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Synthesis of unsymmetric diynes by palladium and cesium fluoride catalyzed coupling of terminal bromoalkynes with alkynylstannane

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The Stille reaction of unsymmetric diynes from terminal bromoalkynes with alkynylstannane in the presence of palladium catalyst and cesium fluoride was studied. The system (bromoalkyne: $PhC{\equiv}CSnMe_3$:$Pd_2(dba)_3$:PPh_3:CsF:18-crown-6) = (1:1:0.015:0.06:2.2:0.1) in toluene at reflux temperature was found to be the most favored. Products were obtained in 31–100% yields. Correlations between calculated electron density, dipole moments and ^{13}C NMR spectral data of synthesized bromoacetylenes and diynes have been carried out. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: Stille coupling; 1-bromoalkynes; alkynylstannane; alkynylsilane; unsymmetric diynes; Pd catalysis; fluoride ion catalysis; phase transfer catalysis

Acetylenic coupling has received considerable attention owing to its utility in the synthesis of natural products and acetylenic oligomers and polymers.

Synthesis of diynes by acetylenic homo- and heterocoupling has been recently reviewed.[1] Among the main methods for the synthesis of unsymmetric butadiynes it is necessary to mention Chodkiewicz and Cadiot coupling in the presence copper(I) salts[2,3] or the $CoCl_2$-mediated coupling of alkynyl Grignard derivatives and 1-haloalkynes,[4] the palladium-mediated reaction of 1-haloalkynes and alkynes,[5] and the two-step synthesis from disiamylalkynylboranes.[6]

Coupling reactions of organostannanes with aryl or unsaturated alkyl halides (Stille coupling) are widely used in organic synthesis.[7,8] Usually the Stille reactions are catalyzed by palladium and palladium(II) complexes. The effect of catalyst, ligands and base on the reaction course, selectivity and yield has been much studied.[9,10] Alkynylstannanes are successively used in such coupling reactions. Thus, Stille reactions for vinyl, alkyl and aryl halides readily proceed in the systems $PhC{\equiv}CSnBu_3/Pd(PPh)_3/CCl_4$,[11] $PhC{\equiv}CSnBu_3/PdCl_2(PPh_3)_2/PhMe$,[12] $PhC{\equiv}CSnBu_3/Pd_2(dba)_3{\cdot}CHCl_3/AsPh_3/PhMe$,[13] $EtOC{\equiv}CSnBu_3/PdCl_2(PPh_3)_2/Bu_4NF/DMF$,[14] $Me_3SiOCH_2C{\equiv}CSnBu_3/PdCl_2(PPh_3)_2/THF$[15] [dba = PhCHCHC(O)CHCHPh]. Recently, detailed investigations of the mechanism of the Stille reaction have also been presented.[16,17] Coupling reactions of acetylenic bromides with alkenyltin compounds in the presence of a $Pd(MeCN)_2Cl_2$/tri(2-furyl)phosphine/*N*-methylpyrrolidinone system were also described.[18] It has been found that unsymmetrical 1,4-biaryl-1,3-butadiynes can be obtained by copper(I)-catalyzed cross-coupling reaction of 1-chloroalkynes and alkynes[19] or alkynylsilanes.[20] However, the use of 1-bromoalkynes in coupling reactions sometimes is connected with some difficulties. These compounds are thermally unstable and undergo some side reactions (reduction, homocoupling, polymerization, etc.).

The aim of the present work was to elaborate a convenient method for synthesis of unsymmetric diynes by interaction of 1-bromoalkynes with alkynylstannane in the presence of palladium complexes and cesium fluoride under phase transfer catalysis (PTC) conditions.

EXPERIMENTAL

^1H NMR spectra were recorded on a Mercury 200 (Varian) instrument using $CDCl_3$ as a solvent and tetramethylsilane (TMS) as internal standard. Mass spectra were registered on a GC–MS HP 6890 (70 eV). Gas chromatography (GC)

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Table 1. The determination of optimal conditions for the preparation of 1-phenyl-4-(2-methyl-5-pyridyl)-1,3-butadiyne (**6**)

M	$Pd_2(dba)_3$ catalyst (%)	L = PPh_3 (%)	CsF (equiv.)	18-Crown-6 (equiv.)	Reaction time (h)	Relative content of products in reaction mixture (GC, %)		
						6	**7**	**6a**
Sn	1.5	6	–	–	30	10	4	5
Sn	1.5	6	0.2	0.1	30	11	3	4
Sn	1.5	6	1.1	0.1	10	60	15	11
Sn	1.5	6	2.2	0.1	9	56	0	23
Sn	5	20	–	–	9	14	3	3
Sn	5	20	0.2	0.1	9	0	0	10
Sn	5	20	2.2	0.1	9	0.3	1	5
Si	1.5	6	–	–	30	0	0	0
Si	1.5	6	2.2	0.1	17	11	0	10
Si	1.5	6	2.2	2.2	6	1	0	1
Si	5	20	2.2	2.2	6	0	0	0

analysis was performed on a Chrom-5 instrument equipped with flame-ionization detector using a glass column packed with 5% OV-101/Chromosorb W-HP (80–100 mesh, 1.2 m × 3 mm, 170–250 °C, 7–10 min). Palladium catalysts, 18-crown-6 (Acros), and 1-trimethylsilyl-2-phenylacetylene and 1-trimethylstannyl-2-phenylacetylene (Aldrich) were used without additional purification. 1-Bromo-2-(2-methyl-5-pyridyl)acetylene (**1**),[21] 1-bromo-2-phenylacetylene (**2**),[21] 1-bromo-2-(*p*-fluorophenyl)acetylene (**3**),[22] 1-bromo-2-(*p*-methoxyphenyl)acetylene (**4**),[23] 1-bromo-2-(1-cyclohexenyl)-acetylene (**5**)[24] were prepared from corresponding alkynes by phase-transfer-catalyzed bromination. The PTC system CBr_4 (0.75 equiv.)/solid KOH/18-crown-6/benzene at room temperature was used.[21]

1-Bromo-2-(*p*-fluorophenyl)acetylene (3)

The reaction was carried out as described[21] over 4 h. 1-Bromo-2-(*p*-fluorophenyl)acetylene (**3**) was isolated in 98% yield. ^1H NMR ($CDCl_3$/TMS) δ ppm: 7.00 (m, 2H, H-2, H-6), 7.43 (m, 2H, H-3, H-5). MS, *m/z* (I, %): 198 (M^+, 100).

1-Bromo-2-(*p*-methoxyphenyl)acetylene (4)

The reaction was carried out as described[21] over 4 h. 1-Bromo-2-(*p*-methoxyphenyl)acetylene (**4**) was isolated in 82% yield. ^1H NMR ($CDCl_3$/TMS) δ ppm: 3.80 (s, 3H, OMe), 6.82 (m, 2H, H-3, H-5), 7.38 (m, 2H, H-2, H-6). MS, m/z (I, %): 210 (M^+, 100).

1-Bromo-2-(1-cyclohexenyl)acetylene (5)

The reaction was carried out as described[21] over 4 h. 1-Bromo-2-(1-cyclohexenyl)acetylene (**5**) was isolated in 24% yield. ^1H NMR ($CDCl_3$/TMS) δ ppm: 1.58 (m, 4H, CH_2-4, CH_2-5), 2.07 (m, 4H, CH_2-3, CH_2-6), 6.13 (m, 1H, CH). MS, *m/z* (I, %): 184 (M^+, 40).

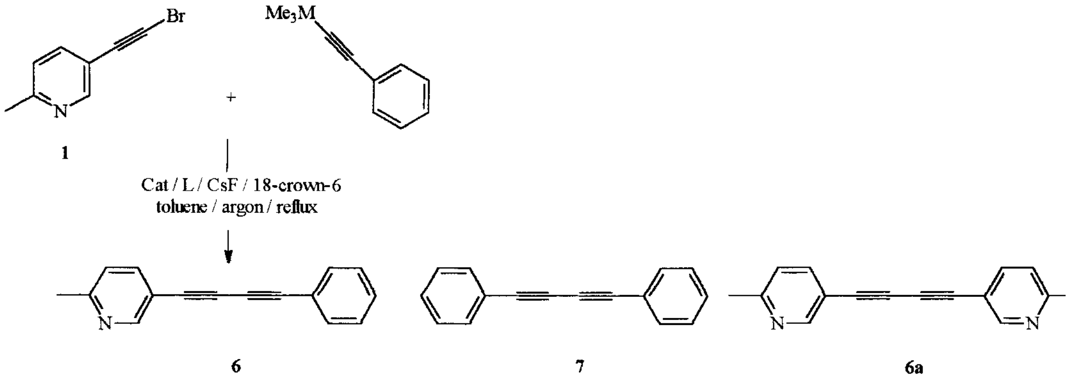
General procedure for the determination of the optimal conditions for 1-phenyl-4-(2-methyl-5-pyridyl)-1,3-butadiyne (6) preparation

The mixture of 1-bromo-2-(2-methyl-5-pyridyl)acetylene (**1**) (0.5 mmol), catalyst, and ligand in toluene (1.5 ml) were stirred over 5 min in an atmosphere of argon at room temperature. 18-Crown-6, dry cesium fluoride and $PhC{\equiv}CSnMe_3$ or $PhC{\equiv}CSiMe_3$ (0.5 mmol) were added to the reaction mixture under stirring in argon. The reaction was carried out under vigorous stirring at reflux temperature in an inert atmosphere over 4–30 h with gas–liquid and GC–mass spectrometry (MS) control. The best catalyst was tris(dibenzylideneacetone)dipalladium(0) [GC yield of *1-phenyl-4-(2-methyl-5-pyridyl)-1,3-butadiyne* (**6**): 56%; only one minor product in 23% yield was present]. The results are shown in Table 1.

General procedure of synthesis of diynes 6–10

The mixture of the corresponding 1-bromoacetylene **1**–**5** (0.5 mmol), tris(dibenzylideneacetone)dipalladium(0) (7 mg, 0.0075 mmol), and triphenylphosphine (8 mg, 0.03 mmol) in toluene (1.5 ml) was stirred over 5 min in an atmosphere of argon at room temperature. 18-Crown-6 (13 mg, 0.05 mmol), dry cesium fluoride (167 mg, 1.1 mmol) and $PhC{\equiv}CSnMe_3$ (133 mg, 0.5 mmol) were added to the reaction mixture under stirring and argon atmosphere. The reaction was carried out under vigorous stirring at reflux temperature in an inert atmosphere over 4–15 h, filtered and evaporated under reduced pressure. The products were isolated by column chromatography using benzene/ethyl acetate (5:1) for **6** and petroleum ether for **7**–**10** as eluents.

The electron density on the carbon atoms of the $-C{\equiv}C-$ group in the bromoalkynes and butadiynes was studied. Quantum chemical calculations were performed with an AM1 Hamiltonian, using the MOPAC 6 program package.[25] The equilibrium geometries were obtained with complete optimization at PRECISE level, using the EF algorithm. The



Scheme 1

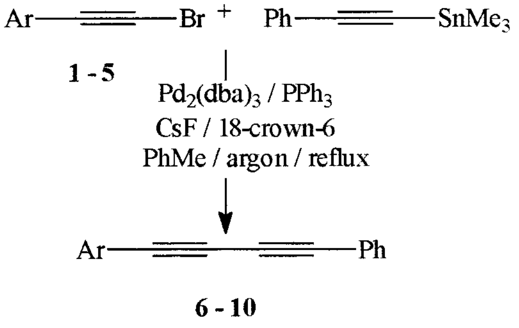
Table 2. Synthesis, ^{1}H NMR and mass spectra data of Ar—C≡C—C≡C—Ph (**6–10**)

Compound	Ar	Reaction time (h)	Isolated yield (%)	^{1}H NMR, δ (ppm)	MS, m/z (I, %)
6	2-Me-5-pyridyl	15	31	2.60 (s, 3H, Me), 7.16 (d, 1H, J = 8.0 Hz, H-3), 7.36 and 7.53 (both m, 5H, Ph), 7.72 (dd, 1H, J_1 = 8.0 Hz, J_2 = 1.8 Hz, H-4), 8.64 (d, 1H, J = 1.8 Hz, H-6)	217 (M^+, 100), 189 (25), 150 (17)
7	Phenyl	8	100	7.34 and 7.51 (both m, 6H and 4H, Ph)	202 (M^+, 100), 174 (5), 150 (10), 98 (5), 74 (5)
8	*p*-*F*-Phenyl	4	52	7.03, 7.34 and 7.51 (all m, 2H, 3H and 4H, Ph and Ar)	220 (M^+, 100), 218 (17), 168 (10), 144 (5), 122 (5), 110 (7), 98 (8), 74 (5), 50 (5)
9	*p*-MeO-phenyl	4	39	3.81 (s, 3H, OMe), 6.85, 7.32 and 7.49 (all m, 2H, 3H and 4H, Ph and Ar)	232 (M^+, 100), 217 (M^+-Me, 46), 189 (52, 163 (17), 150 (10)
10	1-Cyclohexenyl	4	45	1.61 and 2.12 (each m, 4H, cyclohexenyl), 6.31 (m, 1H, cyclohexenyl CH), 7.32 and 7.50 (each m, 3H and 2H, Ph)	206 (M^+, 100), 205 (27), 191 (45), 190 (28), 188 (27), 178 (63), 176 (23), 165 (37), 153 (25), 151 (24), 150 (40), 139 (30), 126 (25), 115 (18), 98 (16), 91 (15), 77 (16), 39 (19)

fully optimized structures present the minimum points on the potential energy surface as the frequency analysis has shown. The calculated electron densities were based on the Coulson charges.

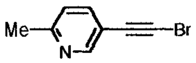
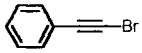
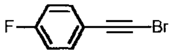
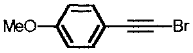
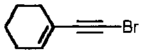
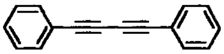
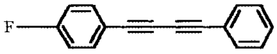
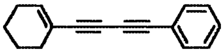
RESULTS AND DISCUSSION

Stille coupling is successfully catalyzed by various palladium(0) or palladium(II) complexes. We have studied the influence of the palladium catalyst and fluoride ion (as process inductor and the base) on the reaction of 1-bromo-2-(2-methyl-5-pyridyl)acetylene (**1**) with 1-trimethylstannyl-2-phenylacetylene. The system (**1**: $PhC\equiv CSnMe_3$:Pd_2(dba)$_3$:PPh_3:CsF:18-crown-6) = (1:1:0.015:0.06:2.2:0.1) in toluene was found to be the most useful (Table 1). In this system the relative content of 1-phenyl-4-(2-methyl-5-pyridyl)-1,3-butadiyne (**6**) in the reaction mixture reached 56% (Table 1). In this case only one coproduct, the diyne **6a**, was detected as a result of acetylene **1** homocoupling (Scheme 1).



Scheme 2

Table 3. ^{13}C NMR spectroscopic data of Ar—C(1)≡C(2)Br and Ar—C(1)≡C(2)—C(3)≡C(4)—Ph

Compound	Structure	δ (ppm)					
		C1	C2	C3	C4	Ph	Ar
1		76.89	52.74	–	–	–	158.02 (C$_2$) 151.73 (C$_6$) 139.23 (C$_4$) 122.72 (C$_3$) 116.85 (C$_5$) 24.32 (CH$_3$)
2		80.02	49.75	–	–	131.94 (*o*) 128.63 (*p*) 128.28 (*m*) 122.63 (*i*)	–
3		79.03	49.58	–	–	–	162.68 (d, ^{1}J = 250.0 Hz[a]) (*p*) 133.85 (d, ^{3}J = 8.5 Hz[a]) (*o*) 118.72 (d, ^{4}J = 3.5 Hz[a]) (*i*) 115.53 (d, ^{2}J = 22.1 Hz[a]) (*m*)
4		79.90	47.82	–	–	–	159.83 (*p*) 133.41 (*o*) 114.75 (*i*) 113.93 (*m*) 55.26 (OCH$_3$)
5		81.82	46.22	–	–	–	136.34[b] (C$_2$) 120.42[b] (C$_1$) 28.81[b] (C$_3$) 25.55[b] (C$_6$) 22.15[b] (C$_4$, C$_5$) 21.33[b]
6		82.39	77.25	73.49	82.60	132.61 (*o*) 129.52 (*p*) 128.53 (*m*) 121.46 (*i*)	158.38 (C$_2$) 152.03 (C$_6$) 139.98 (C$_4$) 123.09 (C$_3$) 116.42 (C$_5$) 24.38 (CH$_3$)
7		81.52	73.89	73.89	81.52	132.46 (*o*) 129.17 (*p*) 128.41 (*m*) 121.76 (*i*)	–
8		80.40	73.72	73.89	81.52	132.48 (*o*) 129.19 (*p*) 128.43 (*m*) 121.64 (*i*)	162.98 (d, ^{1}J = 251 Hz[a]) (*p*) 134.50 (d, ^{3}J = 8.7 Hz[a]) (*o*) 117.87 (d, ^{4}J = 3.7 Hz[a]) (*i*) 115.86 (d, ^{2}J = 22.1 Hz[a]) (*m*)
9		80.99	72.70	74.14	81.79	132.39 (*o*) 129.00 (*p*) 128.38 (*m*) 121.96 (*i*)	160.33 (*p*) 134.09 (*o*) 114.12 (*m*) 113.64 (*i*) 55.30 (OCH$_3$)
10		83.73	71.34	74.17	80.50	132.34 (*o*) 128.87 (*p*) 128.34 (*m*) 122.10 (*i*)	138.88[b] (C$_2$) 119.75[b] (C$_1$) 28.59[b] (C$_3$) 25.90[b] (C$_6$) 22.07[b] (C$_4$, C$_5$) 21.26[b]

[a] ^{19}F–^{13}C coupling constants.

[b] Spectral data for cyclohexenyl substituent.

The presence of a fluoride ion source is important for the successful realization of the reaction. Scott and Stille proposed that cesium fluoride as a coupling additive might cause the formation of Bu_3SnF *in situ*, and would therefore simplify separation of reaction products.[26] Moreover, addition of cesium fluoride might lead to more efficient cross-coupling, perhaps by facilitating transmetallation from tin to palladium. According to literature data, the optimal amount of cesium fluoride to substrates was 2.2 equiv.[27] We have found that without cesium fluoride the reaction rate is significantly lower with regard to substrate **1** conversion (from 100% to 61%) and content of **6** (10%). The optimal amount of cesium fluoride in the Stille diyne synthesis was also found to be 2.2 equiv. to substrates. Decreasing the cesium fluoride amount to 0.2 equiv. lowered the substrate conversion to 58% and led to 11% of **6** in the reaction mixture after 30 h. Coupling in the presence of 1.1 and 2.2 equiv. cesium fluoride was comparable (60% and 56% of **6** respectively). However, in the presence of 1.1 equiv. cesium fluoride the process was less selective: two homocoupling products (**7**[28] and **6a**) were formed.

The use of 5% and 20% of $Pd_2(dba)_3$ and PPh_3 respectively in the absence of cesium fluoride slightly increased the content of the desired product **6** (from 10 to 14%). However, in this case the addition of cesium fluoride caused total substrate polymerization.

The palladium catalysts $Pd(PPh_3)_4$ and $Pd(OAc)_2$ with PPh_3 ligands, as well as CuBr and $Co_2(CO)_8$, were inactive in this reaction. The rhodium complex $[Rh(cod)Cl]_2$ with PPh_3 gave total substrate polymerization.

Similar coupling reactions were also carried out with the silyl acetylene ($Ph-C\equiv CSiMe_3$). However, the reaction of 1-bromo-2-(2-methyl-5-pyridyl)acetylene (**1**) with 1-trimethylsilyl-2-phenylacetylene in the system $Pd_2(dba)_3/PPh_3/CsF/$18-crown-6 (molar ratio **1**:$Ph-C\equiv CSiMe_3$:$Pd_2(dba)_3$:PPh_3:CsF:18-crown-6 = 1:1:0.015:0.06:2.2:0.1) in refluxing toluene afforded the desired product only in 11% yield. This confirms that stannyl acetylene in such types of Stille coupling reaction is favorable in comparison with the silylated one.

The catalytic system $Ar-C\equiv C-Br$ (**1–5**)/1-trimethylstannyl-2-phenylacetylene/$Pd_2(dba)_3$/PPh_3/CsF/18-crown-6 (molar ratio **1–5**:$Ph-C\equiv CSnMe_3$:$Pd_2(dba)_3$:PPh_3:CsF:18-crown-6 = 1:1:0.015:0.06:2.2:0.1) in toluene, as the most active, was used in the synthesis of diynes **6–10**. The products were isolated in yields up to 100% (Table 2, Scheme 2).

The ^{13}C chemical shifts of compounds **1–10** are summarized in Table 3. In general, carbon signals of acetylenes are observed in the 70–85 ppm range. Only the C(2) signals of compounds **1–5** appear much more upfield than other acetylene carbon signals due to the presence of the heavy bromine atom.

The signals of C(2) are also shifted upfield if the *para*-substituent in the aryl ring is the electron donor methoxy group (Table 4). Fluorine in the *para*-position has no real influence on the C(2) shift. The change of the C(1) shift has a more complex nature. The shifts of C(3) and C(4) in butadiynes **8** and **9** nearly coincide with the corresponding shifts in the symmetric diyne **7**.

Table 4. The influence of *para*-substituents in ArC(1)≡C(2)Br and ArC(1)≡C(2)—C(3)≡C(4)Ph on the —C≡C— shifts in ^{13}C spectra

Compound	R	ΔC(1)	ΔC(2)	σ	Ref.
2	H	0	0	0	–
3	F	−1.0	−0.2	0.34	–
4	MeO	−0.1	−1.9	−0.27	–
$MeOC_6H_4C\equiv CBr$	MeO	−0.2	−1.9	−0.27	29
$MeC_6H_4C\equiv CBr$	Me	0.01	−1.0	−0.17	29
$ClC_6H_4C\equiv CBr$	Cl	−1.1	1.3	0.23	29
$O_2NC_6H_4C\equiv CBr$	NO_2	−1.7	6.6	0.76	29
7	H	0	0	0	–
8	F	−1.0	−0.2	0.34	–
9	MeO	−0.5	−1.2	−0.27	–

The incremental shifts of the acetylenic group were calculated to study the influence of the $-C\equiv C-$ group on the shifts of the phenyl carbon atoms in compounds **2** and **6–10** (Table 5).

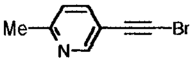
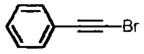
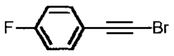
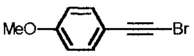
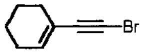
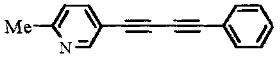
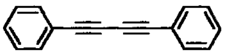
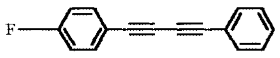
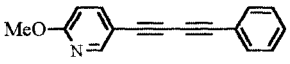
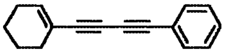
It is shown that the incremental shifts for *ipso*-, *ortho*-, and *meta*-aromatic atoms are similar to the corresponding increments in $Ph-C\equiv CH$ (−6.2, 3.6, −0.4, −0.3)[30] and reflect the shielding character of the triple bond. The *para*-aromatic atoms in **2** and **6–10** are situated downfield in comparison with phenylacetylene.

The electron density on the carbon atoms of $-C\equiv C-$ group in compounds **1–10** was studied (Table 6). According to the calculations the electron density values on the carbon atoms of the acetylenic group are 4.029–4.085, with an exception when there is a bromine at the C(2) atom. In this case the value is in the range 4.298–4.316. Electron-withdrawing substituents in the *para*-position to the acetylenic

Table 5. The substituent chemical shifts of the —C≡C— group in aromatic alkynes and diynes (positive values represent downfield shifts relative to benzene 128.5 ppm, and negative values are highfield shifts)

Compound	*ipso*	*ortho*	*meta*	*para*
2	−5.9	3.4	−0.2	0.1
6	−7.0	4.1	0	1.0
7	−6.7	4.0	−0.1	0.7
8	−6.9	4.0	−0.1	0.7
9	−6.5	3.9	−0.1	0.5
10	−6.4	3.8	−0.2	0.4

Table 6. Electron density and dipole moment data for $\mathrm{Ar{-}C(1){\equiv}C(2)Br}$ and $\mathrm{Ar{-}C(1){\equiv}C(2){-}C(3){\equiv}C(4){-}Ph}$

		Electron density of				
Compound	Structure	C1	C2	C3	C4	Dipole moment *D* of molecule
1		4.047	4.298	–	–	1.700
2		4.047	4.306	–	–	1.105
3		4.052	4.299	–	–	0.536
4		4.041	4.313	–	–	1.961
5		4.046	4.316	–	–	1.390
6		4.080	4.029	4.045	4.070	1.755
7		4.077	4.039	4.039	4.077	0
8		4.084	4.030	4.045	4.070	1.792
9		4.070	4.048	4.036	4.082	1.360
10		4.074	4.053	4.034	4.085	0.452

group lead to an increase of the electron density on the C(1) atom in compounds **1–10**, but the presence of electron-donating substituents results in a decrease. On the contrary, the electron density on the C(2) atom increases in the presence of electron-donor *para*-substituents and decreases in the presence of electron acceptors. The increase of electron density leads to the upfield shifts of the C(2) signals in ^{13}C NMR spectra.

The calculated values of the molecule dipole moments showed the distribution of the positive and negative charges inside the molecule (Table 6). The values of dipole moments range from zero for $\mathrm{PhC{\equiv}CC{\equiv}CPh}$ (**7**) to 1.961 for p-$\mathrm{MeOC_6H_4C{\equiv}CBr}$ (**4**) and demonstrate the degree of polarity of the molecule.

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