Supporting Information

Ligand Free Iron-Catalyzed C (sp\(^3\))-H Amination of Methylarenes with N-Fluorobenzenesulfonimide

Fengyu Bao *, Yuanbo Cao, Wenbo Liu, Junhao Zhu

College of Science, Henan Agricultural University, Zhengzhou 450002, PR China

E-mail: baofengyu@henau.edu.cn

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General information
All chemicals were commercial available and used without purification. All reactions were carried out in air and monitored by thin layer chromatography (TLC). $^1$H and $^{13}$C NMR were measured on a Bruker AVANCE III 400 using tetramethylsilane as an internal standard. In the NMR data, chemical shift ($\delta$, ppm) and integration are recorded. The abbreviations are as follows: s = singlet, d = doublet, t = triplet, m = multiplet. Hertz (Hz) is used for coupling constant (J). HRMS were measured on Agilent 1290-6540 Ultra High Performance Liquid Chromatography-Q-Time of Flight/ High Resolution Mass Spectrometer.

General procedure for the amination reactions of methylarenes
1, 2-Dichlorobenzene (20 mL) was added to a mixture of iron (III) oxalate hexahydrate (0.05 mmol, 10 mol%), methylarenes (0.5 mmol), N-fluorobenzenesulfonimide (NFSI, 0.75 mmol, 1.5 eq). The mixture was stirred and heated in electric heating sleeve at reflux. After the complete consumption of NFSI, the mixture was concentrated in vacuo, and the crude product was purified by a silica gel column chromatography.

Characterization data of compounds 3

N-benzyl-N-(phenylsulfonyl)benzenesulfonamide (3a)

3a was obtained according to the general procedure using toluene and purified by column chromatography (ethyl acetate: petroleum ether = 1: 6). Yield: 113.4 mg (59%); white solid. $^1$HNMR (400 MHz, CDCl$_3$): $\delta$7.77-7.79 (m, 4H), 7.55-7.59 (m, 2H), 7.36-7.44 (m, 6H), 7.21-7.25 (m, 3H), 4.94 (s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 140.0, 134.5, 133.6, 129.2, 128.8, 128.4, 128.1, 52.5. MS m/z: 410.2 ([M+Na]$^+$).

N-(2-methylbenzyl)-N-(phenylsulfonyl)benzenesulfonamide (3b)

3b was obtained according to the general procedure using o-xylene and purified by column chromatography (ethyl acetate: petroleum ether = 1: 6). Yield: 97.8 mg (49%); white solid. $^1$HNMR (400 MHz, CDCl$_3$): $\delta$7.79-7.81 (m, 4H), 7.56-7.60 (m, 2H), 7.41-7.45 (m, 4H), 7.04-7.16 (m, 1H), 7.11 (t, J = 7.36 Hz, 1H), 7.04 (d, J = 7.36 Hz, 1H), 6.95 (t, J = 7.36 Hz, 1H), 5.02 (s, 2H), 2.30 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 140.1, 136.4, 133.6, 132.1, 130.3, 129.3, 128.8, 128.1, 127.8, 126.0, 50.1, 19.2. MS m/z: 424.2 ([M+Na]$^+$).

N-(3-methylbenzyl)-N-(phenylsulfonyl)benzenesulfonamide (3c)

3c was obtained according to the general procedure using m-xylene and purified by column chromatography (ethyl acetate: petroleum ether = 1: 6). Yield: 78.1 mg (39%); white solid. $^1$HNMR (400 MHz, CDCl$_3$): $\delta$ 7.78-7.81 (m, 4H), 7.55-7.59 (m, 2H), 7.41-7.46 (m, 4H), 7.04-7.16 (m,
4H), 4.91 (s, 2H), 2.21 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 140.1, 138.1, 134.2, 133.6, 129.6, 128.8, 128.3, 128.1, 126.2, 52.6, 21.2. MS m/z: 424.2 ([M+Na]$^+$).

N-(4-methylbenzyl)-N-(phenylsulfonyl)benzenesulfonamide (3d)

3d was obtained according to the general procedure using p-xylene and purified by column chromatography (ethyl acetate: petroleum ether = 1: 6). Yield: 104.1 mg (52%); white solid. $^1$HNMR (400 MHz, CDCl$_3$): $\delta$ 7.77-7.80 (m, 4H), 7.57 (t, $J$ = 7.48 Hz, 2H), 7.42 (t, $J$ = 7.88 Hz, 4H), 7.25 (d, $J$ = 7.88 Hz, 2H), 7.03 (d, $J$ = 7.88 Hz, 2H), 4.90 (s, 2H), 2.33 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 140.1, 137.9, 133.5, 131.5, 129.2, 129.0, 128.8, 128.1, 52.3, 21.1. MS m/z: 424.2 ([M+Na]$^+$).

N-(4-ethylbenzyl)-N-(phenylsulfonyl)benzenesulfonamide (3e)

3e was obtained according to the general procedure using 1-ethyl-4-methylbenzene and purified by column chromatography (ethyl acetate: petroleum ether = 1: 8). Yield: 24.5 mg (12%); white solid. $^1$HNMR (400 MHz, CDCl$_3$): $\delta$ 7.76-7.78 (m, 4H), 7.56 (t, $J$ = 7.48 Hz, 2H), 7.41 (t, $J$ = 8.00 Hz, 4H), 7.28 (d, $J$ = 8.00 Hz, 2H), 7.05 (d, $J$ = 8.00 Hz, 2H), 4.91 (s, 2H), 2.62 (q, $J$ = 7.60 Hz, 2H), 1.23 (t, $J$ = 7.60 Hz, 2H), 1.23 (t, $J$ = 7.60 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 144.4, 140.2, 133.5, 131.6, 129.4, 128.8, 128.1, 127.9, 52.4, 28.6, 15.9. MS m/z: 438.2 ([M+Na]$^+$).

N-(4-(tert-butyl)benzyl)-N-(phenylsulfonyl)benzenesulfonamide (3f)

3f was obtained according to the general procedure using 1-(tert-butyl)-4-methylbenzene and purified by column chromatography (ethyl acetate: petroleum ether = 1: 8). Yield: 178.2 mg (80%); white solid. $^1$HNMR (400 MHz, CDCl$_3$): $\delta$ 7.75-7.77 (m, 4H), 7.52-7.57 (m, 2H), 7.38-7.72 (m, 4H), 7.29 (d, $J$ = 8.40 Hz, 2H), 7.24 (d, $J$ = 8.40 Hz, 2H), 4.93 (s, 2H), 1.31 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 151.2, 140.2, 133.5, 131.3, 129.1, 128.7, 128.1, 125.3, 52.4, 34.6, 31.4. HRMS: calculated for C$_{23}$H$_{25}$NO$_4$S$_2$ ([M+Na]$^+$), 466.1123, found, 466.1118.

N-(4-methoxybenzyl)-N-(phenylsulfonyl)benzenesulfonamide (3g)

3g was obtained according to the general procedure using 1-methoxy-4-methylbenzene and purified by column chromatography (ethyl acetate: petroleum ether = 1: 3.5). Yield: 66.6 mg (32%); white solid. $^1$HNMR (400 MHz, CDCl$_3$): $\delta$ 7.80-7.82 (m, 4H), 7.57-7.62 (m, 4H), 7.34 (d, $J$ = 8.76 Hz, 2H), 6.79 (d, $J$ = 8.76 Hz, 2H), 4.90 (s, 2H), 3.83 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 159.5, 140.1, 133.6, 130.8, 128.8, 128.1, 126.6, 113.8, 55.4, 52.1. MS m/z: 440.1 ([M+Na]$^+$).
N-(2-iodobenzyl)-N-(phenylsulfonyl)benzenesulfonamide (3h)

3h was obtained according to the general procedure using 1-iodo-2-methylbenzene and purified by column chromatography (ethyl acetate: petroleum ether = 1: 6.5). Yield: 109.2 mg (43%); white solid. \(^1\)HNMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.89-7.92 (m, 4H), 7.77-7.79 (m, 1H), 7.60-7.64 (m, 2H), 7.46-7.50 (m, 4H), 7.11-7.13 (m, 1H), 7.00-7.04 (m, 1H), 6.85-6.90 (m, 1H), 5.04 (s, 2H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 139.6, 139.3, 136.6, 133.9, 129.2, 129.0, 128.8, 128.4, 128.1, 97.4, 57.4. MS m/z: 536.1 ([M+Na]\(^+\)).

N-(3-iodobenzyl)-N-(phenylsulfonyl)benzenesulfonamide (3i)

3i was obtained according to the general procedure using 1-iodo-3-methylbenzene and purified by column chromatography (ethyl acetate: petroleum ether = 1: 6). Yield: 104.2 mg (41%); white solid. \(^1\)HNMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.81-7.83 (m, 4H), 7.56-7.62 (m, 4H), 7.44-7.48 (m, 4H), 7.30 (d, J = 7.76 Hz, 1H), 6.95 (t, J = 7.76 Hz, 1H), 4.87 (s, 2H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 139.8, 137.7, 137.2, 136.8, 133.9, 130.1, 129.0, 128.2, 128.1, 94.2, 51.6. HRMS: calculated for C\(_{19}\)H\(_{16}\)INO\(_4\)S\(_2\) ([M+H]\(^+\)), 513.9643, found, 513.9639.

N-(4-iodobenzyl)-N-(phenylsulfonyl)benzenesulfonamide (3j)

3j was obtained according to the general procedure using 1-iodo-4-methylbenzene and purified by column chromatography (ethyl acetate: petroleum ether = 1: 6.5). Yield: 108.7 mg (42%); white solid. \(^1\)HNMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.78-7.81 (m, 4H), 7.60 (t, J = 7.56 Hz, 2H), 7.54 (d, J = 8.32 Hz, 2H), 7.45 (t, J = 7.56 Hz, 4H), 7.09 (d, J = 8.32 Hz, 2H), 4.86 (s, 2H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 139.8, 137.5, 134.3, 133.8, 133.9, 130.1, 129.0, 128.2, 128.1, 93.9, 51.9. MS m/z: 536.0 ([M+Na]\(^+\)).

N-(2-iodo-3-methylbenzyl)-N-(phenylsulfonyl)benzenesulfonamide (3k)

3k was obtained according to the general procedure using 2-iodo-1, 3-dimethylbenzene and purified by column chromatography (ethyl acetate: petroleum ether = 1: 4.5). Yield: 108.3 mg (41%); white solid. \(^1\)HNMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.91-7.93 (m, 4H), 7.61-7.65 (m, 2H), 7.47-7.51 (m, 4H), 7.08 (dd, J = 7.48, 1.40 Hz, 1H), 6.91 (t, J = 7.48 Hz, 1H), 6.88 (dd, J = 7.72, 1.48 Hz, 1H), 5.07 (s, 2H), 2.46 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 142.1, 139.5, 137.1, 134.0, 128.9, 128.9, 128.5, 127.6, 125.8, 104.4, 58.6, 29.4. HRMS: calculated for C\(_{20}\)H\(_{18}\)INO\(_4\)S\(_2\) ([M+H]\(^+\)), 527.9800, found, 527.9792.

N-(4-bromobenzyl)-N-(phenylsulfonyl)benzenesulfonamide (3l)

3l was obtained according to the general procedure using 4-bromobenzyl alcohol and purified by column chromatography (ethyl acetate: petroleum ether = 1: 4). Yield: 107.4 mg (41%); white solid. \(^1\)HNMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.81-7.83 (m, 4H), 7.56-7.62 (m, 4H), 7.44-7.48 (m, 4H), 7.09 (dd, J = 7.48 Hz, 1H), 4.86 (s, 2H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 139.8, 137.5, 134.3, 133.8, 133.9, 130.1, 129.0, 128.2, 128.1, 96.1, 51.9. MS m/z: 536.0 ([M+Na]\(^+\)).
3l was obtained according to the general procedure using 1-bromo-4-methylbenzene and purified by column chromatography (ethyl acetate: petroleum ether = 1: 6.5). Yield: 176.1 mg (76%); white solid. $^1$HNMR (400 MHz, CDCl$_3$): $\delta$ 7.79-7.81 (m, 4H), 7.60 (t, J = 7.44 Hz, 2H), 7.45 (t, J = 8.00 Hz, 4H), 7.35 (d, J = 8.00 Hz, 2H), 7.23 (d, J = 8.00 Hz, 2H), 4.87 (s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 139.9, 133.8, 133.6, 131.5, 130.9, 128.9, 128.1, 122.3, 51.8. MS m/z: 488.1 ([M+Na$^+$]).

N-(2-bromo-5-iodobenzyl)-N-(phenylsulfonyl)benzenesulfonamide (3m)

3m was obtained according to the general procedure using 1-bromo-4-iodo-2-methylbenzene and purified by column chromatography (ethyl acetate: petroleum ether = 1: 5). Yield: 85.2 mg (29%); white solid. $^1$HNMR (400 MHz, CDCl$_3$): $\delta$ 7.94-7.96 (m, 4H), 7.65-7.69 (m, 2H), 7.52-7.56 (m, 4H), 7.36 (dd, J = 8.32, 2.08 Hz, 1H), 7.29 (d, J = 2.08 Hz, 1H), 7.20 (d, J = 8.32 Hz, 1H), 5.03 (s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 139.3, 138.1, 137.8, 136.0, 134.3, 134.1, 129.2, 128.3, 122.2, 92.5, 51.7. HRMS: calculated for C$_{19}$H$_{15}$BrINO$_4$S$_2$ ([M+Na$^+$]), 613.8569, found, 613.8565.

N-(4-chlorobenzyl)-N-(phenylsulfonyl)benzenesulfonamide (3n)

3n was obtained according to the general procedure using 1-chloro-4-methylbenzene and purified by column chromatography (ethyl acetate: petroleum ether = 1: 6.5). Yield: 120.5 mg (57%); white solid. $^1$HNMR (400 MHz, CDCl$_3$): $\delta$ 7.79-7.81 (m, 4H), 7.58-7.62 (m, 2H), 7.44-7.48 (m, 4H), 7.30 (d, J = 8.48 Hz, 2H), 7.19-7.21 (m, 2H), 4.89 (s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 139.9, 134.1, 133.8, 133.1, 130.6, 128.9, 128.5, 128.1, 51.7. MS m/z: 444.1 ([M+Na$^+$]).

N-(2-chlorobenzyl)-N-(phenylsulfonyl)benzenesulfonamide (3o)

3o was obtained according to the general procedure using 1-chloro-2-methylbenzene and purified by column chromatography (ethyl acetate: petroleum ether = 1: 6). Yield: 113.3 mg (54%); white solid. $^1$HNMR (400 MHz, CDCl$_3$): $\delta$ 7.89-7.91 (m, 4H), 7.58-7.63 (m, 2H), 7.45-7.49 (m, 4H), 7.28-7.30 (m, 1H), 7.18 (d, J = 7.76 Hz, 1H), 7.11-7.15 (m, 1H), 6.95-6.99 (m, 1H), 5.15 (s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 139.7, 133.9, 132.8, 132.3, 129.4, 129.4, 128.9, 128.8, 128.3, 126.6, 49.8. MS m/z: 444.1 ([M+Na$^+$]).

N-(4-fluorobenzyl)-N-(phenylsulfonyl)benzenesulfonamide (3p)

3p was obtained according to the general procedure using 1-fluoro-4-methylbenzenene and purified by column chromatography (ethyl acetate: petroleum ether = 1: 5). Yield: 116.6 mg (58%); white solid. $^1$HNMR (400 MHz, CDCl$_3$): $\delta$ 7.78-7.81 (m, 4H), 7.57-7.61 (m, 2H), 7.43-7.47 (m, 4H), 7.34-7.38 (m, 2H), 6.90-6.95 (m, 2H), 4.90 (s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 139.9, 134.1, 133.8, 133.1, 130.6, 128.9, 128.5, 128.1, 51.7. MS m/z: 444.1 ([M+Na$^+$]).
MHz, CDCl₃): δ 163.8, 161.4, 139.9, 133.7, 131.2, 131.1, 130.4, 130.4, 128.9, 128.1, 115.4, 115.2, 51.7. HRMS: calculated for C₁₀H₁₆FNO₄S₂ ([M+Na⁺), 428.0403, found, 428.0398.

N-([1, 1'-biphenyl]-4-ylmethyl)-N-(phenylsulfonyl)benzenesulfonamide (3q)

3q was obtained according to the general procedure using 4-methyl-1, 1'-biphenyl and purified by column chromatography (ethyl acetate: petroleum ether = 1: 4.5). Yield: 151.7 mg (66%); white solid. ¹H NMR (400 MHz, CDCl₃): δ 7.81-7.83 (m, 4H), 7.55-7.59 (m, 4H), 7.38-7.48 (m, 11H), 4.99 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 141.0, 140.6, 140.1, 133.6, 133.5, 129.7, 128.9, 128.8, 128.1, 127.5, 127.1, 127.1, 52.3. MS m/z: 486.2 ([M+Na⁺).
N-(4-acetylbenzyl)-N-(phenylsulfonyl)benzenesulfonamide (3u)

3u was obtained according to the general procedure using 1-(p-tolyl)ethan-1-one and purified by column chromatography (ethyl acetate: petroleum ether = 1: 3.5). Yield: 69.7 mg (32%); white solid. 1H NMR (400 MHz, CDCl3): δ 7.80-7.83 (m, 6H), 7.59 (t, J = 7.48 Hz, 2H), 7.44 (t, J = 8.00 Hz, 6H), 4.97 (s, 2H), 2.59 (s, 3H). 13C NMR (100 MHz, CDCl3): δ 197.6, 139.9, 139.7, 136.7, 133.9, 129.0, 128.9, 128.4, 128.1, 51.9, 26.7. MS m/z: 430.2 ([M+H]+).

N-(phenylsulfonyl)-N-(quinolin-8-ylmethyl)benzenesulfonamide (5a)

5a was obtained according to the general procedure using 8-methylquinoline and purified by column chromatography (ethyl acetate: petroleum ether = 1: 2). Yield: 103.4 mg (47%); white solid. 1H NMR (400 MHz, CDCl3): δ 8.91 (dd, J = 4.16, 1.68 Hz, 1H), 8.15 (dd, J = 8.32, 1.68 Hz, 1H), 7.89-7.92 (m, 4H), 7.68 (d, J = 8.32 Hz, 1H), 7.58-7.63 (m, 2H), 7.50-7.53 (m, 1H), 7.42-7.47 (m, 5H), 7.29 (t, J = 7.72 Hz, 1H), 5.82 (s, 2H). 13C NMR (100 MHz, CDCl3): δ 149.5, 145.6, 139.7, 136.3, 133.8, 133.0, 128.9, 128.4, 128.1, 128.0, 127.3, 126.0, 121.2, 49.1. HRMS: calculated for C22H18N2O4S2 ([M+H]+), 439.0786, found, 439.0784.

The radical-trapping experiment

2 equiv of 2, 2, 6, 6-tetramethylpiperidyl-1-oxyl (TEMPO) was added in the amination reaction under the standard reaction conditions. No product could be detected by thin layer chromatography.
\[ \text{Diagram of molecule 3b with chemical shift values and spectra} \]