JOC The Journal of Organic Chemistry

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Pd-Catalyzed Cross-Coupling Reactions of Hydrazones: Regioselective Synthesis of Highly Branched Dienes

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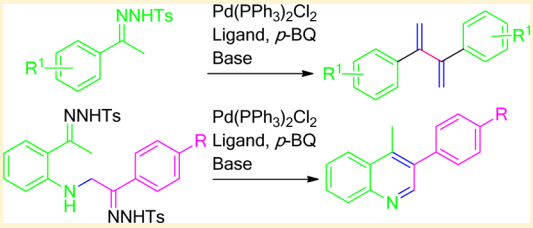
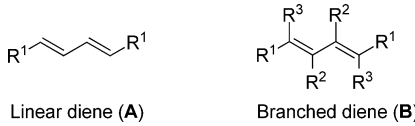
Supporting Information

ABSTRACT: The regioselective formation of highly branched dienes is a challenging task. Design and exploration of alternative working models to achieve such a regioselectivity to accomplish highly branched dienes is considered to be a historical advancement of Heck reaction to construct branched dienes. On the basis of the utility of carbene transfer reactions, in the reaction of hydrazones with Pd(II) under oxidative conditions, we envisioned obtaining a Pd-bis-carbene complex with α-hydrogens, which can lead to branched dienes. Herein, we report a novel Pd-catalyzed selective coupling reaction of hydrazones in the presence of *t*-BuOLi and benzoquinone to form the corresponding branched dienes. The utility of the Pd catalyst for the cross-coupling reactions for synthesizing branched conjugated dienes is rare. The reaction is very versatile and compatible with a variety of functional groups and is useful in synthesizing heterocyclic molecules. We anticipate that this Pd-catalyzed cross-coupling reaction will open new avenues for synthesizing useful compounds.



INTRODUCTION

Transition-metal-mediated cross-coupling reactions have been revolutionary for carbon−carbon-bond-forming reactions, particularly for the synthesis of conjugated dienes and polyenes.[1] Conjugated dienes and polyenes have been accomplished by employing organometallic nucleophiles such as boronic acids and its ester derivatives and organic halides, such as vinyl halides, vinyl sulfonates, and vinyl phosphates.[2] Among the transition-metal-catalyzed reactions for C−C-bond-forming reactions, Pd-catalyzed reactions are the most prominent. Coupling reactions such as Stille, Heck, Suzuki−Miyaura, Sonagashira, Negishi, and Kumada are a few prominent coupling reactions that have found very frequent citations and applications because of their extensive utility in organic synthesis. Ru-catalyzed en-yne metathesis has a remarkable output considering the ease of stereo- and regioselectivity in the construction of 1,3-dienes.[3] However, the challenges faced by chemists in synthesizing complex natural products has prompted the discovery of a large number of coupling reactions that are more efficient and atom economical and that lead to the synthesis of molecular scaffolds that are not easily accessible. Alkenes and 1,3-butadiene derivatives are an important class of organic compounds that can be accessed by Pd-catalyzed cross-coupling reactions. Conjugated dienes are important synthons in organic synthesis and are often synthesized by coupling reactions of alkenes with vinyl halides.[4] Generally, linear dienes such as **A** (Figure 1) can be easily synthesized, whereas the synthesis of branched dienes such as **B** (Figure 1) is cumbersome.[5] The regioselective formation of a branched diene (**B**) is a highly challenging task, which has been rarely achieved by coupling vinyl halides with organometallic reagents. Therefore, the design and exploration



Linear diene (**A**) Branched diene (**B**)

Figure 1. Linear and branched dienes ($R^2 \neq H$; $R^3 \neq H$).

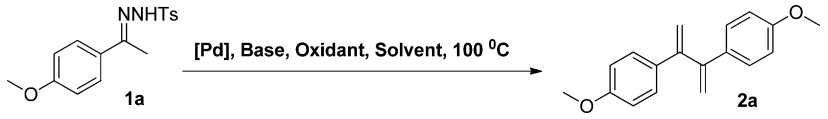
of alternative working models to achieve such a regioselectivity would be considered a historical advancement of the Heck reaction to construct branched dienes of type **B**. A Mizaroki−Heck reaction between an electronically biased olefin and vinyl halide in the presence of Pd can form a conjugated linear diene of type **A**.[6] Similarly, a reaction of olefin with vinyl boronic acid can lead to conjugated branched diene such as **B**.[5] Similarly, branched dienes can be accessed by employing Ru hydride-catalyzed dienyl isomerization reactions.[7] However, using a stoichiometric amount of SmI_2−Ac_2O results in the formation of branched dienes along with rearranged products.[8] Branched dienes can also be accessed using a transmetalation strategy by an organolithium-induced Shapiro reaction.[9] A large amount of precedence in the literature is available to show that there have been devoted efforts for Pd-catalyzed cross-coupling reactions for synthesizing linear conjugated dienes,[10] whereas their utility in synthesizing branched conjugated dienes has not been explored except for a recent report.[8b]

In this context and in light of our earlier study on Pd-catalyzed cross-coupling reactions,[11] we present our recent discovery, a novel Pd-catalyzed selective coupling reaction of hydrazones in the presence of base and oxidant to form the

Received: September 27, 2013
Published: November 18, 2013

   dx.doi.org/10.1021/jo402153t | J. Org. Chem. 2013, 78, 12136−12143

Table 1. Optimization Studies for the Formation of 1,3-Branched Dienes[a]



entry	[Pd]	base	oxidizing agent	ligand	yield (%)[b]
1	$Pd(PPh_3)_2Cl_2$	*t*-BuOLi	none	none	0
2	$Pd(PPh_3)_2Cl_2$	*t*-BuOLi	none	benzoxazole	trace
3	$Pd(PPh_3)_2Cl_2$	*t*-BuOLi	*p*-BQ	benzoxazole (20 mol %)	70
4	$Pd(PPh_3)_2Cl_2$	*t*-BuOLi	*p*-BQ	none	0
5	$Pd(PPh_3)_2Cl_2$	*t*-BuOLi	*p*-BQ	*N*-phenylurea (20 mol %)	trace
6	$Pd(PPh_3)_2Cl_2$	*t*-BuOLi	*p*-BQ	diazabutadiene (20 mol %)	60
7	$Pd(PPh_3)_2Cl_2$	*t*-BuOLi	*p*-BQ	xphos (20 mol %)	65
8	$Pd(PPh_3)_2Cl_2$	*t*-BuOLi	*p*-BQ	PPh_3(20 mol %)	25
9	$Pd(PPh_3)_2Cl_2$	Cs_2CO_3	$(NH4)_2S_2O_8$ (2.5 equiv)	xphos (20 mol %)	trace
10	$Pd(PPh_3)_2Cl_2$	Ag_2CO_3	$(NH4)_2S_2O_8$ (2.5 equiv)	xphos (20 mol %)	trace
11	$Pd(PPh_3)_2Cl_2$	*t*-BuOLi	PIDA (1.5 equiv)	xphos (20 mol %)	nd
12	$Pd(PPh_3)_2Cl_2$	*t*-BuOLi	$Cu(OAc)_2$ (1.3 equiv)	xphos (20 mol %)	nd
13	$Pd(PPh_3)_2Cl_2$	*t*-BuOLi	CuI (1.2 equiv)	xphos (20 mol %)	0
14	$Pd(PPh_3)_2Cl_2$	*t*-BuOLi	CuI (20 mol %)	xphos (20 mol %)	0
15	$Pd(PPh_3)_2Cl_2$	*t*-BuOLi	*p*-BQ	IPr·HCl (20 mol %)	nd
16	$Pd(PPh_3)_2Cl_2$	*t*-BuOLi	*p*-BQ	$P(Cy)_3$ (20 mol %)	40
17	$Pd(PPh_3)_2Cl_2$	*t*-BuOLi	*p*-BQ	bibenzoxazole (20 mol %)	80
18	$Pd(PPh_3)_2Cl_2$	*t*-BuOLi	*p*-BQ	$P(O\text{-}Tol)_3$ (20 mol %)	42
19	$Pd(OAc)_2$	*t*-BuOLi	*p*-BQ	bibenzoxazole (20 mol %)	<10
20	$Pd_2(dba)_3$	*t*-BuOLi	*p*-BQ	bibenzoxazole (20 mol %)	nd
21	$Pd(PPh_3)_4$	*t*-BuOLi	*p*-BQ	bibenzoxazole (20 mol %)	nd
22	$PdCl_2$	*t*-BuOLi	*p*-BQ	bibenzoxazole (20 mol %)	trace
23	$Pd(PPh_3)_2Cl_2$	*t*-BuOLi	*p*-BQ	bibenzoxazole (40 mol %)	84
24	$Pd(PPh_3)_4$	*t*-BuOLi	none	bibenzoxazole (40 mol %)	nd
25	none	*t*-BuOLi	*p*-BQ	bibenzoxazole (40 mol %)	nd

[a]Reaction conditions: **1a** (0.47 mmol), [Pd] (5 mol %), ligand (40 mol %), oxidant (1 mmol), base (1.5 mmol), dioxane (3 mL). [b]Isolated yields. nd, not detected.

corresponding branched dienes. A Pd-catalyzed coupling reaction of tosylhydrazones with a variety of nucleophiles to obtain corresponding dienes has been explored in greater detail by Barluenga and Wang.[12] In developing coupling reactions, Pd chemistry has witnessed exceptional efforts and growth in terms of quantity and quality. Hence, it provides an excellent avenue to accomplish the anticipated conjugated olefins by employing suitable cross-coupling reactions. In this direction, the utility of a carbene complex as the carbon source has been exemplified using carbene chromium(0) complexes in the presence of Pd catalyst or bis-hydrazones in the presence of Rh(II) complexes.[13] Interestingly, these two efforts have led to the formation of corresponding olefins. However, the latter case, which uses a Rh(II) complex, was extensively used to synthesize polycyclic aromatic compounds. Interestingly, none of these methods were adopted to synthesize branched conjugated olefins. Nevertheless, a recent report by Wang and co-workers illustrated the synthesis of branched dienes using a Pd-catalyzed three-component reaction of allenes, aryl halides, and diazo compounds.[14] On the basis of the utility of carbene-transfer reactions,[13a] we postulated that in the reaction of hydrazones with Pd(II) under oxidative conditions it might be possible to obtain a Pd-bis-carbene complex with α-hydrogens, which can lead to branched dienes by facile β-hydride eliminations.

RESULTS AND DISCUSSION

Formation of 1,3-Branched Dienes. To evaluate this hypothesis, we began our studies by employing 4-methoxyacetophenone *N*-tosylhydarazone (**1a**) as a model substrate with a variety of bases, oxidants, and ligands in the presence of a few Pd(II) catalysts (Table 1). An extensive screening study indicated that bistriphenylphosphine palladium dichloride ($Pd(PPh_3)_2Cl_2$) is the most suitable catalyst for this transformation. Initially, the reactions of *N*-tosylhydarazone **1a** using *tert*-BuOLi as base in dioxane at 100 °C, either in the absence or in the presence of ligands, did not furnish expected diene **2a** (entries 1 and 2, Table 1). Because benzoquinone is known to promote reductive elimination in Pd-catalyzed coupling reactions[15] and also can function as a terminal oxidant, we envisioned that benzoquinone may be a suitable oxidant for the present coupling reaction. Hence, performing the same reaction in the presence of benzoquinone resulted in the formation of branched diene **2a** in 70% yield (entry 3). To the best of our knowledge, the formation of a branched diene with Pd(II) catalyst using hydrazone is difficult. Encouraged by this result, we continued our studies (i) using a variety of bases such as *tert*-BuOLi, Cs_2CO_3, and Ag_2CO_3; (ii) a variety of oxidants such as $(NH_4)_2S_2O_8$, PIDA, $Cu(OAc)_2$, and CuI; (iii) ligands such as benzoxazole, bibenzoxazole, *N*-phenylurea, diazabutadiene, XPHOS, *tert*-butyl-XPHOS, PPh_3, $P(o\text{-}Tol)_3$, diethylphosphite, and NHC-precursor (IPr·HCl). After undertaking a thorough screening study, it was found that $Pd(PPh_3)_2Cl_2$ is the most suitable catalyst with benzoquinone as oxidant (2 equiv),

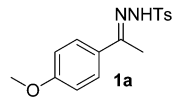
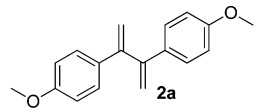
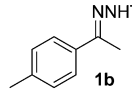
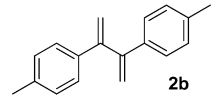
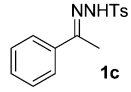
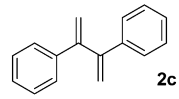
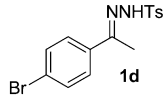
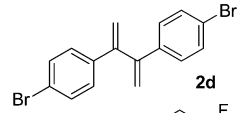
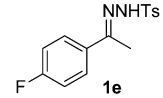
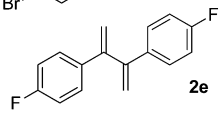
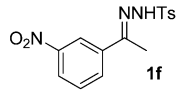
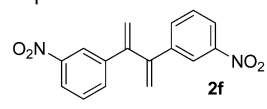
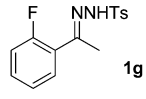
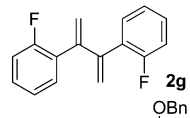
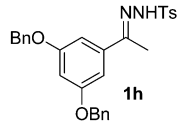
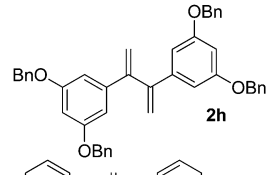
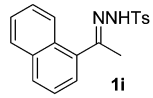
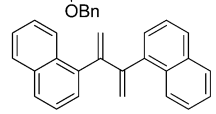
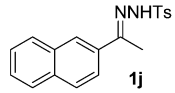
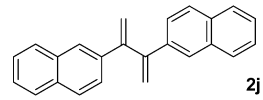
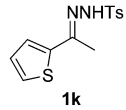
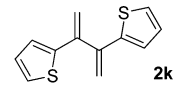
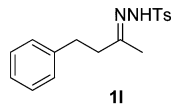
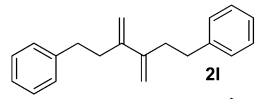
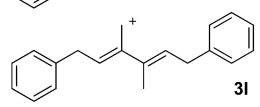
dx.doi.org/10.1021/jo402153t | J. Org. Chem. 2013, 78, 12136−12143

bibenzoxazole as ligand (40 mol %), and *tert*-BuOLi (3 equiv) as base at 100 °C for the homocoupling of **1a** to the product **2a** in good yield (84%, entry 23, Table 1). Furthermore, it was found that the reaction does not proceed with $Pd(PPh_3)_4$ in the absence of oxidant or in the absence of Pd catalyst (entries 24 and 25, Table 1). These observations clearly indicates that Pd(II) is essential for the coupling reaction.

As can be seen in Table 2, a variety of hydrazones were reacted with Pd(II) catalyst under optimal reaction conditions (entry 23, Table 1). The reaction proceeded well with substituted acetophenone derivatives such as **1b−g**. It is noteworthy that acetophenones that were substituted with electron-donating groups (entries 1 and 2, **1a** and **1b**, Table 2) as well as electron-withdrawing groups underwent a smooth reaction under the optimal conditions (entries 4−7, **1d−g**, Table 2). Interestingly, a remarkable chemoselectivity was observed in the reaction of halo-substituted hydrazone derivatives. Under the reaction conditions, no cross-condensation product was observed between the hydrazone and haloarenes in the reaction of bromo-substituted hydrazone derivatives of acetophenone (entry 4. Table 2).[11] To the best of our knowledge, the selectivity observed in these examples is rare.[8b] Furthermore, it was noticed that the reaction is versatile because dibenzyloxy-substituted hydrazone derivatives of acetophenone (**1h**) underwent a smooth reaction to furnish the corresponding branched dienes **2h** in excellent yield (92%, entry 8, Table 2). The scope of the method was extended to study the reaction of hydrazones of naphthyl ethanones. Hence, the reaction of hydrazones of 1-naphthylethanone (**1i**) and 2-naphthylethanone (**1j**) under the optimized conditions yielded the corresponding branched dienes **2i** and **2j** in good yields (entries 9 and 10, Table 2). Additionally, the hydrazone of 1-(thiophen-2-yl)ethanone **1k** furnished the corresponding branched diene **2k** in 92% yield (entry 11, Table 2), indicating that the strategy can be extended to synthesize branched dienes containing heterocyclic compounds. The broad scope of the transformation was further extended by subjecting an unactivated substrate such as hydrazone of 4-phenylbutan-2-one (**1l**) to the optimal reaction conditions to find corresponding branched diene **2l** and **3l** in good yield (71%, 6:4 **2l**/**3l**) (entry 12, Table 2).

Synthesis of Highly Substituted Branched Dienes. Our attempts to employ identical reaction conditions to obtain highly substituted branched dienes were not fruitful. Therefore, in search of suitable reaction conditions, we undertook a screening study by employing the hydrazone of 1,2-diphenylethanone **4a** as a model precursor (Table 3). Earlier conditions using $Pd(PPh_3)_2Cl_2$, benzoquinone as an oxidant, and bibenzoxazole as a ligand (20 mol %) at 100 °C yielded expected product branched diene **5a** as a minor product along with stilbene (**6a**) as a major product (entry 1, Table 3). Therefore, to develop a protocol to obtain the branched dienes, the hydrazone of **4a** was subjected to a variety of reaction conditions (Table 3). As can be seen, increasing the amount of ligand (bibenzaoxazole) to 40 mol % resulted in the formation of **5a** in 56% yield (entry 2, Table 4). Changing the ligand to XPHOS (20 mol %) resulted in the formation of **5a** in 66% yield (entries 3, Table 3). It was found that $PdCl_2$ or $Pd(OAc)_2$ were not useful catalysts, as these reactions did not afford the expected product but resulted in the formation of stilbene **6a** in almost quantitative yields (entries 4 and 5, Table 3). Further enhancement in the formation of branched diene to 80% yield was realized by increasing the amount of XPHOS to 40 mol %

Table 2. Substrate Scope for the Formation of 1,3-Branched Dienes[a]

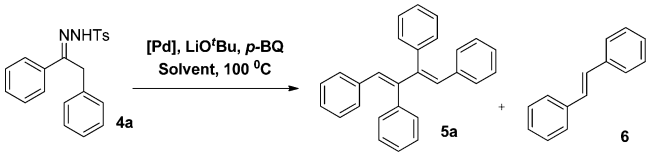
entry	substrate	time (h)	product	yield(%)[a]
1	 **1a**	6	 **2a**	84
2	 **1b**	6	 **2b**	91
3	 **1c**	6	 **2c**	93
4	 **1d**	6	 **2d**	87
5	 **1e**	8	 **2e**	76
6	 **1f**	9	 **2f**	83
7	 **1g**	8	 **2g**	79
8	 **1h**	8	 **2h**	92
9	 **1i**	8	 **2i**	91
10	 **1j**	8	 **2j**	68
11	 **1k**	4	 **2k**	92
12	 **1l**	12	 **2l**	71
		12	 **3l**	

[a]Reaction conditions: **1** (0.4 mmol), $Pd(PPh_3)_2Cl_2$ (5 mol %), bibenzoxazole (40 mol %), *p*-BQ (1 mmol), *t*-BuOLi (1.5 mmol), dioxane (3 mL). [b]Isolated yields.

and performing the reaction in DMF (entry 6). Because ligands are known to have a role in promoting coupling reactions,[16] a more nucleophilic phosphine ligand such as $P(Cy)_3$ was employed for the coupling reaction. However, this reaction resulted in the formation of branched diene **5a** in lower yield (60%), and the formation of stilbene was observed (entry 7,

dx.doi.org/10.1021/jo402153t | J. Org. Chem. 2013, 78, 12136−12143

Table 3. Optimization Studies for the Formation of 1,3-Branched Dienes[a]



entry	[Pd]	ligand	solvent	yield (%)[b] 5a	6
1	$Pd(PPh_3)_2Cl_2$	bibenzoxazole (20 mol %)	dioxane	30	60
2	$Pd(PPh_3)_2Cl_2$	bibenzoxazole (40 mol %)	dioxane	56	40
3	$Pd(PPh_3)_2Cl_2$	xphos (20 mol %)	dioxane	66	33
4	$PdCl_2$	xphos (20 mol %)	dioxane	trace	99
5	$Pd(OAc)_2$	xphos (20 mol %)	dioxane	trace	99
6	$Pd(PPh_3)_2Cl_2$	xphos (20 mol %)	DMF	80	nd
7	$Pd(PPh_3)_2Cl_2$	$P(Cy)_3$ (20 mol %)	dioxane	60	nd
8	$Pd(PPh_3)_2Cl_2$	diethylphosphite (20 mol %)	DMF	90	nd
9	$Pd(PPh_3)_2Cl_2$	diethylphosphite (20 mol %)	DMF (MS 4 Å)	93	nd[c]

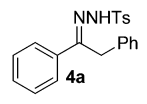
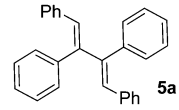
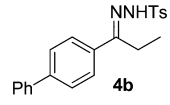
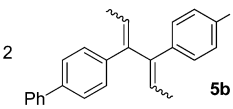
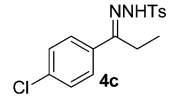
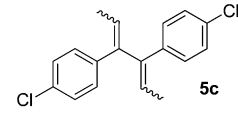
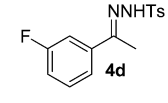
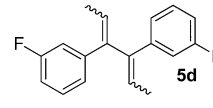
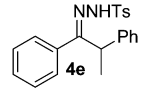
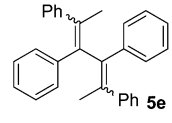
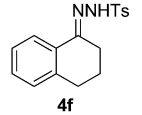
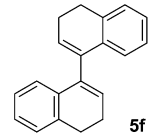
[a]Reaction conditions: **4a** (0.47 mmol), [Pd] (5 mol %), ligand (40 mol %), *p*-BQ (1 mmol), *t*-BuOLi (1.5 mmol), solvent (3 mL). [b]Isolated yields. [c]Molecular sieves (4 Å, 200 mg). nd, not detected.

Table 3). Recently, it was reported that phosphites can strongly bind to Pd(II) complexes.[17] Therefore, we thought that using tri-coordinate phosphite as a ligand could be effective to promote reductive elimination to furnish highly branched dienes and to avoid the formation of undesired olefin. As predicted, using diethylphosphite as a ligand brought a spectacular difference in the formation of product **5a** (90%, entry 8), which was further improved to 93% using molecular sieves (4 Å) in the reaction (93%, entry 9).

With a validated optimal condition in hand, the substrate scope was extended, and the results are tabulated in Table 4. α-Substituted hydrazone derivatives of acetophenone such as **4a** and **4b** under the optimal reaction conditions formed corresponding branched diene **5a** (93%, E/E ratio 100)[18] and **5b** (77%, E/E ratio 71), respectively (entries 1 and 2, Table 4). Similarly, the substrates carrying halogen substitution such as **4c** and **4d** formed the corresponding branched dienes **5c** and **5d** in good yields with expected selectivity (entries 3 and 4, Table 4). Further, tetrasubstituted hydrazone (**4e**) and hydrazone of tetralone (**4f**) furnished corresponding conjugated dienes **5e** and **5f** in 68% and 81%, respectively (entries 5 and 6, Table 4).

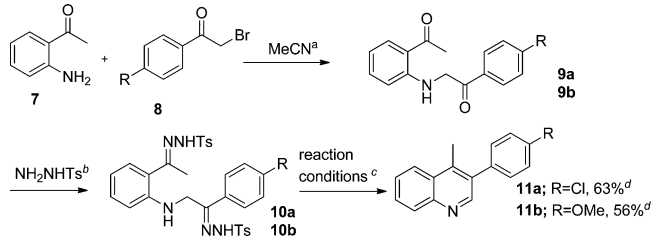
Novel Approach for the Synthesis of Quinolines and Other Applications. The opportunity to form a C−C bond using the present method led us to devise a new strategy for constructing cyclic compounds. Particularly, the syntheses of nitrogen-containing heterocyclic compounds were addressed because they are biologically and pharmaceutically active molecules and widely occur in nature.[19] Among them, the synthesis of quinoline derivatives is attractive owing to their utility in medicinal applications as well as their utility as dyes and antioxidants.[20] In addition, most of the synthetic methods that are available for the synthesis of quinoline adopted the condensation of amines and carbonyl compounds.[21] To test the efficacy of the method, we used diketone derivative 2-((2-acetylphenyl)amino)-1-(4-chlorophenyl)ethanone (**9a**) as the precursor, which was prepared using 1-(2-aminophenyl)-ethanone (**7**) and corresponding phenacyl bromide (**8**) (Scheme 1). The bis-hydrazone of 2-((2-acetylphenyl)-amino)-1-(4-chlorophenyl)ethanone (**10a**) was subjected to the present reaction conditions, resulting in the formation of corresponding quinoline derivative 3-(4-chlorophenyl)-4-methylquinoline **11a** in 63% yield (Scheme 1, also see Supporting

Table 4. Substrate Scope for the Formation of 1,3-Branched Dienes[a]

entry	substrate	time (h)	product	*E*/*E*	yield[b]
1	 4a	11	 5a	100	93
2	 4b	12	 5b	71	77
3	 4c	8	 5c	33:43[c]	82
4	 4d	8	 5d	91	75
5	 4e	12	 5e	50[d]	68
6	 4f	8	 5f	-	81

[a]Reaction conditions: **4** (0.4 mmol), $Pd(PPh_3)_2Cl_2$ (5 mol %), diethylphosphite (40 mol %), *p*-BQ (1 mmol), *t*-BuOLi (1.5 mmol), DMF (3 mL), molecular sieves (4 Å, 200 mg). [b]Isolated yields. [c]E/E to Z/Z isomer ratio. [d]E/Z.

Scheme 1. Synthesis of Quinolines[a]



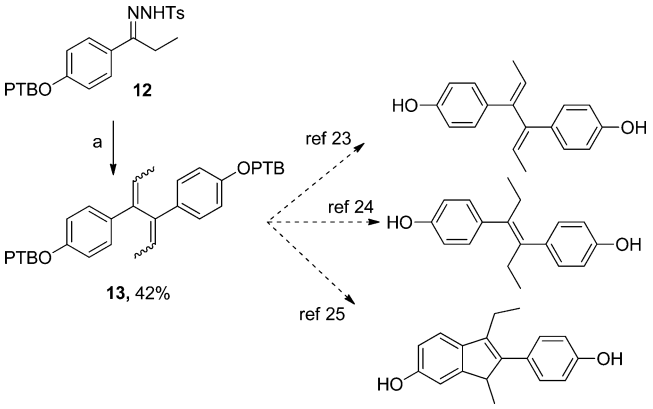
[a]Reaction conditions: (a) **7** (20 mmol), **8** (10 mmol) in MeCN (20 mL), rt, 24 h. (b) $TsNHNH_2$, 1 h, diaoxane. (c) **10** (0.4 mmol), $Pd(PPh_3)_2Cl_2$ (5 mol %), Ligand (40 mol %), *p*-BQ (1 mmol), *t*-BuOLi (1.5 mmol), DMF (3 mL), molecular sieves (4 Å, 200 mg). (d) Isolated yields.

dx.doi.org/10.1021/jo402153t | J. Org. Chem. 2013, 78, 12136−12143

Information Table S1 for screening studies). Similarly, the bis-hydrazone of 2-((2-acetylphenyl)amino)-1-(4-methoxyphenyl)-ethanone (**10b**) underwent a facile reaction to furnish quinoline derivative 3-(4-chlorophenyl)-4-methylquinoline (**11b**) in moderate yield (Scheme 1).

The application of this method is further emphasized by synthesizing dienestrol derivatives, which are estrogen receptors[22] (Scheme 2). As seen in Scheme 1, hydrazone **12**

Scheme 2. Synthesis of Dienestrol Derivatives[a]

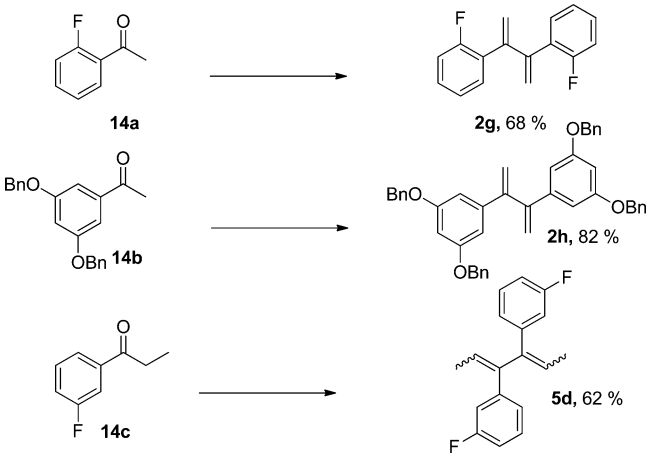


[a]Reaction conditions: **12** (0.4 mmol), $Pd(PPh_3)_2Cl_2$ (5 mol %), ligand (40 mol %), *p*-BQ (1 mmol), *t*-BuOLi (1.5 mmol), DMF (3 mL), molecular sieves (4 Å, 200 mg).

under the optimal conditions furnished corresponding diene **13**, which is a PTB (*p*-tolylbenzyl)-protected dienestrol that can be further manipulated to dienestrol,[23] diethylstilbestrol,[24] and indenestrol[25] using known methods.

One-Pot Reaction Using Ketone as Precursor. The utility of hydrazones as the precursor for Pd-catalyzed cross-coupling reactions led to the idea to employ ketones as precursors to access the corresponding branched dienes in a one-pot reaction. As can be seen in Scheme 3, an in situ one-pot method to synthesize branched dienes using ketones as the precursor is illustrated. 1-(2-Fluorophenyl)ethanone (**14a**) is reacted with tosyl hydrazine followed by the addition of Pd

Scheme 3. One-Pot Reaction[a]

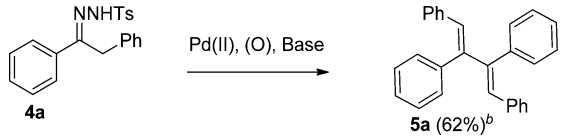


[a]Reaction conditions: (1) $TsNHNH_2$, 1,4-diaoxane. (2) $Pd(PPh_3)_2Cl_2$ (5 mol %), ligand (40 mol %), *p*-BQ (1 mmol), *t*-BuOLi (1.5 mmol), DMF (3 mL), molecular sieves (4 Å, 200 mg).

catalyst under the optimal conditions. As expected, corresponding branched diene **2g** was isolated in 68% yield (Scheme 3). This in situ reaction was further extended to 5-acetyl-1,3-phenylene dibenzoate (**14b**) and 1-(3-fluorophenyl)propan-1-one (**14c**), resulting in the formation of corresponding dienes **2h** and **5d** in good yields (Scheme 3).

To expand the utility of this coupling reaction, a scaling-up study was undertaken (Scheme 4). As can be seen, tosyl hydrazone **4a** (2 g, 5.5 mmol) under the optimized condition furnished prodcut **5a** in 62% isolated yield.

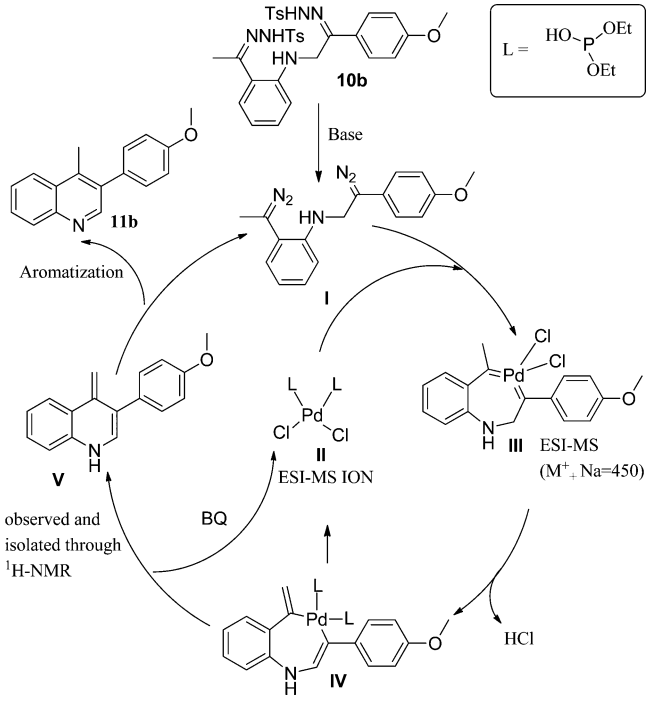
Scheme 4. Scaling-up Experiment[a]



[a]Reaction conditions: **4a** (2 g, 5.5 mmol), $Pd(PPh_3)_2Cl_2$ (5 mol %, 75 mg), diethyl phosphite (300 mg, 40 mol %), *p*-BQ (1.2 g, 11 mmol, 2 equiv), *t*-BuOLi (1.3 g, 16 mmol, 3 equiv), DMF (12 mL), molecular sieves (4 Å, 1 g). [b]Isolated yield.

Mechanistic Studies. A tentative mechanism is proposed in Scheme 5. Bis-hydrazone **10b** in the presence of base forms

Scheme 5. Tentative Mechanism



the corresponding diazo compound (**I**). Furthermore, it was found that the diazo derivative of *p*-methoxy acetophenone (**15**) under the optimal reaction conditions underwent a smooth transformation to corresponding diene **2a** in 67% yield (see Supporting Information, Scheme S1). This experimet indicates that the reaction is probably going through the corresponding diazo intermediate **I**. In addition, $Pd(PPh_3)_2Cl_2$ reacts with ligand to form complex **II** (corresponding signal was observed in ESI-MS, see the Supporting Information). Complex **II** inserts into diazocompound **I** to furnish key intermediate **III** via seven-membered palladacycle. Pd-inserted

dx.doi.org/10.1021/jo402153t | J. Org. Chem. 2013, 78, 12136–12143

complex **III** is a highly reactive species, which cannot be isolated. However, the corresponding molecular ion peak was observed in the ESI-MS spectral analysis of the reaction mixture (see Supporting Information). Furthermore, complex **III** loses HCl to generate complex **IV**, which forms diene **V** and generates Pd(II). Diene **V** aromatizes to **11b**.

CONCLUSIONS

We have discovered a novel Pd-catalyzed selective coupling reaction of hydrazones in the presence of *t*-BuOLi and benzoquinone to form the corresponding branched olefin. The utility of Pd catalyst for the cross-coupling reactions for synthesizing branched conjugated dienes is rare. The reaction is very versatile and compatible with a variety of functional groups. The reaction was well-exploited to show the applicability of the methodology for accessing heterocyclic molecules, which may have good synthetic implications. Additionally, an in situ reaction was conceived using ketones as starting matetials in a one-pot reaction. Considerable progress was made to understand the reaction mechanism, and further work in our laboratory is underway to explore the applications of this reaction.

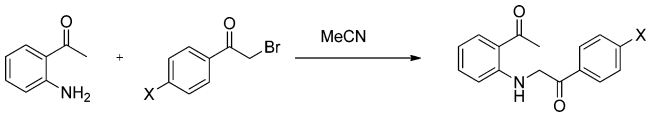
EXPERIMENTAL SECTION

General Procedure for the Homocoupling Reactions of Tosylhydrazones. A well-stirred mixture of *N*-tosylhydrazone (0.4 mmol), *p*-BQ (1 mmol, 2 equiv), bibenzoxazole or diethylphosphite (40 mol %), and $Pd(PPh_3)_2Cl_2$ (0.0067 mmol, 5 mol %) in dioxane (3 mL) under nitrogen was heated at 100 °C. To this hot clear solution was added *t*-BuOLi (1.5 mmol) at 100 °C until the completion of the reaction (monitored by TLC). Then, the reaction mixture was cooled to room temperature, diluted with EtOAc, and passed through a short Celite pad. The solvent was evaporated under reduced pressure and purified on a silica gel column.

General Procedure for the Intramolecular Coupling Reaction of Tosylhydrazones. A well-stirred mixture of bis-*N*-tosylhydrazone (0.4 mmol), *p*-BQ (1 mmol, 2 equiv), diethylphosphite (40 mol %), $Pd(PPh_3)_2Cl_2$ (0.0067 mmol, 5 mol %), and molecular sieves in DMF (3 mL) under nitrogen was heated at 100 °C. To this hot clear solution was added *t*-BuOLi (1.5 mmol) at 100 °C until the completion of the reaction (monitored by TLC). Then, the reaction mixture was cooled to room temperature, diluted with EtOAc, and passed through a short Celite pad. The solvent was evaporated under reduced pressure and purified on a silica gel column.

General Procedure for the Homocoupling Reaction of in Situ Generated Tosylhydrazones. A mixture of ketone (0.4 mmol, 1 equiv) and tosylhydrazide (0.42 mmol, 1.05 equiv) was stirred at 100 °C for 1 h in DMF (1 mL) as solvent. To this were added *p*-benzoquinone (1 mmol, 2 equiv), ligand (40 mol %), and $Pd(PPh_3)_2Cl_2$ (0.0067 mmol) in 1,4-dioxane (3 mL) under nitrogen followed by the addition of *t*-BuOLi (1.5 mmol) at 100 °C until the completion of the reaction (monitored by TLC). Then, the reaction mixture was cooled to room temperature, diluted with EtOAc, and passed through a short Celite pad. The solvent was evaporated under reduced pressure and purified on a silica gel column.

General Procedure for the Preparation of Dicarbonyl Compounds.



Aniline (20 mmol) and bromoacetophenone (10 mmol) were combined in MeCN (20 mL) and allowed to stand at rt for 24 h. Solid aniline-HBr was filtered off, and the filtrate was concentrated under vacuum. The residue was dissolved in EtOAc (100 mL) and extracted sequentially with H_2O (50 mL), 5% citric acid (50 mL), and brine (25 mL). The organic layer was dried (Na_2SO_4), filtered through a pad of silica gel, and in some cases further purified by a silica gel column to yield the product.

*Preparation of 2-((2-Acetylphenyl)amino)-1-(4-chlorophenyl)-ethanone (**9a**).* Yield = 93% (2.66 g), yellow solid, mp 140−143 °C. R_f = 0.4 (EtOAc/hexane 1:5). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.59 (s, 3H), 4.64 (s, 2H), 6.60−6.67 (m, 2H), 7.35 (t, J = 8 Hz, 1H), 7.45 (d, J = 8 Hz, 2H), 7.77 (d, J = 8 Hz, 1H), 7.94 (d, J = 8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.7, 192.7, 149.4, 140.0, 134.9, 133.1, 132.7, 129.2, 129.1, 118.4, 114.9, 11.8, 49.5, 27.8. IR (neat, cm^{-1}): 3325, 2934, 1725, 1780, 1598, 1493, 1443, 1022, 900, 775, 700. HRMS (ESI): calcd for $C_{16}H_{14}ClNO_2$ (M + Na), 310.0611; found, 310.0613.

Preparation of bis-*N*-Tosylhydrazones. *General Procedure for Converting Dicarbonyl Compounds to Bis-N-tosylhydrazones.* A solution of pure dicarbonyl compound (2.0 mmol) in methanol/toluene (3:1 mL) was stirred and heated at 60 °C until the dicarbonyl compound was dissolved. Then, $TsNHNH_2$ (0.763 g, 4.1 mmol, 2.05 equiv) was added to the mixture. After approximately 2 h, the crude products could be obtained as solid precipitates. The precipitates were washed by petroleum ether and kept in a desiccator under vacuum to afford the pure products. If the crude products could not be obtained as solid precipitates after the reaction was completed (TLC), then the solvent was removed by vacuum and the solid was used without further purification. The yields of corresponding *N*-tosylhydrazone derivatives were about ∼80%, and the reaction took 2 h in general (usually 2 mol % TsOH was added to promote the reaction).

Characterization Data. *4,4′-(Buta-1,3-diene-2,3-diyl)bis-(methoxybenzene) (**2a**).* Yield = 84% (52 mg), colorless solid, mp 107−109 °C. R_f = 0.4 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.76 (s, 6H), 5.23 (d, J = 1.4 Hz, 2H), 5.46 (d, J = 1.4 Hz, 2H), 6.78 (d, J = 8.7 Hz, 4H), 7.3 (d, J = 8.8 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.0, 149.3, 132.6, 128.4, 114.3, 113.5, 55.2. IR (neat, cm^{-1}): 3422, 2969, 1597, 1474, 1454, 1168, 1065, 1038. HRMS (ESI): calcd for $C_{18}H_{18}O_2$ (M + H), 267.1385; found, 267.1387. The physical data were identical to those previously reported.[25]

*4,4′-(Buta-1,3-diene-2,3-diyl)bis(methylbenzene) (**2b**).* Yield = 91% (53 mg), colorless solid, mp 57−59 °C. R_f = 0.55 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.29 (s, 6H), 5.25 (d, J = 1.5 Hz, 2H), 5.5 (d, J = 1.5 Hz, 2H), 7.27 (d, J = 7.8 Hz, 4H), 7.59 (d, J = 7.8 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.7, 137.3, 137.1, 128.8, 127.2, 115.3, 21.1. IR (neat, cm^{-1}): 3086, 3923, 1904, 1797, 1605, 1503, 1436, 1183. HRMS (ESI): calcd for$C_{18}H_{18}$ (M + H), 235.1487; found, 235.1483. The physical data were identical to those previously reported.[25]

*Buta-1,3-diene-2,3-diyldibenzene (**2c**).* Yield = 93% (49 mg), colorless solid, mp 44−45 °C. R_f = 0.5(hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.31 (s, 2H), 5.53 (s, 2H), 7.22−7.28 (m, 6H), 7.38−7.4 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.8, 140.2, 128.2, 127.6, 127.5, 116.3. IR (neat, cm^{-1}): 2924, 1598, 1493, 1443, 1022, 900, 775, 700. MS-DI (m/z): 206 (M^+), 191 (M-CH_2), 178 (M-2CH_2). The physical data were identical to those previously reported.[25]

*4,4′-(Buta-1,3-diene-2,3-diyl)bis(bromobenzene) (**2d**).* Yield = 87% (87 mg), colorless solid, mp 78−80 °C. R_f = 0.65 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.3 (d, J = 1.3 Hz, 2H), 5.5 (d, J = 1.3 Hz, 2H), 7.21 (d, J = 8.5 Hz, 4H), 7.38 (d, J = 8.5 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.4, 138.7, 131.4, 129.1, 121.7, 117.0. IR (neat, cm^{-1}): inactive. MS-DI (m/z): 284 (M-HBr), 204 (M-2HBr). The physical data were identical to those previously reported.[26]

*4,4′-(Buta-1,3-diene-2,3-diyl)bis(fluorobenzene) (**2e**).* Yield = 76% (45 mg), colorless solid, mp 48−51. R_f = 0.7 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.29 (d, J = 1.4 Hz, 2H), 5.48 (d, J = 1.4 Hz, 2H), 6.92−6.97 (m, 4H), 7.3−7.34 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.4 (d, J = 250 Hz), 148.7, 136.0, 129.1 (d, J = 7.8 Hz), 116.3, 115.1 (d, J = 21 Hz). IR (neat, cm^{-1}): 3432, 1647, 1033, 1016. MS-DI (m/z): 242 (M^+), 227 (M-CH_2). The physical data were identical to those previously reported.[27]

dx.doi.org/10.1021/jo402153t | J. Org. Chem. 2013, 78, 12136−12143

*3,3′-(Buta-1,3-diene-2,3-diyl)bis(nitrobenzene) (**2f**).* Yield = 83% (55 mg), colorless solid, mp 90−92 °C. R_f = 0.5 (EtOAc/hexane 1:10). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.5 (s, 2H), 5.7 (s, 2H), 7.47 (t, *J* = 8 Hz, 2H), 7.68 (d, *J* = 7 Hz, 2H), 8.12 (d, *J* = 8 Hz, 2H), 8.23 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.4, 146.9, 141.1, 133.4, 129.5, 122.8, 122.3, 119.6. IR (neat, cm^{-1}): 3431, 2919, 1559, 1526, 1348, 1099, 912, 808, 743. HRMS (ESI): calcd for $C_{16}H_{12}N_2O_4$ (M + Na), 319.0695; found, 319.0695.

*2,2′-(Buta-1,3-diene-2,3-diyl)bis(fluorobenzene) (**2g**).* Yield = 79% (46 mg), colorless solid, mp 54−56 °C. R_f = 0.6 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.22 (s, 2H), 5.31 (2H), 7.03−7.13 (m, 4H), 7.24−7.34 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.9 (d, *J* = 246.2 Hz), 143.8, 131.4, 129.2 (d, *J* = 8.6 Hz), 128.4 (d, *J* = 14.3 Hz), 123.8, 119.3, 115.55 (d, *J* = 22.7 Hz). IR (neat, cm^{-1}): 3433, 2924, 2853, 1844, 1616, 1580, 1234, 1200, 918, 758. MS-DI (*m*/*z*): 242 (M^+), 227 (M-CH_2).

*(((Buta-1,3-diene-2,3-diylbis(benzene-5,3,1-triyl)tetrakis(oxy))-tetrakis(methylene))tetrabenzene (**2h**).* Yield = 92% (73 mg), colorless solid, mp 140−142 °C. R_f = 0.4 (EtOAc/hexane 1:20). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.98 (s, 8H), 5.27 (s, 2H), 5.5 (s, 2H), 6.5 (s, 2H), 6.65 (s, 4H), 7.28−7.4 (m, 20H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7, 149.3, 142.2, 136.8, 128.5, 127.9, 127.6, 116.6, 106.9, 101.3, 70.0. IR (neat, cm^{-1}): 3422, 2869, 1587, 1454, 1434, 1158, 1055, 1028, 834. HRMS (ESI): calcd for $C_{44}H_{38}O_4$ (M + H), 631.2848; found, 631.2848.

*1,1′-(Buta-1,3-diene-2,3-diyl)dinaphthalene (**2i**).* Yield = 68% (46 mg), colorless solid, mp 175−177 °C. R_f = 0.35 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.08 (s, 2H), 5.24 (d, *J* = 1, 2H), 7.49−7.55 (m, 8H), 7.85−7.9 (m, 4H), 8.16 (dd, *J* = 8.5 Hz, *J* = 1.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.4, 139.1, 133.6, 132.3, 128.2, 127.6, 126.8, 126.1, 125.9, 125.7, 125.3, 120.8. IR (neat, cm^{-1}): 2922, 2851, 1817, 1593, 1575, 1506, 915, 800, 777. Anal. Calcd for $C_{24}H_{18}$: C, 94.08; H, 5.92. Found: C, 93.97; H, 6.06.

*2,2′-(Buta-1,3-diene-2,3-diyl)dinaphthalene (**2j**).* Yield = 91% (61 mg), colorless solid, mp 142−145 °C. R_f = 0.35 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.46 (d, *J* = 1.4 Hz, 2H), 5.74 (d, *J* = 1.6 Hz, 2H), 7.38−7.4 (m, 4H), 7.6−7.62 (m, 2H), 7.72−7.76 (m, 6H), 7.85 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.7, 137.5, 133.2, 132.8, 128.3, 127.7, 126.6, 125.9, 125.8, 125.5, 116.99. IR (neat, cm^{-1}): 3423, 3055, 1580, 1266, 747. Anal. Calcd for $C_{24}H_{18}$: C, 94.08; H, 5.92. Found: C, 93.97; H, 6.06. The physical data were identical to those previously reported.[26]

*2,2′-(Buta-1,3-diene-2,3-diyl)dithiophene (**2k**).* Yield = 92% (51 mg), brown liquid. R_f = 0.8 (hexane), unstable at rt. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.25 (s, 2H), 5.6 (s, 2H), 6.88−6.91 (m, 2H), 6.94−6.95 (m, 2H), 7.15−7.17 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.5, 142.5, 127.4, 126.0, 124.8, 114.2. IR (neat, cm^{-1}): 3443, 2921, 1662, 1518, 1415, 1236. MS-DI (*m*/*z*): 218 (M^+), 203 (M-CH_2). The physical data were identical to those previously reported.[26]

*(3,4-Dimethylenehexane-1,6-diyl)dibenzene (**2l** and **3l**).* Yield = 71% (62 mg), colorless liquid. R_f = 0.4 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.55−2.61 (m, 4H), 2.73−2.8 (m, 4H), 4.99 (s, 2H), 5.17 (s, 2H), 7.17−7.2 (m, 10H), 7.25−7.31 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.7, 142.2, 138.5, 128.55, 128.53, 128.4, 128.37, 128.3, 126.1, 125.8, 112.2, 36.1, 35.1, 20.47, 14.5. IR (neat, cm^{-1}): 3025, 2922, 2854, 1605, 1454, 1178. MS-DI (*m*/ *z*): 262 (M^+), 171 (M-CH_2Ph). The physical data were identical to those previously reported.[28]

*(1E,3E)-Buta-1,3-diene-1,2,3,4-tetrayltetrabenzene (**5a**).* Yield = 93% (68 mg), colorless solid, mp 170−172 °C. R_f = 0.5 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.3 (s, 2H), 6.73−6.75 (m, 4H), 7.0−7.02 (m, 6H), 7.24−7.32 (m, 4H), 7.37−7.42 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.5, 139.7, 137.2, 131.6, 130.3, 129.4, 128.7, 127.7, 127.3, 126.5. IR (neat, cm^{-1}): 3077, 3056, 3022, 2924, 2852, 1955, 1596, 1490, 1442, 1350, 1027, 866, 761, 753, 692. Anal. Calcd for $C_{28}H_{22}$: C, 93.81; H, 6.19. Found: C, 93.76; H, 6.26. The physical data were identical to those previously reported.[25]

*4,4″-(Hexa-2,4-diene-3,4-diyl)di-1,1′-biphenyl (**5b**).* Yield = 77% (59 mg), colorless solid, mp 231−233 °C. R_f = 0.35 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.52 (d, *J* = 6.6 Hz, 6H), 5.36 (q, *J* = 7 Hz, 2H), 7.27−7.33 (m, 6H), 7.43−7.5 (m, 7H), 7.54−7.66 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.0, 139.2, 139.0, 130.39, 130.28, 128.75, 128.71, 128.67, 127.14, 127.0, 126.9, 126.8, 126.7, 126.6, 126.3. IR (neat, cm^{-1}): 2925, 2853, 1598, 1485, 1333, 1114, 1074, 1020, 907, 849, 765, 737, 691. HRMS (ESI): calcd for $C_{30}H_{26}$ (M + Na), 409.1932; found, 409.1932.

*4,4′-(Hexa-2,4-diene-3,4-diyl)bis(chlorobenzene) (**5c**).* Yield = 82% (55 mg), colorless solid, mp 62−65 °C. R_f = 0.55 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.44 (d, *J* = 6.4 Hz, 6H), 5.25 (q, J = 7 Hz, 2H), 7.08−7.2 (m, 5H), 7.34−7.36 (m, 4H), 7.5 (d, *J* = 6 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.7, 138.0, 131.2, 130.3, 130.0, 129.6, 128.3, 128.1, 127.99, 126.0, 15.2, 12.5. IR (neat, cm^{-1}): 2924, 2853, 1593, 1489, 1263, 1089, 1015, 814, 668. MS-DI (*m*/*z*): 304 (M + 1), 287 (M-CH_3), 275 (M-CH_3CH), 232 (M-2HCl).

*3,3′-(Hexa-2,4-diene-3,4-diyl)bis(fluorobenzene) (**5d**).* Yield = 75% (75 mg), colorless liquid. R_f = 0.5 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.45 (d, *J* = 7 Hz, 6H), 5.26 (q, *J* = 7 Hz, 2H), 6.89 (d, *J* = 10 Hz, 2H), 6.93−6.98 (m, 4H), 7.31−7.36 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.7 (d, *J* = 244 Hz), 141.9 (d, *J* = 7.5 Hz), 129.5 (d, *J* = 8 Hz), 125.99, 125.6 (d, *J* = 2.5 Hz), 116.78 (d, *J* = 20.5 Hz), 113.5 (d, *J* = 21.6 Hz), 15.1. IR (neat, cm^{-1}): 3398, 2927, 2854, 1610, 1582, 1435, 1265, 1069, 785. MS-DI (*m*/*z*): 270 (M^+), 255 (M-CH_3), 241 (M-CH_3CH).

*Hexa-2,4-diene-2,3,4,5-tetrayltetrabenzene (**5e**).* Yield = 68% (68 mg), colorless liquid. R_f = 0.5 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, *J* = 8 Hz, 1 H), 7.38−7.34 (m, 5H), 7.29−7.17 (m, 7H), 7.1−7.04 (m, 3H), 6.94−6.92 (d, *J* = 7.8 Hz, 2H), 6.83 (s, 1H), 6.46 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.9, 142.1, 138.7, 138.3, 137.4, 129.1, 128.9, 128.4, 128.3, 128.1, 127.8, 127.6, 127.1, 126.8, 126.5, 126.4, 126.0, 125.98, 21.1, 17.45. IR (neat, cm^{-1}): 3070, 3026, 3012, 2934, 2862, 1965, 1586, 1480, 1462, 1360, 1037, 866. MS-DI (*m*/*z*) (relative intensity): 386 (100), 356 (13), 281 (73), 265 (16), 219 (40).

*3,3′,4,4′-Tetrahydro-1,1′-binaphthalene (**5f**).* Yield = 81% (50 mg), colorless liquid. R_f = 0.5 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.36−2,41 (m, 4H), 2.88 (t, *J* = 7 Hz, 4H), 6.07 (t, *J* = 4.5 Hz, 2H), 6.90 (d, *J* = 7.7 Hz, 2H), 6.99 (t, *J* = 7.4 Hz, 2H), 7.07 (t, *J* = 7.4 Hz, 2H), 7.14 (d, *J* = 7.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.35, 135.8, 134.7, 127.99, 127.35, 126.7, 126.3, 125.1, 28.2, 23.3. IR (neat, cm^{-1}): 3057, 3017, 2932, 2881, 2829, 2598, 1484, 1450, 1265, 1157, 1039, 939. MS-DI (*m*/*z*): 258 (M^+), 129 (vinyl radical). The physical data were identical to those previously reported.[29]

*4,4′-(Hexa-2,4-diene-3,4-diyl)bis(((4-methylbenzyl)oxy)benzene) (**13**).* Yield = 42% (35 mg), colorless liquid. R_f = 0.4 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.05 (d, *J* = 6.8 Hz, 6H), 2.23 (s, 6H), 6.38 (q, *J* = 6.8 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 4H), 6.95 (d, *J* = 8 Hz, 4H), 7.4 (d, *J* = 8 Hz, 4H), 7.28−7.39 (m, 6H), 7.47 (d, *J* = 8.8 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.1, 136.9, 135.0, 133.9, 132.4, 129.45, 128.5, 125.48, 128.1, 127.46, 114.3, 69.9, 20.8, 16.8. IR (neat, cm^{-1}): 2994, 2843, 1583, 1489, 1243, 1099, 1035. HRMS (ESI): calcd for $C_{34}H_{34}O_2$ (M^+), 474.2559; found, 474.2556.

Characterization Data for Quinolone Derivatives. *3-(4-Chlorophenyl)-4-methylquinoline (**11a**).* Yield = 63% (19 mg), colorless liquid. R_f = 0.4 (EtOAc/hexane 1:5). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.6 (s, 3H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.74 (t, *J* = 7.2 Hz, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 8.14 (d, *J* = 8 Hz, 1H), 8.76 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.1, 147.1, 140.7, 137.1, 133.8, 133.3, 131.2, 130.0, 129.1, 128.7, 127.9, 126.9, 124.2, 22.68. IR (neat, cm^{-1}): 2920, 2850, 1651, 1457, 1261, 1017, 913, 744. HRMS (ESI): calcd for $C_{16}H_{12}ClN$ (M + H), 254.0737; found, 254.0738.

*3-(4-Methoxyphenyl)-4-methylquinoline (**11b**).* Yield = 56% (16 mg), yellow liquid. R_f = 0.35 (EtOAc/hexane 1:5). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.61 (s, 3H), 3.89 (s, 3H), 7.04 (d, *J* = 8 Hz, 2H), 7.32 (d, *J* = 8 Hz, 2H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.72 (t, *J* = 7.8 Hz, 1H), 8.09 (d, *J* = 8.4, 1H), 8.13 (d, *J* = 8.4 Hz, 1H), 8.8 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 151.7, 134.1, 131.5, 131.1, 129.9, 128.7, 128.0, 127.8, 126.7, 126.4, 124.2, 113.9, 55.3, 15.6. IR (neat, cm^{-1}): 2930, 2860, 1641, 1467, 1271, 1027, 903. HRMS (ESI): calcd for $C_{17}H_{15}NO$ (M + H), 250.1232; found, 250.1234.

■ ASSOCIATED CONTENT

Supporting Information

Ligands employed for screening and control studies, Ortep diagram of **5a**, plausible mechanism for stereoselectivity for the formation of highly substituted branched dienes, screening studies for optimization for intramolecular reaction, ^{1}H and ^{13}C spectra and spectral data for all compounds, and reaction of diazo compound **15** with $Pd(PPh_3)_2Cl_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We acknowledge support from IISc, RL Fine Chem, and CSIR (no. 01/2415/10-EMR-II). We thank Dr A. R. Ramesha for useful discussions. D.P.O. thanks UGC for a senior research fellowship.

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