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Regioselectivity in the Addition of Grignard Reagents to Bis(2-benzothiazolyl) Ketone: *C*- vs. *O*-Alkylation Using Aryl Grignard Reagents

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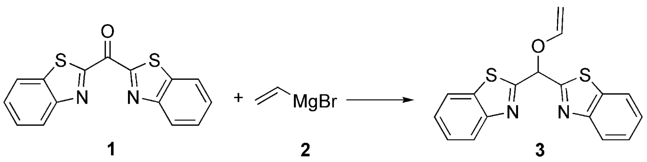
The reaction between bis(2-benzothiazolyl) ketone (**1**) and a series of ring-substituted phenyl Grignard reagents gives, in considerable amount, the unexpected *O*-alkylation product derived from the attack of the Grignard reagent to the carbonyl oxygen atom, thus extending the range of rarely reported cases in which *O*-alkylation can occur. The expected classic 1,2-addition product and that derived from *O*-alkylation have been obtained in a relative molar ratio dependent on the substituent on the phenyl ring. Bis(2-benzothiazolyl) aryl carbinols, the classic 1,2-addition products to the carbonyl group of **1**, were obtained in high yield through an alternative synthetic route that permitted the limit imposed by *O*- vs. *C*-alkylation competition to be overcome.

Introduction

Since their discovery,[1] Grignard reagents represent an efficient and versatile tool able to provide a wide number of intermediates and products useful in both organic and organometallic chemistry.[2] Their addition to carbonyl compounds is one of the most used methods in synthetic organic chemistry. Normally, the reaction proceeds to give alcohols, but in some cases other reactions can take place, depending on the reagents and on the experimental conditions, as extensively studied and reviewed by Holm and Crossland.[3] It is well known,[4] for example, that benzophenone reacts with methylmagnesium bromide to yield the 1,2-addition product, whereas, depending on the Grignard reagent used, other reactions can occur, such as, bimolecular reduction to the pinacol or conjugate addition on the phenyl ring. In particular, *O*-alkylation of Grignard reagents to the carbonyl oxygen atom[3] is a rarely observed reaction: it was found to occur, as a minor reaction, between some Grignard reagents and substrates such as *ortho*-quinones,[5] *ortho*-quinolacetates,[6–8] 9,10-phenanthraquinone,[9] and benzil.[10] In this context, we previously[11] reported that the reaction of vinyl Grignard reagents with bis(2-benzothiazolyl) ketone (**1**) can give the product derived from the addition of the Grignard reagent to the carbonyl oxygen atom. In the case of the reaction between **1** and vinylmagnesium bromide (**2**) the formation of *O*-alkylation product **3** was quantitative after about 15 min at –70 °C (Scheme 1). On the basis of a previous study[12] in which we reported that the reaction of **1** with alkyl-, allyl-, and alkynyl Grignard reagents quantitatively gave the expected carbinols arising from classic 1,2 attack to the carbonyl group, the results obtained in the reaction between **1** and **2** appeared to be as unique as totally unexpected.



Scheme 1. Reaction between bis(2-benzothiazolyl) ketone and vinylmagnesium bromide.

Nevertheless, further investigation evidenced that this particular reactivity is encountered, to a different degree of regioselectivity, also in reactions of **2** with other ketones such as bis(2-thiazolyl)-, bis(2-benzoxazolyl)-, and 2-benzothiazolyl aryl ketones,[13] thus revealing that the *O*-alkylation reaction can occur with a wide number of aromatic ketones bearing at least one group belonging to the pentatomic 1,3-heteroazolic series.

Because it is known that vinyl and aryl Grignard reagents, as well as more general vinyl and aryl compounds, often present close similarities[14] both in the mechanism of formation from the respective halide precursors[14c] and in their properties, as in the C–Mg bond dissociation energy,[3] we thought that phenylmagnesium reagents might also show behavior similar to that found with vinyl Grignard reagents. This might also explain the reported[12] recovery of a mixture of unidentified products and tars from the reaction between **1** and phenyl Grignard reagents and the isolation of the expected carbinol in only 5% yield in the reaction between **1** and *para*-tolylmagnesium bromide.[15] With these considerations in mind, we decided to reinvestigate and to deepen the reaction between compound **1** and a

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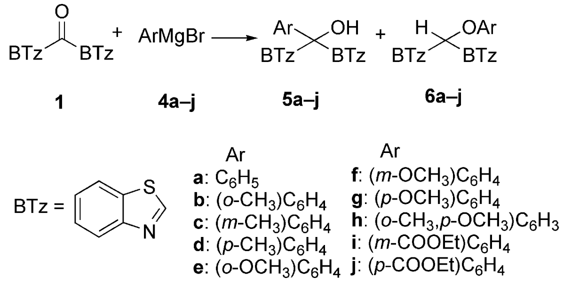
series of ring-substituted phenyl Grignard reagents. Herein we report the results obtained, together with an efficient methodology that permits the limit imposed by *O*- vs. *C*-alkylation competition to be overcome, and to obtain aryl 2-benzothiazolyl carbinols through a simple and clean procedure.

Results and Discussion

The reaction between bis(2-benzothiazolyl) ketone (**1**) and phenylmagnesium bromide (**4a**; Scheme 2) was first carried out under the same experimental conditions as those used in the reaction between **1** and vinylmagnesium bromide (**2**)[11] to make the comparison between the two reactions easier. After 15 min at –70 °C, the ^{1}H NMR spectrum of a sample of the reaction mixture revealed the presence of the starting ketone and a mixture of other products. Quick workup of the reaction mixture (see Experimental Section) followed by flash chromatography of the residue permitted unreacted ketone **1** to be recovered in 60% and the isolation and identification of *C*- and *O*-alkylation products **5a** and **6a**. An *a posteriori* analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed the presence of **5a** and **6a** in a 6:94 relative molar ratio. The reaction was repeated and after 1 h at –70 °C the conversion reached 78%, whereas the relative molar ratio **5a**/**6a** was unchanged. When the reaction was carried out at room temperature with 2.0 equiv. of the Grignard reagent, the ^{1}H NMR spectrum of the crude reaction mixture showed that the conversion reached 91% after 1 h, whereas the relative *C*-/*O*-alkylation ratio was the same. It should be noted that the evaluation of the relative *C*-/*O*-alkylation ratio from the ^{1}H NMR spectrum of these reaction mixtures was more difficult with respect to the case of vinyl Grignard reagents because many of the signals of products **5a** and **6a** were overlapping: for this reason the relative isomeric ratio was calculated from the spectrum of the crude reaction mixture only after separation and identification of the two reaction products by flash chromatography, a procedure that permitted the signals of the respective compounds to be ascertained.



Scheme 2. Reactions between **1** and arylmagnesium reagents **4a**–**j**.

These experiments evidenced that the reaction of **1** with phenylmagnesium bromide is slower with respect to those with alkyl and vinyl Grignard reagents[11–13] (these latter reach high conversion levels after about 15–20 min at –70 °C); in addition, the relative *C*/*O*-alkylation ratio seemed not to be affected by either the reaction temperature or the reaction time.

These preliminary results supported our hypothesis that attack to the carbonyl oxygen atom of **1** could occur not only with vinyl Grignard reagents but also with aryl Grignard reagents. This prompted us to extend this study to a series of substituted phenylmagnesium reagents to see whether the substituents on the phenyl ring could play a role in driving the regioselectivity of the addition.

To improve the conversion without altering the relative ratio of the products, we decided to carry out all reactions with aryl Grignard reagents at room temperature and to quench them after 1 h. Longer reaction times might falsify both the yield and the *C*-/*O*-alkylation relative ratio, because the *O*-alkylation products can slowly decompose, as already reported.[11] With the aim to make the distinction and the relative integration of the ^{1}H NMR signals of the *C*- and the *O*-alkylation products in the crude reaction mixture easier, through comparison of the signals in the methyl region, we chose Grignard reagents **4b**–**j** containing a methyl group on the substituent (Scheme 2).

All reactions between **1** and Grignard reagents **4a**–**j** were carried out in anhydrous THF and at least in duplicate to confirm the reproducibility of the results. The relative isomeric ratio was unaffected by both the reaction temperature and the use of an excess amount (2.5 equiv. were used) of Grignard reagent. However, these reactions must be carried out under a dry argon atmosphere with particular care to avoid the presence of oxygen to minimize the formation of oxidation products as phenol derivatives.[16]

From the data of Table 1 it can be noted, except for *ortho*-substituted Grignard reagents (i.e., **4b**, **4e**, and **4h**), that the *O*-alkylation reaction strongly prevails over the normal *C*-alkylation. These are, to the best of our knowledge, the first reported cases in which aryl Grignard reagents attack the carbonyl oxygen atom to such a high extent. The reverse direction of phenyl Grignard addition to the carbonyl group has been reported only in a few cases and always as minor a reaction[5,10] with yields not exceeding 25% (except

Table 1. *C*- vs. *O*-alkylation in reactions between bis(2-benzothiazolyl) ketone (**1**) and arylmagnesium bromides **4a**–**j**.[a]

Entry	ArMgBr (X)	*C*-product, % Yield[b]	*O*-product, % Yield[b]
1	**4a** (H)	**5a**, 6	**6a**, 94
2	**4b** (o-CH_3)	**5b**, 68[c]	**6b**, 32[c]
3	**4c** (m-CH_3)	**5c**, 20[c]	**6c**, 80[c]
4	**4d** (p-CH_3)	**5d**, 20[c]	**6d**, 80[c]
5	**4e** (o-OCH_3)	**5e**, >97[c]	**6e**, n.d.[c]
6	**4f** (m-OCH_3)	**5f**, 27	**6f**, 73
7	**4g** (p-OCH_3)	**5g**, 20	**6g**, 80
8	**4h** (o-CH_3,p-OCH_3)	**5h**, 64	**6h**, 36
9[d]	**4i** (m-COOEt)	**5i**, 10	**6i**, 90
10[d]	**4j** (p-COOEt)	**5j**, 10	**6j**, 90

[a] Reactions were carried out in THF at room temperature for 60 min. [b] Relative ratio calculated by ^{1}H NMR spectroscopic analysis of the crude reaction mixture. [c] Mean of six determinations. [d] Reaction temperature was 0 °C.

only one case between benzil and mesitylmagnesium bromide,[10] which gave the *O*-arylated product in 60% yield). As shown in Table 1, the reaction with phenylmagnesium bromide (**4a**; Table 1, Entry 1) gave the highest regioselectivity toward the oxygen atom of substrate **1** (the relative ratio carbinol **5a**/phenyl ether **6a** being 6:94), whereas *ortho*-methyl-substituted phenyl Grignard reagent **4b** (Table 1, Entry 2), as well as *ortho*-methoxyphenyl Grignard reagent **4e** (Table 1, Entry 5) gave prevalently (for **4b**) and exclusively (for **4e**) the carbinol derived from classical 1,2-addition. This suggests that steric effects could influence the stereochemical outcome of the addition reaction, probably intervening in the relative spatial approach of the two partners; actually, on going from *ortho*- to *meta*- (Table 1, Entries 3 and 6) and *para*-substituted (Table 1, Entries 4 and 7) tolyl and anisyl Grignard reagents, the relative regioselectivity ratio shifted in favor of the *O*-alkylation products.

It is interesting to note that, as previously found for vinyl ethers,[11,13] compounds **6** are poorly stable and must be stored at –18 °C. In light of the present findings, both the tars recovered in the reaction between **1** and phenylmagnesium halide[12] and the fact that the reaction between *p*-tolylmagnesium bromide (**4d**) and ketone **1** gave carbinol **5d** in only 5% yield[15] after 36 h at 50 °C could now be explained by the formation of the poorly stable *O*-alkylation products in high yields.

The trend observed with compounds **4b**–**g** is followed also by the disubstituted Grignard reagent (4-methoxy-2-methylphenyl)magnesium bromide (**4h**; Table 1, Entry 8) and by Grignard reagents bearing ethoxycarbonyl groups (**4i** and **4j**; Table 1, Entries 9 and 10). However, from the data collected in Table 1, one can evince that probably the steric hindrance on the aryl moiety of the Grignard reagent is not the only factor that drives the regioselectivity of the addition. Actually, a comparison between data obtained with *meta*-substituted reagents **4c**, **4f**, and **4i** (Table 1, Entries 3, 6, and 9) and the corresponding *para*-substituted reagents **4d**, **4g**, and **4j** (Table 1, Entries 4, 7, and 10), shows how on going from *meta*- to *para*-substituted Grignard reagents the relative *C*-/*O*-alkylation ratio does not change significantly. Even if the dissection of the inductive effect from the mesomeric one is a very hard matter, this might be an indication that the intervention of the inductive effect cannot be completely ruled out. If the regioselectivity is only affected by steric hindrance, one might expect that *meta*-substituted reagents give the *O*-alkylation product to a lower extent than the corresponding *para*-substituted one. However, the elucidation of the mechanistic aspects (SET or polar mechanism, or even mixed) of this unusual reactivity is a complex challenge and deserves deepen investigation: first attempts are now in progress.

The difficulty to obtain the products of the classic 1,2-addition of aryl Grignard reagents to the carbonyl group of substrate **1** in good yields, together with the consideration that compounds containing the 2-benzothiazolylmethanol moiety in their framework are interesting intermediates from both mechanistic and synthetic viewpoints[17] and that they are structural motifs present in medicinal and agricultural chemistry,[18] prompted us to turn our attention to a synthetic point of view for which the recovery of both *C*- and *O*-alkylation products (even if in different relative amounts) could represent a limit when the synthesis is directed towards the obtainment of the carbinol.

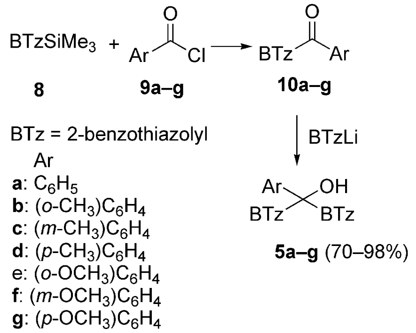
As a first approach, we decided to verify if the classical 1,2-attack could occur exclusively with the use of aryllithium reagents. Aryllithium reagents **7a**–**c** were added in THF at –70 °C to compound **1**.

The results, summarized in Table 2, show that also in this case the reaction did not take place with complete regioselectivity: it follows a trend common to all lithium reagents we used, giving the carbinol as the main product, but always together with a minor amount of *O*-alkylation product. The recovery of a mixture of *C*- and *O*-alkylation products with both aryl Grignard and aryllithium reagents reveals that a clean and quantitative synthesis of bis(2-benzothiazolyl) aryl carbinols cannot be achieved through addition reaction of these organometallic reagents to ketone precursor **1**. After these findings, to overcome the limit imposed by the *O*- vs. *C*-alkylation competition, we planned an alternative synthetic approach focused on the exclusive formation of carbinols **5a**–**g**, as shown in Scheme 3. In the first step, 2-benzothiazolyl aryl ketones **10a**–**g** were prepared from 2-(trimethylsilyl)benzothiazole (**8**) and acyl chlorides **9a**–**g** according to previously reported procedures.[13,19] The addition of 2-lithiobenzothiazole to compounds **10a**–**g** in THF at –70 °C gave after 30 min almost exclusive formation of carbinols **5a**–**g**.

Table 2. *C*- vs. *O*-alkylation from reactions between **1** and aryllithium reagents.[a]

Entry	ArLi (X)	*C*-product, % Yield[b]	*O*-product, % Yield[b]
1	**7a** (H)	**5a**, 80	**6a**, 20
2	**7b** (*o*-CH_3)	**5b**, 78	**6b**, 22
3	**7c** (*p*-OCH_3)	**5g**, 90	**6g**, 10

[a] Reactions carried out in THF at –70 °C for 30 min. [b] Relative ratio calculated by ^{1}H NMR spectroscopic analysis of the crude reaction mixture.



Scheme 3. Synthesis of carbinols **5a**–**g**.

Conclusions

In conclusion, the reaction between variously substituted phenyl Grignard reagents and bis(2-benzothiazolyl) ketone gives *O*-alkylation products derived from attack to the carbonyl oxygen atom in a relative ratio with the classic *C*-alkylation product dependent on the substituent on the phenyl ring. This behavior has been observed, with different *C*-/*O*-alkylation relative ratios, also by using phenyllithium reagents. These findings show that *O*-alkylation of **1** is a characteristic feature not only of vinylmagnesium reagents but also of phenylmagnesium derivatives. Bis(2-benzothiazolyl)phenylmethanol derivatives were obtained in high yield through an alternative synthetic route that permitted the limit imposed by the *O*- vs. *C*-alkylation competition to be overcome.

Experimental Section

General: ^{1}H and ^{13}C NMR spectra were recorded at 300, 400, or 600 MHz and 75.46, 100.56, or 150.8 MHz with a Varian Gemini 300, Varian Mercury 400, or Varian Inova 600 spectrometer, respectively. Chemical shifts are referenced to internal standard TMS (for ^{1}H NMR in $CDCl_3$) and to solvent (δ =77.0 ppm for ^{13}C NMR in $CDCl_3$). GC–MS analyses were performed with a gas chromatograph Agilent 6890 equipped with a (5%-phenyl)methylpolysiloxane column (30 m length, 0.250 mm i.d., 0.25 μm thickness) interfaced to a quadrupole mass detector Agilent 5973 N. Mass spectra and HRMS spectra were recorded at an ionization voltage of 70 eV in the EI mode. Flash chromatography (FC) was performed on silica gel (0.040–0.063 mm). Melting points were recorded with a Büchi apparatus. Compounds **5a**–**j** showed characteristic IR signals at 3650–3300 cm^{-1} (OH) and **6a**–**j** (oils) at 1050–1300 cm^{-1}; in addition, compounds **5i** and **5j** and **6i** and **6j** showed typical ester IR bands around 1735 cm^{-1}. THF was distilled from sodium/benzophenone ketyl. Air- and moisture-sensitive solutions and reagents were handled in dried apparatus under an atmosphere of dry argon using standard Schlenk-type techniques. Acyl chlorides **9a**–**g**, 1,3-benzothiazole, phenyllithium (**7a**), 2-(trimethylsilyl)-1,3-benzothiazole (**8**), and Grignard reagents (except compounds **4i** and **4j**) are commercially available compounds; bis(1,3-benzothiazol-2-yl)methanone (**1**),[12] 1,3-benzothiazol-2-yllithium,[20] and lithium reagents[21] **7b** and **7c** were prepared according to literature procedures and their chemicophysical data were in agreement with those reported. Reactions between arylmagnesium halides and **1** (cases **a**–**h**) gave conversions up to 70%; from the reaction mixtures other compounds were recovered as diaryl coupling products and oxidation products (phenol derivatives). For the preparation of reagents **4i** and **4j** we used the Knochel procedure[22,23] as follows: To a solution of commercially available ethyl 3-iodobenzoate (or ethyl 4-iodobenzoate, 1 mmol) in dry THF (5 mL) kept at 0 °C under an argon atmosphere was added isopropylmagnesium bromide (1.3 equiv.). After 20 min, compound **1** (0.5 mmol) in THF (3 mL) was added. After about 1 h at 0 °C the reaction mixture was quenched with a saturated aqueous solution of $(NH_4)_2SO_4$ and extracted with diethyl ether. The organic layer was washed with brine, dried with anhydrous $MgSO_4$, and concentrated "in vacuo" without warming. The residue was analyzed by ^{1}H NMR spectroscopy, and the products were isolated by FC (petroleum light/diethyl ether, 9:1 to 1:1). This in situ procedure gave *C*- and *O*-alkylation products in low yields (about 30%) besides several side products: 1,1-bis(1,3-benzothiazol-2-yl)-2-methylpropan-1-ol,[20] diethyl biphenyl-4,4′-dicarboxylate [^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.14 (d, *J* = 8.4 Hz, 4 H), 7.69 (d, *J* = 8.4 Hz,4 H), 4.41 (q, *J* = 7.1 Hz, 4 H), 1.42 (t, *J* = 7.1 Hz, 6 H) ppm], ethyl 4-(4-iodobenzoyl)benzoate [^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.16 (d, *J* = 8.7 Hz, 2 H), 7.87 (d, *J* = 8.6 Hz,2 H), 7.81 (d, *J* = 8.7 Hz, 2 H), 7.52 (t, *J* = 8.6 Hz, 2 H), 4.43 (q, *J* = 7.1 Hz, 2 H, CH_2), 1.43 (t, *J* = 7.1 Hz, 3 H, CH_3) ppm. MS: *m*/*z* = 380 [M]$^+$, 335, 231, 203, 177, 149].

Typical Procedure for the Reaction between 1 and Arylmagnesium Bromides: Phenylmagnesium bromide (**4a**; 0.50 mmol) in THF (4.0 mL) was added dropwise at room temperature to a stirred solution of **1** (0.100 g, 0.34 mmol) in THF (5.0 mL). After about 1 h, the reaction mixture was quenched with a saturated aqueous solution of NH_4Cl and extracted with diethyl ether. The organic layer was washed with brine, dried with anhydrous $MgSO_4$, and concentrated in vacuo without warming. The time employed for this workup was about 15 min. The residue was analyzed by ^{1}H NMR spectroscopy, and then products **5a** (0.0064 g, 5%) and **6a** (0.085 g, 67%) were isolated by FC (petroleum light/diethyl ether, 9:1 to 1:1) and fully characterized (all aryl ethers were colorless oils and were stored at –18 °C).

Bis(1,3-benzothiazol-2-yl)(phenyl)methanol (5a): White solid, 0.98 g (75% from **10a**); m.p. 148–150 °C (methanol; ref.[17e] 147–149 °C). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.04 (d, *J* = 7.4 Hz, 2 H), 7.87 (d, *J* = 8.4 Hz, 2 H), 7.80–7.10 (m, 9 H), 6.15 (s, 1 H, OH, exch. with D_2O) ppm. ^{13}C NMR (75.46 MHz, $CDCl_3$, 25 °C): δ = 174.7, 152.3, 142.4, 136.1, 128.6, 128.4, 126.6, 126.1, 125.3, 123.4, 121.7, 80.1 ppm. MS (70 eV, EI): *m*/*z* (%) = 374 (48) [M]$^+$, 269 (26), 240 (36), 161 (47), 134 (49), 105 (100), 77 (96). $C_{21}H_{14}N_2OS_2$ (374.48): calcd. C 67.35, H 3.77, N 7.48; found C 67.31, H 3.78, N 7.45.

Bis(1,3-benzothiazol-2-yl)(2-methylphenyl)methanol (5b): White solid, 1.1 g (80% from **10b**); m.p. 159–160 °C (diethyl ether/light petroleum). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.07–8.01 (m, 2 H), 7.90–7.86 (m, 2 H), 7.51–7.46 (m, 2 H), 7.43–7.37 (m, 2 H), 7.30–7.26 (m, 1 H), 7.23–7.18 (m, 1 H), 7.12–7.06 (m, 1 H), 7.03–6.98 (m, 1 H), 5.91 (s, 1 H, OH, exch. with D_2O), 2.21 (s, 3 H, CH_3) ppm. ^{13}C NMR (100.56 MHz, $CDCl_3$, 25 °C): δ = 175.3, 152.4, 140.2, 138.5, 136.3, 132.6, 129.2, 128.2, 126.2, 125.6, 125.5, 123.6, 121.8, 81.7, 21.2 ppm. MS (70 eV, EI): *m*/*z* (%) = 388 (97) [M]$^+$, 371 (4), 297 (29), 269 (35), 254 (62), 237 (53), 226 (47), 162 (44), 134 (27), 119 (100), 91 (99). $C_{22}H_{16}N_2OS_2$ (388.51): calcd. C 68.01, H 4.15, N 7.21; found C 67.98, H 4.16, N 7.19.

Bis(1,3-benzothiazol-2-yl)(3-methylphenyl)methanol (5c): White solid, 0.95 g (70% from **10c**); m.p. 144–145 °C (diethyl ether/light petroleum). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.08–8.00 (m, 2 H), 7.88–7.81 (m, 2 H), 7.57–7.49 (m, 2 H), 7.49–7.40 (m, 2 H), 7.40–7.31 (m, 2 H), 7.27–7.19 (m, 1 H), 7.15–6.99 (m, 1 H), 6.23 (s, 1 H, OH, exch. with D_2O), 2.31 (s, 3 H, CH_3) ppm. ^{13}C NMR (75.46 MHz, $CDCl_3$, 25 °C): δ = 174.7, 152.3, 142.3, 138.2, 136.1, 129.5, 128.3, 127.1, 126.1, 125.3, 123.8, 123.4, 121.7, 80.1, 21.6 ppm. MS (70 eV, EI): *m*/*z* (%) = 388 (93) [M]$^+$, 371 (6), 297 (25), 269 (38), 254 (59), 237 (58), 226 (41), 162 (50), 134 (22), 119 (100), 91 (92). $C_{22}H_{16}N_2OS_2$ (388.51): calcd. C 68.01, H 4.15, N 7.21; found C 67.96, H 4.16, N 7.20.

Bis(1,3-benzothiazol-2-yl)(4-methylphenyl)methanol (5d): White solid, 1.03 g (75% from **10d**); m.p. 153–154 °C (ref.[15] 154 °C). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.07–8.02 (m, 2 H), 7.89–7.84 (m, 2 H), 7.64–7.58 (m, 2 H), 7.51–7.44 (m, 2 H), 7.42–7.35 (m, 2 H), 7.19–7.13 (m, 2 H), 6.03 (s, 1 H, OH, exch. with D_2O), 2.32 (s, 3 H, CH_3) ppm. ^{13}C NMR (100.56 MHz, $CDCl_3$, 25 °C): δ = 174.9, 152.3, 139.5, 138.7, 136.1, 129.2, 126.6, 126.1, 125.4, 123.4, 121.8, 80.0, 23.8 ppm. MS (70 eV, EI): *m*/*z* (%) = 388 (92) [M]$^+$, 371 (10), 297 (24), 269 (39), 254 (66), 237 (50), 226 (52), 162 (42), 134 (23), 119 (100), 91 (95). $C_{22}H_{16}N_2OS_2$ (388.51): calcd. C 68.01, H 4.15, N 7.21; found C 67.97, H 4.16, N 7.19.

Bis(1,3-benzothiazol-2-yl)(2-methoxyphenyl)methanol (5e): White solid, 1.27 g (90% from **10e**); m.p. 199–200 °C. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): δ = 8.08–8.01 (m, 2 H), 7.92–7.85 (m, 2 H), 7.50–7.43 (m, 2 H), 7.42–7.34 (m, 3 H), 7.28–7.21 (m, 1 H), 7.01–6.90 (m, 2 H), 6.22 (s, 1 H, OH, exch. with D$_2$O), 3.66 (s, 3 H, OCH$_3$) ppm. ^{13}C NMR (100.56 MHz, CDCl$_3$, 25 °C): δ = 174.3, 157.0, 152.9, 135.9, 130.49, 130.46, 128.7, 125.8, 125.1, 123.7, 121.6, 121.2, 112.1, 80.7, 55.8 ppm. MS (70 eV, EI): *m*/*z* (%) = 404 (1) [M]$^+$, 238 (35), 149 (12), 135 (100), 92 (14). MS (ESI+): *m*/*z* = 427 [M + Na]$^+$. $C_{22}H_{16}N_2O_2S_2$ (404.50): calcd. C 65.32, H 3.99, N 6.93; found C 65.29, H 4.00, N 6.91.

Bis(1,3-benzothiazol-2-yl)(3-methoxyphenyl)methanol (5f): White solid, 1.21 g (85% from **10f**); m.p. 126–127 °C. ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ = 8.09–7.99 (m, 2 H), 7.91–7.81 (m, 2 H), 7.62–7.42 (m, 2 H), 7.42–7.32 (m, 4 H), 7.32 (m, 1 H), 6.90–6.81 (m, 1 H), 6.19 (s, 1 H, OH, exch. with D$_2$O), 3.76 (s, 3 H, OCH$_3$) ppm. ^{13}C NMR (75.46 MHz, CDCl$_3$, 25 °C): δ = 174.5, 159.6, 152.2, 143.8, 136.1, 129.5, 126.1, 125.4, 123.4, 121.7, 119.0, 114.0, 112.5, 79.9, 55.2 ppm. MS (70 eV, EI): *m*/*z* (%) = 404 (1) [M]$^+$, 269 (46), 241 (28), 135 (100), 107 (29), 91 (21). $C_{22}H_{16}N_2O_2S_2$ (404.50): calcd. C 65.32, H 3.99, N 6.93; found C 65.30, H 4.00, N 6.90.

Bis(1,3-benzothiazol-2-yl)(4-methoxyphenyl)methanol (5g): White solid, 1.39 g (98% from **10g**); m.p. 182–183 °C. ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ = 8.08–8.02 (m, 2 H), 7.91–7.85 (m, 2 H), 7.65 (d, J = 9.0 Hz, 2 H), 7.52–7.44 (m, 2 H), 7.43–7.35 (m, 2 H), 6.92–6.84 (m, 2 H), 6.03 (s, 1 H, OH, exch. with D$_2$O), 3.78 (s, 3 H, OCH$_3$) ppm. ^{13}C NMR (75.46 MHz, CDCl$_3$, 25 °C): δ = 174.9, 159.8, 152.3, 136.2, 134.6, 128.1, 126.1, 125.4, 123.4, 121.8, 113.8, 79.8, 55.3 ppm. MS (70 eV, EI): *m*/*z* (%) = 404 (1) [M]$^+$, 269 (30), 241 (19), 135 (100), 91 (12). $C_{22}H_{16}N_2O_2S_2$ (404.50): calcd. C 65.32, H 3.99, N 6.93; found C 65.28, H 4.00, N 6.91.

Bis(1,3-benzothiazol-2-yl)(4-methoxy-2-methylphenyl)methanol (5h): Pale-yellow solid, m.p. 136–138 °C. ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ = 8.06–8.00 (m, 2 H), 7.90–7.83 (m, 2 H), 7.55–7.43 (m, 2 H), 7.43–7.33 (m, 2 H), 6.93 (d, J = 9.1 Hz, 1 H), 6.76 (d, J = 2.8 Hz, 1 H), 6.59 (dd, J = 9.1, 2.8 Hz, 1 H), 5.89 (s, 1 H, OH, exch. with D$_2$O), 3.77 (s, 3 H, OCH$_3$), 2.18 (s, 3 H, CH$_3$) ppm. ^{13}C NMR (75.46 MHz, CDCl$_3$, 25 °C): δ = 175.8, 159.9, 152.3, 140.2, 133.3, 132.7, 129.7, 126.2, 125.5, 123.5, 121.8, 118.4, 109.9, 81.3, 51.1, 21.4 ppm. MS (70 eV, EI): *m*/*z* (%) = 418 (1) [M]$^+$, 283 (35), 266 (43), 254 (63), 149 (100), 121 (22), 91 (36). MS (ESI+): *m*/*z* = 441 [M + Na]$^+$. $C_{23}H_{18}N_2O_2S_2$ (418.53): calcd. C 66.00, H 4.33, N 6.69; found C 65.95, H 4.35, N 6.67.

Ethyl 3-[Bis(1,3-benzothiazol-2-yl)(hydroxy)methyl]benzoate (5i): Greasy yellow solid. ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ = 8.54 (dd, J = 1.6, 1.6 Hz, 1 H), 8.10–8.03 (m, 3 H), 8.03–7.98 (m, 1 H), 7.90–7.86 (m, 2 H), 7.53–7.37 (m, 5 H), 6.18 (s, 1 H, OH, exch. with D$_2$O), 4.35 (q, J = 7.2 Hz, 2 H, CH$_2$), 1.36 (t, J = 7.2 Hz, 3 H, CH$_3$) ppm. ^{13}C NMR (100.57 MHz, CDCl$_3$, 25 °C): δ = 174.2, 166.4, 152.2, 142.6, 136.0, 131.2, 129.8, 129.0, 128.6, 127.7, 126.2, 125.6, 123.4, 121.8, 79.6, 61.1, 14.3 ppm. MS (70 eV, EI): *m*/*z* (%) = 446 (100) [M]$^+$, 429 (9), 401 (13), 312 (58), 297 (25), 269 (40), 134 (13). $C_{24}H_{18}N_2O_3S_2$ (446.54): calcd. C 64.47, H 4.07, N 6.27; found C 64.59, H 4.05, N 6.25.

Ethyl 4-[Bis(1,3-benzothiazol-2-yl)(hydroxy)methyl]benzoate (5j): White solid, m.p. 133–135 °C. ^{1}H NMR (600 MHz, CDCl$_3$, 25 °C): δ = 8.06 (d, J = 8.2 Hz, 2 H), 8.04 (d, J = 8.7 Hz, 2 H), 7.92 (d, J = 8.7 Hz, 2 H), 7.88 (d, J = 7.9 Hz, 2 H), 7.51–7.47 (m, 2 H), 7.42–7.38 (m, 2 H), 6.16 (s, 1 H, OH, exch. with D$_2$O), 4.35 (q, J = 7.2 Hz, 2 H, CH$_2$), 1.36 (t, J = 7.2 Hz, 3 H, CH$_3$) ppm. ^{13}C NMR (75.46 MHz, CDCl$_3$, 25 °C): δ = 173.8, 166.1, 160.5, 152.2, 146.5, 136.1, 129.7, 126.6, 126.3, 125.6, 123.5, 121.8, 79.8, 61.0, 14.3 ppm. MS (70 eV, EI): *m*/*z* (%) = 446 (100) [M]$^+$, 429 (5), 401 (11), 312 (55), 297 (30), 269 (46), 135 (17). $C_{24}H_{18}N_2O_3S_2$ (446.54): calcd. C 64.50, H 4.06, N 6.26; found C 64.53, H 4.07, N 6.28.

2,2′-(Phenoxymethylene)bis(1,3-benzothiazole) (6a): ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ = 8.00 (d, J = 8.0 Hz, 2 H), 7.79 (d, J = 7.7 Hz, 2 H), 7.42–7.37 (m, 2 H), 7.33–7.29 (m, 2 H), 7.24–7.19 (m, 2 H), 7.15–7.08 (m, 2 H), 7.02 (s, 1 H, CHO), 6.97–6.92 (m, 2 H) ppm. ^{13}C NMR (75.46 MHz, CDCl$_3$, 25 °C): δ = 168.2, 156.8, 153.0, 135.3, 129.8, 126.2, 125.6, 124.0, 122.8, 121.8, 116.1, 78.5 ppm. MS (70 eV, EI): *m*/*z* (%) = 374 (2) [M]$^+$, 281 (100), 248 (9), 146 (11), 134 (6). HRMS: calcd. for $C_{21}H_{14}N_2OS_2$ 374.0548; found 374.0545.

2,2′-[(2-Methylphenoxy)methylene]bis(1,3-benzothiazole) (6b): ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): δ = 8.09 (d, J = 8.4 Hz, 2 H), 7.87 (d, J = 8.0 Hz, 2 H), 7.53–7.43 (m, 2 H), 7.42–7.32 (m, 2 H), 7.26–7.17 (m, 1 H), 7.11 (s, 1 H, CHO), 7.12–7.00 (m, 2 H), 6.96–6.87 (m, 1 H), 2.49 (s, 3 H, CH$_3$) ppm. ^{13}C NMR (100.57 MHz, CDCl$_3$, 25 °C): δ = 168.6, 154.8, 153.0, 135.2, 131.2, 127.5, 127.0, 126.2, 125.6, 123.9, 122.4, 121.8, 112.8, 78.1, 23.8 ppm. MS (70 eV, EI): *m*/*z* (%) = 388 (3) [M]$^+$, 281 (54), 268 (100), 162 (55), 134 (76). HRMS: calcd. for $C_{22}H_{16}N_2OS_2$ 388.0704; found 388.0709.

2,2′-[(3-Methylphenoxy)methylene]bis(1,3-benzothiazole) (6c): ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ = 8.11–8.05 (m, 2 H), 7.90–7.84 (m, 2 H), 7.51–7.41 (m, 2 H), 7.41–7.33 (m, 2 H), 7.20–7.12 (m, 1 H), 7.08 (s, 1 H, CHO), 7.04–6.93 (m, 2 H), 6.88–6.78 (m, 1 H), 2.31 (s, 3 H, CH$_3$) ppm. ^{13}C NMR (100.57 MHz, CDCl$_3$, 25 °C): δ = 168.4, 156.7, 152.9, 140.0, 135.3, 129.4, 126.2, 125.6, 123.8, 123.7, 121.8, 117.0, 112.7, 78.3, 21.4 ppm. MS (70 eV, EI): *m*/*z* (%) = 388 (5) [M]$^+$, 281 (51), 268 (100), 135 (71). HRMS: calcd. for $C_{22}H_{16}N_2OS_2$ 388.0704; found 388.0708.

2,2′-[(4-Methylphenoxy)methylene]bis(1,3-benzothiazole) (6d): ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): δ = 8.12–8.06 (m, 2 H), 7.89–7.83 (m, 2 H), 7.49–7.43 (m, 2 H), 7.40–7.15 (m, 2 H), 7.08–7.07 (m, 4 H), 7.04 (s, 1 H, CHO), 2.25 (s, 3 H, CH$_3$) ppm. ^{13}C NMR (100.56 MHz, CDCl$_3$, 25 °C): δ = 168.4, 154.7, 152.9, 135.3, 132.2, 130.2, 126.2, 125.6, 123.8, 121.8, 115.9, 78.6, 20.5 ppm. MS (70 eV, EI): *m*/*z* (%) = 388 (7) [M]$^+$, 281 (56), 268 (100), 135 (73). HRMS: calcd. for $C_{22}H_{16}N_2OS_2$ 388.0704; found 388.0700.

2,2′-[(3-Methoxyphenoxy)methylene]bis(1,3-benzothiazole) (6f): ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): δ = 8.11–8.04 (m, 2 H), 7.91–7.84 (m, 2 H), 7.51–7.43 (m, 2 H), 7.43–7.34 (m, 2 H), 7.21–7.10 (m, 1 H), 7.08 (s, 1 H, CHO), 6.79–6.71 (m, 2 H), 6.61–6.54 (m, 1 H), 6.50–6.39 (m, 1 H), 3.77 (s, 3 H, OCH$_3$) ppm. ^{13}C NMR (100.57 MHz, CDCl$_3$, 25 °C): δ = 168.1, 160.9, 157.9, 152.9, 135.3, 130.2, 126.3, 125.7, 123.9, 121.8, 108.7, 107.8, 102.6, 78.4, 55.3 ppm. MS (70 eV, EI): *m*/*z* (%) = 404 (41) [M]$^+$, 388 (45), 372 (30), 282 (10), 268 (100), 162 (65), 135 (59). HRMS: calcd. for $C_{22}H_{16}N_2O_2S_2$ 404.0653; found 404.0655.

2,2′-[(4-Methoxyphenoxy)methylene]bis(1,3-benzothiazole) (6g): ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ = 8.12–8.06 (m, 2 H), 7.94–7.83 (m, 2 H), 7.54–7.43 (m, 2 H), 7.43–7.35 (m, 2 H), 7.11 (d, J = 9.2 Hz, 2 H), 6.98 (s, 1 H, CHO), 6.81 (d, J = 9.2 Hz, 2 H), 3.73 (s, 3 H, OCH$_3$) ppm. ^{13}C NMR (100.57 MHz, CDCl$_3$, 25 °C): δ = 168.5, 155.3, 153.0, 150.9, 135.3, 126.2, 125.6, 123.8, 121.8, 117.4, 114.8, 79.4, 55.6 ppm. MS (70 eV, EI): *m*/*z* (%) = 404 (47) [M]$^+$, 388 (39), 372 (22), 282 (18), 268 (100), 162 (78), 135 (64). HRMS: calcd. for $C_{22}H_{16}N_2O_2S_2$ 404.0653; found 404.0650.

2,2′-[(4-Methoxy-2-methylphenoxy)methylene]bis(1,3-benzothiazole) (6h): ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): δ = 8.10–8.05 (m, 2 H), 7.90–7.84 (m, 2 H), 7.51–7.43 (m, 2 H), 7.42–7.34 (m, 2 H), 6.98

(s, 1 H, CHO), 6.97–6.93 (m, 1 H), 6.79–6.75 (m, 1 H), 6.61–6.54 (m, 1 H), 3.71 (s, 3 H, OCH_3), 2.45 (s, 3 H, CH_3) ppm. ^{13}C NMR (100.57 MHz, $CDCl_3$, 25 °C): δ = 168.8, 154.8, 153.0, 149.0, 135.3, 129.0, 126.2, 123.9, 117.3, 114.2, 110.9, 78.9, 55.5, 16.9 ppm. MS (70 eV, EI): *m*/*z* (%) = 418 (100) $[M]^+$, 403 (38), 386 (15), 282 (38), 268 (16), 135 (10). HRMS: calcd. for $C_{23}H_{18}N_2O_2S_2$ 418.0810; found 418.0806.

Ethyl 3-[Bis(1,3-benzothiazol-2-yl)methoxy]benzoate (6i): ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.03–8.06 (m, 2 H), 7.89 (s, 1 H), 7.92–7.84 (m, 2 H), 7.75–7.68 (m, 1 H), 7.53–7.32 (m, 6 H), 7.15 (s, 1 H, CHO), 4.36 (q, *J* = 7.15 Hz, 2 H, CH_2), 1.38 (t, *J* = 7.15 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100.57 MHz, $CDCl_3$, 25 °C): δ = 167.6, 165.9, 156.6, 152.9, 135.3, 132.3, 129.8, 126.3, 125.7, 124.0, 123.9, 121.8, 120.2, 117.4, 78.6, 14.2 ppm. MS (70 eV, EI): *m*/*z* (%) = 446 (32) $[M]^+$, 401 (4), 281 (33), 165 (10), 135 (10). HRMS: calcd. for $C_{24}H_{18}N_2O_3S_2$ 446.0759; found 446.0762.

Ethyl 4-[Bis(1,3-benzothiazol-2-yl)methoxy]benzoate (6j): ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.13–8.07 (m, 2 H), 8.01 (d, *J* = 9.1 Hz, 2 H), 7.91–7.86 (m, 2 H), 7.54–7.45 (m, 2 H), 7.45–7.37 (m, 2 H), 7.22 (d, *J* = 9.1 Hz, 2 H), 7.17 (s, 1 H, CHO), 4.32 (q, *J* = 7.17 Hz, 2 H, CH_2), 1.35 (t, *J* = 7.17 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100.57 MHz, $CDCl_3$, 25 °C): δ = 167.2, 165.9, 160.1, 152.9, 135.3, 131.7, 126.4, 125.8, 125.0, 123.9, 121.8, 115.6, 78.3, 60.8, 14.3 ppm. MS (70 eV, EI): *m*/*z* (%) = 446 (20) $[M]^+$, 401 (2), 281 (29), 165 (7), 135 (13). MS (ESI+): *m*/*z* = 469 $[M + Na]^+$. MS (ESI–): *m*/*z* = 445. HRMS: calcd. for $C_{24}H_{18}N_2O_3S_2$ 446.0759; found 446.0755.

Synthesis of Compounds 10a–g: Compounds **10a**–**g** were prepared by reaction of 2-(trimethylsilyl)-1,3-benzothiazole (**8**; 2.1 g, 10 mmol) with the corresponding commercially available substituted benzoyl chlorides **9a**–**g**, according to the procedure reported by Jutzi.[19]

1,3-Benzothiazol-2-yl(phenyl)methanone (10a): Yellow solid, 1.86 g (78%); m.p. 98–99 °C (ethanol; ref.[20] 102 °C). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.59 (d, *J* = 8.5 Hz, 2 H), 8.30–8.25 (m, 1 H), 8.08–8.05 (m, 1 H), 7.74–7.55 (m, 5 H) ppm. ^{13}C NMR (75.46 MHz, $CDCl_3$, 25 °C): δ = 185.4, 167.1, 153.9, 137.0, 135.0, 133.9, 131.3, 128.5, 127.6, 126.9, 125.7, 122.2 ppm. MS (70 eV, EI): *m*/*z* (%) = 239 (26) $[M]^+$, 211 (34), 134 (2), 105 (100), 77 (68). HRMS: calcd. for $C_{14}H_9NOS$ 239.0405; found 239.0402. $C_{14}H_9NOS$ (239.29): calcd. C 70.27, H 3.79, N 5.85; found C 70.24, H 3.80, N 5.84. IR ($CHCl_3$): $\tilde{\nu}$ = 1640 cm^{-1}.

1,3-Benzothiazol-2-yl(2-methylphenyl)methanone (10b): White solid, 1.95 g (77%); m.p. 111.4–112.5 °C (CH_3OH). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.22–8.13 (m, 1 H), 8.04–7.94 (m, 2 H), 7.59–7.42 (m, 3 H), 7.38–7.29 (m, 2 H), 2.52 (s, 3 H, CH_3) ppm. ^{13}C NMR (75.46 MHz, $CDCl_3$, 25 °C): δ = 189.1, 167.5, 153.7, 139.0, 137.2, 135.1, 132.0, 131.5, 131.3, 127.6, 126.9, 125.7, 125.2, 122.2, 20.6 ppm. MS (70 eV, EI): *m*/*z* (%) = 253 (37) $[M]^+$, 224 (100), 119 (81), 91 (78). HRMS: calcd. for $C_{15}H_{11}NOS$ 253.0561; found 253.0565. $C_{15}H_{11}NOS$ (253.32): calcd. C 71.12, H 4.38, N 5.53; found C 71.15, H 4.40, N 5.51. IR ($CHCl_3$): $\tilde{\nu}$ = 1652 cm^{-1}.

1,3-Benzothiazol-2-yl(3-methylphenyl)methanone (10c):[24] White solid, 1.97 g (78%); m.p. 72.6–73.5 °C (CH_3OH). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.42–8.35 (m, 1 H), 8.31–8.21 (m, 2 H), 8.04–7.97 (m, 1 H), 7.63–7.51 (m, 2 H), 7.51–7.41 (m, 2 H), 2.47 (s, 3 H, CH_3) ppm. ^{13}C NMR (75.46 MHz, $CDCl_3$, 25 °C): δ = 185.6, 167.2, 153.8, 138.3, 137.0, 135.0, 134.7, 131.4, 128.6, 128.4, 127.5, 126.9, 125.7, 122.1, 21.4 ppm. MS (70 eV, EI): *m*/*z* (%) = 253 (33) $[M]^+$, 225 (53), 119 (100), 91 (52). HRMS: calcd. for $C_{15}H_{11}NOS$ 253.0561; found 253.0563. $C_{15}H_{11}NOS$ (253.32): calcd. C 71.12, H 4.38, N 5.53; found C 71.16, H 4.36, N 5.55. IR ($CHCl_3$): $\tilde{\nu}$ = 1646 cm^{-1}.

1,3-Benzothiazol-2-yl(4-methylphenyl)methanone (10d): White solid, 2.0 g (79%); m.p. 91–93 °C (CH_3OH; ref.[25] 92 °C). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.46–7.24 (m, 8 H), 2.45 (s, 3 H, CH_3) ppm. ^{13}C NMR (75.46 MHz, $CDCl_3$, 25 °C): δ = 184.9, 167.5, 153.4, 145.0, 137.0, 132.4, 125.7, 127.5, 129.3, 126.8, 125.7, 122.5, 21.7 ppm. MS (70 eV, EI): *m*/*z* (%) = 253 (32) $[M]^+$, 225 (43), 119 (100), 91 (50). HRMS: calcd. for $C_{15}H_{11}NOS$ 253.0561; found 253.0558. $C_{15}H_{11}NOS$ (253.32): calcd. C 71.12, H 4.38, N 5.53; found C 71.17, H 4.39, N 5.50. IR ($CHCl_3$): $\tilde{\nu}$ = 1652 cm^{-1}.

1,3-Benzothiazol-2-yl(2-methoxyphenyl)methanone (10e):[26] White solid, 2.04 g (76%); m.p. 115–116 °C. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.19–8.11 (m, 1 H), 8.03–7.95 (m, 1 H), 7.80–7.72 (m, 1 H), 7.60–7.46 (m, 3 H), 7.13–7.00 (m, 2 H), 3.79 (s, 3 H, OCH_3) ppm. ^{13}C NMR (75.46 MHz, $CDCl_3$, 25 °C): δ = 188.0, 167.2, 158.7, 153.6, 137.1, 133.6, 131.1, 127.4, 126.7, 126.2, 125.5, 122.2, 120.3, 112.0, 55.9 ppm. MS (70 eV, EI): *m*/*z* (%) = 269 (14) $[M]^+$, 238 (55), 135 (100), 92 (19). HRMS: calcd. for $C_{15}H_{11}NO_2S$ 269.0511; found 269.0508. $C_{15}H_{11}NO_2S$ (269.32): calcd. C 66.89, H 4.12, N 5.20; found C 66.92, H 4.13, N 5.17. IR ($CHCl_3$): $\tilde{\nu}$ = 1656 cm^{-1}.

1,3-Benzothiazol-2-yl(3-methoxyphenyl)methanone (10f): White solid, 2.0 g (74%); m.p. 104–105 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.29–8.18 (m, 2 H), 8.07–7.98 (m, 2 H), 7.63–7.51 (m, 2 H), 7.51–7.43 (m, 1 H), 7.24–7.20 (m, 1 H), 3.91 (s, 3 H, OCH_3) ppm. ^{13}C NMR (75.46 MHz, $CDCl_3$, 25 °C): δ = 185.1, 167.1, 159.6, 153.9, 137.0, 136.1, 129.5, 127.6, 126.9, 125.8, 124.2, 122.1, 120.6, 115.2, 55.5 ppm. MS (70 eV, EI): *m*/*z* (%) = 269 (54) $[M]^+$, 241 (37), 135 (100), 107 (29). HRMS: calcd. for $C_{15}H_{11}NO_2S$ 269.0511; found 269.0514. $C_{15}H_{11}NO_2S$ (269.32): calcd. C 66.89, H 4.12, N 5.20; found C 66.85, H 4.11, N 5.22. IR ($CHCl_3$): $\tilde{\nu}$ = 1648 cm^{-1}.

1,3-Benzothiazol-2-yl(4-methoxyphenyl)methanone (10g): White solid, 1.9 g (71%); m.p. 122–123 °C (CH_3OH; ref.[27] 123 °C). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.65 (d, *J* = 9.2 Hz, 2 H), 8.26–8.20 (m, 1 H), 8.05–7.98 (m, 1 H), 7.56 (m, 2 H), 7.04 (d, *J* = 9.2 Hz, 2 H), 3.92 (s, 3 H, OCH_3) ppm. ^{13}C NMR (75.46 MHz, $CDCl_3$, 25 °C): δ = 183.1, 167.8, 164.2, 153.7, 136.7, 133.7, 127.6, 126.6, 125.4, 122.0, 113.7, 55.4 ppm. MS (70 eV, EI): *m*/*z* (%) = 269 (6) $[M]^+$, 241 (10), 135 (100). HRMS: calcd. for $C_{15}H_{11}NO_2S$ 269.0511; found 269.0513. $C_{15}H_{11}NO_2S$ (269.32): calcd. C 66.90, H 4.12, N 5.20; found C 66.88, H 4.13, N 5.18. IR ($CHCl_3$): $\tilde{\nu}$ = 1639 cm^{-1}.

Typical Procedure for the Reactions between 1 and Aryllithium Reagents: Phenyllithium (**7a**; 0.25 mmol) in THF (3.0 mL) was added to a stirred solution kept at –70 °C of **1** (0.050 g, 0.17 mmol) in THF (5.0 mL). After about 30 min, the reaction mixture was quenched with a saturated aqueous solution of NH_4Cl and extracted with diethyl ether. The organic layer was washed with brine, dried with anhydrous $MgSO_4$, and concentrated in vacuo without warming. The residue was analyzed by ^1H NMR spectroscopy.

Typical Procedure for the Reactions between 10a–g and 1,3-Benzothiazol-2-yllithium: A solution of *n*-butyllithium (2.5 M in *n*-hexane, 0.15 mL, 3.7 mmol) in THF (3 mL) was added dropwise to a stirred solution kept at –70 °C of 1,3-benzothiazole (0.050 g, 3.7 mmol) in THF (5 mL). After about 15 min, a solution of ketone **10a** (0.84 g, 3.5 mmol) in THF (5 mL) was added dropwise. The reaction course was monitored by TLC and ^1H NMR spectroscopy. After at least 30 min the reaction was quenched with water (3 mL), acidified with 1 M HCl, and extracted with diethyl ether. The organic layer was washed with brine, dried with anhydrous $MgSO_4$, and concentrated in vacuo. After purification by flash chromatography, 0.98 g (75%) of carbinol **5a** was obtained.

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