Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Iridium-Catalyzed Direct C−H Amidation of Anilines with Sulfonyl Azides: Easy Access to 1,2-Diaminobenzenes

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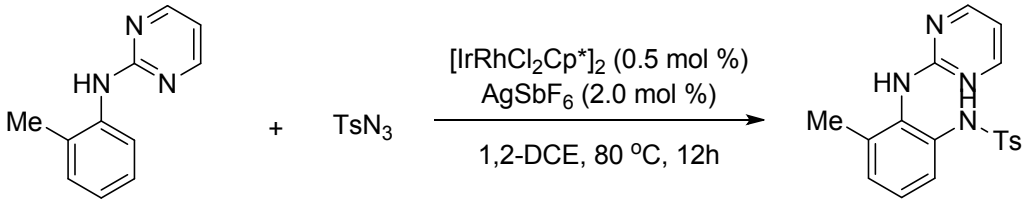
1. General information

Unless otherwise stated, all commercial materials and solvents were used directly without further purification. Melting points were determined in open glass capillaries and were uncorrected.[1]H NMR spectra were recorded on 400 MHz spectrometers, and ^{13}C NMR spectra were recorded on a 100 MHz spectrometer. Chemical shifts (δ in ppm) were referenced to tetramethylsilane (δ = 0 ppm) in $CDCl_3$ or $[d]_6$-DMSO as an internal standard at room temperature. ^{13}C NMR spectra were obtained by using the same NMR spectrometers and were calibrated with $CDCl_3$ or $[d]_6$-DMSO. High-resolution mass spectra (HRMS) were equipped with an ESI source and a TOF detector. Column chromatography was performed on silica gel (70−230 mesh ASTM) using the reported eluents. Thin-layer chromatography (TLC) was carried out on 4×15 cm plates with a layer thickness of 0.2 mm (silica gel 60 F254).

Aniline compounds **1a-j**[1], **1a'**[2] and **1k**[3], and sulfonyl azides **2b-m**[4] were prepared according to the known procedures.

2. The Representative procedure for the synthesis of compounds 3

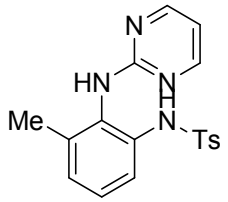


1a **2a** **3aa**

A flame-dried sealed tube was cooled to ambient temperature and filled with N_2. To this flask were added *N*-(*o*-tolyl)pyrimidin-2-amine (**1a**) (92.5 mg, 0.5 mmol), *para*-toluenesulfonyl azide (**2a**) (118.2 mg, 0.6 mmol), $[IrCl_2Cp^*]_2$ (2.0 mg, 0.0025 mmol), $AgSbF_6$ (3.5 mg, 0.01 mmol) and 1,2-DCE (2.0 mL). Then the sealed tube was heated at 80 °C. After 12 h, the reaction mixture was cooled to ambient temperature, filtered through a pad of celite and silica gel, and washed with EtOAc (3 x 10 mL). The solvents were removed under reduced pressure. The residue was purified by silica gel column chromatography (PE/EtOAc/DCM = 10:1:1→5:1:1) to afford the desired

product **3aa** (175 mg, 99%) as a white solid.

3. Preparation and characterization of compounds 3



Synthesis of 4-methyl-*N*-{3-methyl-2-(pyrimidin-2-ylamino)phenyl}benzenesulfonamide (3aa):

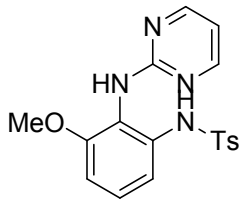
The representative procedure was followed using *N*-(*o*-tolyl)pyrimidin-2-amine (**1a**) (92.5 mg, 0.5 mmol) and *para*-toluenesulfonyl azide (**2a**) (118 mg, 0.6 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM = 10:1:1→5:1:1) to afford the desired product **3aa** (175 mg, 99%) as a white solid.

M. p. = 181−182 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.29 (d, J = 4.8 Hz, 2H), 7.94 (br s, 1H), 7.57 (d, J = 8.1 Hz, 2H), 7.44 (d, J = 8.1 Hz, 1H), 7.21−7.15 (m, 3H), 7.07 (d, J = 7.5 Hz, 1H), 6.71 (t, J = 4.8 Hz, 1H), 6.70 (br s, 1H), 2.38 (s, 3H), 2.18 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 160.9 (C_q), 158.6 (CH), 143.5 (C_q), 137.0 (C_q), 135.3 (C_q), 133.5 (C_q), 130.1 (C_q), 129.4 (CH), 127.9 (CH), 127.3 (CH), 127.1 (CH), 122.3 (CH), 112.6 (CH), 21.5 (CH_3), 18.5 (CH_3).

HRMS (ESI) m/z calcd for $C_{18}H_{19}N_4O_2S$ $[M + H]^+$: 355.1229, Found 355.1228.



Synthesis of *N*-{3-methoxy-2-(pyrimidin-2-ylamino)phenyl}-4-methylbenzenesulfonamide (3ba):

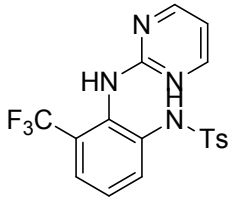
The representative procedure was followed using *N*-(2-methoxyphenyl)pyrimidin-2-amine (**1b**) (100.5 mg, 0.5 mmol) and *para*-toluenesulfonyl azide (**2a**) (118.2 mg, 0.6 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM = 10:1:1→5:1:1) to afford the desired product **3ba** (180 mg, 97%) as a white solid.

M. p. = 188−189 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 9.33 (br s, 1H), 8.39 (d, J = 4.8 Hz, 2H), 7.48 (d, J = 8.2 Hz, 2H), 7.24 (d, J = 8.2 Hz, 1H), 7.18−7.11 (m, 3H), 6.82 (br s, 1H), 6.79−6.73 (m, 2H), 3.80 (s, 3H), 2.37 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 160.7 (C_q), 158.4 (CH), 152.3 (C_q), 143.2 (C_q), 137.4 (C_q), 131.6 (C_q), 129.3 (CH), 126.9 (CH), 125.8 (CH), 122.5 (C_q), 118.8 (CH), 112.7 (CH), 108.1 (CH), 55.9 (CH_3), 21.5 (CH_3).

HRMS (ESI) m/z calcd for $C_{18}H_{19}N_4O_3S$ $[M + H]^+$: 371.1178, Found 371.1178.



Synthesis of 4-methyl-*N*-{2-(pyrimidin-2-ylamino)-3-(trifluoromethyl)phenyl}benzenesulfonamide (3ca):

The representative procedure was followed using *N*-{2-(trifluoromethyl)phenyl}pyrimidin-2-amine (**1c**) (119.5 mg, 0.5 mmol) and *para*-toluenesulfonyl azide (**2a**) (118.2 mg, 0.6 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM = 10:1:1→5:1:1) to afford the desired product **3ca** (192 mg, 94%) as a white solid.

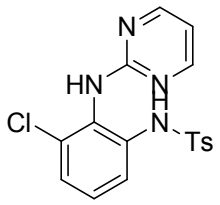
M. p. = 197−198 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.35 (d, J = 4.8 Hz, 2H), 7.97 (br s, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.51 (d, J = 8.0 Hz, 2H), 7.51 (d, J = 8.0 Hz, 1H), 7.40 (dd, J = 8.0, 8.0 Hz, 1H), 7.20 (d, J = 8.0 Hz, 2H), 6.81 (t, J = 4.8 Hz, 1H), 6.58 (br s, 1H), 2.40 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 160.4 (C_q), 158.7 (CH), 143.9 (C_q), 136.6 (C_q), 135.3 (C_q), 129.5 (CH), 129.1 (CH), 127.2 (CH), 127.0 (CH), 126.7 (q, $^2J_{C-F}$ = 29 Hz, C_q), 123.6 (q, $^1J_{C-F}$ = 276 Hz, C_q), 123.6 (q, $^3J_{C-F}$ = 5 Hz, CH), 113.6 (CH), 21.5 (CH_3) (One C_q is invisible).

^{19}F-NMR (376 MHz, $CDCl_3$): δ = −61.4 (s).

HRMS (ESI) m/z calcd for $C_{18}H_{16}F_3N_4O_2S$ $[M + H]^+$: 409.0946, Found 409.0945.



Synthesis of *N*-{3-chloro-2-(pyrimidin-2-ylamino)phenyl}-4-methylbenzenesulfonamide (3da):

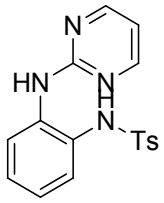
The representative procedure was followed using *N*-(2-chlorophenyl)pyrimidin-2-amine (**1d**) (102.5 mg, 0.5 mmol), *para*-toluenesulfonyl azide (**2a**) (118.2 mg, 0.6 mmol), $[IrCl_2Cp^*]_2$ (4.0 mg, 0.005 mmol) and $AgSbF_6$ (6.9 mg, 0.02 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM = 10:1:1→5:1:1) to afford the desired product **3da** (184 mg, 98%) as a white solid.

M. p. = 203−204 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.57 (br s, 1H), 8.39 (d, J = 8.39 (d, J = 4.8 Hz, 2H), 7.59 (d, J = 8.0 Hz, 1H), 7.50 (d, J = 8.2 Hz, 2H), 7.28 (d, J = 7.6 Hz, 1H), 7.20 (dd, J = 8.0, 7.6 Hz, 1H), 7.17 (d, J = 8.2 Hz, 2H), 6.85 (br s, 1H), 6.83 (t, J = 4.9 Hz, 1H), 2.38 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 160.4 (C_q), 158.6 (CH), 143.6 (C_q), 136.9 (C_q), 133.8 (C_q), 130.0 (C_q), 129.7 (C_q), 129.4 (CH), 127.0 (CH), 126.9 (CH), 126.9 (CH), 124.6 (CH), 113.4 (CH), 21.5 (CH_3).

HRMS (ESI) m/z calcd for $C_{17}H_{16}ClN_4O_2S$ $[M + H]^+$: 375.0682, Found 375.0680.



Synthesis of 4-methyl-*N*-{2-(pyrimidin-2-ylamino)phenyl}benzenesulfonamide (3ea):

The representative procedure was followed using *N*-phenylpyrimidin-2-amine (**1e**) (128.2 mg, 0.75 mmol), *para*-toluenesulfonyl azide (**2a**) (98.5 mg, 0.5 mmol), $[IrCl_2Cp^*]_2$ (4.0 mg, 0.005 mmol) and $AgSbF_6$ (6.9 mg, 0.02 mmol). After 12 h, purification by column chromatography on

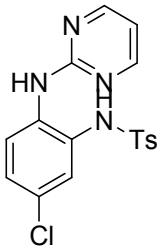
silica gel (PE/EtOAc/DCM = 10:1:1→5:1:1) to afford the desired product **3ea** (115 mg, 68%) as a white solid.

M. p. = 209−210 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.37 (d, J = 4.8 Hz, 2H), 8.03 (br s, 1H), 7.51 (d, J = 8.2 Hz, 2H), 7.45 (d, J = 7.8 Hz, 1H), 7.44 (br s, 1H), 7.35 (d, J = 7.8 Hz, 1H), 7.23 (dd, J = 7.8, 7.5 Hz, 1H), 7.18-7.11 (m, 3H), 6.76 (t, J = 4.8 Hz, 1H), 2.33 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 160.2 (C_q), 158.3 (CH), 143.5 (C_q), 136.7 (C_q), 134.2 (C_q), 129.4 (CH), 129.3 (C_q), 127.8 (CH), 127.5 (CH), 127.1 (CH), 125.5 (CH), 123.8 (CH), 112.7 (CH), 21.5 (CH_3).

HRMS (ESI) m/z calcd for $C_{17}H_{17}N_4O_2S$ $[M + H]^+$: 341.1072, Found 341.1073.



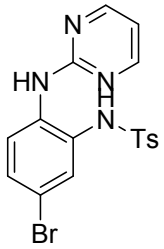
Synthesis of *N*-{5-chloro-2-(pyrimidin-2-ylamino)phenyl}-4-methylbenzenesulfonamide (3fa): The representative procedure was followed using *N*-(4-chlorophenyl)pyrimidin-2-amine (**1f**) (153.8 mg, 0.75 mmol), *para*-toluenesulfonyl azide (**2a**) (98.5 mg, 0.5 mmol), $[IrCl_2Cp^*]_2$ (4.0 mg, 0.005 mmol) and $AgSbF_6$ (6.9 mg, 0.02 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM = 10:1:1→5:1:1) to afford the desired product **3fa** (130 mg, 69%) as a white solid.

M. p. = 223−224 °C.

^{1}H-NMR (400 MHz, [d]$_6$-DMSO): δ = 9.80 (br s, 1H), 8.55 (br s, 1H), 8.37 (d, J = 4.8 Hz, 2H), 7.84 (d, J = 8.8 Hz, 1H), 7.44 (d, J = 8.2 Hz, 2H), 7.26 (dd, J = 8.8, 2.4 Hz, 1H), 7.13−7.07 (m, 3H), 6.85 (t, J = 4.8 Hz, 1H), 2.20 (s, 3H).

^{13}C-NMR (100 MHz, [d]$_6$-DMSO): δ = 159.9 (C_q), 158.4 (CH), 143.7 (C_q), 136.5 (C_q), 134.1 (C_q), 129.9 (CH), 128.6 (C_q), 127.0 (CH), 127.0 (CH), 126.7 (C_q), 125.4 (CH), 113.6 (CH), 21.5 (CH_3) (One CH is invisible).

HRMS (ESI) m/z calcd for $C_{17}H_{16}ClN_4O_2S$ $[M + H]^+$: 375.0682, Found 375.0683.



Synthesis of *N*-{5-bromo-2-(pyrimidin-2-ylamino)phenyl}-4-methylbenzenesulfonamide (3ga):

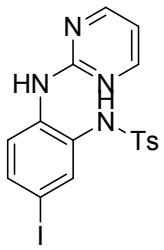
The representative procedure was followed using *N*-(4-bromophenyl)pyrimidin-2-amine (**1g**) (187.5 mg, 0.75 mmol), *para*-toluenesulfonyl azide (**2a**) (98.5 mg, 0.5 mmol), $[IrCl_2Cp^*]_2$ (4.0 mg, 0.005 mmol) and $AgSbF_6$ (6.9 mg, 0.02 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM = 10:1:1→5:1:1) to afford the desired product **3ga** (180 mg, 86%) as a white solid.

M. p. = 220−221 °C.

^{1}H-NMR (400 MHz, [d]$_6$-DMSO): δ = 9.80 (br s, 1H), 8.55 (br s, 1H), 8.37 (d, J = 4.8 Hz, 2H), 7.81 (d, J = 8.8 Hz, 1H), 7.45 (d, J = 8.0 Hz, 2H), 7.37 (dd, J = 8.8, 2.2 Hz, 1H), 7.21 (d, J = 2.2 Hz, 1H), 7.10 (d, J = 8.0 Hz, 2H), 6.84 (t, J = 4.8 Hz, 1H), 2.19 (s, 3H).

^{13}C-NMR (100 MHz, [d]$_6$-DMSO): δ = 159.8 (C_q), 158.4 (CH), 143.7 (C_q), 136.5 (C_q), 134.6 (C_q), 130.0 (CH), 130.0 (CH), 129.8 (CH), 128.7 (C_q), 127.0 (CH), 125.5 (CH), 114.3 (C_q), 113.7 (CH), 21.5 (CH_3).

HRMS (ESI) m/z calcd for $C_{17}H_{16}BrN_4O_2S$ $[M + H]^+$: 419.0177, Found 419.0173.



Synthesis of *N*-{5-iodo-2-(pyrimidin-2-ylamino)phenyl}-4-methylbenzenesulfonamide (3ha):

The representative procedure was followed using *N*-(4-iodophenyl)pyrimidin-2-amine (**1h**) (222.7 mg, 0.75 mmol), *para*-toluenesulfonyl azide (**2a**) (98.5 mg, 0.5 mmol), $[IrCl_2Cp^*]_2$ (4.0 mg, 0.005 mmol) and $AgSbF_6$ (6.9 mg, 0.02 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM = 10:1:1→5:1:1) to afford the desired product **3ha** (198 mg, 85%) as a

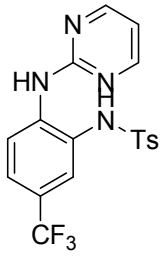
yellow solid.

M. p. = 205−206 °C.

^{1}H-NMR (400 MHz, [d]$_6$-DMSO): δ = 9.73 (br s, 1H), 8.51 (br s, 1H), 8.38 (d, J = 4.8 Hz, 2H), 7.70 (d, J = 8.7 Hz, 1H), 7.52 (dd, J = 8.7, 1.7 Hz, 1H), 7.44 (d, J = 8.1 Hz, 2H), 7.31 (s, 1H), 7.12 (d, J = 8.1 Hz, 2H), 6.85 (t, J = 4.8 Hz, 1H), 2.21 (s, 3H).

^{13}C-NMR (100 MHz, [d]$_6$-DMSO): δ = 159.7 (C_q), 158.4 (CH), 143.7 (C_q), 136.5 (C_q), 136.1 (CH), 135.9 (CH), 135.4 (C_q), 129.8 (CH), 128.5 (C_q), 127.1 (CH), 125.5 (CH), 113.7 (CH), 85.8 (C_q), 21.5 (CH_3).

HRMS (ESI) m/z calcd for $C_{17}H_{16}IN_4O_2S$ $[M + H]^+$: 467.0039, Found 467.0037.



Synthesis of 4-methyl-*N*-{2-(pyrimidin-2-ylamino)-5-(trifluoromethyl)phenyl}benzenesulfonamide (3ia):

The representative procedure was followed using *N*-{4-(trifluoromethyl)phenyl}pyrimidin-2-amine (**1i**) (179.2 mg, 0.75 mmol), *para*-toluenesulfonyl azide (**2a**) (98.5 mg, 0.5 mmol), $[IrCl_2Cp^*]_2$ (4.0 mg, 0.005 mmol) and $AgSbF_6$ (6.9 mg, 0.02 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM = 10:1:1→5:1:1) to afford the desired product **3ia** (149 mg, 73%) as a yellow solid.

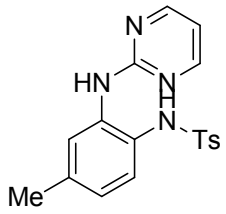
M. p. = 199−200 °C.

^{1}H-NMR (400 MHz, [d]$_6$-DMSO): δ = 9.90 (br s, 1H), 8.73 (br s, 1H), 8.46 (d, J = 4.6 Hz, 2H), 8.22 (d, J = 8.0 Hz, 1H), 7.57 (d, J = 8.0 Hz, 1H), 7.44 (d, J = 8.0 Hz, 2H), 7.22 (s, 1H), 7.14 (d, J = 8.0 Hz, 2H), 6.95 (t, J = 4.6 Hz, 1H), 2.20 (s, 3H).

^{13}C-NMR (100 MHz, [d]$_6$-DMSO): δ = 159.4 (C_q), 158.6 (CH), 143.9 (C_q), 139.3 (C_q), 136.2 (C_q), 129.9 (CH), 127.1 (CH), 126.5 (C_q), 124.9 (q, $^{3}J_{C-F}$ = 4 Hz, CH), 124.5 (q, $^{3}J_{C-F}$ = 4 Hz, CH), 124.2 (q, $^{1}J_{C-F}$ = 259 Hz, C_q), 122.8 (CH), 122.7 (q, $^{2}J_{C-F}$ = 28 Hz, C_q), 114.4 (CH), 21.4 (CH_3).

^{19}F-NMR (376 MHz, [d]$_6$-DMSO): δ = −60.6 (s).

HRMS (ESI) m/z calcd for $C_{18}H_{16}F_3N_4O_2S$ $[M + H]^+$: 409.0946, Found 409.0944.



Synthesis of 4-methyl-*N*-{4-methyl-2-(pyrimidin-2-ylamino)phenyl}benzenesulfonamide (3ja):

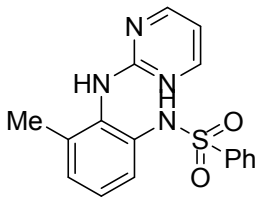
The representative procedure was followed using *N*-(*m*-tolyl)pyrimidin-2-amine (**1j**) (92.5 mg, 0.5 mmol), *para*-toluenesulfonyl azide (**2a**) (118.2 mg, 0.6 mmol), $[IrCl_2Cp^*]_2$ (4.0 mg, 0.005 mmol) and $AgSbF_6$ (6.9 mg, 0.02 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM = 10:1:1→5:1:1) to afford the desired product **3ja** (156 mg, 88%) as a white solid.

M. p. = 209−210 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.36 (d, J = 4.8 Hz, 2H), 7.90 (br s, 1H), 7.50 (d, J = 8.1 Hz, 2H), 7.35 (br s, 1H), 7.28 (d, J = 8.0 Hz, 1H), 7.20 (d, J = 8.0 Hz, 1H), 7.15 (d, J = 8.1 Hz, 2H), 6.94 (d, J = 7.8 Hz, 1H), 6.74 (t, J = 4.8 Hz, 1H), 2.34 (s, 3H), 2.33 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 160.1 (C_q), 158.3 (CH), 143.4 (C_q), 137.8 (C_q), 136.7 (C_q), 134.2 (C_q), 129.4 (CH), 128.1 (CH), 127.2 (CH), 126.4 (C_q), 126.2 (CH), 124.1 (CH), 112.6 (CH), 21.5 (CH_3), 21.1 (CH_3).

HRMS (ESI) m/z calcd for $C_{18}H_{19}N_4O_2S$ $[M + H]^+$: 355.1229, Found 355.1225.



Synthesis of *N*-{3-methyl-2-(pyrimidin-2-ylamino)phenyl}benzenesulfonamide (3ab):

The representative procedure was followed using *N*-(*o*-tolyl)pyrimidin-2-amine (**1a**) (92.5 mg, 0.5 mmol) and benzenesulfonyl azide (**2b**) (109.8 mg, 0.6 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM = 10:1:1→5:1:1) to afford the desired product **3ab**

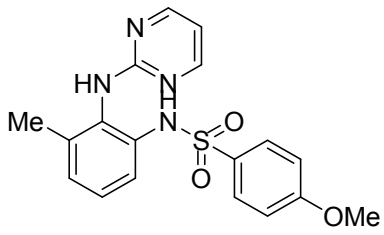
(169 mg, 99%) as a white solid.

M. p. = 175−176 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.33 (d, J = 4.8 Hz, 2H), 7.98 (br s, 1H), 7.65 (d, J = 7.7 Hz, 2H), 7.54 (dd, J = 7.7, 7.7 Hz, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.40 (dd, J = 7.7, 7.7 Hz, 2H), 7.19 (dd, J = 8.0, 7.7 Hz, 1H), 7.09 (d, J = 7.7 Hz, 1H), 6.74 (t, J = 4.8 Hz, 1H), 6.29 (br s, 1H), 2.17 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 160.7 (C_q), 158.6 (CH), 139.9 (C_q), 134.7 (C_q), 133.1 (C_q), 132.7 (CH), 130.5 (C_q), 128.8 (CH), 128.2 (CH), 127.2 (CH), 127.0 (CH), 123.2 (CH), 112.7 (CH), 18.5 (CH_3).

HRMS (ESI) m/z calcd for $C_{17}H_{17}N_4O_2S$ $[M + H]^+$: 341.1072, Found 341.1074.



Synthesis of 4-methoxy-*N*-{3-methyl-2-(pyrimidin-2-ylamino)phenyl}benzenesulfonamide (3ac):

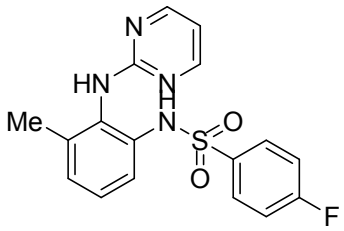
The representative procedure was followed using *N*-(*o*-tolyl)pyrimidin-2-amine (**1a**) (92.5 mg, 0.5 mmol) and 4-methoxybenzenesulfonyl azide (**2c**) (127.8 mg, 0.6 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM = 10:1:1→5:1:1) to afford the desired product **3ac** (183 mg, 99%) as a white solid.

M. p. = 194−195 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.29 (d, J = 4.8 Hz, 2H), 7.89 (br s, 1H), 7.61 (d, J = 8.8 Hz, 2H), 7.44 (d, J = 8.0 Hz, 1H), 7.17 (dd, J = 8.0, 7.7 Hz, 1H), 7.07 (d, J = 7.7 Hz, 1H), 6.85 (d, J = 8.8 Hz, 2H), 6.74 (br s, 1H), 6.70 (t, J = 4.8 Hz, 1H), 3.82 (s, 3H), 2.18 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 162.9 (C_q), 161.0 (C_q), 158.6 (CH), 135.3 (C_q), 133.6 (C_q), 131.5 (C_q), 130.1 (C_q), 129.2 (CH), 127.9 (CH), 127.3 (CH), 122.3 (CH), 114.0 (CH), 112.6 (CH), 55.5 (CH_3), 18.6 (CH_3).

HRMS (ESI) m/z calcd for $C_{18}H_{19}N_4O_3S$ $[M + H]^+$: 371.1178, Found 371.1177.



Synthesis of 4-fluoro-*N*-{3-methyl-2-(pyrimidin-2-ylamino)phenyl}benzenesulfonamide (3ad):

The representative procedure was followed using *N*-(*o*-tolyl)pyrimidin-2-amine (**1a**) (92.5 mg, 0.5 mmol) and 4-fluorobenzenesulfonyl azide (**2d**) (120.6 mg, 0.6 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM = 10:1:1→5:1:1) to afford the desired product **3ad** (177 mg, 99%) as a white solid.

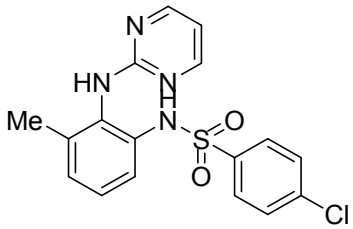
M. p. = 213−214 °C.

^{1}H-NMR (400 MHz, [d]$_6$-DMSO): δ = 9.55 (br s, 1H), 8.34 (br s, 1H), 8.21 (d, J = 4.8 Hz, 2H), 7.63 (dd, J = 8.2, 7.4 Hz, 2H), 7.19 (dd, J = 7.8, 7.8 Hz, 1H), 7.15−7.01 (m, 4H), 6.68 (t, J = 4.8 Hz, 1H), 3.47 (s, 3H).

^{13}C-NMR (100 MHz, [d]$_6$-DMSO): δ = 164.7 (d, $^{1}J_{C-F}$ = 251 Hz, C_q), 161.1 (C_q), 158.3 (CH), 137.8 (C_q), 136.5 (d, $^{4}J_{C-F}$ = 3 Hz, C_q), 132.9 (C_q), 131.9 (C_q), 129.9 (d, $^{3}J_{C-F}$ = 10 Hz, CH), 128.3 (CH), 126.5 (CH), 122.7 (CH), 116.6 (d, $^{2}J_{C-F}$ = 22 Hz, CH), 112.1 (CH), 19.0 (CH_3).

^{19}F-NMR (376 MHz, [d]$_6$-DMSO): δ = −106.3 (s).

HRMS (ESI) m/z calcd for $C_{17}H_{16}FN_4O_2S$ $[M + H]^+$: 359.0978, Found 359.0979.



Synthesis of 4-chloro-*N*-{3-methyl-2-(pyrimidin-2-ylamino)phenyl}benzenesulfonamide (3ae):

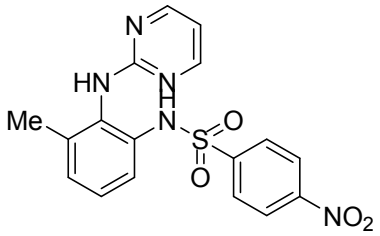
The representative procedure was followed using *N*-(*o*-tolyl)pyrimidin-2-amine (**1a**) (92.5 mg, 0.5 mmol) and 4-chlorobenzenesulfonyl azide (**2e**) (130.2 mg, 0.6 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM = 10:1:1→5:1:1) to afford the desired product **3ae** (185 mg, 99%) as a white solid.

M. p. = 205−206 °C.

^{1}H-NMR (400 MHz, [d]$_6$-DMSO): δ = 9.60 (br s, 1H), 8.31 (br s, 1H), 8.19 (d, J = 4.8 Hz, 2H), 7.53 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 7.8 Hz, 1H), 7.11 (dd, J = 7.8, 7.6 Hz, 1H), 7.06 (d, J = 7.6 Hz, 1H), 6.69 (t, J = 4.8 Hz, 1H), 2.00 (s, 3H).

^{13}C-NMR (100 MHz, [d]$_6$-DMSO): δ = 161.0 (C_q), 158.3 (CH), 138.9 (C_q), 137.9 (C_q), 137.8 (C_q), 132.7 (C_q), 132.0 (C_q), 129.5 (CH), 128.7 (CH), 128.4 (CH), 126.5 (CH), 122.9 (CH), 112.1 (CH), 19.0 (CH_3).

HRMS (ESI) m/z calcd for $C_{17}H_{16}ClN_4O_2S$ $[M + H]^+$: 375.0682, Found 375.0683.



Synthesis of *N*-{3-methyl-2-(pyrimidin-2-ylamino)phenyl}-4-nitrobenzenesulfonamide (3af):

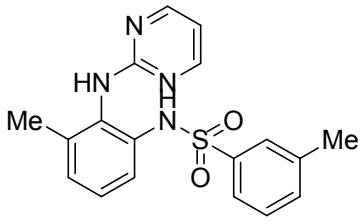
The representative procedure was followed using *N*-(*o*-tolyl)pyrimidin-2-amine (**1a**) (92.5 mg, 0.5 mmol) and 4-nitrobenzenesulfonyl azide (**2f**) (136.8 mg, 0.6 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM = 10:1:1→5:1:1) to afford the desired product **3af** (190 mg, 98%) as a pale yellow solid.

M. p. = 234−235 °C.

^{1}H-NMR (400 MHz, [d]$_6$-DMSO): δ = 9.82 (br s, 1H), 8.26 (br s, 1H), 8.10 (d, J = 4.8 Hz, 2H), 8.06 (d, J = 8.8 Hz, 2H), 7.74 (d, J = 8.8 Hz, 2H), 7.24 (d, J = 7.8 Hz, 1H), 7.15 (dd, J = 7.8, 7.5 Hz, 1H), 7.10 (d, J = 7.5 Hz, 1H), 6.54 (t, J = 4.8 Hz, 1H), 1.96 (s, 3H).

^{13}C-NMR (100 MHz, [d]$_6$-DMSO): δ = 160.9 (C_q), 158.2 (CH), 149.6 (C_q), 145.6 (C_q), 137.7 (C_q), 132.4 (C_q), 132.1 (C_q), 129.1 (CH), 128.3 (CH), 126.5 (CH), 124.8 (CH), 124.1 (CH), 112.0 (CH), 19.0 (CH_3).

HRMS (ESI) m/z calcd for $C_{17}H_{16}N_5O_4S$ $[M + H]^+$: 386.0923, Found 386.0921.



Synthesis of 3-methyl-*N*-{3-methyl-2-(pyrimidin-2-ylamino)phenyl}benzenesulfonamide (3ag):

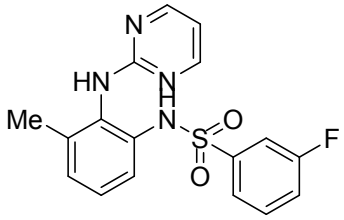
The representative procedure was followed using *N*-(*o*-tolyl)pyrimidin-2-amine (**1a**) (92.5 mg, 0.5 mmol) and 3-methylbenzenesulfonyl azide (**2g**) (118.2 mg, 0.6 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM = 10:1:1→5:1:1) to afford the desired product **3ag** (170 mg, 96%) as a white solid.

M. p. = 176−177 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.33 (d, J = 4.8 Hz, 2H), 7.98 (br s, 1H), 7.49−7.41 (m, 3H), 7.34 (d, J = 7.2 Hz, 1H), 7.28 (d, J = 7.2 Hz, 1H), 7.19 (dd, J = 7.6, 7.6 Hz, 1H), 7.09 (d, J = 7.6 Hz, 1H), 6.72 (t, J = 4.8 Hz, 1H), 6.41 (br s, 1H), 2.33 (s, 3H), 2.18 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 160.8 (C_q), 158.6 (CH), 139.8 (C_q), 139.0 (C_q), 134.9 (C_q), 133.5 (CH), 133.2 (C_q), 130.5 (C_q), 128.6 (CH), 128.2 (CH), 127.4 (CH), 127.2 (CH), 124.2 (CH), 123.2 (CH), 112.6 (CH), 21.3 (CH_3), 18.5 (CH_3).

HRMS (ESI) m/z calcd for $C_{18}H_{19}N_4O_2S$ $[M + H]^+$: 355.1229, Found 355.1230.



Synthesis of 3-fluoro-*N*-{3-methyl-2-(pyrimidin-2-ylamino)phenyl}benzenesulfonamide (3ah):

The representative procedure was followed using *N*-(*o*-tolyl)pyrimidin-2-amine (**1a**) (92.5 mg, 0.5 mmol) and 3-fluorobenzenesulfonyl azide (**2h**) (120.6 mg, 0.6 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM = 10:1:1→5:1:1) to afford the desired product **3ah** (138 mg, 77%) as a white solid.

M. p. = 192−193 °C.

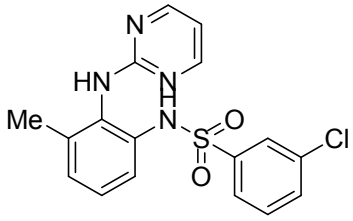
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.33 (d, J = 4.8 Hz, 2H), 8.23 (br s, 1H), 7.45 (d, J = 7.2 Hz, 1H), 7.45 (d, J = 7.2 Hz, 1H), 7.39 (dd, J = 7.8, 7.8 Hz, 1H), 7.34 (d, J = 6.8 Hz, 1H), 7.23 (dd, J = 7.7, 7.5 Hz, 1H), 7.19 (d, J = 7.8 Hz, 1H), 7.11 (d, J = 7.5 Hz, 1H), 6.75 (t, J = 4.8 Hz, 1H), 6.57 (br s, 1H), 2.20 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 162.1 (d, $^1J_{C-F}$ = 251 Hz, C_q), 160.7 (C_q), 158.6 (CH), 142.1 (d,

$^{3}J_{C-F}$ = 7 Hz, C_q), 134.7 (C_q), 132.6 (C_q), 130.6 (C_q), 130.5 (d, $^{3}J_{C-F}$ = 7 Hz, CH), 128.5 (CH), 127.2 (CH), 123.3 (CH), 122.8 (d, $^{4}J_{C-F}$ = 3 Hz, CH), 119.9 (d, $^{2}J_{C-F}$ = 21 Hz, CH), 114.4 (d, $^{2}J_{C-F}$ = 24 H, CH), 112.8 (CH), 18.5 (CH_3).

^{19}F-NMR (376 MHz, $CDCl_3$): δ = −(119.7−110.0) (m).

HRMS (ESI) m/z calcd for $C_{17}H_{16}FN_4O_2S$ $[M + H]^+$: 359.0978, Found 359.0978.



Synthesis of 3-chloro-*N*-{3-methyl-2-(pyrimidin-2-ylamino)phenyl}benzenesulfonamide (3ai):

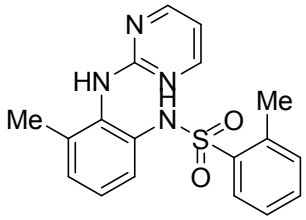
The representative procedure was followed using *N*-(*o*-tolyl)pyrimidin-2-amine (**1a**) (92.5 mg, 0.5 mmol) and 3-chlorobenzenesulfonyl azide (**2i**) (130.5 mg, 0.6 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM = 10:1:1→5:1:1) to afford the desired product **3ai** (186 mg, 99%) as a white solid.

M. p. = 183−184 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.34 (d, J = 4.8 Hz, 2H), 8.27 (s, 1H), 7.60 (br s, 1H), 7.53 (d, J = 7.8 Hz, 1H), 7.49 (d, J = 7.9, 1H), 7.45 (d, J = 7.9, 1H), 7.33 (d, J = 7.9, 7.9 Hz, 1H), 7.21 (dd, J = 7.8, 7.8 Hz, 1H), 7.12 (d, J = 7.8 Hz, 1H), 6.76 (t, J = 4.8 Hz, 1H), 6.53 (br s, 1H), 2.21 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 160.6 (C_q), 158.6 (CH), 141.8 (C_q), 135.0 (C_q), 134.6 (C_q), 132.8 (CH), 132.5 (C_q), 130.8 (C_q), 130.0 (CH), 128.6 (CH), 127.1 (CH), 127.0 (CH), 125.1 (CH), 123.6 (CH), 112.8 (CH), 18.5 (CH_3).

HRMS (ESI) m/z calcd for $C_{17}H_{16}ClN_4O_2S$ $[M + H]^+$: 375.0682, Found 375.0681.



Synthesis of 2-methyl-*N*-{3-methyl-2-(pyrimidin-2-ylamino)phenyl}benzenesulfonamide (3aj):

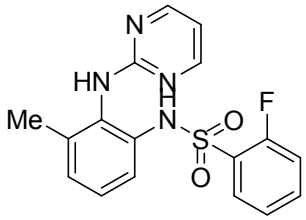
The representative procedure was followed using *N*-(*o*-tolyl)pyrimidin-2-amine (**1a**) (92.5 mg, 0.5 mmol) and 2-methylbenzenesulfonyl azide (**2j**) (118.2 mg, 0.6 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM = 10:1:1→5:1:1) to afford the desired product **3aj** (175 mg, 99%) as a white solid.

M. p. = 164−165 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.35 (d, J = 4.8 Hz, 2H), 8.03 (br s, 1H), 7.87 (d, J = 7.8 Hz, 1H), 7.42 (dd, J = 7.4, 7.4 Hz, 1H), 7.30 (d, J = 7.8 Hz, 1H), 7.24 (d, J = 7.8 Hz, 1H), 7.23 (dd, J = 7.8, 7.8 Hz, 1H), 7.13 (dd, J = 7.8, 7.8 Hz, 1H), 7.05 (d, J = 7.4 Hz, 1H), 6.74 (t, J = 4.8 Hz, 1H), 6.68 (br s, 1H), 2.46 (s, 3H), 2.19 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 161.1 (C_q), 158.6 (CH), 138.2 (C_q), 137.3 (C_q), 135.1 (C_q), 133.5 (C_q), 132.8 (CH), 132.5 (CH), 129.8 (C_q), 129.5 (CH), 127.7 (CH), 127.2 (CH), 126.1 (CH), 121.8 (CH), 112.7 (CH), 20.2 (CH_3), 18.5 (CH_3).

HRMS (ESI) m/z calcd for $C_{18}H_{19}N_4O_2S$ $[M + H]^+$: 355.1229, Found 355.1230.



Synthesis of 2-fluoro-*N*-{3-methyl-2-(pyrimidin-2-ylamino)phenyl}benzenesulfonamide (3ak):

The representative procedure was followed using *N*-(*o*-tolyl)pyrimidin-2-amine (**1a**) (92.5 mg, 0.5 mmol) and 2-fluorobenzenesulfonyl azide (**2k**) (120.6 mg, 0.6 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM = 10:1:1→5:1:1) to afford the desired product **3ak** (171 mg, 95%) as a white solid.

M. p. = 161−162 °C.

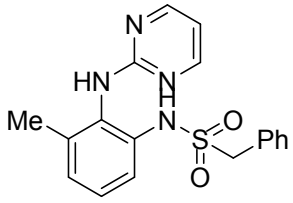
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.50 (br s, 1H), 8.33 (d, J = 4.8 Hz, 2H), 7.78 (dd, J = 7.8, 7.8 Hz, 1H), 7.51 (dd, J = 8.0, 8.0 Hz, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.17 (ddd, J = 7.8, 7.8, 2.0 Hz, 1H), 7.10 (d, J = 8.0 Hz, 1H), 7.09 (dd, J = 7.8, 4.5 Hz, 2H), 6.92 (br s, 1H), 6.75 (t, J = 4.8 Hz, 1H), 2.20 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 160.9 (C_q), 159.2 (d, $^1J_{C-F}$ = 255 Hz, C_q), 158.6 (CH), 135.0 (d, $^3J_{C-F}$ = 8 Hz, CH), 134.8 (C_q), 132.7 (C_q), 130.5 (C_q), 130.4 (CH), 128.3 (CH), 128.3 (d, $^2J_{C-F}$ =

22 Hz, C_q), 127.1 (CH), 124.1 (d, $^4J_{C-F}$ = 4 Hz, CH), 123.1 (CH), 116.8 (d, $^2J_{C-F}$ = 22 Hz, CH), 112.7 (CH), 18.5 (CH_3).

^{19}F-NMR (376 MHz, $CDCl_3$): δ = −(109.8−109.9) (m).

HRMS (ESI) m/z calcd for $C_{17}H_{16}FN_4O_2S$ $[M + H]^+$: 359.0978, Found 359.0979.



Synthesis of *N*-{3-methyl-2-(pyrimidin-2-ylamino)phenyl}-1-phenylmethanesulfonamide (3al):

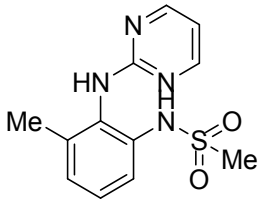
The representative procedure was followed using *N*-(*o*-tolyl)pyrimidin-2-amine (**1a**) (92.5 mg, 0.5 mmol) and phenylmethanesulfonyl azide (**2l**) (118.2 mg, 0.6 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM = 10:1:1→5:1:1) to afford the desired product **3al** (100 mg, 57%) as a white solid.

M. p. = 174−175 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.19 (br s, 1H), 8.16 (d, J = 4.8 Hz, 2H), 7.51 (d, J = 8.0 Hz, 1H), 7.32−7.28 (m, 5H), 7.25 (dd, J = 8.0, 7.8 Hz, 1H), 7.12 (d, J = 7.6 Hz, 1H), 6.58 (t, J = 4.8 Hz, 1H), 6.52 (br s, 1H), 4.38 (s, 2H), 2.24 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 161.1 (C_q), 158.3 (CH), 136.3 (C_q), 134.7 (C_q), 130.8 (CH), 128.8 (C_q), 128.8 (CH), 128.7 (CH), 128.6 (C_q), 127.8 (CH), 127.0 (CH), 119.4 (CH), 112.6 (CH), 58.4 (CH_2), 18.6 (CH_3).

HRMS (ESI) m/z calcd for $C_{18}H_{19}N_4O_2S$ $[M + H]^+$: 355.1229, Found 355.1228.



Synthesis of *N*-{3-methyl-2-(pyrimidin-2-ylamino)phenyl}methanesulfonamide (3am):

The representative procedure was followed using *N*-(*o*-tolyl)pyrimidin-2-amine (**1a**) (92.5 mg, 0.5 mmol) and methanesulfonyl azide (**2m**) (72.6 mg, 0.6 mmol). After 12 h, purification by column

chromatography on silica gel (PE/EtOAc/DCM = 10:1:1→5:1:1) to afford the desired product **3am** (88 mg, 63%) as a white solid.

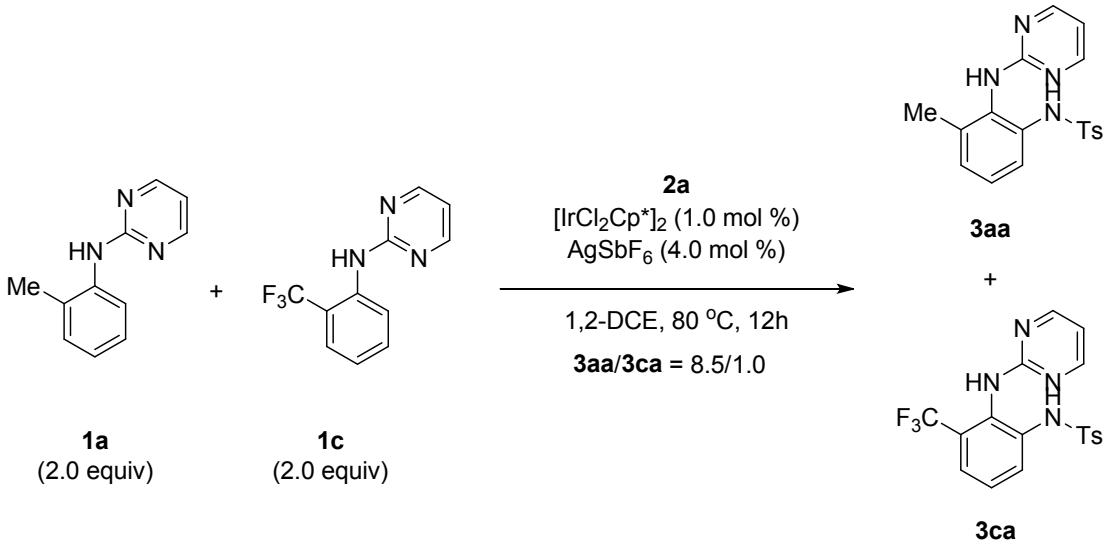
M. p. = 169−171 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.35 (d, J = 4.8 Hz, 2H), 7.79 (br s, 1H), 7.53 (d, J = 8.0 Hz, 1H), 7.26 (dd, J = 8.0, 8.0 Hz, 1H), 7.16 (br s, 1H), 7.15 (d, J = 8.0 Hz, 1H), 6.74 (t, J = 4.8 Hz, 1H), 2.97 (s, 3H), 2.29 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 161.3 (C_q), 158.7 (CH), 135.9 (C_q), 134.1 (C_q), 129.9 (C_q), 127.9 (CH), 127.7 (CH), 121.3 (CH), 113.0 (CH), 39.8 (CH_3), 18.6 (CH_3).

HRMS (ESI) m/z calcd for $C_{12}H_{15}N_4O_2S$ $[M + H]^+$: 279.0916, Found 279.0912.

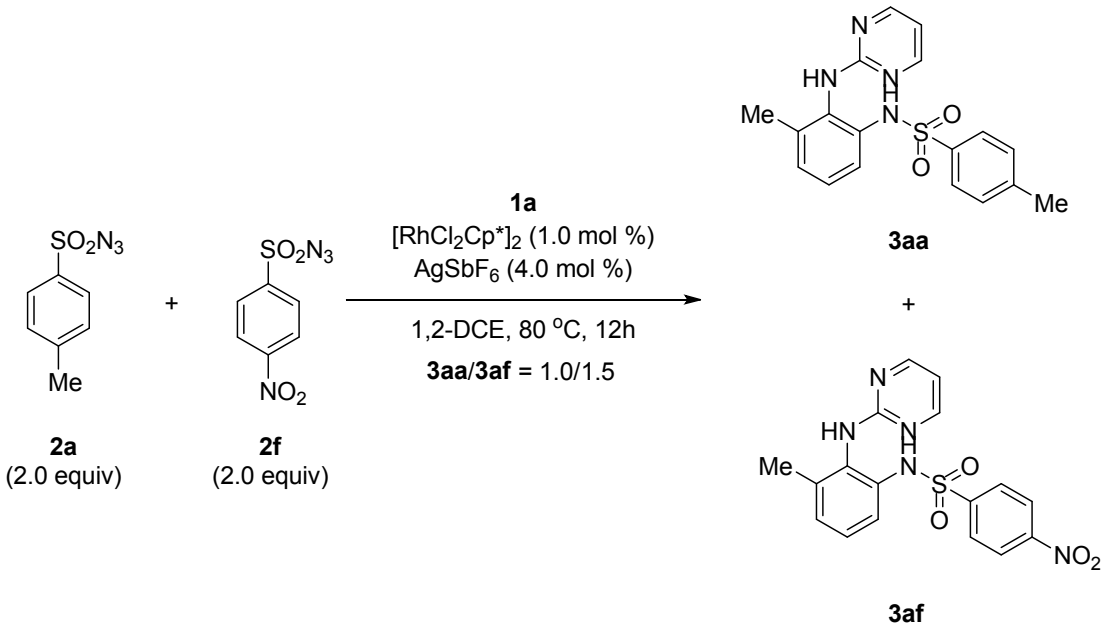
Intermolecular competition experiment with anilines 1a and 1c (Scheme 4)



1a (2.0 equiv) **1c** (2.0 equiv)

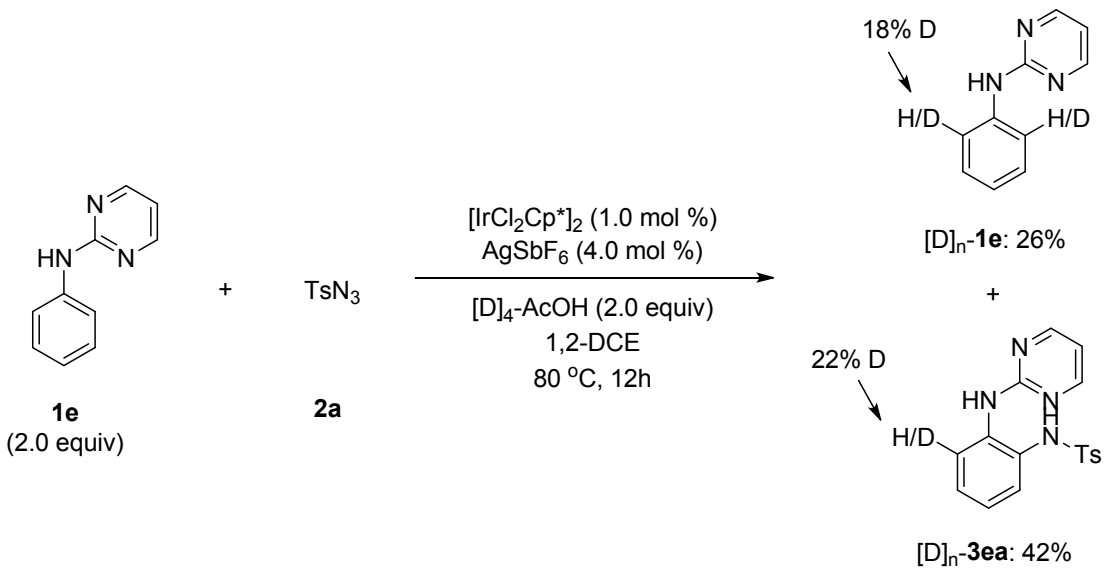
The mixture of *N*-(*o*-tolyl)pyrimidin-2-amine (**1a**) (185.0 mg, 1.0 mmol), *N*-{2-(trifluoromethyl)phenyl}pyrimidin-2-amine (**1c**) (239 mg, 1.0 mmol), *para*-toluenesulfonyl azide (**2a**) (98.5 mg, 0.5 mmol), $[IrCl_2Cp^*]_2$ (4.0 mg, 0.005 mmol), $AgSbF_6$ (6.9 mg, 0.02 mmol) and 1,2-DCE (2.0 mL) was stirred at 80 °C under N_2 for 12 h. The reaction mixture was cooled to ambient temperature, filtered through a pad of celite and silica gel, and washed with EtOAc (3 x 10 mL). The solvents were removed under reduced pressure. The residue was purified by silica gel column chromatography (PE/EtOAc/DCM = 10:1:1→5:1:1→3:1:1) to yield **3ca** (17 mg, 10%) as a pale yellow solid and **3aa** (175 mg, 85%) as a white solid.

Intermolecular competition experiment with sulfonyl azides 2a and 2f (Scheme 5)



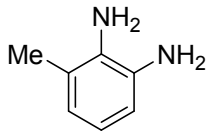
The mixture of *N*-(*o*-tolyl)pyrimidin-2-amine (**1a**) (92.5 mg, 0.5 mmol), *para*-toluenesulfonyl azide (**2a**) (197.0 mg, 1.0 mmol), 4-nitrobenzenesulfonyl azide (**2f**) (228.0 mg, 1.0 mmol), $[IrCl_2Cp^*]_2$ (4.0 mg, 0.005 mmol), $AgSbF_6$ (6.9 mg, 0.02 mmol) and 1,2-DCE (2.0 mL) was stirred at 80 °C under N_2 for 12 h. The reaction mixture was cooled to ambient temperature, filtered through a pad of celite and silica gel, and washed with EtOAc (3 x 10 mL). The solvents were removed under reduced pressure. The residue was purified by silica gel column chromatography (PE/EtOAc/DCM = 10:1:1→5:1:1→3:1:1) to yield **3af** (101 mg, 52%) as a pale yellow solid and **3aa** (62 mg, 35%) as a white solid.

Iridium-catalyzed direct *ortho*-C–H amidation of sulfonyl azide 2a with aniline 1e in 1,2-DCE and $[D]_4$-AcOH (Scheme 6)



A mixture of *N*-phenylpyrimidin-2-amine (**1e**) (342.0 mg, 2.0 mmol), *para*-toluenesulfonyl azide (**2a**) (197.0 mg, 1.0 mmol), $[IrCl_2Cp^*]_2$ (8.0 mg, 0.01 mmol), $AgSbF_6$ (13.8 mg, 0.04 mmol), 1,2-DCE (2.0 mL) and $[D]_4$-AcOH (112 μL, 2.0 mmol) was stirred at 80 °C under N_2 for 12 h. The reaction mixture was cooled to ambient temperature, filtered through a pad of celite and silica gel, and washed with EtOAc (3 x 10 mL). The solvents were removed under reduced pressure. The residue was purified by silica gel column chromatography (PE/EtOAc/DCM = 40:1:1→10:1:1→4:1:1) to give $[D]_n$-**1e** (88 mg, 26%) as a white solid and $[D]_n$-**3ea** (144 mg, 42%) as a white solid. The deuterium incorporation was estimated by ^{1}H-NMR spectroscopy.

Removal of the 2-pyridyl and sulfonyl moieties (Scheme 8)[5]



Synthesis of 3-methylbenzene-1,2-diamine (4aa/4ad):

Procedure 1: 4-Methyl-*N*-{3-methyl-2-(pyrimidin-2-ylamino)phenyl}benzenesulfonamide (**3aa**, 0.2 mmol, 71mg) was dissolved in aqueous HCl (37%, 2.0 mL) in a microwave vial. The vial was heated up to 150 °C (40 W) for 3 h in the microwave oven. The reaction mixture was allowed to cool to ambient temperature and poured into EtOAc (50 mL), and then saturated aqueous $NaHCO_3$ solution was added until the pH was adjusted to 7. The aqueous layer was extracted with EtOAc (3 × 50 mL), the combined organic layers were dried with Na_2SO_4 and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (PE/EtOAc/DCM = 20:1:1→10:1:1→5:1:1) to give **4aa** (13mg, 53%) as a yellow solid.

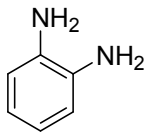
Procedure 2: 4-Methyl-*N*-{3-methyl-2-(pyrimidin-2-ylamino)phenyl}benzenesulfonamide (**3ad**, 0.2 mmol, 71mg) was dissolved in aqueous HCl (37%, 2.0 mL) in a microwave vial. The vial was heated up to 150 °C (40 W) for 3 h in the microwave oven. The reaction mixture was allowed to cool to ambient temperature and poured into EtOAc (50 mL), and then saturated aqueous $NaHCO_3$ solution was added until the pH was adjusted to 7. The aqueous layer was extracted with EtOAc (3 × 50 mL), the combined organic layers were dried with Na_2SO_4 and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (PE/EtOAc/DCM = 20:1:1→10:1:1→5:1:1) to give **4aa** (12mg, 48%) as a yellow solid.

M. p. = 70−71 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 6.72−6.61 (m, 3H), 3.28 (br s, 2H), 3.28 (br s, 2H), 2.23 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 133.9 (C_q), 133.5 (C_q), 123.4 (C_q), 122.1 (CH), 119.2 (CH), 115.1 (CH), 17.4 (CH_3).

HRMS (ESI) m/z calcd for $C_{34}H_{25}O$ $[M + H]^+$: 123.0917, Found 123.0917.



Synthesis of benzene-1,2-diamine (4ea):

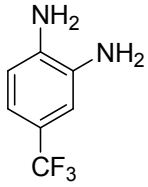
4-Methyl-*N*-{2-(pyrimidin-2-ylamino)phenyl}benzenesulfonamide (**3ea**, 0.2 mmol, 68mg) was dissolved in aqueous HCl (37%, 2.0 mL) in a microwave vial. The vial was heated up to 150 °C (40 W) for 3 h in the microwave oven. The reaction mixture was allowed to cool to ambient temperature and poured into EtOAc (50 mL), and then saturated aqueous $NaHCO_3$ solution was added until the pH was adjusted to 7. The aqueous layer was extracted with EtOAc (3 × 50 mL), the combined organic layers were dried with Na_2SO_4 and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (PE/EtOAc/DCM = 30:1:1→10:1:1→6:1:1) to give **4ea** (13mg, 58%) as a yellow solid.

M. p. = 103−105 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 6.79**–**6.70 (m, 4H), 3.33 (br s, 4H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 134.8 (C_q), 120.3 (CH), 116.8 (CH).

HRMS (ESI) m/z calcd for $C_{34}H_{25}O$ $[M + H]^+$: 109.0766, Found 109.0760.



Synthesis of 4-(trifluoromethyl)benzene-1,2-diamine (4ia):

4-Methyl-*N*-{2-(pyrimidin-2-ylamino)-5-(trifluoromethyl)phenyl}benzenesulfonamide (**3ia**, 0.2 mmol, 82mg) was dissolved in aqueous HCl (37%, 2.0 mL) in a microwave vial. The vial was heated up to 150 °C (40 W) for 3 h in the microwave oven. The reaction mixture was allowed to cool to ambient temperature and poured into EtOAc (50 mL), and then saturated aqueous $NaHCO_3$ solution was added until the pH was adjusted to 7. The aqueous layer was extracted with EtOAc (3 × 50 mL), the combined organic layers were dried with Na_2SO_4 and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (PE/EtOAc/DCM = 20:1:1→10:1:1→5:1:1) to give **4ia** (19mg, 54%) as a white solid.

M. p. = 57−58 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.01 (d, J = 7.8 Hz, 1H), 6.95 (s, 1H), 6.73 (d, J = 7.8 Hz, 1H), 3.56 (br s, 2H), 3.56 (br s, 2H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 138.2 (C_q), 134.1 (C_q), 124.7 (q, $^1J_{C-F}$ = 269 Hz, C_q), 121.8 (q, $^2J_{C-F}$ = 31 Hz, C_q), 117.7 (q, $^3J_{C-F}$ = 4 Hz, CH), 115.5 (CH), 113.5 (q, $^1J_{C-F}$ = 4 Hz, CH).

^{19}F-NMR (376 MHz, $CDCl_3$): $\delta = -61.3$ (s).

HRMS (ESI) m/z calcd for $C_{34}H_{25}O$ $[M + H]^+$: 177.0634, Found 177.0634.

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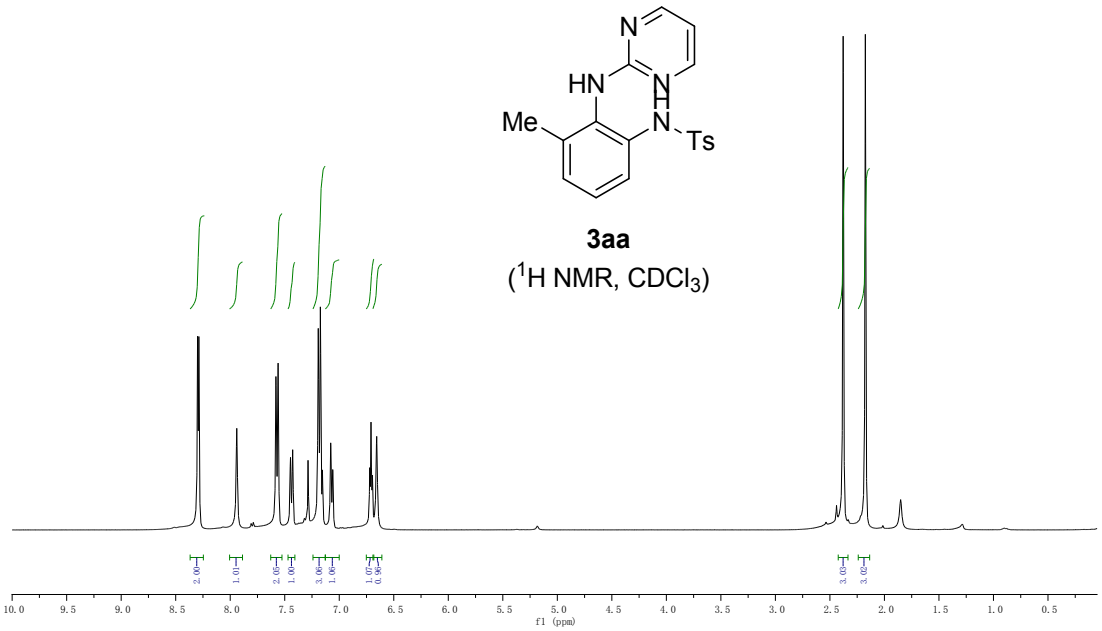
2 J.-H. Chu, H.-P. Huang, W.-T. Hsu, S.-T. Chen and M.-J. Wu, *Organometallics*, 2014, **33**, 1190−1204.

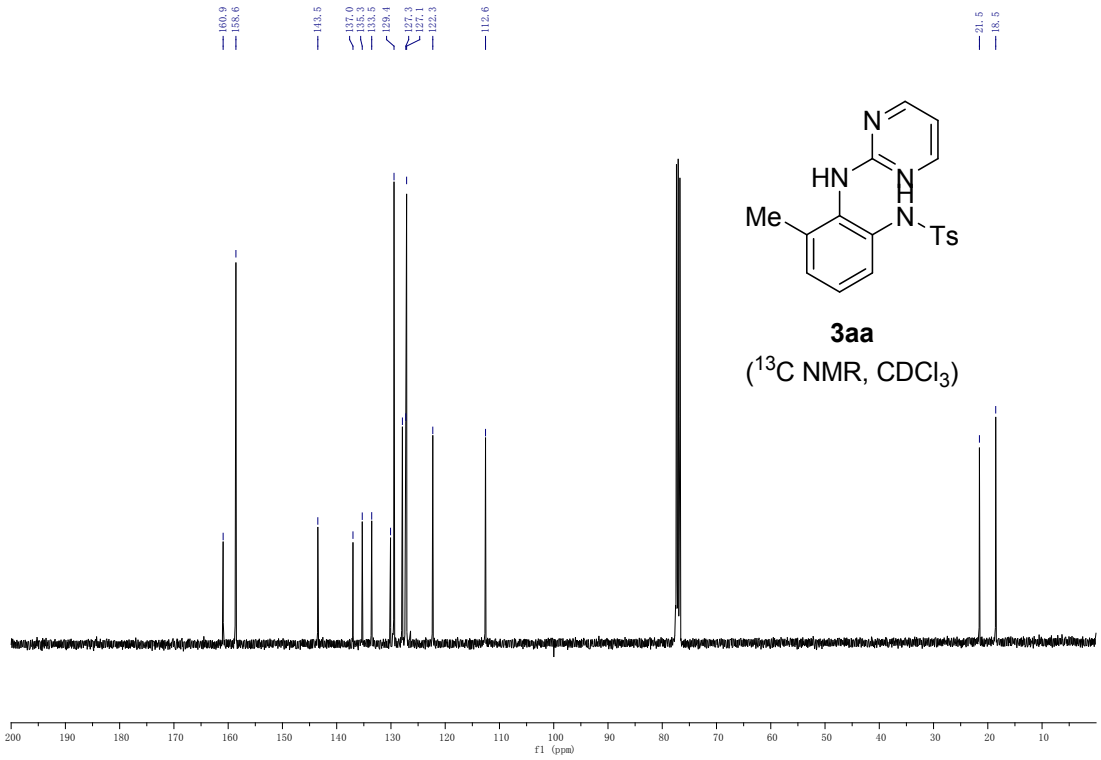
3 I. C. Kogon, *J. Org. Chem.*, 1956, **21**, 1027−1028.

4 a) J. Waser, B. Gaspar, H. Nambu and E. M. Carreira, *J. Am. Chem. Soc.*, 2006, **128**, 11693−11712; b) J. R. Suárez, J. Kwiczak, K. Grenda, M. L. Jimeno and J. L. Chiara, *Adv. Synth. Catal.*, 2013, **355**, 913−918.

5 Z. Ruan, S. Lackner and L. Ackermann, *Angew. Chem. Int. Ed.*, 2016, **55**, 3153–3157.

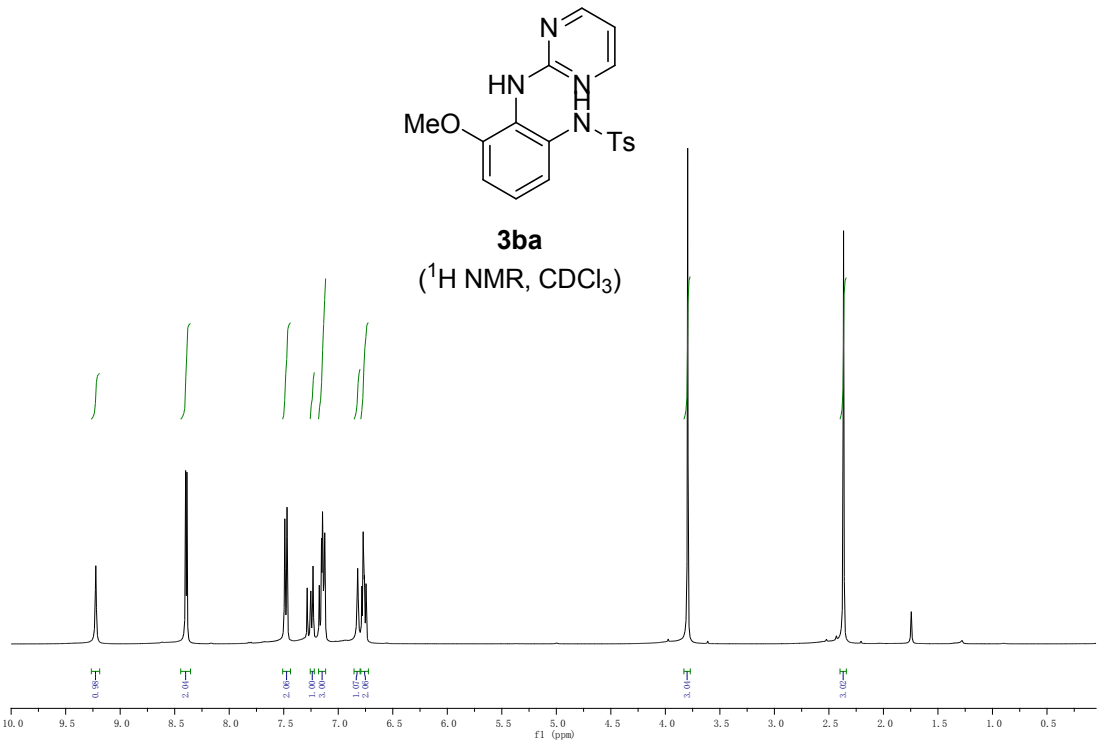
NMR spectra of compounds 3 and 4





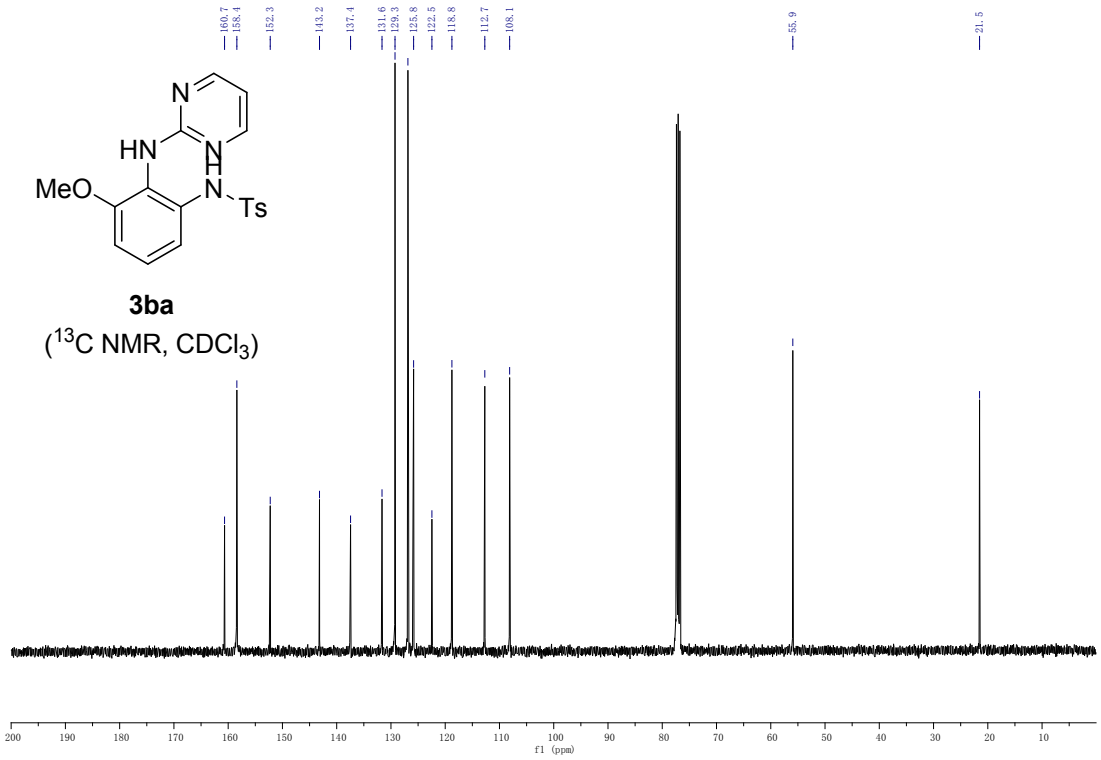
3aa

(^{13}C NMR, $CDCl_3$)



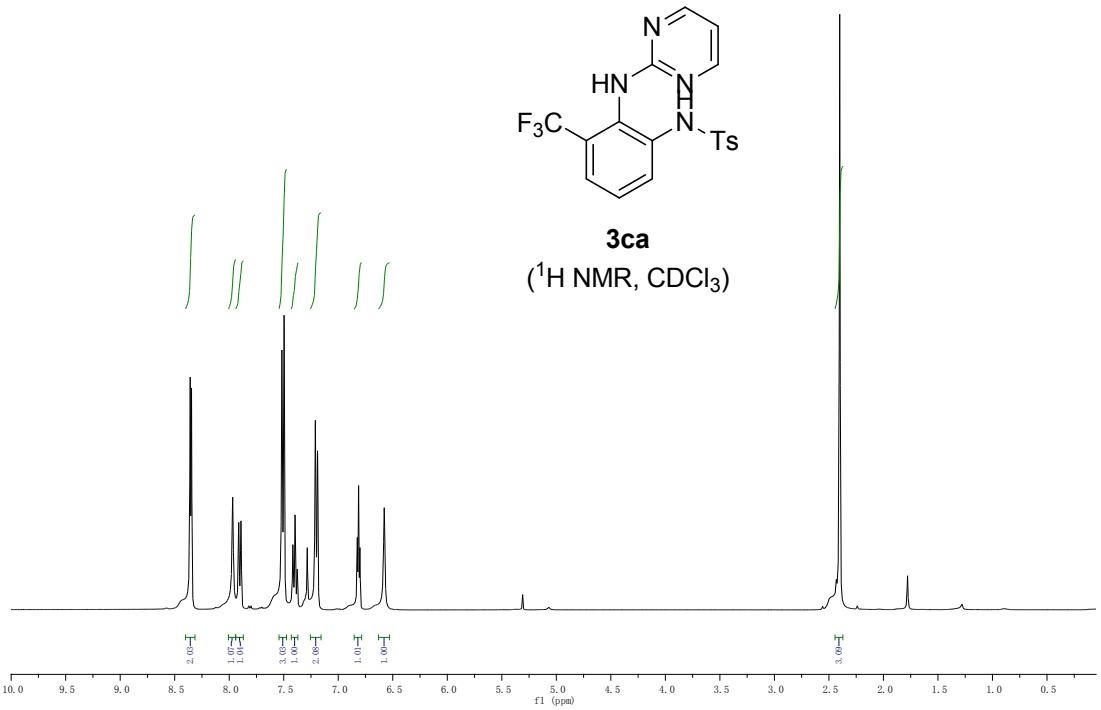
3ba

(^{1}H NMR, $CDCl_3$)



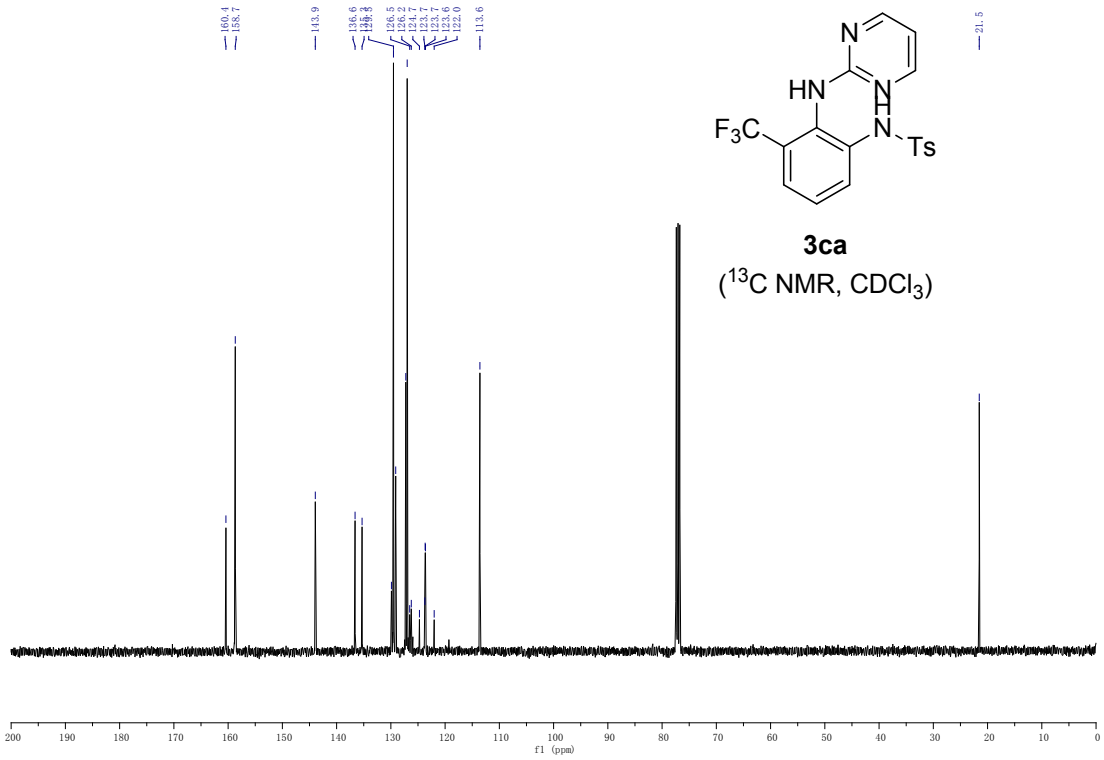
3ba

(^{13}C NMR, $CDCl_3$)



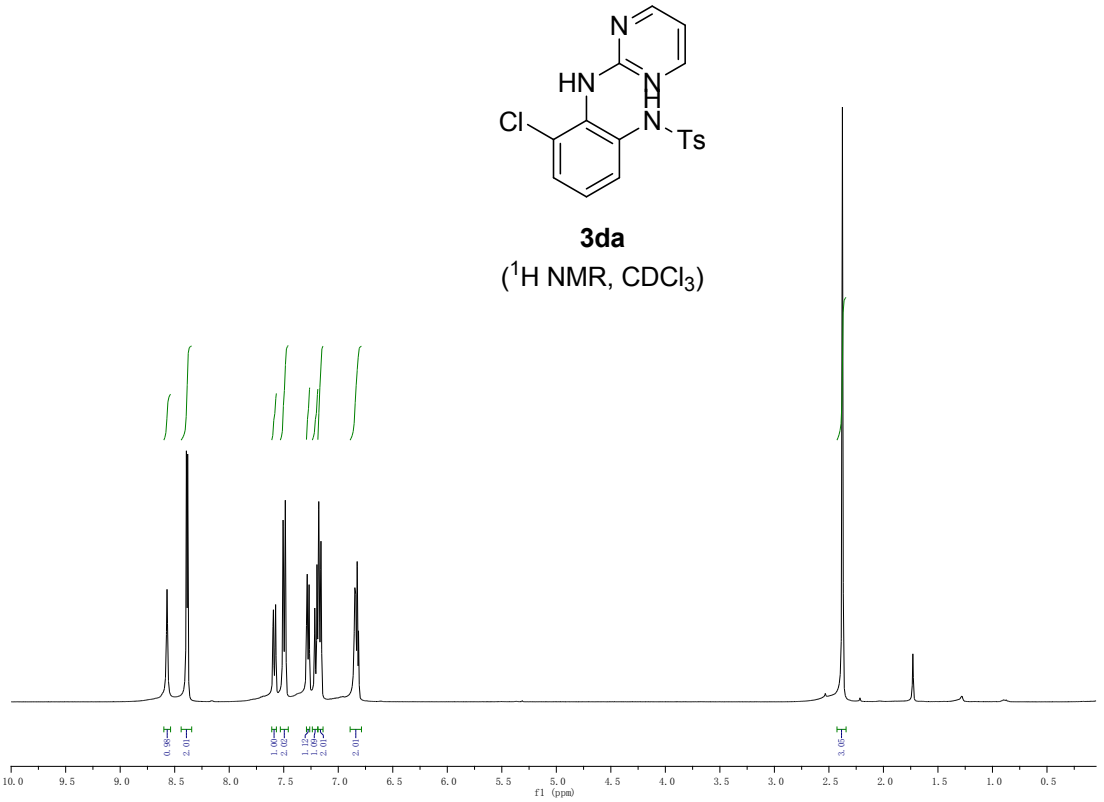
3ca

(^{1}H NMR, $CDCl_3$)



3ca

(^{13}C NMR, $CDCl_3$)



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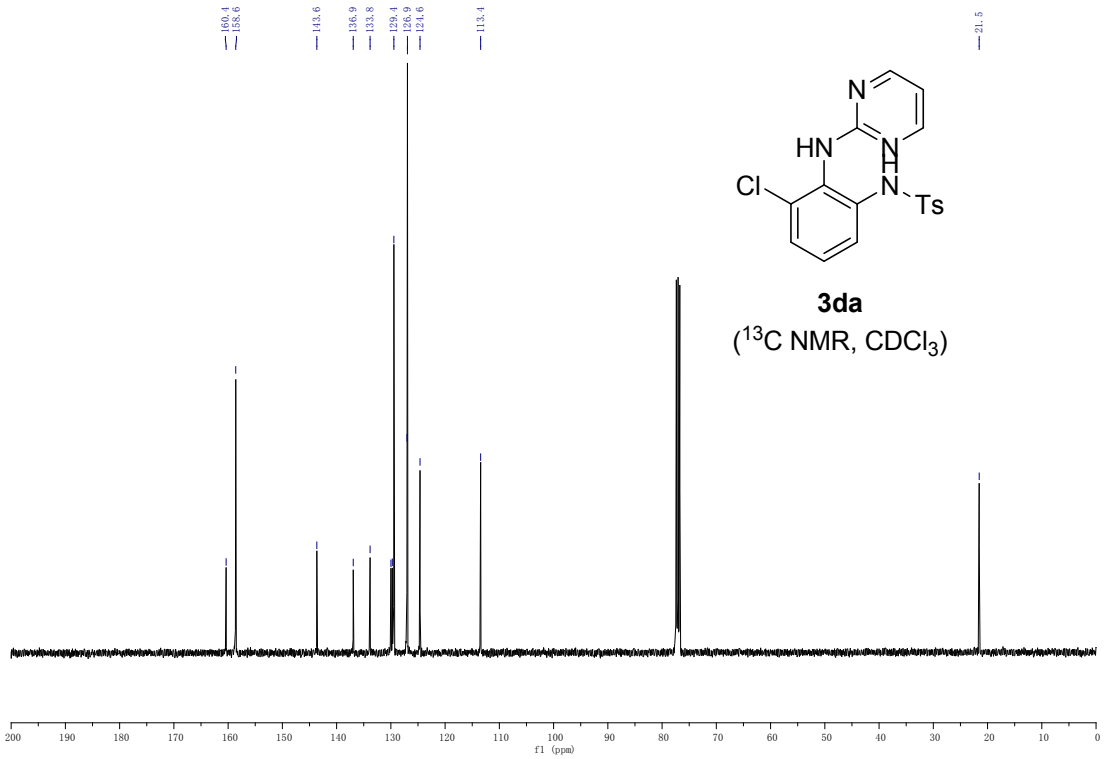
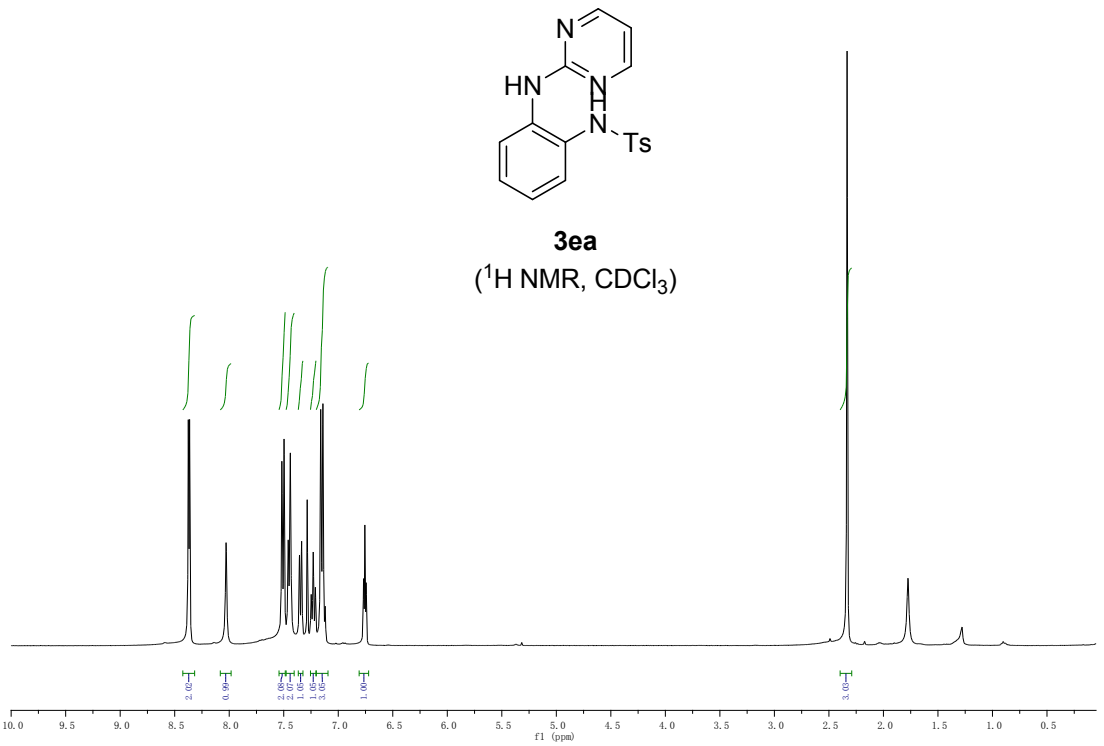
(^{1}H NMR, $CDCl_3$)



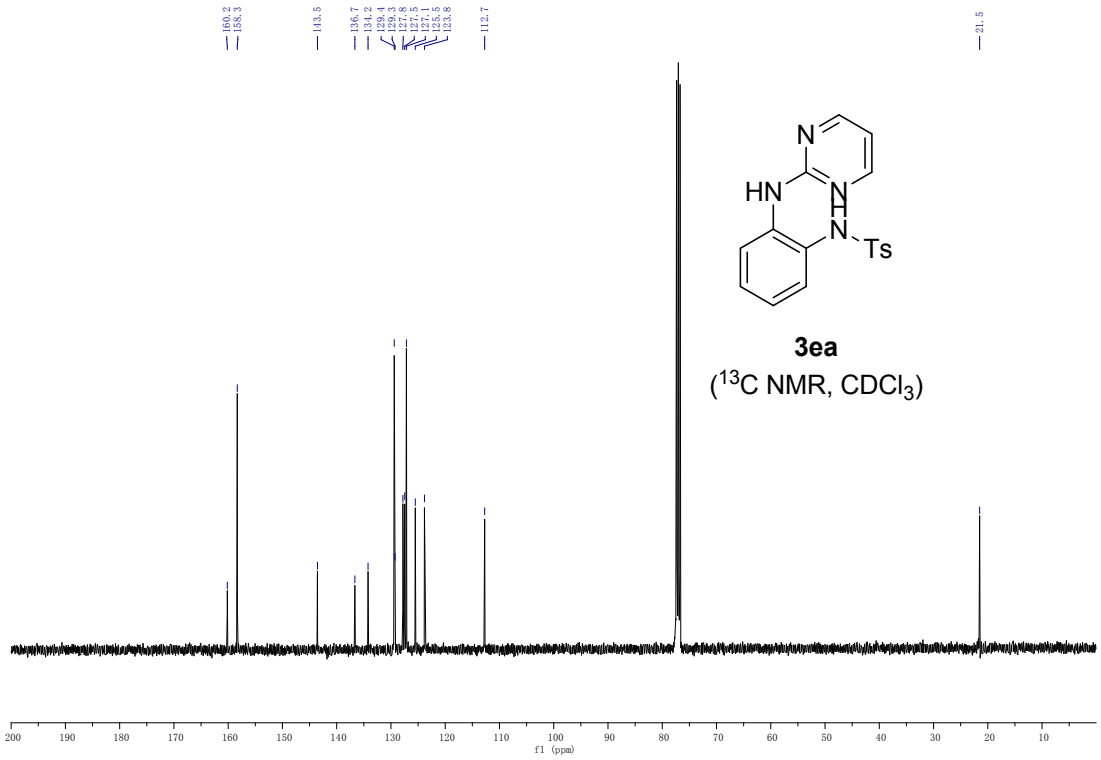
3da

(^{13}C NMR, $CDCl_3$)



3ea

(^{1}H NMR, $CDCl_3$)



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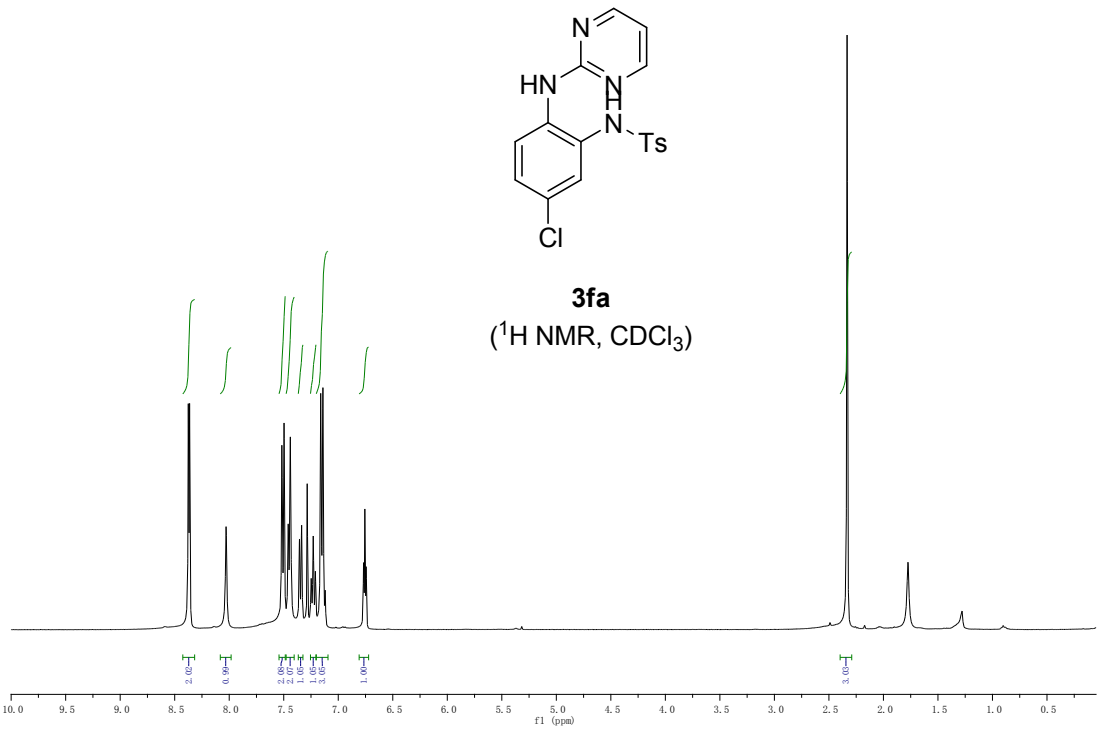
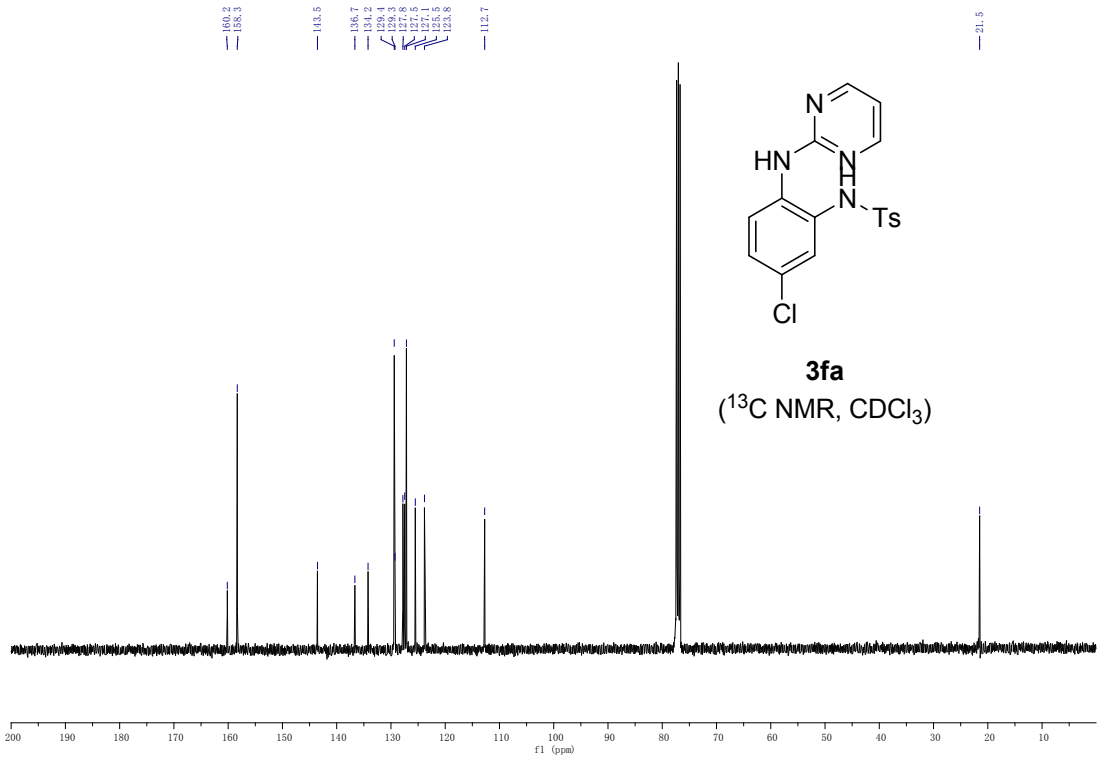
(^{13}C NMR, $CDCl_3$)



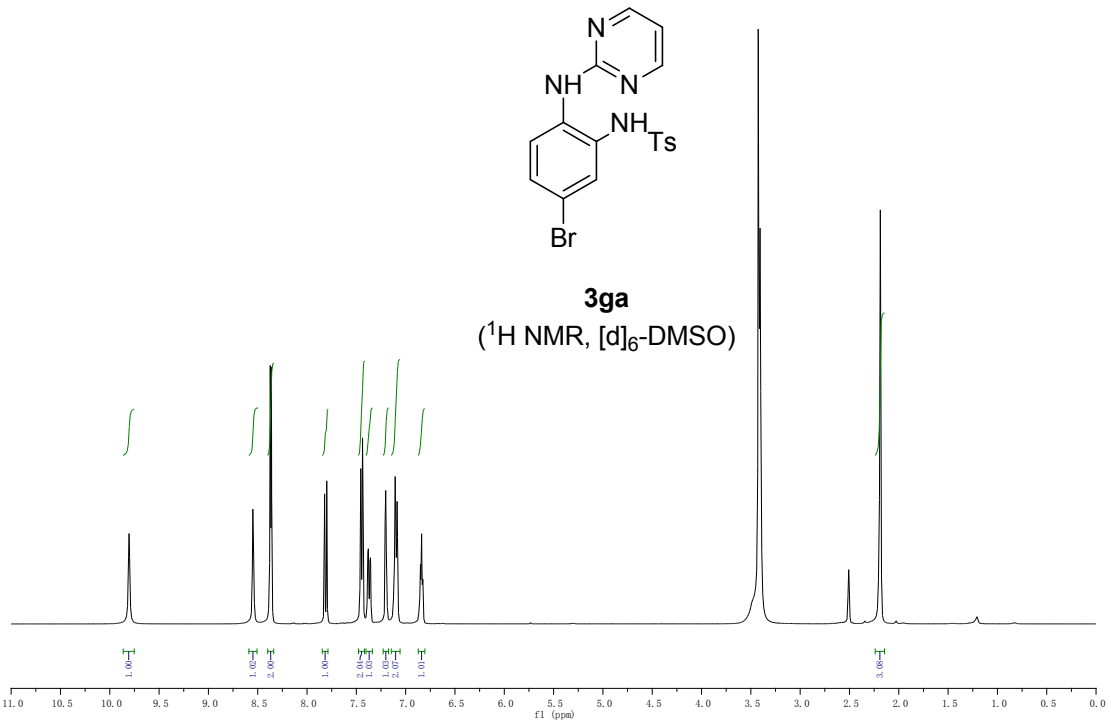
3fa

(^{1}H NMR, $CDCl_3$)



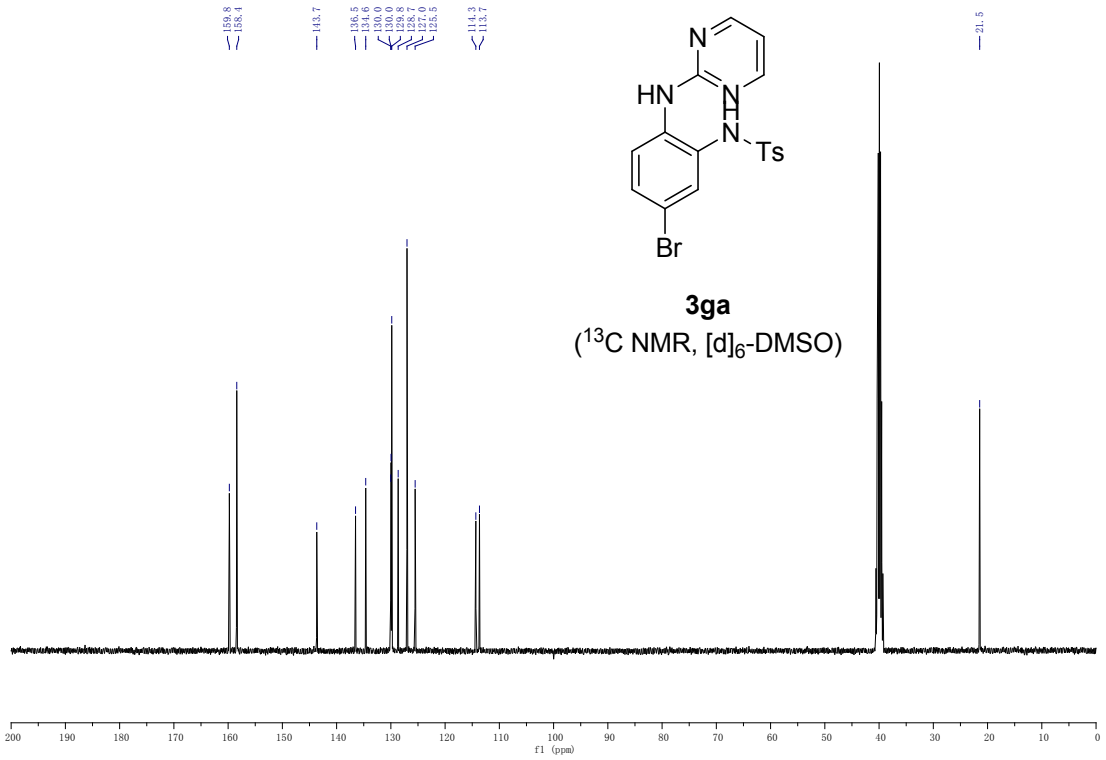
3fa

(^{13}C NMR, $CDCl_3$)



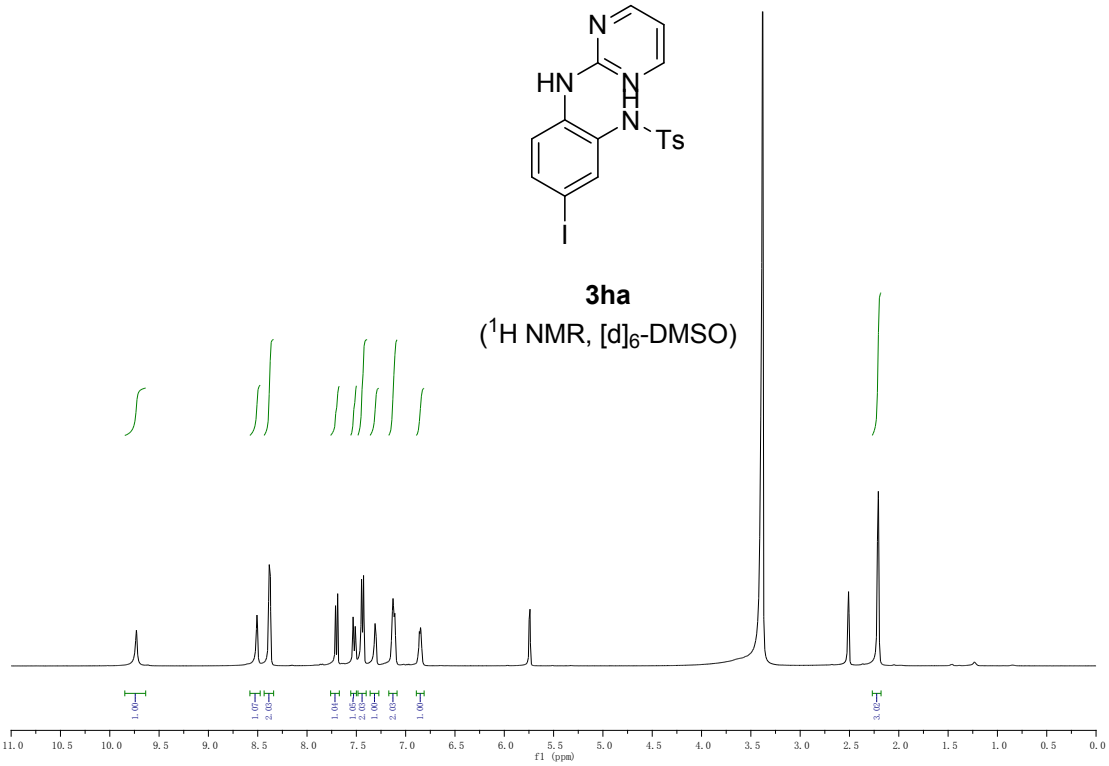
3ga

(^{1}H NMR, $[d]_6$-DMSO)



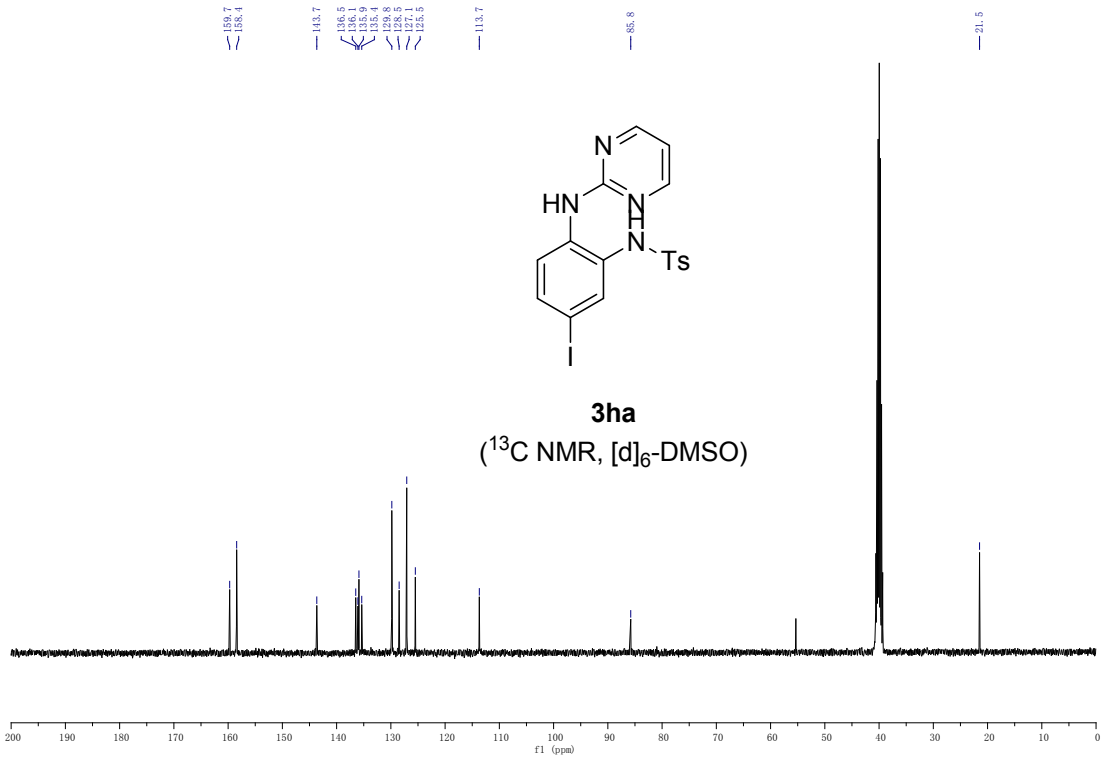
3ga

(^{13}C NMR, [d]$_6$-DMSO)



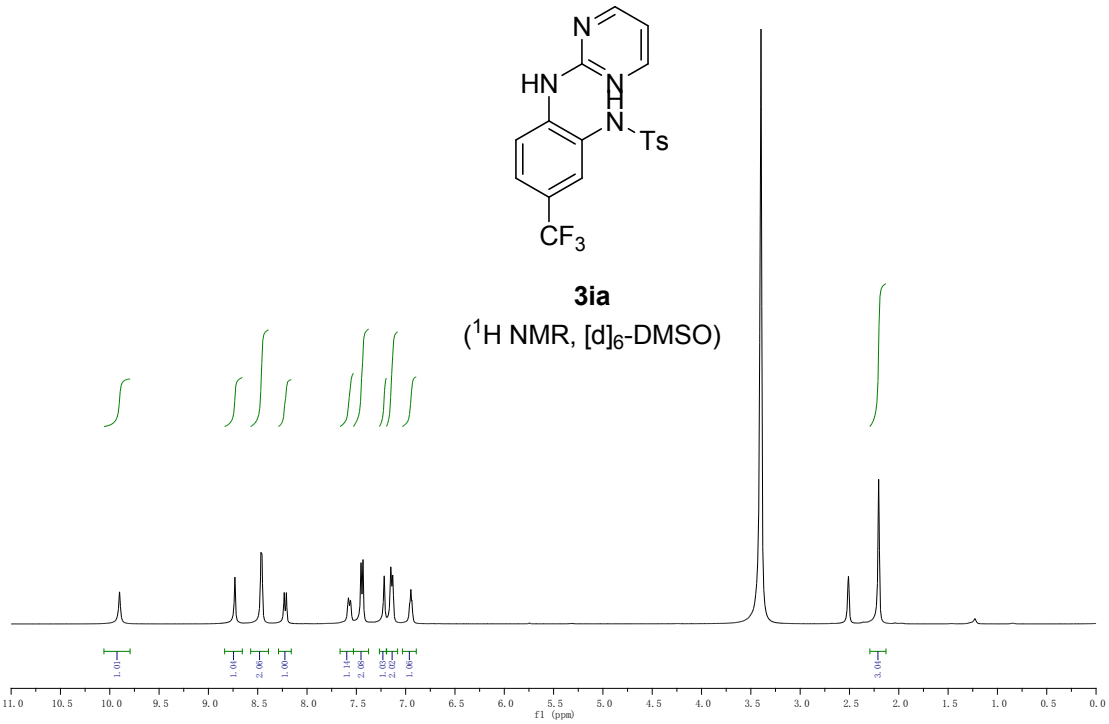
3ha

(^{1}H NMR, [d]$_6$-DMSO)



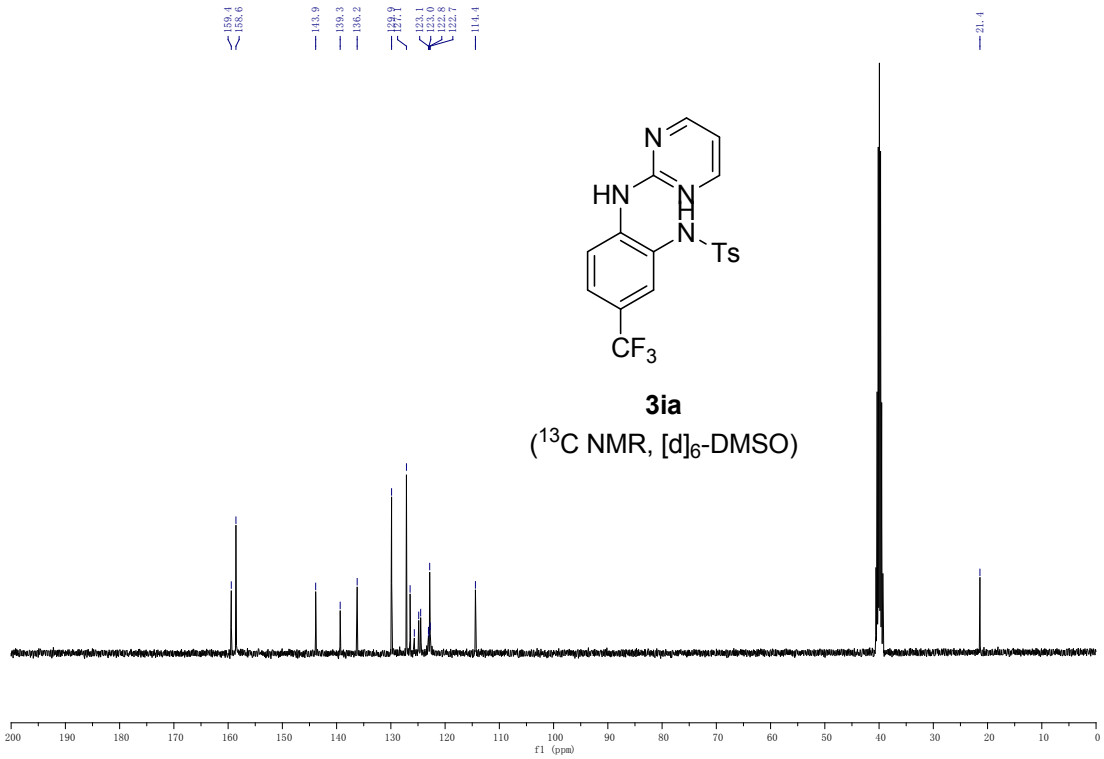
3ha

(^{13}C NMR, [d]$_6$-DMSO)



3ia

(^{1}H NMR, [d]$_6$-DMSO)



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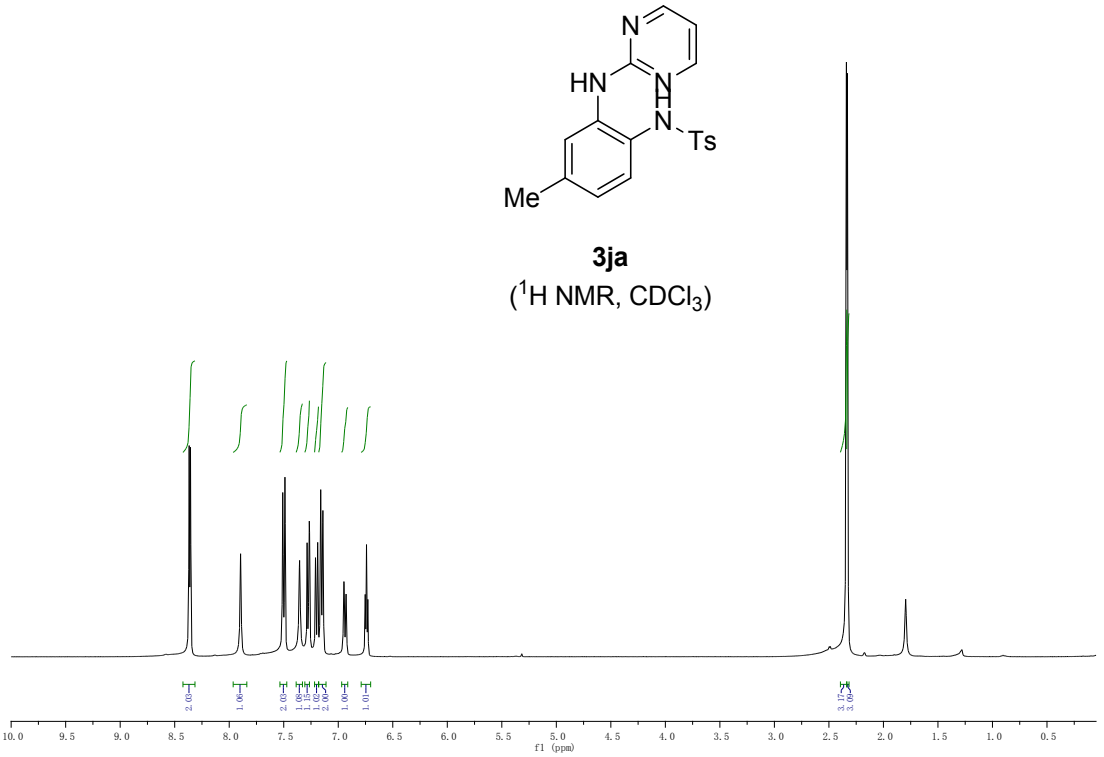
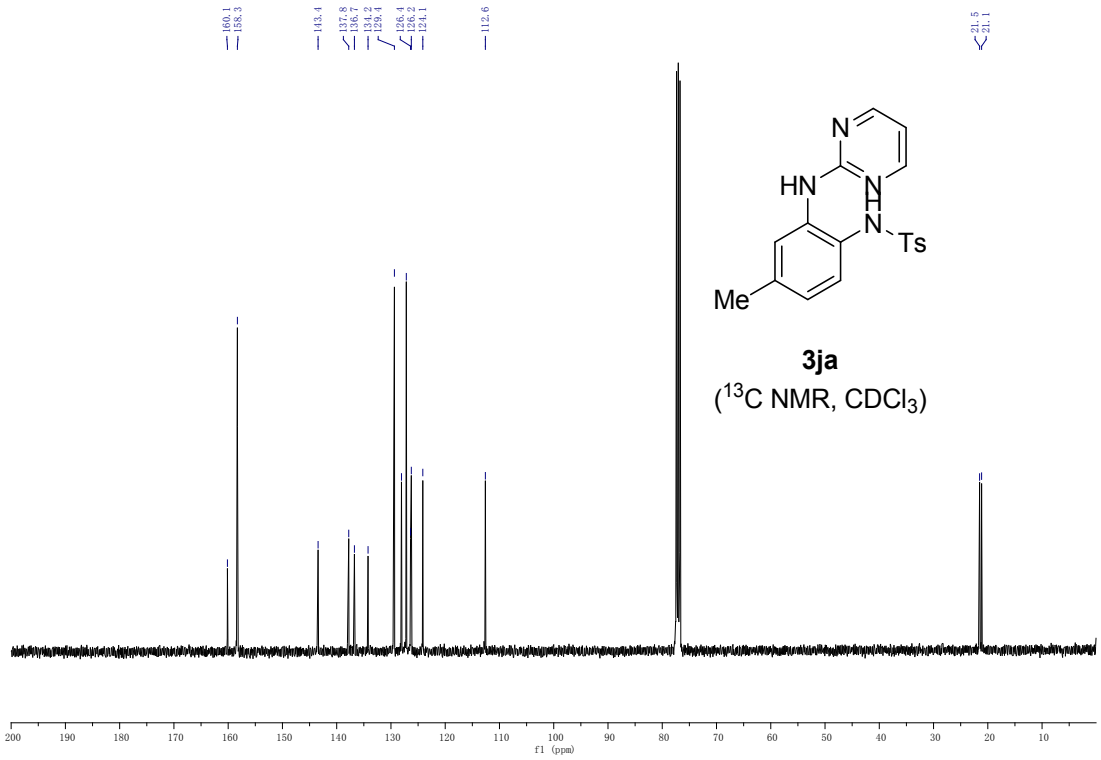


3ja

(^{1}H NMR, $CDCl_3$)



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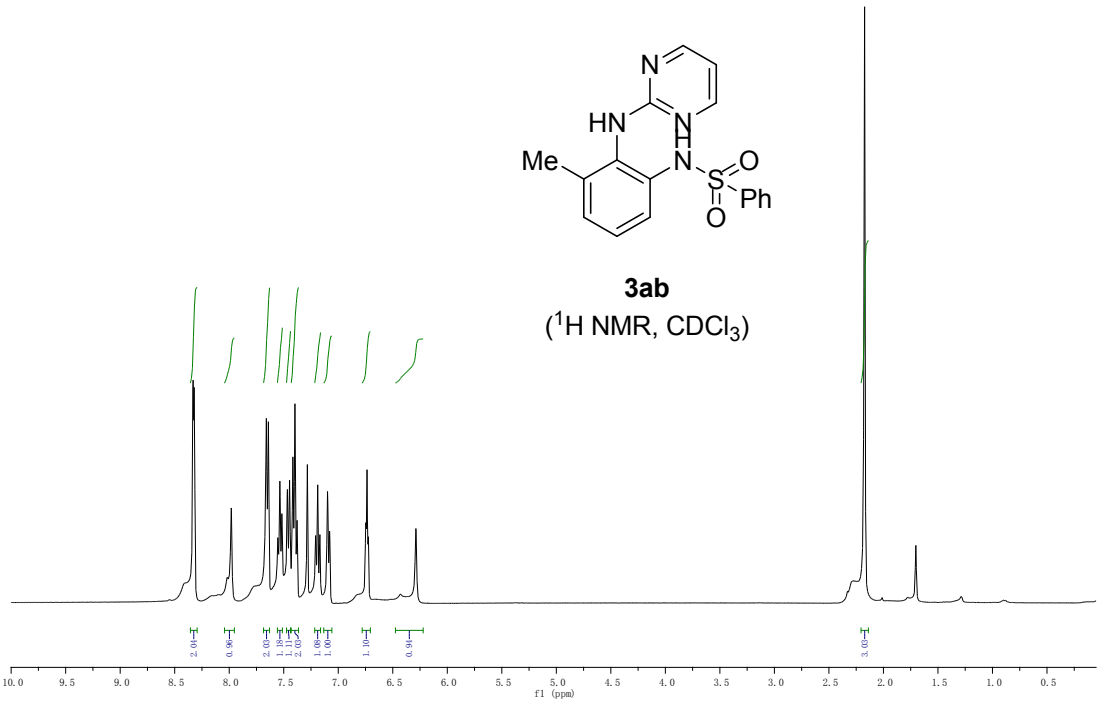
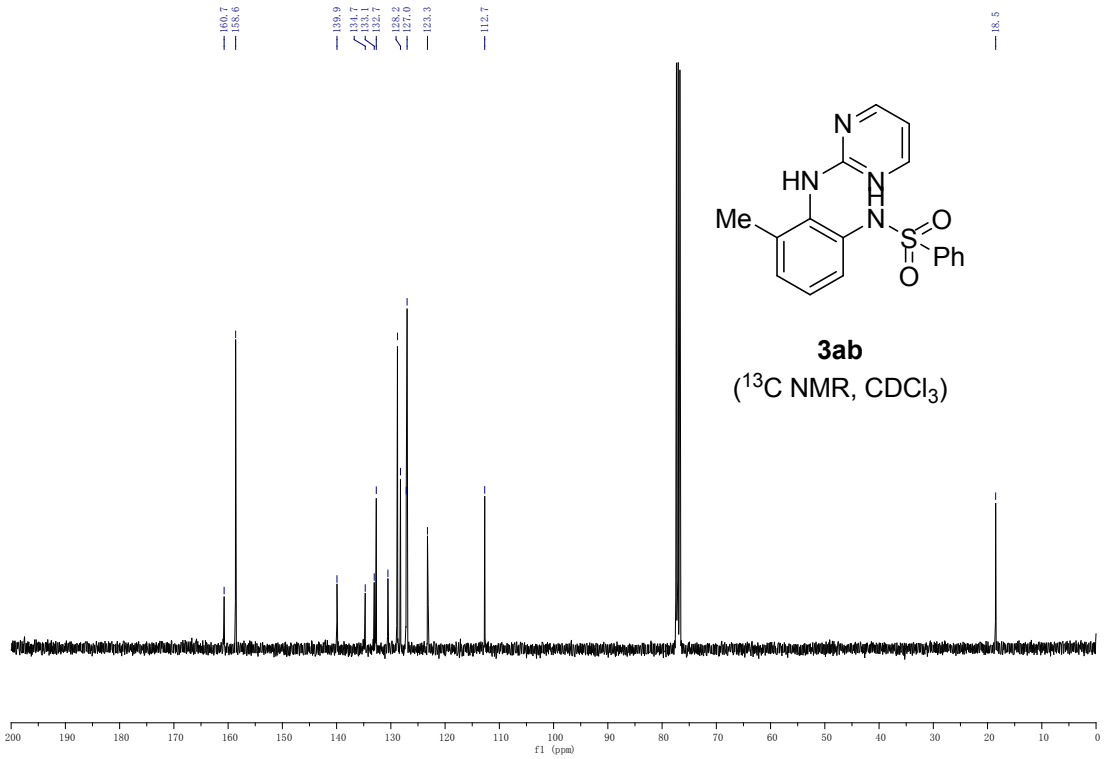


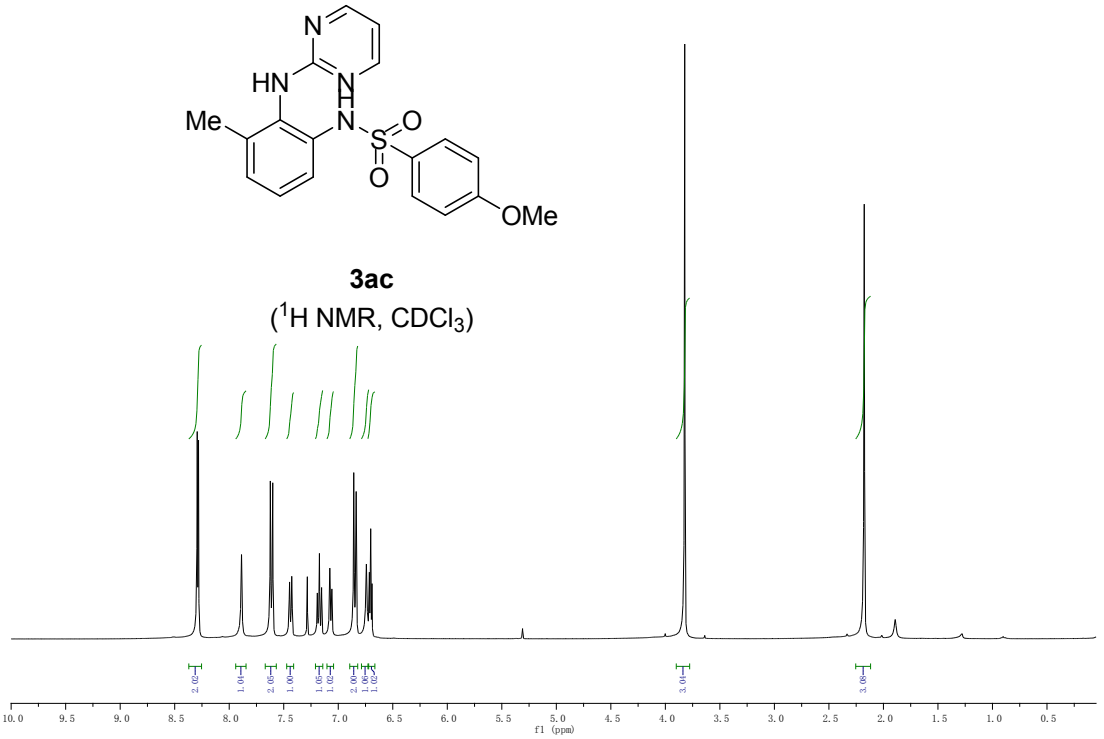
3ab

(^{1}H NMR, $CDCl_3$)



3ab

(^{13}C NMR, $CDCl_3$)



3ac

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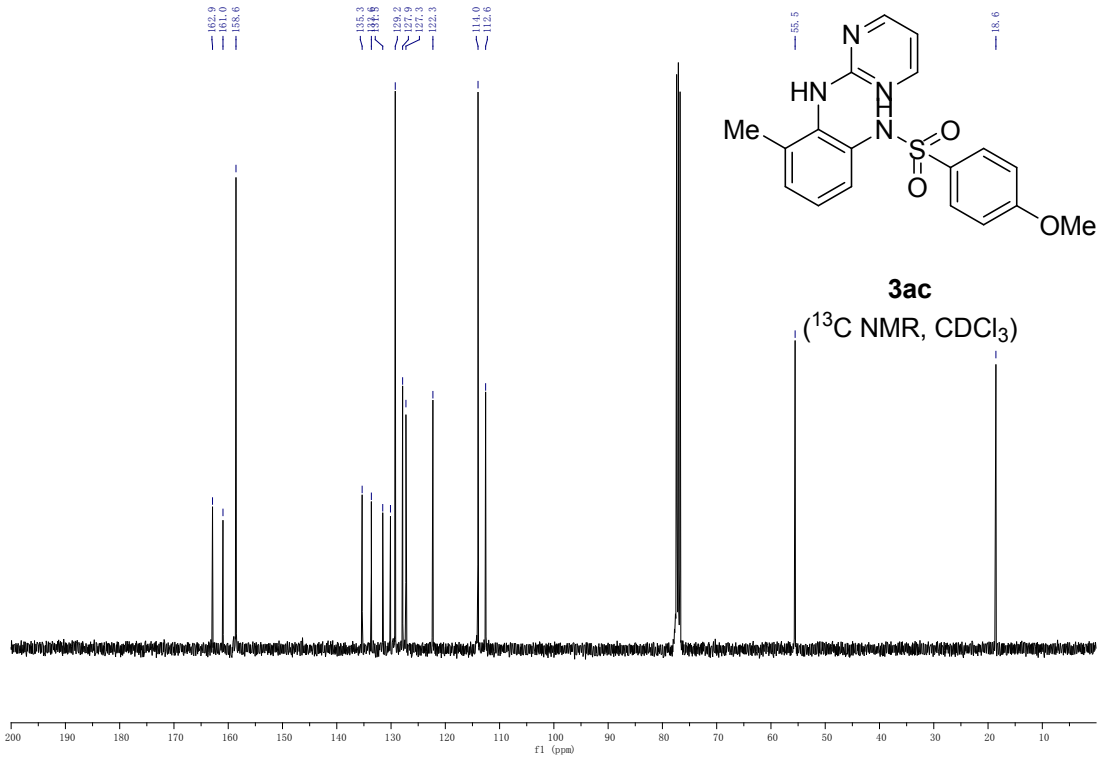

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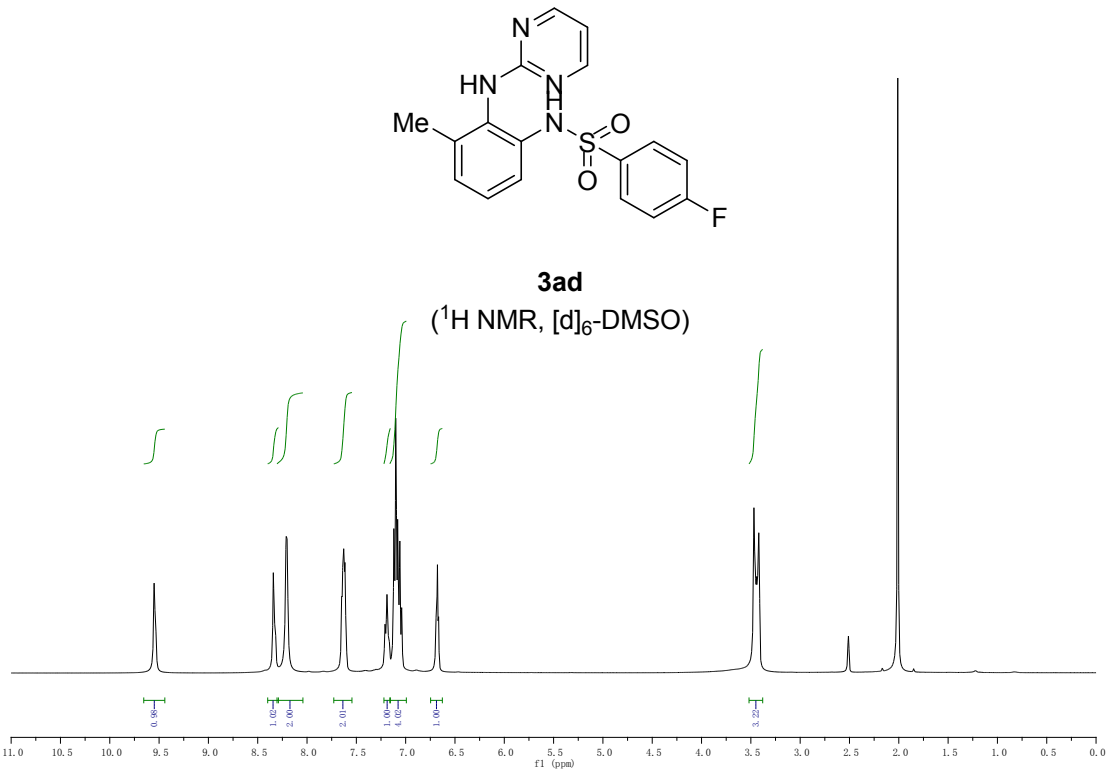
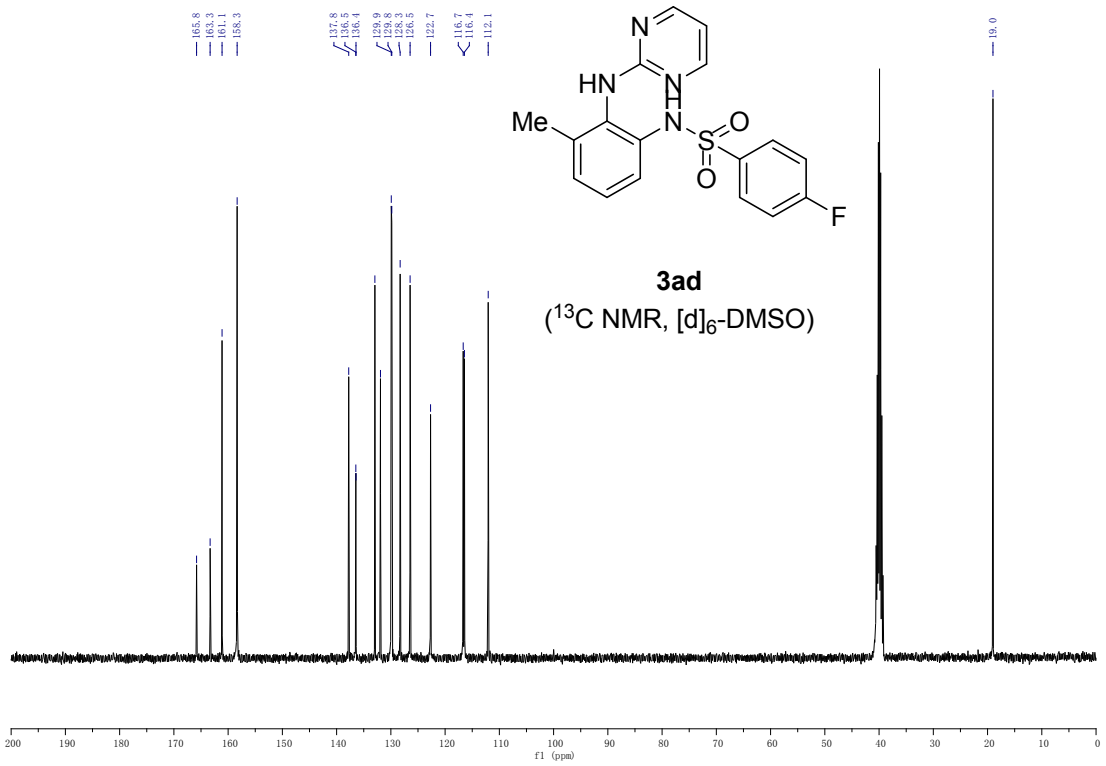


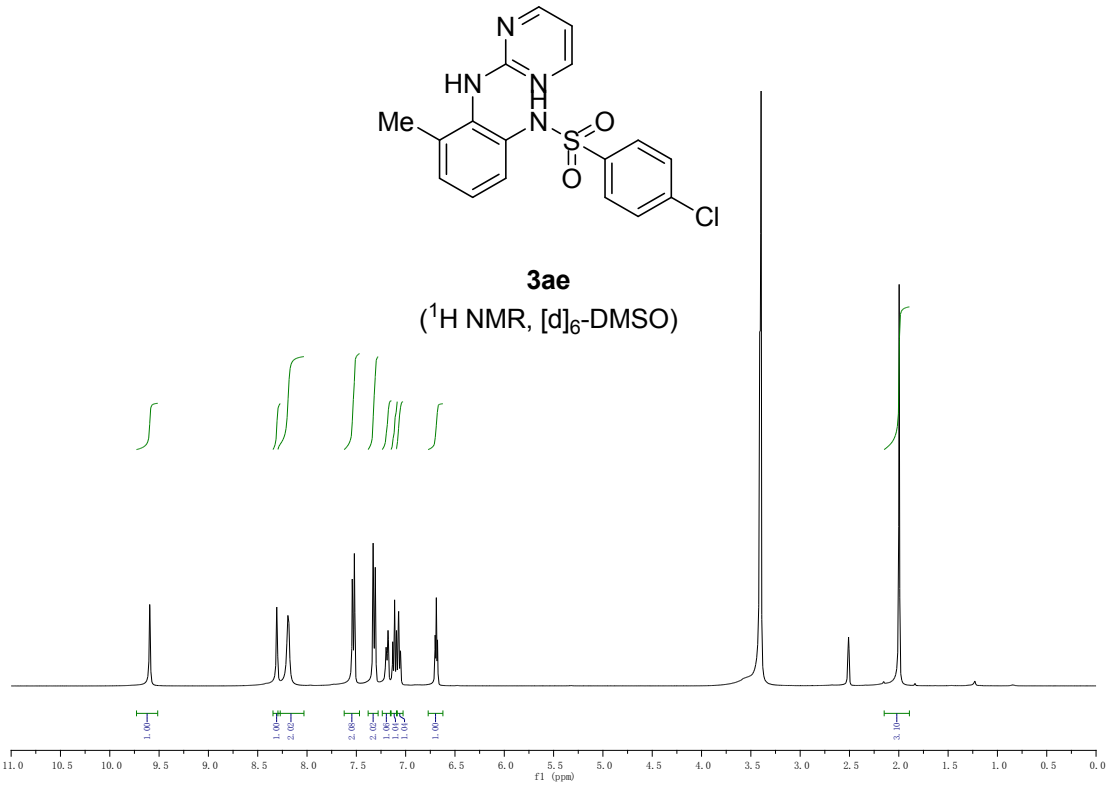
3ad

(^{1}H NMR, $[d]_6$-DMSO)



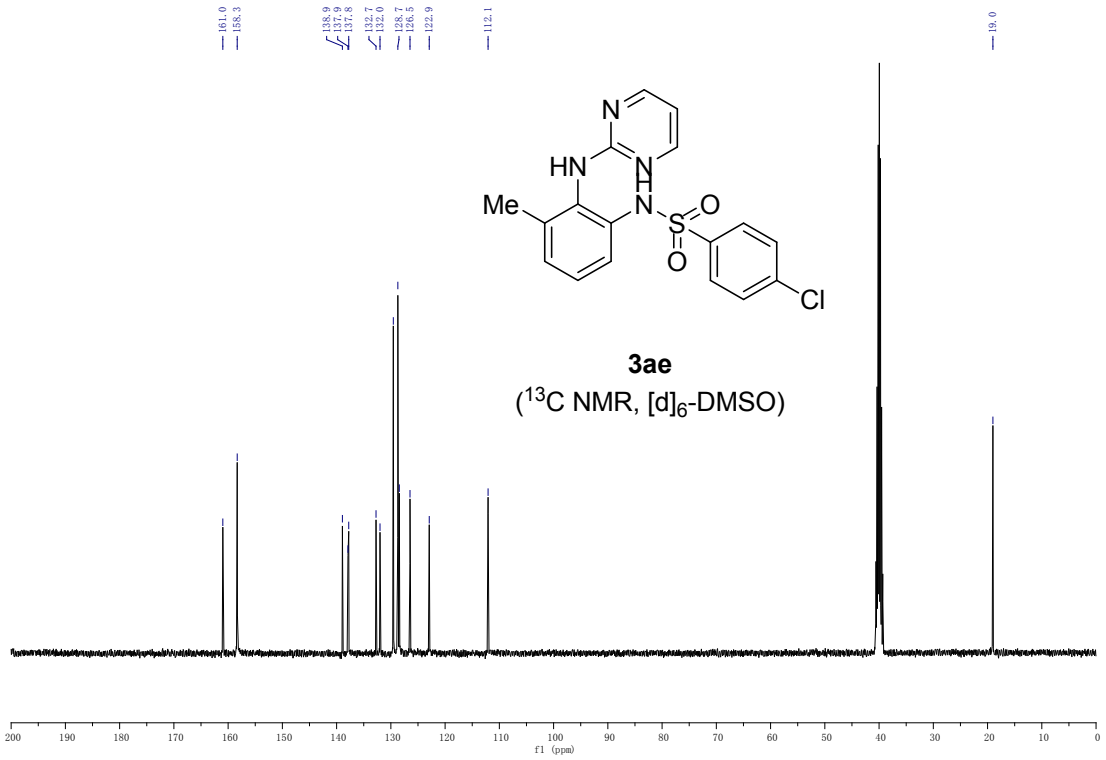
3ad

(^{13}C NMR, [d]$_6$-DMSO)



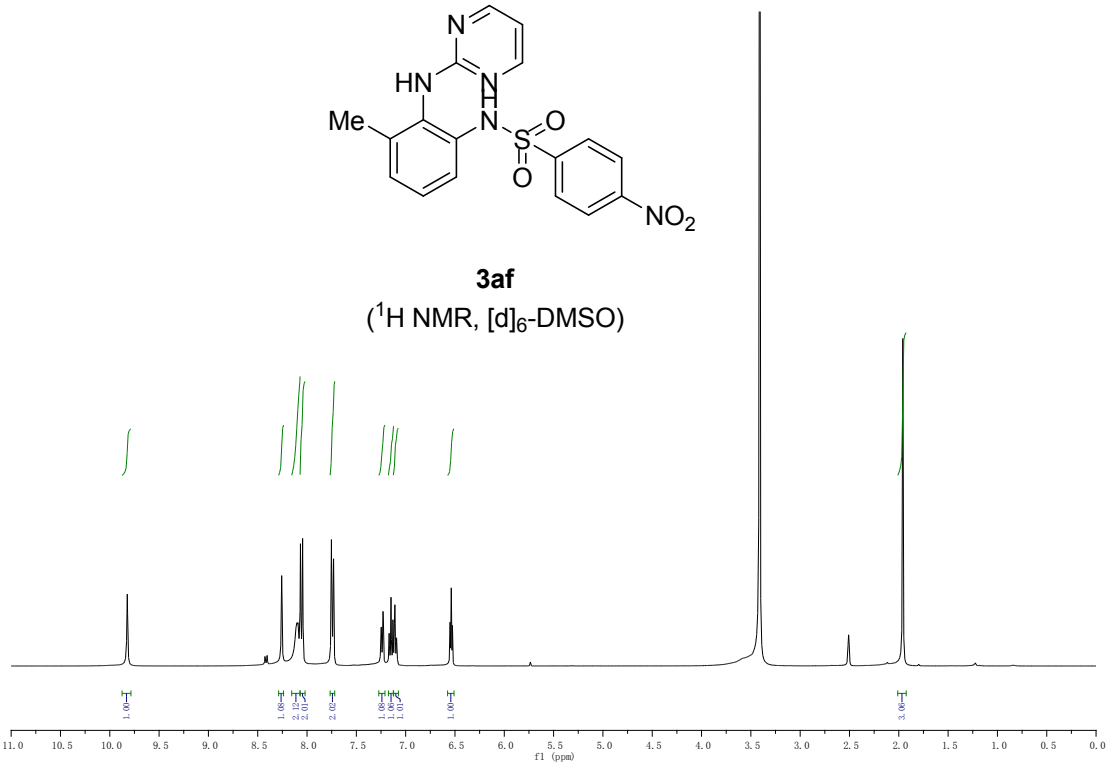
3ae

(^{1}H NMR, [d]$_6$-DMSO)



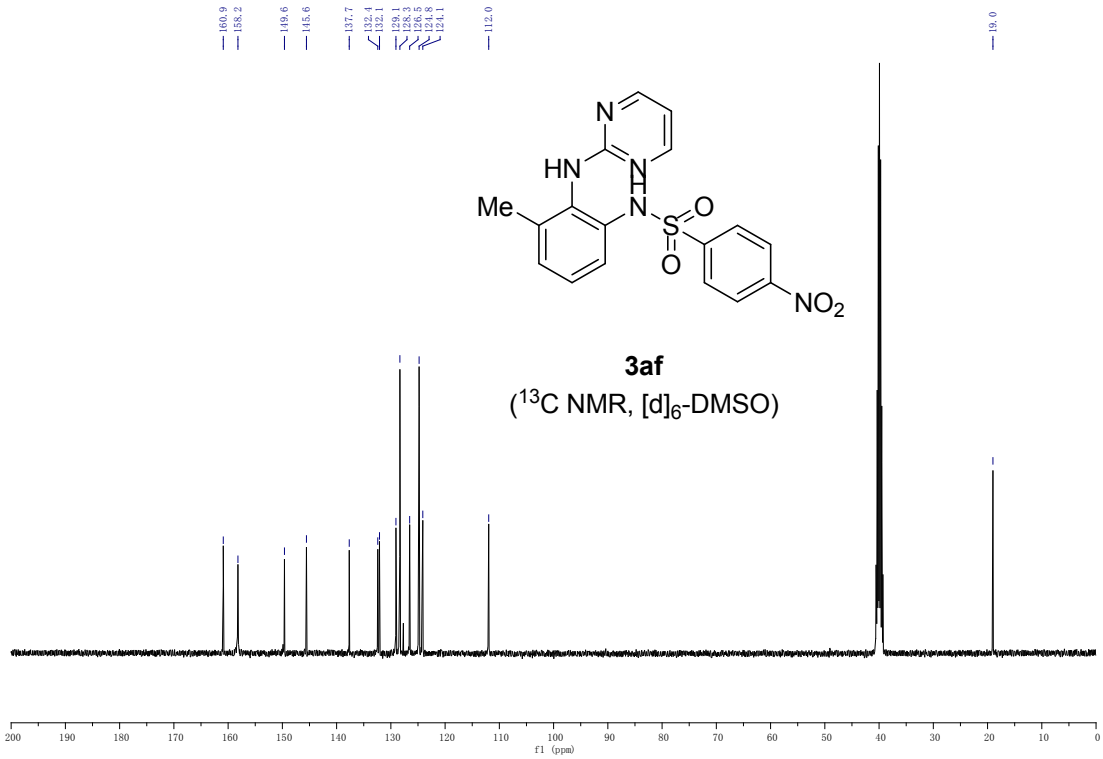
3ae

(^{13}C NMR, [d]$_6$-DMSO)



3af

(^{1}H NMR, [d]$_6$-DMSO)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158.2
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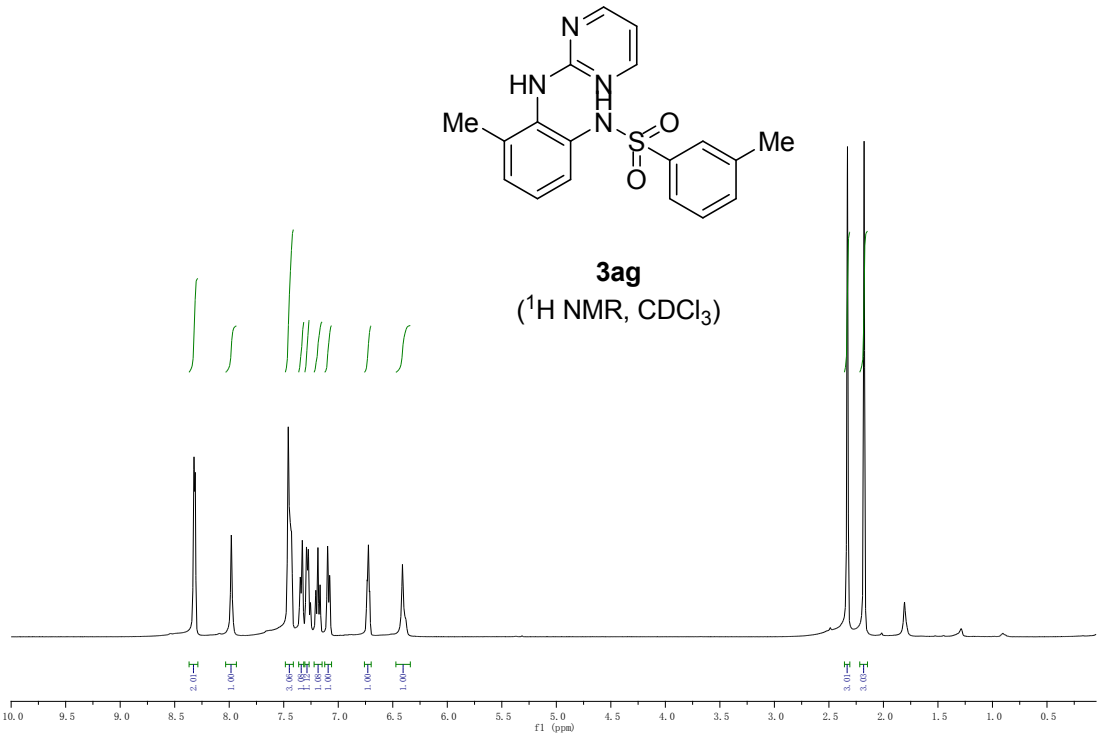
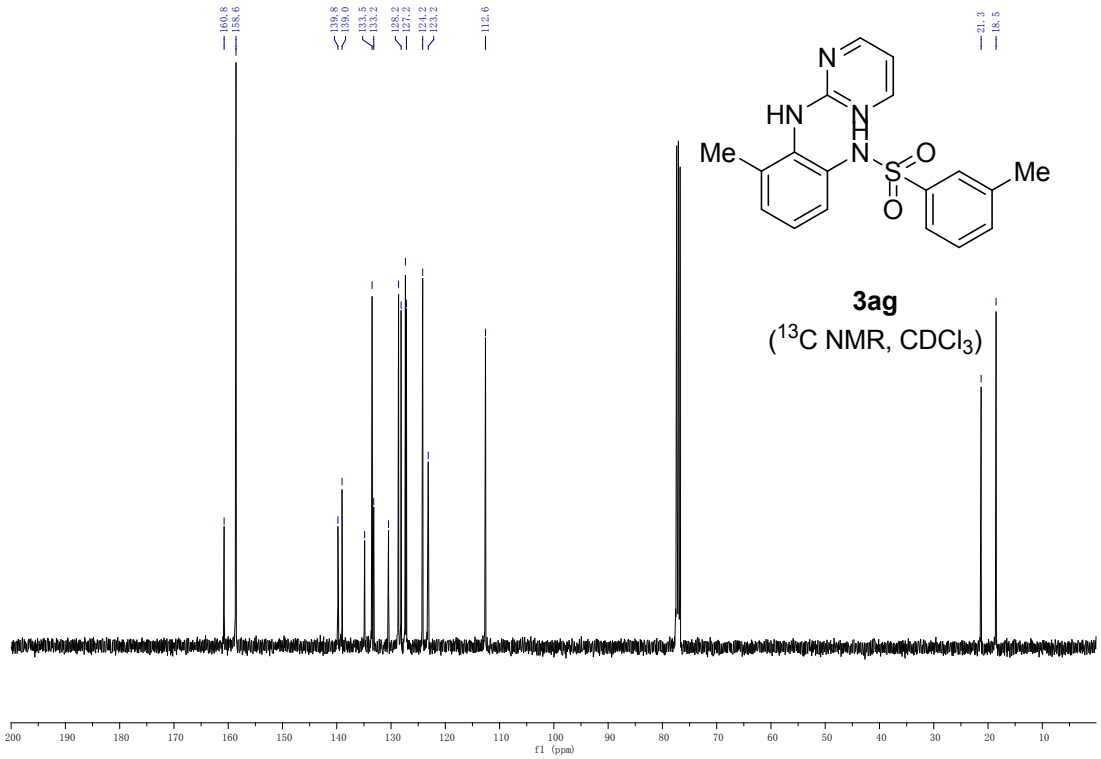
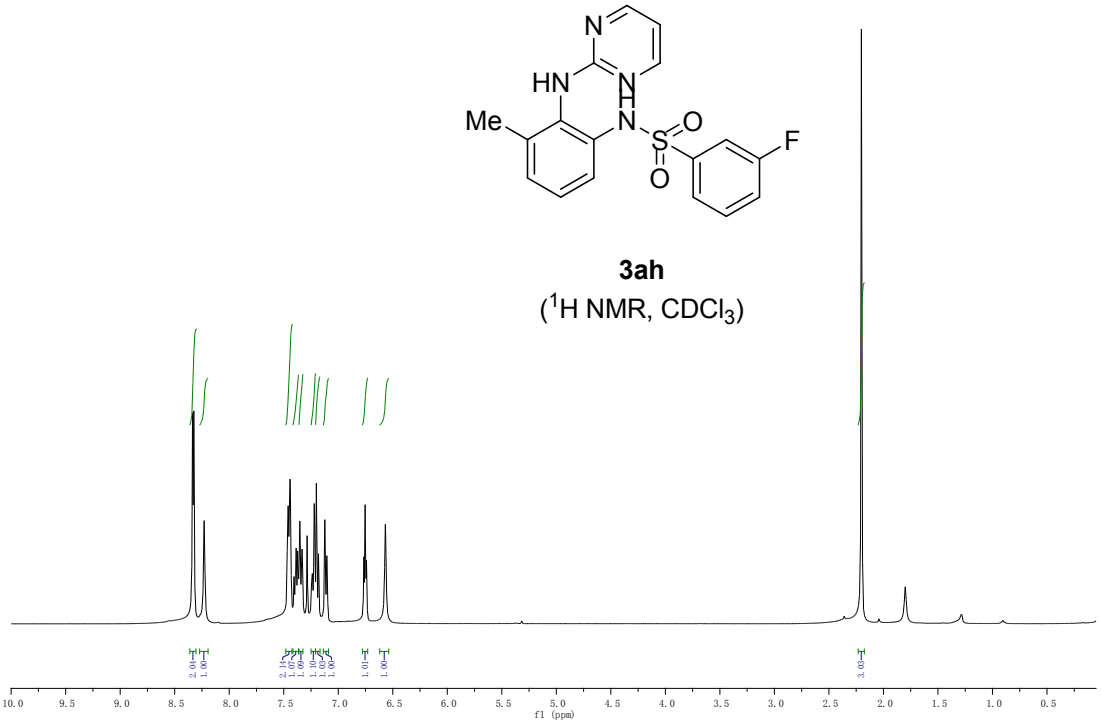
145.6
137.7
132.4
132.1
129.1
128.3
126.5
124.8
124.1
112.0
19.0
N
HN
N
H
Me
N
S
O
O
NO2
3af
(13C NMR, [d]6-DMSO)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


N
HN
N
H
Me
N
S
O
O
Me
3ag
(1H NMR, CDCl3)
2.01
1.00
3.06
1.13
1.08
1.00
1.00
1.00
3.01
3.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)



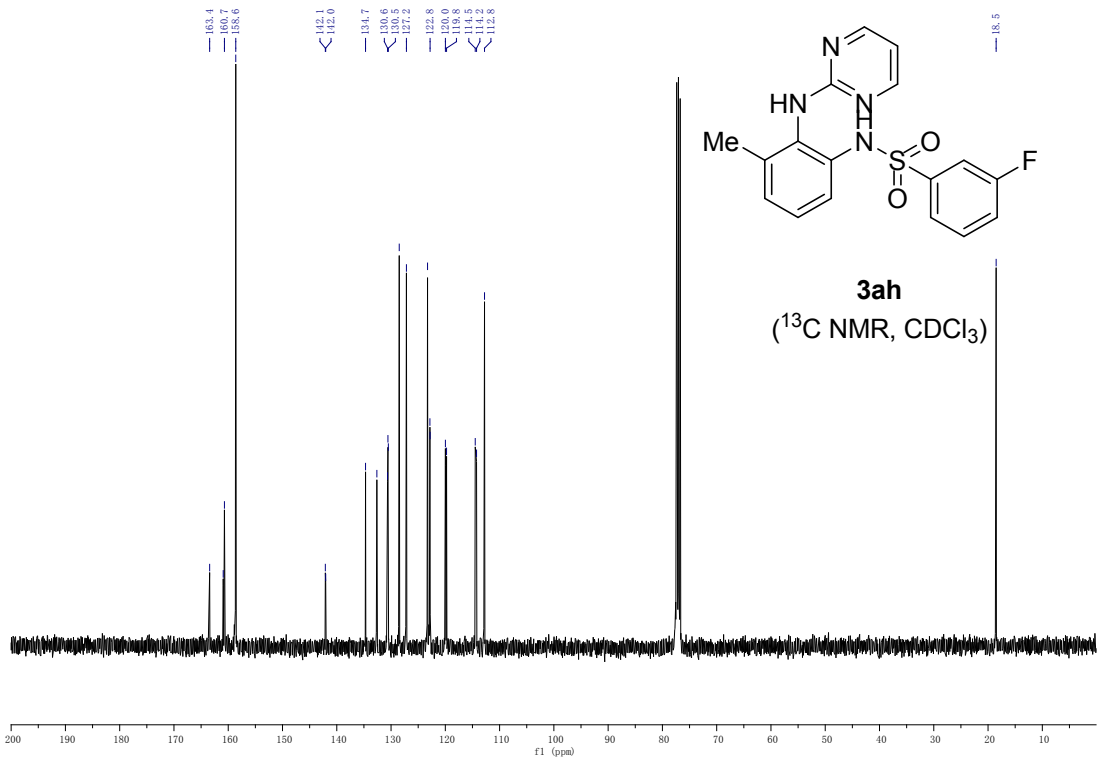
3ag

(^{13}C NMR, $CDCl_3$)



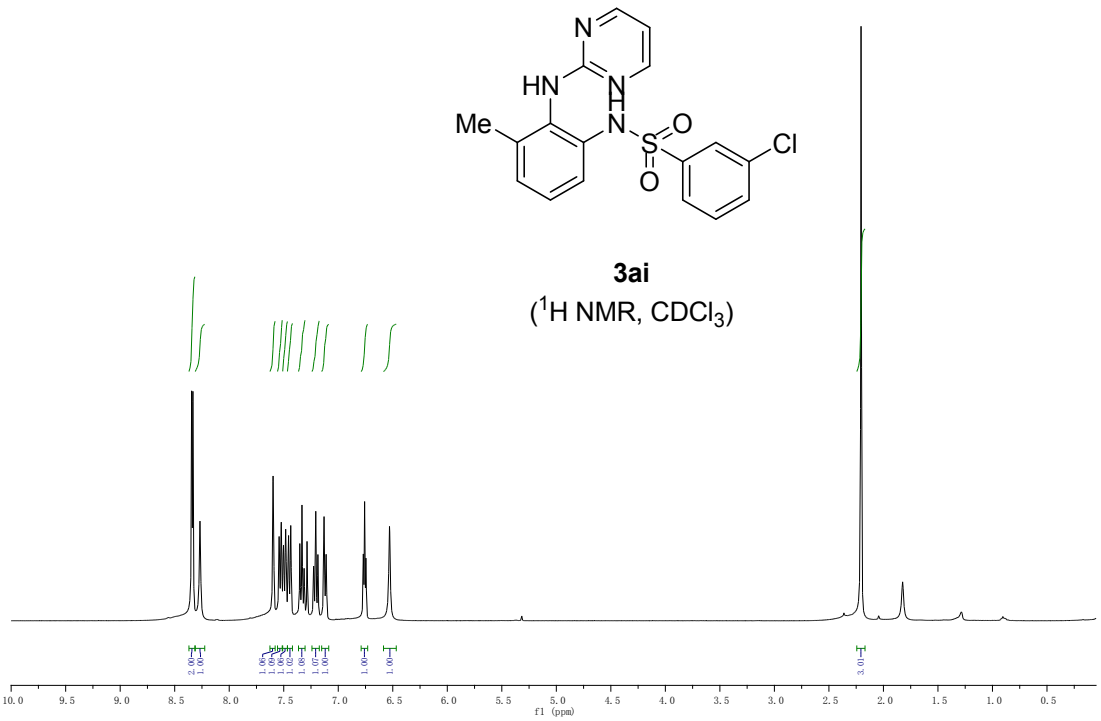
3ah

(^{1}H NMR, $CDCl_3$)



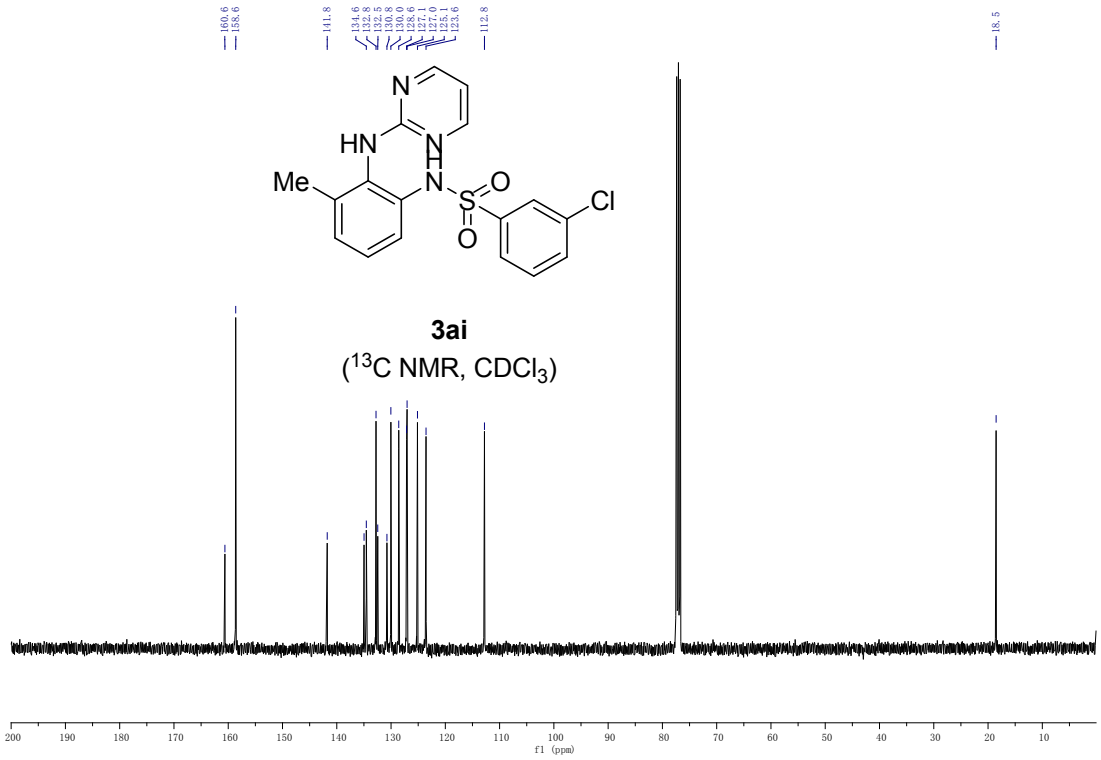
3ah

(^{13}C NMR, $CDCl_3$)



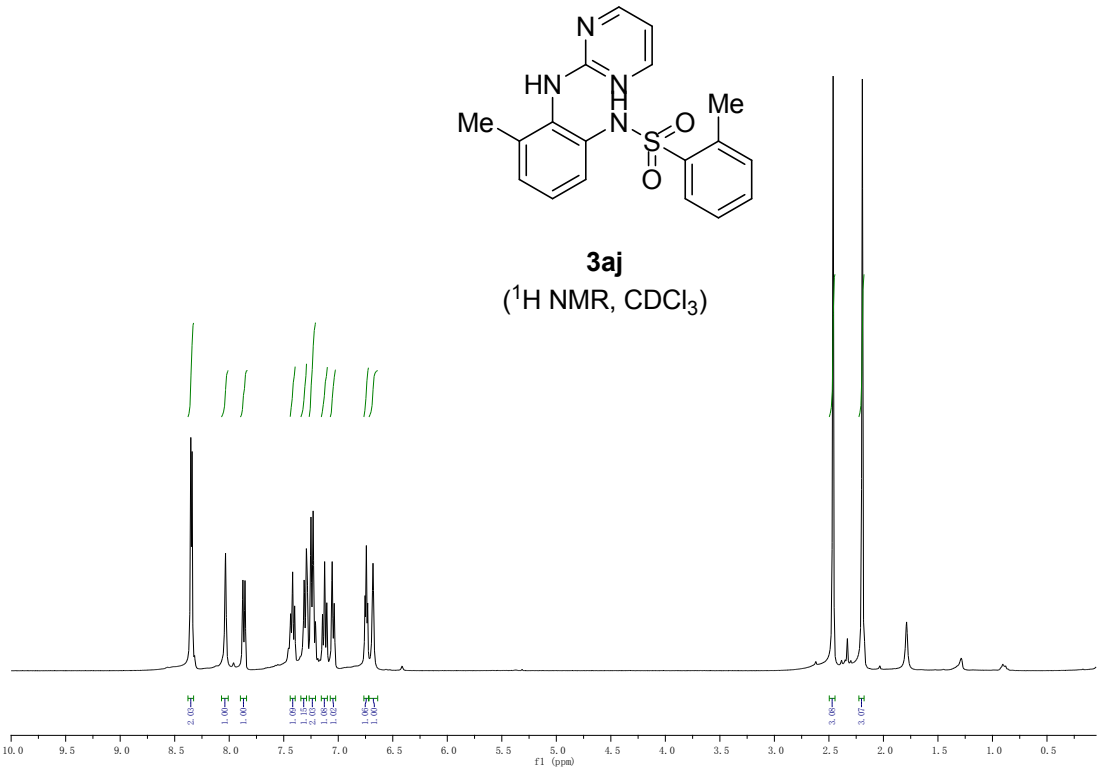
3ai

(^{1}H NMR, $CDCl_3$)



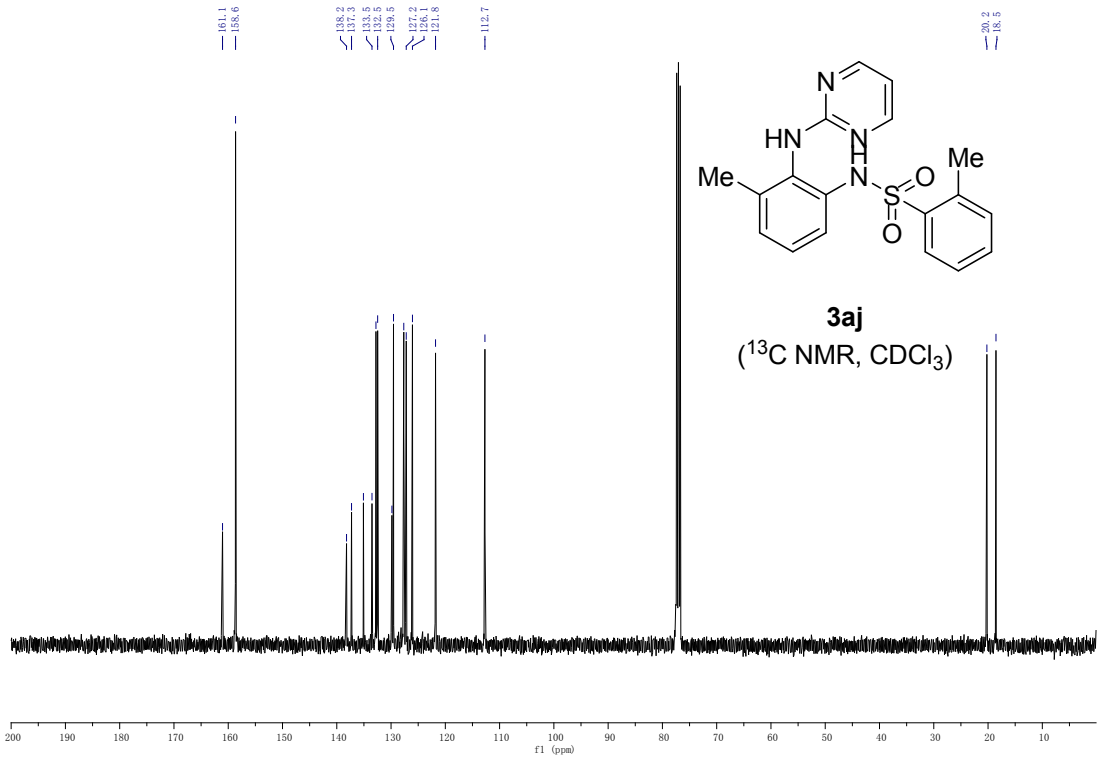
3ai

(^{13}C NMR, $CDCl_3$)



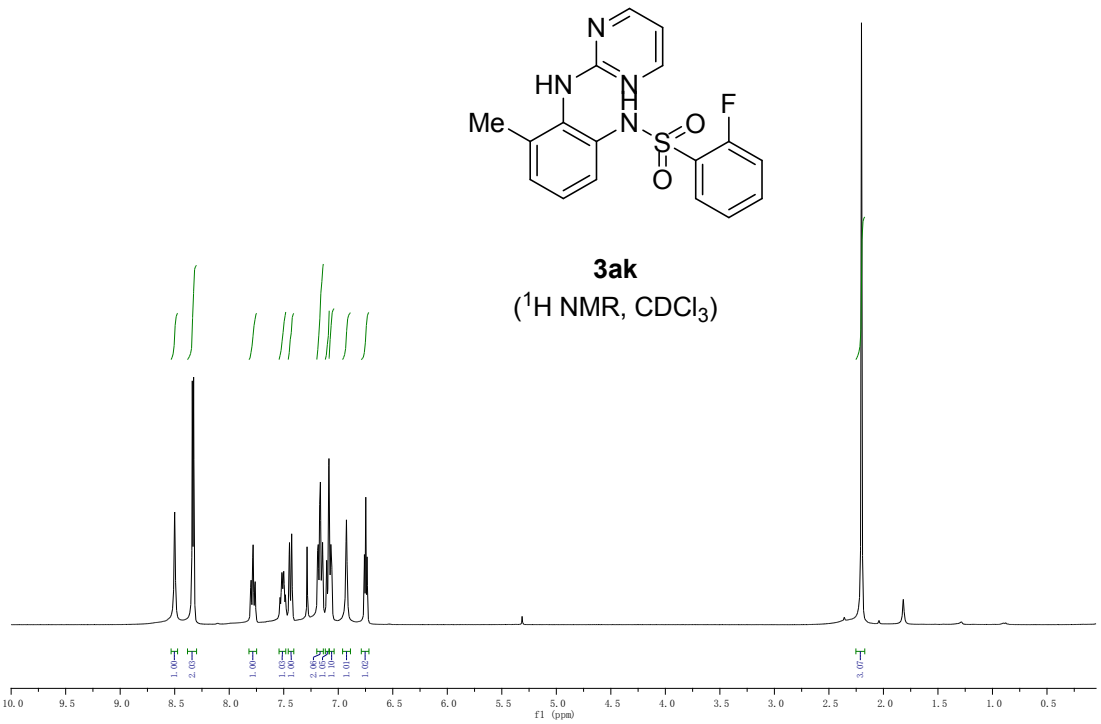
3aj

(^{1}H NMR, $CDCl_3$)



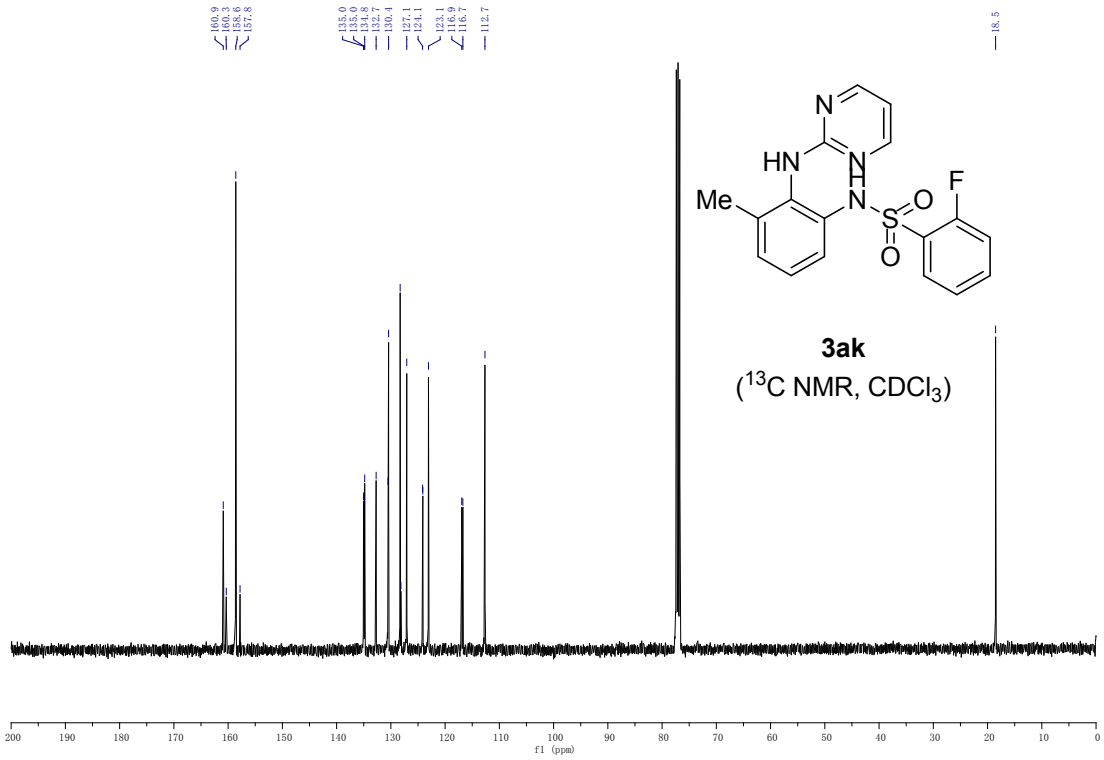
3aj

(^{13}C NMR, $CDCl_3$)



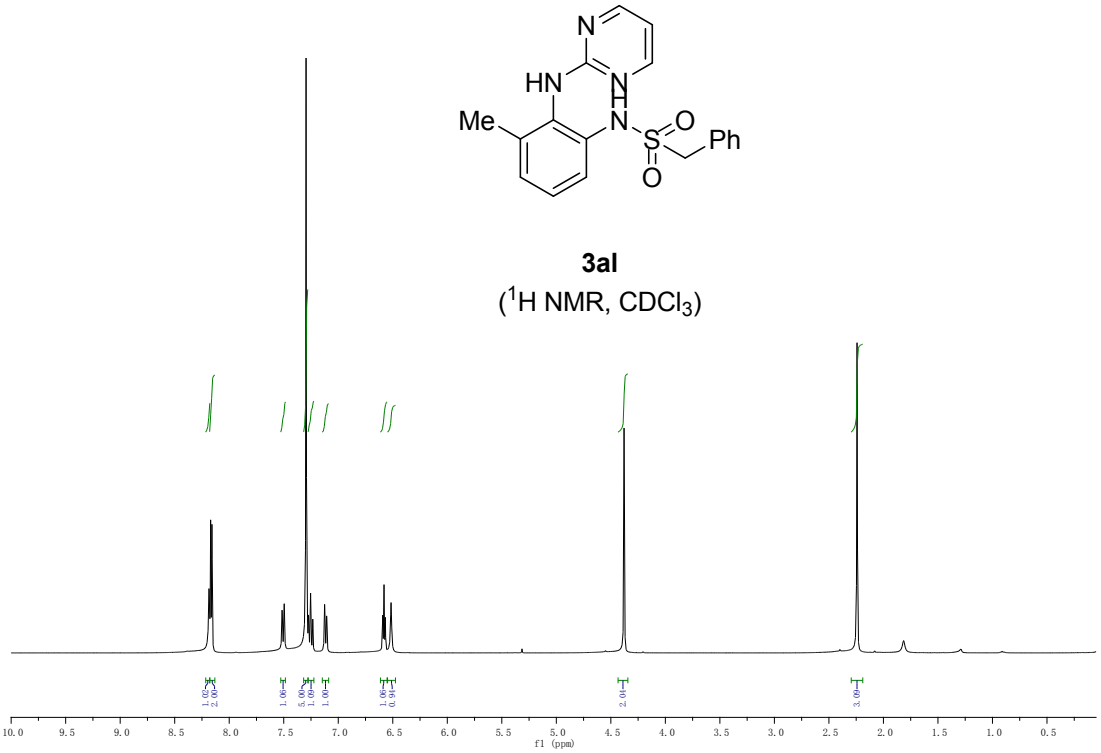
3ak

(^{1}H NMR, $CDCl_3$)



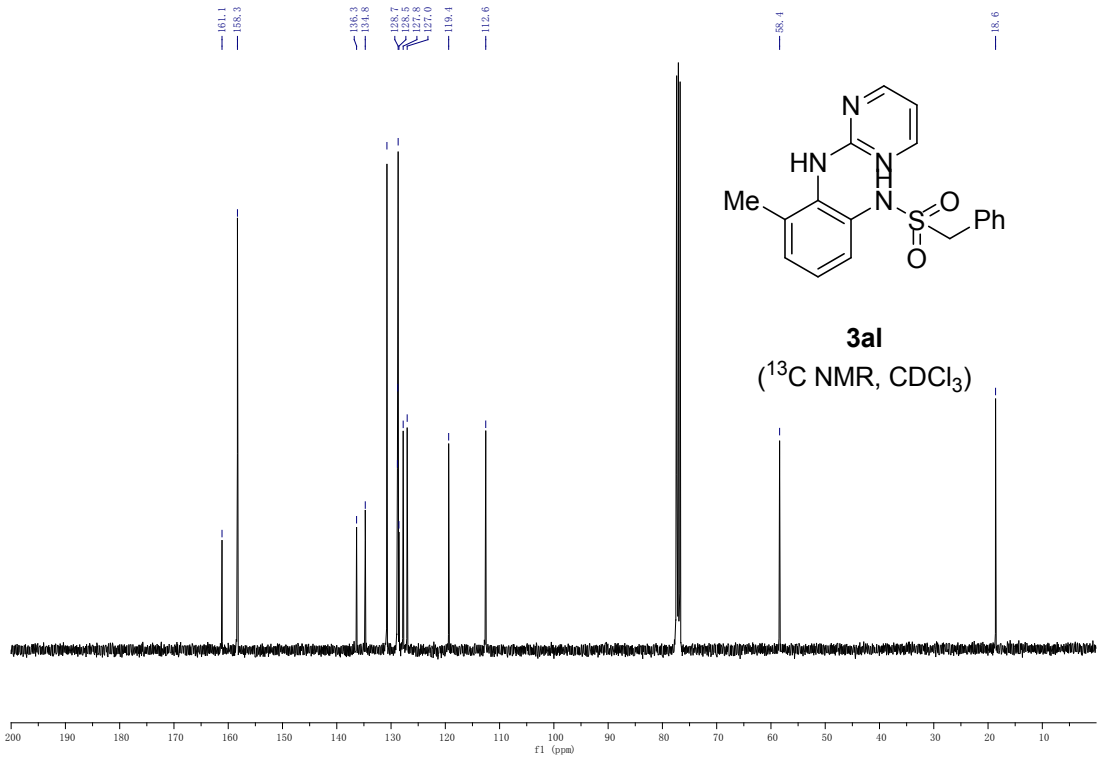
3ak

(^{13}C NMR, $CDCl_3$)



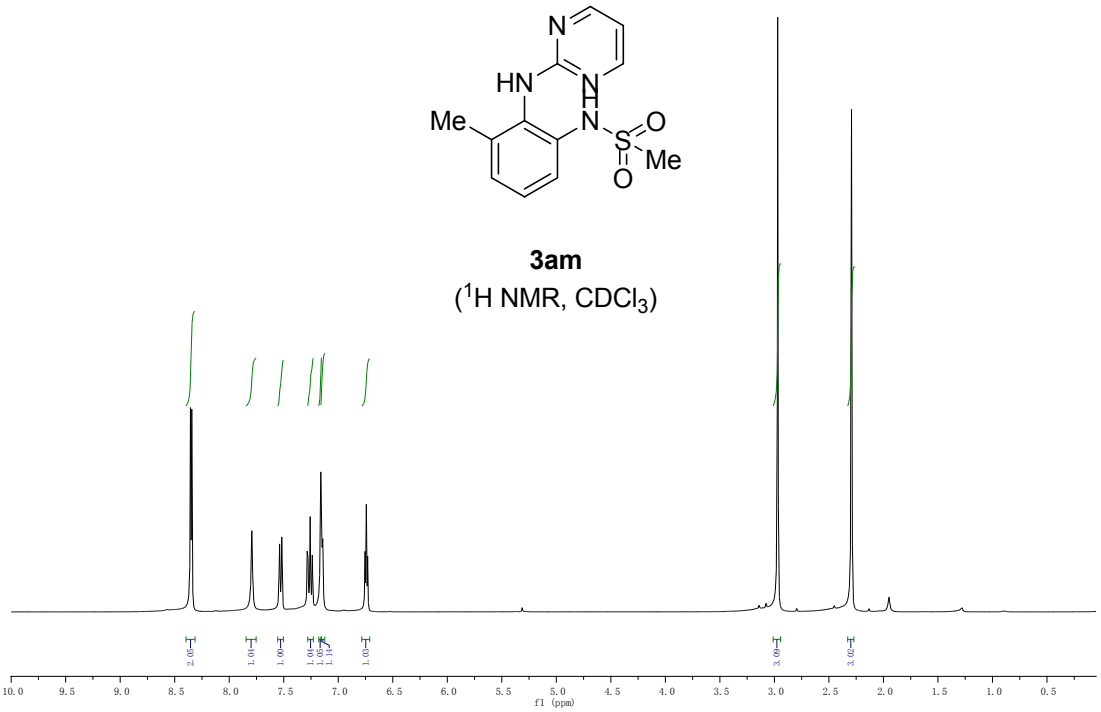
3al

(^{1}H NMR, $CDCl_3$)



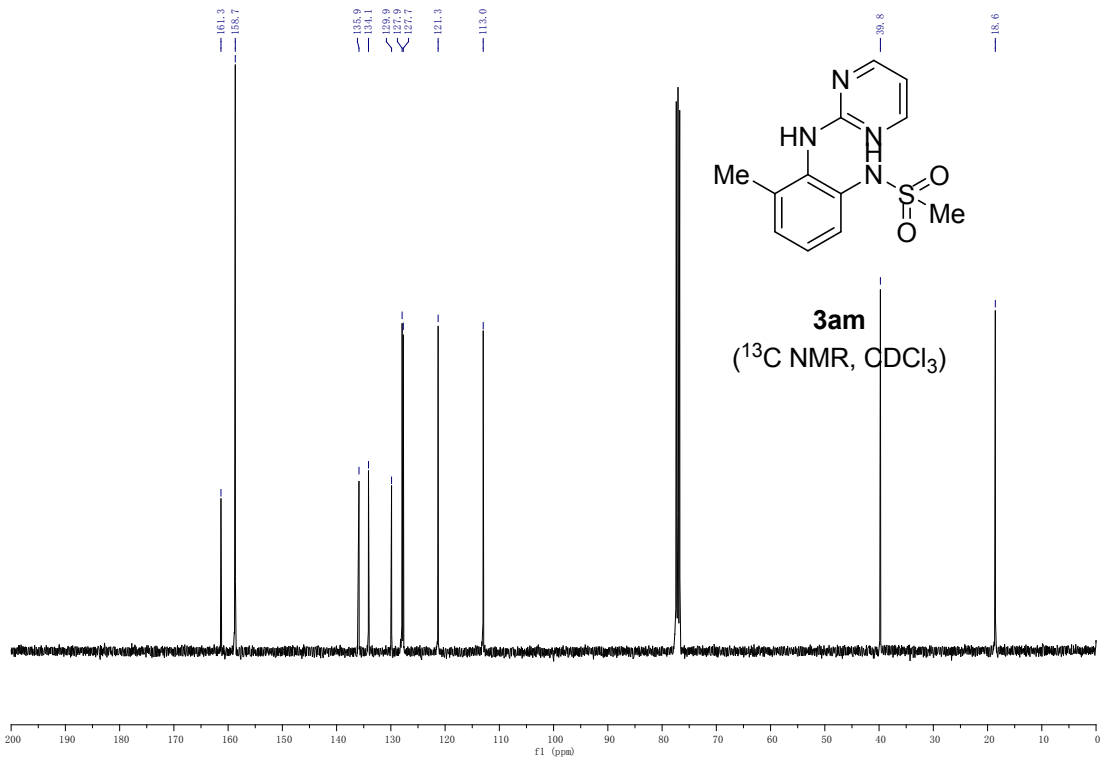
3al

(^{13}C NMR, $CDCl_3$)

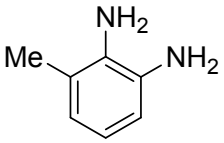


3am

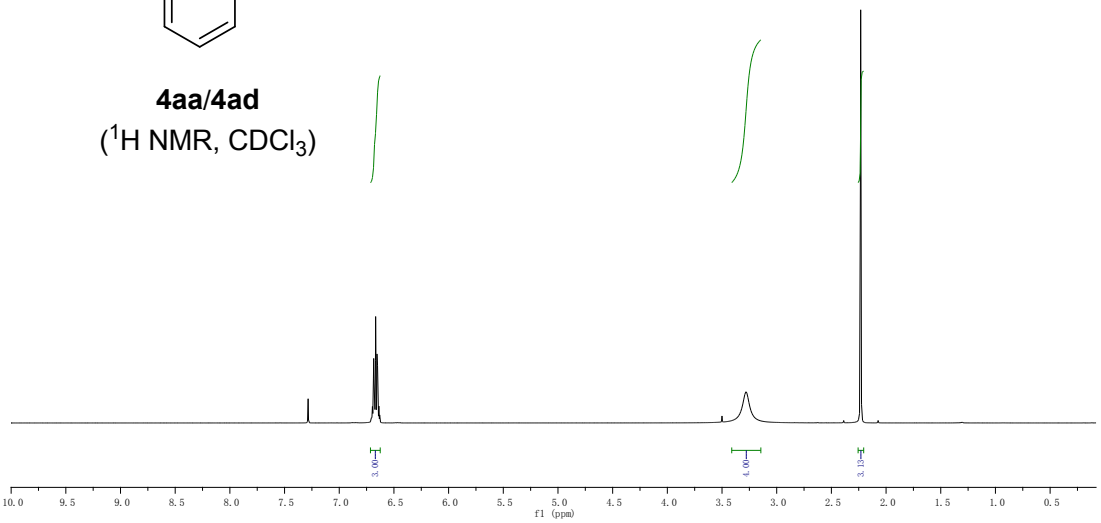
(^{1}H NMR, $CDCl_3$)

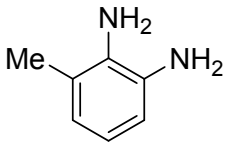


3am
(^{13}C NMR, $CDCl_3$)



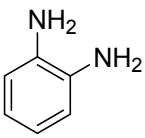
4aa/4ad
(^{1}H NMR, $CDCl_3$)





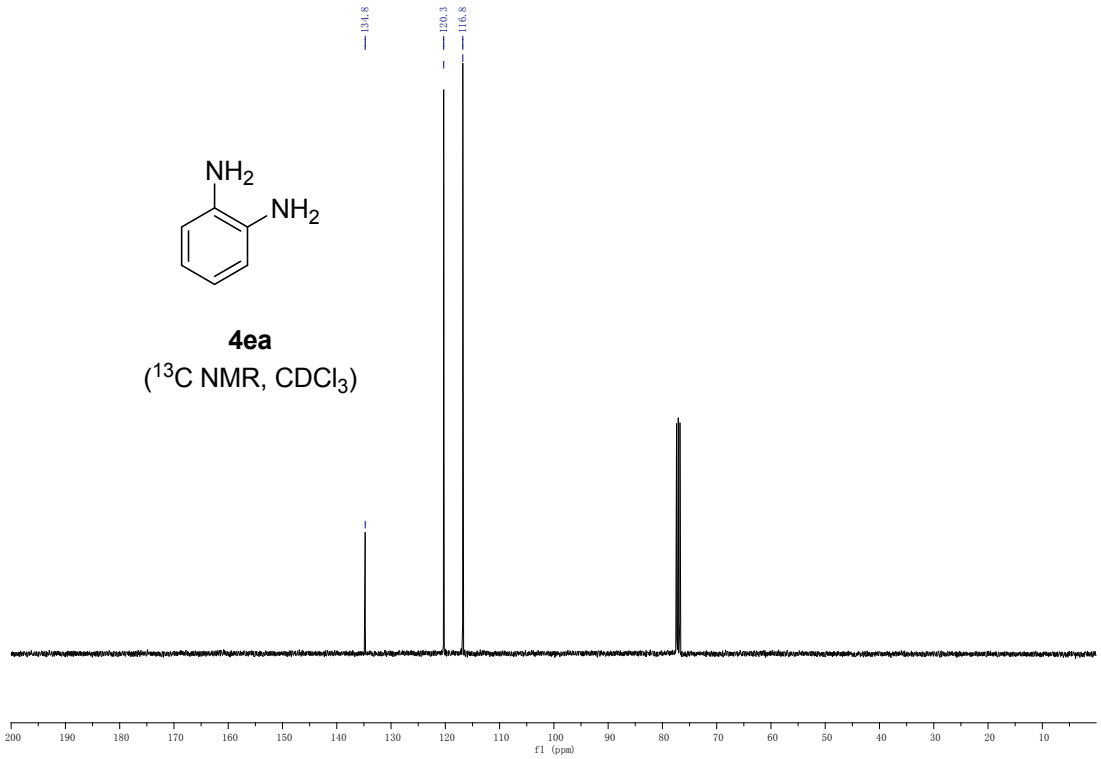
4aa/4ad

(^{13}C NMR, $CDCl_3$)



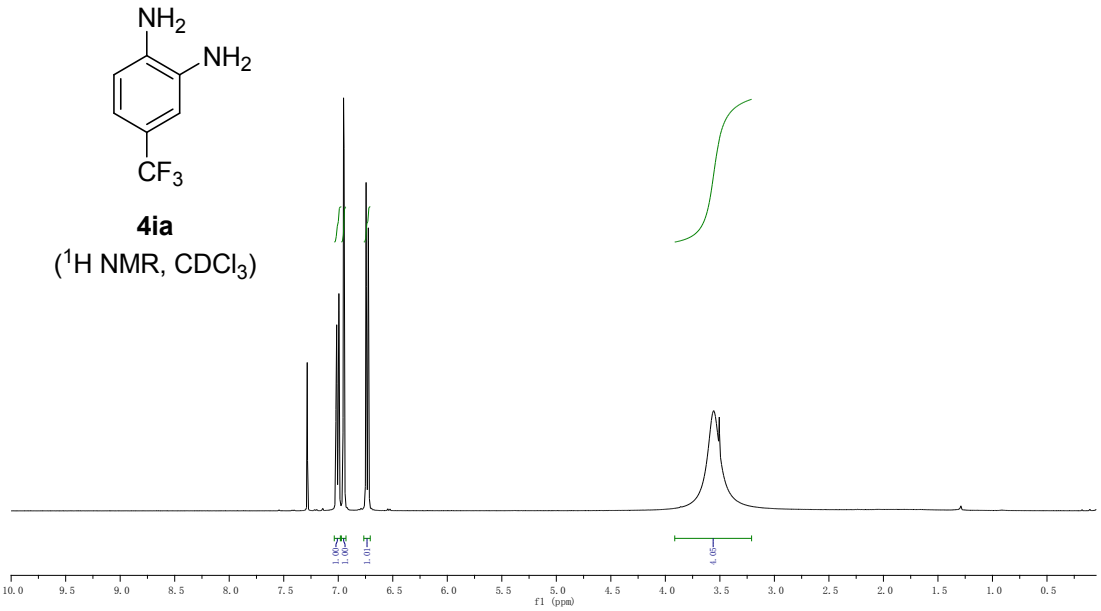
4ea

(^{1}H NMR, $CDCl_3$)



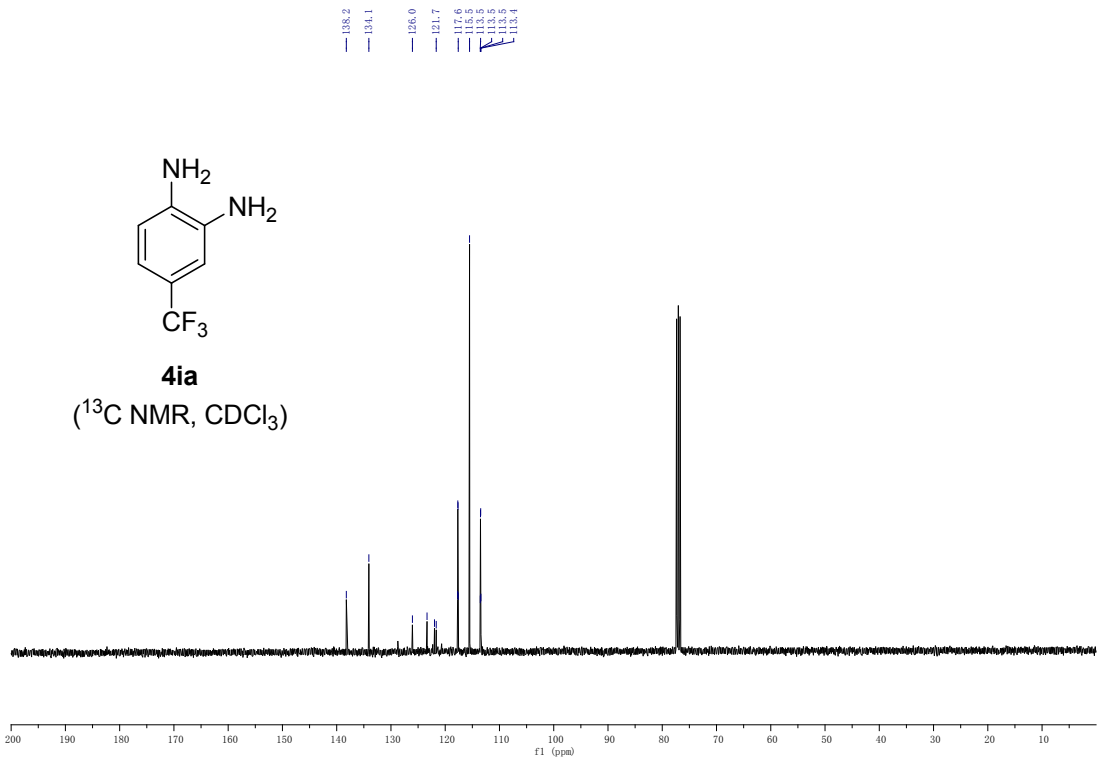
4ea

(^{13}C NMR, $CDCl_3$)



4ia

(^{1}H NMR, $CDCl_3$)



4ia

(^{13}C NMR, $CDCl_3$)