# Supporting Information

## Palladium-catalyzed aminative cross-coupling of aryl thianthrenium salts with arylboronic acid and DPPH

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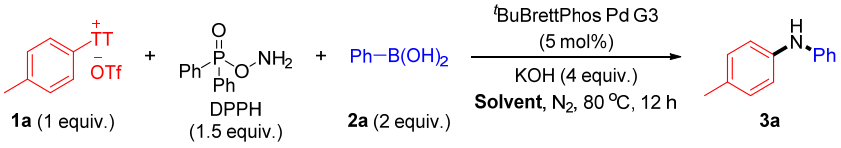
## General information

Unless otherwise stated, all reagents (including all arylboronic acids **2**) were purchased from commercial suppliers and used without further purification. Aryl thianthrenium salts **1** were prepared by following reported methods.[1-3] Analytical thin layer chromatography (TLC) was performed using silica gel plate (0.2 mm thickness). Subsequent to elution, plates were visualized using UV radiation (254 nm). Flash chromatography was performed using Merck silica gel (200-300 mesh) for column chromatography with freshly distilled solvents. IR spectra were recorded on a FT-IR spectrophotometer using KBr optics. $^{1}H$, $^{13}C$, and $^{19}F$ NMR spectra were recorded in $CDCl_3$ on Bruker Avance or Jeol 400 MHz spectrometers. Tetramethylsilane (TMS) served as internal standard for $^{1}H$, $^{13}C$, and $^{19}F$ NMR analysis. High resolution mass spectra (HRMS) were obtained on a Waters Q-TOF Premier Spectrometer (ESI source).

## Optimization of reaction conditions

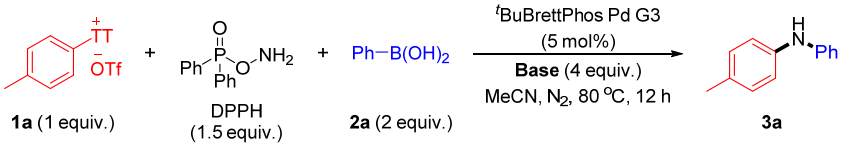
**Table S1.** Optimization of reaction conditions by using different solvents[a]




| Entry | Solvent | Yield (%)[b] |
|---|---|---|
| 1 | MeCN | 51 |
| 2 | PhMe | 0 |
| 3 | $PhCF_3$ | 21 |
| 4 | DMSO | 0 |
| 5 | DMF | 8 |
| 6 | DMA | trace |
| 7 | NMP | 15 |
| 8 | CPME | trace |
| 9 | 1,4-dioxane | 0 |
| 10 | THF | 45 |

[a] The reactions were performed at 80 °C for 12 h under nitrogen atmosphere by using **1a** (0.5 mmol), **2a** (1 mmol), DPPH (0.75 mmol), KOH (2 mmol), and $^{t}$BuBrettPhos Pd G3 (5 mol%) in anhydrous solvent (3 mL). [b] Yields were determined by NMR analysis of crude reaction mixture after work-up by using 1,3,5-trimethoxybenzene as an internal standard.

**Table S2.** Optimization of reaction conditions by using different bases[a]



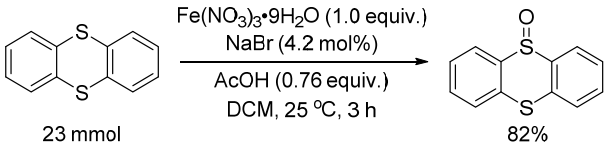

| Entry | Base | Yield (%)[b] |
|---|---|---|
| 1 | $K_3PO_4$ | 0 |
| 2 | $NaHCO_3$ | 0 |
| 3 | $Na_2CO_3$ | 0 |
| 4 | $Cs_2CO_3$ | 60 |
| 5 | LiOH | 0 |
| 6 | NaOH | 49 |
| 7 | KOH | 51 |
| 8 | $^t$BuOLi | 32 |
| 9 | $^t$BuONa | 75 |
| 10 | $^t$BuOK | trace |
| 11 | $CH_3ONa$ | 67 |
| 12 | DBU | 22 |
| 13 | DABCO | 0 |

[a] The reactions were performed at 80 °C for 12 h under nitrogen atmosphere by using **1a** (0.5 mmol), **2a** (1 mmol), DPPH (0.75 mmol), base (2 mmol), and $^t$BuBrettPhos Pd G3 (5 mol%) in anhydrous MeCN (3 mL). [b] Yields were determined by NMR analysis of crude reaction mixture after work-up by using 1,3,5-trimethoxybenzene as an internal standard.

# Experimental procedure

### 1. Preparation of aryl thianthrenium salts

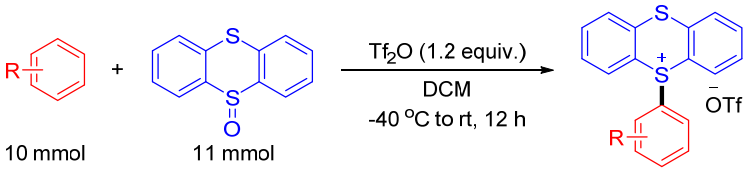
### 1.1 Synthesis of thianthrene *S*-oxide[1]




A 100 mL round-bottom flask equipped with a magnetic stir bar was charged with DCM (50 mL), thianthrene (5.0 g, 23 mmol, 1.0 equiv.), sodium bromide (0.10 g, 0.97 mmol, 4.2 mol%), iron(III) nitrate nonahydrate (9.3 g, 23 mmol, 1.0 equiv.), and acetic acid (1.0 mL, 1.1 g, 17 mmol, 0.76 equiv.). The reaction mixture was stirred at 25 °C for 3 h. After completion of the reaction as monitored by TLC, water (50 mL) was added to the reaction mixture. The organic layer was separated and the aqueous layer was extracted with DCM (50 mL x 2). The organic layers were combined, dried over $Na_2SO_4$, filtered, and the solvent was removed under reduced pressure. The resulting solid was recrystallized from EtOAc. The obtained crystals were collected by filtration, washed with $Et_2O$ (20 mL), and dried in vacuo to afford thianthrene-*S*-oxide in 82% yield (4.38 g) as colorless needle-shaped crystals.

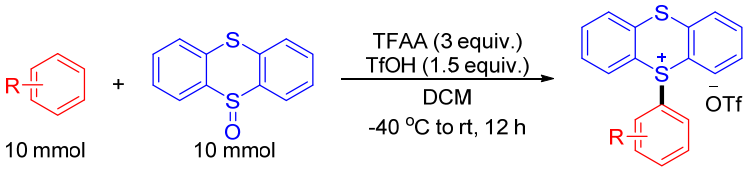
**1.2 Synthesis of aryl thianthrenium salts[2,3]**

**Procedure A:**




A 100 mL round-bottom flask equipped with a magnetic stir bar was charged with arene (10 mmol, 1 equiv.), thianthrene *S*-oxide (2.56 g, 11 mmol, 1.1 equiv.), and DCM (30 mL) under nitrogen atmosphere. The reaction mixture was cooled to -40 °C and trifluoromethanesulfonic anhydride ($Tf_2O$, 2 mL, 12 mmol, 1.2 equiv.) was added dropwise. The reaction mixture was stirred at -40 °C for 30 min, followed by stirring at room temperature for 12 h. After completion of reaction as monitored by TLC, saturated aqueous $NaHCO_3$ solution (30 mL) were added to the reaction mixture. The organic layer was separated and the aqueous layer was extracted with DCM (40 mL x 2). The combined organic extracts were washed with saturated brine, dried over anhydrous $Na_2SO_4$, and concentrated to dryness under reduced pressure. The crude product was purified by crystallization from DCM/$Et_2O$ system to afford the corresponding aryl thianthrenium salt.

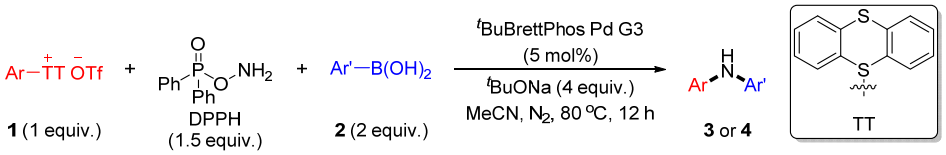
**Procedure B:**




A 100 mL round-bottom flask equipped with a magnetic stir bar was charged with arene (10 mmol, 1.0 equiv.), thianthrene *S*-oxide (2.32 g, 10 mmol, 1 equiv.), and DCM (30 mL) under nitrogen atmosphere. The reaction mixture was cooled to -40 °C and trifluoroacetic anhydride (TFAA, 4.17 mL, 30 mmol, 3 equiv.), and trifluoromethanesulfonic acid (TfOH, 1.3 mL, 15 mmol, 1.5 equiv.) were sequentially added dropwise to the reaction mixture. The reaction mixture was stirred at -40 °C for 30 min, followed by stirring at room temperature for 12 h. After completion of reaction as monitored by TLC, saturated aqueous $NaHCO_3$ solution (30 mL) were added to the reaction mixture. The organic layer was separated and the aqueous layer was extracted with DCM (40 mL x 2). The combined organic extracts were washed with aqueous NaOTf solution (20 mL x 3; 5% (w/w)), dried over anhydrous $Na_2SO_4$, and concentrated to dryness under reduced pressure. The crude product was purified by crystallization from DCM/$Et_2O$ system to afford the corresponding aryl thianthrenium salt.

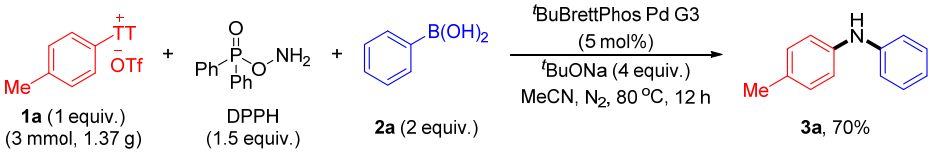
Aryl thianthrenium salts **1a-b** and **1d-n** were synthesized according to Procedure A, and aryl thianthrenium salts **1c** was synthesized by using Procedure B.

**3. Cross-Electrophile Couplings of Aryl Thianthrenium Salts 1 with Arylboronic Acid 2 and DPPH.**



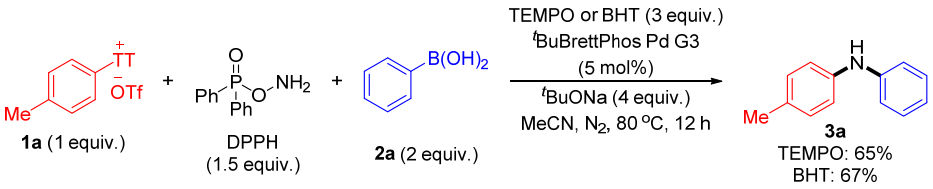

To an oven-dried seal tube equipped with a magnetic stir bar was added aryl thianthrenium salt **1** (0.5 mmol, 1 equiv.), arylboronic acid **2** (1 mmol, 2 equiv.), DPPH (174.9 mg, 0.75 mmol, 1.5 equiv.), $^t$BuBrettPhos Pd G3 (21.4 mg, 0.025 mmol, 5 mol%), and $^t$BuONa (192.2 mg, 2 mmol, 4 equiv.). The seal tube was backfilled with nitrogen for three times followed by the addition of dry MeCN (3 mL). The mixture was stirred at 80 °C for 12 h before quenching with saturated $NaHCO_3$ solution (10 mL) and extracting with EtOAc (20 mL x 3). The organic layers were combined, washed with brine, and dried over anhydrous $Na_2SO_4$. The extracts were concentrated under reduced pressure to afford the crude product, which was further purified through silica gel column chromatography (using EtOAc/petroleum ether as eluents) to yield the product **3** or **4**.

**4. Gram-scale synthesis.**




To an oven-dried seal tube equipped with a magnetic stir bar was added aryl thianthrenium salt **1a** (1369.5 mg, 3 mmol, 1 equiv.), arylboronic acid **2a** (731.6 mg, 6 mmol, 2 equiv.), DPPH (1049.9 mg, 4.5 mmol, 1.5 equiv.), $^t$BuBrettPhos Pd G3 (128.2 mg, 0.15 mmol, 5 mol%), and $^t$BuONa (1.15 g, 12 mmol, 4 equiv.). The seal tube was backfilled with nitrogen for three times followed by the addition of dry MeCN (18 mL). The mixture was stirred at 80 °C for 12 h before quenching with saturated $NaHCO_3$ solution (30 mL) and extracting with EtOAc (60 mL x 3). The organic layers were combined, washed with brine, and dried over anhydrous $Na_2SO_4$. The extracts were concentrated under reduced pressure to afford the crude product, which was further purified through silica gel column chromatography (using EtOAc/petroleum ether as eluents) to yield the product **3a** in 70% yield (385.5 mg).

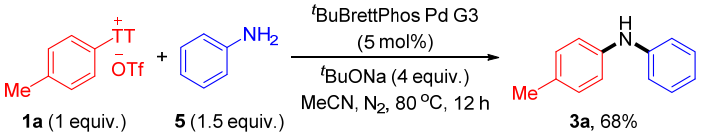
**5. Radical-quenching experiment with TEMPO and BHT.**




To an oven-dried seal tube equipped with a magnetic stir bar was added aryl thianthrenium salt **1a** (228.3 mg, 0.5 mmol, 1 equiv.), arylboronic acid **2a** (121.9 mg, 1 mmol, 2 equiv.), DPPH (174.9 mg, 0.75 mmol, 1.5 equiv.), $^t$BuBrettPhos Pd G3 (21.4 mg, 0.025 mmol, 5 mol%), $^t$BuONa (192.2 mg, 2 mmol, 4 equiv.), and TEMPO (234.4 mg, 1.5 mmol, 3 equiv.) or BHT (330.3 mg, 1.5 mmol, 3 equiv.). The seal tube was backfilled with nitrogen for three times followed by the addition of dry MeCN (3 mL). The mixture was stirred at 80 °C for 12 h before quenching with saturated $NaHCO_3$ solution (10 mL) and extracting with EtOAc (20 mL x 3). The organic layers were combined, washed with brine, and dried over anhydrous $Na_2SO_4$. The extracts were concentrated

under reduced pressure to afford the crude product, which was further purified through silica gel column chromatography (using EtOAc/petroleum ether as eluents) to yield the product **3a** in 65% yield (59.7 mg) or 67% yield (61.4 mg), respectively.

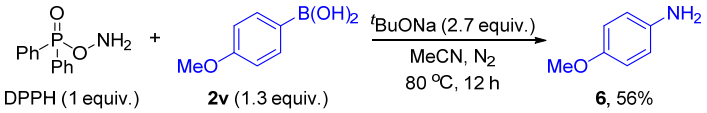
**6. Cross-coupling of aryl thianthrenium salt 1a with aniline 5.**




**1a** (1 equiv.) **5** (1.5 equiv.) **3a**, 68%

To an oven-dried seal tube equipped with a magnetic stir bar was added aryl thianthrenium salt **1a** (228.3 mg, 0.5 mmol, 1 equiv.), aniline **5** (69.8 mg, 0.75 mmol, 1.5 equiv.), $^t$BuBrettPhos Pd G3 (21.4 mg, 0.025 mmol, 5 mol%), and $^t$BuONa (192.2 mg, 2 mmol, 4 equiv.). The seal tube was backfilled with nitrogen for three times followed by the addition of dry MeCN (3 mL). The mixture was stirred at 80 °C for 12 h before quenching with saturated $NaHCO_3$ solution (10 mL) and extracting with EtOAc (20 mL x 3). The organic layers were combined, washed with brine, and dried over anhydrous $Na_2SO_4$. The extracts were concentrated under reduced pressure to afford the crude product, which was further purified through silica gel column chromatography (using EtOAc/petroleum ether as eluents) to yield the product **3a** in 68% yield (62.5 mg).

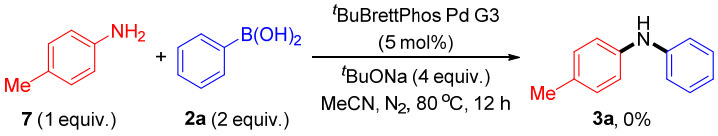
**7. Cross-coupling of DPPH with arylboronic acid 2v.**




DPPH (1 equiv.) **2v** (1.3 equiv.) **6**, 56%

To an oven-dried seal tube equipped with a magnetic stir bar was added arylboronic acid **2v** (98.8 mg, 0.65 mmol, 1.3 equiv.), DPPH (116.6 mg, 0.5 mmol, 1 equiv.), and $^t$BuONa (129.7 mg, 1.35 mmol, 2.7 equiv.). The seal tube was backfilled with nitrogen for three times followed by the addition of dry MeCN (2 mL). The mixture was stirred at 80 °C for 12 h before quenching with saturated $NaHCO_3$ solution (10 mL) and extracting with EtOAc (20 mL x 3). The organic layers were combined, washed with brine, and dried over anhydrous $Na_2SO_4$. The extracts were concentrated under reduced pressure to afford the crude product, which was further purified through silica gel column chromatography (using EtOAc/petroleum ether as eluents) to yield the product **6** in 56% yield (34.3 mg).

**8. Cross-coupling of aniline 7 with arylboronic acid 2a.**

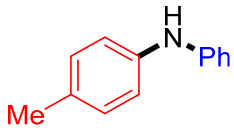



**7** (1 equiv.) **2a** (2 equiv.) **3a**, 0%

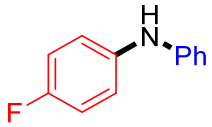
To an oven-dried seal tube equipped with a magnetic stir bar was added aniline **7** (53.6 mg, 0.5 mmol, 1 equiv.), arylboronic acid **2a** (121.9 mg, 1 mmol, 2 equiv.), $^t$BuBrettPhos Pd G3 (21.4 mg, 0.025 mmol, 5 mol%), and $^t$BuONa (192.2 mg, 2 mmol, 4 equiv.). The seal tube was backfilled with nitrogen for three times followed by the addition of dry MeCN (3 mL). The mixture was stirred at 80 °C for 12 h before quenching with saturated $NaHCO_3$ solution (10 mL) and extracting

with EtOAc (20 mL x 3). The organic layers were combined, washed with brine, and dried over anhydrous $Na_2SO_4$. TLC analysis showed that no desired product **3a** was formed in the reaction.

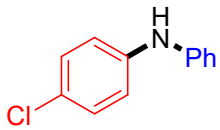
## Characterization data of products



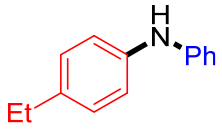

**4-Methyl-*N*-phenylaniline (3a):**[4] This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluant (petroleum ether/EtOAc = 150:1). Yield = 73%, 66.7 mg. White solid. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta$ = 7.22 (ddd, $J$ = 8.3, 7.4, 0.8 Hz, 2H), 7.10 – 7.05 (m, 2H), 6.99 (ddd, $J$ = 8.5, 2.5, 1.5 Hz, 4H), 6.86 (ddd, $J$ = 8.3, 6.8, 1.0 Hz, 1H), 5.59 (s, 1H), 2.29 (s, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** $\delta$ = 143.8, 140.2, 130.9, 129.8, 129.3, 120.2, 118.8, 116.8, 20.7 ppm. **IR (KBr):** $\nu$ = 2915, 1596, 1513, 1499, 1308, 809, 746, 693, 506 cm$^{-1}$. **HRMS (m/z)**: calcd for $C_{13}H_{14}N$ $[M+H]^+$ 184.1121, found: 184.1124.



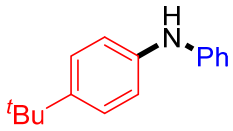

**4-Fluoro-*N*-phenylaniline (3b):**[5] This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluant (petroleum ether/EtOAc = 250:1). Yield = 46%, 43.3 mg. Yellow oil. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta$ = 7.28 – 7.24 (m, 2H), 7.08 – 7.03 (m, 2H), 7.01 – 6.96 (m, 4H), 6.90 (tt, $J$ = 7.4, 1.2 Hz, 1H), 5.59 (s, 1H) ppm. **$^{19}$F NMR (376 MHz, $CDCl_3$):** $\delta$ = -121.89 (s, 1F) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** $\delta$ = 158.0 (d, $J$ = 239.9 Hz), 143.9, 138.8 (d, $J$ = 1.7 Hz), 129.4, 120.54, 120.46, 116.7, 115.9 (d, $J$ = 22.4 Hz) ppm. **IR (KBr):** $\nu$ = 1596, 1509, 1316, 1217, 818, 774, 746, 693 cm$^{-1}$. **HRMS (m/z)**: calcd for $C_{12}H_{11}FN$ $[M+H]^+$ 188.0870, found: 188.0873.



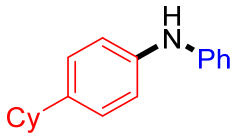

**4-Chloro-*N*-phenylaniline (3c):**[6] This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluant (petroleum ether/EtOAc = 200:1). Yield = 59%, 60.2 mg. Yellow solid. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta$ = 7.32 – 7.27 (m, 2H), 7.24 – 7.20 (m, 2H), 7.08 – 7.04 (m, 2H), 7.02 – 6.95 (m, 3H), 5.69 (s, 1H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** $\delta$ = 142.5, 141.7, 129.4, 129.2, 125.4, 121.4, 118.7, 118.0 ppm. **IR (KBr):** $\nu$ = 3060, 1589, 1504, 1442, 1310, 1089, 750, 691, 503 cm$^{-1}$. **HRMS (m/z)**: calcd for $C_{12}H_{11}ClN$ $[M+H]^+$ 204.0575, found: 204.0581.



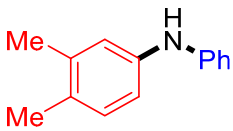

**4-Ethyl-*N*-phenylaniline (3d):**[7] This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluant (petroleum ether/EtOAc = 150:1). Yield = 72%, 70.5 mg. Yellow solid. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta$ = 7.33 – 7.27 (m, 2H), 7.17 (d, $J$ = 8.1 Hz, 2H), 7.08 (dd, $J$ = 8.5, 2.3 Hz, 4H), 6.95 (t, $J$ = 7.3 Hz, 1H), 5.67 (s, 1H), 2.67 (q, $J$ = 7.6 Hz, 2H), 1.30 (t, $J$ = 7.6 Hz, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** $\delta$ =143.8, 140.4, 137.3, 129.2, 128.6, 120.2, 118.7, 116.8, 28.1, 15.8 ppm. **IR (KBr):** $\nu$ = 2961, 2923, 1595, 1514, 1500, 1367, 1312, 742, 692 cm$^{-1}$. **HRMS (m/z)**: calcd for $C_{14}H_{16}N$ $[M+H]^+$ 198.1277, found: 198.1279.




**4-(*tert*-Butyl)-*N*-phenylaniline (3e):**[7] This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluant (petroleum ether/EtOAc = 150:1). Yield = 73%, 81.9 mg. Yellow solid. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta$ = 7.37 – 7.33 (m, 2H), 7.30 (dd, $J$ = 8.5, 7.2 Hz, 2H), 7.11 – 7.06 (m, 4H), 6.94 (tt, $J$ = 7.3, 1.1 Hz, 1H), 5.68 (s, 1H), 1.37 (s, 9H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** $\delta$ = 144.1, 143.6, 140.2, 129.3, 126.1, 120.3, 118.0, 117.0, 34.1, 31.4 ppm. **IR (KBr):** $\nu$ = 2959, 1594, 1515, 1497, 1304, 1265, 743, 692 cm$^{-1}$. **HRMS (m/z)**: calcd for $C_{16}H_{20}N$ $[M+H]^+$ 226.1590, found: 226.1591.

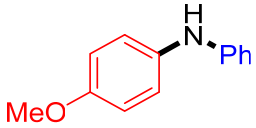



**4-Cyclohexyl-*N*-phenylaniline (3f):**[8] This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluant (petroleum ether/EtOAc = 200:1). Yield = 79%, 99.1 mg. Yellow oil. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta$ = 7.30 – 7.25 (m, 2H), 7.17 – 7.13 (m, 2H), 7.08 – 7.03 (m, 4H), 6.92 (tt, $J$ = 7.3, 1.1 Hz, 1H), 5.64 (s, 1H), 2.53 – 2.45 (m, 1H), 1.94 – 1.85 (m, 4H), 1.81 – 1.75 (m, 1H), 1.43 (td, $J$ = 9.1, 2.8 Hz, 4H), 1.34 – 1.26 (m, 1H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** $\delta$ = 143.7, 141.3, 140.6, 129.2, 127.5, 120.3, 118.5, 117.0, 43.8, 34.6, 26.9, 26.1 ppm. **IR (KBr):** $\nu$ = 2922, 2849, 1598, 1515, 1497, 1312, 745, 693 cm$^{-1}$. **HRMS (m/z)**: calcd for $C_{18}H_{22}N$ $[M+H]^+$ 252.1747, found: 252.1746.

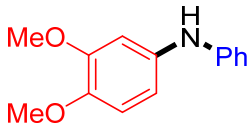



**3,4-Dimethyl-*N*-phenylaniline (3g):**[7] This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluant (petroleum ether/EtOAc = 150:1). Yield = 76%, 74.8 mg. Green solid. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta$ = 7.29 – 7.25 (m, 2H), 7.09 –

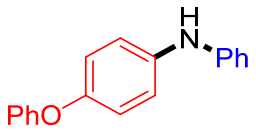
7.02 (m, 3H), 6.94 – 6.87 (m, 3H), 5.59 (s, 1H), 2.26 (s, 3H), 2.25 (s, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** $\delta$ = 143.9, 140.5, 137.5, 130.3, 129.6, 129.2, 120.3, 120.1, 116.8, 116.2, 19.9, 19.0 ppm. **IR (KBr):** $\nu$ = 3389, 2924, 1597, 1502, 1312, 865, 826, 743, 691 $cm^{-1}$. **HRMS (m/z)**: calcd for $C_{14}H_{16}N$ $[M+H]^+$ 198.1277, found: 198.1275.



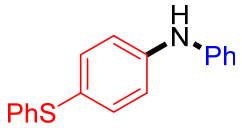

**4-Methoxy-*N*-phenylaniline (3h):**[7] This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluant (petroleum ether/EtOAc = 100:1). Yield = 81%, 80.6 mg. White solid. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta$ = 7.25 – 7.19 (m, 2H), 7.11 – 7.06 (m, 2H), 6.92 (dt, $J$ = 7.7, 1.1 Hz, 2H), 6.89 – 6.81 (m, 3H), 5.51 (s, 1H), 3.81 (s, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** $\delta$ = 155.2, 145.1, 135.7, 129.3, 122.2, 119.5, 115.6, 114.6, 55.6 ppm. **IR (KBr):** $\nu$ = 2831, 1628, 1597, 1512, 1365, 1317, 1168, 774, 751 $cm^{-1}$. **HRMS (m/z)**: calcd for $C_{13}H_{14}NO$ $[M+H]^+$ 199.0997, found: 199.0999.



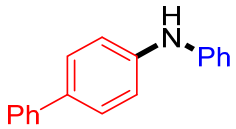

**3,4-Dimethoxy-*N*-phenylaniline (3i):**[9] This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluant (petroleum ether/EtOAc = 12:1). Yield = 69%, 79.6 mg. White solid. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta$ =7.25 – 7.20 (m, 2H), 6.96 – 6.92 (m, 2H), 6.85 (tt, $J$ = 7.3, 1.1 Hz, 1H), 6.80 (d, $J$ = 8.5 Hz, 1H), 6.71 (d, $J$ = 2.5 Hz, 1H), 6.67 (dd, $J$ = 8.5, 2.5 Hz, 1H), 5.54 (s, 1H), 3.86 (s, 3H), 3.82 (s, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** $\delta$ =149.5, 144.8, 144.5, 136.1, 129.3, 119.7, 115.9, 112.04, 111.95, 105.2, 56.2, 55.8 ppm. **IR (KBr):** $\nu$ = 3380, 2833, 1596, 1514, 1261, 1025, 746, 694, 503 $cm^{-1}$. **HRMS (m/z)**: calcd for $C_{14}H_{16}NO_2$ $[M+H]^+$ 230.1176, found: 230.1176.



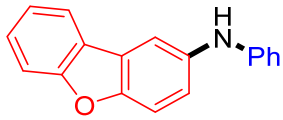

**4-Phenoxy-*N*-phenylaniline (3j):**[10] This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluant (petroleum ether/EtOAc = 200:1). Yield = 44%, 57.8 mg. Grey solid. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta$ = 7.36 – 7.30 (m, 2H), 7.29 – 7.24 (m, 2H), 7.11 – 7.05 (m, 3H), 7.05 – 6.96 (m, 6H), 6.91 (tt, $J$ = 7.4, 1.1 Hz, 1H), 5.62 (s, 1H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** $\delta$ = 158.1, 151.2, 143.9, 138.7, 129.6, 129.4, 122.6 (2C), 120.5, 120.3, 117.9, 116.8 ppm. **IR (KBr):** $\nu$ = 2778, 1509, 1489, 1283, 1229, 1013, 895, 747, 692 $cm^{-1}$. **HRMS (m/z)**: calcd for $C_{18}H_{16}NO$ $[M+H]^+$ 262.1226, found: 262.1221.



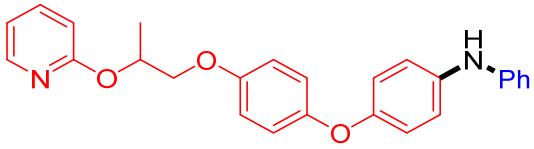

***N*-Phenyl-4-(phenylthio)aniline (3k):**[11] This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluant (petroleum ether/EtOAc = 200:1). Yield = 52%, 71.5 mg. Yellow solid. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta$ = 7.38 – 7.33 (m, 2H), 7.32 – 7.26 (m, 2H), 7.25 – 7.18 (m, 4H), 7.15 – 7.07 (m, 3H), 7.16 – 7.12 (m, 1H), 7.11 – 7.07 (m, 2H), 5.76 (s, 1H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** $\delta$ = 143.7, 142.8, 138.7, 135.3, 129.4, 128.9, 128.0, 125.7, 123.3, 121.9, 118.9, 117.5 ppm. **IR (KBr):** $\nu$ = 2830, 1585, 1505, 1475, 1365, 1313, 750, 741, 689 $cm^{-1}$. **HRMS (m/z)**: calcd for $C_{18}H_{16}NS$ $[M+H]^+$ 278.0998, found: 278.0999.




***N*-Phenyl-[1,1'-biphenyl]-4-amine (3l):**[7] This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluant (petroleum ether/EtOAc = 200:1). Yield = 75%, 92.6 mg. Grey solid. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta$ = 7.64 – 7.61 (m, 2H), 7.58 – 7.54 (m, 2H), 7.50 – 7.45 (m, 2H), 7.38 – 7.32 (m, 3H), 7.20 – 7.18 (m, 1H), 7.17 – 7.16 (m, 2H), 7.15 – 7.14 (m, 1H), 7.03 – 6.98 (m, 1H), 5.82 (s, 1H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** $\delta$ = 142.7, 142.4, 140.8, 133.6, 129.4, 128.7, 127.9, 126.54, 126.47, 121.1, 118.0, 117.7 ppm. **IR (KBr):** $\nu$ = 3025, 1597, 1524, 1504, 1324, 846, 759, 745, 693 $cm^{-1}$. **HRMS (m/z)**: calcd for $C_{18}H_{16}N$ $[M+H]^+$ 246.1277, found: 246.1280.

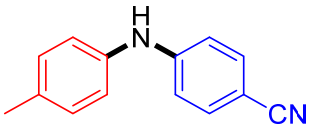



***N*-Phenyldibenzo[*b*,*d*]furan-2-amine (3m):** This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluant (petroleum ether/EtOAc = 100:1). Yield = 66%, 85.4 mg. White solid. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta$ = 7.86 – 7.83 (m, 1H), 7.67 (d, $J$ = 2.4 Hz, 1H), 7.52 (d, $J$ = 8.2 Hz, 1H), 7.46 (d, $J$ = 8.7 Hz, 1H), 7.42 (ddd, $J$ = 8.4, 7.2, 1.4 Hz, 1H), 7.28 (td, $J$ = 7.5, 1.0 Hz, 1H), 7.23 (dd, $J$ = 8.2, 1.0 Hz, 2H), 7.18 (dd, $J$ = 8.7, 2.3 Hz, 1H), 7.00 (dd, $J$ = 8.6, 1.2 Hz, 2H), 6.90 – 6.85 (m, 1H), 5.71 (s, 1H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** $\delta$ =156.8, 152.1, 144.8, 138.1, 129.4, 127.2, 125.0, 124.1, 122.5, 120.68, 120.66, 120.2, 116.3, 112.2, 111.7, 111.6 ppm. **IR (KBr):** $\nu$ = 2830, 1598, 1447, 1358, 1194, 1175, 745, 692, 546 $cm^{-1}$. **HRMS (m/z)**: calcd for $C_{18}H_{14}NO$ $[M+H]^+$ 260.1070, found: 260.1075.

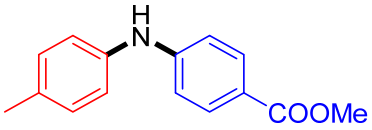



***N*-Phenyl-4-(4-(2-(pyridin-2-yloxy)propoxy)phenoxy)aniline (3n):** This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluant (petroleum

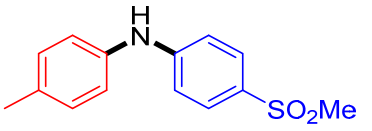
ether/EtOAc = 5:1). Yield = 66%, 135.2 mg. Grey oil. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta$ = 8.15 (ddd, $J$ = 5.1, 2.0, 0.9 Hz, 1H), 7.57 (ddd, $J$ = 8.3, 7.1, 2.0 Hz, 1H), 7.26 – 7.21 (m, 2H), 7.07 – 7.03 (m, 2H), 7.00 – 6.96 (m, 2H), 6.95 – 6.92 (m, 3H), 6.92 – 6.89 (m, 3H), 6.88 – 6.84 (m, 2H), 6.75 (dt, $J$ = 8.3, 0.9 Hz, 1H), 5.64 – 5.55 (m, 2H), 4.18 (dd, $J$ = 9.9, 5.3 Hz, 1H), 4.07 (dd, $J$ = 9.8, 4.8 Hz, 1H), 1.48 (d, $J$ = 6.4 Hz, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** $\delta$ =163.1, 154.8, 152.7, 151.2, 146.7, 144.1, 138.7, 137.8, 129.3, 120.7, 120.1, 119.8, 119.1, 116.7, 116.4, 115.7, 111.6, 71.0, 69.2, 16.9 ppm. **IR (KBr):** $\nu$ = 2931, 2829, 1596, 1569, 1497, 1215, 1142, 777, 747, 512 cm$^{-1}$. **HRMS (m/z)**: calcd for $C_{26}H_{25}N_2O_3$ $[M+H]^+$ 413.1860, found: 413.1861.



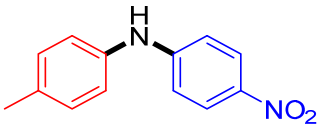

**4-(*p*-Tolylamino)benzonitrile (4b):**[10] This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluant (petroleum ether/EtOAc = 10:1). Yield = 45%, 46.5 mg. White solid. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta$ = 7.47 – 7.43 (m, 2H), 7.17 (d, $J$ = 8.1 Hz, 2H), 7.09 – 7.05 (m, 2H), 6.92 – 6.88 (m, 2H), 6.01 (s, 1H), 2.35 (s, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** $\delta$ = 148.6, 137.1, 134.0, 133.7, 130.1, 122.0, 120.1, 114.3, 100.6, 20.8 ppm. **IR (KBr):** $\nu$ = 2831, 1600, 1514, 1366, 1219, 1111, 828, 545, 500 cm$^{-1}$. **HRMS (m/z)**: calcd for $C_{14}H_{13}N_2$ $[M+H]^+$ 209.1073, found: 209.1076.



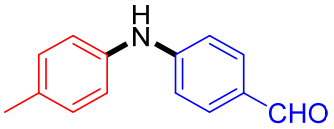

**Methyl 4-(*p*-tolylamino)benzoate (4c):**[12] This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluant (petroleum ether/EtOAc = 10:1). Yield = 74%, 89.8 mg. White solid. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta$ = 7.89 (d, $J$ = 8.7 Hz, 2H), 7.15 (d, $J$ = 8.1 Hz, 2H), 7.08 (d, $J$ = 8.3 Hz, 2H), 6.95 – 6.89 (m, 2H), 5.97 (s, 1H), 3.87 (s, 3H), 2.34 (s, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** $\delta$ = 167.0, 148.7, 137.9, 133.1, 131.5, 130.0, 121.3, 120.4, 113.9, 51.7, 20.8 ppm. **IR (KBr):** $\nu$ = 2939, 1700, 1597, 1527, 1434, 1281, 1171, 773, 504 cm$^{-1}$. **HRMS (m/z)**: calcd for $C_{15}H_{16}NO_2$ $[M+H]^+$ 242.1176, found: 242.1179.



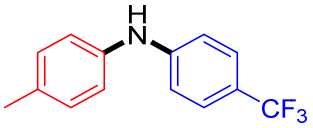

**4-Methyl-*N*-(4-(methylsulfonyl)phenyl)aniline (4d):**[13] This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluant (petroleum ether/EtOAc = 10:1). Yield = 57%, 74.8 mg. Yellow solid. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta$ = 7.74 – 7.69 (m, 2H), 7.17 (d, $J$ = 8.0 Hz, 2H), 7.09 (d, $J$ = 8.1 Hz, 2H), 6.98 – 6.94 (m, 2H), 6.04 (s, 1H), 3.02 (s, 3H), 2.35 (s, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** $\delta$ = 149.8, 143.7, 137.3, 130.3, 129.5, 124.5, 122.3, 114.1, 45.1, 21.0 ppm. **IR (KBr):** $\nu$ = 1592, 1517, 1286, 1136, 1093, 964, 823, 774, 518 cm$^{-1}$. **HRMS (m/z)**: calcd for $C_{14}H_{16}NO_2S$ $[M+H]^+$ 262.0896, found: 262.0894.



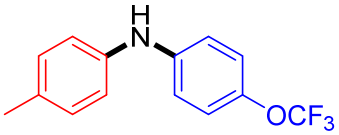
**4-Methyl-*N*-(4-nitrophenyl)aniline (4e):**[14] This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluant (petroleum ether/EtOAc = 10:1). Yield = 76%, 86.6 mg. Yellow solid. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta$ = 8.14 – 8.04 (m, 2H), 7.20 (d, $J$ = 8.1 Hz, 2H), 7.13 – 7.09 (m, 2H), 6.92 – 6.82 (m, 2H), 6.32 (s, 1H), 2.36 (s, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** $\delta$ = 150.8, 139.2, 136.6, 134.7, 130.2, 126.2, 122.6, 113.1, 20.9 ppm. **IR (KBr):** $\nu$ = 3330, 2830, 1607, 1366, 1304, 1179, 1111, 774 cm$^{-1}$. **HRMS (m/z)**: calcd for $C_{13}H_{13}N_2O_2$ $[M+H]^+$ 229.0972, found: 229.0981.



**4-(*p*-Tolylamino)benzaldehyde (4f):**[14] This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluant (petroleum ether/EtOAc = 10:1). Yield = 67%, 70.9 mg. Yellow solid. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta$ = 9.77 (s, 1H), 7.74 – 7.70 (m, 2H), 7.18 (d, $J$ = 8.2 Hz, 2H), 7.11 (d, $J$ = 8.4 Hz, 2H), 6.99 – 6.94 (m, 2H), 6.31 (s, 1H), 2.35 (s, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** $\delta$ = 190.4, 150.5, 137.2, 133.9, 132.2, 130.1, 127.9, 122.1, 113.9, 20.9 ppm. **IR (KBr):** $\nu$ = 3324, 1585, 1568, 1522, 1490, 1336, 1225, 1162, 825 cm$^{-1}$. **HRMS (m/z)**: calcd for $C_{14}H_{14}NO$ $[M+H]^+$ 212.1070, found: 212.1075.

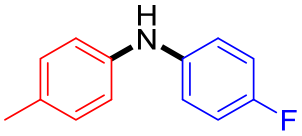


**4-Methyl-*N*-(4-(trifluoromethyl)phenyl)aniline (4g):**[12] This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluant (petroleum ether/EtOAc = 200:1). Yield = 49%, 61.8 mg. White solid. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta$ =7.47 – 7.43 (m, 2H), 7.18 – 7.13 (m, 2H), 7.09 – 7.05 (m, 2H), 7.00 – 6.95 (m, 2H), 5.83 (s, 1H), 2.35 (s, 3H) ppm. **$^{19}$F NMR (376 MHz, $CDCl_3$):** $\delta$ = -61.22 (s, 3F) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** $\delta$ = 147.5, 138.3, 133.0, 130.1, 126.6 (q, $J$ = 3.9 Hz), 124.7 (q, $J$ = 269.2 Hz), 121.02, 120.98 (q, $J$ = 32.5 Hz), 114.6, 20.8 ppm. **IR (KBr):** $\nu$ = 2924, 2778, 1609, 1515, 1326, 1164, 1113, 1068, 828 cm$^{-1}$. **HRMS (m/z)**: calcd for $C_{14}H_{13}F_3N$ $[M+H]^+$ 252.0995, found: 252.0992.

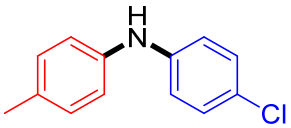


**4-Methyl-*N*-(4-(trifluoromethoxy)phenyl)aniline (4h):**[12] This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluant (petroleum ether/EtOAc =

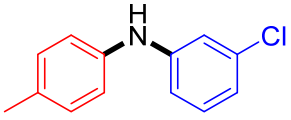
200:1). Yield = 66%, 88.3 mg. Yellow solid. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta$ = 7.15 – 7.07 (m, 4H), 7.03 – 6.95 (m, 4H), 5.64 (s, 1H), 2.33 (s, 3H) ppm. **$^{19}$F NMR (376 MHz, $CDCl_3$):** $\delta$ = -58.21 (s, 3F) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** $\delta$ = 142.9, 142.2, 139.6, 131.7, 130.0, 122.3, 120.6 (q, $J$ = 254.5 Hz), 119.4, 117.0, 20.7 ppm. **IR (KBr):** $\nu$ = 2924, 1520, 1297, 1266, 1204, 1158, 1010, 919, 811 cm$^{-1}$. **HRMS (m/z)**: calcd for $C_{14}H_{13}F_3NO$ $[M+H]^+$ 268.0944, found: 268.0938.



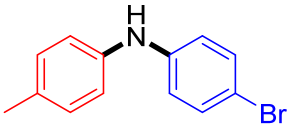

**4-Fluoro-*N*-(*p*-tolyl)aniline (4i):**[12] This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluant (petroleum ether/EtOAc = 200:1). Yield = 72%, 72.5 mg. Brown solid. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta$ = 7.10 – 7.06 (m, 2H), 7.02 – 6.95 (m, 4H), 6.94 – 6.91 (m, 2H), 5.51 (s, 1H), 2.30 (s, 3H) ppm. **$^{19}$F NMR (376 MHz, $CDCl_3$):** $\delta$ = -122.99 (s, 1F) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** $\delta$ = 157.6 (d, $J$ = 239.4 Hz), 141.1, 139.8, 130.5, 129.9, 119.3 (d, $J$ = 7.7 Hz), 117.8, 115.8 (d, $J$ = 22.4 Hz), 20.6 ppm. **IR (KBr):** $\nu$ = 3415, 2830, 1610, 1509, 1365, 1223, 1154, 813, 774 cm$^{-1}$. **HRMS (m/z)**: calcd for $C_{13}H_{13}FN$ $[M+H]^+$ 202.1027, found: 202.1029.



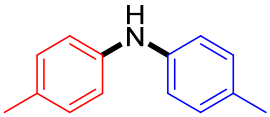

**4-Chloro-*N*-(*p*-tolyl)aniline (4j):**[13] This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluant (petroleum ether/EtOAc = 200:1). Yield = 74%, 80.0 mg. Brown solid. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta$ = 7.21 – 7.17 (m, 2H), 7.13 – 7.09 (m, 2H), 7.01 – 6.97 (m, 2H), 6.95 – 6.91 (m, 2H), 5.60 (s, 1H), 2.33 (s, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** $\delta$ = 142.6, 139.7, 131.4, 129.9, 129.1, 124.6, 119.1, 117.7, 20.7 ppm. **IR (KBr):** $\nu$ = 2889, 2672, 1455, 1262, 1012, 892, 807, 726, 577 cm$^{-1}$. **HRMS (m/z)**: calcd for $C_{13}H_{13}ClN$ $[M+H]^+$ 218.0731, found: 218.0737.



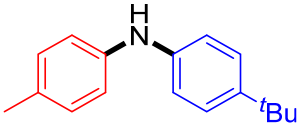

**3-Chloro-*N*-(*p*-tolyl)aniline (4k):**[15] This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluant (petroleum ether/EtOAc = 200:1). Yield = 62%, 67.5 mg. White solid. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta$ = 7.16 – 7.11 (m, 3H), 7.04 – 7.00 (m, 2H), 6.97 (t, $J$ = 2.1 Hz, 1H), 6.84 – 6.80 (m, 2H), 5.65 (s, 1H), 2.33 (s, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** $\delta$ = 145.6, 139.0, 135.0, 132.1, 130.3, 130.0, 120.1, 119.7, 115.7, 114.3, 20.7 ppm. **IR (KBr):** $\nu$ = 3415, 2972, 2830, 1608, 1366, 1162, 1050, 861, 774 cm$^{-1}$. **HRMS (m/z)**: calcd for $C_{13}H_{13}ClN$ $[M+H]^+$ 218.0731, found: 218.0727.



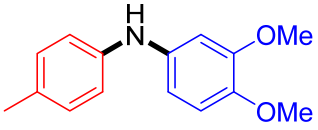

**4-Bromo-*N*-(*p*-tolyl)aniline (4l):**[4] This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluant (petroleum ether/EtOAc = 200:1). Yield = 69%, 90.3 mg. Brown solid. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta$ = 7.19 (d, $J$ = 8.8 Hz, 2H), 7.13 – 7.09 (m, 2H), 7.00 – 6.97 (m, 2H), 6.95 – 6.91 (m, 2H), 5.58 (s, 1H), 2.33 (s, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** $\delta$ = 142.7, 139.8, 131.5, 129.9, 129.2, 124.7, 119.2, 117.8, 20.7 ppm. **IR (KBr):** $\nu$ = 3409, 2830, 1608, 1518, 1365, 1322, 1160, 1090, 774 cm$^{-1}$. **HRMS (m/z)**: calcd for $C_{13}H_{13}BrN$ $[M+H]^+$ 262.0226, found: 262.0219.




**Di-*p*-tolylamine (4m):**[12] This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluant (petroleum ether/EtOAc = 200:1). Yield = 71%, 70.4 mg. White solid. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta$ = 7.10 – 7.06 (m, 4H), 6.98 – 6.94 (m, 4H), 5.52 (s, 1H), 2.31 (s, 6H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** $\delta$ = 141.1, 130.1, 129.8, 117.8, 20.6 ppm. **IR (KBr):** $\nu$ = 3418, 2830, 1609, 1519, 1365, 1320, 1177, 807, 774, 510 cm$^{-1}$. **HRMS (m/z)**: calcd for $C_{14}H_{16}N$ $[M+H]^+$ 198.1277, found: 198.1275.

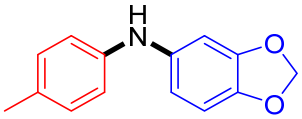



**4-(*tert*-Butyl)-*N*-(*p*-tolyl)aniline (4n):**[12] This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluant (petroleum ether/EtOAc = 200:1). Yield = 75%, 89.9 mg. Yellow oil. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta$ = 7.32 – 7.28 (m, 2H), 7.12 – 7.08 (m, 2H), 7.03 – 6.98 (m, 4H), 5.57 (s, 1H), 2.33 (s, 3H), 1.34 (s, 9H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** $\delta$ = 143.3, 141.0, 140.7, 130.2, 129.7, 126.0, 118.0, 117.0, 34.1, 31.4, 20.6 ppm. **IR (KBr):** $\nu$ = 2961, 1608, 1517, 1364, 1312, 1268, 1190, 816, 774 cm$^{-1}$. **HRMS (m/z)**: calcd for $C_{17}H_{22}N$ $[M+H]^+$ 240.1747, found: 240.1753.

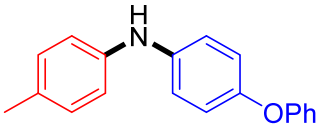



**3,4-Dimethoxy-*N*-(*p*-tolyl)aniline (4o):**[16] This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluant (petroleum ether/EtOAc = 10:1). Yield = 85%, 103.6 mg. Brown oil. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta$ = 7.08 – 7.03 (m, 2H), 6.92 – 6.86 (m, 2H), 6.80 (d, $J$ = 8.5 Hz, 1H), 6.68 (d, $J$ = 2.5 Hz, 1H), 6.62 (dd, $J$ = 8.5, 2.5 Hz, 1H), 5.44 (s, 1H), 3.86 (s, 3H), 3.83 (s, 3H), 2.29 (s, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** $\delta$ = 149.6, 144.1, 142.0, 137.1, 129.8, 129.6, 116.9, 112.2, 110.9, 104.3, 56.3, 55.8, 20.6 ppm. **IR**

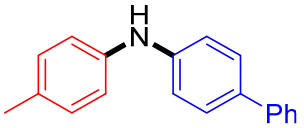
**(KBr):** $\nu$ = 2931, 2831, 1608, 1511, 1463, 1257, 1230, 1135, 1026, 813 $cm^{-1}$. **HRMS (m/z)**: calcd for $C_{15}H_{18}NO_2$ $[M+H]^+$ 244.1332, found: 244.1330.



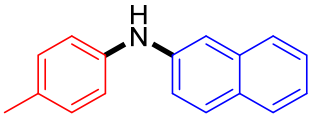
***N*-(*p*-Tolyl)benzo[*d*][1,3]dioxol-5-amine (4p):**[17] This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluant (petroleum ether/EtOAc = 100:1). Yield = 51%, 57.9 mg. Brown oil. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta$ = 7.06 (d, $J$ = 8.1 Hz, 2H), 6.91 – 6.86 (m, 2H), 6.73 (d, $J$ = 8.2 Hz, 1H), 6.66 (d, $J$ = 2.2 Hz, 1H), 6.50 (dd, $J$ = 8.3, 2.2 Hz, 1H), 5.93 (s, 2H), 5.43 (s, 1H), 2.30 (s, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** $\delta$ = 148.1, 142.2, 141.7, 138.2, 129.8 (2C), 117.2, 111.6, 108.5, 101.5, 100.9, 20.6 ppm. **IR (KBr):** $\nu$ = 2887 1517, 1501, 1487, 1242, 1190, 1038, 931, 810 $cm^{-1}$. **HRMS (m/z)**: calcd for $C_{14}H_{14}NO_2$ $[M+H]^+$ 228.1019, found: 228.1016.



**4-Methyl-*N*-(4-phenoxyphenyl)aniline (4q):**[18] This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluant (petroleum ether/EtOAc = 200:1). Yield = 82%, 113.2 mg. Yellow solid. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta$ = 7.36 – 7.30 (m, 2H), 7.09 (ddd, $J$ = 8.5, 7.0, 1.7 Hz, 3H), 7.05 (q, $J$ = 1.5 Hz, 1H), 7.03 – 7.01 (m, 2H), 7.01 – 6.95 (m, 5H), 5.54 (s, 1H), 2.32 (s, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** $\delta$ = 158.3, 129.9, 129.6 (3C), 122.5, 120.6, 119.2, 117.9, 117.7 (3C), 20.6 ppm. **IR (KBr):** $\nu$ = 3023, 1508, 1489, 1263, 1231, 823, 809, 741, 690 $cm^{-1}$. **HRMS (m/z)**: calcd for $C_{19}H_{18}NO$ $[M+H]^+$ 276.1383, found: 276.1379.

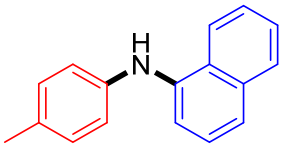


***N*-(*p*-Tolyl)-[1,1'-biphenyl]-4-amine (4r):**[12] This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluant (petroleum ether/EtOAc = 150:1). Yield = 78%, 100.9 mg. White solid. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta$ = 7.64 – 7.60 (m, 2H), 7.57 – 7.52 (m, 2H), 7.50 – 7.44 (m, 2H), 7.35 (td, $J$ = 7.2, 1.3 Hz, 1H), 7.17 (d, $J$ = 8.3 Hz, 2H), 7.14 – 7.07 (m, 4H), 5.72 (s, 1H), 2.38 (s, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** $\delta$ = 143.3, 140.8, 139.9, 132.9, 131.1, 129.9, 128.7, 127.9, 126.4, 119.0, 116.8, 20.7 ppm. **IR (KBr):** $\nu$ = 2913, 1609, 1528, 1515, 1409, 1315, 820, 754, 687 $cm^{-1}$. **HRMS (m/z)**: calcd for $C_{19}H_{18}N$ $[M+H]^+$ 260.1434, found: 260.1435.

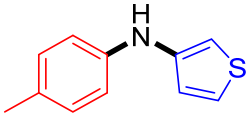


***N*-(*p*-Tolyl)naphthalen-2-amine (4s):**[12] This product was purified by silica gel column

chromatography using petroleum ether/ethyl acetate as eluant (petroleum ether/EtOAc = 200:1). Yield = 82%, 95.7 mg. Brown solid. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta$ = 7.75 – 7.72 (m, 2H), 7.63 (d, $J$ = 8.2 Hz, 1H), 7.42 – 7.36 (m, 2H), 7.29 (ddd, $J$ = 8.1, 6.8, 1.3 Hz, 1H), 7.19 (dd, $J$ = 8.8, 2.4 Hz, 1H), 7.17 – 7.09 (m, 4H), 5.78 (s, 1H), 2.35 (s, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** $\delta$ = 141.7, 140.1, 134.7, 131.4, 129.9, 129.1, 128.8, 127.6, 126.4, 126.3, 123.1, 119.5, 119.3, 110.2, 20.7 ppm. **IR (KBr):** $\nu$ = 2913, 1511, 1310, 1237, 952, 813, 740, 502, 470 $cm^{-1}$. **HRMS (m/z)**: calcd for $C_{17}H_{16}N$ $[M+H]^+$ 234.1277, found: 234.1278.



***N*-(*p*-Tolyl)naphthalen-1-amine (4t):**[17] This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluant (petroleum ether/EtOAc = 200:1). Yield = 56%, 65.8 mg. Red oil. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta$ = 8.05 – 8.01 (m, 1H), 7.89 – 7.85 (m, 1H), 7.55 – 7.47 (m, 3H), 7.38 (t, $J$ = 7.8 Hz, 1H), 7.30 (dd, $J$ = 7.4, 1.2 Hz, 1H), 7.13 – 7.08 (m, 2H), 6.99 – 6.95 (m, 2H), 5.91 (s, 1H), 2.33 (s, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** $\delta$ = 141.7, 139.5, 134.6, 130.4, 129.8, 128.5, 126.9, 126.1, 126.0, 125.5, 122.0, 121.5, 118.4, 114.0, 20.7 ppm. **IR (KBr):** $\nu$ = 2830, 1626, 1606, 1515, 1401, 1366, 1307, 1157, 774 $cm^{-1}$. **HRMS (m/z)**: calcd for $C_{17}H_{16}N$ $[M+H]^+$ 234.1277, found: 234.1277.



***N*-(*p*-Tolyl)thiophen-3-amine (4u):**[19] This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluant (petroleum ether/EtOAc = 200:1). Yield = 42%, 39.6 mg. Brown solid. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta$ = 7.24 (dd, $J$ = 5.1, 3.1 Hz, 1H), 7.07 (dt, $J$ = 8.0, 0.7 Hz, 2H), 6.94 – 6.88 (m, 3H), 6.67 (ddd, $J$ = 3.1, 1.5, 0.7 Hz, 1H), 5.63 (s, 1H), 2.29 (s, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** $\delta$ = 142.3, 142.0, 129.8, 129.5, 125.1, 122.5, 116.2, 104.9, 20.6 ppm. **IR (KBr):** $\nu$ = 2917, 1557, 1515, 1440, 1358, 1311, 1244, 809, 734 $cm^{-1}$. **HRMS (m/z)**: calcd for $C_{11}H_{12}NS$ $[M+H]^+$ 190.0685, found: 190.0684.

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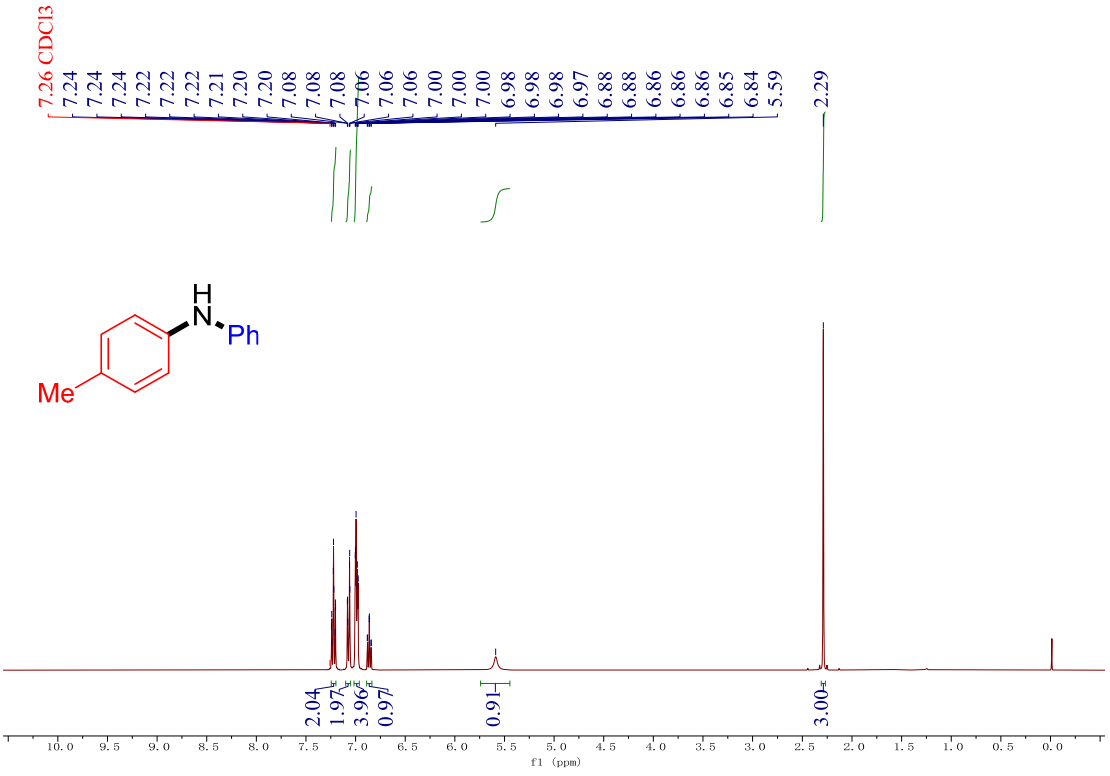
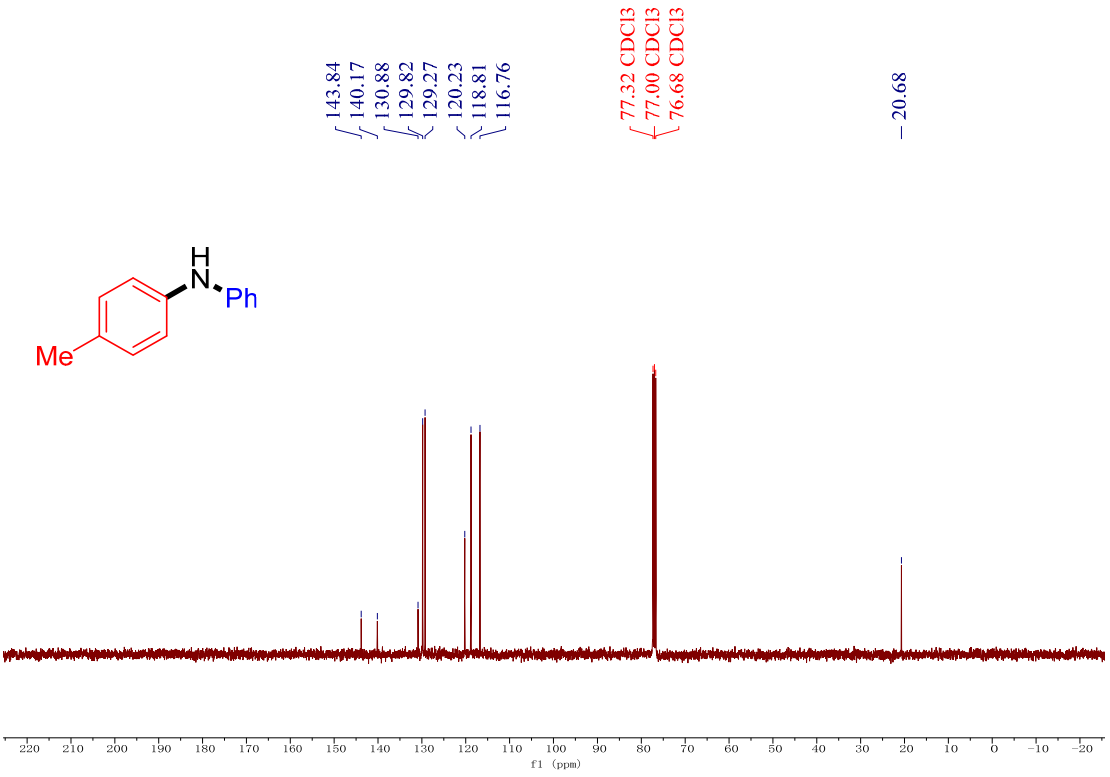
# $^{1}$H, $^{13}$C, and $^{19}$F NMR spectra of products

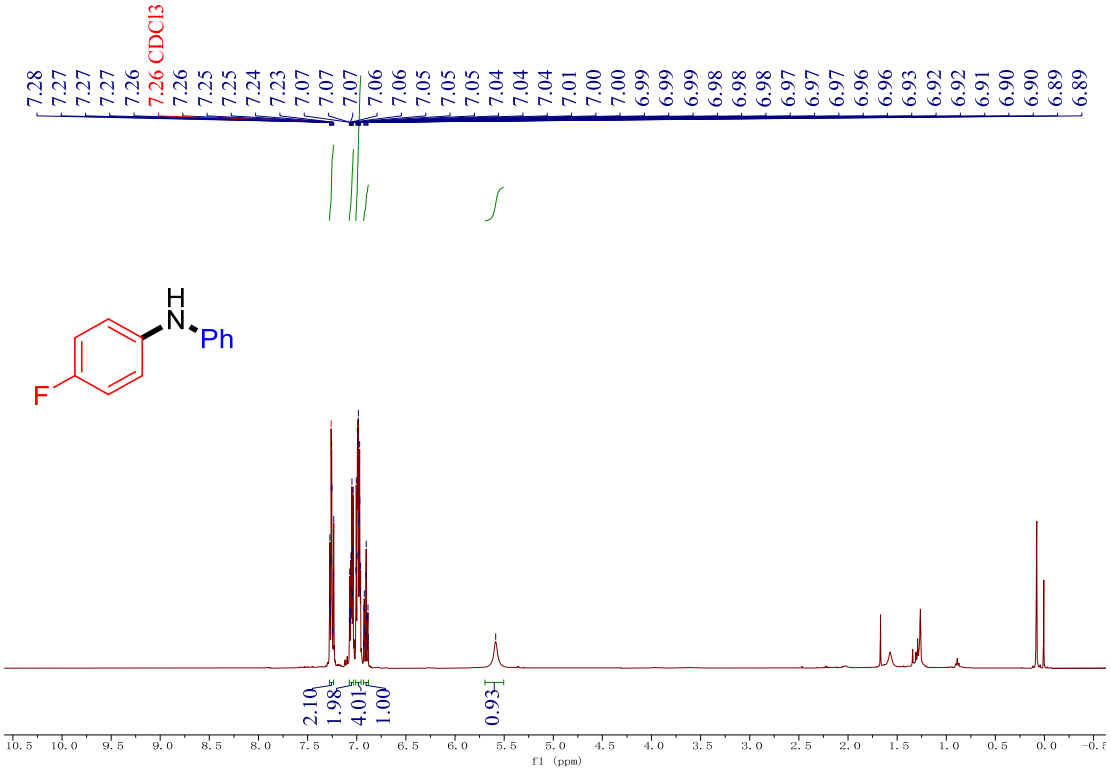
**$^{1}$H NMR spectrum of 3a** (400 MHz, $CDCl_3$)



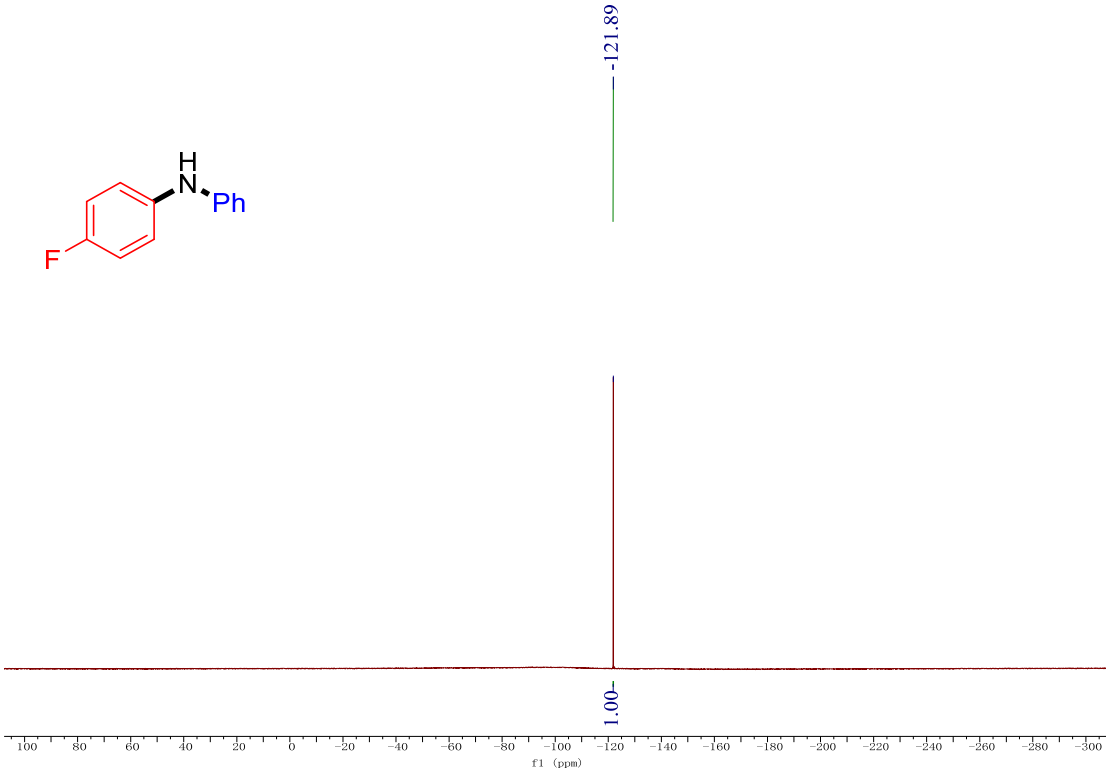

**$^{13}$C NMR spectrum of 3a** (100 MHz, $CDCl_3$)



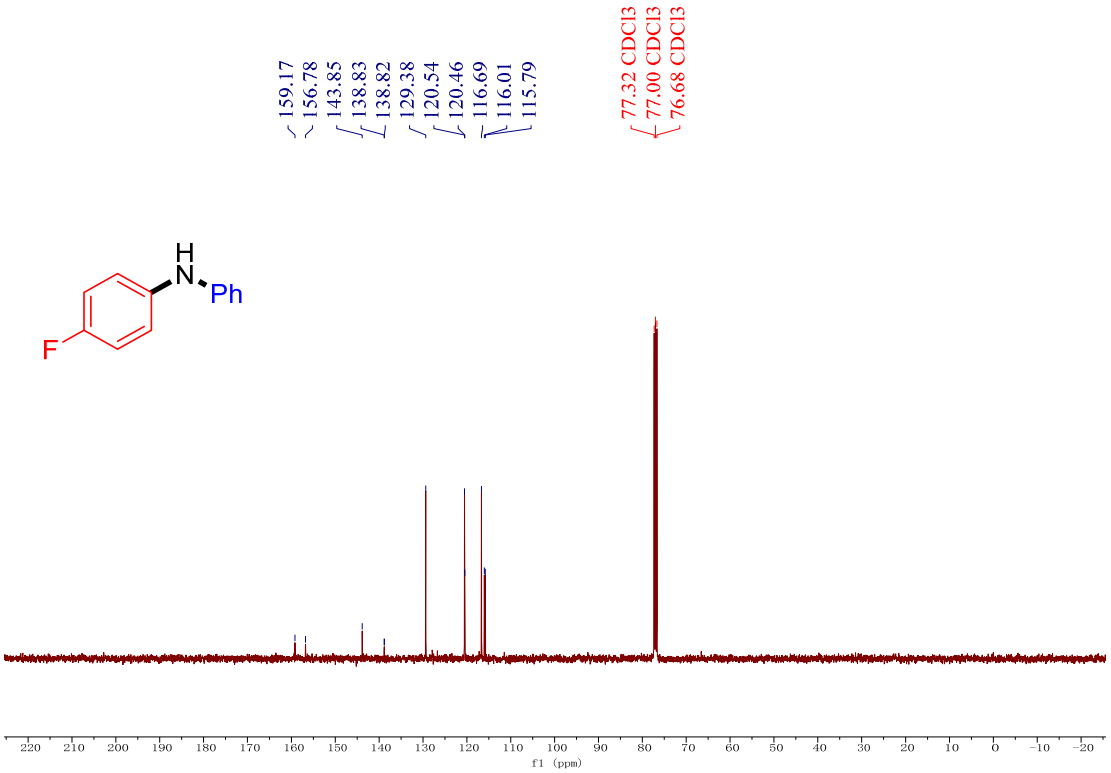
**$^{1}$H NMR spectrum of 3b** (400 MHz, $CDCl_3$)



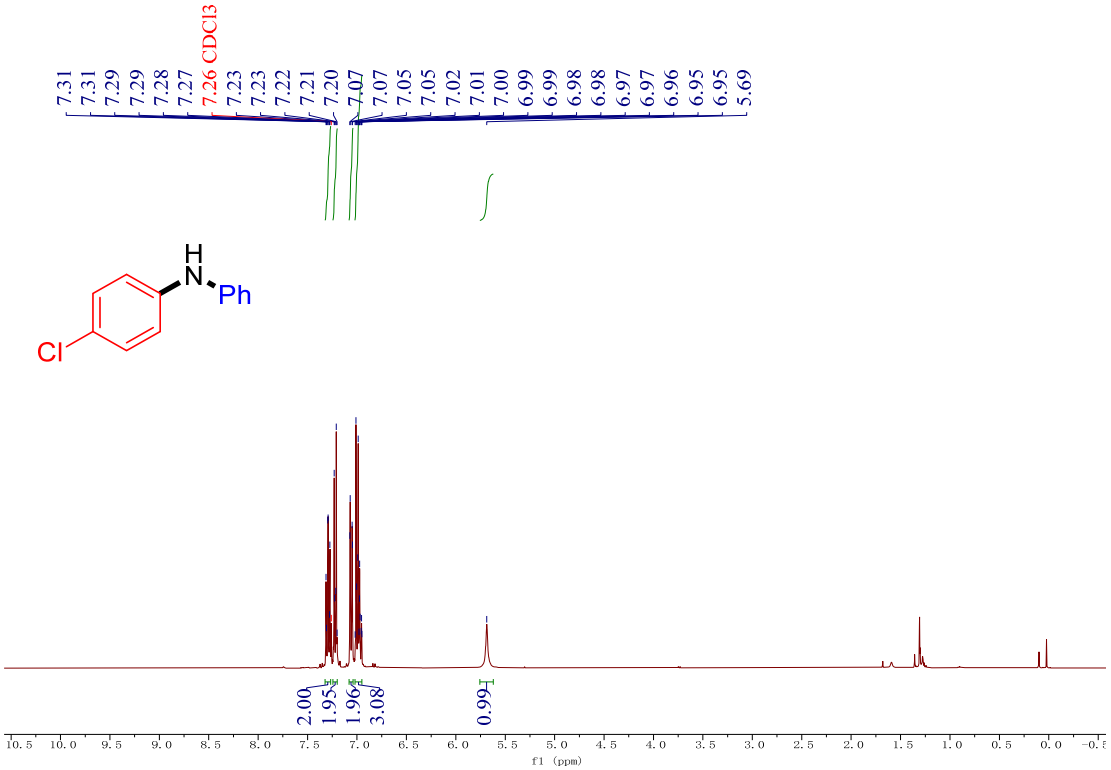

**$^{19}$F NMR spectrum of 3b** (376 MHz, $CDCl_3$)



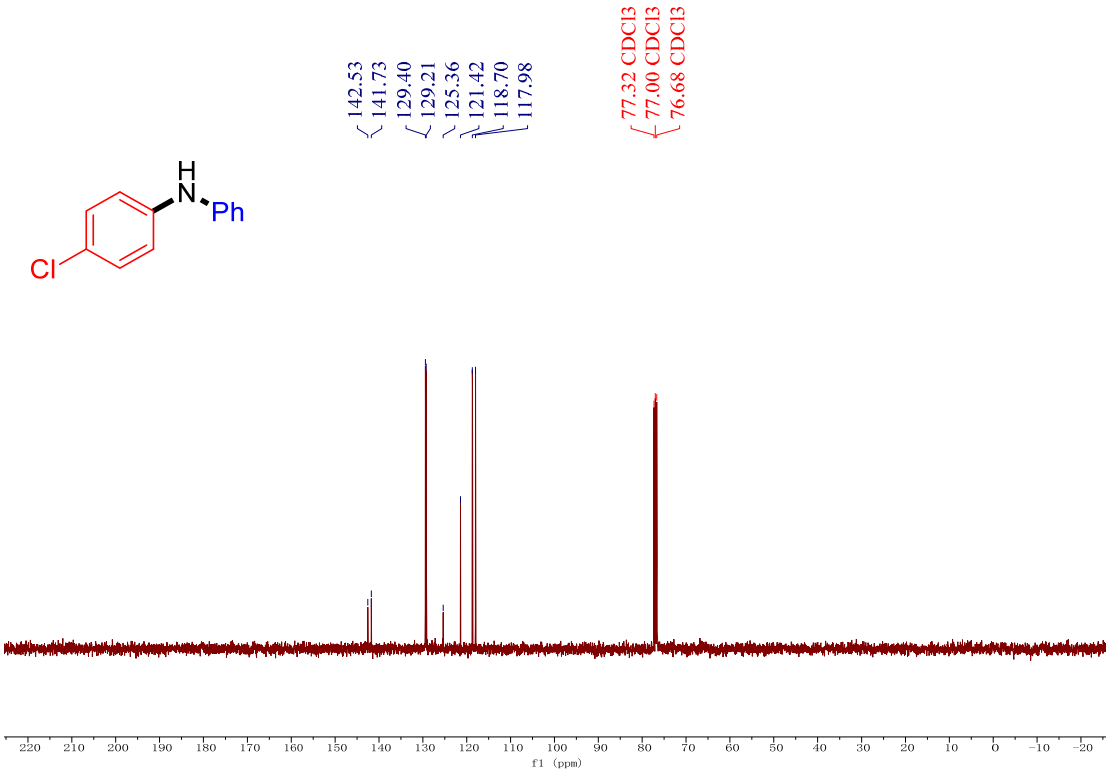
**$^{13}$C NMR spectrum of 3b** (100 MHz, $CDCl_3$)



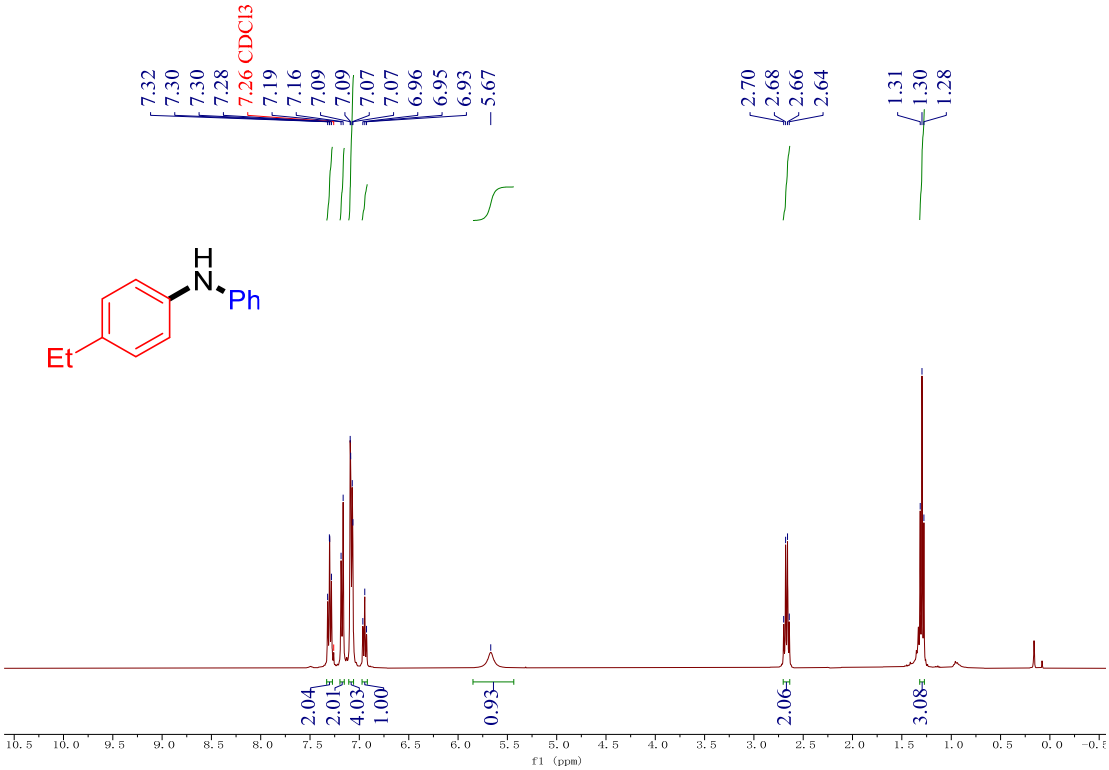

**$^{1}$H NMR spectrum of 3c** (400 MHz, $CDCl_3$)



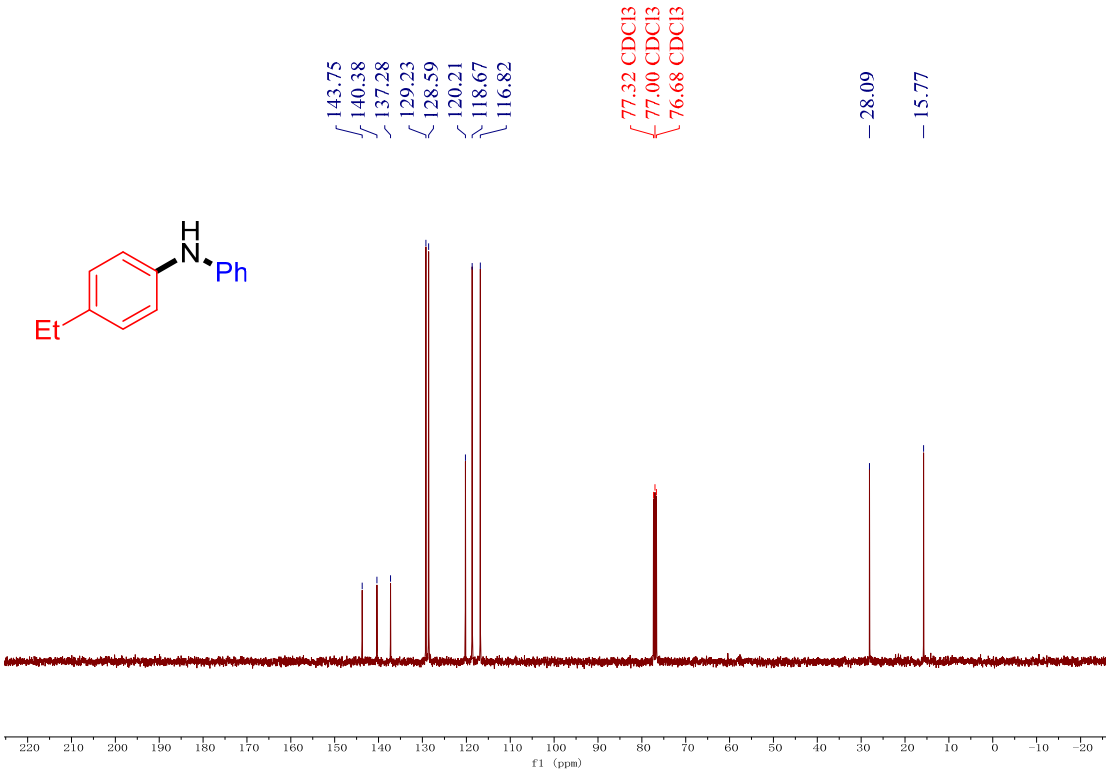
**$^{13}$C NMR spectrum of 3c** (100 MHz, $CDCl_3$)



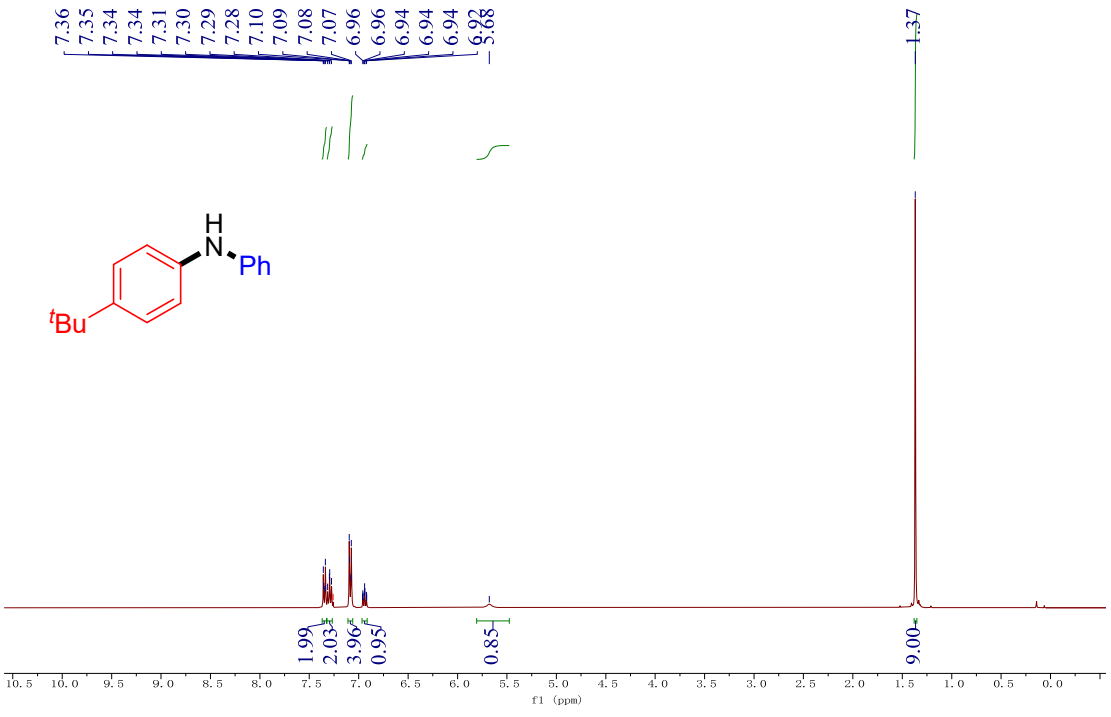

**$^{1}$H NMR spectrum of 3d** (400 MHz, $CDCl_3$)



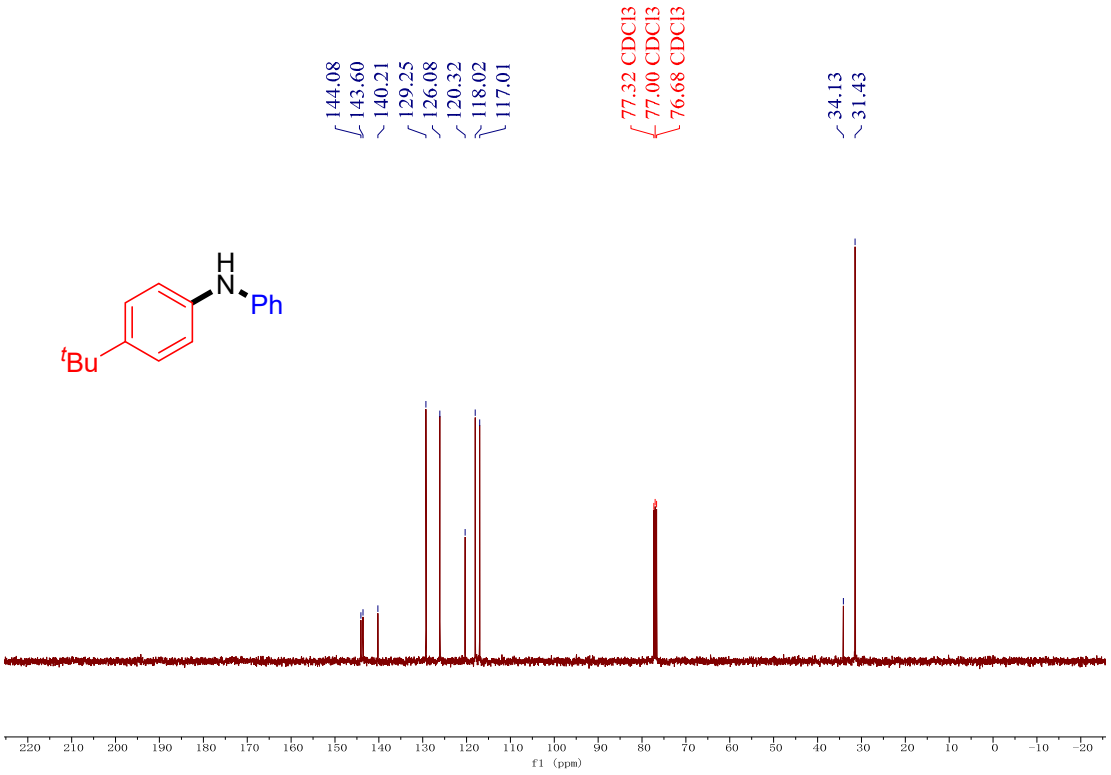
**$^{13}$C NMR spectrum of 3d** (100 MHz, $CDCl_3$)



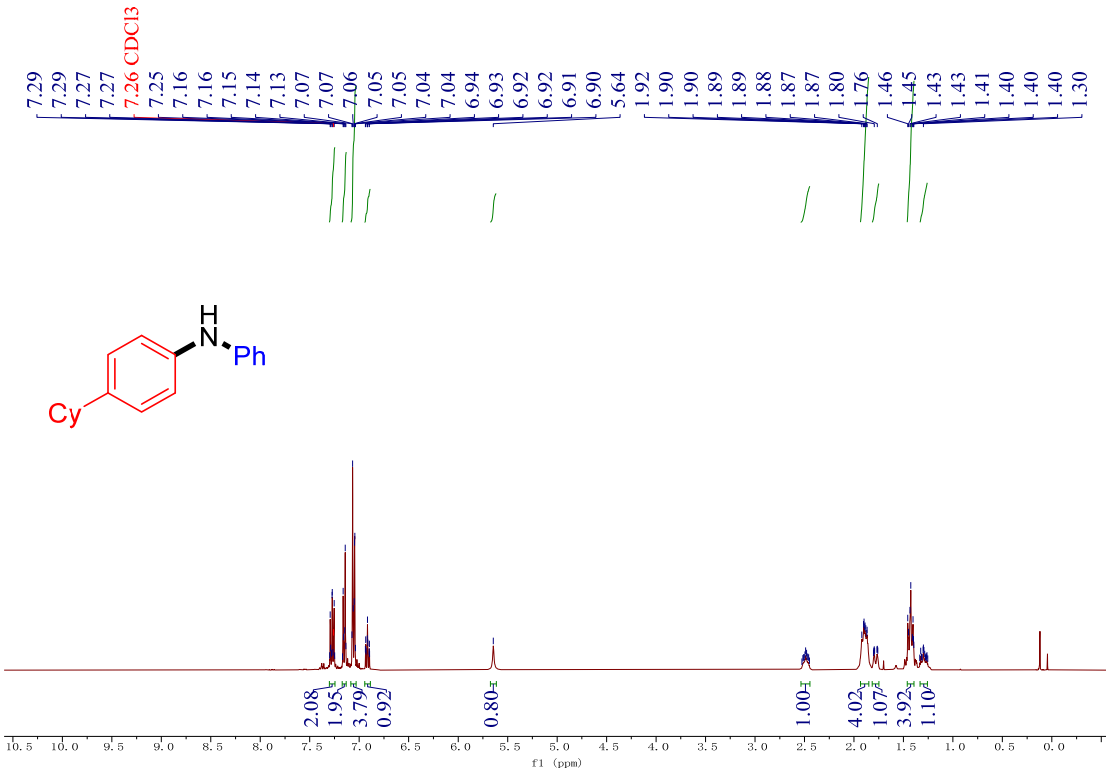

**$^{1}$H NMR spectrum of 3e** (400 MHz, $CDCl_3$)



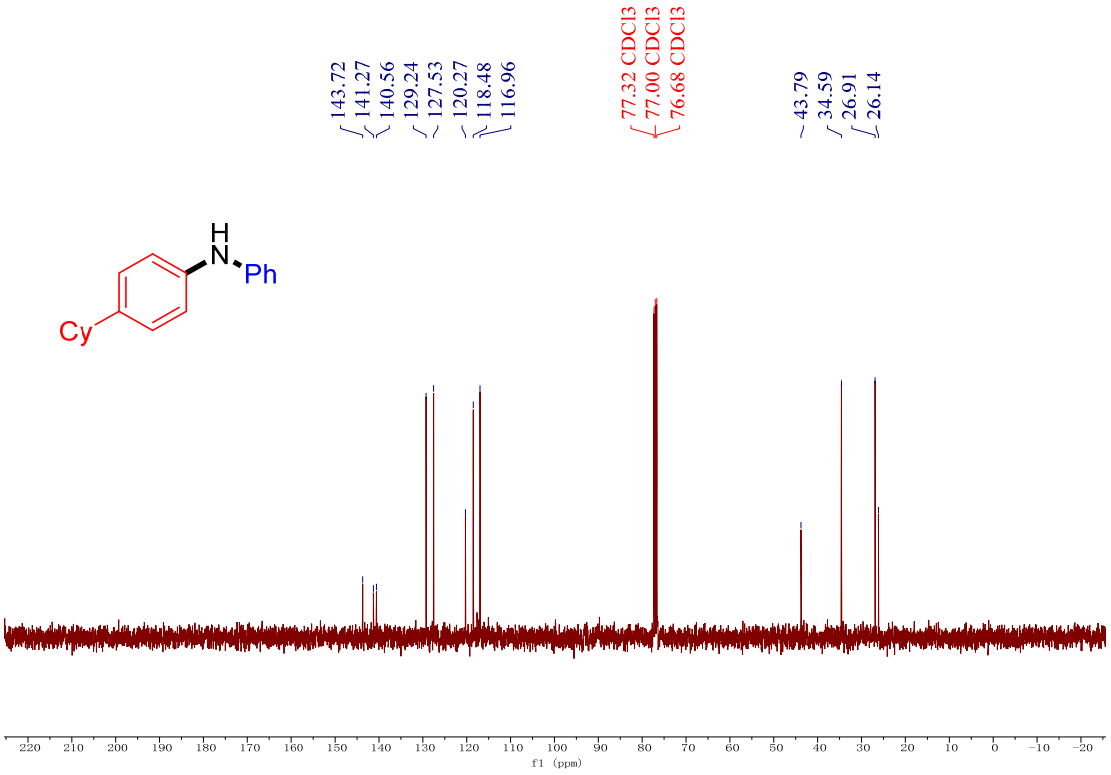
**$^{13}$C NMR spectrum of 3e** (100 MHz, $CDCl_3$)



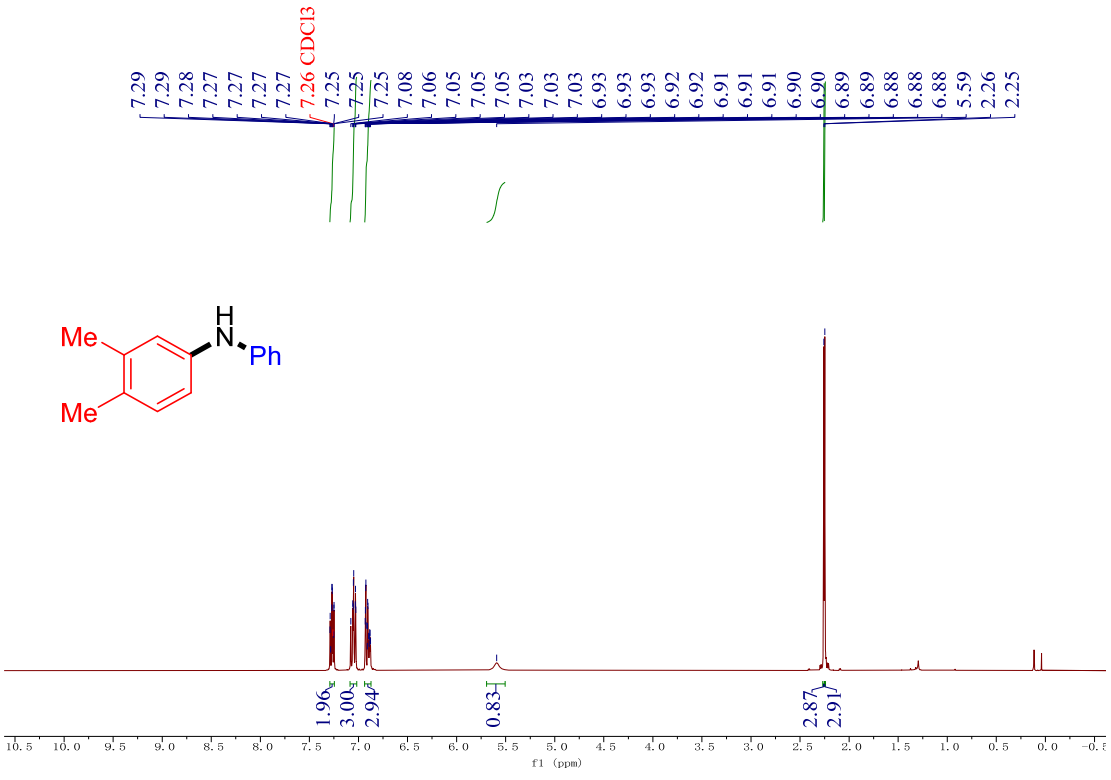

**$^{1}$H NMR spectrum of 3f** (400 MHz, $CDCl_3$)



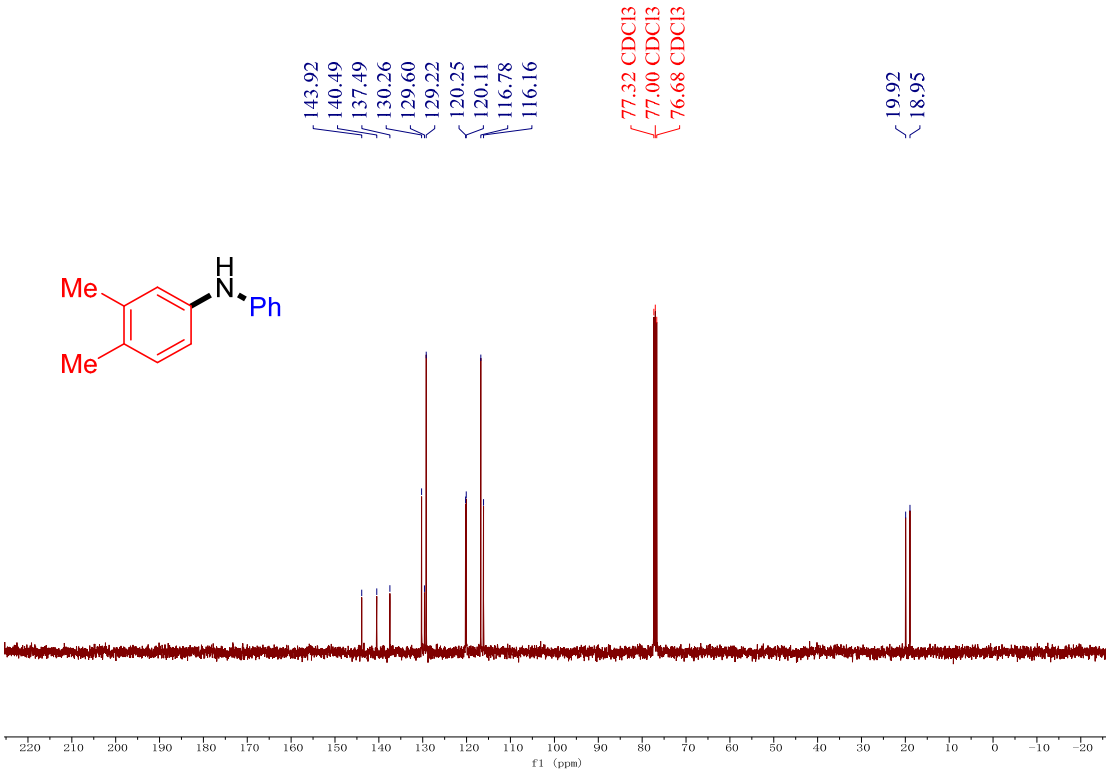
**$^{13}$C NMR spectrum of 3f** (100 MHz, $CDCl_3$)



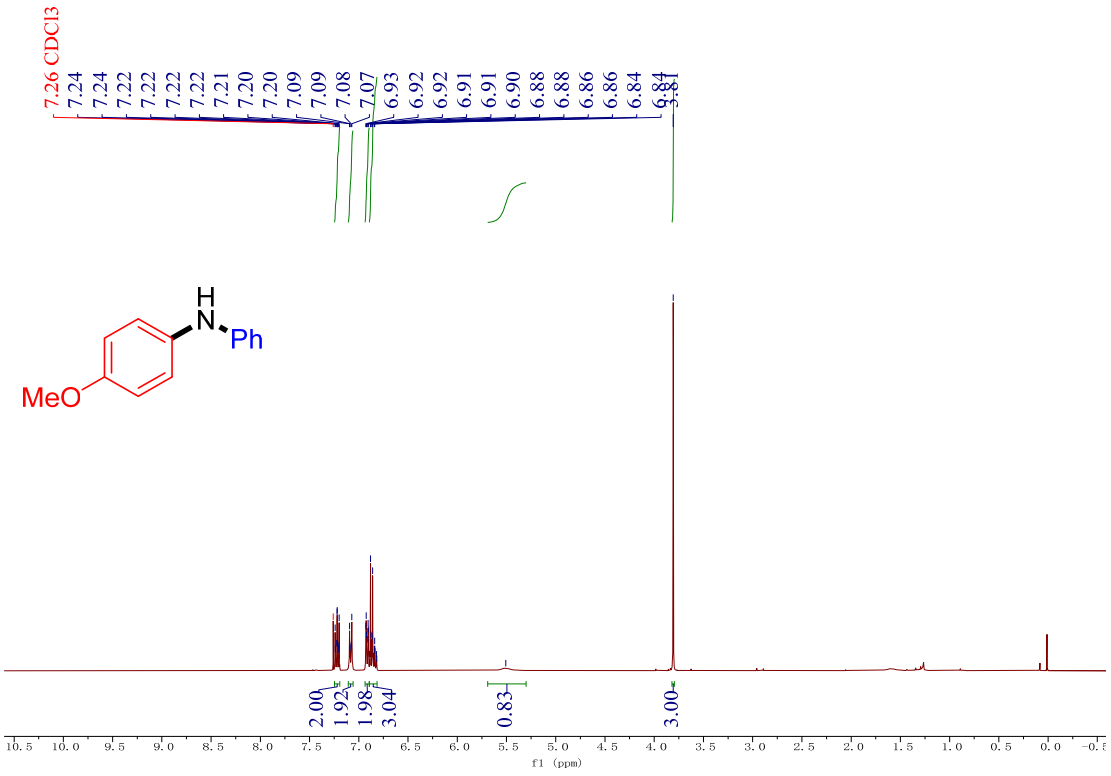

**$^{1}$H NMR spectrum of 3g** (400 MHz, $CDCl_3$)



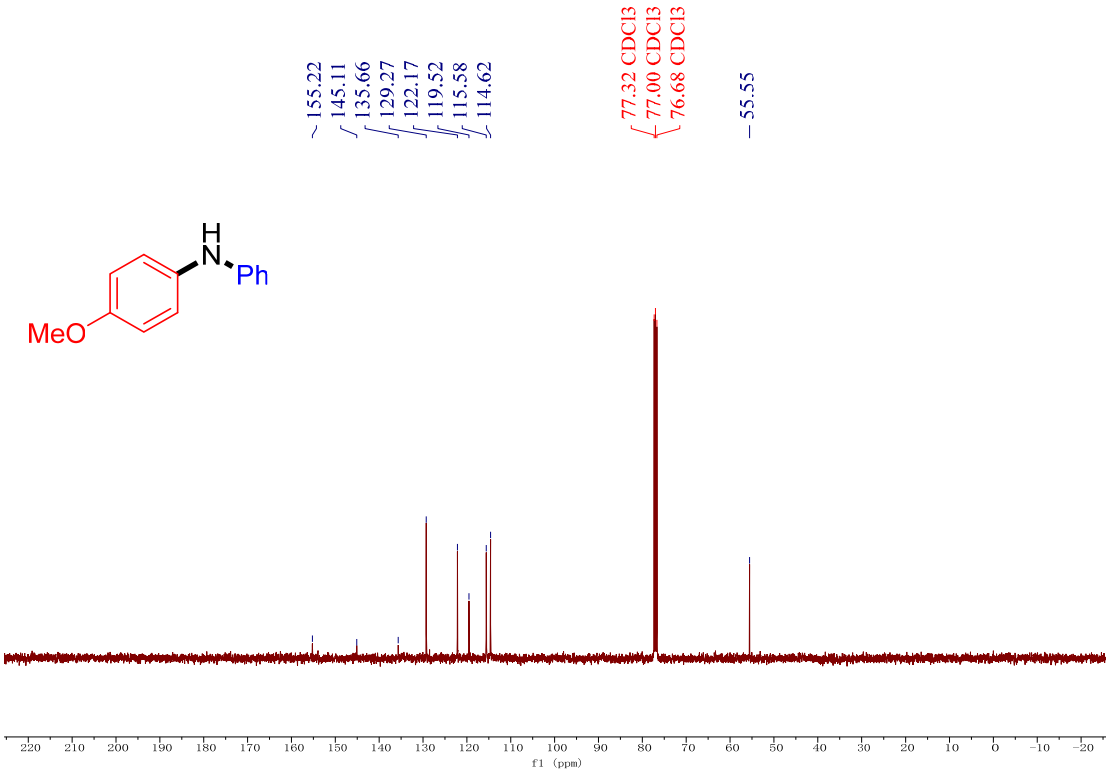
**$^{13}$C NMR spectrum of 3g** (100 MHz, $CDCl_3$)



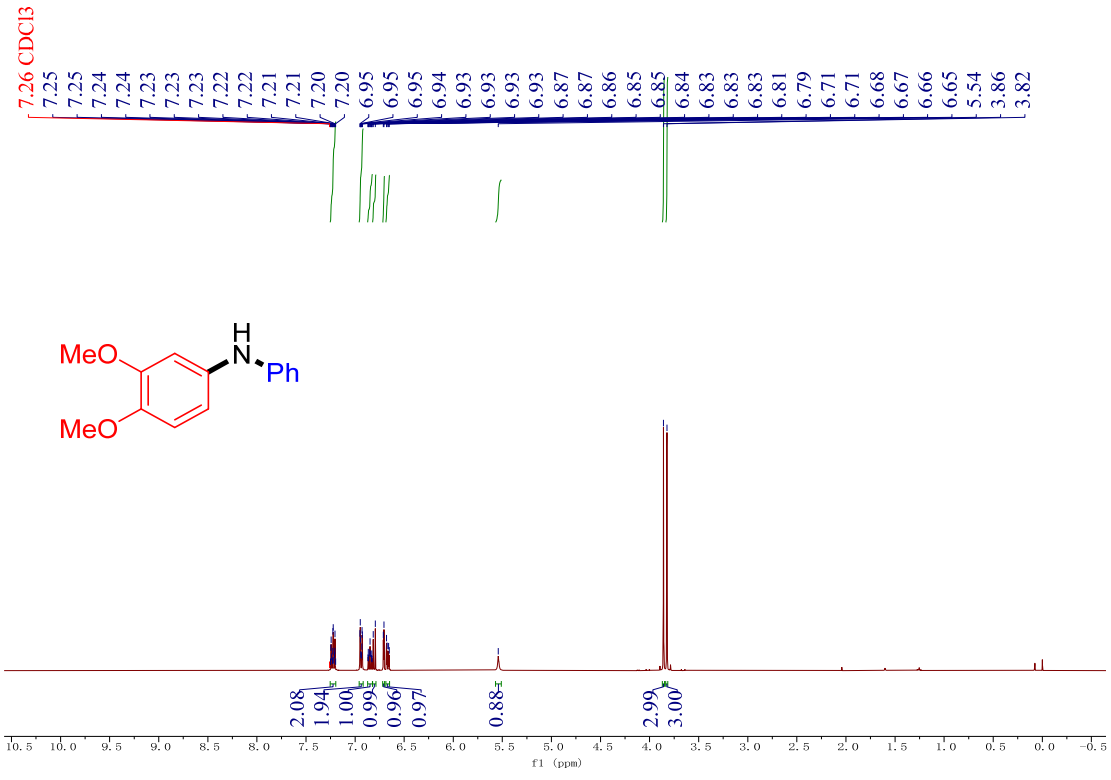

**$^{1}$H NMR spectrum of 3h** (400 MHz, $CDCl_3$)



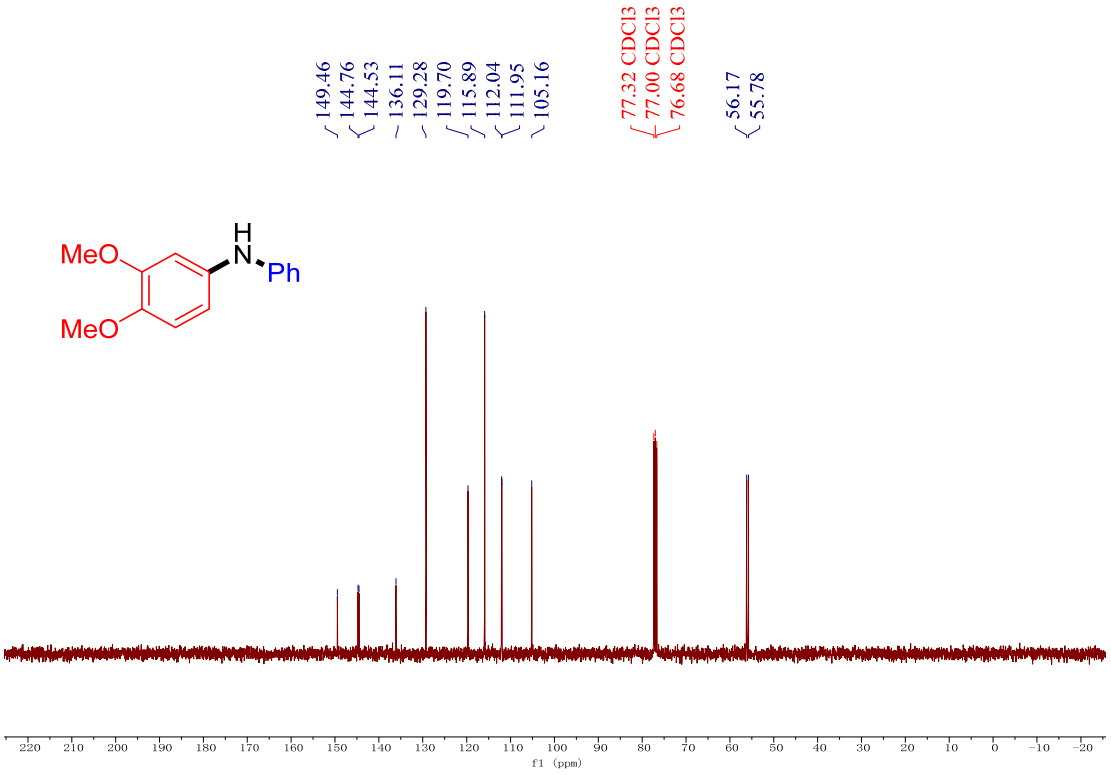
**$^{13}$C NMR spectrum of 3h** (100 MHz, $CDCl_3$)



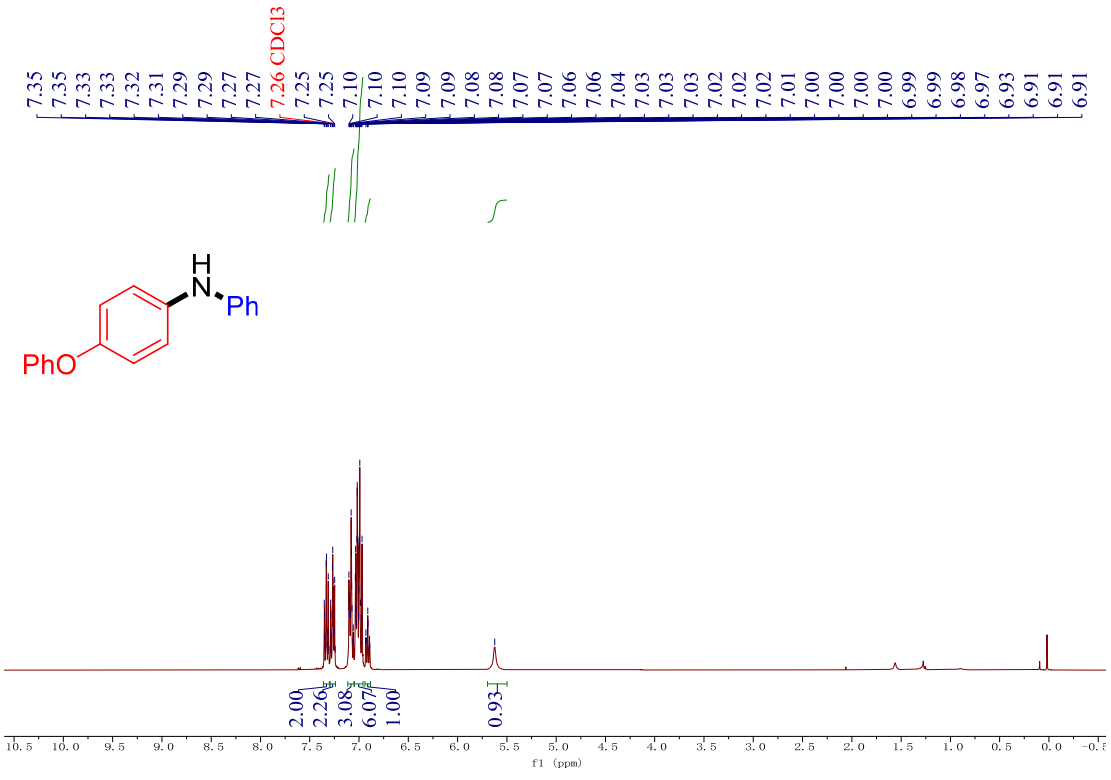

**$^{1}$H NMR spectrum of 3i** (400 MHz, $CDCl_3$)



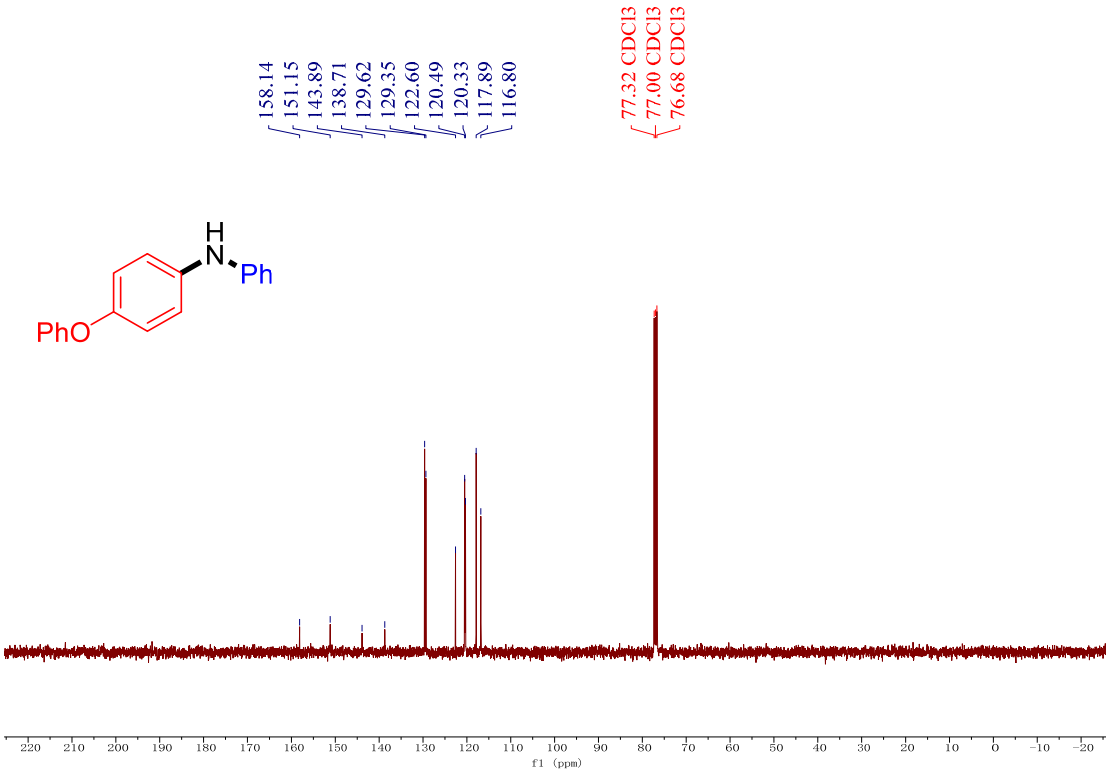
**$^{13}$C NMR spectrum of 3i** (100 MHz, $CDCl_3$)



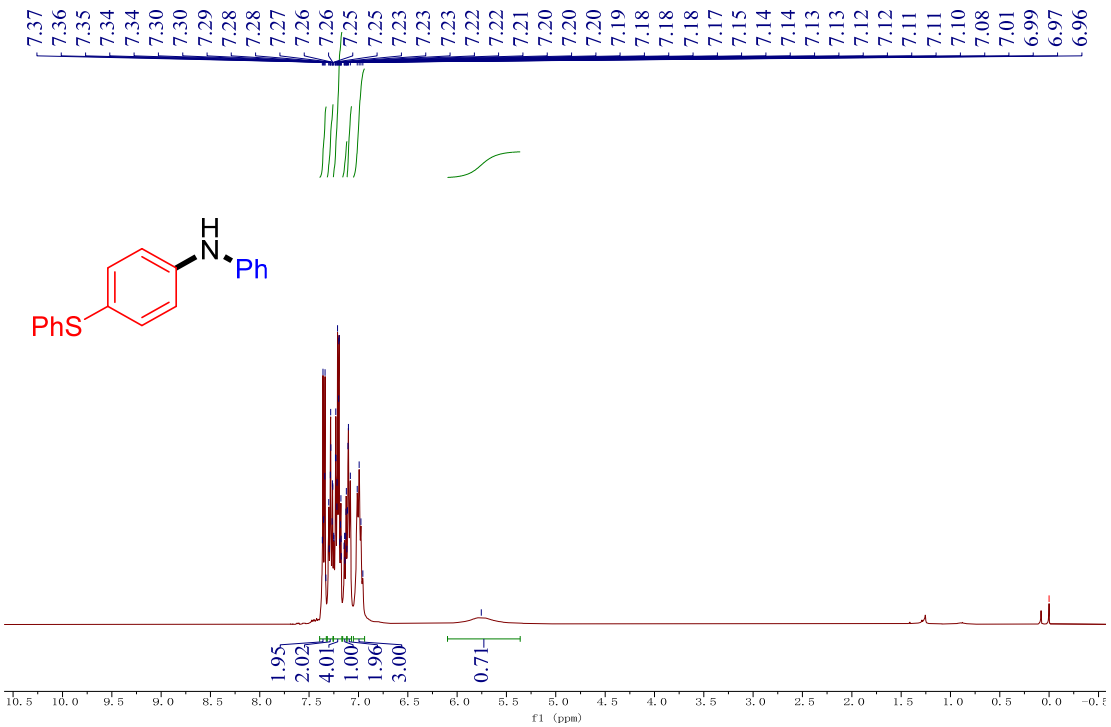

**$^{1}$H NMR spectrum of 3j** (400 MHz, $CDCl_3$)



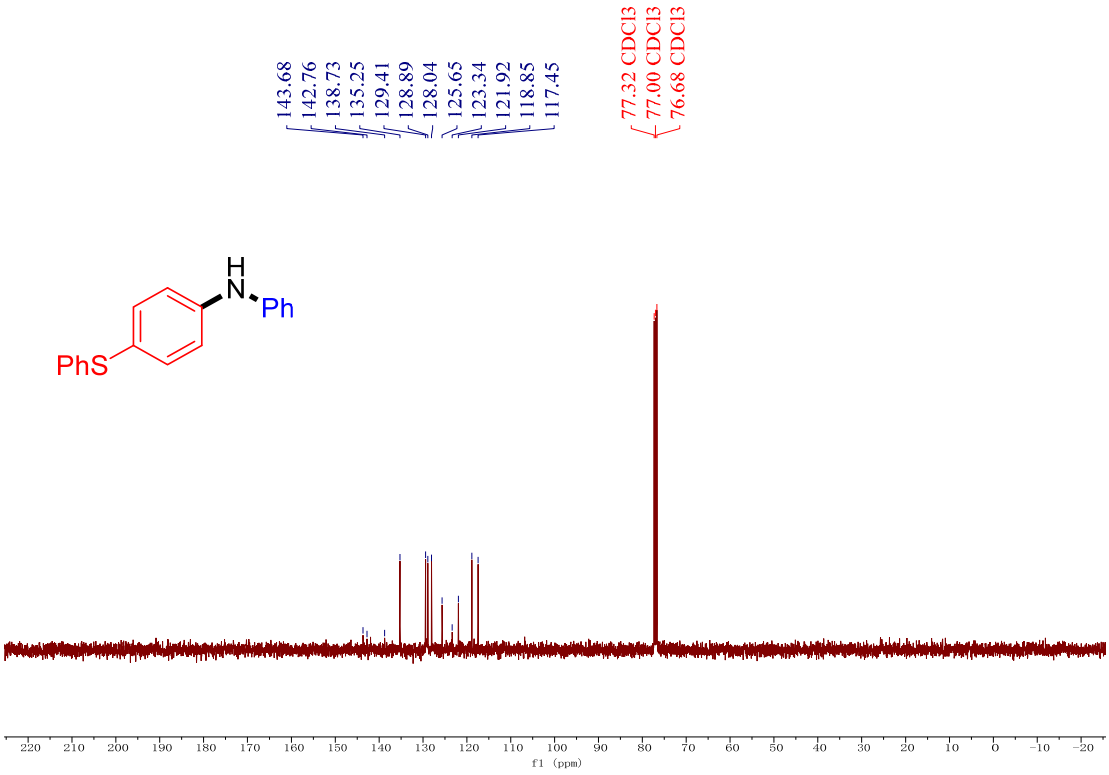
**$^{13}$C NMR spectrum of 3j** (100 MHz, $CDCl_3$)



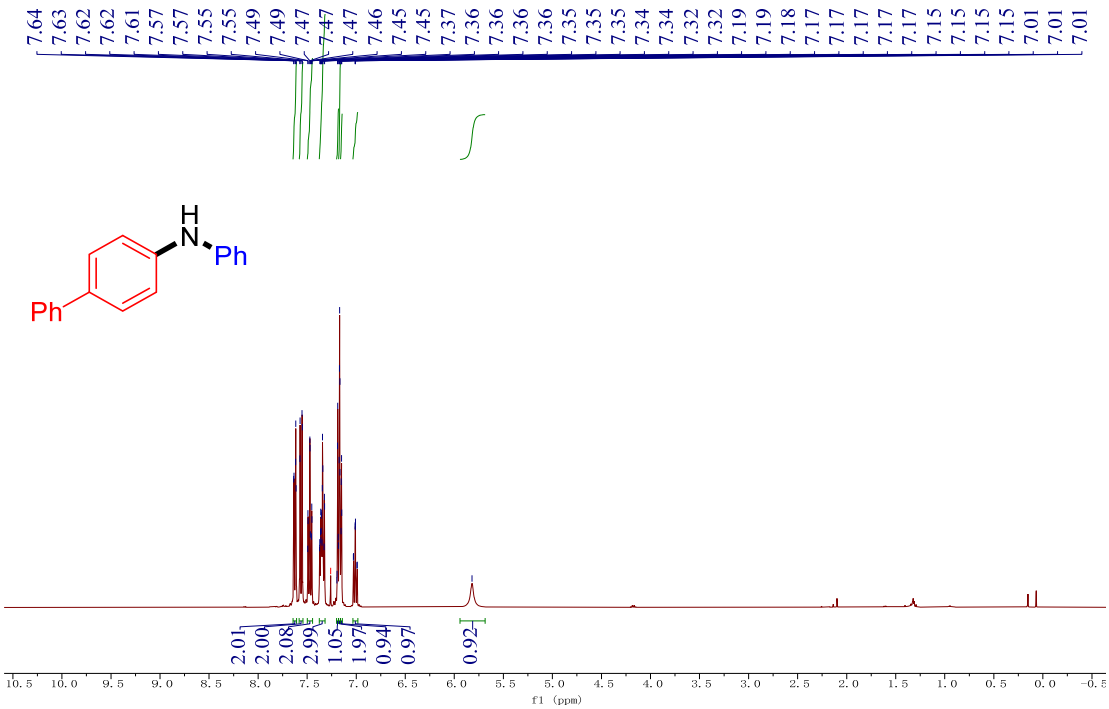

**$^{1}$H NMR spectrum of 3k** (400 MHz, $CDCl_3$)



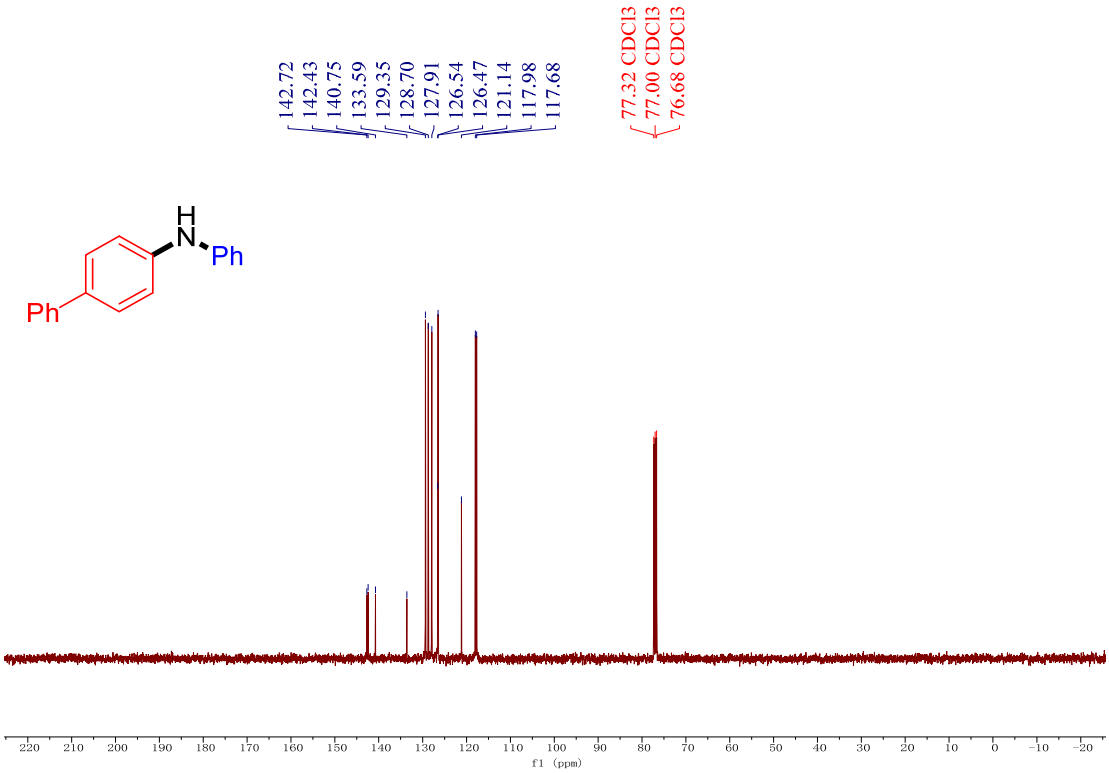
**$^{13}$C NMR spectrum of 3k** (100 MHz, $CDCl_3$)



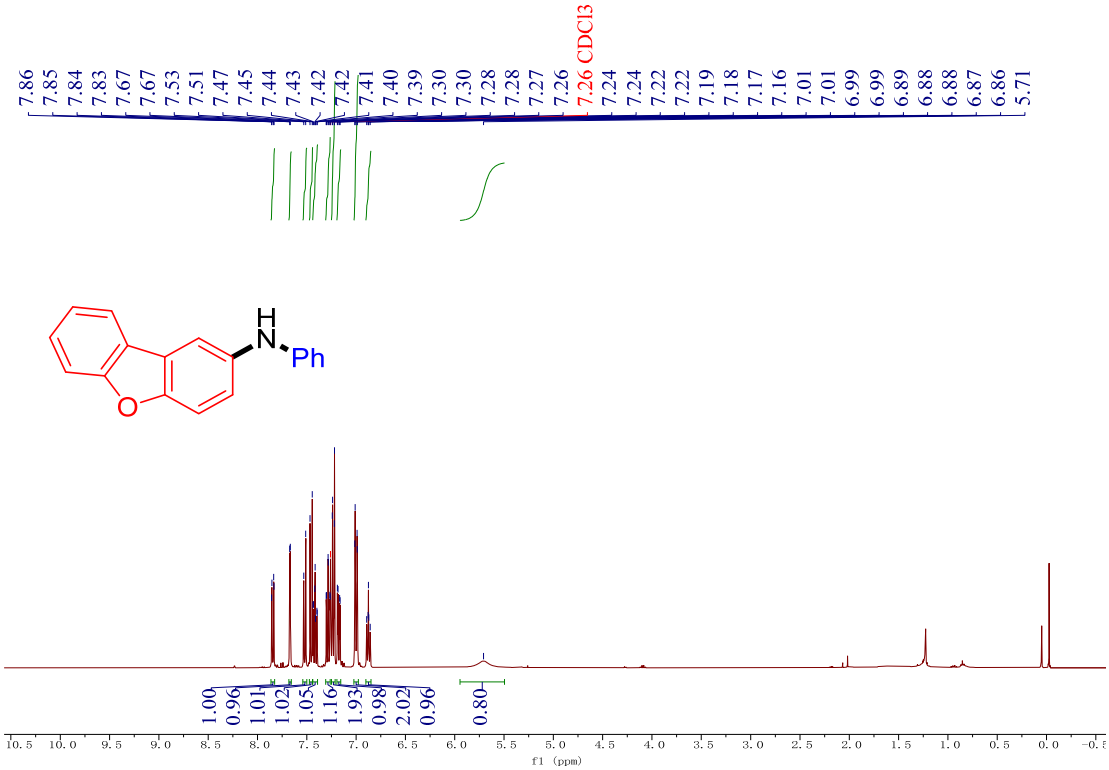

**$^{1}$H NMR spectrum of 3l** (400 MHz, $CDCl_3$)



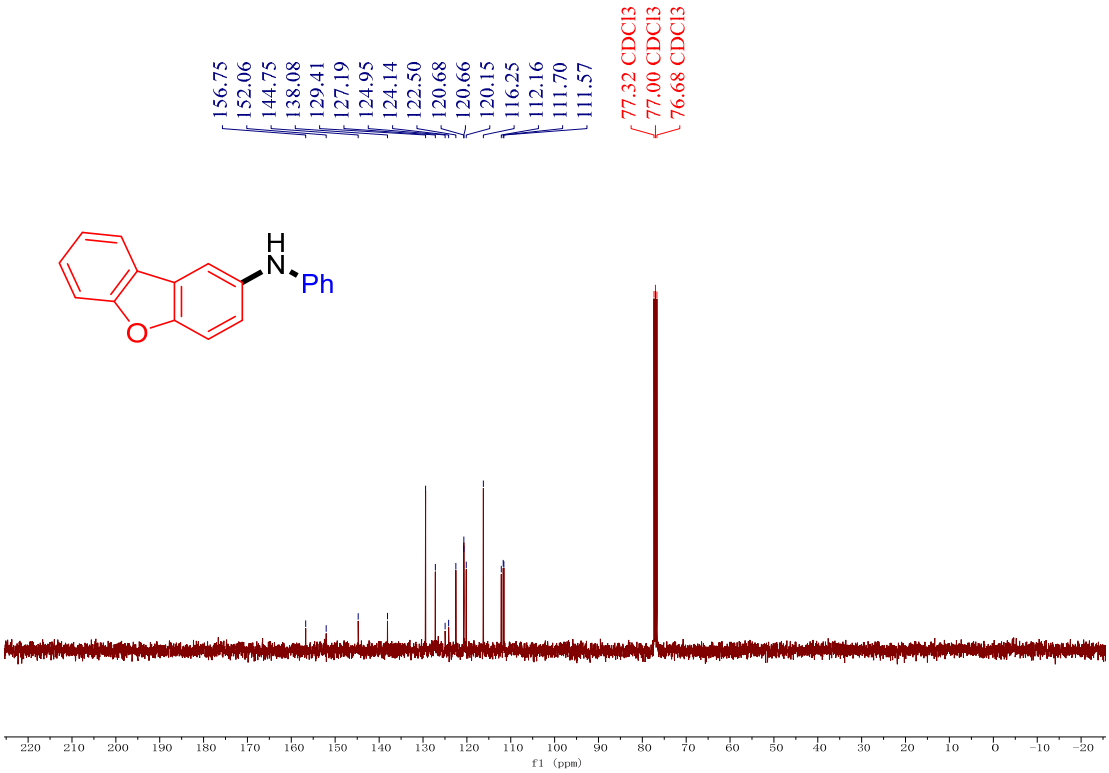
**$^{13}$C NMR spectrum of 3l** (100 MHz, $CDCl_3$)



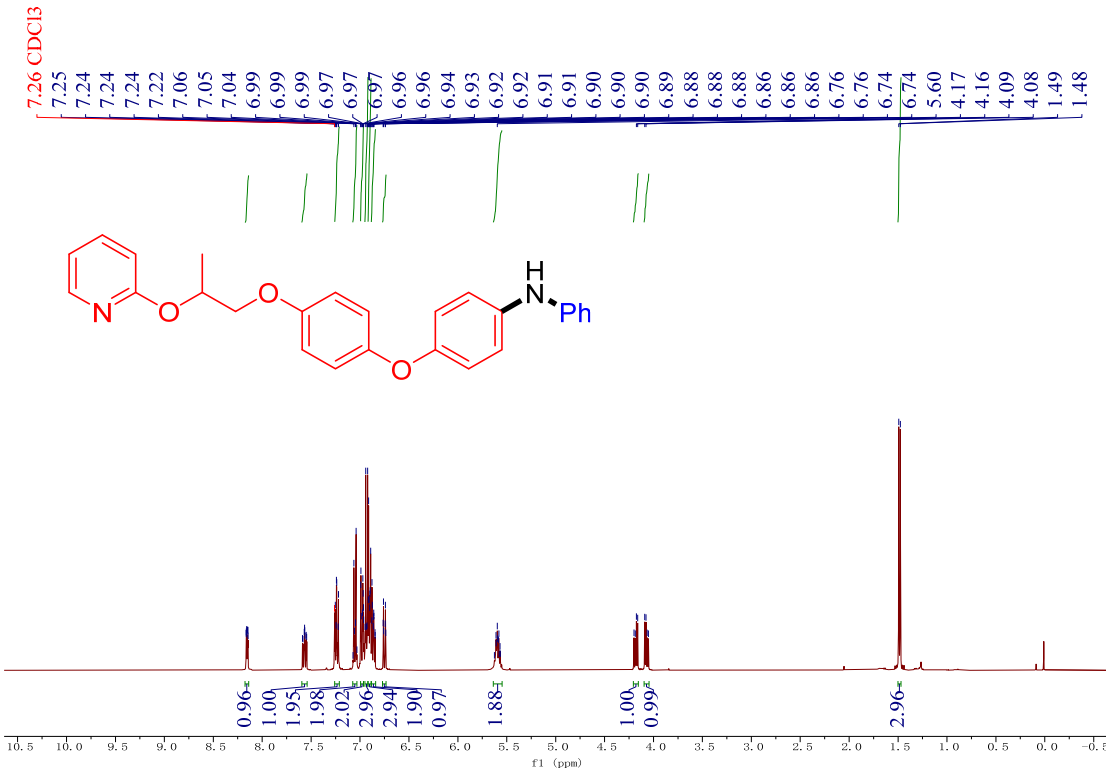

**$^{1}$H NMR spectrum of 3m** (400 MHz, $CDCl_3$)



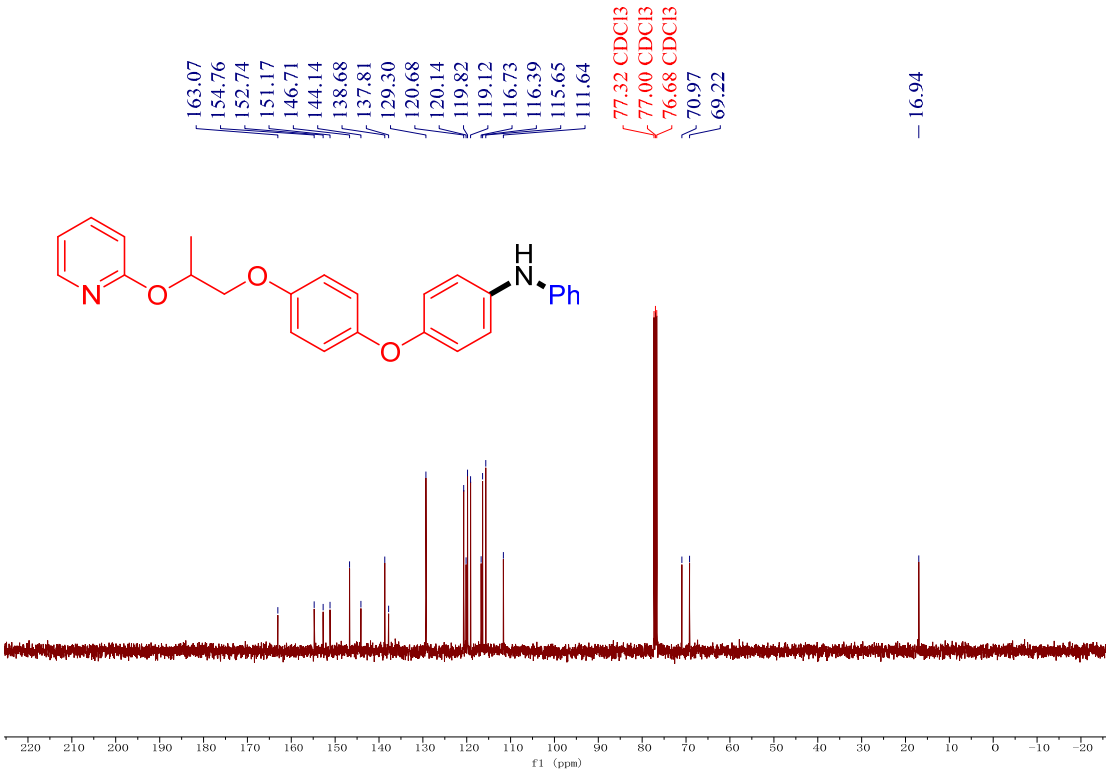
**$^{13}$C NMR spectrum of 3m** (100 MHz, $CDCl_3$)



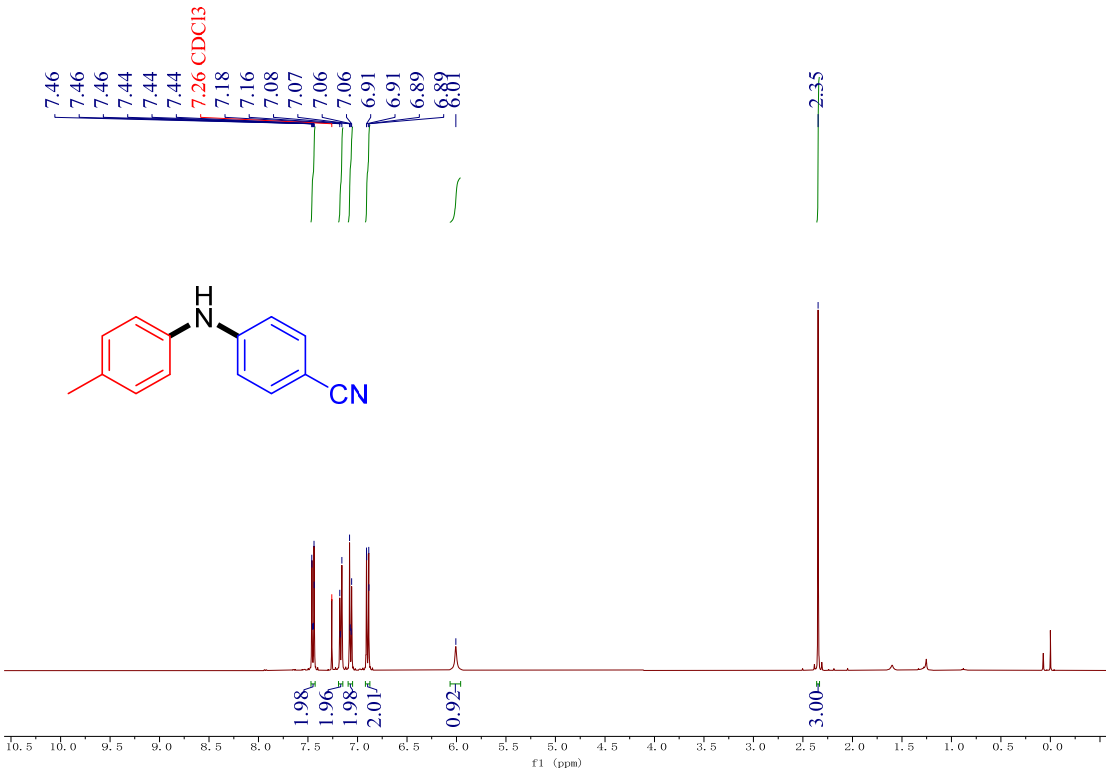

**$^{1}$H NMR spectrum of 3n** (400 MHz, $CDCl_3$)



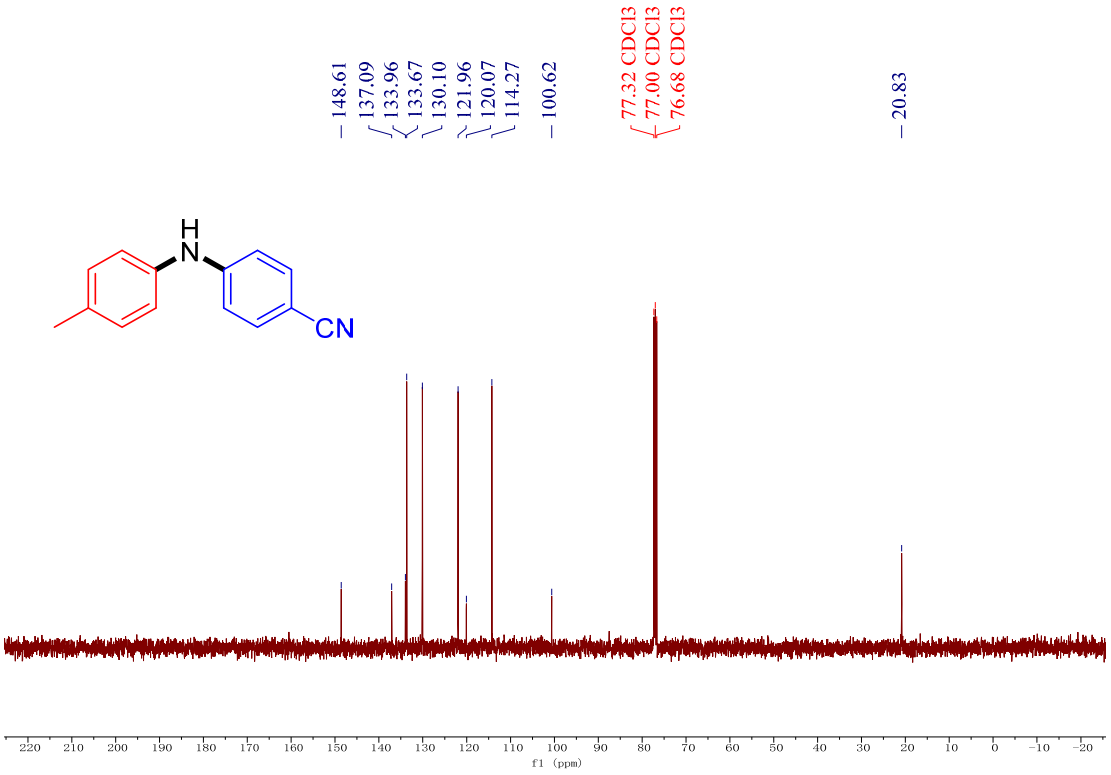
**$^{13}$C NMR spectrum of 3n** (100 MHz, $CDCl_3$)



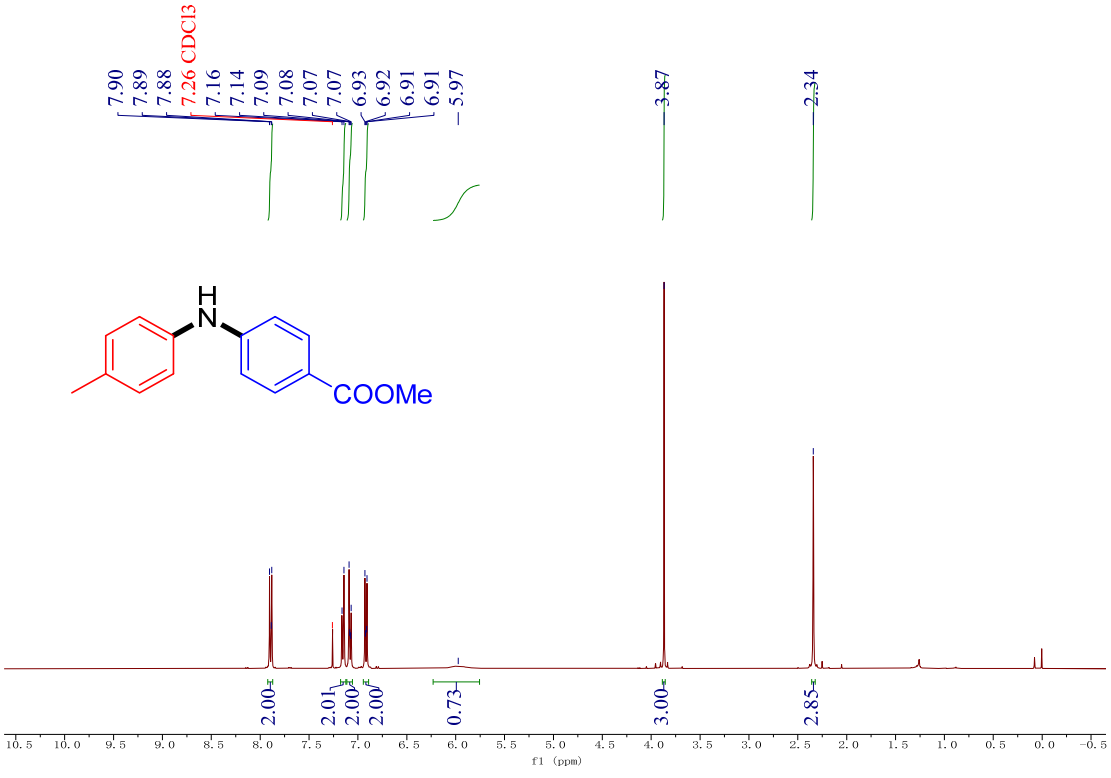

**$^{1}$H NMR spectrum of 4b** (400 MHz, $CDCl_3$)



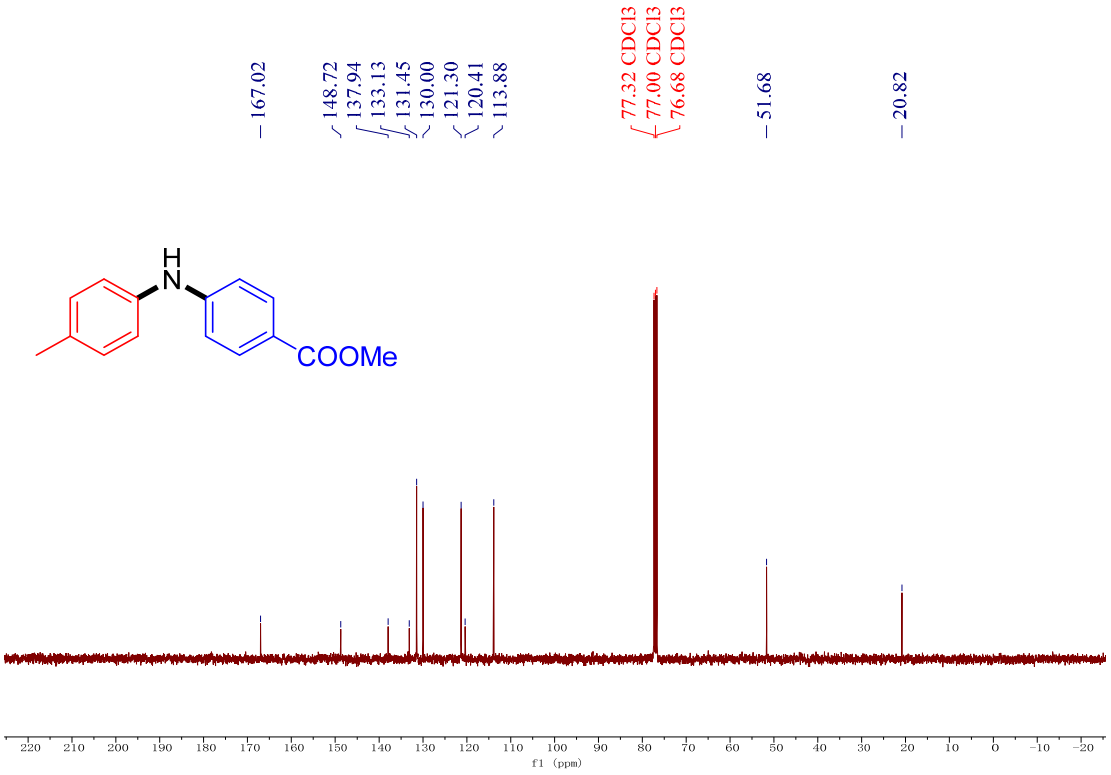
**$^{13}$C NMR spectrum of 4b** (100 MHz, $CDCl_3$)



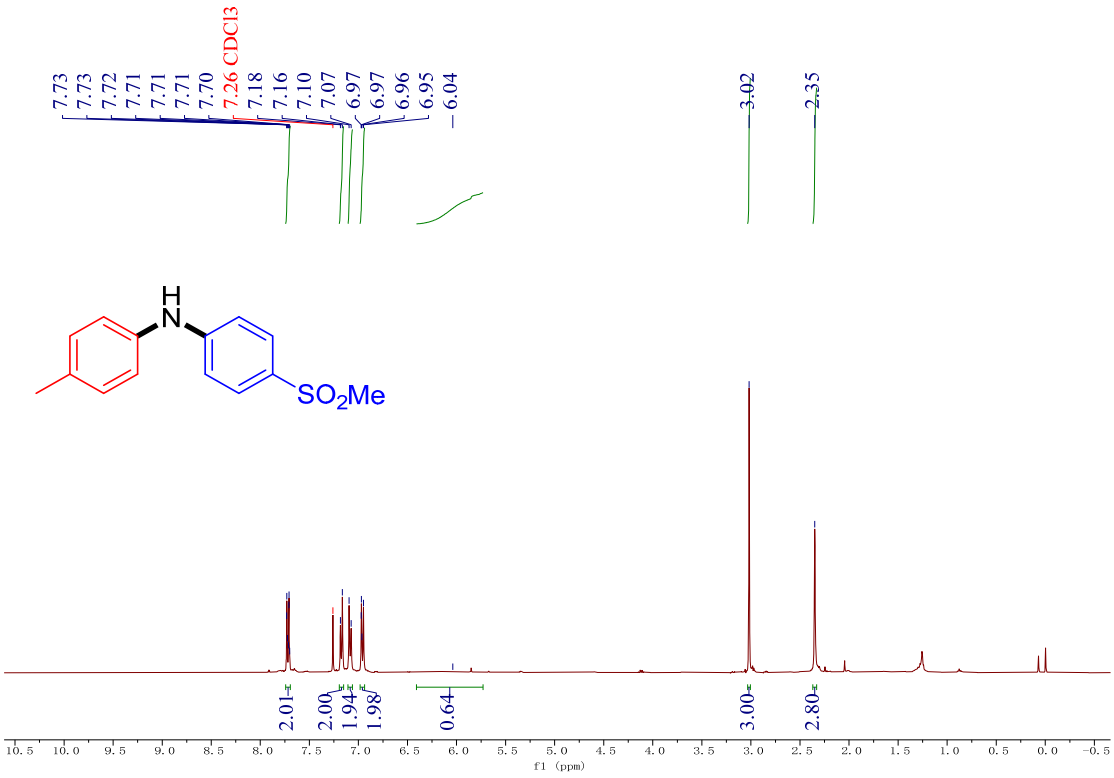

**$^{1}$H NMR spectrum of 4c** (400 MHz, $CDCl_3$)



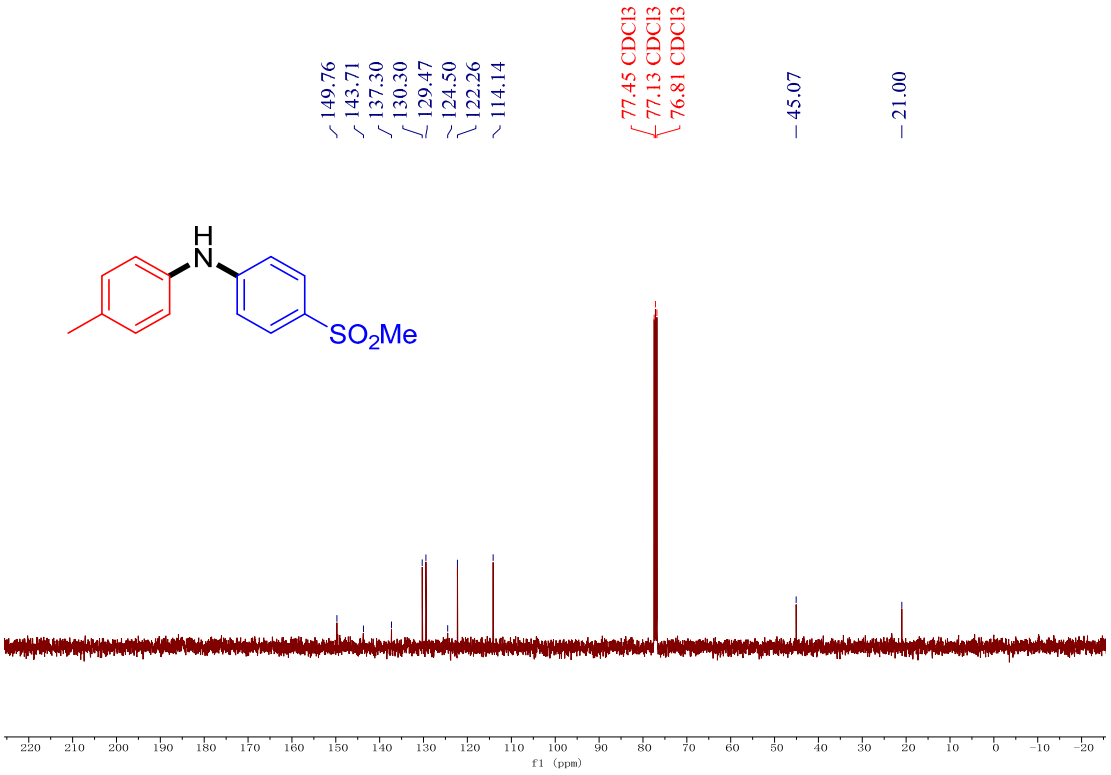
**$^{13}$C NMR spectrum of 4c** (100 MHz, $CDCl_3$)



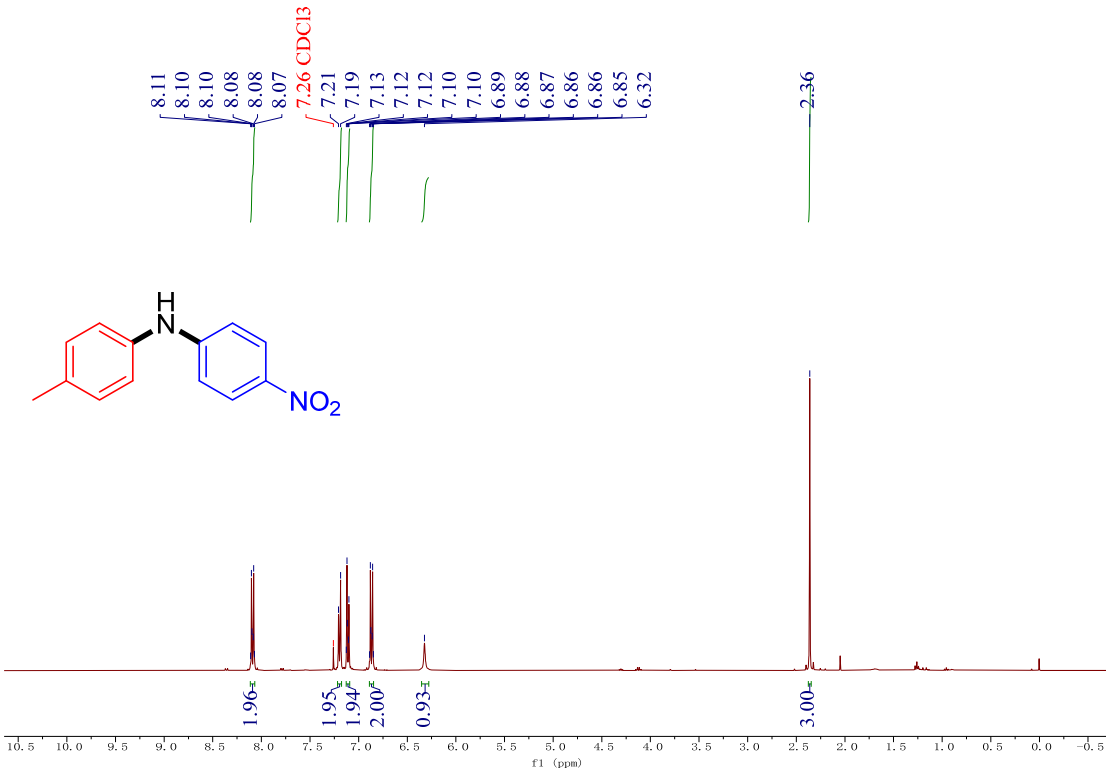

**$^{1}$H NMR spectrum of 4d** (400 MHz, $CDCl_3$)



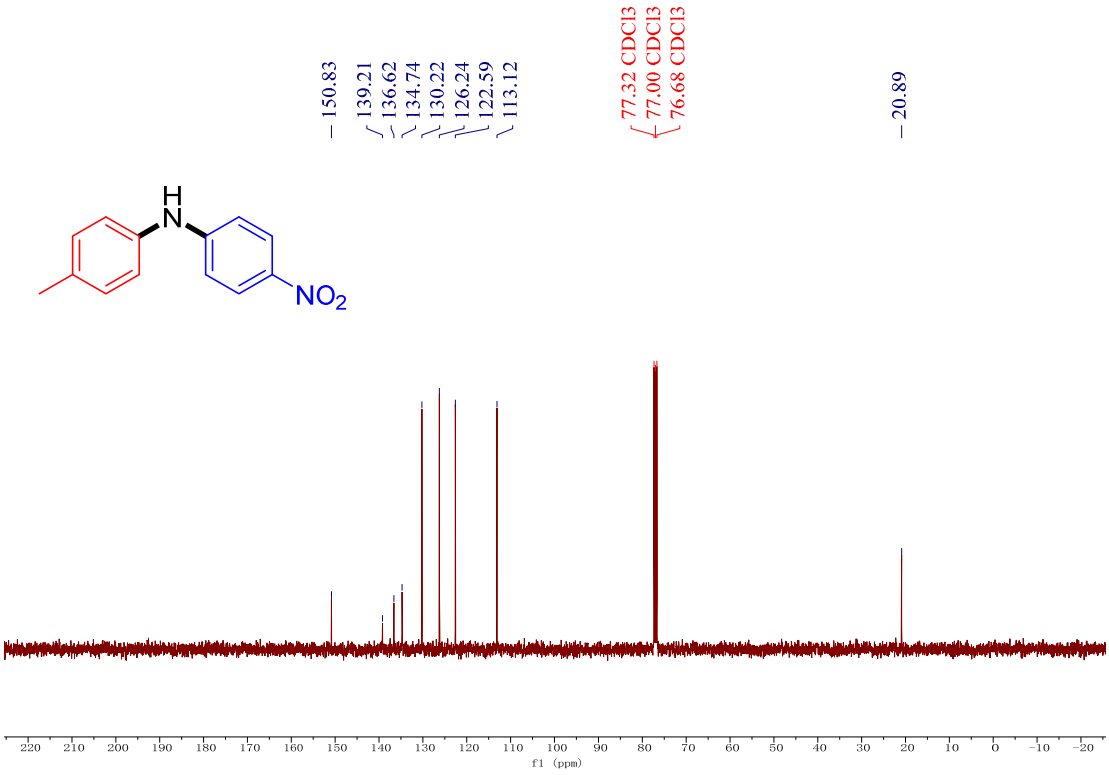
**$^{13}$C NMR spectrum of 4d** (100 MHz, $CDCl_3$)



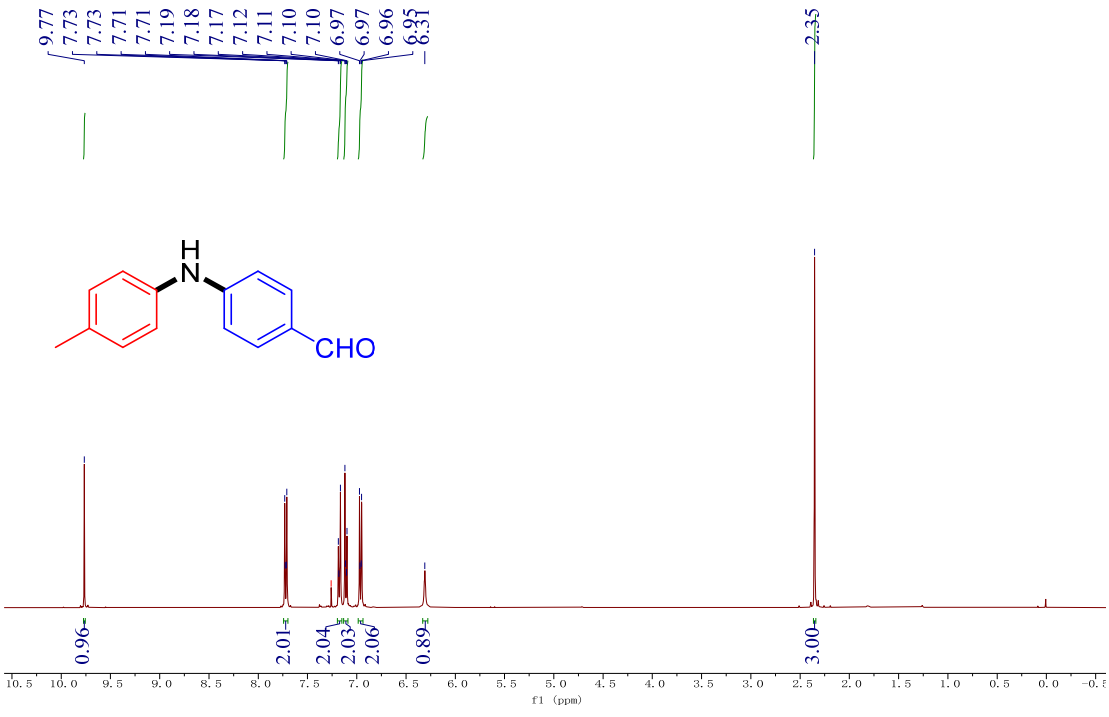

**$^{1}$H NMR spectrum of 4e** (400 MHz, $CDCl_3$)



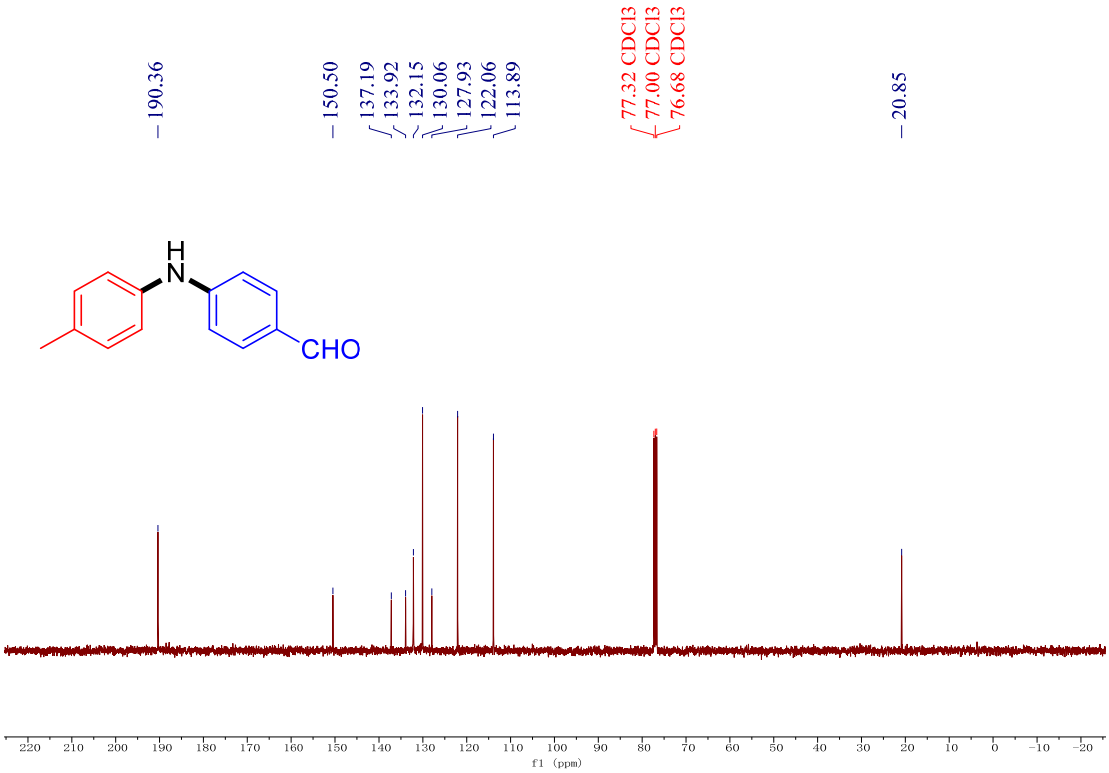
**$^{13}$C NMR spectrum of 4e** (100 MHz, $CDCl_3$)



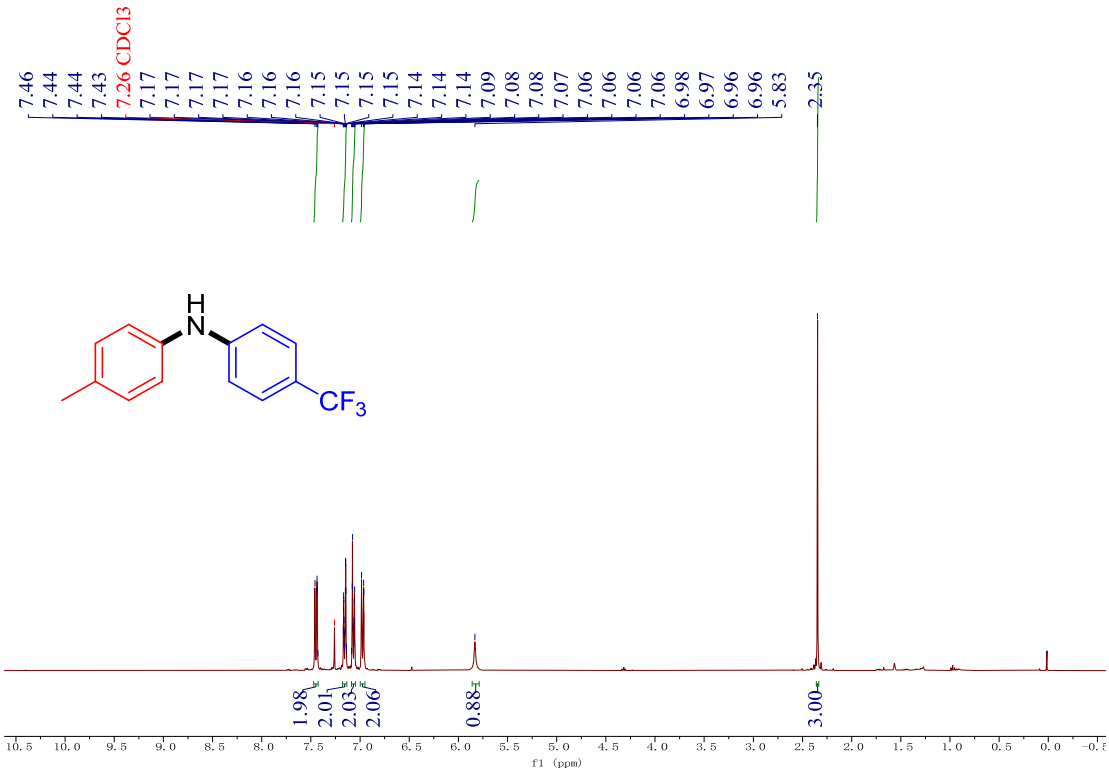

**$^{1}$H NMR spectrum of 4f** (400 MHz, $CDCl_3$)



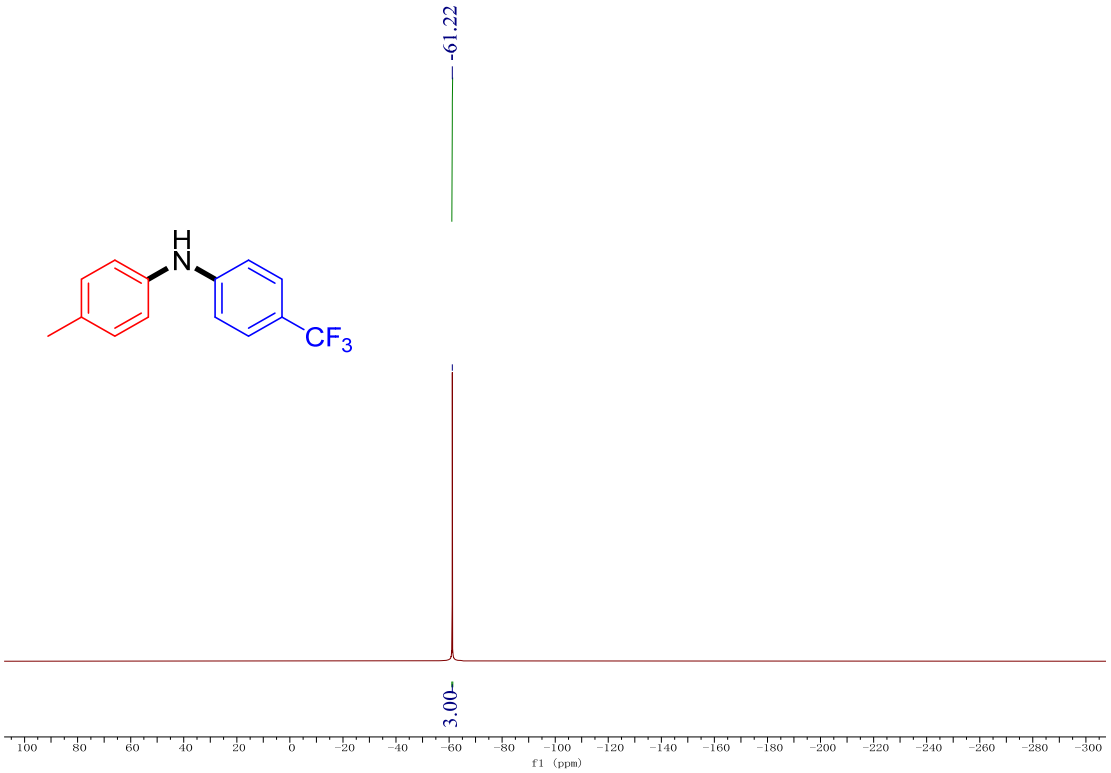
**$^{13}$C NMR spectrum of 4f** (100 MHz, $CDCl_3$)



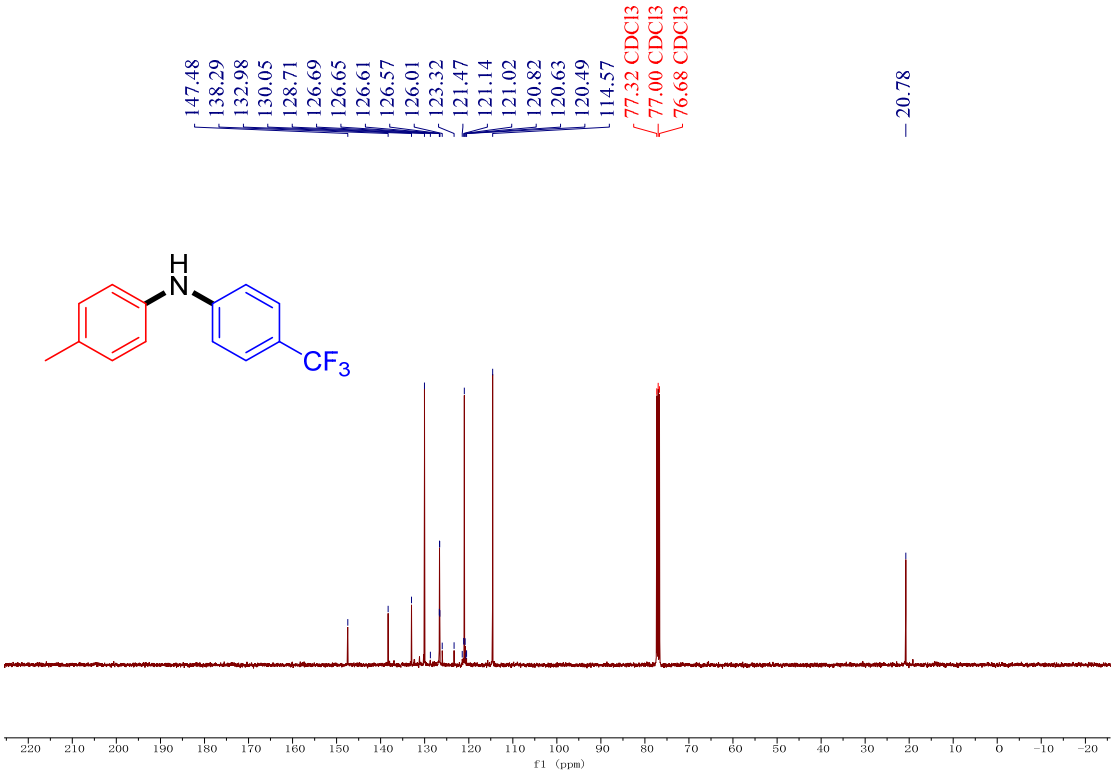

**$^{1}$H NMR spectrum of 4g** (400 MHz, $CDCl_3$)



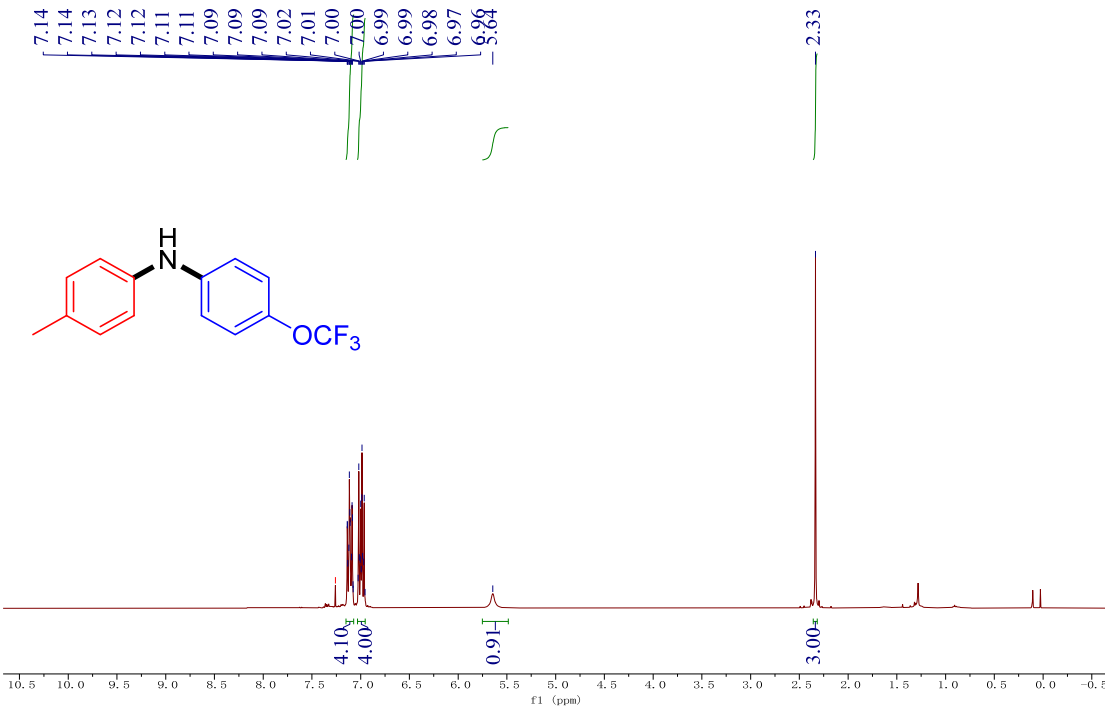
**$^{19}$F NMR spectrum of 4g** (376 MHz, $CDCl_3$)



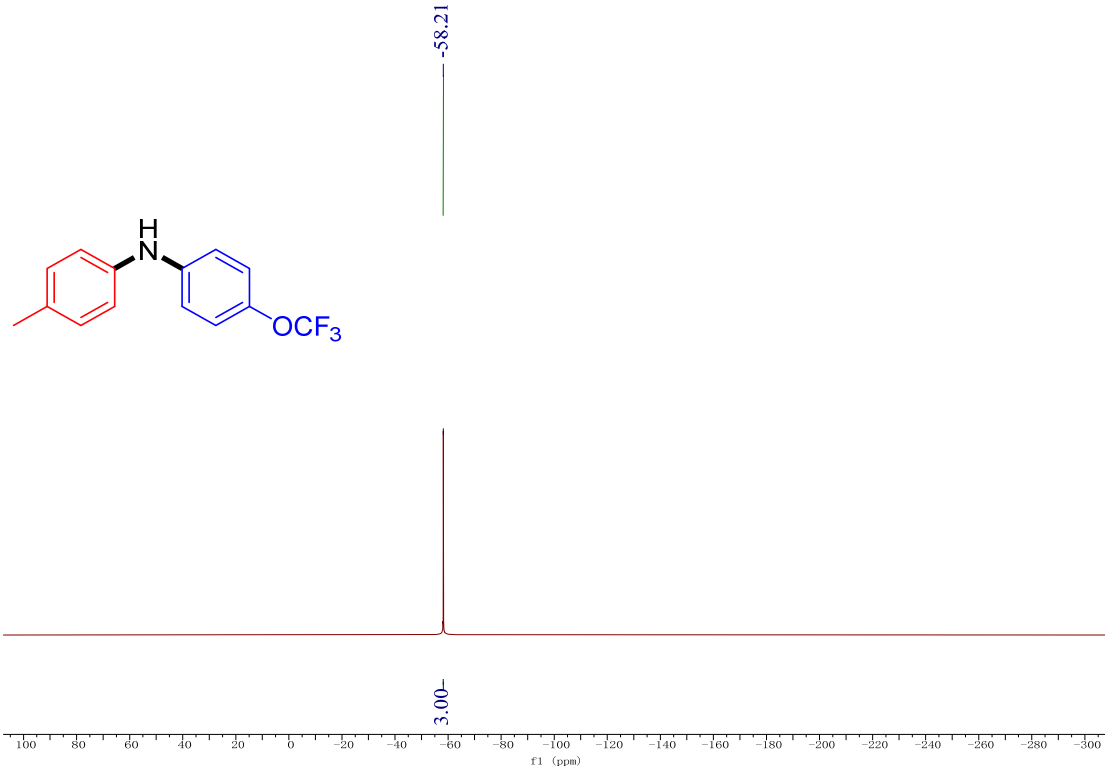

**$^{13}$C NMR spectrum of 4g** (100 MHz, $CDCl_3$)



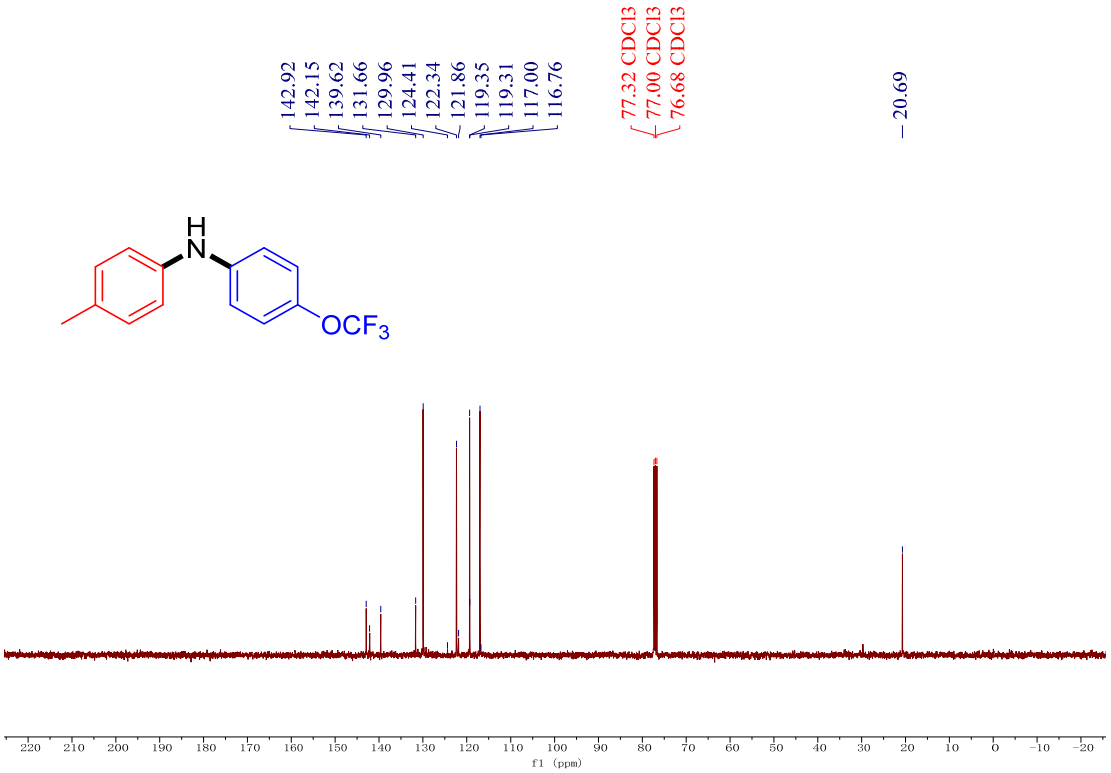
**$^{1}$H NMR spectrum of 4h** (400 MHz, $CDCl_3$)



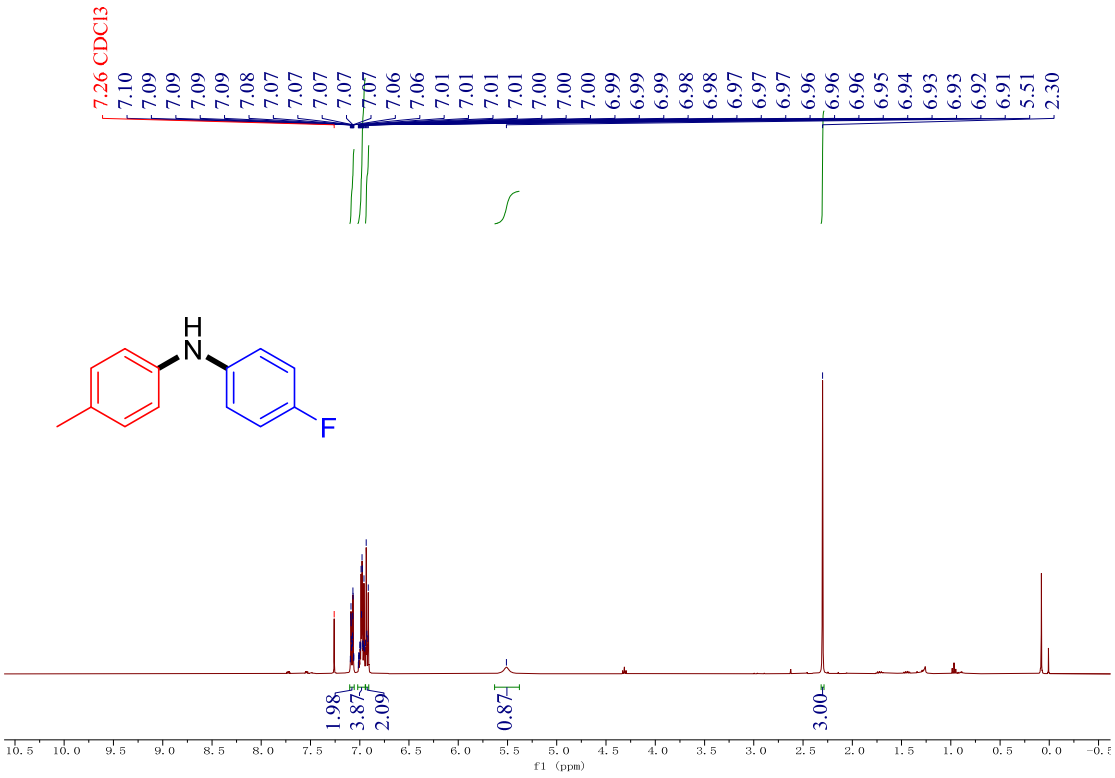

**$^{19}$F NMR spectrum of 4h** (376 MHz, $CDCl_3$)



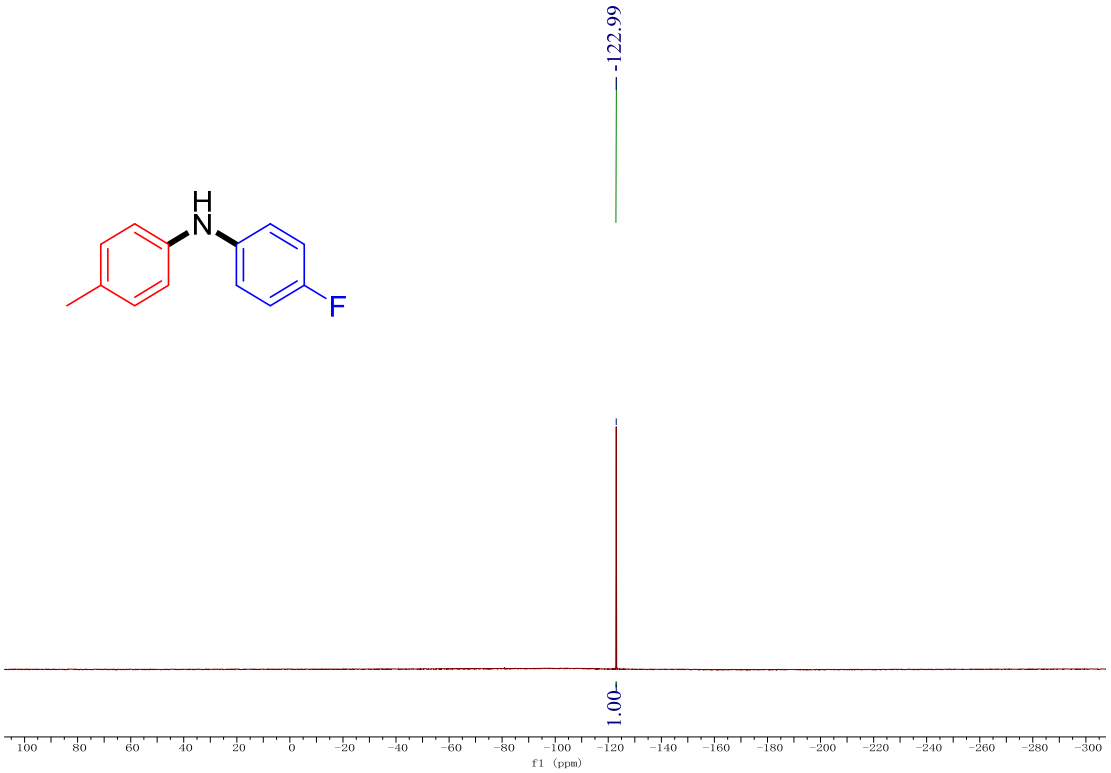
**$^{13}$C NMR spectrum of 4h** (100 MHz, $CDCl_3$)



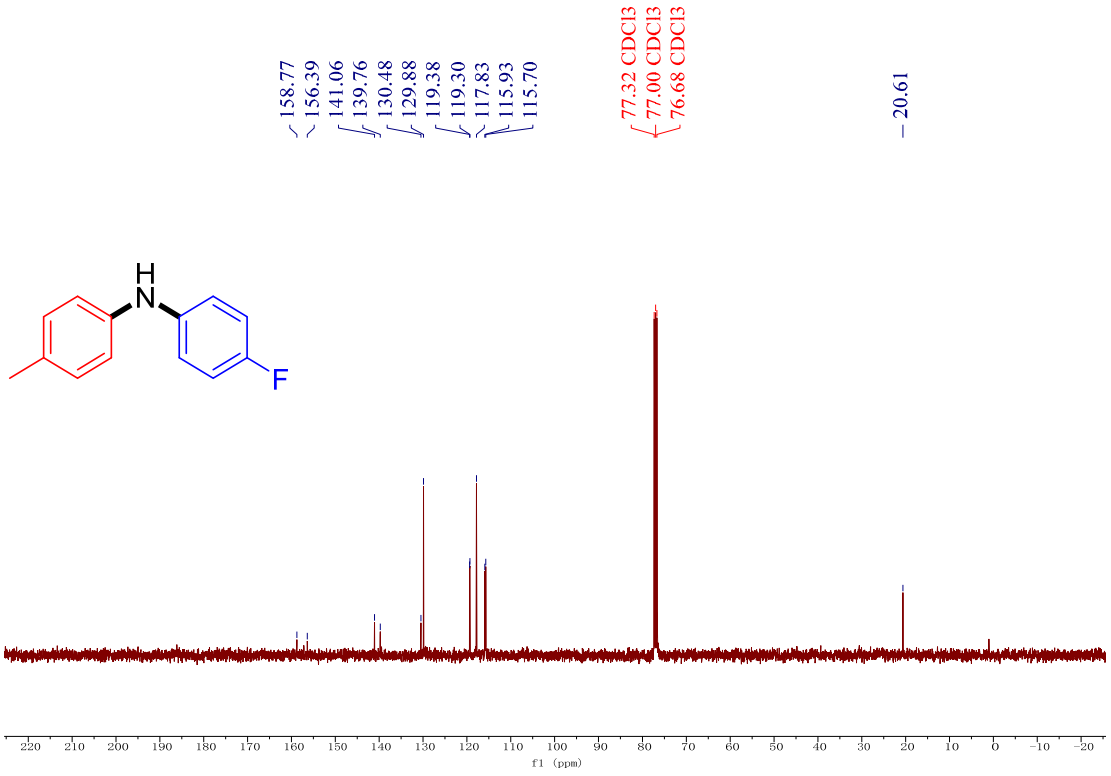

**$^{1}$H NMR spectrum of 4i** (400 MHz, $CDCl_3$)



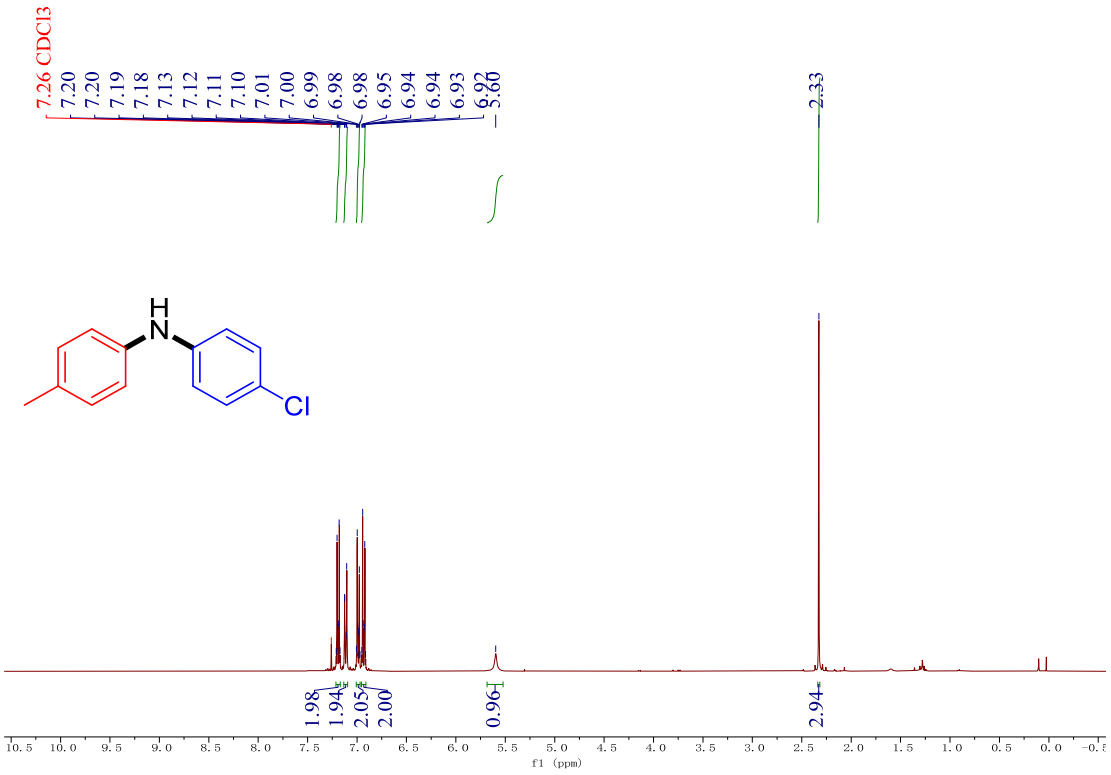
**$^{19}$F NMR spectrum of 4i** (376 MHz, $CDCl_3$)



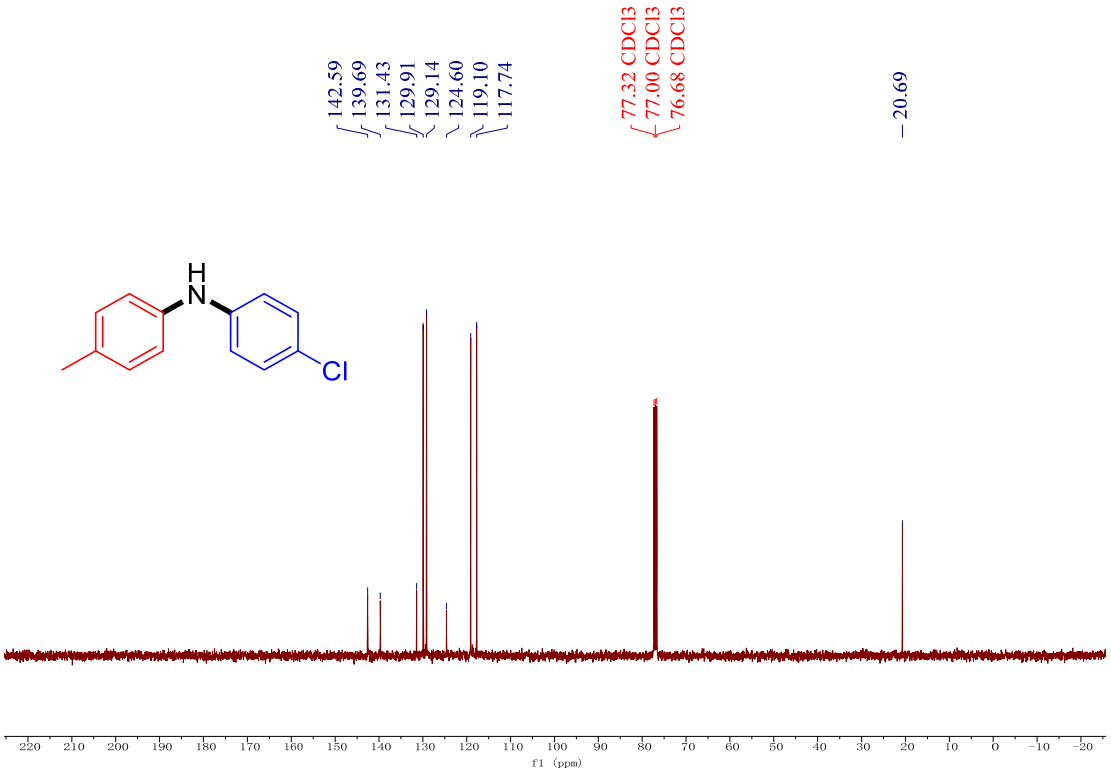

**$^{13}$C NMR spectrum of 4i** (100 MHz, $CDCl_3$)



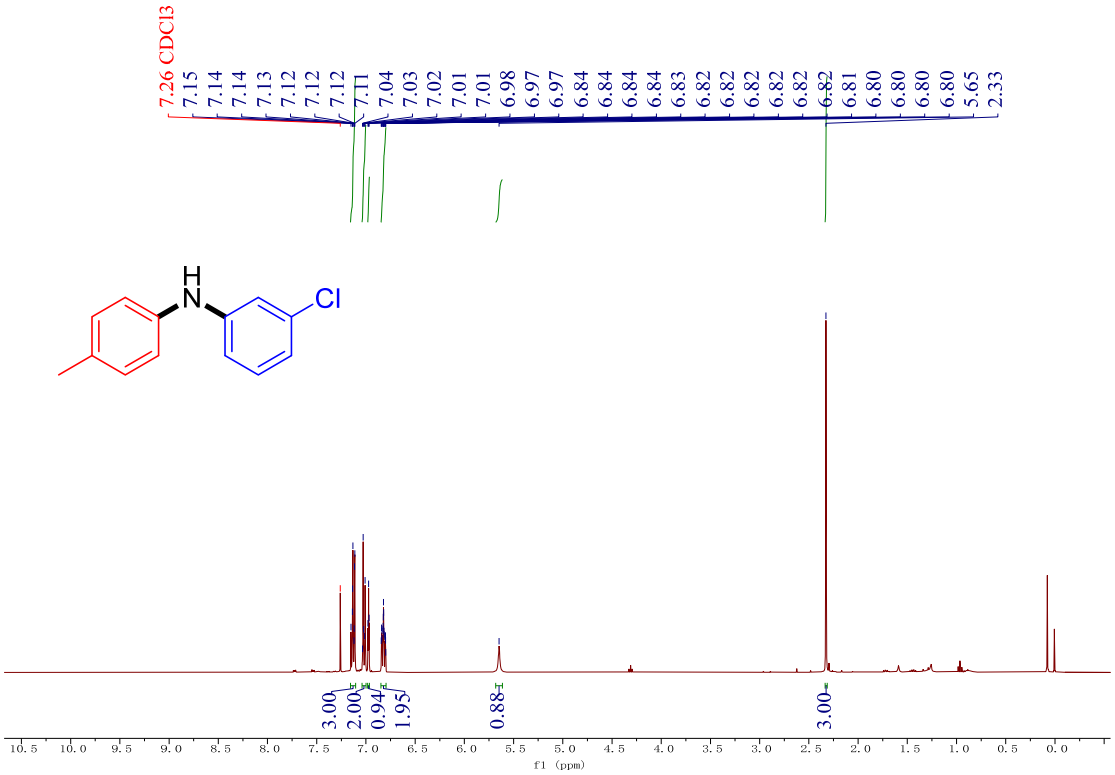
**$^{1}$H NMR spectrum of 4j** (400 MHz, $CDCl_3$)



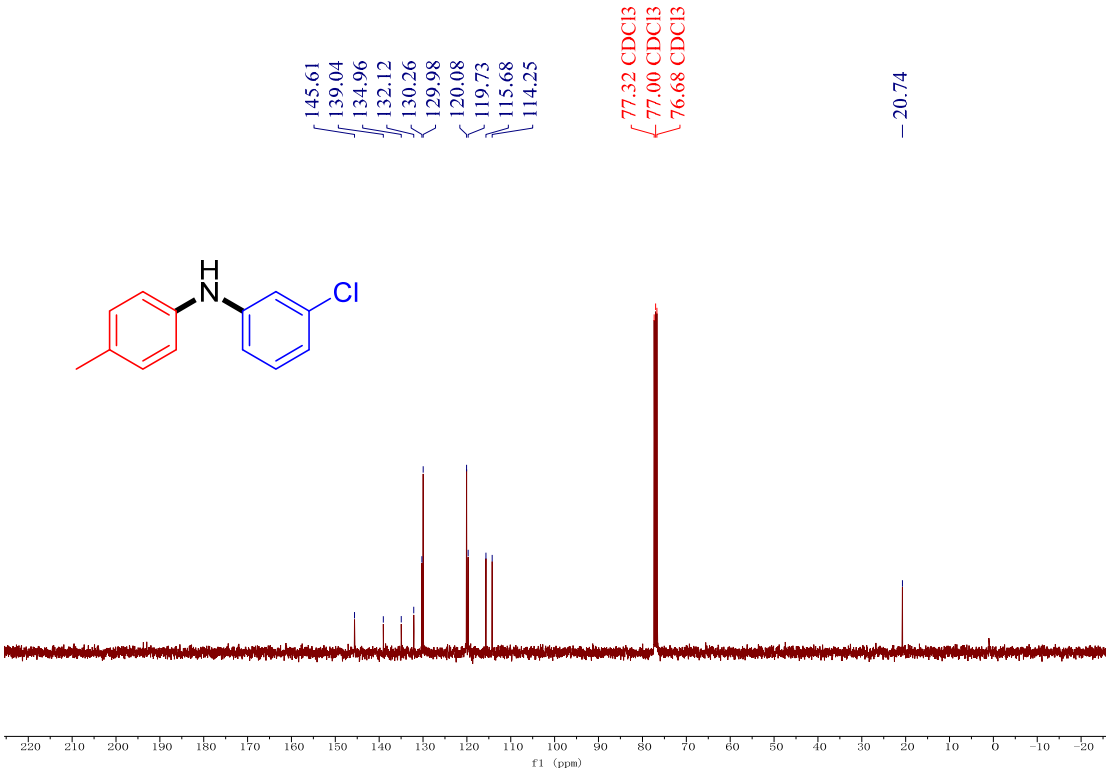

**$^{13}$C NMR spectrum of 4j** (100 MHz, $CDCl_3$)



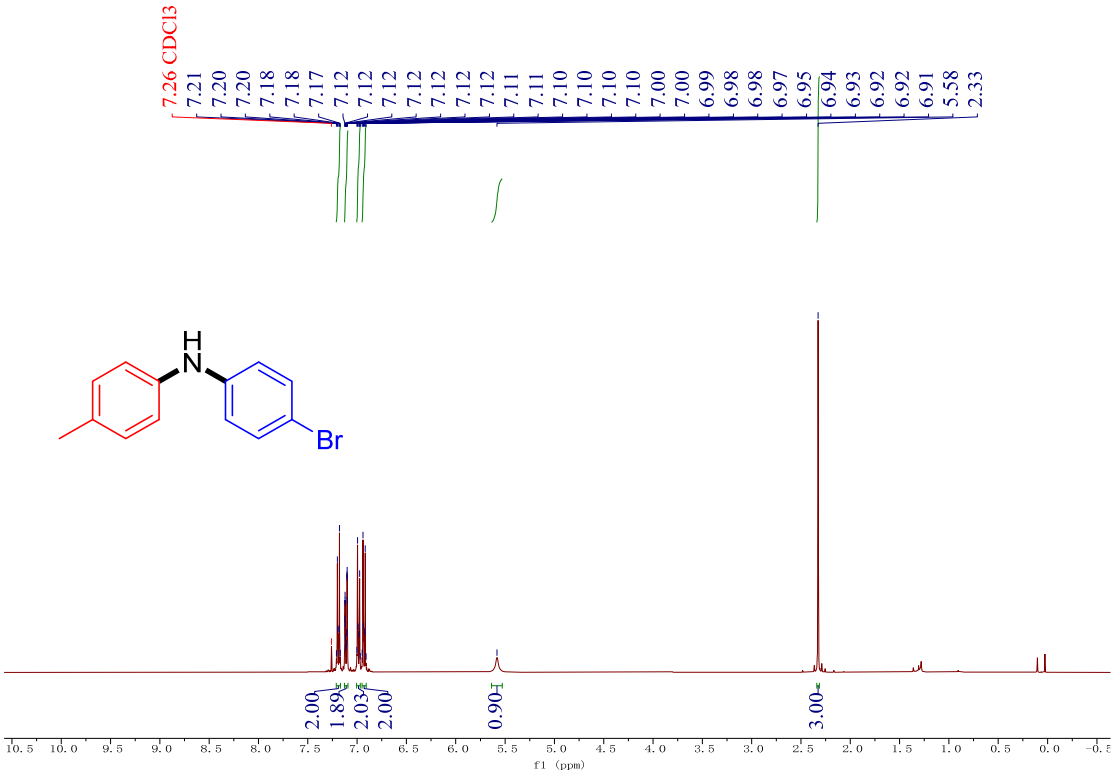
**$^{1}$H NMR spectrum of 4k** (400 MHz, $CDCl_3$)



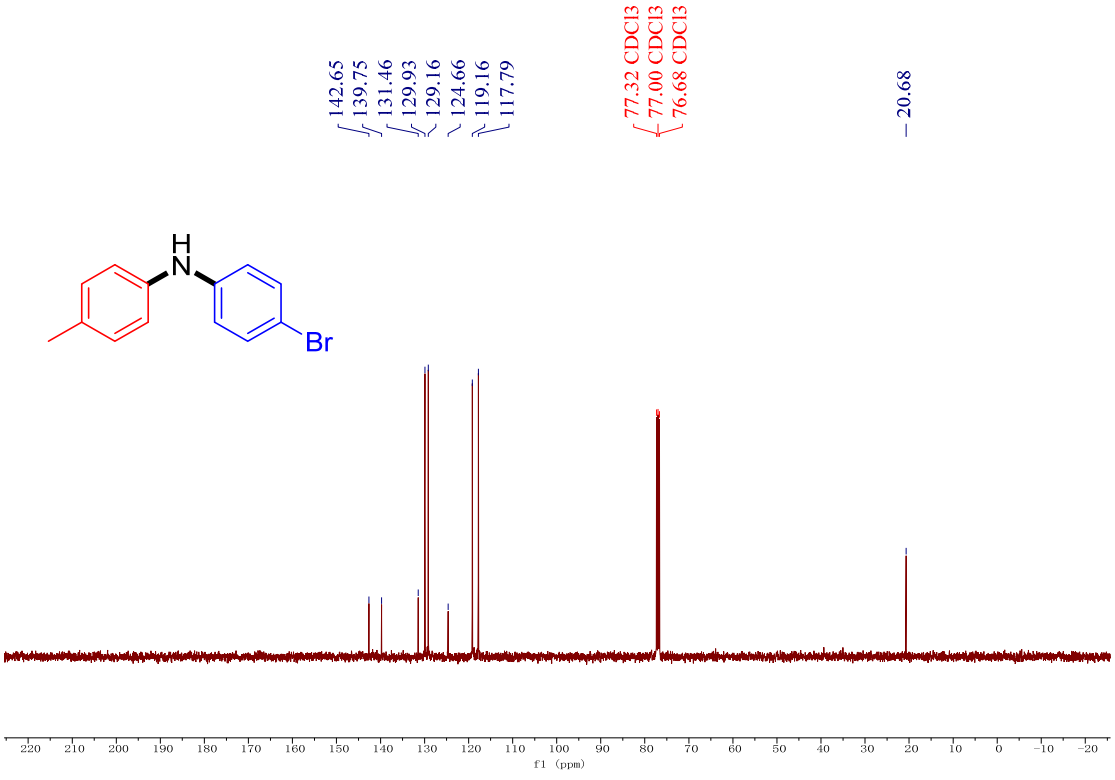

**$^{13}$C NMR spectrum of 4k** (100 MHz, $CDCl_3$)



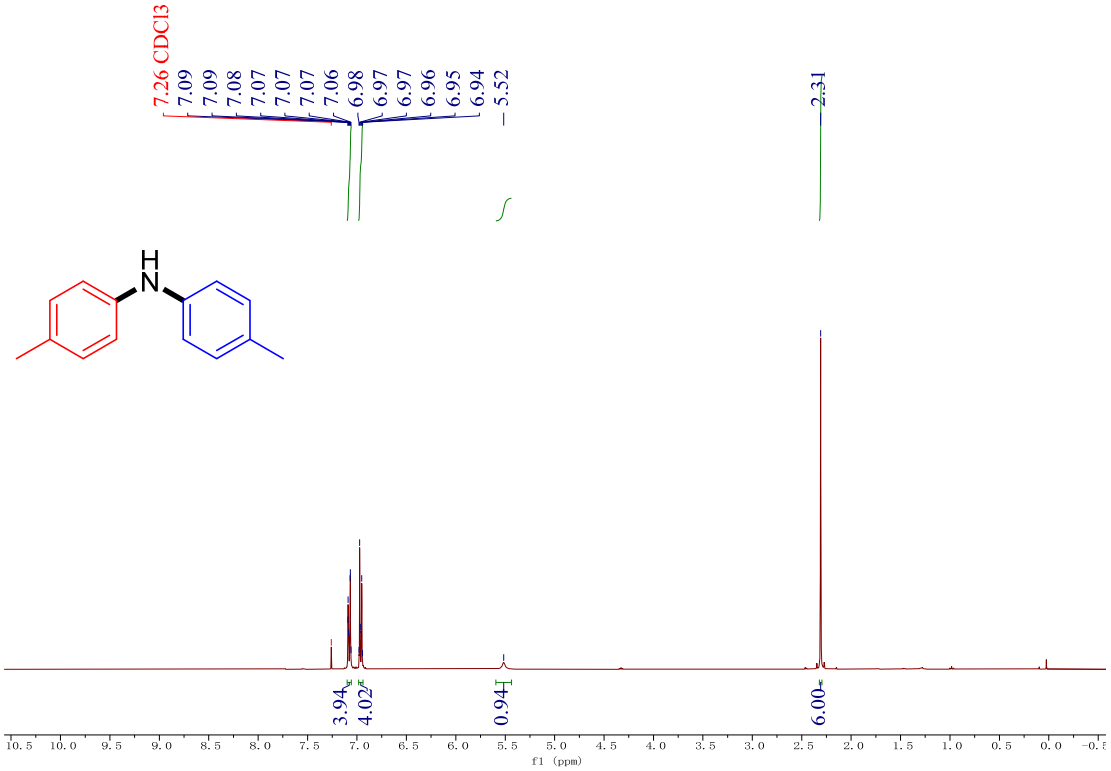
**$^{1}$H NMR spectrum of 4l** (400 MHz, $CDCl_3$)



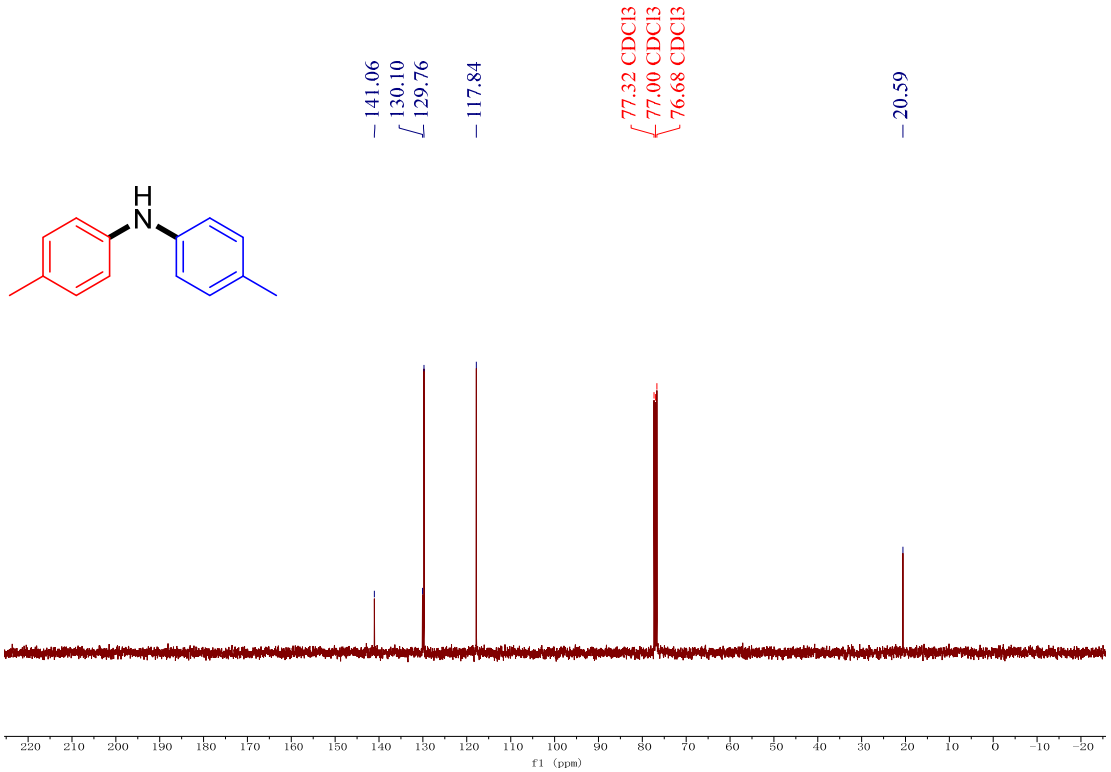

**$^{13}$C NMR spectrum of 4l** (100 MHz, $CDCl_3$)



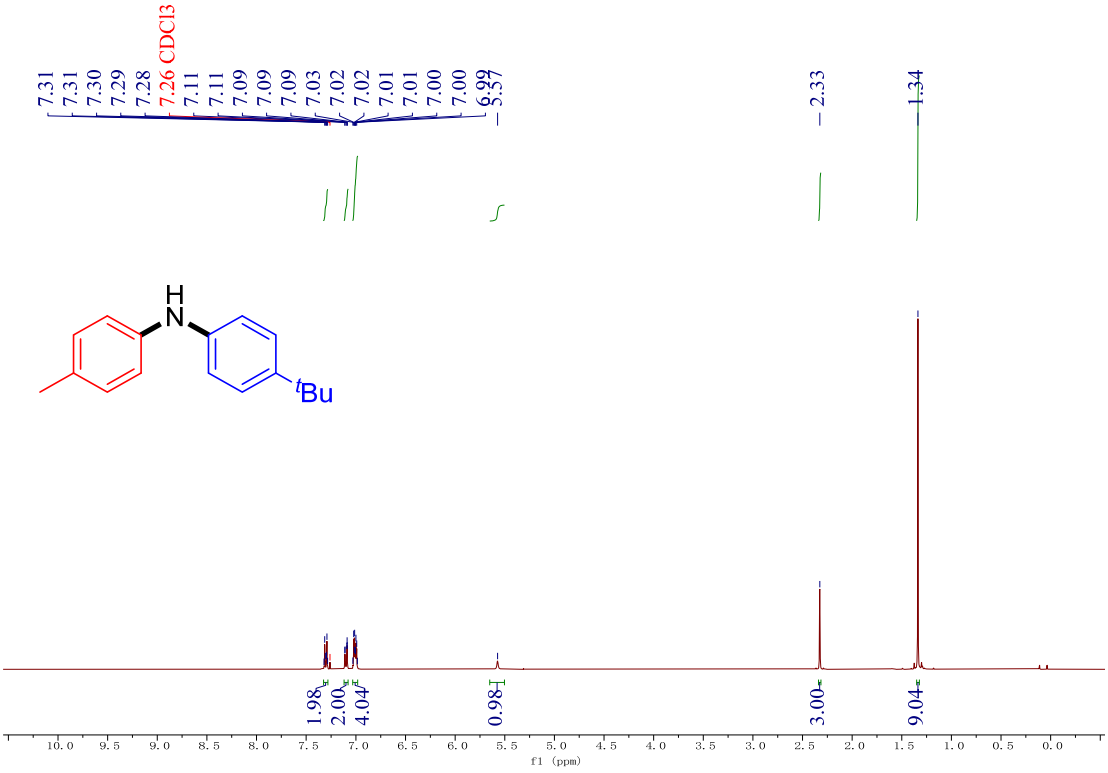
**$^{1}$H NMR spectrum of 4m** (400 MHz, $CDCl_3$)



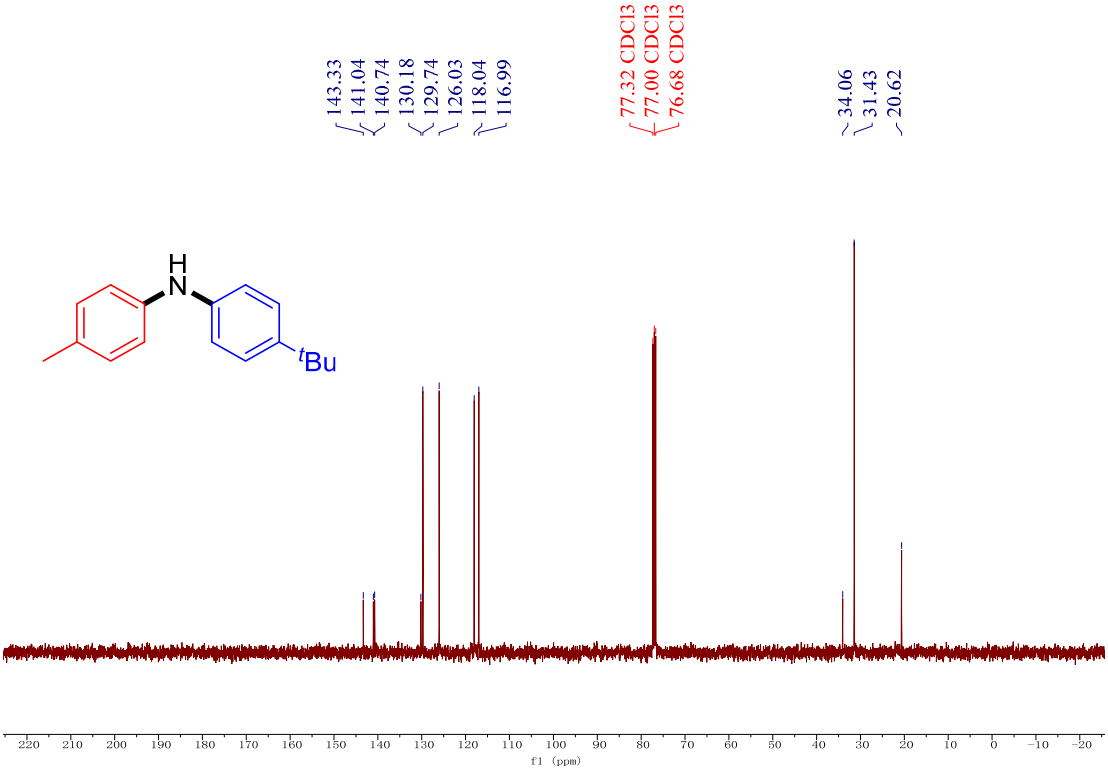

**$^{13}$C NMR spectrum of 4m** (100 MHz, $CDCl_3$)



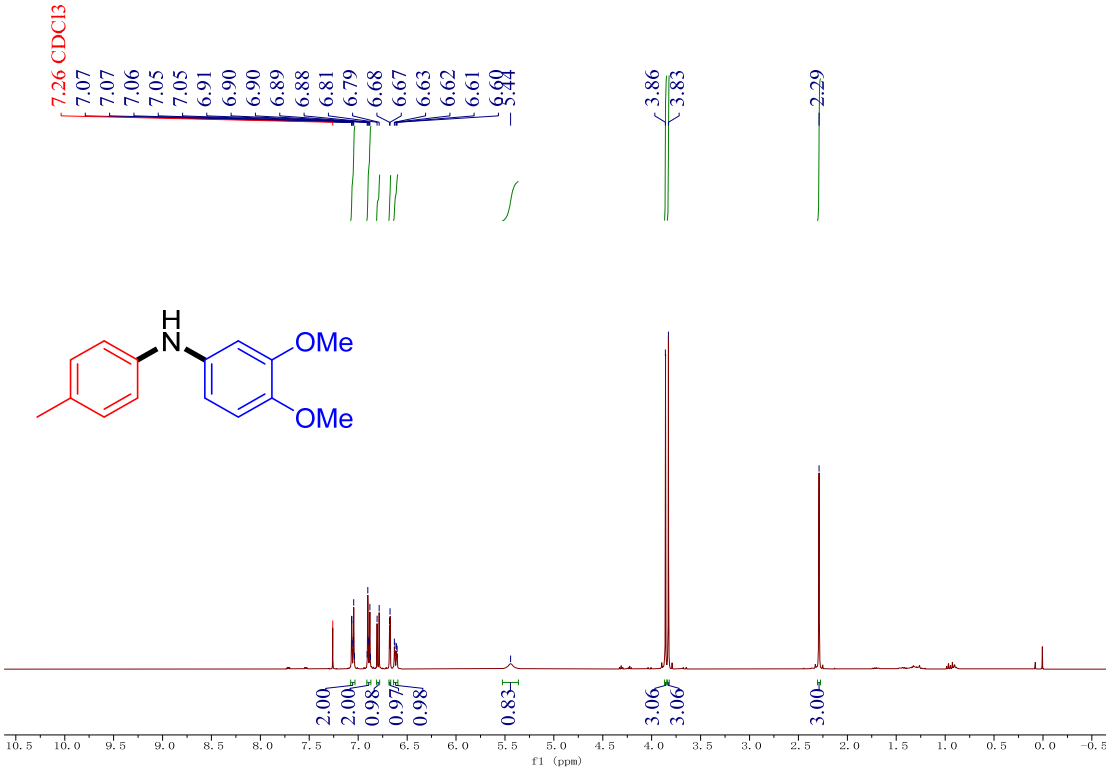
**$^{1}$H NMR spectrum of 4n** (400 MHz, $CDCl_3$)



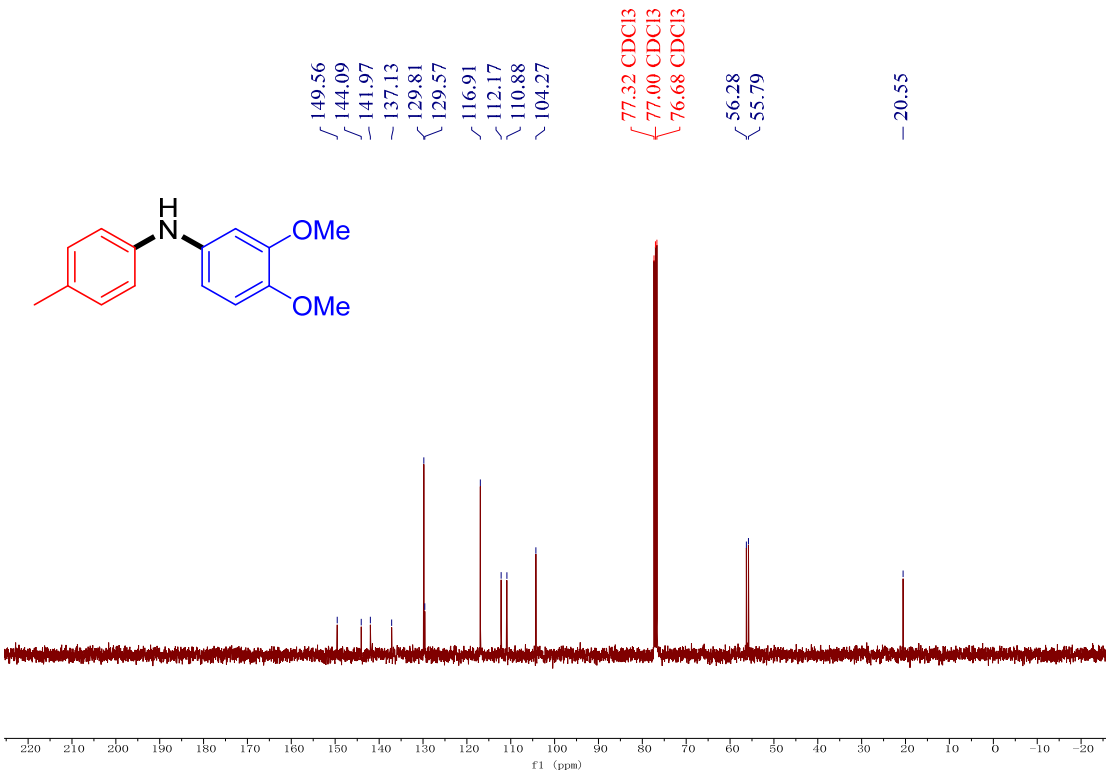

**$^{13}$C NMR spectrum of 4n** (100 MHz, $CDCl_3$)



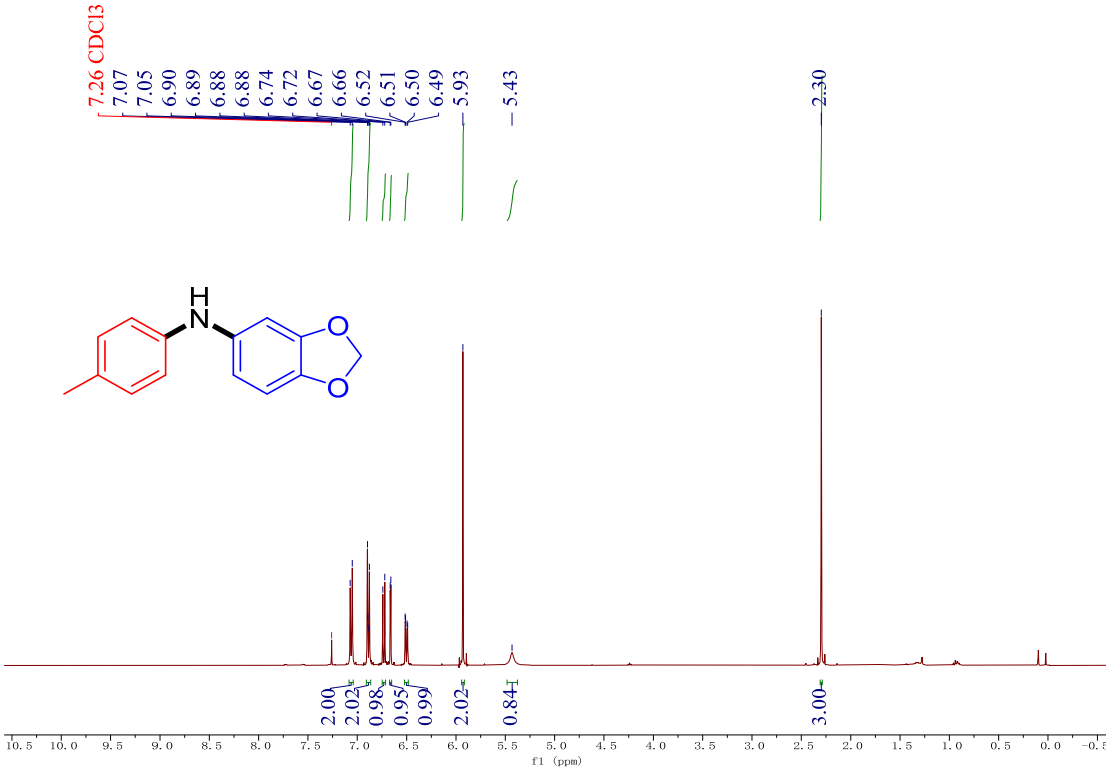
**$^{1}$H NMR spectrum of 4o** (400 MHz, $CDCl_3$)



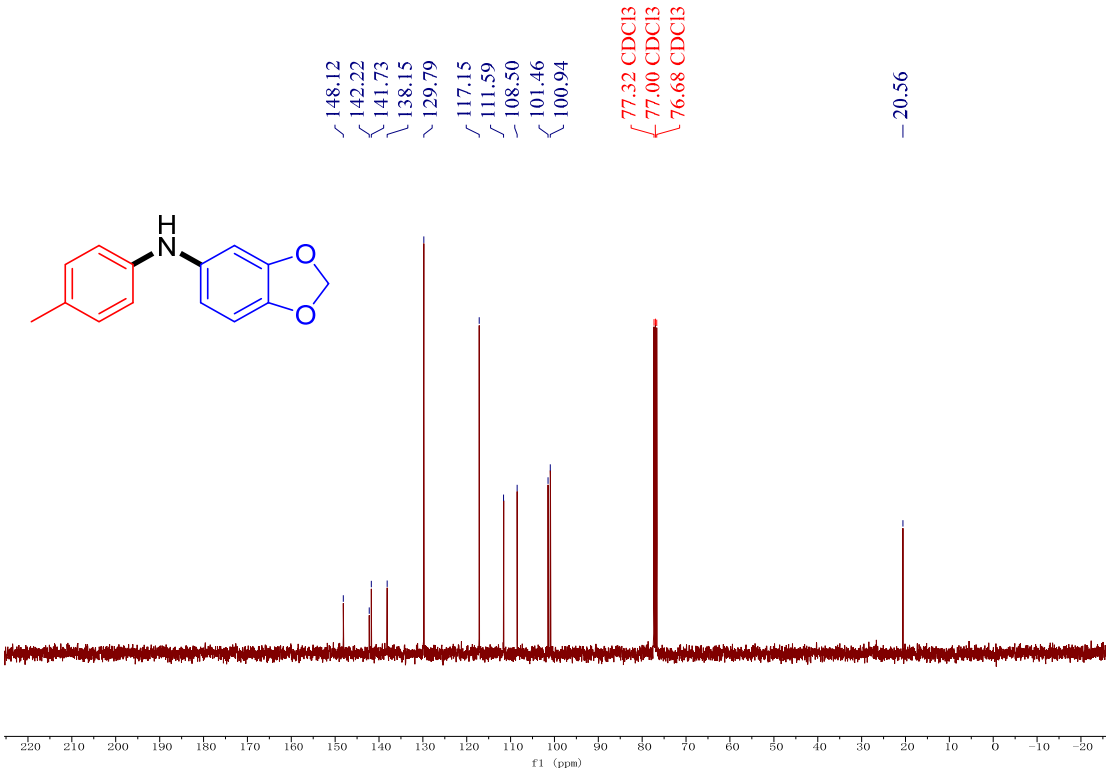

**$^{13}$C NMR spectrum of 4o** (100 MHz, $CDCl_3$)



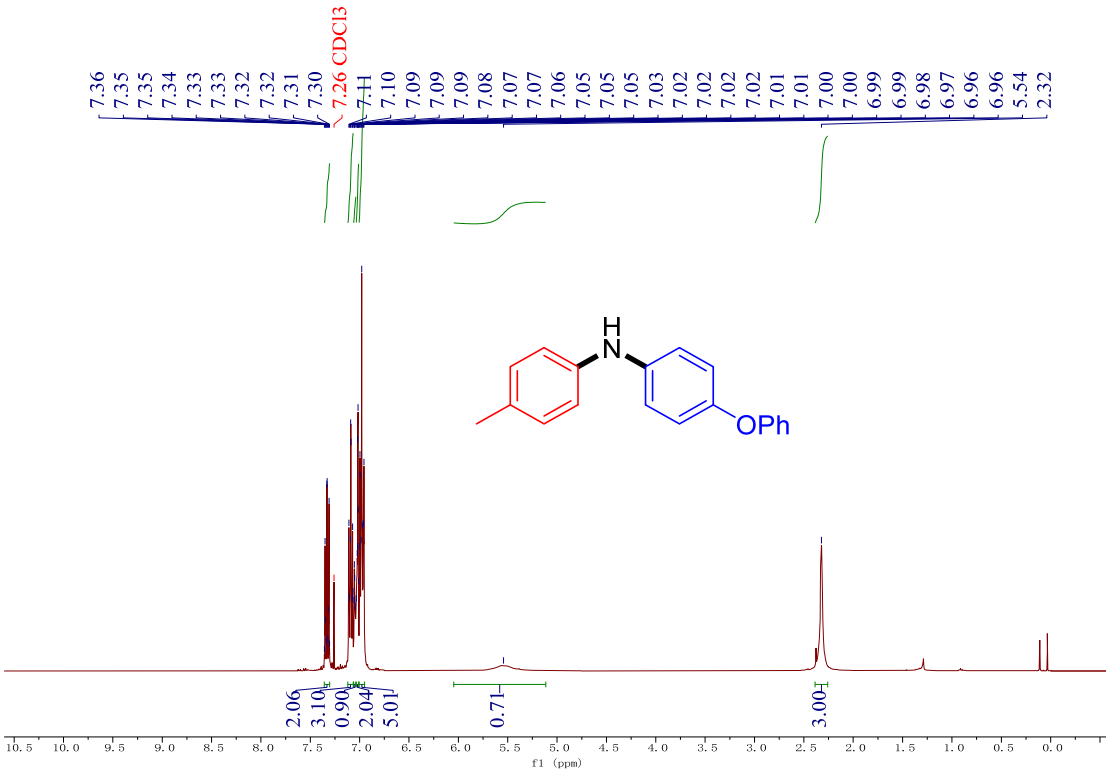
**$^{1}$H NMR spectrum of 4p** (400 MHz, $CDCl_3$)



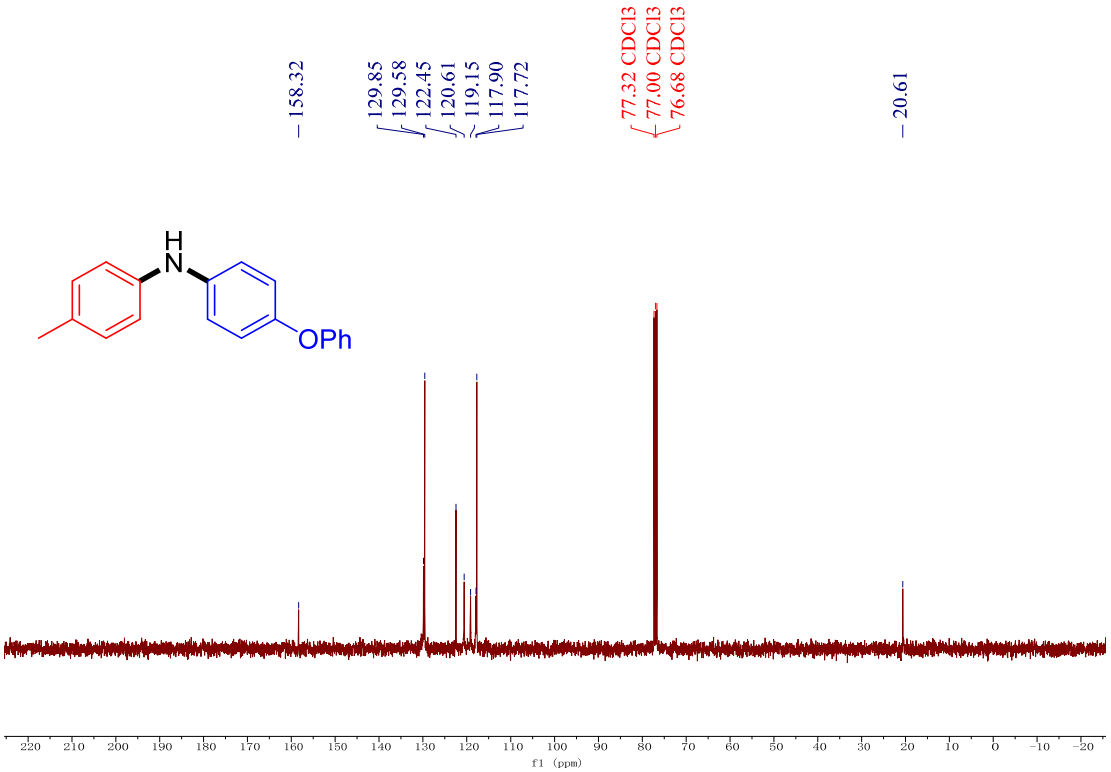

**$^{13}$C NMR spectrum of 4p** (100 MHz, $CDCl_3$)



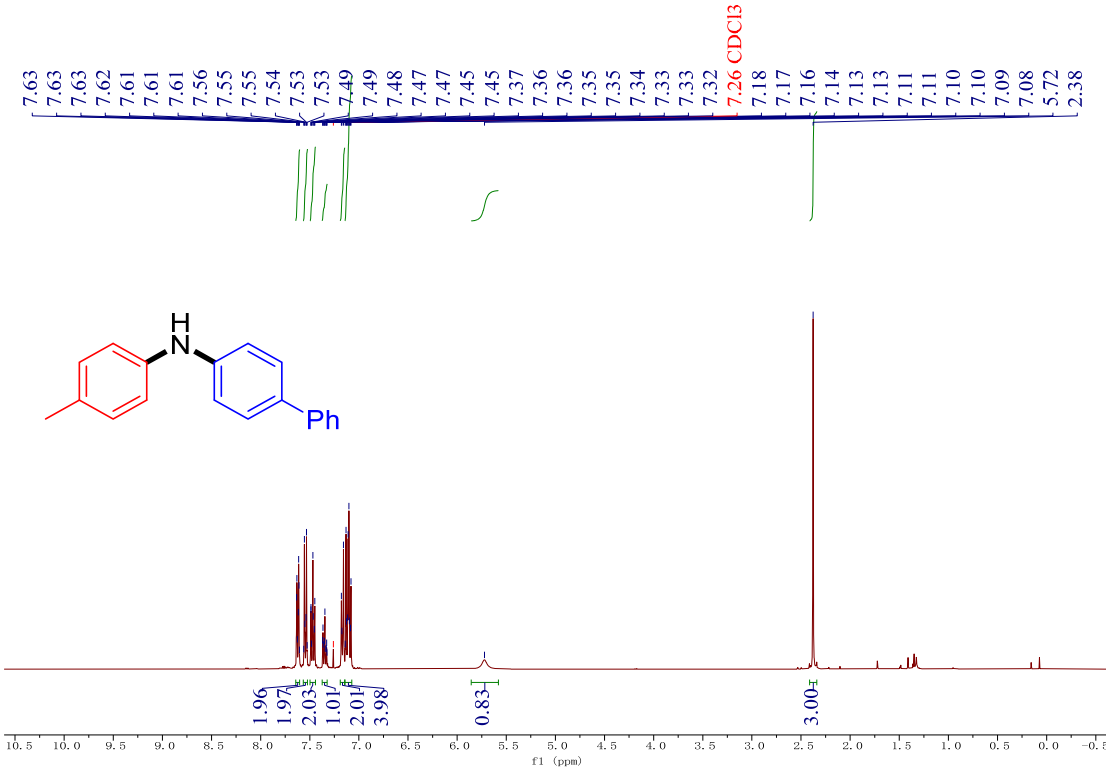
**$^{1}$H NMR spectrum of 4q** (400 MHz, $CDCl_3$)



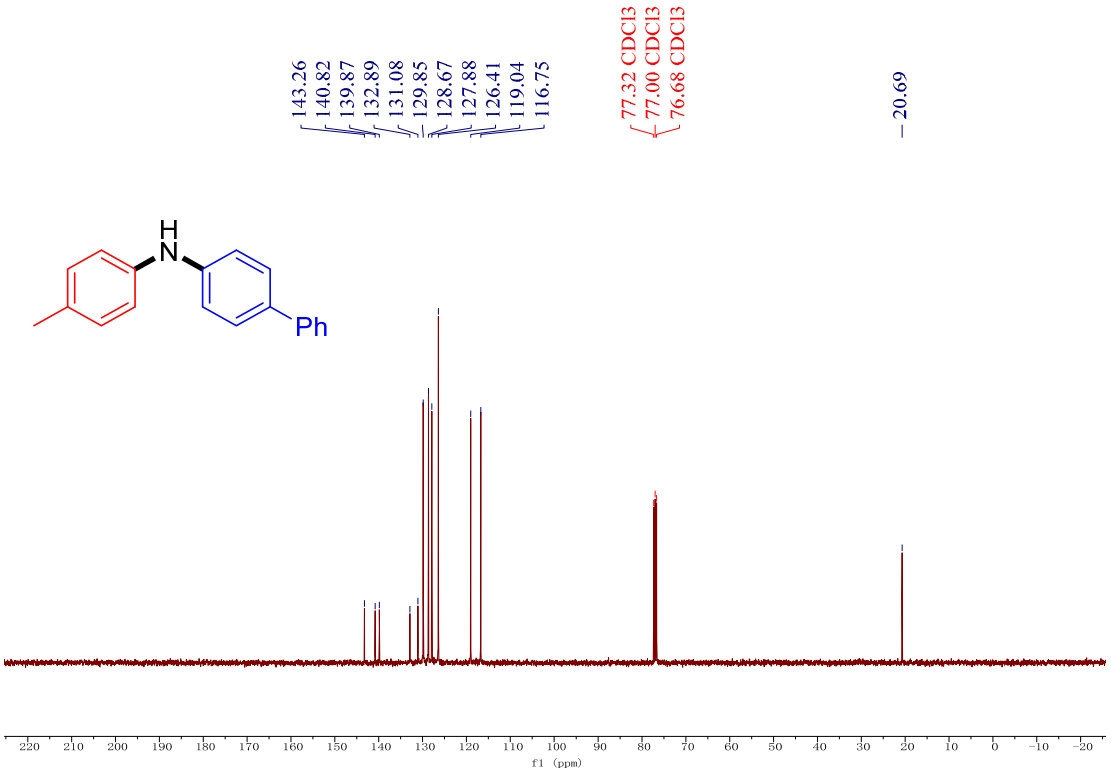

**$^{13}$C NMR spectrum of 4q** (100 MHz, $CDCl_3$)



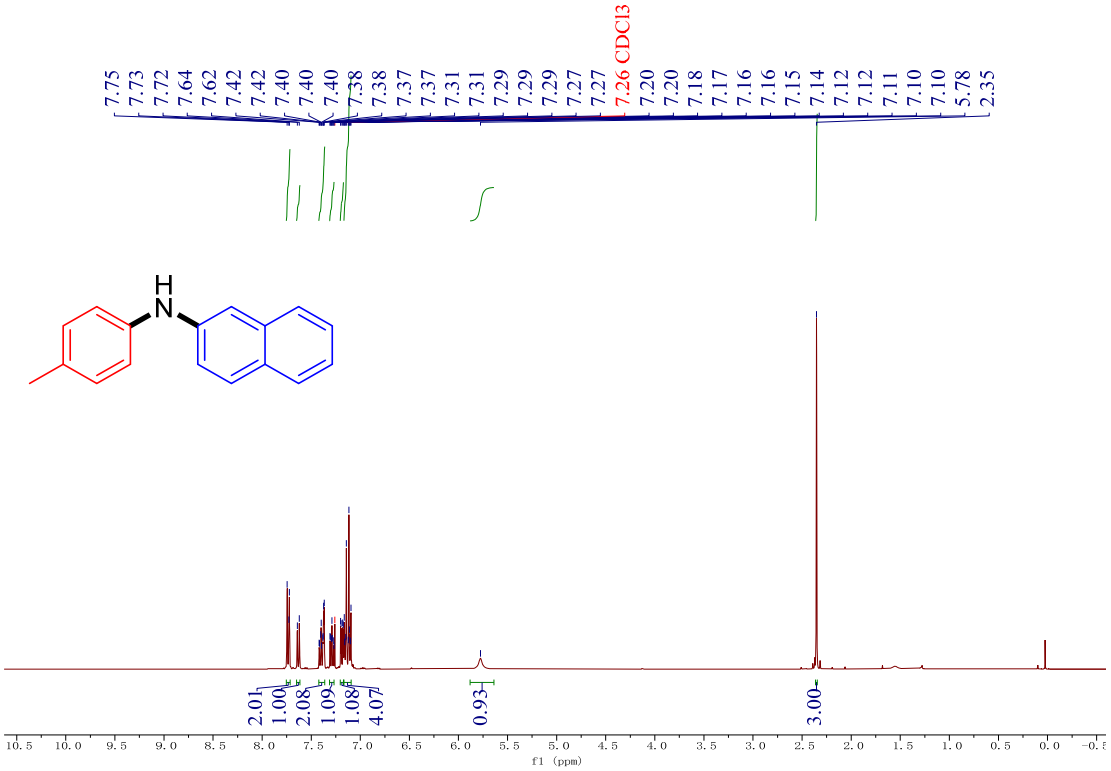
**$^{1}$H NMR spectrum of 4r** (400 MHz, $CDCl_3$)



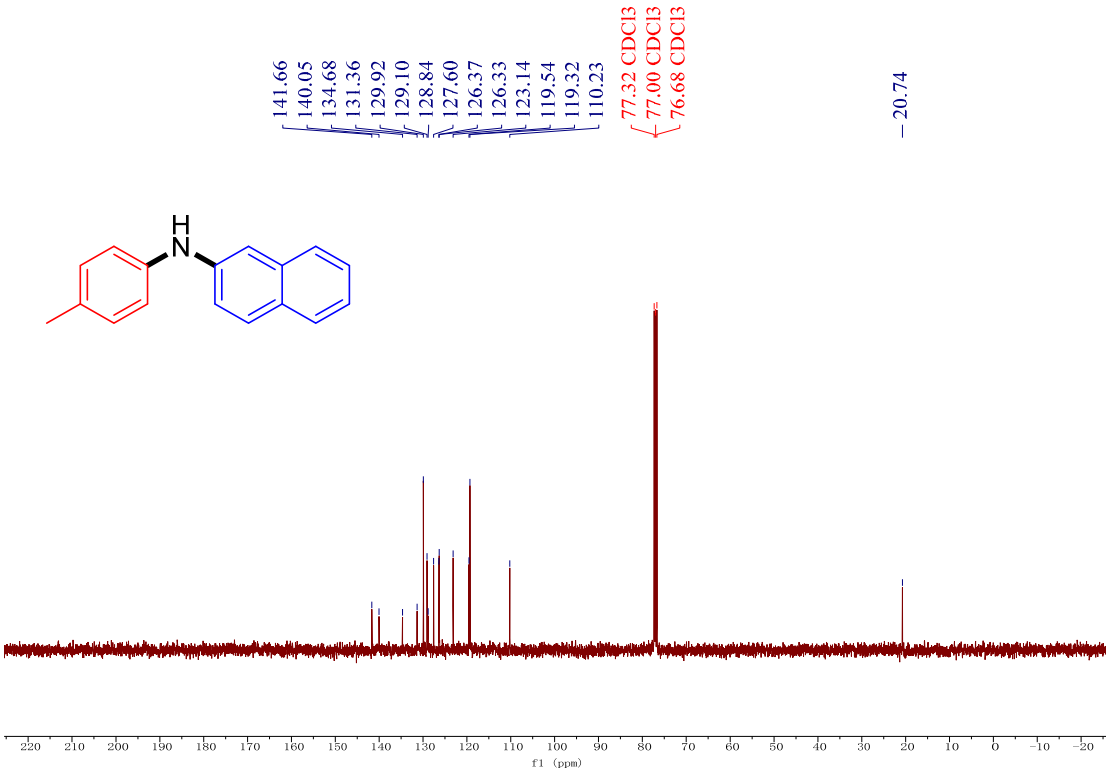

**$^{13}$C NMR spectrum of 4r** (100 MHz, $CDCl_3$)



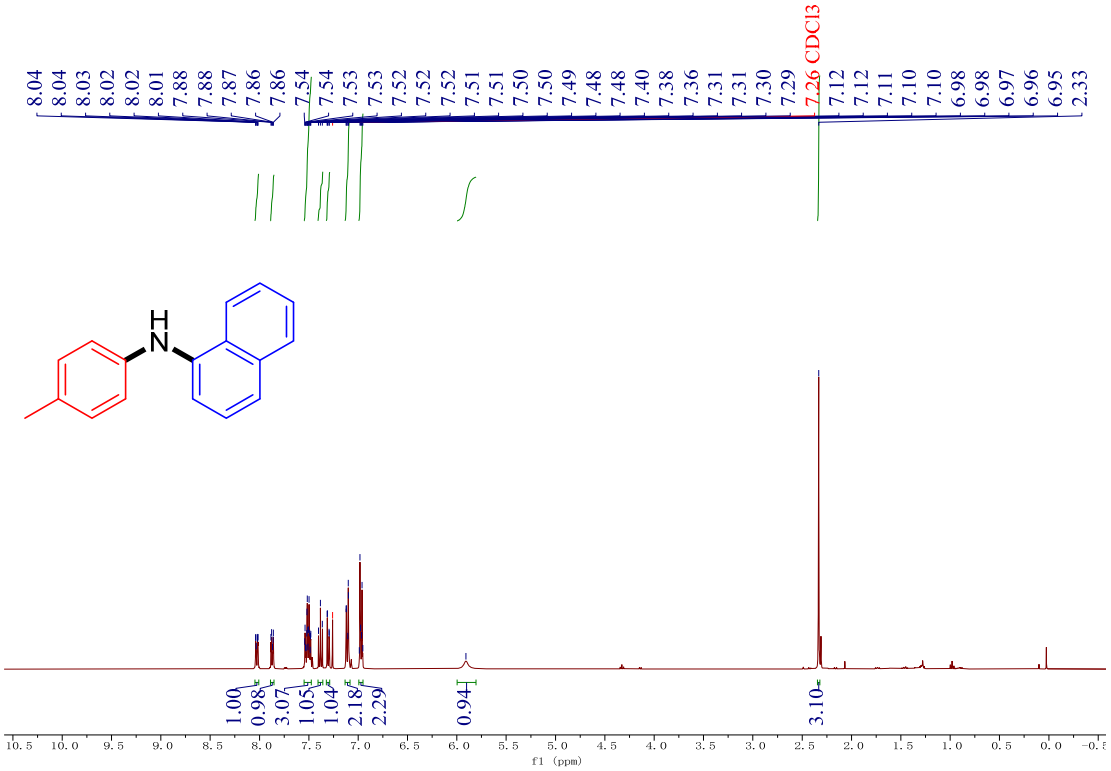
**$^{1}$H NMR spectrum of 4s** (400 MHz, $CDCl_3$)



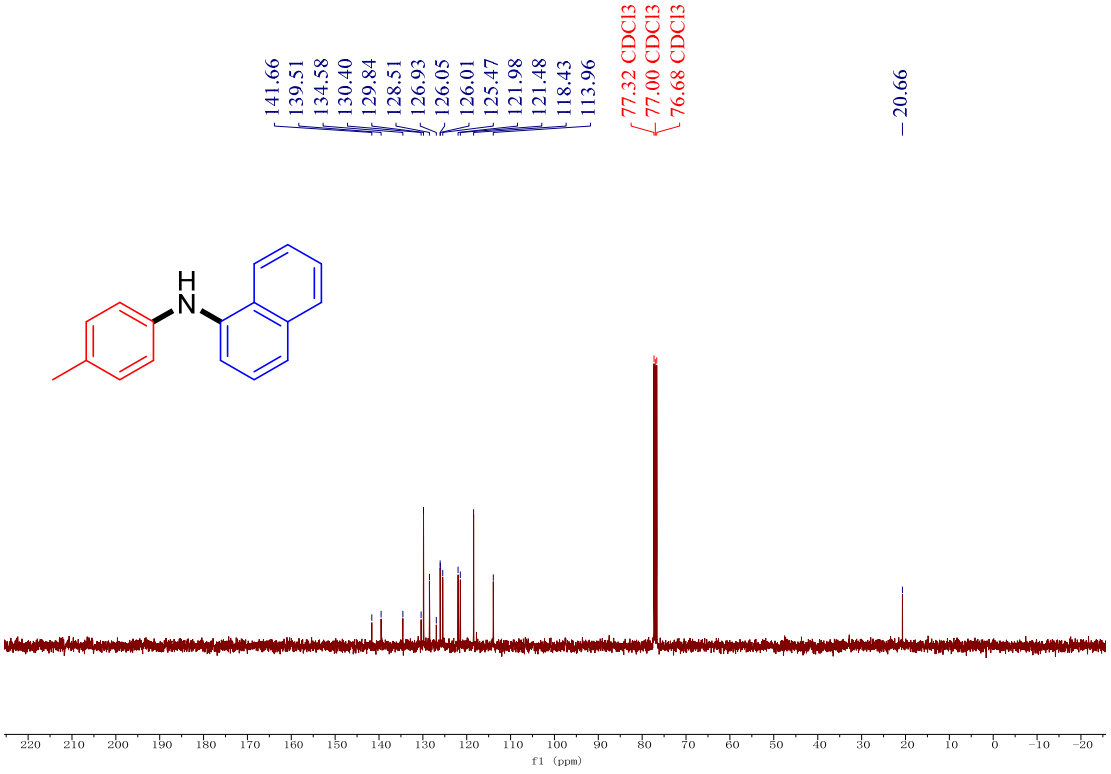

**$^{13}$C NMR spectrum of 4s** (100 MHz, $CDCl_3$)



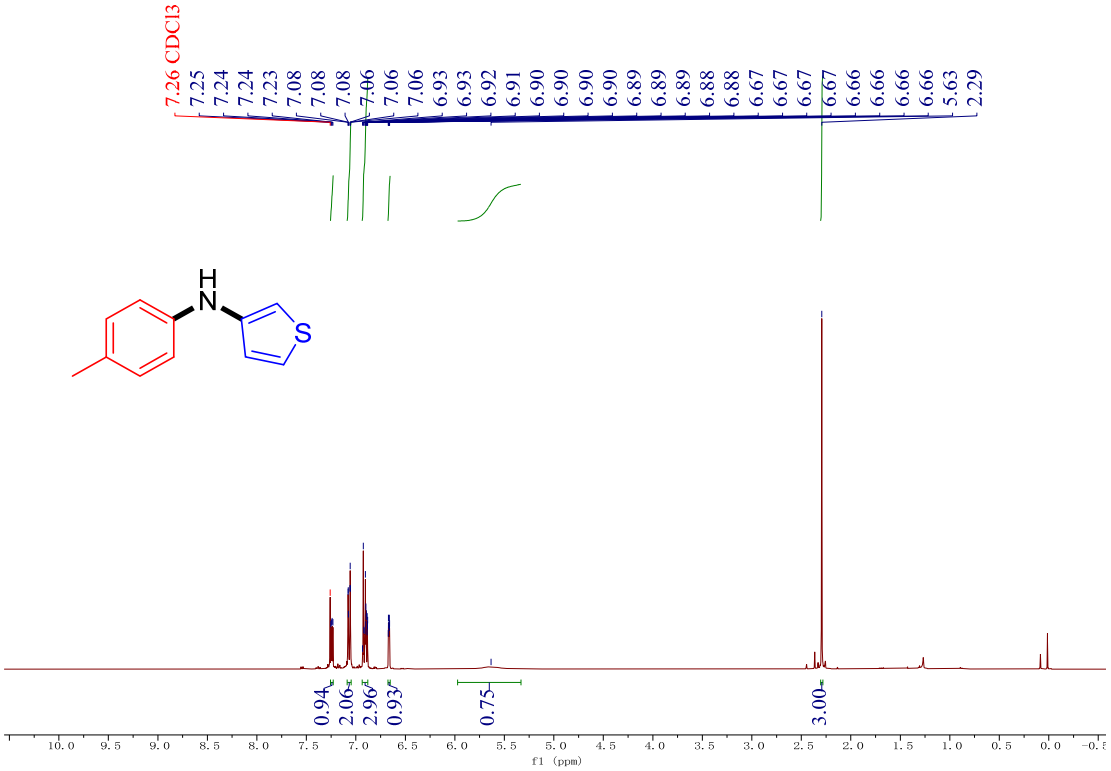
**$^{1}$H NMR spectrum of 4t** (400 MHz, $CDCl_3$)




**$^{13}$C NMR spectrum of 4t** (100 MHz, $CDCl_3$)



**$^{1}$H NMR spectrum of 4u** (400 MHz, $CDCl_3$)




**$^{13}$C NMR spectrum of 4u** (100 MHz, $CDCl_3$)