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Article

One-Pot Synthesis of α-Alkyl Styrene Derivatives

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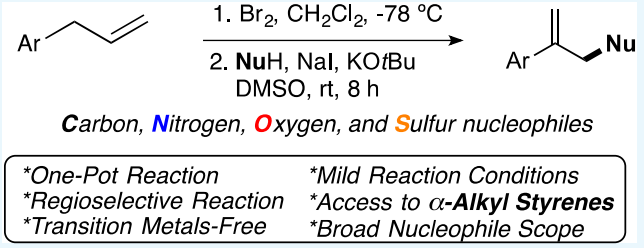
ABSTRACT: There is a significant need to develop more rapid and efficient routes to styrene derivatives, since they are extensively used in polymer sciences. This manuscript reports a one-pot synthesis of an array of α-alkyl styrene derivatives from readily available natural products (i.e., estragole and safrole). This method is regioselective, producing a rearranged adduct, under transition metal-free conditions. This methodology has broad nucleophile scope, even tolerating sterically hindered nucleophiles; it is general for carbon, nitrogen, oxygen, and sulfur nucleophiles.



INTRODUCTION

Polystyrene has had an immeasurable impact on our society. Since its discovery in 1839,[1] polystyrene has found plentiful applications.[2] To meet our daily needs, polystyrene has been prepared in solid and foam forms.[2] In addition, several chemical modifications have been done during the polymerization process or to the styrene monomers, all with the ultimate goal of producing polymers with exceptional or unique physical and chemical properties.[2−4] Copolymerization and/or addition of additives are useful strategies to produce distinctive polymers.[5] For instance, the use of octasulfur (S_8) during vulcanization.[6] Among styrene derivatives, we can find α-methyl styrene, a monomer that has been used to improve the impact and heat-resistance of polymers.[7−9] This is particularly interesting since we can further derivatize α-methyl styrene and even add sulfur moieties to its backbone.

Currently, there are few synthetic methods to produce α-alkyl styrenes. The traditional approach is to use Wittig conditions[10,11] for the conversion of aryl ketones to terminal alkenes (α-alkyl styrenes). Thus far, only simple alkyls bearing groups have been reported using this method (Figure 1, eq 1).[12−14] Alternatively, copper-mediated oxidative coupling of α-methyl styrenes with tertiary alkyl radicals has also produced α-alkyl styrenes (Figure 1, eq 2),[15] but this method obviously requires prior synthesis of the α-methyl styrenes. A regiospecific addition of Grignard reagent to propargyl alcohol has produced hydroxy (OH) derivatives with limited substrate scope (Figure 1, eq 3).[16] These hydroxy derivatives, together with ammonium salts, have been used to prepare both carbon and nitrogen derivatives using metals (Figure 1, eq 4).[17−19] Furthermore, both Suzuki and Heck conditions can produce oxygen and nitrogen derivatives, albeit oxygen or nitrogen moieties have to be preinstalled in the coupling partner (Figure 1, eq 5).[20−22]

Although some of these methods have advantages such as readily available starting materials, they unfortunately have

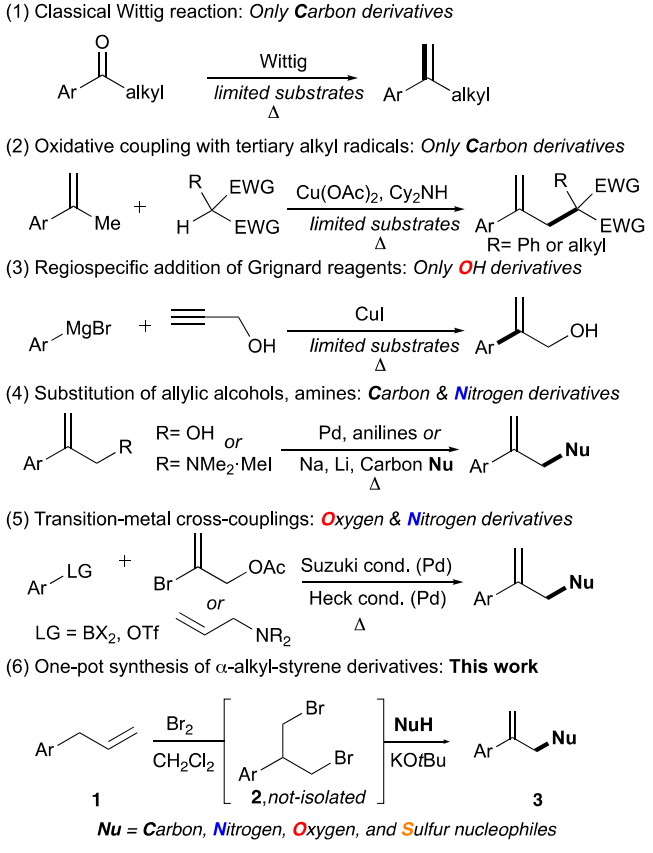


Figure 1. General methods for the synthesis of α-alkyl styrenes.

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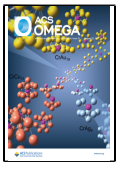

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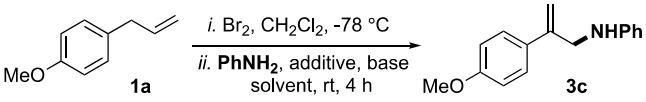
limited substrate scope and require the use of stoichiometric phosphonium salts, base, or metal (e.g., Mg, Na, and Li), while other approaches make use of a transition metal as the catalyst (e.g., Pd and Cu).

All of the above-mentioned synthetic methods have appeared in the literature reflecting the many applications that α-alkyl styrenes can have. For instance, α-alkyl styrenes have been used in Povarov reactions,[23] [6+2] cycloaddition reactions,[24] isomerizations,[12,25] selective hydrocarboxylations,[26] dimerizations,[27,28] fluorocyclizations,[29] allylic fluorinations,[30] in the synthesis of 2-fluoro-2-phenylalkancil acids,[31] among others.[32,33] Therefore, it is valid to say that α-alkyl styrenes have emerged as synthetically useful building blocks. However, despite these various reported synthetic alternatives, it is reasonable to say that a milder, transition metal-free method to synthesize α-alkyl styrenes, with a broader scope, would be extremely useful. To this goal, we herein report a transition metal-free and efficient synthetic protocol that utilizes readily available natural products as starting materials (Figure 1, eq 6). Importantly, our one-pot, two-step procedure is compatible with carbon, oxygen, nitrogen, and sulfur nucleophiles.

RESULTS AND DISCUSSION

To optimize our protocol, we used estragole (**1a**) as the model substrate, as shown in Table 1. Initially, **1a** was subjected to our previously optimized bromination conditions.[34] However, using $CHCl_3$ as a solvent produced a mixture of (di)-brominated products (~ratio 1:1).[35] Therefore, the solvent was changed to CH_2Cl_2, and the reaction was performed at −78 °C. This solvent effect and ratios were reported in 1973 by Dubois et al.[36] After 20 min, 2.1 equivalents of aniline were added and the reaction mixture was stirred for 4 h at room temperature. Unfortunately, the reaction produced only traces of the expected α-alkyl styrene (**3c**) (Table 1, entry 1), even after adding 2.3 equiv of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)[37,38] as base (Table 1, entry 2). Adding NaI (1.0 equiv) as an additive only increased the yield to 11% (Table 1, entry 3). Therefore, we decided to switch solvents for the second step. This time, the solvent (CH_2Cl_2) was removed under reduced pressure and other solvents were added, followed by the addition of 1.5 equiv of aniline and then stirred for 4 h at room temperature. This solvent screening showed that dimethyl sulfoxide (DMSO) is superior to other solvents such as CH_2Cl_2, MeCN, toluene, or dimethylformamide (DMF) (entries 3−7). To our delight, α-alkyl styrene (**3c**) was obtained in 49% (entry 7). With this promising result on hand, we then screened several inorganic bases (entries 9−12), and organic bases (entries 13 to 14), all affording the expected product with yields fluctuating from 14 to 60%, in the presence of 1.0 equiv of NaI. The highest yield (60%) was observed when potassium *tert*-butoxide (KO*t*Bu) was employed as base (entry 12). Further control experiments revealed that longer reactions times, using Cs_2CO_3 as the base, diminished the yield (i.e., 52% in 4 h, while 42% was observed after 8 h) (entries 11 and 15, respectively), presumably due to product decomposition or isomerization.[12,39] Fortunately, KO*t*Bu was tolerated and efficient to afford our expected product **3c** in 66% yield (entry 16). Other additives such as KI, Me_3NI, and TBAI promoted the reaction (not shown), but the yields were low compared to NaI. It is worth noting that in the absence of NaI the yield was 39% yield (entry 17), though the role of NaI was described in our prior reports on liner (*E*)-allylic compounds.[34,39] Hence, we decided to select KO*t*Bu as the base for this transformation, NaI as the additive, and 8 h reaction time (entry 16).

Table 1. Optimization of Reaction Conditions[a]



entry	aniline (equiv)	additive	base (2.3 equiv)	solvent	yield (%)[b]
1	2.1	none	none	CH_2Cl_2	trace
2	1.5	none	DBU	CH_2Cl_2	<5
3	1.5	NaI	DBU	CH_2Cl_2	11
4	1.5	NaI	DBU	MeCN	6
5	1.5	NaI	DBU	toluene	21
6	1.5	NaI	DBU	DMF	44
7	1.5	NaI	DBU	DMSO	49
8	2.1	none	none	DMSO	11
9	1.5	NaI	Na_2CO_3	DMSO	14
10	1.5	NaI	K_2CO_3	DMSO	23
11	1.5	NaI	Cs_2CO_3	DMSO	52
12	1.5	NaI	KO*t*Bu	DMSO	60
13	1.5	NaI	Et_3N	DMSO	31
14	1.5	NaI	*i*-Pr_2EtN	DMSO	28
15	1.5	NaI	Cs_2CO_3	DMSO	45[c]
16	**1.5**	**NaI**	**KO*t*Bu**	**DMSO**	**66**[c]
17	1.5	none	KO*t*Bu	DMSO	39

[a]Reactions were carried out with estragole **1a** (0.5 mmol, 74 mg, 1 equiv), Br_2 (0.65 mmol, 104 mg, 34 μL, 1.3 equiv), in 2.0 mL of CH_2Cl_2 at −78 °C for 30 min. Then, the volatiles were removed. To the crude reaction mixture was added 2.0 mL of solvent, aniline (1.5 equiv), and base (2.3 equiv), at 22 °C and stirred for 4 h. [b]Isolated yields using silica gel flash chromatography. [c]Stirred for 8 h.

With the optimal reaction conditions on hand for the conversion of estragole **1a** to amine-bearing α-alkyl styrenes **3**, we then explored the scope of the one-pot two-step protocol, as shown in Table 2. Estragole **1a** was initially treated with 1.3 equiv of bromine at −78 °C in dichloromethane (DCM). The reaction was monitored by thin-layer chromatography (TLC), and once it was deemed complete (~30 min), the volatiles were removed under reduced pressure. To the crude dibrominated adducts, DMSO, the respective amine/aniline, NaI, and KO*t*Bu were added sequentially and the reaction mixture was stirred for 8 h, at room temperature (Table 2). All reactions were quenched after 8 h for comparative purposes, although small amounts of dibrominated intermediate **2** were still present. In all cases, the reaction proceeds smoothly, in the presence of KO*t*Bu and *N*-nucleophile (azide, alkyl amines, or anilines), to afford the corresponding nitrogen-containing α-alkyl styrene **3**, in moderate to good yields.

To make our study more relevant, two sets of reaction conditions were investigated for every substrate, one using KO*t*Bu and the second with DBU. The yields for the KO*t*Bu-mediated transformation are presented below in Tables 2−5, whereas the yields using DBU are shown in the Supporting Information (Tables SI, 1−3). This study was performed to compare the result from our recently reported regio-and stereoselective nucleophilic addition to miscellaneous terminal olefins.[34,39] In our prior work, DBU was the best base to afford allylic adducts from electron-poor or weak electron-donating substrates. However, for this work, KO*t*Bu was deemed superior base for the observed rearrangement of electron-rich

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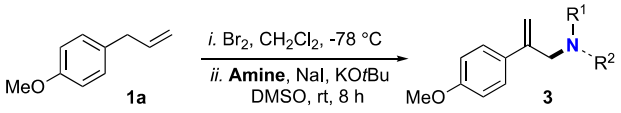
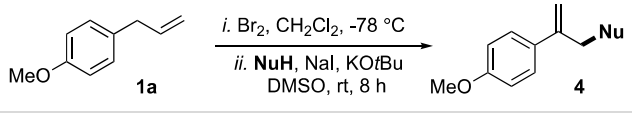
Table 2. Scope of Nitrogen Nucleophiles[a]



entry	Nitrogen-nucleophile	product no.	yield[b] (%)[c]
	Azide		
1	NaN_3	**3a**	66 (60)
	Primary Amines		
2		**3b**	62 (50)
3		**3c**	70 (66)
		1-gram scale =	(63)
4		**3d**	67 (64)
5		**3e**	79 (63)
6		**3f**	59 (53)
	Secondary Amines		
7		**3g**	39 (37)
8		**3h**	70 (65)
9		**3i**	77 (69)
10		**3j**	71 (69)
11		**3k**	77 (69)
12		**3l**	53 (51)
13		**3m**	41 (40)
14		**3n**	63 (54)

[a]Reactions conditions: estragole **1a** (0.5 mmol, 1.0 equiv), bromine (0.65 mmol, 104 mg, 34 μL, 1.3 equiv), in 2.0 mL of CH_2Cl_2 at −78 °C for 30 min. Then, the volatiles were removed. To the crude reaction mixture was added 2 mL of DMSO, NaI (0.50 mmol, 1.0 equiv), amine (0.75 mmol, 1.5 equiv), and KO*t*Bu (1.15 mmol, 2.3 equiv), at 22 °C and stirred for 8 h. [b]Crude ^{1}H NMR yield of reaction using KO*t*Bu as a base, in DMSO-d_6 as the solvent, and mesitylene as the internal standard. [c]Isolated yields based on **1a**, using silica gel flash column chromatography.

Table 3. Scope of Other Nucleophiles[a]



entry	nucleophile	product no.	yield[b] (%)[c]
	Oxygen Nucleophiles		
1	AcOH	**4a**	54 (49)
2		**4b**	26 (22)
3		**4c**	49 (41)
4	R = 4-OMe	**4d**	49 (45)
5	4-Cl	**4e**	51 (45)
6	4-CN	**4f**	54 (31)
7	4-NO_2	**4g**	57 (46)
8	2-NO_2	**4h**	70 (54)
9		**4i**	39 (34)
	Carbon Nucleophiles		
10	R = OMe	**4j**	55 (51)
11	OEt	**4k**	66 (62)
12		**4l**	70 (61)
	Sulfur Nucleophiles		
13		**4m**	48 (48)
14		**4n**	13 (11)

[a]Reactions conditions: estragole **1a** (0.5 mmol, 1.0 equiv), bromine (0.65 mmol, 104 mg, 34 μL, 1.3 equiv), in 2.0 mL of CH_2Cl_2 at −78 °C for 30 min. Then, the volatiles were removed. To the crude reaction mixture was added 2.0 mL of DMSO, NaI (0.50 mmol, 1.0 equiv), nucleophile (0.75 mmol, 1.5 equiv), and KO*t*Bu (1.15 mmol, 2.3 equiv), at 22 °C and stirred for 8 h. [b]Crude ^{1}H NMR yield of reaction using KO*t*Bu as a base, in DMSO-d_6 as the solvent, and mesitylene as the internal standard. [c]Isolated yields based on **1a**, using silica gel flash column chromatography.

substrates (i.e., estragole and safrole). Therefore, it was considered necessary to present a full disclosure of the yields' differences of KO*t*Bu vs DBU. Table 2 contains the scope of nitrogen nucleophiles using KO*t*Bu as a base. The first nitrogen nucleophile for this table was sodium azide, delivering adduct **3a** in 60% isolated yield (Table 2, entry 1). The scope for primary amine nucleophiles included aliphatic and aromatic amines. Hexyl amine gave the adduct **3b** in 50% yield (Table 2, entry 2). Electron-rich and electron-poor aromatic amines

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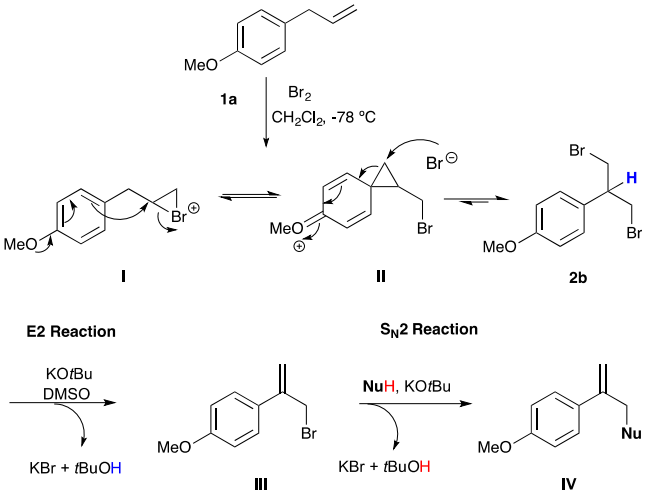
were also good substrates for this transformation with yields up to 66% (Table 2, entries 3−6). In addition, secondary amines afforded their respective tertiary allylamines in good yields

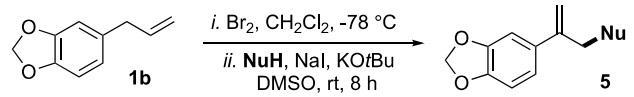
Scheme 1. Proposed Mechanism

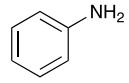
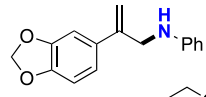
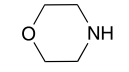
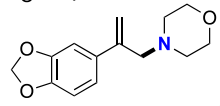
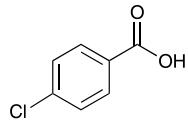
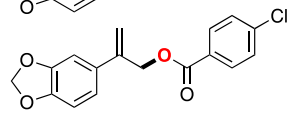
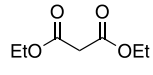
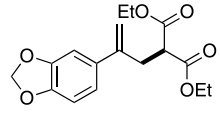


(entries 7−11). Hindered secondary amines,[40] such as diisopropylamine and methylbenzylamine, were also tolerated and afforded the desired products in 37 and 69% yield, respectively (entries 7 and 9). To our delight, diallylamine was an excellent substrate with 65% yield (entry 8). This helps to emphasize the wide-ranging scope of this method, which even provides easy access to triallylamine (**4h**) under mild reaction conditions. Furthermore, heterocycles such as morpholine and piperidine were also compatible and afforded adducts **3j** and **3k** in 69% yield each (entries 10 and 11). Similarly, and to further validate the scope of our synthetic method, phthalimide, 1-benzhydrylpiperazine, and 3-acetyl indole were also used as amine nucleophiles, affording their respective adducts in 51, 40, and 54% isolated yields (Table 2, entries 12−14). It is worth noting that 4-chloro aniline was tolerated, which may be problematic with palladium-catalyzed methods.[41] Overall, the results shown in Table 2 offer strong evidence for the generality of this method.

To further establish the scope of this transformation, assorted oxygen, carbon, and sulfur nucleophiles were also screened (Table 3). In regard to oxygen-containing nucleophiles, aliphatic, aromatic, and conjugated carboxylic acids were viable substrates. For example, acetic acid gave adduct **4a** in 49% yield (entry 1), while glycolic acid and hexanoic acid deliver adduct **4b** and **4c** in 22 and 41%, respectively (entries 2 and 3). Electron-poor and electron-rich benzoic acids were also tolerated, with yields ranging from 31% (**4f**) to 54% (**4h**) (entries 4−8). Furthermore, *trans*-cinnamic acid delivers adduct **4i** in 34% (entry 9). The carbon-based nucleophiles dimethyl malonate, diethyl malonate, and ethyl 3-oxo-3-phenylpropanoate were good substrates and afforded their expected adducts in 51, 62, and 61% yield, respectively (entries 10−12). Additionally, sulfur-containing nucleophiles were also screened. The aliphatic thioacetic acid produced compound **4m** in 48% (Table 3, entry 13). This yield is similar to those yields from carboxylic acids. However, thiobenzoic acid gave adduct **4n** in only 11% (entry 14), presumable due to its difference in nucleophilicity when compared to thioacetic acid. We wish to note explicitly that running all the reactions with

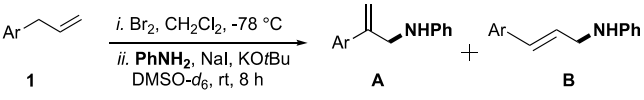
Table 4. Scope of Some Nucleophiles with Safrole[a]

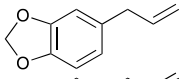
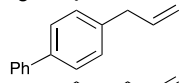
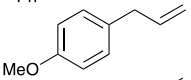
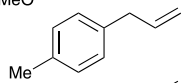
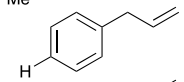
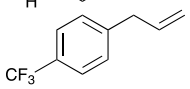


entry	nucleophile	product no.	yield[b] (%)[c]
1			**5a** 75 (72)
2			**5b** 75 (70)
3			**5c** 66 (62)
4			**5d** 54 (50)

[a]Reactions conditions: safrole **1a** (0.5 mmol, 1.0 equiv), bromine (0.65 mmol, 104 mg, 34 μL, 1.3 equiv), in 2.0 mL of CH_2Cl_2 at −78 °C for 30 min. Then, the volatiles were removed. To the crude reaction mixture was added 2.0 mL of DMSO, NaI (0.50 mmol, 1.0 equiv), nucleophile (0.75 mmol, 1.5 equiv), and KO*t*Bu (1.15 mmol, 2.3 equiv), at 22 °C and stirred for 8 h. [b]Crude ^{1}H NMR yield of reaction using KO*t*Bu as a base, in DMSO-d_6 as the solvent, and mesitylene as the internal standard. [c]Isolated yields based on **1b**, using silica gel flash column chromatography.

Table 5. Comparative Study: Electron-Donating Groups (EDG) vs Electron-Withdrawing Groups (EWG)[a]



entry	allylaryl	A, ^{1}H NMR yield[b]	B, ^{1}H NMR yield[b]
1		78	0
2		75	0
3		72	0
4		56	45
5		19	24
6		traces	64[c]
7		0	72

[a]Reactions conditions: allylaryl **1** (0.4 mmol, 1 equiv), Bromine (0.65 mmol, 104 mg, 34 μL, 1.3 equiv), in 2.0 mL of CH_2Cl_2 at −78 °C for 30 min. Then, the volatiles were removed. To the crude reaction mixture was added 2.0 mL of DMSO, NaI (0.50 mmol, 1.0 equiv), aniline (0.75 mmol, 1.5 equiv), and KO*t*Bu (1.15 mmol, 2.3 equiv), at 22 °C and stirred for 8 h. [b]Crude ^{1}H NMR yield of reaction using KO*t*Bu as a base, in DMSO-d_6 as the solvent, and mesitylene as the internal standard. [c]Isolated yield of reaction using DBU as a base.

DBU as base paid off. Specifically, thiobenzoic acid gave adduct **4n** in 50% isolated yield (Table SI, entry 14),

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presumably due to DBU being a milder base, thus eliminating side byproducts. For instance, during mechanism studies, we found that for this specific substrate, a double nucleophilic addition was observed (Scheme S1, eq 5).

On the basis of experimental observations,[35] our previous work,[34,39] and the bromine-mediated rearrangements studies by Dubois[36] and Costa,[42] we propose that estragole undergoes an alkene bromination to form bromonium ion (**I**), which in turn undergoes an intramolecular attack by the electron-rich benzene to form the spiro[2.5] intermediate (**II**). This intermediate can be ring-opened by bromide ion to produce either 2,3-dibromo (**2a**, see the Supporting Information, SI) or 1,3-dibromide intermediate (**2b**). The 1,3-dibromide isomer (**2b**) is the product of a rearrangement step initiated/driven by the formation and ring-opening of the spiro[2.5] intermediate.[43] It is observed in a higher ratio due to its stability and our mild reaction conditions. After this dibromination step, an E2 elimination produces allyl bromide (**III**), enabled by KO*t*Bu. Then, a S_N2 displacement occurs to afford the final adduct (**IV**) (Scheme 1). Additional mechanistic details for this transformation, together with the structural elucidation of key byproducts, are presented in the SI.[35]

In 1984, Costa reported a relatively short study of the bromination of safrole.[42] He reported dibromination ratios (~1:3) favoring the 1,3-dibromide adduct when safrole was used, while Dubois's 1973 study showed ~1:1 ratio of 1,2 and 1,3-dibromo adducts, for estragole. Therefore, we hypothesized that safrole[44] should be a better substrate for our transformation. However, we decided to utilize estragole as the basic substrate to avoid bias in our data. Nonetheless, we also wanted to verify our hypothesis. To do so, we carried out a few representative transformations using safrole as the starting material (Table 4). First, aniline was used as the nitrogen-containing nucleophile and, as expected, adduct **5a** was obtained in 72% isolated yield (Table 4, entry 1), which is 6% higher yield when compared to its congener adduct **3c** (Table 2, entry 3). This confirms our hypothesis. Similarly, morpholine was also an excellent substrate delivering product **5b** in 70% yield (Table 4, entry 2). The oxygen-bearing nucleophile 4-chlorobenzoic acid gave compounds **5c** in 62% yield (Table 4, entry 3). Furthermore, diethyl malonate was also tolerated and afforded product **5d** in 50% (Table 4, entry 4).

Having established the scope of our transformation, we carried out a 1 g scale synthesis using substrates **1a** and aniline. To our delight, the gram-scale procedure gave adduct **3c** in 63% isolated yield (Table 2, entry 3). The former outcome plus broad nucleophiles tolerated demonstrates the scalability and scope of this synthetic method to produce miscellaneous α-alkyl styrenes in good yields. In addition to the observed scope, a comparative study between electron-donating groups (EDG) and electron-withdrawing groups (EWG) attached to allylbenzene was performed (Table 5). The goal was to determine the limits of this transformation. The one-pot two-step approach was performed as usual, except using DMSO-d_6 as the solvent. As previously observed, using safrole as the allylaryl starting material, the only observed product was its rearranged adduct **A** in 78% ^{1}H NMR yield (Table 5, entry 1). Similarly, 4-allyl-1-1′-biphenyl and estragole gave their respective rearranged product in 75 and 72% yield (entries 2 and 3), all bearing EDG. When 1-allyl-4-methylbenzene (weak EDG) was screened, 56% of the rearranged adduct and 45% of the lineal adduct were observed; this is around ~1.2:1 **A**/**B** ratio (entry 4). Then, allylbenzene started to favor the lineal adduct with ~1:1.2 **A**/**B** ratio (entry 5). Furthermore, if DBU was used instead of KO*t*Bu as base, only traces of the rearranged product and 64% isolated yield of the lineal adduct were observed. Finally, 1-allyl-4-(trifluoromethyl)benzene (strong EWG) gave the linear adduct **B** in 72% (entry 7) as the expected and sole product. Thus, corroborating our prior reports.[34,39]

In conclusion, this article reports a straightforward one-pot two-step alternative to α-alkyl styrenes from two natural products (estragole and safrole). The method is general in scope for carbon, nitrogen, oxygen, and sulfur nucleophiles. NaI helped to improve yields for all reactions. KO*t*Bu favors rearrangement adducts, while DBU is a superior base for linear adducts in general. Furthermore, this methodology provided 28 new α-alkyl styrenes from a single starting material (estragole), all potential monomers for polymerization. Therefore, even though the approach is limited to electron-rich substrates, the large number of available nucleophiles can very easily produce hundreds of novel α-alkyl styrenes for use as building blocks in synthesis or material sciences.

EXPERIMENTAL SECTION

General Information. All reactions were carried out under air in oven-dried glassware with magnetic stirring at room temperature. All commercially obtained reagents were used as received. Solvents were dried and degassed from a JC Meyer company solvent purification system. Heating was accomplished by silicone oil bath. Purification of reaction products was carried out by flash column chromatography using silica gel 60 (230−400 mesh). TLC visualization was accompanied with UV light. Concentration in vacuo refers to the removal of volatile solvent using a rotary evaporator attached to a dry diaphragm pump (10−15 mm Hg) followed by pumping to a constant weight with an oil pump (<300 mTorr). ^{1}H NMR spectra, recorded at 300 and 500 MHz, are reported relative to $CDCl_3$ (δ 7.26), DMSO (δ 2.50). ^{1}H NMR coupling constants (J) are reported in Hertz (Hz) and multiplicities are indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet), respectively. Proton-decoupled ^{13}C NMR spectra were recorded at 75 and 125 MHz and reported relative to $CDCl_3$ (δ 77), DMSO-d_6 (δ 39.5). IR experiments were recorded with neat samples on a Bruker α instrument fitted with a diamond ATR sample plate. High-resolution (HR) mass spectra were recorded at the Shimadzu Center Laboratory for Biological Mass Spectrometry at UTA.

General Procedure for the Synthesis of α-Alkyl Styrenes from Estragole. To a 10 mL round-bottom flask was added estragole (74 mg, 0.50 mmol), CH_2Cl_2 (2 mL), at room temperature under air. The mixture was cooled to −78 °C (dry ice/acetone mixture), followed by addition of Br_2 (34 μL, 0.65 mmol) dropwise. The reaction mixture was stirred for 30 min at −78 °C, then the volatiles (mainly DCM) were removed under reduced pressure while in the cold bath. Then, 2 mL of DMSO was added followed by addition of sodium iodide (75 mg, 0.50 mmol), nucleophiles (1.5 equiv, 0.75 mmol), followed by addition of base (2.30 equiv, 1.15 mmol). The reaction was stirred for 8 h while monitored with TLC. The reaction was purified over silica gel using flash column chromatography with hexanes/ethyl acetate mixture to afford the pure product.

*1-(1-Azidoprop-2-en-2-yl)-4-methoxybenzene (**3a**).* Colorless oil (56.8 mg, 60%). IR (neat, cm^{-1}): 3040, 3001, 2935,

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2094, 1244, 1179, and 744. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41 (d, J = 8.0 Hz, 2H), 6.90 (d, J = 9.0 Hz, 2H), 5.54 (s, 1H), 5.25 (s, 1H), 4.12 (s, 2H), and 3.82 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.6, 141.0, 130.3, 127.1, 114.5, 113.9, 55.2, and 55.0 ppm; HRMS (APCI/IT-TOF) m/z: $[M + H - N_2]^+$ calcd for $C_{10}H_{12}NO$ = 162.0913; found 162.0934.

*N-(2-(4-Methoxyphenyl)allyl)hexan-1-amine (**3b**).*[19] Yellow oil (62 mg, 50%). IR (neat, cm^{-1}): 2954, 2927, 1669, 1605, 1245, and 833. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38−7.36 (m, 2H), 6.87−6.85 (m, 2H), 5.35 (s, 1H), 5.20 (s, 1H), 3.79 (s, 3H), 3.67 (s, 2H), 3.19 (br, s, 1H), 2.63 (t, J = 7.5 Hz, 2H), 1.50 (pent, J = 7.5 Hz, 2H), 1.29−1.20 (m, 6H), and 0.85 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.2, 144.4, 131.8, 127.2, 113.8, 112.6, 55.1, 52.8, 48.7, 31.5, 29.2, 26.8, 22.5, and 13.9 ppm; HRMS (APCI/IT-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{26}NO$ = 248.2009; found 248.1959.

*N-(2-(4-Methoxyphenyl)allyl)benzenamine (**3c**).*[17] Yellow oil (79 mg, 66%) 1 g scale = 1.02 g, 63% product. IR (neat, cm^{-1}): 3401, 3051, 2958, 2932, 1677, 1600, 1244, 1118, and 833. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41 (dd, J = 11.5, 3.0 Hz, 2H), 7.20 (dd, J = 9.5, 7.5 Hz, 2H), 6.89 (dd, J = 12.0, 3.0 Hz, 2H), 6.78 (t, J = 7.5 Hz, 1H), 6.70 (d, J = 7.5 Hz, 2H), 5.43 (s, 1H), 5.28 (d, J = 1.1 Hz, 1H), 4.16 (s, 2H), and 3.83 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.4, 146.8, 143.3, 131.3, 129.1, 127.2, 118.3, 113.9, 113.8, 113.7, 112.7, 55.2, and 48.6 ppm; HRMS (APCI/IT-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{18}NO$ = 240.1383; found 240.1341.

*4-Chloro-N-(2-(4-methoxyphenyl)allyl)benzenamine (**3d**).* Yellow oil (88 mg, 64%). IR (neat, cm^{-1}): 3411, 2999, 2931, 1597, 1496, 1176, and 832. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 (d, J = 8.5 Hz, 2H), 7.12 (dd, J = 6.5, 2.0 Hz, 2H), 6.89−6.87 (m, 2H), 6.61 (d, J = 8.5 Hz, 2H), 5.41 (s, 1H), 5.24 (s, 1H), 4.12 (s, 2H), and 3.82 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.4, 145.1, 142.9, 131.1, 129.0, 127.2, 123.2, 115.0, 113.8, 113.0, 55.2, and 48.7 ppm; HRMS (APCI/IT-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{17}ClNO$ = 274.0999; found 274.0908.

*4-Methoxy-N-(2-(4-methoxyphenyl)allyl)benzenamine (**3e**).*[29] Yellow oil (84 mg, 63%). IR (neat, cm^{-1}): 3375, 3009, 2957, 2938, 2838, 2804, 1602, and 1509. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40−7.38 (m, 2H), 6.88 (d, J = 8.5 Hz, 2H), 6.78 (dd, J = 8.5, 2.0 Hz, 2H), 6.67 (d, J = 8.5 Hz, 2H), 5.41 (s, 1H), 5.27 (d, J = 1.0 Hz, 1H), 4.11 (s, 3H), 3.82 (s, 3H), and 3.75 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.3, 152.8, 143.5, 140.7, 131.4, 127.2, 115.2, 114.7, 113.8, 112.7, 55.7, 55.2, and 49.6 ppm; HRMS (APCI/IT-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{20}NO_2$ = 270.1489; found 270.1448.

*4-(Trifluoromethyl)-N-(2-(4-methoxyphenyl)allyl)-benzenamine (**3f**).* Yellow oil (81 mg, 53%). IR (neat, cm^{-1}): 3318, 2933, 2841, 1672, 1599, 1510, 1319, 1105, and 829. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41 (d, J = 8.5 Hz, 2H), 7.38 (dd, J = 8.5, 2.0 Hz, 2H), 6.89 (dd, J = 8.5, 2.0 Hz, 2H), 6.67 (d, J = 8.5 Hz, 2H), 5.43 (s, 1H), 5.24 (s, 1H), 4.18 (s, 2H), and 3.82 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.5, 149.5, 142.7, 130.9, 127.1, 126.7 (J_{CF} = 41.2 Hz), 126.5 (J_{CF} = 4.5 Hz), 124.8 (J_{CF} = 268.3 Hz), 113.9, 112.8, 112.7, 55.2, and 48.0 ppm; HRMS (APCI/IT-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{17}NO$ = 308.1257; found 308.1237.

*N,N-Diisopropyl-2-(4-methoxyphenyl)prop-2-en-1-amine (**3g**).* Yellow oil (46 mg, 37%). IR (neat, cm^{-1}): 2966, 2934, 1664, 1600, 1245, and 833. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42 (d, J = 9.0 Hz, 2H), 6.85 (d, J = 8.5 Hz, 2H), 5.34 (s, 1H), 5.30 (s, 1H), 3.81 (s, 3H), 3.41 (s, 2H), 3.07 (pent, J = 7.0 Hz, 2H), 1.00 (s, 6H), and 0.99 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.8, 147.2, 133.6, 127.4, 113.2, 112.1, 55.1, 49.3, 47.6, and 20.5 ppm; HRMS (APCI/IT-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{26}NO$ = 248.2009; found 248.1940.

*N,N-Diallyl-2-(4-methoxyphenyl)prop-2-en-1-amine (**3h**).* Colorless oil (79 mg, 65%). IR (neat, cm^{-1}): 3076, 3003, 2976, 2834, 1606, 1510, 1245, and 831. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44 (dd, J = 6.5, 2.2 Hz, 2H), 6.87 (dd, J = 6.5, 2.0 Hz, 2H), 5.91−5.83 (m, 2H), 5.39 (d, J = 1.0 Hz, 1H), 5.23 (s, 1H), 5.20 (d, J = 2.0 Hz, 1H), 5.17−5.14 (m, 3H), 3.81 (s, 3H), 3.43 (s, 2H), and 3.12 (d, J = 6.5 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.0, 144.6, 135.6, 132.7, 127.4, 117.4, 113.6, 113.4, 57.6, 56.4, and 55.1 ppm; HRMS (APCI/IT-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{22}NO$ = 244.1696; found 244.1652.

*N-Benzyl-2-(4-methoxyphenyl)-N-methylprop-2-en-1-amine (**3i**).*[45] Yellow oil (92 mg, 69%). IR (neat, cm^{-1}): 3061, 3031, 2933, 1672, 1604, 1245, and 832. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44 (d, J = 9.0 Hz, 2H), 7.33−7.24 (m, 5H), 6.88 (d, J = 8.5 Hz, 2H), 5.43 (s, 1H) 5.23 (s, 1H), 3.83 (s, 3H), 3.55 (s, 2H), 3.39 (s, 2H), and 2.21 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.0, 144.3, 132.4, 129.0, 128.1, 127.5, 126.9, 113.8, 113.4, 62.0, 61.8, 55.2, and 41.9 ppm; HRMS (APCI/IT-TOF) m/z: $[M + H]^+$ calcd for $C_{18}H_{22}NO$ = 268.1696; found 268.1664.

*4-(2-(4-Methoxyphenyl)allyl)morpholine (**3j**).*[19] Yellow oil (80 mg, 69%). IR (neat, cm^{-1}): 2955, 2852, 1606, 1573, 1113, and 833. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49 (dd, J = 8.5, 2.2 Hz, 2H), 6.86 (dd, J = 9.5, 2.0 Hz, 2H), 5.43 (s, 1H) 5.16 (s, 1H), 3.80 (d, J = 2.0 Hz, 3H), 3.69 (s, 4H), 3.33 (s, 2H), and 2.48 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.1, 142.5, 132.4, 127.3, 114.1, 113.4, 66.8, 63.4, 55.1, and 53.3 ppm; HRMS (APCI/IT-TOF) m/z: $[M + H]^+$ calcd for $C_{14}H_{20}NO_2$ = 234.1489; found 234.1442.

*1-(2-(4-Methoxyphenyl)allyl)piperidine (**3k**).*[19] Yellow oil (78 mg, 69%). IR (neat, cm^{-1}): 2997, 2931, 2851, 1606, 1510, 1244, 1112, and 832. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49 (dd, J = 8.5, 2.2 Hz, 2H), 6.86 (dd, J = 7.0, 2.0 Hz, 2H), 5.39 (d, J = 2.0 Hz, 1H) 5.16 (d, J = 1.0 Hz, 1H), 3.81 (s, 3H), 3.29 (s, 2H), 2.42 (br,s, 4H), 1.57 (pent, J = 5.5 Hz, 4H), and 1.43 (d, J = 5.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.0, 143.3, 133.1, 127.3, 113.7, 113.4, 63.7, 55.1, 54.4, 25.8, and 24.3 ppm; HRMS (APCI/IT-TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{22}NO$ = 232.1696; found 232.1656.

*2-(2-(4-Methoxyphenyl)allyl)isoindoline-1,3-dione (**3l**).*[22] White solid (75 mg, 51%). IR (neat, cm^{-1}): 2956, 2921, 2851, 1771, 1702, 1630, 1605, and 1112. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83 (q, J = 2.5 Hz, 2H), 7.69 (q, J = 3.0 Hz, 2H), 7.43 (dd, J = 8.5, 2.2 Hz, 2H), 6.86 (dd, J = 8.5, 2.2 Hz, 2H), 5.36 (s, 1H), 5.08 (s, 1H), 4.67 (s, 2H), and 3.79 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.9, 159.4, 141.6, 133.9, 131.9, 130.8, 127.4, 123.3, 113.7, 112.4, 55.2, and 41.4 ppm; HRMS (APCI/IT-TOF) m/z: $[M + H]^+$ calcd for $C_{18}H_{16}NO_3$ = 294.1125; found 294.1093.

*1-Benzhydryl-4-(2-(4-methoxyphenyl)allyl)piperazine (**3m**).* White gel (78.9 mg, 40%). IR (neat, cm^{-1}): 3062, 2948, 2798, 2760, 1602, 1510, 807, and 703. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52 (dd, J = 6.5, 2.2 Hz, 2H), 7.45 (d, J = 7.0 Hz, 4H), 7.30 (t, J = 7.5 Hz, 4H), 7.20 (t, J = 7.5 Hz, 2H), 6.88 (dd, J = 6.5, 1.5 Hz, 2H), 5.42 (d, J = 2.0 Hz, 1H), 5.18 (s, 1H), 4.25 (s, 1H), 3.82 (s, 3H), 3.36 (s, 2H), and 2.55−2.45 (brs, 8H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.0, 143.2, 142.8, 132.8, 128.3, 127.8, 127.3, 126.7, 113.3 76.2, 63.1, 55.1,

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53.3, and 5.19 ppm; HRMS (APCI/IT-TOF) m/z: $[M + H]^+$ calcd for $C_{27}H_{31}N_2O$ = 399.2431; found 399.2376.

*1-(1-(2-(4-Methoxyphenyl)allyl)-1H-indol-3-yl)ethenone (**3n**).* White solid (83 mg, 54%). IR (neat, cm^{-1}): 2997, 2831, 1718, 1630, 1605, and 1121. ^1H NMR (500 MHz, $CDCl_3$): δ 8.39−8.38 (m, 1H), 7.73 (s, 1H), 7.37−7.29 (m, 5H), 6.87 (dd, J = 7.0, 2.0 Hz, 2H), 5.48 (s, 1H), 5.09 (s, 2H), 4.83 (s, 1H), 3.80 (s, 3H), and 2.49 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.0, 159.7, 141.4, 137.0, 135.0, 130.2, 126.8, 126.2, 123.3, 122.6, 122.5, 117.2, 114.0, 113.6, 109.9, 55.2, 50.5, and 27.5 ppm; HRMS (APCI/IT-TOF) m/z: $[M + H]^+$ calcd for $C_{20}H_{20}NO_2$ = 306.1489; found 306.1448.

*2-(4-Methoxyphenyl)allyl Acetate (**4a**).*[20] White oil (50.5 mg, 49%). IR (neat, cm^{-1}): 2937, 2839, 1735, 1600, 1220, and 1171. ^1H NMR (500 MHz, $CDCl_3$): δ 7.37 (dd, J = 6.9, 2.1 Hz, 2H), 6.88 (dd, J = 6.5, 2.1 Hz, 2H), 5.48 (s, 1H), 5.27 (d, J = 1.2 Hz, 1H), 4.95 (s, 2H), 3.81 (s, 3H), and 2.08 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.7, 159.4, 141.6, 130.3, 129.4, 127.0, 113.7, 65.8, 55.2, and 20.9 ppm; HRMS (APCI/IT-TOF) m/z: $[M + H]^+$ calcd for $C_{12}H_{15}O_3$ = 207.1016; found 207.1010.

*2-(4-Methoxyphenyl)allyl 2-Hydroxyacetate (**4b**).* White gel (24 mg, 22%). IR (neat, cm^{-1}): 3411, 2933, 2838, 1727, 1673, 1510, 1172, and 829. ^1H NMR (500 MHz, $CDCl_3$): δ 7.35 (dd, J = 6.7, 2.5 Hz, 2H), 6.88 (dd, J = 7.0, 2.5 Hz, 2H), 5.50 (s, 1H), 5.28 (s, 1H), 5.08 (s, 2H), 4.16 (s, 2H), and 3.82 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.1, 159.6, 141.1, 130.0, 127.0, 114.4, 113.9, 66.8, 60.6, and 55.2 ppm; HRMS (APCI/IT-TOF) m/z: $[M + H]^+$ calcd for $C_{12}H_{15}O_4$ = 223.0964; found 223.0961.

*2-(4-Methoxyphenyl)allyl Hexanoate (**4c**).* White oil (54 mg, 41%). IR (neat, cm^{-1}): 2956, 2932, 2870, 1734, 1708, 1600, 1246, and 1107. ^1H NMR (500 MHz, $CDCl_3$): δ 7.37 (d, J = 8.5 Hz, 2H), 6.87 (d, J = 9.5 Hz, 2H), 5.46 (s, 1H), 5.26 (s, 1H), 4.96 (s, 2H), 3.81 (s, 3H), 2.31 (t, J = 7.5 Hz, 2H), 1.60 (q, J = 7.5 Hz, 2H), 1.31−1.24 (m, 4H), and 0.87 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.5, 159.4, 141.9, 130.4, 127.0, 113.7, 113.4, 66.5, 55.2, 34.2, 31.2, 24.6, 22.2, and 13.8 ppm; HRMS (APCI/IT-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{23}O_3$ = 263.1641; found 263.1607.

*2-(4-Methoxyphenyl)allyl 4-Methoxybenzoate (**4d**).* Off-white gel (67 mg, 45%). IR (neat, cm^{-1}): 2935, 2838, 1710, 1601, 1022, and 809. ^1H NMR (300 MHz, $CDCl_3$): δ 7.98 (dd, J = 6.9, 2.0 Hz, 2H), 7.44 (dd, J = 6.6, 2.0 Hz, 2H), 6.92−6.87 (m, 4H), 5.52 (s, 1H), 5.36 (d, J = 1.0 Hz, 1H), 5.17 (s, 2H), 3.84 (s, 3H), and 3.81 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.0, 163.3, 159.4, 141.8, 131.6, 130.5, 127.1, 122.4, 113.7, 113.5, 113.3, 66.0, 55.3, and 55.2 ppm; HRMS (APCI/IT-TOF) m/z: $[M + H]^+$ calcd for $C_{18}H_{19}O_4$ = 299.1277; found 299.1245.

*2-(4-Methoxyphenyl)allyl 4-Chlorobenzoate (**4e**).* White solid (68 mg, 45%). IR (neat, cm^{-1}): 3042, 3008, 2960, 2934, 1714, 1628, 1606, 1031, and 708. ^1H NMR (300 MHz, $CDCl_3$): δ 7.95 (dd, J = 6.5, 2.0 Hz, 2H), 7.43 (dd, J = 6.5, 2.0 Hz, 2H), 7.39 (dd, J = 6.5, 2.0 Hz, 2H), 6.89 (dd, J = 7.0, 2.0 Hz, 2H), 5.55 (s, 1H), 5.36 (s, 1H), 5.20 (s, 2H), and 3.81 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.3, 159.5, 141.5, 139.4, 130.9, 130.3, 128.6, 128.4, 127.0, 113.8, 113.7, 66.4, and 55.2 ppm; HRMS (APCI/IT-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{16}ClO_3$ = 303.0782; found 303.0742.

*2-(4-Methoxyphenyl)allyl 4-Cyanobenzoate (**4f**).* Brown solid (45.5 mg, 31%). IR (neat, cm^{-1}): 2968, 2931, 1771, 1717, 1606, 1108, and 825. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.10 (d, J = 8.1 Hz, 2H), 7.72 (d, J = 8.7 Hz, 2H), 7.42 (d, J = 9.0 Hz, 2H), 6.89 (d, J = 8.7 Hz, 2H), 5.55 (s, 1H), 5.36 (s, 1H), 5.23 (s, 2H), and 3.81 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 164.6, 159.5, 141.2, 133.8, 132.1, 130.1, 127.0, 117.9, 116.3, 114.2, 113.8, 67.0, and 55.2 ppm; HRMS (APCI/IT-TOF) m/z: $[M + H]^+$ calcd for $C_{18}H_{16}NO_3$ = 294.1124; found 294.1181.

*2-(4-Methoxyphenyl)allyl 4-Nitrobenzoate (**4g**).*[30] Yellow solid (73 mg, 46%). IR (neat, cm^{-1}): 2998, 2935, 1776, 1717, 1623, 1603, 1101, and 831. ^1H NMR (500 MHz, $CDCl_3$): δ 8.25 (dd, J = 7.0, 2.0 Hz, 2H), 8.17 (dd, J = 7.0, 2.5 Hz, 2H), 7.42 (dd, J = 7.0, 2.0 Hz, 2H), 6.90 (dd, J = 6.5, 2.0 Hz, 2H), 5.56 (s, 1H), 5.37 (s, 1H), 5.25 (s, 2H), and 3.82 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.3, 159.6, 150.2, 141.2, 135.4, 130.7, 130.0, 127.0, 123.6, 123.5, 114.3, 114.0, 113.9, 67.1, and 55.2 ppm; HRMS (APCI/IT-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{15}NO_5$ = 313.0950; found 313.2808.

*2-(4-Methoxyphenyl)allyl 2-Nitrobenzoate (**4h**).* Brown semisolid (84.5 mg, 54%). IR (neat, cm^{-1}): 3041, 2928, 2848, 1731, 1604, 1531, 1125, and 838. ^1H NMR (500 MHz, $CDCl_3$): δ 7.88−7.87 (m, 1H), 7.66−7.57 (m, 3H), 7.40 (dd, J = 6.5, 2.5 Hz, 2H), 6.89 (dd, J = 6.5, 2.5 Hz, 2H), 5.53 (s, 1H), 5.34 (s, 1H), 5.22 (s, 2H), and 3.80 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.1, 159.5, 148.0, 140.8, 132.8, 131.6, 129.9, 129.6, 127.5, 127.0, 123.8, 114.6, 113.8, 67.7, and 55.2 ppm; HRMS (APCI/IT-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{16}NO_5$ = 314.1023; found 314.0981.

*(E)-2-(4-Methoxyphenyl)allyl Cinnamate (**4i**).* White semisolid (50 mg, 34%). IR (neat, cm^{-1}): 2972, 2936, 2836, 1706, 1630, 1248, and 1164. ^1H NMR (500 MHz, $CDCl_3$): δ 7.72 (d, J = 16 Hz, 1H), 7.52−7.40 (m, 2H), 7.43 (d, J = 9.0 Hz, 2H), 7.39 (q, J = 3.0 Hz, 3H), 6.90 (d, J = 8.5 Hz, 2H), 6.47 (d, J = 16 Hz, 1H), 5.53 (s, 1H), 5.35 (s, 1H), 5.11 (s, 2H), and 3.82 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.6, 159.4, 145.1, 141.7, 134.2, 130.3, 130.2, 128.8, 128.0, 127.0, 117.7, 113.8, 113.6, 65.8, and 55.1 ppm; HRMS (APCI/IT-TOF) m/z: $[M + H]^+$ calcd for $C_{19}H_{19}O_3$ = 295.1329; found 295.1296.

*Dimethyl 2-(2-(4-methoxyphenyl)allyl)malonate (**4j**).*[32] Colorless oil (71 mg, 51%). IR (neat, cm^{-1}): 3001, 2954, 2841, 1731, 1245, 1150, and 834. ^1H NMR (500 MHz, $CDCl_3$): δ 7.31 (dd, J = 6.5, 2.0 Hz, 2H), 6.85 (dd, J = 6.5, 2.0 Hz, 2H), 5.23 (s, 1H), 5.03 (d, J = 1 Hz, 1H), 3.79 (s, 3H), 3.68 (s, 6H), 3.53 (t, J = 7.5 Hz, 1H), and 3.09 (d, J = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.3, 159.2, 143.9, 132.0, 127.2, 113.7, 113.2, 55.1, 52.4, 50.7, and 34.5 ppm; HRMS (APCI/IT-TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{19}O_5$ = 279.1227; found 279.1214.

*Diethyl 2-(2-(4-methoxyphenyl)allyl)malonate (**4k**).*[18] Colorless oil (95 mg, 62%). IR (neat, cm^{-1}): 2981, 2939, 1728, 1607, 1246, 1177, 1149, 1031, and 808. ^1H NMR (500 MHz, $CDCl_3$): δ 7.30 (dd, J = 6.7, 2.5 Hz, 2H), 6.84 (dd, J = 6.7, 2.5 Hz, 2H), 5.21 (s, 1H), 5.03 (d, J = 1 Hz, 1H), 4.14 (q, J = 7 Hz, 4H), 3.78 (s, 3H), 3.48 (t, J = 7.5 Hz, 1H), 3.08 (d, J = 7.5 Hz, 2H), and 1.21 (t, J = 7.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.8, 159.2, 143.9, 132.1, 127.2, 113.7, 113.6, 113.1, 61.3, 61.2, 55.1, 50.8, 34.4, and 13.9 ppm; HRMS (APCI/IT-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{23}O_5$ = 307.1540; found 307.1506.

*Ethyl 2-(2-(4-methoxyphenyl)allyl)propanoate (**4l**).* Colorless oil (103 mg, 61%). IR (neat, cm^{-1}): 3058, 2976, 2932, 1682, 1611, 1243, and 1177. ^1H NMR (500 MHz, $CDCl_3$): δ 7.87 (d, J = 9 Hz, 2H), 7.54 (t, J = 7 Hz, 1H), 7.41 (t, J = 7 Hz,

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2H), 7.28 (d, J = 8.5 Hz, 2H), 6.85 (d, J = 8.5 Hz, 2H), 5.19 (s, 1H), 5.04 (s, 1H), 4.46 (t, J = 7 Hz, 1H), 4.09 (q, J = 14, 7, Hz, 2H), 3.81(s, 3H), 3.20 (t, J = 6 Hz, 2H), and 1.14 (t, J = 7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 194.8, 169.3, 159.2, 144.2, 136.2, 133.3, 132.4, 128.5, 127.5, 127.4, 113.7, 113.5, 61.3, 55.2, 52.7, 34.6, and 13.9 ppm; HRMS (APCI/IT-TOF) m/z: $[M + H]^+$ calcd for $C_{21}H_{23}O_4$ = 339.1591; found 339.1546.

*S-2-(4-Methoxyphenyl)allyl Ethanethioate (**4m**).* Brown oil (53 mg, 48%). IR (neat, cm^{-1}): 2933, 2836, 1686, 1600, 1246, and 1110. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 (d, J = 8.5 Hz, 2H), 6.86 (d, J = 8.0 Hz, 2H), 5.37 (s, 1H), 5.25 (s, 1H), 4.02 (s, 2H), 3.81 (s, 3H), and 2.30 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 195.2, 159.4, 142.2, 131.1, 127.1, 114.1, 113.7, 55.2, 33.6, and 30.4 ppm; HRMS (APCI/IT-TOF) m/z: $[M + H]^+$ calcd for $C_{12}H_{15}O_2S$ = 223.0787; found 223.0771.

*S-2-(4-Methoxyphenyl)allyl Benzothioate (**4n**).* Light yellow oil (15 mg, 11%). IR (neat, cm^{-1}): 3049, 3034, 2998, 1714, 1606, 1510, 1246, 906, and 686. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.94 (d, J = 7.5 Hz, 2H), 7.55 (t, J = 7.5 Hz, 1H), 7.44−7.41 (m, 4H), 6.89−6.87 (m, 2H), 5.43 (s, 1H), 5.36 (s, 1H), 4.22 (s, 2H), and 3.81 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 191.4, 159.4, 142.2, 136.8, 133.3, 131.2, 128.5, 127.2, 127.2, 114.4, 113.7, 55.2, and 33.6 ppm; HRMS (APCI/IT-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{17}O_2S$ = 285.0944; found 285.0887.

General Procedure for the Synthesis of α-Alkyl Styrenes from Safrole. To a 10 mL round-bottom flask, was added safrole (81 mg, 0.50 mmol), CH_2Cl_2 (2 mL), at room temperature under air. The mixture was cooled to −78 °C (dry ice/acetone mixture), followed by addition of Br_2 (34 μL, 0.65 mmol) dropwise. After 30 min, the volatile was removed. Then, 2 mL of DMSO was added followed by addition of sodium iodide (75 mg, 0.50 mmol), nucleophiles (1.5 equiv, 0.75 mmol), followed by addition of base (2.30 equiv, 1.15 mmol). The reaction was stirred for 8 h, while monitored with TLC. The reaction was purified over silica gel using flash column chromatography with hexanes/ethyl acetate mixture to afford the pure product.

*N-(2-(Benzo[d][1,3]dioxol-6-yl)allyl)benzenamine (**5a**).* White oil (91 mg, 72%). IR (neat, cm^{-1}): 2899, 1603, 1502, 1490, 1037, and 750. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.21 (td, J = 7.0, 2.0 Hz, 2H), 6.96 (td, J = 9.5, 1.5 Hz, 2H), 6.80 (d, J = 8.0 Hz, 1H), 6.76 (t, J = 7.5 Hz, 1H), 6.67 (d, J = 8.0 Hz, 2H), 5.97 (s, 2H), 5.40 (s, 1H), 5.28 (d, J = 1.0 Hz, 1H), and 4.12 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 147.8, 147.7, 147.3, 143.3, 133.3, 129.1, 119.5, 117.9, 113.2, 113.0, 108.1, 106.6, 101.0, and 48.4 ppm; HRMS (APCI/IT-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{16}NO_2$ = 254.1176; found 254.1130.

*4-(2-(Benzo[d][1,3]dioxol-6-yl)allyl)morpholine (**5b**).* White solid (87 mg, 70%). IR (neat, cm^{-1}): 2855, 2805, 1602, 1011, and 905. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.07 (d, J = 2.0 Hz, 1H), 7.03 (dd, 8.0, 2.0 Hz, 1H), 6.75 (d, J = 8.0 Hz, 1H), 5.93 (s, 2H), 5.39 (d, J = 1.0 Hz, 1H), 5.14 (s, 1H), 3.67 (t, J = 4.5 Hz, 4H), 3.27 (s, 2H), and 2.45 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 147.3, 146.9, 142.7, 134.3, 119.7, 114.8, 107.8, 106.7, 100.8, 66.8, 63.6, and 53.3 ppm; HRMS (APCI/IT-TOF) m/z: $[M + H]^+$ calcd for $C_{14}H_{18}NO_3$ = 248.1281; found 248.1236.

*2-(Benzo[d][1,3]dioxol-6-yl)allyl 4-Chlorobenzoate (**5c**).* White gel (98 mg, 62%). IR (neat, cm^{-1}): 1716, 1591, 1501, 1285, 1014, and 750. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.95 (d, J = 8.5 Hz, 2H), 7.38 (d, J = 8.5 Hz, 2H), 6.95−6.98 (m, 2H), 6.78 (d, J = 8.0 Hz, 1H), 5.95 (s, 2H), 5.50 (s, 1H), 5.36 (s, 1H), and 5.15 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.2, 147.8, 147.4, 141.7, 139.4, 132.0, 130.9, 128.6, 128.3, 119.5, 114.4, 108.1, 106.4, 101.1, and 66.4 ppm; HRMS (APCI/IT-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{14}ClO_4$ = 317.0575; found 317.0548.

*Diethyl 2-(2-(Benzo[d][1,3]dioxol-6-yl)allyl)malonate (**5d**).* Colorless oil (80 mg, 50%). IR (neat, cm^{-1}): 2994, 2903, 1731, 1503, 1230, 1110, and 811. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.86−6.83 (m, 2H), 6.74 (d, J = 8.0 Hz, 1H), 5.93 (s, 2H), 5.19 (s, 1H), 5.03 (d, J = 1.5 Hz, 1H), 4.14 (q, J = 7.0 Hz, 4H), 3.47 (t, J = 8.0 Hz, 1H), 3.04 (d, J = 8.0 Hz, 2H), and 1.22 (t, J = 7.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.8, 147.7, 147.2, 144.1, 134.0, 119.6, 113.8, 108.0, 106.7, 101.0, 61.3, 50.8, 34.6, and 13.9 ppm; HRMS (APCI/IT-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{21}O_6$ = 321.1333; found 321.1290.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c02801.

^{1}H NMR spectra, ^{13}C NMR spectra, and mechanistic studies (PDF)

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Notes

The authors declare no competing financial interest.

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