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Palladium-catalyzed hydroarylation of alkynes with arylboronic acids

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ABSTRACT

Reaction of symmetrical and unsymmetrical alkynes with arylboronic acids, using $PdCl_2$ as catalyst source and *i*-Pr_2NPPh_2 as ligand, afforded trisubstituted alkenes with regioselectivity in good to excellent yields without a common additional acetic acid. Its efficiency has been demonstrated by its good functional groups, high yield and crowded substrates.

1. Introduction

In the past few decades, great attention has been delivered to metal-catalyzed hydroarylation of alkynes due to its fast accessibility to highly functionalized alkenes.[1] The use of organometallic compounds such as arylmagnesium bromide[2] and tetraphenyltin[3] as arylation reagents has been reported in hydroarylation with high selectivity. Of particular note, the arylboron reagents have drawn considerable attention in recent years due to their advantages such as, good functional group tolerance, readily available, as well as air and moiety stability.[4] In 2001, Hayashi and co-workers first reported rhodium-catalyzed addition reaction of arylboronic acid to alkynes.[5] Subsequently, a range of rhodium-catalyzed approaches for unsymmetric addition-type reactions has been developed.[6,7] Then, the nickel-catalyzed[8] selective synthesis of multi-substituted aryl-alkenes and aryl-dienes, copper-catalyzed[9a] conjugate additions of alkynoates with arylboronic acid, cobalt-catalyzed[9b] similarly regio- and stereoselective transformation as well as palladium-catalyzed hydroarylation reaction of alkyne have been reported soon after that.[10,11]

However, palladium-catalyzed approaches for hydroarylation of sterically hindered or electron-deficient substrates often gave poor yields and the regioselectivity of the addition of organometallics to alkynes still need to be improved. Especially, all of reported Pd-catalyzed hydroarylation of alkynes with arylboron must be proceeded in the present of acetic acid as additive,[10,11] thereby, to some extent, the reaction is confined to acid-compatible substrates and equipments.

In our previous report, we have successfully developed some methodologies for palladium-catalyzed additions of organoboronic acids to the carbon–carbon and carbon–heteroatom unsaturated bond.[12] Herein, we wish to report an efficient palladium-catalyzed hydroarylation of alkynes with arylboronic acids, using inorganic base and easily available ligand in common organic solvent, providing multifunctionalized alkenes in one pot with satisfactory yields.

2. Results and discussion

Initially, we examined the ligand effects in the hydroarylation reaction of diphenylacetylene **1a** and 3-methoxyphenylboronic acid **2b** using $PdCl_2$ as the catalyst, and the results were listed in Table 1. As determined by GC–MS analysis (entry 1), treatment of substrate **1a** with arylboronic acid **2b** using $PdCl_2$ as the palladium precursor and K_2CO_3 as the base afforded only a trace amount of the desired product **3ab** in the absence of ligands. When ligand **L1** was used, the reaction gave **3ab** in 5% yield (entry 2). When the common ligand *i*-Pr_2NPPh_2 was employed, we were delight to find that the yield was remarkably improved, and **3ab** was obtained with up to 95% yield (entry 3). Further studies showed that other monophosphine and biphospine ligands such as **L3**–**L8** were essentially inefficient for this hydroarylation reaction (entries 4–9). Subsequently, the effects of bases and solvents were evaluated (entries 10–16). We found that potassium carbonate and cesium carbonate

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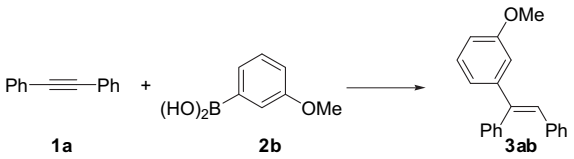
are both suitable bases, but some other bases such as NaOH and Et_3N are ineffective (entries 10–12), THF is the best solvent among the solvents examined, and no reaction occurred in alcohol (entries 14–16). It should be noted that both palladium and bases are necessary, no **3ab** was given in the absence of bases and palladium catalysts (entries 13 and 17). The palladium species screening experiments showed that the reaction could also proceed using other Pd catalysts, such as $Pd(OAc)_2$, $Pd_2(dba)_3$, and $PdCl_2(PhCN)_2$, but all of them were less efficient than $PdCl_2$ (entries 17–20). Moreover, we also examined the amounts of ligand and **2b** (entries 21 and 22). And the results showed that the increased loading of **L2** had little effects on the yield of the reaction; however, the yield was reduced to 75% when using 1.2 equiv of **2b** (entry 22). $Cu(OAc)_2\cdot H_2O$/**L2** and $NiCl_2\cdot 6H_2O$/**L2** catalytic systems show less reactivities (entries 23 and 24).

Table 1
$PdCl_2$-catalyzed hydroarylation of diphenylethyne with phenylboronic acid[a]



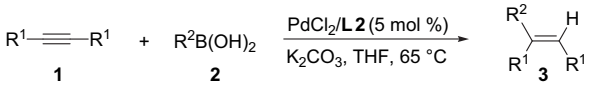
Entry	Pd source	Ligand	Base	Solvent	Yield[b] (%)
1	$PdCl_2$	—	K_2CO_3	THF	Trace
2	$PdCl_2$	(*S*)-Binap **L1**	K_2CO_3	THF	5
3	$PdCl_2$	*i*-Pr_2NPPh_2 **L2**	K_2CO_3	THF	95
4	$PdCl_2$	dppf **L3**	K_2CO_3	THF	Trace
5	$PdCl_2$	PPh_3 **L4**	K_2CO_3	THF	Trace
6	$PdCl_2$	P(4-MeO-C_6H_4)$_3$ **L5**	K_2CO_3	THF	Trace
7	$PdCl_2$	dppp **L6**	K_2CO_3	THF	Trace
8	$PdCl_2$	dppe **L7**	K_2CO_3	THF	Trace
9	$PdCl_2$	$PhNHPPh_2$ **L8**	K_2CO_3	THF	Trace
10	$PdCl_2$	**L2**	NaOH	THF	Trace
11	$PdCl_2$	**L2**	Cs_2CO_3	THF	79
12	$PdCl_2$	**L2**	NEt_3	THF	Trace
13	$PdCl_2$	**L2**	—	THF	NR
14	$PdCl_2$	**L2**	K_2CO_3	DMF	9
15	$PdCl_2$	**L2**	K_2CO_3	Toluene	68
16	$PdCl_2$	**L2**	K_2CO_3	EtOH	Trace
17	—	**L2**	K_2CO_3	THF	NR
18	$Pd(OAc)_2$	**L2**	K_2CO_3	THF	49
19	$Pd_2(dba)_3$	**L2**	K_2CO_3	THF	68
20	$PdCl_2(PhCN)_2$	**L2**	K_2CO_3	THF	86
21	$PdCl_2$	**L2**	K_2CO_3	THF	93[c]
22	$PdCl_2$	**L2**	K_2CO_3	THF	75[d]
23	—[e]	**L2**	K_2CO_3	THF	Trace
24	—[f]	**L2**	K_2CO_3	THF	Trace

NR=No reaction.
[a] Reactions were carried out using **1a** (0.2 mmol), **2a** (2 equiv), $PdCl_2$ (5 mol %), Ligand (5 mol %), and base (3 equiv) in solvent (3 mL) at 65 °C for 24 h.
[b] Isolated yield.
[c] **L2** (10 mol %) was used.
[d] $PhB(OH)_2$·**2a** (1.2 equiv) was used.
[e] $Cu(OAc)_2\cdot H_2O$ (5 mol %) instead of $PdCl_2$.
[f] $NiCl_2\cdot 6H_2O$ (5 mol %) instead of $PdCl_2$.

Under the optimized conditions, we next tried to extend the hydroarylation reaction to other alkynes and arylboronic acids, and results were summarized in Table 2. As we expected, the reaction took place smoothly with good functional group tolerance.

Above all, a variety of diarylacetylenes were examined through the reactions with 3-methoxyphenylboronic acid **2b** (entries 1–7). Both electron-rich and electron-deficient diarylacetylenes underwent the hydroarylation reaction with **2b** in good to excellent yields. It was observed that the reaction of diarylacetylenes **1** bearing electron-rich functional groups with **2b** gave much better yields of hydroarylated product. Diarylacetylenes **1d**, **1e**, and **1f**, reacted smoothly with **2b** to afford **3db**, **3eb**, and **3fb** in 95%, 90%, and 90% yields, respectively (entries 4–6). It was reported that heteroarylboronic acids were not suitable substrates since the heteroatoms may coordinate to transition metal.[13] However, good yield of product **3hb** was furnished in the reaction of di(thiophen-3-yl)acetylene **1h** with **2b** (entry 8). Next, a series of arylboronic acids containing different substituted were investigated. The results showed that the mono-substituted group on the arylboronic acid had little influence on the reaction (entries 9–22). To our delight, a number of functional groups, including ether, halide, formyl, nitro, and cyano groups were readily tolerated in this system. Boronic acids **2c** and **2d** containing a *p*-chloro or *p*-fluoro group, for example, were treated with substrate **1a** using $PdCl_2$/**L2** system smoothly affording the arylated products in 92% and 89% yields, respectively (entries 17 and 18). Diarylacetylenes **1f** bearing chloro group underwent the hydroarylation reaction with arylboronic acids **2a**, **2c**, and **2e**, respectively, to produce corresponding alkenes in excellent yields (entries 14, 19, and 20). In addition, we found that reaction of **1f** with electron-deficient arylboronic acids **2f** and **2g** gave the desired products in relatively lower yields (entries 21 and 22), due to formation of homocoupling and protodeboronation byproducts as determined by GC–MS analysis.

Table 2
$PdCl_2$-catalyzed hydroarylation of alkynes with arylboronic acids[a]



Entry	R^1 (**1**)	R^2 (**2**)	Product	Yield[b] (%)
1	Ph **1a**	3-(OMe)C_6H_4 **2b**	**3ab**	95
2	4-Me–C_6H_4 **1b**	3-(OMe)C_6H_4 **2b**	**3bb**	82
3	3,5-(Me)$_2$–C_6H_3 **1c**	3-(OMe)C_6H_4 **2b**	**3cb**	89
4	4-MeO–C_6H_4 **1d**	3-(OMe)C_6H_4 **2b**	**3db**	95
5	4-F–C_6H_4 **1e**	3-(OMe)C_6H_4 **2b**	**3eb**	90
6	4-Cl–C_6H_4 **1f**	3-(OMe)C_6H_4 **2b**	**3fb**	90
7	3-OHC–C_6H_4 **1g**	3-(OMe)C_6H_4 **2b**	**3gb**	62
8	3-Thienyl **1h**	3-(OMe)C_6H_4 **2b**	**3hb**	80
9	Ph **1a**	Ph **2a**	**3aa**	96
10	4-Me–C_6H_4 **1b**	Ph **2a**	**3ba**	99
11	3,5-(Me)$_2$–C_6H_3 **1c**	Ph **2a**	**3ca**	94
12	4-MeO–C_6H_4 **1d**	Ph **2a**	**3da**	95
13	4-F–C_6H_4 **1e**	Ph **2a**	**3ea**	79
14	4-Cl–C_6H_4 **1f**	Ph **2a**	**3fa**	83
15	4-Me–C_6H_4 **1b**	4-Cl–C_6H_4 **2c**	**3bc**	86
16	4-F–C_6H_4 **1e**	4-Cl–C_6H_4 **2c**	**3ec**	84
17	Ph **1a**	4-Cl–C_6H_4 **2c**	**3ac**	92
18	Ph **1a**	4-F–C_6H_4 **2d**	**3ad**	89
19	4-Cl–C_6H_4 **1f**	4-Cl–C_6H_4 **2c**	**3fc**	86
20	4-Cl–C_6H_4 **1f**	4-F_3C–C_6H_4 **2e**	**3fe**	84
21	4-Cl–C_6H_4 **1f**	4-NC–C_6H_4 **2f**	**3ff**	68
22	4-Cl–C_6H_4 **1f**	3-O_2N–C_6H_4 **2g**	**3fg**	51

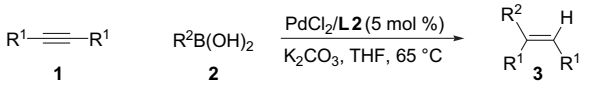
[a] Reactions were carried out using **1** (0.2 mmol), **2** (2 equiv), $PdCl_2$ (5 mol %), **L2** (5 mol %), and K_2CO_3 (3 equiv) in THF (3 mL) at 65 °C for 2–12 h.
[b] Isolated yield.

The steric effect was further examined and results were summarized in Table 3. As shown in Table 3, for most cases, the hydroarylation with hindered substrates also proceeded smoothly in excellent yields. For example, diarylacetylenes **1a**–**e** underwent the reaction successfully with **2i** in quantitative yields (entries 1–4). Naphthylboronic acid **2j** also react with **2a** giving 98% yield of target product (entry 9). Besides, the hydroarylation of dialkylacetylene **1k** with **2a** and **2i** also gave high yields (entries 11 and 12).

Finally, the hydroarylation of unsymmetric alkynes were examined in the hydroarylation reaction (Scheme 1). It has been reported that the aryl alkyl alkyne **1m** is prone to low regioselectivity as a result of the nature of substitutents.[11] However, under the optimal reaction conditions, **1m** could proceed smoothly with arylboronic acid **2a**, **2b**, or **2i** to furnish the corresponding olefins

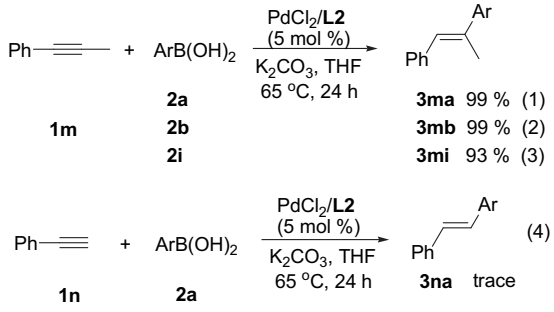
3ma, **3mb**, or **3mi** in excellent yields and regioselectivities (Eqs. 1–3). The addition of the aryl groups occurs exclusively at the β-position of the phenyl group. The ability of the catalytic system to perform the hydroarylation in excellent yields and high regioselectivities may be a consequence of the intrinsic properties (steric and electronic) of the phosphine.[14] Unfortunately, the reaction of phenylacetylene (**1n**) with phenylboronic acid (**2a**) was unsuccessful under the same reaction condition (Eq. 4). May because of C–H of terminal alkynes, in the metal-catalyzed reaction, is so active that could not contain in the present of base.

Table 3
$PdCl_2$-catalyzed hydroarylation of alkynes with arylboronic acids[a]



Entry	1	2	Product	Yield[b] (%)
1	Ph **1a**	2-Me–C_6H_4 **2i**	**3ai**	99
2	4-Me–C_6H_4 **1b**	2-Me–C_6H_4 **2i**	**3bi**	99
3	3,5-$(Me)_2$–C_6H_3 **1c**	2-Me–C_6H_4 **2i**	**3ci**	99
4	4-MeO–C_6H_4 **1d**	2-Me–C_6H_4 **2i**	**3di**	99
5	4-F–C_6H_4 **1e**	2-Me–C_6H_4 **2i**	**3ei**	96
6	3-Thienyl **1h**	2-Me–C_6H_4 **2i**	**3hi**	89
7	2-Me–C_6H_4 **1i**	Ph **2a**	**3ia**	86
8	1-Nap **1j**	Ph **2a**	**3ja**	98
9	Ph **1a**	1-Nap **2j**	**3aj**	98
10	2-Me–C_6H_4 **1i**	2-Me–C_6H_4 **2i**	**3ii**	75
11	*n*-Pr **1k**	Ph **2a**	**3ka**	82
12	*n*-Pr **1k**	2-Me–C_6H_4 **2i**	**3ki**	86

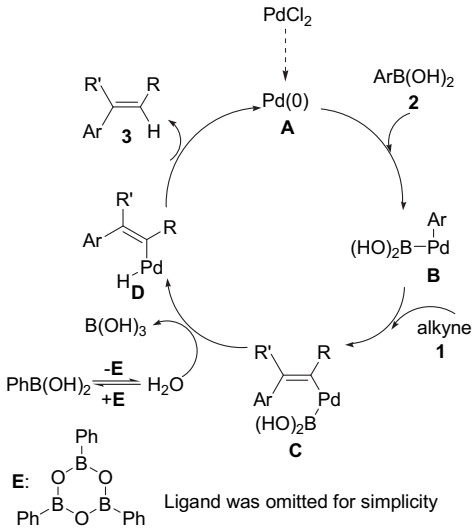
[a] Reactions were carried out using **1** (0.2 mmol), **2** (2 equiv), $PdCl_2$ (5 mol %), **L2** (5 mol %), and K_2CO_3 (3 equiv) in THF (3 mL) at 65 °C for 2–12 h.
[b] Isolated yield.



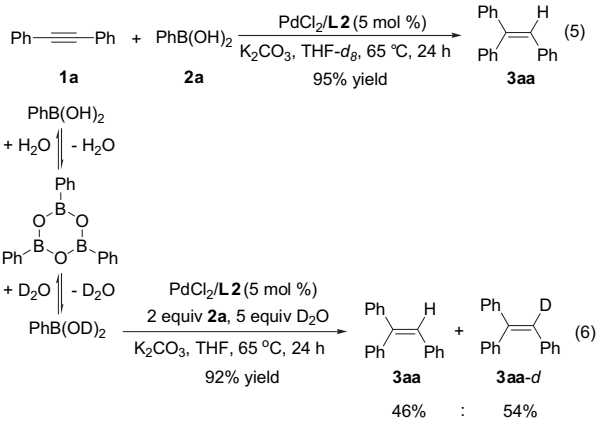
Scheme 1.

The mechanism of the reaction is suggested in Scheme 2. First, the oxidative addition of Pd(0) species **A** with arylboronic acid **2** readily occurs to afford intermediate **B**.[11,15] On the one hand, the employment of electron-rich aminophosphine ligand facilitates this oxidative addition step. However, no reaction could be carried out in the absence of bases, so we think that C–B possible be activated by base. Subsequently, the selective insertion of alkyne **1** into the Pd–C in a *syn* fashion take place to give intermediate **C**. Hydrolysis of **C** followed by reductive elimination of the **D** finally gives the hydroarylating products **3** and regenerates the active Pd(0) species.

To confirm the source of the hydrogen on the vinylic carbon, isotope-labeling study was carried out (Scheme 3). In THF-d_8, **3aa** was almost exclusively formed in excellent yield (Eq. 5). So the hydrogen is not from solvent. There is an equilibrium between $PhB(OH)_2$ and triphenylboroxin,[16] and the process can generate water for hydrolysis. Next, the use of 5 equiv D_2O in THF resulted in the formation of the two products **3aa** and **3aa**-*d* (46:54) (Eq. 6) in 92% isolated yield. Those findings gave direct evidences to support our proposed mechanism.



Scheme 2. Proposed mechanism for palladium-catalyzed hydrophenylation of alkynes with arylboronic acids.



Scheme 3.

The presence of acetic acid has been generally believed to be fundamental for the success of the palladium-catalyzed hydroarylation of alkynes. The present study shows importantly that the alkenylpalladium intermediates **C** could be smoothly hydrolyzed even in basic media. It is noteworthy that no acid is involved in the catalytic cycle.

3. Conclusion

In summary, we have developed a palladium-catalyzed hydroarylation of symmetrical and unsymmetrical alkynes with arylboronic acids by use of the easy-handling *i*-Pr_2NPPh_2 as the ligand and in the presence of inorganic base. This reaction would be a good approach for synthesis of functionalized alkenes. It should be mentioned that the aryl alkyl acetylene (1-phenylpropyne) was firstly transformed to alkenes with high regioselectivity by Pd-catalyzed addition reaction. Further studies on this chemistry and its application of palladium-catalyzed addition protocol are currently underway.

4. Experimental section

4.1. General

Chemical reagents were either purchased or purified by standard techniques. Diarylacetylenes[17] and aminophosphine ligands[14]

were prepared according to the reported procedures. ^{1}H and ^{13}C NMR spectroscopy was performed on both a Bruck-300 spectrometer operating at 300 MHz (^{1}H NMR) and 75 MHz (^{13}C NMR), and ^{19}F NMR spectroscopy was performed on a Bruck-500 spectrometer operating at 470 MHz. TMS (tetramethylsilane) was used as an internal standard and $CDCl_3$ was used as the solvent. Mass spectrometric analysis was performed on GC–MS analysis (SHIMADZU GC–MS-QP2010). Elemental analysis was determined on a Carlo-Erba 1108 instrument. Column chromatography was performed using EM Silica gel 60 (300–400 mesh).

4.2. General procedure for synthesis of trisubstituted olefins

Under a nitrogen atmosphere, a mixture of alkynes **1** (0.2 mmol), arylboronic acid **2** (2 equiv), $PdCl_2$ (5 mol%), **L2** (5 mol%), and K_2CO_3 (3 equiv) in THF (3 mL) was stirred at room temperature for 30 min and then heated to 65 °C for a period of time. After completion of the reaction as indicated by TLC, the reaction mixture was cooled to room temperature. The residue was diluted with EtOAc (5.0 mL) and washed with water (5 mL). Evaporation of the solvent followed by purification on silica gel afforded the corresponding product **3**. The organic layers were dried over $MgSO_4$, concentrated, and purified by flash column chromatography on silica gel to give the desired product.

*4.2.1. (E)-1-(2-Phenyl-2-m-methoxyphenylvinyl)benzene (**3ab**)*[18]. Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.77 (s, 3H), 6.81–6.92 (m, 3H), 6.97 (s, 1H), 7.01–7.22 (m, 8H), 7.30–7.36 (m, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 55.2, 112.8, 113.4, 120.2, 126.8, 127.4, 127.9, 128.3, 128.6, 129.1, 129.5, 130.3, 137.2, 140.2, 142.4, 144.9, 159.4.

*4.2.2. (E)-1-Methyl-4-(2-m-methoxyphenyl-2-p-tolylvinyl) benzene (**3bb**).* Yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.26 (s, 3H), 2.37 (s, 3H), 3.76 (s, 3H), 6.79–6.94 (m, 8H), 7.07–7.23 (m, 5H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.2, 21.3, 55.2, 112.6, 113.3, 120.2, 128.0, 128.7, 129.0, 129.3, 129.4, 130.2, 134.5, 136.5, 136.9, 137.3, 141.5, 145.3, 159.4. IR ($CH_3CO_2C_2H_5$): 3018, 2923, 1594, 1047 cm^{-1}; LRMS (EI, 70 eV) *m*/*z* (%): 314 (M^+, 100), 315 (25), 299 (24), 284 (17). Anal. Calcd for $C_{23}H_{22}O$: C, 87.86; H, 7.05. Found: C, 87.79; H, 6.99.

*4.2.3. (E)-1,3-Dimethyl-5-(2-(3,5-dimethylphenyl)-2-m-methoxyphenylvinyl)benzene (**3cb**).* Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.13 (s, 6H), 2.26 (s, 6H), 3.78 (s, 3H), 6.64–6.75 (m, 3H), 6.82–6.95 (m, 7H), 7.18–7.24 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.22, 21.23, 55.2, 112.4, 113.3, 120.2, 127.5, 127.7, 128.1, 128.5, 128.9, 129.0, 137.0, 137.1, 137.9, 140.1, 142.1, 145.3, 159.4. IR ($CH_3CO_2C_2H_5$): 3038, 3018, 1453, 783 cm^{-1}; LRMS (EI, 70 eV) *m*/*z* (%): 342 (M^+, 100), 327 (13), 312 (17). Anal. Calcd for $C_{25}H_{26}O$: C, 87.68; H, 7.65. Found: C, 87.62; H, 7.72.

*4.2.4. (E)-1-(2-m-Methoxyphenyl-2-p-methoxyphenylvinyl)-4-methoxybenzene (**3db**).* Yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.74 (s, 3H), 3.76 (s, 3H), 3.82 (s, 3H), 6.67–6.69 (m, 2H), 6.79–7.00 (m, 8H), 7.11–7.23 (m, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 55.09, 55.14, 55.2, 112.5, 113.2, 113.4, 114.0, 120.1, 127.5, 129.0, 130.2, 130.7, 131.5, 132.6, 140.1, 145.5, 158.2, 158.8, 159.4. IR ($CH_3CO_2C_2H_5$): 2952, 2835, 1601, 1508, 1248 cm^{-1}; LRMS (EI, 70 eV) *m*/*z* (%): 346 (M^+, 100), 331 (6), 195 (25), 152 (6). Anal. Calcd for $C_{23}H_{22}O_3$: C, 79.74; H, 6.40. Found: C, 79.66; H, 6.36.

*4.2.5. (E)-1-(2-m-Methoxyphenyl-2-p-fluorophenylvinyl)-4-fluorobenzene (**3eb**).* White solid, mp 89–91 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.77 (s, 3H), 6.80–7.04 (m, 10H), 7.12–7.25 (m, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 55.2, 113.2 (d, J_{C-F}=35.8 Hz), 115.0 (d, J_{C-F}=21.4 Hz), 115.6, 115.9, 120.1, 127.4, 129.2, 131.1 (d, J_{C-F}=7.6 Hz), 132.1 (d, J_{C-F}=7.6 Hz), 133.2 (d, J_{C-F}=2.8 Hz), 135.8 (d, J_{C-F}=3.4 Hz), 141.2 (d, J_{C-F}=1.4 Hz), 144.5, 159.5, 161.5 (d, J_{C-F}=246.2 Hz), 162.2 (d, J_{C-F}=245.6 Hz). ^{19}F NMR (470 MHz) δ: −114.3, −114.4. IR ($CH_3CO_2C_2H_5$): 3403, 2924, 2361, 1205 cm^{-1}; LRMS (EI, 70 eV) *m*/*z* (%): 322 (M^+, 100), 289 (15), 288 (12), 183 (14). Anal. Calcd for $C_{21}H_{16}F_2O$: C, 78.25; H, 5.00. Found: C, 78.28; H, 4.94.

*4.2.6. (E)-1-(2-m-Methoxyphenyl-2-p-chlorophenylvinyl)-4-chlorobenzene (**3fb**).* Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.77 (s, 3H), 6.81–6.95 (m, 6H), 7.10–7.32 (m, 7H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 55.2, 113.1, 113.5, 120.2, 127.4, 128.3, 129.0, 129.2, 130.7, 131.7, 132.6, 133.5, 135.4, 138.2, 141.9, 144.1, 159.5. IR ($CH_3CO_2C_2H_5$): 2937, 2360, 1589, 1485, 1092 cm^{-1}; LRMS (EI, 70 eV) *m*/*z* (%): 352 (M^+, 100), 254 (68), 253 (70), 252 (73). Anal. Calcd for $C_{21}H_{16}Cl_2O$: C, 71.00; H, 4.54. Found: C, 69.94; H, 4.57.

*4.2.7. (E)-1-(2-m-Methoxyphenyl-2-m-formylphenylvinyl)-3-formylbenzene (**3gb**).* Yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.80 (s, 3H), 6.84–6.90 (m, 6H), 7.09–7.27 (m, 4H), 7.48–7.88 (m, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 55.2, 113.3, 113.6, 120.2, 127.7, 128.0, 128.8, 129.0, 129.4, 129.5, 131.0, 131.7, 135.1, 136.3, 136.5, 136.8, 137.7, 140.7, 142.8, 143.5, 159.6, 192.0. IR ($CH_3CO_2C_2H_5$): 3379, 2833, 2726, 1698, 1586 cm^{-1}; LRMS (EI, 70 eV) *m*/*z* (%): 342 (M^+, 100), 253 (43), 252 (36), 149 (60). Anal. Calcd for $C_{23}H_{18}O_3$: C, 80.68; H, 5.30. Found: C, 80.65; H, 5.37.

*4.2.8. (Z)-3-(2-m-Methoxyphenyl-2-(thiophen-3-yl)vinyl)thiophene (**3hb**).* Yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.78 (s, 3H), 6.57–6.58 (m, 1H), 6.80–7.26 (m, 9H), 7.38–7.39 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 55.2, 112.6, 112.8, 119.5, 123.0, 124.4, 124.6, 124.7, 125.9, 128.0, 129.1, 129.2, 135.5, 138.9, 140.3, 143.8, 159.4. IR ($CH_3CO_2C_2H_5$): 3100, 2936, 2836, 1592, 1278 cm^{-1}; LRMS (EI, 70 eV) *m*/*z* (%): 298 (M^+, 100), 267 (26), 265 (25), 234 (21). Anal. Calcd for $C_{17}H_{14}OS_2$: C, 68.42; H, 4.73. Found: C, 68.48; H, 4.80.

*4.2.9. 1,1,2-Triphenylethene (**3aa**)*[12f]. Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.97 (s, 1H), 7.01–7.04 (m, 2H), 7.09–7.25 (m, 5H), 7.28–7.35 (m, 8H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 126.7, 127.4, 127.5, 127.6, 127.9, 128.15, 128.18, 128.6, 129.5, 130.4, 137.4, 140.4, 142.6, 143.4.

*4.2.10. (Z)-1-Methyl-4-(2-phenyl-2-p-tolylvinyl)benzene (**3ba**)*[12f]. Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.25 (s, 3H), 2.37 (s, 3H), 6.89 (s, 1H), 6.94–7.07 (m, 4H), 7.10–7.20 (m, 4H), 7.26–7.30 (m, 5H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.2, 21.3, 127.2, 127.5, 127.9, 128.1, 128.7, 129.3, 129.4, 130.2, 134.6, 136.4, 136.9, 137.5, 141.6, 143.8.

*4.2.11. (Z)-1,3-Dimethyl-5-(2-(3,5-dimethylphenyl)-2-phenylvinyl)benzene (**3ca**).* Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.13 (s, 6H), 2.26 (s, 6H), 6.65–6.75 (m, 3H), 6.83–6.96 (m, 4H), 7.23–7.35 (m, 5H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.21, 21.22, 127.2, 127.4, 127.5, 127.7, 127.9, 128.1, 128.4, 128.8, 127.12, 137.14, 138.0, 140.3, 142.3, 143.7. IR ($CH_3CO_2C_2H_5$): 2918, 1598, 1445, 697 cm^{-1}; LRMS (EI, 70 eV) *m*/*z* (%): 312 (M^+, 100), 297 (14), 282 (25). Anal. Calcd for $C_{24}H_{24}$: C, 92.26; H, 7.74. Found: C, 92.20; H, 7.69.

*4.2.12. (Z)-1-(2-Phenyl-2-p-methoxyphenylvinyl)-4-methoxybenzene (**3da**)*[19]. Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.74 (s, 3H), 3.83 (s, 3H), 6.67–6.70 (m, 2H), 6.86–6.89 (m, 3H), 6.98–7.01 (m, 2H), 7.11–7.14 (m, 2H), 7.23–7.31 (m, 5H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 55.09, 55.14, 113.3, 114.0, 127.1, 127.3, 127.4, 128.1, 130.2, 130.7, 131.6, 132.7, 140.2, 143.9, 158.2, 158.7.

*4.2.13. (Z)-1-(2-Phenyl-2-p-fluorophenylvinyl)-4-fluoro benzene (**3ea**).* White solid, mp 61–63 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.80–6.86 (m, 2H), 6.91 (s, 1H), 6.96–7.17 (m, 6H), 7.27–7.31 (m, 5H). ^{13}C

NMR ($CDCl_3$, 75 MHz) δ 115.0 (d, J_{C-F}=21.4 Hz), 115.7 (d, J_{C-F}=21.3 Hz), 127.2, 127.5, 127.7, 128.3, 131.1 (d, J_{C-F}=7.6 Hz), 132.1 (d, J_{C-F}=7.6 Hz), 133.3, 135.9, 141.4, 143.0, 161.5 (d, J_{C-F}=245.6 Hz), 162.2 (d, J_{C-F}=245.5 Hz). ^{19}F NMR (470 MHz) δ: −114.3, −114.5. IR ($CH_3CO_2C_2H_5$): 3400, 2924, 2401, 1505, 1228 cm^{-1}; LRMS (EI, 70 eV) *m*/*z* (%): 292 (M^+, 100), 293 (20), 271 (22), 196 (21). Anal. Calcd for $C_{20}H_{14}F_2$: C, 82.17; H, 4.83. Found: C, 82.11; H, 4.78.

*4.2.14. (Z)-1-(2-Phenyl-2-p-chlorophenylvinyl)-4-chloro benzene (**3fa**).* Colorless oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.89–6.96 (m, 3H), 7.10–7.13 (m, 4H), 7.26–7.31 (m, 7H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 127.3, 127.6, 127.9, 128.28, 128.33, 129.0, 130.7, 131.8, 132.6, 133.5, 135.5, 138.4, 142.0, 142.7. IR ($CH_3CO_2C_2H_5$): 3409, 3025, 2925, 1489, 1090 cm^{-1}; LRMS (EI, 70 eV) *m*/*z* (%): 324 (M^+, 100), 254 (92), 253 (72), 126 (75). Anal. Calcd for $C_{20}H_{14}Cl_2$: C, 73.86; H, 4.34. Found: C, 73.80; H, 4.41.

*4.2.15. (E)-1-Methyl-4-(2-o-chlorophenyl-2-p-tolylvinyl) benzene (**3bc**)[12f].* Yellow oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.26 (s, 3H), 2.37 (s, 3H), 6.86 (s, 1H), 6.90–6.93 (m, 4H), 7.04–7.15 (m, 4H), 7.20–7.26 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.2, 21.3, 128.2, 128.7, 128.8, 129.1, 129.4, 130.1, 131.4, 133.0, 134.3, 136.7, 137.0, 137.2, 140.5, 142.3.

*4.2.16. (E)-1-(2-p-Chlorophenyl-2-p-fluorophenylvinyl)-4-fluorobenzene (**3ec**).* White solid, mp 71–73 °C; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.81–6.88 (m, 3H), 6.95–7.06 (m, 4H), 7.10–7.22 (m, 4H), 7.27–7.29 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 115.1 (d, J_{C-F}=21.3 Hz), 115.9 (d, J_{C-F}=20.6 Hz), 127.6, 128.4, 128.8, 131.1 (d, J_{C-F}=7.6 Hz), 132.0 (d, J_{C-F}=8.3 Hz), 133.0 (d, J_{C-F}=3.4 Hz), 133.6, 135.5 (d, J_{C-F}=3.4 Hz), 140.2 (d, J_{C-F}=2.1 Hz), 141.5, 161.6 (d, J_{C-F}=246.2 Hz), 162.3 (d, J_{C-F}=246.2 Hz). ^{19}F NMR (470 MHz) δ: −113.8, −114.1; IR ($CH_3CO_2C_2H_5$): 2921, 1598, 1504, 1228, 830 cm^{-1}; LRMS (EI, 70 eV) *m*/*z* (%): 326 (M^+, 100), 290 (21), 271 (25), 270 (21). Anal. Calcd for $C_{20}H_{13}ClF_2$: C, 73.51; H, 4.01. Found: C, 73.58; H, 3.94.

*4.2.17. (E)-1-(2-Phenyl-2-p-chlorophenylvinyl)benzene (**3ac**)[12f].* Colorless oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.93 (s, 1H), 6.99–7.03 (m, 2H), 7.11–7.19 (m, 5H), 7.25–7.34 (m, 7H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 126.9, 127.6, 128.0, 128.3, 128.5, 128.7, 128.8, 129.5, 130.3, 133.3, 137.1, 139.9, 141.4, 141.9.

*4.2.18. (E)-1-(2-Phenyl-2-p-fluorophenylvinyl)benzene (**3ad**)[20].* White solid, mp 61–62 °C; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.89 (s, 1H), 6.95–7.03 (m, 4H), 7.10–7.19 (m, 5H), 7.25–7.32 (m, 5H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 115.0 (d, J_{C-F}=21.2 Hz), 126.8, 127.5, 128.0, 128.7, 129.2, 129.3, 129.5, 130.3, 137.2, 139.6 (d, J_{C-F}=2.8 Hz), 140.2, 141.6, 162.4 (d, J_{C-F}=245.5 Hz). ^{19}F NMR (470 MHz) δ: −114.9.

*4.2.19. 1,1,2-Tri-p-chlorophenylethene (**3fc**)[21].* Colorless oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.87 (s, 1H), 6.92–6.95 (m, 2H), 7.07–7.21 (m, 6H), 7.26–7.32 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 127.7, 128.3, 128.5, 128.8, 129.1, 130.2, 130.7, 131.7, 132.8, 133.8, 135.2, 137.9, 140.9, 141.1.

*4.2.20. (Z)-1-(2-p-(Trifluoromethyl)phenyl-2-p-chlorophenylvinyl)-4-chlorobenzene (**3fe**).* White solid, mp 105–108 °C; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.95–6.98 (m, 3H), 7.01–7.16 (m, 4H), 7.31–7.39 (m, 4H), 7.55–7.58 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 125.293 (q, J_{C-F}=3.8 Hz), 127.725 (q, J_{C-F}=270.8 Hz), 127.833, 128.429, 129.162, 129.254, 129.942, 130.804, 131.675, 133.986, 134.940, 137.636, 140.754, 146.192. ^{19}F NMR (470 MHz) δ: −62.4; IR ($CH_3CO_2C_2H_5$): 3041, 2929, 1912, 1325, 1124 cm^{-1}; LRMS (EI, 70 eV) *m*/*z* (%): 392 (M^+, 100), 322 (60), 252 (37), 126 (31). Anal. Calcd for $C_{21}H_{13}Cl_2F_3$: C, 64.14; H, 3.33. Found: C, 64.19; H, 3.40.

*4.2.21. (Z)-1-(2-p-Cyanophenyl-2-p-chlorophenylvinyl)-4-chlorobenzene (**3ff**).* Yellow solid, mp 85–87 °C; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.95–6.98 (m, 3H), 7.08–7.16 (m, 4H), 7.33–7.39 (m, 4H), 7.59–7.62 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 111.1, 118.8, 128.0, 128.5, 129.4, 130.0, 130.8, 131.6, 132.1, 133.4, 134.2, 134.6, 137.2, 140.3, 147.0. IR ($CH_3CO_2C_2H_5$): 3401, 3038, 2226, 1597, 1092 cm^{-1}; LRMS (EI, 70 eV) *m*/*z* (%): 349 (M^+, 100), 351 (63), 279 (86), 278 (60). Anal. Calcd for $C_{21}H_{13}Cl_2N$: C, 72.01; H, 3.74; N, 4.00. Found: C, 72.09; H, N, 3.67.

*4.2.22. (E)-1-(2-m-Nitrophenyl-2-p-chlorophenylvinyl)-4-chlorobenzene (**3fg**).* Yellow solid, mp 91–93 °C; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.97–7.17 (m, 6H), 7.34–8.25 (m, 7H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 122.1, 122.5, 123.5, 128.5, 129.3, 129.5, 129.7, 130.8, 131.6, 133.5, 134.3, 134.6, 137.0, 139.7, 144.4, 148.4. IR ($CH_3CO_2C_2H_5$): 2923, 2358, 1261, 1024, 805 cm^{-1}; LRMS (EI, 70 eV) *m*/*z* (%): 369 (M^+, 100), 371 (69), 252 (97), 126 (52). Anal. Calcd for $C_{20}H_{13}Cl_2NO_2$: C, 64.88; H, 3.54. Found: C, 64.94; H, 3.59.

*4.2.23. (E)-1-(2-Phenyl-2-o-tolylvinyl)benzene (**3ai**)[12f].* Colorless oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.11 (s, 3H), 6.61 (s, 1H), 7.14–7.22 (m, 14H), 7.26–7.29 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.5, 125.6, 126.7, 127.1, 127.4, 128.0, 128.2, 129.4, 129.9, 130.1, 130.2, 130.4, 136.2, 137.4, 140.2, 142.9, 144.0.

*4.2.24. 1,1,2-Tri-o-tolylethene (**3bi**).* Colorless oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.10 (s, 3H), 2.29 (s, 3H), 2.30 (s, 3H), 6.53 (s, 1H), 6.96–7.06 (m, 8H), 7.15–7.27 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.5, 21.19, 21.24, 125.5, 127.2, 128.7, 128.9, 129.2, 129.5, 129.7, 130.1, 130.3, 134.6, 136.3, 136.4, 136.7, 137.4, 142.0, 144.4. IR ($CH_3CO_2C_2H_5$): 3016, 2920, 1508, 1449, 1043 cm^{-1}; LRMS (EI, 70 eV) *m*/*z* (%): 298 (M^+, 100), 283 (33), 193 (33), 105 (29). Anal. Calcd for $C_{23}H_{22}$: C, 92.57; H, 7.43. Found: C, 92.62; H, 7.38.

*4.2.25. (E)-1,3-Dimethyl-5-(2-(3,5-dimethylphenyl)-2-o-tolyl vinyl)-benzene (**3ci**).* Colorless oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.16–2.18 (m, 15H), 6.47 (s, 1H), 6.75–6.84 (m, 6H), 7.16–7.23 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.6, 21.18, 21.21, 125.5, 127.1, 127.2, 127.4, 128.4, 128.7, 130.1, 130.3, 136.2, 137.2, 137.3, 140.1, 142.5, 144.4. IR ($CH_3CO_2C_2H_5$): 3011, 2919, 2861, 1597, 1041 cm^{-1}; LRMS (EI, 70 eV) *m*/*z* (%): 326 (M^+, 100), 220 (39), 207 (52), 205 (51). Anal. Calcd for $C_{25}H_{26}$: C, 91.97; H, 8.03. Found: C, 92.02; H, 8.09.

*4.2.26. (E)-1-(2-p-Methoxyphenyl-2-o-tolylvinyl)-4-methoxy benzene (**3di**).* Yellow oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.99 (s, 3H), 3.66–3.67 (m, 6H), 6.39 (s, 1H), 6.61–6.66 (m, 4H), 6.97–7.13 (m, 8H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.5, 55.0, 55.1, 113.4, 113.5, 125.5, 127.2, 128.6, 130.3, 130.5, 131.0, 132.8, 136.2, 140.7, 144.4, 158.2. IR ($CH_3CO_2C_2H_5$): 2956, 2836, 1604, 1508, 1247 cm^{-1}; LRMS (EI, 70 eV) *m*/*z* (%): 330 (M^+, 100), 222 (18), 209 (26), 121 (18). Anal. Calcd for $C_{23}H_{22}O_2$: C, 83.60; H, 6.71. Found: C, 83.67; H, 6.67.

*4.2.27. (E)-1-(2-o-Tolyl-2-p-fluorophenylvinyl)-4-fluoro benzene (**3ei**).* Colorless oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.08 (s, 3H), 6.56 (s, 1H), 6.85–6.93 (m, 4H), 7.06–7.25 (m, 8H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.5, 115.0 (d, J_{C-F}=16.6 Hz), 115.3 (d, J_{C-F}=16.5 Hz), 125.7, 127.6, 129.0, 130.1, 130.5, 130.9 (d, J_{C-F}=7.6 Hz), 131.5 (d, J_{C-F}=8.3 Hz), 133.2 (d, J_{C-F}=3.4 Hz), 135.9 (d, J_{C-F}=3.4 Hz), 136.2, 141.8 (d, J_{C-F}=1.3 Hz), 143.5, 161.6 (d, J_{C-F}=245.6 Hz), 161.9 (d, J_{C-F}=246.2 Hz). ^{19}F NMR (470 MHz) δ: −114.5, −114.7. IR ($CH_3CO_2C_2H_5$): 2925, 2359, 1599, 1506, 128 cm^{-1}; LRMS (EI, 70 eV) *m*/*z* (%): 306 (M^+, 100), 291 (31), 197 (84), 196 (39). Anal. Calcd for $C_{21}H_{16}F_2$: C, 82.33; H, 5.26. Found: C, 82.37; H, 5.32.

*4.2.28. (E)-3-(2-o-Tolyl-2-(thiophen-3-yl)vinyl)thiophene (**3hi**).* Colorless oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.09 (s, 3H), 6.52 (s, 1H), 6.83–6.84 (m, 1H), 6.91–7.28 (m, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.2, 124.0, 124.2, 124.4, 124.7, 124.8, 125.6, 127.4, 128.1, 128.8,

129.6, 130.3, 136.2, 136.8, 138.7, 141.1, 143.7. IR ($CH_3CO_2C_2H_5$): 3099, 3015, 1452, 863, 769 cm^{-1}; LRMS (EI, 70 eV) *m*/*z* (%): 282 (M^+, 100), 267 (26), 234 (47), 135 (21). Anal. Calcd for $C_{17}H_{14}S_2$: C, 72.30; H, 5.00. Found: C, 72.37; H, 4.94.

*4.2.29. (Z)-1-Methyl-2-(2-phenyl-2-o-tolylvinyl)benzene (**3ia**).* Yellow oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.99 (s, 3H), 2.38 (s, 3H), 6.67–6.82 (m, 2H), 6.97–7.21 (m, 7H), 7.26–7.32 (m, 5H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.8, 20.2, 125.2, 125.8, 126.8, 126.9, 127.1, 127.3, 128.3, 128.4, 128.6, 129.7, 130.2, 130.8, 136.5, 136.7, 136.8, 139.5, 142.0, 142.7; LRMS (EI, 70 eV) *m*/*z* (%): 284 (M^+, 100), 269 (56), 192 (50), 179 (44). Anal. Calcd for $C_{22}H_{20}$: C, 92.91; H, 7.09. Found: C, 92.86; H, 7.15.

*4.2.30. (Z)-1-(2-(Naphthalen-1-yl)-2-phenylvinyl) naphthalene (**3ja**).* White solid, mp 145–147 °C; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.82–6.90 (m, 2H), 7.18–7.51 (m, 12H), 7.69–7.87 (m, 5H), 7.21–7.24 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 124.4, 125.1, 125.5, 125.59, 125.60, 125.9, 126.0, 126.3, 126.4, 126.8, 126.9, 127.2, 127.6, 127.7, 127.9, 128.30, 128.32, 128.5, 132.3, 132.5, 133.3, 133.7, 134.6, 137.6, 142.8, 142.9. IR ($CH_3CO_2C_2H_5$): 3019, 2920, 1487, 1451 cm^{-1}; LRMS (EI, 70 eV) *m*/*z* (%): 356 (M^+, 100), 279 (68). Anal. Calcd for $C_{28}H_{20}$: C, 94.34; H, 5.66. Found: C, 94.39; H, 5.72.

*4.2.31. (E)-1-(2-(Naphthalen-1-yl)-2-phenylvinyl)benzene (**3aj**)*[22]. colorless oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.97 (s, 1H), 7.01–7.04 (m, 2H), 7.09–7.25 (m, 5H), 7.28–7.35 (m, 8H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 126.7, 127.4, 127.5, 127.6, 127.9, 128.15, 128.18, 128.6, 129.5, 130.4, 137.4, 140.4, 142.6, 143.4.

*4.2.32. 1,1,2-Tri-o-tolylethene (**3ii**).* Colorless oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.92 (s, 3H), 2.23 (s, 3H), 2.31 (s, 3H), 6.72–6.84 (m, 3H), 7.00–7.21 (m, 10H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.9, 20.2, 20.7, 125.2, 125.5, 125.6, 126.9, 127.0, 127.1, 128.9, 129.8, 130.1, 130.3, 130.7, 130.76, 130.79, 135.9, 136.2, 136.4, 136.9, 140.0, 142.0, 143.6. IR ($CH_3CO_2C_2H_5$): 3059, 3016, 2923, 1453, 767 cm^{-1}; LRMS (EI, 70 eV) *m*/*z* (%): 298 (M^+, 100), 283 (63), 268 (31), 105 (43). Anal. Calcd for $C_{23}H_{22}$: C, 92.57; H, 7.43. Found: C, 92.62; H, 7.50.

*4.2.33. (E)-4-Phenyl-4-octene (**3ka**)*[2]. Colorless oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.88 (t, *J*=7.5 Hz, 3H), 0.96 (t, *J*=7.5 Hz, 3H), 1.32–1.50 (m, 4H), 2.13–2.21 (m, 2H), 2.45–2.50 (m, 2H), 5.66 (t, *J*=7.2 Hz, 1H), 7.18–7.36 (m, 5H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.0, 21.8, 23.1, 30.6, 31.7, 43.5, 126.3, 128.1, 129.2, 140.0.

*4.2.34. (E)-4-o-Tolyl-4-octene (**3ki**)*[2]. Colorless oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.87 (t, *J*=7.2 Hz, 3H), 0.96 (t, *J*=7.5 Hz, 3H), 1.25–1.32 (m, 2H), 1.41–1.49 (m, 2H), 2.12–2.19 (m, 2H), 2.26–2.34 (m, 5H), 5.24 (t, *J*=7.2 Hz, 1H), 7.02–7.16 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.9, 14.2, 19.9, 21.4, 23.0, 30.1, 33.8, 125.1, 126.2, 129.0, 129.7, 129.9, 135.2, 140.5, 144.6.

*4.2.35. (E)-1,2-Diphenylpropene (**3ma**)*[23]. White solid, mp 80–82 °C; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.27 (s, 3H), 6.83 (s, 1H), 7.19–7.39 (m, 8H), 7.50–7.53 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.4, 126.0, 126.4, 127.2, 127.7, 128.1, 128.3, 129.1, 127.4, 138.3, 143.9.

*4.2.36. (E)-1-Phenyl-2-m-methoxyphenylpropene (**3mb**)*[6b]. Colorless oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.27 (s, 3H), 3.84 (s, 3H), 6.84–6.85 (m, 2H), 7.06–7.37 (m, 8H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.5, 55.2, 59.5, 111.9, 112.4, 118.5, 126.5, 127.8, 128.1, 129.1, 129.2, 137.2, 138.2, 145.5.

*4.2.37. (E)-1-Phenyl-2-o-tolylpropene (**3mi**).* Colorless oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.18 (s, 3H), 2.35 (s, 3H), 6.37 (s, 1H), 7.19–7.25 (m, 5H), 7.37–7.38 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.8, 19.9, 125.6, 126.4, 126.8, 128.0, 128.2, 128.9, 129.1, 130.2, 134.7, 138.0, 139.0, 145.8. IR ($CH_3CO_2C_2H_5$): 3019, 2360, 1598, 1444, 759 cm^{-1}; LRMS (EI, 70 eV) *m*/*z* (%): 208 (M^+, 94), 193 (100), 178 (72), 115 (77). Anal. Calcd for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.32; H, 7.81.

*4.2.38. Compounds **3aa** and **3aa**-d (46:54).* ^1H NMR ($CDCl_3$, 300 MHz) δ 6.96 (m, 0.46H), 7.01–7.33 (m, 15H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 126.7, 127.4, 127.5, 127.6, 127.9, 128.1, 128.2, 128.6, 129.50, 129.52, 130.4, 137.27, 137.34, 140.3, 142.5, 142.6, 143.38, 143.40.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2010.01.086.

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