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A Different Route to the Synthesis of 9,10-Disubstituted Phenanthrenes

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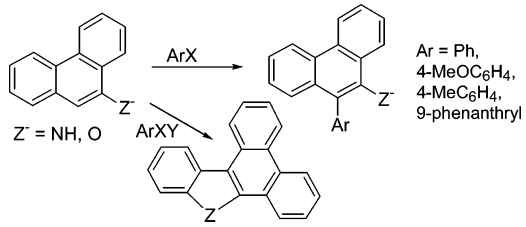

We here report the synthesis of 10-aryl-9-hydroxy- and 10-aryl-9-aminophenanthrenes by reaction of the anions of 9-phenanthrol and 9-aminophenanthrene, respectively, with aryl halides (iodobenzene, 4-iodoanisole, 9-bromophenantrene). Good yields of 9,10-disubstituted phenanthrenes were obtained in these reactions (>75% and ~50% for the 9-amino and 9-hydroxyphenanthrene rings, respectively). Extension of the procedure to the reaction of both anions with *o*-dihalobenzenes leads to the synthesis of the ring closure products (aza- or oxa-indeno[1,2-*l*]phenanthrene), which bear a pentacyclic aromatic condensed ring system, although in lower overall yields (~35%).

The phenanthrene skeleton is found in a number of biologically active natural products. Phenanthro[9,10,*d*] fused heterocycles are some of the derivatives that have been reported to have interesting pharmacological properties.[1] Other promising applications of this type of compounds are based on their photoconducting, optoelectrical, and electroluminescence properties.[2]

Many synthetic schemes have been investigated for the preparation of this aromatic system and derivatives[3] such as photochemical cyclizations of stilbenes,[4] *o*-metalation followed by catalyzed cyclization,[5] intramolecular acylation,[6] base- and light-catalyzed intramolecular cyclization[7] and Lewis acid mediated cyclization.[8] Another approach used is the palladium methodology.[9] This procedure is also widely used in the formation of aryl-aryl bonds, one of the most important tools in modern organic synthesis. Aryl boronic acids (the Suzuki−Miyaura coupling)[10] and arylstannanes (the Stille reaction)[11] are reagents usually employed in these reactions.

The radical nucleophilic substitution mechanism ($S_{RN}1$) is an alternative route to the synthesis of biaryls, particularly, since these reactions are generally carried out under mild conditions and the substrates tolerate many functional groups.[12] This versatility distinguishes the procedure from other methods used such as Kumada, Suzuki, or Stille coupling. Different hydroxybiaryls have been synthesized in good yields by the photoinitiated substitution of haloarenes with arylalcoxides.[13] On the other hand, despite the fact that arylindoles and arylimidazoles can be obtained by this procedure,[14] only one example has been reported for the synthesis of aminobiaryls following this methodology.[15]

These nucleophilic substitutions involve electron transfer steps (ET) and the intermediacy of radical and radical anions. The radicals originate from dissociation

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SCHEME 1

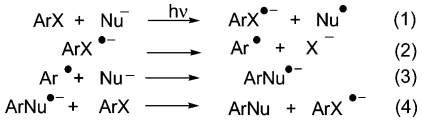


TABLE 1. Photoinitiated Reactions of Aryl Halides with the Anion of 9-Aminophenanthrene (1) and 9-Phenanthrol (4) in Liquid Ammonia[a]

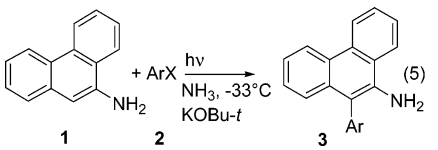
	NuH	ArX	*t*-BuOK		products (% yields)[c]	
expt	M × 10^3	M × 10^3	M × 10^3	X^- (%)[b]	ArH	substitution
1	**1**, 6.1	**2a**, 2.0	13.5	98		**3a**, 100
2[d]	**1**, 4.4	**2a**, 1.8	9.8	100		**3a**, 62
3[e]	**1**, 4.8	**2a**, 1.8	9.8	80		**3a**, 76
4[f]	**1**, 3.8	**2a**, 1.2	7.8	5		
5	**1**, 9.6	**2b**, 3.5	19.7	91	15	**3b**, 80
6[g]	**1**, 9.3	**2b**, 3.2	21.8	98	17	**3b**, 81
7	**1**, 9.2	**2c**, 3.8	22.2	94	12	**3c**, 75
8	**1**, 6.9	**2d**, 2.2	14.3	95	12	**3d**, 93
9	**4**, 10.1	**2a**, 5.0	23.0	100	nq[g]	**5**, 53
10	**1**, 10.5	**6a**, 3.7	20.6	I^- = 77 Br^- = 76		**3a**, 16; **7**, 36
11[h]	**1**, 9.4	**6a**, 2.6	20.1			**3a**, 21; **7**, 31
12	**4**, 10.1	**6b**, 3.1	22.8	I^- = 100		**5**, 26; **8**, 35

[a] Photoinitiated reactions (unless indicated), carried out under nitrogen at −33 °C. Reaction time (180 min). [b] Determined potentiometrically on the basis of the ArX concentration. [c] Determined by GLC and the internal standard method on the basis of the ArX concentration. [d] Di-*tert*-butylnitroxide (43 mmol %). [e] *p*-Dinitrobenzene (42 mmol %). [f] Reaction carried out in the dark. [g] nq = not quantified. [h] Reaction time = 60 min.

of the radical anions of the aromatic substrates (ArX) formed by a photoelectron transfer from the nucleophile (Nu^-) (eqs 1 and 2). The radicals thus formed can react with the nucleophile to give the radical anion of the substitution product (eq 3), responsible to continue the propagation chain of the proposed mechanism (eq 4) (Scheme 1).

In this paper we propose a selective arylation approach, based on the $S_{RN}1$ mechanism, for the preparation of 9,10-disubstituted phenanthrenes. The present synthesis stems from the observation that aryl halides react with 9-phenanthrylamide or 9-phenanthroxide anions under irradiation to give the corresponding 10-aryl derivatives in good yields. Finally, the methodology we report here can be extended to obtain a pentacyclic aromatic ring structure by reaction of either anion with *o*-dihalobenzenes.

The results of the photoinitiated reactions of the anion of 9-aminophenanthrene (**1**) with different aryl halides (**2**) (eq 5) are presented in Table 1.



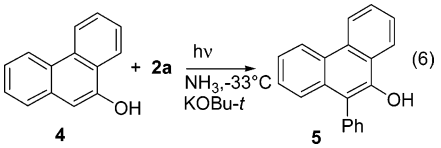
2a: Ar= Ph, X=I
2b: Ar=4-$MeOC_6H_4$, X=I
2c: Ar=4-MeC_6H_4, X=I
2d: Ar= 9-phenanthryl, X=Br

3a: Ar= Ph
3b: Ar=4-$MeOC_6H_4$
3c: Ar=4-MeC_6H_4
3d: Ar= 9-phenanthryl

9-Aminophenanthrene (**1**), the nucleophile precursor, was prepared (81% yield) by reaction of 9-bromophenanthrene (**2d**) with sodium amide in liquid ammonia under laboratory light. When this reaction is performed under irradiation ($\lambda_{max.}$ = 350 nm), the yield of **1** decreased to 68%.[16] The photoinitiated reaction of the anion of **1** with iodobenzene (**2a**) afforded only the product corresponding to substitution at C_{10} of the phenanthrene cycle (**3a**, 100% yield) (eq 5) (Table 1, expt 1). The percentage of substitution obtained with **2a** decreases in the presence of radical or radical anion traps such as di-*tert*-butylnitroxide (DTBN) and *p*-dinitrobenzene (*p*-DNB), respectively (Table 1, expts 2 and 3). Moreover, no substitution occurs in the absence of irradiation (Table 1, expt 4). These facts support the assertion that a nucleophilic substitution with radical and radical anions as intermediates is in play.

Employing this protocol, the reaction of the anion of **1** was examined with the aryl halides (**2b**−**d**). When the reaction was performed with 4-iodoanisole (**2b**), the C_{10}-arylation compound (**3b**) was the main product formed (80% after 1 or 3 h of irradiation) accompanied by the reduction product anisole (15, 17%) (Table 1, expts 5 and 6). High yields of C_{10}-arylation were also obtained by reaction with 4-iodotoluene (**2c**) or 9-bromophenanthrene (**2d**) (75% and 93%, respectively) (Table 1, expts 7 and 8). Hydrogen atom abstraction from the solvent by the radical intermediates is a plausible route to the reduction product (ArH) obtained in these reactions. It is important to mention that the N-arylated product is not formed in any of these reactions despite being formed in approximately 10% when aromatic halides are reacted with 2-naphthylamide anion.[15]

Based on the results obtained with **1**, we investigated the reaction of the anion of 9-phenanthrol **4** with **2a**. The results obtained in this reaction (eq 6) are similar to those obtained by reaction of **2a** with **1**, that is, C_{10} arylation, although in a lower overall yield (53%) (Table 1, expt 9).



1-Iodo-2-methoxynaphthalene is another substrate studied with both anions. Unfortunately, this compound failed to afford arylation with either nucleophile, the main reaction being its reduction to 2-methoxynaphthalene (72% with anion from **4** (liquid ammonia or DMSO) and 60% with anion from **1** (liquid ammonia)). Similar yields of reduction (∼60%) together with nucleophilic substitution (∼40%) were previously obtained when this substrate was reacted with 2-naphthoxide anion.[17]

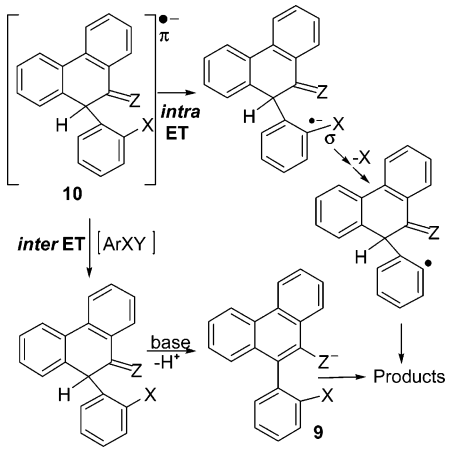
To explain the regiochemistry of the radical-anion coupling, the minimum energy potential surfaces for the reaction of the anions from **1** and **4** with phenyl radicals were calculated with the AM1 procedure (Figures S1 and S2, Supporting Information).[18] According to the energy profile obtained, corroborated with the B3LYP (6-31G*) functional, coupling at either position, N or C_{10} of **1**, is an exothermic step. Despite the fact that N-coupling affords the most stable radical anion, coupling at C_{10}

(16) Other products (phenanthrene 27% and 10-phenanthryl-9-aminophenanthrene (**3d**)) were also formed in this reaction.

(17) Baumgartner, M. T.; Tempesti, T. C.; Pierini, A. B. *Arkivoc* **2003**, part X, 420−433.

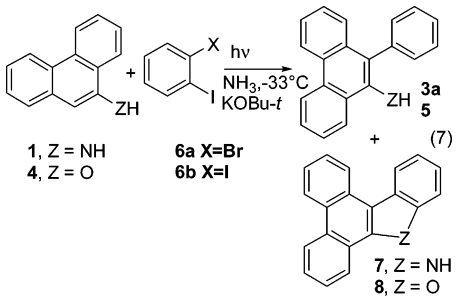
(18) All calculations have been performed with the Gaussian 98 package of programs. For details on the computational procedure, see Supporting Information.

SCHEME 2



occurs with lower activation energy. This profile is similar to the one calculated for the reaction of 2-naphthylamide anion with phenyl radicals. Similarly, with the anion of **4**, the calculation indicates that coupling at C_{10} requires lower activation energy than coupling at oxygen. Moreover, with this anion the reaction at C_{10} affords the most stable radical anion. As expected for reactions under kinetic control, the regiochemistry predicted by the frontier orbital (FO) theory is in agreement with the experimental outcome according to which the C_{10} position is considerably more reactive than the heteroatomic one (see Figure S3, Supporting Information). Besides, the FO comparison between the naphthyl and the phenanthryl rings indicates that the C-substitution is more favored in the phenanthryl system. This fact is also in agreement with the experimental results. That is, whereas the 9-phenanthrylamide anion gives only C-substitution, the 2-naphthylamide anion gives C- and N-substitution in a 9/1 ratio.

On the basis of the promising results obtained with the aryl halides tested, we inspected this experimental strategy as an alternative procedure to the synthesis of the pentacyclic ring systems **7** and **8** by biaryl coupling followed by intramolecular heterocyclization. Within this goal, we studied the reaction of *o*-dihalobenzenes with anions from **1** and **4** (eq 7). *o*-Bromoiodobenzene **6a** reacts with the anion of **1** to afford the reduced substituted product **3a** and the substituted-cyclized compound **7** in 16% and 36% yields, respectively (Table 1, expt 10). On the other hand, compounds **5** and **8** were obtained by reaction of the anion of **4** with *o*-diiodobenzene **6b** (26% and 35% yields, respectively. Table 1, expt 12).



In this system, the monosubstituted compound with retention of halide (**9**, Scheme 2) can be an intermediate in the formation of the cyclic product, as observed in the reaction of substrates **6** with 2-naphthoxide anions.[19] This possibility was inspected in our system by sampling the irradiated reaction of **1** with **6a** at different times (every 15 min; see Figure 1). The monosubstitution product with retention of halide was not detected along the reaction time. Besides, we observed that both compounds, **7** and **3a**, are formed simultaneously, the ratio **7/3a** being unchanged with time.

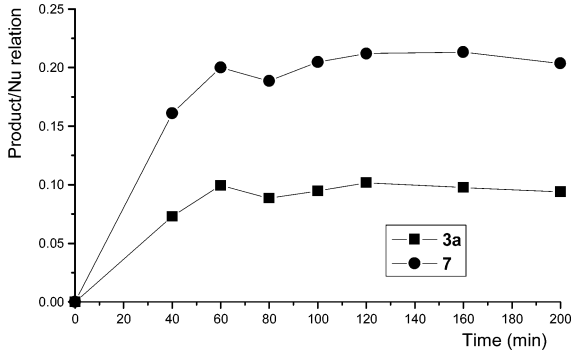
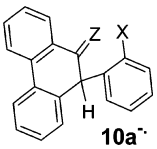
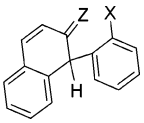


FIGURE 1. Product relationship obtained by sampling the reaction of **1** with *o*-bromoiodobenzene at different irradiation times: (■) **3a**; (●) **7**.

TABLE 2. AM1 Calculated Heats of Formation and C−Br Bond Distances for Monosubstituted Radical Anions

radical anion (RA)	Z	r_{C-Br} (Å) RAπ	r_{C-Br} (Å) RAσ	ΔH_f (kcal/mol) RAπ	ΔH_f (kcal/mol) RAσ	$\Delta\Delta H_{f\sigma-\pi}$ (kcal/mol)
 **10a**$^{\bullet-}$	NH	1.8827	2.0766	72.38	84.52	12.14
	O	1.8766	2.0778	23.39	34.36	10.97
	NH	1.8829	2.0747	60.32	76.36	16.04
	O	1.8810	2.0745	4.35	22.37	18.02

To explain these results, the heat of formation and electronic properties of radical anions **10** (Z = NH or O), formed by coupling of anion from **1** or **4** with an *o*-halophenyl radical, respectively, were calculated, and the results are presented in Table 2.

The most stable radical anions (**10**) calculated have the unpaired spin distribution localized in the π system of the phenanthryl subunit, which is separated from the *o*-haloaryl moiety by an sp^3 carbon. The σ isomer, with an elongated C-halogen bond in which the unpaired electron is located, was also localized on the anionic potential surface. As seen, these intermediates present $\pi-\sigma$ electronic isomerism (Scheme 2).[20]

Despite the fact that the existence of a σ minimum has been attributed to deficiencies of the semiempirical procedure to adequately reproduce the σ surface,[20] the energy difference between the π and the σ species ($\Delta\Delta H_{\sigma-\pi}$) has been shown to be a good indication of the feasibility of the intramolecular ET between both electronic systems.[20] This ET is responsible for the dissociation of the intermediate into radicals and the halide anion.

(19) Baumgartner, M. T.; Pierini, A. B.; Rossi, R. A. *J. Org. Chem.* **1993**, *58*, 2593−2598.

The $\Delta\Delta H_{\sigma-\pi}$ evaluated (Table 2) indicates that in these radical anions the intra-ET is favored for the intermediates that bear a phenanthryl unit ($\Delta\Delta H_{\sigma-\pi}$ less endothermic than for the 2-naphthyl analogues). From these results we can conclude that the preferred reaction pathway followed by intermediates **10** is the intra-ET accompanied by dissociation as opposed to the 2-naphthyl analogues for which the inter-ET to afford monosubstitution is in competition.

In conclusion, we have shown that a series of 9,10-disubstituted phenanthrenes can be regiospecifically prepared by a straightforward and efficient synthetic pathway based on electron-transfer reactions. Furthermore, the methodology we report here can be extended to aryl halides containing a wide variety of organic functional groups compatible with the $S_{RN}1$ mechanism, such as OR, OPh, SAr, COAr, CN, and others. Moreover, the reaction provides an alternative access to the pentacyclic systems **7** and **8** in moderate yields.

Experimental Section

General Methods. ^{1}H NMR and ^{13}C NMR spectra were recorded on a nuclear magnetic resonance spectrometer with $CDCl_3$ as solvent. The position of the aryl substitution on the phenanthryl ring was assigned by comparison of the recorded spectra with those calculated with the ACD labs 4.0 program. All different and possible substitutions on the phenanthryl system of **1** and **4** were evaluated. The procedure was validated by comparison with information reported for the known compound **5**.

Reaction of 9-Bromophenanthrene with Amide Anion. To distilled liquid ammonia (100 mL, −33 °C) were added a catalytic amount of $FeCl_3$ (ca. 5 mg), and then sodium metal (8.3 mmol) in two or three pieces. Once the sodium amide was formed (indicated by bleaching of the blue solution of sodium metal in liquid ammonia), 9-bromophenanthrene (2.5 mmol) was added. After 180 min the reaction was quenched by adding ammonium nitrate in excess, and the ammonia was allowed to evaporate. The residue was dissolved in water (80 mL), and the mixture was extracted with CH_2Cl_2 (3 × 50 mL). The organic extract was dried with $MgSO_4$. The solvent was removed under reduced pressure. After purification of the crude residue by column chromatography (petroleum ether/acetone 9:1) 9-aminophenanthrene (**1**) was obtained: mp 137.5−139 °C (lit.[21] 136−7 °C).

Photoinitiated Reaction of the Anion of 9-Aminophenanthrene (1) with Halobenzenes. The following procedure is representative of these reactions. The reactions were carried out in a 250-mL three-neck round-bottomed flask equipped with nitrogen inlet and magnetic stirrer. To distilled ammonia (100 mL) were added potassium *tert*-butoxide (1.35 mmol) and then 9-aminophenanthrene (0.61 mmol). After 15 min iodobenzene (0.2 mmol) was added, and the reaction mixture was irradiated with two 400-W lamps emitting maximally at 350 nm (air and water refrigerated) for 180 min. The reaction was quenched with an excess of ammonium nitrate. The ammonia was allowed to evaporate, and water (50 mL) was added to the residue and extracted twice with CH_2Cl_2 (20 mL). The iodide ions in the aqueous solution were determined potentiometrically. The organic extract was dried ($MgSO_4$), filtered, and quantified by GLC. The solvent was removed under reduced pressure. The residue after column chromatography (petroleum ether/acetone 9:1) gave 10-phenyl-9-aminophenanthrene (**3a**): ^{1}H NMR δ 4.01 (2H, s, NH_2), 7.24−7.69 (10H, m), 7.93−7.97 (1H, m), 8.61−8.65 (1H, dd), 8.74−8.78 (1H, dd); ^{13}C NMR δ 118.2 (q), 121.6, 121.7 (q), 122.4, 123.1, 123.3, 125.1, 126.6, 126.7, 127.7, 129.4, 130.7 (q), 131.2, 136.6 (q), 137.8 (q); *m/z* 270 (19.7), 269 (100.0), 268 (25.9), 267 (23.8), 239 (9.3), 133.7 (25.3), 126 (16.2), 119 (17.9); HRMS calcd for $C_{20}H_{15}N$ 269.120450, found 269.120693.

10-(4-Methoxyphenyl)-9-aminophenanthrene (3b). Isolated by column chromatography and eluted with petroleum ether/acetone (95:5): mp 179−181 °C; ^{1}H NMR δ 3.91(3H, s, OMe), 4.06 (2H, s, NH_2), 7.08−7.15 (2H, m), 7.28−7.46 (5H, m), 7.60−7.73 (2H, m), 7.93−7.98 (1H, m), 8.60−8.65 (1H, m), 8.73−8.78 (1H, m); ^{13}C NMR δ 55.4, 114.4, 114.9, 118.4 (q), 121.7, 122.4, 123.3, 125.2 (q), 125.3, 126.6, 126.6, 126.7, 129.5 (q), 130.7, 132.3, 133.4 (q), 136.5 (q), 159.2 (q); *m/z* 300 (28.5), 299 (100.0), 254 (13.1), 239 (11.3), 128 (11.3), 127 (16.9), 126 (10.6), 113.1 (11.4); HRMS calcd for $C_{21}H_{17}NO$ 299.131014, found 299.131087.

10-(4-Tolyl)-9-aminophenanthrene (3c). Isolated as an oil by column chromatography and eluted with petroleum ether/acetone (98:2): ^{1}H NMR δ 2.48 (3H, s, Me), 4.05 (2H, s, NH_2), 7.27−7.43 (7H, m), 7.60−7.74 (2H, m), 7.92−7.98 (1H, m), 8.61−8.78 (2H, m); ^{13}C NMR δ 21.3 (CH_3), 118.2 (q), 121.6, 122.4, 122.7 (q), 123.1, 123.3, 125.2, 125.8 (q), 126.5, 126.6, 130.1, 130.6 (q), 131.0, 133.3 (q), 136.7 (q), 137.3 (q); *m/z* 284 (24.4), 283 (100), 282 (18.2), 281 (11.3), 268 (13.1), 267 (27.1), 139 (15.5), 133 (43.9), 119 (12.6); HRMS calcd for $C_{21}H_{17}N$ 283.136100, found 283.137093.

10-(9-Phenanthryl)-9-aminophenanthrene (3d). Isolated by column chromatography and eluted with petroleum ether/acetone (95:5): mp 218−219 °C; ^{1}H NMR δ 4.04 (2H, s, NH_2), 7.13−7.17 (1H, dd), 7.22−7.30 (1H, td), 7.34−7.46 (2H, m), 7.51−7.55 (1H, dd), 7.62−7.79 (5H, m), 7.86 (1H, s), 7.90−7.94 (1H, dd), 7.98−8.03 (1H, m), 8.69 (1H, d), 8.80−8.86 (3H, m); ^{13}C NMR δ 121.6, 122.4, 122.7, 123.0, 123.2, 123.4, 125.1 (q), 125.4, 126.6, 126.7, 126.8, 126.9, 127.0, 127.1, 127.5 (q), 128.7, 128.9 (q), 130.2, 130.3 (q), 131.1 (q), 132.1 (q), 133.4 (q), 133.8 (q), 137.6 (q); *m/z* 370 (29), 369 (100), 368 (31), 367 (34), 366 (11), 365 (16), 352 (14), 184 (10), 183 (18), 182 (33), 177 (17), 176 (39), 175 (16), 168 (13); HRMS calcd for $C_{28}H_{19}N$ 369.151750, found 369.150866.

10-Phenyl-9-phenanthrol (5). Isolated by column chromatography and eluted with petroleum ether/acetone (98:2): mp 144−146 °C (lit.[22] 142−3 °C).

13*H*-13-Aza-indeno[1,2-*l*]phenanthrene (7). Isolated by column chromatography and eluted with petroleum ether/acetone (90:10): mp 193−195 °C (lit.[23] 191−193 °C).

13-Oxa-indeno[1,2-*l*]phenanthrene (8). Isolated by column chromatography and eluted with petroleum ether/acetone (98:2): mp 153−154 °C (lit.[24] 156 °C); ^{1}H NMR δ 7.43−7.53 (2H, m), 7.62−7.81 (5H, m), 8.36−8.41 (1H, m), 8.49−8.54 (1H, m), 8.62−8.67 (1H, dd), 8.73−8.81 (2H, m); ^{13}C NMR δ 111.9, 121.7, 121.7, 123.4, 123.4, 123.8, 124.2, 125.1, 125.4 (q), 127.1, 127.2, 127.4, 128.6 (q), 130.6 (q), 151.2 (q), 155.9 (q); *m/z* 270 (3), 269 (24), 268 (100), 240 (6), 239 (32), 238 (7), 134 (27), 119 (50); HRMS calcd for $C_{20}H_{12}O$ 268.088815, found 268.088570.

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Supporting Information Available: General methods and materials; ^{1}H NMR and ^{13}C NMR spectra of compounds **3a**, **3b**, **3c**, **3d**, and **8**; characterization data for known compounds **1**, **5**, and **7**; energy potential surface for reaction of anions from **1** and **4** with phenyl radical; HOMO of nucleophiles from **1** and **4** and second-order perturbation between frontier MO for the different coupling positions. This material is available free of charge via the Internet at http://pubs.acs.org.

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