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Regioselective Ortho Olefination of Aryl Sulfonamide via Rhodium-Catalyzed Direct C−H Bond Activation

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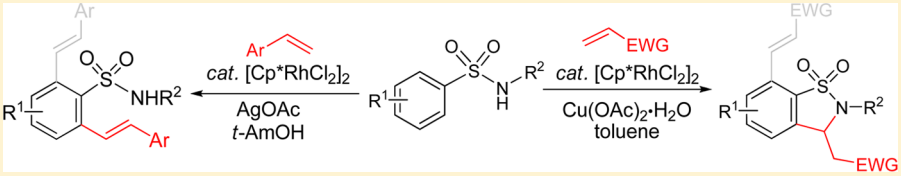
Supporting Information



ABSTRACT: Rh(III)-catalyzed ortho C−H olefination of aryl sulfonamide directed by the SO_2NHAc group is reported. This oxidative coupling process is achieved highly efficiently and selectively with a broad substrate scope. The reactions of *N*-tosylacetamide with acrylate esters afford ortho-alkenylated benzofused five-membered cyclic sulfonamides, whereas styrenes provide the direct diolefination products.

INTRODUCTION

Transition-metal-catalyzed C−H functionalization of arenes represents a step-economical and waste-reducing process, because no prior functionalization of the substrate is necessary.[1] Its synthetic applications have been well identified in the fields of organic synthesis, medicinal chemistry, and materials science.[2] In this regard, the Fujiwara−Moritani reaction[3]—oxidative olefination of normally inert aryl C−H bonds—is an attractive alternative to the traditional Mizoroki−Heck reaction.[4] Among such transformations, palladium(II) complexes have been extensively explored and widely used due to their remarkable activities.[5] Later, after the pioneering work of Satoh and Miura, rhodium(III)[6] and ruthenium(II)[7,8] species were also found to exhibit high catalytic activity in the oxidative alkenylation reactions. In these reactions, the utility of a neighboring directing group has proven to be one of the most promising strategies for ensuring regioselective C−H activation.[9]

Sulfonamide functional groups have long been acclaimed as essential structural motifs presented in drugs such as darunavir, celecoxib, and gliclazide.[10] Meanwhile, sultams (cyclic sulfonamides) have emerged as privileged structures in drug discovery due to their diverse biological properties.[11] In particular, a number of benzofused sultams have shown promising bioactivity for treating disorders of the brain[12] and exhibit broad inhibitory properties against a variety of enzymes (Figure 1).[13] Recent studies reveal that the sulfonamide group can act as a directing group in promoting C−H activation; however, only very limited examples have been documented.[14,15] In 1998, Miura demonstrated the olefination reaction of *N*-(2′-phenylphenyl)benzenesulfonamides with acrylate esters via cleavage of the C−H bond at the 2′-position.[15a] In 2011, Li reported a rhodium(III)-catalyzed C−H olefination of *N*-(1-naphthyl)sulfonamides at the peri position.[15b] Later, this group described a Rh(III)-catalyzed oxidative coupling between *N*-allyl sulfonamides with activated olefins.[15c] For these substrates, the C−H bonds of arenes connected to sulfonamide sulfur atoms are totally inert under the reaction conditions (Scheme 1). With the assistance of $SO_2NHC_6F_5$ as a directing group, Yu reported Pd-catalyzed sulfonamide C−H olefination. The reactions only produce direct alkenylation products, irrespective of the alkenes employed (Scheme 1a).[15d] As a continuation of our interest in Ru- and Rh-catalyzed C−H functionalization,[16] we herein disclose our recent development of Rh-catalyzed regioselective oxidative C−H olefination using SO_2NHAc as a directing

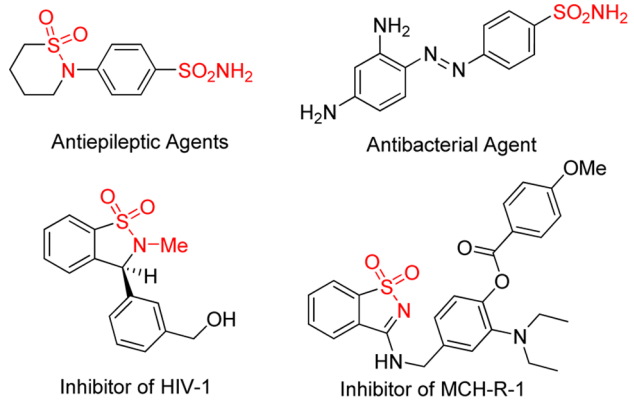


Figure 1. Biologically active molecules containing the sulfonamide or sultam substructure motif.

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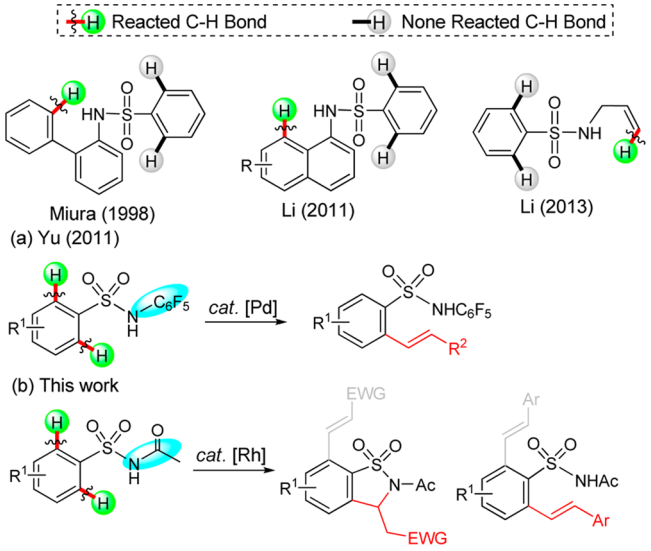
Scheme 1. Sulfonamide Group Directed Oxidative Olefination



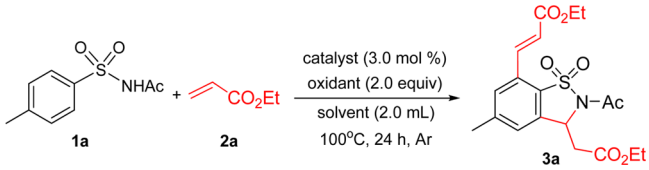
group. The reactions afford ortho-alkenylated benzofused sultam analogues and diolefinated aryl sulfonamides with good yields and a broad reaction scope (Scheme 1b).

RESULTS AND DISCUSSION

We initiated our study with the oxidative olefination of readily available *N*-tosylacetamide (**1a**) and ethyl acrylate (**2a**). After a considerable number of experiments (Table 1),[17] we found that product **3a**, which was formed by dialkenylation at both ortho positions followed by intramolecular hydroamination, was obtained in 93% yield in the presence of $[Cp^*RhCl_2]_2$ (3.0 mol %) and $Cu(OAc)_2{\cdot}H_2O$ (2.0 equiv) in toluene at 100 °C under an Ar atmosphere for 24 h (entry 1, Table 1). No monoalkenylated cycloadduct was observed. The structure of **3a** was confirmed by ^1H and ^{13}C NMR analysis and mass spectrometry. The solvents DME and CH_3CN exhibited negative results (entries 2 and 3). A change of oxidant to AgOAc, Ag_2CO_3, or O_2 led to a low yield or a trace amount of the desired product (entries 4–6). Reducing the amount of $[Cp^*RhCl_2]_2$ from 3.0 to 2.0 mol % provided **3a** in 82% yield (entry 7). It is interesting to find that when switching the ratio of **1a** and **2a** to 1:1 and 2:1, the reactions still gave dominantly the dialkenylation product **3a** and the monoalkenylated cycloadduct was detected in 16% and 25% yields by ^1H NMR, respectively (entries 8 and 9). The reaction efficiency was also sensitive to the reaction temperatures (entry 10). Some other rhodium complexes were also screened. For example, when $[Cp^*Rh(OAc)_2]$ was applied as a catalyst, the reaction still afforded dialkenylation product **3a**, albeit in relatively lower yield (entry 11). However, the cationic rhodium species $[Cp^*Rh(MeCN)_3][SbF_6]_2$, generated in situ by the addition of $AgSbF_6$, totally inhibited the reaction (entry 12). A control experiment confirmed that the transformation did not proceed in the absence of the rhodium catalyst (entry 13). Finally, $[Ru(p\text{-cymene})Cl_2]_2$ displayed no catalytic activity under the present reaction conditions (entry 14).

With the promising optimal conditions, we first investigated the influence of different substituents on the sulfonamide nitrogen atom (Scheme 2). In addition to the acetyl group, the butyryl group was also well suited and gave the product **3b**

Table 1. Optimization of Oxidative Coupling between 1a and 2a[a]



entry	catalyst	oxidant (amt (equiv))	solvent	yield (%)[b]
1	$[Cp^*RhCl_2]_2$	$Cu(OAc)_2{\cdot}H_2O$	toluene	99 (93)[c]
2	$[Cp^*RhCl_2]_2$	$Cu(OAc)_2{\cdot}H_2O$	DME	10
3	$[Cp^*RhCl_2]_2$	$Cu(OAc)_2{\cdot}H_2O$	CH_3CN	NR
4	$[Cp^*RhCl_2]_2$	Ag_2CO_3	toluene	trace
5	$[Cp^*RhCl_2]_2$	AgOAc	toluene	48
6	$[Cp^*RhCl_2]_2$	$Cu(OAc)_2{\cdot}H_2O$ (0.5) + O_2	toluene	trace
7	$[Cp^*RhCl_2]_2$	$Cu(OAc)_2{\cdot}H_2O$	toluene	82[d]
8	$[Cp^*RhCl_2]_2$	$Cu(OAc)_2{\cdot}H_2O$	toluene	54[e]
9	$[Cp^*RhCl_2]_2$	$Cu(OAc)_2{\cdot}H_2O$	toluene	40[f]
10	$[Cp^*RhCl_2]_2$	$Cu(OAc)_2{\cdot}H_2O$	toluene	NR[g]
11	$[Cp^*Rh(OAc)_2]$	$Cu(OAc)_2{\cdot}H_2O$	toluene	65[h]
12	$[Cp^*RhCl_2]_2$/ $AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	toluene	NR[i]
13	none	$Cu(OAc)_2{\cdot}H_2O$	toluene	NR
14	$[Ru(p\text{-cymene})Cl_2]_2$	$Cu(OAc)_2{\cdot}H_2O$	toluene	NR

[a]Reaction conditions: **1a** (0.3 mmol), **2a** (0.9 mmol). [b]Yield determined by ^1H NMR (internal standard: 1,1,2,2-tetrachloroethane). NR = no reaction. [c]Value in parentheses indicates yield after purification. [d]2.0 mol % of $[Cp^*RhCl_2]_2$ was used. [e]**1a**:**2a** (1:1); the monoalkenylated cycloadduct was also formed in 16% yield. [f]**1a**:**2a** (2:1), **2a** (0.3 mmol); the monoalkenylated cycloadduct was also formed in 25% yield. [g]80 °C. [h]4.0 mol % of $[Cp^*Rh(OAc)_2]$ was used. [i]12.0 mol % of $AgSbF_6$ was used.

under the optimized reaction conditions in 97% yield. However, the pivaloyl, *N*-methoxy, and *N*-acrylyl derivatives were completely unreactive.

We next examined the scope of aryl sulfonamides with diverse arene substituents (Scheme 2). Gratifyingly, the reaction proceeded smoothly irrespective of the electronic nature of the substituents to afford the desired products in good to excellent yields. Many important functional groups, such as fluoro, chloro, bromo, methoxy, trifluoromethoxy, and ester substituents, were compatible in the present catalytic reaction (**3d–i**). Surprisingly, in addition to the desired product **3j**, a substrate with a nitro substituent also afforded the nitro group reduced byproduct **3k** in 16% yield. This result suggested that the nitro group might partially act as an oxidant in this reaction. The meta-substituted substrates were then studied. Both naphthalen-2-yl and 3-bromophenyl sulfonyl acetamide reacted with acrylates to form **3l–n** as the sole products. Interestingly, the cyclizations occurred at the sterically more hindered position in compounds **3l–n**, which were confirmed by NOESY spectroscopy of **3l,m**.[17] The exact reason for the selective ring formation is not clear yet, although it seems that the adjacent steric hindrance of meta-substituted group to the alkene could be partially involved. Notably, a substrate bearing a 3-CF_3 moiety underwent the olefination to provide monoolefinic products **4a,b** in moderate yield. The monofunctionalization in **4a,b** might result from the combined electronic and steric effects of the meta-substituted CF_3 group. Ortho-substituted aryl sulfonamides coupled with ethyl acrylate

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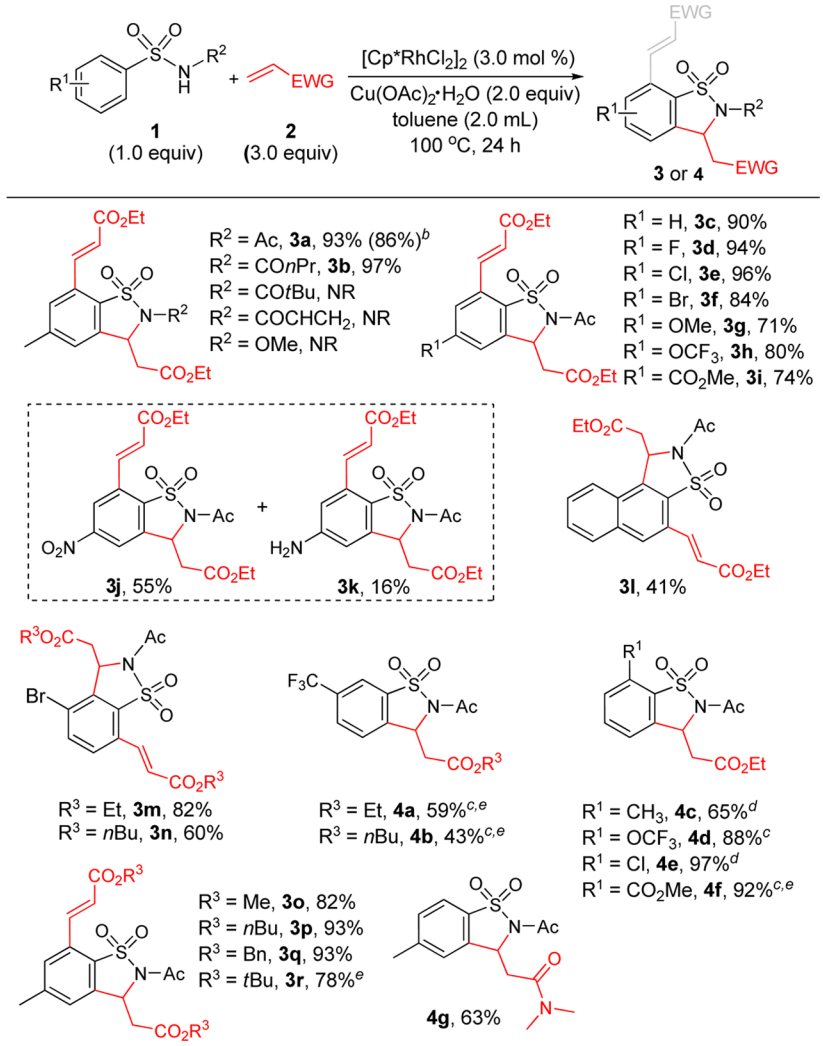
Scheme 2. Rhodium-Catalyzed Oxidative C−H Olefination with Acrylic Acid Esters[a]



[a]Reaction on a 0.3 mmol scale. Yields of isolated products are given. NR = no reaction. [b]The value in parentheses indicates the yield of the reaction on a 3.0 mmol scale. [c]5.0 mol % of $[Cp^*RhCl_2]_2$ was used. [d]2.0 equiv of **2** was used. [e]At 120 °C.

smoothly, leading to the formation of monoalkenylated cyclization products **4c−f**. Moreover, various acrylates, including methyl acrylate, butyl acrylate, benzyl acrylate, and *tert*-butyl acrylate, efficiently reacted with **1a** to produce the corresponding products **3o−r**. In contrast to the acrylate, *N,N*-dimethylacrylamide reacted with **1a** in a 1:1 ratio, resulting in the formation of cyclization product **4g**. Nonetheless, other alkenes bearing electron-withdrawing groups, such as (phenylsulfonyl)ethane, diethyl vinylphosphonate, and ethyl vinyl ketone were not suitable substrates for this reaction and gave the desired products in very low yield (<5%).

Subsequently, styrene was tested as a coupling partner in our catalytic reaction. However, no corresponding alkenylated product was observed under the optimized reaction conditions described above. Thus, the reaction was examined with various solvents and oxidants.[17] It is interesting to see in the present reaction system that copper acetate is advantageous in comparison to silver acetate as an oxidant in the reaction with acrylate esters, while the use of silver acetate gave a better result in the reaction with styrenes. Consequently, it was found that **1a** coupled with styrene **5a** (4.0 equiv) efficiently by employing AgOAc as oxidant and *t*-AmOH as solvent to give the dialkenylated derivative **6a** in 81% yield (entry 1, Table 2). In this reaction, no cyclization process occurred. Under the reaction conditions, various substituted styrenes with either electron-donating or -withdrawing groups were good candidates and produced the corresponding products **6b−h** in moderate to high yield (entries 2−8). The reaction is also tolerant of different substitutions on the aromatic sulfonamides. For example, 4-chloro- and 4-methoxy-substituted aryl sulfonamides also reacted well with **5a** (entries 9 and 10). Examination of the meta-substituted substrate scope revealed that 3-bromophenyl sulfonyl acetamide only produced dialkenylated derivative **6k**, albeit in low yield (entry 11). However, the reaction of a substrate bearing a 3-CF_3 group afforded monoalkenylated product **7a** (entry 12), which is consistent with the result of the reaction with acrylate.

To our delight, the reactions can be easily performed on a large scale; for example, **3a** and **6a** were isolated in 86% (Scheme 2) and 70% yields (Table 2) on a 3.0 mmol scale, respectively. Since the *N*-acyl sulfonamide directing group is relatively labile, it can be easily removed under mildly basic conditions to give **8** (eq 1). The double bond of the enesulfonamide **8** and **6a** can be reduced by $NiCl_2{\cdot}6H_2O$/

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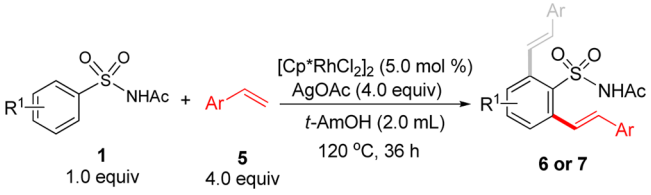
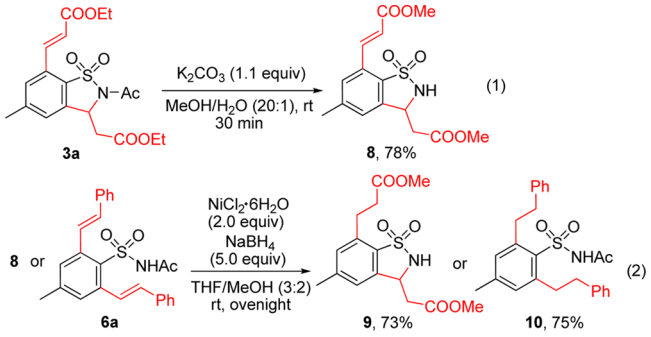
Table 2. Rhodium-Catalyzed Oxidative C−H Olefination of 1 with Styrene[a]



entry	R^1	Ar	product, yield (%)
1	4-Me	Ph	**6a**, 81 (70)[b]
2	4-Me	4-MeC_6H_4	**6b**, 73
3	4-Me	4-$tBuC_6H_4$	**6c**, 80
4	4-Me	4-$MeOC_6H_4$	**6d**, 76
5	4-Me	4-FC_6H_4	**6e**, 87
6	4-Me	4-ClC_6H_4	**6f**, 93
7	4-Me	4-BrC_6H_4	**6g**, 94
8	4-Me	C_6F_5	**6h**, 59
9	4-Cl	Ph	**6i**, 67
10	4-OMe	Ph	**6j**, 56
11	3-Br	Ph	**6k**, 30
12	3-CF_3	Ph	**7a**, 86

[a]Reaction on a 0.3 mmol scale. Yields of isolated products are given. [b]The value in parentheses indicates the yield of the reaction on a 3.0 mmol scale.

$NaBH_4$ to give the saturated products **9** and **10**, respectively (eq 2).

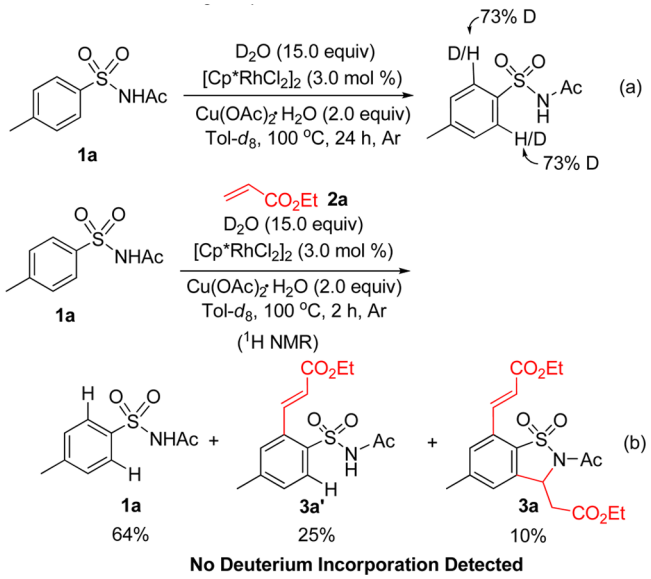


To probe the possible mechanism, we conducted some H/D exchange experiments with isotopically labeled solvents (Scheme 3a). When the reaction of **1a** was conducted with D_2O in the absence of acrylate, 73% deuterium incorporation was observed at the two ortho positions of the aryl ring of **1a** (Scheme 3a). This result suggested that a reversible cyclometalation mode was involved. If the same reaction was conducted in the presence of **2a**, no deuterium incorporation was detected in recovered **1a**, monoalkenylated product **3a′**, and dialkenylated product **3a** (Scheme 3b). This result is similar to those of the investigations by Loh and Zhang.[18] In both experiments, no N−H deuteration was observed, which could be rationalized by the easy N−D/H exchange during the workup on silica gel chromatography.

CONCLUSIONS

In conclusion, we have successfully established the Rh(III)-catalyzed ortho C−H olefination of aryl sulfonamide directed by the SO_2NHAc group. This oxidative coupling process is achieved highly efficiently and selectively with a broad substrate scope. The reactions of *N*-tosylacetamide with acrylate esters

Scheme 3. H/D Exchange Experiment



afford ortho-alkenylated benzofused five-membered cyclic sulfonamides, whereas styrenes provide the directed diolefination products. In Yu's report, $SO_2NHC_6F_5$-directed Pd-catalyzed benzenesulfonamide yielded exclusively the mono-olefinated acyclic product. Thus, our method is complementary to previously reported methods based on the use of palladium catalyst.[15d] Considering the importance of aryl sulfonamides as well as aryl sultams as core structures in pharmacologically active substances, this method should be attractive for both synthetic and medicinal chemistry.

EXPERIMENTAL SECTION

General Procedures. All reactions were carried out under an argon atmosphere using standard Schlenk techniques. ^1H NMR (400 MHz), ^{19}F NMR (376 MHz), and $^{13}C\{^1H\}$ NMR (100 MHz) were recorded with $CDCl_3$ or DMSO-d_6 as solvent. Chemical shifts of ^1H, ^{19}F, and $^{13}C\{^1H\}$ NMR spectra are reported in parts per million (ppm). The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$, δ_H 7.26 ppm, δ_C 77.00 ppm; DMSO-d_6, δ_H 2.50 ppm, δ_C 39.52 ppm). HRMS were measured on FTICR-mass spectrometers. $[Cp^*RhCl_2]_2$ was prepared from $RhCl_3{\cdot}xH_2O$ following a literature procedure.[19]

General Procedure for Synthesis of Substrates 1. *General Procedure I.*[20] The free sulfonamide (4.65 mmol, 1.0 equiv), anhydrous $ZnCl_2$ (63.3 mg, 465 μmol, 0.10 equiv), and Ac_2O (3.95 mL, 41.8 mmol) were mixed and stirred at 23 °C for 1−14 h and then poured into a mixture of EtOAc (50.0 mL) and H_2O (50.0 mL). The layers were separated, and the aqueous layer was extracted with EtOAc. The combined organic layers were dried over Na_2SO_4, concentrated in vacuo, and then purified by silica gel chromatography (eluent EtOAc/petroleum ether 1/3, typically).

General Procedure II.[21] To a cold suspension (0 °C) of 4-methylbenzenesulfonamide (500 mg, 2.92 mmol) and powdered KOH (492 mg, 8.76 mmol, 3.0 equiv) in CH_2Cl_2 (10.0 mL) was added a solution of acyl chloride (2.92 mmol, 1.0 equiv) in CH_2Cl_2 (10.0 mL). The mixture was stirred for 2 h at 23 °C, and water (20 mL) was added. After acidification with 1 N HCl solution (9.0 mL), the product was extracted with EtOAc (3 × 50 mL). The combined organic layers were dried over Na_2SO_4, concentrated in vacuo, and then purified by silica gel chromatography (eluent EtOAc/petroleum ether 1/3, typically).

General Procedure III. Methoxyamine hydrochloride (1003.3 mg, 12.0 mmol, 1.2 equiv) was added to a biphasic mixture of K_2CO_3 (2763.3 mg, 20.0 mmol, 2.0 equiv) in a 2/1 mixture of EtOAc (72

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mL) and H_2O (36 mL). The resulting solution was cooled to 0 °C, followed by dropwise addition of 4-methylbenzene-1-sulfonyl chloride dissolved in a minimum amount of EtOAc. The reaction mixture was stirred overnight while it was warmed to room temperature. Afterward, the phases were separated and the aqueous phase was extracted twice with EtOAc. The combined organic layers were dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The pure products were obtained without any further purification.

All phenylsulfonylacetamides were synthesized according to the literature procedures, and the yields were not optimized. Substrates **1a,b,d−g,i,j,l,m,p** were synthesized through general procedure I. Substrates **1q−s** were synthesized through general procedure II. For the known substrates, ^{1}H and ^{13}C NMR spectral data showed good agreement with the literature data.[22] Below we summarize characterization data for the newly synthesized phenyl sulfonylacetamides.

*N-(4-Fluorophenylsulfonyl)acetamide (**1c**).* This compound was obtained as a white solid (807.6 mg, 80%) by following general procedure I: mp 124−126 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.83 (s, 1H), 8.10 (dd, J = 8.7, 5.0 Hz, 2H), 7.23 (d, J = 8.5 Hz, 2H), 2.08 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 168.3, 165.9 (d, J_{C-F} = 257.2 Hz), 134.2 (d, J_{C-F} = 3.0 Hz), 131.3 (d, J_{C-F} = 9.7 Hz), 116.4 (d, J_{C-F} = 22.8 Hz), 23.5; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −102.4; IR (cm^{-1}) ν 3121, 2901, 2806, 2694, 1694, 1586, 1458, 1350, 1229, 1097, 811, 537; HRMS (ESI) calcd for $C_8H_9FNO_3S$ $[M + H]^+$ 218.0282, found 218.0281.

*Methyl 4-(N-Acetylsulfamoyl)benzoate (**1h**).* This compound was obtained as a white solid (1051.9 mg, 88%) by following general procedure I: mp 188−190 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 12.31 (s, 1H), 8.17 (d, J = 7.9 Hz, 2H), 8.05 (d, J = 7.8 Hz, 2H), 3.90 (s, 3H), 1.94 (s, 3H); $^{13}C\{^1H\}$ NMR (DMSO-d_6, 100 MHz) δ 169.1, 165.1, 143.2, 133.9, 129.9, 128.0, 52.8, 23.3; IR (cm^{-1}) ν 3224, 3108, 2951, 1735, 1565, 1420, 1333, 1300, 1163, 997, 860, 699, 595; HRMS (ESI) calcd for $C_{10}H_{12}NO_5S$ $[M + H]^+$ 258.0431, found 258.0433.

*N-(2-(Trifluoromethoxy)phenylsulfonyl)acetamide (**1k**).* This compound was obtained as a white solid (1184.7 mg, 90%) by following general procedure I: mp 166−168 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 12.53 (s, 1H), 8.07 (d, J = 7.7 Hz, 1H), 7.84 (t, J = 7.9 Hz, 1H), 7.61 (t, J = 6.9 Hz, 2H), 1.95 (s, 3H); $^{13}C\{^1H\}$ NMR (DMSO-d_6, 100 MHz) δ 168.9, 145.1, 136.1, 132.2, 131.1, 127.5, 120.9, 119.9 (q, J_{C-F} = 259.5 Hz), 23.0; ^{19}F NMR (DMSO-d_6, 376 MHz) δ −56.1; IR (cm^{-1}) ν 3096, 2888, 2694, 1698, 1478, 1354, 1205, 1134, 1059, 856, 765, 603; HRMS (ESI) calcd for $C_9H_9F_3NO_4S$ $[M + H]^+$ 284.0199, found 284.0205.

*N-(3-Bromophenylsulfonyl)acetamide (**1n**).* This compound was obtained as a white solid (956.6 mg, 74%) by following general procedure I: mp 131−133 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.44 (s, 1H), 8.18 (s, 1H), 8.02 (d, J = 7.9 Hz, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.45 (t, J = 8.0 Hz, 1H), 2.10 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 168.3, 140.0, 137.2, 131.0, 130.6, 127.0, 122.8, 23.6; IR (cm^{-1}) ν 3088, 2880, 2806, 1702, 1474, 1354, 1155, 1006, 790, 661, 558; HRMS (ESI) calcd for $C_8H_9BrNO_3S$ $[M + H]^+$ 277.9481, found 277.9483.

*N-(3-(Trifluoromethyl)phenylsulfonyl)acetamide (**1o**).* This compound was obtained as a white solid (968.4 mg, 78%) by following general procedure I: mp 125−127 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.65 (s, 1H), 8.31 (d, J = 5.7 Hz, 2H), 7.93 (d, J = 7.8 Hz, 1H), 7.73 (t, J = 8.2 Hz, 1H), 2.11 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 168.4, 139.4, 131.8, 131.7 (d, J_{C-F} = 33.3 Hz), 130.8 (d, J_{C-F} = 3.3 Hz), 129.9, 125.3 (q, J_{C-F} = 3.6 Hz), 123.0 (d, J_{C-F} = 273.0 Hz), 23.5; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −62.8; IR (cm^{-1}) ν 3092, 2888, 2718, 1690, 1495, 1329, 1171, 1118, 1010, 798, 603; HRMS (ESI) calcd for $C_9H_9F_3NO_3S$ $[M + H]^+$ 268.0250, found 268.0250.

*N-Tosylacrylamide (**1s**).* This compound was obtained as a white solid (499.3 mg, 76%) by following general procedure II: mp 158−160 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.49 (bs, 1H), 7.98 (d, J = 8.1 Hz, 2H), 7.35 (d, J = 8.2 Hz, 2H), 6.38 (d, J = 17.0 Hz, 1H), 6.10 (dd, J = 16.7, 10.7 Hz, 1H), 5.83 (d, J = 10.5 Hz, 1H), 2.44 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 162.7, 145.3, 135.3, 131.5, 129.7, 129.6, 128.4, 21.7; IR (cm^{-1}) ν 3622, 3228, 2855, 1702, 1599, 1441, 1325, 1155, 1076, 819, 549; HRMS (ESI) calcd for $C_{10}H_{12}NO_3S$ $[M + H]^+$ 226.0532, found 226.0533.

*N-Methoxy-4-methylbenzenesulfonamide (**1t**).* This compound was obtained as a white solid (2170.8 mg, 90%) by following general procedure III: mp 109−111 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.81 (d, J = 8.3 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H), 7.01 (s, 1H), 3.79 (s, 3H), 2.45 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) 144.9, 133.5, 129.7, 128.5, 65.0, 21.7; IR (cm^{-1}) ν 3224, 2938, 1922, 1590, 1400, 1329, 1159, 1030, 922, 827, 748, 570; HRMS (ESI) calcd for $C_8H_{12}NO_3S$ $[M + H]^+$ 202.0532, found 202.0537.

Preparation of the Product 3 or 4 (General Procedure A). A mixture of sulfonamide **1** (0.30 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (5.6 mg, 0.009 mmol, 3.0 mol %), and $Cu(OAc)_2{\cdot}H_2O$ (120 mg, 0.60 mmol, 2.0 equiv) were weighed in a 50 mL Schlenk tube equipped with a stir bar. Dry toluene (2.0 mL) was added followed immediately by the alkene **2** (0.9 mmol, 3.0 equiv), and the mixture was stirred at 100 °C for 24 h under an Ar atmosphere. Afterward, the vial was cooled to room temperature, diluted with CH_2Cl_2, and transferred to a round-bottom flask. Silica was added to the flask, and the volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel (eluent EtOAc/petroleum ether 1/3, typically).

*Ethyl (N-Acetyl-1,1-dioxo-5-methyl-(E)-7-(ethoxy-3-oxoprop-1-enyl)benzo[d]isothiazol-3-yl)acetate (**3a**).* This compound was obtained as a light yellow solid (115.0 mg, 93%) by following general procedure A: mp 126−128 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.02 (d, J = 15.9 Hz, 1H), 7.55 (s, 1H), 7.34 (s, 1H), 6.63 (d, J = 15.9 Hz, 1H), 5.65 (d, J = 6.2 Hz, 1H), 4.29 (q, J = 7.1 Hz, 2H), 4.14 (q, J = 7.1 Hz, 2H), 3.16−3.10 (m, 1H), 2.93 (dd, J = 16.1, 7.7 Hz, 1H), 2.61 (s, 3H), 2.48 (s, 3H), 1.34 (t, J = 7.1 Hz, 3H), 1.20 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 169.5, 167.3, 165.4, 145.6, 136.1, 135.6, 130.8, 129.4, 128.7, 126.0, 124.4, 61.1, 61.0, 54.7, 39.0, 23.6, 21.8, 14.2, 14.0; IR (cm^{-1}) ν 3560, 3411, 2984, 1735, 1706, 1378, 1275, 1212, 1026, 868, 619; HRMS (ESI) calcd for $C_{19}H_{24}NO_7S$ $[M + H]^+$ 410.1268, found 410.1275.

*Ethyl (N-Butyryl-1,1-dioxo-5-methyl-(E)-7-(ethoxy-3-oxoprop-1-enyl)benzo[d]isothiazol-3-yl)acetate (**3b**).* This compound was obtained as a white solid (128.7 mg, 97%) by following general procedure A: mp 96−98 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.97 (d, J = 15.9 Hz, 1H), 7.52 (s, 1H), 7.31 (s, 1H), 6.58 (d, J = 15.9 Hz, 1H), 5.62 (dd, J = 7.5, 3.2 Hz, 1H), 4.24 (q, J = 7.1 Hz, 2H), 4.08 (t, J = 7.1 Hz, 2H), 3.06 (dd, J = 16.0, 3.3 Hz, 1H), 2.94 (dd, J = 16.2, 7.5 Hz, 1H), 2.91−2.79 (m, 2H), 2.44 (s, 3H), 1.80−1.71 (m, 2H), 1.30 (t, J = 7.1 Hz, 3H), 1.15 (t, J = 7.1 Hz, 3H), 0.98 (t, J = 7.4 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 170.5, 169.4, 165.3, 145.4, 136.1, 135.5, 130.7, 129.6, 128.6, 125.9, 124.3, 61.0, 60.9, 54.6, 39.0, 37.5, 21.7, 17.7, 14.1, 13.9, 13.4; IR (cm^{-1}) ν 3394, 2979, 1731, 1640, 1320, 1179, 1071, 972, 669, 540; HRMS (ESI) calcd for $C_{21}H_{28}NO_7S$ $[M + H]^+$ 438.1581, found 438.1587.

*Ethyl (N-Acetyl-1,1-dioxo-(E)-7-(ethoxy-3-oxoprop-1-enyl)benzo-[d]isothiazol-3-yl)acetate (**3c**).* This compound was obtained as a light yellow solid (106.8 mg, 90%) by following general procedure A: mp 89−91 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.07 (d, J = 15.9 Hz, 1H), 7.76 (d, J = 7.7 Hz, 1H), 7.69 (t, J = 7.7 Hz, 1H), 7.57 (d, J = 7.7 Hz, 1H), 6.64 (d, J = 15.9 Hz, 1H), 5.71 (dd, J = 7.7, 3.3 Hz, 1H), 4.30 (q, J = 7.1 Hz, 2H), 4.13 (q, J = 7.1 Hz, 2H), 3.16 (dd, J = 16.1, 3.3 Hz, 1H), 2.95 (dd, J = 16.1, 7.8 Hz, 1H), 2.62 (s, 3H), 1.35 (t, J = 7.1 Hz, 3H), 1.19 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 169.5, 167.3, 165.3, 135.9, 135.4, 134.3, 132.1, 131.2, 127.8, 125.7, 124.8, 61.2, 61.1, 54.8, 39.0, 23.6, 14.2, 14.0; IR (cm^{-1}) 3564, 3481, 2992, 1731, 1702, 1374, 1283, 1158, 1042, 959, 594; HRMS (ESI) calcd for $C_{18}H_{22}NO_7S$ $[M + H]^+$ 396.1112, found 396.1119.

*Ethyl (N-Acetyl-1,1-dioxo-5-fluoro-(E)-7-(ethoxy-3-oxoprop-1-enyl)benzo[d]isothiazol-3-yl)acetate (**3d**).* This compound was obtained as a light yellow solid (116.1 mg, 94%) by following general procedure A: mp 141−143 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.97 (d, J = 15.8 Hz, 1H), 7.42 (d, J = 9.0 Hz, 1H), 7.30 (t, J = 6.7 Hz, 1H), 6.60 (d, J = 15.8 Hz, 1H), 5.66 (dd, J = 8.0, 2.7 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 4.13 (q, J = 7.1 Hz, 2H), 3.15 (dd, J = 16.4, 3.0 Hz, 1H), 2.91 (dd, J = 16.3, 8.1 Hz, 1H), 2.58 (s, 3H), 1.32 (t, J = 7.1 Hz, 3H),

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1.20 (d, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 169.4, 167.0, 165.7 (d, $J_{C\text{-}F}$ = 257.1 Hz), 164.9, 139.1 (d, $J_{C\text{-}F}$ = 10.4 Hz), 134.3, 134.0 (d, J_{C-F} = 9.0 Hz), 128.2 (d, J_{C-F} = 2.0 Hz), 126.0, 115.3 (d, J_{C-F} = 24.9 Hz), 113.1 (d, J_{C-F} = 25.1 Hz), 61.3, 61.2, 54.5 (d, $J_{C\text{-}F}$ = 2.0 Hz), 38.7, 23.6, 14.1, 13.9; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −101.3; IR (cm^{-1}) ν 3407, 3071, 2988, 1731, 1710, 1382, 1270, 1158, 1038, 959, 860, 632; HRMS (ESI) calcd for $C_{18}H_{24}FN_2O_7S$ $[M + NH_4]^+$ 431.1283, found 431.1285.

*Ethyl (N-Acetyl-1,1-dioxo-5-chloro-(E)-7-(ethoxy-3-oxoprop-1-enyl)benzo[d]isothiazol-3-yl)acetate (**3e**).* This compound was obtained as a light yellow solid (124.3 mg, 96%) by following general procedure A: mp 124−126 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.94 (d, J = 15.8 Hz, 1H), 7.70 (s, 1H), 7.56 (s, 1H), 6.62 (d, J = 15.9 Hz, 1H), 5.65 (d, J = 7.5 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 4.12 (q, J = 7.1 Hz 2H), 3.13 (d, J = 16.4 Hz, 1H), 2.92 (dd, J = 16.3, 8.0 Hz, 1H), 2.58 (s, 3H), 1.32 (t, J = 7.0 Hz, 3H), 1.19 (t, J = 6.7 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 169.3, 167.0, 164.9, 140.8, 137.7, 134.1, 132.6, 130.5, 127.9, 125.9, 125.7, 61.3, 61.2, 54.4, 38.6, 23.6, 14.1, 13.9; IR (cm^{-1}) ν 3075, 2992, 1731, 1702, 1569, 1432, 1266, 1171, 1021, 955, 856, 615; HRMS (ESI) calcd for $C_{18}H_{21}ClNO_7S$ $[M + H]^+$ 430.0722, found 430.0719.

*Ethyl (N-Acetyl-1,1-dioxo-5-bromo-(E)-7-(ethoxy-3-oxoprop-1-enyl)benzo[d]isothiazol-3-yl)acetate (**3f**).* This compound was obtained as a yellow solid (118.7 mg, 84%) by following general procedure A: mp 129−130 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.96 (d, J = 15.9 Hz, 1H), 7.87 (s, 1H), 7.73 (s, 1H), 6.63 (d, J = 15.9 Hz, 1H), 5.66 (dd, J = 8.0, 3.1 Hz, 1H), 4.28 (q, J = 7.1 Hz, 2H), 4.15 (q, J = 7.1 Hz, 2H), 3.14 (dd, J = 16.4, 3.2 Hz, 1H), 2.93 (dd, J = 16.4, 8.0 Hz, 1H), 2.59 (s, 3H), 1.33 (t, J = 7.1 Hz, 3H), 1.21 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 169.3, 167.0, 164.9, 137.7, 134.1, 132.6, 131.0, 130.9, 129.1, 128.7, 126.0, 61.3, 61.2, 54.4, 38.7, 23.6, 14.2, 14.0; IR (cm^{-1}) ν 3075, 2984, 1714, 1565, 1316, 1279, 1167, 1042, 968, 619, 569; HRMS (ESI) calcd for $C_{18}H_{21}BrNO_7S$ $[M + H]^+$ 474.0217, found 474.0220.

*Ethyl (N-Acetyl-1,1-dioxo-5-methoxy-(E)-7-(ethoxy-3-oxoprop-1-enyl)benzo[d]isothiazol-3-yl)acetate (**3g**).* This compound was obtained as a white solid (91.0 mg, 71%) by following general procedure A: mp 147−149 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.97 (d, J = 15.9 Hz, 1H), 7.19 (d, J = 1.9 Hz, 1H), 7.01 (d, J = 1.7 Hz, 1H), 6.60 (d, J = 15.9 Hz, 1H), 5.63 (dd, J = 8.0, 3.2 Hz, 1H), 4.27 (q, J = 7.1 2H), 4.13 (q, J = 7.1 2H), 3.88 (s, 3H), 3.14 (dd, J = 16.2, 3.3 Hz, 1H), 2.89 (dd, J = 16.2, 8.1 Hz, 1H), 2.59 (s, 3H), 1.33 (t, J = 7.1 Hz, 3H), 1.20 (t, J = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 169.7, 167.2, 165.3, 164.1, 138.4, 135.5, 132.7, 124.8, 124.1, 114.4, 109.8, 61.2, 61.0, 56.0, 54.6, 39.1, 23.5, 14.2, 14.0; IR (cm^{-1}) ν 3087, 2979, 2905, 1727, 1710, 1469, 1316, 1287, 1150, 1026, 968, 856, 636; HRMS (ESI) calcd for $C_{19}H_{24}NO_8S$ $[M + H]^+$ 426.1217, found 426.1223.

*Ethyl (N-Acetyl-1,1-dioxo-5-trifluoromethoxy-(E)-7-(ethoxy-3-oxoprop-1-enyl)benzo[d]isothiazol-3-yl)acetate (**3h**).* This compound was obtained as a yellow solid (115.5 mg, 80%) by following general procedure A: mp 101−103 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.01 (d, J = 15.9 Hz, 1H), 7.54 (s, 1H), 7.46 (s, 1H), 6.65 (d, J = 15.9 Hz, 1H), 5.72 (dd, J = 8.4, 3.0 Hz, 1H), 4.30 (q, J = 7.1 Hz, 2H), 4.15 (q, J = 7.1 Hz, 2H), 3.20 (dd, J = 16.4, 3.2 Hz, 1H), 2.90 (dd, J = 16.4, 8.4 Hz, 1H), 2.61 (s, 3H), 1.35 (t, J = 7.1 Hz, 3H), 1.21 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 169.4, 167.0, 164.9, 153.2 (q, J_{C-F} = 1.9 Hz), 138.7, 134.1, 133.6, 130.3, 126.3, 120.0 (d, J_{C-F} = 260.8 Hz), 119.9, 117.5 (d, J_{C-F} = 1.0 Hz), 61.4, 61.3, 54.6, 38.8, 23.6, 14.2, 13.9; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −57.7; IR (cm^{-1}) ν 3407, 3083, 2996, 1710, 1590, 1366, 1258, 1171, 1038, 972, 851, 694; HRMS (ESI) calcd for $C_{19}H_{21}F_3NO_8S$ $[M + H]^+$ 480.0935, found 480.0940.

*Ethyl (N-Acetyl-1,1-dioxo-5-methoxycarbonyl-(E)-7-(ethoxy-3-oxoprop-1-enyl)benzo[d]isothiazol-3-yl) acetate (**3i**).* This compound was obtained as a white solid (101.0 mg, 74%) by following general procedure A: mp 138−140 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.41 (s, 1H), 8.17 (s, 1H), 8.06 (d, J = 15.9 Hz, 1H), 6.74 (d, J = 15.9 Hz, 1H), 5.72 (dd, J = 7.3, 3.3 Hz, 1H), 4.31 (q, J = 7.1 Hz, 2H), 4.13 (q, J = 7.1 Hz, 2H), 3.99 (s, 3H), 3.16 (dd, J = 16.1, 3.4 Hz, 1H), 3.03 (dd, J = 16.1, 7.4 Hz, 1H), 2.63 (s, 3H), 1.35 (t, J = 7.1 Hz, 3H), 1.19 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 169.0, 167.1, 165.0, 164.4, 136.4, 135.7, 135.2, 134.4, 131.5, 128.7, 126.4, 125.7, 61.2, 61.1, 54.8, 53.0, 38.6, 23.6, 14.1, 13.9; IR (cm^{-1}) ν 3398, 3079, 2992, 1723, 1706, 1436, 1362, 1270, 1158, 968, 764, 607; HRMS (ESI) calcd for $C_{20}H_{24}NO_9S$ $[M + H]^+$ 454.1166, found 454.1174.

*Ethyl (N-Acetyl-1,1-dioxo-5-nitro-(E)-7-(ethoxy-3-oxoprop-1-enyl) benzo[d]isothiazol-3-yl)acetate (**3j**).* This compound was obtained as a light yellow solid (72.2 mg, 55%) by following general procedure A: mp 105−107 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.57 (s, 1H), 8.41 (s, 1H), 8.02 (d, J = 15.8 Hz, 1H), 6.78 (d, J = 15.8 Hz, 1H), 5.77 (d, J = 7.4 Hz, 1H), 4.30 (q, J = 6.9 Hz, 2H), 4.13 (q, J = 7.0 Hz, 2H), 3.20 (d, J = 16.5 Hz, 1H), 3.02 (dd, J = 16.4, 7.8 Hz, 1H), 2.60 (s, 3H), 1.34 (t, J = 7.0 Hz, 3H), 1.20 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 169.0, 166.8, 164.6, 151.2, 138.1, 136.5, 133.2, 133.0, 127.2, 122.6, 120.6, 61.43, 61.36, 54.7, 38.2, 23.6, 14.1, 13.9; IR (cm^{-1}) ν 3419, 3091, 2971, 1723, 1552, 1328, 1275, 1167, 1026, 963, 744, 611; HRMS (ESI) calcd for $C_{18}H_{21}N_2O_9S$ $[M + H]^+$ 441.0962, found 441.0966.

*Ethyl (1,1-Dioxo-2-acetyl-5-amino-(E)-7-(ethoxy-3-oxoprop-1-enyl)-benzo[d]isothiazol-3-yl)acetate (**3k**).* This compound was obtained as a brown solid (19.5 mg, 16%) by following general procedure A: mp 157−159 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.91 (d, J = 15.9 Hz, 1H), 6.87 (s, 1H), 6.68 (s, 1H), 6.53 (d, J = 15.9 Hz, 1H), 5.55 (d, J = 7.6 Hz, 1H), 4.44 (s, 2H), 4.27 (q, J = 7.1 Hz, 2H), 4.14 (q, J = 7.1 Hz, 2H), 3.09 (d, J = 16.2 Hz, 1H), 2.88 (dd, J = 16.0, 7.9 Hz, 1H), 2.58 (s, 3H), 1.33 (t, J = 7.1 Hz, 3H), 1.21 (t, J = 7.0 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 169.9, 167.4, 165.6, 152.0, 138.3, 136.2, 132.4, 124.1, 120.6, 113.5, 109.2, 61.1, 61.0, 54.5, 39.2, 23.5, 14.2, 14.0; IR (cm^{-1}) ν 3469, 3378, 3253, 2975, 2913, 1743, 1706, 1631, 1374, 1304, 1196, 1042, 963, 681; HRMS (ESI) calcd for $C_{18}H_{23}N_2O_7S$ $[M + H]^+$ 411.1222, found 411.1222.

*Ethyl (N-Acetyl-1,1-dioxo-(E)-9-(ethoxy-3-oxoprop-1-enyl)-naphtho[1,2-d]isothiazol-3-yl)acetate (**3l**).* This compound was obtained as a white solid (54.4 mg, 41%) by following general procedure A: mp 143−145 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.19 (s, 1H), 8.11 (d, J = 15.9 Hz, 1H), 8.08−8.04 (m, 1H), 8.03−7.98 (m, 1H), 7.74 (dd, J = 6.1, 3.1 Hz, 2H), 6.72 (d, J = 15.8 Hz, 1H), 6.16 (t, J = 3.3 Hz, 1H), 4.29 (q, J = 7.1 Hz, 2H), 4.13 (dd, J = 6.9, 5.2 Hz, 2H), 3.21 (dd, J = 15.6, 3.2 Hz, 1H), 2.93 (dd, J = 15.6, 5.2 Hz, 1H), 2.65 (s, 3H), 1.35 (t, J = 7.1 Hz, 3H), 1.18 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 169.5, 167.1, 165.5, 136.0, 135.3, 133.9, 129.98, 129.96, 129.7, 129.54, 129.47, 126.9, 125.9, 123.8, 123.7, 61.3, 60.9, 54.6, 40.5, 23.5, 14.2, 13.9; IR (cm^{-1}) ν 2918, 1740, 1694, 1329, 1288, 1159, 1035, 757, 512; HRMS (ESI) calcd for $C_{22}H_{24}NO_7S$ $[M + H]^+$ 446.1268, found 446.1271.

*Ethyl (N-Acetyl-1,1-dioxo-4-bromo-(E)-7-(ethoxy-3-oxoprop-1-enyl)benzo[d]isothiazol-3-yl)acetate (**3m**).* This compound was obtained as a yellow solid (116.0 mg, 82%) by following general procedure A: mp 117−119 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.02 (d, J = 15.9 Hz, 1H), 7.85 (d, J = 8.3 Hz, 1H), 7.65 (d, J = 8.3 Hz, 1H), 6.63 (d, J = 15.9 Hz, 1H), 5.64 (t, J = 3.4 Hz, 1H), 4.29 (q, J = 7.1 Hz, 2H), 4.03 (q, J = 7.1 Hz, 2H), 3.31 (dd, J = 15.3, 3.9 Hz, 1H), 3.24 (dd, J = 15.4, 4.3 Hz, 1H), 2.62 (s, 3H), 1.34 (t, J = 7.1 Hz, 3H), 1.10 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 168.6, 167.0, 165.2, 137.9, 134.7, 134.5, 130.3, 129.0, 125.2, 120.2, 61.19, 61.15, 56.2, 35.8, 23.7, 14.2, 13.8 (one signal missing due to overlap); IR (cm^{-1}) ν 2988, 1723, 1648, 1466, 1263, 1117, 1026, 819, 603, 537; HRMS (ESI) calcd for $C_{18}H_{21}BrNO_7S$ $[M + H]^+$ 474.0217, found 474.0215.

*Butyl (N-Acetyl-1,1-dioxo-4-bromo-(E)-7-(butoxy-3-oxoprop-1-enyl)benzo[d]isothiazol-3-yl)acetate (**3n**).* This compound was obtained as a colorless oil (103.2 mg, 60%) by following general procedure A: ^1H NMR ($CDCl_3$, 400 MHz) δ 8.02 (d, J = 15.9 Hz, 1H), 7.85 (d, J = 8.3 Hz, 1H), 7.65 (d, J = 8.3 Hz, 1H), 6.64 (d, J = 15.9 Hz, 1H), 5.64 (t, J = 4.1 Hz, 1H), 4.23 (t, J = 6.7 Hz, 2H), 3.98 (t, J = 6.8 Hz, 2H), 3.32 (dd, J = 15.3, 4.0 Hz, 1H), 3.26 (dd, J = 15.4, 4.3 Hz, 1H), 2.62 (s, 3H), 1.73−1.66 (m, 2H), 1.48−1.40 (m, 4H), 1.23−1.20 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H), 0.86 (t, J = 7.4 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 168.6, 167.0, 165.2, 137.9, 134.7,

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134.58, 134.52, 130.4, 128.9, 125.1, 120.1, 65.09, 65.05, 56.2, 35.8, 30.6, 30.2, 23.6, 19.1, 18.9, 13.68, 13.62; IR (cm^{-1}) ν 2955, 2864, 1711, 1466, 1321, 1254, 1155, 819; HRMS (ESI) calcd for $C_{22}H_{29}BrNO_7S$ $[M + H]^+$ 530.0843, found 530.0849.

*Ethyl (N-Acetyl-1,1-dioxo-6-trifluoromethylbenzo[d]isothiazol-3-yl)acetate (**4a**).* This compound was obtained as a white solid (64.2 mg, 59%) by following general procedure A except using 5.0 mol % of $[Cp^*RhCl_2]_2$ at 120 °C: mp 94−95 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.09 (s, 1H), 7.94 (d, J = 8.2 Hz, 1H), 7.79 (d, J = 8.2 Hz, 1H), 5.77 (d, J = 7.7 Hz, 1H), 4.12 (q, J = 7.1 Hz, 2H), 3.20 (dd, J = 16.4, 1.5 Hz, 1H), 2.95 (dd, J = 16.4, 8.2 Hz, 1H), 2.60 (s, 3H), 1.19 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 169.3, 167.1, 138.7 (d, J_{C-F} = 0.8 Hz), 134.7, 132.8 (q, J_{C-F} = 34.0 Hz), 131.1 (q, J_{C-F} = 3.4 Hz), 126.1, 122.7 (q, J_{C-F} = 273.1 Hz), 119.5 (q, J_{C-F} = 4.0 Hz), 61.3, 55.3, 38.6, 23.6, 14.0; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −62.8; IR (cm^{-1}) ν 3075, 3000, 2946, 2905, 1735, 1714, 1627, 1416, 1312, 1133, 1034, 864, 607, 528; HRMS (ESI) calcd for $C_{14}H_{15}F_3NO_5S$ $[M + H]^+$ 366.0618, found 366.0623.

*Butyl (N-Acetyl-1,1-dioxo-6-trifluoromethylbenzo[d]isothiazol-3-yl)acetate (**4b**).* This compound was obtained as a yellow oil (50.7 mg, 43%) by following general procedure A except using 5.0 mol % of $[Cp^*RhCl_2]_2$ at 120 °C: ^1H NMR ($CDCl_3$, 400 MHz) δ 8.09 (s, 1H), 7.94 (d, J = 8.2 Hz, 1H), 7.79 (d, J = 8.4 Hz, 1H), 5.78 (dd, J = 8.2, 3.0 Hz, 1H), 4.08 (t, J = 6.7 Hz, 2H), 3.22 (dd, J = 16.4, 3.2 Hz, 1H), 2.97 (dd, J = 16.4, 8.2 Hz, 1H), 2.61 (s, 3H), 1.55−1.50 (m, 2H), 1.30−1.24 (m, 2H), 0.88 (t, J = 7.4 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 169.4, 167.2, 138.7, 134.7, 132.9 (q, J_{C-F} = 34.0 Hz), 131.1 (q, J_{C-F} = 3.4 Hz), 126.1, 122.7 (q, J_{C-F} = 273.4 Hz), 119.5 (q, J_{C-F} = 4.0 Hz), 65.2, 55.3, 38.6, 30.3, 23.6, 19.0, 13.6; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −62.8; IR (cm^{-1}) ν 3672, 2971, 2876, 1719, 1329, 1263, 1188, 1084, 591; HRMS (ESI) calcd for $C_{16}H_{19}F_3NO_5S$ $[M + H]^+$ 394.0931, found 394.0933.

*Ethyl (N-Acetyl-1,1-dioxo-7-methylbenzo[d]isothiazol-3-yl)-acetate (**4c**).* This compound was obtained as a yellow oil (61.0 mg, 65%) by following general procedure A except 2.0 equiv of **2a** was used: ^1H NMR ($CDCl_3$, 400 MHz) δ 7.54 (t, J = 7.7 Hz, 1H), 7.34 (t, J = 7.2 Hz, 2H), 5.65 (dd, J = 7.6, 3.3 Hz, 1H), 4.11 (q, J = 7.1 Hz, 2H), 3.12 (dd, J = 16.0, 3.4 Hz, 1H), 2.91 (dd, J = 16.0, 7.7 Hz, 1H), 2.64 (s, 3H), 2.60 (s, 3H), 1.17 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 169.4, 167.3, 135.0, 134.6, 134.0, 131.9, 131.3, 121.9, 60.9, 54.7, 39.0, 23.4, 16.7, 13.8; IR (cm^{-1}) ν 2984, 2930, 1731, 1689, 1370, 1275, 1158, 1100, 1030, 797, 598; HRMS (ESI) calcd for $C_{14}H_{18}NO_5S$ $[M + H]^+$ 312.0900, found 312.0905.

*Ethyl (N-Acetyl-1,1-dioxo-7-trifluoromethoxybenzo[d]isothiazol-3-yl)acetate (**4d**).* This compound was obtained as a white solid (100.5 mg, 88%) by following general procedure A except 5.0 mol % of $[Cp^*RhCl_2]_2$ was used: mp 68−70 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.73 (t, J = 8.0 Hz, 1H), 7.50 (d, J = 7.7 Hz, 1H), 7.43 (d, J = 8.2 Hz, 1H), 5.72 (d, J = 7.8 Hz, 1H), 4.13 (q, J = 6.9 Hz, 2H), 3.17 (d, J = 16.2 Hz, 1H), 2.94 (dd, J = 16.2, 8.0 Hz, 1H), 2.60 (s, 3H), 1.19 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 169.4, 167.2, 144.0, 138.0, 136.0, 125.5, 122.5, 120.1 (d, J_{C-F} = 262.9), 119.5, 61.2, 54.9, 38.9, 23.6, 13.9; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −57.4; IR (cm^{-1}) 3108, 3000, 2930, 1747, 1706, 1490, 1341, 1183, 1113, 1038, 914, 797, 578; HRMS (ESI) calcd for $C_{14}H_{15}F_3NO_6S$ $[M + H]^+$ 382.0567, found 382.0569.

*Ethyl (N-Acetyl-1,1-dioxo-7-chlorobenzo[d]isothiazol-3-yl)-acetate (**4e**).* This compound was obtained as a colorless oil (96.1 mg, 97%) by following general procedure A except 2.0 equiv of **2a** was used: ^1H NMR ($CDCl_3$, 400 MHz) δ 7.62 (t, J = 7.9 Hz, 1H), 7.53 (d, J = 7.9 Hz, 1H), 7.49 (d, J = 7.8 Hz, 1H), 5.68 (dd, J = 7.8, 3.2 Hz, 1H), 4.12 (q, J = 7.1 Hz, 2H), 3.14 (dd, J = 16.2, 3.3 Hz, 1H), 2.93 (dd, J = 16.2, 7.9 Hz, 1H), 2.61 (s, 3H), 1.19 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 169.2, 167.1, 137.6, 135.2, 131.4, 130.7, 128.9, 123.0, 61.0, 54.3, 38.7, 23.5, 13.8; IR (cm^{-1}) ν 3083, 3000, 1739, 1706, 1457, 1333, 1275, 1175, 1026, 972, 802, 594; HRMS (ESI) calcd for $C_{13}H_{15}ClNO_5S$ $[M + H]^+$ 332.0354, found 332.0356.

*Ethyl (N-Acetyl-1,1-dioxo-7-(methoxycarbonyl)benzo[d]-isothiazol-3-yl)acetate (**4f**).* This compound was obtained as a white solid (97.7 mg, 92%) by following general procedure A except using 5.0 mol % of $[Cp^*RhCl_2]_2$ at 120 °C: mp 119−121 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.22 (d, J = 7.3 Hz, 1H), 7.82 (d, J = 7.5 Hz, 1H), 7.78 (t, J = 7.6 Hz, 1H), 5.71 (d, J = 7.6 Hz, 1H), 4.12 (q, J = 7.0 Hz, 2H), 4.04 (s, 3H), 3.16 (d, J = 16.1 Hz, 1H), 2.93 (dd, J = 16.2, 7.8 Hz, 1H), 2.63 (s, 3H), 1.19 (t, J = 7.0 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 169.5, 167.6, 162.9, 137.2, 134.1, 133.8, 131.9, 129.5, 126.6, 61.1, 54.0, 53.1, 39.0, 23.5, 13.9; IR (cm^{-1}) ν 3440, 2979, 2946, 2905, 1731, 1685, 1395, 1283, 1154, 1001, 773, 586; HRMS (ESI) calcd for $C_{15}H_{18}NO_7S$ $[M + H]^+$ 356.0799, found 356.0803.

*Methyl (N-Acetyl-1,1-dioxo-5-methyl-(E)-7-(methoxy-3-oxoprop-1-enyl)benzo[d]isothiazol-3-yl)acetate (**3o**).* This compound was obtained as a white solid (93.7 mg, 82%) by following general procedure A: mp 139−141 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.02 (d, J = 15.9 Hz, 1H), 7.55 (s, 1H), 7.33 (s, 1H), 6.63 (d, J = 15.9 Hz, 1H), 5.65 (dd, J = 7.6, 3.3 Hz, 1H), 3.83 (s, 3H), 3.69 (s, 3H), 3.13 (dd, J = 16.2, 3.4 Hz, 1H), 2.95 (dd, J = 16.2, 7.7 Hz, 1H), 2.61 (s, 3H), 2.48 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 170.0, 167.3, 165.8, 145.7, 136.0, 135.8, 130.7, 129.4, 128.7, 126.0, 123.9, 54.6, 52.0, 38.8, 23.5, 21.8 (one signal missing due to overlap); IR (cm^{-1}) ν 3407, 2955, 1743, 1710, 1635, 1432, 1275, 1229, 1145.9, 968, 856, 673, 623; HRMS (ESI) calcd for $C_{17}H_{20}NO_7S$ $[M + H]^+$ 382.0955, found 382.0958.

*Butyl (N-Acetyl-1,1-dioxo-5-methyl-(E)-7-(butoxy-3-oxoprop-1-enyl)benzo[d]isothiazol-3-yl)acetate (**3p**).* This compound was obtained as a light yellow solid (130.0 mg, 93%) by following general procedure A: mp 77−78 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.01 (d, J = 15.9 Hz, 1H), 7.55 (s, 1H), 7.33 (s, 1H), 6.62 (d, J = 15.9 Hz, 1H), 5.64 (d, J = 5.2 Hz, 1H), 4.22 (t, J = 6.6 Hz, 2H), 4.07 (t, J = 6.6 Hz, 2H), 3.13 (dd, J = 16.1, 2.6 Hz, 1H), 2.93 (dd, J = 16.0, 7.8 Hz, 1H), 2.60 (s, 3H), 2.47 (s, 3H), 1.72−1.65 (m, 2H), 1.57−1.50 (m, 2H), 1.47−1.38 (m, 2H), 1.32−1.23 (m, 2H), 0.95 (t, J = 7.3 Hz, 3H), 0.88 (t, J = 7.3 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 169.5, 167.2, 165.3, 145.5, 136.1, 135.5, 130.7, 129.3, 128.6, 125.9, 124.2, 64.8, 64.7, 54.6, 38.8, 30.5, 30.2, 23.4, 21.7, 19.0, 18.8, 13.6, 13.5; IR (cm^{-1}) ν 3411, 2963, 2867, 1731, 1710, 1635, 1316, 1283, 1187, 1150, 1063, 980, 864, 615; HRMS (ESI) calcd for $C_{23}H_{32}NO_7S$ $[M + H]^+$ 466.1894, found 466.1903.

*Benzyl (N-Acetyl-1,1-dioxo-5-methyl-(E)-7-(benzoxy-3-oxoprop-1-enyl)benzo[d]isothiazol-3-yl)acetate (**3q**).* This compound was obtained as a light yellow solid (148.7 mg, 93%) by following general procedure A: mp 134−136 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.04 (d, J = 15.9 Hz, 1H), 7.46 (s, 1H), 7.42−7.34 (m, 5H), 7.31 (dd, J = 4.8, 2.9 Hz, 3H), 7.29−7.25 (m, 2H), 7.19 (s, 1H), 6.63 (d, J = 15.9 Hz, 1H), 5.64 (dd, J = 7.6, 3.3 Hz, 1H), 5.26 (s, 2H), 5.10 (d, J = 1.9 Hz, 2H), 3.17 (dd, J = 15.9, 3.4 Hz, 1H), 2.98 (dd, J = 15.9, 7.7 Hz, 1H), 2.57 (s, 3H), 2.36 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 169.2, 167.4, 165.2, 145.6, 136.3, 136.0, 135.7, 135.2, 130.7, 129.5, 128.8, 128.57, 128.53, 128.51, 128.4, 128.30, 128.28, 126.0, 124.0, 66.9, 66.7, 54.7, 39.0, 23.6, 21.8 IR (cm^{-1}) ν 3067, 2959, 1731, 1706, 1374, 1308, 1275, 1221, 1167, 963, 748, 702; HRMS (ESI) calcd for $C_{29}H_{31}N_2O_7S$ $[M + NH_4]^+$ 551.1847, found 551.1852.

*tert-Butyl (N-Acetyl-1,1-dioxo-5-methyl-(E)-7-(tert-butoxy-3-oxo-prop-1-enyl)benzo[d]isothiazol-3-yl)acetate (**3r**).* This compound was obtained as a white solid (109.0 mg, 78%) by following general procedure A except for performing the reaction at 120 °C: mp 132−134 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.93 (d, J = 15.8 Hz, 1H), 7.53 (s, 1H), 7.35 (s, 1H), 6.54 (d, J = 15.8 Hz, 1H), 5.62 (dd, J = 8.3, 3.1 Hz, 1H), 3.12 (dd, J = 15.9, 3.2 Hz, 1H), 2.75 (dd, J = 15.9, 8.4 Hz, 1H), 2.60 (s, 3H), 2.45 (s, 3H), 1.53 (s, 9H), 1.40 (s, 9H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 168.9, 167.2, 164.6, 145.3, 136.3, 134.7, 131.0, 129.3, 128.4, 126.1, 125.9, 81.8, 81.2, 54.8, 40.2, 28.0, 27.9, 23.6, 21.8; IR (cm^{-1}) ν 3411, 2992, 2934, 1723 1702, 1378, 1283, 11543, 972, 843, 607, 520; HRMS (ESI) calcd for $C_{23}H_{35}N_2O_7S$ $[M + NH_4]^+$ 483.2159, found 483.2167.

*N,N-Dimethyl(N-acetyl-1,1-dioxo-5-methylbenzo[d]isothiazol-3-yl)acetamide (**4g**).* This compound was obtained as a white solid (58.6 mg, 63%) by following general procedure A: mp 145−147 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.66 (d, J = 8.1 Hz, 1H), 7.62 (s, 1H), 7.36 (d, J = 8.0 Hz, 1H), 5.87 (d, J = 9.6 Hz, 1H), 3.24 (dd, J = 16.1,

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2.0 Hz, 1H), 2.98 (s, 3H), 2.91 (s, 3H), 2.67 (dd, J = 16.2, 9.6 Hz, 1H), 2.59 (s, 3H), 2.44 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 168.9, 167.3, 145.5, 136.4, 130.7, 130.5, 126.4, 121.1, 55.7, 38.7, 37.0, 35.5, 23.7, 22.0; IR (cm^{-1}) ν 2926, 1706, 1649, 1395, 1312, 1263, 1147, 1022, 811, 678, 599; HRMS (ESI) calcd for $C_{14}H_{19}N_2O_4S$ $[M + H]^+$ 311.1060, found 311.1065.

Preparation of the Product 6 or 7 (General Procedure B). A mixture of sulfonamide **1** (0.3 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (9.27 mg, 0.015 mmol, 5.0 mol %), and AgOAc (200.4 mg, 1.2 mmol, 4.0 equiv) were weighed in a 50 mL Schlenk tube equipped with a stir bar. Dry *t*-AmOH (2.0 mL) was added, followed immediately by the styrene **2** (1.2 mmol, 4.0 equiv), and the mixture was stirred at 120 °C for 36 h under an Ar atmosphere. Afterward, the vial was cooled to room temperature, diluted with CH_2Cl_2, and transferred to a round-bottom flask. Silica was added to the flask, and the volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel (eluent EtOAc/petroleum ether 1/3, typically).

(E)-N-(4-Methyl-2,6-distyrylphenylsulfonyl)acetamide ***(6a)***. This compound was obtained as a white solid (100.8 mg, 81%) by following general procedure B: mp 132−134 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.62 (s, 1H), 7.87 (d, J = 16.0 Hz, 2H), 7.44 (d, J = 7.3 Hz, 4H), 7.27 (s, 2H), 7.25−7.13 (m, 6H), 6.75 (d, J = 16.0 Hz, 2H), 2.36 (s, 3H), 1.74 (s, 3H); $^{13}C\{^1H\}$ NMR (DMSO-d_6, 100 MHz) δ 169.4, 143.4, 139.2, 137.1, 131.3, 130.8, 129.0, 128.7, 128.0, 127.6, 127.0, 23.1, 20.8; IR (cm^{-1}) ν 3415, 3253, 3038, 1723, 1557, 1411, 1324, 1146, 963, 847, 652, 520; HRMS (ESI) calcd for $C_{25}H_{24}NO_3S$ $[M + H]^+$ 418.1471, found 418.1466.

(E)-N-(4-Methyl-2,6-bis(4-methylstyryl)phenylsulfonyl)acetamide ***(6b)***. This compound was obtained as a white solid (97.4 mg, 73%) by following general procedure B: mp 227−229 °C; ^1H NMR (DMSO-d_6, 400 MHz) δ 12.46 (s, 1H), 7.91 (d, J = 16.0 Hz, 2H), 7.53−7.50 (m, 6H), 7.22 (d, J = 7.7 Hz, 4H), 6.99 (d, J = 16.0 Hz, 2H), 2.42 (s, 3H), 2.33 (s, 6H), 1.92 (s, 3H); $^{13}C\{^1H\}$ NMR (DMSO-d_6, 100 MHz) δ 169.4, 143.3, 139.3, 137.5, 134.4, 131.2, 130.6, 129.3, 128.8, 126.9, 126.6, 23.2, 20.95, 20.88; IR (cm^{-1}) ν 3689, 3166, 2884, 2689, 1664, 1449, 1341, 1158, 847, 648; HRMS (ESI) calcd for $C_{27}H_{28}NO_3S$ $[M + H]^+$ 446.1784, found 446.1779.

(E)-N-(2,6-Bis(4-tert-butylstyryl)-4-methylphenylsulfonyl)-acetamide ***(6c)***. This compound was obtained as a white solid (126.6 mg, 80%) by following general procedure B: mp 207−209 °C; ^1H NMR (DMSO-d_6, 400 MHz) δ 12.43 (s, 1H), 7.93 (d, J = 16.1 Hz, 2H), 7.54 (d, J = 7.6 Hz, 6H), 7.43 (d, J = 8.2 Hz, 4H), 7.01 (d, J = 16.0 Hz, 2H), 2.42 (s, 3H), 1.92 (s, 3H), 1.30 (s, 18H); $^{13}C\{^1H\}$ NMR (DMSO-d_6, 100 MHz) δ 169.4, 150.6, 143.3, 139.3, 134.4, 131.1, 130.6, 128.7, 126.89, 126.76, 125.5, 34.4, 31.1, 23.2, 20.9; IR (cm^{-1}) ν 3158, 2959, 2863, 1685, 1457, 1349, 1163, 9768, 851, 661, 532; HRMS (ESI) calcd for $C_{33}H_{43}N_2O_3S$ $[M + NH_4]^+$ 547.2989, found 547.2995.

(E)-N-(2,6-Bis(4-methoxystyryl)-4-methylphenylsulfonyl)-acetamide ***(6d)***. This compound was obtained as a yellow solid (109.2 mg, 76%) by following general procedure B: mp 224−226 °C; ^1H NMR (DMSO-d_6, 400 MHz) δ 12.41 (s, 1H), 7.81 (d, J = 16.1 Hz, 2H), 7.55 (d, J = 8.1 Hz, 4H), 7.50 (s, 2H), 7.02−6.95 (m, 6H), 3.79 (s, 6H), 2.41 (s, 3H), 1.91 (s, 3H); $^{13}C\{^1H\}$ NMR (DMSO-d_6, 100 MHz) δ 169.3, 159.2, 143.1, 139.4, 130.8, 130.3, 129.8, 128.4, 128.3, 125.3, 114.1, 55.2, 23.1, 20.8; IR (cm^{-1}) ν 3262, 2934, 2834, 1723, 1615, 1507, 1440, 1245, 1133, 1026, 847, 644, 532; HRMS (ESI) calcd for $C_{27}H_{31}N_2O_5S$ $[M + NH_4]^+$ 495.1948, found 495.1947.

(E)-N-(2,6-Bis(4-fluorostyryl)-4-methylphenylsulfonyl)acetamide ***(6e)***. This compound was obtained as a yellow solid (118.2 mg, 87%) by following general procedure B: mp 257−259 °C; ^1H NMR (DMSO-d_6, 400 MHz) δ 12.49 (s, 1H), 7.90 (d, J = 16.0 Hz, 2H), 7.66 (m, 4H), 7.54 (s, 2H), 7.26 (t, J = 7.9 Hz, 4H), 7.04 (d, J = 16.0 Hz, 2H), 2.42 (s, 3H), 1.93 (s, 3H); $^{13}C\{^1H\}$ NMR (DMSO-d_6, 100 MHz) δ 169.5, 161.9 (d, J_{C-F} = 244.9 Hz), 143.4, 139.1, 133.7 (d, J_{C-F} = 3.0 Hz), 130.8, 130.1, 129.0, 128.9 (d, J_{C-F} = 8.1 Hz), 127.5, 115.6 (d, J_{C-F} = 21.6 Hz), 23.2, 20.9; ^{19}F NMR (DMSO-d_6, 376 MHz) δ −113.8; IR (cm^{-1}) ν 3245, 2926, 1731, 1507, 1325, 1221, 11475, 860, 657; HRMS (ESI) calcd for $C_{25}H_{25}F_2N_2O_3S$ $[M + NH_4]^+$ 471.1549, found 471.1553.

(E)-N-(2,6-Bis(4-chlorostyryl)-4-methylphenylsulfonyl)acetamide ***(6f)***. This compound was obtained as a white solid (135.6 mg, 93%) by following general procedure B: mp 253−255 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.73 (s, 1H), 7.93 (d, J = 16.0 Hz, 2H), 7.45 (d, J = 8.5 Hz, 4H), 7.36 (s, 2H), 7.29 (d, J = 8.4 Hz, 4H), 6.79 (d, J = 16.0 Hz, 2H), 2.46 (s, 3H), 1.88 (s, 3H); $^{13}C\{^1H\}$ NMR (DMSO-d_6, 100 MHz) δ 169.5, 143.5, 138.9, 136.0, 132.4, 130.8, 130.0, 129.2, 128.7, 128.6, 128.3, 23.2, 20.8; IR (cm^{-1}) ν 3419, 3100, 2901, 1669, 1482, 1333, 1158, 1075, 1009, 831, 656, 520; HRMS (ESI) calcd for $C_{25}H_{22}Cl_2NO_3S$ $[M + H]^+$ 486.0692, found 486.0702.

(E)-N-(2,6-Bis(4-bromostyryl)-4-methylphenylsulfonyl)acetamide ***(6g)***. This compound was obtained as a white solid (162.5 mg, 94%) by following general procedure B: mp 231−233 °C; ^1H NMR (DMSO-d_6, 400 MHz) δ 12.52 (s, 1H), 7.97 (d, J = 16.1 Hz, 2H), 7.62 (d, J = 8.5 Hz, 4H), 7.58−7.54 (m, 6H), 7.02 (d, J = 16.1 Hz, 2H), 2.42 (s, 3H), 1.93 (s, 3H); $^{13}C\{^1H\}$ NMR (DMSO-d_6, 100 MHz) δ 169.5, 143.5, 138.9, 136.4, 131.7, 130.8, 130.1, 129.2, 128.9, 128.4, 121.1, 23.2, 20.9; IR (cm^{-1}) ν 3436, 3374, 1706, 1491, 1147, 997, 653, 520; HRMS (ESI) calcd for $C_{25}H_{25}Br_2N_2O_3S$ $[M + NH_4]^+$ 592.9927, found 592.9923.

(E)-N-(4-Methyl-2,6-bis(perfluorostyryl)phenylsulfonyl)acetamide ***(6h)***. This compound was obtained as a brown solid (106.2 mg, 59%) by following general procedure B: mp 196−198 °C; ^1H NMR (DMSO-d_6, 400 MHz) δ 12.36 (s, 1H), 8.23 (d, J = 16.4 Hz, 2H), 7.63 (s, 2H), 6.83 (d, J = 16.5 Hz, 2H), 2.46 (s, 3H), 1.85 (s, 3H); $^{13}C\{^1H\}$ NMR (DMSO-d_6, 100 MHz) δ 170.1, 145.9−145.7 (m), 144.6, 143.5−143.2 (m), 138.9−138.6 (m), 138.4, 136.8−136.2 (m), 130.5, 128.8 (d, J_{C-F} = 205.2 Hz), 116.0, 112.5−112.2 (m), 23.2, 21.0; ^{19}F NMR (DMSO-d_6, 376 MHz) δ −137.74 (dd, J = 23.3, 7.2 Hz), δ −151.10 (t, J = 22.1 Hz), −158.34 (td, J = 23.0, 7.3 Hz); IR (cm^{-1}) ν 3647, 3237, 2930, 1731, 1523, 1499, 1337, 1146, 1005, 847, 656; HRMS (ESI) calcd for $C_{25}H_{14}F_{10}NO_3S$ $[M + H]^+$ 598.0529, found 598.0525.

(E)-N-(4-Chloro-2,6-distyrylphenylsulfonyl)acetamide ***(6i)***. This compound was obtained as a white solid (88.1 mg, 67%) by following general procedure B: mp 227−229 °C; ^1H NMR (DMSO-d_6, 400 MHz) δ 12.67 (s, 1H), 7.93 (d, J = 16.1 Hz, 2H), 7.81 (s, 2H), 7.64 (d, J = 7.4 Hz, 4H), 7.43 (t, J = 7.6 Hz, 4H), 7.34 (t, J = 7.3 Hz, 2H), 7.17 (d, J = 16.1 Hz, 2H), 1.96 (s, 3H); $^{13}C\{^1H\}$ NMR (DMSO-d_6, 100 MHz) δ 169.7, 141.4, 138.0, 136.8, 132.9, 132.1, 128.7, 128.4, 127.4, 127.2, 126.1, 23.1; IR (cm^{-1}) ν 3324, 3017, 1715, 1545, 1350, 1155, 840, 686, 524; HRMS (ESI) calcd for $C_{24}H_{24}ClN_2O_3S$ $[M + NH_4]^+$ 455.1191, found 455.1197.

(E)-N-(4-Methoxy-2,6-distyrylphenylsulfonyl)acetamide ***(6j)***. This compound was obtained as a red solid (72.2 mg, 56%) by following general procedure B: mp 204−206 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.99 (s, 1H), 7.95 (d, J = 16.0 Hz, 2H), 7.52 (d, J = 7.5 Hz, 4H), 7.32 (t, J = 7.5 Hz, 4H), 7.23 (t, J = 3.6 Hz, 2H), 7.02 (s, 2H), 6.83 (d, J = 16.0 Hz, 2H), 3.91 (s, 3H), 1.80 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 168.9, 162.5, 142.7, 136.6, 133.0, 128.7, 128.2, 127.6, 127.0, 114.0, 55.7, 23.0; IR (cm^{-1}) ν 3245, 3021, 1723, 1586, 1411, 1337, 1146, 959, 847, 681, 524; HRMS (ESI) calcd for $C_{25}H_{27}N_2O_4S$ $[M + NH_4]^+$ 451.1686, found 451.1682.

(E)-N-(3-Bromo-2,6-distyrylphenylsulfonyl)acetamide ***(6k)***. This compound was obtained as a light yellow solid (43.1 mg, 30%) by following general procedure B: mp 165−167 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.07 (s, 1H), 8.00 (d, J = 16.1 Hz, 1H), 7.86 (d, J = 8.4 Hz, 1H), 7.55 (d, J = 7.2 Hz, 4H), 7.47 (d, J = 8.4 Hz, 1H), 7.43−7.27 (m, 7H), 6.88 (d, J = 16.1 Hz, 1H), 6.59 (d, J = 16.7 Hz, 1H), 1.90 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 168.0, 139.9, 139.7, 137.5, 136.7, 136.4, 136.0, 133.1, 129.7, 129.0, 128.8, 128.7, 128.44, 128.40, 127.1, 126.9, 126.8, 126.2, 125.0, 23.3; IR (cm^{-1}) ν 3058, 2360, 1686, 1558, 1496, 1457, 1348, 1166, 859, 756, 605; HRMS (ESI) calcd for $C_{24}H_{21}BrNO_3S$ $[M + H]^+$ 482.0420, found 482.0414.

(E)-N-(2-Styryl-5-(trifluoromethyl)phenylsulfonyl)acetamide ***(7a)***. This compound was obtained as brown solid (95.8 mg, 86%) by following general procedure B: mp 165−167 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 9.26 (s, 1H), 8.42 (s, 1H), 7.82 (d, J = 13.2 Hz, 3H), 7.52

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(d, J = 5.1 Hz, 2H), 7.30 (s, 3H), 7.09 (d, J = 15.9 Hz, 1H), 1.95 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 168.8, 140.7, 136.5, 135.8, 135.6, 130.6 (d, J_{C-F} = 3.2 Hz), 129.5 (d, J_{C-F} =34.1 Hz), 129.2, 128.8, 128.7, 128.2 (d, J_{C-F} = 3.5 Hz), 127.4, 123.1 (d, J_{C-F} = 272.6 Hz), 122.5, 23.1; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −62.6; IR (cm^{-1}) ν 3087, 2884, 1681, 1615, 1474, 1328, 1158, 1129, 1080, 885, 615; HRMS (ESI) calcd for $C_{17}H_{15}F_3NO_3S$ $[M + H]^+$ 370.0719, found 370.0717.

Synthetic Transformations of 3a and 6a. *Methyl (1,1-Dioxo-2,3-dihydro-5-methyl-(E)-7-(methoxy-3-oxoprop-1-enyl)benzo[d]-isothiazol-3-yl)acetate (**8**) (Eq 1).* A mixture of **3a** (61.4 mg, 0.15 mmol), K_2CO_3 (22.8 mg, 0.165 mmol, 1.1 equiv) and MeOH/H_2O 20/1 (3.0 mL) was stirred for 0.5 h at room temperature. Methanol was evaporated, and the residue was diluted with EtOAc (25.0 mL) and then washed with brine (20.0 mL). The organic layer was dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography (eluent EtOAc/petroleum ether 1/2) to afford 40.0 mg of **8** in 78% yield as a white solid: mp 123−125 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.04 (d, J = 15.8 Hz, 1H), 7.50 (s, 1H), 7.15 (s, 1H), 6.62 (d, J = 15.9 Hz, 1H), 5.58 (d, J = 21.5 Hz, 1H), 5.03 (br s, 1H), 3.81 (s, 3H), 3.76 (s, 3H), 2.95 (d, J = 17.0 Hz, 1H), 2.79 (dd, J = 16.8, 10.0 Hz, 1H), 2.46 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 171.1, 166.1, 144.6, 139.6, 136.6, 131.7, 130.4, 128.4, 125.4, 123.4, 52.9, 52.4 52.0, 40.2, 21.7; IR (cm^{-1}) ν 3217, 2959, 1712, 1443, 1290, 1179, 1147, 970, 859, 669; HRMS (ESI) calcd for $C_{15}H_{21}N_2O_6S$ $[M + NH_4]^+$ 357.1114, found 357.1120.

*Methyl (1,1-Dioxo-2,3-dihydro-5-methyl-7-(methoxy-3-oxopropanyl)benzo[d]Isothiazol-3-yl)acetate (**9**) (Eq 2).* To a solution of **8** (96 mg, 0.3 mmol) in THF (1.0 mL) and MeOH (0.7 mL) were added $NiCl_2{\cdot}H_2O$ (142.6 mg, 0.6 mmol, 2.0 equiv) and $NaBH_4$ (56.7 mg, 1.5 mmol, 5.0 equiv) at 0 °C under an argon atmosphere. The resulting mixture was stirred overnight and then quenched with water (3.0 mL). The crude mixture was diluted with EtOAc and filtered through a pad of Celite. The filtrate was separated, and the organic layer was washed with water and brine and dried over Na_2SO_4. The solvent was evaporated, and the crude mixture was purified by column chromatography (eluent EtOAc/petroleum ether 1/3) to afford 68.8 mg of **9** in 73% yield as a white solid: mp 91−93 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.14 (s, 1H), 6.98 (s, 1H), 5.69 (d, J = 17.2 Hz, 1H), 5.03−4.96 (m, 1H), 3.72 (s, 3H), 3.64 (s, 3H), 3.22 (t, J = 7.6 Hz, 2H), 2.92 (dd, J = 16.9, 3.0 Hz, 1H), 2.78−2.70 (m, 3H), 2.38 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 172.7, 171.2, 144.4, 138.9, 136.7, 131.4, 131.3, 122.3, 52.9, 52.2, 51.6, 40.3, 34.3, 26.2, 21.6; IR (cm^{-1}) ν 3249, 2967, 1718, 1449, 1291, 1146, 992, 851, 665, 532; HRMS (ESI) calcd for $C_{15}H_{20}NO_6S$ $[M + H]^+$ 342.1006, found 342.1003.

*N-(4-Methyl-2,6-diphenethylphenylsulfonyl)acetamide (**10**) (Eq 2).* To a solution of **6a** (125.3 mg, 0.3 mmol) in THF (1.0 mL) and MeOH (0.7 mL) were added $NiCl_2{\cdot}H_2O$ (142.6 mg, 0.6 mmol, 2.0 equiv) and $NaBH_4$ (56.7 mg, 1.5 mmol, 5.0 equiv) at 0 °C under an argon atmosphere. The resulting mixture was stirred overnight and then quenched with water (3.0 mL). The crude mixture was diluted with EtOAc and filtered through a pad of Celite. The filtrate was separated, and the organic layer was washed with water and brine and dried over Na_2SO_4. The solvent was evaporated, and the crude mixture was purified by column chromatography (eluent EtOAc/petroleum ether 1/2) to afford 94.2 mg of **10** in 75% yield as a white solid: mp 156−158 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.99 (s, 1H), 7.35−7.29 (m, 8H), 7.22 (dd, J = 10.7, 6.4 Hz, 2H), 7.02 (s, 2H), 3.36 (dd, J = 9.8, 6.7 Hz, 4H), 3.01 (dd, J = 9.8, 6.6 Hz, 4H), 2.33 (s, 3H), 1.93 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 168.8, 144.2, 143.8, 141.7, 131.9, 128.6, 128.3, 126.0, 38.6, 37.4, 23.3, 21.1; IR (cm^{-1}) ν 3104, 3025, 2909, 2850, 1686, 1445, 1349, 1167, 831, 656, 511; HRMS (ESI) calcd for $C_{25}H_{28}NO_3S$ $[M + H]^+$ 422.1784, found 422.1787.

Deuteration Experiments. *Scheme 3a.* The reaction between **1a** (0.15 mmol) and D_2O (15 equiv) was carried out in the presence of $[Cp^*RhCl_2]_2$ (3.0 mol %) and $Cu(OAc)_2{\cdot}H_2O$ (2.0 equiv) with Tol-d_8 (1.0 mL) as the solvent at 100 °C for 24 h. After standard workup and purification, a mixture of **1a** and **D-1a** was obtained. ^1H NMR analysis of the mixture showed 73% D was incorporated into the two ortho positions of the sulfonamide aryl ring (see the attached spectrum in the Supporting Information).

Scheme 3b. The reaction of **1a** (0.15 mmol), alkene **2a** (3.0 equiv), and D_2O (15.0 equiv) was carried out in the presence of $[Cp^*RhCl_2]_2$ (3.0 mol %) and $Cu(OAc)_2{\cdot}H_2O$ (2.0 equiv) with Tol-d_8 (1.0 mL) as the solvent at 100 °C for 2 h. Afterward, the vial was cooled to room temperature, diluted with CH_2Cl_2, and transferred to a round-bottom flask. Silica was added to the flask, and volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography (eluent EtOAc/petroleum ether 1/2) on silica gel. Compound **3a** was obtained in 10% yield. The starting material **1a** was recovered in 64% yield, while monoalkenylated product was obtained in 25% yield. These two compounds cannot be separated by the flash column chromatography, and the yield was determined by ^1H NMR. In all of these compounds, no deuterium incorporation was detected (see the attached spectrum in the Supporting Information).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Full spectroscopic data for all new compounds, and details of the optimization. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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