

# A Novel $\text{InCl}_3/\text{SiO}_2$ -Catalyzed Hydroarylation of Arenes with Styrenes under Solvent-Free Conditions

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**Abstract:** A novel  $\text{InCl}_3/\text{SiO}_2$ -catalyzed hydroarylation of various styrenes with arenes has been developed. The reaction can be carried out under solvent-free conditions to afford a series of 1,1-diaryllalkanes in high yields and with good regioselectivities. The catalyst can be reused six times without obvious loss of catalytic activity.

**Key words:** hydroarylation, 1,1-diaryllalkane, heterogeneous catalyst, regioselectivity, solvent-free

Arylation<sup>1</sup> is an important reaction to form new carbon–carbon bond, which can afford many important moieties such as 1,1-diaryllalkanes and 1-aryl-1-heteroalkanes in various valuable biologically active compounds and pharmaceuticals.<sup>2</sup> Recently, hydroarylation reaction has been developed to realize this C–H transformation of arenes and heteroarenes catalyzed by various transition metals.<sup>3</sup> However, these catalysts could not be reused and are not easily removed from the reaction systems after the reaction. As far as we know, heterogeneous catalysts have many advantages in industrial process, such as environmental benign character, easy of recycling, and low cost. Therefore it is important to develop the heterogeneous catalysts which can be used in this hydroarylation.

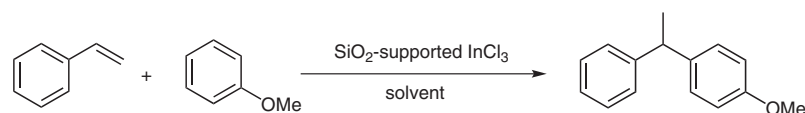
Recently, some publications reported the preparation of heterogeneous catalysts which could be used in hydroarylation.<sup>4</sup> However, these catalysts have been not tested with an exhaustive list of substrates. As far as we know, there is no report about the application of  $\text{InCl}_3$  in the arylation between arene and styrene. Here, we reported a  $\text{Csp}^2$ – $\text{Csp}^2$  bond formation under solvent-free conditions by using indium trichloride immobilized onto the surface of silica gel, allowing the reuse of the catalyst.<sup>5</sup>

We previously reported that  $\text{InCl}_3$  could be successfully applied to the allylation of carbonyl compounds with allylchlorides in water and in carbonyl benzylation.<sup>6</sup> On the basis of our previous experiment we attempted to employ this Lewis acid in hydroarylation. Initial model reactions were carried out with 0.5 mmol of styrene, 0.55 mmol of anisole under 5 mol%  $\text{InCl}_3$  catalyst. After workup, the

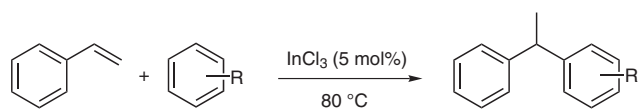
product was obtained in 91% yield with a good regioselectivity (6.6:1). In addition, the reaction could tolerate air and moisture. This result indicated that  $\text{InCl}_3$  was a good catalyst for this arylation reaction. After the reaction, it was difficult to recover the catalyst and reuse it. Therefore we attempted to prepare heterogeneous catalysts by immobilizing  $\text{InCl}_3$  on the surfaces of different supporting materials.

Initially carbon nanotube, diatomite, alumina, PEG2000 (polyethylene glycol), and silica gel were chosen as the supporting materials. After many trials, it was found that silica gel could disperse  $\text{InCl}_3$  well and the  $\text{InCl}_3$  could be immobilized onto the surface of silica gel steadily. This provided us a chance to prepare a heterogeneous catalyst. Subsequently, the reaction was carried out catalyzed by  $\text{InCl}_3$  immobilized onto silica gel. Experimental results showed that 10 mol% of  $\text{InCl}_3/\text{SiO}_2$  could catalyze this reaction smoothly to afford the corresponding product in high yields. This finding intrigued us to investigate the reaction further. The amount of the catalyst, the solvents, and the reaction temperature were screened in order to find the optimal conditions (Table 1). From Table 1, it was found that this reaction could be carried out in acetonitrile and *n*-hexane to generate the corresponding product with in yield of 80% and 78%, respectively, while the reaction did not work in  $\text{CH}_2\text{Cl}_2$  (Table 1, entries 1–3). What is more important was that the reaction could be performed efficiently to produce the product in higher yields under the solvent-free conditions (Table 1, entries 4–7). The reaction yield and rate remained the same as the catalyst loading was decreased from 10 mol% to 5 mol% (Table 1, entries 6 and 7). When the catalyst loading was below 5 mol%, the reaction yield decreased dramatically (Table 1, entry 8). This indicated the best amount of the catalyst was 5 mol% of  $\text{InCl}_3$ . Below 80 °C the reaction was very difficult to initiate while above 80 °C the reaction temperature had little influence on the reaction (Table 1, entries 3, 4, and 9), which showed that the optimal reaction temperature should be 80 °C

After optimization of the reaction conditions, the scope of the reaction substrates was explored. First, the arene component was varied and the results were listed in Table 2. As shown in Table 2, it was found that electron-rich arenes facilitated the reaction. In general, the corresponding 1,1-diaryllalkanes could be isolated in good yields in short

**Table 1** Reaction of Anisole and Styrene under Different Conditions

Entry	Catalyst (mol%)	Solvent	Time (h)	Temp (°C)	Yield (%) <sup>a</sup>
1	10	MeCN	4	80	80
2	10	<i>n</i> -Hexane	4	80	78
3	10	CH <sub>2</sub> Cl <sub>2</sub>	4	40	0
4	10	– <sup>b</sup>	4	100	94
5	10	–	4	80	92
6	10	–	2	80	91
7	5	–	2	80	91
8	5	–	2	80	55
9	5	–	2	r.t.	0

<sup>a</sup> Isolated yield.<sup>b</sup> Solvent-free.**Table 2** Reaction of Different Arenes and Styrene

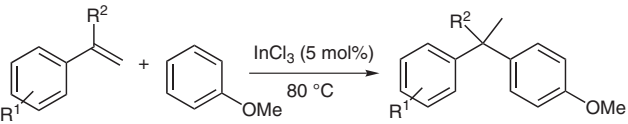
Entry	R	Main product	Time (h)	Regio-selectivity <sup>a</sup>	Yield (%) <sup>b</sup>
1	Me	<b>1a</b>	2	7:1	79
2	1,4-Me <sub>2</sub>	<b>1b</b>	3	–	52
3	1,2-Me <sub>2</sub>	<b>1c</b>	3	8:1	84
4	1,3-Me <sub>2</sub>	<b>1d</b>	2	–	92
5		<b>1e</b>	3	6:1	81
6	OMe	<b>1f</b>	2	6.6:1	81
7	1,2-(OMe) <sub>2</sub>	<b>1g</b>	2	3:1	62
8	1,3-(OMe) <sub>2</sub>	<b>1h</b>	2	–	85
9	OH	<b>1i</b>	2	13.7:1 <sup>c</sup>	88
10	1-OH-4-Me	<b>1j</b>	2	11:1 <sup>d</sup>	95
11	1-Mercapto-4-Me	<b>1k</b>	3	–	71
12		<b>1l</b>	2	5:1 <sup>e</sup>	70

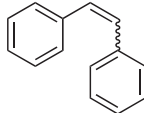
<sup>a</sup> Ratio of *para*-to-*ortho* product.<sup>b</sup> Isolated yield.<sup>c</sup> Ratio of 2-(1-phenylethyl)phenol and 4-(1-phenylethyl)phenol.<sup>d</sup> Ratio of 4-methyl-2-(1-phenylethyl)phenol and 4-methyl-3-(1-phenylethyl)phenol.<sup>e</sup> Ratio of 2-(1-phenylethyl)thiophene and 3-(1-phenylethyl)thiophene.

reaction times (2–3 h). In most cases, the *para*-substituted product was obtained as a major product (Table 2, entries 1, 3–7). When the substituent was a hydroxy group on the aromatic ring, *ortho*-OH product was obtained as a dominant product (Table 2, entries 9 and 10). It is worth noting that a diarylation of 1,3-dimethoxybenzene occurred (Table 2, entry 8), perhaps due to the stronger electron-donating effect of two methoxy groups at *ortho* and *para* positions of the aromatic ring. In addition, for *p*-thiocresol, hydroarylation reaction led to the formation of a thioether, phenethyl(*p*-tolyl)sulfane,<sup>7</sup> possibly due to the strong nucleophilicity of the mercapto group. When thiophene was employed as the reaction substrate, 2-(1-phenylethyl)thiophene was afforded as a main product in 70% yield (Table 2, entry 12).

Following this successful arylation of styrene with various electron-rich arenes, we became interested in the exploration of the scope of styrenes in this hydroarylation (Table 3). As shown in Table 3, anisole could undergo the hydroarylation reaction smoothly with both electron-rich (Table 3, entries 1–4, and 10) and electron-deficient styrenes (Table 3, entries 5–9).

It was observed that electronic effect had little influence on this reaction. It seemed that the substituents at  $\alpha$ -position of carbon–carbon double bond of styrene had an influence on the reaction rate and the regioselectivity. When the steric hindrance of the substituents at  $\alpha$ -position was increased, the regioselectivity was improved (6.6:1 to 99:1) while the reaction time was extended from 2 hours to 18 hours (Table 3, entries 1, 3, and 4). When 1,3-dichloro-2-vinylbenzene was employed as the reaction substrate, the reaction temperature had to raise up to 100 °C to perform this arylation, possibly due to the high steric hindrance of two chloro groups situated next to the car-

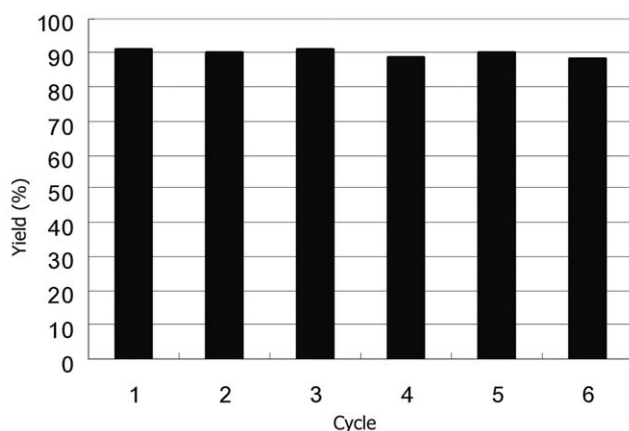
**Table 3** Reactions of Anisole and Various Styrenes<sup>9,10</sup>


Entry	R <sup>1</sup>	R <sup>2</sup>	Main product	Time (h)	Regio-selectivity <sup>a</sup> (%) <sup>b</sup>	Yield (%) <sup>b</sup>
1	H	H	<b>2a</b>	2	6.6:1	91
2	4-Me	H	<b>2b</b>	2	10:1	95
3	H	Me	<b>2c</b>	5	99:1	50
4	H	Ph	<b>2d</b>	18	99:1	72
5	2-Cl	H	<b>2e</b>	4	99:1	93
6	4-Cl	H	<b>2f</b>	4	99:1	90
7	4-F	H	<b>2g</b>	4	7.5:1	86
8 <sup>c</sup>	2,6-Cl <sub>2</sub>	H	<b>2h</b>	10	99:1	50
9	4-CN	H	<b>2i</b>	3	99:1	88
10 <sup>c</sup>		H	<b>2j</b>	15	99:1	85

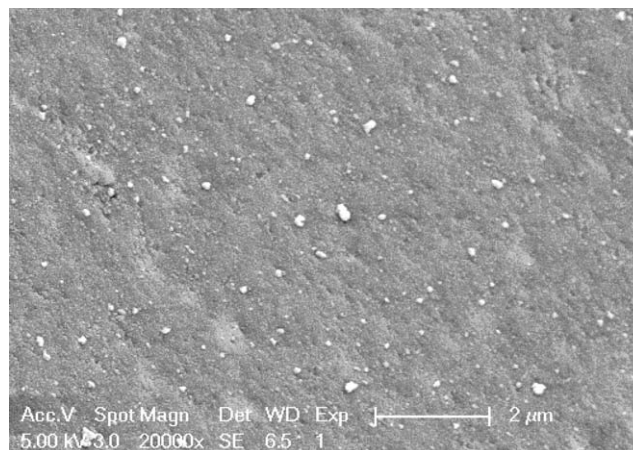
<sup>a</sup> Ratio of *para*-to-*ortho* product.<sup>b</sup> Isolated yield.<sup>c</sup> Heated to 100 °C.

bon-carbon double bond (Table 3, entry 8). When a phenyl group connected the terminal of the double bond in styrene, the reaction rate was decreased dramatically because of the steric hindrance of the phenyl group (Table 3, entry 10).

The recycling of the silica gel supported InCl<sub>3</sub> was also examined. The experimental results about the recycle are presented in Figure 1. For each round in the recycle the reaction product was separated from the reaction mixture,<sup>8</sup> and the new starting materials were added directly into the reaction flask that contained the heterogeneous catalyst.

**Figure 1** Recycling experiments for the hydroarylation reaction

The silica gel immobilized InCl<sub>3</sub> exhibited only a marginal loss of activity after each round. After the fourth round, it took a longer time to achieve a similar yield. Even after the sixth cycle, the catalytic activity of the immobilized InCl<sub>3</sub> was still good enough for this reaction. Because of the simple manipulation and easy recovery, we believed that this catalyst had a potential use in industrial process. In addition, as shown in Figure 2, we also took SEM to determine the image of this catalyst, and it was found that InCl<sub>3</sub> particles were formed with a size of 100–200 nm.

**Figure 2** SEM Image of SiO<sub>2</sub>-supported InCl<sub>3</sub>

In summary, a new heterogeneous catalyst, a silica gel immobilized InCl<sub>3</sub>, has been developed and employed in hydroarylation. By using this developed catalyst, a series of 1,1-diaryllalkanes were obtained in high yields under mild conditions. Compared to the previous hydroarylation reactions, the recovery of the heterogeneous catalyst, solvent-free conditions, simple workup, and broad practicability endowed this transformation to be a practical method for the preparation of 1,1-diaryllalkane derivatives.

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- (5) The catalyst ( $\text{InCl}_3/\text{SiO}_2$ ) was prepared by adding  $\text{SiO}_2$  (500 mg, 200–300 mesh) to a stirred solution of  $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$  (1 mmol) in  $\text{CHCl}_3$  (10 mL) followed by evaporation of the solvent in vacuo.
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- (8) The catalyst can be recovered by washing the mixture with petroleum ether, followed by the removal of the solvent.
- (9) **Typical Procedure for the FC-Arylation of Styrenes**  
In a typical experiment,  $\text{InCl}_3/\text{SiO}_2$  (0.025 mmol, 5 mol%), styrene (0.5 mmol, 1 equiv), and anisole (0.55 mmol, 1.1 equiv) were mixed. The solution was heated at 80 °C for 2 h, cooled down, and gently evaporated under vacuo. The resulting crude mixture was purified by column chromatography on  $\text{SiO}_2$  (gradient hexane to hexane–EtOAc = 100:1) to afford 97 mg (91%) of a colorless oily product.
- (10) **Spectroscopic Data for Products**  
1-Methyl-4-(1-phenylethyl)benzene (**1a**):  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.36–7.10 (m, 9 H), 4.11 (q,  $J$  = 7.2 Hz, 1 H), 2.30 (s, 4 H), 1.60 (d,  $J$  = 7.5 Hz, 3 H).  
1,4-Dimethyl-2-(1-phenylethyl)benzene (**1b**):  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.23–6.95 (m, 9 H), 4.29 (q,  $J$  = 6.9 Hz, 1 H), 2.32 (s, 3 H), 2.18 (s, 2 H), 1.60 (d,  $J$  = 7.2 Hz, 3 H).  
1,2-Dimethyl-4-(1-phenylethyl)benzene (**1c**):  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.20–6.93 (m, 8 H), 4.07 (q,  $J$  = 7.2 Hz, 1 H), 2.20 (s, 6 H), 1.60 (d,  $J$  = 7.2 Hz, 3 H).  
2,4-Dimethyl-1-(1-phenylethyl)benzene (**1d**):  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.27–6.95 (m, 8 H), 4.28 (q,  $J$  = 7.2 Hz, 1 H), 2.29 (s, 3 H), 2.19 (s, 3 H), 1.59 (d,  $J$  = 7.5 Hz, 3 H).  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 146.6, 141.1, 136.0, 135.6, 131.4, 128.4, 127.8, 126.8, 125.9, 40.8, 22.3, 21.0, 19.8. IR (film):  $\nu$  = 3024, 2966, 2926, 2872, 1601, 1493, 1451, 1374, 1307, 1192, 1028, 822, 762, 747, 700  $\text{cm}^{-1}$ . HRMS:  $m/z$  calcd for  $\text{C}_{16}\text{H}_{18}$ : 210.3142; found: 210.3133.  
1,2,3,4-Tetrahydro-6-(1-phenylethyl)naphthalene (**1e**):  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.24–6.92 (m, 8 H), 4.08 (q,  $J$  = 7.2 Hz, 1 H), 2.72 (s, 4 H), 1.76 (s, 4 H), 1.61 (d,  $J$  = 7.5 Hz, 3 H).  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 146.8, 143.6, 137.1, 134.9, 129.2, 128.4, 128.3, 127.7, 126.0, 124.9, 44.6, 29.6, 29.1, 23.4, 22.1. IR (film): 3025, 2928, 2857, 1735, 1601, 1496, 1451, 1373, 1284, 1028, 910, 829, 766, 699  $\text{cm}^{-1}$ . HRMS:  $m/z$  calcd for  $\text{C}_{22}\text{H}_{28}$ : 292.2191; found: 292.2181.  
1-Methoxy-4-(1-phenylethyl)benzene (**1f**):  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.30–7.12 (m, 7 H), 6.82 (d,  $J$  = 8.6 Hz, 2 H), 4.10 (q,  $J$  = 6.9 Hz, 1 H), 3.77 (s, 3 H), 1.76 (d,  $J$  = 7.2 Hz, 3 H).  
1,2-Dimethoxy-4-(1-phenylethyl)benzene (**1g**):  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.28–7.15 (m, 5 H), 6.79 (s, 2 H), 6.72 (s, 1 H), 4.09 (q,  $J$  = 7.5 Hz, 1 H), 3.85 (s, 3 H), 3.82 (s, 3 H), 1.62 (d,  $J$  = 7.2 Hz, 3 H).  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 148.9, 146.7, 139.1, 128.4, 128.3, 127.65, 127.55, 127.5, 126.1, 119.4, 111.3, 111.2, 55.94, 55.87, 44.4, 22.1. IR (film): 3440, 3059, 3025, 2964, 2932, 2872, 2833, 1727, 1602, 1591, 1516, 1451, 1416, 1252, 1236, 1143, 1029, 908, 855, 810, 764, 701  $\text{cm}^{-1}$ . HRMS:  $m/z$  calcd for  $\text{C}_{16}\text{H}_{18}\text{O}_2$ : 242.1307; found: 242.1295.  
1,5-Dimethoxy-2,4-bis(1-phenylethyl)benzene (**1h**):  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.24–7.11 (m, 10 H), 7.00 (s, 1 H), 6.39 (s, 1 H), 4.45 (q,  $J$  = 7.2 Hz, 1 H), 3.73 (s, 1 H), 1.53 (d,  $J$  = 7.2 Hz, 3 H), 1.51 (d,  $J$  = 7.2 Hz, 3 H).  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 156.0, 147.1, 132.2, 128.2, 128.1, 127.68, 127.66, 127.0, 126.8, 126.5, 125.6, 96.0, 55.9, 37.4, 21.3. IR (KBr): 3447, 3024, 2961, 2920, 1610, 1583, 1505, 1491, 1464, 1448, 1293, 1205, 1120, 1033, 839, 821, 757, 744, 697  $\text{cm}^{-1}$ . HRMS:  $m/z$  calcd for  $\text{C}_{24}\text{H}_{26}\text{O}_2$ : 346.1933; found: 346.1922.  
2-(1-Phenylethyl)phenol (**1i**):  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.32–6.73 (s, 8 H), 4.69 (s, 1 H), 4.37 (q,  $J$  = 7.2 Hz, 1 H), 1.63 (d,  $J$  = 7.2 Hz, 3 H).  
4-Methyl-2-(1-phenylethyl)phenol (**1j**):  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.26–7.19 (m, 5 H), 7.03 (s, 3 H), 6.91 (d,  $J$  = 7.8 Hz, 1 H), 6.65 (d,  $J$  = 8.1 Hz, 1 H), 4.33 (q,  $J$  = 7.2 Hz, 1 H), 2.29 (s, 3 H), 1.62 (d,  $J$  = 7.2 Hz, 3 H).  
Phenethyl(*p*-tolyl)sulfane (**1k**):  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.29–7.10 (m, 9 H), 3.13 (t,  $J$  = 7.5 Hz, 2 H), 2.90 (t,  $J$  = 7.8 Hz, 2 H), 2.33 (s, 3 H).  
2-(1-Phenylethyl)thiophene (**1l**):  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.25–7.13 (m, 7 H), 6.57 (d,  $J$  = 4.8 Hz, 1 H), 4.22 (q,  $J$  = 7.2 Hz, 1 H), 1.63 (d,  $J$  = 7.2 Hz, 3 H).  
1-Methoxy-4-(1-*p*-tolylethyl)benzene (**2b**):  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.31–6.97 (m, 6 H), 6.94–6.76 (m, 2 H), 4.06 (q,  $J$  = 7.2 Hz, 1 H), 3.76 (s, 3 H), 2.26 (s, 3 H), 1.59 (d,  $J$  = 7.2 Hz, 3 H).  
1-Methoxy-4-(2-phenylpropan-2-yl)benzene (**2c**):  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.26–7.24 (m, 4 H), 7.16–7.13 (m, 3 H), 6.82–6.79 (m, 2 H), 3.78 (s, 3 H), 1.66 (s, 6 H).  
1-[1-(4-Methoxyphenyl)-1-phenylethyl]benzene (**2d**):  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.28–7.19 (m, 6 H), 7.11–7.10 (m, 3 H), 7.02–6.99 (m, 2 H), 6.79–6.78 (m, 2 H), 3.79 (s, 3 H), 2.16 (s, 6 H).  
1-[1-(2-Chlorophenyl)ethyl]-4-methoxybenzene (**2e**):  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.33 (d,  $J$  = 8.4 Hz, 1 H), 7.20–7.11 (m, 5 H), 6.82 (d,  $J$  = 8.4 Hz, 2 H), 4.60 (q,  $J$  = 7.2

Hz, 1 H), 3.77 (s, 3 H), 1.59 (d,  $J = 6.6$  Hz, 3 H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta = 158.1, 144.2, 137.2, 133.9, 128.8, 128.6, 127.3, 127.0, 113.9, 55.3, 40.2, 21.4$ . IR (KBr): 3435, 3056, 3008, 2959, 2925, 2852, 1628, 1599, 1468, 1431, 1339, 1289, 1243, 1122, 1066, 1049, 1030, 931, 853, 787, 755, 729, 681  $\text{cm}^{-1}$ . HRMS:  $m/z$  calcd for  $\text{C}_{15}\text{H}_{15}\text{ClO}$ : 246.0811; found: 246.0800.

1-[1-(4-Chlorophenyl)ethyl]-4-methoxybenzene (**2f**):  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.23$  (d,  $J = 8.1$  Hz, 2 H), 7.14–7.08 (m, 4 H), 6.82 (d,  $J = 8.7$  Hz, 2 H), 4.07 (q,  $J = 7.2$  Hz, 1 H), 3.77 (s, 3 H), 1.58 (d,  $J = 7.2$  Hz, 3 H).

1-[1-(4-Fluorophenyl)ethyl]-4-methoxybenzene (**2g**):  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.18$ –7.10 (m, 4 H), 6.99–6.91 (m, 2 H), 6.83–6.82 (m, 2 H), 4.10 (q,  $J = 7.2$  Hz, 1 H), 3.79 (s, 3 H), 1.60 (d,  $J = 7.2$  Hz, 3 H).

1-[1-(2,6-Dichlorophenyl)ethyl]-4-methoxybenzene (**2h**):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.48$  (d,  $J = 7.5$  Hz, 1 H), 7.20 (d,  $J = 7.6$  Hz, 3 H), 7.02–6.97 (m, 2 H), 6.77 (d,  $J = 8.1$  Hz, 1 H), 5.11 (q,  $J = 7.3$  Hz, 1 H), 1.70 (d,  $J = 7.4$  Hz, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 157.6, 141.2, 135.5, 131.2, 129.3, 129.0, 127.4, 127.1, 119.8, 110.5, 55.3, 36.3, 15.7$ . IR (KBr): 3433, 3070, 2996, 2962, 2920, 2854, 1590, 1557,

1488, 1459, 1430, 1244, 1124, 1124, 1030, 779, 755, 726  $\text{cm}^{-1}$ . HRMS:  $m/z$  calcd for  $\text{C}_{15}\text{H}_{14}\text{Cl}_2\text{O}$ : 280.0422; found: 280.00410.

4-[1-(4-Methoxyphenyl)ethyl]benzotrile (**2i**):  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.57$ –7.54 (m, 2 H), 7.31–7.26 (m, 2 H), 7.09 (d,  $J = 5.7$  Hz, 2 H), 6.84 (dd,  $J_1 = 2.1$  Hz,  $J_2 = 4.5$  Hz, 2 H), 4.14 (q,  $J = 7.2$  Hz, 1 H), 3.78 (s, 3 H), 1.61 (d,  $J = 7.2$  Hz, 3 H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta = 158.3, 152.5, 136.9, 132.3, 128.6, 128.4, 119.2, 114.1, 109.9, 55.4, 44.2, 21.7$ . IR (film): 3401, 3034, 2966, 2959, 2929, 2840, 2227, 1608, 1509, 1459, 1299, 1247, 1178, 1117, 835, 752  $\text{cm}^{-1}$ . HRMS:  $m/z$  calcd for  $\text{C}_{16}\text{H}_{15}\text{NO}$ : 237.1154; found: 237.1138.

1-Methoxy-3-(1,2-diphenylethyl)benzene (**2j**):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.24$ –7.09 (m, 10 H), 7.00–6.98 (m, 2 H), 6.77 (d,  $J = 8.8$  Hz, 2 H), 4.18 (t,  $J = 7.8$  Hz, 1 H), 3.74 (s, 3 H), 3.3 (d,  $J = 7.8$  Hz, 2 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 158.0, 145.0, 140.5, 136.7, 129.2, 128.4, 128.1, 128.0, 126.2, 125.9, 55.3, 52.3, 42.4$ . IR (KBr): 3444, 3025, 2933, 1610, 1583, 1509, 1453, 1246, 1179, 1035, 833, 740, 697  $\text{cm}^{-1}$ . HRMS:  $m/z$  calcd for  $\text{C}_{21}\text{H}_{20}\text{O}$ : 288.1514; found: 288.1511.

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