

## 150. Preparation of *ortho*-Aryl-benzaldehyde Derivatives via Free-Radical *ipso*-Substitution of an Amidomethyl Group

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Preparation of 2-biarylcarbaldehydes using an intramolecular free-radical *ipso*-substitution is described. The two aryl moieties to be coupled are pre-associated using a glycolamide derivative. An unusual amidomethyl leaving group was successfully employed in this process.

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**1. Introduction.** – Regioselective preparation of substituted biaryl derivatives has recently attracted much attention due to the interesting properties of these compounds and to recent progress in the field of organometallic chemistry<sup>1)</sup>. We report here a free-radical approach to prepare such biaryl derivatives<sup>2)</sup>. The general approach is depicted in *Scheme 1*, the key step being a homolytic *ipso*-substitution of an amidomethyl group. This represents to our knowledge the first attempt to develop an *ipso*-substitution of an alkyl group (amidomethyl group) by an aryl group<sup>3)</sup>. The well-documented stability of 1-amidoalkyl radicals<sup>4)</sup> and re-aromatization<sup>5)</sup> are expected to be driving forces for this process.

**Results and Discussion.** – The critical step is the radical addition at the hindered *ipso*-position. To force the system to react at this position, we have developed an intramolecular version based on a 6-*exo*-cyclization reaction using a glycolamide template. The first aryl moiety is introduced as an *N,O*-acetal, the second one is placed at the N-atom. For this purpose, the *N,O*-acetal **1** was prepared by acetalization of glycolamide (2-hydroxyacetamide) with the 2-bromobenzaldehyde. *N*-Benzoylation of **1** with several

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<sup>1)</sup> For reviews on this topic, see [1–3].

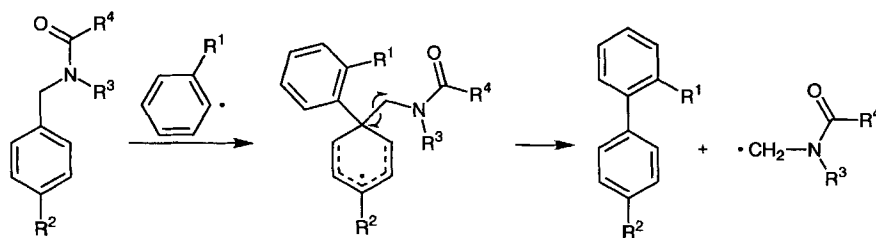
<sup>2)</sup> Radical approaches to biaryl systems using intramolecular *ipso*-substitutions of sulfonates and sulfonamides have been reported [4–6]. Intramolecular radical *ipso*-substitution of alkoxy group has recently been observed [7]. A review on homolytic *ipso*-substitution summarizes the results before 1980 [8]. Examples of radical cyclizations to aromatic rings followed by re-aromatization have been reported [7] [9–11]; for a review, see [12].

<sup>3)</sup> Migration of CN groups via iminyl radical formation and  $\beta$ -fragmentation leading to 1-amidoalkyl radicals have recently been reported [13] [14]. The well-known 1,2-Ph migration of substituted 2-phenylethyl radicals (neophyl rearrangement) can be considered as a special example of intramolecular *ipso*-substitution of an alkyl group; for the mechanism of this rearrangement, see [15].

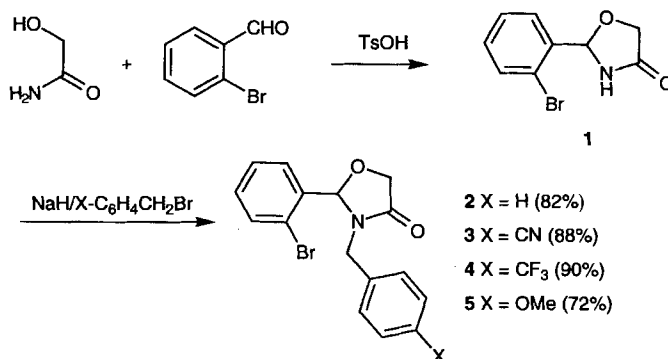
<sup>4)</sup> For a review, see [16]. Recently, we have also reported that acyl radicals derived from *N*-protected amino acids undergo a rapid decarbonylation to the more stable 1-amidoalkyl radicals [17].

<sup>5)</sup> Recently, fragmentation of C,C bond in substituted cyclohexadienyl radicals has been reported [18].

Scheme 1



Scheme 2



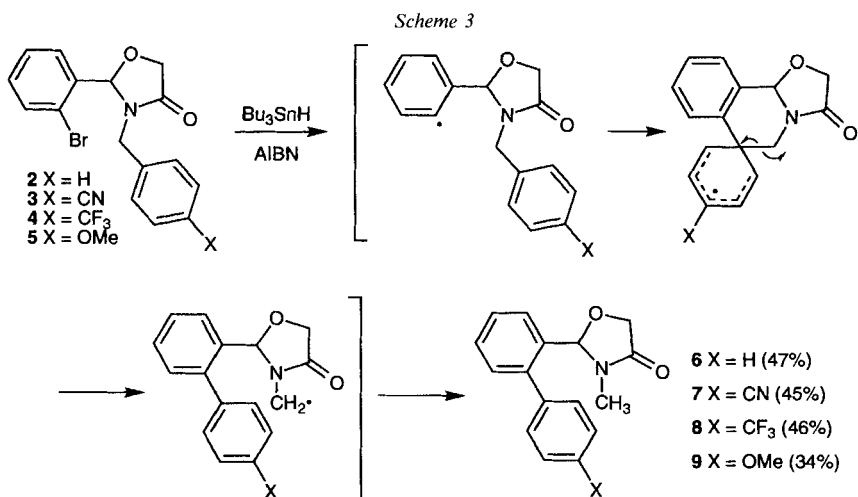
4-substituted benzyl bromides gave the 1,3-oxazolidin-4-one derivatives **2–5** in good yields (Scheme 2).

Treatment of the aryl bromides **2–5** with  $\text{Bu}_3\text{SnH/AIBN}$  using syringe pump addition technique and chromatographic workup (flash column chromatography) gave the biphenyl derivatives **6–9** in moderate yields (34–47%) (Scheme 3). Tetracyclic compounds **10–13**, arising from a cyclization of the radical at the *ortho*-position, were isolated in 6–13% yield, and the reduced products **14–17** were obtained as side products in 26–28% yield (Scheme 3). It was not possible to suppress these side products by further dilution of the reaction mixture. Indeed, reaction with  $\text{Bu}_3\text{SnD}$  showed that reduction is occurring *via* an intramolecular 1,5-H shift from the benzylic  $\text{CH}_2$  group.

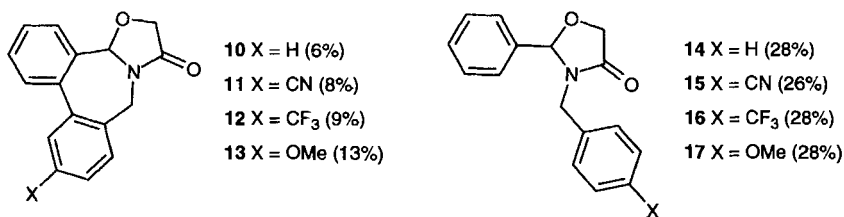
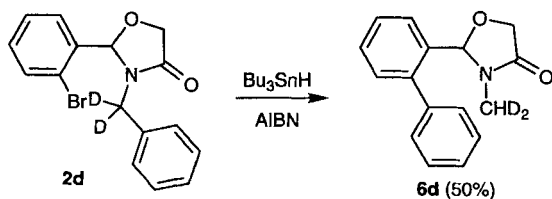
The extent of H-transfer could be dramatically reduced by running the reaction with the deuterated substrate **2d** instead of **2** (Scheme 4). The product of Ph migration **6d** was isolated in 50% yield along with 11% of the tetracycle **10d**, when the reaction was run in refluxing benzene. Products of direct reduction and of D transfer, **14d** and **14d'**, respectively, were also obtained in 11% global yield (**14d/14d'** 1:1, by  $^2\text{H-NMR}$ ). This shows that the deuteration is an effective tool to avoid H-shift in radical reaction<sup>6</sup>.

The final step of the preparation of the 2-aryl-benzaldehydes was the hydrolysis of **6–9** to give **18–21** (Scheme 5). The CN- and the  $\text{CF}_3$ -substituted derivatives **19** and **20**, respectively, were obtained upon heating under reflux a solution of **7** and **8** in 6N HCl (Method A). For compounds **18** and **21**, milder conditions were required. Indeed, in

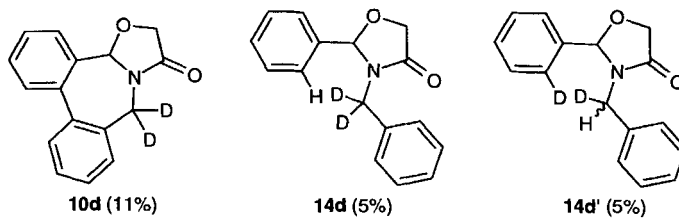
<sup>6</sup>) For former cases using deuterated protective group in radical reactions, see [19].



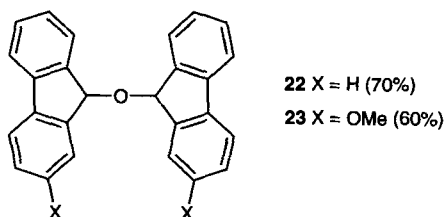
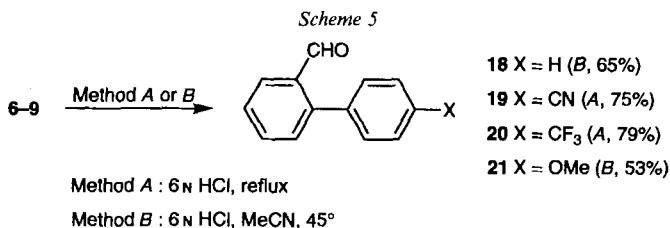
## Side products

*Scheme 4*

## Side products



refluxing HCl (*Method A*), an intramolecular *Friedel-Crafts* alkylation occurred, followed by an acid-catalyzed etherification leading to the difluorenyl ethers **22** and **23**, respectively. Hydrolysis with 6N HCl at 45° in MeCN gave the desired aldehydes **18** and **21** in 65 and 53% yield, respectively.



**Conclusions.** – Formation of C(aryl)–C(aryl) bond using an intramolecular radical *ipso*-substitution reaction of a carbon residue was shown to be possible. Both aryl moieties were linked using a glycolic-acid-based template. Further development of this methodology to synthesize optically active biaryls employing templates derived from enantiomerically pure, commercially available, and cheap  $\alpha$ -hydroxy acids such as lactic and mandelic acids is currently under investigation.

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#### Experimental Part

*General.* THF was freshly distilled from K under N<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>, DMF; and benzene from CaH<sub>2</sub> under N<sub>2</sub>, and toluene from Na under N<sub>2</sub>. Flash column chromatography (FC) and filtration: *Baker silica gel* (0.063–0.200 mm). TCL: *Merck silica gel 60 F<sub>254</sub>* anal. plates; detection either with UV, iodine, or spraying with a soln. of 25 g of phosphomolybdic acid, 10 g of Ce(NH<sub>4</sub>)<sub>2</sub>(NO<sub>3</sub>)<sub>6</sub> · 4 H<sub>2</sub>O, 60 ml of conc. H<sub>2</sub>SO<sub>4</sub>, and 940 ml H<sub>2</sub>O with subsequent heating. M.p.: not corrected; *Büchi Tottoli* apparatus. IR: *Mattson Unicam 5000*; in cm<sup>-1</sup>. NMR: *Varian Gemini 200* (<sup>1</sup>H: 200 MHz, <sup>13</sup>C: 50.3 MHz), *Bruker AM 360* (<sup>1</sup>H: 360 MHz), *Bruker Avance DRX-500* (<sup>1</sup>H: 500 MHz); for <sup>1</sup>H  $\delta$  in ppm relative to CDCl<sub>3</sub> (= 7.27 ppm) and (D<sub>6</sub>)DMSO (= 2.49 ppm); for <sup>13</sup>C,  $\delta$  in ppm relative to CDCl<sub>3</sub> (= 77.1 ppm). <sup>13</sup>C Multiplicities were determined by the APT sequence; coupling constants *J* are given in Hz. MS: *Vacuum Generators Micromass VG 70/70E DS 11-250*; EI (70 eV), CI (CH<sub>4</sub> gas); *m/z* (%). Elemental analysis: *Ilse Beetz*, Microanalytisches Laboratorium, D-96301 Kronach, Germany, and *Ciba Geigy Mikrolabor*, Marly, Switzerland.

*Glycolamide* (= *2-Hydroxyacetamide*) [20]. A soln. of ethyl glycolate (15.0 g, 0.14 mol) in liquid NH<sub>3</sub> (50 ml) was placed in an autoclave and allowed to warm up to r. t. After 24 h, the excess NH<sub>3</sub> was allowed to escape slowly through the gas outlet of the bomb, and the residue was dried under reduced pressure. The crude product was washed with Et<sub>2</sub>O, recrystallized from hexane/THF, and air-dried to yield glycolamide (9.8 g, 90%). White solid.

M. p. 116–116.5°. <sup>1</sup>H-NMR (D<sub>2</sub>O, 200 MHz): 4.10 (s, CH<sub>2</sub>). <sup>13</sup>C-NMR (D<sub>2</sub>O): 181.05 (s, CO); 63.65 (t, CH<sub>2</sub>). EI-MS: 75 (26, M<sup>+</sup>), 46 (46), 44 (100), 32 (35), 31 (24). Anal. calc. for C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub> (75.06): C 32.00, H 6.71, N 18.66; found: C 32.18, H 6.78, N 18.62.

**2-(2-Bromophenyl)-1,3-oxazolidin-4-one (1)** [21]. A soln. of 2-bromobenzaldehyde (13.6 g, 73.5 mmol), glycolamide (5.0 g, 66 mmol), and TsOH (0.13 g, 0.7 mmol) in toluene (150 ml) was heated under reflux for 12 h in a *Dean-Stark* apparatus. After evaporation of toluene, the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub>, washed with H<sub>2</sub>O and brine, and dried (MgSO<sub>4</sub>). Evaporation of the solvent, FC (hexane/AcOEt/THF 7:2:1) and recrystallization from hexane/AcOEt afforded **1** (4.98 g, 31%). White solid. M. p. 132.7–133.5°. <sup>1</sup>H-NMR (200 MHz): 8.08 (br. s, NH); 7.60–7.21 (m, 4 arom. H); 6.47 (dd, *J* = 2.0, 1.6, H–C(2)); 4.42 (A of ABX, *J*<sub>AB</sub> = 14.0, *J*<sub>AX</sub> = 2.0, H–C(5)); 4.33 (B of ABX, *J*<sub>AB</sub> = 14.0, *J*<sub>BX</sub> = 1.5, H–C(5)). <sup>13</sup>C-NMR: 173.32 (s, C(4)); 137.26 (s); 133.25 (d); 131.03 (d); 128.06 (d); 127.50 (d); 122.20 (s, CBr); 87.79 (d, C(2)); 67.42 (t, C(5)). EI-MS: 243 (30, [M + 1]<sup>+</sup>), 242 (47, M<sup>+</sup>), 212 (1), 197 (5), 182 (42), 162 (46), 119 (38), 104 (46), 86 (100), 76 (68), 50 (72). Anal. calc. for C<sub>9</sub>H<sub>8</sub>BrNO<sub>2</sub> (242.07): C 44.66, H 3.33, N 5.79; found: C 44.49, H 3.53, N 5.54.

**General Procedure 1 (GP1).** N-Alkylation of **1**. A soln. of **1** (1.0 g, 4.13 mmol) in THF (10 ml) was added dropwise to a stirred suspension of NaH (55% in paraffin; 0.20 g, 8.3 mmol) in THF (5 ml) at 0°. The mixture was stirred for 30 min at r.t., and the halide (4.5 mmol) was added. After 12 h under reflux, the solvent was evaporated and the residue dissolved in CH<sub>2</sub>Cl<sub>2</sub> (60 ml). The org. layer was washed with H<sub>2</sub>O (3 × 20 ml) and dried (MgSO<sub>4</sub>). The evaporation of the solvent gave the crude product which was purified by FC.

**3-Benzyl-2-(2-bromophenyl)-1,3-oxazolidin-4-one (2)**. According to GP1. From **1** (1.0 g, 4.13 mmol) and PhCH<sub>2</sub>Br (0.78 g, 4.5 mmol). FC (hexane/AcOEt 7:3) gave **2** (1.12 g, 82%). Colorless liquid. <sup>1</sup>H-NMR (200 MHz): 7.58–7.53 (m, 1 arom. H); 7.35–7.06 (m, 8 arom. H); 6.26 (dd, *J* = 1.7, 1.2, H–C(2)); 4.53 (A of ABX, *J*<sub>AB</sub> = 13.7, *J*<sub>AX</sub> = 1.8, H–C(5)); 4.51 (d, *J* = 14.8, 1 H, CH<sub>2</sub>N); 4.39 (B of ABX, *J*<sub>AB</sub> = 13.7, *J*<sub>BX</sub> = 1.2, H–C(5)); 3.72 (d, *J* = 14.8, 1 H, CH<sub>2</sub>N). <sup>13</sup>C-NMR: 170.14 (s, C(4)); 134.94 (s); 134.69 (s); 133.64 (d); 131.41 (d); 129.54 (d); 128.61 (d); 128.32 (d); 127.90 (d); 123.41 (s, CBr); 91.00 (d, C(2)); 67.73 (t, C(5)); 43.95 (t, CH<sub>2</sub>N). EI-MS: 334 (4, [M + 2]<sup>+</sup>), 333 (1, [M + 1]<sup>+</sup>), 332 (6, M<sup>+</sup>), 290 (1), 240 (25), 197 (2), 176 (8), 147 (100), 104 (44), 91 (90), 65 (21), 51 (11). Anal. calc. for C<sub>16</sub>H<sub>14</sub>BrNO<sub>2</sub> (332.19): C 57.85, H 4.25, N 4.22; found: C 57.56, H 4.44, N 4.46.

**3-[(α,α-<sup>2</sup>H<sub>2</sub>)Benzyl]-2-(2-bromophenyl)-1,3-oxazolidin-4-one (2d)**. PhCOMe (680 mg, 5.0 mmol) was added to a slurry of LiAlD<sub>4</sub> (105 mg, 2.5 mmol) in THF (10 ml), and the soln. was stirred 1 h at r.t. The mixture was then treated with sat. aq. Na<sub>2</sub>SO<sub>4</sub> until precipitation of the aluminum salts. After filtration through *Celite* and concentration, the residue was engaged without further purification for the bromide preparation. A soln. of CBr<sub>4</sub> (1.83 g, 5.5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 ml) was added to a soln. of PPh<sub>3</sub> (3.44 g, 13 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 ml) at 0°. After 10 min, a soln. of the alcohol in CH<sub>2</sub>Cl<sub>2</sub> (4 ml) was added, and the soln. was allowed to warm to r.t. and stirred for 2 h. The mixture was concentrated, poured into pentane, and the excess of the phosphine was removed by filtration through *Celite*. Deuterated benzyl bromide (780 mg, 90%) was isolated after filtration through silica gel (pentane). Compound **2d** was obtained according to GP1 starting from **1** (1.09 g, 4.5 mmol) and deuterated benzyl bromide. FC (hexane/AcOEt 7:3) gave **2d** (1.43 g, 73%) as a colorless oil. <sup>1</sup>H- and <sup>13</sup>C-NMR data correspond to those of the undeuterated compound. <sup>2</sup>H-NMR (77 MHz, CHCl<sub>3</sub>): 4.95 (s); 3.76 (s). CI-MS: 364 (27), 362 (27, [M + 43]<sup>+</sup>), 336 (90), 334 (10, [M + 15]<sup>+</sup>), 242 (19), 240 (19), 178 (21), 149 (26).

**2-(2-Bromophenyl)-3-(4-cyanobenzyl)-1,3-oxazolidin-4-one (3)**. According to GP1. From **1** (1.0 g, 4.13 mmol) and 4-cyanobenzyl bromide (0.89 g, 4.5 mmol). FC (hexane/AcOEt 7:3) gave **3** (1.30 g, 88%). Colorless liquid. <sup>1</sup>H-NMR (200 MHz): 7.56–7.49 (m, 3 arom. H); 7.35–7.17 (m, 5 arom. H); 6.33 (dd, *J* = 1.9, 1.4, H–C(2)); 4.71 (d, *J* = 15.2, 1 H, CH<sub>2</sub>N); 4.59 (A of ABX, *J*<sub>AB</sub> = 14.0, *J*<sub>AX</sub> = 2.1, H–C(5)); 4.45 (B of ABX, *J*<sub>AB</sub> = 14.0, *J*<sub>BX</sub> = 1.4, H–C(5)); 4.46 (d, *J* = 15.6, 1 H, CH<sub>2</sub>N). <sup>13</sup>C-NMR: 170.31 (s, C(4)); 140.62 (s); 134.49 (s); 133.56 (d); 132.30 (d); 131.70 (d); 129.56 (d); 128.83 (d); 128.09 (d); 123.29 (s, CBr); 118.38 (s, CN); 111.72 (s, C–CN); 91.04 (d, C(2)); 67.72 (t, C(5)); 43.62 (t, CH<sub>2</sub>N). EI-MS: 359 (1, [M + 2]<sup>+</sup>), 358 (1, [M + 1]<sup>+</sup>), 357 (3, M<sup>+</sup>), 329 (1), 298 (1), 254 (1), 240 (40), 201 (60), 172 (100), 144 (38), 129 (73), 116 (100), 89 (100), 63 (56). Anal. calc. for C<sub>17</sub>H<sub>13</sub>BrN<sub>2</sub>O<sub>2</sub> (357.20): C 57.16, H 3.67, N 7.84; found: C 57.38, H 3.83, N 7.81.

**2-(2-Bromophenyl)-3-[4-(trifluoromethyl)benzyl]-1,3-oxazolidin-4-one (4)**. According to GP1. From **1** (1.0 g, 4.13 mmol) and 4-trifluoromethylbenzyl bromide (1.10 g, 4.5 mmol). FC (hexane/AcOEt 7:3) gave **4** (1.49 g, 90%). Colorless liquid. <sup>1</sup>H-NMR (200 MHz): 7.56–7.46 (m, 3 arom. H); 7.30–7.18 (m, 5 arom. H); 6.31 (dd, *J* = 2.0, 1.4, H–C(2)); 4.78 (d, *J* = 15.2, 1 H, CH<sub>2</sub>N); 4.57 (A of ABX, *J*<sub>AB</sub> = 13.9, *J*<sub>AX</sub> = 2.1, H–C(5)); 4.43 (B of ABX, *J*<sub>AB</sub> = 13.9, *J*<sub>BX</sub> = 1.4, H–C(5)); 3.98 (d, *J* = 15.1, 1 H, CH<sub>2</sub>N). <sup>13</sup>C-NMR: 170.31 (s, C(4)); 139.28 (s); 134.60 (s); 133.62 (d); 131.63 (d); 130.05 (d, <sup>2</sup>J(C,F) = 32.6, C–CF<sub>3</sub>); 129.62 (d); 128.60 (d, 2 arom. C); 128.05 (d); 125.55 (d, <sup>3</sup>J(C,F) = 3.9, 1 arom. C); 125.43 (d, <sup>3</sup>J(C,F) = 3.8, 1 arom. C); 123.96 (q, <sup>1</sup>J(C,F) =

272.2, CF<sub>3</sub>); 123.36 (s, CBr); 91.10 (d, C(2)); 67.74 (t, C(5)); 43.55 (t, CH<sub>2</sub>N). EI-MS: 402 (1, [M + 2]<sup>+</sup>), 401 (3, [M + 1]<sup>+</sup>), 400 (1, M<sup>+</sup>), 399 (5, [M - 1]<sup>+</sup>), 356 (1), 318 (1), 290 (1), 240 (42), 215 (35), 159 (100), 146 (67), 109 (31), 89 (42), 63 (14). Anal. calc. for C<sub>17</sub>H<sub>13</sub>BrF<sub>3</sub>NO<sub>2</sub> (400.19): C 51.02, H 3.27, N 3.50; found: C 51.86, H 3.46, N 3.66.

**2-(2-Bromophenyl)-3-(4-methoxybenzyl)-1,3-oxazolidin-4-one (5).** According to *GP1*. From **1** (1.0 g, 4.13 mmol) and 4-methoxybenzyl chloride (0.70 g, 4.5 mmol). FC (hexane/AcOEt 7:3) gave **5** (1.07 g, 72%). Colorless liquid. <sup>1</sup>H-NMR (200 MHz): 7.57 (d, *J* = 7.7, 1 arom. H); 7.37–7.20 (*m*, 3 arom. H); 7.01 (d, *J* = 8.5, 2 arom. H); 6.78 (d, *J* = 8.6, 2 arom. H); 6.24 (*dd*, *J* = 1.8, 1.7, H-C(2)); 4.87 (d, *J* = 14.6, 1 H, CH<sub>2</sub>N); 4.52 (*A* of *ABX*, *J*<sub>AB</sub> = 13.8, *J*<sub>AX</sub> = 2.2, H-C(5)); 4.38 (*B* of *ABX*, *J*<sub>AB</sub> = 13.8, *J*<sub>BX</sub> = 1.5, H-C(5)); 3.76 (s, MeO); 3.66 (d, *J* = 15.0, 1 H, CH<sub>2</sub>N). <sup>13</sup>C-NMR: 170.12 (s, C(4)); 159.28 (s, C-OMe); 134.82 (s); 133.70 (d); 131.42 (d); 129.76 (d); 129.58 (d); 127.95 (d); 127.06 (s); 123.47 (s, CBr); 114.04 (d); 91.00 (d, C(2)); 67.82 (t, C(5)); 55.22 (q, MeO); 43.42 (t, CH<sub>2</sub>N). EI-MS: 364 (1, [M + 2]<sup>+</sup>), 363 (5, [M + 1]<sup>+</sup>), 362 (2, M<sup>+</sup>), 361 (5, [M - 1]<sup>+</sup>), 338 (1), 304 (1), 252 (1), 224 (3), 195 (1), 177 (100), 146 (65), 121 (86), 78 (34), 51 (13). Anal. calc. for C<sub>17</sub>H<sub>16</sub>BrNO<sub>3</sub> (362.22): C 56.37, H 4.45, N 3.87; found: C 56.76, H 4.57, N 4.07.

**General Procedure 2 (GP2). Radical Reactions.** A degassed soln. of radical precursor (3.01 mmol) in benzene (100 ml) was heated to reflux under an inert atmosphere, treated dropwise (syringe pump) over 18 h with a soln. of Bu<sub>3</sub>SnH (1.00 ml, 3.61 mmol) and 2,2'-azobis[isobutyronitrile] (AIBN; 0.049 g, 0.30 mmol) in benzene (10 ml), and kept for 2 additional h under reflux. The soln. was cooled to r. t., treated with KF (1.5 g, 25.82 mmol) for 24 h, and the solvent was evaporated. The residue was dissolved in hexane (10 ml) and purified by FC (hexane 500 ml and then AcOEt 300 ml). The fraction containing AcOEt was evaporated and purified by FC (hexane/AcOEt 7:3).

**3-Methyl-2-(2-phenylphenyl)-1,3-oxazolidin-4-one (6).** According to *GP2*. From **2** (1.10 g, 3.31 mmol), Bu<sub>3</sub>SnH (1.10 ml, 4.0 mmol), and AIBN (0.060 g, 0.36 mmol). FC (hexane/AcOEt 7:3) gave **6** (0.40 g, 47%) along with **10** (54 mg, 6%) and **14** (0.23 g, 28%).

**Data of 6.** Colorless liquid. <sup>1</sup>H-NMR (200 MHz): 7.49–7.31 (*m*, 9 arom. H); 5.96 (*dd*, *J* = 1.9, 1.6, H-C(2)); 4.37 (*A* of *ABX*, *J*<sub>AB</sub> = 13.7, *J*<sub>AX</sub> = 2.0, H-C(5)); 4.24 (*B* of *ABX*, *J*<sub>AB</sub> = 13.7, *J*<sub>AX</sub> = 1.6, H-C(5)); 2.58 (s, MeN). <sup>13</sup>C-NMR: 170.27 (s, C(4)); 143.07 (s); 133.46 (s); 130.70 (d); 129.54 (d); 129.42 (d); 128.26 (d); 128.17 (d); 127.59 (d); 126.71 (d); 90.33 (d, C(2)); 67.51 (t, C(5)); 26.38 (q, MeN). CI-MS: 255 (63, [M + 2]<sup>+</sup>), 254 (100, [M + 1]<sup>+</sup>), 253 (4, M<sup>+</sup>), 252 (6, [M - 1]<sup>+</sup>), 226 (1), 196 (5), 162 (19), 147 (9), 119 (5), 104 (3), 91 (18), 65 (1). Anal. calc. for C<sub>16</sub>H<sub>15</sub>NO<sub>2</sub> (253.30): C 75.72, H 5.99, N 5.51; found: C 75.61, H 6.07, N 5.60.

**7,9-Dihydro-6H-dibenz[*c,e*]oxazolo[3,2-*a*]azepin-7-one (10).** Colorless liquid. <sup>1</sup>H-NMR (500 MHz): 7.74–7.69 (*m*, 1 arom. H); 7.57–7.26 (*m*, 7 arom. H); 5.85 (*dd*, *J* = 1.1, 1.0, H-C(4a)); 4.83 (d, *J* = 13.6, 1 H, CH<sub>2</sub>N); 4.57 (*A* of *ABX*, *J*<sub>AB</sub> = 13.6, *J*<sub>AX</sub> = 1.1, H-C(6)); 4.47 (*B* of *ABX*, *J*<sub>AB</sub> = 13.6, *J*<sub>BX</sub> = 1.0, H-C(6)); 3.83 (d, *J* = 13.6, 1 H, CH<sub>2</sub>N). <sup>13</sup>C-NMR: 167.61 (s, C(7)); 139.69 (s); 136.82 (s); 133.99 (s); 131.78 (s); 129.50 (d); 129.45 (d); 129.22 (d); 128.81 (d); 128.77 (d); 128.62 (d); 123.34 (d); 88.43 (d, C(4a)); 69.34 (t, C(6)); 43.78 (t, CH<sub>2</sub>N). CI-MS: 253 (18, [M + 2]<sup>+</sup>), 252 (100, [M + 1]<sup>+</sup>), 251 (15, M<sup>+</sup>), 250 (20, [M - 1]<sup>+</sup>), 226 (1), 196 (3), 167 (8), 152 (1), 123 (2), 105 (1), 89 (2), 61 (1). Anal. calc. for C<sub>16</sub>H<sub>15</sub>NO<sub>2</sub> (251.28): C 76.48, H 5.21, N 5.57; found: C 76.52, H 5.54, N 5.40.

**3-Benzyl-2-phenyl-1,3-oxazolidin-4-one (14).** Colorless liquid. <sup>1</sup>H-NMR (200 MHz): 7.42–7.04 (*m*, 10 arom. H); 5.71 (*dd*, *J* = 2.1, 1.5, H-C(2)); 4.97 (d, *J* = 14.6, 1 H, CH<sub>2</sub>N); 4.58 (*A* of *ABX*, *J*<sub>AB</sub> = 13.9, *J*<sub>AX</sub> = 2.0, H-C(5)); 4.42 (*B* of *ABX*, *J*<sub>AB</sub> = 13.9, *J*<sub>BX</sub> = 1.4, H-C(5)); 3.55 (d, *J* = 14.6, 1 H, CH<sub>2</sub>N). <sup>13</sup>C-NMR: 169.97 (s, C(4)); 136.34 (s); 135.15 (s); 130.17 (d); 128.67 (d); 128.28 (d); 127.84 (d); 127.44 (d); 91.77 (d, C(2)); 67.82 (t, C(5)); 43.59 (t, CH<sub>2</sub>N). EI-MS: 255 (63, [M + 2]<sup>+</sup>), 254 (100, [M + 1]<sup>+</sup>), 253 (4, M<sup>+</sup>), 252 (6, [M - 1]<sup>+</sup>), 226 (1), 196 (5), 162 (19), 147 (9), 119 (5), 104 (3), 91 (18), 65 (1). Anal. calc. for C<sub>16</sub>H<sub>15</sub>NO<sub>2</sub> (253.30): C 75.72, H 5.99, N 5.51; found: C 75.76, H 5.98, N 5.44.

**3-[(<sup>2</sup>H<sub>2</sub>)Methyl]-2-(2-phenylphenyl)-1,3-oxazolidin-4-one (6d).** According to *GP2*. From **2d** (244 mg, 0.92 mmol), Bu<sub>3</sub>SnH (0.33 ml, 1.2 mmol), and AIBN (10 mg, 0.1 mmol). FC (hexane/AcOEt 7:3) gave **6d** (119 mg, 50%) along with **10d** (25 mg, 11%) and **14d/14d'** (26 mg, 11%, 1:1 mixture).

**Data of 6d.** Colorless liquid. <sup>1</sup>H- and <sup>13</sup>C-NMR data correspond to those of the undeuterated compound. <sup>2</sup>H-NMR (77 MHz, CHCl<sub>3</sub>): 2.56 (d, *J* = 1.9). CI-MS: 284 (18, [M + 29]<sup>+</sup>), 256 (100, [M + 1]<sup>+</sup>), 165 (24), 102 (19).

**Data of 10d.** Colorless liquid. <sup>1</sup>H- and <sup>13</sup>C-NMR data correspond to those of the undeuterated compound. <sup>2</sup>H-NMR (77 MHz, CHCl<sub>3</sub>): 4.81 (s); 3.80 (s). CI-MS: 282 (13.2, [M + 29]<sup>+</sup>), 254 (100, [M + 1]<sup>+</sup>).

**Data of 14d/14d'.** Colorless liquid. <sup>1</sup>H- and <sup>13</sup>C-NMR data correspond to those of the undeuterated compound. <sup>2</sup>H-NMR (77 MHz, CHCl<sub>3</sub>): 7.32 (s, **14d'**); 4.99 (br. s, **14d** and **14d'**); 3.51 (br. s, **14d** and **14d'**). CI-MS: 284 (6, [M + 29]<sup>+</sup>), 256 (48, [M + 1]<sup>+</sup>).

2-[2-(4-Cyanophenyl)phenyl]-3-methyl-1,3-oxazolidin-4-one (7). According to GP2. From 3 (1.30 g, 3.64 mmol), Bu<sub>3</sub>SnH (1.30 g, 4.45 mmol), and AIBN (0.060 g, 0.36 mmol). FC (hexane/AcOEt 7:3) gave 7 (0.46 g, 45%) along with 11 (80 mg, 8%) and 15 (0.26 g, 26%).

*Data of 7.* White solid. Recrystallized from hexane. *m.p.* 118–118.5°. <sup>1</sup>H-NMR (200 MHz): 7.76 (*d*, *J* = 7.9, 2 arom. H); 7.59–7.39 (*m*, 6 arom. H); 5.85 (*dd*, *J* = 2.0, 1.8, H–C(2)); 4.36 (*A* of *ABX*, *J*<sub>AB</sub> = 14.0, *J*<sub>AX</sub> = 1.9, H–C(5)); 4.27 (*B* of *ABX*, *J*<sub>AB</sub> = 13.8, *J*<sub>BX</sub> = 1.7, H–C(5)); 2.61 (*s*, MeN). <sup>13</sup>C-NMR: 170.19 (*s*, C(4)); 144.09 (*s*); 140.99 (*s*); 133.44 (*s*); 131.99 (*d*); 130.46 (*d*); 130.20 (*d*); 129.89 (*d*); 129.13 (*d*); 127.03 (*d*); 118.43 (*s*, CN); 116.64 (*s*, C–CN); 90.32 (*d*, C(2)); 67.32 (*t*, C(5)); 26.43 (*q*, MeN). EI-MS: 279 (2, [M + 1]<sup>+</sup>), 278 (6, M<sup>+</sup>), 277 (6, [M – 1]<sup>+</sup>), 250 (1), 219 (2), 201 (29), 172 (40), 162 (100), 116 (91), 104 (15), 89 (37), 77 (16), 51 (9). Anal. calc. for C<sub>17</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub> (278.31): C 73.37, H 5.07, N 10.07; found: C 73.11, H 5.09, N 10.03.

7,9-Dihydro-7-oxo-6H-dibenz[*c,e*]oxazolol[3,2-*a*]azepine-12-carbonitrile (11). Colorless liquid. <sup>1</sup>H-NMR (500 MHz): 7.70–7.17 (*m*, 7 arom. H); 5.79 (*dd*, *J* = 2.1, 1.8, H–C(4a)); 4.89 (*d*, *J* = 13.8, 1 H, CH<sub>2</sub>N); 4.55 (*A* of *ABX*, *J*<sub>AB</sub> = 14.6, *J*<sub>AX</sub> = 2.0, H–H(6)); 4.47 (*B* of *ABX*, *J*<sub>AB</sub> = 14.6, *J*<sub>AX</sub> = 1.8, H–C(6)); 3.81 (*d*, *J* = 14.7, 1 H, CH<sub>2</sub>N). <sup>13</sup>C-NMR: 167.50 (*s*, C(7)); 140.88 (*s*); 136.23 (*s*); 134.30 (*s*); 133.71 (*s*); 132.58 (*d*); 131.94 (*d*); 130.21 (*d*); 129.65 (*d*); 129.56 (*d*); 128.61 (*d*); 123.52 (*d*); 117.95 (*s*, CN); 113.17 (*s*, C–CN); 87.69 (*d*, C(4a)); 68.86 (*t*, C(6)); 43.22 (*t*, CH<sub>2</sub>N). EI-MS: 277 (8, [M + 1]<sup>+</sup>), 276 (38, M<sup>+</sup>), 275 (100, [M – 1]<sup>+</sup>), 247 (2), 217 (34), 190 (34), 163 (3), 117 (1), 91 (2). Anal. calc. for C<sub>17</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub> (276.29): C 73.90, H 4.38, N 10.14; found: C 73.94, H 4.22, N 10.11.

3-(4-Cyanobenzyl)-2-phenyl-1,3-oxazolin-4-one (15). Colorless liquid. <sup>1</sup>H-NMR (200 MHz): 7.68–7.15 (*m*, 9 arom. H); 5.79 (*dd*, *J* = 2.0, 1.6, H–C(2)); 4.78 (*d*, *J* = 15.6, 1 H, CH<sub>2</sub>N); 4.59 (*A* of *ABX*, *J*<sub>AB</sub> = 14.1, *J*<sub>AX</sub> = 2.0, H–C(5)); 4.43 (*B* of *ABX*, *J*<sub>AB</sub> = 14.1, *J*<sub>BX</sub> = 1.5, H–C(5)); 3.84 (*d*, *J* = 15.4, 1 H, CH<sub>2</sub>N). <sup>13</sup>C-NMR: 170.31 (*s*, C(4)); 140.79 (*s*); 135.95 (*s*); 132.45 (*d*); 130.54 (*d*); 128.92 (*d*); 127.46 (*d*); 118.37 (*s*, CN); 111.86 (*s*, C–CN); 92.16 (*d*, C(2)); 67.75 (*t*, C(5)); 43.42 (*t*, CH<sub>2</sub>N). EI-MS: 279 (2, [M + 1]<sup>+</sup>), 278 (6, M<sup>+</sup>), 277 (6, [M – 1]<sup>+</sup>), 250 (1), 219 (2), 201 (29), 172 (40), 162 (100), 116 (91), 104 (15), 89 (37), 77 (16), 51 (9). Anal. calc. for H<sub>17</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub> (278.31): C 73.37, H 5.07; found: C 73.04, H 5.22.

3-Methyl-2-{2-[4-(trifluoromethyl)phenyl]phenyl}-1,3-oxazolidin-4-one (8). According to GP2. From 4 (1.49 g, 3.72 mmol), Bu<sub>3</sub>SnH (1.31 g, 4.49 mmol), and AIBN (0.061 g, 0.37 mmol). FC (hexane/AcOEt 7:3) gave 8 (0.55 g, 46%) along with 12 (110 mg, 9%) and 16 (0.28 g, 28%).

*Data of 8.* Colorless liquid. <sup>1</sup>H-NMR (200 MHz): 7.74–7.70 (*d*, *J* = 8.0, 2 arom. H); 7.56–7.32 (*m*, 6 arom. H); 5.89 (*dd*, *J* = 1.9, 1.8, H–C(2)); 4.39 (*A* of *ABX*, *J*<sub>AB</sub> = 13.7, *J*<sub>AX</sub> = 2.0, H–C(5)); 4.28 (*B* of *ABX*, *J*<sub>AB</sub> = 13.7, *J*<sub>BX</sub> = 1.6, H–C(5)); 2.60 (*s*, MeN). <sup>13</sup>C-NMR: 170.32 (*s*, C(4)); 143.05 (*s*); 141.59 (*s*); 133.59 (*s*); 130.59 (*d*); 129.96 (*d*, <sup>2</sup>*J*(C,F) = 32.6, C–CF<sub>3</sub>); 129.87 (*d*, 3 arom. H); 128.90 (*d*); 126.88 (*d*); 125.34 (*d*, <sup>3</sup>*J*(C,F) = 4.0); 125.19 (*d*, <sup>3</sup>*J*(C,F) = 3.9); 124.15 (*q*, MeN). EI-MS: 323 (11, [M + 2]<sup>+</sup>), 322 (54, [M + 1]<sup>+</sup>), 321 (100, M<sup>+</sup>), 320 (10, [M – 1]<sup>+</sup>), 252 (18), 224 (55), 147 (96), 119 (27), 77 (32), 70 (4). Anal. calc. for C<sub>17</sub>H<sub>14</sub>F<sub>3</sub>NO<sub>2</sub> (321.29): C 63.55, H 4.39, N 4.36; found: C 63.66, H 4.31, N 4.27.

7,9-Dihydro-12-(trifluoromethyl)-6H-dibenz[*c,e*]oxazolol[3,2-*a*]azepine-7-one (12). Colorless liquid. <sup>1</sup>H-NMR (200 MHz): 7.75–7.17 (*m*, 7 arom. H); 5.80 (*dd*, *J* = 1.9, 1.8, H–C(4a)); 4.89 (*d*, *J* = 13.7, 1 H, CH<sub>2</sub>N); 4.58 (*A* of *ABX*, *J*<sub>AB</sub> = 14.0, *J*<sub>BX</sub> = 1.5, H–C(6)); 3.81 (*d*, *J* = 13.6, 1 H, CH<sub>2</sub>N). <sup>13</sup>C-NMR: 167.78 (*s*, C(7)); 140.51 (*s*); 135.31 (*s*); 135.22 (*s*); 133.87 (*s*); 131.53 (*d*, <sup>2</sup>*J*(C,F) = 32.2, C–CF<sub>3</sub>); 130.01 (*d*); 129.70 (*d*); 129.38 (*d*); 128.80 (*d*); 126.82 (*d*); 126.22 (*d*, <sup>3</sup>*J*(C,F) = 3.7); 126.17 (*d*, <sup>3</sup>*J*(C,F) = 3.6); 123.82 (*q*, <sup>1</sup>*J*(C,F) = 273.0, CF<sub>3</sub>); 88.06 (*d*, C(2)); 69.12 (*t*, C(5)); 43.30 (*t*, CH<sub>2</sub>N). EI-MS: 323 (11, [M + 2]<sup>+</sup>), 322 (54, [M + 1]<sup>+</sup>), 321 (100, M<sup>+</sup>), 320 (10, [M – 1]<sup>+</sup>), 252 (18), 224 (55), 147 (96), 119 (27), 77 (32), 70 (4). Anal. calc. for C<sub>17</sub>H<sub>12</sub>F<sub>3</sub>NO<sub>2</sub> (319.28): C 63.95, H 3.79, N 4.39; found: C 63.98, H 3.91, N 4.07.

2-Phenyl-3-[4-(trifluoromethyl)benzyl]-1,3-oxazolidin-4-one (16). Colorless liquid. <sup>1</sup>H-NMR (200 MHz): 7.57–7.17 (*m*, 9 arom. H); 5.77 (*dd*, *J* = 2.0, 1.5, H–C(2)); 4.89 (*d*, *J* = 15.2, 1 H, CH<sub>2</sub>N); 4.59 (*A* of *ABX*, *J*<sub>AB</sub> = 14.1, *J*<sub>AX</sub> = 2.0, H–C(5)); 4.43 (*B* of *ABX*, *J*<sub>AB</sub> = 14.0, *J*<sub>BX</sub> = 1.5, H–C(5)); 3.74 (*d*, *J* = 15.1, 1 H, CH<sub>2</sub>N). <sup>13</sup>C-NMR: 170.29 (*s*, C(4)); 139.42 (*s*); 136.10 (*s*); 130.50 (*d*); 129.70 (*d*, <sup>2</sup>*J*(C,F) = 30.3, C–CF<sub>3</sub>); 129.02 (*d*); 128.65 (*d*); 127.51 (*d*); 125.79 (*d*, <sup>3</sup>*J*(C,F) = 4.0); 125.64 (*d*, <sup>3</sup>*J*(C,F) = 3.5); 124.10 (*q*, <sup>1</sup>*J*(C,F) = 271.6, CF<sub>3</sub>); 90.09 (*d*, C(2)); 67.83 (*t*, C(5)); 43.35 (*t*, CH<sub>2</sub>N). EI-MS: 323 (11, [M + 2]<sup>+</sup>), 322 (54, [M + 1]<sup>+</sup>), 321 (100, M<sup>+</sup>), 320 (10, [M – 1]<sup>+</sup>), 252 (18), 224 (55), 147 (96), 119 (27), 77 (32), 70 (4). Anal. calc. for C<sub>17</sub>H<sub>14</sub>F<sub>3</sub>NO<sub>2</sub> (321.29): C 63.55, H 4.39, N 4.36; found: C 63.56, H 4.43, N 4.37.

2-[2-(4-Methoxyphenyl)phenyl]-3-methyl-1,3-oxazolidin-4-one (9). According to GP2. From 5 (850 mg, 2.35 mmol), Bu<sub>3</sub>SnH (820 mg, 2.80 mmol), and AIBN (40 mg, 0.24 mmol). FC (hexane/AcOEt 7:3) gave 9 (226 mg, 34%) along with 13 (86 mg, 13%) and 17 (186 mg, 28%).

*Data of 9.* Colorless liquid. <sup>1</sup>H-NMR (200 MHz): 7.47–7.28 (*m*, 4 arom. H); 7.32 (*d*, *J* = 8.8, 2 arom. H); 6.98 (*d*, *J* = 8.8, 2 arom. H); 5.99 (*dd*, *J* = 1.9, 1.0, H–C(2)); 4.42 (*A* of *ABX*, *J*<sub>AB</sub> = 13.7, *J*<sub>AX</sub> = 1.8, H–C(5)); 4.28 (*B* of *ABX*, *J*<sub>AB</sub> = 13.7, *J*<sub>AX</sub> = 1.0, H–C(5)); 3.86 (*s*, MeO); 2.59 (*s*, MeN). <sup>13</sup>C-NMR: 170.44 (*s*, C(4));

159.30 (s, C–OMe); 142.85 (s); 133.52 (s); 131.64 (s); 130.91 (d); 130.62 (d); 129.57 (d); 127.93 (d); 126.65 (d); 113.81 (d); 90.37 (d, C(2)); 67.59 (t, C(5)); 26.50 (q, MeN). CI-MS: 284 (2,  $[M + 1]^+$ ), 283 (11,  $M^+$ ), 282 (16,  $[M - 1]^+$ ), 252 (100), 175 (36), 147 (19), 133 (12), 77 (48), 70 (43), 51 (31). Anal. calc. for  $C_{17}H_{17}NO_3$  (283.33): C 72.07, H 6.05, N 4.94; found: C 71.90, H 6.09, N 4.80.

**7,9-Dihydro-12-methoxy-6H-dibenz[*c,e*]oxazolo[3,2-*a*]azepin-7-one 13.** Colorless liquid.  $^1H$ -NMR (200 MHz): 7.74–6.90 (*m*, 7 arom. H); 5.85 (*dd*,  $J = 2.0, 1.0$ , H–C(4a)); 4.77 (*d*,  $J = 13.7$ , 1 H,  $CH_2N$ ); 4.57 (*A* of *ABX*,  $J_{AB} = 14.9$ ,  $J_{AX} = 2.2$ , H–C(5)); 4.47 (*B* of *ABX*,  $J_{AB} = 14.9$ ,  $J_{BX} = 1.0$ , H–C(5)); 3.87 (*s*, MeO); 3.76 (*d*,  $J = 13.9$ , 1 H,  $CH_2N$ ).  $^{13}C$ -NMR: 167.47 (*s*, C(7)); 160.12 (*s*, C–OMe); 140.98 (*s*); 136.86 (*s*); 134.17 (*s*); 130.60 (*d*); 129.41 (*d*): 128.65 (*d*); 124.30 (*s*); 123.39 (*d*); 115.23 (*d*); 113.68 (*d*); 88.50 (*d*, C(4a)); 69.41 (*t*, C(6)); 55.56 (*q*, MeO); 43.09 (*t*,  $CH_2N$ ). EI-MS: 282 (7,  $[M + 1]^+$ ), 281 (40,  $M^+$ ), 280 (22,  $[M - 1]^+$ ), 250 (9), 224 (34), 210 (120), 195 (20), 180 (12), 152 (42), 139 (16), 121 (100), 91 (17), 77 (31), 51 (15). Anal. calc. for  $C_{17}H_{15}NO_3$  (281.31): C 72.58, H 5.37, N 4.98; found: C 72.43, H 5.39, N 5.12.

**3-(4-Methoxybenzyl)-2-phenyl-1,3-oxazolidin-4-one (17).** Colorless liquid.  $^1H$ -NMR (200 MHz): 7.44–7.26 (*m*, 5 arom. H); 7.00 (*d*,  $J = 8.6$ , 2 arom. H); 6.87 (*d*,  $J = 8.6$ , 2 arom. H); 5.73 (*dd*,  $J = 1.9, 1.4$ , H–C(2)); 4.93 (*d*,  $J = 14.7$ , 1 H,  $CH_2N$ ); 4.54 (*A* of *ABX*,  $J_{AB} = 13.8$ ,  $J_{AX} = 2.1$ , H–C(5)); 4.37 (*B* of *ABX*,  $J_{AB} = 13.8$ ,  $J_{BX} = 1.5$ , H–C(5)); 3.79 (*s*, MeO); 3.44 (*d*,  $J = 14.8$ , 1 H,  $CH_2N$ ).  $^{13}C$ -NMR: 170.05 (*s*, C(4)); 159.32 (*s*, C–OMe); 136.46 (*s*); 130.28 (*d*); 129.77 (*d*); 128.93 (*d*); 128.61 (*d*); 127.55 (*d*); 127.26 (*s*); 114.15 (*d*); 91.88 (*d*, C(2)); 67.99 (*t*, C(5)); 55.29 (*q*, MeO), 43.14 (*t*,  $CH_2N$ ). CI-MS: 284 (2,  $[M + 1]^+$ ), 283 (11,  $M^+$ ), 282 (16,  $[M - 1]^+$ ), 252 (100), 175 (36), 147 (19), 133 (12), 77 (48), 70 (43), 51 (31). Anal. calc. for  $C_{17}H_{17}NO_3$  (283.33): C 72.07, H 6.05 found: C 71.90, H 6.09.

**General Procedure 3 (GP3). Hydrolysis of Oxazolidinones: Method A.** A soln. of the oxazolidinone (0.72 mmol) in 6N HCl was heated under reflux for 4 h. After dilution with  $H_2O$ , the aq. soln. was extracted with AcOEt. Drying ( $MgSO_4$ ), evaporation of the solvent, and FC gave the pure arom. aldehyde.

**General Procedure 4 (GP4). Hydrolysis of Oxazolidinones: Method B.** A soln. of the oxazolidinone (0.40 mmol) in MeCN (6 ml) was treated with 6N HCl (6 ml) and heated at 60° for 4 h. After addition of  $H_2O$ , the aq. soln. was extracted with AcOEt. Drying ( $MgSO_4$ ), evaporation of the solvent, and FC gave the pure arom. aldehyde.

**2-Phenylbenzaldehyde (18).** According to GP4. From **6** (100 mg, 0.395 mmol). FC (hexane/AcOEt 8:2) afforded **18** (47 mg, 65%). Colorless liquid.  $^1H$ -NMR (200 MHz): 9.74 (*s*, CHO); 7.88–7.17 (*m*, 9 arom. H). Spectral and physical data are in accordance with literature data [22].

**4-(2-Formylphenyl)benzotrile (19).** According to GP3. From **7** (200 mg, 0.72 mmol). FC (hexane/AcOEt 7:3) and recrystallization (hexane/AcOEt) afforded **19** (111 mg, 75%). White solid. M. p. 103–103.5°.  $^1H$ -NMR (200 MHz): 9.95 (*s*, CHO); 8.04 (*d*,  $J = 7.5$ , 1 arom. H); 7.64–7.41 (*m*, 7 arom. H).  $^{13}C$ -NMR: 191.08 (*s*, CHO); 143.42 (*s*); 142.81 (*s*); 133.59 (*s*); 132.13 (*d*); 130.62 (*d*); 128.91 (*d*); 128.66 (*d*); 118.39 (*s*, CN); 112.14 (*s*, C–CN). EI-MS: 207 (100,  $M^+$ ), 206 (98), 178 (60), 151 (78), 126 (10), 104 (89), 89 (14), 76 (70), 63 (24). Anal. calc. for  $C_{14}H_9NO$  (207.23): C 81.14, H 4.38, N 6.76; found: C 81.20, H 4.36, N 6.74.

**2-[4-(Trifluoromethyl)phenyl]benzaldehyde (20).** According to GP3. From **8** (260 mg, 0.81 mmol). FC (hexane/AcOEt 9:1) and recrystallization (hexane) afforded **20** (160 mg, 79%). White solid. M. p. 146–147°.  $^1H$ -NMR (200 MHz): 9.95 (*s*, CHO); 8.05 (*d*,  $J = 7.1$ , 1 arom. H); 7.76–7.41 (*m*, 7 arom. H).  $^{13}C$ -NMR: 191.49 (*s*, CHO); 144.21 (*s*); 141.72 (*s*); 133.79 (*d*); 130.74 (*d*); 130.73 (*d*,  $^2J(C,F) = 19.1$ , C–CF<sub>3</sub>); 130.39 (*d*); 130.12 (*s*); 128.62 (*d*); 128.23 (*d*); 125.52 (*d*,  $^3J(C,F) = 3.8$ ); 125.37 (*d*,  $^3J(C,F) = 3.9$ ); 124.12 (*q*,  $^1J(C,F) = 272.4$ , CF<sub>3</sub>). EI-MS: 250 (61,  $M^+$ ), 249 (100,  $[M - 1]^+$ ), 201 (82), 181 (69), 152 (77), 104 (38), 87 (10), 69 (49), 51 (26). Anal. calc. for  $C_{14}H_9F_3O$  (250.22): C 67.20, H 3.63; found: C 66.69, H 3.90.

**2-(4-Methoxyphenyl)benzaldehyde (21).** According to GP4. From **9** (60 mg, 0.22 mmol). FC (hexane/AcOEt 7:3) afforded **21** (24 mg, 53%). Colorless liquid.  $^1H$ -NMR (500 MHz): 10.0 (*s*, CHO); 8.10 (*d*,  $J = 8.2$ , 1 arom. H); 7.67–6.94 (*m*, 7 arom. H); 3.88 (*s*, MeO).  $^{13}C$ -NMR: 192.71 (*s*, CHO); 159.69 (*s*, C–OMe); 145.67 (*s*); 133.75 (*s*); 133.54 (*d*); 131.31 (*d*); 130.79 (*d*); 130.01 (*s*); 127.62 (*d*); 127.38 (*d*); 113.93 (*d*); 55.41 (*q*, MeO). EI-MS: 213 (67,  $[M + 1]^+$ ), 212 (100,  $M^+$ ), 183 (98), 152 (86), 109 (21), 105 (12), 77 (48). Anal. calc. for  $C_{14}H_{12}O_2$  (212.24): C 79.23, H 5.70; found: C 78.94, H 5.55.

**9-(9H-Fluoren-9-yloxy)-9H-fluorene (22).** According to GP3. From **6** (100 mg, 0.395 mmol). FC (hexane) and recrystallization (hexane) gave **22** (47 mg, 70%). White solid. M. p. 90.5–91°.  $^1H$ -NMR (200 MHz): 7.65–7.59 (*m*, 8 arom. H); 7.41–7.30 (*m*, 8 arom. H); 5.75 (*s*, 2 H–C(9)).  $^{13}C$ -NMR: 143.87 (*s*); 140.05 (*s*); 129.39 (*d*); 128.05 (*d*); 125.86 (*d*); 120.18 (*d*); 57.60 (*d*, CHO). EI-MS: 200 (57), 181 (1), 165 (100), 139 (14), 98 (9), 82 (35), 63 (12). Anal. calc. for  $C_{26}H_{18}O$  (346.42): C 90.14, H 5.24; found: C 90.56, H 4.97.

**2-Methoxy-9-[(2-methoxy-9H-fluoren-9-yl)oxy]-9H-fluorene (23).** According to GP3. From **9** (44 mg, 0.15 mmol). FC (hexane/AcOEt 95:5) and recrystallization (hexane) gave **23** (19 mg, 60%). White solid. M. p.



127–129°. <sup>1</sup>H-NMR (500 MHz): 7.61 (*d*, *J* = 7.5, 2 arom. H); 7.58 (*d*, *J* = 7.6, 2 arom. H); 7.57 (*d*, *J* = 8.3, 2 arom. H); 7.38 (*t*, *J* = 7.6, 2 arom. H); 7.28 (*t*, *J* = 7.6, 2 arom. H); 7.20 (*d*, *J* = 2.5, 2 arom. H); 6.96 (*dd*, *J* = 8.3, 2.4, 2 arom. H); 5.75 (*s*, 2 H–C(9)); 3.88 (*s*, 2MeO). <sup>13</sup>C-NMR: 160.06 (*s*, C–OMe); 143.34 (*s*); 129.35 (*d*); 127.51 (*s*); 126.82 (*d*); 125.66 (*d*); 120.94 (*d*); 119.30 (*d*); 115.53 (*d*); 111.12 (*d*); 57.47 (*d*, CHO); 55.62 (*g*, MeO). EI-MS: 406 (1, *M*<sup>+</sup>), 230 (65), 211 (4), 195 (95), 180 (29), 163 (18), 152 (100), 126 (16), 75 (27). Anal. calc. for C<sub>28</sub>H<sub>22</sub>O<sub>3</sub> (406.480): C 82.74, H 5.46; found: C 83.04, H 5.38.

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