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Copper-catalyzed coupling reactions of alkenyl halides with alkynes in the absence of palladium and ligand

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Abstract—We report herein copper(I)-catalyzed cross-coupling reactions of alkenyl halides with alkynes for the synthesis of 2-alkynyl-buta-1,3-dienes in good to excellent yields. This procedure is the first example for the synthesis of enynes catalyzed by catalytic amount of copper(I) alone in the absence of palladium and any ligand at relatively lower temperature.

1. Introduction

Conjugated enynes are valuable precursors for polysubstituted benzenes[1] and conjugated dienes.[2] Furthermore, enynes also can be found in a variety of naturally occurring compounds such as 6,7-dehydro-stipiamide[3] and mucocin.[4] Among the methods for the synthesis of enynes, transition metal-catalyzed coupling reactions[5] such as the Pd/Cu co-catalyzed Sonogashira coupling reaction between an alkyne and a vinyl halide is the most prevalent one,[6] which are now problematic for industrial use because of the cost of the transition metals. In recent years, copper catalysts, much more cheaper and available ones than normal transition metal catalysts such as palladium and rhodium, have been widely used for the formation of carbon–heteroatom[7] and carbon–carbon bonds.[8] Recently, there has been a resurgence in the development of copper-based methods for the coupling reactions and these methods can also tolerate a wide range of functional groups and substrates. The synthetic scope of these reactions, however, is greatly shrunk by harsh conditions, for example, higher temperatures and air or moisture-sensitive phosphine ligands are required.[7,8] To date, a number of phosphine-free catalysts have been examined for the copper-catalyzed coupling reactions,[9] however, to the best of our knowledge, no paper for the coupling reaction of alkenyl halides with alkynes with copper alone in the absence of any ligand has been reported.[10] Therefore, novel strategies are still in high demand. We previously reported a Pd/Cu co-catalyzed coupling reaction of 2,4-diiodo-but-1-enes with alkynes for the construction of enyne units.[11] In continuing efforts, our attention was drawn to the copper for the same coupling reaction. Herein, we wish to report our new finding that copper(I) iodide alone is used as an efficient catalyst for the cross-coupling reaction of 2,4-halo-but-1-enes with alkynes to give the corresponding enyne products in good to high yields. To date, this is the first example for the C–C coupling reaction catalyzed by copper(I) alone in the absence of palladium and any ligand.[12]

2. Results and discussion

Initial examinations were carried out by the reactions of diiodide **1a** (0.125 mmol) with phenylacetylene **2a** (0.15 mmol) catalyzed by copper(I) iodide (20 mol %) in the presence of various inorganic bases (0.25 mmol) in DMF (1.0 mL).[13] The reactions proceeded smoothly to give the corresponding coupling product **3a** in reasonable to excellent yields as a sole product at 80 °C (Table 1). The best result was obtained using Na_2CO_3 as the base to afford the product **3a** in 95% yield (Table 1, entry 1).

With these optimized reaction conditions in hand, we then turned our interest to the reaction generality. A variety of diiodides **1** and alkynes **2** were examined under these optimal conditions. Satisfactorily, most of the reactions proceeded smoothly to afford the corresponding enynes in good to excellent yields (Table 2). This synthetic method can tolerate aryl alkynes as **2a**, **2b**, and **2c**, substituted with both electron-rich and electron-poor groups, respectively, for a variety of diiodides **1** (Table 2, entries 1–13). The coupling reaction of diiodides **1** with 1-hexyne **2d** also gave the desired products **3o–q** in moderate to good yields, which are superior to

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Keywords: Alkenyl halide; 2-Alkynyl-1,3-buta-dienes; Alkynes; Cross-coupling reaction; Copper catalyst.

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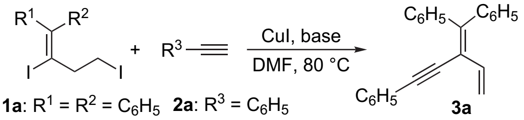
Table 1. Optimization for the coupling reaction of diiodide **1a** with alkyne **2a** catalyzed by CuI (20 mol %)



1a: $R^1 = R^2 = C_6H_5$ **2a**: $R^3 = C_6H_5$ **3a**

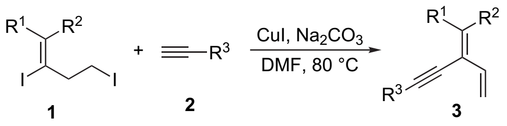
Entry[a]	Base	Yield (%)[b]
1	Na_2CO_3	95
2	K_2CO_3	79
3	$NaHCO_3$	92
4	KOH	50
5	$K_3PO_4 \cdot 3H_2O$	29
6	$KHCO_3$	68
7	HCO_2Na	37
8	CH_3CO_2K	42
9	NaOH	21

[a] All reactions were carried out using **1a** (0.125 mmol), **2a** (0.15 mmol), base (0.25 mmol), and CuI (20 mol %) in DMF (1.0 mL) at 80 °C for 24 h.

[b] Isolated yields.

the previously reported results with co-catalyst of Pd/Cu (Table 2, entries 14–16).[11a]

Table 2. CuI-catalyzed coupling reaction of various diiodides **1** with alkynes **2**



1 **2** **3**

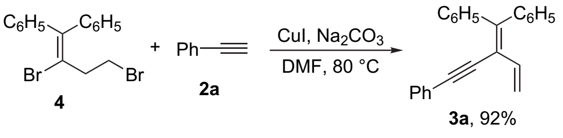
Entry[a]	**1** (R^1/R^2)	**2** (R^3)	Yield (%)[b]
			3
1	**1b** (4-MeC_6H_4/4-MeC_6H_4)	**2a** (C_6H_5)	**3b**, 86
2	**1c** (4-ClC_6H_4/4-ClC_6H_4)	**2a**	**3c**, 60
3	**1d** (4-FC_6H_4/4-FC_6H_4)	**2a**	**3d**, 96
4	**1e** (4-$MeOC_6H_4$/4-$MeOC_6H_4$)	**2a**	**3e**, 99
5	**1f** (Me/4-$EtOC_6H_4$)	**2a**	**3f**, 87
6	**1a** (C_6H_5/C_6H_5)	**2b** (4-$MeOC_6H_4$)	**3g**, 99
7	**1b**	**2b**	**3h**, 99
8	**1e**	**2b**	**3i**, 95
9	**1a**	**2c** (4-ClC_6H_4)	**3j**, 73
10	**1c**	**2c**	**3k**, 71
11	**1b**	**2c**	**3l**, 85
12	**1d**	**2c**	**3m**, 91
13	**1e**	**2c**	**3n**, 84
14[c]	**1a**	**2d** ($^nC_4H_9$)	**3o**, 87
15[c]	**1c**	**2d**	**3p**, 73
16[c]	**1b**	**2d**	**3q**, 41

[a] Otherwise specified, all reactions were carried out using **1** (0.125 mmol), **2** (0.15 mmol), Na_2CO_3 (0.25 mmol), and CuI (20 mol %) in DMF (1.0 mL) at 80 °C for 24 h.

[b] Isolated yields.

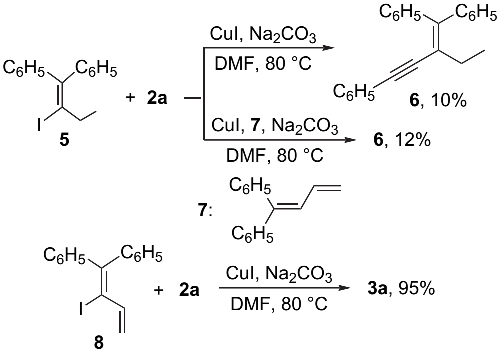
[c] 1-Hexyne of 2.0 equiv was used.

More importantly, we were pleased to find that copper(I) alone catalyzed coupling reaction of dibromide **4** with alkyne **2a** also worked well to give the desired product **3a** in 92% yield (Scheme 1).



Scheme 1. CuI-catalyzed coupling reaction of dibromide **4** with alkyne **2a**.

To further understand this copper(I) alone catalyzed coupling reaction of dihalides with alkynes in the absence of palladium and any ligand, three control experiments using 1,1-diphenyl-2-iodo-but-1-ene **5** or 1,1-diphenyl-2-iodo-buta-1,3-diene **8** and phenylacetylene **2a** as the substrates were performed under identical conditions, respectively (Scheme 2). We found that only 10% of the coupling product **6** was obtained under the optimal conditions as shown in Table 1, entry 1 (Scheme 2). In addition, the yield of **6** was not affected when 1,1-diphenyl-buta-1,3-diene **7** was added as a ligand (Scheme 2). This result excludes the possibility of diene as a ligand in the reaction system. Further studies showed that the reaction of 1,1-diphenyl-2-iodo-but-1,3-diene **8** with phenylacetylene **2a** took place to give the desired product **3a** in 95% yield under the optimized reaction conditions (Scheme 2). This result suggests that the buta-1,3-diene derivative **8**, which is formed from the elimination of HI from substrate **1a** under basic condition, may be a key intermediate in this CuI alone catalyzed effective coupling reaction.



Scheme 2. Three control experiments.

3. Conclusion

In conclusion, we have found a novel CuI alone catalyzed coupling reaction of 2,4-halo-but-1-enes with alkynes in the absence of palladium and any ligand at relatively lower temperature. A variety of enynes were obtained in good to high yields. Efforts are underway to elucidate the mechanistic details and the scope and limitations of this reaction in the laboratory.

4. Experimental section

4.1. General remarks

Melting points are uncorrected. ^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively. Mass and HRMS spectra were recorded by EI and MALDI methods. Organic solvents used were dried by standard methods when necessary. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with silica gel coated plates. Flash column chromatography was carried out using silica gel at increased pressure.

4.2. General procedure for the copper-catalyzed coupling reaction

Under an argon atmosphere, dihalide **1** (0.125 mmol), alkyne **2** (0.15 mmol), Na_2CO_3 (0.25 mmol), CuI (20 mol %), and

DMF (1.0 mL) were added into a Schlenk tube. The reaction mixture was stirred at 80 °C for about 24 h. The solvent was removed under reduced pressure and then the residue was purified by a flash column chromatography.

4.2.1. (3,3′-Diphenylmethylene-pent-4-en-1-ynyl)-benzene (3a).[11a] ^{1}H NMR (CDCl$_3$, 300 MHz, TMS) δ 5.31 (dd, 1H, J=1.8, 10.5 Hz), 5.95 (dd, 1H, J=1.8, 16.8 Hz), 6.59 (dd, 1H, J=10.5, 16.8 Hz), 7.19–7.36 (m, 13H, Ar), 7.49–7.53 (m, 2H, Ar). ^{13}C NMR (CDCl$_3$, 75 MHz, TMS) δ 87.8, 94.8, 117.2, 119.9, 123.6, 127.5, 127.8, 127.9, 128.0, 128.1, 128.3, 130.5, 130.6, 131.4, 134.6, 140.6, 141.9, 149.1.

4.2.2. [3,3′-Di(4-methylphenyl)methylene-pent-4-en-1-ynyl]-benzene (3b).[11a] ^{1}H NMR (CDCl$_3$, 300 MHz, TMS) δ 2.36 (s, 3H, CH$_3$), 2.38 (s, 3H, CH$_3$), 5.27 (dd, 1H, J=1.8, 10.5 Hz), 5.91 (dd, 1H, J=1.8, 16.8 Hz), 6.58 (dd, 1H, J=10.5, 16.8 Hz), 7.07–7.18 (m, 6H, Ar), 7.27–7.37 (m, 5H, Ar), 7.41 (d, 2H, J=8.4 Hz, Ar). ^{13}C NMR (CDCl$_3$, 75 MHz, TMS) δ 21.27, 21.34, 88.1, 94.5, 117.0, 118.9, 123.7, 127.9, 128.16, 128.18, 128.20, 128.7, 130.4, 130.5, 130.6, 131.3, 134.9, 137.6, 137.8, 137.9, 139.1, 149.1.

4.2.3. [3,3′-Di(4-chlorophenyl)methylene-pent-4-en-1-ynyl]-benzene (3c).[11a] ^{1}H NMR (CDCl$_3$, 300 MHz, TMS) δ 5.35 (dd, 1H, J=1.5, 10.2 Hz), 5.98 (dd, 1H, J=1.5, 16.8 Hz), 6.52 (dd, 1H, J=10.2, 16.8 Hz), 7.11 (d, 2H, J=8.4 Hz, Ar), 7.28–7.34 (m, 9H, Ar), 7.42 (d, 2H, J=8.4 Hz, Ar). ^{13}C NMR (CDCl$_3$, 75 MHz, TMS) δ 87.1, 95.6, 118.9, 120.7, 123.1, 127.8, 128.3, 128.39, 128.41, 128.43, 131.4, 131.8, 132.0, 133.9, 134.1, 138.5, 139.9, 146.1.

4.2.4. [3,3′-Di(4-fluoromethylphenyl)methylene-pent-4-en-1-ynyl]-benzene (3d). A pale yellow solid, mp: 119–120 °C. ^{1}H NMR (CDCl$_3$, 300 MHz, TMS) δ 5.34 (dd, 1H, J=1.5, 10.2 Hz), 5.96 (dd, 1H, J=1.5, 16.8 Hz), 6.54 (dd, 1H, J=10.2, 16.8 Hz), 7.01 (d, 2H, J=9.0 Hz, Ar), 7.08 (d, 2H, J=9.0 Hz, Ar), 7.15–7.19 (m, 2H, Ar), 7.29–7.34 (m, 5H, Ar), 7.44–7.50 (m, 2H, Ar). ^{13}C NMR (CDCl$_3$, 75 MHz, TMS) δ 87.4, 95.0, 114.6 (d, $J_{C\text{–}F}$=21.08 Hz), 115.2 (d, $J_{C\text{–}F}$=21.08 Hz), 118.3, 120.1 (d, $J_{C\text{–}F}$=1.35 Hz), 123.2, 128.27, 128.33, 131.3, 132.2, 132.3, 132.4, 134.2, 136.3 (d, $J_{C\text{–}F}$=3.6 Hz), 137.7 (d, $J_{C\text{–}F}$=3.3 Hz), 146.6, 162.4 (d, $J_{C\text{–}F}$=246.75 Hz). IR (CH$_2$Cl$_2$) ν 2928, 2369, 2341, 1597, 1508, 1502, 1489, 1222, 1156, 922 cm^{-1}. MS (%) m/z 342 (M$^+$, 100). HRMS calcd for C$_{24}$H$_{16}$F$_2$: 342.1220. Found: 342.1245.

4.2.5. [3,3′-Di(4-methoxyphenyl)methylene-pent-4-en-1-ynyl]-benzene (3e).[11a] ^{1}H NMR (CDCl$_3$, 300 MHz, TMS) δ 3.81 (s, 3H, CH$_3$O), 3.82 (s, 3H, CH$_3$O), 5.26 (dd, 1H, J=1.8, 10.2 Hz), 5.90 (dd, 1H, J=1.8, 16.8 Hz), 6.61 (dd, 1H, J=10.2, 16.8 Hz), 6.85 (d, 2H, J=8.7 Hz, Ar), 6.88 (d, 2H, J=8.7 Hz, Ar), 7.12 (d, 2H, J=8.7 Hz, Ar), 7.26–7.28 (m, 3H, Ar), 7.34–7.35 (m, 2H, Ar), 7.47 (d, 2H, J=8.7 Hz, Ar). ^{13}C NMR (CDCl$_3$, 75 MHz, TMS) δ 55.2, 88.4, 94.3, 112.8, 113.3, 116.6, 118.0, 123.7, 127.9, 128.2, 131.3, 132.06, 132.13, 133.1, 134.6, 135.1, 148.6, 159.26, 159.32.

4.2.6. [3-Methyl-3-(4-ethoxyphenyl)methylene-pent-4-en-1-ynyl]-benzene (3f).[11a] ^{1}H NMR (CDCl$_3$, 300 MHz, TMS) δ 1.42 (t, 3H, J=7.2 Hz), 2.44 (s, 3H), 4.04 (q, 2H, J=7.2 Hz), 5.13 (d, 1H, J=10.8 Hz), 5.72 (d, 1H, J=17.1 Hz), 6.52 (dd, 1H, J=10.8, 17.1 Hz), 6.88 (d, 2H, J=8.4 Hz, Ar), 7.15 (d, 2H, J=8.4 Hz, Ar), 7.32–7.34 (m, 3H, Ar), 7.52–7.55 (m, 2H, Ar). ^{13}C NMR (CDCl$_3$, 75 MHz, TMS) δ 14.8, 24.5, 63.4, 86.6, 96.0, 114.0, 115.6, 119.1, 123.7, 128.0, 128.3, 129.7, 131.4, 133.4, 133.7, 146.2, 158.3.

4.2.7. 1-Methoxy-4-[diphenylmethylene-pent-4-en-1-ynyl]-benzene (3g).[11a] ^{1}H NMR (CDCl$_3$, 300 MHz, TMS) δ 3.77 (s, 3H, CH$_3$O), 5.29 (dd, 1H, J=1.8, 10.2 Hz), 5.95 (dd, 1H, J=1.8, 17.1 Hz), 6.59 (dd, 1H, J=10.2, 17.1 Hz), 6.80 (d, 2H, J=9.0 Hz, Ar), 7.19–7.35 (m, 10H, Ar), 7.51 (dd, 2H, J=1.8, 8.1 Hz, Ar). ^{13}C NMR (CDCl$_3$, 75 MHz, TMS) δ 55.2, 86.4, 94.9, 113.9, 115.6, 117.7, 120.1, 127.4, 127.67, 127.74, 128.0, 130.5, 130.6, 132.8, 134.7, 140.6, 141.9, 148.3, 159.4.

4.2.8. 1-Methoxy-4-[di(4-methylphenyl)methylene-pent-4-en-1-ynyl]-benzene (3h). A pale yellow solid, mp: 144–146 °C. ^{1}H NMR (CDCl$_3$, 300 MHz, TMS) δ 2.36 (s, 3H), 2.37 (s, 3H), 3.79 (s, 3H, CH$_3$O), 5.25 (dd, 1H, J=1.5, 10.5 Hz), 5.90 (dd, 1H, J=1.5, 16.8 Hz), 6.59 (dd, 1H, J=10.5, 16.8 Hz), 6.82 (d, 2H, J=9.0 Hz, Ar), 7.06–7.16 (m, 6H, Ar), 7.28 (d, 2H, J=9.0 Hz, Ar), 7.42 (d, 2H, J=7.8 Hz, Ar). ^{13}C NMR (CDCl$_3$, 75 MHz, TMS) δ 21.26, 21.34, 55.2, 86.7, 94.6, 113.9, 115.9, 116.9, 119.1, 128.1, 128.7, 130.5, 130.6, 132.8, 135.0, 137.5, 137.6, 138.0, 139.2, 148.4, 159.4. IR (CH$_2$Cl$_2$) ν 3021, 2921, 2856, 2369, 2319, 2200, 1605, 1509, 1502, 1457, 1441, 1284, 1248, 1168, 1034 cm^{-1}. MS (%) m/z 364 (M$^+$, 100), 349 (78). HRMS calcd for C$_{27}$H$_{24}$O (MALDI): 365.1900. Found: 365.1902.

4.2.9. 1-Methoxy-4-[di(4-methoxylphenyl)methylene-pent-4-en-1-ynyl]-benzene (3i).[11a] ^{1}H NMR (CDCl$_3$, 300 MHz, TMS) δ 3.78 (s, 3H, CH$_3$O), 3.81 (s, 3H, CH$_3$O), 3.82 (s, 3H, CH$_3$O), 5.25 (dd, 1H, J=1.8, 10.5 Hz), 5.89 (dd, 1H, J=1.8, 17.1 Hz), 6.60 (dd, 1H, J=10.5, 17.1 Hz), 6.81 (d, 2H, J=8.7 Hz, Ar), 6.85 (d, 2H, J=8.7 Hz, Ar), 6.88 (d, 2H, J=8.7 Hz, Ar), 7.11 (d, 2H, J=8.7 Hz, Ar), 7.29 (d, 2H, J=8.7 Hz, Ar), 7.47 (d, 2H, J=8.7 Hz, Ar). ^{13}C NMR (CDCl$_3$, 75 MHz, TMS) δ 55.19, 55.21, 87.0, 94.3, 112.7, 113.3, 113.9, 115.9, 116.5, 118.2, 132.0, 132.1, 132.7, 133.2, 134.6, 135.1, 147.8, 159.1, 159.2, 159.3.

4.2.10. 1-Chloro-4-(diphenylmethylene-pent-4-en-1-ynyl)-benzene (3j).[11a] ^{1}H NMR (CDCl$_3$, 300 MHz, TMS) δ 5.31 (dd, 1H, J=1.8, 10.5 Hz), 5.91 (dd, 1H, J=1.8, 17.1 Hz), 6.59 (dd, 1H, J=10.5, 17.1 Hz), 7.18–7.27 (m, 6H, Ar), 7.31–7.36 (m, 6H, Ar), 7.47–7.50 (m, 2H, Ar). ^{13}C NMR (CDCl$_3$, 75 MHz, TMS) δ 88.8, 93.6, 117.8, 119.6, 122.0, 127.5, 127.9, 128.0, 128.1, 128.6, 130.4, 130.6, 132.5, 134.0, 134.4, 140.4, 141.8, 149.6.

4.2.11. 1-Chloro-4-[di(4-chlorophenyl)methylene-pent-4-en-1-ynyl]-benzene (3k).[11a] ^{1}H NMR (CDCl$_3$, 300 MHz, TMS) δ 5.35 (dd, 1H, J=1.5, 10.2 Hz), 5.93 (dd, 1H, J=1.5, 16.8 Hz), 6.52 (dd, 1H, J=10.2, 16.8 Hz), 7.11 (d, 2H, J=8.7 Hz, Ar), 7.25–7.42 (m, 10H, Ar). ^{13}C NMR (CDCl$_3$, 75 MHz, TMS) δ 88.1, 94.3, 118.9, 120.5, 121.5, 127.9, 128.5, 128.7, 131.8, 132.1, 132.6, 134.0, 134.1, 134.2, 134.4, 138.4, 139.8, 146.5.

4.2.12. 1-Chloro-4-[di(4-methylphenyl)methylene-pent-4-en-1-ynyl]-benzene (3l). A yellow solid, mp: 134–136 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.36 (s, 3H), 2.37 (s, 3H), 5.26 (dd, 1H, J=1.5, 10.2 Hz), 5.87 (dd, 1H, J=1.5, 14.7 Hz), 6.60 (dd, 1H, J=10.2, 14.7 Hz), 7.06–7.17 (m, 6H, Ar), 7.25 (s, 4H, Ar), 7.39 (d, 2H, J=8.1 Hz, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.27, 21.34, 89.2, 93.3, 117.0, 118.6, 122.2, 128.2, 128.6, 128.7, 130.4, 130.6, 132.5, 133.9, 134.8, 137.70, 137.74, 137.9, 139.0, 149.7. IR (CH_2Cl_2) ν 3022, 2926, 2852, 2370, 2319, 1605, 1505, 1479, 1390, 1091, 1006 cm^{-1}. MS (%) m/z 368 (M$^+$, 99), 353 (91), 318 (100). HRMS calcd for $C_{26}H_{21}Cl$: 368.1332. Found: 368.1338.

4.2.13. 1-Chloro-4-[di(4-fluorophenyl)methylene-pent-4-en-1-ynyl]-benzene (3m). A yellow solid, mp: 142–144 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 5.33 (dd, 1H, J=1.8, 10.8 Hz), 5.92 (dd, 1H, J=1.8, 17.1 Hz), 6.53 (dd, 1H, J=10.8, 17.1 Hz), 6.99–7.09 (m, 4H, Ar), 7.13–7.29 (m, 6H, Ar), 7.42–7.47 (m, 2H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 88.4, 93.8, 114.6 (d, $J_{C\text{–}F}$=21.38 Hz), 115.2 (d, $J_{C\text{–}F}$=21.9 Hz), 118.3, 119.9 (d, $J_{C\text{–}F}$=1.73 Hz), 121.7, 128.7, 132.2, 132.3 (d, $J_{C\text{–}F}$=1.73 Hz), 132.4, 132.5, 134.1, 134.3, 136.1 (d, $J_{C\text{–}F}$=3.53 Hz), 137.7 (d, $J_{C\text{–}F}$=2.85 Hz), 147.1, 162.5 (d, $J_{C\text{–}F}$=247.2 Hz). IR (CH_2Cl_2) ν 3052, 2911, 2385, 2319, 1597, 1509, 1486, 1390, 1228, 1158, 1087, 1013 cm^{-1}. MS (%) m/z 376 (M$^+$, 100), 340 (91). HRMS calcd for $C_{24}H_{15}ClF_2$: 376.0830. Found: 376.0820.

4.2.14. 1-Chloro-4-[di(4-methoxylphenyl)methylene-pent-4-en-1-ynyl]-benzene (3n).[11a] ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 3.737 (s, 3H, CH_3O), 3.744 (s, 3H, CH_3O), 5.17 (dd, 1H, J=2.1, 10.8 Hz), 5.77 (dd, 1H, J=2.1, 16.5 Hz), 6.52 (dd, 1H, J=10.8, 16.5 Hz), 6.49 (d, 2H, J=10.2 Hz, Ar), 6.54 (d, 2H, J=10.2 Hz, Ar), 7.03 (d, 2H, J=8.4 Hz, Ar), 7.17 (s, 4H, Ar), 7.36 (d, 2H, J=8.4 Hz, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 55.2, 89.5, 93.0, 112.8, 113.3, 116.6, 117.7, 122.2, 128.6, 132.06, 132.13, 132.5, 133.0, 133.8, 134.5, 134.9, 149.1, 159.3, 159.4.

4.2.15. 3-Diphenylmethylene-non-1-en-4-yne (3o).[11a] ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.87 (t, 3H, J=7.2 Hz), 1.26–1.55 (m, 4H), 2.33 (t, 2H, J=7.2 Hz), 5.21 (dd, 1H, J=1.8, 10.2 Hz), 5.81 (dd, 1H, J=1.8, 16.5 Hz), 6.53 (dd, 1H, J=10.2, 16.5 Hz), 7.15 (dd, 2H, J=1.8, 7.8 Hz, Ar), 7.24–7.33 (m, 6H, Ar), 7.43 (dd, 2H, J=1.8, 7.8 Hz, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 13.6, 19.3, 21.9, 30.5, 78.0, 96.3, 117.4, 120.4, 127.4, 127.46, 127.50, 128.0, 130.2, 130.6, 135.2, 140.9, 142.0, 147.8.

4.2.16. 3-Di(4-chlorophenyl)methylene-non-1-en-4-yne (3p).[11a] ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.87 (t, 3H, J=6.9 Hz), 1.26–1.52 (m, 4H), 2.33 (t, 2H, J=6.9 Hz), 5.21 (dd, 1H, J=1.8, 10.2 Hz), 5.82 (dd, 1H, J=1.8, 17.1 Hz), 6.53 (dd, 1H, J=10.2, 17.1 Hz), 7.15 (d, 2H, J=7.5 Hz, Ar), 7.26 (d, 2H, J=7.5 Hz, Ar), 7.31 (d, 2H, J=7.5 Hz, Ar), 7.44 (d, 2H, J=7.5 Hz, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 13.6, 19.3, 21.9, 30.5, 78.0, 96.3, 117.4, 120.4, 127.4, 127.5, 127.9, 130.3, 130.6, 135.2, 140.9, 142.0, 147.8.

4.2.17. 3-Di(4-methylphenyl)methylene-non-1-en-4-yne (3q). A colorless liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.88 (t, 3H, J=7.8 Hz), 1.26–1.54 (m, 4H), 2.31–2.35 (m, 8H), 5.17 (dd, 1H, J=2.1, 10.5 Hz), 5.78 (dd, 1H, J=2.1, 16.5 Hz), 6.53 (dd, 1H, J=10.5, 16.5 Hz), 7.03 (d, 2H, J=8.4 Hz, Ar), 7.07 (d, 2H, J=8.4 Hz, Ar), 7.13 (d, 2H, J=8.4 Hz, Ar), 7.33 (d, 2H, J=8.4 Hz, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 13.6, 19.3, 21.2, 21.3, 21.9, 30.6, 78.3, 95.9, 116.7, 119.5, 128.1, 128.6, 130.2, 130.5, 135.5, 137.22, 137.24, 138.1, 139.3, 147.9. IR (CH_2Cl_2) ν 3022, 2950, 2928, 2859, 2207, 1900, 1730, 1682, 1605, 1501, 1442 cm^{-1}. MS (%) m/z 314 (M$^+$, 100). HRMS calcd for $C_{24}H_{26}$: 314.2034. Found: 314.2036.

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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.2007.09.020.

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