JOC*Note*

Facile Formation of Cyclic Aminals through a Brønsted Acid-Promoted Redox Process

Chen Zhang, Sandip Murarka, and Daniel Seidel*

Department of Chemistry and Chemical Biology, Rutgers, The State University of New Jersey, Piscataway, New Jersey 08854

seidel@rutchem.rutgers.edu

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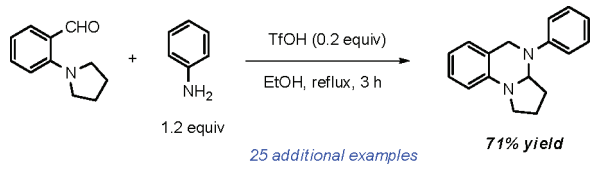
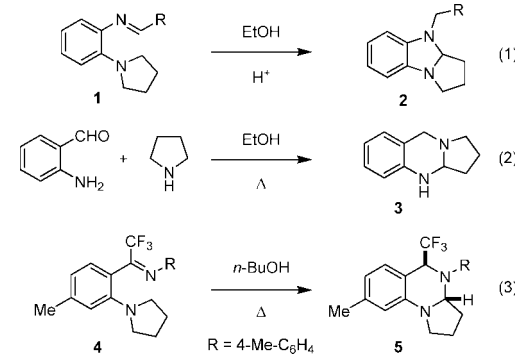


Cyclic aminals were prepared through a Brønsted acid-promoted reaction. This redox neutral process involves iminium ion formation, 1,5 H-transfer, followed by ring closure.

The term "*tert*-amino effect" has been used to describe a diverse number of reactions that proceed via intramolecular, C−C, or C−X bond-forming redox processes within conjugated systems.[1] These reactions involve the functionalization of a C−H bond α to a tertiary amine nitrogen and have also been referred to as "α-cyclization of tertiary amines".[2,3] In the vast majority of cases, these reactions are promoted thermally and relatively little effort has been devoted to developing catalytic approaches.[1] To ultimately expand the scope and applicability of these intriguing transformations, it is desirable to identify catalysts that would allow for milder reaction conditions as well as shorter reaction times. Here we report Brønsted acid-promoted syntheses of aminals from *o*-aminobenzaldehydes and aromatic or aliphatic amines that proceed in a simple single-flask procedure.

A number of aminal forming reactions have been reported that involve α-functionalizations of tertiary amines (eqs 1−3). The acid-catalyzed reaction outlined in eq 1 is an early example of the *tert*-amino effect and is known to occur in the presence of acid, often at room temperature.[4] The initially formed products **2** are typically unstable and known to readily undergo oxidation to the corresponding benzimidazolium salts.[4] We have recently reported a new process in which aminobenzaldehydes react with cyclic amines under thermal conditions to produce aminals such as **3** (eq 2).[5] The formation of both **2** and **3** is thought to involve a 1,6-hydride shift process as the initial step preceding ring closure. Interestingly, only one report has appeared for the mechanistically distinct transformation of imine **4** to aminal **5** (eq 3) that is initiated by a 1,5-hydride shift.[6,7] Heating of **4** in *n*-butanol under reflux for 5 days was reported to provide **5** in 66% yield as a single diastereomer.[6]



We reasoned that this transformation should be readily realized as a single-flask acid-catalyzed procedure that does not require the isolation of the intermediate imine (Scheme 1). Thus, the reaction of *o*-aminobenzaldehydes such as **6** with amines is expected to provide access to potentially useful heterocyclic scaffolds **7**.[8−10]

Brønsted and Lewis acids were evaluated as catalysts for the reaction of aminobenzaldehyde **6** with aniline (Table 1, entries

(1) For reviews, see: (a) Meth-Cohn, O.; Suschitzky, H. *Adv. Heterocycl. Chem.* **1972**, *14*, 211–278. (b) Verboom, W.; Reinhoudt, D. N. *Recl. Trav. Chim. Pays-Bas* **1990**, *109*, 311–324. (c) Meth-Cohn, O. *Adv. Heterocycl. Chem.* **1996**, *65*, 1–37. (d) Quintela, J. M. *Recent Res. Dev. Org. Chem.* **2003**, *7*, 259–278. (e) Matyus, P.; Elias, O.; Tapolcsanyi, P.; Polonka-Balint, A.; Halasz-Dajka, B. *Synthesis* **2006**, 2625–2639.

(2) (a) Jiang, S.; Janousek, Z.; Viehe, H. G. *Bull. Soc. Chim. Belg.* **1993**, *102*, 663–668. (b) Jiang, S.; Janousek, Z.; Viehe, H. G. *Tetrahedron Lett.* **1994**, *35*, 1185–1188. (c) De Boeck, B.; Jiang, S.; Janousek, Z.; Viehe, H. G. *Tetrahedron* **1994**, *50*, 7075–7092. (d) De Boeck, B.; Janousek, Z.; Viehe, H. G. *Tetrahedron* **1995**, *51*, 13239–13246.

(3) These reactions are mechanistically distinct from other oxidative approaches that lead to α-functionalization of tertiary amines. For an excellent review on this topic, see: Campos, K. R. *Chem. Soc. Rev.* **2007**, *36*, 1069–1084.

(4) (a) Meth-Cohn, O.; Naqui, M. A. *Chem. Commun.* **1967**, 1157–1158. (b) Grantham, R. K.; Meth-Cohn, O. *Chem. Commun.* **1968**, 500–502. (c) Grantham, R. K.; Meth-Cohn, O.; Naqui, M. A. *J. Chem. Soc., C* **1969**, 1438–1443. (d) Grantham, R. K.; Meth-Cohn, O. *J. Chem. Soc., C* **1969**, 1444–1448. (e) Clark-Lewis, J. W.; Moody, K.; Thompson, M. J. *Aust. J. Chem.* **1970**, *23*, 1249–1273. (f) Ryabukhin, S. V.; Plaskon, A. S.; Volochnyuk, D. M.; Shivanyuk, A. N.; Tolmachev, A. A. *J. Org. Chem.* **2007**, *72*, 7417–7419. (g) Che, X.; Zheng, L.; Dang, Q.; Bai, X. *Synlett* **2008**, 2373–2375.

(5) Zhang, C.; De, C. K.; Mal, R.; Seidel, D. *J. Am. Chem. Soc.* **2008**, *130*, 416–417.

(6) Verboom, W.; Hamzink, M. R. J.; Reinhoudt, D. N.; Visser, R. *Tetrahedron Lett.* **1984**, *25*, 4309–4312.

(7) In related reactions that involve attempted Vilsmeier formylations of 4-substituted, tertiary anilines, the intermediate iminium salts undergo a number of different rearrangements: (a) Meth-Cohn, O.; Taylor, D. L. *J. Chem. Soc., Chem. Commun.* **1995**, 1463–1464. (b) Meth-Cohn, O.; Cheng, Y. *Tetrahedron Lett.* **1996**, *37*, 2679–2682. (c) Cheng, Y.; Meth-Cohn, O.; Taylor, D. *J. Chem. Soc., Perkin Trans. 1* **1998**, 1257–1262. (d) Patsenker, L. D.; Ermolenko, I. G.; Artyukhova, E. E.; Krasovitskii, B. M. *Chem. Heterocycl. Compd.* **2000**, *36*, 611–612. (e) Patsenker, L. D.; Ermolenko, I. G.; Fedyunyaeva, I. A.; Popova, N. A.; Krasovitskii, B. M. *Chem. Heterocycl. Compd.* **2000**, *36*, 623–625. (f) Patsenker, L. D.; Yermolenko, I. G.; Artyukhova, Y. Y.; Baumer, V. N.; Krasovitskii, B. M. *Tetrahedron* **2000**, *56*, 7319–7323. (g) Cheng, Y.; Liu, Q.-X.; Meth-Cohn, O. *Synthesis* **2000**, 640–642. (h) Cheng, Y.; Liu, Q.-X.; Meth-Cohn, O. *Tetrahedron Lett.* **2000**, *41*, 3475–3478. (i) Cheng, Y.; Jiao, P.; Williams, D. J.; Cohn, O.-M. *J. Chem. Soc., Perkin Trans. 1* **2001**, 44–46. (j) Cheng, Y.; Yang, H.-B.; Liu, B.; Meth-Cohn, O.; Watkin, D.; Humphries, S. *Synthesis* **2002**, 906–910. (k) Cheng, Y.; Wang, B.; Meth-Cohn, O. *Synthesis* **2003**, 2839–2843. (l) Semenova, O. N.; Kudryavtseva, Y. A.; Ermolenko, I. G.; Patsenker, L. D. *Russ. J. Org. Chem.* **2005**, *41*, 1100–1101. (m) Ryabtsova, O. V.; Pozharskii, A. F.; Degtyarev, A. V.; Ozeryanskii, V. A. *Mendeleev Commun.* **2006**, 313–316.

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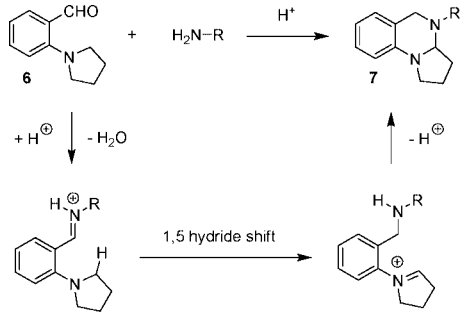
SCHEME 1. Proposed Brønsted Acid-Promoted Process



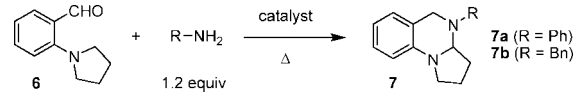
1−14). No formation of **7a** was observed in the absence of acid for a reaction performed in ethanol. The addition of trifluoroacetic acid (20 mol %) to a reaction run at room temperature led to product formation, but the reaction remained incomplete after 48 h (Table 1, entry 1). Under the same conditions but at reflux temperature, the reaction was complete after 12 h and **7a** was isolated in 66% yield (Table 1, entry 2). Addition of excess trifluoroacetic acid (Table 1, entry 7) did not lead to a shortened reaction time but instead resulted in a reduced yield of product **7a**. Other acids are viable catalysts, including Lewis acids such as zinc triflate and ytterbium triflate. Ultimately, triflic acid (20 mol%) was identified as the optimal catalyst with **7a** being isolated in 71% yield (Table 1, entry 8). Ethanol was shown to be the best solvent among those tested.

A different reactivity pattern was seen for the reaction of aminobenzaldehyde **6** with benzylamine (Table 1, entries 15−27). No reaction was observed in the absence or presence of trifluoroacetic acid (20 mol %) at room temperature (Table 1, entry 15). Performing the reaction in the presence of trifluoroacetic acid (20 mol %) under reflux conditions led to full conversion and formation of **7b** in 54% yield (Table 1, entry 16). The maximum yield for **7b** (75%) was obtained when excess trifluoroacetic acid (1.2 equiv) was used (Table 1, entry 21). Other Brønsted and Lewis acids are viable catalysts/promoters of this reaction, but proved less efficient in terms of reaction time and/or yield.

In cases where less than 1 equiv of acid is used to facilitate rearrangement, the actual acid catalyst is presumed to be an ammonium salt. Of course, the nature of the counteranion is expected to have a drastic, if nonobvious role, as complex counterion effects are well-documented in the context of iminium catalysis.[11]

The scope of the reaction of aminobenzaldehyde **6** with different aromatic amines was subsequently evaluated (Table 2, entries 1−9). Electronically diverse anilines with various substitution patterns provided access to products **7** in moderate

TABLE 1. Evaluation of Potential Catalysts[a]



entry	R	catalyst (equiv)	solvent	time [h]	yield [%]
1[b]	Ph	CF_3COOH (0.2)	EtOH	48	38[c]
2	Ph	CF_3COOH (0.2)	EtOH	12	66
3	Ph	CF_3COOH (0.2)	MeCN	5	57
4	Ph	CF_3COOH (0.2)	THF	12	38[c]
5	Ph	CF_3COOH (0.2)	CH_2Cl_2	36	30[c]
6	Ph	CF_3COOH (0.2)	PhH	7	60
7	Ph	CF_3COOH (1.2)	EtOH	12	53
8	Ph	CF_3SO_3H (0.2)	EtOH	3	71
9	Ph	4-Me-$C_6H_4SO_3H$ (0.2)	EtOH	12	53
10	Ph	2,4-$(NO_2)_2$-$C_6H_3SO_3H$ (0.2)	EtOH	12	66
11	Ph	CH_3COOH (0.2)	EtOH	24	50[c]
12	Ph	HCl (1.2)	EtOH	12	71
13	Ph	$Zn(OTf)_2$ (0.1)	EtOH	12	52
14	Ph	$Yb(OTf)_3$ (0.1)	EtOH	12	45
15[b]	Bn	CF_3COOH (0.2)	EtOH	24	NR
16	Bn	CF_3COOH (0.2)	EtOH	24	54
17	Bn	CF_3COOH (0.2)	MeCN	24	57
18	Bn	CF_3COOH (0.2)	THF	24	NR
19	Bn	$MeSO_3H$ (0.2)	EtOH	24	53[c]
20	Bn	4-Me-$C_6H_4SO_3H$ (0.2)	EtOH	24	48[c]
21	Bn	CF_3COOH (1.2)	EtOH	12	75
22	Bn	H_3PO_4 (0.2)	EtOH	24	NR
23	Bn	CH_3COOH (0.2)	EtOH	24	31[c]
24	Bn	CF_3SO_3H (0.2)	EtOH	24	60
25	Bn	HCl (1.2)	EtOH	12	47
26	Bn	$Zn(OTf)_2$ (0.1)	EtOH	24	53
27	Bn	$Yb(OTf)_3$ (0.1)	EtOH	24	53

[a] Reactions were performed in a given solvent (0.1 M) under reflux on a 0.25 mmol scale and were run to full conversion as judged by TLC analysis. [b] Performed at room temperature. [c] Reaction did not go to full conversion.

to good yields. Bulky substituents on both ortho-positions of the aniline moiety were readily accommodated (Table 2, entry 3). Interestingly, the reaction of **6** with 4-cyanoaniline proceeded readily at room temperature to provide the corresponding product **7f** in 50% yield (Table 2, entry 5). The use of heterocyclic amines such as 2-aminopyridine or aminopyrimidine (Table 2, entries 8 and 9) gave rise to products **7i** and **7j** in lower yields, presumably due to the availability of multiple protonation sites that might interfere with the catalytic process. Aliphatic amines were also evaluated in the reaction with aminobenzaldehyde **6** and gave rise to products **7** in good yields (Table 2, entries 10−13), using reaction conditions previously optimized for benzylamine.

The scope of the reaction with regard to the aminobenzaldehyde component is summarized in Table 3. A number of structurally diverse aminobenzaldehydes gave rise to products **9** upon reaction with primary amines in the presence of acid. The required starting materials were readily obtained from 2-fluorobenzaldehyde and the corresponding secondary amines.[12] Aminobenzaldehydes derived from cyclic amines bearing benzylic α C−H bonds were particularly reactive (Table

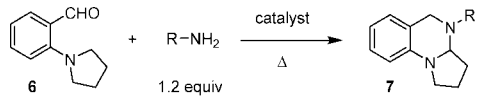
(8) For related, Lewis acid-catalyzed reactions in nonconjugated systems, see: (a) Woelfling, J.; Frank, E.; Schneider, G.; Tietze, L. F. *Eur. J. Org. Chem.* **2004**, 90–100. (b) Pastine, S. J.; McQuaid, K. M.; Sames, D. *J. Am. Chem. Soc.* **2005**, *127*, 12180–12181. (c) Pastine, S. J.; Sames, D. *Org. Lett.* **2005**, *7*, 5429–5431.

(9) For selected publications on the chemistry of aminals and alternate methods for their preparation, see: (a) Campi, E. M.; Jackson, W. R.; McCubbin, Q. J.; Trnacek, A. E. *Aust. J. Chem.* **1994**, *47*, 1061–1070. (b) Alexakis, A.; Mangeney, P. *Adv. Asym. Synth.* **1996**, 93–110. (c) Simon, C.; Peyronel, J.-F.; Rodriguez, J. *Org. Lett.* **2001**, *3*, 2145–2148. (d) Sinha, N.; Jain, S.; Anand, N. *Tetrahedron Lett.* **2004**, *46*, 153–156. (e) Hiersemann, M. Functions bearing two nitrogens. In *Comprehensive Organic Functional Group Transformations II*; Katritzky, A. R. T., RichardJ. K., Ed.; Elsevier Ltd.: Oxford, UK, 2005; Vol. 4, pp 411−441. (f) Rowland, G. B.; Zhang, H.; Rowland, E. B.; Chennamadhavuni, S.; Wang, Y.; Antilla, J. C. *J. Am. Chem. Soc.* **2005**, *127*, 15696–15697. (g) Zhang, Y.; Fu, H.; Jiang, Y.; Zhao, Y. *Org. Lett.* **2007**, *9*, 3813–3816.

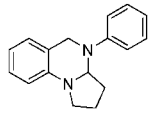
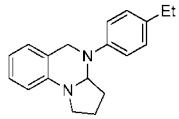
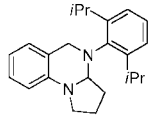
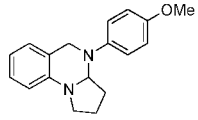
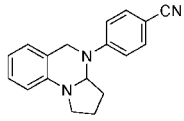
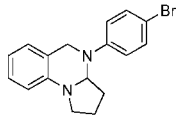
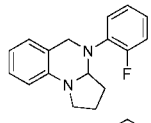
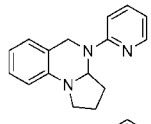
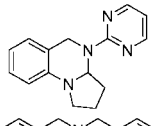
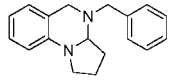
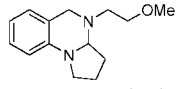
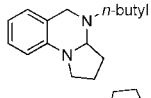
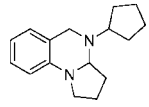
(10) Aminals are found in a number of natural products. For selected examples, see: (a) Braekman, J. C.; Daloze, D.; Pasteels, J. M.; Van Hecke, P.; Declercq, J. P.; Sinnwell, V.; Francke, W. *Z. Naturforsch., C: J. Biosci.* **1987**, *42*, 627–630. (b) Hino, T.; Nakagawa, M. Chemistry and reactions of cyclic tautomers of tryptamines and tryptophans. In *Alkaloids*; Academic Press: New York, 1988; Vol. 34, pp 1−75. (c) Hajicek, J.; Taimr, J.; Budesinsky, M. *Tetrahedron Lett.* **1998**, *39*, 505–508. (d) Crich, D.; Banerjee, A. *Acc. Chem. Res.* **2007**, *40*, 151–161.

(11) For a recent review on iminium catalysis, see: Erkkilae, A.; Majander, I.; Pihko, P. M. *Chem. Rev.* **2007**, *107*, 5416–5470.

TABLE 2. Variation of the Amine Component[a]



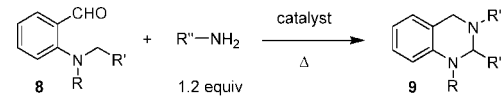
6 7

entry	method	product		time [h]	yield [%]
1	A		**7a**	3	71
2	A		**7c**	12	67
3	A		**7d**	5	71
4	A		**7e**	0.5	57
5	C		**7f**	15	50
6	A		**7g**	1.5	65
7	A		**7h**	6	50
8	A		**7i**	24	35
9	A		**7j**	48	36
10	B		**7b**	24	75
11	B		**7k**	15	70
12	B		**7l**	24	65
13	B		**7m**	24	66

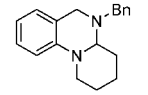
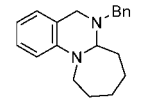
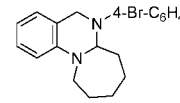
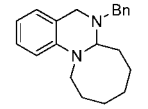
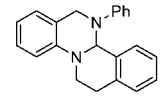
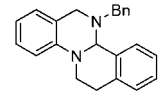
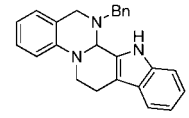
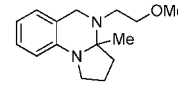
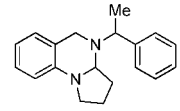
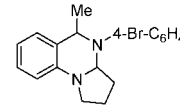
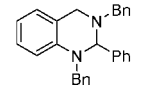
[a] Reactions were performed on a 1 mmol scale in EtOH (0.1 M) and were run to full conversion as judged by TLC analysis. Method A: CF_3SO_3H (0.2 equiv), reflux. Method B: CF_3COOH (1.2 equiv), reflux. Method C: CF_3SO_3H (0.2 equiv), room temperature.

2, entries 5−7), presumably due to the increased hydride donor capabilities of these substrates. Compound **9h** was isolated as a single regioisomer resulting from functionalization at the more hindered position (Table 3, entry 8). This finding likely reflects

TABLE 3. Variation of the Aminobenzaldehyde Component[a]



8 9

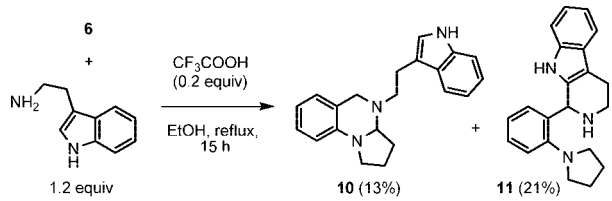
entry	method	product		time [h]	yield [%]
1	B		**9a**	24	65
2	B		**9b**	2	82
3	A		**9c**	1.5	90
4	B		**9d**	1.5	85
5	C		**9e**	12	99
6	B		**9f**	0.5	64
7	B		**9g**	1	74
8	B		**9h**	1	60
9	B		**9i**[b]	15	52
10	A		**9j**[c]	3	65
11	B		**9k**	12	27

[a] Reactions were performed on a 1 mmol scale in EtOH (0.1 M) and were run to full conversion as judged by TLC analysis. Method A: CF_3SO_3H (0.2 equiv), reflux. Method B: CF_3COOH (1.2 equiv), reflux. Method C: CF_3SO_3H (0.2 equiv), room temperature. [b] dr = 59:41. [c] dr = 66:34.

the increased hydride donor capability of a tertiary over a secondary C−H bond. Reaction of **6** with α-methylbenzylamine gave rise to products **9i**as a 59:41 mixture of diastereomers (Table 3, entry 9). Similarly, reaction of 2-pyrrolidinyl acetophenone with 4-bromoaniline resulted in the formation of **9j** as a 66:34 mixture of diastereomers (Table 3, entry 10), illustrating that aminoacetophenones are also viable substrates

(12) (a) Nijhuis, W. H. N.; Verboom, W.; Abu El-Fadl, A.; Harkema, S.; Reinhoudt, D. N. *J. Org. Chem.* **1989**, *54*, 199–209. (b) Nijhuis, W. H. N.; Leus, G. R. B.; Egberink, R. J. M.; Verboom, W.; Reinhoudt, D. N. *Recl. Trav. Chim. Pays-Bas* **1989**, *108*, 172–178. (c) D'yachenko, E. V.; Glukhareva, T. V.; Nikolaenko, E. F.; Tkachev, A. V.; Morzherin, Y. Y. *Russ. Chem. Bull.* **2004**, *53*, 1240–1247.

SCHEME 2. Competing Reaction Pathways



in this transformation. The low isolated yield of product **9k** is likely a reflection of product instability rather than reactivity of the starting material (Table 3, entry 11) as full conversion of the aminobenzaldehyde was observed.

The reaction of **6** with tryptamine was investigated in order to compare the title reaction to a potentially competing Pictet−Spengler pathway. (Scheme 2).[4g] Interestingly, a mixture of both products was obtained with the product resulting from the Pictet−Spengler reaction (**11**) being the predominantly formed species. Although the overall yields of this nonoptimized process are low, the findings demonstrate the relative ease with which acid-catalyzed hydride shift reactions can occur.

In summary, we have shown that reactions involving the "*tert*-amino effect" can be accelerated by Brønsted acids. This allowed for the synthesis of potentially useful and previously unknown aminals under mild conditions, species that are not readily obtainable by other means. The exploration of catalytic approaches to related reactions is ongoing and results will be reported in due course.

Experimental Section

General Procedure A for the Reaction between Aminoaldehydes and Amines. To a stirred solution of aminoaldehyde (1 mmol) in 10 mL of EtOH was added the primary amine (1.2 mmol) and triflic acid (0.2 mmol), followed by heating at reflux. The reaction mixture was monitored by TLC. After the completion of the reaction, 0.3 mL of triethylamine was added. The solution was concentrated in vacuo and the crude product was dissolved in ethyl acetate (20 mL) and washed with 25 mL of 1 M NaOH. The aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with brine (25 mL) and dried with sodium sulfate. The solvent was removed in vacuo and the crude product was purified by column chromatography.

General Procedure B for the Reaction between Aminoaldehydes and Amines. To a stirred solution of aminoaldehyde (1 mmol) in 10 mL of EtOH was added the primary amine (1.2 mmol) and trifluoroacetic acid (1.2 mmol), followed by heating at reflux. The reaction mixture was monitored by TLC. After the completion of the reaction, 1.0 mL of triethylamine was added. The reaction mixture was worked up according to procedure A.

General Procedure C for the Reaction between Aminoaldehydes and Amines. To a stirred solution of aminoaldehyde (1 mmol) in 10 mL of EtOH was added the primary amine (1.2 mmol) and triflic acid (0.2 mmol), followed by stirring at room temperature. The reaction mixture was monitored by TLC. After the completion of the reaction, 0.3 mL of triethylamine was added. The reaction mixture was worked up according to procedure A.

7a: The reaction was carried out according to general procedure A (3 h). The product was obtained as a white solid in 71% yield (R_f 0.34 in 8% EtOAc/Hex); mp 82 − 84 °C; IR (KBr) 3031, 2970, 2937, 2835, 1606, 1596, 1510, 1494, 1477, 1461, 1398, 1363, 1323, 1308, 1256, 1207, 1193, 774, 702 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.32 (app tt, J = 2.0, 3.9 Hz, 2H), 7.22−7.10 (m, 4H), 6.97 (d, J = 7.4 Hz, 1H), 6.69−6.63 (m, 1H), 6.54 (d, J = 8.0 Hz, 1H), 4.65 (dd, J = 5.3, 8.3 Hz, 1H), 4.40 (d, J = 14.9 Hz, 1H), 4.12 (d, J = 14.9 Hz, 1H), 3.47 (app td, J = 3.1, 8.7 Hz, 1H), 3.39 (dd, J = 8.6, 16.2 Hz, 1H), 2.14−1.85 (comp, 3H), 1.80−1.68 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) 150.3, 143.5, 128.9, 127.8, 125.9, 125.2, 124.7, 120.8, 116.2, 111.3, 76.7, 57.3, 47.1, 31.9, 22.2; *m*/*z* (ESIMS) 251.2 $[M + H]^+$.

7b: The reaction was carried out according to general procedure B (24 h). The product was obtained as a colorless oil in 75% yield (R_f 0.24 in 2% EtOAc/DCM); IR (film) 3066, 3025, 2968, 2834, 1606, 1578, 1509, 1483, 1462, 1395, 1369, 1321, 1304, 1160, 1130, 741, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.45−7.26 (comp, 5H), 7.11 (app t, J = 7.5 Hz, 1H), 6.83 (d, J = 7.2 Hz, 1H), 6.59 (app td, J = 0.9, 7.4 Hz, 1H), 6.47 (d, J = 8.0 Hz, 1H), 4.17 (dd, J = 5.3, 8.3 Hz, 1H), 3.95 (d, J = 13.1 Hz, 1H), 3.69 (d, J = 14.8 Hz, 1H), 3.57 (d, J = 14.8 Hz, 1H), 3.50−3.30 (comp, 3H), 2.35−2.25 (m, 1H), 2.19−2.09 (m, 1H), 2.07−1.86 (comp, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) 143.2, 138.3, 129.0, 128.3, 127.6, 127.1, 126.4, 119.4, 115.7, 110.3, 78.4, 56.5, 54.4, 46.6, 31.8, 22.4; *m*/*z* (ESIMS) 265.2 $[M + H]^+$.

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Supporting Information Available: Detailed experimental procedures and characterization data for all new compounds including X-ray structures of **7d**, **9e**, **9f**, and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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