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Iron-Promoted Synthesis of Substituted 1-Halo-1,4-pentadienes by Reaction of 1,3-Diarylpropenes with Ethynylbenzenes via sp^3 C−H Bond Activation

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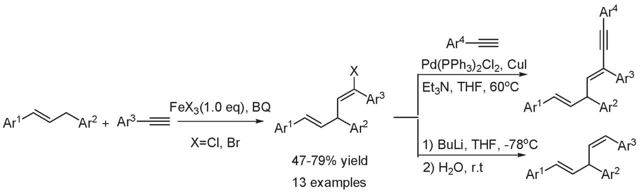

An iron-promoted sp^3 C−H bond activation and C−C bond formation reaction between 1,3-diarylpropenes and ethynylbenzenes was realized with BQ (benzoquinone) as an oxidant. The reaction afforded 1-halo-1,4-pentadiene derivatives in moderate to good yields under mild conditions.

With the emergence of the concepts of "atom economy"[1] and "green chemistry",[2] C−C bond formation via transition-metal-catalyzed C−H bond activation has attracted great attention recently, and a number of excellent results have been obtained.[3] Various oxidative intermolecular cross-dehydrogenative-coupling (CDC) reactions directly between two different C−H bonds have also been developed, such as (i) sp^3 C−H with sp^3 C−H,[4] (ii) sp^2 C−H with sp^2 C−H,[5] (iii) sp^3 C−H with sp^2 C−H,[6] and (iv) sp^3 C−H with sp C−H.[7] Owing to its inexpensive and environmentally benign characteristics, iron salts have emerged as alternative and promising catalysts for a wide range of organic transformations.[8−12] As one of the most abundant metals on earth, iron has been increasingly explored in modern catalysis to discover its unique and novel reactivity toward carbon−carbon and carbon−heteroatom bond formation, which have been typically achieved by rare and expensive transition-metal catalysts. Although the iron-catalyzed formation of C−C and C−heteroatom bonds is becoming popular, the direct formation of C−C bonds through iron-catalyzed C−H bond activation has been reported only in limited cases.[13]

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(1) (a) Trost, B. M. *Acc. Chem. Res.* **2002**, *35*, 695. (b) Trost, B. M. *Angew. Chem.* **1995**, *107*, 285; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 259. (c) Trost, B. M. *Science* **1991**, *254*, 1471.

(2) (a) Winterton, N. *Green Chem.* **2001**, *3*, G73. (b) Anastas, P. T.; Warner, J. C. *Green Chemistry: Theory and Practice*; Oxford University Press: New York, 1998. (c) Anastas, P. T; Kirchhoff, M. M. *Acc. Chem. Res.* **2002**, *35*, 686. (d) Tang, S. L. Y; Smith, R. L; Poliakoff, M. *Green Chem* **2005**, *7*, 761. (e) Sheldon, R. A. *Green Chem.* **2007**, *9*, 1273. (f) Sheldon, R. A. *Chem. Commun.* **2008**, 3352. (g) Horváth, I. T.; Anastas, P. T. Innovations and Green Chemistry. *Chem. Rev.* **2007**, *107*, 2169.

(3) (a) Murai, S.; Kakiuchi, F.; Sekine, S.; Tanaka, Y.; Kamatani, A.; Sonoda, M.; Chatani, N. *Nature* **1993**, *366*, 529. (b) Sonoda, M.; Kakiuchi, F.; Chatani, N.; Murai, S. *J. Organomet. Chem.* **1995**, *504*, 151. (c) Olsson, V. J.; SzabR, K. J. *Angew. Chem.* **2007**, *119*, 7015; *Angew. Chem., Int. Ed.* **2007**, *46*, 6891. (d) Stuart, D. R.; Fagnou, K. *Science* **2007**, *316*, 1172. (e) Ren, H.; Li, Z.; Knochel, P. *Chem. Asian J.* **2007**, *2*, 416. (f) Giri, R.; Maugel, N.; Li, J.; Wang, D.; Breazzano, S. P.; Saunders, L. B.; Yu, J.-Q. *J. Am. Chem. Soc.* **2007**, *129*, 3510. (g) Chen, X.; Goodhue, C. E.; Yu, J.-Q. *J. Am. Chem. Soc.* **2006**, *128*, 12634. (h) Pastine, S. J.; Gribkov, D. V.; Sames, D. *J. Am. Chem. Soc.* **2006**, *128*, 14220. (i) Dong, C.-G.; Hu, Q.-S. *Angew. Chem.* **2006**, *118*, 2347; *Angew. Chem., Int. Ed.* **2006**, *45*, 2289. (j) Chen, X.; Li, J.-J.; Hao, X.-S.; Goodhue, C. E.; Yu, J.-Q. *J. Am. Chem. Soc.* **2006**, *128*, 78. (k) Ackermann, L.; Althammer, A.; Born, R. *Angew. Chem.* **2006**, *118*, 2681; *Angew. Chem., Int. Ed.* **2006**, *45*, 2619. (l) Zaitsev, V. G.; Shabashov, D.; Daugulis, O. *J. Am. Chem. Soc.* **2005**, *127*, 13154. (m) Daugulis, O.; Zaitsev, V. G. *Angew. Chem.* **2005**, *117*, 4114; *Angew. Chem., Int. Ed.* **2005**, *44*, 4046. (n) Crabtree, R. H. *J. Organomet. Chem.* **2004**, *689*, 4083. (o) Murahashi, S.-I.; Komiya, N.; Terai, H.; Nakae, T. *J. Am. Chem. Soc.* **2003**, *125*, 15312. (p) Ritleng, V.; Sirlin, C.; Pfeffer, M. *Chem. Rev.* **2002**, *102*, 1731. (q) Fokin, A. A.; Schreiner, P. R. *Chem. Rev.* **2002**, *102*, 1551. (r) Goossen, L. J. *Angew. Chem.* **2002**, *114*, 3929; *Angew. Chem., Int. Ed.* **2002**, *41*, 3775. (s) Jia, C.; Kitamura, T.; Fujiwara, Y. *Acc. Chem. Res.* **2001**, *34*, 633. (t) Chatani, N.; Asaumi, T.; Yorimitsu, S.; Ikeda, T.; Kakiuchi, F.; Murai, S. *J. Am. Chem. Soc.* **2001**, *123*, 10935. (u) Chen, H.; Schlecht, S.; Semple, T. C.; Hartwig, J. F. *Science* **2000**, *287*, 1995. (v) Dyker, G. *Angew. Chem.* **1999**, *111*, 1808; *Angew. Chem., Int. Ed.* **1999**, *38*, 1698. (w) Naota, T.; Takaya, H.; Murahashi, S. I. *Chem. Rev.* **1998**, *98*, 2599. (x) Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879. (y) Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154. (z) Goldman, A. S. *Nature* **1993**, *366*, 514.

(4) (a) Cheng, D. P.; Bao, W. L. *Adv. Synth. Catal.* **2008**, *350*, 1263. (b) Li, Z.; Cao, L.; Li, C.-J. *Angew. Chem.* **2007***119*, 6625; *Angew. Chem., Int. Ed.* **2007**, *46*, 6505. (c) Zhang, Y.; Li, C.-J. *Eur. J. Org. Chem.* **2007**, 4654. (d) Li, Q.; Wei, Y.; Hao, J.; Zhu, Y.; Wang, L. *J. Am. Chem. Soc.* **2007**, *129*, 5810. (e) Li, Z.; Li, C.-J. *J. Am. Chem. Soc.* **2006**, *128*, 56. (f) Zhang, Y.; Li, C.-J. *J. Am. Chem. Soc.* **2006**, *128*, 4242. (g) Zhang, Y.; Li, C.-J. *Angew. Chem.* **2006**, *118*, 1983; *Angew. Chem., Int. Ed.* **2006**, *45*, 1949. (h) Li, Z.; Li, C.-J. *J. Am. Chem. Soc.* **2005**, *127*, 3672. (i) Li, Z.; Li, C.-J. *Eur. J. Org. Chem.* **2005**, 3173. (j) Brown, S. H.; Crabtree, R. H. *J. Am. Chem. Soc.* **1989**, *111*, 2935.

(5) (a) Hull, K. L.; Sanford, M. S. *J. Am. Chem. Soc.* **2007**, *129*, 11904. (b) Lu, J.; Tan, X.; Chen, C. *J. Am. Chem. Soc.* **2007**, *129*, 7768. (c) Chiong, H. A.; Daugulis, O. *Org. Lett.* **2007**, *9*, 1449. (d) Dwight, T. A.; Rue, N. R.; Charyk, D.; Josselyn, R.; DeBoef, B. *Org. Lett.* **2007**, *9*, 3137. (e) Rech, J. C.; Yato, M.; Duckett, D.; Ember, B.; LoGrasso, P. V.; Bergman, R. G.; Ellman, J. A. *J. Am. Chem. Soc.* **2007**, *129*, 490. (f) Cai, G.; Fu, Y.; Li, Y.; Wan, X.; Shi, Z. *J. Am. Chem. Soc.* **2007**, *129*, 7666. (g) Yokota, T.; Tani, M.; Sakaguchi, S.; Ishii, Y. *J. Am. Chem. Soc.* **2003**, *125*, 1476. (h) Ritleng, V.; Sirlin, C.; Pfeffer, M. *Chem. Rev.* **2002**, *102*, 1731. (i) Tsuji, J.; Nagashima, H. *Tetrahedron.* **1984**, *40*, 2699.

(6) (a) Li, Z.; Li, C.-J. *J. Am. Chem. Soc.* **2005**, *127*, 6968. (b) DeBoef, B.; Pastine, S. J.; Sames, D. *J. Am. Chem. Soc.* **2004**, *126*, 6556.

(7) (a) Li, Z.; Li, C.-J. *Org. Lett.* **2004**, *6*, 4997. (b) Li, Z.; Li, C.-J. *J. Am. Chem. Soc.* **2004**, *126*, 11810. (c) Xu, X.; Li, X. *Org. Lett.* **2009**, *11*, 1027.

(8) For recent reviews, see: (a) Sherry, B. D.; Fürstner, A. *Acc. Chem. Res.* **2008**, *41*, 1500–1511. (b) Correa, A.; Mancheño, O. G.; Bolm, C. *Chem. Soc. Rev.* **2008**, *37*, 1108. (c) Enthaler, S.; Junge, K.; Beller, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 3317. (d) Fürstner, A.; Martin, R.; Krause, H.; Seidel, G.; Goddard, R.; Lehmann, C. W. *J. Am. Chem. Soc.* **2008**, *130*, 8773. (e) Fürstner, A.; Martin, R. *Chem. Lett.* **2005**, *34*, 624. (f) Bolm, C.; Legros, J.; Le Paih, J.; Zani, L. *Chem. Rev.* **2004**, *104*, 6217.

(9) (a) Norinder, J.; Matsumoto, A.; Yoshikai, N.; Nakamura, E. *J. Am. Chem. Soc.* **2008**, *130*, 5858. (b) Volla, C. M. R.; Vogel, P. *Angew. Chem., Int. Ed.* **2008**, *47*, 1305. (c) Lu, Z.; Chai, G. B.; Ma, S. M. *J. Am. Chem. Soc.* **2007**, *129*, 14546.

(10) (a) Carril, M.; Correa, A.; Bolm, C. *Angew. Chem., Int. Ed.* **2008**, *47*, 4862. (b) Correa, A.; Carril, M.; Bolm, C. *Angew. Chem., Int. Ed.* **2008**, *47*, 2880. (c) Bistri, O.; Correa, A.; Bolm, C. *Angew. Chem., Int. Ed.* **2008**, *47*, 586.

(11) (a) Wen, J.; Zhang, J.; Chen, S.-Y.; Li, J.; Yu, X.-Q. *Angew. Chem., Int. Ed.* **2008**, *47*, 8897. (b) Li, Z. P.; Yu, R.; Li, H. J. *Angew. Chem., Int. Ed.* **2008**, *47*, 7497.

(12) (a) Langlotz, B. K.; Wadepohl, H.; Gade, L. H. *Angew. Chem., Int. Ed.* **2008**, *47*, 4670. (b) Shaikh, N. S.; Enthaler, S.; Junge, K.; Beller, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 2497.

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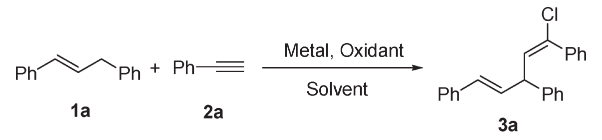
Recently, we reported the indolation reaction of allylic compounds using DDQ as the oxidant via sp^3 C$-$H bond activation and C$-$C bond formation.[14] Due to the achievement of oxidative C$-$H bond activation of allylic compounds, we designed an iron-promoted C$-$C bond-formation reaction.

1-Halo-1,4-pentadiene derivatives are potentially useful intermediates in organic synthesis due to the multifunctionality contained in the molecules, which may be utilized in subsequent substitution and coupling reactions.[15] In addition, 1-halo-1,4-pentadiene derivatives are useful intermediates in the synthesis of some natural products in recent years.[16] In the past few years, several methods to synthesize 1-halo-1,4-pentadiene derivatives or dihalo-1,4-pentadiene derivatives have been developed, mainly using alkynes, aldehydes, and BuLi,[17g] TiX$_4$,[17b,i] BX$_3$,[17a,d,f] FeX$_3$,[17e,h] GaX$_3$[17c] as the reagents. Herein, we report an iron-promoted synthesis of 1-halo-1,4-pentadiene derivatives by the reaction of 1,3-diphenylpropenes with ethynylbenzenes via sp^3 C$-$H bond activation and C$-$C bond formation.

To begin our study, we chose 1,3-diphenylpropene (**1a**) and ethynylbenzene (**2a**) as the standard substrates to search for suitable reaction conditions. BQ (benzoquinone) is a well-known oxidation reagent for organic synthesis.[18] When **1a** and **2a** were mixed with a stoichiometric amount of BQ, no desired product was detected (Table 1, entry 1). Then Bronsted acids such as BF$_3\cdot$Et$_2$O, HOTf, and Fe(OTf)$_3$ were tested, but no desired product was found (Table 1, entries 2, 3, and 5). When ZnCl$_2$ was used, less than 15% desired product was isolated (Table 1, entry 4). This was not a satisfactory result. When FeCl$_3$ and DDQ were used, the yield was improved to 65% (Table 1, entry 7, in DCE at 80 °C). Further, BQ, TBHP, and *tert*-butyl peroxide were screened as the oxidant, for they performed well in C$-$H bond activation reactions. The yield was improved to 70% when BQ was used as the oxidant in DCE at 80 °C (Table 1, entry 10), and no isomers were detected. When we performed the reaction under an atmosphere of dry nitrogen, the desired product also could be obtained in 67% yield (Table 1, entry 11). When the amount of FeCl$_3$ was decreased to 0.33 equiv (total chlorine ~1.0 equiv), the yield was decreased to 51% (Table 1, entry 12). When the amount of FeCl$_3$ was reduced to 0.1 equiv, the desired product was obtained in 15% yield (Table 1, entry 13), suggesting that the second and/or third chlorides in the promoter took part in the reaction. In addition, when 1.0 equiv of FeCl$_3\cdot$6H$_2$O was used, the desired product was also obtained in good yield (Table 1, entry 14). A number of solvents were screened, and the desired product was obtained in moderate yield in toluene, benzene, CH$_2$Cl$_2$, and CHCl$_3$. However, considerable amounts of undesired products were formed in DMF, NMP, and 1,4-dioxane (Table 1, entries 15−21).

TABLE 1. Optimization of the Reaction Conditions[a]



entry	metal (equiv)	oxidant	solvent	temp (°C)	yield (%)
1	none	BQ	DCE	80	ND
2	BF$_3\cdot$Et$_2$O (1.0)	BQ	DCE	80	ND
3	HOTf (1.0)	BQ	DCE	80	ND
4	ZnCl$_2$ (1.0)	BQ	DCE	80	<15
5	Fe(OTf)$_3$ (1.0)	BQ	DCE	80	ND
6	CuCl$_2$ (1.0)	BQ	toluene	100	ND
7	FeCl$_3$ (1.0)	DDQ	DCE	80	65
8	FeCl$_3$ (1.0)	TBHP	DCE	80	trace
9	FeCl$_3$ (1.0)	*tert*-butyl peroxide	DCE	80	ND
10	FeCl$_3$ (1.0)	BQ	DCE	80	70
11[b]	FeCl$_3$ (1.0)	BQ	DCE	80	67
12	FeCl$_3$ (0.3)	BQ	DCE	80	51
13	FeCl$_3$ (0.1)	BQ	DCE	80	15
14	FeCl$_3\cdot$6H$_2$O (1.0)	BQ	DCE	80	64
15	FeCl$_3$ (1.0)	BQ	toluene	100	36
16	FeCl$_3$ (1.0)	BQ	DMF	90	<20
17	FeCl$_3$ (1.0)	BQ	NMP	80	trace
18	FeCl$_3$ (1.0)	BQ	benzene	50	45
19	FeCl$_3$ (1.0)	BQ	1,4-dioxane	80	28
20	FeCl$_3$ (1.0)	BQ	CH$_2$Cl$_2$	50	43
21	FeCl$_3$ (1.0)	BQ	CHCl$_3$	50	68

[a]Unless otherwise specified, the reaction was carried out using 0.5 mmol of **1a**, 0.6 mmol of **2a**, 1.5 mL of solvent, and 0.6 mmol of oxidant in open air atmosphere. [b]The reaction was carried out under an atmosphere of dry nitrogen.

With the optimized reaction conditions established, various substrates were subjected to the reactions, and representative results are summarized in Table 2. Ethynylbenzene with an electron-withdrawing group reacted well with the diarylpropenes under the standard reaction conditions (Table 2, entry 2). However, a moderate yield was achieved when ethynylbenzenes with electron-donating groups were used (Table 2, entries 3−5). Unfortunately, no desired product was obtained when 2-ethynylpyridine (it polymerized rapidly while the reaction temperature rose), 1-ethynyl-4-methoxy-benzene, 2-ethynyl-1,3-dimethylbenzene, and 1-hexyne reacted as the substrates. To expand the scope of the reaction, we further examined the mono- and disubstituted 1,3-diarylpropenes. High yields of the coupling products were obtained when they had an electron-donating group on the aromatic ring, while moderate yields were given if they had an electron-withdrawing group on the aromatic ring

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(13) (a) Yoshikai, N.; Matsumoto, A.; Norinder, J.; Nakamura, E. *Angew. Chem., Int. Ed.* **2009**, *48*, 2925. (c) Ilies, L.; Tsuji, H.; Nakamura, E. *Org. Lett.* **2009**, *11*, 3966. (c) Yoshikai, N.; Matsumoto, A.; Norinder, J.; Nakamura, E. *Synlett* **2010**, 313. (d) Vallée, F.; Mousseau, J. J.; Charette, A. B. *J. Am. Chem. Soc.* **2010**, *132*, 1514. (e) Wei, H.; Hao, C.; Aiwen Lei, L. *Angew. Chem., Int. Ed.* **2010**, *49*, 2004. (f) Jones, W. D.; Foster, G. P.; Putinas, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 5047. (g) Norinder, J.; Matsumoto, A.; Yoshikai, N.; Nakamura, E. *J. Am. Chem. Soc.* **2008**, *130*, 5858. (h) Li, Z.; Cao, L.; Li, C.-J. *Angew. Chem.* **2007**, *119*, 6625; *Angew. Chem., Int. Ed.* **2007**, *46*, 6505. (i) Li, Z.; Yu, R.; Li, H. *Angew. Chem.* **2008**, *120*, 7607; *Angew. Chem., Int. Ed.* **2008**, *47*, 7497. (j) Zhang, Y.; Li, C.-J. *Eur. J. Org. Chem.* **2007**, 4654. (k) Wen, J.; Zhang, J.; Chen, S.-Y.; Li, J.; Yu, X.-Q. *Angew. Chem.* **2008**, *120*, 9029; *Angew. Chem., Int. Ed.* **2008**, *47*, 8897. (l) Li, Y. Z.; Li, B. J.; Lu, X. Y.; Lin, S.; Shi, Z. J. *Angew. Chem., Int. Ed.* **2009**, *48*, 3817. (m) Plietker, B. *Angew. Chem., Int. Ed.* **2006**, *45*, 1469. (n) Plietker, B. *Angew. Chem., Int. Ed.* **2006**, *45*, 6053. (o) Plietker, B.; Dieskau, A.; Möws, K.; Jatsch, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 198. (p) Jegelka, M.; Plietker., B. *Org. Lett.* **2009**, *11*, 3463.

(14) Mo, H. J.; Bao, W. L. *Adv. Synth. Catal.* **2009**, *351*, 2845.

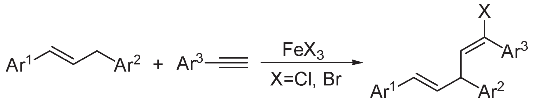
(15) (a) Suzuki, A. *Pure Appl. Chem.* **1986**, *58*, 829. (b) Suzuki, A. *Rev. Heteroatom. Chem.* **1997**, *17*, 271.

(16) Hoye, T. R.; Wang, J. *J. Am. Chem. Soc.* **2005**, *127*, 6950.

(17) (a) Kabalka, G. W.; Wu, Z.; Ju, Y. *Org. Lett.* **2002**, *4*, 1491. (b) Kabalka, G. W.; Wu, Z.; Ju, Y. *Org. Lett.* **2002**, *4*, 3415. (c) Yadav, J. S.; Reddy, B. V. S.; Eeshwaraiah, B.; Gupta, M. K.; Biswas, S. K. *Tetrahedron Lett.* **2005**, *46*, 1161. (d) Kabalka, G. W.; Yao, M.-L.; Borella, S.; Wu, Z. *Chem. Commun.* **2005**, 2492. (e) Miranda, P. O.; Diaz, D. D.; Padron, J. I.; Ramirez, M. A.; Martin, V. S. *J. Org. Chem.* **2005**, *70*, 57. (f) Kabalka, G. W.; Yao, M.-L.; Borella, S.; Wu, Z.; Ju, Y.; Quick, T. *J. Org. Chem.* **2008**, *73*, 2668. (g) Kabalka, G. W.; Borella, S.; Yao, M.-L. *Synthesis* **2008**, 325. (h) Biswas, S.; Maiti, S.; Jana, U. *Eur. J. Org. Chem.* **2009**, 2354. (i) Yao, M.-L.; Quick, T. R.; Wu, Z.; Quinn, M. P.; Kabalka, G. W. *Org. Lett.* **2009**, *11*, 2647.

(18) Hull, K. L.; Sanford, M. S. *J. Am. Chem. Soc.* **2009**, *131*, 9651.

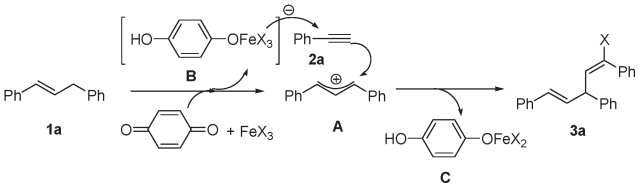
TABLE 2. Iron-Catalyzed/Promoted Synthesis of Substituted 1-Halo-1,4-pentadienes[a]



entry	Ar^1, Ar^2	Ar^3	X	product	yield[b](%)
1	C_6H_5, C_6H_5	C_6H_5	Cl	**3a**	70
2	C_6H_5, C_6H_5	p-Cl-C_6H_4	Cl	**3b**	79
3	C_6H_5, C_6H_5	p-Me-C_6H_4	Cl	**3c**	61
4	C_6H_5, C_6H_5	p-Et-C_6H_4	Cl	**3d**	58
5	C_6H_5, C_6H_5	p-Pr-C_6H_4	Cl	**3e**	55
6	p-Me-C_6H_4, p-Me-C_6H_4	C_6H_5	Cl	**3f**	75
7	p-Cl-C_6H_4, p-Cl-C_6H_4	C_6H_5	Cl	**3g**	56
8	p-Br-C_6H_4, p-Br-C_6H_4	C_6H_5	Cl	**3h**	47
9	p-Cl-C_6H_4, C_6H_5	C_6H_5	Cl	**3i**, **3j**	57
10	C_6H_5, C_6H_5	C_6H_5	Br	**4a**	70[c]
11	C_6H_5, C_6H_5	p-Et-C_6H_4	Br	**4b**	65[c]
12	C_6H_5, C_6H_5	p-Cl-C_6H_4	Br	**4c**	74[c]
13	p-Cl-C_6H_4, p-Cl-C_6H_4	C_6H_5	Br	**4d**	56[c]

[a] 0.5 mmol of diarylpropenes, 0.6 mmol of ethynylbenzenes, 1.5 mL of DCE, 0.6 mmol of BQ, 1.0 equiv of $FeCl_3$, 80 °C, overnight. [b] Based on diarylpropene. [c] 0.5 mmol of diarylpropenes, 0.6 mmol of ethynylbenzenes, 1.5 mL of $CHCl_3$, 0.6 mmol of BQ, 1.0 equiv of $FeBr_3$, 50 °C, overnight.

SCHEME 1. Proposed Mechanism



(Table 2, entries 6−9). No desired product was obtained when (*E*)-4,4′-(prop-1-ene-1,3-diyl)bis(nitrobenzene), (*E*)-4,4′-(prop-1-ene-1,3-diyl)bis(methoxybenzene), (*E*)-4-phenylbut-3-enenitrile, (*E*)-ethyl 4-phenylbut-3-enoate, and allylbenzene were used as the substrates. In the same fashion as using $FeCl_3$ as the promoter, $FeBr_3$-promoted reactions produced bromine-incorporated products **4a**, **4b**, **4c**, and **4d** in 56−74% yield (Table 2, entries 10−13).

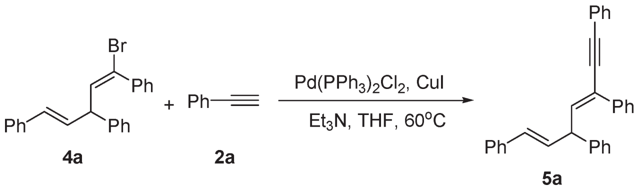
On the basis of these observations, a plausible mechanism is proposed in Scheme 1. First, BQ abstracted a hydride from **1a** to form the conjugated intermediate **A**,[19a] and the reductant **B** electrophilic attacked the ethynylbenzene (**2a**) followed by C−C bond formation with intermediate **A** to give the desired product **3a**.[19b]

Product **3** or **4** can further react with ethynylbenzenes to form 1-yne-3,6-heptadiene derivatives. For example, **4a** was successfully reacted with ethynylbenzene (**2a**) and the product **5a** was obtained in 49% yield (Scheme 2).

To learn the geometry of the halogenated double bond, product **4a** was treated with BuLi; (1*Z*,4*E*)-1,3,5-triphenylpenta-1,4-diene (**6a**) was obtained (see the Supporting Information, NOESY spectrum of **6a**) in 89% yield (Scheme 3), and no isomers were detected.

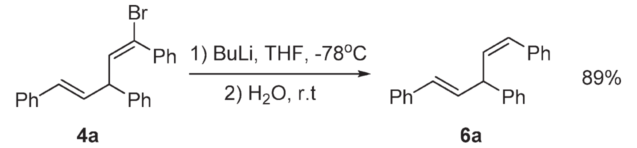
In summary, $FeCl_3$- and $FeBr_3$-promoted synthesis of 1-halopenta-1,4-diene derivatives by the reaction of 1,3-diarylpropenes with ethynylbenzenes has been realized. The present protocol has provided a route to vinylic C−Cl and C−Br bond formation.

SCHEME 2. Palladium-Catalyzed Coupling of 4[a] **with Ethynylbenzene**



[a] Reaction conditions: 0.5 mmol of **4a**, 0.6 mmol of **2a**, 5 mol % of Pd catalyst, 5 mol % of CuI, 1 mmol of Et_3N, 1.5 mL of THF, N_2 protection, 60 °C, overnight.

SCHEME 3. Preparation of (1*Z*,4*E*)-Penta-1,4-dienes from 4[a]



[a] Reaction conditions: (1) 1 mmol of **4a**, 3 mmol of BuLi, 10 mL of dry THF, −78 °C, under an atmosphere of dry nitrogen; (2) 15 mL of H_2O, rt.

Experimental Section

General Procedure for Products 3. A sealed tube was charged with diarylpropenes (0.5 mmol), ethynylbenzenes (0.6 mmol), BQ (0.6 mmol), $FeCl_3$ (0.5 mmol), and DCE (1.5 mL). The mixture was stirred at 80 °C overnight. The reaction mixture was washed with water and extracted with EtOAc. The combined organic layers were dried over anhydrous $MgSO_4$. After evaporation and column chromatography on silica gel (pure petroleum ether), the fraction with an $R_f = 0.4$ was collected to give the desired product.

((1*E*,4*E*)-1-Chloropenta-1,4-diene-1,3,5-triyl)tribenzene (3a). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45−7.21 (m, 15H), 6.47 (d, J = 16 Hz, 1H), 6.35 (dd, J = 6, 16 Hz, 1H), 6.23 (d, J = 10.4 Hz, 1H), 4.34 (dd, J = 6.4, 10.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 48.4, 126.3, 126.8, 127.5, 127.6, 128.3, 128.5, 128.6, 128.8, 128.9, 130.3, 130.7, 131.2, 131.5, 136.91, 136.94, 142.2. IR (neat): 3059, 3026, 1597, 1492, 1445, 966, 906, 729, 694 cm^{-1}. MS (70 eV, EI): m/z = 330.

General Procedure for Products 4. A sealed tube was charged with diarylpropenes (0.5 mmol), ethynylbenzenes (0.6 mmol), BQ (0.6 mmol), $FeBr_3$ (0.5 mmol), and $CHCl_3$ (1.5 mL). The mixture was stirred at 50 °C overnight. The reaction mixture was washed with water and extracted with EtOAc. The combined organic layers were dried over anhydrous $MgSO_4$. After evaporation and column chromatography on silica gel (pure petroleum ether), the fraction with an $R_f = 0.4$ was collected to give the desired product.

((1*E*,4*E*)-1-Bromopenta-1,4-diene-1,3,5-triyl)tribenzene (4a). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43−7.20 (m, 15H), 6.48−6.43 (m, 2H), 6.33 (dd, J=6, 16 Hz, 1H), 4.27 (dd, J=6, 10 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=49.4, 121.3, 126.3, 126.9, 127.6, 127.7, 128.4, 128.5, 128.6, 128.7, 128.8, 130.8, 130.9, 134.5, 137.0, 138.4, 142.0. IR (neat): 3058, 3025, 1597, 1491, 1444, 965, 907, 742, 693 cm^{-1}. MS (70 eV, EI): m/z = 374.

General Procedure for Products 5. A sealed tube was charged with **4** (0.5 mmol), ethynylbenzenes (0.6 mmol), Et_3N (1 mmol), $Pd(PPh_3)_2Cl_2$ (5 mol %), CuI (5 mol %), and THF (1.5 mL) under an atmosphere of dry nitrogen. The mixture was stirred at

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(19) (a) Cheng, D. P.; Bao, W. L. *Adv. Synth. Catal.* **2008**, *350*, 1263. (b) Xu, T.; Yu, Z; Wang, L. *Org. Lett.* **2009**, *11*, 2113.

60 °C overnight. The resulting mixture was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1), and the fraction with an $R_f = 0.5$ was collected to give the desired product.

(3*E*,6*E*)-Hepta-3,6-dien-1-yne-1,3,5,7-tetrayltetrabenzene (5a). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50−7.23 (m, 20H), 6.54−6.47 (m, 2H), 6.40 (dd, J=6, 16 Hz, 1H), 4.56 (dd, J = 6, 10.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 47.9, 88.7, 91.0, 123.3, 124.1, 126.3, 126.7, 127.4, 127.8, 128.0, 128.1, 128.2, 128.4, 128.5, 128.6, 128.7, 128.8, 130.8, 131.5, 137.2, 137.3, 139.3, 142.6. IR (neat): 3025, 2924, 1713, 1597, 1490, 1443, 1362, 1071, 1028, 965, 754, 691 cm^{-1}. MS (70 eV, EI) m/z = 396. HRMS (EI): m/z calcd for $C_{31}H_{24}$ (M^+) 396.1878, found 396.1881.

General Procedure for Products 6. Under an atmosphere of dry nitrogen, BuLi (1.5 mL, 2 M in hexane) was dropped into a solution of **4** (1 mmol) in 10 mL of dry THF at −78 °C. The progress of the reaction was monitored by TLC, and the mixture was stirred until the starting material disappeared. The reaction mixture was quenched with 15 mL of water and extracted with EtOAc (3 × 5 mL). The combined organic layers were dried over anhydrous $MgSO_4$. Evaporation and column chromatography on silica gel afforded **6**.

(1*Z*,4*E*)-Penta-1,4-diene-1,3,5-triyltribenzene (6a). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42−7.23 (m, 15H), 6.69 (d, J = 11.2, 1H), 6.55 (d, J = 16 Hz, 1H), 6.45 (dd, J = 6, 16 Hz, 1H), 5.92 (t, J = 10.4 Hz, 1H), 4.77 (dd, J = 6.4, 10 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 46.9, 126.3, 126.6, 127.0, 127.3, 127.8, 128.3, 128.5, 128.6, 128.7, 129.5, 130.5, 132.3, 132.8, 137.1, 137.4, 143.4. IR (neat): 3024, 2927, 1808, 1598, 1447, 1256, 1075, 1027, 968, 737, 697 cm^{-1}. MS (70 eV, EI): m/z = 296.

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Supporting Information Available: Experimental procedures along with copies of spectra. This material is available free of charge via the Internet at http://pubs.acs.org.