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Sonogashira reaction of aryl halides with propiolaldehyde diethyl acetal catalyzed by a tetraphosphine/palladium complex

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Abstract—All-*cis*-1,2,3,4-Tetrakis(diphenylphosphinomethyl)cyclopentane/$[PdCl(C_3H_5)]_2$ efficiently catalyzes the Sonogashira reaction of propiolaldehyde diethyl acetal with a variety of aryl bromides and chlorides. A minor electronic effect of the substituents of the aryl bromide was observed. Similar reaction rates were observed in the presence of activated aryl bromides such as 4-trifluoromethylbromobenzene and deactivated aryl bromides such as bromoanisole. Turnover numbers up to 95,000 can be obtained for this reaction. Even aryl chlorides and heteroarylbromides or chlorides have been successfully alkynylated with this catalyst. Moreover, a wide variety of substituents on the aryl halide such as fluoro, trifluoromethyl, acetyl, benzoyl, formyl, nitro, dimethylamino or nitrile are tolerated.

1. Introduction

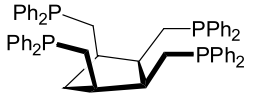
Substituted arylpropiolaldehydes bearing various substituents on the aromatic ring are of great biological interest and are also useful reagents in organic synthesis.[1] The Sonogashira palladium-catalyzed reaction[2] of aryl and heteroaryl halides with propiolaldehyde diethyl acetal is a very powerful method for the synthesis of these arylpropiolaldehydes. However, most of the results have been obtained with very reactive but expensive aryliodides[3–9] and the procedures reported for this reaction require relatively high catalysts loadings (1–10%).[3–12] If the catalytic load of palladium complex could be reduced to a significantly smaller level, this reaction would be much more practical.[13]

In recent years, several thermally stable palladium catalysts have been successfully used for Sonogashira reaction.[14] However, to our knowledge, only triphenylphosphine ligand has been used for the coupling of aryl halides with propiolaldehyde diethyl acetal.[4,5] But this phosphorus ligand can be labile under some coupling conditions especially at elevated temperature and gave palladium black, which is generally inactive. To our knowledge, low-catalyst loading Sonogashira reactions with propiolaldehyde diethyl acetal have not been described.

In order to find more efficient palladium catalysts, we have prepared the tetrapodal phosphine ligand, Tedicyp[15] (Fig. 1). We have reported recently several results obtained in allylic substitution,[15] Suzuki cross-coupling,[16] and Heck reactions.[17] We have also reported the Sonogashira reaction[18] using Tedicyp as ligand in the presence of sterically congested arylbromides,[18b] with arylchlorides[18d] or using alkynols.[18c] Here, in order to further establish the requirements for a successful Sonogashira reaction, we wish to report on the reaction of several aryl and heteroaryl halides with propiolaldehyde diethyl acetal using Tedicyp as ligand.

2. Results and discussion

For this study, based on previous results,[18] DMF was chosen as the solvent and potassium carbonate as the base. The reactions were performed at 130 °C under argon in the presence of a ratio 1/2 of $[Pd(C_3H_5)Cl]_2$/Tedicyp as catalyst. For the reactions performed with aryl bromides or iodobenzene 5% of copper(I) iodide was added as co-catalyst (Scheme 1). The reactions with aryl chlorides were performed without CuI. We have reported recently that for such substrates with our catalyst the presence of CuI often



Tedicyp

Figure 1.

Keywords: Sonogashira reaction; Aryl bromides; Palladium; Catalysis; Tetraphosphine.
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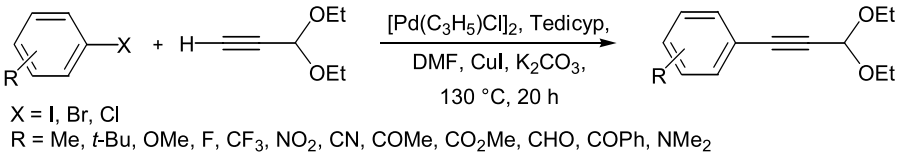


Scheme 1.

led to the formation of side-products such as the dimerization of the alkyne.[18b]

First, we have investigated the Sonogashira reaction of several *para*-substituted aryl bromides with propiolaldehyde diethyl acetal. The results presented in Table 1 disclose a minor effect of the substituents of the aryl bromide. In most cases the reaction performed with propiolaldehyde diethyl acetal proceeds very smoothly in the presence of 0.01% catalyst. We observed that turnover numbers of 6100–95,000 can be achieved with this catalyst for activated substrates such as 4-bromoacetophenone, 4-bromobenzaldehyde, 4-bromobenzophenone, 4-bromobenzonitrile, and 4-fluorobromobenzene (Table 1, entries 2–16). With the deactivated aryl bromides: 4-bromotoluene, 4-*t*butylbromobenzene and 4-bromoanisole slightly lower TONs of 700–10,000 were obtained (Table 1, entries 17–21). The least reactive aryl bromide for this reaction was 4-dimethylaminobromobenzene, but a complete conversion for a ratio substrate/catalyst of 1000 was observed (Table 1, entry 24). The similar TONs obtained with 4-bromobenzophenone and 4-*t*butylbromobenzene (6100 and 9200, respectively) seems to indicate that the oxidative addition of aryl bromides to palladium is not the rate-limiting step of the reaction with this catalyst.

Then, the reaction with propiolaldehyde diethyl acetal was applied to several *meta*- and *ortho*-substituted aryl bromides (Table 2), to aryl chlorides (Table 3) and also to a few heteroaryl halides (Table 4).

The influence of the presence of *meta* and *ortho* substituents on the aryl bromide on the reaction rate is reported in Table 2. As expected very similar TONs were obtained with *meta*-substituted aryl bromides than with the *para*-substituted substrates (Table 2, entries 1–5). *ortho*-Substituents on the aryl bromides generally have a more important effect on the reactions rates of Sonogashira reaction.[18] However, with propiolaldehyde diethyl acetal high TONs were obtained in most cases with the *ortho*- and di-*ortho*-substituted aryl bromides. We observed that the coupling of 2-bromobenzaldehyde, methyl 2-bromobenzoate, 2-bromobenzonitrile, 2-trifluoromethylbromobenzene or 2-fluorobromobenzene proceeds in the presence of 0.01% catalyst (Table 2, entries 8–15). Even the deactivated 2-bromoanisole gave good results in the presence of 0.01% catalyst. Again this observation is also consistent with our suggestion that the rate-limiting step does not involve oxidative addition of the aryl bromide (Table 2, entries 19 and 20).

With 2-bromoacetophenone the formation of an unexpected product was observed (Scheme 2, Table 2, entries 6 and 7). When a ratio substrate/catalyst of 1000 was used, the expected alkynylation product **19a** was obtained together with an other compound, which appears to be **19b**. This

Table 1. Palladium–Tedicyp catalyzed Sonogashira reaction with propiolaldehyde diethyl acetal and aryl halides (Scheme 1)

Entry	Aryl halide	Ratio substrate/catalyst	Product	Yield (%)[a]
1	Iodobenzene	10,000	**1**	100 (92)
2	4-Bromoacetophenone	10,000	**2**	100 (94)
3	4-Bromoacetophenone	100,000	**2**	95
4	4-Bromobenzaldehyde	10,000	**3**	100 (94)
5	4-Bromobenzophenone	1000	**4**	100 (91)
6	4-Bromobenzophenone	10,000	**4**	61
7	Methyl 4-bromobenzoate	1000	**5**	100 (90)
8	Methyl 4-bromobenzoate	10,000	**5**	92
9	4-Bromonitrobenzene	1000	**6**	100 (94)
10	4-Bromonitrobenzene	10,000	**6**	78
11	4-Bromobenzonitrile	10,000	**7**	100 (91)
12	4-Bromobenzonitrile	100,000	**7**	92
13	4-Trifluoromethylbromobenzene	10,000	**8**	100 (90)
14	3,5-bis(Trifluoromethyl)bromobenzene	10,000	**9**	100 (92)
15	4-Fluorobromobenzene	1000	**10**	100 (88)
16	4-Fluorobromobenzene	10,000	**10**	76
17	4-Bromotoluene	1000	**11**	98 (90)
18	4-Bromotoluene	10,000	**11**	70
19	4-*t*Butylbromobenzene	10,000	**12**	100 (92)
20	4-Bromoanisole	10,000	**13**	82 (74)
21	4-Bromoanisole	—[b]	**13**	0
22	2-Bromo-6-methoxynaphthalene	1000	**14**	100 (94)
23	2-Bromo-6-methoxynaphthalene	10,000	**14**	94
24	4-Dimethylaminobromobenzene	1000	**15**	100 (89)

Conditions: Pd–Tedicyp catalyst, ArX (1 equiv), propiolaldehyde diethyl acetal (2 equiv), CuI (0.05 equiv), K_2CO_3 (2 equiv), DMF, 130 °C, 20 h.
[a] GC and NMR conversion; yields in parenthesis are isolated.
[b] Reaction performed with CuI and without Pd catalyst.

Table 2. Palladium–Tedicyp catalyzed Sonogashira reaction with propiolaldehyde diethyl acetal and *meta*- or *ortho*-substituted aryl bromides (Schemes 1 and 2)

Entry	Aryl halide	Ratio substrate/catalyst	Product	Yield (%)[a]
1	3-Bromoacetophenone	10,000	**16**	100 (90)
2	3-Bromoacetophenone	100,000	**16**	50
3	3-Bromonitrobenzene	1000	**17**	100 (89)
4	3-Bromonitrobenzene	10,000	**17**	90
5	3-Bromotoluene	1000	**18**	100 (92)
6	2-Bromoacetophenone	250	**19c**	100 (80)[b]
7	2-Bromoacetophenone	1000	**19a**+**19c**	100 (45 and 42)[b,c]
8	2-Bromobenzaldehyde	10,000	**20**	100 (91)
9	Methyl 2-bromobenzoate	1000	**21**	100 (90)
10	Methyl 2-bromobenzoate	10,000	**21**	67
11	2-Bromobenzonitrile	1000	**22**	100 (87)
12	2-Bromobenzonitrile	10,000	**22**	90
13	2-Trifluoromethylbromobenzene	10,000	**23**	100 (91)
14	2-Fluorobromobenzene	1000	**24**	100 (93)
15	2-Fluorobromobenzene	10,000	**24**	55
16	2-Bromotoluene	1000	**25**	100 (90)
17	1-Bromonaphthalene	1000	**26**	100 (94)
18	1-Bromonaphthalene	10,000	**26**	68
19	2-Bromoanisole	1000	**27**	100 (88)
20	2-Bromoanisole	10,000	**27**	85
21	2,6-Difluorobromobenzene	250	**28**	90 (84)
22	2,6-Difluorobromobenzene	1000	**28**	50
23	2,4,6-Trimethylbromobenzene	1000	**29**	100 (89)
24	2,4,6-Trimethylbromobenzene	10,000	**29**	88
25	2,6-Diethyl-4-methylbromobenzene	1000	**30**	100 (88)
26	9-Bromoanthracene	1000	**31**	100 (90)
27	9-Bromoanthracene	10,000	**31**	40

Conditions: Pd–tedicyp catalyst, ArBr (1 equiv), propiolaldehyde diethyl acetal (2 equiv), CuI (0.05 equiv), K_2CO_3 (2 equiv), DMF, 130 °C, 20 h.
[a] GC and NMR conversion; yields in parenthesis are isolated.
[b] Before filtration on silica gel **19b** was observed (see Scheme 2).
[c] The formation of a mixture of **19a** (45%) and **19c** (42%) (see Scheme 2) was observed.

reaction performed with a ratio substrate/catalyst of 250 led exclusively to **19b**. Acidic treatment or filtration on silica gel of this compound gave the corresponding aldehyde **19c**. The formation of similar cyclization products has already been described for the palladium-catalyzed reactions of 2-iodobenzoic acid or 2-iodobenzyl alcohol and terminal alkynes.[19]

Next, we tried to evaluate the difference of reaction rate between mono- and di-*ortho*-substituted aryl bromides, and we observed that even very hindered aryl bromides could be coupled efficiently with propiolaldehyde diethyl acetal (Table 2, entries 21–27). For example, with 2,4,6-trimethylbromobenzene or 9-bromoanthracene the expected adducts were obtained in 89 and 90% yields, respectively, in the presence of 0.1% catalyst (Table 2, entries 23–27).

Then, the reactivity of a few aryl chlorides was studied (Table 3). These reactions were performed without CuI as co-catalyst. With electron-poor aryl chlorides such as 4-chloroacetophenone, 4-chloronitrobenzene or 4-chlorobenzonitrile the alkynylation products were obtained in good yields in the presence of 1% catalyst (Table 3, entries 1–7). On the other hand the electron-rich 4-chloroanisole led to the adduct **13** in a very low TON of 17 (Table 3, entry 8). Thus, the oxidative-addition of the aryl chlorides be the rate-limiting step of the reaction.

Finally, we have investigated the Sonogashira reaction of nine heteroaryl halides. The results are summarized in Table 4. We have observed in Tables 1 and 2 that with aryl bromides the oxidative addition to the palladium complex is probably not the rate-limiting step of the reaction with this catalyst. Pyridines or quinolines are π-electron deficient.

Table 3. Palladium–Tedicyp catalyzed Sonogashira reaction with propiolaldehyde diethyl acetal and aryl chlorides (Scheme 1)

Entry	Aryl halide	Ratio substrate/catalyst	Product	Yield (%)[a]
1	4-Chloroacetophenone	100	**2**	97 (87)
2	4-Chlorobenzaldehyde	100	**3**	100 (90)
3	4-Chlorobenzaldehyde	250	**3**	100
4	4-Chloronitrobenzene	100	**6**	100 (89)
5	4-Chloronitrobenzene	250	**6**	55
6	4-Chlorobenzonitrile	100	**7**	100 (87)
7	4-Trifluoromethylchlorobenzene	100	**8**	100 (87)
8	4-Chloroanisole	100	**13**	17

Conditions: Pd–Tedicyp catalyst, ArCl (1 equiv), propiolaldehyde diethyl acetal (2 equiv), K_2CO_3 (2 equiv), reactions performed without CuI, DMF, 130 °C, 20 h.
[a] GC and NMR conversion; yields in parenthesis are isolated.

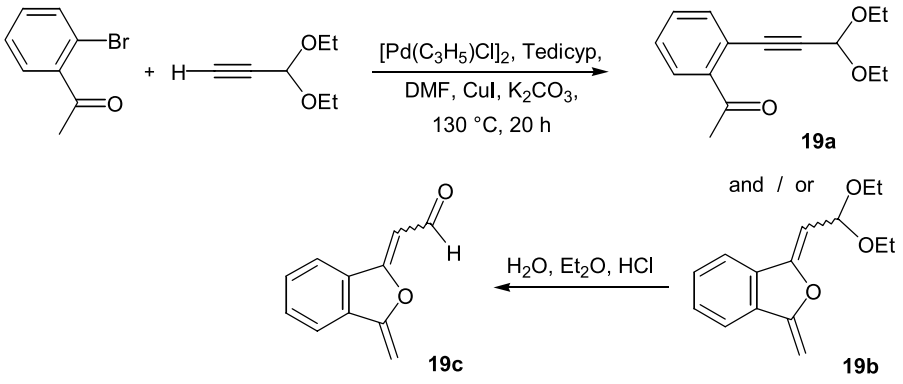
Table 4. Palladium–Tedicyp catalyzed Sonogashira reaction with propiolaldehyde diethyl acetal and heteroaryl halides (Scheme 1)

Entry	Aryl halide	Ratio substrate/catalyst	Product	Yield (%)[a]
1	2-Bromopyridine	1,000	**32**	100 (89)
2	2-Bromopyridine	10,000	**32**	100
3	2-Chloropyridine	100	**32**	100[b]
4	2-Chloropyridine	250	**32**	65[b]
5	3-Bromopyridine	10,000	**33**	100 (93)
6	2-Chloroquinoline	100	**34**	100 (90)[b]
7	2-Chloroquinoline	250	**34**	66[b]
8	3-Bromoquinoline	1000	**35**	100 (94)
9	3-Bromoquinoline	10,000	**35**	52
10	4-Bromoisoquinoline	10,000	**36**	100 (90)
11	5-Bromopyrimidine	1000	**37**	100 (90)
12	5-Bromopyrimidine	10,000	**37**	100
13	2-Bromothiophene	1000	**38**	100 (88)
14	2-Bromothiophene	10,000	**38**	95
15	3-Bromothiophene	100	**39**	100 (90)
16	3-Bromothiophene	1000	**39**	100

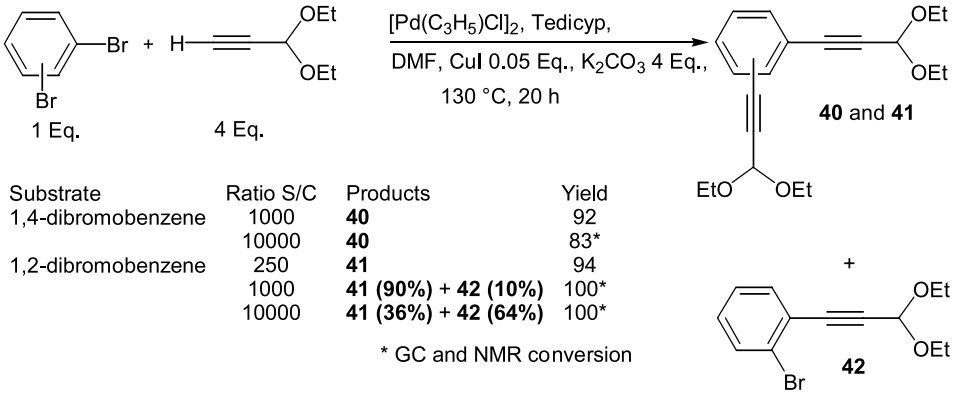
Conditions: Pd–Tedicyp catalyst, ArX (1 equiv), propiolaldehyde diethyl acetal (2 equiv), CuI (0.05 equiv), K_2CO_3 (2 equiv), DMF, 130 °C, 20 h.
[a] GC and NMR conversion; yields in parenthesis are isolated.
[b] Reactions performed without CuI.

Thiophenes or furanes are π-electron excessive. If the oxidative-addition is rate-limiting, the reactions should be slower with thiophenes or furanes than with pyridines or quinolines. In the presence of 2-bromopyridine, 3-bromopyridine, 3-bromoquinoline, 4-bromoisoquinoline, and 5-bromopyrimidine the reactions were performed successfully with 0.1–0.01% catalyst (Table 4, entries 1, 2, 5, and 8–12). Similar reactions rates were observed with 2-bromothiophene and 3-bromothiophene (Table 4, entries 13–16). These results seem to confirm that the oxidative addition of the aryl bromides to palladium is not the rate-limiting step of this reaction. The two heteroaryl chlorides: 2-chloropyridine and 2-chloroquinoline were also successfully alkynylated, but the presence of 0.4% catalyst was required (Table 4, entries 3, 4, 6, and 7).

The synthesis of 1,4- and 1,2-bis(3,3-diethoxyprop-1-ynyl)-benzene **40** and **41** from 1,4- and 1,2-dibromobenzene using 4 equiv of propiolaldehyde diethyl acetal also proceeds in good yields (Scheme 3). With 1,4-dibromobenzene, the



Scheme 2.



Substrate	Ratio S/C	Products	Yield
1,4-dibromobenzene	1000	**40**	92
	10000	**40**	83*
1,2-dibromobenzene	250	**41**	94
	1000	**41 (90%) + 42 (10%)**	100*
	10000	**41 (36%) + 42 (64%)**	100*

* GC and NMR conversion

Scheme 3.

monoaddition product was not observed and the diaddition product **40** was selectively obtained in 92% yield in the presence of 0.1% catalyst. On the other hand, with 1,2-dibromobenzene, if the diaddition product was selectively obtained in the presence of 0.4% catalyst, mixtures of mono and diaddition products **41** and **42** were obtained when ratios substrate/catalyst of 1000 and 10,000 were used. The slower reaction rate observed with 1,2-dibromobenzene probably comes from steric reasons.

In summary, we have established that the Tedicyp–palladium system provides an efficient catalyst for the coupling of aryl bromides with propiolaldehyde diethyl acetal. The uses of this Pd–tetraphosphine catalyst allow the use of low-catalyst loading. This reaction can be performed with as little as 0.01% catalyst with most of the aryl bromides. Due to the high price of palladium, the practical advantage of such low catalyst loadings can become increasingly important for industrial processes. A wide range of functions such as methoxy, fluoro, acetyl, formyl, benzoyl, carboxylate, nitro, nitrile or dimethylamino on the aryl bromide are tolerated. The steric hindrance of the aryl bromide has a minor effect on the reaction rates. Lower TONs were obtained for the coupling of aryl chlorides. With these substrates the use of 1% catalyst was necessary. Some heteroaromatic substrates such as bromo- or chloropyridines, a bromopyrimidine or bromothiophenes have also been used successfully. Moreover, propiolaldehyde diethyl acetal is commercially available and this is a practical advantage of this reaction.

3. Experimental

3.1. General remarks

All reactions were run under argon in Schlenk tubes using vacuum lines. DMF analytical grade was not distilled before use. Potassium carbonate (99+) was used. Commercial propiolaldehyde diethyl acetal was used without purification. The reactions were followed by GC and NMR for high boiling point substrates and by GC for low boiling point substrates. ^{1}H and ^{13}C spectrum were recorded with a Bruker 300 MHz spectrometer in $CDCl_3$ solutions. Chemical shift are reported in ppm relative to $CDCl_3$ (7.25 for ^{1}H NMR and 77.0 for ^{13}C NMR). Flash chromatography were performed on silica gel (230–400 mesh). GC and NMR yields in Tables 1–4 are conversions of the aryl halides into the product calculated with GC and ^{1}H NMR spectrum of the crude mixtures.

3.1.1. Preparation of the Pd–tedicyp catalyst. An oven-dried 40-mL Schlenk tube equipped with a magnetic stirring bar under argon atmosphere, was charged with $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (30 mg, 81 μmol) and Tedicyp (140 mg, 162 μmol). Anhydrous DMF (10 mL) were added, then the solution was stirred at room temperature for 10 min. The appropriate catalyst concentration was obtained by successive dilutions. ^{31}P NMR (162 MHz, $CDCl_3$) δ 25 (w=80 Hz), 19.4 (w=110 Hz).

3.2. General procedure

In a typical experiment, the aryl halide (1 mmol), propiolaldehyde diethyl acetal (0.256 g, 2 mmol or 0.512 g 4 mmol, see Tables 1–4 and Scheme 3), K_2CO_3 (0.276 g, 2 mmol or 0.552 g 4 mmol, see Tables 1–4 and Scheme 3) and CuI for the reactions performed with aryl bromides (0.01 g, 0.05 mmol) were dissolved in DMF (3 mL) under an argon atmosphere. The prepared Pd–Tedicyp catalyst complex (see Tables 1–4) was then transferred to the reaction flask via cannula. The reaction mixture was stirred at 130 °C for 20 h. Then, the product was extracted three times with Et_2O or CH_2Cl_2. (For compound **19c**, the mixture was acidified with an HCl solution (pH 6) then the product was extracted three times with Et_2O). The combined organic layer was dried over $MgSO_4$ and the solvent was removed in vacuo. The crude product was purified by silica gel column chromatography.

3.2.1. 1-Phenyl-3,3-diethoxyprop-1-yne 1. From iodobenzene (0.204 g, 1 mmol), product **1** was obtained in 92% (0.187 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (m, 2H), 7.26 (m, 3H), 5.42 (s, 1H), 3.73 (m, 2H), 3.60 (m, 2H), 1.21 (t, 6H, J=7.1 Hz).

3.2.2. 1-(4-Acetylphenyl)-3,3-diethoxyprop-1-yne 2. From 4-bromoacetophenone (0.199 g, 1 mmol), product **2** was obtained in 94% (0.231 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (d, 2H, J=8.4 Hz), 7.52 (d, 2H, J=8.4 Hz), 5.46 (s, 1H), 3.77 (m, 2H), 3.65 (m, 2H), 2.55 (s, 3H), 1.24 (t, 6H, J=7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.1, 136.7, 132.0, 128.1, 126.6, 91.6, 87.5, 84.1, 61.0, 26.5, 15.0; $C_{15}H_{18}O_3$: Calcd C, 73.15; H, 7.37. Found: C, 72.97; H, 7.43.

3.2.3. 1-(4-Formylphenyl)-3,3-diethoxyprop-1-yne 3. From 4-bromobenzaldehyde (0.185 g, 1 mmol), product **3** was obtained in 94% (0.218 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.79 (d, 2H, J=7.8 Hz), 7.60 (d, 2H, J=7.8 Hz), 5.48 (s, 1H), 3.76 (m, 2H), 3.62 (m, 2H), 1.23 (t, 6H, J=6.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.3, 135.8, 132.4, 129.4, 128.0, 91.6, 88.2, 84.0, 61.1, 15.0; $C_{14}H_{16}O_3$: Calcd C, 72.39; H, 6.94. Found: C, 72.47; H, 7.09.

3.2.4. 1-(4-Benzoylphenyl)-3,3-diethoxyprop-1-yne 4. From 4-bromobenzophenone (0.261 g, 1 mmol), product **4** was obtained in 91% (0.280 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80–7.70 (m, 4H), 7.60–7.52 (m, 3H), 7.45 (t, 2H, J=7.2 Hz), 5.49 (s, 1H), 3.79 (m, 2H), 3.66 (m, 2H), 1.25 (t, 6H, J=6.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.7, 137.3, 137.1, 132.5, 131.7, 129.9, 129.8, 128.3, 125.9, 91.6, 87.2, 84.2, 61.0, 15.0; $C_{20}H_{20}O_3$: Calcd C, 77.90; H, 6.54. Found: C, 77.67; H, 6.74.

3.2.5. 1-(4-Methoxycarbonylphenyl)-3,3-diethoxyprop-1-yne 5. From methyl 4-bromobenzoate (0.215 g, 1 mmol), product **5** was obtained in 90% (0.236 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (d, 2H, J=8.3 Hz), 7.52 (d, 2H, J=8.3 Hz), 5.48 (s, 1H), 3.89 (s, 3H), 3.77 (m, 2H), 3.65 (m, 2H), 1.27 (t, 6H, J=7.2 Hz).

3.2.6. 1-(4-Nitrophenyl)-3,3-diethoxyprop-1-yne 6. From 4-bromonitrobenzene (0.202 g, 1 mmol), product **6** was obtained in 94% (0.234 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16 (d, 2H, J=8.5 Hz), 7.59 (d, 2H, J=8.5 Hz), 5.48 (s, 1H), 3.77 (m, 2H), 3.65 (m, 2H), 1.26 (t, 6H, J=7.2 Hz).

3.2.7. 1-(4-Cyanophenyl)-3,3-diethoxyprop-1-yne 7. From 4-bromobenzonitrile (0.182 g, 1 mmol), product **7** was obtained in 91% (0.209 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (d, 2H, J=8.5 Hz), 7.53 (d, 2H, J=8.5 Hz), 5.47 (s, 1H), 3.77 (m, 2H), 3.65 (m, 2H), 1.26 (t, 6H, J=7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.4, 131.9, 126.7, 118.2, 112.2, 91.5, 88.7, 83.2, 61.1, 15.0; $C_{14}H_{15}NO_2$: Calcd C, 73.34; H, 6.59. Found: C, 73.21; H, 6.47.

3.2.8. 1-(4-Trifluoromethylphenyl)-3,3-diethoxyprop-1-yne 8. From 4-trifluoromethylbromobenzene (0.225 g, 1 mmol), product **8** was obtained in 90% (0.245 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (m, 4H), 5.51 (s, 1H), 3.83 (m, 2H), 3.68 (m, 2H), 1.29 (t, 6H, J=7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.2, 130.5 (q, J=32.4 Hz), 125.6, 125.2 (q, J=3.8 Hz), 123.8 (q, J=274.2 Hz), 91.6, 86.8, 83.6, 61.1, 15.0; $C_{14}H_{15}F_3O_2$: Calcd C, 61.76; H, 5.55. Found: C, 61.66; H, 5.34.

3.2.9. 1-[3,5-Bis(trifluoromethyl)phenyl]-3,3-diethoxyprop-1-yne 9. From 3,5-bis(trifluoromethyl)bromobenzene (0.293 g, 1 mmol), product **9** was obtained in 92% (0.313 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (s, 2H), 7.81 (s, 1H), 5.48 (s, 1H), 3.83 (m, 2H), 3.68 (m, 2H), 1.27 (t, 6H, J=7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.0 (q, J=34.5 Hz), 131.8, 124.5, 122.8 (q, J=272.3 Hz), 122.2 (m), 91.5, 88.0, 81.9, 61.2, 15.0; $C_{15}H_{14}F_6O_2$: Calcd C, 52.95; H, 4.15. Found: C, 52.80; H, 4.39.

3.2.10. 1-(4-Fluorophenyl)-3,3-diethoxyprop-1-yne 10. From 4-fluorobromobenzene (0.175 g, 1 mmol), product **10** was obtained in 88% (0.196 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (dd, 2H, J=5.5, 8.5 Hz), 6.97 (t, 2H, J=8.5 Hz), 5.44 (s, 1H), 3.78 (m, 2H), 3.62 (m, 2H), 1.24 (t, 6H, J=7.2 Hz).

3.2.11. 1-(4-Tolyl)-3,3-diethoxyprop-1-yne 11. From 4-bromotoluene (0.171 g, 1 mmol), product **11** was obtained in 90% (0.196 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (d, 2H, J=8.2 Hz), 7.09 (d, 2H, J=8.2 Hz), 5.47 (s, 1H), 3.80 (m, 2H), 3.64 (m, 2H), 2.32 (s, 3H), 1.25 (t, 6H, J=7.2 Hz).

3.2.12. 1-(4-*tert*-Butylphenyl)-3,3-diethoxyprop-1-yne 12. From 4-*t*butylbromobenzene (0.213 g, 1 mmol), product **12** was obtained in 92% (0.239 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, 2H, J=8.4 Hz), 7.34 (d, 2H, J=8.4 Hz), 5.50 (s, 1H), 3.83 (m, 2H), 3.68 (m, 2H), 1.32 (s, 9H), 1.27 (t, 6H, J=7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.1, 131.6, 125.2, 118.3, 91.5, 85.4, 83.7, 60.9, 34.8, 31.2, 15.1. This compound was characterized by deprotection into the corresponding aldehyde.[20]

3.2.13. 1-(4-Anisyl)-3,3-diethoxyprop-1-yne 13. From 4-bromoanisole (0.187 g, 1 mmol), product **13** was obtained in 74% (0.173 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (d, 2H, J=8.4 Hz), 6.81 (d, 2H, J=8.4 Hz), 5.46 (s, 1H), 3.80 (m, 2H), 3.79 (s, 3H), 3.64 (m, 2H), 1.26 (t, 6H, J=7.2 Hz).

3.2.14. 2-(3,3-Diethoxy-prop-1-ynyl)-6-methoxynaphthalene 14. From 2-bromo-6-methoxynaphthalene (0.237 g, 1 mmol), product **14** was obtained in 94% (0.267 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.65 (m, 2H), 7.45 (dd, 1H, J=8.5, 1.5 Hz), 7.13 (dd, 1H, J=8.7, 2.4 Hz), 7.06 (d, 1H, J=2.4 Hz), 5.53 (s, 1H), 3.85 (s, 3H), 3.83 (m, 2H), 3.68 (m, 2H), 1.29 (t, 6H, J=7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.4, 134.3, 131.8, 129.2, 128.8, 128.2, 126.6, 119.3, 116.6, 105.6, 91.8, 85.6, 83.9, 60.8, 55.1, 15.0; $C_{18}H_{20}O_3$: Calcd C, 76.03; H, 7.09. Found: C, 75.81; H, 7.31.

3.2.15. 1-(4-Dimethylaminophenyl)-3,3-diethoxyprop-1-yne 15. From 4-dimethylaminobromobenzene (0.200 g, 1 mmol), product **15** was obtained in 89% (0.220 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (d, 1H, J=8.9 Hz), 6.59 (d, 1H, J=8.9 Hz), 5.47 (s, 1H), 3.81 (m, 2H), 3.64 (m, 2H), 2.94 (s, 6H), 1.26 (t, 6H, J=7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.3, 132.9, 111.5, 108.4, 92.0, 86.4, 82.1, 60.7, 40.0, 15.1. This compound was characterized by deprotection into the corresponding aldehyde.[21]

3.2.16. 1-(3-Acetylphenyl)-3,3-diethoxyprop-1-yne 16. From 3-bromoacetophenone (0.199 g, 1 mmol), product **16** was obtained in 90% (0.222 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.87 (d, 1H, J=8.0 Hz), 7.62 (d, 1H, J=8.0 Hz), 7.38 (t, 1H, J=8.0 Hz), 5.46 (s, 1H), 3.79 (m, 2H), 3.63 (m, 2H), 2.56 (s, 3H), 1.23 (t, 6H, J=7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.3, 137.0, 136.0, 131.8, 128.6, 128.3, 122.4, 91.6, 85.4, 84.0, 61.0, 26.5, 15.0; $C_{15}H_{18}O_3$: Calcd C, 73.15; H, 7.37. Found: C, 73.41; H, 7.18.

3.2.17. 1-(3-Nitrophenyl)-3,3-diethoxyprop-1-yne 17. From 3-bromonitrobenzene (0.202 g, 1 mmol), product **17** was obtained in 89% (0.222 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28 (s, 1H), 8.15 (d, 1H, J=8.3 Hz), 7.73 (d, 1H, J=8.3 Hz), 7.48 (t, 1H, J=8.3 Hz), 5.46 (s, 1H), 3.79 (m, 2H), 3.63 (m, 2H), 1.24 (t, 6H, J=7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.9, 137.4, 129.3,

126.5, 123.6, 123.4, 91.5, 87.0, 82.4, 61.0, 15.0; $C_{13}H_{15}NO_4$: Calcd C, 62.64; H, 6.07. Found: C, 62.47; H, 5.84.

3.2.18. 1-(3-Tolyl)-3,3-diethoxyprop-1-yne 18. From 3-bromotoluene (0.171 g, 1 mmol), product **18** was obtained in 92% (0.201 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 (m, 2H), 7.17 (t, 1H, J= 7.8 Hz), 7.11 (d, 1H, J=7.8 Hz), 5.46 (s, 1H), 3.81 (m, 2H), 3.64 (m, 2H), 2.30 (s, 3H), 1.25 (t, 6H, J=7.2 Hz).

3.2.19. 1-(2-Benzoylphenyl)-3,3-diethoxyprop-1-yne 19a. From 2-bromoacetophenone (0.199 g, 1 mmol), product **19a** was obtained in 45% (0.111 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (dd, 1H, J=1.1, 7.5 Hz), 7. 57 (dd, 1H, J=1.2, 7.6 Hz), 7.44 (dt, 1H, J=1.1, 7.5 Hz), 7.36 (dt, 1H, J=1.2, 7.6 Hz), 5.52 (s, 1H), 3.84 (s, 3H), 3.80 (m, 2H), 3.69 (m, 2H), 1.25 (t, 6H, J=7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.3, 134.4, 132.3, 131.6, 130.3, 128.4, 122.3, 91.8, 89.3, 83.6, 60.9, 52.1, 15.1; $C_{15}H_{18}O_3$: Calcd C, 73.15; H, 7.37. Found: C, 73.44; H, 7.58. The formation of **19b** was also observed: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55–7.45 (m, 2H), 7.40–7.30 (m, 2H), 5.61 (d, 1H, J= 7.6 Hz), 5.27 (d, 1H, J=7.6 Hz), 4.77 (d, 1H, J=2.6 Hz), 4.47 (d, 1H, J=2.6 Hz), 3.75 (m, 2H), 3.60 (m, 2H), 1.23 (t, 6H, J=7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.6, 153.3, 133.4, 133.3, 130.1 (CH), 129.9 (CH), 120.8 (2CH), 97.2 (CH), 96.1 (CH), 82.5 (=CH_2), 61.3 (CH_2), 15.2 (Me). After HCl hydrolysis of **19b**, **19c** was obtained: ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.25 (d, 1H, J=8.3 Hz), 7.67 (m, 2H), 7.59 (t, 1H, J=7.6 Hz), 7.51 (t, 1H, J=7.6 Hz), 5.75 (d, 1H, J=8.1 Hz), 5.15 (d, 1H, J=3.2 Hz), 5.09 (d, 1H, J=3.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 188.8, 166.3, 157.2, 133.8, 132.5, 132.4, 130.3, 122.1, 120.8, 99.5, 88.0.

3.2.20. 1-(2-Formylphenyl)-3,3-diethoxyprop-1-yne 20. From 2-bromobenzaldehyde (0.185 g, 1 mmol), product **20** was obtained in 91% (0.211 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.49 (s, 1H), 7.89 (d, 1H, J=7.4 Hz), 7.55 (m, 2H), 7.44 (t, 1H, J=7.4 Hz), 5.52 (s, 1H), 3.80 (m, 2H), 3.66 (m, 2H), 1.23 (t, 6H, J=7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.5, 136.1, 133.6, 133.5, 129.1, 127.1, 125.2, 91.6, 91.4, 80.6, 61.2, 15.0; $C_{14}H_{16}O_3$: Calcd C, 72.39; H, 6.94. Found: C, 72.17; H, 6.70.

3.2.21. 1-(2-Methoxycarbonylphenyl)-3,3-diethoxyprop-1-yne 21. From methyl 2-bromobenzoate (0.215 g, 1 mmol), product **21** was obtained in 90% (0.236 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (dd, 1H, J=1.5, 7.7 Hz), 7.56 (dd, 1H, J=1.5, 7.5 Hz), 7.43 (dt, 1H, J=1.5, 7.7 Hz), 7.34 (dt, 1H, J=1.5, 7.5 Hz), 5.50 (s, 1H), 3.87 (s, 3H), 3.82 (m, 2H), 3.66 (m, 2H), 1.23 (t, 6H, J=7.2 Hz).

3.2.22. 1-(2-Cyanophenyl)-3,3-diethoxyprop-1-yne 22. From 2-bromobenzonitrile (0.182 g, 1 mmol), product **22** was obtained in 87% (0.200 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.11 (d, 1H, J=7.8 Hz), 7.50 (m, 2H), 7.41 (t, 1H, J=7.8 Hz), 5.49 (s, 1H), 3.81 (m, 2H), 3.64 (m, 2H), 1.25 (t, 6H, J=7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.7, 132.6, 132.3, 128.9, 125.7, 117.1, 115.4, 91.5, 90.7, 80.9, 61.2, 15.0; $C_{14}H_{15}NO_2$: Calcd C, 73.34; H, 6.59. Found: C, 73.60; H, 6.71.

3.2.23. 1-(2-Trifluoromethylphenyl)-3,3-diethoxyprop-1-yne 23. From 2-trifluoromethylbromobenzene (0.225 g, 1 mmol), product **23** was obtained in 91% (0.248 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (m, 2H), 7.44 (t, 1H, J= 7.6 Hz), 7.40 (t, 1H, J=7.4 Hz), 5.49 (s, 1H), 3.81 (m, 2H), 3.66 (m, 2H), 1.26 (t, 6H, J=7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.6, 131.8 (q, J=30.7 Hz), 131.3, 128.5, 125.7 (q, J=4.9 Hz), 123.3 (q, J=274.0 Hz), 120.2 (q, J=2. 1 Hz), 91.7, 90.1, 80.8, 61.0, 15.0; $C_{14}H_{15}F_3O_2$: Calcd C, 61.76; H, 5.55. Found: C, 61.50; H, 5.72.

3.2.24. 1-(2-Fluorophenyl)-3,3-diethoxyprop-1-yne 24. From 2-fluorobromobenzene (0.175 g, 1 mmol), product **24** was obtained in 93% (0.207 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (t, 1H, J=7.3 Hz), 7.30 (m, 1H), 7.06 (m, 2H), 5.49 (s, 1H), 3.82 (m, 2H), 3.65 (m, 2H), 1.26 (t, 6H, J=7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.8 (d, J=252.4 Hz), 133.6, 130.5 (d, J=7.7 Hz), 123.8 (d, J=3.3 Hz), 115.4 (d, J=21.7 Hz), 110.5 (d, J=15.4 Hz), 91.7, 89.5, 78.6, 61.0, 15.0; $C_{13}H_{15}FO_2$: Calcd C, 70.25; H, 6.80. Found: C, 70.01; H, 6.69.

3.2.25. 1-(2-Tolyl)-3,3-diethoxyprop-1-yne 25. From 2-bromotoluene (0.171 g, 1 mmol), product **25** was obtained in 90% (0.197 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, 1H, J=7.4 Hz), 7.20 (m, 2H), 7.12 (t, 1H, J=7.1 Hz), 5.53 (s, 1H), 3.83 (m, 2H), 3.66 (m, 2H), 2.44 (s, 3H), 1.26 (t, 6H, J=7.2 Hz).

3.2.26. 1-(3,3-Diethoxyprop-1-ynyl)-naphthalene 26. From 1-bromonaphthalene (0.207 g, 1 mmol), product **26** was obtained in 94% (0.239 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.31 (d, 1H, J=8.1 Hz), 7.84 (m, 2H), 7.72 (d, 1H, J=7.3 Hz), 7.57 (t, 1H, J=7.5 Hz), 7.51 (t, 1H, J=7.5 Hz), 7.41 (t, 1H, J=7.5 Hz), 5.64 (s, 1H), 3.90 (m, 2H), 3.73 (m, 2H), 1.29 (t, 6H, J=7.2 Hz).

3.2.27. 1-(2-Anisyl)-3,3-diethoxyprop-1-yne 27. From 2-bromoanisole (0.187 g, 1 mmol), product **27** was obtained in 88% (0.206 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 (dd, 1H, J=1.7, 7.5 Hz), 7.25 (dt, 1H, J=1.7, 8.3 Hz), 6.85 (t, 1H, J=8.3 Hz), 6.82 (d, 1H, J=8.3 Hz), 5.49 (s, 1H), 3.81 (s, 3H), 3.79 (m, 2H), 3.64 (m, 2H), 1.24 (t, 6H, J=7.2 Hz).

3.2.28. 1-(2,6-Difluorophenyl)-3,3-diethoxyprop-1-yne 28. From 2,6-difluorobromobenzene (0.193 g, 1 mmol), product **28** was obtained in 84% (0.202 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 (m, 1H), 6.87 (m, 2H), 5.50 (s, 1H), 3.83 (m, 2H), 3.65 (m, 2H), 1.24 (t, 6H, J=7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.2 (dd, J=5.2, 254.7 Hz), 130.5 (t, J=10.2 Hz), 111.2 (d, J=24.7 Hz), 101.1 (t, J=19.

5 Hz), 94.4, 91.6, 91.3, 61.2, 15.1; $C_{13}H_{14}F_2O_2$: Calcd C, 64.99; H, 5.87. Found: C, 65.13; H, 5.70.

3.2.29. 1-(2,4,6-Trimethylphenyl)-3,3-diethoxyprop-1-yne 29. From 2,4,6-trimethylbromobenzene (0.199 g, 1 mmol), product **29** was obtained in 89% (0.219 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.83 (s, 2H), 5.55 (s, 1H), 3.83 (m, 2H), 3.67 (m, 2H), 2.38 (s, 6H), 2.26 (s, 3H), 1.25 (t, 6H, J=7.2 Hz).

3.2.30. 1-(2,6-Diethyl-4-methylphenyl)-3,3-diethoxyprop-1-yne 30. From 2,6-diethyl-4-methylbromobenzene (0.227 g, 1 mmol), product **30** was obtained in 88% (0.242 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.86 (s, 2H), 5.55 (s, 1H), 3.81 (m, 2H), 3.68 (m, 2H), 2.74 (q, 4H, J=7.6 Hz), 2.30 (s, 3H), 1.24 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.8, 138.6, 126.1, 117.3, 92.1, 91.3, 82.5, 60.8, 27.8, 21.5, 15.1, 15.0; $C_{18}H_{26}O_2$: Calcd C, 78.79; H, 9.55. Found: C, 78.99; H, 9.56.

3.2.31. 9-(3,3-Diethoxy-prop-1-ynyl)-anthracene 31. From 9-bromoanthracene (0.257 g, 1 mmol), product **31** was obtained in 90% (0.274 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.56 (d, 2H, J=8.7 Hz), 8.41 (s, 1H), 7.99 (d, 2H, J=8.5 Hz), 7.59 (t, 2H, J=7.8 Hz), 7.50 (t, 2H, J=7.8 Hz), 5.86 (s, 1H), 4.03 (m, 2H), 3.86 (m, 2H), 1.35 (t, 6H, J=7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.8, 130.9, 128.6, 128.3, 126.7, 126.5, 125.6, 115.7, 95.7, 92.3, 81.9, 61.2, 15.2. This compound was characterized by deprotection into the corresponding aldehyde.[22]

3.2.32. 1-(2-Pyridyl)-3,3-diethoxyprop-1-yne 32. From 2-bromopyridine (0.158 g, 1 mmol), product **32** was obtained in 89% (0.183 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.55 (d, 1H, J=4.8 Hz), 7.60 (t, 1H, J=7.7 Hz), 7.43 (d, 1H, J=7.9 Hz), 7.20 (dd, 1H, J=4.8, 7.0 Hz), 5.44 (s, 1H), 3.77 (m, 2H), 3.62 (m, 2H), 1.21 (t, 6H, J=7.2 Hz).

3.2.33. 1-(3-Pyridyl)-3,3-diethoxyprop-1-yne 33. From 3-bromopyridine (0.158 g, 1 mmol), product **33** was obtained in 93% (0.191 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.74 (m, 1H), 8.60 (m, 1H), 7.77 (d, 1H, J=8.0 Hz), 7.26 (m, 1H), 5.50 (s, 1H), 3.82 (m, 2H), 3.67 (m, 2H), 1.28 (t, 6H, J=7.2 Hz).

3.2.34. 1-(2-Quinolyl)-3,3-diethoxyprop-1-yne 34. From 2-chloroquinoline (0.164 g, 1 mmol), product **34** was obtained in 90% (0.230 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 (d, 1H, J=8.1 Hz), 8.07 (d, 1H, J=8.1 Hz), 7.76 (d, 1H, J=8.1 Hz), 7.69 (t, 1H, J=7.7 Hz), 7.53 (t, 1H, J=7.7 Hz), 7.52 (d, 1H, J=8.1 Hz), 5.54 (s, 1H), 3.84 (m, 2H), 3.69 (m, 2H), 1.26 (t, 6H, J=7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.0, 142.3, 136.1, 130.0, 129.4, 127.4, 127.3, 127.2, 124.2, 91.7, 84.7, 84.6, 61.2, 15.0; $C_{16}H_{17}NO_2$: Calcd C, 75.27; H, 6.71. Found: C, 75.46; H, 6.97.

3.2.35. 1-(3-Quinolyl)-3,3-diethoxyprop-1-yne 35. From 3-bromoquinoline (0.208 g, 1 mmol), product **35** was obtained in 94% (0.240 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.95 (m, 1H), 8.24 (s, 1H), 8.12 (d, 1H, J=8.2 Hz), 7.74 (d, 1H, J=8.4 Hz), 7.69 (t, 1H, J=7.5 Hz), 7.52 (t, 1H, J=7.5 Hz), 5.52 (s, 1H), 3.82 (m, 2H), 3.67 (m, 2H), 1.27 (t, 6H, J=7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.8, 146.9, 138.9, 130.2, 129.3, 127.5, 127.2, 126.9, 115.9, 91.6, 87.6, 82.2, 61.0, 15.0; $C_{16}H_{17}NO_2$: Calcd C, 75.27; H, 6.71. Found: C, 75.28; H, 6.57.

3.2.36. 1-(4-Isoquinolyl)-3,3-diethoxyprop-1-yne 36. From 4-bromoisoquinoline (0.208 g, 1 mmol), product **36** was obtained in 90% (0.230 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.19 (m, 1H), 8.71 (m, 1H), 8.16 (d, 1H, J=8.5 Hz), 7.93 (d, 1H, J=8.2 Hz), 7.74 (t, 1H, J=7.5 Hz), 7.60 (t, 1H, J=7.5 Hz), 5.60 (s, 1H), 3.85 (m, 2H), 3.70 (m, 2H), 1.28 (t, 6H, J=7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.0, 146.7, 135.3, 131.1, 127.8, 127.7, 124.8, 91.7, 80.3, 61.0, 15.1; $C_{16}H_{17}NO_2$: Calcd C, 75.27; H, 6.71. Found: C, 75.47; H, 6.60.

3.2.37. 1-(5-Pyrimidolyl)-3,3-diethoxyprop-1-yne 37. From 5-bromopyrimidine (0.158 g, 1 mmol), product **37** was obtained in 90% (0.186 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.14 (s, 1H), 8.78 (s, 2H), 5.47 (s, 1H), 3.77 (m, 2H), 3.63 (m, 2H), 1.24 (t, 6H, J=7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.9, 157.2, 118.5, 91.5, 91.4, 78.2, 61.2, 15.0; $C_{11}H_{14}N_2O_2$: Calcd C, 64.06; H, 6.84. Found: C, 64.00; H, 6.71.

3.2.38. 1-(2-Thienyl)-3,3-diethoxyprop-1-yne 38. From 2-bromothiophene (0.163 g, 1 mmol), product **38** was obtained in 88% (0.185 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (m, 2H), 6.95 (dd, 1H, J=3.8, 4.9 Hz), 5.48 (s, 1H), 3.80 (m, 2H), 3.64 (m, 2H), 1.26 (t, 6H, J=7.2 Hz).

3.2.39. 1-(3-Thienyl)-3,3-diethoxyprop-1-yne 39. From 3-bromothiophene (0.163 g, 1 mmol), product **39** was obtained in 90% (0.189 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 (d, 1H, J=3.0 Hz), 7.23 (dd, 1H, J=3.0, 5.1 Hz), 7.12 (d, 1H, J=5.1 Hz), 5.45 (s, 1H), 3.79 (m, 2H), 3.64 (m, 2H), 1.24 (t, 6H, J=7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 129.8, 129.7, 125.6, 120.8, 91.7, 84.0, 80.4, 60.9, 15.0; $C_{11}H_{14}O_2S$: Calcd C, 62.83; H, 6.71. Found: C, 62.95; H, 6.84.

3.2.40. 1,4-Bis(3,3-diethoxy-prop-1-ynyl)benzene 40. From 1,4-dibromobenzene (0.236 g, 1 mmol), product **40** was obtained in 92% (0.304 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 (s, 4H), 5.45 (s, 2H), 3.79 (m, 4H), 3.64 (m, 4H), 1.24 (t, 12H, J=7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 131.7, 122.5, 91.7, 86.3, 84.5, 60.9, 15.0; $C_{20}H_{26}O_4$: Calcd C, 72.70; H, 7.93. Found: C, 72.89; H, 7.81.

3.2.41. 1,2-Bis(3,3-diethoxy-prop-1-ynyl)benzene 41. From 1,2-dibromobenzene (0.236 g, 1 mmol), product **41** was obtained in 94% (0.310 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 (m, 2H), 7.25 (m, 2H), 5.48 (s, 2H), 3.82 (m, 4H), 3.66 (m, 4H), 1.24 (t, 12H, J= 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.3, 128.4, 124.7, 91.7, 88.3, 83.5, 60.9, 15.1; $C_{20}H_{26}O_4$: Calcd C, 72.70; H, 7.93. Found: C, 72.67; H, 7.98. The monoaddition product **42** was also isolated ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (d, 1H, J=7.8 Hz), 7.48 (d, 1H, J=7.8 Hz), 7.28–7.10 (m, 2H), 5.52 (s, 1H), 3.86 (m, 2H), 3.66 (m, 2H), 1.27 (t, 6H, J= 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.8, 132.4, 129.9, 126.9, 125.6, 124.2, 91.7, 88.9, 83.5, 61.1, 15.1.

3.3. Registry No.: 1

6142-95-6; **5**, 181419-95-4; **6**, 83758-93-4; **10**, 74929-22-9; **11**, 62358-86-5; **13**, 62358-88-7; **18**, 62358-87-6; **21**, 181419-89-6; **25**, 181419-85-2; **26**, 2375725 (Beilstein Registry Number); **27**, 202391-28-4; **29**, 73057-39-3; **32**, 49836-19-3; **33**, 143952-62-9; **38**, 13781-32-3.

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