Synthesis of 2-(Arylamino)-2-(arylimino)acetamides

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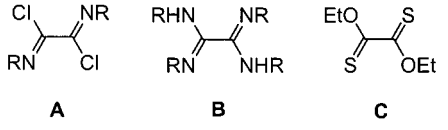
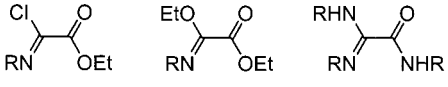
The reaction of 2-(arylamino)-2-oxoacetates with PCl_5 afforded 2-(arylamino)-2,2-dichloroacetates. The reaction of these compounds with aniline derivatives allowed a convenient synthesis of a great variety of 2-(arylamino)-2-(arylimino)acetamides.

Introduction

Oxalic acid derivatives represent versatile synthetic building blocks and have been broadly used as 1,2-dielectrophiles. Symmetrical structures are very common and include, for example, oxalyl chloride,[1,2] dialkyl oxalates,[3] 1,4-dimethylpiperazine-2,3-dione,[4] *N*,*N*′-dimethoxy-*N*,*N*′-dimethylethanediamide,[5] oxaldiimidoyl dichlorides **A**,[6] dialkyl oxaldiimidoates,[7] oxaldiamidines **B**[8] or dithiooxalates **C**.[9] Unsymmetrical derivatives are more rare and include ethyl 2-chloro-2-oxoacetate[10] and related derivatives, such as ethyl 2-(*N*-imidazolyl)-2-oxoacetate[10] and 2-ethoxy-*N*-methoxy-*N*-methyl-2-oxoethaneamide.[10] In addition, unsymmetrical imidoyl derivatives have been reported which include 2-(arylimino)-2-chloroacetates **D**,[11] 2-chloro-2-hydrazonoacetates[12] and 2-alkoxy-2-iminoacetates **E**.[13]



A **B** **C**



D **E** **F**

The synthesis of two examples of ethyl 2-(arylamino)-2,2-dichloroacetates, which can be regarded as hydrochlorides of **D**, was reported as early as in 1877 and a few synthetic applications have been also described.[14] In the course of our study, a number of new 2-amino-2,2-dichloroacetate derivatives were prepared and characterized spectroscopically. In addition, we wish to report the synthesis of 2-(arylamino)-2-(arylimino)acetamides **F** which relies on the reaction of 2-(arylamino)-2,2-dichloroacetates with amines. Alternative methods for the preparation of 2-(arylamino)-2-(arylimino)acetamides are known, however, only a few derivatives have been reported so far.[15,16] An isolated example of a synthesis from a 2-(arylamino)-2,2-dichloroacetate has been previously reported.[15e] However, the preparative scope has not been studied. 2-(Arylamino)-2-(arylimino)acetamides represent structurally and synthetically interesting building blocks. They combine the functional groups of amides and amidines and prototropic shifts and (*E*)/(*Z*) isomerizations can occur. Spectroscopic data are rarely reported in the literature.[16] It is important to note for comparison that the related *symmetrical* diamidines **B** are indeed of considerable structural[17] and practical interest.[8] They represent useful starting materials for the synthesis of tetraaminoalkenes[18] and of many heterocyclic systems[6,19] which are of pharmacological relevance and of interest in the field of material sciences.

Results and Discussion

The reaction of commercially available ethyl 2-chloro-2-oxoacetate (**1**) with aniline gave the known amide **3a**. Treatment of the latter with PCl_5 afforded the known 2-(arylamino)-2,2-dichloroacetate **4a**[14] as a colourless solid.

Spectroscopic analysis of **4a** showed that this compound resides in the form of a 2-amino-2,2-dichloroacetate which can be regarded as a hydrochloride of the corresponding imidoyl chloride. In the ^{13}C NMR spectrum, a characteristic signal was observed at $\delta = 107.68$ ppm which was assigned to the carbon atom attached to the chlorine atoms. As expected, only one low-field signal was observed ($\delta = 160.21$ ppm) which was assigned to the ester group. For

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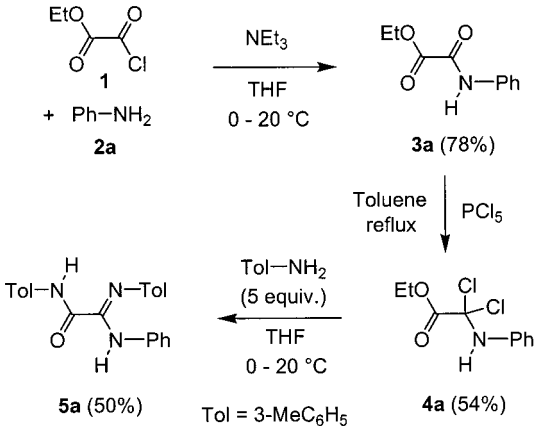
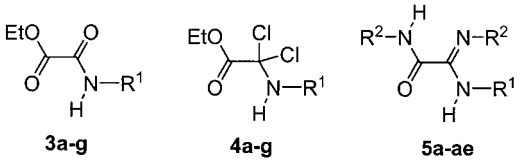
comparison, a low-field signal is generally observed for the imino carbon atom of the yellow oxaldiimidoyl dichlorides **A**. The 2-amino-2,2-dichloroacetates **4** should be stored at −20 °C under argon and exclusion of moisture. Standing of **4a** at room temperature in the presence of air resulted in elimination of HCl and hydrolysis of the imidoyl chloride to give **3a**. The concentration, reaction time and exclusion of moisture were crucial parameters during the optimization of the reaction conditions.



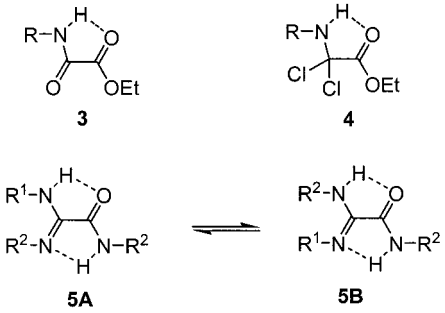
Scheme 1. Synthesis of 2-(arylamino)-2,2-dichloroacetate **4a** and of 2-(arylamino)-2-iminoacetamide **5a**; the assignment of the substituents of the amidine group is arbitrary

Treatment of **4a** with an excess of *m*-toluidine (5 equiv.) resulted in the formation of the 2-(arylamino)-2-iminoacetamide **5a**. The stoichiometry and the temperature proved to be important parameters during the optimization of this reaction (vide infra). The formation of **5a** can be explained by elimination of hydrogen chloride and formation of an imidoyl chloride which was subsequently attacked by the amine. Surprisingly, the ester was completely transformed into the amide despite the mild reaction conditions. All attempts to prepare the ester analogue of **5a**, by variation of the stoichiometry and of the temperature, failed.

The 2-(arylamino)-2-oxoacetates **3a**−**g** were prepared from **1** in 61−87% yield (Table 1). The chlorination (PCl_5) of these compounds afforded the 2-(arylamino)-2,2-dichloroacetates **4a**−**g** in 30−71% yield. The reaction of **4** with aniline derivatives afforded the novel 2-(arylamino)-2-iminoacetamides **5a**−**ae** in 32−73% yields. Functionalized derivatives, containing methoxy, dimethylamino or nitro groups, were successfully prepared.



Inspection of the ^1H NMR spectra of ethyl 2-(arylamino)-2-oxoacetates **3** showed the presence of low-field signals assigned to the NH groups (**3a**−**c**: δ = 8.85−8.88 ppm, in $CDCl_3$). The hydrogen atoms are presumably involved in intramolecular hydrogen bonds N-H···O. For **3e** and **3f**, these signals appear at δ = 10.52−10.60 ppm. Due to the use of [D_6]DMSO, the intramolecular hydrogen bonds are cleaved and replaced by intermolecular hydrogen bonds to the solvent. A low-field shift (δ = 11.30 ppm) was observed for **3g**, due to the presence of the nitro group. Low-field signals were observed also for ethyl 2-(arylamino)-2,2-dichloroacetates **4**. Due to the absence of the amide carbonyl group the signals of **4a**−**c** were shifted to higher field (δ = 8.14−8.21 ppm, in $CDCl_3$) relative to the corresponding signals of **3a**−**c**. A low-field shift was observed for the nitro derivative **4g** (δ = 9.17 ppm, in $CDCl_3$).



Two low-field signals were observed for amidoamidines **5**. The low-field signal was assigned to the amide NH group which is, in $CDCl_3$, involved in a stable hydrogen bond N-H···N (δ = 9.98−10.48 ppm, in $CDCl_3$). The greatest downfield shift was observed for **5ae** containing a nitro group. The second signal in the range of δ = 8.08−8.59 ppm (in $CDCl_3$) can be assigned to the amidine hydrogen atom which is involved in a hydrogen bond N-H···O. The latter is less stable than the hydrogen bond N-H···N. Amidines **5** represent structurally highly flexible molecules, due to 1,3-prototropic shifts (**5A** and **5B**) and (*E*)/(*Z*) isomerizations of the imino and amide groups. At room temperature, a fast equilibrium and coalescence is observed for all amidines **5** reported herein. For example, three broad singlets were observed (in CD_2Cl_2) for the methyl groups of **5n** at δ = 2.12 (6 H), 2.17 (6 H) and 2.35 (3 H) ppm. Upon cooling, coalescence was observed at 233 K and five separated signals appeared at 193 K. Due to the coalescence, broad signals and a reduced number of signals were observed in the ^{13}C NMR spectra of all products at 20 °C.

Our current studies are directed towards the development of further synthetic applications of 2-(arylamino)-2,2-dichloroacetates and 2-(arylamino)-2-iminoacetamides.

Experimental Section

General: All solvents were dried by standard methods and all reactions were carried out under an inert gas. For the ^1H and ^{13}C NMR spectra (^1H NMR: 200, 300 MHz; ^{13}C NMR: 50, 75 MHz) the de-

Table 1. Products and yields; the assignment of the substituents of the amidine group is arbitrary

3, **4**	**5**	R^1	R^2	% (**3**)[a]	% (**4**)[a]	% (**5**)[a]	δ(^{1}H) (**5**)
a	**a**	C_6H_5	3-MeC_6H_4	78	54	50	9.62, 10.54[b]
a	**b**	C_6H_5	2,4-$Me_2C_6H_3$			51	8.06, 10.19[b]
a	**c**	C_6H_5	3,5-$Me_2C_6H_3$			37	8.49, 10.19[b]
a	**d**	C_6H_5	2-(MeO)C_6H_4			54	8.41, 9.89[b]
a	**e**	C_6H_5	4-(Me_2N)C_6H_4			70	–
b	**f**	2-MeC_6H_4	C_6H_5	87	48	73	8.57, 10.21[b]
b	**g**	2-MeC_6H_4	3-MeC_6H_4			36	9.23, 9.88[b]
b	**h**	2-MeC_6H_4	2,4-$Me_2C_6H_3$			60	8.24, 10.38[b]
b	**i**	2-MeC_6H_4	3,5-$Me_2C_6H_3$			55	8.09, 10.21[b]
b	**j**	2-MeC_6H_4	2-(MeO)C_6H_4			50	8.53, 10.25[b]
b	**k**	2-MeC_6H_4	4-(Me_2N)C_6H_4			36	8.35, 10.36[b]
c	**l**	4-MeC_6H_4	C_6H_5	82	31	51	9.62, 10.50[b]
c	**m**	2-MeC_6H_4	3-MeC_6H_4			67	–
c	**n**	2-MeC_6H_4	2,4-$Me_2C_6H_3$			40	8.19, 10.22[c]
c	**o**	2-MeC_6H_4	3,5-$Me_2C_6H_3$			36	8.59, 10.19[c]
c	**p**	2-MeC_6H_4	2-(MeO)C_6H_4			51	8.08, 10.00[b]
c	**q**	2-MeC_6H_4	4-(Me_2N)C_6H_4			50	–
d	**r**	2,4-$Me_2C_6H_3$	C_6H_5	61	48	55	8.51, 10.00[b]
d	**s**	2,4-$Me_2C_6H_3$	3-MeC_6H_4			48	8.51, 10.00[b]
d	**t**	2,4-$Me_2C_6H_3$	2-(MeO)C_6H_4			52	8.53, 10.25[c]
d	**u**	2,4-$Me_2C_6H_3$	4-(Me_2N)C_6H_4			45	–
e	**v**	3,5-$Me_2C_6H_3$	C_6H_5			32	8.50, 10.00[c]
e	**w**	3,5-$Me_2C_6H_3$	3-MeC_6H_4			51	8.40, 10.00[b]
e	**x**	3,5-$Me_2C_6H_3$	2-(MeO)C_6H_4			50	8.51, 10.00[b]
e	**y**	3,5-$Me_2C_6H_3$	4-(Me_2N)C_6H_4			45	–
f	**z**	4-(MeO)C_6H_4	C_6H_5	62	50	55	8.51, 9.99[c]
f	**aa**	4-(MeO)C_6H_4	3-MeC_6H_4			54	8.43, 9.99[c]
f	**ab**	4-(MeO)C_6H_4	2,4-$Me_2C_6H_3$			67	8.08, 10.08[c]
f	**ac**	4-(MeO)C_6H_4	3,5-$Me_2C_6H_3$			62	8.34, 9.98[c]
f	**ad**	4-(MeO)C_6H_4	2-(MeO)C_6H_4			52	8.54, 10.06[c]
g	**ae**	4-(O_2N)C_6H_4	C_6H_5	84	54	55	8.40, 10.48[c]

[a] Yields of isolated products. The assignment of the substituents of the amidine group is arbitrary. Compounds **4a** and **4c** have been previously reported (ref.[14]). [b] [D_6]DMSO. [c] $CDCl_3$.

uterated solvents indicated were used. Mass spectrometric data (MS) were obtained using the electron ionization (70 eV), the chemical ionization (CI, H_2O) or the electrospray ionization technique (ESI). For preparative scale chromatography silica gel (60−200 mesh) was used. Melting points are uncorrected.

General Procedure for the Synthesis of Ethyl 2-(Arylamino)-2-oxoacetates (3): To a THF solution (50 mL) of **1** (10.0 mmol) was added dropwise the corresponding amine **2** (10.0 mmol) at 20 °C. During the reaction a colourless precipitate formed which was removed by filtration. The filtrate was concentrated and dried in vacuo.

Ethyl 2-Oxo-2-(phenylamino)acetate (3a): Starting with **1** (1.36 g, 10.0 mmol) and aniline (0.93 g, 10.0 mmol), **3a** was isolated as a colourless solid (1.50 g, 78%), m.p. 72 °C. IR (KBr): $\tilde{\nu}$ = 701 (m), 760 (s), 1019 (m), 1178 (s), 1236 (w), 1293 (s), 1370 (m), 1445 (m), 1497 (s), 1539 (s), 1600 (s), 1703 (s), 3346 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* = 193 (75) [M^+], 120 (100), 93 (50), 77 (55), 29 (53). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.44 (t, *J* = 7 Hz, 3 H, CH_3), 4.43 (q, *J* = 7 Hz, 2 H, CH_2), 7.17 (t, 2 H, Ar), 7.38 (t, 2 H, Ar), 7.63 (d, 1 H, Ar), 8.85 (s, 1 H, NH) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.94, 63.69, 119.75, 125.45, 129.16, 136.27, 153.83, 160.95 ppm. $C_{10}H_{11}NO_3$ (193.09): calcd. C 62.19, H 5.69, N 7.25; found C 62.31, H 5.90, N 7.36.

Ethyl 2-Oxo-2-(*o*-tolylamino)acetate (3b): Starting with **1** (1.36 g, 10.0 mmol) and *o*-toluidine (1.07 g, 10.0 mmol), **3b** was isolated as a colourless solid (1.80 g, 87%), m.p. 67 °C. IR (KBr): $\tilde{\nu}$ = 755 (m), 101 (w), 1175 (s), 1290 (s), 1372 (w), 1531 (s), 1710 (s), 2984 (w), 3394 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* = 207 (48) [M^+], 134 (100), 105 (55), 91 (60), 29 (62). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.44 (t, *J* = 7.5 Hz, 3 H, CH_3), 2.33 (s, 3 H, CH_3), 4.42 (q, *J* = 7.5 Hz, 2 H, CH_2), 7.13 (d, 1 H, Ar), 7.21 (t, 2 H, Ar), 8.03 (d, 1 H, Ar), 8.85 (s, 1 H, NH) ppm. ^{13}C NMR (50 Hz, $CDCl_3$): δ = 13.93, 17.41, 63.67, 121.59, 125.80, 126.96, 128.29, 130.53, 134.28, 153.83, 161.08 ppm. $C_{11}H_{13}NO_3$ (207.1): calcd. C 63.79, H 6.27, N 6.76; found C 63.33, H 6.53, N 6.61.

Ethyl 2-Oxo-2-(*p*-tolylamino)acetate (3c): Starting with **1** (1.36 g, 10.0 mmol) and *p*-toluidine (1.07 g, 10.0 mmol), **3c** was isolated as a colourless solid (1.70 g, 82%), m.p. 71 °C. IR (KBr): $\tilde{\nu}$ = 497 (m), 698 (w), 816 (m), 1178 (s), 1295 (s), 1366 (w), 1516 (s), 1705 (s), 3338 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* = 207 (100) [M^+], 144 (86), 105 (98), 91 (34), 29 (50). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.41 (t, *J* = 7 Hz, 3 H, CH_3), 2.33 (s, 3 H, CH_3), 4.40 (q, *J* = 7 Hz, 2 H, CH_2), 7.17 (d, 2 H, Ar), 7.53 (d, 2 H, Ar), 8.88 (s, 1 H, NH) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.95, 20.91, 63.61, 119.83, 129.64, 133.76, 135.22, 153.70, 161.04 ppm. $C_{11}H_{13}NO_3$ (207.1): calcd. C 63.79, H 6.27, N 6.76; found C 63.63, H 6.39, N 6.82.

Ethyl 2-[(2′,4′-Dimethylphenyl)amino]-2-oxoacetate (3d): Starting with **1** (1.36 g, 10.0 mmol) and 2,4-xylidine (1.21 g, 10.0 mmol), **3d** was isolated as a colourless solid (1.35 g, 61%), m.p. 58 °C. IR (KBr): $\tilde{\nu}$ = 721 (w), 811 (s), 1021 (s), 1123 (w), 1166 (m), 1289 (s), 1372 (m), 1534 (s), 1695 (s), 1735 (s), 2883 (m), 3219 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* = (66) [M^+], 147 (100), 120 (71), 77 (19), 28 (73).

^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 1.31 (t, *J* = 7 Hz, 3 H, CH_3), 2.14 (s, 3 H, CH_3), 2.26 (s, 3 H, CH_3), 4.30 (q, *J* = 7 Hz, 2 H, CH_2), 7.00 (d, 1 H, Ar), 7.02 (s, 1 H, Ar), 7.18 (d, 1 H, Ar) ppm. ^{13}C NMR (50 MHz, [D$_6$]DMSO): δ = 13.77, 17.49, 20.43, 62.18, 125.46, 126.56, 130.86, 132.05 132.65, 135.62, 155.82, 160.83 ppm. $C_{12}H_{15}NO_3$ (221.26): calcd. C 65.14, H 6.83, N 6.33; found C 64.81, H 6.85, N 6.19.

Ethyl 2-[(3′,5′-Dimethylphenyl)amino]-2-oxoacetate (3e): Starting with **1** (1.36 g, 10.0 mmol) and 3,5-xylidine (10.0 mmol), **3e** was isolated as a colourless solid (1.50 g, 68%), m.p. 130 °C. IR (KBr): ṽ = 719 (s), 859 (s), 1017 (m), 1204 (s), 1267 (s), 1366 (w), 1474 (s), 1559 (s), 1698 (s), 2980 (m), 3349 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* = 221 (87) [M$^+$], 147 (100), 120 (39), 104 (49), 77 (14). ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 1.43 (t, *J* = 7 Hz, 3 H, CH_3), 2.31 (s, 6 H, CH_3), 4.41 (q, *J* = 7 Hz, 2 H, CH_2), 6.80 (s, 1 H, Ar), 7.29 (m, 2 H, Ar), 10.52 (s, 1 H, NH) ppm. ^{13}C NMR (50 MHz, [D$_6$]DMSO): δ = 13.75, 20.96, 62.22, 118.14, 126.17, 137.24, 137.72, 155.53, 160.74 ppm. $C_{12}H_{15}NO_3$ (221.26): calcd. C 65.14, H 6.83, N 6.33; found C 65.09, H 6.83, N 6.10.

Ethyl 2-[(*p*-Methoxyphenyl)amino]-2-oxoacetate (3f): Starting with **1** (1.36 g, 10.0 mmol) and *p*-anisidine (1.24 g, 10.0 mmol), **3f** was isolated as a colourless solid (1.40 g, 62%), m.p. 113 °C. IR (KBr): ṽ = 508 (w), 704 (m), 838 (s), 1021 (s), 1195 (s), 1243 (2), 1294 (s), 1368 (m), 1442 (m), 1512 (s), 1543 (s), 1696 (s), 3352 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* = 223 (67) [M$^+$], 148 (100), 122 (85), 28 (51). ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 1.27 (t, *J* = 7 Hz, 3 H, CH_3), 3.65 (s, 3 H, OCH_3), 4.25 (q, *J* = 7 Hz, 2 H, CH_2), 6.88 (d, 2 H, Ar), 7.63 (d, 2 H, Ar), 10.60 (s, 1 H, NH) ppm. ^{13}C NMR (50 MHz, [D$_6$]DMSO): δ = 13.76, 55.14, 62.21, 113.83, 121.83, 130.47, 155.11, 156.22, 160.81 ppm. $C_{11}H_{13}NO_4$ (223.11): calcd. C 59.21, H 5.82, N 6.27; found C 59.41, H 5.69, N 6.24.

Ethyl 2-[(*p*-Nitrophenyl)amino]-2-oxoacetate (3g): Starting with **1** (1.36 g, 10.0 mmol) and *p*-nitroaniline (1.38 g, 10.0 mmol), **3g** was isolated as a colourless solid (1.90 g, 84%), m.p. 173 °C. IR (KBr): ṽ = 698 (w), 859 (m), 1177 (s), 1305 (s), 1345 (s), 1509 (s), 1561 (m), 1604 (s), 1710 (s), 3343 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* = 238 (82) [M$^+$], 165 (100), 138 (24). ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 1.33 (t, *J* = 7.2 Hz, 3 H, CH_3), 4.33 (q, *J* = 7.2 Hz, 2 H, CH_2), 8.02 (d, 2 H, Ar), 8.22 (d, 2 H, Ar), 11.30 (s, 1 H, NH) ppm. ^{13}C NMR (50 MHz, [D$_6$]DMSO): δ = 13.73, 62.63, 120.33, 124.60, 143.29, 143.54, 155.97, 159.92 ppm. $C_{10}H_{10}N_2O_5$ (238.20): calcd. C 50.42, H 4.23, N 11.76; found C 50.18, H 4.33, N 11.60.

General Procedure for the Synthesis of Ethyl 2-Amino-2,2-dichloroacetates (4): A toluene solution (30 mL) of **3** (10.0 mmol) and of PCl_5 (10.0 mmol) was refluxed for 5 h. The solution was concentrated to 15 mL to give a precipitate. The latter was isolated by filtration and recrystallized from *n*-heptane to give **4** as a colourless solid.

Ethyl 2,2-Dichloro-2-(phenylamino)acetate (4a): Starting with **3a** (1.93 g, 10.0 mmol) and PCl_5 (2.08 g, 10.0 mmol), **4a** was isolated as a colourless solid (1.10 g, 54%). IR (KBr): ṽ = 491 (w), 760, (m), 1019, (w), 1178, (s), 1293, (s), 1540, (s), 1703 (s), 3344 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* = 248 (4) [M$^+$], 246 (8), 119 (100), 91 (31), 77 (41), 27 (64). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.45 (t, *J* = 7 Hz, 3 H, CH_3), 4.30 (q, *J* = 7 Hz, 2 H, CH_2), 7.15 (t, 1 H, Ar), 7.38 (t, 2 H, Ar), 7.58 (d, 2 H, Ar), 8.21 (s, 1 H, NH) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.37, 65.88, 107.68, 120.18, 125.47, 129.19, 136.16, 160.21 ppm. $C_{10}H_{11}Cl_2NO_2$ (248.00): calcd. C 48.42, H 4.43, N 5.64; found C 50.36, H 4.43, N 6.03.

Ethyl 2,2-Dichloro-2-(2′-tolylamino)acetate (4b): Starting with **3b** (2.07 g, 10.0 mmol) and PCl_5 (2.08 g, 10.0 mmol), **4b** was isolated as a colourless solid (1.10 g, 48%), m.p. 104−105 °C. IR (KBr): ṽ = 755 (m), 1014 (w), 1290 (m), 1458 (w), 1532 (m), 1706 (s), 2938 (w), 2938 (w), 3333 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* = 262 (21) [M$^+$], 225 (25), 134 (100), 105 (63), 91 (86), 77 (24). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.45 (t, *J* = 7 Hz, 3 H, CH_3), 2.28 (s, 3 H, CH_3), 4.32 (q, *J* = 7 Hz, 2 H, CH_2), 7.09−7.28 (m, 3 H, Ar), 7.92 (d, 1 H, Ar), 8.19 (s, 1 H, NH) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.32, 17.29, 65.67, 107.75, 122.26, 125.97, 127.06, 129.06, 130.59, 134.22, 160.39 ppm. $C_{11}H_{13}Cl_2NO_2$ (262.01): calcd. C 50.42, H 4.96, N 5.34; found C 50.62, H 5.30, N 5.61.

Ethyl 2,2-Dichloro-2-(4′-tolylamino)acetate (4c): Starting with **3c** (2.07 g, 10.0 mmol) and PCl_5 (2.08 g, 10.0 mmol), **4c** was isolated as a colourless solid (0.80 g, 31%), m.p. 100−101 °C. IR (KBr): ṽ = 498 (m), 703 (w), 817 (m), 1178 (m), 1295 (s), 1368 (w), 1522 (m), 1543 (m), 1599 (w), 1706 (s), 2983 (w), 3336 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* = 262 (27) [M$^+$], 225 (39), 134 (100), 105 (92), 91 (61), 77 (35). ^{1}H NMR (200 MHz, $CDCl_3$):δ = 1.44 (t, *J* = 7 Hz, 3 H, CH_3), 2.33 (s, 3 H, CH_3), 4.31 (q, *J* = 7 Hz, 2 H, CH_2), 7.16 (d, 2 H, Ar), 7.47 (d, 2 H, Ar), 8.14 (s, 1 H, NH) ppm. ^{13}C NMR (50 MHz, $CDCl_3$):δ = 14.38, 20.93, 65.85, 107.77, 120.17, 129.68, 133.67, 135.20, 160.18 ppm. $C_{11}H_{13}Cl_2NO_2$ (262.01): calcd. C 50.42, H 4.96, N 5.34; found C 50.61, H 4.98, N 5.43.

Ethyl 2,2-Dichloro-2-[(2′,4′-dimethylphenyl)amino]acetate (4d): Starting with **3d** (2.21 g, 10.0 mmol) and PCl_5 (2.08 g, 10.0 mmol), **4d** was isolated as a colourless solid (1.35 g, 48%), m.p. 139 °C. IR (KBr): ṽ = 807 (m), 986 (w), 1150 (m), 1291 (m), 1698 (s), 1700 (s), 3272 (w), 3400 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* = 276 (19) [M$^+$], 147 (100), 120 (66), 29 (69). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.43 (t, *J* = 7 Hz, 3 H, CH_3), 2.23 (s, 3 H, CH_3), 2.30 (s, 3 H, CH_3), 4.30 (q, *J* = 7 Hz, 2 H, CH_2), 7.03 (d, 2 H, Ar), 7.73 (d, 1 H, Ar), 8.11 (s, 1 H, NH) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.25, 17.18, 20.84, 65.58, 107.78, 122.43, 127.44, 129.28, 131.18, 131.50, 135.70, 160.33 ppm. $C_{12}H_{15}Cl_2NO_2$ (276.02): calcd. C 52.21, H 5.43, N 5.07; found C 52.04, H 6.45, N 5.03.

Ethyl 2,2-Dichloro-2-[(3′,5′-dimethylphenyl)amino]acetate (4e): Starting with **3e** (2.21 g, 10.0 mmol) and PCl_5 (2.08 g, 10.0 mmol), **4e** was isolated as a colourless solid (1.70 g, 71%), m.p. 159 °C. IR (KBr): ṽ = 719 (s), 859 (s), 1017 (s), 1204 (s), 1267 (s), 1474 (s), 1559 (s), 1615 (s), 1695 (s), 2980 (m), 3349 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* = 275.7 (18) [M$^+$], 147 (100), 104 (51), 77 (29), 29 (80). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.45 (t, *J* = 7.2 Hz, 3 H, CH_3), 2.31 (s, 6 H, CH_3), 4.29 (q, *J* = 7.2 Hz, 2 H, CH_2), 6.82 (s, 1 H, Ar), 7.24 (d, 2 H, Ar), 8.11 (s, 1 H, NH) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 15.05, 21.26, 31.82, 65.78, 107.75, 117.50, 117.84, 127.10, 127.21, 135.98, 138.88, 160.12 ppm. $C_{12}H_{15}NO_2Cl_2$ (276.02): calcd. C 52.21, H 5.43, N 5.07; found C 53.38, H 6.28, N 4.97.

Ethyl 2,2-Dichloro-2-[(4′-methoxyphenyl)amino]acetate (4f): Starting with **3f** (2.23 g, 10.0 mmol) and PCl_5 (2.08 g, 10.0 mmol), **4f** was isolated as a colourless solid (1.20 g, 50%), m.p. 90−91 °C. IR (KBr): ṽ = 834 (s), 1143 (s), 1295 (m), 1512 (s), 1539 (s), 1690 (s), 3271 (m), 3352 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* = 278 (13) [M$^+$], 241 (21), 148 (100), 122 (83), 77 (11), 29 (49). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.44 (t, *J* = 7 Hz, 3 H, CH_3), 3.80 (s, 3 H, OCH_3), 4.42 (q, *J* = 7 Hz, 2 H, CH_2), 6.90 (d, 2 H, Ar), 7.55 (d, 2 H, Ar), 8.78 (s, 1 H, NH) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.30, 55.42, 65.79, 107.75, 114.22, 121.33, 121.85, 129.20, 157.13, 160.17 ppm. $C_{11}H_{13}Cl_2NO_3$ (278.01): calcd. C 47.52, H 4.67, N 5.03; found C 47.25, H 4.66, N 5.25.

Ethyl 2,2-Dichloro-2-[(4′-nitrophenyl)amino]acetate (4g): Starting with **3g** (2.38 g, 10.0 mmol) and PCl_5 (2.08 g, 10.0 mmol), **4g** was

isolated as a colourless solid (1.40 g, 54%), m.p. 159 °C. IR (KBr): $\tilde{\nu}$ = 634 (m), 858 (s), 950 (w), 1113 (s), 1149 (s), 1303 (s), 1343 (s), 1509 (s), 1640 (s), 1710 (s), 1731 (s), 3343 (s), 3386 (s) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 1.45 (t, *J* = 7 Hz, 3 H, CH_3), 4.45 (q, *J* = 7 Hz, 2 H, CH_2), 7.84 (d, 2 H, Ar), 8.27 (d, 2 H, Ar), 9.17 (s, 1 H, NH) ppm. ^{13}C NMR (50 Hz, $CDCl_3$): δ = 13.91, 64.22, 119.56, 119.85, 125.07, 125.15, 141.75, 144.48, 154.13, 160.26 ppm. $C_{10}H_{10}N_2Cl_2O_4$ (293.10): calcd. C 40.97, H 3.41, N 9.55; found C 40.75, H 3.33, N 9.77.

General Procedure for the Synthesis of 2-(Arylamino)-2-iminoacetamides (5): A mixture of **4** (1.0 mmol) and of the amine (5.0 mmol) was stirred at 80 °C for 20 min to give a precipitate. The latter was filtered off and washed with diethyl ether to give **5** as a colourless solid.

2-(Phenylamino)-*N*-(3′-tolyl)-2-(3′-tolylimino)acetamide (5a): Starting with **4a** (0.21 g, 1.0 mmol) and *m*-toluidine (0.53 g, 5.0 mmol), **5a** was isolated as a colourless solid (0.17 g, 50%), m.p. 143 °C. IR (KBr): $\tilde{\nu}$ = 695 (m), 784 (w), 1441 (s), 1504 (s), 1595 (s), 1649 (s), 1687 (s), 3304 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* = 343 (88) [M^+], 223 (100), 209 (32), 106 (45). ^1H NMR (200 MHz, [D_6]DMSO): δ = 2.28 (s, 3 H, CH_3), 2.31 (s, 3 H, CH_3), 6.69−7.66 (m, 3 H, Ar), 9.62 (s, 1 H, NH), 10.54 (s, 1 H, NH) ppm. $C_{22}H_{21}N_3O$ (343.22): calcd. C 76.98, H 6.11, N 12.20; found C 76.61, H 6.60, N 12.30.

***N*-(2′,4′-Dimethylphenyl)-2-[(2′,4′-dimethylphenyl)imino]-2-(phenylamino)acetamide (5b):** Starting with **4a** (0.21 g, 1.0 mmol) and 2,4-xylidine (0.60 g, 5.0 mmol), **5b** was isolated as a colourless solid (0.19 g, 51%), m.p. 122 °C. IR (KBr): $\tilde{\nu}$ = 506 (w), 755 (m), 826 (m), 1313 (w), 1443 (s), 1510 (s), 1540 (s), 1644 (s), 1689 (s), 2918 (w), 3287 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* = 371 (40) [M^+], 251 (50), 132 (58), 121 (100), 120 (55), 77 (30). ^1H NMR (200 MHz, [D_6]DMSO): δ = 2.12 (s, 12 H, CH_3), 6.26 (d, 2 H, Ar), 6.45 (d, 2 H, Ar), 6.74 (s, 2 H, Ar), 7.09−7.48 (m, 3 H, Ar), 7.69−7.71 (d, 2 H, Ar), 8.06 (s, 1 H, NH), 10.19 (s, 1 H, NH) ppm. ^{13}C NMR (50 MHz, [D_6]DMSO): δ = 18.05, 20.60, 119.48, 119.76, 124.56, 125.78, 128.28, 129.08, 130.19, 131.10, 132.29, 132.66, 134.88, 137.13, 141.11, 142.42, 160.28 ppm. $C_{24}H_{25}N_3O$ (371.24): calcd. C 77.64, H 6.73, N 11.31; found C 78.01, H 6.93, N 11.17.

***N*-(3′,5′-Dimethylphenyl)-2-[(3′,5′-dimethylphenyl)imino]-2-(phenylamino)acetamide (5c):** Starting with **4a** (0.21 g, 1.0 mmol) and 3,5-xylidine (0.60 g, 5.0 mmol), **5c** was isolated as a colourless solid (0.19 g, 37%), m.p. 154 °C. MS (EI, 70 eV): *m*/*z* = 371 (100) [M^+], 251 (47), 121 (35), 77 (12), 28 (92). IR (KBr): $\tilde{\nu}$ = 667 (w), 758 (m), 840 (m), 1319 (m), 1440 (s), 1499 (s), 1536 (s), 1594 (s), 1650 (s), 1688 (s), 2916 (w), 3303 (s) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$):δ = 2.05 (s, 12 H, CH_3), 6.29 (s, 4 H, Ar), 6.46 (s, 2 H, Ar), 7.16 (t, *J* = 7 Hz, 1 H, Ar), 7.35 (t, *J* = 8 Hz, 2 H, Ar), 7.66 (d, 2 H, Ar), 8.49 (br., 1 H, NH), 10.19 (br., 1 H, NH) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 20.78, 20.81, 113.05, 117.58, 119.66, 120.08, 120.42, 124.61, 125.41, 129.03, 129.41, 137.06, 137.40, 138.87, 141.54, 146.17, 160.08 ppm. $C_{24}H_{25}N_3O$ (371.24): calcd. C 77.64, H 6.73, N 11.31; found C 77.29, H 7.10, N 11.38.

***N*-(2′-Methoxyphenyl)-2-[(2′-methoxyphenyl)imino]-2-(phenylamino)acetamide (5d):** Starting with **4a** (0.21 g, 1.0 mmol) and *o*-anisidine (0.60 g, 5.0 mmol), **5d** was isolated as a colourless solid (0.20 g, 54%), m.p. 147 °C. IR (KBr): $\tilde{\nu}$ = 692 (w), 750 (s), 1028 (m), 1233(m), 1445 (s), 1516 (s), 1593 (s), 1650 (s), 3346 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* = 375 (58) [M^+], 344 (100), 255 (57), 134 (47), 123 (60), 77 (34), 28 (95). ^1H NMR (200 MHz, [D_6]DMSO): δ = 3.72 (s, 6 H, OCH_3), 6.62−7.13 (m, 9 H, Ar), 7.32 (t, *J* = 8 Hz, 2 H, Ar), 7.61 (d, 2 H, Ar), 8.41 (br., 1 H, NH), 9.89 (br., 1 H, NH) ppm. ^{13}C NMR (50 MHz, [D_6]DMSO): δ = 54.85, 110.47, 119.16, 119.66, 119.76, 121.85, 123.54, 123.68, 128.11, 137.11, 149.88, 159.88 ppm. $C_{22}H_{21}N_3O_3$ (375.22): calcd. C 70.41, H 5.59, N 11.19; found C 70.11, H 5.46, N 11.30.

***N*-[4′-(Dimethylamino)phenyl]-2-{[4′-(dimethylamino)phenyl]imino}-2-(phenylamino)acetamide (5e):** Starting with **4a** (0.21 g, 1.0 mmol) and *N*,*N*-dimethyl-*p*-phenylenediamine (0.68 g, 5.0 mmol), **5e** was isolated as a colourless solid (0.28 g, 70%), m.p. 205 °C. IR (KBr): $\tilde{\nu}$ = 508 (w), 821 (m), 946 (w), 1152 (s), 1365 (s), 1443 (s), 1518 (s), 1600 (s), 1687 (m), 2800 (w), 3425 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* = 401 (70) [M^+], 268 (100), 136 (75), 120 (80). ^1H NMR (200 MHz, $CDCl_3$): δ = 2.80 (s, 6 H, NMe), 3.05 (s, 6 H, NMe), 6.37 (d, 2 H, Ar), 6.55 (d, 2 H, Ar), 6.75 (d, 2 H, Ar), 7.16 (t, 1 H, Ar), 7.38 (t, 2 H, Ar), 7.71 (d, 2 H, Ar), 7.81 (d, 2 H, Ar) ppm. $C_{24}H_{27}N_5O$ (401.24): calcd. C 71.83, H 6.72, N 17.44; found C 72.08, H 7.31, N 17.92.

***N*-Phenyl-2-(phenylimino)-2-(2′-tolylamino)acetamide (5f):** Starting with **4b** (0.22 g, 1.0 mmol) and aniline (0.46 g, 5.0 mmol), **5f** was isolated as a colourless solid (0.24 g, 73%), m.p. 134 °C. IR (KBr): $\tilde{\nu}$ = 507 (m), 693 (s), 755 (s), 834 (w), 1305 (w), 1457 (s), 1506 (s), 1540 (s), 1587 (s), 1643 (s), 1686 (s), 3289 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* = 329 (20) [M^+], 195 (50), 104 (50), 93 (100), 77 (55). ^1H NMR (200 MHz, [D_6]DMSO): δ = 2.36 (s, 3 H, CH_3), 6.66−7.28 (m, 13 H, Ar), 8.17 (d, 1 H, Ar), 8.57 (s, 1 H, NH), 10.21 (s, 1 H, NH) ppm. ^{13}C NMR (50 MHz, [D_6]DMSO): δ = 17.55, 120.93, 121.41, 122.83, 122.98, 124.36, 124.94, 126.86, 127.93, 128.20, 130.46, 135.26, 136.62, 141.20, 146.30, 160.10 ppm. $C_{21}H_{19}N_3O$ (329.21): calcd. C 76.60, H 5.77, N 12.75; found C 76.51, H 6.08, N 12.82.

***N*-(3′-Tolyl)-2-(2′-tolylamino)-2-(3′-tolylimino)acetamide (5g):** Starting with **4b** (0.22 g, 1.0 mmol) and *m*-toluidine (0.53 g, 5.0 mmol), **5g** was isolated as a colourless solid (0.13 g, 36%), m.p. 113.5 °C. Conditions: stirring at 80 °C for 20 min. IR (KBr): $\tilde{\nu}$ = 588 (w), 693 (m), 758 (m), 1301 (m), 1452 (s), 1501 (s), 1539 (s), 1595 (s), 1647 (s), 1686 (s), 2917 (w), 3282 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* = 357 (64) [M^+], 223 (100), 106 (45). ^1H NMR (200 MHz, [D_6]DMSO): δ = 2.15 (s, 3 H, CH_3), 2.23 (s, 6 H, CH_3), 6.36−7.22 (m, 12 H, Ar), 9.23 (br., 1 H, NH), 9.88 (s, 1 H, NH) ppm. ^{13}C NMR (50 MHz, [D_6]DMSO): δ = 17.20, 21.02, 113.48, 117.62, 117.95, 119.65, 121.35, 121.58, 123.13, 124.97, 125.62, 125.92, 128.15, 128.79, 130.15, 132.08, 134.86, 137.39, 138.05, 149.92, 150.09, 160.72 ppm. $C_{23}H_{23}N_3O$ (357.23): calcd. C 77.32, H 6.43, N 11.75; found C 77.74, H 6.75, N 11.45.

***N*-(2′,4′-Dimethylphenyl)-2-[(2′,4′-dimethylphenyl)imino]-2-(2′-tolylamino)acetamide (5h):** Starting with **4b** (0.27 g, 1.0 mmol) and 2,4-xylidine (0.60 g, 5.0 mmol), **5h** was isolated as a colourless solid (0.23 g, 60%), m.p. 124 °C. IR (KBr): $\tilde{\nu}$ = 610 (w), 757 (m), 827 (m), 1293 (w), 1455 (s), 1511 (s), 1542 (s), 1648 (s), 1686 (s), 2917 (w), 3285 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* = 385 (40) [M^+], 251 (60), 132 (45), 121 (100), 120 (45). ^1H NMR (200 MHz, [D_6]DMSO): δ = 2.12 (s, 6 H, CH_3), 2.20 (s, 6 H, CH_3), 2.12 (s, 3 H, CH_3), 6.27−7.24 (m, 10 H, Ar), 8.24 (br., 1 H, NH), 10.38 (s, 1 H, NH) ppm. ^{13}C NMR (50 MHz, [D_6]DMSO): δ = 17.60, 18.08, 20.63, 115.66, 120.44, 121.63, 123.07, 124.68, 125.76, 126.88, 127.27, 127.69, 128.56, 130.22, 130.44, 131.12, 134.32, 135.45, 140.79, 141.28, 160.06 ppm. $C_{25}H_{27}N_3O$ (385.25): calcd. C 77.93, H 7.00, N 10.90; found C 78.24, H 7.18, N 10.98.

***N*-(3′,5′-Dimethylphenyl)-2-[(3′,5′-dimethylphenyl)imino]-2-(2′-tolylamino)acetamide (5i):** Starting with **4b** (0.22 g, 1.0 mmol) and 3,5-xylidine (0.60 g, 5.0 mmol), **5i** was isolated as a colourless solid (0.21 g, 55%), m.p. 141 °C. IR (KBr): $\tilde{\nu}$ = 595 (m), 758 (s), 840 (s), 1455 (s), 1505 (s), 1540 (s), 1599 (s), 1639 (s), 1691 (s), 3289 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* = 385 (30) [M^+], 251 (60), 121 (100),

77 (30). ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 2.05 (s, 12 H, CH$_3$), 2.34 (s, 3 H, CH$_3$), 6.31−6.46 (m, 7 H, Ar), 7.06−7.28 (m, 3 H, Ar), 8.09 (s, 1 H, NH), 10.21 (s, 1 H, NH) ppm. ^{13}C NMR (50 MHz, [D$_6$]DMSO): δ = 17.54, 20.79, 113.02, 120.42, 120.90, 121.21, 124.84, 126.80, 128.21, 130.41, 135.31, 137.40, 141.46, 160.16 ppm. $C_{25}H_{27}N_3O$ (385.25): calcd. C 77.93, H 7.00, N 10.90; found C 77.60, H 6.90, N 10.70.

***N*-(2′-Methoxyphenyl)-2-[(2′-methoxyphenyl)imino]-2-(2′-tolylamino)acetamide (5j):** Starting with **4b** (0.22 g, 1.0 mmol) and *o*-anisidine (0.60 g, 5.0 mmol), **5j** was isolated as a colourless solid (195 mg, 50%), m.p. 143 °C. IR (KBr): ṽ = 594 (w), 744 (s), 765 (m), 1029 (m), 1117 (m), 1454 (s), 1513 (s), 1587 (s), 1638 (s), 3321 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* = 389 (70) [M$^+$], 358 (100), 255 (50), 123 (60). ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 2.34 (s, 2 H, CH$_3$), 3.50 (s, 3 H, OCH$_3$), 3.81 (s, 3 H, OCH$_3$), 6.40−7.28 (m, 13 H, Ar), 8.20 (d, 1 H, Ar), 8.53 (s, 1 H, NH), 10.25 (br., 1 H, NH) ppm. ^{13}C NMR (50 MHz, [D$_6$]DMSO): δ = 17.52, 54.68, 55.17, 109.35, 109.83, 118.86, 119.89, 120.70, 121.98, 123.46, 123.88, 124.62, 124.91, 125.63, 126.77, 127.95, 130.34, 135.52, 135.87, 141.15, 149.65, 151.17, 160.05 ppm. $C_{23}H_{23}N_3O_3$ (389.23): calcd. C 70.96, H 5.90, N 10.76; found C 71.06, H 6.73, N 10.66.

***N*-[4′-(Dimethylamino)phenyl]-2-{[4′-(dimethylamino)phenyl]imino}-2-(2′-tolylamino)acetamide (5k):** Starting with **4b** (0.22 g, 1.0 mmol) and *N*,*N*-dimethyl-*p*-phenylenediamine (0.68 g, 5.0 mmol), **5k** was isolated as a colourless solid (0.15 g, 36%), m.p. 98 °C. IR (KBr): ṽ = 821 (m), 946 (m), 1152 (s), 1366(s), 1458 (s), 1516 (s), 1601 (s), 3338 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* = 415 (100) [M$^+$], 268 (65), 136 (45). ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 2.38 (s, 3 H, CH$_3$), 2.79 (s, 9 H, CH$_3$), 3.05 (s, 3 H, CH$_3$), 6.33−6.85 (m, 8 H, Ar), 7.04−7.31 (m, 3 H, Ar), 7.80 (m, 1 H, Ar), 8.18 (d, 1 H, Ar), 8.35 (s, 1 H, NH), 10.36 (s, 1 H, NH) ppm. ^{13}C NMR (50 MHz, [D$_6$]DMSO): δ = 17.65, 40.38, 40.96, 41.31, 111.70, 112.22, 112.63, 114.02, 120.67, 122.94, 123.53, 123.92, 124.54, 126.81, 128.03, 130.38, 135.65, 136.28, 124.54, 126.81, 128.03, 130.38, 135.65, 136.28, 140.17, 144.07, 147.22, 147.76, 151.44, 160.87 ppm. $C_{25}H_{29}N_5O$ (415.25): calcd. C 72.30, H 6.98, N 16.85; found C 71.00, H 6.85, N 17.98.

***N*-Phenyl-2-(phenylimino)-2-(4′-tolylamino)acetamide (5l):** Starting with **4c** (0.22 g, 1.0 mmol) and aniline (0.46 g, 5.0 mmol), **5l** was isolated as a colourless solid (1.70 g, 51%), m.p. 180 °C. IR (KBr): ṽ = 491 (m), 577 (w), 694 (s), 757 (m), 1314 (w), 1404 (s), 1538 (s), 1589 (s), 1643 (s), 1685 (s), 3296 (s), 3434 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* = 329 (100) [M$^+$], 195 (87), 103 (42), 93 (63), 77 (47), 28 (31). ^{1}H NMR (200 MHz, [D$_6$]DMSO):δ = 2.22 (s, 3 H, CH$_3$), 6.69−7.86 (m, 1 H, Ar), 9.62 (br., 1 H, NH), 10.50 (s, 1 H, NH) ppm. ^{13}C NMR (50 MHz, [D$_6$]DMSO):δ = 20.45, 116.09, 118.65, 119.77, 120.40, 121.13, 122.36, 127.37, 128.44, 129.05, 133.10, 135.26, 140.46, 150.27, 160.46 ppm. $C_{21}H_{19}N_3O$ (329.21): calcd. C 76.61, H 5.77, N 12.75; found C 76.27, H 5.80, N 13.01.

***N*-(3′-Tolyl)-2-(4′-tolylamino)-2-(3′-tolylimino)acetamide (5m):** Starting with **4c** (0.22 g, 1.0 mmol) and *m*-toluidine (0.53 g, 5.0 mmol), **5m** was isolated as a colourless solid (0.24 g, 67%), m.p. 128.5 °C. IR (KBr): ṽ = 495 (w), 697 (s), 917 (m), 1475 (s), 1542 (s), 1588 (s), 1649 (s), 1686 (s), 2919 (w), 3298 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* = 357 (78), 223 (100), 107 (66) ppm. $C_{23}H_{23}N_3O$ (357.23): calcd. C 77.32, H 6.43, N 11.75; found C 77.19, H 6.64, N 11.66.

***N*-(2′,4′-Dimethylphenyl)-2-[(2′,4′-dimethylphenyl)imino]-2-(4′-tolylamino)acetamide (5n):** Starting with **4c** (0.22 g, 1.0 mmol) and 2,4-xylidine (0.60 g, 5.0 mmol), **5n** was isolated as a colourless solid (0.15 g, 39%), m.p. 132 °C. IR (KBr): ṽ = 815 (w), 1484 (m), 1514 (s), 1590 (m), 1643 (s), 1687 (s), 3301 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* = 385 (75) [M$^+$], 251 (78), 132 (55), 121 (100). ^{1}H NMR (200 MHz, CDCl$_3$): δ = 2.12 (s, 6 H, CH$_3$), 2.17 (s, 6 H, CH$_3$), 2.35 (s, 3 H, CH$_3$), 6.29−6.74 (m, 6 H, Ar), 7.18 (d, 2 H, Ar), 7.60 (d, 2 H, Ar), 8.19 (s, 1 H, NH), 10.22 (s, 1 H, NH) ppm. ^{13}C NMR (50 MHz, CDCl$_3$): δ = 18.01, 20.60, 20.88, 115.08, 119.52, 119.71, 121.48, 125.79, 127.24, 127.40, 129.56, 129.67, 130.21, 131.04, 131.29, 133.75, 134.26, 134.58, 135.15, 141.45, 159.89 ppm. $C_{25}H_{27}N_3O$ (385.25): calcd. C 77.93, H 7.00, N 10.90; found C 77.06, H 7.07, N 10.73.

***N*-(3′,5′-Dimethylphenyl)-2-[(3′,5′-dimethylphenyl)imino]-2-(4′-tolylamino)acetamide (5o):** Starting with **4c** (0.22 g, 1.0 mmol) and 3,5-xylidine (0.60 g, 5.0 mmol), **5o** was isolated as a colourless solid (0.14 g, 36%), m.p. 164 °C. MS (EI, 70 eV): *m*/*z* = 385 (26) [M$^+$], 251 (23), 221 (27), 28 (100). IR (KBr): ṽ = 841 (w), 1408 (w), 1494 (s), 1510 (s), 1535 (s), 1593 (s), 1641 (s), 1686 (s), 3334 (m) cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ = 2.05 (s, 12 H, CH$_3$), 2.35 (s, 3 H, CH$_3$), 6.30 (s, 4 H, Ar), 6.46 (s, 2 H, Ar), 7.18 (d, 2 H, Ar), 7.60−7.62 (d, 2 H, Ar), 8.59 (s, 1 H, NH), 10.19 (s, 1 H, NH) ppm. ^{13}C NMR (50 MHz, CDCl$_3$): δ = 20.79, 20.82, 21.22, 113.98, 117.56, 119.75, 119.88, 120.24, 121.64, 125.85, 129.53, 129.66, 134.49, 137.54, 138.94, 139.01, 142.35, 144.19, 159.24 ppm. $C_{25}H_{27}N_3O$ (385.25): calcd. C 77.93, H 7.00, N 10.90; found C 77.61, H 7.54, N 11.01.

***N*-(2′-Methoxyphenyl)-2-[(2′-methoxyphenyl)imino]-2-(4′-tolylamino)acetamide (5p):** Starting with **4c** (0.22 g, 1.0 mmol) and *o*-anisidine (0.60 g, 5.0 mmol), **5p** was isolated as a colourless solid (0.20 g, 51%), m.p. 133 °C. IR (KBr): ṽ = 487 (w), 744 (s), 1029 (m), 1253 (m), 1499 (s), 1517 (s), 1645 (s), 1684 (s), 3288 (w), 3351 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* = 389 (20) [M$^+$], 358 (40), 123 (100), 108 (75), 80 (30). ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 2.34 (s, 3 H, CH$_3$), 3.65 (s, 6 H, OCH$_3$), 6.50−6.66 (m, 6 H, Ar), 6.82 (t, *J* = 7.5 Hz, 2 H, Ar), 7.60 (s, 2 H, Ar), 8.08 (s, 1 H, NH), 10.00 (s, 1 H, NH) ppm. ^{13}C NMR (50 Hz, [D$_6$]DMSO): δ = 20.89, 54.91, 109.53, 119.39, 119.64, 122.76, 124.55, 129.50, 134.12, 134.71, 141.47, 150.45, 159.80 ppm. $C_{23}H_{23}N_3O_3$ (389.23): calcd. C 79.96, H 5.90, N 10.79; found C 70.82, H 5.99, N 10.86.

2-[(2′,4′-Dimethylphenyl)amino]-*N*-phenyl-2-(phenylimino)-acetamide (5r): Starting with **4d** (0.27 g, 1.0 mmol) and aniline (0.46 g, 5.0 mmol), **5r** was isolated as a colourless solid (0.19 g, 55%), m.p. 154 °C. IR (KBr): ṽ = 695 (m), 819 (w), 1444 (s), 1508 (s), 1588 (s), 1630 (s), 1679 (s), 3339 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* = 343 (95) [M$^+$], 223 (40), 195 (100), 104 (50), 93 (90), 77 (40). ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 2.32 (s, 6 H, CH$_3$), 6.39−7.33 (m, 12 H, Ar), 8.00 (d, 1 H, Ar), 8.51 (s, 1 H, NH), 10.00 (br., 1 H, NH) ppm. $C_{22}H_{21}N_3O$ (343.22): calcd. C 76.98, H 6.11, N 12.23; found C 76.82, H 6.71, N 12.15.

2-[(2′,4′-Dimethylphenyl)amino]-*N*-(3′-tolyl)-2-(3′-tolylimino)-acetamide (5s): Starting with **4d** (0.27 g, 1.0 mmol) and *m*-toluidine (0.53 g, 5.0 mmol), **5s** was isolated as a colourless solid (0.18 g, 48%), m.p. 125 °C. IR (KBr): ṽ = 700 (m), 788 (m), 1304 (w), 1543 (s), 1590 (s), 1636 (s), 1688 (s), 3287 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* = 371 (15) [M$^+$], 223 (20), 107 (100), 91 (25), 77 (20). ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 2.11 (s, 6 H, CH$_3$), 2.32 (s, 6 H, CH$_3$), 6.40−7.33 (m, 10 H, Ar), 8.00 (d, 1 H, Ar), 8.51 (s, 1 H, NH), 10.00 (br., 1 H, NH) ppm. $C_{24}H_{25}N_3O$ (371.24): calcd. C 77.64, H 6.73, N 11.31; found C 77.49, H 6.92, N 11.14.

2-[(2′,4′-Dimethylphenyl)amino]-*N*-(2′-methoxyphenyl)-2-[(2′-methoxyphenyl)imino]acetamide (5t): Starting with **4d** (0.27 g, 1.0 mmol) and *o*-anisidine (0.61 g, 5.0 mmol), **5t** was isolated as a colourless solid (0.21 g, 52%), m.p. 133 °C. IR (KBr): ṽ = 744 (m),

1029 (w), 1242 (m), 1516 (s), 1647 (s), 1689 (s), 3305 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* = 403 (65) [M^+], 372 (100), 255 (40), 123 (75). ^1H NMR (200 MHz, $CDCl_3$): δ = 2.30−2.37 (s, 6 H, CH_3), 3.51 (s, 3 H, OCH_3), 3.84 (s, 3 H, OCH_3), 6.40−7.25 (m, 10 H, Ar), 8.03 (d, 1 H, Ar), 8.53 (s, 1 H, NH), 10.25 (br., 1 H, NH) ppm. $C_{24}H_{25}N_3O_3$ (403.24): calcd. C 71.48, H 6.19, N 10.41; found C 71.65, H 6.58, N 10.61.

2-[(3′,5′-Dimethylphenyl)amino]-*N*-phenyl-2-(phenylimino)-acetamide (5v): Starting with **4e** (0.24 g, 1.0 mmol) and aniline (0.46 g, 5.0 mmol), **5v** was isolated as a colourless solid (0.11 g, 32%), m.p. 149 °C. IR (KBr): ṽ = 481 (w), 523 (w), 688 (m), 753 (s), 1320 (w), 1444 (s), 1524 (s), 1598 (s), 1613 (m), 1661 (s), 3289 (s), 3434 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* = 343 (69) [M^+], 195 (100), 93 (86), 77 (90), 65 (35). ^1H NMR (200 MHz, $CDCl_3$): δ = 2.32 (s, 6 H, CH_3), 6.65−6.95 (m, 11 H, Ar), 7.32 (m, 2 H, Ar), 8.50 (s, 1 H, NH), 10.00 (s, 1 H, NH) ppm. $C_{22}H_{21}N_3O$ (343.22): calcd. C 76.98, H 6.11, N 12.23; found C 76.50, H 6.43, N 12.10.

2-[(3′,5′-Dimethylphenyl)amino]-*N*-(3′-tolyl)-2-(3′-tolylimino)-acetamide (5w): Starting with **4e** (0.23 g, 1.0 mmol) and *m*-toluidine (0.53 g, 5.0 mmol), **5w** was isolated as a colourless solid (0.19 g, 51%), m.p. 114 °C. IR (KBr): ṽ = 699 (m), 778 (w), 1453 (m), 1547 (s), 1640 (s), 1684 (s), 3335 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* = 371 (30) [M^+], 223 (68), 107 (100), 91 (50). ^1H NMR (200 MHz, [D_6]DMSO): δ = 2.05 (s, 6 H, CH_3), 2.33 (s, 6 H, CH_3), 6.42−6.90 (m, 9 H, Ar), 7.33 (s, 2 H, Ar), 8.40 (s, 1 H, NH), 10.00 (s, 1 H, NH) ppm. ^{13}C NMR (50 MHz, [D_6]DMSO): δ = 20.91, 21.36, 21.40, 117.43, 119.73, 122.06, 123.81, 126.48, 127.71, 136.88, 137.67, 138.81, 140.23, 160.13 ppm. $C_{24}H_{25}N_3O$ (371.24): calcd. C 77.64, H 6.73, N 11.31; found C 77.31, H 8.12, N 11.27.

2-[(3′,5′-Dimethylphenyl)amino]-*N*-(2′-methoxyphenyl)-2-[(2′-methoxyphenyl)imino]acetamide (5x): Starting with **4e** (0.23 g, 1.0 mmol) and *o*-anisidine (0.60 g, 5.0 mmol), **5x** was isolated as a colourless solid (0.20 g, 50%), m.p. 140 °C. IR (KBr): ṽ = 688 (w), 750 (m), 1113 (m), 1237 (m), 1519 (s), 1642 (s), 1688 (s), 3295 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* = 403 (60) [M^+], 372 (100), 255 (40), 123 (40). ^1H NMR (200 MHz, [D_6]DMSO): δ = 2.32 (s, 6 H, CH_3), 3.50 (s, 3 H, OCH_3), 3.83 (s, 3 H, OCH_3), 6.39 (m, 9 H, Ar), 7.33 (s, 2 H, Ar), 8.51 (s, 1 H, NH), 10.00 (s, 1 H, NH) ppm. ^{13}C NMR (50 MHz, [D_6]DMSO): δ = 21.38, 55.02, 55.08, 109.46, 117.40, 118.83, 119.79, 121.84, 123.87, 124.89, 126.26, 135.76, 137.02, 138.64, 141.13, 149.64, 151.13, 159.98 ppm. $C_{24}H_{25}N_3O_3$ (403.24): calcd. C 71.48, H 6.19, N 10.41; found C 71.77, H 6.98, N 10.27.

2-[(4′-Methoxyphenyl)amino]-*N*-phenyl-2-(phenylimino)acetamide (5z): Starting with **4f** (0.27 g, 1.0 mmol) and aniline (0.46 g, 5.0 mmol), **5z** was isolated as a colourless solid (0.19 g, 55%), m.p. 191 °C. IR (KBr): ṽ = 698 (m), 832 (m), 1029 (w), 1247 (s), 1514 (s), 1634 (s), 1674 (s), 3303 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* = 345 (100) [M^+], 195 (85), 93 (86). ^1H NMR (200 MHz, $CDCl_3$): δ = 3.82 (s, 3 H, OCH_3), 6.65−6.94 (m, 12 H, Ar), 7.57−7.68 (m, 2 H, Ar), 8.51 (s, 1 H, NH), 9.99 (br., 1 H, NH) ppm. $C_{21}H_{19}N_3O_2$ (345.21): calcd. C 73.05, H 5.50, N 12.16; found C 72 54, H 5.89, N 11.91.

2-[(4′-Methoxyphenyl)amino]-*N*-(3′-tolyl)-2-(3′-tolylimino)-acetamide (5aa): Starting with **4f** (0.27 g, 1.0 mmol) and *m*-toluidine (0.53 g, 5.0 mmol), **5aa** was isolated as a colourless solid (0.20 g, 54%), m.p. 153 °C. IR (KBr): ṽ = 697 (w), 830 (w), 1248 (s), 1415 (w), 1513 (s), 1636 (s), 1675 (m), 3307 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* = 374 (90) [M^+], 223 (90), 106 (100), 91 (46). ^1H NMR (200 MHz, $CDCl_3$): δ = 2.04, 2.06 (2 × s, 2 × 3 H, CH_3), 3.82 (s, 3 H, OCH_3), 6.44−6.69 (m, 6 H, Ar), 6.85−6.94 (m, 4 H, Ar), 7.62 (d, 2 H, Ar), 8.43 (s, 1 H, NH), 9.99 (br., 1 H, NH) ppm. $C_{23}H_{23}N_3O_2$ (373.23): calcd. C 73.81, H 6.14, N 11.22; found C 73.91, H 5.77, N 11.28.

***N*-(2′,4′-Dimethylphenyl)-2-[(2′,4′-dimethylphenyl)imino]-2-[(4′-methoxyphenyl)amino]acetamide (5ab):** Starting with **4f** (0.27 g, 1.0 mmol) and 2,4-xylidine (0.60 g, 5.0 mmol), **5ab** was isolated as a colourless solid (0.27 g, 67%), m.p. 144 °C. IR (KBr): ṽ = 829 (s), 1036 (m), 1244 (s), 1414 (m), 1540 (s), 1644 (s), 1682 (s), 3294 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* = 402 (55) [M^+], 251 (51), 132 (65), 121 (100), 77 (22). ^1H NMR (200 MHz, $CDCl_3$): δ = 2.11 (s, 12 H, CH_3), 3.82 (s, 3 H, OCH_3), 6.24−6.30 (m, 4 H, Ar), 6.74 (s, 2 H, Ar), 6.92 (d, 2 H, Ar), 7.62 (d, 2 H, Ar), 8.08 (s, 1 H, NH), 10.08 (br., 1 H, NH) ppm. $C_{25}H_{27}N_3O_2$ (401.25): calcd. C 74.82, H 6.72, N 10.46; found C 74.71, H 6.66, N 10.52.

2-[(4′-Methoxyphenyl)amino]-*N*-(3′,5′-dimethylphenyl)-2-[(3′,5′-dimethylphenyl)imino]acetamide (5ac): Starting with **4f** (0.27 g, 1.0 mmol) and 3,5-xylidine (0.60 g, 5.0 mmol), **5ac** was isolated as a colourless solid (0.25 g, 62%), m.p. 153 °C. IR (KBr): ṽ = 841 (m), 1036 (w), 1245 (m), 1510 (s), 1642 (s), 1681 (s), 3300 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* = 401 (26) [M^+], 251 (28), 121 (100), 77 (50). ^1H NMR (200 MHz, $CDCl_3$): δ = 1.98−2.05 (2 × s, 12 H, CH_3), 3.81 (s, 3 H, OCH_3), 6.26−6.50 (m, 6 H, Ar), 6.92 (d, 2 H, Ar) 7.60 (d, 2 H, Ar), 8.34 (s, 1 H, NH), 9.98 (s, 1 H, NH) ppm. $C_{25}H_{27}N_3O_2$ (401.25): calcd. C 74.82, H 6.72, N 10.46; found C 74.96, H 6.59, N 10.37.

***N*-(2′-Methoxyphenyl)-2-[(4′-methoxyphenyl)amino]-2-[(2′-methoxyphenyl)imino]acetamide (5ad):** Starting with **4f** (0.27 g, 1.0 mmol) and *o*-anisidine (0.61 g, 5.0 mmol), **5ad** was isolated as a colourless solid (0.21 g, 52%), m.p. 144 °C. IR (KBr): ṽ = 742 (m), 1030 (m), 1249 (m), 1514 (s), 1644 (s), 1679 (m), 3354 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* = 406 (80) [M^+], 374 (97), 255 (59), 123 (100), 28 (82). ^1H NMR (200 MHz, $CDCl_3$): δ = 3.80 (s, 9 H, OCH_3), 6.50−7.02 (m, 10 H, Ar), 7.74 (d, 2 H, Ar), 8.54 (br., 1 H, NH), 10.06 (br., 1 H, NH) ppm. $C_{23}H_{23}N_3O_4$ (405.23): calcd. C 68.16, H 5.67, N 10.36; found C 67.84, H 5.83, N 10.38.

2-[(4′-Nitrophenyl)amino]-*N*-phenyl-2-(phenylimino)acetamide (5ae): Starting with **4g** (0.29 g, 1.0 mmol) and aniline (0.46 g, 5.0 mmol), **5ae** was isolated as a colourless solid (0.20 g, 55%), m.p. 192 °C. IR (KBr): ṽ = 528 (w), 694 (m), 1110 (w), 1339 (s), 1502 (s), 1544 (s), 1645 (m), 1691 (m), 3349 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* = 361 (70) [M^+], 195 (69), 93 (64), 28 (100). ^1H NMR (200 MHz, $CDCl_3$): δ = 6.65−6.97 (m, 10 H, Ar), 7.90 (d, 2 H, Ar), 8.30 (d, 2 H, Ar), 8.40 (s, 1 H, NH), 10.48 (s, 1 H, NH) ppm. $C_{20}H_{16}N_4O_3$ (360.20): calcd. C 66.68, H 4.44, N 15.54; found H 66.48, H 4.79, N 15.29.

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[1] Reviews: [1a] P. Langer, *Chem. Eur. J.* **2001**, *7*, 3858. [1b] P. Langer, *Synthesis* **2002**, 441.

[2] [2a] For the cyclization of oxalyl chloride with 1,2-diols, see: T. Iida, T. Itaya, *Tetrahedron* **1993**, *49*, 10511. [2b] For the synthesis of 1,2-diones, see: F. Babudri, V. Fiandanese, G. Marchese, A. Punzi, *Tetrahedron Lett.* **1995**, *36*, 7305. [2c] For the synthesis of furan-2,3-diones, see: C. O. Kappe, G. Kollenz, C. Wentrup, *Heterocycles* **1994**, *38*, 779. [2d] H. Ulrich, A. A. R. Sayigh, *J. Org. Chem.* **1965**, *30*, 2781.

[3] [3a] C. Samarian, H.-W. Wanzlick, *Tetrahedron Lett.* **1974**, *24*, 2125, and references cited therein. [3b] W. Trowitzsch, *Justus Liebigs Ann. Chem.* **1977**, 1707. [3c] C. C. Subramaniam, P. J.

Thomas, V. R. Mamdapur, M. S. Chadha, *Synthesis* **1978**, 468.
[4] U. T. Mueller-Westerhoff, M. Zhou, *J. Org. Chem.* **1994**, *59*, 4988.
[5] [5a] P. Langer, M. Stoll, *Angew. Chem.* **1999**, *111*, 1919; *Angew. Chem. Int. Ed.* **1999**, *38*, 1803. [5b] M. P. Sibi, M. Marvin, R. Sharma, *J. Org. Chem.* **1995**, *60*, 5016.
[6] Review: P. Langer, M. Döring, *Eur. J. Org. Chem.* **2002**, 221.
[7] H. Hoppe, K. Hartke, *Arch. Pharm. (Weinheim Ger.)* **1975**, *308*, 526.
[8] D. Lindauer, R. Beckert, M. Döring, P. Fehling, H. Görls, *J. Prakt. Chem.* **1995**, *337*, 143.
[9] [9a] K. Hartke, H. Hoppe, *Chem. Ber.* **1974**, *107*, 3121. [9b] K. Hartke, A. Kumar, J. Koester, G. Henssen, T. Kissel, *Chem. Ber.* **1982**, *115*, 3096. [9c] K. Hartke, T. Gillmann, *Liebigs Ann. Chem.* **1986**, *10*, 1718.
[10] [10a] C. C. Cjiu, F. Jordan, *J. Org. Chem.* **1994**, *59*, 5763, and references cited therein. [10b] J. S. Nimitz, H. S. Mosher, *J. Org. Chem.* **1981**, *46*, 211.
[11] [11a] V. N. Bodnar, M. O. Lozinskii, V. N. Kalinin, *J. Org. Chem. USSR (Engl. Transl.)* **1987**, *23*, 1991; *Zh. Org. Khim.* **1987**, *23*, 2252. [11b] V. A. Galishev, Yu. T. Struchkovu, T. S. Dolgushina, A. M. Shubnikov, K. A. Potekhin, *Russ. J. Gen. Chem.* **1996**, *66*, 558; *Zh. Obshch. Khim.* **1996**, *66*, 572. [11c] R. Trave, L. Garanti, G. Zecchi, *J. Chem. Soc., Perkin Trans. 1* **1987**, 1533.
[12] [12a] R. Huisgen, F. Koch, *Justus Liebigs Ann. Chem.* **1955**, *591*, 200. [12b] J. Barluenga, F. Fernandez-Mari, E. Aguilar, A. L. Viado, B. Olando, *Tetrahedron Lett.* **1998**, 4887. [12c] A. S. Shawali, A. A. Elghandour, S. M. El-Sheikh, *J. Prakt. Chem.* **2000**, *342*, 96. [12d] G. Cusmano, G. Macaluso, W. Hinz, S. Buscemi, *Heterocycles* **1987**, *26*, 1283. [12e] G. Heubach, *Liebigs Ann. Chem.* **1980**, 1376. [12f] C. A. Coda, G. Desimoni, G. A. Invernizzi, P. Quadrelli, P. P. Righetti, G. Tacconi, *Tetrahedron* **1987**, *43*, 2843. [12g] A. Alemagna, P. del Buttero, E. Licandro, S. Maiorana, R. Trave, *Tetrahedron* **1984**, *40*, 935. [12h] A. Ponti, G. Molteni, *J. Org. Chem.* **2001**, *66*, 5252. [12i] D. A. Bowack, A. Lapworth, *J. Chem. Soc.* **1905**, *87*, 1854.
[13] [13a] E. Csikos, C. Goenczi, B. Podanyi, G. Toth, I. Hermecz, *J. Chem. Soc., Perkin Trans. 1* **1999**, *13*, 1789. [13b] J.-M. Coustard, *Tetrahedron* **1995**, *51*, 10929.
[14] H. Klinger, *Justus Liebigs Ann. Chem.* **1876**, *184*, 261.
[15] For synthetic approaches to 2-amino-2-iminoacetamides, see: [15a] From tetramethyl monoorthooxalate: R. Anschuetz, J. Stiepel, *Justus Liebigs Ann. Chem.* **1899**, *306*, 5; from ethyl 2-chloro-2-iminoacetate: [15b] See ref.[14] From methyl 2-anilino-2,2-dimethoxyacetate: [15c] G. D. Lander, *J. Chem. Soc.* **1907**, *91*, 967. [15d] G. D. Lander, *J. Chem. Soc.* **1901**, *79*, 698. For isolated examples of the use of a 2-amino-2,2-dichloroacetate, see: [15e] H. Klinger, *Justus Liebigs Ann. Chem.* **1876**, *184*, 280.
[16] For a recent report on related hydrazones, see: G. Drutkowski, C. Donner, I. Schulze, P. Frohberg, *Tetrahedron* **2002**, *58*, 5317.
[17] G. Scherer, H.-H. Limbach, *J. Am. Chem. Soc.* **1994**, *116*, 1230.
[18] M. Wenzel, D. Lindauer, R. Beckert, R. Boese, E. Anders, *Chem. Ber.* **1996**, *129*, 39.
[19] [19a] R. Beckert, R. Mayer, *J. Prakt. Chem.* **1982**, *324*, 227. [19b] P. Fehling, M. Döring, F. Knoch, R. Beckert, H. Görls, *Chem. Ber.* **1995**, *128*, 405. [19c] M. Döring P. Fehling, H. Görls, W. Imhof, R. Beckert, D. Lindauer, *J. Prakt. Chem.* **1999**, *341*, 748.

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