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Microwave-Assisted Domino Benzannulation of α-Oxo Ketenes: Preparation of 1,3-Dihydro-2*H*-1,5-benzodiazepin-2-ones

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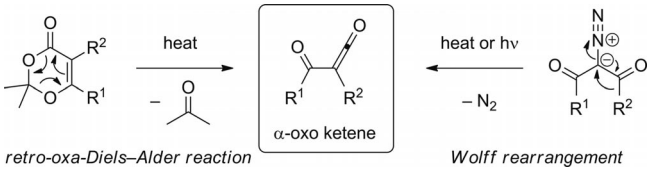
The microwave irradiation of a series of 2-diazo-1,3-diketones in the presence of an *o*-phenylenediamine derivative triggered a domino Wolff rearrangement/nucleophilic addition/intramolecular imination sequence to provide a new synthetic entry to 1,3-dihydr-2*H*-1,5-benzodiazepin-2-ones, a class of molecules with important biological properties.

Introduction

An important focus of contemporary organic synthesis is economy (atom, step, redox, pot economies),[1] and, logically, multiple bond-forming transformations (consecutive, domino, cascade, "one-pot" reactions)[2] have been developed that allow the creation of molecular complexity and functional diversity in a single chemical operation. These transformations are best performed with polyfunctionalized substrates in which the distinct reactive groups react selectively in a well-defined order to give a single product. Densely functionalized molecules such as 1,3-dicarbonyl compounds are particularly attractive for such endeavors[3] and α-oxo ketenes[4] exhibiting two carbonyl groups and one double bond distributed over three carbon atoms fall into this class of compounds. With very few exceptions, α-oxo ketenes are highly reactive molecules, and thus their use in synthesis generally involves their preparation in situ followed by direct trapping with species present in the reaction mixture. The most commonly used method to generate α-oxo ketenes involves the thermal decomposition of 1,3-dioxin-4-ones by a retro-oxa-Diels–Alder reaction (Scheme 1, left).[4] Alternatively, α-oxo ketenes can also be obtained by thermal or photochemical Wolff rearrangement[5] of 2-diazo-1,3-dicarbonyl compounds (Scheme 1, right).



Scheme 1. Most commonly used methods to generate α-oxo ketenes.

We have recently demonstrated that the microwave-assisted Wolff rearrangement of 2-diazoalkane-1,3-diones produces quantitatively the corresponding α-oxo ketenes and that this method could advantageously be applied to domino and/or multicomponent reactions.[6] In this article we report our studies on the domino reactions of 2-diazoalkane-1,3-diones and bis(N-nucleophiles) under microwave irradiation, and our findings that 2-aminoanilines can lead efficiently to bi- and tricyclic 1,3-dihydro-2*H*-1,5-benzodiazepin-2-ones under these conditions.

Results and Discussion

In a previous study we showed that the microwave-assisted Wolff rearrangement is particularly attractive for the clean synthesis of a variety of β-oxo esters and amides.[6a] For example, the microwave irradiation of a 1:1 mixture of the diazo compound **1a** and benzylamine in toluene produced the β-oxo amide **2** in 99% yield and >95% purity without need for purification after removal of the volatiles (Scheme 2). When the same reaction was performed with 2 equiv. of benzylamine, the corresponding β-enamino amide **3** was obtained in the same yield and purity by a very efficient pseudo-three-component reaction (Scheme 2).[7] Note that the Wolff rearrangement is the method of choice for the preparation of the α-oxo ketene

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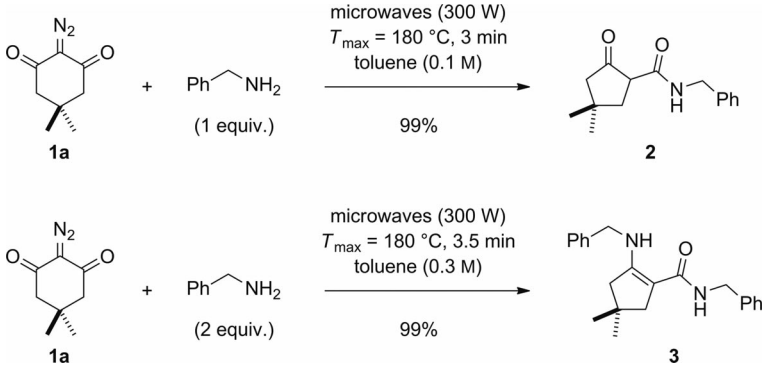


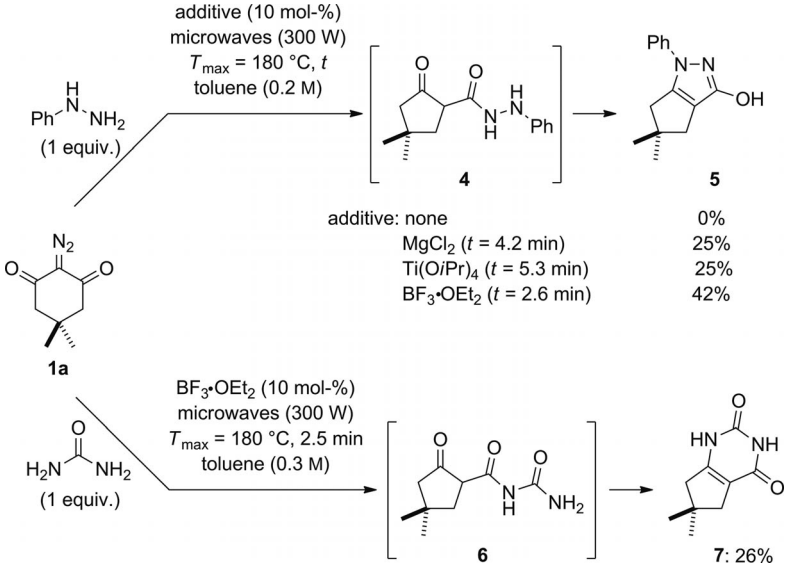
Scheme 2. Reactions of α-oxo ketenes with primary amines.

in this kind of domino reaction, because it avoids the co-production of acetone, which may undergo side-reactions with the nucleophilic amines present in the reaction mixture.

The reactivity of α-oxo ketenes has already proven useful for the preparation of a number of heterocycles,[4,6] and the previous observation triggered our interest in the reactions of 2-diazoalkane-1,3-diones with bis(N-nucleophiles) under microwave irradiation. Our study was initiated by the reactions of the diazo compound **1a** with phenylhydrazine and urea (Scheme 3). In parallel with the earlier results of Capuano et al.,[8] the microwave-assisted Wolff rearrangement of **1a** in the presence of phenylhydrazine afforded the corresponding acylhydrazine **4**, and no heterocycle formation was observed. However, when performed in the presence of a Lewis acid additive, the same reaction evolved by the cyclization of the intermediate acylhydrazine **4** to give the bicyclic pyrazole **5** in low to moderate yields depending on the Lewis acid used. The situation was found to be similar for the reaction between the diazo compound **1a** and urea, which required 10 mol-% of BF_3·OEt_2 to proceed, giving the pyrimidinedione **7** via **6**, albeit in low yield (Scheme 3). Although these reactions could give rise to the heterocyclic products **5** and **7** in a single transformation, they required an additive and were poorly efficient when compared with other related domino reactions of α-oxo ketenes.[6]

We then looked for more efficient and valuable bis(N-nucleophiles), such as 1,2-anilines, targeting diazepine scaffolds. These heterocyclic skeletons, and more particularly 1,5-benzodiazepin-2-ones, are an important class of compounds with a variety of biological activities, including anxiolytic, enzyme-inhibiting, and anti-arrhythmic properties (Figure 1).[9] They are considered as "privileged" scaffolds in medicinal chemistry and drug development.

From the results of our early studies, it was anticipated that the 1,3-dihydro-2*H*-1,5-benzodiazepin-2-one **9a** could be obtained from *o*-phenylenediamine (**8a**) and the α-oxo ketene **10** derived from the diazo compound **1a**. In practice, microwave irradiation of a 1:1 mixture of **1a** and **8a** afforded the desired 1,3-dihydro-2*H*-1,5-benzodiazepin-2-one **9a** in good yield by a domino reaction without the need for additives (Scheme 4). To optimize the time, the reaction was best performed in a sealed reaction vessel under irradiation at the maximum power allowed by the dedicated mono-



Scheme 3. Lewis acid catalyzed domino Wolff rearrangement/heterocyclization of **1a** with phenylhydrazine and urea.

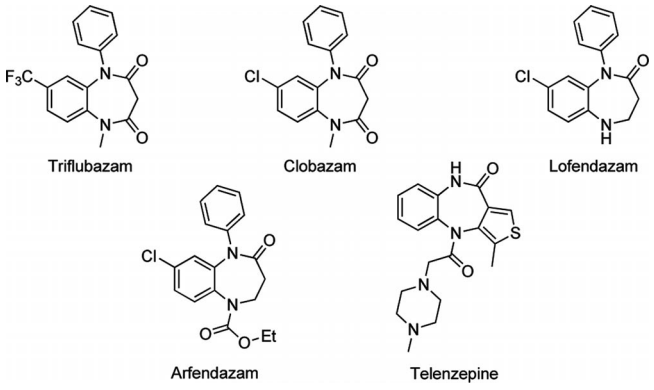
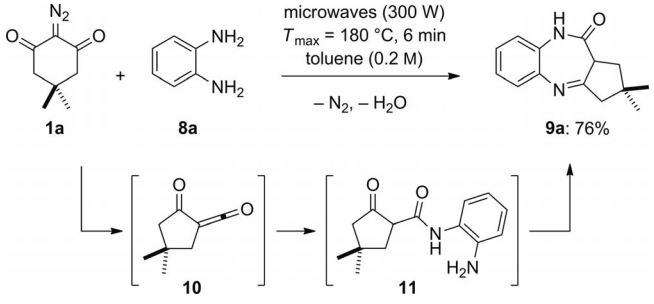


Figure 1. Representative clinically used 1,5-benzodiazepin-2-ones.

mode microwave reactor used (see the Exp. Sect.) until the internal pressure reached 17 bar, or the temperature reached 180 °C, or the total irradiation time reached 6 min.

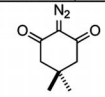
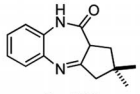
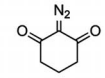
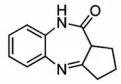
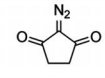
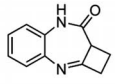
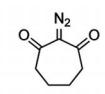
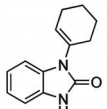
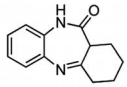
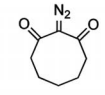
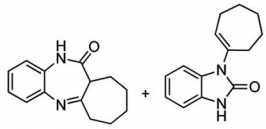
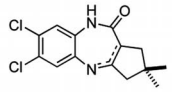
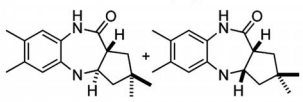
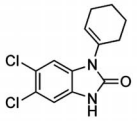
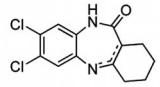
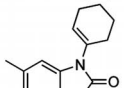
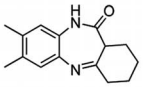


Scheme 4. Domino reaction of α-oxo ketene **10** with diamine **8a**.

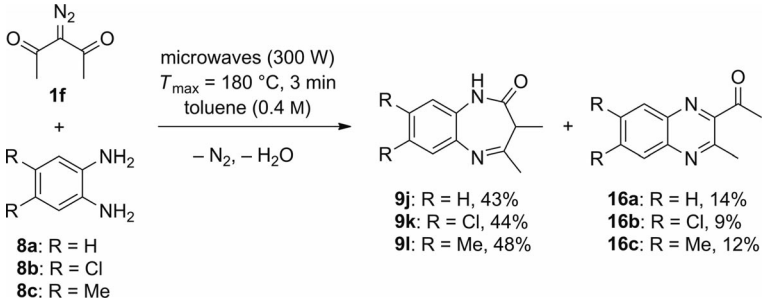
Previous work has established that thermally promoted Wolff rearrangements of cyclic 2-diazoalkane-1,3-diones such as **1a**, which exhibit a blocked s-*Z* conformation, are essentially concerted processes that do not involve the formation of a transient α,α′-dicarbonyl carbene.[5,10] Also, we have verified by monitoring the reaction by LC–MS and NMR spectroscopy that the formation of the β-oxo amide **11** precedes the benzannulation in the domino process. Based on these considerations, the mechanism for the formation of **9a** from **1a** and **8a** under microwave irradiation is believed to involve a concerted Wolff rearrangement of the diazo compound **1a** to give the α-oxo ketene **10**, followed by nucleophilic trapping of the ketene to give the intermediate β-oxo amide **11**, which then undergoes an imination-based benzannulation to give the product **9a** (Scheme 4).

Most of the previous approaches to benzodiazepines of type **9** involve the condensation of *o*-phenylenediamines and β-oxo esters (or synthetic equivalents) via enamino ester intermediates. These reactions were found to be extremely substrate- and conditions-dependent, usually requiring relatively long reaction times (typically hours), and are often complicated by competitive reactions leading to *N*-alkenylbenzimidazol-2-one and/or benzimidazole derivatives.[11] A remarkable feature of this method is that it does not involve an enamino ester intermediate, the formation of the amide bond preceding the formation of the imine bond

Table 1. Domino benzannulation of α-oxo ketenes.

Entry	Diazo compound	Reaction conditions[a]	Product(s)[b]
1	 **1a**	 **8a** (6 min, 0.2 M)	 **9a**: 76%
2	 **1b**	**8a** (1.5 min, 0.4 M)	 **9b**: 55%
3	 **1c**	**8a** (180 °C for 5 min, 0.3 M)	 **9c**: 23%
4	 **1d**	**8a** (3 min, 0.6 M)	 **12d**: 59%
5	**1d**	**8a** (130 °C for 2 min, 0.4 M)	 **9d**: 62%
6	 **1e**	**8a** (4 min, 0.2 M)	 **9e**: 61% **12e**: 19%
7	**1e**	**8a** (130 °C for 2 min, 0.2 M)	**9e**: 57%
8	**1a**	 **8b** (3 min, 0.2 M)	 **9f**: 49% (1:2)
9	**1a**	 **8c** (3 min, 0.4 M, then $NaBH_3CN$ AcOH, MeOH)	 **13g**: 51% **14g**: 18%
10	**1d**	**8b** (5 min, 0.3 M)	 **12h**: 70%
11	**1d**	**8b** (130 °C for 2 min, 0.2 M)	 **9h**: 61% (1:5)
12	**1d**	**8c** (4 min, 0.3 M)	 **12i**: 62%
13	**1d**	**8c** (130 °C for 2 min, 0.2 M)	 **9i**: 73%

[a] Unless otherwise specified (Entries 3, 5, 7, 11, and 13), all reactions were performed in sealed reaction vessels under irradiation at the maximum power allowed by the dedicated monomode microwave reactor used (see the Exp. Sect.) until the internal pressure reached 17 bar, or the temperature reached 180 °C, or the total irradiation time reached 6 min. [b] Yields of the isolated pure compounds were obtained after silica gel flash chromatography.



Scheme 5. Benzannulation reaction with the acyclic diazo compound **1f**.

in the product **9a**. This alternative approach should be more general, faster, and some side-reactions should be suppressed. Thus, the scope and limits of this new domino benzannulation reaction of α-oxo ketenes were studied, and the results are reported in Table 1. With the six- and five-membered cyclic diazo precursors **1b** and **1c**, the corresponding ring-contracted 1,3-dihydro-2*H*-1,5-benzodiazepin-2-ones **9b** and **9c** were obtained in good and low yields, respectively (Entries 2 and 3). With the seven-membered diazo precursor **1d**, the reaction unexpectedly afforded the *N*-cyclohexenylbenzimidazol-2-one **12d** in good yield as the only isolable product (Entry 4). The formation of *N*-alkenylbenzimidazol-2-one byproducts of type **12** has previously been observed in reactions of *o*-phenylenediamines with β-oxo esters,[11] and it has been demonstrated that the benzimidazolones of type **12** are actually obtained by a thermal rearrangement of the benzodiazepinones **9**.[12] Accordingly, the formation of **12d** could essentially be avoided when the reaction between **1d** and **8a** was performed at 130 °C for 2 min, leading efficiently to the 1,3-dihydro-2*H*-1,5-benzodiazepin-2-one **9d** (Entry 5). In the case of the eight-membered cyclic diazo precursor **1e**, both the expected 1,3-dihydro-2*H*-1,5-benzodiazepin-2-one **9e** and the *N*-cycloheptenylbenzimidazol-2-one **12e** were obtained in a 3:1 ratio under the standard reaction conditions (Entry 6), whereas only **9e** was obtained at lower temperature (Entry 7). Similar trends were observed in the reactions with 4,5-dichloro- and 4,5-dimethylbenzene-1,2-diamine (**8b** and **8c**, respectively) as the bis(N-nucleophile). With **8b**, the six-membered diazo compound **1a** gave the corresponding 1,3-dihydro-2*H*-1,5-benzodiazepin-2-one **9f** as a 1:2 mixture of its imine and enamine forms (Entry 8), whereas with **8c**, the benzodiazepinone product **9g** was found somewhat unstable, and thus the crude product was directly reduced by treatment with sodium cyanoborohydride to give the corresponding 1,3,4,5-tetrahydro-2*H*-1,5-benzodiazepin-2-ones **13g** and **14g** in 69% combined yield (*dr* **13g**/**14g** = 2.7:1, Entry 9). Finally, with both diamines **8b** and **8c**, the sharply divergent reactivity of the seven-membered diazo compound **1d** afforded the *N*-cyclohexenylbenzimidazol-2-ones **12h** and **12i**, respectively (Entries 10 and 12). As before, the reactions performed at lower temperature led to the desired benzodiazepinones **9h** (as a 1:5 mixture of regioisomers, Entry 11) and **9i** (Entry 13). The reasons for the propensity of benzodiazepinones **9d**,**h**,**i**, to convert easily into the corresponding *N*-alkenylbenzimidazol-2-ones **12d**,**h**,**i** are not clearly understood.

In the case of the acyclic diazo compound **1f**, the reactions with **8a**–**c** led to the formation of the desired 1,3-dihydro-2*H*-1,5-benzodiazepin-2-ones **9j**–**l**, but, interestingly, these products were always accompanied by minor amounts of the corresponding 2-acetyl-3-methylquinoxalines **16a**–**c** (Scheme 5). The most striking feature of the side-reactions leading to **16a**–**c**[13] is that no Wolff rearrangement occurred in these transformations. We believe that this is due to the unblocked conformation of the acyclic diazo compound **1f**, which probably decomposes thermally to give at least a fraction of the corresponding α,α′-dicarbonyl carbene. In the presence of *o*-phenylenediamines **8a**–**c**, this carbene would undergo an insertion reaction into one N–H bond to give the corresponding 2-amino 1,3-diketones, which would then undergo heterocyclization (intramolecular imination) followed by an aromatizative dehydrogenation step to give the products **16a**–**c**.

Conclusions

The pseudo-three-component reaction of 2-diazodimedone (**1a**) with benzylamine leading to the corresponding enamino amide **3** has been exploited for the selective one-pot construction of various heterocyclic scaffolds of synthetic and biologic importance when bis(N-nucleophiles) are involved as partners. The microwave-assisted reaction with phenylhydrazine or urea required the presence of a catalytic amount of BF_3·OEt to give the pyrazole **5** or the pyrimidinedione **7**, respectively, according to a domino Wolff rearrangement/nucleophilic addition/intramolecular imination sequence. Although not very productive, these reactions are interesting examples of domino reactions of α-oxo ketenes performed in the presence of a Lewis acid. Importantly, the microwave-assisted reactions between the 2-diazo-1,3-diones **1** and the *o*-phenylenediamines **8** in the absence of any additive furnished a series of bi- and tricyclic 1,3-dihydro-2*H*-1,5-benzodiazepin-2-ones **9** according to another domino Wolff rearrangement/nucleophilic addition/intramolecular imination sequence. This reaction has led to a number of interesting observations and represents

a new and advantageously complementary synthetic approach to a valuable class of "drug-like" compounds.

Experimental Section

General: Reactions under microwave irradiation were performed in oven-dried 10 mL sealable Pyrex tubes equipped with a Teflon-coated stirring bar (obtained from CEM). All reactions under microwave irradiation (ν = 2.45 GHz) were performed in a CEM Discover 1-300W system equipped with a built-in pressure measurement sensor and a vertically focused IR temperature sensor. All reagents were obtained from commercial sources and used as supplied unless otherwise stated. Anhydrous toluene was obtained from an MBraun SPS-800 solvent purification system. Petroleum ether refers to the fraction of petroleum ether distilled between 40 and 65 °C. The reactions were monitored by TLC, which was performed on Merck 60F254 plates and visualized with an ethanolic solution of *p*-anisaldehyde and sulfuric acid or an ethanolic solution of molybdophosphoric acid. Flash chromatography was performed with Merck 230–400 mesh silica gel. NMR spectroscopic data were recorded with a Bruker Avance 300 spectrometer in $CDCl_3$, $(CD_3)_2SO$, or C_6D_6. The chemical shifts (δ) are given in ppm relative to the residual non-deuteriated solvent signal for ^1H NMR [$CHCl_3$: δ = 7.26 ppm; $(CH_3)_2SO$: δ = 2.50 ppm; C_6D_6: δ = 7.15 ppm] and relative to the deuteriated solvent signal for ^{13}C NMR [$CDCl_3$: δ = 77.0 ppm; $(CD_3)_2SO$: δ = 39.4 ppm; C_6D_6: δ = 128.02 ppm]; coupling constants (J) are given in Hz. The classical abbreviations are used to describe signal multiplicity. Mass spectra were recorded with a Bruker Esquire 6000 spectrometer equipped with an electrospray ionization source and an ion-trap detector. Melting points were measured with a Büchi B-540 apparatus. HRMS data were obtained from Spectropole (http://www.spectropole.u-3mrs.fr/). Diazo compounds **1a**–**f** were prepared from the corresponding 1,3-diketones by diazo transfer reactions with TsN_3 according to the procedures described in ref.[14] Compound **2** was prepared as described previously.[6a]

Compound 3: A solution of 2-diazodimedone (**1a**; 250 mg, 1.50 mmol) and benzylamine (329 µL, 3.00 mmol) in anhydrous toluene (2 mL) was subjected to microwave irradiation at 300 W for 3.5 min (T_{max} = 180 °C), after which the reaction mixture was cooled to 50 °C with an air flow. Concentration of the reaction mixture followed by high-vacuum removal of the volatiles afforded the clean crude product **3** as a colorless oil (499 mg, 99%) without need for purification. R_f (20% EtOAc/petroleum ether) = 0.59. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.34 (br. s, 1 H), 7.34–7.26 (m, 10 H), 5.18 (br. s, 1 H), 4.49 (d, J = 6.3 Hz, 2 H), 4.34 (d, J = 6.3 Hz, 2 H), 2.36 (s, 2 H), 2.27 (s, 2 H), 1.11 (s, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.8 (C), 160.3 (C), 139.7 (C), 139.4 (C), 128.5 (CH), 128.5 (CH), 128.5 (CH), 128.5 (CH), 127.6 (CH), 127.6 (CH), 127.0 (CH), 126.9 (CH), 126.6 (CH), 126.6 (CH), 93.2 (C), 48.0 (CH_2), 46.2 (CH_2), 44.3 (CH_2), 42.8 (CH_2), 35.7 (C), 29.7 (CH_3), 29.7 (CH_3) ppm. MS (ESI+): m/z = 335 $[M + H]^+$, 357 $[M + Na]^+$, 373 $[M + K]^+$.

Compound 5:[8] Boron trifluoride–diethyl ether (7 µL, 0.05 mmol) was added to a solution of 2-diazodimedone (**1a**; 78 mg, 0.47 mmol) and phenylhydrazine (49 µL, 0.47 mmol) in anhydrous toluene (2 mL), and the resulting mixture was subjected to microwave irradiation at 300 W for 2.6 min (T_{max} = 180 °C), after which the reaction mixture was cooled to 50 °C with an air flow. After removal of the volatiles under vacuum, the resulting crude product was directly purified by flash chromatography eluting with EtOAc/petroleum ether to afford pure **5** (46 mg, 42%) as a red-orange solid. R_f (40% EtOAc/petroleum ether) = 0.69. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.41–7.39 (m, 5 H), 7.19–7.14 (m, 1 H), 2.77 (s, 2 H), 2.48 (s, 2 H), 1.27 (s, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.4 (C), 149.2 (C), 139.6 (C), 129.4 (CH), 129.4 (CH), 124.8 (CH), 118.6 (CH), 118.6 (CH), 111.5 (C), 47.5 (C), 42.5 (CH_2), 37.8 (CH_2), 30.1 (CH_3), 30.1 (CH_3) ppm. MS (ESI+): m/z = 251 $[M + Na]^+$, 267 $[M + K]^+$.

Compound 7:[8] Boron trifluoride–diethyl ether (8 µL, 0.06 mmol) was added to a solution of 2-diazodimedone (**1a**, 98 mg, 0.59 mmol) and urea (35 mg, 0.59 mmol) in anhydrous toluene (2 mL), and the resulting mixture was subjected to microwave irradiation at 300 W for 2.5 min (T_{max} = 180 °C), after which the reaction mixture was cooled to 50 °C with an air flow. After removal of the volatiles under vacuum, the resulting crude product was directly purified by flash chromatography eluting with EtOAc/petroleum ether to afford pure **7** (28 mg, 26%) as a yellow oil. R_f (30% EtOAc/petroleum ether) = 0.26. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.84 (br. s, 1 H), 2.59 (dd, J = 1.8, 1.8 Hz, 2 H), 2.47 (dd, J = 1.8, 1.8 Hz, 2 H), 1.74 (br. s, 1 H), 1.21 (s, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.6 (C), 160.5 (C), 148.8 (C), 111.0 (C), 45.6 (CH_2), 39.9 (CH_2), 36.7 (C), 29.7 (CH_3), 29.7 (CH_3) ppm. MS (ESI+): m/z = 203 $[M + Na]^+$, 219 $[M + K]^+$.

General Procedure for the Synthesis of Compounds 9, 12–14, and/or 16: A solution of 2-diazo 1,3-diketone **1** and *o*-phenylenediamine **8** (1.0 equiv.) in anhydrous toluene (ca. 2 mL) was subjected to microwave irradiation at 300 W until the temperature reached 180 °C, or the pressure reached 17 bar, or for a maximum time of 6 min, after which the reaction mixture was cooled to 50 °C with an air flow. After removal of the volatiles under vacuum, the resulting crude product was directly purified by flash chromatography eluting with EtOAc/petroleum ether to afford pure **9**, **12** and/or **16**.

Compound 9a: According to the general procedure (6 min), the reaction between **1a** (50 mg, 0.30 mmol) and **8a** (33 mg, 0.30 mmol) afforded compound **9a** as an orange oil (52 mg, 76%). R_f (30% EtOAc/petroleum ether) = 0.41. ^1H NMR (300 MHz, C_6D_6): δ = 9.76 (br. s, 1 H), 7.58–7.54 (m, 1 H), 7.02–6.99 (m, 1 H), 6.92–6.89 (m, 2 H), 2.71 (dd, J = 7.0, 13.3 Hz, 1 H), 2.42 (dd, J = 7.0, 9.0 Hz, 1 H), 2.37–2.21 (m, 2 H), 1.43 (dd, J = 9.0, 13.3 Hz, 1 H), 0.94 (s, 3 H), 0.74 (s, 3 H) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 174.9 (C), 169.5 (C), 140.8 (C), 130.0 (C), 128.7 (CH), 126.2 (CH), 124.7 (CH), 122.6 (CH), 50.2 (CH_2), 48.7 (CH), 38.7 (CH_2), 36.7 (C), 28.3 (CH_3), 28.1 (CH_3) ppm. MS (ESI+): m/z = 251 $[M + Na]^+$. HRMS (ESI+): calcd. for $[C_{14}H_{17}N_2O]^+$ $[M + H]^+$ 229.1335; found 229.1332.

Compound 9b: According to the general procedure (1.5 min), the reaction between **1b** (102 mg, 0.74 mmol) and **8a** (80 mg, 0.74 mmol) afforded compound **9b** as an orange oil (82 mg, 55%). R_f (30% EtOAc/petroleum ether) = 0.15. ^1H NMR (300 MHz, $CDCl_3$): δ = 9.28 (br. s, 1 H), 7.36–7.33 (m, 1 H), 7.19–7.16 (m, 2 H), 7.08–7.05 (m, 1 H), 2.87–2.64 (m, 4 H), 2.02–1.95 (m, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 176.3 (C), 168.4 (C), 140.6 (C), 128.7 (C), 127.4 (CH), 126.1 (CH), 124.7 (CH), 122.3 (CH), 48.7 (CH), 35.7 (CH_2), 25.3 (CH_2), 23.5 (CH_2) ppm. MS (ESI+): m/z = 201 $[M + H]^+$, 223 $[M + Na]^+$, 239 $[M + K]^+$, 423 $[2 M + Na]^+$. HRMS (ESI+): calcd. for $[C_{12}H_{13}N_2O]^+$ $[M + H]^+$ 201.1022; found 201.1223.

Compound 9c: A solution of 2-diazocyclopentane-1,3-dione (**1c**; 66 mg, 0.53 mmol) and *o*-phenylenediamine (**8a**; 58 mg, 0.53 mmol) in anhydrous toluene (2 mL) was subjected to microwave irradiation at 180 °C for 5 min (ramp up time: 4 min), after which the reaction mixture was cooled to 50 °C with an air flow. After removal of the volatiles under vacuum, the resulting crude product

was directly purified by flash chromatography eluting with EtOAc/petroleum ether to afford pure **9c** as a pink solid (23 mg, 23%). R_f (50% EtOAc/petroleum ether) = 0.25. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.67 (br. s, 1 H), 7.38–7.35 (m, 1 H), 7.21–7.17 (m, 2 H), 7.07–7.03 (m, 1 H), 3.74 (dd, J = 4.9, 8.8 Hz, 1 H), 3.27–3.21 (m, 2 H), 2.75–2.63 (m, 1 H), 2.47–2.34 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.6 (C), 169.2 (C), 139.2 (C), 128.5 (C), 128.0 (CH), 126.6 (CH), 125.0 (CH), 122.8 (CH), 53.3 (CH), 35.8 (CH_2), 15.2 (CH_2) ppm. MS (ESI+): m/z = 209 $[M + Na]^+$. HRMS (ESI+): calcd. for $[C_{11}H_{11}N_2O]^+$ $[M + H]^+$ 187.2173; found 187.2169.

Compound 12d:[15] According to the general procedure (3 min), the reaction between **1d** (263 mg, 1.73 mmol) and **8a** (194 mg, 1.80 mmol) afforded compound **12d** as a white solid (222 mg, 59%). R_f (80% EtOAc/petroleum ether) = 0.18. M.p. 183–184 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.86 (m, 1 H), 7.15–7.11 (m, 1 H), 7.07–6.97 (m, 3 H), 6.00–5.97 (m, 1 H), 2.41–2.38 (m, 2 H), 2.33–2.28 (m, 2 H), 1.92–1.84 (m, 2 H), 1.79–1.74 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.9 (C), 132.0 (C), 130.6 (C), 128.5 (C), 127.6 (CH), 121.5 (CH), 121.0 (CH), 109.8 (CH), 108.6 (CH), 26.7 (CH_2), 24.7 (CH_2), 22.5 (CH_2), 21.6 (CH_2) ppm. MS (ESI+): m/z = 237 $[M + Na]^+$, 253 $[M + K]^+$, 451 $[2 M + Na]^+$.

Compound 9d:[11c,11f] A solution of 2-diazocycloheptane-1,3-dione (**1d**; 102 mg, 0.67 mmol) and *o*-phenylenediamine (**8a**; 77 mg, 0.71 mmol) in anhydrous toluene (2 mL) was subjected to microwave irradiation at 130 °C for 2 min (ramp up time: 2 min), after which the reaction mixture was cooled to 50 °C with an air flow. After removal of the volatiles under vacuum, the resulting crude product was directly purified by flash chromatography eluting with EtOAc/petroleum ether to afford compound **9d** (88 mg, 62%) as a pale-yellow solid. R_f (40% EtOAc/petroleum ether) = 0.18. M.p. 180–181 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 10.37 (s, 1 H), 7.28–7.23 (m, 1 H), 7.18–7.10 (m, 3 H), 2.73–2.62 (m, 2 H), 2.29–2.12 (m, 2 H), 1.86–1.47 (m, 5 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]-DMSO): δ = 167.6 (C), 165.5 (C), 138.5 (C), 129.9 (C), 126.7 (CH), 125.1 (CH), 123.7 (CH), 121.5 (CH), 44.3 (CH), 34.4 (CH_2), 22.7 (CH_2), 22.5 (CH_2), 21.1 (CH_2) ppm. MS (ESI+): m/z = 215 $[M + H]^+$, 237 $[M + Na]^+$.

Compounds 9e and 12e: According to the general procedure (4 min), the reaction between **1e** (39 mg, 0.24 mmol) and **8a** (27 mg, 0.25 mmol) afforded an inseparable mixture of compounds **12e** and **9e** (43 mg, 80%, **12e**/**9e** = 19:61). **12e:** R_f (50% EtOAc/petroleum ether) = 0.11. ^{1}H NMR (300 MHz, $CDCl_3$, selected resonances): δ = 9.96 (s, 1 H), 6.07 (dd, J = 6.3, 6.3 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, selected resonances): δ = 131.7 (CH), 121.0 (CH), 109.4 (CH), 108.7 (CH), 32.6 (CH_2), 31.4 (CH_2), 27.0 (CH_2), 26.7 (CH_2), 26.1 (CH_2) ppm. **9e:** R_f (50% EtOAc/petroleum ether) = 0.11. ^{1}H NMR (300 MHz, $CDCl_3$, selected resonance): δ = 9.14 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.0 (C), 168.9 (C), 139.4 (C), 129.0 (C), 127.1 (CH), 125.8 (CH), 124.7 (CH), 121.5 (CH), 50.7 (CH), 38.1 (CH_2), 30.5 (CH_2), 28.4 (CH_2), 26.6 (CH_2), 25.4 (CH_2) ppm.

Compound 9e: A solution of 2-diazocyclooctane-1,3-dione (**1e**; 85 mg, 0.51 mmol) and *o*-phenylenediamine (**8a**; 56 mg, 0.52 mmol) in anhydrous toluene (2 mL) was subjected to microwave irradiation at 130 °C for 2 min (ramp up time: 2 min), after which the reaction mixture was cooled to 50 °C with an air flow. After removal of the volatiles under vacuum, the resulting crude product was directly purified by flash chromatography eluting with EtOAc/petroleum ether to afford compound **9e** (65 mg, 57%) as a yellow solid. R_f (50% EtOAc/petroleum ether) = 0.11. M.p. 180–181 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.83 (s, 1 H), 7.38–7.34 (m, 1 H), 7.24–7.15 (m, 2 H), 7.08–7.03 (m, 1 H), 2.76–2.68 (m, 2 H), 2.54–2.46 (m, 1 H), 2.29–1.84 (m, 5 H), 1.64–1.43 (m, 2 H), 1.19–1.08 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.1 (C), 168.9 (C), 139.4 (C), 128.9 (C), 127.1 (CH), 125.8 (CH), 124.7 (CH), 121.4 (CH), 50.7 (CH), 38.2 (CH_2), 30.5 (CH_2), 28.4 (CH_2), 26.6 (CH_2), 25.4 (CH_2) ppm. MS (ESI+): m/z = 229 $[M + H]^+$, 251 $[M + Na]^+$. HRMS (ESI+): calcd. for $[C_{14}H_{17}N_2O]^+$ $[M + H]^+$ 229.1335; found 229.1337.

Compound 9f: According to the general procedure (3 min), the reaction between **1a** (84 mg, 0.51 mmol) and **8b** (90 mg, 0.50 mmol) afforded compound **9f** (74 mg, 49%) as a yellow solid containing the two regioisomeric forms in a 1:2 ratio. **9f (Imine Form):** R_f (40% EtOAc/petroleum ether) = 0.45. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 10.55 (s, 1 H), 7.51 (s, 1 H), 7.35 (s, 1 H), 3.19 (dd, J = 6.9, 8.8 Hz, 1 H), 2.41 (dd, J = 6.9, 8.8 Hz, 1 H), 2.37 (s, 2 H), 1.75 (dd, J = 8.8, 13.2 Hz, 1 H), 1.12 (s), 0.99 (s) ppm. MS (ESI+): m/z = 321/319 $[M + Na]^+$. **9f (Enamine Form):** R_f (40% EtOAc/petroleum ether) = 0.45. M.p. 230–231 °C. ^{1}H NMR (300 MHz, [D$_6$]-DMSO): δ = 8.52 (s, 1 H), 8.33 (s, 1 H), 6.91 (s, 1 H), 6.79 (s, 1 H), 2.23 (s, 4 H), 1.03 (s, 6 H) ppm. ^{13}C NMR (75 MHz/[D$_6$]DMSO): δ = 166.5 (C), 153.1 (C), 134.6 (C), 130.1 (C), 123.9 (C), 123.9 (C), 120.9 (CH), 119.5 (CH), 101.5 (C), 49.6 (CH_2), 45.7 (CH_2), 34.1 (C), 28.9 (CH_3), 28.9 (CH_3) ppm. MS (ESI+): m/z = 321/319 $[M + Na]^+$.

Compounds 13g and 14g: According to the general procedure (3 min), the reaction between **1a** (123 mg, 0.74 mmol) and **8c** (98 mg, 0.72 mmol) afforded crude **9g**, which was not purified. This material was dissolved in MeOH (3 mL) and acetic acid (43 μL, 0.75 mmol), and $NaBH_3CN$ (47 mg, 0.74 mmol) was added at room temperature. After 5 h, the reaction mixture was concentrated, diluted with EtOAc and water, and the organic layer was separated. The aqueous phase was extracted once with EtOAc, and the combined organic layers were washed with brine, dried with anhydrous Na_2SO_4, filtered, and concentrated to give the crude product, which was purified by flash chromatography eluting with EtOAc/petroleum ether to afford first compound **13g** (72 mg, 51%) as a white solid and then **14g** (25 mg, 18%) as a white solid. **13g:** R_f (30% EtOAc/petroleum ether) = 0.18. M.p. 211–212 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.59 (s, 1 H), 6.53 (s, 1 H), 6.43 (s, 1 H), 3.88 (ddd, J = 9.0, 9.0, 9.0 Hz, 1 H), 3.81 (s, 1 H), 2.95 (ddd, J = 9.0, 9.0, 9.0 Hz, 1 H), 2.18–2.10 (m, 7 H), 2.05 (dd, J = 7.2, 12.4 Hz, 1 H), 1.76 (dd, J = 9.0, 13.6 Hz, 1 H), 1.45 (dd, J = 9.0, 12.1 Hz, 1 H), 1.10 (s, 3 H), 1.09 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 174.0 (C), 135.0 (C), 133.5 (C), 126.8 (C), 123.7 (CH), 120.6 (C), 119.8 (CH), 59.6 (CH), 50.3 (CH), 50.1 (CH_2), 39.9 (CH_2), 37.1 (C), 30.8 (CH_3), 30.4 (CH_3), 18.9 (CH_3), 18.3 (CH_3) ppm. MS (ESI+): m/z = 259 $[M + H]^+$, 281 $[M + Na]^+$, 297 $[M + K]^+$. HRMS (ESI+): calcd. for $[C_{16}H_{23}N_2O]^+$ $[M + H]^+$ 259.1805; found 259.1806. **14g:** R_f (30% EtOAc/petroleum ether) = 0.15. M.p. 224–225 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.61 (s, 1 H), 6.71 (s, 1 H), 6.69 (s, 1 H), 4.10 (ddd, J = 6.3, 9.0, 9.0 Hz, 1 H), 3.25 (br. s, 1 H), 3.01 (ddd, J = 6.3, 9.0, 9.0 Hz, 1 H), 2.32 (dd, J = 6.3, 13.2 Hz, 1 H), 2.18 (s, 6 H), 1.79–1.53 (m, 3 H), 1.16 (s, 3 H), 0.98 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 175.0 (C), 138.7 (C), 133.6 (C), 131.6 (C), 128.7 (C), 123.0 (CH), 122.8 (CH), 66.7 (CH), 48.1 (CH_2), 46.9 (CH), 40.8 (CH_2), 36.6 (C), 30.1 (CH_3), 30.1 (CH_3), 19.0 (CH_3), 18.9 (CH_3) ppm. MS (ESI+): m/z = 259 $[M + H]^+$, 281 $[M + Na]^+$, 297 $[M + K]^+$. HRMS (ESI+): calcd. for $[C_{16}H_{23}N_2O]^+$ $[M + H]^+$ 259.1805; found 259.1802.

Compound 12h: According to the general procedure (5 min), the reaction between **1d** (95 mg, 0.62 mmol) and **8b** (111 mg, 0.62 mmol) afforded compound **12h** as a pink solid (124 mg, 70%).

R_f (50% EtOAc/petroleum ether) = 0.22. M.p. 256–257 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 11.19 (s, 1 H), 7.17 (s, 1 H), 7.16 (s, 1 H), 5.88–5.86 (m, 1 H), 2.28–2.20 (m, 4 H), 1.77–1.61 (m, 4 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 152.7 (C), 131.2 (C), 130.1 (C), 128.3 (C), 126.7 (CH), 122.8 (C), 122.6 (C), 110.0 (CH), 109.3 (CH), 25.9 (CH_2), 23.9 (CH_2), 21.9 (CH_2), 20.9 (CH_2) ppm. MS (ESI+): *m*/*z* = 307/305 [M + Na]$^+$. HRMS (ESI+): calcd. for [$C_{13}H_{13}N_2OCl_2$]$^+$ [M + H]$^+$ 283.0399; found 283.0400.

Compound 9h: A solution of 2-diazocycloheptane-1,3-dione (**1d**; 100 mg, 0.66 mmol) and diamine **8b** (116 mg, 0.65 mmol) in anhydrous toluene (2 mL) was subjected to microwave irradiation at 130 °C for 2 min (ramp up time: 2 min), after which the reaction mixture was cooled to 50 °C with an air flow. After removal of the volatiles under vacuum, the resulting crude product was directly purified by flash chromatography eluting with EtOAc/petroleum ether to afford compound **9h** (112 mg, 61%) as a yellow solid containing the two regioisomeric forms of **9h** in a 1:5 ratio. R_f (50% EtOAc/petroleum ether) = 0.45. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 10.5 (s, 1 H, enamine form), 8.95 (s, 1 H, imine form), 7.51 (s, 1 H), 7.46 (s, 1 H), 7.33 (s, 1 H, enamine form), 7.00 (s, 1 H), 6.97 (s, 1 H), 2.79–2.65 (m), 2.30–2.07 (m), 1.85–1.82 (m), 1.71–1.45 (m) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 169.5 (C), 168.3 (C), 167.4 (C), 152.3 (C), 138.3 (C), 138.0 (C), 131.0 (C), 130.0 (C), 127.8 (CH), 126.8 (C), 125.3 (C), 124.4 (C), 123.9 (C), 122.5 (CH), 120.6 (CH), 119.9 (CH), 105.2 (C), 44.8 (CH), 34.5 (CH_2), 30.4 (CH_2), 25.0 (CH_2), 22.6 (CH_2), 22.3 (CH_2), 21.8 (CH_2), 21.7 (CH_2), 20.9 (CH_2) ppm. MS (ESI+): *m*/*z* = 307/305 [M + Na]$^+$.

Compound 12i: According to the general procedure (4 min), the reaction between **1d** (158 mg, 1.04 mmol) and **8c** (147 mg, 1.08 mmol) afforded compound **12i** as a white solid (156 mg, 62%). R_f (40% EtOAc/petroleum ether) = 0.15. M.p. 256–257 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.5 (br. s, 1 H), 6.93 (s, 1 H), 6.76 (s, 1 H), 5.97–5.94 (m, 1 H), 2.40–2.38 (m, 2 H), 2.34–2.26 (m, 8 H), 1.92–1.84 (m, 2 H), 1.80–1.74 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.0 (C), 132.2 (C), 129.6 (C), 129.1 (C), 128.7 (C), 127.2 (CH), 126.3 (C), 110.9 (CH), 109.5 (CH), 26.7 (CH_2), 24.6 (CH_2), 22.5 (CH_2), 21.6 (CH_2), 19.8 (CH_3), 19.7 (CH_3) ppm. MS (ESI+): *m*/*z* = 265 [M + Na]$^+$, 281 [M + K]$^+$. HRMS (ESI+): calcd. for [$C_{15}H_{19}N_2O$]$^+$ [M + H]$^+$ 243.1492; found 243.1490.

Compound 9i: A solution of 2-diazocycloheptane-1,3-dione (**1d**; 98 mg, 0.65 mmol) and diamine **8c** (89 mg, 0.65 mmol) in anhydrous toluene (2 mL) was subjected to microwave irradiation at 130 °C for 2 min (ramp up time: 2 min), after which the reaction mixture was cooled to 50 °C with an air flow. After removal of the volatiles under vacuum, the resulting crude product was directly purified by flash chromatography eluting with EtOAc/petroleum ether to afford compound **9i** as a yellow solid (115 mg, 73%). R_f (50% EtOAc/petroleum ether) = 0.25. M.p. 173–174 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 10.19 (s, 1 H), 7.03 (s, 1 H), 6.86 (s, 1 H), 2.68–2.59 (m, 2 H), 2.25–2.14 (m, 8 H), 1.85–1.45 (m, 5 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 167.2 (C), 164.3 (C), 136.5 (C), 133.5 (C), 131.9 (C), 127.6 (C), 127.1 (CH), 121.8 (CH), 44.3 (CH), 34.4 (CH_2), 22.7 (CH_2), 22.6 (CH_2), 21.2 (CH_2), 18.8 (CH_3), 18.6 (CH_3) ppm. MS (ESI+): *m*/*z* = 243 [M + H]$^+$, 265 [M + Na]$^+$. HRMS (ESI+): calcd. for [$C_{15}H_{19}N_2O$]$^+$ [M + H]$^+$ 243.1492; found 243.1492.

Compounds 9j and 16a:[13] According to the general procedure (3 min), the reaction between **1f** (93 mg, 0.73 mmol) and **8a** (80 mg, 0.74 mmol) afforded first **16a** (20 mg, 14%) and then **9j** (59 mg, 43%) as yellow solids. **16a:** R_f (40% EtOAc/petroleum ether) = 0.65. M.p. 86–87 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.11 (dd, *J* = 1.2, 8.2 Hz, 1 H), 8.04 (dd, *J* = 1.2, 8.5 Hz, 1 H), 7.83 (ddd, *J* = 1.5, 7.6, 8.5 Hz, 1 H), 7.75 (ddd, *J* = 1.5, 7.5, 8.2 Hz, 1 H), 2.96 (s, 3 H), 2.84 (s, 3 H) ppm; NH resonances not detected. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 201.3 (C), 153.0 (C), 147.1 (C), 142.5 (C), 139.7 (C), 132.0 (CH), 129.8 (CH), 129.5 (CH), 128.3 (CH), 27.7 (CH_3), 24.3 (CH_3) ppm. MS (ESI+): *m*/*z* = 189 [M + H]$^+$, 211 [M + Na]$^+$, 227 [M + K]$^+$. **9j:** R_f (40% EtOAc/petroleum ether) = 0.15. M.p. 167–168 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.16 (br. s, 1 H), 7.35–7.32 (m, 1 H), 7.22–7.15 (m, 2 H), 7.10–7.05 (m, 1 H), 2.81 (q, *J* = 6.9 Hz, 1 H), 2.24 (s, 3 H), 1.47 (d, *J* = 6.9 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.8 (C), 166.3 (C), 139.1 (C), 128.8 (C), 127.0 (CH), 125.9 (CH), 124.8 (CH), 121.5 (CH), 44.0 (CH), 23.0 (CH_3), 10.9 (CH_3) ppm. MS (ESI+): *m*/*z* = 189 [M + H]$^+$, 211 [M + Na]$^+$, 227 [M + K]$^+$. HRMS (ESI+): calcd. for [$C_{11}H_{13}N_2O$]$^+$ [M + H]$^+$ 189.1022; found 189.1020.

Compounds 9k and 16b: According to the general procedure (3 min), the reaction between **1f** (118 mg, 0.94 mmol) and **8b** (166 mg, 0.93 mmol) afforded first **16b** (21 mg, 9%) and then **9k** (106 mg, 44%) as yellow and white solids, respectively. **16b:** R_f (30% EtOAc/petroleum ether) = 0.80. M.p. 144–145 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.24 (s, 1 H), 8.15 (s, 1 H), 2.94 (s, 3 H), 2.80 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 200.6 (C), 154.4 (C), 147.8 (C), 141.3 (C), 138.4 (C), 136.7 (C), 134.3 (C), 130.2 (CH), 129.1 (CH), 27.7 (CH_3), 24.4 (CH_3) ppm. MS (ESI+): *m*/*z* = 279/277 [M + Na]$^+$. **9k:** R_f (30% EtOAc/petroleum ether) = 0.20. M.p. 205–206 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 10.6 (s, 1 H), 7.47 (s, 1 H), 7.33 (s, 1 H), 2.81 (q, *J* = 6.9 Hz, 1 H), 2.12 (s, 3 H), 1.31 (d, *J* = 6.9 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]-DMSO): δ = 168.3 (C), 167.2 (C), 138.6 (C), 129.8 (C), 127.5 (CH), 126.9 (C), 125.3 (C), 122.5 (CH), 44.2 (CH), 22.6 (CH_3), 10.7 (CH_3) ppm. MS (ESI+): *m*/*z* = 259/257 [M + H]$^+$, 281/279 [M + Na]$^+$. HRMS (ESI+): calcd. for [$C_{11}H_{11}Cl_2N_2O$]$^+$ [M + H]$^+$ 257.0243; found 257.0247.

Compounds 9l and 16c:[13] According to the general procedure (3 min), the reaction between **1f** (160 mg, 1.27 mmol) and **8c** (173 mg, 1.27 mmol) afforded first **16c** (34 mg, 12%) and then **9l** (132 mg, 48%) as white solids. **16c:** R_f (40% EtOAc/petroleum ether) = 0.59. M.p. 130–131 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.85 (s, 1 H), 7.77 (s, 1 H), 2.93 (s, 3 H), 2.81 (s, 3 H), 2.50 (s, 3 H), 2.49 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 201.5 (C), 152.1 (C), 146.3 (C), 143.0 (C), 141.6 (C), 140.1 (C), 138.7 (C), 128.7 (CH), 127.4 (CH), 27.7 (CH_3), 24.3 (CH_3), 20.6 (CH_3), 20.1 (CH_3) ppm. MS (ESI+): *m*/*z* = 237 [M + Na]$^+$. **9l:** R_f (40% EtOAc/petroleum ether) = 0.12. M.p. 181–182 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.72 (s, 1 H), 7.10 (s, 1 H), 6.80 (s, 1 H), 2.80 (q, *J* = 6.9 Hz, 1 H), 2.24 (s, 6 H), 2.22 (s, 3 H), 1.45 (d, *J* = 6.9 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.5 (C), 165.1 (C), 137.2 (C), 134.8 (C), 133.5 (C), 127.5 (CH), 126.5 (C), 121.9 (CH), 43.9 (CH), 22.9 (CH_3), 19.2 (CH_3), 19.1 (CH_3), 11.0 (CH_3) ppm. MS (ESI+): *m*/*z* = 217 [M + H]$^+$, 239 [M + Na]$^+$, 255 [M + K]$^+$. HRMS (ESI–): calcd. for [$C_{13}H_{15}N_2O$]$^-$ [M – H]$^-$ 215.1190; found 215.1195.

Supporting Information (see footnote on the first page of this article): NMR spectra of all new compounds.

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