Highly Selective $sp^3$ C-N Bond Activation of Tertiary Anilines Modulated by Steric and Thermodynamic Factors

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Electronic Supplementary Information

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General:
All solvents are anhydrous. TBN and TEMPO were purchased from commercial source and used without further purification. Flash chromatography was carried out with silica gel (200-300 mesh). Analytical TLC was performed with silica gel GF254 plates, and the products were visualized by UV detection. $^1$H NMR and $^{13}$C NMR (400 MHz, 600MHz and 100 MHz, 150MHZrespectively) spectra were recorded in CDCl$_3$. Chemical shifts ($\delta$) are reported in ppm using TMS as internal standard and spin-spin coupling constants (J) are given in Hz. The high resolution mass spectra (HRMS) were measured on an electrospray ionization (ESI) apparatus using time of flight (TOF) mass spectrometry.

General Experimental Procedure

![Diagram of reaction procedure](image)

A solution of 1 (1 mmol) and TEMPO (10 mol %) in MeCN (10 mL) or 1,4-dioxane (10 mL) was mixed fully, then TBN (1.5 eq) was added dropwise under air atmosphere. The reaction solution was stirred under room temperature. After completion monitored by TLC (by UV visualization), the solvent was removed under reduced pressure. The products were separated by silica gel column chromatography eluted with petroleum ether/acetone (v/v 50:1) to afford the products.

Measurement of KIE
The deuterated substrate d$_3$-1d was synthesized by the nucleophilic substitution between N,4-dimethylaniline and CD$_3$I under basic condition. The reaction of d$_3$-1d was performed under the standard reaction conditions, and the KIE value was obtained by $^1$H NMR of the products mixture.

Analytical data for compounds

$N$-(4-Bromophenyl)-$N$-methylnitrous amide (2a) $^1$
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.60 (d, $J = 9.0$ Hz, 2H), 7.44 (d, $J = 9.0$ Hz, 2H), 3.43 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 141.3, 132.5, 120.6, 120.3, 31.1. HRMS (ESI): Calc’d for C$_7$H$_7$BrN$_2$O $^+\text{H}^+$, 214.9815; found, 214.9815.

$N$-(4-Chlorophenyl)-$N$-methylnitrous amide (2b) $^1$

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$^1$H NMR (400 MHz, CDCl$_3$) δ 7.48 (d, $J = 9.1$ Hz, 2H), 7.43 (d, $J = 9.1$ Hz, 2H), 3.42 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 140.8, 132.9, 129.6, 120.1, 31.2. HRMS (ESI): Calc’d for C$_7$H$_7$ClN$_2$O + H$^+$, 171.0320; found, 171.0321.

\[ \text{N-(4-Iodophenyl)-N-methylnitrous amide (2c)} \]

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.60 (d, $J = 9.0$ Hz, 2H), 7.44 (d, $J = 9.0$ Hz, 2H), 3.43 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 142.0, 138.5, 120.5, 91.6, 31.0. HRMS (ESI): Calc’d for C$_7$H$_7$IN$_2$O + H$^+$, 262.9676; found, 262.9665.

\[ \text{N-Methyl-N-(p-tolyl)nitrous amide (2d)} \]

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.42 (d, $J = 8.5$ Hz, 1H), 7.27 (d, $J = 8.3$ Hz, 1H), 3.44 (s, 3H), 2.40 (s, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 139.9, 137.3, 129.9, 119.3, 31.7, 20.9. HRMS (ESI): Calc’d for C$_8$H$_{10}$N$_2$O + H$^+$, 151.0866; found, 151.0871.

\[ \text{N-Methyl-N-(4-(trifluoromethyl)phenyl)nitrous amide (2e)} \]

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.71 (d, $J = 8.7$ Hz, 2H), 7.67 (d, $J = 8.7$ Hz, 2H), 3.44 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 144.9, 128.9 (q, $J_{C,F} = 33.0$ Hz), 126.7 (q, $J_{C,F} = 3.8$ Hz), 123.8 (q, $J_{C,F} = 271.9$ Hz), 118.4, 30.5. HRMS (ESI): Calc’d for C$_8$H$_7$F$_3$N$_2$O + H$^+$, 205.0583; found, 205.0574.

\[ \text{N-(4-Formylphenyl)-N-methylnitrous amide (2f)} \]

$^1$H NMR (400 MHz, CDCl$_3$) δ 9.99 (s, 1H), 7.96 (d, $J = 8.5$ Hz, 2H), 7.72 (d, $J = 8.4$ Hz, 2H), 3.44 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 190.9, 146.7, 134.5, 131.1, 118.2, 30.3. HRMS (ESI): Calc’d for C$_8$H$_8$N$_2$O$_2$ + H$^+$, 165.0659; found, 165.0659.

\[ \text{Methyl 4-(methyl(nitroso)amino)benzoate (2g)} \]

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.08 (d, $J = 6.7$ Hz, 2H), 7.59 (d, $J = 7.4$ Hz, 2H), 3.89 (s, 3H), 3.41 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 166.1, 145.6, 131.0, 128.4, 117.8, 52.2, 30.4. HRMS (ESI): Calc’d for C$_9$H$_{10}$N$_2$O$_3$ + H$^+$, 195.0764; found, 195.0758.
N-Methyl-N-(4-nitrophenyl)nitrous amide (2h)
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.31 (d, $J = 9.2$ Hz, 2H), 7.74 (d, $J = 9.1$ Hz, 2H), 3.45 (s, 3H); $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 147.1, 145.9, 125.2, 117.9, 30.1; HRMS (ESI): Calc’d for C$_7$H$_7$N$_3$O$_3$ + H$^+$, 182.0560; found, 182.0557.

N-Methyl-N-phenyl nitrous amide (2i)$^1$
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.53 (d, $J = 8.4$ Hz, 2H), 7.46 (t, $J = 7.9$ Hz, 2H), 7.35 (t, $J = 7.3$ Hz, 1H), 3.45 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 142.3, 129.4, 127.3, 119.2, 31.4. HRMS (ESI): Calc’d for C$_7$H$_8$N$_2$O + H$^+$, 137.0709; found, 137.0717.

N-(2-Bromophenyl)-N-methyl nitrous amide (2j)
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.42 (d, $J = 8.5$ Hz, 1H), 7.27 (d, $J = 8.3$ Hz, 1H), 3.44 (s, 1H), 2.40 (s, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 141.6, 133.9, 130.8, 128.5, 128.3, 119.9, 35.4. HRMS (ESI): Calc’d for C$_7$H$_7$BrN$_2$O + H$^+$, 214.9815; found, 214.9805.

N-(3-Chlorophenyl)-N-methyl nitrous amide (2k)$^2$
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.58 (t, $J = 1.8$ Hz, 1H), 7.48 – 7.44 (m, 1H), 7.41 (t, $J = 7.9$ Hz, 1H), 7.36 – 7.31 (m, 1H), 3.43 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 143.3, 135.2, 130.5, 127.1, 119.0 , 116.8, 31.0. HRMS (ESI): Calc’d for C$_7$H$_7$ClN$_2$O + H$^+$, 171.0320; found, 171.0316.

N-Methyl-N-(m-tolyl) nitrous amide (2l)$^1$
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.38 – 7.27 (m, 3H), 7.15 (d, $J = 7.1$ Hz, 1H), 3.42 (s, 3H), 2.40 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 142.2, 139.5, 129.2, 128.1, 119.9, 116.3, 31.6, 21.5. HRMS (ESI): Calc’d for C$_8$H$_{10}$N$_2$O + H$^+$, 151.0866; found, 151.0867.
**N-(4-Bromo-2-methylphenyl)-N-methylnitrous amide (2m)**

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.50 (d, $J = 1.9$ Hz, 1H), 7.44 (dd, $J = 8.2$, 2.0 Hz, 1H), 7.10 (d, $J = 8.4$ Hz, 1H), 3.35 (s, 3H), 2.22 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 140.5, 136.0, 134.4, 130.1, 127.1, 122.8, 35.1, 18.1. HRMS (ESI): Calc’d for C$_8$H$_9$BrN$_2$O + H$^+$, 228.9971; found, 228.9967.

![Structure of N-(4-Bromo-2-methylphenyl)-N-methylnitrous amide (2m)](image)

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**N-(2-Chloro-4-methylphenyl)-N-methylnitrous amide (2n)**

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.35 (s, 1H), 7.28 (d, $J = 8.1$ Hz, 1H), 7.18 (d, $J = 8.0$ Hz, 1H), 3.37 (s, 3H), 2.40 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 141.0, 137.5, 131.1, 129.7, 128.5, 127.6, 35.2, 20.9. HRMS (ESI): Calc’d for C$_8$H$_9$ClN$_2$O + H$^+$, 185.0476; found, 185.0468.

![Structure of N-(2-Chloro-4-methylphenyl)-N-methylnitrous amide (2n)](image)

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**N-Methyl-N-(pyridin-2-yl)nitrous amide (2o)**

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.46 (d, $J = 4.3$ Hz, 1H), 7.98 (d, $J = 8.4$ Hz, 1H), 7.77 (t, $J = 7.8$ Hz, 1H), 7.20 (dd, $J = 7.2$, 5.0 Hz, 1H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 154.5, 147.9, 138.3, 121.6, 112.67, 28.2. ESI-MS m/z (relative intensity): 137 (40.1%), 107 (90.0%), 78 (100%).

![Structure of N-Methyl-N-(pyridin-2-yl)nitrous amide (2o)](image)

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**N-Ethyl-N-(p-tolyl)nitrous amide (2p)**

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.39 (d, $J = 8.1$ Hz, 2H), 7.26 (d, $J = 7.9$ Hz, 2H), 4.04 (q, $J = 7.2$ Hz, 2H), 2.38 (s, 3H), 1.15 (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 139.0, 137.3, 130.0, 119.7, 39.4, 20.9, 11.7. HRMS (ESI): Calc’d for C$_9$H$_{12}$N$_2$O + H$^+$, 165.1022; found, 165.1019.

![Structure of N-Ethyl-N-(p-tolyl)nitrous amide (2p)](image)

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**N-Propyl-N-(p-tolyl)nitrous amide (2q)**

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.39 (d, $J = 8.2$ Hz, 2H), 7.25 (d, $J = 8.0$ Hz, 2H), 4.00 – 3.93 (m, 2H), 2.38 (s, 3H), 1.62 – 1.50 (m, 2H), 0.87 (t, $J = 7.4$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 139.2, 137.3, 130.0, 119.9, 45.5, 20.9, 19.9, 11.4. HRMS (ESI): Calc’d for C$_{10}$H$_{14}$N$_2$O + H$^+$, 179.1179; found, 179.1181.

![Structure of N-Propyl-N-(p-tolyl)nitrous amide (2q)](image)

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**N-Butyl-N-(p-tolyl)nitrous amide (2r)**

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.38 (d, $J = 8.1$ Hz, 2H), 7.24 (d, $J = 8.0$ Hz, 2H), 4.03 – 3.95 (m, 2H), 2.38 (s, 3H), 1.56 – 1.45 (m, 2H), 1.34 – 1.23 (m, 2H), 0.88 (t, $J = 7.3$ Hz, 3H). $^{13}$C NMR
(101 MHz, CDCl₃) δ 139.2, 137.3, 130.0, 119.8, 43.8, 28.5, 20.9, 20.3, 13.6. HRMS (ESI): Calc’d for C₁₁H₁₆N₂O + H⁺, 193.1335; found, 193.1335.

\[
\begin{align*}
\text{N-Pentyl-}\text{N-(p-tolyl)nitrous amide (2s)} \\
\text{H NMR (400 MHz, CDCl}_3\text{) } &\delta 7.38 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 4.05 – 3.91 (m, 2H), 2.38 (s, 3H), 1.57 – 1.47 (m, 2H), 1.31 – 1.21 (m, 4H), 0.85 (t, J = 6.8 Hz, 3H). \text{C NMR (101 MHz, CDCl}_3\text{) } &\delta 139.2, 137.2, 130.0, 119.8, 44.0, 29.1, 26.1, 22.2, 20.9, 13.8. \text{HRMS (ESI): Calc’d for C}_{12}H_{18}N₂O + H⁺, 207.1492; found, 207.1483.
\end{align*}
\]

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\begin{align*}
\text{N-Isobutyl-}\text{N-(p-tolyl)nitrous amide (2t)} \\
\text{H NMR (400 MHz, CDCl}_3\text{) } &\delta 7.39 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 3.89 (d, J = 7.5 Hz, 2H), 2.38 (s, 3H), 2.05 – 1.90 (m, 1H), 0.82 (d, J = 6.9 Hz, 6H). \text{C NMR (101 MHz, CDCl}_3\text{) } &\delta 137.3, 130.0, 120.1, 50.1, 26.6, 20.9, 20.2, 19.8. \text{HRMS (ESI): Calc’d for C}_{11}H_{16}N₂O + H⁺, 193.1328.
\end{align*}
\]

\[
\begin{align*}
\text{N-Isopropyl-}\text{N-(p-tolyl)nitrous amide (2u)} \\
\text{Mixture of two isomers: H NMR (400 MHz, CDCl}_3\text{) } &\delta 7.32 – 7.16 (m, 6.6H), 6.83 (d, J = 7.8 Hz, 1.6H), 5.25 – 5.18 (m, 1.4H), 5.05 (m, 1H), 2.41 (s, 4H), 2.37 (s, 3H), 1.44 (d, J = 6.8 Hz, 6H), 1.16 (d, J = 6.9 Hz, 8H); \text{C NMR (101 MHz, CDCl}_3\text{) } &\delta 139.4, 138.9, 136.8, 133.6, 130.0, 129.7, 127.4, 126.0, 56.0, 46.1, 22.0, 21.2, 21.1, 19.7. \text{HRMS (ESI): Calc’d for C}_{10}H_{14}N₂O + Na⁺, 201.1004; found, 201.0996.
\end{align*}
\]

\[
\begin{align*}
\text{N-Phenyl-}\text{N-(p-tolyl)nitrous amide (2v)} \\
mixture of two isomers: H NMR (400 MHz, CDCl}_3\text{) } &\delta 7.51 (t, J = 7.5 Hz, 1H), 7.48 – 7.38 (m, 4H), 7.32 (d, J = 8.1 Hz, 4H), 7.27 – 7.20 (m, 2H), 7.10 (d, J = 7.8 Hz, 1H), 6.98 (d, J = 7.8 Hz, 2H), 2.43 (s, 3H), 2.40 (s, 2H). \text{C NMR (101 MHz, CDCl}_3\text{) } &\delta 142.7, 140.2, 139.7, 137.1, 134.1, 130.5, 129.9, 129.7, 129.4, 129.3, 127.5, 127.2, 126.9, 120.0, 119.6, 21.3, 21.0. \text{HRMS (ESI): Calc’d for C}_{13}H_{12}N₂O + Na⁺, 235.0847; found, 235.0845.
\end{align*}
\]
**N,N-Di-p-tolyl nitrous amide (2w)**

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.30 (dd, $J = 8.6$, 2.1 Hz, 4H), 7.20 (d, $J = 8.2$ Hz, 2H), 6.96 (d, $J = 8.3$ Hz, 2H), 2.41 (s, 3H), 2.38 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 140.3, 139.5, 136.9, 134.4, 130.4, 129.9, 127.0, 119.8, 21.3, 21.0. HRMS (ESI): Calc’d for C$_{14}$H$_{14}$N$_2$O + Na$, 249.1004$, found, 249.1001.

![N,N-Di-p-tolyl nitrous amide (2w)](image)

**N-(4-(Dimethylamino)phenyl)-N-methyl nitrous amide (5a)**

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.35 (d, $J = 8.9$ Hz, 2H), 6.76 (d, $J = 9.0$ Hz, 2H), 3.42 (s, 3H), 2.99 (s, 6H); $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 149.9, 132.1, 121.2, 112.6, 40.6, 32.6; HRMS (ESI): Calc’d for C$_9$H$_{13}$N$_3$O + H$^+$, 180.1131; found, 180.1131.

![N-(4-(Dimethylamino)phenyl)-N-methyl nitrous amide (5a)](image)

**N,N’-(1,4-Phenylene)bis(N-methyl nitrous amide) (5b)**

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.65 (s, 4H), 3.46 (s, 6H); $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 141.1, 119.81, 31.2; HRMS (ESI): Calc’d for C$_8$H$_{10}$N$_4$O$_2$ + Na$, 217.0702$, found, 217.0693.

![N,N’-(1,4-Phenylene)bis(N-methyl nitrous amide) (5b)](image)

**N-Allyl-N-(p-tolyl) nitrous amide (7a)**

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.42 (d, $J = 8.1$ Hz, 2H), 7.24 (d, $J = 8.0$ Hz, 2H), 5.79 – 5.66 (m, 1H), 5.16 (d, $J = 10.4$ Hz, 1H), 5.07 (d, $J = 17.3$ Hz, 1H), 4.60 (d, $J = 5.1$ Hz, 2H), 2.38 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 139.4, 137.3, 130.0, 129.6, 119.5, 118.0, 46.8, 21.0. HRMS (ESI): Calc’d for C$_{10}$H$_{12}$N$_2$O + H$^+$, 177.1022; found, 177.1015.

![N-Allyl-N-(p-tolyl) nitrous amide (7a)](image)

**N-Benzyl-N-(4-methoxyphenyl) nitrous amide (7b)**

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.40 (d, $J = 9.1$ Hz, 2H), 7.31 – 7.19 (m, 3H), 7.08 (d, $J = 6.6$ Hz, 2H), 6.93 (d, $J = 9.1$ Hz, 2H), 5.21 (s, 2H), 3.80 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 159.0, 135.0, 134.4, 128.8, 127.6, 127.3, 121.7, 114.6, 55.5, 47.9. HRMS (ESI): Calc’d for C$_{14}$H$_{14}$N$_2$O$_2$ + H$^+$, 243.1128; found, 243.1130.

![N-Benzyl-N-(4-methoxyphenyl) nitrous amide (7b)](image)

**N-Benzyl-N-(p-tolyl) nitrous amide (7c)**

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.41 (d, $J = 8.4$ Hz, 2H), 7.32 – 7.15 (m, 5H), 7.08 (d, $J = 7.1$ Hz, 2H), 5.23 (s, 2H), 2.37 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 139.4, 137.4, 130.0, 128.8, 127.5, 127.1, 119.7, 47.4, 20.9. HRMS (ESI): Calc’d for C$_{16}$H$_{14}$N$_2$O + H$^+$, 227.1179; found, 227.1175.
**N-Benzyl-N-(4-bromophenyl)nitrous amide (7d)**

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.53 (d, $J = 8.9$ Hz, 2H), 7.41 (d, $J = 8.9$ Hz, 2H), 7.34 – 7.20 (m, 3H), 7.05 (d, $J = 6.7$ Hz, 2H), 5.21 (s, 2H).$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 140.7, 133.9, 132.5, 128.9, 127.8, 126.9, 120.8, 120.7, 46.8.HRMS (ESI): Calc’d for C$_{13}$H$_{11}$BrN$_2$O + H$^+$, 291.0128; found, 291.0123.

**N-Benzyl-N-(4-cyanophenyl)nitrous amide (7e)**

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.69 (s, 4H), 7.34 – 7.20 (m, 3H), 7.02 (d, $J = 6.6$ Hz, 2H), 5.23 (s, 2H).$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 145.0, 133.6, 133.4, 129.1, 128.0, 126.6, 118.5, 118.1, 110.4, 45.9.HRMS (ESI): Calc’d for C$_{14}$H$_{11}$N$_3$O + Na$^+$, 260.0800; found, 260.0795.

**N-Methyl-N-(4-cyanophenyl)nitrous amide (7e')**

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.75 (d, $J = 9.0$ Hz, 2H), 7.69 (d, $J = 8.9$ Hz, 2H), 3.42 (s, 3H).$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 145.5, 133.6, 118.3, 118.1, 110.3, 30.0.HRMS (ESI): Calc’d for C$_8$H$_7$N$_3$O + H$^+$, 162.0662; found, 162.0658.

**Solvent effect on the selected examples**

1. **Solvent effect on 1i and 1l**

For substrates 1i and 1l, when MeCN was employed as the solvent, N-nitrosoanilines were isolated in lower yields, and nitration on para-position occurred inevitably. While using 1,4-dioxane as the solvent, only trace amount of nitration products were detected.
2. Solvent effect on reaction selectivity

The selectivity was also affected by solvent effect. For unsymmetric substrate 1p, when the reaction was performed in MeCN, a mixture of C-N cleavage products were isolated, in which demethylation was favored (ratio: 82:14). However, in 1,4-dioxane, only trace amount of the de-ethylation product was detected by GC-MS, and the desired product 2p was obtained in 91% yield.

Similar results were also obtained for N-allylanilines. In MeCN, a mixture were afforded, and the C-N cleavage on N-allyl bond was preferred. In 1,4-dioxane, the N-Me cleavage was inhibited.

In the cases of N-benzyl-N-methylanilines, MeCN as the solvent gave higher site-selectivity, favoring N-Me cleavage. Furthermore, 1,4-dioxane as the solvent resulted in lower conversion of the substrates (about 80%) under air atmosphere (under O\textsubscript{2} balloon, full conversion could be realized). The exact reason of this solvent effect remains unknown at current stage.
\[
\text{Me-}^\text{N} \text{Bn} \quad \xrightarrow{\text{TBN (1.5 eq)}} \quad \text{Bn-}^\text{N} \text{NO} \quad \xrightarrow{\text{TEMPO (0.1 eq)}} \quad \text{Me-}^\text{N} \text{NO} + \text{Me-}^\text{N} \text{NO}
\]

air, r.t., solvent

3h

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References

$^1$H and $^{13}$C spectra