Copper-Catalyzed Intermolecular Carboamination of Alkenes Induced by Visible Light

SUPPORTING INFORMATION

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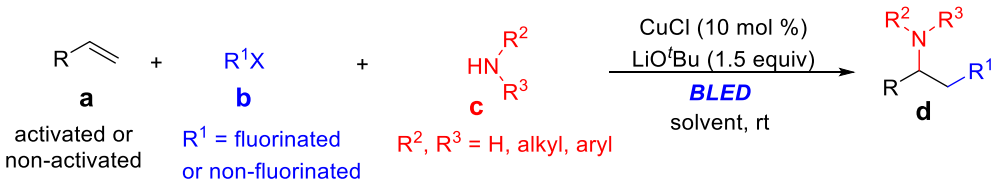
CONTENTS

1. General Experimental Information

NMR spectra were recorded at room temperature on the following spectrometers: Agilent (400 MHz), VARIAN (400 MHz) and Bruker (400 MHz). Chemical shifts are given in ppm and coupling constants in Hz. ^{1}H spectra were calibrated in relation to the reference measurement of TMS (0.00 ppm). ^{13}C spectra were calibrated in relation to deuterated solvents, namely $CDCl_3$ (77.16 ppm). The following abbreviations were used for ^{1}H NMR spectra to indicate the signal multiplicity: s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet) as well as combinations of them. When combinations of multiplicities are given the first character noted refers to the largest coupling constant. High performance liquid chromatography (HPLC) was carried out with Agilent 1260 Infinity on a UV spectrophotometric detector (Agilent). For ESI^{+}-spectra an EI^{-}HR (GC-TOF) spectrometer was applied. Infrared Spectroscopy (IR) was processed on an FT-IR spectrometer named Nicolet 380. The method is denoted in brackets. For the most significant bands the wave number $\tilde{\nu}$ (cm^{-1}) is given. Analytical Thin Layer Chromatography (TLC) was purchased from Jiangyou, Yantai, China. Blue LED lamps (40 W; Kessill A160WE Tuna Blue) were used to irradiate the reaction mixtures.

Chemicals were purchased from commercial suppliers. Unless stated otherwise, all the substrates and solvents were purified and dried according to standard methods prior to use. Reactions requiring inert conditions were carried out in glove box.

2. Experimental Details



Scheme 1. Copper-catalyzed carboamination of alkenes induced by visible light

(1). General Procedure A

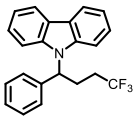
In a nitrogen-filled glovebox, an oven-dried 4 mL vial, CuCl (2.0 mg, 0.02 mmol, 10 mol %), LiO^{t}Bu (24.0 mg, 0.3 mmol, 1.5 equiv), the amine (0.3 mmol, 1.5 equiv) were dissolved in CH_3CN (1.5 mL). The mixture was stirred for 5-10 min. Then, alkene substrate (0.20 mmol, 1.0 equiv) was added, followed by the alkyl iodide (0.4 mmol, 2.0 equiv). The reaction mixture was irradiated with 40 W Kessil blue LED lamps (two or three reactions with one lamps), placed ~3.5 cm away, for 60 h. The mixture was washed with Water (2 mL), and brine (10 mL) sequentially, dried over Na_2SO_4. The organic layer was concentrated under vacuum. The residue was purified by column chromatography on silica gel with a gradient eluent of petroleum ether (PE) and ethyl acetate (EA) to afford the product.

(2). General Procedure B

In a nitrogen-filled glovebox, an oven-dried 4 mL vial, CuCl (2.0 mg, 0.02 mmol, 10 mol %) and *race*-BINOL (11.5 mg, 0.040 mmol, 20 mol %), LiO^{t}Bu (24.0 mg, 0.3 mmol, 1.5 equiv), were dissolved in CH_3CN (1.5 mL) and DMA (0.3 mL). The mixture was stirred for 5-10 min. Then, the amine (0.3 mmol, 1.5 equiv) was added and the mixture stirred for another 5-10 min. Next, alkene substrate (0.20 mmol, 1.0 equiv) was added, followed by the alkyl iodide (0.4 mmol, 2.0 equiv). The reaction mixture was irradiated with 40 W Kessil blue LED lamps (two or three reactions with one lamps), placed ~3.5 cm away, for 60 h. The mixture was washed with Water (2 mL), and brine (10 mL) sequentially, dried over Na_2SO_4. The organic layer was concentrated under vacuum. The residue was purified by column chromatography on silica gel with a gradient eluent of petroleum ether (PE) and ethyl acetate (EA) to afford the product.

3. Synthesis and Characterization of Products

9-(4,4,4-Trifluoro-1-phenylbutyl)-9*H*-carbazole d1

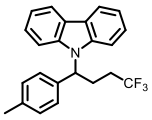


According to the general procedure A, this reaction was conducted in 0.4 mmol scale. **d1** (115.8 mg, 0.328 mmol) was prepared from 9*H*-carbazole (100.3 mg, 0.6 mmol), styrene (41.7 mg, 0.4 mmol) and 1,1,1-trifluoro-2-iodoethane (168.0 mg, 0.4 mmol) as white solid in 82% yield by column chromatography on silica gel with a gradient eluent of PE.

1 mmol scale: In a nitrogen-filled glovebox, an oven-dried 20 mL vial, CuCl (9.9 mg, 0.1 mmol, 10 mol %), LiO^{t}Bu (120.1 mg, 1.5 mmol, 1.5 equiv), 9*H*-carbazole (250.8 mg, 1.5 mmol, 1.5 equiv)

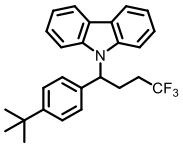
were dissolved in CH_3CN (7.5 mL). The mixture was stirred for 5-10 min. Then, styrene (104.2 mg, 1.0 mmol, 1.0 equiv) was added, followed by the 1,1,1-trifluoro-2-iodoethane (419.9 mg, 2.0 mmol, 2.0 equiv). The reaction mixture was irradiated with 40 W Kessil blue LED lamps (with one lamps), placed ~3.5 cm away, for 60 h. The mixture was washed with Water (10 mL), and brine (20 mL) sequentially, dried over Na_2SO_4. The organic layer was concentrated under vacuum. The residue was purified by column chromatography on silica gel with a gradient eluent of petroleum ether (PE) to afford the product **d1** (247.4 mg, 0.70 mmol) in 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.7 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.31 – 7.16 (m, 9H), 5.92 (dd, *J* = 11.5, 4.7 Hz, 1H), 3.00 – 2.87 (m, 1H), 2.84 – 2.73 (m, 1H), 2.13 – 1.96 (m, 1H), 1.77 – 1.59 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.0, 139.0, 129.0, 127.9, 127.0 (d, *J* = 276.4 Hz), 126.6, 126.0, 123.6, 120.6, 119.6, 110.0, 56.1, 31.1 (q, *J* = 29.0 Hz), 24.3 (d, *J* = 2.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.1 (t, *J* = 10.7 Hz, 3F). IR (neat) cm^{-1} ṽ: 2926.5, 1450.6, 1252.0, 1141.2, 749.1, 697.7. HRMS (EI (+), 70 eV): $C_{22}H_{18}NF_3$ calcd. $[M]^+$: 353.1391, found: 353.1385.

9-(4,4,4-Trifluoro-1-(p-tolyl)butyl)-9*H*-carbazole d2



According to the general procedure A, this reaction was conducted in 0.2 mmol scale. **d2** (55.1 mg, 0.150 mmol) was prepared from 9*H*-carbazole (50.2 mg, 0.3 mmol), 1-methyl-4-vinylbenzene (23.6 mg, 0.2 mmol) and 1,1,1-trifluoro-2-iodoethane (84.0 mg, 0.4 mmol) as white solid in 75% yield by column chromatography on silica gel with a gradient eluent of PE. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.7 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.31 – 7.18 (m, 4H), 7.10 (dd, *J* = 23.2, 8.0 Hz, 4H), 5.88 (dd, *J* = 11.3, 4.5 Hz, 1H), 2.99 – 2.83 (m, 1H), 2.82 – 2.69 (m, 1H), 2.28 (s, 3H), 2.09 – 1.95 (m, 1H), 1.75 – 1.58 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.0, 137.6, 136.0, 129.6, 127.0 (d, *J* = 276.5 Hz), 126.5, 126.0, 123.5, 120.6, 119.5, 110.1, 56.0, 31.2 (d, *J* = 29.1 Hz), 24.3(d, *J* = 2.7 Hz), 21.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.1 (t, *J* = 10.7 Hz, 3F). IR (neat) cm^{-1} ṽ: 2920.0, 1449.5, 1233.0, 1142.4, 745.7, 723.6. HRMS (EI (+), 70 eV): $C_{23}H_{20}NF_3$ calcd. $[M]^+$: 367.1548, found: 367.1541.

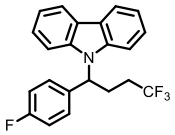
9-(1-(4-(Tert-butyl)phenyl)-4,4,4-trifluorobutyl)-9*H*-carbazole d3



According to the general procedure A, this reaction was conducted in 0.2 mmol scale. **d3** (62.2 mg, 0.152 mmol) was prepared from 9*H*-carbazole (50.2 mg, 0.3 mmol), 1-(*tert*-butyl)-4-vinylbenzene (32.1 mg, 0.2 mmol) and 11,1,1-trifluoro-2-iodoethane (84.0 mg, 0.4 mmol) as white solid in 76% yield by column chromatography on silica gel with a gradient eluent of PE. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.7 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 8.9 Hz, 4H), 7.26 (t, *J* = 7.4 Hz, 2H), 7.21 (d, *J* = 8.2 Hz, 2H), 5.92 (dd, *J* = 11.4, 4.7 Hz, 1H), 3.03 – 2.89 (m, 1H), 2.86 – 2.71 (m, 1H), 2.13 – 1.99 (m, 1H), 1.78 – 1.64 (m, 1H), 1.29 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.9, 140.1, 136.0, 127.0 (d, *J* = 276.3 Hz), 126.3, 126.0, 125.8, 123.5, 120.6, 119.5, 110.1, 56.0, 34.6, 31.4, 31.2 (d, *J* = 29.0 Hz), 24.4 (d, *J* = 2.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.1 (t, *J* =

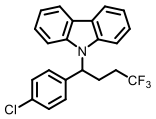
10.7 Hz, 3F). IR (neat) cm^{-1} ṽ: 2920.0, 1450.2, 1233.1, 1144.4, 1126.6, 745.8, 720.5, 584.8. HRMS (EI (+), 70 eV): $C_{26}H_{26}NF_3$ calcd. $[M]^+$: 409.2017, found: 409.2026.

9-(4,4,4-Trifluoro-1-(4-fluorophenyl)butyl)-9*H*-carbazole d4



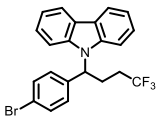
According to the general procedure A, this reaction was conducted in 0.2 mmol scale. **d4** (55.7 mg, 0.150 mmol) was prepared from 9*H*-carbazole (50.2 mg, 0.3 mmol), 1-fluoro-4-vinylbenzene (24.4 mg, 0.2 mmol) and 1,1,1-trifluoro-2-iodoethane (84.0 mg, 0.4 mmol) as white solid in 75% yield by column chromatography on silica gel with a gradient eluent of PE. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.8 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.28 – 7.14 (m, 6H), 6.95 (t, *J* = 8.5 Hz, 2H), 5.87 (dd, *J* = 11.4, 4.1 Hz, 1H), 3.01 – 2.85 (m, 1H), 2.81 – 2.67 (m, 1H), 2.12 – 1.93 (m, 1H), 1.76 – 1.57 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3 (d, *J* = 247.1 Hz), 139.9, 134.8, 128.2, 126.9 (d, *J* = 276.7 Hz), 126.1, 123.6, 120.7, 119.8, 116.0, 115.8, 109.9, 55.6, 31.1 (q, *J* = 29.3 Hz), 24.42 (d, *J* = 2.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.1 (t, *J* = 10.6 Hz, 3F), -114.3– -114.4 (m, 1F). IR (neat) cm^{-1} ṽ: 2923.3, 1450.3, 1235.3, 1144.9, 747.3, 724.3, 497.5. HRMS (EI (+), 70 eV): $C_{22}H_{17}NF_4$ calcd. $[M]^+$: 371.1297, found: 371.1296.

9-(1-(4-Chlorophenyl)-4,4,4-trifluorobutyl)-9*H*-carbazole d5



According to the general procedure A, this reaction was conducted in 0.2 mmol scale. **d5** (56.6 mg, 0.146 mmol) was prepared from 9*H*-carbazole (50.2 mg, 0.3 mmol), 1-chloro-4-vinylbenzene (27.7 mg, 0.2 mmol) and 1,1,1-trifluoro-2-iodoethane (84.0 mg, 0.4 mmol) as white solid in 73% yield by column chromatography on silica gel with a gradient eluent of PE. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.7 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.24 (t, *J* = 7.7 Hz, 6H), 7.15 (d, *J* = 8.4 Hz, 2H), 5.85 (dd, *J* = 11.5, 4.4 Hz, 1H), 2.97 – 2.84 (m, 1H), 2.79 – 2.67 (m, 1H), 2.09 – 1.94 (m, 1H), 1.73 – 1.59 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.8, 137.6, 133.8, 129.1, 128.0, 126.9 (d, *J* = 276.4 Hz), 126.1, 123.6, 120.7, 119.8, 109.9, 55.6, 31.0 (q, *J* = 29.3 Hz), 24.3 (d, *J* = 2.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.1 (t, *J* = 10.6 Hz, 3F). IR (neat) cm^{-1} ṽ: 2922.1, 1449.6, 1234.0, 1140.8, 746.6, 723.4, 563.0. HRMS (EI (+), 70 eV): $C_{22}H_{17}NF_3Cl$ calcd. $[M]^+$: 387.1002, found: 387.1003.

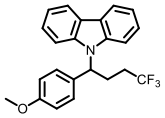
9-(1-(4-Bromophenyl)-4,4,4-trifluorobutyl)-9*H*-carbazole d6



According to the general procedure A, this reaction was conducted in 0.2 mmol scale. **d6** (65.7 mg, 0.152 mmol) was prepared from 9*H*-carbazole (50.2 mg, 0.3 mmol), 1-bromo-4-vinylbenzene (36.6 mg, 0.2 mmol) and 1,1,1-trifluoro-2-iodoethane (84.0 mg, 0.4 mmol) as white solid in 76% yield by column chromatography on silica gel with a gradient eluent of PE. ^{1}H NMR (400 MHz, $CDCl_3$)

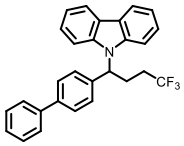
δ 8.12 (d, *J* = 7.7 Hz, 2H), 7.37 (dd, *J* = 11.9, 8.2 Hz, 4H), 7.28 – 7.17 (m, 4H), 7.09 (d, *J* = 8.2 Hz, 2H), 5.83 (dd, *J* = 11.5, 4.4 Hz, 1H), 2.96 – 2.84 (m, 1H), 2.78 – 2.67 (m, 1H), 2.10 – 1.94 (m, 1H), 1.74 – 1.57 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.8, 138.1, 132.1, 128.3, 126.8 (d, *J* = 260.1 Hz), 126.1, 123.6, 122.0, 120.7, 119.8, 109.9, 55.6, 31.0 (d, *J* = 29.1 Hz), 24.2 (d, *J* = 2.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.1 (t, *J* = 10.6 Hz, 3F). IR (neat) cm^{-1} ṽ: 2922.1, 1449.5, 1234.0, 1141.2, 1117.8, 745.8, 722.7, 560.8. HRMS (EI (+), 70 eV): $C_{22}H_{17}NF_3Br$ calcd. $[M]^+$: 431.0496, found: 431.0491.

9-(4,4,4-Trifluoro-1-(4-methoxyphenyl)butyl)-9*H*-carbazole d7



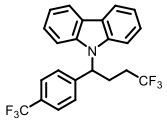
According to the general procedure A, this reaction was conducted in 0.2 mmol scale. **d7** (63.6 mg, 0.166 mmol) was prepared from 9*H*-carbazole (50.2 mg, 0.3 mmol), 1-methoxy-4-vinylbenzene (26.8 mg, 0.2 mmol) and 1,1,1-trifluoro-2-iodoethane (84.0 mg, 0.4 mmol) as white solid in 83% yield by column chromatography on silica gel with a gradient eluent of PE. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.7 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.32 – 7.19 (m, 4H), 7.16 (d, *J* = 8.4 Hz, 2H), 6.80 (d, *J* = 8.5 Hz, 2H), 5.87 (dd, *J* = 11.2, 4.5 Hz, 1H), 3.74 (s, 3H), 2.96 – 2.83 (m, 1H), 2.80 – 2.67 (m, 1H), 2.12 – 1.97 (m, 1H), 1.75 – 1.61 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2, 140.0, 131.0, 127.8, 127.0 (d, *J* = 276.5 Hz), 126.0, 123.5, 120.6, 119.5, 114.2, 110.0, 55.6, 55.3, 31.2 (q, *J* = 29.1 Hz), 24.3 (d, *J* = 2.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.1 (t, *J* = 10.7 Hz, 3F). IR (neat) cm^{-1} ṽ: 2921.6, 1450.6, 1248.1, 1180.4, 747.6, 723.3, 565.1. HRMS (EI (+), 70 eV): $C_{23}H_{20}NOF_3$ calcd. $[M]^+$: 383.1497, found: 383.1488.

9-(1-([1,1'-Biphenyl]-4-yl)-4,4,4-trifluorobutyl)-9*H*-carbazole d8



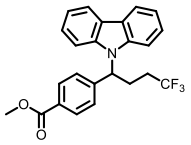
According to the general procedure A, this reaction was conducted in 0.2 mmol scale. **d8** (64.4 mg, 0.150 mmol) was prepared from 9*H*-carbazole (50.2 mg, 0.3 mmol), 4-vinyl-1,1'-biphenyl (26.8 mg, 0.2 mmol) and 1,1,1-trifluoro-2-iodoethane (84.0 mg, 0.4 mmol) as white solid in 75% yield by column chromatography on silica gel with a gradient eluent of PE. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.7 Hz, 2H), 7.45 (dd, *J* = 11.8, 8.0 Hz, 4H), 7.39 – 7.31 (m, 4H), 7.31 – 7.17 (m, 7H), 5.89 (dd, *J* = 11.4, 4.5 Hz, 1H), 3.01 – 2.87 (m, 1H), 2.83 – 2.70 (m, 1H), 2.10 – 1.94 (m, 1H), 1.75 – 1.59 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.7, 140.3, 140.0, 138.0, 128.9, 127.6, 127.5, 127.1, 126.99 (d, *J* = 276.4 Hz), 126.98, 126.1, 123.6, 120.7, 119.7, 110.1, 55.9, 31.1 (q, *J* = 29.4 Hz), 24.3 (d, *J* = 2.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.4 (t, *J* = 10.6 Hz, 3F). IR (neat) cm^{-1} ṽ: 2922.2, 1450.4, 1233.6, 1141.7, 748.7, 722.4, 585.9. HRMS (EI (+), 70 eV): $C_{28}H_{22}NF_3$ calcd. $[M]^+$: 429.1704, found: 429.1713.

9-(4,4,4-Trifluoro-1-(4-(trifluoromethyl)phenyl)butyl)-9*H*-carbazole d9



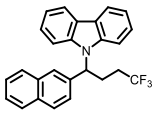
According to the general procedure A, this reaction was conducted in 0.2 mmol scale. **d9** (59.8 mg, 0.142 mmol) was prepared from 9*H*-carbazole (50.2 mg, 0.3 mmol), 1-(trifluoromethyl)-4-vinylbenzene (34.4 mg, 0.2 mmol) and 1,1,1-trifluoro-2-iodoethane (84.0 mg, 0.4 mmol) as white solid in 71% yield by column chromatography on silica gel with a gradient eluent of PE. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.7 Hz, 2H), 7.56 (d, *J* = 8.1 Hz, 2H), 7.39 (dd, *J* = 14.7, 7.6 Hz, 4H), 7.27 (dd, *J* = 16.8, 8.5 Hz, 4H), 5.96 (dd, *J* = 11.6, 4.0 Hz, 1H), 3.05 – 2.91 (m, 1H), 2.87 – 2.75 (m, 1H), 2.13 – 2.00 (m, 1H), 1.78 – 1.64 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1, 139.8, 130.3 (q, *J* = 32.7 Hz), 127.0, 126.9 (d, *J* = 276.3 Hz), 126.2, 126.0 (q, *J* = 3.7 Hz), 123.7, 120.8, 120.0, 109.8, 55.8, 31.0 (q, *J* = 29.2 Hz), 24.3 (d, *J* = 2.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7 (s, 3F), -66.2 (t, *J* = 10.6 Hz, 3F). IR (neat) cm^{-1} ṽ: 2920.0, 1451.2, 1321.1, 1114.2, 1067.4, 748.4, 722.8. HRMS (EI (+), 70 eV): $C_{28}H_{22}NF_3$ calcd. $[M]^+$: 429.1704, found: 429.1713.

Methyl 4-(1-(9*H*-carbazol-9-yl)-4,4,4-trifluorobutyl)benzoate d10



According to the general procedure A, this reaction was conducted in 0.2 mmol scale. **d10** (58.4 mg, 0.142 mmol) was prepared from 9*H*-carbazole (50.2 mg, 0.3 mmol), methyl-4-vinylbenzoate (32.4 mg, 0.2 mmol) and 1,1,1-trifluoro-2-iodoethane (84.0 mg, 0.4 mmol) as white solid in 71% yield by column chromatography on silica gel with a gradient eluent of PE / EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.7 Hz, 2H), 7.94 (d, *J* = 8.2 Hz, 2H), 7.43 – 7.33 (m, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.26 – 7.14 (m, 4H), 5.92 (dd, *J* = 11.5, 4.3 Hz, 1H), 3.86 (s, 3H), 3.01 – 2.87 (m, 1H), 2.84 – 2.72 (m, 1H), 2.11 – 1.98 (m, 1H), 1.75 – 1.63 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 144.1, 139.8, 130.2, 129.8, 126.9 (d, *J* = 276.4 Hz), 126.6, 126.1, 123.6, 120.7, 119.9, 109.8, 55.9, 52.3, 31.0 (dd, *J* = 58.4, 29.3 Hz), 24.2 (d, *J* = 2.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.1 (t, *J* = 10.6 Hz, 3F). IR (neat) cm^{-1} ṽ: 2951.8, 1719.4, 1451.2, 1280.1, 1112.1, 750.2, 724.3. HRMS (EI (+), 70 eV): $C_{24}H_{20}NO_2F_3$ calcd. $[M]^+$: 411.1446, found: 411.1442.

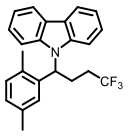
9-(4,4,4-Trifluoro-1-(naphthalen-2-yl)butyl)-9*H*-carbazole d11



According to the general procedure A, this reaction was conducted in 0.2 mmol scale. **d11** (45.8 mg, 0.170 mmol) was prepared from 9*H*-carbazole (50.2 mg, 0.3 mmol), 2-vinylnaphthalene (30.8 mg, 0.2 mmol) and 1,1,1-trifluoro-2-iodoethane (84.0 mg, 0.4 mmol) as white solid in 71% yield by column chromatography on silica gel with a gradient eluent of PE / EA = 100/1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.7 Hz, 2H), 7.85 (s, 1H), 7.81 – 7.70 (m, 2H), 7.66 (d, *J* = 8.6 Hz, 1H), 7.46 (p, *J* = 7.2 Hz, 2H), 7.39 – 7.26 (m, 4H), 7.22 (dd, *J* = 12.9, 5.8 Hz, 2H), 7.17 (d, *J* = 8.5 Hz, 1H), 6.03 (dd, *J* = 11.3, 4.4 Hz, 1H), 3.12 – 2.98 (m, 1H), 2.96 – 2.84 (m, 1H), 2.15 – 2.00 (m, 1H), 1.79

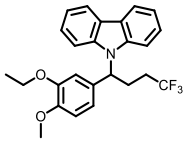
– 1.63 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.1, 136.6, 133.3, 132.9, 128.9, 128.2, 127.8, 127.0 (d, *J* = 276.2 Hz), 126.6, 126.5, 126.1, 125.0, 124.9, 123.6, 120.7, 119.7, 110.0, 56.2, 31.2 (q, *J* = 29.0 Hz), 24.1 (d, *J* = 2.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.0 (t, *J* = 10.7 Hz, 3F). IR (neat) cm^{-1} ṽ: 2921.0, 1451.4, 1249.9, 1126.1, 1026.6, 745.1, 718.7, 474.0. HRMS (EI (+), 70 eV): $C_{26}H_{20}NF_3$ calcd. $[M]^+$: 403.1548, found: 403.1545.

9-(1-(2,5-Dimethylphenyl)-4,4,4-trifluorobutyl)-9*H*-carbazole d12



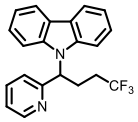
According to the general procedure A, this reaction was conducted in 0.2 mmol scale. **d12** (61.0 mg, 0.160 mmol) was prepared from 9*H*-carbazole (50.2 mg, 0.3 mmol), 1,2-dimethyl-4-vinylbenzene (26.4 mg, 0.2 mmol) and 1,1,1-trifluoro-2-iodoethane (84.0 mg, 0.4 mmol) as white solid in 80% yield by column chromatography on silica gel with a gradient eluent of PE / EA = 100/1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.7 Hz, 2H), 7.52 (s, 1H), 7.40 – 7.29 (m, 4H), 7.28 – 7.16 (m, 2H), 7.05 (d, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 7.6 Hz, 1H), 5.83 (dd, *J* = 10.1, 5.2 Hz, 1H), 2.94 – 2.80 (m, 1H), 2.76 – 2.64 (m, 1H), 2.44 (s, 3H), 2.30 – 2.12 (m, 1H), 1.90 – 1.83 (m, 1H), 1.82 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.0, 136.4, 135.6, 135.0, 131.6, 128.9, 127.4, 127.0 (d, *J* = 276.3 Hz), 125.9, 123.4, 120.5, 119.4, 110.0, 54.7, 31.6 (d, *J* = 28.9 Hz), 24.9 (d, *J* = 2.7 Hz), 21.6, 19.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.1 (t, *J* = 10.7 Hz, 3F). IR (neat) cm^{-1} ṽ: 2919.7, 1450.9, 1257.9, 1128.6, 1026.2, 746.7, 720.6, 516.8. HRMS (EI (+), 70 eV): $C_{24}H_{22}NF_3$ calcd. $[M]^+$: 381.1704, found: 381.1710.

9-(1-(3-Ethoxy-4-methoxyphenyl)-4,4,4-trifluorobutyl)-9*H*-carbazole d13



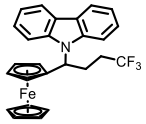
According to the general procedure A, this reaction was conducted in 0.2 mmol scale. **d13** (72.7 mg, 0.170 mmol) was prepared from 9*H*-carbazole (50.2 mg, 0.3 mmol), 2-ethoxy-1-methoxy-4-vinyl-benzene (35.7 mg, 0.2 mmol) and 1,1,1-trifluoro-2-iodoethane (84.0 mg, 0.4 mmol) as white solid in 85% yield by column chromatography on silica gel with a gradient eluent of PE / EA = 20/1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.7 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 2H), 7.31 – 7.17 (m, 4H), 6.82 (d, *J* = 8.3 Hz, 1H), 6.74 (d, *J* = 8.4 Hz, 1H), 6.67 (s, 1H), 5.84 (dd, *J* = 11.1, 4.5 Hz, 1H), 3.85 (dt, *J* = 14.4, 7.1 Hz, 1H), 3.78 (s, 3H), 3.74 (dd, *J* = 16.3, 7.4 Hz, 1H), 2.94 – 2.80 (m, 1H), 2.77 – 2.65 (m, 1H), 2.12 – 1.95 (m, 1H), 1.73 – 1.59 (m, 1H), 1.25 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.0, 148.6, 140.0, 131.4, 127.0 (d, *J* = 276.7 Hz), 125.9, 123.5, 120.6, 119.5, 118.7, 111.6, 111.4, 110.7, 110.1, 64.4, 55.9, 55.8, 31.1 (q, *J* = 28.9 Hz), 24.4 (d, *J* = 2.3 Hz), 14.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.4 (t, *J* = 10.7 Hz, 3F). IR (neat) cm^{-1} ṽ: 2929.8, 1450.0, 1251.2, 1137.9, 1025.5, 748.1, 723.5, 421.8. HRMS (EI (+), 70 eV): $C_{25}H_{24}NO_2F_3$ calcd. $[M]^+$: 427.1759, found: 427.1755.

9-(4,4,4-Trifluoro-1-(pyridin-2-yl)butyl)-9*H*-carbazole d14



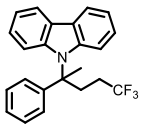
According to the general procedure A, this reaction was conducted in 0.2 mmol scale. **d14** (36.2 mg, 0.102 mmol) was prepared from 9*H*-carbazole (50.2 mg, 0.3 mmol), 2-ethoxy-1-methoxy-4-vinyl-benzene (21.0 mg, 0.2 mmol) and 1,1,1-trifluoro-2-iodoethane (84.0 mg, 0.4 mmol) as yellow solid in 51% yield by column chromatography on silica gel with a gradient eluent of PE / EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 4.4 Hz, 1H), 8.12 (d, *J* = 7.7 Hz, 2H), 8.07 (d, *J* = 7.8 Hz, 1H), 7.49 – 7.34 (m, 4H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.26 – 7.19 (m, 2H), 7.19 – 7.14 (m, 1H), 6.85 (d, *J* = 7.9 Hz, 1H), 5.93 (dd, *J* = 10.6, 5.2 Hz, 1H), 3.24 – 3.07 (m, 1H), 2.98 – 2.82 (m, 1H), 2.26 – 2.07 (m, 1H), 1.89 – 1.71 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 149.1, 139.6, 137.0, 127.1 (d, *J* = 276.5 Hz), 126.1, 125.9, 123.6, 122.9, 122.4, 120.6, 120.4, 119.7, 119.5, 110.7, 110.0, 58.25, 31.2 (q, *J* = 29.0 Hz), 23.4 (d, *J* = 2.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.0 (t, *J* = 10.8 Hz, 3F). IR (neat) cm^{-1} ṽ: 3048.3, 1432.1, 1254.9, 1119.1, 1024.7, 748.2, 723.5. HRMS (EI (+), 70 eV): $C_{21}H_{17}N_2F_3$ calcd. $[M]^+$: 354.1344, found: 354.1348.

9-(4,4,4-Trifluoro-1-Ferrocenebutyl)-9*H*-carbazole d15



According to the general procedure A, this reaction was conducted in 0.2 mmol scale. **d15** (70.1 mg, 0.152 mmol) was prepared from 9*H*-carbazole (50.2 mg, 0.3 mmol), vinylferrocene (42.4 mg, 0.2 mmol) and 1,1,1-trifluoro-2-iodoethane (84.0 mg, 0.4 mmol) as yellow solid in 76% yield by column chromatography on silica gel with a gradient eluent of PE / EA = 100/0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 5.5 Hz, 2H), 7.51 (s, 2H), 7.34 – 7.07 (m, 4H), 5.89 (dd, *J* = 11.7, 3.5 Hz, 1H), 4.51 (s, 1H), 4.16 (s, 1H), 4.13 (s, 4H), 4.00 (s, 2H), 2.88 – 2.74 (m, 1H), 2.69 – 2.57 (m, 1H), 2.09 – 1.92 (m, 1H), 1.82 – 1.62 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 127.1 (d, *J* = 276.5 Hz), 126.1, 125.5, 120.5, 119.3, 111.7, 108.2, 86.9, 69.1, 68.71, 68.66, 67.7, 67.0, 54.1, 31.0 (q, *J* = 28.8 Hz), 24.9 (d, *J* = 2.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.7 (td, *J* = 10.8, 3.8 Hz, 3F). IR (neat) cm^{-1} ṽ: 3058.3, 1450.0, 1245.3, 1138.7, 746.2, 721.3, 479.4, 421.7. HRMS (DART (+)): $C_{26}H_{22}NF_3Fe$ calcd. $[M]^+$: 461.1048, found: 461.1046.

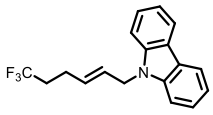
9-(5,5,5-Trifluoro-2-phenylpentan-2-yl)-9*H*-carbazole d16



According to the general procedure A, this reaction was conducted in 0.2 mmol scale. **d16** (38.9 mg, 0.106 mmol) was prepared from 9*H*-carbazole (50.2 mg, 0.3 mmol), prop-1-en-2-ylbenzene (23.6 mg, 0.2 mmol) and 1,1,1-trifluoro-2-iodoethane (84.0 mg, 0.4 mmol) as white solid in 53% yield by column chromatography on silica gel with a gradient eluent of PE. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 6.9, 1.9 Hz, 2H), 7.37 – 7.26 (m, 6H), 7.25 – 7.16 (m, 5H), 3.22 (td, *J* = 13.1, 4.8 Hz, 1H), 2.61 (td, *J* = 13.0, 3.6 Hz, 1H), 2.32 (s, 3H), 2.16 – 2.04 (m, 1H), 1.38 – 1.19 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.7, 141.0, 129.2, 127.4, 127.2 (d, *J* = 276.3 Hz), 125.7, 125.0, 124.5,

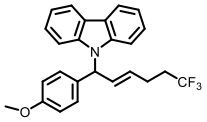
120.1, 119.5, 113.5, 65.5, 31.9, 31.6 (d, J = 2.5 Hz), 29.1 (q, J = 28.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.1 (t, J = 10.7 Hz, 3F). IR (neat) cm^{-1} ṽ: 3054.2, 1443.0, 1252.6, 1135.0, 1060.7, 747.3, 702.8. HRMS (EI (+), 70 eV): $C_{23}H_{20}NF_3$ calcd. $[M]^+$: 367.1548, found: 367.1549.

(*E*)-9-(6,6,6-trifluorohex-2-en-1-yl)-9*H*-carbazole d17



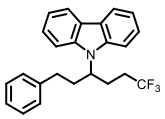
According to the general procedure A, this reaction was conducted in 0.2 mmol scale. **d17** (30.3 mg, 0.100 mmol) was prepared from 9*H*-carbazole (50.2 mg, 0.3 mmol), buta-1,3-diene (1 mol/L in THF, 200ul, 0.2 mmol) and 11,1,1-trifluoro-2-iodoethane (84.0 mg, 0.4 mmol) in 50% yield by column chromatography on silica gel with a gradient eluent of PE. The ratio of regioisomer > 10:1, major regioisomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 7.7 Hz, 1H), 7.45 (t, J = 7.6 Hz, 1H), 7.35 (d, J = 8.1 Hz, 1H), 7.24 (t, J = 7.4 Hz, 1H), 5.69 (dt, J = 15.2, 4.9 Hz, 1H), 5.54 – 5.43 (m, 1H), 4.86 (d, J = 4.6 Hz, 1H), 2.23 (dd, J = 14.6, 6.8 Hz, 1H), 2.13 – 1.95 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.4, 129.6, 126.9 (d, J = 276.5 Hz), 126.2, 125.9, 123.1, 120.5, 119.2, 108.8, 44.5, 33.4 (d, J = 28.4 Hz), 24.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.3 (t, J = 10.7 Hz, 3F). IR (neat) cm^{-1} ṽ: 2962.8, 1458.7, 1259.7, 1092.8, 1019.7, 798.5. HRMS (EI (+), 70 eV): $C_{18}H_{16}NF_3$ calcd. $[M]^+$: 303.1235, found: 303.1240.

(*E*)-9-(6,6,6-trifluoro-1-(4-methoxyphenyl)hex-2-en-1-yl)-9*H*-carbazole d18



According to the general procedure A, this reaction was conducted in 0.2 mmol scale. **d18** (49.1 mg, 0.120 mmol) was prepared from 9*H*-carbazole (50.2 mg, 0.3 mmol), (*E*)-1-(buta-1,3-dien-1-yl)-4-methoxybenzene (32.0 mg, 0.2 mmol) and 1,1,1-trifluoro-2-iodoethane (84.0 mg, 0.4 mmol) as white solid in 60% yield by column chromatography on silica gel with a gradient eluent of PE. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 7.6 Hz, 2H), 7.34 (t, J = 7.6 Hz, 2H), 7.28 – 7.21 (m, 4H), 7.16 (d, J = 8.5 Hz, 2H), 6.82 (d, J = 8.5 Hz, 2H), 6.38 (d, J = 6.9 Hz, 1H), 6.28 (dd, J = 15.2, 6.8 Hz, 1H), 5.73 – 5.59 (m, 1H), 3.77 (s, 3H), 2.36 (dd, J = 15.0, 7.0 Hz, 2H), 2.22 – 2.06 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2, 140.0, 131.8, 131.0, 128.4, 128.3, 126.9 (d, J = 276.7 Hz), 125.6, 123.6, 120.4, 119.3, 114.2, 110.5, 59.0, 55.4, 33.4 (q, J = 28.5 Hz), 25.0 (d, J = 3.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.3 (t, J = 10.5 Hz, 3F). IR (neat) cm^{-1} ṽ: 2921.9, 1510.8, 1450.3, 1248.2, 1125.2, 749.1, 723.4. HRMS (EI (+), 70 eV): $C_{25}H_{22}NOF_3$ calcd. $[M]^+$: 409.1653, found: 409.1655.

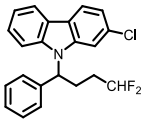
9-(6,6,6-Trifluoro-1-phenylhexan-3-yl)-9*H*-carbazole d19



According to the general procedure A, this reaction was conducted in 0.3 mmol scale, for 72 h. **d19** (45.7 mg, 0.12 mmol) was prepared from 9*H*-carbazole (75.2 mg, 0.45 mmol), but-3-en-1-ylbenzene (39.7 mg, 0.3 mmol) and 1,1,1-trifluoro-2-iodoethane (126.0 mg, 0.6 mmol) as white solid in 40% yield by column chromatography on silica gel with a gradient eluent of PE. ^{1}H NMR (400 MHz,

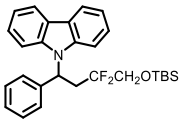
$CDCl_3$) δ 8.14 (dd, *J* = 18.0, 7.3 Hz, 2H), 7.58 (d, *J* = 8.1 Hz, 1H), 7.44 (d, *J* = 4.0 Hz, 2H), 7.33 – 7.26 (m, 2H), 7.24 – 7.13 (m, 4H), 6.97 (d, *J* = 7.4 Hz, 2H), 4.72 – 4.57 (m, 1H), 2.81 – 2.57 (m, 2H), 2.43 (dt, *J* = 14.8, 7.0 Hz, 2H), 2.38 – 2.26 (m, 1H), 2.26 – 2.11 (m, 1H), 2.06 – 1.85 (m, 1H), 1.77 – 1.60 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.8, 128.6, 128.5, 127.0 (d, *J* = 275.9 Hz), 126.3, 126.0, 125.8, 120.9, 120.4, 119.4, 119.3, 111.2, 108.8, 54.4, 35.2, 32.7, 31.1 (q, *J* = 28.9 Hz), 26.1 (d, *J* = 2.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.3 (t, *J* = 10.7 Hz, 3F). IR (neat) cm^{-1} ṽ: 2962.7, 1452.4, 1259.2, 1087.3, 1021.8, 798.5, 749.6. HRMS (EI (+), 70 eV): $C_{24}H_{22}NF_3$ calcd. $[M]^+$: 381.1704, found: 381.1703.

2-Chloro-9-(4,4-difluoro-1-phenylbutyl)-9*H*-carbazole d20



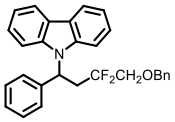
According to the general procedure A, this reaction was conducted in 0.2 mmol scale. **d20** (39.2 mg, 0.106 mmol) was prepared from 2-chloro-9*H*-carbazole (60.5 mg, 0.3 mmol), styrene (20.8 mg, 0.2 mmol) and 1,1-difluoro-2-iodoethane (76.8 mg, 0.4 mmol) as white solid in 53% yield by column chromatography on silica gel with a gradient eluent of PE. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.8 Hz, 1H), 8.01 (d, *J* = 8.3 Hz, 1H), 7.40 – 7.34 (m, 1H), 7.32 – 7.24 (m, 8H), 7.20 (dd, *J* = 8.3, 1.7 Hz, 1H), 5.85 (dd, *J* = 11.0, 5.5 Hz, 1H), 5.92 – 5.56 (m, 1H), 2.85 – 2.68 (m, 2H), 1.91 – 1.72 (m, 1H), 1.52 – 1.39 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.7, 140.4, 138.9, 131.7, 129.0, 128.0, 126.6, 126.2, 123.0, 122.1 121.4, 120.5, 120.1, 120.0, 116.6 (t, *J* = 239.5 Hz), 110.5, 110.1, 56.9, 31.2 (t, *J* = 21.4 Hz), 23.8 (t, *J* = 5.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.8 – -118.6 (m, 2F). IR (neat) cm^{-1} ṽ: 2922.6, 1591.2, 1436.1, 1322.0, 1123.5, 809.1, 743.2, 698.2. HRMS (EI (+), 70 eV): $C_{22}H_{18}NF_2Cl$ calcd. $[M]^+$: 369.1096, found: 369.1100.

9-(4-((Tert-butyldimethylsilyl)oxy)-3,3-difluoro-1-phenylbutyl)-9*H*-carbazole d21



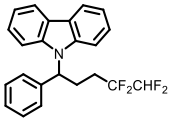
According to the general procedure A, this reaction was conducted in 0.2 mmol scale. **d21** (65.2 mg, 0.140 mmol) was prepared from 9*H*-carbazole (50.2 mg, 0.3 mmol), styrene (20.8 mg, 0.2 mmol) and (2-bromo-2,2-difluoroethoxy)(*tert*-butyl)dimethylsilane (110.1 mg, 0.4 mmol) as colorless oil in 70% yield by column chromatography on silica gel with a gradient eluent of PE / EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.7 Hz, 2H), 7.43 – 7.27 (m, 6H), 7.23 (dd, *J* = 13.6, 6.1 Hz, 5H), 6.31 (dd, *J* = 8.4, 4.0 Hz, 1H), 3.57 (q, *J* = 11.4 Hz, 1H), 3.43 – 3.12 (m, 3H), 0.78 (s, 9H), -0.07 (s, 3H), -0.17 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.8, 139.4, 128.8, 128.6 (d, *J* = 193.9 Hz), 127.7, 126.6, 125.8, 123.6, 120.5, 119.4, 110.4, 64.4 (t, *J* = 26.8 Hz), 51.1, 35.1, 25.8, 18.3, -5.6, -5.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -103.1 – -104.2 (m, 1F), -107.4 – -108.6 (m, 1F). IR (neat) cm^{-1} ṽ: 2928.7, 1451.9, 1120.9, 838.5, 748.2, 723.1. HRMS (EI (+), 70 eV): $C_{28}H_{33}NOF_2Si$ calcd. $[M]^+$: 465.2299, found: 465.2301.

9-(4-(Benzyloxy)-3,3-difluoro-1-phenylbutyl)-9*H*-carbazole d22



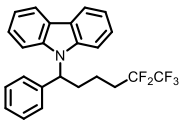
According to the general procedure A, this reaction was conducted in 0.2 mmol scale. **d22** (58.3 mg, 0.132 mmol) was prepared from 9*H*-carbazole (50.2 mg, 0.3 mmol), styrene (20.8 mg, 0.2 mmol) and ((2-bromo-2,2-difluoroethoxy)methyl)benzene (100.4 mg, 0.4 mmol) as colorless oil in 66% yield by column chromatography on silica gel with a gradient eluent of PE / EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.7 Hz, 2H), 7.43 – 7.27 (m, 6H), 7.26 – 7.15 (m, 8H), 7.09 – 6.99 (m, 2H), 6.28 (dd, *J* = 9.3, 2.9 Hz, 1H), 4.07 (s, 2H), 3.48 – 3.32 (m, 2H), 3.27 – 2.98 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.8, 139.2, 137.0, 128.9, 128.5, 128.0, 127.9, 127.8, 126.6, 125.9, 123.6 (t, *J* = 121.7 Hz), 120.5, 119.4, 110.4, 73.6, 70.3 (dd, *J* = 35.1, 29.6 Hz), 51.25, 35.3 (t, *J* = 23.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -99.1 – -100.3 (m, 1F), -104.9 – -106.2 (m, 1F). IR (neat) cm^{-1} ṽ: 2920.1, 1450.5, 1219.8, 1097.2, 746.5, 695.5. HRMS (EI (+), 70 eV): $C_{29}H_{25}NOF_2$ calcd. $[M]^+$: 441.1904, found: 441.1908.

9-(4,4,5,5-Tetrafluoro-1-phenylpentyl)-9*H*-carbazole d23



According to the general procedure A, this reaction was conducted in 0.2 mmol scale. **d23** (58.6 mg, 0.152 mmol) was prepared from 9*H*-carbazole (50.2 mg, 0.3 mmol), styrene (20.8 mg, 0.2 mmol) and 1,1,2,2-tetrafluoro-3-iodopropane (96.8 mg, 0.4 mmol) as white solid in 76% yield by column chromatography on silica gel with a gradient eluent of PE. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.7 Hz, 2H), 7.40 – 7.34 (m, 2H), 7.33 – 7.21 (m, 9H), 5.92 (dd, *J* = 11.1, 5.1 Hz, 1H), 5.57 (tt, *J* = 53.8, 2.8 Hz, 1H), 3.08 – 2.77 (m, 2H), 2.09 – 1.86 (m, 1H), 1.73 – 1.56 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.1, 139.3, 128.9, 127.9, 126.6, 126.0, 123.6, 120.6, 119.56, 115.3 (dt, *J* = 82.1, 35.1 Hz), 110.1, 108.9 (dt, *J* = 249.4, 40.7 Hz), 56.7, 27.3 (t, *J* = 22.4 Hz), 22.8 (t, *J* = 3.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.9 (dt, *J* = 18.2, 13.6 Hz, 2F), -133.2 – -136.6 (m, 2F). IR (neat) cm^{-1} ṽ: 2917.8, 1450.5, 1229.8, 1078.9, 749.7, 691.1. HRMS (EI (+), 70 eV): $C_{23}H_{19}NF_4$ calcd. $[M]^+$: 385.1454, found: 385.1457.

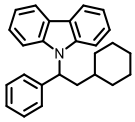
9-(5,5,6,6,6-Pentafluoro-1-phenylhexyl)-9*H*-carbazole d24



According to the general procedure A, this reaction was conducted in 0.2 mmol scale. **d24** (46.7 mg, 0.112 mmol) was prepared from 9*H*-carbazole (50.2 mg, 0.3 mmol), styrene (20.8 mg, 0.2 mmol) and 1,1,1,2,2-pentafluoro-4-iodobutane (109.6 mg, 0.4 mmol) as white solid in 56% yield by column chromatography on silica gel with a gradient eluent of PE. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.6 Hz, 2H), 7.41 – 7.33 (m, 2H), 7.32 – 7.18 (m, 8H), 5.89 (dd, *J* = 10.7, 4.8 Hz, 1H), 2.88 – 2.56 (m, 2H), 2.09 – 1.86 (m, 2H), 1.68 – 1.56 (m, 1H), 1.39 – 1.29 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.2, 139.7, 128.9, 127.7, 126.7, 126.2 (dd, *J* = 71.6, 33.2 Hz), 125.8, 123.5, 120.6, 119.4, 116.6 (dd, *J* = 187.8, 36.8 Hz), 110.1, 57.0, 31.1, 30.2 (t, *J* = 22.1 Hz), 18.04. ^{19}F NMR (376

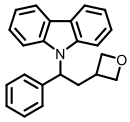
MHz, $CDCl_3$) δ -85.70 (s, 3F), -118.22 (t, *J* = 18.6 Hz, 2F). IR (neat) cm^{-1} ṽ: 2963.1, 1450.6, 1260.5, 1091.0, 1018.6, 798.5, 747.7. HRMS (EI (+), 70 eV): $C_{24}H_{20}NF_5$ calcd. $[M]^+$: 417.1516, found: 417.1511.

9-(2-Cyclohexyl-1-phenylethyl)-9*H*-carbazole d25



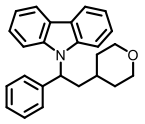
According to the general procedure A, this reaction was conducted in 0.2 mmol scale. **d25** (42.4 mg, 0.120 mmol) was prepared from 9*H*-carbazole (50.2 mg, 0.3 mmol), styrene (20.8 mg, 0.2 mmol) and iodocyclohexane (84.0 mg, 0.4 mmol) as white solid in 60% yield by column chromatography on silica gel with a gradient eluent of PE. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.7 Hz, 2H), 7.42 – 7.30 (m, 4H), δ 7.29 – 7.15 (m, 7H), 5.99 (dd, *J* = 10.1, 5.2 Hz, 1H), 2.61 – 2.49 (m, 1H), 2.40 – 2.29 (m, 1H), 1.71 – 1.47 (m, 5H), 1.11 – 0.94 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.9, 128.7, 127.4, 126.9, 125.6, 123.4, 122.2, 120.4, 119.0, 110.4, 54.8, 39.7, 34.5, 34.1, 33.2, 26.5, 26.1, 26.0. IR (neat) cm^{-1} ṽ: 2920.2, 1482.0, 1448.8, 1329.8, 745.6, 720.8, 695.7. HRMS (EI (+), 70 eV): $C_{26}H_{27}N$ calcd. $[M]^+$: 353.2144, found: 353.2149.

9-(2-(Oxetan-3-yl)-1-phenylethyl)-9*H*-carbazole d26



According to the general procedure A, this reaction was conducted in 0.2 mmol scale. **d26** (34.7 mg, 0.106 mmol) was prepared from 9*H*-carbazole (50.2 mg, 0.3 mmol), styrene (20.8 mg, 0.2 mmol) and 3-iodooxetane (73.6 mg, 0.4 mmol) as white solid in 53% yield by column chromatography on silica gel with a gradient eluent of PE / EA = 20/1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.7 Hz, 2H), 7.43 – 7.27 (m, 7H), 7.25 – 7.13 (m, 4H), 5.81 (dd, *J* = 11.6, 4.1 Hz, 1H), 4.61 – 4.54 (m, 1H), 4.50 (t, *J* = 6.2 Hz, 1H), 4.12 – 4.04 (m, 1H), 3.89 (t, *J* = 6.2 Hz, 1H), 3.07 – 2.95 (m, 1H), 2.93 – 2.82 (m, 1H), 2.69 – 2.54 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.0, 139.6, 128.9, 127.7, 126.6, 125.8, 123.4, 120.6, 119.4, 109.9, 77.0, 76.9, 55.1, 34.6, 33.0. IR (neat) cm^{-1} ṽ: 2946.0, 1448.5, 1328.5, 1218.6, 969.1, 745.1, 717.9, 699.9. HRMS (EI (+), 70 eV): $C_{23}H_{21}NO$ calcd. $[M]^+$: 327.1623, found: 327.1621.

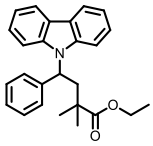
9-(1-Phenyl-2-(tetrahydro-2*H*-pyran-4-yl)ethyl)-9*H*-carbazole d27



According to the general procedure A, this reaction was conducted in 0.2 mmol scale. **d27** (36.3 mg, 0.102 mmol) was prepared from 9*H*-carbazole (50.2 mg, 0.3 mmol), styrene (20.8 mg, 0.2 mmol) and 4-iodotetrahydro-2*H*-pyran (84.8 mg, 0.4 mmol) as white solid in 51% yield by column chromatography on silica gel with a gradient eluent of PE / EA = 20/1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.7 Hz, 2H), 7.43 – 7.30 (m, 4H), 7.30 – 7.16 (m, 7H), 6.00 (dd, *J* = 10.9, 4.8 Hz, 1H), 3.85 (dd, *J* = 11.5, 2.5 Hz, 1H), 3.78 (d, *J* = 11.3 Hz, 1H), 3.17 – 3.02 (m, 2H), 2.81 – 2.66 (m, 1H), 2.37 (ddd, *J* = 13.9, 8.8, 4.9 Hz, 1H), 1.82 (d, *J* = 12.7 Hz, 1H), 1.48 – 1.28 (m, 4H).^{13}C NMR (101

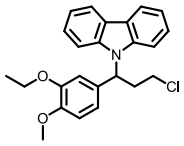
MHz, $CDCl_3$) δ 140.4, 128.8, 127.5, 126.7, 125.8, 123.5, 120.5, 119.2, 110.2, 67.8, 67.7, 54.3, 39.2, 33.6, 33.0, 32.0. IR (neat) cm^{-1} ṽ: 2920.1, 1449.2, 1326.3, 1218.6, 969.1, 745.1, 717.9, 699.9. HRMS (EI (+), 70 eV): $C_{25}H_{25}NO$ calcd. $[M]^+$: 355.1936, found: 355.1935.

Ethyl 4-(9*H*-carbazol-9-yl)-2,2-dimethyl-4-phenylbutanoate d28



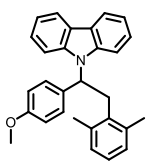
According to the general procedure A, this reaction was conducted in 0.2 mmol scale. **d28** (43.9 mg, 0.114 mmol) was prepared from 9*H*-carbazole (50.2 mg, 0.3 mmol), styrene (20.8 mg, 0.2 mmol) and ethyl 2-iodo-2-methylpropanoate (96.8 mg, 0.4 mmol) as white solid in 57% yield by column chromatography on silica gel with a gradient eluent of PE / EA = 15/1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.7 Hz, 2H), 7.46 – 7.30 (m, 5H), 7.26 – 7.13 (m, 7H), 6.01 (dd, *J* = 10.0, 3.0 Hz, 1H), 3.67 – 3.56 (m, 1H), 3.41 – 3.30 (m, 1H), 3.14 (dd, *J* = 14.6, 10.1 Hz, 1H), 2.75 (dd, *J* = 14.6, 3.1 Hz, 1H), 1.24 (s, 3H), 0.96 (s, 3H), 0.88 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.8, 140.6, 128.6, 127.4, 126.6, 125.9, 125.6, 123.5, 120.3, 119.2, 110.7, 60.5, 54.2, 42.1, 41.8, 26.0, 25.7, 13.8. IR (neat) cm^{-1} ṽ: 2974.8, 1720.1, 1449.8, 1323.0, 1136.9, 1025.4, 746.4, 722.3. HRMS (EI (+), 70 eV): $C_{26}H_{27}NO_2$ calcd. $[M]^+$: 385.2042, found: 385.2044.

9-(3-Chloro-1-(3-ethoxy-4-methoxyphenyl)-propyl)-9*H*-carbazole d29



According to the general procedure A, this reaction was conducted in 0.2 mmol scale. **d29** (32.3 mg, 0.082 mmol) was prepared from 9*H*-carbazole (50.2 mg, 0.3 mmol), 2-ethoxy-1-methoxy-4-vinyl-benzene (35.7 mg, 0.2 mmol) and CH_2Cl_2 (0.2 mL) as yellow solid in 41% yield by column chromatography on silica gel with a gradient eluent of PE / EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.7 Hz, 2H), 7.41 – 7.32 (m, 4H), 7.24 – 7.19 (m, 2H), 6.85 (d, *J* = 8.2 Hz, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 6.69 (s, 1H), 6.16 (dd, *J* = 10.5, 3.4 Hz, 1H), 3.92 – 3.84 (m, 1H), 3.82 (s, 3H), 3.80 – 3.72 (m, 1H), 3.43 (dd, *J* = 10.7, 4.5 Hz, 1H), 3.16 – 3.03 (m, 2H), 2.92 – 2.80 (m, 1H), 1.27 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.7, 148.5, 140.0, 133.3, 125.9, 125.6, 123.6, 120.4, 119.5, 119.0, 118.8, 111.8, 111.4, 110.7, 110.3, 64.4, 56.1, 56.0, 52.2, 17.6, 14.7. IR (neat) cm^{-1} ṽ: 2931.5, 1450.9, 1233.2, 1138.2, 749.0, 724.2. HRMS (EI (+), 70 eV): $C_{24}H_{24}NO_2Cl$ calcd. $[M]^+$: 393.1496, found: 393.1498.

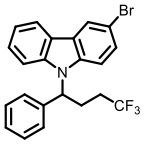
9-(2-(2,6-Dimethylphenyl)-1-(4-methoxyphenyl)ethyl)-9*H*-carbazole d30



According to the general procedure A, this reaction was conducted in 0.2 mmol scale. **d30** (24.3 mg, 0.06 mmol) was prepared from 9*H*-carbazole (50.2 mg, 0.3 mmol), 1-methoxy-4-vinylbenzene (26.8

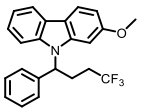
mg, 0.2 mmol) and 2-iodo-1,3-dimethylbenzene (92.8 mg, 0.4 mmol) as yellow solid in 30% yield by column chromatography on silica gel with a gradient eluent of PE / EA = 100/1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.00 (m, 2H), 7.31 – 7.21 (m, 5H), 7.14 (dd, *J* = 7.6, 6.2 Hz, 4H), 6.85 – 6.78 (m, 2H), 6.58 (s, 1H), 6.42 – 6.34 (m, 2H), 6.01 (dd, *J* = 9.5, 5.4 Hz, 1H), 3.75 (s, 3H), 3.73 – 3.59 (m, 2H), 2.46 – 2.37 (m, 1H), 1.98 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 140.4, 138.1, 137.6, 132.19, 129.2, 128.2, 128.0, 126.6, 125.3, 123.3, 120.1, 118.8, 114.0, 110.4, 58.6, 55.3, 37.5, 21.1. IR (neat) cm^{-1} ṽ: 2918.1, 1599.8, 1510.9, 1450.3, 1245.1, 1178.1, 746.9, 721.0. HRMS (EI (+), 70 eV): $C_{29}H_{27}NO$ calcd. $[M]^+$: 405.2093, found: 405.2101.

3-Bromo-9-(4,4,4-trifluoro-1-phenylbutyl)-9*H*-carbazole d31



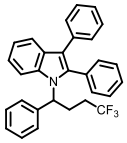
According to the general procedure A, this reaction was conducted in 0.2 mmol scale. **d31** (67.4 mg, 0.156 mmol) was prepared from 3-bromo-9*H*-carbazole (73.8 mg, 0.3 mmol), styrene (20.8 mg, 0.2 mmol) and 1,1,1-trifluoro-2-iodoethane (84.0 mg, 0.4 mmol) as white solid in 78% yield by column chromatography on silica gel with a gradient eluent of PE / EA = 100/1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 8.06 (d, *J* = 7.7 Hz, 1H), 7.40 (dd, *J* = 14.5, 7.8 Hz, 2H), 7.33 – 7.18 (m, 7H), 7.11 (d, *J* = 8.7 Hz, 1H), 5.87 (dd, *J* = 11.2, 4.6 Hz, 1H), 2.96 – 2.70 (m, 2H), 2.12 – 1.95 (m, 1H), 1.75 – 1.57 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.5, 138.6, 129.0, 128.7, 128.1, 126.9 (d, *J* = 276.2 Hz), 126.8, 126.5, 125.4, 123.4, 122.5, 120.9, 120.1, 112.6, 111.6, 110.1, 56.3, 31.1 (q, *J* = 29.3 Hz), 24.2 (d, *J* = 2.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.1 (t, *J* = 10.6 Hz, 3F). IR (neat) cm^{-1} ṽ: 2972.7, 1443.3, 1253.0, 1138.3, 1022.8, 743.9, 696.0. HRMS (EI (+), 70 eV): $C_{22}H_{17}NF_3Br$ calcd. $[M]^+$: 431.0496, found: 431.0493.

2-Methoxy-9-(4,4,4-trifluoro-1-phenylbutyl)-9*H*-carbazole d32



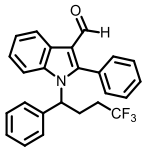
According to the general procedure A, this reaction was conducted in 0.2 mmol scale. **d32** (64.4 mg, 0.168 mmol) was prepared from 3-methoxy-9H-carbazole (59.2 mg, 0.3 mmol), styrene (20.8 mg, 0.2 mmol) and 1,1,1-trifluoro-2-iodoethane (84.0 mg, 0.4 mmol) as white solid in 84% yield by column chromatography on silica gel with a gradient eluent of PE / EA = 100/1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 14.2, 8.1 Hz, 2H), 7.35 – 7.26 (m, 5H), 7.25 – 7.15 (m, 3H), 6.85 (d, *J* = 8.5 Hz, 1H), 6.74 (s, 1H), 5.85 (dd, *J* = 11.4, 4.6 Hz, 1H), 3.80 (s, 3H), 2.99 – 2.85 (m, 1H), 2.83 – 2.72 (m, 1H), 2.15 – 1.98 (m, 1H), 1.80 – 1.65 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 141.4, 140.1, 138.9, 129.0, 128.0, 127.0 (d, *J* = 276.3 Hz), 126.6, 124.7, 123.8, 121.3, 119.8, 119.7, 117.5, 109.9, 107.7, 94.8, 56.1, 55.7, 31.1 (q, *J* = 29.2 Hz), 24.1 (d, *J* = 2.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.1 (t, *J* = 10.7 Hz, 3F). IR (neat) cm^{-1} ṽ: 2923.2, 1459.7, 1231.4, 1140.8, 1115.2, 1021.1, 741.5, 696.8. HRMS (EI (+), 70 eV): $C_{23}H_{20}NOF_3$ calcd. $[M]^+$: 383.1497, found: 383.1500.

2,3-Diphenyl-1-(4,4,4-trifluoro-1-phenylbutyl)-1*H*-indole d33



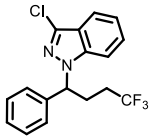
According to the general procedure A, this reaction was conducted in 0.2 mmol scale. **d33** (64.7 mg, 0.142 mmol) was prepared from 2,3-diphenyl-1*H*-indole (80.8 mg, 0.3 mmol), styrene (20.8 mg, 0.2 mmol) and 1,1,1-trifluoro-2-iodoethane (84.0 mg, 0.4 mmol) as white solid in 71% yield by column chromatography on silica gel with a gradient eluent of PE / EA = 100/1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.8 Hz, 1H), 7.44 – 7.22 (m, 14H), 7.17 (dd, *J* = 16.8, 7.5 Hz, 2H), 7.08 (dd, *J* = 17.9, 8.1 Hz, 2H), 5.52 (dd, *J* = 11.2, 4.7 Hz, 1H), 2.83 – 2.67 (m, 1H), 2.62 – 2.49 (m, 1H), 1.87 – 1.72 (m, 1H), 1.52 – 1.40 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.9, 138.8, 135.0, 134.9, 132.0, 131.2, 130.1, 129.0, 128.9, 128.6, 128.5, 128.3, 127.7, 127.4 (d, *J* = 272.2 Hz), 126.4, 125.9, 122.4, 120.7, 120.3, 116.2, 112.7, 57.1, 30.9 (q, *J* = 29.5 Hz), 25.1 (d, *J* = 2.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.3 (t, *J* = 10.6 Hz, 3F). IR (neat) cm^{-1} ṽ: 2921.8, 1452.9, 1253.8, 1136.0, 1024.3, 738.4, 697.1. HRMS (EI (+), 70 eV): $C_{30}H_{24}NF_3$ calcd. $[M]^+$: 455.1861, found: 455.1871.

2-Phenyl-1-(4,4,4-trifluoro-1-phenylbutyl)-1*H*-indole-3-carbaldehyde d34



According to the general procedure A, this reaction was conducted in 0.2 mmol scale. **d34** (49.7 mg, 0.122 mmol) was prepared from 2-phenyl-1*H*-indole-3-carbaldehyde (66.4 mg, 0.3 mmol), styrene (20.8 mg, 0.2 mmol) and 1,1,1-trifluoro-2-iodoethane (84.0 mg, 0.4 mmol) as white solid in 61% yield by column chromatography on silica gel with a gradient eluent of PE / EA = 100/1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.72 (s, 1H), 8.48 (d, *J* = 7.9 Hz, 1H), 7.55 (d, *J* = 3.3 Hz, 2H), 7.49 – 7.40 (m, 3H), 7.39 – 7.29 (m, 4H), 7.25 – 7.21 (m, 2H), 7.18 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.07 (d, *J* = 8.4 Hz, 1H), 5.54 (dd, *J* = 11.0, 5.2 Hz, 1H), 2.82 – 2.55 (m, 2H), 1.88 – 1.76 (m, 1H), 1.64 – 1.46 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.2, 152.3, 138.3, 134.9, 131.8, 130.4, 129.9, 129.3, 129.1, 128.7, 128.3, 126.6 (d, *J* = 276.5 Hz), 126.3, 126.1, 124.3, 123.7, 122.7, 116.4, 112.8, 57.8, 30.9 (dd, *J* = 58.8, 29.5 Hz), 24.84 (d, *J* = 2.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.3 (t, *J* = 10.6 Hz, 3F). IR (neat) cm^{-1} ṽ: 2920.8, 1653.9, 1415.6, 1129.8, 1024.0, 747.0, 698.0. HRMS (EI (+), 70 eV): $C_{25}H_{20}NOF_3$ calcd. $[M]^+$: 407.1497, found: 407.1499.

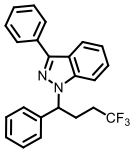
3-Chloro-1-(4,4,4-trifluoro-1-phenylbutyl)-1*H*-indazole d35



According to the general procedure A, this reaction was conducted in 0.2 mmol scale. **d35** (33.9 mg, 0.100 mmol) was prepared from 3-chloro-1*H*-indazole (45.8 mg, 0.3 mmol), styrene (20.8 mg, 0.2 mmol) and 1,1,1-trifluoro-2-iodoethane (84.0 mg, 0.4 mmol) as white solid in 50% yield by column chromatography on silica gel with a gradient eluent of PE / EA = 100/1. ^{1}H NMR (400 MHz, $CDCl_3$)

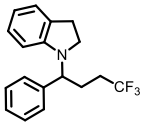
δ 7.67 (d, *J* = 8.1 Hz, 1H), 7.41 – 7.34 (m, 1H), 7.34 – 7.22 (m, 6H), 7.19 (t, *J* = 7.4 Hz, 1H), 5.57 (dd, *J* = 9.8, 5.7 Hz, 1H), 3.00 – 2.88 (m, 1H), 2.54 (dt, *J* = 14.5, 6.3 Hz, 1H), 2.25 – 2.05 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.2, 139.6, 133.9, 129.1, 128.4, 127.9, 127.1 (d, *J* = 276.3 Hz), 126.7, 121.8, 121.7, 120.1, 109.5, 61.9, 31.2 (q, *J* = 29.1 Hz), 27.8 (d, *J* = 2.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.7 (t, *J* = 10.8 Hz, 3F). IR (neat) cm^{-1} ṽ: 2922.6, 1255.4, 1141.9, 1068.5, 1029.0, 798.4, 743.1, 699.4. HRMS (EI (+), 70 eV): $C_{17}H_{14}N_2ClF_3$ calcd. $[M]^+$: 338.0798, found: 338.0802.

3-Phenyl-1-(4,4,4-trifluoro-1-phenylbutyl)-1*H*-indazole d36



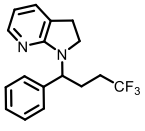
According to the general procedure A, this reaction was conducted in 0.2 mmol scale. **d36** (41.1 mg, 0.108 mmol) was prepared from 3-phenyl-1*H*-indazole (58.3 mg, 0.3 mmol), styrene (20.8 mg, 0.2 mmol) and 1,1,1-trifluoro-2-iodoethane (84.0 mg, 0.4 mmol) as white solid in 54% yield by column chromatography on silica gel with a gradient eluent of PE / EA = 100/1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.1 Hz, 1H), 7.65 – 7.59 (m, 1H), 7.55 – 7.45 (m, 3H), 7.44 – 7.36 (m, 3H), 7.34 – 7.29 (m, 3H), 7.21 – 7.13 (m, 2H), 5.77 (dd, *J* = 11.3, 5.0 Hz, 1H), 2.81 – 2.68 (m, 1H), 2.65 – 2.53 (m, 1H), 1.82 – 1.70 (m, 1H), 1.53 – 1.42 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.2, 143.8, 138.5, 133.5, 130.3, 130.3, 129.5, 129.3, 129.1, 128.3, 126.6 (d, *J* = 276.3 Hz), 126.2, 123.2, 123.0, 120.7, 112.6, 58.6, 30.8 (d, *J* = 29.5 Hz), 25.5 (d, *J* = 2.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.8 (t, *J* = 10.8 Hz). IR (neat) cm^{-1} ṽ: 2922.8, 1254.5, 1140.5, 1024.8, 741.8, 696.9. HRMS (EI (+), 70 eV): $C_{23}H_{19}N_2F_3$ calcd. $[M]^+$: 380.1500, found: 380.1496.

1-(4,4,4-Trifluoro-1-phenylbutyl)indoline d37



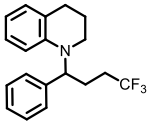
According to the general procedure B, this reaction was conducted in 0.2 mmol scale. **d37** (45.8 mg, 0.150 mmol) was prepared from indoline (35.8 mg, 0.3 mmol), styrene (20.8 mg, 0.2 mmol) and 1,1,1-trifluoro-2-iodoethane (84.0 mg, 0.4 mmol) as yellow oil in 75% yield by column chromatography on silica gel with a gradient eluent of PE. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.25 (m, 4H), 7.04 (t, *J* = 7.2 Hz, 2H), 6.60 (t, *J* = 7.3 Hz, 1H), 6.50 (d, *J* = 8.1 Hz, 1H), 4.69 – 4.63 (m, 1H), 3.41 (dd, *J* = 15.4, 8.9 Hz, 1H), 3.19 (dd, *J* = 18.1, 8.7 Hz, 1H), 3.06 – 2.80 (m, 2H), 2.45 – 2.04 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.3, 139.0, 129.7, 128.7, 127.8, 127.4 (d, *J* = 276.1 Hz), 127.5, 124.8, 117.3, 106.7, 57.9, 46.7, 31.4 (dd, *J* = 51.7, 22.9 Hz), 28.2, 24.0 (d, *J* = 2.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.1 (t, *J* = 10.4 Hz, 3F). IR (neat) cm^{-1} ṽ: 2960.2, 1257.7, 1138.2, 1021.1, 798.8, 743.3. HRMS (EI (+), 70 eV): $C_{18}H_{18}NF_3$ calcd. $[M]^+$: 305.1391, found: 305.1398.

1-(4,4,4-Trifluoro-1-phenylbutyl)-2,3-dihydro-1*H*-pyrrolo[2,3-b]pyridine d38



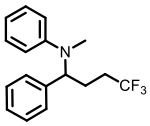
According to the general procedure B, this reaction was conducted in 0.2 mmol scale. **d38** (37.4 mg, 0.122 mmol) was prepared from 2,3-dihydro-1*H*-pyrrolo[2,3-b]pyridine (36.1 mg, 0.3 mmol), styrene (20.8 mg, 0.2 mmol) and 1,1,1-trifluoro-2-iodoethane (84.0 mg, 0.4 mmol) as yellow oil in 61% yield by column chromatography on silica gel with a gradient eluent of PE / EA = 50/1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 4.6 Hz, 1H), 7.38 – 7.29 (m, 4H), 7.26 (ddd, *J* = 9.6, 4.4, 1.9 Hz, 1H), 7.13 (dd, *J* = 7.0, 1.4 Hz, 1H), 6.42 (dd, *J* = 6.9, 5.4 Hz, 1H), 5.51 – 5.42 (m, 1H), 3.45 (ddd, *J* = 9.9, 9.0, 5.6 Hz, 1H), 3.12 (dt, *J* = 10.3, 8.5 Hz, 1H), 3.01 – 2.82 (m, 2H), 2.36 – 2.13 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6, 145.7, 138.8, 131.3, 128.8, 127.9, 127.8, 127.4 (d, *J* = 276.0 Hz), 122.9, 112.5, 54.6, 43.4, 31.6 (q, *J* = 28.9 Hz), 25.7, 23.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.2 (t, *J* = 10.8 Hz, 3F). IR (neat) cm^{-1} ṽ: 2961.9, 1260.1, 1091.4, 1019.1, 798.6. HRMS (EI (+), 70 eV): $C_{17}H_{17}N_2F_3$ calcd. $[M]^+$: 306.1344, found: 306.1351.

1-(4,4,4-Trifluoro-1-phenylbutyl)-1,2,3,4-tetrahydroquinoline d39



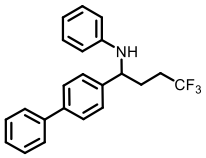
According to the general procedure B, this reaction was conducted in 0.2 mmol scale. **d39** (45.4 mg, 0.142 mmol) was prepared from 1,2,3,4-tetrahydroquinoline (40.0 mg, 0.3 mmol), styrene (20.8 mg, 0.2 mmol) and 1,1,1-trifluoro-2-iodoethane (84.0 mg, 0.4 mmol) as yellow oil in 71% yield by column chromatography on silica gel with a gradient eluent of PE / EA = 100/1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.25 (m, 5H), 7.09 – 7.02 (m, 1H), 6.98 (d, *J* = 7.3 Hz, 1H), 6.77 (d, *J* = 8.3 Hz, 1H), 6.60 (td, *J* = 7.3, 0.8 Hz, 1H), 5.06 (dd, *J* = 8.7, 6.2 Hz, 1H), 3.11 (ddd, *J* = 11.8, 8.3, 3.8 Hz, 1H), 3.03 – 2.92 (m, 1H), 2.74 (t, *J* = 6.3 Hz, 2H), 2.38 – 2.12 (m, 4H), 1.94 – 1.65 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.8, 140.1, 129.7, 128.7, 127.5, 127.44, 127.37 (d, *J* = 275.3 Hz), 127.3, 123.0, 116.2, 110.8, 58.2, 42.3, 31.6 (q, *J* = 28.8 Hz), 28.6, 23.2 (d, *J* = 2.6 Hz), 22.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.2 (t, *J* = 10.6 Hz, 3F). IR (neat) cm^{-1} ṽ: 2926.9, 1497.3, 1255.7, 1138.4, 745.1, 700.2. HRMS (EI (+), 70 eV): $C_{19}H_{20}NF_3$ calcd. $[M]^+$: 319.1548, found: 319.1552.

***N*-methyl-*N*-(4,4,4-trifluoro-1-phenylbutyl)aniline d40**



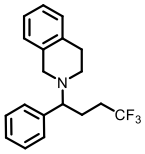
According to the general procedure B, this reaction was conducted in 0.2 mmol scale. **d40** (37.6 mg, 0.128 mmol) was prepared from *N*-methylaniline (32.2 mg, 0.3 mmol), styrene (20.8 mg, 0.2 mmol) and 1,1,1-trifluoro-2-iodoethane (84.0 mg, 0.4 mmol) as yellow oil in 64% yield by column chromatography on silica gel with a gradient eluent of PE / EA = 100/1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.19 (m, 6H), 6.84 (d, *J* = 8.3 Hz, 2H), 6.77 (t, *J* = 7.3 Hz, 1H), 5.00 (dd, *J* = 9.1, 5.5 Hz, 1H), 2.66 (s, 3H), 2.42 – 2.05 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.6, 140.0, 129.5, 128.9, 127.6, 127.5 (d, *J* = 294.9 Hz), 127.1, 117.6, 113.5, 60.7, 31.58 (t, *J* = 14.4 Hz), 24.11 (d, *J* = 2.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.3 (t, *J* = 10.5 Hz, 3F). IR (neat) cm^{-1} ṽ: 2924.5, 1502.3, 1252.7, 1138.4, 749.7, 696.5. HRMS (EI (+), 70 eV): $C_{17}H_{18}NF_3$ calcd. $[M]^+$: 293.1391, found: 293.1399.

***N*-(1-([1,1'-biphenyl]-4-yl)-4,4,4-trifluorobutyl)aniline d41**



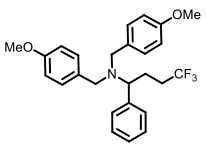
According to the general procedure B, this reaction was conducted in 0.2 mmol scale. **d41** (43.4 mg, 0.122 mmol) was prepared from aniline (27.9 mg, 0.3 mmol), 4-vinyl-1,1'-biphenyl (36.1 mg, 0.2 mmol) and 1,1,1-trifluoro-2-iodoethane (84.0 mg, 0.4 mmol) as yellow solid in 61% yield by column chromatography on silica gel with a gradient eluent of PE / EA = 50/1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.51 (m, 4H), 7.45 – 7.36 (m, 4H), 7.33 (dd, *J* = 8.3, 6.4 Hz, 1H), 7.12 (dd, *J* = 8.4, 7.5 Hz, 2H), 6.68 (t, *J* = 7.3 Hz, 1H), 6.57 (d, *J* = 7.7 Hz, 2H), 4.44 (t, *J* = 6.6 Hz, 1H), 4.02 (s, 1H), 2.33 – 2.19 (m, 1H), 2.18 – 2.02 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.9, 141.5, 140.8, 140.6, 129.4, 128.9, 127.8, 127.5, 127.18 (d, *J* = 276.2 Hz), 127.17, 126.9, 118.1, 113.6, 56.9, 30.9 (dd, *J* = 42.1, 15.7 Hz), 29.8 (d, *J* = 5.9 Hz). IR (neat) cm^{-1} ṽ: 2926.7, 1503.9, 1257.7, 1089.7, 1021.5, 798.5, 694.3. HRMS (EI (+), 70 eV): $C_{22}H_{20}NF_3$ calcd. $[M]^+$: 355.1548, found: 355.1552.

2-(4,4,4-Trifluoro-1-phenylbutyl)-1,2,3,4-tetrahydroisoquinoline d42



According to the general procedure B, this reaction was conducted in 0.2 mmol scale. **d42** (46.0 mg, 0.144 mmol) was prepared from 1,2,3,4-tetrahydroisoquinoline (40.0 mg, 0.3 mmol), styrene (20.8 mg, 0.2 mmol) and 1,1,1-trifluoro-2-iodoethane (84.0 mg, 0.4 mmol) as yellow oil in 72% yield by column chromatography on silica gel with a gradient eluent of PE / EA = 100/1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.26 (m, 5H), 7.13 – 7.04 (m, 3H), 7.02 – 6.95 (m, 1H), 3.73 – 3.51 (m, 3H), 2.93 – 2.74 (m, 3H), 2.61 – 2.47 (m, 1H), 2.35 – 2.21 (m, 1H), 2.16 – 1.90 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.0, 135.0, 134.6, 128.8, 128.6, 128.5, 127.8, 127.5 (d, *J* = 275.9 Hz), 126.8, 126.2, 125.7, 68.1, 53.2, 47.6, 30.8 (q, *J* = 28.5 Hz), 29.5, 25.3 (d, *J* = 2.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.4 (t, *J* = 10.2 Hz, 3F). IR (neat) cm^{-1} ṽ: 2922.1, 1252.4, 1128.2, 1090.3, 740.2, 702.3. HRMS (EI (+), 70 eV): $C_{19}H_{20}NF_3$ calcd. $[M]^+$: 319.1548, found: 319.1549.

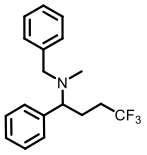
4,4,4-Trifluoro-*N*,*N*-bis(4-methoxybenzyl)-1-phenylbutan-1-amine d43



According to the general procedure B, this reaction was conducted in 0.2 mmol scale. **d43** (47.0 mg, 0.106 mmol) was prepared from bis(4-methoxybenzyl)amine (77.2 mg, 0.3 mmol), styrene (20.8 mg, 0.2 mmol) and 1,1,1-trifluoro-2-iodoethane (84.0 mg, 0.4 mmol) as black oil in 53% yield by column chromatography on silica gel with a gradient eluent of PE / EA = 100/1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (t, *J* = 7.3 Hz, 1H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.24 (dd, *J* = 16.7, 7.9 Hz, 6H), 6.89 (d, *J* = 8.4 Hz, 4H), 3.81 (s, 6H), 3.76 (d, *J* = 13.5 Hz, 2H), 3.71 – 3.64 (m, 1H), 3.04 (d, *J* = 13.5 Hz, 2H), 2.43 – 2.27 (m, 2H), 2.03 – 1.88 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 137.5, 131.9,

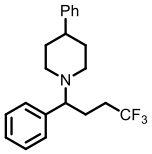
130.0, 128.9, 128.3, 127.60, 127.60 (d, J = 282.6 Hz), 113.9, 60.6, 55.4, 55.37, 52.8, 31.8 (d, J = 28.0 Hz), 23.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.3 (t, J = 10.8 Hz, 3F). IR (neat) cm^{-1} ṽ: 2924.1, 1493.2, 1258.9, 1025.1, 799.0, 747.7, 695.5. HRMS (EI (+), 70 eV): $C_{26}H_{28}NO_2F_3$ calcd. $[M]^+$: 443.2072, found: 443.2079.

_N_-benzyl-4,4,4-trifluoro-_N_-methyl-1-phenylbutan-1-amine d44



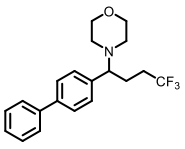
According to the general procedure B, this reaction was conducted in 0.2 mmol scale. **d44** (41.2 mg, 0.134 mmol) was prepared from *N*-methyl-1-phenylmethanamine (36.4 mg, 0.3 mmol), styrene (20.8 mg, 0.2 mmol) and 1,1,1-trifluoro-2-iodoethane (84.0 mg, 0.4 mmol) as yellow oil in 67% yield by column chromatography on silica gel with a gradient eluent of PE / EA = 100/1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 2H), 7.34 – 7.27 (m, 5H), 7.26 – 7.21 (m, 3H), 3.56 (dd, J = 13.6, 6.2 Hz, 2H), 3.26 (d, J = 13.4 Hz, 1H), 2.31 – 2.18 (m, 2H), 2.10 (s, 3H), 2.06 – 1.91 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.7, 138.4, 128.8, 128.7, 128.43, 128.41, 127.7, 127.6 (d, J = 276.1 Hz), 127.1, 66.6, 58.8, 37.6, 31.2 (q, J = 28.6 Hz), 25.0 (d, J = 2.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.2 (t, J = 10.8 Hz, 3F). IR (neat) cm^{-1} ṽ: 2950.8, 1452.7, 1252.0, 1130.5, 734.7, 699.5. HRMS (EI (+), 70 eV): $C_{18}H_{20}NF_3$ calcd. $[M]^+$: 307.1548, found: 307.1542.

4-Phenyl-1-(4,4,4-trifluoro-1-phenylbutyl)piperidine d45



According to the general procedure B, this reaction was conducted in 0.2 mmol scale. **d45** (48.6 mg, 0.140 mmol) was prepared from 4-phenylpiperidine (48.4 mg, 0.3 mmol), styrene (20.8 mg, 0.2 mmol) and 1,1,1-trifluoro-2-iodoethane (84.0 mg, 0.4 mmol) as yellow oil in 70% yield by column chromatography on silica gel with a gradient eluent of PE / EA = 100/1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (t, J = 7.2 Hz, 21H), 7.33 – 7.21 (m, 5H), 7.20 – 7.13 (m, 3H), 3.48 (t, J = 7.0 Hz, 1H), 3.08 (d, J = 10.3 Hz, 1H), 2.96 (d, J = 11.0 Hz, 1H), 2.42 – 2.31 (m, 1H), 2.28 – 1.65 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 128.7, 128.5, 128.4, 127.8, 127.5 (d, J = 276.2 Hz), 127.0, 126.3, 68.8, 53.0, 48.7, 42.8, 33.8 (d, J = 23.2 Hz), 31.1 (q, J = 28.7 Hz), 29.8, 24.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.2 (t, J = 10.7 Hz, 3F). IR (neat) cm^{-1} ṽ: 2962.3, 1261.7, 1141.7, 1097.0, 799.4, 702.5. HRMS (EI (+), 70 eV): $C_{21}H_{24}NF_3$ calcd. $[M]^+$: 347.1861, found: 347.1865.

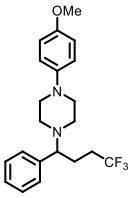
4-(1-([1,1'-Biphenyl]-4-yl)-4,4,4-trifluorobutyl)morpholine d46



According to the general procedure B, this reaction was conducted in 0.2 mmol scale. **d46** (52.4 mg, 0.150 mmol) was prepared from morpholine (26.1 mg, 0.3 mmol), 4-vinyl-1,1'-biphenyl (36.1 mg,

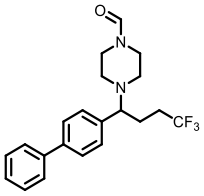
0.2 mmol) and 1,1,1-trifluoro-2-iodoethane (84.0 mg, 0.4 mmol) as yellow oil in 75% yield by column chromatography on silica gel with a gradient eluent of PE / EA = 100/1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 12.9, 4.8 Hz, 4H), 7.44 (dd, *J* = 10.4, 4.8 Hz, 2H), 7.38 – 7.31 (m, 1H), 7.29 – 7.22 (m, 2H), 3.75 – 3.64 (m, 4H), 3.34 (t, *J* = 6.7 Hz, 1H), 2.48 – 2.40 (m, 4H), 2.24 – 2.11 (m, 1H), 2.11 – 1.89 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.7, 137.8, 128.93, 128.91, 127.50 (d, *J* = 276.1 Hz), 127.49, 127.3, 127.2, 68.6, 67.3, 50.9, 30.7 (q, *J* = 28.7 Hz), 24.8 (d, *J* = 2.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.2 (t, *J* = 10.7 Hz, 3F). IR (neat) cm^{-1} ṽ: 2956.3, 1252.8, 1116.0, 1005.6, 764.6, 697.5. HRMS (EI (+), 70 eV): $C_{20}H_{22}NOF_3$ calcd. $[M]^+$: 349.1653, found: 349.1650.

1-(4-Methoxyphenyl)-4-(4,4,4-trifluoro-1-phenylbutyl)piperazine d47



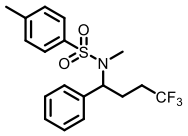
According to the general procedure B, this reaction was conducted in 0.2 mmol scale. **d47** (53.7 mg, 0.142 mmol) was prepared from 1-(4-methoxyphenyl)piperazine (57.8 mg, 0.3 mmol), styrene (20.8 mg, 0.2 mmol) and 1,1,1-trifluoro-2-iodoethane (84.0 mg, 0.4 mmol) as yellow oil in 71% yield by column chromatography on silica gel with a gradient eluent of PE / EA = 100/1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (t, *J* = 7.2 Hz, 2H), 7.31 – 7.26 (m, 1H), 7.24 (dd, *J* = 6.1, 4.6 Hz, 2H), 6.90 – 6.77 (m, 4H), 3.75 (s, 3H), 3.40 (t, *J* = 6.7 Hz, 1H), 3.05 (t, *J* = 4.9 Hz, 4H), 2.58 (d, *J* = 5.4 Hz, 4H), 2.26 – 2.13 (m, 1H), 2.11 – 1.86 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.9, 145.8, 138.7, 128.54, 128.52, 127.8, 127.5 (d, *J* = 276.2 Hz), 118.3, 114.5, 68.5, 55.7, 51.0, 50.2, 30.8 (q, *J* = 28.6 Hz), 25.0 (d, *J* = 2.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.3 (t, *J* = 10.8 Hz, 3F). IR (neat) cm^{-1} ṽ: 2951.0, 1510.9, 1242.8, 1131.5, 822.4, 702.8. HRMS (EI (+), 70 eV): $C_{21}H_{25}N_2OF_3$ calcd. $[M]^+$: 378.1919, found: 378.1926.

4-(1-([1,1'-Biphenyl]-4-yl)-4,4,4-trifluorobutyl)piperazine-1-carbaldehyde d48



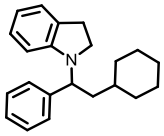
According to the general procedure B, this reaction was conducted in 0.2 mmol scale. **d48** (41.4 mg, 0.110 mmol) was prepared from piperidine-4-carbaldehyde (34.0 mg, 0.3 mmol), 4-vinyl-1,1'-biphenyl (36.1 mg, 0.2 mmol) and 1,1,1-trifluoro-2-iodoethane (84.0 mg, 0.4 mmol) as yellow solid in 55% yield by column chromatography on silica gel with a gradient eluent of PE / EA = 50/1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.58 (dd, *J* = 7.5, 5.2 Hz, 4H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.3 Hz, 1H), 7.27 – 7.21 (m, 2H), 3.54 (t, *J* = 5.0 Hz, 2H), 3.48 (t, *J* = 6.9 Hz, 1H), 3.40 – 3.30 (m, 2H), 2.56 – 2.36 (m, 4H), 2.26 – 2.10 (m, 2H), 2.08 – 1.94 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7, 141.0, 140.6, 136.8, 129.0, 128.8, 127.6, 127.4 (d, *J* = 276.3 Hz), 127.3, 127.2, 68.1, 50.5, 49.3, 46.0, 40.3, 31.0 (q, *J* = 28.8 Hz), 24.7 (d, *J* = 2.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.2 (t, *J* = 10.6 Hz, 3F). IR (neat) cm^{-1} ṽ: 2919.9, 1671.9, 1252.6, 1127.0, 1003.5, 697.9. HRMS (EI (+), 70 eV): $C_{21}H_{23}N_2OF_3$ calcd. $[M]^+$: 376.1762, found: 376.1760.

_N_,4-dimethyl-_N_-(4,4,4-trifluoro-1-phenylbutyl)benzenesulfonamide d49



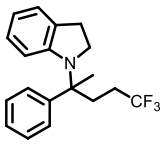
According to the general procedure B, this reaction was conducted in 0.2 mmol scale. **d49** (63.9 mg, 0.172 mmol) was prepared from *N*,4-dimethylbenzenesulfonamide (55.6 mg, 0.3 mmol), styrene (20.8 mg, 0.2 mmol) and 1,1,1-trifluoro-2-iodoethane (84.0 mg, 0.4 mmol) as yellow oil in 86% yield by column chromatography on silica gel with a gradient eluent of PE / EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.3 Hz, 2H), 7.33 – 7.23 (m, 5H), 7.13 (dt, *J* = 6.0, 3.2 Hz, 2H), 5.12 (dd, *J* = 8.4, 6.1 Hz, 1H), 2.61 (s, 3H), 2.42 (s, 3H), 2.18 – 1.98 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 137.1, 137.0, 129.8, 128.8, 128.3, 127.9, 127.2, 127.0 (d, *J* = 276.1 Hz), 59.1, 31.5 (q, *J* = 29.1 Hz), 28.74, 23.23 (d, *J* = 2.8 Hz), 21.60. ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.4 (t, *J* = 10.2 Hz, 3F). IR (neat) cm^{-1} ṽ: 2926.4, 1335.5, 1256.2, 1144.6, 981.9, 715.6, 546.5. HRMS (EI (+), 70 eV): $C_{18}H_{20}NO_2F_3S$ calcd. $[M]^+$: 371.1167, found: 371.1159.

1-(2-Cyclohexyl-1-phenylethyl)indoline d50



According to the general procedure B, this reaction was conducted in 0.2 mmol scale. **d50** (36.7 mg, 0.120 mmol) was prepared from indoline (35.8 mg, 0.3 mmol), styrene (20.8 mg, 0.2 mmol) and iodocyclohexane (84.0 mg, 0.4 mmol) as yellow oil in 60% yield by column chromatography on silica gel with a gradient eluent of PE / EA = 100/1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 4H), 7.24 – 7.18 (m, 1H), 7.05 – 6.96 (m, 2H), 6.53 (ddd, *J* = 16.4, 11.5, 4.3 Hz, 2H), 4.75 (t, *J* = 7.7 Hz, 1H), 3.45 (ddd, *J* = 9.6, 8.7, 6.8 Hz, 1H), 3.22 (dt, *J* = 9.9, 8.3 Hz, 1H), 3.00 – 2.78 (m, 2H), 1.91 – 1.76 (m, 4H), 1.70 – 1.51 (m, 4H), 1.38 – 1.30 (m, 1H), 1.22 – 1.15 (m, 2H), 1.06 – 0.93 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.6, 140.9, 129.7, 128.4, 128.0, 127.4, 127.1, 124.6, 116.4, 106.3, 55.7, 46.8, 38.8, 34.4, 33.7, 33.6, 28.2, 26.7, 26.4, 26.3. IR (neat) cm^{-1} ṽ: 2921.1, 1260.1, 1088.7, 1021.6, 798.5, 739.4. HRMS (EI (+), 70 eV): $C_{22}H_{27}N$ calcd. $[M]^+$: 305.2144, found: 305.2151.

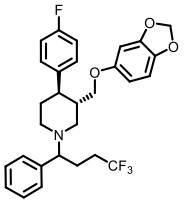
1-(5,5,5-Trifluoro-2-phenylpentan-2-yl)indoline d51



According to the general procedure B, this reaction was conducted in 0.2 mmol scale. **d51** (41.5 mg, 0.130 mmol) was prepared from indoline (35.8 mg, 0.3 mmol), prop-1-en-2-ylbenzene (23.6 mg, 0.2 mmol) and 1,1,1-trifluoro-2-iodoethane (84.0 mg, 0.4 mmol) as brown oil in 65% yield by column chromatography on silica gel with a gradient eluent of PE / EA = 100/1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.5 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.28 (d, *J* = 7.3 Hz, 1H), 7.06 (d, *J* = 7.1 Hz, 1H), 6.69 (t, *J* = 7.7 Hz, 1H), 6.58 (t, *J* = 7.3 Hz, 1H), 5.63 (d, *J* = 8.0 Hz, 1H), 3.61 (td, *J* = 8.4,

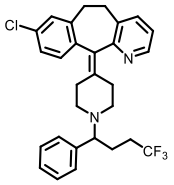
2.7 Hz, 1H), 3.44 (dt, *J* = 11.7, 9.1 Hz, 1H), 3.12 – 2.92 (m, 2H), 2.16 (dd, *J* = 19.2, 6.3 Hz, 1H), 2.04 – 1.88 (m, 2H), 1.82 – 1.69 (m, 1H), 1.54 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.8, 144.3, 131.5, 128.8, 127.5 (d, *J* = 276.0 Hz), 127.2, 126.5, 126.4, 124.3, 117.9, 112.2, 60.6, 48.9, 35.9 (d, *J* = 2.6 Hz), 29.6 (d, *J* = 28.5 Hz), 28.4, 17.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.2 (t, *J* = 10.5 Hz, 3F). IR (neat) cm^{-1} ṽ: 2925.5, 1453.5, 1254.3, 1132.3, 744.9, 701.4. HRMS (EI (+), 70 eV): $C_{19}H_{20}NF_3$ calcd. $[M]^+$: 319.1548, found: 319.1549.

(3*S*,4*R*)-3-((benzo[d][1,3]dioxol-5-yloxy)methyl)-4-(4-fluorophenyl)-1-(4,4,4-trifluoro-1-phenylbutyl)piperidine d52



According to the general procedure B, this reaction was conducted in 0.2 mmol scale. **d52** (38.2 mg, 0.074 mmol) was prepared from (3*S*,4*R*)-3-((benzo[d][1,3]dioxol-5-yloxy)methyl)-4-(4-fluorophenyl)piperidine (98.8 mg, 0.3 mmol), styrene (20.8 mg, 0.2 mmol) and 1,1,1-trifluoro-2-iodoethane (84.0 mg, 0.4 mmol) as brown oil in 37% yield by column chromatography on silica gel with a gradient eluent of PE / EA = 50/1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.28 (m, 3H), 7.24 – 7.17 (m, 2H), 7.17 – 7.05 (m, 2H), 6.94 (td, *J* = 8.7, 1.8 Hz, 2H), 6.61 (dd, *J* = 8.4, 6.7 Hz, 1H), 6.30 (dd, *J* = 22.0, 2.4 Hz, 1H), 6.09 (ddd, *J* = 17.1, 8.5, 2.5 Hz, 1H), 5.85 (d, *J* = 2.1 Hz, 2H), 3.59 – 3.46 (m, 2H), 3.38 (ddd, *J* = 16.8, 9.3, 7.4 Hz, 1H), 3.25 (dd, *J* = 44.2, 10.5 Hz, 1H), 2.97 (dd, *J* = 33.8, 10.9 Hz, 1H), 2.38 – 1.95 (m, 8H), 1.91 – 1.77 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 127.59 (d, *J* = 276.0 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8, 160.4, 154.5, 148.3, 141.7, 139.9 (d, *J* = 2.5 Hz), 138.2, 128.9, 128.6, 128.4, 127.7, 115.6, 115.4, 108.0, 105.7, 101.2, 98.1, 69.7, 68.5, 56.4, 52.6, 51.7, 48.2, 44.5, 42.7, 34.9, 31.1 (q, *J* = 28.6 Hz), 24.8 (d, *J* = 10.1 Hz), 14.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.1 (t, *J* = 10.8 Hz, 3F), -116.4 – -116.6 (m, 1F). IR (neat) cm^{-1} ṽ: 2919.6, 1486.5, 1181.6, 1130.9, 1037.1, 830.7, 702.4. HRMS (EI (+), 70 eV): $C_{29}H_{29}NO_3F_4$ calcd. $[M]^+$: 515.2084, found: 515.2088.

8-Chloro-11-(1-(4,4,4-trifluoro-1-phenylbutyl)piperidin-4-ylidene)-6,11-dihydro-5H-benzo-[5,6]cyclohepta[1,2-b]pyridine d53

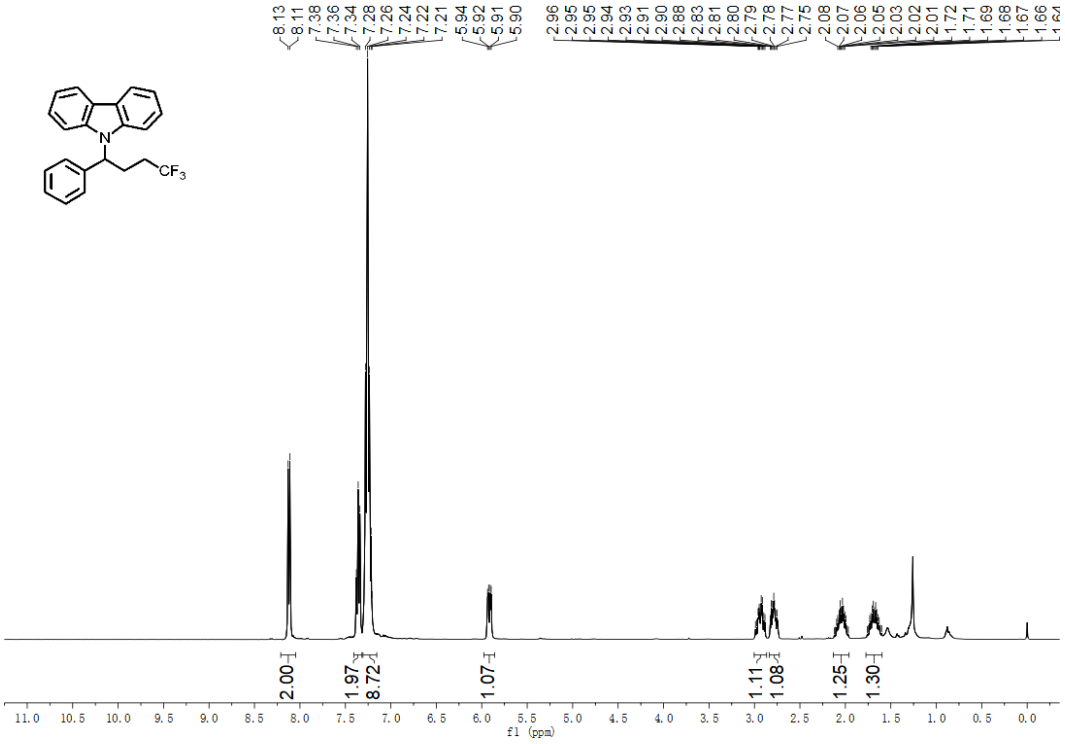


According to the general procedure B, this reaction was conducted in 0.2 mmol scale. **d53** (38.8 mg, 0.078 mmol) was prepared from 8-chloro-11-(piperidin-4-ylidene)-6,11-dihydro-5*H*-benzo[5,6]-cyclohepta[1,2-b]pyridine (93.2 mg, 0.3 mmol), styrene (20.8 mg, 0.2 mmol) and 1,1,1-trifluoro-2-iodoethane (84.0 mg, 0.4 mmol) as brown oil in 39% yield by column chromatography on silica gel with a gradient eluent of PE / EA = 50/1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (td, *J* = 4.6, 1.5 Hz, 1H), 7.42 – 7.36 (m, 1H), 7.33 – 7.25 (m, 3H), 7.18 – 7.13 (m, 2H), 7.12 – 7.07 (m, 3H), 7.07 – 7.01 (m, 1H), 3.41 (t, *J* = 6.8 Hz, 1H), 3.35 – 3.20 (m, 2H), 2.82 – 2.64 (m, 4H), 2.57 – 2.40 (m, 2H),

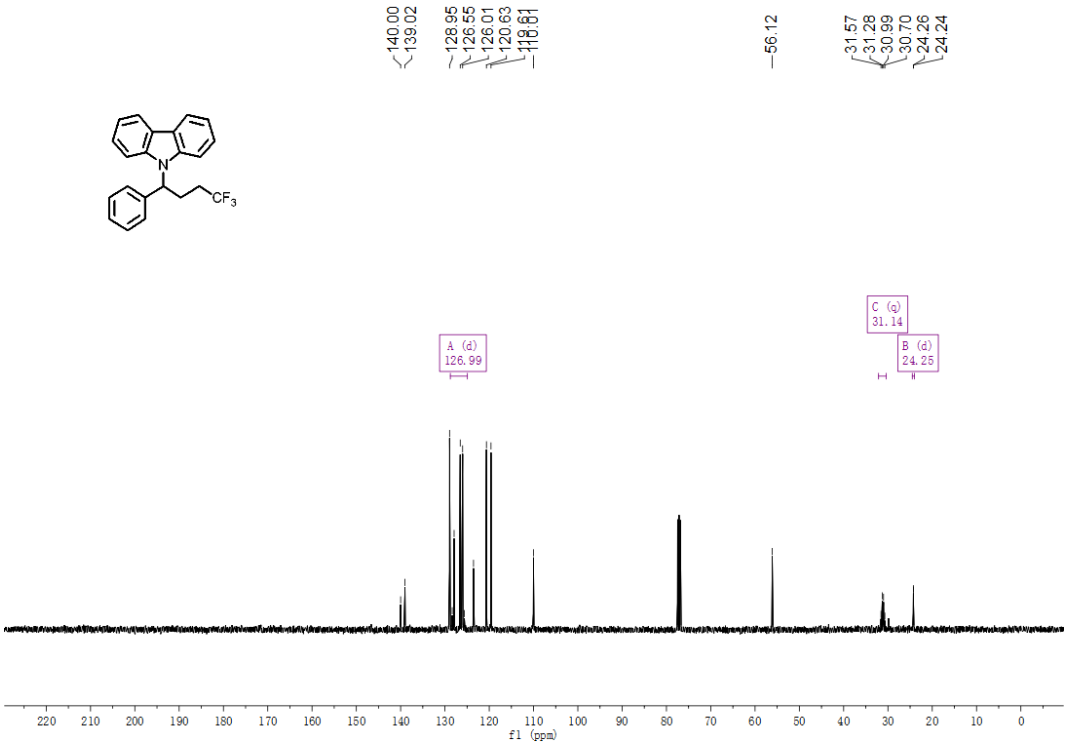
2.36 – 2.27 (m, 2H), 2.21 – 2.06 (m, 3H), 2.04 – 1.89 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.7, 146.7, 139.6, 139.2, 138.6, 137.8, 137.3, 133.5, 132.7, 132.5, 131.0, 129.0, 128.4, 127.6, 127.5 (d, J = 276.2 Hz), 126.4, 122.2, 68.3, 52.2, 50.7, 31.9, 31.5, 31.4, 31.2, 31.0 (d, J = 26.4 Hz), 24.98 (d, J = 2.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.2 (t, J = 10.7 Hz, 3F). IR (neat) cm^{-1} ṽ: 2921.6, 1477.2, 1252.9, 1099.9, 999.3, 730.8, 701.5. HRMS (EI (+), 70 eV): $C_{29}H_{28}N_2F_3Cl$ calcd. $[M]^+$: 496.1893, found: 496.1892.

4. Copies of NMR spectra

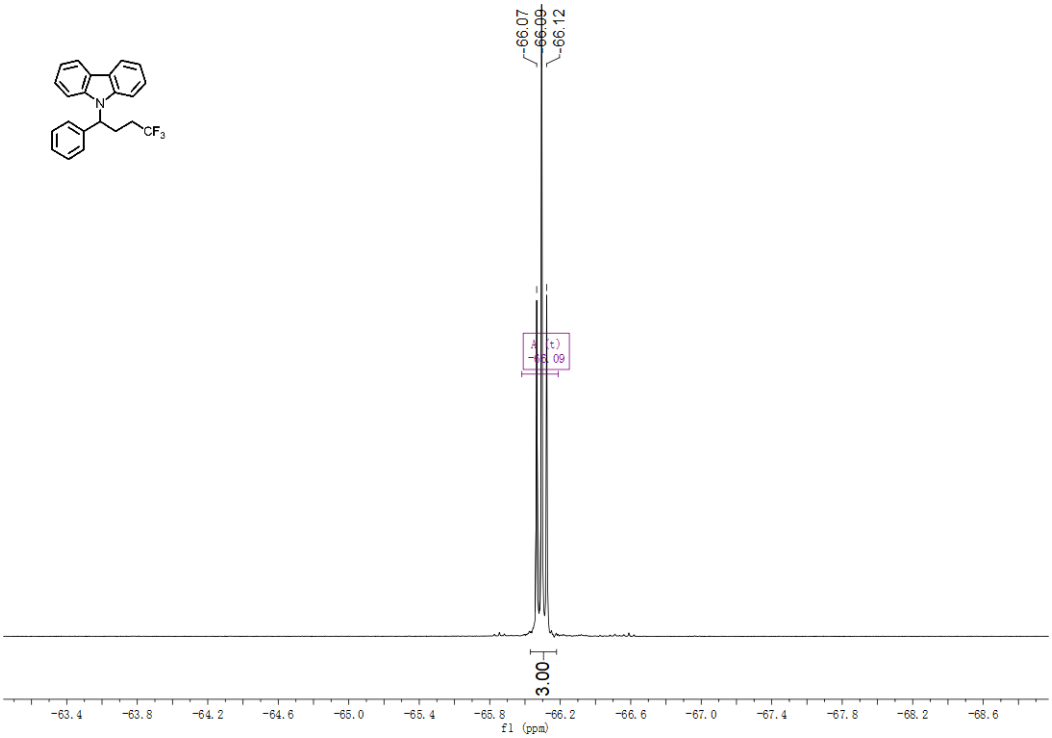
d1 ^{1}H NMR



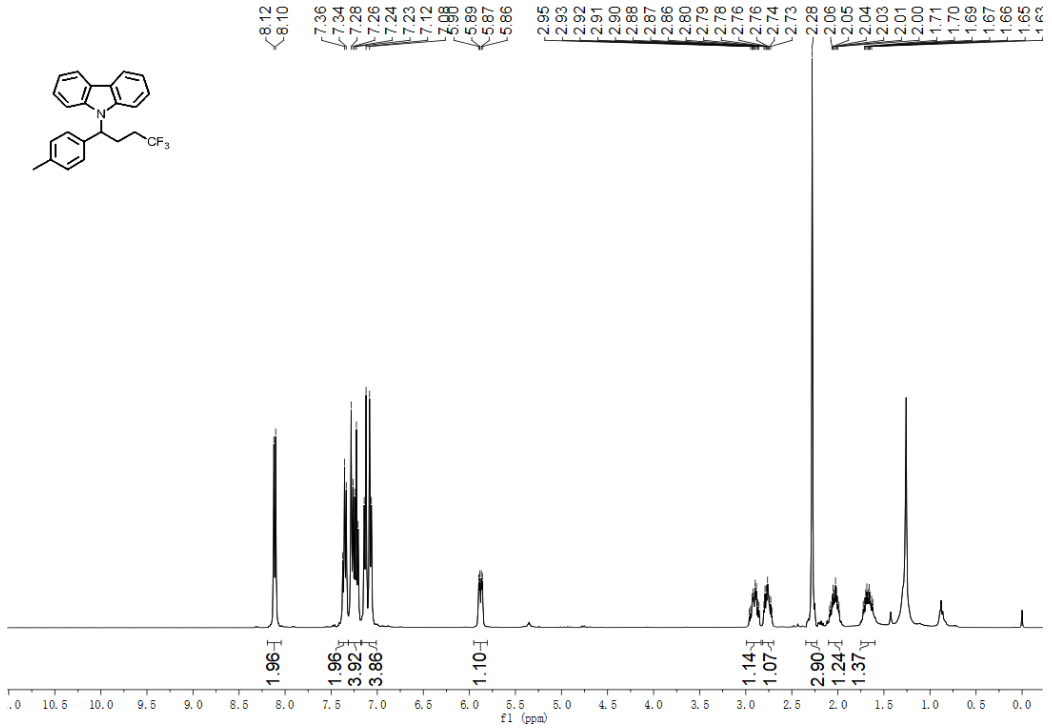
d1 ^{13}C NMR



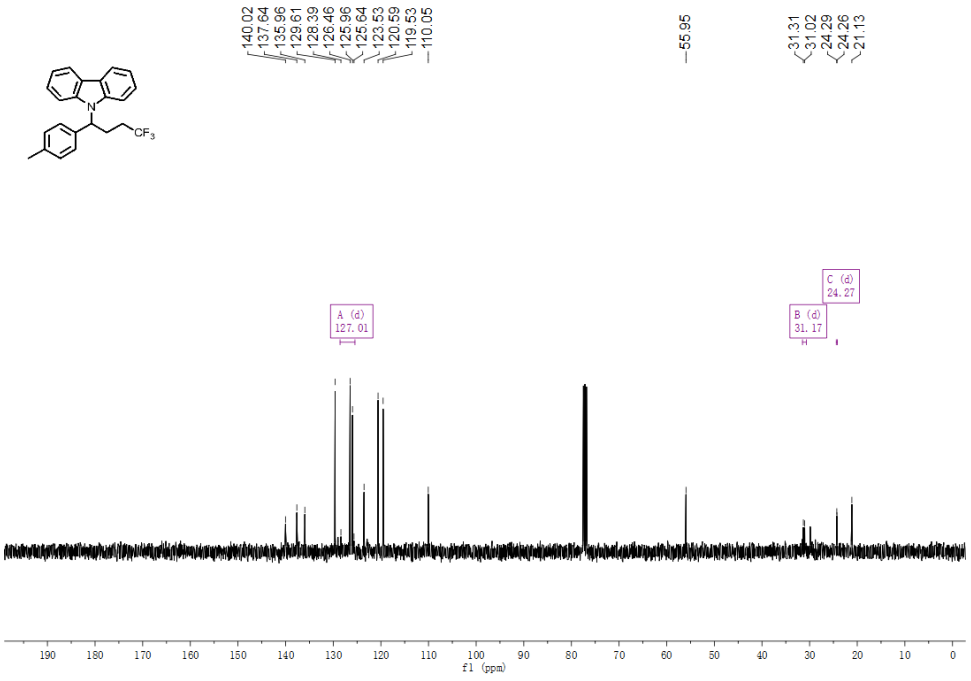
d1 ^{19}F NMR



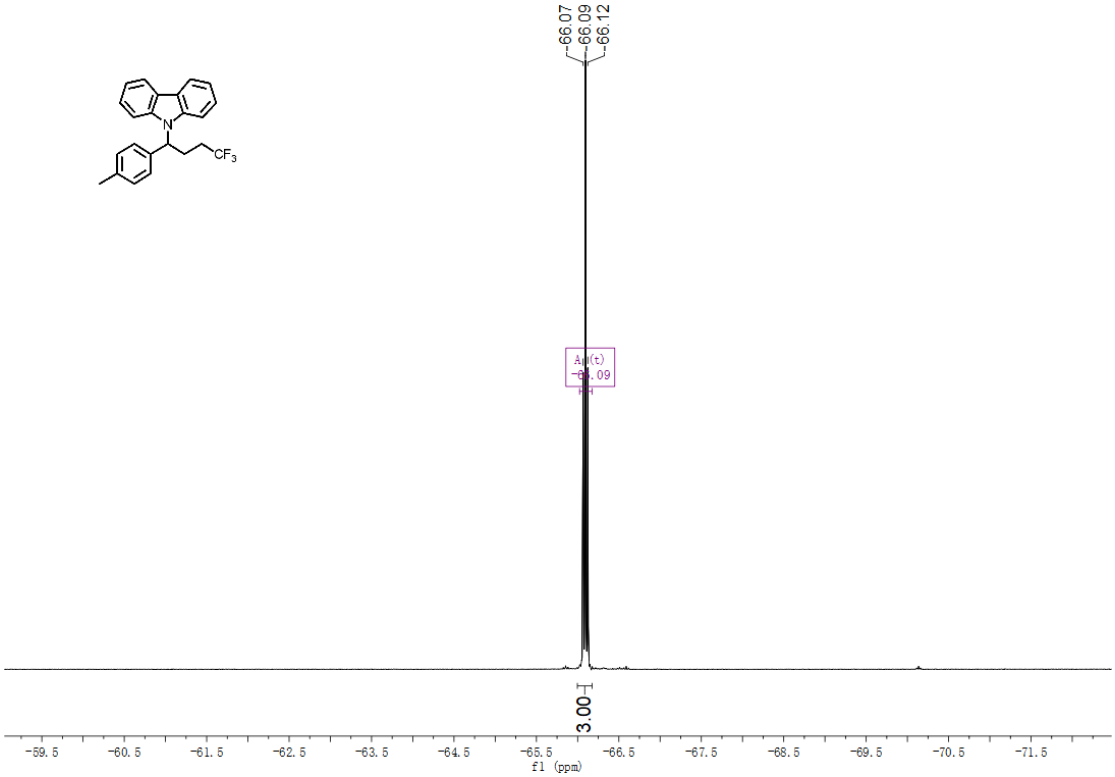
d2 ^{1}H NMR



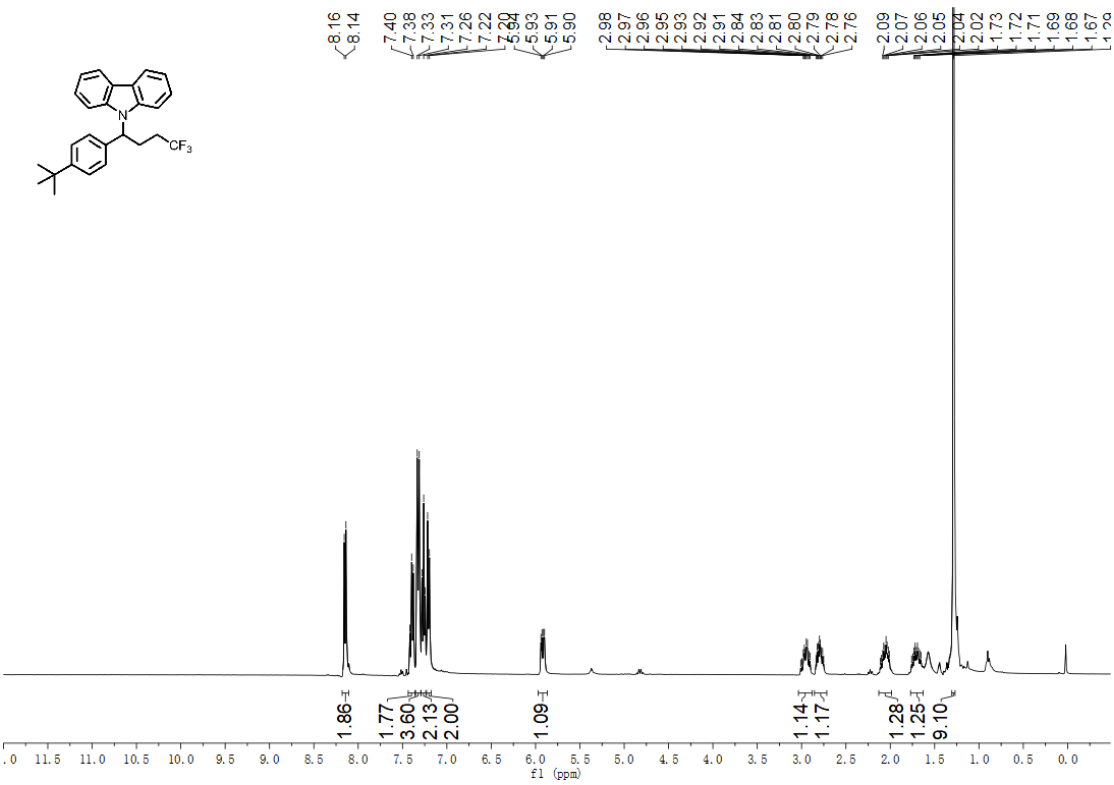
d2 ^{13}C NMR



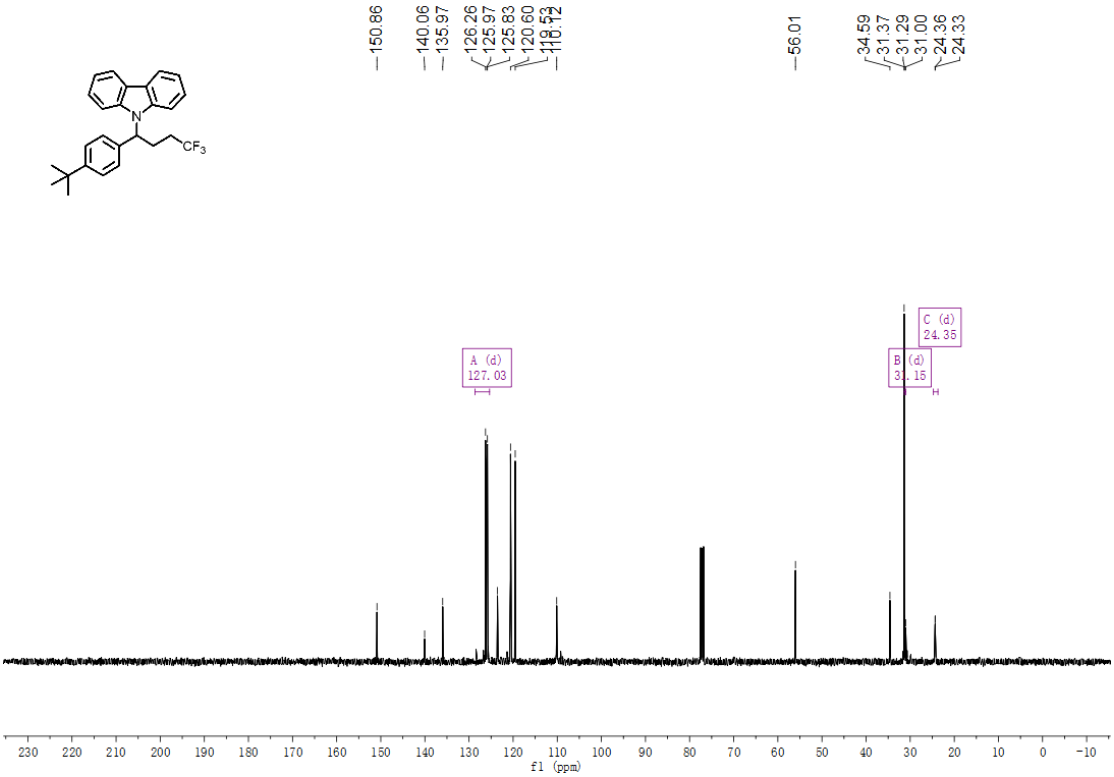
d2 ^{19}F NMR



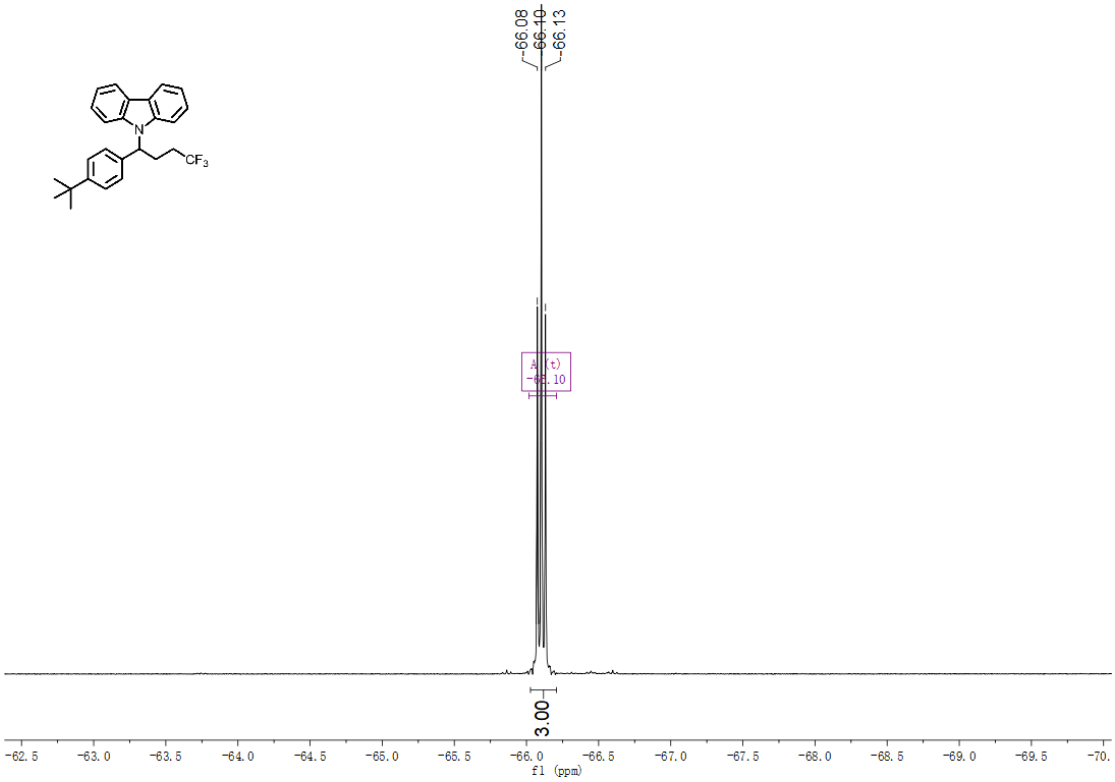
d3 ^{1}H NMR



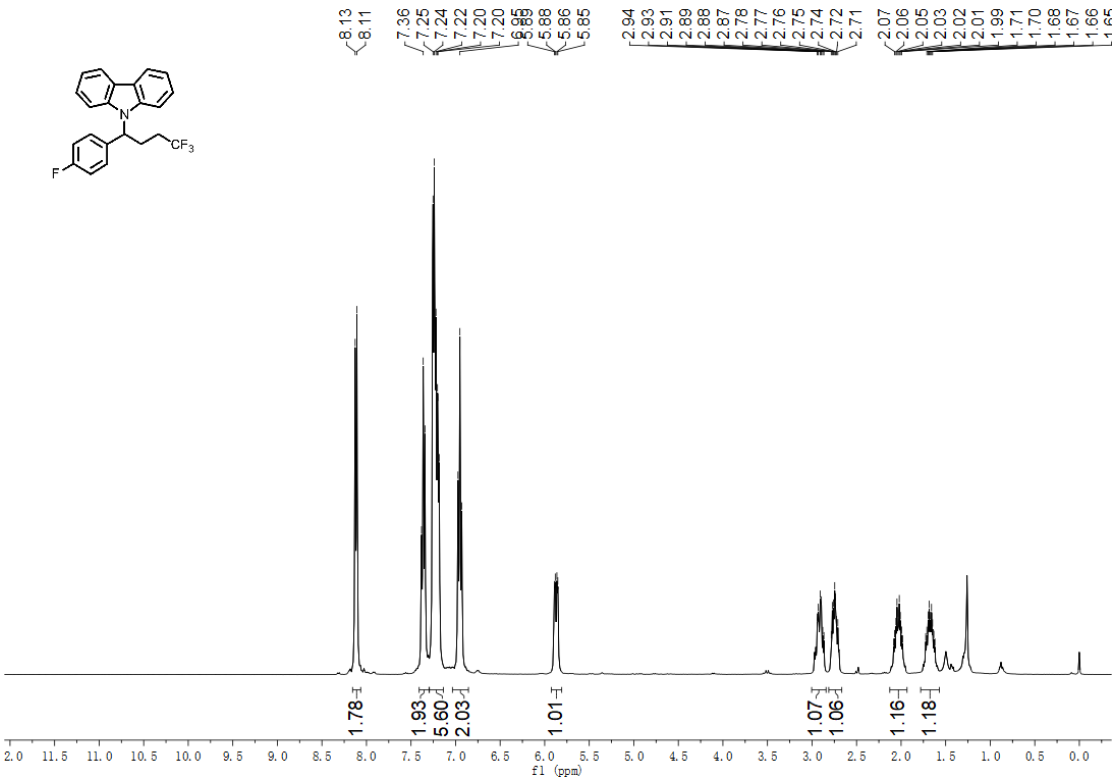
d3 ^{13}C NMR



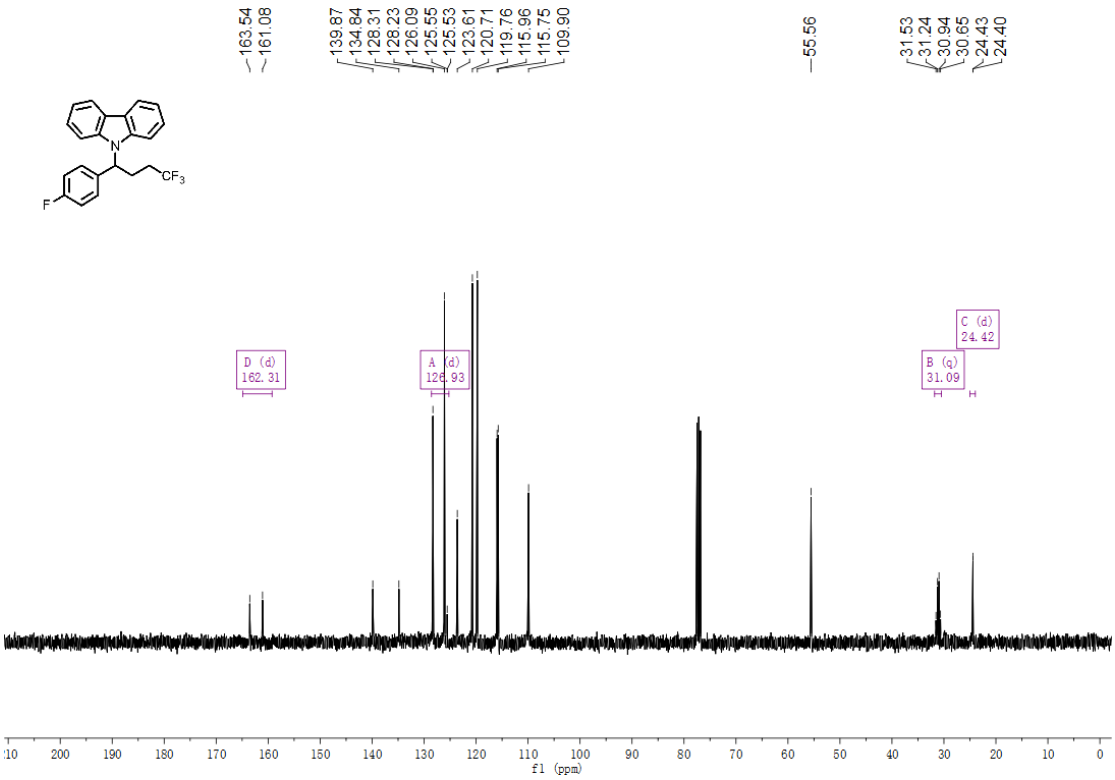
d3 ^{19}F NMR



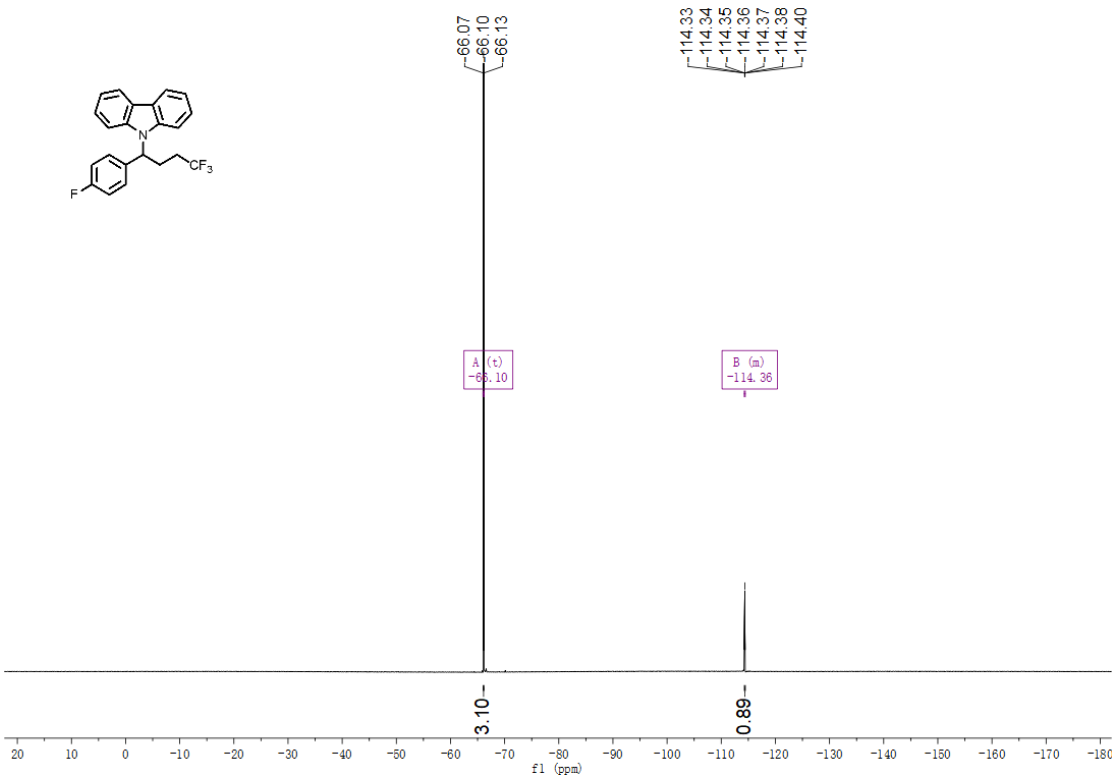
d4 ^{1}H NMR



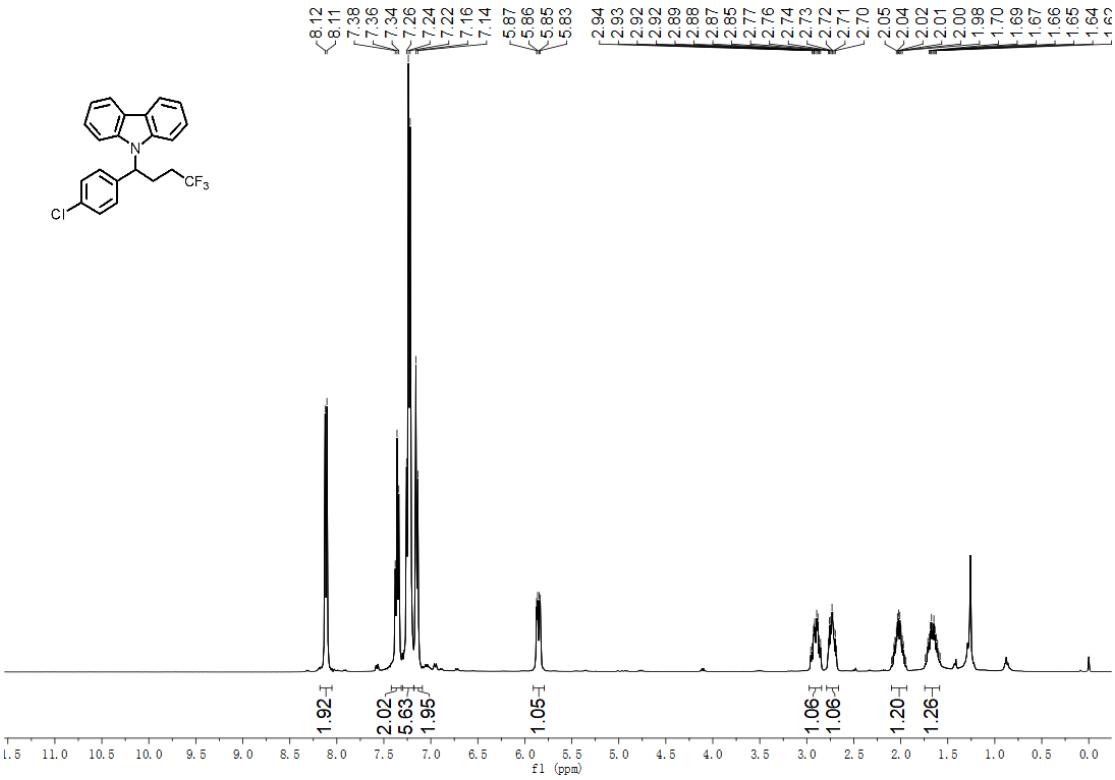
d4 ^{13}C NMR



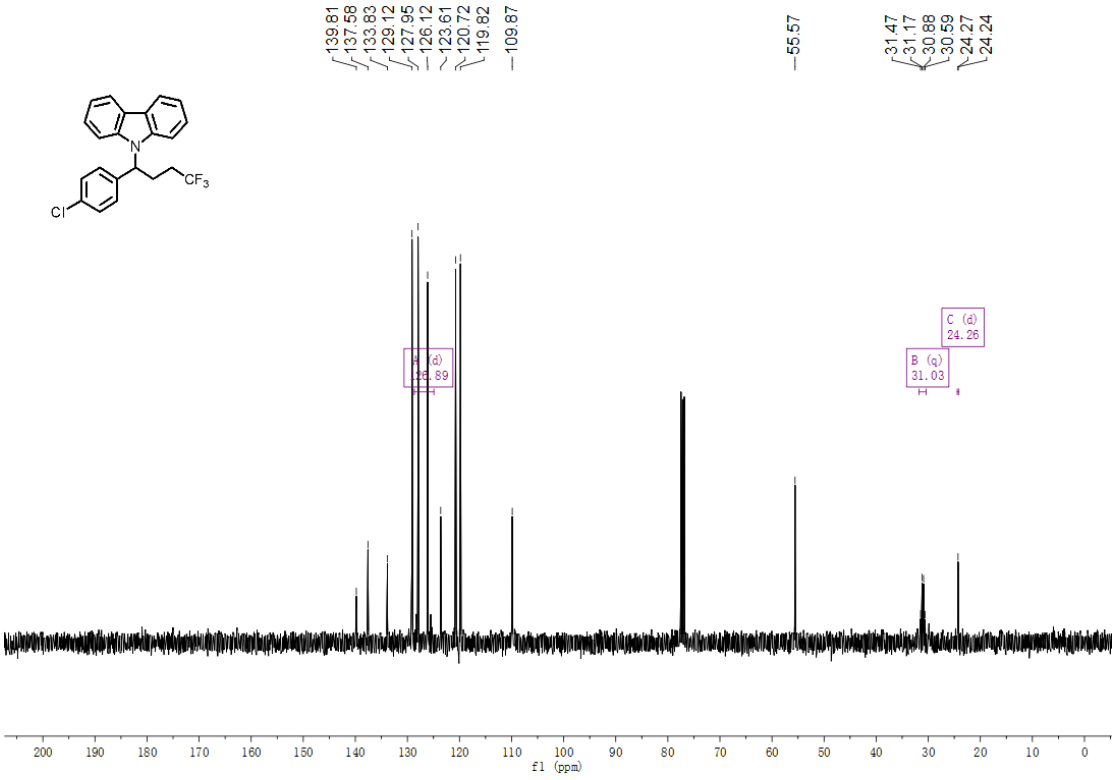
d4 ^{19}F NMR



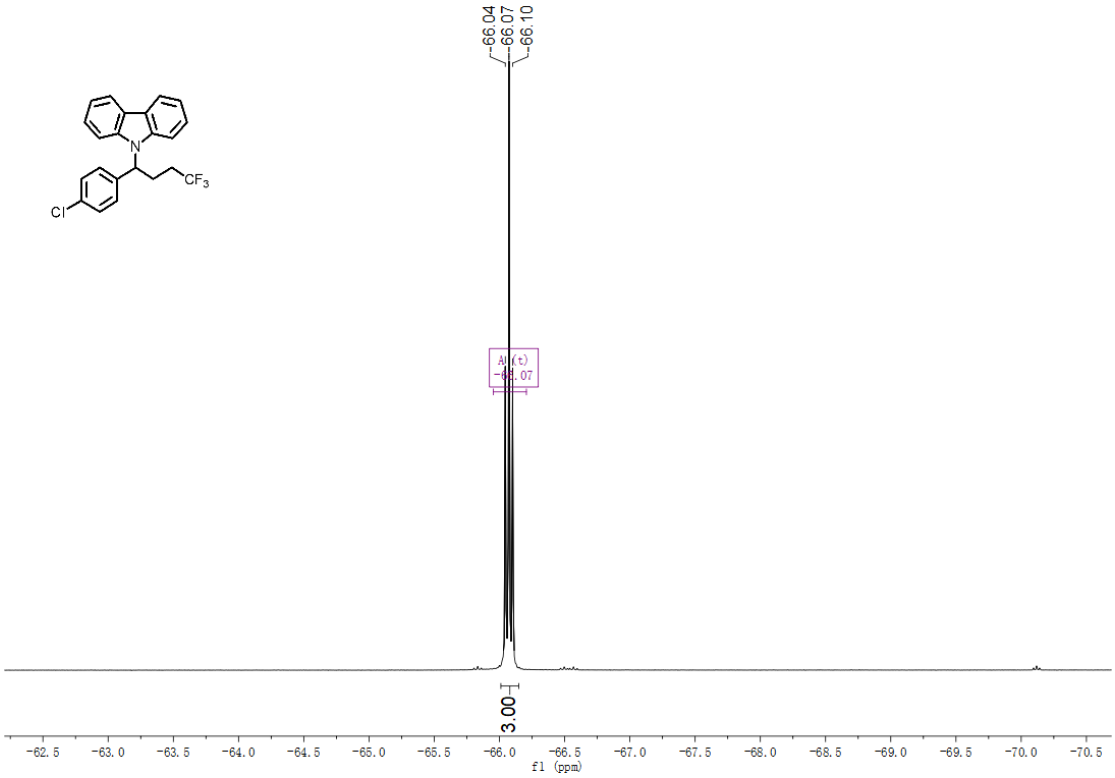
d5 ^{1}H NMR



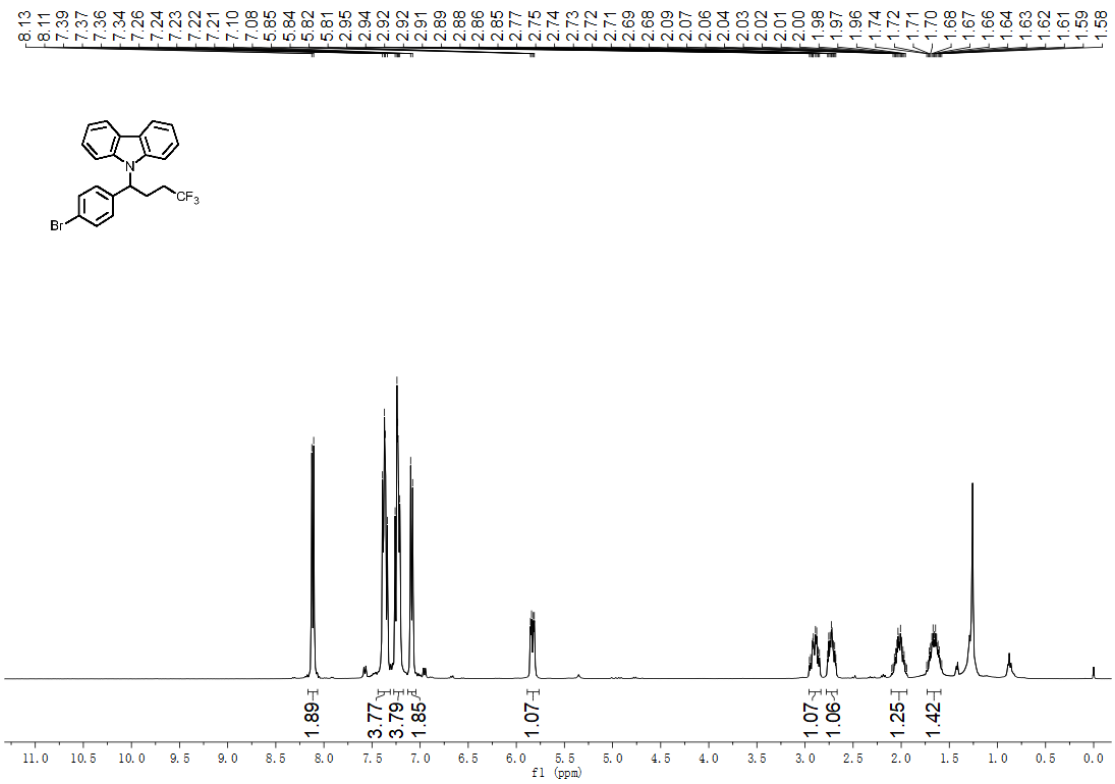
d5 ^{13}C NMR



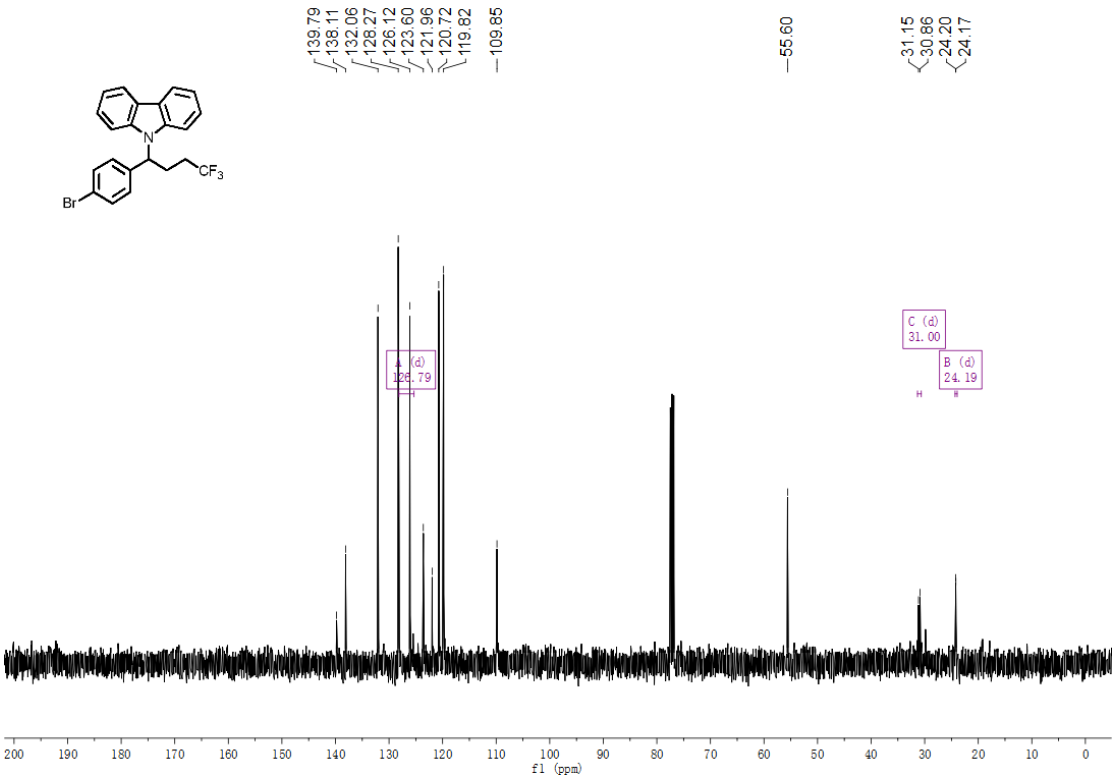
d5 ^{19}F NMR



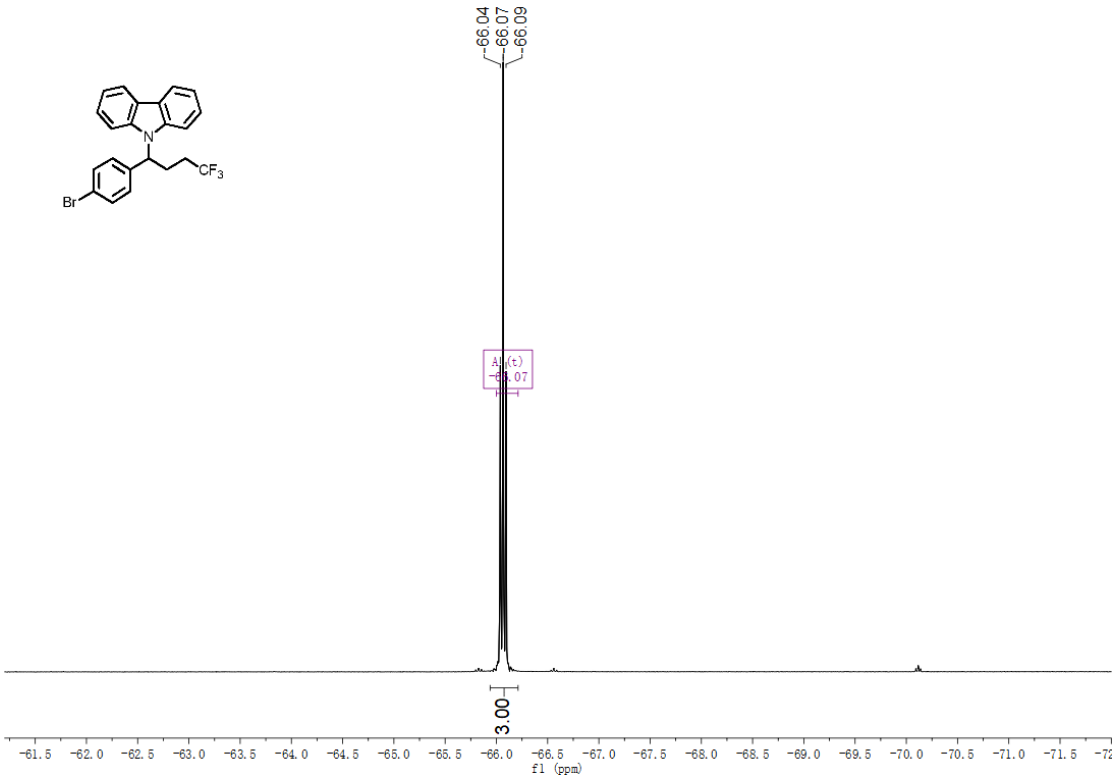
d6 ^{1}H NMR



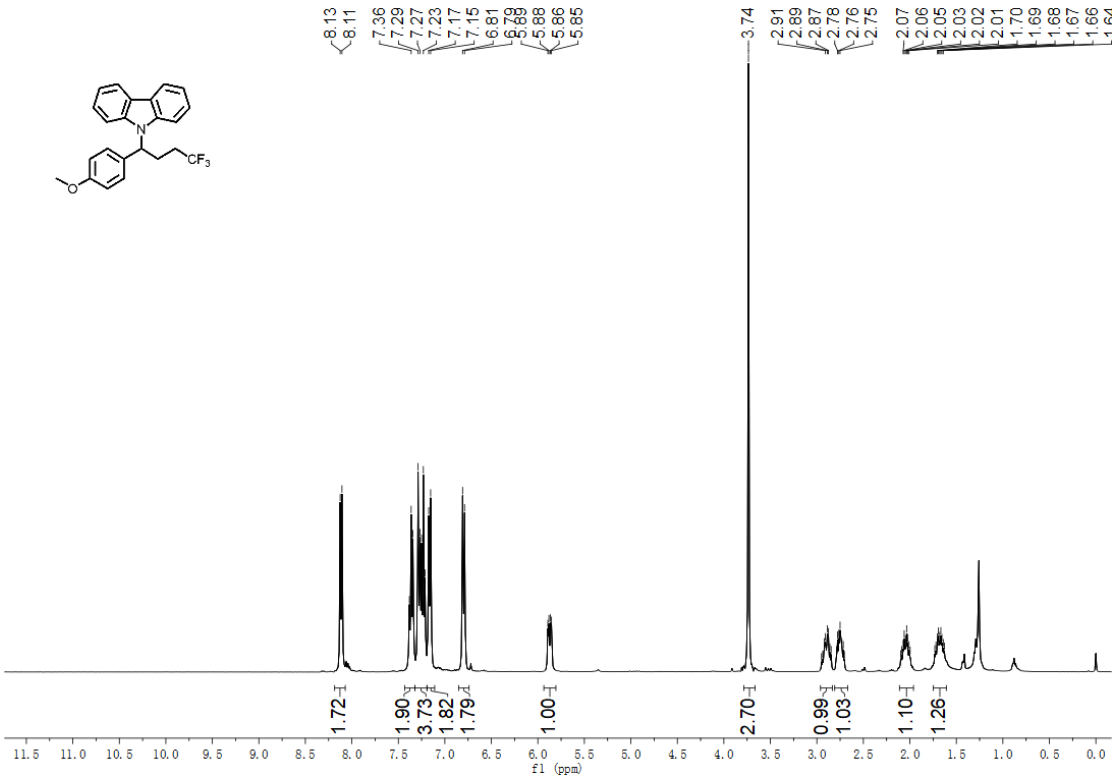
d6 ^{13}C NMR



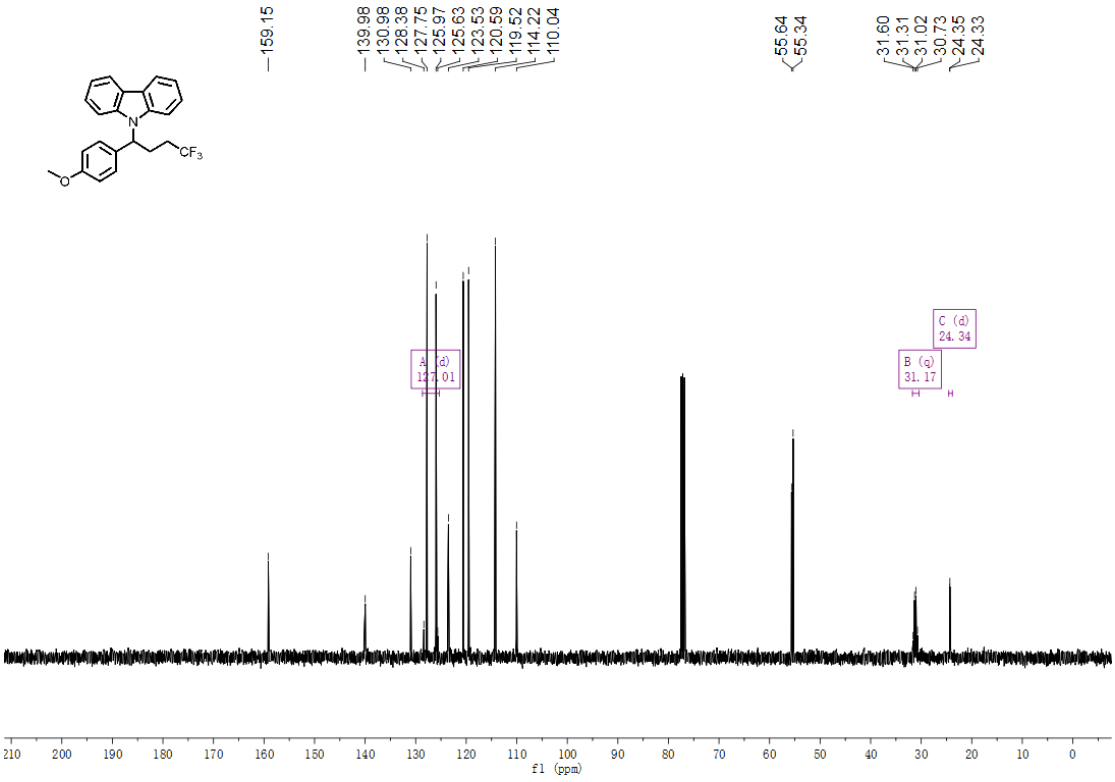
d6 ^{19}F NMR



d7 ^{1}H NMR



d7 ^{13}C NMR



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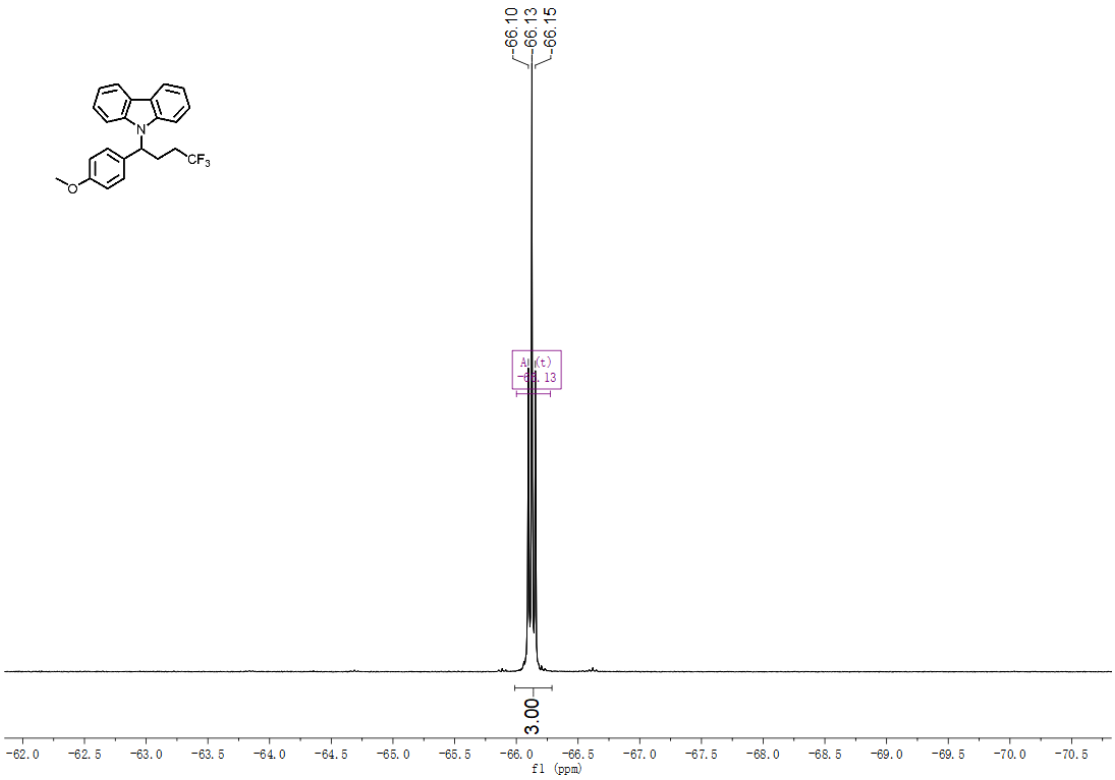
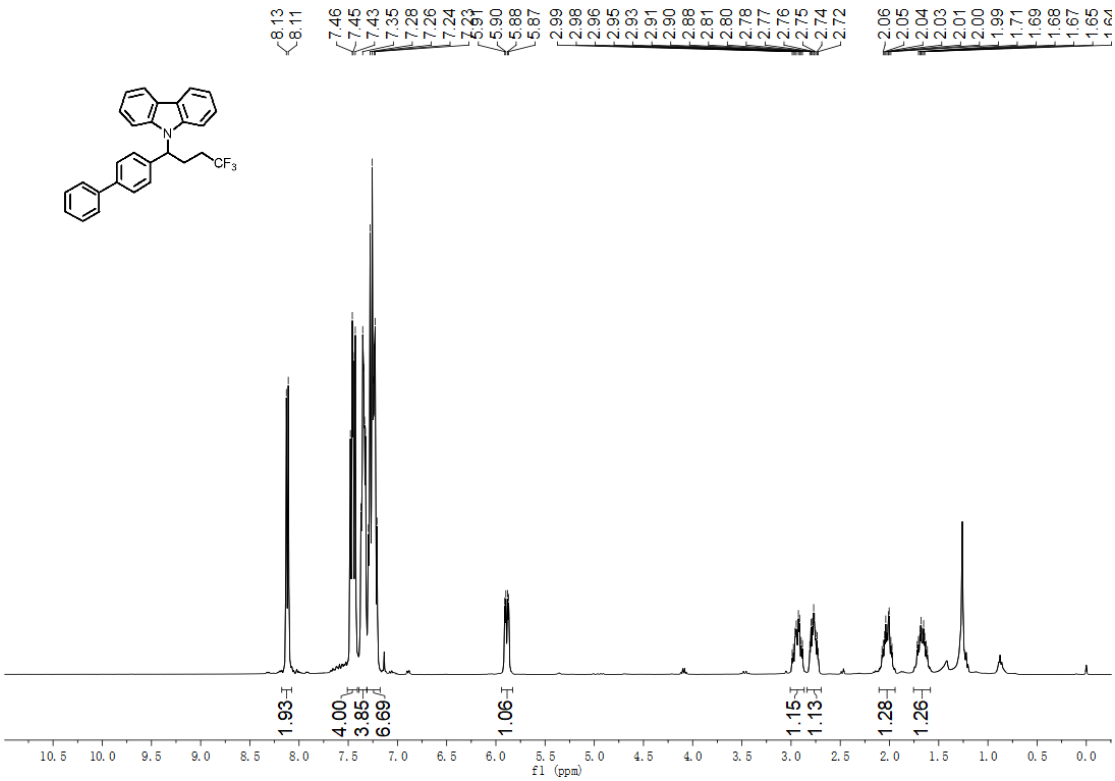
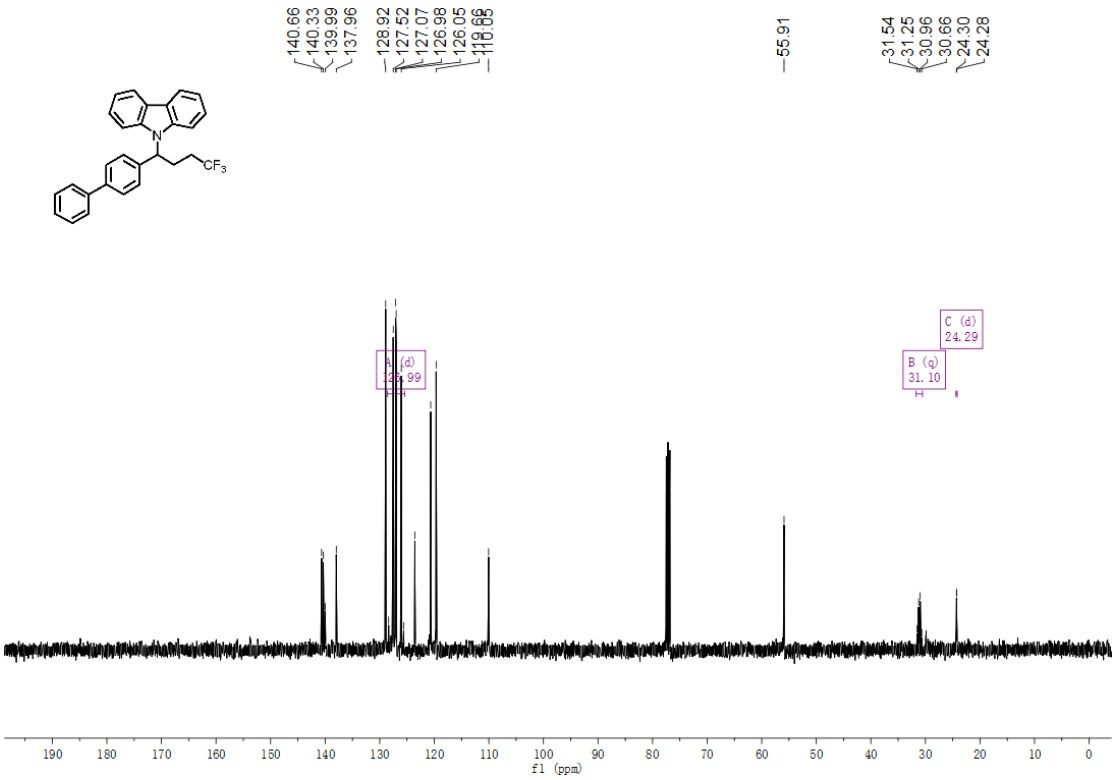


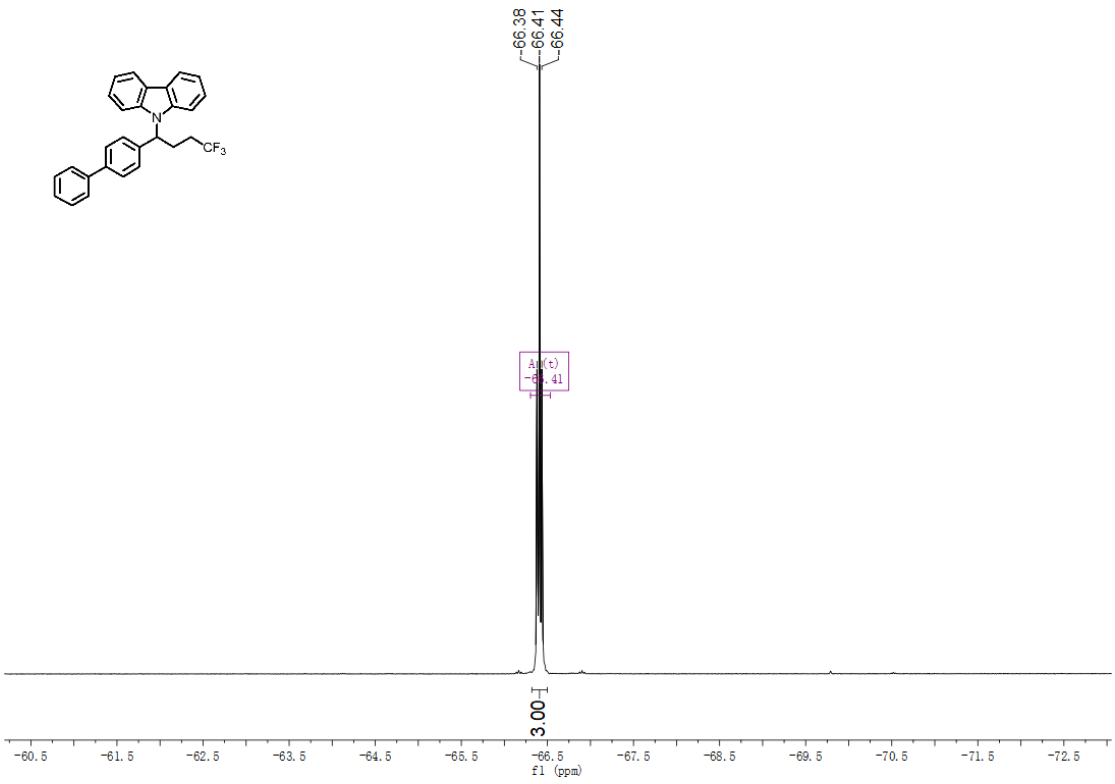
d8 ^{1}H NMR



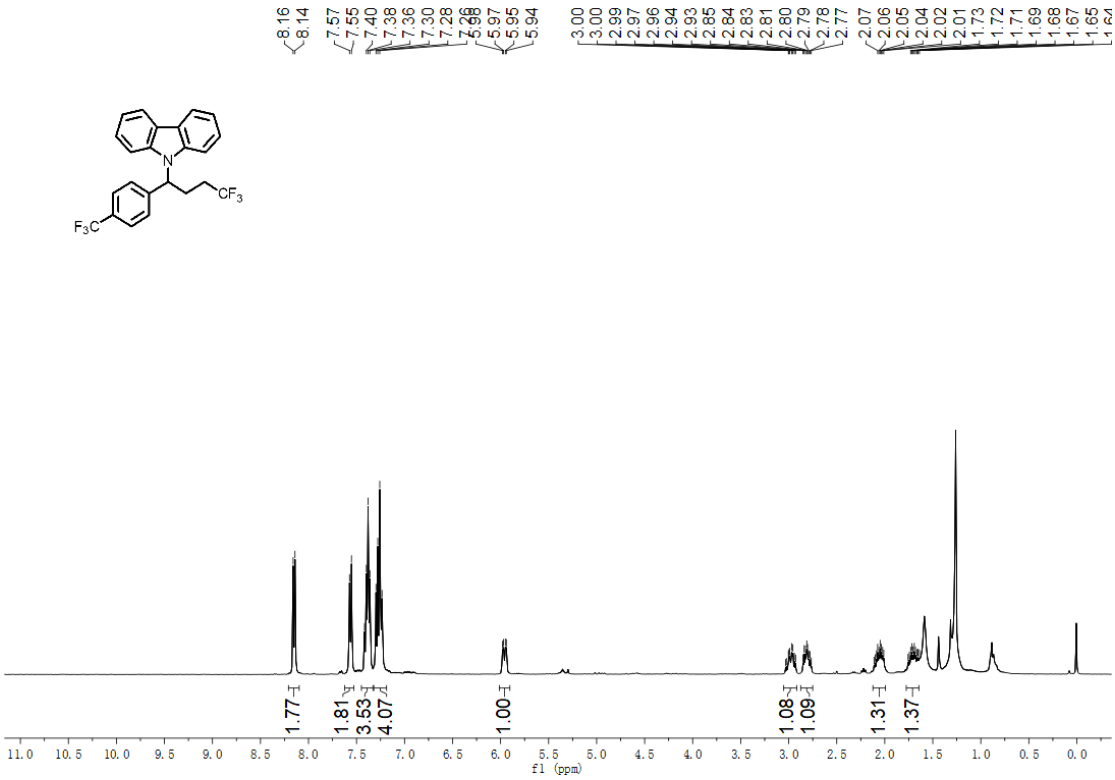
d8 ^{13}C NMR



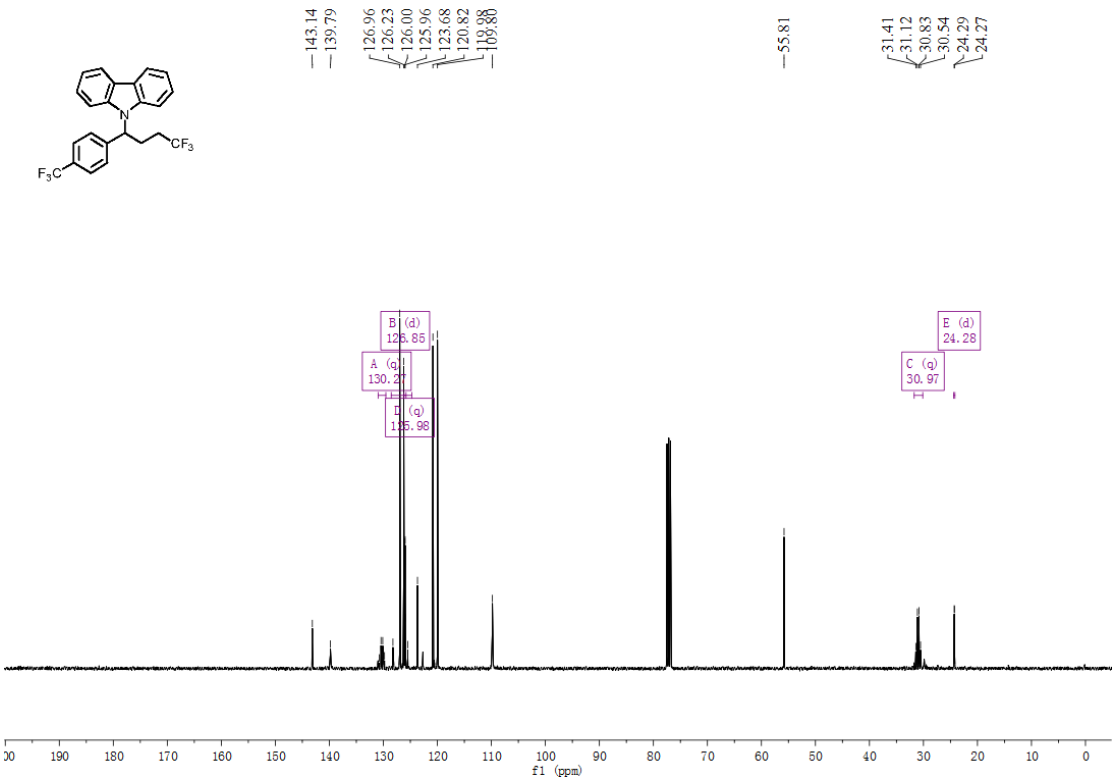
d8 ^{19}F NMR



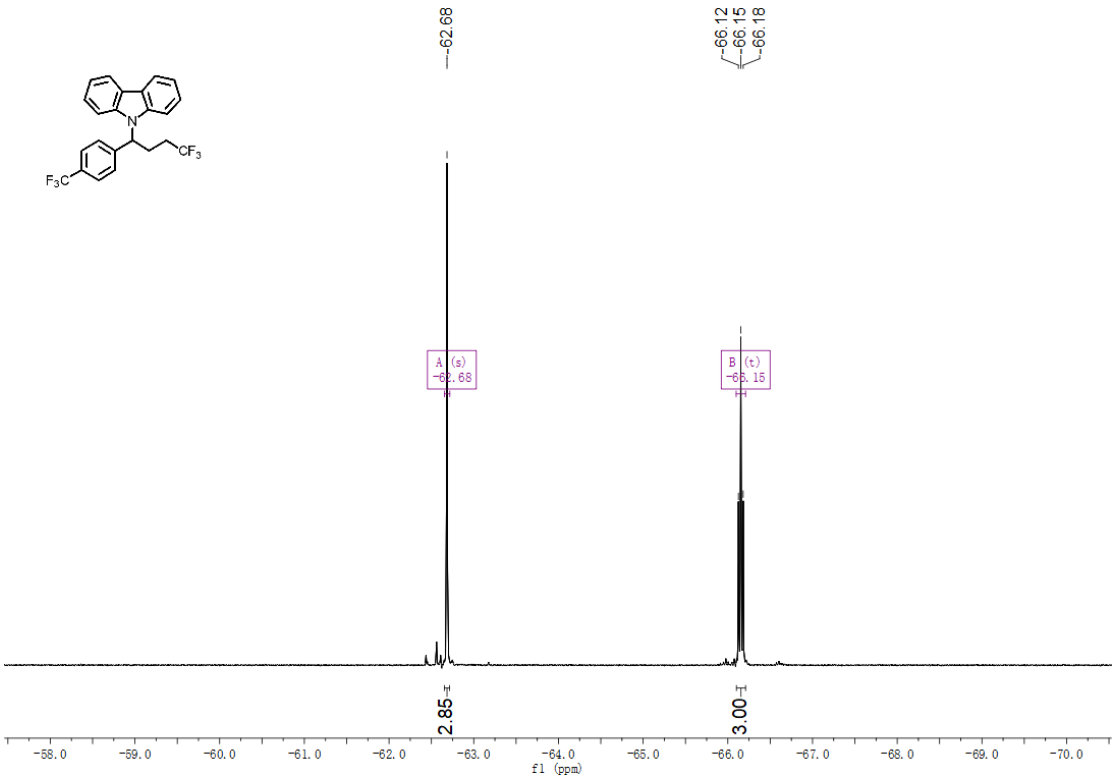
d9 ^{1}H NMR



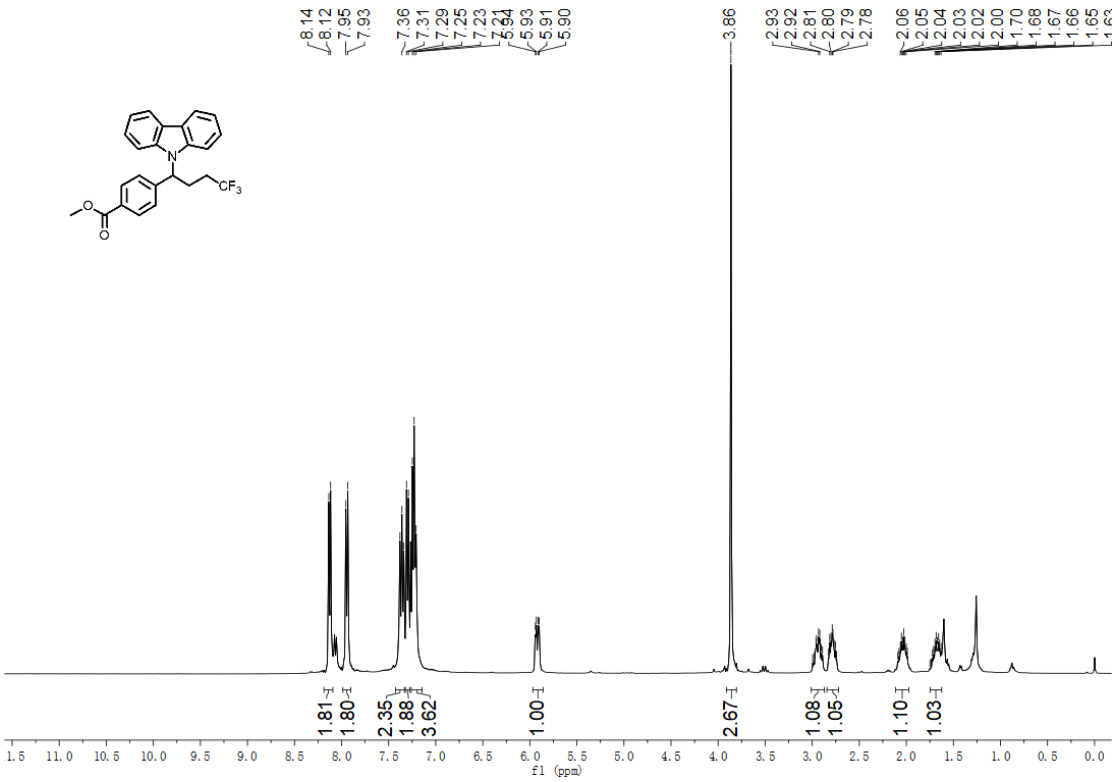
d9 ^{13}C NMR



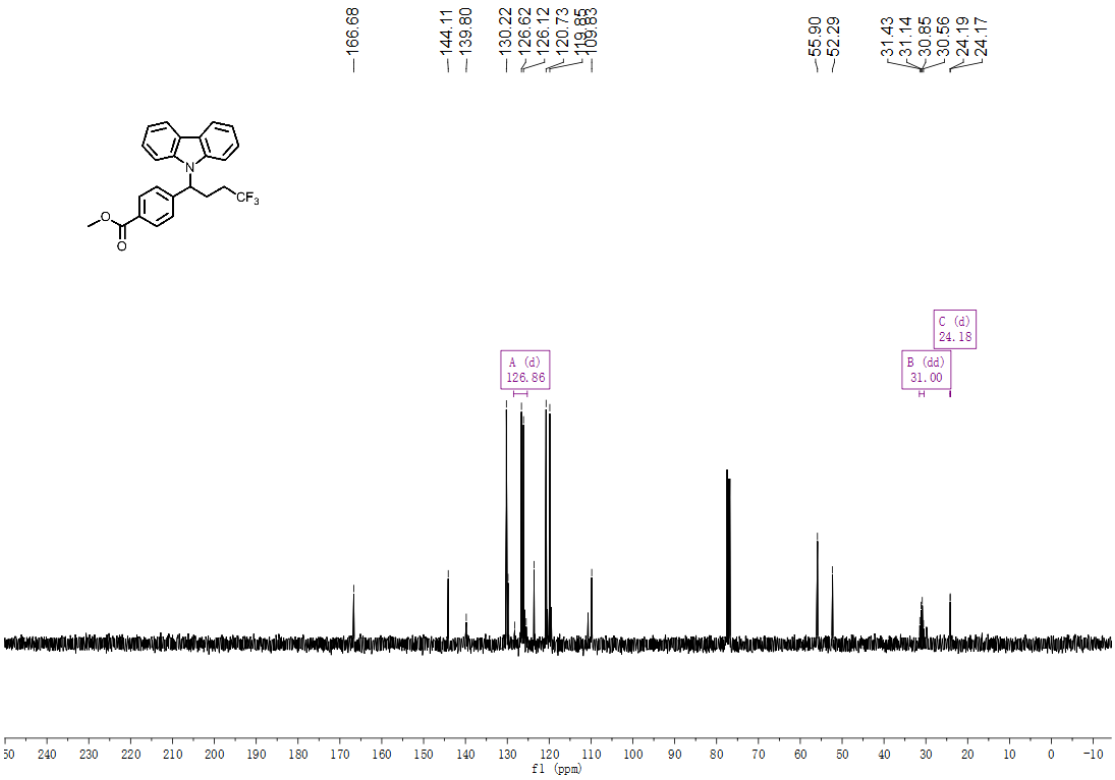
d9 ^{19}F NMR



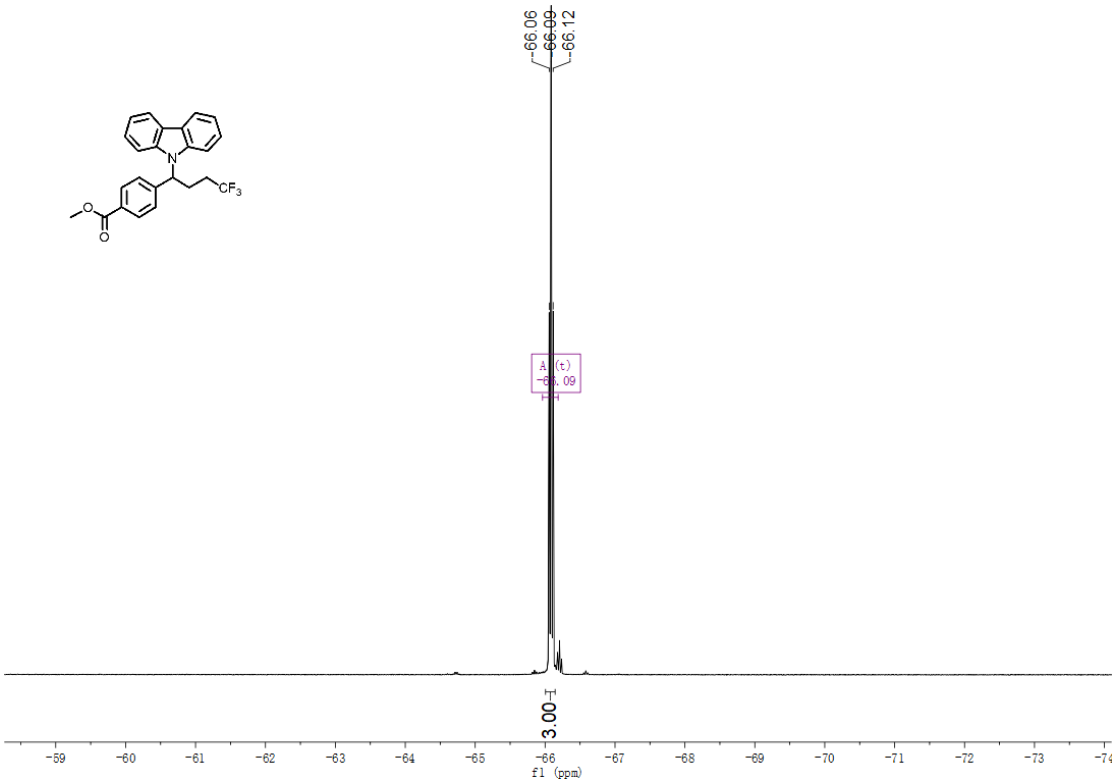
d10 ^{1}H NMR



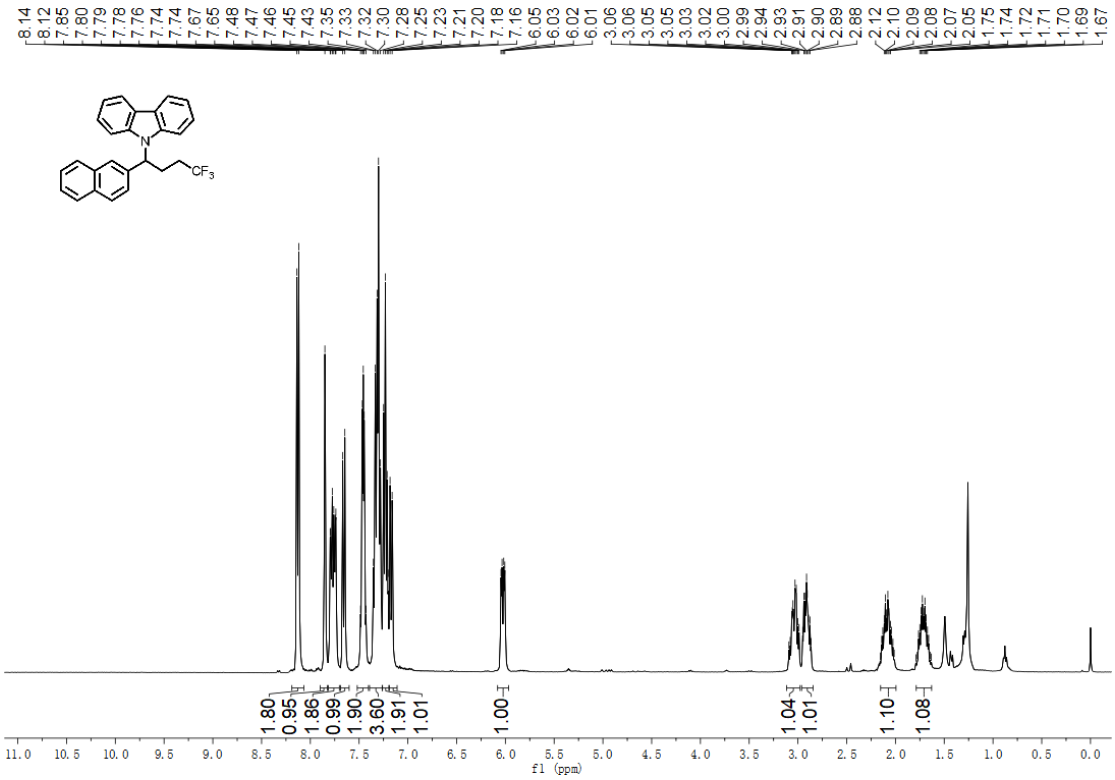
d10 ^{13}C NMR



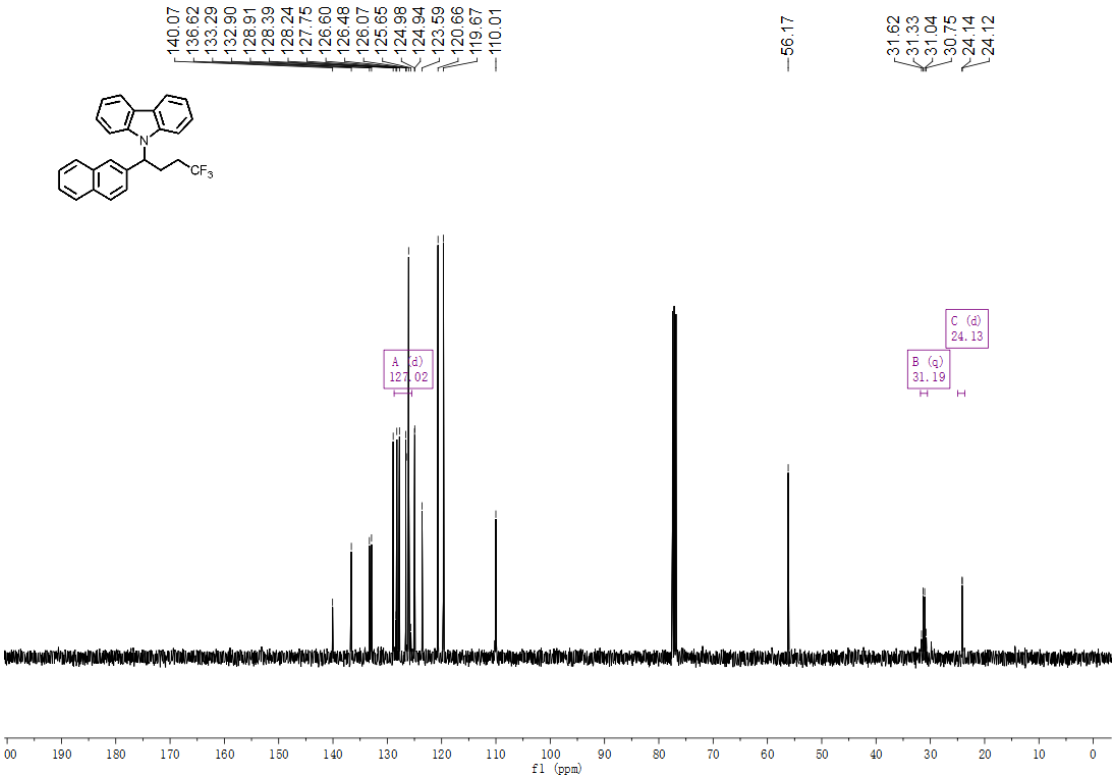
d10 ^{19}F NMR



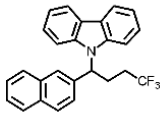
d11 ^{1}H NMR



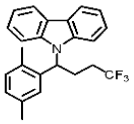
d11 ^{13}C NMR



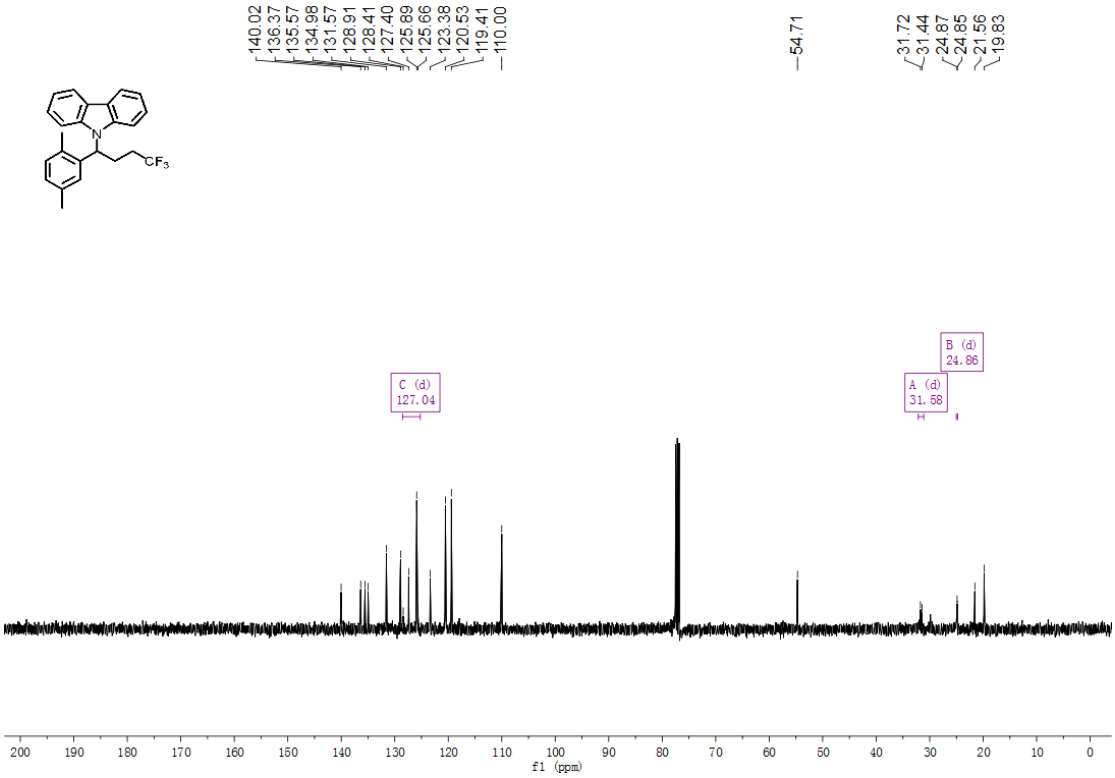
d11 ^{19}F NMR



d12 ^{1}H NMR



d12 ^{13}C NMR



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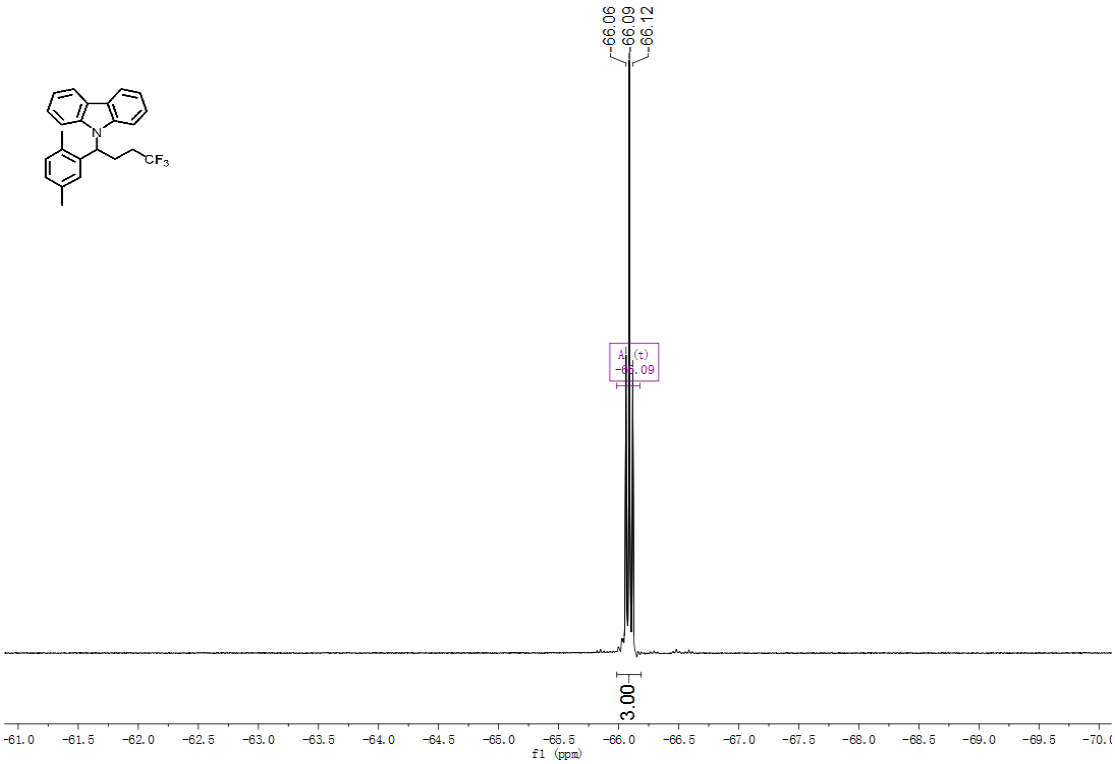
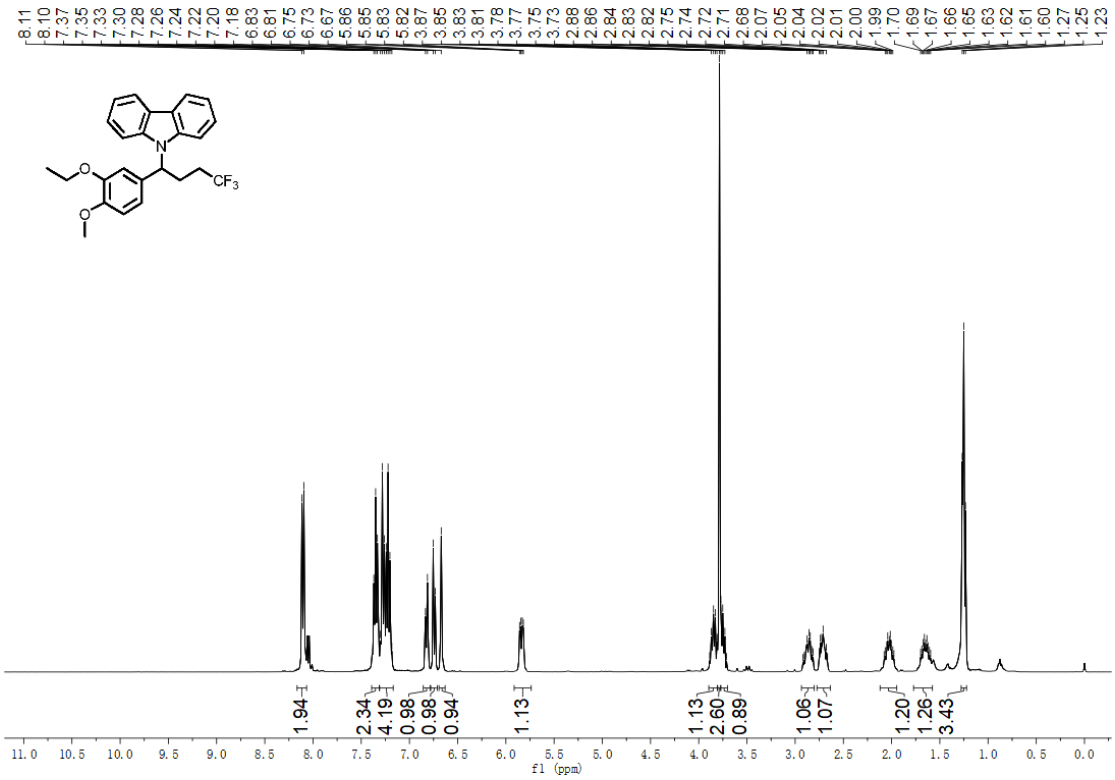
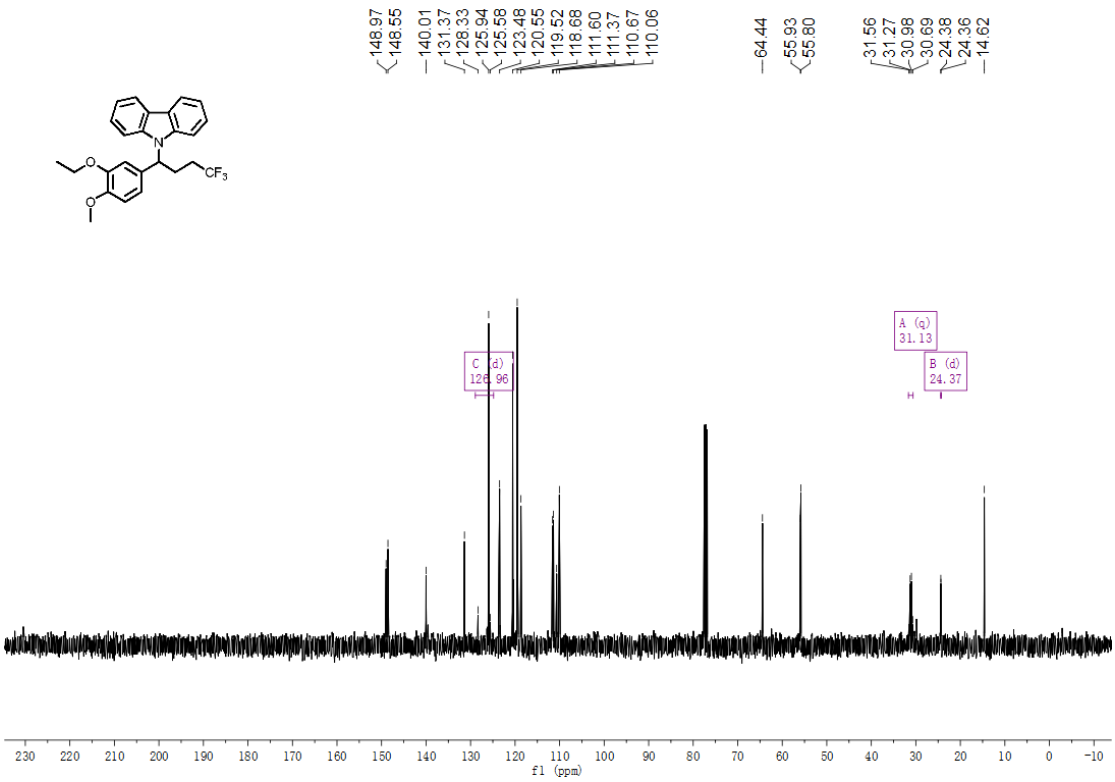


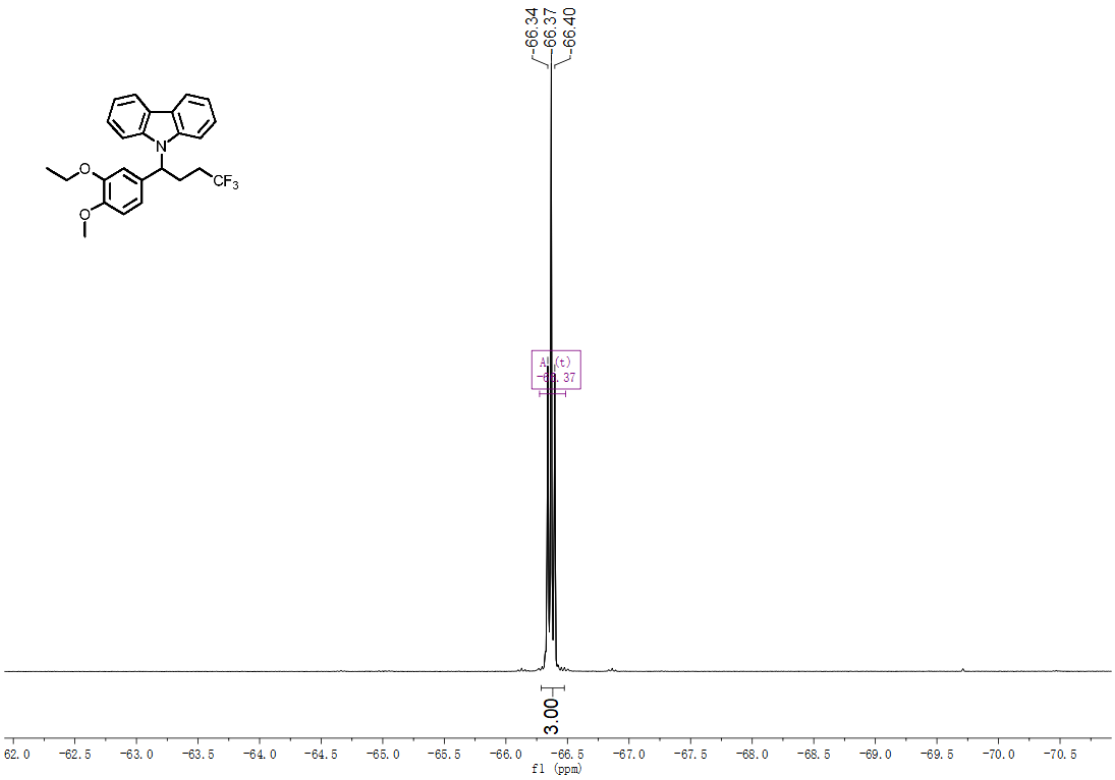
d13 ^{1}H NMR



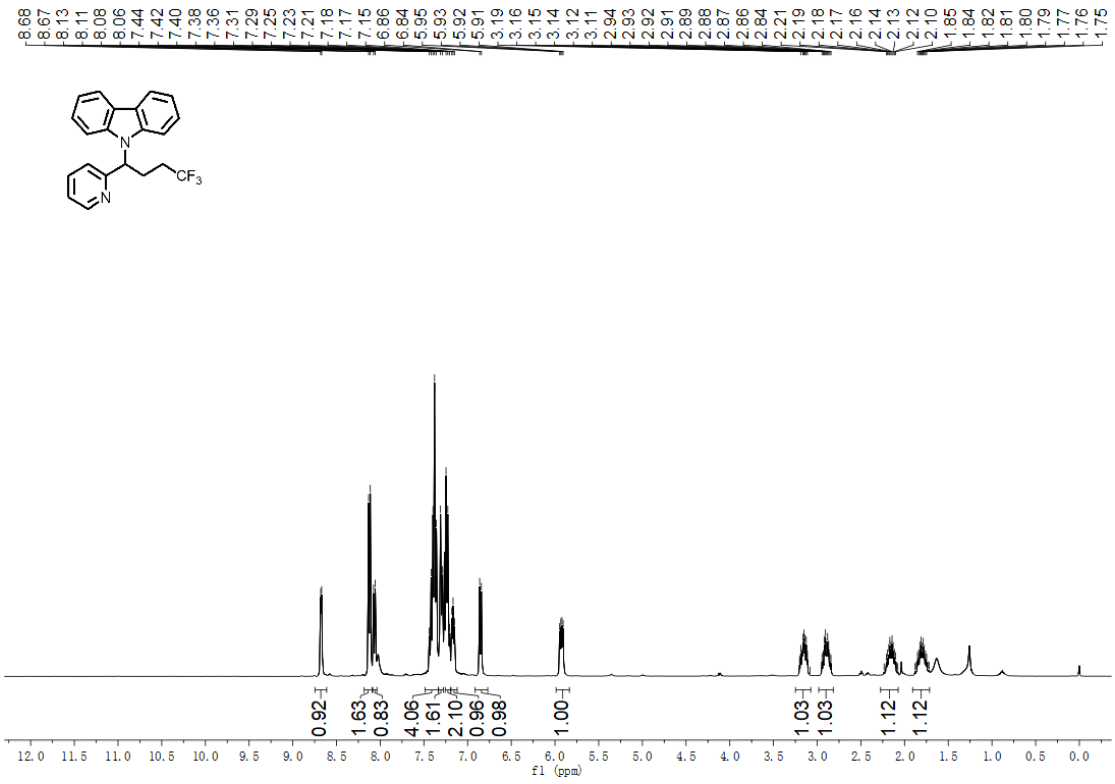
d13 ^{13}C NMR



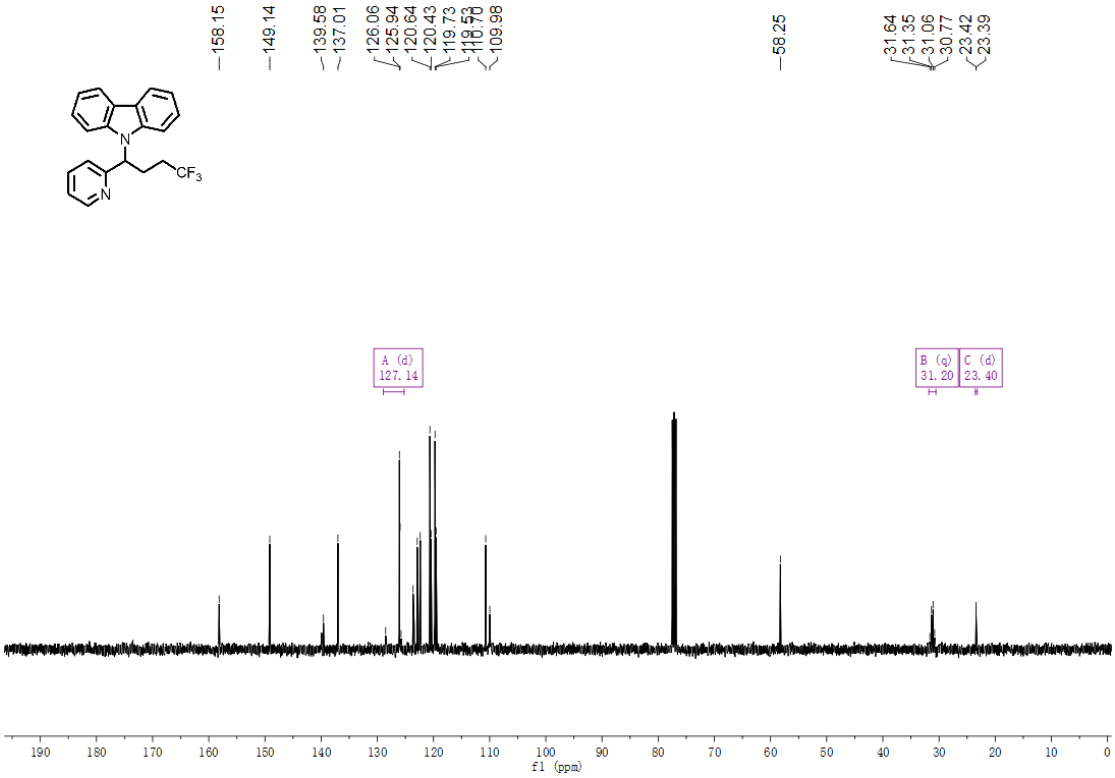
d13 ^{19}F NMR



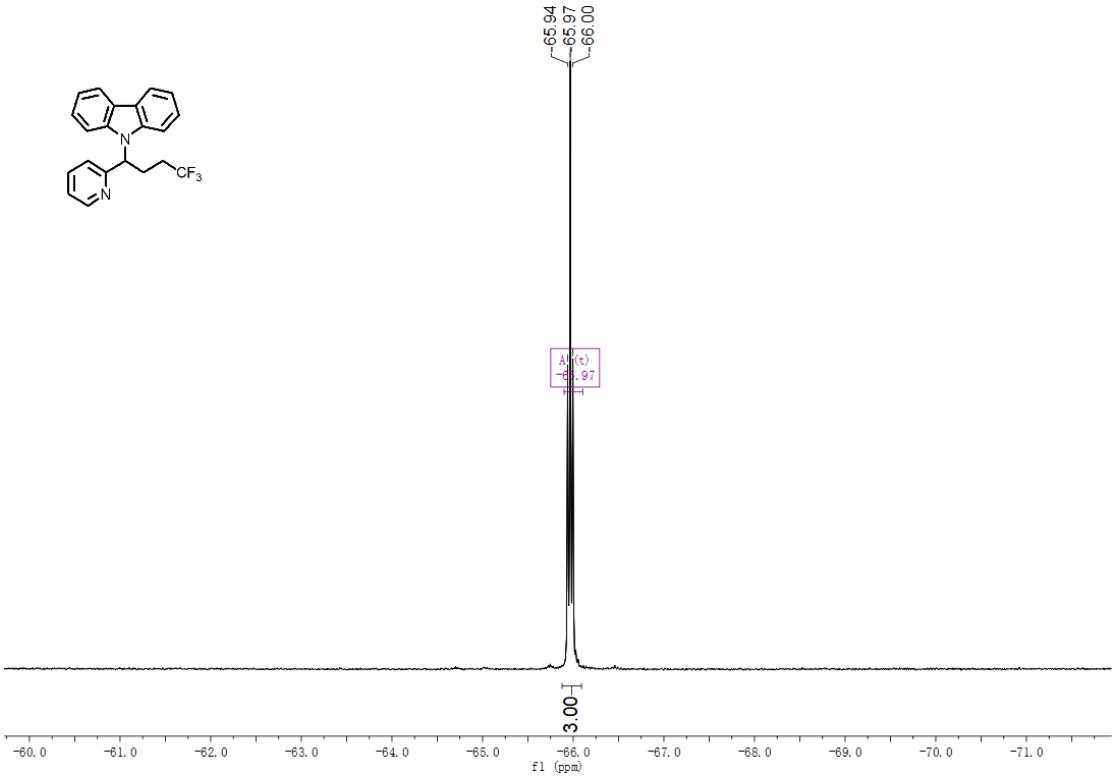
d14 ^{1}H NMR



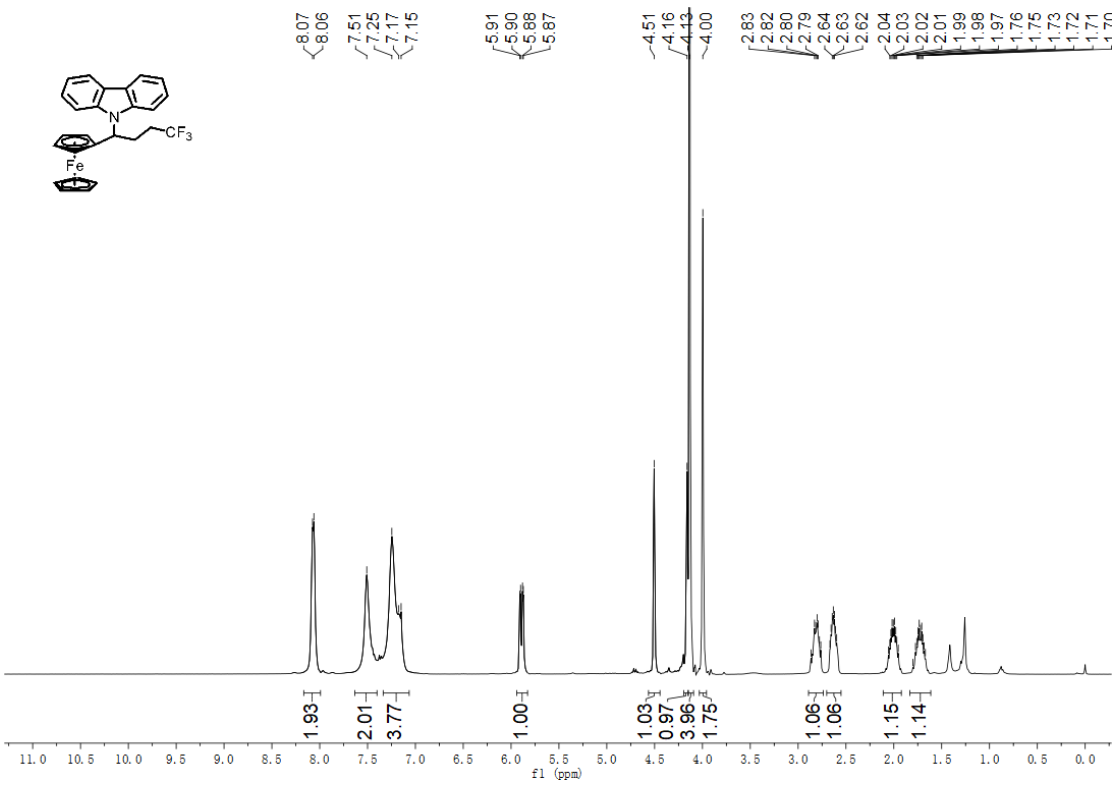
d14 ^{13}C NMR



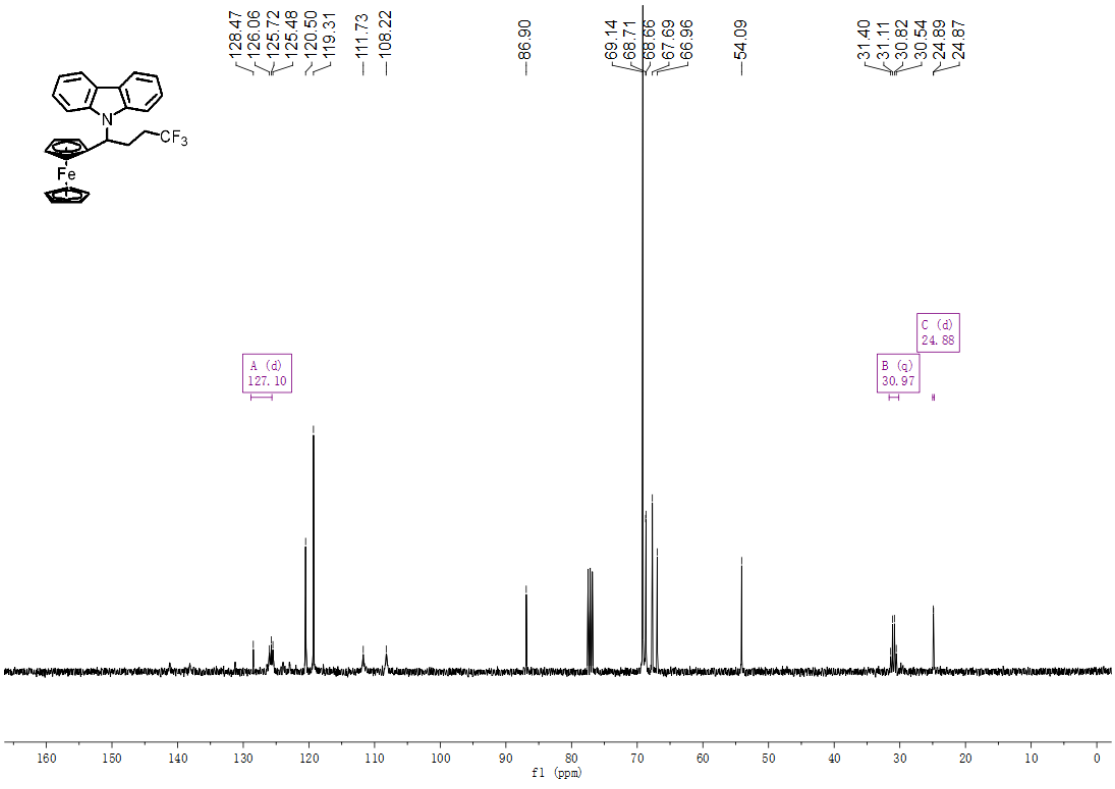
d14 ^{19}F NMR



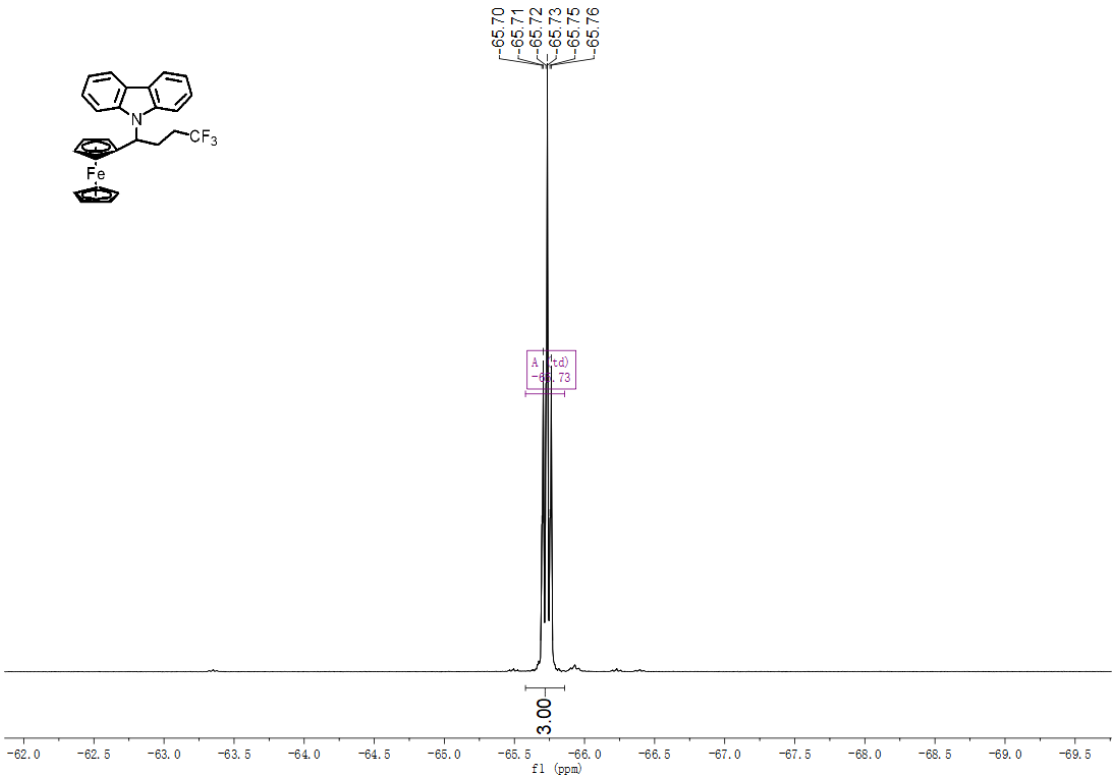
d15 ^{1}H NMR



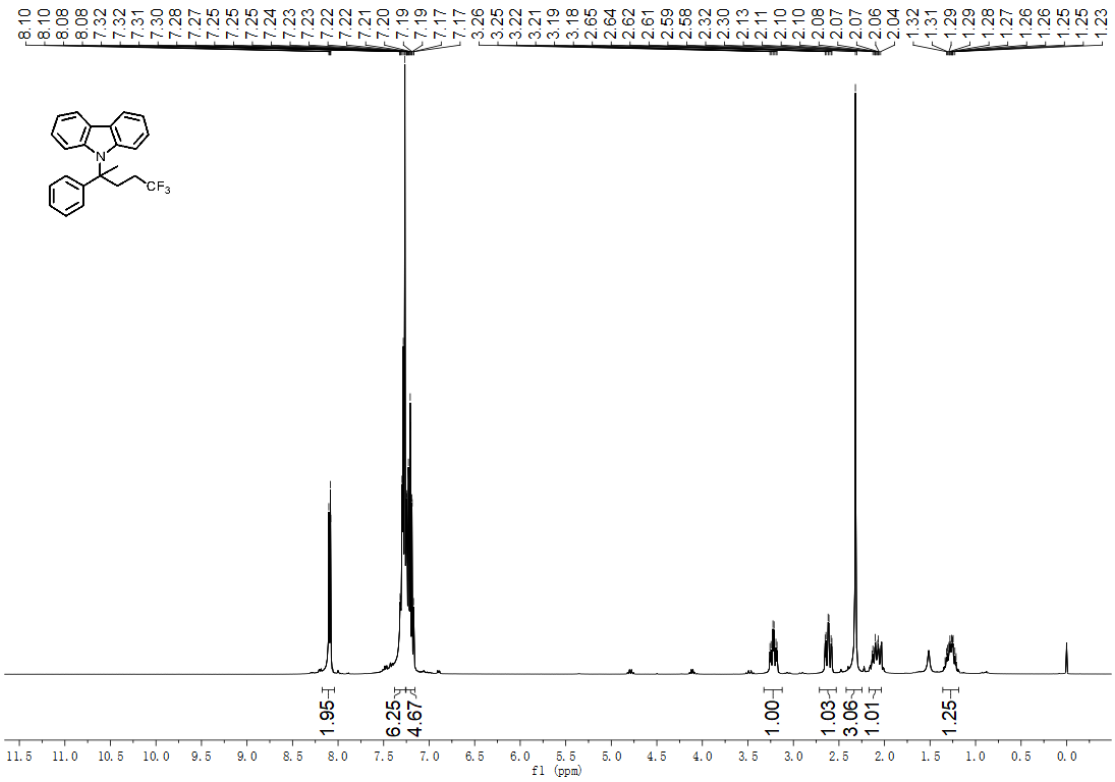
d15 ^{13}C NMR



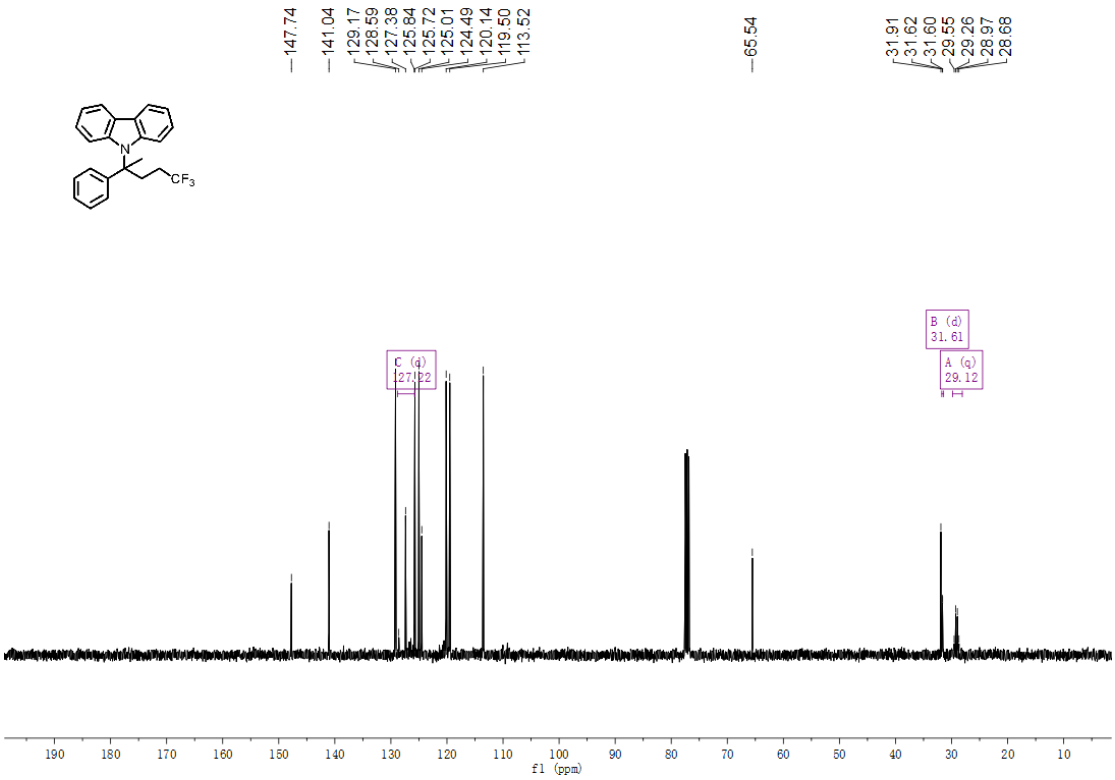
d15 ^{19}F NMR



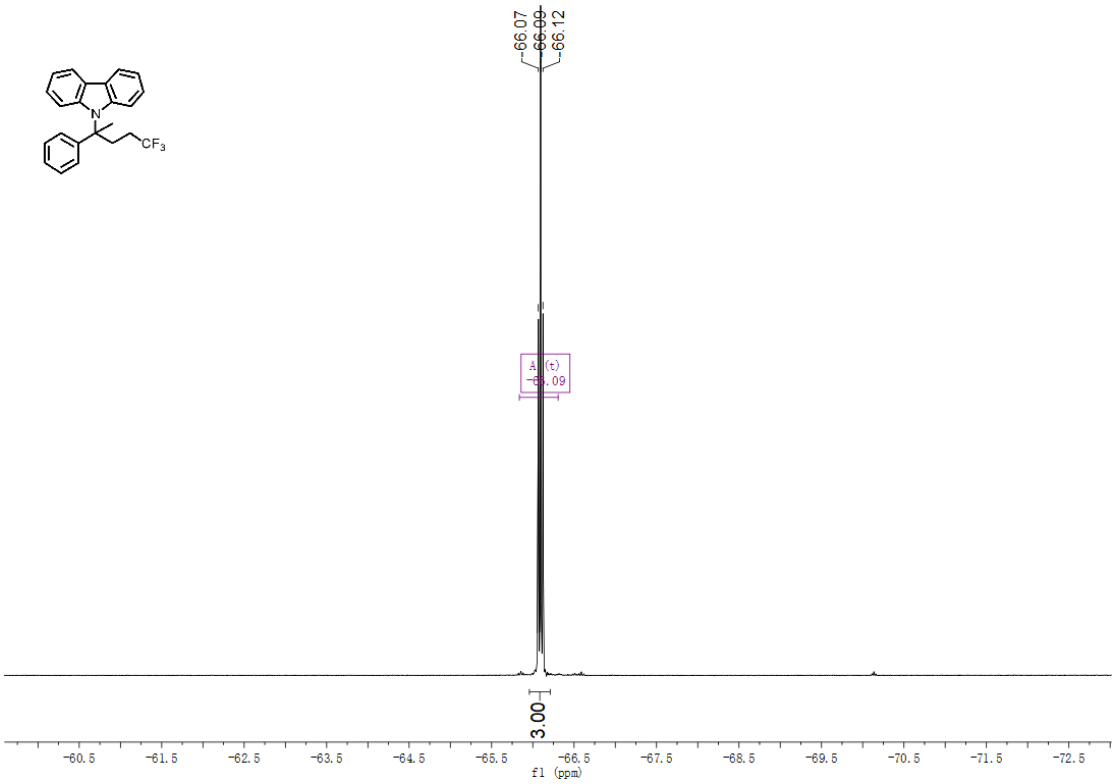
d16 ^{1}H NMR



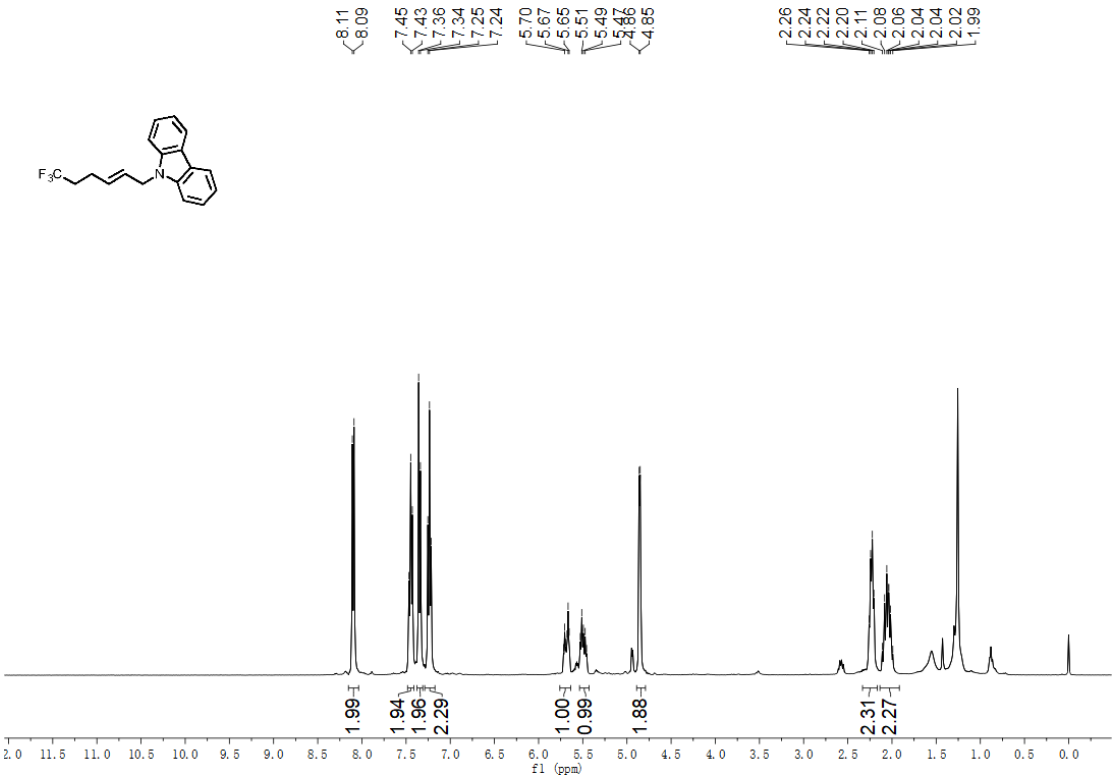
d16 ^{13}C NMR



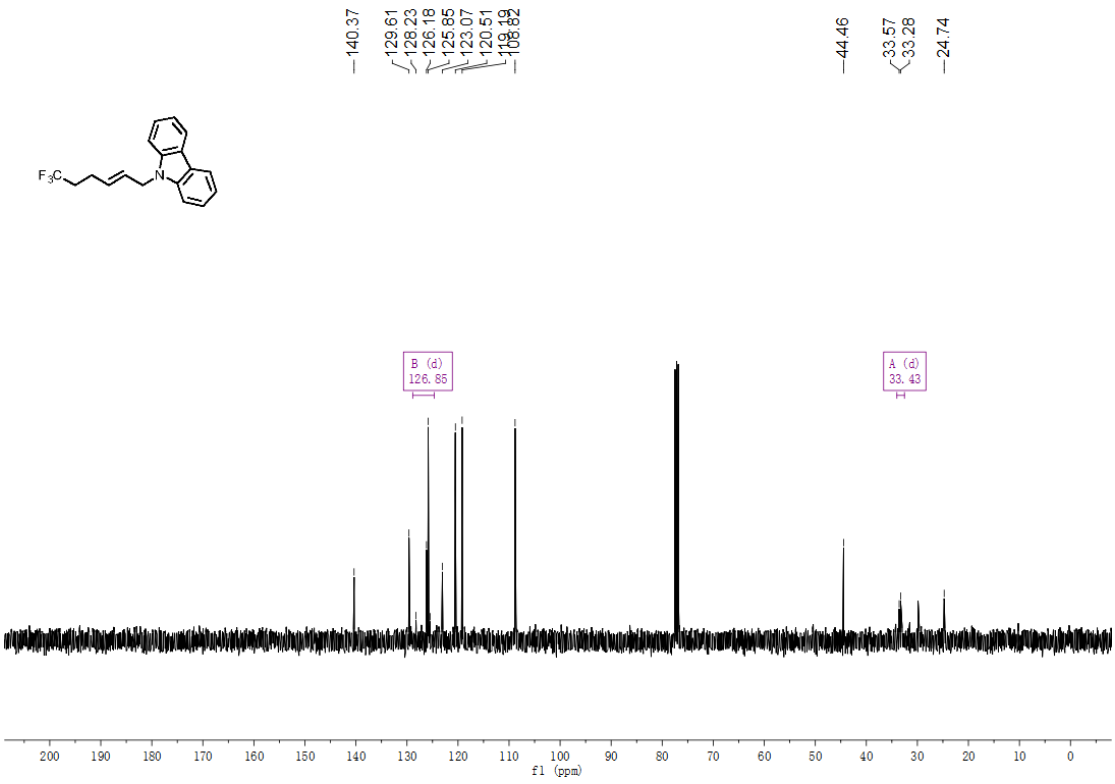
d16 ^{19}F NMR



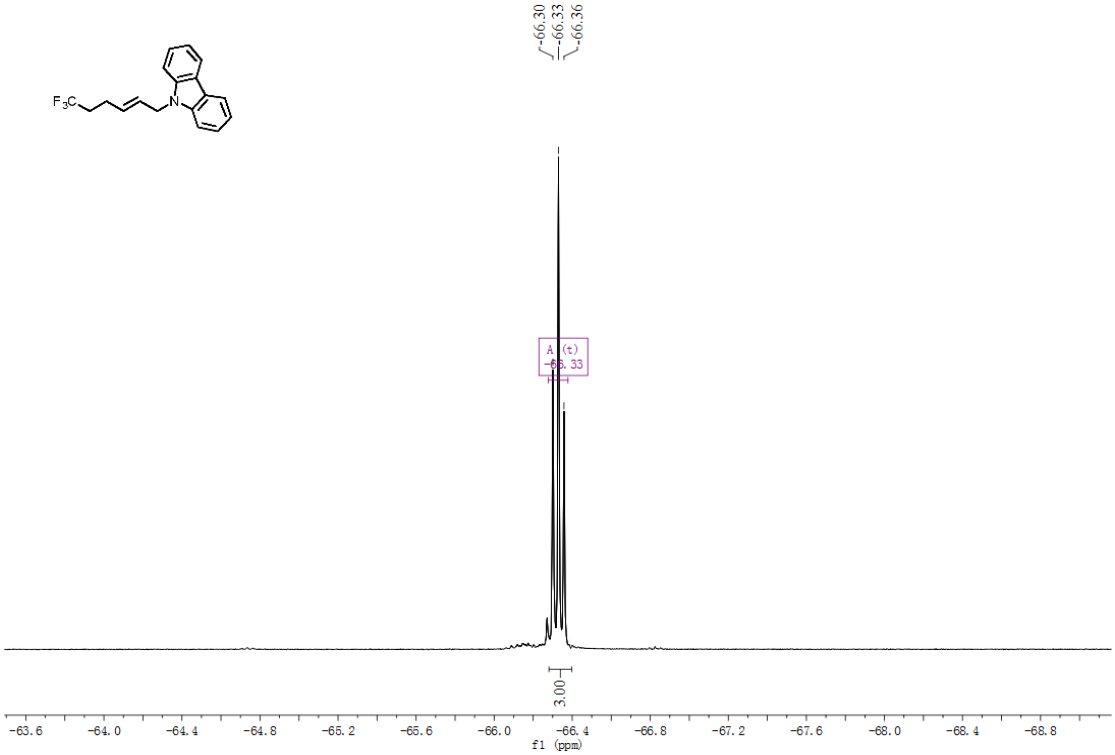
d17 ^{1}H NMR



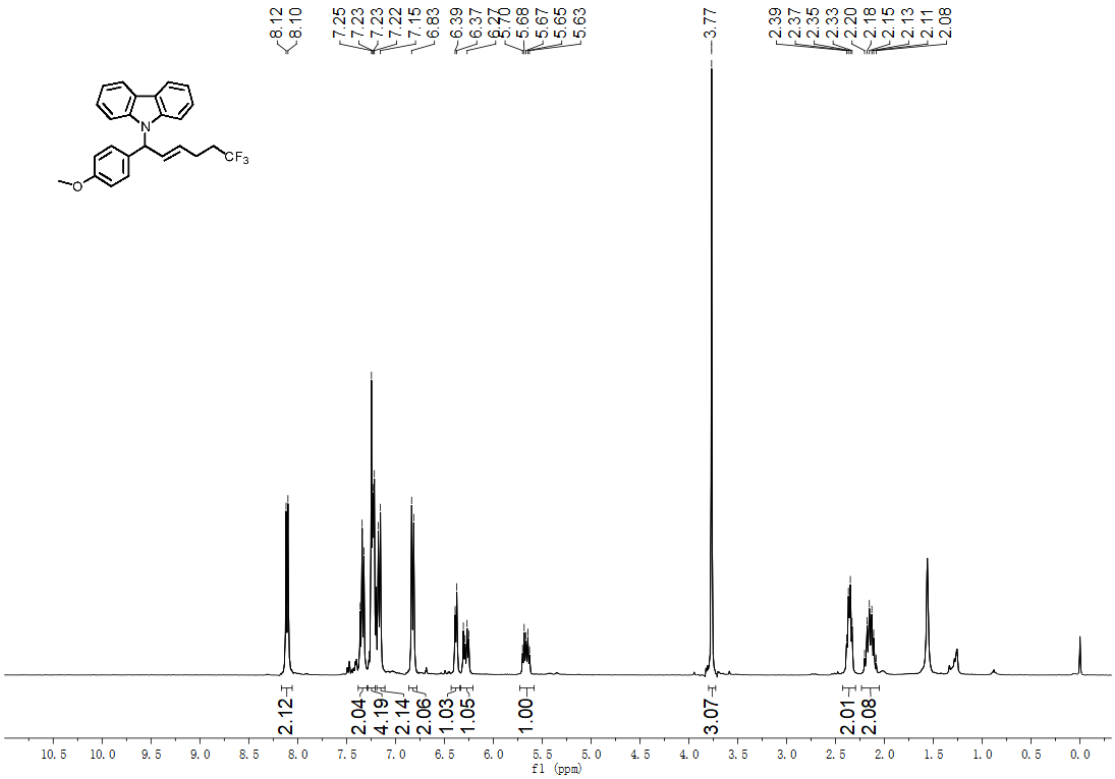
d17 ^{13}C NMR



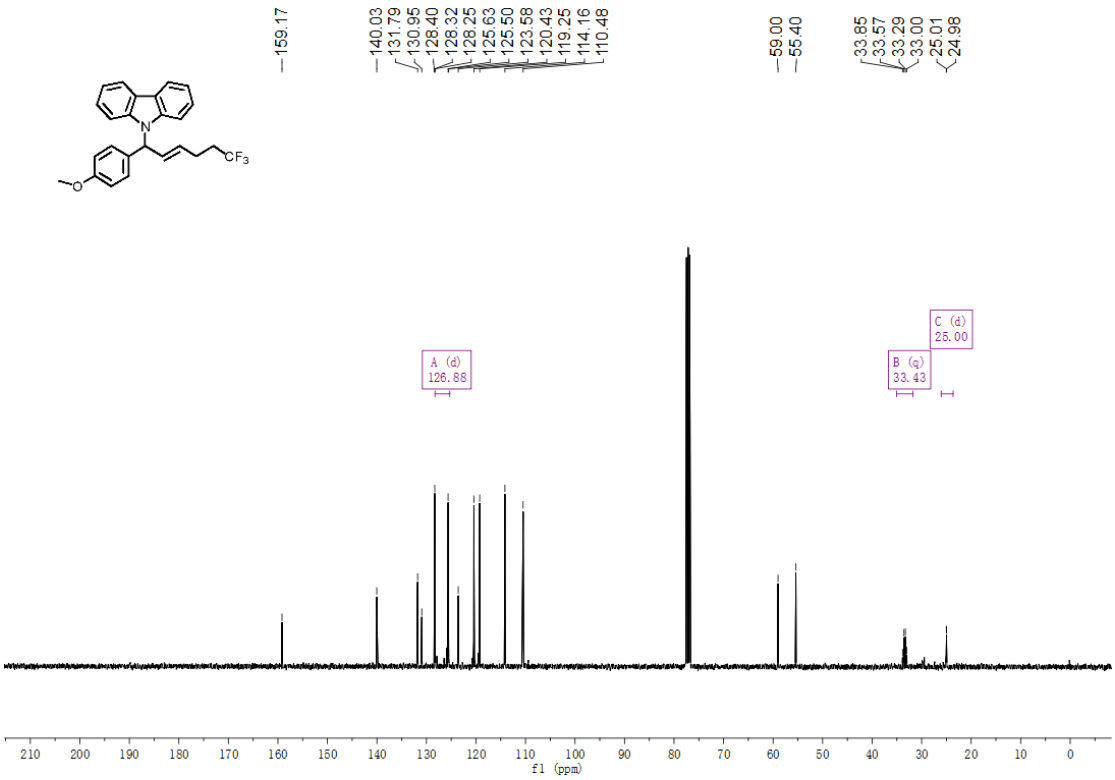
d17 ^{19}F NMR



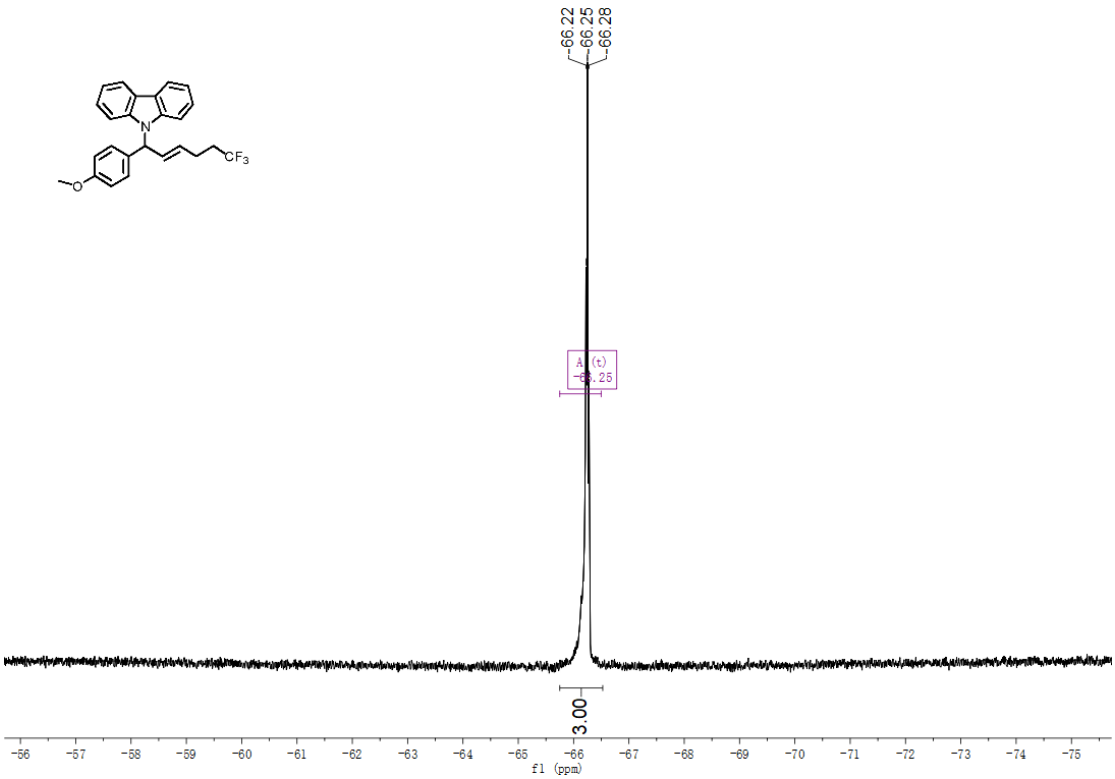
d18 ^{1}H NMR



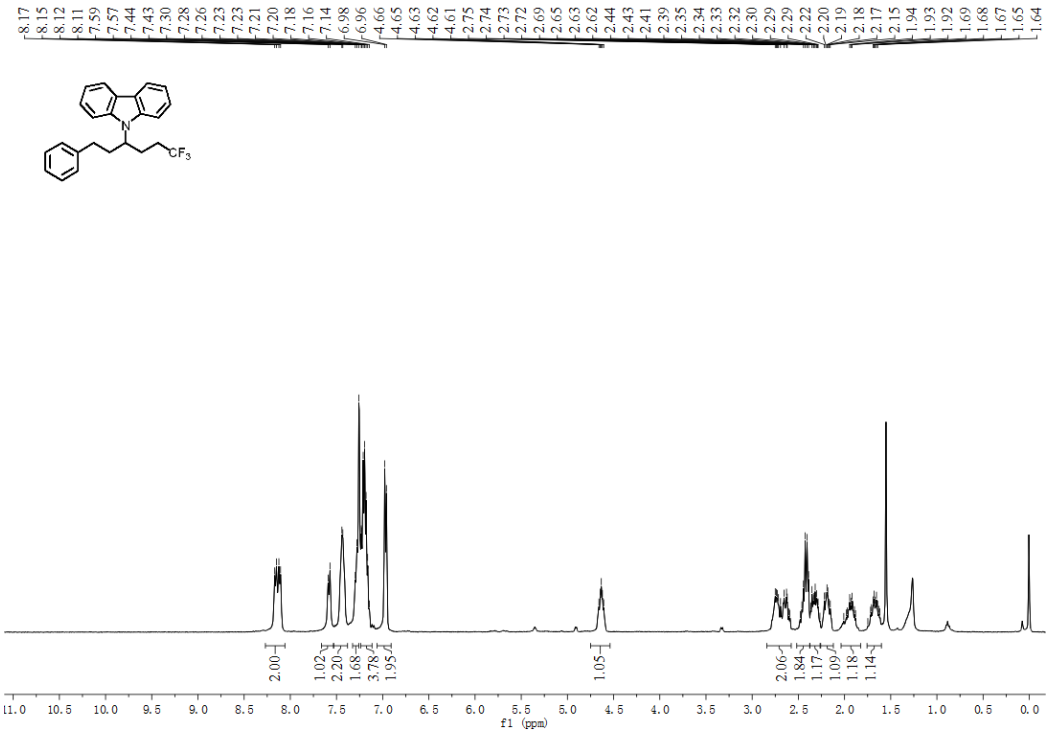
d18 ^{13}C NMR



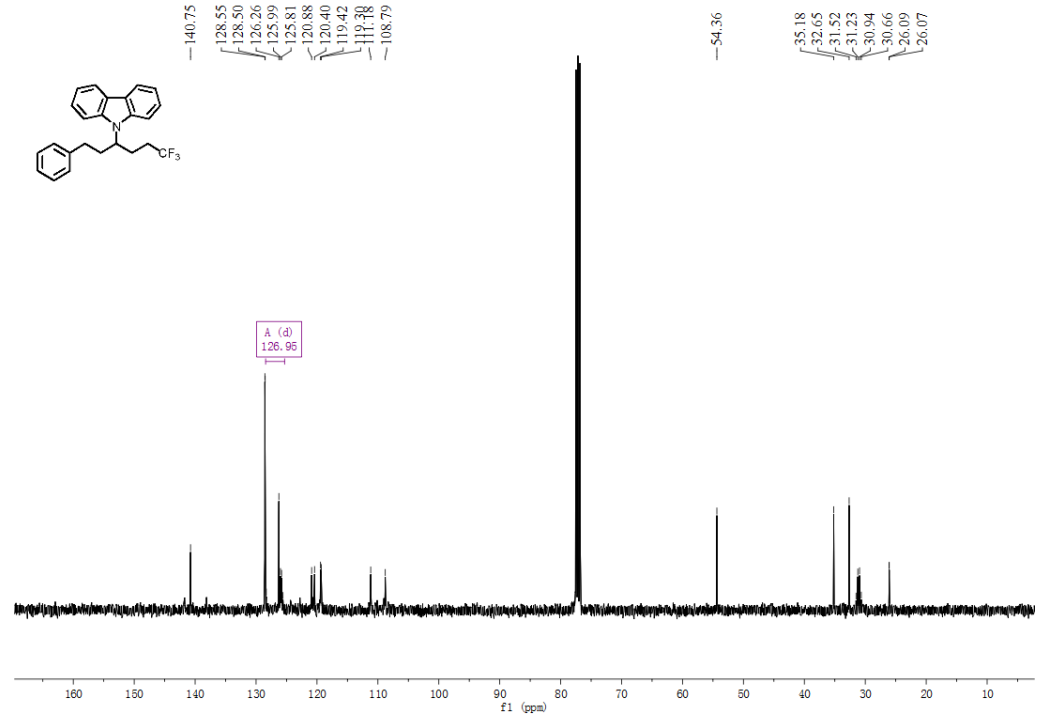
d18 ^{19}F NMR



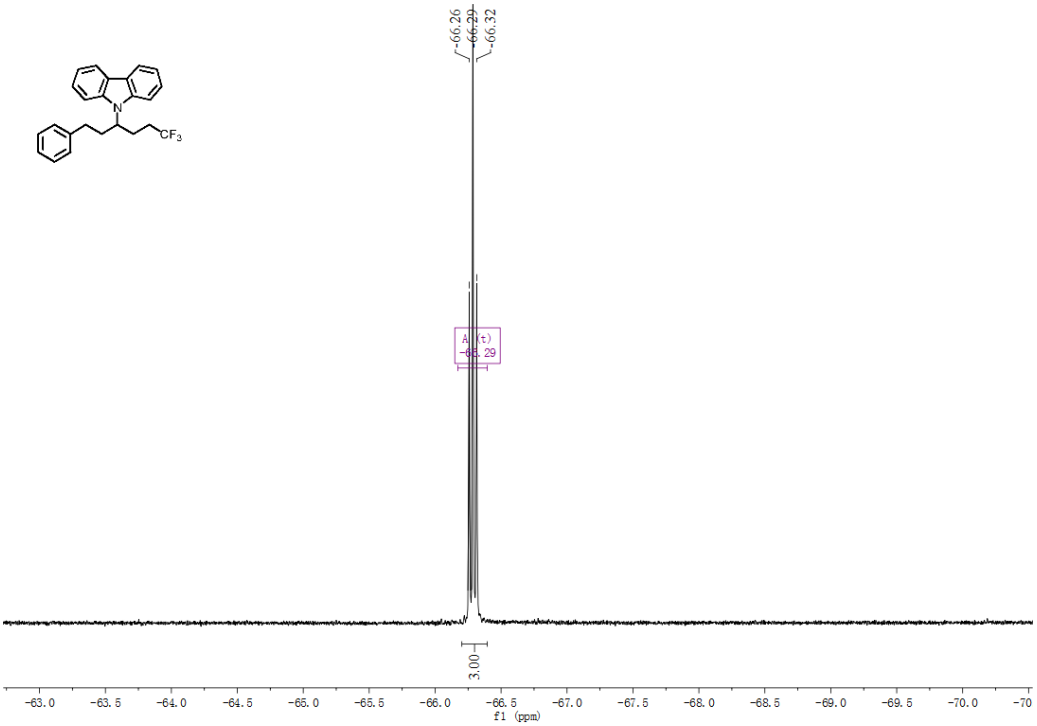
d19 ^{1}H NMR



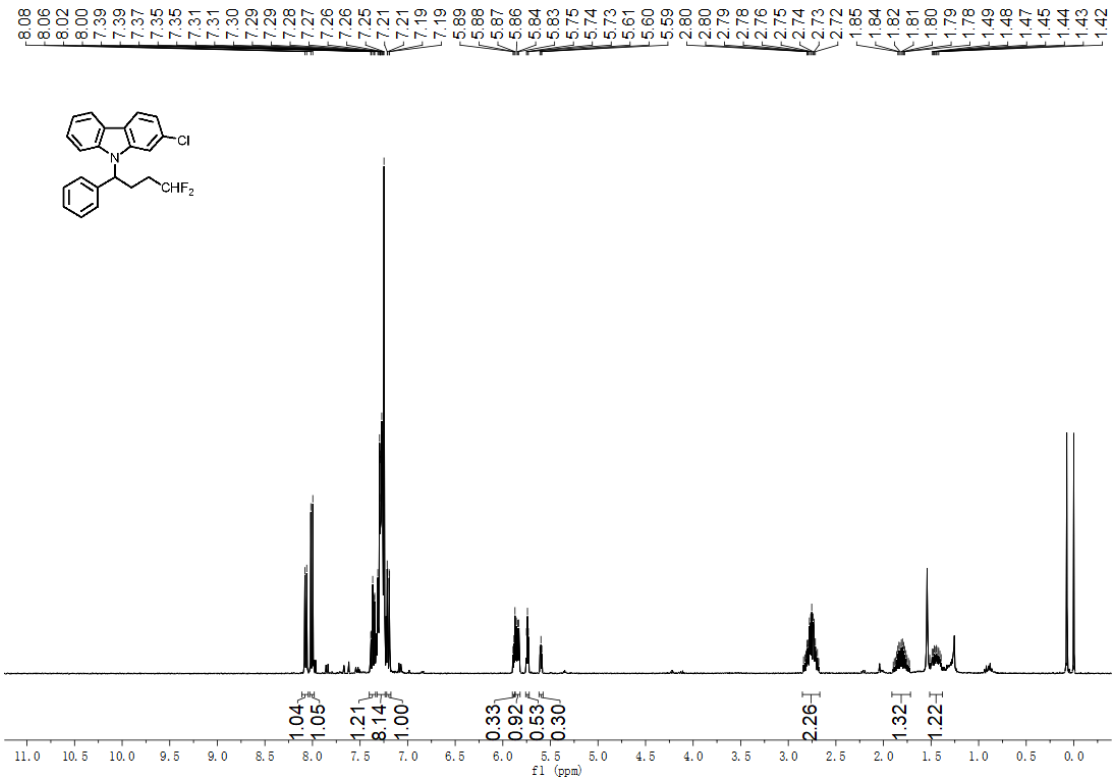
d19 ^{13}C NMR



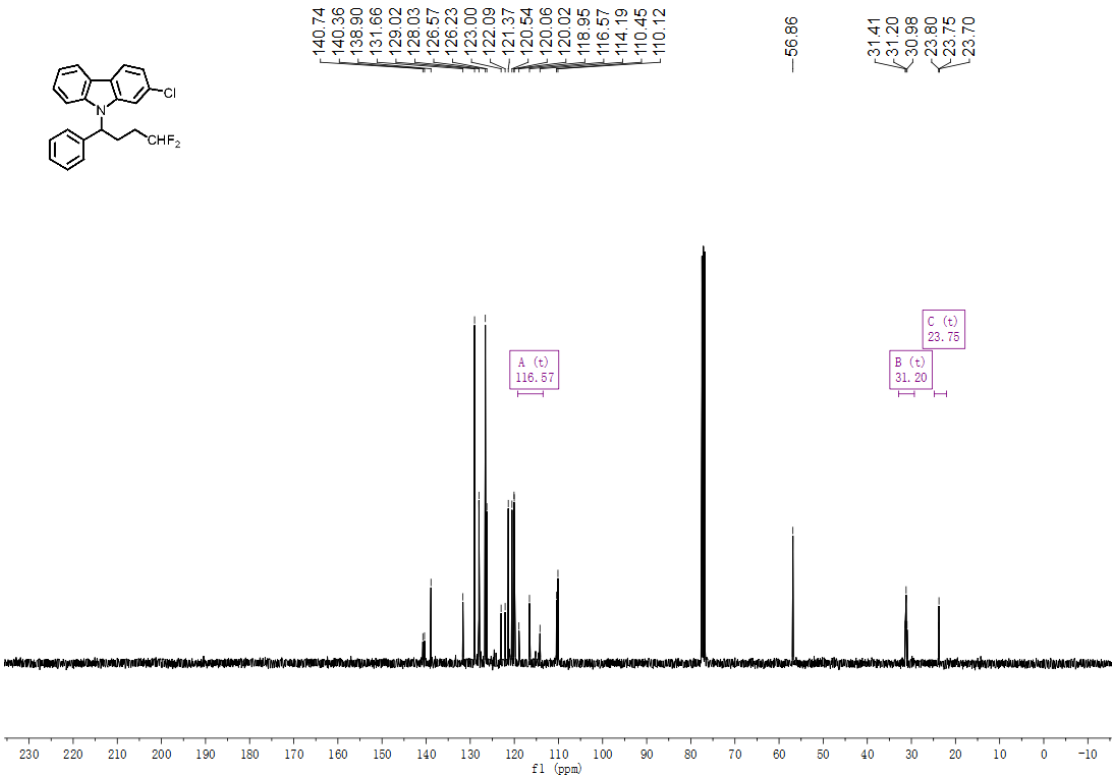
d19 ^{19}F NMR



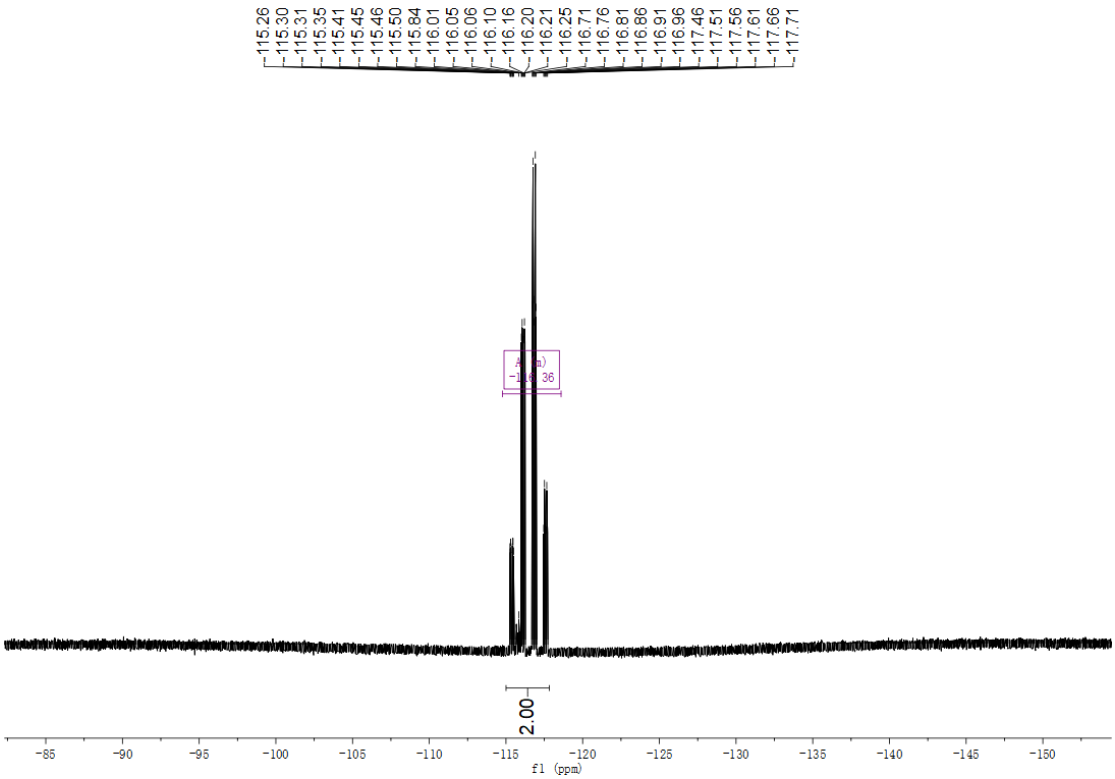
d20 ^{1}H NMR



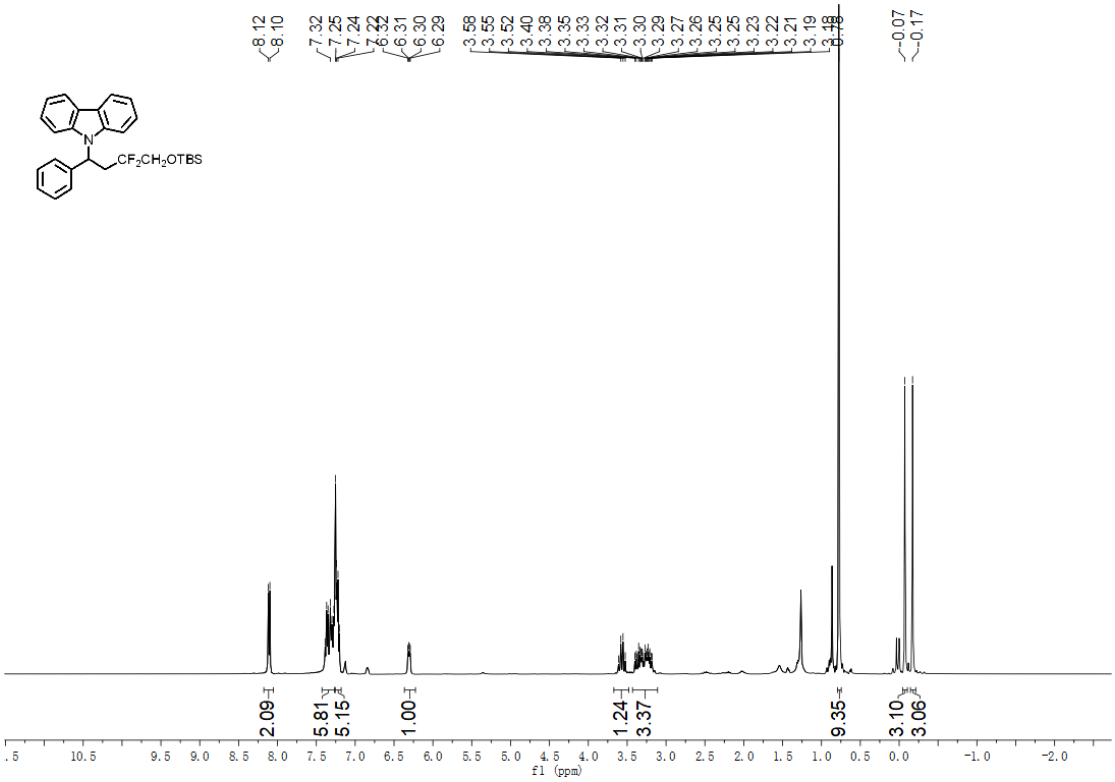
d20 ^{13}C NMR



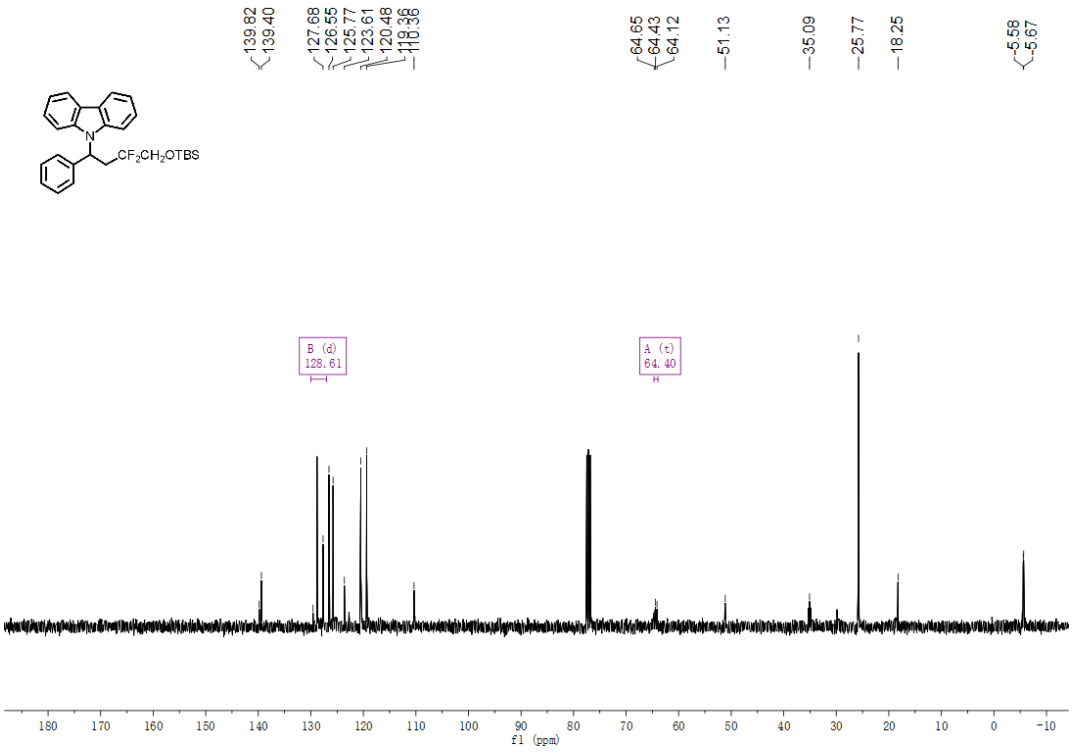
d20 ^{19}F NMR



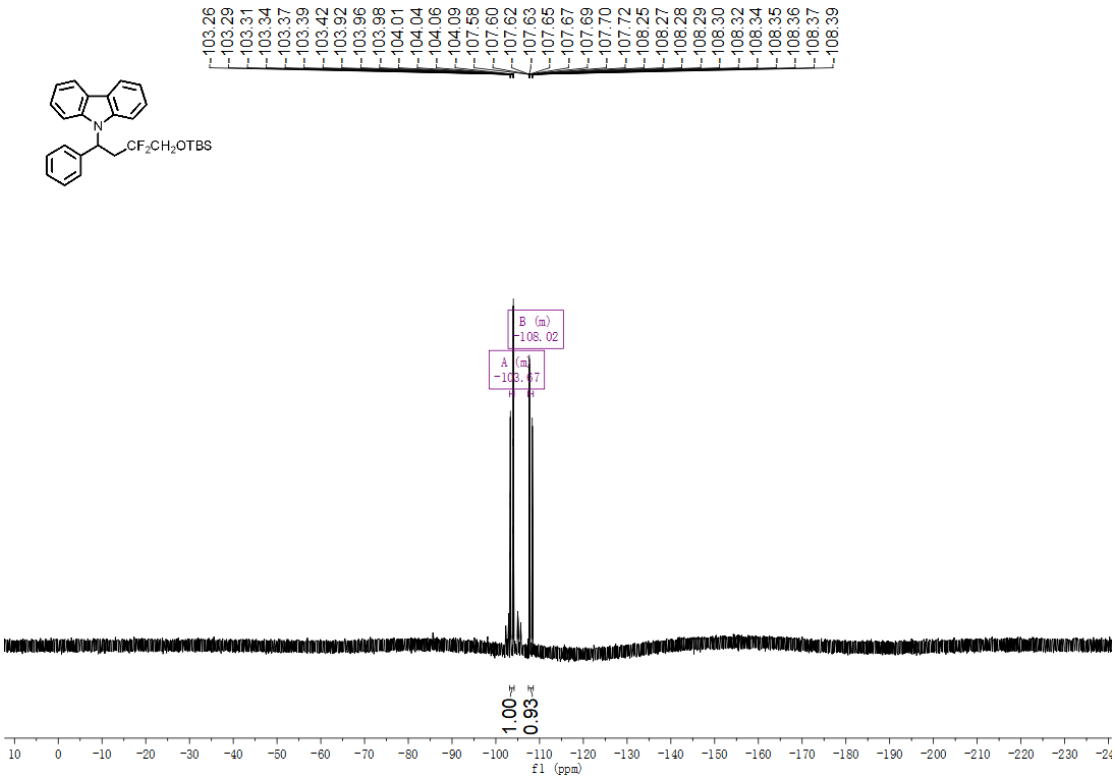
d21 ^{1}H NMR



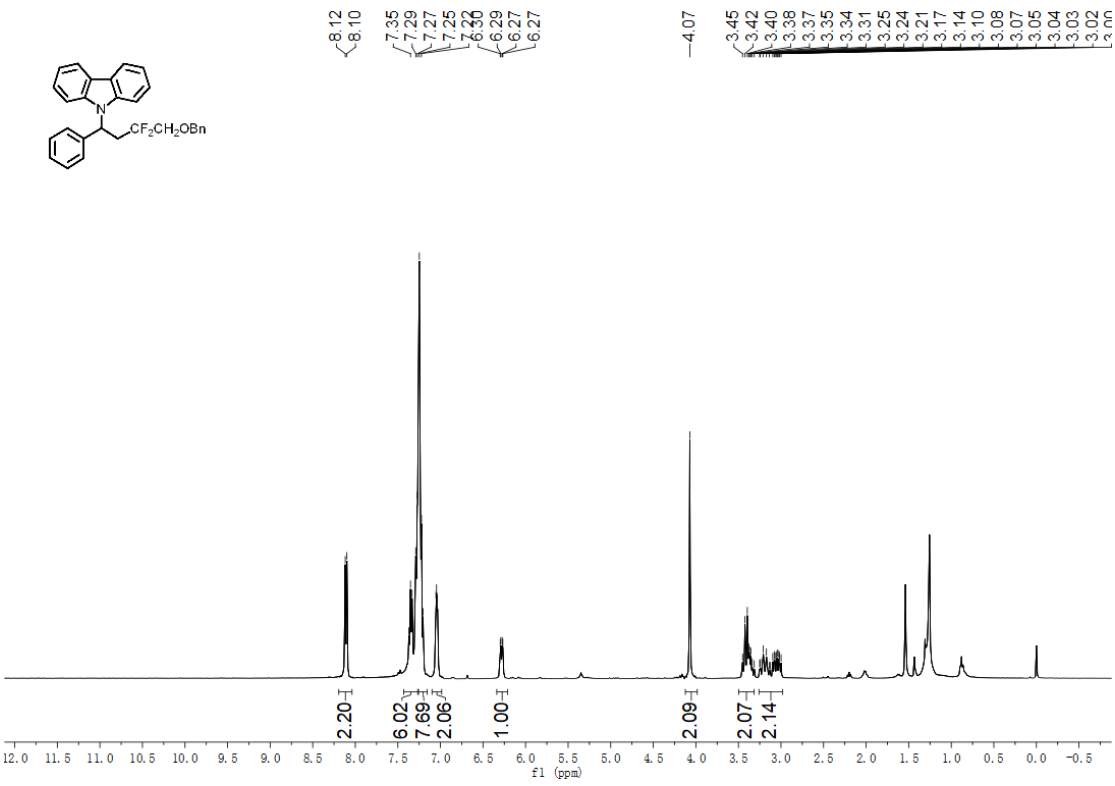
d21 ^{13}C NMR



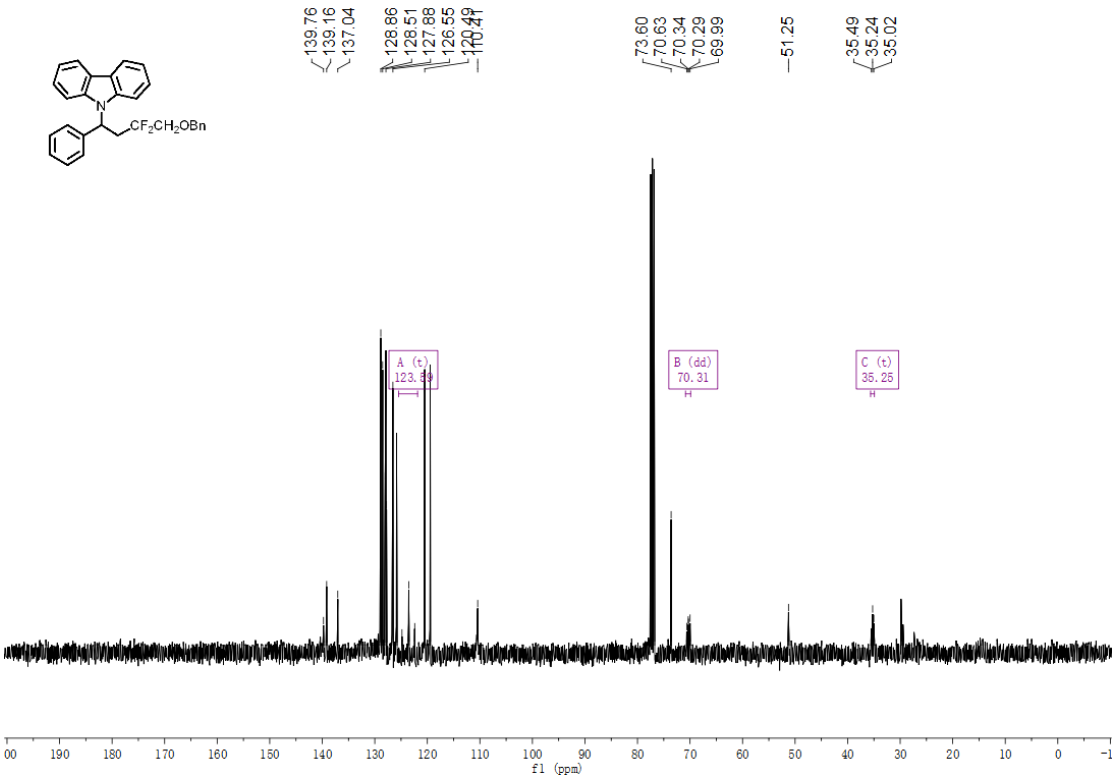
d21 ^{19}F NMR



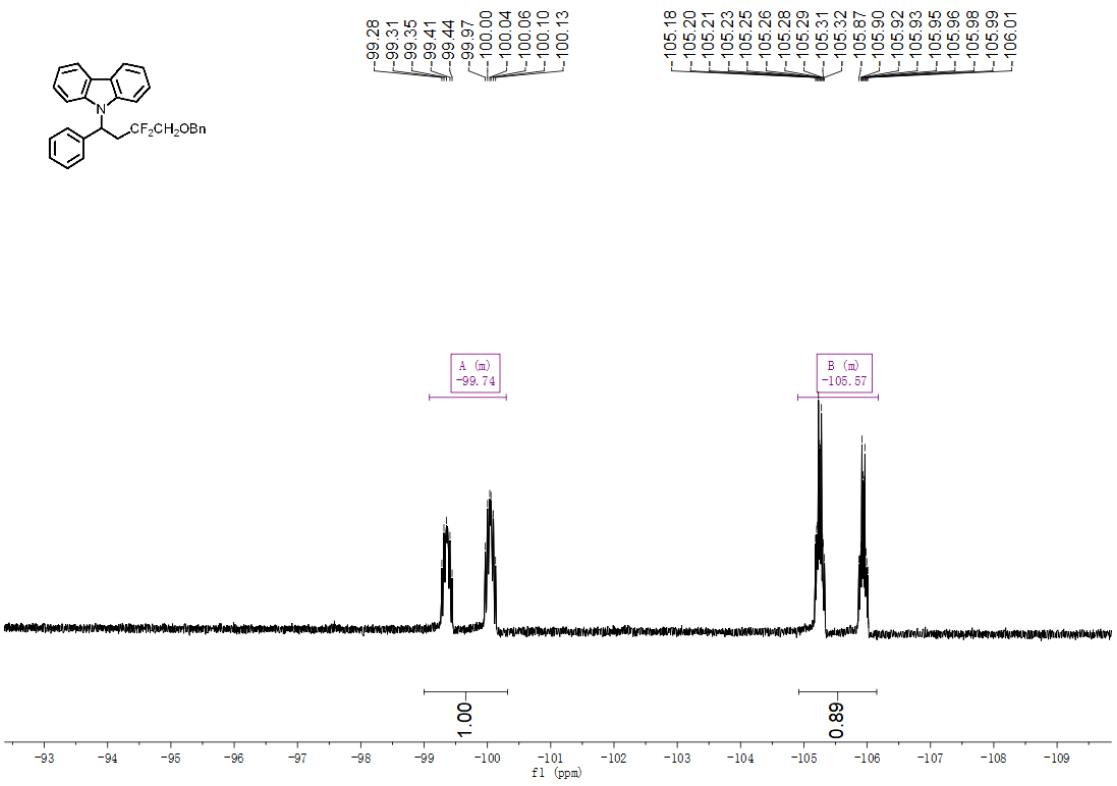
d22 ^{1}H NMR



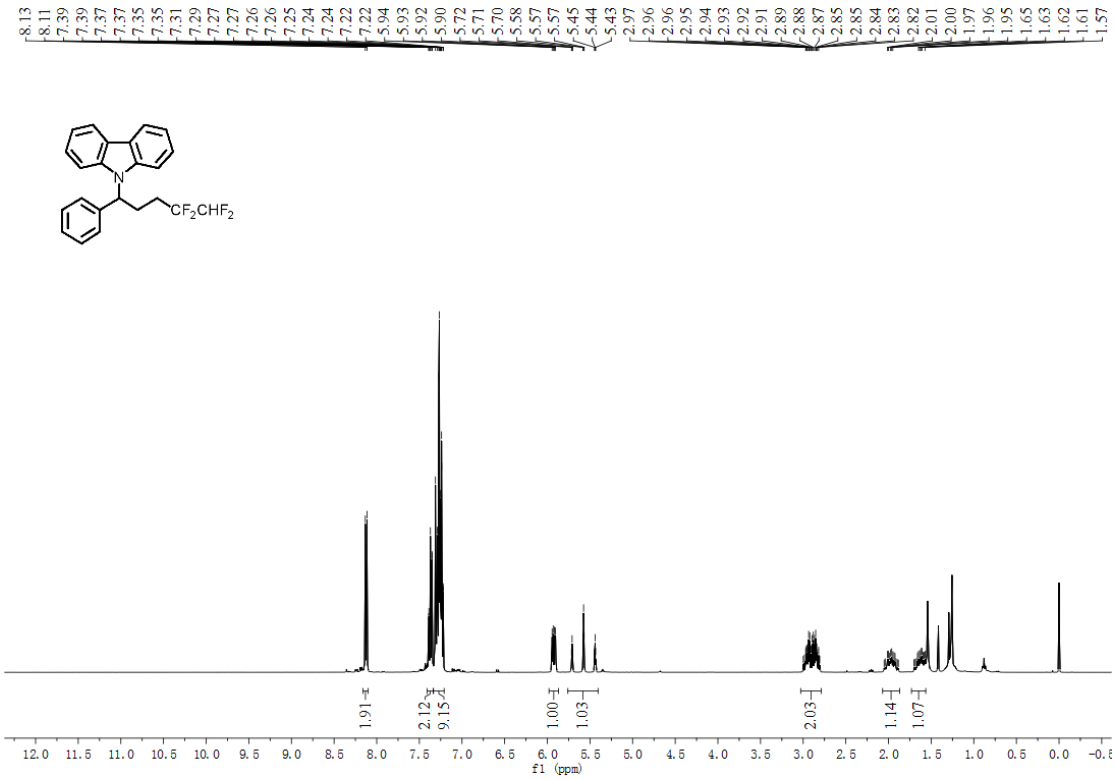
d22 ^{13}C NMR



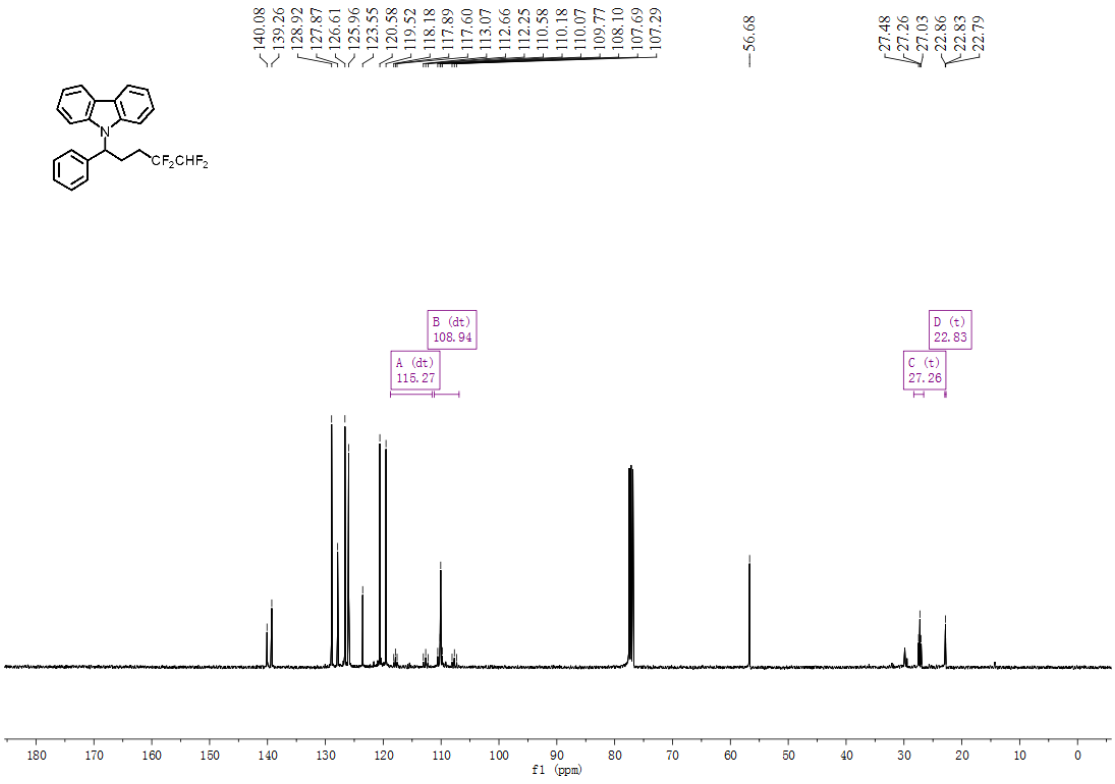
d22 ^{19}F NMR



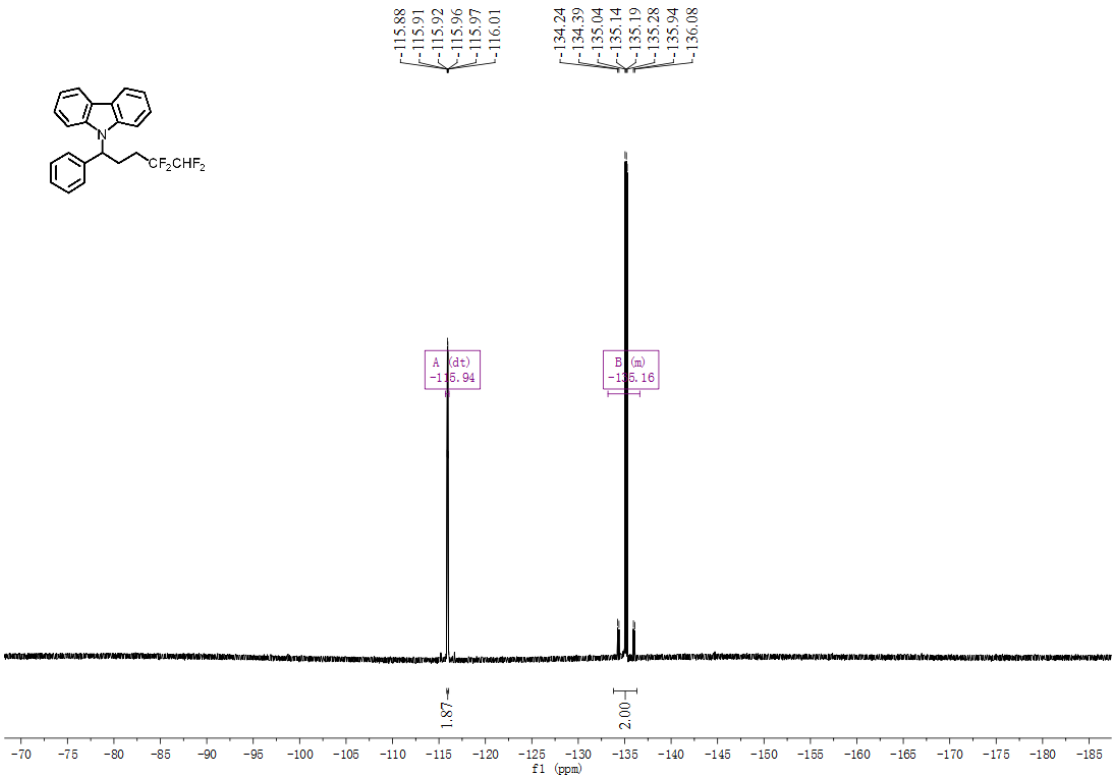
d23 ^{1}H NMR



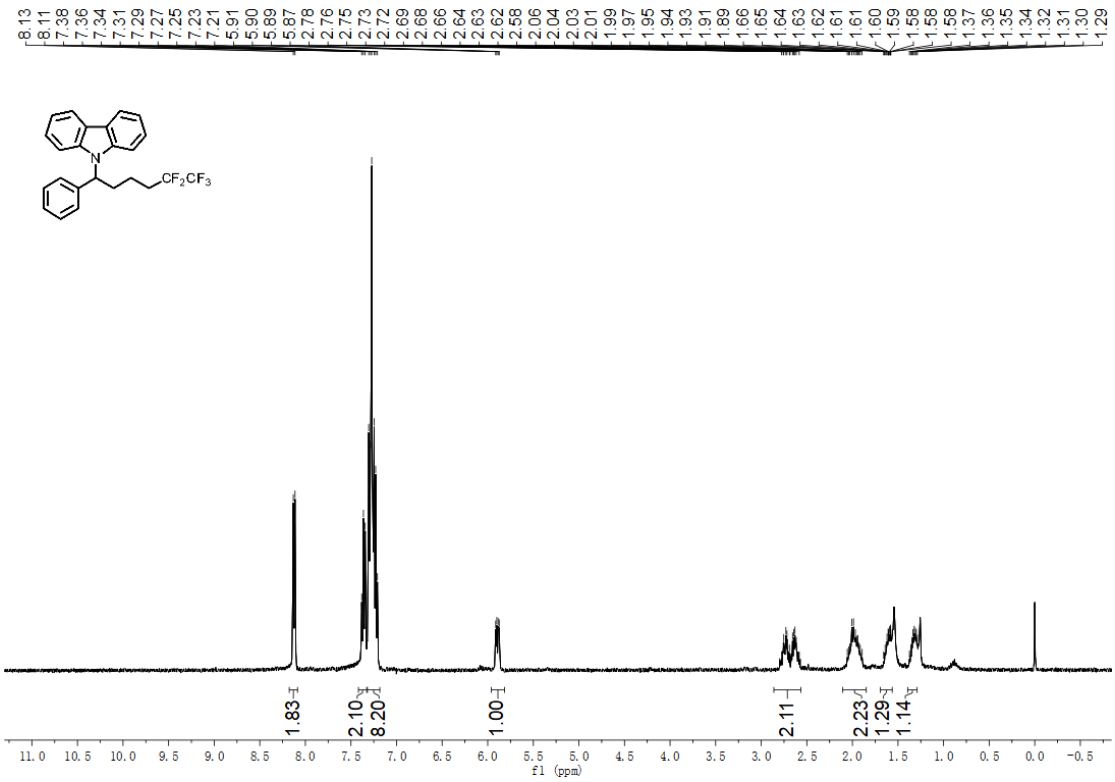
d23 ^{13}C NMR



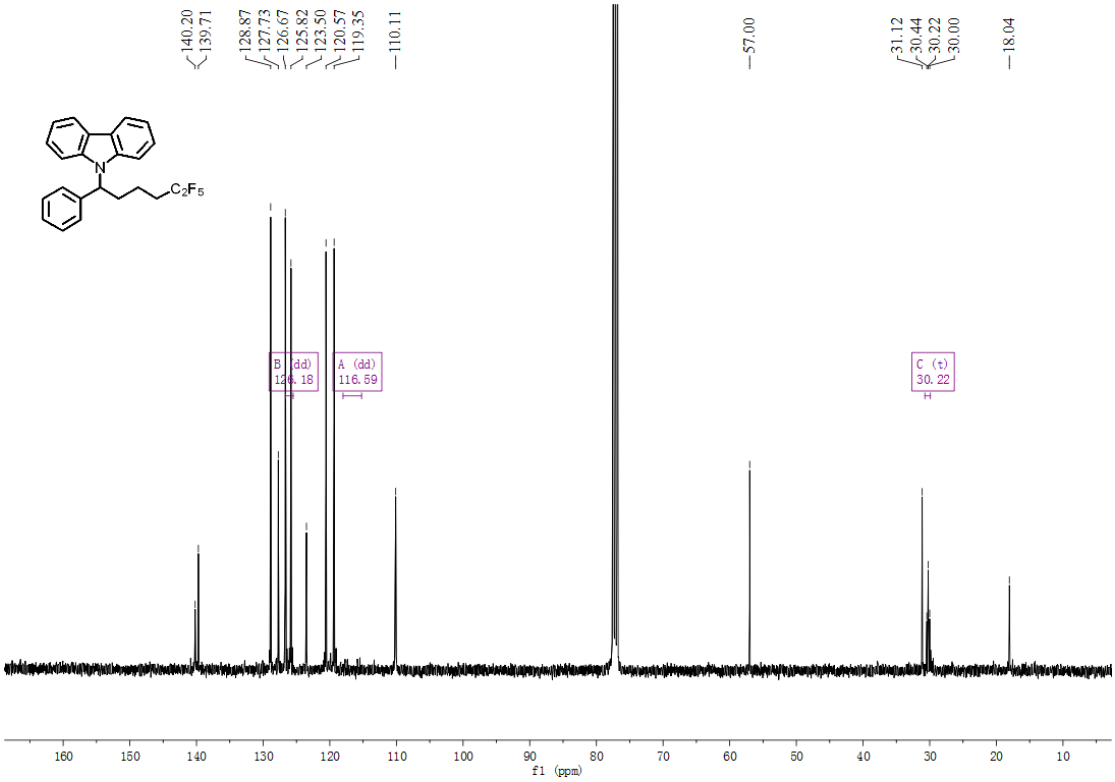
d23 ^{19}F NMR



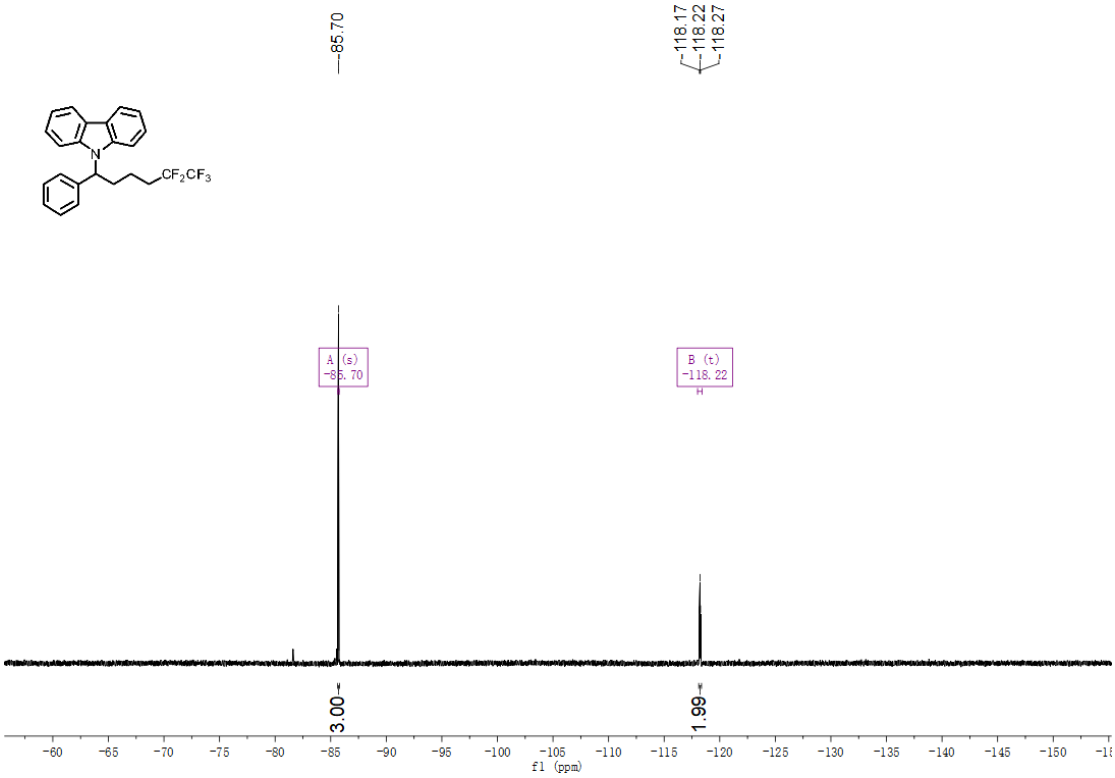
d24 ^{1}H NMR



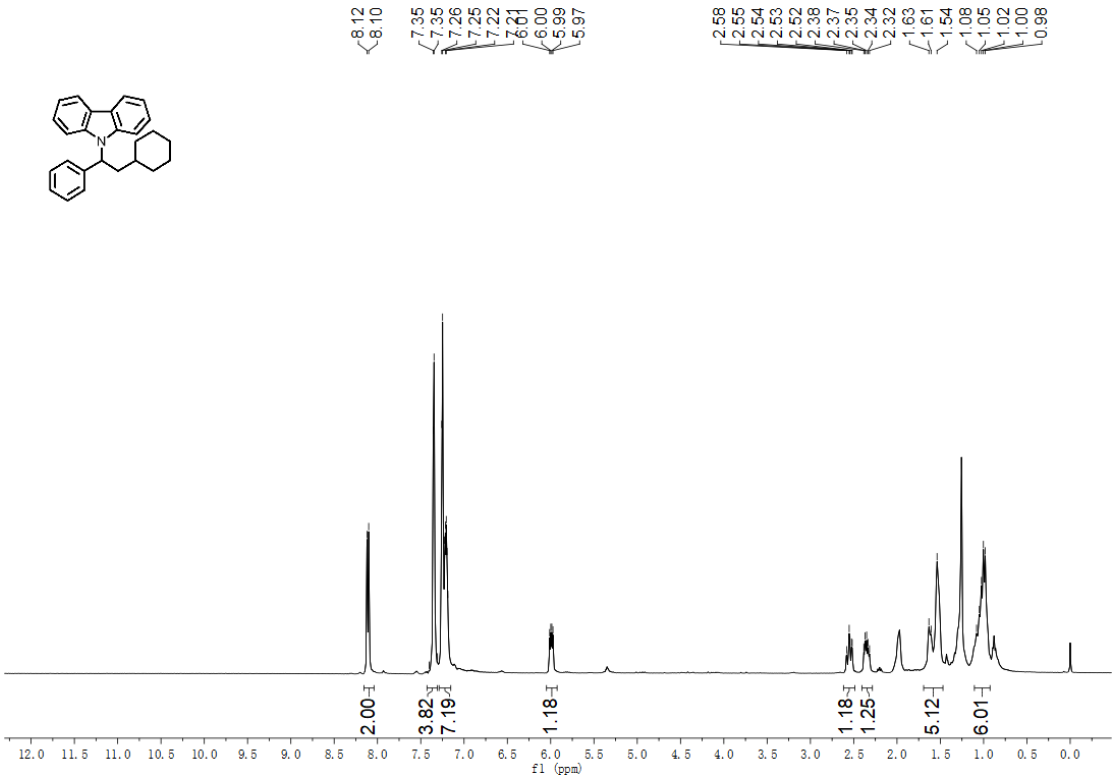
d24 ^{13}C NMR



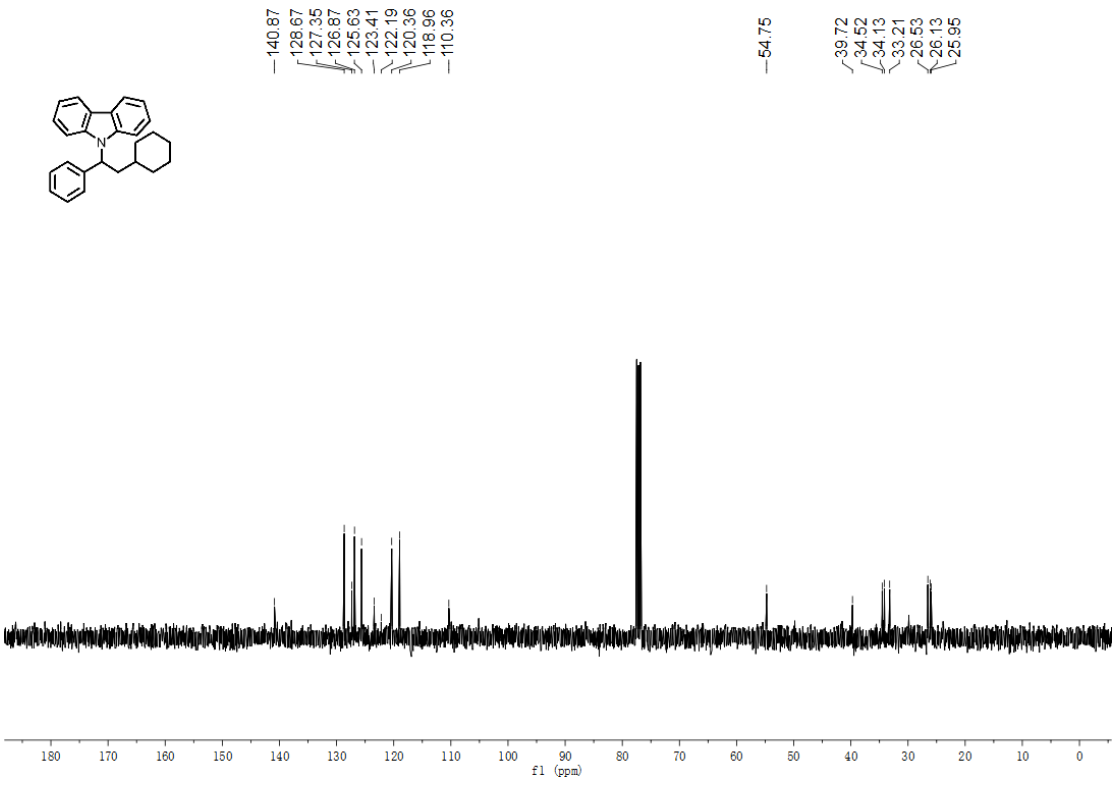
d24 ^{19}F NMR



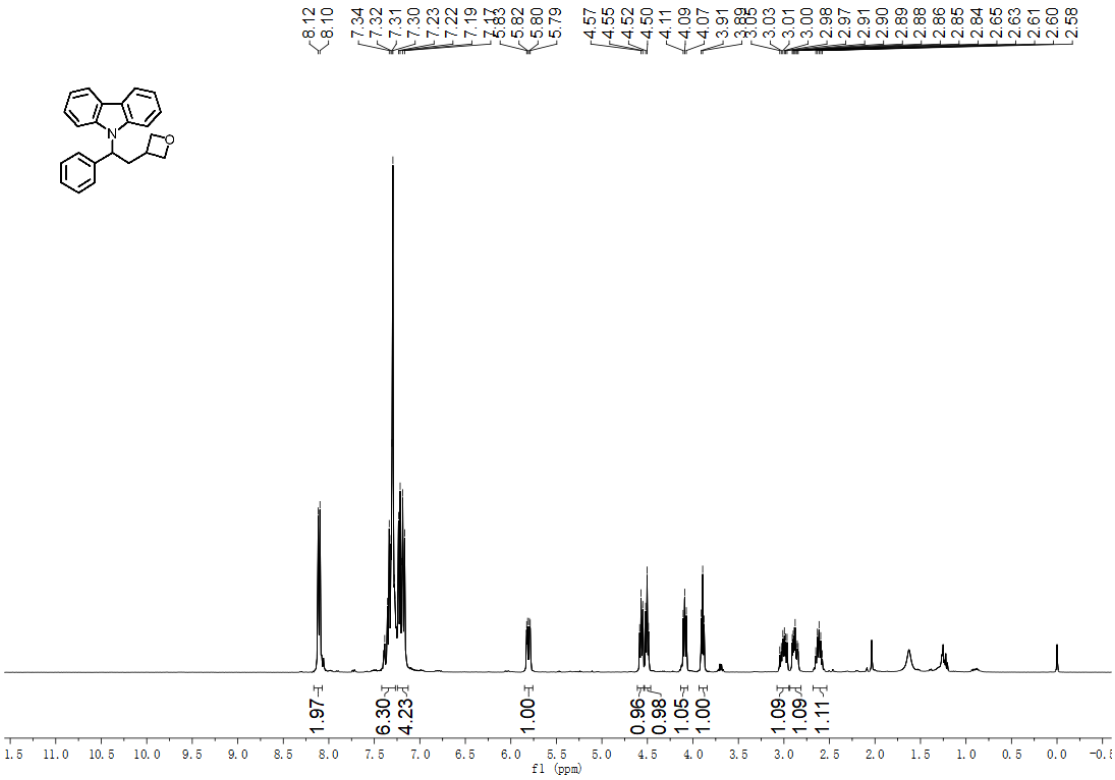
d25 ^{1}H NMR



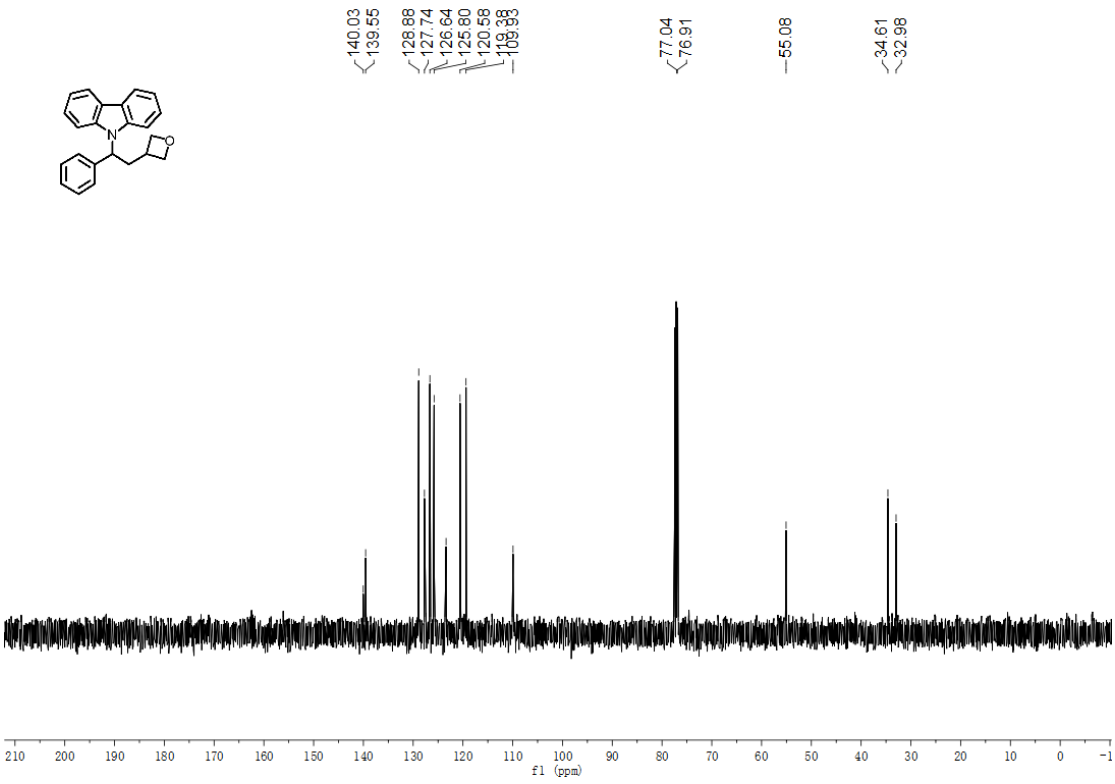
d25 ^{13}C NMR



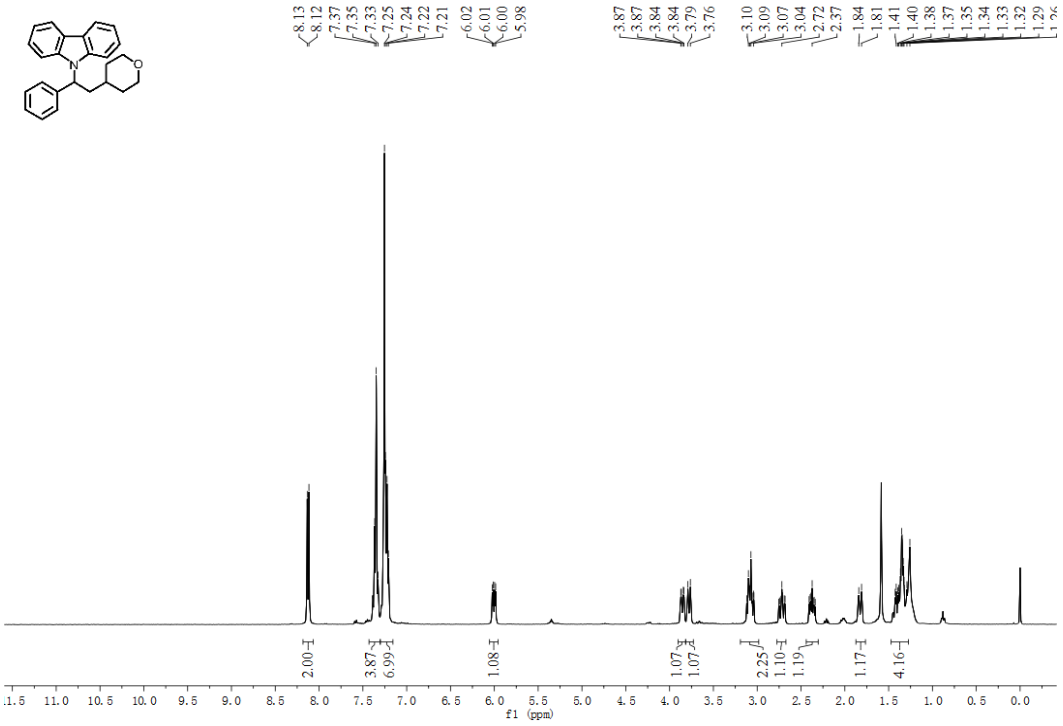
d26 ^{1}H NMR



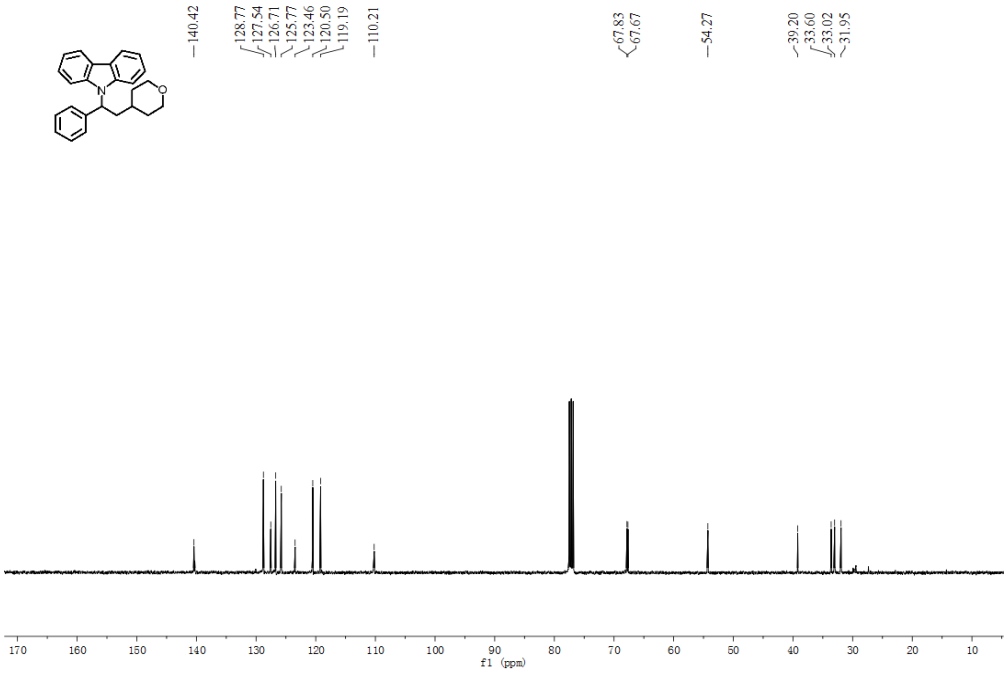
d26 ^{13}C NMR



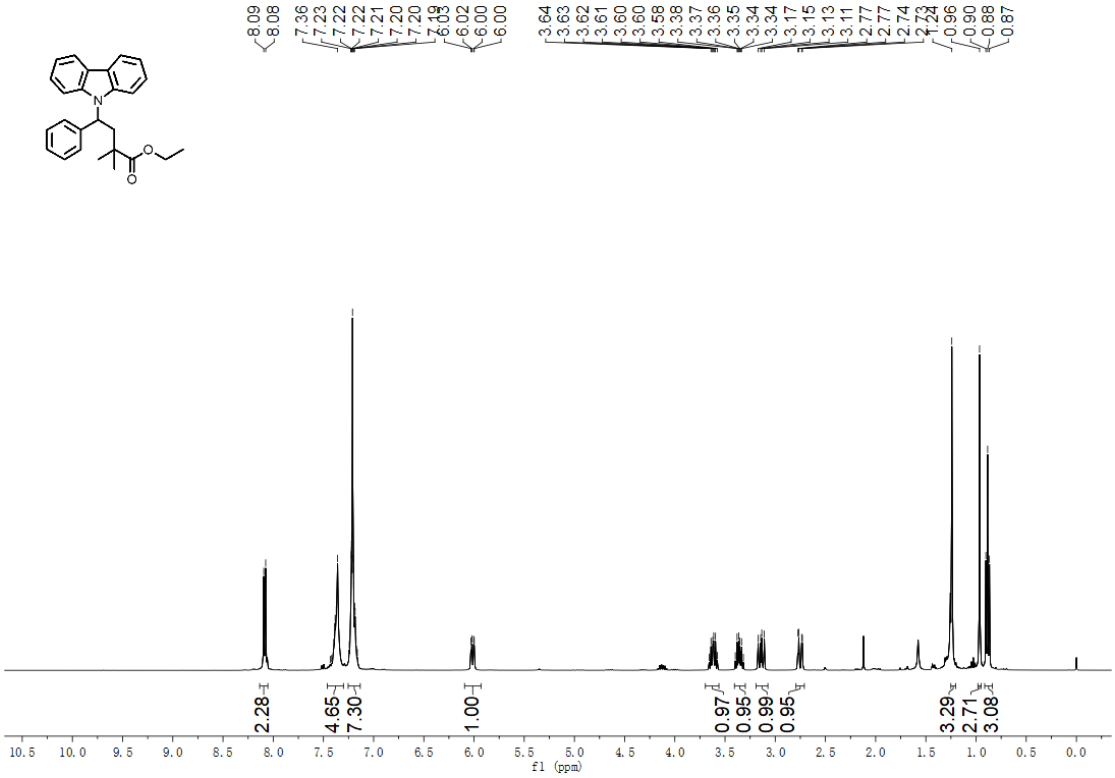
d27 ^{1}H NMR



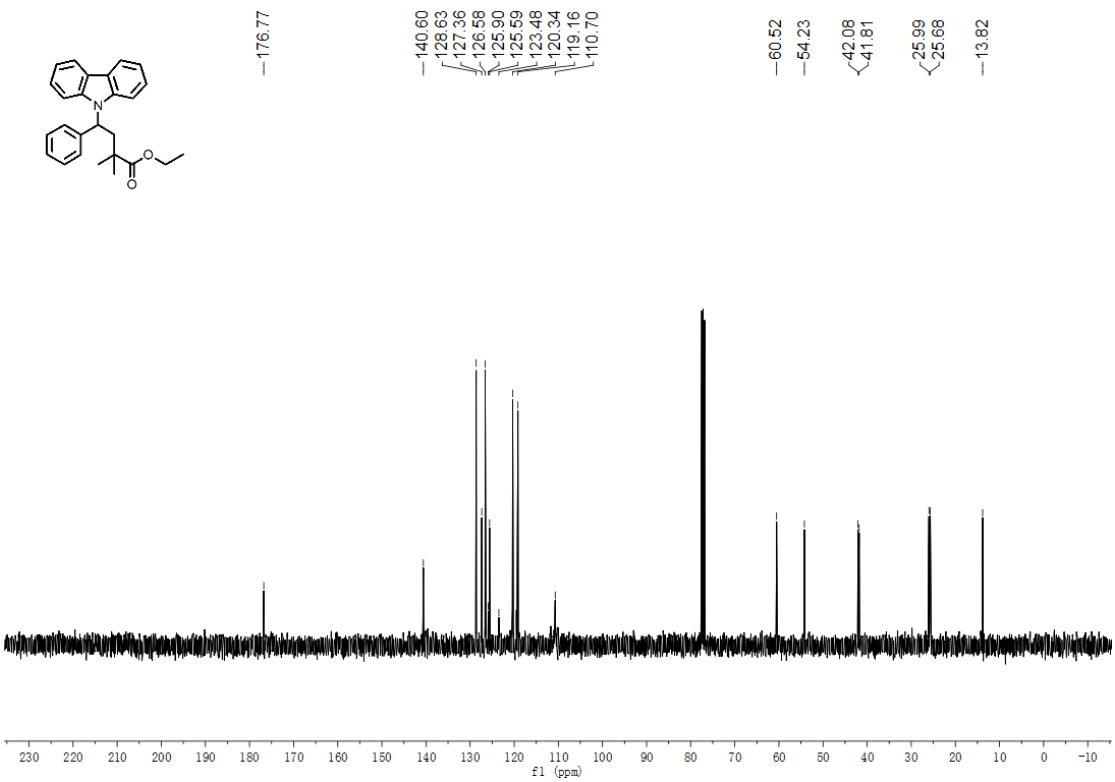
d27 ^{13}C NMR



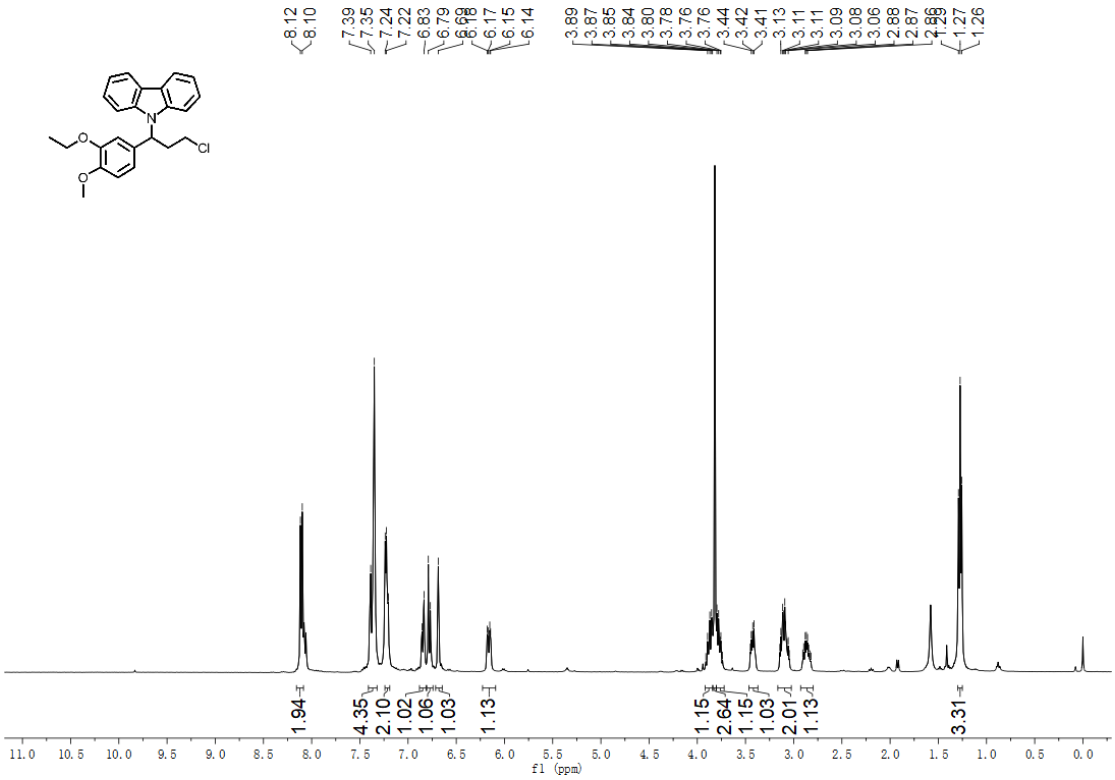
d28 ^{1}H NMR



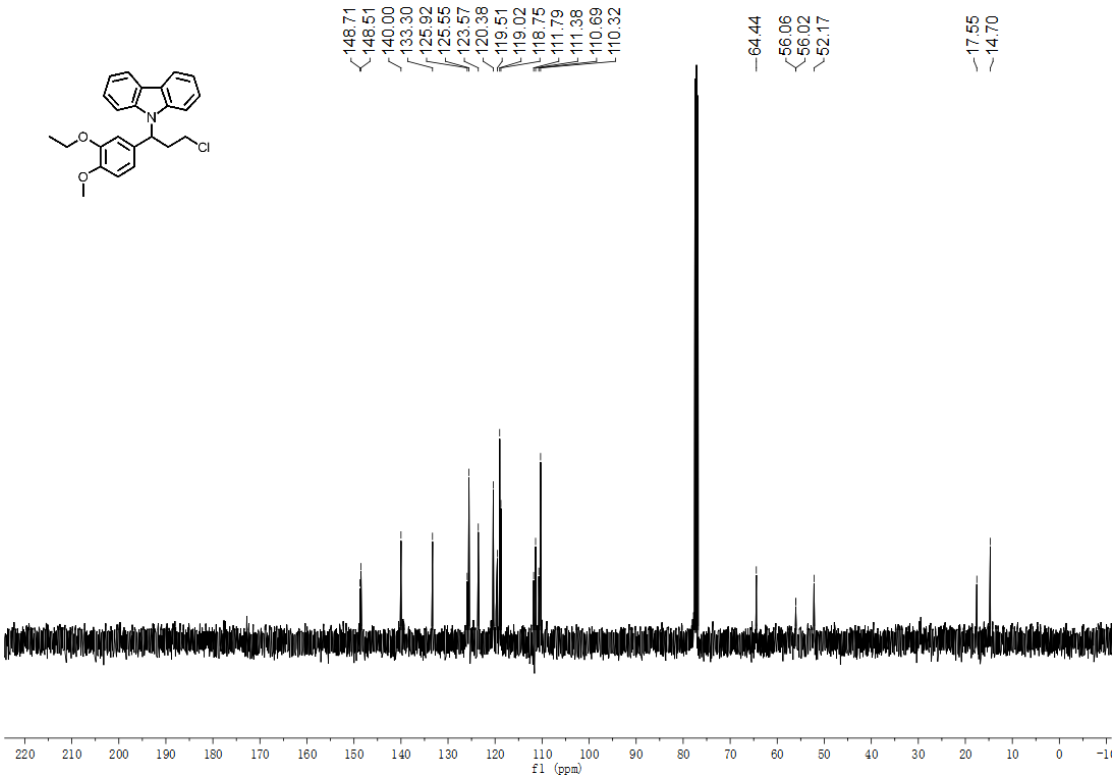
d28 ^{13}C NMR



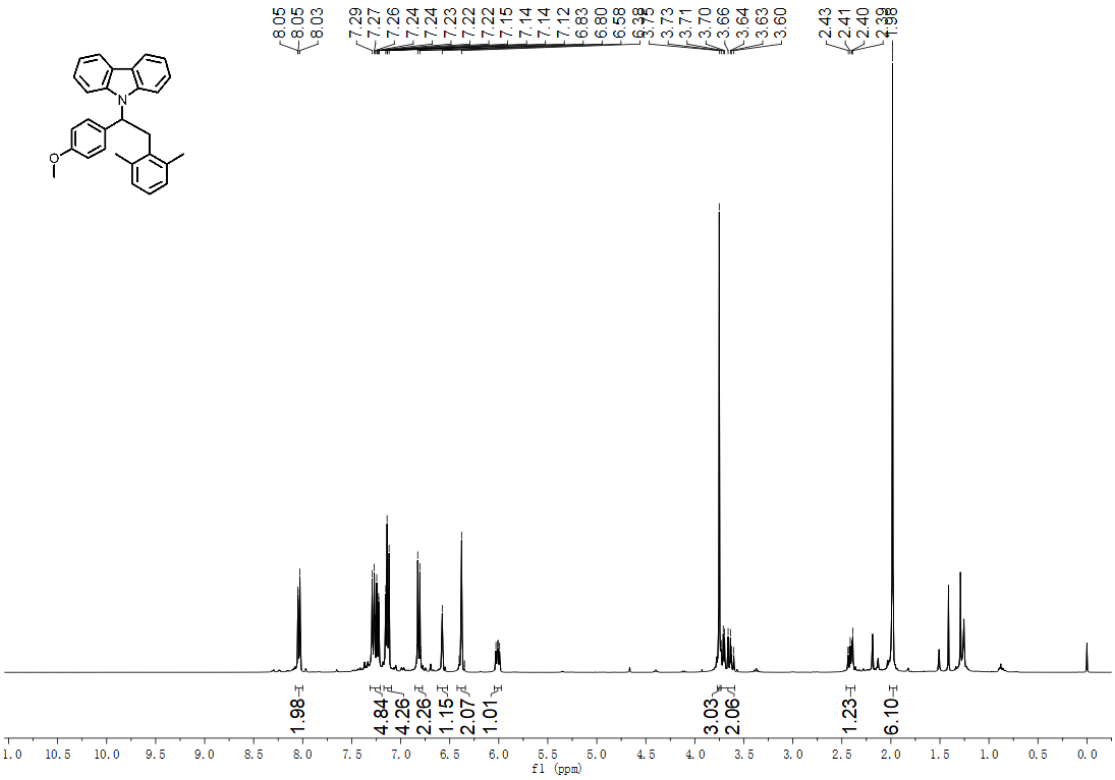
d29 ^{1}H NMR



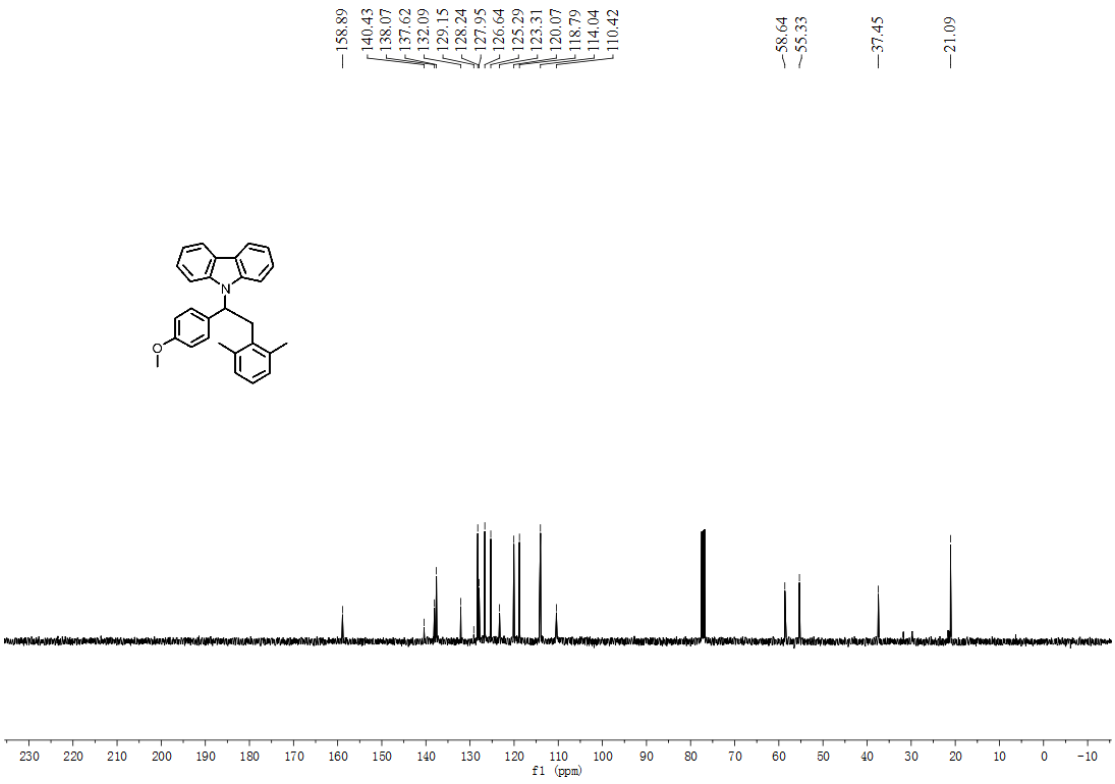
d29 ^{13}C NMR



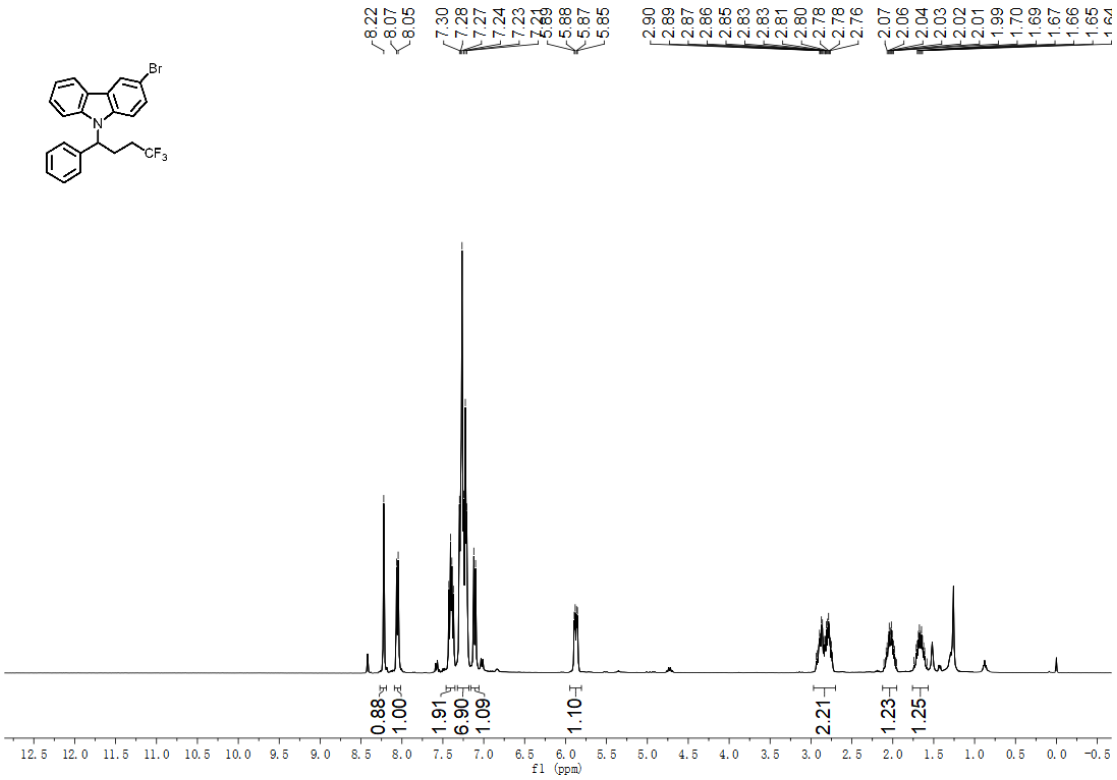
d30 ^{1}H NMR



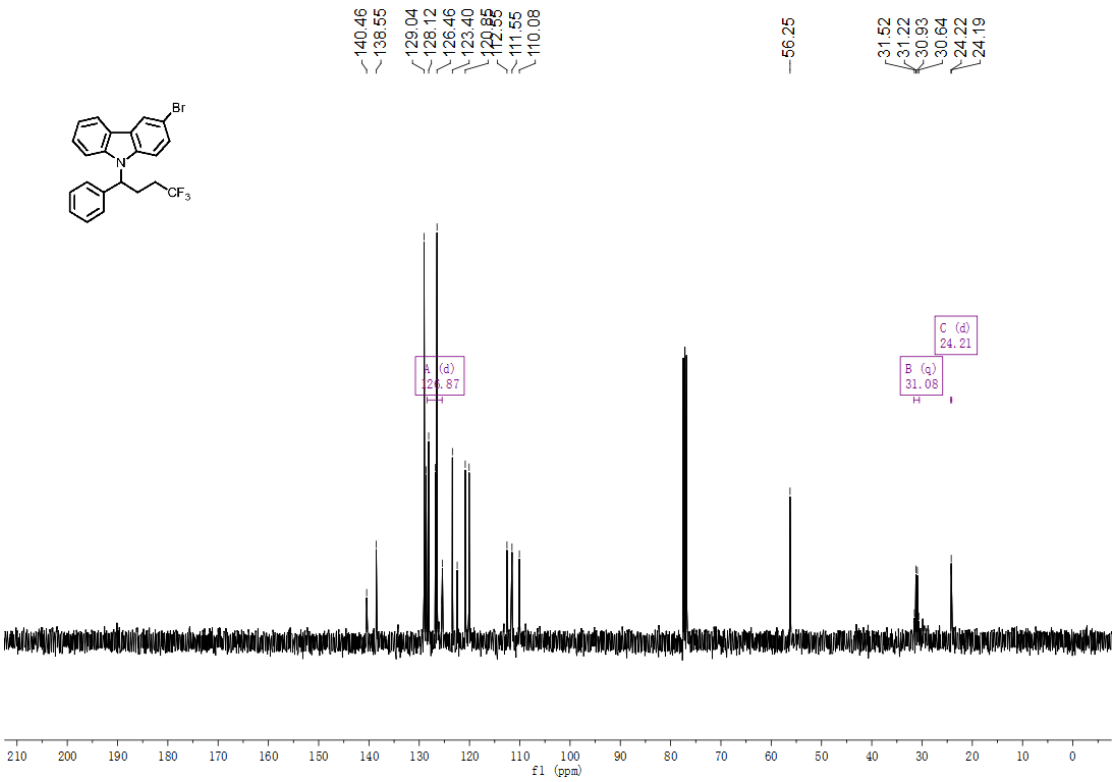
d30 ^{13}C NMR



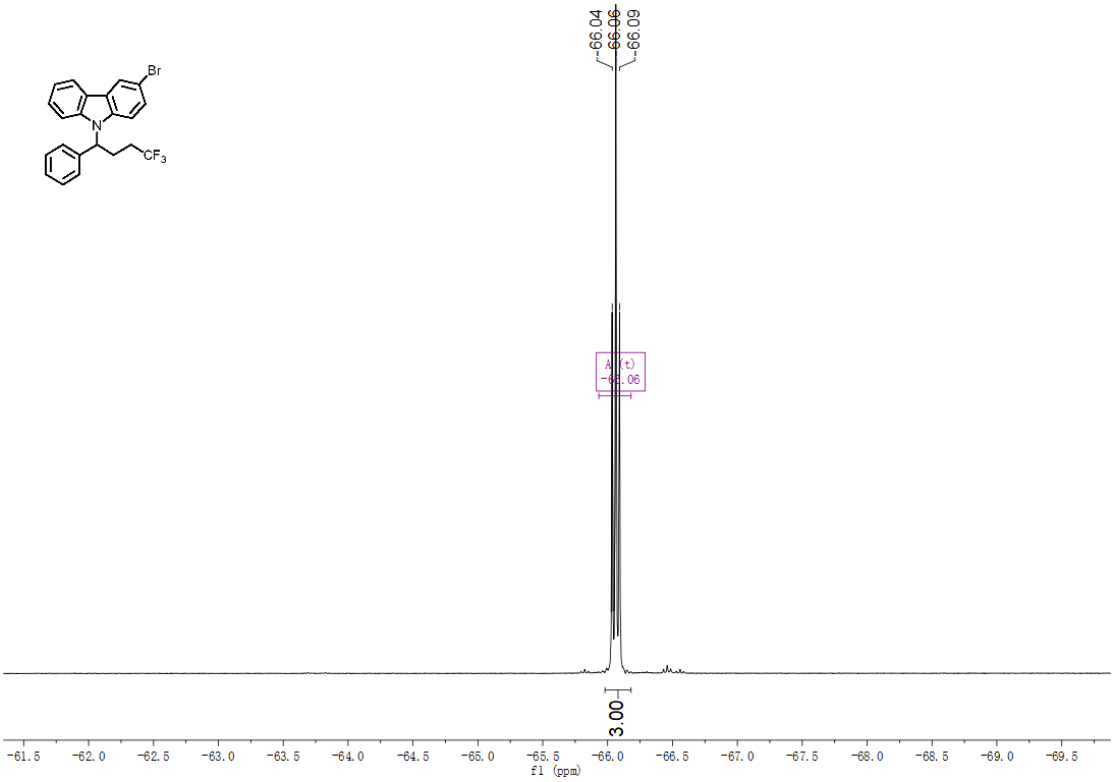
d31 ^{1}H NMR



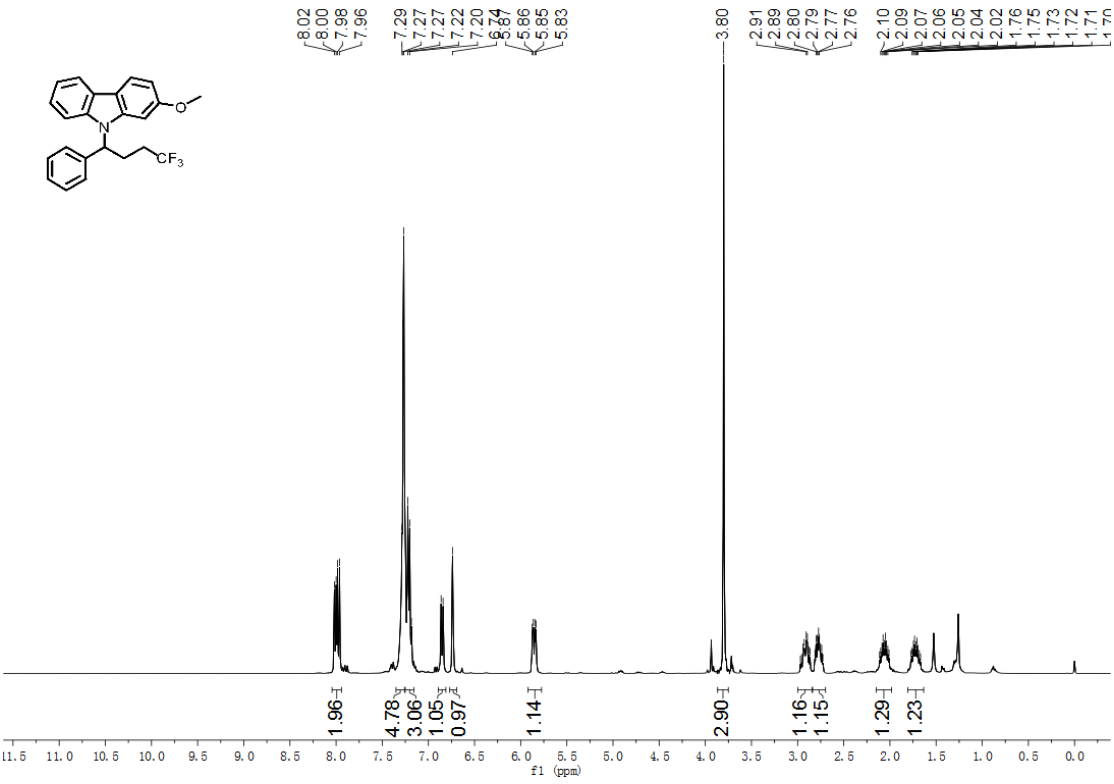
d31 ^{13}C NMR



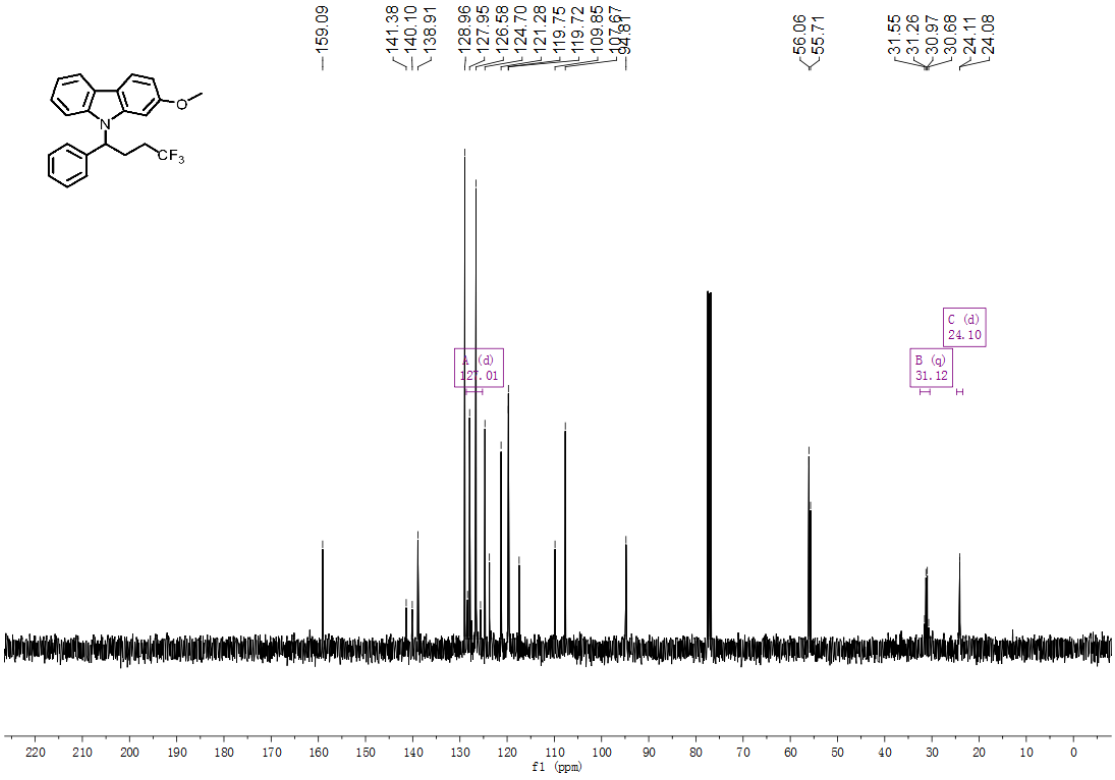
d31 ^{19}F NMR



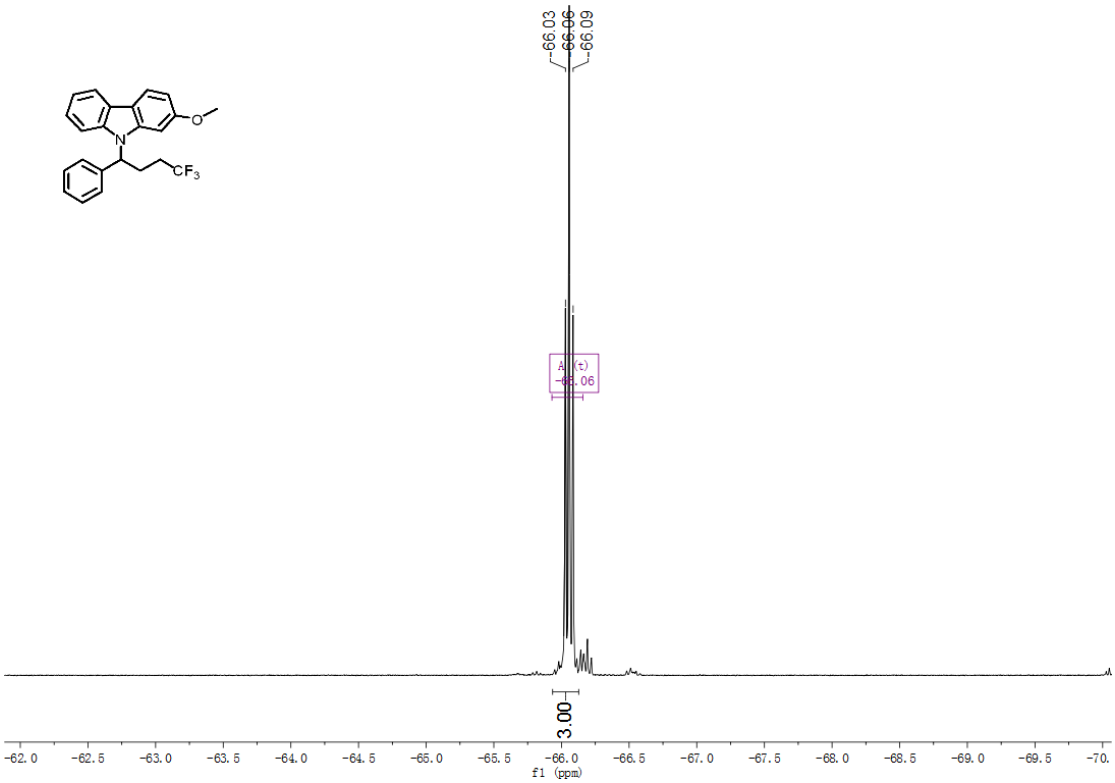
d32 ^{1}H NMR



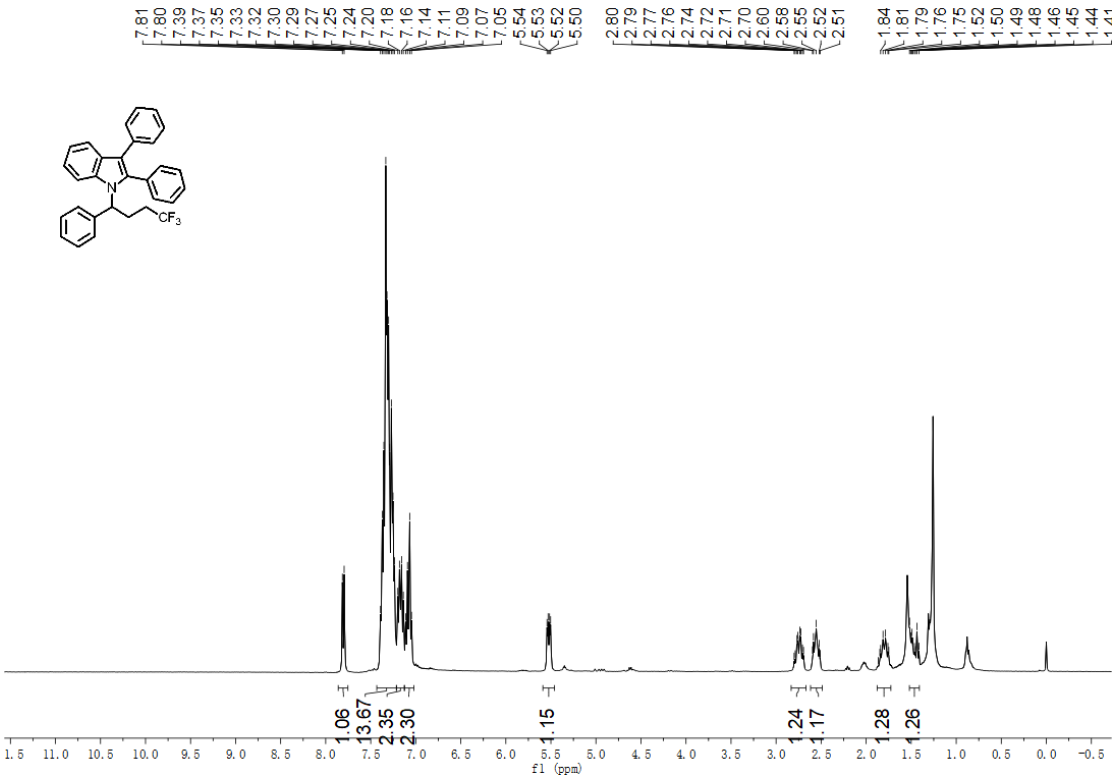
d32 ^{13}C NMR



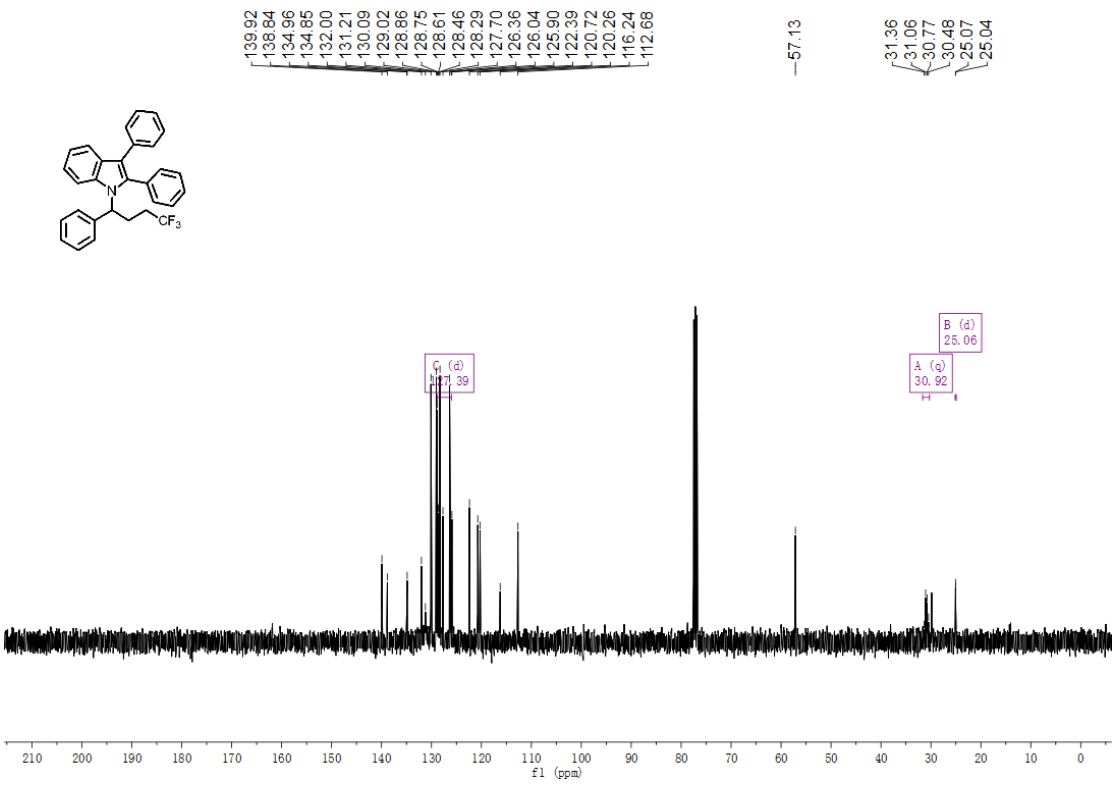
d32 ^{19}F NMR



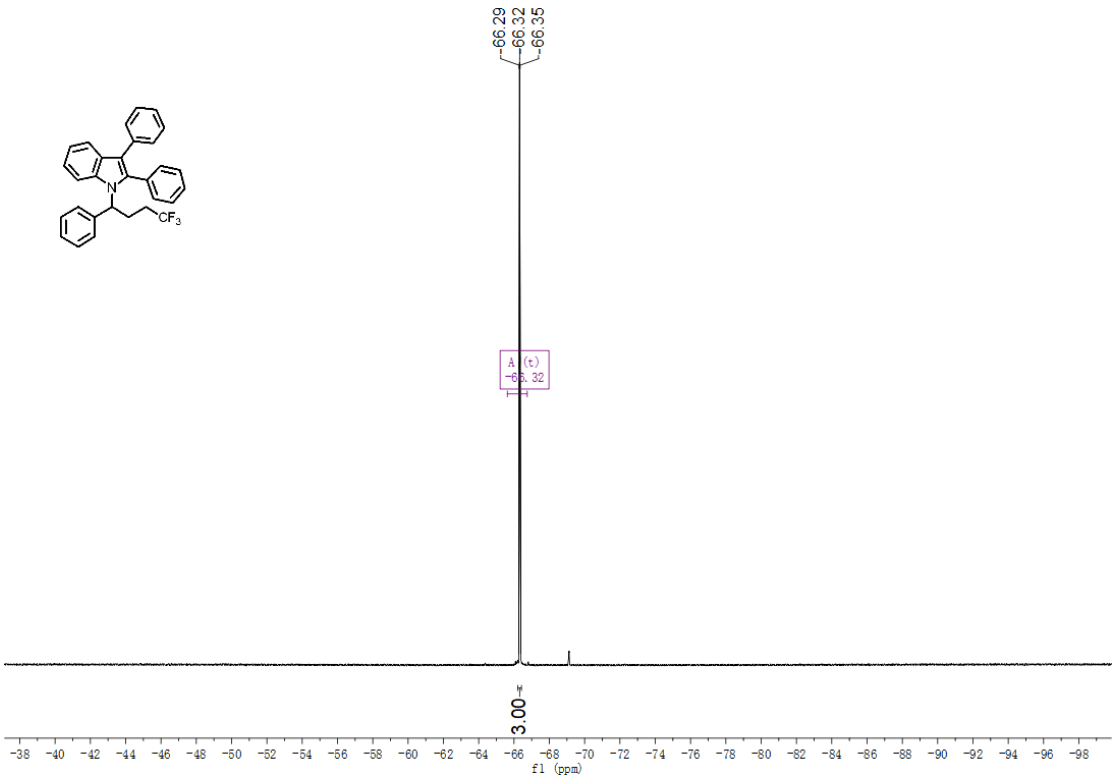
d33 ^{1}H NMR



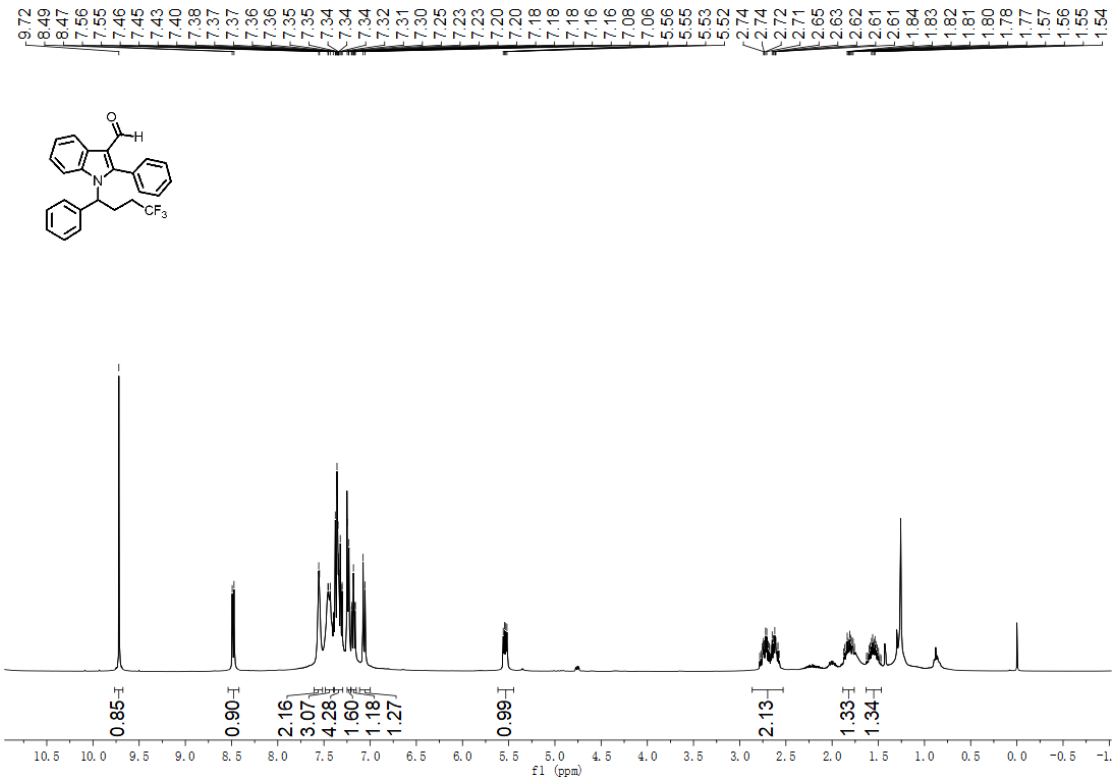
d33 ^{13}C NMR



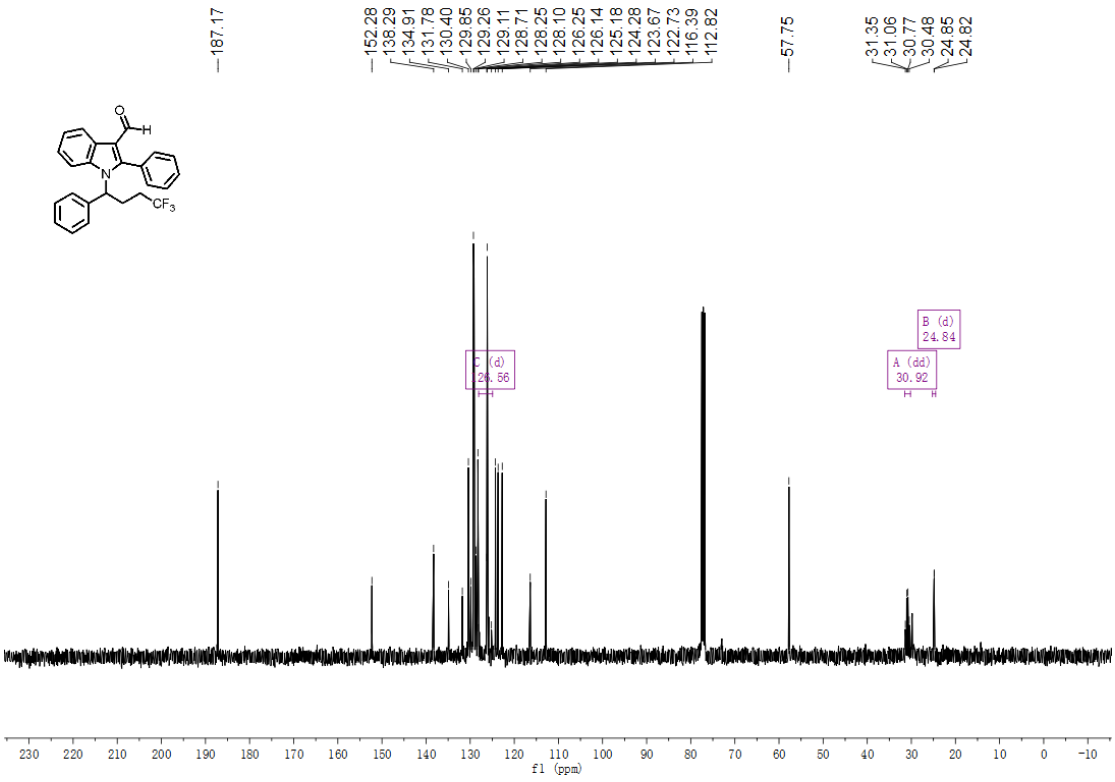
d33 ^{19}F NMR



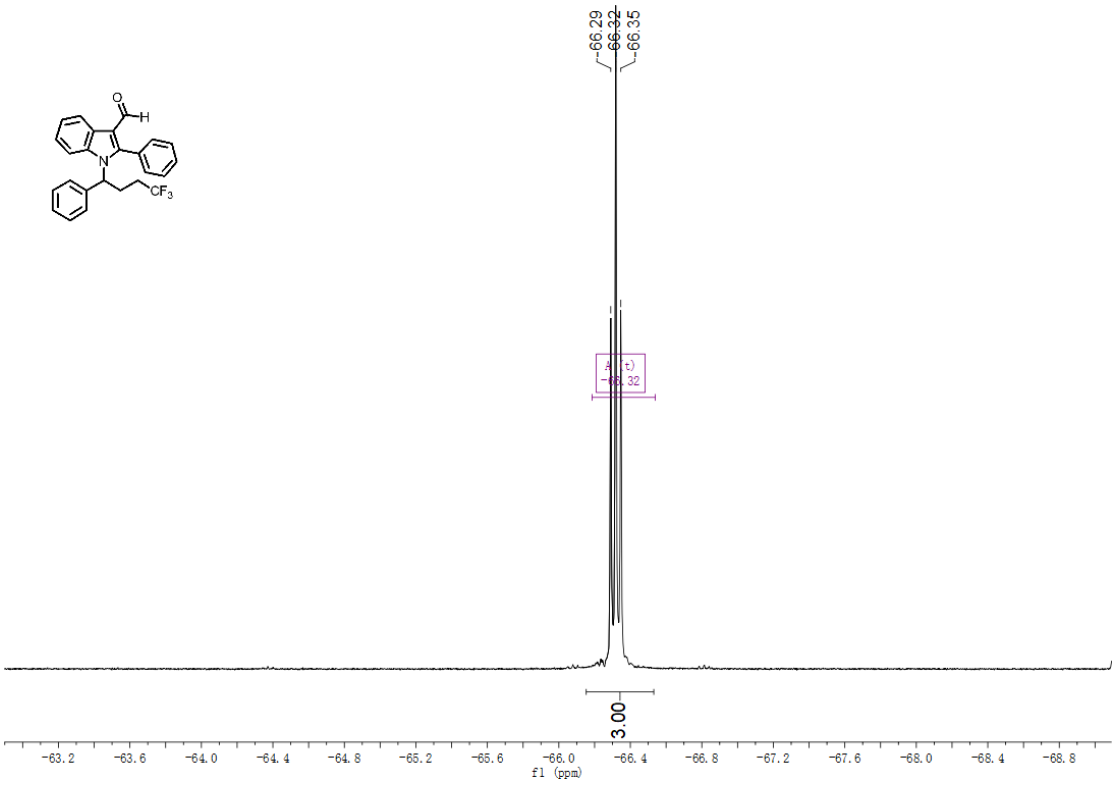
d34 ^{1}H NMR



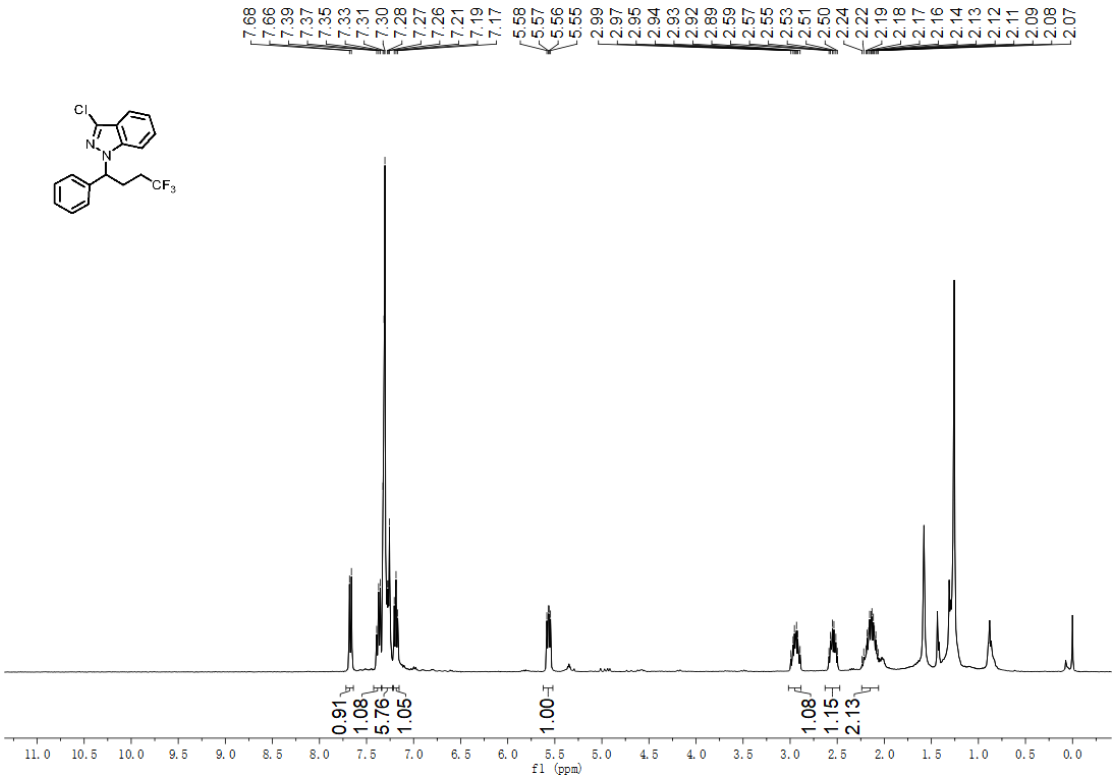
d34 ^{13}C NMR



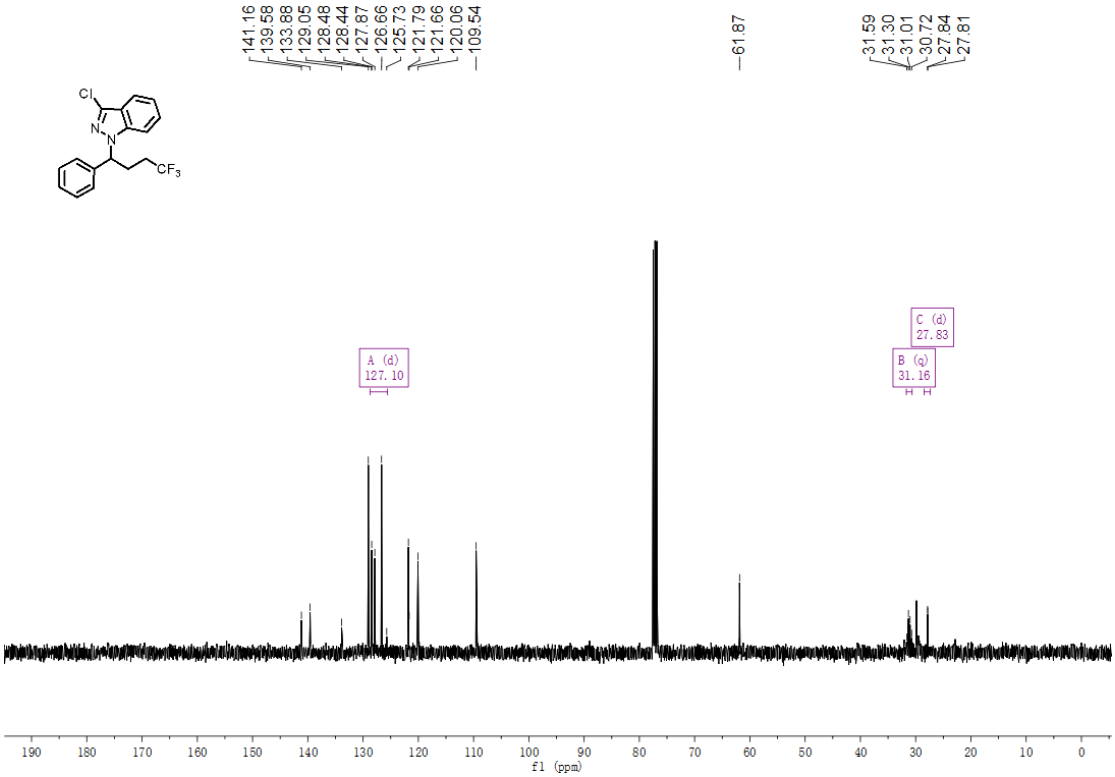
d34 ^{19}F NMR



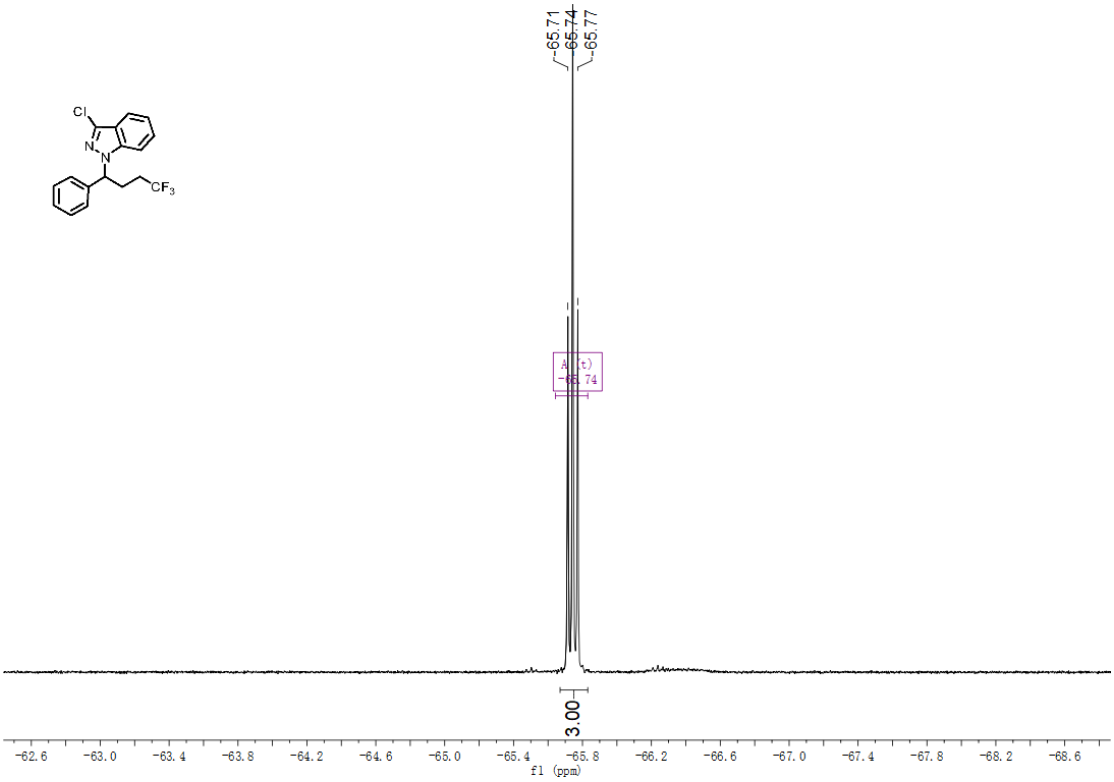
d35 ^{1}H NMR



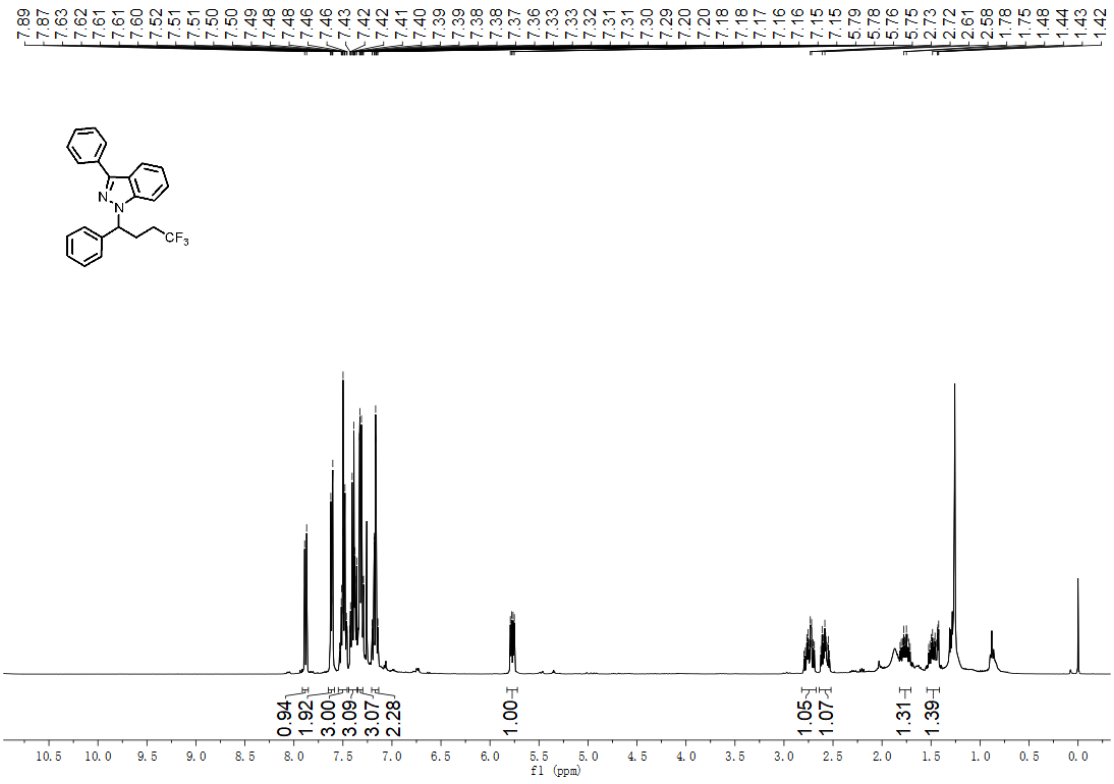
d35 ^{13}C NMR



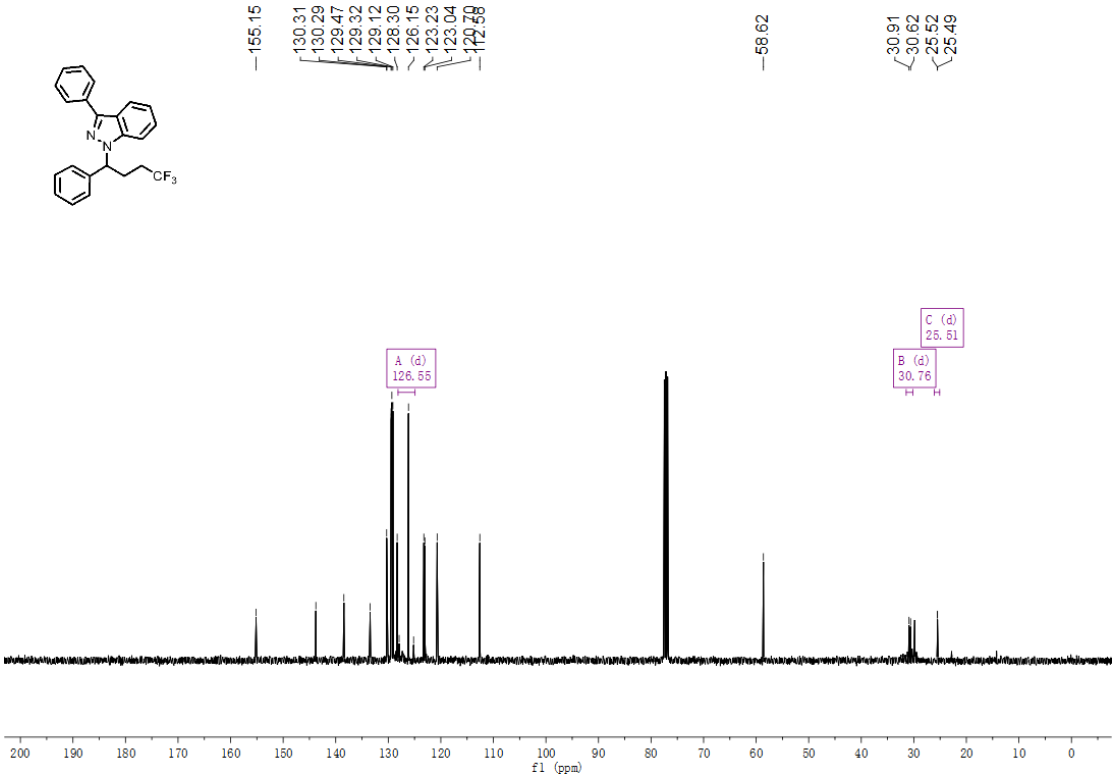
d35 ^{19}F NMR



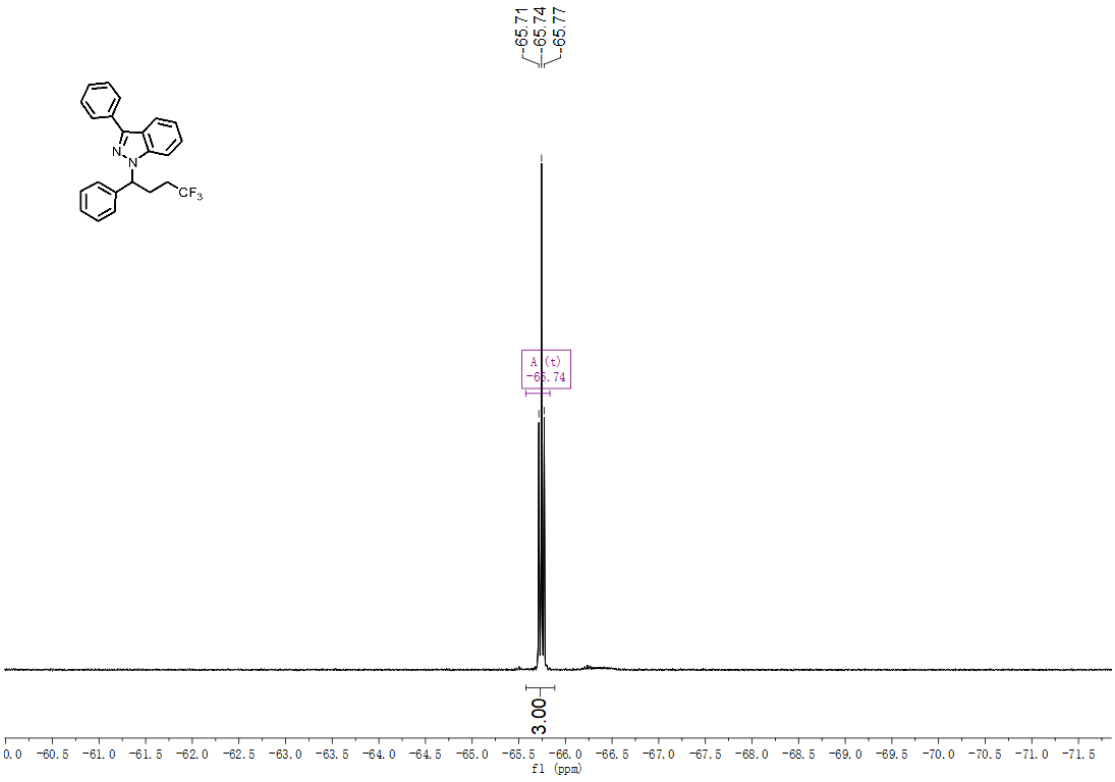
d36 ^{1}H NMR



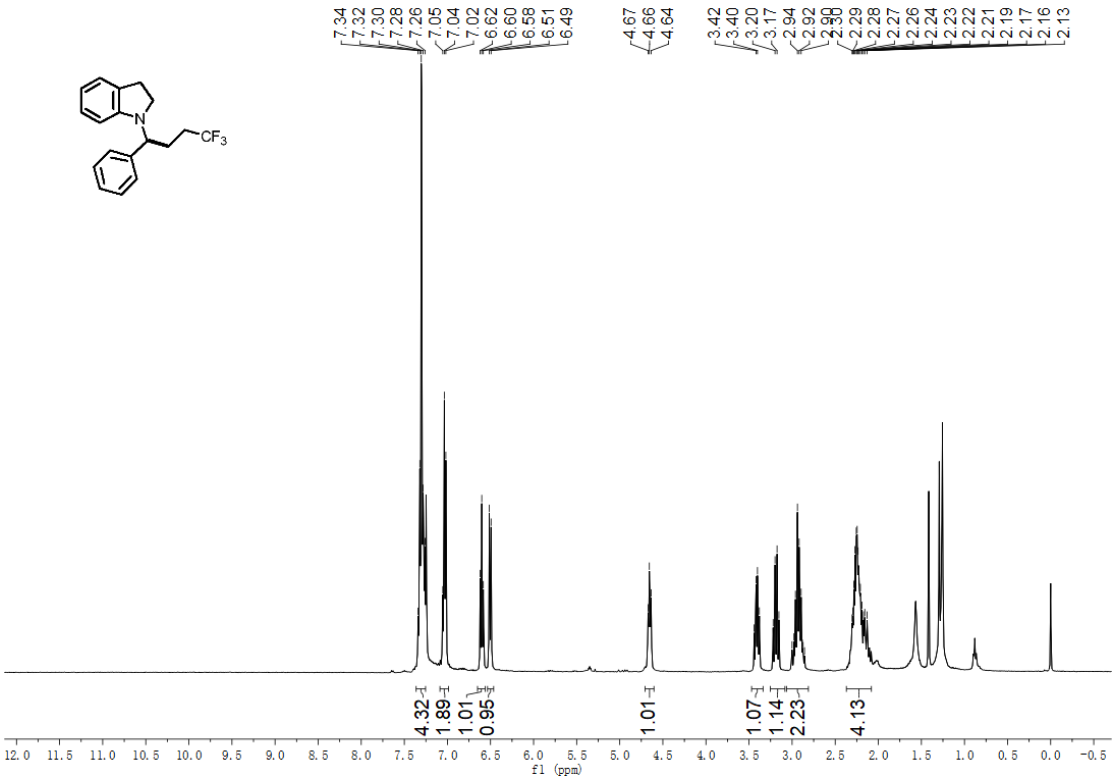
d36 ^{13}C NMR



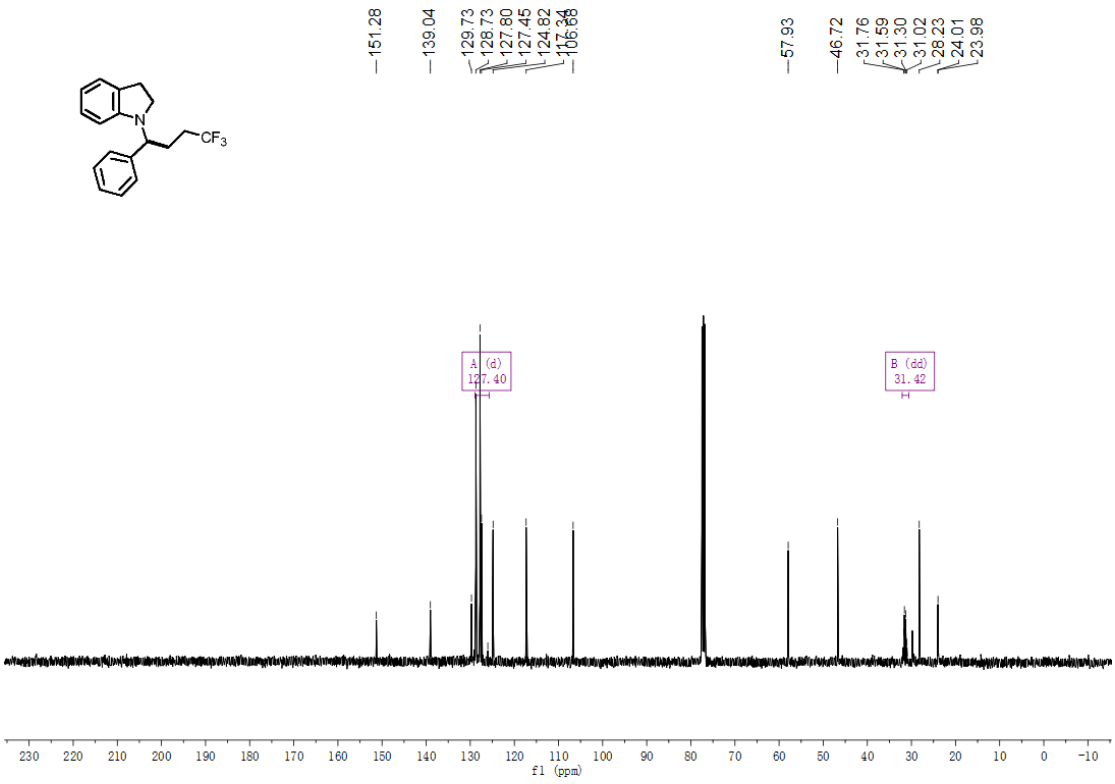
d36 ^{19}F NMR



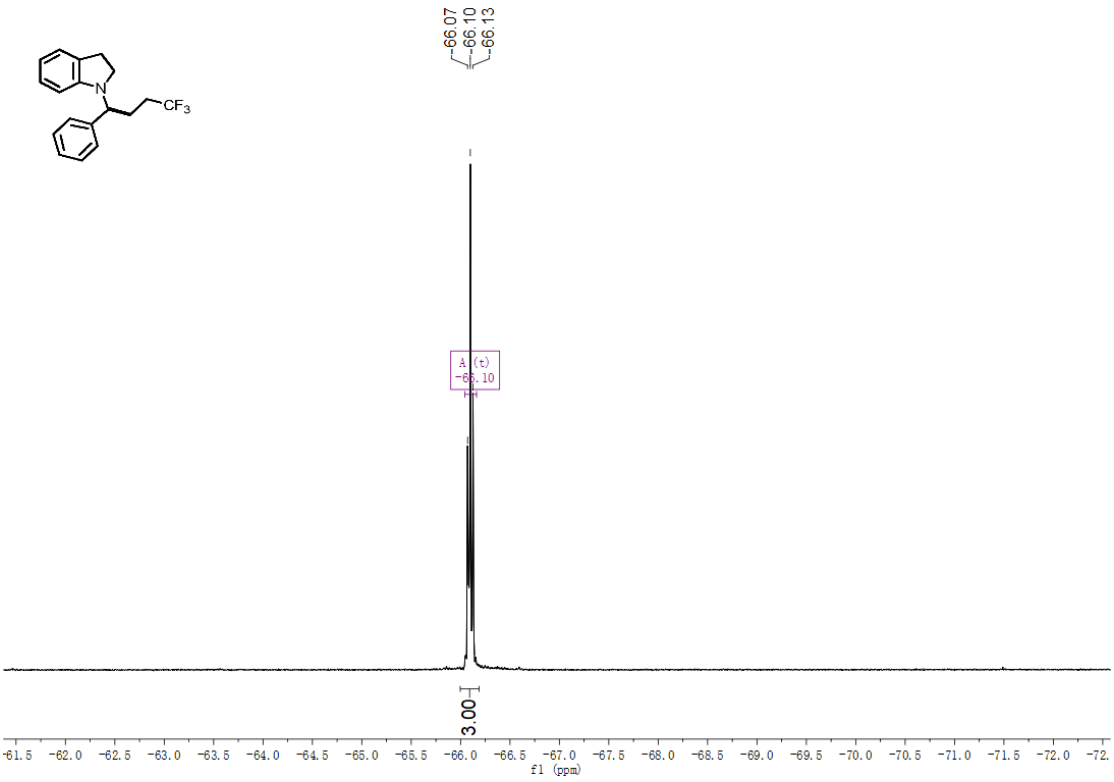
d37 ^{1}H NMR



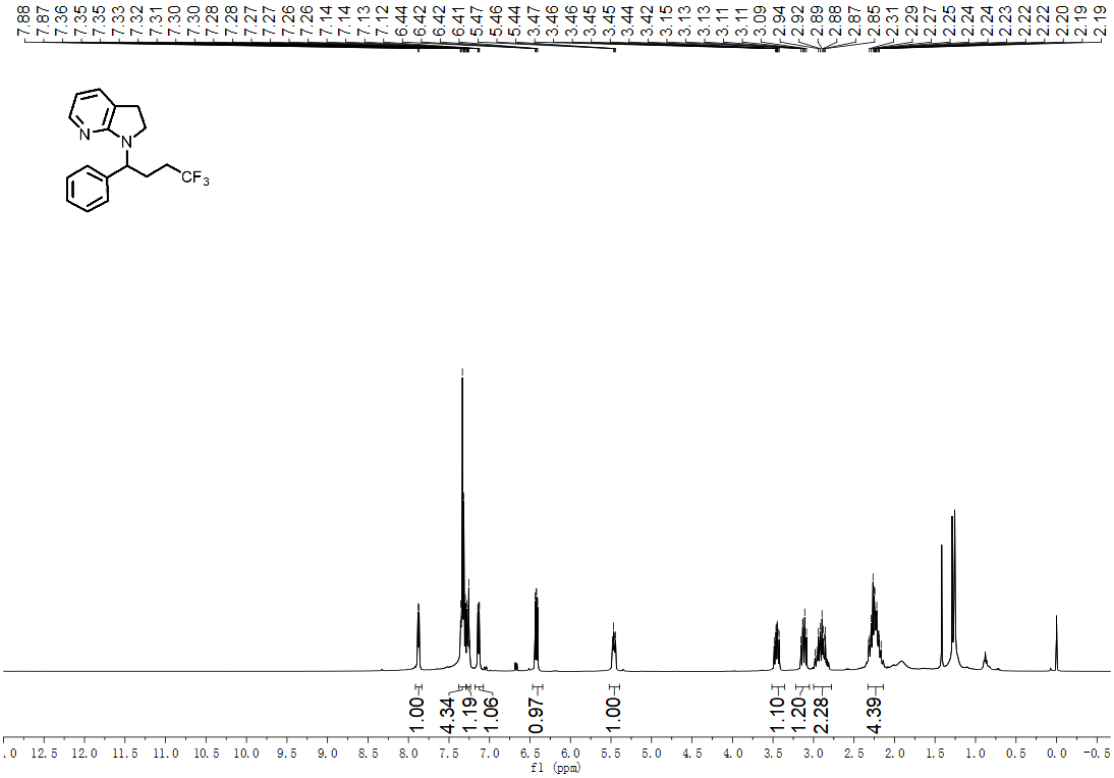
d37 ^{13}C NMR



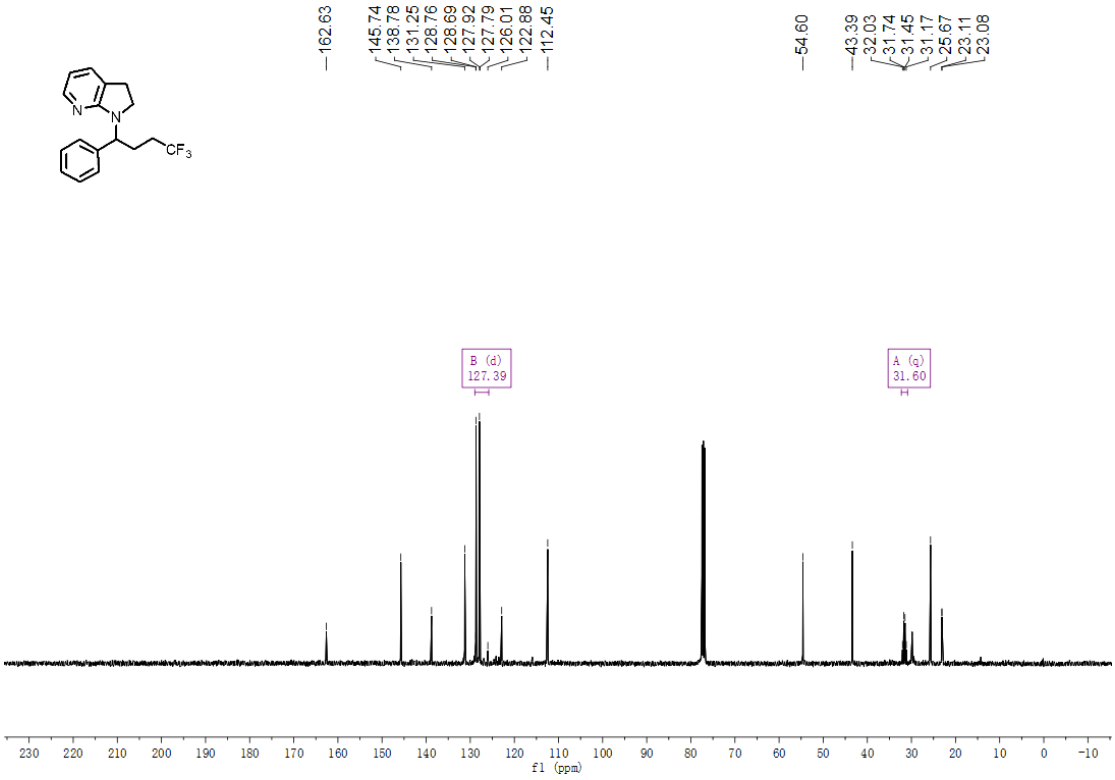
d37 ^{19}F NMR



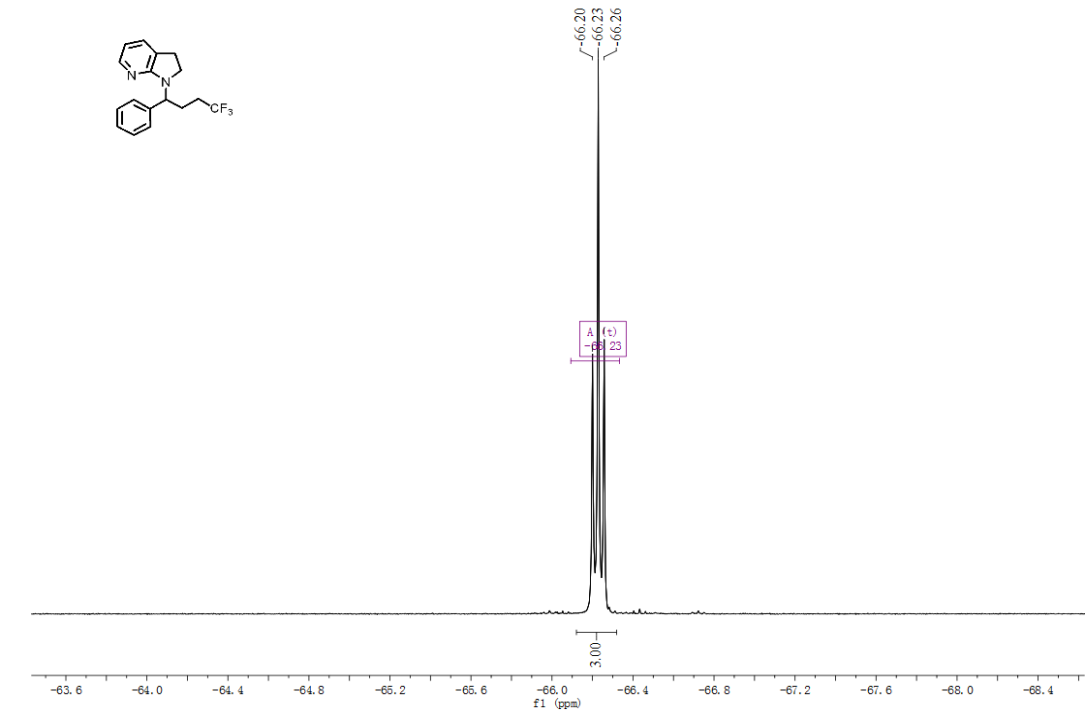
d38 ^{1}H NMR



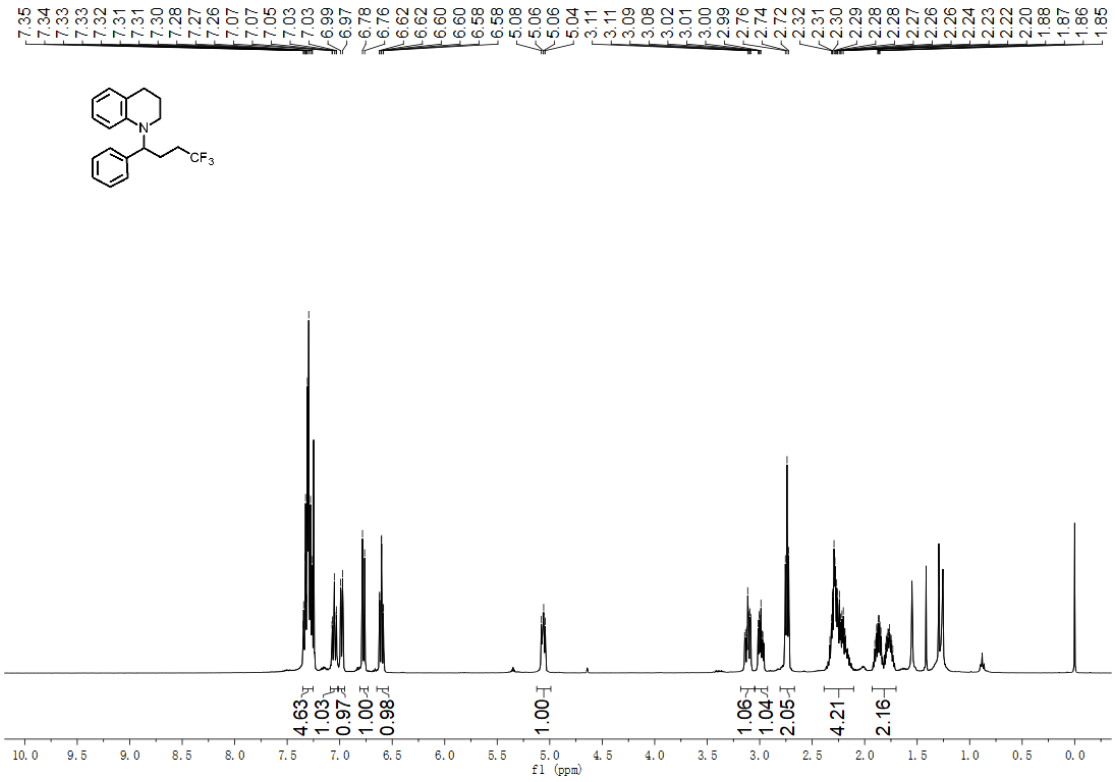
d38 ^{13}C NMR



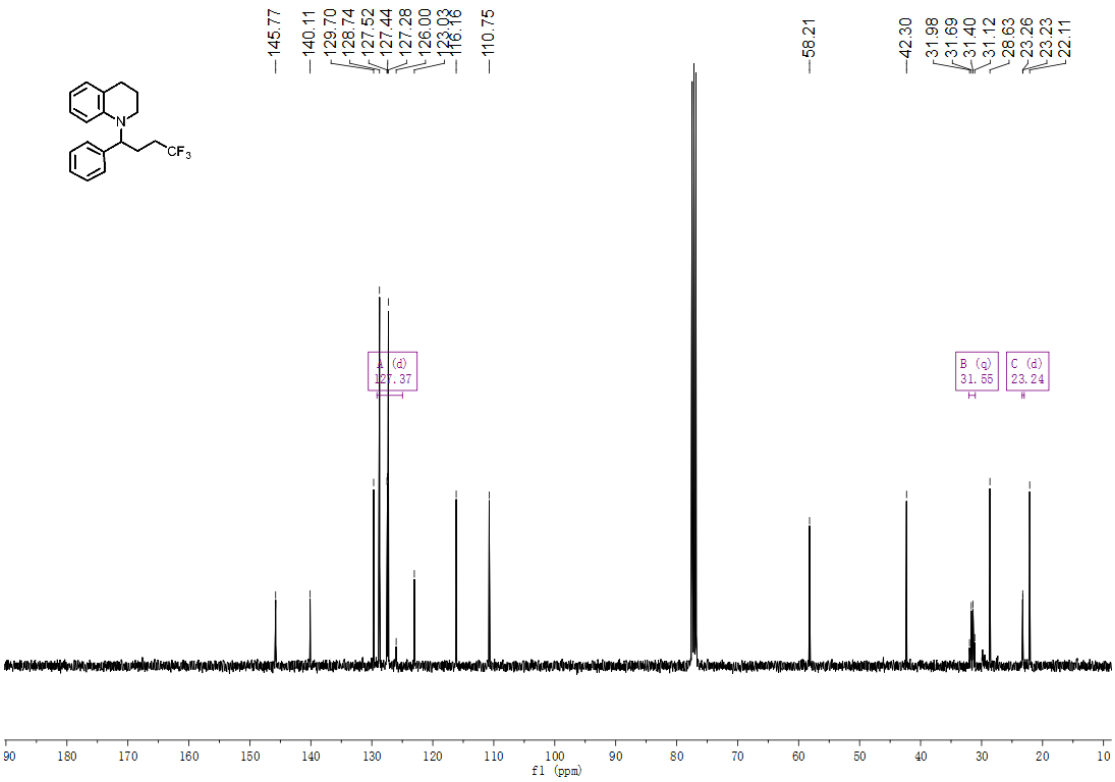
d38 ^{19}F NMR



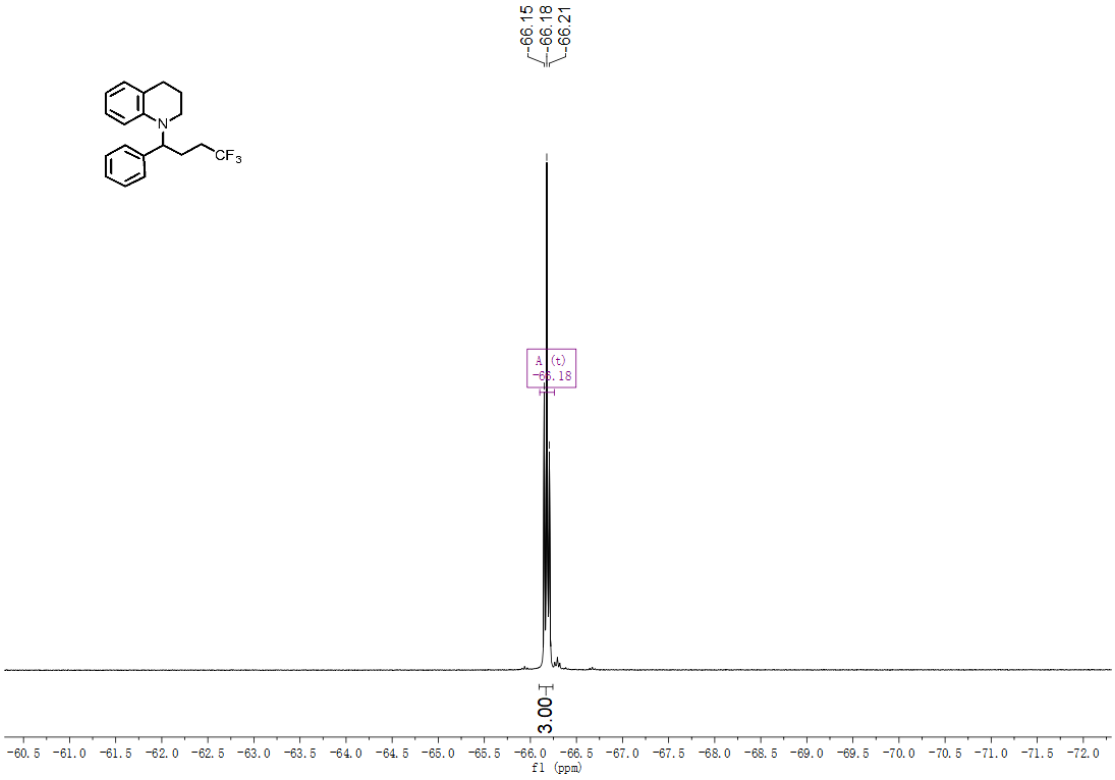
d39 ^{1}H NMR



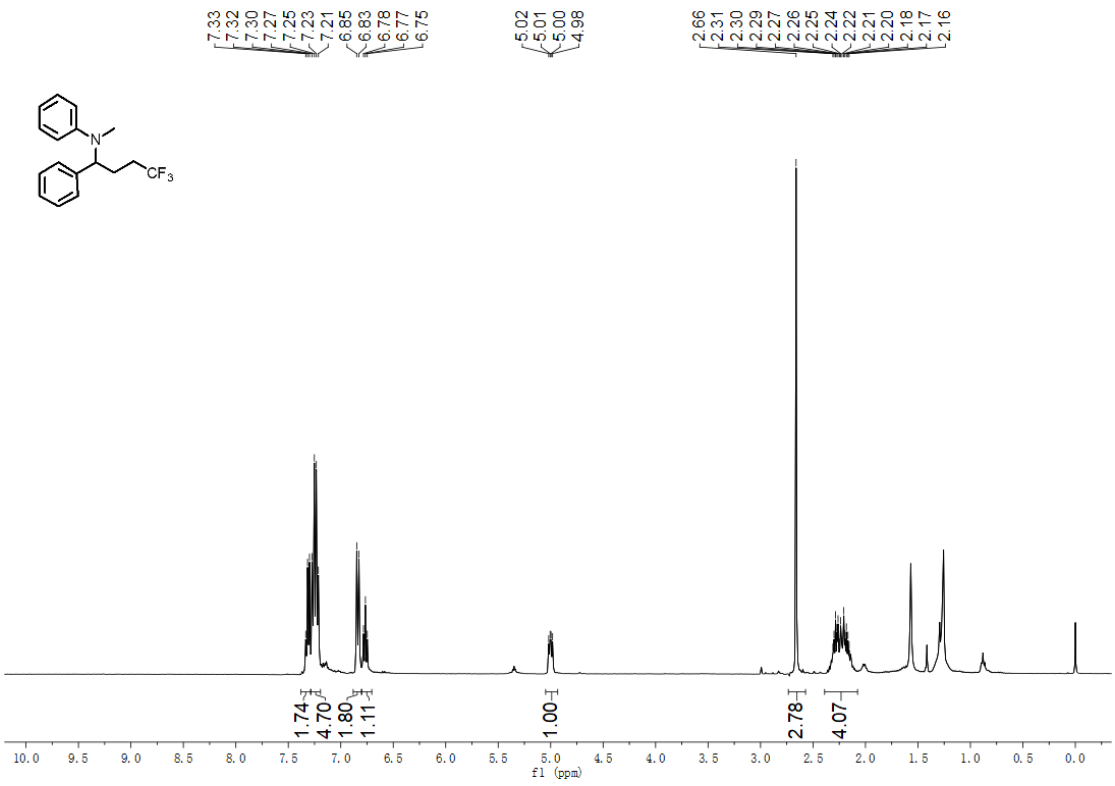
d39 ^{13}C NMR



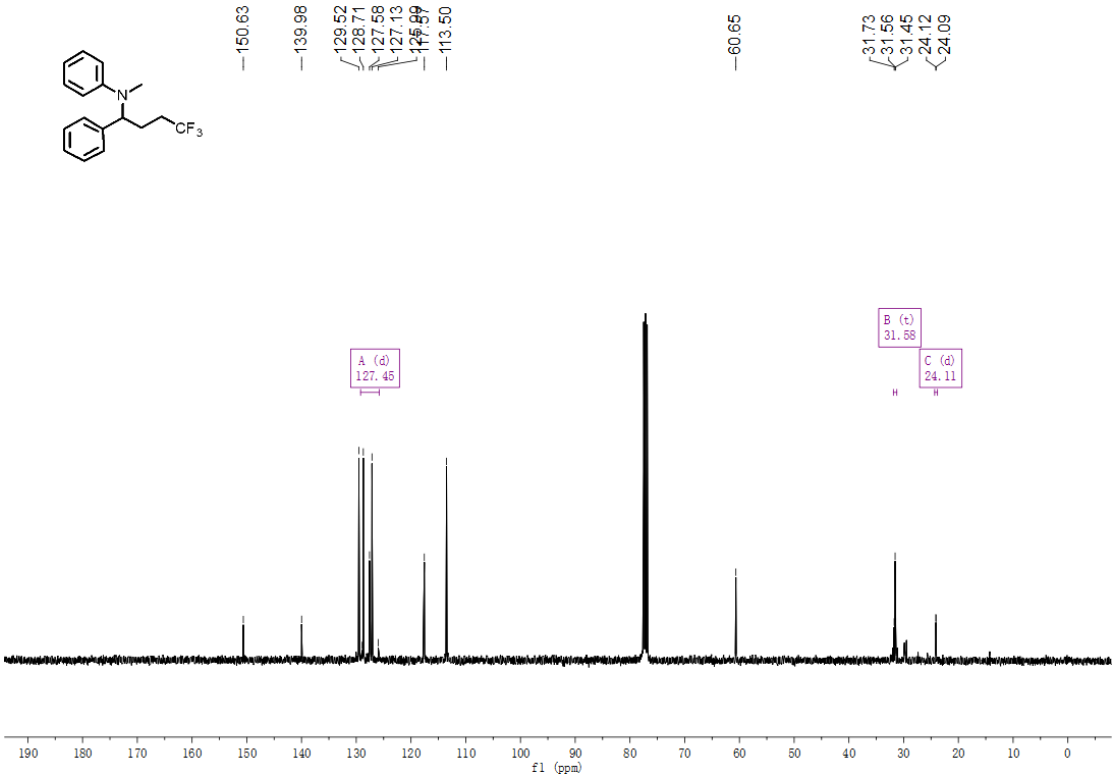
d39 ^{19}F NMR



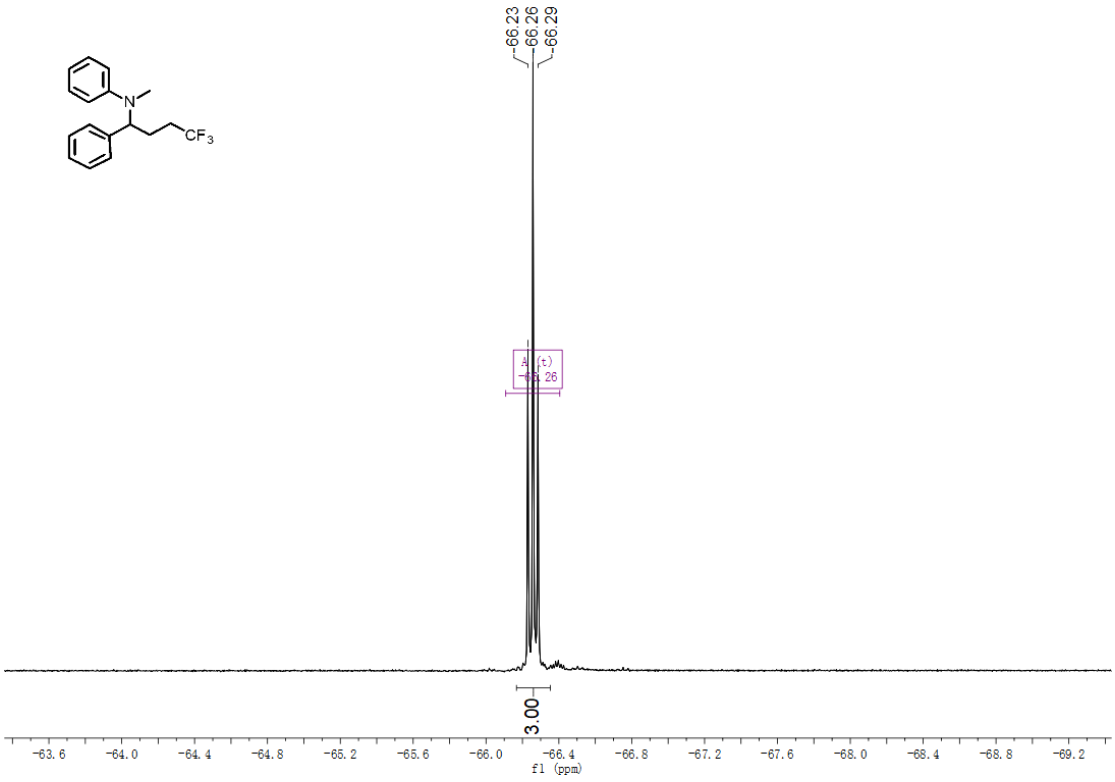
d40 ^{1}H NMR



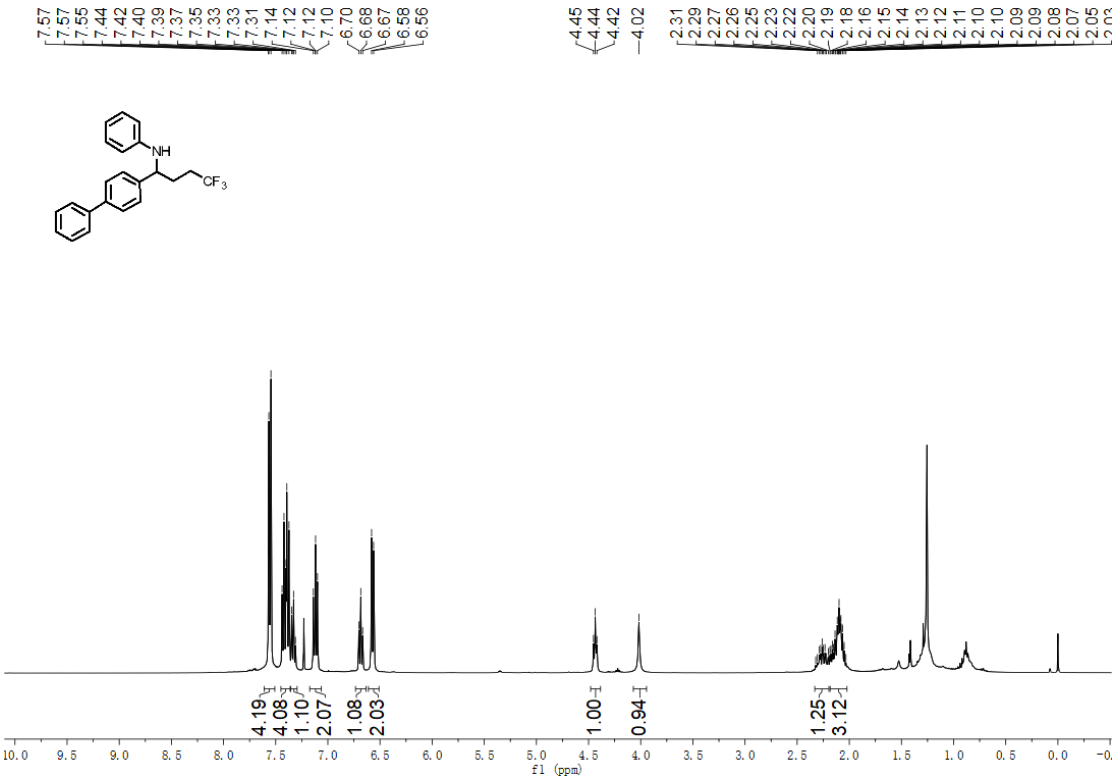
d40 ^{13}C NMR



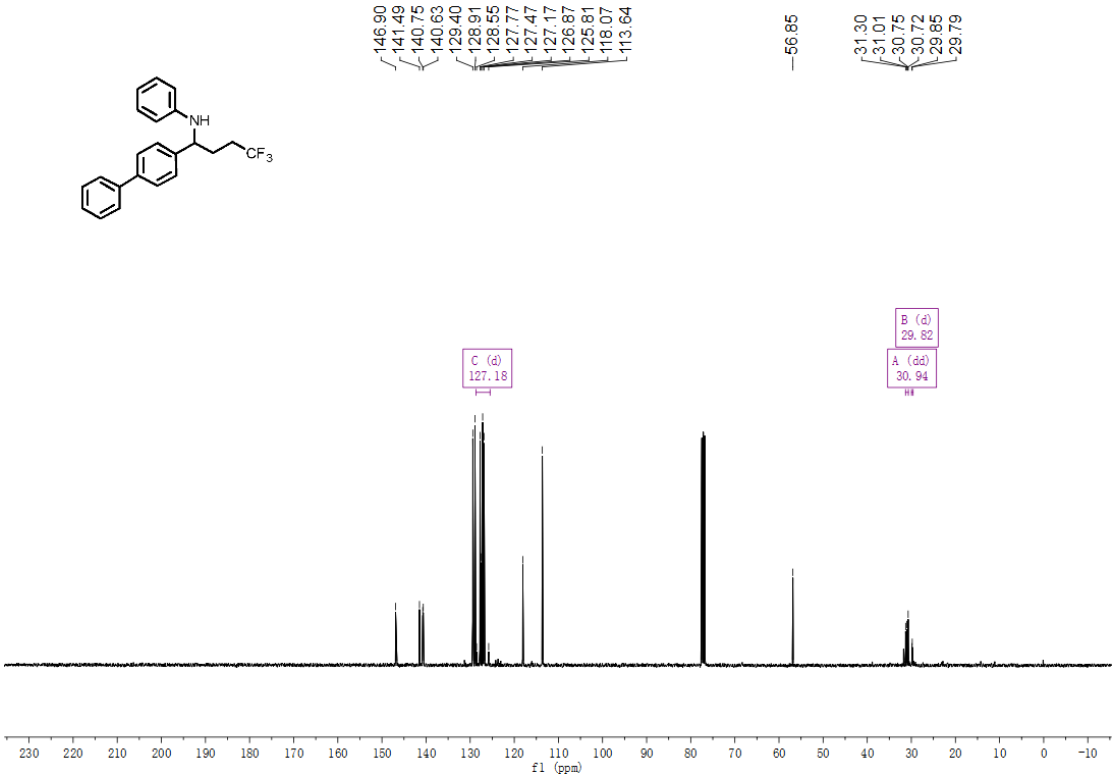
d40 ^{19}F NMR



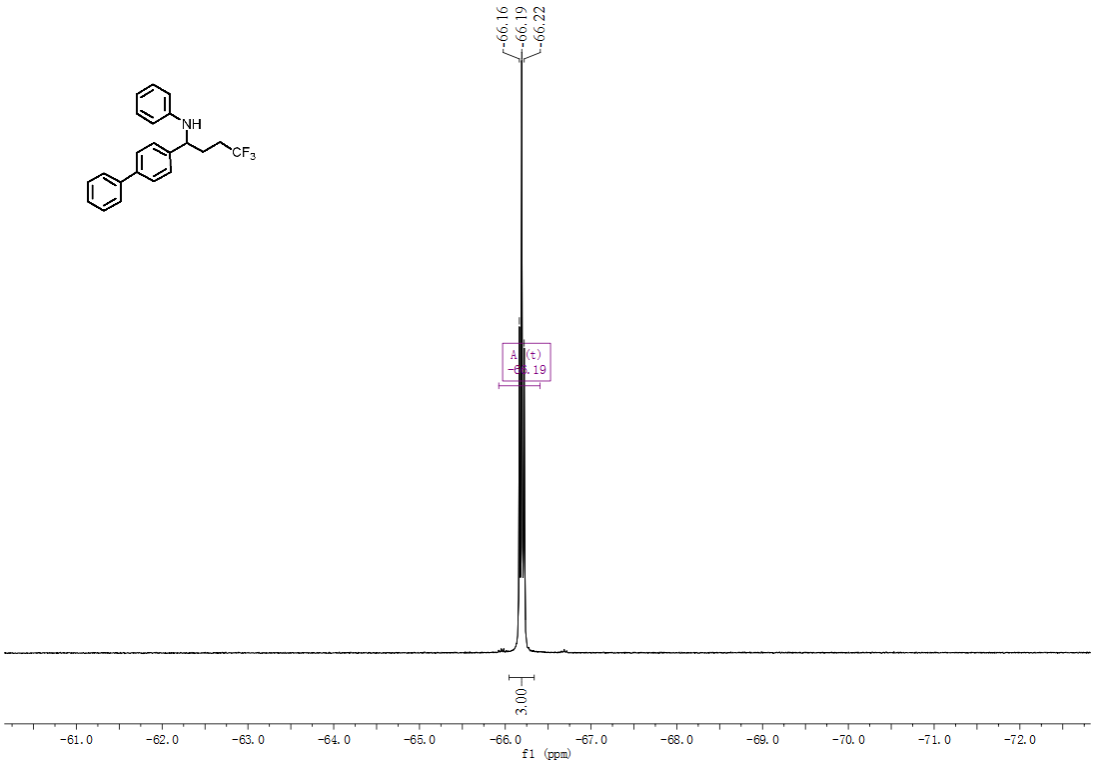
d41 ^{1}H NMR



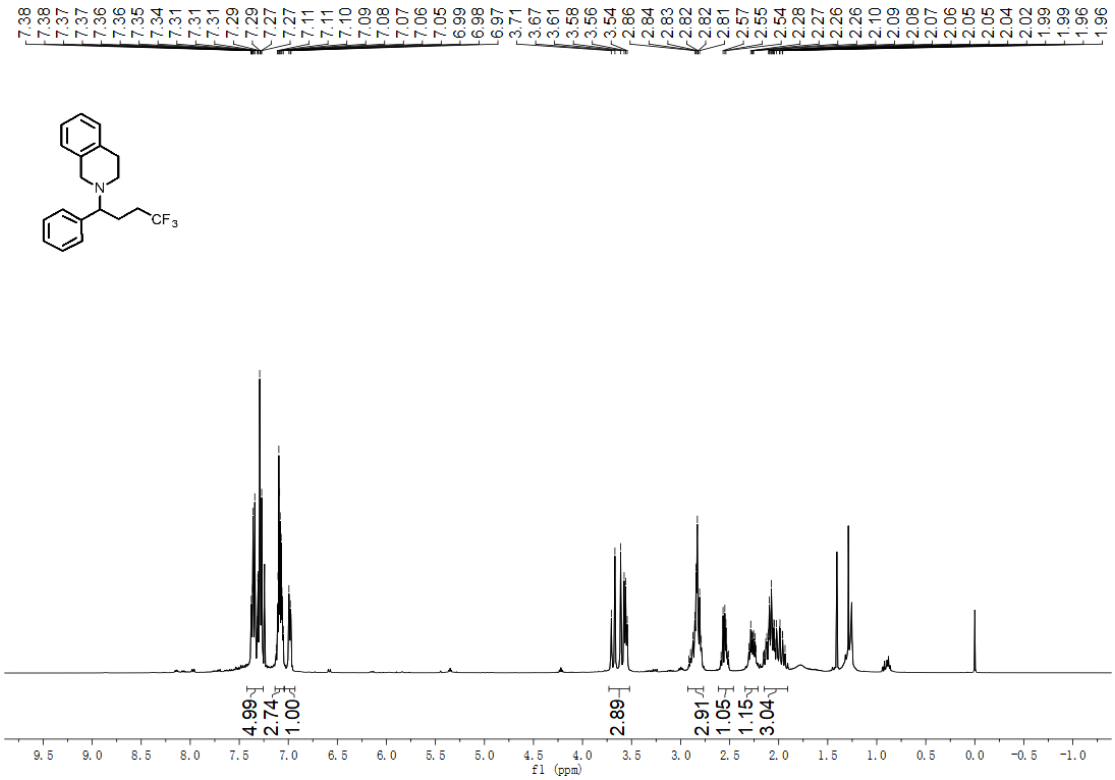
d41 ^{13}C NMR



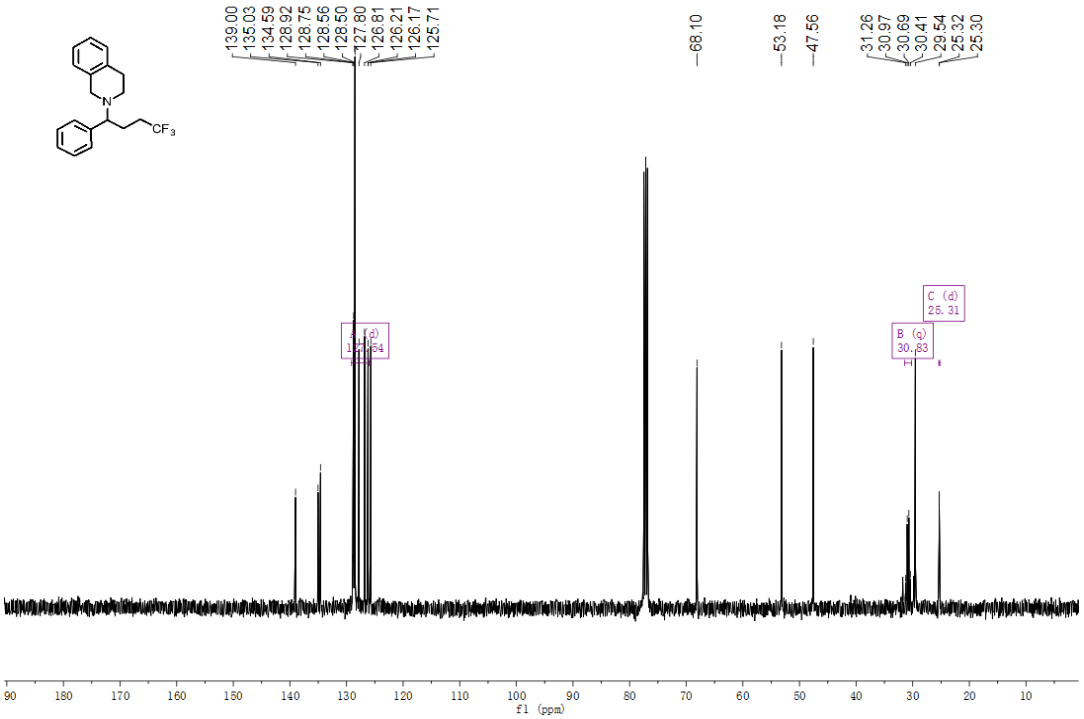
d41 ^{19}F NMR



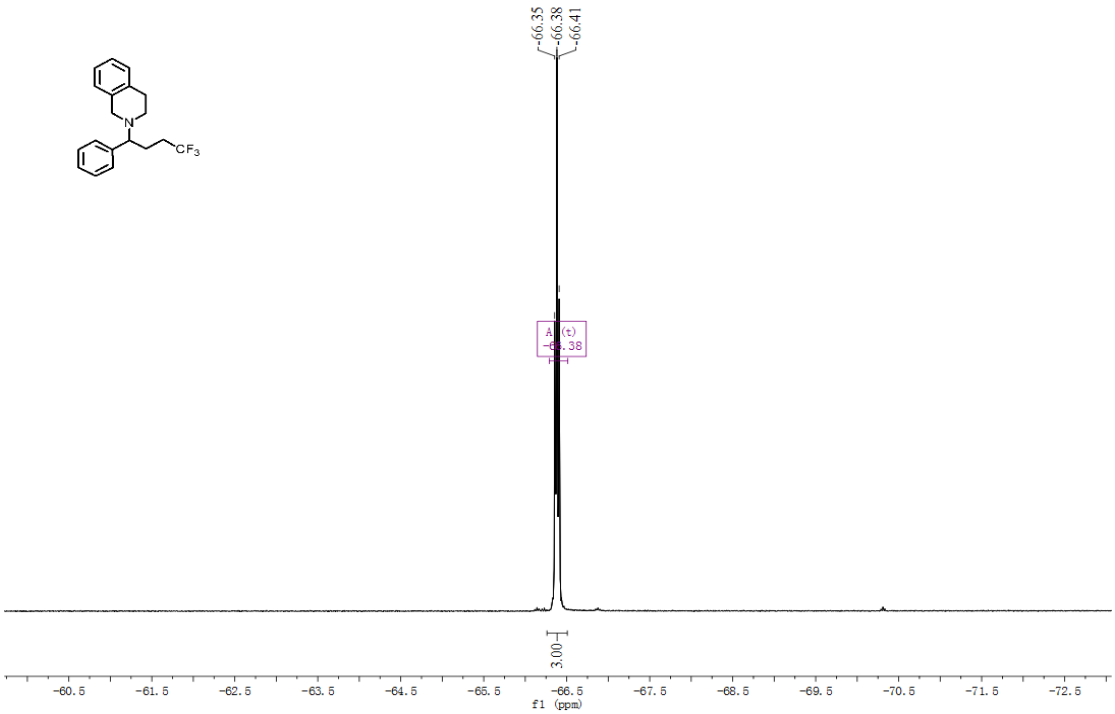
d42 ^{1}H NMR



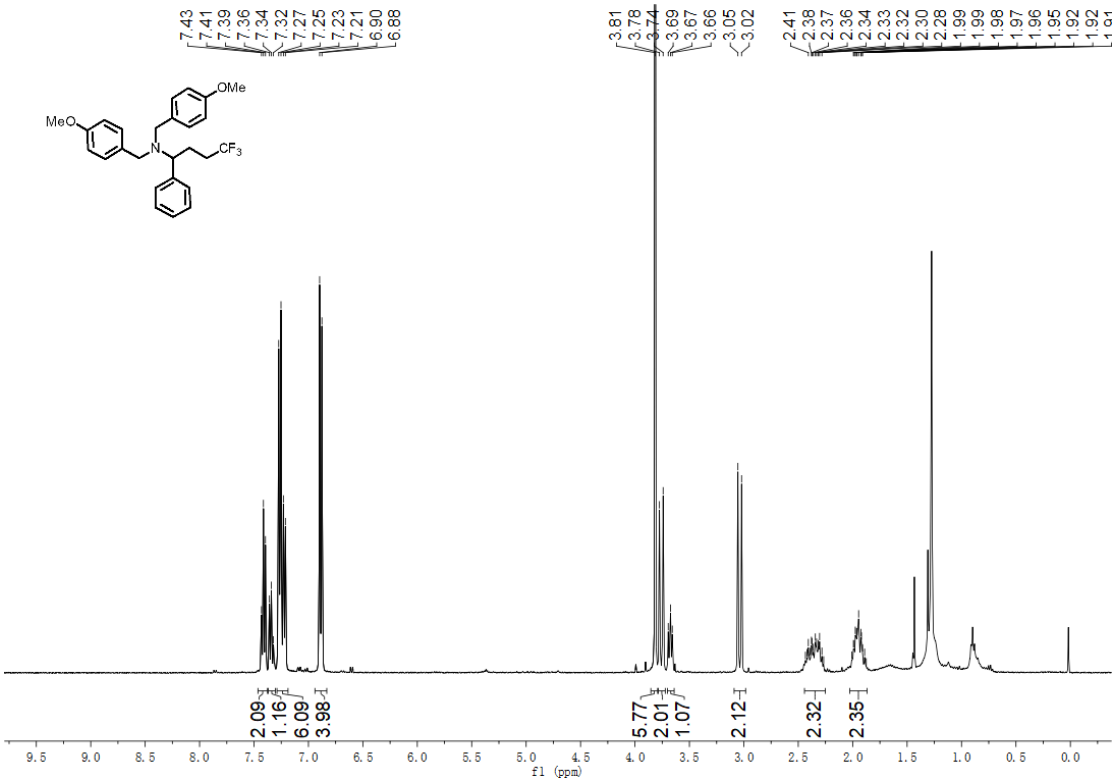
d42 ^{13}C NMR



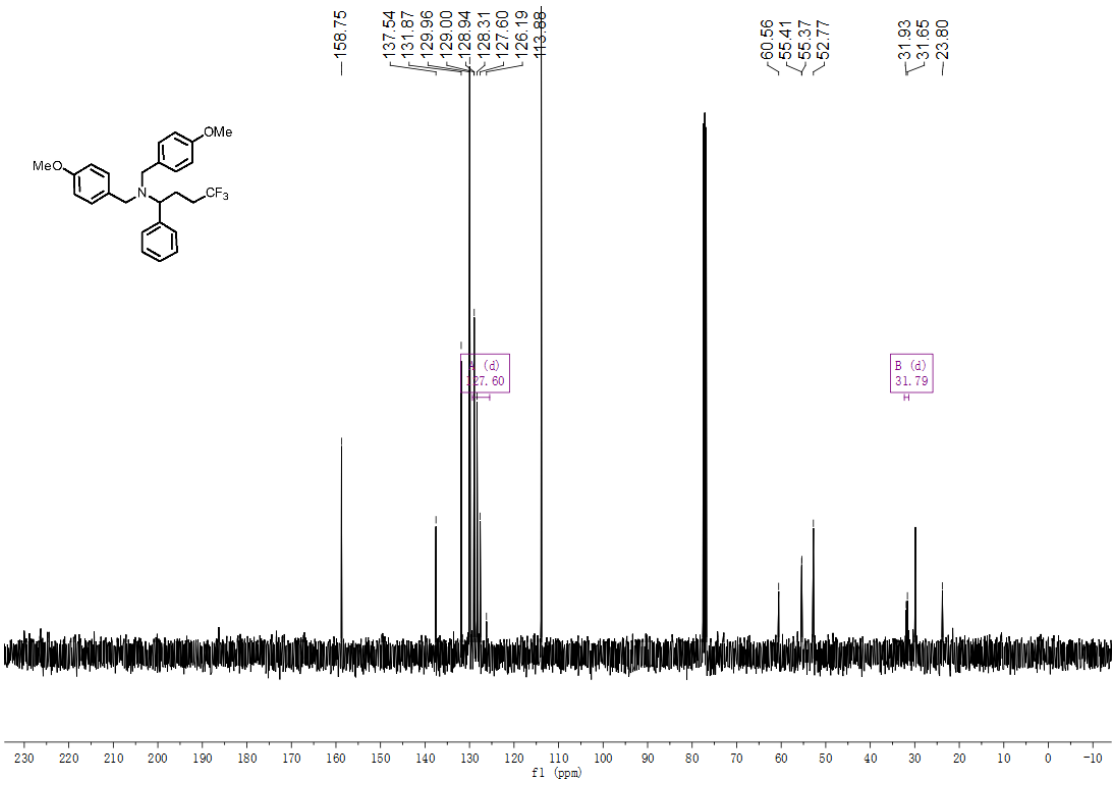
d42 ^{19}F NMR



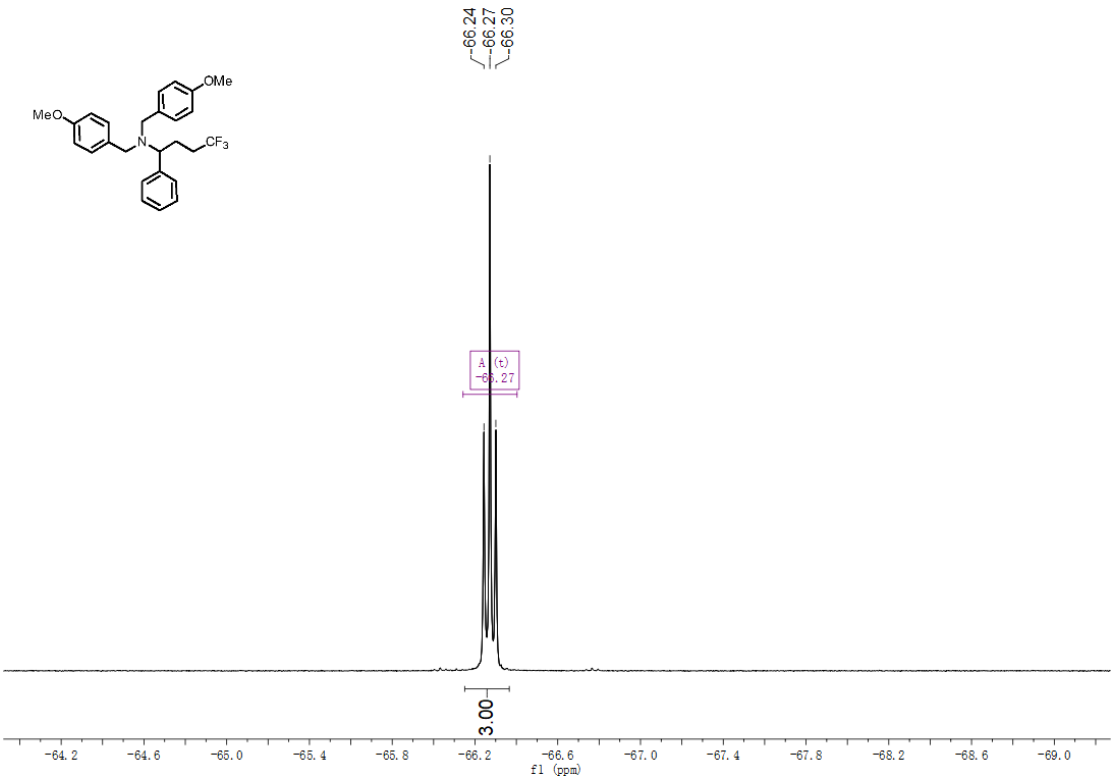
d43 ^{1}H NMR



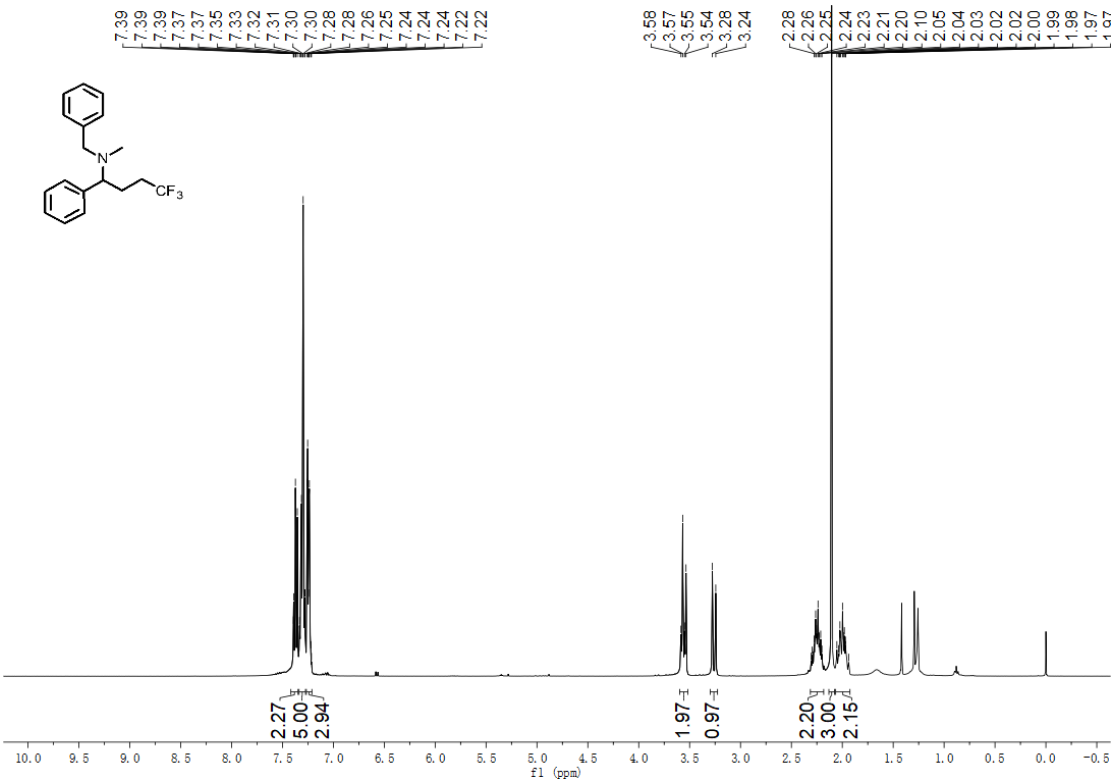
d43 ^{13}C NMR



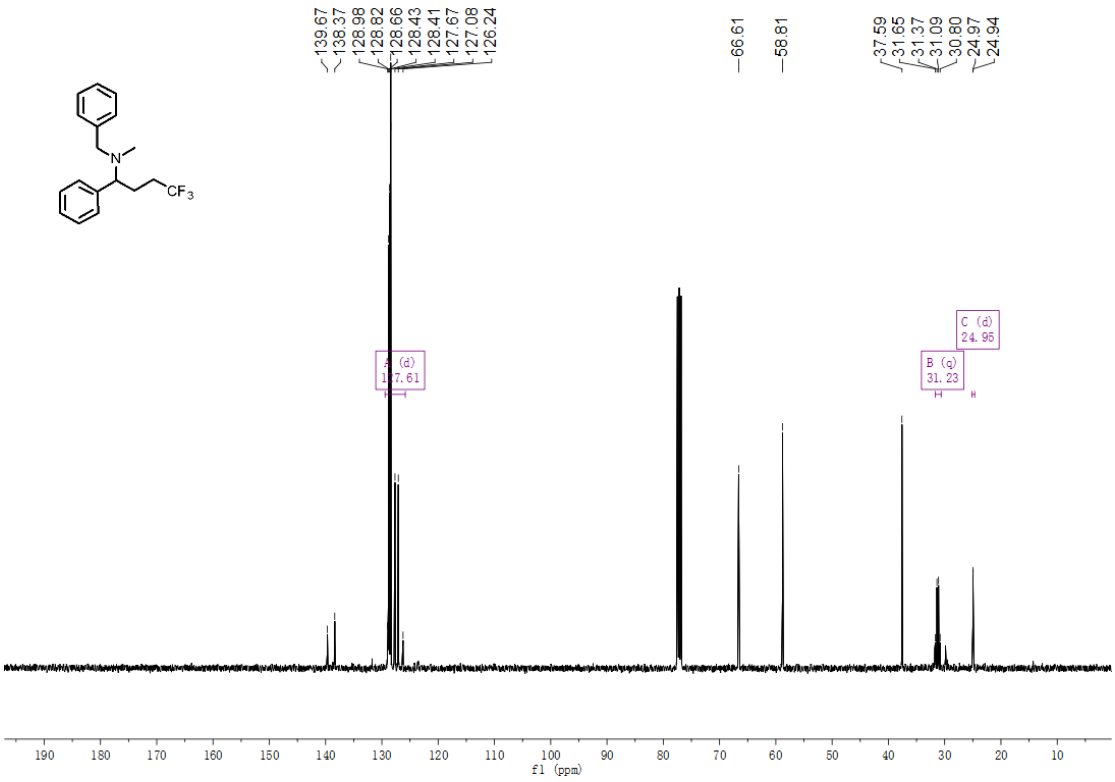
d43 ^{19}F NMR



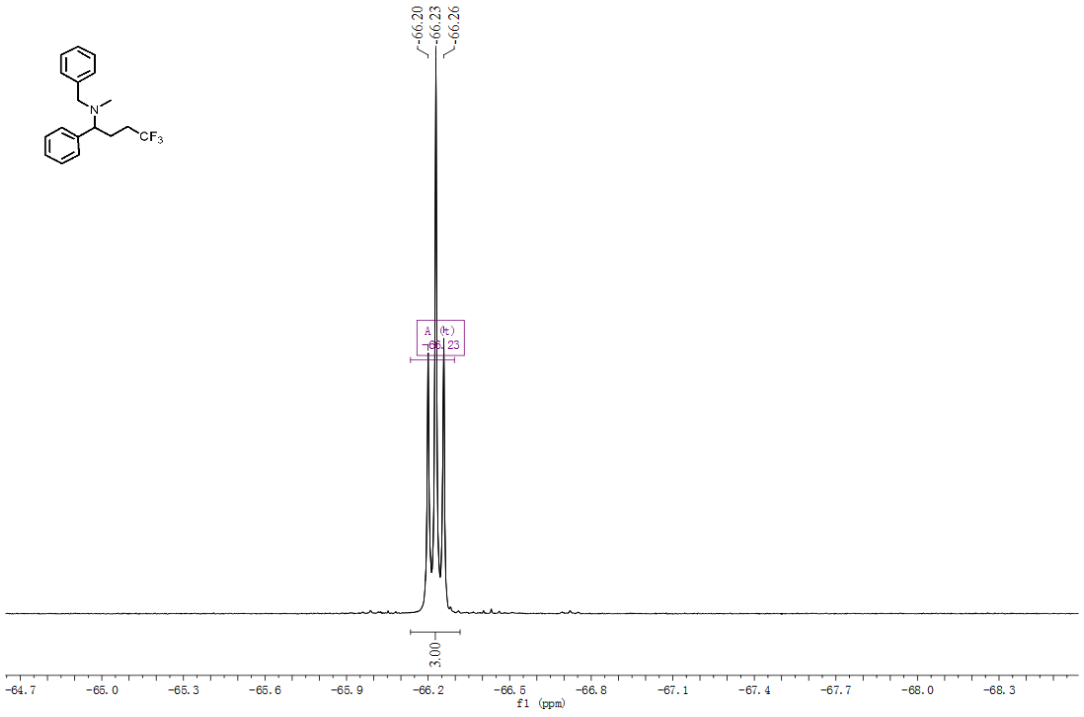
d44 ^{1}H NMR



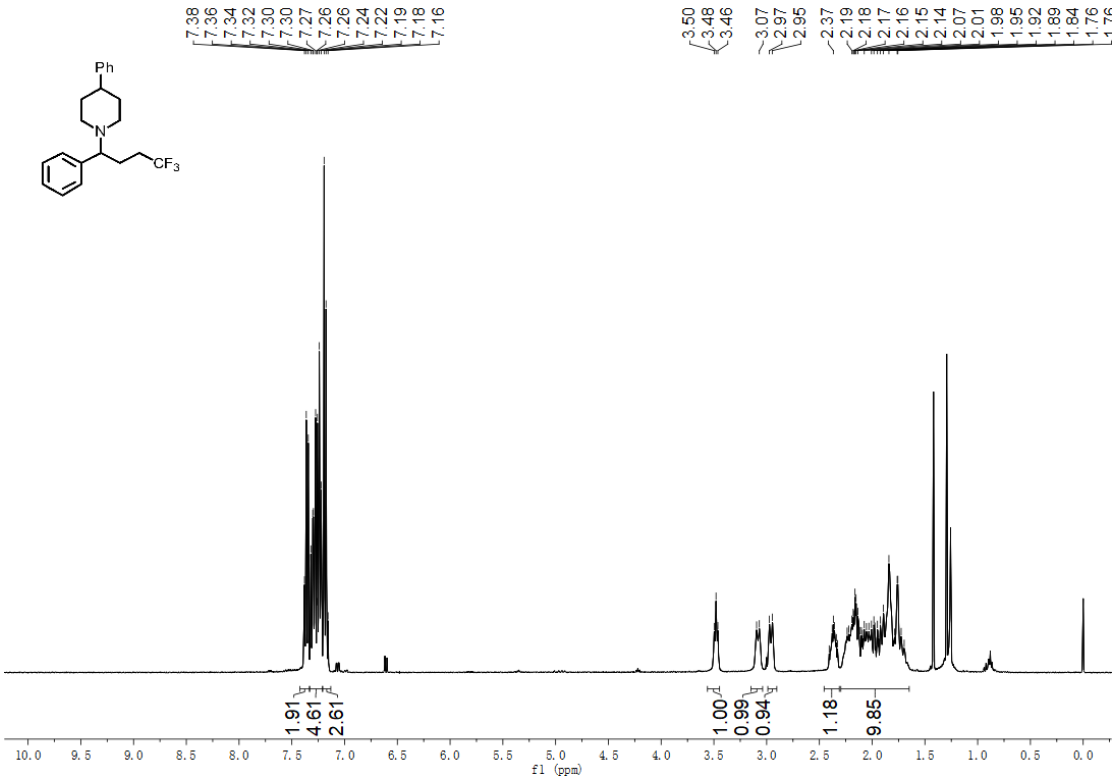
d44 ^{13}C NMR



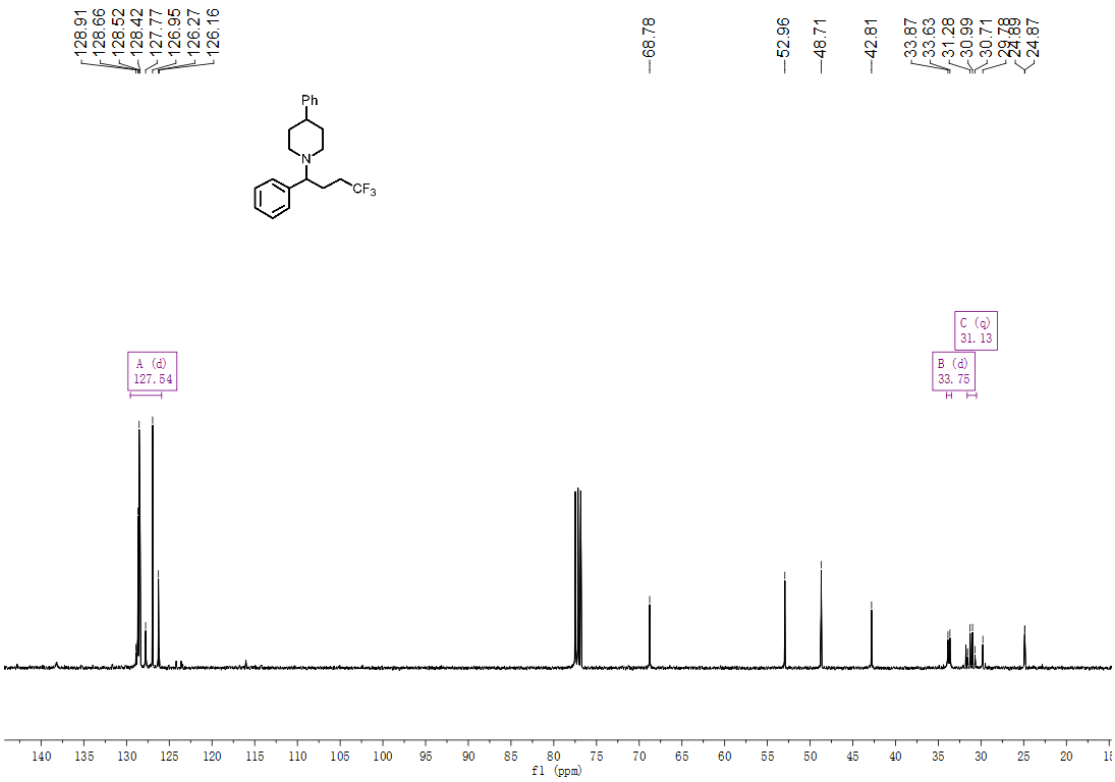
d44 ^{19}F NMR



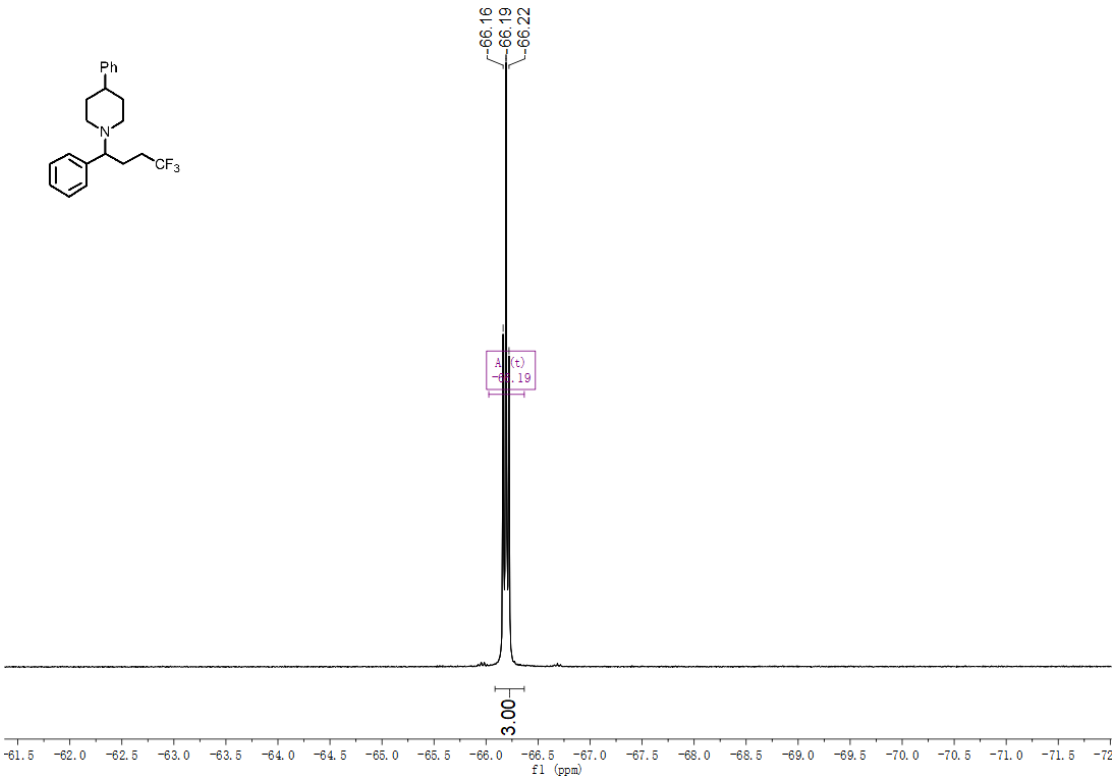
d45 ^{1}H NMR



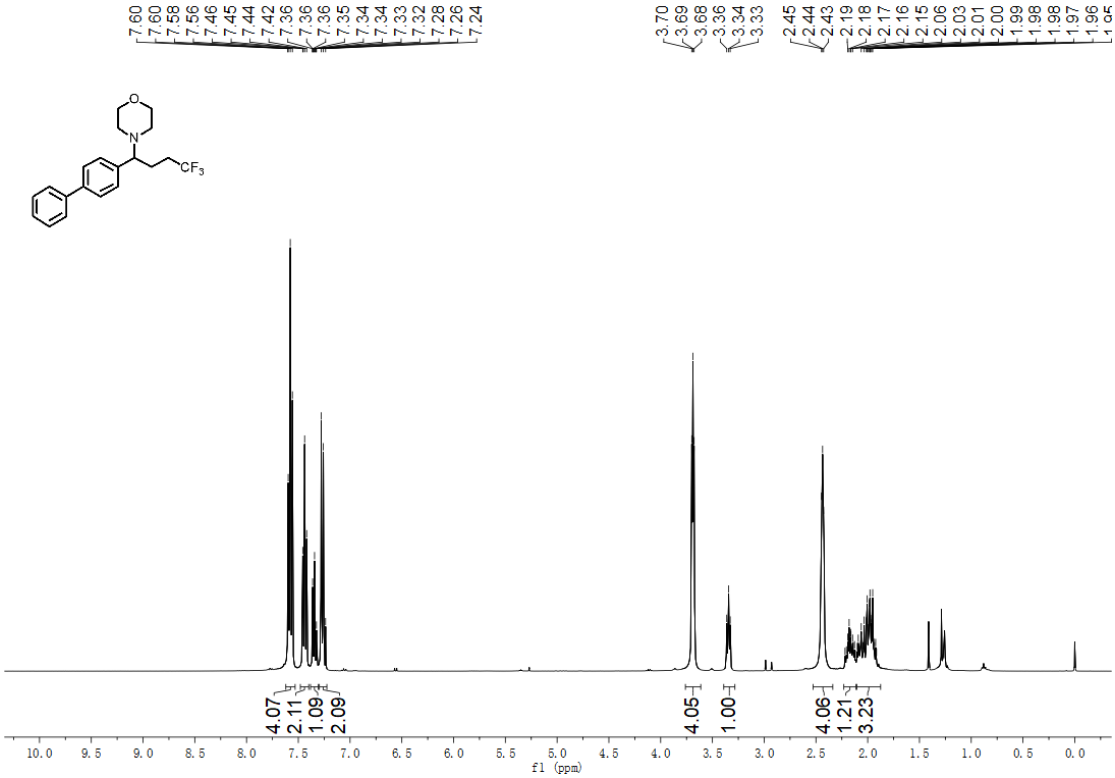
d45 ^{13}C NMR



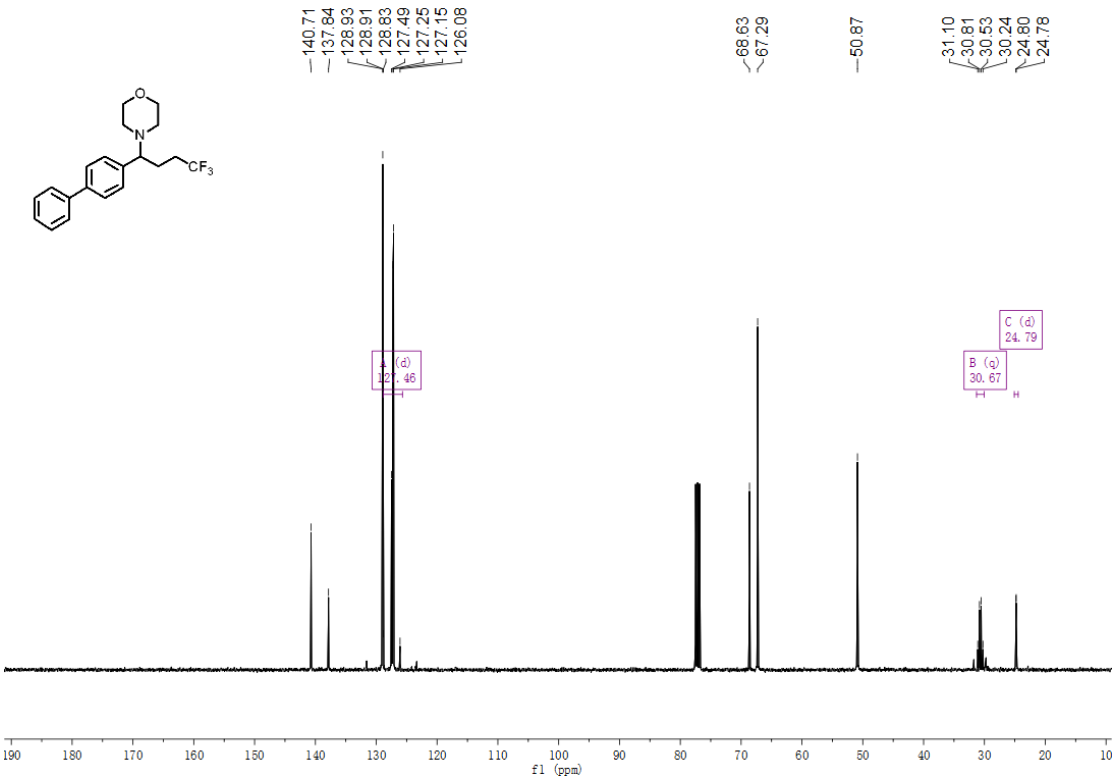
d45 ^{19}F NMR



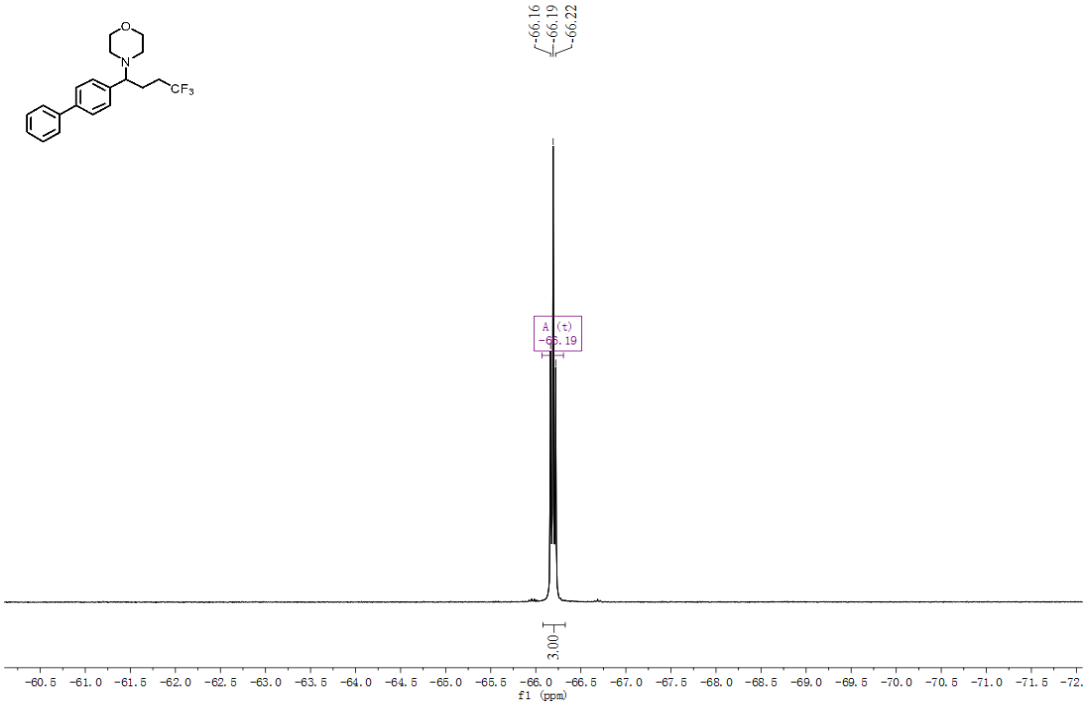
d46 ^{1}H NMR



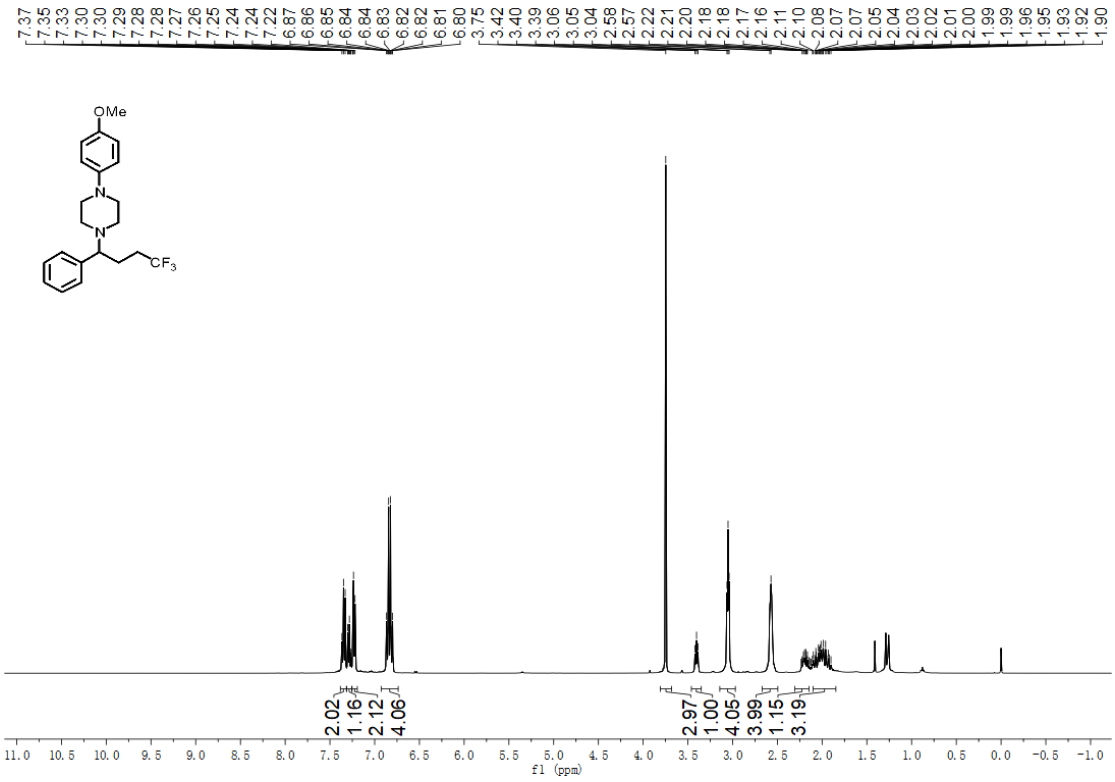
d46 ^{13}C NMR



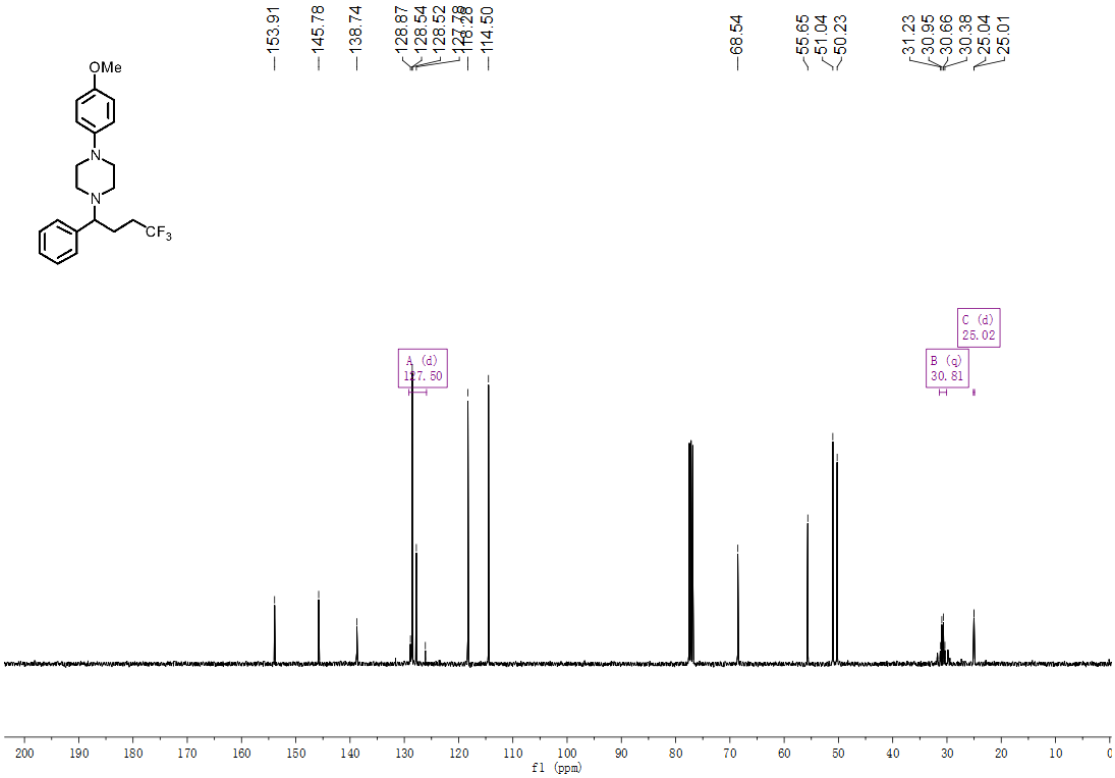
d46 ^{19}F NMR



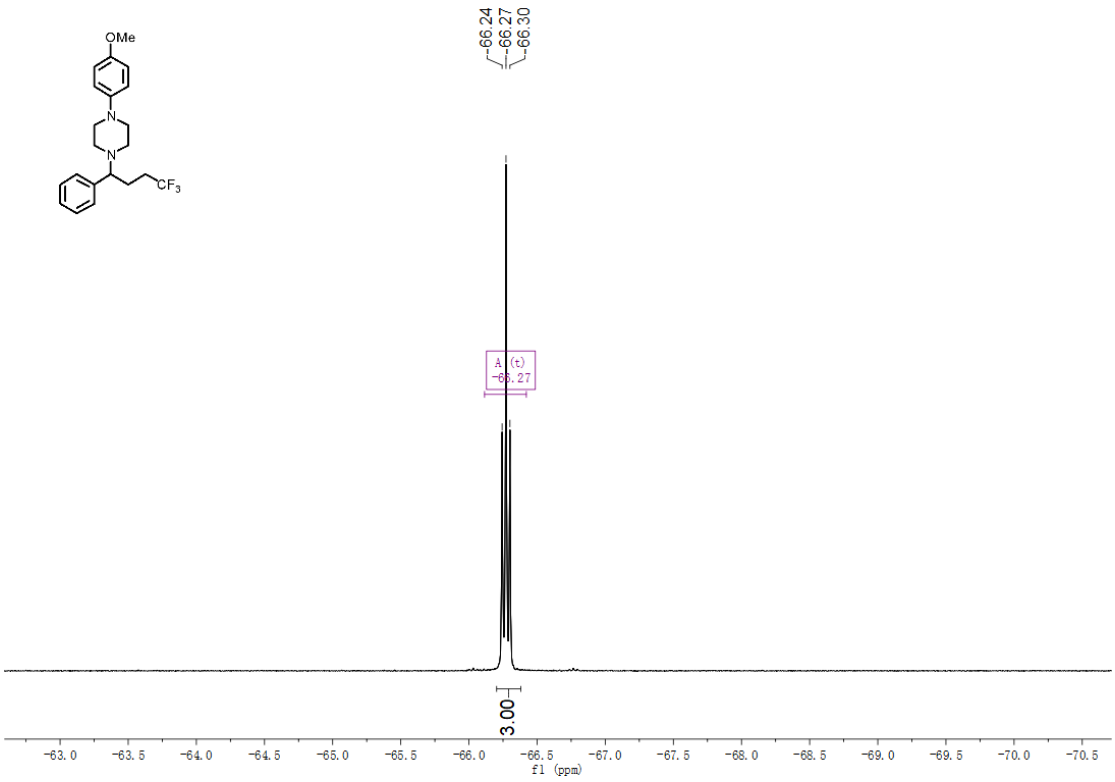
d47 ^{1}H NMR



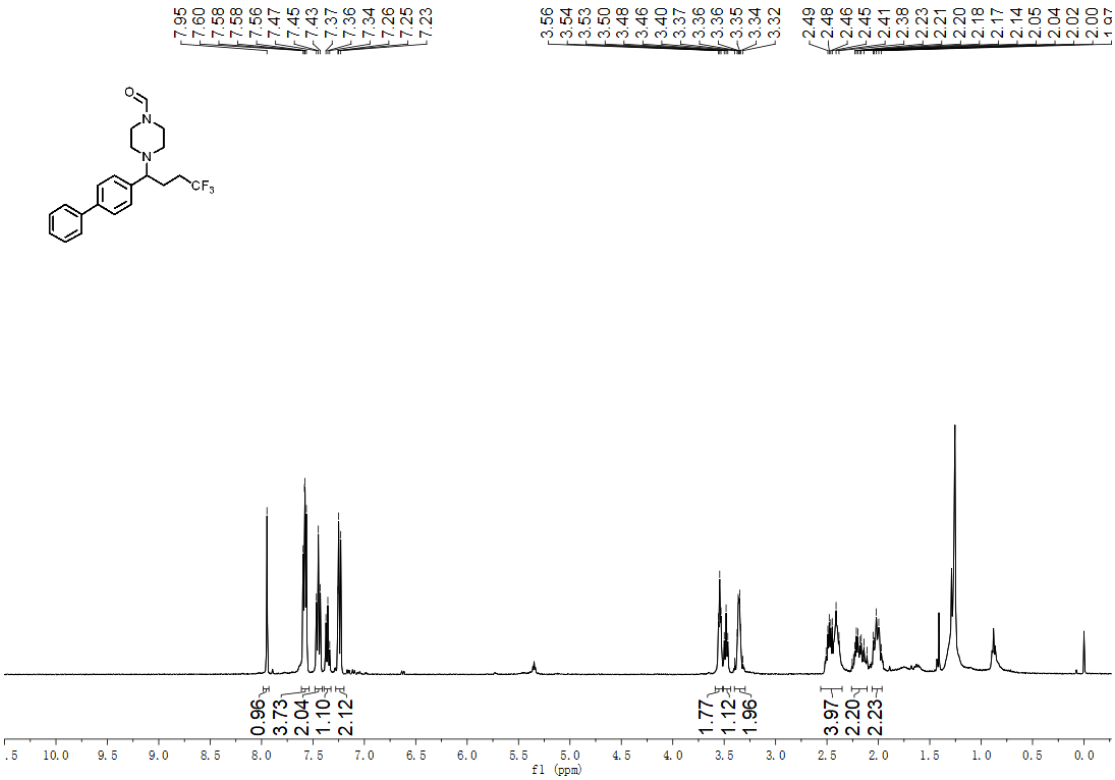
d47 ^{13}C NMR



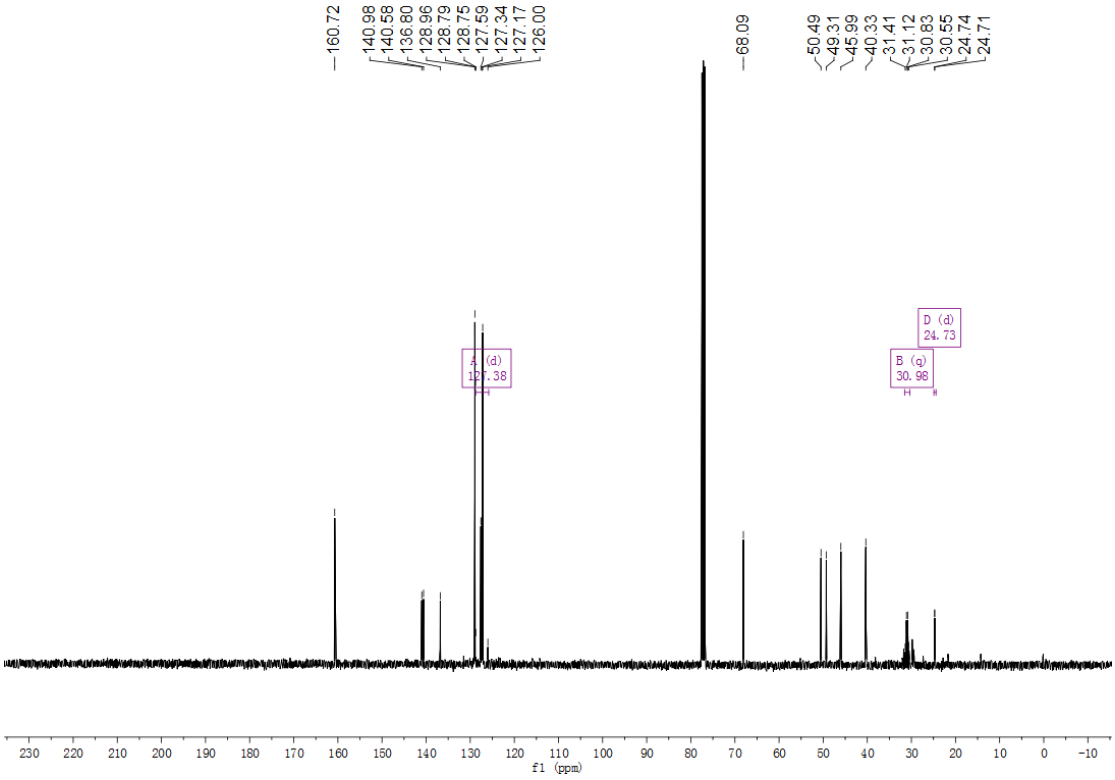
d47 ^{19}F NMR



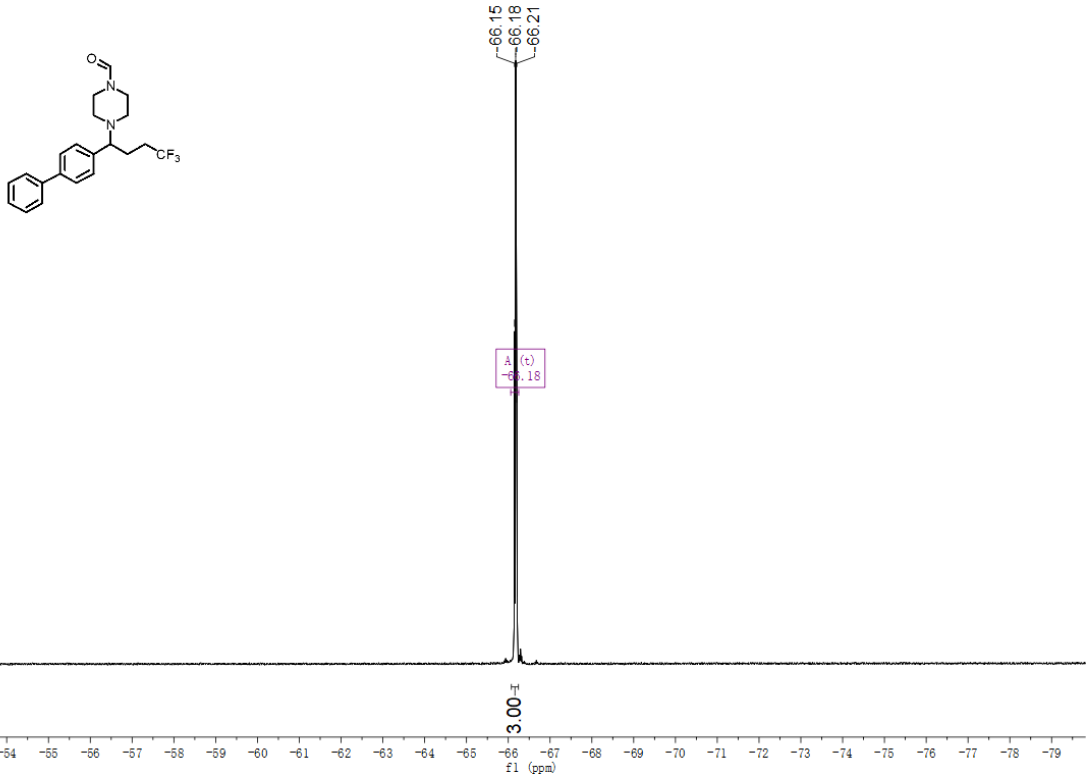
d48 ^{1}H NMR



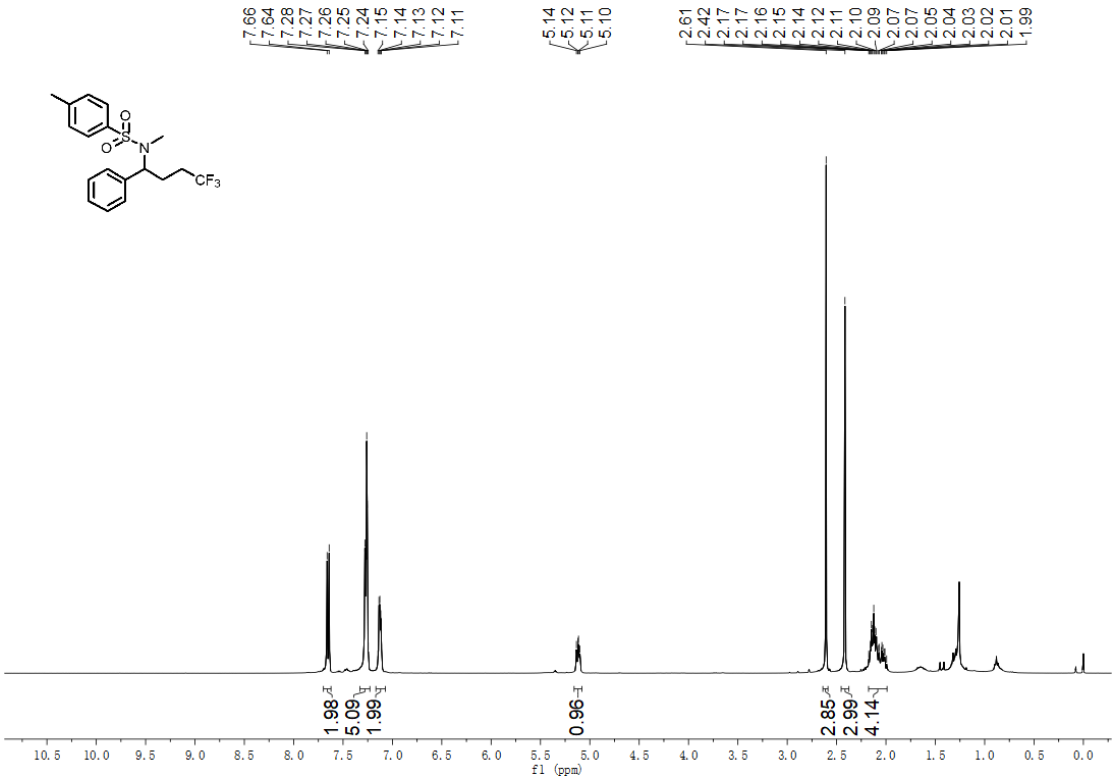
d48 ^{13}C NMR



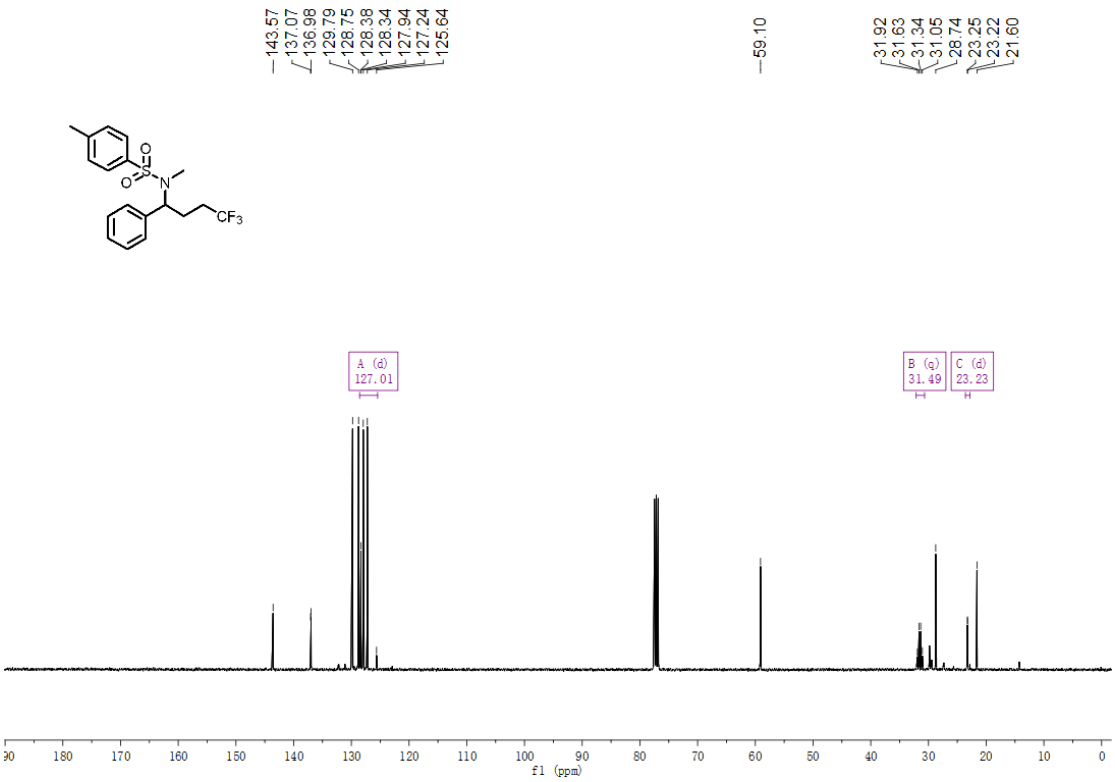
d48 ^{19}F NMR



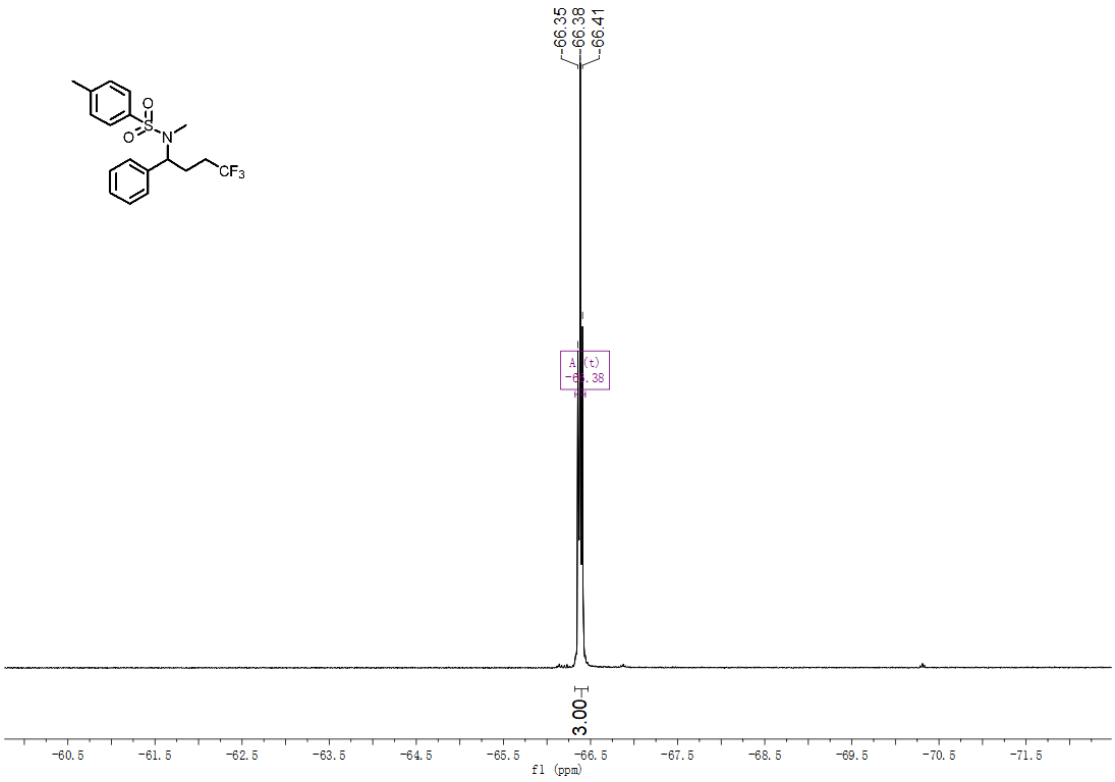
d49 ^{1}H NMR



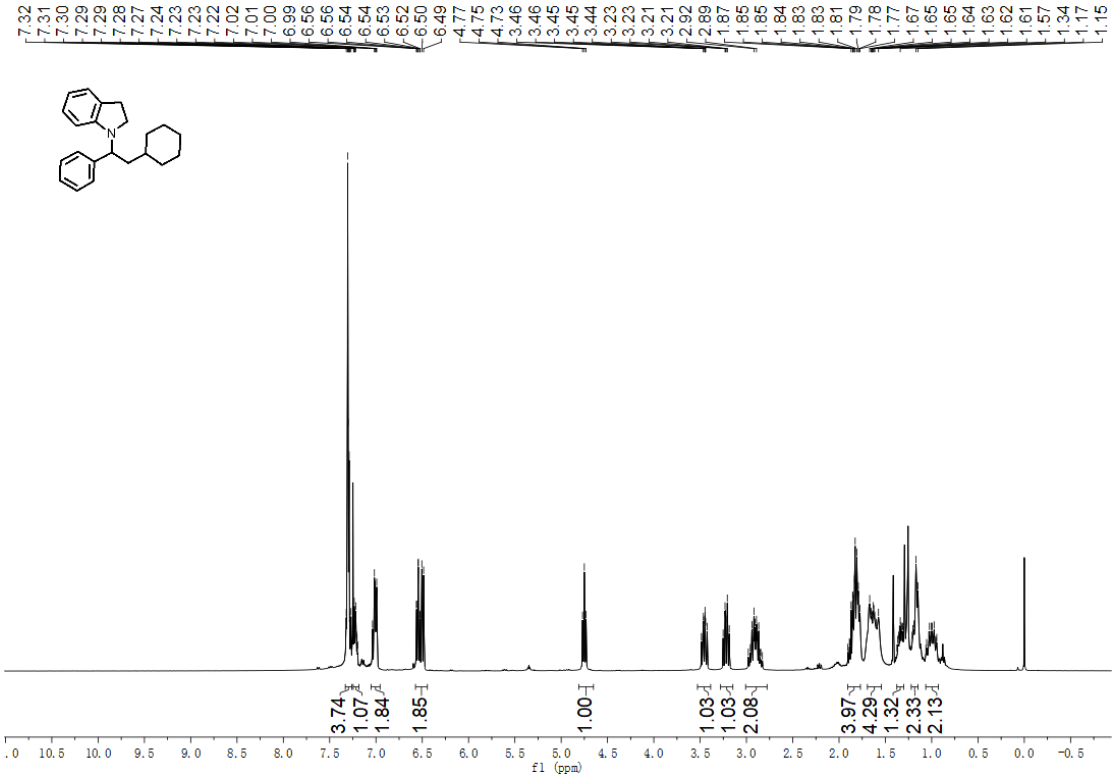
d49 ^{13}C NMR



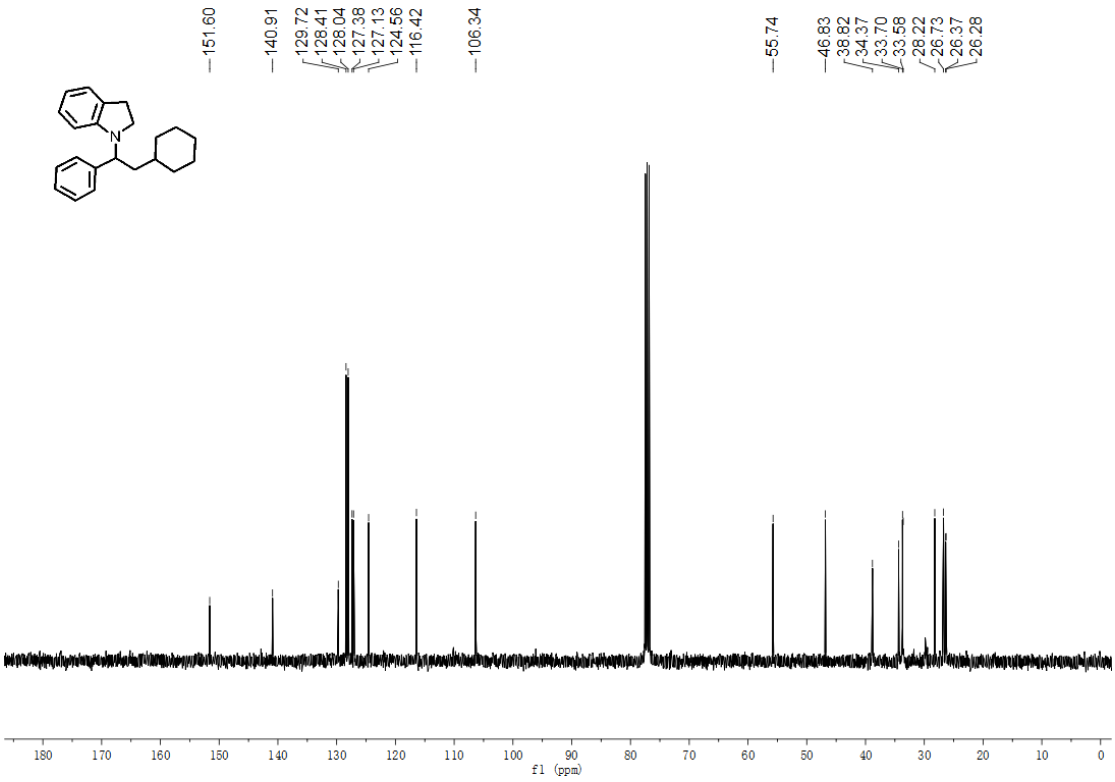
d49 ^{19}F NMR



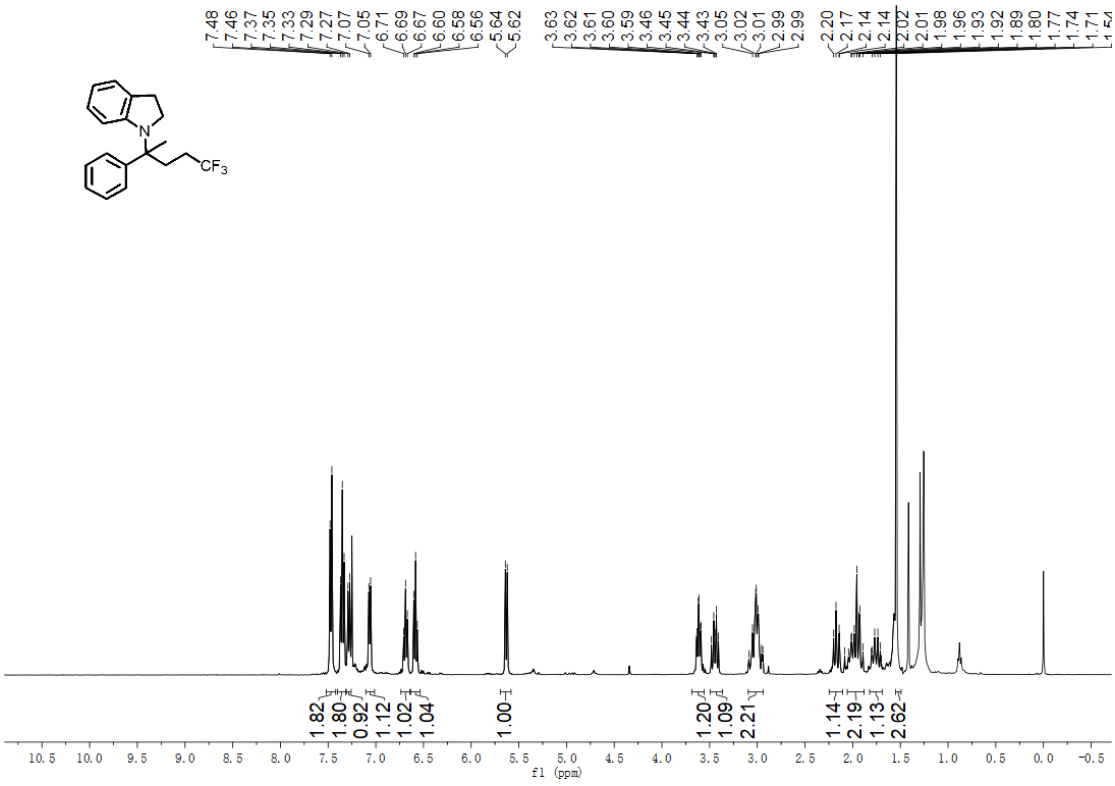
d50 ^{1}H NMR



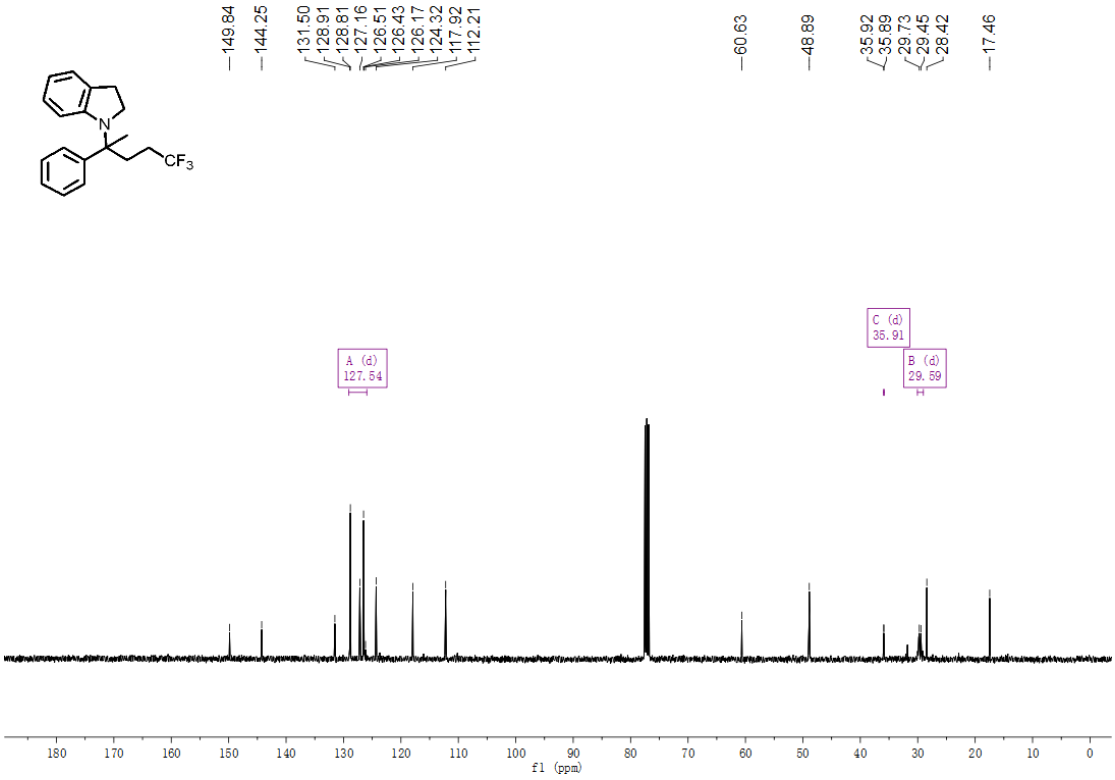
d50 ^{13}C NMR



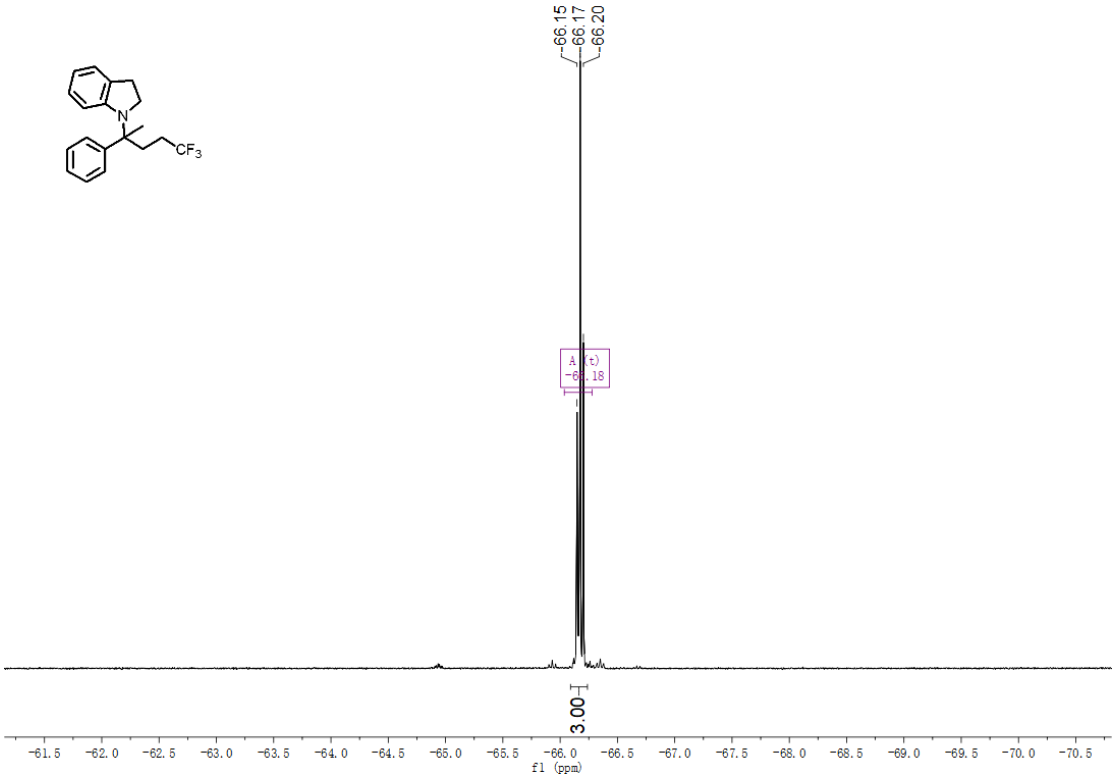
d51 ^{1}H NMR



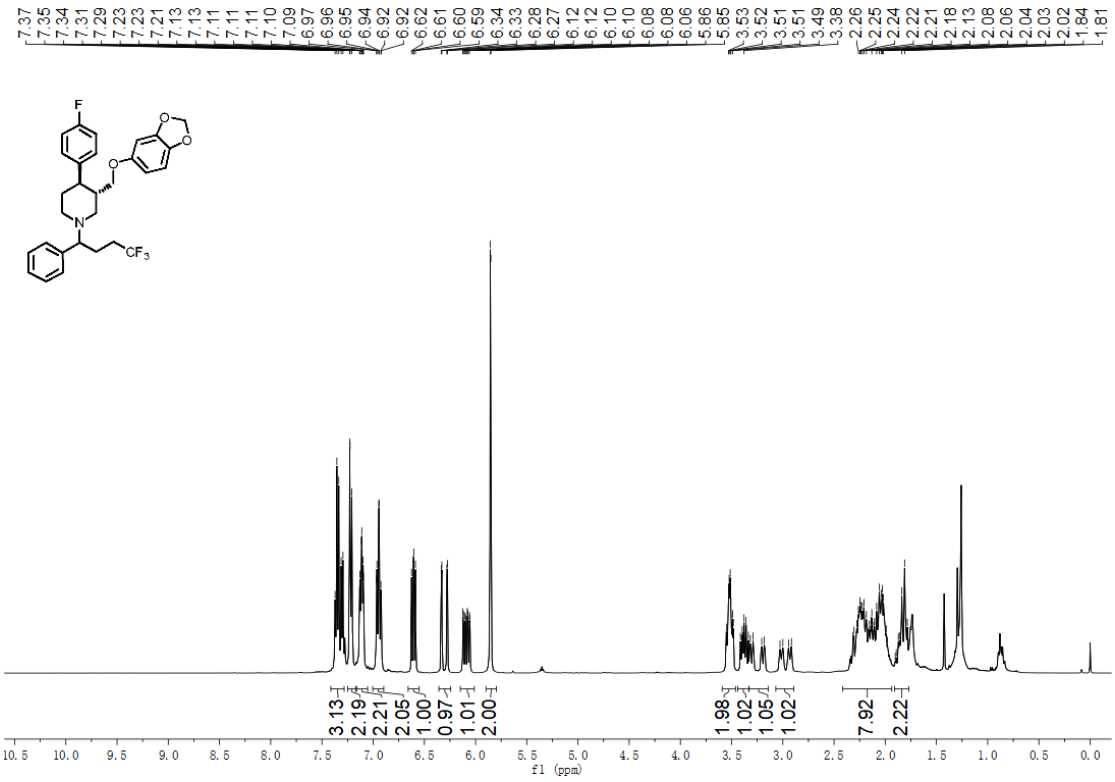
d51 ^{13}C NMR



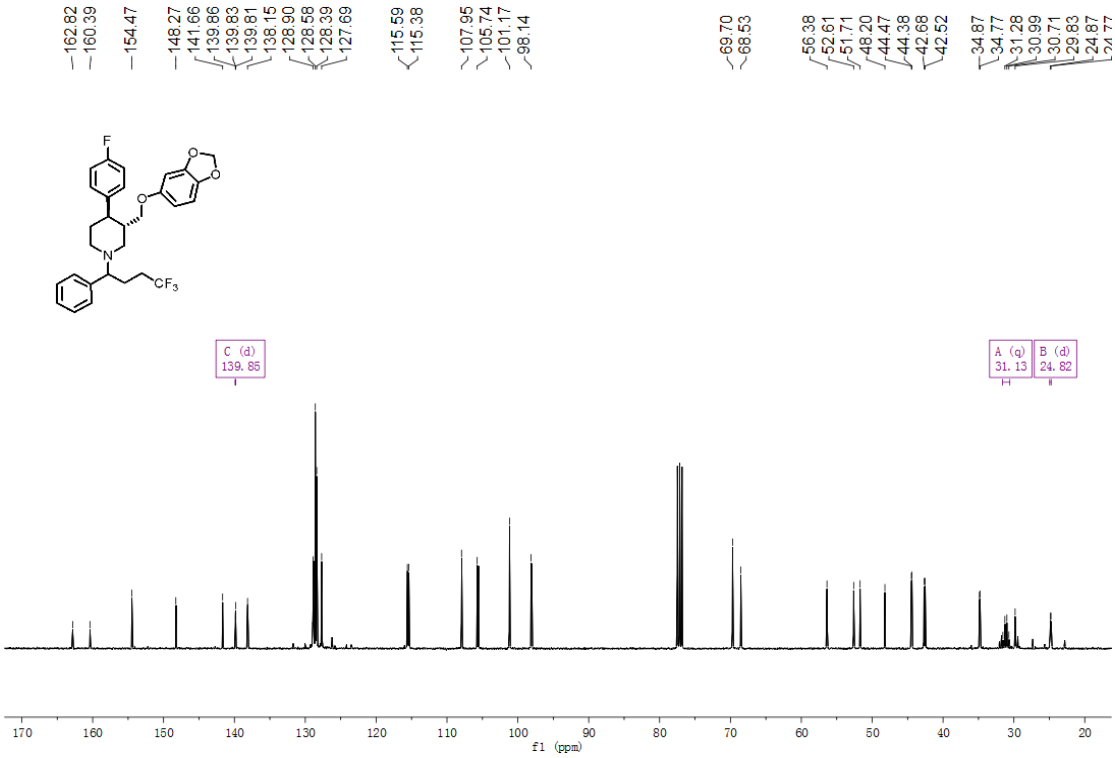
d51 ^{19}F NMR



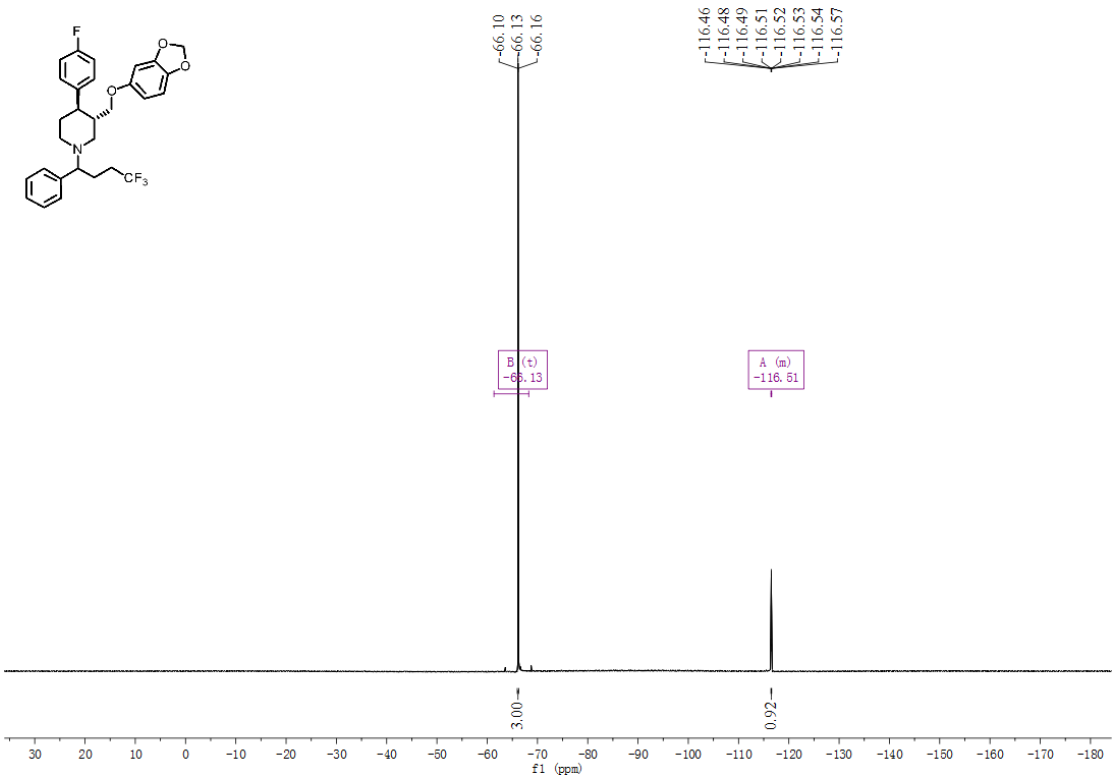
d52 ^{1}H NMR



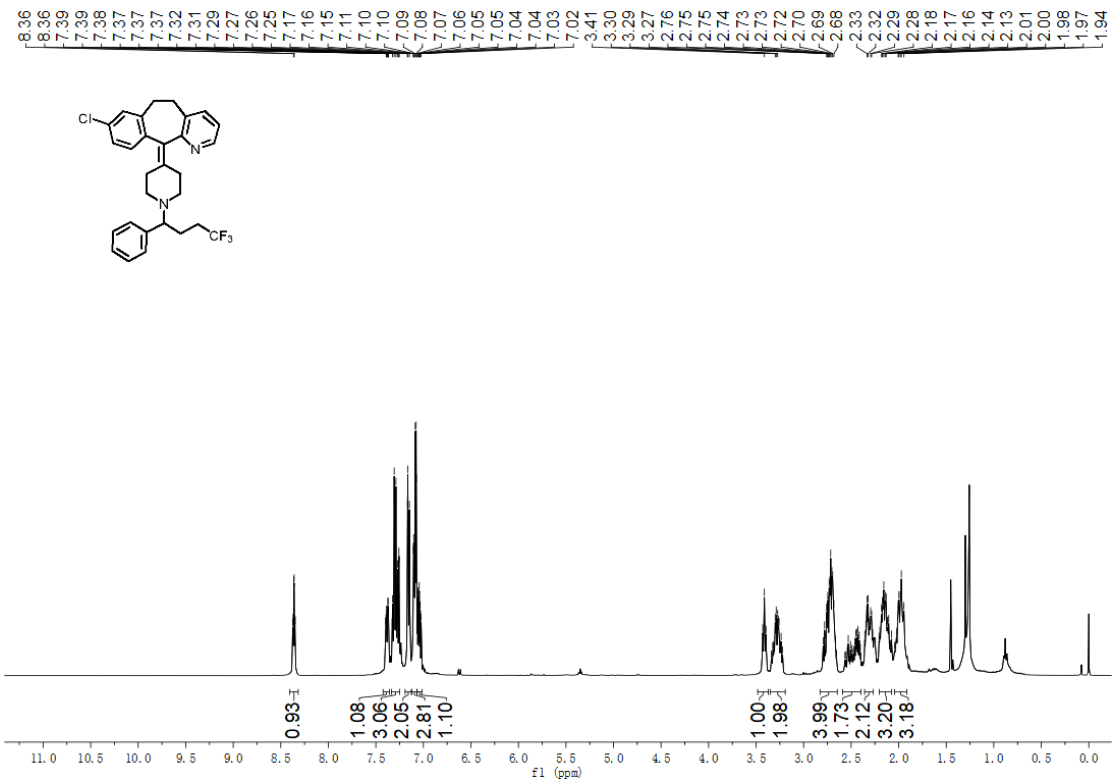
d52 ^{13}C NMR



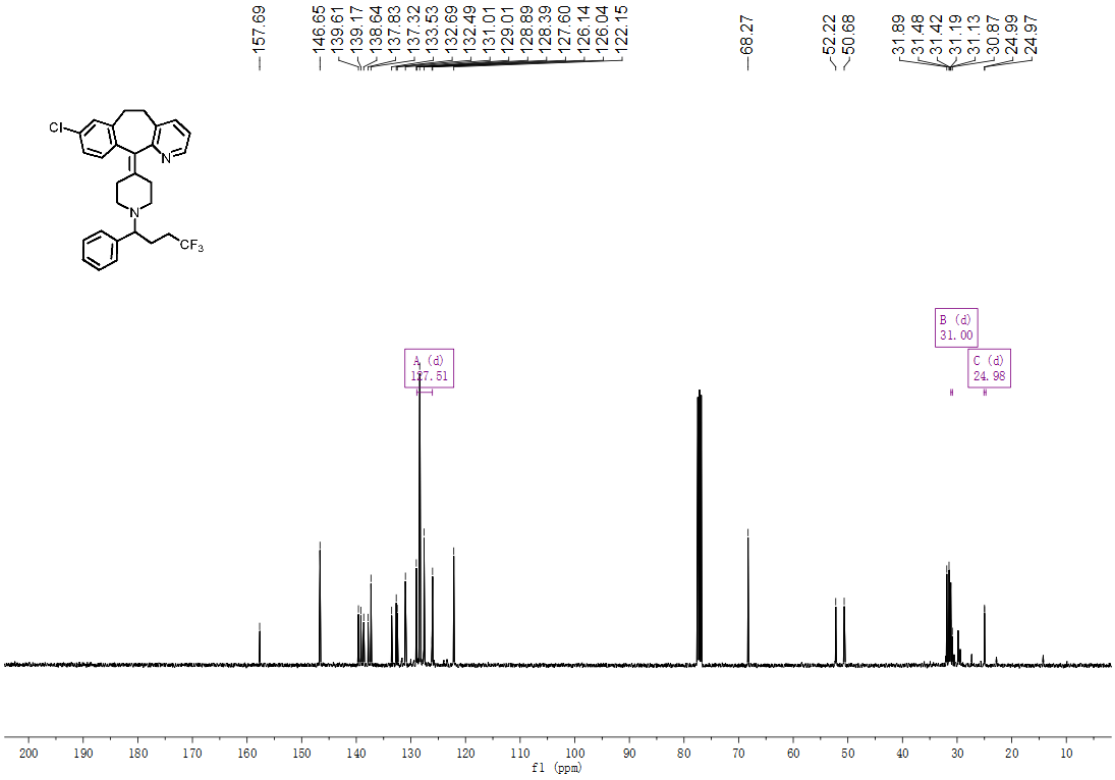
d52 ^{19}F NMR



d53 ^{1}H NMR



d53 ^{13}C NMR



d53 ^{19}F NMR