

# Atom-Efficient Vinylic Arylations with Triarylbismuths as Substoichiometric Multicoupling Reagents under Palladium Catalysis

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The first atom-efficient arylation of vinylic iodides was achieved by using triarylbismuths as substoichiometric multicoupling reagents under palladium catalysis. Vinylic iodides were efficiently coupled with electronically divergent

triarylbismuths to furnish the corresponding arylated products in short reaction times.

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## Introduction

The coupling reaction of organic electrophiles with organometallic reagents is highly demanding methodology for natural product synthesis and other applications in organic synthesis.<sup>[1]</sup> Given their importance in industry,<sup>[2]</sup> the search for new nucleophilic<sup>[3]</sup> and electrophilic<sup>[4]</sup> coupling partners is inevitable to enrich this chemistry for further applications in organic synthesis. With a view to develop a new class of nucleophilic organometallic reagents that can serve in substoichiometric amounts with respect to electrophilic partners, we have unraveled novel and atom-efficient reactivity of triarylbismuths<sup>[5]</sup> for C–C bond formation reactions under palladium catalysis.<sup>[6,7]</sup>

Heck arylation is a novel strategy for the synthesis of substituted alkenes.<sup>[8]</sup> However, arylation of vinylic substrates through cross-coupling provides a facile approach for the synthesis of highly substituted alkenes.<sup>[9]</sup> Further, chemoselective arylation is often a difficult task in the presence of functionalities that are more labile under metal conditions. So, development of a task-specific, new catalytic protocol is usually driven by the relative reactivity of the nucleophilic and electrophilic coupling partners. In cross-coupling reactions, this amenability thus depends on the nucleophilic coupling partner and its reactivity under metal-catalyzed conditions.

In general, vinylic substrates react efficiently under metal-catalyzed conditions.<sup>[9,10]</sup> However, the reactivity profiles of these substrates vary depending on the nature of the leaving groups, such as triflates, bromides, iodides, and phosphonates. This variance in reactivity usually depends on the relative ability of these substrates to oxidatively add

to a metal center and their own stability in the presence of a metal catalyst.<sup>[11]</sup> As a result, vinylic iodides are relatively less studied, as they are more labile in comparison with other vinylic substrates.

Recently, vinylic phosphonates were used as more-stable coupling partners for Suzuki cross-couplings.<sup>[9e]</sup> As is well known, vinylic systems are an important class of compounds in synthetic organic chemistry. Further, development of new coupling reactions with vinylic substrates is highly desirable due to their key role in the synthesis of several natural products.<sup>[1]</sup> In continuation of our interest to develop more efficient cross-coupling reactions under relatively mild catalytic conditions, we extended our efforts towards coupling reactions of vinylic iodides with triarylbismuths. During these efforts we have indeed found that the cross-coupling of triarylbismuths with vinylic iodides is efficient under palladium catalysis. We report here for the first time the palladium-catalyzed arylation of vinylic iodides with functionalized triarylbismuths.

## Results and Discussion

In our initial optimization efforts, we investigated the coupling of 4-iodo-1,2-dihydronaphthalene with triphenylbismuth under palladium-catalyzed conditions (Table 1). The coupling reaction studied under different conditions revealed that cesium carbonate in *N,N*-dimethylacetamide (DMA) was the right combination to afford good cross-coupling conversion to give 4-phenyl-1,2-dihydronaphthalene in short reaction time (Table 1, Entry 9). Other carbonates of sodium, potassium, and barium did not produce respectable conversion in DMA solvent (Table 1, Entries 1–3). Whereas cesium carbonate as base in *N*-methyl-2-pyrrolidone (NMP) and *N,N*-dimethylformamide (DMF) solvents furnished reasonable conversion, the reactivity was poor in THF and 1,4-dioxane solvents (Table 1, Entries 4–7). The coupling reaction carried out at

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80 °C did not improve the conversion (Table 1, Entry 8). Further, loading of different amounts of base proved that 1.2 equiv. is required to obtain better product conversion (Table 1, Entries 9–13). In the absence of cross-coupling with the vinyl iodide, we have invariably observed the formation of biphenyl as a homocoupling side product from triphenylbismuth in our coupling reactions. It is known that triarylbismuths usually form homocoupling biaryls under catalytic palladium conditions.<sup>[12a,12b]</sup> However, the amount of biphenyl varied with respect to cross-coupling conversion. Under the optimized protocol (Table 1, Entry 9), biphenyl was formed in 12% isolated yield along with 72% isolated yield of the cross-coupling product.

Table 1. Screening conditions.<sup>[a]</sup>

Entry	Base (equiv.)	Solvent	Conversion [%] <sup>[c]</sup>
1	K <sub>2</sub> CO <sub>3</sub> (1.21)	DMA	29
2	Na <sub>2</sub> CO <sub>3</sub> (1.21)	DMA	48
3	Ba <sub>2</sub> CO <sub>3</sub> (1.21)	DMA	13
4	Cs <sub>2</sub> CO <sub>3</sub> (1.21)	DMF	88 (63) <sup>[c]</sup>
5	Cs <sub>2</sub> CO <sub>3</sub> (1.21)	NMP	70
6	Cs <sub>2</sub> CO <sub>3</sub> (1.21)	Dioxane	8
7	Cs <sub>2</sub> CO <sub>3</sub> (1.21)	THF	2
8	Cs <sub>2</sub> CO <sub>3</sub> (1.21)	DMA	68 <sup>[d]</sup>
9	Cs <sub>2</sub> CO <sub>3</sub> (1.21)	DMA	90 (72)
10	Cs <sub>2</sub> CO <sub>3</sub> (0.91)	DMA	70
11	Cs <sub>2</sub> CO <sub>3</sub> (0.61)	DMA	71
12	Cs <sub>2</sub> CO <sub>3</sub> (0.30)	DMA	57
13	None	DMA	7

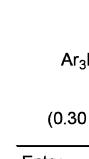
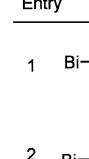
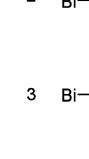
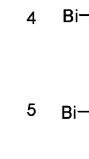
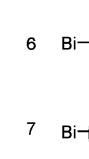
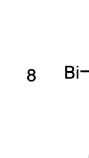
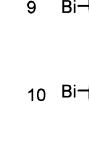
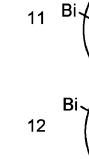
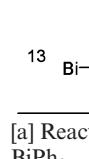
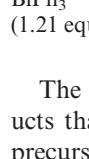
[a] Reaction conditions: Vinyl iodide (1 equiv.), BiPh<sub>3</sub> (0.303 equiv.), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.0273 equiv.), base (1.21 equiv.), solvent (3 mL), 60 °C. [b] Conversions are based on GC analysis. [c] Isolated yields are given in parenthesis.<sup>[13]</sup> [d] At 80 °C.

Thus, we have successfully driven the reaction towards cross-coupling and obtained the arylation of vinyl iodides with cesium carbonate in DMA at 60 °C for 1 h as optimized conditions with the PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> catalytic system (Table 1, Entry 9). After obtaining the effective arylation of vinylic iodides with triphenylbismuth, it was of interest to further study the cross-coupling ability of diverse triarylbismuths with 4-iodo-1,2-dihydronaphthalene under the above established protocol.

The arylations carried out with various functionalized triarylbismuths were very successful and we obtained high yields of the corresponding 4-aryl-1,2-dihydronaphthalenes through facile arylation reaction of 4-iodo-1,2-dihydronaphthalene (Table 2). Thus, a diverse range of functionalized triarylbismuths reacted smoothly under the present palladium protocol. In elaboration, triarylbismuths with functional groups such as halide and formyl groups reacted chemoselectively. Other triarylbismuths substituted with methyl, methoxy, ethoxy, or acetyl groups also reacted efficiently. This study clearly established the striking reactivity of electronically divergent triarylbismuths for arylations of

4-iodo-1,2-dihydronaphthalene under the established protocol. The heteroarylation carried out with trithiophen-2-ylbismuth also furnished 2-(3,4-dihydronaphthalen-1-yl)thiophene (**2m**) as the product in high yield (Table 2, Entry 13).

Table 2. Vinylic arylation with different triarylbismuths.<sup>[a,b]</sup>

Entry	Ar <sub>3</sub> Bi	Vinyl iodide	Product	Yield [%] <sup>[a,b]</sup>
1	Bi(Ph) <sub>3</sub>			<b>2a</b> 72
2	Bi(Ph-Me) <sub>3</sub>	"		<b>2b</b> 77
3	Bi(Ph-OMe) <sub>3</sub>	"		<b>2c</b> 64
4	Bi(Ph-OEt) <sub>3</sub>	"		<b>2d</b> 87
5	Bi(Ph-F) <sub>3</sub>	"		<b>2e</b> 87
6	Bi(Ph-Cl) <sub>3</sub>	"		<b>2f</b> 70
7	Bi(Ph-OMe) <sub>3</sub>	"		<b>2g</b> 85
8	Bi(Ph-Me) <sub>3</sub>	"		<b>2h</b> 83
9	Bi(Ph-COMe) <sub>3</sub>	"		<b>2i</b> 80
10	Bi(Ph-CHO) <sub>3</sub>	"		<b>2j</b> 77
11	Bi(Ph-Naph) <sub>3</sub>	"		<b>2k</b> 85
12	Bi(Ph-OMe-Naph) <sub>3</sub>	"		<b>2l</b> 78
13	Bi(SPh) <sub>3</sub>	"		<b>2m</b> 84

[a] Reaction conditions: 4-Iodo-1,2-dihydronaphthalene (1 equiv.), BiPh<sub>3</sub> (0.303 equiv.), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.0273 equiv.), Cs<sub>2</sub>CO<sub>3</sub> (1.21 equiv.), DMA (3 mL), 60 °C, 1 h. [b] Isolated yields.<sup>[13]</sup>

The functionalized 4-aryl-1,2-dihydronaphthalene products that are obtained in this coupling reaction are useful precursors for the synthesis of substituted naphthalenes and

also other derivatives.<sup>[14]</sup> Earlier, these compounds were synthesized either through Suzuki-type cross-coupling reactions involving the corresponding vinylic triflate or the Grignard addition reaction to  $\alpha$ -tetralone followed by acid-mediated elimination.<sup>[14a,14b]</sup> The present method of obtaining 4-aryl-1,2-dihydronaphthalenes through the coupling reaction of triarylbismuths with 4-iodo-1,2-dihydronaphthalene has a definitive advantage in terms of atom-efficient coupling ability of triarylbismuths and also short reaction times. It is to note that in these reactions triarylbismuths were employed in substoichiometric amounts with respect to the vinylic iodide.

The efficient reactivity that was observed with 4-iodo-1,2-dihydronaphthalene led us to further explore the coupling reactivity of triarylbismuths with 1-iodo-cyclohexenes and 1-iodo-cyclooctene under the present protocol. As summarized in Table 3, these reactions provided moderate to good yields of the corresponding arylated products.<sup>[9g]</sup>

Table 3. Arylations of cycloalkenyl iodides.<sup>[a–c]</sup>

Entry	Ar <sub>3</sub> Bi	Vinyl Iodide	Substituted alkene	Yield [%] <sup>[a]</sup>
1	Bi( <i>Ph</i> ) <sub>3</sub>	Ph-I	Ph-Ph	3a 57
2	Bi( <i>Ph</i> ) <sub>3</sub>	Ph-CH <sub>2</sub> -I	Ph-CH <sub>2</sub> -Ph	3b 60
3	Bi( <i>Ph</i> -Me) <sub>3</sub>	"	Ph-CH <sub>2</sub> -Ph-Me	3c 61
4	Bi( <i>Ph</i> -OMe) <sub>3</sub>	"	Ph-CH <sub>2</sub> -Ph-OMe	3d 65
5	Bi( <i>Ph</i> ) <sub>3</sub>	Cyclohex-1-yl-I	Cyclohex-1-yl-Ph	3e 73

[a] Reaction conditions: Vinylic iodide (1 equiv.), BiPh<sub>3</sub> (0.303 equiv.), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.0273 equiv.), Cs<sub>2</sub>CO<sub>3</sub> (1.21 equiv.), DMA (3 mL), 60 °C, 1 h. [b] Isolated yields.<sup>[13]</sup> [c] Minor amounts of alkenyl iodides remained unreacted after 1 h, as 0.1 equiv. in excess was employed for the reactions.

Next, we have focused on arylation studies of  $\alpha$ -iodostyrenes with triarylbismuths for the synthesis of 1,1-diarylethylene derivatives. The coupling reactions of various functionalized  $\alpha$ -iodostyrenes were studied with triarylbismuths as illustrated in Table 4. In general, these coupling reactions afforded the corresponding 1,1-diaryl products in high yields. Further, the reaction of  $\alpha$ -iodostyrene containing a *p*-bromo substituent reacted chemoselectively at the vinylic terminus (Table 4, Entries 7–9). Coupling reactions carried out with the corresponding naphthyl derivatives, that is, 2-(1-iodovinyl)naphthalene, also showed good reactivity, furnishing the corresponding arylated products in high yields (Table 4, Entries 10–12).

Table 4. Coupling of  $\alpha$ -iodostyrenes.<sup>[a,b]</sup>

Entry	Ar <sub>3</sub> Bi	Vinyl Iodide	Disubstituted alkene	Yield [%] <sup>[a]</sup>
1	Bi( <i>Ph</i> ) <sub>3</sub>	Ph-I	MeO-Ph-Ph	4a 71
2	Bi( <i>Ph</i> -OMe) <sub>3</sub>	"	MeO-Ph-Ph	4b 73
3	Bi( <i>Ph</i> -OEt) <sub>3</sub>	"	EtO-Ph-Ph	4c 70
4	Bi( <i>Ph</i> -OMe) <sub>3</sub>	Me-Ph-I	MeO-Ph-Ph-Me	4d 75
5	Bi( <i>Ph</i> -OMe) <sub>3</sub>	"	MeO-Ph-Ph-Me	4e 65
6	Bi( <i>Ph</i> -OEt) <sub>3</sub>	"	EtO-Ph-Ph-Me	4f 73
7	Bi( <i>Ph</i> -OMe) <sub>3</sub>	Br-Ph-I	MeO-Ph-Ph-Br	4g 78
8	Bi( <i>Ph</i> -OMe) <sub>3</sub>	"	MeO-Ph-Ph-Br	4h 82
9	Bi( <i>Ph</i> -OEt) <sub>3</sub>	"	EtO-Ph-Ph-Br	4i 80
10	Bi( <i>Ph</i> ) <sub>3</sub>	Naph-1-yl-I	Naph-1-yl-Naph	4j 76
11	Bi( <i>Ph</i> -Me) <sub>3</sub>	"	Me-Ph-Ph-Naph	4k 75
12	Bi( <i>Ph</i> -OMe) <sub>3</sub>	"	MeO-Ph-Ph-Naph	4l 71

[a] Reaction conditions: Vinylic iodide (1 equiv.), BiPh<sub>3</sub> (0.303 equiv.), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.0273 equiv.), Cs<sub>2</sub>CO<sub>3</sub> (1.21 equiv.), DMA (3 mL), 60 °C, 1 h. [b] Isolated yields.<sup>[13]</sup>

Thus, the arylation of  $\alpha$ -iodostyrenes with triarylbismuths was obtained under relatively mild and faster reaction conditions in comparison with the known reactivity of  $\alpha$ -bromostyrenes with arylboronic acids. The cross-coupling of  $\alpha$ -bromostyrenes with arylboronic acids was carried out at 130 °C for longer reaction times under palladium catalysis.<sup>[10a]</sup>

The 1,1-diarylene obtained in the above coupling are useful precursors for the synthesis of biologically active compounds<sup>[15]</sup> and for other useful synthetic transformations. The Wittig olefination of ketones or Grignard addition to carbonyl compounds and subsequent elimination procedures were reported for the synthesis of these com-

pounds, in addition to cross-coupling methods. The present method of obtaining these compounds through arylation of  $\alpha$ -iodostyrenes with triarylbismuths provides easy access to the functionalized unsymmetrical 1,1-diarylalkenes in an atom-efficient manner.

Similar to earlier couplings,<sup>[1e,12a,12c]</sup> the reaction mechanism may involve the initial oxidative addition of alkenyl iodide to the Pd<sup>0</sup> center<sup>[11]</sup> followed by a transmetalation step involving triarylbismuths, which subsequently furnishes the cross-coupling product through reductive elimination.<sup>[12a]</sup> The proposed mechanism also takes into consideration the higher reactivity of alkenyl iodides towards the Pd<sup>0</sup> center.<sup>[11]</sup> Additionally, the rationale is also based on the known cross-coupling reactivity of organobismuth compounds<sup>[12c]</sup> and the general cross-coupling reaction mechanism involving other organometallic reagents.<sup>[1e]</sup> After initial involvement of triarylbismuth in transmetalation, the subsequent transmetalations would involve reactions with di- or monoarylbismuth reagents. This way, all the three aryl groups would efficiently participate as multicoupling reagents. Also, the formation of biaryl as a side product indicates initial oxidative addition of triarylbismuth to Pd<sup>0</sup>. So, the coupling mechanism also goes through further transmetalation with vinylic iodide and subsequent reductive elimination to the product. However, given the reactivity of vinylic iodides with the Pd<sup>0</sup> center, it is most likely initiated through its oxidative addition as given in the first option. In any case, more specific studies are needed to understand the mechanism clearly.

## Conclusions

We have demonstrated efficient vinylic arylations using triarylbismuths under palladium catalytic conditions. The novel coupling reactivity of vinylic iodides with triarylbismuths provided easy access to 4-aryl-1,2-dihydronaphthalenes, 1-aryl-substituted cycloalkenes, and 1,1-diarylalkenes in good to high yields. The stoichiometric loadings of the triarylbismuth reagents with respect to the vinylic iodides under relatively mild conditions and short reaction times successfully demonstrated the high and efficient reactivity of triarylbismuths in carbon–carbon bond-forming reactions under palladium catalysis. Further, this is the first time that a cross-coupling study of triarylbismuths has been combined with vinylic iodides under palladium catalysis.

## Experimental Section

**General:** All reactions were performed under a nitrogen atmosphere by using Schlenk techniques. Standard procedures were followed to purify solvents prior to use. Thin-layer chromatography and gas chromatography (Clarus 500, Perkin–Elmer) was used to analyze the crude reaction mixtures. Crude products were purified by column chromatography (230–400 mesh silica gel). Melting points reported are uncorrected. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with a JEOL-Lambda 400 MHz spectrometer in CDCl<sub>3</sub> as solvent and the chemical shift ( $\delta$ ) values are expressed in parts per million (ppm). IR spectra were recorded with a Bruker vector 22-FTIR

spectrophotometer. High-resolution mass spectra were recorded using electrospray (ES) technique with a Waters HAB213 Q-ToF Premier Micromass spectrometer. Triarylbismuths<sup>[5]</sup> and vinyl iodides<sup>[16]</sup> were prepared according to literature procedures.

**Representative Procedure:** A hot, oven-dried Schlenk tube was charged with 4-iodo-1,2-dihydronaphthalene (211 mg, 0.825 mmol, 1 equiv.), Ph<sub>3</sub>Bi (110 mg, 0.25 mmol, 0.303 equiv.), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (15.8 mg, 0.0225 mmol, 0.0273 equiv.), Cs<sub>2</sub>CO<sub>3</sub> (326 mg, 1.0 mmol, 1.21 equiv.), and dry DMA (3 mL) under a nitrogen atmosphere. The contents were stirred at 60 °C in an oil bath for 1 h. After the reaction was complete, the contents were cooled to room temperature, acidified with dilute HCl (10 mL), and then extracted with ethyl acetate (15 mL × 3). The combined organic extract was further washed with water (2 × 15 mL) and brine (15 mL) and dried with anhydrous MgSO<sub>4</sub>. The solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (petroleum ether) to obtain 4-phenyl-1,2-dihydronaphthalene (**2a**) as a colorless liquid. Yield: 111 mg (72%). The yield was calculated with respect to the reactivity of 0.9 equiv. of Bi-Ph from triphenylbismuth (0.3 equiv.) used.

For all the reactions, yields were calculated considering the three aryl groups from triarylbismuth for cross-coupling. Thus, 0.3 equiv. of BiAr<sub>3</sub> is equal to 0.9 equiv. of Bi-Ar, and 0.9 equiv. of cross-coupling product (0.75 mmol) corresponds to 100% yield.

**4-Phenyl-1,2-dihydronaphthalene (2a):**<sup>[9b]</sup> Colorless liquid (111 mg, 72%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.04–7.42 (m, 9 H, Ar-H), 6.13 (t,  $J$  = 4.6 Hz, 1 H, 3-H), 2.90 (t,  $J$  = 7.9 Hz, 2 H, 1-H), 2.43–2.48 (m, 2 H, 2-H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 140.7, 139.8, 136.7, 135.0, 128.7, 128.1, 127.6, 127.5, 127.0, 126.9, 126.1, 125.4, 28.2, 23.5 ppm. IR (film):  $\tilde{\nu}$  = 3055, 3023, 2931, 2882, 2829, 1598, 1486, 1443, 1040, 1020, 786, 756, 737 cm<sup>-1</sup>. HRMS (ESI): calcd. for C<sub>16</sub>H<sub>15</sub> [M + H]<sup>+</sup> 207.1174; found 207.1178.

**4-(4-Methylphenyl)-1,2-dihydronaphthalene (2b):** Colorless liquid (127 mg, 77%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.01–7.26 (m, 8 H, Ar-H), 6.07 (t,  $J$  = 4.6 Hz, 1 H, 3-H), 2.85 (t,  $J$  = 7.9 Hz, 2 H, 1-H), 2.36–2.44 (m, 5 H, 2-H and CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 139.7, 137.8, 136.7, 136.6, 135.2, 128.8, 128.6, 127.4, 127.1, 126.8, 126.1, 125.4, 28.3, 23.5, 21.1 ppm. IR (film):  $\tilde{\nu}$  = 2951, 2922, 2852, 2835, 1654, 1606, 1509, 1290, 1249, 1180, 1149, 1116, 1030, 900, 834 cm<sup>-1</sup>. HRMS (ESI): calcd. for C<sub>17</sub>H<sub>17</sub> [M + H]<sup>+</sup> 221.1330; found 221.1331.

**4-(3,4-Dihydronaphthalen-1-yl)phenyl methyl ether (2c):** Pale-yellow liquid (114 mg, 64%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.25 (d,  $J$  = 8.8 Hz, 2 H, Ar-H), 7.06–7.20 (m, 3 H, Ar-H), 7.00 (d,  $J$  = 7.3 Hz, 1 H, Ar-H), 6.88 (d,  $J$  = 8.8 Hz, 2 H, Ar-H), 6.02 (t,  $J$  = 4.6 Hz, 1 H, 3-H), 3.80 (s, 3 H, -OCH<sub>3</sub>), 2.81 (t,  $J$  = 7.9 Hz, 2 H, 1-H), 2.33–2.38 (m, 2 H, 2-H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 158.7, 139.2, 136.8, 135.2, 133.1, 129.7, 127.4, 126.8, 126.1, 125.3, 113.5, 55.2, 28.3, 23.4 ppm. IR (film):  $\tilde{\nu}$  = 3017, 2932, 2832, 1606, 1509, 1487, 1288, 1245, 1176, 1034, 820, 767, 740 cm<sup>-1</sup>. HRMS (ESI): calcd. for C<sub>17</sub>H<sub>17</sub>O [M + H]<sup>+</sup> 237.1279; found 237.1279.

**4-(3,4-Dihydronaphthalen-1-yl)phenyl ethyl ether (2d):** Colorless liquid (163 mg, 87%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.28–7.31 (m, 2 H, Ar-H), 7.06–7.24 (m, 4 H, Ar-H), 6.93–6.95 (m, 2 H, Ar-H), 6.08 (t,  $J$  = 4.6 Hz, 1 H, 3-H), 4.10 (q,  $J$  = 7.0 Hz, 2 H, OCH<sub>2</sub>CH<sub>3</sub>), 2.88 (t,  $J$  = 7.9 Hz, 2 H, 1-H), 2.40–2.45 (m, 2 H, 2-H), 1.48 (t,  $J$  = 7.0 Hz, 3 H, OCH<sub>2</sub>CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 158.1, 139.3, 136.8, 135.2, 133.0, 129.7, 127.4, 126.8, 126.1, 125.3, 114.1, 63.4, 28.3, 23.4, 14.8 ppm. IR (film):  $\tilde{\nu}$  = 3061, 2978, 2932, 1721, 1654, 1600, 1509, 1247, 1045,

922, 824, 758, 697 cm<sup>-1</sup>. HRMS (ESI): calcd. for C<sub>18</sub>H<sub>19</sub>O [M + H]<sup>+</sup> 251.1436; found 251.1338.

**4-(4-Fluorophenyl)-1,2-dihydroronaphthalene (2e):** Colorless liquid (146 mg, 87%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 6.89–7.31 (m, 8 H, Ar-H), 6.04 (t, J = 4.6 Hz, 1 H, 3-H), 2.83 (t, J = 7.9 Hz, 2 H, 1-H), 2.36–2.41 (m, 2 H, 2-H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 162.1 [d, <sup>1</sup>J<sub>C,F</sub> = 243.5 Hz], 138.9, 136.7, 134.9, 130.2 (d, <sup>3</sup>J<sub>C,F</sub> = 7.4 Hz), 127.7, 127.5, 127.0, 126.2, 125.2, 115.0 (d, <sup>2</sup>J<sub>C,F</sub> = 21.4 Hz), 28.2, 23.4 ppm. IR (film): ν = 3067, 2928, 1717, 1663, 1598, 1505, 1227, 1158, 1054, 1014, 834, 783, 757 cm<sup>-1</sup>. HRMS (ESI): calcd. for C<sub>16</sub>H<sub>14</sub>F [M + H]<sup>+</sup> 225.1080; found 225.1085.

**4-(4-Chlorophenyl)-1,2-dihydroronaphthalene (2f):** Pale-yellow liquid (126 mg, 70%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.04–7.30 (m, 7 H, Ar-H), 6.90 (d, J = 7.6 Hz, 1 H, Ar-H), 6.02 (t, J = 4.6 Hz, 1 H, 3-H), 2.79 (t, J = 7.9 Hz, 2 H, 1-H), 2.32–2.37 (m, 2 H, 2-H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 139.2, 138.9, 136.7, 134.7, 132.9, 130.0, 128.4, 128.0, 127.6, 127.1, 126.2, 125.2, 28.1, 23.4 ppm. IR (film): ν = 3062, 3025, 2934, 1717, 1662, 1587, 1487, 1400, 1266, 1091, 1014, 822, 763, 738 cm<sup>-1</sup>. HRMS (ESI): calcd. for C<sub>16</sub>H<sub>14</sub>Cl [M + H]<sup>+</sup> 241.0784; found 241.0782.

**3-(3,4-Dihydroronaphthalen-1-yl)phenyl methyl ether (2g):** Pale-yellow liquid (151 mg, 85%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 6.85–7.29 (m, 8 H, Ar-H), 6.08 (t, J = 4.6 Hz, 1 H, 3-H), 3.79 (s, 3 H, OCH<sub>3</sub>), 2.84 (t, J = 7.9 Hz, 2 H, 1-H), 2.36–2.41 (m, 2 H, 2-H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 159.4, 142.2, 139.7, 136.7, 134.9, 129.1, 127.6, 127.5, 126.9, 126.2, 125.4, 121.2, 114.1, 112.7, 55.2, 28.2, 23.4 ppm. IR (film): ν = 3023, 2935, 2833, 1662, 1598, 1485, 1289, 1044, 782, 759, 740, 701 cm<sup>-1</sup>. HRMS (ESI): calcd. for C<sub>17</sub>H<sub>17</sub>O [M + H]<sup>+</sup> 237.1279; found 237.1276.

**4-(3-Methylphenyl)-1,2-dihydroronaphthalene (2h):** Pale-yellow liquid (137 mg, 83%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.08–7.48 (m, 8 H, Ar-H), 6.15 (t, J = 4.8 Hz, 1 H, 3-H), 2.93 (t, J = 7.8 Hz, 2 H, 1-H), 2.45–2.50 (m, 5 H, 1-H and CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 140.7, 139.9, 137.7, 136.7, 135.1, 129.4, 128.0, 127.7, 127.4, 127.3, 126.8, 126.1, 125.8, 125.4, 28.2, 23.4, 21.4 ppm. IR (film): ν = 3023, 2927, 1662, 1602, 1485, 1451, 1273, 1042, 787, 759, 739, 705 cm<sup>-1</sup>. HRMS (ESI): calcd. for C<sub>17</sub>H<sub>17</sub> [M + H]<sup>+</sup> 221.1330; found 221.1330.

**1-[4-(3,4-Dihydroronaphthalen-1-yl)phenyl]ethanone (2i):** Pale-yellow solid (149 mg, 80%). M.p. 84–86 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.00 (d, J = 7.8 Hz, 2 H, Ar-H), 7.48 (d, J = 8.0 Hz, 2 H, Ar-H), 7.12–7.25 (m, 3 H, Ar-H), 6.98 (d, J = 7.6 Hz, 1 H, Ar-H), 6.19 (t, J = 4.6 Hz, 1 H, 3-H), 2.89 (t, J = 7.9 Hz, 2 H, 1-H), 2.66 (s, 3 H, COCH<sub>3</sub>), 2.43–2.50 (m, 2 H, 2-H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 197.7, 145.8, 139.2, 136.7, 135.9, 134.4, 128.9, 128.8, 128.4, 128.3, 127.6, 127.3, 126.3, 125.2, 28.1, 26.5, 23.5 ppm. IR (KBr): ν = 3021, 2943, 2885, 2831, 1675, 1601, 1555, 1308, 1267, 1185, 1111, 1037, 953, 787, 770, 748, 692, 644 cm<sup>-1</sup>. HRMS (ESI): calcd. for C<sub>18</sub>H<sub>17</sub>O [M + H]<sup>+</sup> 249.1279; found 249.1275.

**4-(3,4-Dihydroronaphthalen-1-yl)benzaldehyde (2j):** White solid (135 mg, 77%). M.p. 53–55 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 10.02 (s, 1 H, CHO), 7.88 (d, J = 8.3 Hz, 2 H, Ar-H), 7.51 (d, J = 8.0 Hz, 2 H, Ar-H), 7.08–7.21 (m, 3 H, Ar-H), 6.93 (d, J = 7.3 Hz, 1 H, Ar-H), 6.17 (t, J = 4.6 Hz, 1 H, 3-H), 2.84 (t, J = 7.9 Hz, 2 H, 1-H), 2.39–2.45 (m, 2 H, 2-H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 191.8, 147.3, 139.2, 136.7, 135.3, 134.2, 129.7, 129.3, 127.7, 127.4, 126.3, 125.2, 28.1, 23.5 ppm. IR (KBr): ν = 3023, 2927, 2851, 2829, 1699, 1602, 1209, 1167, 1092, 1019, 827, 811, 767, 740, 701, 669 cm<sup>-1</sup>. HRMS (ESI): calcd. for C<sub>17</sub>H<sub>15</sub>O [M + H]<sup>+</sup> 235.1123; found 235.1126.

**3,4-Dihydro-1,2'-binaphthalene (2k):** Pale-yellow solid (163 mg, 85%). M.p. 52–53 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.83–7.86

(m, 4 H, Ar-H), 7.45–7.50 (m, 3 H, Ar-H), 7.01–7.24 (m, 4 H, Ar-H), 6.21 (t, J = 4.6 Hz, 1 H, 3-H), 2.89 (t, J = 7.9 Hz, 2 H, 1-H), 2.43–2.48 (m, 2 H, 2-H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 139.9, 138.3, 136.8, 135.1, 133.5, 132.6, 128.1, 127.9, 127.5, 127.3, 127.0, 126.2, 126.0, 125.6, 125.5, 28.3, 23.6 ppm. IR (KBr): ν = 3052, 3015, 2932, 2879, 2827, 1593, 1481, 1446, 1426, 1270, 1188, 1155, 1125, 1041, 859, 823, 800, 769, 742, 659 cm<sup>-1</sup>. HRMS (ESI): calcd. for C<sub>20</sub>H<sub>17</sub> [M + H]<sup>+</sup> 257.1330; found 257.1337.

**3,4-Dihydro-1,2'-binaphthalen-6'-yl methyl ether (2l):** Pale-yellow solid (168 mg, 78%). M.p. 114–116 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.62–7.67 (m, 3 H, Ar-H), 7.35 (d, J = 8.5 Hz, 1 H, Ar-H), 6.94–7.16 (m, 6 H, Ar-H), 6.10 (t, J = 4.6 Hz, 1 H, 3-H), 3.85 (s, 3 H, OCH<sub>3</sub>), 2.80 (t, J = 7.9 Hz, 2 H, 1-H), 2.33–2.38 (m, 2 H, 2-H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 157.6, 139.8, 136.8, 136.1, 135.2, 133.7, 129.4, 129.0, 127.7, 127.5, 127.0, 126.9, 126.4, 126.2, 125.5, 118.8, 105.7, 55.3, 28.3, 23.6 ppm. IR (KBr): ν = 3054, 3021, 2945, 2878, 2828, 1627, 1598, 1459, 1270, 1249, 1160, 1028, 988, 967, 945, 887, 854, 830, 813, 779, 767, 742, 675, 622 cm<sup>-1</sup>. HRMS (ESI): calcd. for C<sub>21</sub>H<sub>19</sub>O [M + H]<sup>+</sup> 287.1436; found 287.1438.

**2-(3,4-Dihydroronaphthalen-1-yl)thiophene (2m):** Pale-yellow solid (134 mg, 84%). M.p. 70–72 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.39–7.41 (m, 1 H, Ar-H), 7.19–7.30 (m, 4 H, Ar-H), 7.06–7.11 (m, 2 H, Ar-H), 6.33 (t, J = 4.8 Hz, 1 H, 3-H), 2.87 (t, J = 7.9 Hz, 2 H, 1-H), 2.41–2.46 (m, 2 H, 2-H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 142.5, 136.6, 134.4, 132.8, 129.1, 127.5, 127.2, 127.0, 126.3, 125.5, 125.2, 124.0, 28.0, 23.4 ppm. IR (KBr): ν = 3098, 3060, 3027, 2926, 2880, 2825, 1477, 1428, 1272, 1095, 1021, 822, 771, 740, 709, 618 cm<sup>-1</sup>. HRMS (ESI): calcd. for C<sub>14</sub>H<sub>13</sub>S [M + H]<sup>+</sup> 213.0738; found 213.0735.

**Cyclohex-1-en-1-ylbenzene (3a):**<sup>[9b]</sup> Colorless liquid (68 mg, 57%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.12–7.33 (m, 5 H, Ar-H), 6.04–6.07 (m, 1 H, 2-H), 2.32–2.37 (m, 2 H, CH<sub>2</sub>), 2.12–2.17 (m, 2 H, CH<sub>2</sub>), 1.69–1.75 (m, 2 H, CH<sub>2</sub>), 1.57–1.64 (m, 2 H, CH<sub>2</sub>) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 142.7, 136.6, 128.1, 126.4, 124.9, 124.7, 27.4, 25.8, 23.0, 22.1 ppm. IR (film): ν = 3028, 2927, 2856, 1642, 1598, 1493, 1444, 1075, 1033, 758, 741, 693 cm<sup>-1</sup>. HRMS (ESI): calcd. for C<sub>12</sub>H<sub>14</sub> [M]<sup>+</sup> 158.1096; found 158.1096.

**4-tert-Butylcyclohex-1-en-1-yl)benzene (3b):**<sup>[17a]</sup> Colorless liquid (97 mg, 60%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.14–7.33 (m, 5 H, Ar-H), 6.05–6.07 (m, 1 H, 2-H), 2.37–2.44 (m, 2 H, CH<sub>2</sub>), 2.16–2.20 (m, 1 H, 4-H), 1.90–1.94 (m, 2 H, CH<sub>2</sub>), 1.22–1.30 (m, 2 H, CH<sub>2</sub>), 0.85 (s, 9 H, tBu) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 142.2, 136.4, 128.1, 126.4, 124.9, 43.8, 32.2, 28.8, 27.4, 27.2, 24.4 ppm. IR (film): ν = 3060, 2957, 2869, 1722, 1688, 1449, 1366, 1018, 757, 699 cm<sup>-1</sup>. HRMS (ESI): calcd. for C<sub>16</sub>H<sub>22</sub> [M]<sup>+</sup> 214.1722; found 214.1725.

**1-(4-tert-Butylcyclohex-1-en-1-yl)-4-methylbenzene (3c):**<sup>[17b]</sup> White solid (105 mg, 61%). M.p. 67–69 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.28 (d, J = 8.1 Hz, 2 H, Ar-H), 7.11 (d, J = 8.1 Hz, 2 H, Ar-H), 6.09 (t, J = 2.7 Hz, 1 H, 2-H), 2.22–2.54 (m, 6 H, CH<sub>3</sub>, CH<sub>2</sub>, and 4-H), 1.93–2.00 (m, 2 H, CH<sub>2</sub>), 1.28–1.40 (m, 2 H, CH<sub>2</sub>), 0.91 (s, 9 H, tBu) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 139.4, 136.1, 136.0, 128.8, 124.8, 124.0, 43.8, 32.2, 28.8, 27.4, 27.2, 24.4, 21.0 ppm. IR (KBr): ν = 3031, 2959, 2870, 1644, 1511, 1467, 1284, 1256, 1180, 1038, 829, 802, 775 cm<sup>-1</sup>. HRMS (ESI): calcd. for C<sub>17</sub>H<sub>24</sub> [M]<sup>+</sup> 228.1878; found 228.1876.

**1-(4-tert-Butylcyclohex-1-en-1-yl)-4-methoxybenzene (3d):**<sup>[17b]</sup> White solid (119 mg, 65%). M.p. 78–80 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.32 (d, J = 8.6 Hz, 2 H, Ar-H), 6.85 (d, J = 8.8 Hz, 2 H, Ar-H), 6.04 (t, J = 2.8 Hz, 1 H, 2-H), 3.80 (s, 3 H, OCH<sub>3</sub>),

2.21–2.51 (m, 3 H,  $\text{CH}_2$  and 4-H), 1.92–1.99 (m, 2 H,  $\text{CH}_2$ ), 1.24–1.38 (m, 2 H,  $\text{CH}_2$ ), 0.91 (s, 9 H,  $t\text{Bu}$ ) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 158.4, 135.7, 134.9, 125.8, 123.2, 113.5, 55.2, 43.8, 32.2, 28.9, 27.4, 27.2, 27.2, 24.4 ppm. IR (KBr):  $\tilde{\nu}$  = 3023, 2949, 2867, 1644, 1512, 1390, 1362, 1258, 1208, 848, 817, 799, 773  $\text{cm}^{-1}$ . HRMS (ESI): calcd. for  $\text{C}_{17}\text{H}_{25}\text{O}$  [ $\text{M} + \text{H}]^+$  245.1905; found 245.1906.

**1-Phenylcyclooctene (3e):**<sup>[17a]</sup> Colorless liquid (102 mg, 73%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.09–7.39 (m, 5 H, Ar-H), 5.89–5.98 (m, 1 H, 2-H), 2.52–2.62 (m, 2 H,  $\text{CH}_2$ ), 2.17–2.25 (m, 2 H,  $\text{CH}_2$ ), 1.47–1.58 (m, 8 H,  $4 \times \text{CH}_2$ ) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 143.2, 140.2, 128.1, 127.9, 126.3, 125.7, 29.9, 29.4, 28.4, 27.4, 26.9, 26.1 ppm. IR (film):  $\tilde{\nu}$  = 3023, 2921, 2850, 1597, 1491, 1468, 1446, 1020, 757, 695  $\text{cm}^{-1}$ . HRMS (ESI): calcd. for  $\text{C}_{14}\text{H}_{18}$  [ $\text{M}]^+$  186.1409; found 186.1402.

**1-Methoxy-3-(1-phenylvinyl)benzene (4a):**<sup>[17c]</sup> Pale-yellow liquid (115 mg, 73%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.22–7.32 (m, 6 H, Ar-H), 6.85–6.92 (m, 3 H, Ar-H), 5.45 (s, 2 H, = $\text{CH}_2$ ), 3.78 (s, 3 H,  $\text{OCH}_3$ ) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 159.4, 149.9, 142.9, 141.3, 129.0, 128.2, 128.1, 127.7, 120.8, 114.3, 113.9, 113.1, 55.2 ppm. IR (film):  $\tilde{\nu}$  = 3055, 2933, 2833, 1576, 1487, 1327, 1284, 1239, 1182, 1046, 897, 777, 698  $\text{cm}^{-1}$ . HRMS (ESI): calcd. for  $\text{C}_{15}\text{H}_{15}\text{O}$  [ $\text{M} + \text{H}]^+$  211.1123; found 211.1128.

**1-Methoxy-4-(1-phenylvinyl)benzene (4b):**<sup>[10a]</sup> Pale-yellow solid (101 mg, 64%). M.p. 61–63  $^\circ\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.26–7.33 (m, 7 H, Ar-H), 6.86 (d,  $J$  = 8.6 Hz, 2 H, Ar-H), 5.39 (s, 1 H, = $\text{CH}_2$ ), 5.35 (s, 1 H, = $\text{CH}_2$ ), 3.82 (s, 3 H,  $\text{OCH}_3$ ) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 159.2, 149.4, 141.7, 133.9, 129.3, 128.2, 128.0, 127.6, 113.4, 112.9, 55.2 ppm. IR (KBr):  $\tilde{\nu}$  = 3030, 2951, 2834, 1658, 1508, 1289, 1249, 1178, 1150, 1028, 901, 841, 784, 746, 707  $\text{cm}^{-1}$ . HRMS (ESI): calcd. for  $\text{C}_{15}\text{H}_{15}\text{O}$  [ $\text{M} + \text{H}]^+$  211.1123; found 211.1126.

**1-Ethoxy-4-(1-phenylvinyl)benzene (4c):** Pale-yellow solid (118 mg, 70%). M.p. 72–73  $^\circ\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.24–7.33 (m, 7 H, Ar-H), 6.82–6.85 (m, 2 H, Ar-H), 5.38 (d,  $J$  = 1.2 Hz, 1 H, = $\text{CH}_2$ ), 5.33 (d,  $J$  = 1.2 Hz, 1 H, = $\text{CH}_2$ ), 4.04 (q,  $J$  = 7.1 Hz, 2 H,  $\text{OCH}_2\text{CH}_3$ ), 1.41 (t,  $J$  = 7.0 Hz, 3 H,  $\text{OCH}_2\text{CH}_3$ ) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 158.7, 149.6, 141.8, 133.8, 129.3, 128.3, 128.0, 127.5, 114.1, 112.7, 63.4, 14.8 ppm. IR (KBr):  $\tilde{\nu}$  = 3033, 2981, 2929, 1656, 1507, 1445, 1392, 1244, 1180, 1045, 899, 843, 783, 707  $\text{cm}^{-1}$ . HRMS (ESI): calcd. for  $\text{C}_{16}\text{H}_{17}\text{O}$  [ $\text{M} + \text{H}]^+$  225.1279; found 225.1279.

**1-Methoxy-3-[1-(4-methylphenyl)vinyl]benzene (4d):** Pale-yellow liquid (126 mg, 75%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.11–7.24 (m, 5 H, Ar-H), 6.83–6.92 (m, 3 H, Ar-H), 5.42 (d,  $J$  = 1.0 Hz, 1 H, = $\text{CH}_2$ ), 5.39 (s, 1 H, = $\text{CH}_2$ ), 3.77 (s, 3 H,  $\text{OCH}_3$ ), 2.35 (s, 3 H,  $\text{CH}_3$ ) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 159.4, 149.8, 143.2, 138.4, 137.4, 129.0, 128.8, 128.1, 120.9, 113.9, 113.6, 113.1, 55.2, 21.1 ppm. IR (film):  $\tilde{\nu}$  = 3001, 2924, 1656, 1511, 1485, 1455, 1284, 1241, 1180, 1043, 966, 874, 835, 782, 750, 702  $\text{cm}^{-1}$ . HRMS (ESI): calcd. for  $\text{C}_{16}\text{H}_{17}\text{O}$  [ $\text{M} + \text{H}]^+$  225.1279; found 225.1279.

**1-Methoxy-4-[1-(4-methylphenyl)vinyl]benzene (4e):** Pale-yellow solid (110 mg, 65%). M.p. 73–74  $^\circ\text{C}$ .<sup>[17d]</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.22–7.28 (m, 4 H, Ar-H), 7.13 (d,  $J$  = 8.3 Hz, 2 H, Ar-H), 6.83–6.86 (m, 2 H, Ar-H), 5.31–5.33 (m, 2 H, = $\text{CH}_2$ ), 3.81 (s, 3 H,  $\text{OCH}_3$ ), 2.35 (s, 3 H,  $\text{CH}_3$ ) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 159.2, 149.3, 138.9, 137.4, 134.2, 129.3, 128.8, 128.1, 113.4, 112.2, 55.3, 21.1 ppm. IR (KBr):  $\tilde{\nu}$  = 3009, 2952, 2834, 1654, 1509, 1290, 1248, 1180, 1029, 900, 834, 759, 730  $\text{cm}^{-1}$ . HRMS (ESI): calcd. for  $\text{C}_{16}\text{H}_{17}\text{O}$  [ $\text{M} + \text{H}]^+$  225.1279; found 225.1275.

**1-Ethoxy-4-[1-(4-methylphenyl)vinyl]benzene (4f):** White solid (130 mg, 73%). M.p. 49–51  $^\circ\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  =

7.21–7.28 (m, 4 H, Ar-H), 7.12 (d,  $J$  = 7.8 Hz, 2 H, Ar-H), 6.83 (d,  $J$  = 8.3 Hz, 2 H, Ar-H), 5.33 (s, 1 H, = $\text{CH}_2$ ), 5.30 (s, 1 H, = $\text{CH}_2$ ), 4.03 (q,  $J$  = 7.1 Hz, 2 H,  $\text{OCH}_2\text{CH}_3$ ), 2.35 (s, 3 H,  $\text{CH}_3$ ), 1.41 (t,  $J$  = 7.0 Hz, 3 H,  $\text{OCH}_2\text{CH}_3$ ) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 158.6, 149.3, 138.9, 137.3, 133.9, 129.3, 128.7, 128.1, 114.0, 112.1, 63.4, 21.1, 14.8 ppm. IR (KBr):  $\tilde{\nu}$  = 3025, 2978, 2923, 2853, 1651, 1605, 1510, 1245, 1176, 1090, 1019, 923, 890, 760  $\text{cm}^{-1}$ . HRMS (ESI): calcd. for  $\text{C}_{17}\text{H}_{19}\text{O}$  [ $\text{M} + \text{H}]^+$  239.1436; found 239.1436.

**1-[1-(4-Bromophenyl)vinyl]-3-methoxybenzene (4g):** Pale-yellow liquid (178 mg, 82%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.45–7.48 (m, 2 H, Ar-H), 7.21–7.29 (m, 3 H, Ar-H), 6.85–6.91 (m, 3 H, Ar-H), 5.48 (d,  $J$  = 1.0 Hz, 1 H, = $\text{CH}_2$ ), 5.46 (s, 1 H, = $\text{CH}_2$ ), 3.80 (s, 3 H,  $\text{OCH}_3$ ) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 159.5, 148.9, 142.4, 140.2, 131.2, 129.8, 129.2, 121.7, 120.7, 114.8, 113.9, 113.3, 55.2 ppm. IR (film):  $\tilde{\nu}$  = 3002, 2933, 2834, 1660, 1585, 1486, 1462, 1322, 1285, 1236, 1177, 1072, 1046, 834, 785, 752  $\text{cm}^{-1}$ . HRMS (ESI): calcd. for  $\text{C}_{15}\text{H}_{14}\text{BrO}$  [ $\text{M} + \text{H}]^+$  and  $[\text{M} + \text{H} + 2]^+$  289.0228 and 291.0208; found 289.0229 and 291.0060.

**1-Bromo-4-[1-(4-methoxyphenyl)vinyl]benzene (4h):** White solid (169 mg, 78%). M.p. 82–84  $^\circ\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.45–7.47 (m, 2 H, Ar-H), 7.20–7.26 (m, 4 H, Ar-H), 6.86–6.88 (m, 2 H, Ar-H), 5.41 (s, 1 H, = $\text{CH}_2$ ), 5.35 (s, 1 H, = $\text{CH}_2$ ), 3.83 (s, 3 H,  $\text{OCH}_3$ ) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 159.5, 148.5, 140.7, 133.4, 131.2, 129.9, 129.3, 121.6, 113.6, 113.3, 55.3 ppm. IR (KBr):  $\tilde{\nu}$  = 3006, 2953, 2929, 2834, 1604, 1482, 1292, 1250, 1178, 900, 840, 787, 758  $\text{cm}^{-1}$ . HRMS (ESI): calcd. for  $\text{C}_{15}\text{H}_{14}\text{BrO}$  [ $\text{M} + \text{H}]^+$  and  $[\text{M} + \text{H} + 2]^+$  289.0228 and 291.0208; found 289.0226 and 291.0168.

**1-Bromo-4-[1-(4-ethoxyphenyl)vinyl]benzene (4i):** White solid (182 mg, 82%). M.p. 76–78  $^\circ\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.22–7.34 (m, 6 H, Ar-H), 6.81–6.86 (m, 2 H, Ar-H), 5.31–5.40 (m, 2 H, = $\text{CH}_2$ ), 4.03 (q,  $J$  = 7.0 Hz, 2 H,  $\text{OCH}_2\text{CH}_3$ ), 1.41 (t,  $J$  = 7.0 Hz, 3 H,  $\text{OCH}_2\text{CH}_3$ ) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 158.8, 148.5, 140.8, 133.2, 131.2, 129.9, 129.2, 121.6, 114.1, 113.2, 63.4, 14.8 ppm. IR (KBr):  $\tilde{\nu}$  = 2980, 2925, 1641, 1604, 1507, 1480, 1391, 1287, 1248, 1180, 1147, 844, 729, 716  $\text{cm}^{-1}$ . HRMS (ESI): calcd. for  $\text{C}_{16}\text{H}_{16}\text{BrO}$  [ $\text{M} + \text{H}]^+$  and  $[\text{M} + \text{H} + 2]^+$  303.0385 and 305.0364; found 303.0383 and 305.0210.

**2-(1-Phenylvinyl)naphthalene (4j):**<sup>[9e]</sup> Pale-yellow liquid (131 mg, 76%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.75–7.84 (m, 5 H, Ar-H), 7.34–7.49 (m, 7 H, Ar-H), 5.59 (d,  $J$  = 1.0 Hz, 1 H, = $\text{CH}_2$ ), 5.55 (d,  $J$  = 1.2 Hz, 1 H, = $\text{CH}_2$ ) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 150.0, 141.5, 138.9, 133.3, 132.9, 128.3, 128.2, 127.7, 127.6, 127.5, 127.2, 126.3, 126.1, 126.0, 114.7 ppm. IR (film):  $\tilde{\nu}$  = 3054, 2922, 1610, 1492, 1444, 1382, 1270, 1143, 1119, 1018, 895, 858, 820, 777, 749, 711, 696  $\text{cm}^{-1}$ . HRMS (ESI): calcd. for  $\text{C}_{18}\text{H}_{15}$  [ $\text{M} + \text{H}]^+$  231.1174; found 231.1176.

**2-[1-(4-Methylphenyl)vinyl]naphthalene (4k):** Pale-yellow liquid (137 mg, 75%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.75–7.80 (m, 4 H, Ar-H), 7.40–7.46 (m, 3 H, Ar-H), 7.25 (d,  $J$  = 8.3 Hz, 2 H, Ar-H), 7.13 (d,  $J$  = 7.8 Hz, 2 H, Ar-H), 5.49–5.50 (m, 2 H, = $\text{CH}_2$ ), 2.35 (s, 3 H,  $\text{CH}_3$ ) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 149.9, 139.1, 138.6, 137.5, 133.3, 132.9, 128.9, 128.2, 128.1, 127.6, 127.2, 126.4, 126.0, 125.9, 114.1, 21.1 ppm. IR (film):  $\tilde{\nu}$  = 3055, 3023, 2923, 1653, 1607, 1538, 1276, 1236, 1018, 951, 859, 771, 752  $\text{cm}^{-1}$ . HRMS (ESI): calcd. for  $\text{C}_{19}\text{H}_{17}$  [ $\text{M} + \text{H}]^+$  245.1330; found 245.1338.

**2-[1-(4-Methoxyphenyl)vinyl]naphthalene (4l):** White solid (139 mg, 71%). M.p. 92–94  $^\circ\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.77–7.83 (m, 4 H, Ar-H), 7.44–7.47 (m, 3 H, Ar-H), 7.29–7.31 (m, 2 H, Ar-H)

H), 6.86–6.88 (m, 2 H, Ar-H), 5.47 (s, 2 H, =CH<sub>2</sub>), 3.82 (s, 3 H, OCH<sub>3</sub>) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 159.4, 149.5, 139.2, 134.0, 133.3, 132.9, 129.4, 128.1, 127.5, 127.2, 126.5, 126.1, 125.9, 113.6, 113.4, 55.3 ppm. IR (KBr): ν = 3058, 2954, 2853, 1680, 1626, 1508, 1464, 1361, 1280, 1018, 941, 859, 821, 746 cm<sup>-1</sup>. HRMS (ESI): calcd. for C<sub>19</sub>H<sub>17</sub>O [M + H]<sup>+</sup> 261.1279; found 261.1279.

**Supporting Information** (see footnote on the first page of this article): Spectroscopic data and HPLC traces of new compounds.

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- [1] a) K. C. Nicolaou, P. G. Bulger, D. Sarlah, *Angew. Chem. Int. Ed.* **2005**, *44*, 4442–4489; b) J. Hassan, M. Sevignon, C. Gozzi, E. Schulz, M. Lemaire, *Chem. Rev.* **2002**, *102*, 1359–1469; c) S. Kotha, K. Lahiri, D. Kashinath, *Tetrahedron* **2002**, *58*, 9633–9695; d) A. Roglans, A. Pla-Quintana, M. Moreno-Manas, *Chem. Rev.* **2006**, *106*, 4622–4643; e) L. Yin, J. Liebscher, *Chem. Rev.* **2007**, *107*, 133–173.
- [2] a) J.-P. Corbet, G. Mignani, *Chem. Rev.* **2006**, *106*, 2651–2710; b) A. M. Rouhi, *Chem. Eng. News* **2004**, *82*, 49–58.
- [3] a) S. Darses, J.-P. Genet, *Chem. Rev.* **2008**, *108*, 288–325; b) G. A. Molander, N. Ellis, *Acc. Chem. Res.* **2007**, *40*, 275–286; c) S. E. Denmark, C. S. Regens, *Acc. Chem. Res.* **2008**, *41*, 1486–1499.
- [4] a) C. Peng, Y. Wang, J. Wang, *J. Am. Chem. Soc.* **2008**, *130*, 1566–1567; b) S. R. Dubbaka, P. Vogel, *J. Am. Chem. Soc.* **2003**, *125*, 15292–15293; c) J. Barluenga, P. Moriel, C. Valdes, F. Aznar, *Angew. Chem. Int. Ed.* **2007**, *46*, 5587–5590.
- [5] H. Suzuki, Y. Matano (Eds.), *Organobismuth Chemistry*, Elsevier, Amsterdam, **2001**.
- [6] M. L. N. Rao, V. Venkatesh, D. Banerjee, *Synfacts* **2008**, *4*, 406–406.
- [7] a) M. L. N. Rao, D. N. Jadhav, D. Banerjee, *Tetrahedron* **2008**, *64*, 5762–5772; b) M. L. N. Rao, V. Venkatesh, D. N. Jadhav, *J. Organomet. Chem.* **2008**, *693*, 2494–2498; c) M. L. N. Rao, V. Venkatesh, D. Banerjee, *Tetrahedron* **2007**, *63*, 12917–12926; d) M. L. N. Rao, D. Banerjee, D. N. Jadhav, *Tetrahedron Lett.* **2007**, *48*, 6644–6647; e) M. L. N. Rao, D. Banerjee, D. N. Jadhav, *Tetrahedron Lett.* **2007**, *48*, 2707–2711; f) M. L. N. Rao, V. Venkatesh, D. N. Jadhav, *Tetrahedron Lett.* **2006**, *47*, 6975–6978; g) M. L. N. Rao, D. N. Jadhav, V. Venkatesh, *Tetrahedron Lett.* **2009**, *50*, 4268–4271.
- [8] I. P. Beletskaya, A. V. Cheprakov, *Chem. Rev.* **2000**, *100*, 3009–3066.
- [9] a) J. K. Stille, B. L. Groh, *J. Am. Chem. Soc.* **1987**, *109*, 813–817; b) A. G. Martinez, J. O. Barcina, M. R. C. Heras, A. F. Cerezo, *Organometallics* **2001**, *20*, 1020–1023; c) C. A. Busacca, M. C. Eriksson, R. Fiaschi, *Tetrahedron Lett.* **1999**, *40*, 3101–3104; d) J. A. Miller, *Tetrahedron Lett.* **2002**, *43*, 7111–7114; e) A. L. Hansen, J.-P. Ebran, T. M. Gogsig, T. Skrydstrup, *Chem. Commun.* **2006**, 4137–4139; f) J. Takagi, K. Takahashi, T. Ishiyama, N. Miyaura, *J. Am. Chem. Soc.* **2002**, *124*, 8001–8006; g) A. F. Littke, C. Dai, G. C. Fu, *J. Am. Chem. Soc.* **2000**, *122*, 4020–4028.
- [10] a) F. Berthioli, H. Doucet, M. Santelli, *Eur. J. Org. Chem.* **2003**, 1091–1096; b) N. Miyaura, M. Satoh, A. Suzuki, *Tetrahedron Lett.* **1986**, *27*, 3745–3748; c) M. P. Jennings, E. A. Cork, P. V. Ramachandran, *J. Org. Chem.* **2000**, *65*, 8763–8766; d) W. Dohle, F. Kopp, G. Cahiez, P. Knochel, *Synlett* **2001**, 1901–1904; e) M. Shimizu, K. Tanaka, T. Kurahashi, K. Shimono, T. Hiyama, *Chem. Lett.* **2004**, *33*, 1066–1067; f) G. A. Molander, B. J. Rahn, D. C. Shubert, S. E. Bonde, *Tetrahedron Lett.* **1983**, *24*, 5449–5452.
- [11] A. Jutand, S. Negri, *Organometallics* **2003**, *22*, 4229–4237.
- [12] a) D. H. R. Barton, N. Ozbalik, M. Ramesh, *Tetrahedron* **1988**, *44*, 5661–5668; b) T. Ohe, T. Tanaka, M. Kuroda, C. S. Cho, K. Ohe, S. Uemura, *Bull. Chem. Soc. Jpn.* **1999**, *72*, 1851–1855; c) M. L. N. Rao, S. Shimada, O. Yamazaki, M. Tanaka, *J. Organomet. Chem.* **2002**, *659*, 117–120; d) M. L. N. Rao, S. Shimada, M. Tanaka, *Org. Lett.* **1999**, *1*, 1271–1273; e) M. L. N. Rao, O. Yamazaki, S. Shimada, T. Tanaka, Y. Suzuki, M. Tanaka, *Org. Lett.* **2001**, *3*, 4103–4105.
- [13] For all the reactions, yields were calculated considering the three aryl groups from triarylbismuth for coupling. Thus, 0.3 equiv. of BiAr<sub>3</sub> is equal to 0.9 equiv. of Bi-Ar, and 0.9 equiv. of cross-coupling product corresponds to 100% yield. In these reactions minor amounts of the corresponding biaryls were also formed. As we have used 0.1 equiv. of vinylic iodides in excess to stoichiometric ratio, minor amounts of iodides remained unreacted after 1 h reaction time.
- [14] a) M. C. Carreno, M. Gonzalez-Lopez, A. Latorre, A. Urbano, *J. Org. Chem.* **2006**, *71*, 4956–4964; b) M. C. Carreno, M. Gonzalez-Lopez, A. Latorre, A. Urbano, *Synlett* **2005**, 1601–1605; c) G. Adam, J. Andrieux, M. Plat, *Tetrahedron* **1982**, *38*, 2403–2410; d) J.-C. Lorenz, J. Long, Z. Yang, S. Xue, Y. Xie, Y. Shi, *J. Org. Chem.* **2004**, *69*, 327–334.
- [15] a) M. M. Faul, A. M. Ratz, K. A. Sullivan, W. G. Trankle, L. L. Winneroski, *J. Org. Chem.* **2001**, *66*, 5772–5782; b) D. A. Barda, Z.-Q. Wang, T. C. Britton, S. S. Henry, G. E. Jagdmann, D. S. Coleman, M. P. Johnson, S. L. Andis, D. D. Schoepp, *Bioorg. Med. Chem. Lett.* **2004**, *14*, 3099–3102; c) P. Nussbaumer, G. Dorfstatter, M. A. Grassberger, I. Leitner, J. G. Meingassner, K. Thirring, A. Stutz, *J. Med. Chem.* **1993**, *36*, 2115–2120.
- [16] D. H. R. Barton, G. Bashiardes, J.-L. Fourrey, *Tetrahedron Lett.* **1983**, *24*, 1605–1608.
- [17] a) N. Yoshikai, H. Mashima, E. Nakamura, *J. Am. Chem. Soc.* **2005**, *127*, 17978–17979; b) J. Barluenga, M. Tomas-Gamasa, P. Moriel, F. Aznar, C. Valdes, *Chem. Eur. J.* **2008**, *14*, 4792–4795; c) M. Fischer, P. Wan, *J. Am. Chem. Soc.* **1999**, *121*, 4555–4562; d) W. E. McEwen, M. Gilliland, B. I. Sparr, *J. Am. Chem. Soc.* **1950**, *72*, 3212–3213.

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