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Practical Synthesis of β-Carbonyl Phenyltetrazolesulfones and Investigations of Their Reactivities in Organocatalysis

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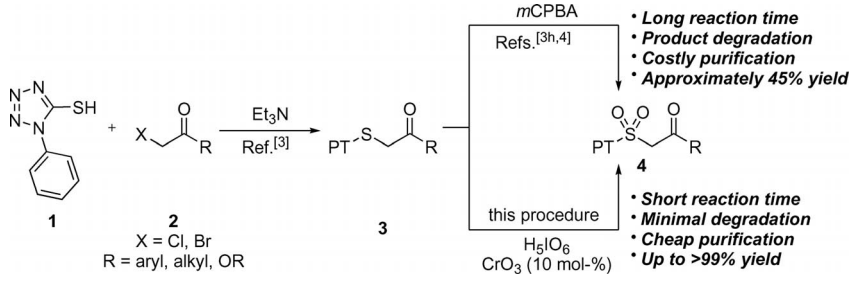
A practical synthesis of β-carbonyl phenyltetrazolesulfones, useful for a series of enantioselective reactions, is shown. Aryl, alkyl and ester carbonyl compounds all proved to be efficiently synthesised, leading to products in up to >99 % yield over two steps. During this procedure, no special attention to conditions or laborious purification by chromatography is needed. Furthermore, X-ray crystallography, kinetic studies, as well as NMR and IR investigations provide insights into the reactivities of these compounds in organocatalysis.

Introduction

The development of asymmetric organocalytic approaches towards synthetically valuable target molecules has evolved into a highly credited area.[1] Several examples pointing out the advantages of using organocatalysis for synthetic applications have been published,[2] and organocatalysis is thus a field that has emerged from focussing mainly on methodology developments to also being applied in the synthesis of important target molecules. However, considering the synthesis of a given molecule, the easy availability of all chemicals involved should be taken into account. As such, reactions leading to attractive products in high yields and stereoselectivities might still suffer from expenses or difficulties in, for example, the synthesis of starting materials compared to established routes.

Recently, the synthetic value of employing sulfones in asymmetric organocatalysis has been demonstrated,[1i,1j,3] giving access to highly important enantioenriched compounds. For example, the use of β-oxo phenyltetrazolesulfones combined with α,β-unsaturated aldehydes and a prolinol-derived catalyst has led to the stereoselective formation of both β-alkynylated and β-alkenylated aldehydes.[3h] This procedure provided the first enantioselective catalytic formation of enantioenriched 4-ynals, and therefore represents an example of the utility of organocatalysis as a unique tool for solving specific problems. However, a drawback of the method was the expensive synthesis of the β-oxo phenyltetrazolesulfones, particularly attributed to a costly and complicated purification process. Due to the instability of these compounds on normal silica gel, column chromatography could only be carried out with special stationary-phase powder (Iatrobeads 6RS-8060). Furthermore,



Scheme 1. Early and present approaches towards β-carbonyl phenyltetrazolesulfones **4**. PT = phenyltetrazole.

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degradation processes were observed during prolonged reaction times (days), which were often necessary for reasonable conversion to product **4** (Scheme 1, upper reaction). These setbacks resulted in yields generally in the range of only 45%. For β-ester derivatives of phenyltetrazolesulfones, the purification is performed by using normal silica, and no degradation during the oxidation step is observed.[4] However, long reaction times are still required.

Herein, we wish to present an efficient, fast and high-yielding procedure for the formation of β-carbonyl phenyltetrazolesulfones. During a two-step process, only ambient and simple conditions are applied, no laborious purification is needed, and cheap starting materials are used to isolate the products in up to 99% yield (Scheme 1, lower reaction). Furthermore, in order to obtain information concerning the reactivities of these compounds, several crystal structures, as well as kinetic studies and IR spectroscopic investigations are presented.

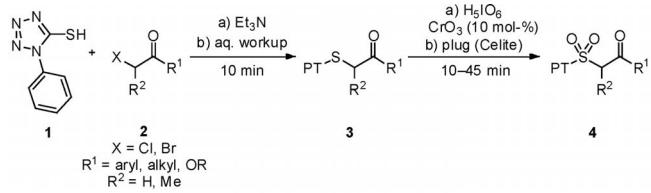
Results and Discussion

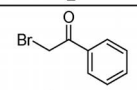
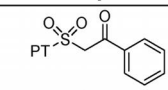
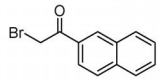
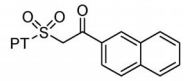
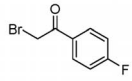
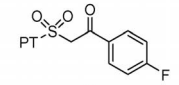
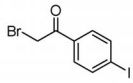
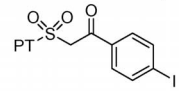
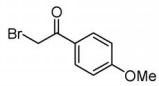
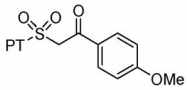
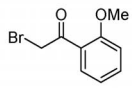
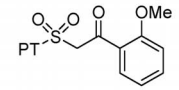
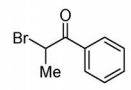
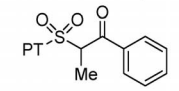
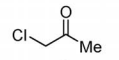
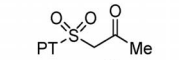
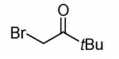
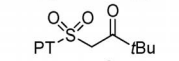
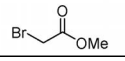
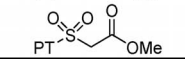
The formation of β-carbonyl phenyltetrazolesulfones **4** was conducted from 1-phenyl-1*H*-tetrazole-5-thiol (PTSH; **1**) and α-halogenated ketones or esters **2** in a two-step procedure (Table 1). First, intermediate **3** was formed and isolated by employing a known procedure,[3h] i.e. reaction of **1** and **2** in CH_2Cl_2 in the presence of Et_3N, followed by aqueous workup. Having unsuccessfully employed various oxidative systems, e.g. dioxirane[5b,5c] or ammonium molybdate and hydrogen peroxide,[5d–5f] in the oxidation of **3**, we turned our attention towards chromium-catalysed procedures. As such, we found that the oxidation of **3** can be carried out by using H_5IO_6 and catalytic amounts of CrO_3, which leads to **4** within 10–45 min.[5a] A cheap and easy purification process allows the isolation of **4** in high yields with minimal degradation.[5a] As shown in the scheme of Table 1, purification consists of a filtration through Celite to obtain products **4**, which by ^{1}H NMR spectroscopy are in general found to contain less than 5% impurities. Analytically pure samples were obtained in good yields by a simple recrystallisation.

Having found an efficient protocol for the formation of the β-carbonyl phenyltetrazolesulfones **4**, we investigated the scope by variation of the α-halogenated ketones or esters **2** with respect to the R^1 and R^2 substituents (Table 1). The standard reaction was performed on a 1 mmol scale; however, experiments at a 5 mmol scale for R^1 = OMe gave comparable yields of compound **4j**, which shows the practical use of this procedure. The results in Table 1 are the yields before and after recrystallisation.

Initially, various α-halogenated aryl ketones **2** (R^1 = aryl) were tested. Phenyl derivative **4a** was synthesised in 91% yield over both steps, and 70% after recrystallisation. Enlarging the aromatic skeleton to a naphthyl unit results in a similar outcome; however, the recrystallisation process proved slightly more efficient to yield 81% of product **4b**. Employment of an electron-withdrawing substituent, such as a 4-fluorophenyl moiety, resulted in a mixture consisting of 91% of **4c** before purification, the remaining 9% being mainly 1-phenyl-1*H*-tetrazol-5-ol (PTOH) formed by degradation. However, pure **4c** was obtained in 60% yield upon recrystallisation. Remarkably, in the synthesis of **4d** containing a 4-iodophenyl moiety, which is less electron-withdrawing, but more susceptible to oxidation, a yield of 86% was obtained. It should be noted that this starting material cannot be used in the procedure with *m*CPBA as oxidant due to oxidation of the iodo substituent. Electron-donating groups, such as 4- and 2-methoxy substituents, are equally well tolerated, forming products **4e** and **4f** in 90% and 94% yields, respectively. Modification of the R^2 group to a

Table 1. Scope of the new procedure for the formation of **4** from **1** and **2**.[a]



Entry	2	4	Yield (%)[b,c]
1			**4a**: 91 (70)
2			**4b**: 90 (81)
3			**4c**: –[d] (60)
4			**4d**: 86 (73)
5			**4e**: 90 (78)
6			**4f**: 94 (74)
7			**4g**: 96 (88)
8			**4h**: 90 (80)
9			**4i**: >99 (–)[e]
10			**4j**: 98 (82)

[a] Formation of **3** is performed with **2** (1.0 mmol), **1** (1.1 equiv., 1.1 mmol), and Et_3N (1.1 equiv., 1.1 mmol) in CH_2Cl_2 (5 mL). Formation of **4** is performed with **3** (amount produced in previous step, expected to be 1.0 mmol), H_5IO_6 (3 equiv., 3.0 mmol), and CrO_3 (0.1 equiv., 0.1 mmol) in MeCN. [b] Isolated yield over the two steps. [c] Values in parentheses are yields after a single recrystallisation. [d] 91% pure by ^{1}H NMR spectroscopy. [e] Did not crystallize.

methyl unit resulted in an outcome similar to **4a**–**f** with a 96% yield of **4g**. Recrystallisation afforded **4g** in 88% overall yield, corresponding to 94% per reaction step.

According to the general procedure, high yields were also achieved for aliphatic products (R^1 = alkyl). Starting from chloroacetone, methyl-substituted β-oxo phenyltetrazolesulfone product **4h** was obtained in 90% and 80% yield, before and after recrystallisation, respectively. Likewise, the *tert*-butyl product **4i** was formed in >99% yield; however, recrystallisation was not possible for this compound. Finally, a single example of an ester product, the methyl ester **4j**, was produced in 98% yield and in 82% yield after a single recrystallisation.

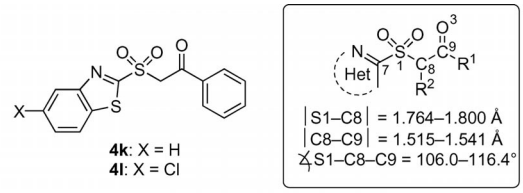
Having established the substrate capacity of this procedure, kinetic studies for the reaction shown in Table 2 were performed for selected β-carbonyl phenyltetrazolesulfones (**4a**–**c**,**e**–**h**,**j**) and related benzothiazole and 5-chlorobenthiazole derivatives **4k**,**l**.[6] In addition, crystal structures were obtained of **4a**–**c**,**e**–**h**,**j**–**l** (Figure 1).[7] Of particular interest is to relate the various observed reaction rates with the structural information and NMR and IR spectroscopic data. In this regard, the angles and bond lengths of the bonds at C-8 should be expected to be of importance. Furthermore, ^{1}H NMR and ^{13}C NMR shifts of 8-H and C-8, respectively, have been extracted, and IR measurements of the C-9=O-3 carbonyl bond were compared. The data are given in Table 2 and in the Supporting Information.

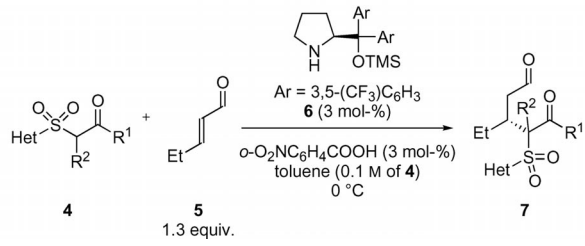
The kinetic measurements revealed that compounds **4a**–**l** can be divided in three groups of compounds with similar reactivities. The compounds belonging to the most reactive group are **4a**,**c** with a TOF_{50} of >10 h^{-1}, followed by **4b**,**e** with a TOF_{50} of approximately 5 h^{-1}. The slowest reactions were observed for the group of **4f**,**h**,**j** with a TOF_{50} of approximately 2 h^{-1}. It should be noted that, performing the reactions with **4a** without acid additive (2-$O_2NC_6H_4CO_2H$) or with NaOAc, led to reactivities <2 h^{-1} (see Supporting Information). Nucleophile **4g** containing a methyl group as R^2 was unreactive. The benzothiazole derivatives **4k**,**l** showed limited conversion (<25%).

Crystal structures showed that the bond lengths of the C8–S1 bond vary from 1.764 to 1.800 Å, corresponding to a C–S single bond. Likewise, the C8–C9 bond lengths are 1.515–1.541Å, equivalent to a C–C single bond. Furthermore, the S1–C8–C9 bond angles are 106.0–116.4°, values typical for tetrahedral structures. These values are all very similar for the structures and they do not provide a rationale to interpret the differences in reaction rates.

On the contrary, the dihedral angle of S1–C8–C9–O3 reveals a weak correlation between this angle and the observed reactivities. The phenyltetrazole compounds **4a**–**j** seem to be more reactive when the S1–C8–C9–O3 dihedral angle is close to 0°. Thus, it is plausible to be of importance whether the conformation of the molecule is ready to adopt the sp^2-hybridised enol form or not. Whereas rotation about the bonds is likely, the conformations of the crystal structures should represent some of the most stable conformations in solution as well.

Table 2. Selected torsion angles, IR data, and TOF_{50} values of **4**.





	S1–C8–C9–O3 [°]	ν(C=O) [cm^{-1}]	TOF_{50}[a] [h^{-1}]
4a	3.5	1687	16.7
4b	–4.9	1679	6.9
4c	0.8	1686	11.1
4e	0.3	1675	5.1
4f	–82.3	1664	1.6
4g	89.1	1682	0[b]
4h	39.3	1726	1.6
4j	–8.8	1740	2.4
4k	–5.2	1683	0[c]
4l	1.6	1683	0[c]

[a] Turn-over frequency at 50% conversion for the reaction between **4** and **5**, catalysed by **6**. [b] No conversion. [c] Conversion does not exceed 25%.

This is supported by the fact that the group of slowest reacting substrates (**4f**,**h**,**j**) has an S1–C8–C9–O3 dihedral angle considerably deviating from 0°. For example, compound **4h** has an S1–C8–C9–O3 dihedral angle of 39.3°. This correlates with a very slow reactivity of **4h** of 1.6 h^{-1}.[8] The equally slow-reacting 2-MeO-substituted substrate **4f** has a significantly different conformation with an S1–C8–C9–O3 dihedral angle of –82.3°, and the methoxy group is conceivably shielding the nucleophile when approaching **5**. Compound **4g** with R^2 = Me is unreactive, likely due to steric congestion at the C8 unit of the nucleophile by the methyl group, hindering its approach to the electrophile.

Both the ^{1}H and ^{13}C NMR spectroscopic data, for the 8-H and C-8 atoms, respectively, seem not to correlate with the differences in reaction rates (see Supporting Information for NMR spectroscopic data). Therefore, NMR spectroscopy seems not to be an appropriate tool for predicting reactivities with this type of nucleophiles.

IR data for the C-9=O-3 carbonyl bond correlate with the observed rates for the directly comparable phenyltetrazole compounds with R^1 = Ar (**4a**–**c**,**e**,**f**). The lower the observed wavenumber $\tilde{\nu}$(C-9=O-3), the lower the reaction rate. Thus, the group of most reactive compounds (**4a**,**c**) has $\tilde{\nu}$(C-9=O-3) = 1687 cm^{-1} and 1686 cm^{-1} for **4a** and **4c**, respec-

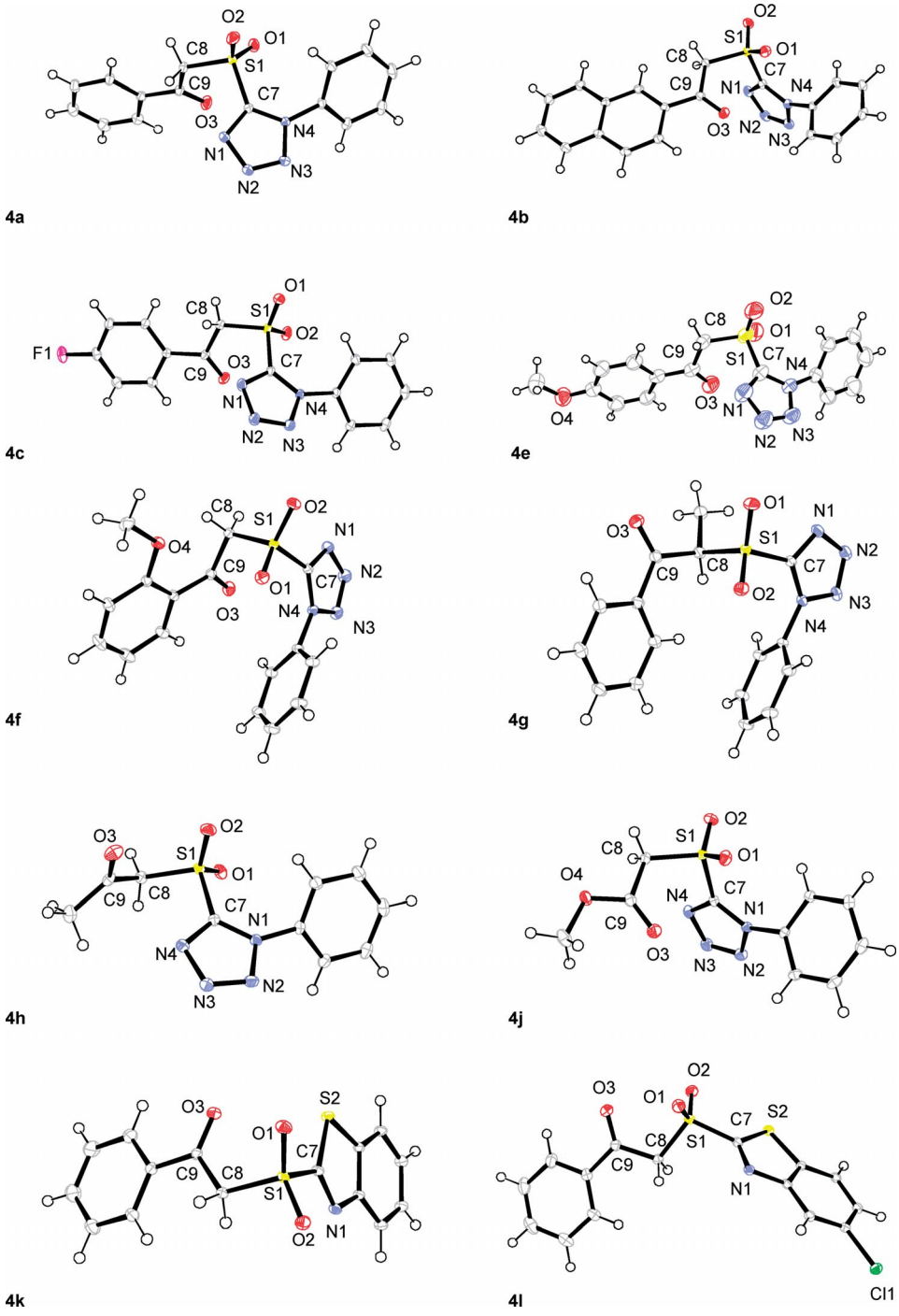


Figure 1. ORTEP[9] plots at 50% ellipsoid probability of crystal structures of **4a**–**l**.

tively. The group of moderately reactive compounds (**4b**,**e**) has $\tilde{\nu}$(C-9=O-3) = 1679 cm^{-1} and 1675 cm^{-1} for **4b** and **4e**, respectively. In this context, the lower reactivity of the naphthyl derivative **4b** and 4-MeO derivative **4e** correlates well with their observed lower IR frequencies. We propose that this difference in reactivity can be explained by their different electronic properties, since their conformations, as determined by X-ray crystallography, should be well suited for enol formation. Finally, in the group of slowest reacting substrates (**4f**,**h**,**j**), **4f** has $\tilde{\nu}$(C-9=O-3) = 1664 cm^{-1}, suggesting low reactivity. As the R^1 substituents of both **4h** and **4j** differ considerably from the aryl moieties in the other substrates, $\tilde{\nu}$(C-9=O-3) can not be compared.

Whereas X-ray crystallography gives information concerning the steric bulk and conformation of the discussed nucleophiles, IR spectroscopy reflects the electronic effects of the R^1 substituent on the C-9=O-3 carbonyl bond. From the data collected it becomes apparent that both steric and electronic effects govern the reactivity of phenyltetrazole compounds in the organocatalytic addition to α,β-unsatu-

rated aldehydes. Since the reaction mechanism seems to require acid-catalysed enol formation, lone-pair-donating R^1 substituents, such as the 2-$MeOC_6H_4$ and 4-$MeOC_6H_4$ groups, can explain a slower reaction, due to less enol formation. Electron-withdrawing substituents on the other hand may decrease the nucleophilicity of the formed enol, again resulting in a slower reaction, as observed in the small decrease in reactivity of **4c** vs. **4a**.

Interestingly, the benzothiazole derivatives **4k**,**l** have similar dihedral angles and NMR and IR spectroscopic data as the most reactive phenyltetrazole compounds, but show only minimal reactivity. We attribute this discrepancy to stereoelectronic differences of phenyltetrazole and benzothiazole moieties, apparently not evident in any of these experimental data. Whereas these compounds are not suitable for the β-alkynylation and β-alkenylation of α,β-unsaturated aldehydes, they are successfully employed in a range of analogous reactions.[6]

Conclusions

A practical synthesis of β-carbonyl phenyltetrazolesulfones has been devised. In general, high yields were obtained (up to 99%), and the products were isolated with high purity after a single recrystallization. Furthermore, X-ray crystallography, kinetic studies and NMR and IR spectral investigations have provided a number of insights of the internal properties of these compounds. Besides the α-methylated compound **4g**, all other β-carbonyl phenyltetrazoles **4a**–**j** were found to be reactive in the organocatalytic addition to pentenal, demonstrating again the broad applicability of this reaction.[3h] Correlation between reactivity and analytical data has been observed and provides insight into both the steric and electronic effects governing the reactivity of these compounds.

Experimental Section

General Procedure for the Formation of β-Carbonyl Phenyltetrazolesulfones 4a–j: The respective α-halocarbonyl compound **2** (1.0 mmol) was dissolved in CH_2Cl_2 (5 mL), and 1-phenyl-1*H*-tetrazole-5-thiol (1.1 mmol, 1.1 equiv.) was added. Then Et_3N (1.1 mmol, 1.1 equiv.) was added slowly. The reaction mixture was stirred for 10–60 min and monitored by TLC. Upon consumption of **2**, the organic phase was washed with 2 M HCl and satd. aq. Na_2CO_3. The organic phase was concentrated, and the crude sulfide **3** used without further purification in the next step. Finely crushed periodic acid (3.0 mmol, 3 equiv.) was suspended in MeCN (5 mL) and the mixture stirred for 30 min until a clear solution was obtained. CrO_3 (0.1 mmol, 0.1 equiv.) was added. Then the sulfide **3** was added as a solid. Immediate formation of a precipitate was observed. Alternatively, periodic acid and **3** were premixed and stirred for 30 min before addition of CrO_3. The reaction was monitored by ^{1}H NMR spectroscopy and/or TLC and was complete after 10–45 min. A pad of Celite (8 cm in diameter and 5 cm in height) was wetted with pentane. Then water (25 mL) was added to the MeCN solution and the mixture adsorbed to the Celite. The adsorbed product was washed with pentane (75 mL), and then the product was washed off the Celite with CH_2Cl_2 (250 mL). The organic phase was dried with Na_2SO_4. Removal of the solvent gave product **4** of high purity (<5% impurities). Recrystallisation was effected by dissolving the crude product in hot toluene or CH_2Cl_2 (1–2 mL), filtering the solution through glass wool and layering the solution with iPr_2O (ca. 2 mL) and hexane (ca. 10 mL). After standing overnight, the mother liquor could be decanted and the pure product dried under high vacuum.

1-Phenyl-2-(1-phenyl-1*H*-tetrazol-5-ylsulfonyl)ethanone (4a): According to the general procedure, compound **4a** was obtained in 91% yield (70% yield after recrystallisation from toluene and iPr_2O) as a colorless crystalline solid (m.p. 86–89 °C). ^{1}H NMR ($CDCl_3$): δ = 7.88 (d, J = 7.8 Hz, 2 H, ar-H), 7.80–7.56 (m, 6 H, ar-H), 7.51 (t, J = 7.8 Hz, 2 H, ar-H), 5.32 (s, 2 H, 8-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 186.8, 153.6, 135.0, 134.8, 132.9, 131.5, 129.5 (2 C), 129.1 (2 C), 128.6 (2 C), 125.7 (2 C), 62.1 (1 C, C-8) ppm. IR (Nujol): $\tilde{\nu}$ = 3065, 2961, 2915, 1687 (s), 1595, 1580, 1497, 1449, 1356 (s), 1301, 1212, 1158, 1015, 982, 885, 823, 754, 686 cm^{-1}. HRMS: calcd. for $C_{15}H_{12}N_4NaO_3S$ [M + Na] 351.0528; found 351.0536.

Supporting Information (see footnote on the first page of this article) Additional experimental details and full characterization of all new compounds.

Acknowledgments

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[7] See the Supporting Information for crystal structure information. CCDC-790871, -790872, -790873, -790874, -790875, -790876, -790877, -790878, -790879, -790880 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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