0 equiv.) Reaction time: 12 h. The crude was purified by flash column chromatography (AcOH:EtOAc:PE = = 1:2:97 to 1:5:94, v/v/v) to afford compound **2b** as a pale yellow solid (89% yield, 39.5 mg) and compound **4a** as a pale yellow oil (90% yield, 28 mg), respectively.

3-(4-Chlorophenyl)-1-(trifluoromethyl)indolizine (2b):

TLC (SiO_2) $R_f = 0.80$ (hexanes/ethyl acetate = 9:1), [UV light]

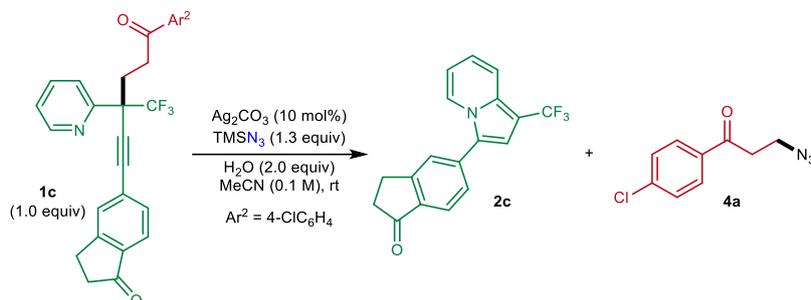
mp 95-96 °C

^1H NMR (400 MHz, CDCl_3) δ 8.16 (dt, $J = 7.2, 1.2$ Hz, 1H), 7.64 (dq, $J = 9.1, 1.1$ Hz, 1H), 7.45 (d, $J = 0.8$ Hz, 4H), 7.00 (s, 1H), 6.93 (ddd, $J = 9.1, 6.6, 1.0$ Hz, 1H), 6.64 (td, $J = 6.9, 1.3$ Hz, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 133.9, 131.6 (q, $J = 4.0$ Hz), 129.7, 129.5, 129.4, 124.7 (q, $J = 266.6$ Hz), 124.4, 122.7, 120.6, 118.0, 112.3 (q, $J = 3.0$ Hz), 112.3, 103.2 (q, $J = 37.4$ Hz).

^{19}F NMR (376 MHz, CDCl_3) δ -54.8.

HRMS (ESI) m/z : $[M+H]^+$ Calcd for $C_{15}H_{10}ClF_3N$ 296.0448; Found 296.0451.



Compound **2c** was synthesized according to **General Procedure B** using **1c** (72 mg, 0.15 mmol, 1.0 equiv.) Reaction time: 12 h. The crude was purified by flash column chromatography (AcOH:EtOAc:PE = 1:5:94 to 1:20:79, v/v/v) to afford compound **2c** as a yellow solid (87% yield, 41 mg) and compound **4a** as a pale yellow oil (83% yield, 26 mg), respectively.

5-(1-(Trifluoromethyl)indolizin-3-yl)-2,3-dihydro-1H-inden-1-one (2c):

TLC (SiO₂) R_f = 0.34 (hexanes/ethyl acetate = 4:1), [UV light]

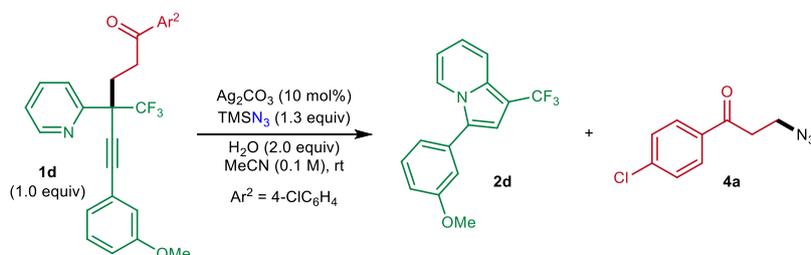
mp 204-205 °C

¹H NMR (400 MHz, CDCl₃) δ 8.35 (d, $J = 7.2$ Hz, 1H), 7.86 (d, $J = 7.9$ Hz, 1H), 7.67 (d, $J = 12.3$ Hz, 2H), 7.56 (d, $J = 8.0$ Hz, 1H), 7.12 (s, 1H), 7.00 (dd, $J = 9.1, 6.6$ Hz, 1H), 6.72 (t, $J = 6.9$ Hz, 1H), 3.29-3.16 (m, 2H), 2.76 (td, $J = 5.6, 2.4$ Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 206.0, 156.1, 137.3, 136.3, 132.3 (q, $J = 4.0$ Hz), 127.0, 125.7, 124.7, 124.5, 124.5 (q, $J = 266.6$ Hz), 122.9, 121.2, 118.2, 113.4 (q, $J = 3.0$ Hz), 112.7, 103.8 (q, $J = 37.4$ Hz), 36.4, 25.9.

¹⁹F NMR (376 MHz, CDCl₃) δ -55.0.

HRMS (ESI) m/z : $[M+H]^+$ Calcd for $C_{18}H_{13}F_3NO$ 316.0944; Found 316.0946.



Compound **2d** was synthesized according to **General Procedure B** using **1d** (68.6 mg, 0.15 mmol, 1.0 equiv.) Reaction time: 12 h. The crude was purified by flash column chromatography

(AcOH:EtOAc:PE = 1:2:97, v/v/v) to afford compound **2d** as a colorless oil (70% yield, 30.5 mg) and compound **4a** as a pale yellow oil (79% yield, 25 mg), respectively.

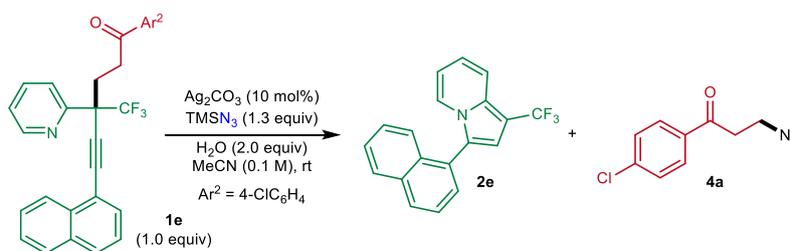
3-(3-Methoxyphenyl)-1-(trifluoromethyl)indolizine (2d):

¹H NMR (400 MHz, CDCl₃) δ 8.28 (d, *J* = 7.2 Hz, 1H), 7.64 (d, *J* = 9.1 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.15-7.09 (m, 1H), 7.05 (t, *J* = 2.1 Hz, 1H), 7.02 (d, *J* = 3.0 Hz, 1H), 6.97-6.89 (m, 2H), 6.67-6.59 (m, 1H), 3.85 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 160.2, 132.4, 131.5 (q, *J* = 3.3 Hz), 130.3, 125.6, 124.9 (q, *J* = 266.6 Hz), 123.2, 120.9, 120.5, 118.0, 114.2, 113.6, 112.2 (q, *J* = 3.1 Hz), 112.1, 102.9 (q, *J* = 37.0 Hz), 55.5.

¹⁹F NMR (376 MHz, CDCl₃) δ -54.7.

HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₁₆H₁₃F₃NO 292.0944; Found 292.0942.



Compound **2e** was synthesized according to **General Procedure B** using **1e** (71.7 mg, 0.15 mmol, 1.0 equiv.) Reaction time: 12 h. The crude was purified by flash column chromatography (AcOH:EtOAc:PE = 1:2:97 to 1:5:94, v/v/v) to afford compound **2e** as a pale yellow oil (79% yield, 36.9 mg) and compound **4a** as a pale yellow oil (73% yield, 23 mg), respectively.

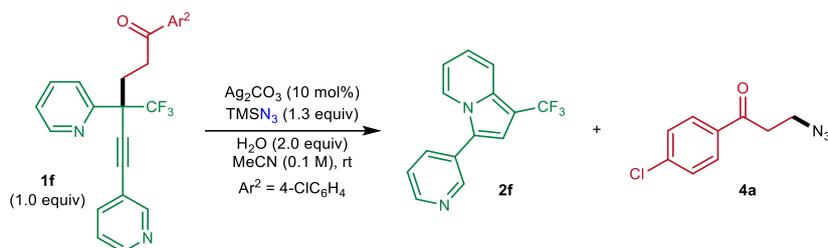
3-(Naphthalen-1-yl)-1-(trifluoromethyl)indolizine (2e):

¹H NMR (400 MHz, CDCl₃) δ 7.98-7.91 (m, 2H), 7.70 (dd, *J* = 9.2, 1.1 Hz, 1H), 7.59-7.48 (m, 4H), 7.45-7.37 (m, 2H), 7.11 (s, 1H), 6.93 (ddd, *J* = 9.2, 6.6, 1.0 Hz, 1H), 6.49 (td, *J* = 6.9, 1.2 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 133.9, 132.2, 131.1 (q, *J* = 3.3 Hz), 129.5, 129.4, 128.7, 128.3, 127.0, 126.4, 125.7, 125.4, 123.7, 123.6, 120.3, 117.8, 113.5 (q, *J* = 3.0 Hz), 111.7, 102.6 (q, *J* = 37.1 Hz).

¹⁹F NMR (376 MHz, CDCl₃) δ -54.3.

HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₁₉H₁₃F₃N 312.0995; Found 312.0988.



Compound **2f** was synthesized according to **General Procedure B** using **1f** (64 mg, 0.15 mmol, 1.0 equiv.) Reaction time: 12 h. The crude was purified by flash column chromatography (5-10% EtOAc in PE) to afford compound **2f** as a pale yellow solid (59% yield, 23 mg) and compound **4a** as a pale yellow oil (70% yield, 22 mg), respectively.

3-(Pyridin-3-yl)-1-(trifluoromethyl)indolizine (**2f**):

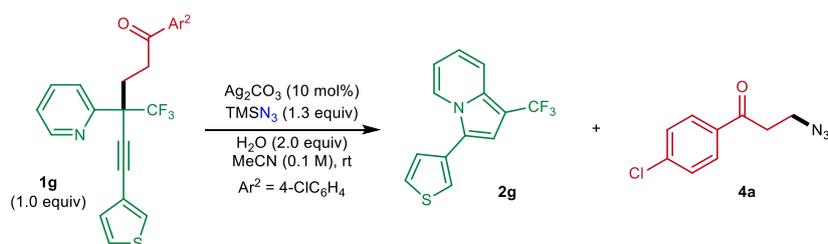
mp 71-72 °C

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.83 (s, 1H), 8.73-8.57 (m, 1H), 8.19 (dt, $J = 7.2, 1.1$ Hz, 1H), 7.86 (dt, $J = 7.9, 1.9$ Hz, 1H), 7.68 (dq, $J = 9.2, 1.2$ Hz, 1H), 7.45 (dd, $J = 7.9, 4.8$ Hz, 1H), 7.08 (s, 1H), 6.99 (ddd, $J = 9.1, 6.6, 1.0$ Hz, 1H), 6.70 (td, $J = 6.9, 1.3$ Hz, 1H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 149.4, 149.0, 135.7, 132.1, 127.4, 124.5 (q, $J = 266.6$ Hz), 123.9, 122.5, 122.0, 121.0, 118.2, 113.0 (q, $J = 3.0$ Hz), 112.6, 103.6 (q, $J = 37.5$ Hz).

$^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -55.0.

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_{10}\text{F}_3\text{N}_2$ 263.0791; Found 263.0787.



Compound **2g** was synthesized according to **General Procedure B** using **1g** (65 mg, 0.15 mmol, 1.0 equiv.) Reaction time: 12 h. The crude was purified by flash column chromatography (100% PE to 10% EtOAc in PE) to afford compound **2g** as a colorless oil (77% yield, 30.8 mg) and compound **4a** as a pale yellow oil (86% yield, 27 mg), respectively.

3-(Thiophen-3-yl)-1-(trifluoromethyl)indolizine (**2g**):

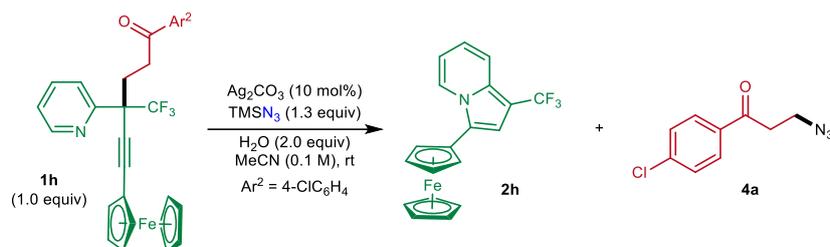
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.21 (dt, $J = 7.2, 1.1$ Hz, 1H), 7.63 (dp, $J = 9.0, 1.1$ Hz, 1H), 7.48 (dd, $J = 4.9, 3.0$ Hz, 1H), 7.44 (dd, $J = 2.9, 1.3$ Hz, 1H), 7.29 (dd, $J = 5.0, 1.3$ Hz, 1H), 7.03 (s, 1H),

6.93 (ddd, $J = 9.2, 6.6, 1.0$ Hz, 1H), 6.66 (td, $J = 6.9, 1.3$ Hz, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 131.4, 131.2 (q, $J = 3.1$ Hz), 127.5, 126.6, 124.8 (d, $J = 265.7$ Hz), 123.3, 122.8, 121.1, 120.2, 117.9, 112.1 (2C), 102.7 (q, $J = 37.4$ Hz).

^{19}F NMR (376 MHz, CDCl_3) δ -54.7.

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{13}\text{H}_9\text{F}_3\text{NS}$ 268.0402; Found 268.0383.



Compound **2h** was synthesized according to **General Procedure B** using **1h** (80 mg, 0.15 mmol, 1.0 equiv.) Reaction time: 12 h. The crude was purified by flash column chromatography ($\text{AcOH}:\text{EtOAc}:\text{PE} = 1:1.5:97.5$ to $1:5:94$, v/v/v) to afford compound **2h** as a yellow solid (89% yield, 49.2 mg) and compound **4a** as a pale yellow oil (92% yield, 29 mg), respectively.

(2h):

TLC (SiO_2) $R_f = 0.71$ (hexanes/ethyl acetate = 9:1), [UV light]

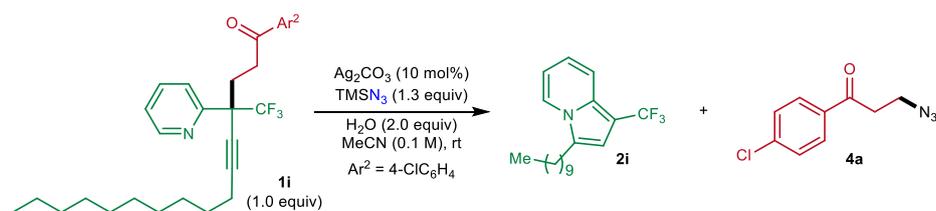
mp 110-111 °C

^1H NMR (400 MHz, CDCl_3) δ 8.58 (dd, $J = 7.2, 1.2$ Hz, 1H), 7.65-7.58 (m, 1H), 7.00 (s, 1H), 6.92 (dd, $J = 9.1, 6.5$ Hz, 1H), 6.76-6.69 (m, 1H), 4.53 (t, $J = 2.0$ Hz, 2H), 4.38 (t, $J = 1.8$ Hz, 2H), 4.20 (d, $J = 0.8$ Hz, 5H).

^{13}C NMR (101 MHz, CDCl_3) δ 131.3 (q, $J = 3.0$ Hz), 124.8 (q, $J = 266.6$ Hz), 124.1, 122.3, 119.5, 117.8, 112.1 (q, $J = 3.0$ Hz), 111.5, 102.4 (q, $J = 37.4$ Hz), 76.7, 69.1, 68.7, 67.3.

^{19}F NMR (376 MHz, CDCl_3) δ -54.5.

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{15}\text{F}_3\text{FeN}$ 370.0501; Found 370.0456.



Compound **2i** was synthesized according to **General Procedure B** using **1i** (74 mg, 0.15 mmol, 1.0

equiv.) Reaction time: 12 h. The crude was purified by flash column chromatography (AcOH:EtOAc:PE = 1:1:98 to 1:3:96, v/v/v) to afford compound **2i** as a colorless oil (81% yield, 39.5 mg) and compound **4a** as a pale yellow oil (84% yield, 26.4 mg), respectively.

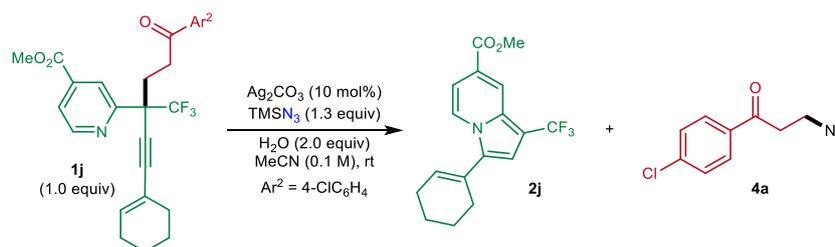
3-Decyl-1-(trifluoromethyl)indolizine (2i):

¹H NMR (400 MHz, CDCl₃) δ 7.77 (dt, *J* = 7.1, 1.2 Hz, 1H), 7.58 (dq, *J* = 9.2, 1.2 Hz, 1H), 6.89-6.83 (m, 1H), 6.75 (s, 1H), 6.65 (td, *J* = 6.8, 1.3 Hz, 1H), 2.80-2.73 (m, 2H), 1.81-1.70 (m, 2H), 1.47-1.39 (m, 2H), 1.35-1.24 (m, 12H), 0.92-0.85 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 130.5 (q, *J* = 3.0 Hz), 125.1, 125.1 (q, *J* = 266.6 Hz), 122.2, 119.0, 117.7, 111.3, 109.7 (q, *J* = 3.0 Hz), 101.3 (q, *J* = 36.4 Hz), 31.9, 29.6, 29.6, 29.5, 29.4, 29.3, 27.0, 25.7, 22.7, 14.1.

¹⁹F NMR (376 MHz, CDCl₃) δ -54.2.

HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₁₉H₂₇F₃N 326.2090; Found 326.2091.



Compound **2j** was synthesized according to **General Procedure B** using **1j** (73 mg, 0.15 mmol, 1.0 equiv.) Reaction time: 6 h. The crude was purified by flash column chromatography (AcOH:EtOAc:PE = 1:2:97 to 1:5:94, v/v/v) to afford compound **2j** as a yellow oil (75% yield, 36.4 mg) and compound **4a** as a pale yellow oil (78% yield, 24.5 mg), respectively.

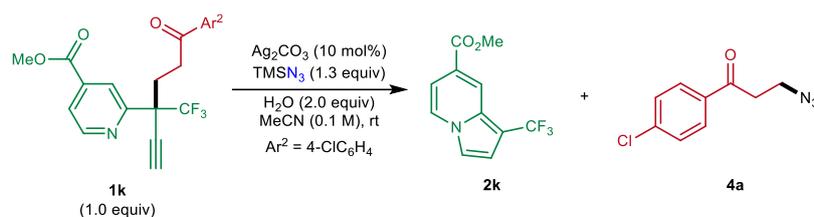
Methyl 3-(cyclohex-1-en-1-yl)-1-(trifluoromethyl)indolizine-7-carboxylate (2j):

¹H NMR (400 MHz, CDCl₃) δ 8.33 (dt, *J* = 2.1, 1.0 Hz, 1H), 8.17 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.18 (dd, *J* = 7.5, 1.8 Hz, 1H), 6.93 (s, 1H), 6.12 (tt, *J* = 3.8, 1.7 Hz, 1H), 3.94 (s, 3H), 2.37-2.33 (m, 2H), 2.31-2.26 (m, 2H), 1.86-1.79 (m, 2H), 1.78-1.71 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 165.9, 129.9, 129.6, 129.1, 127.9, 124.2 (q, *J* = 267.6 Hz), 123.3, 121.2, 120.7, 112.2 (q, *J* = 3.0 Hz), 110.5, 107.0 (q, *J* = 37.3 Hz), 52.3, 28.9, 25.5, 22.7, 21.9.

¹⁹F NMR (376 MHz, CDCl₃) δ -55.0.

HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₁₇H₁₇F₃NO₂ 324.1206; Found 324.1204.



Compound **2k** was synthesized according to **General Procedure B** using **1k** (61.5 mg, 0.15 mmol, 1.0 equiv.) Reaction time: 12 h. The crude was purified by flash column chromatography (AcOH:EtOAc:PE = 1:5:94, v/v/v) to afford compound **2k** as a pale yellow viscous oil (95% yield, 34.6 mg) and compound **4a** as a pale yellow oil (87% yield, 27.3 mg), respectively.

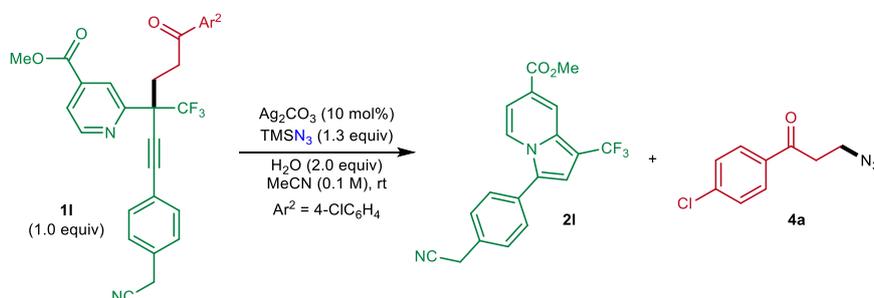
Methyl 1-(trifluoromethyl)indolizine-7-carboxylate (2k):

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.38-8.33 (m, 1H), 7.97 (dd, $J = 7.2, 1.1$ Hz, 1H), 7.39 (d, $J = 2.9$ Hz, 1H), 7.22 (dd, $J = 7.3, 1.7$ Hz, 1H), 7.07 (d, $J = 2.8$ Hz, 1H), 3.94 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 165.8, 129.2 (q, $J = 2.9$ Hz), 125.0, 124.1 (q, $J = 267.6$ Hz), 121.8, 121.0, 114.9, 113.8 (q, $J = 3.3$ Hz), 110.9, 107.1 (q, $J = 37.2$ Hz), 52.4.

$^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -55.0.

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{11}\text{H}_9\text{F}_3\text{NO}_2$ 244.0580; Found 244.0580.



Compound **2l** was synthesized according to **General Procedure B** using **1l** (78.7 mg, 0.15 mmol, 1.0 equiv.) Reaction time: 12 h. The crude was purified by flash column chromatography (5-20% EtOAc in petroleum ether) to afford compound **2l** as a yellow solid (65% yield, 35 mg) and compound **4a** as a pale yellow oil (82% yield, 25.7 mg), respectively.

Methyl 3-(4-(cyanomethyl)phenyl)-1-(trifluoromethyl)indolizine-7-carboxylate (2l):

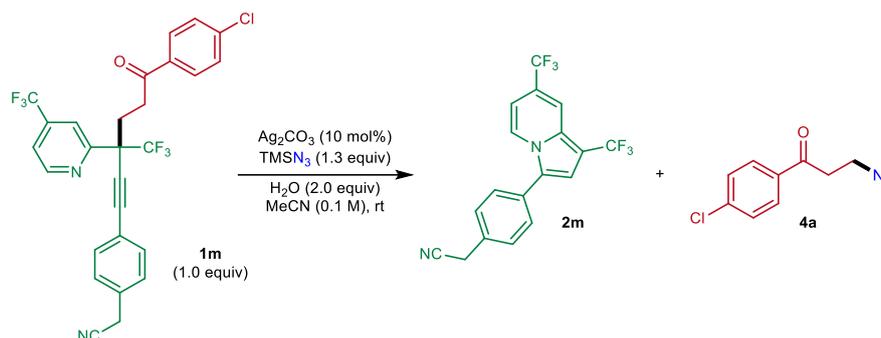
mp 130-131 °C

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.42 (dt, $J = 2.0, 1.1$ Hz, 1H), 8.20 (dd, $J = 7.5, 1.0$ Hz, 1H), 7.61-7.55 (m, 2H), 7.54-7.48 (m, 2H), 7.24 (dd, $J = 7.5, 1.8$ Hz, 1H), 7.14 (s, 1H), 3.96 (s, 3H), 3.85 (s, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 165.6, 130.4, 130.0 (q, $J = 2.9$ Hz), 129.3, 129.0, 126.9, 124.0 (d, $J = 266.4$ Hz), 122.2, 121.9, 121.3, 117.4, 114.1 (q, $J = 3.2$ Hz), 111.4, 107.8 (d, $J = 37.4$ Hz), 52.5, 23.5.

^{19}F NMR (376 MHz, CDCl_3) δ -55.2.

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{14}\text{F}_3\text{N}_2\text{O}_2$ 359.1002; Found 359.1000.



Compound **2m** was synthesized according to **General Procedure B** using **1m** (53.4 mg, 0.10 mmol, 1.0 equiv.) Reaction time: 48 h. The crude was purified by flash column chromatography (EtOAc:PE = 8:92 to 18:82, v/v) to afford compound **2m** as a white solid (83% yield, 30.6 mg) and compound **4a** as a pale yellow oil (89% yield, 18.6 mg), respectively.

(2m):

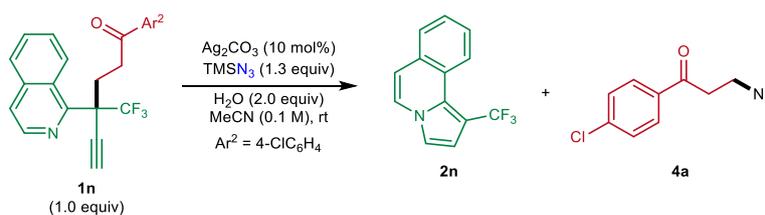
mp 128-129 °C

^1H NMR (500 MHz, CDCl_3) δ 8.27 (d, $J = 7.4$ Hz, 1H), 7.97 (s, 1H), 7.59-7.50 (m, 4H), 7.15 (s, 1H), 6.82 (dd, $J = 7.6, 1.9$ Hz, 1H), 3.86 (s, 2H).

^{13}C NMR (126 MHz, CDCl_3) δ 130.6, 130.1, 129.4, 129.0, 126.6, 124.0 (q, $J = 267.19$ Hz), 123.4, 123.4 (q, $J = 272.2$ Hz), 122.3 (d, $J = 34.0$ Hz), 117.4, 116.3 (q, $J = 4.8$ Hz), 113.9 (q, $J = 2.7$ Hz), 108.0 (q, $J = 2.6$ Hz), 107.1 (d, $J = 37.8$ Hz), 23.5.

^{19}F NMR (471 MHz, CDCl_3) δ -55.2, -63.7.

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{11}\text{F}_6\text{N}_2$ 369.0821; Found 369.0817.



Compound **2n** was synthesized according to **General Procedure B** using **1n** (60 mg, 0.15 mmol, 1.0 equiv.) Reaction time: 12 h. The crude was purified by flash column chromatography (0-5% EtOAc in petroleum ether) to afford compound **2n** as a pale yellow oil (45% yield, 15.9 mg) and compound **4a** as a pale yellow oil (69% yield, 21.7 mg), respectively.

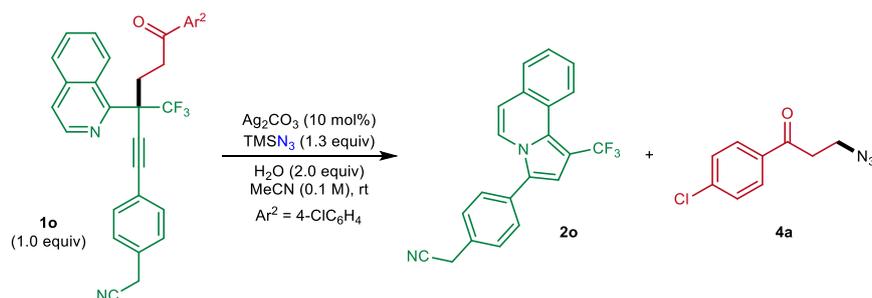
1-(Trifluoromethyl)pyrrolo[2,1-*a*]isoquinoline (2n):

¹H NMR (400 MHz, CDCl₃) δ 8.35 (d, *J* = 8.3 Hz, 1H), 7.74 (d, *J* = 7.2 Hz, 1H), 7.61 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.56 (ddd, *J* = 8.4, 7.2, 1.5 Hz, 1H), 7.46 (ddd, *J* = 8.2, 7.2, 1.2 Hz, 1H), 7.21 (d, *J* = 3.0 Hz, 1H), 6.96 (d, *J* = 3.0 Hz, 1H), 6.89 (d, *J* = 7.3 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 128.2, 128.1, 127.3, 127.0, 124.8 (q, *J* = 267.7 Hz), 124.5, 124.3 (q, *J* = 5.1 Hz), 124.1, 114.4, 113.1, 111.7 (q, *J* = 5.1 Hz), 106.2 (q, *J* = 37.4 Hz).

¹⁹F NMR (376 MHz, CDCl₃) δ -55.5.

HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₁₃H₉F₃N 236.0682; Found 236.0680.



Compound **2o** was synthesized according to **General Procedure B** using **1o** (77.5 mg, 0.15 mmol, 1.0 equiv.) Reaction time: 12 h. The crude was purified by flash column chromatography (AcOH:EtOAc:PE = 1:5:94 to 1:10:89, v/v/v) to afford compound **2o** as a yellow solid (92% yield, 48.3 mg) and compound **4a** as a pale yellow oil (80% yield, 25 mg), respectively.

2-(4-(1-(Trifluoromethyl)pyrrolo[2,1-*a*]isoquinolin-3-yl)phenyl)acetonitrile (2o):

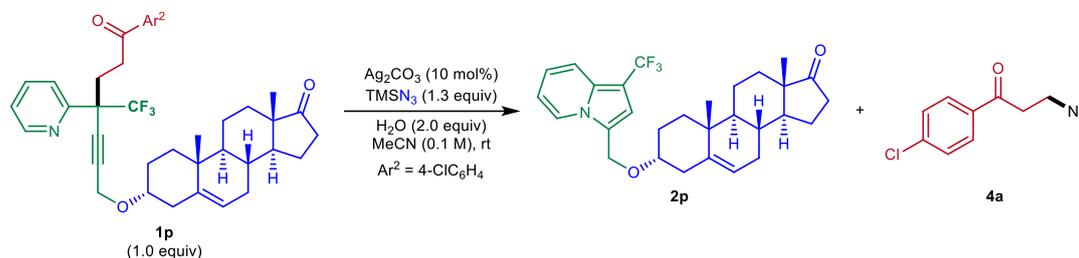
mp 120-121 °C

¹H NMR (500 MHz, CDCl₃) δ 8.40 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 7.4 Hz, 1H), 7.63 (d, *J* = 7.9 Hz, 1H), 7.59 (t, *J* = 7.7 Hz, 1H), 7.57-7.53 (m, 2H), 7.51-7.44 (m, 3H), 7.01 (s, 1H), 6.90 (d, *J* = 7.5 Hz, 1H), 3.82 (s, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 130.9, 130.0, 129.7, 128.7, 128.3, 128.1 (q, *J* = 3.6 Hz), 128.1, 127.2, 127.2, 126.3, 124.8 (q, *J* = 265.8 Hz), 124.6, 124.4 (q, *J* = 5.0 Hz), 121.5, 117.5, 113.4, 112.1 (q, *J* = 4.5 Hz), 106.5 (q, *J* = 37.3 Hz), 23.5.

^{19}F NMR (376 MHz, CDCl_3) δ -55.6.

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{14}\text{F}_3\text{N}_2$ 351.1104; Found 351.1102.



Compound **2p** was synthesized according to **General Procedure B** using **1p** (65 mg, 0.1 mmol, 1.0 equiv.) Reaction time: 12 h. The crude was purified by flash column chromatography (10% EtOAc in PE) to afford compound **2p** as a pale yellow oil (87% yield, 42.2 mg) and compound **4a** as a pale yellow oil (82% yield, 17.1 mg), respectively.

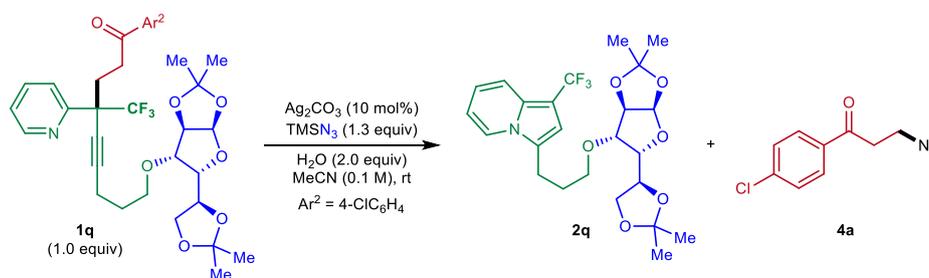
(2p):

^1H NMR (400 MHz, CDCl_3) δ 8.11 (dt, $J = 7.1, 1.1$ Hz, 1H), 7.60 (dq, $J = 9.2, 1.2$ Hz, 1H), 6.97 (ddd, $J = 9.2, 6.6, 1.0$ Hz, 1H), 6.93 (s, 1H), 6.72 (td, $J = 6.9, 1.3$ Hz, 1H), 5.37-5.35 (m, 1H), 4.80 (s, 2H), 3.31-3.23 (m, 1H), 2.49-2.42 (m, 1H), 2.39-2.34 (m, 1H), 2.30-2.21 (m, 1H), 2.15-2.02 (m, 2H), 1.98-1.82 (m, 4H), 1.74-1.58 (m, 4H), 1.57-1.42 (m, 3H), 1.39-1.14 (m, 3H), 1.02 (s, 3H), 0.88 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 140.8, 131.9 (q, $J = 3.2$ Hz), 124.7 (q, $J = 266.6$ Hz), 123.9, 121.2, 120.8, 120.7, 117.6, 112.9 (q, $J = 3.0$ Hz), 111.8, 101.5 (q, $J = 37.3$ Hz), 77.7, 61.2, 51.8, 50.2, 47.5, 38.9, 37.0 (2C), 35.8, 31.5, 31.4, 30.8, 28.2, 21.9, 20.4, 19.4, 13.6.

^{19}F NMR (376 MHz, CDCl_3) δ -54.6.

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{29}\text{H}_{35}\text{F}_3\text{NO}_2$ 486.2614; Found 486.2607.



Compound **2q** was synthesized according to **General Procedure B** using **1q** (98 mg, 0.15 mmol, 1.0 equiv.) Reaction time: 3 h. The crude was purified by flash column chromatography (5-10%

EtOAc in petroleum ether) to afford compound **2q** as a pale yellow oil (93% yield, 67.7 mg) and compound **4a** as a pale yellow oil (76% yield, 23.9 mg), respectively.

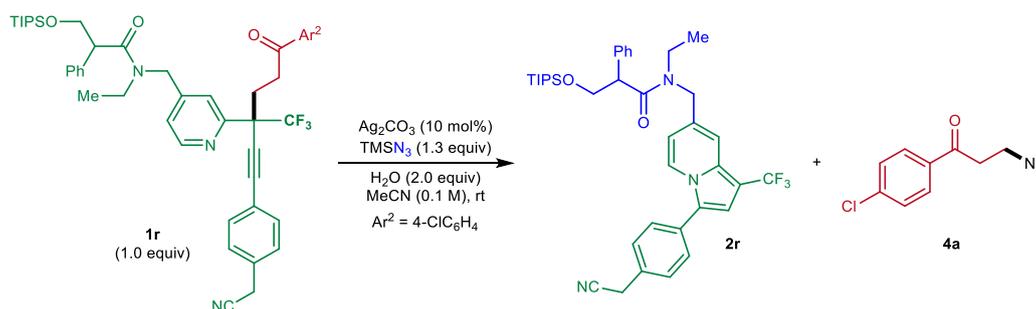
(2q):

¹H NMR (400 MHz, CDCl₃) δ 7.83 (dd, *J* = 7.1, 1.2 Hz, 1H), 7.59 (dq, *J* = 9.1, 1.1 Hz, 1H), 6.92-6.85 (m, 1H), 6.81 (s, 1H), 6.67 (td, *J* = 6.9, 1.3 Hz, 1H), 5.88 (d, *J* = 3.7 Hz, 1H), 4.53 (d, *J* = 3.7 Hz, 1H), 4.39-4.34 (m, 1H), 4.14-4.10 (m, 2H), 4.02 (dd, *J* = 8.6, 5.5 Hz, 1H), 3.90 (d, *J* = 3.1 Hz, 1H), 3.74-3.69 (m, 1H), 3.59-3.53 (m, 1H), 3.00-2.88 (m, 2H), 2.05-1.96 (m, 2H), 1.50 (s, 3H), 1.44 (s, 3H), 1.31 (d, *J* = 1.6 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 130.6 (q, *J* = 3.6 Hz), 125.0 (q, *J* = 266.6 Hz), 123.9, 122.2, 119.2, 117.8, 111.8, 111.5, 110.2 (q, *J* = 3.1 Hz), 109.1, 105.3, 101.4 (q, *J* = 37.0 Hz), 82.2, 81.3, 72.3, 68.9, 67.5, 27.2, 26.8 (2C), 26.2, 25.3, 22.0.

¹⁹F NMR (376 MHz, CDCl₃) δ -54.2.

HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₂₄H₃₁F₃NO₆ 486.2098; Found 486.2092.



Compound **2r** was synthesized according to **General Procedure B** using **1r** (83 mg, 0.1 mmol, 1.0 equiv.) Reaction time: 12 h. The crude was purified by flash column chromatography (0-15% EtOAc in PE) to afford compound **2r** as a yellow oil (77% yield, 51 mg) and compound **4a** as a pale yellow oil (78% yield, 16.3 mg), respectively.

(2r):

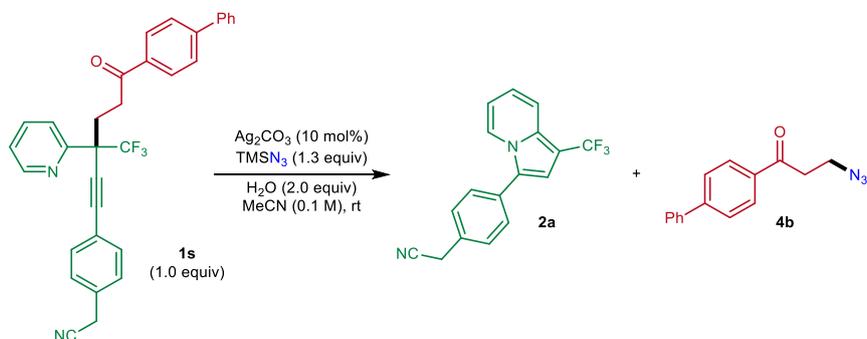
¹H NMR (400 MHz, CDCl₃) δ 8.12-8.06 (m, 1H), 7.55-7.25 (m, 10H), 7.02-6.97 (m, 1H), 6.61-6.39 (m, 1H), 4.81-4.47 (m, 1H), 4.46-4.37 (m, 2H), 4.05-3.94 (m, 1H), 3.87-3.82 (m, 3H), 3.56-3.16 (m, 2H), 1.15-0.96 (m, 24H).

¹³C NMR (101 MHz, CDCl₃) δ 172.2, 171.8, 137.0, 137.0, 131.6, 131.3 (q, *J* = 3.3 Hz), 131.0, 129.6, 129.0, 128.8, 128.8, 128.7, 128.3, 127.4, 127.4, 124.8, 124.6, 123.2, 122.9, 117.6, 115.8, 115.3, 112.8, 112.4, 111.1, 102.8 (d, *J* = 37.2 Hz), 67.1, 67.0, 52.2, 52.0, 50.0, 47.7, 41.6, 41.1, 29.7,

23.5, 18.0, 17.9, 14.1, 12.5, 11.9.

^{19}F NMR (376 MHz, CDCl_3) δ -54.7, -54.8.

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{38}\text{H}_{47}\text{F}_3\text{N}_3\text{O}_2\text{Si}$ 662.3384; Found 662.3376.



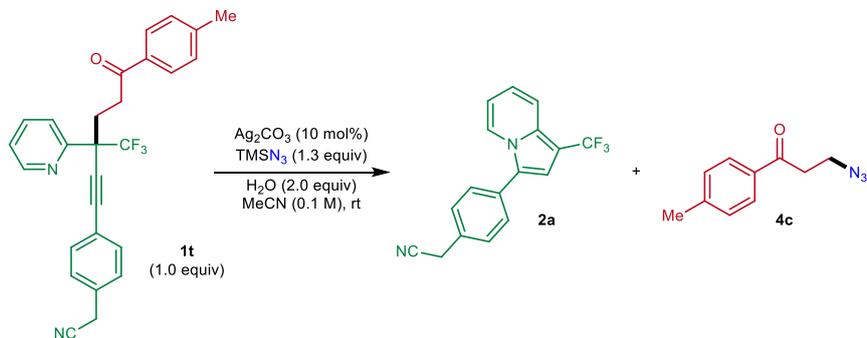
According to **General Procedure B** using **1s** (76 mg, 0.15 mmol, 1.0 equiv.) Reaction time: 12 h. The crude was purified by flash column chromatography (AcOH:EtOAc:PE = 1:5:94 to 1:20:79, v/v/v) to afford compound **2a** as a pale yellow solid (85% yield, 38.2 mg) and compound **4b** as a pale yellow oil (78% yield, 29.4 mg), respectively.

1-([1,1'-Biphenyl]-4-yl)-3-azidopropan-1-one (**4b**):

^1H NMR (400 MHz, CDCl_3) δ 8.09-8.01 (m, 2H), 7.76-7.68 (m, 2H), 7.67-7.61 (m, 2H), 7.51-7.45 (m, 2H), 7.44-7.38 (m, 1H), 3.76 (t, $J = 6.5$ Hz, 2H), 3.28 (t, $J = 6.5$ Hz, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 196.7, 146.2, 139.7, 135.1, 129.0, 128.7, 128.4, 127.4, 127.3, 46.2, 37.7.

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{15}\text{H}_{14}\text{N}_3\text{O}$ 252.1131; Found: 252.1132.



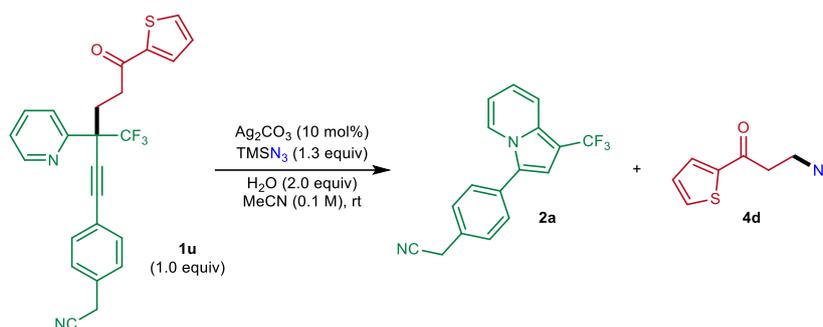
According to **General Procedure B** using **1t** (67 mg, 0.15 mmol, 1.0 equiv.) Reaction time: 12 h. The crude was purified by flash column chromatography (AcOH:EtOAc:PE = 1:5:94 to 1:20:79, v/v/v) to afford compound **2a** as a pale yellow solid (90% yield, 40.5 mg) and compound **4c** as a

pale yellow oil (87% yield, 24.7 mg), respectively.

3-Azido-1-(*p*-tolyl)propan-1-one (4c):²

¹H NMR (400 MHz, CDCl₃) δ 7.86 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 3.73 (t, *J* = 6.5 Hz, 2H), 3.22 (t, *J* = 6.5 Hz, 2H), 2.42 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 196.8, 144.4, 134.0, 129.4, 128.2, 46.3, 37.5, 21.7.



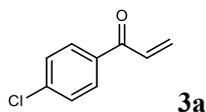
According to **General Procedure B** using **1u** (65.8 mg, 0.15 mmol, 1.0 equiv.) Reaction time: 12 h. The crude was purified by flash column chromatography (AcOH:EtOAc:PE = 1:6:93 to 1:20:79, v/v/v) to afford compound **2a** as a pale yellow solid (70% yield, 31.5 mg) and compound **4d** as a pale yellow oil (65% yield, 17.6 mg), respectively.

3-Azido-1-(thiophen-2-yl)propan-1-one (4d):³

¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, *J* = 3.8 Hz, 1H), 7.66 (d, *J* = 4.8 Hz, 1H), 7.14 (t, *J* = 4.4 Hz, 1H), 3.71 (t, *J* = 6.5 Hz, 2H), 3.17 (t, *J* = 6.5 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 190.1, 143.7, 134.4, 132.4, 128.4, 46.3, 38.4.

1-(4-Chlorophenyl)prop-2-en-1-one

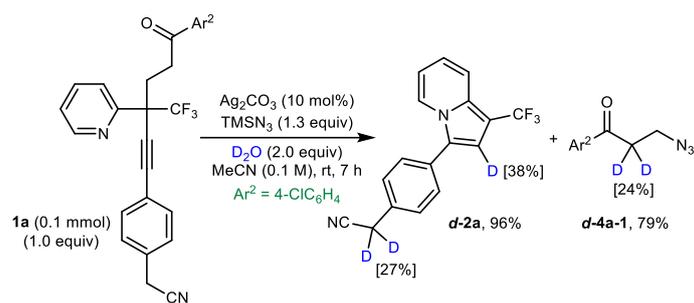


TLC (SiO₂) R_f = 0.61 (hexanes/ethyl acetate = 9:1), [UV light]

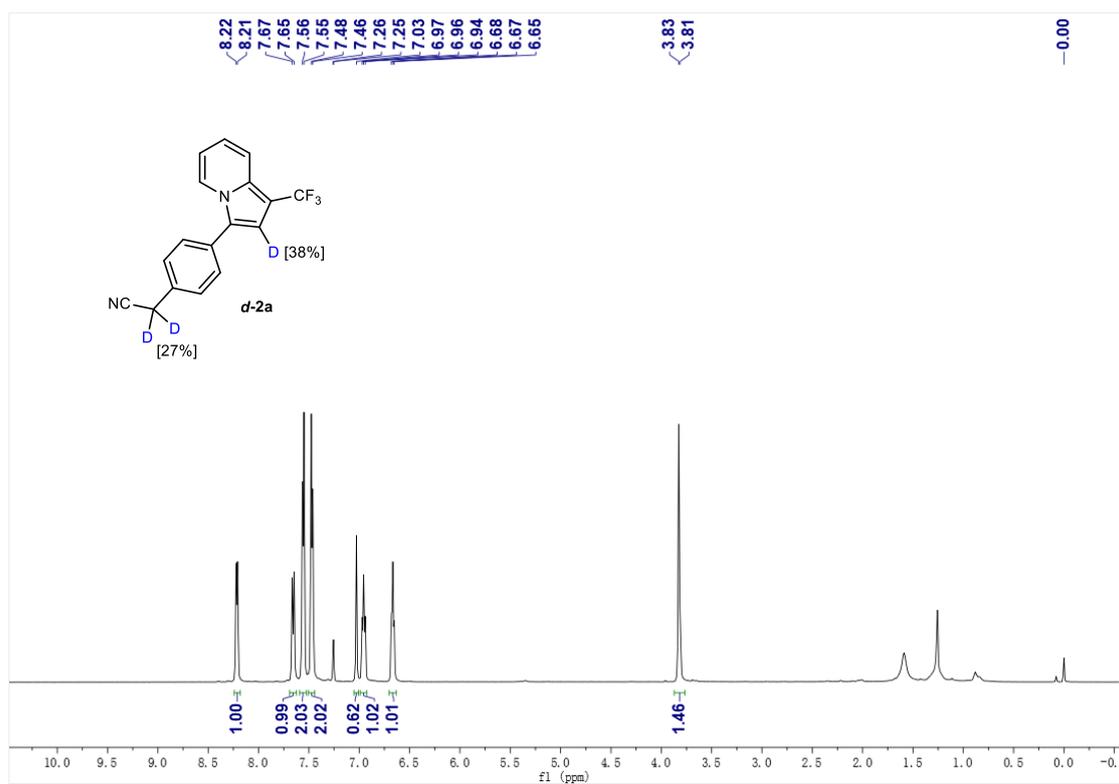
¹H NMR (400 MHz, CDCl₃) δ 7.92-7.86 (m, 2H), 7.49-7.44 (m, 2H), 7.12 (dd, *J* = 17.1, 10.6 Hz, 1H), 6.45 (dd, *J* = 17.1, 1.6 Hz, 1H), 5.96 (dd, *J* = 10.6, 1.6 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 189.78, 139.49, 135.56, 131.94, 130.68, 130.11, 128.98.

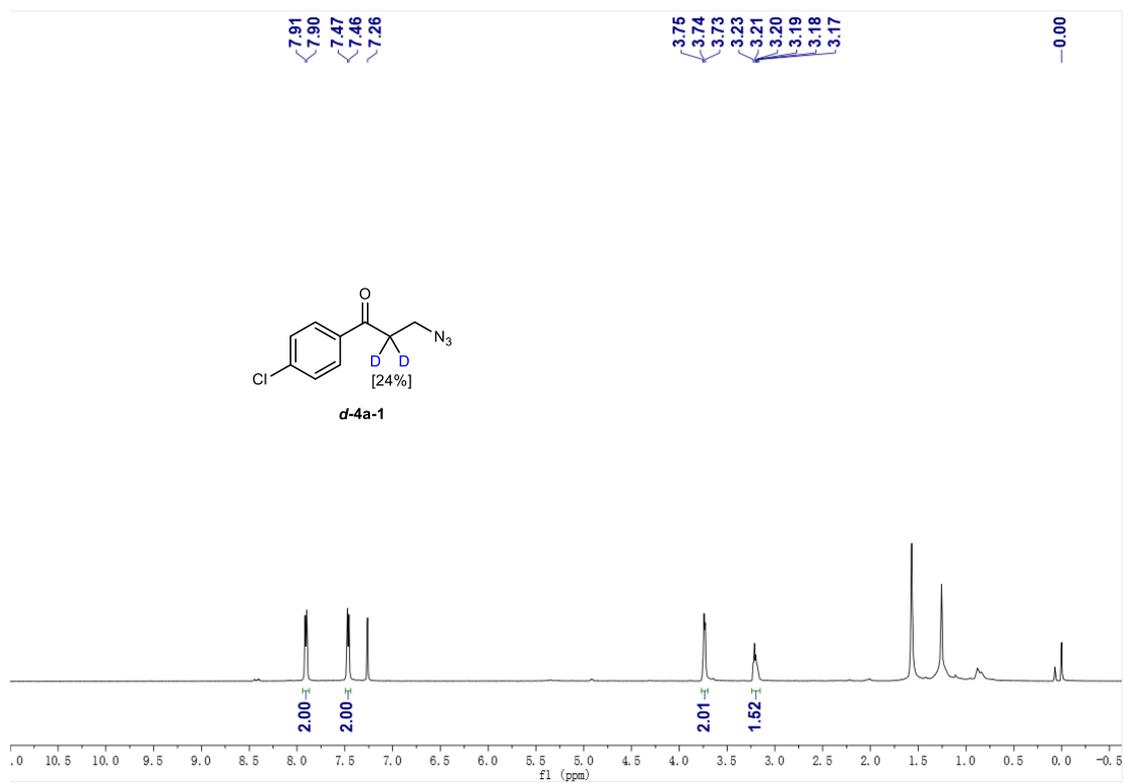
4. Mechanistic studies

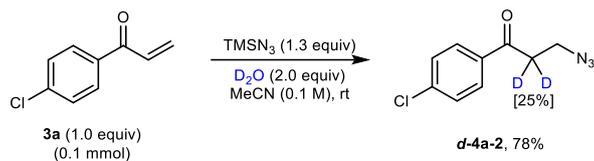


^1H NMR spectra of compound **d-2a** in CDCl_3 (500 MHz):

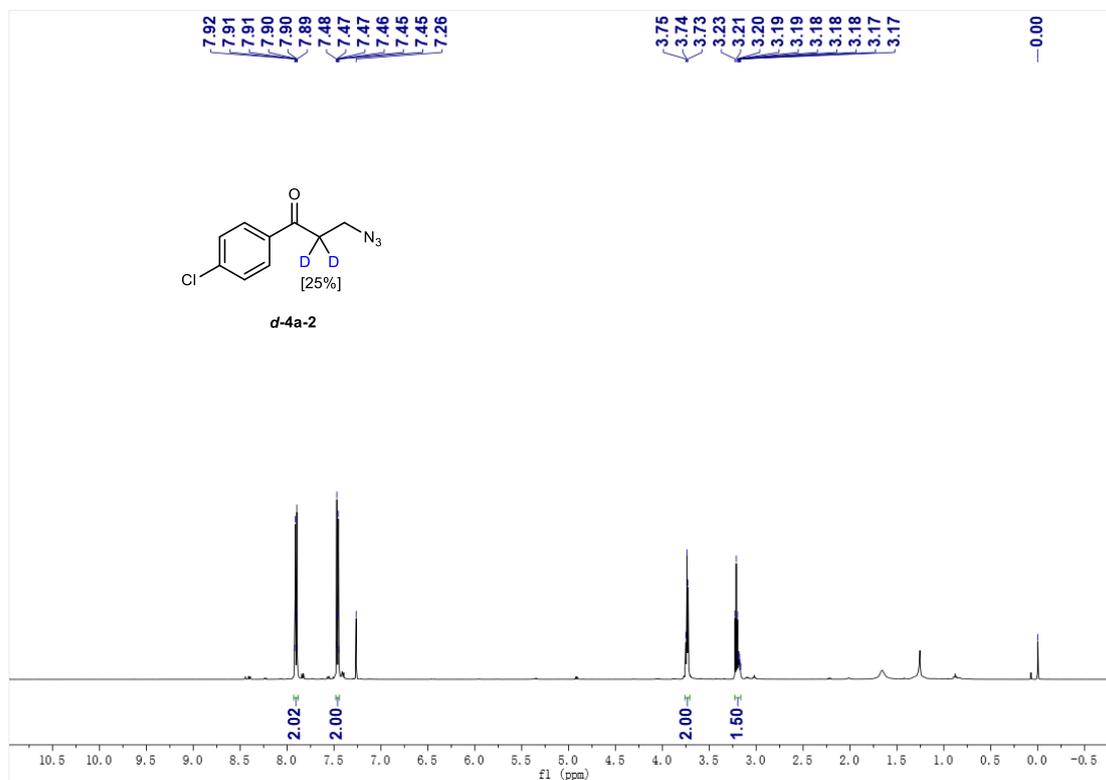


¹H NMR spectra of compound **d-4a-1** in CDCl₃ (500 MHz):





¹H NMR spectra of compound **d-4a-2** in CDCl₃ (500 MHz):



5. X-ray single crystal data of **2a**

A view of the molecular structure of compound **2a** (thermal ellipsoids are shown with a 30% probability level). Single crystals of compound **2a** suitable for the X-ray crystal structure analysis were obtained by the slow evaporation of a solution of compound **2a** in PE/dichloromethane at 2-8 °C. CCDC deposition number of **2a**: 2121294.

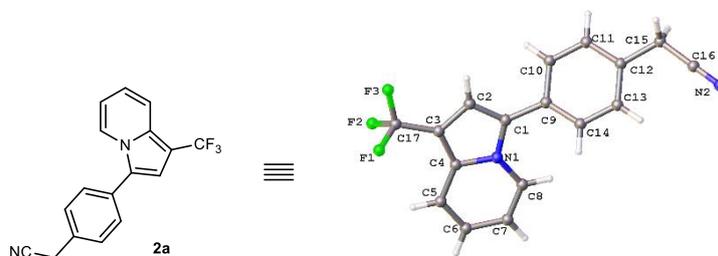


Table S1. The crystal parameters of **2a**

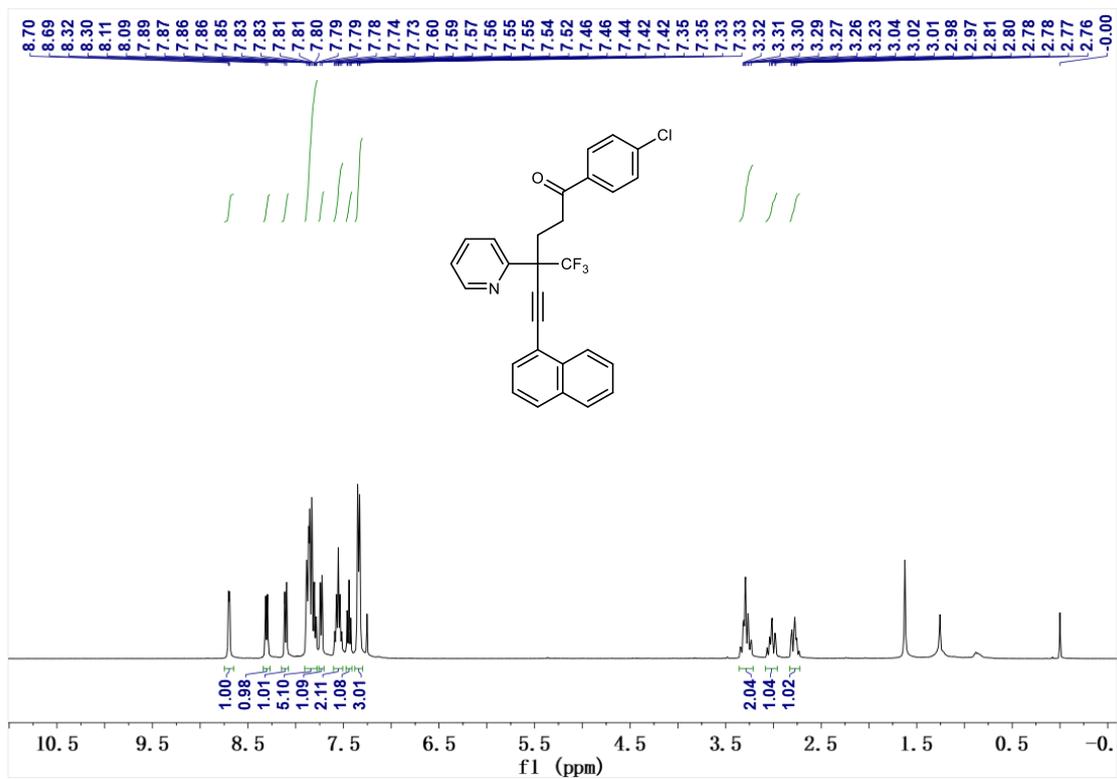
Empirical formula	C ₁₇ H ₁₁ F ₃ N ₂
Formula weight	300.28
Temperature/K	288(11)
Crystal system	monoclinic
Space group	P21/c
a/Å	9.1862(4)
b/Å	22.9415(7)
c/Å	7.2169(2)
α/°	90
β/°	113.012(4)
γ/°	90
Volume/Å ³	1399.90(9)
Z	4
ρ _{calc} /cm ³	1.425
μ/mm ⁻¹	0.964
F(000)	616.0
Crystal size/mm ³	30.14 × 0.1 × 0.08
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	7.708 to 147.64
Index ranges	-11 ≤ h ≤ 10, -28 ≤ k ≤ 28, -8 ≤ l ≤ 8
Reflections collected	2829
Data/restraints/parameters	2829/58/237
Goodness-of-fit on F ²	1.065
Final R indexes [I ≥ 2σ (I)]	R1 = 0.0769, wR2 = 0.2039
Final R indexes [all data]	R1 = 0.0790, wR2 = 0.2058
Largest diff. peak/hole / e Å ⁻³	0.62/-0.45

6. References

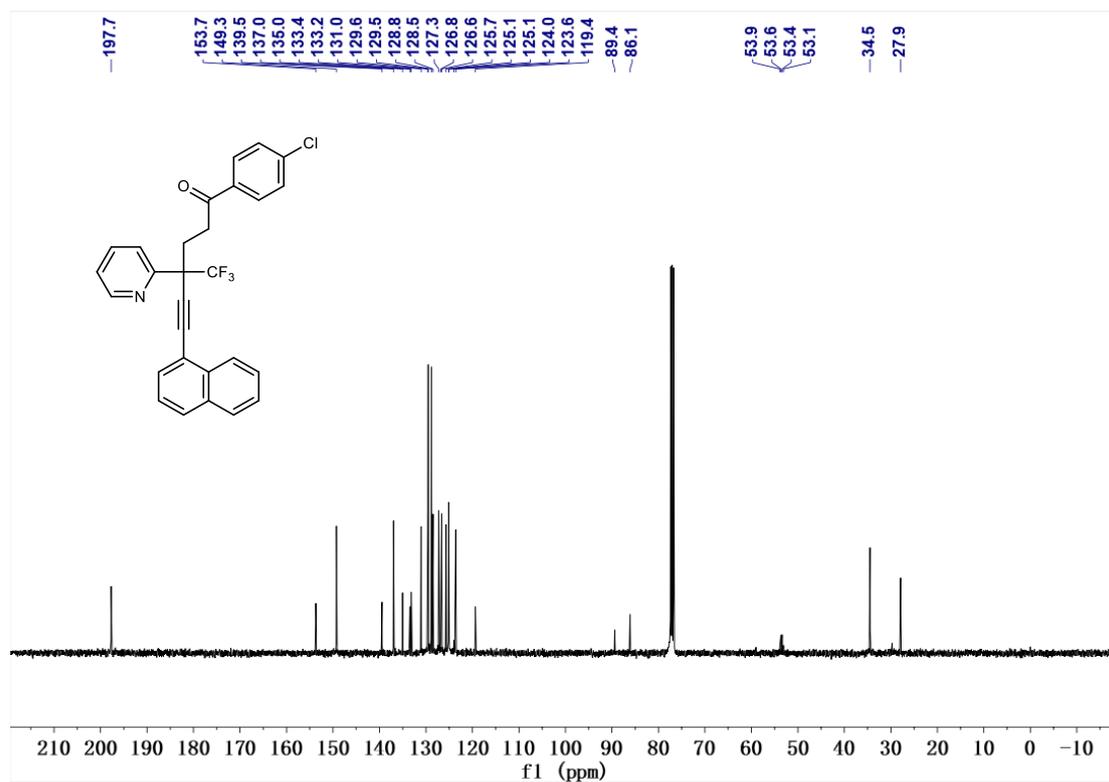
- [1] S.-J. Chen, G.-S. Chen, T. Deng, J.-H. Li, Z.-Q. He, L.-S. Liu, H. Ren, Y.-L. Liu, *Org. Lett.* **2022**, *24*, 702-707.
- [2] A. S. Carlson, C. Calcanas, R. M. Brunner, J. J. Topczewski, *Org. Lett.* **2018**, *20*, 1604-1607.
- [3] R. P. Shirke, S. S. V. Ramasastry, *Org. Lett.* **2017**, *19*, 5482-5485.
- [4] F. Verma, P. Shukla, S. R. Bhardiya, M. Singh, A. Rai, V. K. Rai, *Adv. Synth. Catal.* **2019**, *361*, 1247-1252.

7. Copies of NMR spectra

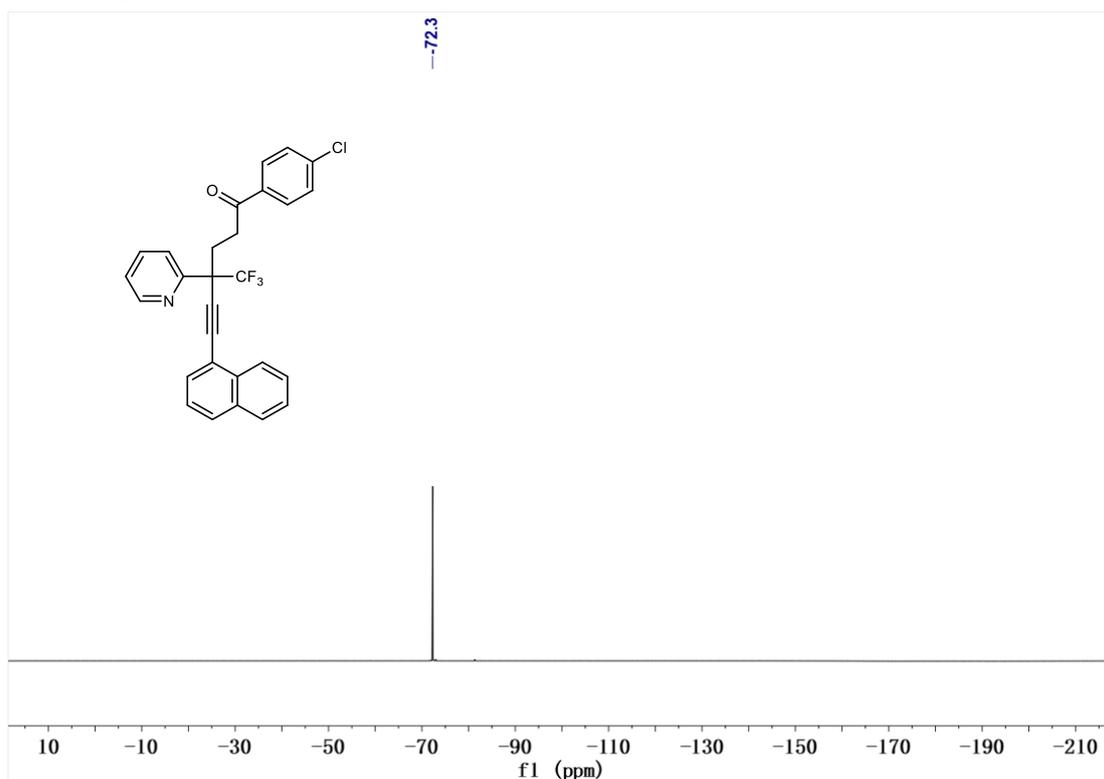
^1H NMR spectra of compound **1e** in CDCl_3 (400 MHz):



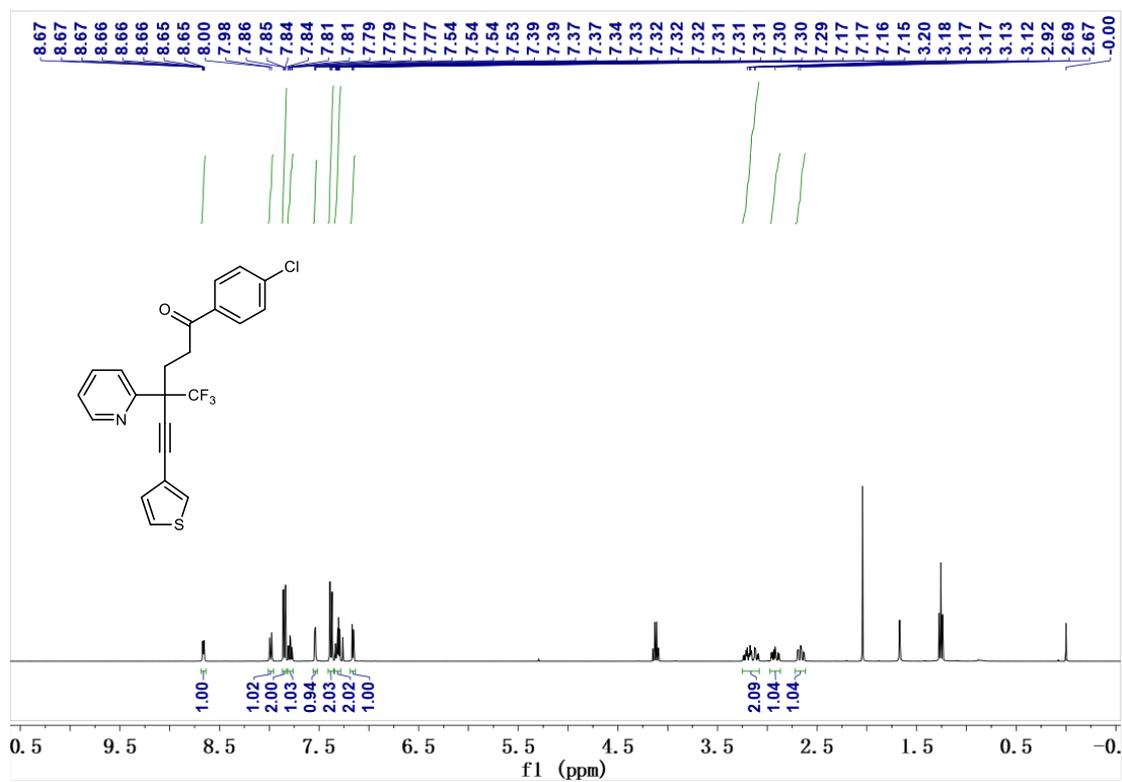
^{13}C NMR spectra of compound **1e** in CDCl_3 (101 MHz):



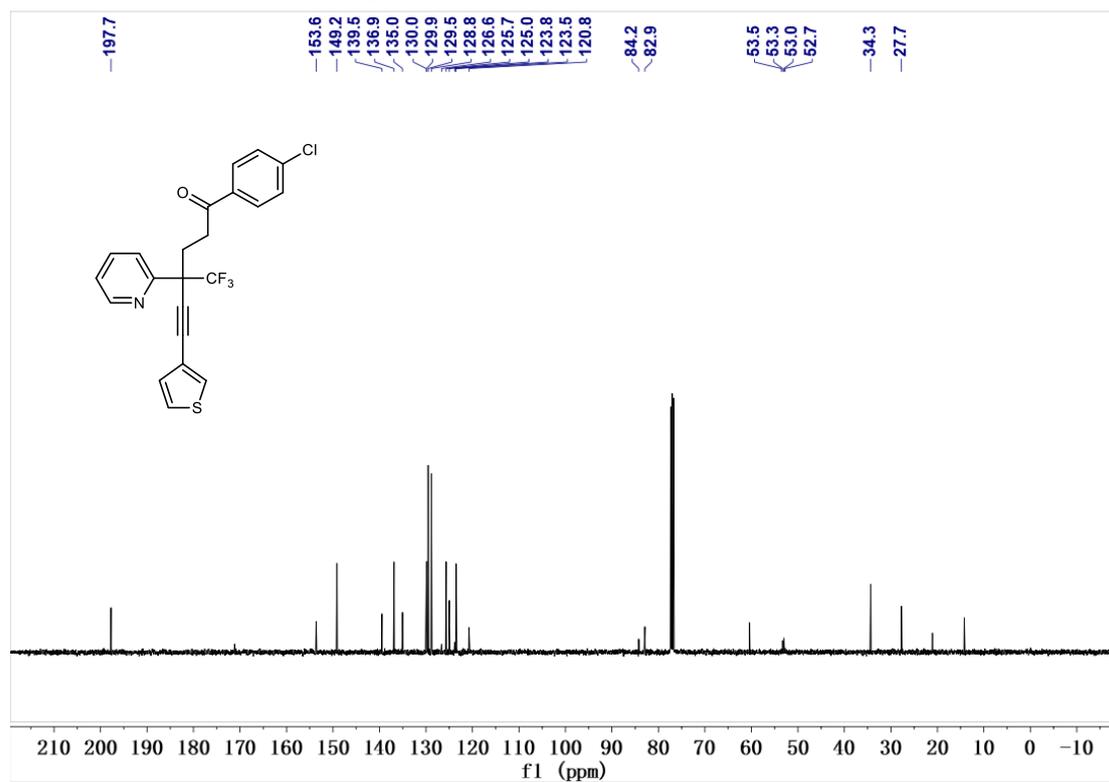
^{19}F NMR spectra of compound **1e** in CDCl_3 (376 MHz):



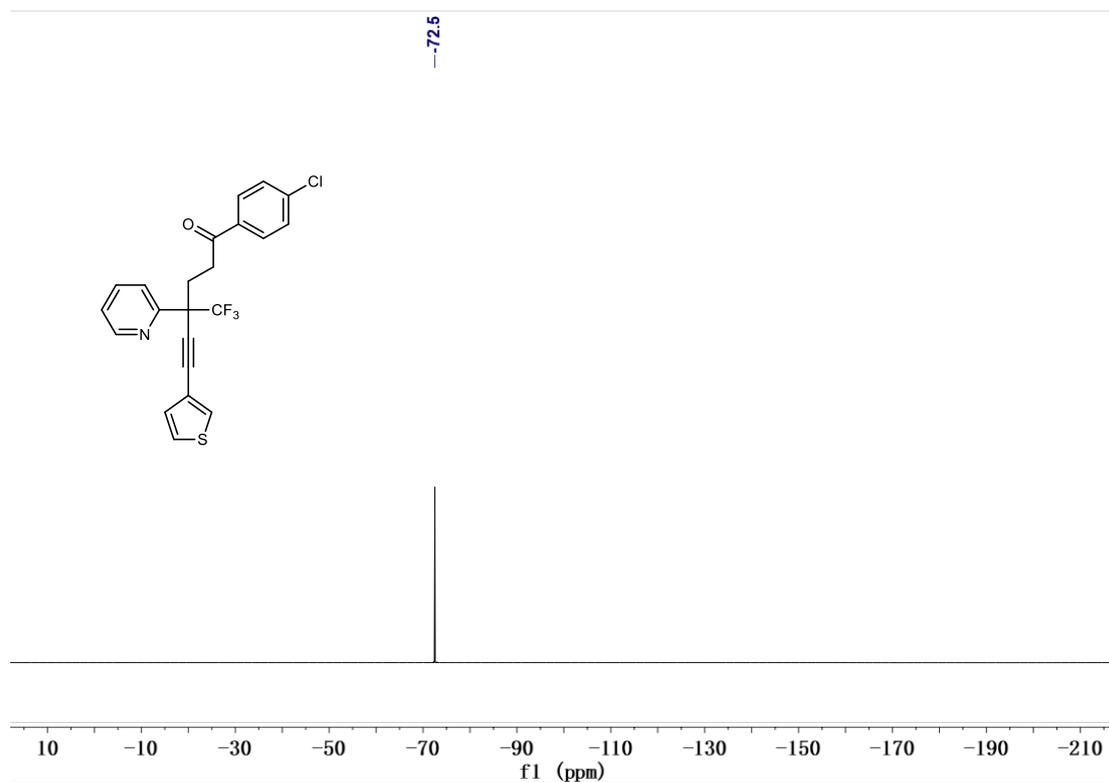
^1H NMR spectra of compound **1g** in CDCl_3 (400 MHz):



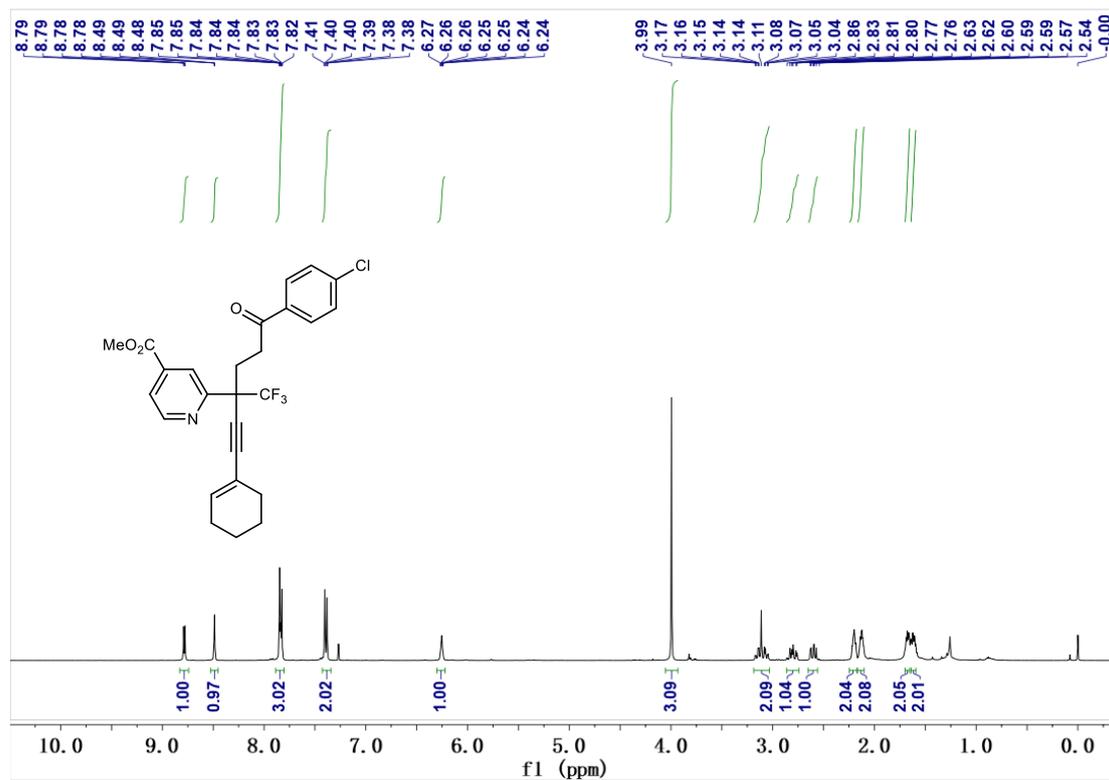
^{13}C NMR spectra of compound **1g** in CDCl_3 (101 MHz):



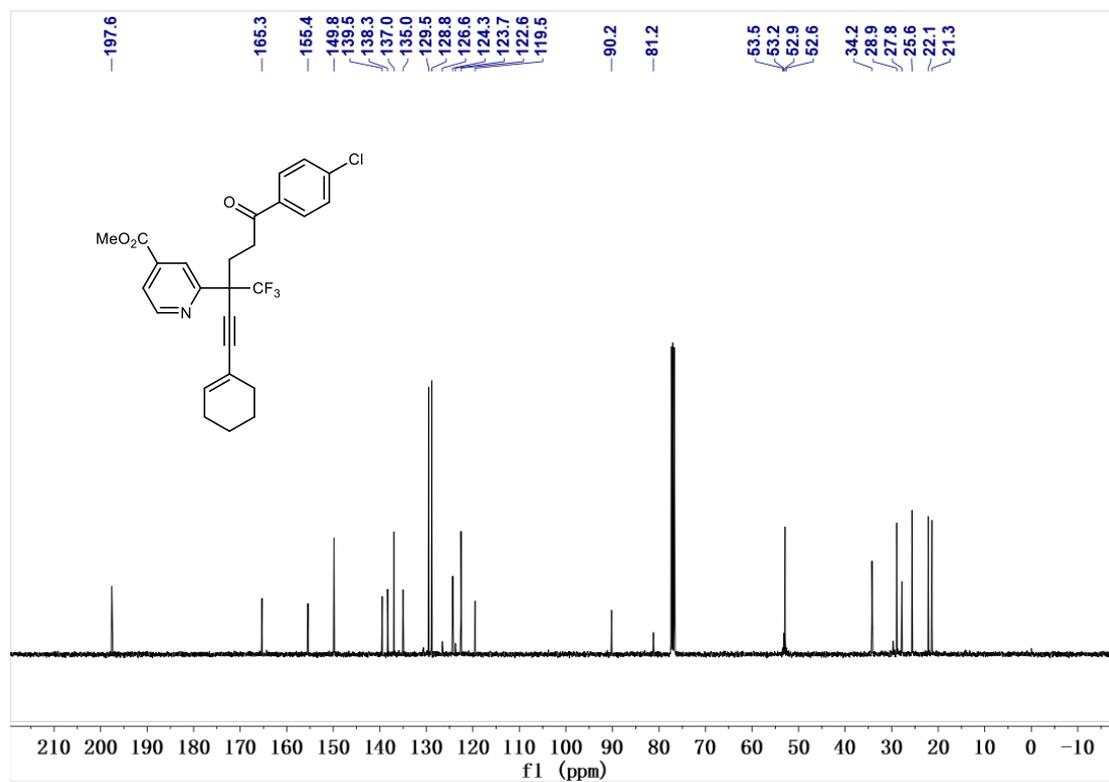
^{19}F NMR spectra of compound **1g** in CDCl_3 (376 MHz):



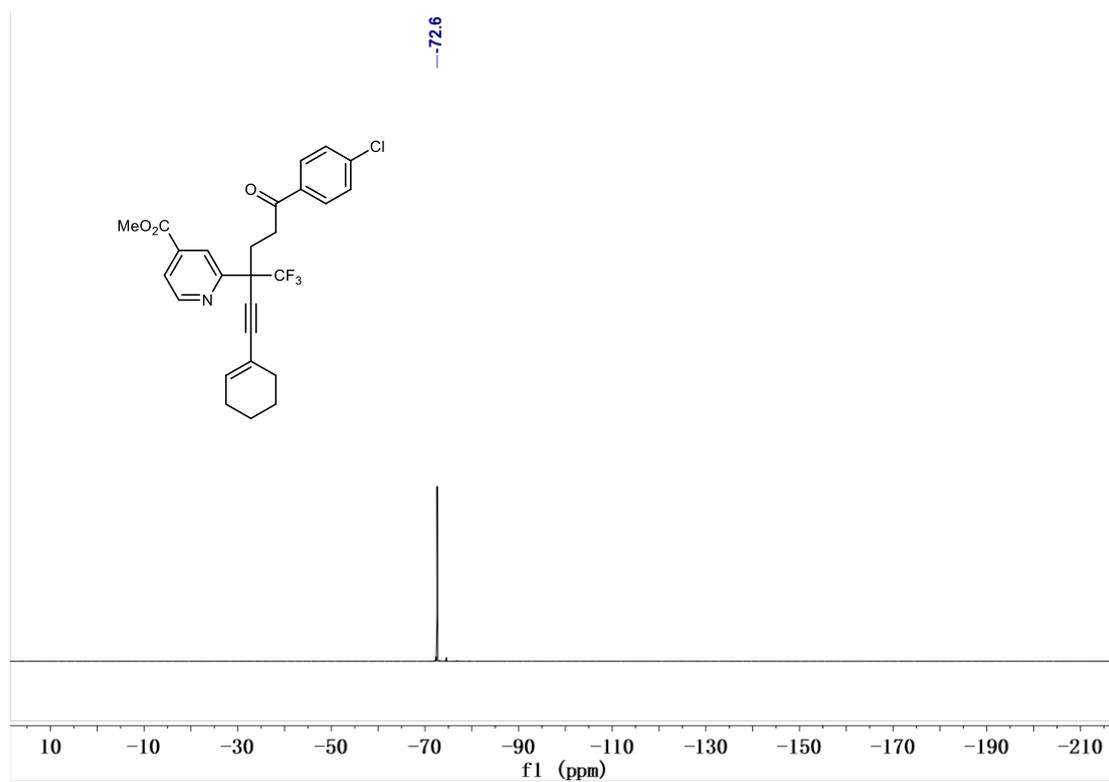
¹H NMR spectra of compound **1j** in CDCl₃ (400 MHz):



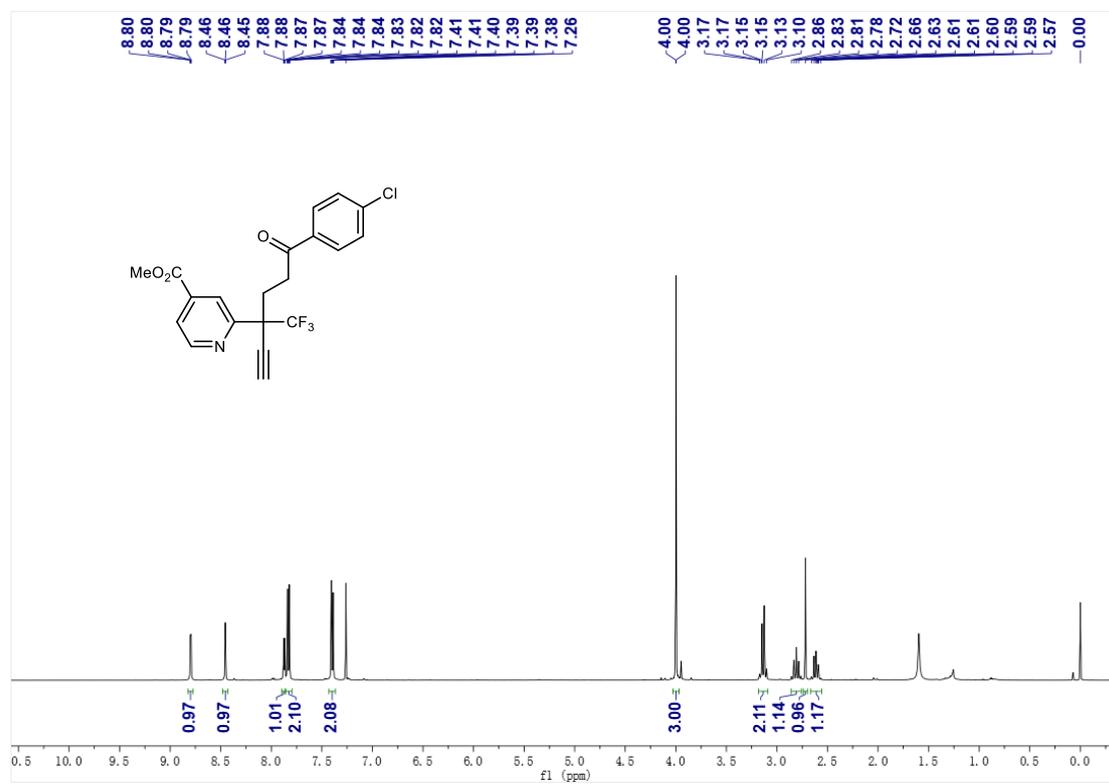
¹³C NMR spectra of compound **1j** in CDCl₃ (101 MHz):



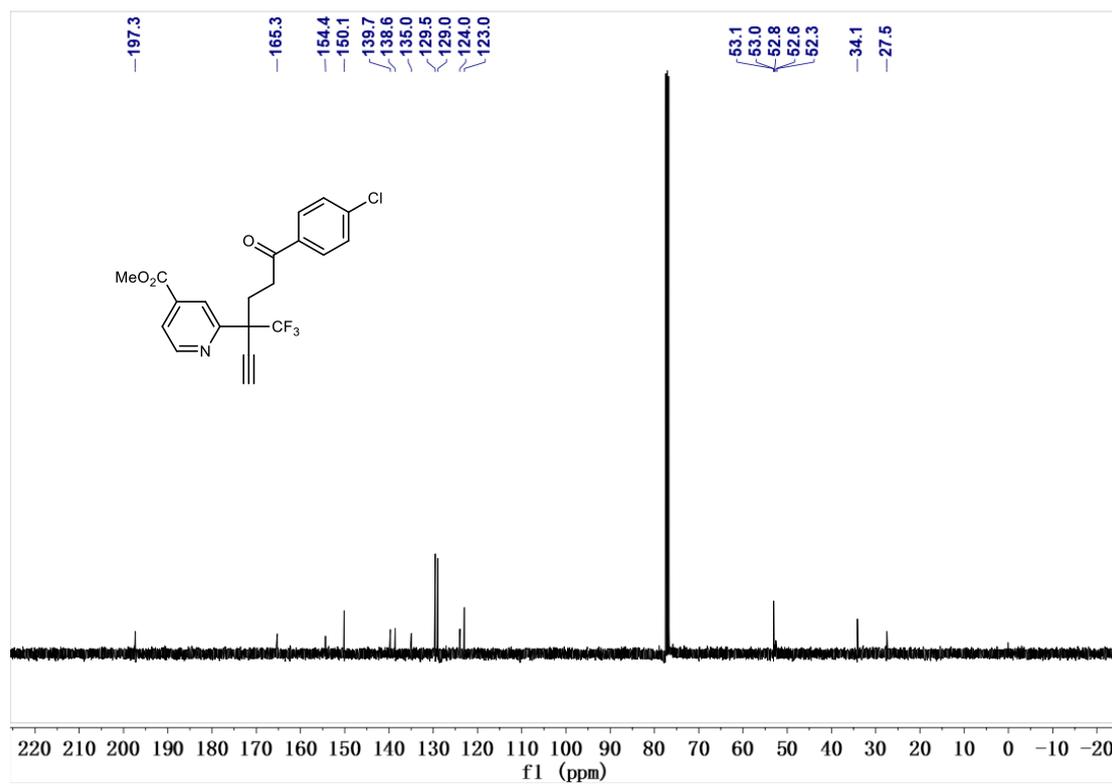
^{19}F NMR spectra of compound **1j** in CDCl_3 (376 MHz):



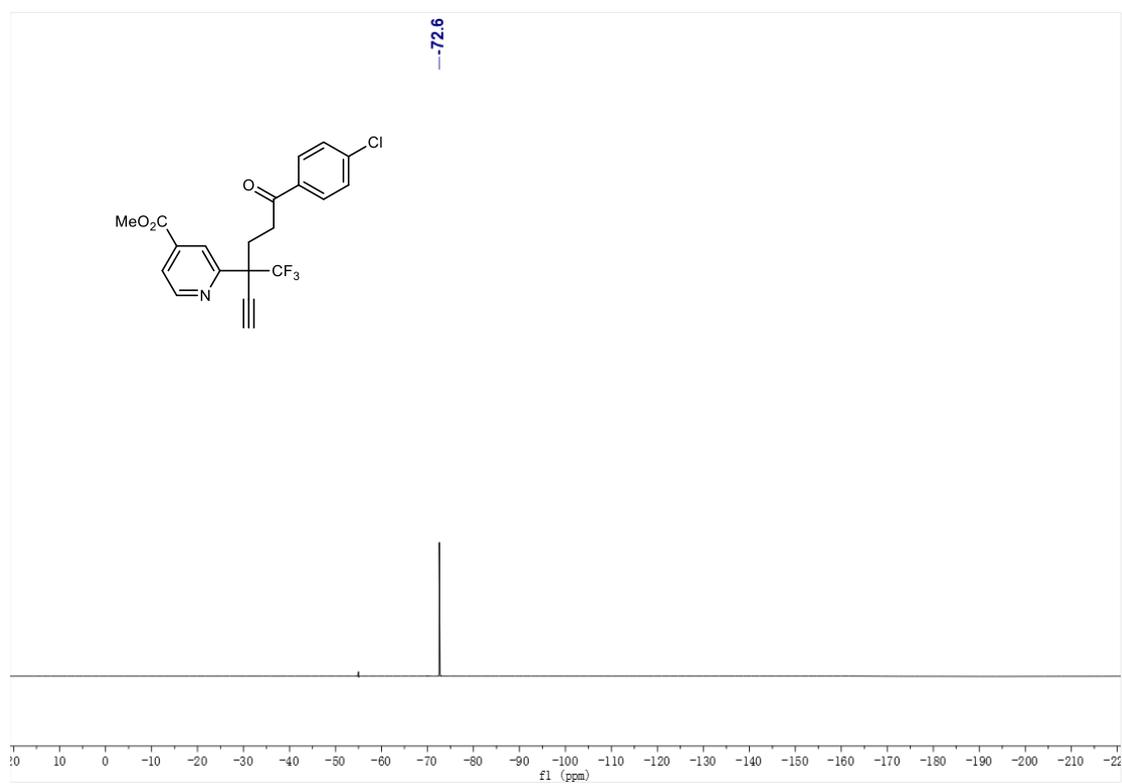
^1H NMR spectra of compound **1k** in CDCl_3 (400 MHz):



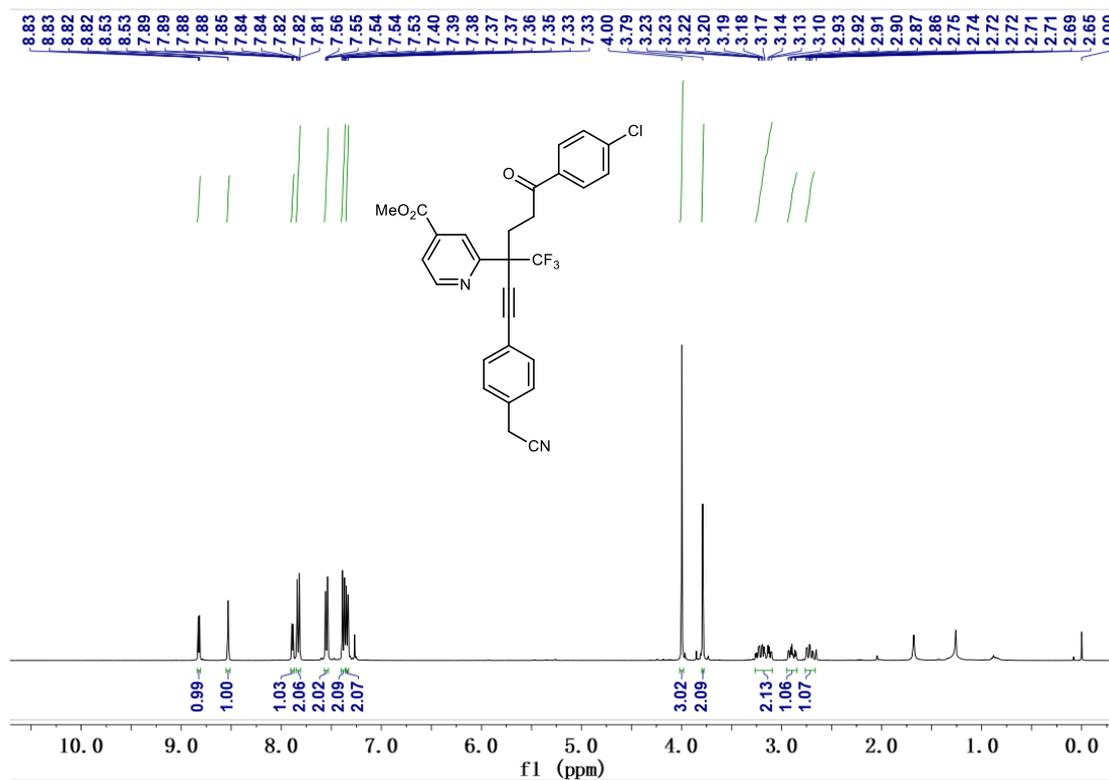
¹³C NMR spectra of compound **1k** in CDCl₃ (101 MHz):



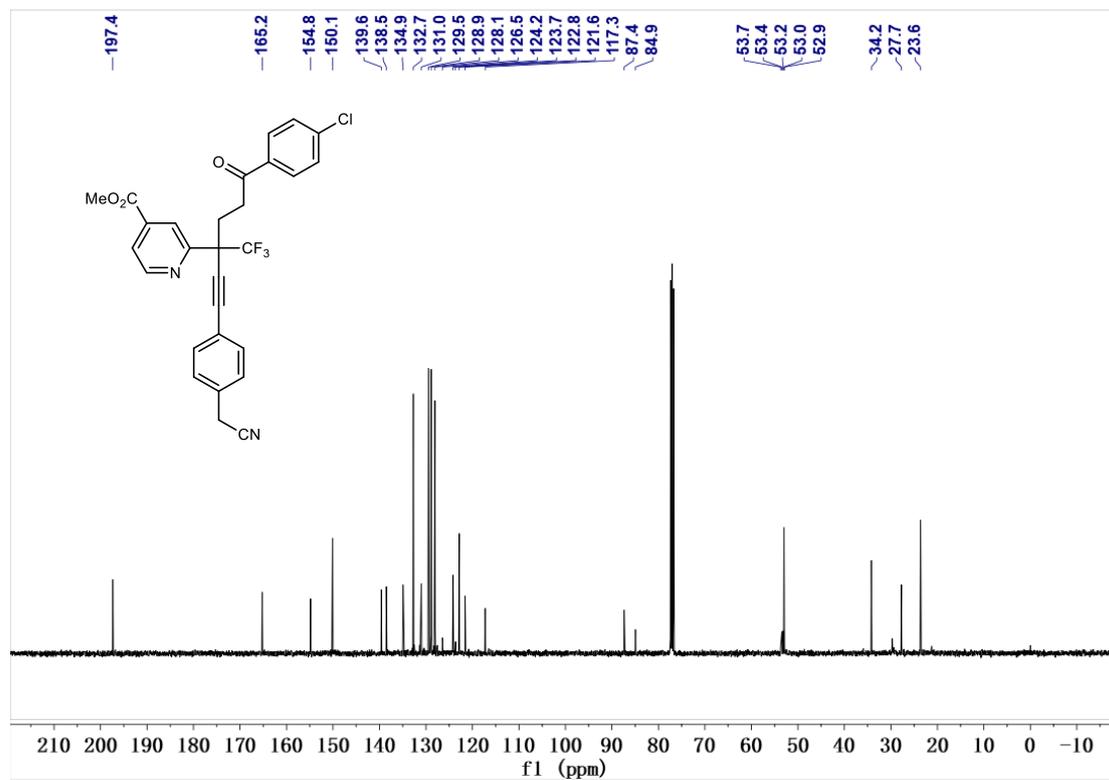
¹⁹F NMR spectra of compound **1k** in CDCl₃ (471 MHz):



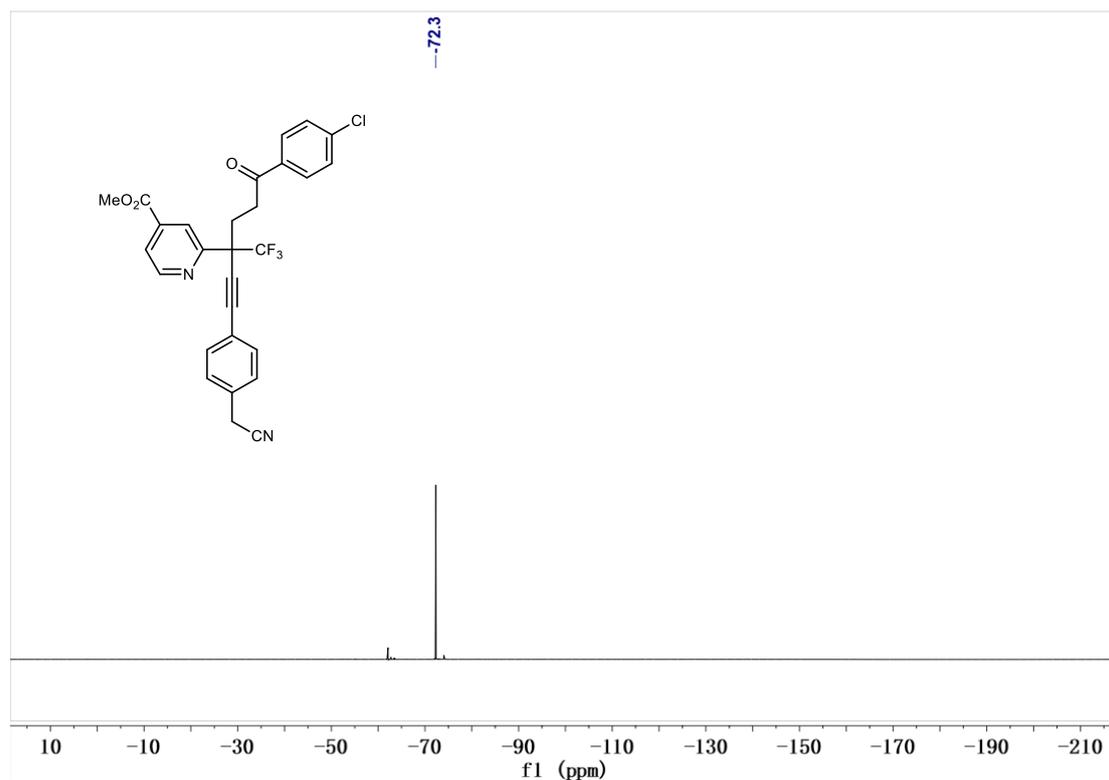
¹H NMR spectra of compound **11** in CDCl₃ (400 MHz):



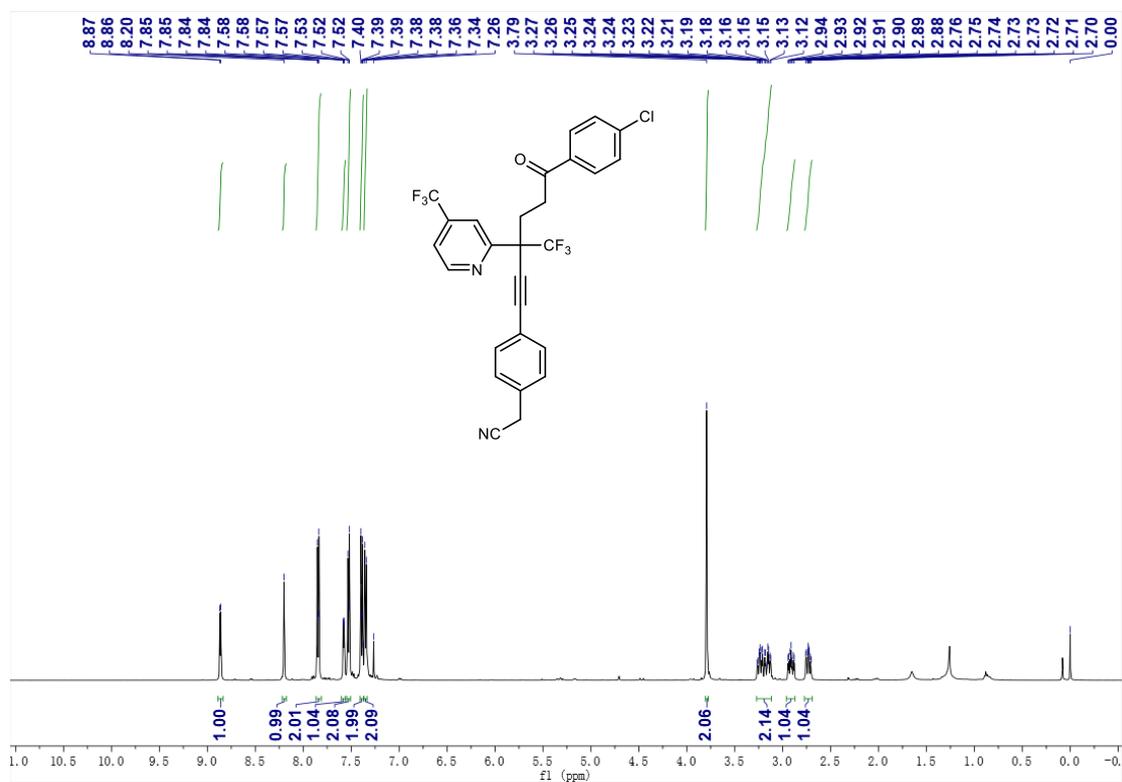
¹³C NMR spectra of compound **11** in CDCl₃ (101 MHz):



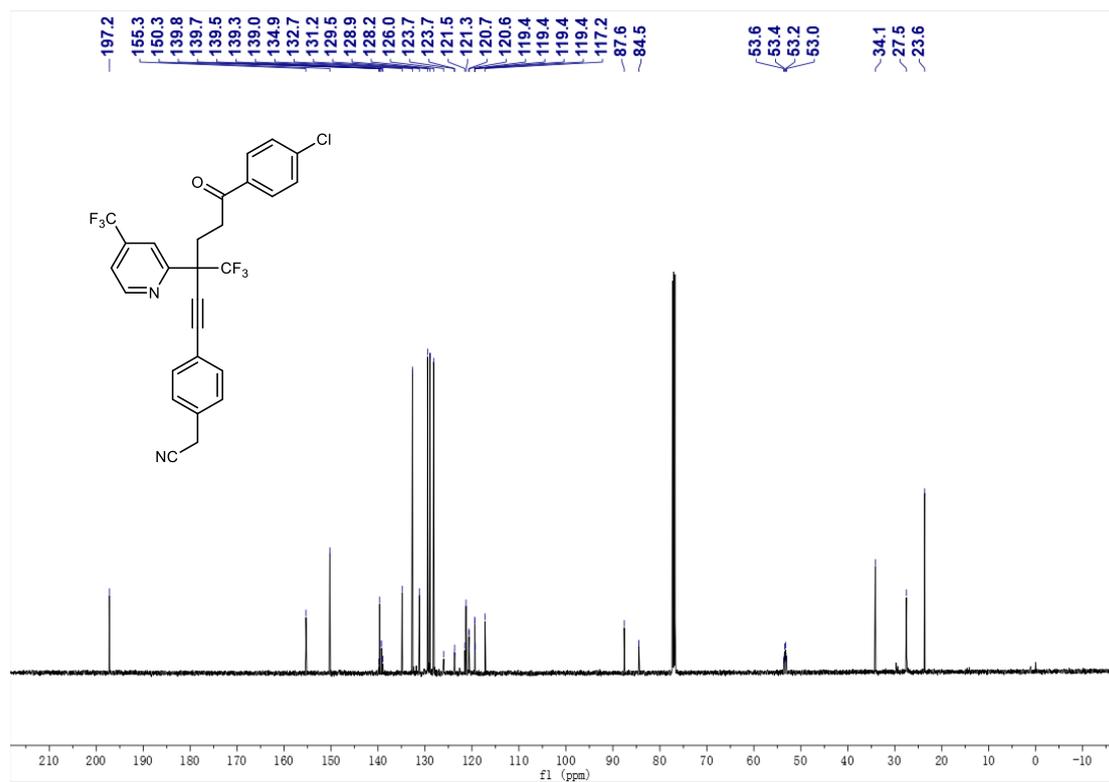
^{19}F NMR spectra of compound **1l** in CDCl_3 (376 MHz):



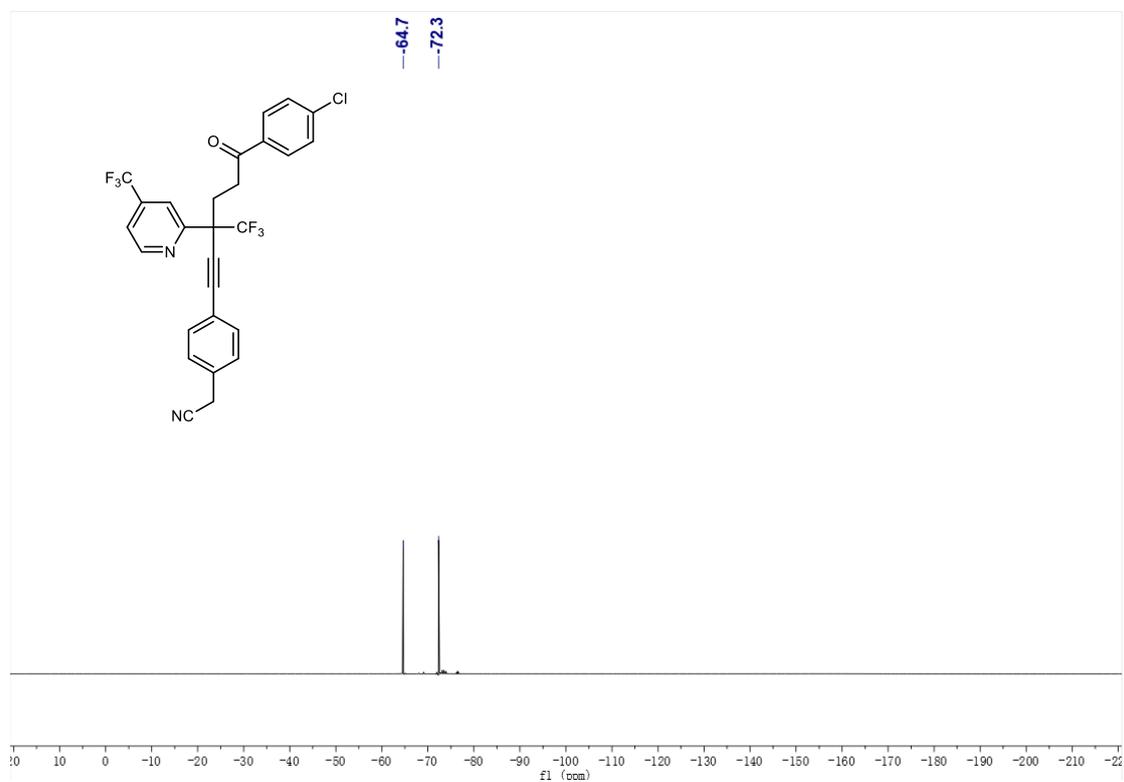
^1H NMR spectra of compound **1m** in CDCl_3 (500 MHz):



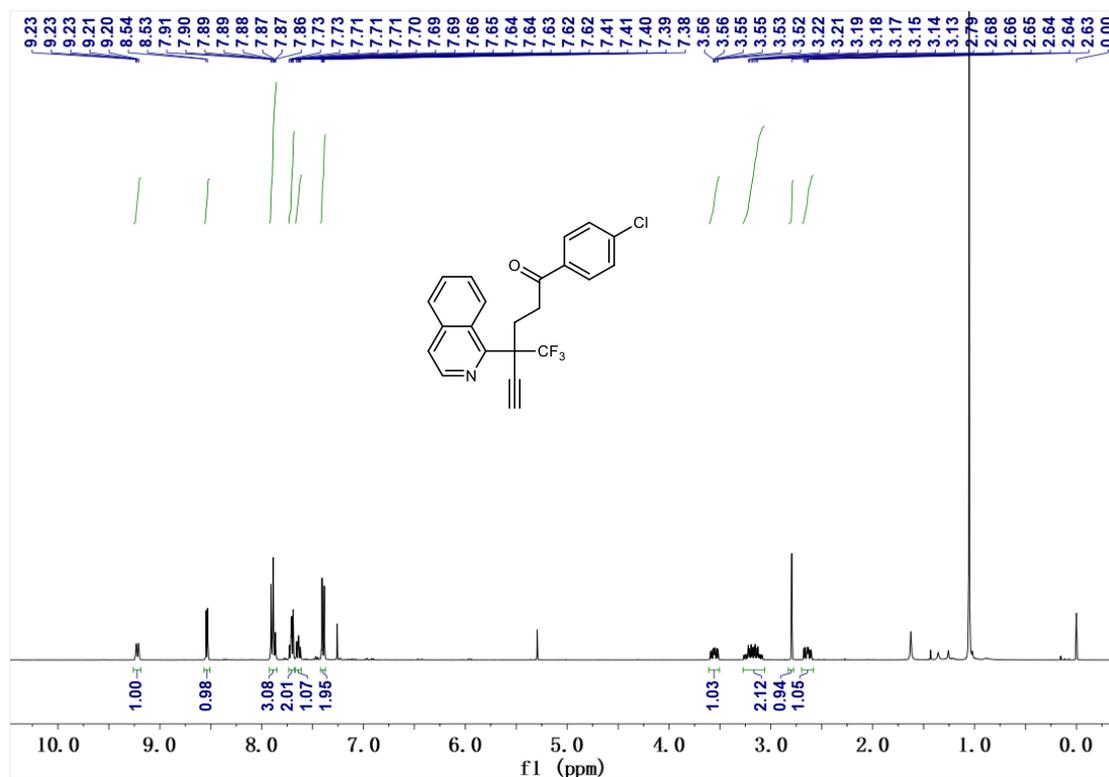
^{13}C NMR spectra of compound **1m** in CDCl_3 (126 MHz):



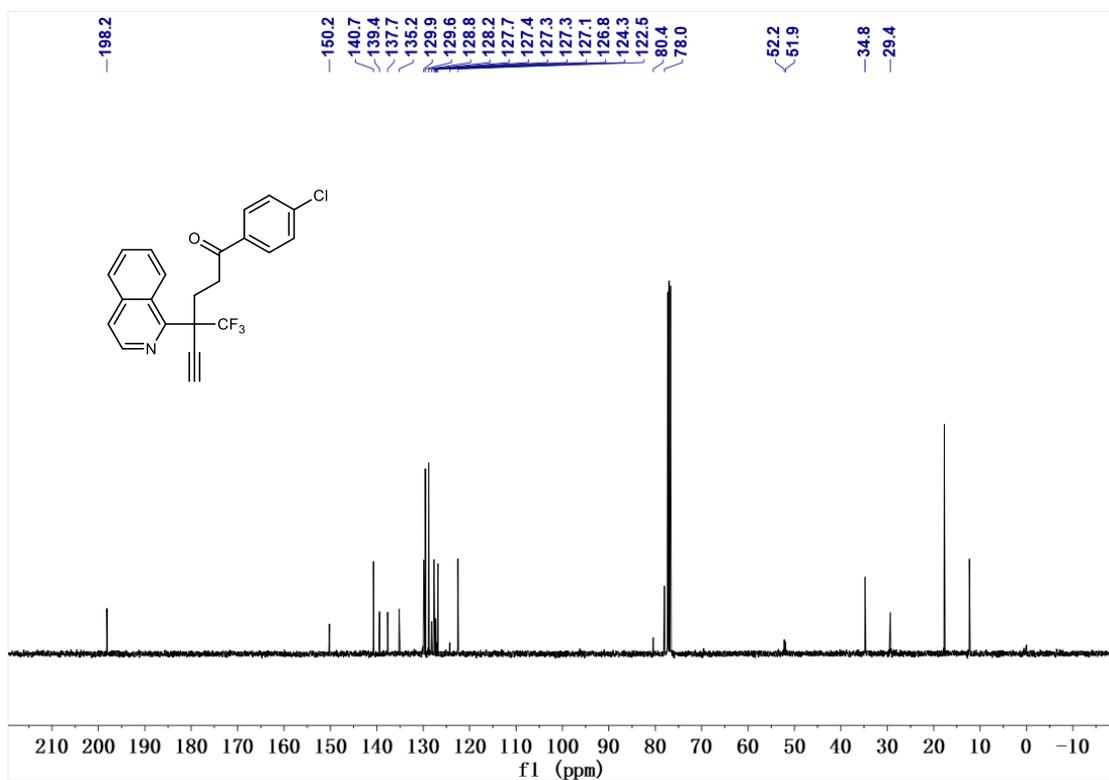
^{19}F NMR spectra of compound **1m** in CDCl_3 (471 MHz):



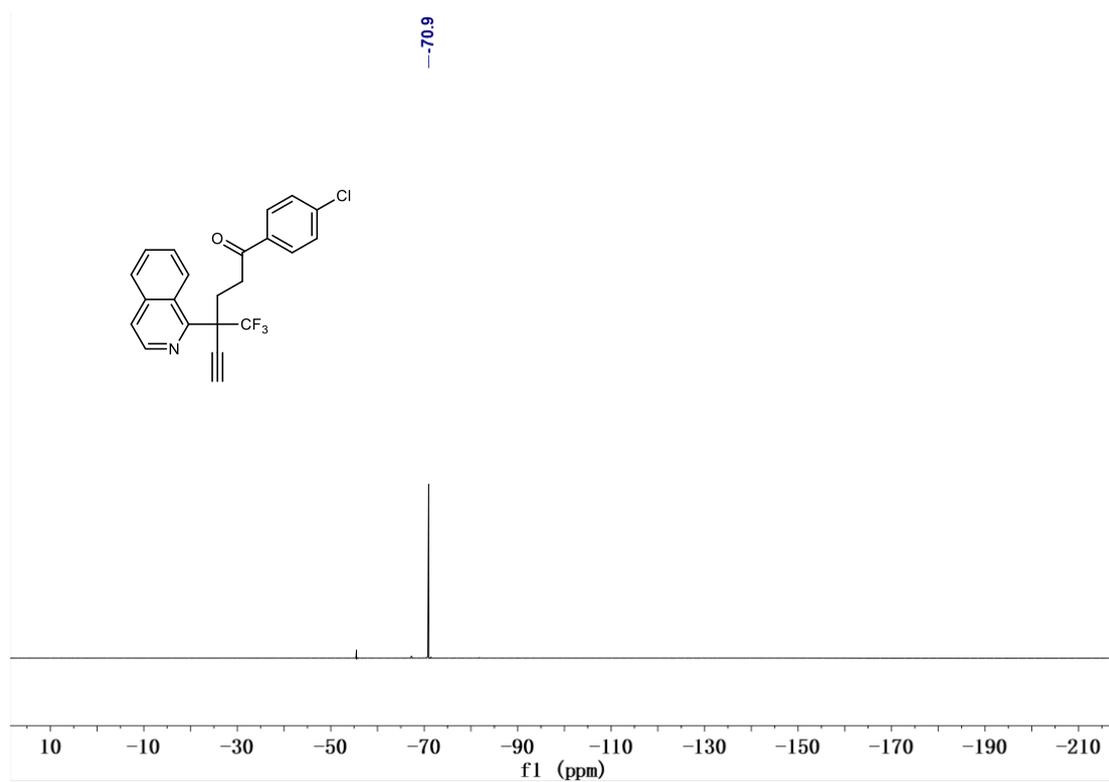
¹H NMR spectra of compound **1n** in CDCl₃ (400 MHz):



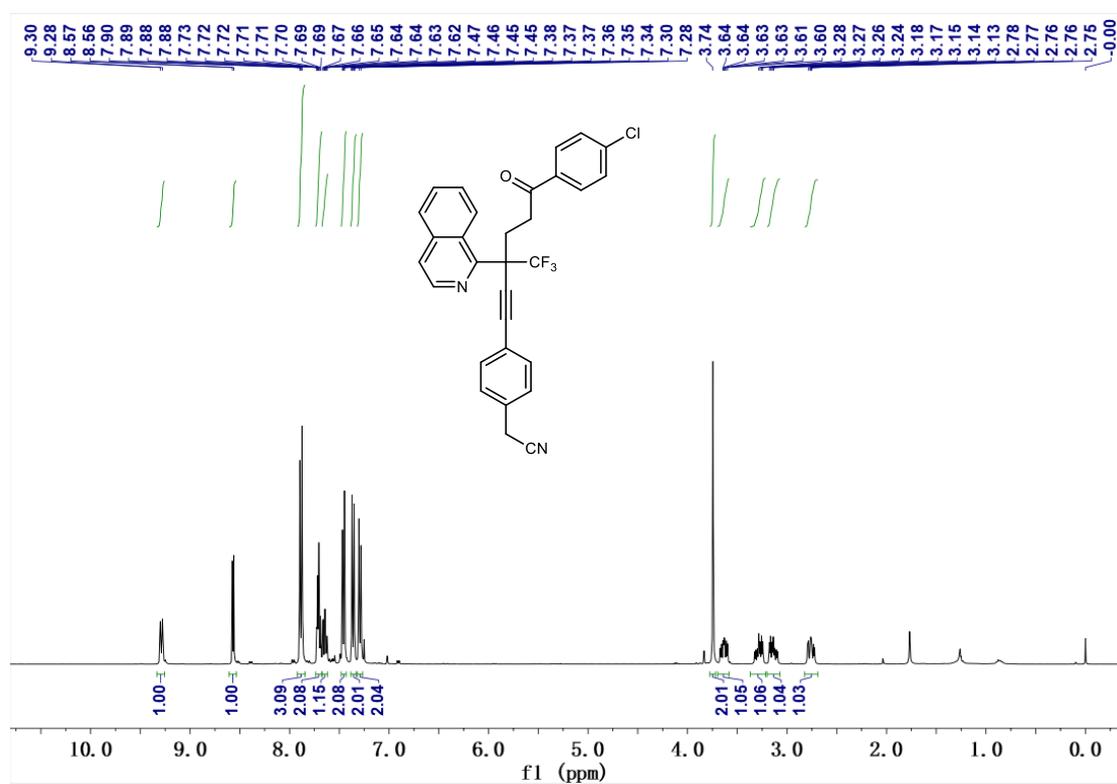
¹³C NMR spectra of compound **1n** in CDCl₃ (101 MHz):



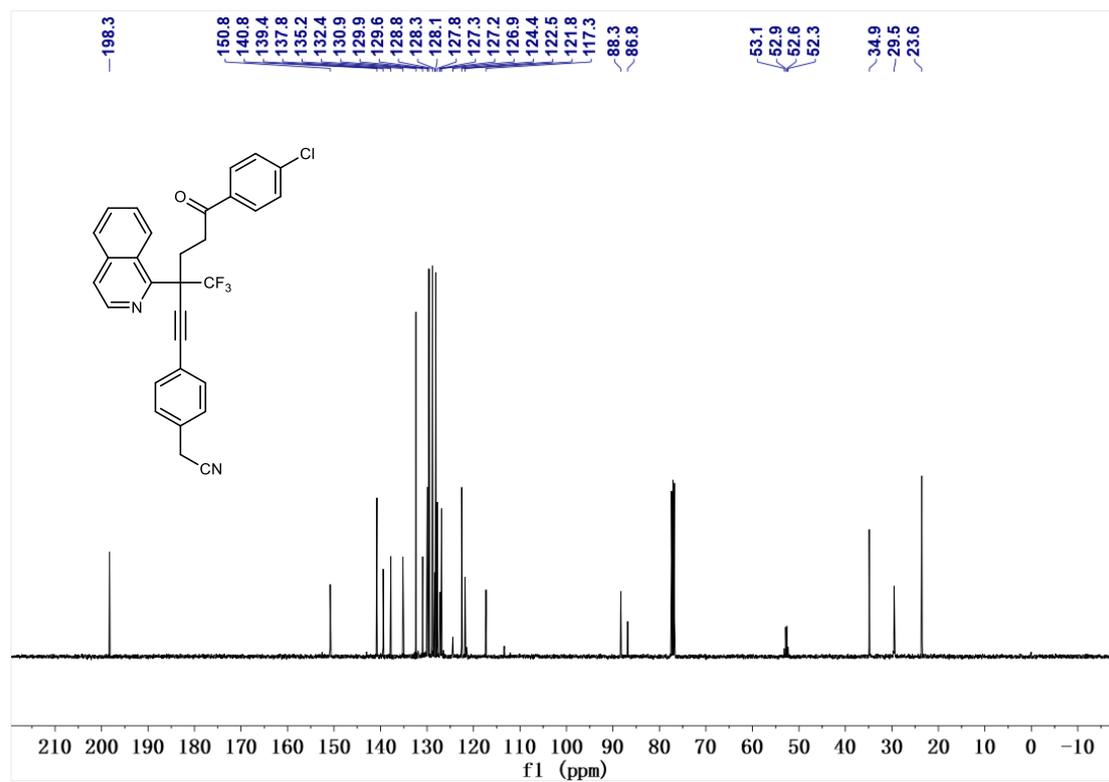
^{19}F NMR spectra of compound **1n** in CDCl_3 (376 MHz):



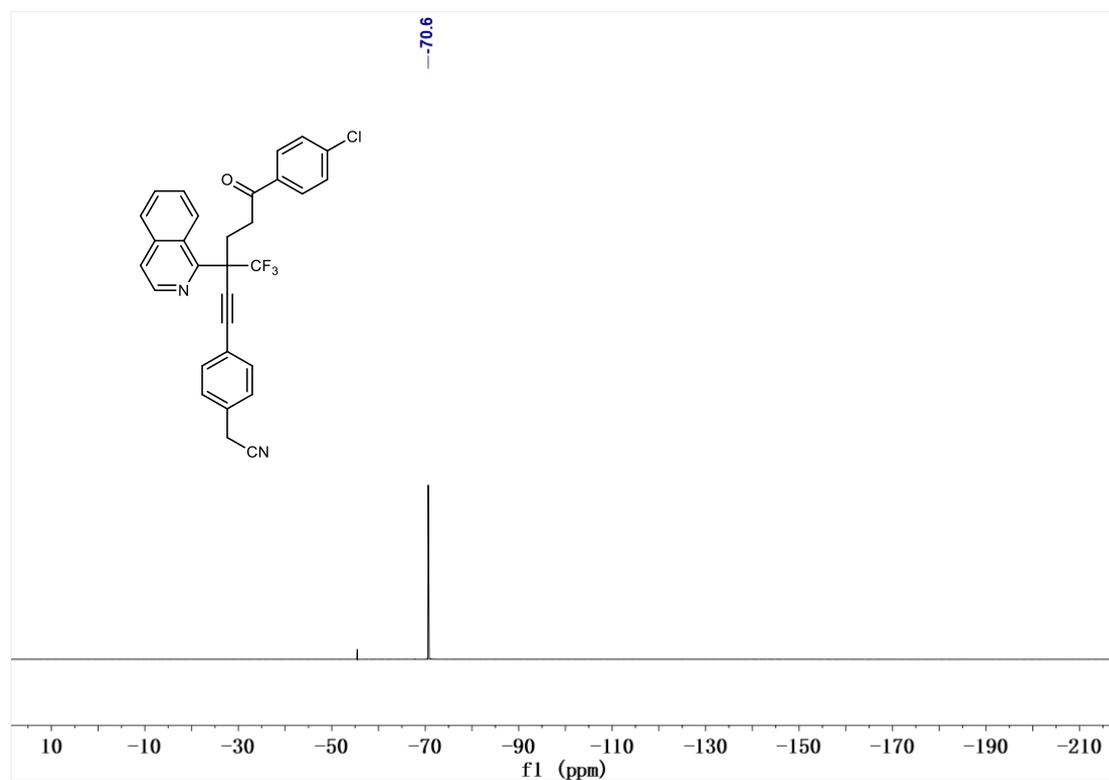
^1H NMR spectra of compound **1o** in CDCl_3 (400 MHz):



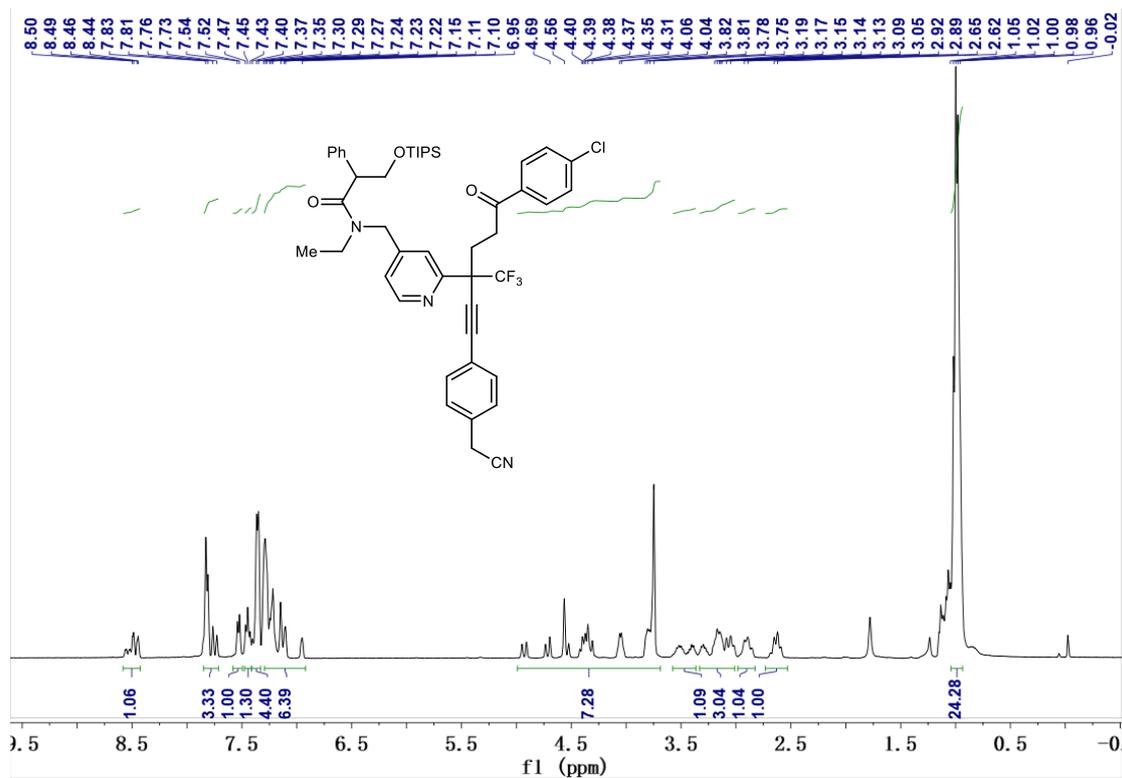
^{13}C NMR spectra of compound **1o** in CDCl_3 (101 MHz):



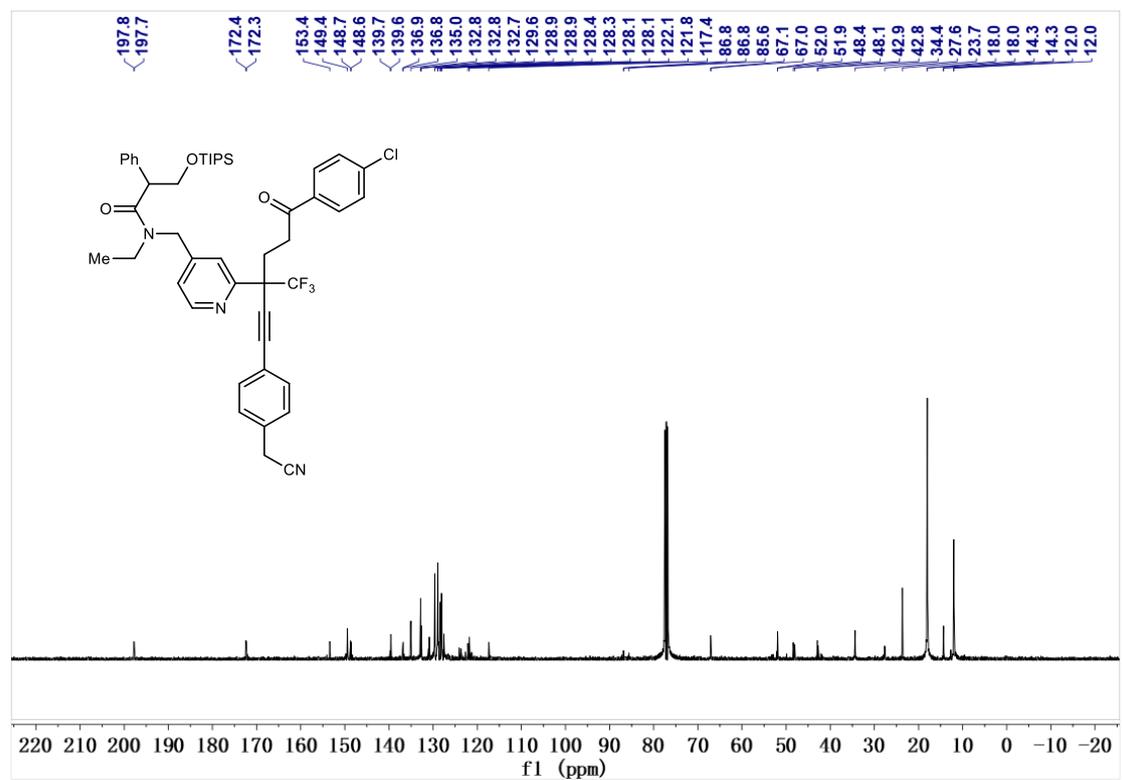
^{19}F NMR spectra of compound **1o** in CDCl_3 (471 MHz):



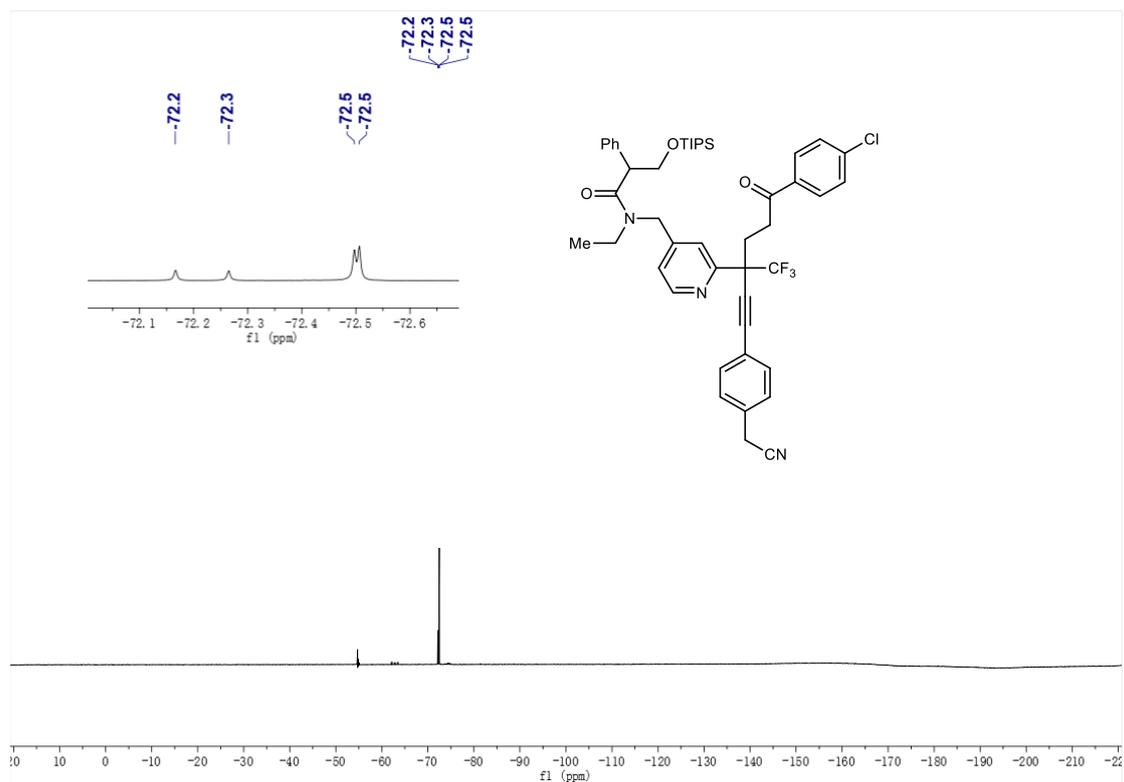
^1H NMR spectra of compound **1r** in CDCl_3 (400 MHz):



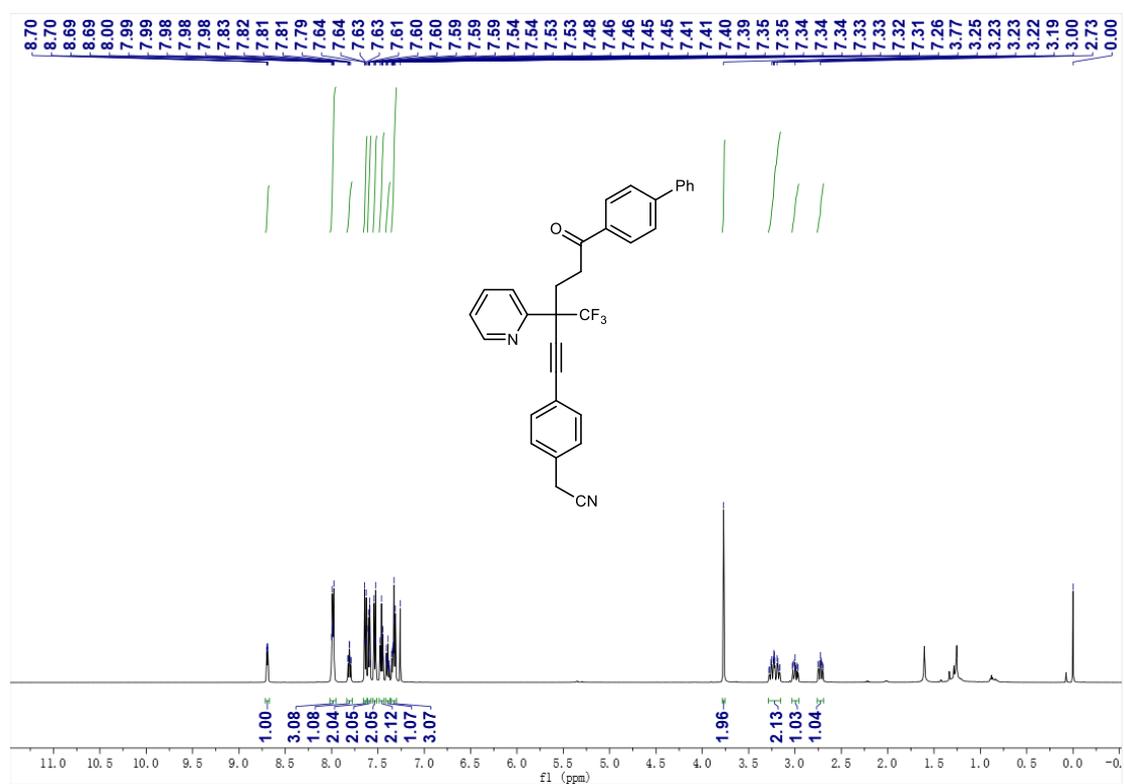
^{13}C NMR spectra of compound **1r** in CDCl_3 (101 MHz):



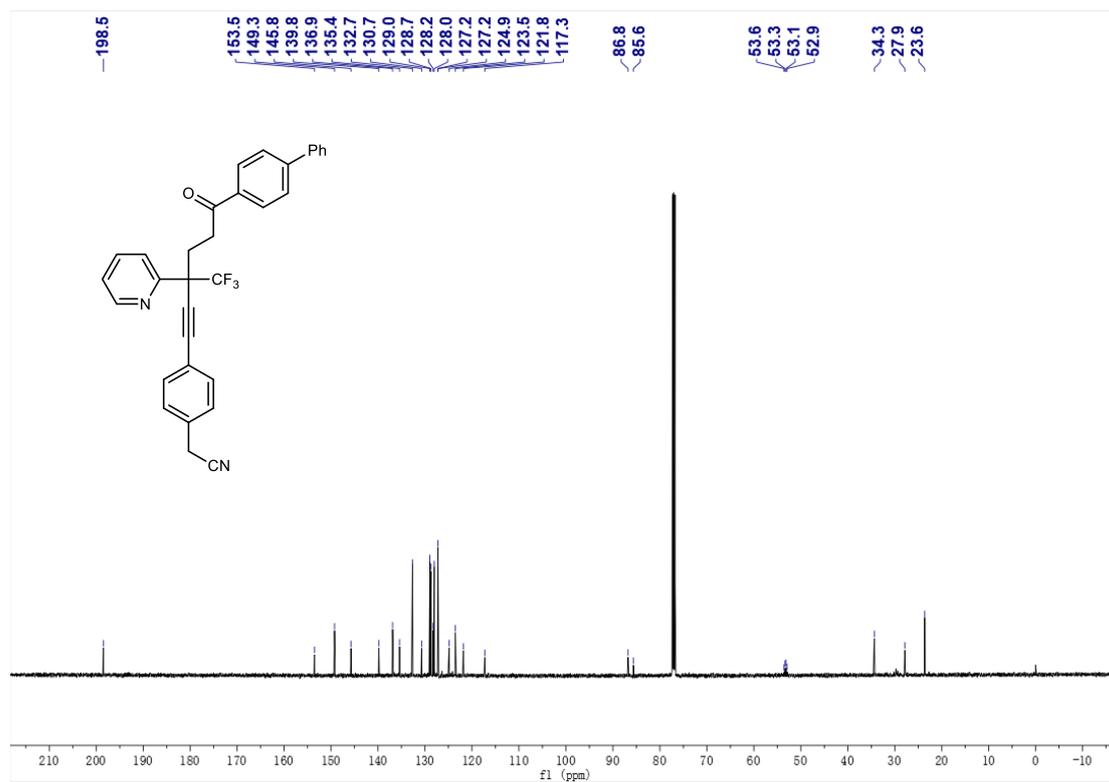
^{19}F NMR spectra of compound **1r** in CDCl_3 (471 MHz):



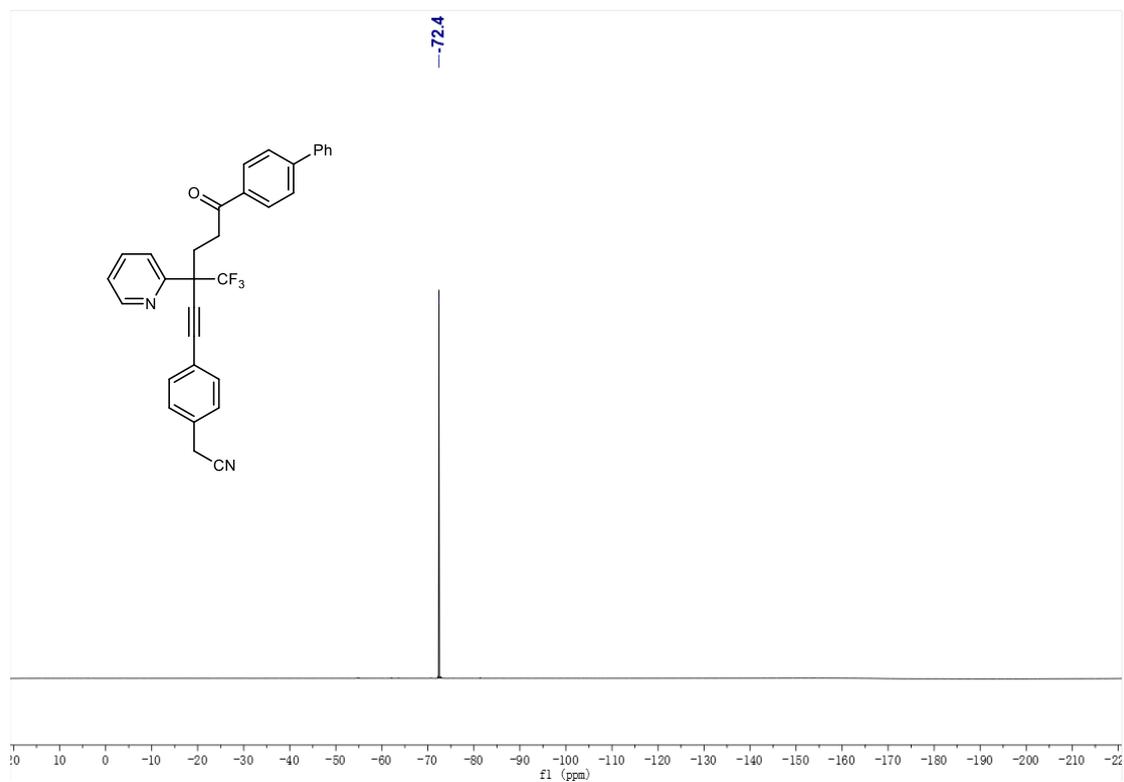
^1H NMR spectra of compound **1s** in CDCl_3 (500 MHz):



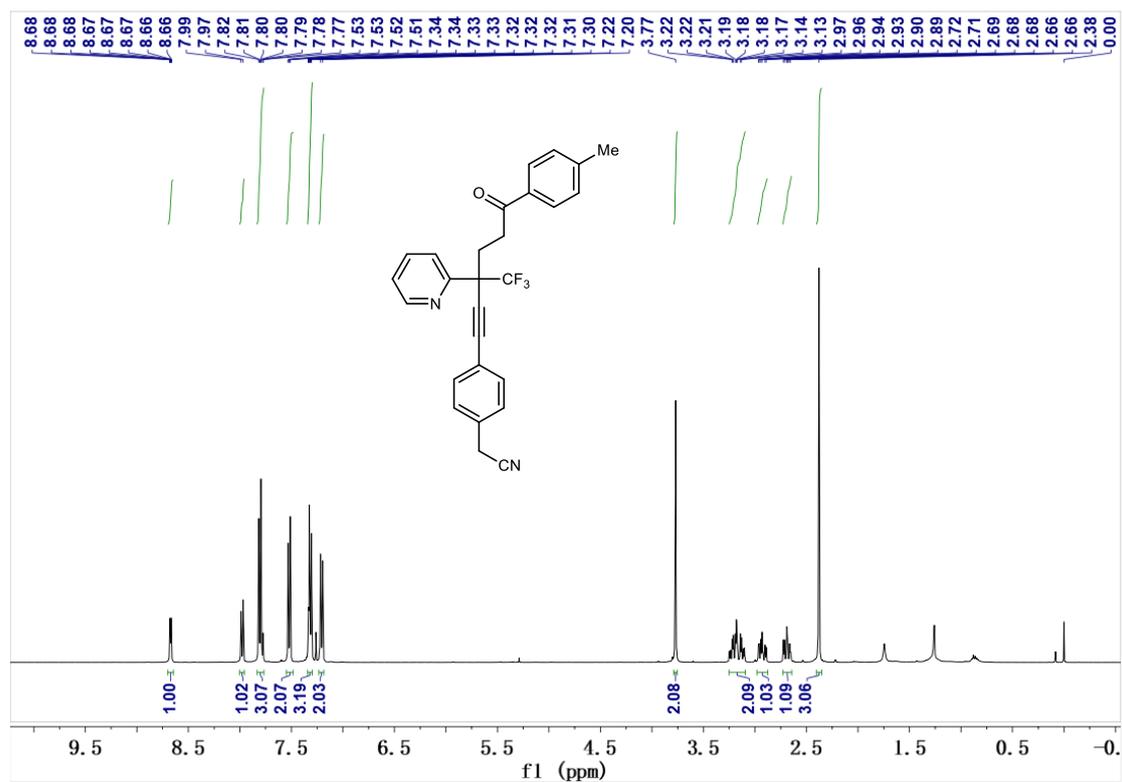
^{13}C NMR spectra of compound **1s** in CDCl_3 (126 MHz):



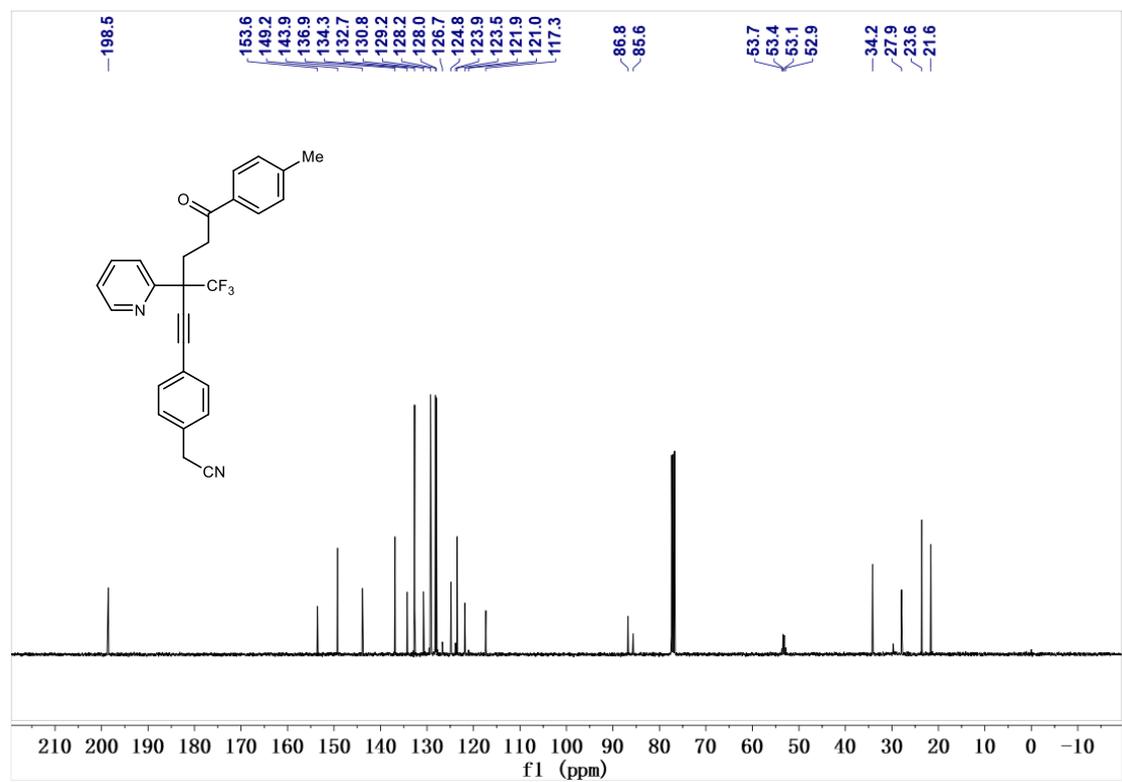
^{19}F NMR spectra of compound **1s** in CDCl_3 (471 MHz):



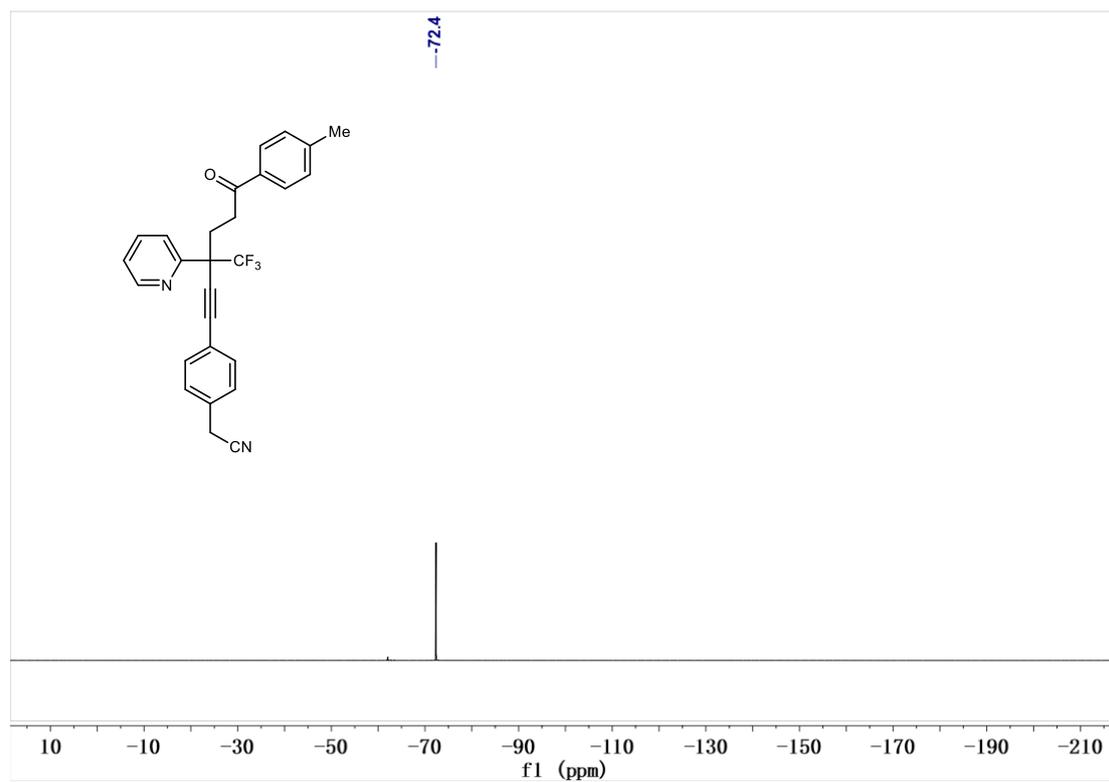
¹H NMR spectra of compound **1t** in CDCl₃ (400 MHz):



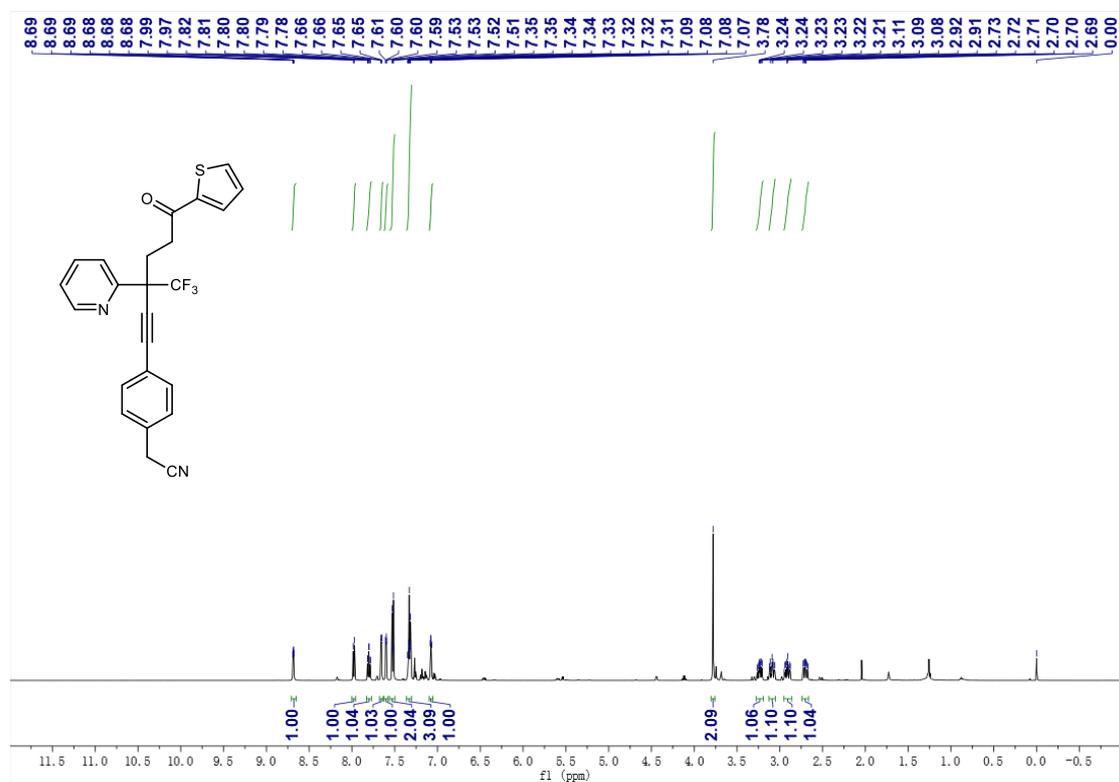
¹³C NMR spectra of compound **1t** in CDCl₃ (101 MHz):



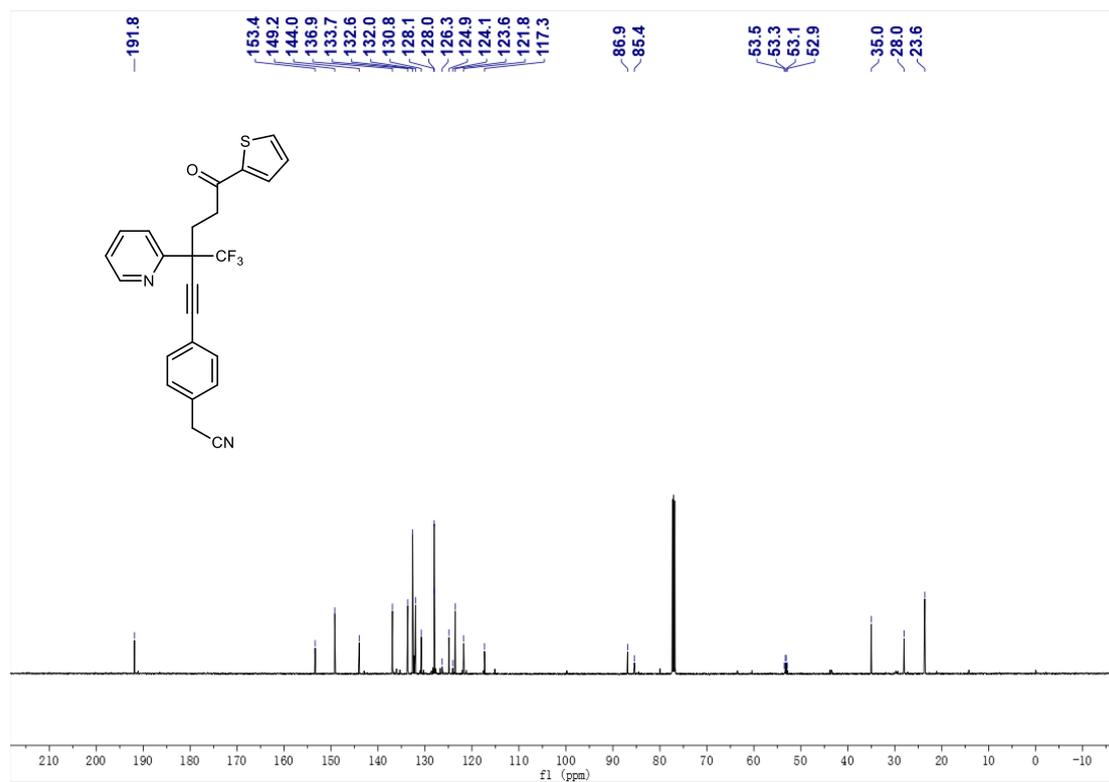
^{19}F NMR spectra of compound **1t** in CDCl_3 (376 MHz):



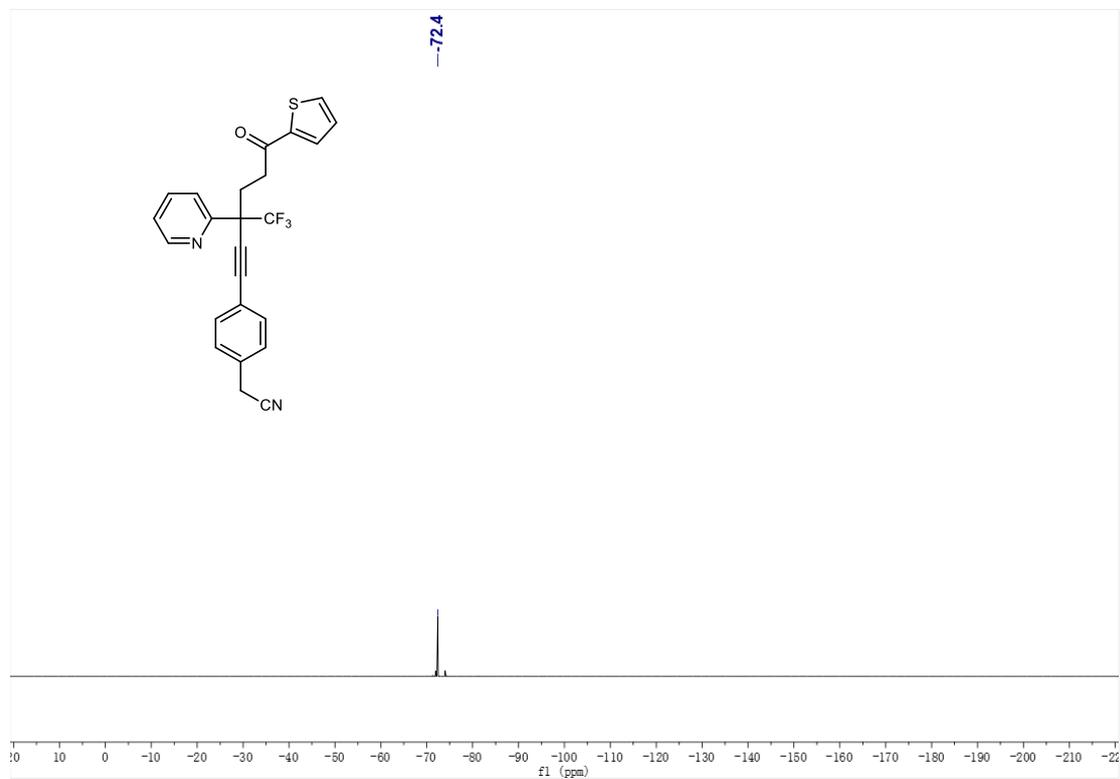
^1H NMR spectra of compound **1u** in CDCl_3 (500 MHz):



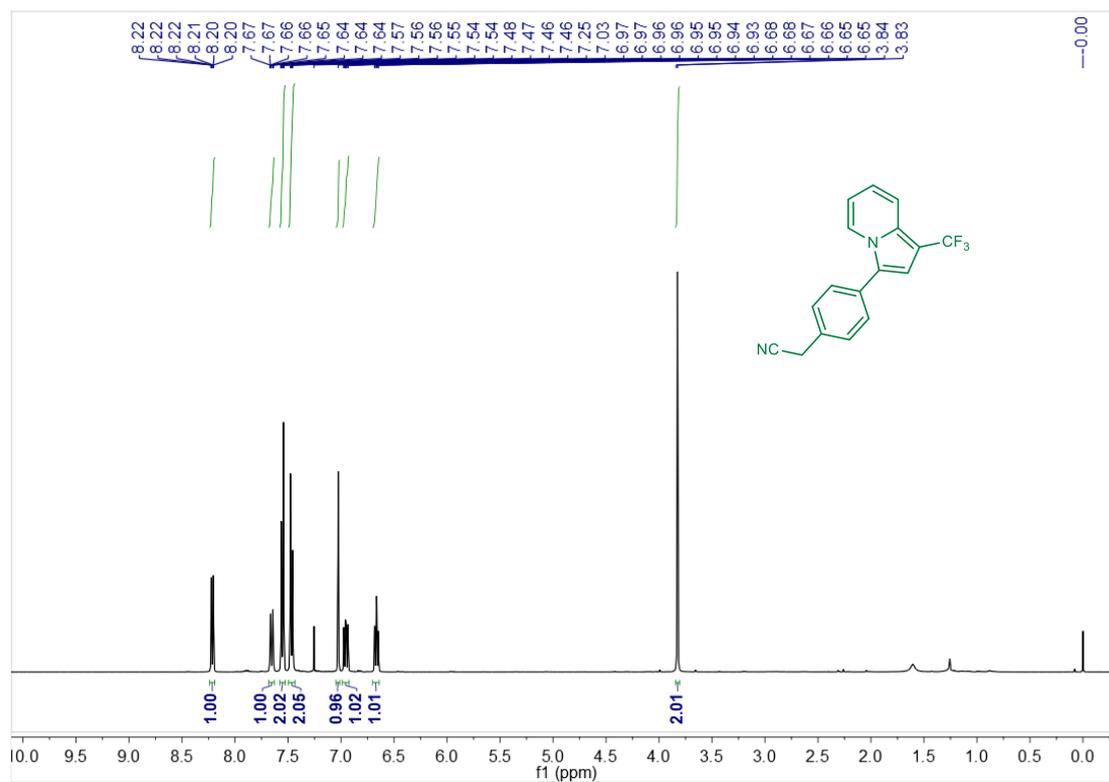
^{13}C NMR spectra of compound **1u** in CDCl_3 (126 MHz):



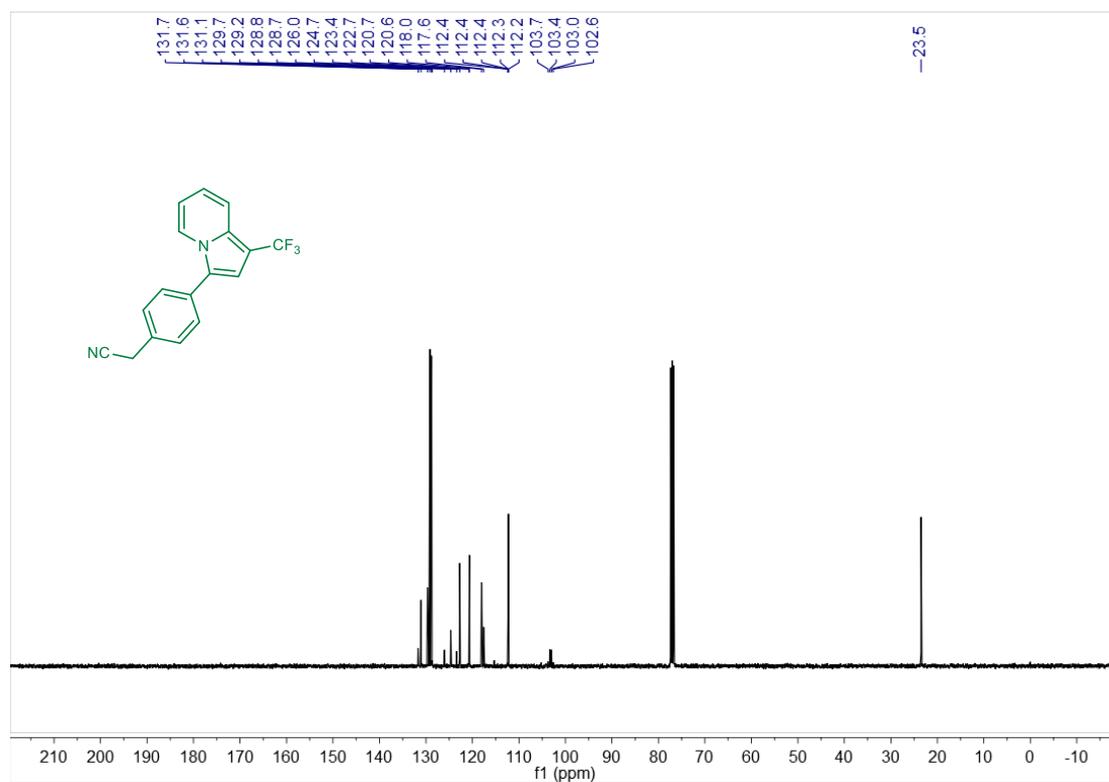
^{19}F NMR spectra of compound **1u** in CDCl_3 (471 MHz):



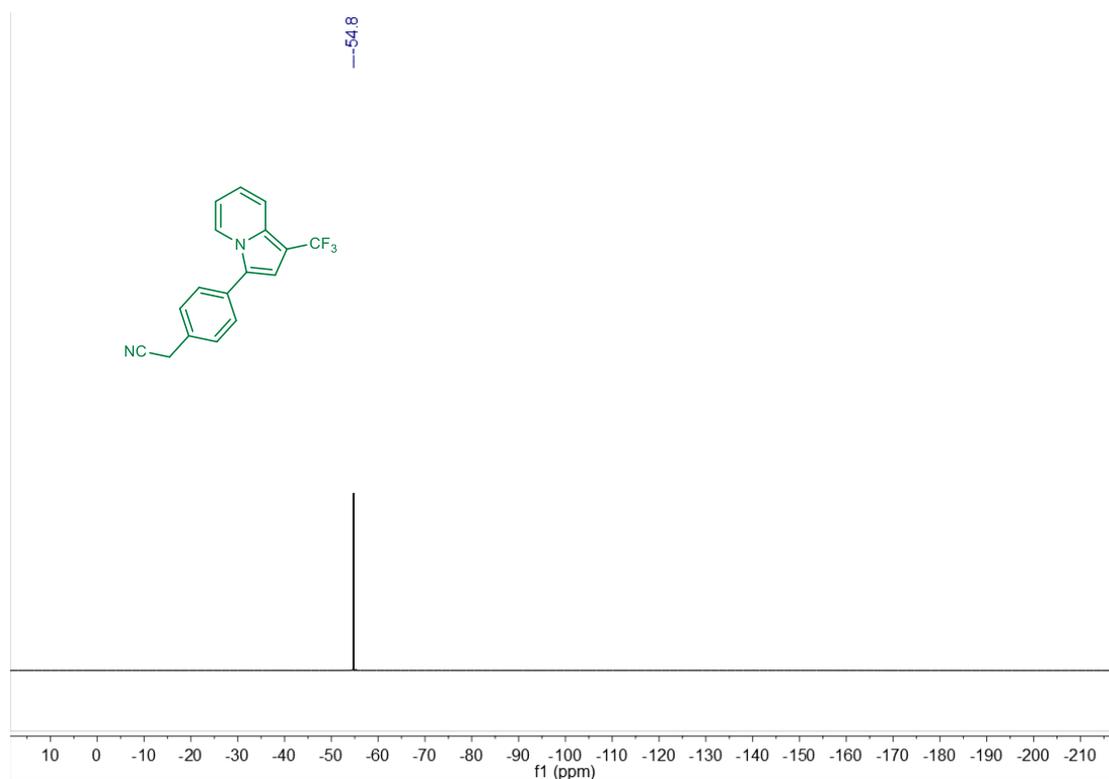
¹H NMR spectra of compound **2a** in CDCl₃ (400 MHz):



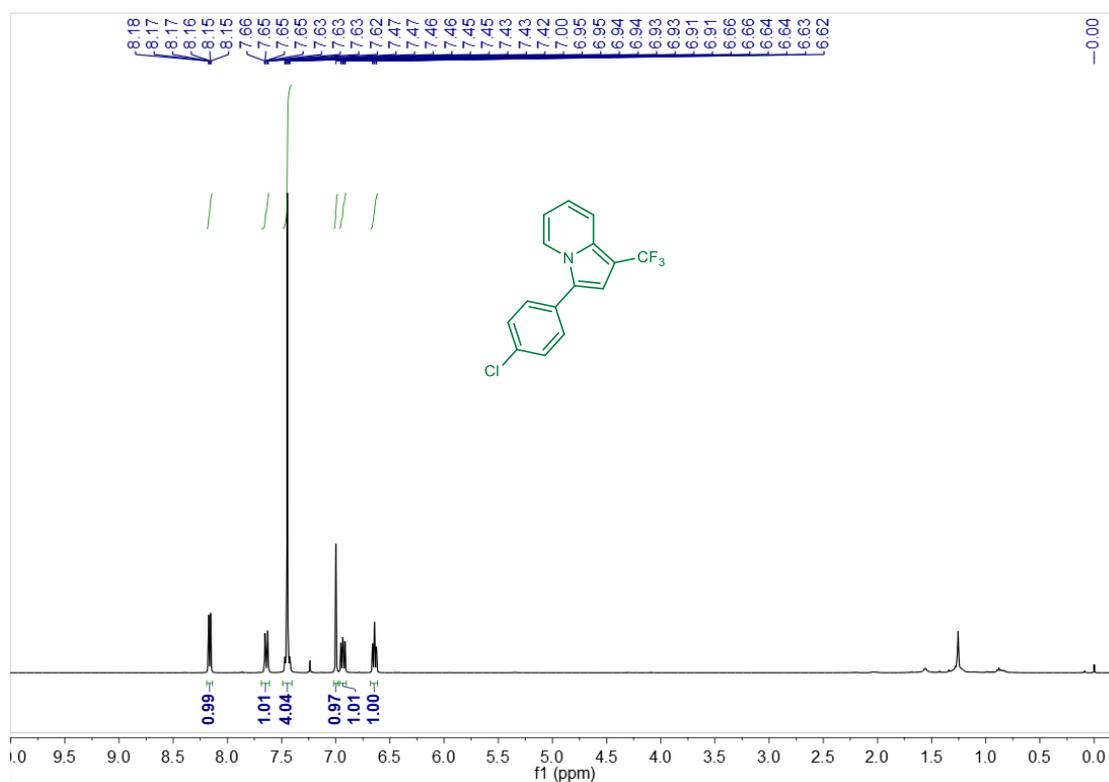
¹³C NMR spectra of compound **2a** in CDCl₃ (101 MHz):



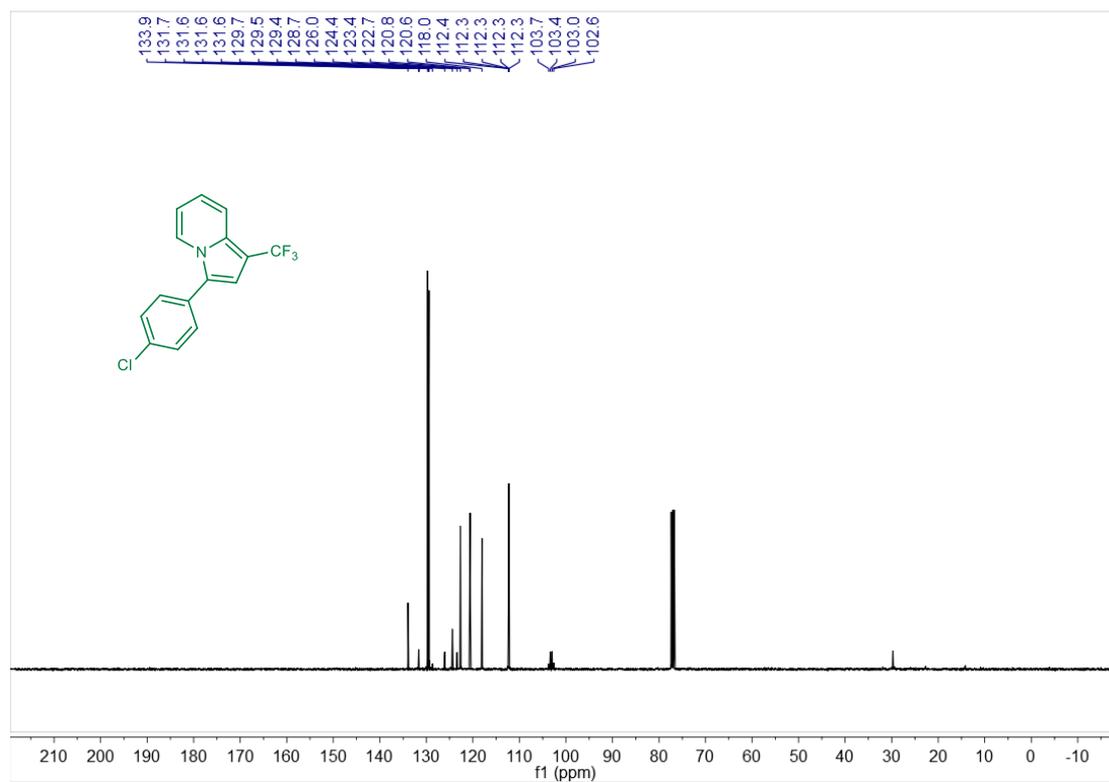
^{19}F NMR spectra of compound **2a** in CDCl_3 (376 MHz):



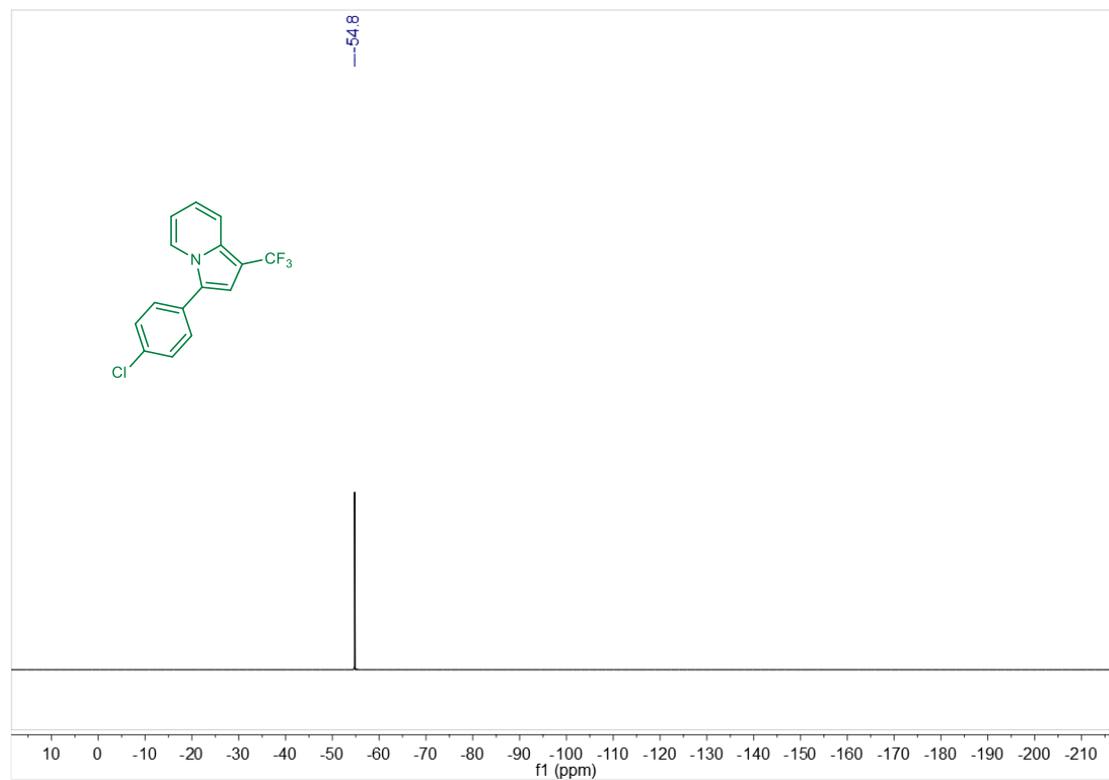
^1H NMR spectra of compound **2b** in CDCl_3 (400 MHz):



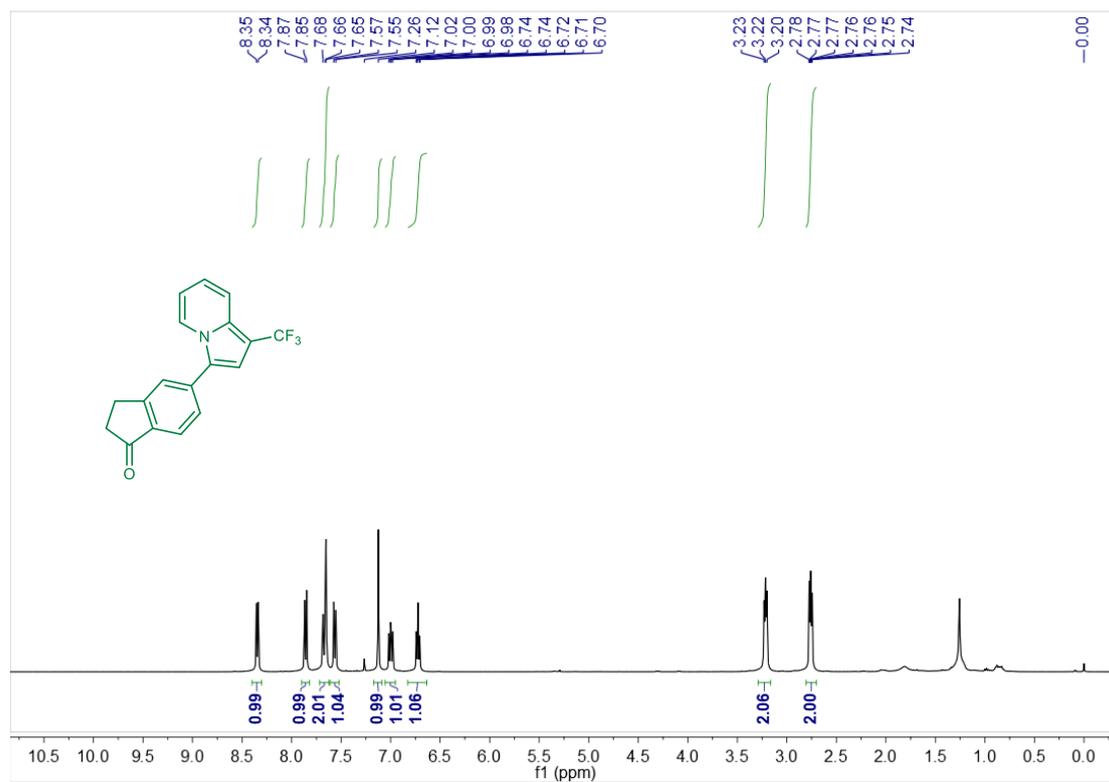
^{13}C NMR spectra of compound **2b** in CDCl_3 (101 MHz):



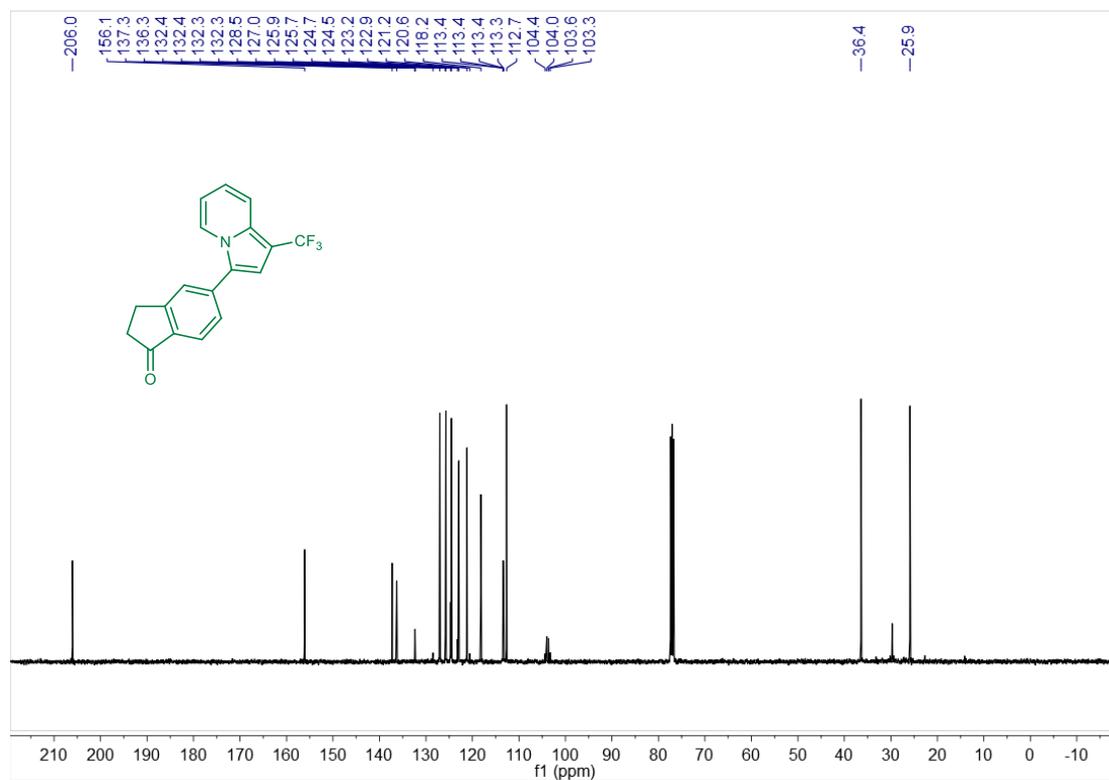
^{19}F NMR spectra of compound **2b** in CDCl_3 (376 MHz):



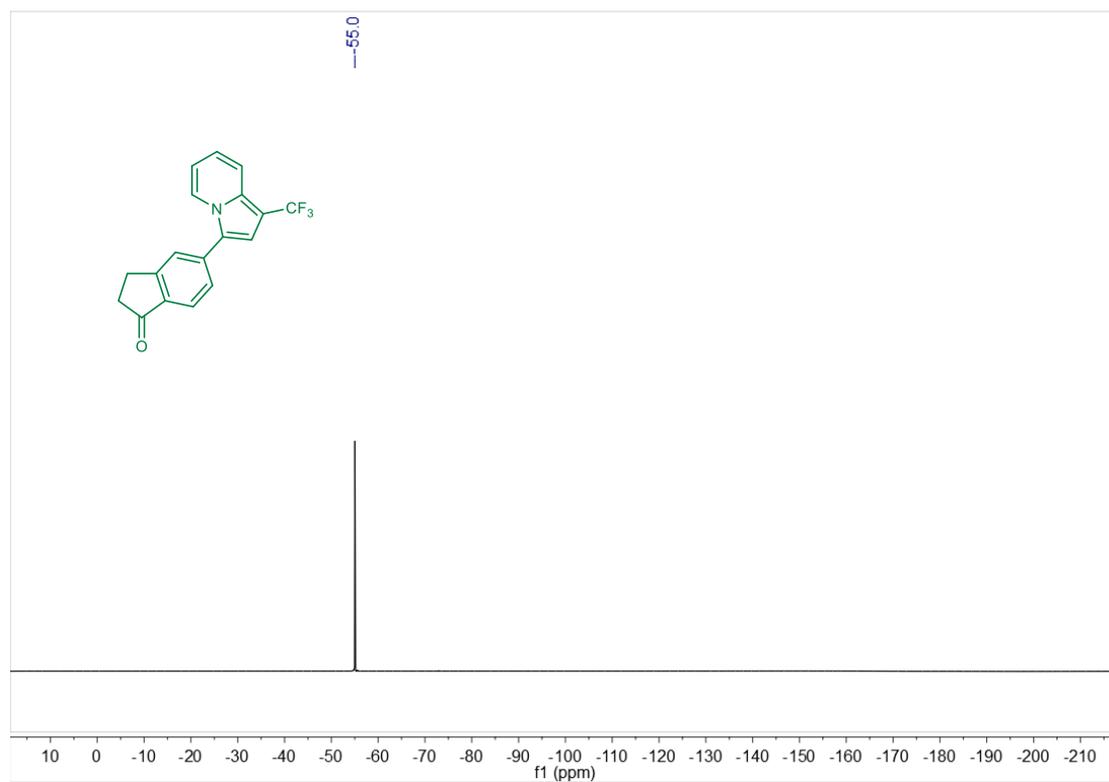
¹H NMR spectra of compound **2c** in CDCl₃ (400 MHz):



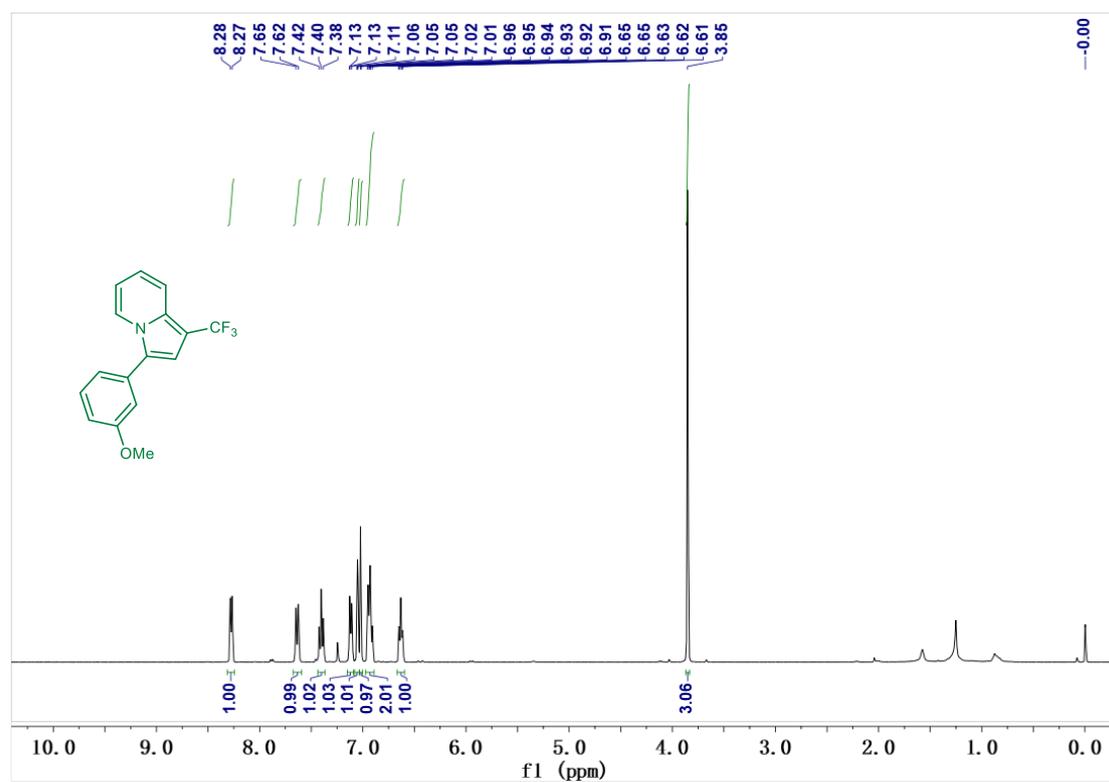
¹³C NMR spectra of compound **2c** in CDCl₃ (101 MHz):



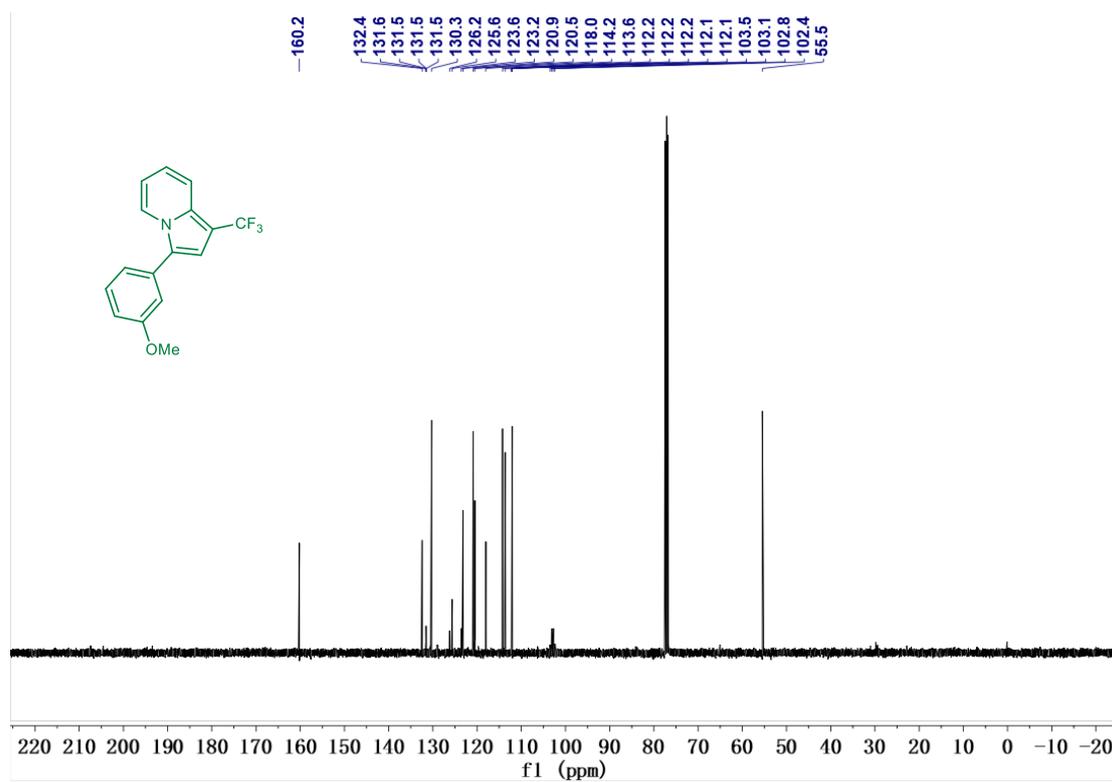
^{19}F NMR spectra of compound **2c** in CDCl_3 (376 MHz):



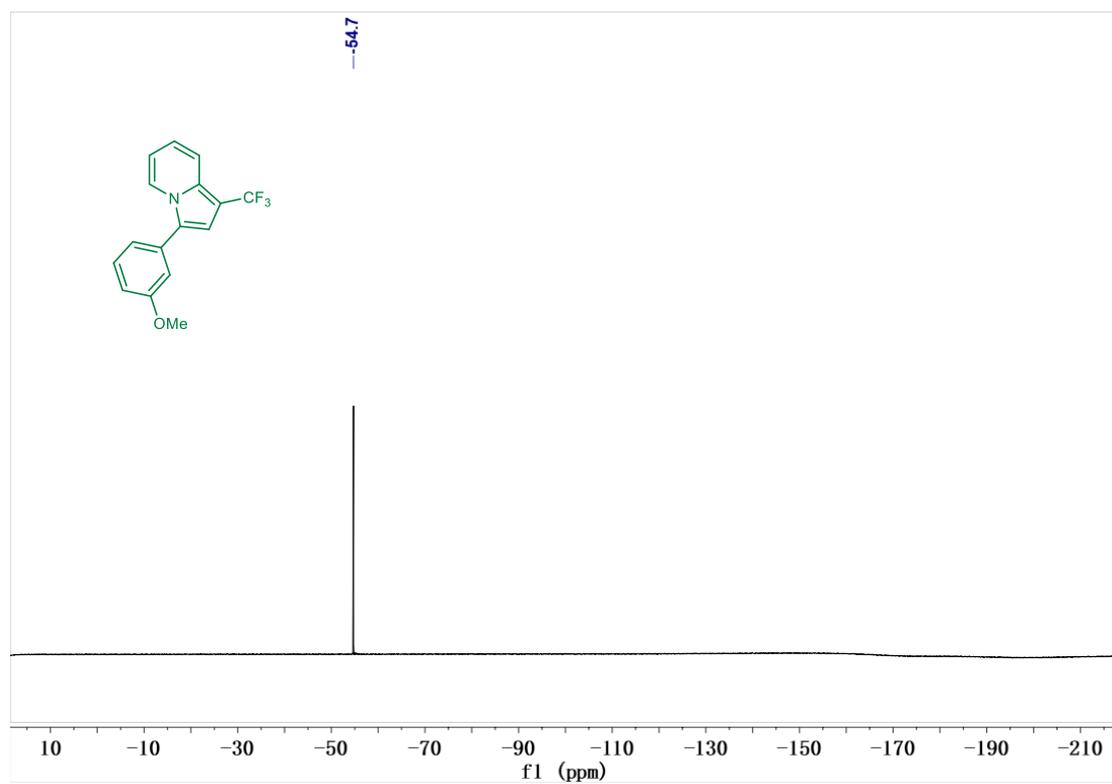
^1H NMR spectra of compound **2d** in CDCl_3 (400 MHz):



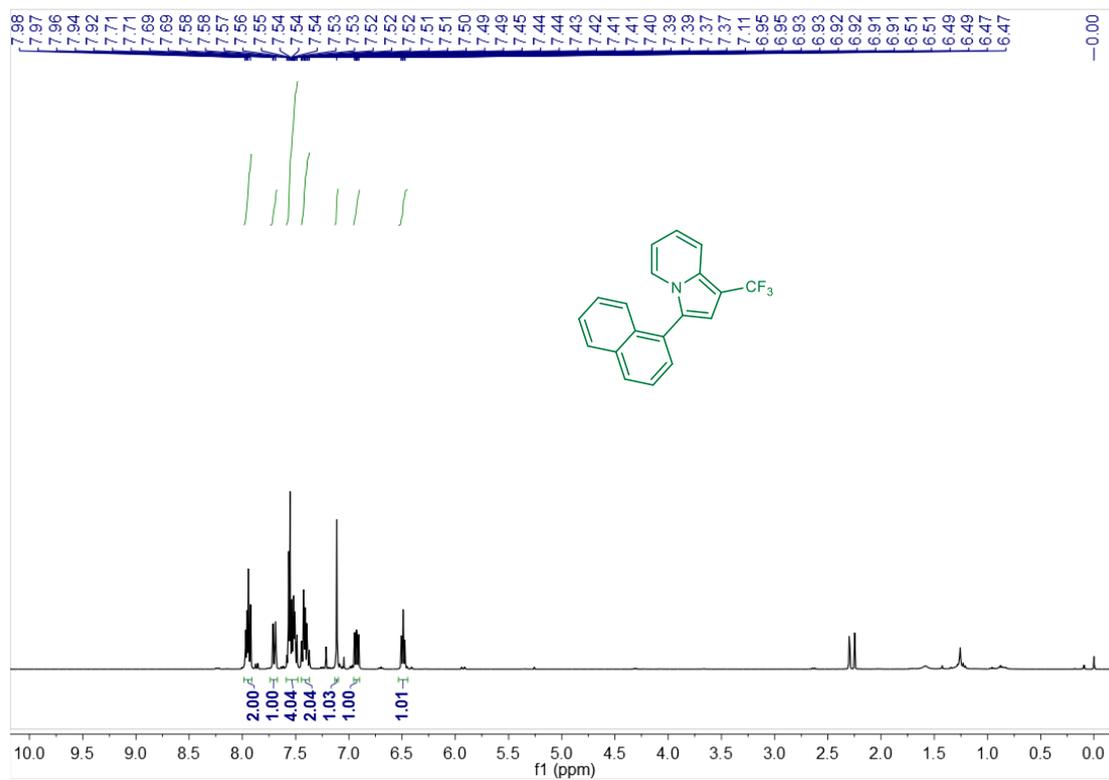
¹³C NMR spectra of compound **2d** in CDCl₃ (101 MHz):



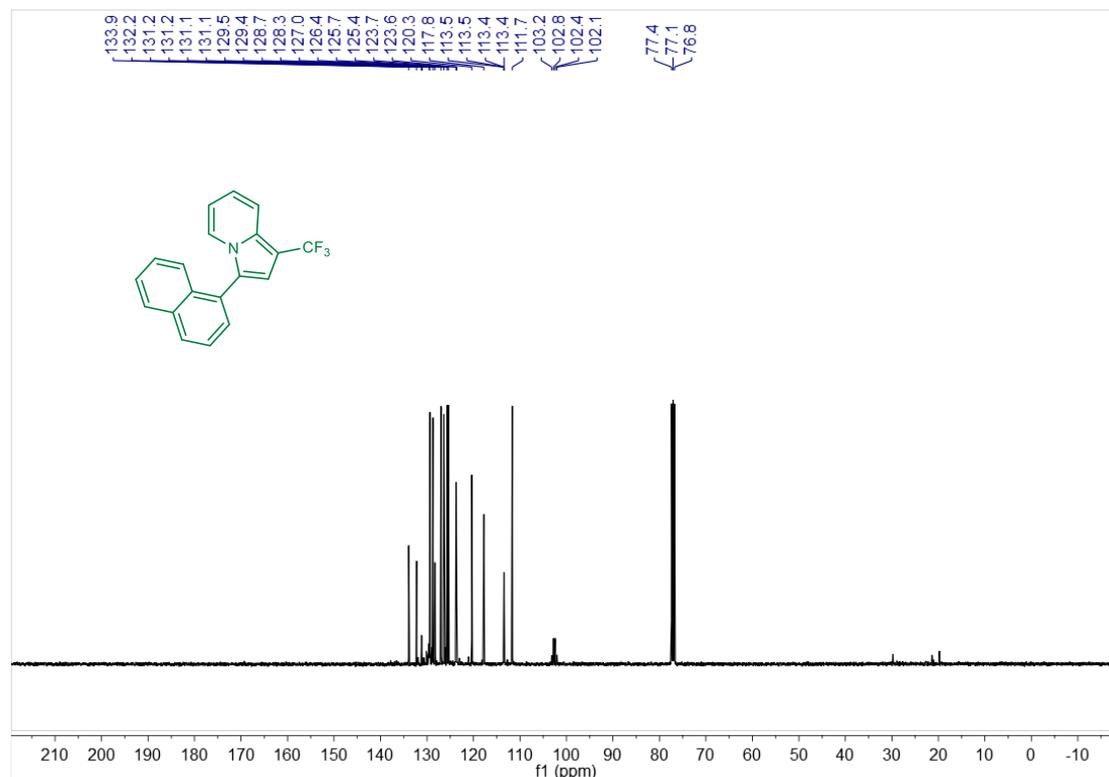
¹⁹F NMR spectra of compound **2d** in CDCl₃ (376 MHz):



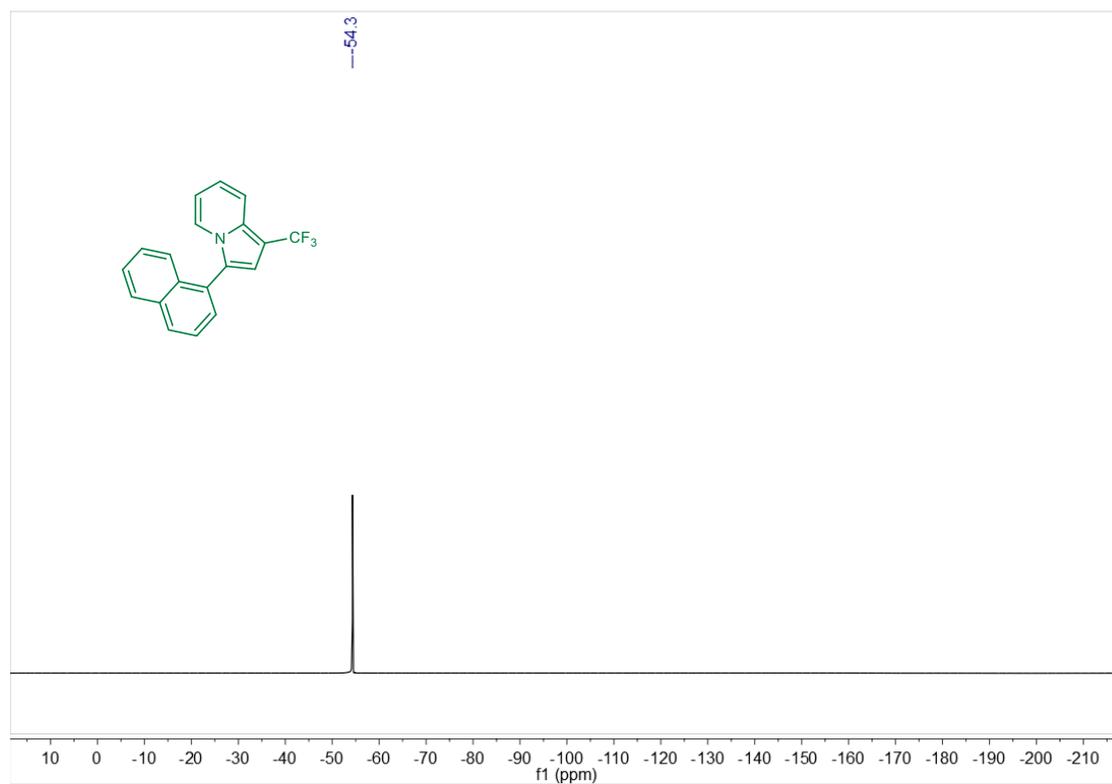
¹H NMR spectra of compound **2e** in CDCl₃ (400 MHz):



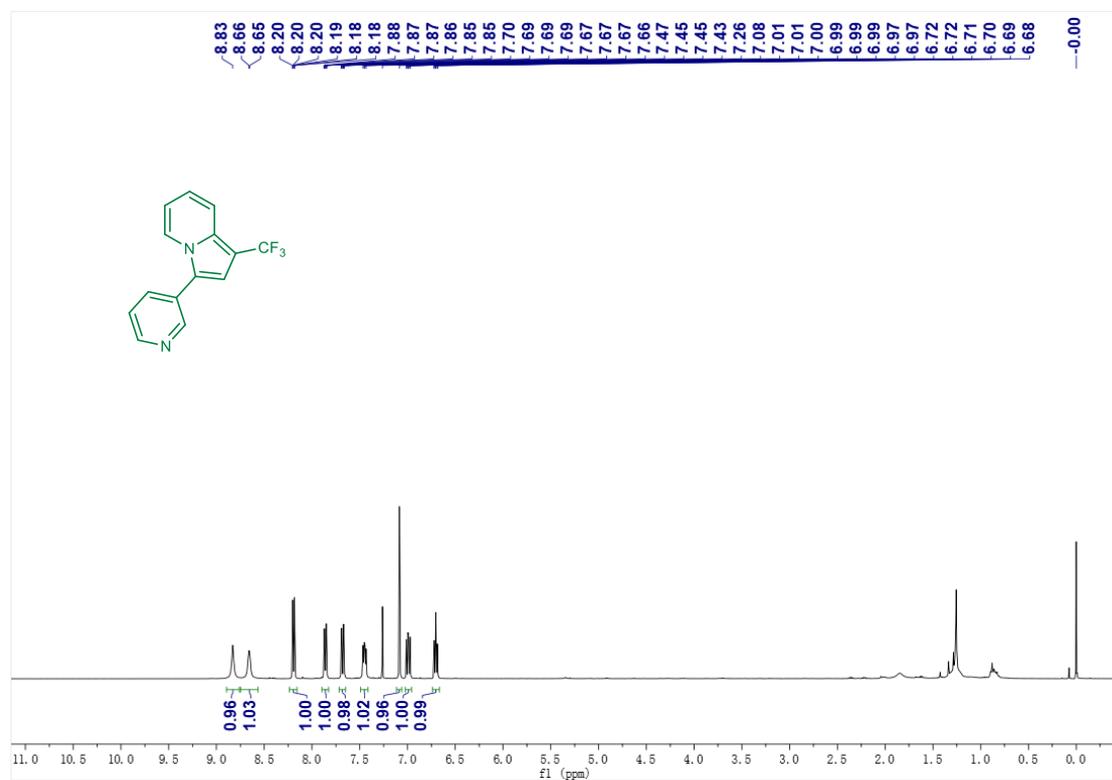
¹³C NMR spectra of compound **2e** in CDCl₃ (101 MHz):



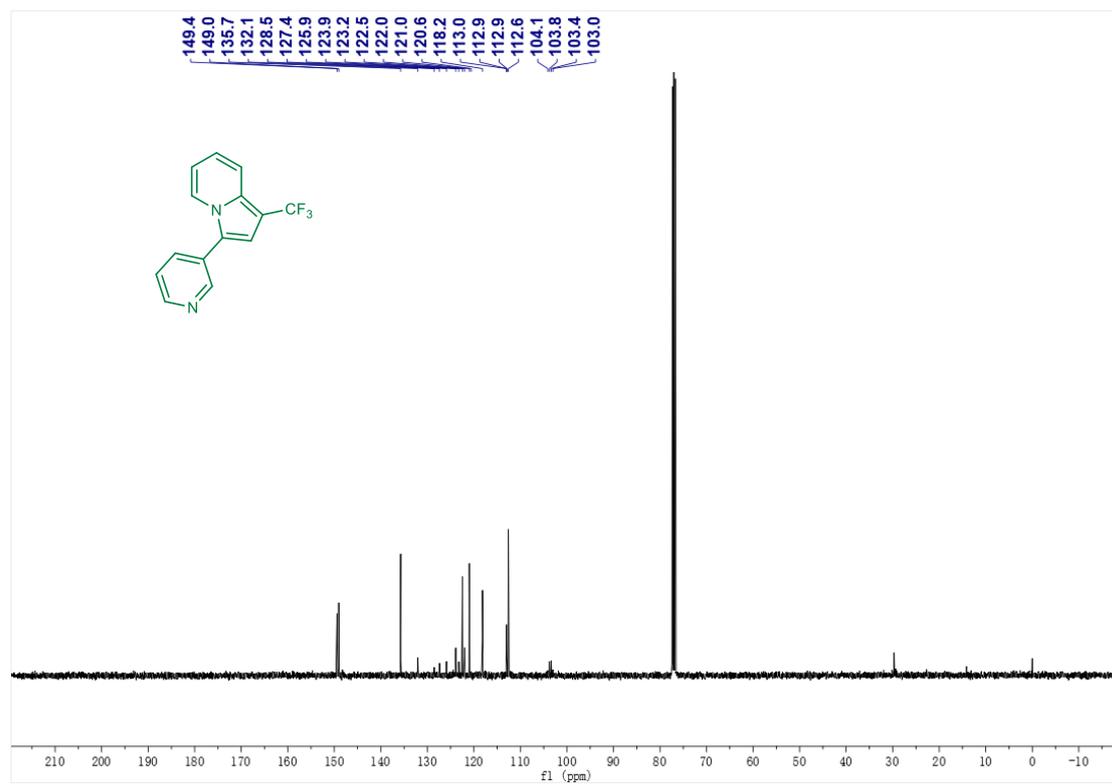
^{19}F NMR spectra of compound **2e** in CDCl_3 (376 MHz):



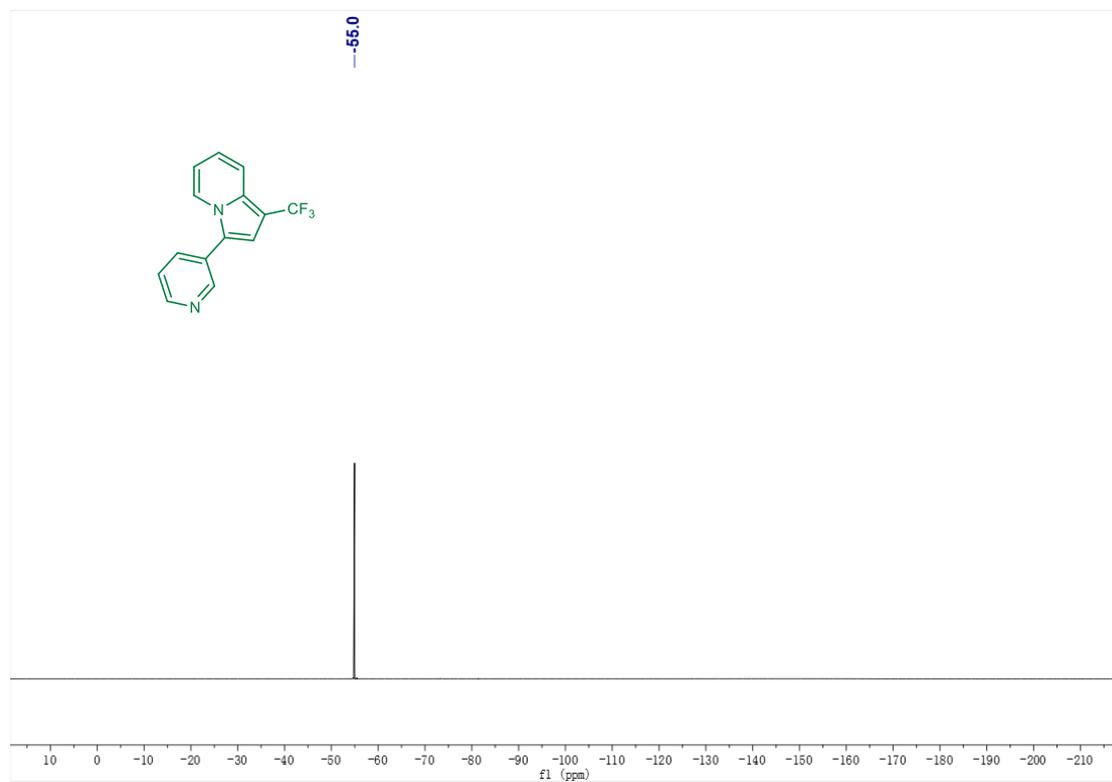
^1H NMR spectra of compound **2f** in CDCl_3 (400 MHz):



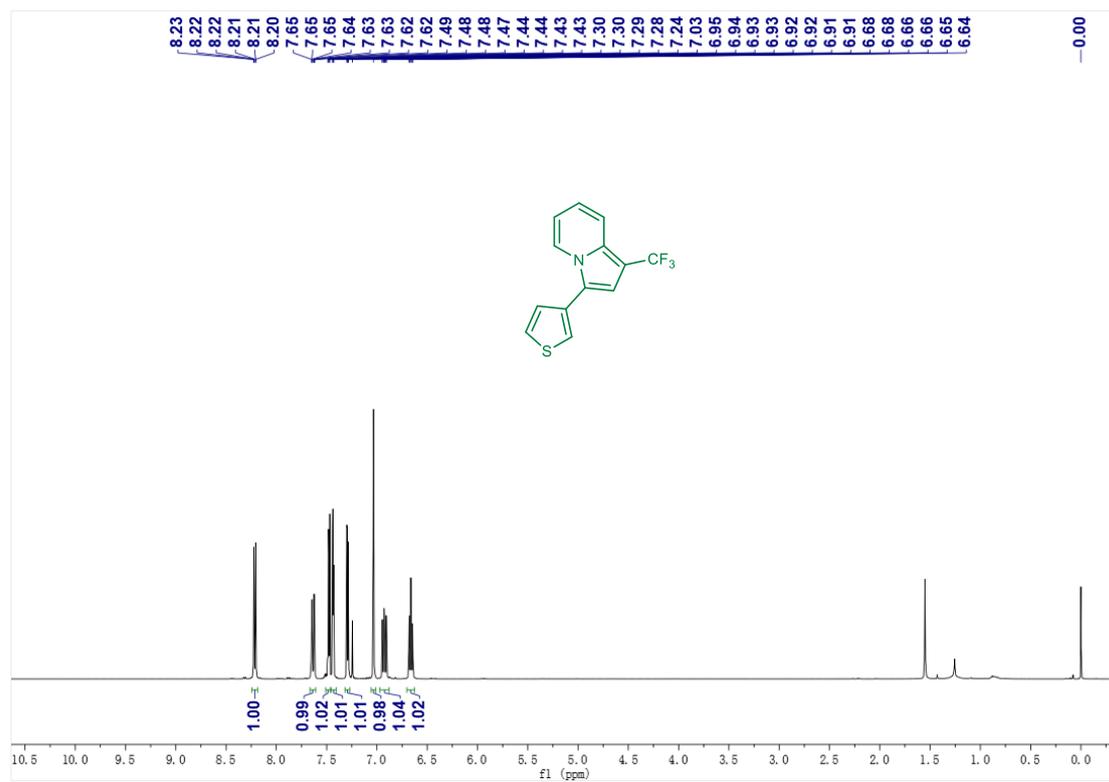
^{13}C NMR spectra of compound **2f** in CDCl_3 (101 MHz):



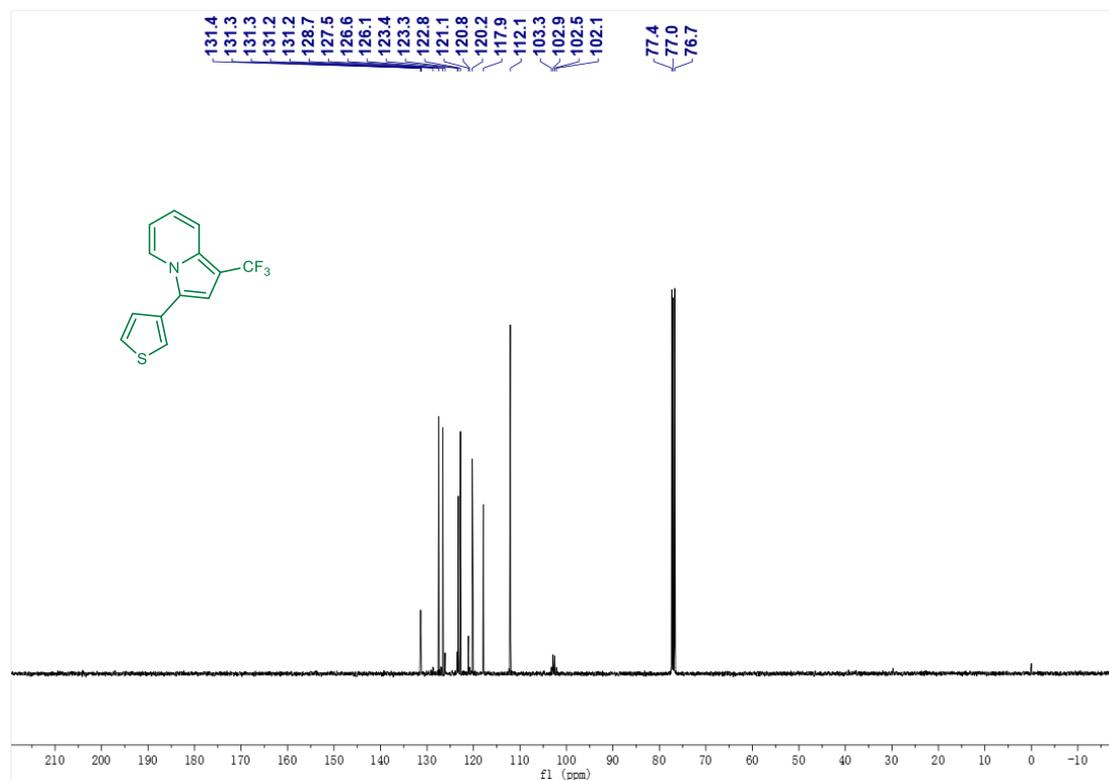
^{19}F NMR spectra of compound **2f** in CDCl_3 (376 MHz):



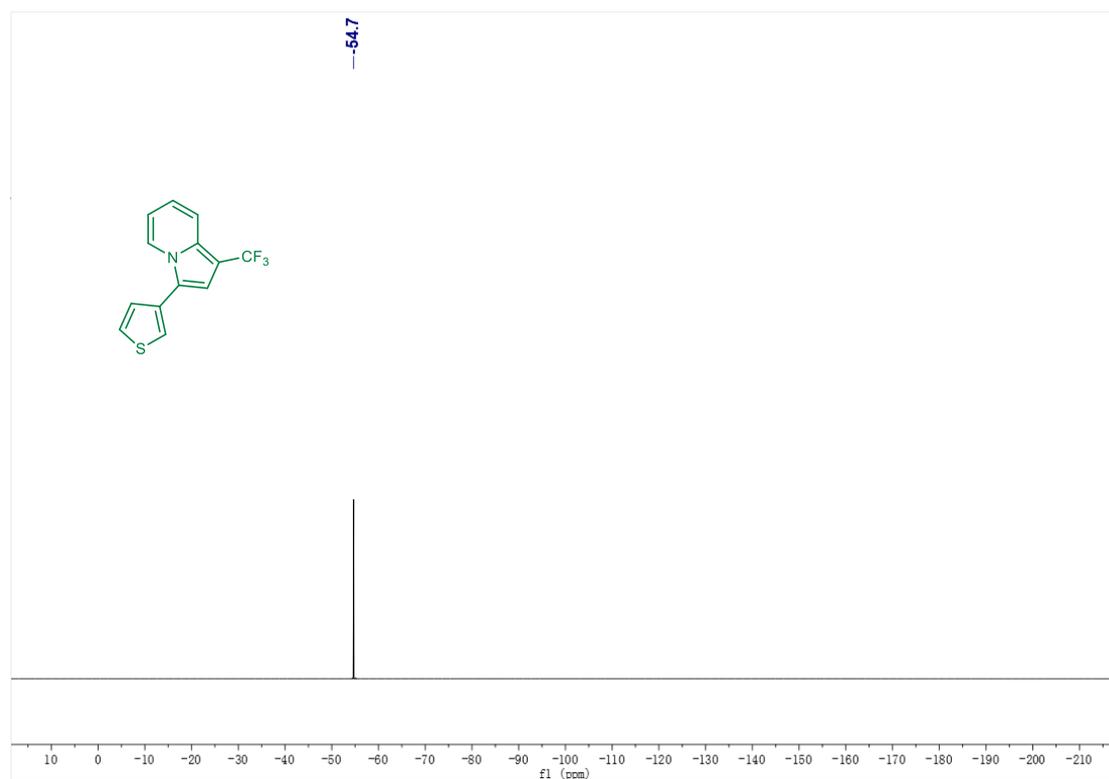
^1H NMR spectra of compound **2g** in CDCl_3 (400 MHz):



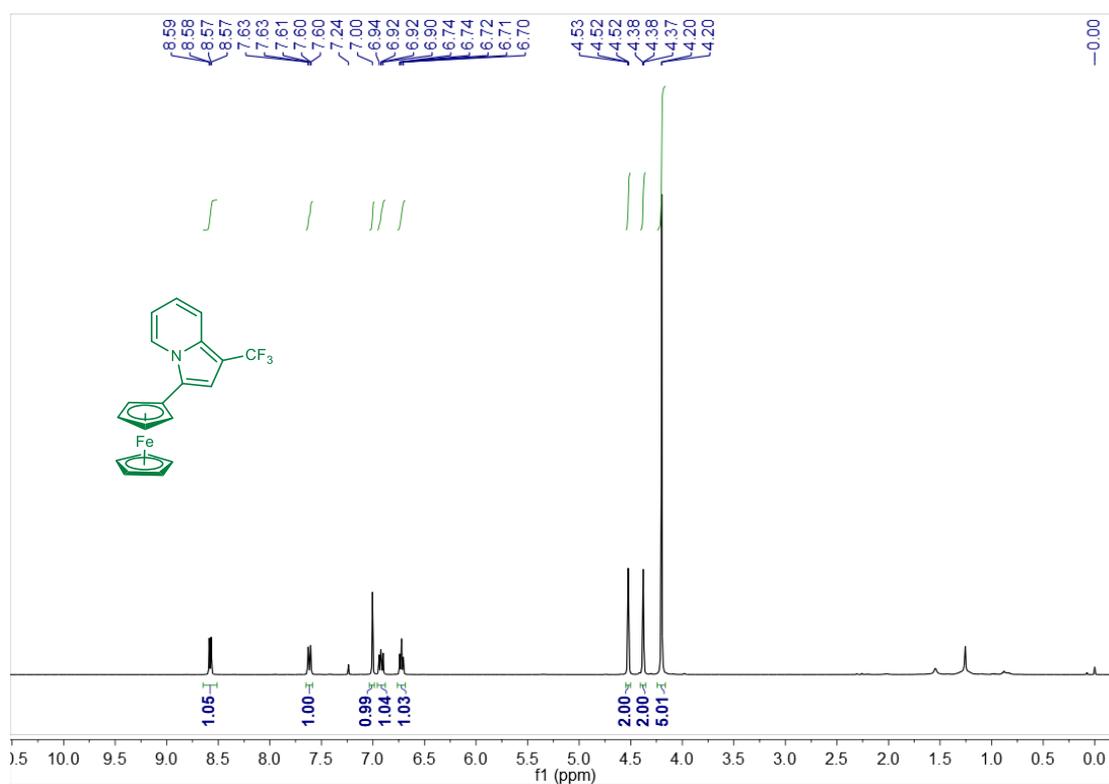
^{13}C NMR spectra of compound **2g** in CDCl_3 (101 MHz):



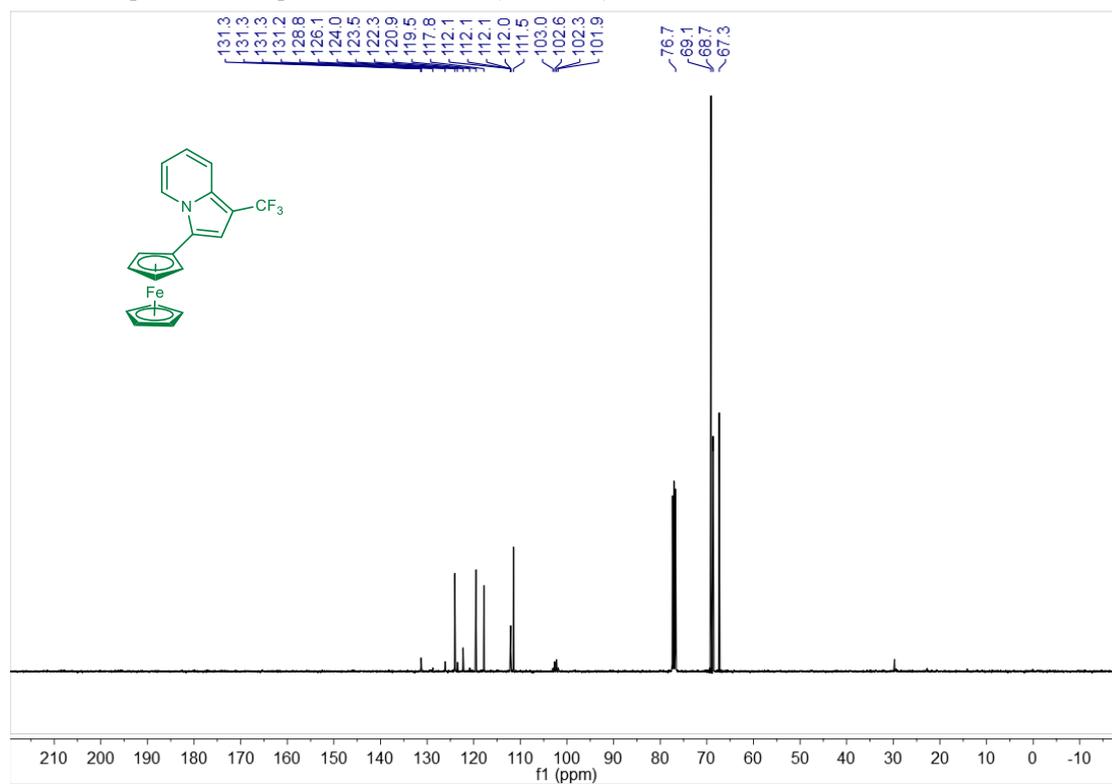
^{19}F NMR spectra of compound **2g** in CDCl_3 (376 MHz):



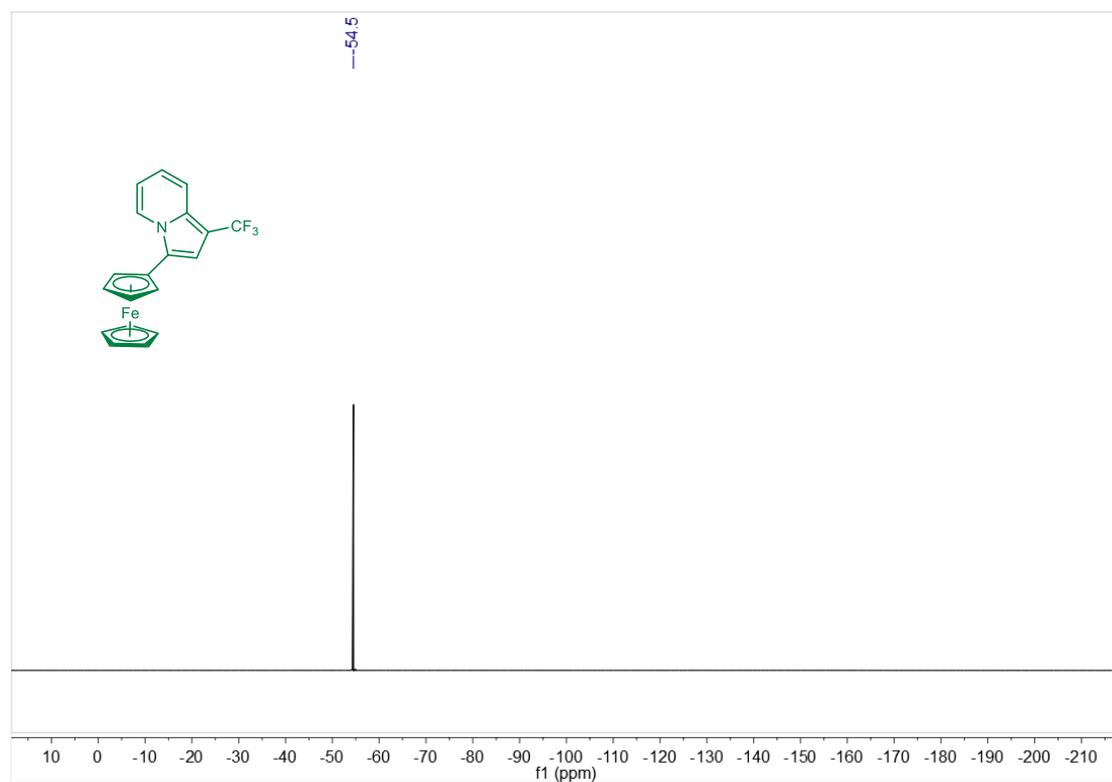
^1H NMR spectra of compound **2h** in CDCl_3 (400 MHz):



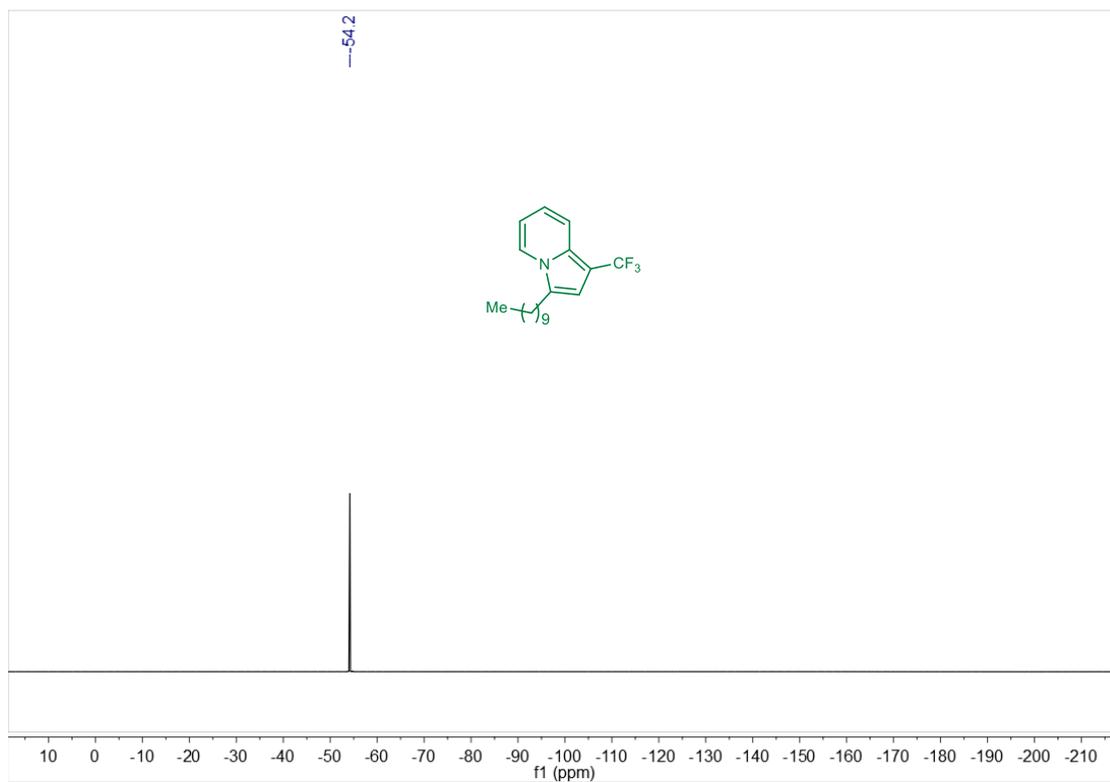
^{13}C NMR spectra of compound **2h** in CDCl_3 (101 MHz):



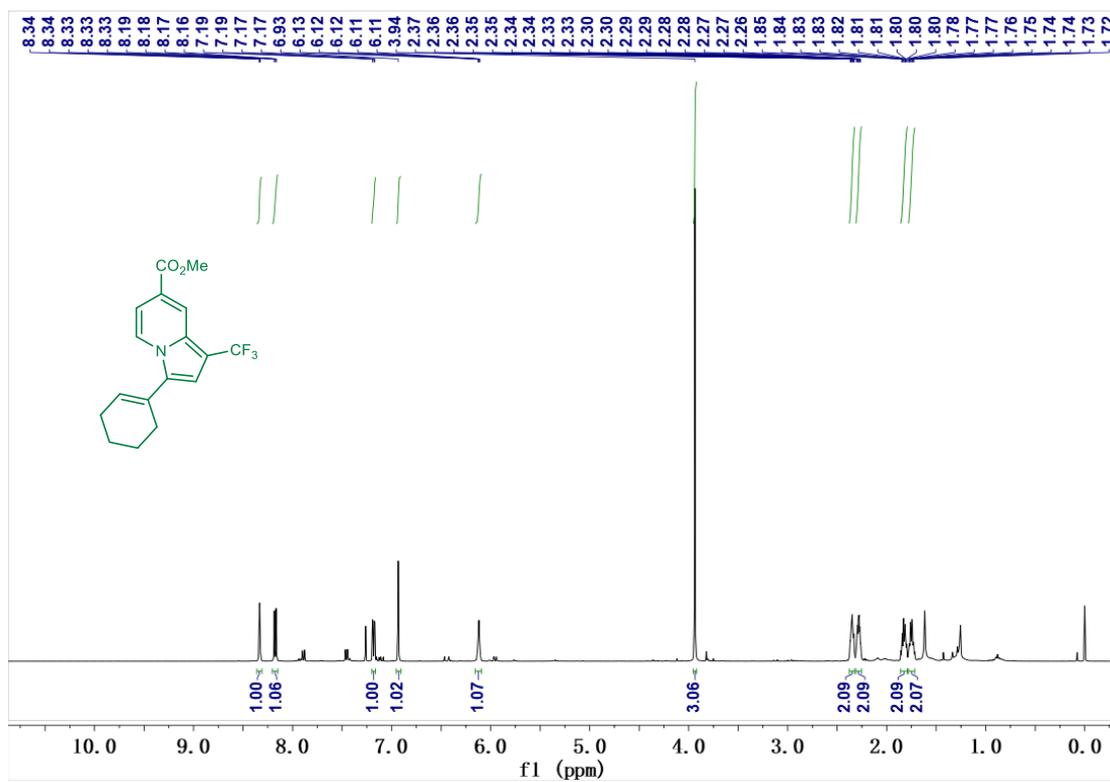
^{19}F NMR spectra of compound **2h** in CDCl_3 (376 MHz):



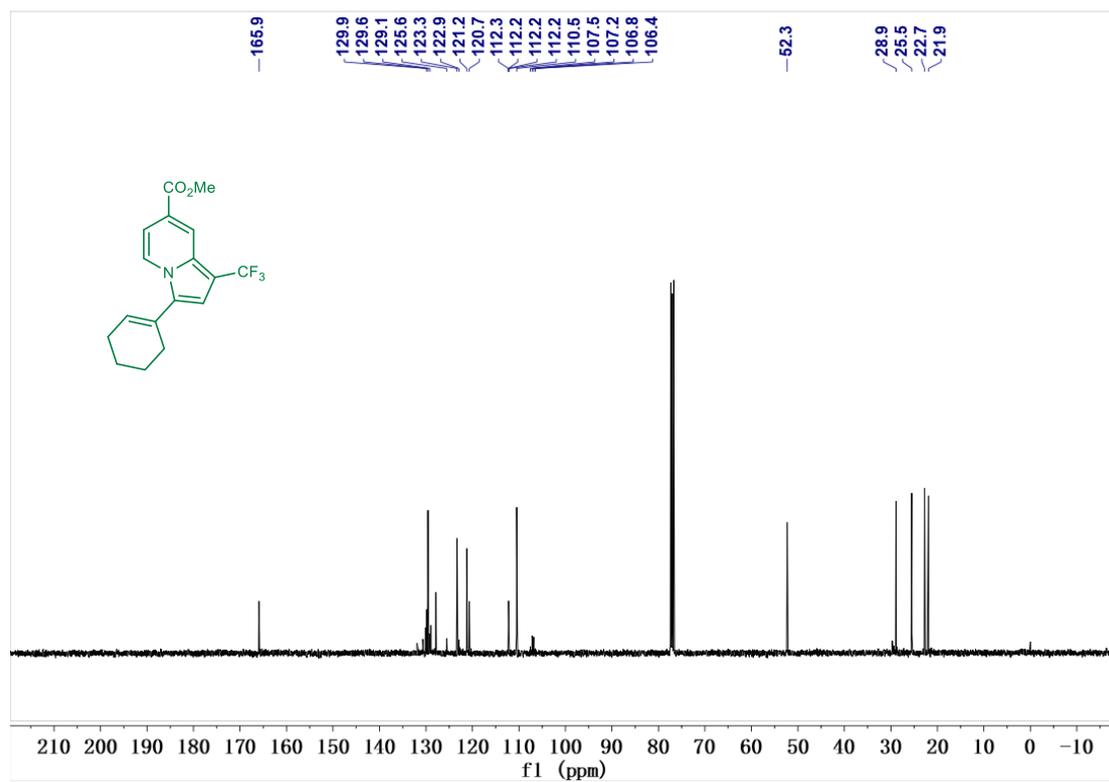
^{19}F NMR spectra of compound **2i** in CDCl_3 (376 MHz):



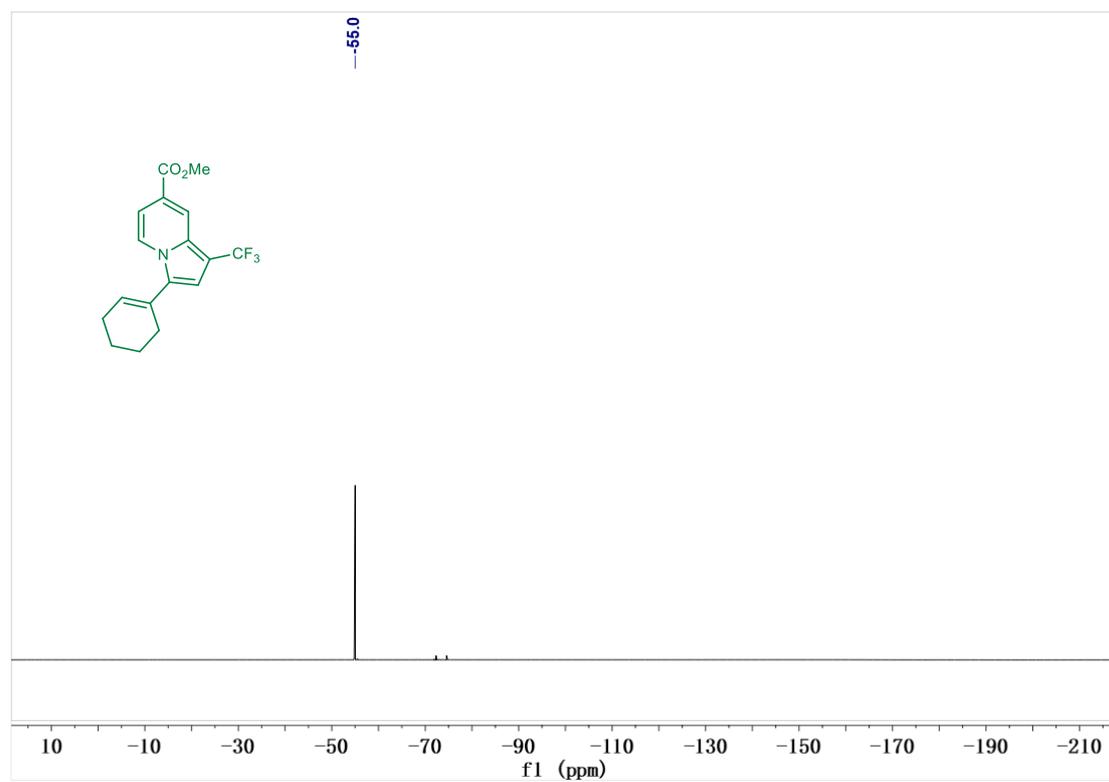
^1H NMR spectra of compound **2j** in CDCl_3 (400 MHz):



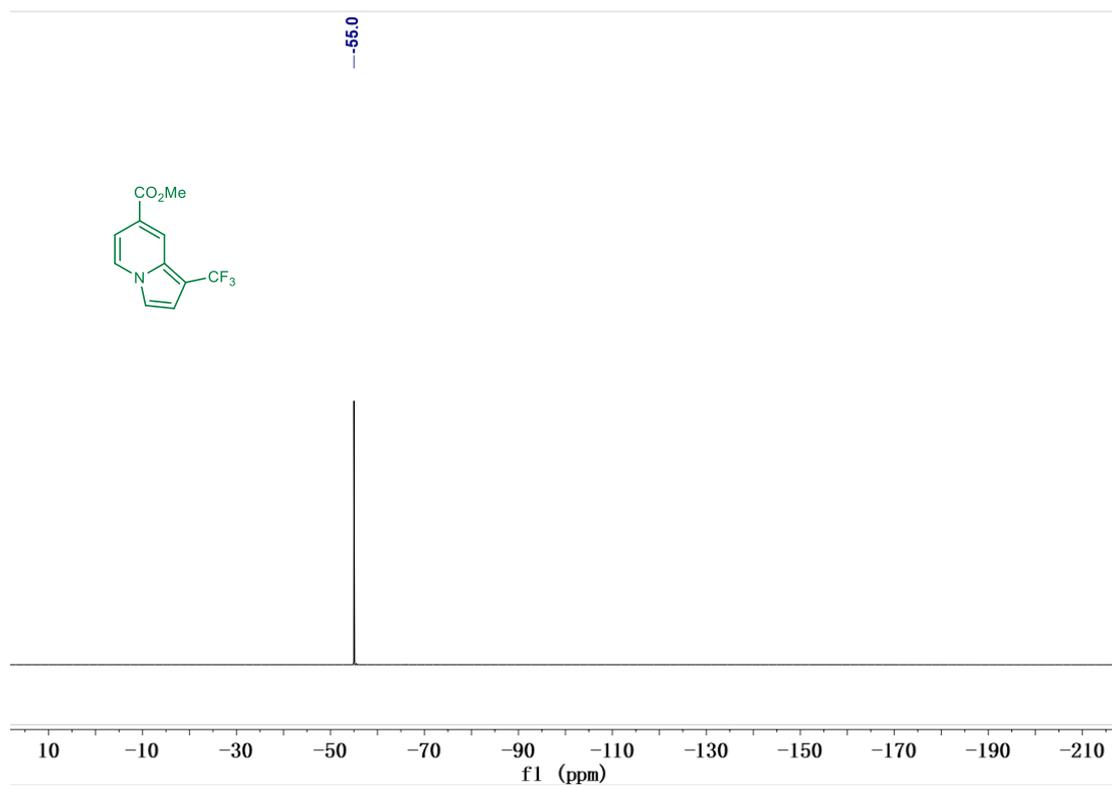
^{13}C NMR spectra of compound **2j** in CDCl_3 (101 MHz):



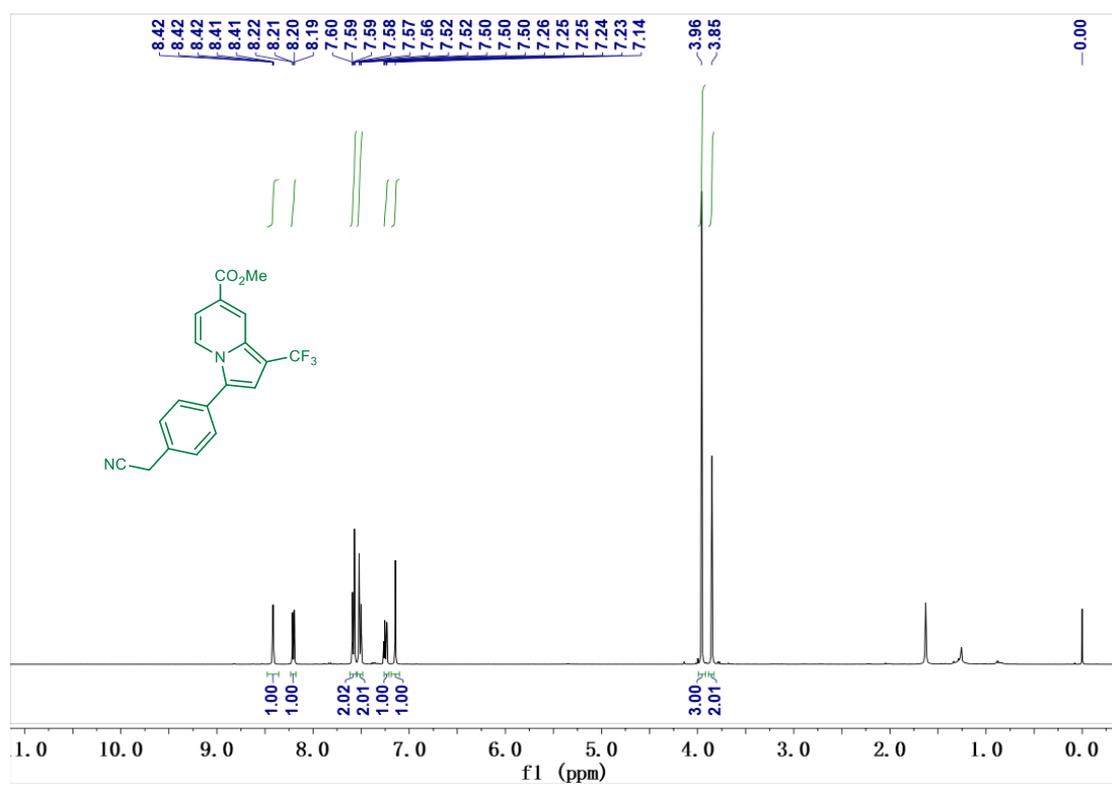
^{19}F NMR spectra of compound **2j** in CDCl_3 (376 MHz):



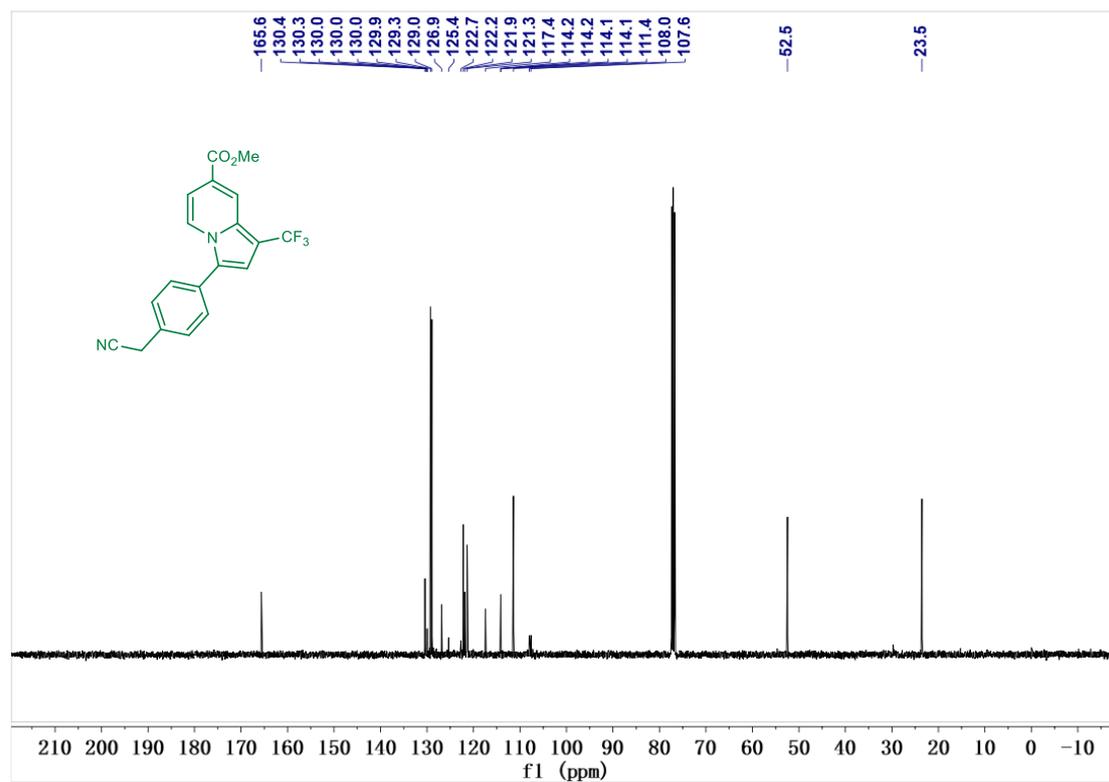
^{19}F NMR spectra of compound **2k** in CDCl_3 (376 MHz):



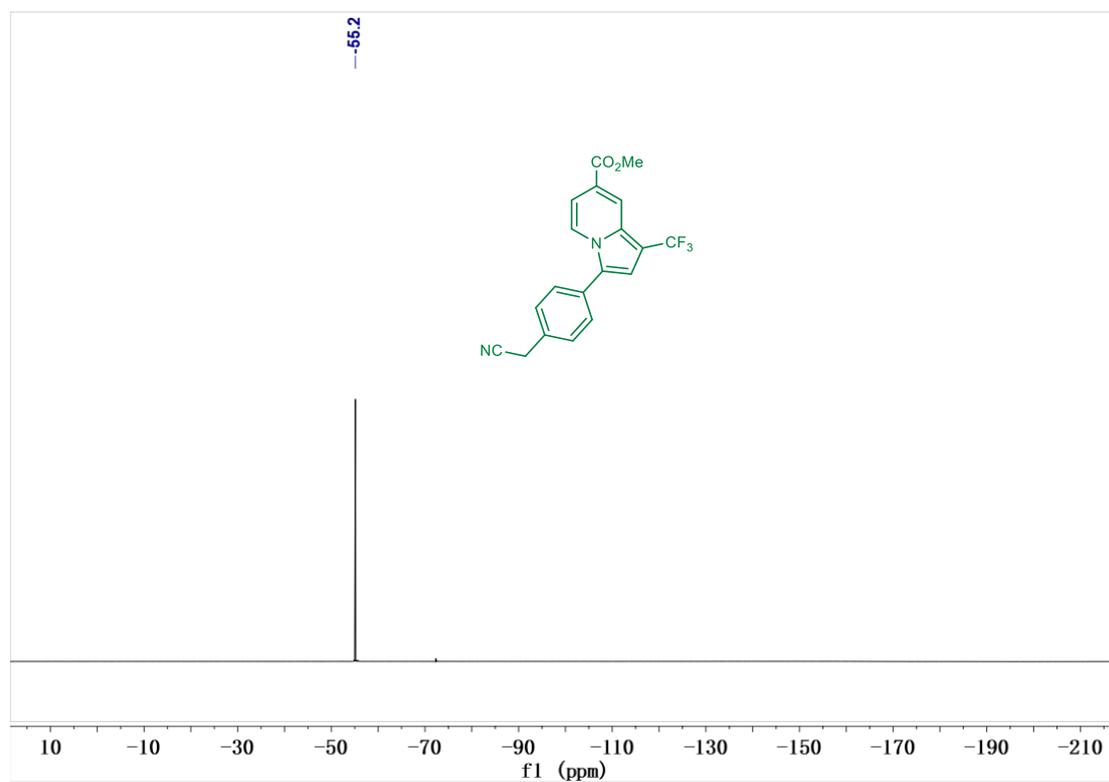
^1H NMR spectra of compound **2l** in CDCl_3 (400 MHz):



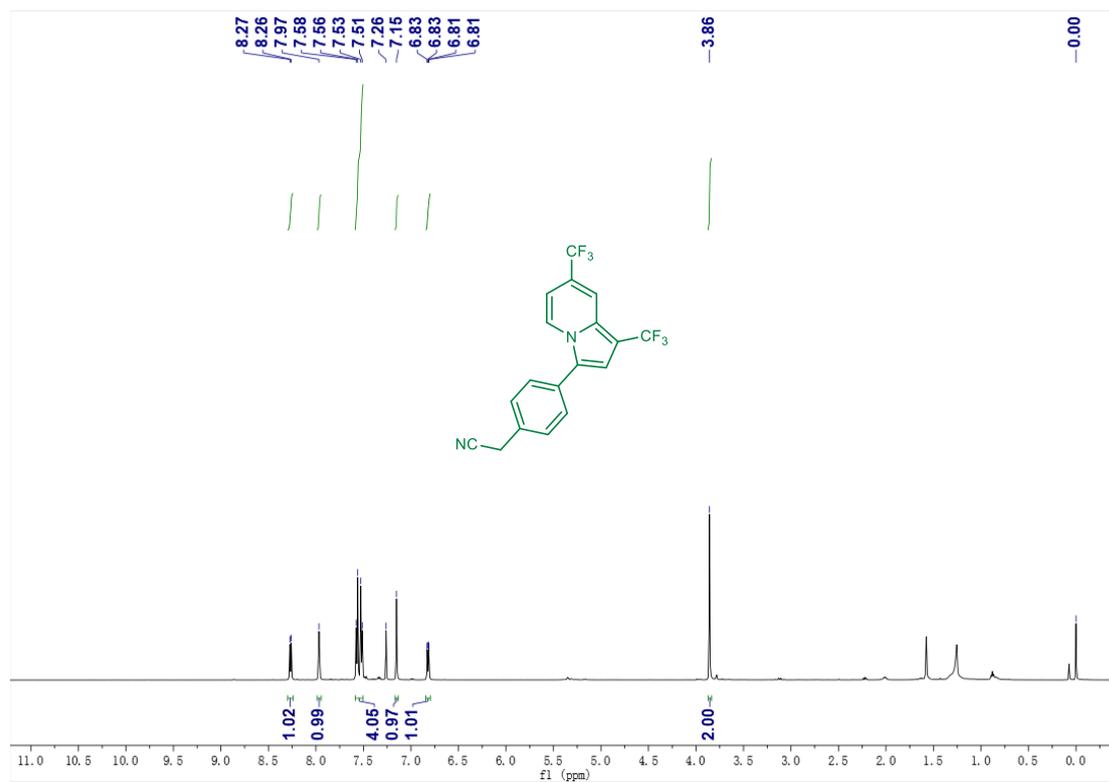
^{13}C NMR spectra of compound **21** in CDCl_3 (101 MHz):



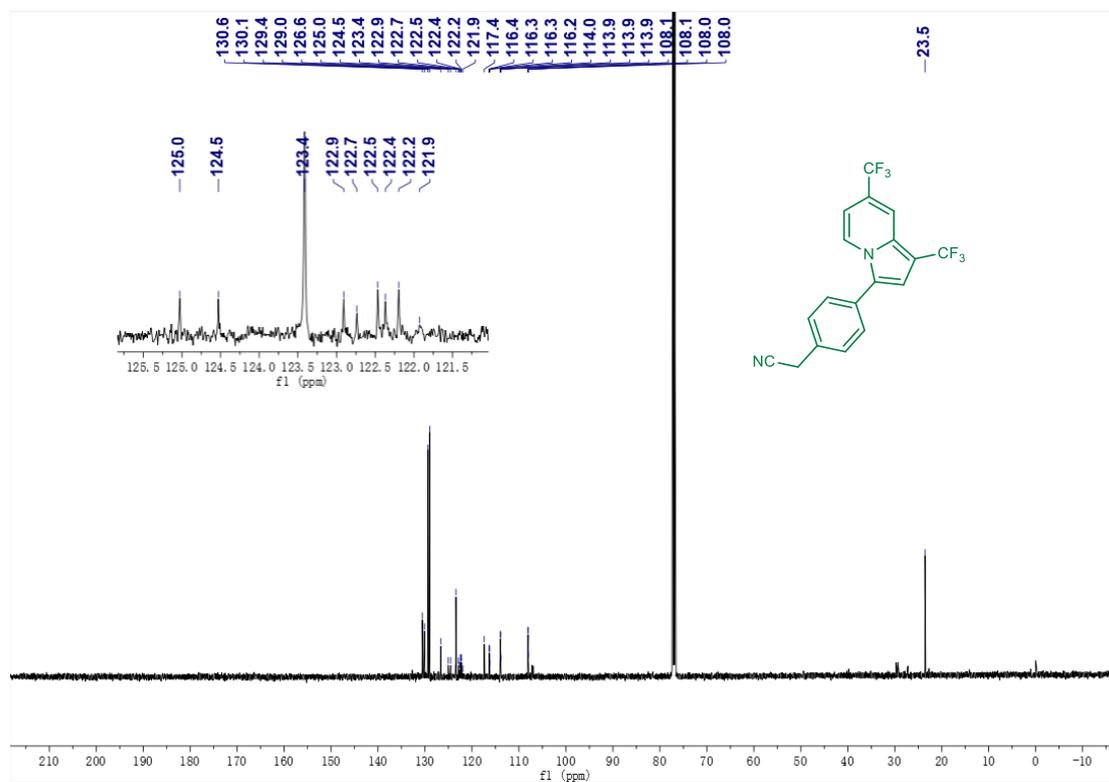
^{19}F NMR spectra of compound **21** in CDCl_3 (376 MHz):



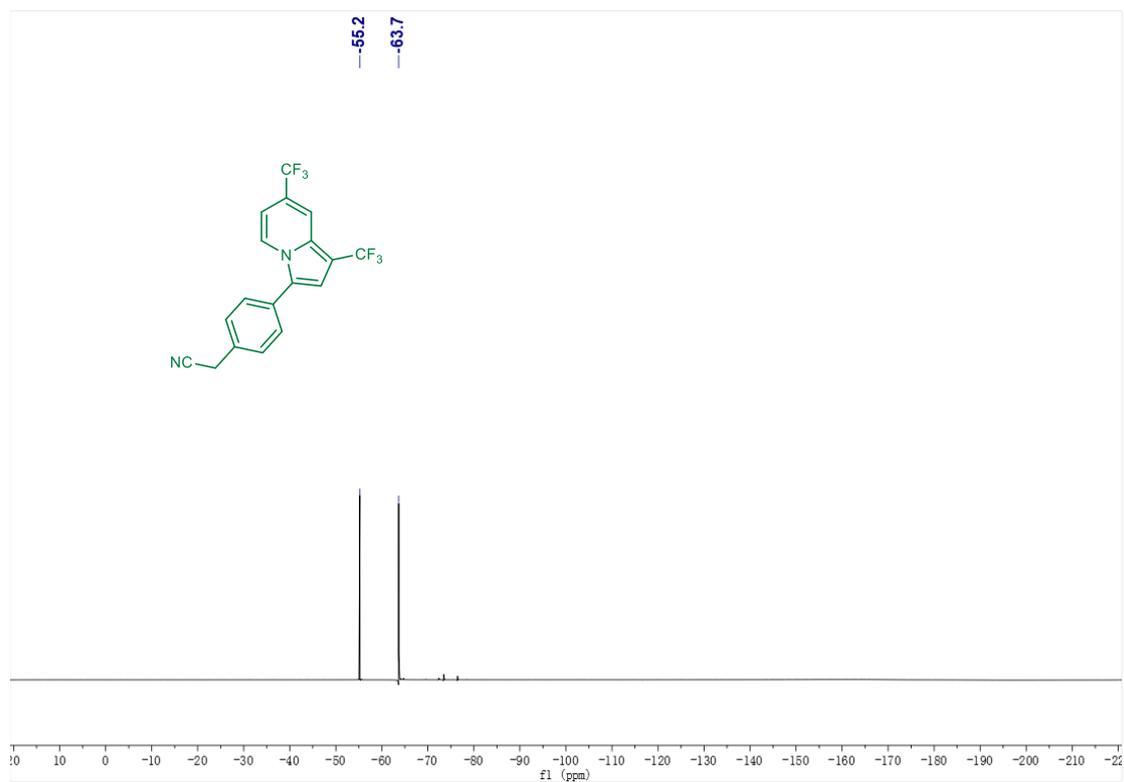
^1H NMR spectra of compound **2m** in CDCl_3 (500 MHz):



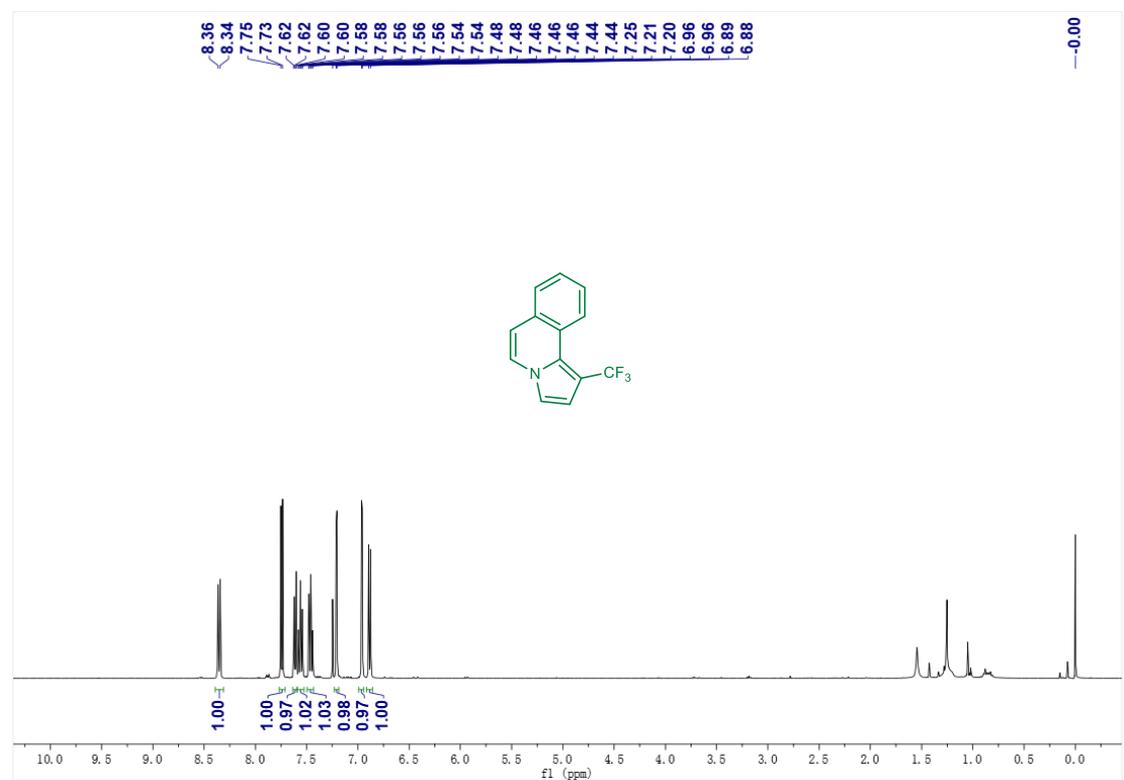
^{13}C NMR spectra of compound **2m** in CDCl_3 (126 MHz):



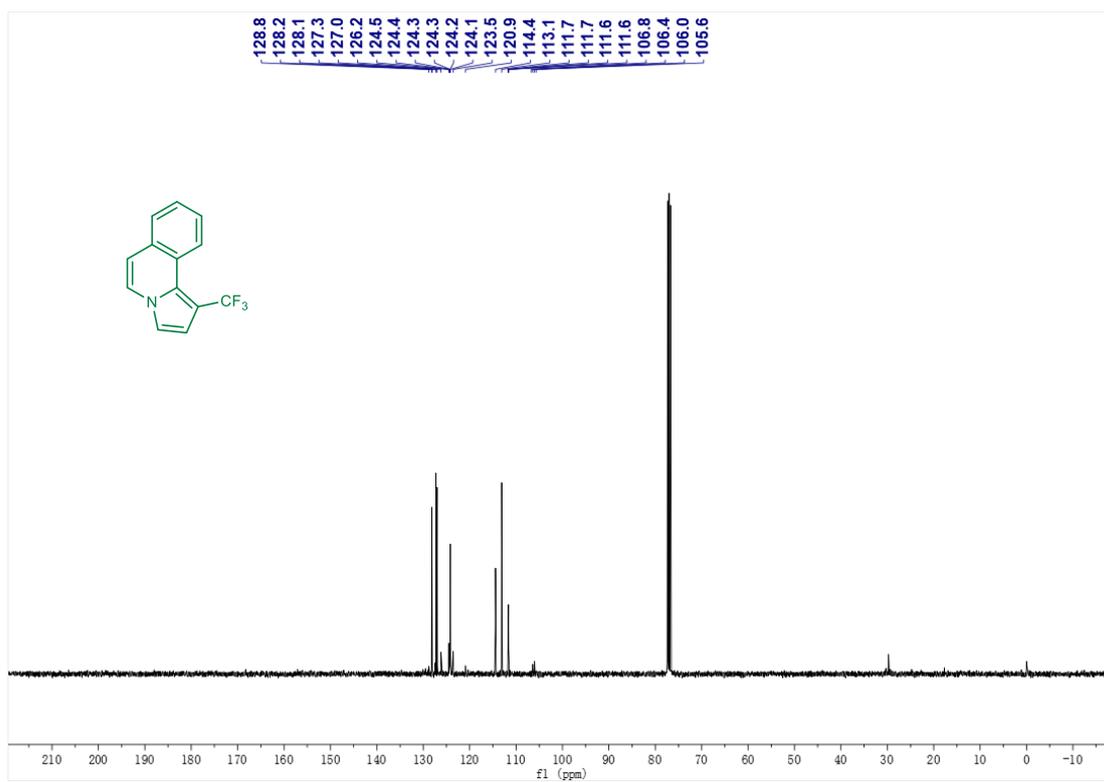
^{19}F NMR spectra of compound **2m** in CDCl_3 (471 MHz):



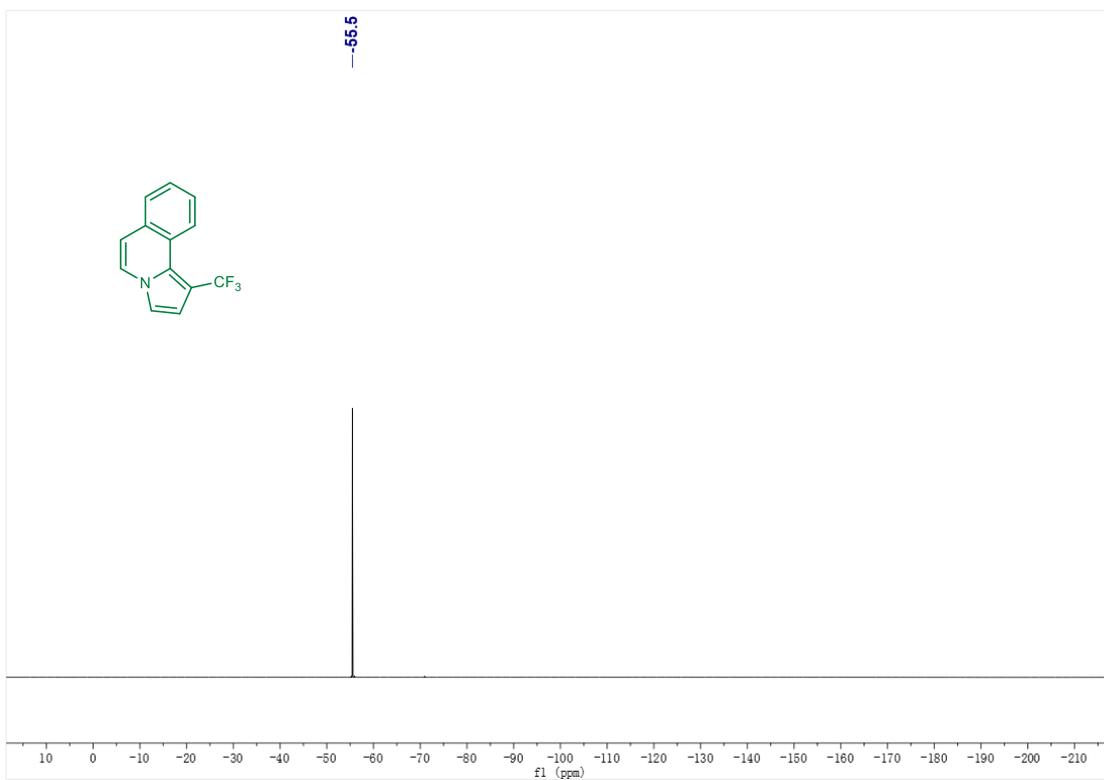
^1H NMR spectra of compound **2n** in CDCl_3 (400 MHz):



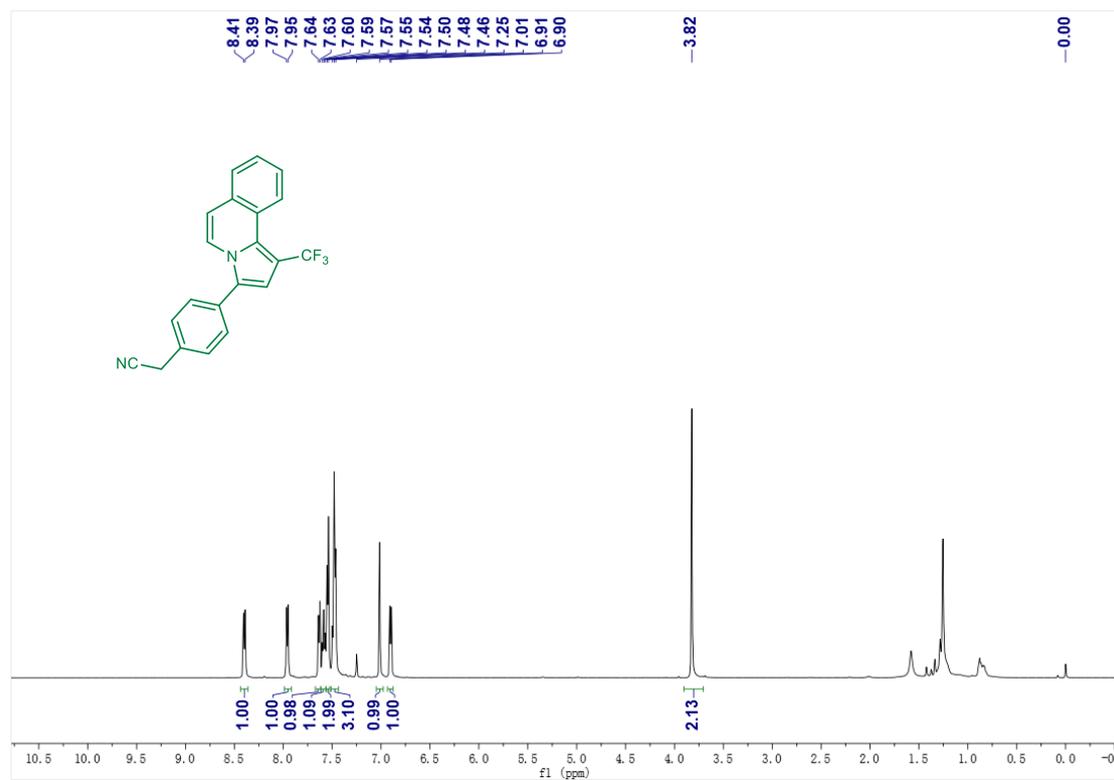
^{13}C NMR spectra of compound **2n** in CDCl_3 (101 MHz):



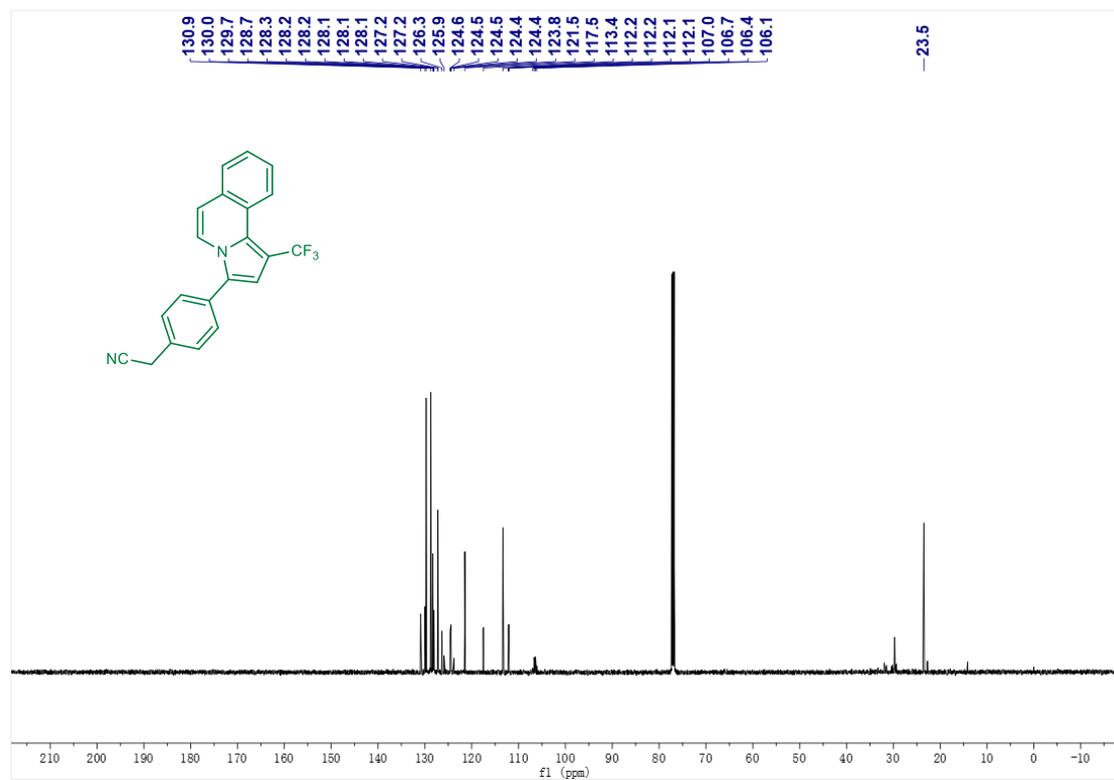
^{19}F NMR spectra of compound **2n** in CDCl_3 (376 MHz):



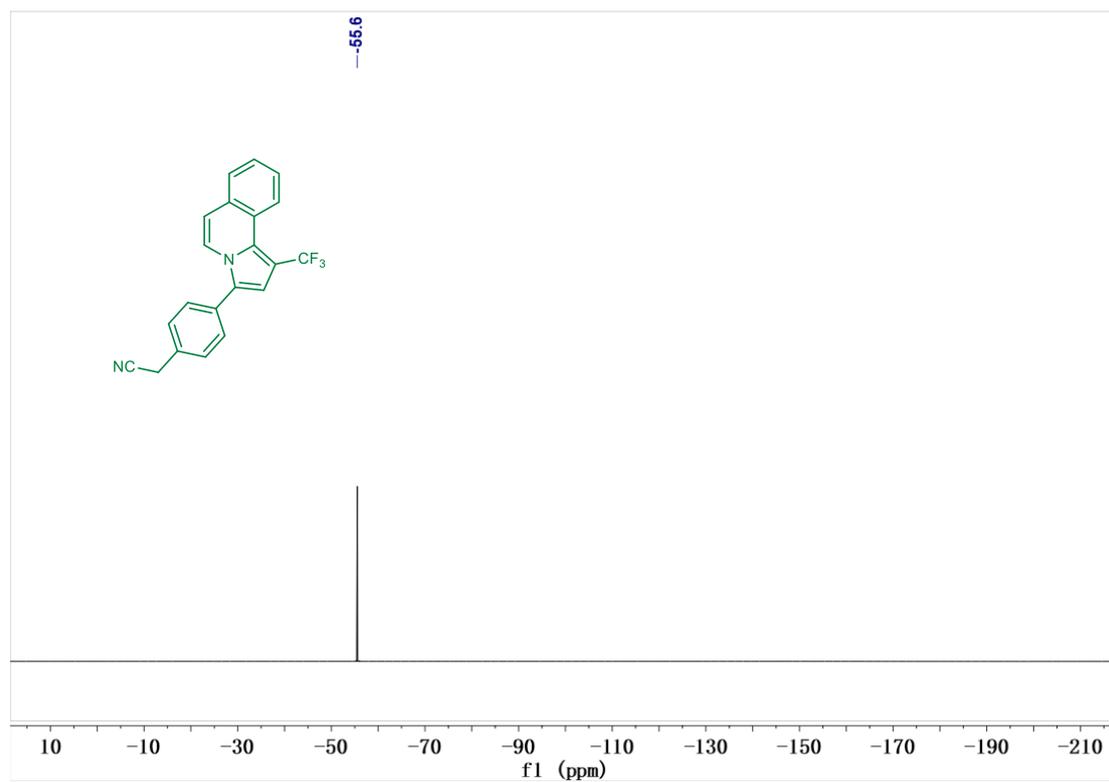
¹H NMR spectra of compound **2o** in CDCl₃ (500 MHz):



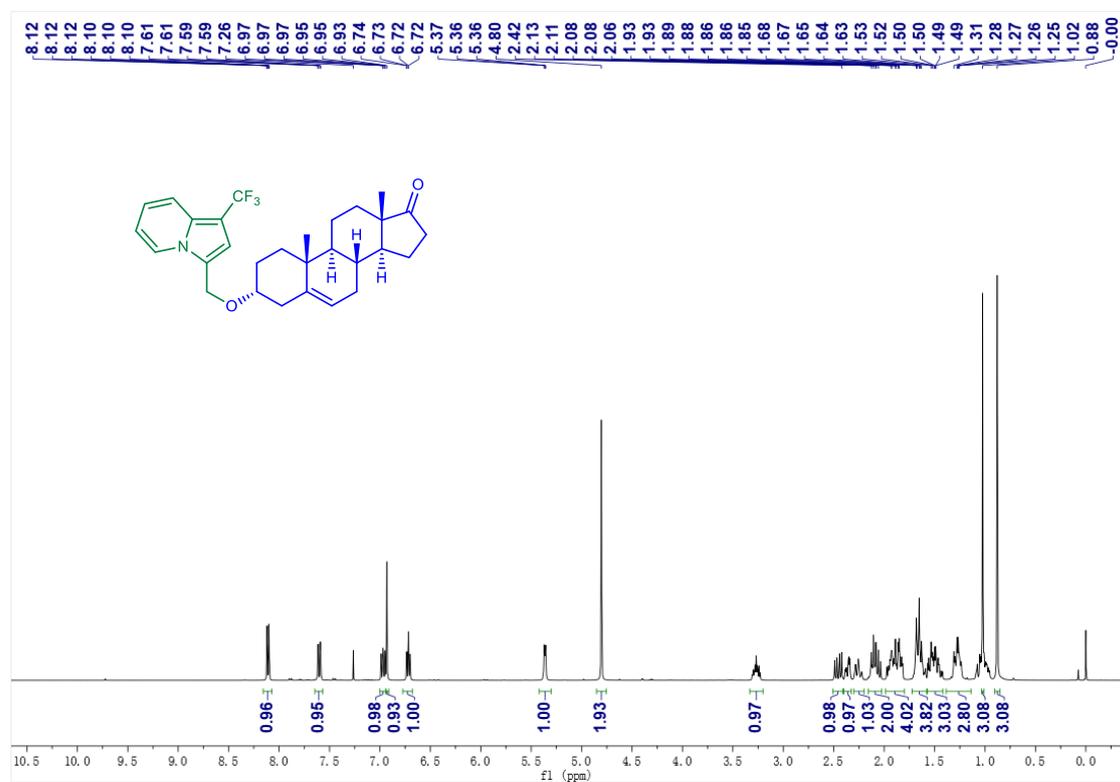
¹³C NMR spectra of compound **2o** in CDCl₃ (126 MHz):



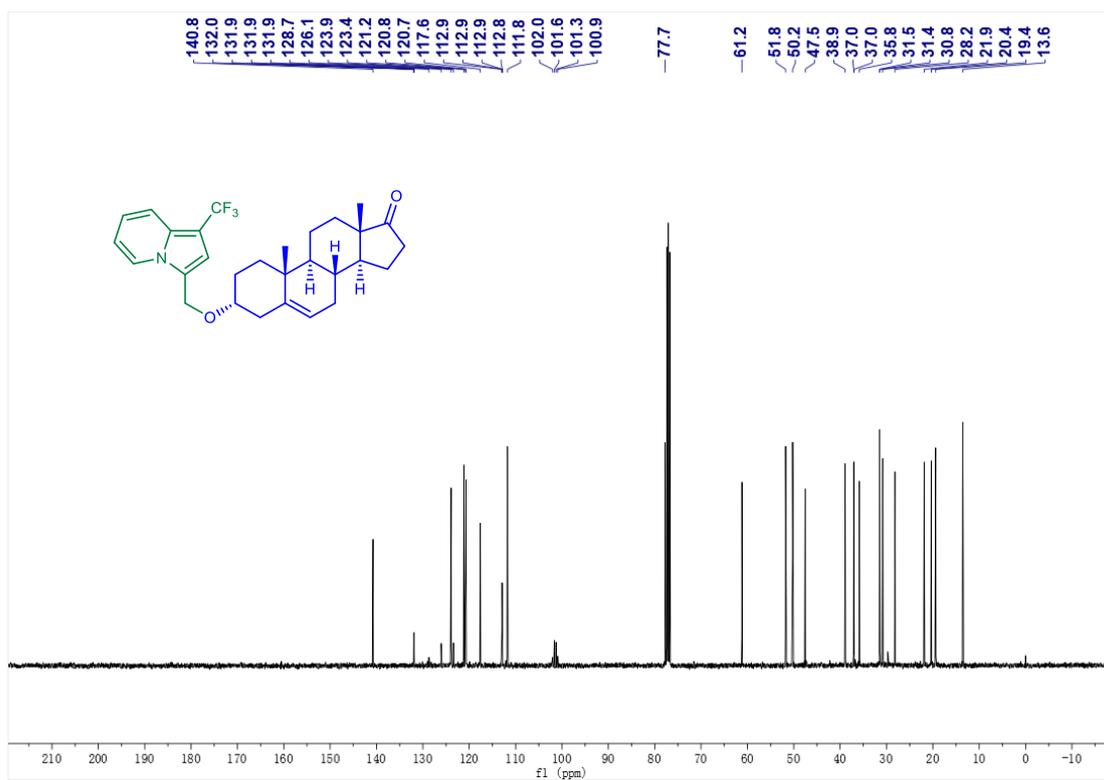
^{19}F NMR spectra of compound **2o** in CDCl_3 (376 MHz):



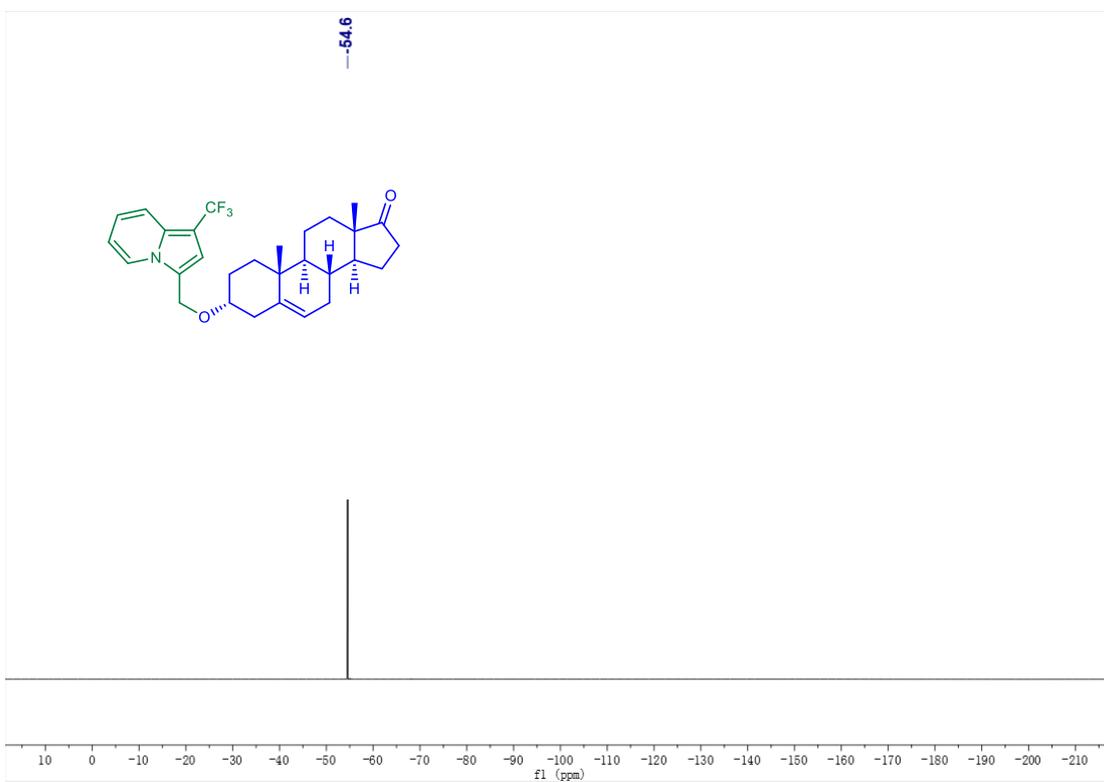
^1H NMR spectra of compound **2p** in CDCl_3 (400 MHz):



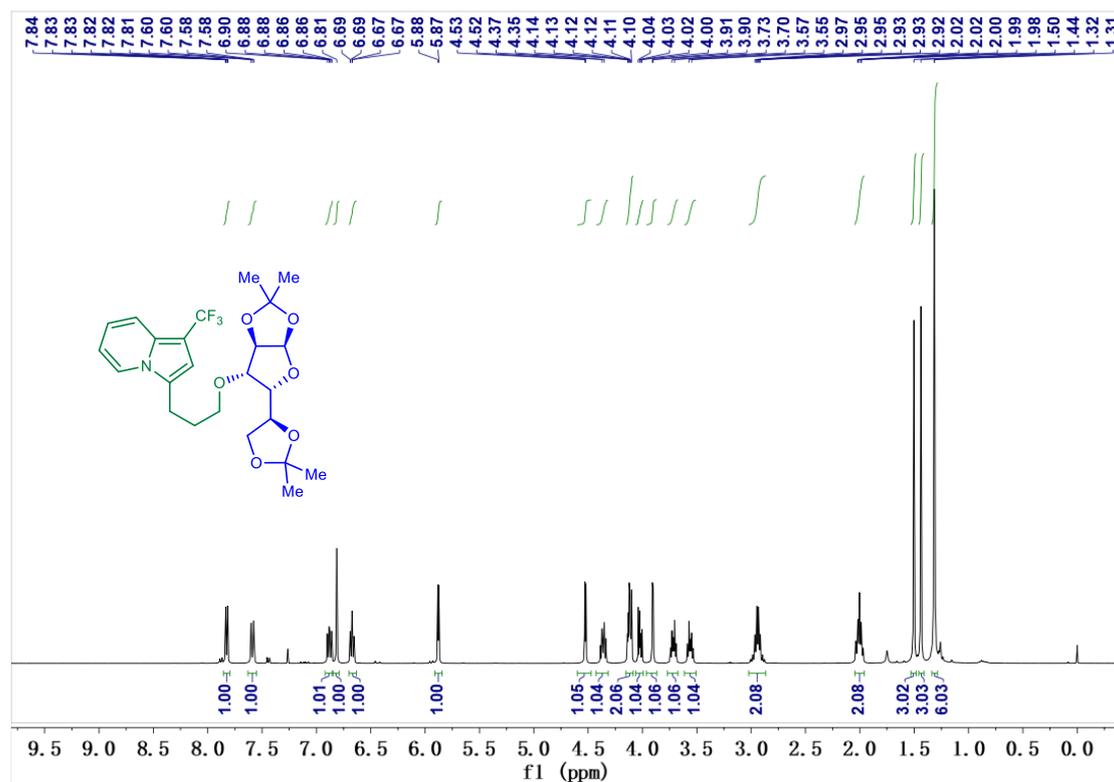
¹³C NMR spectra of compound **2p** in CDCl₃ (101 MHz):



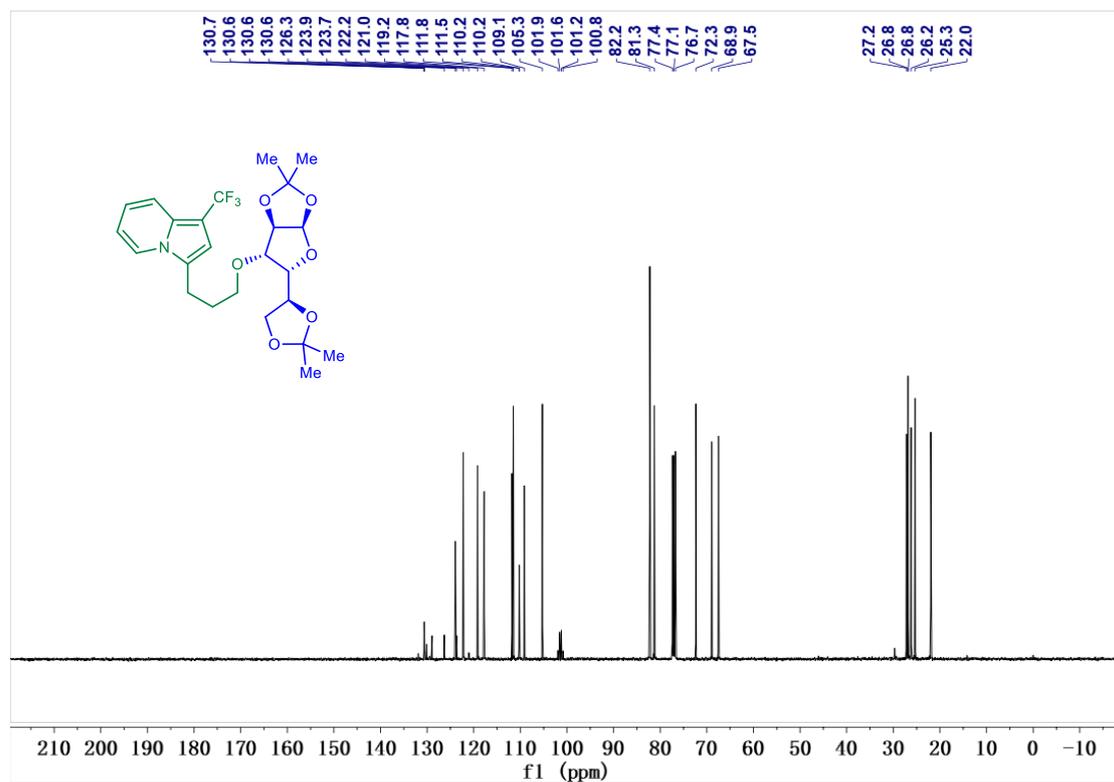
¹⁹F NMR spectra of compound **2p** in CDCl₃ (376 MHz):



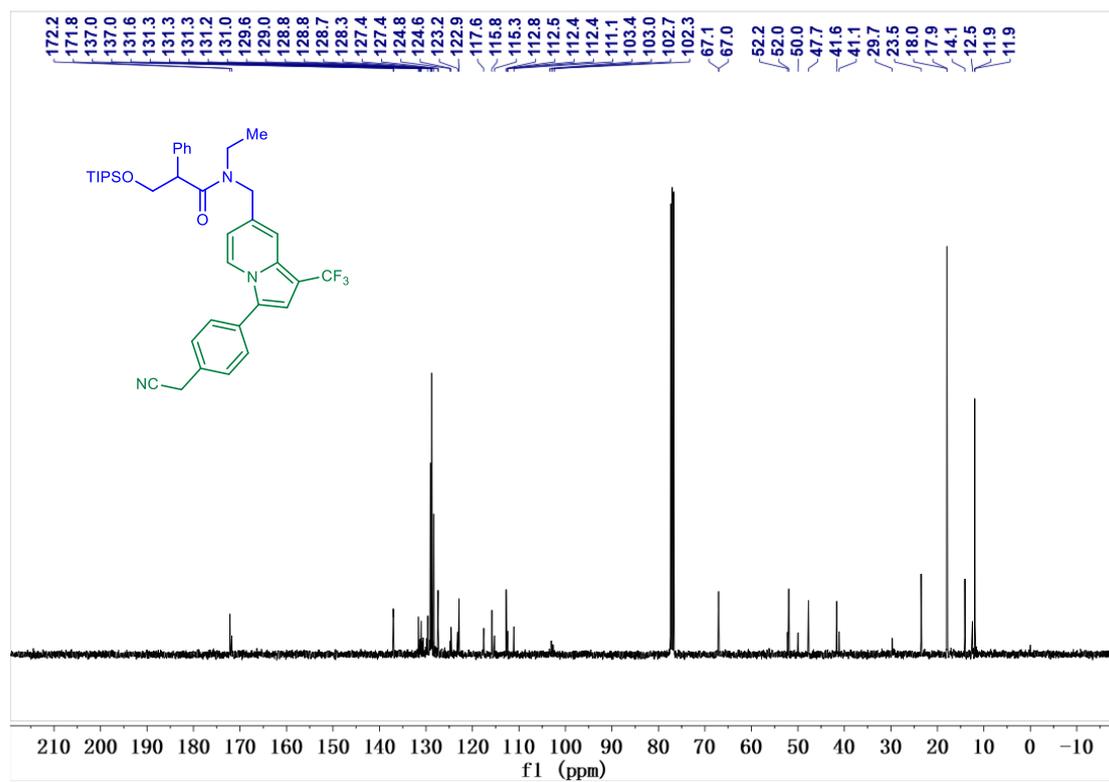
¹H NMR spectra of compound **2q** in CDCl₃ (400 MHz):



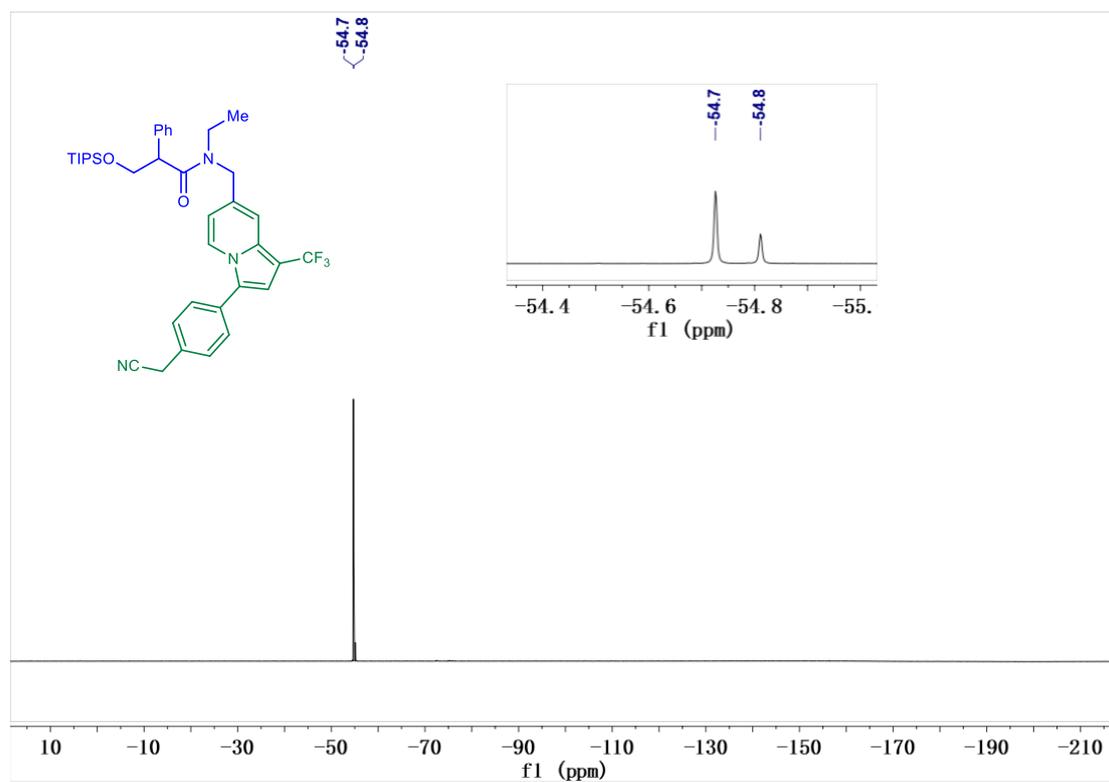
¹³C NMR spectra of compound **2q** in CDCl₃ (101 MHz):



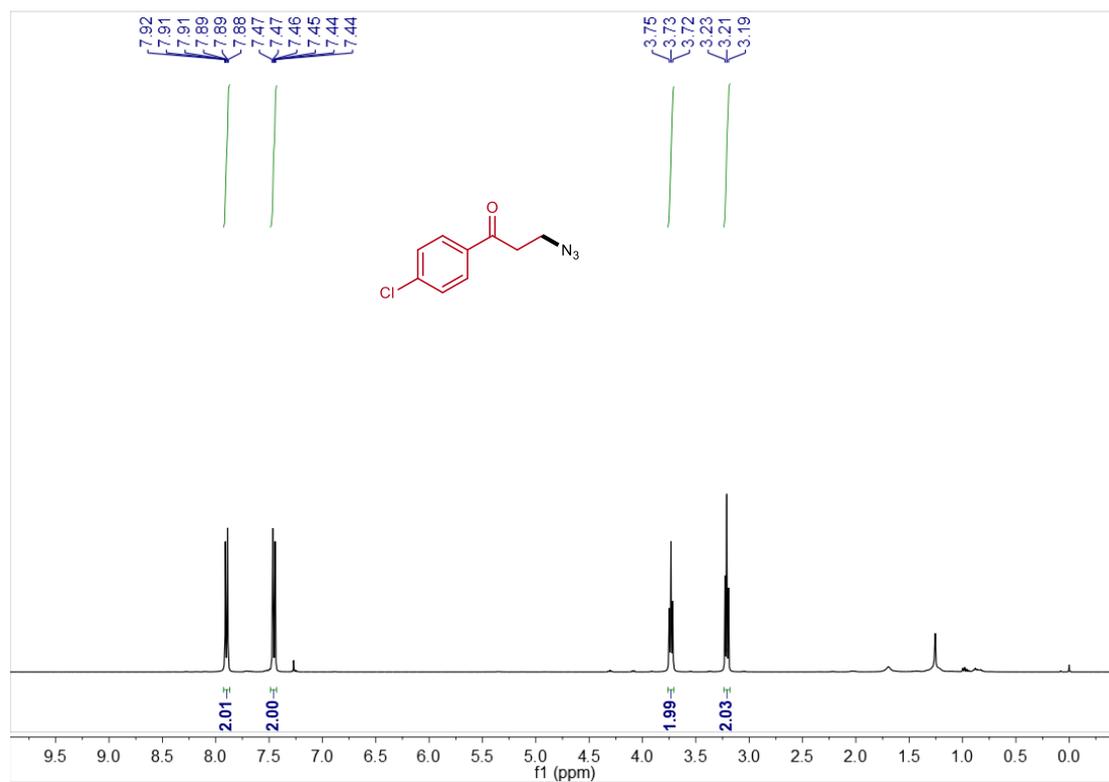
^{13}C NMR spectra of compound **2r** in CDCl_3 (101 MHz):



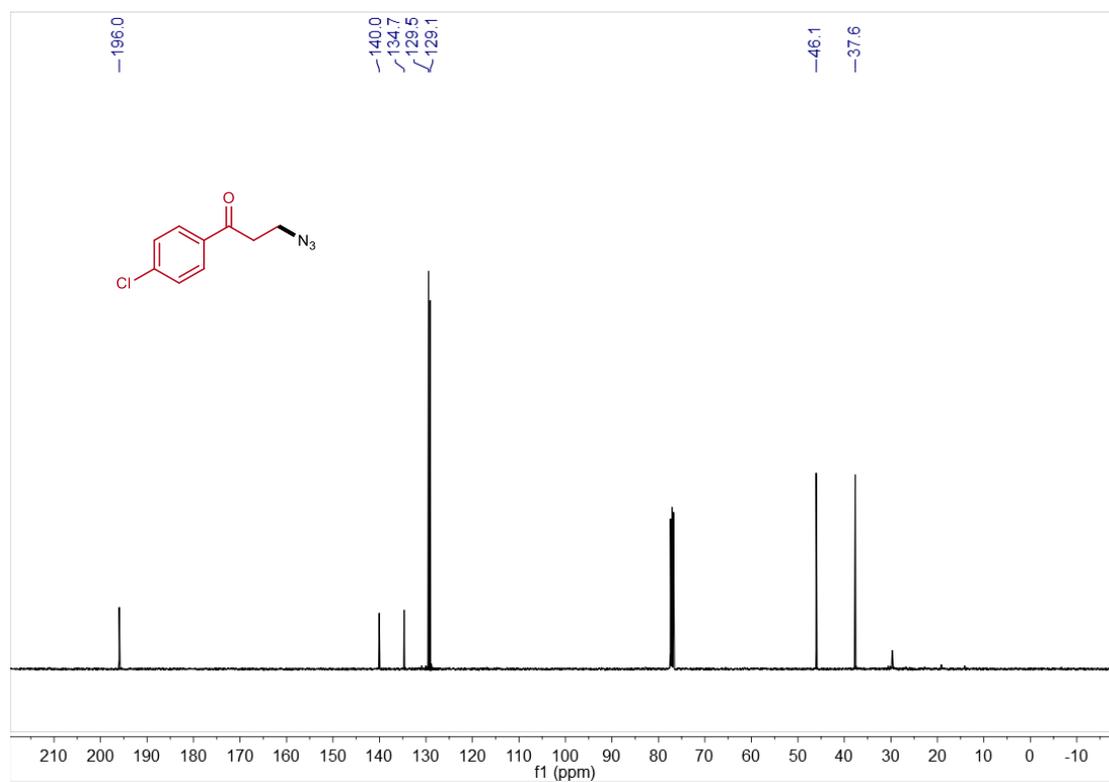
^{19}F NMR spectra of compound **2r** in CDCl_3 (376 MHz):



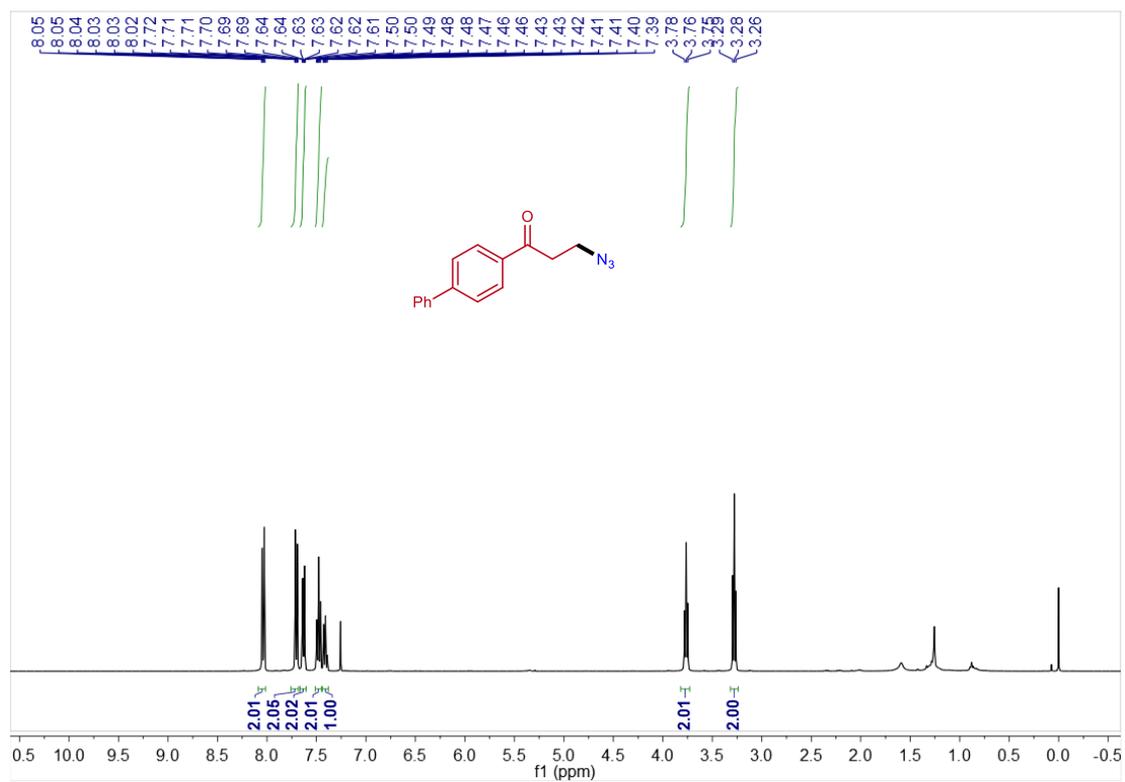
¹H NMR spectra of compound **4a** in CDCl₃ (400 MHz):



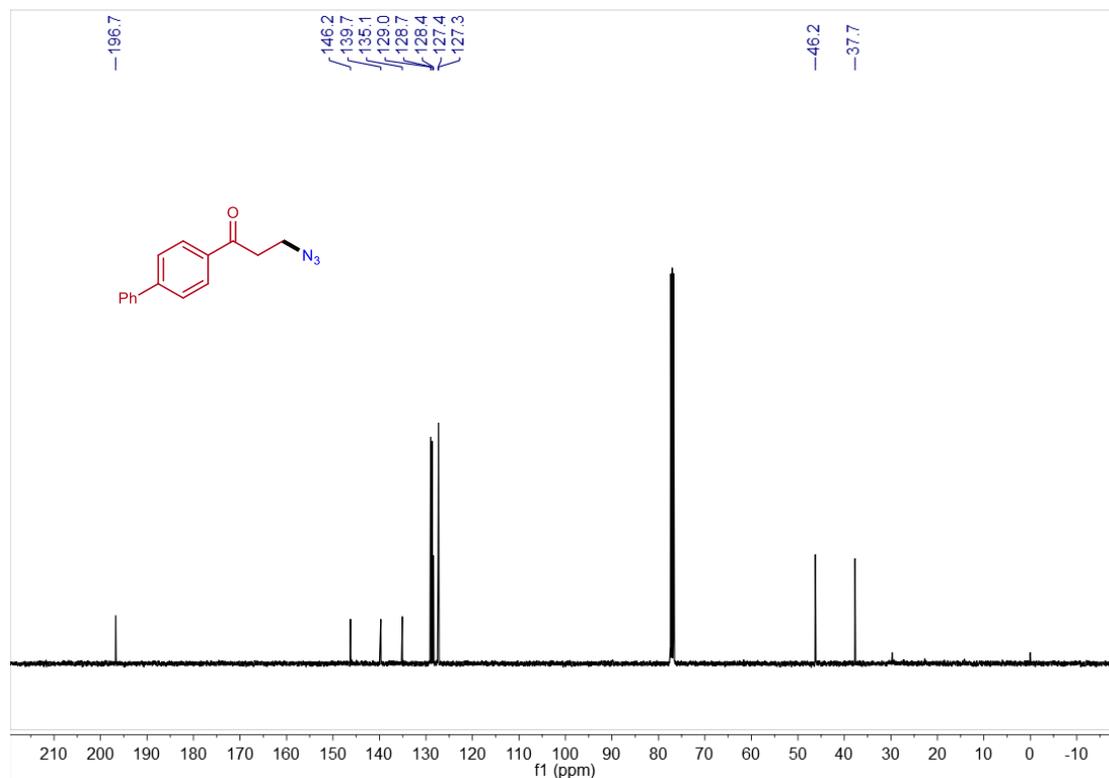
¹³C NMR spectra of compound **4a** in CDCl₃ (101 MHz):



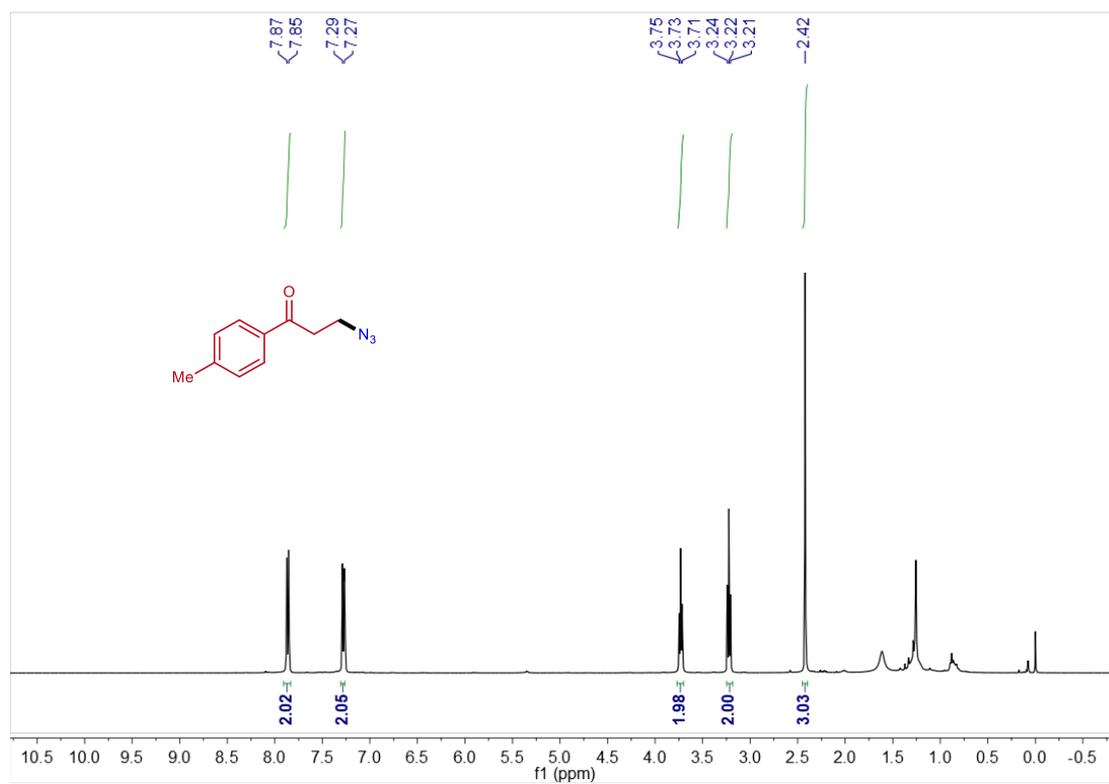
^1H NMR spectra of compound **4b** in CDCl_3 (400 MHz):



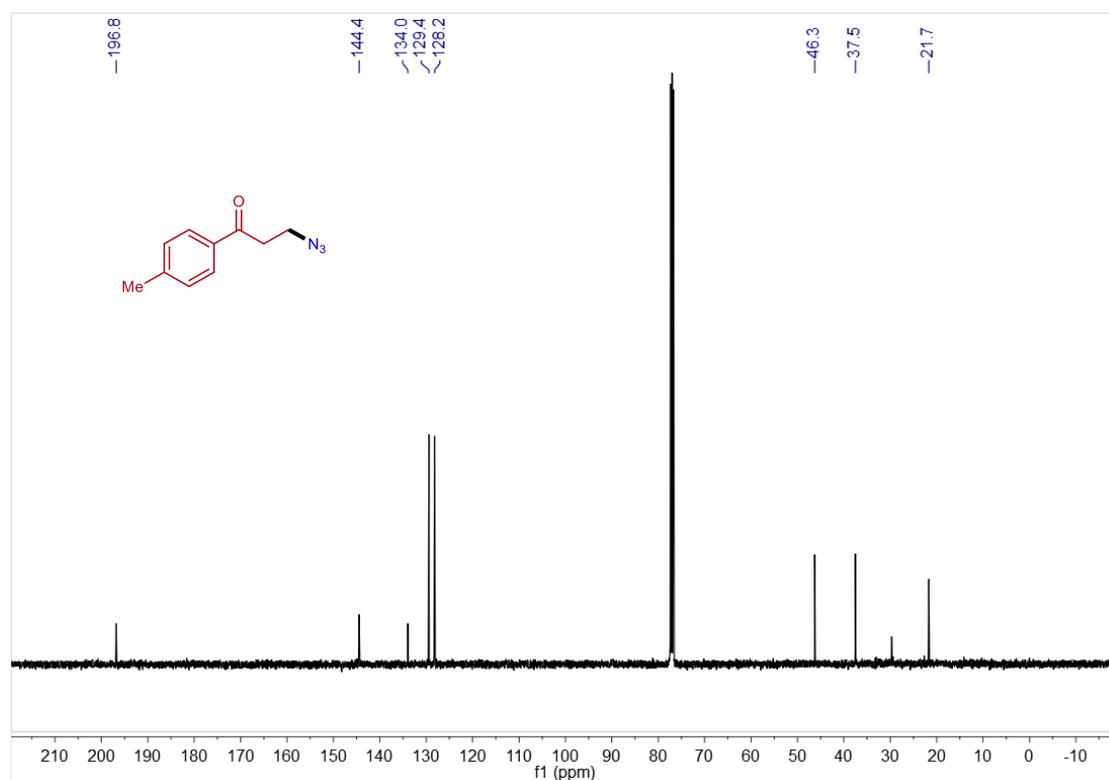
^{13}C NMR spectra of compound **4b** in CDCl_3 (101 MHz):



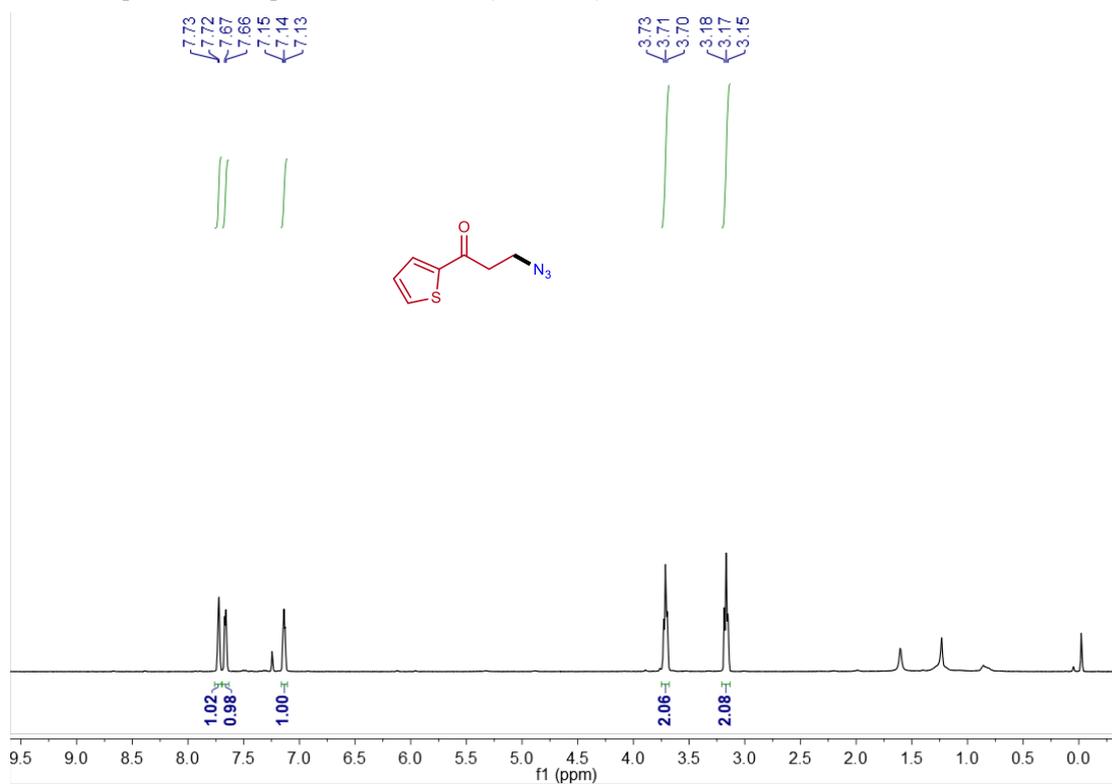
¹H NMR spectra of compound **4c** in CDCl₃ (400 MHz):



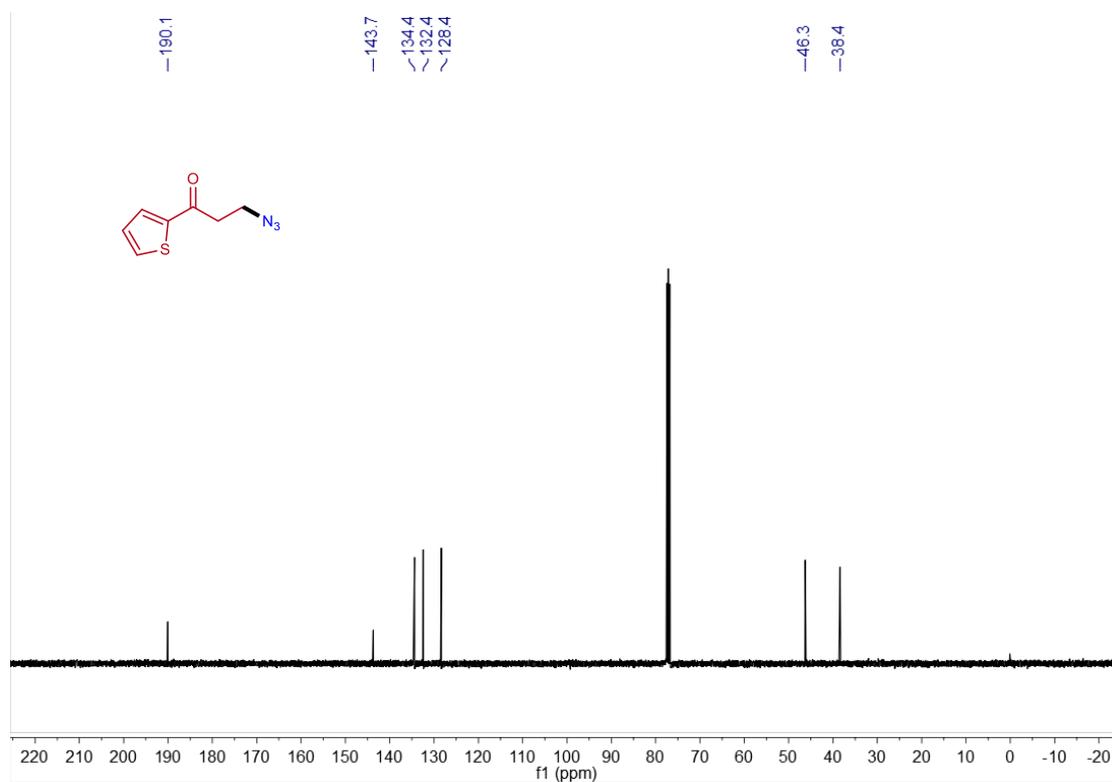
¹³C NMR spectra of compound **4c** in CDCl₃ (101 MHz):



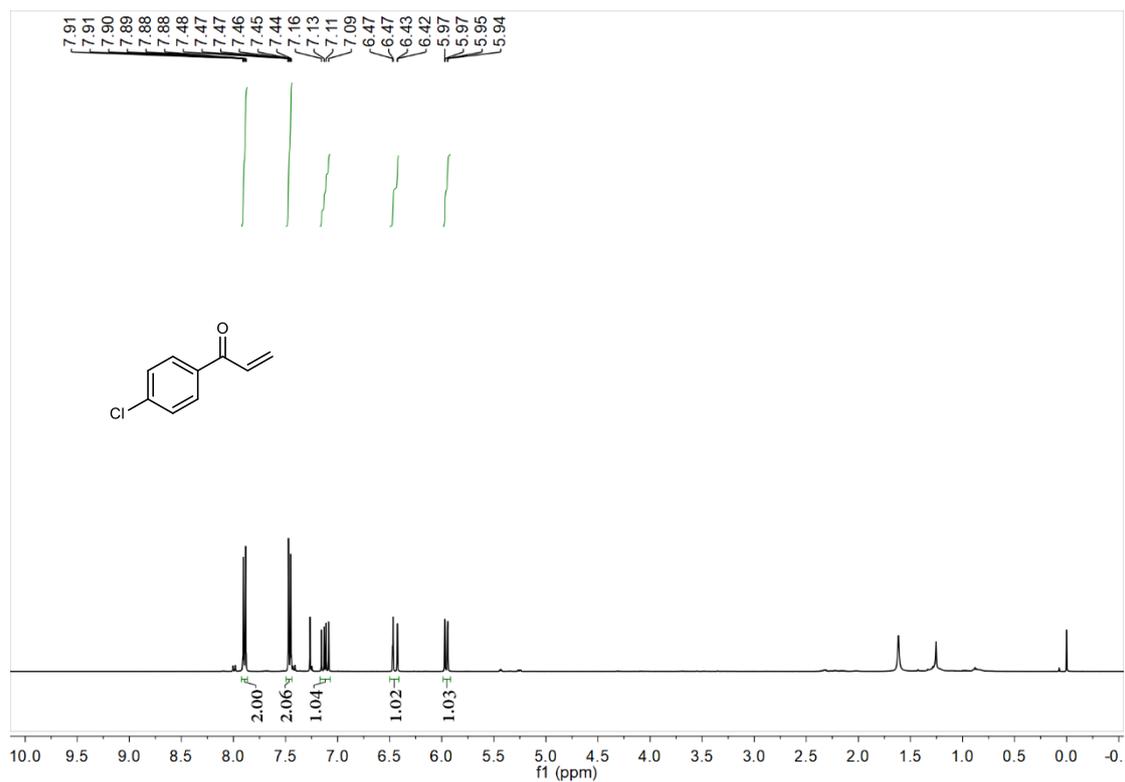
^1H NMR spectra of compound **4d** in CDCl_3 (400 MHz):



^{13}C NMR spectra of compound **4d** in CDCl_3 (101 MHz):



^1H NMR spectra of compound **3a** in CDCl_3 (400 MHz):



¹³C NMR spectra of compound **3a** in CDCl₃ (101 MHz):

