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Smooth Photocatalytic Preparation of 2-Substituted 1,3-Benzodioxoles

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Abstract: A mild and general method for the synthesis of potentially bioactive 2-substituted-1,3-benzodioxoles is presented. This is based on the photocatalyzed activation of methylene hydrogen atoms in the presence of tetrabutylammonium decatungstate (TBADT). The method gave yields ranging from 46–77% with no interference by benzene ring substituents, such as OR, COOMe, Me, or CHO. The OH group interfered, but protection regenerated the reactivity. 5-Chloro-1,3-benzodioxole was converted into a safrole derivative through a one-pot process involving two consecutive irradiations, at 366 nm for the photocatalyzed alkylation at position 2 and at 310 nm for the alkylation at position 5.

Keywords: alkylation · benzodioxoles · C–H activation · photocatalysis · radical reactions

Introduction

The 1,3-benzodioxole moiety is present in many biologically active molecules with antitumor, antioxidant, antibacterial, and insecticidal activity. A few examples among many are Tadalafil (a PDE5 inhibitor used for the treatment of erectile dysfunction with the commercial name of Cialis), the well-known methamphetamine Ecstasy (a psychoactive drug), Safrole (a sassafras plant extract, formerly used in perfumery but nowadays banned because of its weak carcinogenic activity), and piperonyl butoxide (widely employed as a pesticide synergist). The marked biological activity that the 1,3-benzodioxole fragment imparts to these molecules depends on the presence of the methylenedioxy moiety, which is known to inhibit some enzymes and to promote Cytochrome P-450 induction.[1,2] This has stimulated studies aimed both at the preparation of 1,3-benzodioxole derivatives in view of their possible cytotoxic and antitumor activity[3] and to the isolation from plants of bioactive constituents of such a structure.[4]

Less attention has been paid to 2-substituted-1,3-benzodioxoles, considered to be less bioactive. However, there is some indication in the literature that introducing an alkyl or substituted alkyl group at position 2 modifies the activity[5] or makes it specific towards some classes of enzymes (e.g. for epoxide hydrolase)[6] rather than eliminating it. These compounds are usually prepared by condensation of a (substituted) catechol and a carbonyl derivative,[7,8] although the method is unsatisfactory when using low-boiling aldehydes or ketones.[9] The alternative derivatization at position 2 of the preformed 1,3-benzodioxole ring has likewise been applied with some success for the introduction of a chlorine or of a O-bonded substituent.[10,11]

The introduction of a C-bonded substituent has been rarely reported (see the Discussion Section). An appealing entry would involve H abstraction leading to the 1,3-benzodioxol-2-yl radical and trapping, a process for which photocatalysis[12] has been shown to be a valid option. In particular, tetrabutylammonium decatungstate salt ($(n\mathrm{Bu_4N})_4\mathrm{W_{10}O_{32}}$, TBADT) is a robust and easily prepared[13] photocatalyst[14] that has proven effective for the activation of C–H bonds in various classes of organic molecules, including aldehydes,[15] amides,[16] and even cycloalkanes.[17] Excited TBADT abstracts a hydrogen atom from the reagent and is regenerated by back H transfer in the last step of the reaction, so that light is actually the stoichiometric reagent[18] (see Scheme 12). The carbon radical thus formed is the key intermediate for the mild alkylation of enones, unsaturated esters, and nitriles.[14a] Preliminary experiments[13,19] showed that α-oxyalkyl radicals were likewise easily obtained by hydrogen abstraction from a few ethers and one acetal. Accordingly, it appeared worthwhile to test the alkylation at position 2 of 1,3-benzodioxoles by TBADT photocatalysis.

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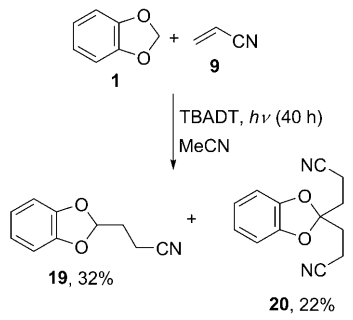
Results

The TBADT-photocatalyzed reaction of a few 1,3-benzodioxoles (**1**–**8**) with electrophilic alkenes (**9**–**18**) was studied to assess the feasibility and the scope of the reaction. Blank experiments showed that parent 1,3-benzodioxole (**1**) was not appreciably consumed when irradiated in neat acetonitrile for 40 h by means of phosphor-coated lamps (λ_{irr} = 366 nm, see the Experimental Section and Supporting information) and to a modest degree (ca. 10%) when in the presence of TBADT (2 mol%), although no byproducts were detected by GC analysis. Moreover, in the absence of TBADT, **1** was likewise unreactive when irradiated in the presence of acrylonitrile (**9**).

Parent benzodioxole: The photolysis of an acetonitrile mixture of **1** (0.11 M), **9** (0.1 M), and TBADT (2×10^{-3} M) efficiently led to the formation of nitrile **19** as the major product (32% yield) along with dinitrile **20** (22%, Scheme 1).



Scheme 1.

The use of a slight excess of **1** was required to obtain the best overall alkylation yield. To our delight, the reaction with dimethyl maleate (**10**) under the same conditions gave diester **21** in 63% yield as the exclusive product (Scheme 2 and Table 1). Doubling the concentrations of both reagents (**1**: 0.22 M, **10**: 0.2 M) led likewise to the formation of **21** in similar yields and with a comparable irradiation time (40 h). Moreover, (*E*)-2-hexenal gave substituted aldehyde **22** in a satisfactory yield (56%), with no competitive activation of

Table 1. Photocatalyzed preparation of 2-substituted-1,3-benzodioxoles.[a]

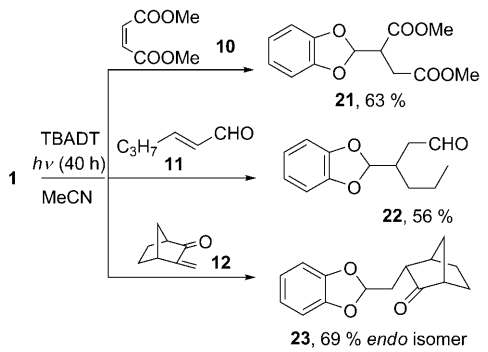
Entry	Benzodioxole (0.11 M)	Olefin (0.1 M)	Products (yields [%])[b]
1	**1** (R = R^1 = H)	**9**	**19** (32), **20** (22)
2	**1**	**10**	**21** (63, 65[c])
3	**1**	**11**	**22** (56)
4	**1**	**12**	**23** (69)[d]
5[e]	**1**	**13**	**24** (66), **25** (22)
6	**2** (R = COOMe; R^1 = H)	**14**	**26** (65)
7	**3** (R = Cl; R^1 = H)	**15**	**27** (56)
8	**3**	**16**	**28** (51)
9	**4** (R = CH_3; R^1 = H)	**17**	**29** (70)
10	**5** (R = CH_2OAc; R^1 = H)	**18**	**30** (46)
11	**5**	**17**	**31** (61)
12	**6** (R = CHO; R^1 = H)	**10**	**32** (60)
13	**7** (R = OCOOEt; R^1 = H)	**14**	**33** (75)
14	**8** (R = H; R^1 = Me	**9**	**34** (65)
15[e]	**8**	**13**	**35** (77)

[a] Reaction conditions: **1**–**8**, (0.11 M), **9**–**18** (0.1 M), TBADT (2×10^{-3} M) in MeCN irradiated at 366 nm until the olefin was consumed (40 h). [b] Isolated yields; no other significant photoproduct was detected by GC-MS analysis. [c] **1**, (0.22 M), **10** (0.2 M). [d] The *endo* isomer has been obtained exclusively. [e] Irradiation time: 24 h.

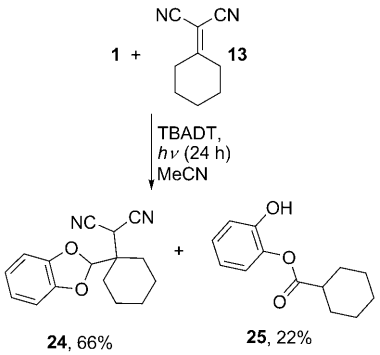
the aldehyde hydrogen atom that could compete with the dioxolane CH_2 as a hydrogen donor; a bulky α,β-unsaturated ketone such as **12** gave the *endo* isomer[20] of norbornanone **23** as the exclusive product in 69% yield (Scheme 2).

The alkylation was extended to tetrasubstituted electrophilic alkenes by using 1,1-dinitrile **13**. With **13** the reaction was successful, although the expected product **24** (66% yield) was accompanied by an open-chain byproduct in which malononitrile was lost (**25**, 22%, Scheme 3). To assess whether compound **25** was a secondary photoproduct, a MeCN solution of **24** (0.1 M) was irradiated at 366 nm for 18 h but the starting dinitrile was not consumed.

On the other hand, **24** reacted (60% consumption) when irradiated in the presence of TBADT for the same time as in the original reaction, with the formation of a significant amount of **25**. The photocatalyzed reaction between **1** and



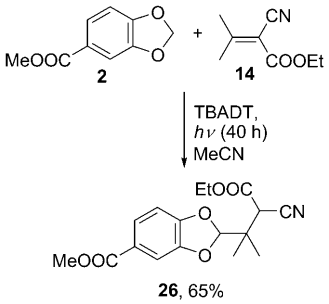
Scheme 2.



Scheme 3.

13 was further explored under buffered conditions in the presence of solid $NaHCO_3$. In this case, the yield of compound **24** was unaffected, whereas a new compound with *m*/*z*: 202 (as detected by GC-MS analysis, see the Discussion Section) was formed at the expense of **25**.

Substituted 1,3-benzodioxoles: A few derivatives were next considered to determine the tolerance of substituents. Ester **2** was tested with tetrasubstituted olefins. With isopropylidene malonate only a sluggish photoreaction occurred, albeit formation of the desired adduct was detected by GC analysis. With isopropylidene cyanoacetate (**14**), however, it reacted completely (40 h irradiation) and functionalized benzodioxole **26** was formed as the only adduct in a satisfactory yield (65%, Scheme 4). With piperonylic acid, on the other hand, no useful reaction occurred.

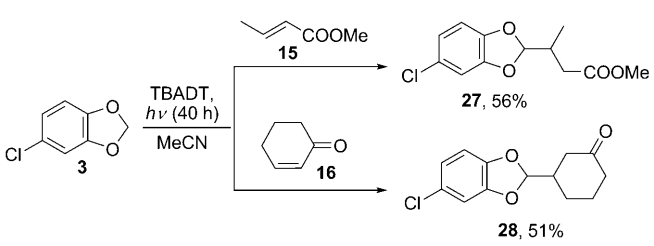


Scheme 4.

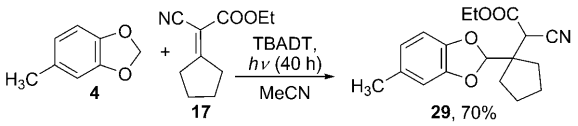
5-Chloro-1,3-benzodioxole (**3**) is known to undergo smooth heterolytic cleavage of the Ar–Cl bond upon direct irradiation.[22,23] Under the present photocatalytic conditions, however, no chloride-free products were detected in the presence of either methyl crotonate (**15**) or cyclohexenone (**16**), in which the alkylation products **27** and **28**, respectively, were formed in a decent yield (50–60%, Scheme 5).

5-Methyl-1,3-benzodioxole (**4**) gave the expected cyanoester **29** in 70% isolated yield in the presence of the olefin **17** and TBADT (Scheme 6), with no interference by benzylic hydrogen atoms.

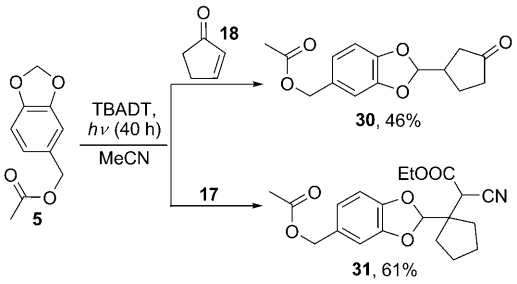
On the contrary, piperonyl alcohol gave no adduct after 40 h irradiation in the presence of cyclopentenone **18** and TBADT. On the other hand, protection of the benzylic –OH group as a *tert*-butyldimethylsilyl ether (–OTBS) allowed the sluggish formation of a new product, as determined by GC analysis. Protection as an acetate (benzodioxole **5**) was more effective and under these conditions a complete reaction and formation of alkylated products **30** (46% isolated yield with cyclopentenone **18**) and **31** (61% with cyanoester **17**, Scheme 7) were achieved.



Scheme 5.

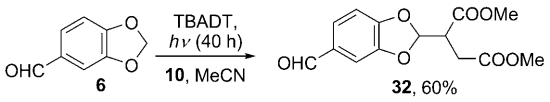


Scheme 6.



Scheme 7.

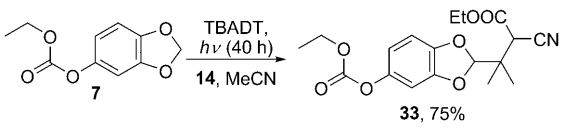
Piperonal (**6**) was chosen to assess the competition with the aromatic aldehyde group, recently demonstrated to be effectively activated by TBADT photocatalysis.[13,15b,21] In the experiment, activation of the benzodioxole CH_2 was exclusive, as witnessed by the reaction with maleate **10** to yield **32** (Scheme 8).



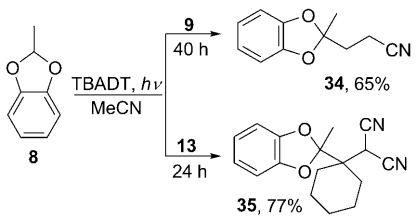
Scheme 8.

A phenolic group interfered, however, and 3,4-methylenedioxyphenol (sesamol) was only partially consumed (ca. 30%) under photocatalyzed conditions in the presence of alkene **14**, but no adduct was detected. Protection of the OH group as a carbonate (**7**), however, regenerated the reactivity, as illustrated in Scheme 9.

Interference by substituents at the CH_2 group was next investigated by reacting the 2-methyl derivative **8**. A clean photocatalyzed addition was obtained both with a β-unsubstituted (acrylonitrile **9**, to give nitrile **34** in 65% isolated yield) and with a β,β-disubstituted alkene (dinitrile **13**, to give benzodioxole **35** in a 77% yield, Scheme 10).



Scheme 9.



Scheme 10.

One-pot, consecutive photochemical functionalization: The last reaction considered was a proof of concept for the one-pot functionalization of 1,3-benzodioxole based on two consecutive photochemical steps, namely, both the photocatalytic reaction described in the present work and the recently reported arylation via a phenyl cation.[23,24] As mentioned above, chlorobenzodioxole **3** was functionalized only at the CH_2 under TBADT photocatalysis (Scheme 5). The reaction was repeated with alkene **14** and, by the usual irradiation at 366 nm, afforded adduct **36** (not isolated, Scheme 11). Addition of water and allyltrimethylsilane (**37**) to the crude photolysate and further irradiation at a shorter wavelength (310 nm) caused Ar–Cl bond scission and the formation of safrole derivative **38** in 35% yield (from **14**) along with some byproducts (such as dechlorinated compound **1** and safrole, <5% overall) arising from excess **3** still present during the second photochemical step. The role of water is that of enhancing polarity and favoring chloride anion loss,[22] while hindering a possible second TBADT photocatalytic alkylation.[25]

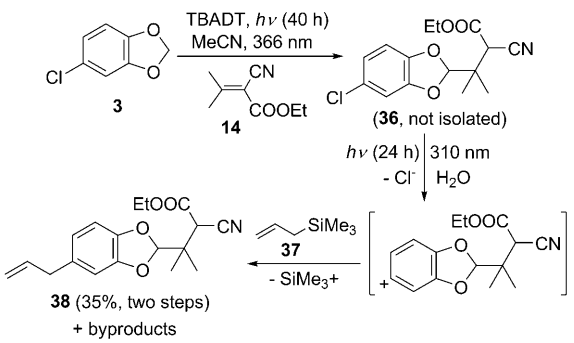
Discussion

The generation of α-oxy and α,α-dioxy radicals from ethers or 1,3-dioxolanes is easily obtained.[26,27] As an example, such radicals are generated by treatment of ethers with pyrophoric Me_2Zn (2 equiv) and $BF_3{\cdot}Et_2O$ (2 equiv),[26a] with *N*-hydroxyphthalimide as the catalyst in the presence of benzoyl peroxide at 80 °C[26c] or under a Et_3B (6 equiv)/air system.[26d] The photochemical activation of the α-oxy C–H bonds likewise occurs by using a 40% equivalent of a photomediator, such as benzophenone.[27] Thus, the known procedures require a large amount of activator and a large excess of the ether (from 15 to 250 equiv, in some cases used as the reaction medium[27a]).

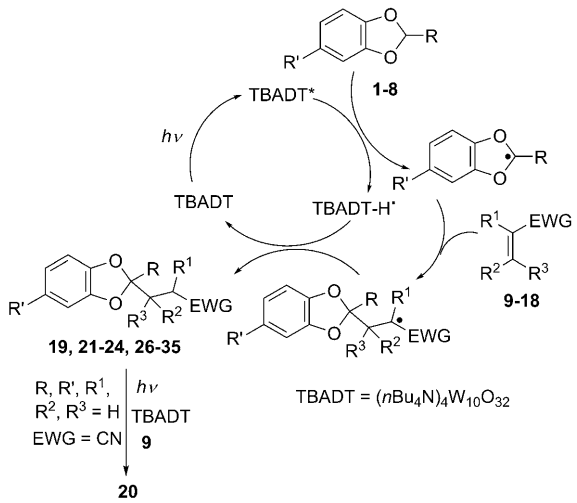
As for the specific case of 1,3-benzodioxole, only sparse results have been reported.[28,29] Thus, generation of the 1,3-benzodioxol-2-yl radical by using *tert*-butoxyl radicals as initiators at 140 °C led to ring opening[28] and only a poor alkylation occurred in the presence of nucleophilic olefins.[28] α-Oxy radicals have been recently generated from 1,3-benzodioxole by using dimethylzinc (6 equiv)/air and shown to add to *N*-sulfinyl imines in a satisfactory yield, but the starting dioxole had to be used in a large excess (250 equiv).[29] To our knowledge, no substituted 1,3-benzodioxoles have been tested in such reactions.

On the other hand, the anionic activation in 1,3-benzodioxole derivatives is troublesome due to the low acidity of the CH_2 hydrogen atoms, which require a strong base for deprotonation. Furthermore, the treatment of 1,3-benzodioxole with lithium or sodium diethylamide leads to reductive cleavage of the ether bond and to ring opening[30] and more elaborate alternatives have been considered, for example, a preliminary chlorination.[31]

On the contrary, the present method by means of TBADT photocatalysis, summarized in Scheme 12, was demonstrated to be a viable alternative for the mild preparation of 2-substituted-1,3-benzodioxoles via radicals. The reaction requires only 10% excess reagent, operates at a reasonable starting concentration, and is experimentally very simple. The effective activation at room temperature avoids the above-mentioned cleavage of radicals[28] and avoids inhibition by an alkyl substituent at position 2 (see the case of 2-methylbenzodioxole **8**). On the other hand, this characteristic may lead to double alkylation, as seen in the formation of compound **20** from **1** and acrylonitrile, a phenomenon that is limited to this nonhindered alkene, however. In the other cases the alkylation is indeed clean and general in scope. Apparently, as long as a hydrogen atom is present at position 2, alkylation at this position is



Scheme 11.



Scheme 12. EWG = electron-withdrawing group.

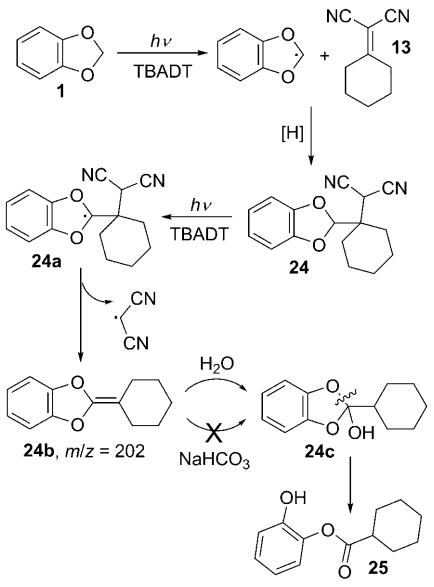
exclusive as shown in the cases of intramolecular selectivity above. For example, no significant (<1%) reaction at a benzylic position (**4**, **5**) or at an aromatic aldehyde group (**6**) takes place.

However, the phenolic O–H bond in sesamol (BDE estimated around 86–88 kcal mol^{-1})[32] interfered and the benzylic hydrogen atoms in piperonyl alcohol (87.5 kcal mol^{-1} for benzyl alcohol)[32] completely inhibited the reaction. In both cases, however, protection of the OH group as a carbonate or as an ester regenerated the reactivity and allowed an easy derivatization of the benzodioxole. A detailed study on the origin of such an interesting chemoselectivity is currently under investigation.

In a single case a secondary process was detected, namely, the reaction between **1** and dinitrile **13** in which loss of malononitrile from the primary product is significant (see Scheme 13).[33] This can be rationalized by a secondary hydrogen abstraction from **24** to yield radical **24a** and, by loss of the stable dicyanomethyl radical,[34] vinyl acetal **24b** (*m*/*z*: 202, identified by GC-MS) and ester **25** via **24c** by addition of adventitious water. The last reaction was catalyzed by a trace of acid since addition of bicarbonate prevented any thermal reaction of **24b**.[35] This secondary conversion probably occurs to some degree in all of the reactions from benzodioxoles **1**–**7**, but has no consequence because back hydrogen transfer from reduced TBADT is faster than addition to alkenes, except when a nonhindered radical reacts with the least-hindered alkene, namely, acrylonitrile, as indeed for the case of **20** from **19** (Scheme 12). This general scheme was confirmed by the preparation of **35** for which stability was assured by the lack of any methylene hydrogen atom in position 2 (see Scheme 10).

1,1-Disubstituted olefins, such as **13**, **14**, and **17**, have been proven to be the best radical traps among the olefins tested in this work. In fact, high alkylation yields and short irradiation times were obtained, despite the sterical hindrance in the β-position (see the Experimental Section).

In the case of 5-chloro-1,3-benzodioxole (**3**), either the Ar–Cl or the methylene C–H bonds were photoactivated depending on the irradiation wavelength and the reaction media used and an uncommon one-pot synthesis by two consecutive photochemical reactions was achieved (see Scheme 11).



Scheme 13.

Conclusion

A smooth synthesis of (mostly new) 2-substituted-1,3-benzodioxoles has been disclosed. This exploits the TBADT photocatalytic (2% equiv) chemoselective activation of the methylene hydrogen atoms in 1,3-benzodioxole derivatives. The reaction takes place under mild conditions and offers an unprecedented, general access for the preparation of a class of compounds of potential biological activity.

Experimental Section

General: NMR spectra were recorded on a 300 MHz spectrometer. The attributions were made on the basis of ^{1}H and ^{13}C NMR spectra, as well as DEPT experiments; chemical shifts are reported in ppm downfield from TMS. Compounds **1**, **3**, **4**, **6**, **9**–**12**, **15**, **16**, **18**, and **37** were commercially available and compounds **1**, **3**, **4**, **9**–**12**, **15**, **16**, **18**, and **37** were freshly distilled before use. Acetonitrile (HPLC purity grade) was purchased from Carlo Erba and used as received. Compound **5** was synthesized by starting from equimolar amounts of piperonyl alcohol and acetyl chloride in CH_2Cl_2 in the presence of 1.1 equiv of triethylamine (colorless oil, quantitative yield). Spectroscopic data of compound **5** are in accordance with the literature.[37] Compounds **2**,[38] **7**,[39] **8**,[9] **13**,[40] **14**,[41] and **17**[42] were synthesized according to published procedures.

General procedure for the photocatalyzed synthesis of 2-substituted 1,3-benzodioxole: A solution (30 mL) of a 1,3-benzodioxole (**1**–**8**, 0.11 M) and an olefin (**9**–**18**, 0.1 M) in the presence of TBADT[13] (200 mg, 2×10^{-3} M) in MeCN was poured in quartz tubes and purged for 10 min with nitrogen, serum capped, and then irradiated for 24–40 h with 12 15 W phosphor-coated lamps (emission centered at 366 nm) by means of a multilamps apparatus (Helios Italquartz, Italy). The solvent was removed in vacuo from the photolyzed solutions and the products isolated by purification of the residue by column chromatography (cyclohexane/ethyl acetate as eluants).

Photochemical reaction between 1,3-benzodioxole (1) and acrylonitrile (9): 1,3-benzodioxole (**1**, 380 μL, 3.3 mmol, 0.11 M), acrylonitrile (**9**, 200 μL, 3.0 mmol, 0.10 M), and TBADT (200 mg, 0.06 mmol, 2×10^{-3} M) were dissolved in acetonitrile (30 mL) and irradiated for 40 h at 366 nm. After removing the solvent in vacuo and purification of the residue by column chromatography (silica gel, eluent: cyclohexane/ethyl acetate 99:1), 3-(1,3-benzodioxol-2-yl)propanenitrile (**19**, 168 mg, 32%) and 3,3′-(1,3-benzodioxol-2,2-diyl)dipropanenitrile (**20**, 151 mg, 22%) were obtained as colorless oils (overall yield: 54%). Compound **20** solidified upon standing.

*3-(1,3-Benzodioxol-2-yl)propanenitrile (**19**)*: ^{1}H NMR ($CDCl_3$): $\delta=2.3$ (dt, $J=8$, 4 Hz, 2H), 2.6 (t, $J=8$ Hz, 2H), 6.2 (d, $J=4$ Hz, 1H), 6.8–6.9 ppm (m, 4H); ^{13}C NMR ($CDCl_3$): $\delta=10.8$ (CH_2), 30.0 (CH_2), 108.4 (CH), 108.7 (CH), 118.5, 121.8 (CH), 147.0 ppm; IR (neat): $\tilde{\nu}=1236$, 1485, 2252 cm^{-1}; elemental analysis calcd (%) for $C_{10}H_9NO_2$: C 68.56, H 5.18, N 8.00; found: C 68.5, H 5.2 N 8.1.

*3,3′-(1,3-Benzodioxol-2,2-diyl)dipropanenitrile (**20**)*: M.p. 68–71 °C; ^{1}H NMR ($CDCl_3$): $\delta=2.3$ (t, $J=8$ Hz, 4H), 2.6 (t, $J=8$ Hz, 4H), 6.8–

6.9 ppm (m, 4H); ^{13}C NMR ($CDCl_3$): $\delta=10.9$ (CH_2), 33.7 (CH_2), 108.8 (CH), 115.5, 118.4 , 122.2 (CH), 146.6 ppm; IR (KBr): $\tilde{\nu}=1237$, 1485, 2250 cm^{-1}; elemental analysis calcd (%) for $C_{13}H_{12}N_2O_2$: C 68.41, H 5.30, N 12.27; found: C 68.4, H 5.4, N 12.1.

Dimethyl 2-(1,3-benzodioxol-2-yl)succinate (21): 1,3-Benzodioxole (**1**, 380 μL, 3.3 mmol, 0.11 M), dimethyl maleate (**10**, 375 μL, 3.0 mmol, 0.10 M), and TBADT (200 mg, 0.06 mmol, 2×10^{-3} M) were dissolved in acetonitrile (30 mL) and irradiated for 40 h at 366 nm. After removing the solvent in vacuo and purification of the residue by column chromatography (silica gel, eluant: cyclohexane/ethyl acetate 9:1), dimethyl 2-(1,3-benzodioxol-2-yl)succinate (**21**, 503 mg, 63%) was obtained as a colorless oil, which solidified upon standing. A similar yield (65%) was obtained when a solution containing **1** (0.22 M) and **10** (0.2 M) was irradiated for 40 h. M.p. 76–79 °C; ^{1}H NMR ($CDCl_3$): $\delta=2.7$–3.0 (2H; AB part of an ABX system), 3.4–3.5 (1H; X part of an ABX system), 3.8 (s, 3H), 3.9 (s, 3H), 6.4 (d, $J=4$ Hz, 1H), 6.8–6.9 ppm (m, 4H); ^{13}C NMR ($CDCl_3$): $\delta=29.1$ (CH_2), 46.3 (CH), 51.9 (CH_3), 52.5 (CH_3), 108.5 (CH), 109.0 (CH), 121.8 (CH), 146.9, 170.0, 171.6 ppm; IR (KBr): $\tilde{\nu}=1238$, 1488, 1728 cm^{-1}; elemental analysis calcd (%) for $C_{13}H_{14}O_6$: C 58.64, H 5.30; found: C 58.7, H 5.3.

3-(1,3-Benzodioxol-2-yl)hexanal (22): 1,3-Benzodioxole (**1**, 380 μL, 3.3 mmol, 0.11 M), *trans*-2-hexenal (**11**, 350 μL, 3.0 mmol, 0.10 M), and TBADT (200 mg, 0.06 mmol, 2×10^{-3} M) were dissolved in acetonitrile (30 mL) and irradiated for 40 h at 366 nm. After removing the solvent in vacuo and purification of the residue by column chromatography (silica gel, eluant: cyclohexane/ethyl acetate 95:5), 3-(1,3-benzodioxol-2-yl)-hexanal (**22**, 370 mg, 56%) was obtained as a colorless oil. ^{1}H NMR ($CDCl_3$): $\delta=0.9$–1.1 (m, 3H), 1.3–1.5 (m, 3H), 1.5–1.7 (m, 1H), 2.3–2.5 (m, 1H), 2.5–2.7 (m, 2H), 6.1 (d, $J=5$ Hz, 1H), 6.7–6.8 (m, 4H), 9.8 ppm (s, 1H); ^{13}C NMR ($CDCl_3$): $\delta=14.0$ (CH_3), 20.0 (CH_2), 31.3 (CH_2), 37.4 (CH), 42.2 (CH_2), 108.3 (CH), 112.2 (CH), 121.5 (CH), 147.4, 147.5, 200.9 ppm; IR (neat): $\tilde{\nu}=1236$, 1486, 1727 cm^{-1}; elemental analysis calcd (%) for $C_{13}H_{16}O_3$: C 70.89, H 7.32; found: C 70.8, H 7.4.

3-(1,3-Benzodioxol-2-ylmethyl)bicyclo[2.2.1]heptan-2-one (23): 1,3-Benzodioxole (**1**, 380 μL, 3.3 mmol, 0.11 M), 3-methylene-2-norbornanone (**12**, 370 μL, 3.0 mmol, 0.10 M), and TBADT (200 mg, 0.06 mmol, 2×10^{-3} M) were dissolved in acetonitrile (30 mL) and irradiated for 40 h at 366 nm. After removing the solvent in vacuo and purification of the residue by column chromatography (silica gel, eluant: cyclohexane/ethyl acetate 9:1), 3-(1,3-benzodioxol-2-ylmethyl)bicyclo[2.2.1]heptan-2-one (**23**, 506 mg, 69%, *endo* isomer) was obtained as a colorless oil, which solidified upon standing. M.p. 45–47 °C; ^{1}H NMR ($CDCl_3$): $\delta=1.3$–1.5 (m, 1H), 1.5–1.8 (m, 4H), 1.8–2.0 (m, 2H), 2.2–2.4 (m, 2H), 2.6–2.8 (m, 2H), 6.2 (d, $J=4$ Hz, 1H), 6.8–6.9 ppm (m, 4H); ^{13}C NMR ($CDCl_3$): $\delta=21.3$ (CH_2), 25.3 (CH_2), 30.9 (CH_2), 37.1 (CH_2), 39.2 (CH), 48.6 (CH), 49.8 (CH), 108.4 (CH), 110.5 (CH), 121.4 (CH), 147.3, 147.4, 218.2 ppm; IR (KBr): $\tilde{\nu}=1234$, 1484, 1742 cm^{-1}; elemental analysis calcd (%) for $C_{15}H_{16}O_3$: C 73.75, H 6.60; found: C 73.8, H 6.5.

Photochemical reaction between 1,3-benzodioxole (1) and cyclohexylidene malononitrile (13): 1,3-Benzodioxole (**1**, 380 μL, 3.3 mmol, 0.11 M), cyclohexylidene malononitrile (**13**, 430 μL, 3.0 mmol, 0.10 M), and TBADT (200 mg, 0.06 mmol, 2×10^{-3} M) were dissolved in acetonitrile (30 mL) and irradiated for 24 h at 366 nm. After removing the solvent in vacuo and purification of the residue by column chromatography (silica gel, eluant: cyclohexane/ethyl acetate 9:1), 2-[1-(1,3-benzodioxol-2-yl)cyclohexyl]malononitrile (**24**, 531 mg, 66%) and 2-hydroxyphenyl cyclohexanecarboxylate (**25**, 145 mg, 22%) were obtained as colorless oils (overall yield: 88%). Compound **24** solidified upon standing.

*2-[1-(1,3-Benzodioxol-2-yl)cyclohexyl]malononitrile (**24**)*: M.p. 80–83 °C; ^{1}H NMR ($CDCl_3$): $\delta=1.5$–1.8 (m, 6H), 1.8–1.9 (m, 2H), 2.0–2.1 (m, 2H), 4.1 (s, 1H), 6.3 (s, 1H), 6.8–6.9 ppm (m, 4H); ^{13}C NMR ($CDCl_3$): $\delta=20.8$ (2CH_2), 24.6 (CH_2), 27.5 (CH), 28.6 (2CH_2), 44.1, 109.0 (2CH), 110.5 (CH), 111.2, 122.2 (2CH), 146.7 ppm; IR (KBr): $\tilde{\nu}=1234$, 1484, 2251 cm^{-1}; elemental analysis calcd (%) for $C_{16}H_{16}N_2O_2$: C 71.62, H 6.01, N 10.44; found: C 71.7, H 6.0, N 10.5; MS *m*/*z*: 269 $[M+1]^+$ (20), 122 (100).

*2-Hydroxyphenyl cyclohexanecarboxylate (**25**)*: ^{1}H NMR ($CDCl_3$): $\delta=$ 1.3–1.5 (m, 3H), 1.6–1.8 (m, 3H), 1.8–1.9 (m, 2H), 2.0–2.2 (m, 2H), 2.6 (dt, $J=11$, 4 Hz, 1H), 5.7 (br s, 1H), 6.8–7.0 (m, 2H), 7.0–7.2 ppm (m, 2H); ^{13}C NMR ($CDCl_3$): $\delta=25.2$ (2 CH_2), 25.5 (CH_2), 28.9 (2 CH_2), 43.1 (CH), 117.7 (CH), 120.8 (CH), 122.2 (CH), 126.7 (CH), 138.7, 147.1, 174.6 ppm; IR (neat): $\tilde{\nu}=3403$, 1732, 1598, 1231, 1162 cm^{-1}; elemental analysis calcd for $C_{13}H_{16}O_3$: C 70.89, H 7.32; found: C 70.8, H 7.3; MS *m*/*z*: 220 $[M]^+$ (10), 110 (80), 83 (80), 55 (100); the same reaction, when performed in the presence of $NaHCO_3$ (200 mg) yielded malononitrile **24** again and a new byproduct, namely, 2-cyclohexylidene-1,3-benzodioxole (**24b**), as identified by GC-MS analysis (MS *m*/*z*: 203 $[M+1]^+$ (100), 174 (30), 146 (20), 135 (20), 83 (20)).

Methyl 2-(3-cyano-4-ethoxy-2-methyl-4-oxobutan-2-yl)-1,3-benzodioxole-5-carboxylate (26): Methyl 1,3-benzodioxole-5-carboxylate (**2**, 595 mg, 3.3 mmol, 0.11 M), ethyl isopropylidene cyanoacetate (**14**, 460 mg, 3.0 mmol, 0.10 M), and TBADT (200 mg, 0.06 mmol, 2×10^{-3} M) were dissolved in acetonitrile (30 mL) and irradiated for 40 h at 366 nm. After removing the solvent in vacuo and purification of the residue by column chromatography (silica gel, eluant: cyclohexane/ethyl acetate 9:1), methyl 2-(3-cyano-4-ethoxy-2-methyl-4-oxobutan-2-yl)-1,3-benzodioxole-5-carboxylate (**26**, 650 mg, 65%, equimolar mixture of two diastereoisomers) was obtained as a colorless oil. ^{1}H NMR ($CDCl_3$, mixture of diastereoisomers): $\delta=1.2$ (s, 3H), 1.25 (t, $J=7$ Hz, 3H), 1.3 (s, 3H), 3.8 (s, 1H), 3.9 (s, 3H), 4.3 (q, $J=7$ Hz, 2H), 6.2 (s, 1H), 6.8 (dd, $J=8$, 4 Hz, 1H), 7.5 (dd, $J=4$, 2 Hz, 1H), 7.7 ppm (dt, $J=8$, 2 Hz, 1H); ^{13}C NMR ($CDCl_3$, mixture of diastereoisomers): $\delta=13.8$ (CH_3), 18.4 (CH_3), 18.5 (CH_3), 19.7 (CH_3), 42.0, 43.4 (CH), 43.5 (CH), 52.0 (CH_3), 62.8 (CH_2), 107.7 (CH), 107.8 (CH), 109.2 (CH), 109.3 (CH), 114.0 (CH), 114.8, 124.3, 124.4, 125.3 (CH), 125.4 (CH), 147.5, 147.6, 151.2, 151.3, 164.2, 166.1 ppm; IR (neat): $\tilde{\nu}=1259$, 1284, 1497, 1719, 1745, 2251 cm^{-1}; elemental analysis calcd for $C_{17}H_{19}NO_6$: C 61.25, H 5.75, N 4.20; found: C 61.2, H 5.8, N 4.3.

Methyl 3-(5-chloro-1,3-benzodioxol-2-yl)butanoate (27): 5-Chloro-1,3-benzodioxole (**3**, 385 μL, 3.3 mmol, 0.11 M), methyl crotonate (**15**, 320 μL, 3.0 mmol, 0.10 M), and TBADT (200 mg, 0.06 mmol, 2×10^{-3} M) were dissolved in acetonitrile (30 mL) and irradiated for 40 h at 366 nm. After removing the solvent in vacuo and purification of the residue by column chromatography (silica gel, eluant: cyclohexane/ethyl acetate 95:5), methyl 3-(5-chloro-1,3-benzodioxol-2-yl)butanoate (**27**, 431 mg, 56%, equimolar mixture of two diastereoisomers) was obtained as a colorless oil. ^{1}H NMR ($CDCl_3$, mixture of diastereoisomers): $\delta=1.1$ (d, $J=7$ Hz, 3H), 2.2–2.4 (m, 1H), 3.6–3.7 (m, 2H), 3.7 (s, 3H), 6.1 (d, $J=4$ Hz, 1H), 6.6–6.7 (m, 1H), 6.7–6.8 ppm (m, 2H); ^{13}C NMR ($CDCl_3$, mixture of diastereoisomers): $\delta=13.3$ (CH_3), 13.3 (CH_3), 34.7 (CH_2), 34.7 (CH), 51.6 (CH_3), 108.4 (CH), 109.1 (CH), 114.1 (CH), 121.0 (CH), 125.9, 146.6, 148.4, 172.3 ppm; IR (neat): $\tilde{\nu}=1236$, 1484, 1737 cm^{-1}; elemental analysis calcd (%) for $C_{12}H_{13}ClO_4$: C 56.15, H 5.10; found: C 56.0, H 5.1.

3-(5-Chloro-1,3-benzodioxol-2-yl)cyclohexanone (28): 5-Chloro-1,3-benzodioxole (**3**, 385 μL, 3.3 mmol, 0.11 M), 2-cyclohexenone (**16**, 290 μL, 3.0 mmol, 0.10 M), and TBADT (200 mg, 0.06 mmol, 2×10^{-3} M) were dissolved in acetonitrile (30 mL) and irradiated for 40 h at 366 nm. After removing the solvent in vacuo and purification of the residue by column chromatography (silica gel, eluant: cyclohexane/ethyl acetate 95:5), methyl 3-(5-chloro-1,3-benzodioxol-2-yl)cyclohexanone (**28**, 431 mg, 51%, equimolar mixture of two diastereoisomers) was obtained as a colorless oil. ^{1}H NMR ($CDCl_3$, mixture of diastereoisomers): $\delta=1.6$–1.8 (m, 2H), 2.0–2.1 (m, 1H), 2.1–2.2 (m, 1H), 2.3–2.5 (m, 4H), 2.5–2.6 (m, 1H), 6.0 (d, $J=3$ Hz, 1H), 6.6–6.7 (m, 1H), 6.7–6.8 ppm (m, 2H); ^{13}C NMR ($CDCl_3$, mixture of diastereoisomers): $\delta=24.4$ (CH_2), 40.6 (CH_2), 41.2 (CH_2), 42.7 (CH), 108.5 (CH), 109.2 (CH), 113.3 (CH), 121.1 (CH), 126.1, 146.4, 148.2, 209.4 ppm; IR (neat): $\tilde{\nu}=1238$, 1485, 1715 cm^{-1}; elemental analysis calcd (%) for $C_{13}H_{13}ClO_3$: C 61.79, H 5.19; found: C 61.9; H 5.0.

Ethyl 2-cyano-2-[1-(5-methyl-1,3-benzodioxol-2-yl)cyclopentyl]acetate (29): 5-Methyl-1,3-benzodioxole (**4**, 3.3 mmol, 0.11 M), cyclopentylidene cyanoacetate (**17**, 538 mg, 3.0 mmol, 0.10 M), and TBADT (200 mg, 0.06 mmol, 2×10^{-3} M) were dissolved in acetonitrile (30 mL) and irradiated for 40 h at 366 nm. After removing the solvent in vacuo and purification of the residue by column chromatography (silica gel, eluant: cyclohexane/ethyl acetate 95:5), ethyl 2-cyano-2-[1-(5-methyl-1,3-benzodioxol-

2-yl)cyclopentyl]acetate (**29**, 70%, 662 mg, equimolar mixture of two diastereoisomers) was obtained as a colorless oil. ^{1}H NMR ($CDCl_3$, mixture of diastereoisomers): $\delta = 1.2$ (t, $J = 7$ Hz, 3H), 1.7–1.9 (m, 4H), 1.9–2.1 (m, 4H), 2.3 (s, 3H), 3.8 (s, 1H), 4.2 (q, $J = 7$ Hz, 2H), 6.1 (s, 1H), 6.5–6.7 ppm (m, 3H); ^{13}C NMR ($CDCl_3$, mixture of diastereoisomers): $\delta =$ 13.6 (CH_3), 21.1 (CH_3), 25.7 (CH_2), 26.1 (CH_2), 31.2 (CH_2), 32.2 (CH_2), 42.6 (CH), 52.1, 62.7 (CH_2), 107.7 (CH), 107.8 (CH), 109.3 (CH), 109.4 (CH), 112.7 (CH), 115.8, 121.5 (CH), 121.6 (CH), 131.5, 131.6, 145.3, 145.4, 147.5, 147.6, 164.9 ppm; IR (neat): $\tilde{\nu} = 1246$, 1495, 1746, 2249 cm^{-1}; elemental analysis calcd (%) for $C_{18}H_{21}NO_4$: C 68.55, H 6.71, N 4.44; found: C 68.6, H 6.7, N 4.3.

[2-(3-Oxocyclopentyl)-1,3-benzodioxol-5-yl]methyl acetate (30): 1,3-Benzodioxol-5-ylmethyl acetate (**5**, 641 mg, 3.3 mmol, 0.11 M), 2-cyclopentenone (**18**, 250 μL, 3.0 mmol, 0.10 M), and TBADT (200 mg, 0.06 mmol, 2×10^{-3} M) were dissolved in acetonitrile (30 mL) and irradiated for 40 h at 366 nm. After removing the solvent in vacuo and purification of the residue by column chromatography (silica gel, eluant: cyclohexane/ethyl acetate 9:1), [2-(3-oxocyclopentyl)-1,3-benzodioxol-5-yl]methyl acetate (**30**, 381 mg, 46%, equimolar mixture of two diastereoisomers) was obtained as a colorless oil. ^{1}H NMR ($CDCl_3$, mixture of diastereoisomers): $\delta = 2.0$–2.2 (m, 1H), 2.1 (s, 3H), 2.2–2.5 (m, 5H), 2.8–2.9 (m, 1H), 5.0 (s, 2H), 6.1 (d, $J = 4$ Hz, 1H), 6.6–6.7 (m, 1H), 6.8–6.9 ppm (m, 2H); ^{13}C NMR ($CDCl_3$, mixture of diastereoisomers): $\delta = 20.9$ (CH_3), 22.8 (CH_2), 37.3 (CH_2), 38.3 (CH_2), 40.3 (CH), 66.1 (CH_2), 107.9 (CH), 108.7 (CH), 108.8 (CH), 112.8 (CH), 122.2 (CH), 129.6, 147.7, 170.8, 216.9 ppm; IR (neat): $\tilde{\nu} = 1244$, 1499, 1742 cm^{-1}; elemental analysis calcd (%) for $C_{15}H_{16}O_5$: C 65.21, H 5.84; found: C 65.3, H 5.9.

When the irradiation was performed on piperonyl alcohol protected as *tert*-butyldimethylsilyl ether (−OTBS, prepared by standard reaction with TBSCl[43]) the formation of a new product was likewise observed, though in a sluggish way.

Ethyl 2-{1-[5-(acetoxymethyl)-1,3-benzodioxol-2-yl]cyclopentyl}-2-cyanoacetate (31): 1,3-Benzodioxol-5-ylmethyl acetate (**5**, 641 mg, 3.3 mmol, 0.11 M), cyclopentylidene cyanoacetate (**17**, 538 mg, 3.0 mmol, 0.10 M), and TBADT (200 mg, 0.06 mmol, 2×10^{-3} M) were dissolved in acetonitrile (30 mL) and irradiated for 40 h at 366 nm. After removing the solvent in vacuo and purification of the residue by column chromatography (silica gel, eluant: cyclohexane/ethyl acetate 9:1), ethyl 2-{1-[5-(acetoxymethyl)-1,3-benzodioxol-2-yl]cyclopentyl}-2-cyanoacetate (**31**, 61%, equimolar mixture of two diastereoisomers) was obtained as a colorless oil. ^{1}H NMR ($CDCl_3$, mixture of diastereoisomers): $\delta = 1.2$ (t, $J = 7$ Hz, 3H), 1.6–1.8 (m, 4H), 1.8–2.0 (m, 4H), 2.1 (s, 3H), 3.8 (s, 1H), 4.2 (q, $J = 7$ Hz, 2H), 4.9 (s, 2H), 6.1 (s, 1H), 6.6–6.8 ppm (m, 3H); ^{13}C NMR ($CDCl_3$, mixture of diastereoisomers): $\delta = 13.6$ (CH_3), 20.8 (CH_3), 25.7 (CH_2), 26.0 (CH_2), 31.2 (CH_2), 32.1 (CH_2), 42.7 (CH), 52.1 (C), 62.7 (CH_2), 65.9 (CH_2), 107.9 (CH), 108.0 (CH), 108.7 (CH), 108.8 (CH), 113.2 (CH), 115.7, 122.2 (CH), 122.3 (CH), 129.8, 129.9, 147.5, 147.6, 147.7, 147.8, 164.8, 170.6 ppm; IR (neat): $\tilde{\nu} = 1239$, 1499, 1738, 2250 cm^{-1}; elemental analysis calcd (%) for $C_{20}H_{23}NO_6$: C 64.33, H 6.21, N 3.75; found: C 64.3, H 6.2, N 3.7.

Dimethyl 2-(5-formyl-1,3-benzodioxol-2-yl)succinate (32): Piperonal (**6**, 495 mg, 3.3 mmol, 0.11 M), dimethyl maleate (**10**, 375 μL, 3.0 mmol, 0.10 M), and TBADT (200 mg, 0.06 mmol, 2×10^{-3} M) were dissolved in acetonitrile (30 mL) and irradiated for 40 h at 366 nm. After removing the solvent in vacuo and purification of the residue by column chromatography (silica gel, eluant: cyclohexane/ethyl acetate 8:2), dimethyl 2-(5-formyl-1,3-benzodioxol-2-yl)succinate (**32**, 530 mg, 60%, equimolar mixture of two diastereoisomers) was obtained as a colorless oil. ^{1}H NMR ($CDCl_3$, mixture of diastereoisomers): $\delta = 2.6$–2.9 (2H; AB part of an ABX system), 3.5–3.6 (1H; X part of an ABX system), 3.7 (s, 3H), 3.8 (s, 3H), 6.6 (d, $J = 4$ Hz, 1H), 6.8–6.9 (m, 1H), 7.2–7.3 (m, 1H), 7.4–7.5 (m, 1H), 9.8 ppm (s, 1H); ^{13}C NMR ($CDCl_3$, mixture of diastereoisomers): $\delta = 29.0$ (CH_2), 29.3 (CH_2), 46.2 (CH), 52.0 (CH_3), 52.6 (CH_3), 106.9 (CH), 108.3 (CH), 110.7 (CH), 128.5 (CH), 128.6 (CH), 131.9, 148.2, 152.4, 169.5, 171.3, 190.0 ppm; IR (neat): $\tilde{\nu} = 1257$, 1493, 1690, 1740 cm^{-1}; elemental analysis calcd for $C_{14}H_{14}O_7$: C 57.14, H 4.80; found: C 57.2, H 4.9.

Ethyl 2-cyano-3-[5-(ethoxycarbonyloxy)1,3-benzodioxol-2-yl]-3-methylbutanoate (33): 1,3-Benzodioxol-5-yl ethyl carbonate (**7**, 694 mg, 3.3 mmol, 0.11 M), ethyl isopropylidene cyanoacetate (**14**, 460 mg, 3.0 mmol, 0.10 M), and TBADT (200 mg, 0.06 mmol, 2×10^{-3} M) were dissolved in acetonitrile (30 mL) and irradiated for 40 h at 366 nm. After removing the solvent in vacuo and purification of the residue by column chromatography (silica gel, eluant: cyclohexane/ethyl acetate 9:1), ethyl 2-cyano-3-[5-(ethoxycarbonyloxy)1,3-benzodioxol-2-yl]-3-methylbutanoate (**33**, 818 mg, 75%, equimolar mixture of two diastereoisomers) was obtained as a colorless oil. ^{1}H NMR ($CDCl_3$, mixture of diastereoisomers): $\delta = 1.2$ (s, 3H), 1.25 (t, $J = 7$ Hz, 3H), 1.3 (s, 3H), 1.4 (t, $J = 7$ Hz, 3H), 3.8 (s, 1H), 4.2 (q, $J = 7$ Hz, 2H), 4.3 (q, $J = 7$ Hz, 2H), 6.1 (s, 1H), 6.6–6.8 ppm (m, 3H); ^{13}C NMR ($CDCl_3$, mixture of diastereoisomers): $\delta = 13.8$ (CH_3), 14.1 (CH_3), 18.6 (CH_3), 20.0 (CH_3), 41.9 (C), 43.4 (CH), 43.5 (CH), 62.9 (CH_2), 64.9 (CH_2), 103.2 (CH), 103.2 (CH), 107.7 (CH), 107.8 (CH), 113.7 (CH), 113.8 (CH), 114.1 (CH), 114.9 (C), 145.3, 145.5, 147.7, 153.7, 164.3 ppm; IR (neat): $\tilde{\nu} = 1240$, 1494, 1746, 1760, 2251 cm^{-1}; elemental analysis calcd (%) for $C_{18}H_{21}NO_7$: C 59.50, H 5.83, N 3.85; found: C 59.5, H 5.8, N 3.7.

3-(2-Methyl-1,3-benzodioxol-2-yl)propanenitrile (34): 2-Methyl-1,3-benzodioxole (**8**, 449 mg, 3.3 mmol, 0.11 M), acrylonitrile (**9**, 200 μL, 3.0 mmol, 0.10 M), and TBADT (200 mg, 0.06 mmol, 2×10^{-3} M) were dissolved in acetonitrile (30 mL) and irradiated for 40 h at 366 nm. After removing the solvent in vacuo and purification of the residue by column chromatography (silica gel, eluant: cyclohexane/ethyl acetate 95:5), 3-(2-methyl-1,3-benzodioxol-2-yl)propanenitrile (**34**, 369 mg, 65%) was obtained as a colorless oil. ^{1}H NMR ($CDCl_3$): $\delta = 1.6$ (s, 3H), 2.3 (t, $J =$ 7 Hz, 2H), 2.6 (t, $J = 7$ Hz, 2H), 6.7–6.8 ppm (m, 4H); ^{13}C NMR ($CDCl_3$): $\delta = 10.9$ (CH_2), 24.0 (CH_3), 34.3 (CH_2), 108.3 (CH), 115.9, 118.5, 121.2 (CH), 146.4 ppm; IR (neat): $\tilde{\nu} = 1239$, 1487, 2252 cm^{-1}; elemental analysis calcd (%) for $C_{11}H_{11}NO_2$: C 69.83, H 5.86, N 7.40; found: C 69.8, H 5.8, N 7.3.

2-[1-(2-Methyl-1,3-benzodioxol-2-yl)cyclohexyl]malononitrile (35): 2-Methyl-1,3-benzodioxole (**8**, 449 mg, 3.3 mmol, 0.11 M), cyclohexylidene malononitrile (**13**, 430 μL, 3.0 mmol, 0.10 M), and TBADT (200 mg, 0.06 mmol, 2×10^{-3} M) were dissolved in acetonitrile (30 mL) and irradiated for 24 h at 366 nm. After removing the solvent in vacuo and purification of the residue by column chromatography (silica gel, eluant: cyclohexane/ethyl acetate 95:5), 2-[1-(2-methyl-1,3-benzodioxol-2-yl)cyclohexyl]malononitrile (**35**, 652 mg, 77%) was obtained as a colorless solid (m.p.: 165–167 °C). ^{1}H NMR ($CDCl_3$): $\delta = 1.2$–1.4 (m, 3H), 1.7 (s, 3H), 1.7–1.9 (m, 5H), 2.1–2.2 (m, 2H), 4.3 (s, 1H), 6.8–6.9 ppm (m, 4H); ^{13}C NMR ($CDCl_3$): $\delta = 20.8$ (CH_2), 20.9 (CH), 24.4 (CH_2), 24.4 (CH_3), 27.9 (CH_2), 49.0, 108.9 (CH), 111.8, 119.6, 121.8 (CH), 146.4 ppm; IR (KBr): $\tilde{\nu} = 1241$, 1486, 2251 cm^{-1}; elemental analysis calcd (%) for $C_{17}H_{18}N_2O_2$: C 72.32, H 6.43, N 9.92; found: C 72.2, H 6.5, N 9.9.

Ethyl 3-(5-allyl-1,3-benzodioxol-2-yl)-2-cyano-3-methylbutanoate (38): 5-Chloro-1,3-benzodioxole (**3**, 385 μL, 3.3 mmol, 0.11 M), ethyl isopropylidene cyanoacetate (**14**, 460 mg, 3.0 mmol, 0.10 M), and TBADT (200 mg, 0.06 mmol, 2×10^{-3} M) was dissolved in acetonitrile (30 mL) and irradiated for 40 h at 366 nm. Water (6 mL) and allyltrimethylsilane (**37**, 2.87 mL, 18 mmol, 0.5 M) were added to the crude photolyzed mixture. The resulting solution was purged for 10 min with nitrogen, serum capped, and then irradiated with 10 15 W phosphor-coated lamps (emission centered at 310 nm) for 24 h. After removing the solvent in vacuo and purification of the residue by column chromatography (silica gel, eluant: cyclohexane/ethyl acetate 95:5), ethyl 3-(5-allyl-1,3-benzodioxol-2-yl)-2-cyano-3-methylbutanoate (**38**, 331 mg, 35%, as a mixture of diastereoisomers) was obtained as a colorless oil. ^{1}H NMR ($CDCl_3$, mixture of diastereoisomers): $\delta = 1.2$ (s, 3H), 1.25 (t, $J = 7$ Hz, 3H), 1.3 (s, 3H), 3.3 (m, 2H), 3.8 (s, 1H), 4.3 (q, $J = 7$ Hz, 2H), 5.1–5.2 (m, 2H), 5.8–6.0 (m, 1H), 6.1 (s, 1H), 6.6–6.8 ppm (m, 3H); ^{13}C NMR ($CDCl_3$, mixture of diastereoisomers): $\delta = 13.7$ (CH_3), 18.6 (CH_3), 20.0 (CH_3), 39.8 (CH_2), 41.9, 43.5 (CH), 62.7 (CH_2), 107.8 (CH), 107.9 (CH), 108.7 (CH), 108.8 (CH), 113.0 (CH), 115.0 (C), 115.7 (CH_2), 121.3 (CH), 121.4 (CH), 134.0, 134.1, 137.3 (CH), 145.7, 145.8, 147.5, 147.6, 164.4 ppm; IR (neat): $\tilde{\nu} = 1259$, 1496, 1746, 2250 cm^{-1}; elemental analysis calcd (%) for $C_{18}H_{21}NO_4$: C 68.55, H 6.71, N 4.44; found: C 68.6, H 6.7, N 4.3.

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