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A DDQ-promoted metal-free cross-coupling of 1,3-diarylpropynes with hydroxyl via Sp^3 C–H bond activation to form C–O bond

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ABSTRACT

A metal-free coupling reaction between 1,3-diarylpropynes and alcohols/phenols/acids via propargylic sp^3 C–H bonds activation and C–O bond formation reaction promoted by DDQ was realized. The reaction afforded series of propargyl ethers, propargyl esters and propargyl ketals.

1. Introduction

The formation of carbon–heteroatom bonds from a common intermediate is of great significance to the drug discovery and production process.[1] In particular, the construction of an ether linkage adjacent to a sterically hindered carbon centre is important for the synthesis of many biologically active compounds.[2] The conventional method for ether synthesis is the direct S_N2-type O-alkylation (Williamson ether synthesis). However, this protocol is sometimes synthetically impractical owing to the strong basicity of the alkoxide anion, which may be incompatible with other functional groups presented in the system.[3] Therefore some modified methods were developed,[4–6] for example, transition metal-catalyzed cross-coupling of aryl halides with phenols or alcohols.[4b,c,e,f,l] However, transition metal-based protocols, although successful, usually have some inherent limitations, such as moisture sensitivity, costly metal catalysts and environmental toxicity.[4c] With the prevalence of 'atom economy'[7] and 'green chemistry',[8] the cross-coupling reaction for constructing C–O bonds without any metal catalysts via C–H functionalization has attracted great interest.

Propargyl ethers/esters are useful structural motifs that can serve as substrates or intermediates in countless transformations,[9] especially in the synthesis of allenes. In the past few years, only few methods were reported to prepare propargyl ethers/esters.[10] However, using transition metal catalysts, such as Au or Ru compounds is costly and environmental harmful.[10a,c] Recently, Gevorgyan and co-workers used phenylethynyl bromide and ketones as the substrates with KHMDS/NaO^{t}Bu as the strong base to synthesize the propargyl ethers,[10b] but the substrates were costly and not easy to obtain with their limitations in structure. So it is meaningful and worthy of directly using propargylic sp^3 C–H bonds and hydroxyl without any metal catalyst to form propargyl ethers/esters.

For the construction of C–O bonds, our group reported a metal-free coupling reaction to form C–O bonds between 1,3-diarylpropenes and alcohols promoted by DDQ, which afforded a new path to synthesize various types of C–O bonds.[11] Recently, both 1,3-diarylpropynes and 1,3-diarylpropenes were reported to react with 1,3-dicarbonyl compounds to form C–C bonds by our group.[12] By comparing these, it suggested that the coupling reaction of 1,3-diarylpropenes was faster and more simple, and the desired product of 1,3-diarylpropenes was more stable and the yield was higher than the desired substituted product of 1,3-diarylpropynes. Thus the formation of C–O bonds between 1,3-diarylpropynes and hydroxyl directly still remains a challenge. Herein we report a metal-free oxidative coupling reaction promoted by DDQ between 1,3-diarylpropynes and alcohols/phenols/acids to form a series of propargyl ethers, esters and ketals.

2. Discussion

To begin our study, 1-phenyl-3-(4′-methoxyl)phenylpropyne and ethanol were chosen as the standard substrates to search for suitable reaction conditions. When 1-phenyl-3-(4′-methoxyl) phenylpropyne and ethanol were mixed in 1 mL CH_2Cl_2 with a stoichiometric amount of DDQ, 0.1 equiv of CuBr as the catalyst,

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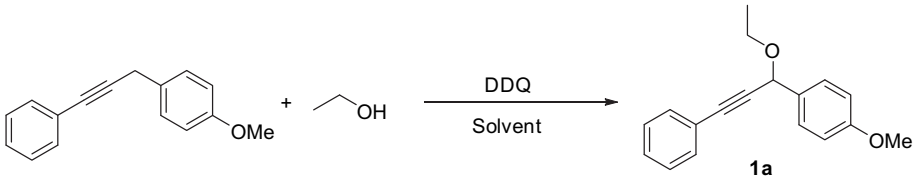
the desired product was isolated in 61% yield (Table 1, entry 1). Then the same reaction was taken without any metal catalyst. Surprisingly, the yield of the desired product was improved to 73% (Table 1, entry 2). The reactions of 1,3-diarylpropynes and alcohols finished in 2 h, which is longer than the reactions of 1,3-diarylpropenes and alcohols.[11] By decreasing the amount of DDQ to 0.5 equiv, the product was obtained in 42% yield (Table 1, entry 3). Only 29% yield of the product was isolated when 1.5 equiv of DDQ was used (Table 1, entry 4). Further, different temperatures were screened, which suggested that the reaction performed best under 0 °C (Table 1, entries 2, 5 and 6). A number of solvents were screened and the desired product was obtained in moderate yield in DCE, toluene, $CHCl_3$, DMF, THF and benzene. However, considerable amounts of undesired products were formed in CH_3NO_2, cyclohexane and 1,4-dioxane (Table 1, entries7–16).

Table 1
Screening of reaction conditions[a]



1a

Entry	Metal	Oxidant/equiv	Solvent	Temp (°C)	Yield[b] (%)
1	CuBr (0.1 equiv)	DDQ/1.0	CH_2Cl_2	0	61
2	None	DDQ/1.0	CH_2Cl_2	0	73
3	None	DDQ/0.5	CH_2Cl_2	0	43
4	None	DDQ/1.5	CH_2Cl_2	0	29
5	None	DDQ/1.0	CH_2Cl_2	rt	47
6	None	DDQ/1.0	CH_2Cl_2	50	20
7	None	DDQ/1.0	DCE	0	63
8	None	DDQ/1.0	Toluene	0	50
9	None	DDQ/1.0	$CHCl_3$	0	58
10	None	DDQ/1.0	CH_3CN	0	55
11	None	DDQ/1.0	CH_3NO_2	0	47
12	None	DDQ/1.0	DMF	0	65
13	None	DDQ/1.0	THF	0	61
14	None	DDQ/1.0	Cyclohexane	0	30
15	None	DDQ/1.0	1,4-Dioxane	0	49
16	None	DDQ/1.0	Benzene	0	59

[a] 1-Phenyl-3-(4′-methoxyl)phenylpropyne (0.25 mmol), 0.27 mmol of ethanol, 1 mL of solvent, 2 h.
[b] Isolated yield.

With the optimized reaction conditions established, we further explored the generality and efficiency of the DDQ-mediated oxidative cross-coupling reaction between various 1,3-diarylpropyne compounds with different alcohols, and a series of products were obtained in Table 2. Alcohols with electron-withdrawing groups reacted well with the 1,3-diarylpropynes under the standard condition (**1c**, **g** and **h**). However, a moderate yield was achieved when alcohols with electron-donating groups were used (**1b**, **f** and **i**). The steric effect caused the lower yield of the product (**1f**). Various 1,3-diarylpropyne compounds were also examined. High yields of the coupling products were obtained when there were electron-donating group on the aromatic ring (**1j**, **l** and **m**), while moderate yields were given if electron-withdrawing group existed (**1n**).

After screening the alcohols, phenols were used as the substrates to react with 1,3-diarylpropynes. For the stronger acidity of phenols, the cross-coupling reaction finished in 30 min, and a series of propargyl phenyl ethers were obtained in Table 3. The substituent effects were the same as the alcohols. Phenols with electron-withdrawing groups reacted well with the 1,3-diarylpropynes under the standard reaction condition (**2b** and **e**), and a moderate yield was achieved when phenols with electron-donating groups were used (**2c**, **d** and **g**). For 1,3-diarylpropynes, electron-donating substituents were favourable to obtain high yields (**2a**, **i**, **k** and **l**), but electron-withdrawing groups were disfavourable (**2j**). This means that the 1,3-diarylpropynes were oxidized to cations as intermediates.

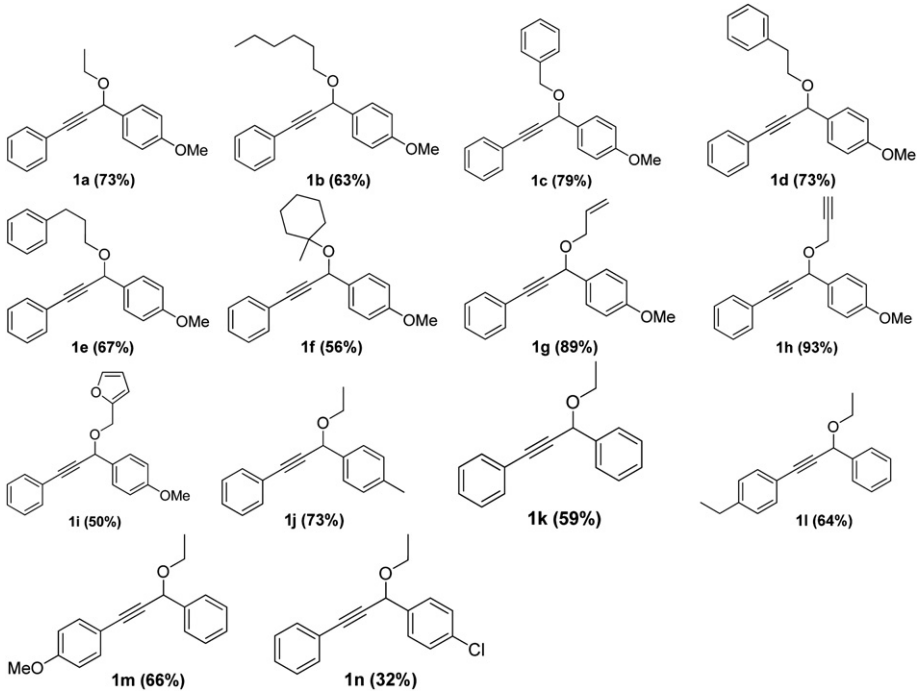
When ethane-1,2-diol and 2,2-dimethylpropane-1,3-diol were used as the substrate, **3a** and **3b** were isolated in high yields (Scheme 1). Thus a series of propargyl ketals can be easily obtained. Unfortunately, when we use pyrocatechol as the substrate, trace of the desired product was obtained. Then we used **1a** as the substrate to react with methanol, only less than 20% yield of desired unsymmetric ketal product was obtained.

To expand the scope of the reaction, the reaction of 1,3-diarylpropynes with several acids were also tested. Firstly, we chose 1-phenyl-3-(4′-methoxyl)phenylpropyne and acetic acid as the standard substrates. For the poor nucleophilicity of the acetic acid, the yield of the desired product was not satisfactory under the reaction condition of alcohols (Table 4, entry 2). Thus different reaction temperatures were screened, and a moderate yield of desired product (**4a**) was isolated when the reaction was taken under the room temperature (Table 4, entry 2). But the yield of the desired product decreased to 17% when the reaction was taken under 50 °C (Table 4, entry 3). When we decreased the reaction time, the yield of the product increased slowly, and 30 min would be the most suitable reaction time (Table 4, entries 2, 4, 5 and 6).

With the suitable reaction condition established, a series of propargyl esters were obtained in Table 5. Both aromatic and aliphatic acids can react with 1,3-diarylpropynes. But the yields of esters were lower than ethers, maybe the stability of esters were lower than ethers. The yields of aromatic esters were lower than the corresponding aliphatic esters (**4a**–**c**). The electron-donating groups on 1,3-diarylpropynes were also beneficial to the formation of esters (**4a**, **b**). Thus most types of propargyl C–O bonds have been formed.

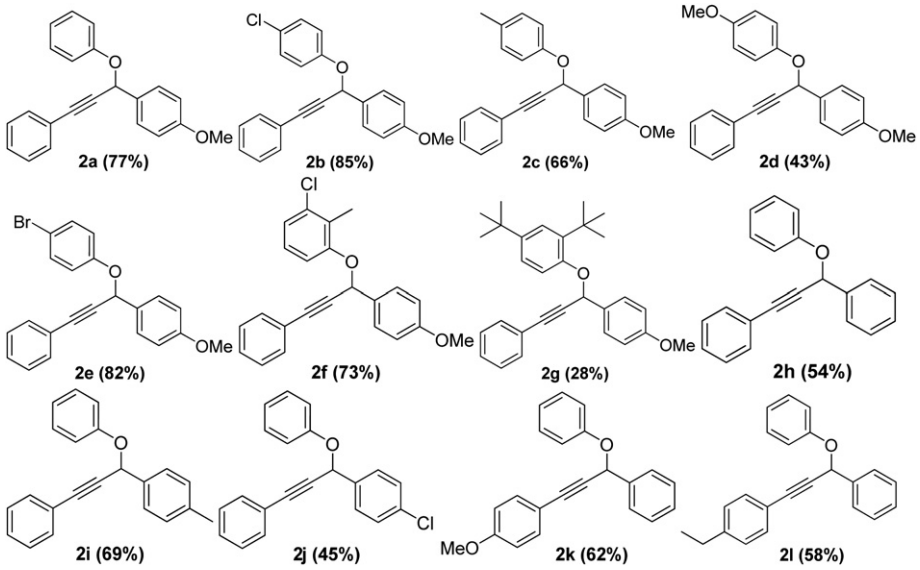
According to literature[11,12a] and based on our experiments, a possible mechanism was proposed in Scheme 2. The formation of product may have two pathways, hydride transferred directly from propargylic position and/or hydrogen abstraction after an electron was transferred from the propargylic triple bond to DDQ. However, sole products **1l**, **m** and **n** were obtained, respectively. The incoming nucleophile attacks mainly at the original benzylic cation position. This means the mechanism of hydride abstraction may be more possible.

Table 2
Formation of propargyl ethers between 1,3-diarylpropynes and alcohols[a,b]



[a] 1,3-Diarylpropynes (0.25 mmol), 0.27 mmol of alcohols, 0.25 mmol of DDQ, 1 mL of CH_2Cl_2, 0 °C, 2 h.
[b] Isolated yield.

Table 3
Formation of propargyl ethers between 1,3-diarylpropynes and phenols[a,b]



[a] 1,3-Diarylpropynes (0.25 mmol), 0.27 mmol of phenols, 0.25 mmol of DDQ, 1 mL of CH_2Cl_2, 0 °C, 30 min.
[b] Isolated yield.

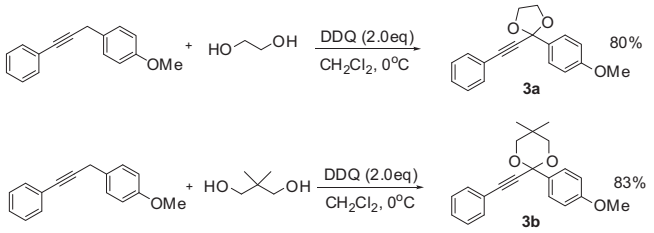
3. Conclusion

In summary, we have developed an efficient cross-coupling reaction between 1,3-diarylpropynes and alcohols/phenols/acids to form C–O bonds via sp^3 C–H bond activation promoted by DDQ. This provides a wide scope of propargyl ethers/esters and propargyl ketals in scientific research.

4. Experimental section

4.1. General procedure for products 1

To a 5 mL round-bottom flask with a mixture of 1,3-diarylpropynes (0.25 mmol) and alcohol (0.3 mmol) in CH_2Cl_2 (1 mL), DDQ (0.27 mmol) was added at 0 °C. The resulting mixture

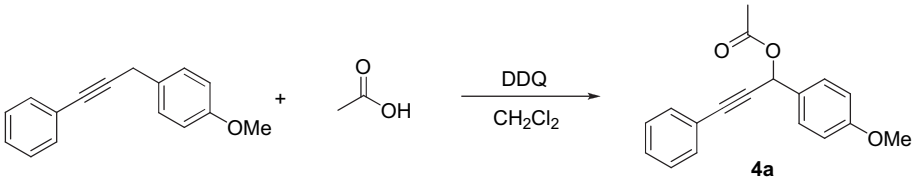


Scheme 1.

was stirred for 1 h. Purification was done by column chromatography on silica gel (petroleum ether/ethyl acetate=20/1), and the fraction with an R_f=0.6 was collected to give the desired product.

*4.1.1. 1-(1-Ethoxy-3-phenylprop-2-ynyl)-4-methoxybenzene (**1a**).* Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.53–7.46 (m, 4H), 7.33–7.30 (m, 3H), 6.94–6.91 (m, 2H), 5.35 (s, 1H), 3.82 (s, 3H), 3.80–3.59 (m, 2H), 1.28 (t, J=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=15.2, 55.3, 63.7, 71.4, 87.0, 87.5, 113.8, 122.7, 128.2, 128.3, 128.8, 131.2, 131.7, 159.6. IR (neat): 3058, 2926, 2857, 2221, 1609, 1512, 1465, 1249, 1170, 1077, 1036, 921, 828, 753, 690 cm^{-1}. MS (70 eV, EI) m/z=266.

Table 4
Screening of cross-coupling reaction conditions between 1,3-diarylpropynes and acids[a]

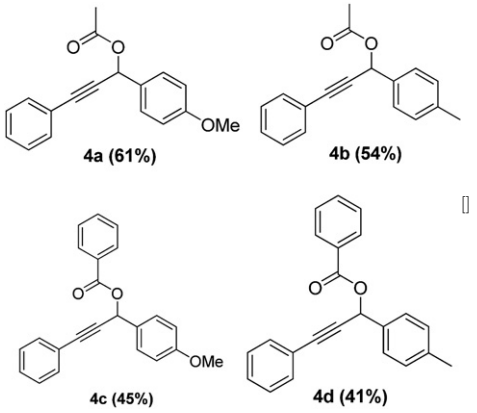


4a

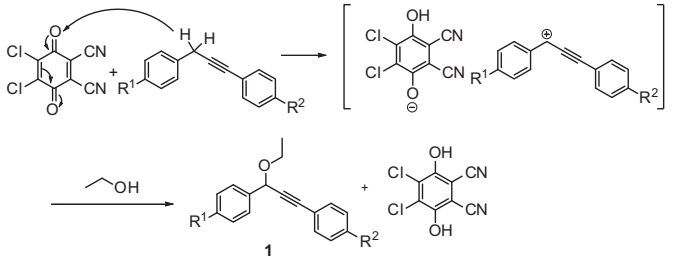
Entry	Temp (°C)	Time (min)	Yield[b] (%)
1	0	120	29
2	rt	120	36
3	50	120	17
4	rt	60	45
5	rt	30	61
6	rt	10	57

[a] 1-Phenyl-3-(4′-methoxyl)phenylpropyne (0.25 mmol), 0.27 mmol of acetic acid, 1 mL of CH_2Cl_2.
[b] Isolated yield.

Table 5
Formation of propargyl esters between 1,3-diarylpropynes and acids[a,b]



[a] 1,3-Diarylpropynes (0.25 mmol), 0.27 mmol of acids, 0.25 mmol of DDQ, 1.5 mL of CH_2Cl_2, room temperature, 30 min.
[b] Isolated yield.



Scheme 2. A possible mechanism.

*4.1.2. 1-(1-(Hexyloxy)-3-phenylprop-2-ynyl)-4-methoxybenzene (**1b**).* Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.52–7.46 (m, 4H), 7.33–7.30 (m, 3H), 6.92 (d, J=8.4 Hz, 2H), 5.34 (s, 1H), 3.82 (s, 3H), 3.73–3.51 (m, 2H), 1.66–1.60 (m, 2H), 1.40–1.26 (m, 6H), 0.88 (t, J=6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=13.9, 22.5, 25.8, 29.6, 31.5, 55.2, 68.2, 71.4, 87.0, 87.5, 113.7, 122.7, 128.1, 128.3, 128.7, 131.2, 131.7, 159.5. IR (neat): 3056, 2927, 2856, 2223, 1610, 1511, 1461, 1247, 1173, 1076, 1034, 916, 827, 755, 691 cm^{-1}. MS (70 eV, EI) m/z=322. HRMS (EI): m/z calcd for $C_{22}H_{26}O_2$ (M^+): 322.1933. Found, 322.1931.

*4.1.3. 1-(1-(Benzyloxy)-3-phenylprop-2-ynyl)-4-methoxybenzene (**1c**).* Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.51–7.21 (m, 12H), 6.90 (d, J=8.4 Hz, 2H), 5.38 (s, 1H), 4.75–4.66 (m, 2H), 3.79 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=55.2, 69.8, 70.5, 87.0, 87.6, 113.8, 122.6, 127.6, 128.1, 128.2, 128.3, 128.4, 128.9, 130.8, 131.7, 137.8, 159.7. IR (neat): 3056, 2926, 2859, 2227, 1609, 1511, 1491, 1457, 1302, 1248, 1173, 1031, 917, 830, 753, 693 cm^{-1}. MS (70 eV, EI) m/z=328. HRMS (EI): m/z calcd for $C_{23}H_{20}O_2$ (M^+): 328.1463. Found, 328.1465.

*4.1.4. 1-Methoxy-4-(1-phenethoxy-3-phenylprop-2-ynyl)benzene (**1d**).* Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.45–7.42 (m, 4H), 7.29–7.17 (m, 8H), 6.87 (d, J=8.8 Hz, 2H), 5.34 (s, 1H), 3.93–3.71 (m, 2H), 3.78 (s, 3H), 2.94 (t, J=7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=36.2, 55.2, 68.9, 71.6, 87.1, 87.3, 113.7, 122.6, 126.1, 128.17, 128.2, 128.4, 128.8, 128.9, 130.9, 131.7, 138.8, 159.6. IR (neat): 3061, 3028, 2923, 2855, 2221, 1608, 1510, 1457, 1247, 1173, 1070, 1032, 828, 753, 693 cm^{-1}. MS (70 eV, EI) m/z=342. HRMS (EI): m/z calcd for $C_{24}H_{22}O_2$ (M^+): 342.1620. Found, 342.1624.

*4.1.5. 1-Methoxy-4-(3-phenyl-1-(3-phenylpropoxy)prop-2-ynyl)benzene (**1e**).* Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.51–7.13 (m, 12H), 6.91–6.88 (m, 2H), 5.31 (s, 1H), 3.79 (s, 3H), 3.75–3.50 (m, 2H), 2.71 (t, J=7.6 Hz, 2H), 1.98–1.90 (m, 2H). ^{13}C NMR (100 MHz,

$CDCl_3$): δ=31.2, 32.3, 55.2, 67.2, 71.6, 87.1, 87.4, 113.8, 122.6, 125.6, 128.17, 128.2, 128.3, 128.5, 128.8, 131.1, 131.7, 141.9, 159.6. IR (neat): 3056, 3028, 2924, 2855, 2223, 1609, 1510, 1453, 1247, 1173, 1070, 1033, 915, 828, 753, 693 cm^{-1}. MS (70 eV, EI) m/z=356. HRMS (EI): m/z calcd for $C_{25}H_{24}O_2$ (M^+): 356.1776. Found, 356.1777.

*4.1.6. 1-Methoxy-4-(1-(1-methylcyclohexyloxy)-3-phenylprop-2-ynyl)benzene (**1f**).* Light yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ=7.52–7.29 (m, 7H), 6.90 (d, J=9.2 Hz, 2H), 5.44 (s, 1H), 3.87 (s, 3H), 2.01–1.97 (m, 2H), 1.78–1.75 (m, 2H), 1.58–1.22 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=24.1, 24.2, 24.3, 25.7, 31.8, 32.9, 55.2, 68.5, 75.5, 86.2, 88.3, 113.7, 122.8, 128.1, 128.2, 128.6, 131.7, 131.9, 159.4. IR (neat): 3056, 3000, 2929, 2855, 2225, 1610, 1510, 1448, 1246, 1173, 1065, 1032, 946, 825, 755, 691 cm^{-1}. MS (70 eV, EI) m/z=334. HRMS (EI): m/z calcd for $C_{23}H_{26}O_2$ (M^+): 334.1933. Found, 334.1930.

*4.1.7. 1-(1-(Allyloxy)-3-phenylprop-2-ynyl)-4-methoxybenzene (**1g**).* Light yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ=7.53–7.30 (m, 7H), 6.92 (d, J=8.8 Hz, 2H), 6.04–5.94 (m, 1H), 5.40 (s, 1H), 5.38–5.21 (m, 2H), 4.26–4.13 (m, 2H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=55.2, 68.9, 70.6, 87.1, 87.3, 113.8, 117.6, 122.6, 128.2, 128.4, 128.8, 130.9, 131.7, 134.3, 159.6. IR (neat): 3056, 2925, 2853, 2226, 1610, 1511, 1460, 1302, 1247, 1173, 1034, 924, 827, 756, 691 cm^{-1}. MS (70 eV, EI) m/z=278. HRMS (EI): m/z calcd for $C_{19}H_{18}O_2$ (M^+): 278.1307. Found, 278.1301.

*4.1.8. 1-Methoxy-4-(3-phenyl-1-(prop-2-ynyloxy)prop-2-ynyl)benzene (**1h**).* Light yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ=7.53–7.24 (m, 7H), 6.93–6.89 (m, 2H), 5.59 (s, 1H), 4.44–4.24 (m, 2H), 3.81 (s, 3H), 2.48 (t, J=2.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=55.16, 55.23, 70.1, 74.8, 79.4, 86.1, 87.8, 113.9, 122.3, 128.2, 128.5, 129.1, 130.0, 131.7, 159.8. IR (neat): 3290, 3056, 2926, 2856, 2225, 1610, 1511, 1443, 1302, 1248, 1174, 1055, 1031, 927, 827, 756, 689 cm^{-1}. MS (70 eV, EI) m/z=276. HRMS (EI): m/z calcd for $C_{19}H_{16}O_2$ (M^+): 276.1150. Found, 276.1146.

*4.1.9. 2-((1-(4-Methoxyphenyl)-3-phenylprop-2-ynyloxy)methyl)furan (**1i**).* Light yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ=7.52–7.25 (m, 8H), 6.91 (d, J=8.8 Hz, 2H), 6.39–6.35 (m, 2H), 5.41 (s, 1H), 4.67 (d, J=4.8 Hz, 2H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=55.3, 61.7, 70.4, 86.7, 87.7, 109.8, 110.3, 113.8, 122.6, 128.2, 128.5, 129.0, 130.5, 131.8, 142.9, 151.4, 159.7. IR (neat): 3059, 2931, 2858, 2226, 1641, 1463, 1248, 1176, 1075, 1031, 922, 831, 751, 689 cm^{-1}. MS (70 eV, EI) m/z=318. HRMS (EI): m/z calcd for $C_{21}H_{18}O_3$ (M^+): 318.1256. Found, 318.1253.

*4.1.10. 1-(1-Ethoxy-3-phenylprop-2-ynyl)-4-methylbenzene[1] (**1j**).* Light yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ=7.50–7.19 (m, 9H), 5.36 (s, 1H), 3.83–3.58 (m, 2H), 2.37 (s, 3H), 1.29 (t, J=7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=15.1, 21.1, 63.7, 71.7, 87.0, 87.4, 122.7, 127.4, 128.1, 128.3, 129.1, 131.7, 136.0, 138.0. IR (neat): 3056, 2923, 2863, 2222, 1718, 1599, 1512, 1489, 1444, 1305, 1176, 1073, 1023, 889, 812, 754, 691 cm^{-1}. MS (70 eV, EI) m/z=250.

*4.1.11. (3-Ethoxyprop-1-yne-1,3-diyl)dibenzene[1] (**1k**).* Light yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ=7.60–7.30 (m, 10H), 5.39 (s, 1H), 3.85–3.59 (m, 2H), 1.31–1.26 (t, J=7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=15.1, 63.8, 71.8, 87.17, 87.19, 122.6, 127.4, 128.1, 128.2, 128.3, 128.4, 131.7, 138.9. IR (neat): 3059, 2974, 2926, 2223, 1599, 1489, 1449, 1309, 1160, 1070, 1027, 917, 885, 755, 692 cm^{-1}. MS (70 eV, EI) m/z=236.

*4.1.12. 1-(3-Ethoxy-3-phenylprop-1-ynyl)-4-ethylbenzene (**1l**).* Light yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ=7.65–7.36 (m, 7H), 7.18 (d, J=8.4 Hz, 2H), 5.43 (s, 1H), 3.88–3.63 (m, 2H), 2.68 (q, J_1=7.6 Hz, J_2=15.2 Hz, 2H), 1.32 (t, J=6.8 Hz, 3H), 1.27 (t, J=7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=15.1, 15.2, 28.7, 63.8, 71.8, 86.5, 87.4, 119.7, 127.4, 127.7, 128.2, 128.4, 131.7, 139.0, 144.8. IR (neat): 3030, 2968, 2928, 2870, 2223, 1510, 1452, 1308, 1162, 1070, 1021, 972, 918, 885, 751, 697 cm^{-1}. MS (70 eV, EI) m/z=264. HRMS (EI): m/z calcd for $C_{19}H_{20}O$ (M^+): 264.1514. Found, 264.1517.

*4.1.13. 1-(3-Ethoxy-3-phenylprop-1-ynyl)-4-methoxybenzene (**1m**).* Light yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ=7.61–7.34 (m, 7H), 6.85 (d, J=8.8 Hz, 2H), 5.39 (s, 1H), 3.82 (s, 3H), 3.82–3.59 (m, 2H), 1.30 (t, J=6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=15.1, 55.2, 63.7, 71.9, 85.8, 87.1, 113.8, 114.7, 127.4, 128.1, 128.4, 133.2, 139.1, 159.6. IR (neat): 3061, 2972, 2925, 2222, 1747, 1605, 1508, 1453, 1289, 1173, 1070, 1030, 885, 831, 753, 698 cm^{-1}. MS (70 eV, EI) m/z=266. HRMS (EI): m/z calcd for $C_{18}H_{18}O_2$ (M^+): 266.1307. Found, 266.1309.

*4.1.14. 1-Chloro-4-(1-ethoxy-3-phenylprop-2-ynyl)benzene[1] (**1n**).* Light yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ=7.54–7.31 (m, 9H), 5.36 (s, 1H), 3.85–3.57 (m, 2H), 1.28 (t, J=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=15.1, 63.9, 71.1, 86.6, 87.5, 122.3, 128.2, 128.5, 128.55, 128.7, 131.7, 134.0, 137.5. IR (neat): 3060, 2975, 2870, 2221, 1596, 1488, 1444, 1290, 1169, 1081, 1014, 915, 890, 754, 690 cm^{-1}. MS (70 eV, EI) m/z=270.

4.2. General procedure for products 2

To a 5 mL round-bottom flask with a mixture of 1,3-diarylpropynes (0.25 mmol) and phenol (0.3 mmol) in CH_2Cl_2 (1 mL), DDQ (0.27 mmol) was added at 0 °C. The resulting mixture was stirred for 0.5 h. Purification was done by 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.

*4.2.1. 1-Methoxy-4-(1-phenoxy-3-phenylprop-2-ynyl)benzene (**2a**).* Light yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ=7.60 (d, J=8.8Hz, 2H), 7.45–6.94 (m, 12H), 6.00 (s, 1H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=55.6, 70.7, 86.9, 88.5, 114.3, 116.7, 121.8, 122.6, 128.5, 128.9, 129.2, 129.6, 130.5, 132.0, 157.9, 160.2. IR (neat): 3056, 3004, 2930, 2834, 2225, 1591, 1489, 1460, 1303, 1249, 1219, 1173, 1110, 1074, 1031, 962, 870, 752, 689 cm^{-1}. MS (70 eV, EI) m/z=314. HRMS (EI): m/z calcd for $C_{22}H_{18}O_2$ (M^+): 314.1307. Found, 314.1301.

*4.2.2. 1-Chloro-4-(1-(4-methoxyphenyl)-3-phenylprop-2-ynyloxy) benzene (**2b**).* Light yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ=7.56 (d, J=8.4 Hz, 2H), 7.43–7.23 (m, 7H), 7.05 (d, J=9.2 Hz, 2H), 6.94 (d, J=8.8 Hz, 2H), 5.93 (s, 1H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=55.3, 70.8, 86.0, 88.5, 114.0, 117.8, 122.0, 126.5, 128.2, 128.7, 128.9, 129.2, 129.7, 131.7, 156.0, 160.0. IR (neat): 3060, 3028, 2925, 2857, 2227, 1610, 1511, 1486, 1302, 1249, 1224, 1173, 1091, 1032, 960, 872, 755, 690 cm^{-1}. MS (70 eV, EI) m/z=349. HRMS (EI): m/z calcd for $C_{22}H_{17}ClO_2$ (M^+): 348.0917. Found, 348.0912.

*4.2.3. 1-Methoxy-4-(3-phenyl-1-(p-tolyloxy)prop-2-ynyl)benzene (**2c**).* Light yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ=7.58 (d, J=8.8 Hz, 2H), 7.44–7.27 (m, 5H), 7.09 (d, J=8.4 Hz, 2H), 7.02 (d, J=8.8 Hz, 2H), 6.93 (d, J=8.8 Hz, 2H), 5.94 (s, 1H), 3.81 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=20.5, 55.2, 70.6, 86.7, 88.0, 113.9, 116.3, 122.3, 128.1, 128.5, 128.8, 129.7, 130.3, 130.8, 131.7, 155.4, 159.8. IR (neat): 3061, 3033, 3000, 2923, 2856, 2224, 1610, 1508, 1460, 1303, 1248, 1219, 1173, 1110, 1032, 964, 873, 755, 690 cm^{-1}. MS (70 eV, EI) m/z=328. HRMS (EI): m/z calcd for $C_{23}H_{20}O_2$ (M^+): 328.1463. Found, 328.1459.

*4.2.4. 1-Methoxy-4-(1-(4-methoxyphenoxy)-3-phenylprop-2-ynyl) benzene (**2d**).* Light yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ=7.59–6.82 (m, 13H), 5.89 (s, 1H), 3.83 (s, 3H), 3.77 (s, 3H). ^{13}C

NMR (100 MHz, $CDCl_3$): δ=55.2, 55.6, 71.7, 86.7, 88.1, 113.9, 114.4, 118.1, 128.1, 128.3, 128.5, 128.9, 130.3, 131.7, 151.5, 154.5, 159.8. IR (neat): 3058, 2929, 2835, 2223, 1609, 1505, 1461, 1302, 1247, 1210, 1174, 1107, 1032, 964, 873, 755, 691 cm^{-1}. MS (70 eV, EI) m/z=344. HRMS (EI): m/z calcd for $C_{23}H_{20}O_3$ (M^+): 344.1412. Found, 344.1417.

*4.2.5. 1-Bromo-4-(1-(4-methoxyphenyl)-3-phenylprop-2-ynyloxy) benzene (**2e**).* Light yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ=7.59–6.94 (m, 13H), 5.95 (s, 1H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=55.3, 70.7, 85.9, 88.6, 113.8, 114.0, 118.2, 122.0, 128.2, 128.7, 128.9, 129.6, 131.7, 132.1, 159.8. IR (neat): 3056, 2926, 2856, 2223, 1610, 1511, 1484, 1303, 1250, 1223, 1173, 1109, 1071, 1032, 960, 872, 755, 690 cm^{-1}. MS (70 eV, EI) m/z=393. HRMS (EI): m/z calcd for $C_{22}H_{17}BrO_2$ (M^+): 392.0412. Found, 392.0405.

*4.2.6. 1-Chloro-3-(1-(4-methoxyphenyl)-3-phenylprop-2-ynyloxy)-2-methylbenzene (**2f**).* Light yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ=7.58 (d, J=8.4 Hz, 12H), 7.43–6.94 (m, 9H), 5.94 (s, 1H), 3.84 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=13.1, 55.2, 71.3, 86.3, 88.2, 112.8, 113.9, 122.1, 122.4, 126.4, 128.2, 128.6, 128.7, 129.6, 130.1, 131.6, 135.1, 156.5, 159.9. IR (neat): 3062, 2928, 2827, 2228, 1610, 1462, 1249, 1172, 1070, 1031, 962, 855, 751, 689 cm^{-1}. MS (70 eV, EI) m/z=363. HRMS (EI): m/z calcd for $C_{23}H_{19}ClO_2$ (M^+): 362.1074. Found, 362.1072.

*4.2.7. 2,4-Di-tert-butyl-1-(1-(4-methoxyphenyl)-3-phenylprop-2-ynyloxy)benzene (**2g**).* Light yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ=7.49–6.82 (m, 12H), 5.67 (s, 1H), 3.82 (s, 3H), 1.42 (s, 9H), 1.31 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=29.8, 31.6, 34.3, 35.0, 39.5, 55.2, 86.1, 88.7, 113.8, 114.1, 123.2, 124.4, 126.5, 128.3, 128.7, 129.7, 131.5, 131.7, 136.8, 142.3, 150.5, 158.7. IR (neat): 2955, 2924, 2857, 2221, 1608, 1461, 1298, 1248, 1176, 1115, 1035, 882, 824, 755, 690 cm^{-1}. MS (70 eV, EI) m/z=426. HRMS (EI): m/z calcd for $C_{30}H_{34}O_2$ (M^+): 426.2559. Found, 426.2561.

*4.2.8. (3-Phenoxyprop-1-yne-1,3-diyl)dibenzene[2] (**2h**).* Light yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ=7.72 (d, J=7.6 Hz, 2H), 7.49–7.04 (m, 13H), 6.08 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=70.7, 86.3, 88.4, 116.3, 121.6, 122.2, 127.4, 128.2, 128.66, 128.7, 129.4, 131.8, 138.0, 157.6. IR (neat): 3060, 3033, 2922, 2856, 2225, 1592, 1489, 1450, 1306, 1220, 1173, 1075, 1030, 965, 863, 751, 689 cm^{-1}. MS (70 eV, EI) m/z=284.

*4.2.9. 1-Methyl-4-(1-phenoxy-3-phenylprop-2-ynyl)benzene (**2i**).* Light yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ=7.61 (d, J=8.0 Hz, 2H), 7.49–7.02 (m, 12H), 6.06 (s, 1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=21.2, 70.6, 86.6, 88.2, 116.3, 121.6, 122.3, 127.4, 128.2, 128.6, 129.4, 131.8, 135.1, 138.6, 157.6. IR (neat): 3061, 2921, 2853, 2224, 1592, 1489, 1445, 1304, 1220, 1176, 1074, 1030, 964, 872, 751, 689 cm^{-1}. MS (70 eV, EI) m/z=298. HRMS (EI): m/z calcd for $C_{22}H_{18}O$ (M^+): 298.1358. Found, 298.1359.

*4.2.10. 1-Chloro-4-(1-phenoxy-3-phenylprop-2-ynyl)benzene (**2j**).* Light yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ=7.64 (d, J=8.8 Hz, 2H) 7.47–7.02 (m, 12H), 6.04 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=70.0, 85.9, 88.6, 116.3, 121.8, 122.0, 128.3, 128.4, 128.7, 128.8, 129.4, 131.8, 134.6, 136.6, 157.3. IR (neat): 3059, 2919, 2227, 1593, 1489, 1406, 1305, 1220, 1173, 1089, 1014, 966, 871, 751, 688 cm^{-1}. MS (70 eV, EI) m/z=319. HRMS (EI): m/z calcd for $C_{21}H_{15}ClO$ (M^+): 318.0811. Found, 318.0807.

*4.2.11. 1-Methoxy-4-(3-phenoxy-3-phenylprop-1-ynyl)benzene (**2k**).* Light yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ=7.70 (d, J=7.6 Hz, 2H), 7.47–7.00 (m, 10H), 6.84 (d, J=8.8 Hz, 2H), 6.06 (s, 1H), 3.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=55.2, 70.8, 85.0, 88.4, 113.8, 116.3, 121.5, 127.4, 128.3, 128.6, 128.62, 129.3, 133.3, 138.2, 157.6, 159.9. IR (neat): 3056, 2922, 2856, 2224, 1724, 1601, 1491, 1455, 1290, 1221, 1172, 1107, 1076, 1030, 963, 863, 751, 693 cm^{-1}. MS (70 eV, EI) m/z=314. HRMS (EI): m/z calcd for $C_{22}H_{18}O_2$ (M^+): 314.1307. Found, 314.1309.

*4.2.12. 1-Ethyl-4-(3-phenoxy-3-phenylprop-1-ynyl)benzene (**2l**).* Light yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ=7.74–7.02 (m, 14H), 6.08 (s, 1H), 2.63 (q, J_1=8 Hz, J_2=11.2 Hz, 2H), 1.25 (q, J=7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=15.3, 28.8, 70.8, 85.7, 88.6, 116.3, 119.4, 121.6, 127.4, 127.8, 128.6, 129.4, 131.8, 138.1, 145.2, 157.6. IR (neat): 3056, 3030, 2964, 2926, 2862, 2225, 1593, 1492, 1453, 1306, 1221, 1174, 1076, 1026, 965, 863, 750, 693 cm^{-1}. MS (70 eV, EI) m/z=312. HRMS (EI): m/z calcd for $C_{23}H_{20}O$ (M^+): 312.1514. Found, 312.1517.

4.3. General procedure for products 3

To a 5 mL round-bottom flask with a mixture of 1,3-diarylpropynes (0.25 mmol) and diol (0.3 mmol) in CH_2Cl_2 (1 mL), DDQ (0.55 mmol) was added at 0 °C. The resulting mixture was stirred for 1 h. Purification was done by column chromatography on silica gel (petroleum ether/ethyl acetate=10/1), and the fraction with an R_f=0.6 was collected to give the desired product.

*4.3.1. 2-(4-Methoxyphenyl)-2-(phenylethynyl)-1,3-dioxolane (**3a**).* Light yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ=7.72 (d, J=8.8 Hz, 2H), 7.52–7.32 (m, 5H), 6.94 (d, J=8.8 Hz, 2H), 4.35–4.31 (m, 2H), 4.22–4.18 (m, 2H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=55.3, 65.1, 85.6, 86.4, 113.5, 113.9, 121.9, 127.5, 128.2, 128.8, 131.9, 132.9, 160.3. IR (neat): 3060, 2923, 2856, 2198, 1632, 1595, 1510, 1489, 1462, 1287, 1251, 1165, 1077, 1027, 967, 830, 756, 689 cm^{-1}. MS (70 eV, EI) m/z=280. HRMS (EI): m/z calcd for $C_{18}H_{16}O_3$ (M^+): 280.1099. Found, 280.1097.

*4.3.2. 2-(4-Methoxyphenyl)-5,5-dimethyl-2-(phenylethynyl)-1,3-dioxane (**3b**).* Light yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ=7.80 (d, J=8.8 Hz, 2H), 7.58–7.37 (m, 5H), 6.95 (d, J=8.8 Hz, 2H), 4.25 (d, J=10.8 Hz, 2H), 3.85 (s, 3H), 3.66 (d, J=10.8 Hz, 2H), 1.33 (s, 3H), 0.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=22.0, 23.2, 29.9, 55.3, 73.4, 84.7, 88.3, 96.0, 113.5, 122.0, 127.2, 128.4, 128.9, 131.9, 133.6, 160.1. IR (neat): 3058, 2954, 2864, 2221, 1612, 1513, 1489, 1464, 1279, 1208, 1172, 1087, 1036, 982, 831, 756, 690 cm^{-1}. MS (70 eV, EI) m/z=322. HRMS (EI): m/z calcd for $C_{21}H_{22}O_3$ (M^+): 322.1569. Found, 322.1571.

4.4. General procedure for products 4

To a 5 mL round-bottom flask with a mixture of 1,3-diarylpropynes (0.25 mmol) and acid (0.3 mmol) in CH_2Cl_2 (1 mL), DDQ (0.27 mmol) was added at room temperature. The resulting mixture was stirred for 30 min. Purification was done by column chromatography on silica gel (petroleum ether/ethyl acetate=10/1), and the fraction with an R_f=0.5 was collected to give the desired product.

*4.4.1. 1-(4-Methoxyphenyl)-3-phenylprop-2-ynyl acetate (**4a**).* Light yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ=7.56 (d, J=6.8 Hz, 2H), 7.51–7.32 (m, 5H), 6.94 (d, J=6.8 Hz, 2H), 6.68 (s, 1H), 3.84 (s, 3H), 2.13 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=21.2, 55.3, 65.8, 85.8, 86.8, 114.0, 122.2, 128.3, 128.7, 129.38, 129.4, 131.9, 160.1, 169.9. IR (neat): 3056, 2956, 2925, 2862, 2222, 1738, 1492, 1453, 1306, 1219, 1176, 1077, 963, 875, 755, 690 cm^{-1}. MS (70 eV, EI) m/z=280.

*4.4.2. 3-Phenyl-1-p-tolylprop-2-ynyl acetate (**4b**).* Light yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ=7.53–7.23 (m, 9H), 6.70 (s, 1H), 2.40 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=21.1, 21.2, 66.0, 85.8, 86.8, 122.2, 127.8, 128.2, 128.7, 129.3, 131.9, 134.3, 138.9, 169.8.

IR (neat): 3058, 2952, 2926, 2227, 1735, 1491, 1309, 1223, 1174, 1075, 962, 871, 753, 691 cm^{-1}. MS (70 eV, EI) m/z=264.

*4.4.3. 1-(4-Methoxyphenyl)-3-phenylprop-2-ynyl benzoate (**4c**).* Light yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ=8.11 (d, J=6.0 Hz, 2H), 7.67–7.27 (m, 10H), 6.97 (d, J=6.8 Hz, 2H), 6.93 (s, 1H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=55.3, 66.4, 85.9, 87.2, 114.0, 122.2, 128.2, 128.3, 128.7, 128.8, 129.4, 129.5, 129.9, 131.9, 133.1, 160.1, 165.5. IR (neat): 3062, 2957, 2929, 2226, 1738, 1310, 1222, 1176, 1076, 961, 875, 755, 693 cm^{-1}. MS (70 eV, EI) m/z=342. HRMS (EI): m/z calcd for $C_{23}H_{18}O_3$ (M^+): 342.1256. Found, 342.1252.

*4.4.4. 3-Phenyl-1-p-tolylprop-2-ynyl benzoate (**4d**).* Light yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ=8.16–7.27 (m, 14H), 6.98 (s, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=21.2, 66.5, 85.8, 87.1, 122.2, 127.8, 128.2, 128.3, 128.7, 129.3, 129.9, 131.9, 133.1, 134.4, 138.8, 165.4. IR (neat): 3061, 2956, 2928, 2221, 1732, 1309, 1227, 1169, 1071, 961, 872, 752, 691 cm^{-1}. MS (70 eV, EI) m/z=326. HRMS (EI): m/z calcd for $C_{23}H_{18}O_2$ (M^+): 326.1307. Found, 326.1303.

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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.2011.05.030.

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