

Electronic Supplementary Information

Csp³-H bond functionalization of amines via tunable iminium ions: divergent synthesis of trifluoromethylated arylamines

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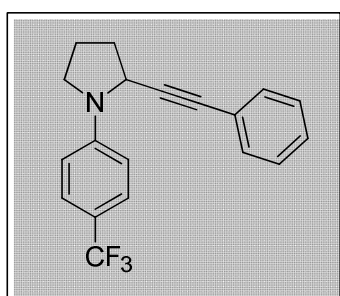
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I. General Information

All reagents were purchased from commercial sources and used without further purification. All products were monitored by TLC and purified by flash column chromatography on silica gel (300–400 mesh). Melting points were uncorrected. NMR spectra were obtained on a Bruker AVANCE 600 MHz spectrometer (600 MHz for ^1H NMR; 150 MHz for ^{13}C NMR; 565 MHz for ^{19}F NMR). ^1H NMR and ^{13}C NMR were determined with TMS as the internal standard. ^{19}F NMR was determined with $\text{C}_6\text{H}_5\text{F}$ as external reference. All chemical shifts are given in ppm. High-resolution mass spectra (HRMS) were obtained using a Bruker microTOF II focus spectrometer (ESI).

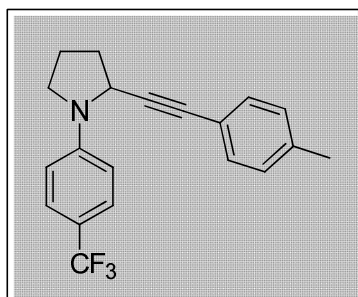
II. Experimental procedure and characterization data



4a: 2-(phenylethynyl)-1-(4-(trifluoromethyl)phenyl)pyrrolidine

To the solution of 4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone (125 mg, 0.50 mmol), phenylacetylene (138 μL , 1.25 mmol), copper(II) bromide (16.8 mg, 0.075 mmol), 4-methoxyphenol (74.4 mg, 0.6 mmol) in toluene (1 mL) in a sealed tube was added pyrrolidine (42 μL , 0.5 mmol) and reacted at 180 $^\circ\text{C}$. After 20 minutes, the reaction was cooled down to room temperature and purified by column chromatography directly on silica gel (PE/EtOAc = 60 : 1) to afford **4a** (97 mg, 61%).

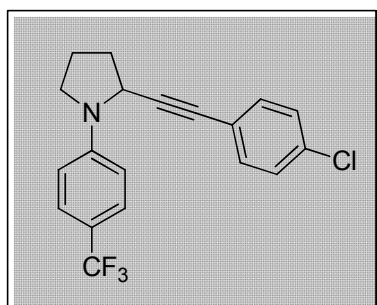
Brown liquid. ^1H NMR (600 MHz, CDCl_3): δ 7.47 (d, J = 8.4 Hz, 2H), 7.37 – 7.32 (m, 2H), 7.29 – 7.23 (m, 3H), 6.76 (d, J = 8.4 Hz, 2H), 4.63 – 4.54 (m, 1H), 3.53 – 3.44 (m, 1H), 3.37 – 3.26 (m, 1H), 2.34 – 2.21 (m, 3H), 2.14 – 2.06 (m, 1H). ^{13}C NMR (150 MHz, CDCl_3): δ 148.7, 131.7, 128.2(2), 126.3 (q, J = 3.9 Hz), 125.5 (q, J = 268.5 Hz), 122.8, 117.8 (q, J = 32.4 Hz), 116.0, 88.7, 83.1, 50.1, 47.7, 33.8, 24.2. ^{19}F NMR (565 MHz, CDCl_3) δ -60.7. IR (KBr, cm^{-1}): 3057, 2951, 2872, 2647, 2227, 1885, 1706, 1615, 1531, 1489, 1325, 1108. HRMS (ESI-TOF) Calcd for $\text{C}_{19}\text{H}_{17}\text{F}_3\text{N}$ ($\text{M}+\text{H}$) $^+$ 316.1314. Found 316.1308.



4b: 2-(*p*-tolylethynyl)-1-(4-(trifluoromethyl)phenyl)pyrrolidine

To the solution of 4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone (125 mg, 0.50 mmol), 4-ethynyltoluene (145.2 mg, 1.25 mmol), copper(II) bromide (16.8 mg, 0.075 mmol), 4-methoxyphenol (74.4 mg, 0.6 mmol) in toluene (1 mL) in a sealed tube was added pyrrolidine (42 μ L, 0.5 mmol) and reacted at 180 $^{\circ}$ C. After 20 minutes, the reaction was cooled down to room temperature and purified by column chromatography directly on silica gel (PE/EtOAc = 60 : 1) to afford **4b** (105 mg, 64%).

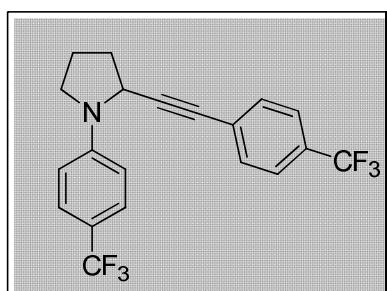
Brown liquid. $^1\text{H NMR}$ (600 MHz, CDCl_3): δ 7.46 (d, $J = 8.4$ Hz, 2H), 7.24 (d, $J = 7.8$ Hz, 2H), 7.05 (d, $J = 7.8$ Hz, 2H), 6.75 (d, $J = 8.4$ Hz, 2H), 4.57 – 4.53 (m, 1H), 3.53 – 3.44 (m, 1H), 3.36 – 3.23 (m, 1H), 2.30 (s, 3H), 2.30 – 2.22 (m, 3H), 2.17 – 2.03 (m, 1H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3): δ 148.7, 138.3, 131.6, 128.9, 126.3 (q, $J = 3.8$ Hz), 125.2 (q, $J = 268.2$ Hz), 119.7, 117.7 (q, $J = 32.4$ Hz), 111.9, 87.9, 83.2, 50.2, 47.7, 33.9, 24.2, 21.4. $^{19}\text{F NMR}$ (565 MHz, CDCl_3) δ -60.7. **IR** (KBr, cm^{-1}): 3028, 2975, 2870, 2646, 2225, 1887, 1614, 1531, 1383. **HRMS** (ESI-TOF) Calcd for $\text{C}_{20}\text{H}_{19}\text{F}_3\text{N}$ (M+H) $^+$ 330.1464. Found 330.1466.



4c: 2-((4-chlorophenyl)ethynyl)-1-(4-(trifluoromethyl)phenyl)pyrrolidine

To the solution of 4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone (125 mg, 0.50 mmol), 4-chlorophenylacetylene (145.2 mg, 1.25 mmol), copper(II) bromide (16.8 mg, 0.075 mmol), 4-methoxyphenol (74.4 mg, 0.6 mmol) in toluene (1 mL) in a sealed tube was added pyrrolidine (42 μ L, 0.5 mmol) and reacted at 180 $^{\circ}$ C. After 20 minutes, the reaction was cooled down to room temperature and purified by column chromatography directly on silica gel (PE/EtOAc = 60 : 1) to afford **4c** (93 mg, 53%).

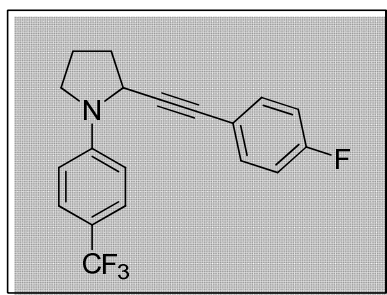
Brown liquid. $^1\text{H NMR}$ (600 MHz, CDCl_3): δ 7.47 (d, $J = 8.4$ Hz, 2H), 7.27 (d, $J = 8.4$ Hz, 2H), 7.23 (d, $J = 8.4$ Hz, 2H), 6.74 (d, $J = 8.4$ Hz, 2H), 4.62 – 4.53 (m, 1H), 3.54 – 3.45 (m, 1H), 3.40 – 3.27 (m, 1H), 2.28 (t, $J = 3.6$ Hz, 3H), 2.17 – 2.08 (m, 1H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3): δ 148.6, 134.2, 132.9, 128.5, 126.3 (q, $J = 3.6$ Hz), 125.2 (q, $J = 268.5$ Hz), 121.3, 118.0 (q, $J = 32.3$ Hz), 111.9, 89.7, 82.0, 50.1, 47.7, 33.8, 24.2. $^{19}\text{F NMR}$ (565 MHz, CDCl_3) δ -60.8. **IR** (KBr, cm^{-1}): 3056, 2976, 2854, 2647, 2227, 1889, 1704, 1615, 1530, 1488. **HRMS** (ESI-TOF) Calcd for $\text{C}_{19}\text{H}_{16}\text{ClF}_3\text{N}$ (M+H) $^+$ 350.0918. Found 350.0909.



4d: 1-(4-(trifluoromethyl)phenyl)-2-((4-(trifluoromethyl)phenyl)ethynyl)pyrrolidine

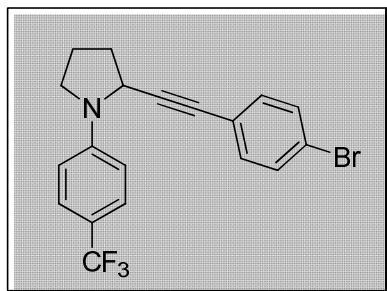
To the solution of 4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone (125 mg, 0.50 mmol), 4-(trifluoromethyl)phenylacetylene (213 mg, 1.25 mmol), copper(II) bromide (16.8 mg, 0.075 mmol), 4-methoxyphenol (74.4 mg, 0.6 mmol) in toluene (1 mL) in a sealed tube was added pyrrolidine (42 μ L, 0.5 mmol) and reacted at 180 $^{\circ}$ C. After 20 minutes, the reaction was cooled down to room temperature and purified by column chromatography directly on silica gel (PE/EtOAc = 60 : 1) to afford **4d** (105 mg, 55%).

Colorless liquid. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.51 (d, $J = 8.4$ Hz, 2H), 7.48 (d, $J = 8.4$ Hz, 2H), 7.44 (d, $J = 8.4$ Hz, 2H), 6.75 (d, $J = 8.4$ Hz, 2H), 4.59 (d, $J = 6.0$ Hz, 1H), 3.50 (m, 1H), 3.34 (m, 1H), 2.40 – 2.22 (m, 3H), 2.22 – 2.04 (m, 1H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 148.6, 132.0, 130.0 (q, $J = 32.6$ Hz), 126.6, 126.4 (q, $J = 3.6$ Hz), 125.2 (q, $J = 270.2$ Hz), 125.1 (q, $J = 3.8$ Hz), 123.9 (q, $J = 272.1$ Hz), 118.1 (q, $J = 32.6$ Hz), 111.9, 91.4, 81.8, 50.1, 47.7, 33.7, 24.2. $^{19}\text{F NMR}$ (565 MHz, CDCl_3) δ -60.8(2). **IR** (KBr, cm^{-1}): 3057, 2980, 2875, 1706, 1615, 1530, 1489, 1287, 1203. **HRMS** (ESI-TOF) Calcd for $\text{C}_{20}\text{H}_{16}\text{F}_6\text{N}$ ($\text{M}+\text{H}$) $^+$ 384.1181. Found 384.1190.

**4e: 2-((4-fluorophenyl)ethynyl)-1-(4-(trifluoromethyl)phenyl)pyrrolidine**

To the solution of 4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone (125 mg, 0.50 mmol), 4-fluorophenylacetylene (150 mg, 1.25 mmol), copper(II) bromide (16.8 mg, 0.075 mmol), 4-methoxyphenol (74.4 mg, 0.6 mmol) in toluene (1 mL) in a sealed tube was added pyrrolidine (42 μ L, 0.5 mmol) and reacted at 180 $^{\circ}$ C. After 20 minutes, the reaction was cooled down to room temperature and purified by column chromatography directly on silica gel (PE/EtOAc = 60 : 1) to afford **4e** (83 mg, 50%).

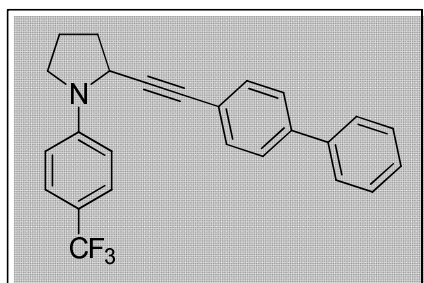
Colorless liquid. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.48 (d, $J = 8.4$ Hz, 2H), 7.39 – 7.29 (m, 2H), 6.96 (t, $J = 8.4$ Hz, 2H), 6.76 (d, $J = 8.4$ Hz, 2H), 4.57 (d, $J = 6.0$ Hz, 1H), 2.56 – 2.45 (m, 1H), 3.40 – 3.28 (m, 1H), 2.36 – 2.23 (m, 3H), 2.18 – 2.06 (m, 1H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 163.2 (d, $J = 249.5$ Hz), 148.6, 133.6 (d, $J = 8.3$ Hz), 126.3 (d, $J = 3.8$ Hz), 125.2 (d, $J = 270.0$ Hz), 118.8 (d, $J = 3.5$ Hz), 118.0 (q, $J = 32.6$ Hz), 115.5, 115.4, 111.9, 88.4, 82.0, 50.1, 47.7, 33.8, 24.2. $^{19}\text{F NMR}$ (565 MHz, CDCl_3) δ -60.8, -111.1. **IR** (KBr, cm^{-1}): 2927, 1709, 1615, 1530, 1506, 1325, 1109. **HRMS** (ESI-TOF) Calcd for $\text{C}_{19}\text{H}_{16}\text{F}_4\text{N}$ ($\text{M}+\text{H}$) $^+$ 334.1213. Found 334.1223.



4f: 2-((4-bromophenyl)ethynyl)-1-(4-(trifluoromethyl)phenyl)pyrrolidine

To the solution of 4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone (125 mg, 0.50 mmol), 4-bromophenylacetylene (226 mg, 1.25 mmol), copper(II) bromide (16.8 mg, 0.075 mmol), 4-methoxyphenol (74.4 mg, 0.6 mmol) in toluene (1 mL) in a sealed tube was added pyrrolidine (42 μ L, 0.5 mmol) and reacted at 180 $^{\circ}$ C. After 20 minutes, the reaction was cooled down to room temperature and purified by column chromatography directly on silica gel (PE/EtOAc = 50 : 1) to afford **4f** (106 mg, 54%).

Colorless liquid. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.48 (d, $J = 8.4$ Hz, 2H), 7.39 (d, $J = 8.4$ Hz, 2H), 7.21 (d, $J = 8.4$ Hz, 2H), 6.74 (d, $J = 8.4$ Hz, 2H), 4.57 (d, $J = 6.0$ Hz, 1H), 3.50 (t, $J = 8.4$ Hz, 1H), 3.34 (dd, $J = 15.4, 8.0$ Hz, 1H), 2.33 – 2.24 (m, 3H), 2.19 – 2.05 (m, 1H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 148.6, 133.1, 131.5, 126.3 (q, $J = 3.6$ Hz), 125.2 (q, $J = 270.3$ Hz), 122.4, 121.7, 118.0 (q, $J = 32.6$ Hz), 111.9, 89.9, 82.1, 50.1, 47.7, 33.8, 24.2. $^{19}\text{F NMR}$ (565 MHz, CDCl_3) δ -60.8. **IR** (KBr, cm^{-1}): 3055, 2950, 2872, 1889, 1707, 1614, 1530, 1486, 1325, 1110. **HRMS** (ESI-TOF) Calcd for $\text{C}_{19}\text{H}_{16}\text{BrF}_3\text{N}$ ($\text{M}+\text{H}$) $^+$ 394.0413. Found 394.0422.

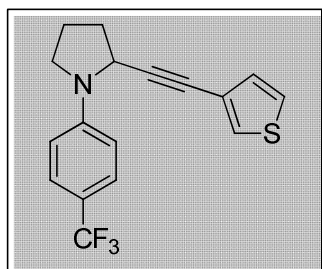


4g: 2-([1,1'-biphenyl]-4-ylethynyl)-1-(4-(trifluoromethyl)phenyl)pyrrolidine

To the solution of 4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone (125 mg, 0.50 mmol), 4-ethynyl-1,1'-biphenyl (222 mg, 1.25 mmol), copper(II) bromide (16.8 mg, 0.075 mmol), 4-methoxyphenol (74.4 mg, 0.6 mmol) in toluene (1 mL) in a sealed tube was added pyrrolidine (42 μ L, 0.5 mmol) and reacted at 180 $^{\circ}$ C. After 20 minutes, the reaction was cooled down to room temperature and purified by column chromatography directly on silica gel (PE/EtOAc = 50 : 1) to afford **4g** (84 mg, 43%).

Light yellow solid; mp: 128-129 $^{\circ}$ C; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.56 (d, $J = 7.8$ Hz, 2H), 7.53 – 7.46 (m, 4H), 7.46 – 7.40 (m, 4H), 7.34 (t, $J = 7.2$ Hz, 1H), 6.78 (d, $J = 8.4$ Hz, 2H), 4.62 (d, $J = 6.0$ Hz, 1H), 3.53 (t, $J = 6.0$ Hz, 1H), 3.43 – 3.30 (m, 1H), 2.39 – 2.25 (m, 3H), 2.21 – 2.08 (m, 1H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 148.7, 140.9, 140.3, 132.1, 128.8, 127.6, 127.0, 126.9, 126.3 (q, $J = 3.8$ Hz), 121.7, 111.9, 89.4, 83.0, 50.2, 47.7, 33.9, 24.2. $^{19}\text{F NMR}$ (565 MHz, CDCl_3) δ -60.8. **IR** (KBr, cm^{-1}): 2921, 2852, 1614, 1532, 1322, 1098. **HRMS** (ESI-TOF) Calcd for

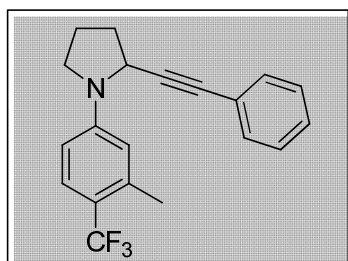
C₂₅H₂₁F₃N (M+H)⁺ 392.1621. Found 392.1618.



4h: 2-(thiophen-3-ylethynyl)-1-(4-(trifluoromethyl)phenyl)pyrrolidine

To the solution of 4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone (125 mg, 0.50 mmol), 3-ethynylthiophene (135 mg, 1.25 mmol), copper(II) bromide (16.8 mg, 0.075 mmol), 4-methoxyphenol (74.4 mg, 0.6 mmol) in toluene (1 mL) in a sealed tube was added pyrrolidine (42 μ L, 0.5 mmol) and reacted at 180 °C. After 20 minutes, the reaction was cooled down to room temperature and purified by column chromatography directly on silica gel use pure petroleum ether to afford **4h** (87 mg, 54%).

Colorless liquid. ¹H NMR (600 MHz, CDCl₃) δ 7.47 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 2.4 Hz, 1H), 7.19 (dd, *J* = 4.8, 3.0 Hz, 1H), 7.02 (d, *J* = 4.8 Hz, 1H), 6.74 (d, *J* = 8.4 Hz, 2H), 4.55 (d, *J* = 7.2 Hz, 1H), 3.55 – 3.40 (m, 1H), 3.38 – 3.23 (m, 1H), 2.39 – 2.19 (m, 3H), 2.16 – 2.01 (m, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 148.6, 129.9, 128.6, 126.3 (q, *J* = 3.6 Hz), 125.3 (q, *J* = 270.3 Hz), 125.2, 121.8, 117.8 (q, *J* = 32.6 Hz), 111.9, 88.3, 78.2, 50.1, 47.6, 33.8, 24.2. ¹⁹F NMR (565 MHz, CDCl₃) δ -60.7. IR (KBr, cm⁻¹): 3108, 2977, 2872, 2644, 2221, 1887, 1708, 1615, 1531, 1328. HRMS (ESI-TOF) Calcd for C₁₇H₁₅F₃NS (M+H)⁺ 322.0872. Found 322.0874.

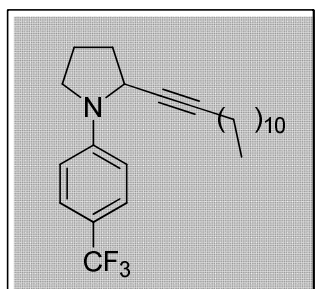


4i: 1-(3-methyl-4-(trifluoromethyl)phenyl)-2-(phenylethynyl)pyrrolidine

To the solution of 3-methyl-4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone (132 mg, 0.50 mmol), phenylacetylene (138 μ L, 1.25 mmol), copper(II) bromide (16.8 mg, 0.075 mmol), 4-methoxyphenol (74.4 mg, 0.6 mmol) in toluene (1 mL) in a sealed tube was added pyrrolidine (42 μ L, 0.5 mmol) and reacted at 180 °C. After 20 minutes, the reaction was cooled down to room temperature and purified by column chromatography directly on silica gel use pure petroleum ether to afford **4i** (89 mg, 54%).

Colorless liquid. ¹H NMR (600 MHz, CDCl₃) δ 7.45 (d, *J* = 8.4 Hz, 1H), 7.43 – 7.30 (m, 2H), 7.30 – 7.20 (m, 3H), 6.70 – 6.50 (m, 2H), 4.56 (d, *J* = 6.6 Hz, 1H), 3.59 – 3.42 (m, 1H), 3.40 – 3.25 (m, 1H), 2.44 (s, 3H), 2.37 – 2.17 (m, 3H), 2.15 – 2.00 (m, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 148.6, 137.6, 131.8, 128.3, 128.2, 127.1 (q, *J* = 5.4 Hz), 125.7 (q, *J* = 271.5 Hz), 122.9, 116.7 (q, *J* = 30.1 Hz), 115.2, 109.1, 89.0, 83.1, 50.1, 47.7, 33.9, 24.2, 19.8. ¹⁹F NMR (565 MHz, CDCl₃) δ -59.3. IR (KBr, cm⁻¹): 3061, 2977, 2873, 2623, 1706, 1613, 1376, 1314, 1117. HRMS

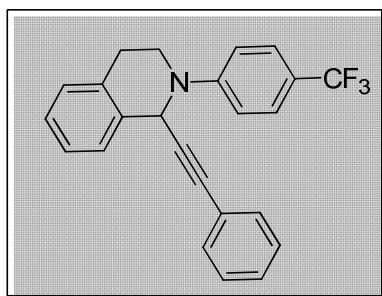
(ESI-TOF) Calcd for $C_{20}H_{19}F_3N$ (M+H)⁺ 330.1464. Found 330.1473.



4j: 1-(4-(trifluoromethyl)phenyl)-2-(undec-1-yn-1-yl)pyrrolidine

To the solution of 4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone (125 mg, 0.50 mmol), 1-tridecyne (225 mg, 1.25 mmol), copper(II) bromide (16.8 mg, 0.075 mmol), 4-methoxyphenol (74.4 mg, 0.6 mmol) in toluene (1 mL) in a sealed tube was added pyrrolidine (42 μ L, 0.5 mmol) and reacted at 180 °C. After 20 minutes, the reaction was cooled down to room temperature and purified by column chromatography directly on silica gel use pure petroleum ether to afford **4j** (82 mg, 42%).

Colorless liquid. ¹H NMR (600 MHz, CDCl₃) δ 7.45 (d, J = 8.4 Hz, 2H), 6.70 (d, J = 8.4 Hz, 2H), 4.34 (s, 1H), 3.50 – 3.40 (m, 1H), 3.28 (dd, J = 15.6, 7.8 Hz, 1H), 2.24 – 2.11 (m, 5H), 2.08 – 2.00 (m, 1H), 1.46 – 1.41 (m, 2H), 1.32 – 1.20 (m, 16H), 0.88 (t, J = 7.2 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 148.7, 126.2 (q, J = 3.8 Hz), 125.0 (q, J = 270.5 Hz), 117.7 (q, J = 32.5 Hz), 111.9, 83.6, 79.5, 49.8, 47.6, 34.1, 31.9, 29.7, 29.6, 29.5, 29.3, 29.1, 28.8, 28.7, 24.1, 22.7, 18.6, 14.1. ¹⁹F NMR (565 MHz, CDCl₃) δ -61.7. IR (KBr, cm⁻¹): 2925, 2854, 1711, 1615, 1529, 1376, 1325, 1112. HRMS (ESI-TOF) Calcd for $C_{24}H_{35}F_3N$ (M+H)⁺ 394.2716. Found 374.2712.

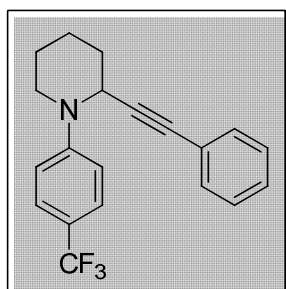


4k: 1-(phenylethynyl)-2-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydroisoquinoline

To the solution of 4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone (125 mg, 0.50 mmol), phenylacetylene (138 μ L, 1.25 mmol), copper(II) bromide (16.8 mg, 0.075 mmol), 4-methoxyphenol (74.4 mg, 0.6 mmol) in toluene (1 mL) in a sealed tube was added 1,2,3,4-tetrahydroisoquinoline (67 mg, 0.5 mmol) and reacted at 180 °C. After 20 minutes, the reaction was cooled down to room temperature and purified by column chromatography directly on silica gel (PE/EtOAc = 60 : 1) to afford **4k** (138 mg, 73%).

Colorless liquid. ¹H NMR (600 MHz, CDCl₃): δ 7.54 (d, J = 8.4 Hz, 2H), 7.38 (t, J = 4.8 Hz, 1H), 7.31 (d, J = 8.4 Hz, 2H), 7.28 – 7.18 (m, 6H), 7.09 (d, J = 8.4 Hz, 2H), 5.67 (s, 1H), 3.85 – 3.77 (m, 1H), 3.74 – 3.36 (m, 1H), 3.16 – 3.02 (m, 2H). ¹³C NMR (150 MHz, CDCl₃): δ 151.3, 134.9, 134.4, 131.7, 128.7, 128.3, 128.1, 127.5, 127.3, 126.6, 126.5 (q, J = 3.6 Hz), 124.8 (q, J = 269.0

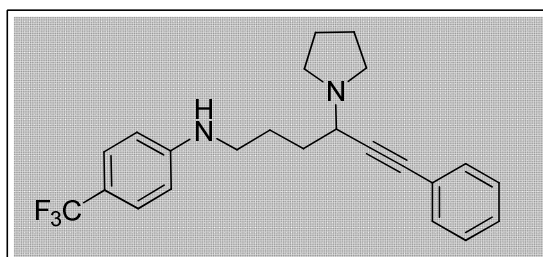
Hz), 122.6, 120.0 (q, $J = 32.6$ Hz), 114.2, 87.9, 84.4, 50.9, 43.2, 28.7. ^{19}F NMR (565 MHz, CDCl_3) δ -61.1. IR (KBr, cm^{-1}): 3027, 2924, 2849, 1616, 1525, 1380, 1328, 1112. HRMS (ESI-TOF) Calcd for $\text{C}_{24}\text{H}_{19}\text{F}_3\text{N}$ (M+H) $^+$ 378.1464. Found 378.1459.



4l: 2-(phenylethynyl)-1-(4-(trifluoromethyl)phenyl)piperidine

To the solution of 4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone (125 mg, 0.50 mmol), phenylacetylene (138 μL , 1.25 mmol), copper(II) bromide (16.8 mg, 0.075 mmol), 4-methoxyphenol (74.4 mg, 0.6 mmol) in toluene (1 mL) in a sealed tube was added piperidine (42 μL , 0.5 mmol) and reacted at 180 $^\circ\text{C}$. After 20 minutes, the reaction was cooled down to room temperature and purified by column chromatography directly on silica gel (PE/Et $_3$ N = 40 : 1) to afford **4l** (32 mg, 20%).

Colorless liquid. ^1H NMR (600 MHz, CDCl_3) δ 7.50 (d, $J = 9.0$ Hz, 2H), 7.37 – 7.33 (m, 2H), 7.28 – 7.25 (m, 3H), 7.05 (d, $J = 9.0$ Hz, 2H), 4.82 (s, 1H), 3.56 (d, $J = 12.6$ Hz, 1H), 3.21 (td, $J = 12.6, 3.0$ Hz, 1H), 2.03 (d, $J = 13.2$ Hz, 1H), 1.98 – 1.83 (m, 3H), 1.76 – 1.67 (m, 2H). ^{13}C NMR (150 MHz, CDCl_3) δ 153.4, 131.8, 128.2, 128.1, 126.2 (q, $J = 3.8$ Hz), 122.9, 116.2, 100.0, 86.7, 85.7, 49.3, 45.2, 31.2, 25.7, 20.0. ^{19}F NMR (565 MHz, CDCl_3) δ -61.4. IR (KBr, cm^{-1}): 2924, 2852, 1613, 1521, 1489, 1442, 1328, 1114. HRMS (ESI-TOF) Calcd for $\text{C}_{20}\text{H}_{19}\text{F}_3\text{N}$ (M+H) $^+$ 330.1416. Found 330.1407.

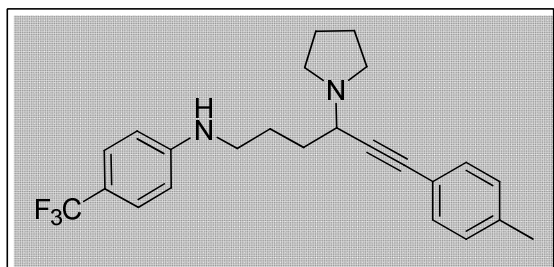


5a: N-(6-phenyl-4-(pyrrolidin-1-yl)hex-5-yn-1-yl)-4-(trifluoromethyl)aniline

To the solution of 4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone (125 mg, 0.50 mmol), phenylacetylene (99 μL , 0.9 mmol), copper(II) bromide (16.8 mg, 0.075 mmol) in toluene (1 mL) in a sealed tube was added pyrrolidine (126 μL , 1.5 mmol) and reacted at 150 $^\circ\text{C}$. After 20 minutes, the reaction was cooled down to room temperature and purified by column chromatography directly on silica gel (PE/EtOH/NEt $_3$ = 120: 6: 1) to afford **5a** (162 mg, 84%).

Brown liquid. ^1H NMR (600 MHz, CDCl_3): δ 7.41–7.38 (m, 2H), 7.37 (d, $J = 8.4$ Hz, 2H), 7.33 – 7.25 (m, 3H), 6.56 (d, $J = 8.4$ Hz, 2H), 4.38 (s, 1H), 3.74 (t, $J = 7.2$ Hz, 1H), 3.27 – 3.13 (m, 2H), 2.84 – 2.64 (m, 4H), 1.97 – 1.76 (m, 8H). ^{13}C NMR (150 MHz, CDCl_3): δ 150.7, 131.7, 128.2, 128.0, 126.5 (q, $J = 3.6$ Hz), 125.0 (q, $J = 268.1$ Hz), 118.2 (q, $J = 31.5$ Hz), 123.1, 111.6, 87.5,

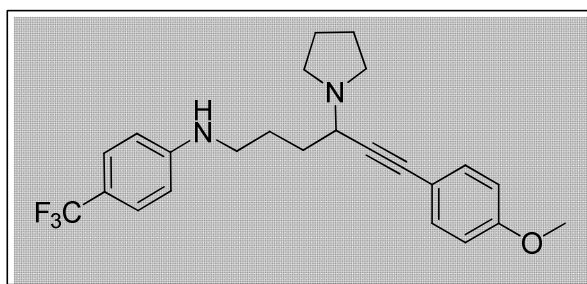
85.7, 54.5, 49.6, 43.1, 32.7, 26.2, 23.5. ^{19}F NMR (565 MHz, CDCl_3) δ -60.8. IR (KBr, cm^{-1}): 3430, 3257, 2957, 2190, 1891, 1614, 1531, 1485, 1326, 1107. HRMS (ESI-TOF) Calcd for $\text{C}_{23}\text{H}_{26}\text{F}_3\text{N}_2$ ($\text{M}+\text{H}$) $^+$ 387.2052. Found 387.2043.



5b: N-(4-(pyrrolidin-1-yl)-6-(p-tolyl)hex-5-yn-1-yl)-4-(trifluoromethyl)aniline

To the solution of 4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone (125 mg, 0.50 mmol), 4-ethynyltoluene (104.5 mg, 0.9 mmol), copper(II) bromide (16.8 mg, 0.075 mmol) in toluene (1 mL) in a sealed tube was added pyrrolidine (126 μL , 1.5 mmol) and reacted at 150 $^\circ\text{C}$. After 20 minutes, the reaction was cooled down to room temperature and purified by column chromatography directly on silica gel (PE/EtOH/ NEt_3 = 120: 6: 1) to afford **5b** (134 mg, 67%).

Brown liquid. ^1H NMR (600 MHz, CDCl_3): δ 7.36 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H), 6.55 (d, J = 8.4 Hz, 2H), 4.30 (s, 1H), 3.72 (t, J = 7.0 Hz, 1H), 3.18 (q, J = 6.6 Hz, 2H), 2.78 – 2.66 (m, 4H), 2.33 (s, 3H), 1.96 – 1.77 (m, 8H). ^{13}C NMR (150 MHz, CDCl_3): δ 150.8, 138.1, 131.6, 129.0, 126.6 (q, J = 3.8 Hz), 125.1 (q, J = 268.1 Hz), 120.0, 118.3 (q, J = 32.1 Hz), 111.6, 86.8, 85.9, 54.6, 49.7, 43.2, 32.8, 26.3, 23.6, 21.4. ^{19}F NMR (565 MHz, CDCl_3) δ -60.8. IR (KBr, cm^{-1}): 3415, 3255, 2958, 2220, 1892, 1620, 1488, 1325, 1123, 1010. HRMS (ESI-TOF) Calcd for $\text{C}_{24}\text{H}_{28}\text{F}_3\text{N}_2$ ($\text{M}+\text{H}$) $^+$ 401.2199. Found 401.2206.

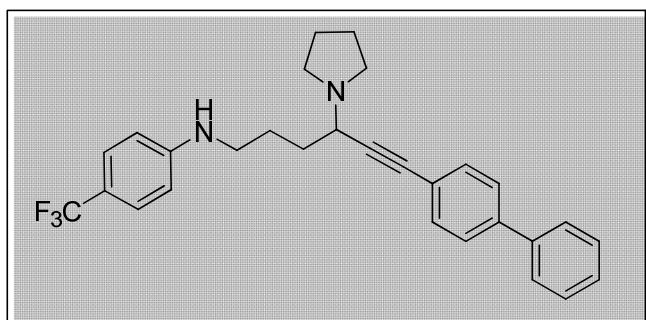


5c: N-(6-(4-methoxyphenyl)-4-(pyrrolidin-1-yl)hex-5-yn-1-yl)-4-(trifluoromethyl)aniline

To the solution of 4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone (125 mg, 0.50 mmol), 1-ethynyl-4-methoxybenzene (0.119 g, 0.9 mmol), copper(II) bromide (16.8 mg, 0.075 mmol) in toluene (1 mL) in a sealed tube was added pyrrolidine (126 μL , 1.5 mmol) and reacted at 150 $^\circ\text{C}$. After 20 minutes, the reaction was cooled down to room temperature and purified by column chromatography directly on silica gel (PE/EtOH/ NEt_3 = 120: 7: 1) to afford **5c** (171 mg, 82%).

Brown liquid. ^1H NMR (600 MHz, CDCl_3): δ 7.37 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 9.0 Hz, 2H), 6.82 (d, J = 9.0 Hz, 2H), 6.57 (d, J = 8.4 Hz, 2H), 4.39 (s, 1H), 3.80 (s, 3H), 3.77 – 3.70 (m, 1H), 3.20 (q, J = 6.0 Hz, 2H), 2.78 – 2.67 (m, 4H), 2.01 – 1.75 (m, 8H). ^{13}C NMR (150 MHz, CDCl_3): δ 159.4, 150.8, 133.1, 126.5 (q, J = 3.5 Hz), 125.3 (q, J = 268.7 Hz), 118.3 (q, J = 32.4 Hz), 115.2,

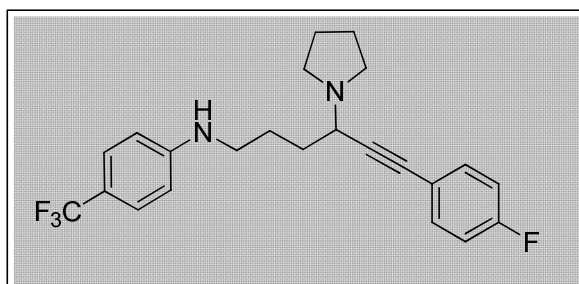
113.9, 111.6, 85.9, 85.5, 55.3, 54.6, 49.7, 43.2, 32.8, 26.2, 23.5. ^{19}F NMR (565 MHz, CDCl_3) δ -60.9. IR (KBr, cm^{-1}): 3414, 2955, 2642, 2539, 2218, 2053, 1889, 1615, 1508, 1415, 1326. HRMS (ESI-TOF) Calcd for $\text{C}_{24}\text{H}_{28}\text{F}_3\text{N}_2\text{O}$ ($\text{M}+\text{H}$) $^+$ 417.2148. Found 417.2157.



5d: *N*-(6-([1,1'-biphenyl]-4-yl)-4-(pyrrolidin-1-yl)hex-5-yn-1-yl)-4-(trifluoromethyl)aniline

To the solution of 4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone (125 mg, 0.50 mmol), 4-ethynylbiphenyl (160 mg, 0.9 mmol), copper(II) bromide (16.8 mg, 0.075 mmol) in toluene (1 mL) in a sealed tube was added pyrrolidine (126 μL , 1.5 mmol) and reacted at 150 $^\circ\text{C}$. After 20 minutes, the reaction was cooled down to room temperature and purified by column chromatography directly on silica gel (PE/EtOH/ NEt_3 = 120: 6: 1) to afford **5d** (162 mg, 70%).

Brown liquid. ^1H NMR (600 MHz, CDCl_3): δ 7.56 (d, J = 7.2 Hz, 2H), 7.54 – 7.51 (m, 2H), 7.48 – 7.42 (m, 4H), 7.40 – 7.33 (m, 3H), 6.56 (d, J = 8.4 Hz, 2H), 4.37 (s, 1H), 3.76 (t, J = 7.2 Hz, 1H), 3.25 – 3.10 (m, 2H), 2.85 – 2.65 (m, 4H), 1.99 – 1.75 (m, 8H). ^{13}C NMR (150 MHz, CDCl_3): δ 150.7, 140.8, 140.3, 132.1, 128.8, 127.6, 126.9, 127.0, 126.5 (q, J = 3.5 Hz), 125.1 (q, J = 268.4 Hz), 122.0, 118.3 (q, J = 32.3 Hz), 111.6, 88.3, 85.6, 54.6, 49.6, 43.1, 32.7, 26.2, 23.5. ^{19}F NMR (565 MHz, CDCl_3) δ -60.8. IR (KBr, cm^{-1}): 3423, 3232, 3031, 2955, 2249, 1889, 1726, 1616, 1534, 1485, 1326, 1108. HRMS (ESI-TOF) Calcd for $\text{C}_{29}\text{H}_{30}\text{F}_3\text{N}_2$ ($\text{M}+\text{H}$) $^+$ 463.2356. Found 463.2362.

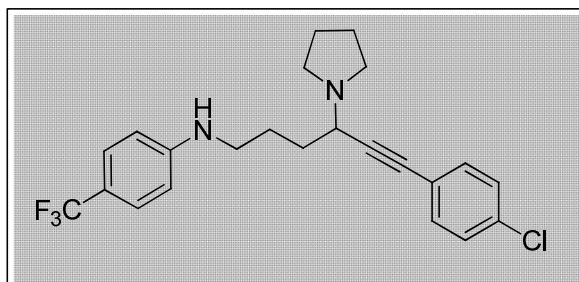


5e: *N*-(6-(4-fluorophenyl)-4-(pyrrolidin-1-yl)hex-5-yn-1-yl)-4-(trifluoromethyl)aniline

To the solution of 4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone (125 mg, 0.50 mmol), 4-fluorophenylacetylene (108 mg, 0.9 mmol), copper(II) bromide (16.8 mg, 0.075 mmol) in toluene (1 mL) in a sealed tube was added pyrrolidine (126 μL , 1.5 mmol) and reacted at 150 $^\circ\text{C}$. After 20 minutes, the reaction was cooled down to room temperature and purified by column chromatography directly on silica gel (PE/EtOH/ NEt_3 = 120: 6: 1) to afford **5e** (156 mg, 77%).

Brown liquid. ^1H NMR (600 MHz, CDCl_3): δ 7.40 – 7.33 (m, 4H), 6.97 (t, J = 8.4 Hz, 2H), 6.55 (d, J = 8.4 Hz, 2H), 4.39 (s, 1H), 3.78 – 3.66 (m, 1H), 3.18 (q, J = 6.0 Hz, 2H), 2.84 – 2.62 (m,

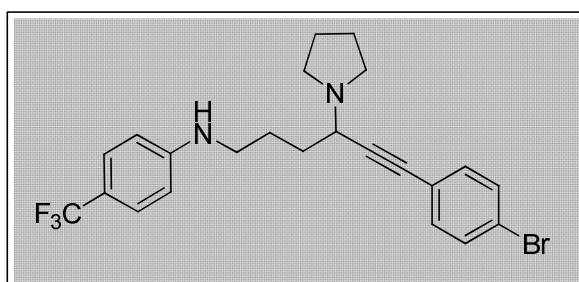
4H), 1.93 – 1.74 (m, 8H). ^{13}C NMR (150 MHz, CDCl_3): δ 162.2 (d, $J = 247.4$ Hz), 150.7, 133.4 (d, $J = 8.1$ Hz), 126.5 (q, $J = 3.6$ Hz), 125.0 (q, $J = 268.4$ Hz), 119.1 (d, $J = 3.5$ Hz), 118.2 (q, $J = 32.3$ Hz), 115.4 (d, $J = 21.8$ Hz), 111.5, 87.2, 84.6, 54.4, 49.6, 43.1, 32.6, 26.1, 23.5. ^{19}F NMR (565 MHz, CDCl_3) δ -60.8, -111.3. IR (KBr, cm^{-1}): 3428, 3259, 3046, 2958, 2875, 2280, 1890, 1617, 1535, 1506, 1326, 1109. HRMS (ESI-TOF) Calcd for $\text{C}_{23}\text{H}_{25}\text{F}_4\text{N}_2$ ($\text{M}+\text{H}$) $^+$ 405.1948. Found 405.1953.



5f: N-(6-(4-chlorophenyl)-4-(pyrrolidin-1-yl)hex-5-yn-1-yl)-4-(trifluoromethyl)aniline

To the solution of 4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone (125 mg, 0.50 mmol), 1-chloro-4-ethynylbenzene (0.122 g, 0.9 mmol), copper(II) bromide (16.8 mg, 0.075 mmol) in toluene (1 mL) in a sealed tube was added pyrrolidine (126 μL , 1.5 mmol) and reacted at 150 $^\circ\text{C}$. After 20 minutes, the reaction was cooled down to room temperature and purified by column chromatography directly on silica gel (PE/EtOH/ $\text{NEt}_3 = 120: 6: 1$) to afford **5f** (155 mg, 74%).

Brown liquid. ^1H NMR (600 MHz, CDCl_3): δ 7.37 (d, $J = 8.4$ Hz, 2H), 7.31 (d, $J = 8.4$ Hz, 2H), 7.25 (d, $J = 8.4$ Hz, 2H), 6.55 (d, $J = 8.4$ Hz, 2H), 4.38 (s, 1H), 3.79 – 3.69 (m, 1H), 3.18 (q, $J = 6.0$ Hz, 2H), 2.77 – 2.65 (m, 4H), 1.98 – 1.73 (m, 8H). ^{13}C NMR (150 MHz, CDCl_3): δ 150.7, 133.9, 132.9, 128.5, 126.5 (q, $J = 3.8$ Hz), 125.6 (q, $J = 268.7$ Hz), 121.6, 118.2 (q, $J = 32.3$ Hz), 111.5, 88.7, 84.5, 54.4, 49.6, 43.1, 32.6, 26.1, 23.5. ^{19}F NMR (565 MHz, CDCl_3) δ -60.8. IR (KBr, cm^{-1}): 3425, 2959, 2644, 2281, 1895, 1618, 1535, 1488, 1326, 1111. HRMS (ESI-TOF) Calcd for $\text{C}_{23}\text{H}_{25}\text{ClF}_3\text{N}_2$ ($\text{M}+\text{H}$) $^+$ 421.1653. Found 421.1658.

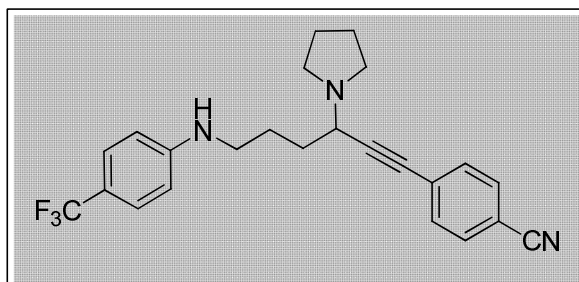


5g: N-(6-(4-bromophenyl)-4-(pyrrolidin-1-yl)hex-5-yn-1-yl)-4-(trifluoromethyl)aniline

To the solution of 4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone (125 mg, 0.50 mmol), 1-bromo-4-ethynylbenzene (0.163 g, 0.9 mmol), copper(II) bromide (16.8 mg, 0.075 mmol) in toluene (1 mL) in a sealed tube was added pyrrolidine (126 μL , 1.5 mmol) and reacted at 150 $^\circ\text{C}$. After 20 minutes, the reaction was cooled down to room temperature and purified by column chromatography directly on silica gel (PE/EtOH/ $\text{NEt}_3 = 120: 6: 1$) to afford **5g** (179 mg,

77%).

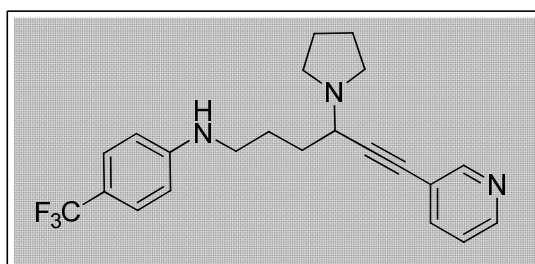
Brown liquid. $^1\text{H NMR}$ (600 MHz, CDCl_3): δ 7.42 – 7.38 (m, 2H), 7.36 (d, $J = 8.4$ Hz, 2H), 7.26 – 7.22 (m, 2H), 6.54 (d, $J = 8.4$ Hz, 2H), 4.54 (s, 1H), 3.78 – 3.70 (m, 1H), 3.20 – 3.12 (m, 2H), 2.82 – 2.64 (m, 4H), 1.92 – 1.76 (m, 8H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3): δ 150.7, 133.1, 131.4, 126.4 (q, $J = 3.6$ Hz), 125.9 (q, $J = 268.4$ Hz), 122.1, 121.9, 118.1 (q, $J = 32.3$ Hz), 111.5, 88.7, 84.7, 54.4, 49.6, 43.0, 32.4, 26.0, 23.5. $^{19}\text{F NMR}$ (565 MHz, CDCl_3) δ -60.9. **IR** (KBr, cm^{-1}): 3426, 3255, 2956, 2874, 2181, 1896, 1617, 1485, 1326, 1109. **HRMS** (ESI-TOF) Calcd for $\text{C}_{23}\text{H}_{25}\text{BrF}_3\text{N}_2$ ($\text{M}+\text{H}$) $^+$ 465.1148. Found 465.1148.



5h: 4-(3-(pyrrolidin-1-yl)-6-((4-(trifluoromethyl)phenyl)amino)hex-1-yn-1-yl)benzonitrile

To the solution of 4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone (125 mg, 0.50 mmol), 4-ethynylbenzonitrile (0.114 g, 0.9 mmol), copper(II) bromide (16.8 mg, 0.075 mmol) in toluene (1 mL) in a sealed tube was added pyrrolidine (126 μL , 1.5 mmol) and reacted at 150 $^\circ\text{C}$. After 20 minutes, the reaction was cooled down to room temperature and purified by column chromatography directly on silica gel (PE/EtOH/ $\text{NEt}_3 = 120: 6: 1$) to afford **5h** (138 mg, 67%).

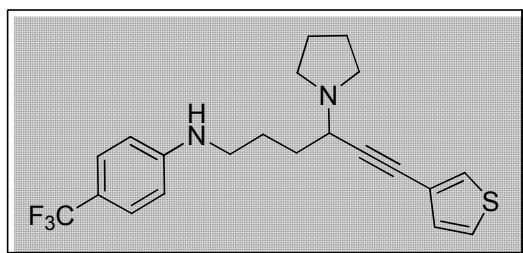
Brown liquid. $^1\text{H NMR}$ (600 MHz, CDCl_3): δ 7.56 (d, $J = 8.4$ Hz, 2H), 7.45 (d, $J = 8.4$ Hz, 2H), 7.37 (d, $J = 8.4$ Hz, 2H), 6.57 (d, $J = 8.4$ Hz, 2H), 4.55 – 4.32 (m, 1H), 3.77 (t, $J = 6.6$ Hz, 1H), 3.20 (q, $J = 5.4$ Hz, 2H), 2.81 – 2.65 (m, 4H), 1.95 – 1.76 (m, 8H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3): δ 150.7, 132.2, 131.9, 128.0, 126.4 (q, $J = 3.9$ Hz), 125.0 (q, $J = 268.5$ Hz), 118.4, 118.2 (q, $J = 32.1$ Hz), 111.5, 111.2, 92.7, 84.2, 54.4, 49.6, 43.0, 32.4, 26.0, 23.4. $^{19}\text{F NMR}$ (565 MHz, CDCl_3) δ -60.8. **IR** (KBr, cm^{-1}): 3399, 2958, 2874, 2227, 1919, 1617, 1536, 1326, 1108. **HRMS** (ESI-TOF) Calcd for $\text{C}_{24}\text{H}_{25}\text{F}_3\text{N}_3$ ($\text{M}+\text{H}$) $^+$ 412.1995. Found 412.1999.



5i: N-(6-(pyridin-3-yl)-4-(pyrrolidin-1-yl)hex-5-yn-1-yl)-4-(trifluoromethyl)aniline

To the solution of 4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone (125 mg, 0.50 mmol), 3-ethynylpyridine (0.093 g, 0.9 mmol), copper(II) bromide (16.8 mg, 0.075 mmol) in toluene (1 mL) in a sealed tube was added pyrrolidine (126 μL , 1.5 mmol) and reacted at 150 $^\circ\text{C}$. After 20 minutes, the reaction was cooled down to room temperature and purified by column chromatography directly on silica gel (PE/EtOH/ $\text{NEt}_3 = 120: 6: 1$) to afford **5i** (110 mg, 57%).

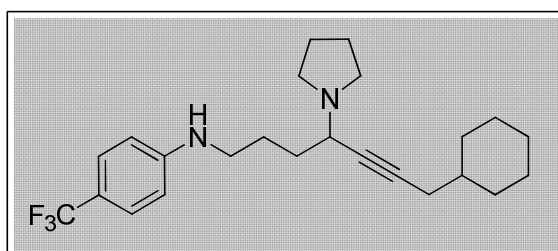
Brown liquid. $^1\text{H NMR}$ (600 MHz, CDCl_3): δ 8.65 (s, 1H), 8.50 (dd, $J = 4.8, 1.8$ Hz, 1H), 7.66 (dt, $J = 7.8, 1.8$ Hz, 1H), 7.37 (d, $J = 8.4$ Hz, 2H), 7.22 (dd, $J = 7.8, 4.8$ Hz, 1H), 6.57 (d, $J = 8.4$ Hz, 2H), 4.31 (s, 1H), 3.83 – 3.74 (m, 1H), 3.26 – 3.17 (m, 2H), 2.83 – 2.67 (m, 4H), 1.97 – 1.78 (m, 8H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3): δ 152.2, 150.7, 148.3, 138.5, 126.4 (q, $J = 3.9$ Hz), 124.8 (q, $J = 268.4$ Hz), 122.9, 120.1, 118.1 (q, $J = 32.3$ Hz), 111.5, 91.1, 82.4, 54.4, 49.6, 43.0, 32.4, 26.0, 23.4. $^{19}\text{F NMR}$ (565 MHz, CDCl_3) δ -62.8. **IR** (KBr, cm^{-1}): 3299, 2956, 2874, 2223, 1891, 1616, 1536, 1330, 1107. **HRMS** (ESI-TOF) Calcd for $\text{C}_{22}\text{H}_{25}\text{F}_3\text{N}_2$ ($\text{M}+\text{H}$) $^+$ 388.1995. Found 388.2002.



5j: N-(4-(pyrrolidin-1-yl)-6-(thiophen-3-yl)hex-5-yn-1-yl)-4-(trifluoromethyl)anilin

To the solution of 4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone (125 mg, 0.50 mmol), 3-ethynylthiophene (0.097 g, 0.9 mmol), copper(II) bromide (16.8 mg, 0.075 mmol) in toluene (1 mL) in a sealed tube was added pyrrolidine (126 μL , 1.5 mmol) and reacted at 150 $^\circ\text{C}$. After 20 minutes, the reaction was cooled down to room temperature and purified by column chromatography directly on silica gel (PE/EtOH/ $\text{NEt}_3 = 120: 6: 1$) to afford **5j** (177 mg, 78%).

Brown liquid. $^1\text{H NMR}$ (600 MHz, CDCl_3): δ 7.41 – 7.34 (m, 3H), 7.23 (dd, $J = 4.8, 3.0$ Hz, 1H), 7.06 (d, $J = 4.8$ Hz, 1H), 6.55 (d, $J = 8.4$ Hz, 2H), 4.38 (s, 1H), 3.78 – 3.68 (m, 1H), 3.24 – 3.11 (m, 2H), 2.83 – 2.61 (m, 4H), 1.94 – 1.76 (m, 8H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3): δ 150.7, 130.0, 128.3, 126.5 (q, $J = 3.5$ Hz), 125.9 (q, $J = 268.7$ Hz), 125.2, 122.0, 118.3 (q, $J = 3.5$ Hz), 111.5, 87.1, 80.6, 54.5, 49.6, 43.1, 32.7, 26.2, 23.5. $^{19}\text{F NMR}$ (565 MHz, CDCl_3) δ -60.8. **IR** (KBr, cm^{-1}): 3422, 3259, 3108, 2955, 2874, 2221, 1889, 1616, 1535, 1327, 1110. **HRMS** (ESI-TOF) Calcd for $\text{C}_{21}\text{H}_{24}\text{F}_3\text{N}_2\text{S}$ ($\text{M}+\text{H}$) $^+$ 393.1607. Found 393.1612.

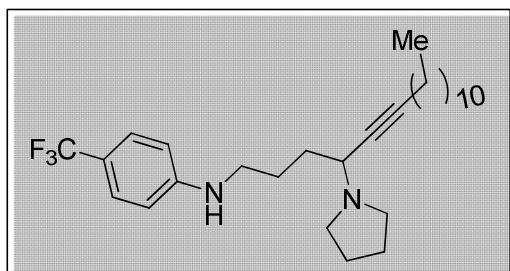


5k: N-(7-cyclohexyl-4-(pyrrolidin-1-yl)hept-5-yn-1-yl)-4-(trifluoromethyl)aniline

To the solution of 4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone (125 mg, 0.50 mmol), 3-cyclohexyl-propyne (0.110 g, 0.9 mmol), copper(II) bromide (16.8 mg, 0.075 mmol) in toluene (1 mL) in a sealed tube was added pyrrolidine (126 μL , 1.5 mmol) and reacted at 150 $^\circ\text{C}$. After 20 minutes, the reaction was cooled down to room temperature and purified by column chromatography directly on silica gel (PE/EtOH/ $\text{NEt}_3 = 120: 3: 1$) to afford **5k** (128 mg, 63%).

Brown liquid. $^1\text{H NMR}$ (600 MHz, CDCl_3): δ 7.37 (d, $J = 8.4$ Hz, 2H), 6.55 (d, $J = 8.4$ Hz, 2H), 4.41 (s, 1H), 3.55 – 3.42 (m, 1H), 3.15 (d, $J = 7.2$ Hz, 2H), 2.76 – 2.52 (m, 4H), 2.09 (d, $J = 6.6$

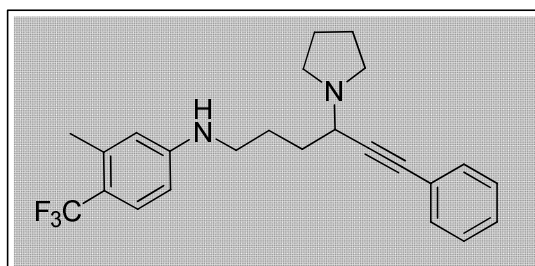
Hz, 2H), 1.90 – 1.83 (m, 1H), 1.82 – 1.68 (m, 11H), 1.68 – 1.61 (m, 1H), 1.48 – 1.37 (m, 1H), 1.32 – 1.18 (m, 2H), 1.18 – 1.06 (m, 1H), 1.05 – 0.92 (m, 2H). ^{13}C NMR (150 MHz, CDCl_3): δ 150.8, 126.5 (q, $J = 3.9$ Hz), 125.0 (q, $J = 268.5$ Hz), 118.1 (q, $J = 32.4$ Hz), 111.5, 84.4, 78.6, 54.2, 49.5, 43.2, 37.5, 33.1, 32.7, 26.5, 26.3, 26.2, 26.1, 23.5. ^{19}F NMR (565 MHz, CDCl_3) δ -60.9. IR (KBr, cm^{-1}): 3256, 2925, 2222, 1887, 1725, 1617, 1536, 1326, 1111. HRMS (ESI-TOF) Calcd for $\text{C}_{24}\text{H}_{34}\text{F}_3\text{N}_2$ ($\text{M}+\text{H}$) $^+$ 407.2669. Found 407.2686.



5l: N-(4-(pyrrolidin-1-yl)heptadec-5-yn-1-yl)-4-(trifluoromethyl)aniline

To the solution of 4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone (125 mg, 0.50 mmol), 1-tridecyne (0.162 g, 0.9 mmol), copper(II) bromide (16.8 mg, 0.075 mmol) in toluene (1 mL) in a sealed tube was added pyrrolidine (126 μL , 1.5 mmol) and reacted at 150 $^\circ\text{C}$. After 20 minutes, the reaction was cooled down to room temperature and purified by column chromatography directly on silica gel (PE/EtOH/ $\text{NEt}_3 = 120: 3: 1$) to afford **5l** (148 mg, 64%).

Brown liquid. ^1H NMR (600 MHz, CDCl_3): δ 7.37 (d, $J = 8.4$ Hz, 2H), 6.55 (d, $J = 8.4$ Hz, 2H), 4.41 (s, 1H), 3.54 – 3.44 (m, 1H), 3.19 – 3.10 (m, 2H), 2.73 – 2.56 (m, 4H), 2.23 – 2.16 (m, 2H), 1.92 – 1.83 (m, 1H), 1.82 – 1.68 (m, 7H), 1.54 – 1.45 (m, 2H), 1.43 – 1.33 (m, 2H), 1.33 – 1.20 (m, 14H), 0.88 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3): δ 150.8, 126.4 (q, $J = 3.9$ Hz), 125.0 (q, $J = 268.2$ Hz), 118.2 (q, $J = 32.3$ Hz), 111.5, 85.7, 76.8, 54.1, 49.4, 43.2, 33.0, 31.9, 29.6(2), 29.5, 29.3, 29.1, 29.0, 28.8, 26.2, 23.5, 22.6, 18.6, 14.0. ^{19}F NMR (565 MHz, CDCl_3) δ -60.9. IR (KBr, cm^{-1}): 3428, 2926, 2855, 1618, 1535, 1327, 1111. HRMS (ESI-TOF) Calcd for $\text{C}_{28}\text{H}_{44}\text{F}_3\text{N}_2$ ($\text{M}+\text{H}$) $^+$ 465.3451 Found 465.3463.

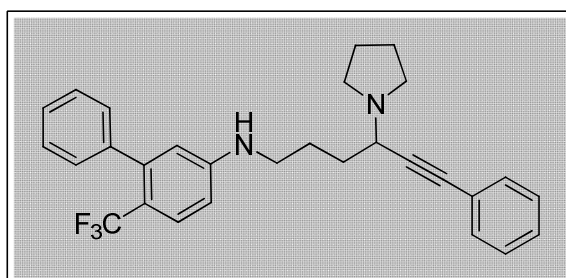


5m: 3-methyl-N-(6-phenyl-4-(pyrrolidin-1-yl)hex-5-yn-1-yl)-4-(trifluoromethyl)aniline

To the solution of 3-methyl-4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone (132 mg, 0.50 mmol), phenylacetylene (99 μL , 0.9 mmol), copper(II) bromide (16.8 mg, 0.075 mmol) in toluene (1 mL) in a sealed tube was added pyrrolidine (126 μL , 1.5 mmol) and reacted at 150 $^\circ\text{C}$. After 20 minutes, the reaction was cooled down to room temperature and purified by column chromatography directly on silica gel (PE/EtOH/ $\text{NEt}_3 = 120: 6: 1$) to afford **5m** (136 mg, 68%).

Brown liquid. ^1H NMR (600 MHz, CDCl_3): δ 7.42 – 7.38 (m, 2H), 7.35 (d, $J = 8.4$ Hz, 1H), 7.29

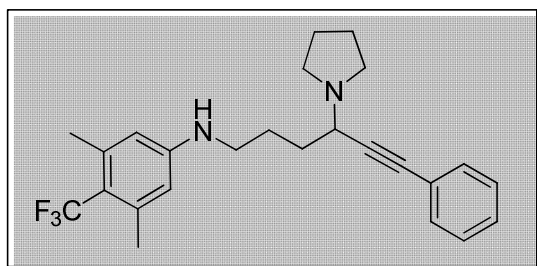
– 7.25 (m, 3H), 6.38 (s, 1H), 6.36 (d, $J = 8.4$ Hz, 1H), 4.47 – 4.04 (m, 1H), 3.73 (t, $J = 6.6$ Hz, 1H), 3.17 (t, $J = 7.8$ Hz, 2H), 2.80 – 2.66 (m, 4H), 2.36 (s, 3H), 1.93 – 1.78 (m, 8H). ^{13}C NMR (150 MHz, CDCl_3): δ 150.5, 137.8, 131.6, 128.2, 128.0, 127.2 (q, $J = 5.6$ Hz), 125.4 (q, $J = 270.0$ Hz), 123.1, 116.8 (q, $J = 30.0$ Hz), 114.9, 108.4, 87.5, 85.7, 54.5, 49.6, 43.1, 32.6, 26.2, 23.5, 19.5 (d, $J = 2.25$ Hz). ^{19}F NMR (565 MHz, CDCl_3) δ -59.4. IR (KBr, cm^{-1}): 3421, 3261, 2957, 2874, 2225, 1882, 1614, 1313, 1114. HRMS (ESI-TOF) Calcd for $\text{C}_{24}\text{H}_{28}\text{F}_3\text{N}_2$ (M+H) $^+$ 401.2199. Found 401.2198.



5n: *N*-(6-phenyl-4-(pyrrolidin-1-yl)hex-5-yn-1-yl)-6-(trifluoromethyl)-[1,1'-biphenyl]-3-amine

To the solution of 6-(trifluoromethyl)-6-((trimethylsilyl)oxy)-[1,1'-biphenyl]-3(6*H*)-one (163 mg, 0.50 mmol), phenylacetylene (99 μL , 0.9 mmol), copper(II) bromide (16.8 mg, 0.075 mmol) in toluene (1 mL) in a sealed tube was added pyrrolidine (126 μL , 1.5 mmol) and reacted at 150 $^\circ\text{C}$. After 20 minutes, the reaction was cooled down to room temperature and purified by column chromatography directly on silica gel (PE/EtOH/ $\text{NEt}_3 = 120: 6: 1$) to afford **5n** (120 mg, 52%).

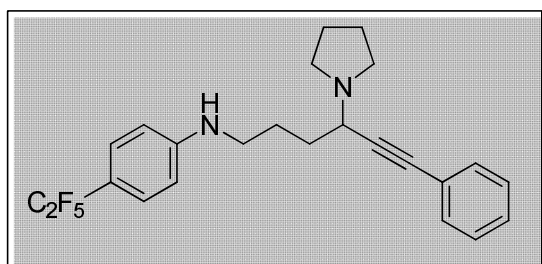
Brown liquid. ^1H NMR (600 MHz, CDCl_3): δ 7.47 (d, $J = 9.0$ Hz, 1H), 7.39 – 7.26 (m, 10H), 6.53 (d, $J = 9.0$ Hz, 1H), 6.41 (s, 1H), 4.38 (s, 1H), 3.71 (t, $J = 6.6$ Hz, 1H), 3.18 (q, $J = 5.4$ Hz, 2H), 2.82 – 2.60 (m, 4H), 1.96 – 1.75 (m, 8H). ^{13}C NMR (150 MHz, CDCl_3): δ 150.0, 142.7, 140.6, 131.6, 128.7, 128.2, 128.0, 127.6 (q, $J = 3.6$ Hz), 127.2, 125.0 (q, $J = 270.3$ Hz), 123.0, 116.6 (q, $J = 30.3$ Hz), 115.0, 110.1, 87.5, 85.7, 54.5, 49.6, 43.1, 32.6, 26.2, 23.5. ^{19}F NMR (565 MHz, CDCl_3) δ -54.8. IR (KBr, cm^{-1}): 3423, 3254, 3056, 2955, 2874, 2248, 1886, 1611, 1488, 1308, 1122. HRMS (ESI-TOF) Calcd for $\text{C}_{29}\text{H}_{30}\text{F}_3\text{N}_2$ (M+H) $^+$ 463.2356. Found 463.2350.



5o: 3,5-dimethyl-*N*-(6-phenyl-4-(pyrrolidin-1-yl)hex-5-yn-1-yl)-4-(trifluoromethyl)aniline

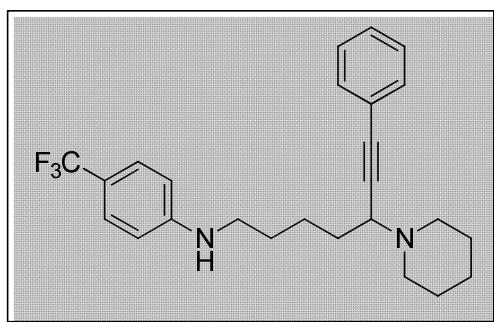
To the solution of 3,5-dimethyl-4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone (139 mg, 0.50 mmol), phenylacetylene (99 μL , 0.9 mmol), copper(II) bromide (16.8 mg, 0.075 mmol) in toluene (1 mL) in a sealed tube was added pyrrolidine (126 μL , 1.5 mmol) and reacted at 150 $^\circ\text{C}$. After 20 minutes, the reaction was cooled down to room temperature and purified by column chromatography directly on silica gel (PE/EtOH/ $\text{NEt}_3 = 120: 6: 1$) to afford **5o** (139 mg, 67%).

Brown liquid. $^1\text{H NMR}$ (600 MHz, CDCl_3): δ 7.43 – 7.37 (m, 2H), 7.30 – 7.24 (m, 3H), 6.21 (s, 2H), 4.12 (s, 1H), 3.78 – 3.69 (m, 1H), 3.16 (t, $J = 6.6$ Hz, 2H), 2.84 – 2.65 (m, 4H), 2.36 (q, $J = 3.6$ Hz, 6H), 1.92 – 1.77 (m, 8H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3): δ 149.5, 138.7 (q, $J = 2.3$ Hz), 131.6, 128.2, 128.0, 126.7 (q, $J = 272.4$ Hz), 123.1, 115.6 (q, $J = 28.5$ Hz), 113.1, 87.6, 85.7, 54.5, 49.6, 42.9, 32.6, 26.3, 23.5, 21.6 (q, $J = 4.1$ Hz). $^{19}\text{F NMR}$ (565 MHz, CDCl_3) δ -51.9. **IR** (KBr, cm^{-1}): 3417, 2935, 2874, 1608, 1295, 1140, 1094, 1030. **HRMS** (ESI-TOF) Calcd for $\text{C}_{25}\text{H}_{30}\text{F}_3\text{N}_2$ ($\text{M}+\text{H}^+$) 415.2356. Found 415.2363.



5p: 4-(perfluoroethyl)-N-(6-phenyl-4-(pyrrolidin-1-yl)hex-5-yn-1-yl)aniline

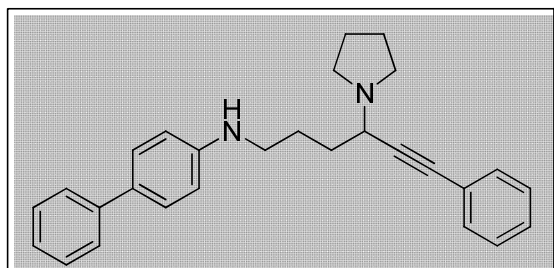
To the solution of 4-(perfluoroethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone (150 mg, 0.50 mmol), phenylacetylene (99 μL , 0.9 mmol), copper(II) bromide (16.8 mg, 0.075 mmol) in toluene (1 mL) in a sealed tube was added pyrrolidine (126 μL , 1.5 mmol) and reacted at 150 $^\circ\text{C}$. After 20 minutes, the reaction was cooled down to room temperature and purified by column chromatography directly on silica gel (PE/EtOH/ $\text{NEt}_3 = 120: 7: 1$) to afford **5p** (73 mg, 40%). Brown liquid. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.43 – 7.38 (m, 2H), 7.33 (d, $J = 8.4$ Hz, 2H), 7.30 – 7.27 (m, 3H), 6.58 (d, $J = 8.4$ Hz, 2H), 4.42 (s, 1H), 3.75 (t, $J = 7.2$ Hz, 1H), 3.20 (s, 2H), 2.74 (dd, $J = 37.8, 7.8$ Hz, 4H), 1.98 – 1.77 (m, 8H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 150.9, 131.7, 128.2, 128.0, 127.6 (t, $J = 6.0$ Hz), 123.1, 119.4 (tq, $J_1 = 286.0$ Hz, $J_2 = 36.9$ Hz), 114.8 (tq, $J_1 = 250.3$ Hz, $J_2 = 36.6$ Hz), 111.7, 87.6, 85.7, 54.5, 49.6, 43.1, 32.7, 26.2, 23.5. $^{19}\text{F NMR}$ (565 MHz, CDCl_3) δ -85.0, -113.2. **IR** (KBr, cm^{-1}): 3421, 3033, 2955, 2874, 1615, 1530, 1287, 1203, 1087. **HRMS** (ESI-TOF) Calcd for $\text{C}_{24}\text{H}_{26}\text{F}_5\text{N}_2$ ($\text{M}+\text{H}^+$) 436.1938. Found 436.1930.



5q: N-(7-phenyl-5-(piperidin-1-yl)hept-6-yn-1-yl)-4-(trifluoromethyl)aniline

To the solution of 4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone (125 mg, 0.50 mmol), phenylacetylene (99 μL , 0.9 mmol), copper(II) bromide (16.8 mg, 0.075 mmol) in toluene (1 mL) in a sealed tube was added piperidine (127 μL , 1.5 mmol) and reacted at 150 $^\circ\text{C}$. After 20 minutes, the reaction was cooled down to room temperature and purified by column chromatography directly on silica gel (PE/EtOH/ $\text{NEt}_3 = 120: 5: 1$) to afford **5q** (60 mg, 29%). Brown liquid. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.42 (d, $J = 8.4$ Hz, 2H), 7.37 (d, $J = 8.4$ Hz, 2H),

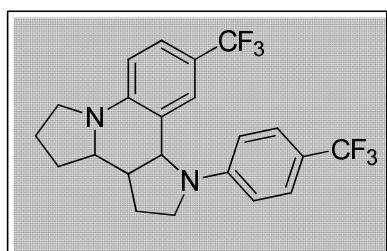
7.32 – 7.27 (m, 3H), 6.56 (d, $J = 8.4$ Hz, 2H), 3.98 (s, 1H), 3.50 (dd, $J = 12.6, 6.6$ Hz, 1H), 3.16 (dd, $J = 12.4, 6.6$ Hz, 2H), 2.75 – 2.60 (m, 2H), 2.55 – 2.42 (m, 2H), 1.82 – 1.73 (m, 2H), 1.70 – 1.55 (m, 8H), 1.50 – 1.41 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 150.7, 131.7, 128.2, 127.9, 126.5 (q, $J = 3.6$ Hz), 125.0 (q, $J = 270.1$ Hz), 123.3, 118.4 (q, $J = 32.6$ Hz), 111.6, 87.7, 85.9, 58.4, 43.3, 33.0, 28.9, 26.2, 24.5, 24.3. ^{19}F NMR (565 MHz, CDCl_3) δ -60.4. IR (KBr, cm^{-1}): 3423, 3057, 2934, 2858, 2805, 2750, 1888, 1725, 1617, 1327, 1109. HRMS (ESI-TOF) Calcd for $\text{C}_{25}\text{H}_{30}\text{F}_3\text{N}_2$ (M+H) $^+$ 415.2356. Found 415.2349.



5r: N-(6-phenyl-4-(pyrrolidin-1-yl)hex-5-yn-1-yl)-[1,1'-biphenyl]-4-amine

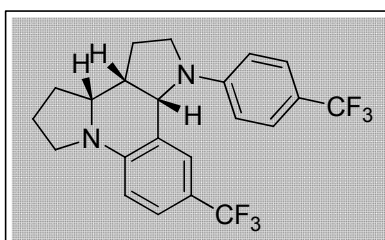
To the solution of 1-((trimethylsilyloxy)-[1,1'-biphenyl]-4(1H)-one (129 mg, 0.50 mmol), phenylacetylene (99 μL , 0.9 mmol), copper(II) bromide (16.8 mg, 0.075 mmol) in toluene (1 mL) in a sealed tube was added pyrrolidine (126 μL , 1.5 mmol) and reacted at 150 $^\circ\text{C}$. After 20 minutes, the reaction was cooled down to room temperature and purified by column chromatography directly on silica gel (PE/EtOAc/ $\text{NEt}_3 = 120: 20: 1$) to afford **5r** (43 mg, 22%).

Brown liquid. ^1H NMR (600 MHz, CDCl_3) δ 7.52 (d, $J = 7.8$ Hz, 2H), 7.45 – 7.40 (m, 4H), 7.37 (t, $J = 7.8$ Hz, 2H), 7.31 – 7.26 (m, 3H), 7.23 (t, $J = 7.8$ Hz, 1H), 6.66 (d, $J = 8.4$ Hz, 2H), 3.98 (s, 1H), 3.75 (t, $J = 7.8$ Hz, 1H), 3.22 (d, $J = 7.8$ Hz, 2H), 2.82 – 2.66 (m, 4H), 1.95 – 1.78 (m, 8H). ^{13}C NMR (150 MHz, CDCl_3) δ 147.8, 141.3, 131.7, 129.9, 128.6, 128.2, 127.9, 127.9, 126.2, 125.9, 123.2, 112.9, 87.8, 85.6, 54.6, 49.7, 43.7, 32.8, 26.6, 23.5. IR (KBr, cm^{-1}): 3409, 3025, 2951, 2872, 2811, 1879, 1612, 1526, 1489, 1443, 1322. HRMS (ESI-TOF) Calcd for $\text{C}_{28}\text{H}_{31}\text{N}_2$ (M+H) $^+$ 395.2482. Found 395.2492.



6: 10-(trifluoromethyl)-1-(4-(trifluoromethyl)phenyl)-2,3,3a,3b,4,5,6,11b-octahydro-1H-dipyrrolo[1,2-a:3',2'-c]quinoline

To the solution of 4-(trifluoromethyl)-4-((trimethylsilyloxy)cyclohexa-2,5-dienone (125 mg, 0.50 mmol), 4-methoxyphenol (124 mg, 1 mmol) in toluene (1 mL) in a 25 mL round-bottomed flask was added pyrrolidine (42 μL , 0.50 mmol) and reacted at 80 $^\circ\text{C}$. After 40 minutes, the reaction was cooled down to room temperature and purified by column chromatography directly on silica gel (PE/EtOAc/ $\text{NEt}_3 = 120: 7: 1$) to afford crude product of **6** (91 mg, 85%), the dr value is about 2.5: 1.

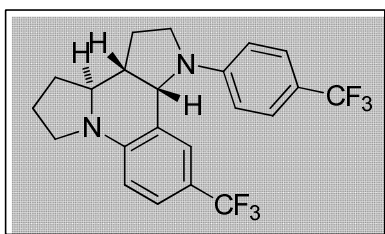


6a:

10-(trifluoromethyl)-1-(4-(trifluoromethyl)phenyl)-2,3,3a,3b,4,5,6,11b-octahydro-1H-dipyrrolo[1,2-a:3',2'-c]quinoline

The crude product of **6** was purified by column chromatography on silica gel (PE/EtOAc/NEt₃ = 120: 4: 1) to afford **6a** (60 mg, 56%).

White solid: m.p. 174–175 °C ¹H NMR (600 MHz, CDCl₃): δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.38 (s, 1H), 7.31 (d, *J* = 8.4 Hz, 1H), 6.78 (d, *J* = 8.4 Hz, 2H), 6.40 (d, *J* = 8.4 Hz, 1H), 5.08 (d, *J* = 6.6 Hz, 1H), 3.87 – 3.78 (m, 1H), 3.45 (t, *J* = 9.0 Hz, 1H), 3.41 (t, *J* = 9.6 Hz, 1H), 3.36 – 3.28 (m, 2H), 2.58 – 2.50 (m, 1H), 2.20 – 2.12 (m, 1H), 2.12 – 2.06 (m, 1H), 2.06 – 1.93 (m, 2H), 1.80 – 1.65 (m, 2H). ¹³C NMR (150 MHz, CDCl₃): δ 150.6, 145.2, 126.7 (q, *J* = 3.6 Hz), 125.6 (q, *J* = 4.1 Hz), 125.2 (q, *J* = 268.4 Hz), 125.4 (q, *J* = 3.6 Hz), 125.0 (q, *J* = 268.7 Hz), 121.2, 117.5 (q, *J* = 32.1 Hz), 117.1 (q, *J* = 3.3 Hz), 110.5, 109.8, 57.5, 56.0, 47.4, 46.7, 39.5, 30.3, 23.4, 23.2. ¹⁹F NMR (565 MHz, CDCl₃) δ -60.7(2). IR (KBr, cm⁻¹): 2974, 2907, 2867, 2644, 1880, 1615, 1525, 1383, 1325, 1147. HRMS (ESI-TOF) Calcd for C₂₀H₂₀F₆N₂Na (M+Na)⁺ 425.1423 Found 425.1436.



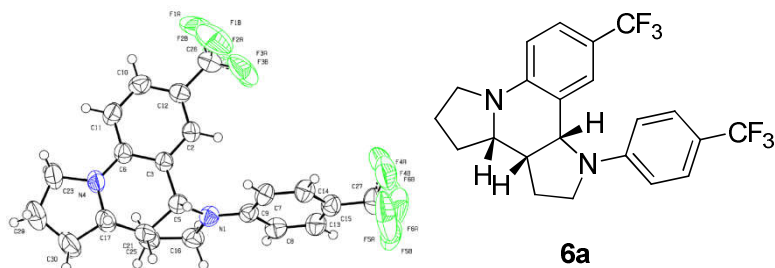
6a':

10-(trifluoromethyl)-1-(4-(trifluoromethyl)phenyl)-2,3,3a,3b,4,5,6,11b-octahydro-1H-dipyrrolo[1,2-a:3',2'-c]quinoline

The crude product of **6** was purified by column chromatography on silica gel (PE/EtOAc/NEt₃ = 120: 4: 1) to afford **6a'** (31 mg, about 29%).

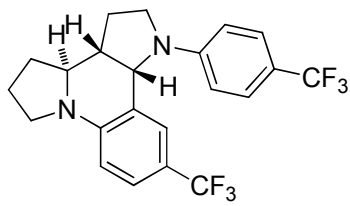
Yellow viscous liquid; ¹H NMR (600 MHz, CDCl₃): δ 7.49 – 7.41 (m, 3H), 7.23 (s, 1H), 6.72 (d, *J* = 8.4 Hz, 1H), 6.65 (d, *J* = 8.4 Hz, 2H), 4.43 (d, *J* = 8.4 Hz, 1H), 3.69 (t, *J* = 8.4 Hz, 1H), 3.47 (td, *J* = 9.0, 3.6 Hz, 1H), 3.37 (td, *J* = 9.6, 6.6 Hz, 1H), 3.03 – 2.94 (m, 1H), 2.88 – 2.76 (m, 1H), 2.65 – 2.56 (m, 1H), 2.35 – 2.21 (m, 2H), 2.21 – 2.11 (m, 1H), 2.06 – 1.95 (m, 1H), 1.89 – 1.72 (m, 2H). ¹³C NMR (150 MHz, CDCl₃): δ 151.0, 149.5, 127.0, 126.4 (q, *J* = 3.9 Hz), 125.1 (q, *J* = 279.2 Hz), 125.0 (q, *J* = 3.9 Hz), 124.8 (q, *J* = 269.3 Hz), 123.7 (q, *J* = 3.5 Hz), 120.3 (q, *J* = 3.2 Hz), 118.6 (q, *J* = 3.6 Hz), 112.1, 111.9, 63.4, 59.5, 49.0, 47.8, 46.9, 32.2, 30.3, 22.3. ¹⁹F NMR (565 MHz, CDCl₃) δ -60.9, -61.1. IR (KBr, cm⁻¹): 2924, 2852, 1614, 1530, 1327, 1104, 1067. HRMS (ESI-TOF) Calcd for C₂₀H₂₀F₆N₂Na (M+Na)⁺ 425.1423 Found 425.1436.

IV. Crystal Data and OPTEP Drawing

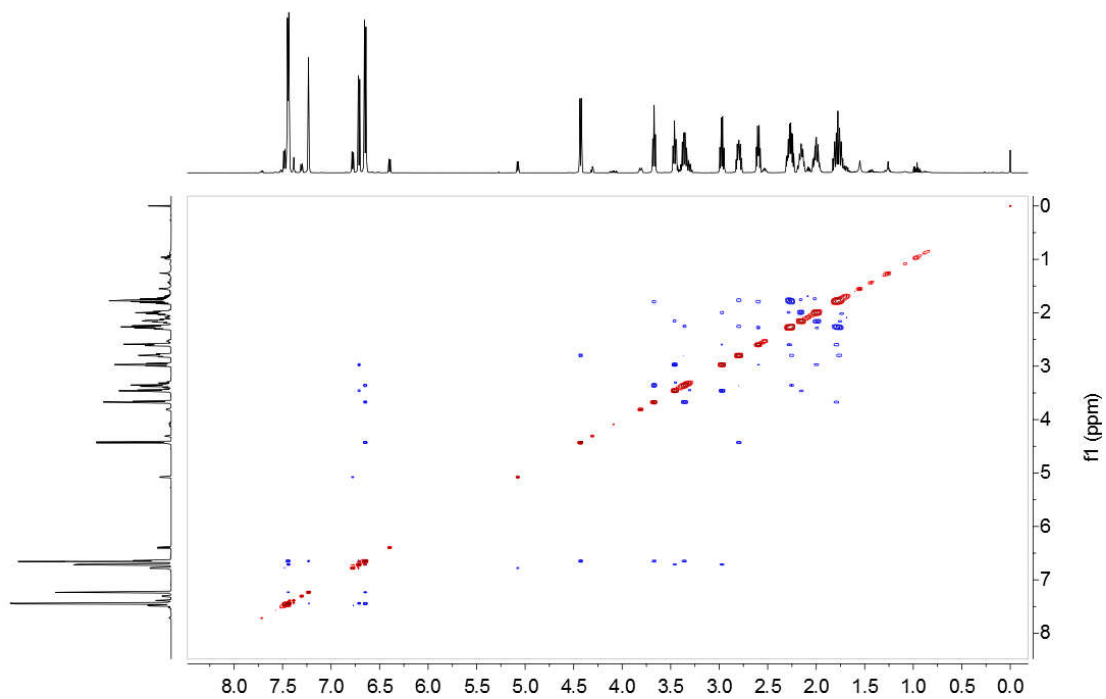


Crystal data:

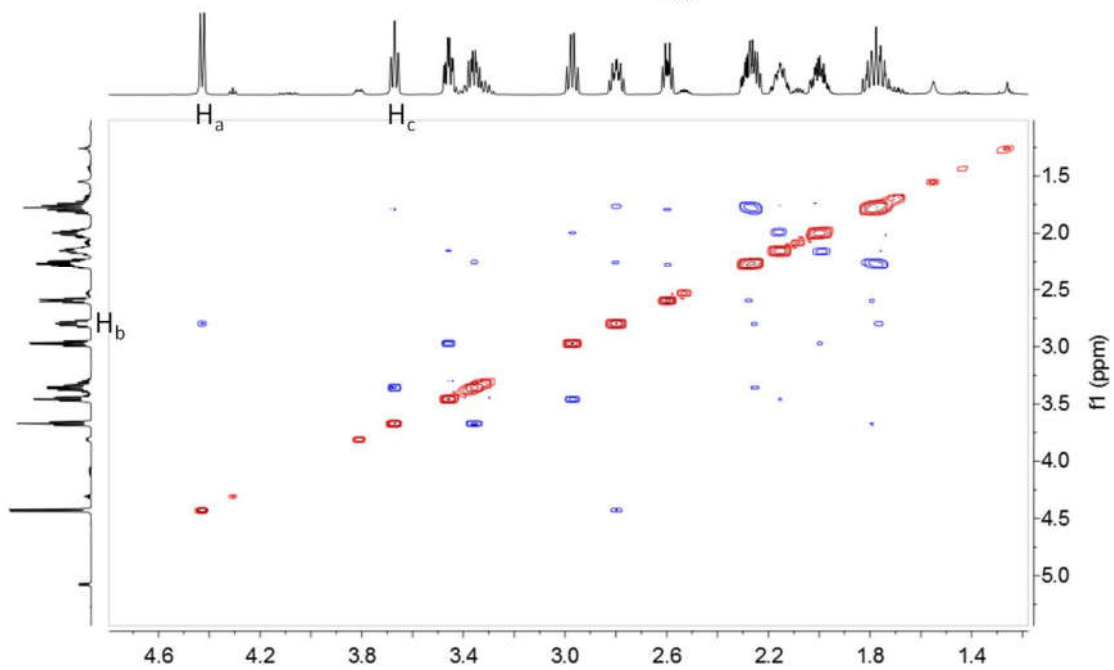
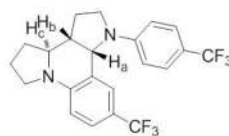
Empirical formula	C ₂₂ H ₂₀ F ₆ N ₂
Formula weight	426.40
Crystal system	Monoclinic
Space group	P 21/c
a (Å)	9.6136(7)
b (Å)	15.5641(12)
c (Å)	13.7093(11)
α (deg)	90
β (deg)	104.355(2)
γ (deg)	90
Volume (Å ³)	1987.2(3)
Z	4
Calculated density (mg/m ³)	1.425
Absorption coefficient (mm ⁻¹)	0.124
F(000)	880.0
Theta range for data collection (deg)	2.680 to 25.721
Reflections collected/unique	3781/2487
Goodness-of-fit on F ²	1.083
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0520, WR2 = 0.1166
R indices (all data)	R1 = 0.0921, WR2 = 0.1460



V. NOE Spectra of 6a'

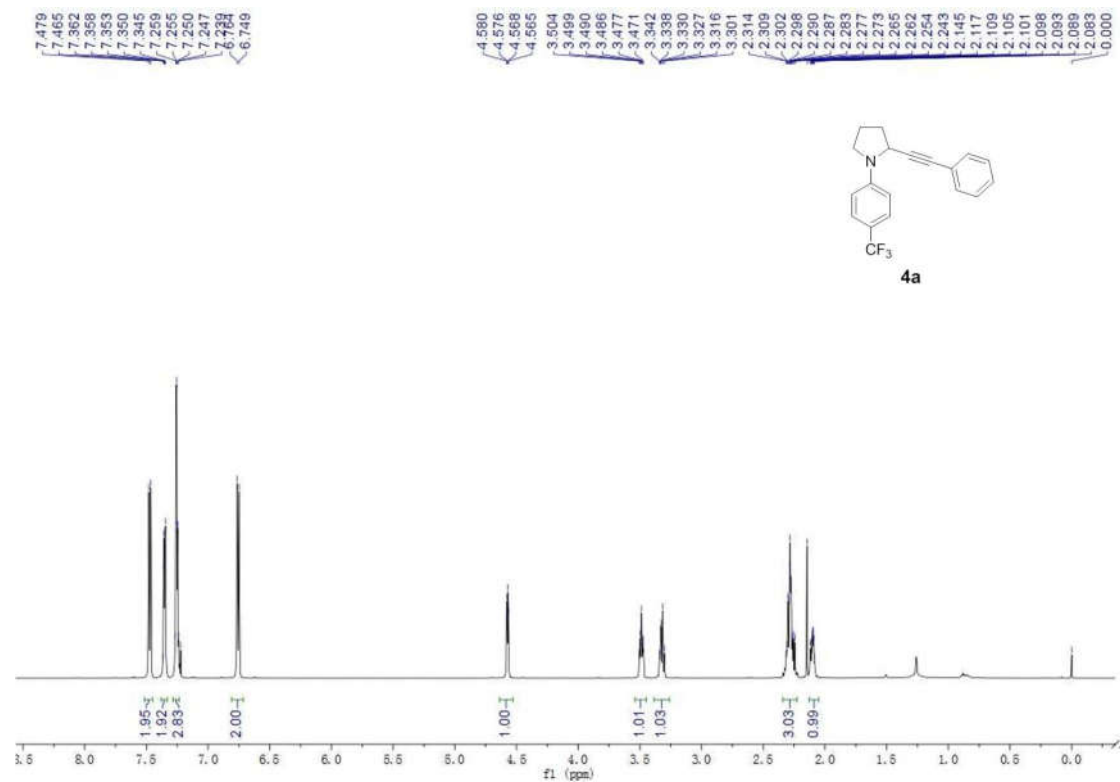


H_b and H_c have no interaction.

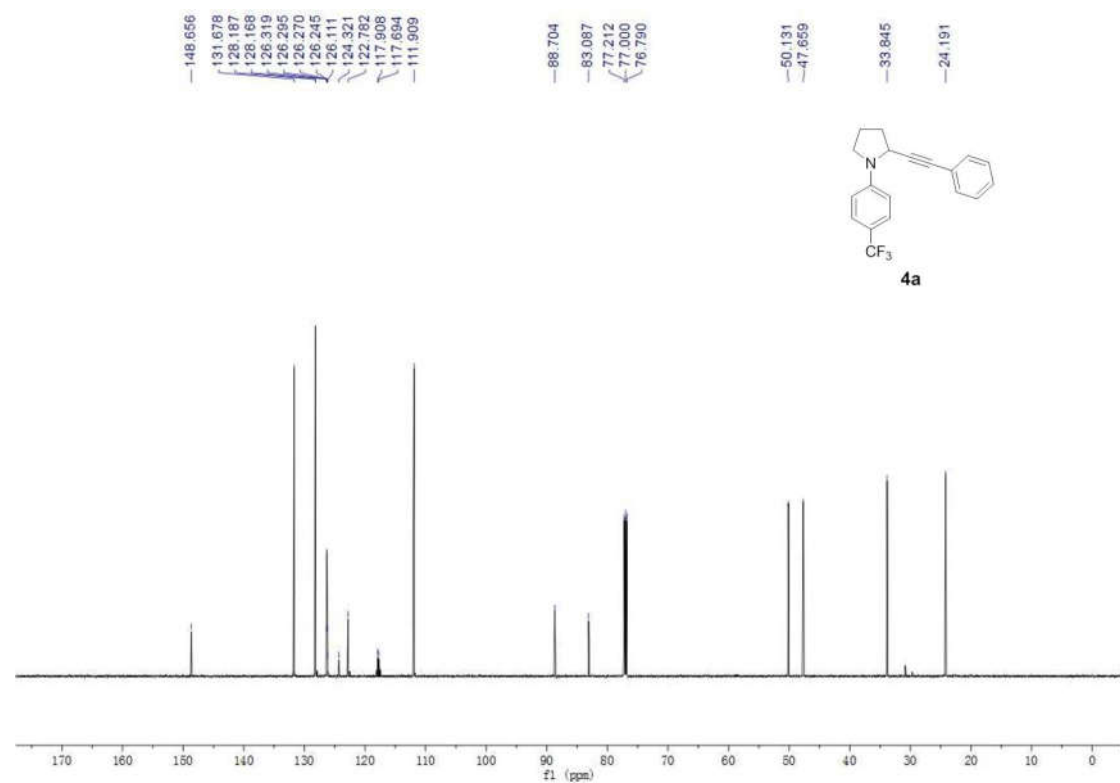


VI. Copies of ^1H NMR, ^{13}C NMR and ^{19}F NMR Spectra.

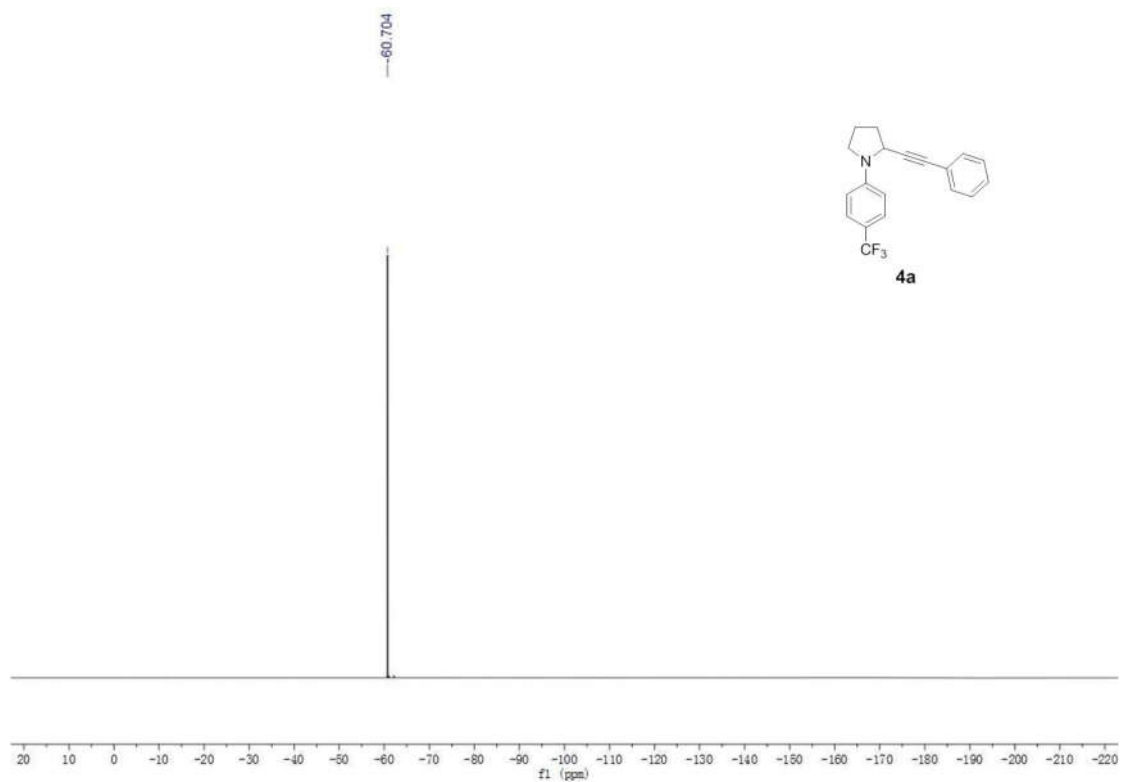
^1H spectrum(600 MHz, CDCl_3) of compound 4a



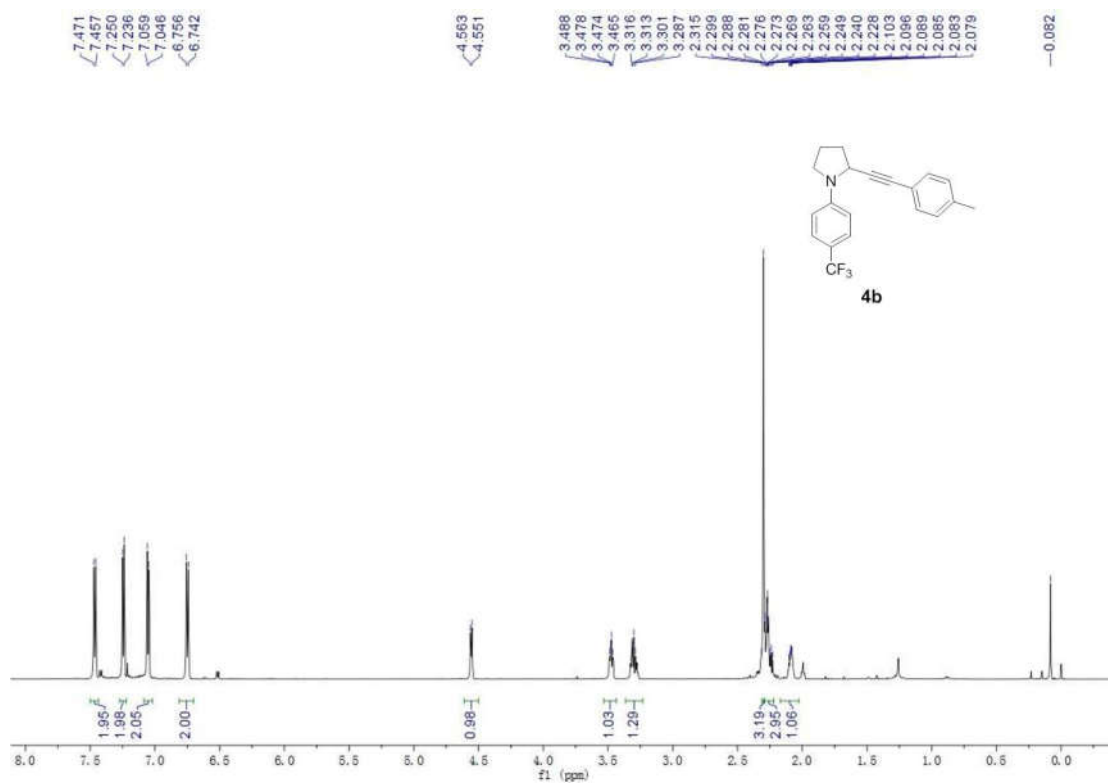
^{13}C spectrum(150 MHz, CDCl_3) of compound 4a



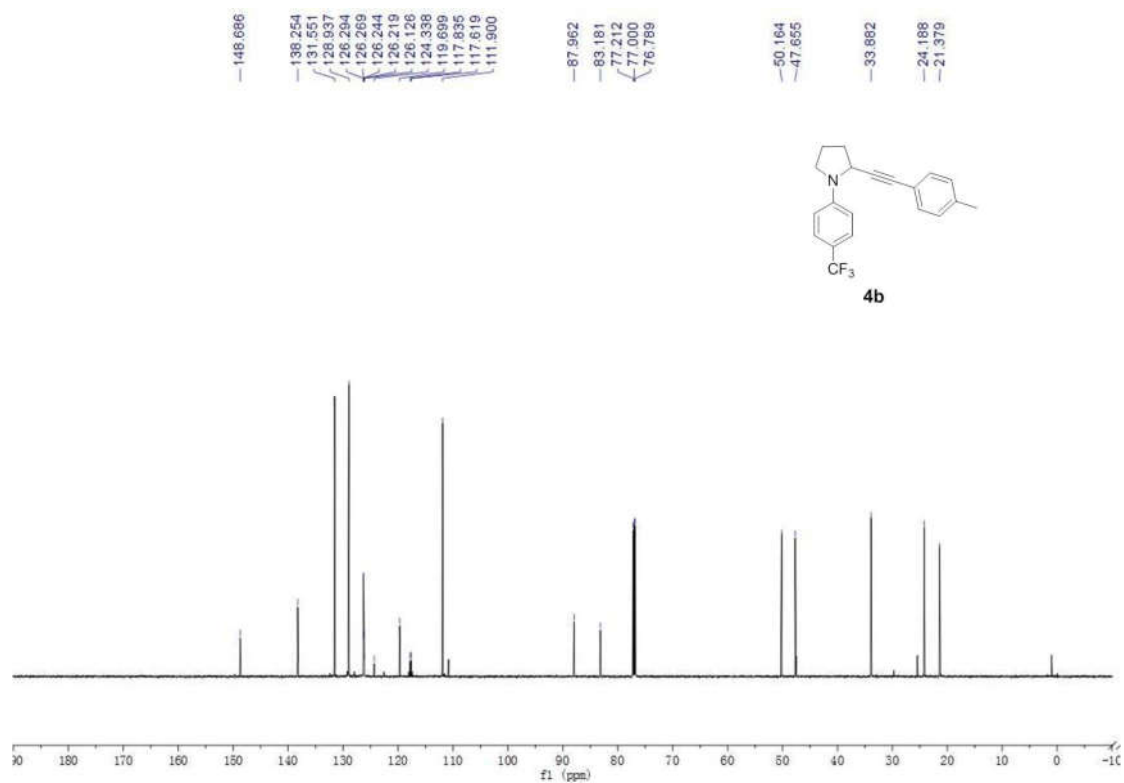
¹⁹F spectrum(565 MHz, CDCl₃) of compound 4a



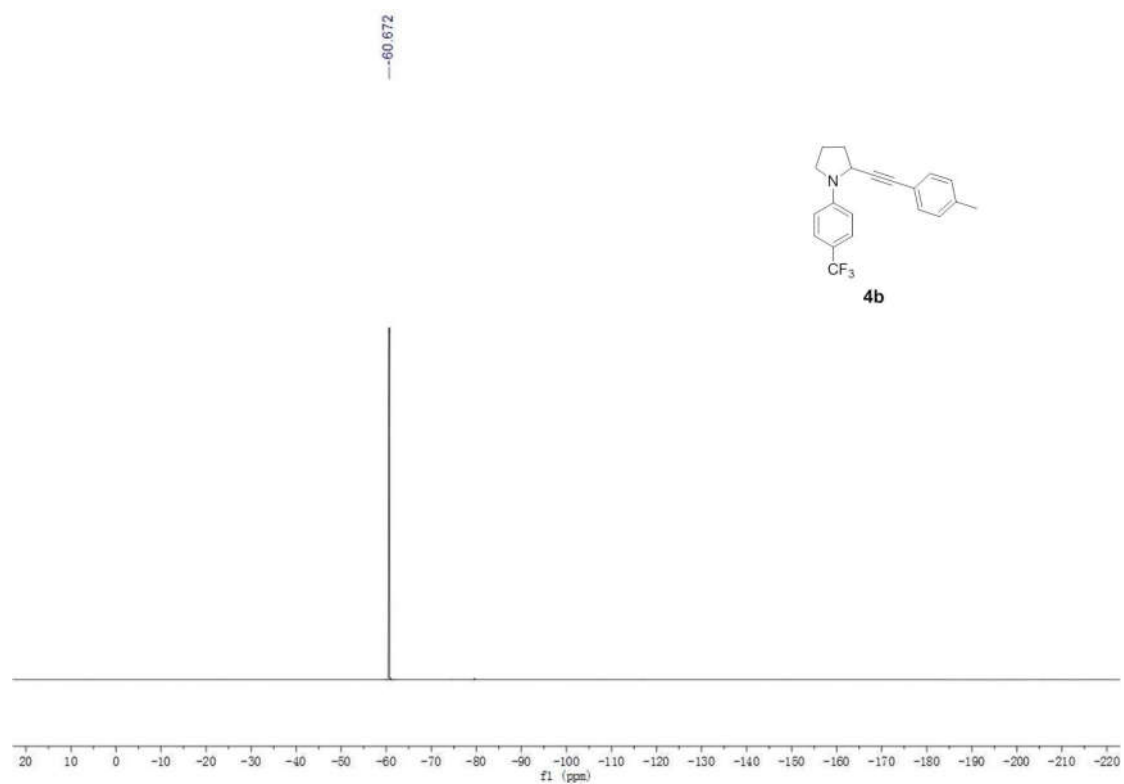
¹H spectrum(600 MHz, CDCl₃) of compound 4b



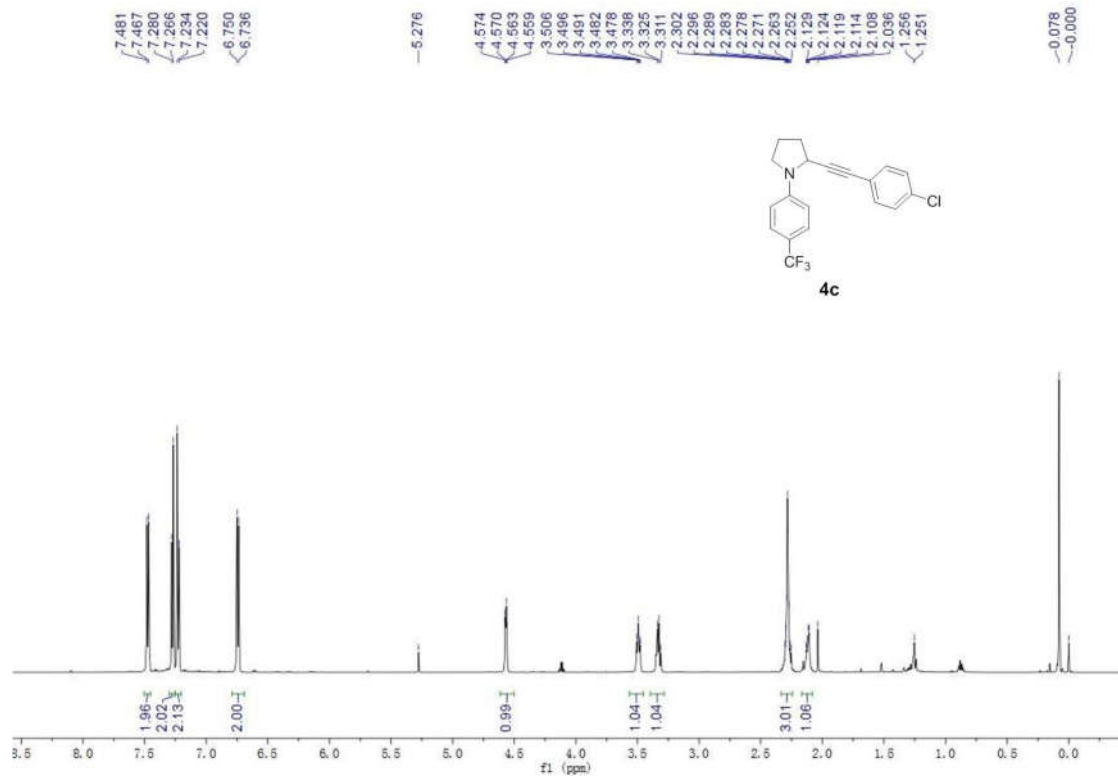
¹³C spectrum(150 MHz, CDCl₃) of compound 4b



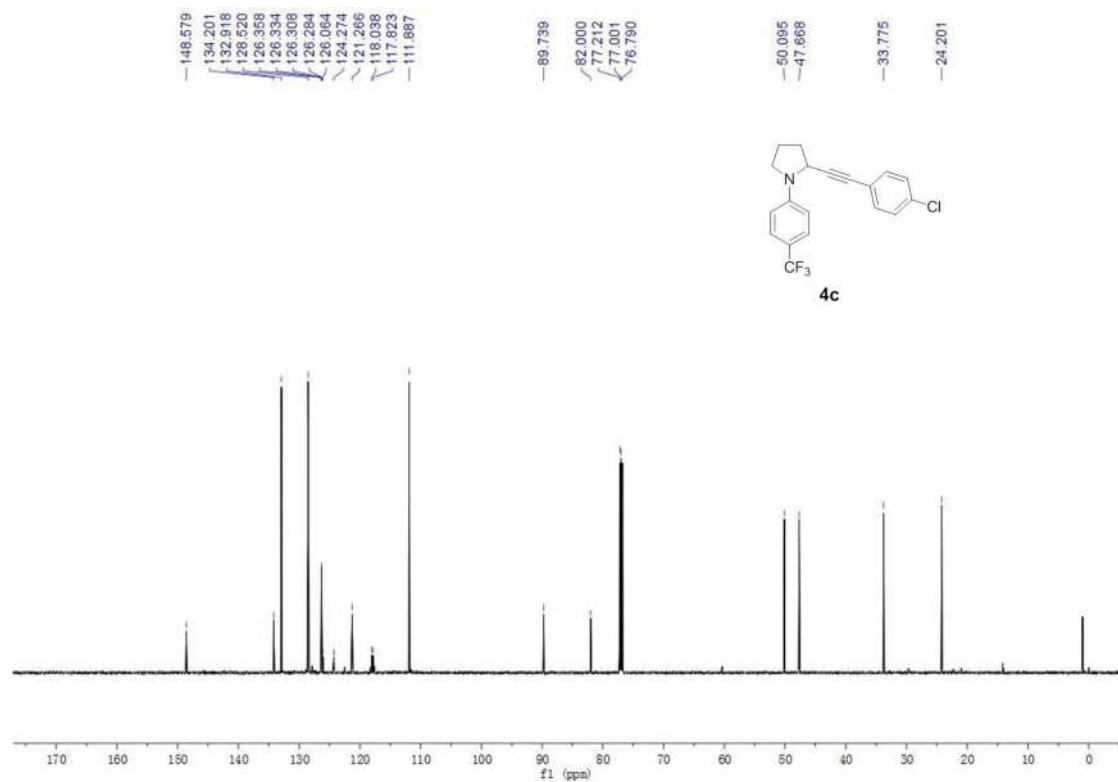
¹⁹F spectrum(565 MHz, CDCl₃) of compound 4b



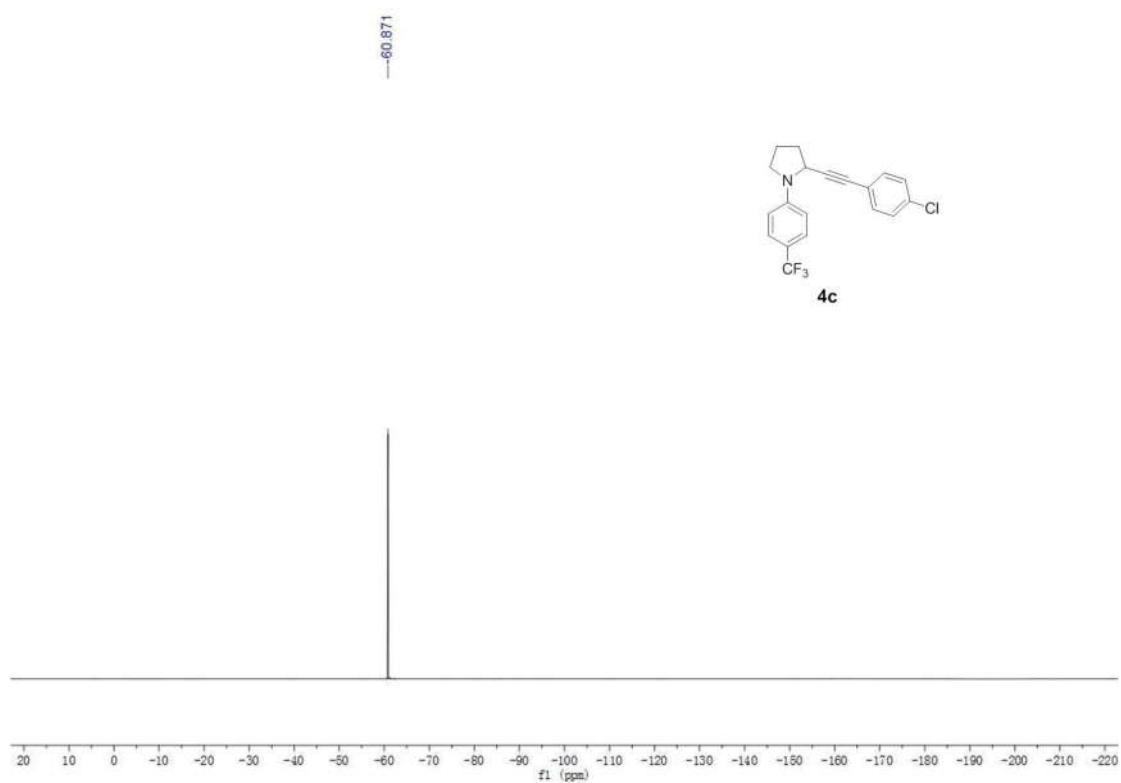
¹H spectrum(600 MHz, CDCl₃) of compound 4c



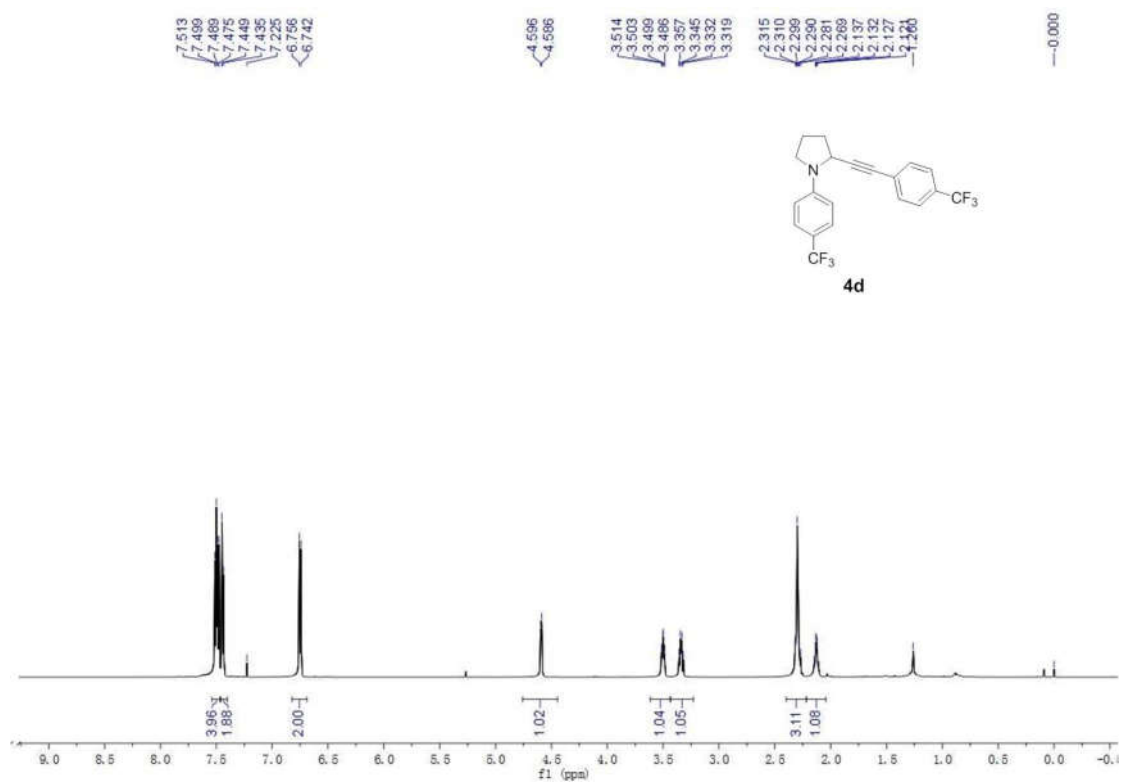
¹³C spectrum(150 MHz, CDCl₃) of compound 4c



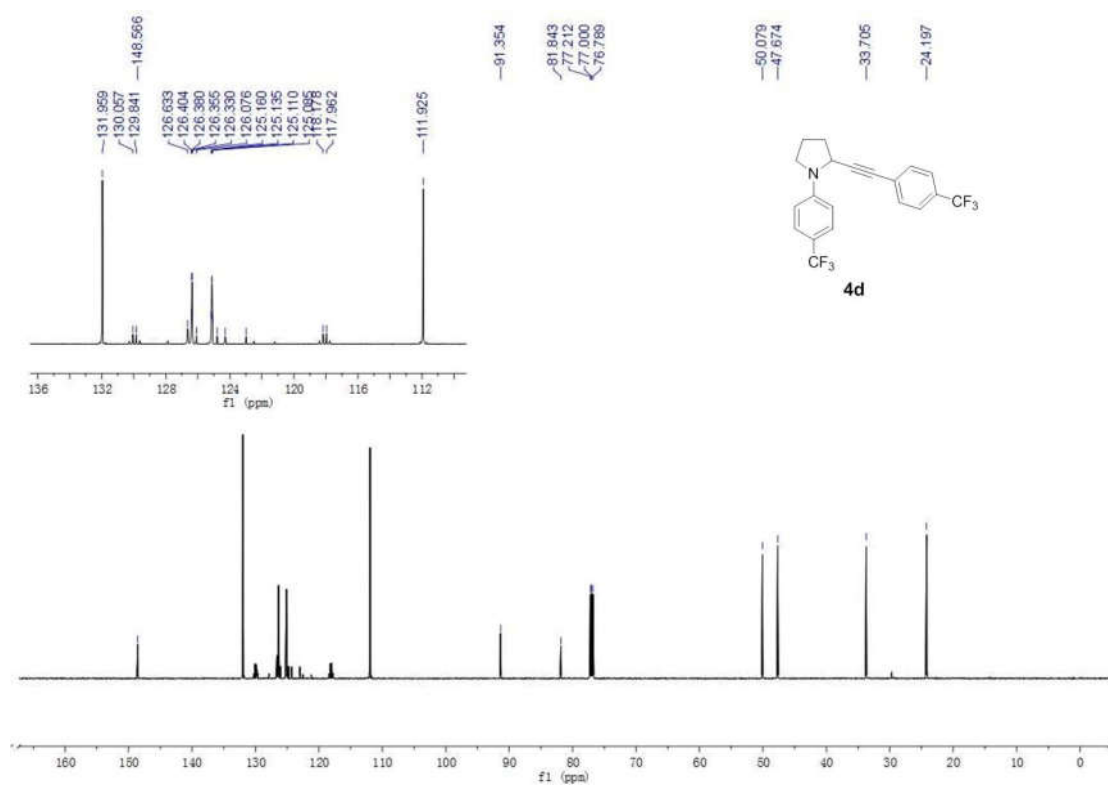
¹⁹F spectrum(565 MHz, CDCl₃) of compound 4c



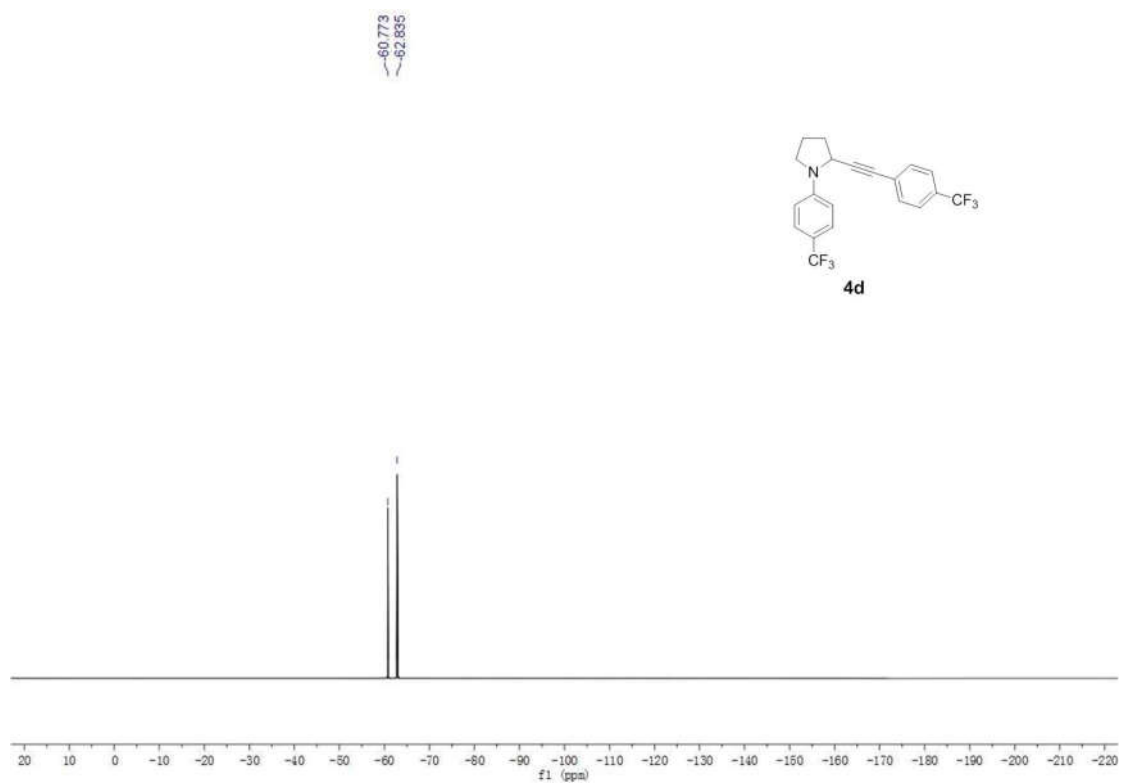
¹H spectrum(600 MHz, CDCl₃) of compound 4d



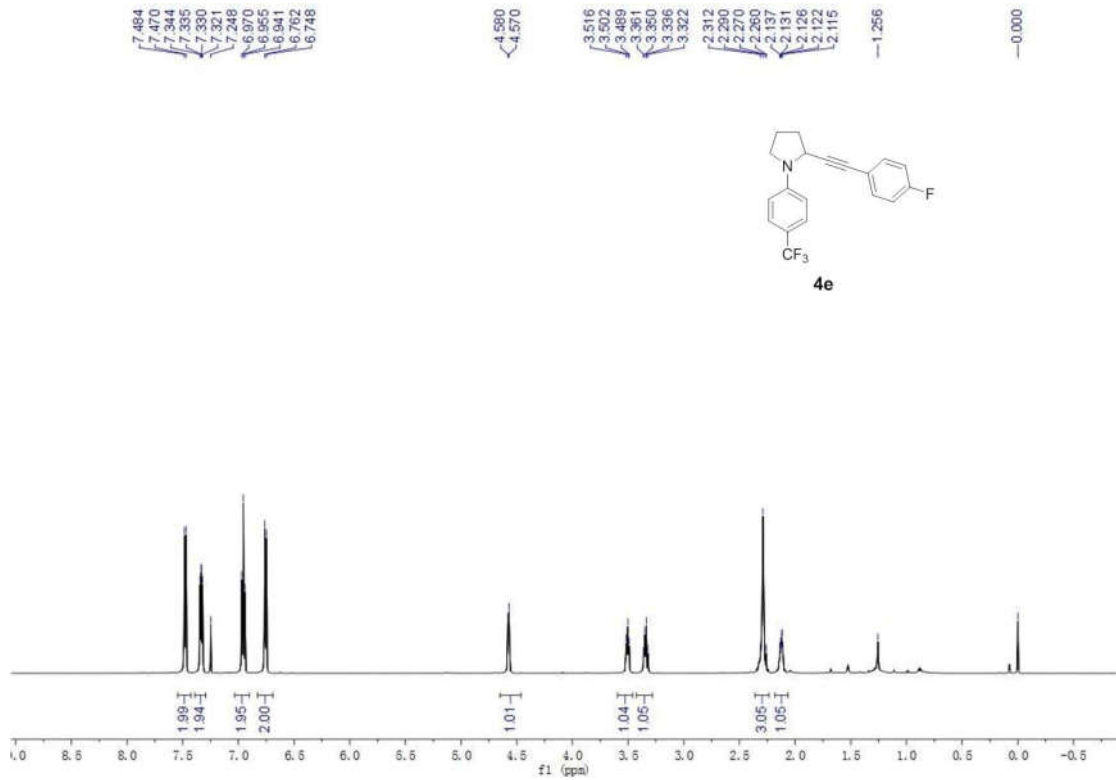
¹³C spectrum(150 MHz, CDCl₃) of compound 4d



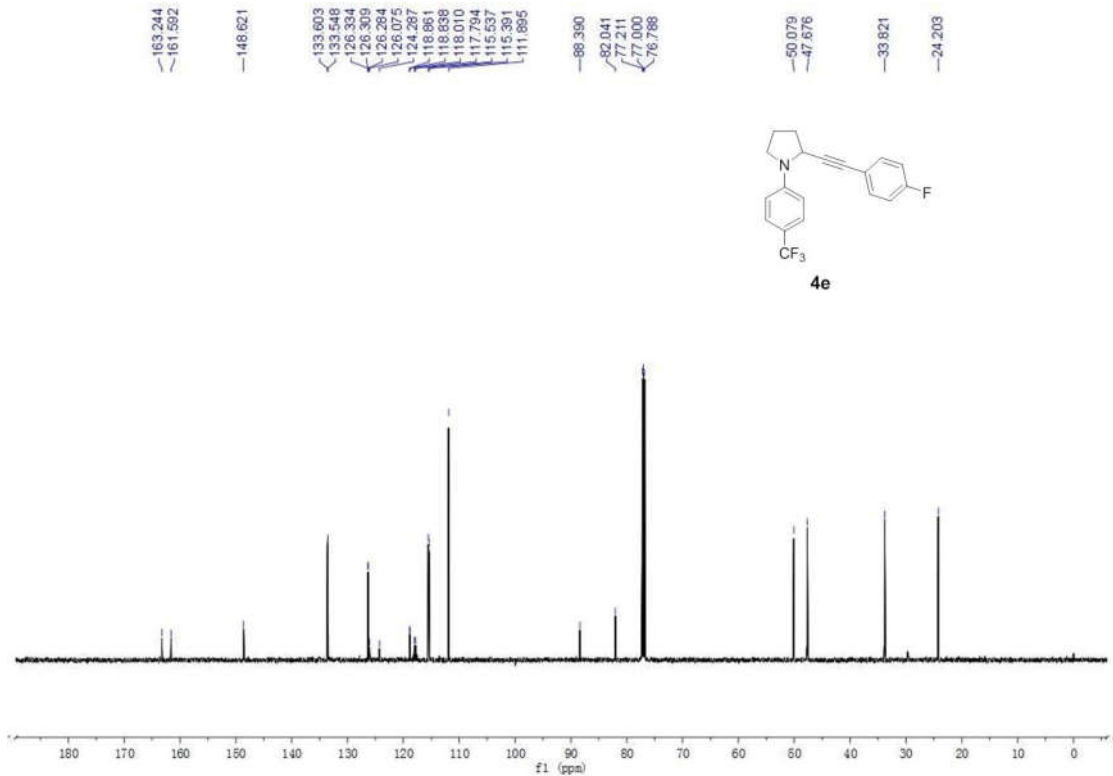
¹⁹F spectrum(565 MHz, CDCl₃) of compound 4d



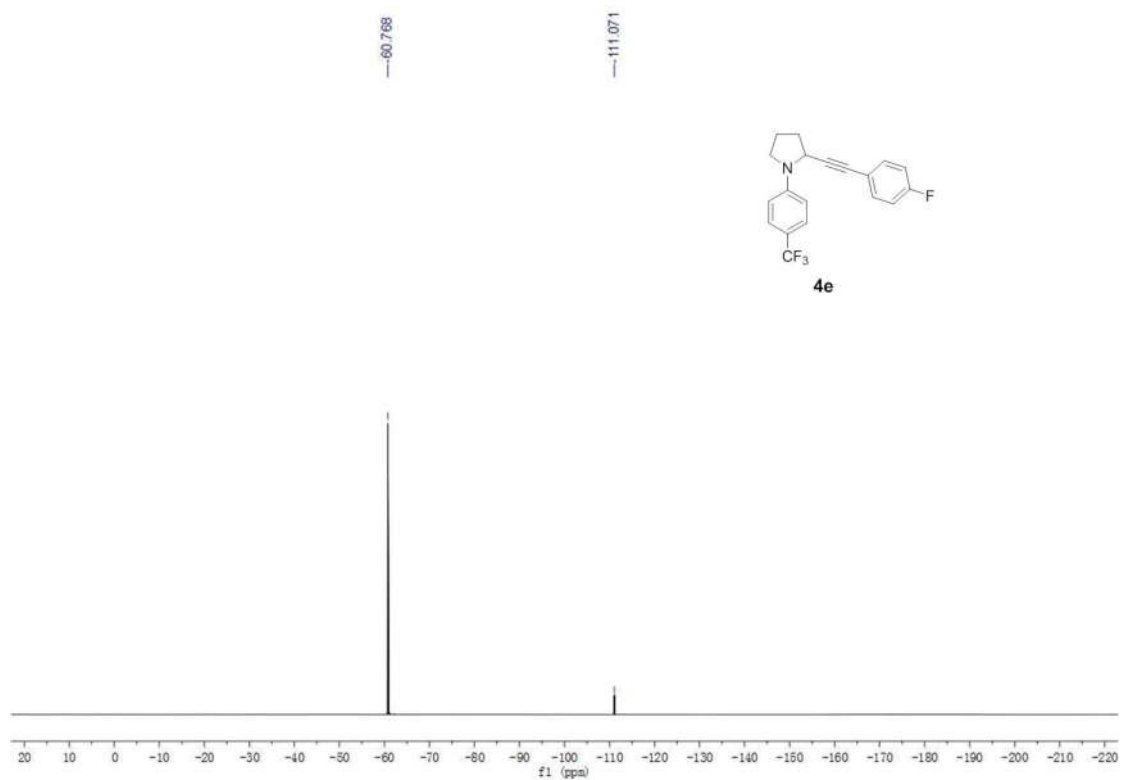
¹H spectrum(600 MHz, CDCl₃) of compound 4e



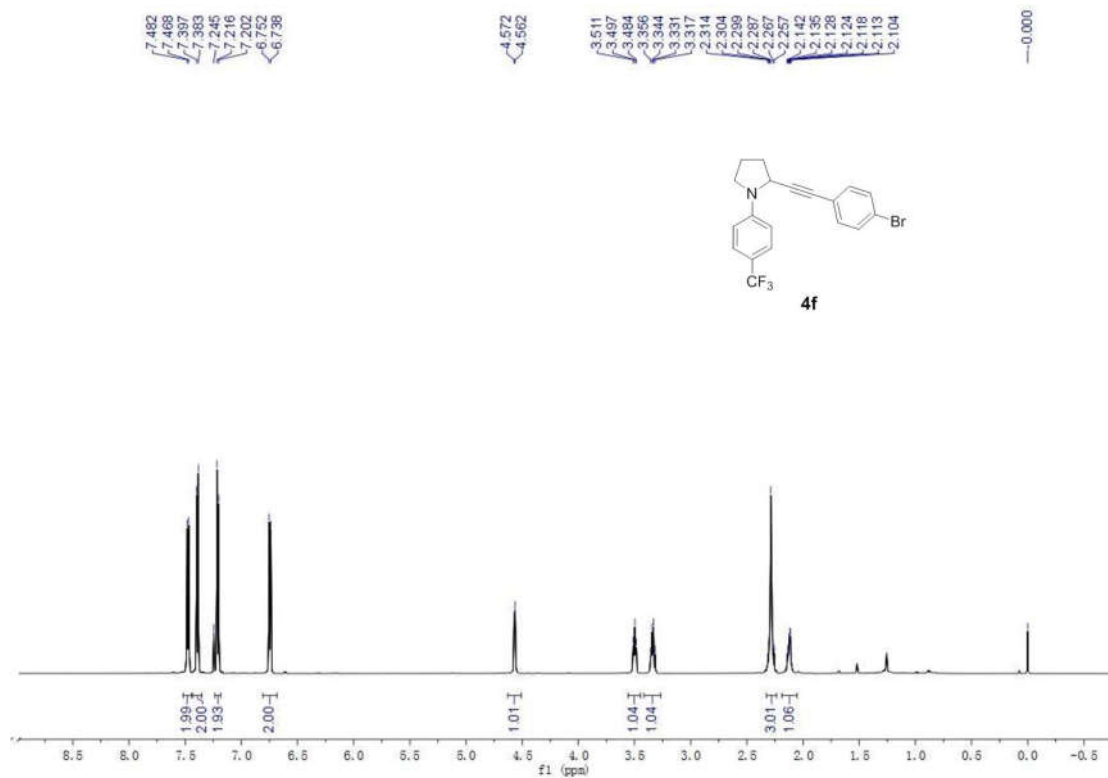
¹³C spectrum(150 MHz, CDCl₃) of compound 4e



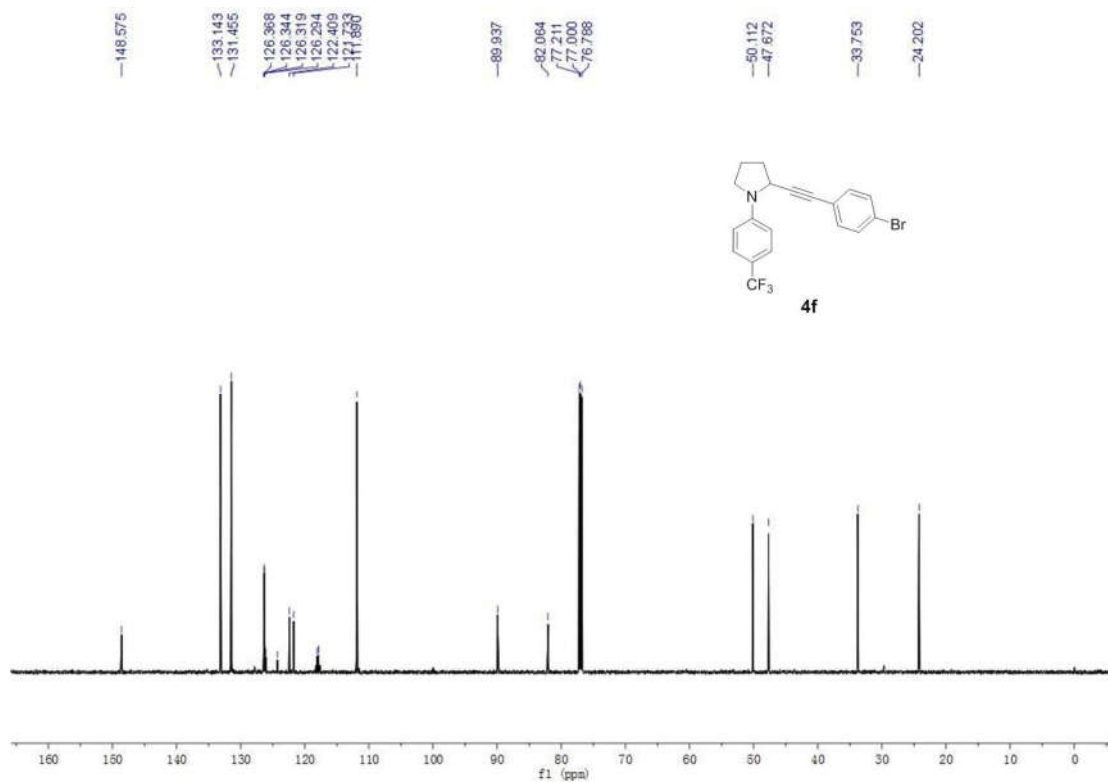
^{19}F spectrum(565 MHz, CDCl_3) of compound 4e



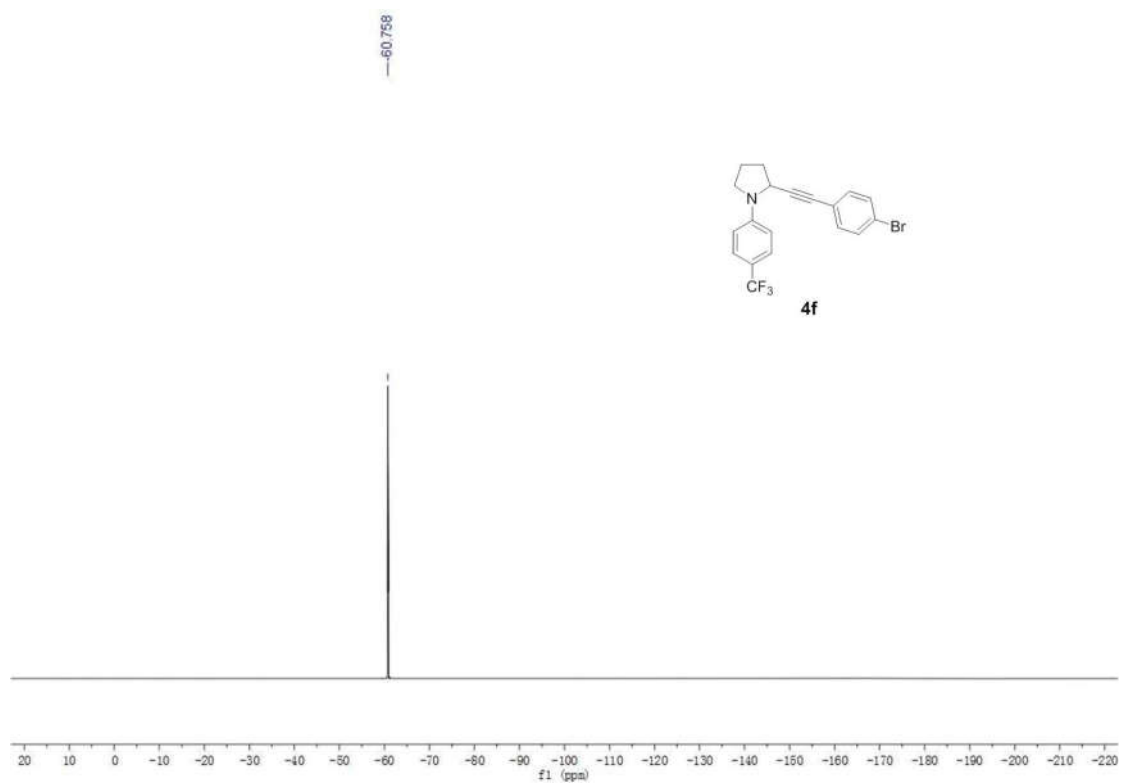
^1H spectrum(600 MHz, CDCl_3) of compound 4f



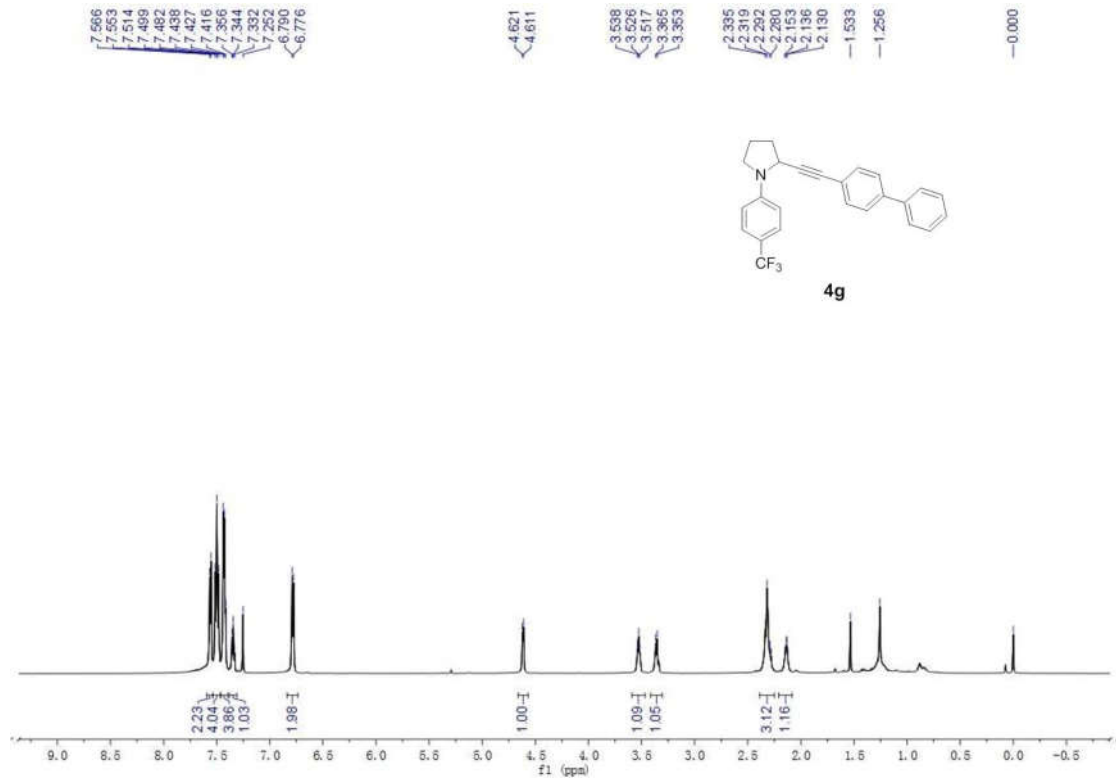
¹³C spectrum(150 MHz, CDCl₃) of compound 4f



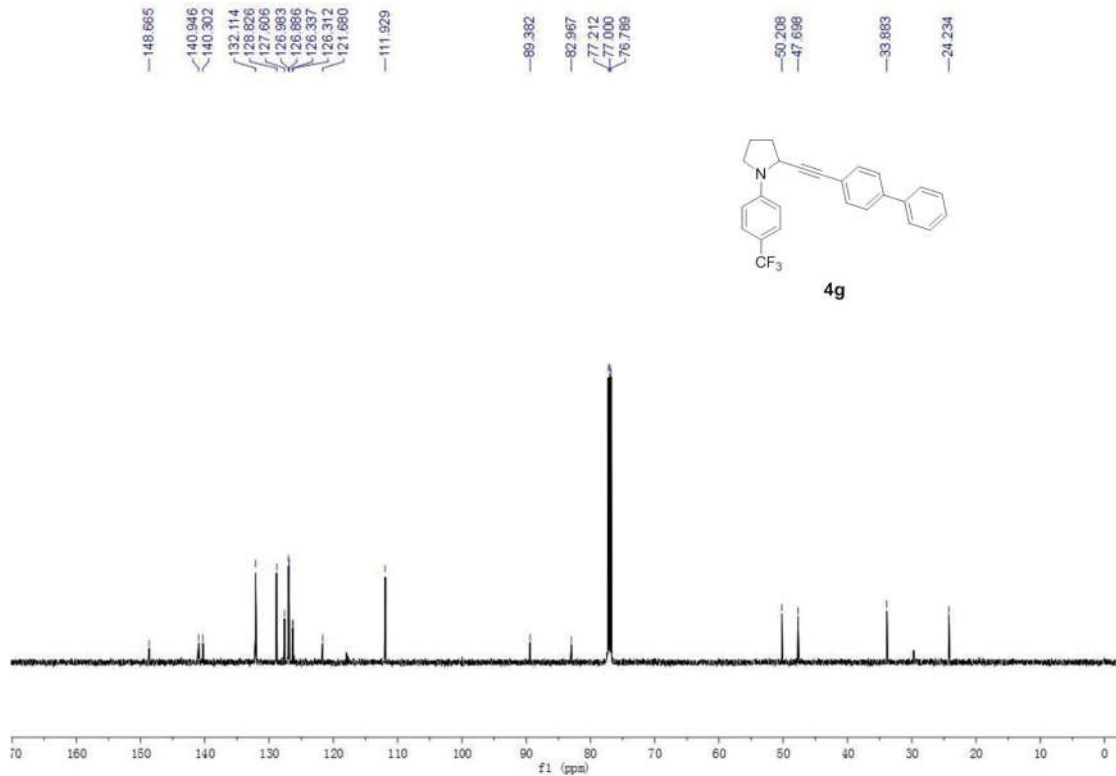
¹⁹F spectrum(565 MHz, CDCl₃) of compound 4f



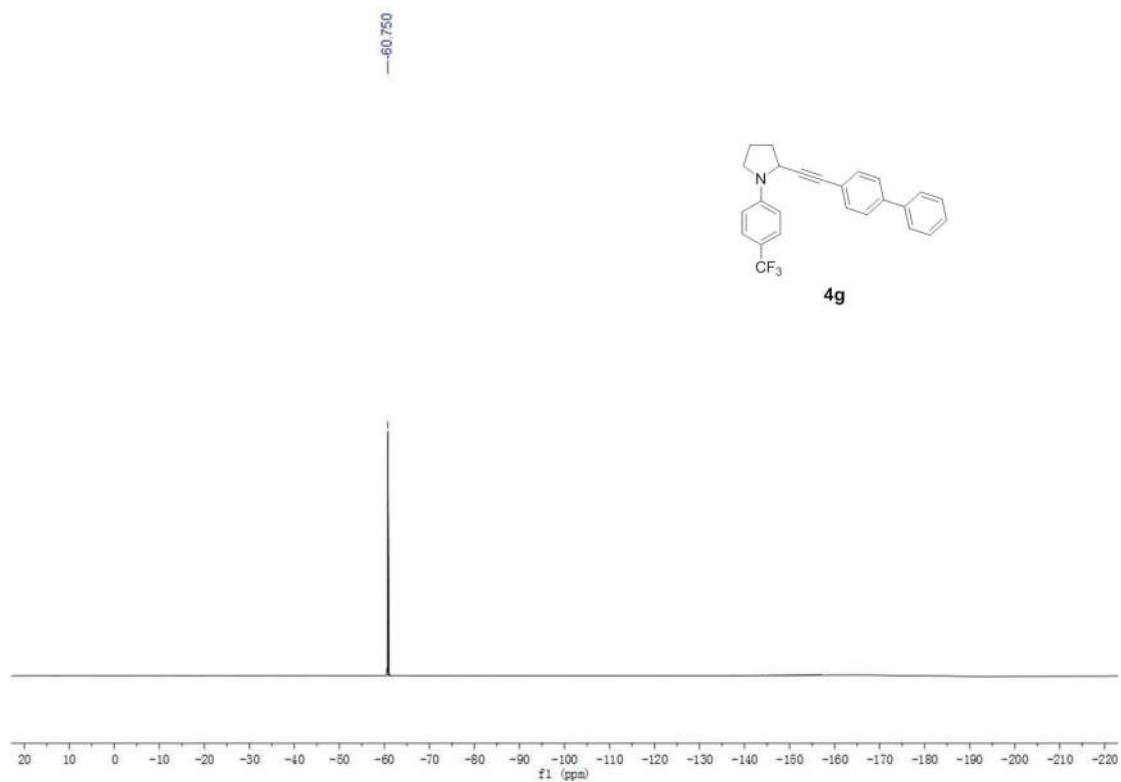
¹H spectrum(600 MHz, CDCl₃) of compound 4g



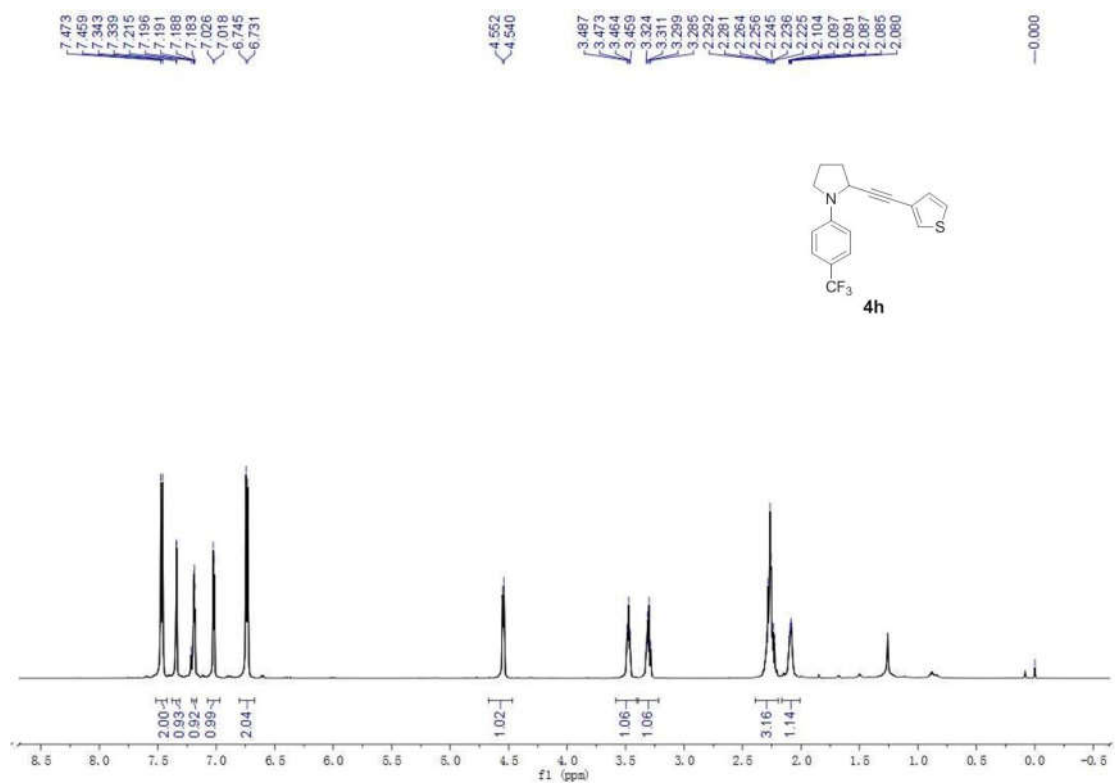
¹³C spectrum(150 MHz, CDCl₃) of compound 4g



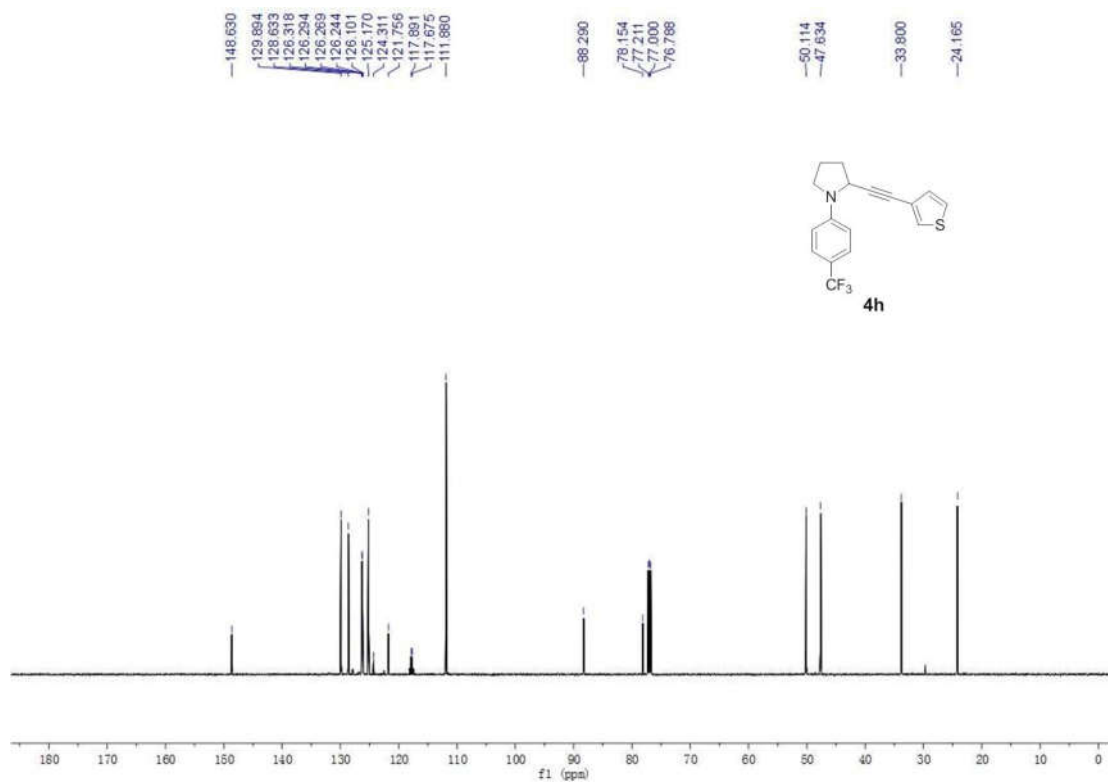
^{19}F spectrum(565 MHz, CDCl_3) of compound 4g



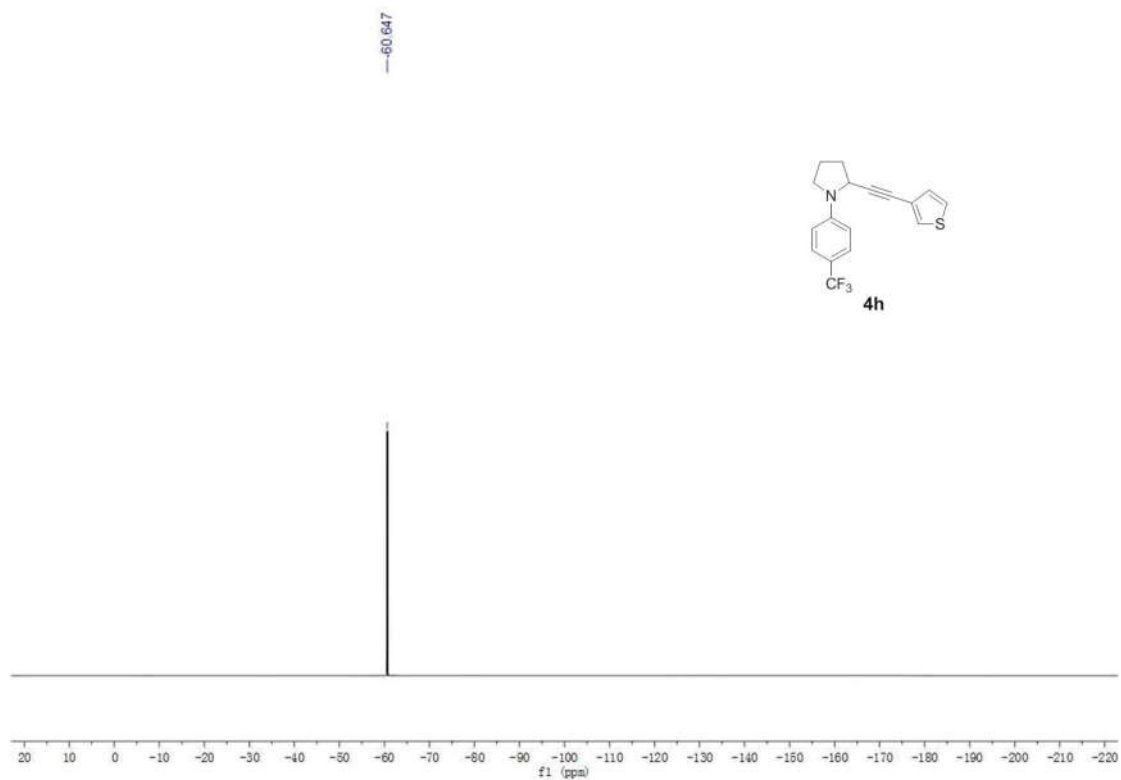
^1H spectrum(600 MHz, CDCl_3) of compound 4h



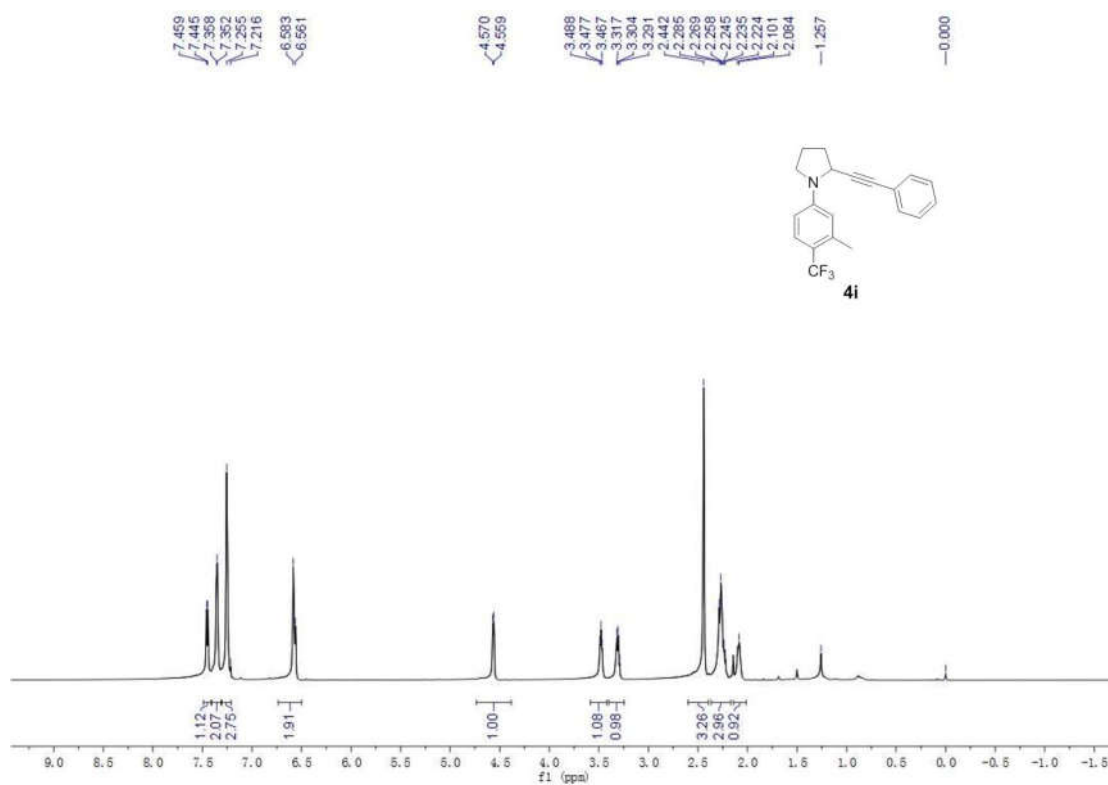
^{13}C spectrum(150 MHz, CDCl_3) of compound 4h



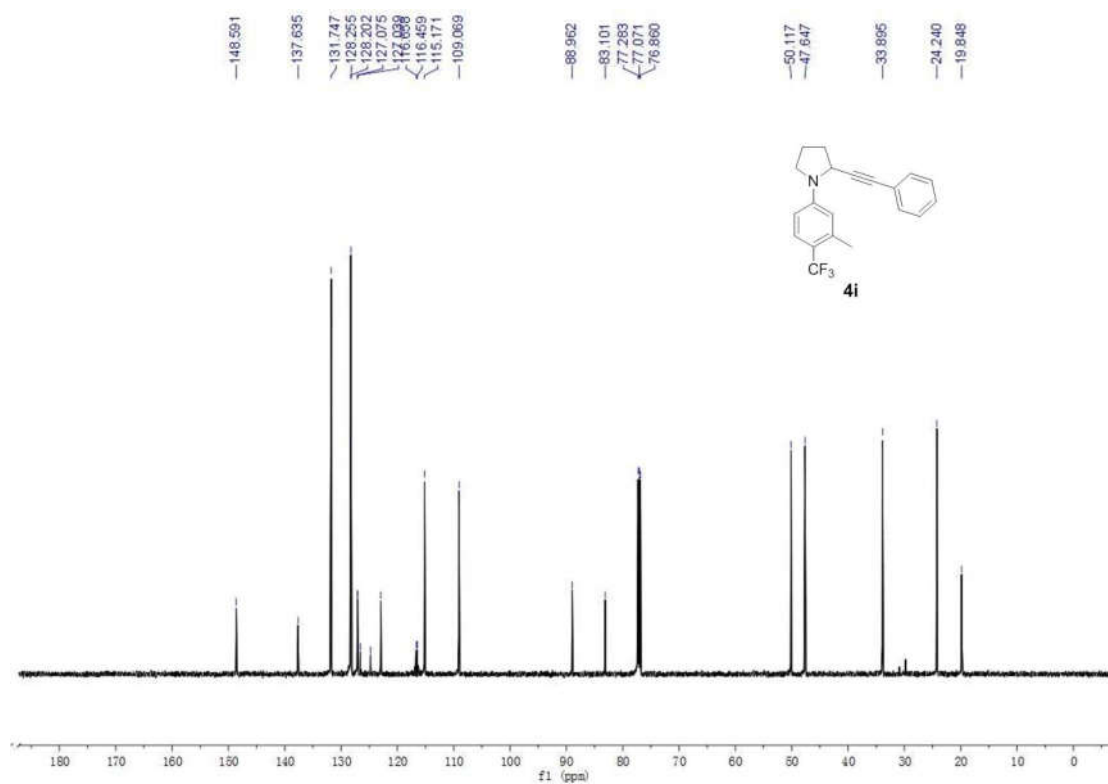
^{19}F spectrum(565 MHz, CDCl_3) of compound 4h



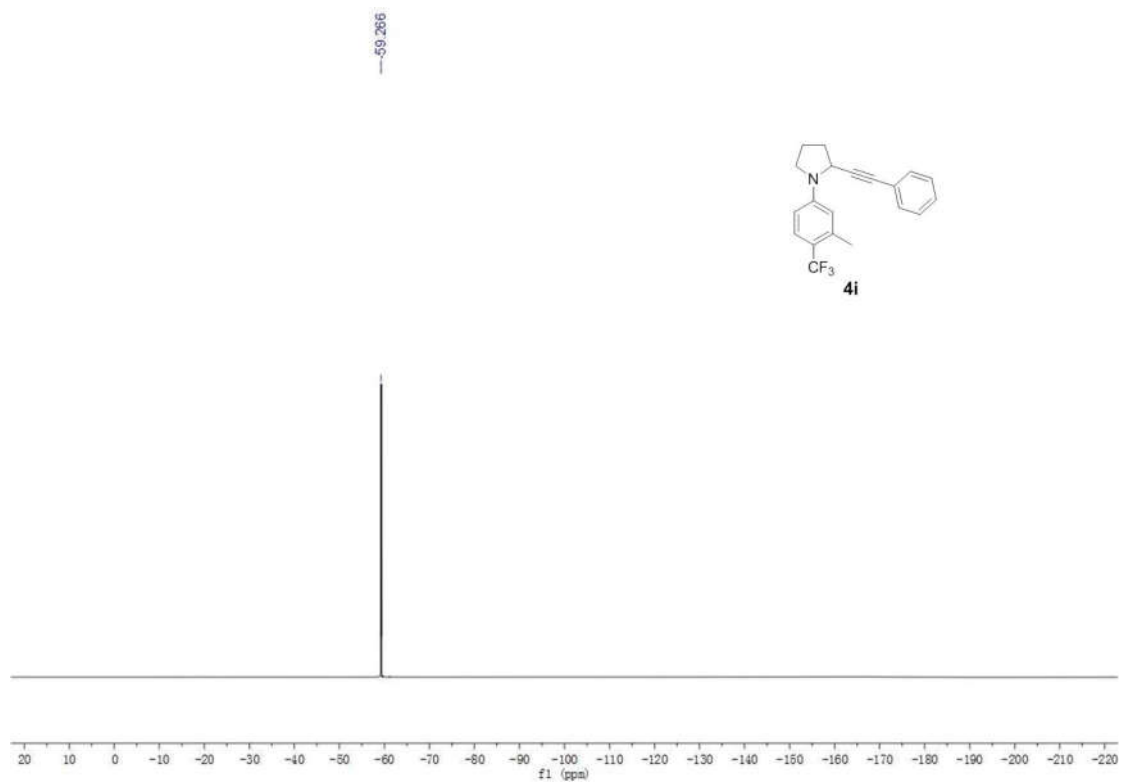
¹H spectrum(600 MHz, CDCl₃) of compound 4i



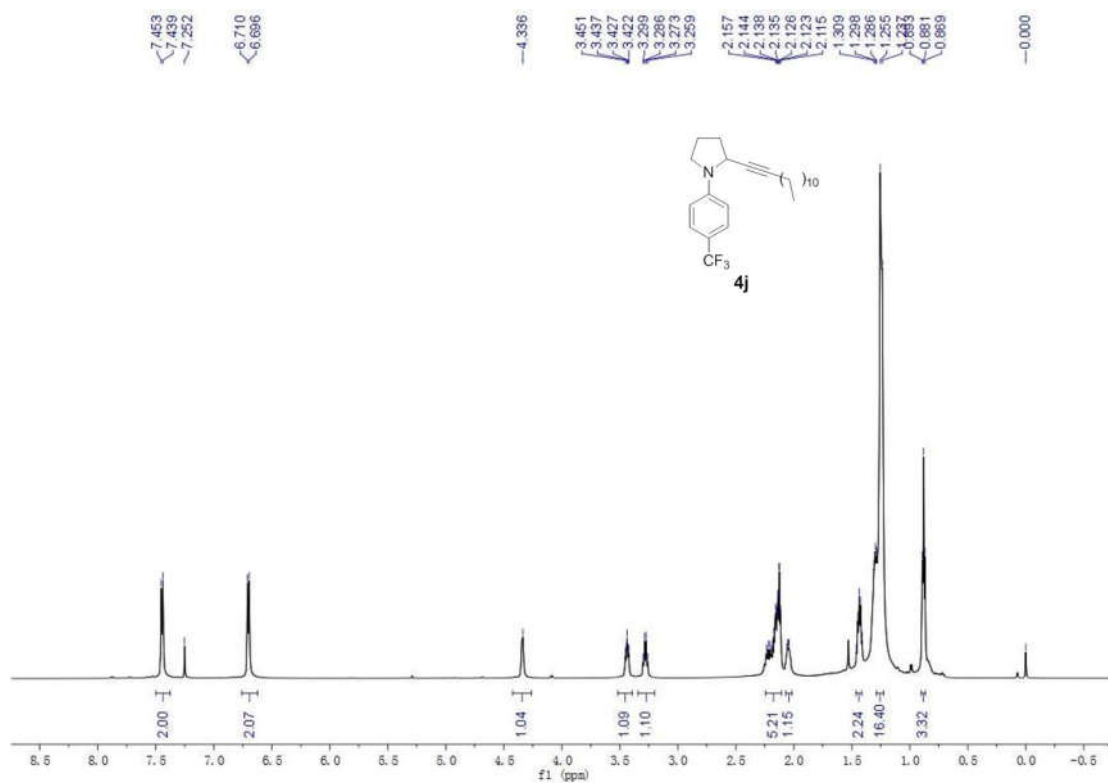
¹³C spectrum(150 MHz, CDCl₃) of compound 4i



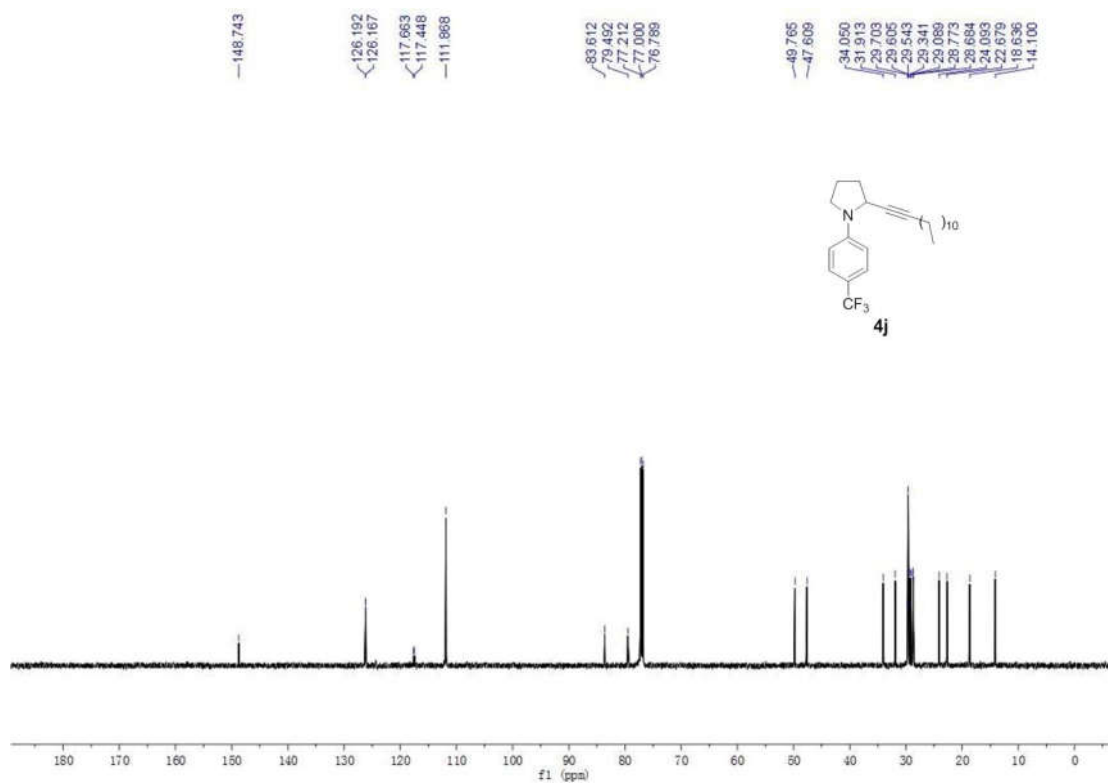
¹⁹F spectrum(565 MHz, CDCl₃) of compound 4i



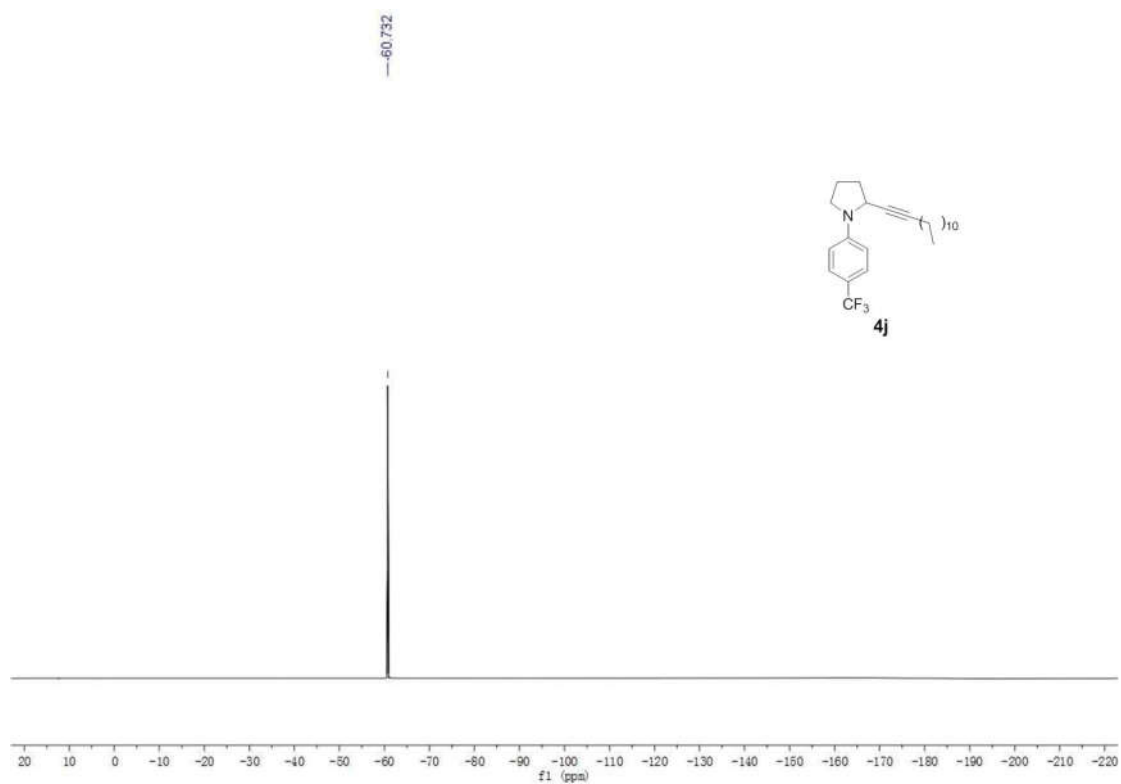
¹H spectrum(600 MHz, CDCl₃) of compound 4j



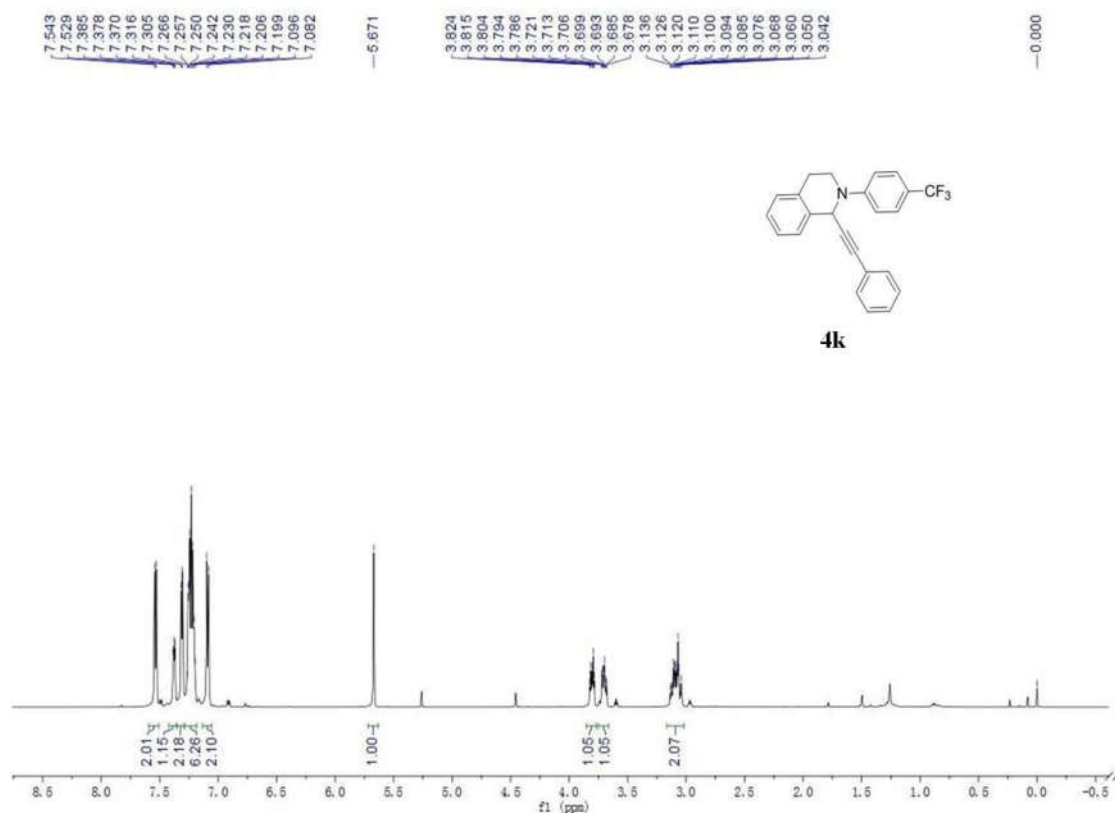
¹³C spectrum(150 MHz, CDCl₃) of compound 4j



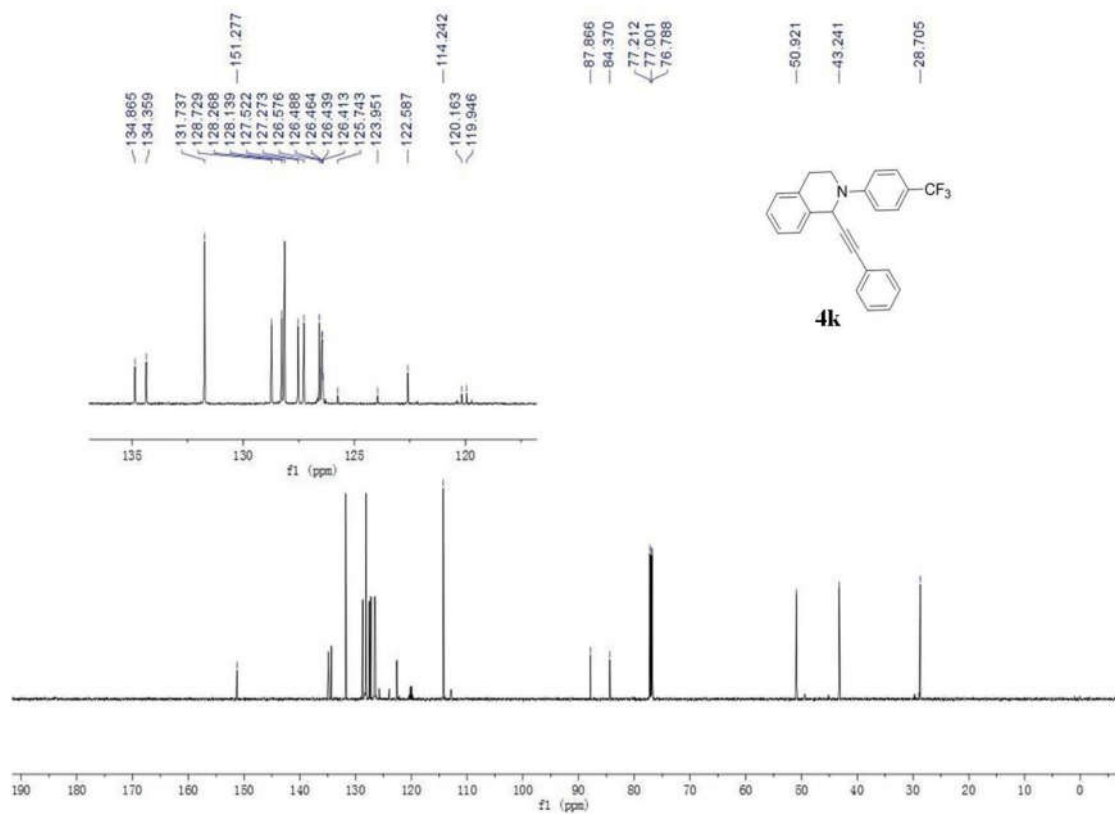
¹⁹F spectrum(565 MHz, CDCl₃) of compound 4j



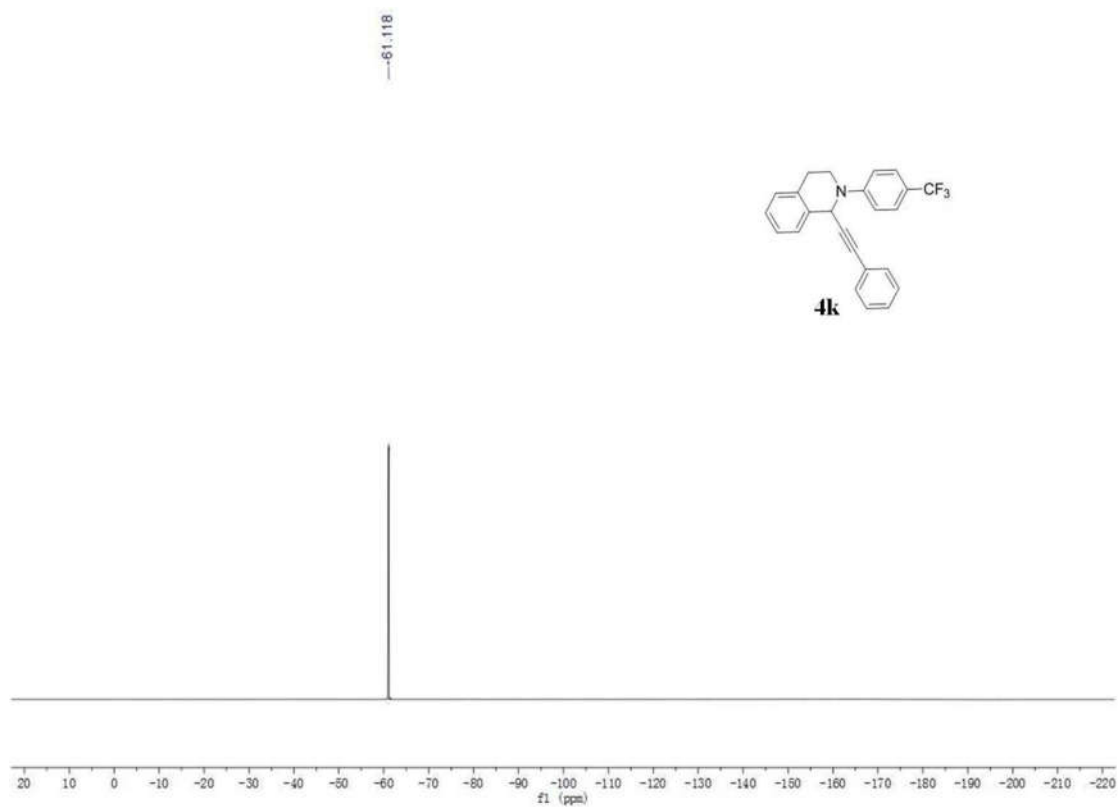
¹H spectrum(600 MHz, CDCl₃) of compound 4k



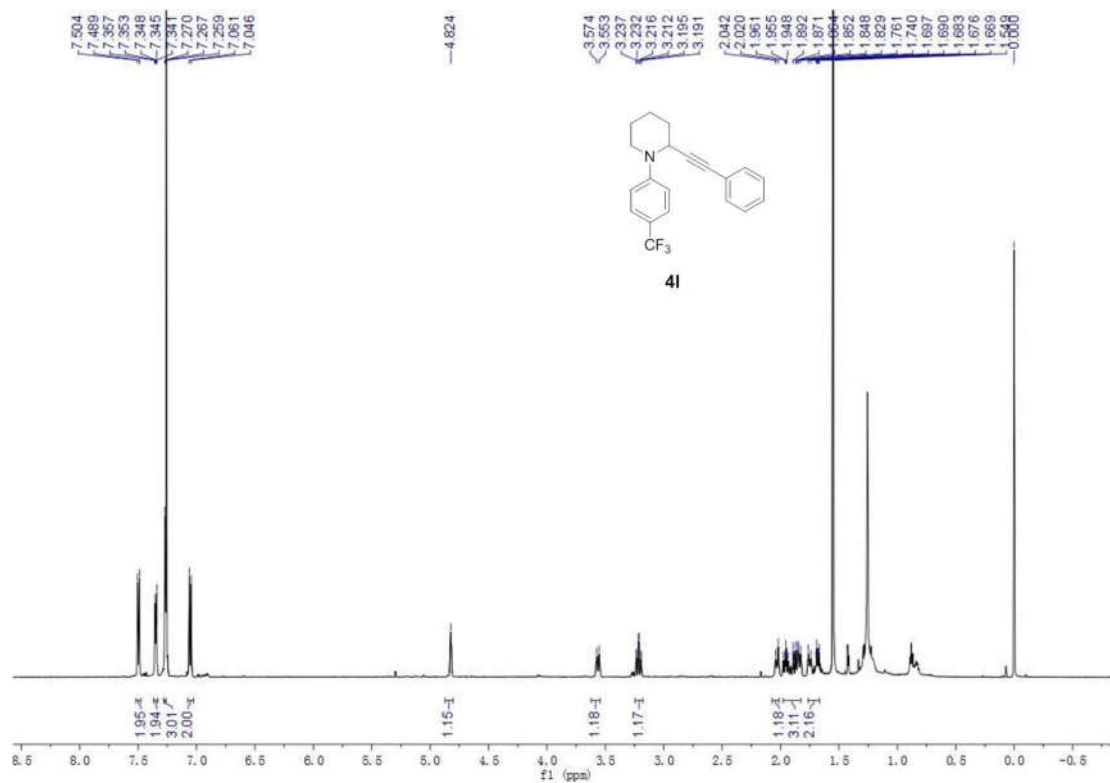
¹³C spectrum(150 MHz, CDCl₃) of compound 4k



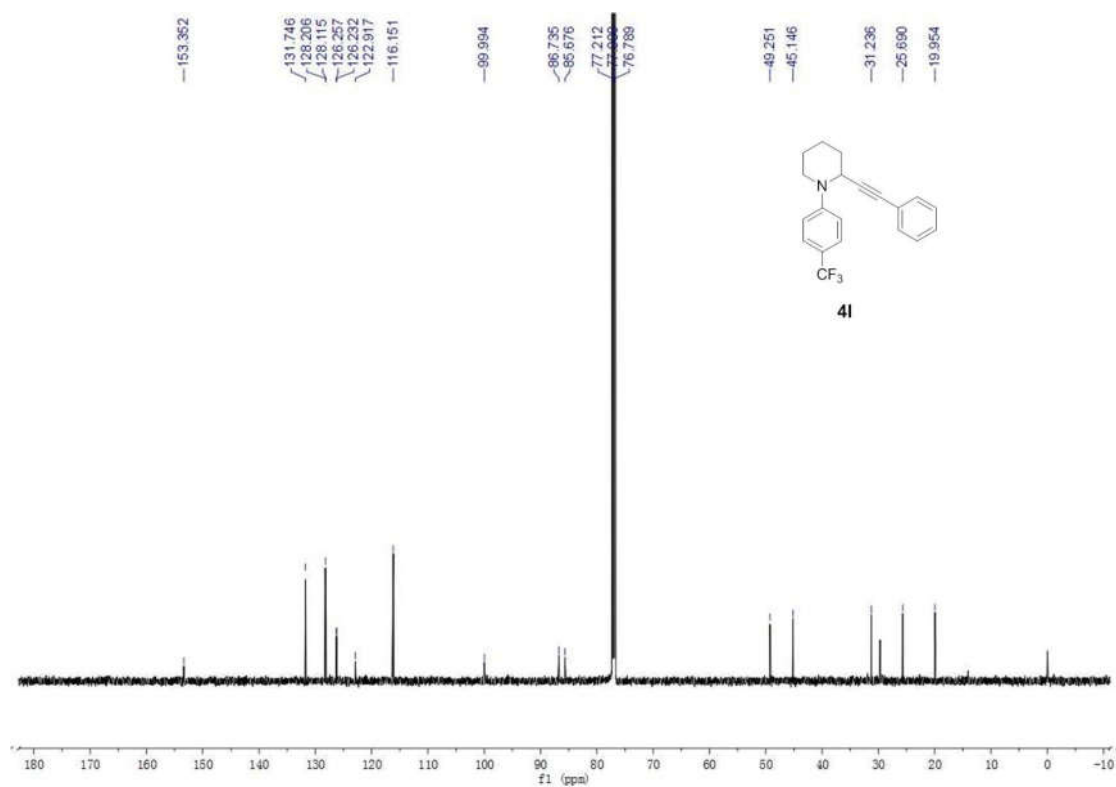
¹⁹F spectrum(565 MHz, CDCl₃) of compound 4k



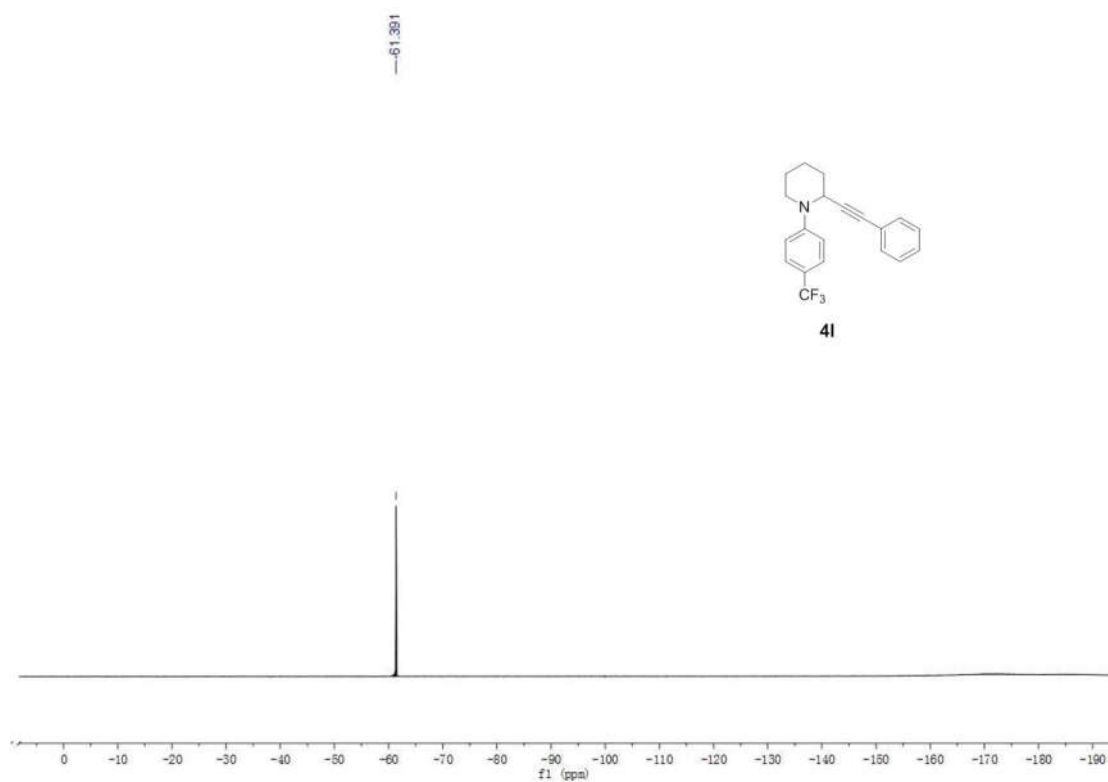
¹H spectrum(600 MHz, CDCl₃) of compound 4l



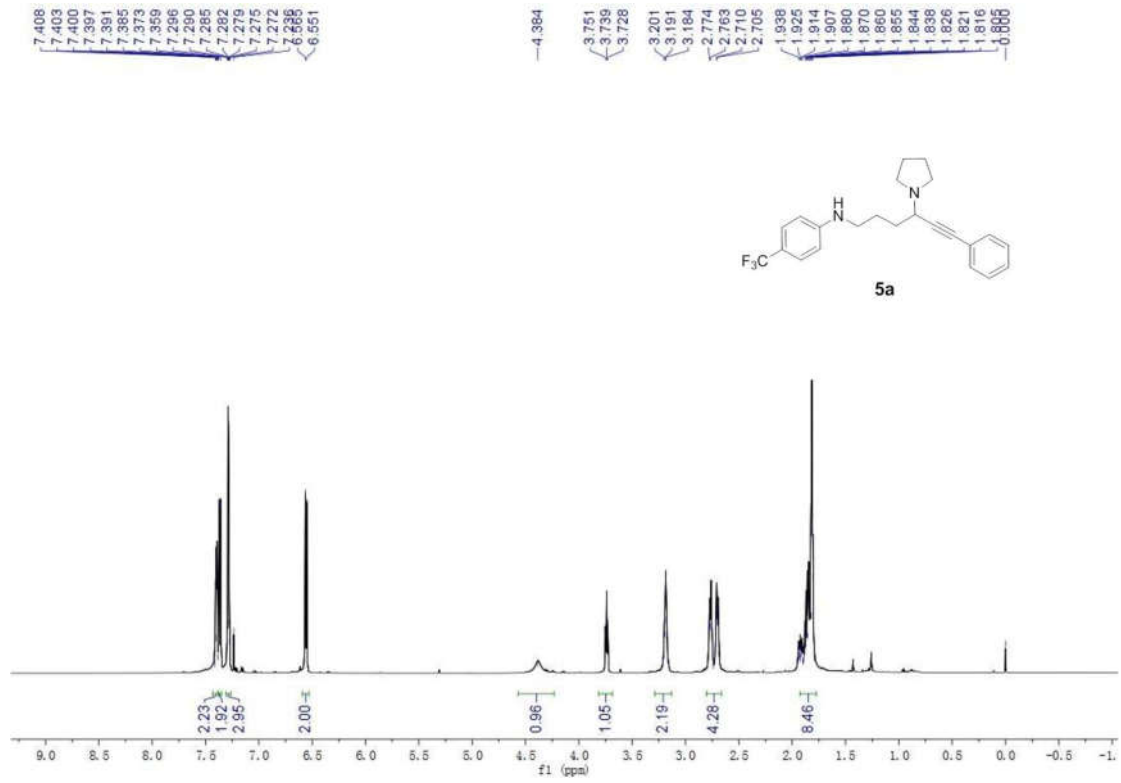
¹³C spectrum(150 MHz, CDCl₃) of compound 4I



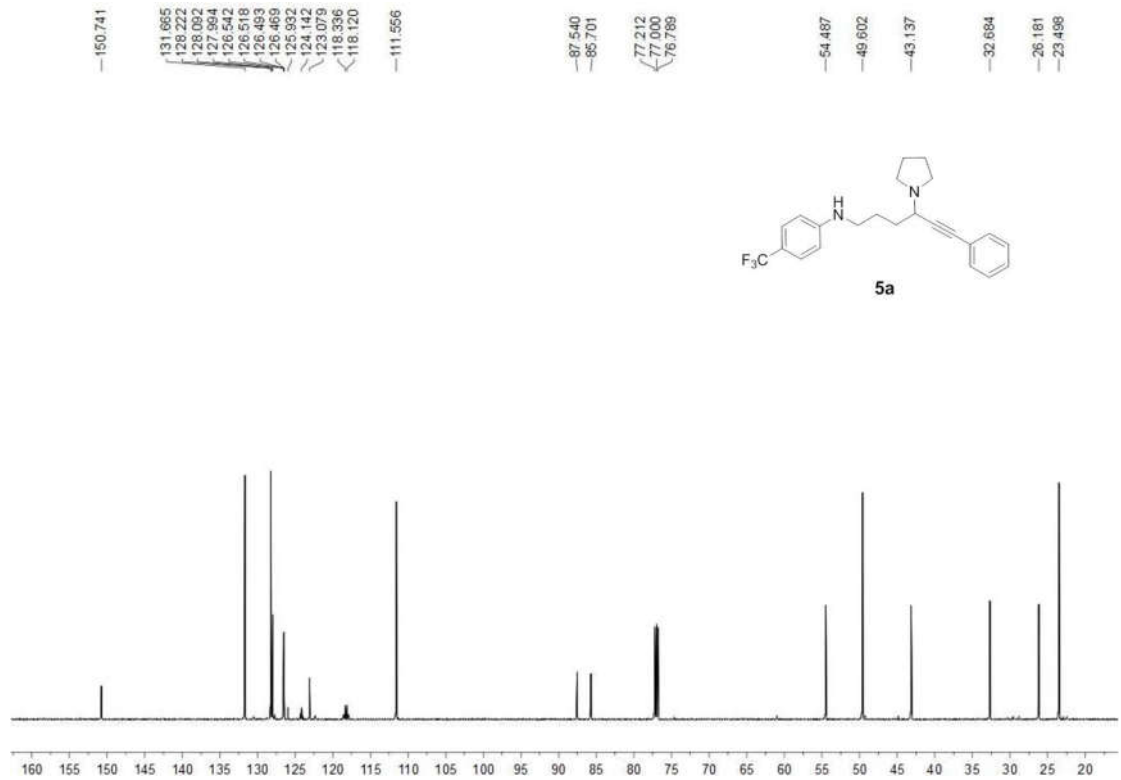
¹⁹F spectrum(565 MHz, CDCl₃) of compound 4I



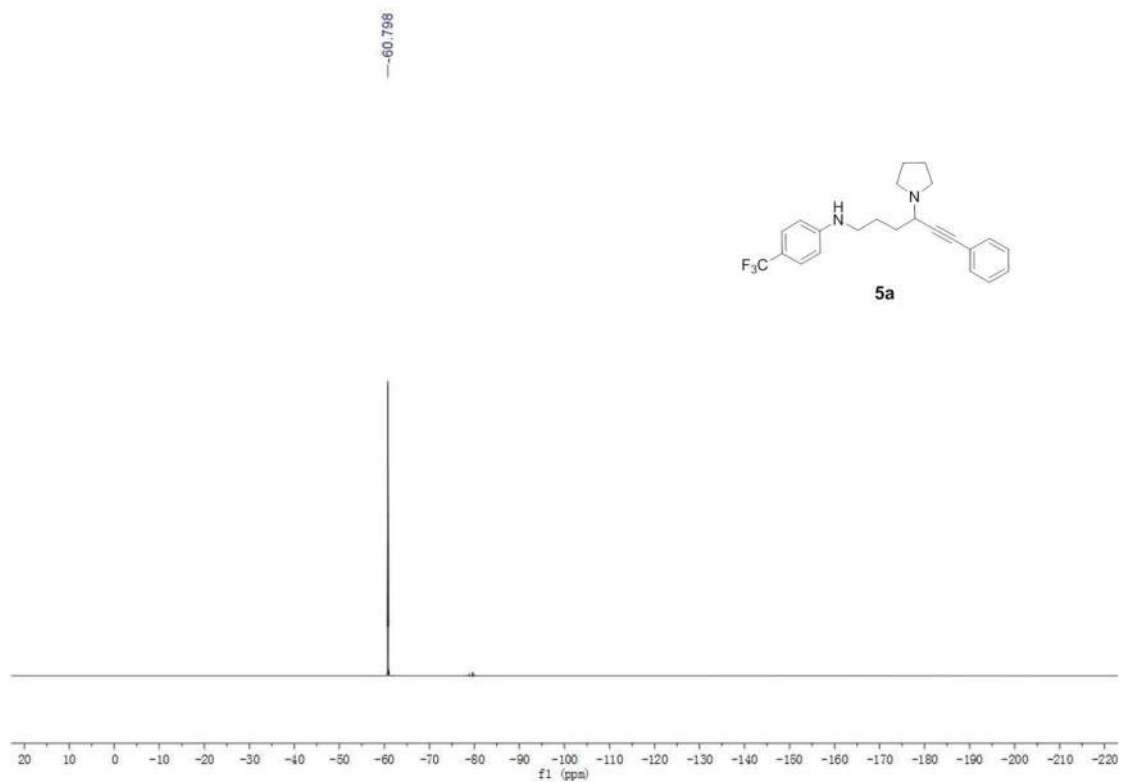
¹H spectrum(600 MHz, CDCl₃) of compound 5a



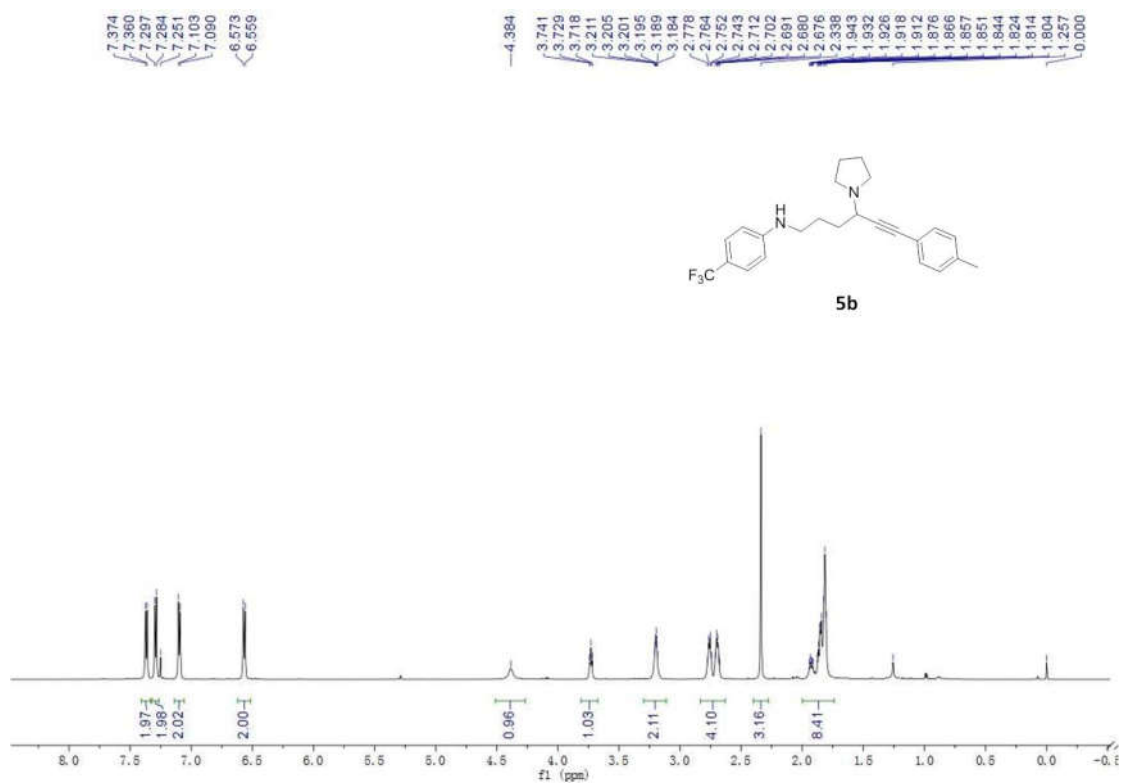
¹³C spectrum(150 MHz, CDCl₃) of compound 5a



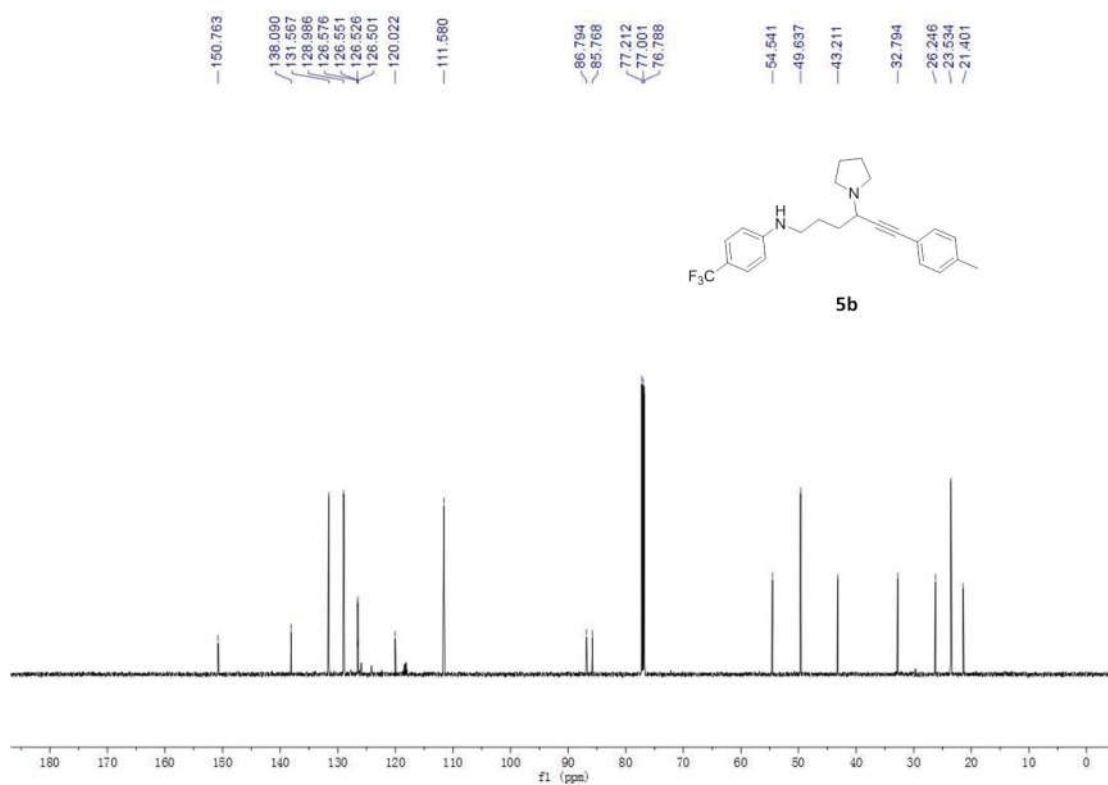
^{19}F spectrum(565 MHz, CDCl_3) of compound 5a



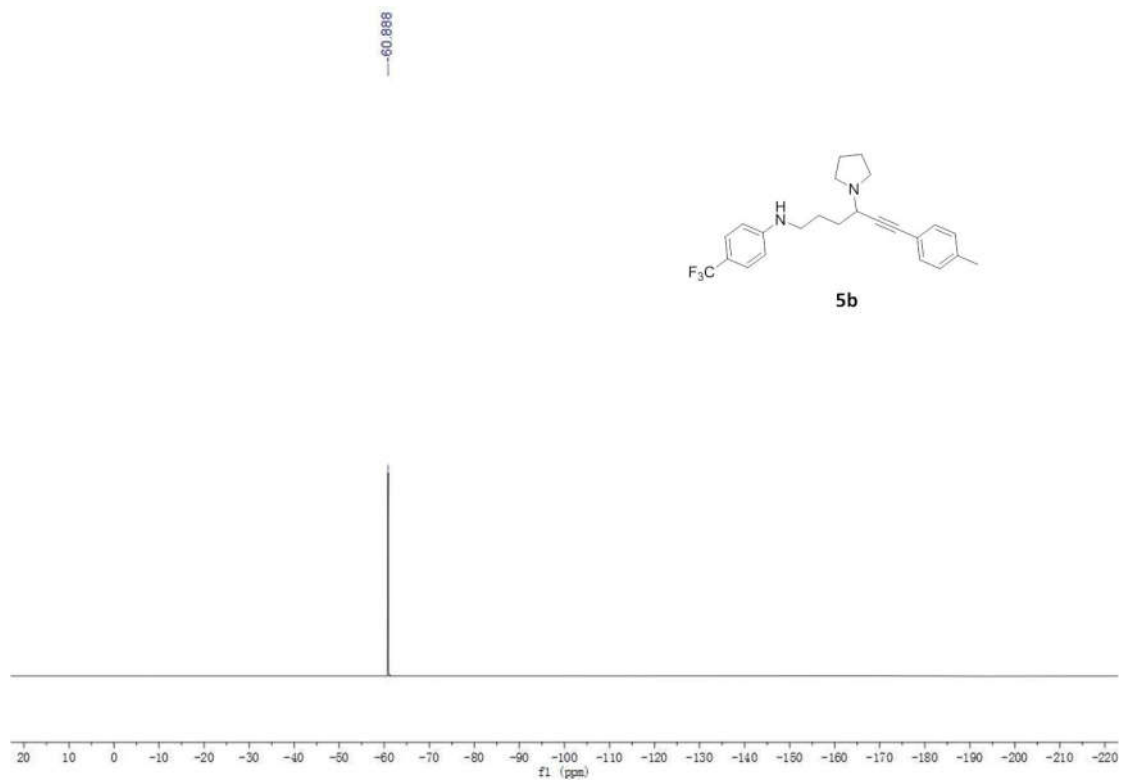
^1H spectrum(600 MHz, CDCl_3) of compound 5b



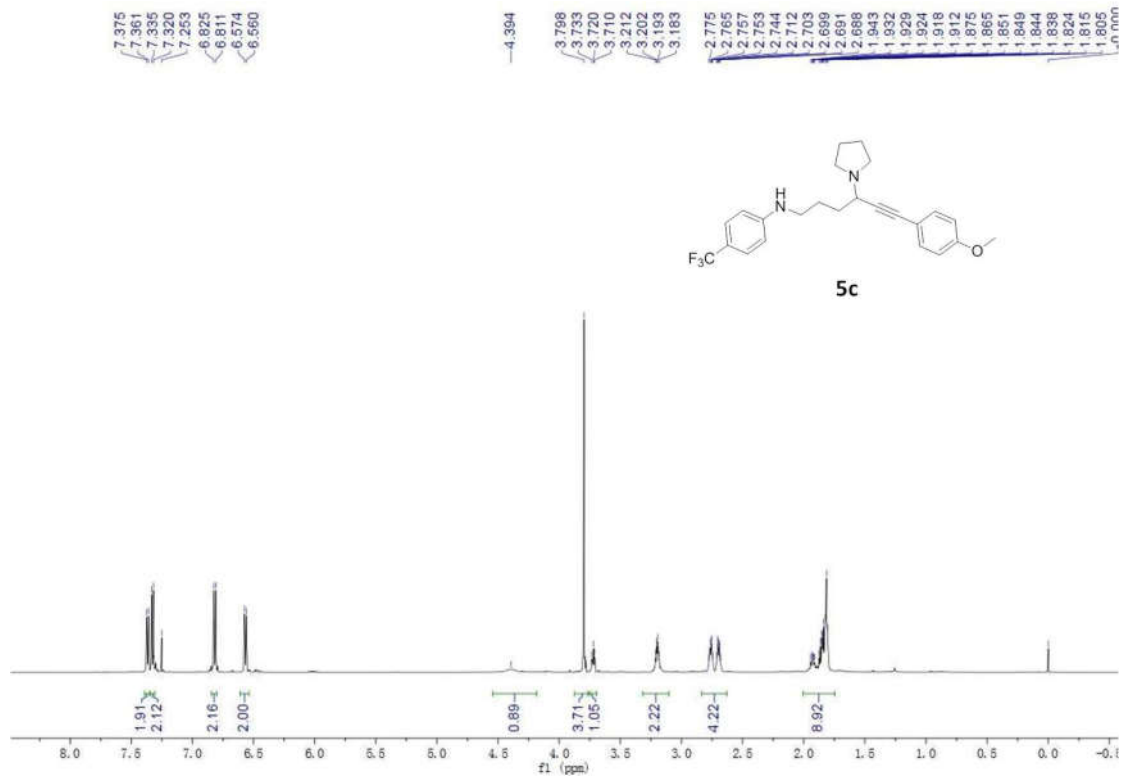
^{13}C spectrum(150 MHz, CDCl_3) of compound 5b



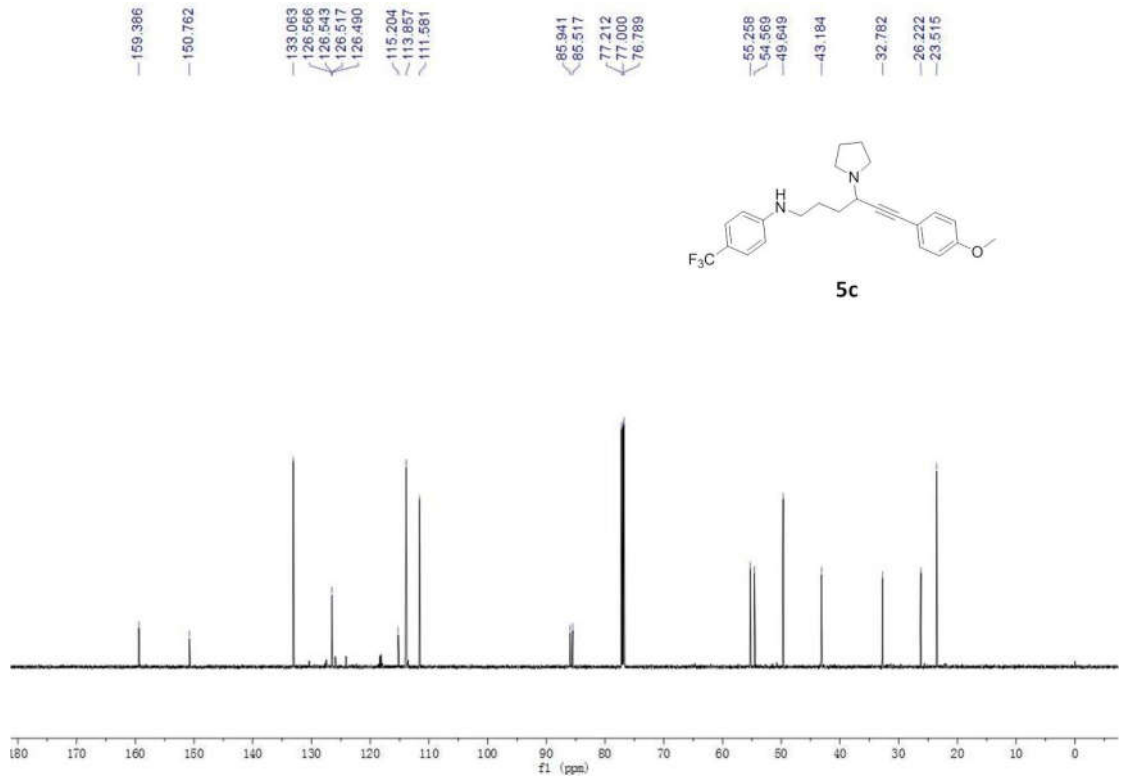
^{19}F spectrum(565 MHz, CDCl_3) of compound 5b



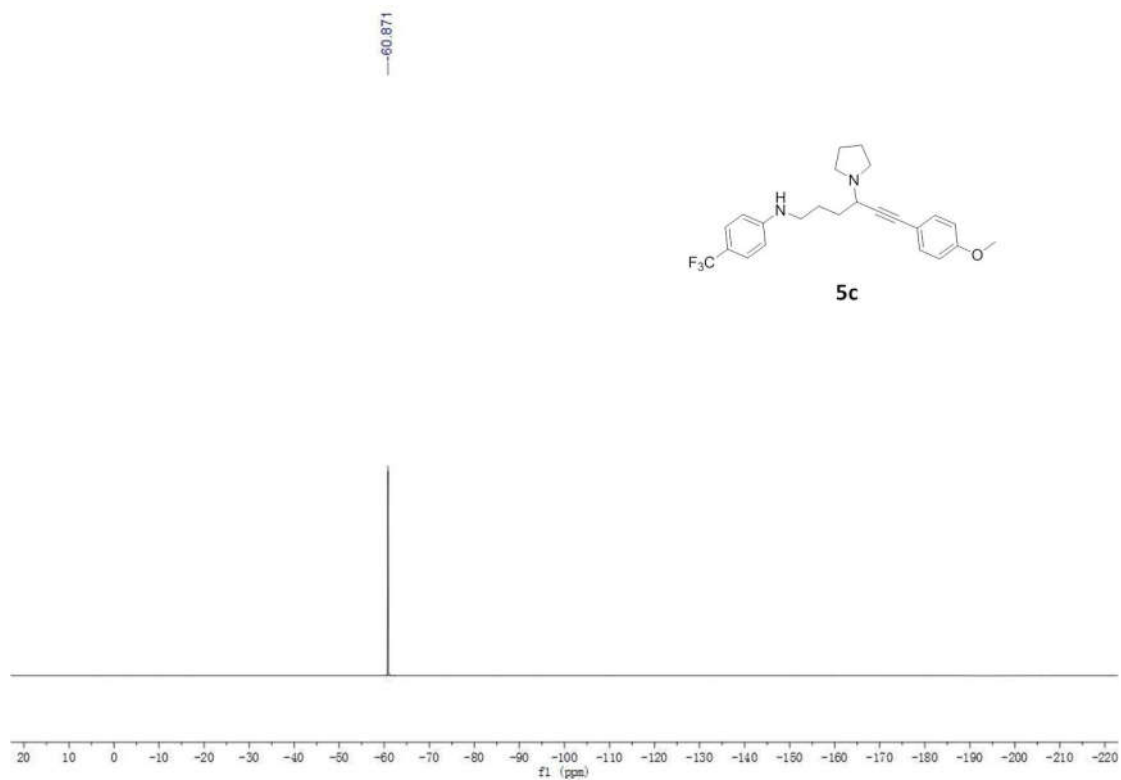
¹H spectrum(600 MHz, CDCl₃) of compound 5c



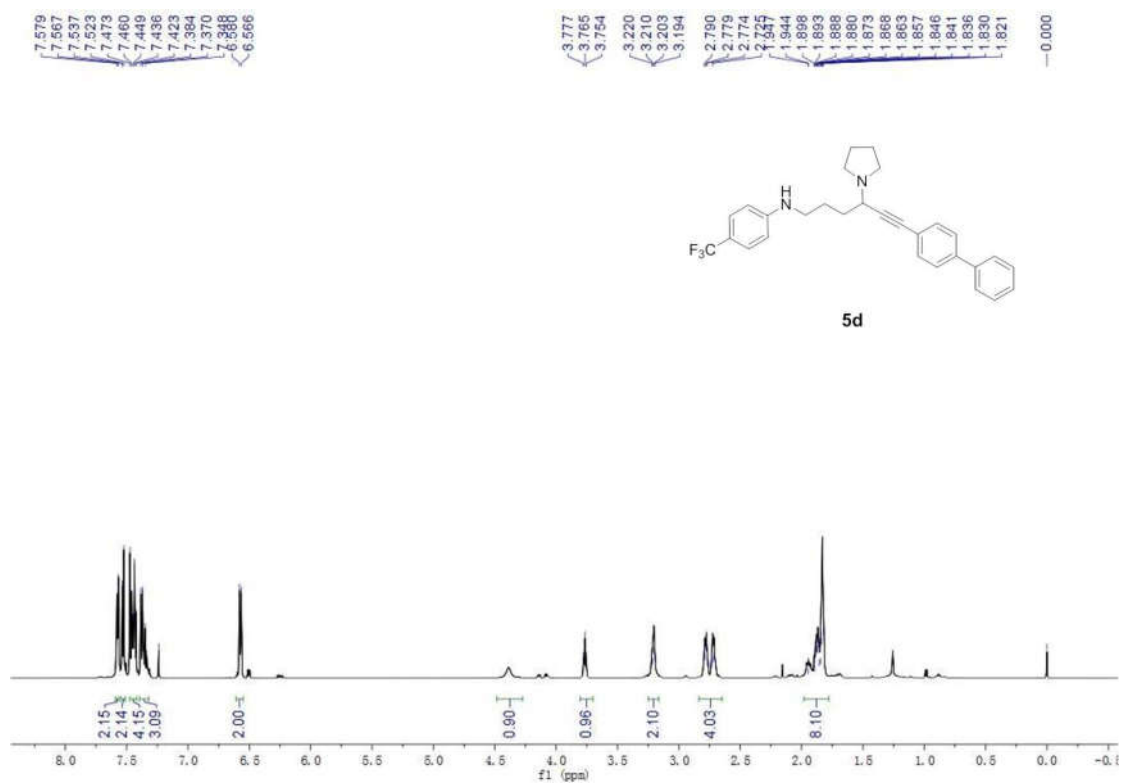
¹³C spectrum(150 MHz, CDCl₃) of compound 5c



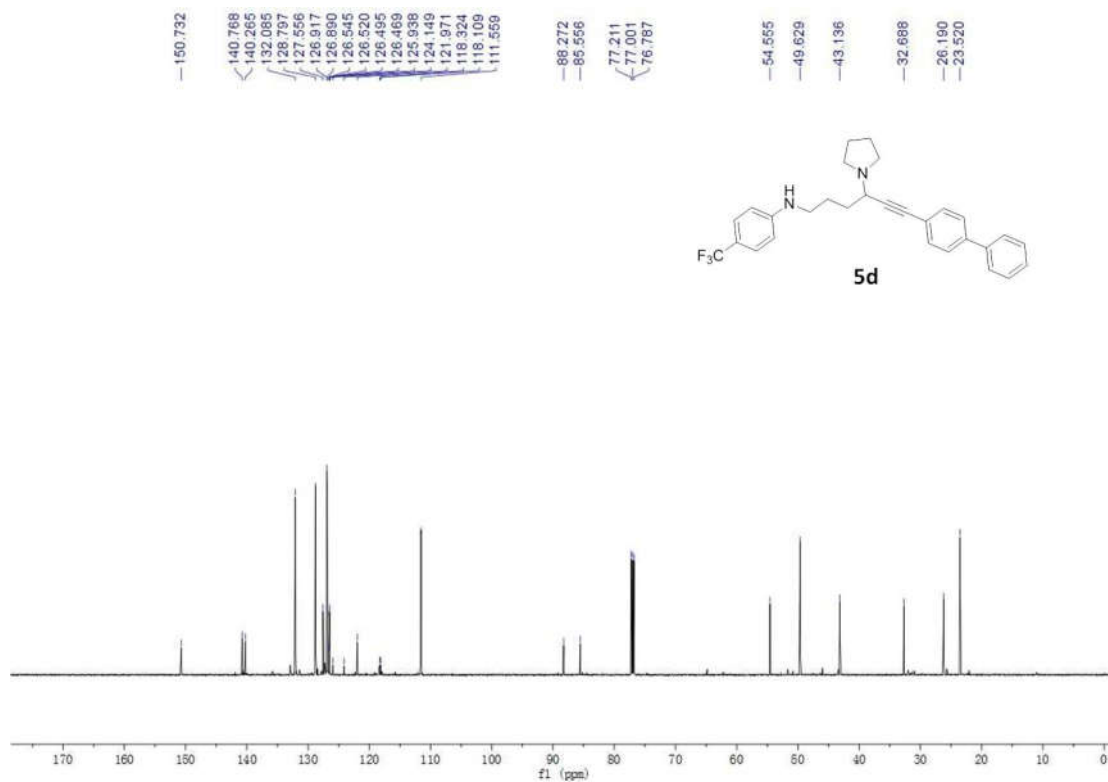
^{19}F spectrum(565 MHz, CDCl_3) of compound 5c



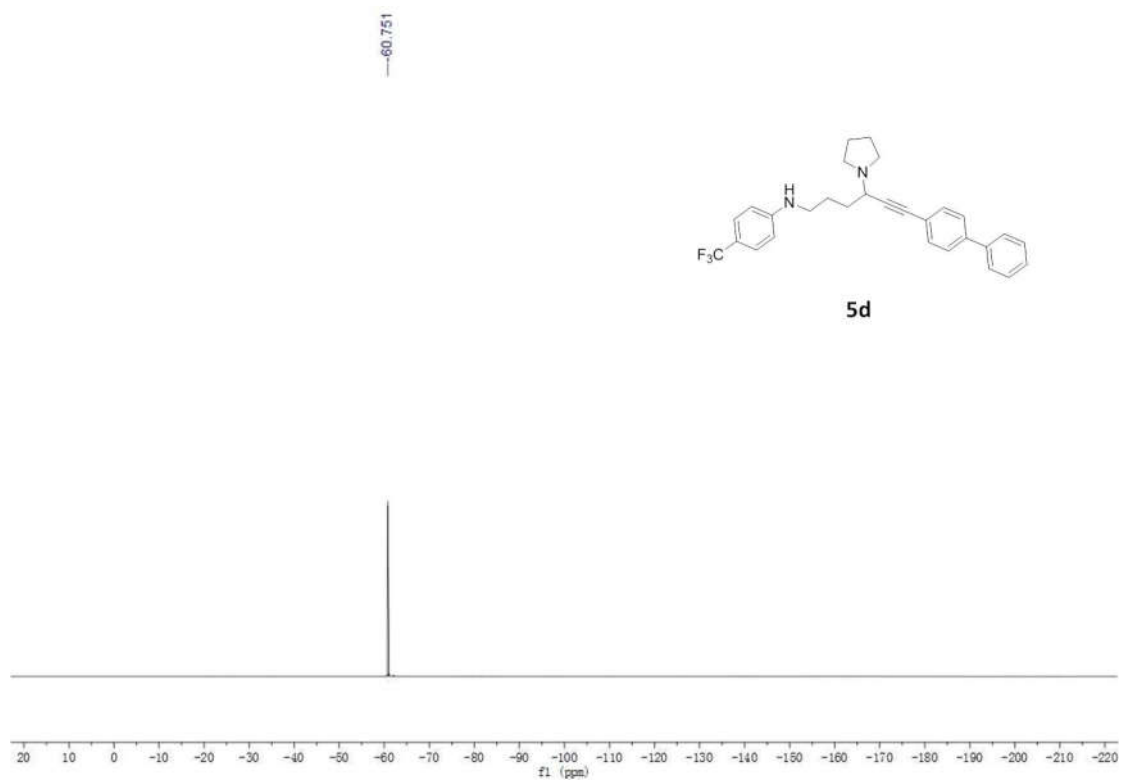
^1H spectrum(600 MHz, CDCl_3) of compound 5d



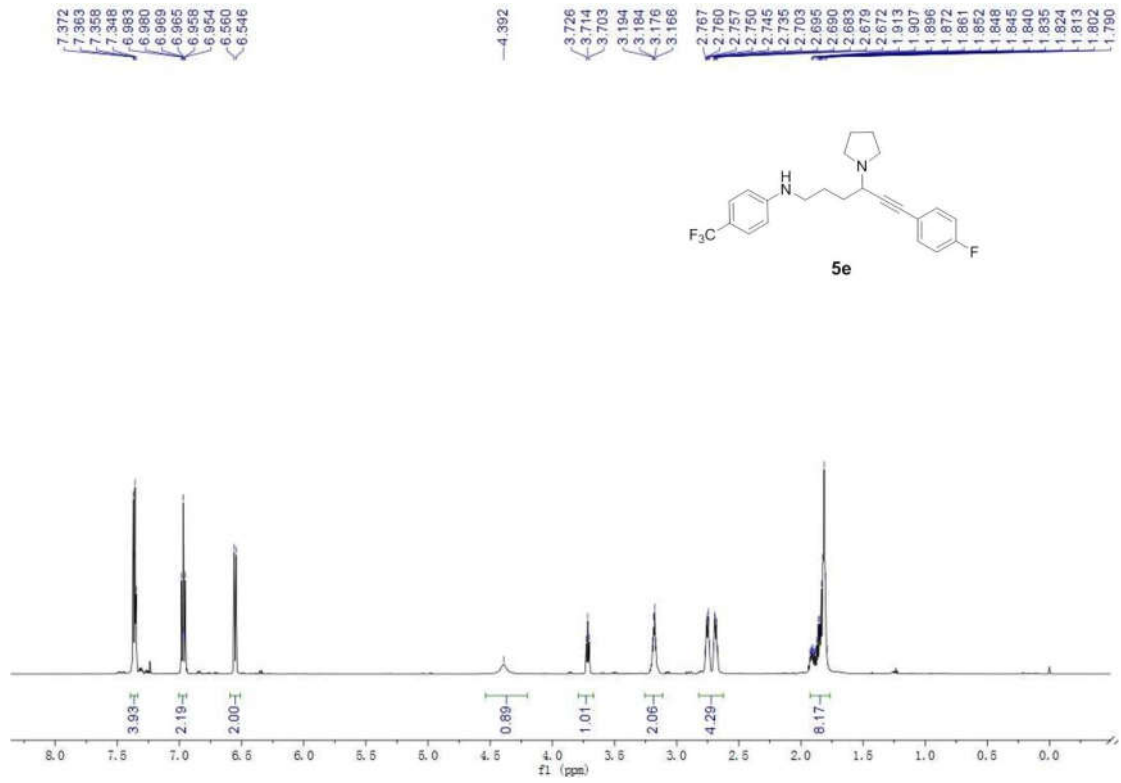
^{13}C spectrum(150 MHz, CDCl_3) of compound 5d



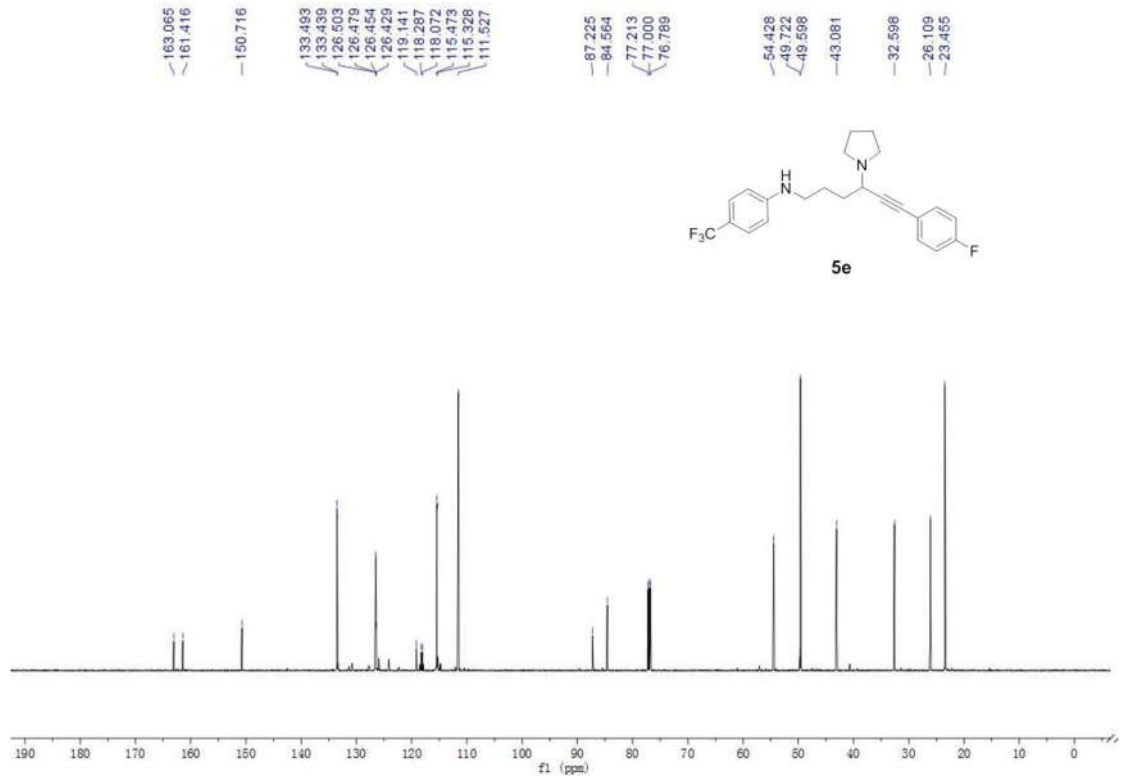
^{19}F spectrum(565 MHz, CDCl_3) of compound 5d



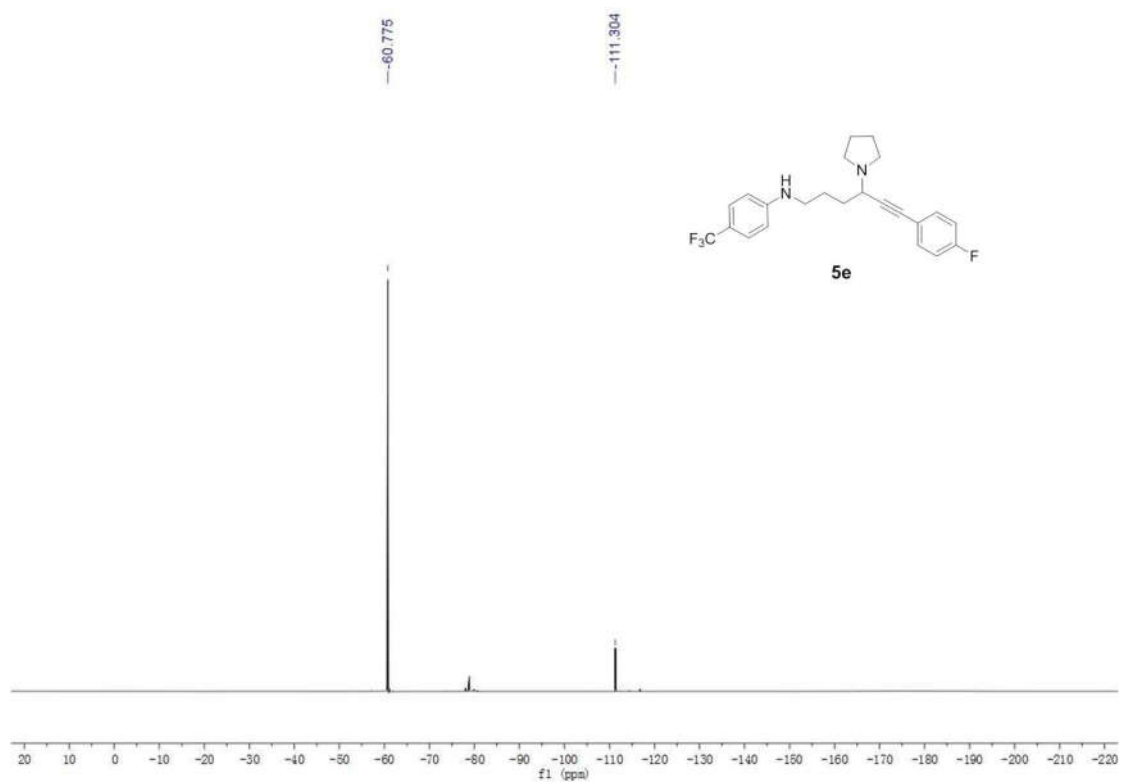
¹H spectrum(600 MHz, CDCl₃) of compound 5e



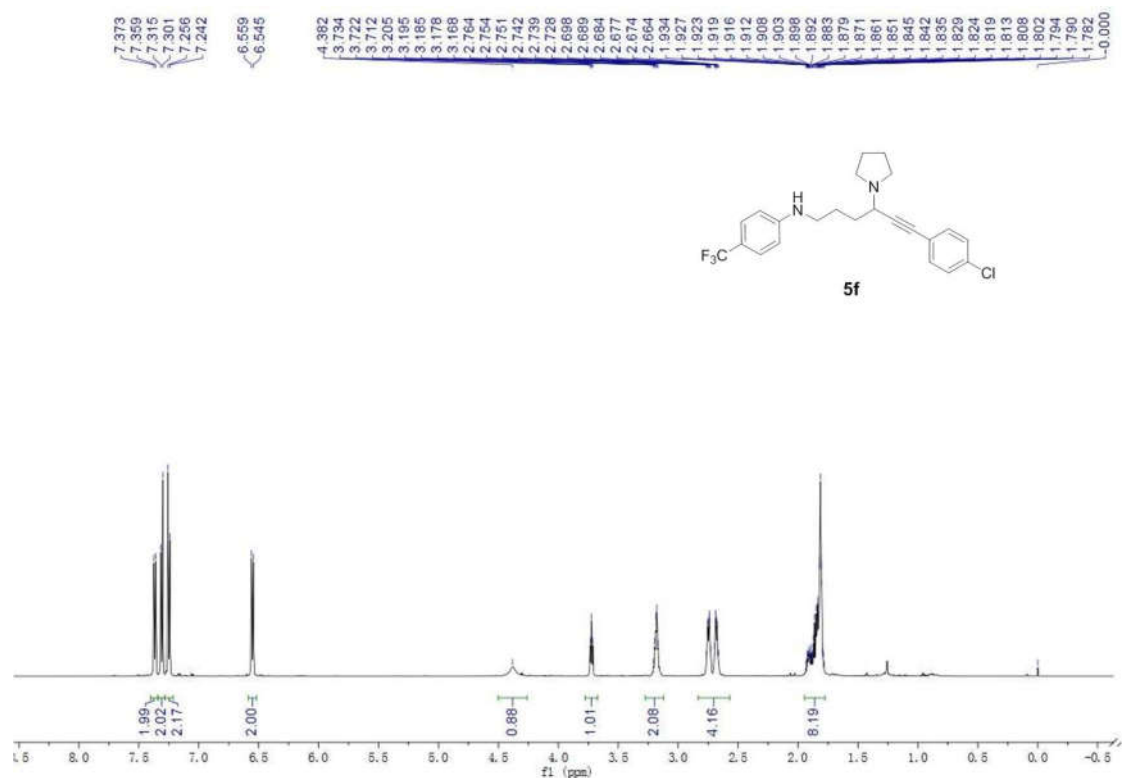
¹³C spectrum(150 MHz, CDCl₃) of compound 5e



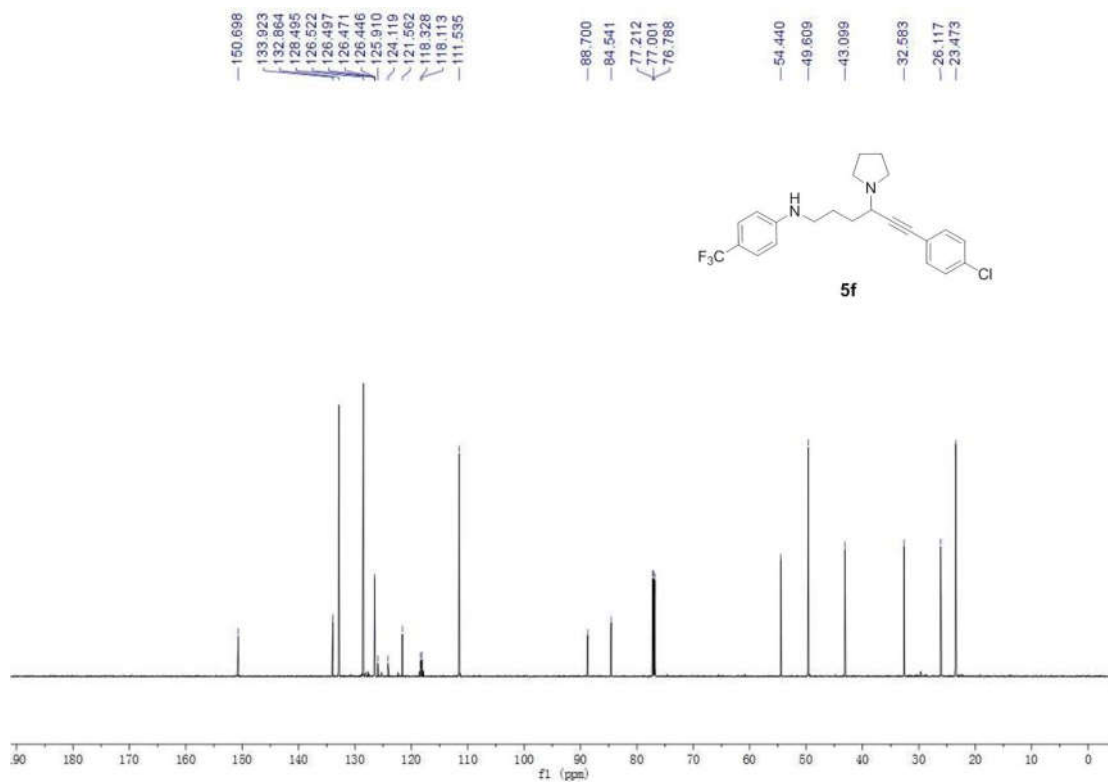
^{19}F spectrum(565 MHz, CDCl_3) of compound 5e



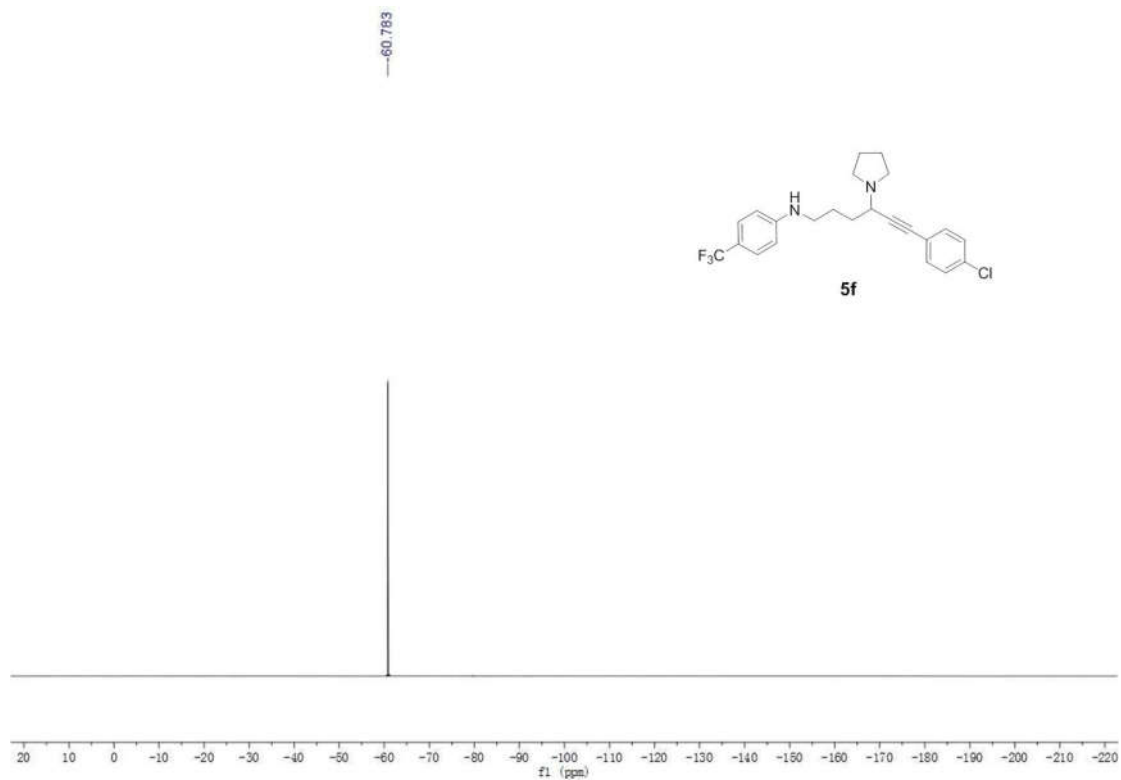
^1H spectrum(600 MHz, CDCl_3) of compound 5f



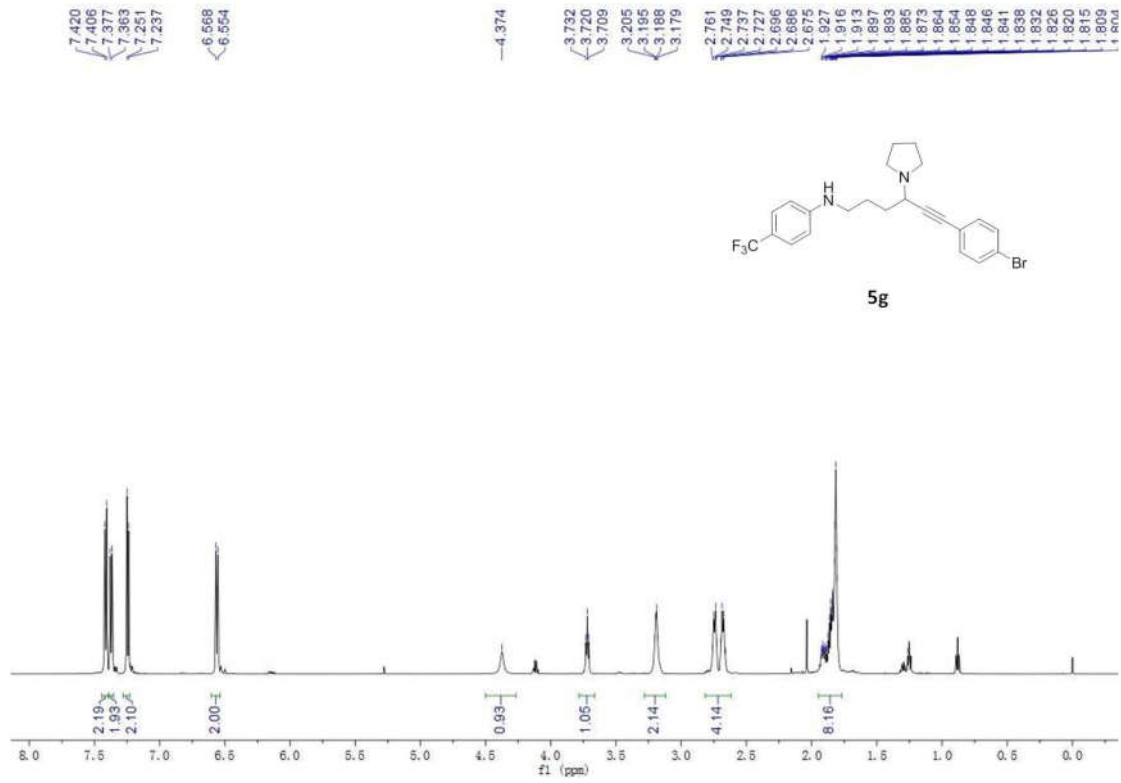
^{13}C spectrum (150 MHz, CDCl_3) of compound 5f



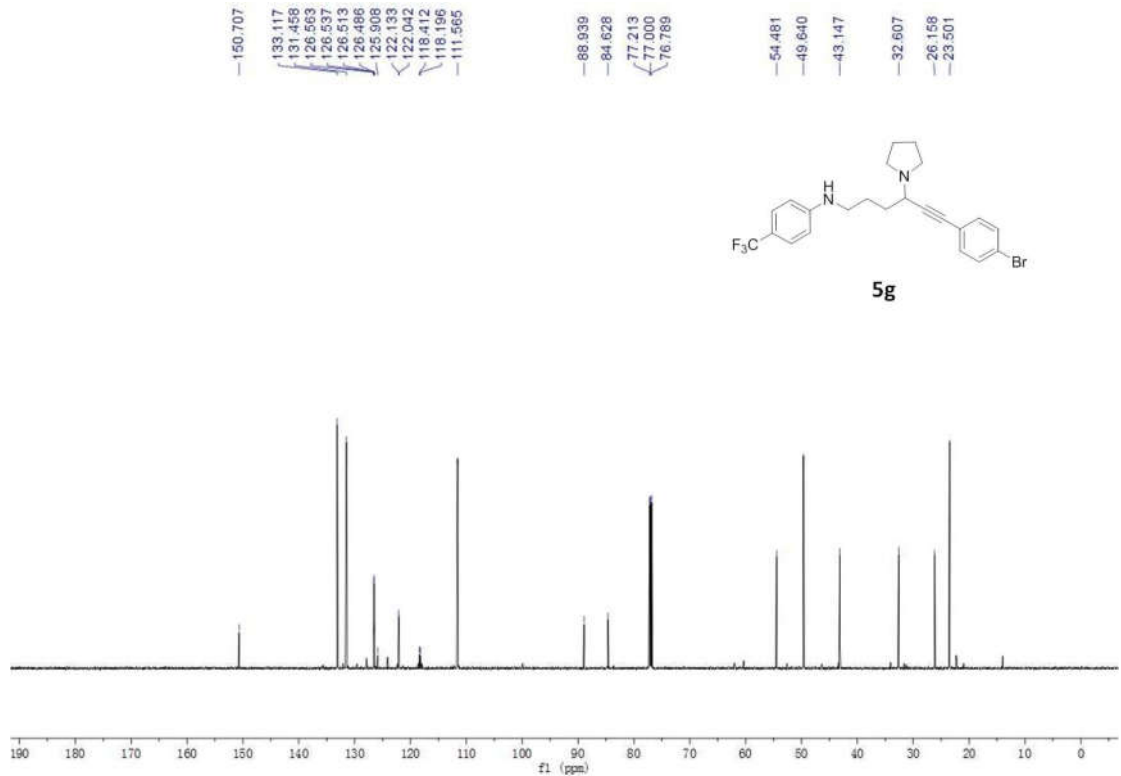
^{19}F spectrum (565 MHz, CDCl_3) of compound 5f



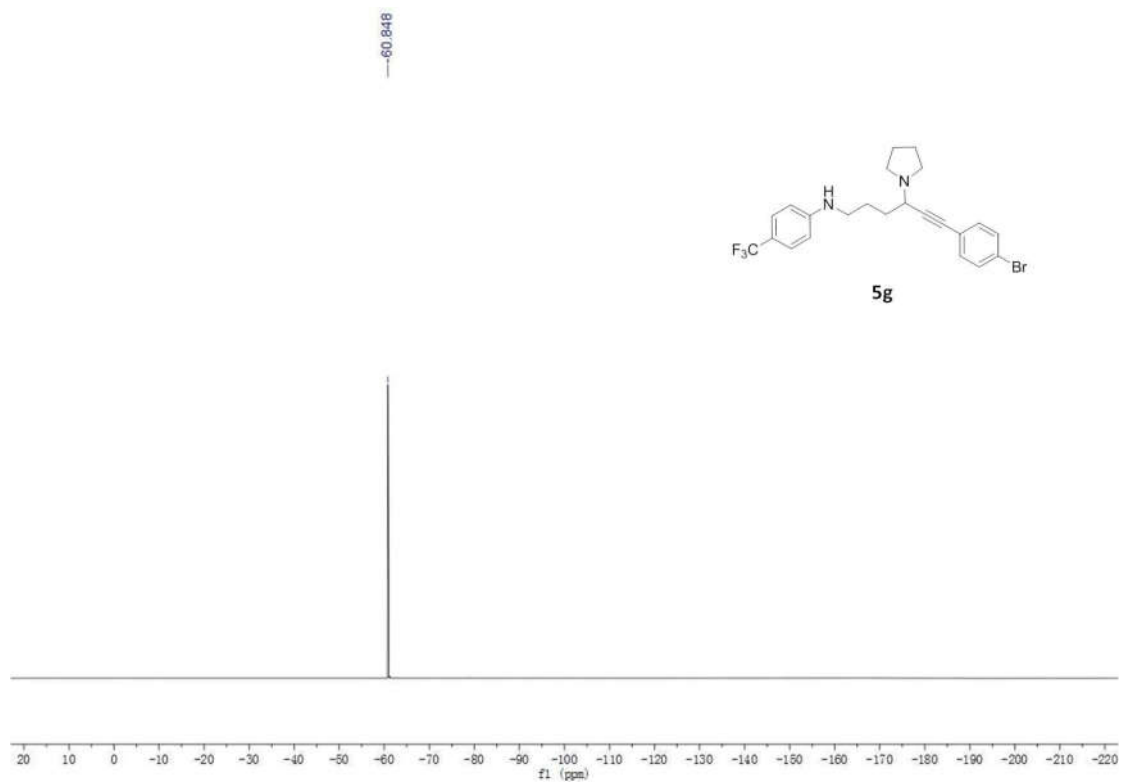
¹H spectrum(600 MHz, CDCl₃) of compound 5g



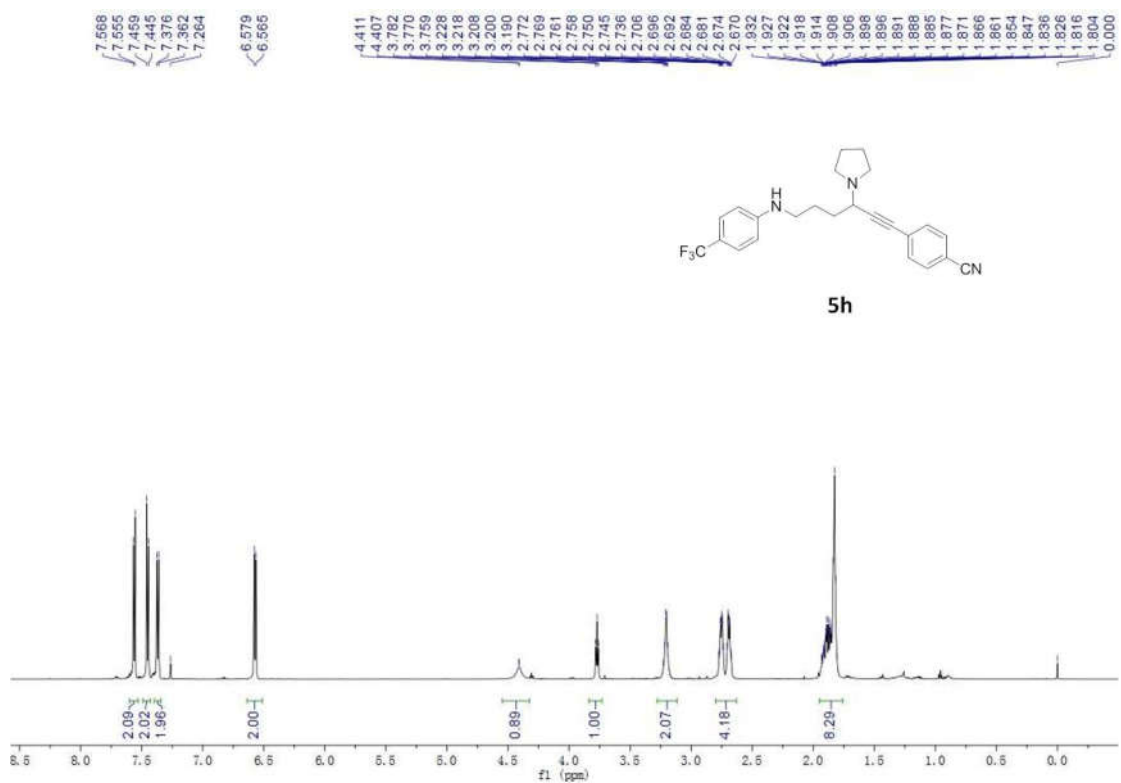
¹³C spectrum(150 MHz, CDCl₃) of compound 5g



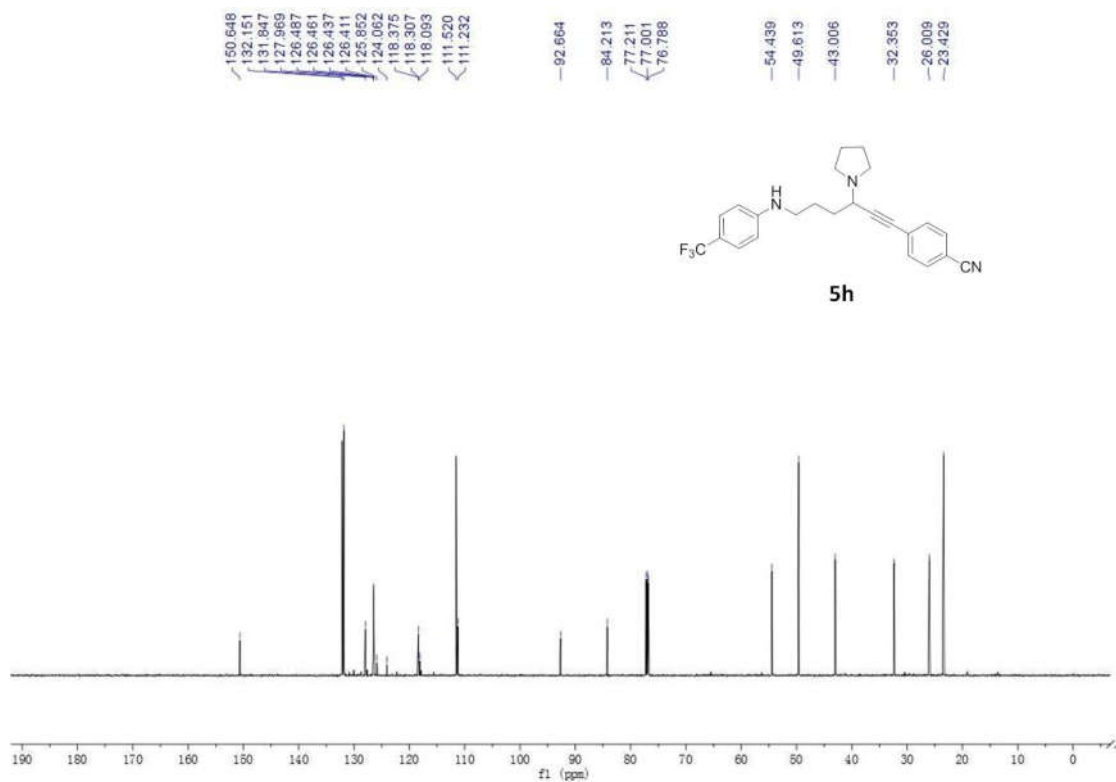
^{19}F spectrum (565 MHz, CDCl_3) of compound 5g



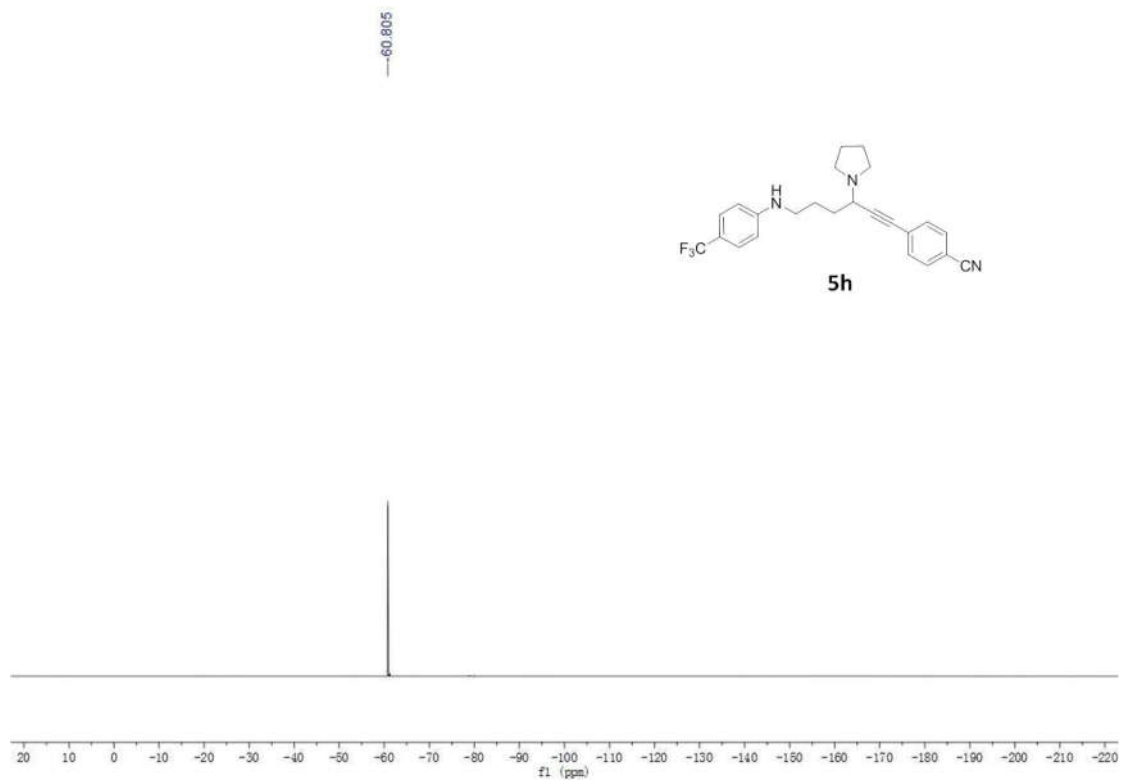
^1H spectrum (600 MHz, CDCl_3) of compound 5h



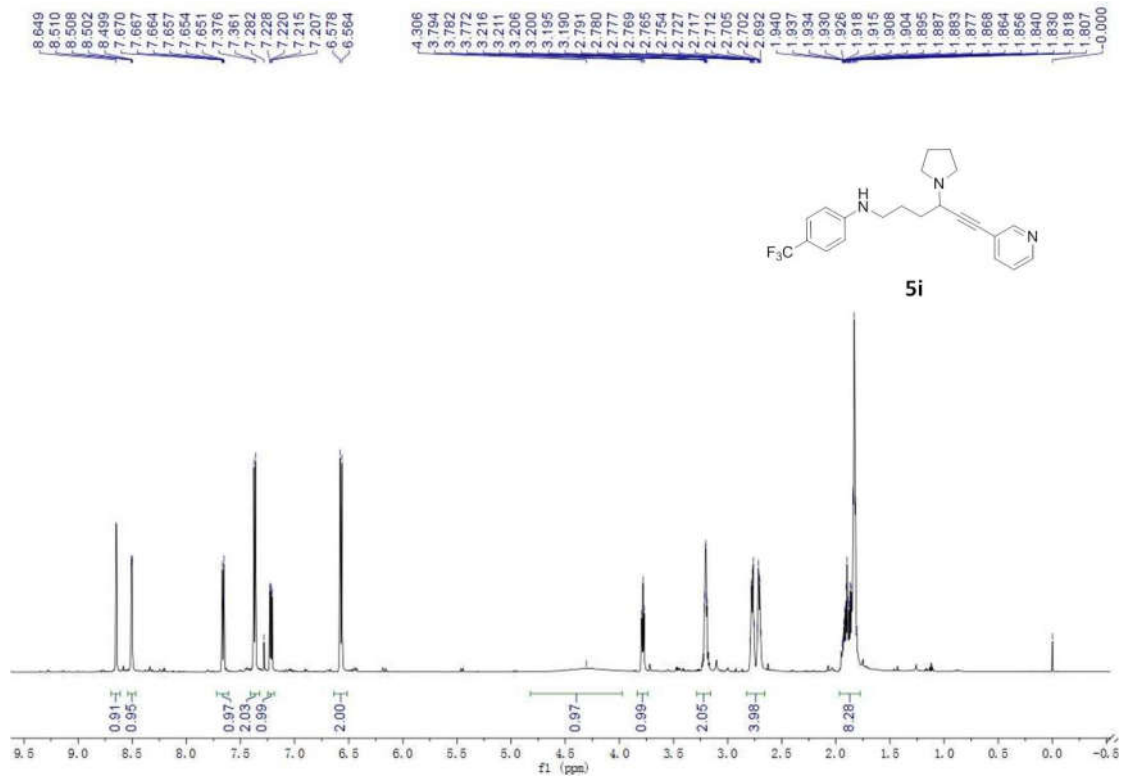
^{13}C spectrum(150 MHz, CDCl_3) of compound 5h



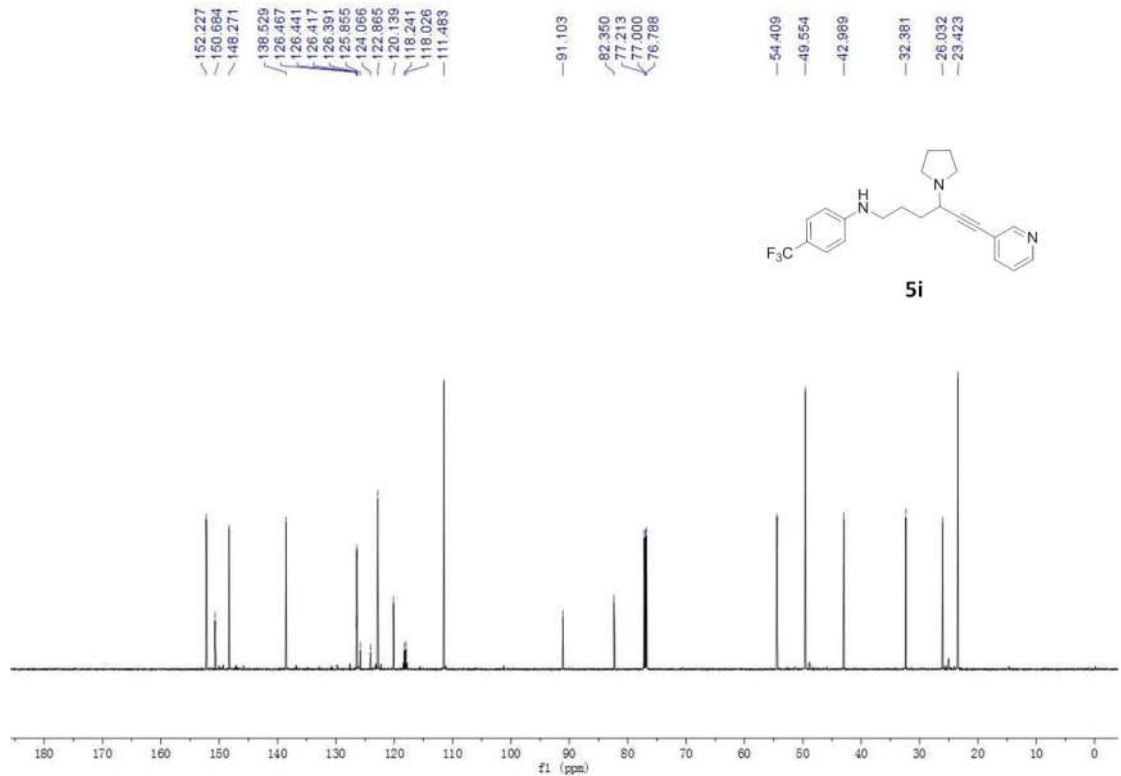
^{19}F spectrum(565 MHz, CDCl_3) of compound 5h



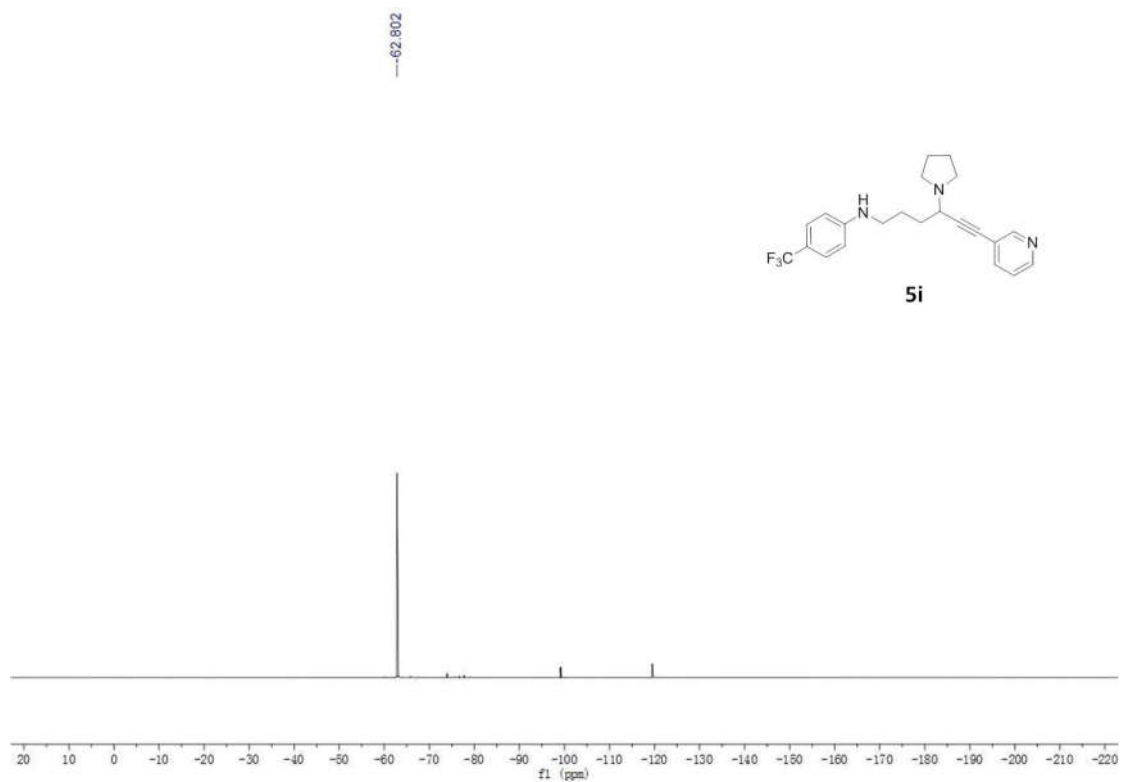
¹H spectrum(600 MHz, CDCl₃) of compound 5i



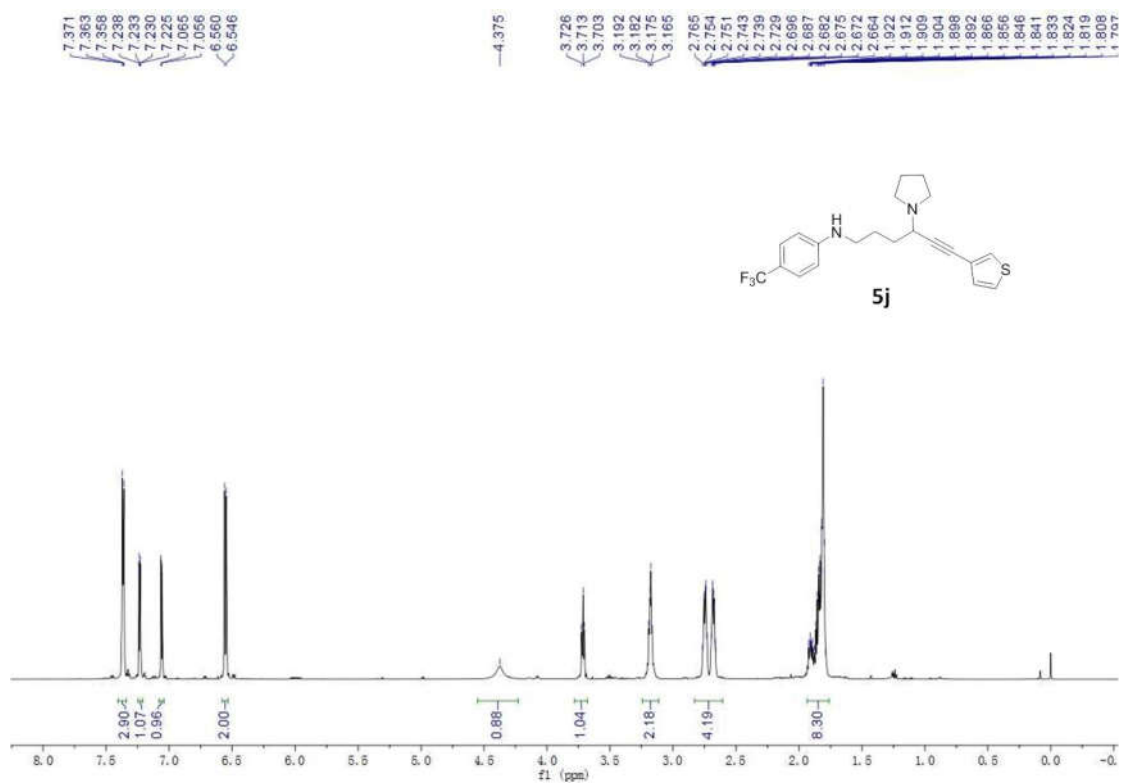
¹³C spectrum(150 MHz, CDCl₃) of compound 5i



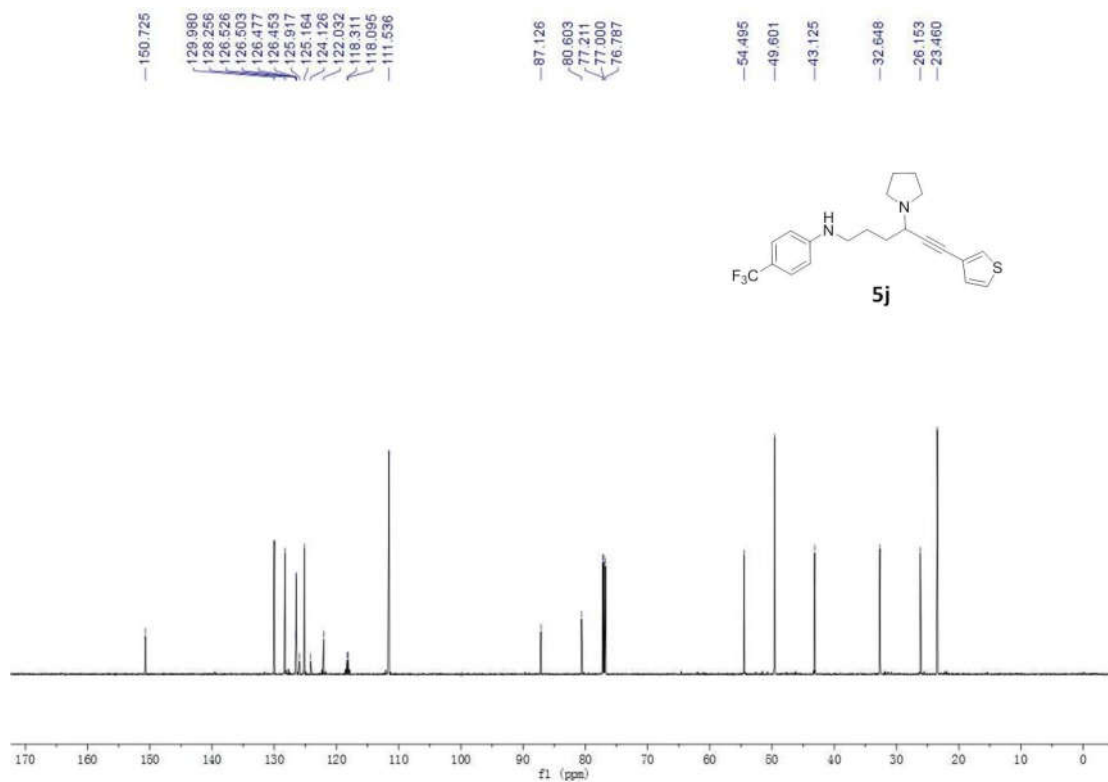
^{19}F spectrum(565 MHz, CDCl_3) of compound **5i**



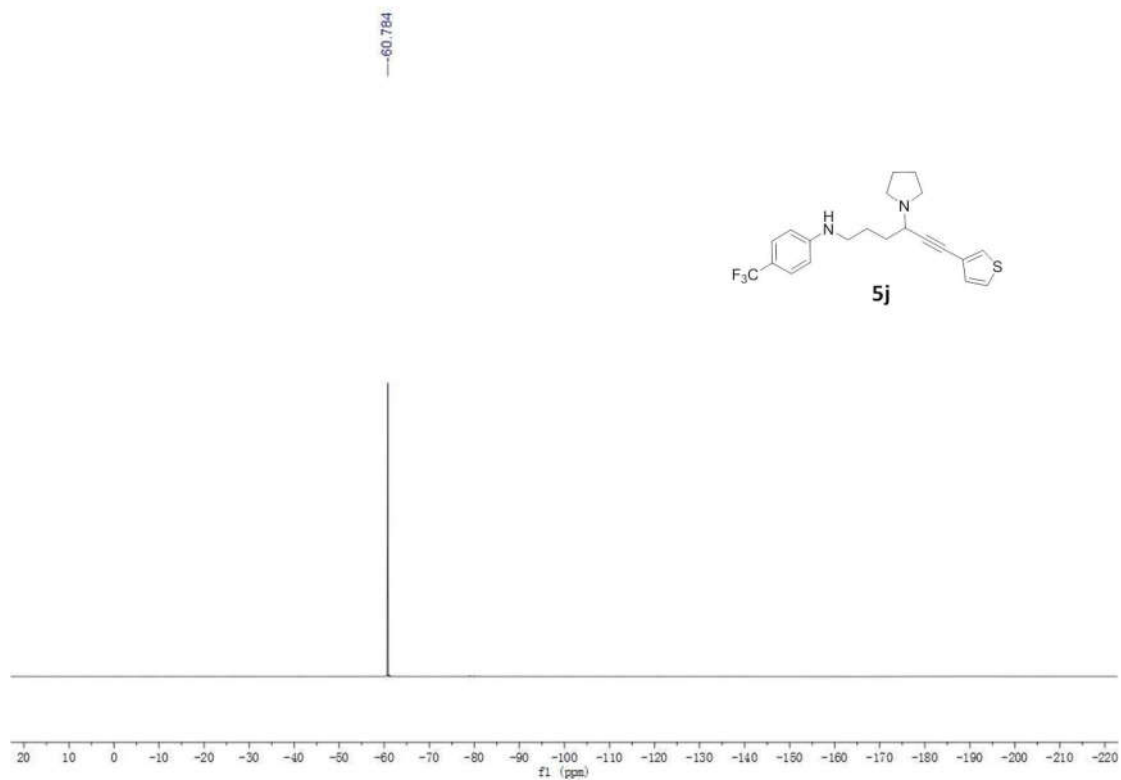
^1H spectrum(600 MHz, CDCl_3) of compound **5j**



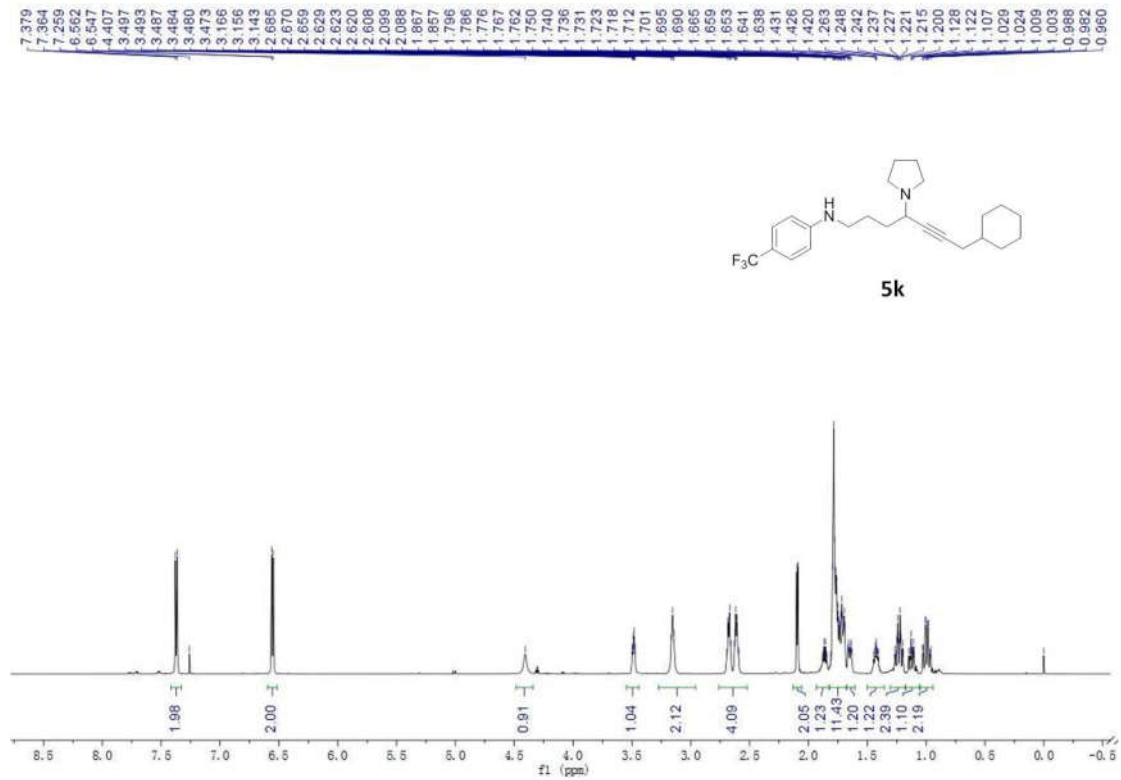
^{13}C spectrum(150 MHz, CDCl_3) of compound 5j



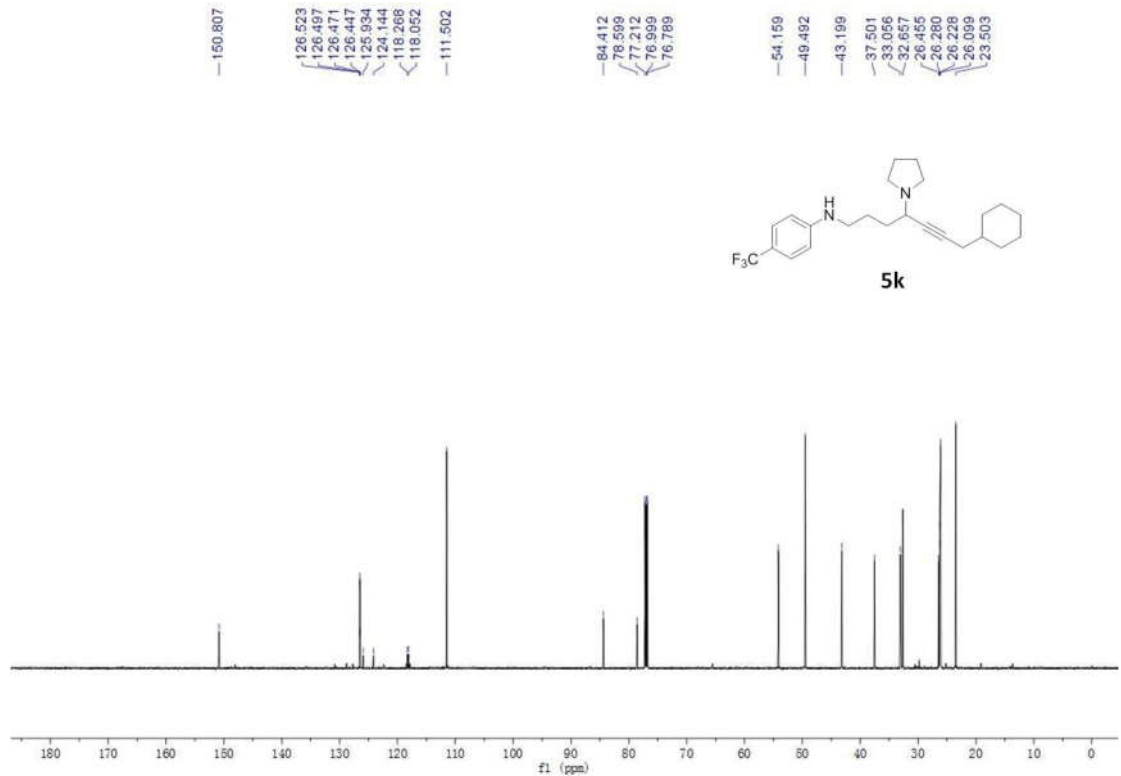
^{19}F spectrum(565 MHz, CDCl_3) of compound 5j



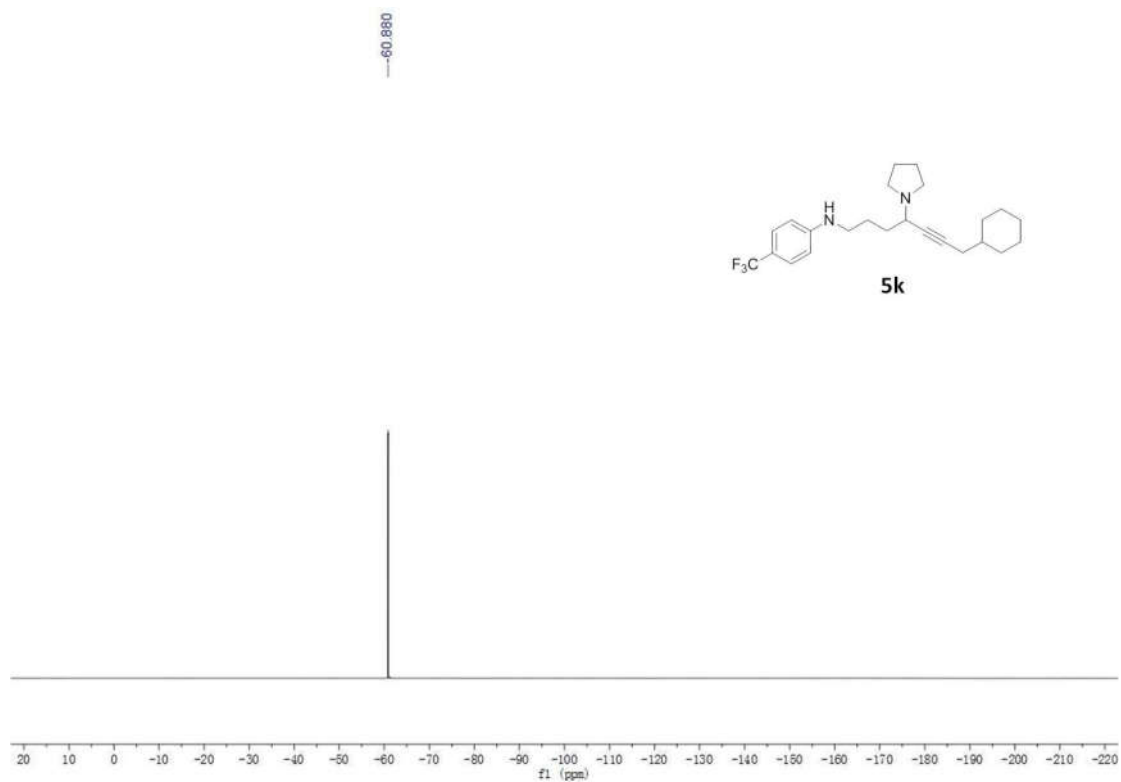
¹H spectrum(600 MHz, CDCl₃) of compound 5k



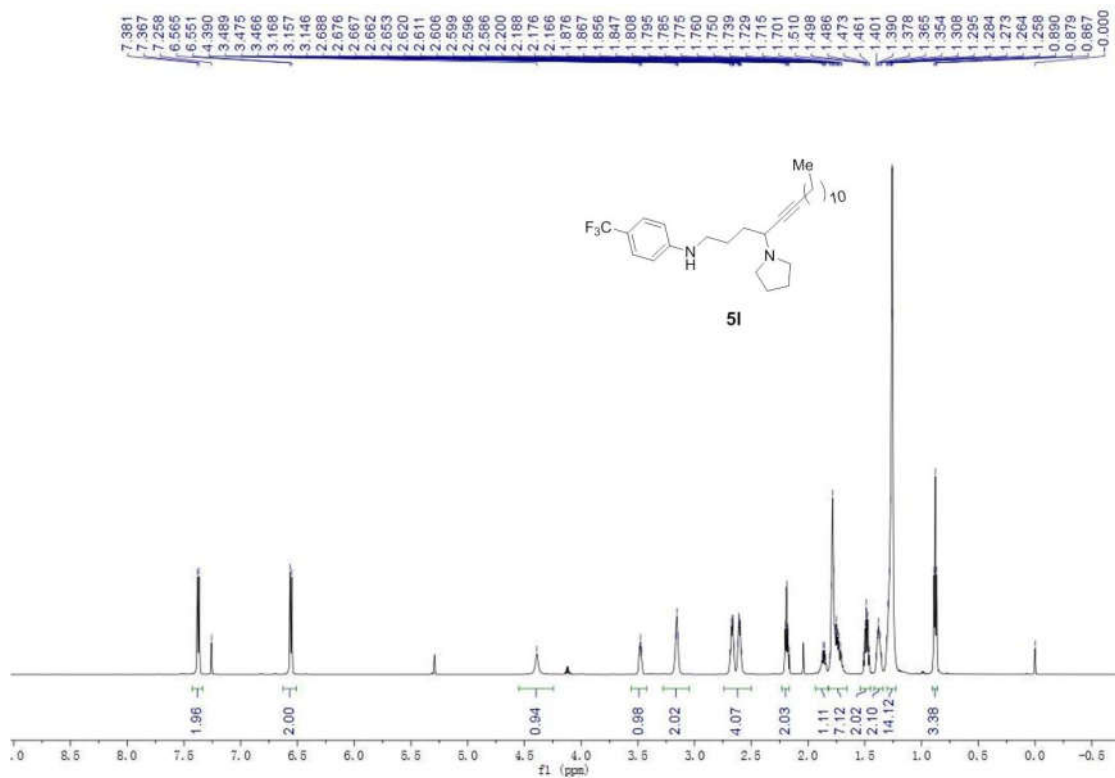
¹³C spectrum(150 MHz, CDCl₃) of compound 5k



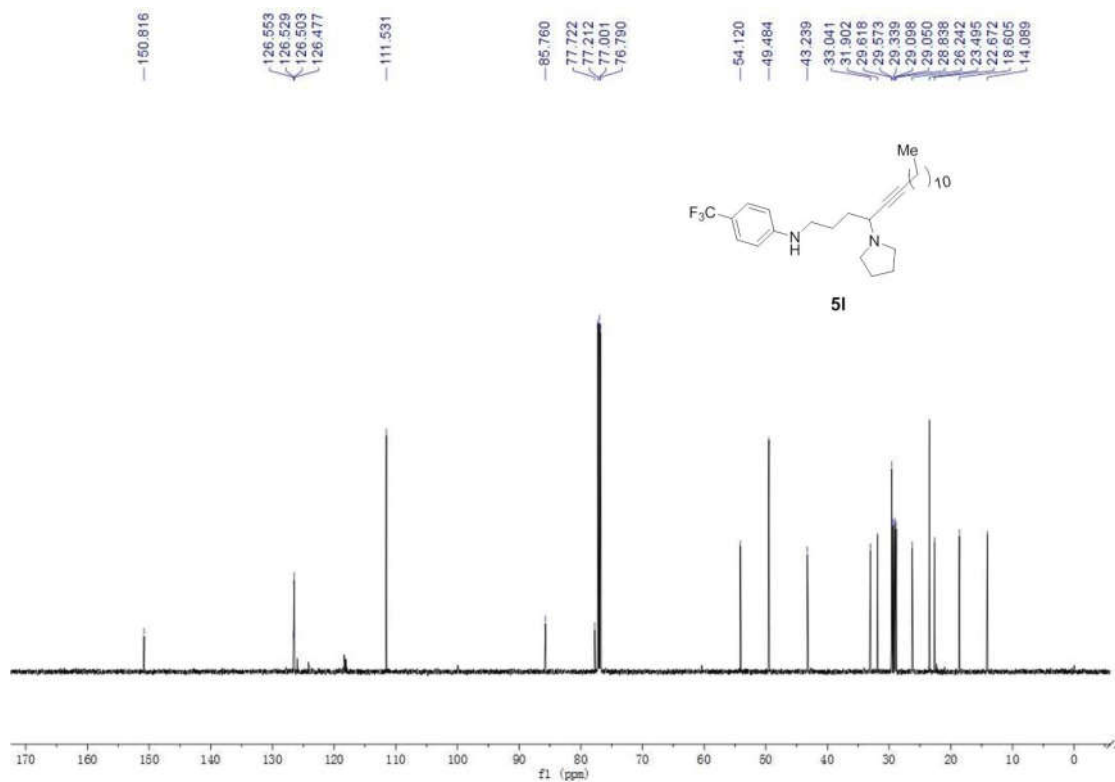
^{19}F spectrum(565 MHz, CDCl_3) of compound 5k



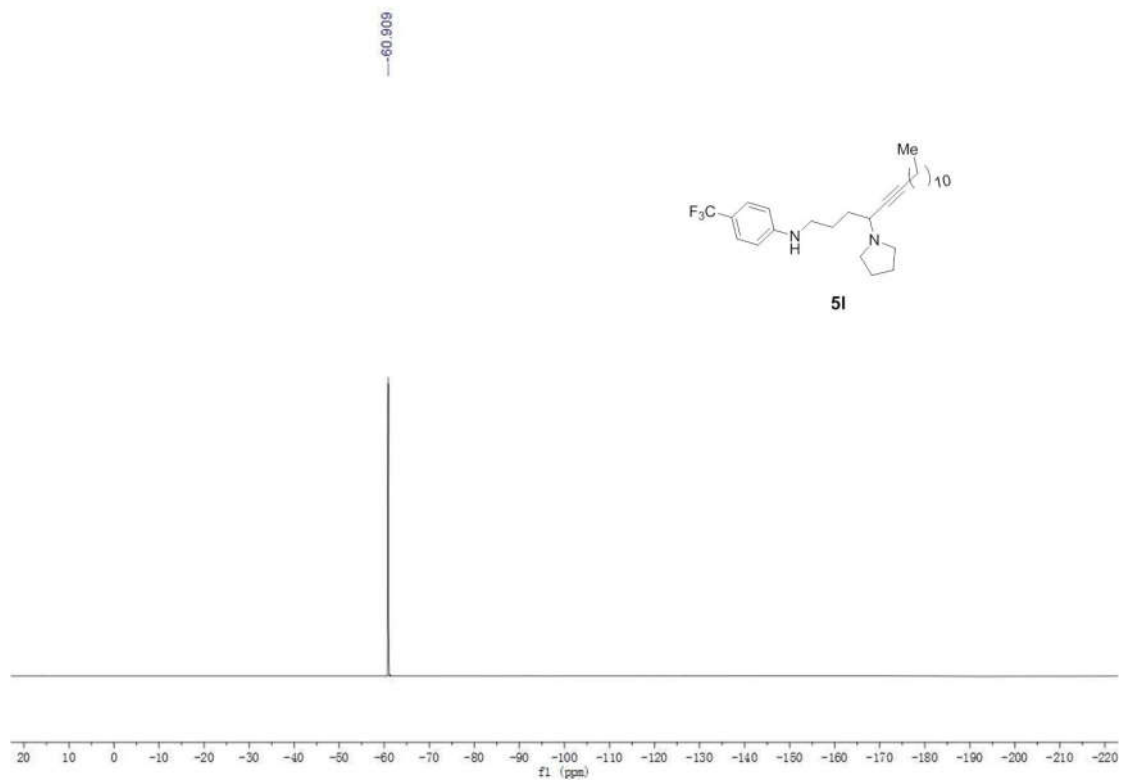
^1H spectrum(600 MHz, CDCl_3) of compound 5l



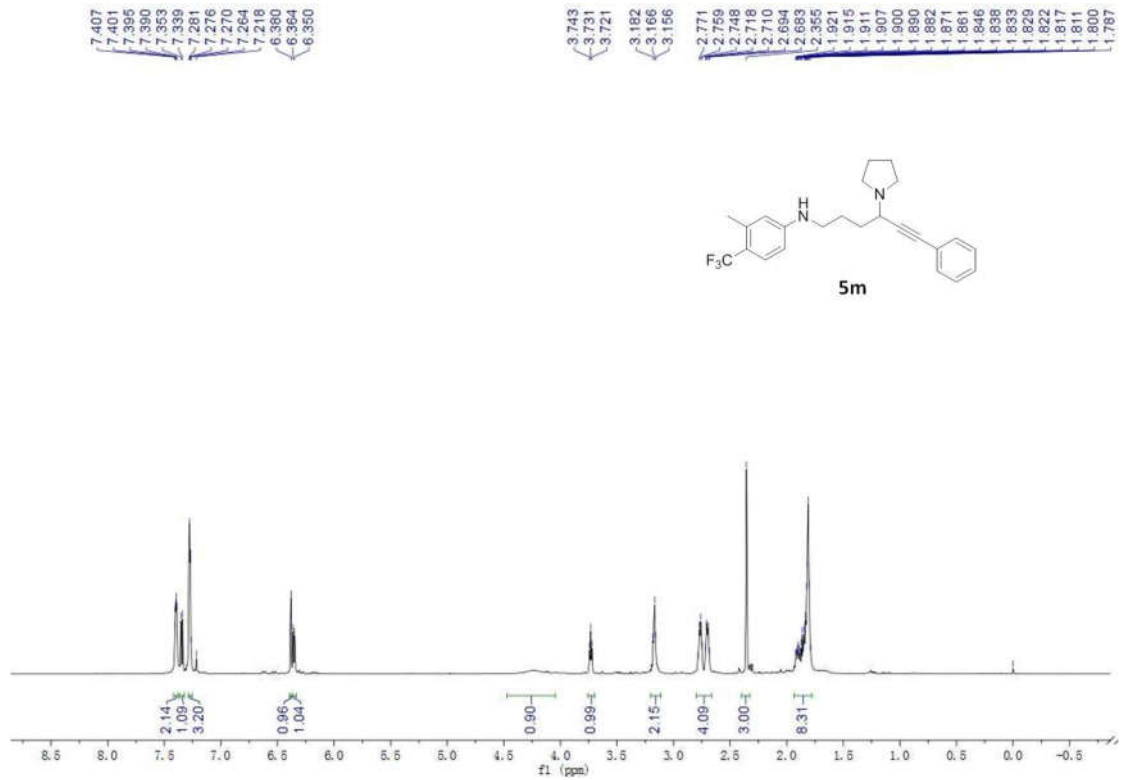
¹³C spectrum(150 MHz, CDCl₃) of compound 5I



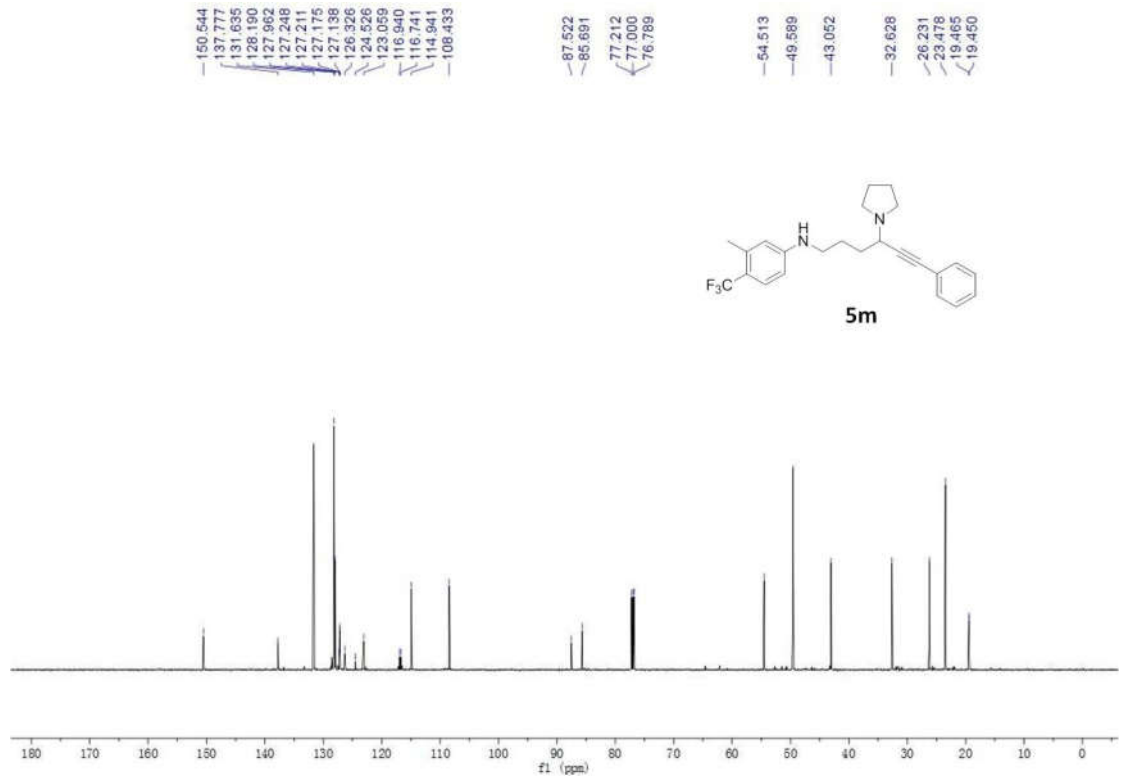
¹⁹F spectrum(565 MHz, CDCl₃) of compound 5I



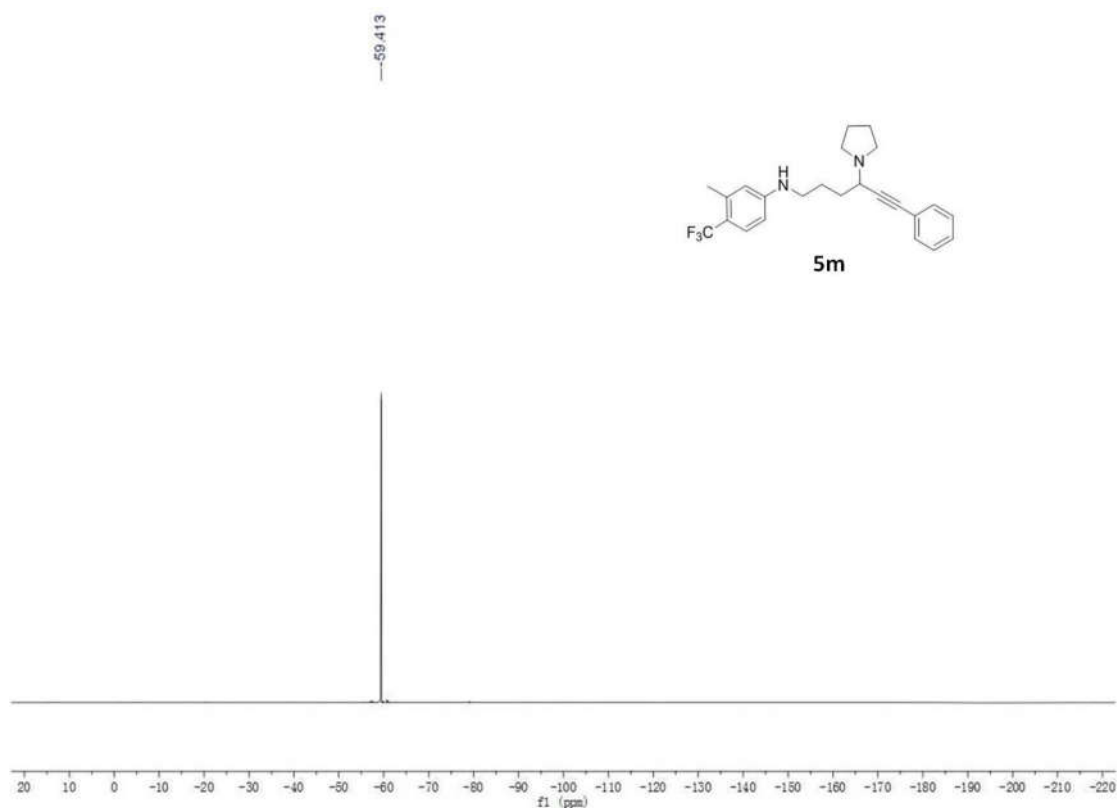
¹H spectrum(600 MHz, CDCl₃) of compound 5m



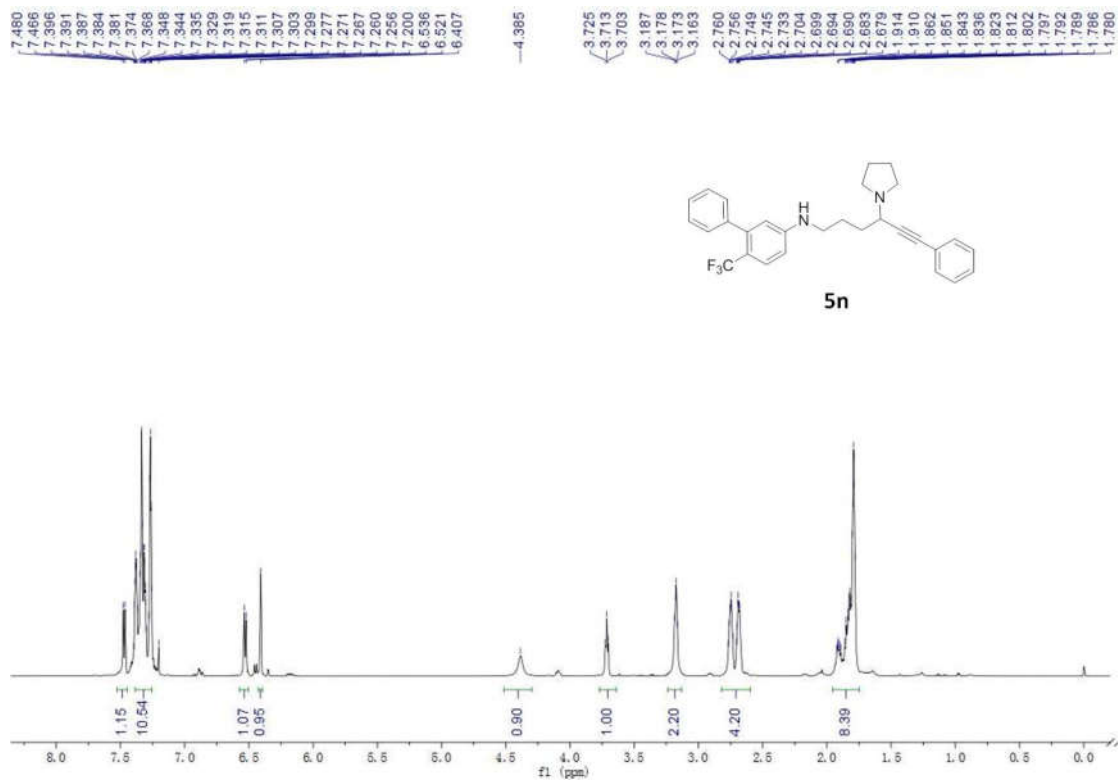
¹³C spectrum(150 MHz, CDCl₃) of compound 5m



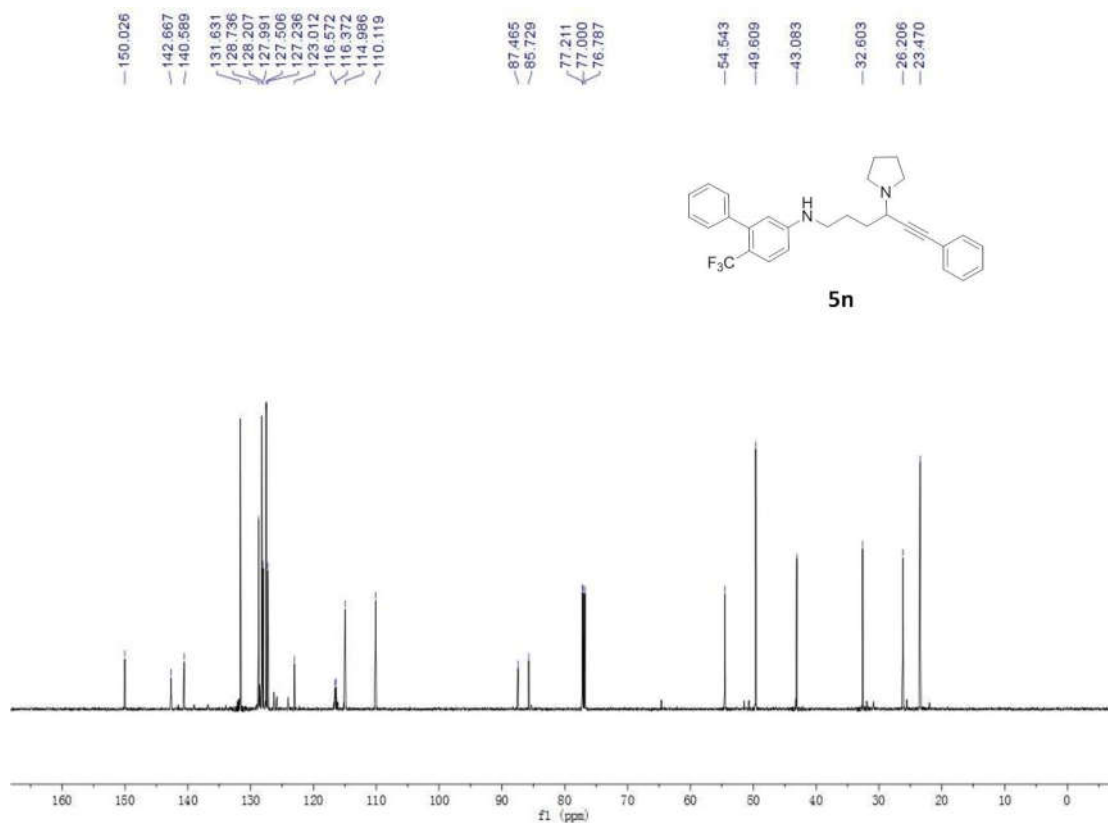
^{19}F spectrum(565 MHz, CDCl_3) of compound 5m



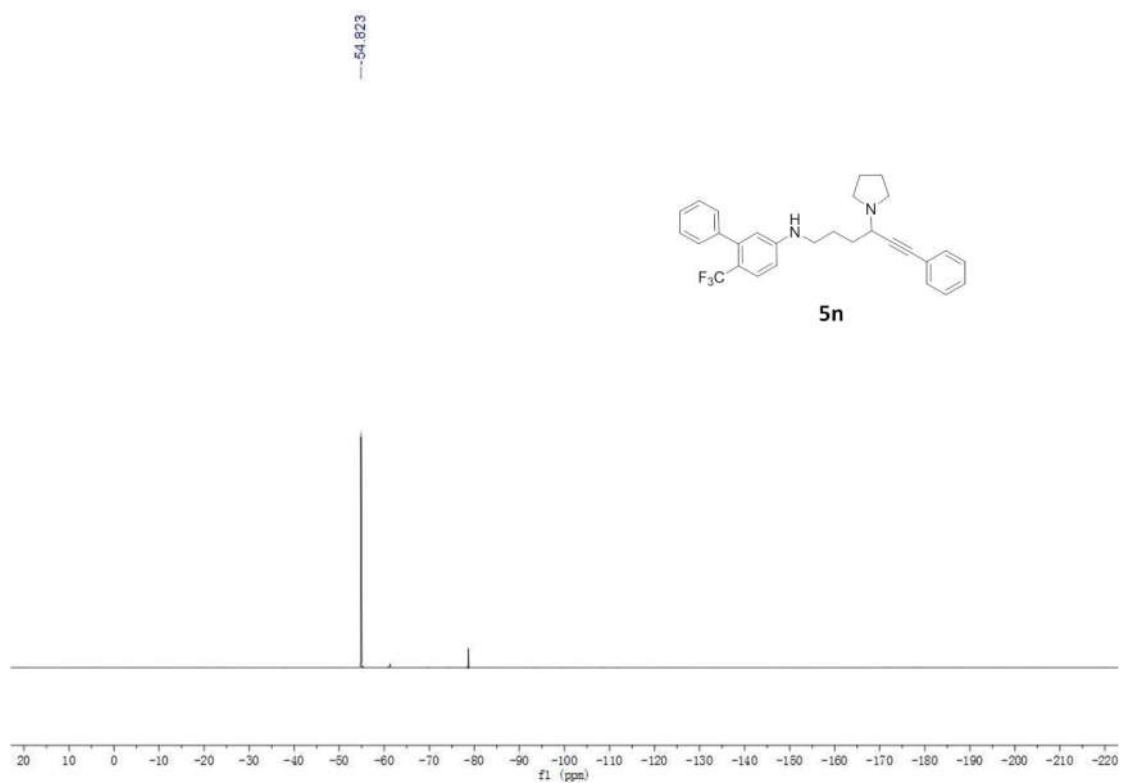
^1H spectrum(600 MHz, CDCl_3) of compound 5n



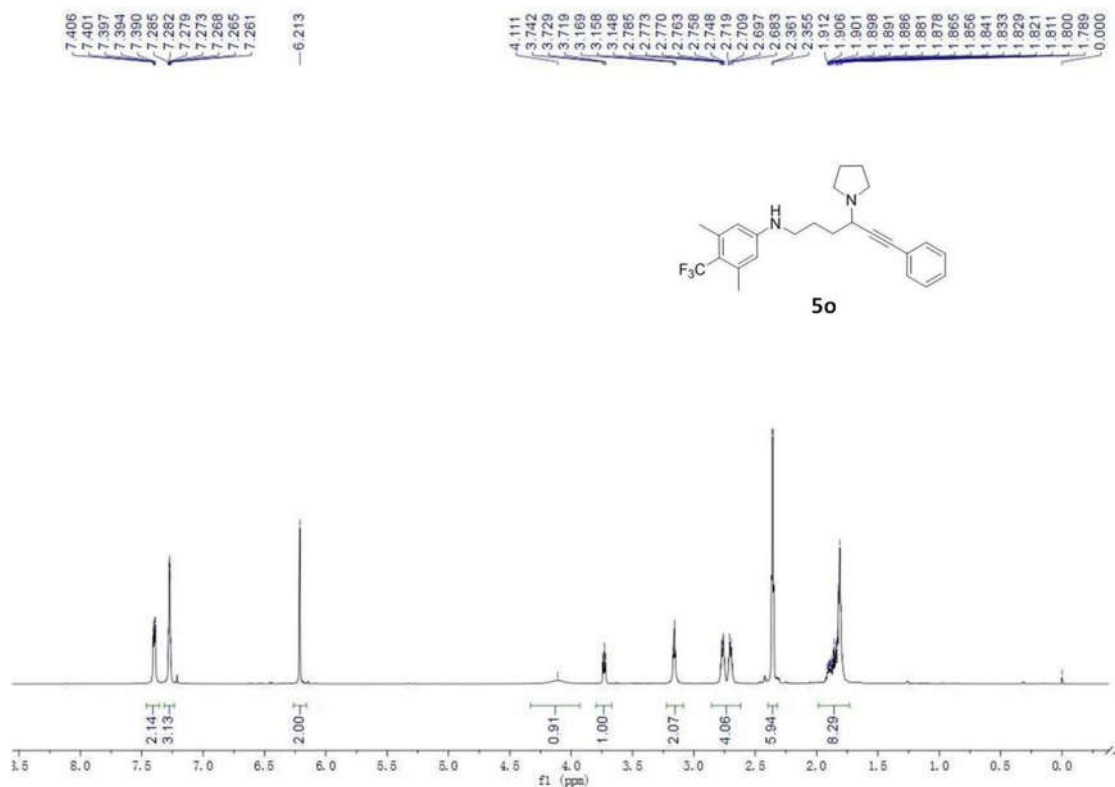
^{13}C spectrum(150 MHz, CDCl_3) of compound 5n



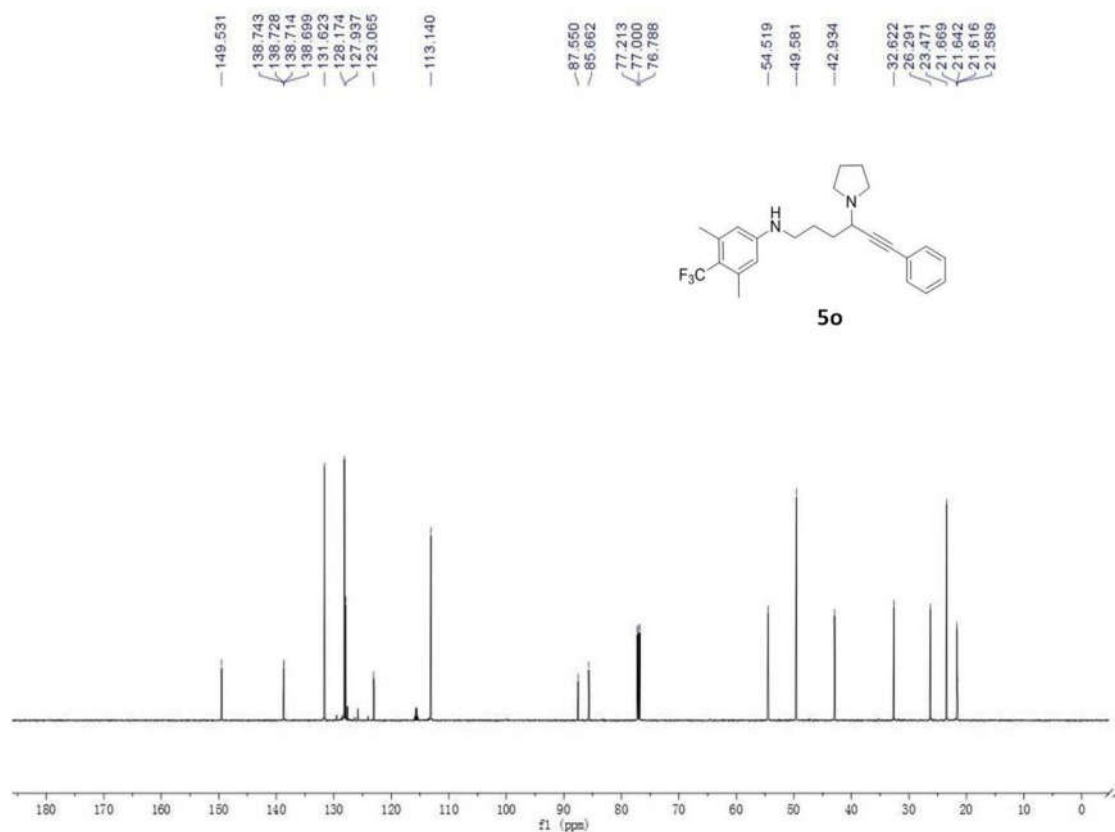
^{19}F spectrum(565 MHz, CDCl_3) of compound 5n



¹H spectrum(600 MHz, CDCl₃) of compound 5o



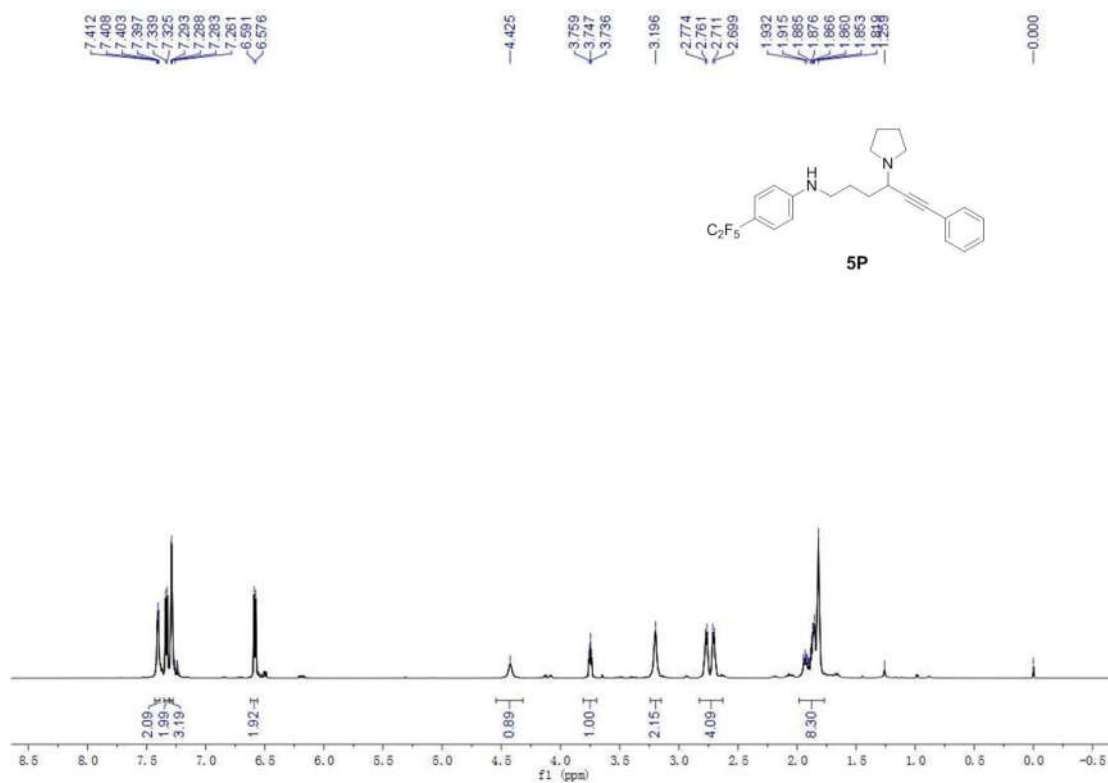
¹³C spectrum(150 MHz, CDCl₃) of compound 5o



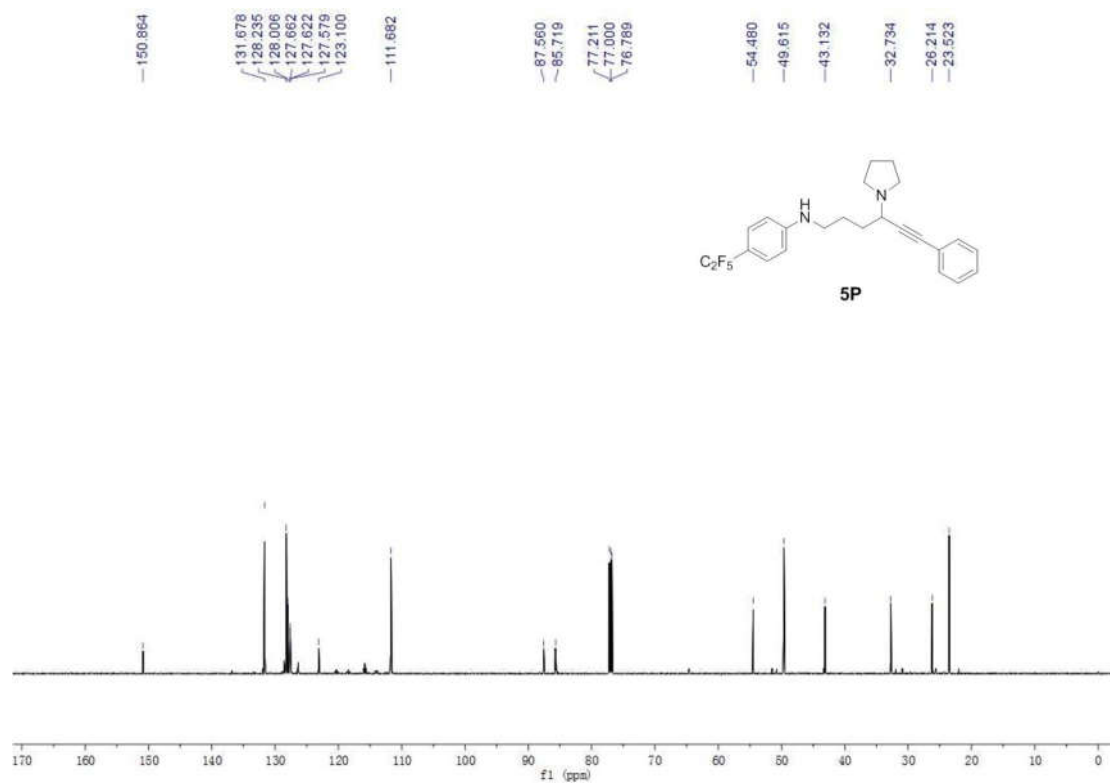
^{19}F spectrum(565 MHz, CDCl_3) of compound 5o



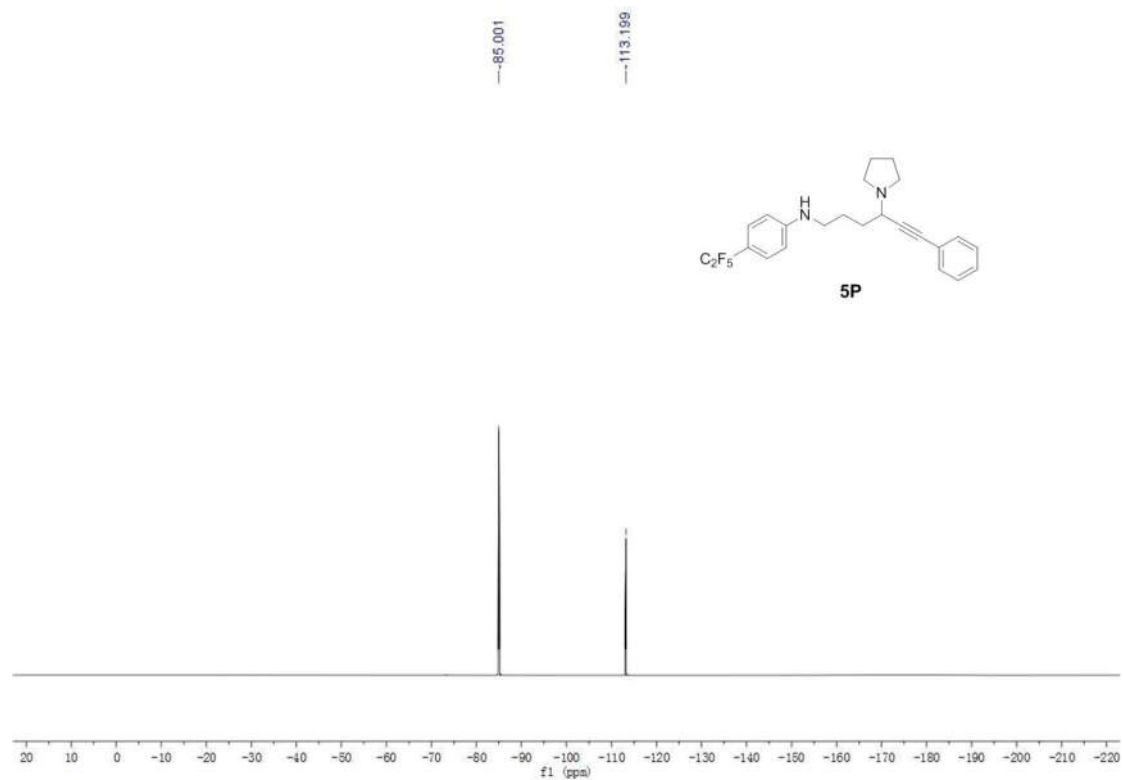
^1H spectrum(600 MHz, CDCl_3) of compound 5p



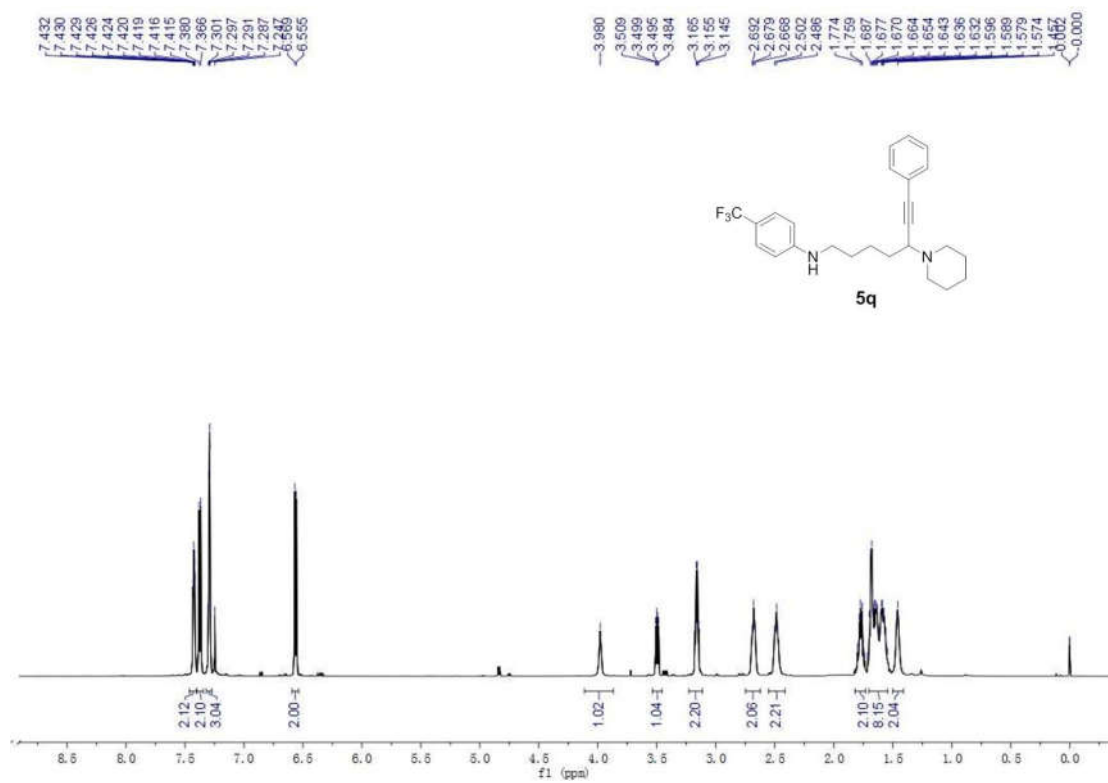
^{13}C spectrum(150 MHz, CDCl_3) of compound 5p



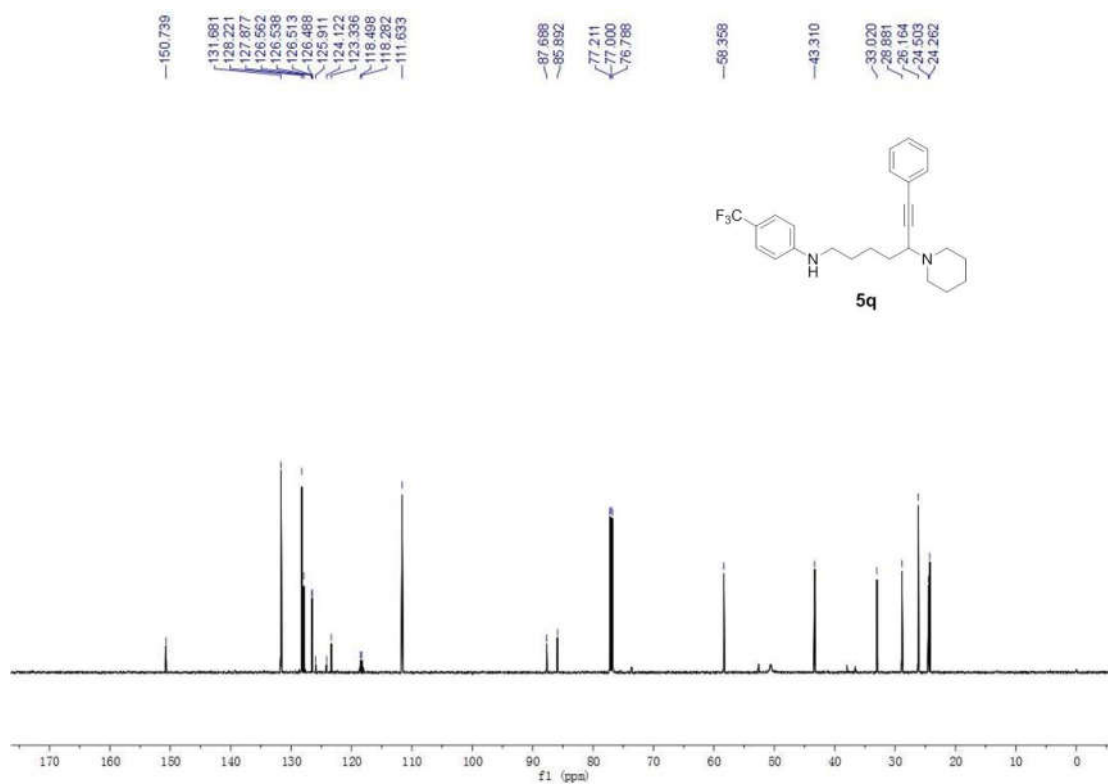
^{19}F spectrum(565 MHz, CDCl_3) of compound 5p



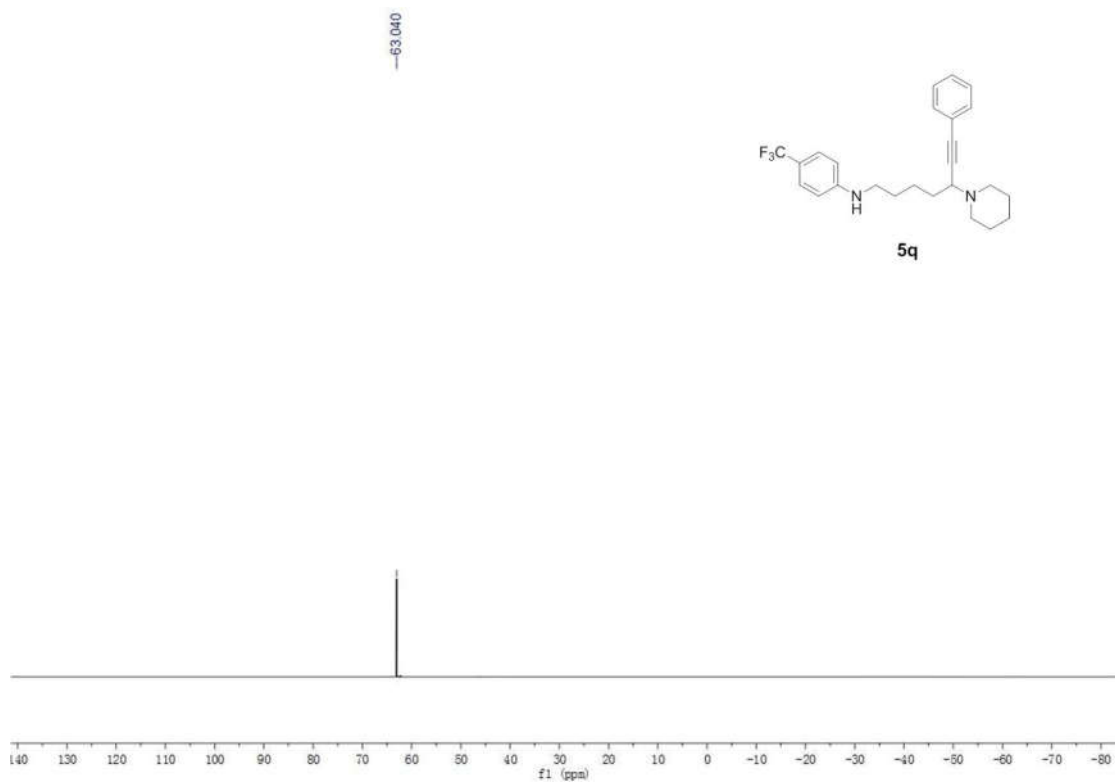
¹H spectrum(600 MHz, CDCl₃) of compound 5q



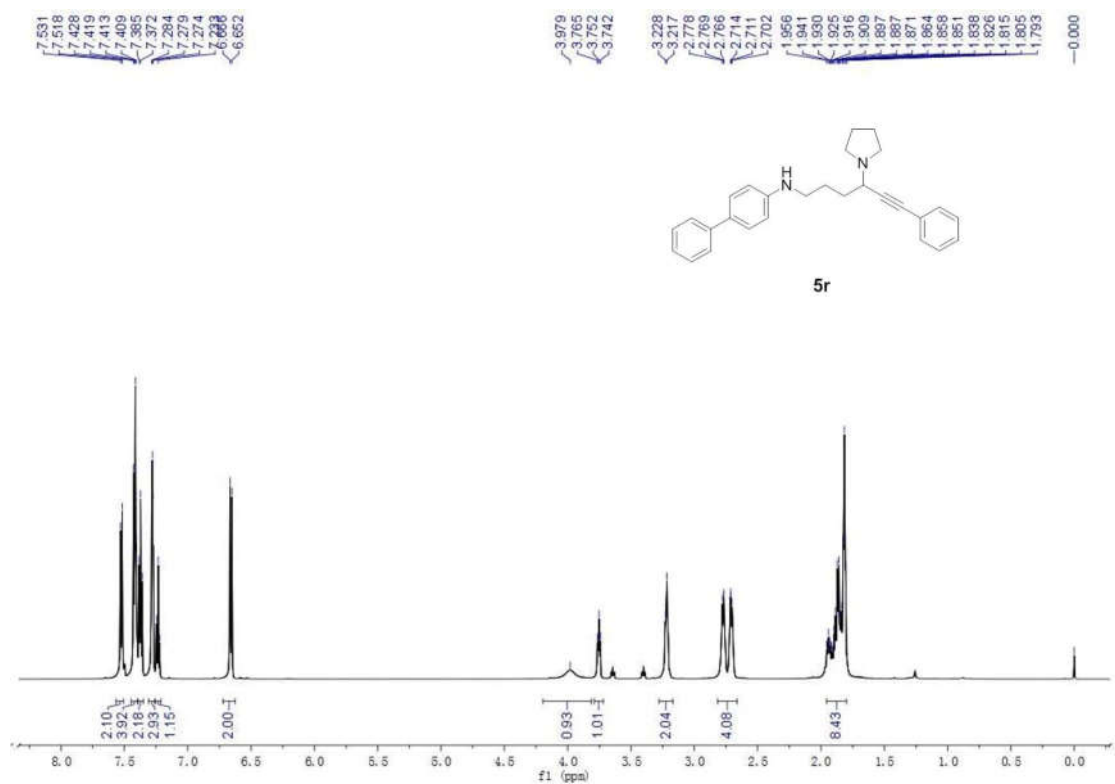
¹³C spectrum(150 MHz, CDCl₃) of compound 5q



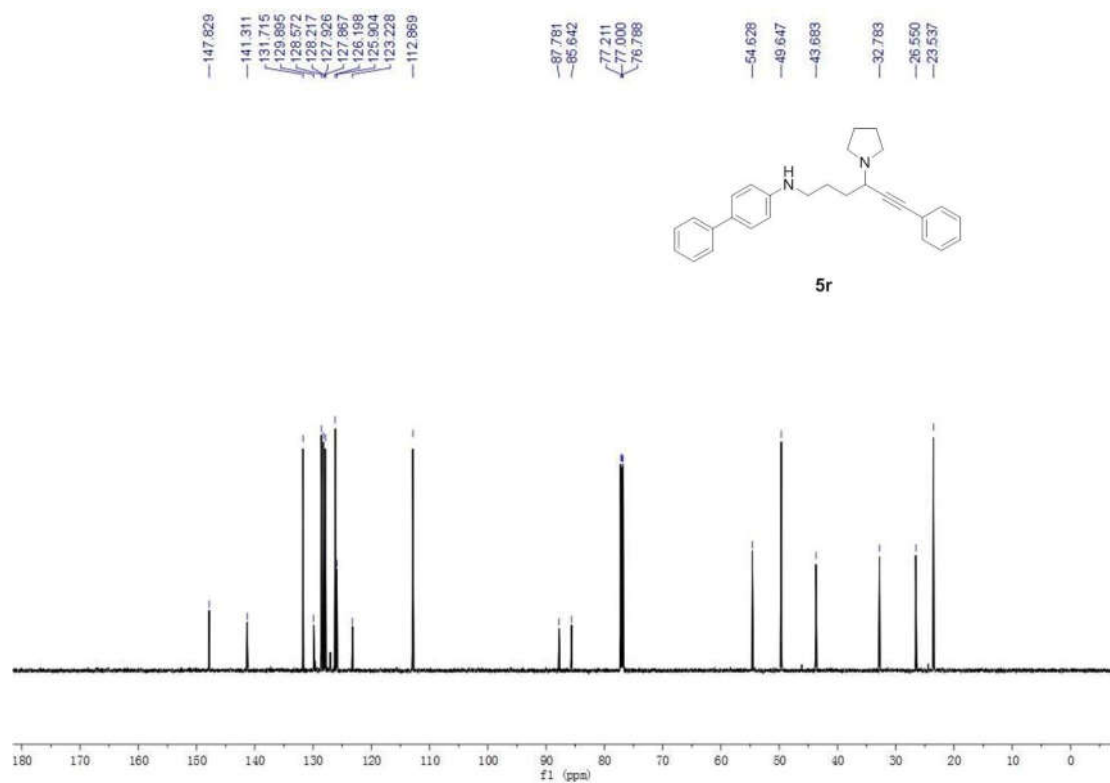
¹⁹F spectrum(565 MHz, CDCl₃) of compound 5q



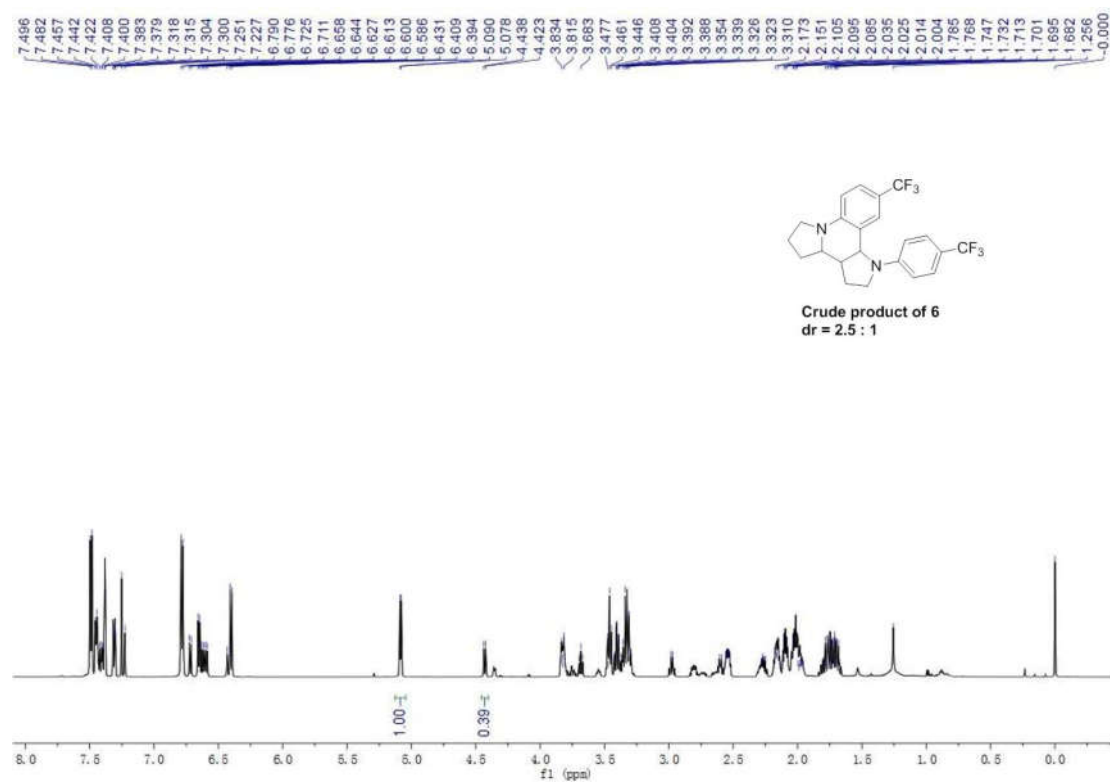
¹H spectrum(600 MHz, CDCl₃) of compound 5r



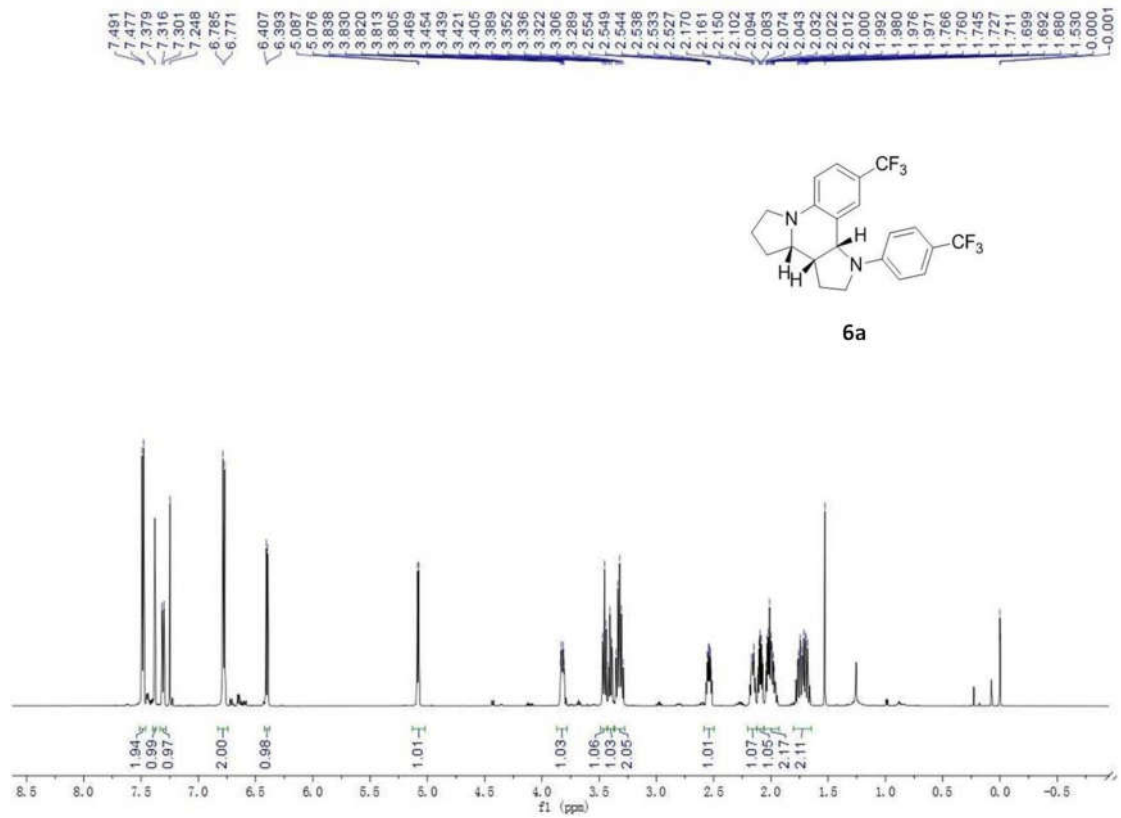
¹³C spectrum(150 MHz, CDCl₃) of compound 5r



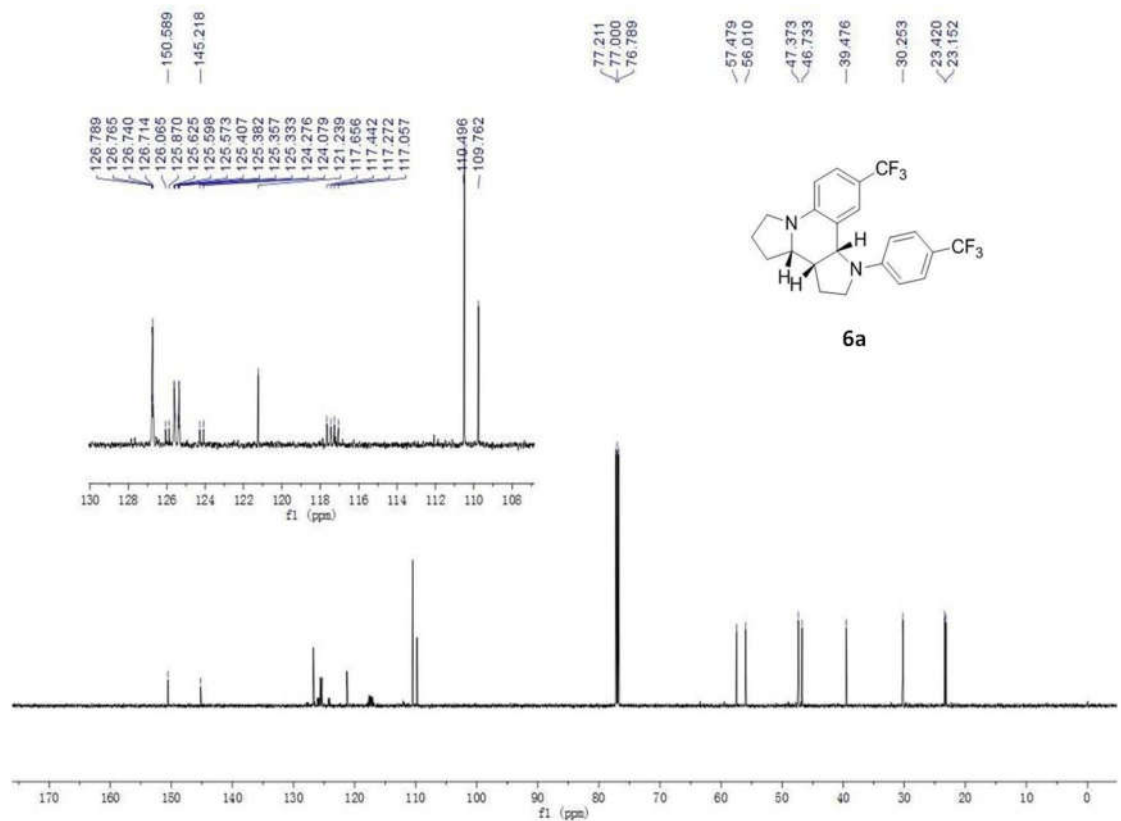
¹H spectrum(600 MHz, CDCl₃) of crude compound 6



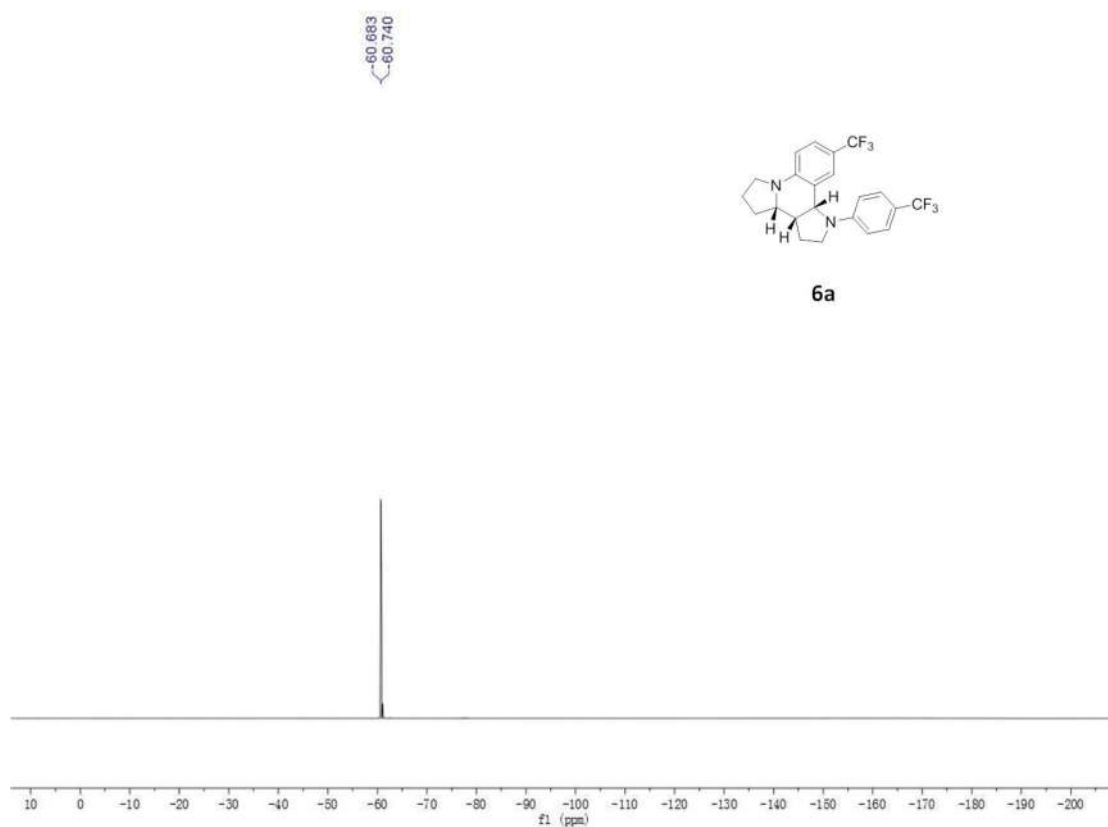
¹H spectrum(600 MHz, CDCl₃) of compound 6a



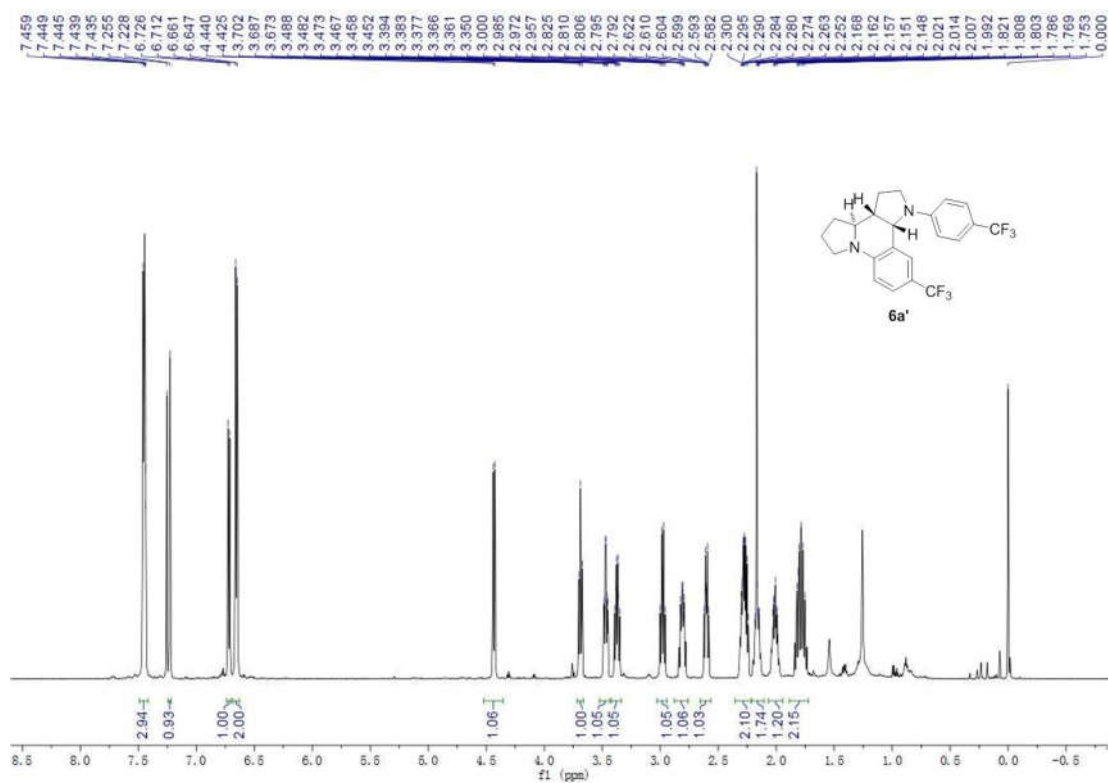
¹³C spectrum(150 MHz, CDCl₃) of compound 6a



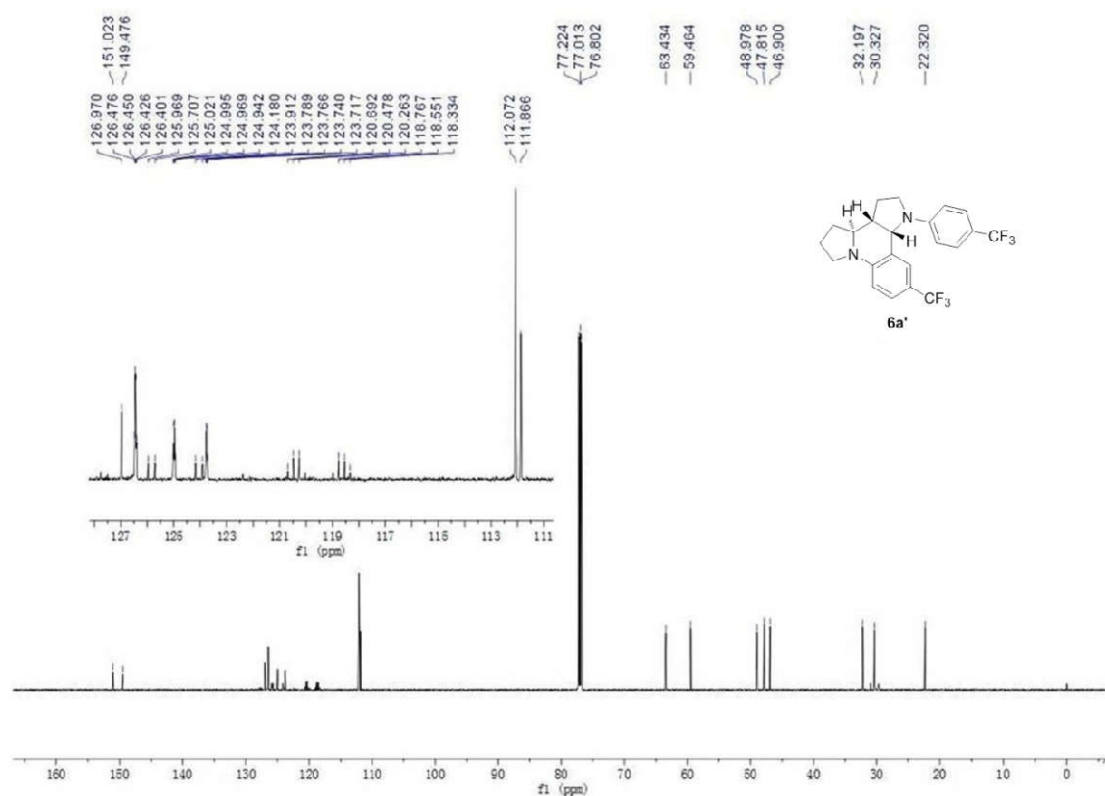
^{19}F spectrum (565 MHz, CDCl_3) of compound 6a



^1H spectrum (600 MHz, CDCl_3) of compound 6a'



^{13}C spectrum(150 MHz, CDCl_3) of compound **6a'**



^{19}F spectrum(565 MHz, CDCl_3) of compound **6a'**

