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Cobalt-Catalyzed Direct Electrochemical Cross-Coupling between Aryl or Heteroaryl Halides and Allylic Acetates or Carbonates

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Abstract: The electroreduction of a mixture of functionalized aromatic or heteroaromatic bromides or chlorides and allylic compounds such as acetates or carbonates in an electrochemical cell fitted with a sacrificial iron anode affords, in the presence of cobalt halide associated with pyridine as ligand in acetonitrile or DMF, the corresponding coupling product in good yields.

Introduction

The arylallyl skeleton is the basic structure of many natural products[1] like estragol (p-$CH_3O-C_6H_4CH_2CH=CH_2$), eugenol (2-$CH_3O-C_6H_4OH$-4-$CH_2CH=CH_2$), osmorhyzol (1,3-di-$CH_3O-C_6H_4$-4-$CH_2CH=CH_2$), etc. Substitution reactions of allylic halides with aromatic organometallic reagents have provided an important route for the synthesis of these allylic compounds. However, a large class of useful compounds is hardly accessible from aromatic Grignard reagents,[2] i.e., those bearing a reactive functional group such as aldehydes, esters, ketones, or nitriles on the aromatic nuclei. Alternatively, arylzinc compounds are convenient reagents owing to their high functional group tolerance and their good reactivity in the presence of the soluble salt $CuCN \cdot 2LiCl$.[3] Using this approach, Knochel reported the coupling reaction between arylzinc reagents and various electrophiles,[4] namely, allylic halides. In the same manner, arylpalladium species prepared in situ from arylmercuric and palladium-(II) salts can react with allylic halides at room temperature to produce allylaromatic compounds.[5] Although organomercuric reagents exhibit a good functional group compatibility, their high toxicity is well-known.

Allylic stannanes can be prepared from allylic acetates derivatives[6] and coupled with aryl halides by a palladium catalysis.[7] In that case, the best results were obtained from aryl bromides.

Palladium complexes have proven to be the most versatile catalyst. The discovery of these catalysts in allylic substitution is one of the milestones in organic synthesis. Although the advent of Pd(0) has solved a number of industrial problems, this catalyst has a major limitation: the cost of Pd becomes prohibitive for industrial application when the catalytic turnover is low.

Hence, developing new catalytic systems are of particular importance. As a matter of fact, Mo,[8] Zr,[9] Pt,[10] and Rh[11] complexes have been studied. In most cases, only very reactive substrates such as allylic carbonates provide good yields.

A few years ago, in our laboratory, the electrochemical reduction of aryl halide and allylic compounds[12] was reported in DMF in the presence of a catalytic amount of $NiBr_2$-2,2'-bipyridine at 60 °C. This method presents two major drawbacks: (1) Elimination of nickel is now recommended for environmental reasons. (2) Allylic acetate must be introduced slowly all along the electrolysis since the oxidative addition of electrogenerated Ni^0-bpy is faster on allylic compounds than on aryl halides.

Recently, we have discovered a more simple catalytic system involving cobalt halides used in DMF—pyridine or acetonitrile—pyridine mixtures. This catalyst allowed us to achieve the electrochemical synthesis of mono-[13] and dizinc[14] species and was applied to the synthesis of arylpyridines,[15] arylpyrimidines,[16] and even conjugate addition of aromatic halides onto activated olefins[17] using the sacrificial anode process.

Previously, Iqbal[18] has described that allylation of 1,3-dicarbonyl compounds could be achieved with allyl acetates in the presence of catalytic amounts of cobalt-(II) chloride in 1,2-dichloroethane in high yields.

We describe in this paper the scope of this electrochemical procedure using the cobalt—pyridine complex in DMF or acetonitrile in the field of arylation of allylic acetate and derivatives (eq 1) from aryl bromides or chlorides. We first studied the coupling reaction between aryl bromides substituted by electron-donating or electron-withdrawing groups and allyl acetate catalyzed by cobalt bromide in acetonitrile/pyridine mixture (v/v = 9/1).

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(2) (a) Kharasch, M. S.; Reinmuth, O. In *Grignard Reactions of Nonmetallic Substances*; Coustable: London, 1954. (b) Hayashi, T.; Konishi, M.; Yokota, K.-i.; Kumada, M. *J. Chem. Soc., Chem. Commun.* **1981**, 313. (c) Hayashi, T.; Konishi, M.; Yokota, K.-i.; Kumada, M. *J. Organomet. Chem.* **1985**, *285*, 359.

(3) Zhu, L.; Wehmeyer, R. M.; Rieke, R. D. *J. Org. Chem.* **1991**, *56*, 1445.

(4) Knochel, P.; Singer, R. D. *Chem. Rev.* **1993**, *93*, 2117.

(5) Heck, R. F. *J. Am. Chem. Soc.* **1968**, *90*, 5531.

(6) Kosugi, M.; Sasazawa, K.; Shimizu, Y.; Migita, T. *Chem. Lett.* **1977**, 301.

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(8) (a) Trost, B. M.; Merlic, C. A. *J. Am. Chem. Soc.* **1990**, *112*, 9590. (b) Malkov, A. V.; Baxendale, I. R.; Dvorak, D.; Mansfield, D. J.; Kocovsky, P. *J. Org. Chem.* **1999**, *64*, 2737.

(9) (a) Temple, J. S.; Schwartz, J. *J. Am. Chem. Soc.* **1980**, *102*, 7382. (b) Temple, J. S.; Riediker, M.; Schwartz, J. *J. Am. Chem. Soc.* **1982**, *104*, 1310.

(10) Kurosawa, H.; Ogoshi, S.; Kawasaki, Y.; Murai, S.; Miyoshi, M.-a.; Ikeda, I. *J. Am. Chem. Soc.* **1990**, *112*, 2813.

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(16) Gosmini, C.; Nédélec, J.-Y.; Périchon, J. *Tetrahedron Lett.* **2000**, *41*, 201.

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(18) Maikap, G. C.; Madhava Reddy, M.; Mukhopadhyay, M.; Bhatia, B.; Iqbal, J. *Tetrahedron* **1994**, *50*, 9145.

$$X= Br, Cl$$
$$Y= OCOMe, OCO_2Me$$

$$(1)$$
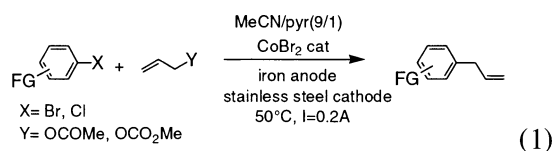
The mechanism is complex and should involve the transitory electrogenerated Co(I)−pyridine species, closely associated with allyl and its oxidative addition on aryl halide. Electroanalytical investigations are in progress, and results will be soon reported.

Results and Discussion

All reactions are conducted in a one-compartment cell already described,[19] using a consumable iron anode and a stainless steel cathode. Commercial solvents are used without purification. The ionic conductivity of the medium is ensured by addition of NBu_4BF_4 as supporting electrolyte. Electrolyses are run at constant current intensity of 0.2 A (0.01 A/cm^2), at 50 °C, and under an inert atmosphere of argon. They are quenched after total consumption of ArX. The cathodic potential during the electrolysis remains at ca. −1.1 V/SCE, which is the potential of formation of the Co(I) complex from CoX_2- pyridine[20] in the acetonitrile medium. In a typical experiment, 50 mL of a mixture of solvent (45 mL of acetonitrile or DMF and 5 mL of pyridine) containing 7.5 mmol of ArBr (0.15 M), 20 mmol of allyl acetate (0.4 M), 1 mmol of $CoBr_2$ (0.02 M), and 0.5 mmol of NBu_4BF_4 (0.01 M) was introduced in the cell. Results obtained in acetonitrile−pyridine from phenyl bromides substituted by an electron-donating or electron-withdrawing groups and allyl acetate are reported in Table 1.

In our case, allylic substrate is totally introduced in the cell at the beginning of the electrolysis, unlike the electrochemical process using nickel complex as catalyst.[12] All the starting product ArBr is consumed at 4F/mol.

Several metals can be used as anodes such as aluminum and zinc, but iron gives better yields in coupling product. In the absence of pyridine as cobalt−ligand in acetonitrile or DMF, only a small amount of arylallyl is formed, the major product being ArH. In fact, we have reported in a previous paper the efficiency of pyridine to stabilize the electrogenerated active cobalt species.[21]

Results are similar if the electrolysis is carried out at 50 or 70 °C, but the coupling yield decreases if the reaction is carried out at room temperature.

These results show that this new method gives high yields of coupling product from aryl bromides substituted either by electron-withdrawing (Table 1, entries 1−10) or electron-donating (Table 1, entry 11) groups. Furthermore, the yields do not depend on the position of the functional group on the aromatic nucleus (Table 1, entries 1 and 8 or entries 2 and 10). With a ketone (Table 1, entry 3) or with an amide (Table 1, entry 5) as substituent, lower yields are obtained in this standard condition. The

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TABLE 1. Coupling Reaction between Substituted Aryl Bromides and Allyl Acetate

entry	FG	Product	yields %[a]
1	p-COOEt	EtOOC— **1**	70
2	p-CN	NC— **2**	64
3	p-COMe	MeOC— **3**	41
4	p-CF₃	F₃C— **4**	62
5	p-CONH₂	H₂NOC— **5**	30
6	p-F	F— **6**	51
7	m-CF₃	F₃C— **7**	57
8	m-COOEt	EtOOC— **8**	64
9	m-Cl	Cl— **9**	58
10	o-CN	CN— **10**	63
11	p-OMe	MeO— **11**	74

[a] Isolated yields, based on initial ArBr.

starting compounds are converted into ArAr in the case of *p*-bromoacetophenone and into ArH in the case of *p*-bromobenzamide. The coupling with *m*-bromochlorobenzene (Table 1, entry 9) shows that only the carbon−bromine bond is reactive toward allyl acetate. Nevertheless, electroreductive coupling reaction can be extended to aryl chlorides providing that we modify the conditions described before.

Then, we studied the coupling reaction between aryl chlorides and allyl acetate. In the conditions used previously with aryl bromides, i.e., 1 mmol of cobalt bromide catalyst for 7.5 mmol of aromatic halide and 20 mmol of allyl acetate, aryl chloride is not totally consumed. By use of a larger amount of $CoBr_2$ (0.2 equiv per equiv of ArCl), all the aromatic chloride is consumed, but the reaction proceeds slowly. To increase the reaction rate, 0.4 equiv of $CoBr_2$ per ArCl was introduced in the medium and allyl acetate is introduced in lower amounts (2 equiv per ArCl).

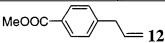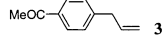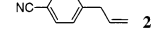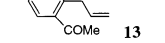Reaction conditions are reported in eq 2 and results in Table 2.
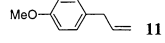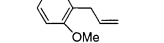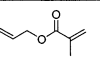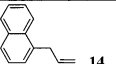

$$(2)$$
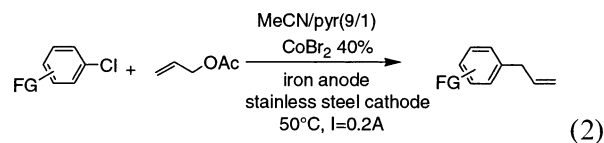
Aryl chlorides substituted by an electron-withdrawing group (Table 2, entries 12−15) give good to high yields even in the case of ortho-substituted aryl chloride. With *o*-chloroacetophenone (Table 2, entry 15), 50% yield of allylic product is isolated, with the byproduct being ArH.

TABLE 2. Coupling Reaction between Substituted Aryl Chlorides and Allyl Acetate

Entry	FG	Product	yields %[a]
12	p-COOMe	MeOOC—⟨ ⟩—⧸⧹ **12**	81
13	p-COMe	MeOC—⟨ ⟩—⧸⧹ **3**	60
14	p-CN	NC—⟨ ⟩—⧸⧹ **2**	66
15	o-COMe	⟨ ⟩—⧸⧹ COMe **13**	50
16	p-OMe	MeO—⟨ ⟩—⧸⧹ **11**	< 5
17	o-OMe	⟨ ⟩—⧸⧹ OMe	< 5

[a] Isolated yields, based on initial ArCl.

TABLE 3. Coupling Reaction between Aromatic Halides and Various Allylic Esters

Entry	ArX	Allylic ester	Product	yields %[a]
18	⟨naphthyl⟩–Br	⧸⧹O–CO–C(Me)=CH₂	⟨naphthyl⟩–⧸⧹ **14**	86
19	NC—⟨ ⟩—Cl	⧸⧹O–CO–C(Me)=CH₂	NC—⟨ ⟩—⧸⧹ **2**	76
20	NC—⟨ ⟩—Cl	⧸⧹O–CO–nC₆H₁₃	NC—⟨ ⟩—⧸⧹ **2**	58
21	MeOOC—⟨ ⟩—Cl	⧸⧹⧸O–CO–Me	MeOOC—⟨ ⟩—⧸⧹ **15** ; MeOOC—⟨ ⟩—⧸ **16**	51 (**15**) ; 19 (**16**)
22	EtOOC—⟨ ⟩—Br	Ph⧸⧹O–CO–Me	EtOOC—⟨ ⟩—⧸⧹ Ph **17**	52
23	NC—⟨ ⟩—Cl	Ph⧸⧹O–CO–Me	NC—⟨ ⟩—⧸⧹ Ph	0

[a] Isolated yields, based on initial ArX.

However, if the substituent is an electron-donating group (Table 2, entries 16 and 17), only traces of the coupling product are obtained, and the main product formed is also ArH. Only 15% of ArCl is consumed. In this case, Co(I) associated to allylic acetate reacts too slowly with ArCl. The main reaction was found to be the oxidative addition of Co(I) to allyl acetate generating the corresponding hexadiene.

This process can also be extended to aryl iodides but their higher reactivity leads to a higher formation of the dimer ArAr during the electrolysis.

The reactions involving substituted allylic derivatives generally give the linear or branched products due to allylic transposition. The ratio of the α- and γ-allylation depends on the nature of the organometallic intermediates.[7] So, we have attempted to study the influence of the groups born by both the allylic bond or the ester leaving group. Results are reported in Table 3.

We have first studied the effect of the ester leaving group (Table 3, entries 1−3). Good yields are obtained with allyl methacrylate (Table 3, entries 18−19). The

TABLE 4. Coupling Reaction between Heteroaromatic Halides and Allyl Methacrylate

Entry	HetArX	Product	yields %[a]
24	⟨3-bromothiophene⟩	⟨3-allylthiophene⟩ **18**	70
25	⟨2-bromothiophene⟩	⟨2-allylthiophene⟩ **19**	20
26	⟨2-chlorothiophene⟩	⟨2-allylthiophene⟩ **19**	63
27	⟨4-chloro-2-methylquinoline⟩	⟨2-methylquinoline propenyl⟩ **20**	69

[a] Isolated yields, based on initial HetArX.

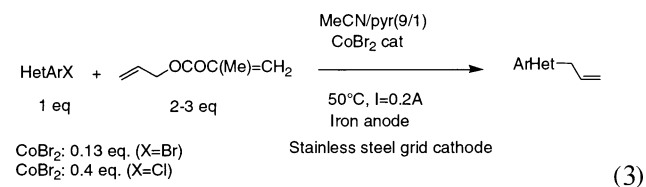yields poorly depend on the ester leaving group (Table 2, entry 14 and Table 3, entries 19−20), but with the methacrylate one, the yield is slightly higher, probably due to the conjugated double bond.

The regiochemistry of the reaction has also been studied with crotyl and cinnamyl acetates (Table 3, entries 21−23). With the crotyl acetate, a mixture of the S$_N$2 and S$_N$2′ allylic products is observed. However, the major product formed in this reaction is the unbranched product **15** (S$_N$2) like the electrochemical process using a nickel complex catalysis described in our laboratory.[12] With cinnamyl acetate, the only product formed is the linear one **17** (Table 3, entry 22) due to the steric hindrance of phenyl group on the double bond. Nevertheless, with this allylic acetate, the aryl halide must be reactive (ArBr). Indeed, aryl chloride substituted by an electron-withdrawing group (Table 3, entry 23) is not reactive enough toward the bulky allyl−cobalt complex and generates ArH. As a matter of fact, electrolysis of allylic acetates without aromatic halide in the medium leads to the dimerization of the allylic moiety and, in a minor way, to the reduction products of allylic substrates. Work is still in progress to elucidate the mechanism of the carbon−carbon bond formation in this process.

We have extended this process to the coupling between several heteroaromatic halides with allyl methacrylate according to eq 3 which gave the best results with

$$\text{HetArX} + \text{⧸⧹OCOC(Me)=CH}_2 \xrightarrow[\substack{50°C, I=0.2A \\ \text{Iron anode} \\ \text{Stainless steel grid cathode}}]{\substack{\text{MeCN/pyr(9/1)} \\ \text{CoBr}_2 \text{ cat}}} \text{ArHet⧸⧹}$$

1 eq   2-3 eq

CoBr₂: 0.13 eq. (X=Br)
CoBr₂: 0.4 eq. (X=Cl)   (3)
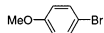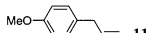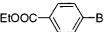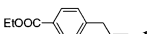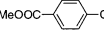
aromatic halides. The conditions are similar to those used with aromatic halides. With a chlorine atom, the amounts of CoBr₂ should be higher than that obtained with a bromine, owing to the lower reactivity of aryl chlorides. Results are reported in Table 4.

The yields depend on the reactivity of each heteroaromatic halide. 2-Bromothiophene, which is more reactive versus 3-bromothiophene,[22] mainly leads to the reduction product (Table 4, entry 25). The reaction provides good yields (70 and 63%) with 3-bromothiophene and 2-chlo-

(22) Schulz, E.; Fahmi, K.; Lemaire, M. *Acros Org. Acta* **1995**, *1*, 10.

TABLE 5. Coupling Reaction between Substituted Aryl Halides and Allyl Methyl carbonate

Entry	ArX	Product	yields %[a]
28	MeO—⟨ ⟩—Br	MeO—⟨ ⟩—CH₂CH=CH₂ **11**	50
29	EtOOC—⟨ ⟩—Br	EtOOC—⟨ ⟩— **1**	53 (**1**)
		MeOOC—⟨ ⟩— **12**	26 (**12**)
30	MeOOC—⟨ ⟩—Cl	MeOOC—⟨ ⟩— **12**	26

[a] Isolated yields, based on initial ArX.

rothiophene (less reactive than 2-bromothiophene) (Table 4, entries 24 and 26). In the case of 4-chloroquinaldine (Table 4, entry 27), isomerization of the allylic product takes place and leads to the arylvinyl product in a good yield (69%).

Allyl methyl carbonate can also react with aryl bromides or chlorides according to eq 4. Results are reported

$$GF-\!\!\langle\ \rangle\!\!-X + \diagup\!\!\diagdown OCO_2Me \xrightarrow[\substack{50°C, I=0.2A \\ \text{Iron anode} \\ \text{Stainless steel grid cathode}}]{\substack{\text{MeCN/pyr(9/1)} \\ CoBr_2 \text{ cat}}} GF-\!\!\langle\ \rangle\!\!-\diagup\!\!\diagdown$$
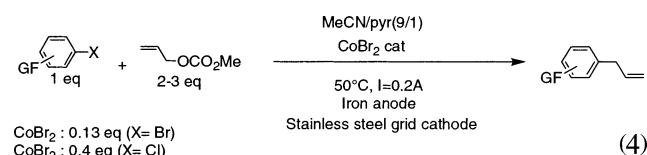
CoBr₂ : 0.13 eq (X= Br)
CoBr₂ : 0.4 eq (X= Cl)   (4)

in Table 5.

Allyl carbonates have been shown to be very reactive allylic substrates.[8–11] Good yields are obtained with aryl bromides substituted by either an electron-donating group (Table 5, entry 28) or electron-withdrawing allyl carbonates (Table 5, entry 29). The reaction with ethyl 4-bromobenzoate gives 53% of the expected allylic product and 26% of aryllallyl resulting from a trans-esterification reaction due to the high reactivity of methyl carbonate group in nucleophilic substitutions. However, with an aryl chloride (even activated by an electron-withdrawing substituent) (Table 5, entry 30), the yield is lower. In this case, allylic substrate is too reactive toward Co(I) species and gives the hydrogenation and dimerization products.

Attempts with allylic halides (bromides or chlorides) gave few coupling products. In that case, Co(I) reacts very quickly with these species leading to hexadiene.

In conclusion, we have discovered a new cobalt-catalyzed coupling reaction[23] of various functionalized aryl or heteroaryl halides with different allylic substrates (especially acetates). The corresponding arylallyls are obtained in good yields. This simple experimental procedure appears to be a mild and useful method for the synthesis of various arylallyl compounds. This catalytic reaction is a convenient route for the nucleophilic substitution with aryl halides. Studies are now in progress to elucidate the electrochemical reaction mechanism.

Experimental Section

GC analysis was carried out using a 25-m capillary column. Mass spectra were recorded with a spectrometer coupled to a gas chromatograph (30 m). Column chromatography was per-

(23) Fillon, H.; Gosmini, C.; Périchon, J. Patent application 01/08808, France, July 3, 2001.

formed on silica gel 60, 70−230 mesh. ¹H, ¹³C, and ¹⁹F spectra were recorded in CDCl₃ at 200 MHz with TMS as an internal standard.

The electrochemical cell has been described previously.[19] All solvents and reagents were purchased and used without further purification. DMF, acetonitrile, and pyridine were stored under argon. Cobalt bromide was used as obtained commercially.

General Procedure for the Coupling of Aryl Bromides with Allyl Acetate. In an undivided cell using a consumable iron anode and a stainless steel grid as the cathode, CoBr₂ (0.219 g, 1 mmol), ArBr (7.5 mmol), and allyl acetate (2.002 g, 20 mmol) were placed in a mixture solvent of acetonitrile/pyridine or dimethylformamide/pyridine (45 mL/5 mL). The ionic conductivity of the medium is ensured by addition of NBu₄BF₄ (0.165 g, 0.5 mmol) as supporting electrolyte. The solution was electrolyzed under argon and heated at 50 °C at current constant intensity of 0.2 A (0.01 A/cm²) until aryl bromide wholly reacted. The solution was hydrolyzed with HCl (2 N) and extracted with diethyl ether, the organic layer was washed with brine and dried, and the solvent was evaporated under vacuum. Coupling products were isolated by column chromatography on silica gel with pentane/ether as eluent.

General Procedure for the Coupling of Aryl Chlorides with Allyl Acetate. The procedure used for aryl chlorides is the same as that for aryl bromides excepted for amounts of CoBr₂ (0.438 g, 2 mmol), ArCl (5 mmol), and allyl acetate (1.001 g, 10 mmol).

Registry Numbers (Provided by the Authors): 4-allyl-benzoic acid ethyl ester (**1**), 19819−94−4; 4-allyl-benzonitrile (**2**), 51980−05−3; 1-(4−allyl−phenyl)ethanone (**3**), 62929−84−5; 1-allyl-4-trifluoromethyl-benzene (**4**), 1813−97−4; 4-allyl-ben-zamide (**5**), 104699−51−6; 1-allyl-4-fluoro-benzene (**6**), 1737−16−2; 1-allyl-3-trifluoromethyl-benzene (**7**), 1813−96−3; 3-allyl-benzoic acid ethyl ester (**8**), 372510−70−8; 1-allyl-3-chloro-benzene (**9**), 3840−17−3; 2-allyl-benzonitrile (**10**), 61463−61−4; 1-allyl-4-methoxy-benzene (**11**), 140−67−0; 4-allyl-benzoic acid methyl ester (**12**), 20849−84−7; 1-(2−allyl−phenyl)etha-none (**13**), 64664−07−9; 1-allyl-naphthalene (**14**), 2489−86−3; 4-but-2-enyl-benzoic acid methyl ester (**15**), 161112−49−8; 3-al-lyl-thiophene (**18**), 33934−92−8; 2-allyl-thiophene (**19**), 20849−87−0.

Product Analysis. *4-(1-Methyl-allyl)-benzoic Acid Methyl Ester* (**16**). Yield: 19%. ¹H NMR (200 MHz) δ (ppm): 7.96 (d, 2H, *J* = 8.0 Hz), 7.39 (d, 2H, *J* = 8.0 Hz), 5.52 (m, 1H), 5.04 (m, 2H), 3.87 (s, 3H), 3.40 (m, 1H), 1.33 (d, 3H, *J* = 7.0 Hz). ¹³C NMR (50 MHz) δ (ppm): 166.7, 150.7, 146.4, 132.6, 128.8, 128.0, 113.6, 51.6, 43.0, 22.2. MS. *m/z* (%): 190 (22) [M], 175 (21), 159 (28), 132 (12), 131 (100), 129 (17), 116 (18), 115 (28), 91 (30). IR (neat): 3000, 1720, 1610 cm⁻¹. Anal. Calcd for C₁₂H₁₄O₂: C, 75.76; H, 7.42; O, 16.82. Found: C, 74.74; H, 7.08; O, 15.93.

4-(3-Phenyl-prop-2-enyl)-benzoic Acid Ethyl Ester (**17**). Yield: 52%. ¹H NMR (200 MHz) δ (ppm): 8.01 (d, 2H, *J* = 8.2 Hz), 7.24 (m, 7H), 6.47 (d, 1H, *J* = 15.8 Hz), 6.33 (td, 1H, *J* = 15.8 and 6.2 Hz), 4.38 (q, 2H, *J* = 7.1 Hz), 3.59 (d, 2H, *J* = 6.2 Hz), 1.39 (t, 3H, *J* = 7.1 Hz). ¹³C NMR (50 MHz) δ (ppm): 166.5, 145.6, 145.4, 137.1, 131.7, 129.7, 128.6, 128.5, 128.0, 127.2, 126.1, 60.7, 39.2, 14.2. MS. *m/z* (%): 266 (45) [M], 237 (30), 221 (21), 193 (100), 192 (23), 178 (33), 115 (62). IR (neat): 3040, 3000, 1730, 1620 cm⁻¹. Anal. Calcd for C₁₈H₁₈O₂: C, 79.91; H, 6.85; O, 12.31. Found: C, 79.70; H, 6.82; O, 12.48.

2-Methyl-4-(prop-2-enyl)-quinoline (**20**). Yield: 69%. ¹H NMR (200 MHz) δ (ppm): 7.91 (m, 2H), 7.51 (m, 1H), 7.31 (m, 1H), 7.12 (s, 1H), 6.87 (dd, 1H, *J* = 15.5 and 1.6 Hz), 6.25 (m, 1H), 2.58 (s, 3H), 1.85 (dd, 3H, *J* = 6.7 and 1.6 Hz). ¹³C NMR (50 MHz) δ (ppm): 158.4, 147.9, 143.6, 132.6, 129.1, 128.7, 125.8, 125.3, 124.4, 123.3, 117.9, 25.0, 18.9. MS. *m/z* (%): 184 (19) [M + 1], 183 (100) [M], 181 (12), 169 (48), 168 (37), 167 (18). IR (neat): 2940, 1600 cm⁻¹. Anal. Calcd for C₁₃H₁₃N: C, 85.21; H, 7.15; N, 7.64. Found: C, 85.23; H, 7.35; N, 7.42.

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