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Intramolecular homolytic aromatic substitution of alkyl 2-benzimidazolyl sulfones as a means of entry into alkyl radicals for organic synthesis

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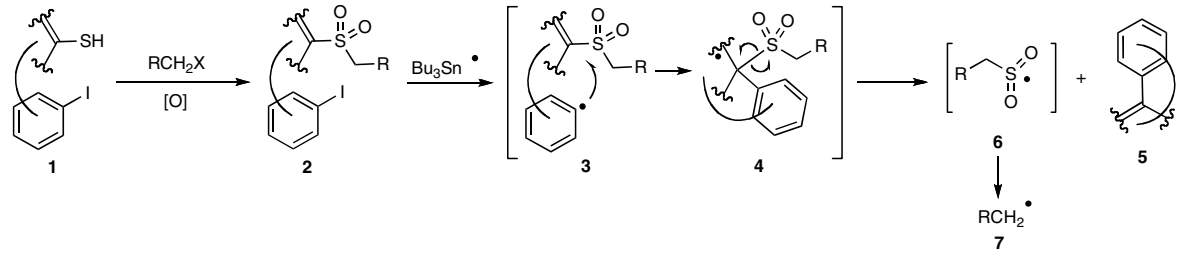
Abstract

The intramolecular radical aromatic substitution of heteroaryl sulfones by tethered aryl radicals has been investigated as a source of alkyl radicals. The 1-(2-iodobenzyl)benzimidazole-2-sulfonyl system was found to be the most effective, while a tetrazole-based system did not undergo the desired radical aromatic substitution at all. Application of the benzimidazole-based system to the generation of alkyl radical and their subsequent use in radical cyclizations was demonstrated.

Ongoing projects in our laboratory required the use of alkyl radical precursors beyond the halides, chalcogenides, and thiocarbonyl derivatives traditionally employed.[1,2] Nitroalkanes met many of our requirements[1–3] but still suffered from several limitations, most notably the high acidity of the α-hydrogen. Looking for another group with powerful electron-withdrawing properties but lower acidity of the α-hydrogens, we focused our attention on the sulfones. As this group is somewhat inert to direct displacement by tributyltin hydride and its surrogates, and does not take part in intramolecular homolytic substitution reactions at sulfur[1] we focused our attention on alkyl radical generation by intramolecular *ipso*-type substitution of alkyl aryl sulfones.

The susceptibility of aryl sulfones toward *ipso* intramolecular homolytic substitution is well known.[2] This reaction typically involves attack of a C-centered radical upon the *ipso* position of an aryl-sulfone, the cyclic radical



Scheme 1. General strategy for the generation of alkyl radicals from arylsulfones.

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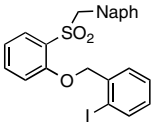
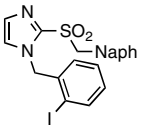
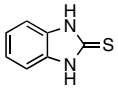
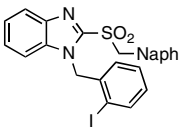
intermediate then fragments resulting in the formation of a sulfonyl radical. The earliest example of this reaction involved the attack of an alkyl radical on an aryl sulfonamide resulting in the transfer of the aryl group to the alkane.[2] Subsequently, this reaction has been widely employed in the synthesis of novel fused hetero-cycles and biaryls, with the focus on products derived from the aryl moiety of the initial alkyl aryl sulfone.[3–6] We envisaged an alternative application of this chemistry with the emphasis on the alkylsulfonyl radical expelled in the *ipso*-substitution process as a precursor, via extrusion of sulfur dioxide,[7] as an alkyl radical progenitor.

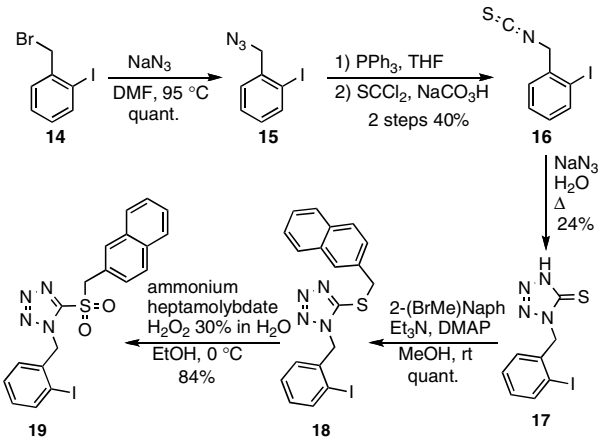
The general strategy foreseen here (Scheme 1) involves the synthesis of a system in which an aryl iodide trigger is tethered to an aromatic thiol; this thiol **1** can then be alkylated and subsequently oxidized to a sulfone **2**. While generally stable to typical synthetic manipulations this sulfone **2** undergoes *ipso*-substitution upon generation of the aryl radical **3** resulting in ejection of the alkyl sulfonyl radical **6**, which rapidly extrudes sulfur dioxide to leave the desired alkyl radical **7**.

A series of sulfones were synthesized based on aromatic thiols containing a second heteroatom for installation of the 2-iodobenzyl 'trigger'. The 2-methylnaphthalenyl radical was chosen as a model radical leaving group because of the characteristic chemical shift of methyl singlet at δ 2.48 in the product, which makes identification of a successful reaction by NMR possible. Compounds **9**, **11**, and **13** (Table 1) were constructed by sequential alkylations of the base compound followed by oxidation.[8] A tetrazole-based system **19** was constructed (Scheme 2) from the isothiocyanate **16** by way of a [3+2] cycloaddition in aqueous solution.[9–11]

Radical reactions were performed by syringe pump controlled addition of an AIBN/tributyltin hydride solution to

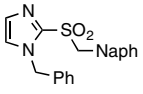
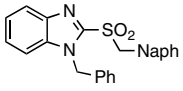
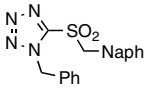
Table 1
Synthesis of arylsulfones for screening

Base	Yield 3-step synthesis[9]	Compound
 **8**	77, 70, 85	 **9**
 **10**	86, 92, 98	 **11**
 **12**	33, 59, 51	 **13**



Scheme 2. Synthesis tetrazole-based system **19**.[12]

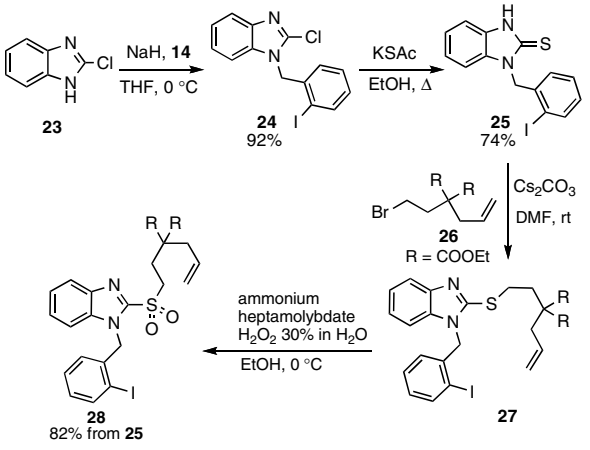
Table 2
Screening of arylsulfones for S_Hi

Arylsulfone	NMR Yield 2-methylnaphthalene (%)	Other products
9	0	Mixture of dehalogenated and cyclized products
11	10–20	 **20** 4:1, 20:product
13	40–50	 **21** 28%
19	0	 **22** 88%

a refluxing solution of the various alkyl aryl sulfones in order to minimize the concentration of stannane in an effort to reduce premature trapping of the aryl radical (Table 2). Not surprisingly, inspection of the reaction mixture of the 2-mercaptophenol-based system **9** by ^{1}H NMR spectroscopy did not show evidence of successful homolytic aromatic substitution, as indicated by the absence of 2-methylnaphthalene. Rather, a complex mixture of dehalogenated starting material and biaryl compounds, presumably the result of addition of the aryl radical to solvent and possibly the 3-position of the alkoxy benzene ring, was produced. Subjecting **11** to the same conditions resulted in simple dehalogenation of the majority of the starting material. However, the formation of 2-methylnaphthalene in 10–20% yield gave some grounds for optimism. The benzimidazole system **13** was the most successful precursor producing moderate amounts of product in the screening reaction.

Two aspects of the tetrazole-based system **19** make it quite interesting in the context of aromatic homolytic substitution. First, this system is the most electron deficient of the systems studied making it highly susceptible to nucleophilic aromatic substitution, as exemplified by its widespread application in the Kocienski modification of the Julia benzothiazole-based olefination.[12] Secondly, the use of the tetrazole ring eliminates the possibility of the initial aryl radical being trapped via an intramolecular 1,5-hydrogen transfer[13–15] a process, which could play a role in the poor conversion of imidazole-based system **11**. Unfortunately, the propensity of this system toward nucleophilic aromatic substitution does not extend to radical aromatic substitution, and the only reaction observed with **19** was its clean conversion to the dehalogenated starting material **22**; there was no evidence for the formation of 2-methylnaphthalene in this reaction.

Having established the supremacy of the benzimidazole nucleus in the desired radical aromatic substitution a 1(2-iodobenzyl)benzimidazole-2-thiol, which can be easily incorporated into substrates as an alkyl radical precursor, was synthesized. Thus, commercially available 2-chlorobenzimidazole **23** was treated with base and alkylated with 2-iodobenzyl bromide **14**. The resulting chlorobenzimidazole **24** was converted to thione **25** by nucleophilic displacement of chloride **24** with KSAc.[16] This synthesis of **25** was practical and scalable for the efficient preparation of larger quantities. For the purpose of this investigation, the challenge of the generation of a primary alkyl radical was chosen. Introduction of **25**[17] into an alkyl compound from the alkyl halide was completed in an efficient 2-step sequence (Scheme 3).



Scheme 3. Synthesis and incorporation of precursor **25**.

Table 3
Generation and cyclization of alkyl radical **34** from sulfone **28**

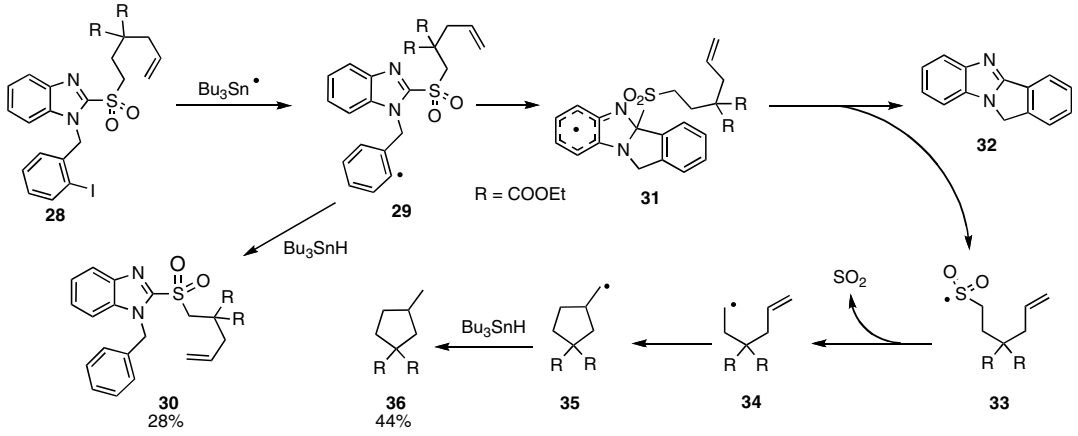
Propagating reagent	Solvent	Addition time (h)	Yield of **36** (%)
Bu_3SnH	Toluene	3	36
Bu_3SnH	Toluene	5	44
Bu_3SnH	Benzene	8	35
TTMSH	Benzene	Immediate	**30**
TTMSH	Benzene	5	A

Starting material **28** was recovered unchanged from this reaction.

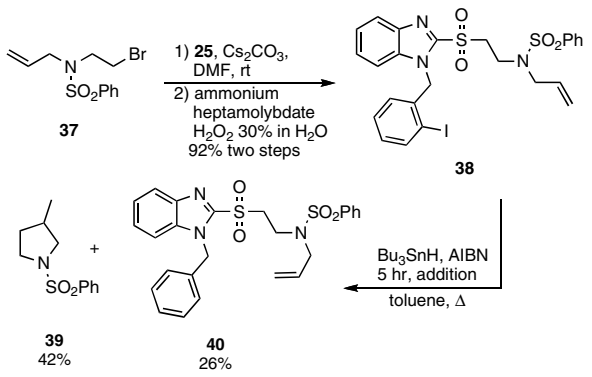
Syringe pump controlled treatment of the alkyl arylsulfone **28**[18] in refluxing toluene with a solution of AIBN and tributyltin hydride over 5 h (Scheme 4); resulted in successful generation of the cyclized product **36**[19] in 44% yield along with 28% of the dehalogenated starting material **30**. Attempts to further suppress premature trapping of the aryl radical by varying the addition time proved unsuccessful (Table 3). Use of tris(trimethylsilyl) silane as a propagating agent resulted in either complete dehalogenation of the aryl iodide or failure of the reaction to propagate.

A second example involves a sulfonamide **37**.[20] Again, the precursor **25** was incorporated smoothly into the alkyl system, resulting in a yield of 92% over two steps (Scheme 5). The methyl-pyrrolidine **39**[21] product of the 5-*exo*-cyclization of the alkyl radical was recovered in moderate yield on treatment of **38** with tributyltin hydride.

In conclusion, a system has been designed which can be effectively used as a precursor for alkyl radicals from sulfones. The 2-thiobenzimidazole **25** can be incorporated into an alkyl system in a facile 2-step sequence. The resulting



Scheme 4. Generation of alkyl radical **34** from sulfone **28**.



Scheme 5. Alkyl radical generation via sulfone **38**.

sulfone can then be used to generate the corresponding alkyl radical under typical AIBN/tributyltin hydride mediated conditions.

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8. *General synthesis of compounds* **9**, **11**, *and* **13**. To a solution of 2-thio imidazole/phenol (2.0 mmol) and 2-(bromomethyl)naphthalene (486 mg, 2.2 mmol) dissolved in DCM (10 mL) and CH_3CN (5 mL) were added Et_3N (3.0 mmol) and DMAP (5 mg). The reaction mixture was stirred 2 h at rt, the solvent was then removed in vacuo and the residue was taken up in DCM (25 mL) and washed with water (2×25 mL) the organic layer was concentrated in vacuo and the residue was purified by silica gel column chromatography. A solution of the resulting thioether (1.17 mmol) and 2-iodobenzyl bromide (1.4 mmol) in DMF (10 mL) was treated with K_2CO_3 (1.75 mmol). The reaction mixture was stirred at rt for 14 h before it was partitioned between EtOAc (25 mL) and water (30 mL), the organic layer was then washed with brine and dried with Na_2SO_4. The solvent was removed in vacuo and the residue was purified by silica gel chromatography. Oxidation of the resulting thioether (1.25 mmol) was undertaken with catalytic ammonium heptamolybdate (154 mg, 10 mol %) in EtOH (5 mL). To this solution was added H_2O_2 (30% in water, 2.0 mL); after stirring for 14 h the reaction mixture was partitioned between water (20 mL) and EtOAc (20 mL), the organic layer was evaporated and the residue was purified by silica gel column chromatography. *2-[2′-(2-Iodobenzyloxy)phenylsulfonylmethyl]naphthalene* (**9**) as a white solid, mp 147–149 °C, ^{1}H NMR (500 MHz, $CDCl_3$): 4.75 (s, 2H), 5.30 (s, 2H), 6.99 (t, $J = 7.5$ Hz, 1H), 7.27 (dd, $J = 1.5$, 8.5 Hz, 1H), 7.43–7.47 (m, 2H), 7.51 (t, $J = 8.0$ Hz, 1H), 7.56 (dt, $J = 1.5$, 7.5 Hz, 1H), 7.63 (s, 1H), 7.69–7.78 (m, 4H), 7.89–7.92 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): 60.9, 75.2, 96.9, 113.6, 121.4, 125.5, 126.3, 126.5, 126.8, 127.7, 127.9, 128.3, 129.0, 129.2, 130.1, 130.6, 131.4, 133.1, 135.7, 137.9, 139.3, 156.2. *1-(2-Iodobenzyl)-2-(naphthylmethylsulfonyl)imidazole* (**11**) as a white solid ^{1}H NMR (500 MHz, $CDCl_3$): 4.67 (s, 2H), 4.75 (s, 2H), 6.15 (s, 1H), 6.60 (s, 1H), 6.79 (s, 2H), 7.21–7.25 (m, 1H), 7.25 (s, 1H), 7.74–7.51 (m, 2H), 7.52 (s, 1H), 7.64–7.83 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): 55.4, 62.5, 98.5, 124.1, 124.7, 126.8, 127.1, 127.8, 128.1, 128.3, 128.65, 128.74, 130.0, 130.2, 130.9, 133.1, 133.3, 138.4, 139.5, 140.4; Anal. Calcd for $C_{21}H_{17}IN_2O_2S$: C, 51.65; H, 3.51. Found: C, 51.83; H, 3.61. *1-(2-Iodobenzyl)-2-(2-naphthylmethyl sulfonyl)benzimidazole* (**13**) a white solid. Mp 148–150 °C, ^{1}H NMR (500 MHz, $CDCl_3$): 4.99 (s, 2H), 5.05 (s, 2H), 5.92 (d, $J = 8.0$ Hz, 1H), 6.61 (t, $J = 7.5$ Hz, 1H), 6.78 (t, $J = 7.5$ Hz, 1H), 6.96 (d, $J = 8.5$ Hz, 1H), 7.25 (dd,$J = 2.0$, 8.0 Hz, 1H), 7.33 (dt, $J = 1.0$, 8.0 Hz, 1H), 7.41–7.48 (m, 2H), 7.51 (t, $J = 1.0$, 7.5 Hz, 1H), 7.64 (d, $J = 7.5$ Hz, 1H), 7.70–7.74 (m, 3H), 7.82 (d, $J = 8.0$ Hz, 1H), 8.00–8.03 (m, 1H).
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11. *1-(2-Iodobenzyl)-5-thiotetrazole* (**17**). Sodium azide (325 mg, 5.0 mmol) and **16** (0.9 g, 3.3 mmol) were dissolved in water (10 mL) and DMF (5 mL). The reaction mixture was heated to 100 °C for 24 h, at which point it was then acidified to pH 5 and extracted with EtOAc (3×25 mL), the organic layer was washed with brine and dried with Na_2SO_4. The solvent was removed in vacuo and the residue was purified by silica gel column chromatography (eluent: 50% to neat EtOAc in hexanes) to afford **17** (250 mg, 0.79 mmol, 24%). ^{1}H NMR (500 MHz, CD_3OD): 5.48 (s, 2H), 7.07 (dt, $J = 1.5$, 7.5 Hz, 1H), 7.71 (dd, $J = 1.5$, 7.5 Hz, 1H), 7.36 (dt, $J = 1.5$, 8.0 Hz, 1H), 7.93 (dd, $J = 1.5$, 8.0 Hz, 1H); ^{13}C NMR (125 MHz, CD_3OD): 54.4, 99.6, 128.4, 128.9, 129.7, 136.8, 139.6, 145.0. *1-(2-Iodobenzyl)-5-(naphthylmethylthio)tetrazole* (**18**). To a solution of **17** (200 mg, 0.629 mmol), Et_3N (135 μL, 0.950 mmol) and DMAP (5 mg) was added 2-bromomethyl naphthalene (153 mg, 692 μmol). The reaction mixture was kept stirring at rt for 3 h before the solvent was removed in vacuo. The residue was partitioned between EtOAc and satd $NaHCO_3$ (25 mL each), the organic layer was then evaporated and the residue was purified by silica gel column chromatography to afford the title compound **18** (286 mg, 0.629 mmol, quant. yield) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): 4.67 (s, 2H), 5.31 (s, 2H), 6.62 (dd, $J = 1.5$, 7.5 Hz, 1H), 6.94 (dt, $J = 1.5$, 7.5 Hz, 1H), 7.09 (dt, $J = 1.5$, 7.5 Hz, 1H), 7.43 (dd, $J = 2.0$, 8.0 Hz, 1H), 7.45–7.48 (m, 2H), 7.75–7.80 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): 38.4, 55.4, 97.9, 126.5, 126.6, 126.7, 127.7, 128.0, 128.3, 128.6, 128.8, 130.4, 132.9, 133.0, 133.2, 135.4, 139.8, 154.1; EI-HRMS calcd [M]+: 458.00621, found: 458.00710. *1-(2-Iodobenzyl)-5-(naphthylmethylsulfonyl)tetrazole* (**19**). Ammonium heptamolybdate (75 mg) and **18** (250 mg, 0.545 mmol) were taken up in EtOH (5 mL) and H_2O_2 (30% in water, 1 mL) was added. The reaction mixture was kept stirring for 24 h before being filtered through a plug of silica (eluent: EtOAc), evaporation of the solvent in vacuo afforded the title compound **19**. (225 mg, 0.46 mmol, 84%). ^{1}H NMR (500 MHz, $CDCl_3$): 5.00 (s, 2H), 5.36 (s, 2H), 6.26 (d, $J = 7.5$ Hz, 1H), 6.81 (t, $J = 7.5$ Hz, 1H), 6.88 (t, $J = 7.5$ Hz, 1H), 7.33 (d, $J = 8.0$ Hz, 1H), 7.52–7.58 (m, 2H), 7.71–7.85 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): 57.3, 62.8, 98.2, 122.2, 127.1, 127.6, 127.8, 128.3, 128.4. 128.6, 129.2, 130.4, 131.6, 133.1, 133.5, 135.0, 139.8, 152.2.
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17. *1-(2-Iodobenzyl)-2-thiobenzimidazole* (**25**). Compound **24** (3.4 g, 9.2 mmol) was dissolved in EtOH (30 mL) and THF (10 mL), to this solution was added KSAc (1.27 g, 11.1 mmol). The reaction mixture was heated to 70 °C and stirred for 24 h, at which point TLC

confirmed consumption of **24**. The solvent was then removed in vacuo and the residue was taken up in water (50 mL) and extracted with EtOAc (3 × 50 mL), the organic layer was then washed with brine and concentrated. The residue was initially subjected to silica gel column chromatography (eluent: 20% EtOAc in hexanes). However, recrystallization from a solution of 15% EtOAc in hexanes was needed for complete purification of the title product and afforded **25** (2.5 g, 6.8 mmol, 74%) as a white fluffy solid. Mp 220–222 °C, ^{1}H NMR (500 MHz, CD_3OD): 5.51 (s, $J = 2$H), 6.71 (d, $J = 8.0$ Hz, 1H), 6.90 (d, $J = 8.0$ Hz, 1H), 6.95 (dt, $J = 1.5$, 8.0 Hz, 1H), 7.10 (dt, $J = 1.5$, 8.0 Hz, 1H), 7.15–7.20 (m, 2H), 7.25 (d, $J = 7.5$ Hz, 1H), 7.87 (dd, $J = 1.5$, 7.5 Hz, 1H); ^{13}C NMR (125 MHz, CD_3OD): 52.4, 97.1, 109.8, 110.1, 122.9, 123.6, 127.1, 128.5, 129.2, 131.1, 132.5, 137.1, 139.5, 169.2.

18. *4,4-Bis(ethoxycarbonyl)-6-[1-(2-iodobenzyl)-2-benzimidazolesulfonyl]-1-hexene* (**28**). A solution of **25** (298 mg, 0.8 mmol) and **26** (250 mg, 0.8 mmol) in DMF (10 mL) was treated with Cs_2CO_3 (390 mg, 1.2 mmol) and stirred for 12 h at rt. The reaction mixture was poured into water (50 mL) and extracted with EtOAc (3 × 25 mL) the organic layer was then washed with brine and evaporated affording thioether **27**. The crude thioether was taken up in THF and EtOH (5 mL each), to this solution was added a suspension of ammonium heptamolybdate (50 mg, 40 μmol) in H_2O_2 (30% in water, 2.5 mL). The reaction was kept stirring for 24 h before being poured into water (50 mL) and extracted with EtOAc (3 × 25 mL), the organic layer was washed with brine and dried with Na_2SO_4. The solvent was then evaporated and the residue was purified by silica gel column chromatography (eluent: 10% EtOAc in hexanes) to afford **28** (409 mg, 0.655 mmol, 82%) as a crystalline solid. Mp 96–99 °C, ^{1}H NMR (500 MHz, $CDCl_3$): 1.25 (t, $J = 7.0$ Hz, 6H), 2.43–2.46 (m, 2H), 2.66 (d, $J = 7.5$ Hz, 2H), 3.69–3.73 (m, 2H), 4.18–4.22 (m, 4H), 5.11 (d, $J = 10.0$ Hz, 1H), 5.14 (dd, $J = 1.5$, 17.0 Hz, 1H), 5.60–5.70 (m, 1H), 5.81 (s, 2H), 6.49 (d, $J = 7.5$ Hz, 1H), 6.97 (t, $J = 7.5$ Hz, 1H), 7.15–7.20 (m, 2H), 7.36–7.39 (m, 2H), 7.86–7.90 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): 14.1, 25.5, 37.7, 50.9, 53.9, 56.2, 61.9, 96.9, 11.5, 120.2, 121.9, 124.4, 126.4, 126.7, 128.9, 129.7, 131.3, 135.4, 137.2, 139.7, 141.1, 147.3; ESI-HRMS calcd [M+H]+: 625.08693, found: 625.0852.

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20. *N-Allyl-N-[2-(2-iodobenzyl)-1-benzimidazoylethylsulfonyl]-N-phenylsulfonamide* (**29**). A colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): 3.72–3.75 (m, 2 H), 3.85 (d, $J = 6.5$ Hz, 2H), 3.90–3.93 (m, 2H), 5.17 (dd, $J = 1.5$, 21.5 Hz, 1H), 5.20 (dd, $J = 1.5$, 28.5 Hz, 1H), 5.60–5.68 (m, 1H), 5.79 (s, 2H), 6.48 (dd, $J = 1.0$, 7.5 Hz, 1H), 6.98 (dt, $J = 1.0$, 7.5 Hz, 1H), 7.21 (dd, $J = 1.5$, 7.0 Hz, 1H), 7.37–7.44 (m, 2H), 7.50 (t, $J = 8.0$ Hz, 2H), 7.59 (t, $J = 8.0$ Hz, 1H), 7.79 (dd, $J = 1.0$, 8.0 Hz, 2H), 7.90 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): 41.4, 52.0, 53.9, 54.3, 96.9, 111.6, 120.6, 121.8, 124.6, 126.7, 127.3, 129.0, 129.4, 129.8, 132.1, 133.1, 135.5, 137.1, 138.6, 139.7, 140.9, 147.2.

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