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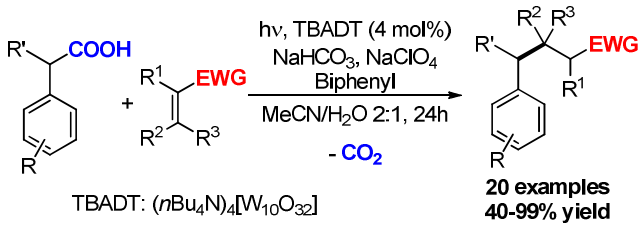
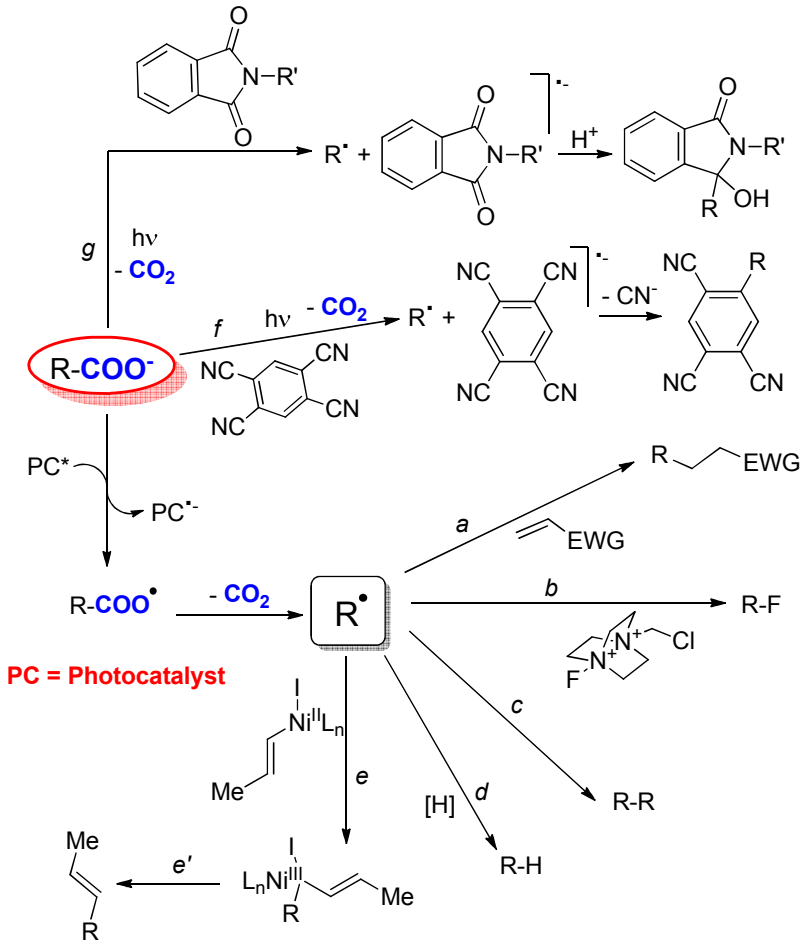


Abstract: Arylacetic acids were used as source of benzyl radicals under tetrabutylammonium decatungstate photocatalyzed conditions for the benzylation of electron-poor olefins. The reaction proceeds smoothly in a mixed aqueous medium (MeCN/H_2O 2:1) in the presence of $NaHCO_3$, $NaClO_4$ and an electron transfer agent (biphenyl). The reaction tolerates a wide variety of functional groups on the aromatic ring (whether electron-donating or electron-withdrawing), and can be extended to heteroaromatic analogues. The olefins have the double role of radical trap and electron-acceptor. The present approach can also be extended to arylpropionic acids (including the nonsteroidal anti-inflammatory drugs ibuprofen and flurbiprofen), as well as mandelic acid derivatives.

Introduction

Carboxylic acids are versatile organic compounds that have stimulated growing attention in recent years. In particular, they have been adopted in decarboxylative couplings,[1] exploiting the role of the -COOH group as "traceless activating agent".[2] Most of these reactions took place under thermal conditions with the help of a metal catalyst (often based on silver).[3] Decarboxylation is likewise a smooth route for the generation of radicals. A recent approach involved the photocatalytic monoelectronic oxidation of carboxylate anions followed by carbon dioxide loss from the thus formed RCOO$^{\bullet}$ intermediates.[4] The photogenerated carbon-centered radicals were then used in several reactions, as summarized in Scheme 1.

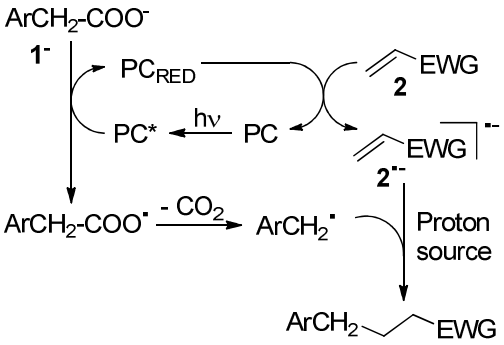
Scheme 1. Carboxylic Acids as Radical Precursors



A typical case is the conjugate addition onto electron-poor olefins (Scheme 1, path a)[2,5] or allyl sulfones[6] forming a new C-C bond. Efficient fluorinating agents (e.g. Selectfluor) were likewise used for C-F bond formation (path b).[7] In rare instances, the stability of the radical allowed for a dimerization process (path c),[8] whereas the presence of a reducing agent (e.g. a thiol) led to an overall removal of the carboxylic acid group (path d).[9] Dual catalytic processes combining a photocatalyst (PC) with a metal catalyst (e.g. based on Ni) involved trapping of the photogenerated radical by the metal complex (path e) and products were then formed from the resulting adduct (path e').[10] A particular case is the photoinduced electron transfer between a carboxylate anion and an organic compound, such as cyanobenzenes (path f)[11,12] or phthalimides (path g)[13] causing an overall functionalization of the latter.

One of the critical steps of these reactions is the decarboxylation of the $RCOO^{\bullet}$ intermediate, that is particularly efficient only when the resulting radical ($R^{\bullet}$) is stabilized. Accordingly, secondary or tertiary alkyl radicals, along with α-amino (from the corresponding aminoacids) or α-oxy radicals, were mainly used in synthetic processes. Benzyl radicals were generated from phenylacetic acids and used as well, but not in the benzylation of olefins, due to the lack of reactivity of these radicals towards C=C double bonds. A way to overcome the problem makes use of easily reducible olefins.[14-16] Scheme 2 shows our proposed plan to benzylate olefins starting from phenylacetic acids **1** (used as the corresponding carboxylate anions $\mathbf{1}^{-}$). The photocatalytic generation of the benzyl radical should be followed by regeneration of the photocatalyst via reaction with the olefin (**2**). In such a way, the high reactivity of the resulting radical anion $\mathbf{2}^{\bullet-}$ should be sufficient to trap $ArCH_2^{\bullet}$, finally leading to the desired compound.

Scheme 2. Proposed Route for the Benzylation of Electron-poor Olefins



Apart from photocatalytic applications, the use of arylacetic acids in photochemical processes has been only sparsely reported.[17] Under direct irradiation conditions, the photoelimination of CO_2 often took place and triggered the desired process. Early studies demonstrated that the loss of CO_2 is pH-dependent. In particular, the involvement of radical intermediates was postulated when phenylacetic acids were irradiated, while the formation of benzyl anions was claimed when irradiating the corresponding sodium salts.[18,19] A recent application deals with materials science and involved the irradiation of thioxanthone acetic acid ammonium salts that were used as efficient photobase generators to trigger a polymerization.[20] In another instance, the -COOH moiety was used as electrofugal group in the route to α,n-didehydrotoluenes (DHTs) starting from isomeric (n-chlorophenyl)acetic acids.[21] Furthermore, the decarboxylation of arylacetic acids is of particular interest in pharmacokinetic studies, since this process is the main responsible for the *in vivo* photodecomposition of several nonsteroidal anti-inflammatory drugs (NSAIDs).[17]

As part of our ongoing interest in photocatalyzed C-C bond formation reactions, in this paper we describe the use of tetrabutylammonium decatungstate (TBADT; $(n\text{Bu}_4\text{N})_4[\text{W}_{10}\text{O}_{32}]$) as a convenient, cheap and robust photocatalyst for the benzylation of electron-poor olefins via decarboxylation of easily available arylacetic acids. In the last years, we found that TBADT is particularly efficient in hydrogen atom transfer reactions[22] and, to a minor extent, as photoredox

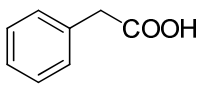
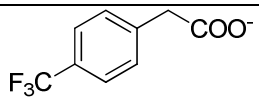
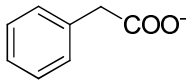
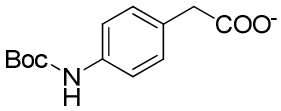
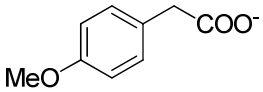
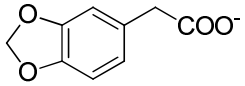
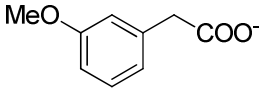
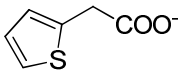
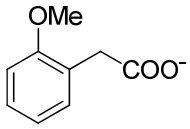
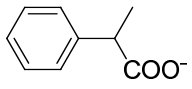
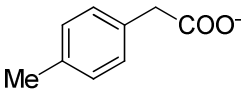
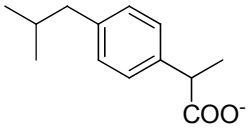
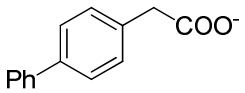
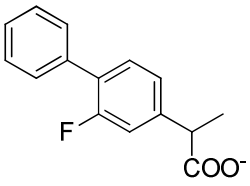
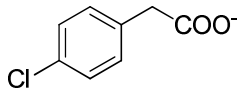
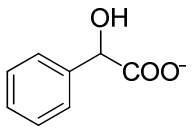
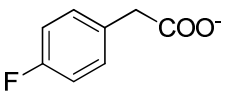
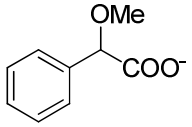
catalyst.[14] The excited state of TBADT rapidly decays into a reactive form (a relaxed excited state, named **wO**, a virtually unknown species).[23] Accordingly, the reduction potential of **wO** in the excited state, $E(\mathbf{wO}/[W_{10}O_{32}]^{5-})$, can only be estimated ranging from + 2.26 to + 2.61 V vs SCE,[14,24] thus making feasible the oxidation of carboxylates, whose oxidation potentials $E(\text{R-COO}^{\bullet}/\text{R-COO}^{-})$ fall in the + 1-1.6 V vs SCE range.[7d,25,26]

Results and Discussion

To check the feasibility of the proposed plan reported in Scheme 2, we initially measured by cyclic voltammetry the oxidation potentials of parent phenylacetic acid **1a** and of the carboxylate anions **1a-q**$^{-}$ (as the tetrabutylammonium salts; Table 1), as well as the reduction potentials of the electron-poor olefins **2a-e** (Table 2) employed in this work. In the case of derivatives **1a** and **1a-q**$^{-}$, typically irreversible or quasi reversible redox behaviors were observed.[27] For this reason, the data reported in Table 1 refer to $E_{1/2}^{OX}$ (half-wave potential) values of the oxidation process, better appreciated by plotting the cyclic voltammogram in the semi-differential mode. In the case of phenylacetic acid **1a** in acetonitrile (in the presence of $n\text{Bu}_4\text{N}^{+}\text{ClO}_4^{-}$ 0.1 M as the supporting electrolyte), an oxidation wave was registered at + 2.51 V vs SCE,[28] partially superimposed with the anodic oxidation of the solvent (see Figure S1 in Supporting Information for details). By contrast carboxylate anions **1a-q**$^{-}$, obtained upon addition of a base (1 equiv. of a 1.0 N $n\text{Bu}_4\text{N}^{+}\text{OH}^{-}$ in MeOH was used), showed oxidation waves in the + 0.91 (for **1j**$^{-}$) to + 1.39 (for **1i**$^{-}$) V vs SCE range (Table 1; see also Figure S1).

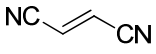
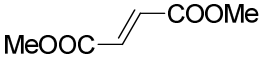
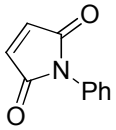
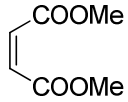
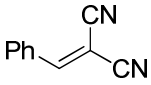
The electrochemical investigation on electron-poor olefins **2** was performed in acetonitrile (in the presence of $n\text{Bu}_4\text{N}^{+}\text{ClO}_4^{-}$ 0.1 M as the supporting electrolyte) and showed a reversible redox behavior. For this reason, the $E_{1/2}^{RED}$ values could be approximated with the formal redox potentials ($E^{0\prime}$; Table 2), in accordance with a previous work by our group.[14] The analysis revealed that the reduction potentials for **2a-e** range between - 1.09 (for **2b**)[14] and - 1.65 (for **2e**)[14] V vs SCE, with the newly investigated derivative **2c** showing a reduction potential at - 1.20 V vs SCE (Table 2).

Table 1. Oxidation Potentials of Phenylacetic acid 1a and of Carboxylates (1a-q$^-$) Studied in the Present Work.

Arylacetic Acid **1**	$E_{1/2}^{OX}$ (**1**$^{\bullet}$/**1**$^-$) [V vs SCE]	Arylacetic Acid **1**	$E_{1/2}^{OX}$ (**1**$^{\bullet}$/**1**$^-$) [V vs SCE]
 **1a**	+ 2.51[a]	 **1i**$^-$	+ 1.39
 **1a**$^-$	+ 1.27	 **1j**$^-$	+ 0.91
 **1b**$^-$	+ 0.99	 **1k**$^-$	+ 0.97
 **1c**$^-$	+ 1.17	 **1l**$^-$	+ 1.05
 **1d**$^-$	+ 1.07	 **1m**$^-$	+ 1.07
 **1e**$^-$	+ 1.17	 **1n**$^-$	+ 1.11
 **1f**$^-$	+ 1.11	 **1o**$^-$	+ 1.04
 **1g**$^-$	+ 1.25	 **1p**$^-$	+ 1.16
 **1h**$^-$	+ 1.21	 **1q**$^-$	+ 0.97

[a] $E_{1/2}^{OX}$ (**1**$^{\bullet+}$/**1**) [V vs SCE] value has been reported.

Table 2. Reduction Potentials of the Electron-poor Olefins (2a-e) Studied in the Present Work.

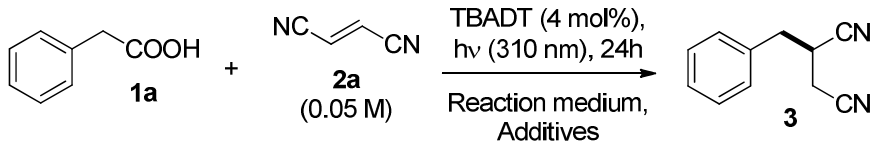
Electron-poor Olefin **2**	$E^{0'}$ (**2**/**2**$^{\bullet-}$) [V vs SCE]	Electron-poor Olefin **2**	$E^{0'}$ (**2**/**2**$^{\bullet-}$) [V vs SCE]
 **2a**	- 1.31[a]	 **2d**	- 1.47[a]
 **2b**	- 1.09[a]	 **2e**	- 1.65[a]
 **2c**	- 1.20		

[a] Data taken from Ref. 14.

Initial experiments were carried out on the reaction between parent phenylacetic acid (**1a**) and fumaronitrile (**2a**) to give benzylsuccinonitrile **3** (Table 3). When an equimolar (0.05 M) solution of **1a** and **2a** in acetonitrile in the presence of TBADT (4 mol%) was irradiated for 24h (λ_{em} centered at 310 nm), the expected product was not detected by GC analysis (entry 1). When shifting to mixed aqueous media, however, small amounts of **3** were formed (entries 2, 3). The role of additives was next evaluated. Comparable results were obtained in the presence of sodium hydrogencarbonate alone (1 equiv.; entry 4), or when it was coupled with sodium perchlorate (1 equiv.; entry 5), with the yield never exceeding 20%, despite an almost quantitative consumption of **2a** (> 90%). By contrast, the addition of biphenyl had a tremendous effect and raised the formation of **3** up to 83% (entries 6, 7). Other experiments (entries 8-10) demonstrated that the presence of all of the three additives ($NaHCO_3$, $NaClO_4$ and biphenyl) was mandatory for the success of the reaction and that a bivalent perchlorate ($Mg(ClO_4)_2$) was less beneficial than $NaClO_4$ (entry 11). Interestingly, a good yield (69% GC yield, entry 12) was likewise observed in the absence of biphenyl when increasing

the amount of acid (up to 1.5 equiv.). Blank experiments demonstrated the crucial role of both TBADT and light in the desired process (entries 13, 14).

Table 3. Optimization of the Reaction Conditions.[a]

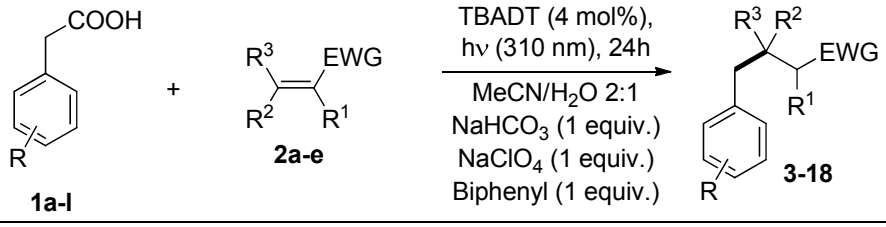


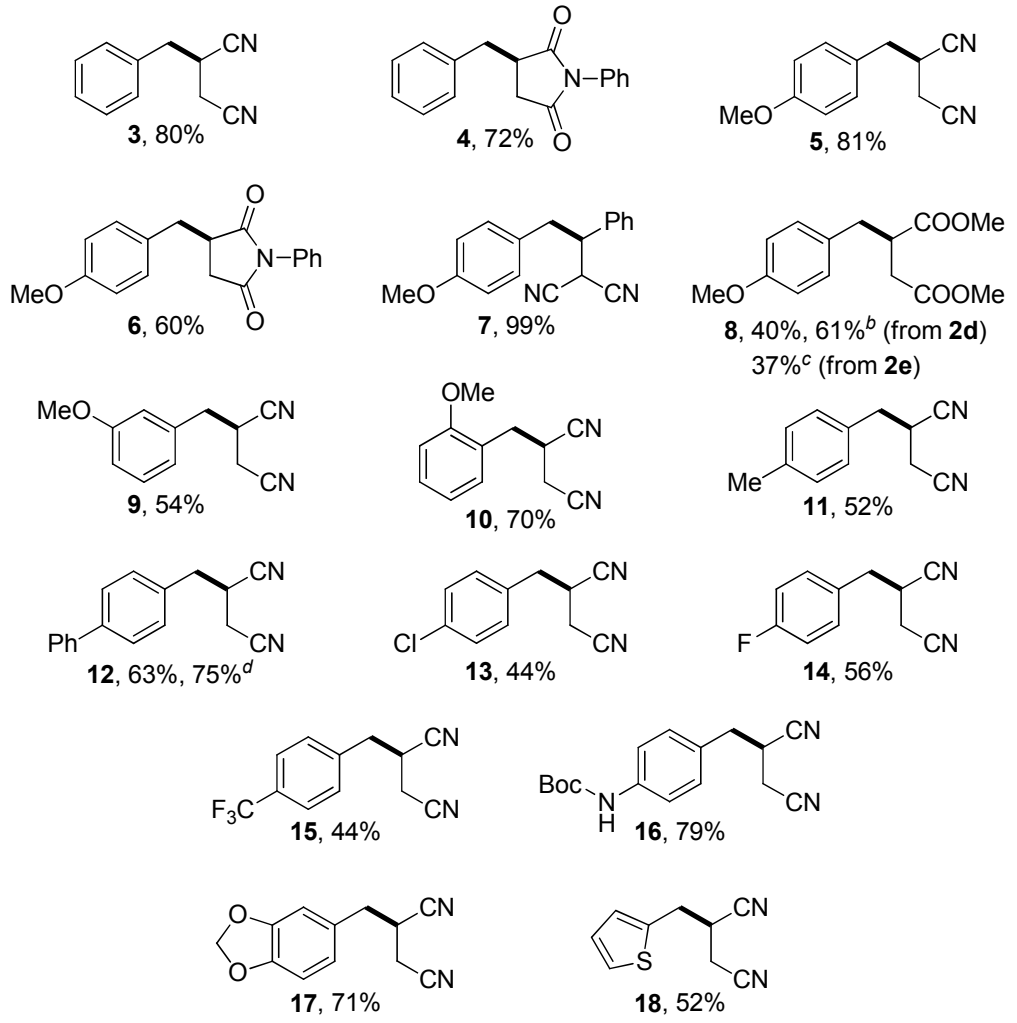
Entry	**1a** (equiv.)	Reaction medium	Additives	**3** Yield (%)[b]
1	1.0	MeCN	-	n.d.
2	1.0	MeCN-H_2O 5/1	-	trace
3	1.0	MeCN-H_2O 2/1	-	14
4	1.0	MeCN-H_2O 2/1	$NaHCO_3$ (1.0 equiv.)	17
5	1.0	MeCN-H_2O 2/1	$NaHCO_3$ (1.0 equiv.) $NaClO_4$ (1.0 equiv.)	20
6	1.0	MeCN-H_2O 2/1	$NaHCO_3$ (1.0 equiv.) $NaClO_4$ (1.0 equiv.) Biphenyl (0.5 equiv.)	52
7	**1.0**	**MeCN-H_2O 2/1**	**$NaHCO_3$ (1.0 equiv.)** **$NaClO_4$ (1.0 equiv.)** **Biphenyl (1.0 equiv.)**	**83**
8	1.0	MeCN-H_2O 2/1	$NaHCO_3$ (1.0 equiv.) Biphenyl (1.0 equiv.)	61
9	1.0	MeCN-H_2O 2/1	$NaClO_4$ (1.0 equiv.) Biphenyl (1.0 equiv.)	13
10	1.0	MeCN-H_2O 2/1	Biphenyl (1.0 equiv.)	23
11	1.0	MeCN-H_2O 2/1	$NaHCO_3$ (1.0 equiv.) $Mg(ClO_4)_2$ (1.0 equiv.) Biphenyl (1.0 equiv.)	53
12	1.5	MeCN-H_2O 2/1	$NaHCO_3$ (1.5 equiv.) $NaClO_4$ (1.0 equiv.)	69
13[c]	1.0	MeCN-H_2O 2/1	$NaHCO_3$ (1.0 equiv.) $NaClO_4$ (1.0 equiv.) Biphenyl (1.0 equiv.)	8[d]
14[e]	1.0	MeCN-H_2O 2/1	$NaHCO_3$ (1.0 equiv.) $NaClO_4$ (1.0 equiv.) Biphenyl (1.0 equiv.)	n.d.[f]

[a] Reaction conditions: **1a** (0.15 mmol), **2a** (0.15 mmol), $(n\text{Bu}_4\text{N})_4[\text{W}_{10}\text{O}_{32}]$ (TBADT, 4 mol%) in 3 mL of the chosen reaction medium. [b] Gas Chromatography (GC) yields based on the amount of 3 vs an internal standard, n-octanol; the consumption of 2a was always › 90%, except where otherwise noted. [c] No TBADT used. [d] The formation of by-products has been

observed by GC analysis. [e] In the absence of light. [f] No consumption (< 5%) of the olefin was observed.

Table 4. Benzylation of Electron-poor Olefins via Decarboxylation of Arylacetic Acids.[a]





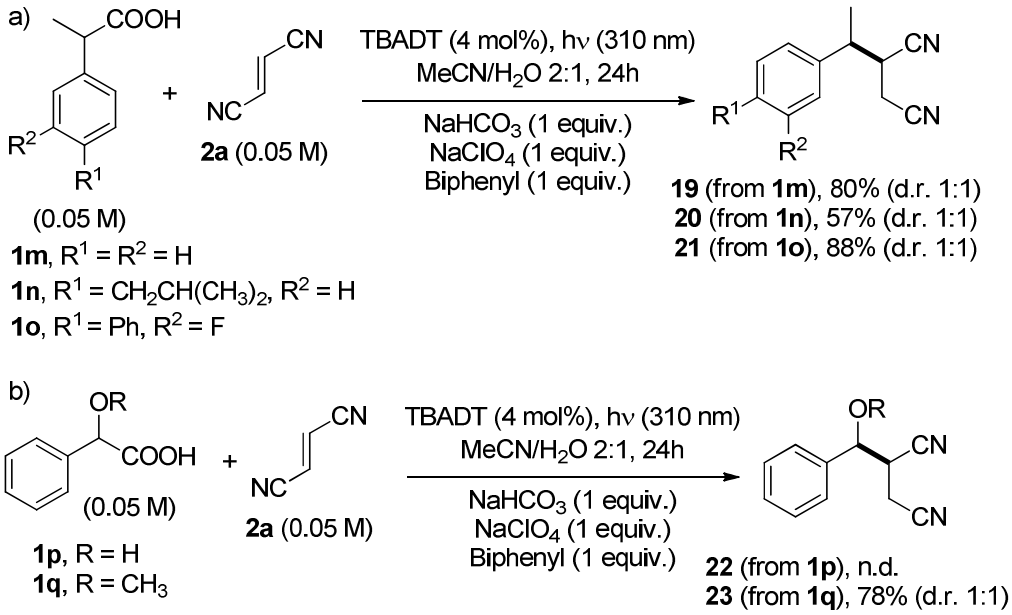
[a] Reactions carried out on a 0.75 mmol scale (0.05 M); all data are the average of two experiments. Isolated yields by silica gel chromatography (see Experimental Section). [b] Conditions from Table 1, entry 8. [c] Yield based on 75% consumption of **2e**. [d] Reaction carried out in the absence of biphenyl.

Having the optimized conditions in hand (entry 7, Table 3), we next evaluated the scope of the reaction (Table 4), by investigating different combinations of arylacetic acids **1** (see Table 1) and electron-poor olefins **2** (see Table 2). The reaction of phenylacetic acid **1a** with fumaronitrile **2a** and *N*-phenyl maleimide **2b** gave products **3** and **4** in 80% and 72% isolated yield, respectively. The reaction was next extended to 4-methoxyphenylacetic acid **1b**, that gave products **5-7** in good to excellent yields in the reaction with **2a**, **2b** and benzylidenemalononitrile **2c**. By contrast, the reaction of **1b** with dimethyl fumarate **2d** gave only a modest yield (40%) of adduct **8**, that was increased (61% yield) when using an excess of **1b** (1.5 equiv., biphenyl omitted). When repeating the synthesis of **8** by using isomeric dimethyl maleate **2e** as the radical trap, the process was sluggish giving the desired product in 37% yield (with only 75% consumption of **2e**). The reactions of 3-methoxy (**1c**) and 2-methoxy (**1d**) phenylacetic acids likewise gave adducts **9** and **10** in 54 and 70% yield, respectively, in the reaction with **2a**. Aliphatic (in 4-methylphenylacetic acid **1e**) or aromatic (in 4-biphenylacetic acid **1f**) groups in the *para*- position were tolerated and the expected adducts with fumaronitrile were obtained in 52% and 63% yields, respectively (compounds **11**, **12**). In the latter case, product **12** was likewise formed in a good yield (75%) in the absence of biphenyl. Electron-withdrawing substituted 4-chloro (**1g**), 4-fluoro (**1h**) and 4-trifluoromethyl (**1i**) phenylacetic acids underwent addition onto fumaronitrile to give compounds **13-15** in decent yields (45-55% range). 4-Aminophenylacetic acid was likewise tested, but was not soluble under the optimized reaction conditions. Protection of the amino group as carbamate in 4-(*tert*-butoxycarbonylamino)phenylacetic acid **1j** restored the usual reactivity to give adduct **16** in good yield (79%) upon reaction with **2a**. The reaction could be extended to substrates bearing two substituents on the aromatic ring, as well as to heteroaryl substituted acetic acids, as demonstrated by (3,4-methylenedioxy)phenylacetic acid **1k** and 2-thiopheneacetic acid **1l**, that reacted with **2a** to give, respectively, compounds **17** and **18**.

Next, we shifted our attention to 2-arylpropionic acids, as reported in Scheme 3a. In particular, parent 2-phenylpropionic acid **1m** gave adduct **19** in 80% yield as a 1:1 diastereomeric mixture.

Furthermore, since several NSAIDs pertain to this family, we subjected two very well-known drugs to our reaction conditions. Indeed, both ibuprofen (**1n**) and flurbiprofen (**1o**) gave the expected adducts **20** and **21** in 57% and 88% isolated yield (as 1:1 diastereomeric mixtures), respectively. Finally, we tested the effect of oxygen-based substituents in the benzylic position (Scheme 3b). Thus, when using mandelic acid **1p**, benzaldehyde was detected (by GC analysis) as the exclusive product at the expense of the expected adduct **22**. However, when employing α-methoxyphenylacetic acid **1q**, the usual reactivity was restored, allowing to isolate product **23** in 78% yield as a 1:1 diastereomeric mixture in the reaction with **2a**.

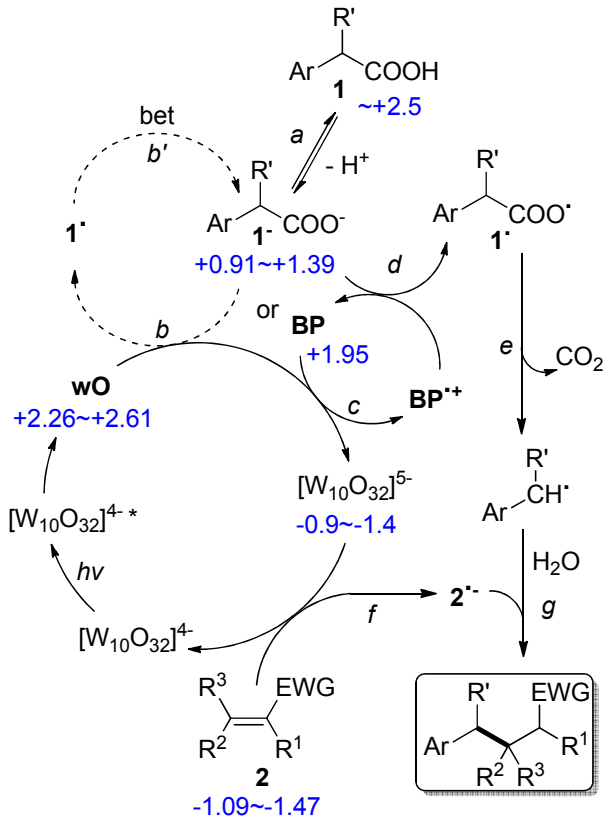
Scheme 3. Reactivity of: a) 2-Phenylpropionic Acids and b) Mandelic Acid Derivatives



The present work compares favorably with other decarboxylative photocatalytic strategies employing arylacetic acids and is complementary to them, since this is one of the rare examples of electron-poor olefins benzylation.[14-16] The proposed reaction mechanism is gathered in Scheme 4 and is strengthened by the electrochemical investigation reported above. Given the unknown

reduction potential of **wO** (up to + 2.61 V vs SCE),[14,24] the occurrence of an electron transfer from **1a** ($E_{1/2}^{OX}$ (**1a**$^{\bullet+}$/**1a**) = + 2.51 V vs SCE, Table 1) to **wO** cannot be excluded. The efficiency of this process, however, is expected to be very low, as also confirmed by the reaction carried out in neat acetonitrile, where no product **3** has been detected in the reaction with **2a** (Table 3, entry 1). By contrast, when in the anionic form the -COO^- group functions as an electroauxiliary moiety,[29] since it lowers the oxidation potential of the substrate with respect to the corresponding unsubstituted derivative and also drives the selectivity. Thus, the reaction takes place significantly only on the carboxylate anions **1**$^-$ (much better electron donors than the protonated forms **1**; see Scheme 4, path a). It is interesting to note that the reaction medium did not affect the stability of the decatungstate anion, while this does not tolerate strongly basic conditions.[30] Thus, excitation of the $[W_{10}O_{32}]^{4-}$ cluster populates the highly oxidizing **wO** state (see above),[14,24] capable to accept an electron from the carboxylate anion **1**$^-$ (path b; dashed arrow).

Scheme 4. Proposed Reaction Mechanism. Selected Redox Potentials (V vs SCE) of the Species Involved are Reported in Blue Color



However, this step is not efficient *per se*, as supported by the low yields observed in entries 2-5, Table 3. Two main reasons may explain this behavior. Given that both $\mathbf{1}^-$ and **wO** are negatively charged, an electrostatic repulsion may hamper path b. Otherwise, a back electron transfer (bet, path b') may be involved, preventing the otherwise fast decarboxylation (reported to be in the order of 10^{10} s^{-1})[31] of the thus formed $ArCH_2$-$COO^{\bullet}$ radical ($\mathbf{1}^{\bullet}$).

The key point to the success of the present reaction is the use of biphenyl (**BP**).[32,33] Thus, **BP** ($E(\mathbf{BP}^{\bullet+}/\mathbf{BP})$ = + 1.95 V vs SCE)[34] can be oxidized (in competition with $\mathbf{1}^-$) to the corresponding long-lived radical cation $\mathbf{BP}^{\bullet+}$ (path c). $\mathbf{BP}^{\bullet+}$ is then capable of oxidizing $\mathbf{1}^-$ to $\mathbf{1}^{\bullet}$ (path d), that in turn loses CO_2 to give the corresponding benzyl radical (path e). **BP** has the role of electron transfer agent[35] and it is able to overcome the electrostatic repulsion between $\mathbf{1}^-$ and **wO** and to separate $\mathbf{1}^{\bullet}$ from $[W_{10}O_{32}]^{5-}$, preventing bet and leading to a productive oxidation of $\mathbf{1}^-$ (in turn triggering decarboxylation). The actual concentration of **BP** (1 equiv., Table 3) must be high enough to prevent any competitive (yet, unproductive) direct oxidation of $\mathbf{1}^-$. The presence of $NaClO_4$ is

likewise important in favoring the electron transfer process.[14,36] Another important point is related to the trapping of ArR'CH$^{\bullet}$. Benzyl radicals are rather stable species, quite difficult to trap and with a marked tendency to dimerize.[8] As previously demonstrated by our group, this limitation can be overcome by having recourse to easily reducible olefins (see above).[14] Indeed, the olefins have a role in the regeneration of the photocatalyst (path f) by the concomitant conversion into the corresponding radical anions (**2**$^{\bullet-}$). The reduction potential of the deactivated photocatalyst has been estimated to lie in the - 0.9 to - 1.4 V vs SCE range. This is due to the possible involvement of the highly reducing $[W_{10}O_{32}]^{6-}$ species, in turn obtained via disproportionation of the mono-reduced form $[W_{10}O_{32}]^{5-}$.[14] As a result, the C-C bond forming step occurs via a radical-radical anion coupling (path g), leading to the desired product upon addition of a proton (from the aqueous solvent). This behavior has been confirmed in the present system, where the least two reducible olefins used, *viz.* isomeric dimethyl fumarate **2d** and dimethyl maleate **2e**, both gave product **8** in a modest yield, with an efficiency proportional to their reduction potentials (the more negative the reduction potential, the worse the efficiency).[14] An excess of the acid (**1b**$^{-}$), however, ameliorated the performance of the reaction with **2d** (61% yield, even in the absence of biphenyl), highlighting that the limitations related to path b (see above) can be overcome by increasing the absolute concentration of the electron donor.

As for the employed acids, despite their oxidation potentials span over a quite large range (*ca.* 0.5 V, from + 0.91 for **1j**$^{-}$ to + 1.39 for **1i**$^{-}$ V vs SCE; Table 1), the reaction proceeds satisfactorily, demonstrating the potential of TBADT as photoredox catalyst. The presence of a biphenyl moiety in compound **1f** allowed the reaction to proceed even in the absence of the electron transfer agent. Another interesting case is the selective activation of the -COOH group in (3,4-methylenedioxy)phenylacetic acid **1k**, despite the presence of the two methylene hydrogen atoms, likewise prone to be activated under TBADT photocatalyzed conditions.[30] Phenylpropionic acids behave quite similarly to the corresponding C2-homologues despite the stability imparted by the methyl group to the resulting benzyl radical. Different is the case of mandelic acid derivatives,

where the presence of the benzylic -OH group in **1p** completely diverted the reactivity, leading to a formal decarboxylation/oxidation rather than the desired C-C bond formation, as previously observed.[9b,37] However, when using substrate **1q** bearing a α-methoxy substituent, the usual reactivity was restored.

Conclusions

The present work demonstrates that C-C bond forming reactions starting from arylacetic acids and easily reducible olefins are feasible. The success of the protocol is based on the use of TBADT as photoredox catalyst and the -COOH moiety in the role of electroauxiliary group. The reaction requires a fine tuning of the conditions and a mixed aqueous solvent is mandatory to solubilize all the compounds present in solution. Interestingly, biphenyl, acting as an electron transfer agent, has a fundamental role in improving the performance of the reaction. Further work is currently ongoing in our lab to extend the present methodology to other classes of carboxylic acids.

EXPERIMENTAL SECTION

General

Compounds **1** and **2** were commercially available and used as received, except for 4-(*tert*-butoxycarbonylamino)phenylacetic acid (**1j**)[38] and benzylidenemalononitrile (**2c**)[39] that were synthesized according to published procedures. The photocatalyst TBADT has been prepared according to a published procedure.[40] Acetonitrile and water (HPLC purity grade) used as solvents were commercially available and used as received. NMR spectra were recorded on a 300 MHz spectrometer; the attributions were made on the basis of ^{1}H and ^{13}C NMR, as well as DEPT experiments, and chemical shifts reported in ppm downfield from TMS. Reactions were monitored by gas chromatographic (GC) analyses (HP-5 capillary column) using *n*-octanol as an internal standard.

The electrochemical measurements were carried out by a computer-controlled electrochemical analyzer. Electrochemical measurements (cyclic voltammetry) were performed in a three-electrode cell (volume 10 mL; acetonitrile as solvent, nBu$_4$N$^+$ClO$_4^-$ 0.1 M as the supporting electrolyte, 2 mM concentration of the tested compound)[26] at glassy carbon (diameter: 3 mm) as the working electrode, Pt wire as the auxiliary electrode, and Ag/AgCl (3 M NaCl) as the reference electrode. Scan speed was 100 mV·s^{-1}. The potential ranges investigated for oxidations were: 0/+3.0 V and 0/+2.0 V vs Ag/AgCl (3 M NaCl) for **1a** and **1a-q**$^-$, respectively. By contrast, for reduction processes the 0/-2.0V vs Ag/AgCl (3 M NaCl) range has been explored. The potentials measured were then referred to SCE by applying the equation:

$$E\ (\text{vs SCE}) = E\ (\text{vs Ag/AgCl; 3 M NaCl}) - 35\ \text{mV}$$

General Procedure for the TBADT-photocatalyzed Decarboxylative Benzylation of Electron-poor Olefins. An acetonitrile/water 2:1 solution (15 mL) of the acid **1** (0.75 mmol, 0.05 M, 1 equiv.) and the olefin **2** (1 equiv.), in the presence of TBADT (2×10^{-3} M, 4 mol%), $NaHCO_3$ (1 equiv.), $NaClO_4$ (1 equiv.) and biphenyl (1 equiv.), was poured in a quartz tube and purged for 3 minutes with nitrogen, septum capped and irradiated for 24h in a multi-lamp apparatus fitted with 10×15W phosphor-coated lamps (emission centered at 310 nm). The solvent was removed under reduced pressure from the photolyzed solution and the product isolated by purification of the residue by column chromatography (hexane/ethyl acetate as eluants).

*2-Benzylsuccinonitrile (**3**).* Colorless oil (102 mg, 80% yield). Purification: silica gel chromatography (hexane/ethyl acetate 8:2). Spectroscopic data of **3** were in accordance with the literature.[41] Anal. Calcd. for $C_{11}H_{10}N_2$: C, 77.62; H, 5.92; N, 16.46. Found: C: 77.7; H 5.8; N, 16.2.

*3-Benzyl-1-phenylpyrrolidine-2,5-dione (**4**).* White solid (143 mg, 72% yield). Purification: silica gel chromatography (hexane/ethyl acetate 8:2). M.p. 123-125 °C (Lit.[14] 128-130 °C). Spectroscopic

data of **4** were in accordance with the literature.[14] Anal. Calcd. for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28. Found: C, 76.8; H, 5.9; N, 5.2.

*2-(4-Methoxybenzyl)succinonitrile (**5**).* Colorless oil (122 mg; 81% yield). Purification: silica gel chromatography (hexane/ethyl acetate 8:2). Spectroscopic data of **5** were in accordance with the literature.[14] Anal. Calcd. for $C_{12}H_{12}N_2O$: C, 71.98; H, 6.04; N, 13.99. Found: C, 72.0; H, 6.2; N, 13.9.

*3-(4-Methoxybenzyl)-1-phenylpyrrolidine-2,5-dione (**6**).* Off-white solid (133 mg, 60% yield). Purification: silica gel chromatography (hexane/ethyl acetate 8:2). M.p. 128-130 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.49-7.35 (m, 3H), 7.19-7.12 (m, 4H), 6.86 (d, *J* = 8.7 Hz, 2H), 3.80 (s, 3H) 3.33-3.24 (m, 1H), 3.19-3.03 (m, 2H), 2.88 (dd, *J* = 18, 9 Hz, 1H), 2.64 (dd, *J* = 18, 5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 178.5, 175.5, 159.0, 132.0, 130.4, 129.3, 128.8, 128.7, 126.6, 114.4, 55.4, 41.6, 35.8, 33.4. Anal. Calcd. for $C_{18}H_{17}NO_3$: C, 73.20; H, 5.80; N, 4.74. Found: C, 73.2; H, 5.9; N, 4.6.

*2-(2-(4-Methoxyphenyl)-1-phenylethyl)malononitrile (**7**).* Colorless oil (205 mg; 99% yield). Purification: silica gel chromatography (hexane/ethyl acetate 8:2). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.48-7.33 (m, 5H), 7.09 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.5 Hz, 2H), 3.86 (d, *J* = 5.1 Hz, 1H), 3.79 (s, 3H), 3.44-3.38 (m, 1H), 3.21 (d, *J* = 8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 159.1, 136.6, 130.1, 129.3, 129.2, 128.6, 128.2, 114.7, 112.3, 111.6, 55.4, 48.7, 37.8, 28.5. Anal. Calcd. for $C_{18}H_{16}N_2O$: C, 78.24; H, 5.84; N, 10.14. Found: C, 78.2; H, 5.9; N, 10.0.

*Dimethyl 2-(4-methoxybenzyl)succinate (**8**).* Colorless oil (80 mg; 40% yield). Purification: silica gel chromatography (hexane/ethyl acetate 8:2). Spectroscopic data of **8** were in accordance with the literature.[41] Anal. Calcd. for $C_{14}H_{18}O_5$: C, 63.15; H, 6.81. Found: C, 63.2; H, 6.7.

*2-(3-Methoxybenzyl)succinonitrile (**9**).* Colorless oil (81 mg; 54% yield). Purification: silica gel chromatography (hexane/ethyl acetate 8:2). Spectroscopic data of **9** were in accordance with the

literature.[14] Anal. Calcd. for $C_{12}H_{12}N_2O$: C, 71.98; H, 6.04; N, 13.99. Found: C, 71.8; H, 6.1; N, 13.9.

*2-(2-Methoxybenzyl)succinonitrile (**10**).* Colorless oil (105 mg; 70% yield). Purification: silica gel chromatography (hexane/ethyl acetate 8:2). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.31 (td, J = 8, 2 Hz, 1H), 7.21 (dd, J = 7, 1 Hz, 1H), 6.95 (td, J = 7, 1 Hz, 1H), 6.90 (d, J = 8.3 Hz, 1H), 3.85 (s, 3H), 3.41-3.23 (m, 1H), 3.16-3.00 (m, 2H), 2.71-2.54 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 157.4, 131.3, 129.6, 123.1, 121.0, 119.1, 115.9, 110.7, 55.4, 32.9, 28.3, 20.4. Anal. Calcd. for $C_{12}H_{12}N_2O$: C, 71.98; H, 6.04; N, 13.99. Found: C, 71.9; H, 6.2; N, 13.8.

*2-(4-Methylbenzyl)succinonitrile (**11**).* Colorless oil (72 mg; 52% yield). Purification: silica gel chromatography (hexane/ethyl acetate 9:1). Spectroscopic data of **11** were in accordance with the literature.[42] Anal. Calcd. for $C_{12}H_{12}N_2$: C, 78.23; H, 6.57; N, 15.21. Found: C, 78.2; H, 6.7; N, 15.1.

*2-([1,1'-Biphenyl]-4-ylmethyl)succinonitrile (**12**).* White solid (116 mg, 63% yield). Purification: silica gel chromatography (hexane/ethyl acetate 8:2). M.p.: 117-119 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.62-7.57 (m, 4H), 7.48-7.43 (m, 2H), 7.40-7.33 (m, 3H), 3.26-3.08 (m, 3H), 2.70 (d, J = 6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 141.3, 140.4, 133.4, 129.7, 129.0, 128.1, 127.8, 127.2, 118.6, 115.6, 36.8, 30.2, 20.3. Anal. Calcd. for $C_{17}H_{14}N_2$: C, 82.90; H, 5.73; N, 11.37. Found: C, 82.8; H, 5.9; N, 11.3.

*2-(4-Chlorobenzyl)succinonitrile (**13**).* White solid (68 mg, 44% yield). Purification: silica gel chromatography (hexane/ethyl acetate 8:2). M.p.: 79-82 °C (Lit.[43] 80-82 °C). The spectroscopic data of **13** were in accordance with the literature.[14] Anal. Calcd. for $C_{11}H_9ClN_2$: C, 64.56; H, 4.43; N, 13.69. Found: C, 64.4; H, 4.5; N, 13.6.

*2-(4-Fluorobenzyl)succinonitrile (**14**).* Colorless oil, that solidified upon standing (79 mg, 56% yield). Purification: silica gel chromatography (hexane/ethyl acetate 8:2). M.p.: 82-85 °C (Lit.[43] 84-

86 °C). Spectroscopic data of **14** were in accordance with the literature.[43] Anal. Calcd. for $C_{11}H_9FN_2$: C, 70.20; H, 4.82; N, 14.88. Found: C, 70.1; H, 4.9; N, 14.8.

*2-(4-(Trifluoromethyl)benzyl)succinonitrile (**15**).* Colorless oil (79 mg, 44% yield). Purification: silica gel chromatography (hexane/ethyl acetate 8:2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 3.28-3.08 (m, 3H), 2.70 (d, *J* = 5.9 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.6 (s), 130.5 (q, *J* = 33 Hz), 129.7 (s), 126.2 (q, *J* = 4 Hz), 123.7 (q, *J* = 272 Hz), 118.5 (s), 115.5 (s), 36.8 (s), 30.0 (s), 20.4 (s). Anal. Calcd. for $C_{12}H_9F_3N_2$: C, 60.51; H, 3.81; N, 11.76. Found: C, 60.4; H, 3.9; N, 11.8.

*tert-Butyl (4-(2,3-dicyanopropyl)phenyl)carbamate (**16**).* White solid (169 mg, 79% yield). Purification: silica gel chromatography (hexane/ethyl acetate 8:2). M.p.: 146-148 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.5 Hz, 2H), 7.20 (d, *J* = 8.5 Hz, 2H), 6.49 (s, 1H), 3.24-2.88 (m, 3H), 2.63 (d, *J* = 5.9 Hz, 2H), 1.52 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.8, 138.5, 129.9, 128.8, 119.2, 119.1, 118.6, 115.6, 36.5, 30.3, 28.5, 20.1. Anal. Calcd. for $C_{16}H_{19}N_3O_2$: C, 67.35; H, 6.71; N, 14.73. Found: C, 67.2; H, 6.9; N, 14.6.

*2-(1,3-Benzodioxol-5-ylmethyl)succinonitrile (**17**).* Colorless oil (114 mg; 71% yield). Purification: silica gel chromatography (hexane/ethyl acetate 8:2). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.79 (d, *J* = 8.0 Hz, 1H), 6.76-6.69 (m, 2H), 5.97 (s, 2H), 3.18-2.91 (m, 3H), 2.65 (d, *J* = 6.3 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 148.3, 147.6, 128.0, 122.6, 118.7, 115.7, 109.3, 108.9, 101.4, 36.8, 30.3, 20.1. Anal. Calcd. for $C_{12}H_{10}N_2O_2$: C, 67.28; H, 4.71; N, 13.08. Found: C, 67.2; H, 4.9; N, 13.0.

*2-(Thiophen-2-ylmethyl)succinonitrile (**18**).* Slightly yellow oil (69 mg; 52% yield). Purification: silica gel chromatography (hexane/ethyl acetate 8:2). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.29 (dd, *J* = 5, 2 Hz, 1H), 7.12-6.97 (m, 2H), 3.43-3.13 (m, 3H), 2.75-2.67 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 135.9, 127.8, 127.6, 125.9, 118.4, 115.5, 31.3, 30.4, 20.0. Anal. Calcd. for $C_9H_8N_2S$: C, 61.34; H, 4.58; N, 15.90. Found: C, 61.4; H, 4.7; N, 15.8.

*2-(1-Phenylethyl)succinonitrile (**19**).* Colorless oil (111 mg; 80% yield; 1:1 mixture of diastereoisomers). Purification: silica gel chromatography (hexane/ethyl acetate 9:1). Spectroscopic data of **19** were in accordance with the literature.[14] Anal. Calcd. for $C_{12}H_{12}N_2$: C, 78.23; H, 6.57; N, 15.21. Found: C, 78.1; H, 6.6; N, 15.2

*2-(1-(4-Isobutylphenyl)ethyl)succinonitrile (**20**).* Colorless oil (103 mg; 57% yield; 1:1 mixture of diastereoisomers). Purification: silica gel chromatography (hexane/ethyl acetate 9:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28-7.12 (m, 8H), 3.22-2.95 (m, 4H), 2.65-2.37 (m, 8H), 1.93-1.82 (m, 2H), 1.57 (d, *J* = 7 Hz, 3H), 1.56 (d, *J* = 7 Hz, 3H), 0.93 (d, *J* = 7 Hz, 6H), 0.92 (d, *J* = 7 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.1, 142.0, 137.5, 136.0, 130.2, 129.9, 127.6, 126.8, 118.5, 117.9, 116.0, 115.7, 45.1, 45.1, 41.1, 39.7, 36.1, 35.8, 30.3, 22.5, 22.5, 20.1, 19.7, 19.5, 19.2. Anal. Calcd. for $C_{16}H_{20}N_2$: C, 79.96; H, 8.39; N, 11.66. Found: C, 79.9; H, 8.5; N, 11.5.

*2-(1-(2-Fluoro-[1,1'-biphenyl]-4-yl)ethyl)succinonitrile (**21**).* White thick paste (184 mg; 88% yield; 1:1 mixture of diastereoisomers). Purification: silica gel chromatography (hexane/ethyl acetate 8:2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56-6.99 (m, 16H), 3.35-3.10 (m, 2H), 3.09-2.92 (m, 2H), 2.73-2.63 (m, 2H), 2.55-2.44 (m, 2H), 1.59 (d, *J* = 7 Hz, 3H), 1.58 (d, *J* = 7 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.9 (d, *J* = 248 Hz), 159.8 (d, *J* = 248 Hz), 141.4 (d, *J* = 7 Hz), 140.0 (d, *J* = 7 Hz), 135.1 (d, *J* = 8 Hz), 135.1 (d, *J* = 8 Hz), 131.9 (d, *J* = 4 Hz), 131.6 (d, *J* = 4 Hz), 129.3 (d, *J* = 14 Hz), 129.2 (d, *J* = 14 Hz), 129.1, 129.0, 128.7, 128.7, 128.6, 128.2, 128.1, 127.5, 124.0 (d, *J* = 3 Hz), 123.3 (d, *J* = 3 Hz), 118.0, 117.6, 115.7, 115.6 (d, *J* = 23 Hz), 115.4, 114.8 (d, *J* = 23 Hz), 40.8, 39.7, 35.9, 35.6, 20.2, 19.6, 19.3. Anal. Calcd. for $C_{18}H_{15}FN_2$: C, 77.68; H, 5.43; N, 10.07. Found: C, 77.6; H, 5.5; N, 10.0.

*2-(Methoxy(phenyl)methyl)succinonitrile (**23**).* Colorless oil (117 mg; 78% yield; 1:1 mixture of diastereoisomers). Purification: silica gel chromatography (hexane/ethyl acetate 8:2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53-7.34 (m, 10H), 4.49-4.43 (m, 2H), 3.35 (s, 3H), 3.31 (s, 3H), 3.26-3.11 (m, 2H), 2.97-2.60 (m, 4H). ^{13}C NMR (75 MHz, CDCl3) δ 135.8, 135.8, 129.7, 129.6, 129.2, 129.2,

127.1, 126.9, 117.0, 116.9, 115.9, 115.8, 81.0, 80.8, 57.5, 57.4, 36.7, 36.3, 18.4, 17.8. Anal. Calcd. for $C_{12}H_{12}N_2O$: C, 71.98; H, 6.04; N, 13.99. Found: C, 71.8; H, 6.1; N, 13.9.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. Copies of ^{1}H NMR and ^{13}C NMR of all compounds; details on the electrochemical investigation and on the optimization of reaction conditions (PDF).

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Notes

The authors declare no competing financial interest.

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