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# Structure-reactivity relationships in (2-hydroxyethyl)benzophenone photoremovable protecting Groups

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ABSTRACT

A detailed study of substituent effects on the photochemical conversion of esters of (2-hydroxyethyl)benzophenone to the carboxylic acid was performed with the aim of improving on the reactivity of the parent, which was first reported decades ago. Over 20 derivatives were prepared, 10 of which exhibit some level of photochemical reactivity, but none of them is appreciably better than the original. The reaction did not respond to a thioxanthone as a sensitizer or the inclusion of base to facilitate elimination. Solvent effects on the reaction also seem to be small, with the exception of the perfluorphenyl analog, which is totally unreactive in hexanes but behaves normally in methanol or acetonitrile. These neglected protecting groups may still prove useful in organic synthesis, with fairly rapid deprotection even with long-wavelength irradiation.

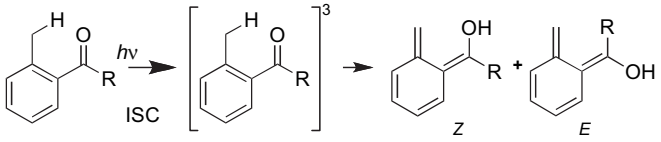


## 1. Introduction

Photochemically removable protecting groups are key elements of a variety of current technologies, including the fabrication of DNA microarrays. Many protecting groups for deoxyribose hydroxyls have been investigated for this application. The two most prominent are both nitroaromatics: the NPPoc group developed by Pfleiderer[1] and the MeNPoc group developed by Holmes.[2] The latter derivatives are currently used for fabrication of commercial Affymetrix microarrays, while the former are used with the maskless array synthesizers as practiced by NimbleGen and Febit. The NPPoc group undergoes a beta-elimination reaction to give a hemi-carbonate that decarboxylates. The MeNPoc group undergoes an internal redox reaction to release the hemi-carbonate.

There are many issues with nitrobenzyl photochemically removable protecting groups, such as: their chemical yields are most often <100%; they give a nitrosocarbonyl by-product with a significant UV absorption and sometimes problematic chemical reactivity; they are typically poor chromophores: their native $\varepsilon$ is too low, and their native $\lambda_{max}$ is too blue, meaning that substituents must be added to shift the absorption to the red, out of the range of the DNA being synthesized; consequently, they may be subject to the common wavelength/reactivity compensation, i.e., as $\lambda_{max}$ increases, $\Phi$ decreases because the excited state energy decreases. MeNPoc in particular has the drawback of ca. 90% cycle yields in DNA synthesis, but is the only photoremovable group that can be removed in the absence of solvent, which provides virtues for large-scale manufacture. There are a limited number[3] of other fundamental organic compound frameworks that exhibit sufficiently desirable photochemical traits to be effective as protecting groups. This work explored the photochemical manifold of a neglected photoremovable protecting group skeleton.

The photoenolization of aryl ketones bearing an *ortho*-alkyl group that includes an alpha-hydrogen (Scheme 1) is an interesting photochemical reaction that has an analogy in the photochemical behavior of the NPPoc group, yet it has been poorly explored for deprotection compared to nitroaromatic groups. The reaction proceeds via the triplet excited state, which is easily reached owing to the rapid intersystem crossing known for aryl ketones. This triplet can be converted to two stereoisomeric dienols. The proximity of the hydrogen in the (*Z*)-dienol to the terminal alkene facilitates an intramolecular transfer of this hydrogen, which converts it back to starting material. Consequently this enol has a shorter lifetime than the (*E*)-dienol, which does not




**Scheme 1.**

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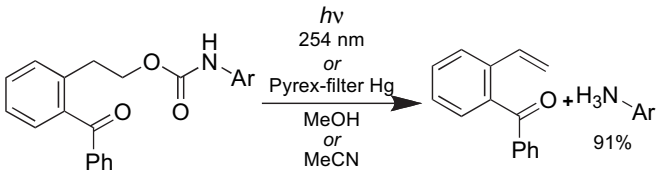
have such favorable proximity. This energy-wasting reversion to starting material reduces the product quantum yield and the rate of any reactions involving these dienols. One example is available for the use of photoenolization to trigger photoremoval of a protecting group by beta-elimination. In 1976 work of Ullman and Tseng,[4] a benzophenone bearing an ethylene linker and a leaving group was shown to undergo photochemical deprotection (Scheme 2). This is a triplet reaction, as naphthalene quenches a reactive triplet state that has a 1 μs lifetime. The product quantum yield $\Phi_{prod}$ correlates with leaving group ability, and the photoenolization quantum yield $\Phi_{photenol}$ appears to be ~0.45, close to the $\Phi_{prod}$ of 0.47 when the leaving group is the very reactive tosylate (rather than the carbamate shown). Therefore, photoenolization is rate-determining with good leaving groups, and $\Phi_{photenol} \equiv \Phi_{prod}$. It is conceivable that the 0.45 $\Phi_{photenol}$ reflects only the formation of the (*E*)-dienol, with the (*Z*) rapidly reverting to starting material. With poorer leaving groups, elimination is rate-determining, and some dienol reverts to starting material, so $\Phi_{prod} < \Phi_{photenol}$. This is the case when a carbamate is the leaving group, as shown. The product quantum yield for this reactant could be marginally increased (to 0.28) by the inclusion of a weak base in the reaction mixture, which presumably facilitates the elimination step at the expense of reversion to starting material.



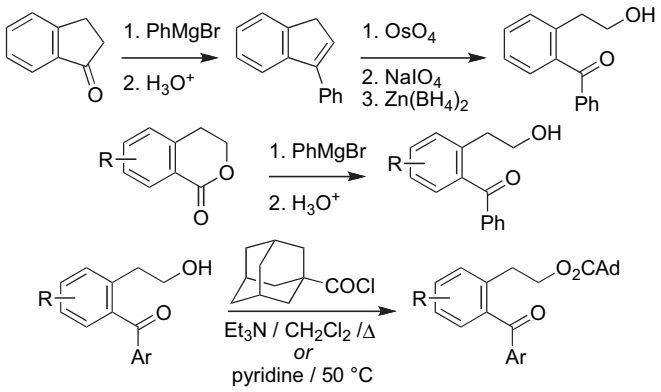

**Scheme 2.**

Another example of this type of reaction with an acetophenone derivative has been reported.[5] This reactant releases a carboxylic acid in respectable isolated yield upon irradiation. Its reaction is quenched by oxygen, as expected for a triplet reactive excited state. However, the simple acetophenone chromophore is far less absorbing than the benzophenone used by Ullman, and the reaction is very slow.

We aimed to modify the structure of the parent (2-hydroxyethyl)benzophenone chromophore to increase its absorptivity at the longer wavelengths more compatible with UV-absorbing biomolecules like proteins and nucleic acids and to enhance its photochemical reactivity (both chemical and quantum yield) to offer an alternative to nitrobenzyl systems for photochemical deprotection.

## 2. Results

Two principal methods were used to prepare the target (2-hydroxyethyl)benzophenone derivatives (Scheme 3). The first is essentially the route used by Ullman. An indanone is submitted to phenyl Grignard addition and dehydration, and the resulting indene is subjected to oxidative cleavage, reduction, and re-oxidation. His route was modified in two ways: osmylation followed by periodate cleavage is more convenient than ozonolysis, and zinc borohydride[6] is selective for reduction of the aldehyde over the benzophenone and obviates the over-reduction and re-oxidation step used by Ullman. The second method is direct Grignard addition to an isochromanone. Once the alcohols were in hand, they were converted to their adamantanoate esters by one of two methods. Adamantanoic acid was chosen so that the chemical yield of deprotection could be directly determined without risk of loss of a volatile acid.




**Scheme 3.**

All of the prepared compounds that exhibited photoreactivity in hexane (and two that do not) are collected in Chart 1, and the specific routes and procedures for their syntheses are provided in the Supplementary data. General procedures representing each of the steps in Scheme 3 are provided in the Experimental section. All of the compounds prepared were directly compared against the parent chromophore reported by Ullman in the form of compound **1**. For comparison to a photochemically removable group already used in DNA synthesis, the adamantanoyl derivative of (*o*-nitrophenyl)propanol (**2**) was also prepared. Absorption properties of compounds in Chart 1 are given in Table 1. This includes absorption at 366 nm, our desired reaction wavelength, as well as at 300 nm, which was examined when it became apparent that simple modifications to the parent chromophore would not lead to large leaps in efficiency. Many other analogs were prepared that showed no photoreactivity, and some of their structures and absorption properties are given in the Supplementary data. For all compounds prepared in this work, their UV spectra were recorded in hexane solvent.

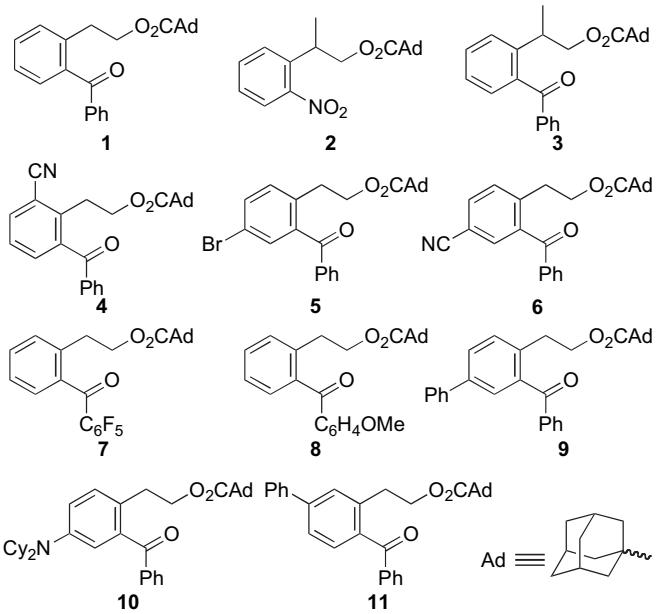



**Chart 1.**

The photochemical reactivity of these (hydroxyethyl)benzophenone analogs was assessed by irradiating solutions at 1 mM in hexane or acetonitrile for 30 min using the long-wavelength phosphor lamps (ca. 366 nm) in a Rayonet photochemical reactor. The extent of conversion was determined by the integration of the

**Table 1**
Absorption and photochemical properties of compounds in Chart 1

| Compound | $\varepsilon_{366}$ | $\varepsilon_{300}$ | % Conversion (hex) | % Conversion (acn) | % Conversion (MeOH, 300 nm) |
|---|---|---|---|---|---|
| **1** | 77 | 501 | 65 | 63 | 72 |
| **2** | 261 | 1048 | 100 | 100 | 62 |
| **3** | 34 | 98 | 0 | 0 | 0 |
| **4** | 94 | 494 | 53 | 51 | 59 |
| **5** | 83 | 916 | 53 | 49 | 62 |
| **6** | 90 | 688 | 54 | 49 | 60 |
| **7** | 45 | 889 | 0 | 41 | 49 |
| **8** | 100 | 1526 | 69 | 70 | 84 |
| **9** | 93 | 1323 | 59 | 64 | 69 |
| **10** | 114 | 1087 | 54 | 76 | 67 |
| **11** | 174 | 1662 | 64 | 63 | 58 |
| **1**+IPTX | — | — | — | 28 | — |
| **2**+IPTX | — | — | — | 100 | — |
| **8**+IPTX | — | — | — | 39 | — |

carbinol $CH_2$ in the starting materials versus the vinyl $CH_2$ in the styrene product in the NMR spectrum of the crude reaction mixture. These experiments were performed in triplicate. In selected cases, this conversion was verified by product isolation, purification, and styrene yield determination. A preparative irradiation was conducted on **1** and the styrene product was isolated in 58% yield, nearly the % conversion found from NMR. This indicates that the styrene is stable under these reaction conditions and that the NMR integration is a fair indication of the conversion. Subsequent experiments also used the 300 nm lamps in the Rayonet with methanol as solvent.

None of these (hydroxyethyl)benzophenone derivatives approached the reactivity of the NPPoc chromophore **2**. The best reactant observed was **8**, which is only a slight improvement on **1**. Its enhanced absorption due to the *p*-methoxy group is likely the reason for this observation.

Sensitization of the reaction with isopropylthioxanthone was also examined for compounds **1**, **2**, and **8**, at 366 nm in acetonitrile. The two (hydroxyethyl)benzophenone derivatives showed reduced conversion. For all compounds that underwent photoreactions, reactions were attempted in hexane with the inclusion of 1 mM diisopropylethylamine, but it had no effect on the conversion. Preparative irradiation of **1** for 2 h at 366 nm gave adamantanecarboxylic acid in 75% isolated yield.

## 3. Discussion

Many aspects of the results are perplexing. Comparison of the photochemically reactive compounds (Chart 1) to those that are not reactive (Chart S1) reveals the dilemma. Methoxy substitution at the *para* position of the phenyl ring (**8**) gives the best compound, but methoxy substitution at the 4-position of the substituted ring (**S4**) abolishes photoreactivity. Bromination at the 5-position of the substituted ring (**5**) is tolerated, but bromination at the 4-position (**S5**) abolishes photoreactivity. Phenyl substitution at the 4-position of the substituted ring (**11**) gives a compound with the greatest absorption of all compounds prepared, but this does not translate to improved conversion. Unusual behavior is exhibited by the perfluorophenyl analog **7**, as it is unreactive in hexanes but reacts normally in polar solvents. Some observations are understandable. Introduction of a methyl group at the benzylic position to give compound **3** was expected to stabilize the photoenol via alkyl substitution, much as was noted with the aci-nitro intermediate in the photochemical elimination of nitrophenylpropyl derivatives.[7] However, compound **3** is totally unreactive, which can be explained by its much-reduced absorption. Evidently, steric interactions between the methyl group and the adjacent benzoyl group cause the latter to rotate out of conjugation with the substituted ring. This observation illustrates the difference between structure-reactivity relationships in the nitrophenethyl groups and the (hydroxyethyl)benzophenones. Likewise the ineffectiveness of the addition of base, which was useful in the initial work on the NPPoc group. Another illustration is the lack of any gain in photoreactivity from 5-phenyl substitution (**11**), whereas this modification is very effective in nitrophenethyl groups.[7]

The tendency for the (*Z*)-dienols produced by photoenolization to revert to starting material, as shown in their lifetimes, can be modified by aromatic substituents.[8] In particular, electron-withdrawing influences (a cyano group or a pyridine nitrogen) in conjugation with the enol lengthen its lifetime. Compounds **4** and **6** were designed to exploit this effect to increase the lifetime of the dienol intermediates, shown in Chart 2. The fact that neither had significantly improved performance may indicate that dienol lifetime does not limit the efficiency of this photochemical deprotection. It was likewise envisioned that increasing the acidity of the photoenol through inductive effects could favor its ionization to the dienolate, which would be more effective in displacing the leaving group; hence, **7** was prepared. Again, the lack of a benefit of this change suggests that the dienol acidity is not a key determinant of photochemical reaction efficiency.

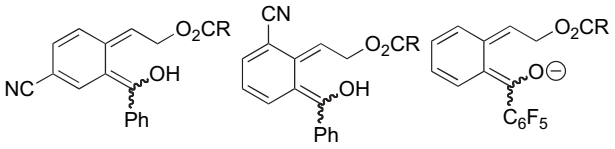



**Chart 2.**

Compound **8** represents the only example among the many strategies attempted to provide even a modest benefit. It is also interesting that there is little enhancement in photoreactivity by moving the irradiation wavelength deeper into the UV absorption bands of these materials.

One typically expects that a change in a chromophore can modify the nature of its excited state, both in terms of its multiplicity and electronic configuration. Though this work did not address multiplicity, we intrinsically assumed that these are triplet reactions. It is crucial for the reaction of interest here that the excited state of the ketone be $n,\pi^*$, since its radical-like character favors abstraction of the benzylic hydrogen. In benzophenones with a variety of substituents (H, Cl, OMe), the triplet state is $n,\pi^*$ in both polar and non-polar solvents. With strong donor substituents (e.g., *p*-dimethylaminobenzophenone), there is a lower energy $\pi,\pi^*$ excited state configuration and a concomitant low reactivity toward C–H bonds in polar solvent. These traits are only partially expressed here. With the addition of a methoxy substituent, the photoreaction is unaffected, but only when it is added to the proper ring. With the addition of a dimethylamino substituent (**S8**), the photoreaction is abolished in either polar or non-polar media. The lack of reactivity of the naphthyl and biphenyl analogs **S6** and **S7** is presumably because these long conjugated $\pi$-systems favor $\pi,\pi^*$ excited states, rendering them unable to follow the mechanistic pathway of **1**.

## 4. Conclusion

While it has not been possible by straightforward manipulation of subsitutents to substantially improve upon the photochemical performance of (2-hydroxyethyl)benzophenone esters, photochemical behavior that bears further investigation has been discovered. Among the interesting observations is a profound solvent effect on the photochemistry of perfluorophenyl compound **7** that could be profitably exploited in selective deprotection photochemistry.

## 5. Experimental

### 5.1. General

All reagents were purchased from Aldrich or Acros Organics and used without further purification. All moisture-sensitive reactions were performed in oven-dried glassware under a nitrogen or argon atmosphere. Dry solvents were from a Glass Contour Solvent Purification System. Flash column chromatography was carried out on EM Reagents Silica Gel 60 (230–400 mesh). Thin-layer chromatography (TLC) was performed using Merck EMD TLC Silica Gel 60 $F_{254}$ plates. $^1$H NMR spectra were obtained on a Varian MVX-300 (300 MHz), or a Varian INOVA 400 (400 MHz) spectrometer. Chemical shifts are reported in parts per million using tetramethylsilane ($\delta$ 0.0) as an internal standard. $^{13}$C NMR spectra were obtained on a Varian MVX-300 (75 MHz) or a Varian INOVA 400 (100 MHz) spectrometer and chemical shift were reported in parts per million using $CDCl_3$ ($\delta$ 77.0) as an internal standard. IR spectra were obtained using a Perkin–Elmer Spectrum One FT-IR spectrometer. UV spectra were obtained using Cary 50 UV–vis–NIR spectrophotometers from Varian, Inc.

### 5.2. General procedure for the dihydroxylation of an indene. 1-Phenyl-2,3-dihydro-1*H*-indene-1,2-diol (S9)

To a solution of *N*-methylmorpholine-*N*-oxide (975 mg, 8.32 mmol) in 40:3:3 acetone, water, and *tert*-butanol (18 mL) was added osmium tetroxide (28 mg, 0.11 mmol, 2 mol %). A solution of 3-phenyl-*1H*-indene (1.00 g, 5.55 mmol) was slowly added in acetone (8 mL) and the reaction mixture was allowed to stir for 12 h at rt. Any remaining osmium tetroxide was destroyed by the addition of $NaBH_4$ (10 mg). The mixture was evaporated to dryness, dissolved in ethyl acetate (30 mL), washed with brine (2×10 mL), dried, and evaporated. The resulting brown crude material was purified by silica gel column chromatography with ethyl acetate–hexanes (1:9) to yield a colorless solid (225 mg, 51%). Mp 107 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 2.59 (d, $J$=6.3 Hz, 3H), 3.00 (dd, $J$=5.7, 15.9 Hz, 1H), 3.11 (s, 1H), 3.25 (dd, $J$=6.6, 15.9 Hz, 1H), 4.45 (dd, $J$=4.2, 8.1 Hz, 1H), 7.15 (d, $J$=4.5 Hz, 1H), 7.28–7.36 (m, 8H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 37.9, 81.1, 84.0, 120.2, 120.4, 121.4, 122.4, 122.6, 123.2, 124.1, 135.9, 138.7, 140.1. IR (film): 3371, 2962, 2893, 1654, 1525, 1497, 1454, 1411, 1360, 1304, 1216, 1157, 1124 cm$^{-1}$. HRMS (ESI): calcd for $C_{15}H_{13}O_2$ (M−H): 225.0916; found: 225.0923.

### 5.3. General procedure for the periodate cleavage of an indene diol. 2-(2-Benzoylphenyl)propanal

To a methanolic solution (30 mL) of 3-methyl-1-phenyl-2,3-dihydro-1*H*-indene-1,2-diol (260 mg, 1.08 mmol) was added an aqueous solution (6 mL) of $NaIO_4$ (290 mg, 1.35 mmol). After stirring at rt for 30 min, the reaction mixture was filtered and the filtrate was concentrated by evaporation. The residue was diluted with water (14 mL) and this solution was extracted with ethyl acetate (2×15 mL). The combined organic extracts were washed with brine, dried, and evaporated to give the title aldehyde (234 mg, 91%) as a colorless gum. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 1.43 (d, $J$=6.9 Hz, 3H), 1.71 (s, 6H), 3.99 (q, $J$=6.9 Hz, 1H), 7.28–7.85 (m, 9H), 9.76 (s, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 15.3, 27.6, 49.4, 126.9, 128.7, 128.8, 129.3, 129.5, 129.8, 130.6, 131.4, 133.8, 137.8, 137.9, 198.0, 200.9. IR (film): 3060, 2929, 1704, 1658, 1595, 1578, 1485, 1447, 1315, 1267, 1152, 1122 cm$^{-1}$. HRMS (ESI): calcd for $C_{16}H_{15}O_2$ (M+H$^+$): 239.1072; found: 239.1080. This compound was not routinely purified before the next step.

### 5.4. General procedure for the zinc borohydride reduction to give a (2-hydroxyethyl)benzophenone. (2-(1-Hydroxypropan-2-yl)phenyl)(phenyl)methanone (S13)

Freshly fused $ZnCl_2$ (2.0 g, 15 mmol) was taken up in THF (15 mL), added to $NaBH_4$ (solid, 1.7 g, 45 mmol), and allowed to stir at rt for 24 h under nitrogen. The mixture was filtered quickly and the cooled (−10 °C) filtrate (1 mL) was directly added to a cooled (−10 °C) THF solution of aldehyde (500 mg, 2.10 mmol) with constant stirring. After 10 min at −10 °C, the reaction was quenched by the slow addition of cold water. The mixture was evaporated to dryness and the residue was partitioned between ethyl acetate and water. The organic phase was washed with brine, dried and evaporated to give a white semisolid, which on purification by silica gel chromatography (ethyl acetate/hexanes 2:23) gave the title alcohol (332 mg, 66%) as a colorless gum. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 1.40 (d, $J$=6.6 Hz, 3H), 2.48 (d, $J$=7.5 Hz, 1H), 2.80 (s, 1H), 3.11–3.16 (m, 1H), 3.87 (t, $J$=7.5 Hz, 1H), 6.92 (d, $J$=7.5 Hz, 1H), 7.11–7.37 (m, 8H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 16.0, 43.3, 88.8, 123.8, 125.4, 126.6, 127.5, 127.8, 128.2, 129.0, 129.9, 131.1, 143.8, 144.4, 145.7. IR (film): 3366, 2969, 2926, 1602, 1493, 1475, 1446, 1173, 1107 cm$^{-1}$. HRMS (ESI): calcd for $C_{16}H_{17}O_2$ (M+H$^+$): 241.1229; found: 241.1233.

### 5.5. General procedure for organometallic addition to isochroman-1-ones to give a (2-hydroxyethyl)benzophenone

To a solution of isochroman-1-one (200 mg, 1.35 mmol) in 5 mL THF was added phenylmagnesium bromide (3 M solution in ether, 0.57 mL, 1.25 equiv). After stirring for 3 h, excess Grignard reagent was destroyed by the addition of water, and the organic solvents were evaporated under reduced pressure. The solid white residue was dissolved in ethyl acetate, washed with water, and brine, dried (anhydrous $Na_2SO_4$) and evaporated under reduced pressure. The resulting colorless gum was purified by silica gel column chromatography (ethyl acetate/hexanes 3:22) to obtain (2-hydroxyethyl)benzophenone (**S10**) (186 mg, 61%) as a colorless oil. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 1.57 (s, 1H), 2.96 (t, $J$=6.0, 2H), 3.91 (m, 2H), 7.28–7.38 (m, 4 h), 7.42–7.53 (m, 3H), 7.58–7.64 (m, 1H), 7.81–7.84 (m, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 36.5, 64.1, 125.8, 128.1, 128.7, 129.6, 130.8, 131.2, 131.3, 133.7, 137.8, 138.7, 139.2, 199.1. This compound is known from Ullman, of course.[4]

### 5.6. General procedure 1 for acylation with adamantanoyl chloride. 2-(2-Nitrophenyl)propyl adamantanoate (2)

To a solution of 2-(2-nitrophenyl)propanol (240 mg, 1.32 mmol) in 15 mL dichloromethane in a screw-top vial under a nitrogen atmosphere were added adamantanecarbonyl chloride (392 mg, 1.98 mmol) and triethylamine (265 mg, 2.62 mmol). The vial was closed tightly and heated at 50 °C for 6 h. The solution was washed with water (2×10 mL) and brine, dried, and evaporated. The brown residue was purified by silica gel chromatography (hexanes) giving the title ester (360 mg, 59%) as a light brown transparent gum. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 1.36 (d, $J$=7.2 Hz, 3H), 1.64–1.73 (m, 6H), 1.76 (d, $J$=2.7 Hz, 6H), 1.97 (s, 3H), 3.67–3.74 (m, 1H), 4.16–4.27 (m, 2H), 7.34 (t, $J$=6.9 Hz, 1H), 7.34 (dt, $J$=1.2, 7.8 Hz, 1H), 7.48 (dd, $J$=1.2, 7.8 Hz, 1H), 7.57 (dt, $J$=1.2, 7.5 Hz, 1H), 7.34 (d, $J$=1.5, 8.4 Hz, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 18.1, 28.1, 33.5, 36.6, 38.9, 40.9, 68.0, 124.3, 127.6, 128.6, 132.7, 137.7, 150.7, 177.5. IR (film): 2905, 2851, 1724, 1523, 1452, 1353, 1226, 1183, 1103 cm$^{-1}$. HRMS (ESI): calcd for $C_{20}H_{25}NNaO_4$ (M+Na$^+$): 366.1681; found: 366.1690. UV $\lambda_{max}$, $\varepsilon$ (hexane): 254, 3041.

### 5.7. General procedure 2 for acylation of a (2-hydroxyethyl)-benzophenone with adamantanoyl chloride. 2-Benzoylphenethyl adamantanoate (1)

To a solution of (2-hydroxyethyl)benzophenone (400 mg, 1.77 mmol) in dry pyridine (2 mL) was added adamantanecarbonyl chloride (525 mg, 2.65 mmol). After stirring at 50 °C for 2 h, the pyridine was evaporated under reduced pressure. The final traces of pyridine were removed by addition of toluene and evaporation of the azeotrope. The residual brown solid was dissolved in ethyl acetate (15 mL), washed with water (10 mL) and brine (10 mL), dried, and evaporated to give a brownish sticky residue that was purified by silica gel column chromatography (2% ethyl acetate–hexanes) to give **1** (558 mg, 81%). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 1.68–1.73 (m, 6H), 1.81 (d, $J$=2.7 Hz, 6H), 1.97 (s, 3H), 3.03 (t, $J$=6.6 Hz, 2H), 4.25 (t, $J$=6.6 Hz, 2H), 7.29–7.49 (m, 6H), 7.49–7.52 (m 1H), 7.71–7.74 (m, 2H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 27.8, 32.5, 36.4, 38.7, 40.5, 64.3, 125.8, 128.3, 129.0, 130.2, 131.1, 133.1, 137.2, 137.6, 138.5, 177.3, 197.9. IR (film): 2904, 2851, 1724, 1662, 1597, 1579, 1448, 1344, 1315, 1266, 1248, 1182 cm$^{-1}$. HRMS (ESI): calcd for $C_{26}H_{29}O_3$ ($M+H^+$): 389.2111; found: 389.2121, calcd for $C_{26}H_{28}NaO_3$ ($M+Na^+$): 411.1931; found: 411.1940.

### 5.8. Photochemistry

UV spectra were recorded in hexane. Photochemical reactivity was assessed by making up a solution at 1 mM in hexane (also in some cases including 1 mM diisopropylethylamine), acetonitrile or methanol and irradiating each solution for 30 min using 366 or 300 nm lamps in a Rayonet photochemical reactor. The percent conversion was determined by NMR analysis of the crude reaction mixture after evaporation.

## Acknowledgements

Financial support from Samsung is appreciated. Mass spectra were obtained on an instrument purchased with NSF grant CHE0541848. Dr. Goutam Biswas provided valued assistance in the analysis of some samples.

## Supplementary data

Narrative of routes for the synthesis of compounds that are photochemically reactive. Experimental descriptions for the synthesis of compounds **1** and **3**–**11**. Structures and UV properties of prepared compounds that are not photochemically reactive. $^1$H NMR and $^{13}$C NMR spectra for **1**–**11** and compounds **S15**–**S17**, **S19**–**S20**, **S26**–**S27**, and **S29** (55 pages total). Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2010.02.087.

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