Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information (SI)

Manganese-Mediated Reductive *N*,*N*-Dialkylation of Nitroarenes: A dramatic NiI_2 effect

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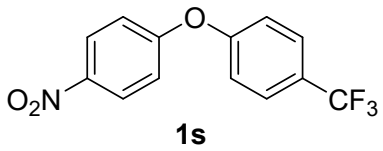
1. General Information

Unless otherwise specified, all reagents are commercially obtained. All nitro compounds are purchased from Adamas, Energy Chemical, Accela or 3A Company. Manganese was purchased from Alfa Aesar. Nickel iodide was purchased from 3A. Nickel nano powder (with 50 nm diameter) was purchased from Adamas. Nickel nano powder (with 1 μm diameter) was purchased from 3A. NMP was purchased from Aladdin and activated with 3Å molecular sieve before use. All reactions were carried out in Ar atmosphere. Thin layer chromatography (TLC) was carried out on 0.2-0.3 mm (Shanxi nuotai Biotechnology Co., Ltd.) silica gel plate. Silica gel (300-400 mesh) (Shanxi nuotai Biotechnology Co., Ltd.) was used for column chromatography separation. Fourier transform infrared spectrometer (vertex 70) for infrared characterization; Reaction monitoring was performed by GC-MS-QP2010 SE; High resolution mass spectrometry was performed on waters synapt G2 Si Q-TOF mass spectrometer.; ^{1}H, ^{13}C and ^{19}F were recorded by nuclear magnetic resonance spectrometer (brukeravance III 300MHz) and (AVANCE III HD 400MHz) (^{1}H NMR), 101 MHz (^{13}C NMR) and 376 MHz (^{19}F NMR). 1H chemical shifts were given in parts per million (ppm), $CDCl_3$ (^{1}H NMR is 7.26 ppm, ^{13}C NMR is 77.0 ppm) was used as reference, and ^{1}H data were reported as follows: chemical shifts (ppm) Multiplicity (s = single line state, d = double line state, t = three line state, q = four line state, dd = double line state of double line state, m = double line state, bs = wide single line state), coupling constant (Hz) and integral.

2. Synthesis of substrates 1s and 10.

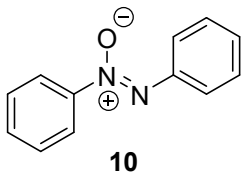
Synthesis of 1-Nitro-4-(4-(trifluoromethoxy)phenoxy)benzene (1s)[1]



1s

Phenol (1.62 g, 10 mmol), 1-fluoro-4-nitrobenzene (705.5 mg, 5 mmol), and Na_2CO_3 (10 mmol, 1.05 g), were suspended in DMF (5 mL) and heated. The reaction was followed by TLC, and after completion (approximately 24 h), the desired product was extracted with dichloromethane. The crude product was purified by flash chromatography, petroleum ether/ethyl acetate (100/1, v/v) as eluent to give compound **1s** (yellow liquid, 1.17 g, 4.1 mmol, 82% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 8.26 (d, *J* = 9.0 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 9.0 Hz, 2H).

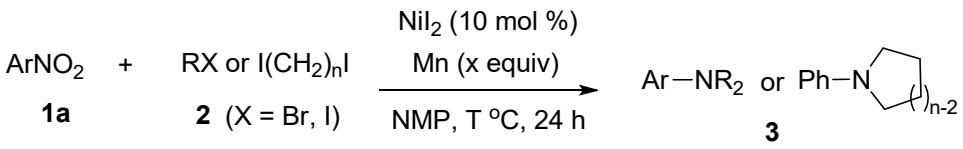
Synthesis of 1,2-diphenyldiazene 1-oxide (10)[2]



10

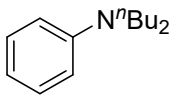
Selenium dioxide (1.0 mmol, 0.2 equiv.) and arylamine (5.0 mmol, 1.0 equiv.) were treated with 30% hydrogen peroxide (5 mL) and the mixture was stirred at room temperature for 3 h. Afterwards, the aqueous reaction mixture was extracted with ethyl acetate (3 × 5 mL). The combined organic phases were washed with brine (10 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The crude material was purified by flash chromatography petroleum ether/ethyl acetate (10/1, v/v) as eluent to give compound **10** (yellow liquid, 0.32 g, 1.6 mmol, 64% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 8.32 (d, *J* = 8.1 Hz, 2H), 8.17 (d, *J* = 7.5 Hz, 2H), 7.57–7.47 (m, 5H), 7.40 (t, *J* = 7.2 Hz, 1H).

3. General Procedure for the Synthesis of *N, N*-Dialkyl Anilines



Under an argon atmosphere, NiI_2, Mn, NMP, **1a** and **2** were sequentially added to a 25 mL reaction tube, stirred at T °C for 24 hours, and checked by TLC. After the reaction was complete, a small amount of water (3 mL) was added and ethyl acetate (3 × 5 mL) was used for the extraction; the organic phases were combined, dried over anhydrous sodium sulfate, concentrated in vacuum, and separated by column chromatography to obtain **3**.

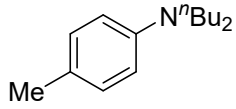
***N,N*-Dibutylbenzenamine (3a)[3]**



3a

Synthesized according to General Procedure using nitrobenzene (51 μL, 0.50 mmol, 1 eq), *n*-Bu-I (227 μL, 2.0 mmol, 4 eq), NiI_2 (15.6 mg, 0.05 mmol, 10 mol%), Mn (96.2 mg, 1.75 mmol, 3.5 eq) and NMP (1.0 mL) at 120 °C for 24 hours. The crude products were purified by column chromatography with petroleum ether/ethyl acetate (100/1, v/v) as eluent to give compound **3a** (yellow liquid, 85.5 mg, 0.416 mmol, 83% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 7.20 (t, J = 7.2 Hz, 2H), 6.65–6.59 (m, 3H), 3.25 (t, J = 7.5 Hz, 4H), 1.61–1.51 (m, 4H), 1.41–1.31 (dt, J = 14.9, 7.3 Hz, 4H), 0.95 (t, J = 7.2 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 148.2, 129.1, 115.1, 111.7, 50.7, 29.4, 20.4, 14.0.

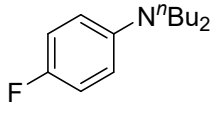
***N, N*-Dibutyl-4-methylbenzenamine (3b)[3]**



3b

Synthesized according to General Procedure using 1-methyl-4-nitrobenzene (68.6 mg, 0.50 mmol, 1 eq), *n*-Bu-I (227 μL, 2.0 mmol, 4 eq), NiI_2 (15.6 mg, 0.05 mmol, 10 mol%), Mn (96.2 mg, 1.75 mmol, 3.5 eq) and NMP (1.0 mL) at 120 °C for 24 hours. The crude products were purified by column chromatography with petroleum ether/ethyl acetate (100/1, v/v) as eluent to give compound **3b** (yellow liquid, 77.0 mg, 0.351 mmol, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.01 (d, J = 8.4 Hz, 2H), 6.58 (d, J = 8.8 Hz, 2H), 3.22 (t, J = 7.6 Hz, 4H), 2.23 (s, 3H), 1.58–1.50 (m, 4H), 1.38–1.29 (m, 4H), 0.94 (t, J = 7.2 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 146.2, 129.7, 124.3, 112.2, 51.0, 29.4, 20.4, 20.1, 14.0.

***N, N*-Dibutyl-4-fluorobenzenamine (3c)[3]**

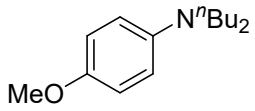


3c

Synthesized according to General Procedure using 1-fluoro-4-nitrobenzene (70.7 mg, 0.50 mmol, 1 eq), *n*-Bu-I (227 μL, 2.0 mmol, 4 eq), NiI_2 (15.6 mg, 0.05 mmol, 10 mol%), Mn (96.2 mg, 1.75 mmol, 3.5 eq) and NMP (1.0 mL) at 130 °C for 24 hours. The crude products were purified by column chromatography with petroleum ether/ethyl acetate (200/1, v/v) as eluent to give compound **3c** (yellow liquid, 78.5 mg, 0.350 mmol, 70% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 6.91 (t, J = 9.0Hz, 2H), 6.57 (dd, J = 9.2, 4.3 Hz, 2H), 3.21 (t, J = 7.5 Hz , 4H), 1.58–1.48 (m, 4H), 1.40–1.26 (m, 4H), 0.95 (t, J = 7.2 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 154.8 (d, $^1J_{C\text{-}F}$ = 234.3 Hz), 145.1, 115.4 (d, $^2J_{C\text{-}F}$ = 22.2 Hz), 113.1 (d, $^3J_{C\text{-}F}$ = 8.0 Hz), 51.4, 29.4, 20.4,

14.0; ^{19}F NMR (376 MHz, $CDCl_3$, ppm) δ -130.84 (s, 1F).

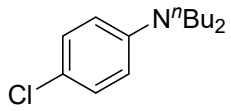
_N,N_-Dibutyl-4-methoxybenzenamine (3d)[4]



3d

Synthesized according to General Procedure using 1-methoxy-4-nitrobenzene (76.6 mg, 0.50 mmol, 1 eq), *n*-Bu-I (227 μL, 2.0 mmol, 4 eq), NiI_2 (15.6 mg, 0.05 mmol, 10 mol%), Mn (96.2 mg, 1.75 mmol, 3.5 eq) and NMP (1.0 mL) at 120 ℃ for 24 hours. The crude products were purified by column chromatography with petroleum ether/ethyl acetate (50/1, v/v) as eluent to give compound **3d** (yellow liquid, 55.9 mg, 0.237 mmol, 47% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 6.81 (d, *J* = 9.2 Hz, 2H), 6.65 (d, *J* = 8.8 Hz, 2H), 3.75 (s, 3H), 3.17 (t, *J* = 7.6 Hz 4H), 1.54–1.32 (m, 4H), 1.30–1.28 (m, 4H), 0.93 (t, *J* = 7.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 151.0, 143.4, 114.8, 114.4, 55.9, 51.7, 29.5, 20.4, 14.0.

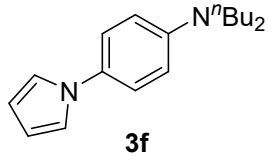
_N,N_-Dibutyl-4-chlorobenzenamine (3e)[5]



3e

Synthesized according to General Procedure using 1-chloro-4-nitrobenzene (78.8 mg, 0.50 mmol, 1 eq), *n*-Bu-I (227 μL, 2.0 mmol, 4 eq), NiI_2 (15.6 mg, 0.05 mmol, 10 mol%), Mn (109.9 mg, 2.0 mmol, 4 eq) and NMP (1.0 mL) at 120 ℃ for 24 hours. The crude products were purified by column chromatography with petroleum ether/ethyl acetate (200/1, v/v) as eluent to give compound **3e** (yellow liquid, 36.9 mg, 0.153 mmol, 31% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.11 (d, *J* = 9.3 Hz, 2H), 6.53 (d, *J* = 9.0 Hz, 2H), 3.22 (t, *J* = 7.5 Hz, 4H), 1.58–1.39 (m, 4H), 1.40–1.25 (m, 4H), 0.94 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 146.8, 128.9, 119.8, 112.9, 50.9, 29.3, 20.3, 14.0.

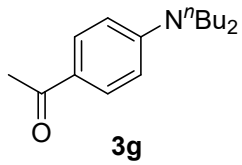
_N,N_-Dibutyl-4-(1H-pyrrol-1-yl)aniline (3f)



3f

Synthesized according to General Procedure using 1-(4-nitrophenyl)-1H-pyrrole (94.1 mg, 0.50 mmol, 1 eq), *n*-Bu-I (227 μL, 2.0 mmol, 4 eq), NiI_2 (15.6 mg, 0.05 mmol, 10 mol%), Mn (96.2 mg, 1.75 mmol, 3.5 eq) and NMP (1.0 mL) at 130 ℃ for 24 hours. The crude products were purified by column chromatography with petroleum ether/ethyl acetate (200/1, v/v) as eluent to give compound **3f** (brown liquid, 81.3 mg, 0.301 mmol, 60% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 7.21 (d, 2H), 6.95 (t, *J* = 2.0 Hz, 2H), 6.64 (d, *J* = 9.0 Hz, 2H), 6.28 (t, *J* = 2.0 Hz, 2H), 3.26 (t, *J* = 7.4 Hz, 4H), 1.62–1.52 (m, 4H), 1.42–1.29 (m, 4H), 0.96 (t, *J* = 7.3 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 146.5, 130.0, 122.5, 119.7, 112.0, 109.0, 50.9, 29.3, 20.3, 14.0; IR (neat, cm^{-1}) 3101, 3048, 2950, 2867, 1616, 1525, 1461, 1368, 1330, 1225; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{27}N_2$ 271.2174; Found 271.2169.

1-[4-(Dibutylamino)phenyl]ethenone (3g)[6]

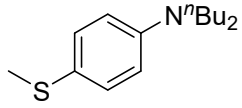


3g

Synthesized according to General Procedure using 1-(4-nitrophenyl)ethan-1-one (82.6 mg, 0.50 mmol, 1 eq), *n*-Bu-I (227 μL, 2.0 mmol, 4 eq), NiI_2 (15.6 mg, 0.05 mmol, 10 mol%), Mn (96.2 mg, 1.75 mmol, 3.5 eq) and NMP (1.0 mL) at 120 ℃ for 24 hours. The crude products were purified by column chromatography with petroleum ether/ethyl acetate (20/1, v/v) as eluent to give compound **3g** (colorless liquid, 48.0 mg, 0.194 mmol, 39% yield). ^{1}H NMR (400

MHz, $CDCl_3$, ppm) δ 7.83 (d, *J* = 9.2 Hz, 2H), 6.58 (d, *J* = 9.2 Hz, 2H), 3.32 (t, *J* = 7.6 Hz 4H), 2.48 (s, 3H), 1.63–1.55 (m, 4H), 1.41–1.32 (m, 4H), 0.96 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 195.9, 151.5, 130.7, 124.5, 110.1, 50.7, 29.2, 25.8, 20.2, 13.9.

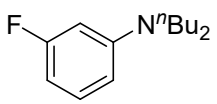
***N,N*-Dibutyl-4-(methylthio)aniline (3h)**



3h

Synthesized according to General Procedure using methyl(4-nitrophenyl)sulfane (84.6 mg, 0.50 mmol, 1 eq), *n*-Bu-I (227 μL, 2.0 mmol, 4 eq), NiI_2 (15.6 mg, 0.05 mmol, 10 mol%), Mn (96.2 mg, 1.75 mmol, 3.5 eq) and NMP (1.0 mL) at 120 ℃ for 24 hours. The crude products were purified by column chromatography with petroleum ether/ethyl acetate (50/1, v/v) as eluent to give compound **3h** (colorless liquid, 27.5 mg, 0.109 mmol, 22% yield). ^1H NMR (300 MHz, $CDCl_3$, ppm) δ 7.28 (d, *J* = 8.7 Hz, 2H), 6.61 (d, *J* = 8.7 Hz, 2H), 3.29 (t, *J* = 7.5 Hz 2H), 2.92 (s, 3H), 2.75 (t, *J* = 7.5 Hz 2H), 1.60–1.50 (m, 4H), 1.58–1.30 (m, 4H), 0.97–0.86 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 148.7, 134.1, 120.3, 112.3, 52.5, 38.3, 36.5, 31.6, 28.9, 21.9, 20.4, 14.0, 13.7; IR (neat, cm^{-1}) 3089, 2927, 2866, 1598, 1500, 1459, 1369, 1210, 812; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{26}NS$ 252.1786; Found 252.1769.

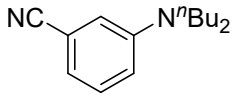
***N,N*-Dibutyl-3-fluoroaniline (3i)**



3i

Synthesized according to General Procedure using 1-fluoro-3-nitrobenzene (70.7 mg, 0.50 mmol, 1 eq), *n*-Bu-I (227 μL, 2.0 mmol, 4 eq), NiI_2 (15.6 mg, 0.05 mmol, 10 mol%), Mn (96.2 mg, 1.75 mmol, 3.5 eq) and NMP (1.0 mL) at 120 ℃ for 24 hours. The crude products were purified by column chromatography with petroleum ether/ethyl acetate (100/1, v/v) as eluent to give compound **3i** (colorless liquid, 54.1 mg, 0.241 mmol, 48% yield). ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.12 (q, *J* = 8.5, 7.9 Hz, 1H), 6.41–6.38 (m, 1H), 6.34–6.30 (m, 2H), 3.25 (t, *J* = 7.6 Hz 4H), 1.62–1.54 (m, 4H), 1.41–1.32 (m, 4H), 0.98 (t, *J* = 7.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 164.4 (d, $^1J_{C\text{-}F}$ = 241.4 Hz), 150.0 (d, $^3J_{C\text{-}F}$ = 11.1 Hz), 130.1, 107.2, 101.4 (d, $^3J_{C\text{-}F}$ = 9.1 Hz), 98.4 (d, $^2J_{C\text{-}F}$ = 26.3 Hz), 50.9, 29.3, 20.3, 14.0; ^{19}F NMR (376 MHz, $CDCl_3$, ppm) δ -112.87 (s, 1F); IR (neat, cm^{-1}) 3038, 2952, 2867, 1618, 1573, 1502, 1460, 1368, 825, 749; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{23}FN$ 224.1815; Found 224.1809.

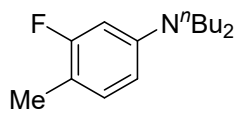
3-(Dibutylamino)benzonitrile (3j)[7]



3j

Synthesized according to General Procedure using 3-nitrobenzonitrile (74.1 mg, 0.50 mmol, 1 eq), *n*-Bu-I (227 μL, 2.0 mmol, 4 eq), NiI_2 (15.6 mg, 0.05 mmol, 10 mol%), Mn (96.2 mg, 1.75 mmol, 3.5 eq) and NMP (1.0 mL) at 120 ℃ for 24 hours. The crude products were purified by column chromatography with petroleum ether/ethyl acetate (50/1, v/v) as eluent to give compound **3j** (yellow green liquid, 65.0 mg, 0.282 mmol, 56% yield). ^1H NMR (300 MHz, $CDCl_3$, ppm) δ 7.25–7.19 (m, 1H), 6.86–6.80 (m, 3H), 3.25 (t, *J* = 7.5 Hz, 4H), 1.59–1.49 (m, 4H), 1.41–1.29 (m, 4H), 0.96 (t, *J* = 7.5 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 148.0, 129.7, 119.9, 118.1, 115.5, 114.1, 112.8, 50.6, 29.0, 20.2, 13.9

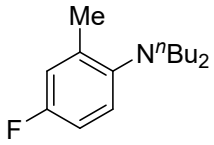
***N,N*-Dibutyl-3-fluoro-4-methylaniline (3k)[7]**



3k

Synthesized according to General Procedure using 2-fluoro-1-methyl-4-nitrobenzene (77.6 mg, 0.50 mmol, 1 eq), *n*-Bu-I (227 μL, 2.0 mmol, 4 eq), NiI_2 (15.6 mg, 0.05 mmol, 10 mol%), Mn (96.2 mg, 1.75 mmol, 3.5 eq) and NMP (1.0 mL) at 120 ℃ for 24 hours. The crude products were purified by column chromatography with petroleum ether/ethyl acetate (50/1, v/v) as eluent to give compound **3k** (yellow liquid, 75.7 mg, 0.321 mmol, 64% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 6.95 (t, J = 9.6 Hz, 1H), 6.33–6.27 (m, 2H), 3.20 (t, J =7.6Hz, 4H), 2.14 (s, 3H), 1.57–1.50 (m, 4H), 1.38–1.26 (m, 4H), 0.94 (t, J = 7.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 162.3 (d, $^1J_{C\text{-}F}$ = 241.4 Hz), 148.1 (d, $^3J_{C\text{-}F}$ = 10.0 Hz), 131.5 (d, $^3J_{C\text{-}F}$ = 8.1 Hz), 110.4 (d, $^2J_{C\text{-}F}$ = 18.2 Hz), 107.3, 98.8 (d, $^2J_{C\text{-}F}$ = 27.3 Hz), 50.9, 29.4, 20.4, 14.0, 13.4; ^{19}F NMR (376 MHz, $CDCl_3$, ppm) δ -116.89 (s, 1F).

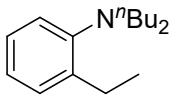
***N,N*-Dibutyl-4-fluoro-3-methylaniline (3l)**



3l

Synthesized according to General Procedure using 4-fluoro-2-methyl-1-nitrobenzene (77.6 mg, 0.50 mmol, 1 eq), *n*-Bu-I (283 μL, 2.5 mmol, 5 eq), NiI_2 (15.6 mg, 0.05 mmol, 10 mol%), Mn (96.2 mg, 1.75 mmol, 3.5 eq) and NMP (1.0 mL) at 120 ℃ for 24 hours. The crude products were purified by column chromatography with petroleum ether/ethyl acetate (100/1, v/v) as eluent to give compound **3l** (yellow liquid, 57.8 mg, 0.243 mmol, 48% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 7.04 (dd, J = 8.7, 5.5 Hz, 1H), 6.90–6.80 (m , 2H), 2.85 (t, J = 6.9Hz, 4H), 2.29 (s, 3H), 1.41–1.21 (m, 8H), 0.87 (t, J = 6.9 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 158.8 (d, $^1J_{C\text{-}F}$ = 242.4 Hz), 146.5 (d, $^4J_{C\text{-}F}$ = 3.0 Hz), 137.7 (d, $^3J_{C\text{-}F}$ = 7.1 Hz), 123.6 (d, $^3J_{C\text{-}F}$ = 9.1 Hz), 117.0 (d, $^2J_{C\text{-}F}$ = 21.2 Hz), 112.4 (d, $^2J_{C\text{-}F}$ = 21.2 Hz), 54.5, 29.5, 20.5, 18.2, 14.0; ^{19}F NMR (376 MHz, $CDCl_3$, ppm) δ -120.57 (s, 1F); IR (neat, cm^{-1}) 303, 2958, 2932, 2865, 2812, 1612, 159, 1499, 1463, 1377; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{25}FN$ 238.1971; Found 238.1966.

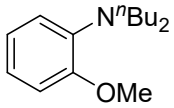
***N,N*-Dibutyl-2-ethylaniline (3m)**



3m

Synthesized according to General Procedure using 1-ethyl-2-nitrobenzene (75.6 mg, 0.50 mmol, 1 eq), *n*-Bu-I (227 μL, 2.0 mmol, 4 eq), NiI_2 (15.6 mg, 0.05 mmol, 10 mol%), Mn (109.9 mg, 2.0 mmol, 4.0 eq) and NMP (1.0 mL) at 120 ℃ for 24 hours. The crude products were purified by column chromatography with petroleum ether/ethyl acetate (80/1, v/v) as eluent to give compound **3m** (yellow liquid, 62.9 mg, 0.268 mmol, 54% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.23 (t, J = 5.2 Hz, 1H), 7.13–7.10 (m, 2H), 7.03 (td, J = 6.8, 5.9, 2.6 Hz, 1H), 2.87 (t, J = 7.6 Hz, 4H), 2.73 (q, J = 7.6 Hz, 2H), 1.42–1.34 (m, 4H), 1.24 (dt, J = 26.8, 7.4 Hz, 7H), 0.86 (t, J = 7.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 150.3, 141.4, 128.8, 125.9, 123.7, 122.6, 54.7, 29.7, 23.3, 20.6, 14.9, 14.1; IR (neat, cm^{-1}) 3057, 2950, 2922, 2853, 2810, 1595, 1482, 1456, 1375, 1108, 756; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{28}N$ 234.2222; Found 234.2220.

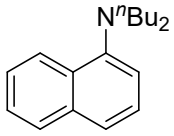
***N,N*-Dibutyl-2-methoxyaniline (3n)**



3n

Synthesized according to General Procedure using 1-methoxy-2-nitrobenzene (51 μL, 0.50 mmol, 1 eq), *n*-Bu-I (227 μL, 2.0 mmol, 4 eq), NiI_2 (15.6 mg, 0.05 mmol, 10 mol%), Mn (96.2 mg, 1.75 mmol, 3.5 eq) and NMP (1.0 mL) at 120 ℃ for 24 hours. The crude products were purified by column chromatography with petroleum ether/ethyl acetate (40/1, v/v) as eluent to give compound **3n** (yellow liquid, 61.2 mg, 0.260 mmol, 52% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 7.00–6.85 (m, 4H), 3.82 (s, 3H), 3.07 (t, *J* = 7.2 Hz, 4H), 1.48–1.38 (m, 4H), 1.33–1.21 (m, 4H), 0.87 (t, *J* = 76.3 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 153.8, 140.0, 122.4, 121.6, 120.5, 111.8, 55.4, 52.7, 29.2, 20.6, 14.0; IR (neat, cm^{-1}) 3038, 2948, 2865, 1592, 1499, 1459, 1378, 1241, 1034, 743; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{26}NO$ 236.2014; Found 236.1996.

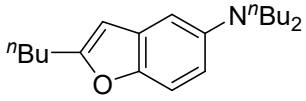
***N,N*-Dibutylnaphthalen-1-amine (3o)[8]**



3o

Synthesized according to General Procedure using 1-nitronaphthalene (86.6 mg, 0.50 mmol, 1 eq), *n*-Bu-I (283 μL, 2.5 mmol, 5 eq), NiI_2 (15.6 mg, 0.05 mmol, 10 mol%), Mn (109.9 mg, 2.0 mmol, 4.0 eq) and NMP (1.0 mL) at 120 ℃ for 24 hours. The crude products were purified by column chromatography with petroleum ether/ethyl acetate (100/1, v/v) as eluent to give compound **3o** (colorless liquid, 87.8 mg, 0.343 mmol, 69% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 8.31 (d, *J* = 9.6 Hz, 1H), 7.80 (d, *J* = 9.3 Hz, 1H), 7.52 (d, *J* = 9.0 Hz, 1H), 7.45–7.36 (m, 3H), 7.16 (d, *J* = 7.2 Hz, 1H), 3.11 (t, *J* = 7.2 Hz, 4H), 1.52–1.42 (m, 4H), 1.34–1.21 (m, 4H), 0.84 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 148.6, 134.9, 131.1, 128.1, 125.6, 125.5, 125.0, 124.2, 123.1, 117.9, 54.0, 29.3, 20.5, 14.0.

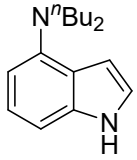
***N,N*,2-Tributylbenzofuran-5-amine (3p)**



3p

Synthesized according to General Procedure using 2-butyl-5-nitrobenzofuran (109.6 mg, 0.50 mmol, 1 eq), *n*-Bu-I (227 μL, 2.0 mmol, 4 eq), NiI_2 (15.6 mg, 0.05 mmol, 10 mol%), Mn (96.2 mg, 1.75 mmol, 3.5 eq) and NMP (1.0 mL) at 130 ℃ for 24 hours. The crude products were purified by column chromatography with petroleum ether/ethyl acetate (40/1, v/v) as eluent to give compound **3p** (yellow liquid, 93.1 mg, 0.309 mmol, 62% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 7.26 (d, *J* = 9.0 Hz, 1H), 6.79 (d, *J* = 2.4 Hz, 1H), 6.69 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.28 (s, 1H), 3.25 (t, *J* = 7.2 Hz, 4H), 2.74 (t, *J* = 7.5 Hz, 2H), 1.78–1.68 (m, 2H), 1.62–1.52 (m, 4H), 1.47–1.31 (m, 6H), 0.97 (t, *J* = 7.5 Hz 9H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 159.8, 148.0, 145.1, 129.7, 111.2, 110.6, 104.2, 101.7, 52.3, 29.8, 29.4, 28.2, 22.2, 20.4, 14.0, 13.8; IR (neat, cm^{-1}) 3098, 2950, 2865, 1616, 1475, 1368, 1249, 1204, 1010; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{32}NO$ 302.2484; Found 302.2478.

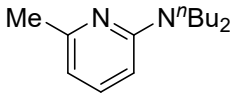
***N,N*-Dibutyl-1H-indol-4-amine (3q)**



3q

Synthesized according to General Procedure using 4-nitro-1H-indole (81.1 mg, 0.50 mmol, 1 eq), *n*-Bu-I (227 μL, 2.0 mmol, 4 eq), NiI_2 (15.6 mg, 0.05 mmol, 10 mol%), Mn (96.2 mg, 1.75 mmol, 3.5 eq) and NMP (1.0 mL) at 120 ℃ for 24 hours. The crude products were purified by column chromatography with petroleum ether/ethyl acetate (10/1, v/v) as eluent to give compound **3q** (black liquid, 26.3 mg, 0.108 mmol, 22% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 8.07 (s, 1H), 7.12–7.06 (m, 2H), 6.95 (d, J = 8.1 Hz 1H), 6.54 (d, J = 7.8 Hz 1H), 3.33 (t, J = 7.8 Hz 4H), 1.65–1.55 (m, 4H), 1.41–1.29 (m, 4H), 0.90 (t, J = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 144.7, 137.4, 122.6, 121.8, 121.0, 107.3, 103.5, 102.1, 52.2, 29.7, 20.6, 14.1; IR (neat, cm^{-1}) 3405, 3055, 2948, 2865, 1659, 1582, 1506, 1461, 1368, 741; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{25}N_2$ 245.2018; Found 245.2013.

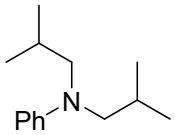
***N,N*-Dibutyl-6-methylpyridin-2-amine (3r)[9]**



3r

Synthesized according to General Procedure using 2-methyl-6-nitropyridine (69.1 mg, 0.50 mmol, 1 eq), *n*-Bu-I (227 μL, 2.0 mmol, 4 eq), NiI_2 (15.6 mg, 0.05 mmol, 10 mol%), Mn (96.2 mg, 1.75 mmol, 3.5 eq) and NMP (1.0 mL) at 120 ℃ for 24 hours. The crude products were purified by column chromatography with petroleum ether/ethyl acetate (30/1, v/v) as eluent to give compound **3r** (yellow liquid, 25.9 mg, 0.117 mmol, 24% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 7.30–7.25 (m, 1H), 6.32 (d, J = 6.9 Hz, 1H), 6.21 (d, J = 8.7 Hz, 1H), 3.43 (t, J = 7.5 Hz, 4H), 2.35 (s, 3H), 1.61–1.51 (m, 4H), 1.40–1.30 (m, 4H), 0.95 (t, J = 7.5 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 157.6, 156.6, 137.1, 109.7, 102.1, 48.1, 29.9, 24.7, 20.3, 14.0.

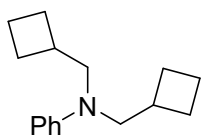
***N,N*-Diisobutylaniline (3s)[10]**



3s

Synthesized according to General Procedure using nitrobenzene (51 μL, 0.50 mmol, 1 eq), 1-iodo-2-methylpropane (345 μL, 2.5 mmol, 5 eq), NiI_2 (15.6 mg, 0.05 mmol, 10 mol%), Mn (109.9 mg, 2.0 mmol, 4 eq) and NMP (1.0 mL) at 120 ℃ for 24 hours. The crude products were purified by column chromatography with petroleum ether/ethyl acetate (100/1, v/v) as eluent to give compound **3s** (yellow liquid, 34.0 mg, 0.165 mmol, 33% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 7.31–7.25 (m, 2H), 6.75–6.68 (m, 3H), 3.23 (d, J = 7.2 Hz, 4H), 2.24–2.11 (m, 2H), 0.99 (d, J = 6.7 Hz, 12H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 148.2, 128.9, 115.0, 112.4, 60.4, 26.3, 20.4.

***N,N*-Dis(cyclobutylmethyl)aniline (3t)**

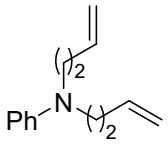


3t

Synthesized according to General Procedure using nitrobenzene (21 μL, 0.20 mmol, 1 eq), (bromomethyl)cyclobutene (201 μL, 1.2 mmol, 6 eq), NiI_2 (6.3 mg, 0.02 mmol, 10 mol%), Mn (38.5 mg, 0.7 mmol, 3.5 eq) and NMP (1.0 mL) at 120 ℃ for 24 hours. The crude products were purified by column chromatography with petroleum ether/ethyl acetate (50/1, v/v) as eluent to give compound **3t** (yellow liquid, 16.9 mg, 0.073 mmol, 37% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 7.28 (t, J = 8.6 Hz, 2H), 6.63 (t, J = 8.7 Hz, 3H), 3.31 (d, J = 6.8 Hz, 4H), 2.66 (p, J = 7.5 Hz, 2H), 2.08–1.95 (m, 4H), 1.88–1.65 (m, 8H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 148.9, 129.0, 115.6, 112.6, 57.1, 34.4, 27.2, 18.7; IR (neat, cm^{-1}) 3015, 2976, 2842, 1607, 1506, 1456,

1363, 1260, 749, 696; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{24}N$ 230.1909; Found 230.1911.

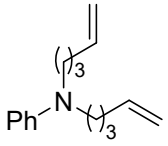
***N,N*-Di(but-3-en-1-yl)aniline (3u)**



3u

Synthesized according to General Procedure using nitrobenzene (21 μL, 0.20 mmol, 1 eq), 4-bromopent-1-ene (122 μL, 1.2 mmol, 6 eq), NiI_2 (6.3 mg, 0.02 mmol, 10 mol%), KI (199.2 mg, 1.2 mmol, 6 eq), TMSCl (102 μL, 0.8 mmol, 4 eq), Zn (78.5 mg, 1.2 mmol, 6 eq) and NMP (0.4 mL) at 120 ℃ for 24 hours. The crude products were purified by column chromatography with petroleum ether/ethyl acetate (200/1, v/v) as eluent to give compound **3u** (yellow liquid, 19.7 mg, 0.098 mmol, 49% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.18–7.13 (m, 2H), 6.9 (t, J = 8.4 Hz, 3H), 5.81–5.71 (m, 2H), 5.06–4.97 (m, 4H), 3.29 (t, J = 7.2 Hz, 4H), 2.27 (q, J = 7.2 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 157.3, 147.7, 135.8, 129.3, 116.4, 115.7, 111.9, 50.6, 31.7; IR (neat, cm^{-1}) 3077, 2935, 2875, 1640, 1604, 1506, 1456, 1363, 1217; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{20}N$ 202.1596; Found 202.1590.

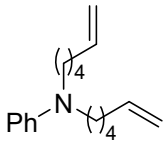
***N,N*-Di(pent-4-en-1-yl)aniline (3v)**



3v

Synthesized according to General Procedure using nitrobenzene (51 μL, 0.50 mmol, 1 eq), 5-bromopent-1-ene (198 μL, 2.0 mmol, 4 eq), NiI_2 (15.6 mg, 0.05 mmol, 10 mol%), Mn (96.2 mg, 1.75 mmol, 3.5 eq) and NMP (1.0 mL) at 120 ℃ for 24 hours. The crude products were purified by column chromatography with petroleum ether/ethyl acetate (50/1, v/v) as eluent to give compound **3v** (yellow liquid, 58.1 mg, 0.253 mmol, 51% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.21 (dd, J = 15.6, 6.8 Hz, 2H), 6.63 (t, J = 8.0 Hz, 3H), 5.89–5.79 (m, 2H), 5.07–4.98 (m, 4H), 3.29–3.25 (m, J = 7.6 Hz, 4H), 2.12–2.06 (m, 4H), 1.71–1.64 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 148.0, 138.1, 129.2, 115.4, 114.9, 111.8, 50.4, 31.2, 26.3; IR (neat, cm^{-1}) 3072, 2932, 2870, 1747, 2601, 1504, 1454, 1364, 1280, 745, 693; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{24}N$ 230.1909; Found 230.1889.

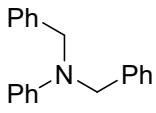
***N,N*-Di(hex-5-en-1-yl)aniline (3w)**



3w

Synthesized according to General Procedure using nitrobenzene (51 μL, 0.50 mmol, 1 eq), 6-bromopent-1-ene (267 μL, 2.0 mmol, 4 eq), NiI_2 (15.6 mg, 0.05 mmol, 10 mol%), Mn (96.2 mg, 1.75 mmol, 3.5 eq) and NMP (1.0 mL) at 120 ℃ for 24 hours. The crude products were purified by column chromatography with petroleum ether/ethyl acetate (50/1, v/v) as eluent to give compound **3w** (yellow liquid, 59.0 mg, 0.229 mmol, 46% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.16–7.10 (m, 2H), 6.56(t, J = 8.0 Hz, 3H), 5.79–5.69 (m, 2H), 4.97–4.87 (m, 4H), 3.18 (t, J = 7.6 Hz, 4H), 2.02 (q, J = 7.2 Hz, 4H), 1.56–1.48 (m, 4H), 1.38–1.31 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 148.1, 138.6, 129.2, 115.2, 114.6, 111.7, 50.9, 33.6, 26.7, 26.4. IR (neat, cm^{-1}) 3086, 3043, 2926, 2862, 2838, 1643, 1601, 1506, 1456, 1368, 1261, 749, 693; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{28}N$ 258.2222; Found 258.2219.

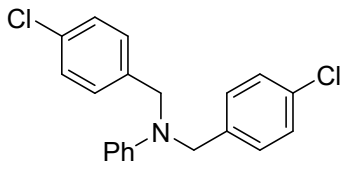
***N,N*-Dibenzylaniline (3x)[11]**



3x

Synthesized according to General Procedure using nitrobenzene (21 μL, 0.20 mmol, 1 eq), (bromomethyl)benzene (144 μL, 1.2 mmol, 6 eq), NiI_2 (6.3 mg, 0.02 mmol, 10 mol%), Mn (65.9 mg, 1.2 mmol, 6 eq) and NMP (0.4 mL) at 120 ℃ for 24 hours. The crude products were purified by column chromatography with petroleum ether/ethyl acetate (50/1, v/v) as eluent to give compound **3x** (yellow liquid, 39.1 mg, 0.144 mmol, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.25–7.13 (m, 10H), 7.16 (t, J = 8.4 Hz, 2H), 6.66–6.60 (m, 3H), 4.56 (s, 4H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 149.1, 138.6, 129.2, 128.6, 126.8, 126.6, 116.7, 112.4, 54.2.

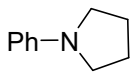
_N_-(3-Chlorobenzyl)-_N_-(4-chlorobenzyl)aniline (3y)[11]



3y

Synthesized according to General Procedure using nitrobenzene (21 μL, 0.20 mmol, 1 eq), 1-(bromomethyl)-4-chlorobenzene (246 mg, 1.2 mmol, 6 eq), NiI_2 (6.3 mg, 0.02 mmol, 10 mol%), Mn (65.9 mg, 1.2 mmol, 6 eq) and NMP (0.4 mL) at 120 ℃ for 24 hours. The crude products were purified by column chromatography with petroleum ether/ethyl acetate (100/1, v/v) as eluent to give compound **3y** (yellow liquid, 49.5 mg, 0.144 mmol, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.19 (t, J = 8.4 Hz, 4H), 7.12–7.07 (m, 6H), 6.68–6.61 (m, 3H), 4.49 (s, 4H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 148.7, 136.9, 132.7, 129.4, 128.8, 128.1, 117.4, 112.7, 53.8.

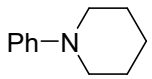
1-Phenylpyrrolidine (3z)[12]



3z

Synthesized according to General Procedure using nitrobenzene (21 μL, 0.20 mmol, 1 eq), 1,4-diiodobutane (133 μL, 1.0 mmol, 5 eq), NiI_2 (6.3 mg, 0.02 mmol, 10mol%), Mn (54.9 mg, 1.0 mmol, 5 eq) and NMP (0.4 mL) at 120 ℃ for 24 hours. The crude products were purified by column chromatography with petroleum ether/ethyl acetate (50/1, v/v) as eluent to give compound **3z** (yellow liquid, 19.9 mg, 0.136 mmol, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.22 (t, J = 7.2 Hz, 2H), 6.65 (t, J = 7.2 Hz, 1H), 6.56 (d, J = 7.6 Hz, 2H), 3.27 (t, J = 6.8 Hz, 4H), 2.00–1.97 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 147.9, 129.1, 115.3, 111.6, 47.5, 25.4.

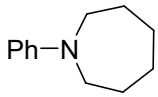
1-Phenylpiperidine (3aa)[12]



3aa

Synthesized according to General Procedure using nitrobenzene (21 μL, 0.20 mmol, 1 eq), 1,5-diiodopentane (149 μL, 1.0 mmol, 5 eq), NiI_2 (6.3 mg, 0.02 mmol, 10 mol%), Mn (54.9 mg, 1.0 mmol, 5 eq) and NMP (0.4 mL) at 120 ℃ for 24 hours. The crude products were purified by column chromatography with petroleum ether/ethyl acetate (50/1, v/v) as eluent to give compound **3aa** (yellow liquid, 20.6 mg, 0.128 mmol, 64% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.20–7.16 (m, 2H), 6.87 (d, J = 8.0 Hz, 2H), 6.75 (t, J = 7.2 Hz, 1H), 3.08 (t, J = 5.6 Hz, 4H), 1.67–1.61 (m, 4H), 1.53–1.47 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 152.3, 129.0, 119.2, 116.6, 50.7, 25.9, 24.3.

1-Phenylazepane (3ab)[13]

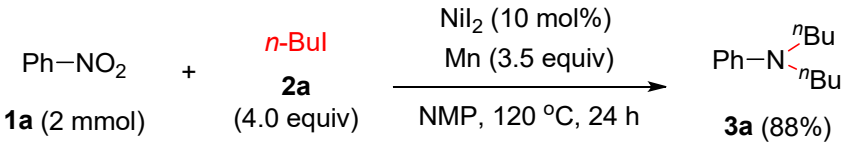


3ab

Synthesized according to General Procedure using nitrobenzene (21 μL, 0.20 mmol, 1 eq), 1,6-diiodohexane (164 μL, 1.0 mmol, 5 eq), NiI_2 (6.3 mg, 0.02 mmol, 10 mol%), Mn (54.9 mg, 1.0 mmol, 5 eq) and NMP (0.4 mL) at 120 ℃ for 24 hours. The crude products were purified by column chromatography with petroleum ether/ethyl acetate (200/1, v/v) as eluent to give compound **3ab** (yellow liquid, 16.1 mg, 0.092 mmol, 46% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 7.21 (t, J = 8.4 Hz, 2H), 6.69 (d, J = 8.4 Hz, 2H), 6.62 (t, J = 7.2 Hz, 1H), 3.45 (t, J = 6.0 Hz, 4H), 1.79 (s, 4H), 1.58–1.52 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 148.9, 129.3, 115.1, 111.2, 49.1, 27.8, 27.2.

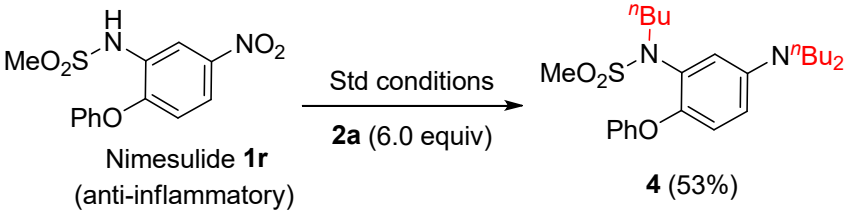
4. Synthetic Applications

4.1. Scale experiment

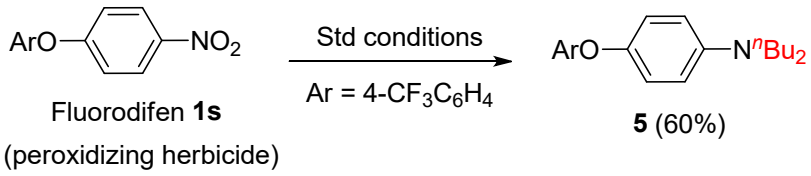


In order to prove the applicability of the reaction, NiI_2 (64.3 mg, 0.2 mmol, 10 mol%), Mn (384.6 mg, 7.0 mmol, 3.5 eq) NMP (4.0 ml), nitrobenzene **1a** (204 μL, 2.0 mmol, 1 eq) and *n*-Bu-I (908 μL, 8.0 mol, 4 eq) were added to a 25 ml reaction flask in argon atmosphere, and the reaction was carried out at 120 °C for 24 hours. Afterwards, the crude reaction mixture was extracted with ethyl acetate and the organic phase was combined. The crude products were purified by column chromatography with petroleum ether/ethyl acetate (100/1, v/v) as eluent to give compound **3a** (yellow liquid, 360.8 mg, 1.76 mmol, 88% yield).

4.2 Modification of drug and pesticide



Under standard conditions, using Nimesulide **1r** (30.8 mg, 0.10 mmol, 1 eq), *n*-Bu-I (68 μL, 0.6 mmol, 6 eq), NiI_2 (3.1 mg, 0.01 mmol, 10 mol%), Mn (19.5 mg, 0.35 mmol, 3.5 eq) and NMP (0.4 mL) at 120 ℃ for 24 hours. The crude products were purified by column chromatography with petroleum ether/ethyl acetate (50/1, v/v) as eluent to give compound **4** (yellow liquid, 23.7 mg, 0.053 mmol, 53% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 7.37 (t, J = 7.6 Hz, 2H), 7.19–7.11 (m, 2H), 7.06–7.03 (d, J = 7.6 Hz, 2H), 6.31 (dd, J = 8.9, 2.8 Hz, 1H), 5.93 (d, J = 2.8 Hz, 1H), 3.57 (s, 2H), 3.14–3.08 (t, J = 7.4 Hz, 4H), 2.93 (s, 3H), 1.36 (m, 12H), 0.87 (q, J = 7.4 Hz, 9H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 156.0, 155.1, 149.0, 134.4, 129.8, 123.8, 119.3, 115.5, 106.4, 101.0, 50.8, 50.0, 38.8, 31.0, 29.2, 20.1, 19.7, 13.8; IR (neat, cm^{-1}) 3069, 2972, 2921, 2871, 1614, 1566, 1513, 1339, 1226; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{39}N_2O_3S$ 447.2681; Found 447.2682.9

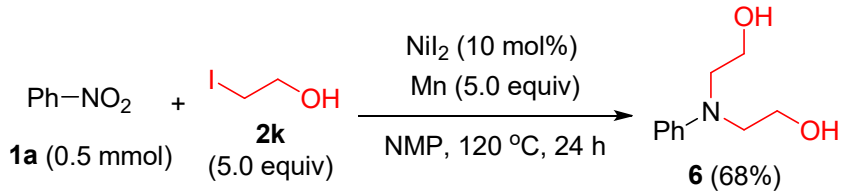


Fluorodifen **1s**
(peroxidizing herbicide)

5 (60%)

Under standard conditions, using **1s** (56.6 mg, 0.20 mmol, 1 eq), *n*-Bu-I (114 μL, 1.0 mmol, 5 eq), NiI_2 (6.3 mg, 0.02 mmol, 10 mol%), Mn (38.5 mg, 0.7 mmol, 3.5 eq) and NMP (0.4 mL) at 120 °C for 24 hours. The crude products were purified by column chromatography with petroleum ether/ethyl acetate (100/1, v/v) as eluent to give compound **5** (brown liquid, 43.9 mg, 0.120 mmol, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.51 (d, J = 8.7 Hz, 2H), 6.98 (d, J = 8.7 Hz, 2H), 6.92 (d, J = 9. Hz, 2H), 6.63 (d, J = 9.1 Hz, 2H), 3.25 (t, J = 6.4 Hz , 4H), 1.61–1.54 (m, 4H), 1.41–1.32 (m, 4H), 0.96 (t, J = 7.3 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 162.2, 145.9, 144.5, 127.1 (d, $^1J_{C\text{-}F}$ = 270.0 Hz), 126.9 (dd, $^3J_{C\text{-}F}$ = 3.0 Hz), 123.4 (t, $^2J_{C\text{-}F}$ = 32.0 Hz), 121.6, 116.4, 112.8, 51.1, 29.4, 20.4, 14.0; ^{19}F NMR (376 MHz, $CDCl_3$, ppm) δ -61.52 (s, 3F); IR (neat, cm^{-1}) 3050, 2943, 2866, 1615, 1511, 1464, 1325, 1247, 831; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{27}F_3NO$ 366.2045; Found 366.2027.

4.3 Synthetic drug intermediates 6



1a (0.5 mmol)

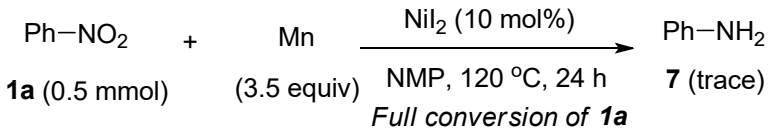
2k
(5.0 equiv)

6 (68%)

Under standard conditions, using nitrobenzene **1a** (51 μL, 0.50 mmol, 1 eq), 2-iodoethan-1-ol **2k** (200 μL, 2.5 mmol, 5 eq), NiI_2 (15.6 mg, 0.05 mmol, 10 mol%), Mn (96.2 mg, 1.75 mmol, 3.5 eq) and NMP (1.0 mL) at 120 °C for 24 hours. The crude products were purified by column chromatography with petroleum ether/ethyl acetate (1/5, v/v) as eluent to give compound **6** (yellow liquid, 61.9 mg, 0.341 mmol, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.23 (dd, J = 8.7, 7.3 Hz, 2H), 6.73 (t, J = 7.2 Hz, 1H), 6.68 (d, J = 8.2 Hz, 2H), 4.00 (s, 2H), 3.80 (t, J = 4.8 Hz, 4H), 3.54 (t, J = 4.9 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 147.7, 129.2, 116.8, 112.5, 60.7, 55.3.

5. Mechanistic Studies

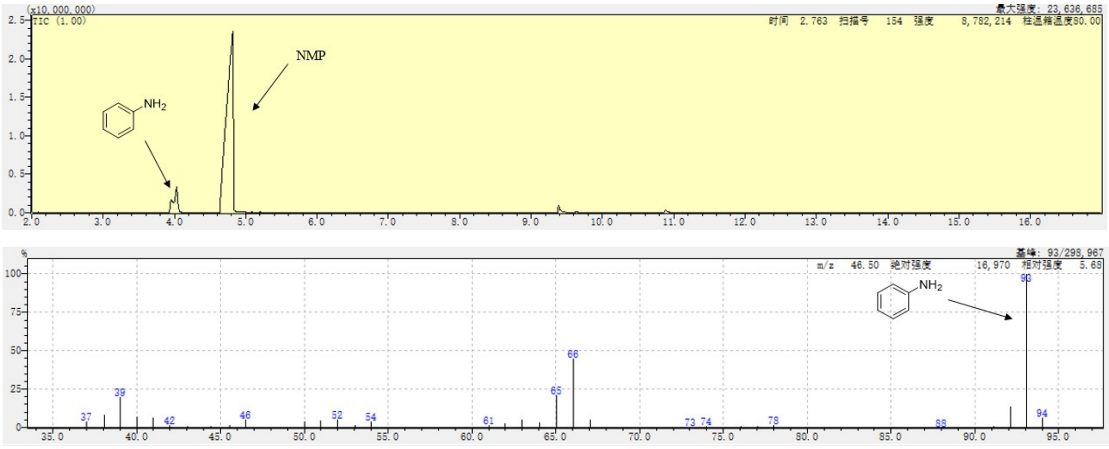
5.1. Reduction of nitrobenzene



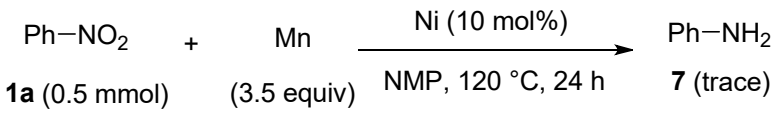
(i) Without NiI_2, <5% conversion of **1a**
(ii) In air with NiI_2,: 59% conversion of **1a**

In the glove box, NiI_2 (15.5mg, 0.05 mmol, 10 mol%), Mn (96.2 mg, 1.75 mmol, 3.5 eq) NMP (1.0 ml) and nitrobenzene **1a** (51 μL, 0.5 mmol, 1 eq) were added to a 25 ml reaction flask in argon atmosphere, and the reaction was carried out at 120 °C for 24 hours. By GC-MS observation, a trace amount of aniline **7** was found. In addition, the reaction condition was changed to experiment under air, and the result was that the ^{1}H NMR yield was only 59%. As a comparison, without adding NiI_2, no change was observed.

Figure S1. GC-MS spectrum of **7**



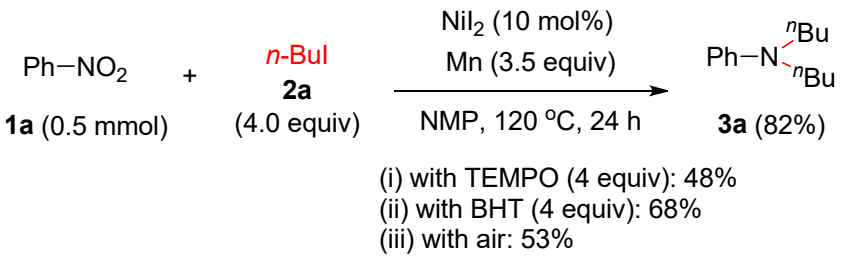
5.2. Reduction of nitrobenzene with Ni nanoparticle



with Ni nanoparticle (50 nm or 1 μm diameter): <5% conversion of **1a**

In the glove box, nickel nano powder (with 50 nm or 1 μm diameter) (2.9 mg, 0.05 mmol, 10 mol%), Mn (96.2 mg, 1.75 mmol, 3.5 eq), NMP (1.0 ml) and nitrobenzene **1a** (51 μL, 0.5 mmol, 1 eq) were added to a 25 ml reaction flask in argon atmosphere, and the reaction was carried out at 120 °C for 24 hours. By ^{1}H-NMR analysis, no change was observed.

5.3. Reaction with radial scavengers



In order to verify whether free radicals are involved in the reaction, we did a set of control experiments by adding 4 eq TEMPO or BHT to the standard condition system respectively, and ^{1}H NMR obtained 48% and 68% yields. In addition, the reaction condition was changed to experiment under air, and the result was that the ^{1}H NMR yield was only 53%.

5.4. Investigation of possible intermediates

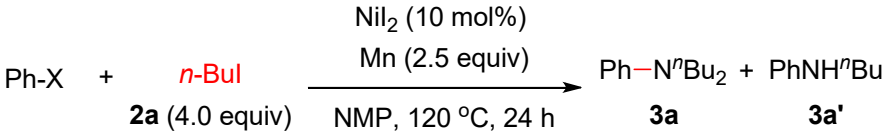
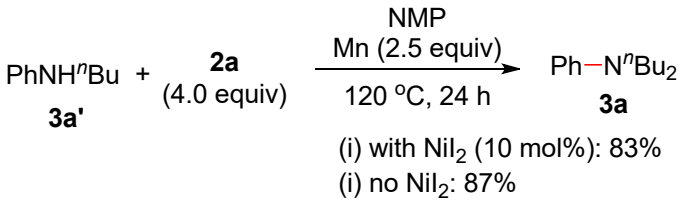


Table S1. Nuclear magnetic yield of possible intermediates

entries	intermediate	yield **3a** (%)	yield **3a'** (%)
1	PhN=O	41%	--
2	PhNH-OH	80%	--
3	PhNH-OH , w/o NiI_2	77%	--
4	1/2 Ph−N^{+}(O^{-})=N−Ph	24%	--
5	1/2 PhN=NPh	20%	--
6	1/2 PhNHNHPh	31%	--
7	$PhNH_2$	19%	37%

Under the standard conditions, the Mn was reduced to 2.5 eq. The yields of different intermediates to **3a** were examined by ^{1}H NMR, and it was found that only *N*-phenyl hydroxylamine yields were the closest to the model reaction.

5.5. Reaction of 3a' with 2a



The *N*-butyl aniline **3a'** was reacted with **2a** under the standard condition except that Mn was 2.5 eq, and the yield was 83% identified by ^{1}H NMR; the crude yield was 87% without NiI_2.

6. References

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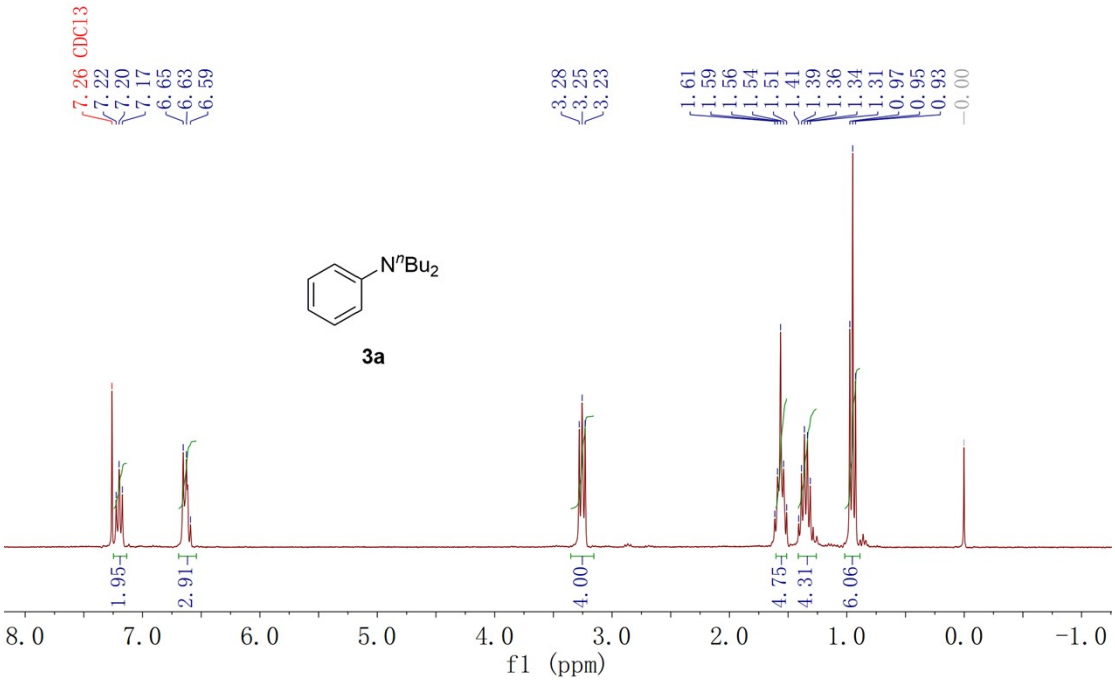
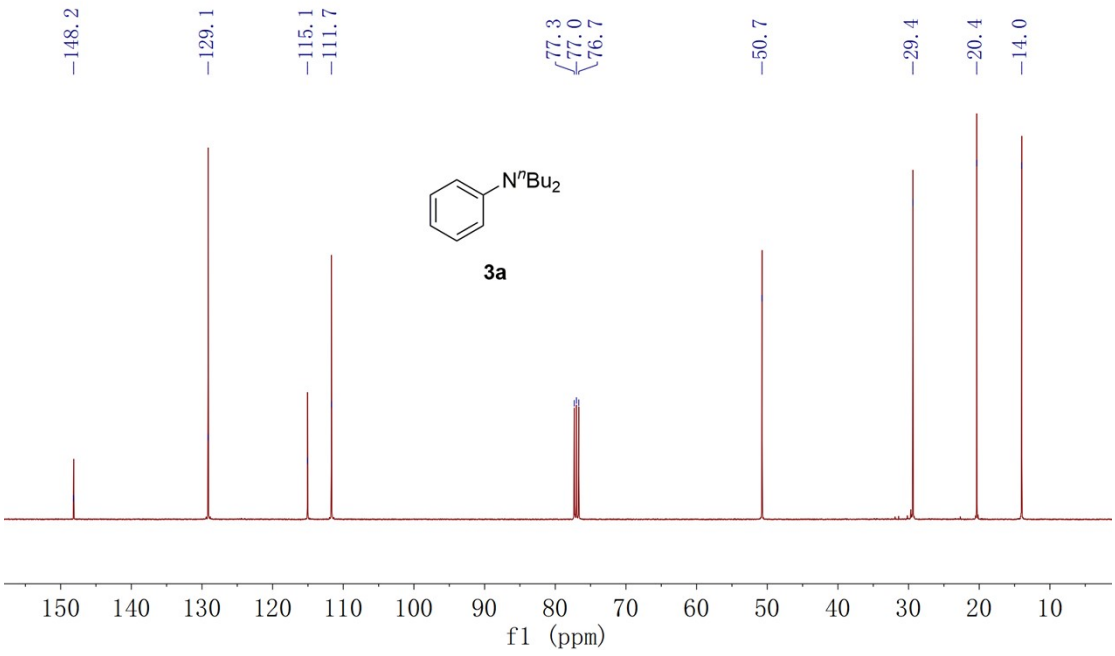
7. ^{1}H, ^{13}C and ^{19}F NMR Spectra

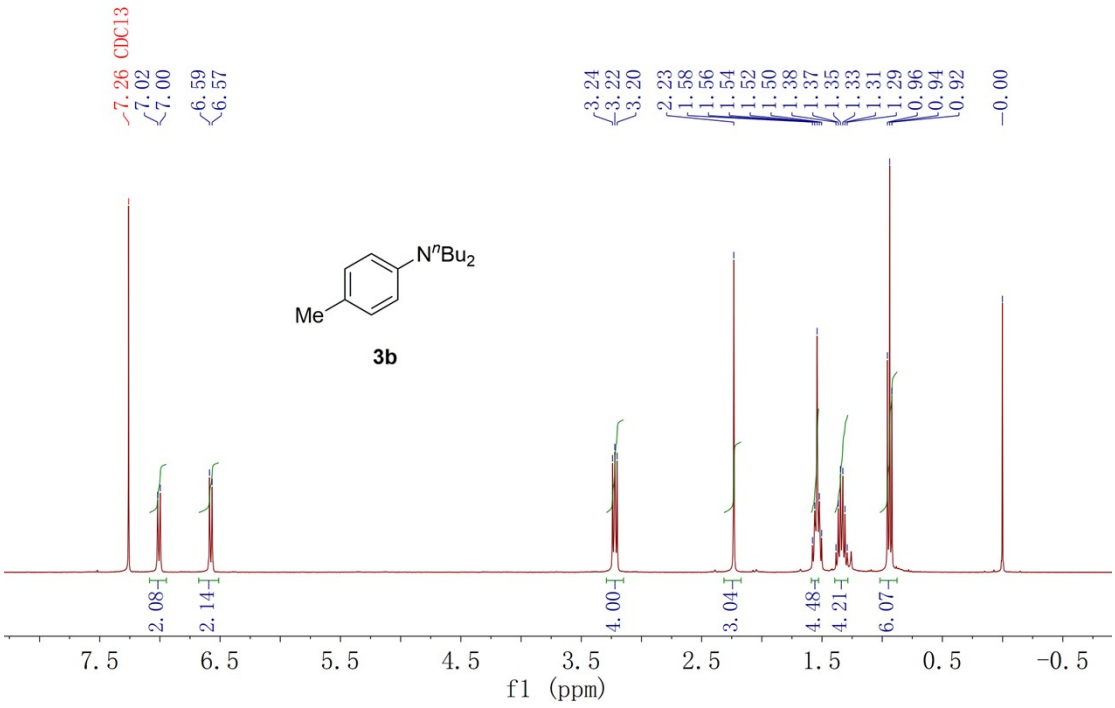
^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of compound **3a**



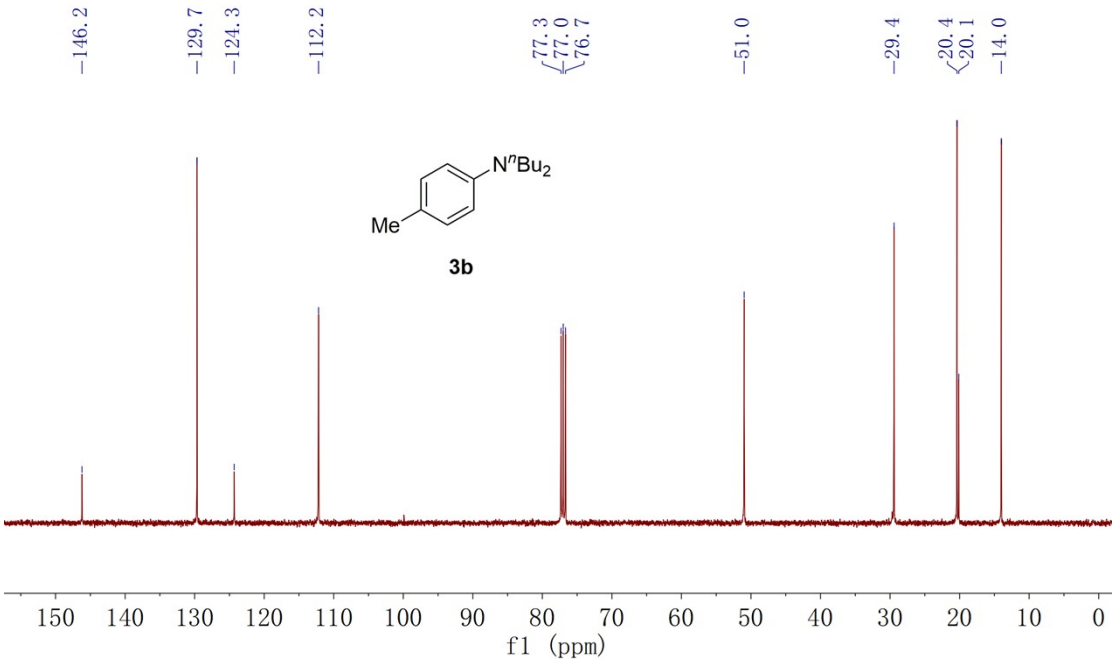
^{13}C NMR ($CDCl_3$, 101 MHz) spectrum of compound **3a**



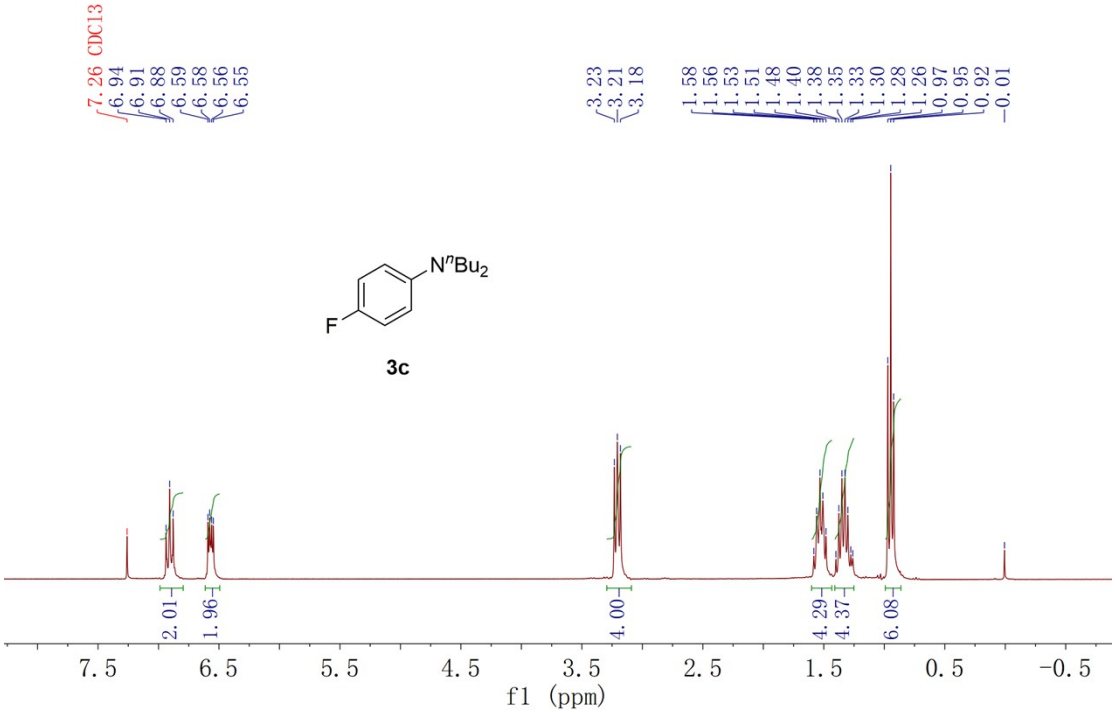
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **3b**



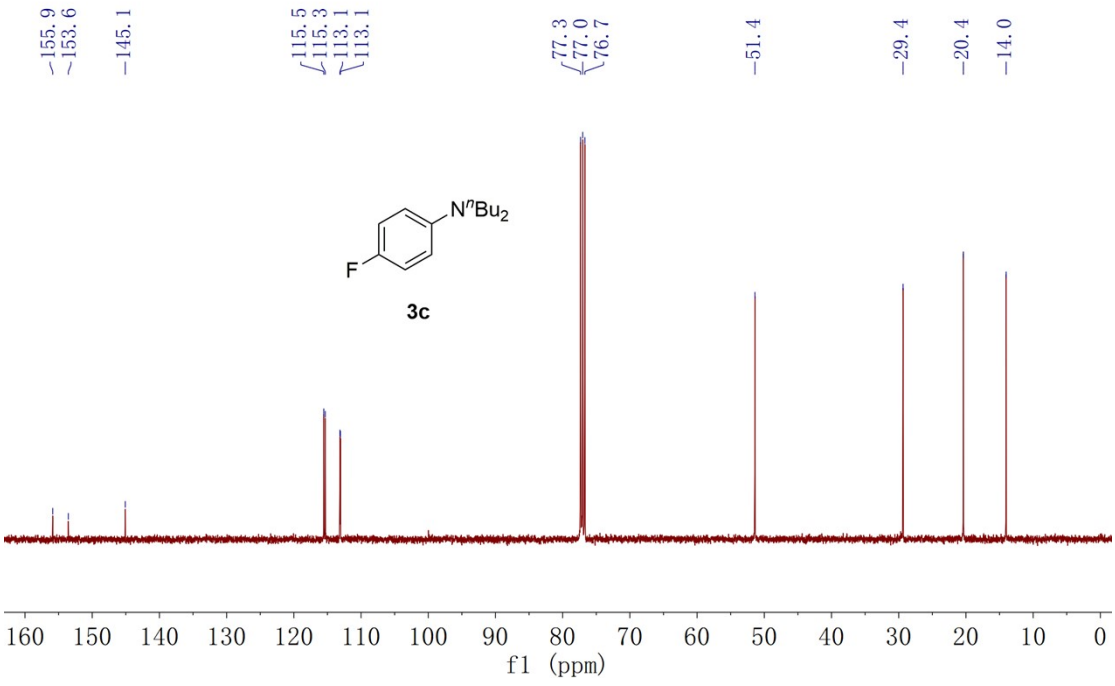
^{13}C NMR ($CDCl_3$, 101 MHz) spectrum of compound **3b**



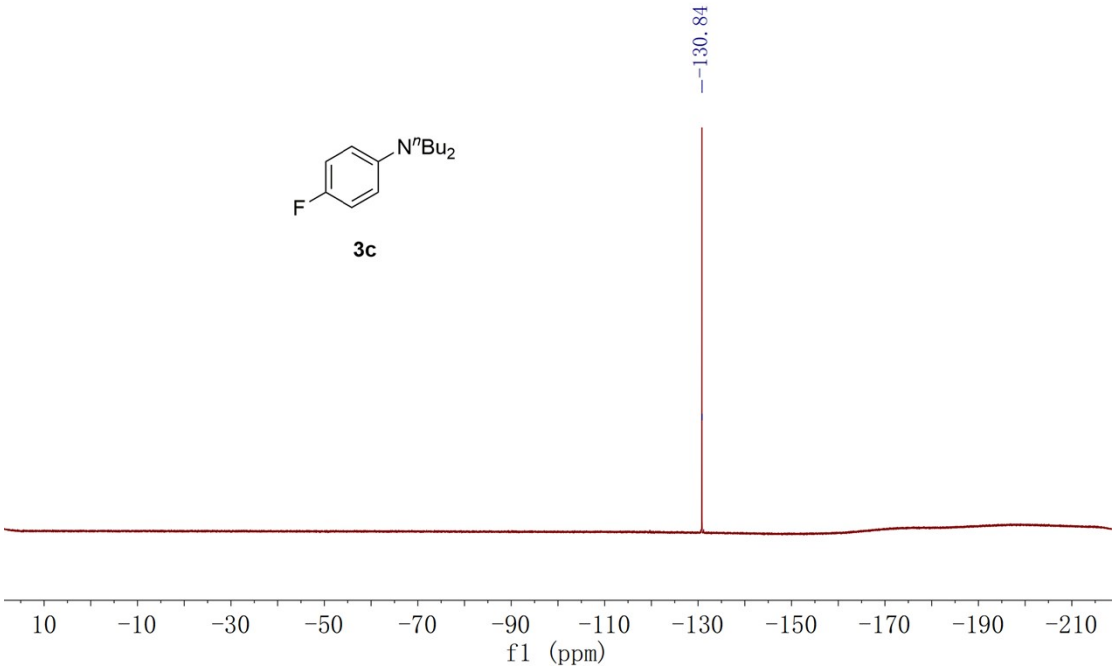
^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of compound **3c**



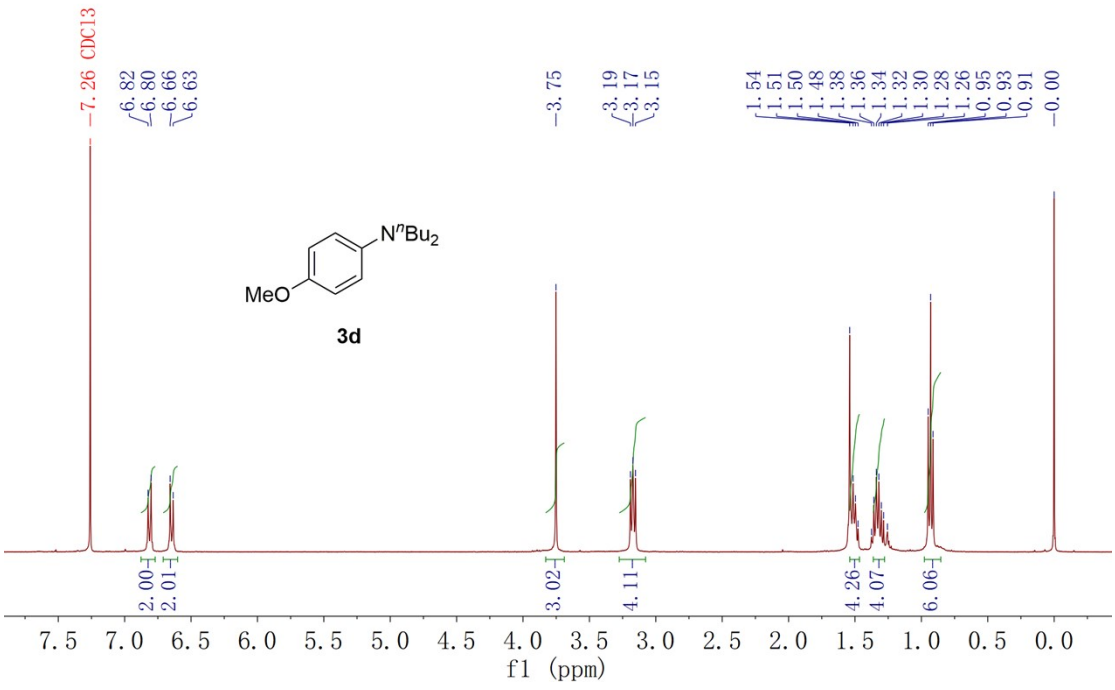
^{13}C NMR ($CDCl_3$, 101 MHz) spectrum of compound **3c**



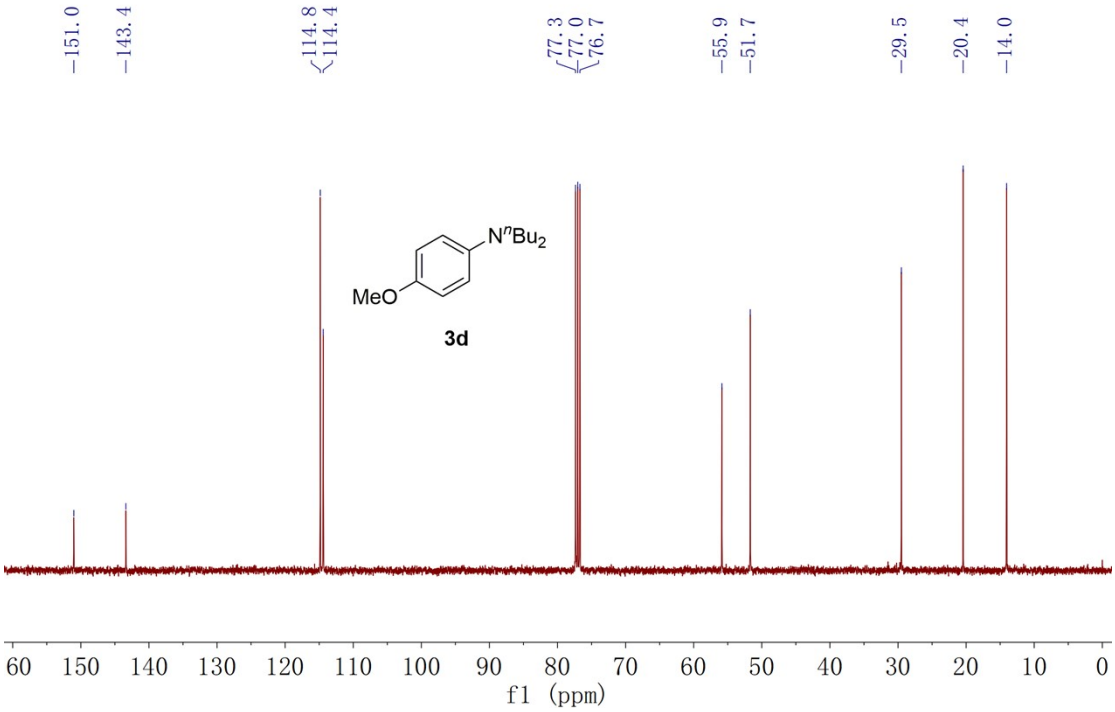
^{19}F NMR ($CDCl_3$, 376 MHz) spectrum of compound **3c**



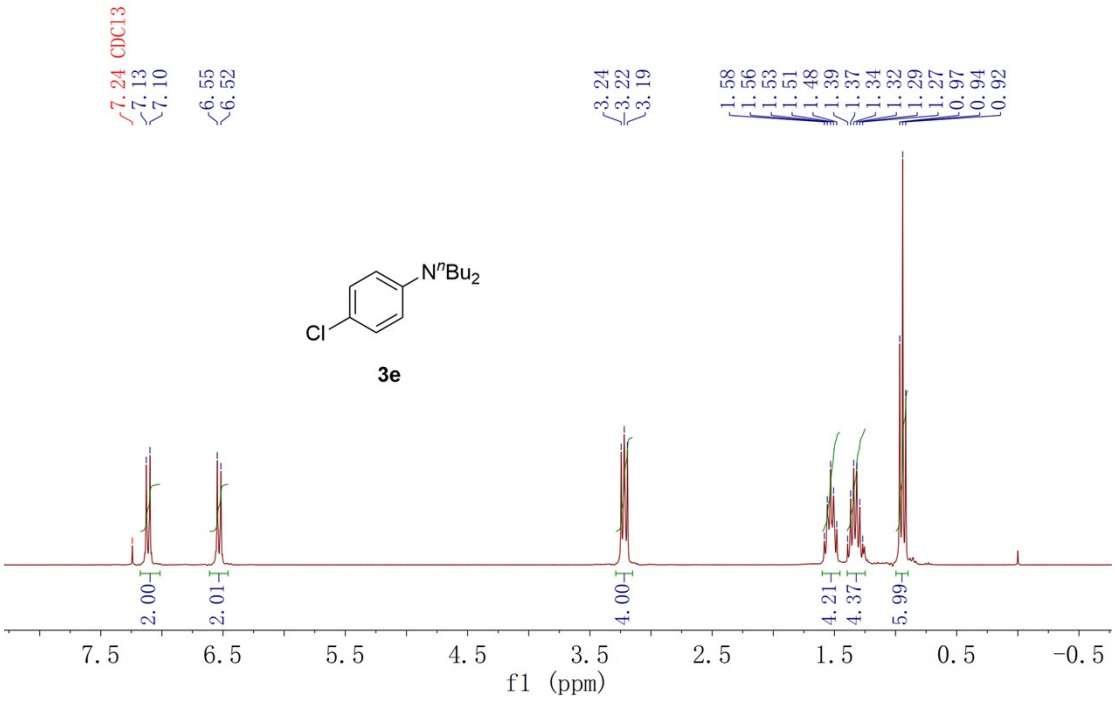
^1H NMR ($CDCl_3$, 400 MHz) spectrum of compound **3d**



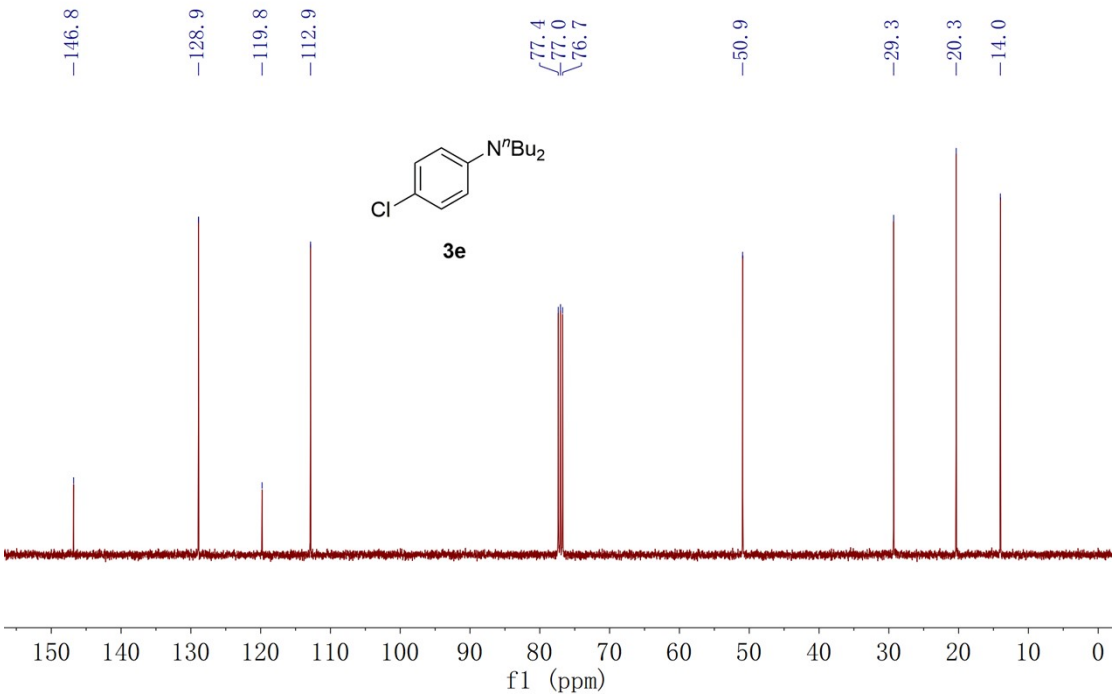
^{13}C NMR ($CDCl_3$, 101 MHz) spectrum of compound **3d**



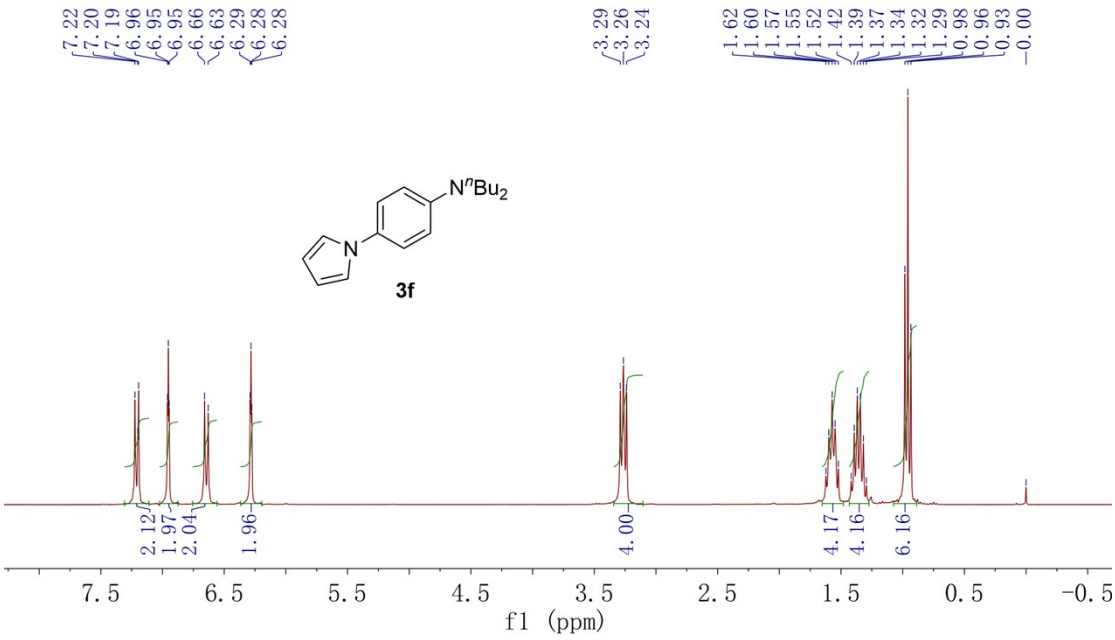
^1H NMR ($CDCl_3$, 300 MHz) spectrum of compound **3e**



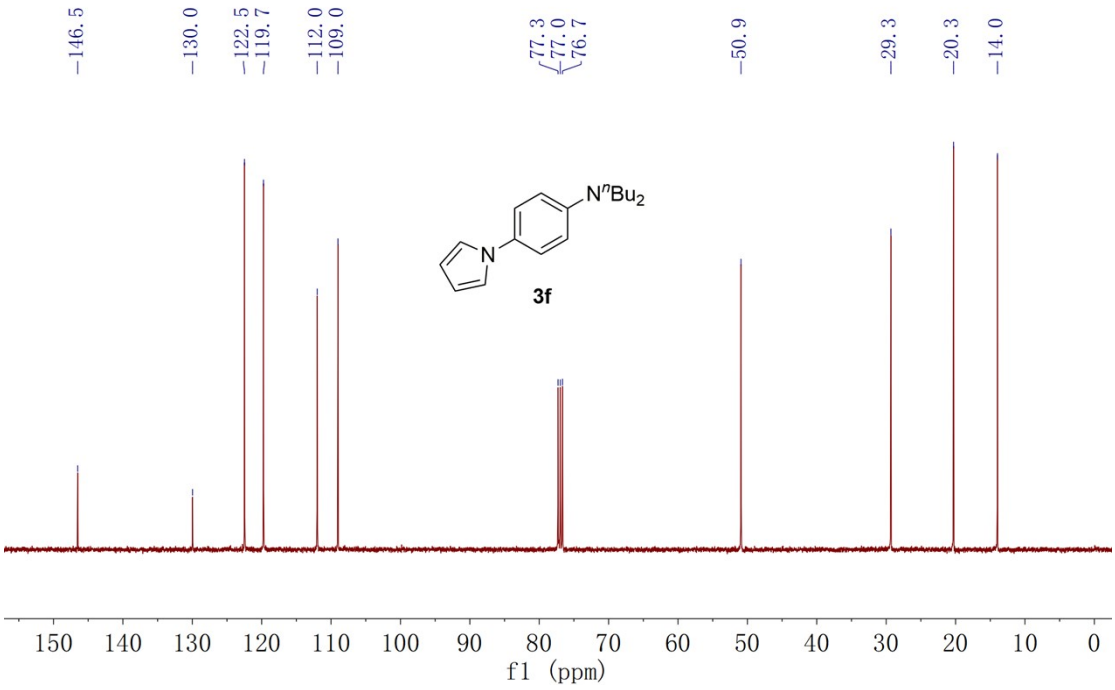
^{13}C NMR ($CDCl_3$, 101 MHz) spectrum of compound **3e**



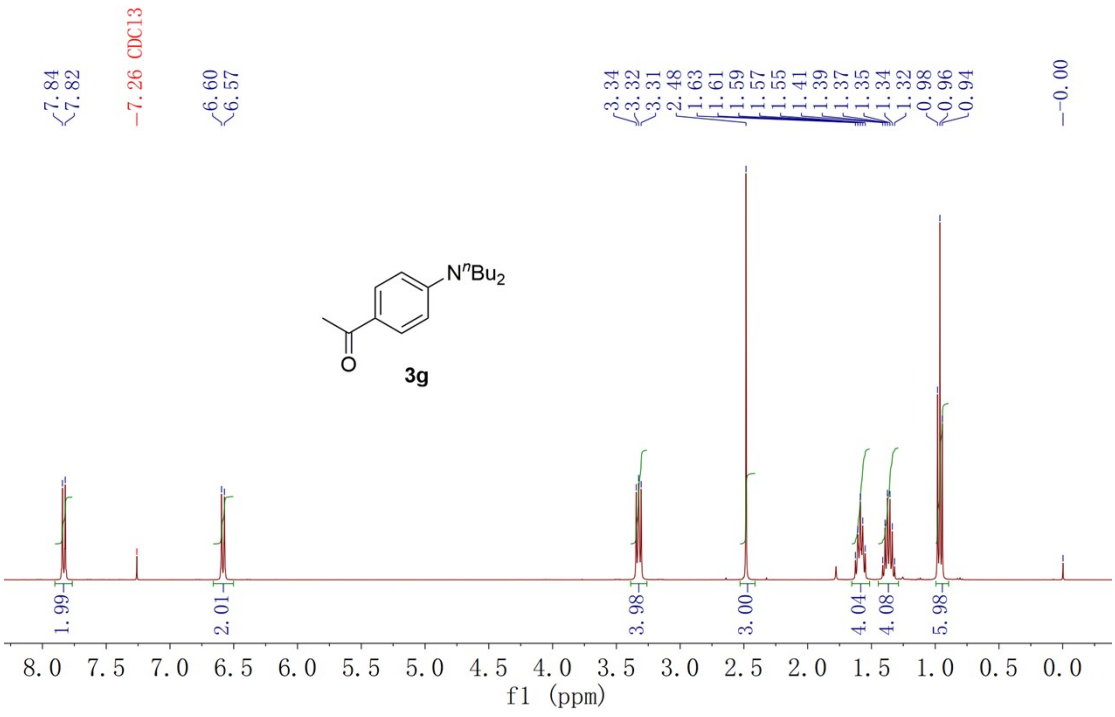
^1H NMR ($CDCl_3$, 300 MHz) spectrum of compound **3f**



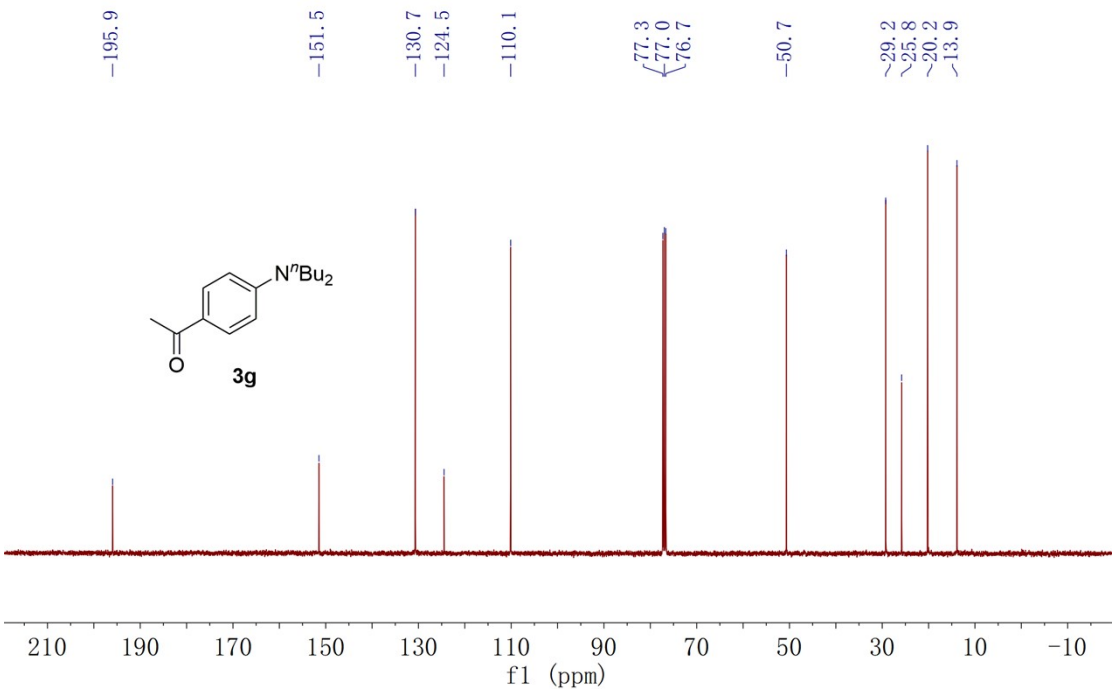
^{13}C NMR ($CDCl_3$, 101 MHz) spectrum of compound **3f**



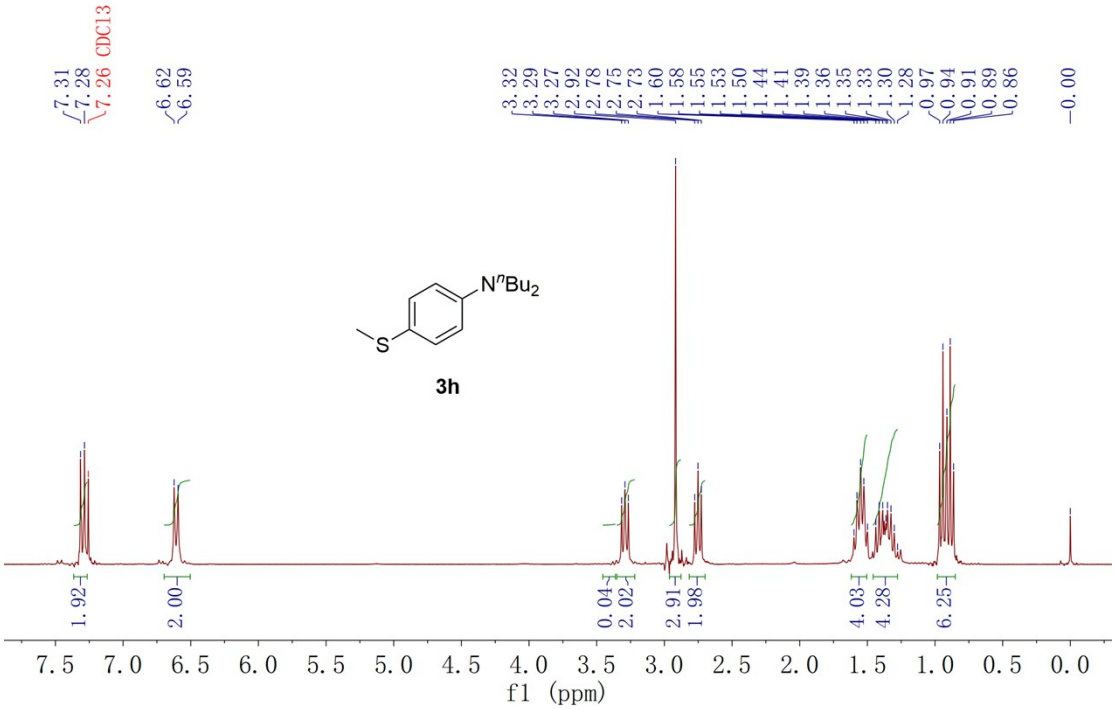
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **3g**



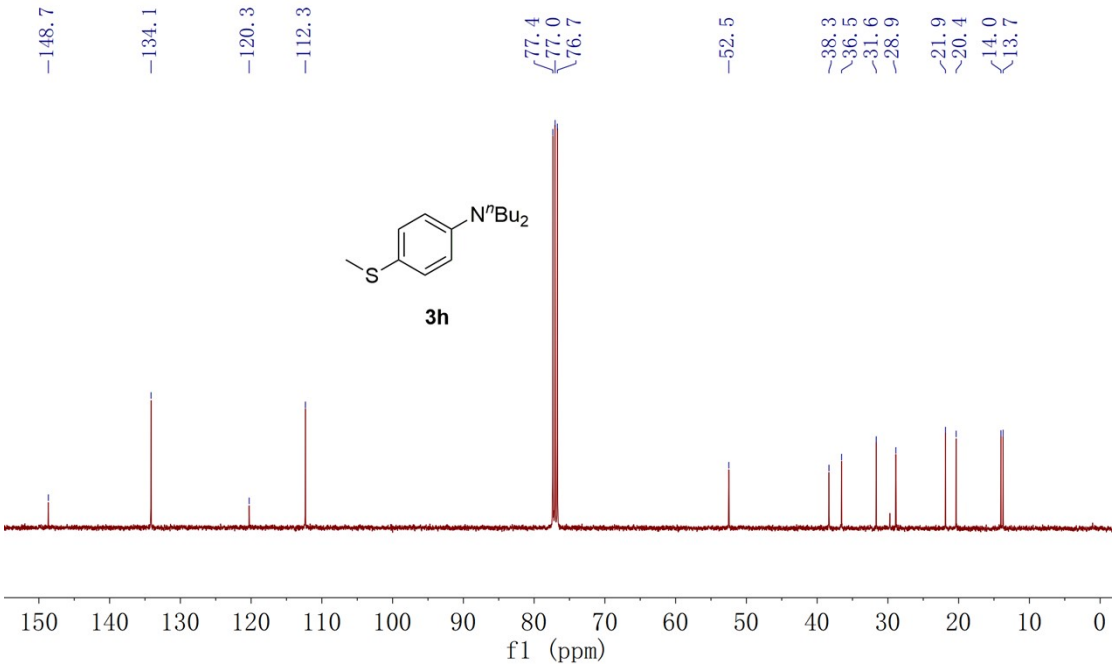
^{13}C NMR ($CDCl_3$, 101 MHz) spectrum of compound **3g**



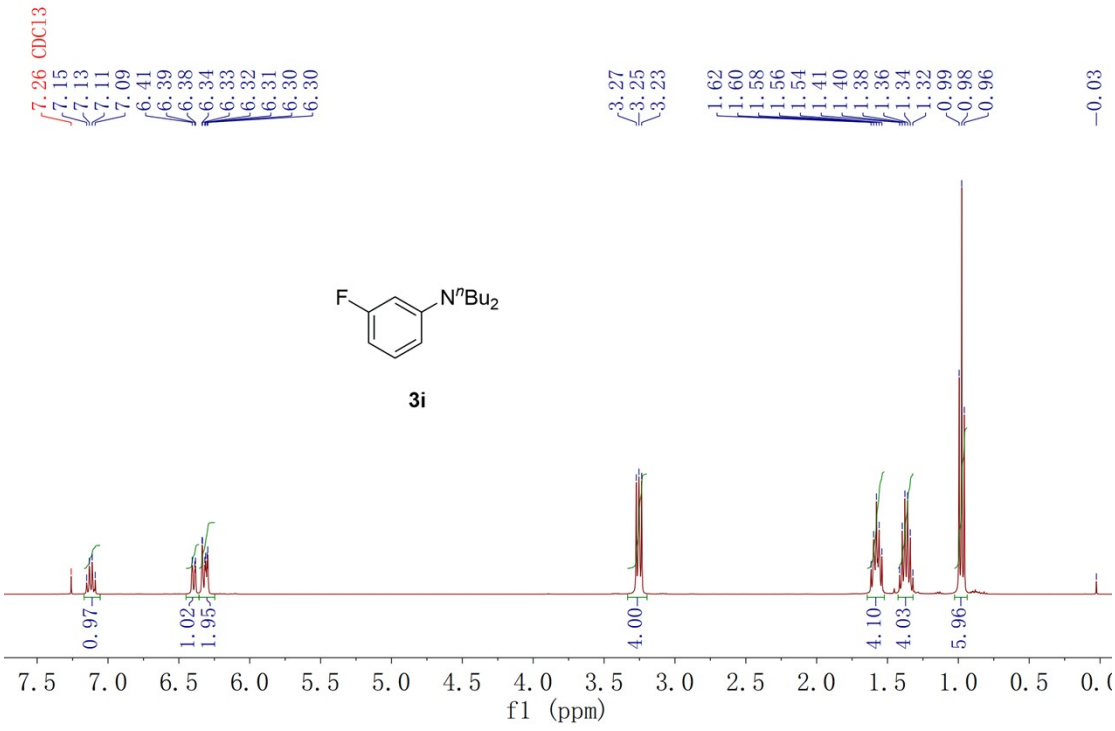
^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of compound **3h**



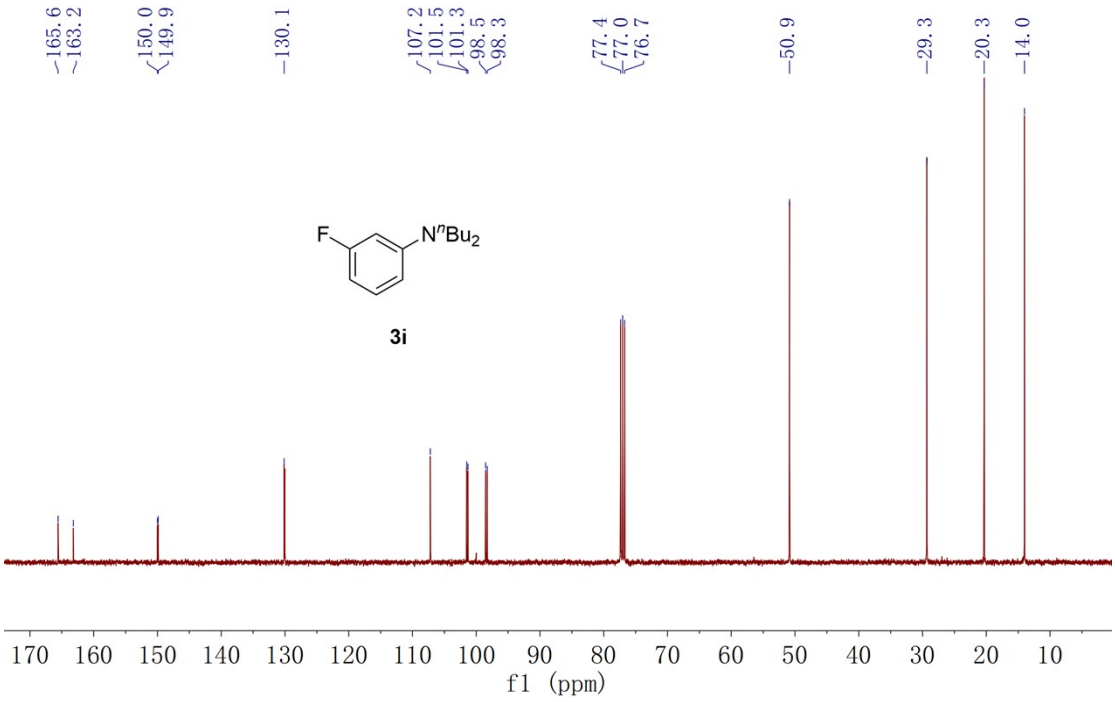
^{13}C NMR ($CDCl_3$, 101 MHz) spectrum of compound **3h**



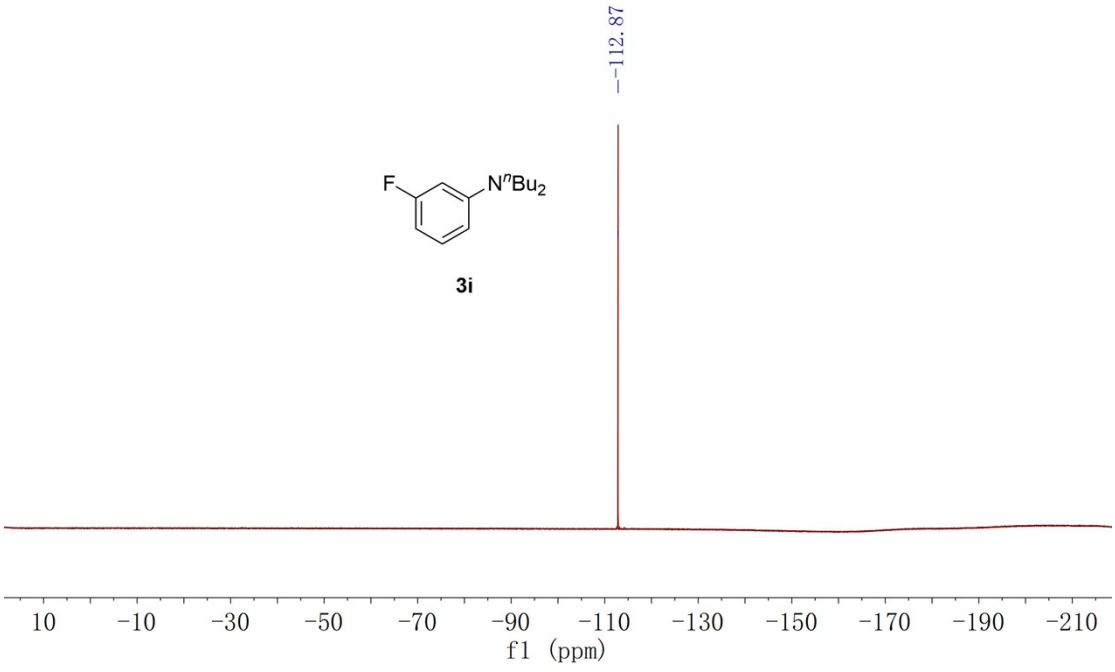
^1H NMR ($CDCl_3$, 400 MHz) spectrum of compound **3i**



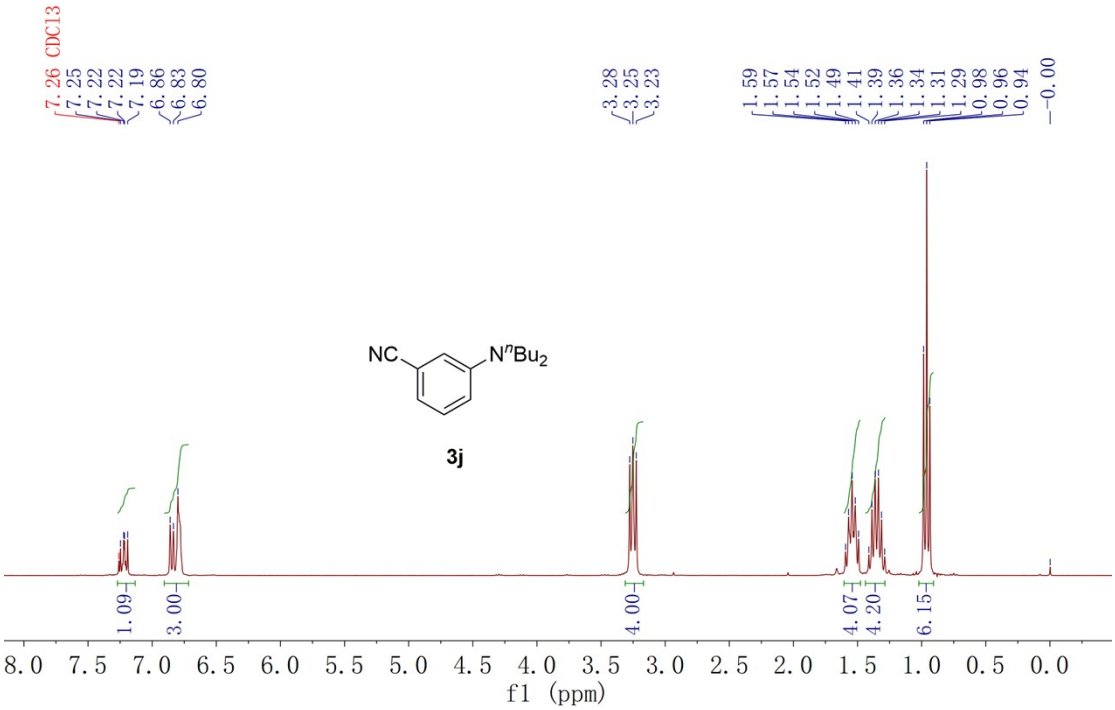
^{13}C NMR ($CDCl_3$, 101 MHz) spectrum of compound **3i**



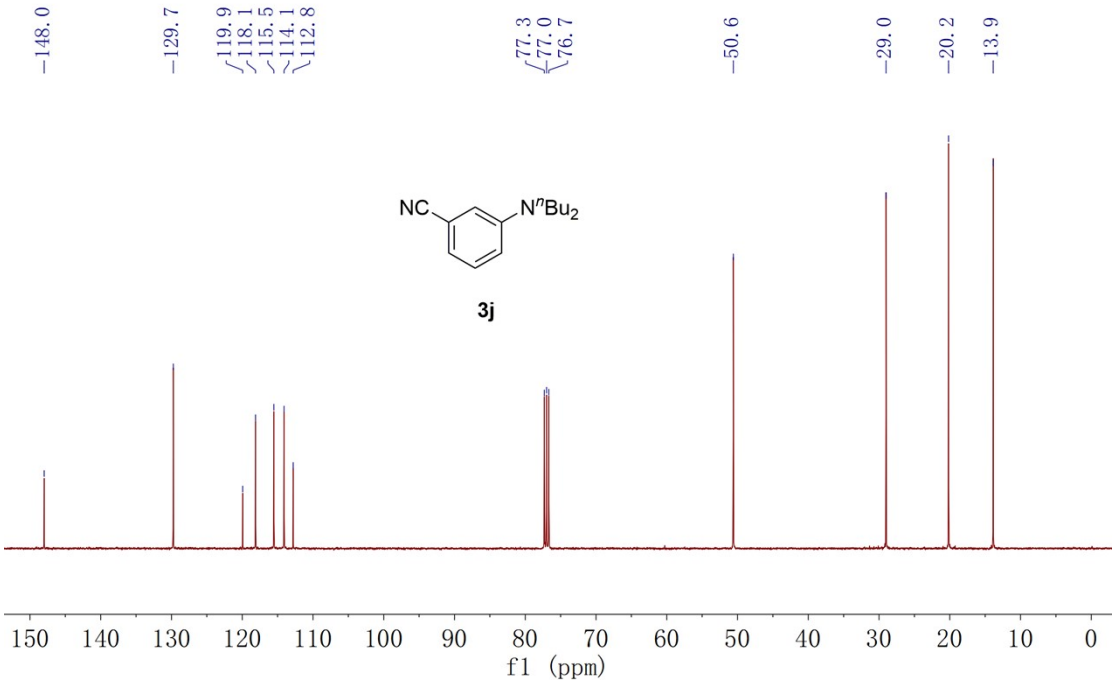
^{19}F NMR ($CDCl_3$, 376 MHz) spectrum of compound **3i**



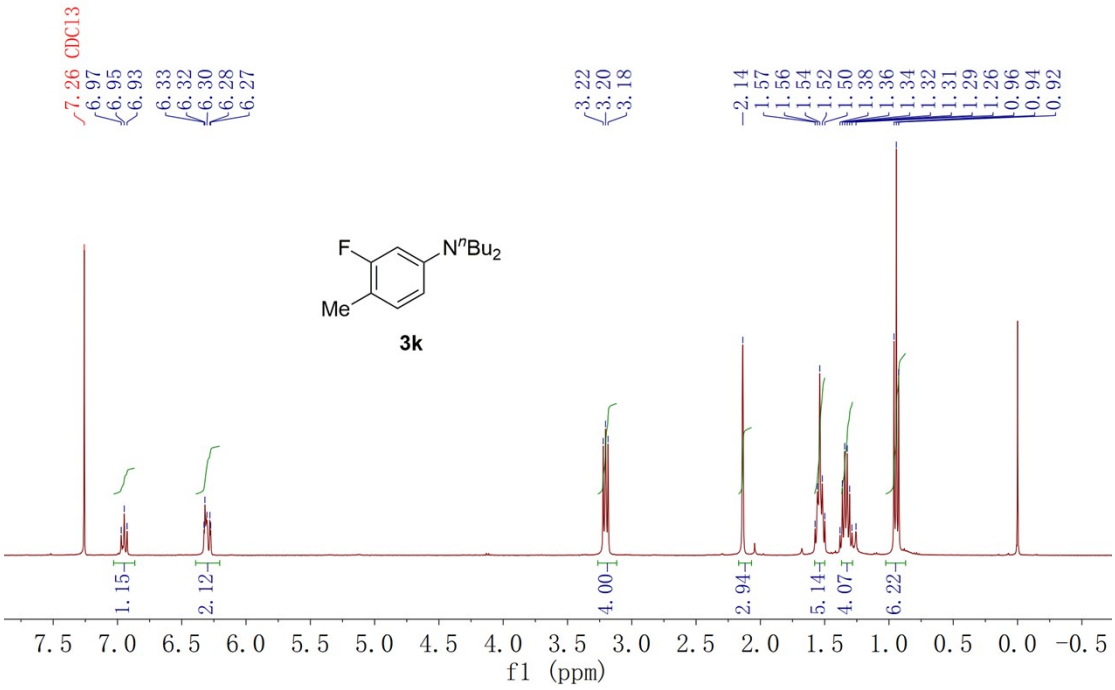
^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of compound **3j**



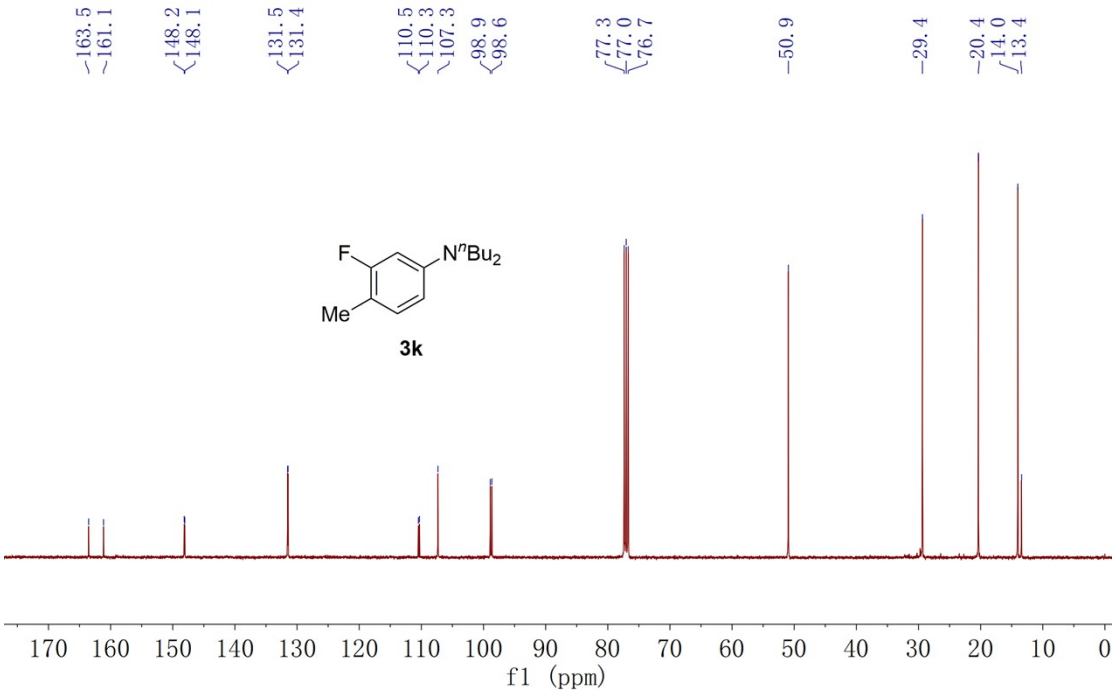
^{13}C NMR ($CDCl_3$, 101 MHz) spectrum of compound **3j**



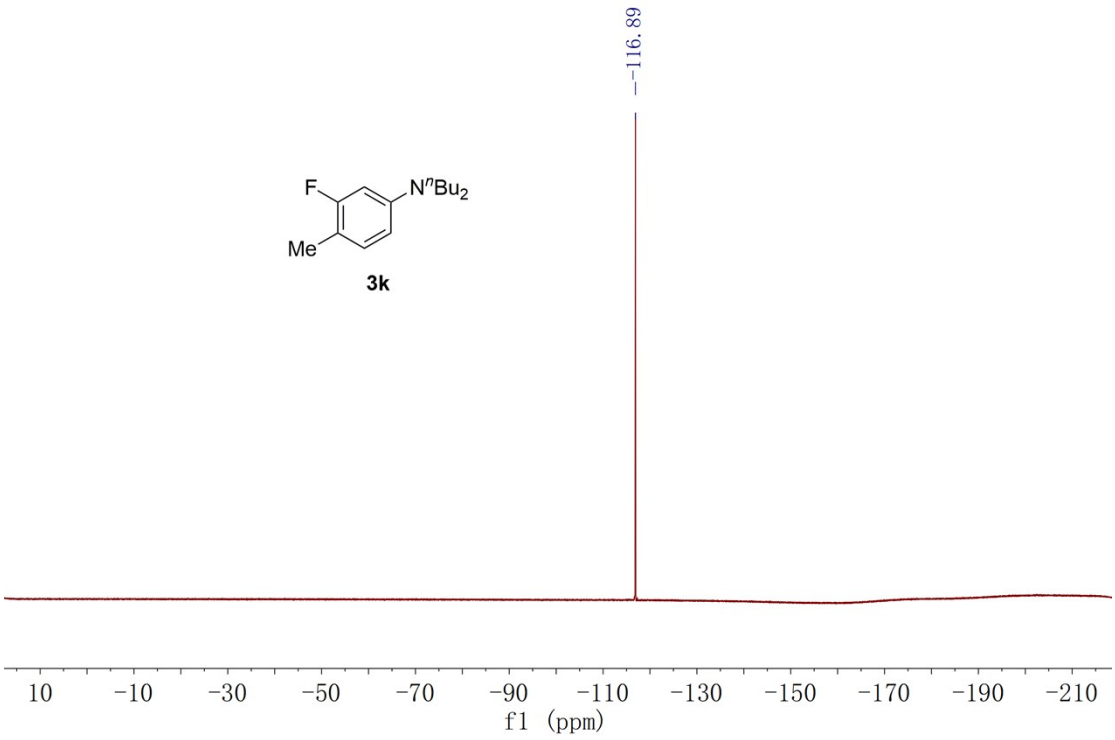
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **3k**



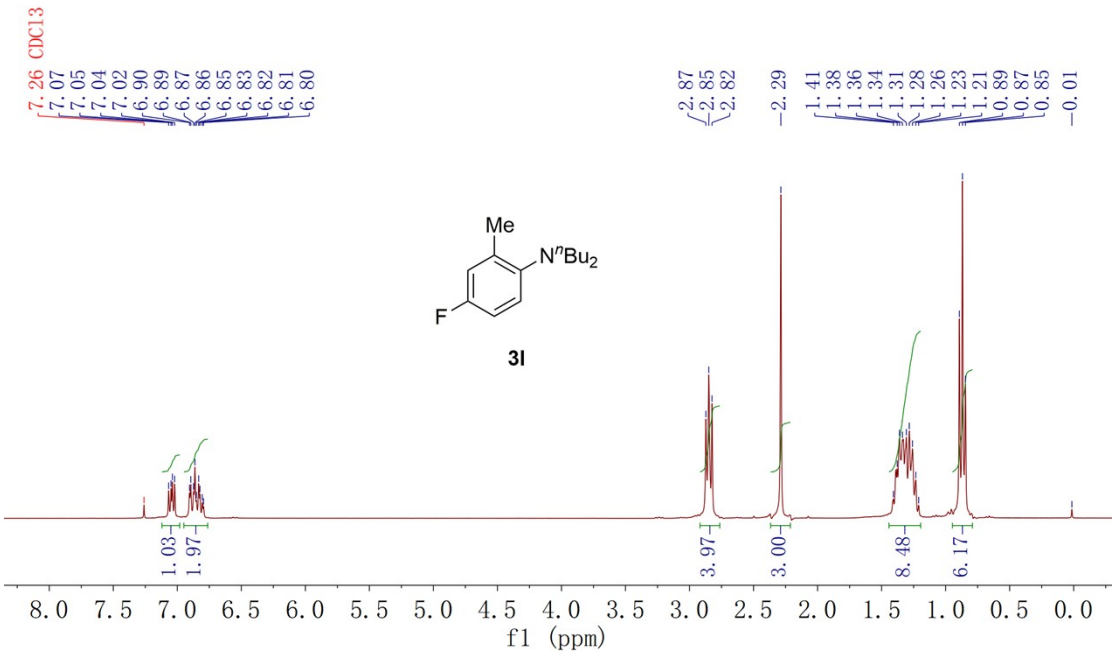
^{13}C NMR ($CDCl_3$, 101 MHz) spectrum of compound **3k**



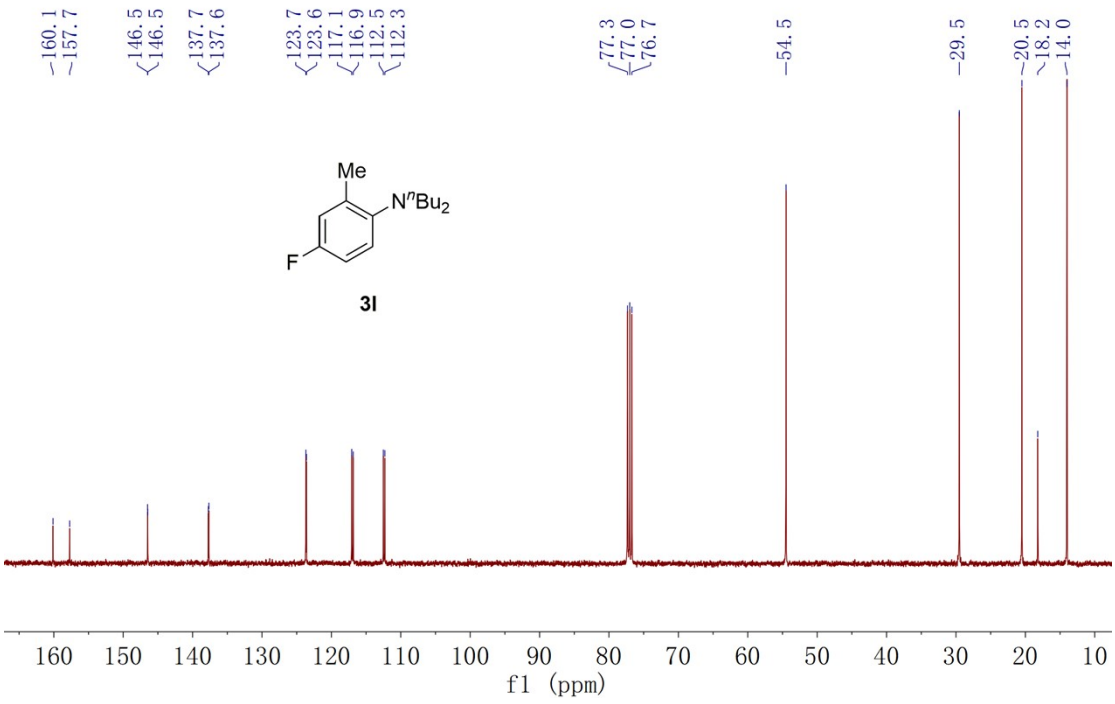
^{19}F NMR ($CDCl_3$, 376 MHz) spectrum of compound **3k**



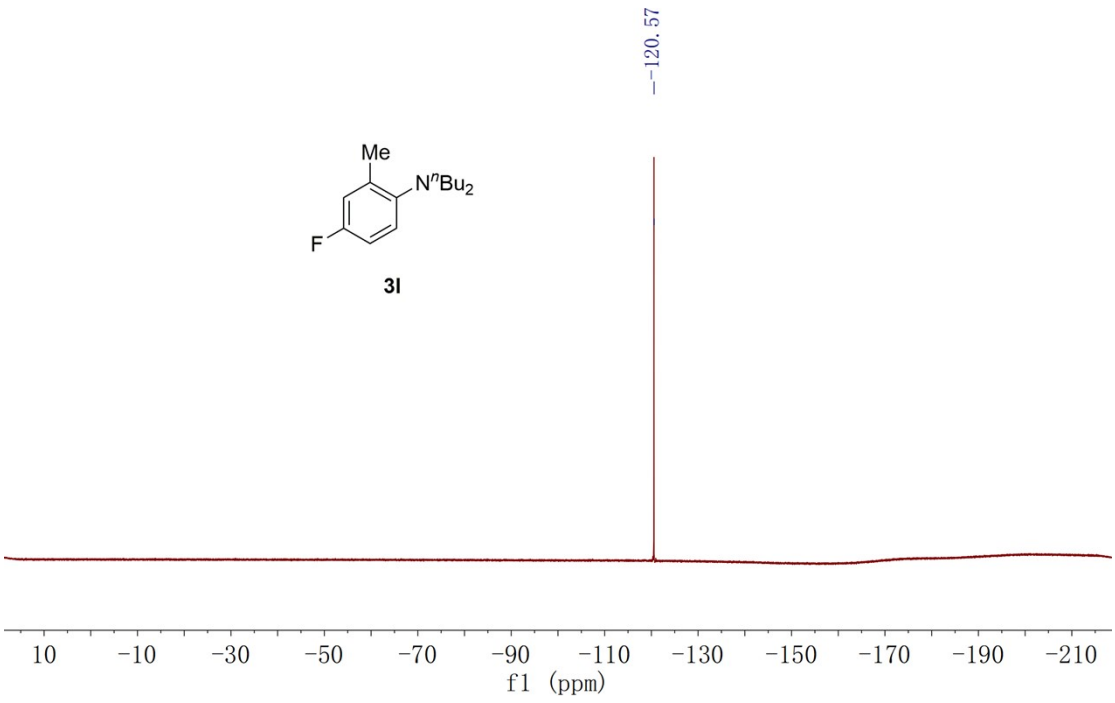
^1H NMR ($CDCl_3$, 300 MHz) spectrum of compound **3l**



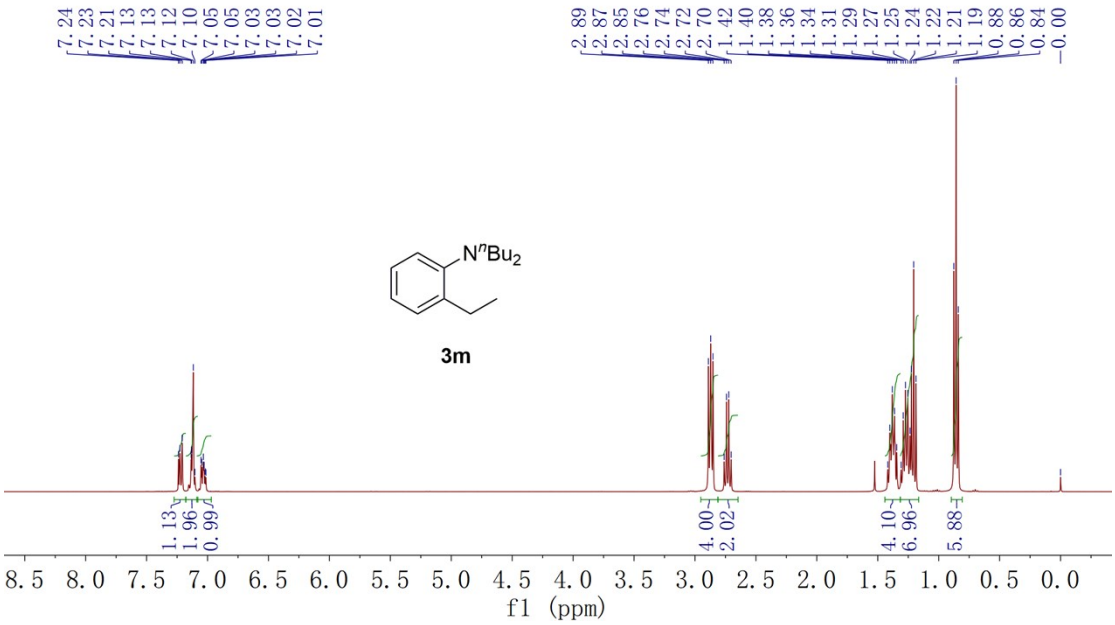
^{13}C NMR ($CDCl_3$, 101 MHz) spectrum of compound **3l**



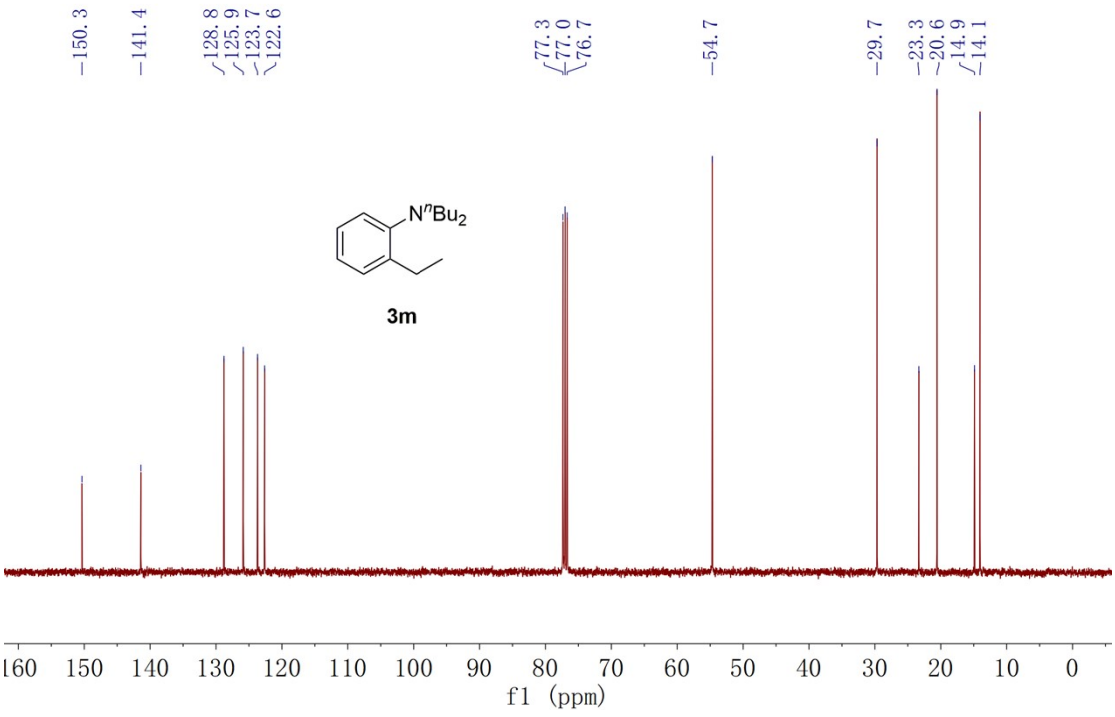
^{19}F NMR ($CDCl_3$, 376 MHz) spectrum of compound **3l**



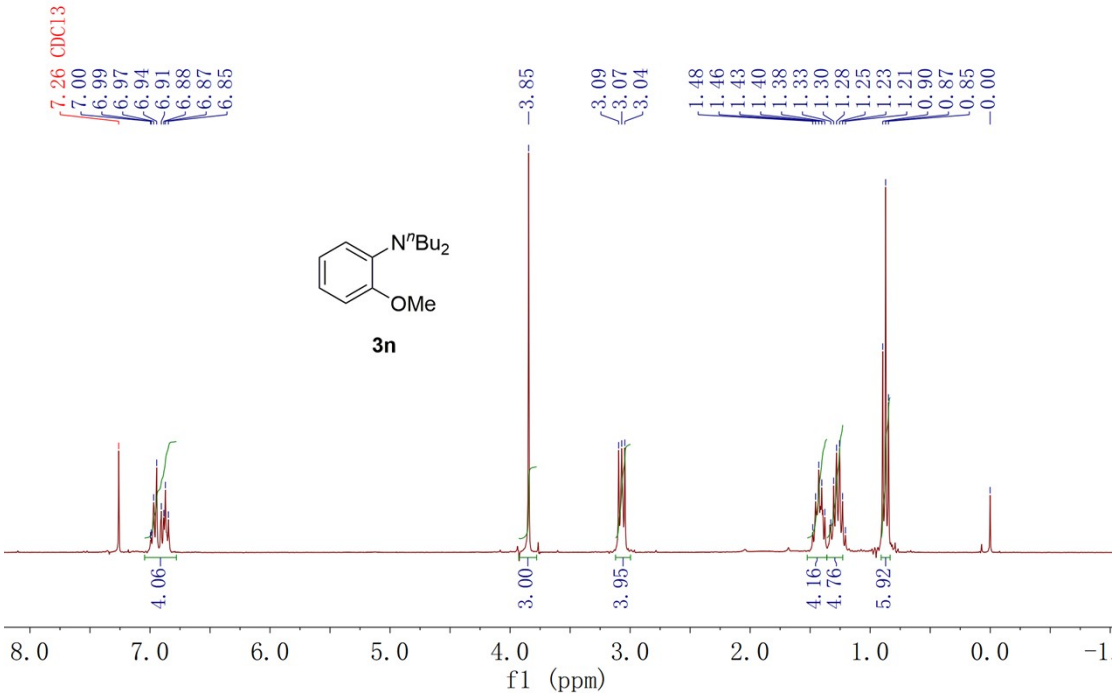
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **3m**



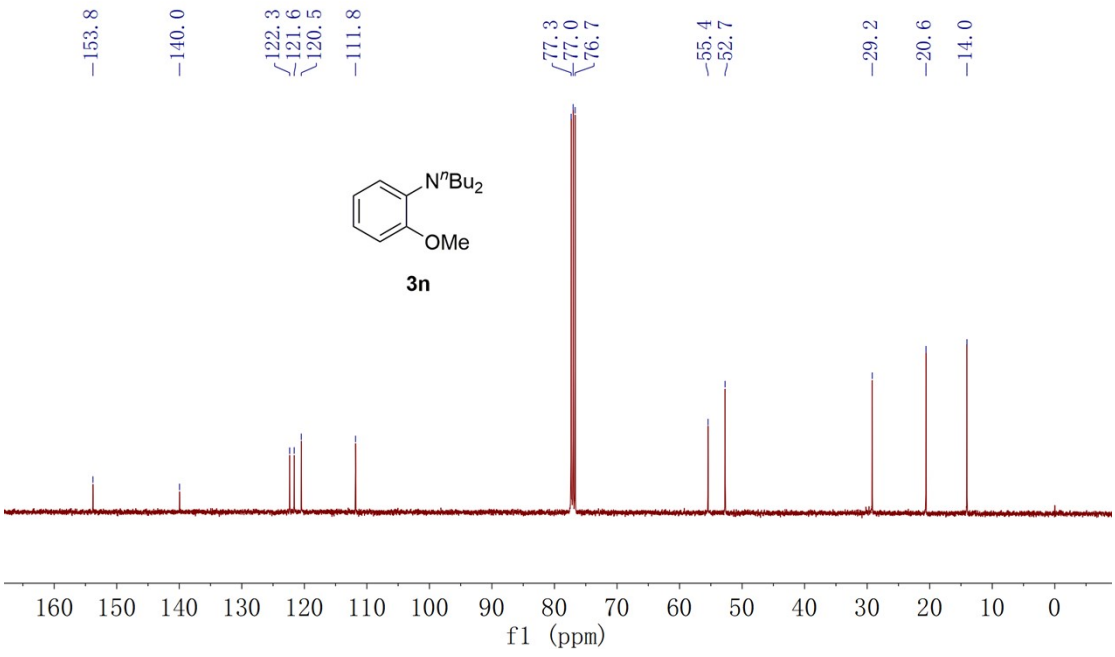
^{13}C NMR ($CDCl_3$, 101 MHz) spectrum of compound **3m**



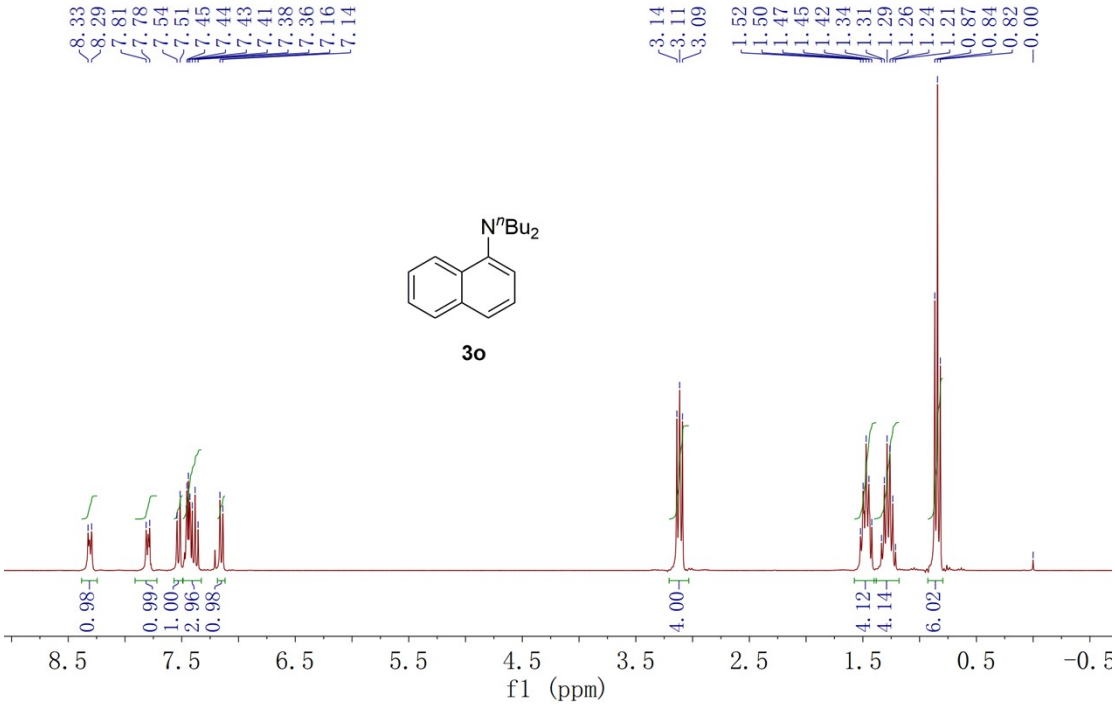
^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of compound **3n**



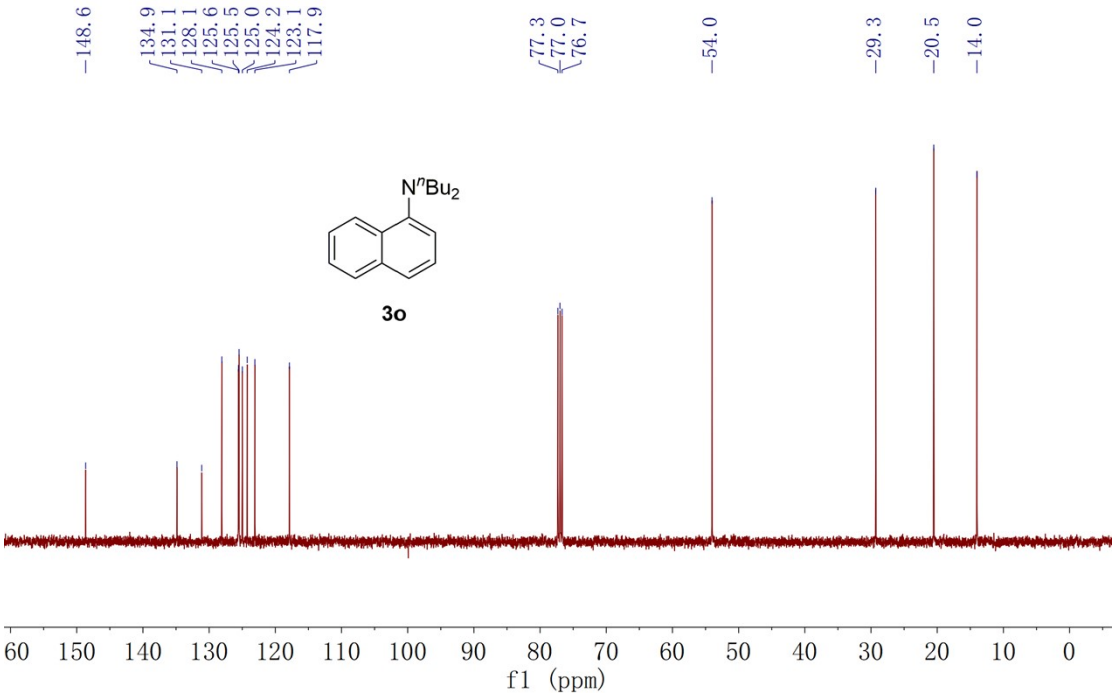
^{13}C NMR ($CDCl_3$, 101 MHz) spectrum of compound **3n**



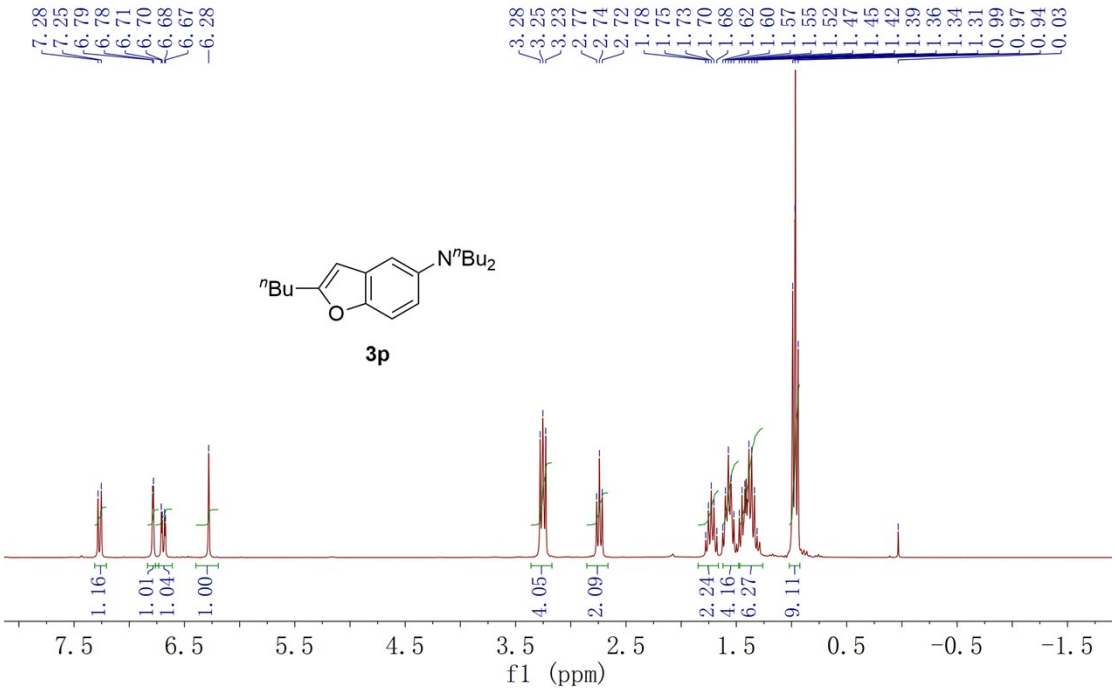
^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of compound **3o**



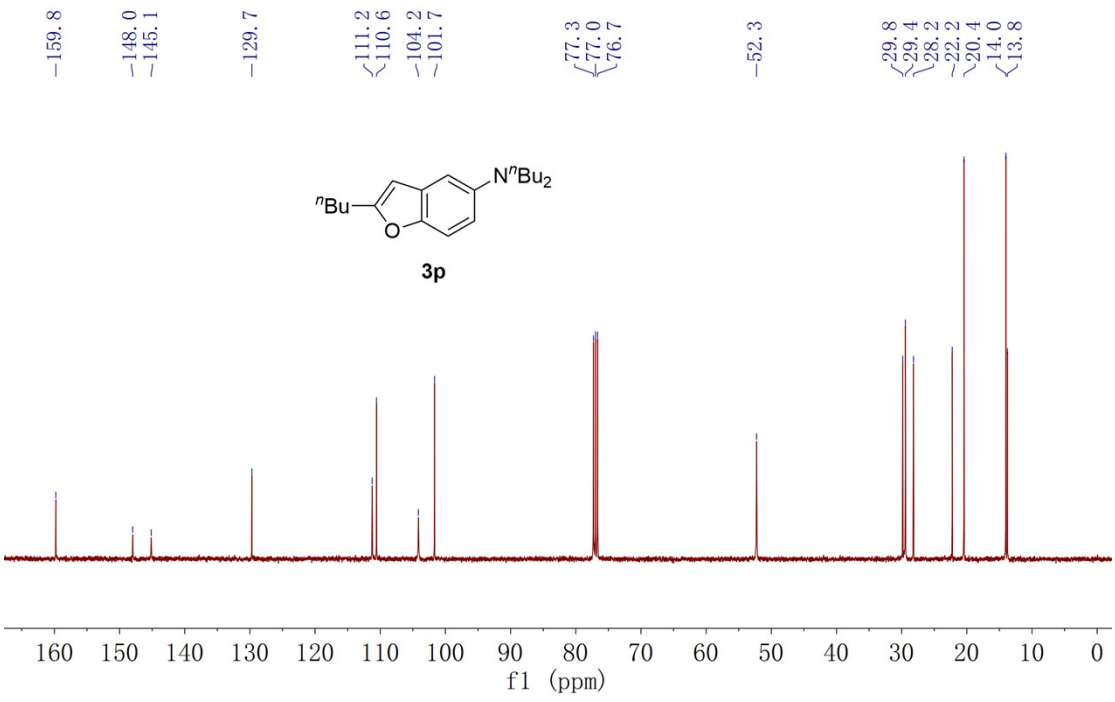
^{13}C NMR ($CDCl_3$, 101 MHz) spectrum of compound **3o**



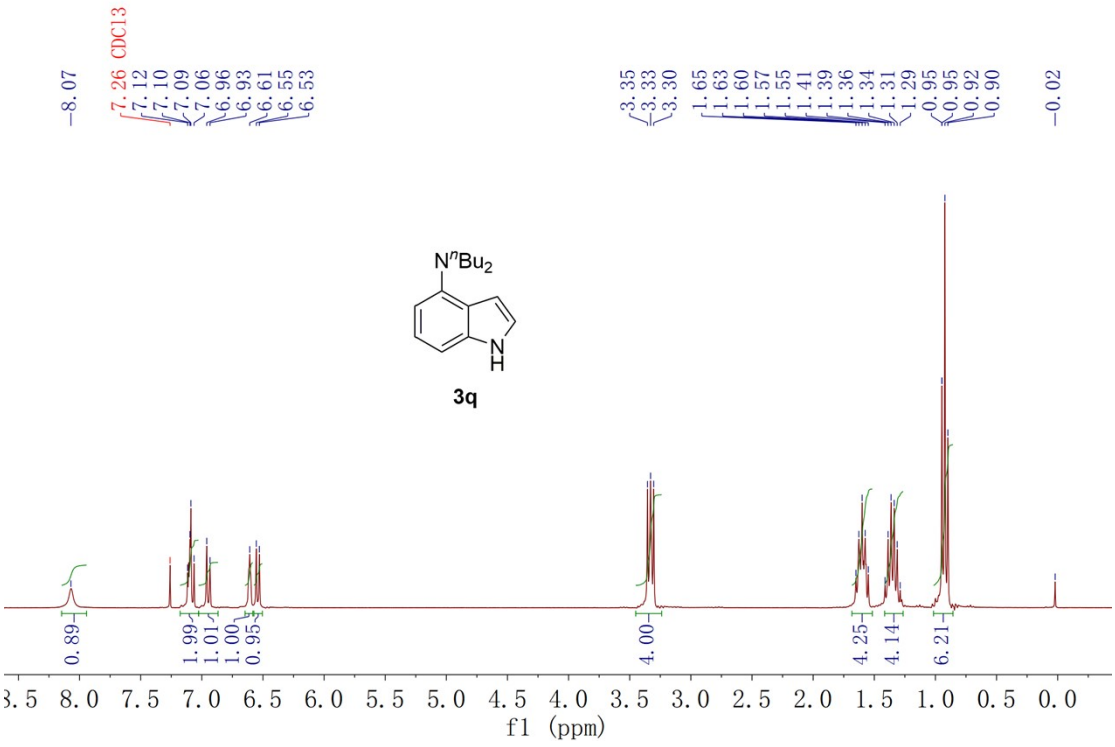
^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of compound **3p**



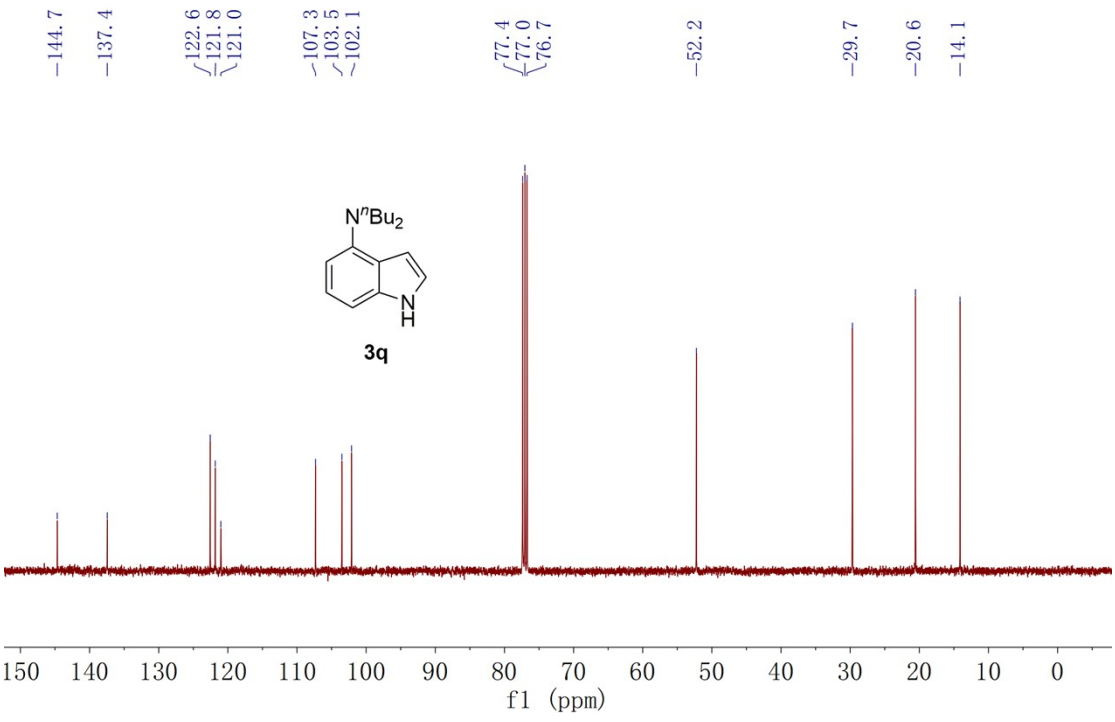
^{13}C NMR ($CDCl_3$, 101 MHz) spectrum of compound **3p**



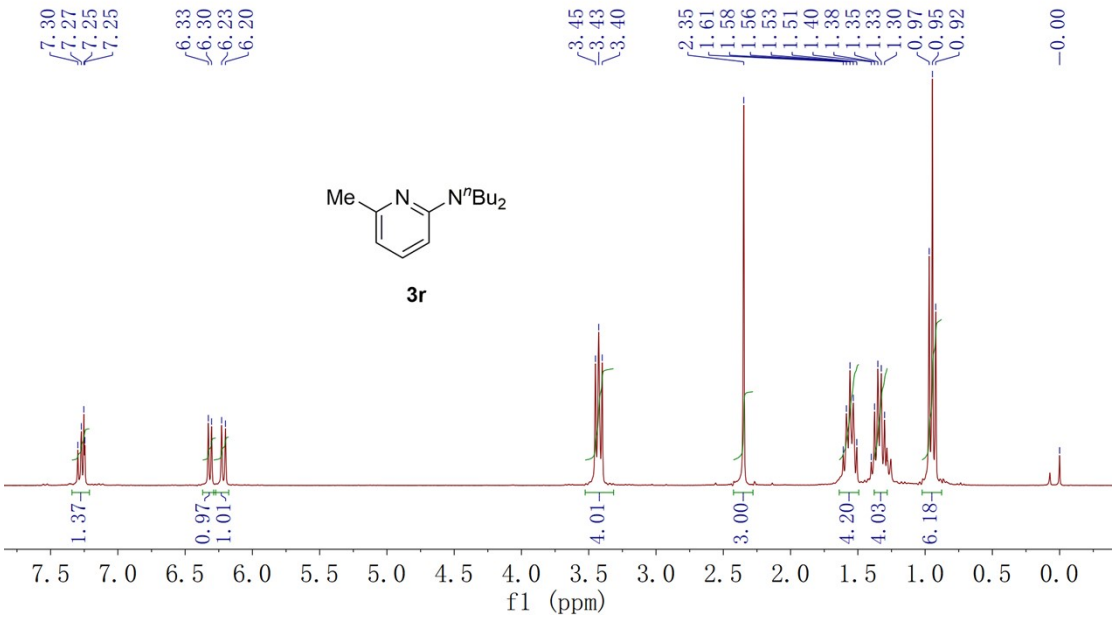
^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of compound **3q**



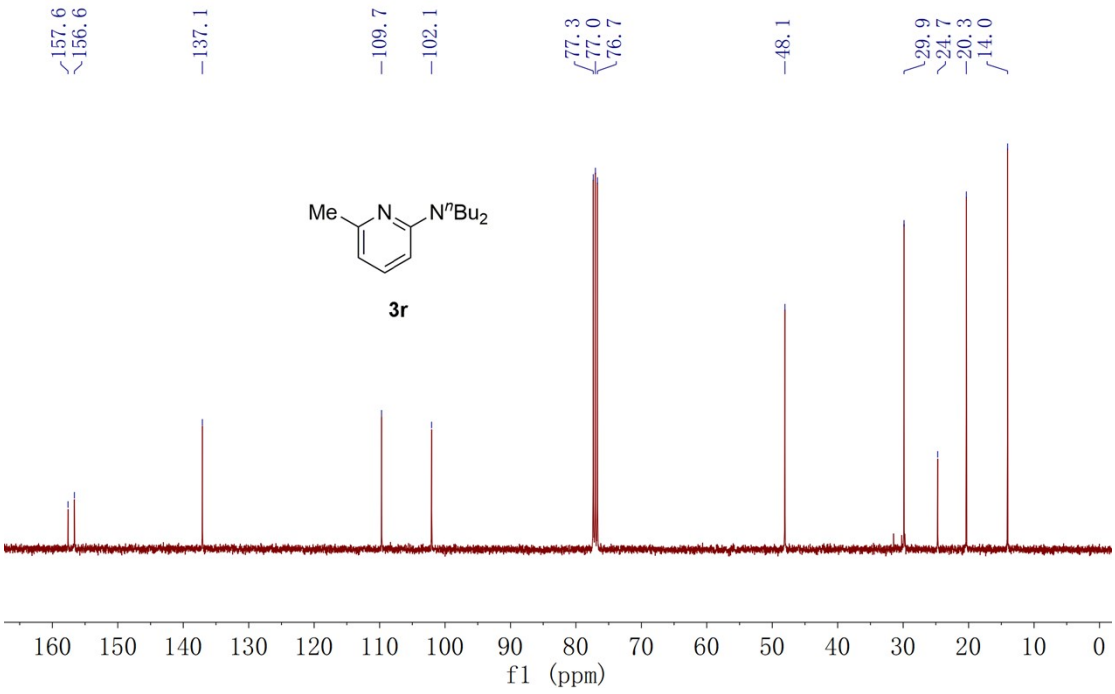
^{13}C NMR ($CDCl_3$, 101 MHz) spectrum of compound **3q**



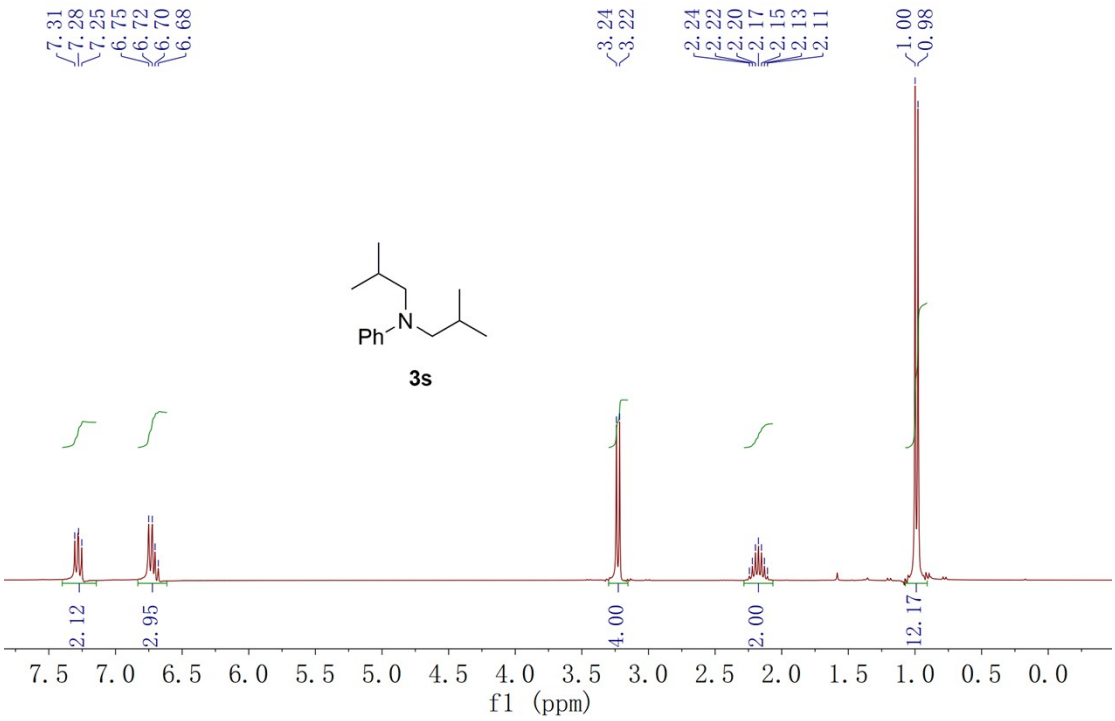
^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of compound **3r**



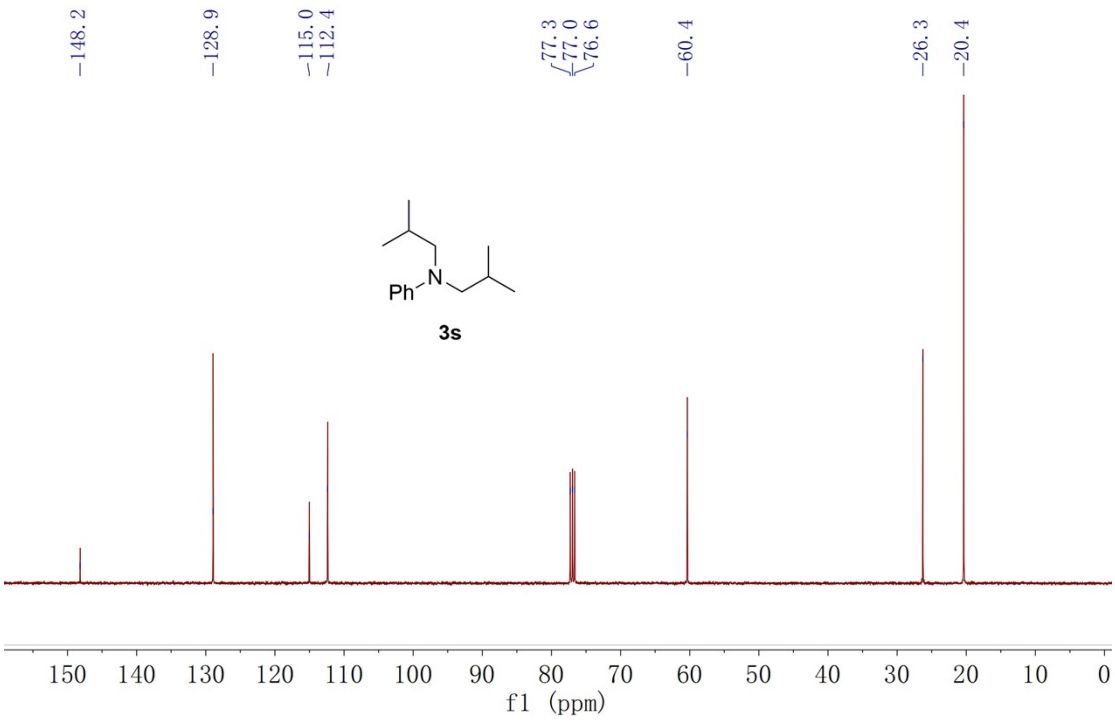
^{13}C NMR ($CDCl_3$, 101 MHz) spectrum of compound **3r**



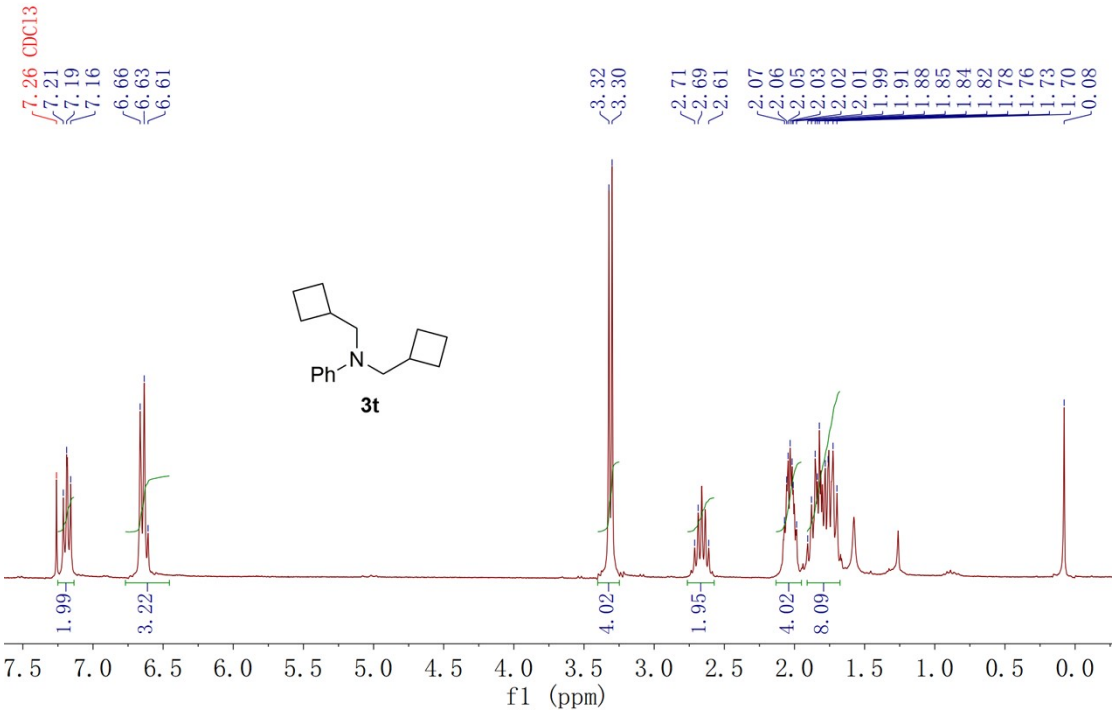
^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of compound **3s**



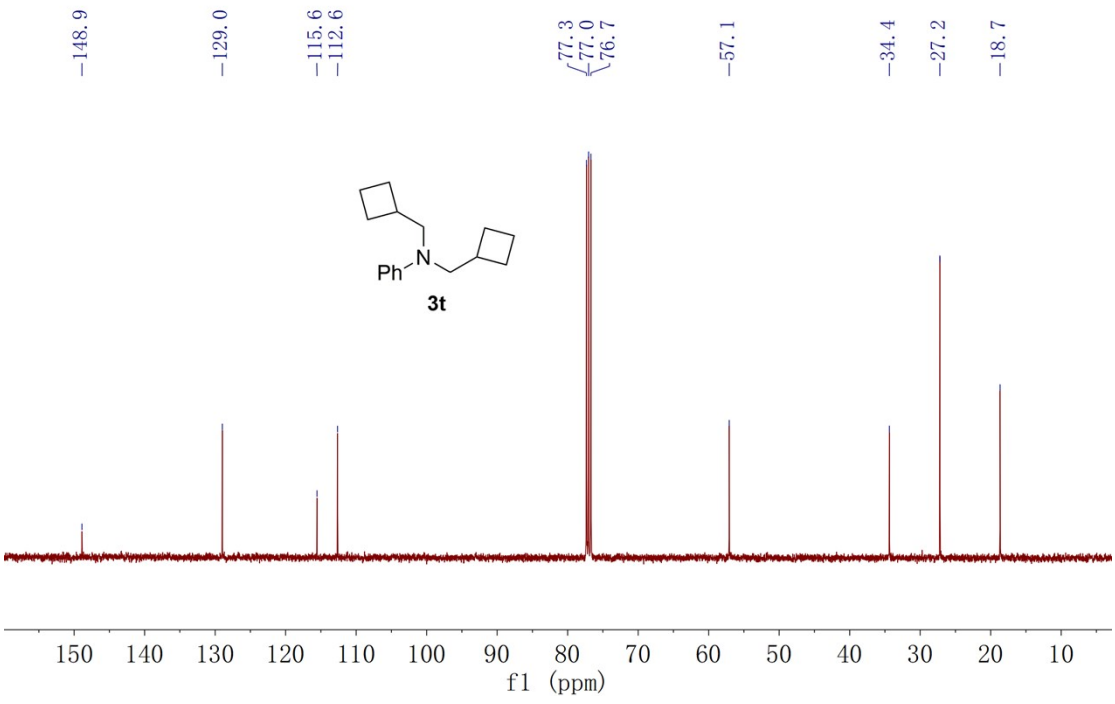
^{13}C NMR ($CDCl_3$, 101 MHz) spectrum of compound **3s**



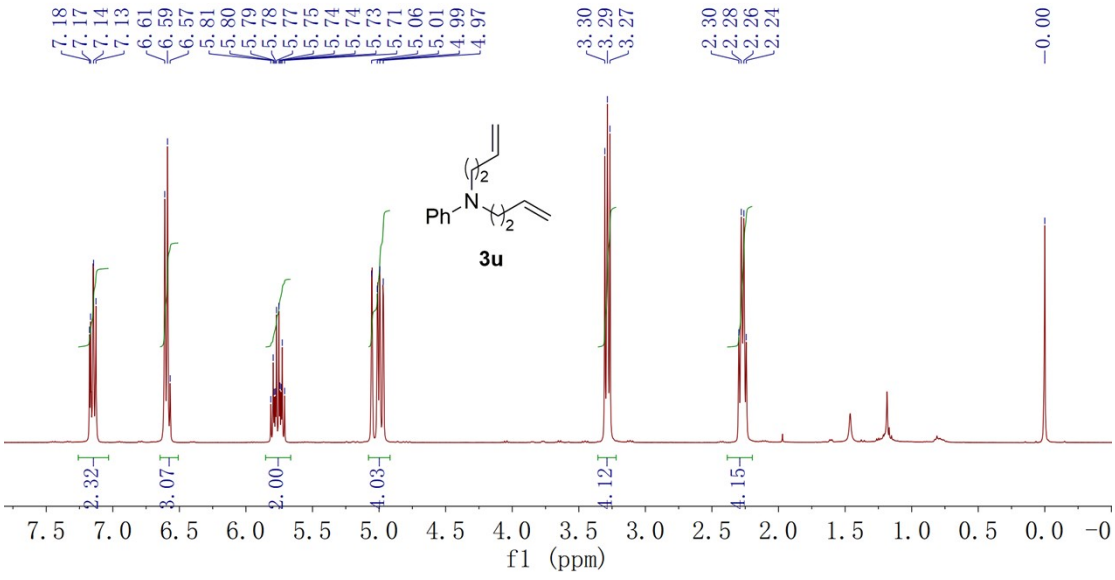
^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of compound **3t**



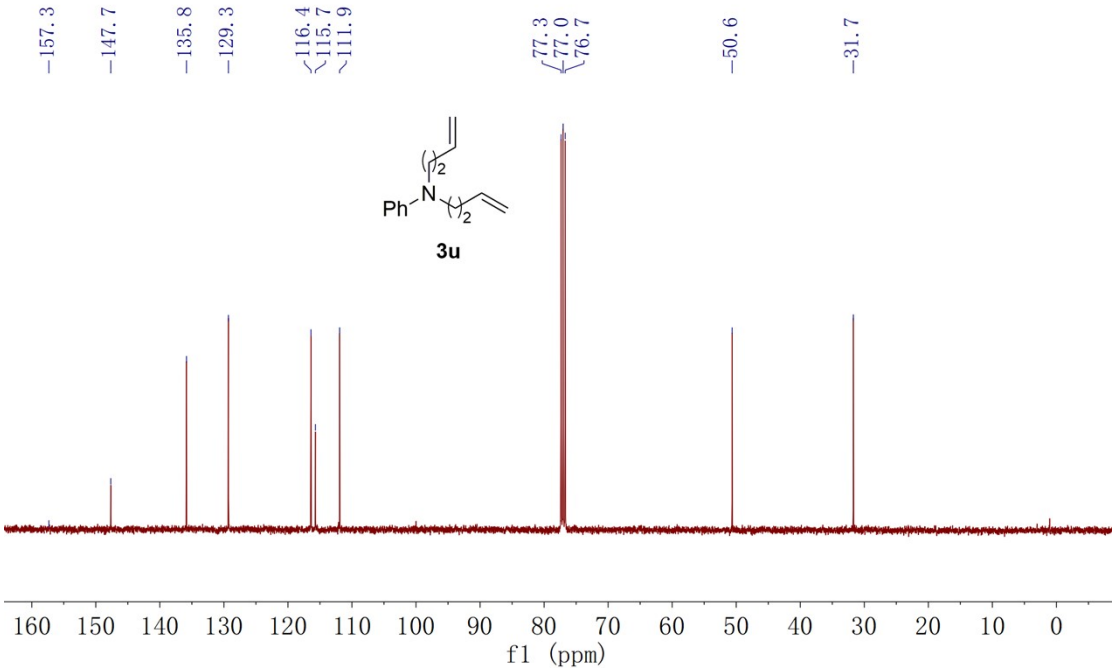
^{13}C NMR ($CDCl_3$, 101 MHz) spectrum of compound **3t**



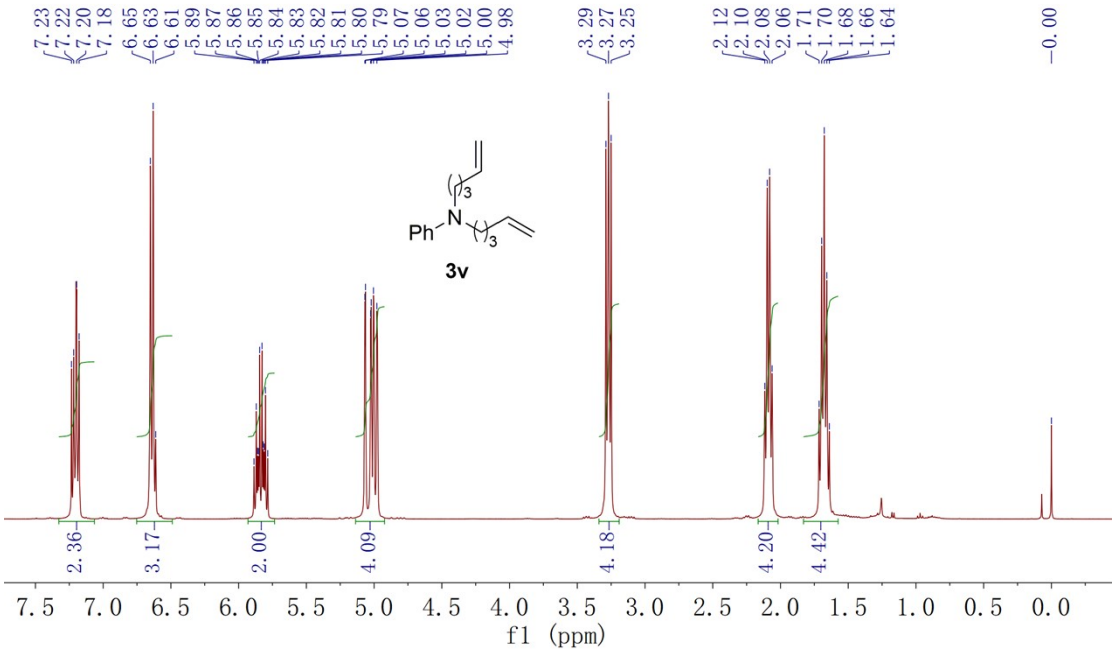
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **3u**



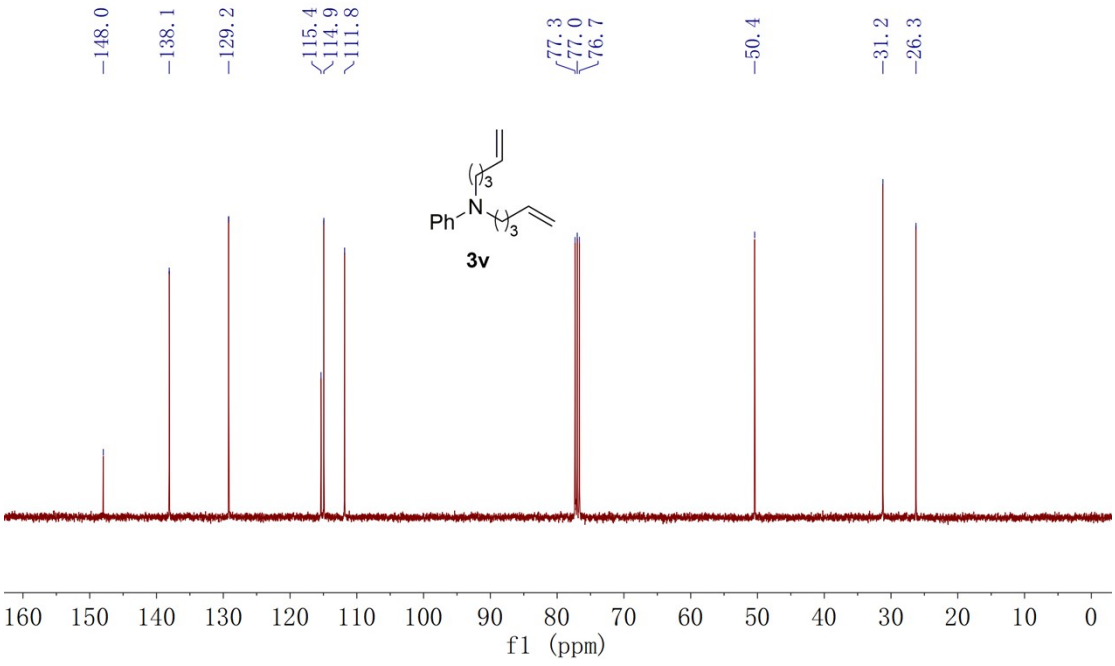
^{13}C NMR ($CDCl_3$, 101 MHz) spectrum of compound **3u**



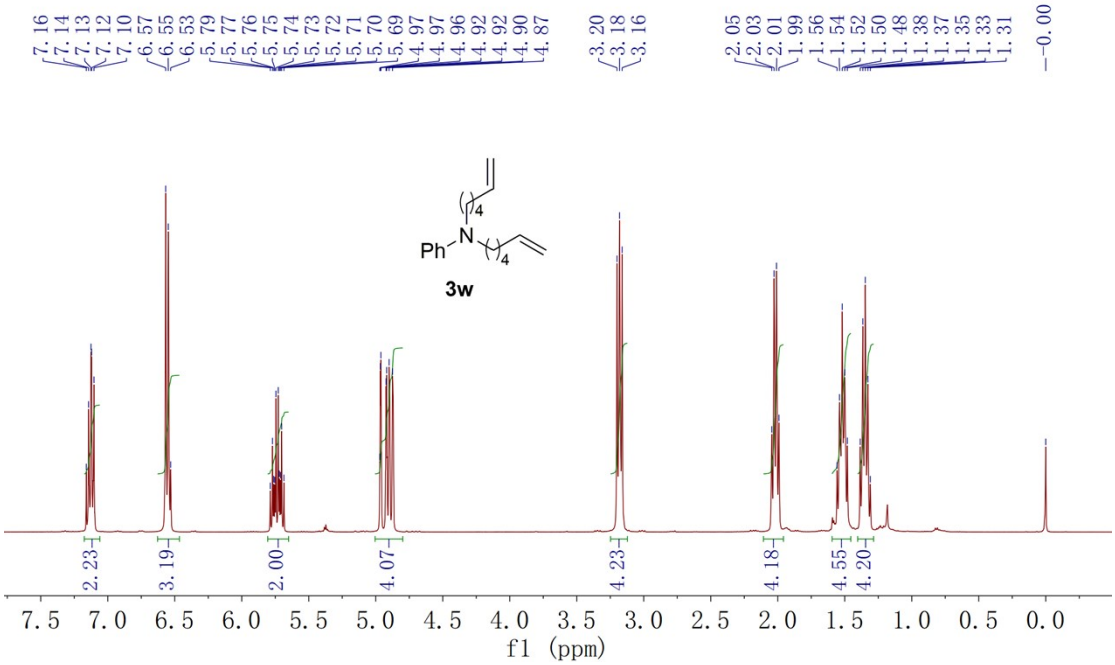
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **3v**



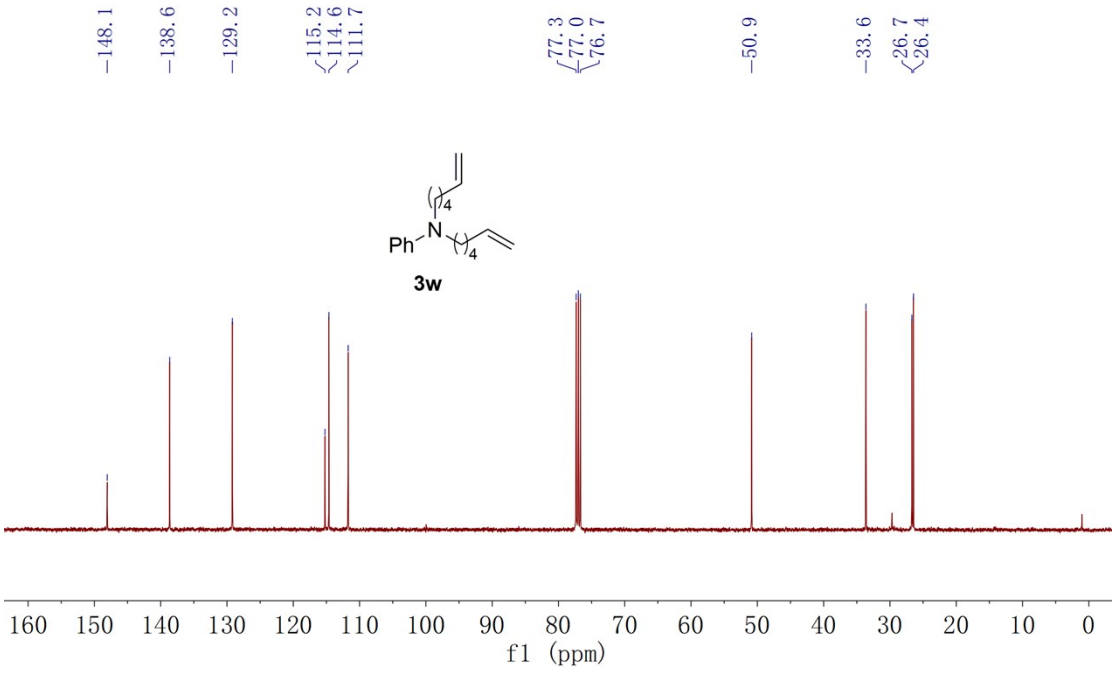
^{13}C NMR ($CDCl_3$, 101 MHz) spectrum of compound **3v**



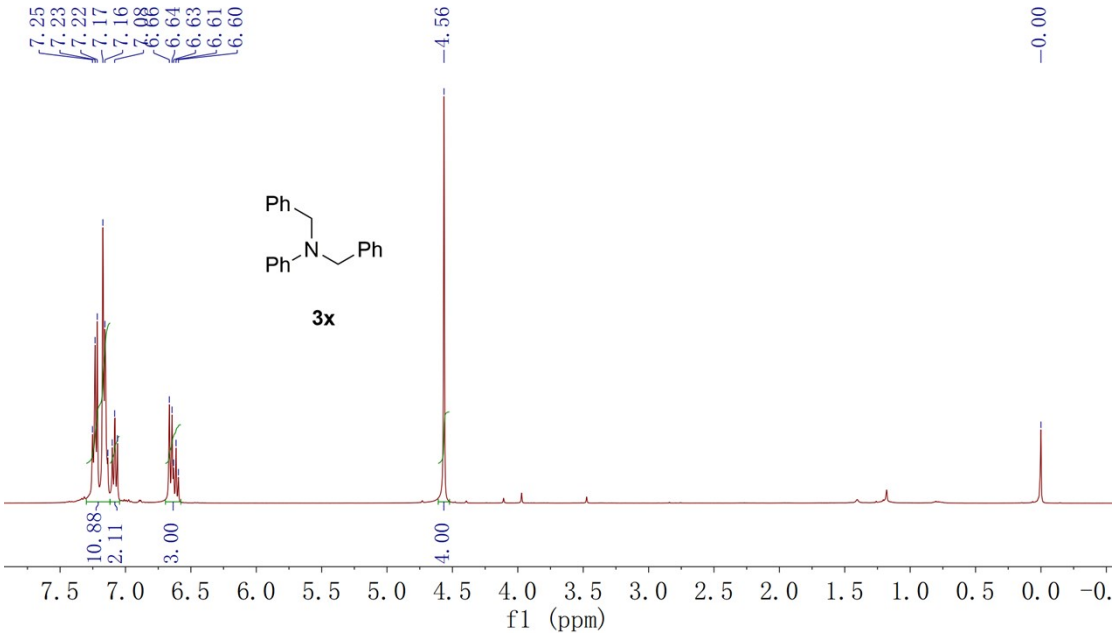
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **3w**



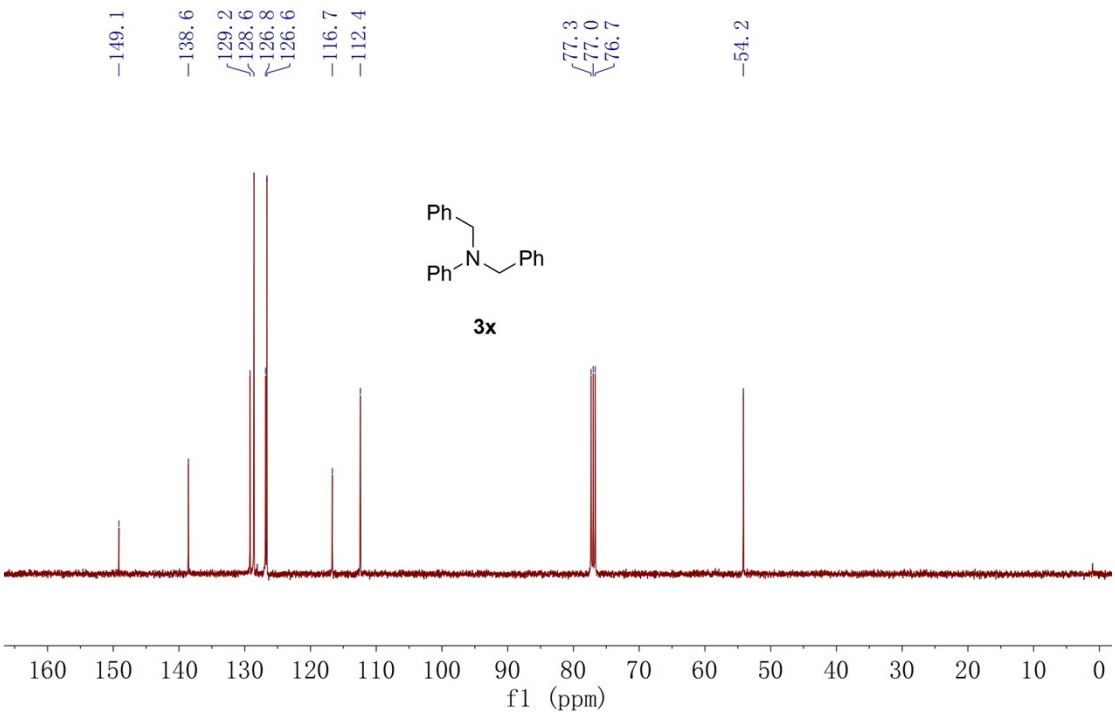
^{13}C NMR ($CDCl_3$, 101 MHz) spectrum of compound **3w**



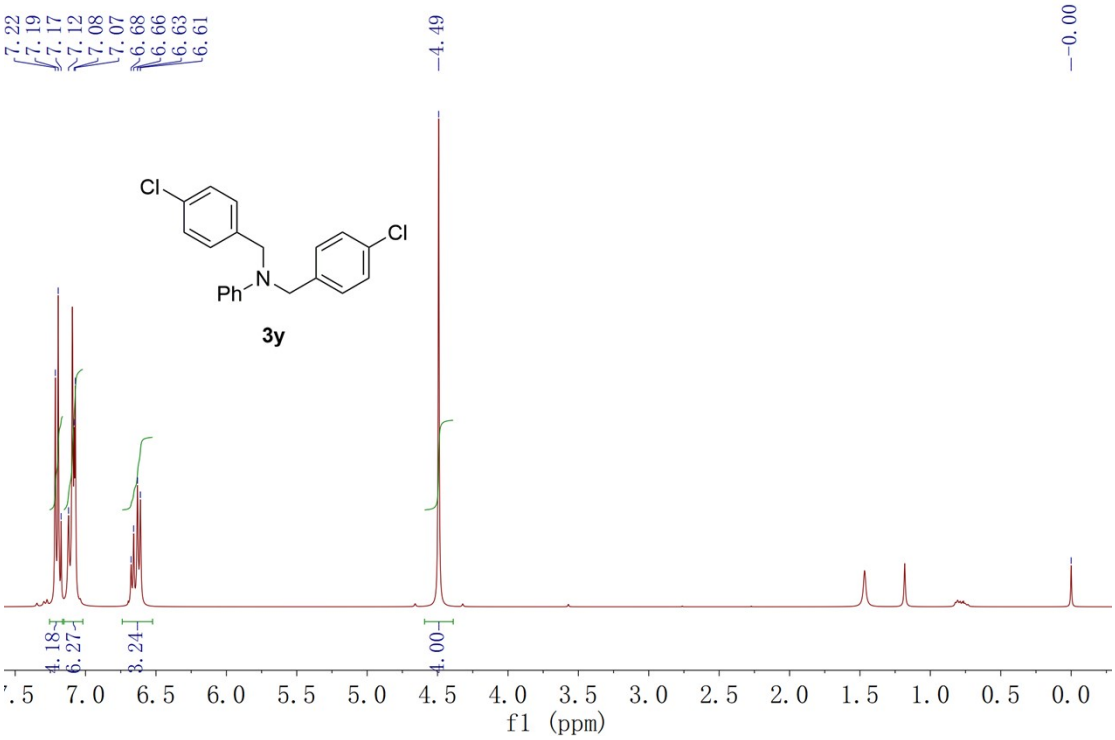
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **3x**



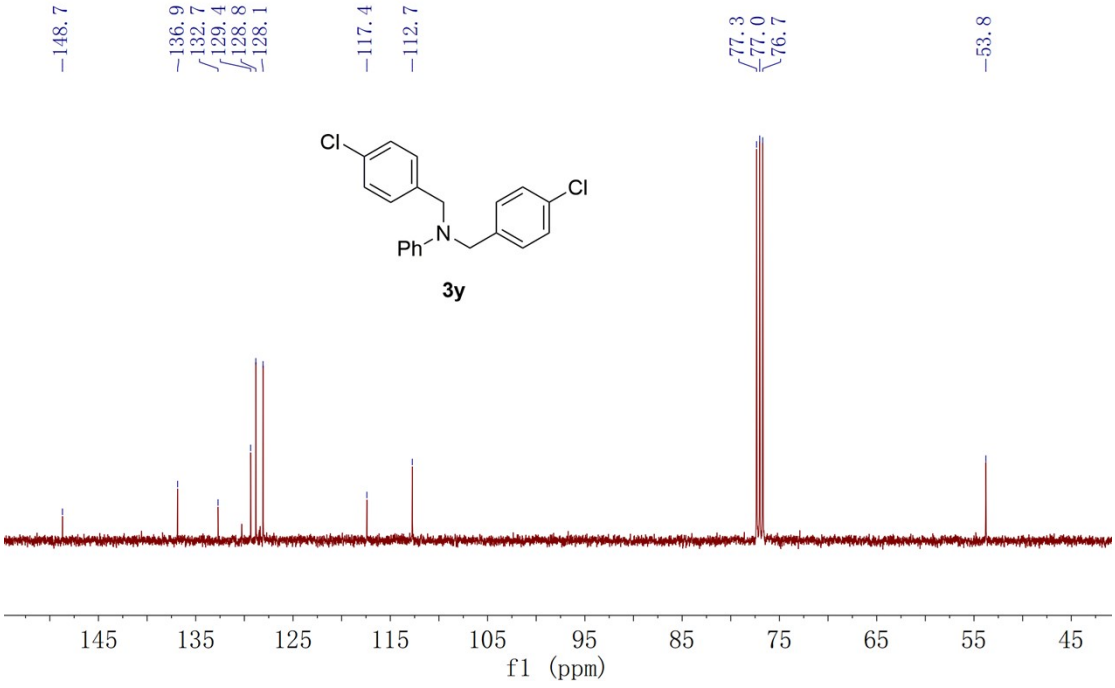
^{13}C NMR ($CDCl_3$, 101 MHz) spectrum of compound **3x**



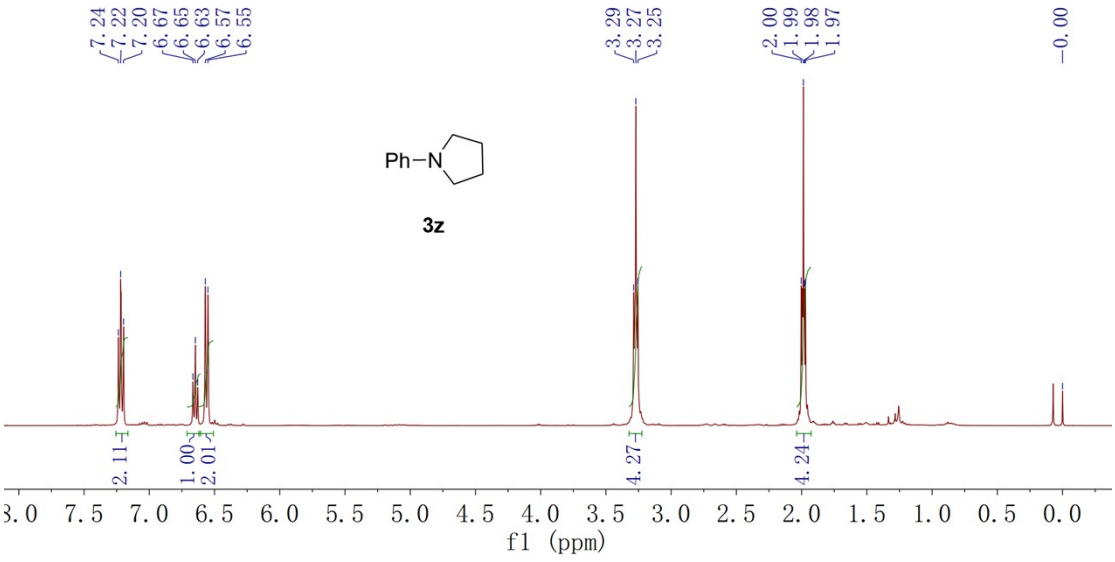
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **3y**



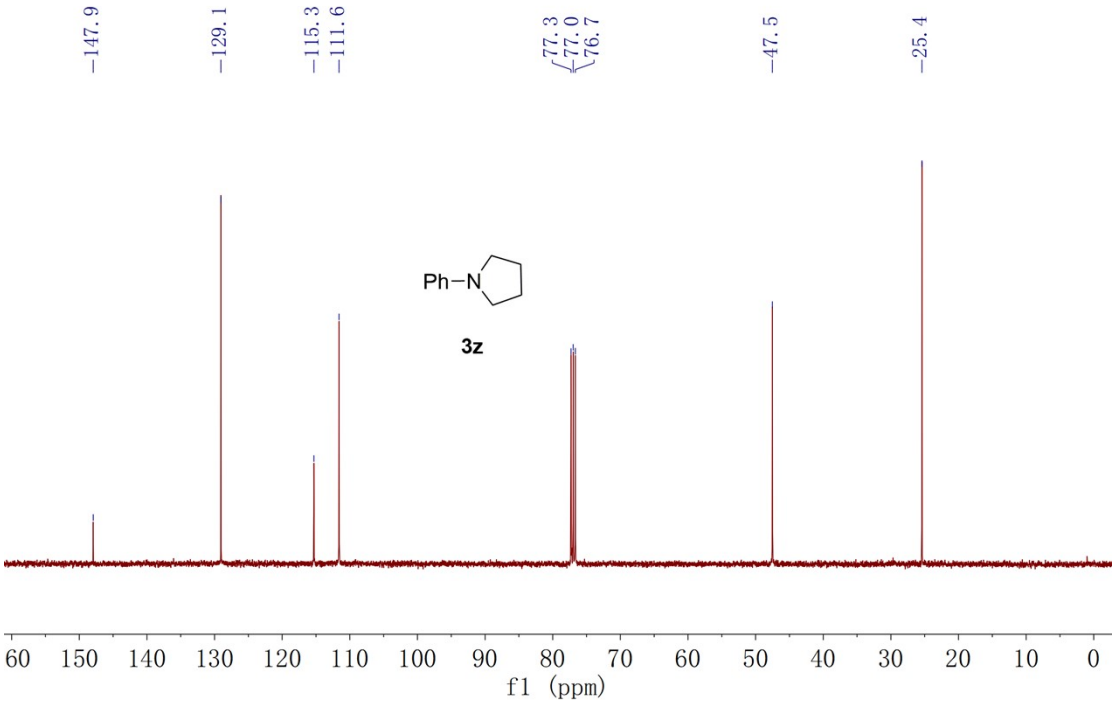
^{13}C NMR ($CDCl_3$, 101 MHz) spectrum of compound **3y**



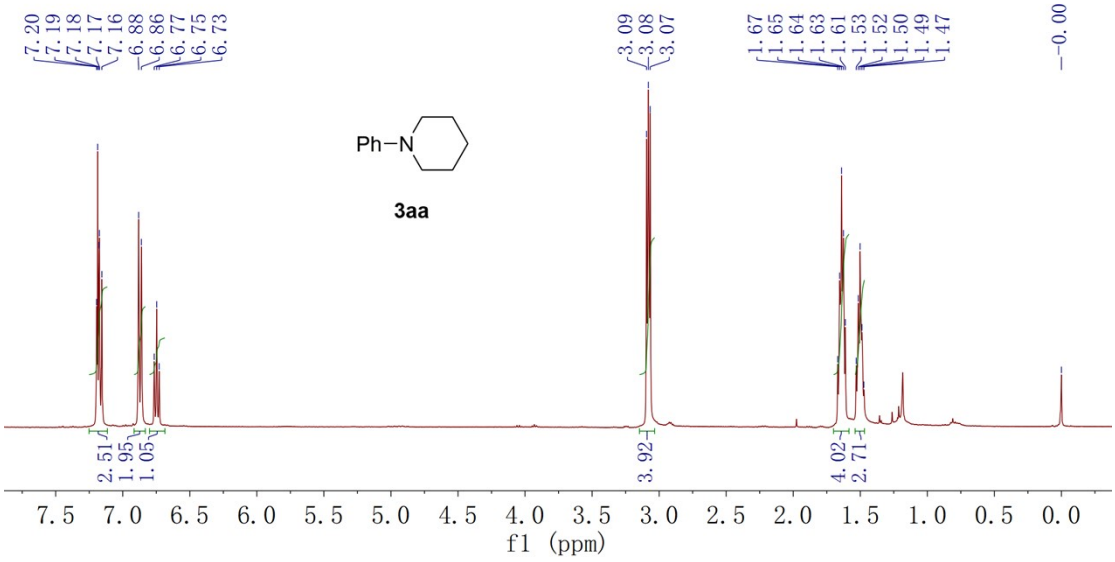
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **3z**



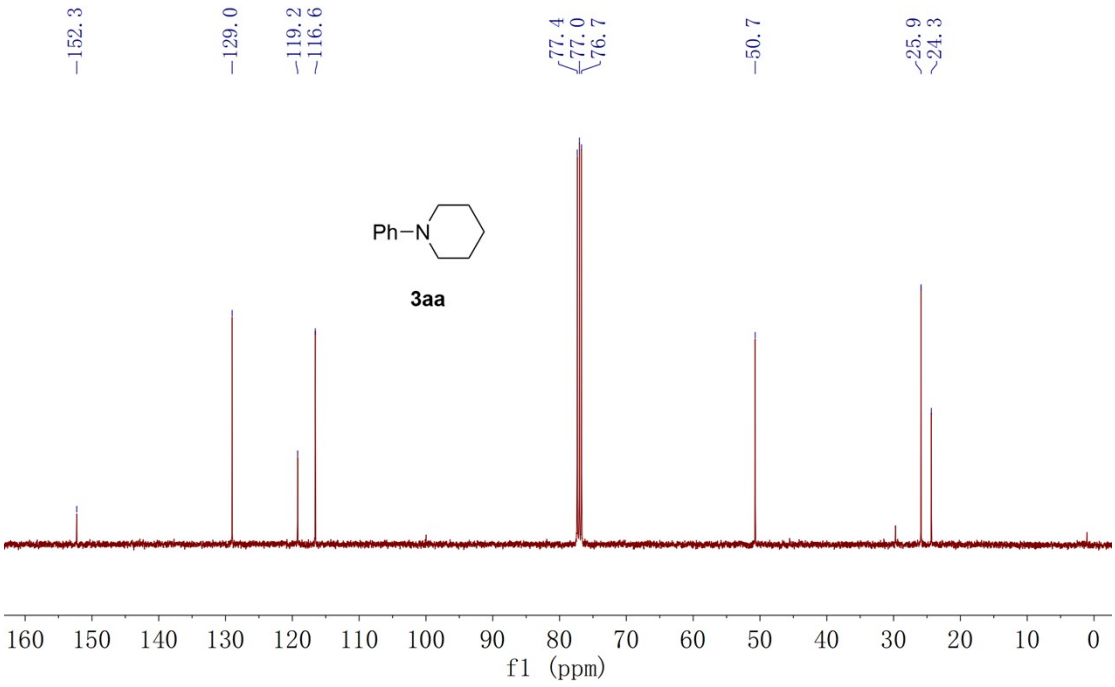
^{13}C NMR ($CDCl_3$, 101 MHz) spectrum of compound **3z**



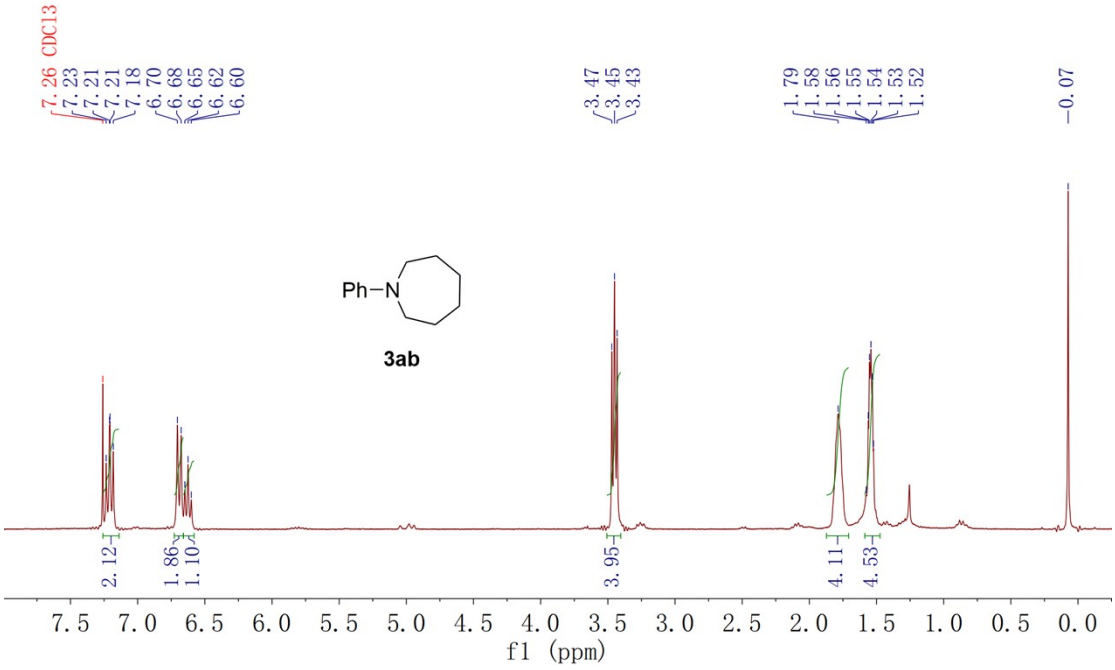
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **3aa**



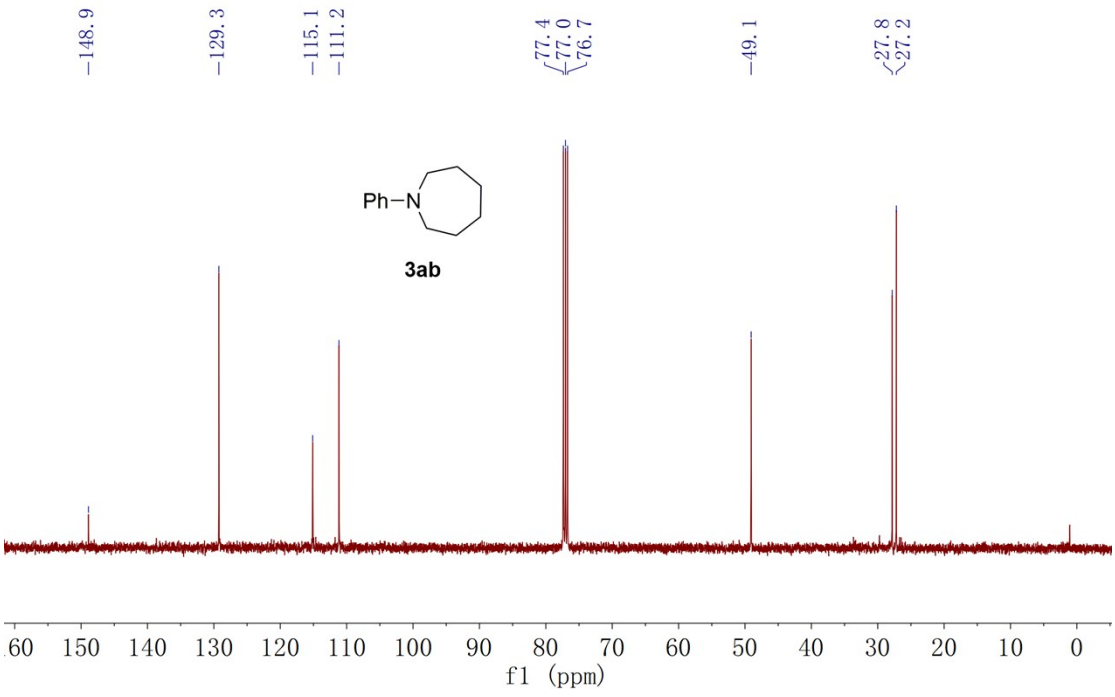
^{13}C NMR ($CDCl_3$, 101 MHz) spectrum of compound **3aa**



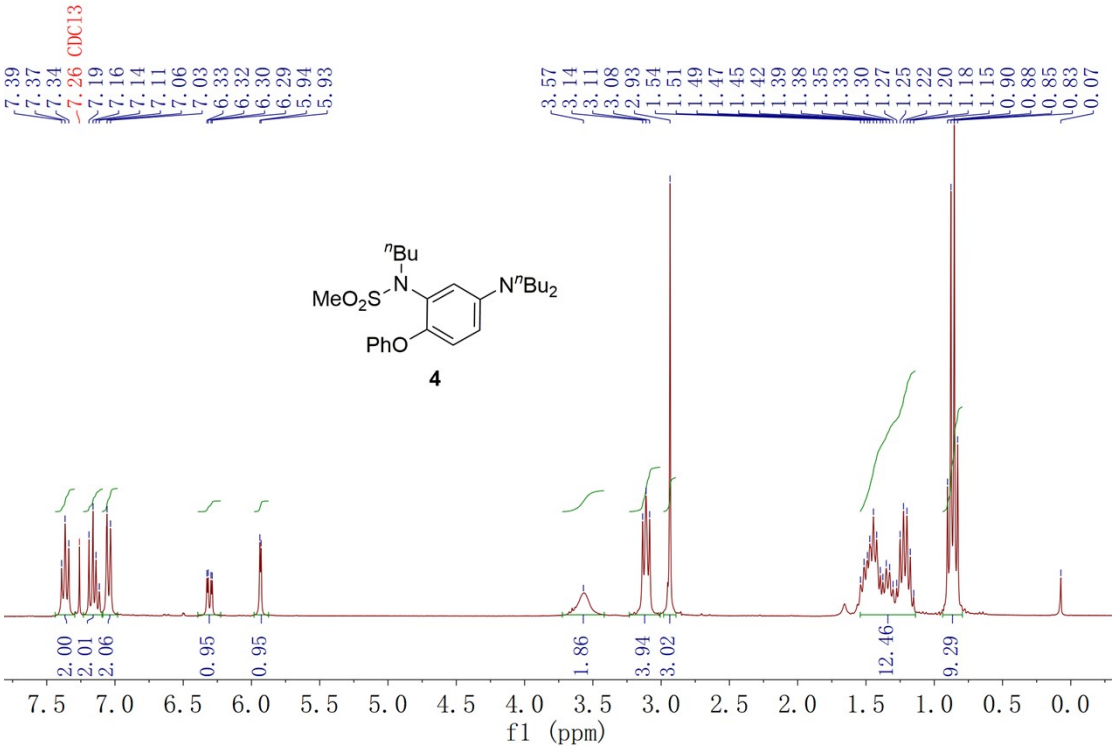
^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of compound **3ab**



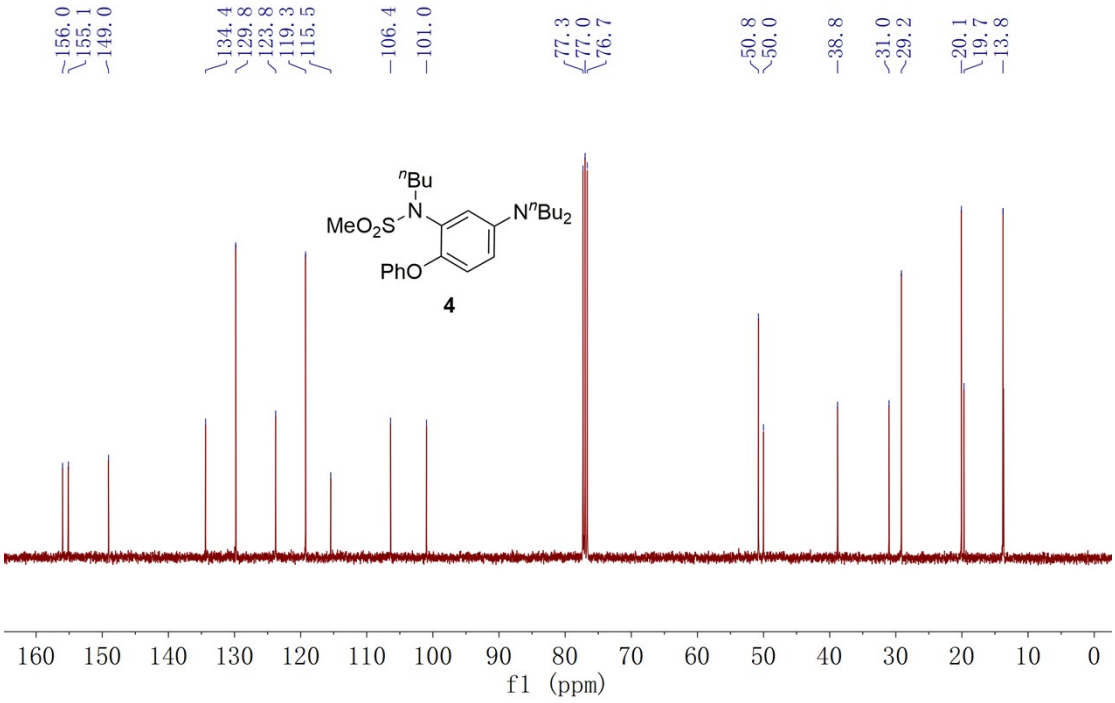
^{13}C NMR ($CDCl_3$, 101 MHz) spectrum of compound **3ab**



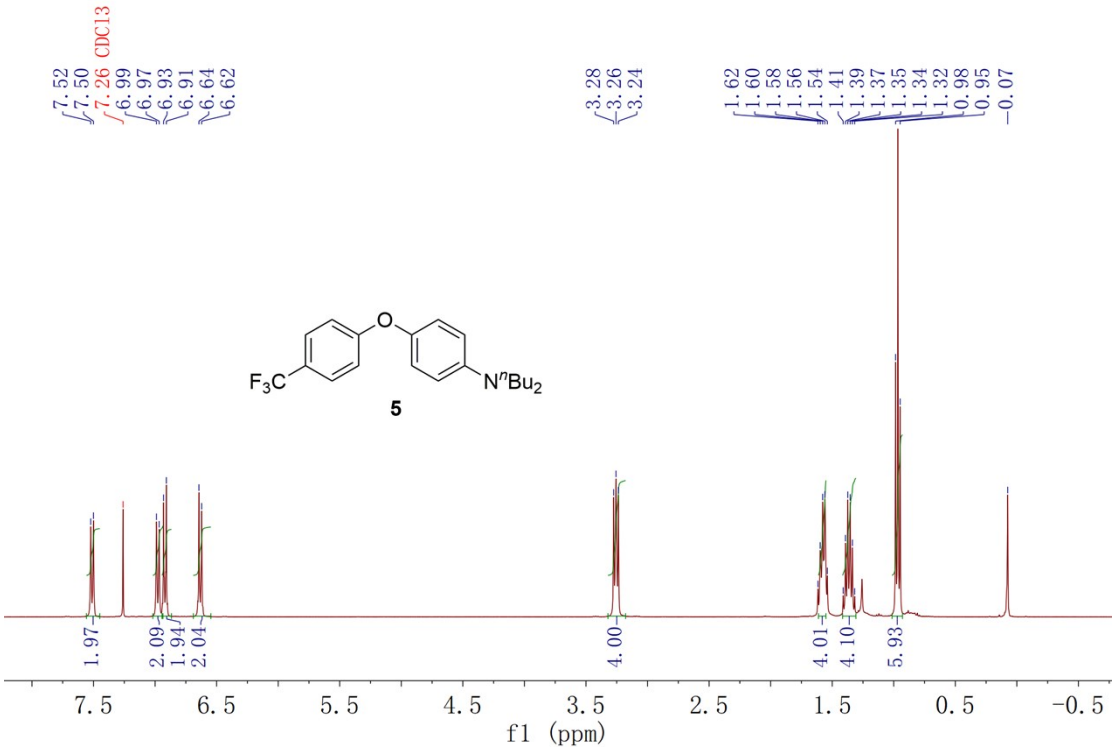
^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of compound **4**



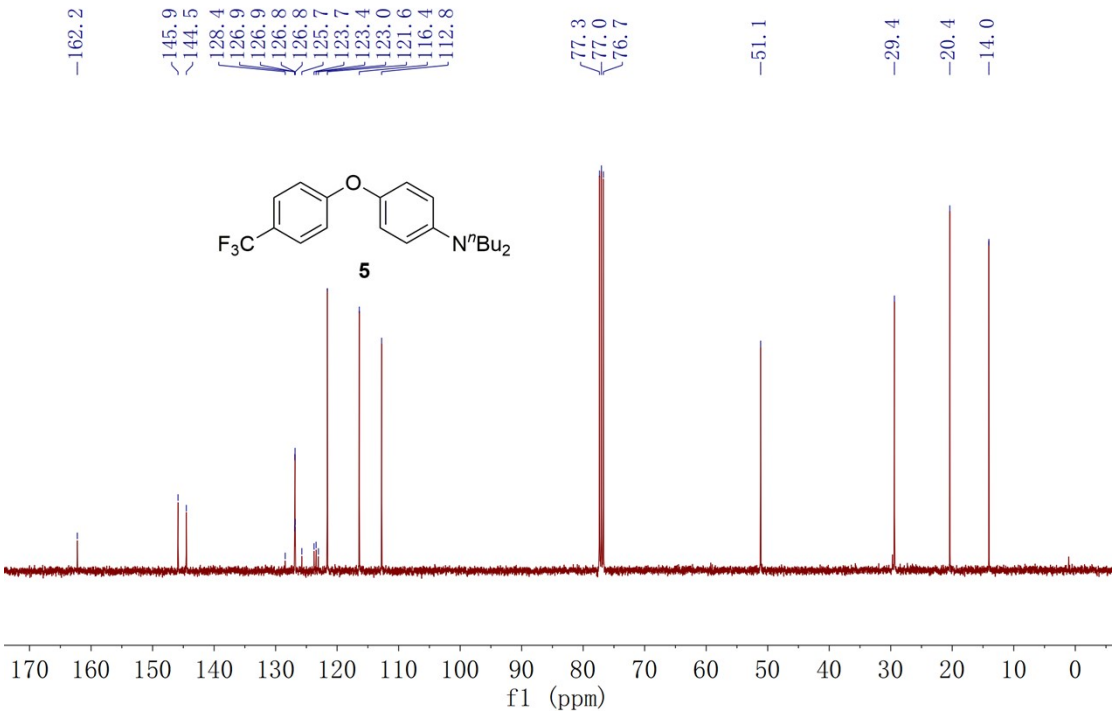
^{13}C NMR ($CDCl_3$, 101 MHz) spectrum of compound **4**



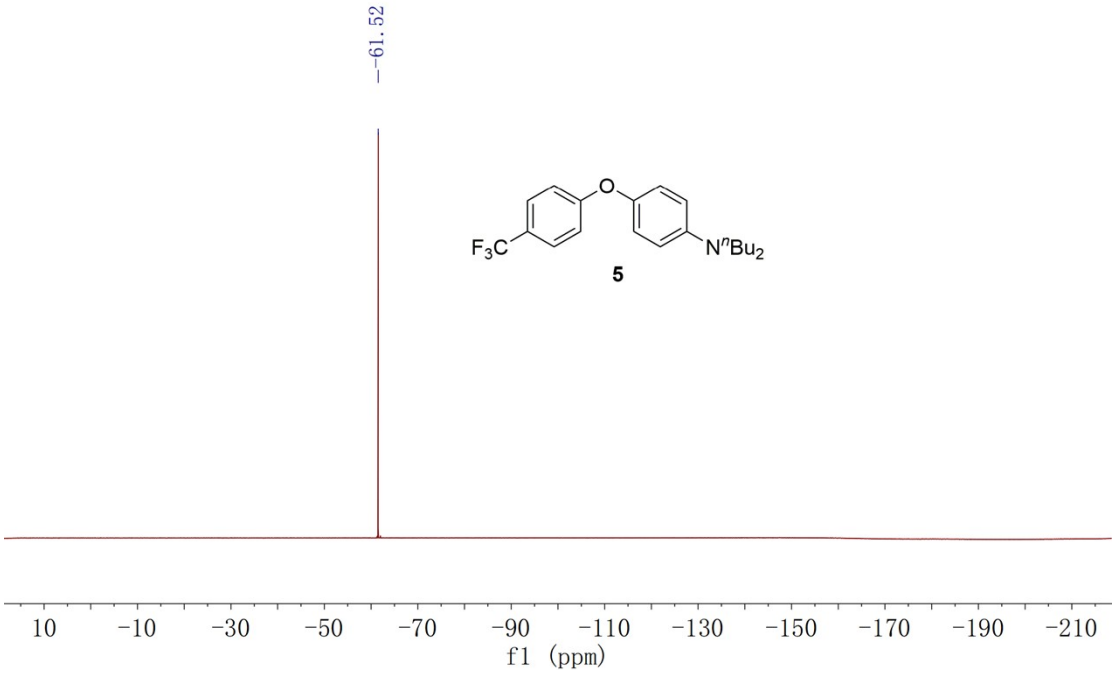
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **5**



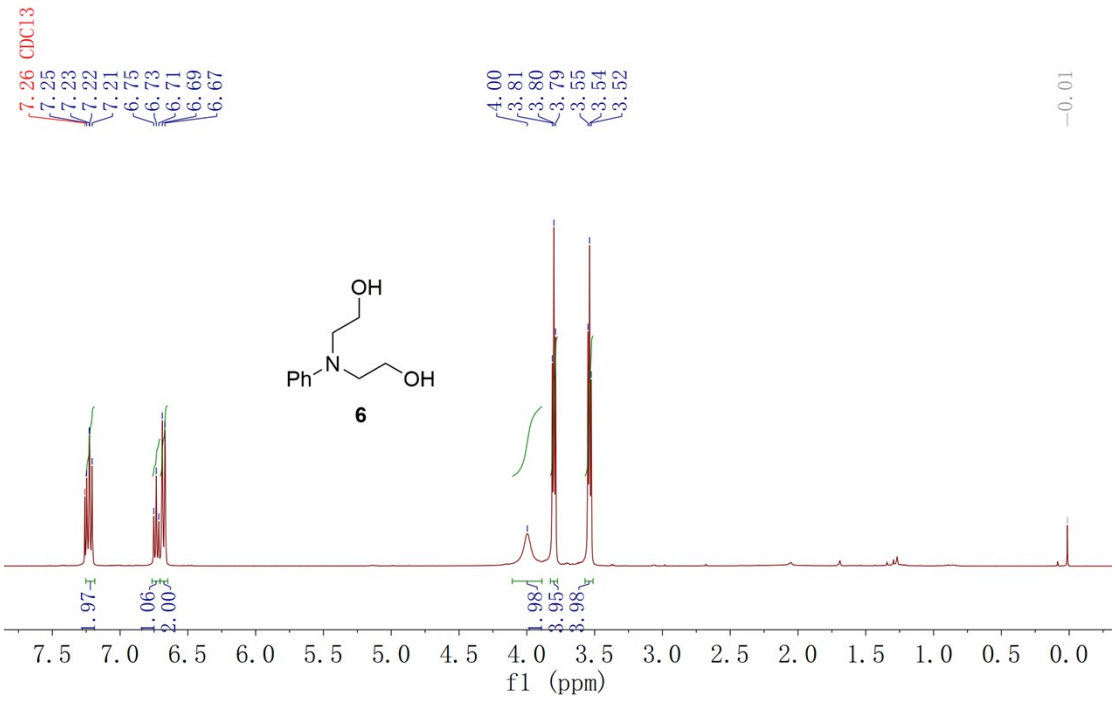
^{13}C NMR ($CDCl_3$, 101 MHz) spectrum of compound **5**



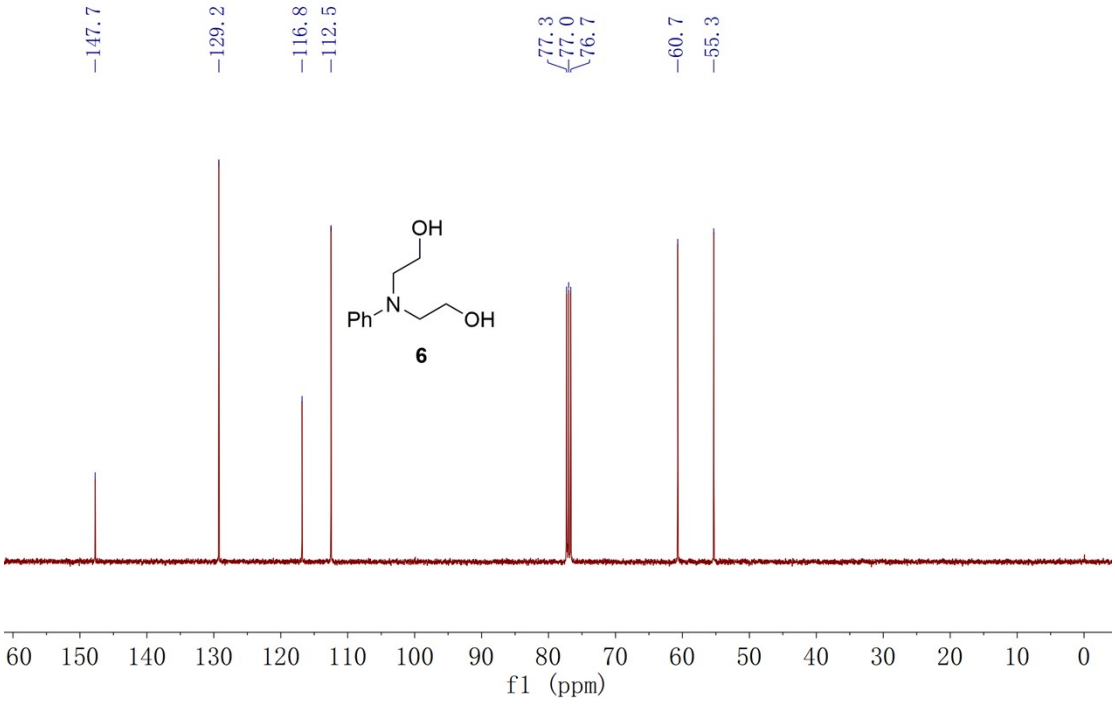
^{19}F NMR ($CDCl_3$, 376 MHz) spectrum of compound **5**



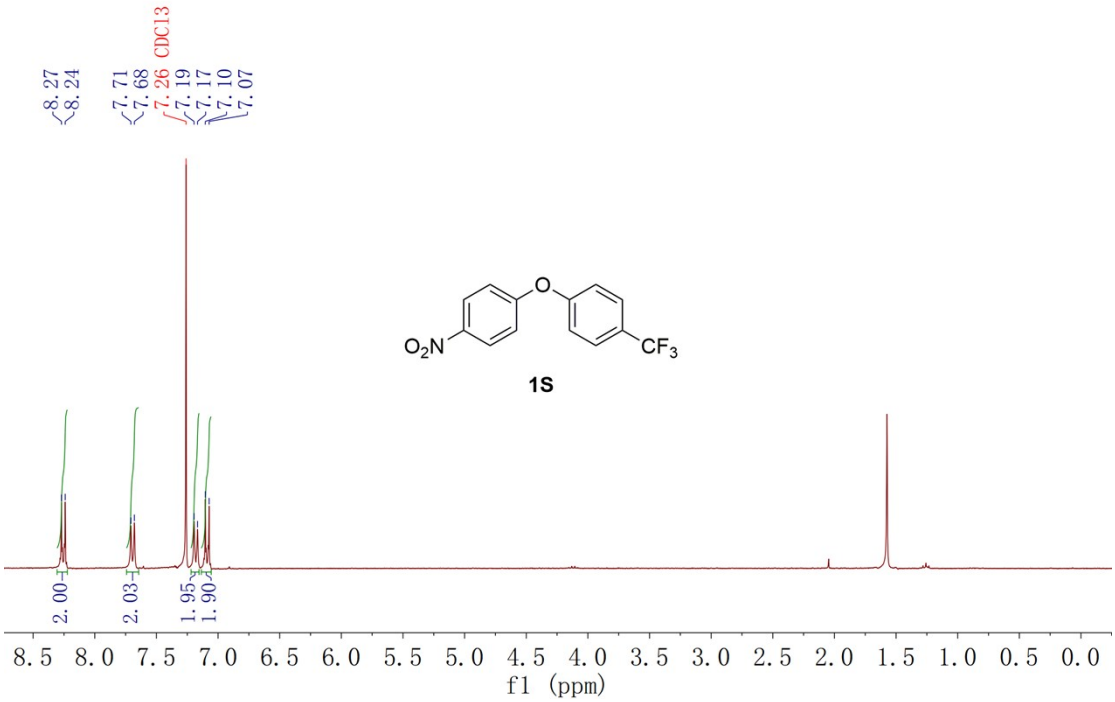
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **6**



^{13}C NMR ($CDCl_3$, 101 MHz) spectrum of compound **6**



^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of compound **1s**



^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of compound **10**