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Photochemical Electron Transfer Mediated Addition of Naphthylamine Derivatives to Electron-Deficient Alkenes

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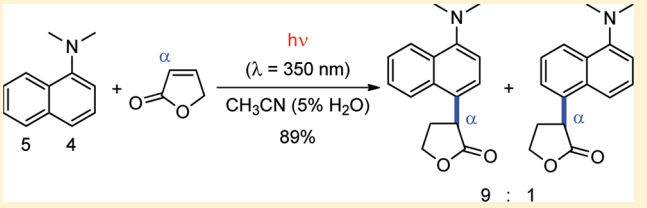
Supporting Information

ABSTRACT: Using photochemical electron transfer, *N*,*N*-dimethylnaphthylamine derivatives are added to α,β-unsaturated carboxylates. The addition takes place exclusively in the α-position of electron-deficient alkenes and mainly in the 4-position of *N*,*N*-dimethylnaphthalen-1-amine. A minor regioisomer results from the addition in the 5-position of this naphthylamine. A physicochemical study reveals that the fluorescence quenching of *N*,*N*-dimethylnaphthalen-1-amine is diffusion-controlled and that the back electron transfer is highly efficient. Therefore no transformation is observed at lower concentrations. To overcome this limitation and to induce an efficient transformation, minor amounts of water or another proton donor as well as an excess of the naphthylamine derivative are necessary. A mechanism involving a contact radical ion pair is discussed. Isotopic labeling experiments reveal that no hydrogen is directly transferred between the substrates. The hydrogen transfer to the furanone moiety observed in the overall reaction therefore results from an exchange with the reaction medium. An electrophilic oxoallyl radical generated from the furanone reacts with the naphthylamine used in excess. Concerning some mechanistic details, the reaction is compared with radical and electrophilic aromatic substitutions. The transformation was carried out with a variety of electron-deficient alkenes. Sterically hindered furanone derivatives are less reactive under standard conditions. In a first experiment, such a compound was transformed using heterogeneous electron transfer photocatalysis with TiO_2.



INTRODUCTION

Photochemical reactions considerably enrich the methodology in organic synthesis.[1] Frequently, mild reaction conditions are applied and no activating reagents (acids, bases, metals, etc.) are necessary, which opens perspectives in the context of a sustainable chemistry.[2] The electron configuration completely changes when molecules are electronically excited, and thus their chemical properties also significantly change with respect to the ones in the ground state.[3] For instance, electron transfer between two molecules in the ground state is possible only when the energy of the highest occupied molecular orbital (HOMO) of the donor molecule is energetically higher than the lowest unoccupied molecular orbital (LUMO) of the acceptor molecule. The electron transfer is then exothermic. When one of these reaction partners is photochemically excited, electron transfer is also possible in cases where the ground state HOMO of the donor molecule is energetically lower than the LUMO of the acceptor. The endothermicity of a corresponding electron transfer in the ground state is compensated by the excitation energy.[4−7] Thus photochemical electron transfer considerably enriches the redox chemistry of organic molecules. Kinetics of the photochemical electron transfer are determined by Marcus theory.[6,8] Recently, we used such processes to develop an efficient method for the addition of simple tertiary amines to alkenes.[9,10] In this case, electron transfer sensitizers such as electron donor substituted aromatic ketones were used as efficient homogeneous catalysts.[11,12] The same reaction was carried out with inorganic semiconductors such as TiO_2 or ZnS as efficient heterogeneous photocatalysts.[13] In cases of homogeneous photocatalysis, initially generated radical ions undergo proton transfer from the radical cation to the radical anion, thus generating neutral radicals. The latter intermediates undergo radical chain reactions. Such reactions can be controlled by addition of thiocarbonyl compounds, which reversibly add to the radical intermediates and thus control the outcome.[14,15] These transformations have also been successfully applied to radical polymerization.[16,17] In a variety of such photocatalytic reactions very interesting for

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synthetic applications, sacrificial electron donors or acceptors are needed.[11,18]

All of these reactions are more or less complex processes leading to the formation of a carbon−carbon bond. Reactions have also been reported in which such a bond formation is induced by photochemical electron transfer between the two reaction partners without intervention of a sacrificial electron donor or acceptor or a sensitizer. For instance, tertiary amines have been added to electronically excited α,β-unsaturated ketones in this way.[19,20] Photochemical analogues of the Suzuki, Sonogashira, or Heck reactions as well as addition of aromatic compounds to alkenes have been carried out by excitation of electron-rich benzene derivatives.[21] Reactions involving direct photochemical electron transfer between the substrates have been performed with phthalimide derivatives.[10,22] All of these transformations are particularly interesting since they do not need any metal activation. In many cases, however, leaving groups are involved, which leads to the formation of byproduct. In this context, we were interested in reactions in which neither leaving groups nor electron transfer sensitizers are involved. Thus only photochemical electron transfer between the substrates will induce the transformation. Herein, we report on the regioselective addition of naphthylamine derivatives to electron-deficient alkenes. In this transformation, the alkene is formally inserted in a relatively strong aromatic C−H bond. Currently, in the field of organometallic chemistry, such transformations are intensively investigated in the context of "C−H activation".[23−25] Activation of thermodynamically stable C−H bonds is also intensively studied in biochemistry or chemical biology.[26]

RESULTS AND DISCUSSION

We started our investigation with the reaction of *N*,*N*-dimethylnaphthalen-1-amine **1** with furan-2[5*H*]-one **2** in acetonitrile as solvent and in the presence of water (Scheme 1). Naphthylamine **1** was added in excess. The best results were obtained when a 0.1 M solution of furanone **2** was irradiated in the presence of 15 equiv of the amine **1** (Table 1, entry 2). Larger amounts (entry 1) do not improve the yields. No significant transformation was observed when the proportions of substrates were inversed (furanone **2** (1.5 mol L^{-1}) with respect to the naphthylamine **1** (0.1 mol L^{-1})). Small amounts of water were crucial for the transformation. Best results were obtained when the reaction mixture contained 4% of water. (In the case of higher water amounts, the reaction mixture became heterogeneous and naphthylamine **1** deposited.) Two regioisomers **3a,b** were obtained in a ratio of 9/1. Surprisingly when compared to the large majority of ground state reactions[27,28] of α,β-unsaturated carbonyl or carboxyl compounds, the addition of **1** occurred only in the α-position of furanone **2**. In similar reactions, the β-position of **2** is more electrophilic. When compared to well established reactivity of α,β-unsaturated carboxyl compounds, it must be stated that α-functionalization of such compounds, for example, in the case of the Baylis−Hillman reaction,[28,29] is more difficult. Recently, a similar Lewis acid catalyzed reaction was published.[30] In the electronically excited state of furanones and depending on the mechanism, selective C−C bond formation occurs in the α-position of furanones[31] or α,β-unsaturated carbonyl compounds.[32−34] In these cases, the α-regioselectivity is essentially linked to the biradical structure of the T_1 ($^3\pi\pi^*$) state of such compounds. It is also surprising that the minor regioisomer **3b** results from addition in the 5-position of compound **1**. In electrophilic substitutions in the ground state of such naphthalene derivatives carrying an electron-donating substituent in the 1-position, the transformation in position 2 dominates over the one in position 5.[35−38]

Scheme 1. Photochemical Addition of Naphthylamine Derivative 1 to Furanone 2

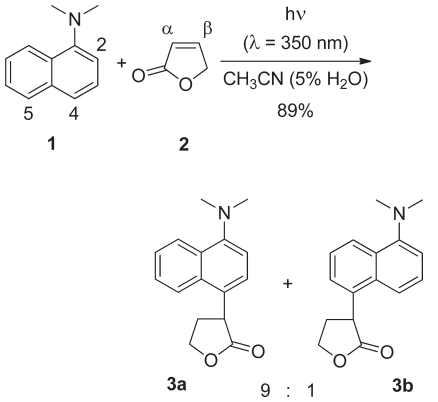

Table 1. Irradiation Time and Yields of the Reaction between Compounds 1 and 2 Depending on the Excess of Amine 1 in the Reaction Mixture (Scheme 1)

entry	amine equiv	amine concn (mol L^{-1})	irradiation time (h)	yield (%)
1	50	3.1	6	92
2	15	1.5	6	89
3	10	1.1	17	62
4	5	0.6	24	*a*

[a] Only traces of the products were detected by NMR.

To obtain mechanistic information, isotopic labeling experiments were carried out. During the transformation, a hydrogen atom in position 4 of the naphthylamine derivative **1** is removed (formation of the major isomer **3a** in a formal electrophilic aromatic substitution) while a hydrogen atom is added in the β-position of furanone **2** (Scheme 2). Deuterium labeling may lead to information about the origin of the hydrogen in this position, and more general mechanistic conclusions should also be possible. We first checked whether hydrogen in the β-position of products **3a,b** may originate from the naphthalene compound **1**. However, when deuterated compounds **4** or **5** were transformed, no deuterium was detected in the β-position of the reaction products (Scheme 2, eq 1). Deuterium transfer to the furanone did not occur either from the methyl group or from the most reactive 4-position of the naphthylamine derivative. The yields and the ratio of regioisomers did not change when the isotopically marked compounds were transformed. These results with isotopic labeling are quite different from those that we have previously published in the context of sensitized photochemical electron transfer reactions.[39−41] To check whether hydrogen is transferred from the reaction medium, first acetonitrile-d_3 was used. In this case, no deuterium was detected on the lactone moiety of the products. However, when D_2O was used, deuterium incorporation was observed in the β-position of the lactone moiety of products **8a,b** (incorporation of one deuterium >90%). We concluded that a protic solvent or cosolvent is necessary for

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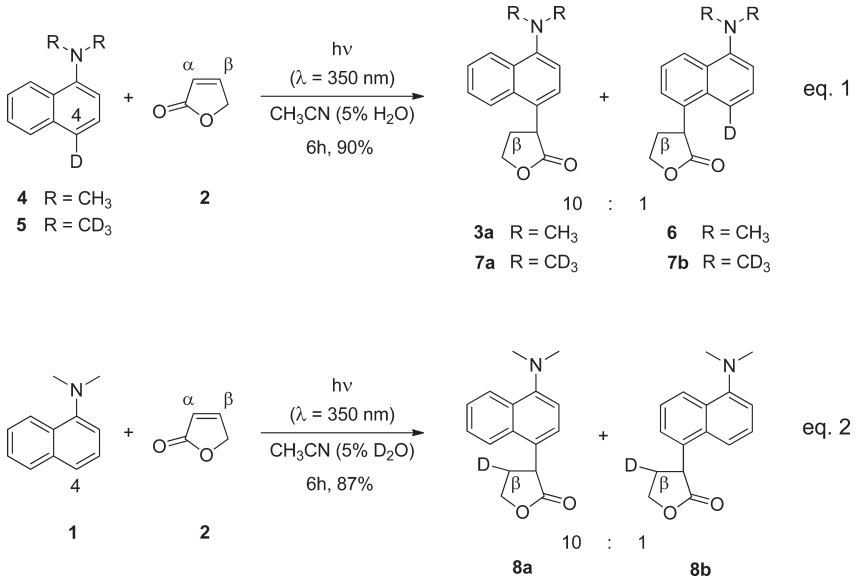
Scheme 2. Photochemical Addition of Deuterated Naphthylamine Derivatives 4 and 5 to Furanone 2[a]



[a] The conversion was complete after 6 h of irradiation.

the successful transformation. Two additional experiments confirmed this interpretation. When compounds **1** and **2** were irradiated in CD_3OD, deuterated compounds **8a,b** were obtained in 85% yield and with the same ratio of regioisomers; 10 h of irradiation was needed for complete conversion. No conversion was observed when water-free acetonitrile was used. We also observed a slow conversion in the presence of water traces in acetonitrile. The use of protic solvents or cosolvents, water in particular, is essential for the reactivity.

Similar observations concerning regioselectivity or deuterium transfer have been made in photochemical transformations of electron-rich aromatic compounds with acrylates.[42,43] In these previously reported transformations, the reaction competes with [2 + 2] or [2 + 3] photocycloaddition.[44]

Using the Norrish type II reaction of butyrophenone as actinometer,[45−47] we have measured a product quantum yield of 0.1 for the optimized reaction conditions (Table 1, entry 2). It must be pointed out that the quantum yield decreases significantly when the naphthylamine concentration is diminished, as illustrated by the reaction times and yields in Table 1, or when the proton source is removed.

To get insight into the primary photophysical steps, physicochemical studies have been carried out. The quenching reaction of *N*,*N*-dimethyl-1-naphthylamine **1** with 2[5*H*]-furanone **2** was found to be diffusion controlled. Steady state and time-resolved fluorescence measurements yielded identical values of $2.0 \pm 0.2 \times 10^{10}$ M^{-1} s^{-1} for the quenching constant, revealing that the nature of the quenching is purely dynamic according to the simple Einstein−Smoluchowski equation ($k_{diff} = 8RT/3\eta$). Under the applied conditions (solution in pure acetonitrile at 25 °C), the fluorescence lifetime of the fluorophore amounts to 4.4 ns (under Ar), whereas for the fluorescence quantum yield a value of 0.20 was obtained. No photoproduct formation could be observed. We therefore assume that efficient back- electron transfer occurs.

Upon addition of 1% of bidistilled water to the fluorophore−quencher solutions, no spectral changes were detected. The recorded absorption and fluorescence spectra do not give any indication for complex formation in ground or excited state, so that exciplex formation is not thought to occur under the conditions applied. Within experimental error, the quenching constants determined from quantum yields and lifetime measurements are identical to the ones obtained in the case where no water was added. The observations indicate that water has no influence on the primary quenching step.

To favor excited state complex formation, it was attempted to lower the dielectric constant of the solution by studying the reaction in solvents or solvent mixtures of different permittivity. The following solvents were tested but all of them were found to react with the excited state of the fluorophore, indicated by a decrease in both, the fluorescence lifetime as well as the quantum yield: propyl acetate, benzyl acetate, methyl-*iso*-butylketone, 1-hexanol, 1-butanol, butanone, toluene, THF, *n*-hexane, *tert*-butyl benzene.

On the basis of our observations, we suggest the mechanism depicted in Scheme 3. After photochemical excitation of naphthylamine **1**, an electron transfer may take place from the amine **1** to the furanone **2** leading to a radical ion pair. Using the Weller equation,[4,5,48] the ΔG_{ET} of this photochemical is estimated to −0.37 eV (−8.5 kcal/mol), which is in agreement with our previous observations of fast fluorescence quenching of amine **1**.[49]

$$\Delta G_{ET} = E^{\circ}(D^{+}/D) - E^{\circ}(A/A^{-}) - E_{0-0} - w \qquad (3)$$

The redox potentials of the substrates have been determined by cyclic voltametry (vs ferrocene/ferrocenium): $E_p(\mathbf{1}^{+}/\mathbf{1})$ = +0.39 V, $E_p(\mathbf{2}/\mathbf{2}^{-})$ = −2.75 V. The energy gap between the frontier orbitals (E_{0-0}) approximately corresponds to the excitation energy, which can be determined by UV−vis spectroscopy. Especially in cases of low Stokes shifts, a better value of the HOMO/LUMO energy difference is obtained when the 0−0 transition between the S_0 and the S_1 potential energy surface is determined from UV−vis absorption and fluorescence spectra (Figure 1).[50] The corresponding energy of 3.39 eV is determined from the intersection (λ_{inter} = 365 nm) of the absorption and the

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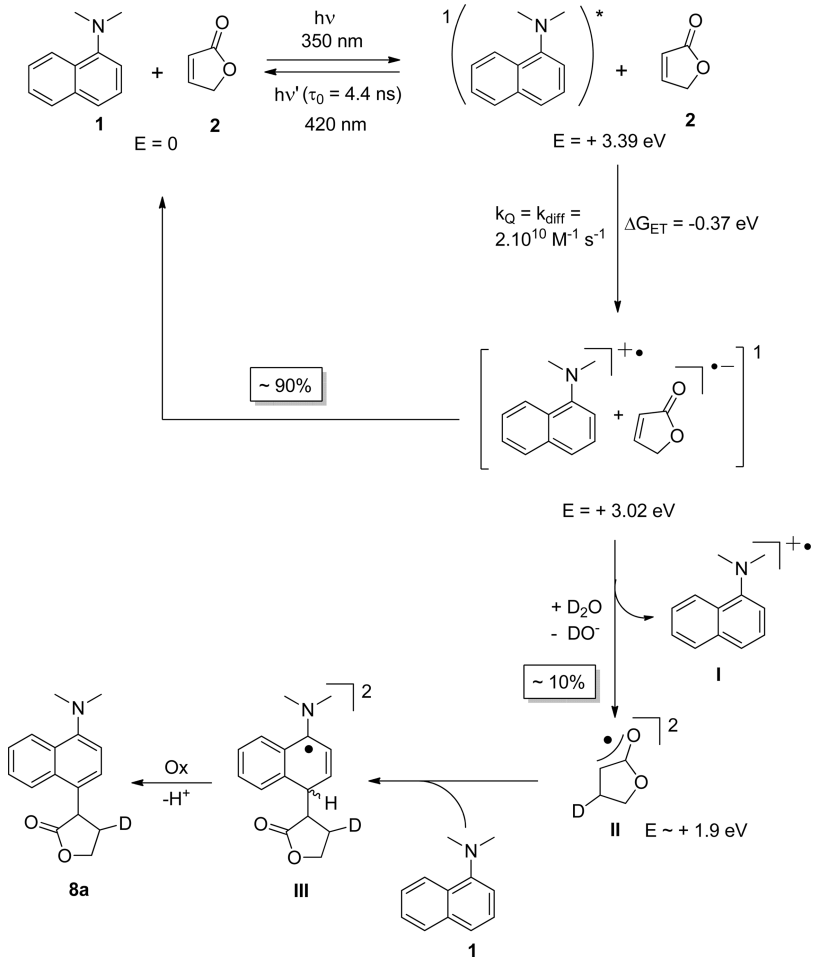
Scheme 3. Mechanism of the Photochemical Electron Transfer Mediated Addition of Naphthylamine Derivative 1 to Furanone 2



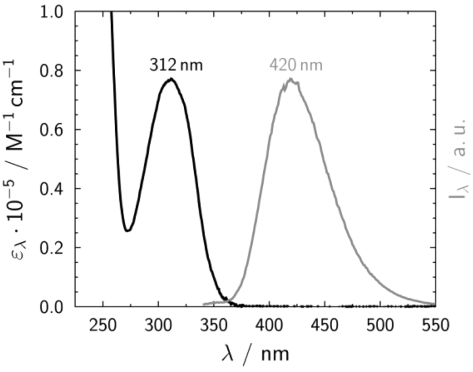


Figure 1. Absorption and normalized fluorescence spectra of naphthylamine derivative **1**.

normalized emission spectra. The value for *w* is +0.12 eV. This term corresponds to the free enthalpy gained by bringing the ions to encounter distance in acetonitril as solvent.[51] In contrast, cyclic voltametry is considered to take into account free ions.

The productivity of photochemical electron transfer mediated reactions frequently suffers from back electron transfer, which leads to the regeneration of the substrates. In our case, this electron transfer is efficient. To induce a chemical reaction, a competitive trapping process is needed. Protonation of the radical anion by the reaction medium fulfills this task and leads to the radical cation **I** and the oxoallyl radical **II**. Obviously, proton transfer from the radical cation to the radical anion[19,31,52] in the radical ion pair does not occur. It has been suggested that a very polarized exciplex may be protonated or deuterated, leading directly to the formation of intermediates such as **I** and **II**.[42] However, as photochemical electron transfer is exothermic and given the polarity of the solvent applied, we assume the formation of a radical ion pair. Furthermore, we have no evidence for the formation of such an exciplex intermediate. Electrophilic oxoallyl radicals such as **II** are easily trapped by nucleophilic reaction partners.[14,46,53] In the present case, this occurs through addition of the naphthylamine derivative **1**, which is therefore needed in excess. Despite the trapping process and as indicated by the product quantum yield ($\Phi = 0.1$) and the efficient fluorescence quenching of **1** by the furanone **2**, about 90% of the radical ion pair reacts via back electron transfer to regenerate the substrates **1** and **2**. As in the case of α-aminoalkyl radicals,[13,39,54] the resulting intermediate **III** is easily oxidized, and after deprotonation, the final product **8a** is obtained. Although the product yield of the overall reaction is high, no details on the last mechanistic step can be indicated here. For instance, the oxidation of intermediate **III** might occur by electron transfer from this

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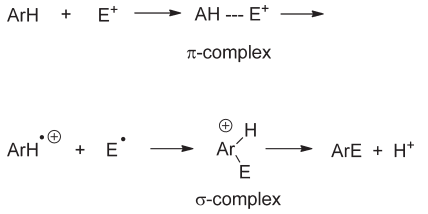
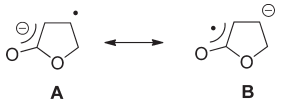
Scheme 4. General Mechanism of Electrophilic Substitution Involving Single Electron Transfer



Scheme 5. Mesomeric Structures of the Radical Anion of Furanone 2

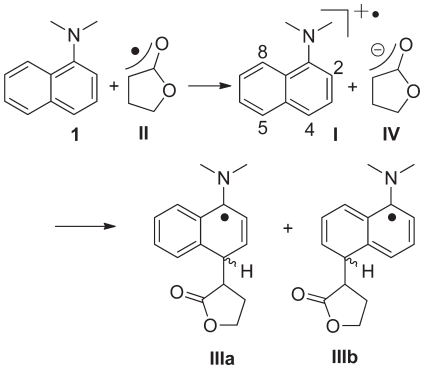


species to the radical cation **I**. Similar inter- and intramolecular radical aromatic substitutions have been reported several times in the literature[55−57] (see also ref 39).

The overall reaction as depicted in Scheme 1 resembles an electrophilic aromatic substitution.[35,58] Although frequently supposed in the past,[59] only recently has electron transfer been proven to be involved in some of these reactions.[60] In particular, nitration and nitrosylation was discussed in this context.[61−63] In view of these results, the electron transfer from the aromatic compound ArH to the electrophile E^+ takes place (Scheme 4). Radical combination leads to the σ-complex (Wheland intermediate). Often the electron transfer step is rate-limiting in the overall reaction. In our case (Scheme 3), such an electron transfer at the ground state is endothermic (E = +3.02 eV). Between the substrates, only photochemical induced electron transfer is exothermic, thus enabling the reaction. Furthermore, it should be pointed out that in our case a neutral but electrophilic oxoallyl radical adds to an electron-rich aromatic system and a σ-complex intermediate is formed after oxidation of the resulting intermediate **III** (see below).

When compared to electrophilic substitution, one must also point out that the electrophilic site of α,β-unstaturated lactone is the β-position. Therefore, one should observe reaction at this position, which would also be in accordance with the Michael reaction as already mentionned.[27,28,38] The observed regiospecific α-addition in our reaction is due to previous protonation of the radical anion in the β-position as outlined in Schemes 2 and 3. To explain this unusual selectivity, the structure of the radical anion must be discussed. This species possesses two main mesomeric structures, **A** and **B** (Scheme 5). Protonation is expected at the enolate oxygen (**A**) since this atom is the most electronegative one. In a previous mechanistic study using deuterium labeling, an alkoxyfuranone molecule in solution was reduced to a radical anion.[9,39,41] The latter was deuterated at the enolate oxygen, and after tautomerization of the enol, deuterium was detected in the α-position of the lactone. The same photochemical reaction was carried out with inorganic semiconductors such as TiO_2 or ZnS in their function as photochemical electron transfer sensitizers.[40,41] In this case, the same radical anion of an alkoxyfuranone is adsorbed at the surface of a negatively charged semiconductor particle (see also ref 13) and is protonated in its β-position. Obviously, the radical anion intermediate in this heterogeneous reaction is better represented by the mesomeric structure **B** (Scheme 5). In analogy to these previous observations, we conclude that protonation of the furanone part in the present reaction also occurs in a confined structure in which the furanone radical anion is firmly bound in an ion pair to the naphthylamine partner as depicted in Scheme 3. As already mentioned above, a protonation in the β-position of acryl derivatives was discussed in cases where the acrylate is bound in a polarized exciplex.[42]

Scheme 6. Electrophilic Aromatic Substitution with Electrophilic Radical II and Naphthylamine Derivative 1 Involving Single Electron Transfer As Outlined in Scheme 4



Naphthalene derivatives carrying an electron donor substituent in position 1 generally undergo electrophilic substitution mainly in the 4-position and to a less extent in the 2-position.[35,36,38] In the present case, however, the minor product results from a transformation in the 5-position (Schemes 1 and 2). Similar unusual regioselectivities have also been observed in some radical aromatic substitution reactions with naphthalene derivatives.[57] Such results are explained by a two-step mechanism as depicted in Scheme 6. As shown in the general mechanism (Scheme 4), single electron transfer is involved that leads to the radical cation **I** and to the enolate **IV**. In this context, it should be pointed out that radicals carrying electron-withdrawing substituents such carbonyl or carboxyl groups are easily reduced.[64] The corresponding neutral σ-complexes **IIIa** and **IIIb** are formed by charge combination. In such a step, the regioselectivity is controlled by the charge or the electron density in the intermediates. It has been shown previously that in radical cations of naphthalenes carrying an electron-donor substituent in the 1-position the positive charge density may be higher in position 5 than in position 2.[57,65] We have determined the overall electron densities in the radical cation **I** using HF calculations (Figure 2). In positions in which electrophilic substitution can occur, the lowest electron density is detected in position 4 (−0.106). The main product **IIIa** results from a reaction in this position. The electron density in position 2 (−0.172) is significantly higher than that in position 5 (−0.127). Therefore, the formation of the minor regioisomer **IIIb** results from a transformation in the latter position. A relatively low electron density is also detected in position 8 (−0.128). Most probably, due to steric hindrance, no reaction occurs in this position.[66,67]

Compound **3a** is a 2-(4-(dialkylamino)naphthalen-1-yl)propanoic acid derivative. Such compounds possess a variety of pharmaceutical activities.[68] To obtain a first glance of the scope of the reaction, structural variations have been carried out on the

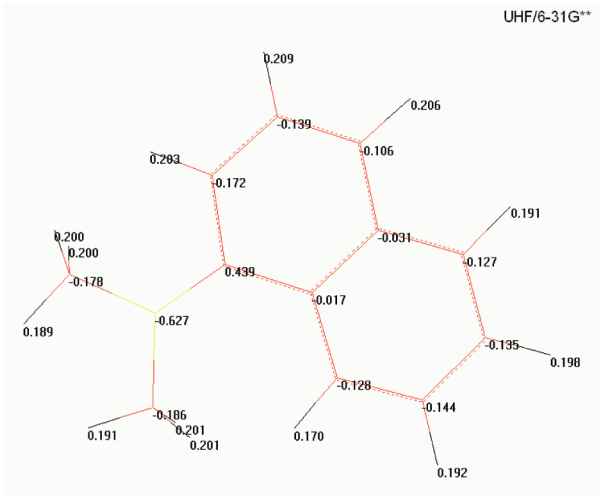
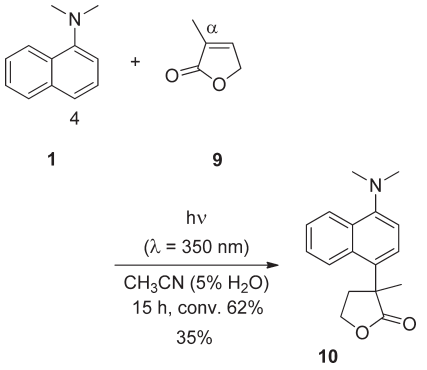


Figure 2. Overall charge distribution in the radical cation **I**.

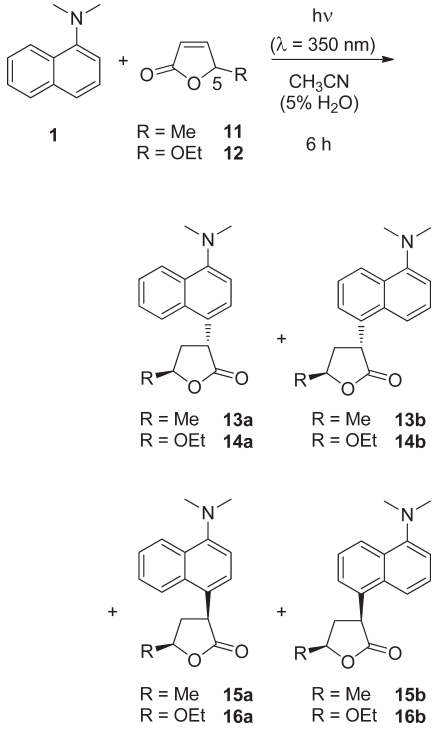
Scheme 7. Photochemical Addition of Naphthylamine Derivative 1 to Furanone 9 Carrying a Methyl Group in the α Position



substrates. First, the structure of the furanone was modified by addition of substituents in different positions. When 3-methyl-2[5*H*]-furanone **9** transformed under the optimized reaction conditions, compound **10** was isolated in moderate yields (Scheme 7). Furthermore, the reaction was considerably slower when compared to the transformation of furanone **2**. After 15 h of irradiation, only 62% of **9** was transformed and the adduct **10** was isolated with yield of 35% (selectivity 57%). Only one regioisomer was obtained resulting from a selective reaction in position 4 of the naphthylamine **1**. The reduced reactivity may be explained by the increased steric hindrance of the α-position in compound **9**. Nevertheless, it must be pointed out that it remains sufficient to establish a quaternary sp^3-hybridized center carrying 4 carbon substituents.[69]

We next investigated the reaction of furanones **11** and **12** carrying a substituent in the 5-position with the naphthylamine derivative **1** (Scheme 8, Table 2). Lower yields were obtained when compared to the parent compound **2** (Scheme 1, Table 1). On the basis of the previous mechanistic discussion, this observation may be explained by a hindered formation of the key intermediates such as the radical ion pair (compare Scheme 3). Steric effects reduce the interaction of the π systems of the

Scheme 8. Dia- and Regioselective Addition of Naphthylamine Derivative 1 to Furanones 11 and 12 Carrying a Subsitutent in Position 5



substrates[70] and also the addition of the corresponding oxoallyl radical with the naphthylamine **1**. This addition of **1** occurred preferentially *anti* with respect to the substituent in position 5 leading to compounds **13a,b** and **14a,b**. In both cases, the diastereoisomers were separated by column chromatography. The corresponding fractions contained a mixture of regioisomers **a** and **b**. For this 1,3 chiral induction, the diastereoselectivity was moderate when compared to the 1,2 chiral induction with comparable compounds (for instance, 1,2 chiral induction in the addition reactions at the β-position).[71−73] The ratio of regioisomers was almost the same for the major (**13a,b** and **14a,b**) and the minor diastereoisomer (**15a,b** and **16a,b**).

Methylcrotonate **17** and dimethylfumarate **18** have successfully been transformed with amine **1** under the same reaction conditions (Scheme 9, eq 4 and 5). In the case of **17**, the expected adducts **19a,b** have been isolated in a 9/1 ratio of regioisomers. The reaction of **18** also lead to the expected adducts **20a,b** with the a comparable ratio of regioisomers (Scheme 9, eq 5). Additionally, compound **21** was formed in minor amounts. This product resembles to compounds, that have been obtained by photochemically induced radical tandem addition cyclization reactions[39,40,71] (see also refs 74 and 75). Under the applied reaction conditions, its formation can be explained by the mechanism depicted in Scheme 10. After photochemical excitation of the naphthylamine derivative **1**, electron transfer occurs according the mechanism depicted in Scheme 2 leading to the radical ion pair **V** and **VI**. Instead of protonation of the radical anion **VI** by the reaction medium, proton transfer occurs from the radical cation **V** to **VI**. This competitive acid base reaction may be favored by the presence of two basic centers (ester functions) in the radical anion **VI**.

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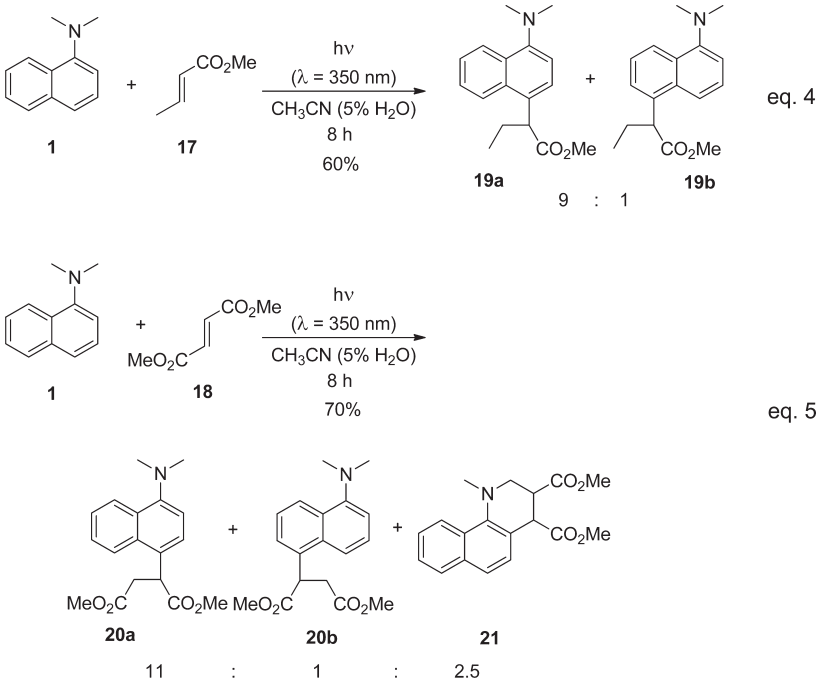
Table 2. Diastereoselective Addition of 1 with Furanones 11 and 12 Carrying a Substituent in Position 5 (Scheme 7)

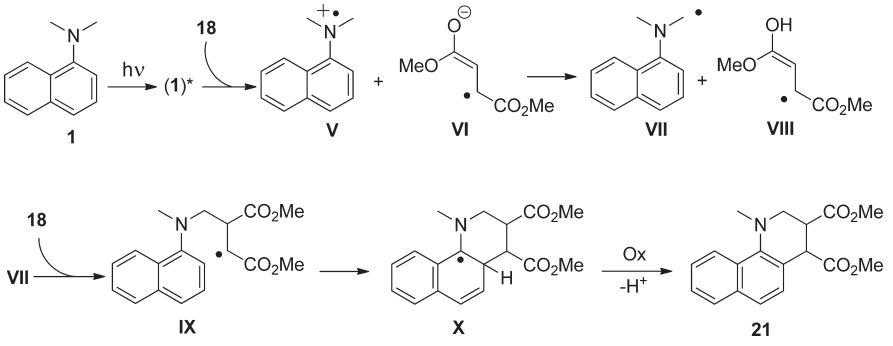
		major diastereoisomer (*anti* addition)		minor diastereoismer(*syn* addition)		
R		**a**/**b**[a]	yield (%)	**a**/**b**[a]	yield (%)	ratio of diastereoisomers
Me	**11**	11/1	45	10/1	13	3.5
OEt	**12**	10/1	25	10/1	10	2.5

[a] Ratio of regioisomers.

Scheme 9. Photochemical Addition of Naphthylamine Derivative 1 to Acyclic α,β-Unsaturated Esters 17 and 18



Scheme 10. Mechanism of Formation of Minor Product 21



Thus the neutral radicals **VII** and **VIII** are formed. The α-aminoalkyl radical **VII** easily adds to the electron-deficient double bond of **18** to form intermediate **IX**.[53,76] Cyclization (**X**) and rearomatization lead to the final product **21**. In principal, the fumaric ester **18** may also act as electron transfer sensitizer.[11,39,40] However, since the absorption coefficient of **18** at λ = 350 nm is very low and **1** possessing a higher one at this wavelength is used in excess, such a mechanism should be excluded.

We also investigated the transformation of *N*,*N*-dimethylnaphthalen-2-amine **22** (Scheme 11, eq 6) which is a regioisomer of **1**. When **22** was irradiated under standard conditions in the presence of furanone **2**, compound **23** was obtained in high yield as the sole reaction product. A C−C bond was formed between the carbon 1 of the naphthylamine derivative **22** and the α carbon of furanone **2**. The reaction rate was lower when compared to the transformation of **1** (Scheme 1, Table 1) which may be explained by an increased steric hindrance. Indeed, in

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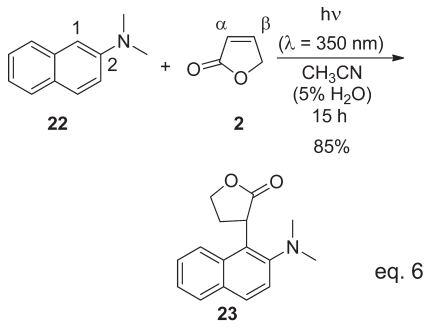
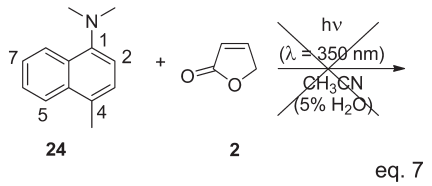
Scheme 11. Photochemical Reactivity of Naphthylamine Derivatives 22 and 24 with Furanone 2 under Standard Conditions





NMR spectra of compound **23** which was recorded at room temperature, conformational rigidity (atropisomerism[77]) was detected. On the other hand, the reactivity concerning electrophilic aromatic substitutions at the 1 position is particularly high in such compounds.[35,37,78]

In the case of the transformation of *N*,*N*-dimethylnaphthalen-1-amine **1**, we observed the favored addition of the furanone **2** in position 4 and a reduced reactivity in position 5 (Scheme 1). We wonder whether we could direct the major reactivity into position 5 or eventually into positions 2 or 7 by blocking position 4 by a methyl substituent in compound **24** (Scheme 11, eq 7). These positions are more or less reactive in electrophilic substitutions.[35−37] However, under the standard reaction conditions and after 20 h of irradiation, no transformation was observed.

As already pointed out, sterically hindered and less planar electron-deficient alkenes were hardly transformed under the described reaction conditions (Scheme 8, Table 2). Obviously, the formation of the key intermediates (radical ion pair) and addition of the oxoallyl radical (compare **II** in Scheme 2) are difficult in such cases. Thus menthyloxyfuranone **25** could not successfully be transformed, although the photochemical electron transfer is more exothermic ($\Delta G_{ET} = -0.60$ eV) than in the case of **2** ($\Delta G_{ET} = -0.39$ eV). The reduction potential of furanone **25** has been determined by cyclic voltammetry (vs ferrocene/ferrocenium) in acetonitrile: $E_p^{red}(\mathbf{25}/\mathbf{25}^-) = -2.52$ V.

We wonder whether such compounds may be transformed when photocatalysis is applied, and we were particularly interested in using heterogeneous photocatalysis with inorganic semiconductors such as TiO_2. Generally, such conditions are applied for purification of waste waters.[79] However, this heterogeneous photocatalysis was also applied to organic synthesis.[80] During our studies on the radical addition of tertiary amines to electron-deficient alkenes[13] making use of this photocatalysis, it became evident that the structure of the radical anion of the furanone **2** (Scheme 5) and in particular the mesomeric structure **B** plays an important role.[40] As outlined above, this structure in the radical ion pair (Scheme 3) explains the regioselective protonation in the β-position of this intermediate. On the basis of these mechanistic similarities with a common intermediate possessing the same polarization, we concluded that TiO_2 heterogeneous photocatalysis might also enable the addition of naphthylamine **1** to less or unreactive alkenes. To prove this hypothesis, we performed the reaction of naphthylamine **1** with menthyloxyfuranone **25** (Scheme 12). Using the standard reaction conditions discussed above, no transformation took place. Using homogeneous photocatalysis with Michler's ketone as electron transfer sensitizer,[39] the transformation could not be carried out.[47] However, when both substrates **1** and **25** were irradiated in the presence of TiO_2 (16 mg, 0.2 mmol in 20 mL), a selective transformation was observed and the two diastereomeric adducts **26** and **27** were obtained in a ratio of 1/3.3 (53% of diastereomeric excess), which is comparable to that observed in the homogeneous reaction with furanones **11** and **12** (Scheme 8, Table 2). A higher excess of the amine **1** was necessary, and no addition of water or another proton source was required to induce the transformation. In particular, the addition of water would have favored photochemical degradation of the organic substrates.[79] As already pointed out above, for this 1,3 chiral induction the diastereoselectivity was moderate when compared to that of the 1,2 chiral induction with comparable compounds, for instance, in addition reactions in the β-position.[71−73]

For the moment, it is difficult to propose a mechanism. For similar transformations, it has been suggested that after formation of an electron hole pair in the semiconductor particle by light absorption, electron transfer occurs from the donor molecule to the particle, which quenches the hole.[81−83] A critical step is the transfer of the electron in the conduction band to the acceptor molecule thus leading to the formation of a radical anion. A characteristic observation in such reactions is the formation of a reduction side product of the acceptor molecule.[83] In our case, such a product (**28**) was indeed observed (Scheme 12).[84] On the other hand, the redox potential of **25** ($E(\mathbf{25}/\mathbf{25}^-) = -2.52$ V (vs fercene/ferrocenium)) seems not to allow such an electron transfer from the conduction band of TiO_2 ($E_{cb} = -1.2$ V (vs fercene/ferrocenium)).[85] In the present case, the TiO_2 containing suspension was irradiated in the presence of large amounts of amine **1**, leading to efficient electron transfer from the amine to the semiconductor particle. In the absence of an appropriate acceptor, appreciable negative charge can thus be built up on the particle, which induces also the otherwise less favorable reduction processes.[85,86] The electron transfer from the conduction band to the alkoxyfuranone **25** may also be facilitated by the fact that it is adsorbed at the particle surface via an interaction of the carboxyl oxygen with a Ti ion.

Alternatively, an electron transfer from the excited naphthylamine derivative **1** to the adsorbed furanone **25** may be considered. The resulting radical ion pair should react in the usual way (compare Scheme 3). In this context it should be noted that **1** is used in excess (2.5 mol L^{-1}). Further investigations are necessary to depict a more precise mechanism.

Structure Determination of Photochemical Products. Compounds **3a,b** (Scheme 1) have been isolated as a chromatographically inseparable 9/1 mixture of regioisomers. The determination of the position of the butyrolactone fragment on the naphthylamine moiety of each isomer is crucial and has been carried out by NMR spectroscopy (500 MHz proton

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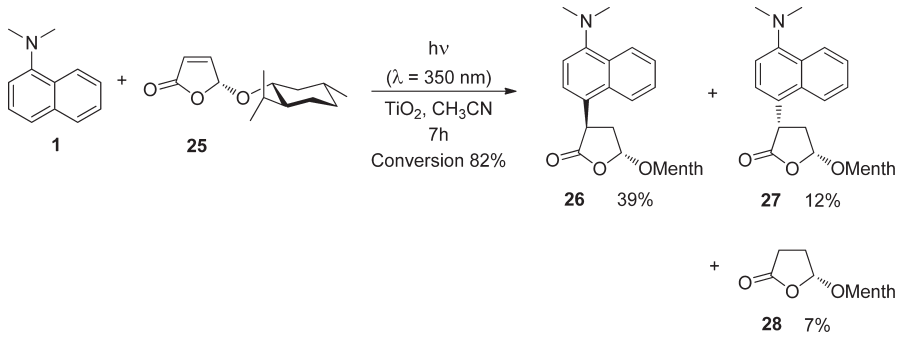
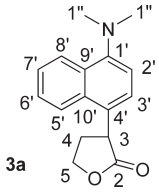
Scheme 12. Addition of Naphthylamine Derivative 1 to Menthyloxyfuranone 25 Using Heterogeneous Photocatalysis with TiO_2[a]



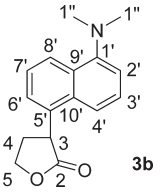
[a] The yields are based on the conversion.

Table 3. NMR Data of Compound 3a (Scheme 1)



^{13}C (ppm)		^{1}H (ppm)	multip, J (Hz)	attribution	HMBC correlation
178.3	Q			2	
150.9	Q			1′	1′ → 8′,2′,3′
132.4	Q			10′	10′ → 8′, 3′
129.3	Q			9′	9′ → 5′, 2′
127.4	Q			4′	4′ → 5′, 2′, 3
126.3	CH	7.53	m	6′	
125.3	CH	7.30	d, 7.8	3′	
125.2	CH	8.33	m	8′	
125.1	CH	7.53	m	7′	
123.4	CH	7.86	m	5′	
113.6	CH	7.05	d, 7.8	2′	
66.7	CH_2	4.48	ddt, 4.8, 8.0, 9.0	5	
45.2	CH_3	2.89	s	1″	
42.6	CH	4.44	m	3	
31.5	CH_2	2.82	dddd, 4.8, 7.1, 9.0, 12.9	4	
		2.42	dq (virt), 12.9, 8.0	4	

Table 4. NMR Data of Compound 3b (Scheme 1)



^{13}C (ppm)		^{1}H (ppm)	multip, J (Hz)	attribution	HMBC correlation
177.9	Q			2	
151.8	Q			1′	
133.4	Q			5′	5′ → 4′, 7′
132.6	Q			10′	10′ → 8′, 3′, 6′
129.5	Q			9′	9′ → 2′, 7′, 4′
126.4	CH	7.47	dd, 7.7, 8.2	3′	
125.1	CH	7.38	d, 6.9	6′	
124.6	CH	7.47	dd, 6.9, 8.5	7′	
124.5	CH	8.28	d, 8.5	8′	
117.7	CH	7.56	d, 8.2	4′	
114.1	CH	7.13	d, 7.5	2′	
[a]	CH_2	4.48	ddt, 4.8, 8.0, 9.0	5	
45.3	CH_3	2.89	s	1″	
43.2	CH	4.49	m	3	
31.6	CH_2	2.80	m	4	
		2.42	m	4	

[a] Uncertain ^{13}C NMR attribution

resonance frequency). Using additionally two-dimensional NMR techniques (COSY, HSQC, HMBC), chemical shifts of almost all protons and ^{13}C atoms have been detected and attributed (Tables 3 and 4). HMBC correlations as well as the coupling motives of protons 3′ in **3a** and **3b** and of proton 6′ in **3b** are particularly indicative. The addition of the naphthylamine derivative in the 3- or α-position of the furanone is also detected by the HMBC correlation. The structures of *syn* and *anti* isomers (**13a** and **15a**) have been determined with NOESY correlations (Figure 3).

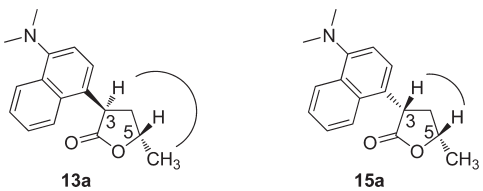


Figure 3. Structure determination of the diastereoisomers **13a** and **15a** (compare Scheme 9) by detection of NOESY correlations.

CONCLUSION

The addition of naphthylamine derivatives to the electron-deficient double bond of furanones has been efficiently carried out with yields up to 90%. Fluorescence quenching of *N*,*N*-dimethylnaphthalen-1-amine by the furanone is diffusion-controlled, and the back electron transfer in the resulting radical ion pair is highly efficient. Therefore, no transformation is observed at lower substrate concentrations. To induce a chemical

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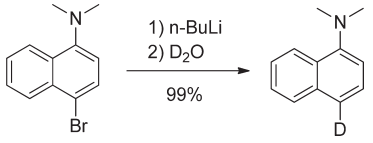
reaction in this inherently unreactive system, two reaction parameters must be modified: water or another proton source must be added, and the naphthylamine must be used in excess in the reaction mixture. Under these conditions the transformation becomes highly efficient. The radical anion of the furanone is protonated, and the resulting electrophilic oxoallyl radical reacts with *N*,*N*-dimethylnaphthalen-1-amine by radical aromatic substitution. Thus back electron transfer in the radical ion pair becomes less dominant. It should further be pointed out that this transformation involving aromatic C−H activation does not need chemical activation with metal compounds or other reagents. Light acts as traceless reagent. The reactivity decreases when sterically encumbering or conformationally mobile substituents are attached to the electron-deficient alkene. First investigations indicate that in such cases, the reactivity may be enhanced when heterogeneous photochemical electron transfer catalysis is applied with inorganic semiconductors such as TiO_2.

EXPERIMENTAL SECTION

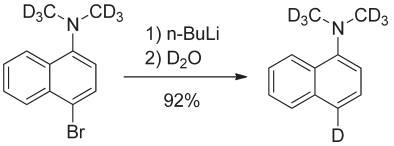
NMR spectra were recorded at frequencies of 250 MHz for ^{1}H and 62 MHz for ^{13}C or 500 MHz for ^{1}H and 125 MHz for ^{13}C. Chemical shifts are given in ppm relative to TMS using residual solvent signals as secondary references. UV Irradiations have been performed with Rayonet reactors at λ = 350 nm. The reaction mixture was irradiated in pyrex tubes (ϕ = 0.9 cm). Preparative chromatography was carried out with silica gel 60A. TLC was carried out with Kieselgel 60F254 plates form Merck.

Synthesis of 4-Deutero-*N*,*N*-dimethylnaphthalen-1-amine 4



At −40 °C and under argon atmosphere, a solution of 4-bromo-*N*,*N*-dimethylnaphthalen-1-amine[87] (10 g, 40 mmol) in ether (140 mL) was added to a solution of *n*-butyllithium in hexane (48 mL, 1.6 M). The resulting mixture was stirred for 1 h. The color changed from red to brown. Deuterium oxide (8.6 mL) was then added. After 3 h at −30 °C the reaction mixture was additionally stirred overnight at room temperature. Water (10 mL) was added, and the mixture was extracted three times with ether (20 mL). The organic phases were dried with $MgSO_4$. After evaporation of the solvent, the residue was distilled. Yield: 6.84 (99%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.92 (s, 6H), 7.09 (d, J = 7.4 Hz, 1H), 7.41 (d, J = 7.4 Hz, 1H), 7.46−7.52 (m, 2H), 7.84 (m, 1H), 8.26 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 45.3, 114.0, 122.6 (t, J = 24.5 Hz), 124.2, 125.2, 125.7, 125.8, 128.4, 128.9, 134.9, 150.9; IR (film) ν 2939, 1575 cm^{-1}. HRSM (ESI + H): m/z calcd for $C_{12}H_{13}DN$ 173.1189, found 173.1182 $[M + H]^+$.

Synthesis of 4-Deutero-*N*,*N*-bis(trideuteromethyl)-naphthalen-1-amine5



At −40 °C and under argon atmosphere, a solution of 4-bromo-*N*,*N*-dimethylnaphthalen-1-amine (19.9 g, 77.6 mmol) in ether (300 mL) was added to a solution of *n*-butyllithium in hexane (93.5 mL, 1.6 M). The resulting mixture was stirred for 2 h. The color changed from red to brown. Deuterium oxide (16.7 mL) was then added. After 3 h at −30 °C the reaction mixture was additionally stirred overnight at room temperature. Water (15 mL) was added, and the mixture was extracted three times with ether (20 mL). The organic phases were dried with $MgSO_4$. After evaporation of the solvent, the residue was distilled. Yield: 13.87 (92%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11 (d, J = 7.4 Hz, 1H), 7.44 (d, J = 7.4 Hz, 1H), 7.51 (m, 1H), 7.54 (m, 1H), 7.87 (dd, J = 7.6/1.4 Hz, 1H), 8.30 (dd, J = 8.0/1.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 44.4 (sept, J = 20.2 Hz), 113.9, 122.6 (t, J = 24.4 Hz), 124.2, 125.2, 125.8, 125.8, 128.4, 128.9, 134.9, 150.9; IR (film) ν 2939, 1582 cm^{-1}. HRSM (ESI + H): m/z calcd for $C_{12}H_7D_7N$ 179.1566, found 179.1557 $[M + H]^+$.

Standard Procedure for Photochemical Transformation of Naphthylamine Derivatives with Electron-Deficient Alkenes under Homogeneous Reaction Conditions. A solution of the α,β-unsaturated ester (1 equiv), the naphthylamine derivative (15 equiv), and water (0.38 mL) in acetonitrile (7 mL) was purged with argon for 20 min before being irradiated until maximal conversion. After evaporation of solvent and water, the residue was purified by flash chromatography (eluent, ethyl acetate/petroleum ether, 1:9). In most cases, mixtures were isolated. Signal attributions in NMR spectroscopy were carried out with two-dimensional spectra (see also Supporting Information).

Compounds 3a,b. A mixture of *N*,*N*-dimethylnaphthalen-1-amine **1** (2.44 g, 14.25 mmol) and furan-2[5*H*]-one **2** (80 mg, 0.95 mmol) was irradiated for 6 h. Compounds **3a,b** were isolated as a 9:1 mixture of regioisomers. Yield: 215 mg (89%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.42 (dq (virt), J = 12.9/8.0 Hz, 1H, maj), 2.42 (m, 1H, min), 2.80 (m, 1H, min), 2.82 (dddd, J = 4.8/7.1/9.0/12.9 Hz, 1H, maj), 2.89 (s, 6H, maj), 2.89 (s, 6H, min), 4.44 (m, 1H, maj), 4.48 (ddt, J = 4.8/8.0/9.0 Hz, 2H maj), 4.49 (m, 2H, min), 7.05 (d, J = 7.8 Hz, 1H, maj), 7.13 (d, J = 7.5 Hz, 1H, min), 7.30 (d, J = 7.8 Hz, 1H, maj), 7.38 (d, J = 6.9 Hz, 1H, min), 7.47 (dd, J = 7.5/8.2 Hz, 1H, min), 7.47 (dd, J = 6.9/8.5 Hz, 1H, min), 7.53 (m, 2H, maj), 7.86 (m, 1H, maj), 8.28 (d, J = 8.5, 1H, min), 8.33 (m, 1H, maj); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.5 (maj), 31.6 (min), 42.6 (maj), 43.2 (min), 45.2 (maj), 45.3 (min), 66.7 (maj), 113.6 (maj), 114.1 (min), 117.7 (min), 123.4 (maj), 124.5 (min), 124.6 (min), 125.1 (min), 125.1 (maj), 125.2 (maj), 125.3 (maj), 126.3 (maj), 126.4 (min), 127.4 (maj), 129.3 (maj), 129.5 (min), 132.4 (maj), 132.6 (min), 133.4 (min), 150.9 (maj), 151.8 (min), 177.9 (min), 178.1 (maj); IR (film) ν 2940, 1771, 1582 cm^{-1}. HRSM (ESI + H): m/z calcd for $C_{16}H_{18}NO_2$ 256.1338, found 256.1331 $[M + H]^+$. Anal. Calcd for $C_{16}H_{17}NO_2$ (255.31): C 75.27, H 6.71, N 5.49. Found: C 74.86, H 6.70, N 5.31.

Compounds 7a,b. A mixture of 4-deutero-*N*,*N*-D_6-dimethylnaphthalen-1-amine **5** (2.54 g, 14.25 mmol) and furan-2[5*H*]-one **2** (80 mg, 0.95 mmol) was irradiated for 6 h. Compounds **7a,b** were isolated as a 10:1 mixture of regioisomers. Yield: 224 mg (90%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.39−259 (m, 1H, maj), 2.79−2.86 (m, 1H, maj), 4.47 (m, 1H, maj), 4.47 (m, 2H, maj), 7.03 (d, J = 7.7 Hz, 1H, maj), 7.11 (d, J = 7.5 Hz, min), 7.30 (d, J = 7.7 Hz, 1H, maj), 7.37 (d, J = 6.9 Hz, 1H, min), 7.45 (m, 1H, min), 7.46 (m, 1H, min), 7.53 (m, 1H, maj), 7.54 (m, 1H, maj), 7.86 (d, J = 8.6 Hz, 1H, maj), 8.27 (d, J = 8.5 Hz, 1H, min), 8.32 (d, J = 9.0 Hz, 1H, maj); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.7 (maj), 31.8 (min), 42.7 (min), 42.8 (maj), 42.7−44.9 (sep, J = 20.1 Hz, maj), 66.8 (min), 66.9 (maj), 113.6 (maj), 114.1 (min), 123.4 (maj), 124.6 (min), 124.7 (min), 125.2 (maj), 125.3 (maj), 125.4 (maj), 126.4 (maj), 127.3 (maj), 129.5 (maj), 129.7 (min), 132.5 (maj), 132.6 (min), 133.4 (min), 151.1 (maj), 178.2 (maj); IR (KBr) ν 2912, 1761, 1581 cm^{-1}. HRSM (ESI + H): m/z calcd for $C_{16}H_{12}D_6NO_2$ 262.1714, found 262.1704 $[M + H]^+$.

Compounds 8a,b. A mixture of *N*,*N*-dimethylnaphthalen-1-amine **1** (2.44 g, 14.25 mmol) and furan-2[5*H*]-one **2** (80 mg, 0.95 mmol) was irradiated for 6 h. Deuteriumoxide (0.375 mL) was used instead of water. Compounds **8a,b** were isolated as a 10:1 mixture of regioisomers. Yield: 224 mg (87%). Incorporation of 1 deuterium >90%. ^{1}H NMR (500

MHz, $CDCl_3$) δ 2.74 (m, 1H, maj), 2.91 (s, 6H, maj), 4.19 (m, 3H, min), 4.38−4.46 (m, 3H, maj), 7.08 (d, J = 7.7 Hz, 1H, maj), 7.16 (d, J = 7.1 Hz, 1H, min), 7.34 (d, J = 7.7 Hz, 1H, maj), 7.42 (d, J = 6.8 Hz, 1H, min), 7.55−7.59 (m, 2H, maj), 7.91 (m, 1H, maj), 8.40 (m, 1H, maj); ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.76-31.07 (t, J = 19.7 Hz, maj), 42.3 (maj), 42.9 (min), 44.9 (maj), 45.1 (min), 60.1 (min), 66.4 (maj), 113.4 (maj), 114.0 (min), 117.5 (min), 123.3 (maj), 124.2 (min), 124.2 (min), 124.7 (min), 124.9 (maj), 124.9 (maj), 125.1 (maj), 126.3 (min), 126.2 (min), 127.3 (maj), 129.1 (maj), 129.2 (min), 132.2 (maj), 132.5 (min), 133.3 (min), 150.7 (maj), 151.8 (min), 178.0 (maj), 178.2 (min); IR (film) ν 2940, 1771, 1582 cm^{-1}. HRSM (ESI + H): m/z calcd for $C_{16}H_{17}DNO_2$ 257.1336, found 257.1333 $[M + H]^+$.

Compound 10. A mixture of *N*,*N*-dimethylnaphthalen-1-amine **1** (2.44 g, 14.25 mmol) and 3-methylfuran-2[5*H*]-one **2** (93.2 mg, 0.95 mmol) was irradiated for 15 h. the conversion attained 62%. Compound **10** was isolated with a yield of 90 mg (35%, selectivity: 57%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.89 (s, 3H), 2.41 (ddd, J = 6.7/8.2/13.1 Hz, 1H), 2.89 (s, 6H), 3.09 (ddd, J = 5.8/7.4/13.1 Hz, 1H), 4.30 (ddd, J = 6.7/7.4/13.9 Hz, 1H), 4.42 (ddd, J = 5.8/8.2/13.9 Hz, 1H), 7.00 (d, J = 8.0 Hz, 1H), 7.40 (d, J = 8.0 Hz, 1H), 7.50 (m, 1H), 7.51 (m, 1H), 7.91 (m, 1H), 8.37 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 24.5, 38.2, 45.3, 47.8, 65.8, 113.2, 124.7, 124.8, 125.2, 125.9, 125.9, 125.9, 130.3, 131.2, 151.3, 181.4; IR (film) ν 2939, 1771, 1585 cm^{-1}. HRSM (ESI + H): m/z calcd for $C_{17}H_{20}NO_2$ 270.1494, found 270.1490 $[M + H]^+$.

Transformation of 5-Substituted Furanone 11. A mixture of *N*,*N*-dimethylnaphthalen-1-amine **1** (4.88 g, 28.5 mmol) and 5-methylfuran-2[5*H*]-one **11** (186 mg, 1.9 mmol) was irradiated for 6 h. After evaporation, the product mixture was separated by column chromatography. A first fraction of 250 mg (45%) contained compounds a 11/1 mixture of the regioisomers **13a,b**. A second fraction of 68 mg (13%) contained a 10/1 mixture of regioisomers **15a,b**. Thus the diastereoisomers were separated.

Compounds 13a,b. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.48 (d, J = 6.2 Hz, 1H, maj), 2.42−2.48 (m, 2H, maj), 2.88 (s, 6H, maj), 2.89 (s, 6H, min), 4.55 (dd, J = 6.0/8.5 Hz, 1H, maj), 4.6 (dd, J = 6.6/8.0 Hz, 1H, min), 4.77 (m, 1H, maj), 7.02 (d, J = 7.8 Hz, 1H, maj), 7.12 (d, J = 7.4 Hz, 1H, min), 7.26 (d, J = 7.8 Hz, 1H, maj), 7.34 (d, J = 6.9 Hz, 1H, min), 7.42−7.48 (m, 2H, min), 7.51−7.55 (m, 2H, maj), 7.84 (m, 1H, maj), 8.26 (d, J = 8.5 Hz, 1H, min), 8.32 (m, 1H, maj); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.0 (maj), 38.8 (maj), 38.9 (min), 43.8 (maj), 44.4 (min), 45.3 (2x, maj), 44.5 (2x, min), 75.7 (maj), 113.6 (maj), 114.3 (min), 117.9 (min), 123.5 (maj), 124.6 (min), 124.7 (maj), 125.3 (maj), 126.5 (maj), 126.6 (min), 127.4 (maj), 129.6 (maj), 132.4 (maj), 132.5 (min), 133.8 (min), 151.0 (maj), 177.9 (min), 178.1 (maj); IR (film) ν 2938, 1771, 1582 cm^{-1}. HRSM (ESI + H): m/z calcd for $C_{17}H_{20}NO_2$ 270.1494, found 270.1491 $[M + H]^+$.

Compounds 15a,b. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.53 (d, J = 6.1 Hz, 1H, maj), 2.08 (ddd, J = 5/6/11.5 Hz, 1H, maj), 2.88 (s, 6H, maj, min), 4.52 (dd, J = 9.1/11.8 Hz, 1H, maj), 4.58 (m, 1H), 4.74 (m, 1H), 7.06 (d, J = 7.7 Hz, 1H), 7.11 (d, J = 7.3 Hz, 1H, min), 7.36 (d, J = 7.7 Hz, 1H, maj), 7.43−7.47 (m, 3H, min), 7.51−7.53 (m, 2H, maj), 7.56 (d, J = 9.1 Hz, 1H, min), 7.85 (m, 1H, maj), 8.27 (d, J = 8.3 Hz), 8.33 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.2 (maj), 39.8 (maj), 39.9 (min), 44.8 (maj), 45.3 (2x, maj), 45.4 (2x, min), 75.3 (maj), 113.8 (maj), 114.2 (min), 117.7 (min), 123.4 (maj), 124.5 (min), 124.6 (min), 125.1 (maj), 125.3 (maj), 125.9 (maj), 126.3 (maj), 126.4 (min), 127.5 (maj), 129.4 (maj), 129.6 (min), 132.6 (maj), 132.8 (min), 133.5 (min), 152.0 maj), 151.9 (min), 177.3 (min), 177.5 (maj); IR (film) ν 2936, 1764, 1582 cm^{-1}. HRSM (ESI + H): m/z calcd for $C_{17}H_{20}NO_2$ 270.1494, found 270.1497 $[M + H]^+$.

Transformation of 5-Substituted Furanone 12. A mixture of *N*,*N*-dimethylnaphthalen-1-amine **1** (4.88 g, 28.5 mmol) and 5-ethoxyfuran-2[5*H*]-one **12** (243 mg, 1.9 mmol) was irradiated for 6 h. After evaporation, the product mixture was separated by column chromatography. A first fraction of 143 mg (25%) contained compounds a 10/1 mixture of the regioisomers **14a,b**. A second fraction of 60 mg (10%) contained a 10/1 mixture of regioisomers **16a,b**. Thus the diastereoisomers were separated.

Compounds 14a,b. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.31 (t, J = 7.0 Hz, 3H, maj), 2.55 (m, 1H, maj), 2.74, (dd, J = 9.1/13.1 Hz, 1H), 2.88 (s, 6H, maj), 3.68 (dq J = 9.0/7.0 Hz, 1H, maj), 3.96 (dq J = 9.0/7.0 Hz, 1H, maj), 4.68 (t (virt), J = 9.7 Hz, 1H, maj), 5.65 (d, J = 5.4 Hz, 1H, maj), 7.05 (d, J = 7.7 Hz, 1H, maj), 7.12 (d, J = 7.3 Hz, 1H, min), 7.31 (d, J = 7.7 Hz, 1H, maj), 7.38 (d, J = 6.9 Hz, 1H, min), 7.44−7.48 (m, 2H, min), 7.51−7.53 (m, 2H, maj), 7.56 (d, J = 8.8 Hz, 1H, min), 7.85 (m, 1H, maj), 8.28 (d, J = 8.4 Hz, 1H, min), 8.33 (m, 1H, maj); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.1 (maj), 38.5 (maj), 38.6 (min), 41.6 (maj), 42.1 (min), 45.3 (maj), 45.4 (min), 65.3 (maj), 102.1 (maj), 113.8 (maj), 114.3 (min), 117.8 (min), 123.4 (maj), 124.6 (min), 124.9 (min), 125.2 (maj), 125.3 (maj), 125.8 (maj), 126.5 (maj), 127.5 (maj), 129.4 (maj), 132.6 (maj), 132.8 (min), 133.4 (min), 151.0 (maj), 151.8 (min), 177.6 (maj); IR (film) ν 2938, 1778, 1583 cm^{-1}. HRSM (ESI + H): m/z calcd for $C_{18}H_{22}NO_3$ 300.1600, found 300.1591 $[M + H]^+$.

Compounds 16a,b. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.28 (t, J = 7.0 Hz, 3H, maj), 2.34 (m, 1H, maj), 2.88 (m, 6H, maj), 3.02 (m, 1H, maj), 3.70 (dq J = 9.0/7.0 Hz, 1H, maj), 4.00 (dq J = 9.0/7.0 Hz, 1H, maj), 4.49 (dd, J = 8.3/10.0 Hz, 1H, maj), 4.54 (dd, J = 8.3/10.2 Hz, 1H, min), 5.67 (t (virt), J = 4.9/5.3 Hz, 1H, maj), 7.05 (d, J = 7.8 Hz, 1H, maj), 7.12 (d, J = 7.4 Hz, 1H, min), 7.41 (d, J = 7.8 Hz, 1H, maj), 7.41−7.47 (m, 3H, min), 7.52 (m, 2H, maj), 7.55 (d, J = 9.3 Hz, 1H, min), 7.87 (m, 1H, maj), 8.27 (d, J = 7.5 Hz, 1H, min), 8.33 (m, 1H, maj); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.1 (maj), 37.4 (maj), 37.6 (min), 42.7 (maj), 43.3 (min), 45.3 (maj), 45.4 (min), 66.1 (maj), 103.1 (maj), 104.5 (min), 113.8 (maj), 114.2 (min), 117.9 (min), 123.5 (maj), 124.7 (min), 124.8 (min), 125.1 (maj), 125.2 (maj), 126.0 (maj), 126.4 (maj), 127.8 (maj), 129.4 (maj), 132.5 (maj), 151.0 (maj), 151.9 (min), 176.4 (min), 177.5 (maj); IR (film) ν 2938, 1773, 1582 cm^{-1}. HRSM (ESI + H): m/z calcd for $C_{18}H_{22}NO_3$ 300.1600, found 300.1595 $[M + H]^+$.

Compounds 19a,b. A mixture of *N*,*N*-dimethylnaphthalen-1-amine **1** (2.44 g, 14.25 mmol) and methylcrotonate **17** (95 mg, 0.95 mmol) was irradiated for 8 h. Compounds **8a,b** were isolated as a 9:1 mixture of regioisomers. Yield: 115 mg (60%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.00 (t, J = 7.3 Hz, 3H, maj), 1.00 (3H, min), 1.96 (dp, J = 6.6/7.3 Hz, 1H, maj), 1.96 (1H, min), 2.29 (dp, J = 8.2/7.3 Hz, 1H, maj), 2.29 (1H, min), 2.90 (s, 6H, maj), 2.90 (6H, min), 3.66 (s, 3H, maj), 4.25 (dd, J = 6.7/8.2 Hz, 1H, maj), 4.31 (dd, J = 6.7/8.2 Hz, 1H, min), 7.08 (d, J = 7.8 Hz, 1H, maj), 7.12 (d, J = 7.4 Hz, 1H, min), 7.43 (d, J = 7.8 Hz, 1H, maj), 7.47 (dd, J = 7.4/8.5 Hz, 1H, min), 7.47−7.49 (m, 1H, min), 7.51 (m, 1H, min), 7.52 (m, 1H, maj), 7.54 (m, 1H, maj), 7.83 (d, J = 8.5 Hz, 1H, min), 8.13 (dd, J = 1.3/7.8 Hz, 1H, maj), 8.25 (d, J = 8.1 Hz, 1H, min), 8.33 (dd, J = 1.6/7.8 Hz, 1H, min); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.7 (maj), 12.7 (min), 26.5 (maj), 26.6 (min), 45.4 (maj), 45.5 (min), 48.4 (maj), 48.9 (min), 52.1 (maj), 113.9 (maj), 114.0 (min), 118.1 (min), 123.6 (maj), 123.8 (min), 124.8 (min), 124.9 (min), 124.9 (maj), 125.0 (maj), 125.1 (maj), 126.2 (min), 126.2 (maj), 129.3 (maj), 129.6 (min), 130.0 (maj), 132.9 (maj), 133.1 (min), 135.8 (min), 150.3 (maj), 151.8 (maj), 175.0 (min), 175.2 (maj); IR (film) ν 2948, 1734, 1583, 1169 cm^{-1}. HRSM (ESI + Na): m/z calcd for $C_{17}H_{21}NO_2Na$ 294.1470, found 294.1475 $[M + Na]^+$.

Compounds 20a,b and 21. A mixture of *N*,*N*-dimethylnaphthalen-1-amine **1** (2.44 g, 14.25 mmol) and dimethylfumarate **18** (137 mg, 0.95 mmol) was irradiated for 8 h. Compounds **20a,b** and **21** were isolated as a 11:1:2.5 mixture. Yield: 205 mg (69%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.74 (dd, J = 4.3/17.1 Hz, 1H, maj), 2.74 (m, 1H, min), 2.88 (s, 6H, maj), 2.88 (s, 6H, min), 3.05 (s, 3H, **21**), 3.27 (dd, J = 11.5/13.4 Hz, **21**), 3.34 (dd, J = 10.4/17.1 Hz, 1H, maj), 3.34 (m, 1H, min), 3.60 (dd, J = 3.6/13.4 Hz, 1H, **21**), 3.68 (s, 3H, maj), 3.68 (s, 3H, min), 3.71 (s, 3H, maj), 3.71 (s, 3H, min), 3.79 (s, 3H, **21**), 3.82 (s, 3H, min),

4.35 (d, J = 10.3 Hz, 1H, **21**), 4.87 (dd, J = 4.3/10.4 Hz, 1H, maj), 4.93 (dd, J = 4.4/10.5 Hz, 1H, min), 7.02 (d, J = 7.8 Hz, 1H, maj), 7.12 (d, J = 7.4 Hz, 1H, min), 7.30 (d, J = 7.8 Hz, 1H, maj), 7.37 (m, 1H, min), 7.38 (m, 1H, **21**), 7.44 (m, 1H, min), 7.45 (m, 1H, **21**), 7.48 (m, 1H, min), 7.49 (m, 2H, **21**), 7.52 (m, 1H, maj), 7.54 (m, 1H, maj), 7.77 (d, J = 7.4 Hz, 1H, **21**), 7.77 (m, 1H, min), 8.08 (dd, J = 1.0/8.1 Hz, maj), 8.17 (d, J = 8.3 Hz, 1H, **21**), 8.25 (d, J = 8.3 Hz, 1H, min), 8.31 (dd, J = 1.4/8.0 Hz, 1H, maj); ^{13}C NMR (125 MHz, $CDCl_3$) δ 36.9 (**21**), 37.6 (maj), 37.6 (min), 42.8 (maj), 43.2 (min), 44.2 (**21**), 45.3 (maj), 45.3 (min), 46.2 (**21**), 52.0 (maj), 52.3 (**21**), 52.4 (**21**), 52.5 (maj), 52.7 (**21**), 113.7 (maj), 114.3 (min), 117.8 (min), 120.8 (**21**), 123.4 (maj), 123.7 (**21**), 124.0 (**21**), 124.5 (min), 125.2 (maj), 125.6 (**21**), 125.8 (**21**), 126.0 (**21**), 126.6 (maj), 128.4 (maj), 128.5 (**21**), 129.4 (maj), 129.7 (min), 132.3 (maj), 132.5 (min), 133.9 (**21**), 144.2 (**21**), 150.8 (min), 150.9 (maj), 172.4 (min), 172.5 (maj), 173.6 (**21**), 174.1 (**21**), 174.2 (min), 174.3 (maj); IR (film) ν 2951, 1733, 1582, 1160 cm^{-1}. HRSM (ESI + Na): m/z calcd for $C_{18}H_{21}NO_4Na$ 338.1368, found 338.1367 [M + Na]$^+$ (maj, min).

Compound 23. A mixture of *N,N*-dimethylnaphthalen-2-amine **22** (2.44 g, 14.25 mmol) and furan-2[5*H*]-one **2** (80 mg, 0.95 mmol) was irradiated for 15 h. Compound **23** was isolated as with a yield of 205 mg (85%). Due to conformational restrictions, NMR spectra recorded in $CDCl_3$ at room temperature had domains with low resolution. ^{1}H NMR (500 MHz, DMSO-d_6, 80 °C) δ 2.38−2.48 (m, 2H), 2.65 (s, 6H), 4.45 (dd, J = 8.8/16.9 Hz, 1H), 4.57 (dt (virt), J = 3.2/8.8 Hz, 1H), 4.94 (t (virt), J = 9.8 Hz, 1H), 7.42−7.58 (m, 3H), 7.89 (m, 3H); ^{13}C NMR (125 MHz, DMSO-d_6, 80 °C) δ 29.2, 37.6, 44.9, 65.7, 120.6, 123.3, 124.2, 125.8, 128.1, 128.6, 131.3 (2×), 131.4, 150.1, 177.2; IR (KBr) ν 2936, 1761, 1451, 1183 cm^{-1}. HRSM (ESI + H): m/z calcd for $C_{16}H_{18}NO_2$ 256.1338, found 256.1335 [M + H]$^+$.

Transformation of 5-Menthyloxyfuran-2[5*H*]-one 25 Using Heterogeneous Photocatalysis. Photochemical transformation of the *N,N*-dimethylnaphthalen-1-amine **1** with 5-menthyloxyfuran-2[5*H*]-one **25** under heterogeneous photocatalytic conditions. A suspension of menthyloxyfuranone **25** (250 mg, 1.05 mmol), *N,N*-dimethylnaphthalen-1-amine **1** (8.55 mg, 53 mmol), and TiO_2 (99% anatase purchased from ACROS) (16 mg, 0.2 mmol) in acetonitrile (40 mL) was filled in pyrex tubes (ϕ = 2 cm) and purged with argon for 30 min before being irradiated at λ = 350 nm (Rayonet). During irradiation, the suspension was stirred with a magnetic stirring bar. After 7 h of irradiation and filtration over Celite, the solvent and the amine excess were evaporated. The residue was subjected to column chromatography (eluent, ethyl acetate/petroleum ether, 1:5). A first fraction of 136 mg (32%, selectivity 39%) contained **26**; $[\alpha]^{21}_D$ = 29.4 (c 0.320 in CH_2Cl_2). A second fraction contained a mixture of compounds **25**, **27**, and the reduction product **28**. The proportion of different constituents was determined by ^{1}H NMR spectroscopy. Yield of **27**: 43 mg (10%, selectivity 12%). Yield of **28**:[39] 15 mg (6%, selectivity 7%).

Compound 26. ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.85 (d, J = 6.8 Hz, 3H), 0.94 (d, J = 6.8 Hz, 6H), 0.76−1.09 (m, 3H), 1.18−1.50 (m, 2H), 1.61−1.75 (m, 2H), 2.10−2.30 (m, 2H), 2.56 (ddd, J = 13.2/10.7/5.4 Hz, 1H), 2.73 (dd, J = 13.2/8.8 Hz, 1H), 2.90 (s, 6H), 3.68 (dt, J = 10.7/4.1 Hz, 1H), 7.34 (d, J = 7.8 Hz, 1H), 7.41−7.60 (m, 2H), 7.86 (m, 1H), 8.34 (m, 1H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 15.6, 21.0, 22.2, 23.0, 25.6, 31.3, 34.3, 38.7, 39.8, 41.7, 45.1, 47.8, 76.6, 98.3, 113.6, 123.2, 125.0, 125.2, 125.8, 126.2, 127.3, 129.3, 132.4, 151.0, 177.2; IR (KBr) ν 2959, 1789, 1455, 1199 cm^{-1}; MS (EI) m/z (%) 409 (26) [M]$^+$, 226 (100), 197 (38), 182 (12), 153 (14). Anal. Calcd for $C_{26}H_{35}NO_3$ (409.56): C 76.25, H 8.61, N 3.42. Found: C 76.78, H 9.11, N 3.42.

Compound 27. ^{1}H NMR (250 MHz, $CDCl_3$) (only signals that are attributable are reported) δ 2.86 (s, 6H), 3.52 (dt, J = 10.6/4.2 Hz, 1H), 4.47 (dd, J = 10.5/7.2 Hz, 1H), 5.90 (dd, J = 6.1/4.0 Hz, 1H), 7.02 (d, J = 7.8 Hz, 1H), 7.39 (d, J = 7.6 Hz, 1H), 7.47−7.58 (m, 2H), 7.86 (m, 1H), 8.32 (m, 1H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 15.6, 21.0, 22.2, 22.9, 25.2, 31.3, 34.2, 37.4, 39.6, 42.9, 45.2, 47.7, 77.4, 99.2, 113.4, 123.5, 125.0, 125.1, 125.9, 126.2, 127.9, 129.4, 132.4, 150.9, 176.6.

Physicochemical Studies. The solvent acetonitrile (Baker, HPLC grade) was dried over molecular sieve (3 Å), redistilled, and stored under argon atmosphere. All samples to be measured contained 2.2×10^{-5} M *N,N*-dimethyl-1-naphthylamine **1** and were prepared and kept under argon atmosphere. For the Stern−Volmer quenching series the liquid quencher 2[5*H*]-furanone **2** was directly added into the cuvette with the help of a Hamilton syringe in stepwise concentrations up to 0.06 M. When the influence of water on the reaction was studied, the samples were prepared in the same way, except that 1% of bidistilled water was deliberately added before measurement. Absorption spectra were recorded on a Shimadzu UV-3101-PC UV−vis−NIR spectrophotometer. Steady state fluorescence measurements (excitation 312 nm) were carried out using a Jobin Yvon Fluoromax-2 spectrofluorimeter, while the corresponding time-resolved fluorescence measurements were performed on a custom-built LED-based modulation fluorimeter (excitation LED 340 nm, cutoff filter GG 400) that has been described elsewhere.[88] During all fluorescence experiments the sample cuvette was thermostatted to 298 K (25 °C). Fluorescence quantum yields were determined against 2.2×10^{-5} M quinine hemisulfate in 0.5 M H_2SO_4 (excitation 347.5 nm, Φ = 0.546).

Cyclic Voltammetry of Furanones 2 and 25. Cyclic voltammetry was carried out with an Autolab PGSTAT12 potentiostat from ECO Chemie coupled to an electrochemical cell with three electrodes. A platinum disk was used as working electrode with a Pt wire as counter. $Ag/AgNO_3$ was used as reference electrode. Solutions of the furanone derivatives **2** and **25** or *N,N*-dimethylnaphthylamine **1** (10^{-3} mol L^{-1}) in acetonitrile containing Bu_4NPF_6 (0.1 mol L^{-1}) have been measured with a scan rate of 100 mV s^{-1}. Fc^+/Fc was used as internal reference. Furan-2[5*H*]-one **2**: E_p^{red} = −2.75 V. 5-Menthyloxyfuran-2[5*H*]-one **25**: E_p^{red} = −2.52 V. *N,N*-Dimethylnaphthylamine **1**: E_p^{ox} = +0.39 V.

Quantum Chemical Calculations. Quantum chemical calculations for the radical cation **I** were performed using HyperChem 5.11 Prof: Geometry optimization was carried out with 3-21G to C_S symmetry. Calculations on the optimized structure were carried out with UHF/6-31 G**.

■ ASSOCIATED CONTENT

Supporting Information. Tables with two dimentional NMR data of compounds **10**, **19a**, **19b**, **20a**, **20b**, **21**, and **26**; NOE of compound **26**; copies of ^{1}H NMR and ^{13}C NMR spectra and cyclic voltametry of *N,N*-dimethylnaphthylamine **1**, furanone **2**, and 5-menthyloxyfuranone **25**; atom coordinates of the radical cation **I**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(67) A direct reaction of radical **II** with **1** (Scheme 6) without previous electron transfer is improbable. In a corresponding direct reaction of electrophilic trifluoromethyl radicals with 1-aminonaphthalene, 1-amino-2-(trifluoromethyl)naphthalene, and 1-amino-4-(trifluoromethyl)naphthalene were isolated in a 1/1 ratio. In this case, no reaction was detected in position 4. Strekowski, L.; Hojjat, M.; Patterson, S. E.; Kiselyov, A. S. *J. Heterocycl. Chem.* **1994**, *31*, 1413–1416.

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