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Metal-Free Synthesis of Imido Derivatives by Direct Oxidation of α-Amido Sulfones

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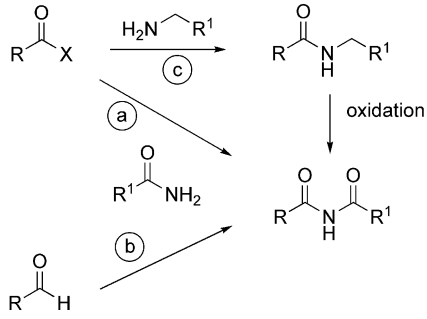
Oxidation of α-amidoaryl sulfones with *m*-chloroperoxybenzoic acid under mild conditions readily provides the corresponding imides in satisfactory yields. The overall process probably involves formation of an *N*-acyliminium ion intermediate, which by attack of the peroxyacid anion generates the final imido derivatives.

Introduction

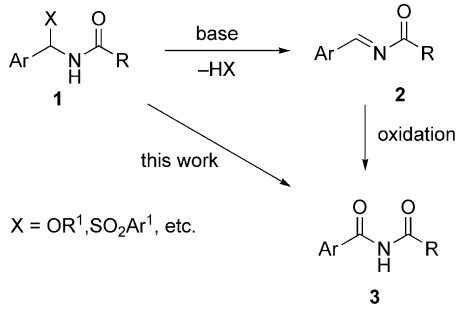
The generation of imide bonds in molecular frameworks is of paramount interest in synthesis because of the presence of this functional group in a plethora of materials and compounds endowed of practical interest. The imido group constitutes the core unit in several biologically active compounds of natural[1] and synthetic origin.[2] Furthermore, imides are also pivotal moieties in several organic processes.[3] Preparation of linear imides by direct reaction of reactive carboxylic acid derivatives with amides is not as efficient as the corresponding amidation procedure carried out by using amino compounds (Scheme 1, path a).[4] A valid alternative to this procedure has been envisaged in the direct coupling of amides with aldehydes under metal-catalyzed oxidative conditions (Scheme 1, path b).[5] A totally different approach to the synthesis of imides involves preliminary formation of the amide bond and thereafter oxidation of the nitrogen-bearing carbon (Scheme 1, path c).[6] Formation of imides, in variable amount, has been observed in some oxidative processes aimed at the preparation of *N*-acyloxaziridines from the corresponding *N*-acylimines.[7]

To have preferential formation of imides from *N*-Boc benzaldimines with the use of pure sodium *m*-chloroperoxybenzoate, low temperatures and strictly anhydrous reaction conditions are required.[8] Although *N*-acylimines can be prepared by following different synthetic procedures,[9] a very popular method for their formation employs a suitable precursor of type **1**, which under basic conditions undergoes an elimination reaction leading to *N*-acylimine **2** (Scheme 2). The stability of *N*-acylimines is strongly affected by the nature of the imino substituent, as only the presence of aryl groups allows proper isolation of compounds **2** that can be oxidatively converted into imides **3**.[10] The



Scheme 1. General synthetic strategies for the preparation of imides.

poor shelf stability of *N*-acylimines would make advisable the search for a direct procedure for the preparation of imides **3** starting directly from bench-stable amido derivatives **1**, thus avoiding manipulation of compounds **2**.



Scheme 2. Synthesis of imides via *N*-acylimino derivatives.

Among various systems available for this purpose, α-amido sulfones **1** (X = SO_2Ar^1) have demonstrated wide versatility that has allowed them to be used in several processes, including asymmetric synthesis.[11] In this paper we disclose a new procedure to directly convert α-amido sulfones into imides by using commercial *m*-chloroperoxybenzoic acid under mild reaction conditions and without the need of any added metal promoter.

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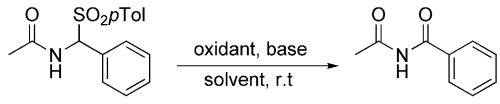
Results and Discussion

Many synthetic procedures make use of metal-based reagents or catalysts to promote oxidations of organic substrates. However, the utilization of metals is often associated to some practical troubles caused by their toxicity and environmental sustainability. Therefore, we decided to test several metal-free oxidant systems with different solvent/base combinations on model substrate **1a** for the synthesis of imide **3a** (Table 1).

Table 1. Optimization studies for oxidation of α-amido sulfone **1a**.



1a **3a**

Entry	Oxidant (equiv.)	Base (equiv.)	Solvent	Yield [%][a,b]
1	*t*BuOOH (2)	DBU (1.1)[c]	CH_2Cl_2	0
2	UHP (2)[d]	DBU (1.1)	CH_2Cl_2	26
3	*m*-CPBA (2)[e]	DBU (1.1)	CH_2Cl_2	43
4	*m*-CPBA (3)	DBU (1.1)	CH_2Cl_2	61
5	*m*-CPBA (4)	DBU (1.1)	CH_2Cl_2	77
6	*m*-CPBA (4)	DBU (1.1)	MeCN	58
7	*m*-CPBA (4)	–	CH_2Cl_2	13
8	*m*-CPBA (4)	DBU (0.5)	CH_2Cl_2	57
9	*m*-CPBA (4)	TMG (1.1)[f]	CH_2Cl_2	84

[a] Yield of pure isolated product. [b] Reactions were carried out at room temperature, reaction time 4.0 h. [c] 1,8-Diazabicyclo[5.4.0] uncec-7-ene. [d] Urea–hydrogen peroxide complex. [e] Commercial *m*-CPBA contains 77% weight of peroxyacid. [f] 1,1,3,3-Tetramethylguanidine.

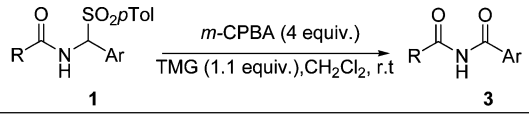
Initially 1,8-diazabicyclo[5.4.0]uncec-7-ene (DBU) was chosen as a base for its known aptitude to provide elimination of the arylsulfonyl group from α-amido sulfones, but its combination with *t*BuOOH did not provide the expected product (Table 1, Entry 1). Encouraging results were obtained with the use of urea–hydrogen peroxide complex (UHP) and commercial *m*-chloroperoxybenzoic acid (*m*-CPBA), so we decided to use the latter reagent for further optimization studies (Table 1, Entries 2 and 3). An increase of up to four equivalents of peroxyacid proved to be beneficial for the chemical yield of imide **3a**, whereas changing dichloromethane with acetonitrile gave a reduced yield of product (Table 1, Entries 4–6). At this point, we were concerned with the role played by the base in this procedure, because the large amount of peroxyacid used and the observation that better results were recorded when the base was added to the mixture of **1a** and the peracid seemed to exclude its role in the formation of the *N*-acylimine. As a matter of fact, when the reaction was carried out without any added base, product **3a** was still obtained although in a reduced yield (Table 1, Entry 7). An increase in the amount of the base to 0.5 equiv. provided an increase in the yield, confirming that its presence was mandatory for successful oxidation (Table 1, Entry 8). Finally, a survey of other basic systems revealed that 1,1,3,3-tetramethylguanidine (TMG) is the base of choice for the efficient conversion of α-amido sulfones into the corresponding imides (Table 1, Entry 9). Several attempts at using α-amidoalkyl sulfones for this conversion led only to disappointing results, as the starting material seems quite unreactive under these conditions. Finally, other known precursors of *N*-acylimines were tested to evidence their behavior in the oxidation process. The *N*-acetyl benzotriazolyl derivative (**1**: R = Me, Ar = Ph, X = 1-benzotriazolyl)[12] is totally unreactive under our conditions, whereas the *N*-acetyl methoxy derivative (**1**: R = Me, Ar = Ph, X = OMe) was converted into imide **3a** only in modest yield (40%).[13]

A number of different α-amidoaryl sulfones **1** bearing alkyl and aryl substituents in the amido portion were converted into imides **3** under our optimized conditions (Table 2, Entries 1–5).

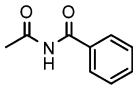
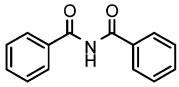
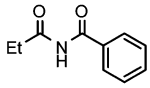
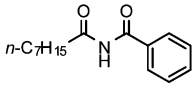
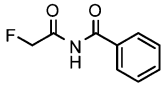
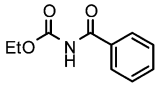
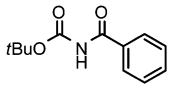
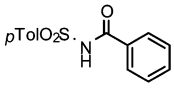
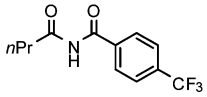
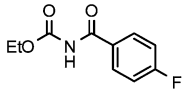
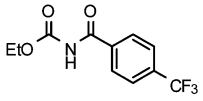
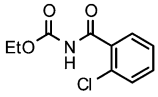
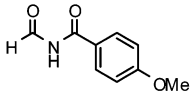
Carbamoyl sulfones can also be used for this purpose and even the acid-sensitive *tert*-butoxylcarbonyl group is well tolerated by the applied reaction conditions (Table 2, Entries 6 and 7).[14] The synthetic interest in *N*-tosylated amido derivatives[15] prompted us to verify the suitability of our oxidizing system also for an *N*-*p*-tosylamidophenyl sulfone, and we were delighted to observe that this substrate can be converted into the corresponding imide **3h** in satisfactory yield (Table 2, Entry 8). Substituents in the aryl portion of α-amido sulfones **1** have a sensible effect on the reactivity, as the presence of electron-withdrawing groups generally gives superior results to those obtained in the presence of electron-donating groups (Table 2, Entries 9–11 vs. Entry 13). However, when the substituent is situated in close proximity to the reacting center, a decrease in reactivity is observed, as in the case of the formation of imide **3l** bearing a chloride in the 2-position of the aromatic ring (Table 2, Entry 12). A particular behavior was observed with α-amido sulfone **1n** bearing a 2-chloroethylamido group that under usual conditions gave an equimolar, inseparable mixture of expected imide **3n** and unsaturated imide **3o** clearly generated by an elimination process (Scheme 3). After exploiting several different reaction conditions, we were unable to selectively drive the process toward a single product; therefore, the crude product mixture obtained after workup operation was treated with TMG in dichloromethane, allowing recovery of unsaturated imide **3o** in 76% overall yield.

Various observations recorded during trial experiments and those evidenced on different substrates reported in Table 2 support a mechanism strictly related to that proposed by Vidal and co-workers for the formation of byproduct imides observed during oxidation of *N*-acylimines.[8] Because of the acidic conditions in which our process is carried out, we consider as a probable intermediate in our process the formation of *N*-acyliminium ion **4** formed by elimination of *p*-toluenesulfinic acid from α-amido sulfone **1** (Scheme 4).[16] This highly reactive electrophilic species is able to react with the anion of *m*-chloroperoxybenzoic acid partially generated by the added base TMG leading to intermediate **5**. The favorable equilibrium among the acid and its anionic counterpart is mandatory for a successful pro-

Table 2. Oxidation of α-amido sulfones **1** to imides **3**.

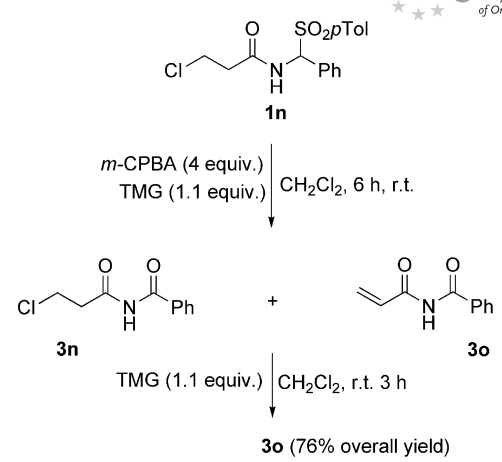


1 **3**

Entry		Imide[a]	*t* [h]	Yield [%][b]
1	**3a**		4	84
2	**3b**		4	50
3	**3c**		4	55
4	**3d**		5	69
5	**3e**		15	53
6	**3f**		4	68
7	**3g**		6	70
8	**3h**		4	65[c]
9	**3i**		15	73
10	**3j**		4	85
11	**3k**		4	80
12	**3l**		4	40
13	**3m**		15	46

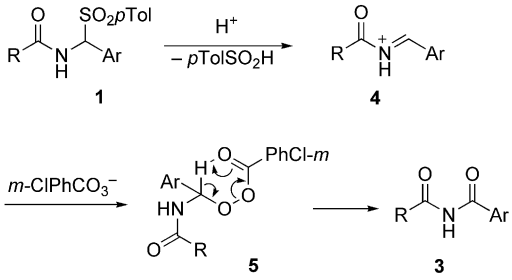
[a] α-Amido sulfone (1 mmol), *m*-CPBA (4 mmol) in dichloromethane; (10 mL) then TMG (1.1 mmol) at room temperature. [b] Yield of pure, isolated products. [c] Reaction carried out on *N*-tosylamidophenyl sulfone.

cess. As a matter of fact, the absence of any added base results in a poor conversion (Table 1, Entry 7), whereas a large amount of base equally provided disappointing results, reducing the acidity level of the reaction medium. The subsequent oxidative rearrangement of intermediate **5** is largely dependent on the acidity of the benzylic proton and this accounts for the better results obtained when electron-



Scheme 3. Synthesis of *N*-acryloylbenzamide **3o**.

withdrawing groups are located in the aromatic ring of substrates **1**. The modest results evidenced in the formation of imide **3l** bearing a 2-chlorophenyl group (Table 2, Entry 12) may be attributable to the steric hindrance that makes attack of the peroxyacid anion to *N*-acyliminium ion **4** difficult.



Scheme 4. Plausible mechanism for the oxidation of α-amidoaryl sulfones.

Conclusions

In summary, imides can be obtained in satisfactory yields by direct oxidation of α-amidoaryl sulfones by using commercial *m*-chloroperoxybenzoic acid at room temperature. The procedure is effective for the preparation of arylimides bearing functionalized *N*-alkanoyl, *N*-alkoxycarbonyl, aryl, and *p*-toluenesulfonyl substituents. The experimental conditions required for this process suggest an *N*-acyliminium ion as a reactive intermediate, which upon addition of the peroxyacid anion and subsequent intramolecular rearrangement affords the imido derivative.

Experimental Section

General Remarks: ^{1}H NMR spectra were recorded at 400 MHz with a Varian Mercury Plus 400. ^{13}C NMR spectra were recorded at 100 MHz. Mass spectra were carried out by the EI technique (70 eV) with a GC–MS Agilent Technologies 6850 Serie II/5973 Inert. Microanalyses were performed with a CHNS-O analyzer Model EA 1108 from Fisons Instruments. IR spectra were recorded

with a Perkin–Elmer Paragon 500 FTIR. All chemical used were commercial. α-Amido sulfones **1** were prepared as described previously.[17]

General Procedure for the Synthesis of Imides 3a–m: To a stirred solution of α-amido sulfone **1** (1 mmol) in CH_2Cl_2 (10 mL) was added *m*-chloroperoxybenzoic acid (77% pure, 4 mmol) at room temperature. TMG (1.1 mmol) was added dropwise, and the mixture was stirred for the appropriate amount of time (see Table 2) at the same temperature. The mixture was diluted with CH_2Cl_2 (30 mL) and then washed with aqueous sodium hydrogensulfite (2.5%, 2 × 10 mL) and saturated $NaHCO_3$ (2 × 10 mL). The organic phase was dried with $MgSO_4$ and after evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography (hexanes/ethyl acetate, 6:4).

***N*-Acetylbenzamide (3a):** Yield: 0.137 g (84%). White solid. M.p. 115–117 °C. IR (nujol): $\tilde{\nu}$ = 679, 1204, 1481, 1499, 1600, 1678, 1735, 3064, 3273 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.60 (s, 3 H, CH_3), 7.45–7.53 (m, 2 H, ArH), 7.56–7.63 (m, 1 H, ArH), 7.85–7.91 (m, 2 H, ArH), 9.06 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.9, 128.0, 129.2, 132.9, 133.5, 166.1, 173.9 ppm. MS (EI): *m*/*z* (%) = 163 (25) $[M]^+$, 162 (21), 105 (100), 77 (42), 51 (13), 43 (18). $C_9H_9NO_2$ (163.17): calcd. C 66.25, H 5.56, N 8.58; found C 66.34, H 5.48, N 8.66.

***N*-Benzoylbenzamide (3b):** Yield: 0.112 g (50%). White solid. M.p. 146–148 °C. IR (nujol): $\tilde{\nu}$ = 706, 1221, 1470, 1675, 1702, 3030, 3242 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.50 (m, 4 H, ArH), 7.53–7.60 (m, 2 H, ArH), 7.83–7.89 (m, 4 H, ArH), 9.49 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 128.3, 128.9, 133.2, 133.7, 167.1 ppm. MS (EI): *m*/*z* (%) = 225 (24) $[M]^+$, 197 (9), 122 (6), 105 (100), 77 (55), 51 (17). $C_{14}H_{11}NO_2$ (225.24): calcd. C 74.65, H 4.92, N 6.22; found C 74.83, H 5.03, N 6.13.

***N*-Propanoylbenzamide (3c):** Yield: 0.098 g (55%). White solid. M.p. 97–99 °C. IR (nujol): $\tilde{\nu}$ = 804, 1079, 1208, 1243, 1366, 1470, 1600, 1678, 1711, 3068, 3285 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.20 (t, $^3J_{H,H}$ = 7.3 Hz, 3 H, CH_3), 3.02 (q, $^3J_{H,H}$ = 7.3 Hz, 2 H, CH_2), 7.45–7.52 (m, 2 H, ArH), 7.55–7.62 (m, 1 H, ArH), 7.86–7.93 (m, 2 H, ArH), 9.13 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 8.4, 31.4, 128.0, 129.1, 133.1, 133.4, 166.0, 177.7 ppm. MS (EI): *m*/*z* (%) = 177 (30) $[M]^+$, 149 (19), 122 (28), 105 (100), 77 (54), 51 (18). $C_{10}H_{11}NO_2$ (177.20): calcd. C 67.78, H 6.26, N 7.90; found C 67.63, H 6.19, N 7.99.

***N*-Octanoylbenzamide (3d):** Yield: 0.171 g (69%). White solid. M.p. 64–66 °C. IR (nujol): $\tilde{\nu}$ = 773, 1185, 1237, 1465, 1508, 1676, 1707, 3064, 3320 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, $^3J_{H,H}$ = 6.8 Hz, 3 H, CH_3), 1.22–1.45 (m, 8 H, 4 CH_2), 1.66–1.76 (m, 2 H, CH_2), 2.99 (t, $^3J_{H,H}$ = 7.3 Hz, 2 H, CH_2CO), 7.46–7.53 (m, 2 H, ArH), 7.57–7.63 (m, 1 H, ArH), 7.85 (d, *J* = 7.7 Hz, 2 H, ArH), 8.66 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.3, 22.9, 24.4, 29.3, 29.4, 31.9, 37.8, 127.8, 129.2, 133.1, 133.4, 165.7, 176.5 ppm. MS (EI): *m*/*z* (%) = 247 (2) $[M]^+$, 176 (40), 163 (47), 122 (50), 105 (100), 77 (51), 57 (13), 41 (16). $C_{15}H_{21}NO_2$ (247.33): calcd. C 72.84, H 8.56, N 5.66; found C 73.02, H 8.65, N 5.58.

***N*-2-Fluoroacetylbenzamide (3e):** Yield: 0.096 g (53%). White solid. M.p. 119–122 °C. IR (nujol): $\tilde{\nu}$ = 801, 912, 1049, 1240, 1401, 1602, 1683, 1712, 3075, 3300 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.43 (d, $^2J_{H,H}$ = 47.9 Hz, 2 H, CH_2F), 7.48–7.54 (m, 2 H, ArH), 7.59–7.65 (m, 1 H, ArH), 7.89–7.94 (m, 2 H, ArH), 9.52 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 80.4, 82.2, 128.1, 129.3, 131.4, 134.0, 166.1, 171.2, 172.4 ppm. MS (EI): *m*/*z* (%) = 181 (17) $[M]^+$, 161 (14), 105 (100), 103 (31), 77 (57), 81 (18). $C_9H_8FNO_2$ (181.16): calcd. C 59.67, H 4.45, N 7.73; found C 59.49, H 4.37, N 7.79.

Ethyl *N*-Benzoylcarbamate (3f): Yield: 0.131 g (68%). White solid. M.p. 110–112 °C. IR (nujol): $\tilde{\nu}$ = 804, 1026, 1077, 1206, 1242, 1366, 1469, 1600, 1677, 1710, 3068, 3289 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.33 (t, $^3J_{H,H}$ = 7.3 Hz, 3 H, CH_3), 4.30 (q, $^3J_{H,H}$ = 7.3 Hz, 2 H, CH_2), 7.44–7.51 (m, 2 H, ArH), 7.54–7.61 (m, 1 H, ArH), 7.79–7.85 (m, 2 H, ArH), 8.22 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.4, 62.6, 127.8, 129.1, 133.2, 133.3, 151.3, 165.1 ppm. MS (EI): *m*/*z* (%) = 177 (29), 149 (18), 122 (27), 105 (100), 77 (55), 51 (18). $C_{10}H_{11}NO_3$ (193.20): calcd. C 62.17, H 5.74, N 7.25; found C 62.01, H 5.65, N 7.33.

***tert*-Butyl *N*-Benzoylcarbamate (3g):** Yield: 0.155 g (70%). White solid. M.p. 149–151 °C. IR (nujol): $\tilde{\nu}$ = 936, 1128, 1217, 1480, 1501, 1677, 1747, 3074, 3252 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.52 (s, 9 H, *t*Bu), 7.41–7.48 (m, 2 H, ArH), 7.51–7.58 (m, 1 H, ArH), 7.77–7.83 (m, 2 H, ArH), 8.08 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.2, 82.9, 127.7, 128.9, 132.9, 133.5, 149.9, 165.5 ppm. MS (EI): *m*/*z* (%) = 147 (55), 105 (100), 77 (80), 51 (27), 50 (17). $C_{12}H_{15}NO_3$ (221.25): calcd. C 65.14, H 6.83, N 6.33; found C 65.25, H 6.72, N 6.36.

***N*-Benzoyl-*p*-toluenesulfonamide (3h):** Yield: 0.179 g (65%). White solid. M.p. 93–95 °C. IR (nujol): $\tilde{\nu}$ = 661, 775, 1164, 1344, 1456, 1593 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.49 (s, 3 H, $ArCH_3$), 5.45 (s, 1 H, NH), 7.37–7.50 (m, 7 H, ArH), 7.93 (d, $^3J_{H,H}$ = 8.5 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.0, 128.4, 128.9, 129.6, 130.2, 130.8, 131.6, 131.7, 146.6 ppm. MS (EI): *m*/*z* (%) = 259 (19), 195 (8), 155 (66), 104 (14), 91 (100), 77 (17), 65 (23), 51 (11). $C_{14}H_{13}NO_3S$ (275.32): calcd. C 61.07, H 4.76, N 5.09; found C 60.91, H 4.82, N 4.96.

***N*-Butyryl-(4-trifluoromethyl)benzamide (3i):** Yield: 0.190 g (73%). White solid. M.p. 135–138 °C. IR (nujol): $\tilde{\nu}$ = 693, 764, 867, 1066, 1670, 1683, 1713, 3277 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.03 (t, $^3J_{H,H}$ = 7.3 Hz, 3 H, CH_3), 1.70–1.81 (m, 2 H, CH_2), 2.98 (t, $^3J_{H,H}$ = 7.3 Hz, 2 H, CH_2), 7.77 (d, $^3J_{H,H}$ = 8.5 Hz, 2 H, ArH), 7.98 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H, ArH), 8.85 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9, 17.7, 39.8, 126.1, 126.2, 126.3, 126.4, 128.4, 136.4, 164.7, 176.2, 176.3 ppm. MS (EI): *m*/*z* (%) = 259 (9) $[M]^+$, 244 (10), 231 (22), 190 (58), 173 (100), 145 (68), 125 (9), 95 (12), 71 (25), 55 (16), 43 (37). $C_{12}H_{12}F_3NO_2$ (259.22): calcd. C 55.60, H 4.67, N 5.40; found C 55.72, H 4.73, N 5.50.

Ethyl *N*-(4-Fluorobenzoyl)carbamate (3j): Yield: 0.180 g (85%). White solid. M.p. 91–93 °C. IR (nujol): $\tilde{\nu}$ = 777, 1161, 1231, 1505, 1600, 1704, 1768, 3031, 3333 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.34 (t, $^3J_{H,H}$ = 7.3 Hz, 3 H, CH_3), 4.30 (q, $^3J_{H,H}$ = 7.3 Hz, 2 H, CH_2), 7.12–7.19 (m, 2 H, ArH), 7.82–7.89 (m, 2 H, ArH), 8.08 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.5, 62.8, 116.1, 116.4, 130.4, 130.5, 164.5, 167.0 ppm. MS (EI): *m*/*z* (%) = 165 (8), 139 (51), 123 (100), 95 (76), 75 (27), 50 (10), 44 (10). $C_{10}H_{10}FNO_3$ (211.19): calcd. C 56.87, H 4.77, N 6.63; found C 56.71, H 4.80, N 6.70.

Ethyl *N*-(4-Trifluoromethylbenzoyl)carbamate (3k): Yield: 0.208 g (80%). White solid. M.p. 119–122 °C. IR (nujol): $\tilde{\nu}$ = 777, 1032, 1113, 1192, 1326, 1498, 1692, 1754, 3066, 3303 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.30 (t, $^3J_{H,H}$ = 7.3 Hz, 3 H, CH_3), 4.19–4.30 (m, 2 H, CH_2), 7.69 (d, $^3J_{H,H}$ = 7.7 Hz, 2 H, ArH), 7.94 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H, ArH), 8.21 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.4, 62.9, 125.9, 126.0, 126.1, 126.2, 128.4 ppm. MS (EI): *m*/*z* (%) = 215 (26), 196 (10), 173 (100), 145 (89), 125 (9), 95 (13), 75 (16), 50 (9), 31 (9). $C_{11}H_{10}F_3NO_3$ (261.20): calcd. C 50.58, H 3.86, N 5.36; found C 50.38, H 3.95, N 5.47.

Ethyl *N*-(2-Chlorobenzoyl)carbamate (3l): Yield: 0.091 g (40%). White solid. M.p. 76–78 °C. IR (nujol): $\tilde{\nu}$ = 775, 1163, 1215, 1501,

1602, 1711, 1766, 3042, 3301 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.26 (t, $^3J_{H,H}$ = 7.3 Hz, 3 H, CH_3), 4.20 (q, $^3J_{H,H}$ = 7.3 Hz, 2 H, CH_2), 7.29–7.36 (m, 1 H, ArH), 7.37–7.41 (m, 2 H, ArH), 7.50 (d, $^3J_{H,H}$ = 7.3 Hz, 1 H, ArH), 8.34 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.3, 62.7, 127.2, 129.5, 130.0, 130.6, 132.0, 134.4, 151.0, 166.4 ppm. MS (EI): *m*/*z* (%) = 181 (27), 141 (28), 139 (100), 137 (37), 111 (38), 75 (26), 50 (12). $C_{10}H_{10}ClNO_3$ (227.64): calcd. C 52.76, H 4.43, N 6.15; found C 52.63, H 4.48, N 6.23.

***N*-Formyl-(4-methoxy)benzamide (3m):** Yield: 0.082 g (46%). White solid. M.p. 201–203 °C. IR (nujol): $\tilde{\nu}$ = 749, 840, 1017, 1178, 1214, 1373, 1461, 1579, 1604, 1670, 1718, 3260 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.91 (s, 3 H, CH_3O), 7.09 (d, $^3J_{H,H}$ = 9.0 Hz, 2 H, ArH), 8.08 (d, $^3J_{H,H}$ = 9.0 Hz, 2 H, ArH), 9.28 (s, 1 H, CHO), 10.41 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.5, 114.3, 130.7, 163.4, 164.3, 205.6 ppm. MS (EI): *m*/*z* (%) = 179 (16) $[M]^+$, 151 (47), 135 (100), 107 (13), 92 (17), 77 (22), 64 (11). $C_9H_9NO_3$ (179.17): calcd. C 60.33, H 5.06, N 7.82; found C 60.25, H 5.15, N 7.99.

***N*-Acryloylbenzamide (3o):** To a CH_2Cl_2 (20 mL) solution of the crude mixture of products **3n** and **3o** obtained by treating sulfone **1n** (1 mmol) according to the general procedure was added TMG (2.0 mmol). The solution was stirred for 3 h at room temperature and then washed with 1 N HCl (2 × 5 mL) and brine (2 × 5 mL). The organic phase was dried with $MgSO_4$ and after evaporation of the solvent under reduced pressure the crude product was purified by column chromatography (hexanes/ethyl acetate, 6:4). Yield: 0.133 g (76%). Yellow solid. M.p. 94–97 °C. IR (nujol): $\tilde{\nu}$ = 747, 849, 976, 1167, 1241, 1303, 1467, 1597, 1666, 1703, 3269 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.87 (dd, $^2J_{H,H}$ = 1.7 Hz, $^3J_{H,H}$ = 10.3 Hz, 1 H, CH_2), 6.51 (dd, $^2J_{H,H}$ = 1.7 Hz, $^3J_{H,H}$ = 17.1 Hz, 1 H, CH_2), 7.39 (dd, $^3J_{H,H}$ = 10.7 Hz, $^3J_{H,H}$ = 17.1 Hz, 1 H, CH), 7.45–7.61 (m, 3 H, ArH), 7.85–7.91 (m, 2 H, ArH), 9.19 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 128.1, 129.2, 129.9, 130.6, 132.2, 133.6, 133.7, 166.1, 168.1 ppm. MS (EI): *m*/*z* (%) = 175 (11) $[M]^+$, 147 (15), 105 (100), 77 (55), 55 (23), 51 (19). $C_{10}H_9NO_2$ (175.19): calcd. C 68.56, H 5.18, N 8.00; found C 68.75, H 5.28, N 7.96.

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