

Supporting Information

Direct Reductive Amination of Aromatic Aldehydes Catalyzed by Gold(I) Complex Under Transfer Hydrogenation Conditions

Ming Zhang,^a Hongwei Yang,^a Yan Zhang,^a Chengjian Zhu,^{*a,b} Wei Li,^c Yixiang Cheng,^{*a}
Hongwen Hu.^a

^a *State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China*

^b *State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China*

^c *School of Pharmacy, Nanjing University of Chinese Medicine, Nanjing 210046, PR China.*

Fax: +86-25-83594886; E-mail: cjzhu@nju.edu.cn

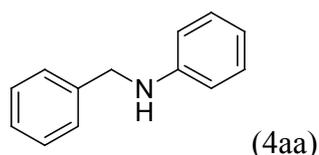
Table of contents

General information	s2
General procedure for the direct reductive amination of aromatic aldehydes	s2
Characterization data of compounds	s3
References	s9
The ¹ H and ¹³ C NMR spectra of compounds	s10

General Information: All reagents were obtained from commercial suppliers and used without further purification. The reaction was carried out at room temperature without exclusion of air or moisture from the reaction mixture. The reaction was monitored by TLC on silica-gel plates (GF 254). ^1H and ^{13}C NMR spectra were recorded on a Bruker APX-300 spectrometer at room temperature in CDCl_3 using tetramethylsilane (TMS) as the internal standard. HRESIMS were recorded on an Agilent 6210 TOF LC/MS equipped with an electrospray ionization (ESI) probe operating in positive or negative ion mode. All yields mentioned referred to isolated yields. Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad resonance.

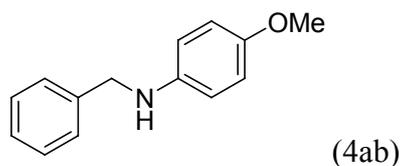
General procedure for the direct reductive amination of aromatic aldehydes:

A mixture of $(\text{PPh}_3)\text{AuCl}$ (0.02 mmol), AgOTf (0.02 mmol) in dichloromethane was stirred at room temperature. After 10 minutes, amine (2 mmol), aldehyde (2 mmol) and Hantzsch ester (2.5 mmol) was subsequently added into the stirring solution. The reaction was monitored by TLC on silica-gel plates (GF 254). After the reaction was complete, the mixture was concentrated under vacuum and then purification by flash chromatography to afford the corresponding product.



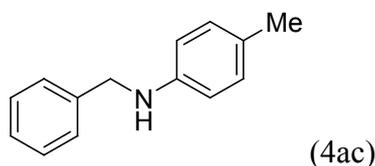
N-benzylbenzenamine (4aa)⁽¹⁾

^1H NMR (CDCl_3 , 300 MHz) δ =7.37-7.25 (m, 5H), 7.19-7.12 (m, 2H), 6.73-6.68 (m, 1H), 6.63-6.60 (m, 2H), 4.30 (s, 2H), 3.98 (br, 1H). ^{13}C NMR (CDCl_3 , 75 MHz) δ =148.2, 139.5, 129.4, 128.7, 127.6, 127.3, 117.7, 113.0, 48.5.



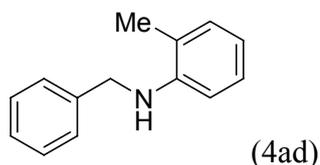
N-benzyl-4-methoxybenzenamine (4ab)⁽²⁾

^1H NMR (CDCl_3 , 300 MHz) δ =7.35-7.20 (m, 5H), 6.76-6.72 (m, 2H), 6.58-6.52 (m, 2H), 4.22 (s, 2H), 3.68 (s, 3H), 3.51 (br, 1H). ^{13}C NMR (CDCl_3 , 75 MHz) δ =152.2, 142.5, 139.7, 128.6, 127.6, 127.2, 114.9, 114.2, 55.8, 49.2.



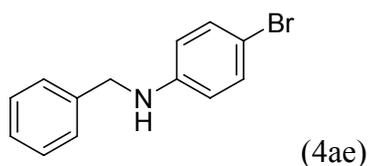
N-benzyl-4-methylbenzenamine (4ac)⁽³⁾

^1H NMR (CDCl_3 , 300 MHz) δ =7.36-7.21 (m, 5H), 6.97-6.95 (m, 2H), 6.56-6.51 (m, 2H), 4.26 (s, 2H), 3.40 (br, 1H), 2.22 (s, 3H). ^{13}C NMR (CDCl_3 , 75 MHz) δ =146.0, 139.8, 129.8, 128.7, 127.6, 127.2, 126.8, 113.1, 48.7, 20.5.



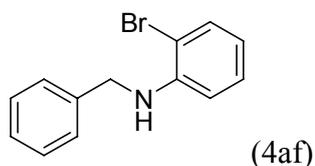
N-benzyl-2-methylbenzenamine (4ad)⁽³⁾

^1H NMR (CDCl_3 , 300 MHz) δ =7.37-7.24 (m, 5H), 7.10-7.04 (m, 2H), 6.68-6.57 (m, 2H), 4.32 (s, 2H), 3.60 (br, 1H), 2.12 (s, 3H). ^{13}C NMR (CDCl_3 , 75 MHz) δ =146.1, 139.6, 130.1, 128.7, 127.5, 127.3, 127.2, 121.9, 117.2, 110.1, 48.3, 17.6.



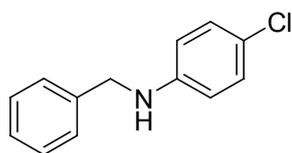
N-benzyl-4-bromobenzenamine (4ae)⁽³⁾

^1H NMR (CDCl_3 , 300 MHz) δ =7.33-7.18 (m, 7H), 6.48-6.43 (m, 2H), 4.25 (s, 2H) 3.87 (br, 1H). ^{13}C NMR (CDCl_3 , 75 MHz) δ =147.1, 138.9, 132.0, 128.8, 127.5, 127.4, 114.5, 109.2, 48.3.



N-benzyl-2-bromobenzenamine (4af)⁽⁴⁾

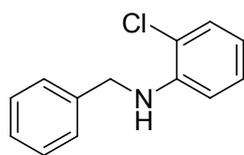
^1H NMR (CDCl_3 , 300 MHz) δ =7.43-7.39 (m, 1H), 7.33-7.23 (m, 5H), 7.12-7.06 (m, 1H), 6.58-6.51 (m, 2H), 4.64 (br, 1H), 4.34 (s, 2H). ^{13}C NMR (CDCl_3 , 75 MHz) δ =144.9, 138.8, 132.5, 128.8, 128.6, 127.4, 127.3, 118.1, 111.7, 109.8, 48.1.



(4ag)

N-benzyl-4-chlorobenzamide (4ag)⁽³⁾

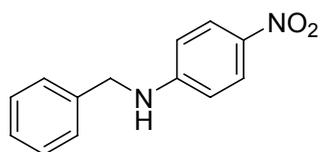
^1H NMR (CDCl_3 , 300 MHz) δ =7.34-7.23 (m, 5H), 7.09-7.04 (m, 2H), 6.51-6.46 (m, 2H), 4.24 (s, 2H), 3.40 (br, 1H). ^{13}C NMR (CDCl_3 , 75 MHz) δ =146.7, 139.0, 129.1, 128.8, 127.5, 127.4, 122.1, 114.0, 48.4.



(4ah)

N-benzyl-2-chlorobenzamide (4ah)⁽¹⁾

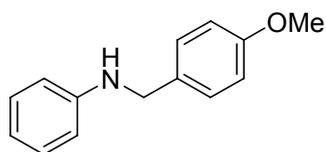
^1H NMR (CDCl_3 , 300 MHz) δ =7.32-7.22 (m, 6H), 7.07-7.02 (m, 1H), 6.62-6.57 (m, 2H), 4.67 (br, 1H), 4.33 (s, 2H). ^{13}C NMR (CDCl_3 , 75 MHz) δ =143.9, 138.9, 129.2, 128.8, 128.0, 127.5, 127.4, 119.2, 117.6, 111.7, 47.9.



(4ai)

N-benzyl-4-nitrobenzamide (4ai)⁽⁵⁾

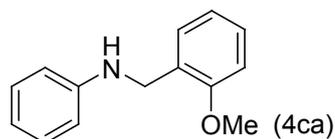
^1H NMR (CDCl_3 , 300 MHz) δ =8.09-8.04 (m, 2H), 7.39-7.30 (m, 5H), 6.59-6.54 (m, 2H), 4.94 (br, 1H), 4.43 (s, 2H). ^{13}C NMR (CDCl_3 , 75 MHz) δ =153.3, 137.5, 129.0, 127.9, 127.4, 126.5, 111.4, 47.7.



(4ba)

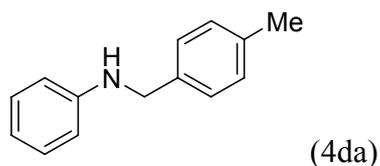
N-(4-methoxybenzyl)benzenamine (4ba)⁽⁶⁾

¹H NMR (CDCl₃, 300 MHz) δ= 7.41-7.27 (m, 4H), 7.01-6.98 (m, 2H), 6.87-6.82 (m, 1H), 6.75-6.72 (m, 2H), 4.34 (s, 2H), 3.89 (br, 1H), 3.89 (s, 3H). ¹³C NMR (CDCl₃, 75 MHz) δ=158.8, 148.2, 131.4, 129.4, 128.8, 117.5, 114.0, 112.8, 55.2, 47.7.



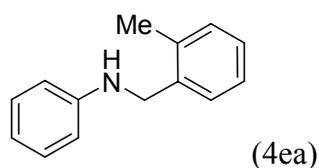
N-(2-methoxybenzyl)benzenamine (4ca)⁽⁷⁾

¹H NMR (CDCl₃, 300 MHz) δ=7.27-7.09 (m, 4H), 6.89-6.81 (m, 2H), 6.68-6.59 (m, 3H), 4.29 (s, 2H), 3.96 (br, 1H), 3.71(s, 3H). ¹³C NMR (CDCl₃, 75 MHz) δ=157.4, 148.4, 129.2, 128.9, 128.3, 127.4, 120.6, 117.3, 113.1, 110.3, 55.3, 43.4.



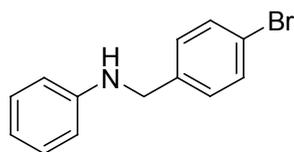
N-(4-methylbenzyl)benzenamine (4da)⁽²⁾

¹H NMR (CDCl₃, 300 MHz) δ=7.25-7.12 (m, 6H), 6.72-6.59 (m, 3H), 4.24 (s, 2H), 3.80 (br, 1H), 2.32 (s, 3H). ¹³C NMR (CDCl₃, 75 MHz) δ=148.3, 138.9, 136.4, 129.4, 129.3, 127.6, 117.6, 112.9, 48.2, 21.2.



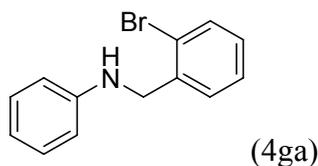
N-(2-methylbenzyl)benzenamine (4ea)⁽⁸⁾

¹H NMR (CDCl₃, 300 MHz) δ=7.29-7.27 (m, 1H), 7.20-7.12 (m, 5H), 6.72-6.66 (m, 1H), 6.59-6.56 (m, 2H), 4.20 (s, 2H), 3.67 (br, 1H), 2.33 (s, 3H). ¹³C NMR (CDCl₃, 75 MHz) δ=148.3, 137.1, 136.3, 130.4, 129.3, 128.3, 127.4, 126.2, 117.5, 112.7, 46.4, 18.9.



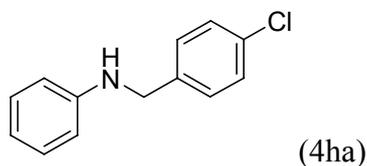
N-(4-bromobenzyl)benzenamine (4fa)⁽²⁾

¹H NMR (CDCl₃, 300 MHz) δ=7.44-7.39 (m, 2H), 7.21-7.11 (m, 4H), 6.73-6.67 (m, 1H), 6.58-6.54 (m, 2H), 4.23 (s, 2H), 3.81 (br, 1H). ¹³C NMR (CDCl₃, 75 MHz) δ=147.9, 138.2, 132.8, 129.4, 128.8, 117.8, 113.0, 47.6.



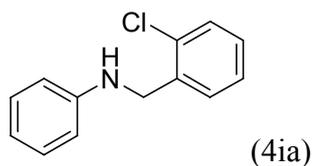
N-(2-bromobenzyl)benzenamine (4ga)⁽⁴⁾

¹H NMR (CDCl₃, 300 MHz) δ=7.54-7.51 (m, 1H), 7.36-7.33 (m, 1H), 7.22-7.04 (m, 4H), 6.72-6.66 (m, 1H), 6.57-6.53 (m, 2H), 4.33 (s, 2H), 3.93 (br, 1H). ¹³C NMR (CDCl₃, 75 MHz) δ= 147.8, 138.2, 132.8, 129.3, 129.2, 128.7, 127.6, 123.3, 117.8, 112.9, 48.4.



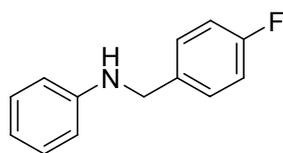
N-(4-chlorobenzyl)benzenamine (4ha)⁽¹⁾

¹H NMR (CDCl₃, 300 MHz) δ=7.43-7.38 (m, 2H), 7.19-7.11 (m, 4H), 6.73-6.67 (m, 1H), 6.57-6.54 (m, 2H), 4.21 (s, 2H), 3.79 (br, 1H). ¹³C NMR (CDCl₃, 75 MHz) δ=148.1, 138.4, 132.9, 129.5, 128.8, 117.9, 113.1, 47.5.



N-(2-chlorobenzyl)benzenamine (4ia)⁽⁹⁾

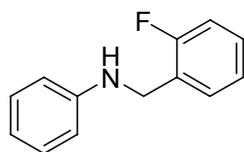
¹H NMR (CDCl₃, 300 MHz) δ=7.39-7.32 (m, 2H), 7.19-7.11 (m, 4H), 6.72-6.67 (m, 1H), 6.59-6.56 (m, 2H), 4.38 (s, 2H), 3.98 (br, 1H). ¹³C NMR (CDCl₃, 75 MHz) δ= 147.8, 136.7, 133.2, 129.6, 129.4, 129.0, 128.4, 127.0, 117.8, 112.9, 45.9.



(4ja)

N-(4-fluorobenzyl)benzenamine (4ja)⁽¹⁰⁾

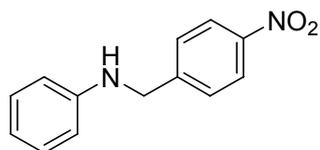
¹H NMR (CDCl₃, 300 MHz) δ=7.31-7.26 (m, 2H), 7.18-7.12 (m, 2H), 7.03-6.96 (m, 2H), 6.73-6.68 (m, 1H), 6.60-6.57 (m, 2H), 4.24 (s, 2H) 3.84 (br, 1H). ¹³C NMR (CDCl₃, 75 MHz) δ=163.8, 160.6, 148.2, 135.5, 129.5, 129.2, 129.1, 117.9, 115.7, 115.4, 113.1, 47.6.



(4ka)

N-(2-fluorobenzyl)benzenamine (4ka)

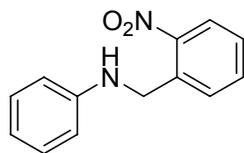
¹H NMR (CDCl₃, 300 MHz) δ=7.34-7.29 (m, 1H), 7.22-7.11 (m, 3H), 7.05-6.97 (m, 2H), 6.71-6.66 (m, 1H), 6.60-6.57 (m, 2H), 4.33 (s, 2H), 3.76 (br, 1H). ¹³C NMR (CDCl₃, 75 MHz) δ=160.9 (d, *j*=244.1), 147.9, 129.4 (d, *j*=41.2), 129.3, 128.8 (d, *j*=7.9), 126.4 (d, *j*=14.3), 124.2 (d, *j*=3.4), 117.8, 115.3 (d, *j*=21.9), 112.9, 41.8 (d, *j*=4.4). HRESIMS: (m/z) 202.1011 (M+H).



(4la)

N-(4-nitrobenzyl)benzenamine (4la)⁽⁶⁾

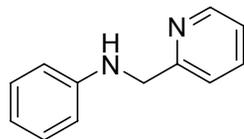
¹H NMR (CDCl₃, 300 MHz) δ=8.15-8.12 (m, 2H), 7.51-7.46 (m, 2H), 7.18-7.12 (m, 2H), 6.75-6.70 (m, 1H), 6.58-6.55 (m, 2H), 4.44 (s, 2H) 3.87 (br, 1H). ¹³C NMR (CDCl₃, 75 MHz) δ=147.7, 147.4, 147.0, 129.3, 127.6, 123.7, 118.0, 112.9, 47.4.



(4ma)

N-(2-nitrobenzyl)benzenamine (4ma)⁽¹¹⁾

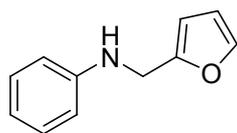
^1H NMR (CDCl_3 , 300 MHz) δ =8.05-8.02 (m, 1H), 7.65-7.63 (m, 1H), 7.55-7.50 (m, 1H), 7.41-7.35 (m, 1H), 7.17-7.11 (m, 2H), 6.73-6.68 (m, 1H), 6.56-6.53 (m, 2H), 4.69 (s, 2H), 4.27 (br, 1H). ^{13}C NMR (CDCl_3 , 75 MHz) δ =147.5, 135.7, 133.7, 129.8, 129.4, 128.0, 125.2, 118.0, 112.9, 48.4.



(4na)

N-((pyridin-2-yl)methyl)benzenamine (4na)⁽⁵⁾

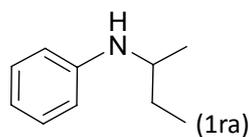
^1H NMR (CDCl_3 , 300 MHz) δ =8.55-8.53 (m, 1H), 7.60-7.55 (m, 1H), 7.28 (d, j =7.8Hz, 1H), 7.18-7.10 (m, 3H), 6.72-6.62 (m, 3H), 4.42 (s, 2H), 4.19 (br, 1H). ^{13}C NMR (CDCl_3 , 75 MHz) δ =158.6, 149.1, 147.9, 136.7, 129.2, 122.1, 121.6, 117.5, 113.0, 49.2.



(4oa)

N-((furan-2-yl)methyl)benzenamine (4oa)⁽⁶⁾

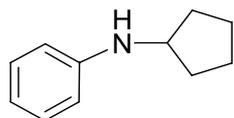
^1H NMR (CDCl_3 , 300 MHz) δ =7.32 (m, 1H), 7.19-7.12 (m, 2H), 6.74-6.69 (m, 1H), 6.64-6.61 (m, 2H), 6.29-6.27 (m, 1H), 6.19-6.18 (m, 1H), 4.22 (s, 2H), 3.74 (br, 1H). ^{13}C NMR (CDCl_3 , 75 MHz) δ =152.8, 147.7, 141.9, 129.3, 118.0, 113.2, 110.4, 107.0, 41.5.



(1ra)

N-sec-butylbenzenamine (1pa)⁽¹²⁾

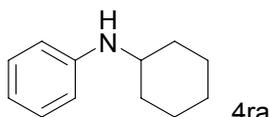
^1H NMR (CDCl_3 , 300 MHz) δ =7.14 (t, j =7.8, 2H), 6.64 (t, j =7.8, 1H), 6.55 (d, j =7.8, 2H), 3.48 (br, 1H), 3.43-3.34 (m, 1H), 1.62-1.39 (m, 2H), 1.14 (d, j =6.6, 3H), 0.93 (t, j =7.8, 7.5, 3H). ^{13}C NMR (CDCl_3 , 75 MHz) δ = 147.7, 129.3, 116.8, 113.1, 49.8, 29.7, 20.3, 10.5.



(4qa)

N-cyclopentylbenzenamine (4qa) ⁽¹²⁾

¹H NMR (CDCl₃, 300 MHz) δ=7.18-7.12 (m, 2H), 6.68-6.56 (m, 3H), 3.79-3.71 (m, 1H), 3.60 (br, 1H), 2.04-1.93 (m, 2H), 1.75-1.53 (m, 4H), 1.48-1.38 (m, 2H). ¹³C NMR (CDCl₃, 75 MHz) δ= 148.4, 129.4, 117.1, 113.5, 54.8, 33.8, 24.4.



4ra

N-cyclohexylbenzenamine (4ra) ⁽³⁾

¹H NMR (CDCl₃, 300 MHz) δ=7.18-7.11 (m, 2H), 6.67-6.55 (m, 3H), 3.39-3.19 (m, 1H), 2.07-2.02 (m, 2H), 1.78-1.61 (m, 3H), 1.43-1.07 (m, 5H). ¹³C NMR (CDCl₃, 75 MHz) δ= 147.5, 129.3, 116.9, 113.3, 51.8, 33.6, 26.1, 25.1.

Reference

- (1) W. Y. Liao, Y. F. Chen, Y. X. Liu, H. G. Duan, J. L. Petersen and X. D. Shi, *Chem. Commun.*, 2009, 6436.
- (2) B. Sreedhar, P. S. Reddy and D. K. Debi, *J. Org. Chem.*, 2009, **74**, 8806.
- (3) C. T. Yang, Y. Fu, Y. B. Huang, J. Yi, Q. X. Guo and L. Liu, *Angew. Chem. Int. Ed.*, 2009, **48**, 7398.
- (4) I. Shibata, T. Suwa, E. Sugiyama and A. Baba, *Synlett*, 1998, **10**, 1081.
- (5) R. J. He, P. H. Toy and Y. L. Lam, *Adv. Synth. Catal.*, 2008, **350**, 54.
- (6) P. D. Pham, P. Bertus and S. Legoupy, *Chem. Commun.*, 2009, 6207.
- (7) K. I. Fujita, Y. Enoki and R. Yamaguchi, *Tetrahedron*, 2008, **64**, 1943.
- (8) R. Y. Lai, C. I. Lee and S. T. Liu, *Tetrahedron*, 2008, **64**, 1213.
- (9) S. V. Kessar, R. Gopal and M. Singh, *Tetrahedron*, 1973, **29**, 167.
- (10) M. S. Kwon, S. Kim, S. Park, W. Bosco, R. K. Chidrala and J. Park, *J. Org. Chem.*, 2009, **74**, 2877.
- (11) M. M. Joseph and D. E. Jacob, *Indian J. Chem., Sect B.*, 2004, **43**, 432.
- (12) L. Xu, D. Zhu, F. Wu, R. L. Wang and B. S. Wan, *Tetrahedron*, 2005, **61**, 6553.

