Rh- AND Ru-COMPLEX-CATALYZED DIMERIZATION OF ARYLETHYNES IN AQUEOUS ENVIRONMENT

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Complexes $[RhCl(PPh_3)_3]$ and $[Ru(CHPh)Cl_2(PCy_3)_2]$ efficiently catalyzed the dimerization of arylethynes to the corresponding 1,4-substituted enynes in aqueous environment in the presence of sodium dodecyl sulfate. The Rh catalyst exhibited almost exclusive preference for the formation of *E*-isomers, the Ru one exhibits strong preference for the formation of *Z*-isomers.

Keywords: Dimerizations; Rhodium; Ruthenium; Water chemistry; Terminal alkines; Enynes; Arylacetylenes.

In the last two decades, development of organic reactions in an aqueous environment has become a highly attractive area. Special interest is devoted to the reactions catalyzed with transition metal complexes because of their resemblance to enzymatic processes[1]. It has been recently shown that alkynes can undergo a wide array of transformations in water or aqueous environment[2]. Interestingly, the area of alkyne dimerization[3] to 1,3-enynes in water has been somewhat neglected. This is rather surprising because this class of compounds can be used as building blocks in the synthesis of natural compounds[4], biologically active substances[5], or intermediates used in material chemistry[6]. The only exceptions are the recently reported *Z*-selective dimerization of alkynes in the presence of Ru catalyst with a tripodal phosphine ligand[7] and *E*-selective process catalyzed with a Rh complex containing sulfonated phosphine ligands[8]. Generally, the dimerization of a terminal alkyne RC≡CH may result in the formation of several isomeric hydrocarbons but the main products are usually (*E*)- and (*Z*)-RCH=CHC≡CR. The dimerization can be catalyzed with a number of transition metal com-

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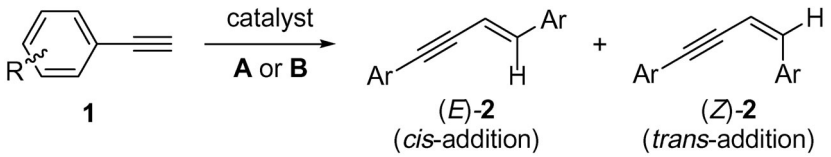
plexes of Ru (refs[7,9]), Rh (refs[8,10]), Ir (ref.[11]), Pd (ref.[12]), Ni (ref.[13]), Ti (ref.[14]), and lanthanide[15] compounds. The selectivity in the formation of (*E*)- or (*Z*)-enynes depends on a number of factors such as the reaction mechanism, structural features of the reacting alkynes, and the catalyst. The most frequently used Rh-complex-catalyzed dimerization usually proceeds with high or exclusive *E*-selectivity (formally a *cis*-addition to the triple bond). On the other hand, in case of the Ru-complex-catalyzed reactions, the ligand environment around the central Ru atom plays a significant role in controlling the *E*/*Z* ratio in the products[9]. The preferential selectivity has been explained either in terms of the ligand steric effect (a Ru complex with bulky PCy_3 showed high *Z*-selectivity, whereas the analogous complex with the less sterically demanding PMe_3 ligand exhibited *E*-selectivity)[9c] or by the existence of different reactive species[9g].

RESULTS AND DISCUSSION

Since there is lack of information on the scope and stereoselectivity of alkyne dimerization in an aqueous environment, we decided to explore the possibility of carrying out the dimerization of alkynes to (*E*)- or (Z)-enynes in water, catalyzed with commercially available Rh and Ru complexes ($[RhCl(PPh_3)_3]$ – Wilkinson catalyst and $[Ru(CHPh)Cl_2(PCy_3)_2]$ – 1st generation Grubbs catalyst) in the presence of surfactant sodium dodecyl sulfate (SDS). The surfactant has been used previously to accelerate a number of various reactions in water or aqueous environment[16,17]. The reactions were carried out under two different reaction conditions: A (catalysts (5 mole %), water and SDS); B catalysts (5 mole %), water, toluene 10% v/v, SDS)



SCHEME 1

(Scheme 1).

Initially, the dimerization of alkynes was tested with the Wilkinson catalyst, $[RhCl(PPh_3)_3]$, under both conditions. The reaction proceeded with reasonable yields (19–86%) only under conditions B, with excellent *E*-selectivity (Table I). In most cases, the dimerization proceeded with good yields of the *para*-isomers **1b**–**1g** (entries 2–7), *meta*-isomers of **1h**–**1j**

(entries 8–10), and *ortho*-isomers **1k**–**1n** (entries 11–14) of substituted arylethynes. As to other alkynes, successful dimerization was performed with ferrocenylethyne **1o** (entry 15). It is worth mentioning that *E*-selectivity was better than in the case of previously reported results, e.g. $[RhCl(CO)(PPh_3)_2]/K_2CO_3/MeI/THF$ [10b]. Interestingly, ethynes such as 3-ethynylphenol, 3-ethynylpyridine, 6-ethynylpurine, prop-2-yn-1-yl benzoate, 3-phenylpropyne, and {2-deoxy-3,5-bis[*O*-(*p*-toluoyl)]-α-D-ribofuranosyl}ethyne[10c] did not react. In the case of 3-ethynylpyridine and 6-ethynylpurine, coordination of the central Rh atom to lone electron pairs of heteroatoms saturating its coordination sites may account for the lack of reactivity. On the other hand, the lack of reactivity of alkylalkynes remains a puzzle, because their facile dimerization in aprotic solvents was reported previously[10b,10c]. The obtained data are also in agreement with the generally accepted three-step reaction mechanism: (i) oxidative addition of the alkynyl C–H bond onto the central rhodium atom giving a rhodium hy-

TABLE I
$[RhCl(PPh_3)_3]$-catalyzed dimerization of alkynes **1** to enynes **2**

Entry	Alkyne	R	*E*-**2**/*Z*-**2**	Yield, %[a]
1	**1a**	H	>99:1	78
2	**1b**	4-Me_2N	>99:1	19[b]
3	**1c**	4-MeO	>99:1	18
4	**1d**	4-Me	>99:1	86
5	**1e**	4-Cl	>99:1	59
6	**1f**	4-CF_3	>99:1	62
7	**1g**	4-CN	>99:1	22[c]
8	**1h**	3-Me	>99:1	83
9	**1i**	3-Cl	>99:1	56
10	**1j**	3-CF_3	>99:1	25
11	**1k**	2-MeO	>99:1	48
12	**1l**	2-Me	>99:1	69
13	**1m**	2-Cl	>99:1	57[d]
14	**1n**	2-CF_3	>99:1	44
15	**1o**	FcC≡CH	>99:1	29[e]

Conditions B. [a] Isolated yields. [b] 9% of the starting **1b**. [c] 26% of the starting **1g**. [d] 40% of the starting **1m**. [e] 14% of the starting **1o**.

dride, (ii) hydrorhodation of the second alkyne, and (iii) reductive elimination of a vinyl-alkynyl-rhodium intermediate[8,10].

Our attention was then shifted to catalysis with $[Ru(CHPh)Cl_2(PCy_3)_2]$. From the general point of view, it should be mentioned that its use resulted in the preferential formation of (*Z*)-enynes (Table II). The dimerization of phenylethyne **1a** proceeded under both conditions A and B uneventfully to give a mixture of (*E*)- and (*Z*)-enynes **2a** in the 1:5 ratio. Interestingly, phenylethynes bearing electron-donating groups **1b** (4-Me_2N), **1c** (4-MeO), and **1k** (2-MeO), did not undergo dimerization (entries 3–6, 21 and 22). Similarly, (4-cyanophenyl)ethyne **1g** did not react (entries 13 and 14), either. In all other cases, the alkynes afforded the corresponding enynes usually as mixtures of (*E*)- and (*Z*)-isomers in various ratios. As to the difference in the reaction conditions, the dimerization running under conditions B gave higher yields and better *Z*-selectivity. This difference is nicely demonstrated in the dimerization of **1f**, **1h**, **1j**, and **1l**. Thus, enynes **2f** were obtained in the yields of 75% (*E*/*Z* 1:10) and 89% (*E*/*Z* 1:19) (entries 11 and 12), enynes **2h** in the yields of 51% (*E*/*Z* 1:5) and 83% (*E*/*Z* 1:7) (entries 15 and 16), enynes **2j** in the yields of 38% (*E*/*Z* 1:10) and 58% (*E*/*Z* 1:17) (entries 19 and 20), and enynes **2l** in the yields of 40% (*E*/*Z* 1:2) and 71% (*E*/*Z* 1:4) (entries 23 and 24). Only the dimerization of **1n** under conditions A gave rise to higher yields of enynes **2n** and better selectivity ratio (entries 27 and 28). In this respect, higher yields of the products were obtained under condition A also for **1d** (entries 7 and 8), **1i** (entries 17 and 18), and **1m** (entries 25 and 26), but with lower *E*/*Z* selectivity than under conditions B. Under conditions A, [4-(dimethylamino)phenyl]ethyne **2b** and (4-methoxyphenyl)ethyne **2c** underwent hydration of the triple bond affording the corresponding acetophenones; under conditions B, they did not react. In addition to the above mentioned unsuccessful dimerizations, ethynes such as 3-ethynylphenol, 3-ethynylpyridine, 6-ethynylpurine, prop-2-yn-1-yl benzoate, 3-phenylpropyne, and {2-deoxy-3,5-bis[*O*-(*p*-toluoyl)]-α-D-ribofuranosyl}ethyne[10c] did not react under any conditions used (probably for the same reasons as in the Rh-catalyzed case), either. The positive effect of the presence of toluene was especially significant when solid alkynes were dimerized; the reaction of ferrocenylethyne **1o** did not proceed under conditions A. Since better results for the dimerization were obtained under conditions B (in a mixture of water and toluene), it is reasonable to assume that the presence of toluene had a positive effect on the solubilization of the catalysts and reactants prior to the formation of micelles with SDS.

The course of the reaction is more complex since the preferential formation of *Z*- or *E*-isomers was observed. Although all proposed reaction mech-

TABLE II
$[Ru(CHPh)Cl_2(PCy_3)_2]$-catalyzed dimerization of alkynes **1** to enynes **2**

Entry	Alkyne	R	Conditions	*E*-**2**/*Z*-**2**	Yield, %[a]
1	**1a**	H	A	1:5	96
2			B	1:5	98
3	**1b**	4-Me_2N	A		–[b]
4			B		n.r.[c]
5	**1c**	4-MeO	A		–[b]
6			B		n.r.[c]
7	**1d**	4-Me	A	1:10	95
8			B	1:20	34
9	**1e**	4-Cl	A	1:19	46
10			B	1:10	90
11	**1f**	4-CF_3	A	1:13	75
12			B	1:19	89
13	**1g**	4-CN	A		n.r.[c]
14			B		n.r.[c]
15	**1h**	3-Me	A	1:5	51
16			B	1:7	83
17	**1i**	3-Cl	A	1:5	94
18			B	1:8	90
19	**1j**	3-CF_3	A	1:10	38
20			B	1:17	58
21	**1k**	2-MeO	A		n.r.[c]
22			B		n.r.[c]
23	**1l**	2-Me	A	1:2	40
24			B	1:4	71
25	**1m**	2-Cl	A	1:4	68
26			B	1:5	18
27	**1n**	2-CF_3	A	1:10	66
28			B	1:3	28
29	**1o**	FcC≡CH	B	1:1	30[d]

[a] Isolated yields. [b] Hydration of alkyne. [c] No reaction. [d] 30% of the starting **1o**.

anisms presume the formation of alkylidene ruthenium species as one the probable intermediates, they differ in the origin of *E*/*Z* selectivity. The preferential formation of *Z*-isomers was reported for the dimerization carried out with Ru-carbene[9g] and other Ru complexes[7,9a–9c]; on the other hand, *E*-selectivity was reported as well[9c,9d,9h]. In addition, the change from *E*- to *Z*-selectivity was attributed either to the bulkiness of phosphine ligands[9c] or the presence of protic additives[9e]. In view of the foregoing, it is at this point difficult to speculate on the effect of water on preferential *Z*-selectivity.

CONCLUSIONS

We have shown that stable and commercially available rhodium and ruthenium complexes such as $[RhCl(PPh_3)_3]$ and $[Ru(CHPh)Cl_2(PCy_3)_2]$ were able to efficiently dimerize arylethynes to the corresponding enynes in an aqueous environment. Under these conditions, the Rh catalyst had higher selectivity in the formation of (*E*)-enynes than that reported for the reaction carried out in aprotic solvents. In addition, so far the largest set of phenylalkynes was converted selectively to the corresponding *E*-enynes. The catalysis with the Ru complex was more complicated, but it exhibited preferential selectivity for the (*Z*)-enynes in most cases. The scope of the reaction with respect to substituents on the benzene ring was somewhat restricted: phenylalkynes bearing electron-donating groups (e.g. Me_2N or MeO) or strongly coordinating ligands (e.g. CN) either did not react or the hydration of the triple bond was observed. Further study focusing on the use of other amphiphiles (e.g. the recently reported polyoxyethanyl α-tocopheryl sebacate (PTS)[18]) with elucidation of the roles of water on the reaction course is under way and will be reported in due course.

EXPERIMENTAL

All solvents were used as obtained. $[RhCl(PPh_3)_3]$ was prepared by the previously reported procedure[19]. $[Ru(CHPh)Cl_2(PCy_3)_2]$ and alkynes were purchased from Sigma–Aldrich. NMR spectra (δ, ppm; *J*, Hz) were recorded in $CDCl_3$ solutions on a Varian Unity 300 Inova instrument at 300 MHz (^1H) and 75.6 MHz (^{13}C) and are referenced to the Me_4Si signal. IR spectra (cm^{-1}) were recorded on a Bruker IFS 88 instrument using ATR technics. Mass spectra were recorded on a Finnigan Mat Incos 50 spectrometer. HR MS were recorded on a ZAB-SEQ VG Analytical spectrometer.

$[RhCl(PPh_3)_3]$-Catalyzed Dimerization. General Procedure

$[RhCl(PPh_3)_3]$ (0.025 mmol, 23 mg), alkyne (0.5 mmol), toluene (0.4 ml) and water (3.6 ml) were placed into a vial flask. SDS (1 mmol, 288 mg) was then added, and the solution was

stirred at 50 °C for 15 h. The reaction mixture was then extracted with Et_2O (2 × 5 ml). The combined organic fractions were washed with brine (5 ml) and dried over anhydrous $MgSO_4$. After removal of the solvents in vacuo, the residue was purified by column chromatography on silica gel (hexane/EtOAc 6:1). The products were obtained as yellowish liquids in the yields given below. Their spectral data were in agreement with those published previously.

(E)-1,4-Diphenylbut-1-en-3-yne (*E*-**2a**). Yield 40 mg (78%)[15c,20].

(E)-1,4-Bis[4-(dimethylamino)phenyl]but-1-en-3-yne (*E*-**2b**). Yield 14 mg (19%)[10b].

(E)-1,4-Bis(4-methoxyphenyl)but-1-en-3-yne (*E*-**2c**). Yield 12 mg (18%)[9g,20].

(E)-1,4-Bis(4-methylphenyl)but-1-en-3-yne (*E*-**2d**). Yield 50 mg (86%)[21].

(E)-1,4-Bis(4-chlorophenyl)but-1-en-3-yne (*E*-**2e**). Yield 40 mg (59%)[20].

(E)-1,4-Bis[4-(trifluoromethyl)phenyl]but-1-en-3-yne (*E*-**2f**). Yield 53 mg (62%)[10b,20].

(E)-1,4-Bis(4-cyanophenyl)but-1-en-3-yne (*E*-**2g**). Yield 14 mg (22%)[10b].

(E)-1,4-Bis(3-methylphenyl)but-1-en-3-yne (*E*-**2h**). Yield 48 mg (83%). ^{1}H NMR: 2.34 s, 3 H; 2.36 s, 3 H; 6.36 d, *J* = 16.2, 1 H; 6.99 d, *J* = 16.2, 1 H; 7.11–7.30 m, 8 H. ^{13}C NMR: 21.2, 21.4, 88.7, 91.8, 108.0, 123.2, 123.5, 127.0, 128.2, 128.5, 128.6, 129.1, 129.4, 132.1, 136.3, 138.0, 138.3, 141.3. IR: 3027, 2920, 1582, 1484, 1453, 1091, 1040, 782, 703, 690. HR MS (EI) for $C_{18}H_{16}$ calculated: 232.125201, found: 232.124879.

(E)-1,4-Bis(3-chlorophenyl)but-1-en-3-yne (*E*-**2i**). Yield 44 mg (56%). ^{1}H NMR: 6.36 d, *J* = 16.2, 1 H; 6.97 d, *J* = 16.2, 1 H; 7.26–7.46 m, 8 H. ^{13}C NMR: 89.5, 91.0, 109.2, 124.5, 124.9, 126.2, 128.2, 128.7, 129.6, 129.7, 130.0, 131.4, 134.2, 134.8, 137.9, 140.4. IR: 1590, 1561, 1474, 1096, 1077, 950, 881, 804, 782, 709, 702, 681. HR MS (EI) for $C_{16}H_{10}Cl_2$ calculated: 272.015956, found: 272.015645.

(E)-1,4-Bis[3-(trifluoromethyl)phenyl]but-1-en-3-yne (*E*-**2j**). Yield 21 mg (25%). ^{1}H NMR: 6.44 d, *J* = 16.2, 1 H; 7.09 d, *J* = 16.2, 1 H; 7.45–7.65 m, 6 H; 7.66 s, 1 H; 7.74 s, 1 H. ^{13}C NMR: 89.7, 91.1, 109.6, 123.0, 123.0, 124.1, 124.9, 125.0, 125.3, 125.4, 128.3, 128.4, 128.91, 129.3, 129.4, 134.6, 136.8, 140.5. IR: 1332, 1167, 1128, 1073, 695. HR MS (EI) for $C_{16}H_{10}F_6$ calculated: 340.068670, found: 340.068276.

(E)-1,4-Bis(2-methoxyphenyl)but-1-en-3-yne (*E*-**2k**). Yield 32 mg (48%)[15c,20].

(E)-1,4-Bis(2-methylphenyl)but-1-en-3-yne (*E*-**2l**). Yield 40 mg (69%)[15c,21].

(E)-1,4- Bis(2-chlorophenyl)but-1-en-3-yne (*E*-**2m**). Yield 39 mg (57%)[22].

(E)-1,4-Bis[(2-trifluoromethyl)phenyl]but-1-en-3-yne (*E*-**2n**). Yield 32 mg (44%)[20].

(E)-1,4-(Diferrocenyl)but-1-en-3-yne (*E*-**1o**). Yield 30 mg (29%)[20].

[Ru(CHPh)Cl_2(PCy_3)$_2$]-Catalyzed Dimerization. General Procedure

Method A. First generation Grubbs catalyst (0.025 mmol, 20.5 mg), alkyne (0.5 mmol), and water (4 ml) were placed in a vial. SDS (1 mmol, 288 mg) was then added, and the solution was stirred at 50 °C for 15 h. The reaction mixture was then extracted with Et_2O (2 × 5 ml). The combined organic fractions were washed with brine (5 ml) and dried over anhydrous $MgSO_4$. After removal of the solvents in vacuo, the residue was purified by column chromatography on silica gel (hexane/EtOAc 6:1). The products were obtained as yellowish liquids in the yields given below. Their spectral data were in agreement with those published previously.

Method B. First generation Grubbscatalyst (0.025 mmol, 20.5 mg), alkyne (0.5 mmol), toluene (0.4 ml), and water (3.6 ml) were placed in a vial. SDS (1 mmol, 288 mg) was then added, and the solution was stirred at 50 °C for 15 h. The reaction mixture was then ex-

tracted with Et_2O (2 × 5 ml). The combined organic fractions were washed with brine (5 ml) and dried over anhydrous $MgSO_4$. After removal of the solvents in vacuo, the residue was purified by column chromatography on silica gel (hexane/EtOAc 6:1). The products were obtained as yellowish liquids in the yields given below. Their spectral data were in agreement with those published previously.

(Z)- and (E)-1,4-Diphenylbut-1-en-3-yne (*Z*-**2a** and *E*-**2a**). Methods *A* and *B* 49 mg (96%) and 50 mg (98%), respectively. *Z*/*E* mixture (5:1)[7,15c,20,23].

(Z)- and (E)-1,4-Bis(4-methylphenyl)but-1-en-3-yne (*Z*-**2d** and *E*-**2d**). Method *A* 55 mg (95%). *Z*/*E* mixture (10:1). Method *B* 20 mg (34%). *Z*/*E* mixture (20:1)[7,9g,10b].

(Z)- and (E)-1,4-Bis(4-chlorophenyl)but-1-en-3-yne (*Z*-**2e** and *E*-**2e**). Method *A* 31 mg (46%). *Z*/*E* mixture (19:1). Method *B* 61 mg (90%). *Z*/*E* mixture (10:1)[15a,20].

(Z)- and (E)-1,4-Bis[4-(trifluoromethyl)phenyl]but-1-en-3-yne (*Z*-**2f** and *E*-**2f**). Method *A* 64 mg (75%). *Z*/*E* mixture (13:1). Method *B* 76 mg (89%). *Z*/*E* mixture (19:1)[15a,20,21].

(Z)- and (E)-1,4-Bis(3-methylphenyl)but-1-en-3-yne (*Z*-**2h** and *E*-**2h**). Method *A* 38 mg (51%). *Z*/*E* mixture (5:1). Method *B* 48 mg (83%). *Z*/*E* mixture (7:1). *Z*-**2h**. ^{1}H NMR: 2.34 s, 3 H; 2.38 s, 3 H; 5.88 d, *J* = 12, 1 H; 6.65 d, *J* = 12, 1 H; 7.21–7.31 m, 6 H; 7.68–7.71 m, 1 H; 7.81 m, 1 H. ^{13}C NMR: 21.2, 21.5, 88.1, 96.0, 107.2, 123.3, 126.0, 128.2, 128.3, 129.2, 129.2, 129.4, 132.0, 136.5, 137.7, 138.1, 138.6. IR: 3032, 2918, 1579, 1489, 1448, 1095, 1038, 786, 707, 685. HR MS (EI) for $C_{18}H_{16}$ calculated: 232.125201, found: 232.124913.

(Z)- and (E)-1,4-Bis(3-chlorophenyl)but-1-en-3-yne (*Z*-**2i** and *E*-**2i**). Method *A* 64 mg (94%). *Z*/*E* mixture (5:1). Method *B* 61 mg (90%). *Z*/*E* mixture (8:1). *Z*-**2i**. ^{1}H NMR: 5.93 d, *J* = 12, 1 H; 6.66 d, *J* = 12, 1 H; 7.27–7.58 m, 7 H; 8.09 s, 1 H. ^{13}C NMR: 88.8, 95.2, 108.5, 124.8, 127.1, 128.3, 128.5, 128.8, 129.6, 129.6, 129.7, 131.3, 134.2, 134.3, 137.8, 138.0. IR: 1585, 1559, 1468, 1073, 806, 779, 711, 700, 685. HR MS (EI) for $C_{16}H_{10}Cl_2$ calculated: 272.015956, found: 272.015787.

(Z)- and (E)-1,4-Bis[3-(trifluoromethyl)phenyl]but-1-en-3-yne (*Z*-**2j** and *E*-**2j**). Method *A* 31 mg (38%). *Z*/*E* mixture (10:1). Method *B* 49 mg (58%). *Z*/*E* mixture (17:1). *Z*-**2j**. ^{1}H NMR: 6.01 d, *J* = 12, 1 H; 6.77 d, *J* = 12, 1 H; 7.47–7.83 m, 7 H; 8.43 s, 1 H. ^{13}C NMR: 88.8, 95.2, 108.8, 123.9, 124.9, 124.9, 125.1, 125.2, 128.3, 128.4, 128.9, 129.0, 131.5, 131.9, 132.2, 134.5, 136.9, 137.9. IR: 1336, 1175, 1131, 1085, 689. HR MS (EI) for $C_{16}H_{10}F_6$ calculated: 340.068670, found: 340.068309.

(Z)- and (E)-1,4-Bis(2-methylphenyl)but-1-en-3-yne (*Z*-**2l** and *E*-**2l**). Method *A* 23 mg (40%). *Z*/*E* mixture (2:1). Method *B* 41 mg (71%). *Z*/*E* mixture (4:1)[15c,21].

(Z)- and (E)-1,4-Bis(2-chlorophenyl)but-1-en-3-yne (*Z*-**2m** and *E*-**2m**). Method *A* 46 mg (68%). *Z*/*E* mixture (4:1). Method *B* 12 mg (18%). *Z*/*E* mixture (5:1)[15c,22].

(Z)- and (E)-1,4-Bis[2-(trifluoromethyl)phenyl]but-1-en-3-yne (*Z*-**2n** and *E*-**2n**). Method *A* 56 mg (66%). *Z*/*E* mixture (10:1). Method *B* 24 mg (28%). *Z*/*E* mixture (3:1). *Z*-**2n**. ^{1}H NMR: 5.93 d, *J* = 11.7, 1 H; 6.66 d, *J* = 11.7, 1 H; 7.27–7.39 m, 6 H; 7.48–7.49 m, 1 H; 8.09–8.10 m, 1 H. ^{13}C NMR: 88.8, 95.2, 108.5, 124.8, 127.1, 128.3, 128.6, 128.8, 129.6, 129.6, 129.7, 131.3, 134.2, 134.3, 137.8, 138.0. IR: 1340, 1173, 1119, 1085, 693. HR MS (EI) for $C_{16}H_{10}F_6$ calculated: 340.068670, found: 340.069158[21].

(Z)- and (E)-1,4-Di(ferrocenyl)but-1-en-3-yne (*Z*-**2o** and *E*-**2o**). Method *B* 31 mg (30%). *Z*/*E* mixture (1:1)[20,23].

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