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# Photoarylation of Alkenes and Heteroaromatics by Dibromo-BINOLs in Aqueous Solution

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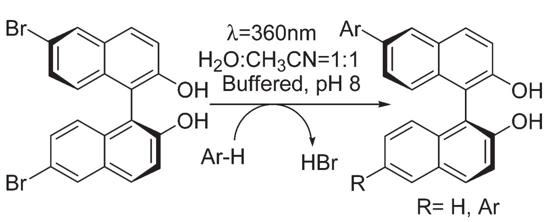
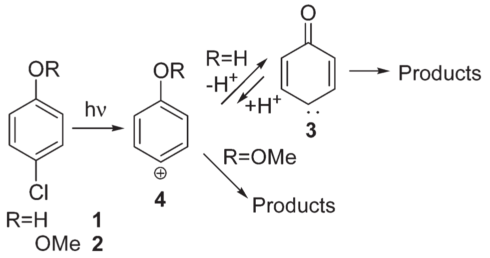
*Received February 24, 2010*



The photochemistry of 6,6′-dibromo-BINOL (BINOL = 2,2′-dihydroxy-1,1′-binaphthyl) under mild basic conditions and its methyl and triisopropylsilyl ethers has been investigated in neat and aqueous acetonitrile through product distribution analysis and laser flash photolysis. Arylation and alkylation have been successfully achieved in the presence of allyltrimethylsilane, ethyl vinyl ether, pyrrole, pyridine, thiophene, benzene, and indole. Such a photoreactivity offers a metal and protecting group free synthetic protocol toward mono- and disubstituted 6-aryl/alkyl BINOLs, since the BINOL chirality is preserved in the photoactivation process.

The activation of carbon−halogen bonds in aryl halides, by photoexcitation, has been studied for decades by classic product distribution analysis[1] and fast kinetic techniques, such as laser flash photolysis (LFP), detecting the generated transient species by means of UV/vis.[2] The mechanistic investigations propelled the exploitation of such a reactivity for synthetic applications[3] and photodegradation of organic pollutants in water.[4] Recently, the reactivity has been extended to organic solvents, suggesting new synthetic applications for a metal free arylation/alkylation process.[5] Nevertheless, synthetic protocols based on the mild photoactivation in aqueous solvents are still scarce.[6] The photoreactivity of the 4-chlorophenol (**1**) and its methyl ether (**2**) as prototypes of aryloxy halides has been rationalized as a heterolytic process generating both 4-oxocyclohexa-2,5-dienylidene carbene (**3**) and 4-hydroxyphenyl cation (**4**). The carbene **3** has been proposed to arise from the deprotonation of the **4** (Scheme 1). The latter has successfully been trapped by several $\pi$-nucleophiles. Despite the great effort on mechanistic and synthetic aspects related to the photoreactivity of **1** and **2**, only very recently the photoreactivity of both the 6-bromonaphthols **5a**−**d**[7] and the 1,6-dibromonaphthols **6a**−**d** (Scheme 2),[8] has been investigated in the presence of aromatics, heteroaromatic, and alkenes.

**SCHEME 1. Photogeneration of 4-Oxocyclohexa-2,5-dienylidene Carbene (3) and 4-Hydroxyphenyl Cation (4) from Chlorophenol 1 and Chloroanisole 2**



The reactive triplet carbenes **5C** and **6C**, photogenerated from the bromonaphthols **5a** and **6a** (Scheme 2), have been shown to be the key intermediates involved in the reactivity, by LFP and trapping experiments.[7,8] These carbene intermediates have been efficiently trapped by $O_2$ generating the detectable carbonyl oxides **5CO**[7] and **6CO**,[8] which exhibit a broad absorbance centered at 580 and 680 nm, respectively.

From a synthetic point of view, 6,6′-dibromo-BINOL (**8**) is much more interesting than the 6-bromonaphthol, since it is widely used as precursor in the synthesis of both 6,6′-disubstituted chiral ligands,[9] and several helicates with different cavity sizes and chemical properties.[10] The above aspects, conjugated with the interest of our group in the

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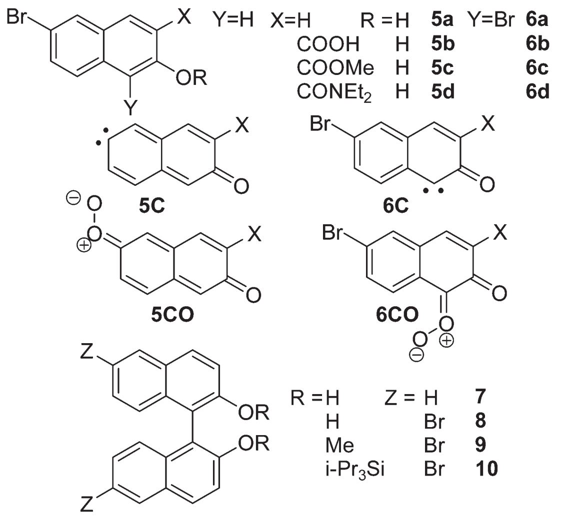
DOI: 10.1021/jo100349h

**SCHEME 2**



photoreactivity of BINOL-derivatives,[11−13] prompted us to explore the photochemistry of 6,6′-dibromo-BINOL (**8**) and the methyl and silyl ethers **9** and **10** (Scheme 2) in the presence of alkenes and heterocycles, to assess whether the reactivity of the resulting transient carbene may be exploited for the synthesis of functionalized BINOLs.

The photoreactivity of 6,6′-dibromo-BINOL (**8**) was first explored in $1 \times 10^{-3}$ M solution by irradiation with four lamps (15 W) centered at 310 nm. The reaction was investigated in cyclohexane, 2-propanol (IPA), acetonitrile (ACN), and aqueous acetonitrile 1:1 NaPi buffer (phosphate) at pH 8. In cyclohexane a very sluggish mixture was recovered both in the absence and in the presence of oxygen with the formation of uncharacterized oligomer products. The main isolated product was BINOL (**7**), in a very low yield (10%), in aqueous ACN without oxygen. No photoreactivity was detected in neat ACN. **7** became the only product through a clean and quantitative reductive dehalogenation process in IPA.

We next investigated the photoreactivity of **8** in the presence of both an equimolar amount of triethylamine (TEA) and several arenes and alkenes in large excess ($5 \times 10^{-2}$ M) in ACN solution. The choice of using TEA had been suggested by our previous studies on 6-bromonaphthols (**5a−d**),[6,7] where we observed an important improvement of the photoproduct yields, using a diluted solution of the amine. In addition, the presence of TEA induces a red shift in the UV−vis spectra of **8**, allowing us also to explore the reactivity at 360 nm. The irradiation at 360 nm in the presence of pyrrole, thiophene, 1*H*-indole, ethyl vinyl ether (EVE), allyltrimethylsilane, pyridine, and benzene in ACN solution with the addition of TEA gave reaction mixtures containing three types of adducts: (i) 6,6′-disubstituted BINOLs (**11a**, **14a**, **15a**), (ii) 6-monosubstituted BINOLs (**11b−15b**, **17b**) (Scheme 3), and (iii) BINOL (**7**). The irradiation of **8** in the presence of morpholine afforded only **7**, resulting from a clean reductive dehalogenation process. The methyl ether **9** and the triisopropylsilyl (TIPS) ether **10** were both stable upon irradiation at 310 and 360 nm after 5 h.

**SCHEME 3. Photoreactivity of 6,6′-Dibromo-BINOL (8) in the Presence of Arenes and Alkenes**

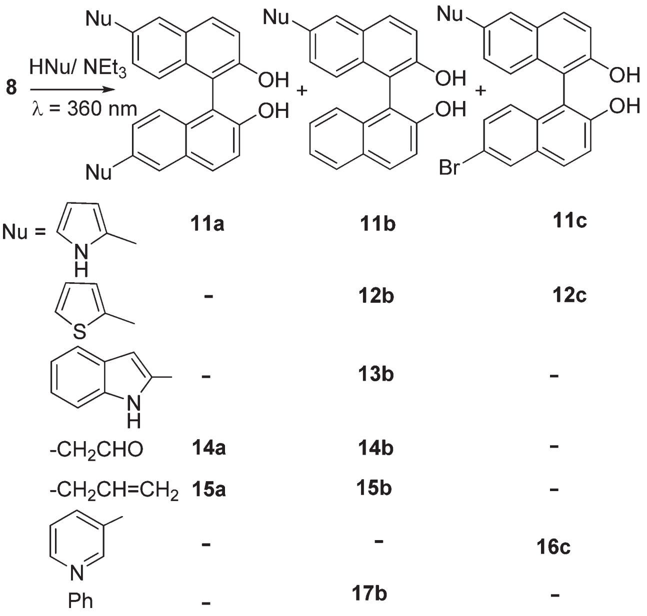


**TABLE 1. Product Distribution from the Irradiation of 8 in Acetonitrile, neat Benzene, and Pyridine[a]**

| HNu[b] | consumption (%) | products (% yield)[c] |
|---|---|---|
| pyrrole | 100 | **7** (5), **11a** (38), **11b** (55) |
| thiophene | 80 | **7** (32), **12b** (35) |
| 1*H*-indole | 80 | **7** (23), **13b** (49) |
| ethyl vinyl ether | 60 | **7** (25), **14a** (6), **14b** (18) |
| allyltrimethylsilane | 100 | **7** (18), **15a** (22), **15b** (59) |
| pyridine | 25[d] | **16c** (25) |
|  | 98[e] | **16c** (95) |
|  | 70[f] | **7** (70) |
| benzene | 30[g] | **7** (5), **17b** (24) |
|  | 57[h] | **7** (15), **17b** (42) |
| morpholine | 100 | **7** (95) |
| IPA | 100[i] | **7** (95) |

[a] Irradiation time 1 h, at 360 nm, $T = 30$ °C. $[\mathbf{8}] = 1 \times 10^{-3}$ M. [b] $[\text{HNu}] = 5 \times 10^{-2}$ M. [c] The product yields have been determined by HPLC. [d] In anhydrous pyridine without $NEt_3$. [e] In anhydrous pyridine without $NEt_3$, after 12 h of irradiation. [f] In neat acetonitrile with pyridine and $NEt_3$. [g] In neat benzene. [h] In neat acetonitrile with 1 M benzene. [i] In neat IPA.

The product yields and reactant consumption irradiating **8** in neat benzene, pyridine, and acetonitrile in the presence of $\pi$- and n-nucleophiles are listed in Table 1. Morpholine and TEA, similarly to IPA, act as H-donor rather than nucleophiles, affording almost a quantitative conversion to **7**, through a clean reductive dehalogenation process. $\pi$-Nucleophiles undergo an arylation/alkylation process, producing a mixture of mono- and bis-arylated/alkylated BINOLs, with the former product being always the major one. The irradiation in ACN in the presence of anhydrous pyridine and TEA, used as base, yields **7**. The photoreaction becomes less efficient by using pyridine without TEA, since it requires longer irradiation time to generate the monoarylated-monobromo BINOL **16c**, but overall the photoreaction becomes a cleaner process, free from the reductive dehalogenation.

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**TABLE 2. Product Distribution from the Irradiation of 8 in MeCN: NaPi Buffer pH 8 (1:1)**[a]

| HNu[b] | consumption (%) | products (% yield)[c] |
|---|---|---|
| pyrrole | 98 | **7** (2), **11a** (62), **11b** (33) |
| thiophene | 80 | **7** (8), **12b** (69) |
| 1*H*-indole | 75 | **7** (4), **13b** (70) |
| ethyl vinyl ether | 50 | **7** (21), **14a** (10), **14b** (19) |
| allyltrimethylsilane | 99 | **7** (9), **15a** (47), **15b** (42) |

[a] Irradiation time 1.5 h, at 360 nm, $T$ = 30 °C. [**8**] = $1 \times 10^{-3}$ M. [b] [HNu] = $5 \times 10^{-2}$ M. [c] The product yields have been determined by HPLC.

In fact, when pyridine is used instead of TEA, no H atom donor is present in solution and no dehalogenation mechanism is observed (Table 1). The product distribution appears to be similar to that arising from the photoreactivity of 6-bromo-2-naphthols (**5a−d**)[7] and 1,6-dibromo-2-naphthol derivatives (**6a−d**).[8]

In these photoreactions the presence of a base is always required in order to trap the generated acidity (HBr) and improve the conversion. Unfortunately the presence of TEA makes more efficient the competitive photodehalogenation process due to its H-donor character. Therefore, in order to minimize the reductive dehalogenation process and to improve the efficiency of the arylation/alkylation pathways, we decided to run the irradiation in buffered aqueous acetonitrile ($H_2O$:MeCN = 1:1; NaPi buffer, pH 8). Product yields and conversions, listed in Table 2, suggest that the selectivity of the arylation/alkylation vs the reductive dehalogenation process is improved under mild basic aqueous solution.

To clarify the mechanism, we run the reaction at low conversion of the reactant **8** (< 20%), monitoring the photoarylation process by time-dependent product distribution analysis in ACN in the presence of TEA. The irradiation of **8** (in a merry-go-round photoreactor, with 4 lamps at 15 W, 360 nm; ca. 25 °C, and Ar purged) in the presence of pyrrole after 10 min afforded a crude containing the bis-substituted adduct **11a** (4%), the monosubstituted derivative **11b** (10%), and the monosubstituted-monobromo **11c** (18%) together with unreacted starting material (65%). The photoproduct **11c** reaches its maximum after 10 min of irradiation. Longer irradiation time causes a decrease of **11c** and a parallel rising of both **11a** and **11b**. The irradiation of **8** in the presence of thiophene after 10 min afforded a crude containing the monosubstituted derivative **12b** (15%) and **12c** (14%) together with unreacted starting material (69%).

To evaluate the potential application of this photoarylation/alkylation reaction for synthetic purposes, we had to asses the retention of the BINOL configuration in the photoarylation process. Therefore, we decided to investigate the photochemistry of the purified chiral (*R*)-**8**. We irradiated (*R*)-**8** at 360 nm both in the presence of pyrrole and TEA in ACN and in a 1:1 mixture ACN/water (buffered, pH 8), affording the chiral adduct (*R*)-**11b** (55%, 33% yields, respectively), with complete retention of the binol moiety configuration. The configuration assignment of (*R*)-**11b** has been achieved by chiral HPLC chromatography, comparing the crude arising from the irradiation of (*R*)-**8** to the crude of the same reaction run on racemic **8** (Supporting Information, Figure S1).

The photoactivation processes of **8** has also been studied by LFP. Flashing a solution of **8**, at 266 nm (4 mJ/pulse, Nd:YAG laser), in neat acetonitrile and aqueous acetonitrile (pH 8, buffered conditions), yielded an intense transient absorbance centered at $\lambda_{max}$ = 460 nm (Figure 1), which was efficiently quenched by $O_2$.

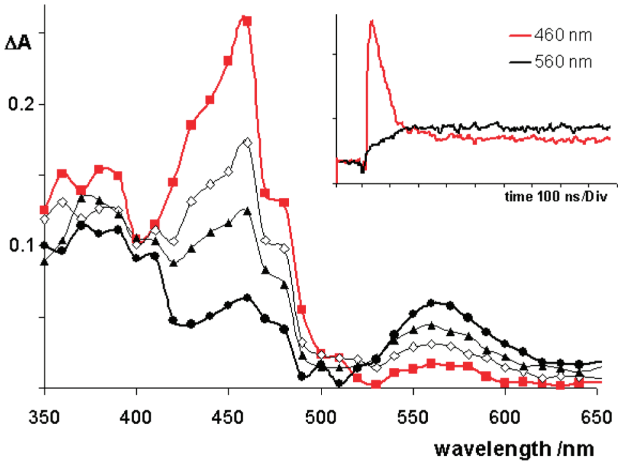
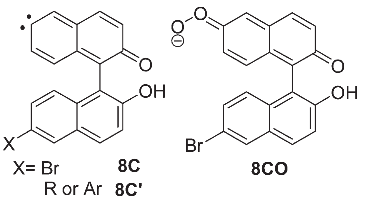


**FIGURE 1.** Transient absorption spectra of **8** in acetonitrile: $H_2O$ = 1:1 with $Et_3N$ ($5 \times 10^{-3}$ M) and $O_2$. The spectra were taken immediately after the laser pulse (red line), and 0.04, 0.10, and 0.15 μs after the laser pulse, respectively (black lines). The inset shows the decay traces monitored at 470 and 560 nm.

**SCHEME 4**



The above transient has been attributed to the triplet excited state of **8** ($^3$**8***) taking into account the spectroscopic similarity of the triplet state of **5a** ($^3$**5a***, $\lambda_{max}$ 460 nm).[7] Although very similar transients have been recorded also for the methyl and TIPS ethers **9** and **10**, respectively, their lifetimes were not affected by TEA addition. The decay profile of such a transient absorbance follows mainly a second order kinetic, in the absence of $O_2$. The decay trace of $^3$**8*** became a single exponential upon addition of TEA, in the concentration range $3 \times 10^{-4}$ to $5 \times 10^{-3}$ M [$k_2 = 3(\pm0.5) \times 10^8$ $M^{-1}$ $s^{-1}$, which was slightly faster than the quenching of $^3$**5a***, $k_2 = 9(\pm1.0) \times 10^7$ $M^{-1}$ $s^{-1}$],[7] where in the presence of $O_2$ a second transient with a broad absorbance centered at 560 nm was detected (Figure 1). The latter is almost superimposable to the absorbance recently assigned to the carbonyl oxide **5-CO** (λ 580 nm, Scheme 2). Due to the striking similarities of the transient species detected and the similar reactivity of **8** in comparison to **5a**, we believe that the transient with absorbance centered at 560 nm has to be assigned to the carbonyl oxide **8CO**, resulting from the trapping of the triplet carbene by molecular oxygen (Scheme 4). Therefore, the synthesis of the 6,6′-disubstituted (**11a**, **14a**, **15a**) and 6-monosubstituted BINOLs (**11b−15b**, **17b**) achieved by irradiation can be rationalized as a sequential photogeneration of the two BINOL-carbenes **8C** and **8C′** (Scheme 4).

In summary, we have described the arylation of alkenes and arenes by 6,6′-dibromo-BINOL using a mild (360 nm) photochemical protocol in acetonitrile and in aqueous buffered solution (pH 8). Mono- and bis-functionalized BINOLs at 6,6′ positions were achieved with good conversions. The reaction yields were improved under aqueous condition, since the competing reductive dehalogenation process became much less efficient. The bis-arylated/alkylated adducts were the main photoproducts in the presence of electron rich $\pi$-nucleophiles, such as pyrrole and trimethylallylsilane. Since it has been shown that the configuration of the BINOL moiety is preserved in the photoactivation process, the described photoreactivity represents a metal and protecting group free synthetic protocol, toward mono- and disubstituted 6-aryl/alkyl BINOLs, via a photogenerated electrophilic triplet carbene intermediate.

## Experimental Section

**8−10** have been synthesized via standard synthetic procedures already published.[14−16]

**General Procedure for the Irradiation of 8 in the Presence of Heteroaromatics in ACN.** An argon-purged solution of **8** (133 mg, 0.3 mmol), freshly distilled pyrrole (1.01 g, 15 mmol), and $Et_3N$ (121 mg, 0.6 mmol) in 300 mL of ACN was irradiated for 1 h by using argon-purged solutions in Pyrex tubes (20 mL) and a multilamp reactor fitted with four 15 W lamps, with maximum emission centered at 360 nm. Chromatographic separation (cyclohexane:ethyl acetate = 7:3) following solvent removal by vacuum concentration gave 47 mg of **11a** (38%, yield) and 61 mg of **11b** (55%, yield).

**6,6′-Bis(1*H*-pyrrol-2-yl)-[1,1′]-binaphthalenyl-2,2′-diol (11a):** pale green solid; mp >180 °C dec; $^1$H NMR ($CDCl_3$) $\delta$ 5.50 (br s, 1H), 6.30−6.35 (m, 2H), 6.55−6.60 (m, 2H), 6.85−6.90 (m, 2H), 7.15−7.25 (m, 2H), 7.35−7.55 (m, 4H), 7.85−8.05 (m, 4H), 8.55 (br s, 1H). $^{13}$C NMR ($CDCl_3$) $\delta$ 106.3, 110.2, 118.2, 119.0, 121.8, 124.0, 124.7, 124.8, 127.5, 128.6, 129.7, 131.1, 131.7, 152.3. Anal. Calcd for $C_{28}H_{20}N_2O_2$: C, 80.75; H, 4.84; N, 6.73; O, 7.68. Found: C, 80.59; H, 4.92; N, 6.70.

**6-(1*H*-Pyrrol-2-yl)-[1,1′]-binaphthalenyl-2,2′-diol (11b):** pale green solid; mp >210 °C dec; $^1$H NMR ($CDCl_3$) $\delta$ 5.05 (s, 1H), 6.30−6.35 (m, 1H), 6.85−6.94 (m, 1H), 7.10−7.25 (m, 2H), 7.30−7.50 (m, 5H), 7.85−8.05 (m, 4H), 8.55 (br s, 1H). $^{13}$C NMR ($CDCl_3$) $\delta$ 106.2, 110.2, 110.6, 111.0, 117.7, 118.2, 119.0, 121.8, 124.0, 124.1, 124.6, 124.8, 127.4, 128.3, 128.6, 129.3, 129.7, 131.0, 131.4, 131.79, 131.84, 133.2, 152.3, 152.6. Anal. Calcd for $C_{24}H_{17}NO_2$: C, 82.03; H, 4.88; N, 3.99; O, 9.11. Found: C, 81.91; H, 4.90; N, 3.93.

**General Procedure for the Irradiation of 8 in the Presence of Alkenes in Aqueous ACN.** An argon-purged solution of **8** (130 mg, 0.29 mmol), freshly distilled allyltrimethylsilane (1.71 g, 15 mmol), and NaPi Buffer pH 8 ($2 \times 10^{-3}$ M) in 300 mL of aqueous ACN (1:1) was irradiated for 1.5 h by using argon-purged solutions in Pyrex tubes (20 mL) and a multilamp reactor fitted with four 15 W lamps, with maximum emission centered at 360 nm. After ACN evaporation, the remaining aqueous suspension was extracted 5 times with $CH_2Cl_2$. Chromatographic separation (cyclohexane:ethyl acetate = 7:3), following $CH_2Cl_2$ removal by vacuum concentration gave 50 mg of **15a** (47%, yield) and 40 mg of **15b** (42%, yield).

**6,6′-Diallyl-[1,1′]-binaphthalenyl-2,2′-diol (15a):** pale yellow solid; Mp >185 °C dec; $^1$H NMR ($CDCl_3$) $\delta$ 3.50 (d, $J$ = 6.5 Hz, 4H), 5.00 (s, 2H), 5.05−5.20 (m, 4H), 5.95−6.15 (m, 2H), 7.15 (dd, $J$ = 5.0, 1.5 Hz, 2H), 7.20 (d, J = 5.0 Hz, 2H), 7.35 (d, $J$ = 8.5 Hz, 2H), 7.70 (s, 2H), 7.90 (d, $J$ = 10.0 Hz, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 39.9, 110.7, 116.0, 117.7, 124.2, 127.1, 128.8, 129.5, 130.8, 131.8, 135.6, 137.1, 152.2. Anal. Calcd for $C_{26}H_{22}O_2$: C, 85.22; H, 6.05; O, 8.73. Found: C, 85.46; H, 6.12.

**6-Allyl-[1,1′]-binaphthyl-2,2′-diol (15b):** pale yellow solid; mp 130−132 °C; $^1$H NMR ($CDCl_3$) $\delta$ 3.50 (d, $J$ = 6.5 Hz, 2H), 5.00 (s, 1H), 5.05 (s, 1H), 5.10−5.20 (m, 2H), 5.90−6.20 (m, 1H), 7.05−7.25 (m, 2H), 7.30−7.45 (m, 4H), 7.70 (s, 2H), 7.85−8.05 (m, 3H); $^{13}$C NMR ($CDCl_3$) $\delta$ 39.9, 110.6, 110.8, 116.0, 117.6, 117.7, 123.9, 124.1, 124.2, 127.1, 127.4, 128.4, 128.9, 129.3, 129.5, 130.9, 131.3, 131.8, 133.3, 135.7, 137.1, 152.2, 152.6. Anal. Calcd for $C_{23}H_{18}O_2$: C, 84.64; H, 5.56; O, 9.80. Found: C, 84.64; H, 5.60.

**Acknowledgment.** Financial support from the Italian Ministry of University and Research (MIUR, FIRB-Ideas Project RBID082ATK_003) and the Italian Association for Cancer Research (Associazione Italiana per la Ricerca sul Cancro, or AIRC Grant No. 5826) is gratefully acknowledged.

**Supporting Information Available:** General Experimental Methods and characterization data for **11c**, **12b**,**c**, **13b**, **14a**,**b**, **16c**, and **17b** and $^1$H NMR and $^{13}$C NMR spectra for the adducts **11a−c 12b**,**c 13b**, **14a**,**b 15a**,**b 16c**, and **17b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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