Supporting Information

Visible Light-Promoted [3+2] Cyclization Reaction of Vinyl Azides with Perfluoroalkyl-Substituted-Imidoyl Sulfoxonium Ylides

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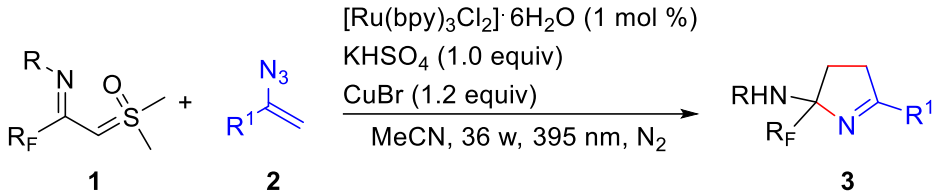
I. General Information:

All reagents were purchased and used as received from their respective suppliers unless otherwise noted. Perfluoroalkyl -substituted imidoyl sulfoxonium ylides **1** were synthesized according to known literature procedure.[1] Vinyl azides **2** were prepared according to the previous reported method.[2] Chromatography was carried on flash silica gel (300-400 mesh). All reactions were monitored by TLC, which was performed on percolated aluminum sheets of silica gel 60 (F254). Unless noted, the ^{1}H NMR spectra were recorded at 500 MHz and 600 MHz in $CDCl_3$, the ^{13}C NMR spectra were recorded at 151 MHz in $CDCl_3$ with TMS as internal standard, and the ^{19}F NMR spectra were recorded at 565 MHz in $CDCl_3$. All coupling constants (*J* values) were reported in Hertz (Hz). High-resolution mass spectra (HRMS) were obtained using a Bruker microTOF II focus spectrometer (ESI). UV-vis absorption analysis using HITACHI U-3900. The light source were used 18×2 W purple LEDs (manufacturer: GANGSHI lighting, model: PAR38, wavelength range: 380-410 nm, λ max = 395 nm), with wrap in foil, less than 5cm from the light source to the irradiation vessel.

II. General Procedure for the Preparation of 3 (3aa as example):

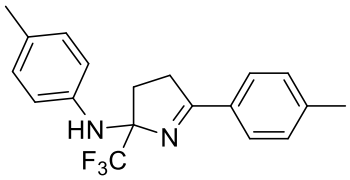


A sealed tube equipped with a magnetic stir bar was charged with perfluoroalkyl -substituted imidoyl sulfoxonium ylide **1a** (0.6 mmol, 166.4 mg), vinyl azide **2a** (0.2 mmol, 31.8 mg), $[Ru(bpy)_3Cl_2]$. $6H_2O$ (0.002 mmol, 1.5 mg), $KHSO_4$ (0.2 mmol, 27.2 mg), CuBr (0.24 mmol, 34.4 mg) and dry MeCN (2.0 mL) were added. The mixture was then stirred at room temperature under N_2 atmosphere and irradiated with 395nm LEDs for 72 h. After the reaction was complete, the reaction mixture was concentrated, and the residue was purified by silica gel column chromatography (EtOAc/petroleum ether = 1:50, V/V) to give the product **3aa** (48.5 mg, 73%) as a yellow solid.

A gram-scale synthesis of compound 3aa:

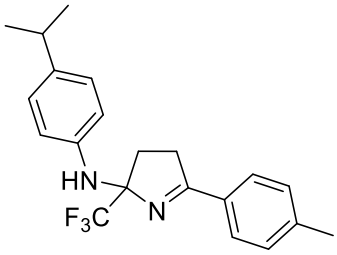
An oven-dried vial equipped with a magnetic stir bar was charged with perfluoroalkyl -substituted imidoyl sulfoxonium ylide **1a** (18.0 mmol, 4.99 g), vinyl azide **2a** (6.0 mmol, 0.96 g), $[Ru(bpy)_3Cl_2]$. $6H_2O$ (0.06 mmol, 44.9 mg), $KHSO_4$ (6.0 mmol, 0.82 g), CuBr (7.2 mmol, 1.03 g) and dry MeCN (50.0 mL) were added. Subsequently, the reaction mixture was stirred at room temperature under N_2 atmosphere and irradiated with 395nm LEDs for 72 h. After the reaction was complete, the reaction mixture was concentrated, and the residue was purified by silica gel column chromatography (EtOAc/petroleum ether = 1:50, V/V) to give the product **3aa** (1.20 g, 60%) as a yellow solid.

***N*,5-di-*p*-Tolyl-2-(trifluoromethyl)-3,4-dihydro-2*H*-pyrrol-2-amine (3aa):**



Yellow solid; mp: 86 – 88 °C; 48.5 mg, 73% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.1 Hz, 2H, Ar), 7.25 (d, *J* = 2.9 Hz, 2H, Ar), 6.97 (d, *J* = 8.1 Hz, 2H, Ar), 6.79 (d, *J* = 8.3 Hz, 2H, Ar), 4.22 (s, 1H, -NH-), 3.06 (ddd, *J* = 16.2, 9.7, 6.2 Hz, 1H, -CH_2-), 2.93 – 2.85 (m, 1H, -CH_2-), 2.48 (ddd, *J* = 14.4, 9.8, 4.8 Hz, 1H, , -CH_2-), 2.40 (s, 3H, -CH_3), 2.38 – 2.31 (m, 1H, -CH_2-), 2.24 (s, 3H, -CH_3); ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.7 (C=N), 142.2 (Ar), 140.5 (Ar), 130.9 (Ar), 130.4 (Ar), 129.5 (Ar), 129.3 (Ar), 128.4 (Ar), 125.7 (q, *J* = 286.3 Hz, -CF_3), 120.8 (Ar), 93.1 (q, *J* = 33.1 Hz, $CF_3\underline{C}NH$), 35.9 (-CH_2-), 27.7 (-CH_2-), 21.6 (-CH_3), 20.6 (-CH_3); ^{19}F NMR (565 MHz, $CDCl_3$) δ -80.27 (-CF_3). HRMS (ESI-TOF): $[M + H]^+$ calculated for $C_{19}H_{20}F_3N_2^+$: 333.1573, found: 333.1572.

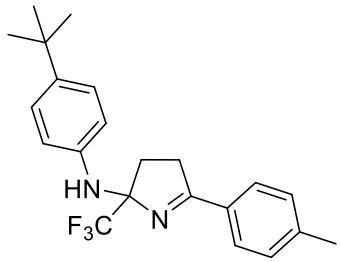
***N*-(4-Isopropylphenyl)-5-(*p*-tolyl)-2-(trifluoromethyl)-3,4-dihydro-2*H*-pyrrol-2-amine (3ba):**



Colorless liquid; 49.0 mg, 68% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.1 Hz, 2H, Ar), 7.23 (d, *J* = 7.8 Hz, 2H, Ar), 7.02 (d, *J* = 8.3 Hz, 2H, Ar), 6.79 (d, *J* = 8.4 Hz, 2H, Ar), 4.27 (s, 1H, -NH-), 3.07 (ddd, *J* = 16.4, 9.6, 6.4 Hz, 1H, -CH_2-), 2.96 – 2.89 (m, 1H, -CH_2-), 2.79 (p, *J* = 6.9 Hz, 1H, $CH_3C\underline{H}CH_3$), 2.49 (ddd, *J* = 14.2, 9.7, 4.6 Hz, 1H, -CH_2-), 2.39 (s, 3H, -CH_3), 2.35 (dd, *J* = 13.2, 8.8 Hz, 1H, -CH_2-), 1.18 (s, 3H, -CH_3), 1.17 (s, 3H, -CH_3); ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.6 (C=N), 141.2 (Ar), 140.6 (Ar), 139.8 (Ar), 129.4 (Ar), 128.3 (Ar), 127.3 (Ar), 125.8 (Ar), 124.7 (q,

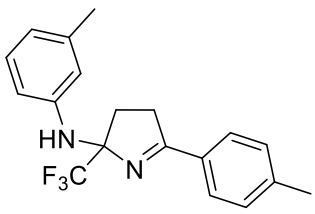
J = 286.4 Hz, -CF_3), 119.0 (Ar), 92.0 (q, *J* = 27.8 Hz, $CF_3\underline{C}NH$), 34.8 (-CH_2-), 32.2 ($CH_3\underline{C}HCH_3$), 26.7 (-CH_2-), 23.1 ($\underline{C}H_3CHCH_3$), 23.0 ($CH_3CH\underline{C}H_3$), 20.5 (-CH_3); ^{19}F NMR (565 MHz, $CDCl_3$) δ -80.24 (-CF_3). HRMS (ESI-TOF): $[M + H]^+$ calculated for $C_{21}H_{24}F_3N_2^+$: 361.1886, found: 361.1887.

_N_-(4-(Tert-Butyl)phenyl)-5-(_p_-tolyl)-2-(trifluoromethyl)-3,4-dihydro-2_H_-pyrrol-2-amine (3ca):



Colorless liquid; 51.7 mg, 69% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.1 Hz, 2H, Ar), 7.24 (d, *J* = 9.2 Hz, 2H, Ar), 7.18 (d, *J* = 8.6 Hz, 2H, Ar), 6.79 (d, *J* = 8.6 Hz, 2H, Ar), 4.30 (s, 1H, -NH-), 3.10 (ddd, *J* = 16.4, 9.6, 6.5 Hz, 1H, -CH_2-), 3.02 – 2.94 (m, 1H, -CH_2-), 2.52 (ddd, *J* = 14.2, 9.7, 4.6 Hz, 1H, -CH_2-), 2.40 (s, 3H, -CH_3), 2.40 – 2.34 (m, 1H, -CH_2-), 1.25 (s, 9H, -CH_3); ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.7 (C=N), 143.7 (Ar), 142.2 (Ar), 140. 6 (Ar), 130.4 (Ar), 129.3 (Ar), 128.5 (Ar), 128.4 (Ar), 125.8 (Ar), 125.7 (q, *J* = 286.9 Hz, -CF_3), 119.2 (Ar), 92.9 (q, *J* = 27.2 Hz, $CF_3\underline{C}NH$), 35.9 (-CH_2-), 34.0 (-$\underline{C}(CH_3)_3$), 31.4 (-$C(\underline{C}H_3)_3$), 27.8 (-CH_2-), 21.6 (-CH_3); ^{19}F NMR (565 MHz, $CDCl_3$) δ -80.26 (-CF_3). HRMS (ESI-TOF): $[M + H]^+$ calculated for $C_{22}H_{26}F_3N_2^+$: 375.2043, found: 375.2051.

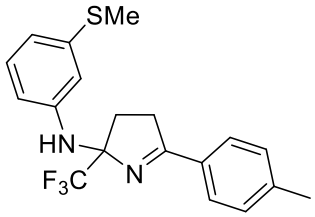
_N_-(_m_-tolyl)-5-(_p_-tolyl)-2-(trifluoromethyl)-3,4-dihydro-2_H_-pyrrol-2-amine (3da):



Colorless liquid; 41.2 mg, 62% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.1 Hz, 2H, Ar), 7.18 – 7.14 (m, 2H, Ar), 6.96 (t, *J* = 7.7 Hz, 1H, Ar), 6.63 – 6.56 (m, 3H,

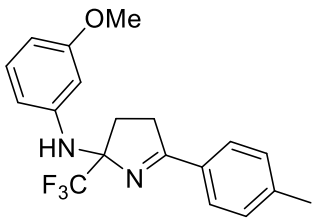
Ar), 4.26 (s, 1H, -NH-), 3.03 (ddd, *J* = 16.5, 9.6, 6.5 Hz, 1H, -CH_2-), 2.92 (ddd, *J* = 17.3, 9.9, 4.5 Hz, 1H, -CH_2-), 2.46 (ddd, *J* = 14.1, 9.7, 4.5 Hz, 1H, -CH_2-), 2.32 (s, 3H, -CH_3), 2.29 (dd, *J* = 8.9, 6.4 Hz, 1H, -CH_2-), 2.16 (s, 3H, -CH_3); ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.8 (C=N), 142.2 (Ar), 141.3 (Ar), 137.7 (Ar), 129.3 (Ar), 128.3 (Ar), 127.8 (Ar), 127.3 (Ar), 124.7 (q, *J* = 286.9 Hz, -CF_3), 120.5 (Ar), 119.0 (Ar), 115.0 (Ar), 91.8 (q, *J* = 27.9 Hz, CF_3CNH), 35.0 (-CH_2-), 27.0 (-CH_2-), 20.5 (-CH_3), 20.5 (-CH_3); ^{19}F NMR (565 MHz, $CDCl_3$) δ -80.13 (-CF_3). HRMS (ESI-TOF): $[M + H]^+$ calculated for $C_{19}H_{20}F_3N_2^+$: 333.1573, found: 333.1578.

_N_-(3-(methylthio)phenyl)-5-(_p_-tolyl)-2-(trifluoromethyl)-3,4-dihydro-2_H_-pyrrol-2-amine (3ea):



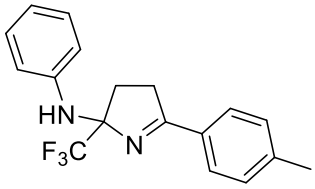
Yellow solid; mp: 68 – 70 °C; 43.7 mg, 60% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.1 Hz, 2H, Ar), 7.25 (d, *J* = 7.9 Hz, 2H, Ar), 7.08 (t, *J* = 7.9 Hz, 1H, Ar), 6.94 – 6.70 (m, 2H, Ar), 6.63 (d, *J* = 8.0 Hz, 1H, Ar), 4.43 (s, 1H, -NH-), 3.18 – 3.04 (m, 2H, -CH_2-), 2.58 (ddd, *J* = 14.0, 9.4, 4.6 Hz, 1H, -CH_2-), 2.41 (s, 3H, -CH_3), 2.39 (s, 3H, -CH_3), 2.37 – 2.32 (m, 1H, -CH_2-); ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.1 (C=N), 144.0 (Ar), 142.5 (Ar), 139.1 (Ar), 130.3 (Ar), 129.4 (Ar), 129.3 (Ar), 128.4 (Ar), 125.6 (q, *J* = 287.1 Hz, -CF_3), 118.6 (Ar), 116.2 (Ar), 115.3 (Ar), 92.7 (q, *J* = 28.1 Hz, CF_3CNH), 36.0 (-CH_2-), 28.4 (-CH_2-), 21.6 (-CH_3), 15.6 (-SMe); ^{19}F NMR (565 MHz, $CDCl_3$) δ -80.02 (-CF_3). HRMS (ESI-TOF): $[M + H]^+$ calculated for $C_{19}H_{20}F_3N_2S^+$: 365.1294, found: 365.1299.

_N_-(3-methoxyphenyl)-5-(_p_-tolyl)-2-(trifluoromethyl)-3,4-dihydro-2_H_-pyrrol-2-amine (3fa):



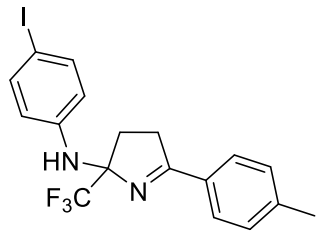
Colorless liquid; 46.0 mg, 66% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 – 7.77 (m, 2H, Ar), 7.25 (d, *J* = 8.1 Hz, 2H, Ar), 7.07 (t, *J* = 8.0 Hz, 1H, Ar), 6.48 – 6.38 (m, 3H, Ar), 4.42 (s, 1H, -NH-), 3.71 (s, 3H, $-OCH_3$), 3.18 – 3.05 (m, 2H, $-CH_2-$), 2.57 (ddd, *J* = 14.0, 9.4, 4.6 Hz, 1H, $-CH_2-$), 2.41 (s, 4H, $-CH_2-$, $-CH_3$); ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.9 (C=N), 160.3 (Ar), 144.7 (Ar), 142.4 (Ar), 130.3 (Ar), 129.7 (Ar), 129.3 (Ar), 128.4 (Ar), 125.6 (q, *J* = 287.1 Hz, $-CF_3$), 111.3 (Ar), 105.9 (Ar), 104.5 (Ar), 93.2 (q, *J* = 28.1 Hz, $CF_3\underline{C}NH$), 55.1 ($-OCH_3$), 36.0 ($-CH_2-$), 28.2 ($-CH_2-$), 21.6 ($-CH_3$). ^{19}F NMR (565 MHz, $CDCl_3$) δ -80.13 ($-CF_3$). HRMS (ESI-TOF): $[M + H]^+$ calculated for $C_{19}H_{20}F_3N_2O^+$: 349.1522, found: 349.1522.

***N*-Phenyl-5-(*p*-tolyl)-2-(trifluoromethyl)-3,4-dihydro-2*H*-pyrrol-2-amine (3ga):**



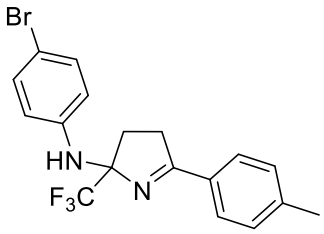
White solid; mp: 115 – 116 °C; 47.8 mg, 75% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.1 Hz, 2H, Ar), 7.25 (d, *J* = 7.9 Hz, 2H, Ar), 7.17 (t, *J* = 7.9 Hz, 2H, Ar), 6.86 (d, *J* = 7.9 Hz, 3H, Ar), 4.40 (s, 1H, -NH-), 3.13 (ddd, *J* = 16.5, 9.5, 6.7 Hz, 1H, $-CH_2-$), 3.07 – 2.99 (m, 1H, $-CH_2-$), 2.56 (ddd, *J* = 14.0, 9.6, 4.5 Hz, 1H, $-CH_2-$), 2.41 (s, 3H, $-CH_3$), 2.40 – 2.33 (m, 1H, $-CH_2-$).; ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.8 (C=N), 142.3 (Ar), 141.3 (Ar), 129.3 (Ar), 128.3 (Ar), 128.0 (Ar), 127.4 (Ar), 124.6 (q, *J* = 286.9 Hz, $-CF_3$), 119.6 (Ar), 117.9 (Ar), 91.7 (q, *J* = 33.5 Hz, $CF_3\underline{C}NH$), 34.9 ($-CH_2-$), 27.0 ($-CH_2-$), 20.5 ($-CH_3$); ^{19}F NMR (565 MHz, $CDCl_3$) δ -80.16 ($-CF_3$). HRMS (ESI-TOF): $[M + H]^+$ calculated for $C_{18}H_{18}F_3N_2^+$: 319.1417, found: 319.1416.

***N*-(4-Iodophenyl)-5-(*p*-tolyl)-2-(trifluoromethyl)-3,4-dihydro-2*H*-pyrrol-2-amine (3ha):**



Yellow liquid; 66.6 mg, 75% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.1 Hz, 2H, Ar), 7.43 (d, *J* = 8.8 Hz, 2H, Ar), 7.26 – 7.22 (m, 2H, Ar), 6.65 (d, *J* = 8.7 Hz, 2H, Ar), 4.42 (s, 1H, -NH-), 3.18 – 3.08 (m, 2H, -CH_2-), 2.58 (ddd, *J* = 14.0, 8.9, 5.0 Hz, 1H, -CH_2-), 2.41 (s, 3H, -CH_3), 2.30 (dt, *J* = 14.6, 8.1 Hz, 1H, -CH_2-); ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.3 (C=N), 143.3 (Ar), 142.6 (Ar), 137.7 (Ar), 130.1 (Ar), 129.4 (Ar), 128.4 (Ar), 125.6 (q, *J* = 287.4 Hz, -CF_3), 120.2 (Ar), 92.4 (q, *J* = 28.2 Hz, $CF_3\underline{C}NH$), 82.1 (Ar), 36.0 (-CH_2-), 28.7 (-CH_2-), 21.6 (-CH_3); ^{19}F NMR (565 MHz, $CDCl_3$) δ -79.89 (-CF_3). HRMS (ESI-TOF): $[M + H]^+$ calculated for $C_{18}H_{17}F_3IN_2^+$: 445.0383, found: 445.0383.

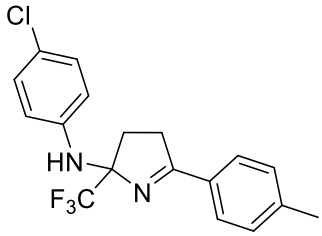
***N*-(4-Bromophenyl)-5-(*p*-tolyl)-2-(trifluoromethyl)-3,4-dihydro-2*H*-pyrrol-2-amine (3ia):**



White solid; mp: 97 – 98 °C; 55.6 mg, 70% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.1 Hz, 2H, Ar), 7.20 – 7.17 (m, 4H, Ar), 6.69 (d, *J* = 8.8 Hz, 2H, Ar), 4.32 (s, 1H, -NH-), 3.11 – 2.99 (m, 2H, -CH_2-), 2.50 (ddd, *J* = 14.0, 9.5, 4.6 Hz, 1H, -CH_2-), 2.34 (s, 3H, -CH_3), 2.26 – 2.20 (m, 1H, -CH_2-); ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.2 (C=N), 142.6 (Ar), 145.6 (Ar), 131.8 (Ar), 130.1 (Ar), 129.4 (Ar), 128.4 (Ar), 125.6 (q, *J* = 287.2 Hz, -CF_3), 120.1 (Ar), 112.7 (Ar), 92.5 (q, *J* = 28.1 Hz, $CF_3\underline{C}NH$), 35.9 (-CH_2-), 28.6 (-CH_2-), 21.6 (-CH_3); ^{19}F NMR (565 MHz, $CDCl_3$) δ -79.96 (-CF_3).

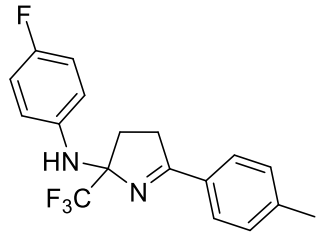
HRMS (ESI-TOF): $[M + H]^+$ calculated for $C_{18}H_{17}BrF_3N_2^+$: 397.0522, found: 397.0520.

_N_-(4-Chlorophenyl)-5-(_p_-tolyl)-2-(trifluoromethyl)-3,4-dihydro-2_H_-pyrrol-2-amine (3ja):



White solid; mp: 90 – 92 °C; 50.8 mg, 72% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.0 Hz, 2H, Ar), 7.25 (d, *J* = 7.0 Hz, 2H, Ar), 7.12 (d, *J* = 8.6 Hz, 2H, Ar), 6.81 (d, *J* = 8.6 Hz, 2H, Ar), 4.37 (s, 1H, -NH-), 3.03 – 3.17 (m, 2H, -CH_2-), 2.56 (ddd, *J* = 14.1, 9.5, 4.6 Hz, 1H, -CH_2-), 2.41 (s, 3H, -CH_3), 2.29 (dt, *J* = 14.7, 8.1 Hz, 1H, -CH_2-); ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.2 (C=N), 142.5 (Ar), 142.1 (Ar), 130.1 (Ar), 129.4 (Ar), 128.9 (Ar), 128.4 (Ar), 125.6 (Ar), 125.6 (q, *J* = 287.1 Hz, -CF_3), 120.0 (Ar), 92.6 (q, *J* = 28.1 Hz, CF_3CNH), 35.9 (-CH_2-), 28.5 (-CH_2-), 21.6 (-CH_3); ^{19}F NMR (565 MHz, $CDCl_3$) δ -79.98 (-CF_3). HRMS (ESI-TOF): $[M + H]^+$ calculated for $C_{18}H_{17}ClF_3N_2^+$: 353.1027, found: 353.1024.

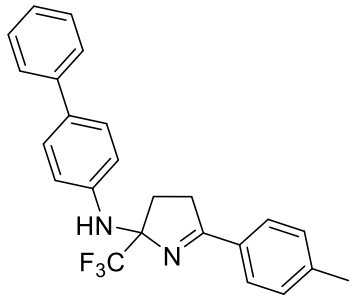
_N_-(4-Fluorophenyl)-5-(_p_-tolyl)-2-(trifluoromethyl)-3,4-dihydro-2_H_-pyrrol-2-amine (3ka):



Colorless liquid; 43.7 mg, 65% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 – 7.77 (m, 2H, Ar), 7.25 (d, J = 3.2 Hz, 2H, Ar), 6.92 – 6.84 (m, 4H, Ar), 4.19 (s, 1H, -NH-), 3.06 (ddd, J = 17.3, 9.8, 5.9 Hz, 1H, -CH_2-), 2.86 (ddd, J = 17.4, 9.8, 4.9 Hz, 1H, -CH_2-), 2.48 (ddd, J = 14.5, 9.8, 5.0 Hz, 1H, -CH_2-), 2.41 (s, 3H, -CH_3), 2.29 – 2.24 (m,

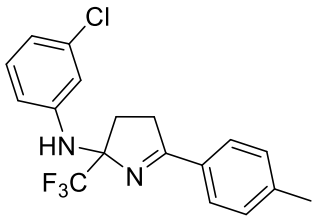
1H, -CH_2-); ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.9 (C=N), 158.5 (d. *J* = 240.5 Hz, Ar), 142.4 (Ar), 139.1 (d, *J* = 2.6 Hz, Ar), 130.3 (Ar), 129.3 (Ar), 128.3 (Ar), 125.6 (q, *J* = 286.0 Hz, -CF_3), 122.9 (d, *J* = 7.7 Hz, Ar), 115.5 (d, *J* = 22.3 Hz, Ar), 93.2 (q, *J* = 27.6 Hz, CF_3<u>C</u>NH), 35.7 (-CH_2-), 27.9 (-CH_2-), 21.6 (-CH_3); ^{19}F NMR (565 MHz, $CDCl_3$) δ -80.23 (-CF_3), -122.13 (Ar-F). HRMS (ESI-TOF): $[M + H]^+$ calculated for $C_{18}H_{17}F_4N_2^+$: 337.1322, found: 337.1332.

_N_-([1,1'-biphenyl]-4-yl)-5-(_p_-tolyl)-2-(trifluoromethyl)-3,4-dihydro-2_H_-pyrrol-2-amine (3la):



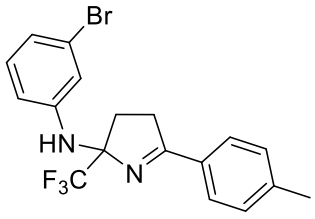
Yellow solid; mp: 106 – 108 °C; 43.4 mg, 55% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.1 Hz, 2H, Ar), 7.52 (d, *J* = 7.6 Hz, 2H, Ar), 7.43 – 7.37 (m, 4H, Ar), 7.25 (t, *J* = 3.9 Hz, 3H, Ar), 6.92 (d, *J* = 8.5 Hz, 2H, Ar), 4.49 (s, 1H, -NH-), 3.21 – 3.08 (m, 2H, -CH_2-), 2.61 (ddd, *J* = 14.0, 9.3, 4.7 Hz, 1H, -CH_2-), 2.46 – 2.42 (m, 1H, -CH_2-), 2.41 (s, 3H, -CH_3); ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.0 (C=N), 142.8 (Ar), 142.4 (Ar), 140.8 (Ar), 133.3 (Ar), 130.3 (Ar), 129.3 (Ar), 128.7 (Ar), 128.5 (Ar), 128.4 (Ar), 127.6 (Ar), 126.5 (Ar), 125.7 (q, *J* = 287.1 Hz, -CF_3), 118.8 (Ar), 92.7 (q, *J* = 28.1 Hz, CF_3<u>C</u>NH), 36.0 (-CH_2-), 28.3 (-CH_2-), 21.6 (-CH_3); ^{19}F NMR (565 MHz, $CDCl_3$) δ -80.05 (-CF_3). HRMS (ESI-TOF): $[M + H]^+$ calculated for $C_{24}H_{22}F_3N_2^+$: 395.1730, found: 395.1720.

_N_-(3-chlorophenyl)-5-(_p_-tolyl)-2-(trifluoromethyl)-3,4-dihydro-2_H_-pyrrol-2-amine (3ma):



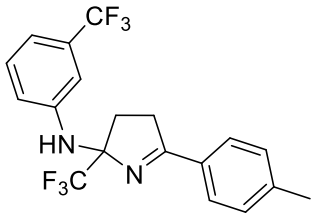
Yellow liquid; 48.0 mg, 68% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.1 Hz, 2H, Ar), 7.27 – 7.23 (m, 2H, Ar), 7.07 (t, *J* = 8.1 Hz, 1H, Ar), 6.88 (s, 1H, Ar), 6.80 (d, *J* = 7.9 Hz, 1H, Ar), 6.74 – 6.70 (m, 1H, Ar), 4.49 (s, 1H, -NH-), 3.19 – 3.15 (m, 2H, -CH_2-), 2.65 – 2.59 (m, 1H, -CH_2-), 2.41 (s, 3H, -CH_3), 2.34 (dd, *J* = 14.8, 7.4 Hz, 1H, -CH_2-); ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.3 (C=N), 144.8 (Ar), 142.6 (Ar), 134.6 (Ar), 130.1 (Ar), 129.9 (Ar), 129.4 (Ar), 128.4 (Ar), 125.6 (q, *J* = 287.4 Hz, -CF_3), 112.0 (Ar), 117.6 (Ar), 115.8 (Ar), 92.4 (q, *J* = 28.4 Hz, CF_3CNH), 36.0 (-CH_2-), 28.8 (-CH_2-), 21.6 (-CH_3); ^{19}F NMR (565 MHz, $CDCl_3$) δ -79.87 (-CF_3). HRMS (ESI-TOF): $[M + H]^+$ calculated for $C_{18}H_{17}ClF_3N_2^+$: 353.1027, found: 353.1028.

_N_-(3-bromophenyl)-5-(_p_-tolyl)-2-(trifluoromethyl)-3,4-dihydro-2_H_-pyrrol-2-amine (3na):



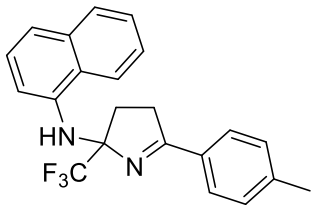
Yellow liquid; 50.1 mg, 63% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.1 Hz, 2H, Ar), 7.27 – 7.23 (m, 2H, Ar), 7.05 – 6.99 (m, 2H, Ar), 6.97 – 6.91 (m, 1H, Ar), 6.80 – 6.75 (m, 1H, Ar), 4.47 (s, 1H, -NH-), 3.21 – 3.10 (m, 2H, -CH_2-), 2.62 (ddd, *J* = 13.9, 8.3, 5.5 Hz, 1H, -CH_2-), 2.41 (s, 3H, -CH_3), 2.34 (dd, *J* = 14.9, 7.2 Hz, 1H, -CH_2-); ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.4 (C=N), 145.0 (Ar), 142.6 (Ar), 130.2 (Ar), 130.1 (Ar), 129.4 (Ar), 128.5 (Ar), 125.6 (q, *J* = 287.4 Hz, -CF_3), 122.9 (Ar), 122.7 (Ar), 120.5 (Ar), 116.2 (Ar), 92.4 (q, *J* = 28.4 Hz, CF_3CNH), 36.0 (-CH_2-), 28.8 (-CH_2-), 21.6 (-CH_3); ^{19}F NMR (565 MHz, $CDCl_3$) δ -79.87 (-CF_3). HRMS (ESI-TOF): $[M + H]^+$ calculated for $C_{18}H_{17}BrF_3N_2^+$: 397.0522, found: 397.0527.

5-(*p*-tolyl)-2-(trifluoromethyl)-*N*-(3-(trifluoromethyl)phenyl)-3,4-dihydro-2*H*-pyrrol-2-amine (3oa):



Yellow liquid; 44.0 mg, 57% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.1 Hz, 2H, Ar), 7.27 – 7.23 (m, 3H, Ar), 7.14 (s, 1H, Ar), 7.06 (d, *J* = 7.7 Hz, 1H, Ar), 7.03 (d, *J* = 8.2 Hz, 1H, Ar), 4.59 (s, 1H, -NH-), 3.25 – 3.11 (m, 2H, -CH_2-), 2.65 (ddd, *J* = 14.0, 8.5, 5.4 Hz, 1H, -CH_2-), 2.41 (s, 3H, -CH_3), 2.31 (dt, *J* = 15.2, 8.7 Hz, 1H, -CH_2-); ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.5 (C=N), 144.1 (Ar), 142.7 (Ar), 131.3 (q, *J* = 32.0 Hz, Ar), 130.1 (Ar), 129.4 (Ar), 129.4 (Ar), 128.4 (Ar), 125.6 (q, *J* = 287.4 Hz, -CF_3), 124.1 (q, *J* = 273.2 Hz, -CF_3), 120.4 (Ar), 116.4 (q, *J* = 3.8 Hz, Ar), 114.1 (Ar), 92.3 (q, *J* = 28.5 Hz, $CF_3\underline{C}NH$), 35.9 (-CH_2-), 29.1 (-CH_2-), 21.6 (-CH_3); ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.90 (Ar-CF_3), -79.80 (-CF_3). HRMS (ESI-TOF): $[M + H]^+$ calculated for $C_{19}H_{17}F_6N_2^+$: 387.1290, found: 387.1290.

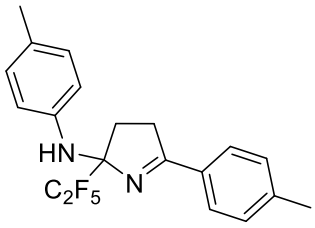
***N*-(Naphthalen-1-yl)-5-(*p*-tolyl)-2-(trifluoromethyl)-3,4-dihydro-2*H*-pyrrol-2-amine (3pa):**



Colorless liquid; 44.2 mg, 60% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.3 Hz, 1H, Ar), 7.71 (d, *J* = 8.1 Hz, 3H, Ar), 7.43 – 7.35 (m, 3H, Ar), 7.18 – 7.15 (m, 3H, Ar), 6.92 (d, *J* = 7.4 Hz, 1H, Ar), 4.62 (s, 1H, -NH-), 2.91 (ddd, *J* = 17.2, 9.9, 6.0 Hz, 1H, -CH_2-), 2.61 (ddd, *J* = 17.4, 10.0, 4.8 Hz, 1H, -CH_2-), 2.38 – 2.34 (m, 1H, -CH_2-), 2.33 (s, 3H, -CH_3), 2.18 (ddd, *J* = 15.0, 9.9, 6.1 Hz, 1H, -CH_2-); ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.5 (C=N), 142.3 (Ar), 138.1 (Ar), 134.4 (Ar), 130.4 (Ar), 129.4 (Ar),

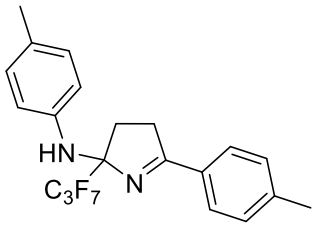
129.3 (Ar), 128.4 (Ar), 128.3 (Ar), 125.9 (Ar), 125.8 (Ar), 125.7 (Ar), 125.5 (q, *J* = 285.2 Hz, -CF_3), 123.2 (Ar), 122.2 (Ar), 118.4 (Ar), 93.8 (q, *J* = 27.6 Hz, $CF_3\underline{C}NH$), 36.0 (-CH_2-), 26.4 (-CH_2-), 21.6 (-CH_3); ^{19}F NMR (565 MHz, $CDCl_3$) δ -80.65 (-CF_3). HRMS (ESI-TOF): $[M + H]^+$ calculated for $C_{22}H_{20}F_3N_2^+$: 369.1573, found: 369.1578.

2-(Perfluoroethyl)-*N*,5-di-*p*-tolyl-3,4-dihydro-2*H*-pyrrol-2-amine (3qa):



Yellow liquid; 40.5 mg, 53% yield. ^1H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.1 Hz, 2H, Ar), 7.24 (d, *J* = 7.8 Hz, 2H, Ar), 6.97 (d, *J* = 8.2 Hz, 2H, Ar), 6.77 (d, *J* = 8.2 Hz, 2H, Ar), 4.16 (s, 1H, -NH-), 2.99 (ddd, *J* = 16.1, 9.7, 5.9 Hz, 1H, -CH_2-), 2.84 – 2.77 (m, 1H, -CH_2-), 2.59 (ddd, *J* = 14.4, 9.8, 4.9 Hz, 1H, -CH_2-), 2.41 (s, 3H, -CH_3), 2.39 – 2.33 (m, 1H, -CH_2-), 2.24 (s, 3H, -CH_3); ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.1 (C=N), 142.2 (Ar), 140.3 (Ar), 131.0 (Ar), 130.5 (Ar), 129.8 (Ar), 129.5 (Ar), 129.3 (Ar), 128.4 (Ar), 121.0 (Ar), 117.6 (qt, *J* = 288.1 Hz, 36.2 Hz, C-F), 93.9 (t, *J* = 23.4 Hz, $CF_3\underline{C}NH$), 36.0 (-CH_2-), 27.7 (-CH_2-), 21.6 (-CH_3), 20.6 (-CH_3); ^{19}F NMR (565 MHz, $CDCl_3$) δ -78.09, -121.10, -121.59, -122.75, -123.24. HRMS (ESI-TOF): $[M + H]^+$ calculated for $C_{20}H_{20}F_5N_2^+$: 383.1541, found: 383.1545.

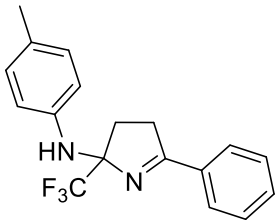
2-(Perfluoroethyl)-*N*,5-di-*p*-tolyl-3,4-dihydro-2*H*-pyrrol-2-amine (3ra):



Yellow liquid; 38.9 mg, 45% yield. ^1H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.2 Hz, 2H, Ar), 7.24 (d, *J* = 7.9 Hz, 2H, Ar), 6.96 (d, *J* = 8.1 Hz, 2H, Ar), 6.83 – 6.74 (m, 2H, Ar), 4.12 (s, 1H, -NH-), 2.97 (ddd, *J* = 17.4, 9.8, 5.5 Hz, 1H, -CH_2-), 2.75 (ddd, *J* =

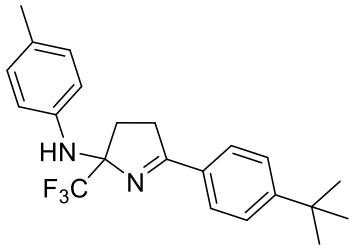
17.3, 9.8, 5.1 Hz, 1H, -CH_2-), 2.57 (ddd, *J* = 14.7, 9.8, 5.1 Hz, 1H, -CH_2-), 2.40 (s, 4H, -CH_2-, -CH_3), 2.23 (s, 3H, -CH_3); ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.0 (C=N), 142.2 (Ar), 140.2 (Ar), 131.2 (Ar), 130.5 (Ar), 129.5 (Ar), 129.3 (Ar), 128.4 (Ar), 121.4 (Ar), 118.0 (dt, *J* = 288.3 Hz, 34.4 Hz, C-F), 116.4 (tt, *J* = 263.2 Hz, 28.4 Hz, C-F), 111.2 (dt, *J* = 230.1 Hz, 37.1 Hz, C-F), 94.9 (t, *J* = 23.7 Hz, CF_3CNH), 35.9 (-CH_2-), 27.8 (-CH_2-), 21.6 (-CH_3), 20.6 (-CH_3); ^{19}F NMR (565 MHz, $CDCl_3$) δ -80.78, -117.91 – -117.99 (m), -118.46 (qd, *J* = 11.1, 3.5 Hz), -118.90 (q, *J* = 10.3 Hz), -119.39 (t, *J* = 10.3 Hz), -121.85 (dd, *J* = 10.5, 2.6 Hz), -122.36 (dd, *J* = 10.6, 2.6 Hz), -123.59 (dd, *J* = 11.1, 3.5 Hz), -124.10 (dd, *J* = 10.8, 3.5 Hz). HRMS (ESI-TOF): [M + H]$^+$ calculated for $C_{21}H_{20}F_7N_2^+$: 433.1509, found: 433.1505.

5-Phenyl-*N*-(*p*-tolyl)-2-(trifluoromethyl)-3,4-dihydro-2*H*-pyrrol-2-amine (3ab):



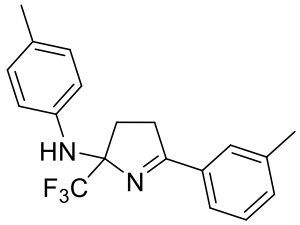
Yellow solid; mp: 82 – 83 °C; 45.8 mg, 72% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 – 7.88 (m, 2H, Ar), 7.52 – 7.48 (m, 1H, Ar), 7.44 (td, *J* = 7.0, 1.5 Hz, 2H, Ar), 6.98 (d, *J* = 8.0 Hz, 2H, Ar), 6.83 – 6.79 (m, 2H, Ar), 4.23 (s, 1H, -NH-), 3.09 (ddd, *J* = 17.2, 9.8, 6.1 Hz, 1H, -CH_2-), 2.91 (ddd, *J* = 17.4, 9.9, 4.8 Hz, 1H, -CH_2-), 2.50 (ddd, *J* = 14.4, 9.8, 4.9 Hz, 1H, -CH_2-), 2.39 – 2.33 (m, 1H, -CH_2-), 2.24 (s, 3H, -CH_3); ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.8 (C=N), 140.4 (Ar), 133.1 (Ar), 131.7 (Ar), 131.0 (Ar), 129.5 (Ar), 128.6 (Ar), 128.3 (Ar), 125.6 (q, *J* = 286.3 Hz, -CF_3), 120.9 (Ar), 93.2 (q, *J* = 27.5 Hz, CF_3CNH), 35.9 (-CH_2-), 27.7 (-CH_2-), 20.6 (-CH_3); ^{19}F NMR (565 MHz, $CDCl_3$) δ -80.24 (-CF_3). HRMS (ESI-TOF): [M + H]$^+$ calculated for $C_{18}H_{18}F_3N_2^+$: 319.1417, found: 319.1415.

5-(4-(*tert*-Butyl)phenyl)-*N*-(*p*-tolyl)-2-(trifluoromethyl)-3,4-dihydro-2*H*-pyrrol-2-amine (3ac):



Colorless liquid; 43.4 mg, 58% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.4 Hz, 2H, Ar), 7.46 (d, *J* = 8.4 Hz, 2H, Ar), 6.98 (d, *J* = 8.2 Hz, 2H, Ar), 6.80 (d, *J* = 8.3 Hz, 2H, Ar), 4.25 (s, 1H, -NH-), 3.09 (ddd, *J* = 16.3, 9.7, 6.3 Hz, 1H, -CH_2-), 2.93 (ddd, *J* = 17.3, 9.9, 4.7 Hz, 1H, -CH_2-), 2.48 (td, *J* = 9.6, 5.6 Hz, 1H, -CH_2-), 2.38 – 2.33 (m, 1H, -CH_2-), 2.24 (s, 3H, -CH_3), 1.35 (s, 9H, -CH_3); ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.6 (C=N), 155.3 (Ar), 140.6 (Ar), 130.8 (Ar), 130.4 (Ar), 129.5 (Ar), 128.2 (Ar), 125.7 (q, *J* = 286.3 Hz, -CF_3), 125.5 (Ar), 120.7 (Ar), 93.2 (q, *J* = 27.6 Hz, $CF_3\underline{C}NH$), 35.9 (-CH_2-), 35.0 (-$\underline{C}(CH_3)_3$), 31.2 (-$C(\underline{C}H_3)_3$), 27.7 (-CH_2-), 20.6 (Ar-$\underline{C}H_3$); ^{19}F NMR (565 MHz, $CDCl_3$) δ -80.33 (-CF_3). HRMS (ESI-TOF): $[M + H]^+$ calculated for $C_{22}H_{26}F_3N_2^+$: 375.2043, found: 375.2040.

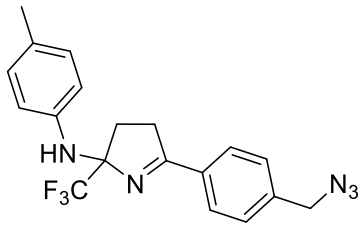
5-(*m*-Tolyl)-*N*-(*p*-tolyl)-2-(trifluoromethyl)-3,4-dihydro-2*H*-pyrrol-2-amine (3ad):



Colorless liquid; 45.2 mg, 68% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (s, 1H, Ar), 7.67 – 7.62 (m, 1H, Ar), 7.32 (d, *J* = 5.4 Hz, 2H, Ar), 6.98 (d, *J* = 8.2 Hz, 2H, Ar), 6.80 (d, *J* = 8.3 Hz, 2H, Ar), 4.25 (s, 1H, -NH-), 3.08 (ddd, *J* = 16.2, 9.7, 6.2 Hz, 1H, -CH_2-), 2.91 (ddd, *J* = 17.4, 9.9, 4.8 Hz, 1H, -CH_2-), 2.50 (td, *J* = 9.7, 4.9 Hz, 1H, -CH_2-), 2.41 (s, 3H, -CH_3), 2.36 (d, *J* = 5.9 Hz, 1H, -CH_2-), 2.25 (s, 3H, -CH_3); ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.0 (C=N), 140.5 (Ar), 138.4 (Ar), 133.1 (Ar), 132.5 (Ar), 131.0 (Ar), 129.5 (Ar), 128.8 (Ar), 128.5 (Ar), 125.6 (q, *J* = 286.1 Hz, -CF_3), 125.6 (Ar), 120.8 (Ar), 93.2 (q, *J* = 27.6 Hz, $CF_3\underline{C}NH$), 36.0 (-CH_2-), 27.6 (-CH_2-),

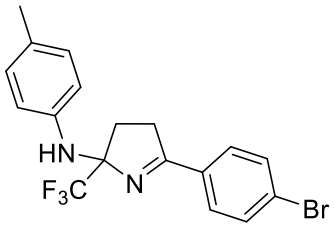
21.3 (-CH_3), 20.6 (-CH_3); ^{19}F NMR (565 MHz, $CDCl_3$) δ -80.28 (-CF_3). HRMS (ESI-TOF): $[M + H]^+$ calculated for $C_{19}H_{20}F_3N_2^+$: 333.1573, found: 333.1582.

5-(4-(Azidomethyl)phenyl)-*N*-(*p*-tolyl)-2-(trifluoromethyl)-3,4-dihydro-2*H*-pyrrol-2-amine (3ae):



Colorless liquid; 49.3 mg, 66% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.2 Hz, 2H, Ar), 7.39 (d, *J* = 8.3 Hz, 2H, Ar), 6.98 (d, *J* = 8.1 Hz, 2H, Ar), 6.81 (d, *J* = 8.4 Hz, 2H, Ar), 4.40 (s, 2H, -C$\underline{H_2}N_3$), 4.23 (s, 1H, -NH-), 3.08 (ddd, *J* = 17.2, 9.8, 6.0 Hz, 1H, -CH_2-), 2.89 (ddd, *J* = 17.4, 9.9, 4.9 Hz, 1H, -CH_2-), 2.50 (ddd, *J* = 14.5, 9.8, 4.9 Hz, 1H, -CH_2-), 2.38 (dt, *J* = 10.2, 5.5 Hz, 1H, -CH_2-), 2.24 (s, 3H, -CH_3); ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.3 (C=N), 140.3 (Ar), 139.1 (Ar), 133.0 (Ar), 131.2 (Ar), 129.5 (Ar), 128.9 (Ar), 128.3 (Ar), 125.7 (q, *J* = 286.3 Hz, -CF_3), 121.0 (Ar), 93.2 (q, *J* = 27.6 Hz, $CF_3\underline{C}NH$), 54.4 (, -$\underline{C}H_2N_3$), 35.9 (-CH_2-), 27.7 (-CH_2-), 20.6 (-CH_3); ^{19}F NMR (565 MHz, $CDCl_3$) δ -80.22 (-CF_3). HRMS (ESI-TOF): $[M + H]^+$ calculated for $C_{19}H_{19}F_3N_5^+$: 374.1587, found: 374.1582.

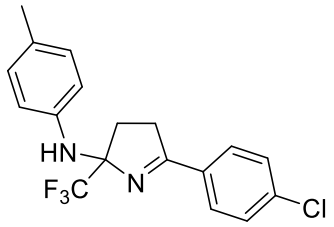
5-(4-Bromophenyl)-*N*-(*p*-tolyl)-2-(trifluoromethyl)-3,4-dihydro-2*H*-pyrrol-2-amine (3af):



White solid; mp: 117 – 118 °C; 55.6 mg, 70% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.5 Hz, 2H, Ar), 7.57 (d, *J* = 8.5 Hz, 2H, Ar), 6.98 (d, *J* = 8.1 Hz, 2H, Ar), 6.79 (d, *J* = 8.3 Hz, 2H, Ar), 4.20 (s, 1H, -NH-), 3.03 (ddd, *J* = 16.0, 9.7, 5.9 Hz, 1H, -

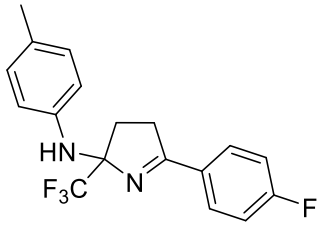
CH_2-), 2.88 – 2.80 (m, 1H, -CH_2-), 2.49 (ddd, *J* = 14.5, 9.8, 5.0 Hz, 1H, -CH_2-), 2.36 (dd, *J* = 10.0, 5.0 Hz, 1H, -CH_2-), 2.24 (s, 3H, -CH_3); ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.7 (C=N), 140.2 (Ar), 131.9 (Ar), 131.9 (Ar), 131.4 (Ar), 129.8 (Ar), 129.5 (Ar), 126.5 (Ar), 125.5 (q, *J* = 286.1 Hz, -CF_3), 121.2 (Ar), 93.3 (q, *J* = 27.6 Hz, CF_3CNH), 35.7 (-CH_2-), 27.8 (-CH_2-), 20.6 (-CH_3); ^{19}F NMR (565 MHz, $CDCl_3$) δ -80.26 (-CF_3). HRMS (ESI-TOF): $[M + H]^+$ calculated for $C_{18}H_{17}BrF_3N_2^+$: 397.0522, found: 397.0531.

5-(4-Chlorophenyl)-*N*-(*p*-tolyl)-2-(trifluoromethyl)-3,4-dihydro-2*H*-pyrrol-2-amine (3ag):



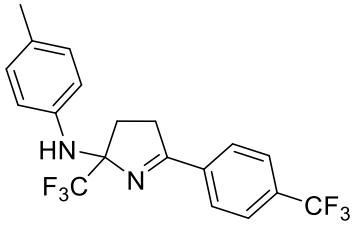
Yellow liquid; 48.0 mg, 68% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.6 Hz, 2H, Ar), 7.41 (d, *J* = 8.6 Hz, 2H, Ar), 6.98 (d, *J* = 8.1 Hz, 2H, Ar), 6.80 (d, *J* = 8.3 Hz, 2H, Ar), 4.21 (s, 1H, -NH-), 3.04 (ddd, *J* = 15.9, 9.8, 5.9 Hz, 1H, -CH_2-), 2.84 (ddd, *J* = 17.4, 9.9, 4.9 Hz, 1H, -CH_2-), 2.50 (ddd, *J* = 14.5, 9.8, 5.0 Hz, 1H, -CH_2-), 2.36 (dq, *J* = 15.0, 7.3, 6.7 Hz, 1H, -CH_2-), 2.24 (s, 3H, -CH_3); ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.6 (C=N), 140.3 (Ar), 138.0 (Ar), 131.5 (Ar), 131.3 (Ar), 129.6 (Ar), 129.5 (Ar), 128.9 (Ar), 125.5 (q, *J* = 286.1 Hz, -CF_3), 121.2 (Ar), 93.3 (q, *J* = 27.8 Hz, CF_3CNH), 35.8 (-CH_2-), 27.8 (-CH_2-), 20.6 (-CH_3); ^{19}F NMR (565 MHz, $CDCl_3$) δ -80.22 (-CF_3). HRMS (ESI-TOF): $[M + H]^+$ calculated for $C_{18}H_{17}ClF_3N_2^+$: 353.1027, found: 353.1033.

5-(4-Fluorophenyl)-*N*-(*p*-tolyl)-2-(trifluoromethyl)-3,4-dihydro-2*H*-pyrrol-2-amine (3ah):



Yellow liquid; 41.7 mg, 62% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 – 7.80 (m, 2H, Ar), 7.08 – 7.02 (m, 2H, Ar), 6.91 (d, *J* = 8.1 Hz, 2H, Ar), 6.76 – 6.71 (m, 2H, Ar), 4.15 (s, 1H, -NH-), 3.02 – 2.95 (m, 1H, -CH_2-), 2.80 (ddd, *J* = 17.3, 10.0, 4.9 Hz, 1H, -CH_2-), 2.43 (ddd, *J* = 14.5, 9.8, 4.9 Hz, 1H, -CH_2-), 2.32 – 2.27 (m, 1H, -CH_2-), 2.17 (s, 3H, -CH_3); ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.5 (C=N), 163.9 (d, *J* = 252.6 Hz, Ar), 139.3 (Ar), 130.1 (Ar), 129.5 (d, *J* = 8.76 Hz, Ar), 128.5 (Ar), 128.4 (d, *J* = 3.0 Hz, Ar), 124.5 (q, *J* = 286.3 Hz, -CF_3), 119.9 (Ar), 114.7 (d, *J* = 21.9 Hz, Ar), 92.1 (q, *J* = 27.6 Hz, $CF_3\underline{C}NH$), 34.8 (-CH_2-), 26.9 (-CH_2-), 19.5 (-CH_3); ^{19}F NMR (565 MHz, $CDCl_3$) δ -80.26 (-CF_3), -107.70 (tt, *J* = 8.6, 5.5 Hz, Ar-F). HRMS (ESI-TOF): $[M + H]^+$ calculated for $C_{18}H_{17}F_4N_2^+$: 337.1322, found: 337.1322.

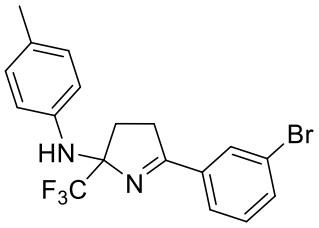
_N_-(_p_-tolyl)-2-(trifluoromethyl)-5-(4-(trifluoromethyl)phenyl)-3,4-dihydro-2_H_-pyrrol-2-amine (3ai):



Yellow solid; mp: 93 – 95 °C; 44.0 mg, 57% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.1 Hz, 2H, Ar), 7.69 (d, *J* = 8.2 Hz, 2H, Ar), 6.98 (d, *J* = 8.1 Hz, 2H, Ar), 6.80 (d, *J* = 8.3 Hz, 2H, Ar), 4.21 (s, 1H, -NH-), 3.07 (ddd, *J* = 15.8, 9.8, 5.8 Hz, 1H, -CH_2-), 2.89 – 2.82 (m, 1H, -CH_2-), 2.52 (ddd, *J* = 14.6, 9.8, 5.1 Hz, 1H, -CH_2-), 2.39 (ddd, *J* = 14.8, 9.9, 6.0 Hz, 1H, -CH_2-), 2.24 (s, 3H, -CH_3); ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.5 (C=N), 140.1 (Ar), 136.2 (Ar), 133.3 (q, *J* = 32.8 Hz, Ar), 131.7 (Ar), 129.6 (Ar), 128.6 (Ar), 125.6 (q, *J* = 3.8 Hz, Ar), 125.5 (q, *J* = 283.9 Hz, -CF_3), 125.4 (q, *J* = 286.0 Hz, -CF_3), 121.6 (Ar), 93.4 (q, *J* = 27.8 Hz, $CF_3\underline{C}NH$), 35.9 (-CH_2-),

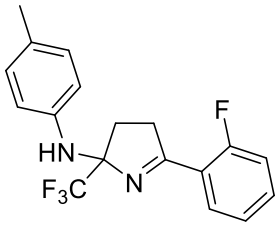
27.7 (-CH_2-), 20.6 (-CH_3); ^{19}F NMR (565 MHz, $CDCl_3$) δ -63.00 (Ar-CF_3), -80.27 (-CF_3). HRMS (ESI-TOF): $[M + H]^+$ calculated for $C_{19}H_{17}F_6N_2^+$: 387.1290, found: 387.1287.

5-(3-Bromophenyl)-N-(*p*-tolyl)-2-(trifluoromethyl)-3,4-dihydro-2*H*-pyrrol-2-amine (3aj):



Yellow liquid; 46.1 mg, 58% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (s, 1H, Ar), 7.78 (d, *J* = 7.8 Hz, 1H, Ar), 7.62 (d, *J* = 8.0 Hz, 1H, Ar), 7.31 (t, *J* = 7.9 Hz, 1H, Ar), 6.99 (d, *J* = 8.1 Hz, 2H, Ar), 6.80 (d, *J* = 8.3 Hz, 2H, Ar), 4.21 (s, 1H, -NH-), 3.04 (ddd, *J* = 15.9, 9.7, 5.9 Hz, 1H, -CH_2-), 2.87 – 2.79 (m, 1H, -CH_2-), 2.50 (ddd, *J* = 14.5, 9.8, 4.9 Hz, 1H, -CH_2-), 2.40 – 2.34 (m, 1H, -CH_2-), 2.25 (s, 3H, -CH_3); ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.5 (C=N), 140.2 (Ar), 135.0 (Ar), 134.6 (Ar), 131.5 (Ar), 131.2 (Ar), 130.1 (Ar), 129.6 (Ar), 126.9 (Ar), 125.5 (q, *J* = 287.5 Hz, -CF_3), 122.9 (Ar), 121.3 (Ar), 93.3 (q, *J* = 27.8 Hz, CF_3CNH), 35.8 (-CH_2-), 27.7 (-CH_2-), 20.6 (-CH_3); ^{19}F NMR (565 MHz, $CDCl_3$) δ -80.27 (-CF_3). HRMS (ESI-TOF): $[M + H]^+$ calculated for $C_{18}H_{17}BrF_3N_2^+$: 397.0522, found: 397.0530.

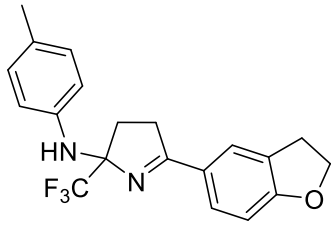
5-(2-Fluorophenyl)-N-(*p*-tolyl)-2-(trifluoromethyl)-3,4-dihydro-2*H*-pyrrol-2-amine (3ak):



Yellow liquid; 32.3 mg, 48% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (td, *J* = 7.7, 1.7 Hz, 1H, Ar), 7.46 (tdd, *J* = 7.2, 5.1, 1.7 Hz, 1H, Ar), 7.24 – 7.19 (m, 1H, Ar), 7.08

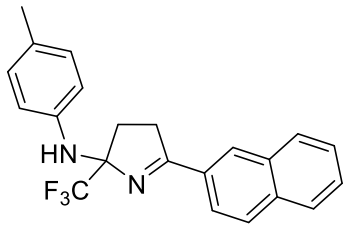
– 7.12 (m, 1H, Ar), 6.99 (d, *J* = 8.1 Hz, 2H, Ar), 6.81 (d, *J* = 8.3 Hz, 2H, Ar), 4.22 (s, 1H, -NH-), 3.17 (dtd, *J* = 12.4, 6.6, 6.2, 3.1 Hz, 1H, -CH_2-), 2.96 (ddd, *J* = 18.0, 9.1, 4.4 Hz, 1H, -CH_2-), 2.49 (td, *J* = 9.6, 4.9 Hz, 1H, -CH_2-), 2.35 (td, *J* = 9.0, 4.7 Hz, 1H, -CH_2-), 2.25 (s, 3H, -CH_3); ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.3 (C=N), 162.8 (Ar), 161.1 (Ar), 140.3 (Ar), 133.3 (d, *J* = 8.8 Hz, Ar), 131.2 (Ar), 130.7 (d, *J* = 3.0 Hz, Ar), 129.5 (Ar), 125.6 (q, *J* = 286.1 Hz, -CF_3), 124.4 (d, *J* = 3.2 Hz, Ar), 121.0 (Ar), 116.4 (d, *J* = 22.5 Hz, Ar), 91.2 (q, *J* = 20.8 Hz, CF_3<u>C</u>NH), 38.8 (d, *J* = 8.2 Hz, -CH_2-), 28.0 (d, *J* = 2.3 Hz, -CH_2-), 20.6 (-CH_3); ^{19}F NMR (565 MHz, $CDCl_3$) δ -80.22 (-CF_3), -111.73 (ddd, *J* = 11.6, 7.8, 4.6 Hz, Ar-F). HRMS (ESI-TOF): $[M + H]^+$ calculated for $C_{18}H_{17}F_4N_2^+$: 337.1322, found: 337.1320.

5-(2,3-Dihydrobenzofuran-5-yl)-*N*-(*p*-tolyl)-2-(trifluoromethyl)-3,4-dihydro-2*H*-pyrrol-2-amine (3al):



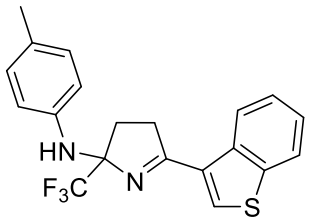
Colorless liquid; 48.3 mg, 67% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 – 7.86 (m, 1H, Ar), 7.58 (dd, *J* = 8.3, 1.7 Hz, 1H, Ar), 6.97 (d, *J* = 8.2 Hz, 2H, Ar), 6.79 (dd, *J* = 8.4, 2.9 Hz, 3H, Ar), 4.63 (t, *J* = 8.7 Hz, 2H, -C<u>H$_2$</u>CH$_2$-), 4.22 (s, 1H, -NH-), 3.23 (t, *J* = 8.7 Hz, 2H, -C<u>H$_2$</u>CH$_2$-), 3.04 (ddd, *J* = 16.3, 9.7, 6.2 Hz, 1H, -CH_2-), 2.89 (ddd, *J* = 17.2, 9.9, 4.7 Hz, 1H, -CH_2-), 2.47 (ddd, *J* = 14.3, 9.8, 4.8 Hz, 1H, -CH_2-), 2.33 (ddd, *J* = 14.7, 10.0, 6.4 Hz, 1H, -CH_2-), 2.24 (s, 3H, -CH_3); ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.2 (C=N), 163.3 (Ar), 140.7 (Ar), 130.7 (Ar), 129.6 (Ar), 129.5 (Ar), 127.9 (Ar), 126.0 (Ar), 125.2 (Ar), 125.7 (q, *J* = 286.3 Hz, -CF_3), 120.4 (Ar), 109.1 (Ar), 92.9 (q, *J* = 27.5 Hz, CF_3<u>C</u>NH), 72.0 (-O<u>C</u>H$_2$-), 35.8 (-CH_2-), 29.2 (-CH_2-), 27.8 (-CH_2-), 20.6 (-CH_3); ^{19}F NMR (565 MHz, $CDCl_3$) δ -80.26 (-CF_3). HRMS (ESI-TOF): $[M + H]^+$ calculated for $C_{20}H_{20}F_3N_2O^+$: 361.1522, found: 361.1520.

5-(Naphthalen-2-yl)-*N*-(*p*-tolyl)-2-(trifluoromethyl)-3,4-dihydro-2*H*-pyrrol-2-amine (3am):



White solid; mp: 105 – 107 °C; 53.0 mg, 72% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (s, 1H, Ar), 8.14 (dd, *J* = 8.6, 1.5 Hz, 1H, Ar), 7.89 (q, *J* = 8.2, 7.7 Hz, 3H, Ar), 7.58 – 7.51 (m, 2H, Ar), 6.98 (d, *J* = 8.1 Hz, 2H, Ar), 6.83 (d, *J* = 8.3 Hz, 2H, Ar), 4.27 (s, 1H, -NH-), 3.21 (ddd, *J* = 16.1, 9.7, 6.0 Hz, 1H, -CH_2-), 3.06 – 2.98 (m, 1H, -CH_2-), 2.55 (ddd, *J* = 14.5, 9.8, 4.9 Hz, 1H, -CH_2-), 2.42 (ddd, *J* = 14.6, 9.8, 6.3 Hz, 1H, -CH_2-), 2.24 (s, 3H, -CH_3); ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.7 (C=N), 140.4 (Ar), 135.0 (Ar), 132.8 (Ar), 131.1 (Ar), 130.6 (Ar), 129.5 (Ar), 129.3 (Ar), 128.9 (Ar), 128.4 (Ar), 127.8 (Ar), 127.7 (Ar), 126.6 (Ar), 125.6 (q, *J* = 285.8 Hz, -CF_3), 124.7 (Ar), 121.0 (Ar), 93.3 (q, *J* = 27.6 Hz, $CF_3\underline{C}NH$), 35.9 (-CH_2-), 27.7 (-CH_2-), 20.6 (-CH_3); ^{19}F NMR (565 MHz, $CDCl_3$) δ -80.19 (-CF_3). HRMS (ESI-TOF): $[M + H]^+$ calculated for $C_{22}H_{20}F_3N_2^+$: 369.1573, found: 369.1578.

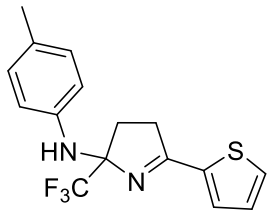
5-(Benzo[*b*]thiophen-3-yl)-*N*-(*p*-tolyl)-2-(trifluoromethyl)-3,4-dihydro-2*H*-pyrrol-2-amine (3an):



Colorless liquid; 48.7 mg, 65% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.02 (d, *J* = 8.1 Hz, 1H, Ar), 7.87 (d, *J* = 8.1 Hz, 1H, Ar), 7.83 (s, 1H, Ar), 7.53 – 7.50 (m, 1H, Ar), 7.45 – 7.42 (m, 1H, Ar), 6.98 (d, *J* = 8.2 Hz, 2H, Ar), 6.84 (d, *J* = 8.3 Hz, 2H, Ar), 4.27 (s, 1H, -NH-), 3.16 (ddd, *J* = 16.2, 9.8, 6.1 Hz, 1H, -CH_2-), 3.04 – 2.98 (m, 1H, -CH_2-), 2.48 (ddd, *J* = 14.4, 9.8, 4.9 Hz, 1H, -CH_2-), 2.32 (ddd, *J* = 14.7, 9.9, 6.2 Hz,

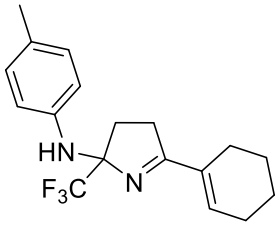
1H, -CH_2-), 2.24 (s, 3H, -CH_3); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.8 (C=N), 140.5 (Ar), 140.1 (Ar), 136.8 (Ar), 133.5 (Ar), 131.0 (Ar), 130.6 (Ar), 129.5 (Ar), 126.4 (Ar), 125.7 (q, *J* = 286.3 Hz, -CF_3), 125.5 (Ar), 125.4 (Ar), 122.3 (Ar), 120.9 (Ar), 93.8 (q, *J* = 27.6 Hz, CF_3<u>C</u>NH), 37.5 (-CH_2-), 27.1 (-CH_2-), 20.6 (-CH_3); ^{19}F NMR (565 MHz, $CDCl_3$) δ -80.14 (-CF_3). HRMS (ESI-TOF): $[M + H]^+$ calculated for $C_{20}H_{18}F_3N_2S^+$: 375.1137, found: 375.1132.

5-(Thiophen-2-yl)-*N*-(*p*-tolyl)-2-(trifluoromethyl)-3,4-dihydro-2*H*-pyrrol-2-amine (3ao):



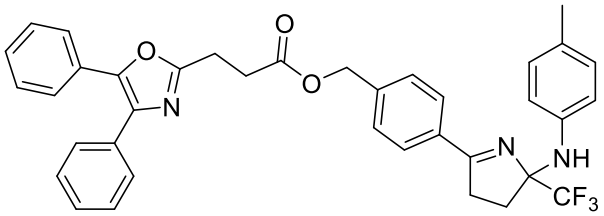
Yellow liquid; 47.4 mg, 73% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 – 7.74 (m, 1H, Ar), 7.65 – 7.61 (m, 1H, Ar), 7.36 (dd, *J* = 5.0, 2.9 Hz, 1H, Ar), 6.98 (d, *J* = 8.1 Hz, 2H, Ar), 6.79 (d, *J* = 8.3 Hz, 2H, Ar), 4.22 (s, 1H, -NH-), 3.04 (ddd, *J* = 16.4, 9.7, 6.3 Hz, 1H, -CH_2-), 2.91 – 2.85 (m, 1H, -CH_2-), 2.48 (td, *J* = 9.7, 4.9 Hz, 1H, -CH_2-), 2.36 – 2.30 (m, 1H, -CH_2-), 2.24 (s, 3H, -CH_3); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.8 (C=N), 140.5 (Ar), 136.6 (Ar), 130.9 (Ar), 129.5 (Ar), 129.3 (Ar), 127.1 (Ar), 126.5 (Ar), 125.1 (q, *J* = 285.4 Hz, -CF_3), 120.7 (Ar), 93.2 (q, *J* = 27.6 Hz, CF_3<u>C</u>NH), 36.7 (-CH_2-), 27.6 (-CH_2-), 20.6 (-CH_3); ^{19}F NMR (565 MHz, $CDCl_3$) δ -80.21 (-CF_3). HRMS (ESI-TOF): $[M + H]^+$ calculated for $C_{16}H_{16}F_3N_2S^+$: 325.0981, found: 325.0978.

5-(Cyclohex-1-en-1-yl)-N-(*p*-tolyl)-2-(trifluoromethyl)-3,4-dihydro-2*H*-pyrrol-2-amine (3ap):



Colorless liquid; 35.5 mg, 55% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.98 (d, *J* = 8.0 Hz, 2H, Ar), 6.77 – 6.74 (m, 2H, Ar), 6.38 (dq, *J* = 4.0, 2.3, 1.9 Hz, 1H, -C=C<u>H</u>), 4.18 (s, 1H, -NH-), 2.82 (ddd, *J* = 16.6, 9.7, 6.6 Hz, 1H, -CH_2-), 2.74 – 2.68 (m, 1H, -CH_2-), 2.51 – 2.41 (m, 2H, -CH_2-), 2.40 – 2.35 (m, 1H, -CH_2-), 2.25 (s, 3H, -CH_3), 2.18 – 2.24 (m, 3H, -CH_2-), 1.71 – 1.67 (m, 2H, -CH_2-), 1.64 (dtd, *J* = 10.9, 6.0, 2.5 Hz, 2H, -CH_2-); ^{13}C NMR (151 MHz, $CDCl_3$) δ 179.0 (C=N), 140.8 (Ar), 137.8 (Ar), 134.4 (Ar), 130.3 (Ar), 129.4 (C=C), 125.8 (q, *J* = 286.7 Hz, -CF_3), 119.9 (Ar), 92.6 (q, *J* = 27.5 Hz, CF_3<u>C</u>NH), 34.7 (-CH_2-), 27.7 (-CH_2-), 26.2 (-CH_2-), 24.9 (-CH_2-), 22.1 (-CH_2-), 21.8 (-CH_2-), 20.6 (-CH_3); ^{19}F NMR (565 MHz, $CDCl_3$) δ -80.15 (-CF_3). HRMS (ESI-TOF): $[M + H]^+$ calculated for $C_{18}H_{22}F_3N_2^+$: 323.1730, found: 323.1734.

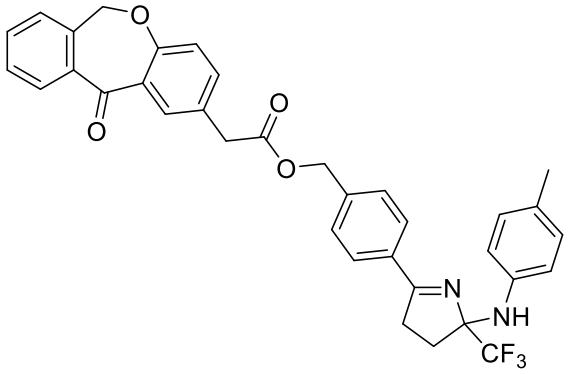
4-(2-(*p*-Tolylamino)-2-(trifluoromethyl)-3,4-dihydro-2*H*-pyrrol-5-yl)benzyl 3-(4,5-diphenyloxazol-2-yl)propanoate (3aq):



Colorless liquid; 68.6 mg, 55% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 – 7.77 (m, 2H, Ar), 7.61 (dt, *J* = 6.0, 1.5 Hz, 2H, Ar), 7.56 – 7.52 (m, 2H, Ar), 7.39 (d, *J* = 8.0 Hz, 2H, Ar), 7.36 – 7.29 (m, 6H, Ar), 6.97 (d, *J* = 7.9 Hz, 2H, Ar), 6.84 – 6.75 (m, 2H, Ar), 5.21 (s, 2H, -COOC<u>H</u>$_2$-), 4.21 (s, 1H, -NH-), 3.21 (t, *J* = 7.3 Hz, 2H, -CH_2-), 3.00 (t, *J* = 7.4 Hz, 3H, -CH_2-), 2.82 (ddd, *J* = 17.3, 9.9, 4.9 Hz, 1H, -CH_2-), 2.48 (ddd, *J* = 14.4, 9.8, 4.9 Hz, 1H, -CH_2-), 2.35 (td, *J* = 9.1, 8.5, 4.8 Hz, 1H, -CH_2-), 2.24 (s, 3H, -CH_3); ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.4 (C=N), 171.8 (C=O), 161.6 (-O<u>C</u>=N-), 145.5 (Ar), 140.4 (Ar), 139.6 (Ar), 135.1 (Ar), 132.8 (Ar), 132.4 (Ar), 131.2 (Ar), 129.5

(Ar), 128.9 (Ar), 128.7 (Ar), 128.6 (Ar), 128.6 (Ar), 128.5 (Ar), 128.1 (Ar), 128.0 (Ar), 127.9 (Ar), 126.5 (Ar), 125.6 (q, *J* = 286.2 Hz, -CF_3), 121.1 (Ar), 93.2 (q, *J* = 27.5 Hz, CF_3<u>C</u>NH), 65.9 (-O<u>C</u>H_2Ph), 35.9 (-CH_2-), 31.1 (-CH_2-), 27.7 (-CH_2-), 23.5 (-CH_2-), 20.6 (-CH_3); ^{19}F NMR (565 MHz, $CDCl_3$) δ -80.20 (-CF_3). HRMS (ESI-TOF): $[M + H]^+$ calculated for $C_{37}H_{33}F_3N_3O_3^+$: 624.2469, found: 624.2468.

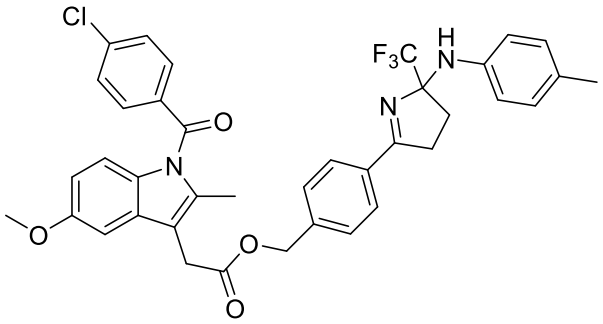
4-(2-(*p*-Tolylamino)-2-(trifluoromethyl)-3,4-dihydro-2*H*-pyrrol-5-yl)benzyl 2-(11-oxo-6,11-dihydrodibenzo[*b*,*e*]oxepin-2-yl)acetate (3ar):



Colorless liquid; 62.3 mg, 52% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 (d, *J* = 2.4 Hz, 1H, Ar), 7.88 (dd, *J* = 13.6, 7.8 Hz, 3H, Ar), 7.56 (t, *J* = 7.4 Hz, 1H, Ar), 7.47 (t, *J* = 7.6 Hz, 1H, Ar), 7.42 (dd, *J* = 8.4, 2.4 Hz, 1H, Ar), 7.36 – 7.39 (m, 3H, Ar), 7.03 (d, *J* = 8.4 Hz, 1H, Ar), 6.98 (d, *J* = 8.0 Hz, 2H, Ar), 6.80 (d, *J* = 8.0 Hz, 2H, Ar), 5.19 (d, *J* = 3.0 Hz, 4H, -CH_2-), 4.22 (s, 1H, -NH-), 3.71 (s, 2H, -CH_2-), 3.06 (ddd, *J* = 16.4, 9.8, 6.0 Hz, 1H, -CH_2-), 2.87 (ddd, *J* = 17.3, 9.9, 4.9 Hz, 1H, -CH_2-), 2.49 (ddd, *J* = 14.5, 9.8, 4.9 Hz, 1H, -CH_2-), 2.36 (ddd, *J* = 14.8, 9.8, 6.2 Hz, 1H, -CH_2-), 2.24 (s, 3H, -CH_3); ^{13}C NMR (151 MHz, $CDCl_3$) δ 190.8 (C=O), 177.4 (C=N), 171.1 (-COO-), 160.6 (Ar), 140.4 (Ar), 140.3 (Ar), 139.5 (Ar), 136.3 (Ar), 135.5 (Ar), 132.9 (Ar), 132.8 (Ar), 132.5 (Ar), 131.2 (Ar), 129.5 (Ar), 129.5 (Ar), 129.3 (Ar), 128.6 (Ar), 128.1 (Ar), 127.9 (Ar), 127.5 (Ar), 125.6 (q, *J* = 286.4 Hz, -CF_3), 125.2 (Ar), 121.2 (Ar), 121.1 (Ar), 93.2 (q, *J* = 27.6 Hz, CF_3<u>C</u>NH), 73.7 (Ph<u>C</u>H_2O), 66.1 (-COO<u>C</u>H_2Ph), 40.2 (Ph<u>C</u>H_2CO), 35.9 (-CH_2-), 27.7 (-CH_2-), 20.6 (-CH_3); ^{19}F NMR (565 MHz, $CDCl_3$) δ -80.26 (-CF_3). HRMS (ESI-TOF): $[M + H]^+$ calculated for $C_{35}H_{30}F_3N_2O_4^+$:

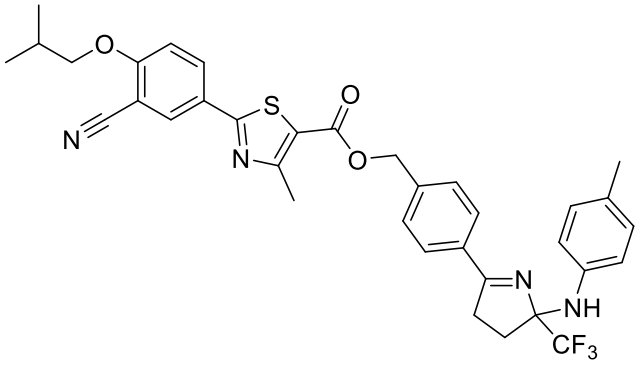
599.2152, found: 599.2155.

4-(2-(*p*-Tolylamino)-2-(trifluoromethyl)-3,4-dihydro-2*H*-pyrrol-5-yl)benzyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate (3as):



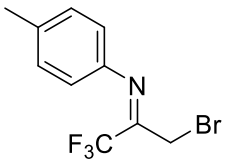
Colorless liquid; 79.8 mg, 58% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.2 Hz, 2H, Ar), 7.66 – 7.62 (m, 2H, Ar), 7.46 – 7.42 (m, 2H, Ar), 7.33 (d, *J* = 8.0 Hz, 2H, Ar), 6.97 (d, *J* = 8.0 Hz, 2H, Ar), 6.92 (d, *J* = 2.5 Hz, 1H, Ar), 6.88 (d, *J* = 9.0 Hz, 1H, Ar), 6.82 – 6.77 (m, 2H, Ar), 6.67 (dd, *J* = 9.0, 2.5 Hz, 1H, Ar), 5.17 (s, 2H, -$COOCH_2$-), 4.24 (s, 1H, -NH-), 3.75 (s, 3H, -OMe), 3.73 (s, 2H, -$COCH_2$-), 3.05 (ddd, *J* = 17.3, 9.7, 6.0 Hz, 1H, -CH_2-), 2.87 (ddd, *J* = 17.3, 9.9, 4.9 Hz, 1H, -CH_2-), 2.49 (ddd, *J* = 14.4, 9.8, 4.9 Hz, 1H), 2.37 (s, 3H, -CH_3), 2.35 (q, *J* = 7.8, 6.5 Hz, 1H, -CH_2-), 2.23 (s, 3H, -PhCH_3); ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.3 (C=N), 170.5 (-COO-), 168.3 (-CONRR, -CH_2-'), 156.1 (Ar), 140.4 (Ar), 139.5 (Ar), 139.3 (Ar), 136.0 (Ar), 133.9 (Ar), 133.0 (Ar), 131.2 (Ar), 131.1 (Ar), 130.8 (Ar), 130.6 (Ar), 129.5 (Ar), 129.2 (Ar), 128.6 (Ar), 128.0 (Ar), 125.6 (q, *J* = 286.3 Hz, -CF_3), 121.0 (Ar), 115.0 (Ar), 112.3 (Ar), 111.8 (Ar), 101.3 (Ar), 93.2 (q, *J* = 27.6 Hz, $CF_3\underline{C}NH$), 66.1 (-COO$\underline{C}H_2$Ph), 55.6 (-OCH_3), 35.9 (-CH_2-), 30.4 (-$\underline{C}H_2$COO-), 27.8 (-CH_2-), 20.6 (-PhCH_3), 13.4 (-CH_3); ^{19}F NMR (565 MHz, $CDCl_3$) δ -80.16 (-CF_3). HRMS (ESI-TOF): $[M + H]^+$ calculated for $C_{38}H_{34}ClF_3N_3O_4^+$: 688.2184, found: 688.2177.

4-(2-(*p*-Tolylamino)-2-(trifluoromethyl)-3,4-dihydro-2*H*-pyrrol-5-yl)benzyl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (3at):



Colorless liquid; 59.5 mg, 46% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (d, *J* = 2.3 Hz, 1H, Ar), 8.09 (dd, *J* = 8.8, 2.3 Hz, 1H, Ar), 7.93 (d, *J* = 8.2 Hz, 2H, Ar), 7.50 (d, *J* = 8.0 Hz, 2H, Ar), 6.99 (dd, *J* = 17.2, 8.5 Hz, 3H, Ar), 6.84 – 6.76 (m, 2H, Ar), 5.37 (s, 2H), 3.90 (d, *J* = 6.5 Hz, 2H), 3.08 (ddd, *J* = 17.4, 9.8, 6.0 Hz, 1H), 2.90 (ddd, *J* = 17.4, 9.9, 4.8 Hz, 1H, -CH_2-), 2.77 (s, 3H), 2.51 (ddd, *J* = 14.4, 9.8, 4.9 Hz, 1H, -CH_2-), 2.37 (ddd, *J* = 15.0, 9.8, 6.1 Hz, 1H, -CH_2-), 2.24 (s, 3H), 2.23 – 2.18 (m, 1H, -CH_2-), 1.09 (d, *J* = 6.7 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.3 (C=N), 167.6 (-COO-), 162.6 (Ar), 161.9 (Ar), 161.7 (Ar), 140.3 (Ar), 139.2 (Ar), 133.1 (Ar), 132.6 (Ar), 132.2 (Ar), 131.2 (Ar), 129.5 (Ar), 128.7 (Ar), 128.1 (Ar), 125.9 (Ar), 125.6 (q, *J* = 286.3 Hz, -CF_3), 121.2 (Ar), 121.0 (Ar), 115.3 (-CN), 112.7 (Ar), 103.0 (Ar), 93.2 (q, *J* = 27.8 Hz, CF_3CNH), 75.7 (-CH_2OPh-), 66.3 (-COOCH_2-), 35.9 (-CH_2-), 28.2 (CH_3CHCH_3), 27.7 (-CH_2-), 20.6 (-PhCH_3), 19.1 (CH_3CHCH_3), 17.6 (CH_3CHCH_3); ^{19}F NMR (565 MHz, $CDCl_3$) δ -80.24 (-CF_3). HRMS (ESI-TOF): $[M + H]^+$ calculated for $C_{35}H_{34}F_3N_4O_3S^+$: 647.2298, found: 647.2292.

(*E*)-3-bromo-1,1,1-trifluoro-*N*-(*p*-tolyl)propan-2-imine (6a):

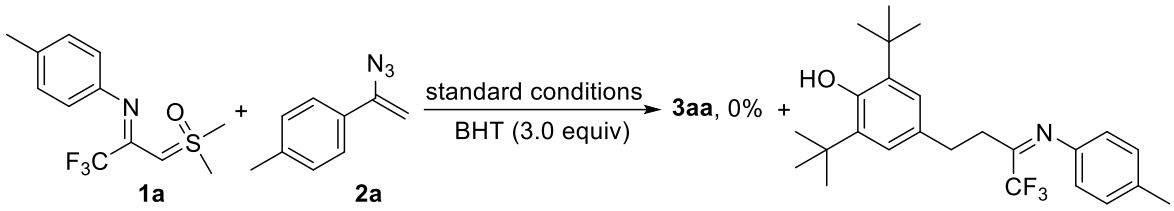


Yellow liquid; 31.6 mg, 47% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.14 (d, *J* = 8.0 Hz, 2H, Ar), 6.80 (d, *J* = 8.3 Hz, 2H, Ar), 3.79 (s, 2H, -CH_2-), 2.28 (s, 3H, -CH_3); ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.9 (q, *J* = 33.7 Hz, -C=N), 142.6 (Ar), 135.1 (Ar), 128.9 (Ar), 119.2 (Ar), 118.3 (q, *J* = 279.7 Hz, -CF_3), 19.9 (-CH_2-), 15.5 (-CH_3); ^{19}F

NMR (565 MHz, $CDCl_3$) δ -70.02 ($-CF_3$). HRMS (ESI-TOF): $[M + H]^+$ calculated for $C_{10}H_{10}BrF_3N^+$: 279.9943, found: 279.9945.

III. Mechanistic Studies

Radical intermediate quench reactions



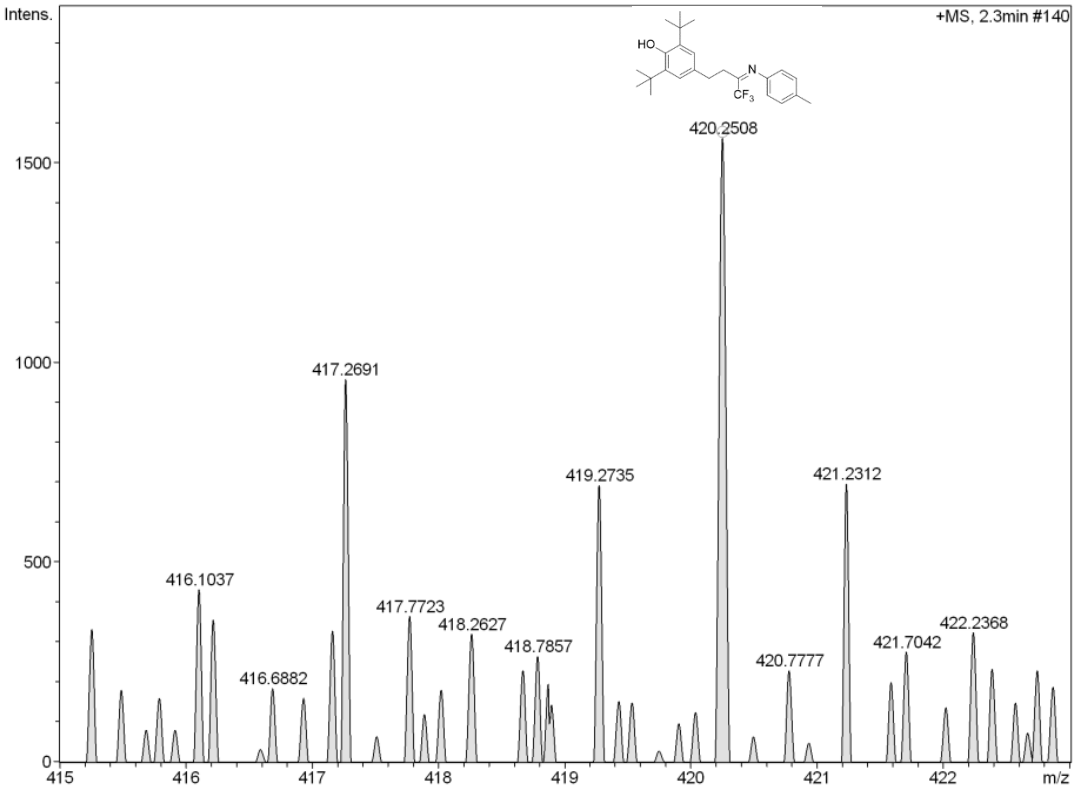
detected by HRMS
$[M + H^+]$ = 420.2509
found: 420.2508

Analysis Info

Analysis Name	D:\Data\user\D2023\Dd399_9_01_21587.d	Acquisition Date	3/9/2023 10:35:10 AM
Method	sample-3min-100%acn.m		
Sample Name	Dd399	Operator	BDAL@DE
Comment		Instrument / Ser#	micrOTOF 213750.10328

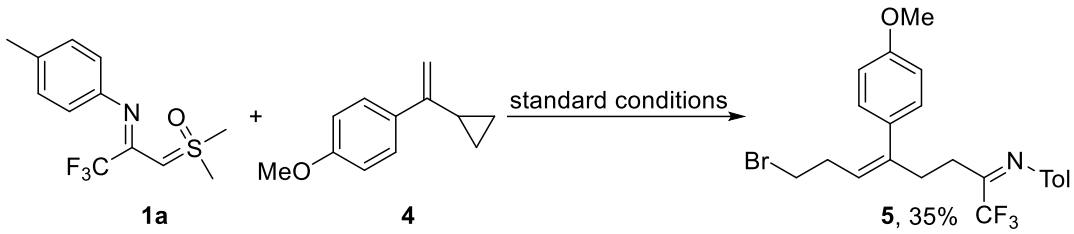
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	8.0 l/min
Scan End	1500 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
420.2508	1	C25H33F3NO	420.2509	0.3	162.6	1	100.00	8.5	even	ok

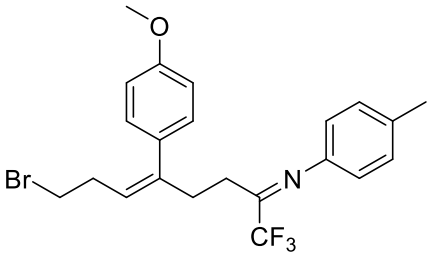
Radical clock experiment



1a **4** **5**, 35%

A sealed tube equipped with a magnetic stir bar was charged with perfluoroalkyl -substituted imidoyl sulfoxonium ylide **1a** (0.6 mmol, 166.4 mg), 1-(1-cyclopropylvinyl)-4-methoxybenzene **4** (0.2 mmol, 34.8 mg), $[Ru(bpy)_3Cl_2]$. $6H_2O$ (0.002 mmol, 1.50 mg), $KHSO_4$ (0.2 mmol, 27.2 mg), CuBr (0.24 mmol, 34.4 mg) and dry MeCN (2.0 mL) were added. The mixture was then stirred at room temperature under N_2 atmosphere and irradiated with 395nm LEDs for 72 h. After the reaction was complete, the solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography (EtOAc/petroleum ether = 1:100, V/V) to give the product **5** (31.8 mg, 35%) as a yellow liquid.

(5*Z*)-8-Bromo-1,1,1-trifluoro-5-(4-methoxyphenyl)-*N*-(*p*-tolyl)oct-5-en-2-imine (5):



Yellow liquid; 31.8 mg, 35% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (d, *J* = 7.9 Hz, 2H, Ar), 6.98 (d, *J* = 8.6 Hz, 2H, Ar), 6.73 (d, *J* = 8.6 Hz, 2H, Ar), 6.68 (d, *J* = 8.0 Hz, 2H, Ar), 5.53 (t, *J* = 7.2 Hz, 1H, -CH=C), 3.79 (s, 3H, -OMe), 3.29 (t, *J* = 6.9 Hz, 2H, $-CH_2-$), 2.57 (dd, *J* = 11.0, 6.1 Hz, 2H, $-CH_2-$), 2.48 – 2.43 (m, 2H, $-CH_2-$), 2.43 – 2.39 (m, 2H, $-CH_2-$), 2.39 (s, 3H, $-CH_3$); ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.57 (q, *J* = 32.8 Hz, C=N), 158.99 (Ar), 145.06 (Ar), 139.39 (Ar), 134.48 (Ar), 132.78 (Ar), 129.91 (Ar), 126.98 (Ar), 124.62 (Ar), 119.95 (q, *J* = 279.4 Hz, $-CF_3$), 118.09 (C=C),

113.76 (C=C), 55.25 (-OCH_3), 32.20 (-CH_2-), 31.44 (-CH_2-), 27.44 (-CH_2-), 26.69 (-CH_2-), 20.96 (-CH_3); ^{19}F NMR (565 MHz, $CDCl_3$) δ -72.63 (-CF_3). HRMS (ESI-TOF): $[M + H]^+$ calculated for $C_{22}H_{24}BrF_3NO^+$: 454.0988, found: 454.0997.

UV-vis spectrum

UV-vis absorption of six solutions are reported. As follows: perfluoroalkyl -substituted imidoyl sulfoxonium ylide **1a** (0.08 mmol in 200 mL MeCN); vinyl azide **2a** (0.1 mmol in 200 mL MeCN); [$Ru(bpy)_3Cl_2$]. $6H_2O$ (0.005 mmol in 200 mL MeCN); perfluoroalkyl -substituted imidoyl sulfoxonium ylide **1a** (0.08 mmol) and [$Ru(bpy)_3Cl_2$]. $6H_2O$ (0.005 mmol) in 200 mL MeCN; vinyl azide **2a** (0.1 mmol) and [$Ru(bpy)_3Cl_2$]. $6H_2O$ (0.005 mmol) in 200 mL MeCN; perfluoroalkyl -substituted imidoyl sulfoxonium ylide **1a** (0.08 mmol), vinyl azide **2a** (0.1 mmol) and [$Ru(bpy)_3Cl_2$]. $6H_2O$ (0.005 mmol) in 200 mL MeCN.

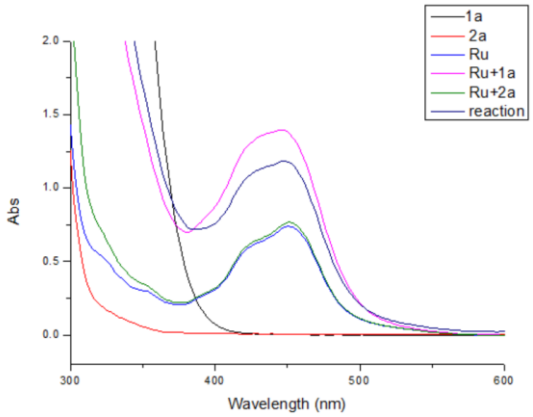


Figure 1. UV−Vis Absorption Spectrum

Cyclic Voltammetry Experiments

For the electrochemical measurements, a three-electrode system connected to an electrochemical station was used: A reference electrode, Ag/AgCl in 0.1 M KCl; A glassy carbon electrode as the working electrode; and a Pt wire as the counter electrode. All electrochemical measurements were performed in degassed MeCN

under dry N_2 atmosphere. CV spectra of **1a** is reported at 3 mM in 0.1 M NBu_4PF_6 in degassed MeCN with scan rate 100 mV/s.

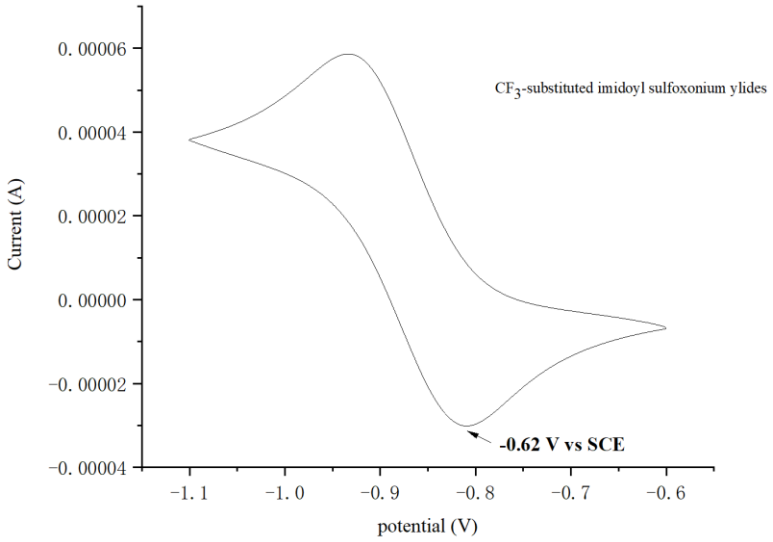


Figure 2. Cyclic Voltammetry (CV) Experiments

Stern-Volmer Quenching Experiments

Emission intensities were recorded using an spectrofluorimeter. All $[Ru(bpy)_3Cl_2].6H_2O$ solutions were excited at 500 nm and the emission intensity at 615 nm was observed. First, the emission spectrum of a 5×10^{-5} M solution of $[Ru(bpy)_3Cl_2].6H_2O$ in MeCN was collected. Then, appropriate amount of quencher was added to the measured solution and the emission spectrum of the sample was collected.

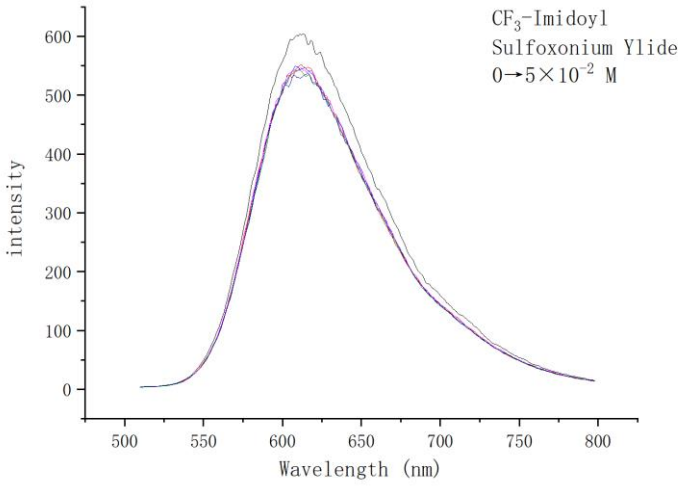


Figure 3. [Ru(bpy)$_3$Cl$_2$]. 6H$_2$O Emission Quenching by CF$_3$-substituted imidoyl sulfoxonium ylide **1a**

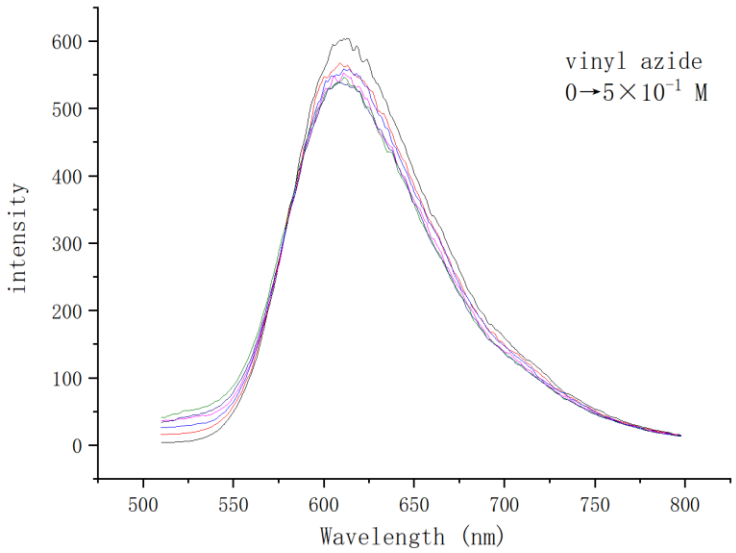


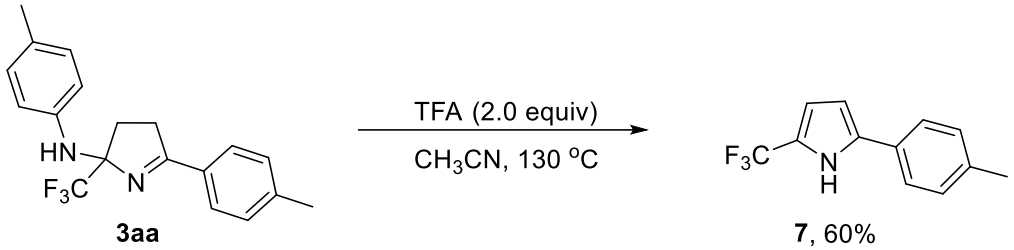
Figure 4. [Ru(bpy)$_3$Cl$_2$]. 6H$_2$O Emission Quenching by vinyl azide **2a**

References:

1. (a) Caiuby, C. A. D.; de Jesus, M. P.; Burtoloso, A. C. B. *α*-Imino Iridium Carbenes from Imidoyl Sulfoxonium Ylides: Application in the One-Step Synthesis of Indoles. *J. Org. Chem.* **2020**, *85*, 7433–7445. (b) Wen, S.; Tian, Q.; Chen, Y.; Zhang, Y.; Cheng, G. Annulation of CF$_3$−Imidoyl Sulfoxonium Ylides with 1,3-Dicarbonyl Compounds: Access to 1,2,3-Trisubstituted 5 −Trifluoromethylpyrroles. *Org. Lett.* **2021**, *23*, 7407−7411. (c) Zhang, Y.; Ling, S.; Li, P.; Chen, Z.; Wu, X. F. Rh(III)-Catalyzed Dual C–H Activation/Cascade Annulation of Benzimidates and CF$_3$-Imidoyl Sulfoxonium Ylides for the Synthesis of Trifluoromethyl-Decorated Benzo[*de*][1,8]naphthyridines. *Org. Lett.* **2022**, *24*, 8864−8869.

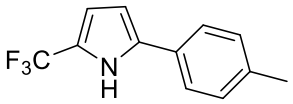
2. (a) Ning, Y.; Ji, Q.; Liao, P.; Anderson, E. A.; Bi, X. Silver-Catalyzed Stereoselective Aminosulfonylation of Alkynes. *Angew. Chem., Int. Ed.* **2017**, *56*, 13805–13808. (b) Zhang, Y.; Jiang, B.; Liu, P.; Liu, X. Et$_2$Zn-Mediated Radical (3 + 2) Cycloaddition of Vinyl Azides with Ethyl Iododifluoroacetate to Access 3,3-Difluoro-γ-lactams. *J. Org. Chem.* **2023**, *88*, 14634–14639.

IV. Synthetic procedures and analytical data of compound 7:



To a solution of **3aa** (0.2 mmol, 66.5 mg) and TFA (0.4 mmol) in CH_3CN (2.0 mL) was added into a 10.0 mL sealed tube. Then the mixture was stirred at 130 °C for 6 h. After the complete consumption of **3aa** (TLC), the mixture was treated with saturated sodium bicarbonate solution (50 mL) and extracted with DCM (3 × 15 mL). The combined organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure to yield the corresponding crude product, which was purified by silica gel chromatography (EtOAc /Petroleum Ether = 1/10, V/V) to give **7** (27.0 mg, 60%) as a white solid.

2-(*p*-Tolyl)-5-(trifluoromethyl)-1*H*-pyrrole (7)：



White solid; mp: 42 – 43 °C; 27.0 mg, 60% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.59 (s, 1H, -NH-), 7.41 – 7.38 (m, 2H, Ar), 7.22 (d, *J* = 7.9 Hz, 2H, Ar), 6.62 – 6.63 (m, 1H, Ar), 6.45 – 6.43 (m, 1H, Ar), 2.37 (s, 3H, $-CH_3$); ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.6 (Ar), 135.1 (Ar), 129.7 (Ar), 128.6 (Ar), 124.5 (Ar), 121.3 (q, *J* = 266.1 Hz, $-CF_3$), 120.4 (q, *J* = 39.6 Hz, Ar), 111.5 (q, *J* = 2.9 Hz, Ar), 106.0 (Ar), 21.2 ($-CH_3$); ^{19}F NMR (565 MHz, $CDCl_3$) δ -59.25 ($-CF_3$). HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{12}H_{10}F_3NNa^+$: 248.0657, found: 248.0658.

V. ORTEP Drawing of Compound 3aa:

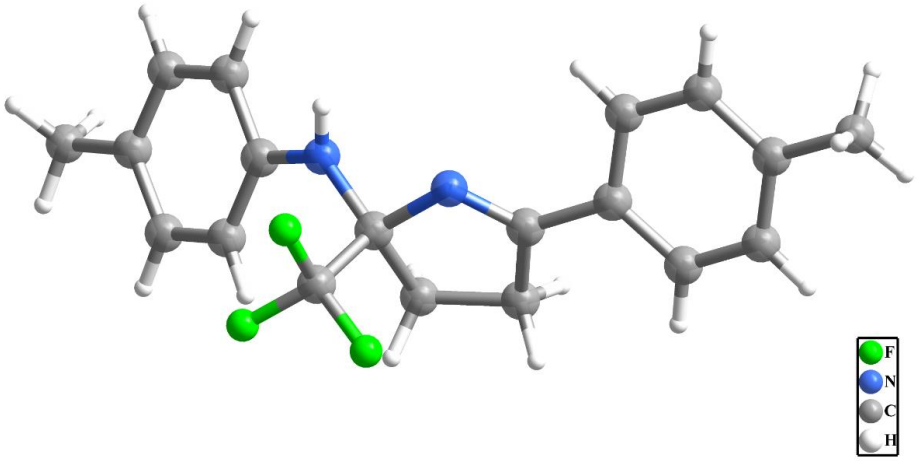


Figure 5. The ORTEP drawing of crystal 3aa (The ellipsoid contour percent probability level is 50%).

Method of Crystallization: The compounds **3aa** was recrystallized from mixed solvents of ethyl acetate and petroleum ether at 25 ˚C.

Introduction of crystal measuring instrument: X-ray single-crystal data of **3aa** was collected by a Bruker D8 Venture diffractometer (Mo Kα radiation, λ = 0.71073 Å (Cu Kα radiation, λ = 1.54178 Å)) at 293(2) K. The adsorption corrections were conducted by a multiscan technique. All the structures were solved via direct method and refined by the full-matrix least-squares technique using the SHELXL-2014 program. Anisotropic thermal parameters were used to refine the non-hydrogen atoms and hydrogen atoms were contained in calculated positions, refining with isotropic thermal parameters locating at those of the parent atoms.

VI. Copies of ^{1}H NMR, ^{13}C NMR and ^{19}F NMR Spectra of Compounds 3 and 5-7:

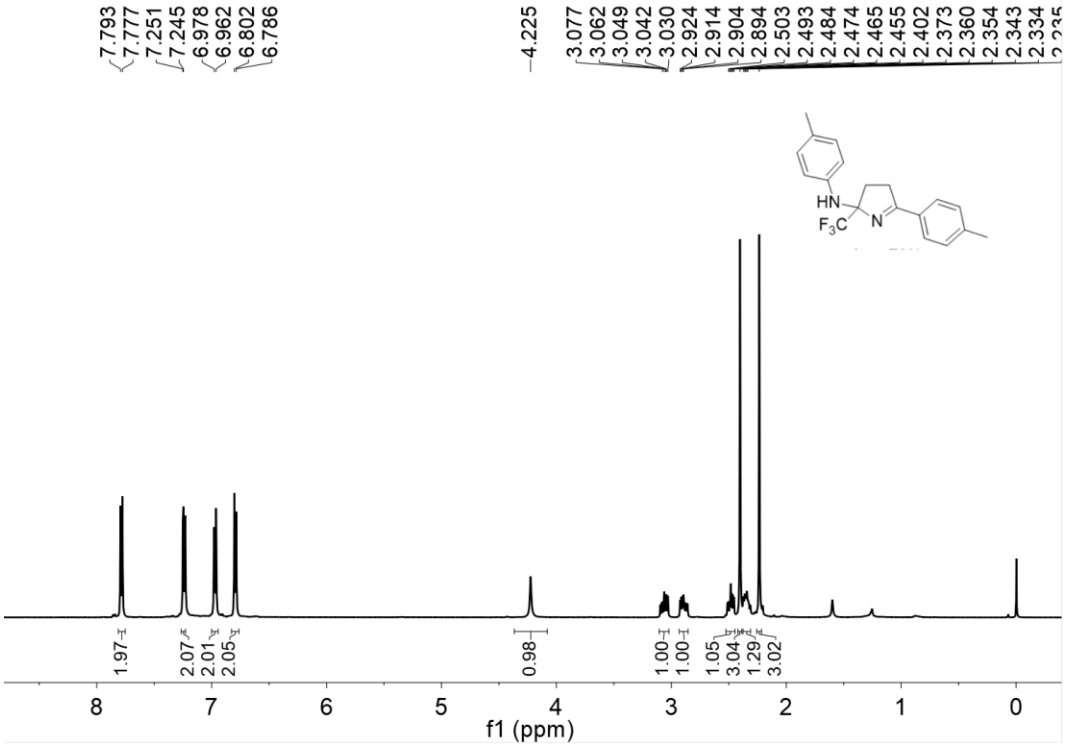


Figure 6. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3aa**

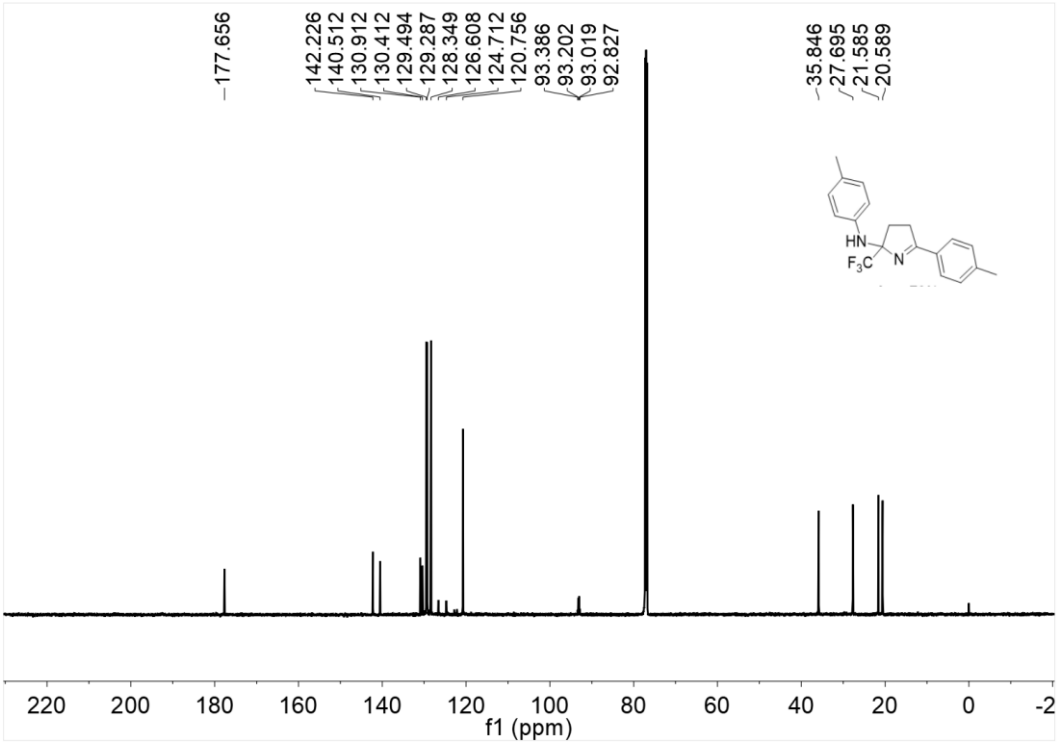


Figure 7. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3aa**

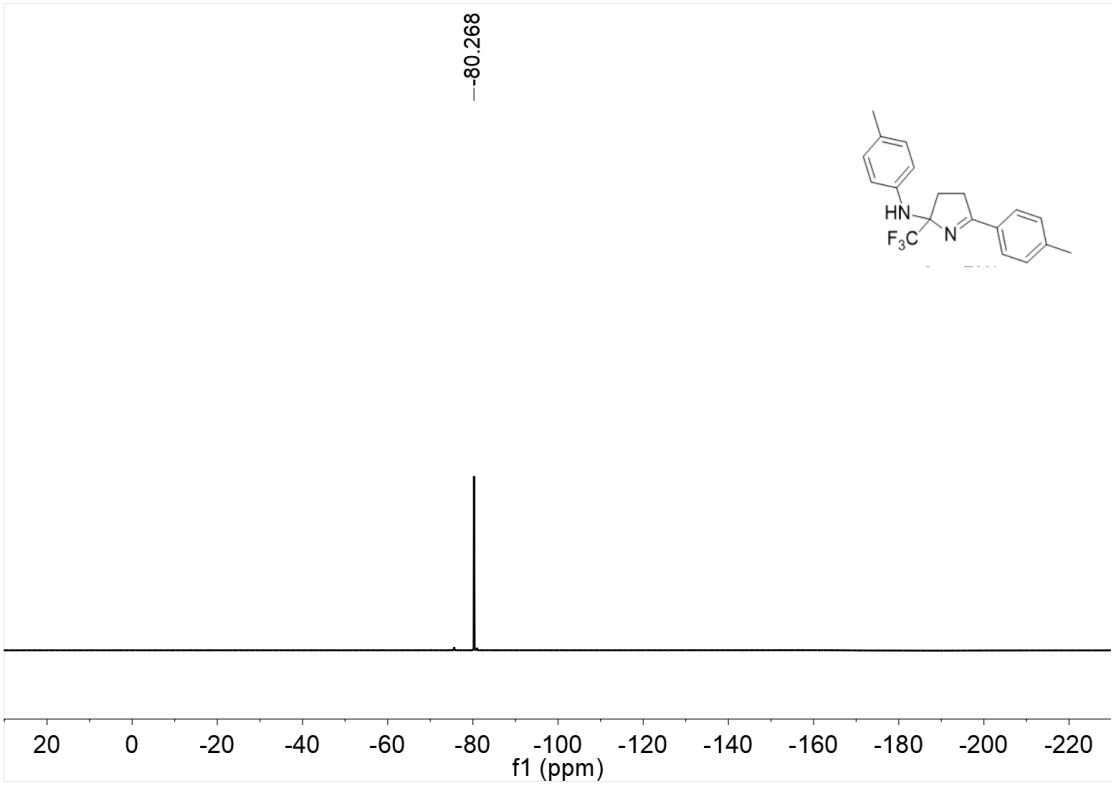


Figure 8. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **3aa**

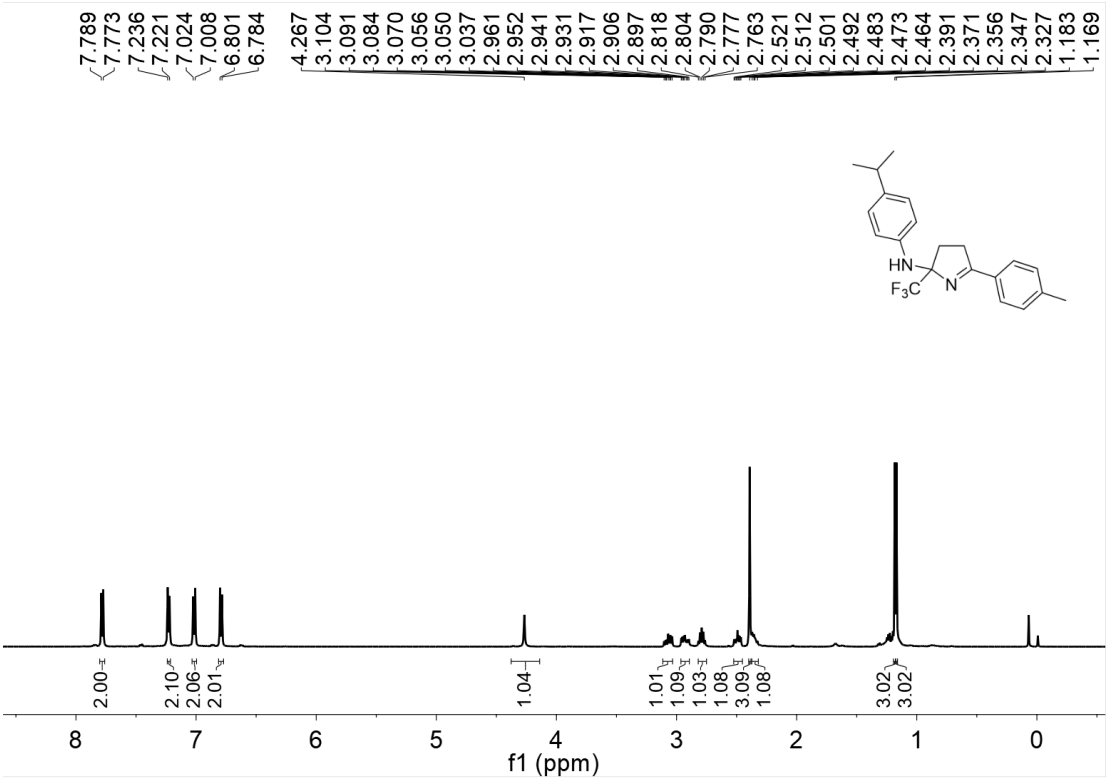


Figure 9. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3ba**

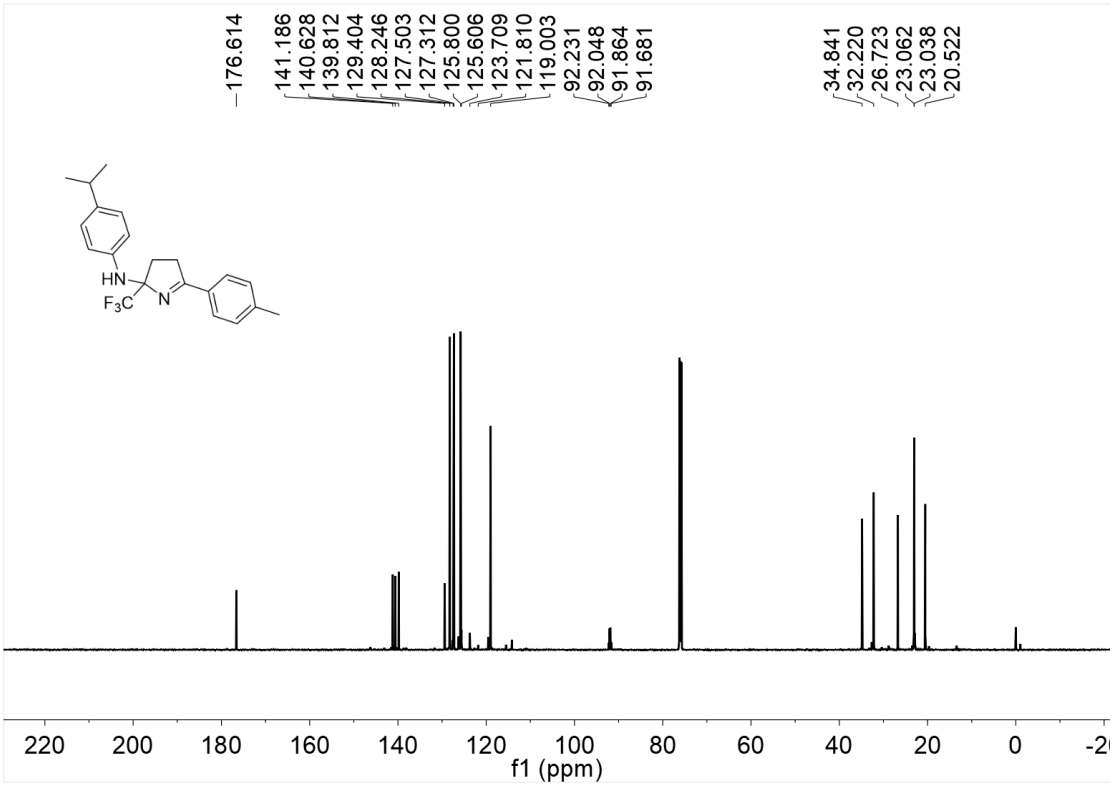


Figure 10. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ba**

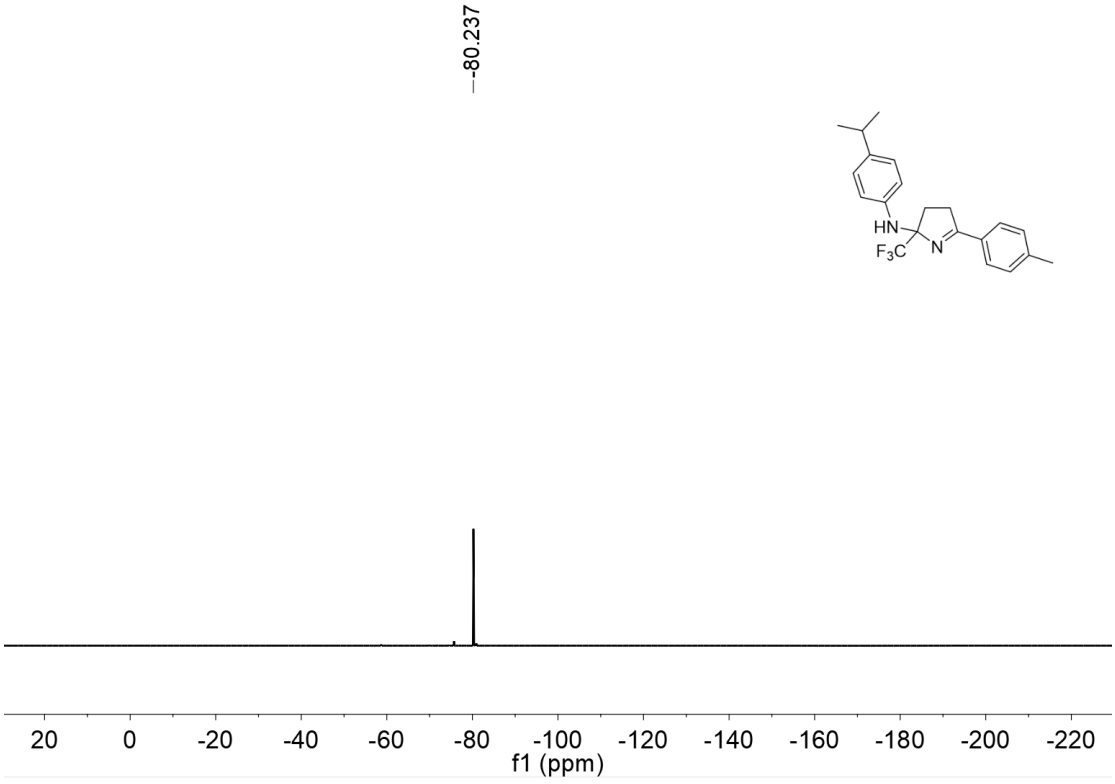


Figure 11. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **3ba**

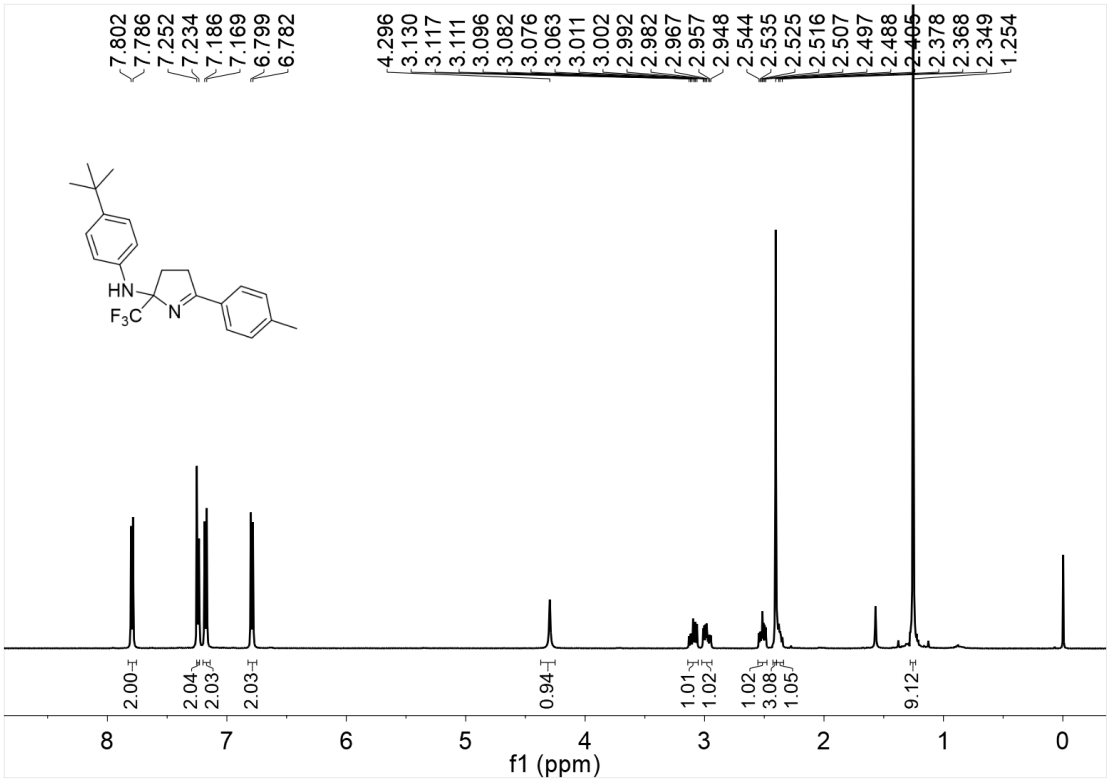


Figure 12. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3ca**

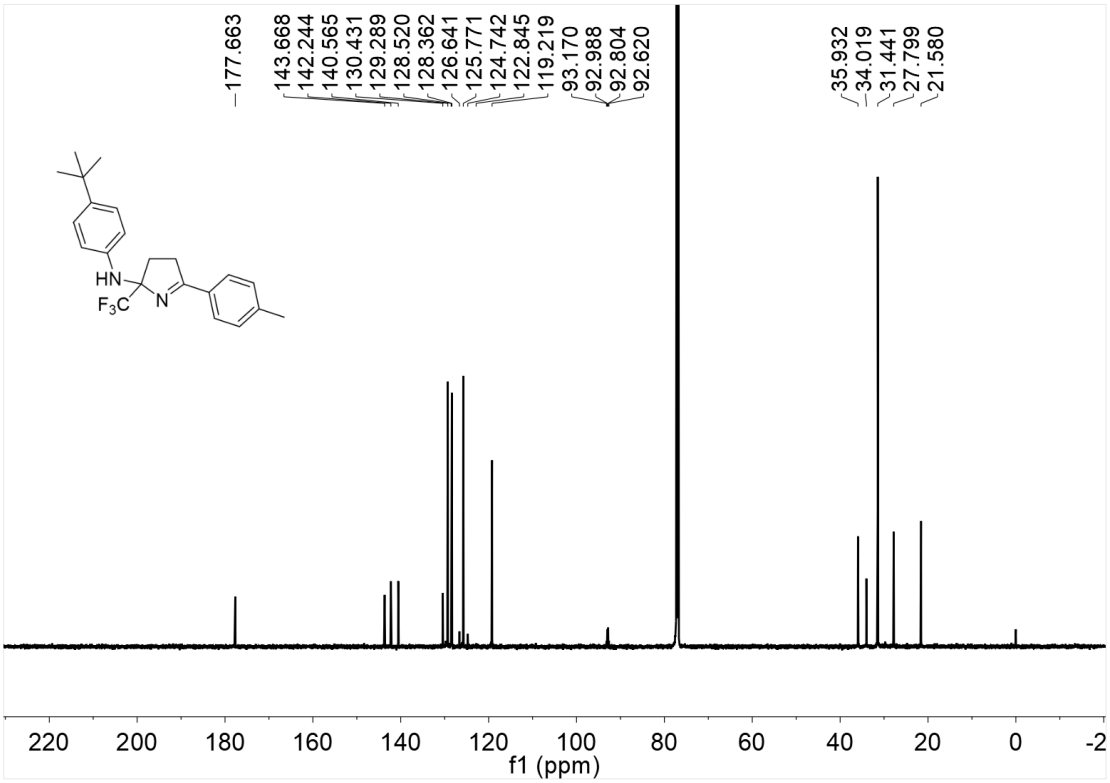


Figure 13. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ca**

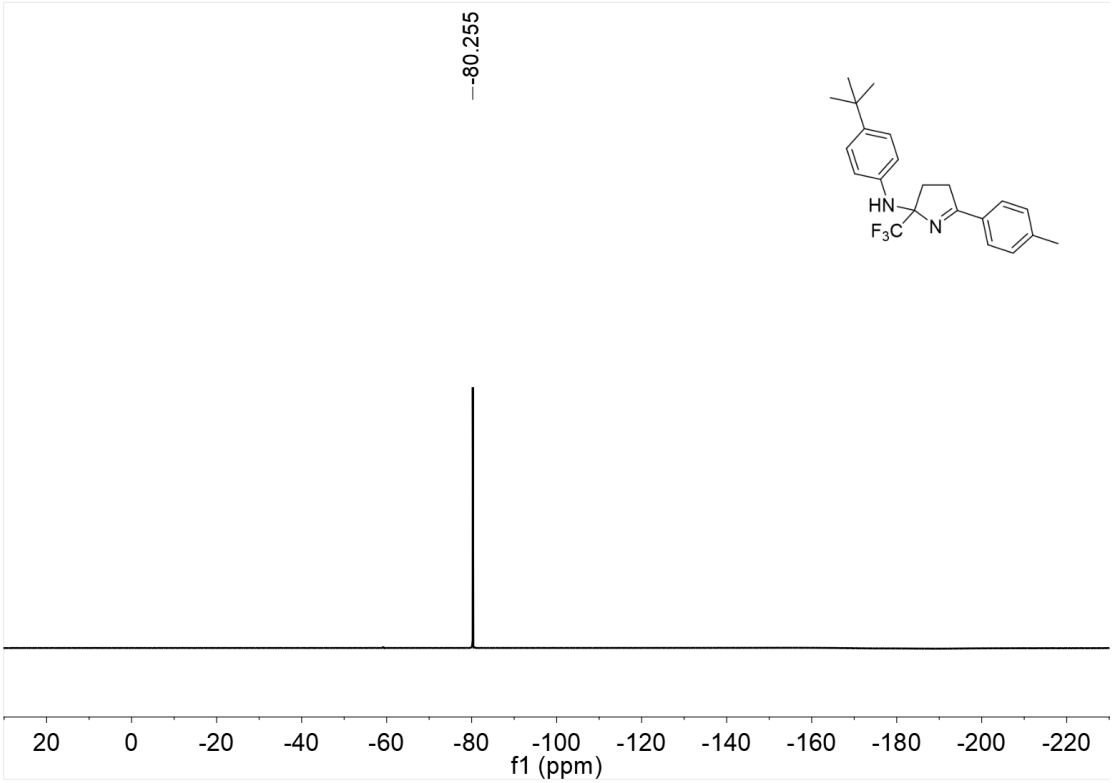


Figure 14. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **3ca**

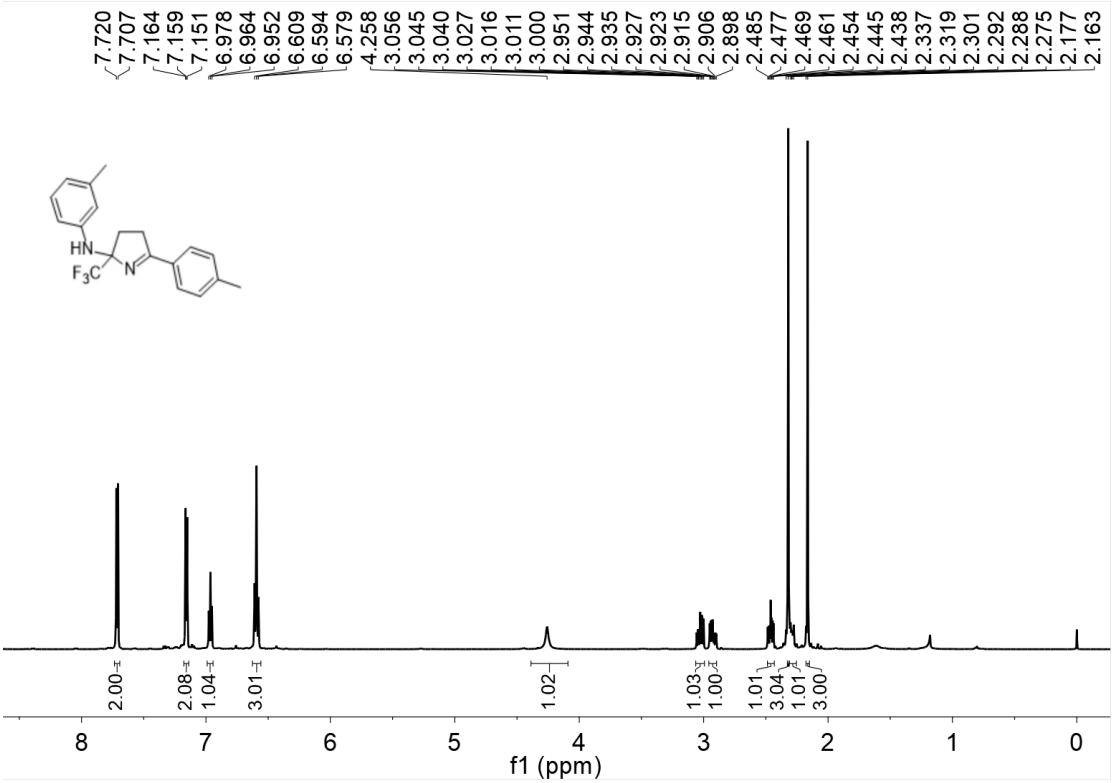


Figure 15. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3da**

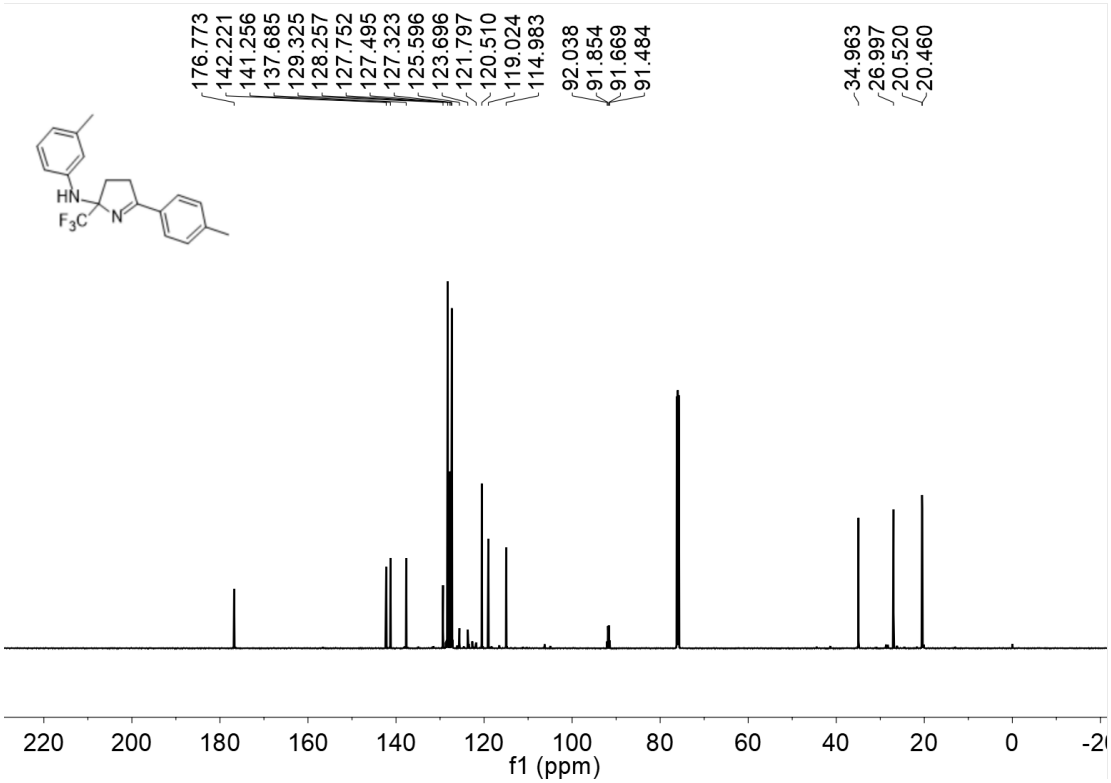


Figure 16. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3da**

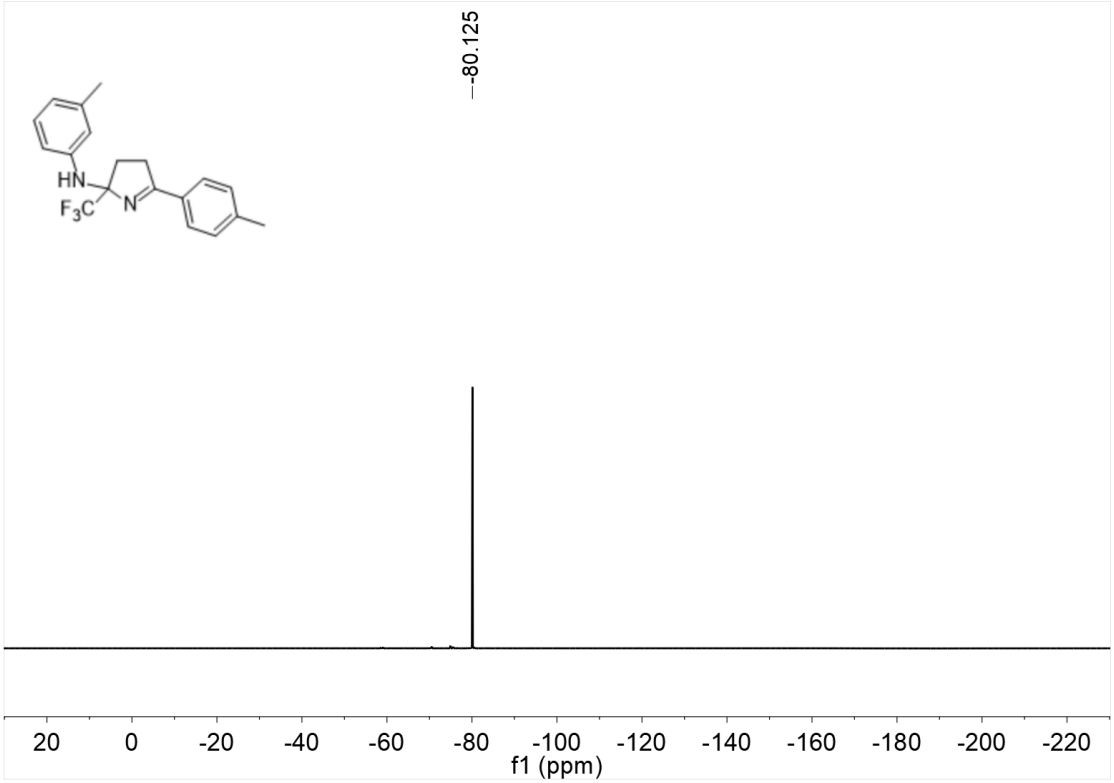


Figure 17. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **3da**

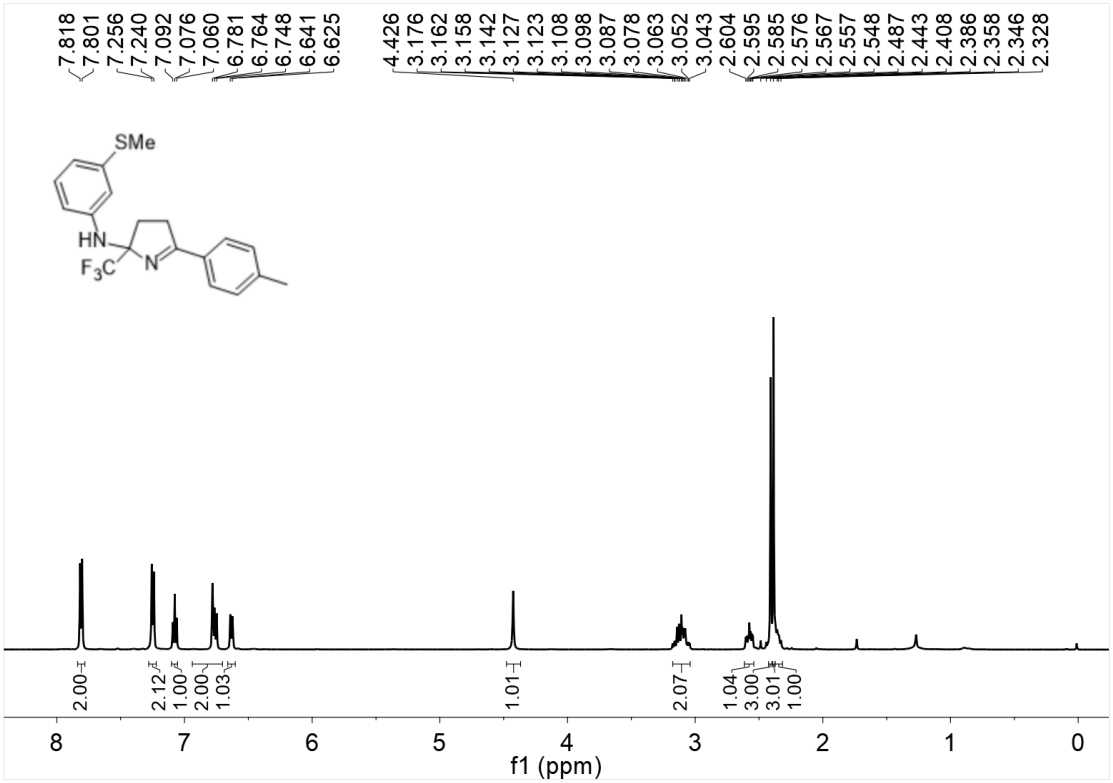


Figure 18. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3ea**

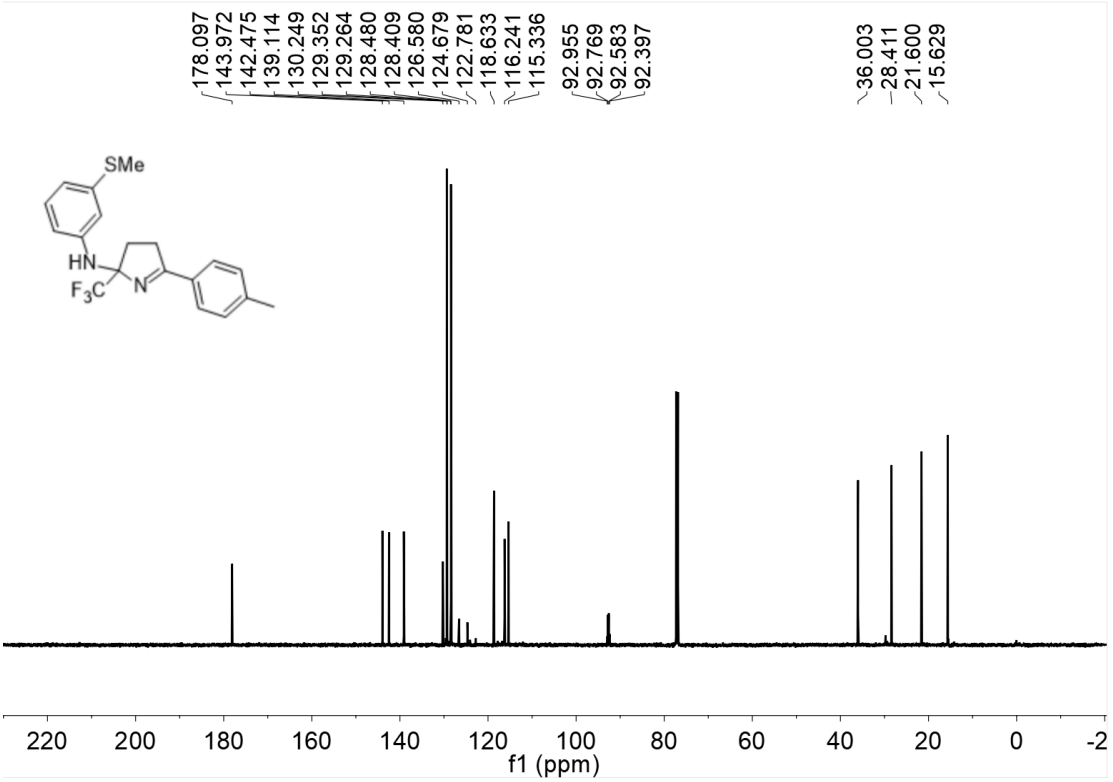


Figure 19. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ea**

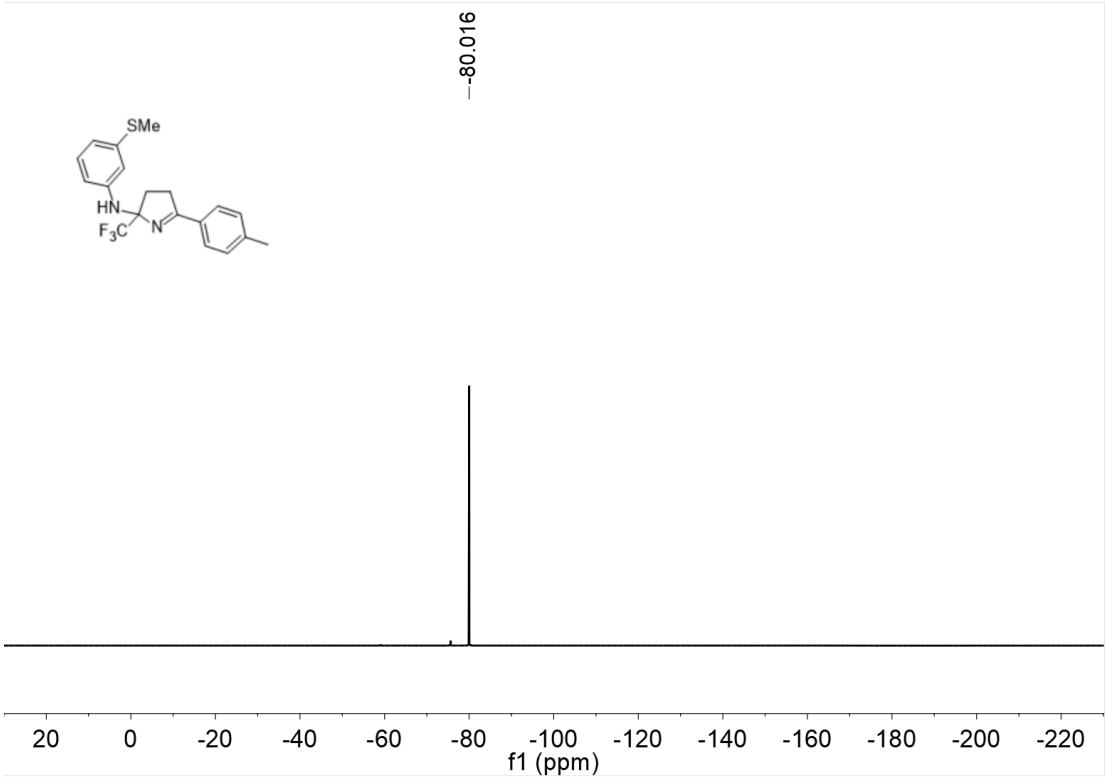


Figure 20. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **3ea**

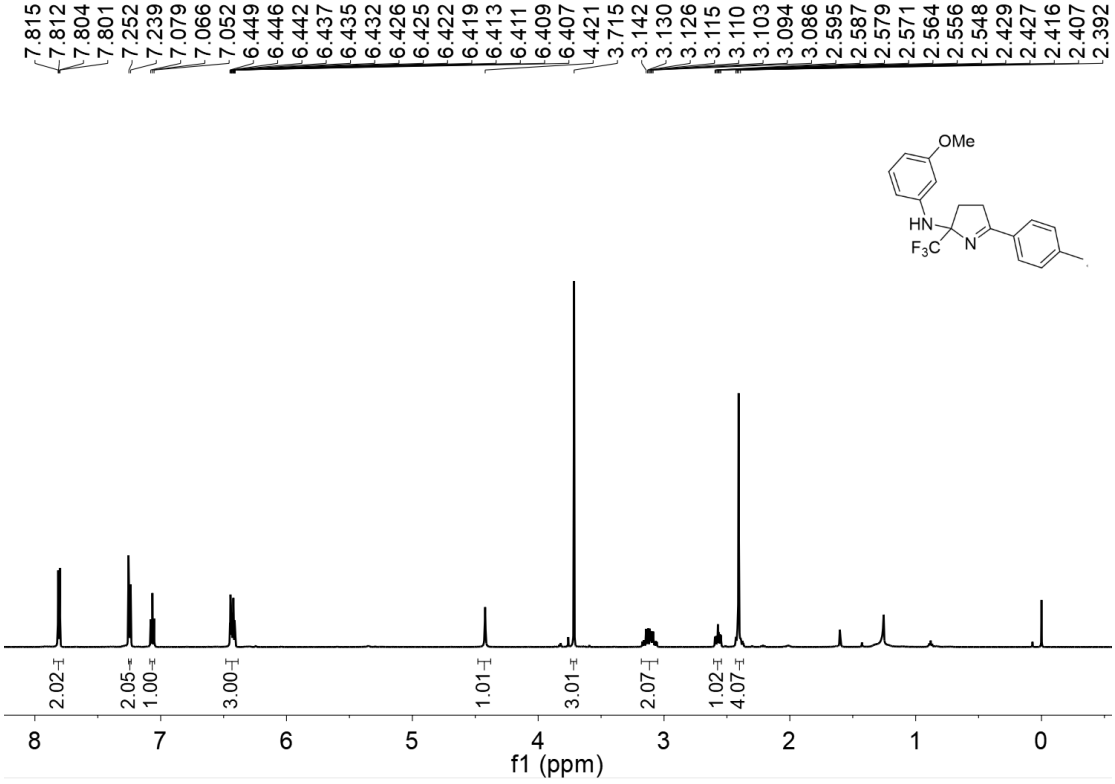


Figure 21. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3fa**

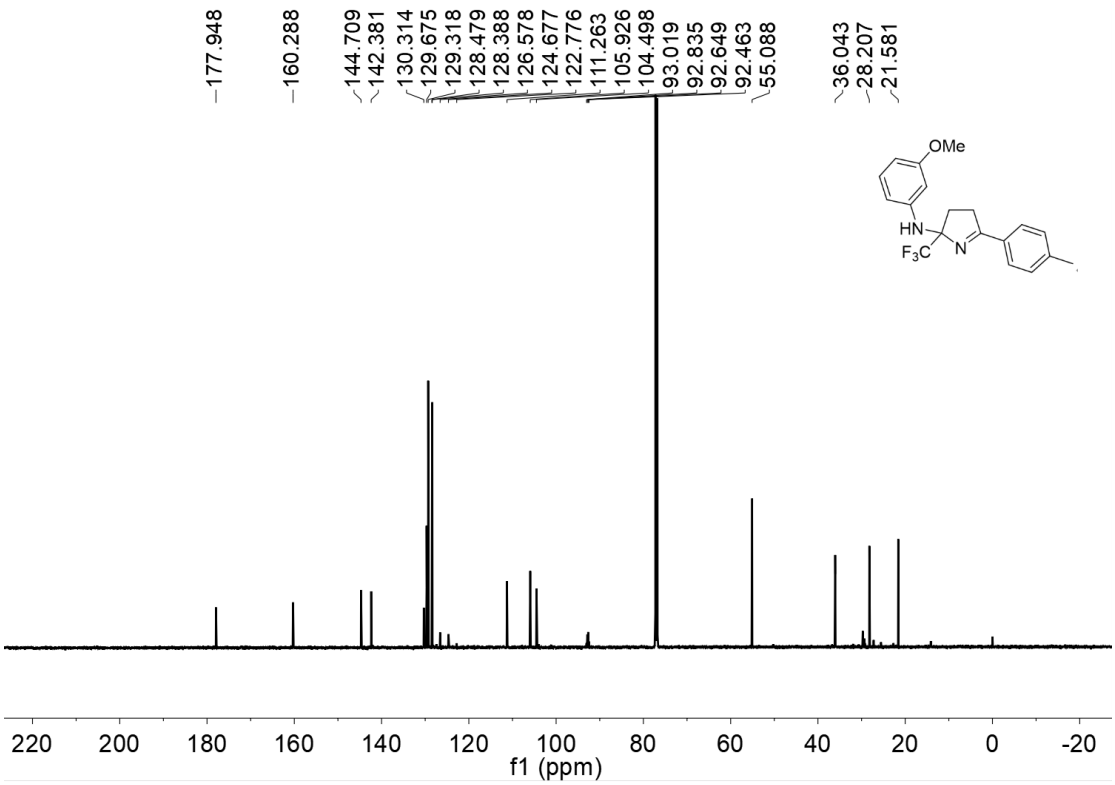


Figure 22. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3fa**

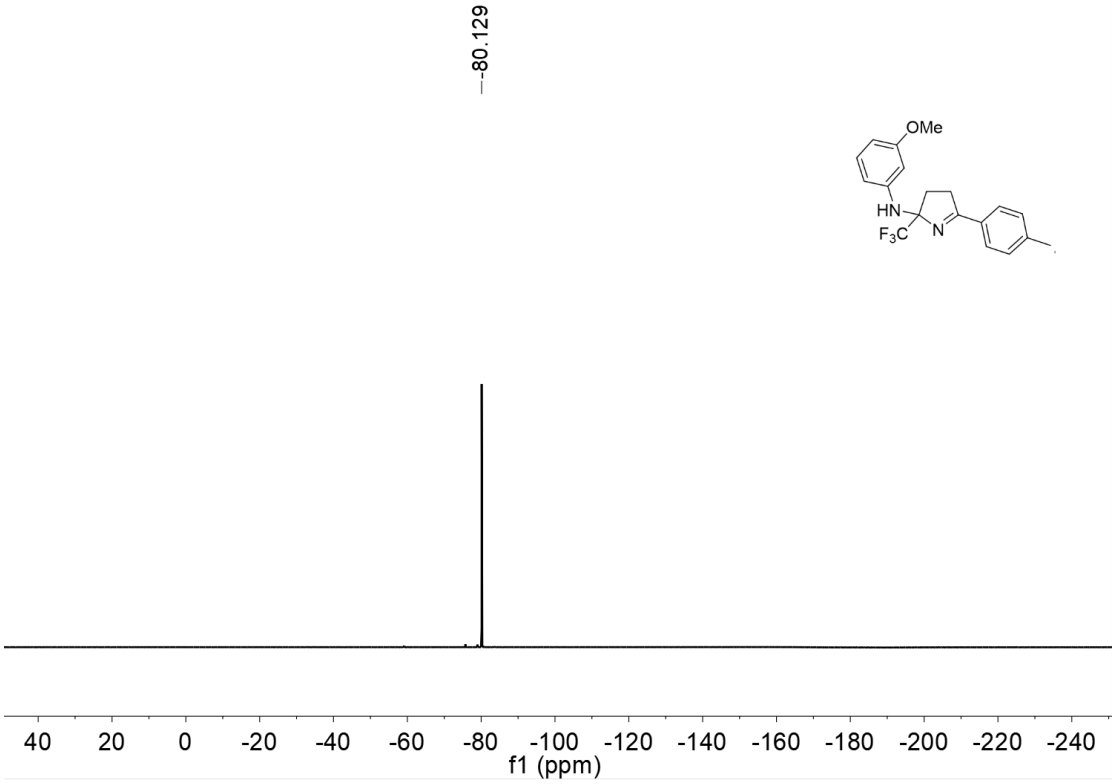


Figure 23. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **3fa**

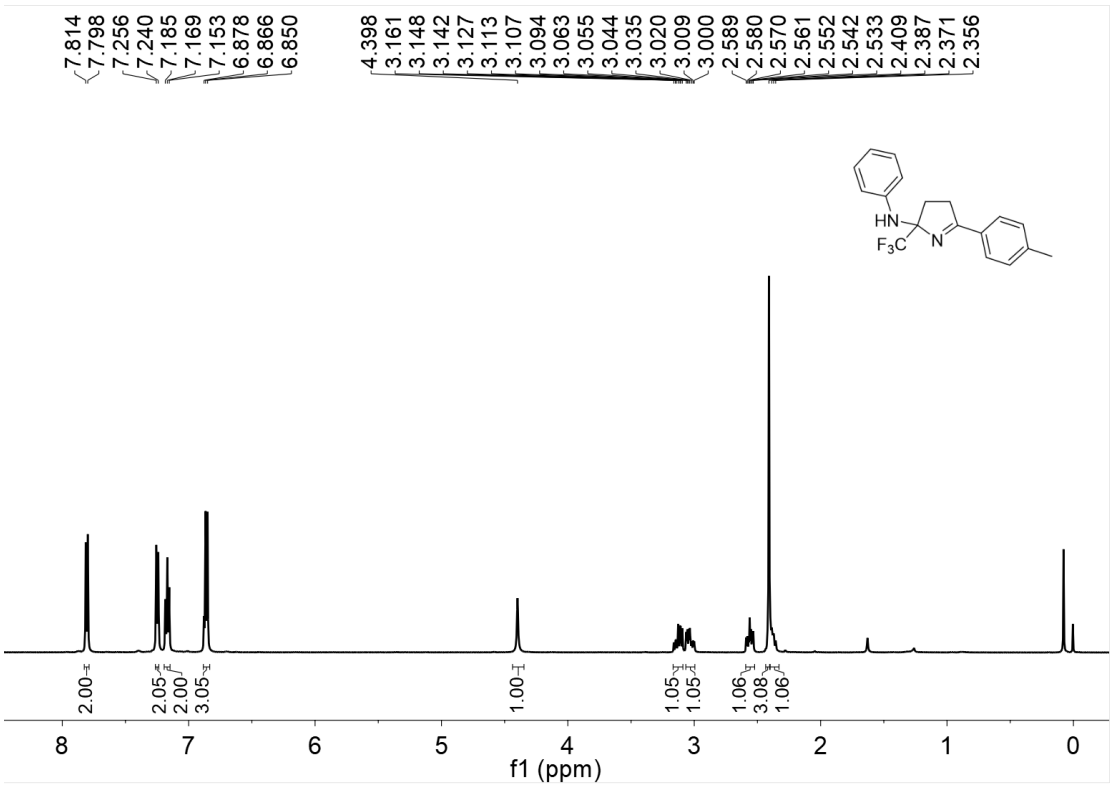


Figure 24. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3ga**

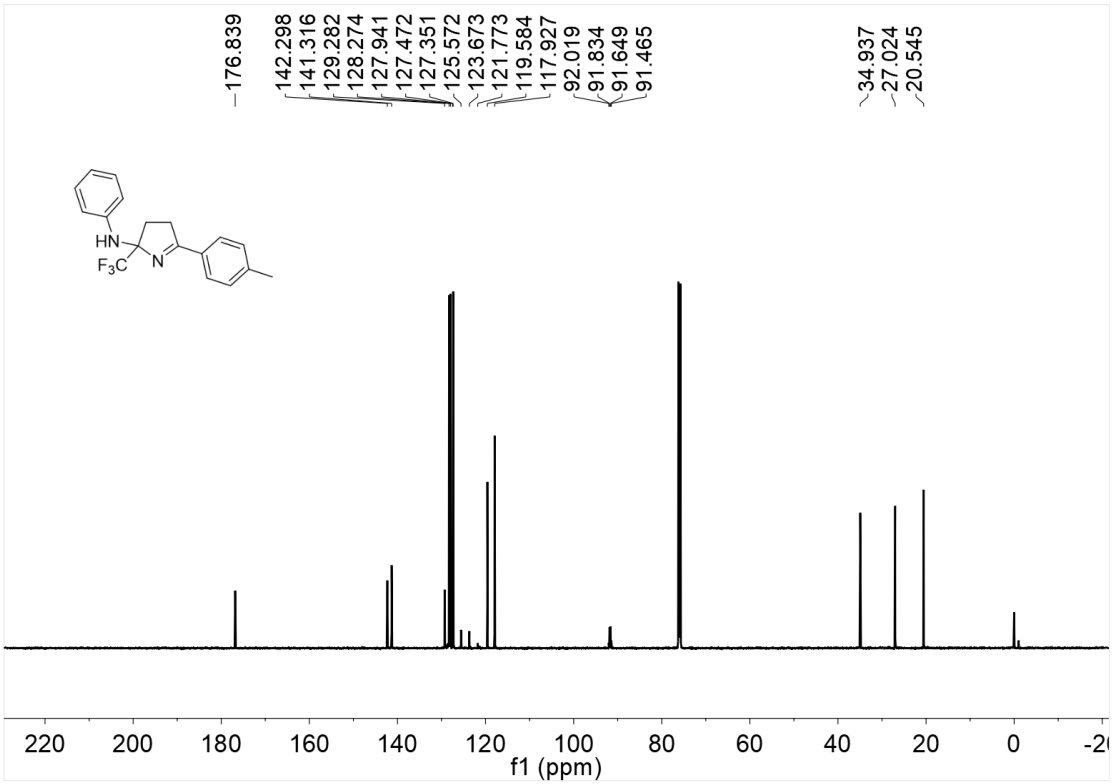


Figure 25. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ga**

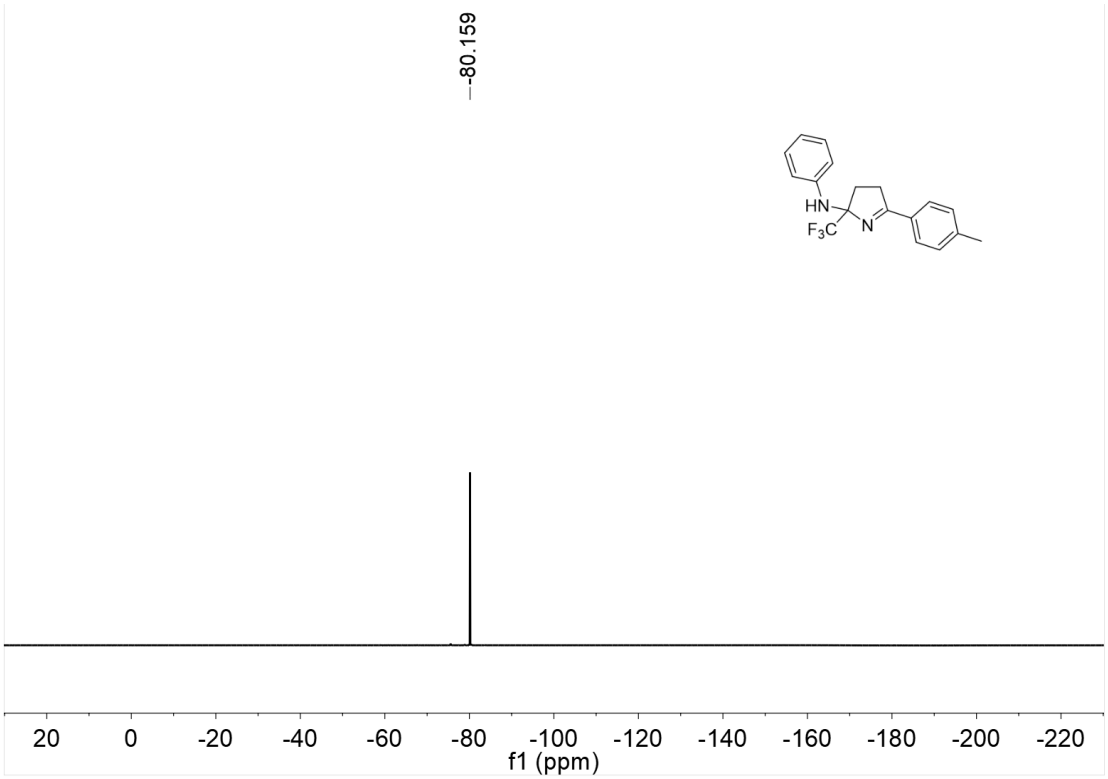


Figure 26. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **3ga**

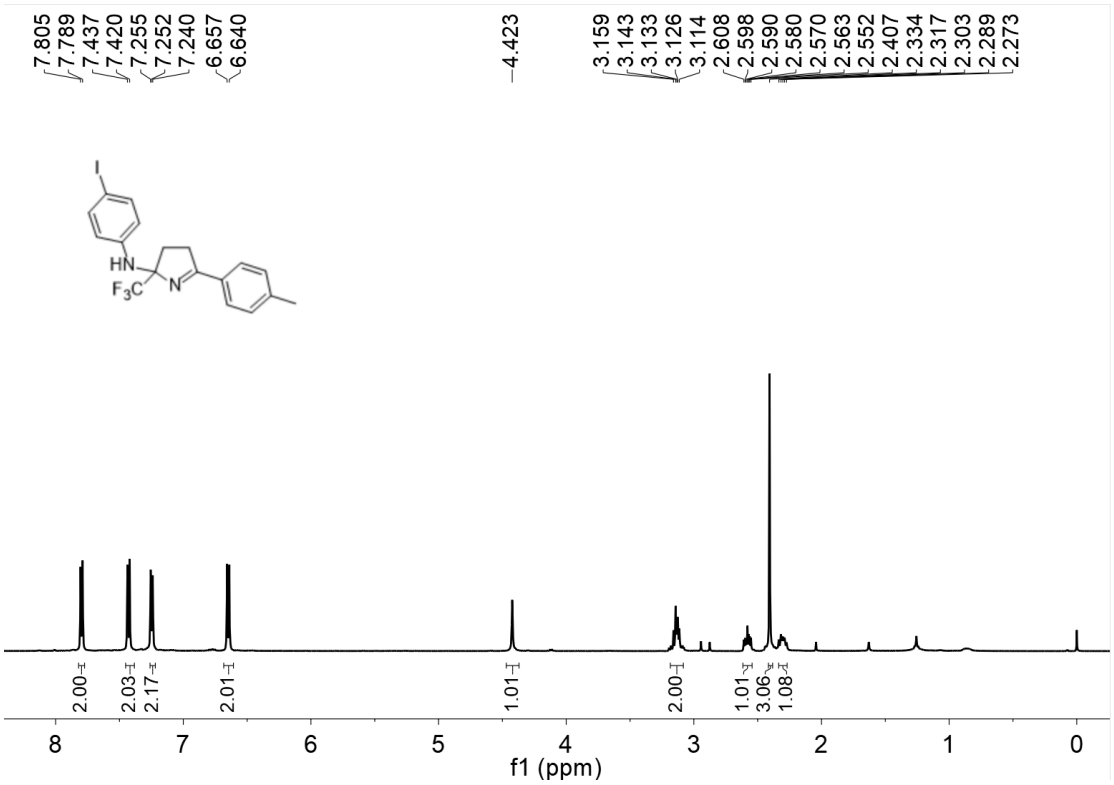


Figure 27. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3ha**

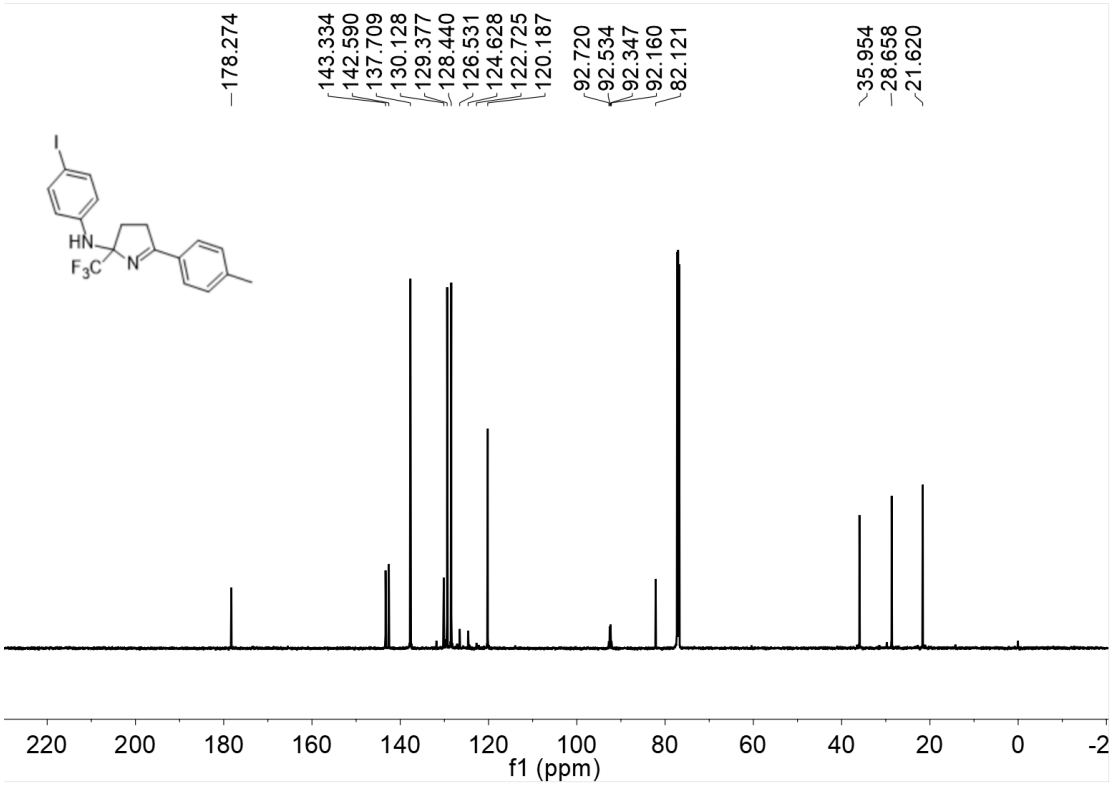


Figure 28. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ha**

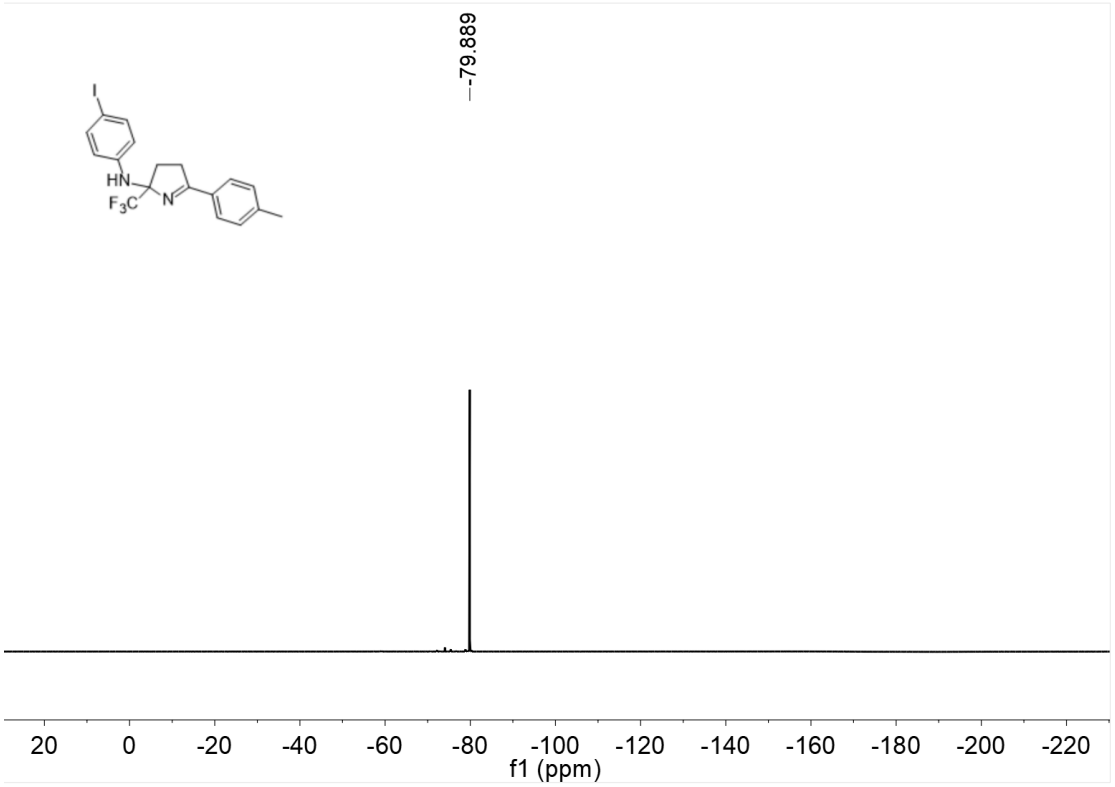


Figure 29. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **3ha**

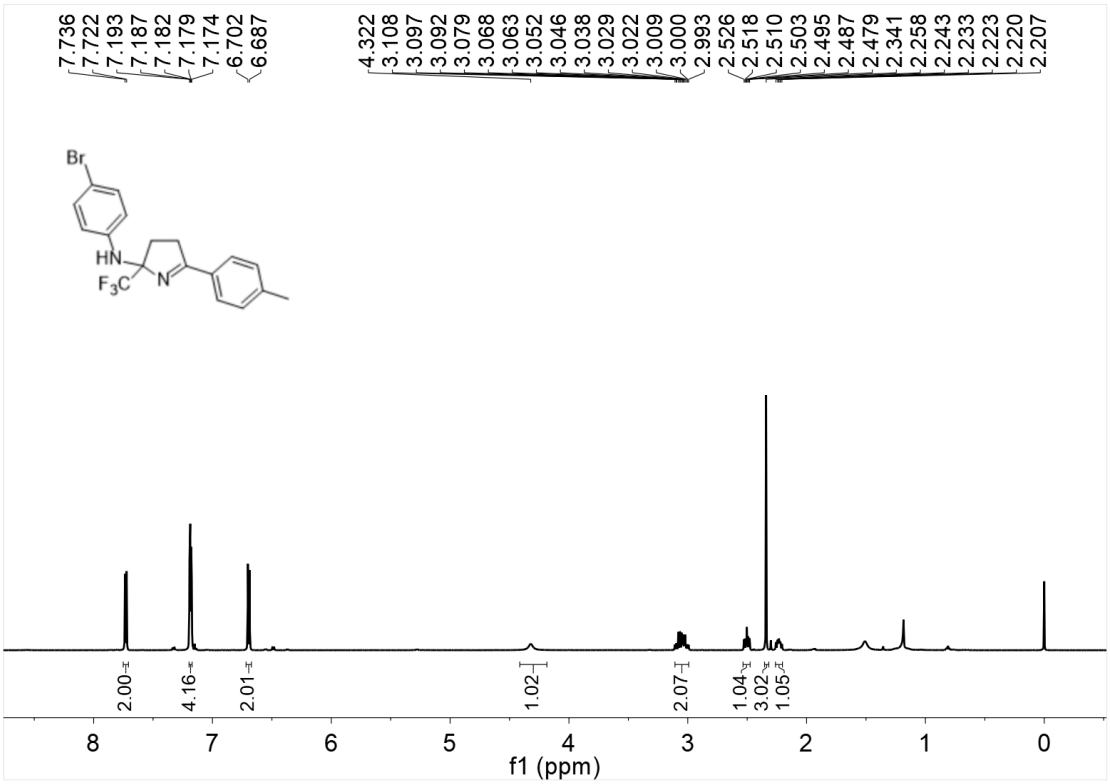


Figure 30. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3ia**

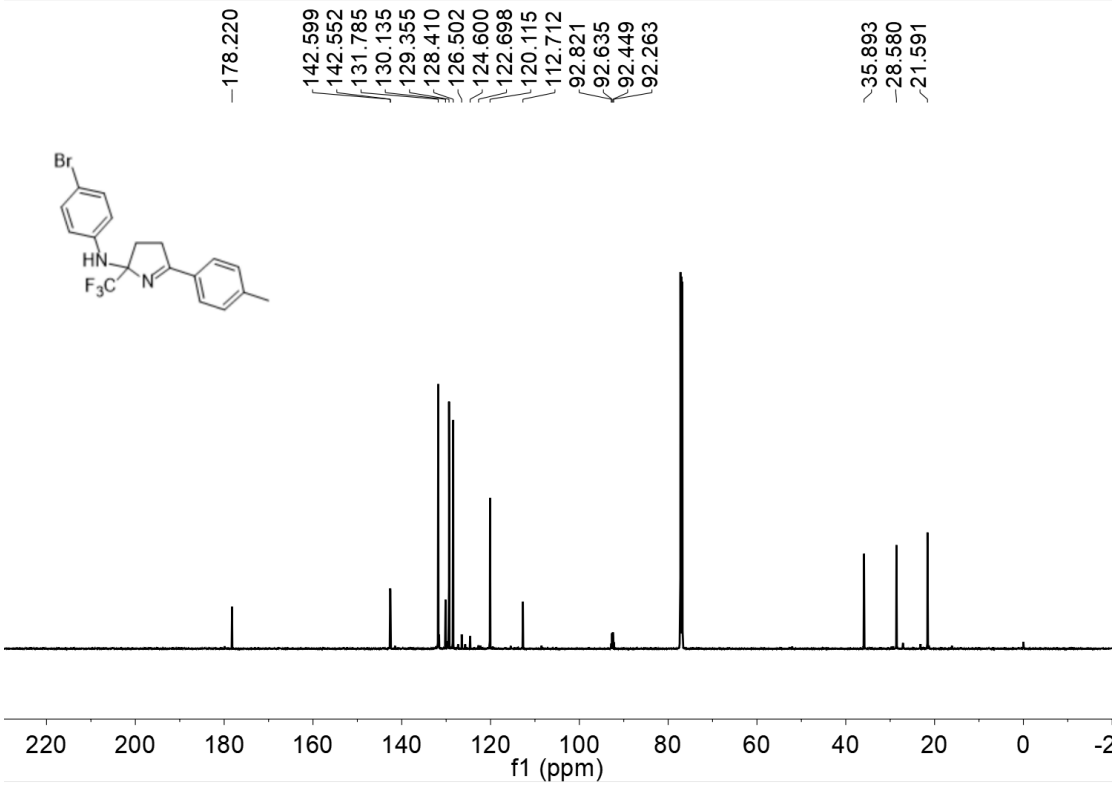


Figure 31. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ia**

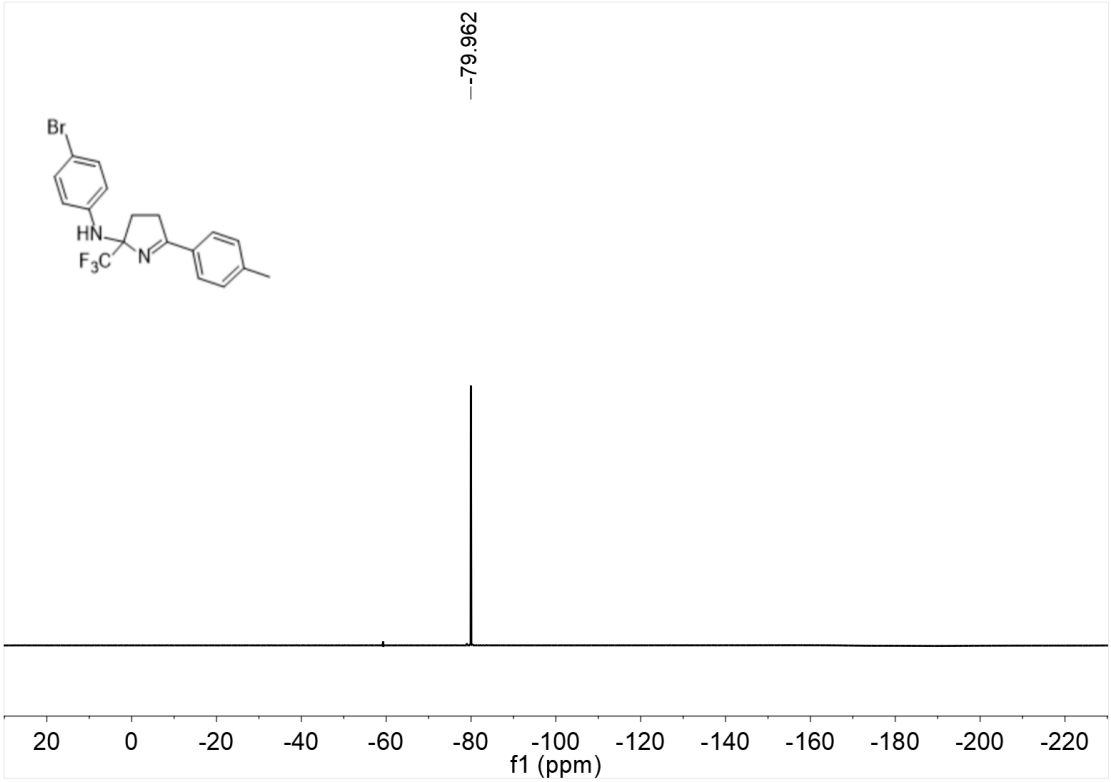


Figure 32. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **3ia**

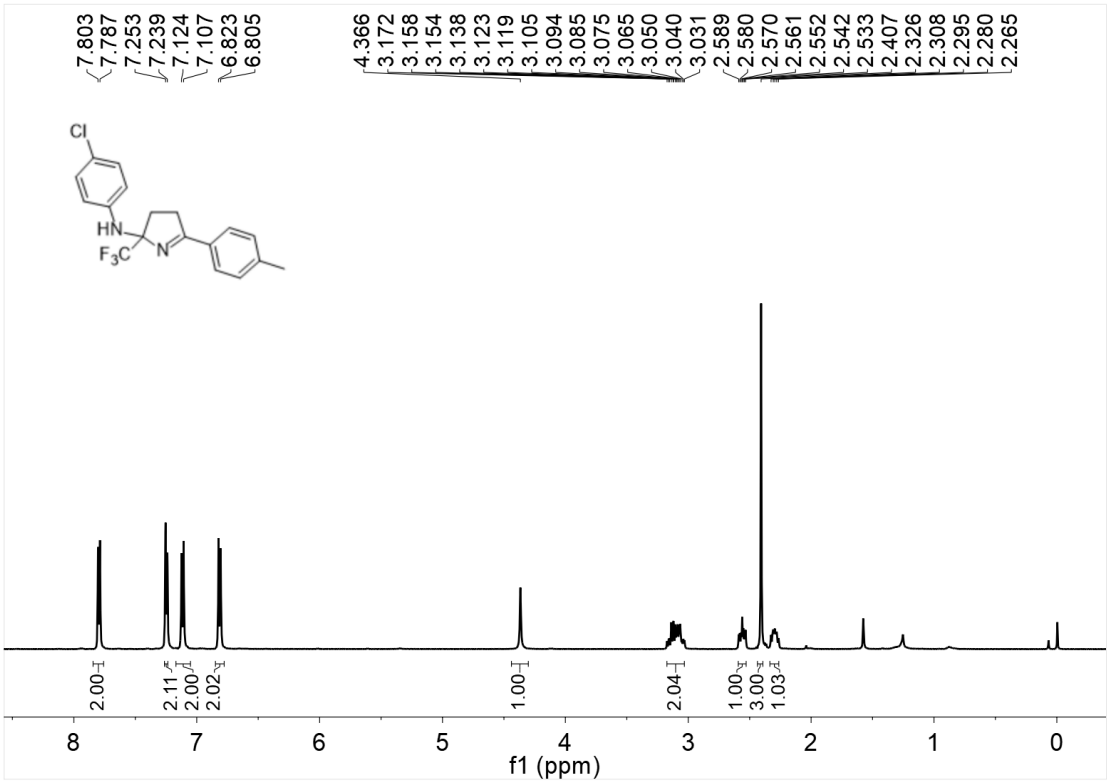


Figure 33. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3ja**

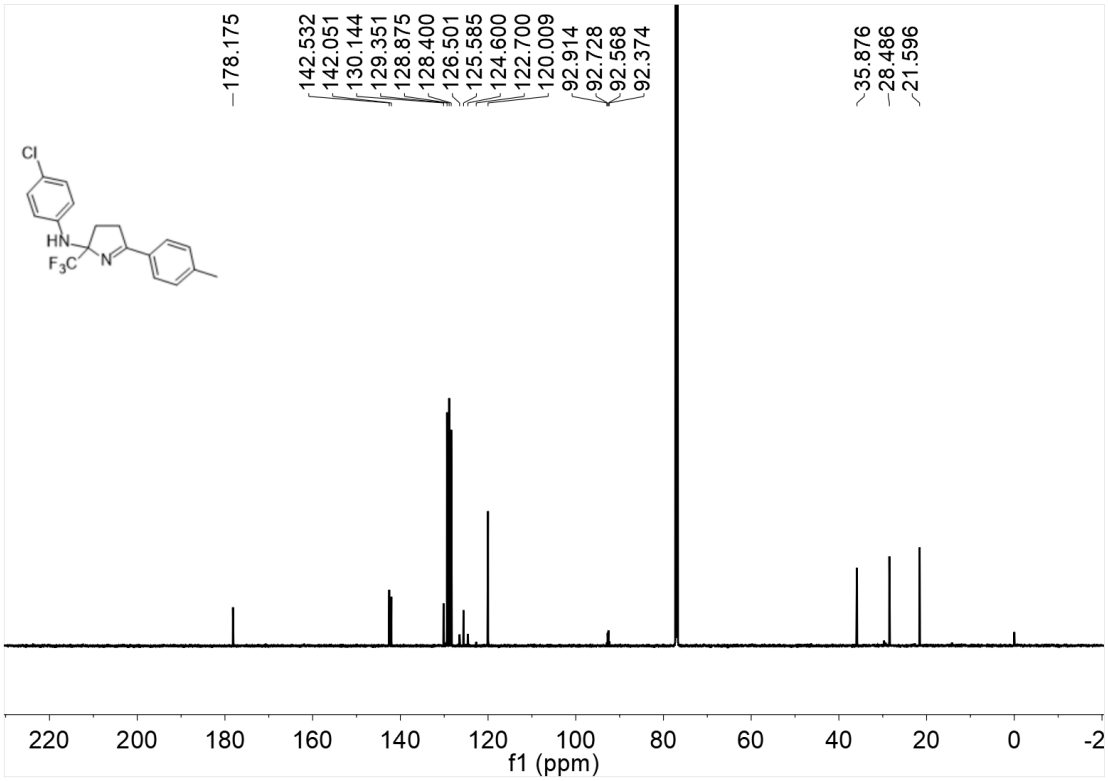


Figure 34. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ja**

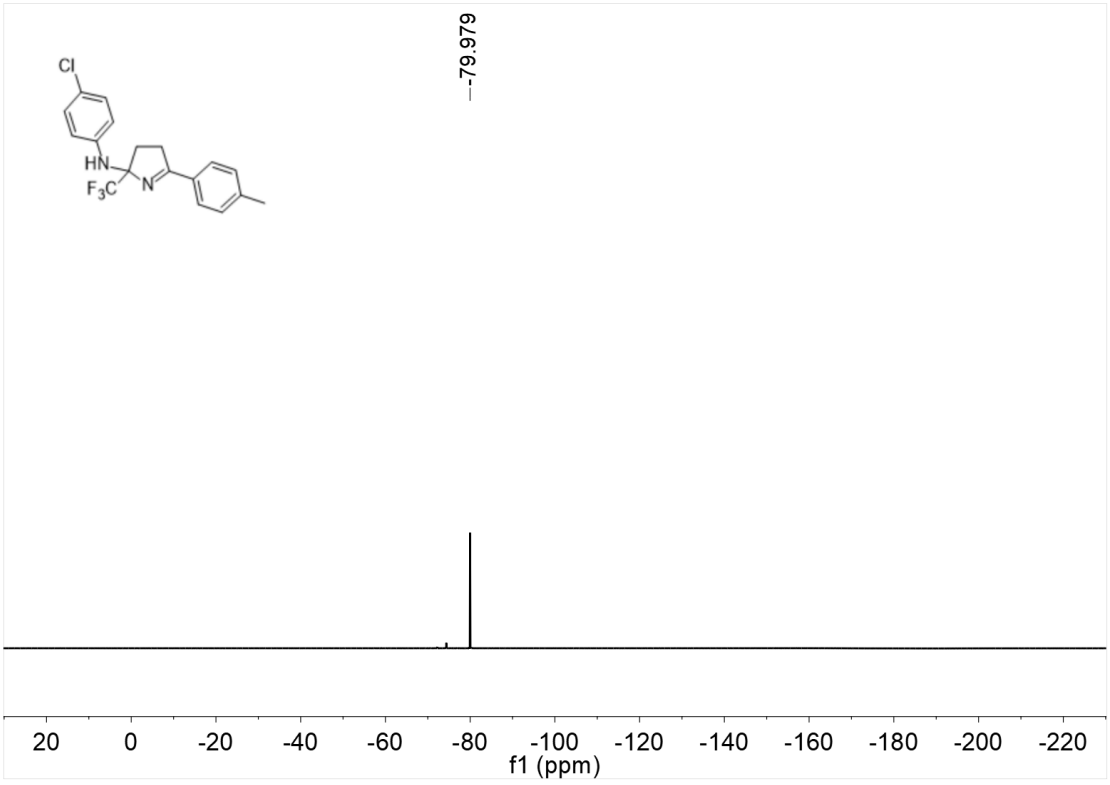


Figure 35. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **3ja**

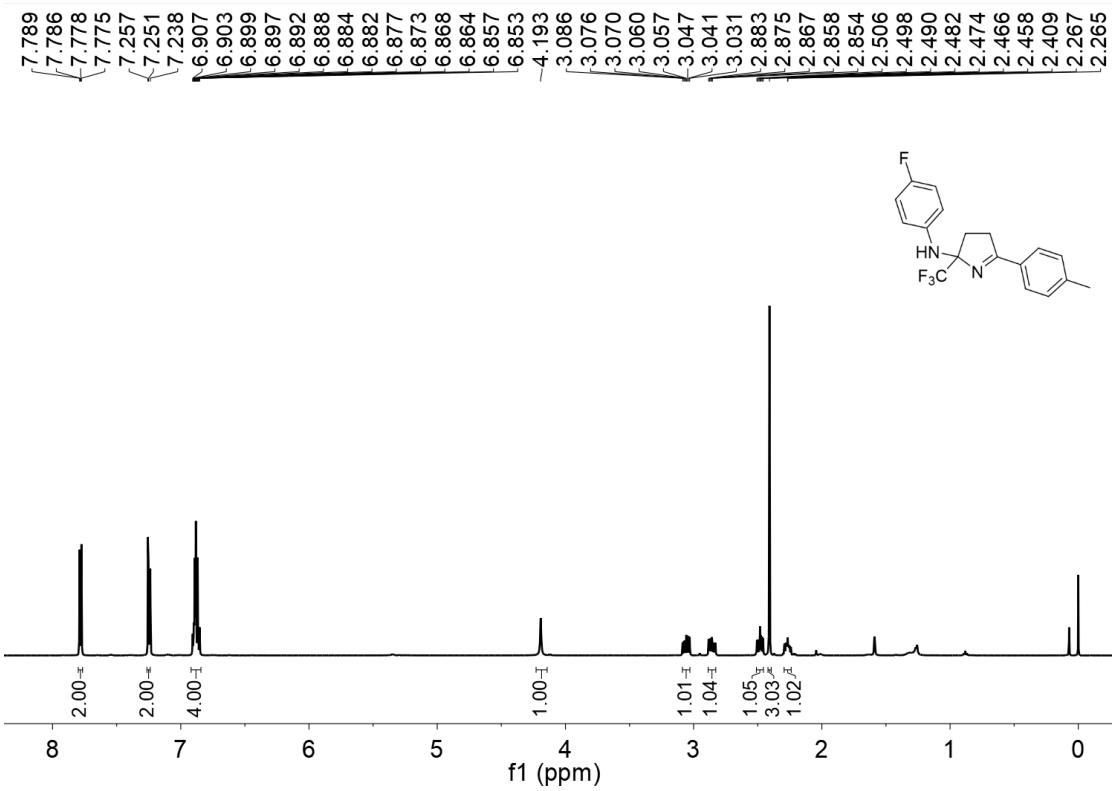


Figure 36. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3ka**

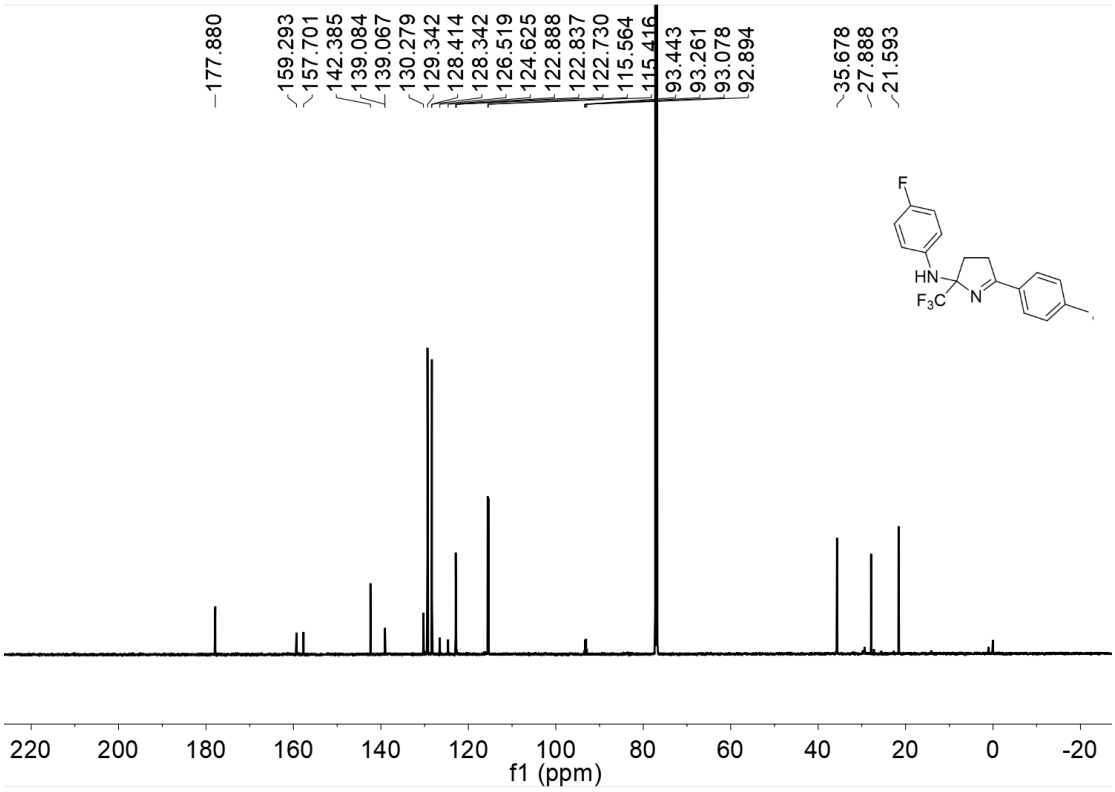


Figure 37. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ka**

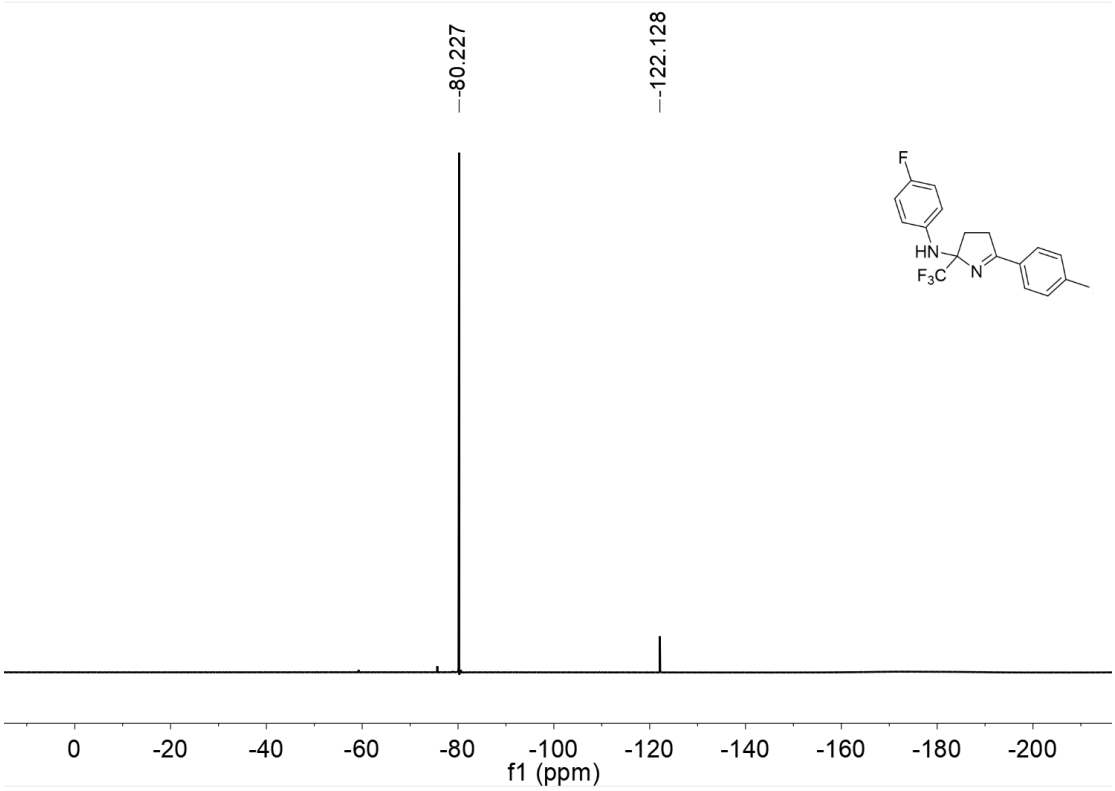


Figure 38. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **3ka**

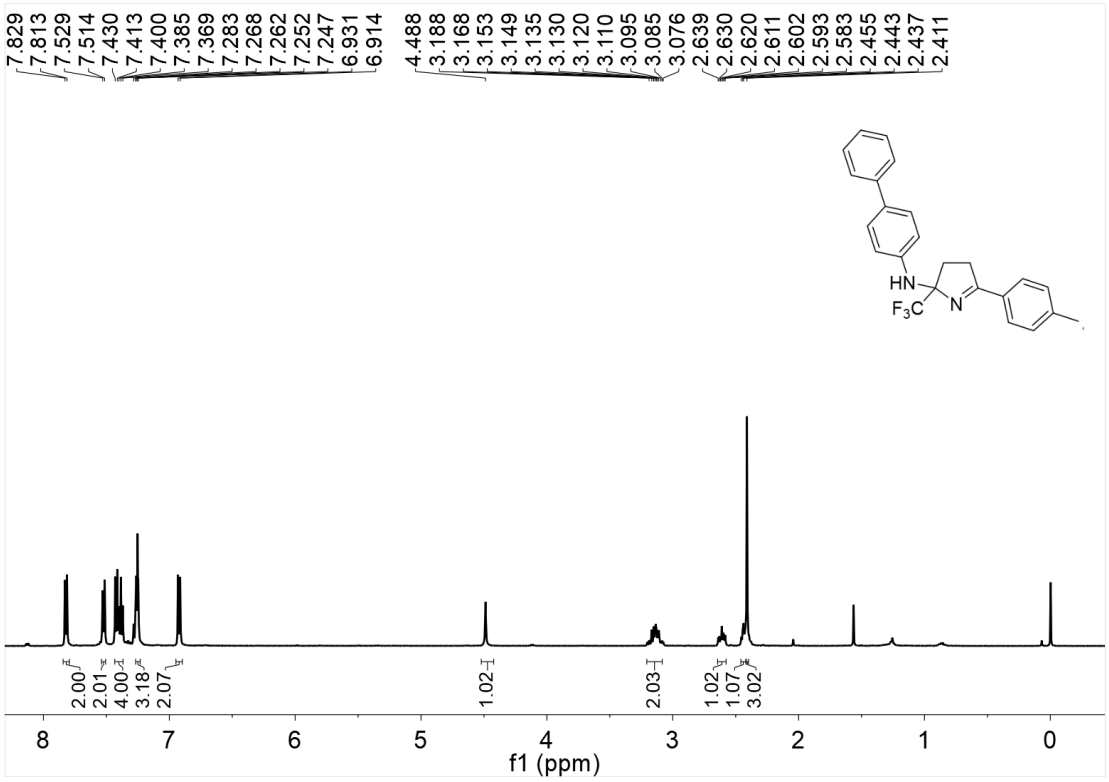


Figure 39. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3la**

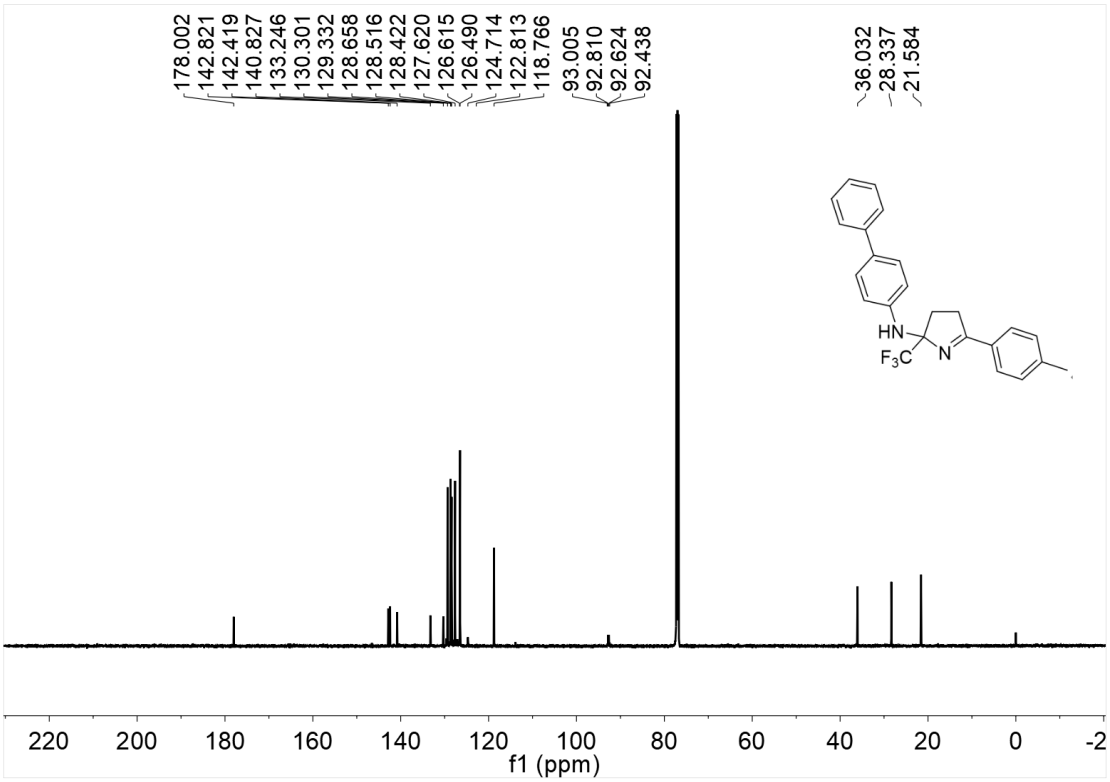


Figure 40. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3la**

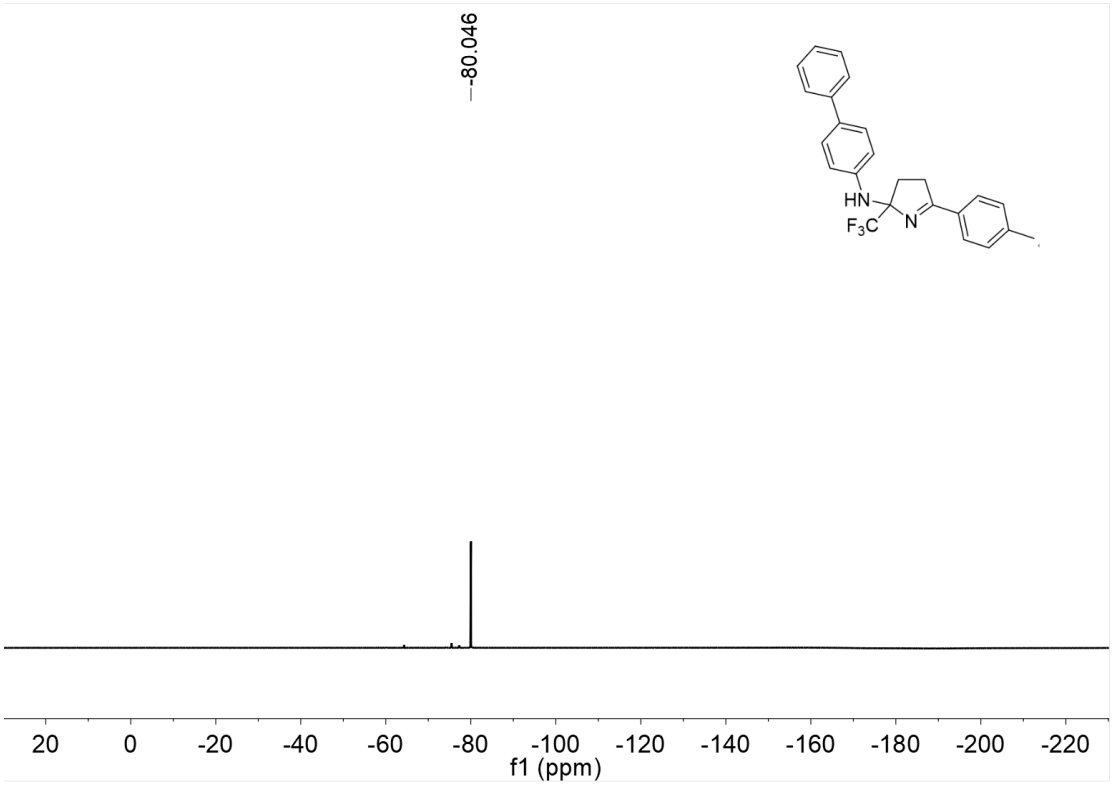


Figure 41. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **3la**

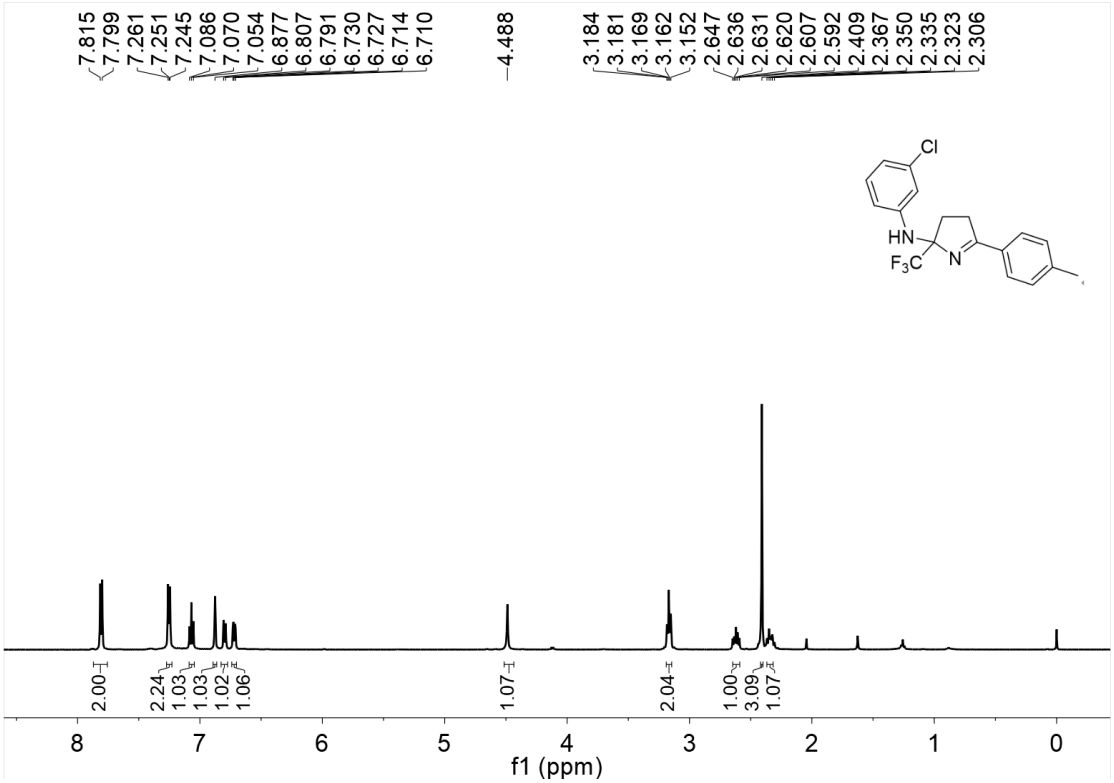


Figure 42. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3ma**

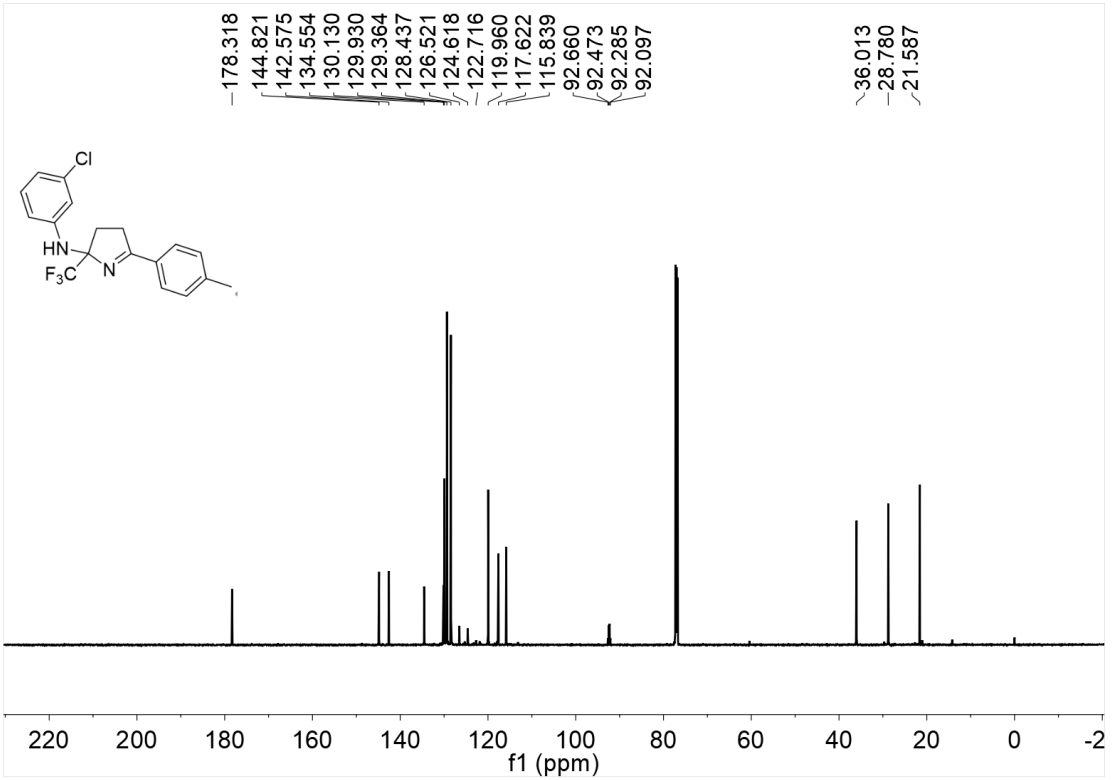


Figure 43. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ma**

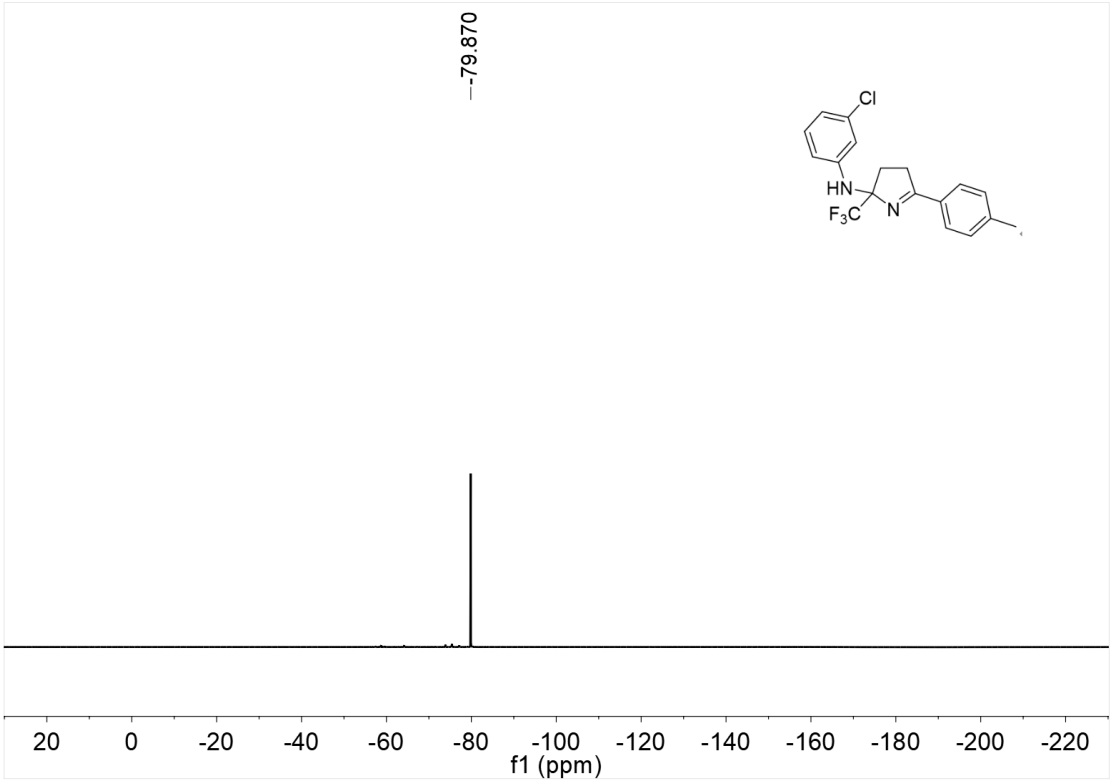


Figure 44. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **3ma**

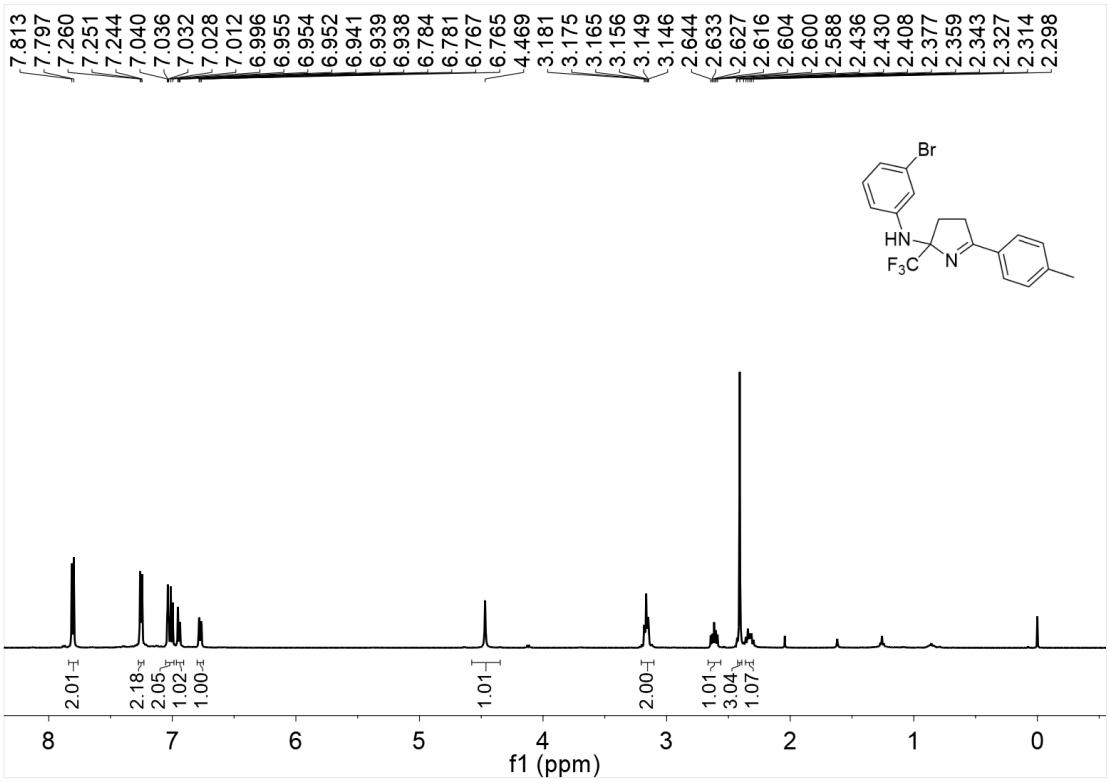


Figure 45. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3na**

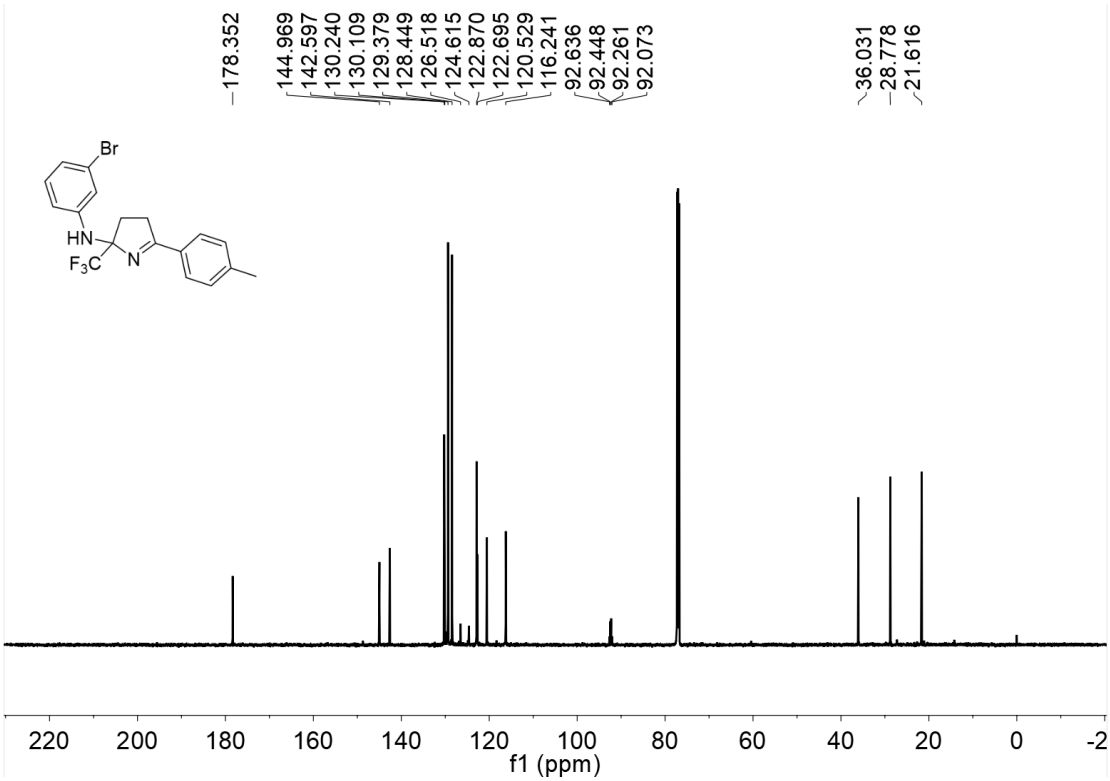


Figure 46. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3na**

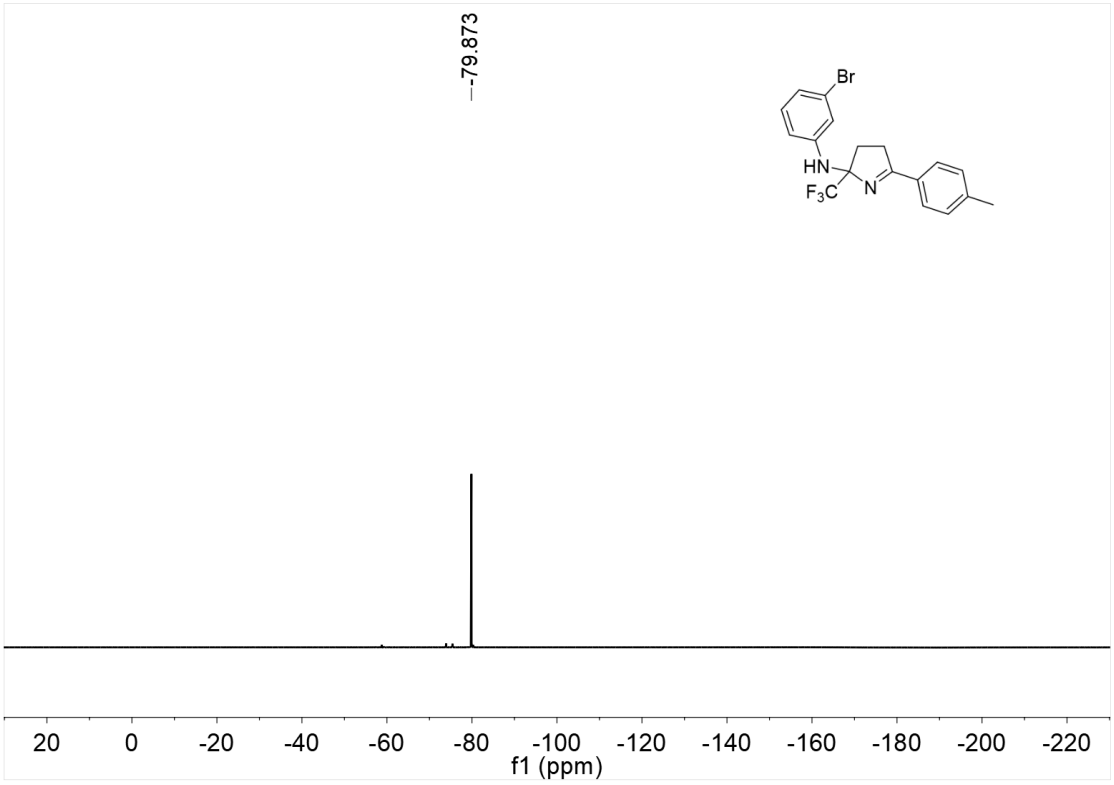


Figure 47. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **3na**

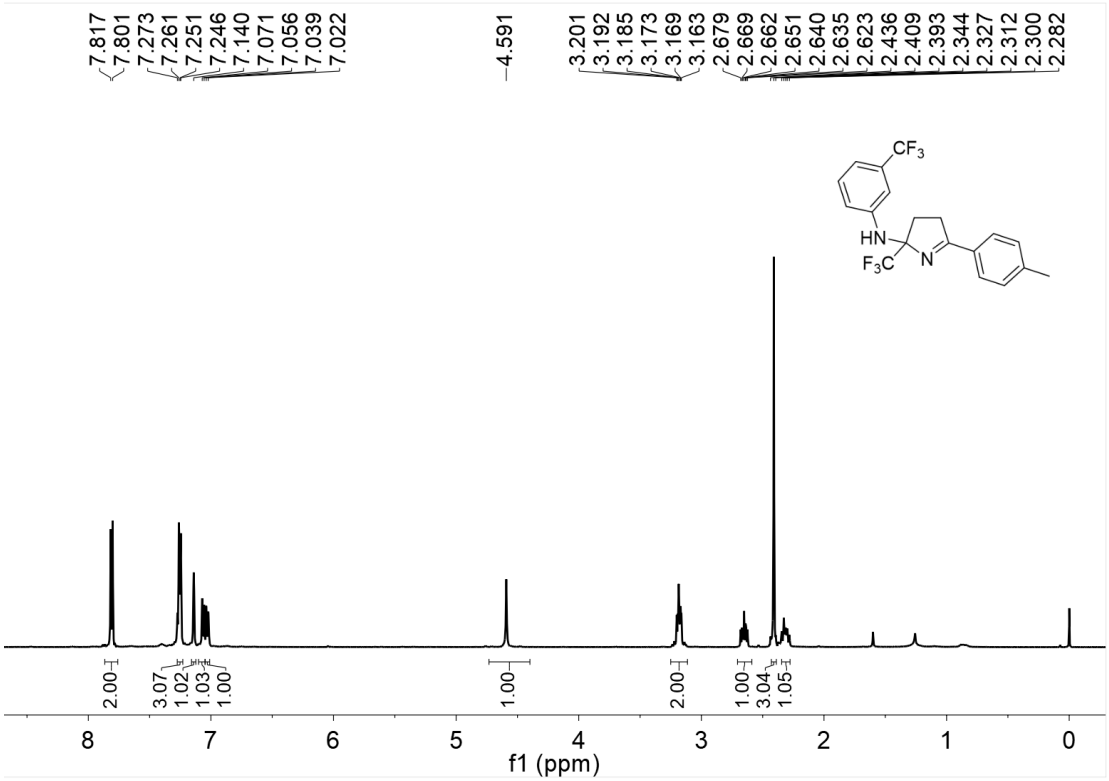


Figure 48. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3oa**

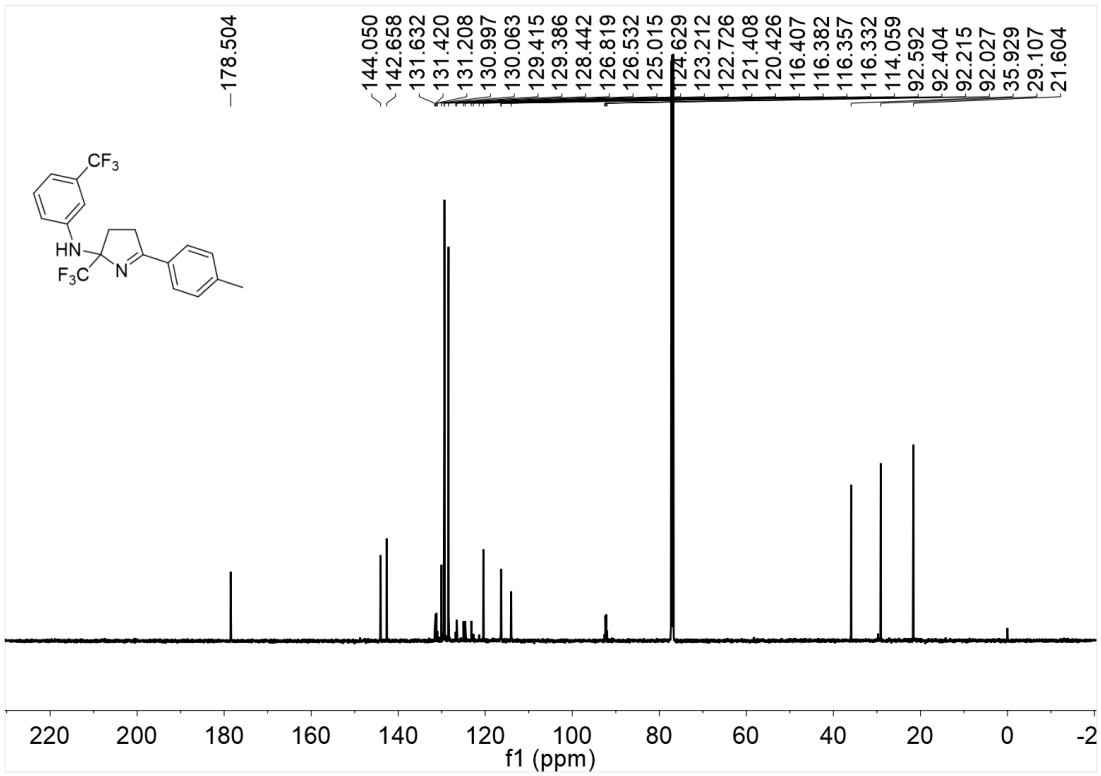


Figure 49. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3oa**

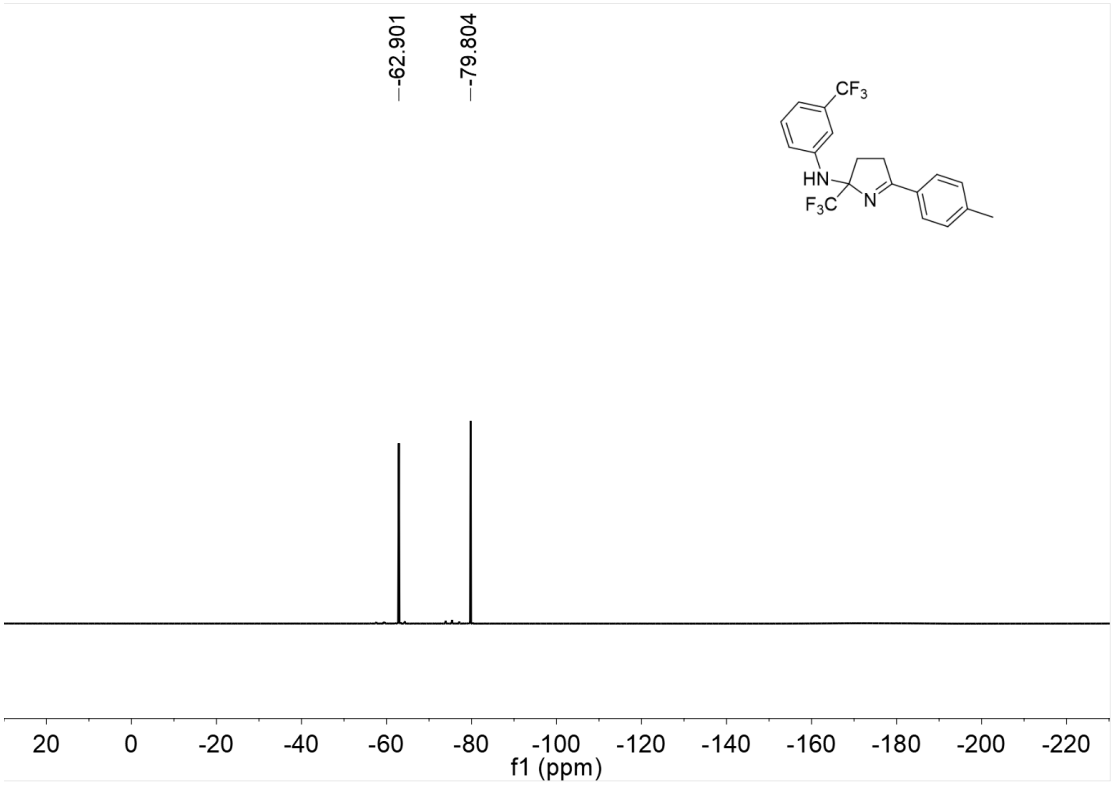


Figure 50. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **3oa**

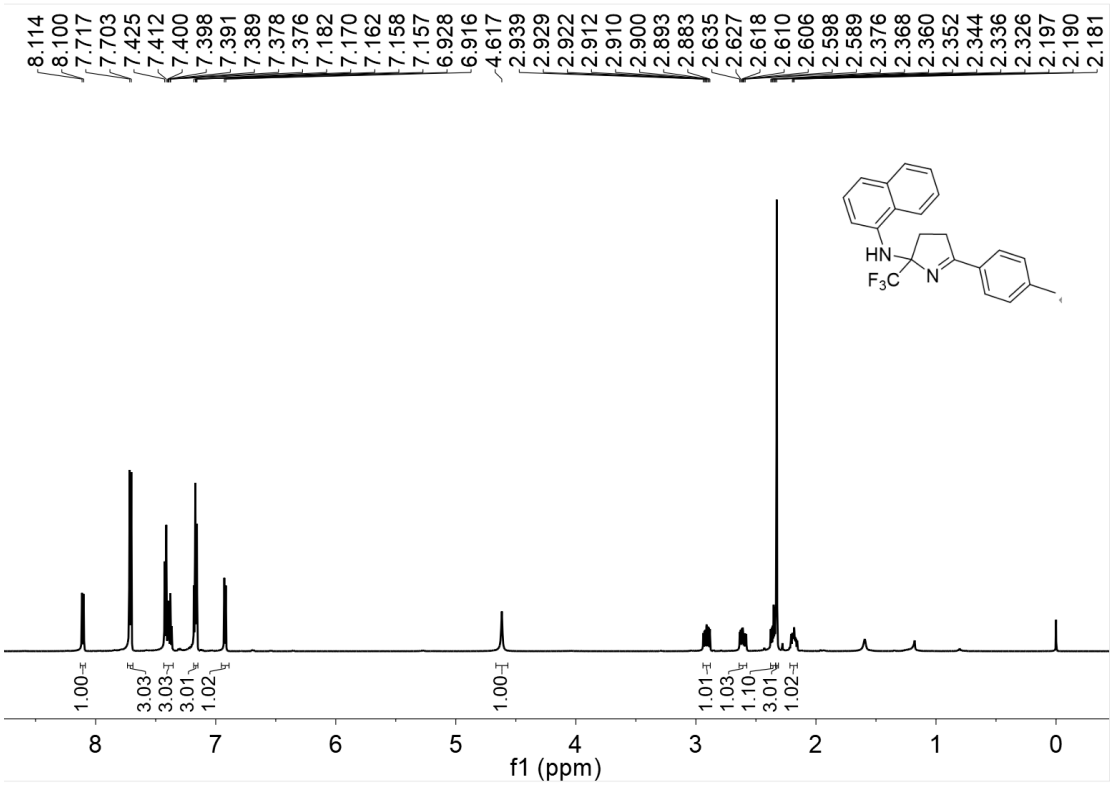


Figure 51. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3pa**

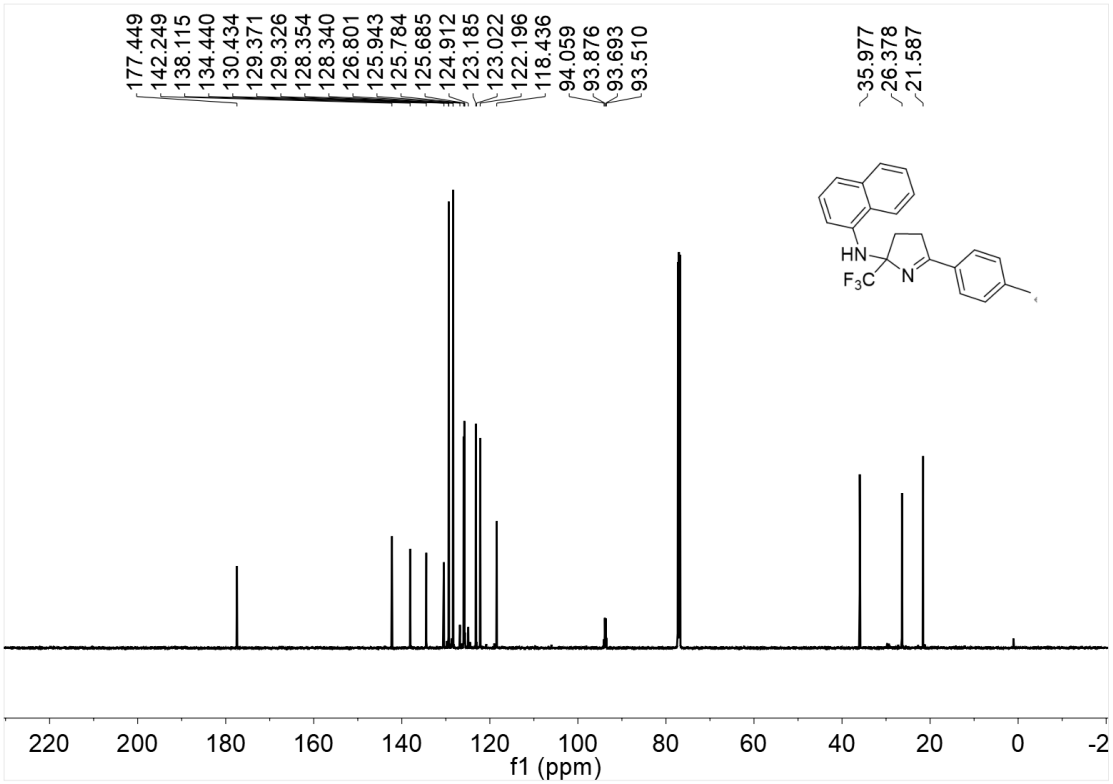


Figure 52. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3pa**

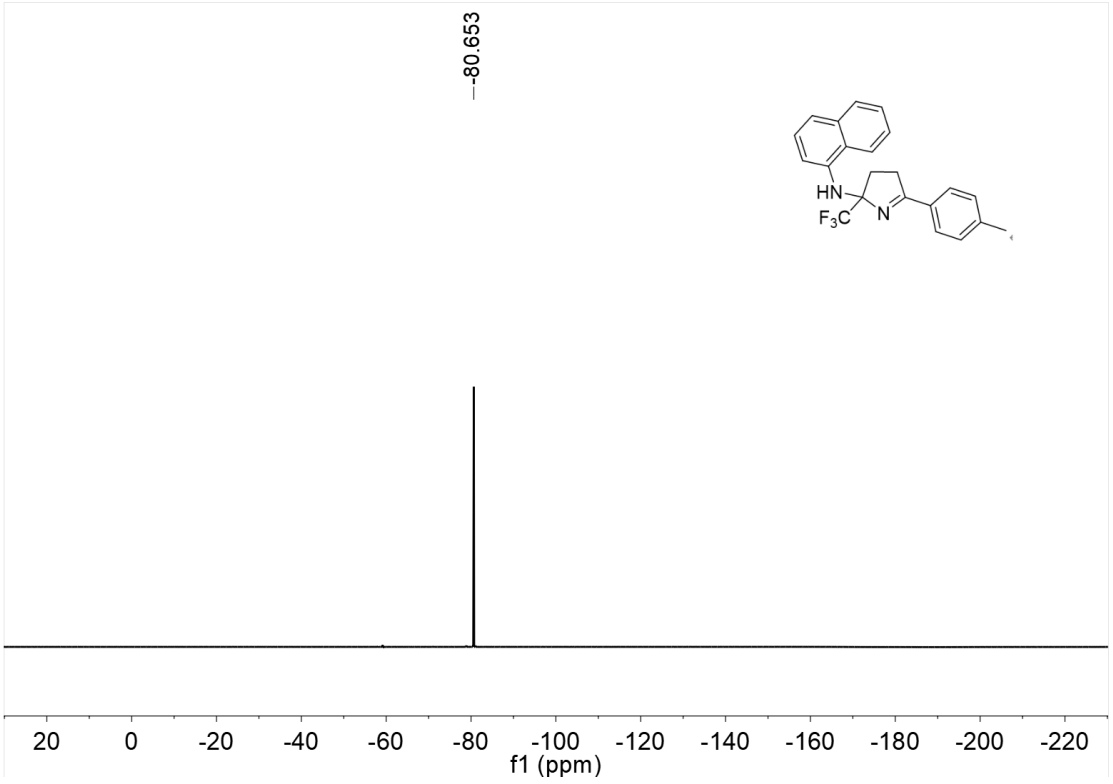


Figure 53. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **3pa**

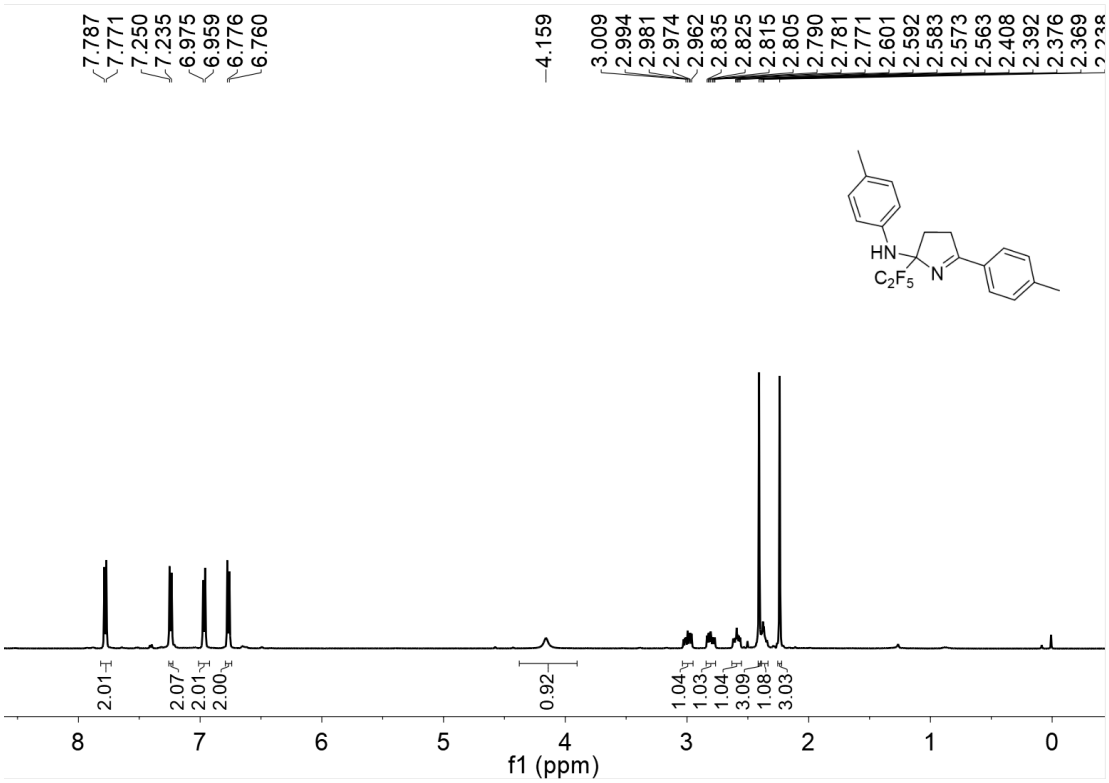


Figure 54. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3qa**

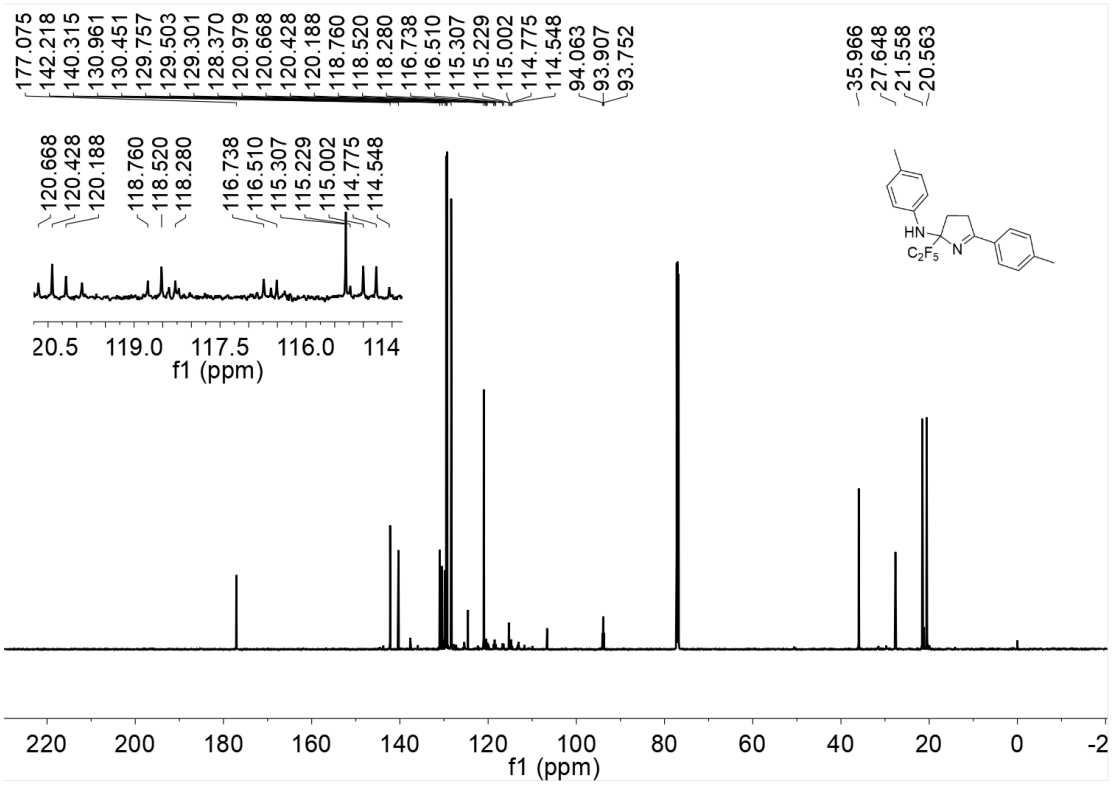


Figure 55. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3qa**

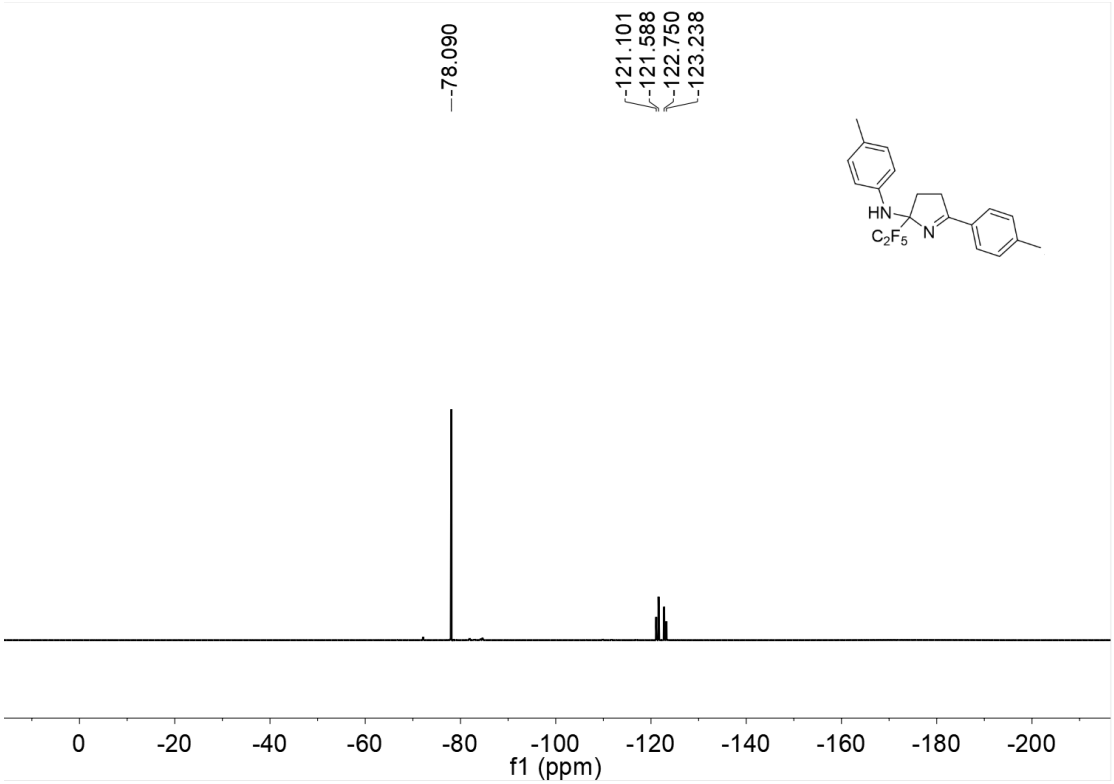


Figure 56. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **3qa**

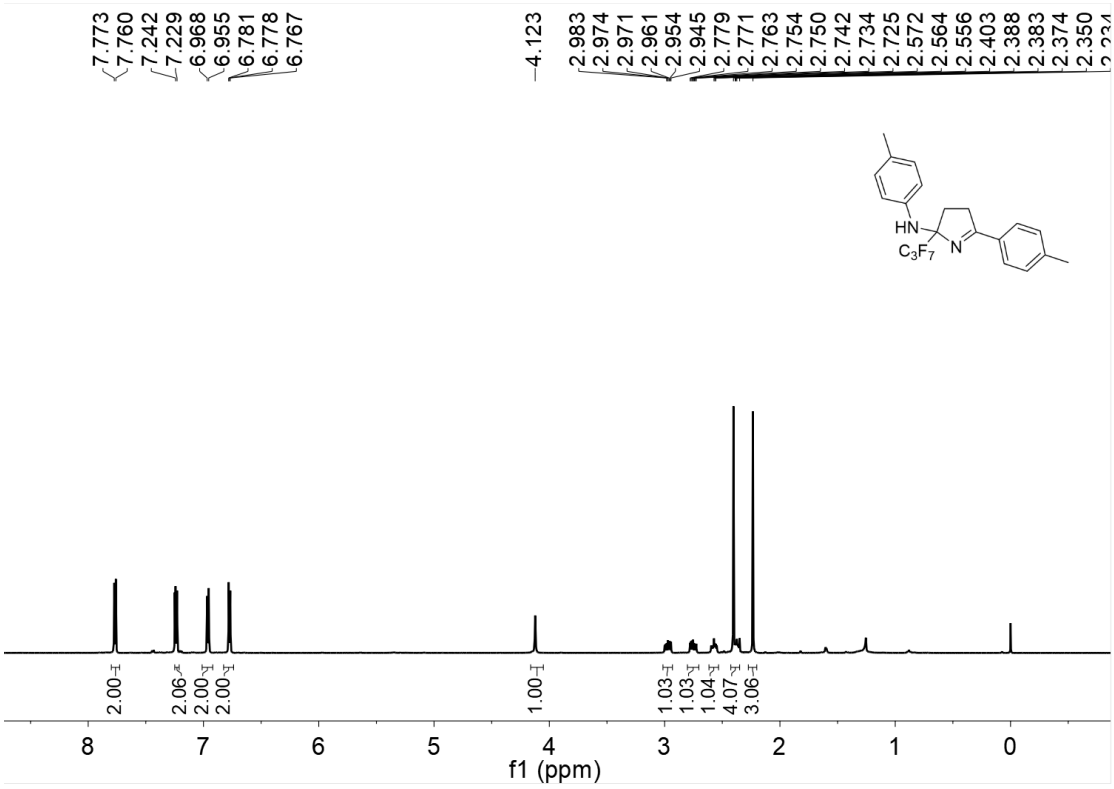


Figure 57. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3ra**

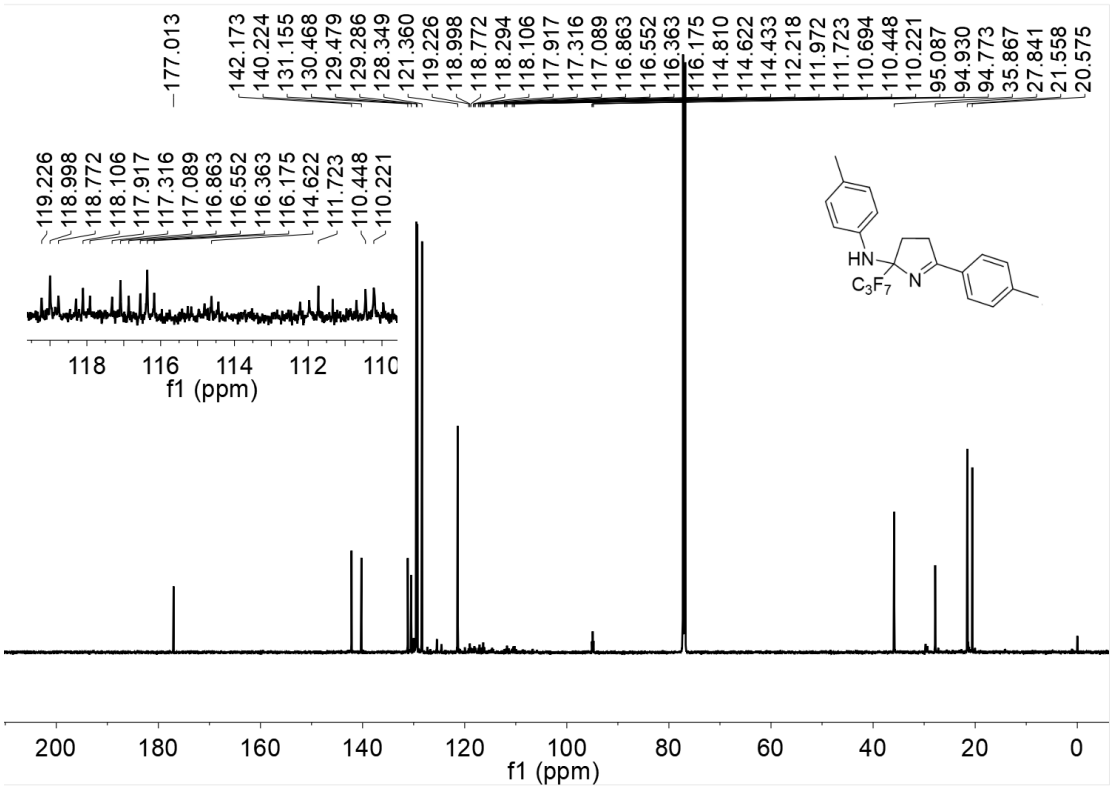


Figure 58. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ra**

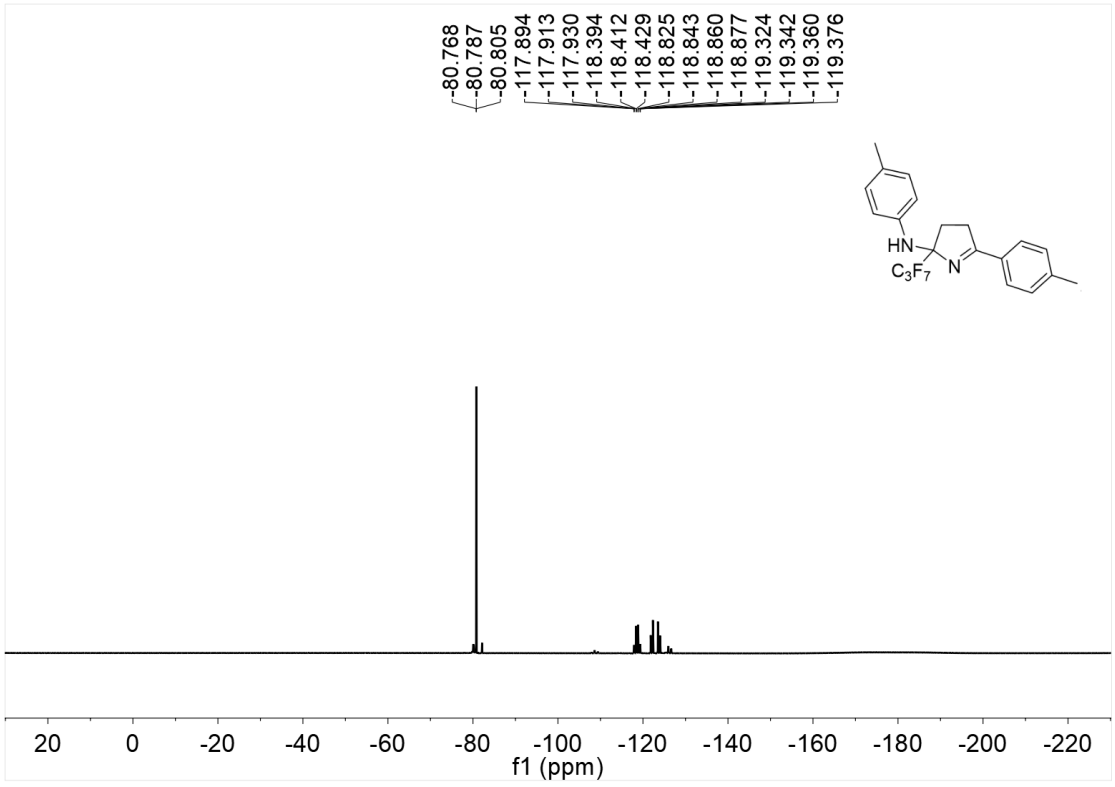


Figure 59. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **3ra**

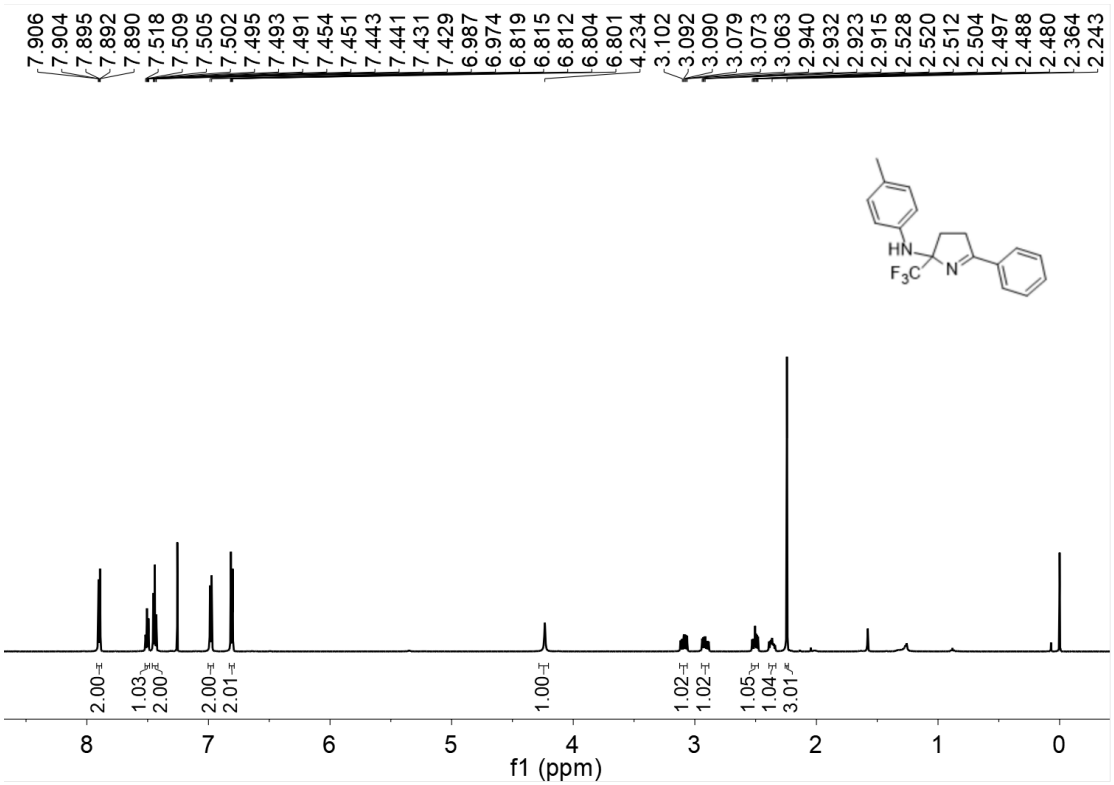


Figure 60. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3ab**

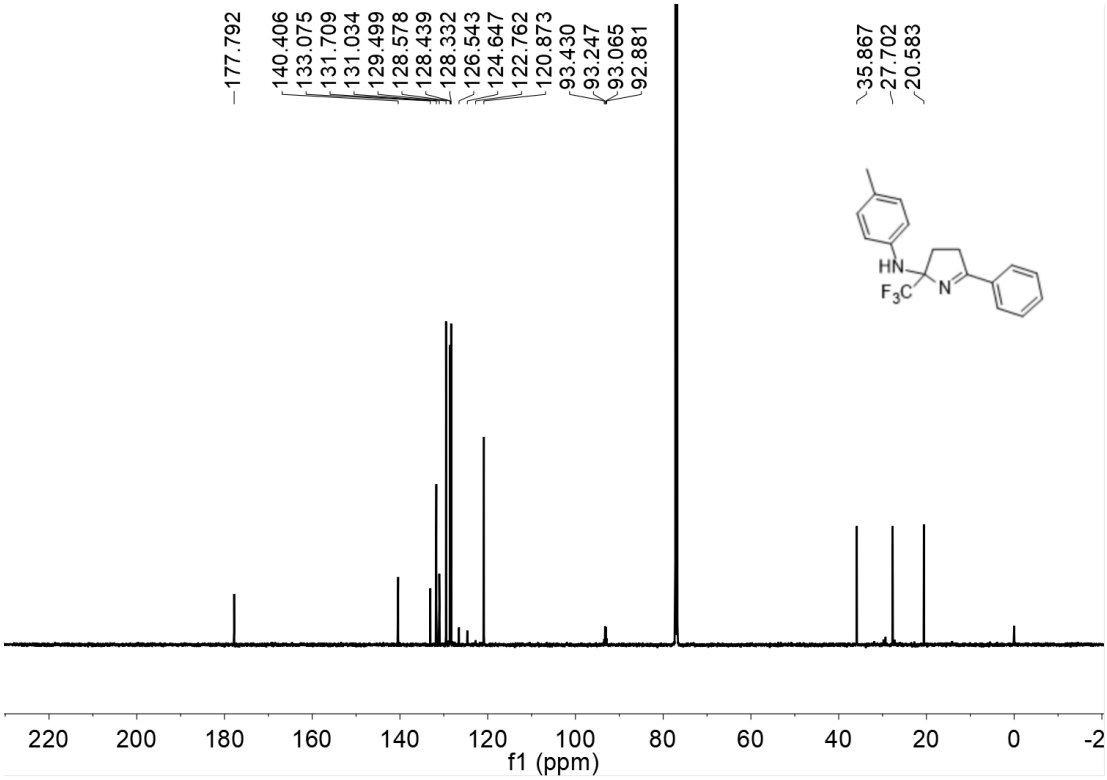


Figure 61. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ab**

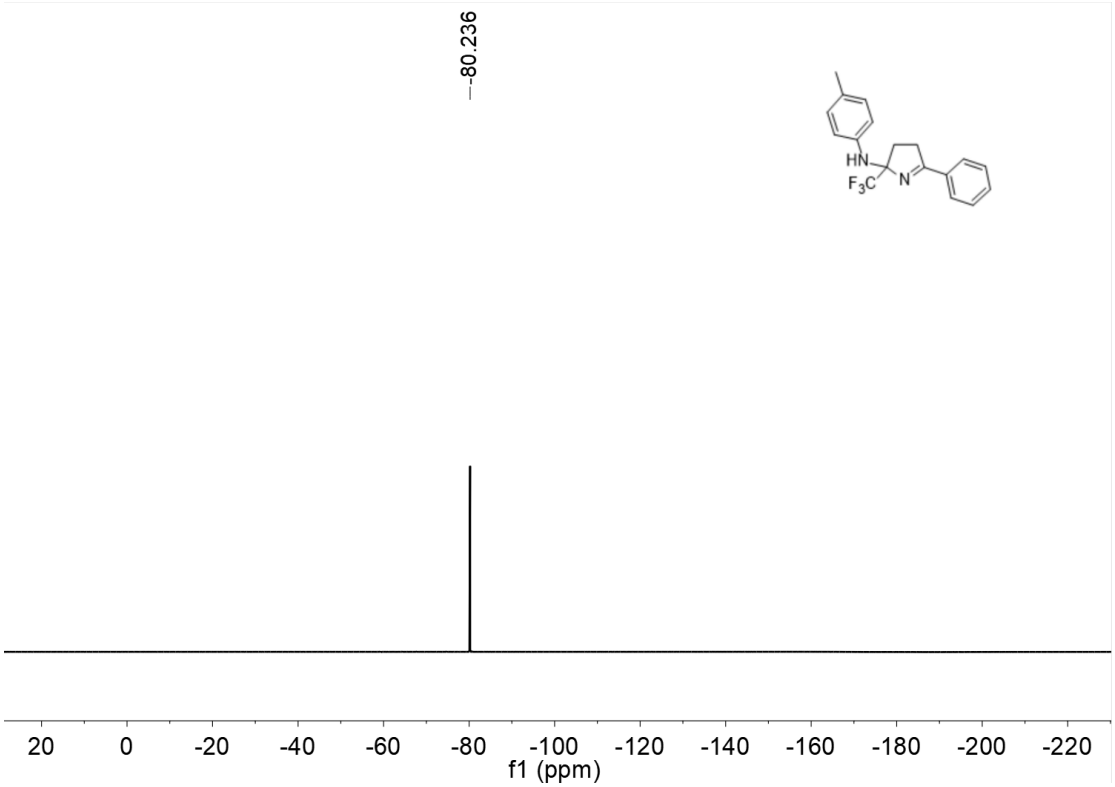


Figure 62. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **3ab**

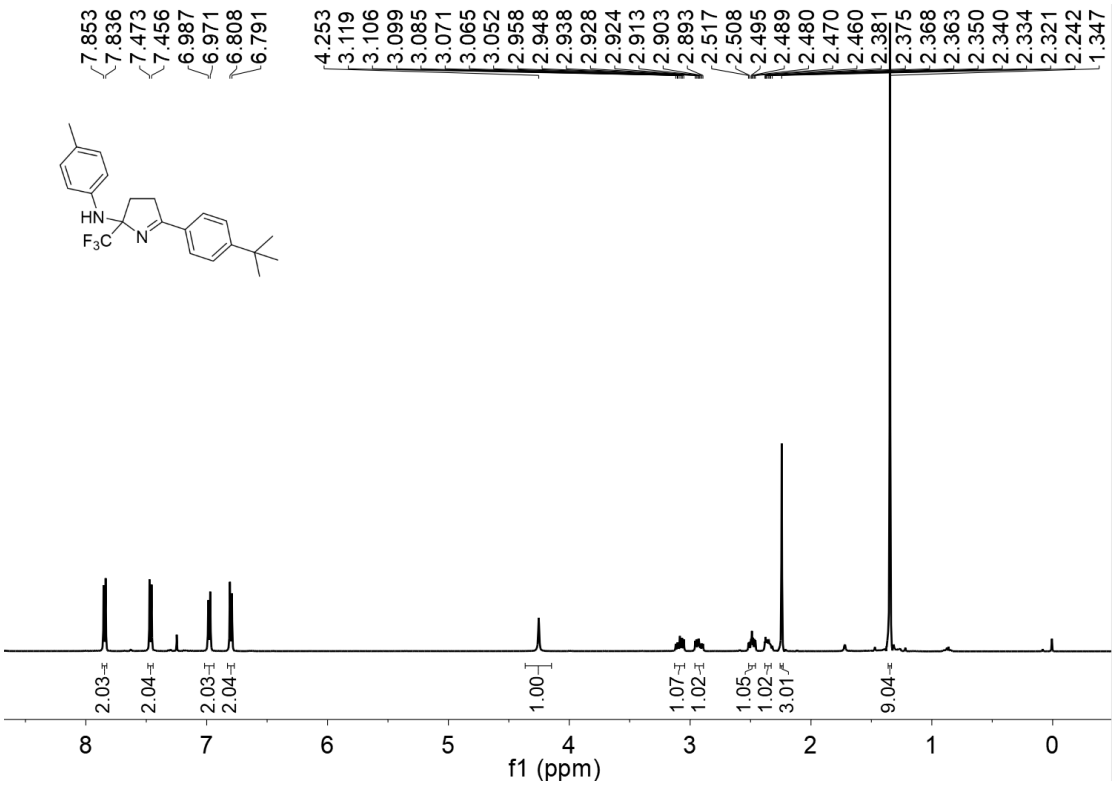


Figure 63. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3ac**

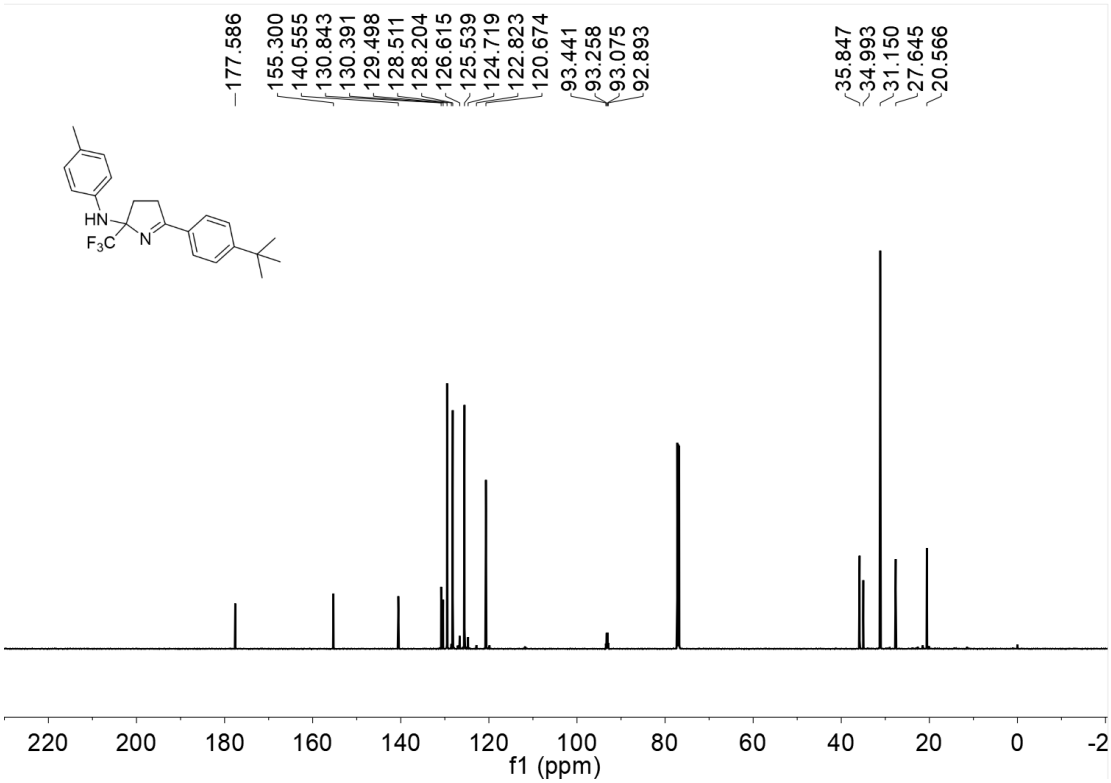


Figure 64. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ac**

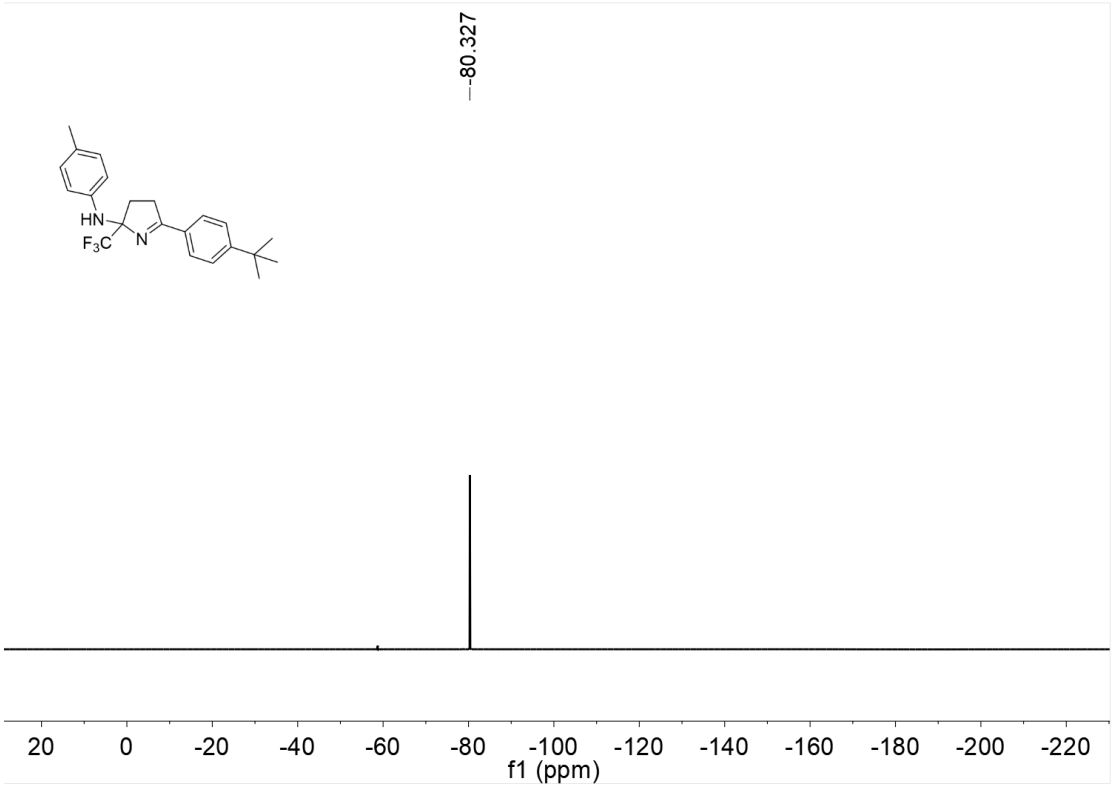


Figure 65. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **3ac**

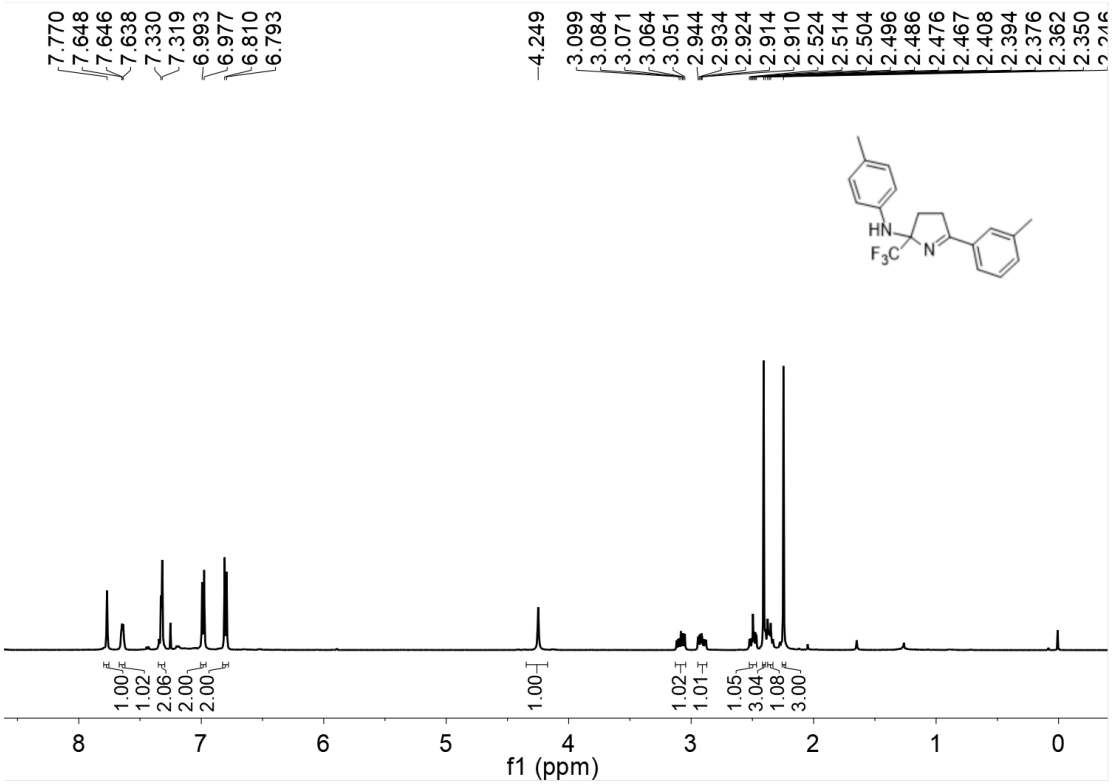


Figure 66. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3ad**

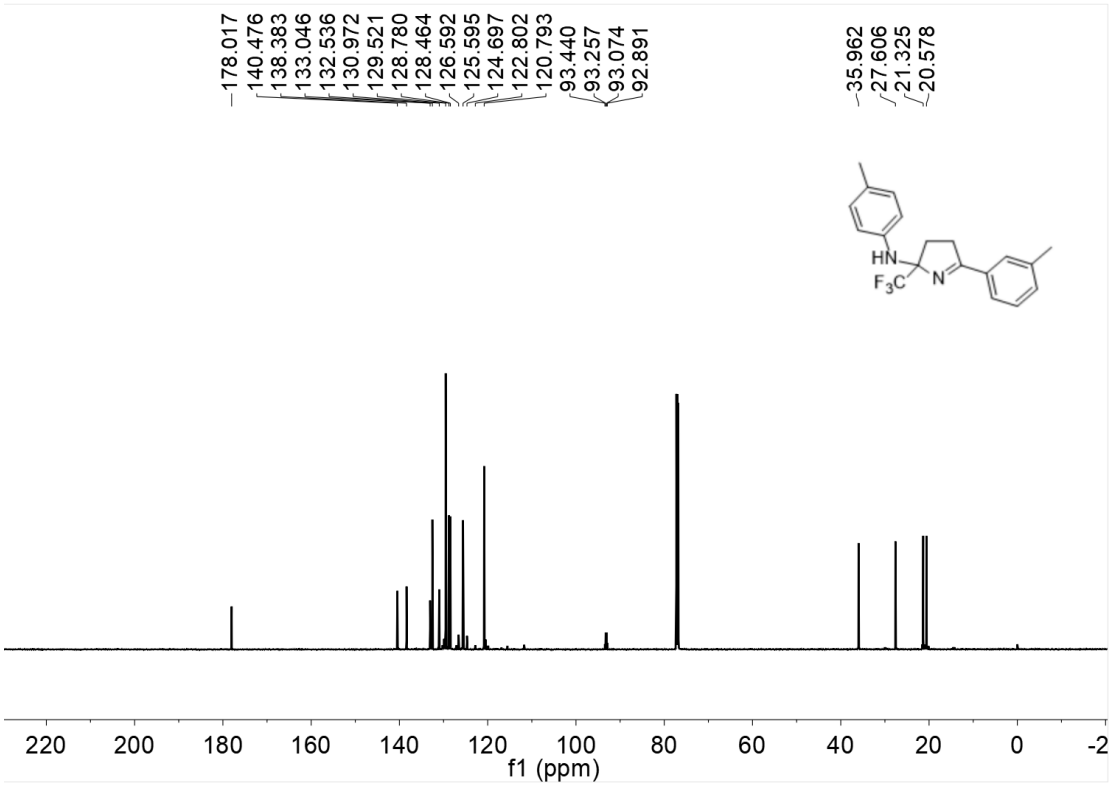


Figure 67. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ad**

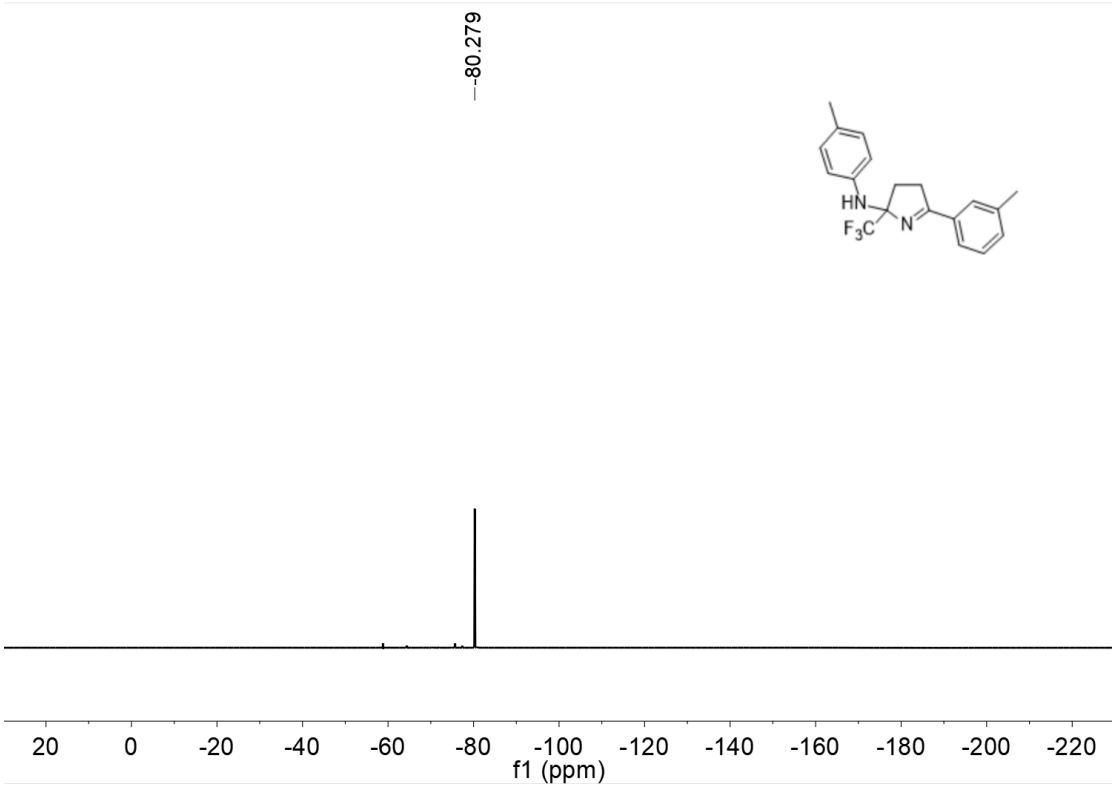


Figure 68. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **3ad**

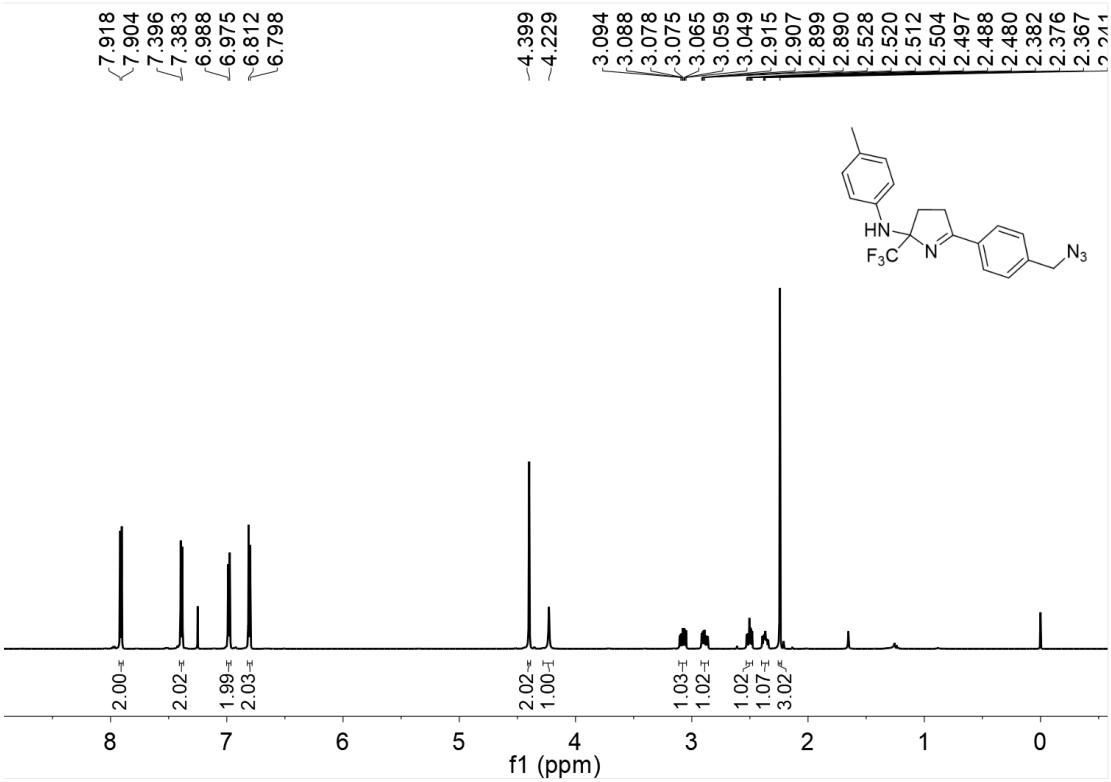


Figure 69. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3ae**

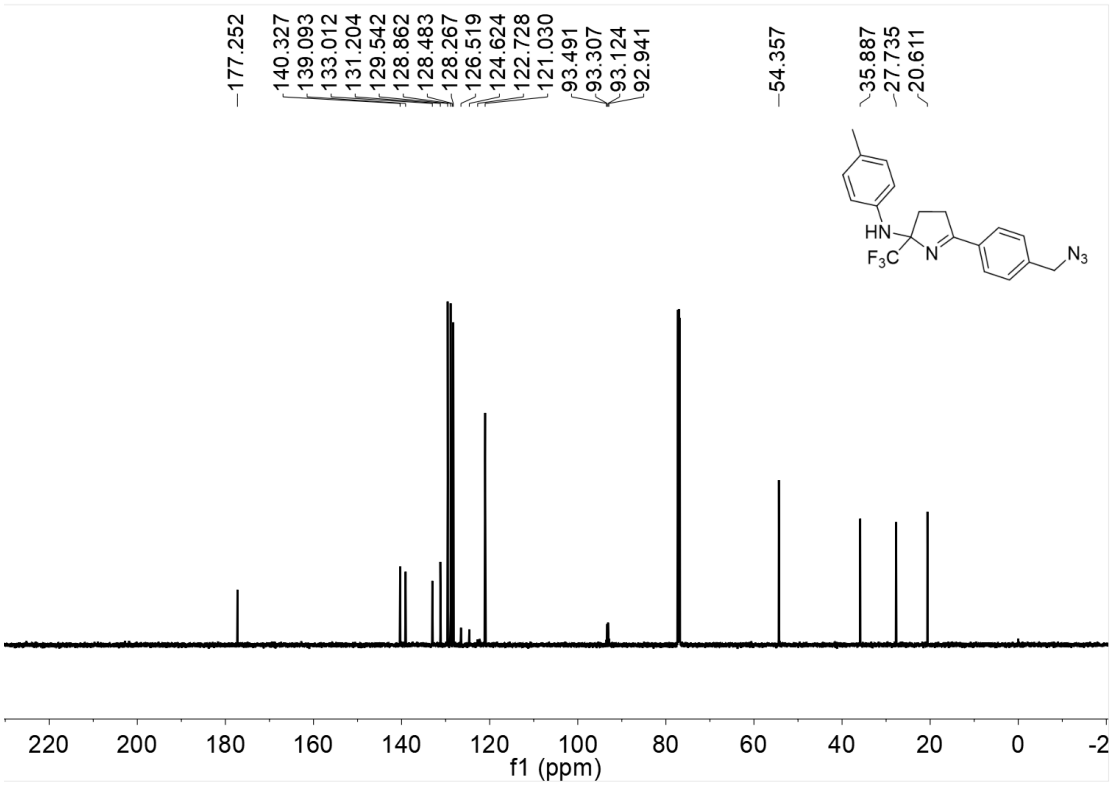


Figure 70. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ae**

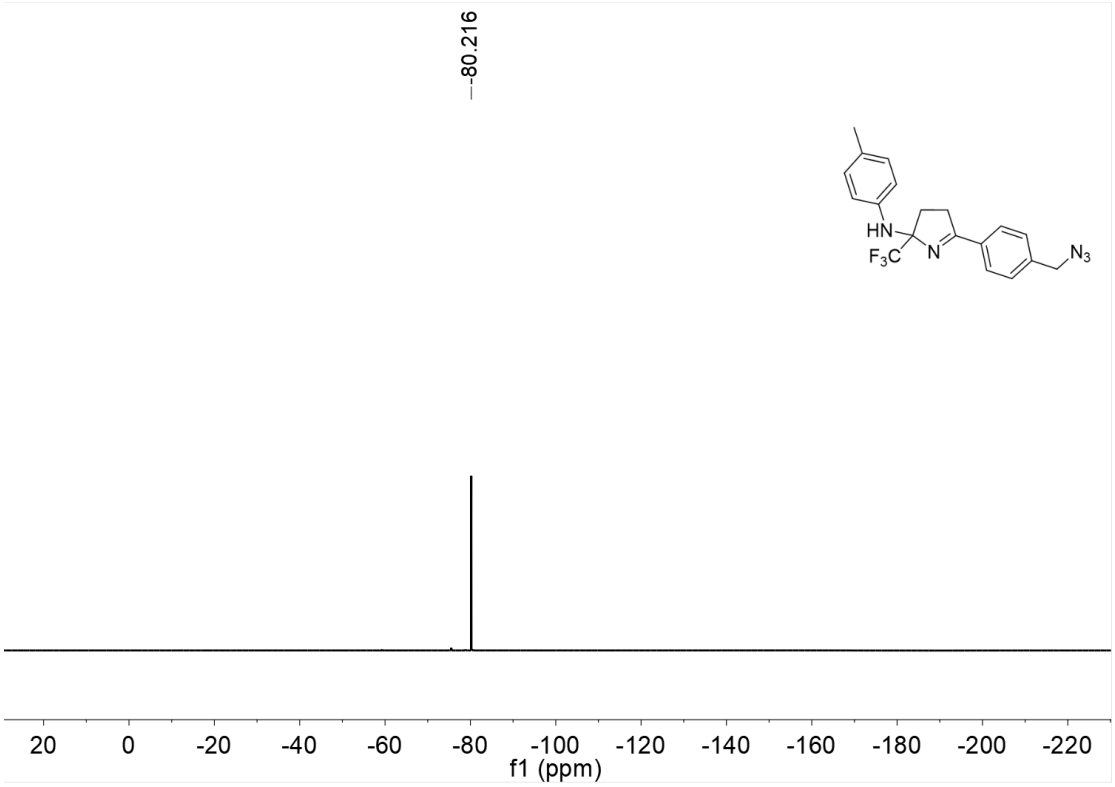


Figure 71. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **3ae**

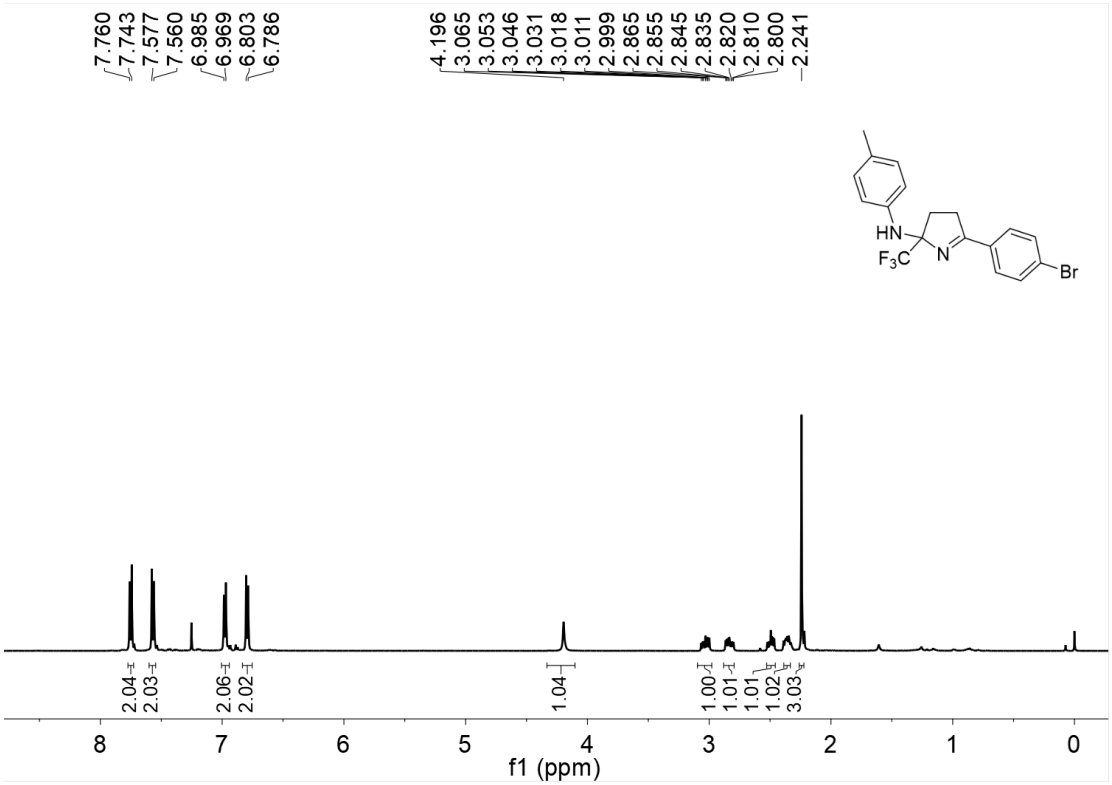


Figure 72. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3af**

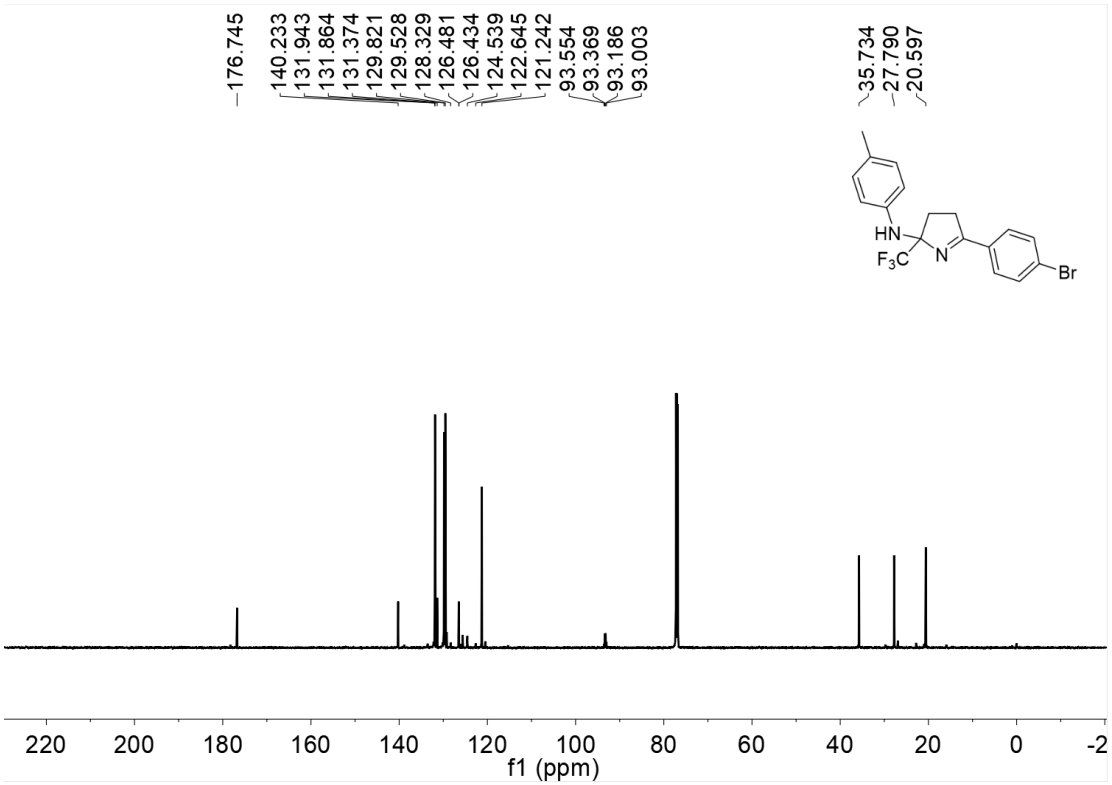


Figure 73. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3af**

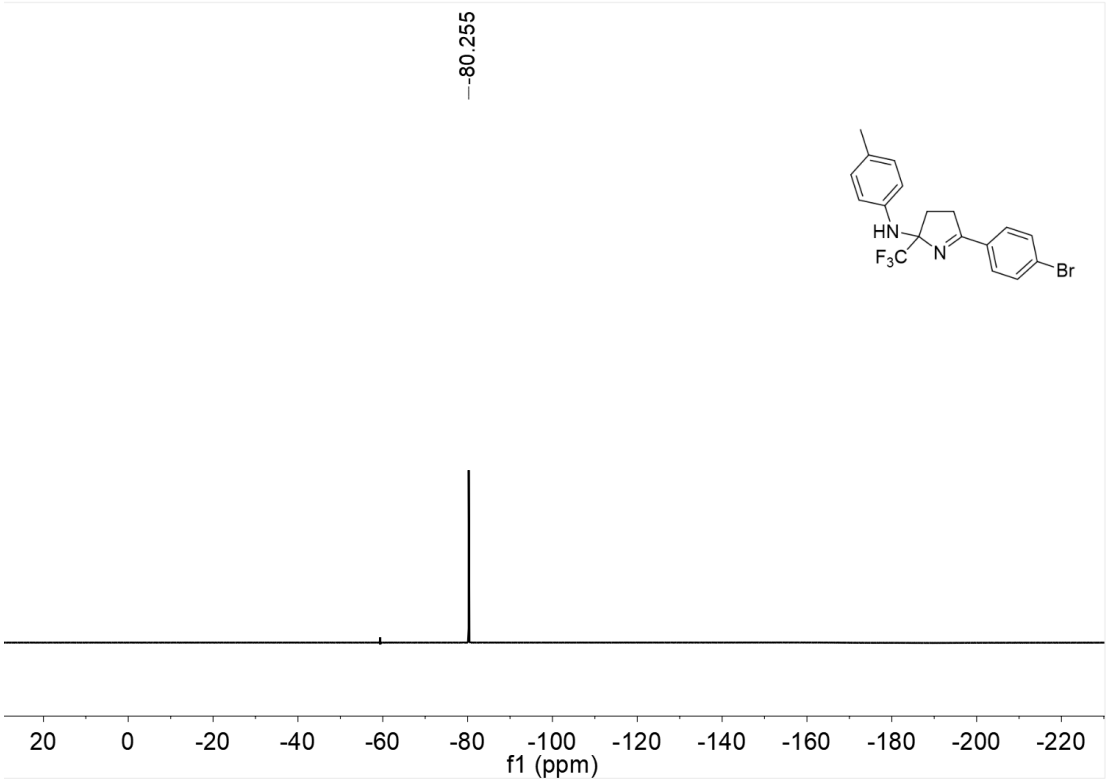


Figure 74. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **3af**

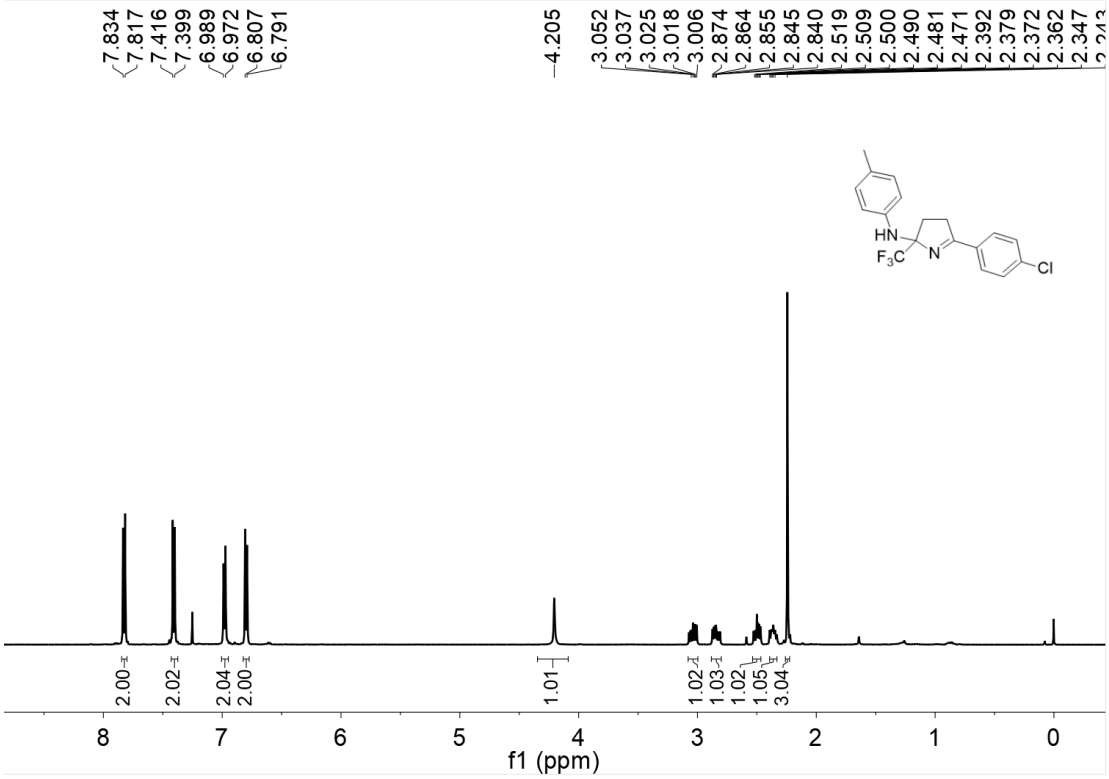


Figure 75. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3ag**

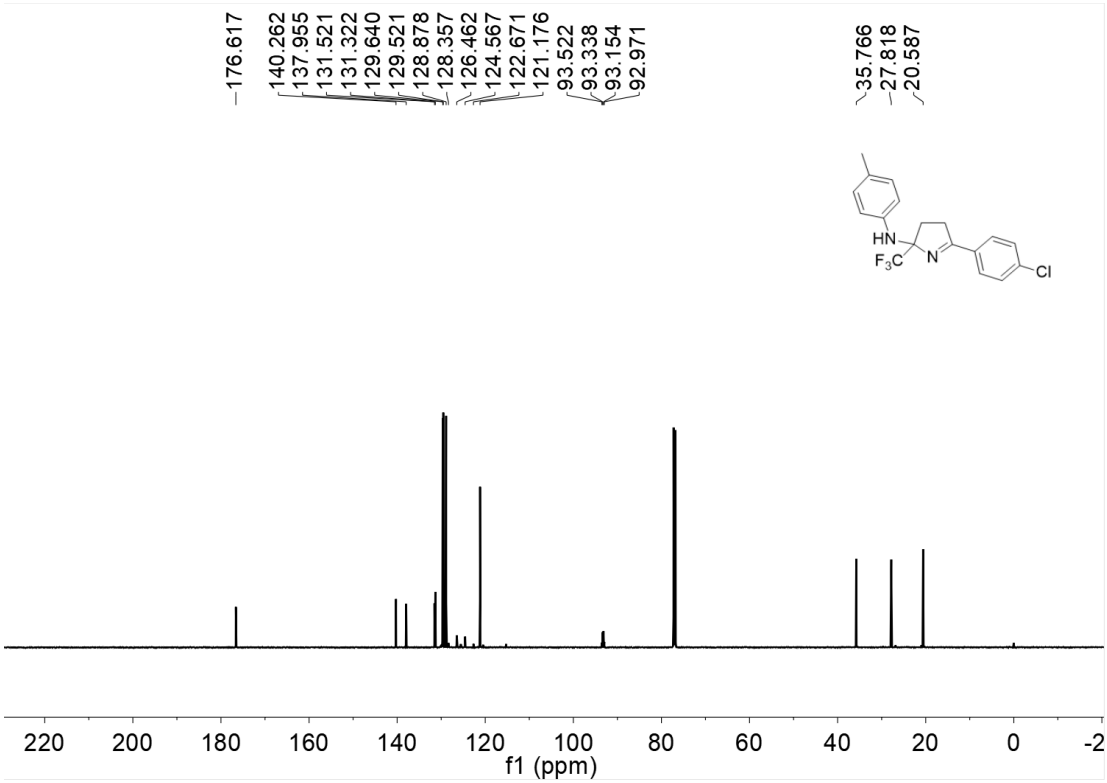


Figure 76. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ag**

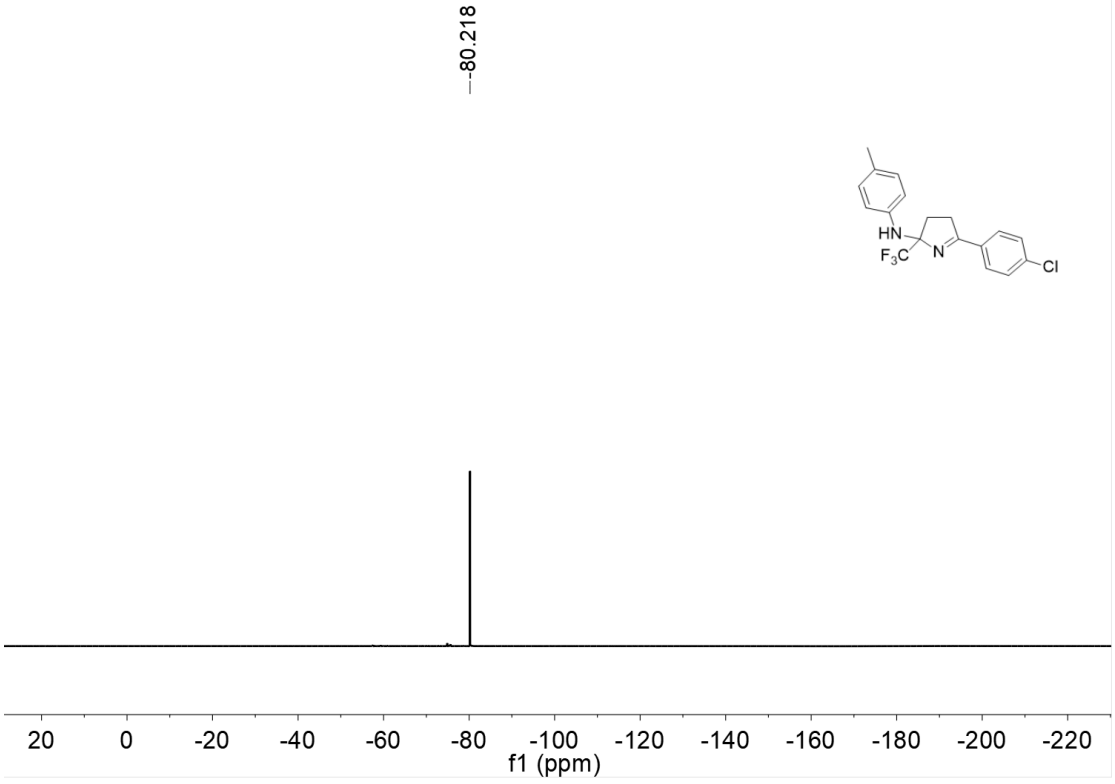


Figure 77. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **3ag**

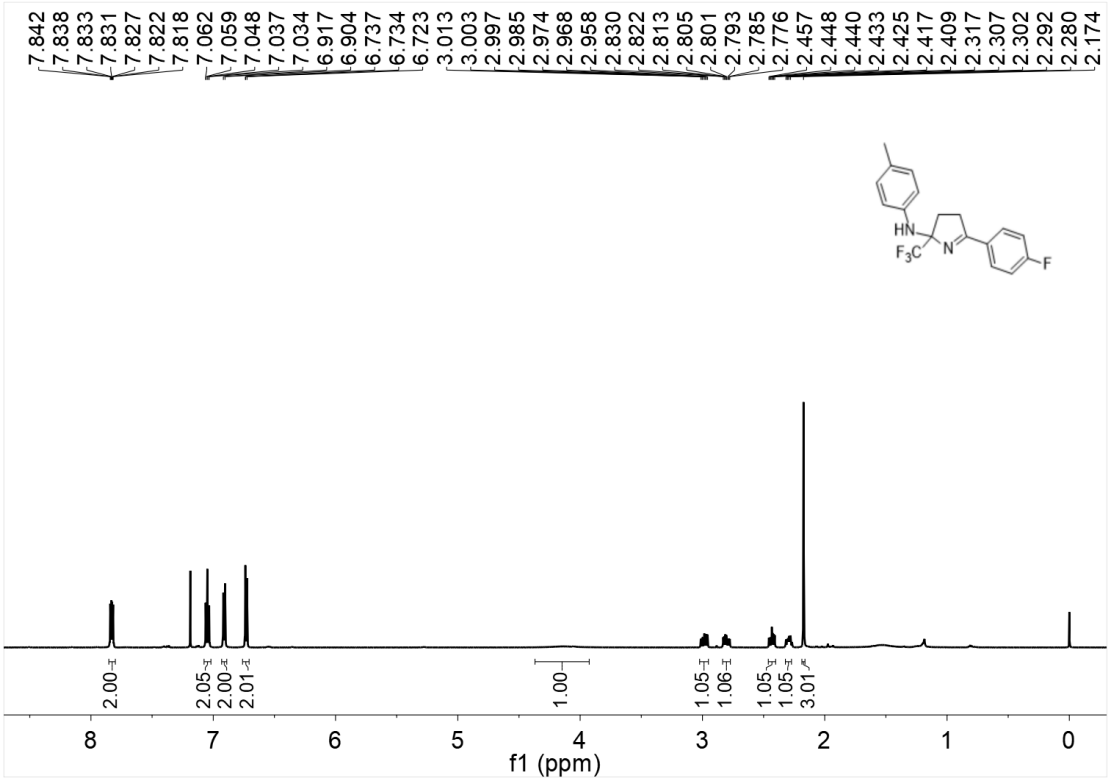


Figure 78. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3ah**

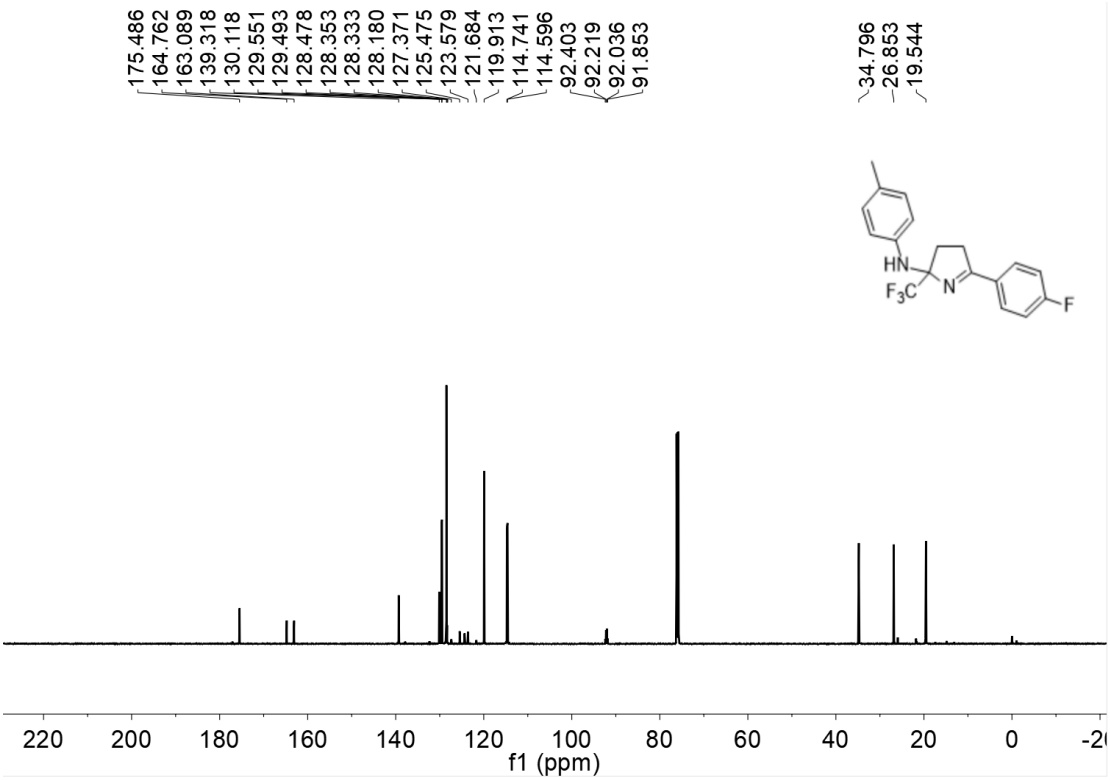


Figure 79. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ah**

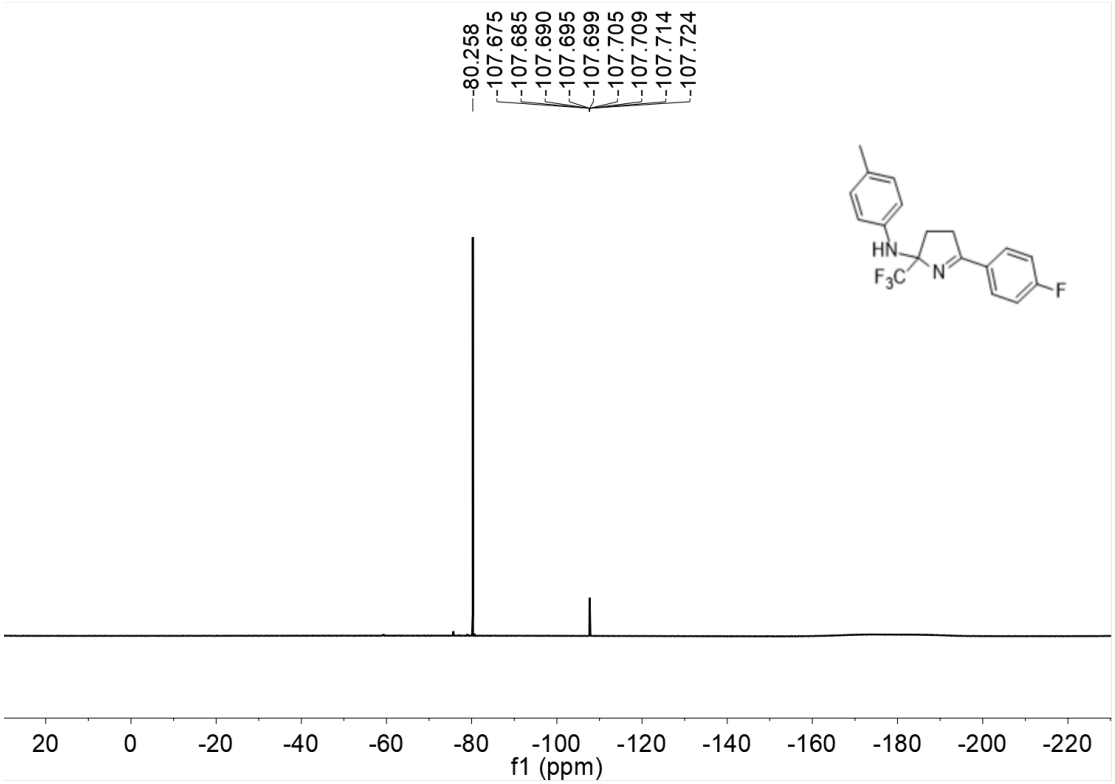


Figure 80. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **3ah**

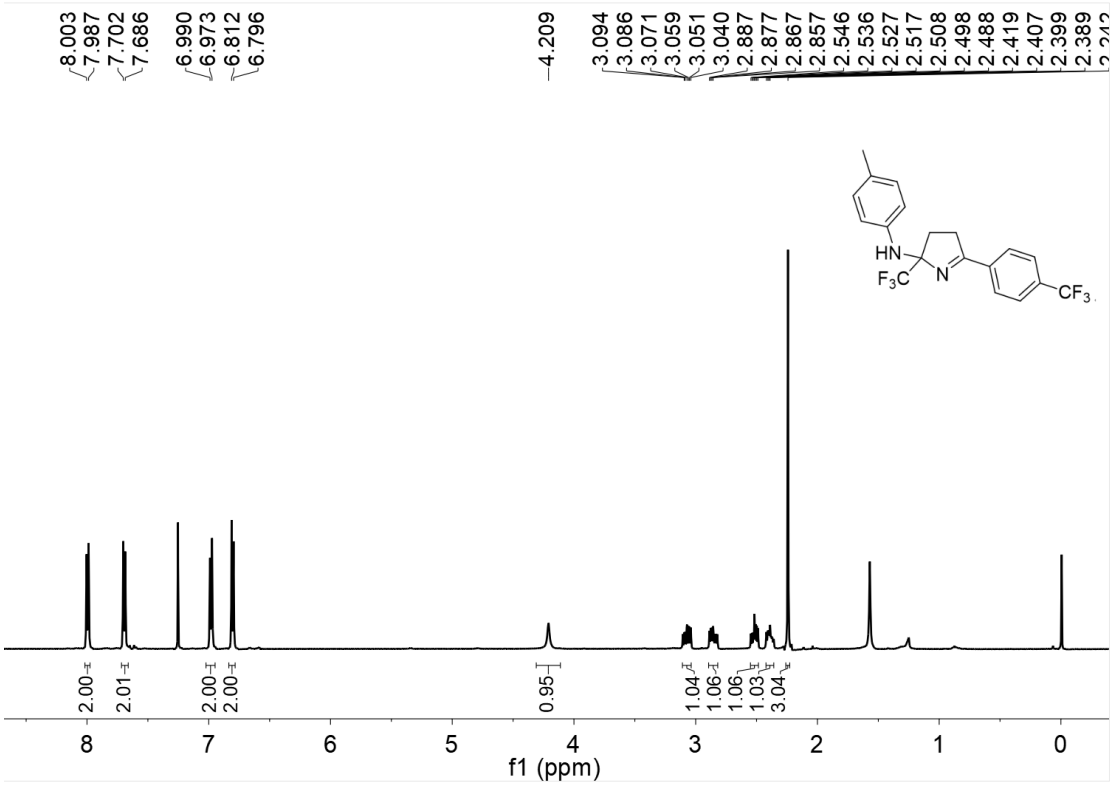


Figure 81. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3ai**

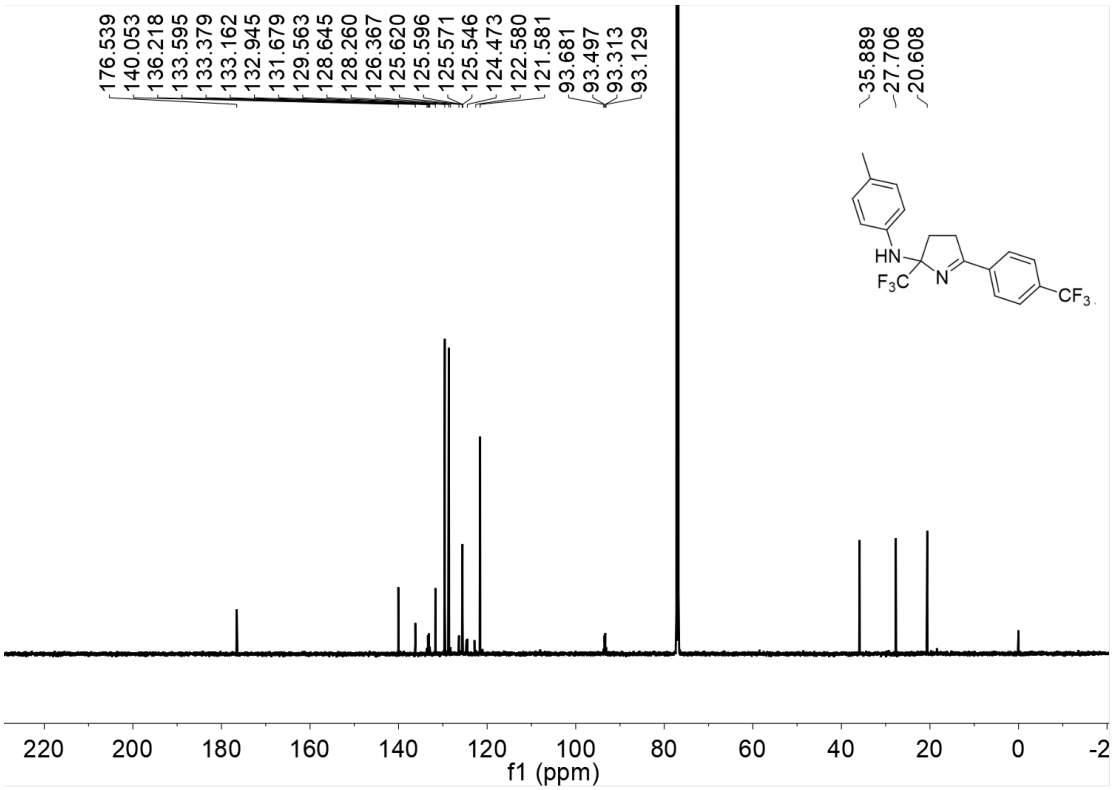


Figure 82. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ai**

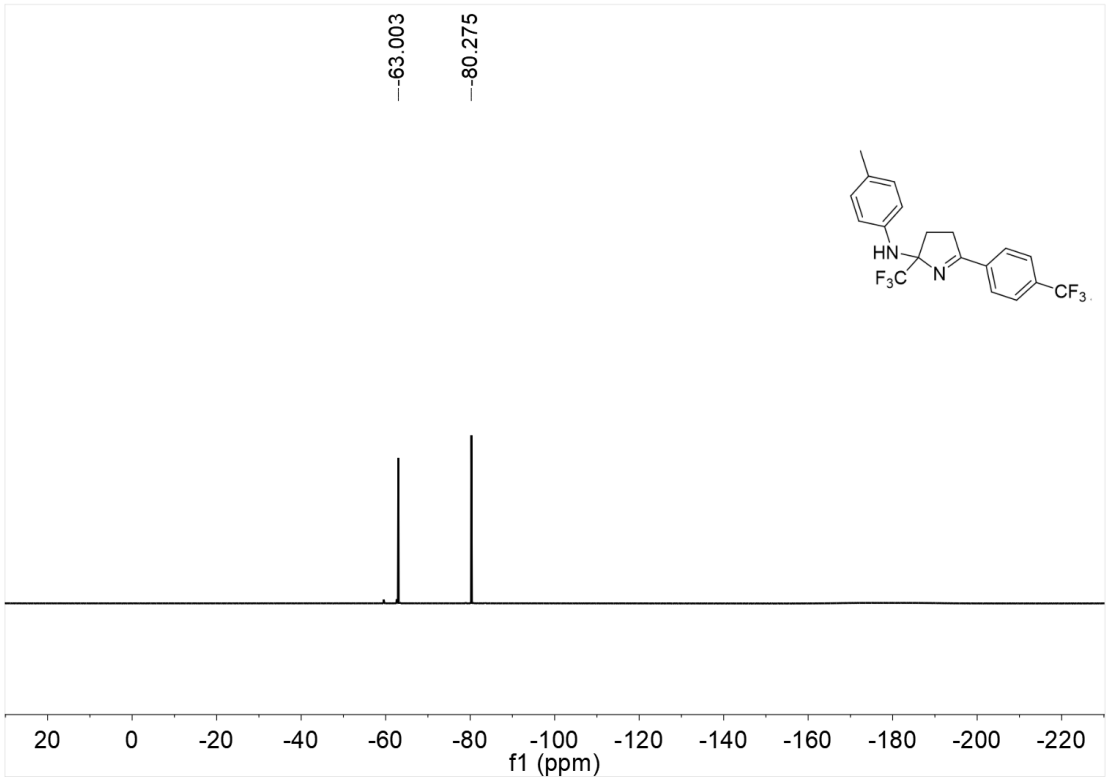


Figure 83. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **3ai**

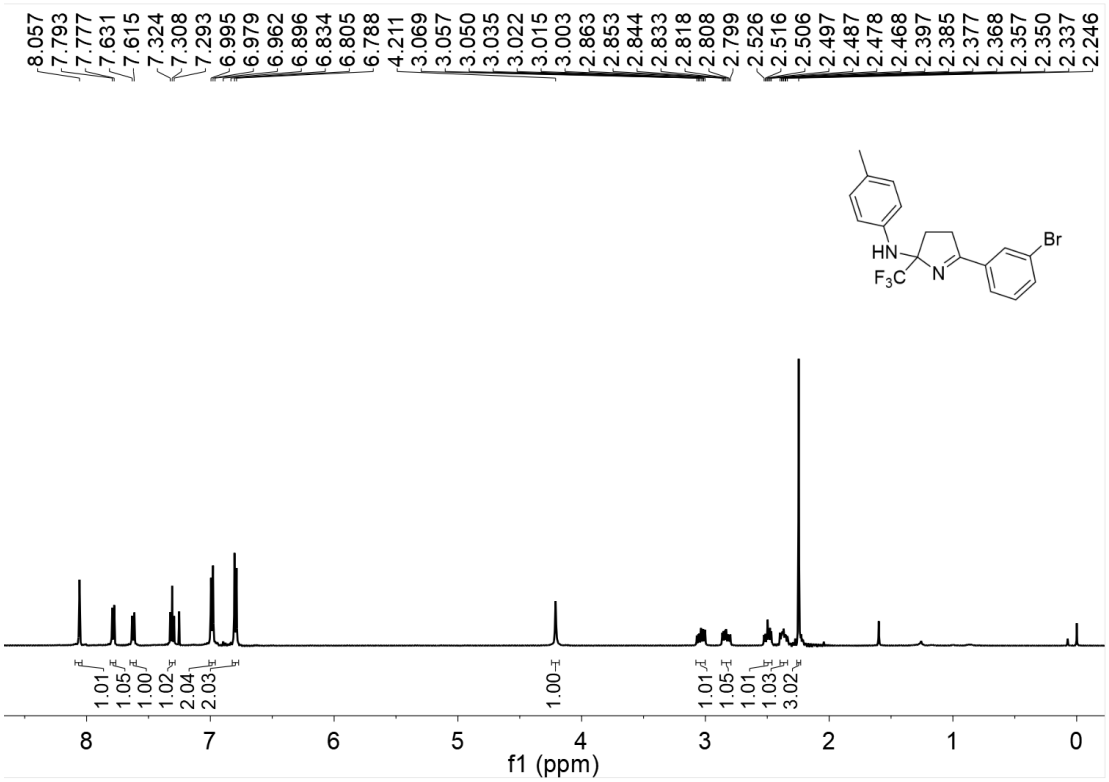


Figure 84. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3aj**

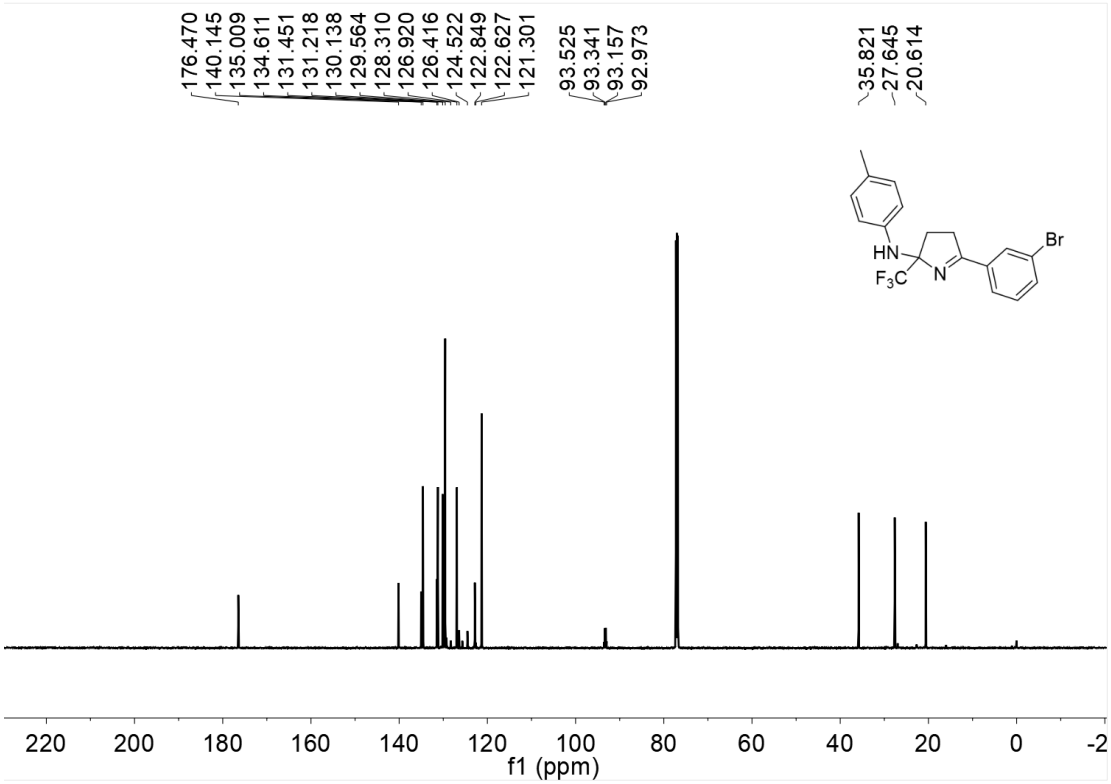


Figure 85. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3aj**

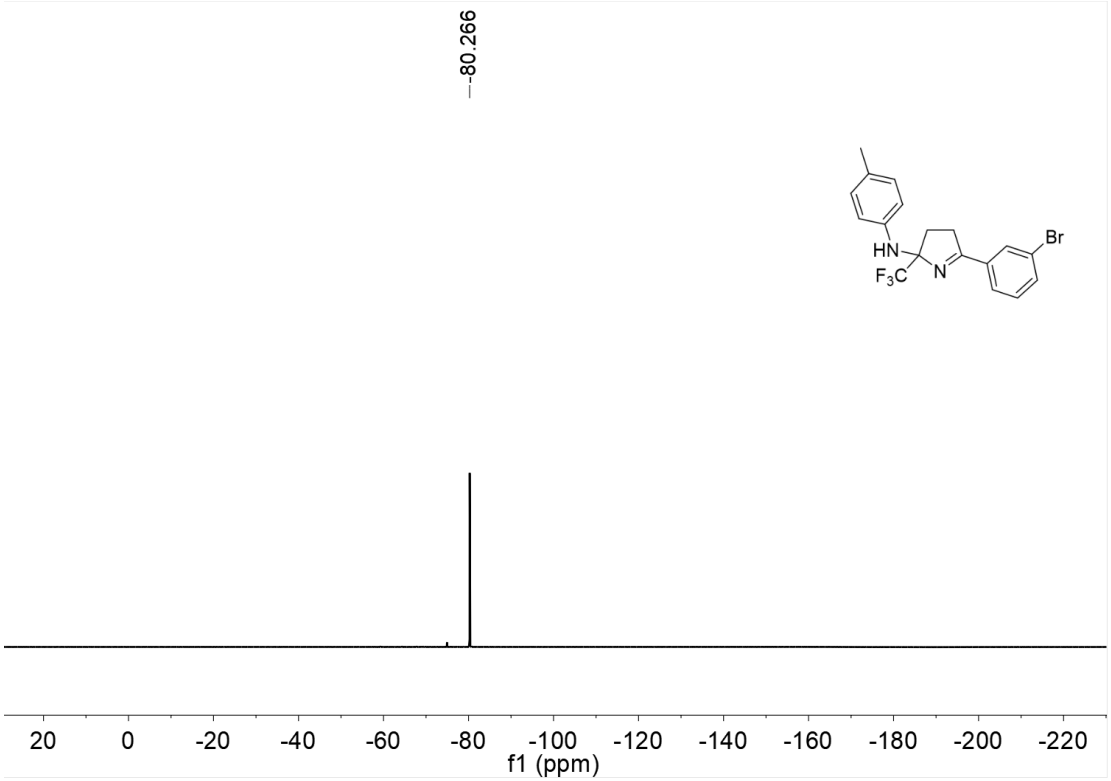


Figure 86. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **3aj**

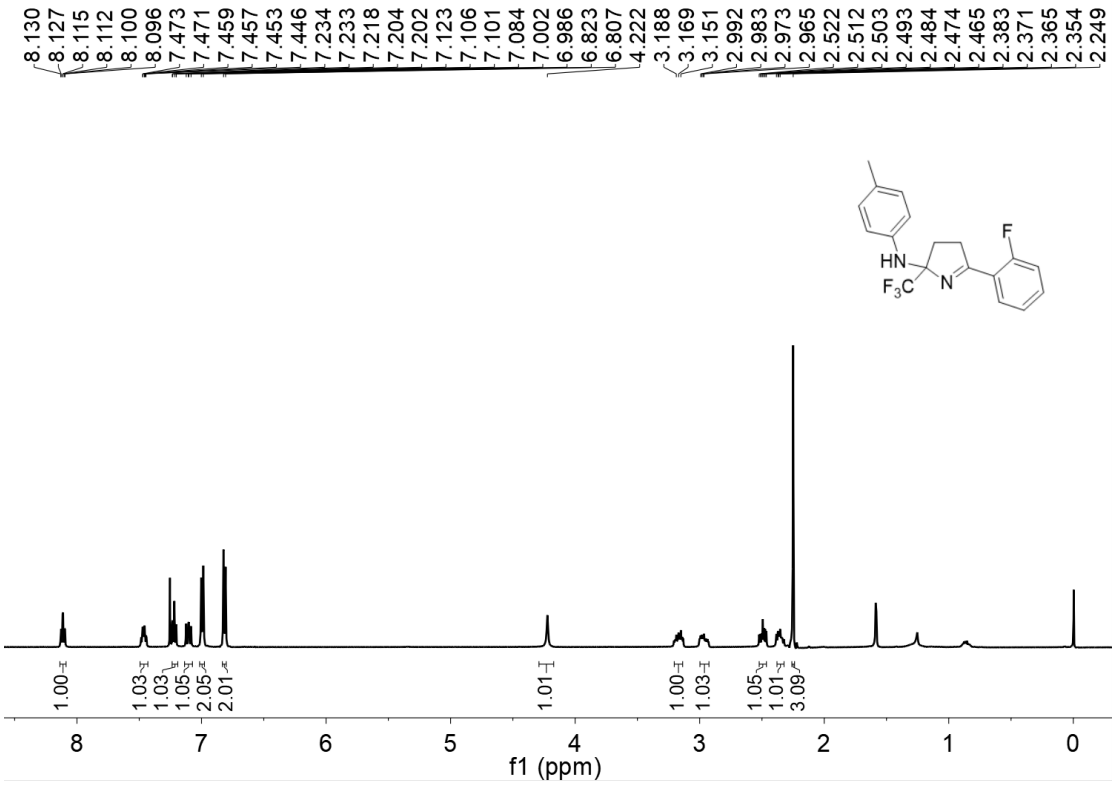


Figure 87. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3ak**

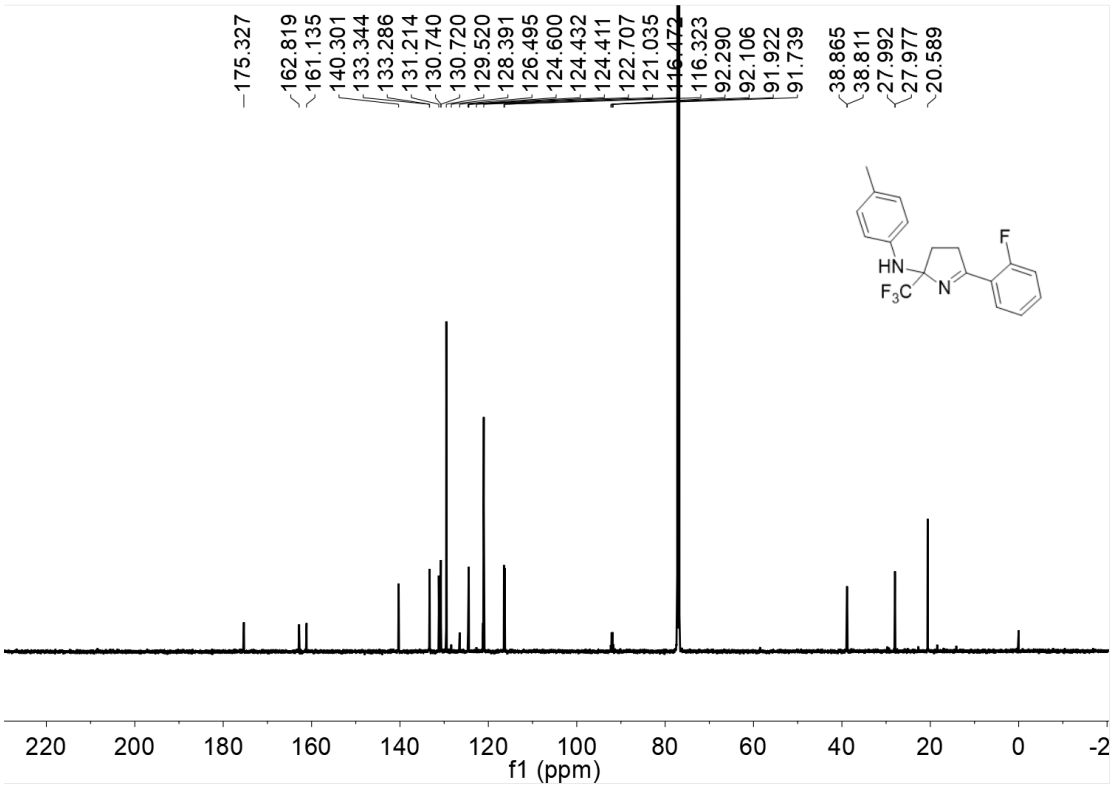


Figure 88. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ak**

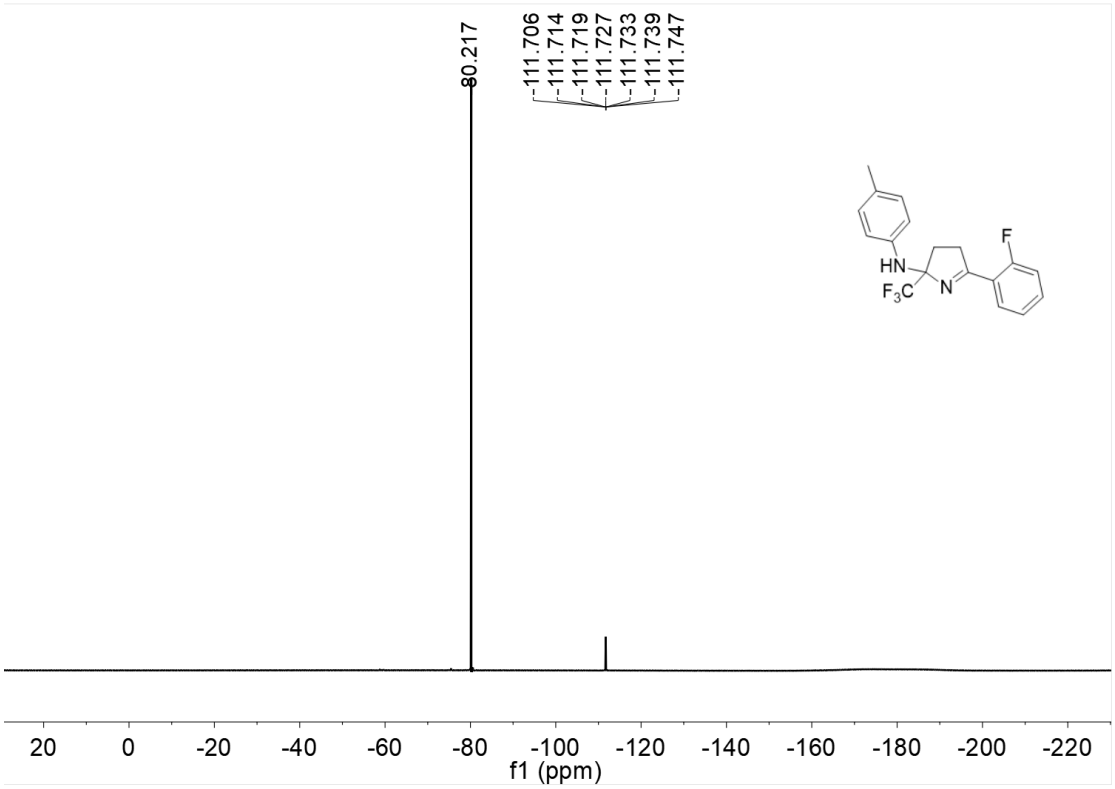


Figure 89. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **3ak**

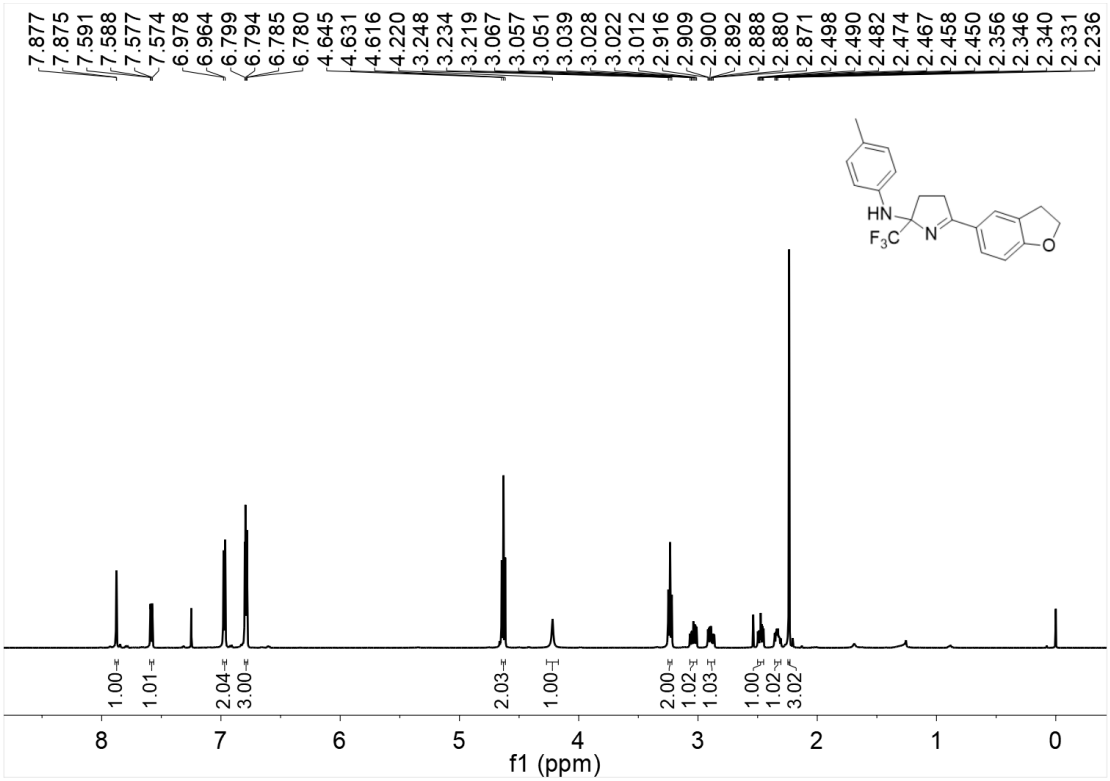


Figure 90. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3al**

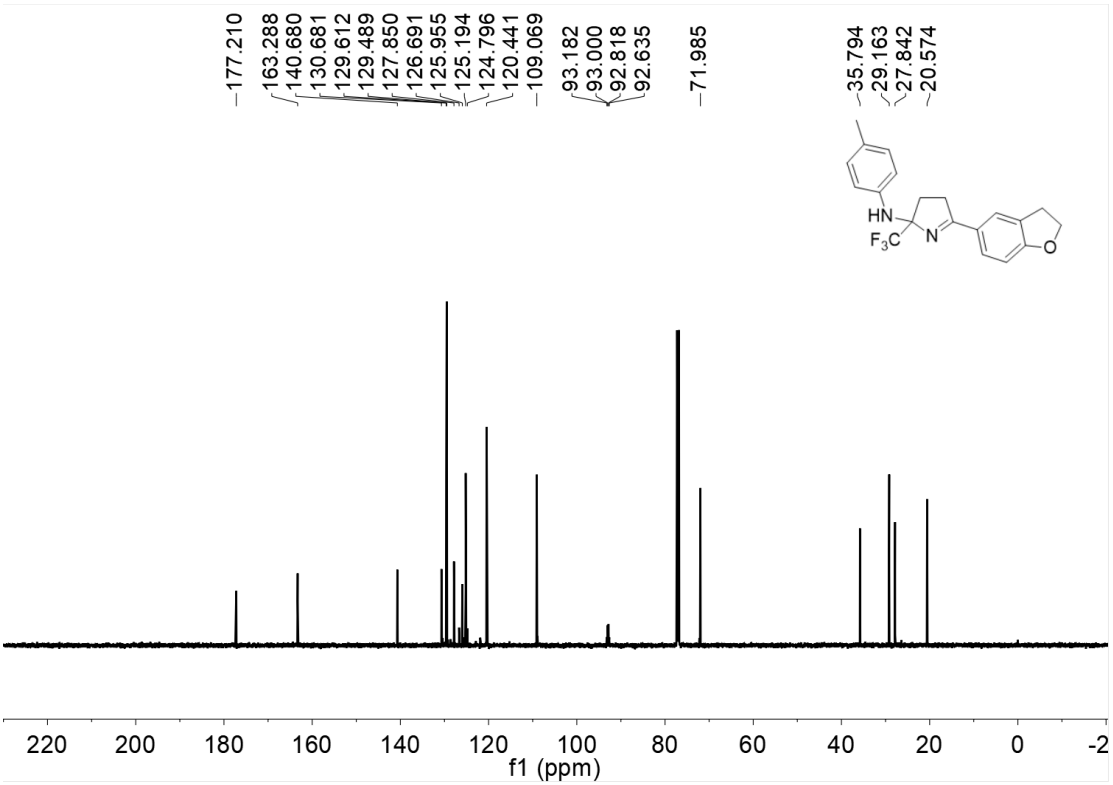


Figure 91. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3al**

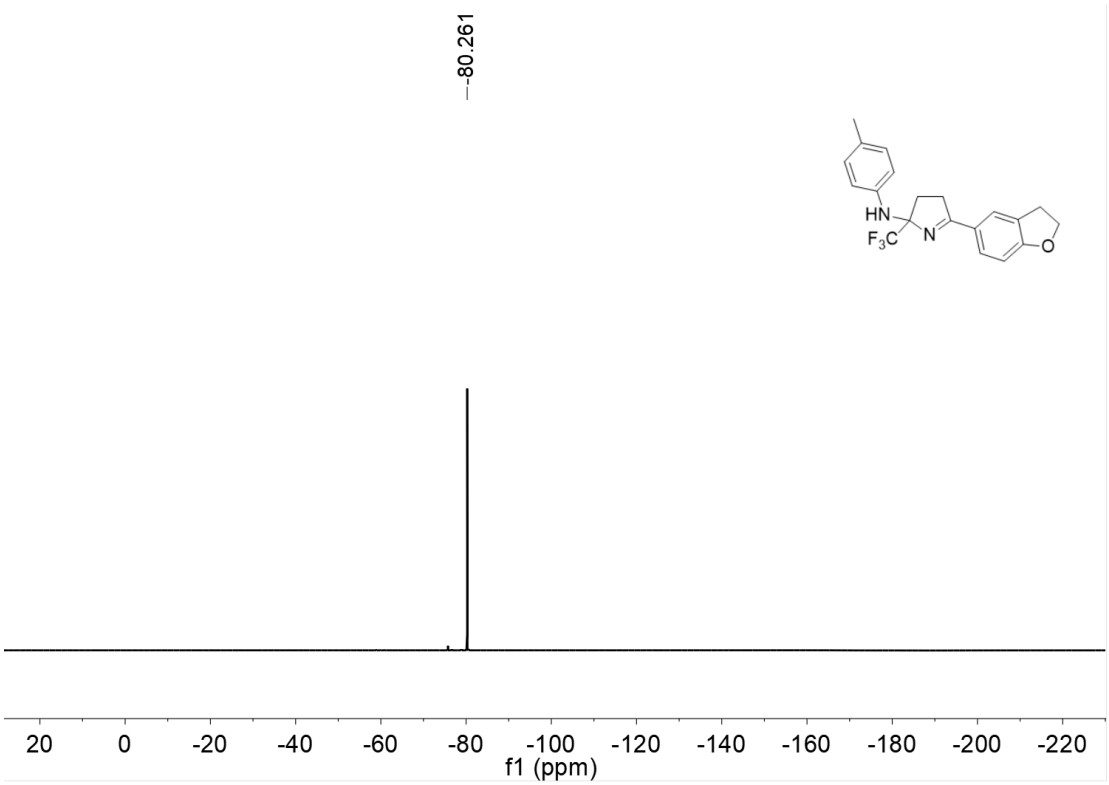


Figure 92. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **3al**

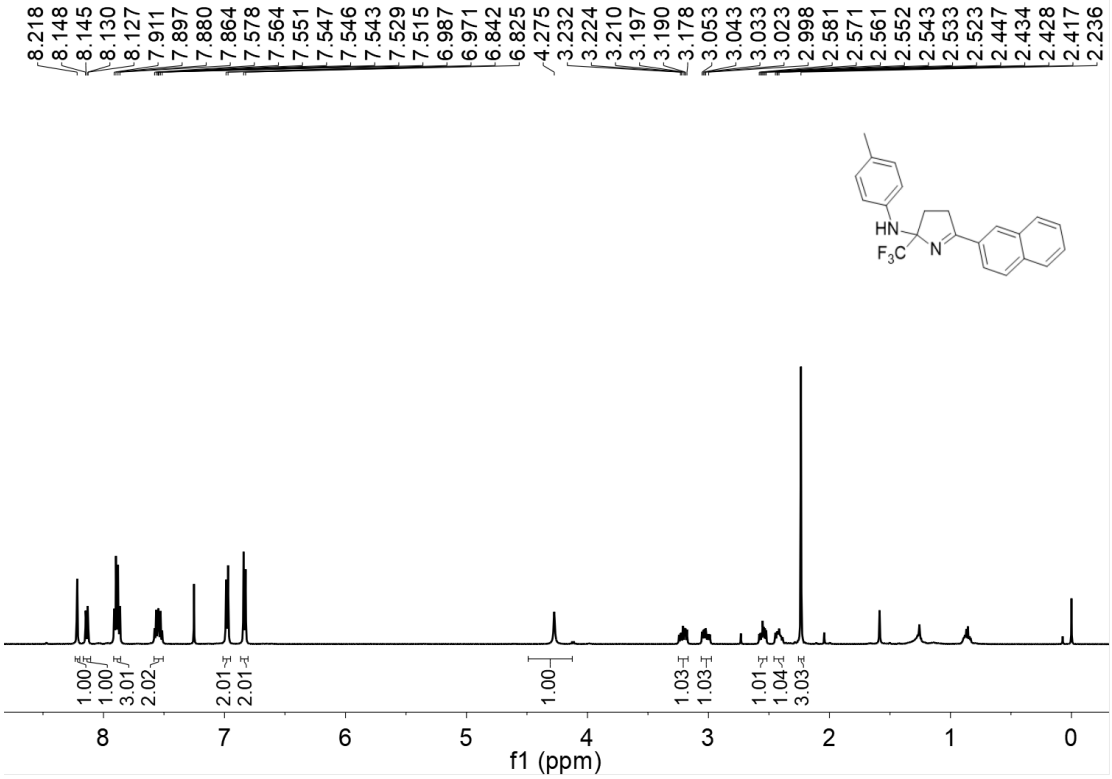


Figure 93. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3am**

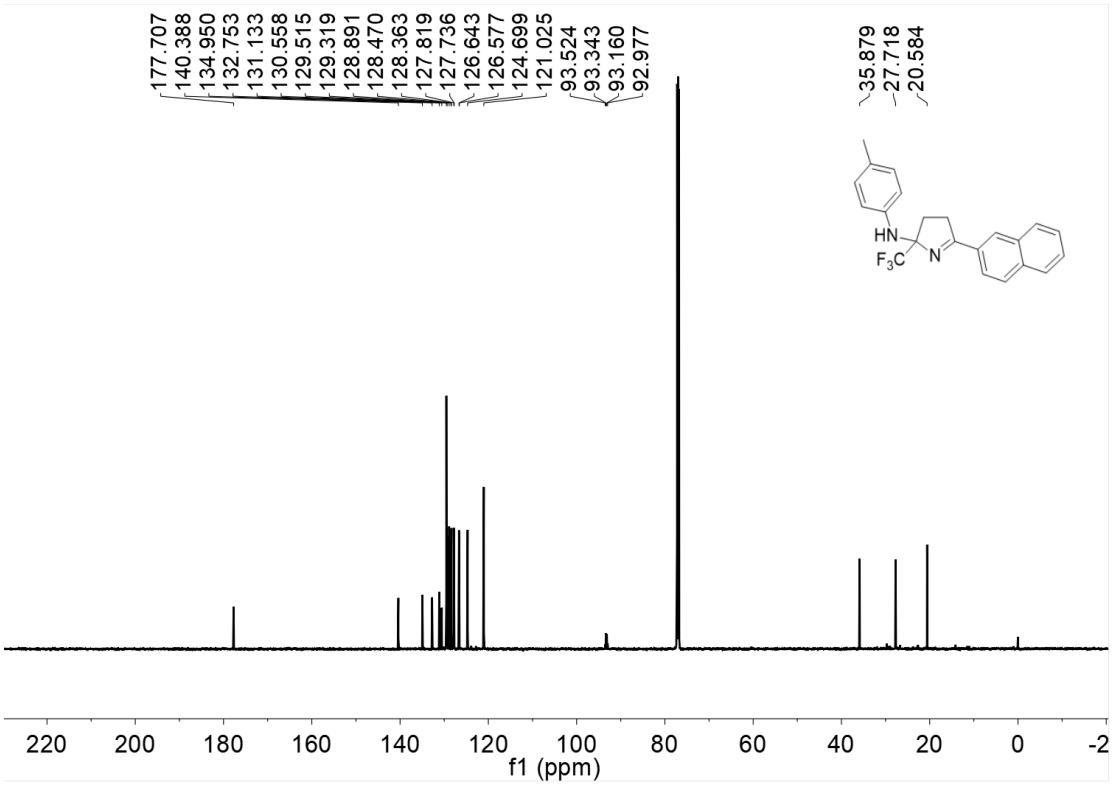


Figure 94. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3am**

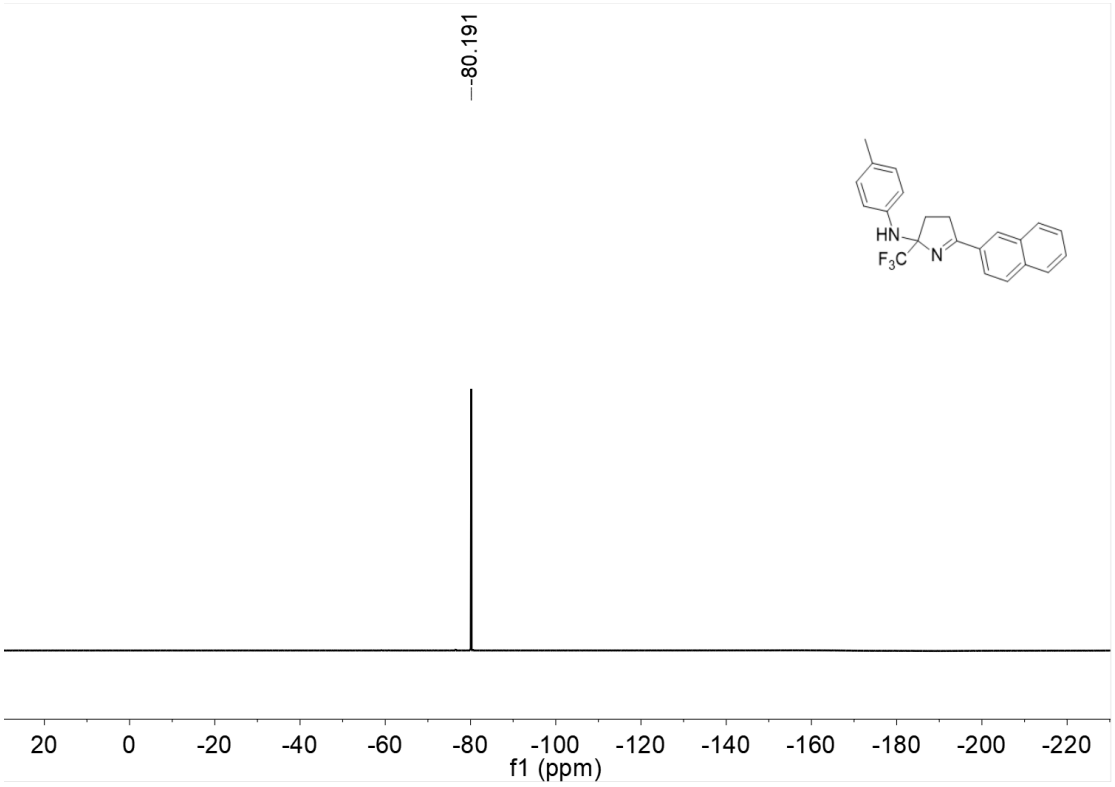


Figure 95. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **3am**

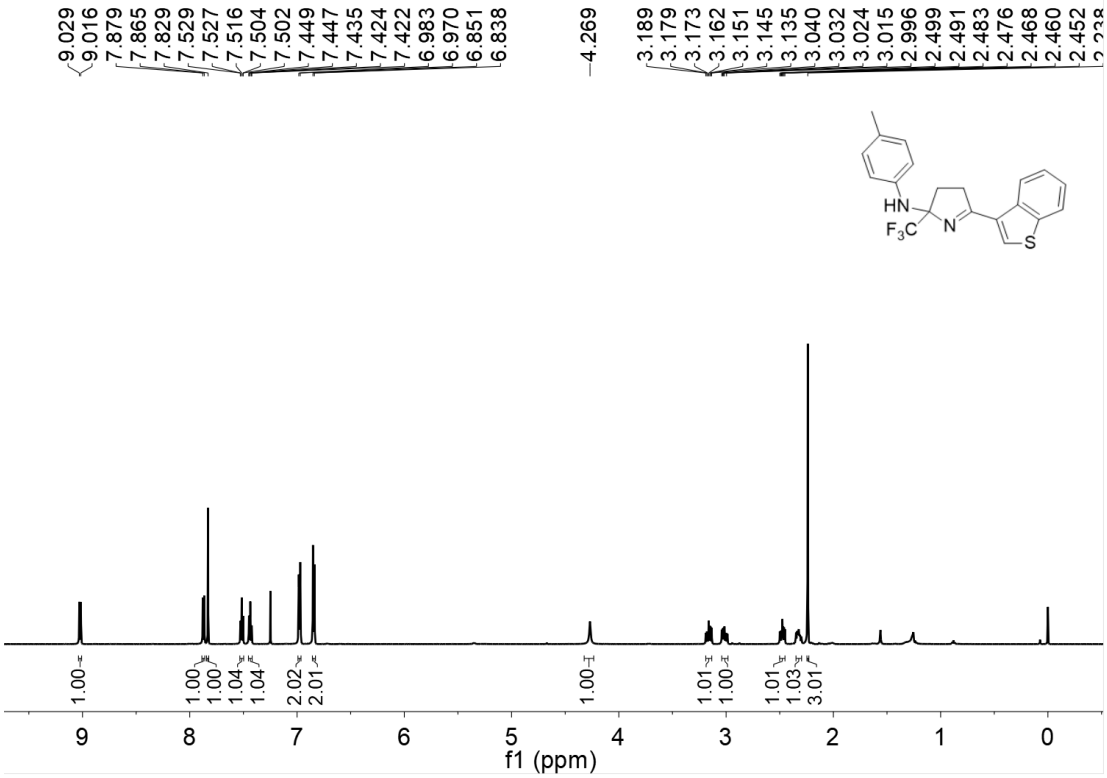


Figure 96. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3an**

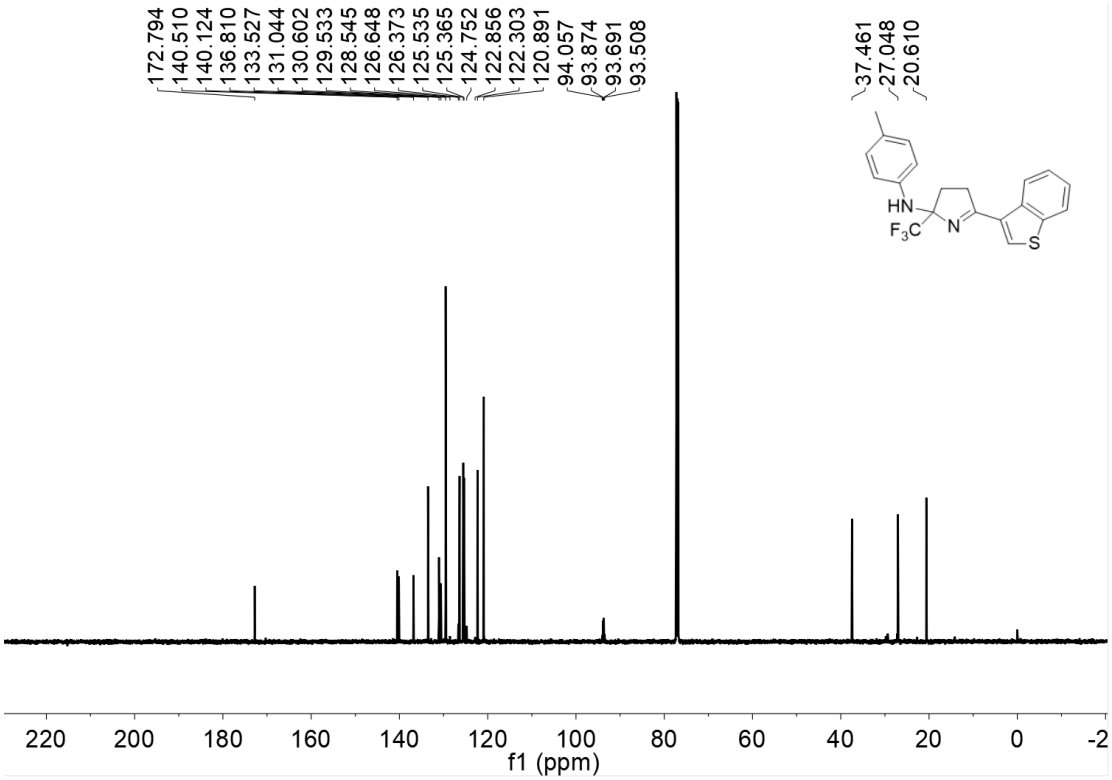


Figure 97. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3an**

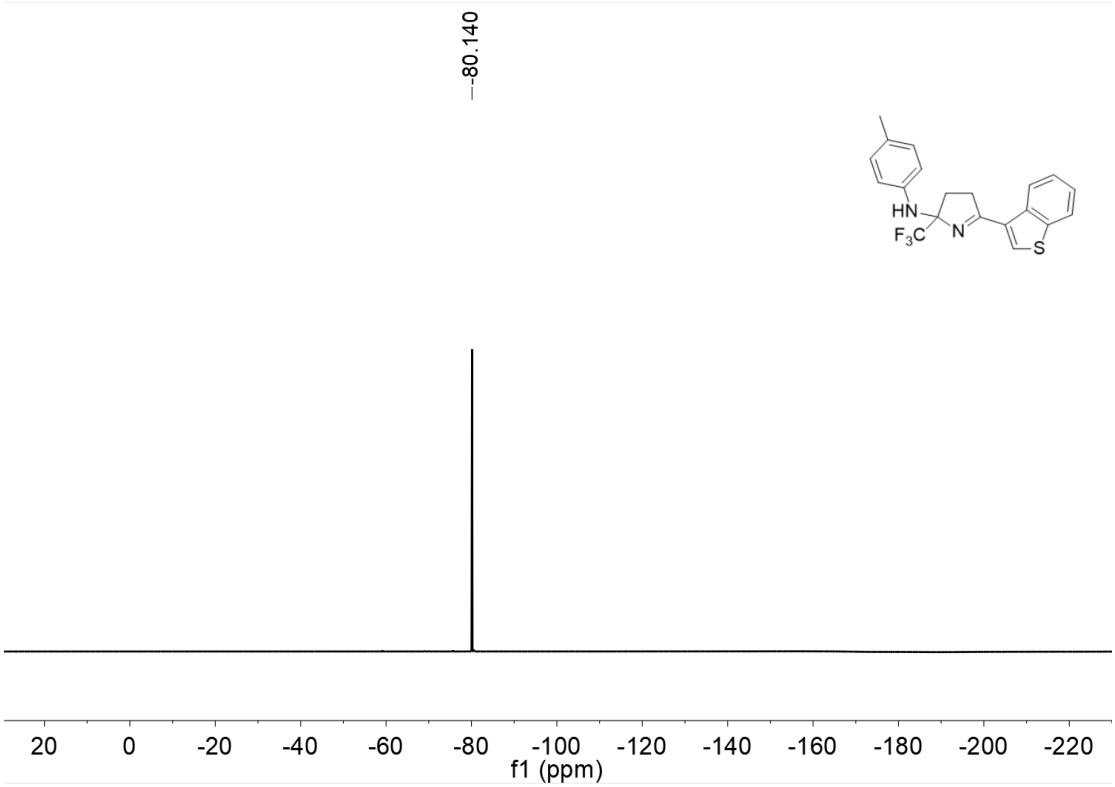


Figure 98. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **3an**

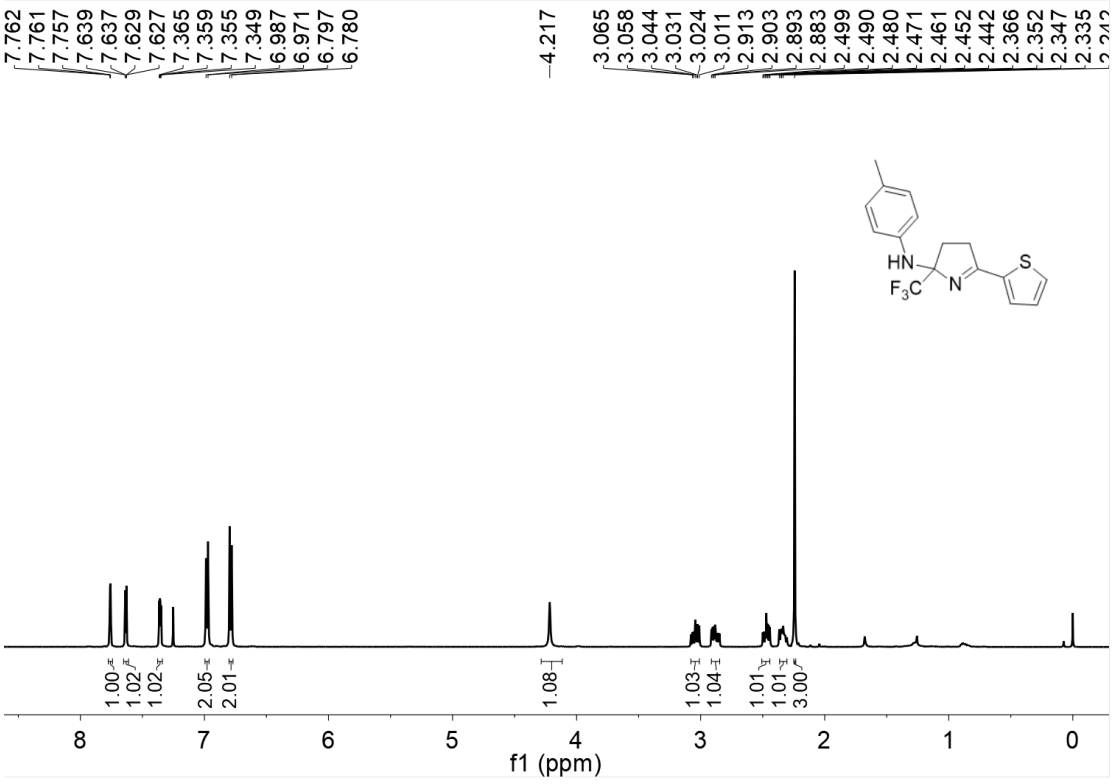


Figure 99. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3ao**

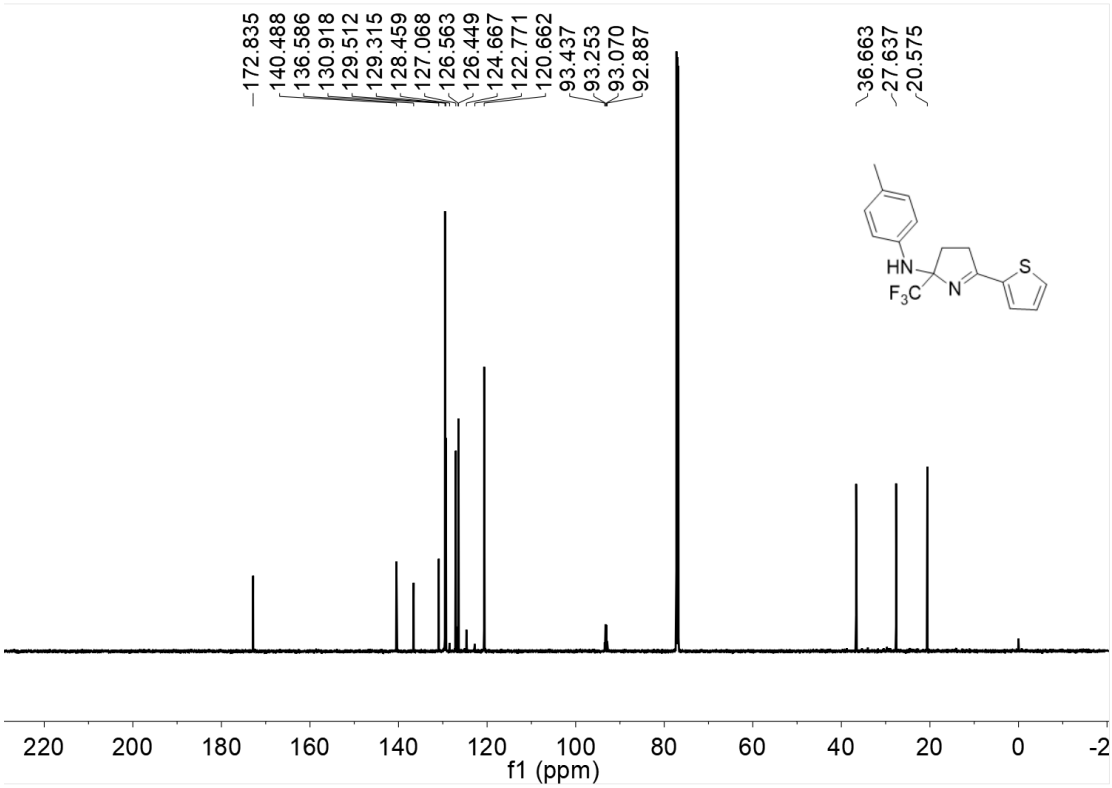


Figure 100. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ao**

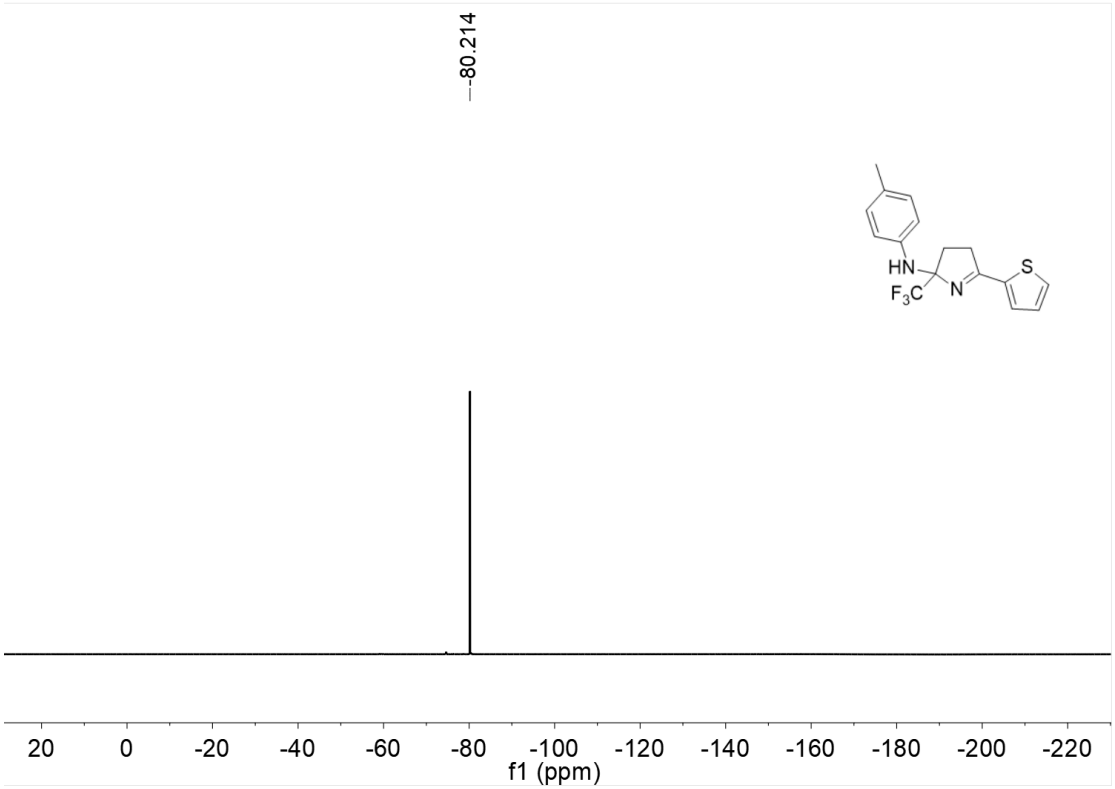


Figure 101. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **3ao**

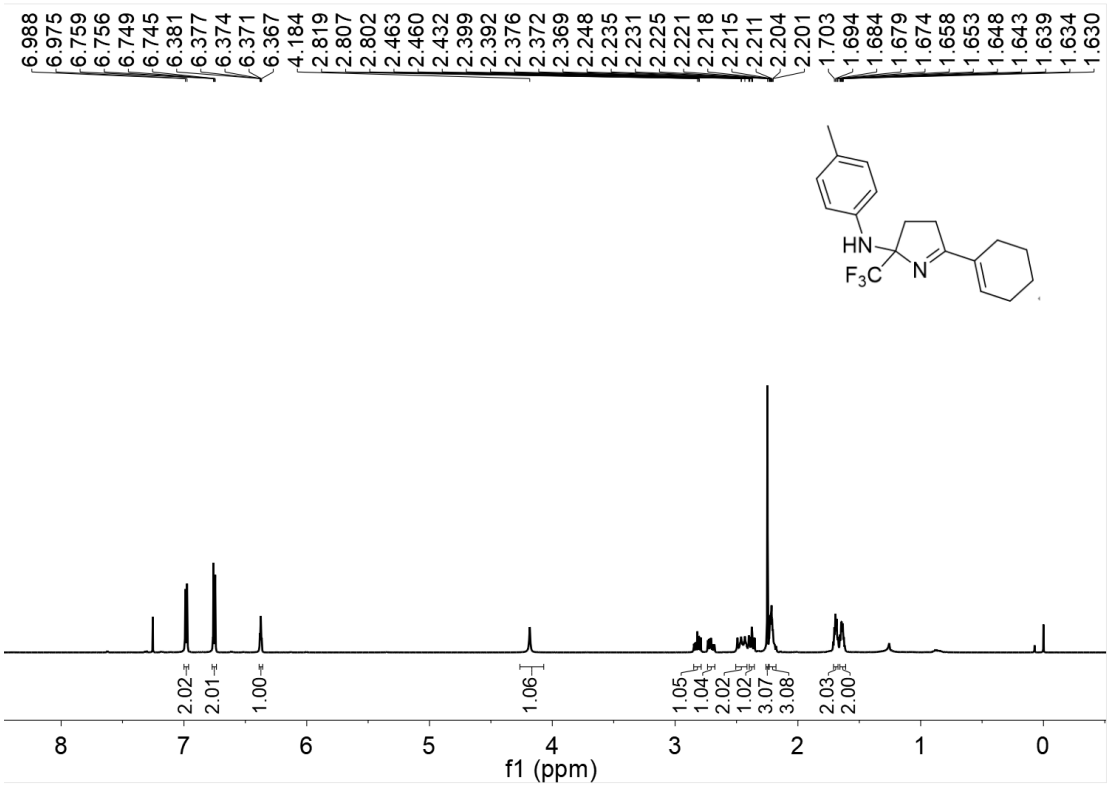


Figure 102. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3ap**

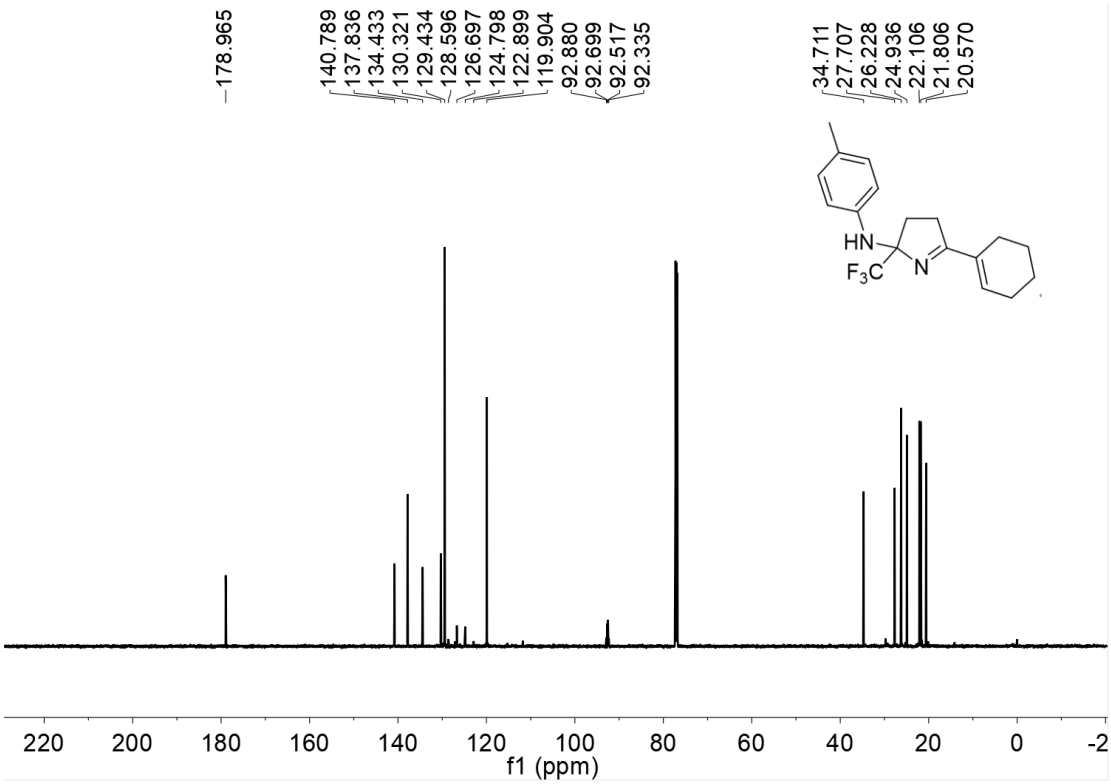


Figure 103. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ap**

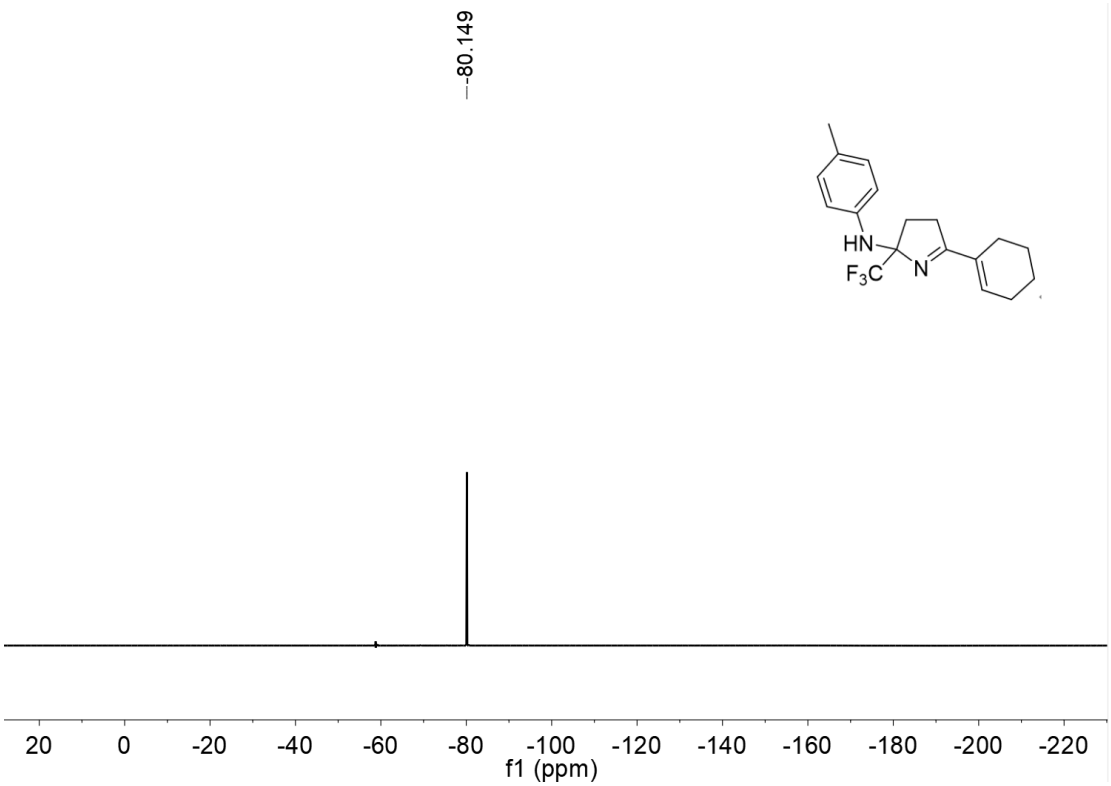


Figure 104. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **3ap**

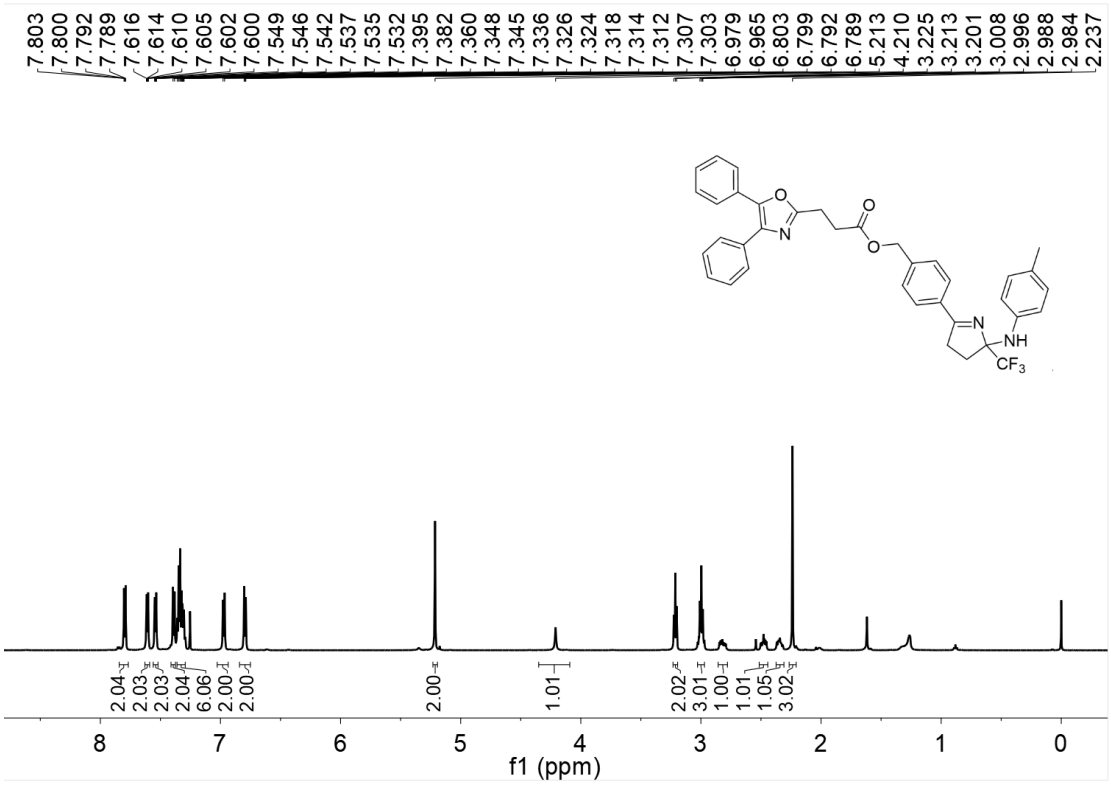


Figure 105. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3aq**

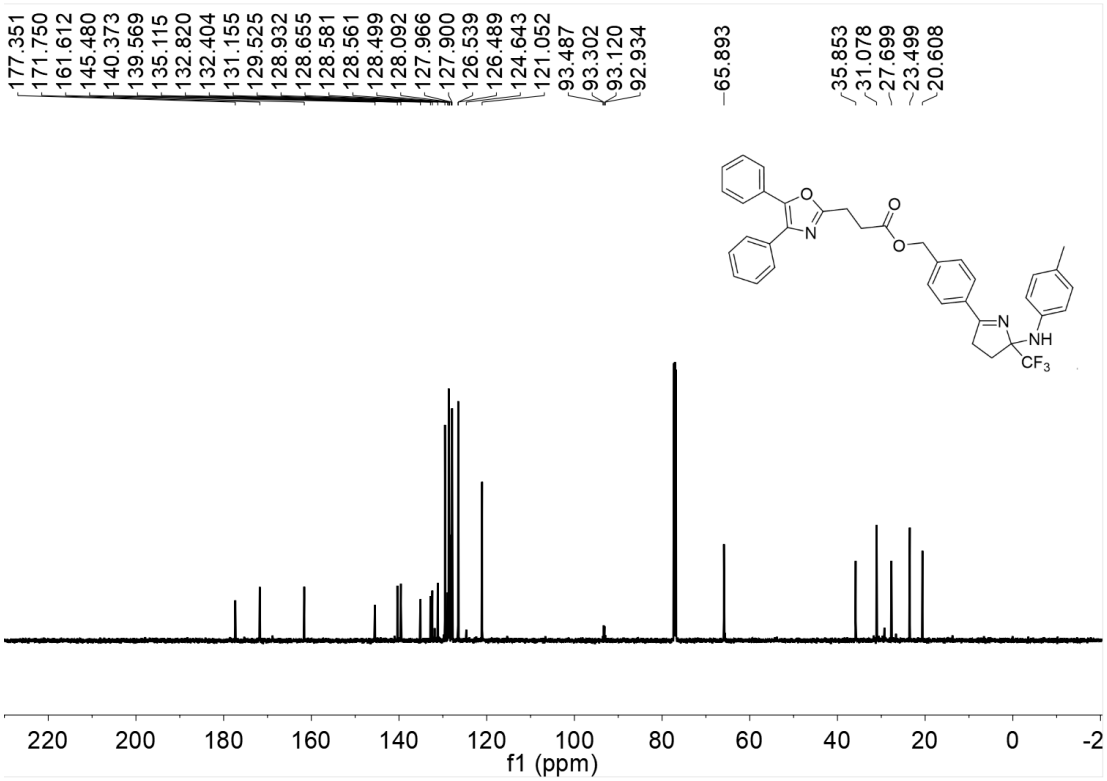


Figure 106. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3aq**

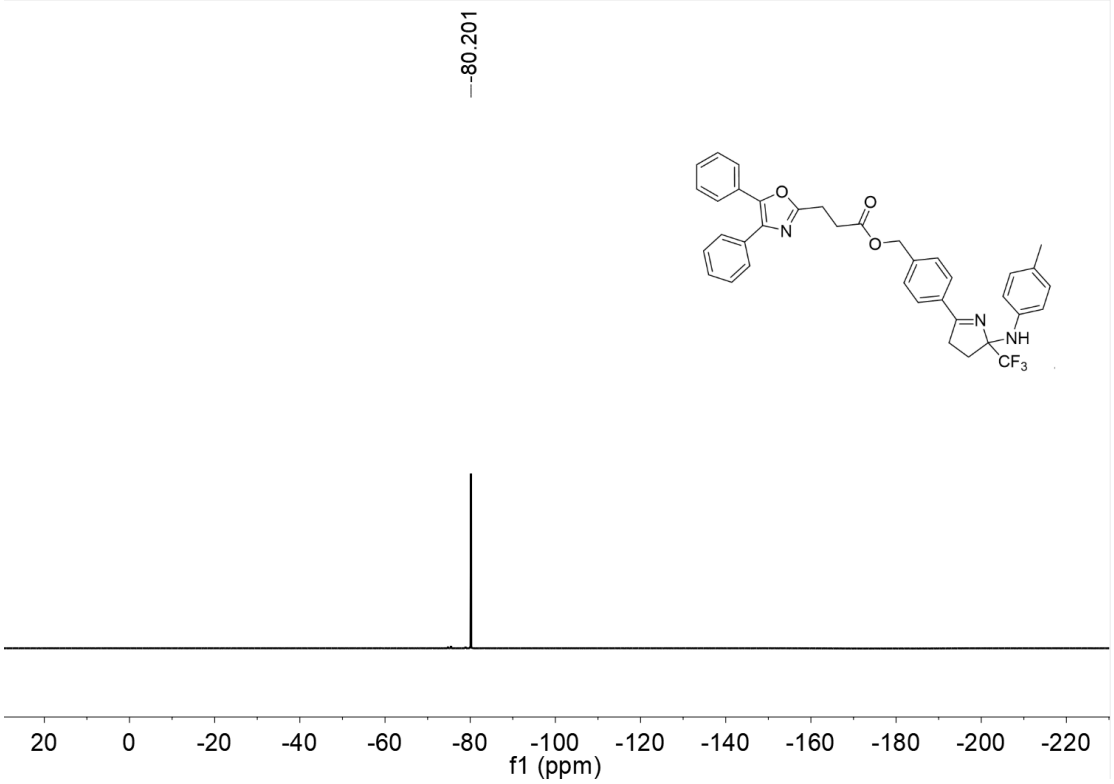


Figure 107. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **3aq**

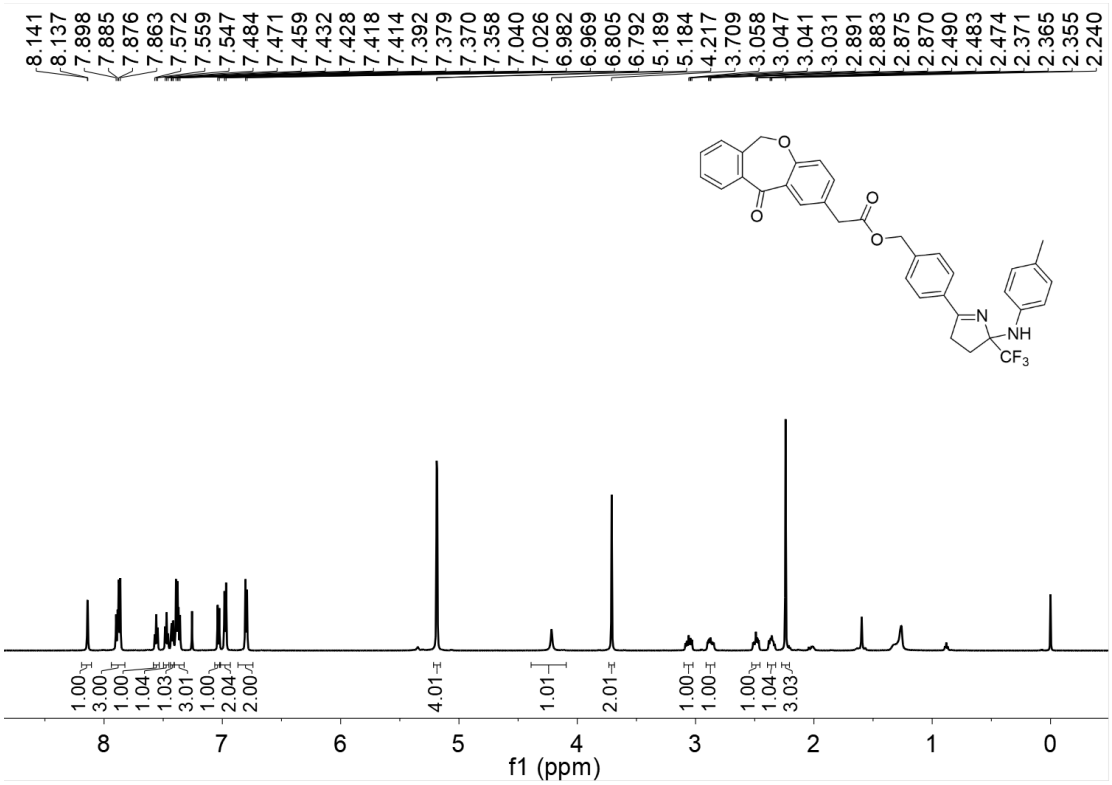


Figure 108. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3ar**

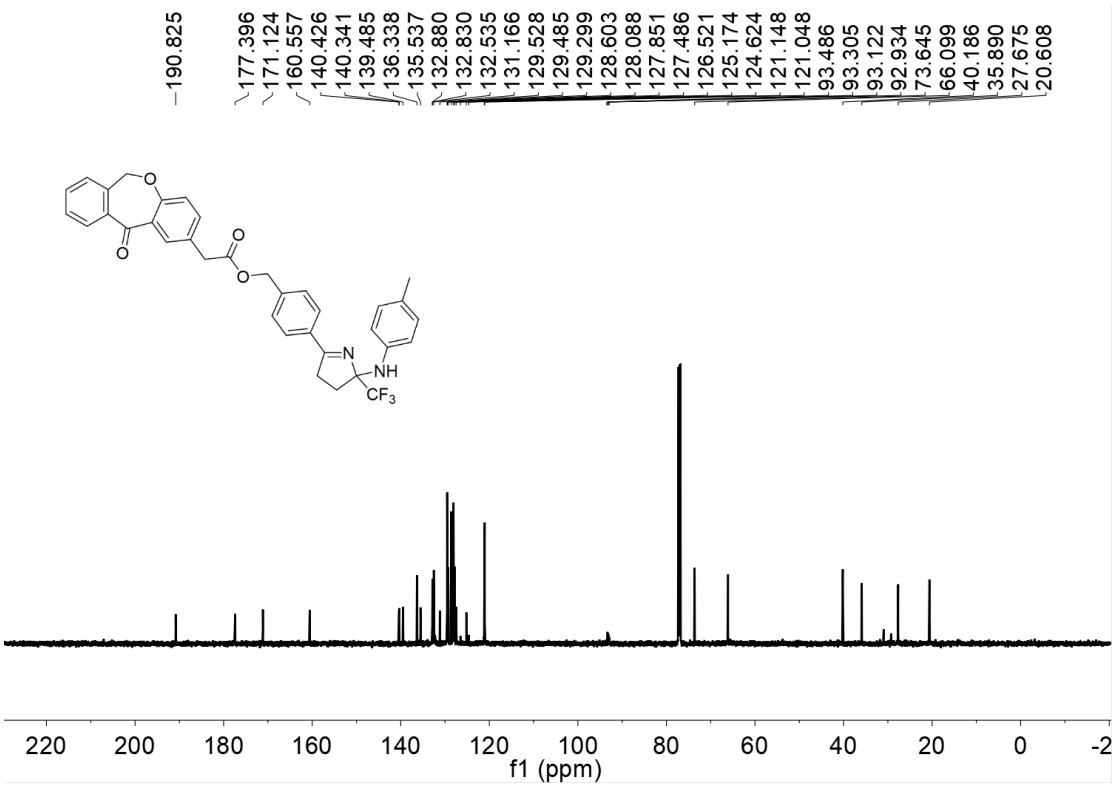


Figure 109. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ar**

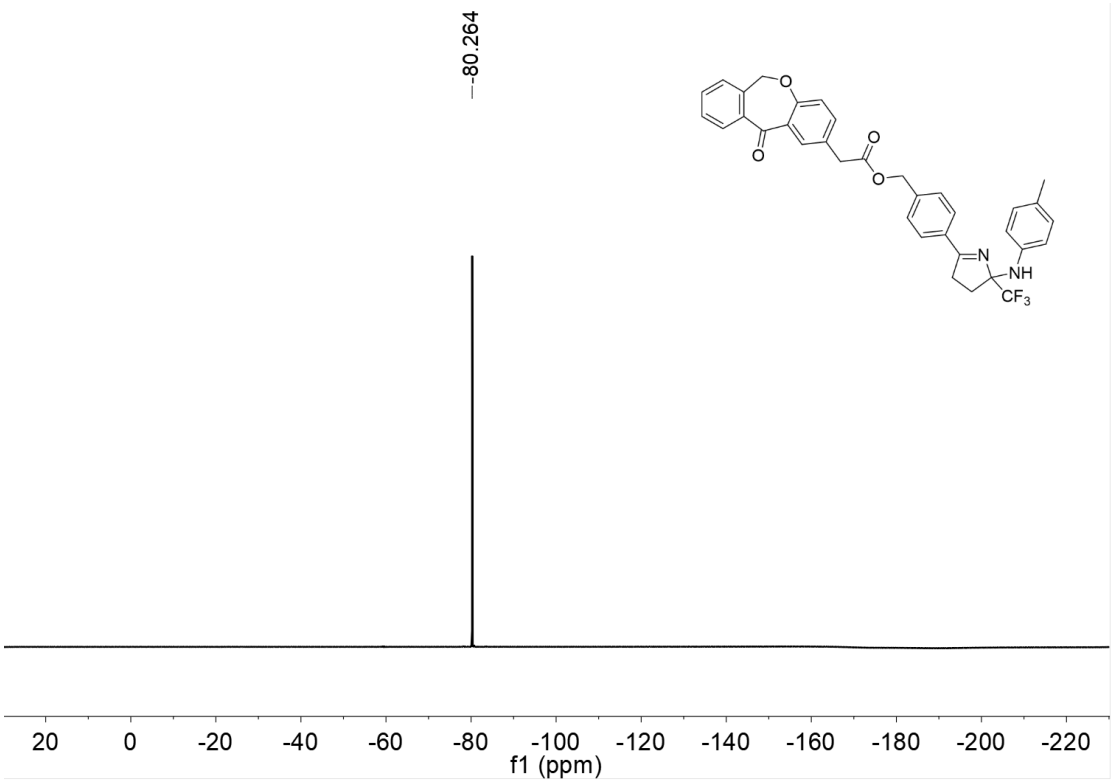


Figure 110. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **3ar**

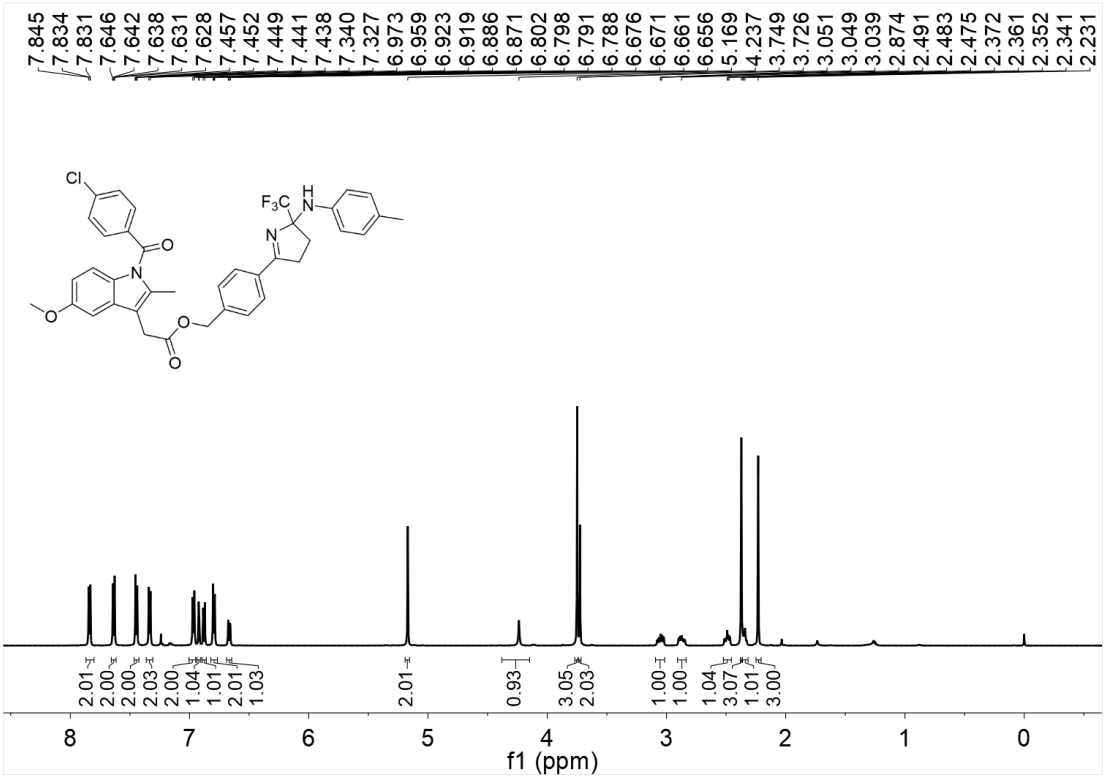


Figure 111. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3as**

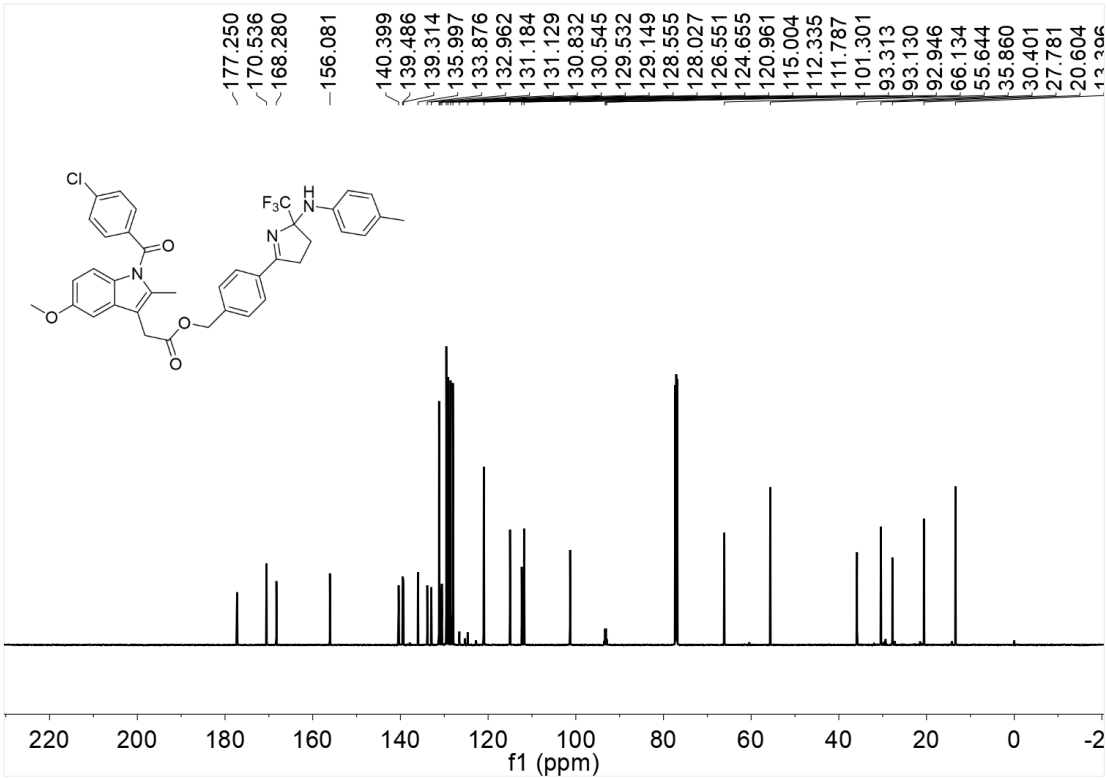


Figure 112. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3as**

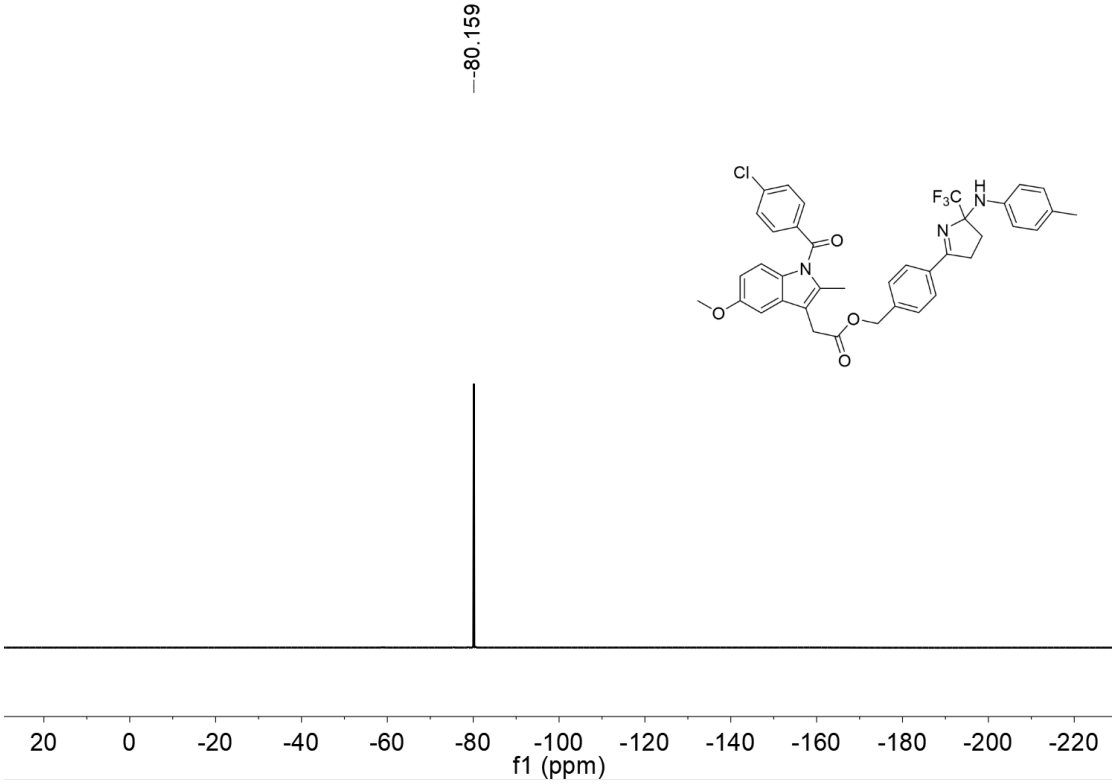


Figure 113. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **3as**

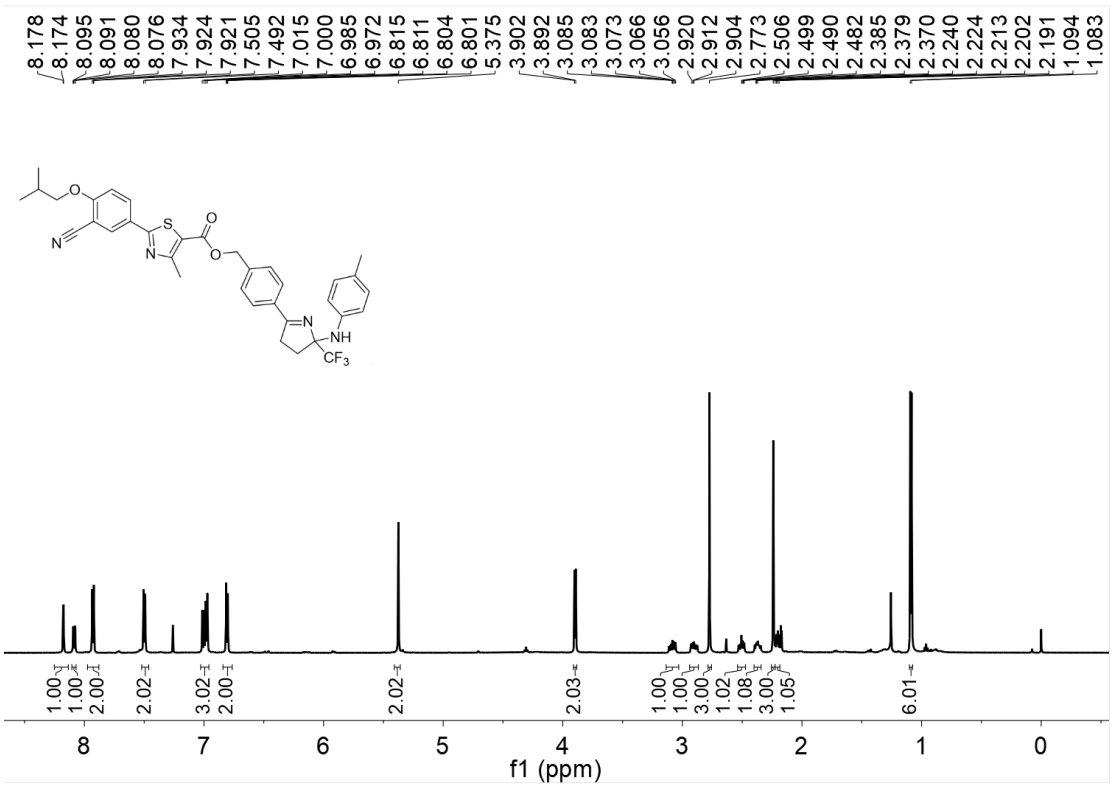


Figure 114. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3at**

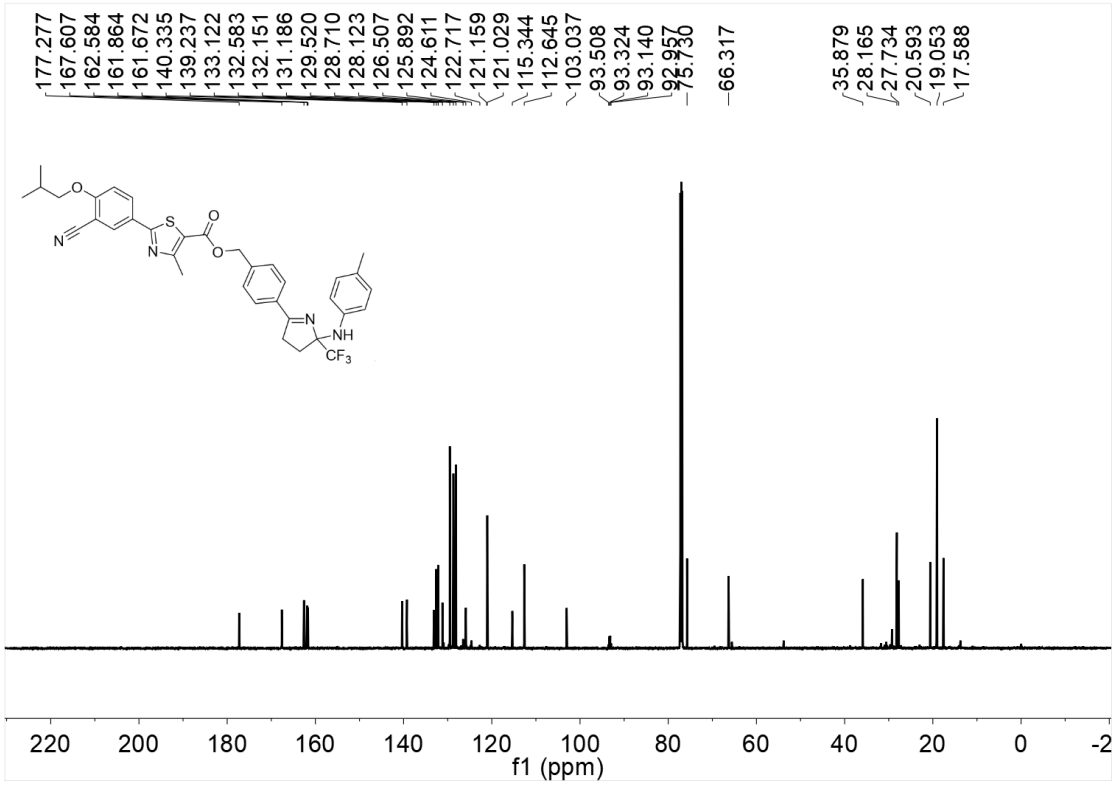


Figure 115. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3at**

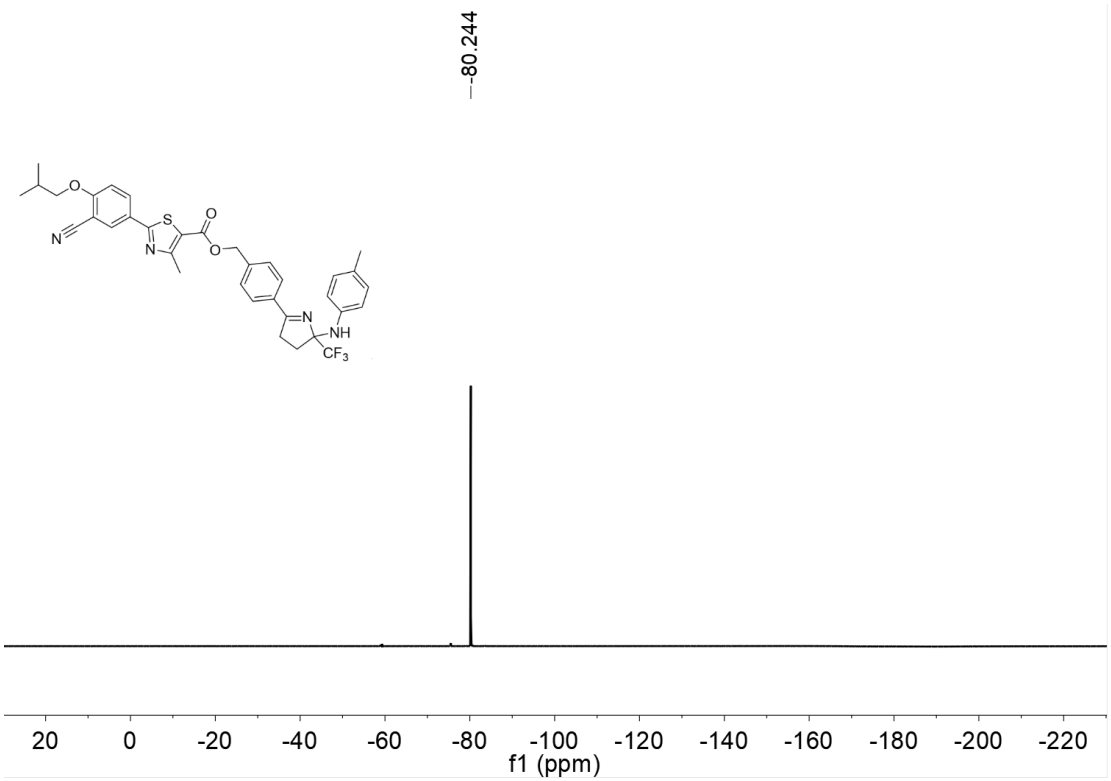


Figure 116. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **3at**

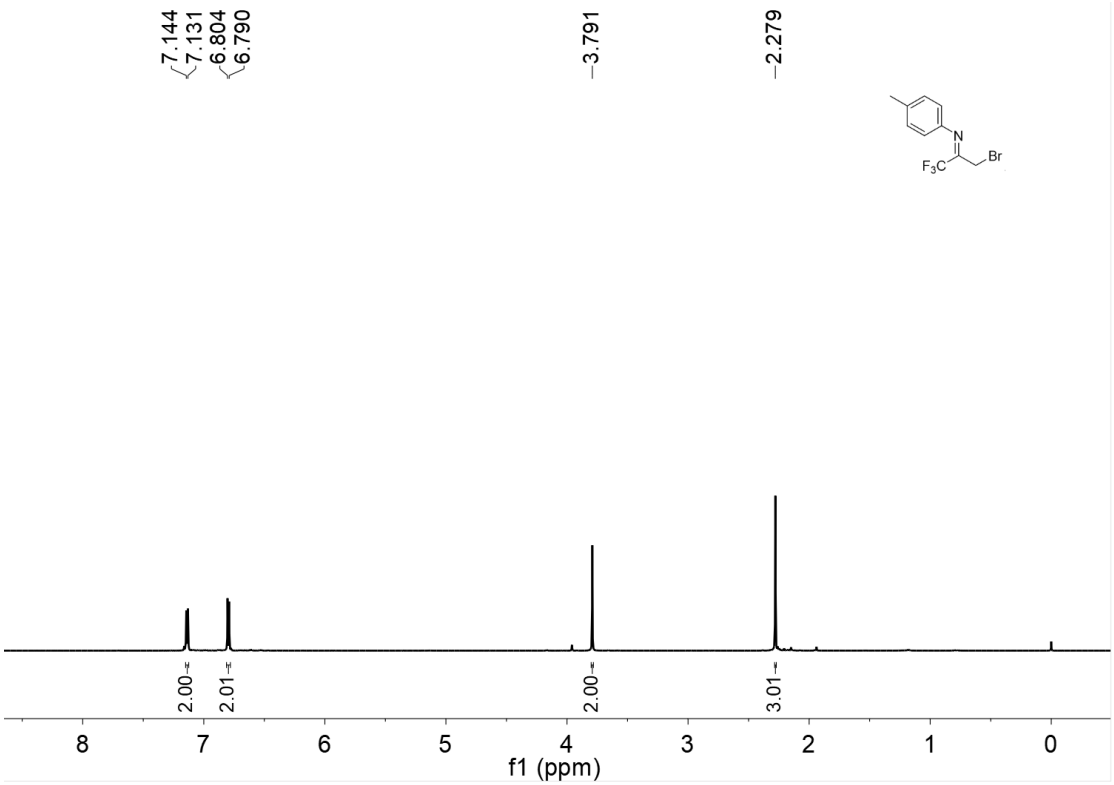


Figure 117. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **6a**

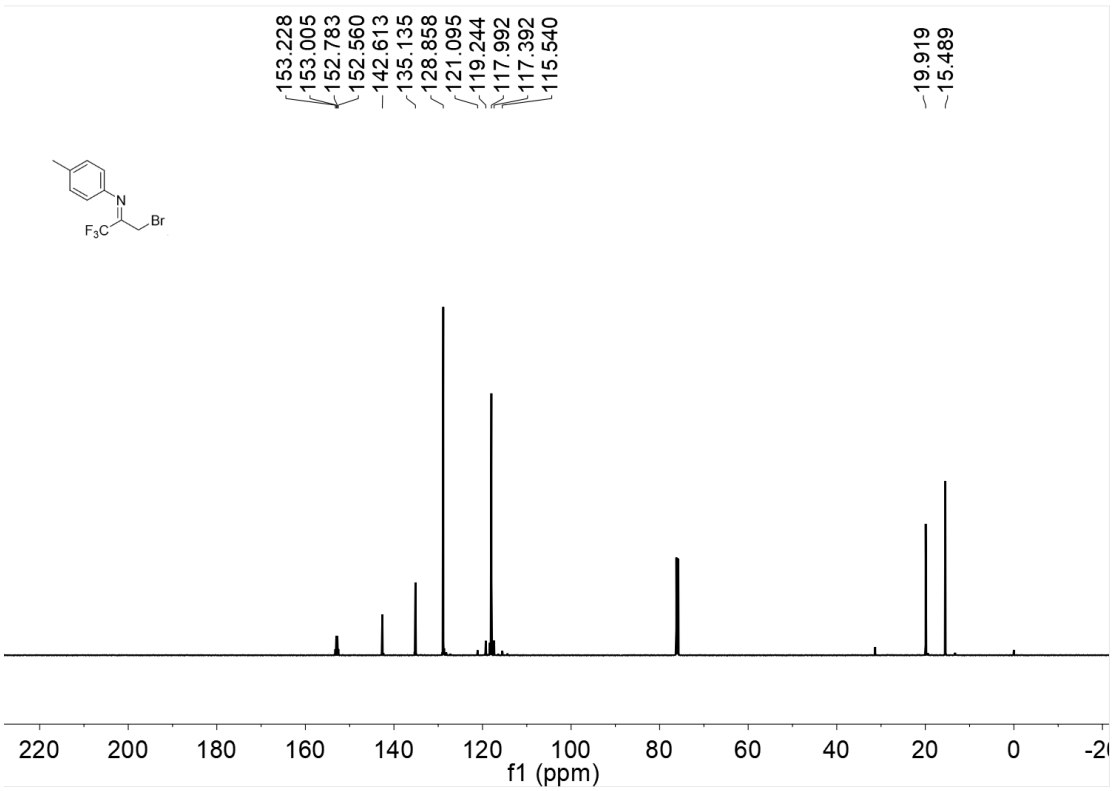


Figure 118. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **6a**

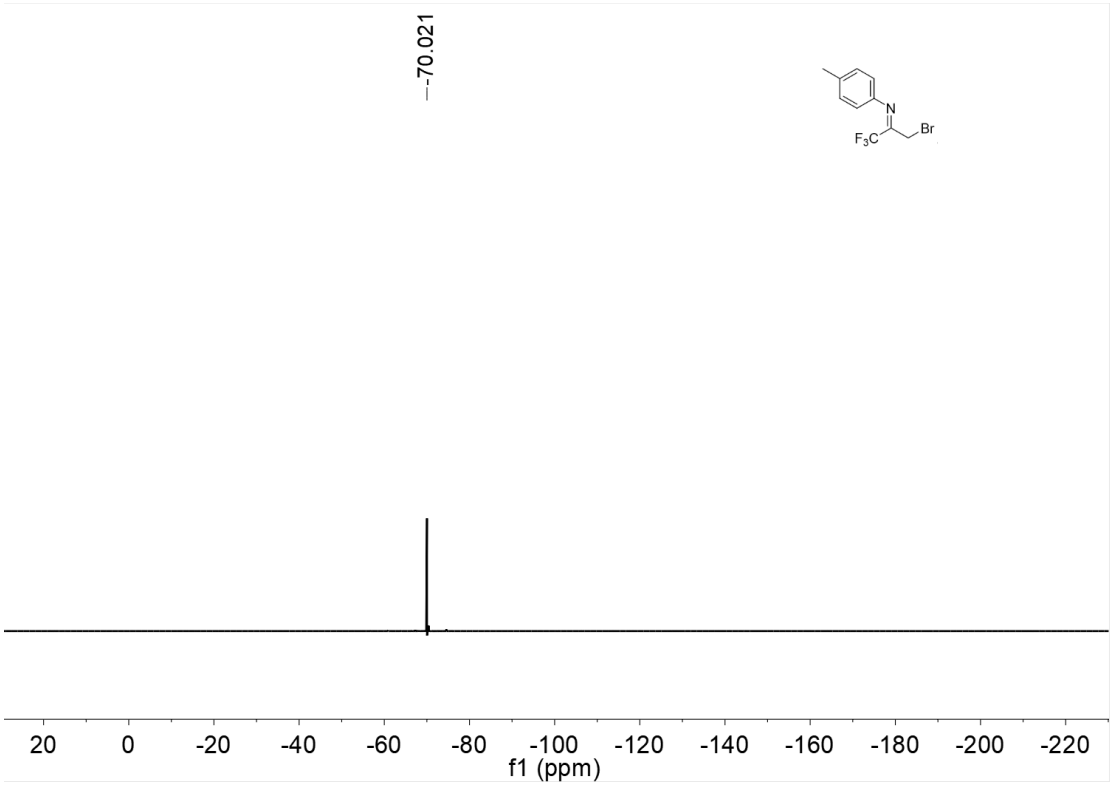


Figure 119. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **6a**

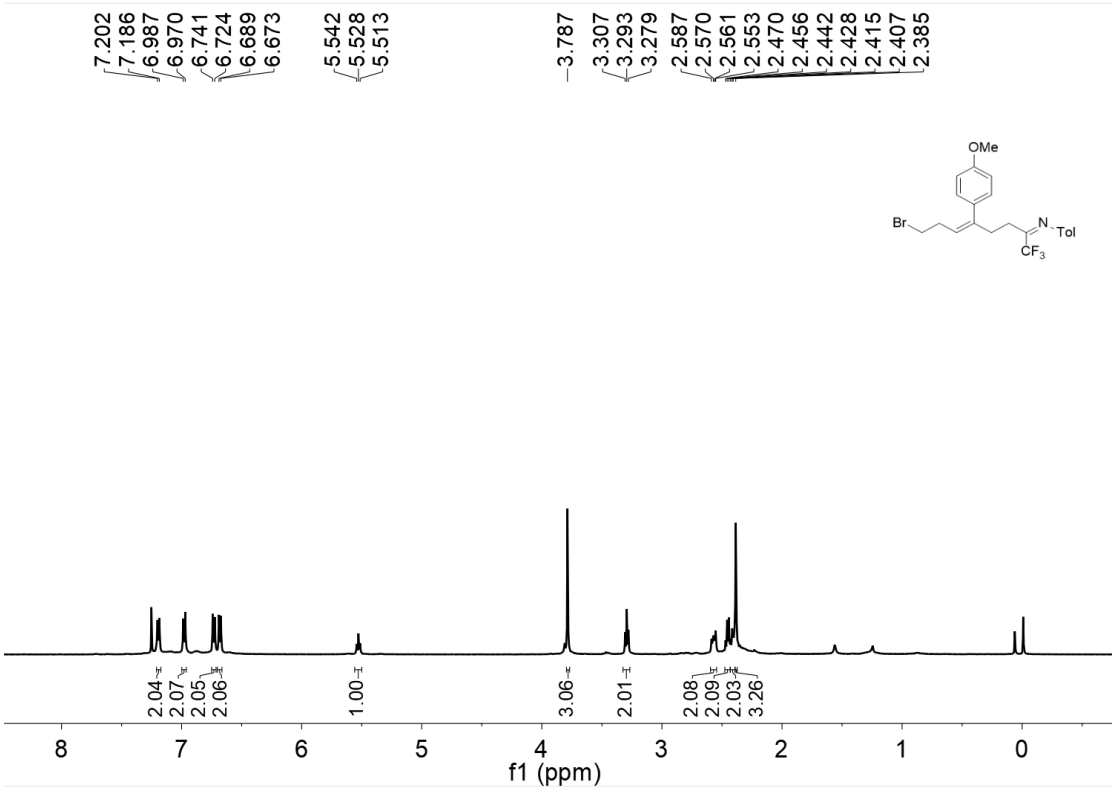


Figure 120. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **5**

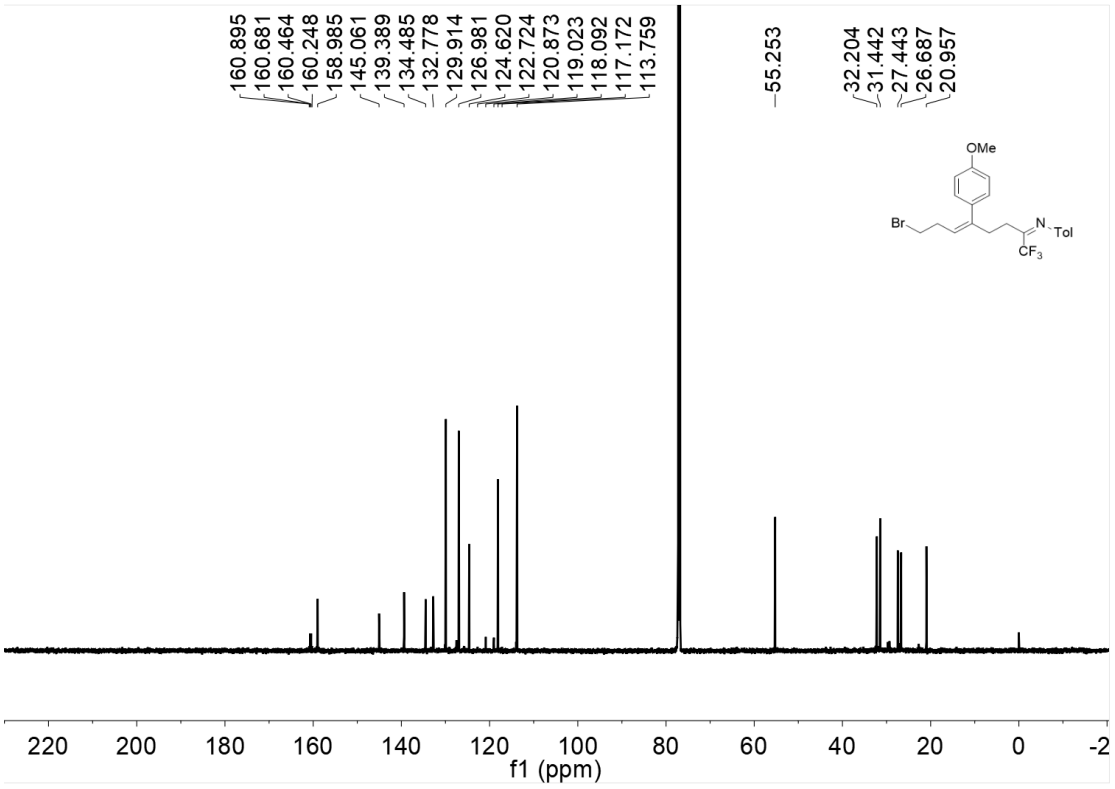


Figure 121. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **5**

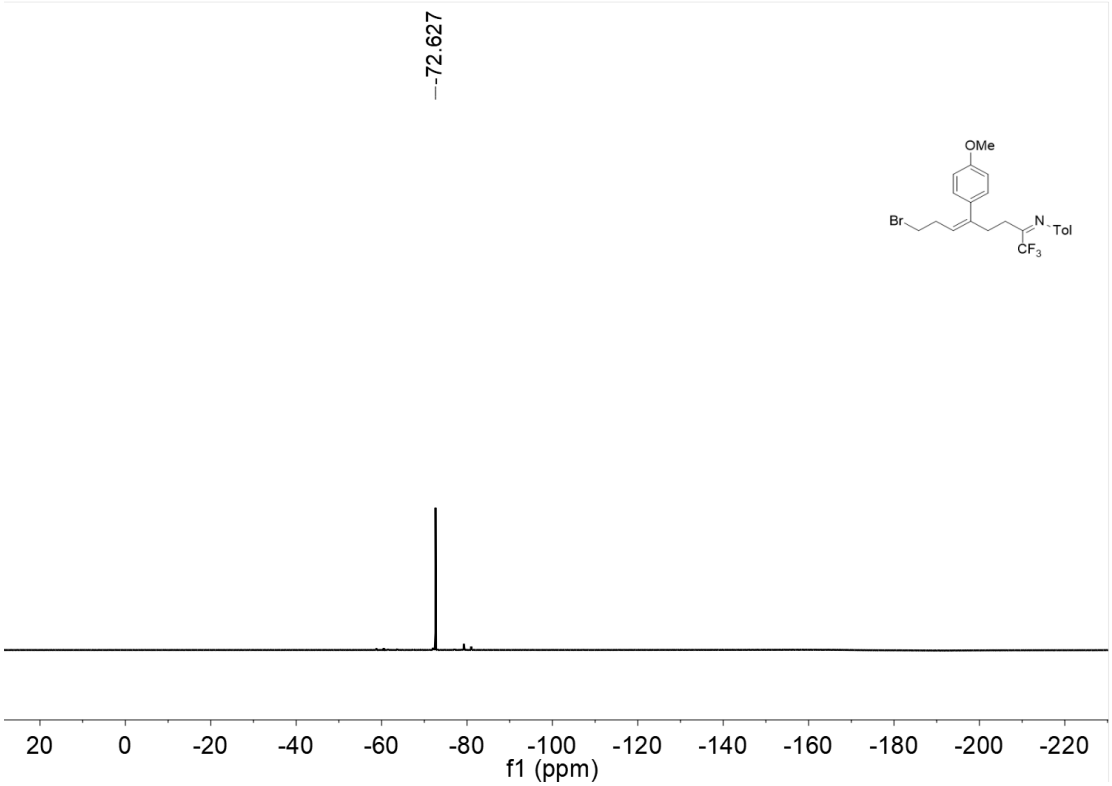


Figure 122. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **5**

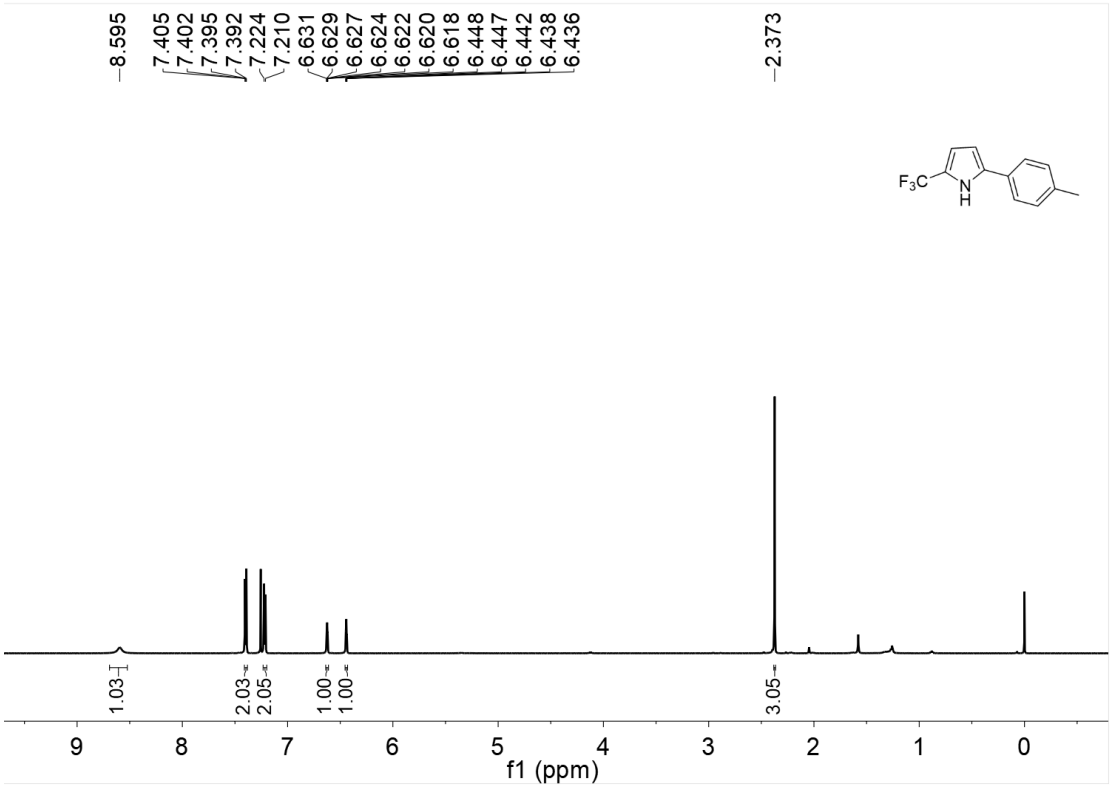


Figure 123. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **7**

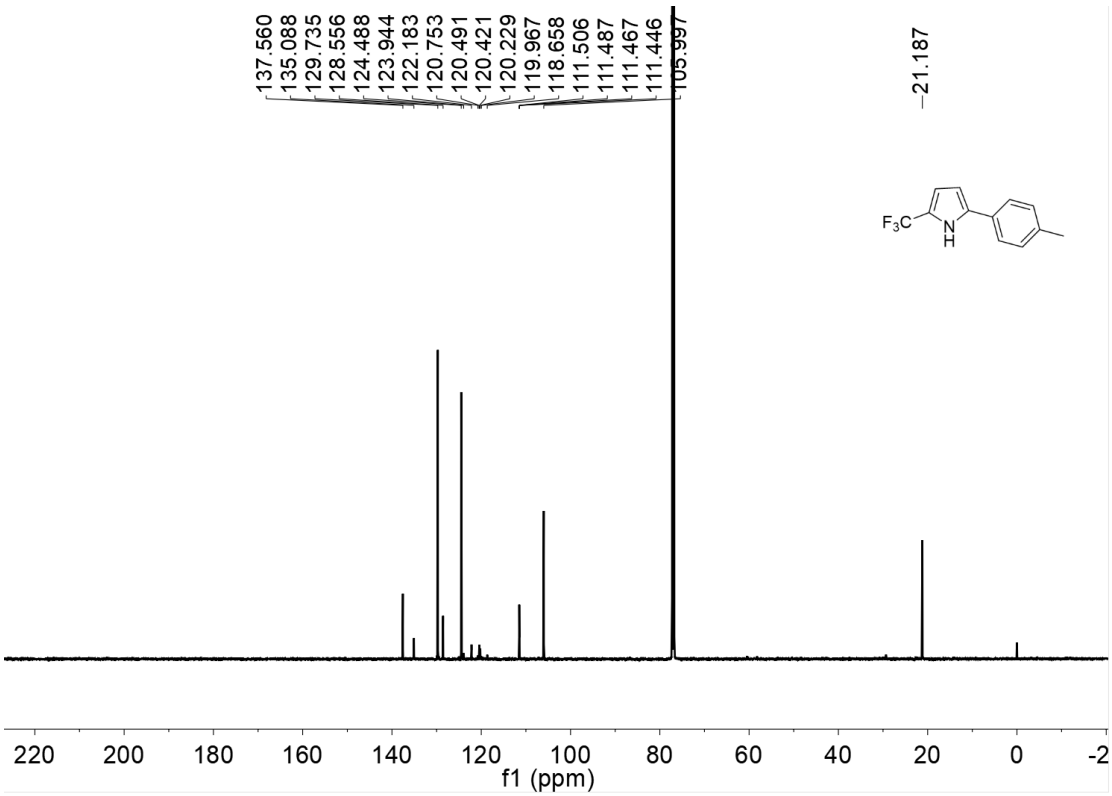


Figure 124. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **7**

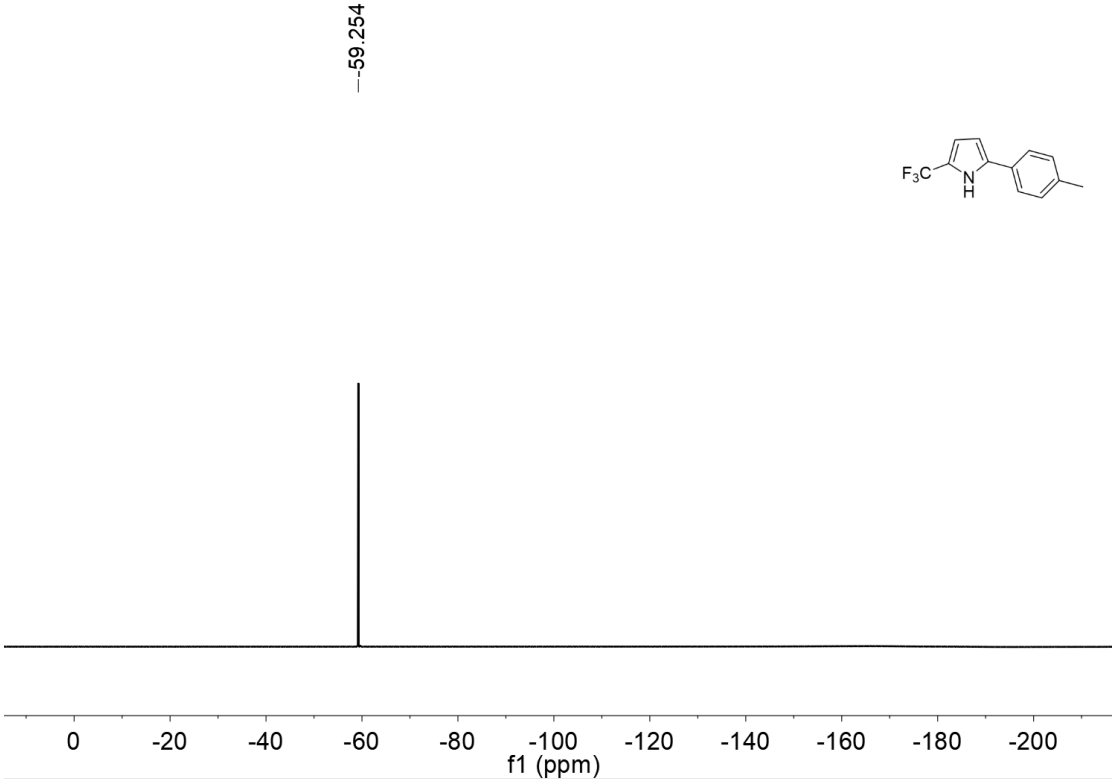


Figure 125. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **7**