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Regioselectivity in the Addition of Vinylmagnesium Bromide to Heteroarylic Ketones: *C*- versus *O*-Alkylation

Carla Boga,* Rayk Stengel, Rodolphe Abdayem, Erminia Del Vecchio, Luciano Forlani, and Paolo E. Todesco

Dipartimento di Chimica Organica "A. Mangini", Viale Risorgimento, 4, 40136-Bologna, Italy

boga@ms.fci.unibo.it

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The reactivity of heteroarylic ketones toward vinylmagnesium bromide (**2**) and the regiochemistry of the addition were investigated. The reactivity drastically increases when the carbonyl is conjugated with at least one aza group and the regiochemistry of the addition of the vinyl Grignard reagent depends on the carbonyl compound: in the series of di(heteroazolyl) ketones the *O*-alkylation product was observed as unique with di(1,3-benzothiazol-2-yl) ketone, and in different relative ratios with respect to the classic *C*-alkylation product with di(1,3-thiazol-2-yl) ketone, (1,3-benzothiazol-2-yl) (1,3-thiazol-2-yl) ketone, and di(1,3-benzoxazol-2-yl) ketone, whereas di(*N*-methylbenzimidazol-2-yl) ketone gave the exclusive formation of the carbinol. This behavior can be explained by the intervention of the delocalization power of the heterocyclic ring and this was confirmed by the results obtained from the reaction between vinylmagnesium bromide and a series of mixed (1,3-benzothiazol-2-yl) (para-substituted phenyl) ketones, that showed a relative *O*-/*C*-alkylation ratio dependent on the nature and on the electronic effect of the substituent on the phenyl ring. The results are in agreement with the existence of intermediate species bearing a negative charge on the benzylic carbonyl carbon atom, and make the *O*-alkylation reaction between vinyl Grignard reagents and carbonyl compounds no longer a rare case, since it was observed with a number of heterocyclic carbonyl compounds, such as (1,3-benzothiazol-2-yl) aryl ketones and di(heteroaryl) ketones of the pentatomic 1,3-heteroazolic series.

Introduction

The addition of Grignard reagents to carbonyl compounds is well recognized as one of the most important reactions in synthetic organic chemistry. Although more than 100 years have passed since Grignard published his paper on the preparation of these organometallics,[1] new synthetic developments involving these compounds are still in progress.[2] Usually, the reaction gives alcohols arising from the 1,2 nucleophilic attack to carbonyl, but in some cases, depending on the structure of the Grignard reagent, of the substrate or on the solvent used, it does not follow the classic pathway and unexpected products can be recovered, as was extensively studied and recently reviewed by Holm and Crossland.[3] It is well-known,[4] for example, that benzophenone reacts with methylmagnesium bromide yielding the 1,2-addition product, whereas with cyclohexyl or isobutyl Grignard reagents reduction to the alcohol takes place. In addition, neopentylmagnesium halides cause a bimolecular reduction to the pinacol, whereas *tert*-butyl Grignard reagents gave not only the classic 1,2-addition but also a conjugate addition on the phenyl ring. The *O*-alkylation of Grignard reagents to the carbonylic oxygen[3] is a rarely observed reaction: it was found to occur, as a minor reaction, between some Grignard reagents and substrates such as orthoquinones,[5] orthoquinolacetates,[6−8] 9,10-phenanthraquinone,[9] and benzil.[10] We recently found[11] that the addition of vinylmagnesium bromide (**2**) to di(1,3-benzothiazol-2-yl) ketone (**1**) gives quantitatively the *O*-alkylation product **3** (Scheme 1).

This reaction also occurs with substituted vinyl Grignard compounds, whereas nonvinyl Grignard reagents give, exclusively and quantitatively in a few minutes, the product of the classic 1,2-attack.[12] In addition, the regioselectivity seems to be highly influenced by the groups bonded to the carbonyl: actually, the reaction between

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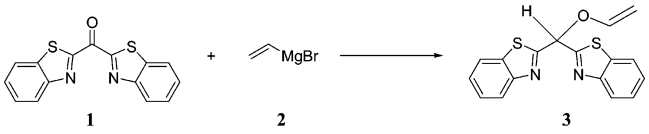

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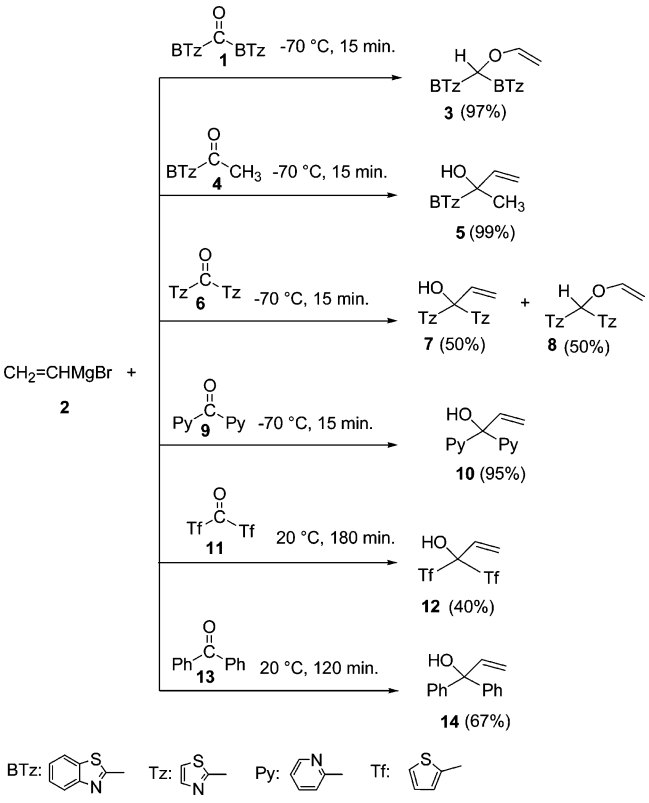

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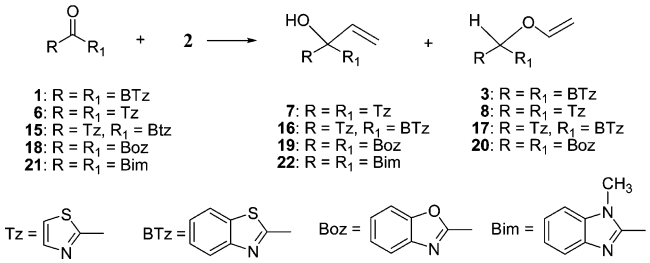


TABLE 1. *C*- versus *O*-Alkylation from Reactions between Di(heteroaryl) Ketones and Vinylmagnesium Bromide (2)[a]

entry	ketone	*C*-alkylation (%)[b]	*O*-alkylation (%)[b]
1	**6**	**7** (50)	**8** (50)
2	**15**	**16** (10)	**17** (90)
3	**1**		**3** (>97)[c]
4	**18**	**19** (50)	**20** (50)
5	**21**	**22** (>97)[c]	

[a] Reactions carried out in THF at −70 °C for 15 min with an equimolar ratio of reagents, in all cases the conversion was up to 90%. [b] Relative ratio calculated from ^{1}H NMR of crude reaction mixture. [c] In these cases the NMR spectra showed only the presence of one regioisomer.

2 and 1-(1,3-benzothiazol-2-yl)-1-ethanone (**4**) give only the corresponding carbinol (**5**), whereas with di(1,3-thiazol-2-yl) ketone (**6**) an equimolar mixture of *C*- and *O*-alkylation products (**7** and **8**) is produced (Scheme 2). These findings suggested that the presence of two thiazolic groups on the substrate is a fundamental requisite to drive the regiochemistry of the reaction toward the *O*-alkylation, which increases with use of the corresponding benzo derivative owing to its anellation effect. Furthermore, it is of interest to note that the addition to compound **1** of all the Grignard reagents we used proved to be complete in about 15 min and gave the corresponding addition products in quantitative yield, showing thus a behavior unusual for aromatic ketones.

On the basis of these previous findings and with the aim of investigating and deepening the role of the groups bonded to the carbonyl, both in increasing the carbonyl reactivity and in driving the regiochemistry of the attack, we synthesized some selected heteroarylic ketones and we tested their behavior with vinylmagnesium bromide (**2**), chosen because of its exclusive preference for the *O*-alkylation with ketone **1**. Herein we report the results obtained.

Results and Discussion

Since our previous findings[11] (Scheme 1) showed that ketones containing a thiazolic group react with organomagnesium compounds more rapidly than benzophenone, and that vinyl Grignard reagents gave *O*-alkylation only when two thiazolyl (or benzothiazolyl) groups are linked to the carbonyl, we first wanted to investigate the effect of the aza group and, for this purpose, we carried out the reaction of vinylmagnesium bromide (**2**) with di(2-pyridinyl) ketone (**9**) (bearing only aza groups) and with a substrate in which only a sulfur atom is present in the heterocyclic ring, namely di(2-thienyl) ketone (**11**).

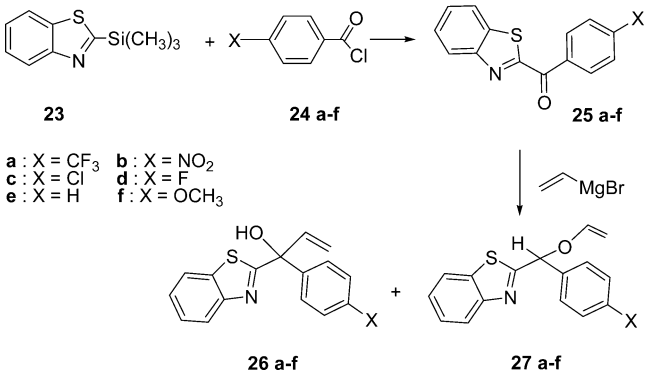
Scheme 2 shows the results obtained, together with some of those previously reported,[11] in order to make an easier comparison. As shown in Scheme 2, ketones bearing at least one aza group in the β position with respect to the carbonyl (i.e. compounds **1**, **4**, **6**, and **9**) quantitatively undergo the addition reaction in a few minutes at −70 °C, whereas di(thienyl) ketone (**11**) and benzophenone (**13**) gave lower conversion and only at higher temperatures and reaction times. This suggests that the observed considerable increase of the reactivity of the substrate toward the addition of the Grignard reagent can be caused by the coordination of the magnesium by the azolic nitrogen.

Furthermore, the results obtained show that the *O*-alkylation requires a carbonyl bonded to two thiazolic groups and that, on going from di(1,3-thiazol-2-yl) ketone (**6**) to its monobenzo derivative **15** and to the dibenzo derivative **1** (Scheme 3) the regioselectivity toward the oxygen atom drastically increases (Table 1, entries 1−3).

These findings induced us to check the possibility that the *O*-alkylation also occurs with other ketones of the aromatic benzocondensated pentatomic 1,3-heteroazolic series. For this purpose we synthesized di(1,3-benzoxazol-2-yl) ketone (**18**) and bis(*N*-methyl-benzimidazol-2-yl) ketone (**21**) and we carried out the reaction between these and compound **2** (Scheme 3), which gave the results collected in Table 1.

A comparison of the results obtained with ketones **1**, **18**, and **21** (Table 1, entries 3−5) shows that the absolute

SCHEME 4



preference toward *O*-alkylation observed with compound **1** halved on passing to di(1,3-benzoxazol-2-yl) ketone (**18**) and is completely lost when benzimidazolyl derivate **21** was used. These results induced us to hypothesize that the observed trend of regioselectivity toward the carbonylic oxygen could depend on the electronic delocalization power of the heterocyclic ring. It has been reported[13] that the fraction of π-charge transferred from a negatively charged trigonal carbon atom to an adjacent X group can be calculated from ^{13}C shift/π charge relationships. The charge demand (C_X) of the substituent group X represents a quantitative measure of its capacity to delocalize the negative charge (thus reflecting its mesomeric electron-withdrawing power). For azole derivatives C_X gradually diminish on passing from thiazolyl to oxazolyl and to (*N*-methyl)imidazolyl substituents (or their benzo-fused analogues).[14] Even if the regioselectivity of our systems cannot be ascribed to this factor alone, the fact that the charge demand scale reported for the pentatomic 1,3-heteroazolic series parallels the regioselectivity toward the oxygen reported in Table 1 seems to suggest the possibility of the intervention of an intermediate bearing a negative charge on the carbonylic carbon adjacent to the aromatic ring. If this is true, it could be predictable that *O*-alkylation might occur also with ketones bearing both one benzothiazolyl group and one phenyl ring substituted with electron-withdrawing groups.

To verify this hypothesis we prepared, from 2-(trimethylsilyl)-1,3-benzothiazole (**23**) and para-substituted benzoyl chlorides **24a**−**f** (Scheme 4), the series of (1,3-benzothiazol-2-yl) aryl ketones **25a**−**f** in which the phenyl ring contains in the para position groups characterized by different mesomeric and/or inductive effect.

The reactions between compounds **25a**−**f**, as well as all those herein reported, and vinylmagnesium bromide (**2**) (Scheme 4) were carried out in duplicate and the reaction mixture was quenched and analyzed by ^{1}H NMR spectroscopy. Since it was observed that some 1,3-benzothiazol-2-yl-methane derivatives are susceptible to oxidation[15,16] and that the vinyl ether **3** decomposes[11] after storage for many days in acidic solution and is water- and air-sensitive giving the starting carbonyl compound **1**, we monitored the reaction mixtures over a period of time of about 6 h and we observed that in present cases the *C*-/*O*-alkylation ratio was unchanged.

TABLE 2. *C*- versus *O*-Alkylation from Reactions between Compounds 25a−f and Vinylmagnesium Bromide (2)[a]

entry	ketone 25 (X)	*C*-alkylation product **26** (%)[b]	*O*-alkylation product **27** (%)[b]
1	**25a** (CF_3)	**26a** (33)	**27a** (67)
2	**25b** (NO_2)	**26b** (50)	**27b** (50)
3	**25c** (Cl)	**26c** (60)	**27c** (40)
4	**25d** (F)	**26d** (86)	**27d** (14)
5	**25e** (H)	**26e** (90)	**27e** (10)
6	**25f** (OCH_3)	**26f** (>97)[c]	

[a] Reactions carried out in THF at −70 °C for 20 min with a 1:1.2 molar ratio between **25** and **2**, conversions up to 70%. [b] Relative ratio calculated from ^{1}H NMR of the crude reaction mixture. [c] In this case the NMR spectra showed only the presence of the carbinol.

The results, reported in Table 2, also show that with (1,3-benzothiazol-2-yl) aryl ketones the reaction generally led to both possible regioisomers in different relative ratios. Despite the apparent complexity, the regiochemical outcome shows characteristic features, the relative amount of *C*- and *O*-alkylation product being dependent on the electronic effect of the substituent on the phenyl ring. The substitution of one benzothiazolyl group of compound **1** with a phenyl ring (Table 2, entry 5) allows, even if to a very limited extent, the *O*-alkylation product, according to the hypothesis that the regioselectivity of the attack is affected by the delocalization power of the groups linked to the carbonyl. The result obtained with *p*-fluoro derivative **25d** (entry 4) also agrees with this trend, since the substitution, in the aromatic ring, of a hydrogen atom with a fluorine atom produces very little change in the electronic effects. The preference for the *C*-alkylation product **26** is exclusive with the 1,3-benzothiazol-2-yl(4-methoxyphenyl)methanone (**25f**, entry 6) and decreases on going toward ketones bearing more electron-withdrawing substituents, in agreement with the σ_p values trend of the substituents.[17] This behavior seems not to be followed by 1,3-benzothiazol-2-yl[4-(trifluoromethyl)phenyl]methanone (**25a**, entry 1) and 1,3-benzothiazol-2-yl(4-nitrophenyl)methanone (**25b**, entry 2), a higher ratio of *O*-/*C*-alkylation products for the nitro-substituted substrate **25b** with respect to **25a** being expected. It is worth noting, however, that reactions between nitro- and nitrosoarenes and organomagnesium reagents[18−20] have been reported to be very complex,

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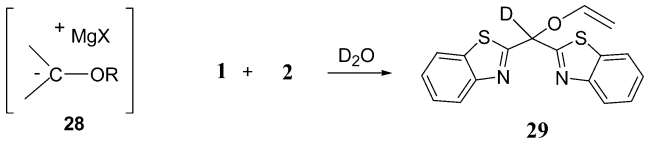
SCHEME 5



giving a mixture of products. It has also been reported[20] that the nitro group is much more reactive with Grignard reagents than carbonyl functions of esters and ketones; in our case, from the reaction between **25b** and vinylmagnesium bromide (**2**), the vinyl ether **27b** and the carbinol **26b** are isolated as the main products thus indicating that the carbonyl of **25b** is more reactive than that of nitro group present in the substrate, and this is probably due to the strong electron-withdrawing effect of the groups bonded to the carbonyl.

All these results seem to be in agreement with the hypothesis of the formation, in the reaction pathway for the *O*-alkylation, of an intermediate species bearing a negative charge on the benzylic carbon (structure **28** of Scheme 5), that can result both from a radicalic and an ionic attack of the Grignard reagent to the carbonylic oxygen atom.

This might also be supported by studies[21] on the delocalization effect of the radical spin in para-substituted benzylic systems, which showed a poor dependence on the substituent. However, we tried to trap the carbanionic species resulting from the reaction between compound **1** and organomagnesium reagent **2** and for this purpose we quenched the reaction mixture with D_2O: after the workup, the ^1H NMR spectrum of the crude reaction product showed the absence of the benzylic proton signal, in agreement with the formation of deuterated compound **29** (Scheme 5). This result confirmed the hypothesis of the formation of an intermediate **28**-like species.

Conclusions

The present investigation showed that the reactivity of heteroaromatic ketones toward Grignard reagents drastically increases when the carbonyl is conjugated with at least one aza group and that the presence of such a functionality is not the only one responsible for driving the regiochemistry of the addition of vinyl Grignard reagents toward the *O*-alkylation product. This unexpected and rarely reported *O*-alkylation became important in the reaction between vinylmagnesium bromide (**2**) and a series of di(heteroazolyl) ketones: the *O*-alkylation product, which was observed as the unique reaction product with di(1,3-benzothiazol-2-yl) ketone (**1**) was recovered, in different relative ratios with respect to the classic *C*-alkylation product, also using di(1,3-thiazol-2-yl) ketone, (1,3-benzothiazol-2-yl)(1,3-thiazol-2-yl) ketone, and di(1,3-benzoxazol-2-yl) ketone, whereas bis(*N*-methylbenzimidazol-2-yl) ketone gave the exclusive formation of the carbinol. This behavior suggested the great importance of the delocalization power of the heterocyclic ring on the regiochemistry of the addition, which was confirmed by the results obtained from the reaction between **2** and a series of mixed (1,3-benzothiazol-2-yl) (para-substituted phenyl) ketones, which showed the relative *O*-/*C*-alkylation ratio to be dependent on the nature and on the electronic effect of the substituent on the phenyl ring. These results are in agreement with the existence of intermediate species bearing a negative charge on the benzylic carbonyl carbon atom, the *O*-alkylation reaction seeming to be dependent on the delocalization of this charge.

In conclusion, according to the results herein reported the *O*-alkylation reaction between vinyl Grignard reagents and carbonyl compounds can no longer be considered a rare case, since it occurs with a great number of heterocyclic carbonyl compounds, such as (1,3-benzothiazol-2-yl) aryl ketones and di(heteroaryl) ketones of the pentatomic 1,3-heteroazolic series.

Experimental Section

Di(2-pyridinyl) ketone (**9**) is commercially available, compounds **11**,[22] **18**,[16b] and **21**[23] were prepared according to literature, and their chemicophysical data are in agreement with those reported.

Preparation of 1,3-benzothiazol-2-yl(1,3-thiazol-2-yl)-methanone (15): *n*-BuLi (1.27 mL, 2.6 mmol; 2.5 M in *n*-hexane) diluted in THF (2.0 mL) was added dropwise at −70 °C to a solution of 0.18 mL (2.6 mmol) of thiazole in 3.0 mL of THF. After 15 min a solution (0.5 g, 2.6 mmol, in 5.0 mL of THF) of benzothiazole-2-carboxylic acid methyl ester, prepared from 2-(trimethylsilyl)-1,3-benzothiazole (**23**) and methyl chloroformiate according to Jutzi's procedure,[24] was added. After 15 min at −70 °C the reaction mixture was treated with aqueous sat. NH_4Cl solution and extracted with diethyl ether. The organic layer was washed with "brine", dried over anhydrous Na_2SO_4, filtered, and concentrated. FC of the residue gave 0.48 g (1.95 mmol, 75%) of **15**: mp 146−148 °C (from CH_3OH); R_f 0.20 (7:3 petroleum ether:diethyl ether); ^1H NMR (300 MHz, $CDCl_3$) δ 7.50−7.62 (m, 2H), 7.85 (d, 1H, J = 3.0 Hz), 7.99 (dd, 1H, J = 8.7 Hz, J = 1.6 Hz), 8.23 (d, 1H, J = 3.0 Hz), 8.30 (dd, 1H, J = 6.7 Hz, J = 1.6 Hz); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ 122.3, 126.2, 127.3, 128.2, 128.3, 137.7, 145.7, 153.3, 162.2, 163.0, 175.1; MS (70 eV, EI) *m/z* (%) 246 [M^+, 84], 218 (100), 162 (27), 134 (30), 112 (68); HRMS calcd for $C_{11}H_6N_2OS_2$ 245.9922, found 245.9920. Anal. Calcd for $C_{11}H_6N_2OS_2$: C, 53.64; H, 2.46; N, 11.37. Found: C, 53.61; H, 2.48; N, 11.34. IR ($CHCl_3$) (ν, cm^{-1}) 1663.

Synthesis of compounds 25a−f: Compounds **25a−f** were prepared by reaction between 2-(trimethylsilyl)-1,3-benzothiazole **23** and the corresponding commercially available para-substituted benzoyl chlorides **24a−f**, according to the procedure reported by Jutzi.[24]

1,3-Benzothiazol-2-yl[4-(trifluoromethyl)phenyl]methanone (25a): white solid, yield 75%; mp 114−116 °C (from $CHCl_3$); R_f 0.70 (1:1 dichloromethane:petroleum ether); ^1H NMR (300 MHz, $CDCl_3$) δ 7.59 (td, 2H, J = 7.2 Hz, J = 1.6 Hz), 7.82 (d, 2H, J = 8.1 Hz), 8.00−8.06 (m, 1H), 8.22−8.27 (m, 1H), 8.66 (d, 2H, J = 8.1 Hz); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ 123.6 (q, J = 273.1 Hz, CF_3), 122.2, 125.4 (q, J = 3.5 Hz, $CH-C-CF_3$), 125.9, 127.2, 128.0, 131.5, 134.8 (q, J = 32.8 Hz, $C-CF_3$), 137.1, 137.8, 153.8, 166.2, 184.4; MS (70 eV, EI) *m/z* (%) 307 [M^+, 43], 279 (68), 173 (100), 145 (95); HRMS calcd for $C_{15}H_8F_3NOS$ 307.0279, found 307.0274. Anal. Calcd for $C_{15}H_8F_3NOS$: C, 58.63; H, 2.62; N, 4.56. Found: C, 58.61; H, 2.64, N; 4.58. IR ($CHCl_3$) (ν, cm^{-1}) 1656.

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1,3-Benzothiazol-2-yl(4-nitrophenyl)methanone (25b): yellow solid, yield 70%; mp 183−185 °C (from $CHCl_3$) (lit.[15] mp 181−184 °C); R_f 0.62 (2:1 dichloromethane:petroleum ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55−7.68 (m, 2H), 8.02−8.08 (m, 1H), 8.23−8.30 (m, 1H), 8.40 (d, 2H, J = 8.6 Hz), 8.75 (d, 2H, J = 8.6 Hz); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ 122.3, 123.5, 126.0, 127.3, 128.3, 132.3, 137.2, 139.7, 150.6, 153.8, 165.8, 183.9; MS (70 eV, EI) *m/z* (%) 284 (M^+, 48), 256 (88), 150 (100), 104 (71), 92 (41), 76 (70); HRMS calcd for $C_{14}H_8N_2O_3S$ 284.0256, found 284.0258. Anal. Calcd for $C_{14}H_8N_2O_3S$: C, 59.15; H, 2.84; N, 9.85. Found: C, 59.14; H, 2.86; N, 9.88. IR ($CHCl_3$) (ν, cm^{-1}) 1685.

1,3-Benzothiazol-2-yl(4-chlorophenyl)methanone (25c): white solid, yield 80%; mp 108−109 °C (from CH_3OH) (lit.[25] mp 102−103 °C); R_f 0.70 (4:6 dichloromethane:petroleum ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 (d, 2H, J = 8.7 Hz), 7.46−7.63 (m, 2H), 7.96−8.04 (m, 1H), 8.18−8.26 (m, 1H), 8.55 (d, 2H, J = 8.7 Hz); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ 122.1, 125.7, 127.0, 127.7, 128.8, 132.6, 133.1, 137.0, 140.5, 153.7, 166.7, 183.8; MS (70 eV, EI) *m/z* (%) 273 (15) [M^+], 245 (19), 139 (71), 111 (100), 75 (86); HRMS calcd for $C_{14}H_8ClNOS$ 273.0015, found 273.0011. Anal. Calcd for $C_{14}H_8ClNOS$: C, 61.43; H, 2.95; N, 5.12. Found: C, 61.40; H, 2.97; N, 5.10. IR ($CHCl_3$) (ν, cm^{-1}) 1644.

1,3-Benzothiazol-2-yl(4-fluorophenyl)methanone (25d): white solid, yield 70%; mp 121−122 °C (from methanol); R_f 0.42 (4:6 dichloromethane:petroleum ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15−7.25 (m, 2H), 7.48−7.62 (m, 2H), 7.95−8.04 (m, 1H), 8.16−8.25 (m, 1H), 8.60−8.72 (m, 2H); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ 115.7 (d, J = 22.0 Hz), 122.1, 125.6, 126.9, 127.6, 134.1 (d, J = 9.2 Hz), 134.1 (d, J = 217 Hz), 153.8, 164.6, 167.0, 168.0, 183.4; MS (70 eV, EI) *m/z* (%) 257 [M^+, 25], 229 (52), 123 (100), 95 (43); HRMS calcd for $C_{14}H_8FNOS$ 257.0311, found 257.0309. Anal. Calcd for $C_{14}H_8FNOS$: C, 65.36; H, 3.13; N, 5.44. Found: C, 65.34; H, 3.16; N, 5.47. IR ($CHCl_3$) (ν, cm^{-1}) 1649.

1,3-Benzothiazol-2-yl(phenyl)methanone (25e): yellow solid; yield 78%; mp 98−99 °C (from ethanol) (lit.[15] mp 95−98 °C); R_f 0.70 (8:2 petroleum ether:diethyl ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55−7.74 (m, 5H), 8.05−8.08 (m, 1H), 8.25−8.30 (m, 1H), 8.59 (d, 2H, J = 8.5 Hz); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ 122.2, 125.7, 126.9, 127.6, 128.5, 131.3, 133.9, 135.0, 137.0, 153.9,167.1, 185.4; MS (70 eV, EI) *m/z* 239 [M^+, 26], 211 (34), 134 (2), 105 (100), 77 (68); HRMS calcd for $C_{14}H_9NOS$ 239.0405, found 239.0403. Anal. Calcd for $C_{14}H_9NOS$: C, 70.27; H, 3.79; N, 5.85. Found: C, 70.24; H, 3.80; N, 5.84. IR ($CHCl_3$) (ν, cm^{-1}) 1640.

1,3-Benzothiazol-2-yl(4-methoxyphenyl)methanone (25f): white solid, yield 72%; mp 122−123 °C (from CH_3OH) (lit.[26] mp 123 °C); R_f 0.60 (1:1 dichloromethane:petroleum ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.92 (s, 3H), 7.04 (d, 2H, J = 9.2 Hz), 7.56 (td, 2H, J = 8.2 Hz, J = 2.1 Hz), 7.98−8.05 (m, 1H), 8.20−8.26 (m, 1H), 8.65 (d, 2H, J = 9.2 Hz); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ 55.4, 113.7, 122.0, 125.4, 126.6, 127.2, 127.6, 133.7, 136.7, 153.7, 164.2, 167.8, 183.1; MS (70 eV, EI) *m/z* (%) 269 [M^+, 6], 241 (10), 135 (100); HRMS calcd for $C_{15}H_{11}NO_2S$ 269.0511, found 269.0514. Anal. Calcd for $C_{15}H_{11}NO_2S$: C, 66.90; H, 4.12; N, 5.20. Found: C, 66.88; H, 4.15; N, 5.18. IR ($CHCl_3$) (ν, cm^{-1}) 1639.

Reactions between Ketones and Vinylmagnesium Bromide (2). General procedure: Vinylmagnesium bromide (**2**) (0.41 mmol) in THF (3.0 mL) was added dropwise to a stirred solution of carbonyl compound (0.34 mmol) in THF (3.0 mL), cooled at − 70 °C. After about 20 min. the reaction mixture was quenched with saturated aqueous $(NH_4)_2SO_4$, stirred while being warmed to room temperature, and extracted with diethyl ether. The organic layers were washed with "brine", dried over anhydrous Na_2SO_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, and then the products were isolated by FC and fully characterized. The vinyl ethers, stored at −18 °C, are stable for many years.

1,1-Di(2-pyridinyl)-2-propen-1-ol (10): colorless oil; R_f 0.76 (2:8 petroleum ether:diethyl ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.24 (dd, 1H, J = 10.4 Hz, J = 1.5 Hz), 5.50 (dd, 1H, J = 17.0 Hz, J = 1.5 Hz), 6.57 (br s, 1H, OH), 6.88 (dd, 1H, J = 17.0 Hz, J = 10.4 Hz), 7.11−7.16 (m, 2H), 7.61−7.67 (m, 2H), 7.76−7.79 (m, 2H), 8.49−8.52 (m, 2H); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ 78.1, 113.6, 121.3, 122.2, 136.8, 142.4, 147.6, 162.6; MS (70 eV, EI) *m/z* (%) 212 [M^+, 4], 195 (39), 185 (20), 134 (59), 106 (66), 78 (100); HRMS calcd for $C_{13}H_{12}N_2O$ 212.0950, found 212.0948. Anal. Calcd for $C_{13}H_{12}N_2O$: C, 73.57; H, 5.70: N, 13.20. Found: C, 73.54; H, 5.72; N, 13.18. IR ($CHCl_3$) (ν, cm^{-1}) 3323, 1586, 1464, 1434, 1156, 997, 928.

1,1-Di(2-thienyl)-2-propen-1-ol (12): pale yellow oil, R_f 0.50 (7:3 petroleum ether:diethyl ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.72 (br s, 1H, OH), 5.30 (d, 1H, J = 10.4 Hz), 5.47 (d, 1H, J = 17.0 Hz), 6.52 (dd, 1H, J = 17.0 Hz, J = 10.4 Hz), 6.94−6.99 (m, 4H), 7.28 (dd, 2H, J = 4.4 Hz, J = 2.0 Hz); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ 75.8, 113.0, 125.3, 125.5, 126.7, 142.4, 150.1; MS (70 eV, EI) *m/z* (%) 222 [M^+, 13], 205 (4), 195 (9), 111 (100), 97 (30); HRMS calcd for $C_{11}H_{10}OS_2$ 222.0173, found 222.0170. Anal. Calcd for $C_{11}H_{10}OS_2$: C, 59.43; H, 4.53. Found: C, 59.41; H, 4.54. IR ($CHCl_3$) (ν, cm^{-1}) 3678, 3617, 1614, 1519, 1416, 1045, 927.

1-(1,3-Benzothiazol-2-yl)-1-(1,3-thiazol-2-yl)-2-propen-1-ol (16): R_f 0.35 (7:3 petroleum ether:diethyl ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.40 (d, 1H, J = 8.0 Hz), 5.48 (s, 1H, OH), 5.70 (d, 1H, J = 15.0 Hz), 6.65 (dd, 1H, J = 15.0 Hz, J = 8.0 Hz), 7.25−7.60 (m, 2H), 7.80−7.95 (m, 2H), 8.00−8.10 (m, 2H); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ 78.5, 115.8, 120.6, 121.6, 123.3, 125.4, 126.2, 135.3, 139.7, 142.4, 151.8, 173.4, 173.5; MS (70 eV, EI) *m/z* (%) 274 [M^+, 45], 257 (16), 246 (28), 135 (35), 58 (100); HRMS calcd for $C_{13}H_{10}N_2OS_2$ 274.0235, found 274.0233. Anal. Calcd for $C_{13}H_{10}N_2OS_2$: C, 56.91; H, 3.67: N, 10.21. Found: C, 56.89; H, 3.69; N, 10.19. IR ($CHCl_3$) (ν, cm^{-1}) 3615, 1635, 1485, 1370, 1025, 848.

1,3-Benzothiazol-2-yl(1,3-thiazol-2-yl)methyl vinyl ether (17): colorless oil; R_f 0.40 (7:3 petroleum ether:diethyl ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.31 (dd, 1H, J = 6.8 Hz, J = 2.8 Hz), 4.63 (dd, 1H, J = 14.0 Hz, J = 2.8 Hz), 6.65 (s, 1H), 6.62 (dd, 1H, J = 14.0 Hz, J = 6.8 Hz), 7.25−7.60 (m, 2H), 7.80−7.95 (m, 2H), 8.00−8.10 (m, 2H); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ 77.9, 92.3, 120.8, 121.9, 123.8, 125.9, 126.3, 135.3, 143.2. 149.2, 152.8, 166.9, 168.4; MS (70 eV, EI) *m/z* (%) 274 [M^+, 7], 231 (100), 218 (2), 198 (44), 146 (48); HRMS calcd for $C_{13}H_{10}N_2OS_2$ 274.0235, found 274.0234. Anal. Calcd for $C_{13}H_{10}N_2OS_2$: C, 56.91; H, 3.67: N, 10.21. Found: C, 56.90; H, 3.68; N, 10.20. IR ($CHCl_3$) (ν, cm^{-1}) 3617, 1641, 1488, 1385, 1045, 877.

1,1-Di(1,3-benzoxazol-2-yl)-2-propen-1-ol (19): R_f 0.15 (7:3 petroleum ether:diethyl ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.70 (br s, 1H, OH), 5.64 (d, 1H, J = 10.5 Hz), 5.91 (d, 1H, J = 17.0 Hz), 6.82 (dd, 1H, J = 17.0 Hz, J = 10.5 Hz), 7.30−7.50 (m, 4H), 7.50−7.65 (m, 2H), 7.76−7.89 (m, 2H); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ 72.9, 111.2, 118.3, 120.7, 124.9, 125.9, 133.9, 140.5, 151.1, 163.9; MS (70 eV, EI) *m/z* (%) 292 [M^+, 40], 275 (4), 264 (8), 119 (100); HRMS calcd for $C_{17}H_{12}N_2O_3$ 292.0848, found 292.0850. Anal. Calcd for $C_{17}H_{12}N_2O_3$: C, 69.86; H, 4.14; N, 9.58. Found: C, 69.85; H, 4.16; N, 9.61. IR ($CHCl_3$) (ν, cm^{-1}) 3590, 1035, 895.

Di(1,3-benzoxazol-2-yl)methyl vinyl ether (20): R_f 0.20 (7:3 petroleum ether:diethyl ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.33 (dd, 1H, J = 6.6 Hz, J = 3.3 Hz), 4.65 (dd, 1H, J = 14.3 Hz, J = 3.3 Hz), 6.54 (s, 1H), 6.68 (dd, 1H, J = 14.3 Hz, J = 6.6 Hz), 7.30−7.50 (m, 4H), 7.50−7.65 (m, 2H), 7.55−7.88 (m, 2H); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ 69.9, 91.8, 111.3, 120.9, 125.0, 126.2, 140.2, 149.2, 151.3, 159.1; MS (70 eV, EI) *m/z* (%) 292 [M^+, 38], 264 (9), 249 (100); HRMS calcd for $C_{17}H_{12}N_2O_3$

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292.0848, found 292.0847. Anal. Calcd for $C_{17}H_{12}N_2O_3$: C, 69.86; H, 4.14; N, 9.58. Found: C, 69.84; H, 4.13; N, 9.60. IR ($CHCl_3$) (ν, cm^{-1}) 3600, 1016, 848.

1,1-Bis(1-methyl-1*H*-benzimidazol-2-yl)-2-propen-1-ol (22): orange solid; mp 143−145 °C (from CH_3OH); R_f 0.56 (diethyl ether); ^1H NMR (300 MHz, $CDCl_3$) δ 3.58 (s, 6H), 5.28 (d, 1H, J = 17.0 Hz), 5.50 (d, 1H, J = 10.0 Hz), 5.95−6.10 (br s, 1H, OH), 7.02 (dd, 1H, J = 17.0 Hz, J = 10.0 Hz), 7.25−7.35 (m, 6H), 7.78−7.85 (m, 2H); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ 50.7, 73.3, 109.5, 116.8, 120.0, 122.5, 123.4, 137.1, 137.7, 140.8, 152.7; MS (70 eV, EI) *m/z* (%) 318 [M^+, 51], 301 (26), 291 (18), 170 (59), 159 (100), 133 (74), 55 (87); HRMS calcd for $C_{19}H_{18}N_4O$ 318.1481, found 318.1480. Anal. Calcd for $C_{19}H_{18}N_4O$: C, 71.68; H, 5.70; N, 17.60. Found: C, 71.65; H, 5.73; N, 17.63. IR ($CHCl_3$) (ν, cm^{-1}) 3617, 3402, 1656, 1614, 1500, 1465, 1335, 1049, 965, 893.

1-(1,3-Benzothiazol-2-yl)-1-[4-(trifluoromethyl)phenyl]-2-propen-1-ol (26a): colorless oil; R_f 0.20 (8:2 petroleum ether:diethyl ether); ^1H NMR (300 MHz, $CDCl_3$) δ 4.10 (s, 1H, OH), 5.47 (d, 1H, J = 10.9 Hz), 5.52 (d, 1H, J = 17.5 Hz), 6.69 (dd, 1H, J = 17.5 Hz, J = 10.9 Hz), 7.36−7.44 (m, 1H), 7.46−7.53 (m, 1H), 7.58−7.65 (m, 2H), 7.70−7.76 (m, 2H), 7.84−7.90 (m, 1H), 8.00−8.05 (m, 1H); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ 82.9, 123.8 (q, J = 278.0 Hz, CF_3), 116.4, 121.7, 123.3, 125.4, 125.5 (q, J = 3.8 Hz, $CH{-}C{-}CF_3$), 126.3, 126.8, 130.7 (q, J = 34.9 Hz, $C{-}CF_3$), 135.3, 140.5, 149.3, 152.7, 176.0; MS (70 eV, EI) *m/z* (%) 335 [M^+, 58], 318 (77), 308 (27), 292 (99), 223 (78), 135 (100); HRMS calcd for $C_{17}H_{12}F_3NOS$ 335.0592, found 335.0588. Anal. Calcd for $C_{17}H_{12}F_3NOS$: C, 60.89; H, 3.61; N, 4.18. Found: C, 60.87; H, 3.64; N, 4.16. IR ($CHCl_3$) (ν, cm^{-1}) 3536, 1460, 1365, 1323, 1168, 1130, 1069, 1016, 844.

1-(1,3-Benzothiazol-2-yl)-1-(4-nitrophenyl)-2-propen-1-ol (26b): yellow oil; R_f 0.11 (8:2 petroleum ether:diethyl ether); ^1H NMR (300 MHz, $CDCl_3$) δ 4.35 (s, 1H, OH), 5.48 (d, 1H, J = 10.5 Hz), 5.52 (d, 1H, J = 17.0 Hz), 6.71 (dd, 1H, J = 17.0 Hz, J = 10.5 Hz), 7.35−7.60 (m, 2H), 7.80 (d, 2H, J = 8.5 Hz), 7.72−7.95 (m, 1H), 7.90−8.10 (m, 1H), 8.18 (d, 2H, J = 8.5 Hz); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ 78.6, 116.8, 121.7, 123.3, 125.1, 125.6, 126.4, 127.1, 135.2, 140.2, 147.4, 149.9, 152.6, 175.4; MS (70 eV, EI) *m/z* (%) 312 [M^+, 97], 295 (80), 283 (21), 269 (34), 223 (48), 162 (49), 135 (100); HRMS calcd for $C_{16}H_{12}N_2O_3S$ 312.0569, found 312.0571. Anal. Calcd for $C_{16}H_{12}N_2O_3S$: C, 61.53; H, 3.87; N, 8.97. Found: C, 61.51; H, 3.89; N, 9.00. IR ($CHCl_3$) (ν, cm^{-1}) 3594, 3364, 1603, 1523, 1351, 1259, 1099, 1015, 938, 854.

1-(1,3-Benzothiazol-2-yl)-1-(4-chlorophenyl)-2-propen-1-ol (26c): white solid, mp 115−117 °C (from CH_3OH); R_f 0.30 (8:2 petroleum ether:diethyl ether); ^1H NMR (300 MHz, $CDCl_3$) δ 4.00 (br s, 1H, OH), 5.45 (d, 1H, J = 10.5 Hz), 5.51 (d, 1H, J = 17.1 Hz), 6.67 (dd, 1H, J = 17.1 Hz, J = 10.5 Hz), 7.30−7.60 (m, 6H), 7.87 (dd, 1H, J = 7.3 Hz, J = 0.7 Hz), 8.02 (dd, 1H, J = 8.1 Hz, J = 0.7 Hz); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ 78.7, 116.1, 121.7, 123.2, 125.3, 126.2, 128.0, 128.5, 134.1, 135.4, 140.7, 141.7, 152.7, 176.5; MS (70 eV, EI) *m/z* (%) 301 [M^+, 24], 284 (10), 246 (10), 162 (30), 139 (30), 135 (73), 111 (37), 55 (100); HRMS calcd for $C_{16}H_{12}ClNOS$ 301.0328, found 301.0332. Anal. Calcd for $C_{16}H_{12}ClNOS$: C, 63.68; H, 4.01; N, 4.64. Found: C, 63.65; H, 4.03; N, 4.67. IR ($CHCl_3$) (ν, cm^{-1}) 3678, 3594, 3425, 1591, 1488, 1094, 1015, 942, 893, 820.

1-(1,3-Benzothiazol-2-yl)-1-(4-fluorophenyl)-2-propen-1-ol (26d): white solid, mp 148−150 °C (from CH_3OH); R_f 0.21 (8:2 petroleum ether:diethyl ether); ^1H NMR (300 MHz, $CDCl_3$) δ 3.99 (br s, 1H, OH), 5.44 (d, 1H, J = 10.5 Hz), 5.51 (d, 1H, J = 17.1 Hz), 6.67 (dd, 1H, J = 17.1 Hz, J = 10.5 Hz), 6.98−7.10 (m, 2H), 7.30−7.60 (m, 4H), 7.83−7.90 (m, 1H), 7.98−8.06 (m, 1H); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ 78.7, 115.3 (d, J = 21.6 Hz), 115.9, 121.8, 123.3, 125.3, 126.2, 128.5 (d, J = 8.1 Hz), 139.4 (d, J = 60 Hz), 141.0, 152.8, 160.9, 164.1, 176.5; MS (70 eV, EI) *m/z* (%) 285 [M^+, 27], 268 (51), 257 (22), 190 (6), 151 (18), 135 (100), 95 (54); HRMS calcd for $C_{16}H_{12}FNOS$ 285.0624, found 285.0621. Anal. Calcd for $C_{16}H_{12}FNOS$: C, 67.35; H, 4.24; N, 4.91. Found: C, 67.31; H, 4.23; N, 4.92. IR ($CHCl_3$) (ν, cm^{-1}) 3571, 3410, 1599, 1504, 1164, 1080, 935, 893, 843.

1-(1,3-Benzothiazol-2-yl)-1-phenyl-2-propen-1-ol (26e): white solid, mp 113−115 °C (from CH_3OH); R_f 0.32 (8:2 petroleum ether:diethyl ether); ^1H NMR (300 MHz, $CDCl_3$) δ 3.85 (s, 1H, OH), 5.45 (dd, 1H, J = 10.5 Hz, J = 0.8 Hz), 5.55 (dd, 1H, J = 17.1 Hz, J = 0.8 Hz), 6.73 (dd, 1H, J = 17.1 Hz, J = 10.5 Hz), 7.32−7.61 (m, 7H), 7.87 (dd, 1H, J = 8.0 Hz, J = 1.4 Hz), 8.04 (dd, 1H, J = 8.2 Hz, J = 0.8 Hz); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ 79.1, 115.6, 121.7, 123.3, 125.2, 126.1, 126.4, 128.2, 128.3, 128.5, 141.1, 143.3, 152.8, 176.7; MS (70 eV, EI) *m/z* 267 [M^+, 49], 250 (58), 239 (23), 224 (32), 212 (17), 190 (10), 162 (31), 135 (64), 105 (100), 77 (86), 55 (77); HRMS calcd for $C_{16}H_{13}NOS$ 267.0718, found 267.0720. Anal. Calcd for $C_{16}H_{13}NOS$: C, 71.88; H, 4.90; N, 5.24. Found: C, 71.85; H, 4.89; N, 5.22. IR ($CHCl_3$) (ν, cm^{-1}) 3686, 3594, 3433, 1675, 1591, 1492, 1320, 1068, 1026, 931, 893.

1-(1,3-Benzothiazol-2-yl)-1-(4-methoxyphenyl)-2-propen-1-ol (26f): white solid, mp 78−80 °C (from methanol); R_f 0.40 (6:4 petroleum ether:diethyl ether); ^1H NMR (300 MHz, $CDCl_3$) δ 4.04 (s, 3H), 4.29 (s, 1H, OH), 5.67 (dd, 1H, J = 10.5 Hz, J = 0.9 Hz), 5.78 (dd, 1H, J = 17.1 Hz, J = 0.9 Hz), 6.94 (dd, 1H, J = 17.1 Hz, J = 10.5 Hz), 7.13 (d, 2H, J = 9.0 Hz), 7.55−7.65 (m, 1H), 7.65−7.75 (m, 1H), 7.74 (d, 2H, J = 9.0 Hz), 8.10 (d, 1H, J = 8.0 Hz), 8.19 (d, 1H, J = 8.2 Hz); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ 55.2, 78.8, 113.7, 115.3, 121.6, 123.1, 125.0, 126.0, 127.8, 135.4, 135.5, 141.1, 152.8, 159.3, 177.4; MS (70 eV, EI) *m/z* (%) 297 [M^+, 11], 279 (4), 162 (21), 135 (100), 108 (16); HRMS calcd for $C_{17}H_{15}NO_2S$ 297.0824, found 297.0821. Anal. Calcd for $C_{17}H_{15}NO_2S$: C, 68.66; H, 5.08; N, 4.71. Found: C, 68.64; H, 5.10; N, 4.68. IR ($CHCl_3$) (ν, cm^{-1}) 3693, 3586, 3471, 1607, 1511, 1435, 1301, 1252, 1175, 1038, 988, 896, 832.

1,3-Benzothiazol-2-yl[4-(trifluoromethyl)phenyl]-methyl vinyl ether (27a): colorless oil, R_f 0.45 (8:2 petroleum ether:diethyl ether); ^1H NMR (300 MHz, $CDCl_3$) δ 4.26 (dd, 1H, J = 6.8 Hz, J = 2.5 Hz), 4.52 (dd, 1H, J = 14.3 Hz, J = 2.5 Hz), 6.36 (s, 1H), 6.56 (dd, 1H, J = 14.3 Hz, J = 6.8 Hz), 7.39 (td, 1H, J = 8.0 Hz, J = 1.3 Hz), 7.49 (td, 1H, J = 7.3 Hz, J = 1.3 Hz), 7.65 (d, 2H, J = 8.2 Hz), 7.72 (d, 2H, J = 8.2 Hz), 7.88 (dd, 1H, J = 8.2 Hz, J = 1.9 Hz), 8.03 (dd, 1H, J = 8.2 Hz, J = 0.6 Hz); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ 79.5, 91.8, 121.8, 123.3, 123.8 (q, J = 272.3 Hz, CF_3), 125.5, 125.7 (q, J = 3.6 Hz, $CH{-}C{-}CF_3$), 126.2, 126.9, 130.7 (q, J = 32.6 Hz, $C{-}CF_3$), 134.9, 141.9, 149.3, 152.6, 171.4; MS (70 eV, EI) *m/z* (%) 335 [M^+, 8], 292 (100), 223 (78); HRMS calcd for $C_{17}H_{12}F_3NOS$ 335.0592, found 335.0589. IR ($CHCl_3$) (ν, cm^{-1}) 3536, 1639, 1620, 1324, 1171, 1133, 1069, 1016, 959, 845.

1,3-Benzothiazol-2-yl(4-nitrophenyl)methyl vinyl ether (27b): pale yellow oil; R_f 0.24 (8:2 petroleum ether:diethyl ether); ^1H NMR (400 MHz, $CDCl_3$) δ 4.28 (dd, 1H, J = 6.7 Hz, J = 2.8 Hz), 4.51 (dd, 1H, J = 14.2 Hz, J = 2.8 Hz), 6.36 (s, 1H), 6.58 (dd, 1H, J = 14.2 Hz, J = 6.7 Hz), 7.36−7.52 (m, 2H), 7.76 (d, 2H, J = 8.5 Hz), 7.85−7.90 (m, 1H), 7.98−8.03 (m, 1H), 8.24 (d, 2H, J = 8.5 Hz); ^{13}C NMR (100.56 MHz, $CDCl_3$) δ 79.2, 92.1, 121.9, 123.4, 124.0, 125.6, 126.4, 127.5, 135.0, 144.9, 147.9, 149.3, 152.8, 170.4; MS (70 eV, EI) *m/z* (%) 312 [M^+, 9], 284 (12), 269 (57), 223 (100); HRMS calcd for $C_{16}H_{12}N_2O_3S$ 312.0569, found 312.0571. IR ($CHCl_3$) (ν, cm^{-1}) 3620, 1525, 1346, 1223, 1187, 1046, 928, 852.

1,3-Benzothiazol-2-yl(4-chlorophenyl)methyl vinyl ether (27c): colorless oil; R_f 0.50 (8:2 petroleum ether:diethyl ether); ^1H NMR (300 MHz, $CDCl_3$) δ 4.23 (dd, 1H, J = 6.8 Hz, J = 2.5 Hz), 4.50 (dd, 1H, J = 14.2 Hz, J = 2.5 Hz), 6.26 (s, 1H), 6.55 (dd, 1H, J = 14.2 Hz, J = 6.8 Hz), 7.36 (d, 2H, J = 8.4 Hz), 7.33−7.42 (m, 1H), 7.42−7.55 (m, 1H), 7.51 (d, 2H, J = 8.4 Hz), 7.87 (d, 1H, J = 8.0 Hz), 8.01 (d, 1H, J = 8.2 Hz); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ 79.6, 91.6, 121.8, 123.3, 125.4, 126.1, 128.0, 128.9, 134.5, 135.0, 136.6, 149.4, 152.7, 171.7; MS (70 eV, EI) *m/z* (%) 301 [M^+, 6], 258 (65), 223 (100), 139 (6), 111 (23); HRMS calcd for $C_{16}H_{12}ClNOS$ 301.0328, found

301.0330. IR ($CHCl_3$) (ν, cm^{-1}) 3609, 3533, 1641, 1622, 1488, 1316, 1187, 1095, 1015, 958, 843.

1,3-Benzothiazol-2-yl(4-fluorophenyl)methyl vinyl ether (27d): colorless oil; R_f 0.39 (8:2 petroleum ether:diethyl ether); ^1H NMR (300 MHz, $CDCl_3$) δ 4.22 (dd, 1H, J = 6.6 Hz, J = 2.5 Hz), 4.50 (dd, 1H, J = 14.3 Hz, J = 2.5 Hz), 6.25 (s, 1H), 6.55 (dd, 1H, J = 14.3 Hz, J = 6.6 Hz), 6.98−7.14 (m, 2H), 7.34−7.60 (m, 4H), 7.83−7.92 (m, 1H), 7.97−8.07 (m, 1H); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ 79.8, 91.5, 115.7 (d, J = 21.8 Hz), 121.8, 123.3, 125.3, 126.1, 128.5 (d, J = 8.4 Hz), 134.5 (d, J = 80 Hz), 149.5, 152.9, 161.1, 164.4, 171.8; MS (70 eV, EI) *m/z* (%) 285 [M^+, 4], 242 (100), 123 (11); HRMS calcd for $C_{16}H_{12}FNOS$ 285.0624, found 285.0622. IR ($CHCl_3$) (ν, cm^{-1}) 3627, 1639, 1624, 1506, 1200, 1183, 1160, 1057, 1016, 955, 928, 841.

1,3-Benzothiazol-2-yl(phenyl)methyl vinyl ether (27e): colorless oil; R_f 0.49 (8:2 petroleum ether:diethyl ether); ^1H NMR (400 MHz, $CDCl_3$) δ 4.22 (dd, 1H, J = 6.3 Hz, J = 2.5 Hz), 4.51 (dd, 1H, J = 14.0 Hz, J = 2.5 Hz), 6.28 (s, 1H), 6.58 (dd, 1H, J = 14.0 Hz, J = 6.3 Hz), 7.52−7.72 (m, 7H), 8.05 (dt, 1H, J = 8.7 Hz, J = 1.6 Hz, J = 0.9 Hz), 8.27 (dt, 1H, J = 7.2 Hz, J = 2.2 Hz, J = 0.6 Hz); ^{13}C NMR (100.56 MHz, $CDCl_3$) δ 80.4, 91.3, 121.8, 123.3, 125.2, 126.0, 126.7, 128.7, 128.8, 135.1, 138.1, 149.7, 152.9, 172.1; MS (70 eV, EI) *m/z* (%) 267 [M^+, 2], 239 (2), 224 (100), 190 (2), 112 (10); HRMS calcd for $C_{16}H_{13}NOS$ 267.0718, found 267.0722. IR ($CHCl_3$) (ν, cm^{-1}) 3597, 1597, 1479, 1289, 1183, 1118, 932, 890, 837.

2-[1-(1,3-Benzothiazol-2-yl)-1-deuterio-2-propenyl]-1,3-benzothiazole (29): Compound **29** was obtained following the general procedure described above, with the modification that the reaction mixture was quenched with deuterium oxide (isotopic purity: 99.990%), treated with anhydrous sodium sulfate, filtered, and analyzed by ^1H, ^{13}C NMR, and mass spectrometry. ^1H NMR (300 MHz, CD_3COCD_3) δ 4.47 (dd, 1H, J = 6.6 Hz, J = 2.5 Hz), 4.83 (dd, 1H, J = 14.0 Hz, J = 2.5 Hz), 6.94 (dd, 1H, J = 14.0 Hz, J = 6.6 Hz), 7.53−7.76 (m, 4H), 8.17 (dd, 2H, J = 8.1 Hz, J = 1.2 Hz), 8.26 (dd, 2H, J = 8.7 Hz, J = 1.4 Hz); ^{13}C NMR (75.46 MHz, CD_3COCD_3) δ 79.3 (t, J_{C-D} = 23 Hz), 93.0, 123.5, 124.7, 127.1, 127.7, 136.6, 150.9, 154.2, 169.1; MS (70 eV, EI) *m/z* (%) 325 [M^+, 6], 324 (12), 282 (68), 281 (100), 268 (10), 248 (11), 162 (13), 146 (17), 134 (17).

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Supporting Information Available: General experimental details and copies of ^1H NMR and ^{13}C NMR spectra of compounds **25a**, **25d**, and **27a**−**e**. This material is available free of charge via the Internet at http://pubs.acs.org.

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