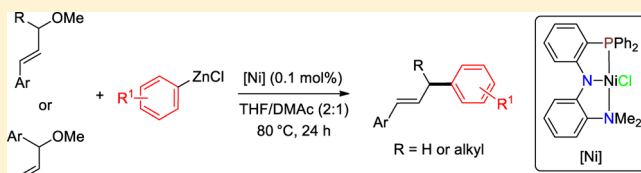


## Pincer-Nickel-Catalyzed Allyl-Aryl Coupling between Allyl Methyl Ethers and Arylzinc Chlorides

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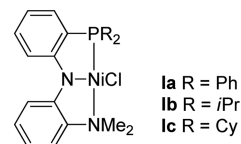
## Supporting Information

**ABSTRACT:** The *P,N,N*-pincer nickel complex [Ni(Cl){N-(2-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>)(2'-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>)}]-catalyzed allyl-aryl coupling was studied. The reaction of allyl methyl ethers, including (1-methoxyallyl)arenes and (3-methoxyprop-1-en-1-yl)arenes, with arylzinc chlorides afforded linear (*E*)-alkenes in high yields, whereas the reaction of (*E*)-1-methoxytridec-2-ene with *p*-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>ZnCl generated a mixture of linear and branched alkenes.



The 1,3-diarylpropenes are useful intermediates in the synthesis of natural products and biologically active molecules.<sup>1</sup> A powerful synthetic method for 1,3-diarylpropenes is transition metal-catalyzed allyl-aryl coupling. Allylic halides and allylic phosphates are often used as electrophilic substrates.<sup>2,3</sup> Recently, allylic alcohol, allylic esters, and allylic ethers have received considerable attention in these transformations. However, reactions of allylic alcohol and allylic esters mainly center on their cross-coupling with organoboron reagents.<sup>4</sup> A few other coupling reactions of allylic esters, with organosilicon reagents and copper(I) enolates as well as reductive coupling with organic halides, have also been performed.<sup>5</sup> The reported reactions of allylic ethers include Suzuki-type coupling,<sup>6</sup> Kumada-type coupling,<sup>7</sup> and couplings with organolithium reagents<sup>8</sup> or through sp<sup>2</sup> C–H bond activation.<sup>9</sup> For example, the reaction of allyl phenyl ethers with arylboronic acids in water under the catalysis of PdCl<sub>2</sub>(DPEphos) affords 3-arylprop-1-enes.<sup>6a</sup> Allyl methyl ethers were demonstrated to react with Grignard reagents under the catalysis of CoCl<sub>2</sub>/phosphine.<sup>7a</sup> Despite the excellent results achieved, investigations on transition metal-catalyzed allylic arylation of allylic partners is still limited. It is necessary to further explore the reactivity of allylic alcohol derivatives and develop a methodology to construct allyl-aryl systems.

In the past several years, we have focused on developing highly active catalyst systems for transition metal-catalyzed C–C cross-coupling reactions.<sup>10</sup> Recently, we demonstrated that *P,N,N*-pincer nickel complexes **Ia–Ic** can catalyze cross-couplings of arylzinc reagents with aryl chlorides or aryltrimethylammonium triflates, and complex **Ia** exhibited high catalytic activity.<sup>10c,d</sup> On the basis of these findings, we intended to study the reaction of arylzinc reagents with allylic ethers to synthesize 1,3-diarylpropenes using the pincer nickels as catalyst.



The reaction of cinnamyl methyl ether with 4-(dimethylamino)phenylzinc chloride was employed to screen catalysts and optimize reaction conditions, and the results are listed in Table S1 in the Supporting Information. The catalytic properties of complexes **Ia–Ic** were evaluated using similar reaction conditions to those of the **Ia**-catalyzed reaction of aryltrimethylammonium triflates with arylzinc chlorides, which we reported earlier.<sup>10d</sup> Thus, the reaction was run in a 2:1 mixture of THF and NMP at 65 °C for 24 h using 0.1 mol % of catalyst loadings. Each of the complexes was demonstrated to be catalytically active. Complex **Ia** resulted in the cross-coupling product in 82% yield, and **Ib** and **Ic** led to 77 and 75% yields, respectively (entries 1–3, Table S1). Examination of the reaction temperature showed that the **Ia**-catalyzed reaction could not give the desired product at room temperature and generated a corresponding product in 55% yield at 45 °C and 87% yield at 80 °C, respectively (entries 4–6, Table S1). A reaction temperature higher than 80 °C cannot further increase the product yield. Then, we examined the solvent effect using **Ia** as the catalyst at 80 °C. A series of solvents, including THF, THF/toluene (2:1), THF/dioxane (2:1), and THF/DMA (2:1) were tested (entries 6–10, Table S1). The results showed that a 2:1 mixture of THF and DMA was the best solvent. 99% GC yield and 91% isolated yield could be achieved (entry 10, Table 1). A higher isolated yield (97%) of the cross-coupling product was achieved when 2.0 equiv of 4-(dimethylamino)-phenylzinc chloride was used (entry 11, Table S1). In these

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**Table 1.** Ia-Catalyzed Cross-Coupling of (*E*)-(3-Methoxyprop-1-en-1-yl)benzene with Arylzinc Chlorides<sup>a</sup>

| $\text{Ph}-\text{CH}=\text{CH}-\text{OMe} + \text{Ar}-\text{ZnCl} \xrightarrow[\text{THF/DMAc (2:1), 80 } ^\circ\text{C, 24 h}]{\text{Ia (0.1 mol\%)}} \text{Ar}-\text{CH}=\text{CH}-\text{Ph}$ |    |         |                        |
|---|----|---------|------------------------|
| Entry   | Ar | Product | Yield (%) <sup>b</sup> |
| 1   |    |         | 97                     |
| 2   |    |         | 96                     |
| 3   |    |         | 94 <sup>c</sup>        |
| 4   |    |         | 92 <sup>c</sup>        |
| 5   |    |         | 89                     |
| 6   |    |         | 91                     |
| 7   |    |         | 89                     |
| 8   |    |         | 82                     |
| 9   |    |         | 96                     |
| 10  |    |         | 97                     |
| 11  |    |         | 94                     |
| 12  |    |         | 92                     |
| 13  |    |         | 90                     |
| 14  |    |         | 88                     |
| 15  |    |         | 86                     |
| 16  |    |         | 84                     |
| 17  |    |         | 82                     |

<sup>a</sup>The reactions were carried out using 0.5 mmol cinnamyl methyl ether and 1.0 mmol arylzinc chloride according to the conditions indicated by the above equation; the zinc reagents were prepared from corresponding Grignard reagents and ZnCl<sub>2</sub> in the presence of 2 equiv of LiCl. <sup>b</sup>Isolated yield. <sup>c</sup>Catalyst loading of 0.01 mol %.

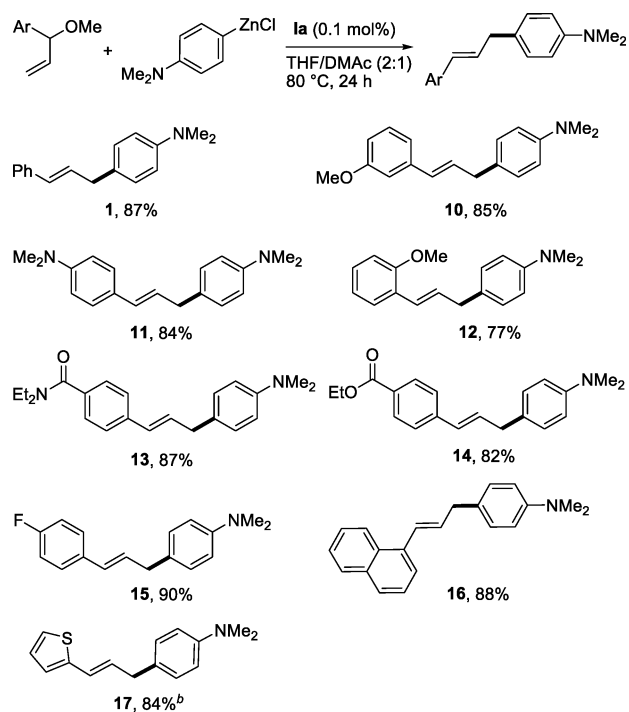
reactions, a homocoupling product of the zinc reagent was also observed. In the absence of a nickel catalyst, the reaction cannot give any desired product (entry 12, Table S1). In addition, a test of the salt effect showed that the zinc reagent, 4-(dimethylamino)phenylzinc chloride, prepared from the corresponding Grignard reagent and ZnCl<sub>2</sub> in the presence of 2 equiv of LiCl, gave a better reaction result than those prepared from *p*-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>Li and ZnCl<sub>2</sub>, *p*-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>MgBr and ZnCl<sub>2</sub>, or *p*-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>Li and ZnCl<sub>2</sub> in the presence of 1 equiv of MgBr<sub>2</sub> (entries 13–15, Table S1). This implies that both lithium and magnesium ions play important roles in the reaction. This may be due to the presence of a multimetallic synergistic effect in the reaction process.<sup>11</sup> The role of LiCl additive may also involve breaking the aggregation of ArZnCl with the coproduct MgCl<sub>2</sub> through forming a trimetallic adduct and enhancing the reactivity of the zinc reagents by forming more nucleophilic zincates.<sup>11,12</sup>

Next, we examined cross-coupling of cinnamyl methyl ether with different arylzinc reagents under the optimized reaction conditions. 4-Methoxyphenylzinc chloride exhibited similar reactivity to 4-(dimethylamino)phenylzinc chloride. As electron-rich nucleophiles, both 4-(dimethylamino)phenylzinc chloride and 4-methoxyphenylzinc chloride can react smoothly with cinnamyl methyl ether in the presence of 0.01 mol % of Ia, giving corresponding products **1** and **2** in excellent yields (entries 1 and 2, Table 1). Similar reactions using benzo[1,3]-dioxol-5-ylzinc chloride, *p*-tolylzinc chloride, phenylzinc chloride, and (1,1'-biphenyl)-4-ylzinc chloride as nucleophiles also led to high product yields, but 0.1 mol % catalyst loadings

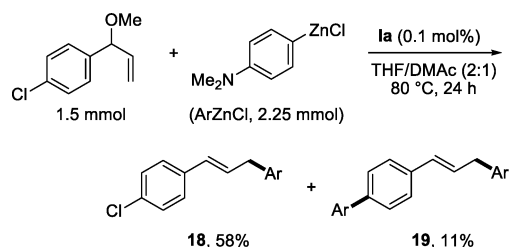
were necessary (entries 3–6, Table 1). Several fused arylzinc reagents, including naphthalen-2-ylzinc chloride, 6-methoxynaphthalen-2-ylzinc chloride, and phenanthren-9-ylzinc chloride, were also tested (entries 7–9, Table 1). They exhibited good reactivity in the reaction with cinnamyl methyl ether under the optimized conditions. Each reaction proceeded smoothly and gave an excellent product yield. The electron-poor arylzinc reagent 4-(trifluoromethyl)phenylzinc chloride, heteroarylzinc reagents 2-furylzinc chloride and 2-thienylzinc chloride, and alkylzinc reagent 3-phenylpropylzinc chloride were also tested for catalyzed cross-coupling with cinnamyl methyl ether. However, none of them gave the desired cross-coupling product, and the ether was not consumed in these reactions. 4-(Trifluoromethyl)phenylzinc chloride has lower nucleophilicity compared with those of the substituted phenylzinc reagents mentioned above. The weak nucleophilicity may lead to failure of the transmetalation reaction in the catalytic cycle (see below). Both 2-furylzinc chloride and 2-thienylzinc chloride are electron-rich nucleophilic reagents. However, the Lewis acids in the system, such as LiCl, MgCl<sub>2</sub>, and ZnCl<sub>2</sub> may combine with the 2-furyl and 2-thienyl groups through coordination. The combination results in a decrease of their nucleophilicity. In the case of 3-phenylpropylzinc chloride, we guess that the unsuccessful reaction may be due to a difficult reductive elimination in the catalytic process.

Furthermore, we examined the reactivity of various branched ethers using 4-(dimethylamino)phenylzinc chloride as the nucleophilic reagent. When 3-aryl-3-methoxyprop-1-enes were used as the electrophiles to react with 4-(dimethylamino)phenylzinc chloride under the optimized conditions, (*E*)-*N,N*-dimethyl-4-(3-arylallyl)aniline (**1** and **10–17**) rather than *N,N*-dimethyl-4-(1-arylallyl)aniline were formed (Scheme 1). That is to say, allylic rearrangements occurred in the reaction process to selectively provide linear rather than branched coupling products. In addition, among these substrates, both 1-methoxy-2-(1-methoxyallyl)benzene and 2-(1-methoxyallyl)thiophene exhibited relatively low reactivity. The former gave lower product yield (77%) compared with other substrates under the same conditions, and the latter required higher catalyst loading (1 mol % of Ia) to drive the reaction to completion. This may be due to steric hindrance of the substrate for the former and catalyst poisoning by the thienyl group for the latter. The reaction tolerated functional groups, such as C(O)OEt, C(=O)NEt<sub>2</sub>, and F groups. However, the reaction of 1-chloro-4-(1-methoxyallyl)benzene with 4-(dimethylamino)phenylzinc chloride gave a mixture of (*E*)-4-(3-(4-chlorophenyl)allyl)-*N,N*-dimethylaniline (**18**) and (*E*)-4'-(3-(4-(dimethylamino)phenyl)prop-1-enyl)-*N,N*-dimethylbiphenyl-4-amine (**19**) in 58 and 11% isolated yield, respectively (Scheme 2). From the product distribution, it seems that the allyl C–O bond is more reactive than the aryl C–Cl bond.

Reactivity of several 1-aryl-3-alkyl-3-methoxypropenes was also examined, and the results are presented in Scheme 3. The reaction of 1-phenyl-3-alkyl-3-methoxypropenes with 4-(dimethylamino)phenylzinc chloride proceeded smoothly under the optimized conditions, and no allylic rearrangements were observed whether the alkyl group is Me, Et, *n*Bu, or *i*Pr. However, bulkier alkyl groups in the electrophilic substrates result in lower product yields. For example, the reaction of the 3-position methyl derivative with 4-(dimethylamino)phenylzinc chloride gave 91% yield of cross-coupling product **20**, but the reaction of the 3-position isopropyl derivative gave 80% product yield. Heteroarylallyl methyl ether (*E*)-2-(3-methoxy-

**Scheme 1. Ia-Catalyzed Cross-Coupling of 3-Aryl-3-methoxy-prop-1-enes with  $p$ -Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>ZnCl<sup>a</sup>**


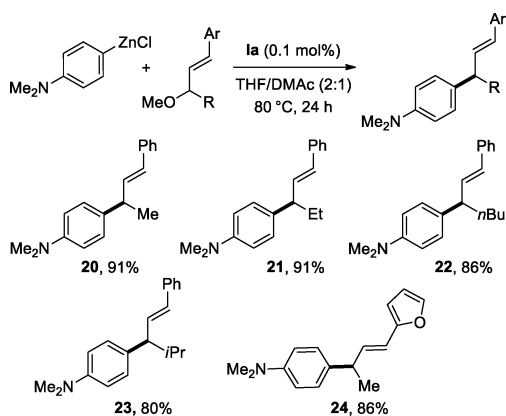
<sup>a</sup>The reactions were carried out on a 0.5 mmol scale, and 2.0 equiv of zinc reagent was employed. The zinc reagents were prepared from corresponding Grignard reagents and ZnCl<sub>2</sub> in the presence of 2 equiv of LiCl. Isolated product yields are reported. <sup>b</sup>**Ia** was employed at 1 mol %.

**Scheme 2. Ia-Catalyzed Reaction of 1-Chloro-4-(1-methoxyallyl)benzene with  $p$ -Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>ZnCl**


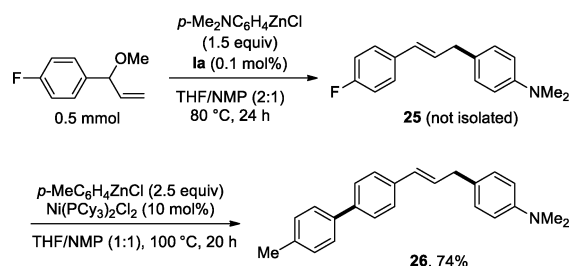
ylbut-1-en-1-yl)furan was also demonstrated to be a good electrophile in the cross-coupling. Its reaction with 4-(dimethylamino)phenylzinc chloride afforded (*E*)-4-(4-(furan-2-yl)but-3-en-2-yl)-*N,N*-dimethylaniline **24** in 86% yield.

As shown in **Scheme 1**, the catalytic reaction can tolerate the C<sub>Ar</sub>–F bond in the arylallyl ether. Our previous work showed that the C<sub>Ar</sub>–F bond can be catalytically cleaved and coupled to a zinc reagent using Ni(PCy<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> as catalyst.<sup>10</sup> Hence, we tried to install two different aryl groups into the fluorinated arylallyl ether in a one-pot reaction. The results demonstrated that the reaction could be performed well and gave 74% overall yield (**Scheme 4**). The nickel complex **Ia** used in the first step did not affect the following reaction. The excess zinc reagent in the first step was consumed due to its homocoupling.

The **Ia**-catalyzed reaction of cinnamyl methyl ether with  $p$ -Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>ZnCl was not affected by the 1,1-diphenylethene additive. The reaction run under the optimized conditions in the presence of 1,1-diphenylethene (1.0 equiv) gave 95% yield

**Scheme 3. Ia-Catalyzed Cross-Coupling of 1-Aryl-3-alkyl-3-methoxypropenes with  $p$ -Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>ZnCl<sup>a</sup>**


<sup>a</sup>The reactions were carried out on a 0.5 mmol scale, and 2.0 equiv of zinc reagent was employed. The zinc reagents were prepared from corresponding Grignard reagents and ZnCl<sub>2</sub> in the presence of 2 equiv of LiCl. Isolated product yields are reported.

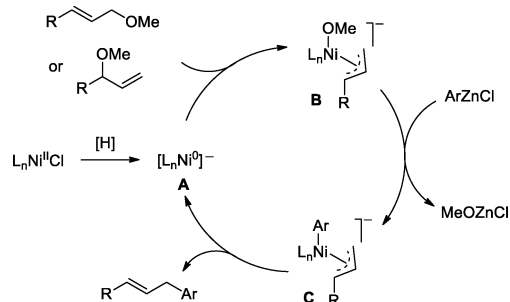
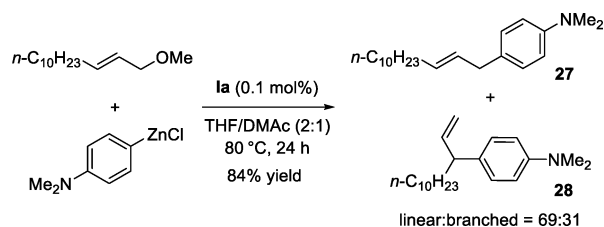
**Scheme 4. Sequential Cross-Coupling of 1-Fluoro-4-(1-methoxyallyl)benzene**


of the cross-coupling product. This ruled out the possibility of a free radical mechanism. No reaction occurred between cinnamyl methyl ether and an equiv of **Ia** in THF at 80 °C (bath temperature). However, a reaction between cinnamyl methyl ether and an equiv of Ni(0) species prepared in situ from Ni(COD)<sub>2</sub> and lithiated (2-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>)NH(2'-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>), supposing [Li{N(2-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>)(2'-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>)}] (**II**) did occur in THF at 80 °C, and cinnamyl methyl ether was completely consumed in 24 h. Attempts to isolate the formed nickel complexes were unsuccessful. The combination of Ni(COD)<sub>2</sub> and **II** effectively catalyzed the cross-coupling of cinnamyl methyl ether with  $p$ -Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>ZnCl in THF/DMA (2:1) at 80 °C and 0.1 mol % Ni(COD)<sub>2</sub>/**II**, leading to the desired product in 95% yield. These experimental facts showed that the catalytically active species may be a Ni(0) complex. The allylic rearrangements shown in **Scheme 1** support a  $\pi$ -allylnickel intermediate formed in the catalytic process. A proposed catalytic cycle is outlined in **Scheme 5**. In the catalytic cycle, the tridentate ligand may be hemilabile. In intermediates **B** and **C**, the ligand is expected to adopt a didentate coordination mode, which keeps an 18e configuration of the central metals in the intermediates.

The regioselectivity of the reactions is probably the result of both maximizing conjugation and minimizing steric hindrance in the coupling of the zinc reagent with the putative  $\pi$ -allylnickel intermediate, and the conjugation seems to act predominantly. This conjecture is supported by the reactions shown in **Schemes 3** and **6**. In the reaction shown in **Scheme 6**, the aliphatic group substituted allyl methyl ether (*E*)-1-



Scheme 5. A Proposed Catalytic Cycle

Scheme 6. Ia-Catalyzed Reaction of (*E*)-1-Methoxytridec-2-ene with *p*-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>ZnCl

methoxytridec-2-ene with *p*-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>ZnCl resulted in a mixture of linear and branched regioisomers in a ratio of 69:31 (based on <sup>1</sup>H NMR integration), whereas the reactions of the aryl group substituted allyl methyl ether with *p*-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>ZnCl gave only linear isomers.

In summary, we have demonstrated a pincer-nickel complex [Ni(Cl){N(2-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>)(2'-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>)}] (Ia) that can effectively catalyze cross-coupling of allyl methyl ethers with arylzinc reagents under mild conditions with low catalyst loadings. The reaction shows high regioselectivity when (1-methoxyallyl)arenes or (3-methoxyprop-1-en-1-yl)arenes were employed as the electrophilic substrates, giving linear (*E*)-alkenes in high yields. Aliphatic group substituted allyl methyl ether (*E*)-1-methoxytridec-2-ene also exhibited good reactivity with *p*-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>ZnCl under the same conditions but formed a mixture of linear and branched regioisomers. The reaction may proceed through a Ni(0)/Ni(II) process with  $\pi$ -allylnickel intermediates, but the exact mechanism is not presently clear.

## EXPERIMENTAL SECTION

**General Information.** All air- or moisture-sensitive manipulations were performed under nitrogen using standard Schlenk techniques. Toluene and dioxane were distilled under nitrogen over sodium; THF was distilled under nitrogen over sodium/benzophenone; NMP and DMA were dried over 4 Å molecular sieves, fractionally distilled under reduced pressure, and stored under a nitrogen atmosphere. *N,N*-Diethyl-4-formylbenzamide,<sup>13</sup> ethyl 4-(1-hydroxyallyl)benzoate,<sup>14</sup> (*E*)-(3-methoxyprop-1-en-1-yl)benzene,<sup>9b</sup> 1-fluoro-4-(1-methoxyallyl)benzene,<sup>15</sup> and 1-chloro-4-(1-methoxyallyl)benzene<sup>15</sup> were prepared according to literature procedures. Grignard reagents were prepared according to reported methods.<sup>16</sup> Arylzinc chlorides were prepared from ZnCl<sub>2</sub> and an equiv of ArMgBr in the presence of 2 equiv of LiCl. All other chemicals and solvents were obtained from commercial vendors and used as received. NMR spectra were recorded on a 400 MHz NMR spectrometer at ambient temperature. The chemical shifts of <sup>1</sup>H NMR spectra were referenced to TMS, and the chemical shifts of <sup>13</sup>C NMR spectra were referenced to internal solvent resonances ( $\delta_{\text{CDCl}_3}$  = 77.0 ppm). High-resolution mass spectra (HR-MS) were acquired in ESI mode using an Orbitrap mass analyzer.

**Synthesis of Allyl Methyl Ethers.** *Synthesis of (1-Methoxyallyl)benzene.*<sup>17</sup> Vinylmagnesium bromide (9.0 mL, 1.0 M solution in

THF, 9.0 mmol) was added dropwise to a stirred solution of benzaldehyde (0.61 mL, 6.00 mmol) in THF (15 mL) at −78 °C. The resulting solution was warmed to room temperature and stirred for 4 h. Ice water (20 mL) was added slowly to the mixture after which ethyl acetate (20 mL) was added. The organic layer was separated, and the aqueous phase was extracted with ethyl acetate (2 × 20 mL). The combined organic phase was washed with brine (20 mL), dried over MgSO<sub>4</sub>, and evaporated to dryness by rotary evaporation to give 1-phenylprop-2-en-1-ol with a yield of 0.44 g (55%). This product was used in the next step without further purification.

1-Phenylprop-2-en-1-ol (0.44 g, 3.28 mmol) was dissolved in THF (10 mL) and added dropwise to a stirred suspension of NaH (0.27 g, 60% dispersion in mineral oil, 6.75 mmol) in THF (15 mL) at 0 °C. The mixture was warmed to room temperature and stirred for 1 h. Then, MeI (0.62 mL, 9.96 mmol) was added dropwise to the stirred mixture. The resulting mixture was stirred overnight at room temperature. Ice water (20 mL) was added slowly to the mixture after which ethyl acetate (20 mL) was added. The organic layer was separated, and the aqueous phase was extracted with ethyl acetate (2 × 20 mL). The combined organic phase was then washed with brine (20 mL), dried over MgSO<sub>4</sub>, and evaporated to dryness by rotary evaporation. The residue was purified by column chromatography (eluted with petroleum ether/EtOAc (100:1 v/v)) to yield (1-methoxyallyl)benzene as a clear oil with a yield of 0.46 g (52% overall yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  3.33 (d, *J* = 1.1 Hz, 3H), 4.62 (d, *J* = 6.7 Hz, 1H), 5.19–5.30 (m, 2H), 5.89–5.98 (m, 1H), 7.26–7.38 (m, 5H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  56.4, 84.7, 116.3, 126.8, 127.7, 128.4, 138.8, 140.9.

The same procedure as for (1-methoxyallyl)benzene was used to prepare the other 3-aryl-3-methoxyprop-1-enes.

**1-Methoxy-3-(1-methoxyallyl)benzene.** Eluent: petroleum ether/EtOAc (60:1 v/v). Colorless oil, yield 0.74 g (69%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  3.33 (s, 3H), 3.81 (s, 3H), 4.59 (d, *J* = 6.7 Hz, 1H), 5.19–5.22 (m, 1H), 5.28 (dt, *J* = 16.8, 1.2 Hz, 1H), 5.88–5.96 (m, 1H), 6.81–6.84 (m, 1H), 6.88–6.92 (m, 2H), 7.26 (t, *J* = 7.9 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  55.2, 56.4, 84.6, 112.1, 113.3, 116.3, 119.2, 129.4, 138.6, 142.5, 159.8. HR-MS: *m/z* 179.10701 [M + H]<sup>+</sup>; calcd for C<sub>11</sub>H<sub>15</sub>O<sub>2</sub>, 179.10666.

**4-(1-Methoxyallyl)-*N,N*-dimethylaniline.** Eluent: petroleum ether/EtOAc (60:1 v/v). Colorless oil, yield 0.49 g (42%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  2.94 (s, 6H), 3.29 (s, 3H), 4.54 (d, *J* = 6.5 Hz, 1H), 5.16 (dt, *J* = 10.4, 1.2 Hz, 1H), 5.24 (dt, *J* = 17.2, 1.4 Hz, 1H), 5.91–6.00 (m, 1H), 6.72 (d, *J* = 8.8 Hz, 2H), 7.19 (d, *J* = 8.8 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  40.6, 56.0, 84.4, 112.5, 115.4, 127.9, 128.5, 139.2, 150.3. HR-MS: *m/z* 192.13924 [M + H]<sup>+</sup>; calcd for C<sub>12</sub>H<sub>18</sub>NO, 192.13829.

**1-Methoxy-2-(1-methoxyallyl)benzene.** Eluent: petroleum ether/EtOAc (60:1 v/v). Colorless oil, yield 0.38 g (36%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  3.33 (s, 3H), 3.83 (s, 3H), 5.10 (d, *J* = 6.3 Hz, 1H), 5.12–5.15 (m, 1H), 5.24–5.29 (m, 1H), 5.89–5.98 (m, 1H), 6.88 (dd, *J* = 8.3, 0.9 Hz, 1H), 6.98 (dt, *J* = 7.6, 1.1 Hz, 1H), 7.23–7.27 (m, 1H), 7.37 (dd, *J* = 7.6, 1.8 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  55.4, 56.5, 77.9, 110.6, 115.3, 120.8, 127.0, 128.5, 129.2, 138.1, 156.8. HR-MS: *m/z* 179.10614 [M + H]<sup>+</sup>; calcd for C<sub>11</sub>H<sub>15</sub>O<sub>2</sub>, 179.10666.

**1-(1-Methoxyallyl)naphthalene.**<sup>18</sup> Eluent: petroleum ether/EtOAc (100:1 v/v). Colorless oil, yield 0.97 g (82%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  3.39 (s, 3H), 5.21–5.26 (m, 1H), 5.29–5.36 (m, 2H), 6.10–6.19 (m, 1H), 7.45–7.52 (m, 3H), 7.56 (d, *J* = 7.1 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.84–7.88 (m, 1H), 8.16–8.21 (m, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  56.6, 82.7, 116.7, 124.0, 124.9, 125.4, 125.5, 125.9, 128.4, 128.8, 131.0, 134.0, 136.2, 138.1.

**2-(1-Methoxyallyl)thiophene.** Eluent: petroleum ether/EtOAc (100:1 v/v). Yellow oil, 0.36 g (39%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  3.36 (s, 3H), 4.87 (d, *J* = 6.8 Hz, 1H), 5.28 (dt, *J* = 10.0, 1.2 Hz, 1H), 5.35 (dt, *J* = 17.2, 1.3 Hz, 1H), 5.94–6.03 (m, 1H), 6.96–6.98 (m, 2H), 7.26–7.29 (m, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  56.3, 80.2, 117.2, 124.9, 125.3, 126.5, 137.8, 144.5. HR-MS: *m/z* 123.02583 [M-MeO]<sup>+</sup>; calcd for C<sub>7</sub>H<sub>7</sub>S, 123.02630.

**Synthesis of (*E*)-(3-Methoxybut-1-en-1-yl)benzene.**<sup>19</sup> MeLi (6.3 mL, 1.3 M solution in Et<sub>2</sub>O, 8.19 mmol) was added dropwise to a

solution of cinnamaldehyde (0.95 mL, 7.54 mmol) in Et<sub>2</sub>O (15 mL) at –78 °C with stirring. The resulting mixture was warmed to room temperature and stirred for 4 h. Ice water (20 mL) was added slowly to the mixture. The organic layer was separated, and the aqueous phase was extracted with ethyl acetate (3 × 15 mL). The combined organic phase was washed with brine (20 mL), dried over MgSO<sub>4</sub>, and evaporated to dryness by rotary evaporation to give (*E*)-4-phenylbut-3-en-2-ol with a yield of 0.943 g (85%). This product was used in the next step without further purification.

A solution of (*E*)-4-phenylbut-3-en-2-ol (0.943 g, 6.36 mmol) in THF (10 mL) was added dropwise to a stirred suspension of NaH (0.51 g, 60% dispersion in mineral oil, 12.75 mmol) in THF (15 mL) at 0 °C. The mixture was warmed to room temperature and stirred for 1 h. Then, MeI (1.2 mL, 19.27 mmol) was added dropwise to the mixture. The resulting mixture was stirred overnight at room temperature. Ice water (20 mL) was added slowly to the mixture after which ethyl acetate (20 mL) was added. The organic layer was separated, and the aqueous phase was extracted with ethyl acetate (2 × 20 mL). The combined organic phase was washed with brine (20 mL), dried over MgSO<sub>4</sub>, and evaporated to dryness by rotary evaporation. The residue was purified by column chromatography (eluted with petroleum ether/EtOAc (100:1 v/v)) to yield (*E*)-(3-methoxybut-1-en-1-yl)benzene as a clear oil with a yield of 0.93 g (76% overall yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 1.33 (d, *J* = 6.3 Hz, 3H), 3.32 (s, 3H), 3.86–3.93 (m, 1H), 6.09 (dd, *J* = 16.0, 7.7 Hz, 1H), 6.53 (d, *J* = 16.0 Hz, 1H), 7.21–7.27 (m, 1H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.38–7.41 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 21.5, 56.0, 78.1, 126.4, 127.6, 128.6, 131.3, 131.4, 136.6.

The same procedure as for (*E*)-(3-methoxybut-1-en-1-yl)benzene was used to prepare the other (3-alkyl-3-methoxyprop-1-en-1-yl)benzenes and 2-(3-methoxybut-1-en-1-yl)furan.

**(*E*)-(3-Methoxypent-1-en-1-yl)benzene.**<sup>20</sup> Eluent: petroleum ether/EtOAc (100:1 v/v). Colorless oil, yield 0.95g (72%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.93 (t, *J* = 7.5 Hz, 3H), 1.53–1.65 (m, 1H), 1.66–1.78 (m, 1H), 3.32 (s, 3H), 3.62 (q, *J* = 7.2 Hz, 1H), 6.04 (dd, *J* = 16.0, 8.0 Hz, 1H), 6.53 (d, *J* = 16.0 Hz, 1H), 7.22–7.27 (m, 1H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.40 (d, *J* = 7.1 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 9.8, 28.5, 56.3, 84.0, 126.4, 127.6, 128.6, 130.3, 132.4, 136.7. HR-MS: *m/z* 177.12757 [M + H]<sup>+</sup>; calcd for C<sub>12</sub>H<sub>17</sub>O, 177.12739.

**(*E*)-(3-Methoxyhept-1-en-1-yl)benzene.** Eluent: petroleum ether/EtOAc (100:1 v/v). Colorless oil, yield 1.19 g (78%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.90 (t, *J* = 7.0 Hz, 3H), 1.27–1.42 (m, 4H), 1.50–1.62 (m, 1H), 1.63–1.76 (m, 1H), 3.31 (s, 3H), 3.68 (q, *J* = 7.2 Hz, 1H), 6.05 (dd, *J* = 15.9, 8.0 Hz, 1H), 6.52 (d, *J* = 16.0 Hz, 1H), 7.22–7.26 (m, 1H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.40 (d, *J* = 7.0 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 14.0, 22.7, 27.6, 35.4, 56.2, 82.7, 126.4, 127.6, 128.6, 130.6, 132.2, 136.7. HR-MS: *m/z* 205.15914 [M + H]<sup>+</sup>; calcd for C<sub>14</sub>H<sub>21</sub>O, 205.15869.

**(*E*)-(3-Methoxy-4-methylpent-1-en-1-yl)benzene.** Eluent: petroleum ether/EtOAc (100:1 v/v). Colorless oil, yield 0.88 g (62%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.91 (d, *J* = 6.8 Hz, 3H), 0.97 (d, *J* = 6.7 Hz, 3H), 1.81–1.89 (m, 1H), 3.31 (s, 3H), 3.39 (dd, *J* = 7.8, 6.6 Hz, 1H), 6.06 (dd, *J* = 16.0, 8.2 Hz, 1H), 6.51 (d, *J* = 16.0 Hz, 1H), 7.22–7.27 (m, 1H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.41 (d, *J* = 7.4 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 18.3, 18.7, 33.0, 56.6, 88.1, 126.4, 127.6, 128.6, 128.8, 133.1, 136.8. HR-MS: *m/z* 191.14351 [M + H]<sup>+</sup>; calcd for C<sub>13</sub>H<sub>19</sub>O, 191.14304.

**(*E*)-2-(3-Methoxybut-1-en-1-yl)furan.** Eluent: petroleum ether/EtOAc (100:1 v/v). Yellow oil, yield 0.77 g (67%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 1.31 (d, *J* = 6.4 Hz, 3H), 3.31 (s, 3H), 3.81–3.89 (m, 1H), 6.04 (dd, *J* = 15.9, 7.5 Hz, 1H), 6.24 (d, *J* = 3.3 Hz, 1H), 6.34–6.38 (m, 2H), 7.35 (d, *J* = 1.7 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 21.4, 56.1, 77.7, 107.8, 111.2, 119.5, 130.2, 141.9, 152.3. HR-MS: *m/z* 153.09103 [M + H]<sup>+</sup>; calcd for C<sub>9</sub>H<sub>13</sub>O<sub>2</sub>, 153.09101.

**Synthesis of *N,N*-diethyl-4-(1-methoxyallyl)benzamide.** Vinylmagnesium bromide (4.2 mL, 1.0 M solution in THF, 4.2 mmol) was added dropwise to a stirred solution of *N,N*-diethyl-4-formylbenzamide (0.82 g, 4.0 mmol) in THF (8 mL) at 0 °C. The resulting solution was warmed to room temperature and stirred for 4

h. Ice water (15 mL) was added slowly to the mixture after which ethyl acetate (15 mL) was added. The organic layer was separated, and the aqueous phase was extracted with ethyl acetate (2 × 15 mL). The combined organic phase was washed with brine (15 mL), dried over MgSO<sub>4</sub>, and evaporated to dryness by rotary evaporation to give *N,N*-diethyl-4-(1-hydroxyallyl)benzamide with a yield of 0.49 g (53%). This product was used in the next step without further purification.

*N,N*-Diethyl-4-(1-hydroxyallyl)benzamide (0.49 g, 2.1 mmol) was dissolved in THF (4 mL) and added dropwise to a stirred suspension of NaH (0.13 g, 60% dispersion in mineral oil, 3.15 mmol) in THF (5 mL) at 0 °C. The mixture was warmed to room temperature and stirred for 1 h. MeI (0.4 mL, 6.3 mmol) was added dropwise to the stirred mixture. The resulting mixture was stirred overnight at room temperature. Ice water (10 mL) was added slowly to the mixture after which ethyl acetate (10 mL) was added. The organic layer was separated, and the aqueous phase was extracted with ethyl acetate (2 × 10 mL). The combined organic phase was then washed with brine (10 mL), dried over MgSO<sub>4</sub>, and evaporated to dryness by rotary evaporation. The residue was purified by column chromatography (eluted with petroleum ether/EtOAc (4:1 v/v)) to give *N,N*-diethyl-4-(1-methoxyallyl)benzamide as a clear oil with a yield of 0.44 g (85%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 1.11 (b, 3H), 1.25 (b, 3H), 3.26 (b, 2H), 3.35 (s, 3H), 3.54 (b, 2H), 4.64 (d, *J* = 6.9 Hz, 1H), 5.24 (d, *J* = 10.3 Hz, 1H), 5.30 (d, *J* = 17.2 Hz, 1H), 5.85–5.94 (m, 1H), 7.36 (s, 4H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 12.9, 14.2, 39.2, 43.3, 56.4, 84.3, 116.8, 126.5, 126.8, 136.5, 138.3, 141.9, 171.1. HR-MS: *m/z* 248.16476 [M + H]<sup>+</sup>; calcd for C<sub>15</sub>H<sub>22</sub>O<sub>2</sub>N, 248.16451.

**Synthesis of Ethyl 4-(1-Methoxyallyl)benzoate.** NaH (0.12 g, 60% dispersion in mineral oil, 3.0 mmol) was added to a stirred solution of ethyl 4-(1-hydroxyallyl)benzoate (0.41 g, 2.0 mmol) and MeI (0.50 mL, 8.0 mmol) in THF (6 mL) at 0 °C in one portion. The resulting mixture was stirred at 0 °C for 30 min and then stirred overnight at room temperature. Ice water (10 mL) was added slowly to the mixture after which ethyl acetate (10 mL) was added. The organic layer was separated, and the aqueous phase was extracted with ethyl acetate (2 × 10 mL). The combined organic phase was washed with brine (10 mL), dried over MgSO<sub>4</sub>, and evaporated to dryness by rotary evaporation. The residue was purified by column chromatography (eluted with petroleum ether/EtOAc (60:1 v/v)) to afford ethyl 4-(1-methoxyallyl)benzoate as a clear oil with a yield of 0.24 g (54%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 1.39 (t, *J* = 7.2 Hz, 3H), 3.34 (s, 3H), 4.37 (q, *J* = 7.2 Hz, 2H), 4.67 (d, *J* = 6.8 Hz, 1H), 5.24 (dt, *J* = 1.2, 10.4 Hz, 1H), 5.30 (dt, *J* = 1.4, 17.2 Hz, 1H), 5.84–5.92 (m, 1H), 7.40 (d, *J* = 8.4 Hz, 2H), 8.03 (d, *J* = 8.4 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 14.3, 56.5, 60.9, 84.3, 117.2, 126.6, 129.7, 129.8, 138.1, 145.9, 166.4. HR-MS: *m/z* 221.11687 [M + H]<sup>+</sup>; calcd for C<sub>13</sub>H<sub>17</sub>O<sub>3</sub>, 221.11722.

**Synthesis of (*E*)-1-Methoxytridec-2-ene.** (*E*)-1-Methoxytridec-2-ene was prepared on a 6 mmol scale according to the second step of the procedure for (*E*)-(3-methoxybut-1-en-1-yl)benzene. (*E*)-1-Methoxytridec-2-ene was purified by column chromatography (eluted with petroleum ether/EtOAc (100:1 v/v)) to give a pale yellow oil with a yield of 1.03 g (81%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.88 (t, *J* = 6.8 Hz, 3H), 1.20–1.43 (m, 16H), 2.04 (q, *J* = 7.0 Hz, 2H), 3.32 (s, 3H), 3.86 (d, *J* = 6.3 Hz, 2H), 5.50–5.59 (m, 1H), 5.66–5.75 (m, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 14.1, 22.7, 29.1, 29.2, 29.3, 29.5, 29.59, 29.61, 31.9, 32.3, 57.6, 73.3, 126.0, 135.1. HR-MS: *m/z* 213.22104 [M + H]<sup>+</sup>; calcd for C<sub>14</sub>H<sub>29</sub>O, 213.22129.

**General Procedure for the Cross-Coupling of Allyl Methyl Ethers with Arylzinc Chlorides.** A Schlenk tube was charged with allyl methyl ether (0.5 mmol), DMA (1.05 mL), and a solution of complex **1a** (0.1 mL, 0.005 M solution in THF, 0.0005 mmol). To the stirred mixture was added ArZnCl solution (2 mL, 0.5 M solution in THF, 1.0 mmol) by syringe. The reaction mixture was stirred at 80 °C for 24 h. Water (10 mL) and several drops of glacial acetic acid were added successively. The mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic phases were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, concentrated by rotary evaporation, and purified by column chromatography (silica gel).



**4-Cinnamyl-*N,N*-dimethylaniline (1).**<sup>21</sup> Eluent: petroleum ether/EtOAc (60:1 v/v), yield of 0.115 g (97%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 2.92 (s, 6H), 3.46 (d, *J* = 6.4 Hz, 2H), 6.34 (dt, *J* = 15.6, 6.4 Hz, 1H), 6.43 (d, *J* = 15.6 Hz, 1H), 6.72 (d, *J* = 8.7 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.28 (t, *J* = 7.6 Hz, 2H), 7.35 (d, *J* = 7.1 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 38.4, 40.9, 113.1, 126.1, 126.9, 128.2, 128.4, 129.3, 130.2, 130.3, 137.7, 149.3.

**1-Cinnamyl-4-methoxybenzene (2).**<sup>4d</sup> Eluent: petroleum ether/EtOAc (100:1 v/v), yield 0.108 g (96%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 3.48 (d, *J* = 6.5 Hz, 2H), 3.79 (s, 3H), 6.33 (dt, *J* = 15.6, 6.4 Hz, 1H), 6.43 (d, *J* = 15.6 Hz, 1H), 6.85 (d, *J* = 8.7 Hz, 2H), 7.15 (d, *J* = 8.8 Hz, 2H), 7.18–7.21 (m, 1H), 7.28 (t, *J* = 7.6 Hz, 2H), 7.33–7.36 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 38.4, 55.3, 113.9, 126.1, 127.0, 128.5, 129.6, 129.7, 130.7, 132.1, 137.5, 158.0.

**5-Cinnamylbenzo[d][1,3]dioxole (3).**<sup>22</sup> Eluent: petroleum ether/EtOAc (100:1 v/v), yield 0.106 g (89%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 3.45 (d, *J* = 6.7 Hz, 2H), 5.91 (s, 2H), 6.30 (dt, *J* = 15.8, 6.7 Hz, 1H), 6.43 (d, *J* = 15.8 Hz, 1H), 6.65–6.78 (m, 3H), 7.17–7.22 (m, 1H), 7.28 (t, *J* = 7.5 Hz, 2H), 7.35 (d, *J* = 7.3 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 39.0, 100.8, 108.2, 109.2, 121.4, 126.1, 127.1, 128.5, 129.3, 131.0, 133.9, 137.4, 145.9, 147.7.

**1-Cinnamyl-4-methylbenzene (4).**<sup>4d</sup> Eluent: petroleum ether, yield 0.095 g (91%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 2.33 (s, 3H), 3.51 (d, *J* = 6.5 Hz, 2H), 6.34 (dt, *J* = 15.7, 6.5 Hz, 1H), 6.44 (d, *J* = 15.8 Hz, 1H), 7.13 (s, 4H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.28 (t, *J* = 7.5 Hz, 2H), 7.35 (d, *J* = 7.8 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 21.0, 38.9, 126.1, 127.0, 128.5, 128.5, 129.2, 129.5, 130.8, 135.7, 137.1, 137.5.

**(*E*)-Prop-1-ene-1,3-diylidibenzene (5).**<sup>23</sup> Eluent: petroleum ether, yield 0.086 g (89%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 3.55 (d, *J* = 6.6 Hz, 2H), 6.36 (dt, *J* = 15.7, 6.6 Hz, 1H), 6.46 (d, *J* = 15.8 Hz, 1H), 7.17–7.26 (m, 4H), 7.27–7.33 (m, 4H), 7.34–7.37 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 39.3, 126.1, 126.2, 127.1, 128.47, 128.48, 128.7, 129.2, 131.1, 137.5, 140.2.

**4-Cinnamyl-1,1'-biphenyl (6).**<sup>24</sup> Eluent: petroleum ether, yield 0.110 g (82%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 3.56 (d, *J* = 6.6 Hz, 2H), 6.32–6.41 (m, 1H), 6.47 (d, *J* = 15.8 Hz, 1H), 7.15–7.22 (m, 1H), 7.24–7.44 (m, 9H), 7.50–7.60 (m, 4H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 38.9, 126.1, 127.0, 127.06, 127.11, 127.2, 128.5, 128.7, 129.0, 129.1, 131.2, 137.4, 139.1, 139.2, 141.0.

**2-Cinnamyl-naphthalene (7).**<sup>24</sup> Eluent: petroleum ether, yield 0.117 g (96%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 3.71 (d, *J* = 6.2 Hz, 2H), 6.43 (dt, *J* = 15.8, 6.4 Hz, 1H), 6.51 (d, *J* = 15.9 Hz, 1H), 7.21 (t, *J* = 7.3 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.34–7.40 (m, 3H), 7.41–7.48 (m, 2H), 7.68 (s, 1H), 7.76–7.83 (m, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 39.5, 125.3, 126.0, 126.2, 126.7, 127.1, 127.4, 127.5, 127.6, 128.0, 128.5, 129.1, 131.3, 132.2, 133.7, 137.4, 137.6.

**2-Cinnamyl-6-methoxynaphthalene (8).** Eluent: petroleum ether/EtOAc (100:1 v/v). White solid, yield 0.119 g (87%); mp 86–88 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 3.66 (d, *J* = 6.2 Hz, 2H), 3.90 (s, 3H), 6.42 (dt, *J* = 15.8, 6.2 Hz, 1H), 6.49 (d, *J* = 15.9 Hz, 1H), 7.09–7.14 (m, 2H), 7.17–7.22 (m, 1H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.32–7.39 (m, 3H), 7.60 (s, 1H), 7.68 (d, *J* = 8.4 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 39.3, 55.3, 105.7, 118.7, 126.1, 126.6, 126.9, 127.1, 127.9, 128.5, 129.0, 129.1, 129.3, 131.1, 133.2, 135.3, 137.5, 157.3. HR-MS: *m/z* 275.14306 [M + H]<sup>+</sup>; calcd for C<sub>20</sub>H<sub>19</sub>O, 275.14304.

**9-Cinnamylphenanthrene (9).**<sup>25</sup> Elute: petroleum ether, yield 0.137 g (93%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 4.02 (d, *J* = 5.6 Hz, 2H), 6.50 (d, *J* = 16 Hz, 1H), 6.56 (dt, *J* = 15.9, 5.8 Hz, 1H), 7.15–7.21 (m, 1H), 7.27 (t, *J* = 7.5 Hz, 2H), 7.32–7.35 (m, 2H), 7.53–7.68 (m, 5H), 7.81–7.84 (m, 1H), 8.11–8.14 (m, 1H), 8.65 (d, *J* = 8.1 Hz, 1H), 8.71–8.74 (m, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 36.7, 122.5, 123.2, 124.7, 126.1, 126.2, 126.3, 126.62, 126.64, 126.8, 127.1, 128.2, 128.48, 128.51, 129.9, 130.7, 131.3, 131.7, 131.9, 134.5, 137.4.

**(*E*)-4-(3-(3-Methoxyphenyl)allyl)-*N,N*-dimethylaniline (10).** Eluent: petroleum ether/EtOAc (60:1 v/v). Colorless oil, yield 0.113 g (85%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 2.93 (s, 6H), 3.46 (d, *J* = 5.9 Hz, 2H), 3.80 (s, 3H), 6.29–6.45 (m, 2H), 6.70–6.78 (m, 3H), 6.90 (s, 1H), 6.95 (d, *J* = 7.6 Hz, 1H), 7.12 (d, *J* = 8.4 Hz, 2H), 7.20 (t, *J* = 7.9 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 38.3, 40.9, 55.2, 111.2,

112.7, 113.0, 118.8, 128.1, 129.3, 129.4, 130.2, 130.5, 139.2, 149.3, 159.8. HR-MS: *m/z* 268.16965 [M + H]<sup>+</sup>; calcd for C<sub>18</sub>H<sub>22</sub>NO, 268.16959.

**(*E*)-4,4'-(Prop-1-ene-1,3-diyl)bis(*N,N*-dimethylaniline) (11).** Eluent: petroleum ether/EtOAc (50:1 v/v). Colorless oil, yield 0.118 g (84%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 2.91 (s, 6H), 2.93 (s, 6H), 3.42 (d, *J* = 6.8 Hz, 2H), 6.13 (dt, *J* = 15.7, 6.9 Hz, 1H), 6.35 (d, *J* = 15.7 Hz, 1H), 6.66 (d, *J* = 8.8 Hz, 2H), 6.71 (d, *J* = 8.6 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.8 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 38.4, 40.6, 41.9, 112.6, 113.1, 126.0, 126.5, 126.9, 129.0, 129.2, 130.2, 149.2, 149.7. HR-MS: *m/z* 281.20126 [M + H]<sup>+</sup>; calcd for C<sub>19</sub>H<sub>25</sub>N<sub>2</sub>, 281.20123.

**(*E*)-4-(3-(2-Methoxyphenyl)allyl)-*N,N*-dimethylaniline (12).** Eluent: petroleum ether/EtOAc (60:1 v/v). White solid, yield 0.103 g (77%); mp 68–70 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 2.91 (s, 6H), 3.48 (d, *J* = 7.0 Hz, 2H), 3.83 (s, 3H), 6.33 (dt, *J* = 15.8, 7.1 Hz, 1H), 6.71 (d, *J* = 8.8 Hz, 2H), 6.79 (d, *J* = 15.8 Hz, 1H), 6.82–6.91 (m, 2H), 7.12 (d, *J* = 8.8 Hz, 2H), 7.14–7.20 (m, 1H), 7.41 (dd, *J* = 7.6, 1.7 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 38.9, 40.9, 55.4, 110.8, 113.1, 120.6, 125.0, 126.6, 126.8, 127.9, 128.6, 129.2, 130.8, 149.3, 156.4. HR-MS: *m/z* 268.16943 [M + H]<sup>+</sup>; calcd for C<sub>18</sub>H<sub>22</sub>NO, 268.16959.

**(*E*)-4-(3-(4-(Dimethylamino)phenyl)prop-1-enyl)-*N,N*-diethylbenzamide (13).** Eluent: petroleum ether/EtOAc (4:1 v/v). Colorless oil, yield 0.146 g (87%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 1.09 (b, 3H), 1.22 (b, 3H), 2.91 (s, 6H), 3.24 (b, 2H), 3.45 (d, *J* = 5.2 Hz, 2H), 3.52 (b, 2H), 6.34–6.44 (m, 2H), 6.71 (d, *J* = 8.8 Hz, 2H), 7.10 (d, *J* = 8.8 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 12.8, 14.1, 38.3, 39.1, 40.7, 43.2, 112.9, 125.8, 126.5, 127.6, 129.2, 129.4, 131.4, 135.4, 138.4, 149.2, 171.1. HR-MS: *m/z* 337.22699 [M + H]<sup>+</sup>; calcd for C<sub>22</sub>H<sub>29</sub>ON<sub>2</sub>, 337.22744.

**(*E*)-Ethyl 4-(3-(4-(Dimethylamino)phenyl)prop-1-enyl)benzoate (14).** Eluent: petroleum ether/EtOAc (60:1 v/v). Colorless oil, yield 0.127 g (82%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 1.38 (t, *J* = 7.2 Hz, 3H), 2.92 (s, 6H), 3.47 (d, *J* = 5.2 Hz, 2H), 4.36 (q, *J* = 7.2 Hz, 2H), 6.41–6.52 (m, 2H), 6.72 (d, *J* = 8.8 Hz, 2H), 7.11 (d, *J* = 8.8 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.95 (d, *J* = 8.4 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 14.3, 38.4, 40.8, 60.8, 113.0, 125.9, 127.4, 128.7, 129.3, 129.5, 129.8, 133.1, 142.1, 149.4, 166.5. HR-MS: *m/z* 310.17966 [M + H]<sup>+</sup>; calcd for C<sub>20</sub>H<sub>24</sub>O<sub>2</sub>N, 310.18016.

**(*E*)-4-(3-(4-Fluorophenyl)allyl)-*N,N*-dimethylaniline (15).** Eluent: petroleum ether/EtOAc (100:1 v/v). Colorless oil, yield 0.115 g (90%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 2.91 (s, 6H), 3.43 (d, *J* = 6.6 Hz, 2H), 6.25 (dt, *J* = 15.7, 6.6 Hz, 1H), 6.38 (d, *J* = 15.7 Hz, 1H), 6.71 (d, *J* = 8.7 Hz, 2H), 6.96 (t, *J* = 8.7 Hz, 2H), 7.10 (d, *J* = 8.7 Hz, 2H), 7.26–7.32 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 38.3, 40.8, 113.0, 115.3 (d, *J* = 21.6 Hz), 127.5 (d, *J* = 7.9 Hz), 128.0, 129.1, 129.3, 130.0 (d, *J* = 2.1 Hz), 133.9 (d, *J* = 3.2 Hz), 149.3, 161.9 (d, *J* = 246.6 Hz). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ –115.65. HR-MS: *m/z* 256.14943 [M + H]<sup>+</sup>; calcd for C<sub>17</sub>H<sub>19</sub>NF, 256.14960.

**(*E*)-*N,N*-Dimethyl-4-(3-(naphthalen-1-yl)allyl)aniline (16).** Eluent: petroleum ether/EtOAc (100:1 v/v). Colorless oil, yield 0.126 g (88%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 2.93 (s, 6H), 3.58 (d, *J* = 6.9 Hz, 2H), 6.37 (dt, *J* = 15.4, 6.9 Hz, 1H), 6.74 (d, *J* = 8.7 Hz, 2H), 7.13–7.20 (m, 3H), 7.41 (t, *J* = 7.8 Hz, 1H), 7.44–7.52 (m, 2H), 7.57 (d, *J* = 7.1 Hz, 1H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.81–7.84 (m, 1H), 8.12 (d, *J* = 7.8 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 38.8, 40.9, 113.1, 123.6, 124.0, 125.59, 125.62, 125.8, 127.3, 127.6, 128.2, 128.4, 129.3, 131.2, 133.4, 133.6, 135.5, 149.4. HR-MS: *m/z* 288.17419 [M + H]<sup>+</sup>; calcd for C<sub>21</sub>H<sub>22</sub>N, 288.17468.

**(*E*)-*N,N*-Dimethyl-4-(3-(thiophen-2-yl)allyl)aniline (17).** Eluent: petroleum ether/EtOAc (60:1 v/v). Yellow oil, yield 0.102 g (84%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 2.92 (s, 6H), 3.42 (d, *J* = 6.8 Hz, 2H), 6.19 (dt, *J* = 15.6, 6.8 Hz, 1H), 6.52 (d, *J* = 15.6 Hz, 1H), 6.71 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 3.2 Hz, 1H), 6.90–6.94 (m, 1H), 7.08 (d, *J* = 5.2 Hz, 1H), 7.10 (d, *J* = 8.8 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 38.1, 40.9, 113.0, 123.2, 123.5, 124.5, 127.2, 127.7, 129.3, 130.2, 142.9, 149.3. HR-MS: *m/z* 244.11487 [M + H]<sup>+</sup>; calcd for C<sub>15</sub>H<sub>18</sub>NS, 244.11545.

(*E*)-4-(3-(4-Chlorophenyl)allyl)-*N,N*-dimethylaniline (**18**). Eluent: petroleum ether/EtOAc (100:1 v/v). Colorless oil, yield 0.236 g (1.5 mmol scale, 58%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 2.92 (s, 6H), 3.44 (d, *J* = 5.5 Hz, 2H), 6.26–6.39 (m, 2H), 6.72 (d, *J* = 8.6 Hz, 2H), 7.10 (d, *J* = 8.6 Hz, 2H), 7.22–7.28 (m, 4H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 38.3, 40.9, 113.0, 127.3, 127.8, 128.5, 129.1, 129.3, 131.0, 132.4, 136.2, 149.3. HR-MS: *m/z* 272.12000, 274.11694 [M + H]<sup>+</sup>; calcd for C<sub>17</sub>H<sub>19</sub>N<sup>35</sup>Cl 272.12005, C<sub>17</sub>H<sub>19</sub>N<sup>37</sup>Cl 274.11710.

(*E*)-4'-(3-(4-(Dimethylamino)phenyl)prop-1-en-1-yl)-*N,N*-dimethyl-[1,1'-biphenyl]-4-amine (**19**). Eluent: petroleum ether/EtOAc (50:1 v/v). White solid, yield 0.059 g (1.5 mmol scale, 11%); mp 147 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 2.92 (s, 6H), 2.98 (s, 6H), 3.47 (d, *J* = 6.5 Hz, 2H), 6.35 (dt, *J* = 15.7, 6.6 Hz, 1H), 6.45 (d, *J* = 15.8 Hz, 1H), 6.72 (d, *J* = 8.8 Hz, 2H), 6.79 (d, *J* = 8.9 Hz, 2H), 7.13 (d, *J* = 8.8 Hz, 2H), 7.38 (d, *J* = 8.3 Hz, 2H), 7.47–7.52 (m, 4H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 38.4, 40.6, 40.9, 112.8, 113.1, 126.2, 126.4, 127.4, 128.3, 128.9, 129.3, 129.5, 130.1, 135.5, 139.7, 149.3, 149.9. HR-MS: *m/z* 357.23239 [M + H]<sup>+</sup>; calcd for C<sub>25</sub>H<sub>29</sub>N<sub>2</sub>, 357.23253.

(*E*)-*N,N*-Dimethyl-4-(4-phenylbut-3-en-2-yl)aniline (**20**).<sup>21</sup> Eluent: petroleum ether/EtOAc (100:1 v/v), yield 0.114 g (91%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 1.43 (d, *J* = 7.0 Hz, 3H), 2.92 (s, 6H), 3.51–3.60 (m, 1H), 6.36–6.39 (m, 2H), 6.72 (d, *J* = 8.8 Hz, 2H), 7.15 (d, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 7.3 Hz, 1H), 7.27 (t, *J* = 7.6 Hz, 2H), 7.33–7.36 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 21.2, 40.8, 41.5, 112.9, 126.1, 126.8, 127.83, 127.86, 128.4, 133.6, 136.1, 137.8, 149.3.

(*E*)-*N,N*-Dimethyl-4-(1-phenylpent-1-en-3-yl)aniline (**21**). Eluent: petroleum ether/EtOAc (100:1 v/v). Colorless oil, yield 0.121 g (91%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.91 (t, *J* = 7.4 Hz, 3H), 1.74–1.84 (m, 2H), 2.92 (s, 6H), 3.22 (q, *J* = 7.2 Hz, 1H), 6.31 (dd, *J* = 15.8, 7.0 Hz, 1H), 6.37 (d, *J* = 15.9 Hz, 1H), 6.72 (d, *J* = 8.7 Hz, 2H), 7.12 (d, *J* = 8.7 Hz, 2H), 7.17 (t, *J* = 7.2 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 2H), 7.34 (d, *J* = 7.2 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 12.3, 28.7, 40.8, 49.9, 112.9, 126.1, 126.8, 128.2, 128.4, 128.8, 132.5, 135.0, 137.9, 149.2. HR-MS: *m/z* 266.19022 [M + H]<sup>+</sup>; calcd for C<sub>19</sub>H<sub>24</sub>N, 266.19033.

(*E*)-*N,N*-Dimethyl-4-(1-phenylhept-1-en-3-yl)aniline (**22**). Eluent: petroleum ether/EtOAc (100:1 v/v). Colorless oil, yield 0.126 g (86%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.87 (t, *J* = 7.1 Hz, 3H), 1.25–1.38 (m, 4H), 1.71–1.80 (m, 2H), 2.92 (s, 6H), 3.31 (q, *J* = 7.2 Hz, 1H), 6.30 (dd, *J* = 15.8, 6.8 Hz, 1H), 6.36 (d, *J* = 15.8 Hz, 1H), 6.72 (d, *J* = 8.8 Hz, 2H), 7.12 (d, *J* = 8.7 Hz, 2H), 7.16 (t, *J* = 7.2 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 3H), 7.32–7.35 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 14.0, 22.7, 29.9, 35.6, 40.8, 48.1, 112.9, 126.1, 126.8, 128.2, 128.4, 128.5, 132.8, 135.3, 137.9, 149.2. HR-MS: *m/z* 294.22208 [M + H]<sup>+</sup>; calcd for C<sub>21</sub>H<sub>28</sub>N, 294.22163.

(*E*)-*N,N*-Dimethyl-4-(4-methyl-1-phenylpent-1-en-3-yl)aniline (**23**). Eluent: petroleum ether/EtOAc (100:1 v/v). Colorless oil, yield 0.112 g (80%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.82 (d, *J* = 6.6 Hz, 3H), 0.98 (d, *J* = 6.6 Hz, 3H), 1.95–2.05 (m, 1H), 2.92 (s, 6H), 2.94–3.00 (m, 1H), 6.34–6.38 (m, 2H), 6.71 (d, *J* = 8.6 Hz, 2H), 7.10 (d, *J* = 8.7 Hz, 2H), 7.16 (t, *J* = 7.2 Hz, 1H), 7.26 (t, *J* = 7.5 Hz, 2H), 7.34 (d, *J* = 7.8 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 20.9, 21.1, 33.2, 40.8, 56.5, 112.9, 126.1, 126.7, 128.4, 128.5, 129.6, 132.4, 133.9, 137.9, 149.1. HR-MS: *m/z* 280.20642 [M + H]<sup>+</sup>; calcd for C<sub>20</sub>H<sub>26</sub>N, 280.20598.

(*E*)-4-(4-(Furan-2-yl)but-3-en-2-yl)-*N,N*-dimethylaniline (**24**). Eluent: petroleum ether/EtOAc (60:1 v/v). Yellow oil, yield 0.104 g (86%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 1.40 (d, *J* = 7.0 Hz, 3H), 2.92 (s, 6H), 3.48–3.56 (m, 1H), 6.12–6.19 (m, 2H), 6.30–6.38 (m, 2H), 6.72 (d, *J* = 8.7 Hz, 2H), 7.12 (d, *J* = 8.6 Hz, 2H), 7.28 (d, *J* = 1.2 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 21.1, 40.8, 41.3, 106.3, 111.1, 113.0, 116.8, 127.9, 133.3, 135.1, 141.2, 149.3, 153.4. HR-MS: *m/z* 242.15391 [M + H]<sup>+</sup>; calcd for C<sub>16</sub>H<sub>20</sub>NO, 242.15394.

(*E*)-*N,N*-Dimethyl-4-(3-(4'-methyl-[1,1'-biphenyl]-4-yl)allyl)aniline (**26**). Eluent: petroleum ether/EtOAc (80:1 v/v). White solid, yield 0.121 g (74%); mp 107–108 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 2.38 (s, 3H), 2.92 (s, 6H), 3.47 (d, *J* = 6.4 Hz, 2H), 6.37 (dt, *J* = 15.7, 6.4 Hz, 1H), 6.46 (d, *J* = 15.8 Hz, 1H), 6.72 (d, *J* = 8.7 Hz, 2H), 7.12 (d, *J* = 8.8 Hz, 2H), 7.23 (d, *J* = 7.8 Hz, 2H), 7.40 (d, *J* = 8.3 Hz, 2H),

7.47–7.52 (m, 4H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 21.1, 38.4, 40.9, 113.1, 126.4, 126.7, 126.9, 128.2, 129.3, 129.4, 129.9, 130.2, 136.5, 136.9, 138.0, 139.6, 149.3. HR-MS: *m/z* 328.20599 [M + H]<sup>+</sup>; calcd for C<sub>24</sub>H<sub>26</sub>N, 328.20598.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02151.

Table on catalyst evaluation and optimization of reaction conditions and copies of NMR spectra of allyl methyl ethers and the cross-coupling products (PDF)

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### Notes

The authors declare no competing financial interest.

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