Visible-Light-Induced Decarboxylative C–H Adamantylation of Azoles at Ambient Temperature

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Abstract The visible-light-promoted oxidant-free decarboxylative C–H adamantylation of azoles was accomplished under ambient reaction conditions. The novel acridinium photocatalyst and cobalt synergistic catalysis enabled the C–H adamantylation under oxidant-free reaction conditions. This C–H adamantylation strategy proved viable for a wide range of substituted azoles, including benzothiazole, benzoxazole, and benzimidazoles as well as caffeine derivatives, providing an expedient access to 2-adamantyl-substituted azoles.

Key words photocatalysis, C–H functionalization, decarboxylation, cobalt, acridinium salts, oxidant-free, adamantylation, azoles

Adamantane, a strain-free molecule consisting of three fused cyclohexane rings, has attracted significant attention because of its unique structural features and properties. For instance, the adamantyl moiety represents a key scaffold in several biologically active compounds and clinical therapeutics. The incorporation of the adamantyl group to polymers significantly improves their physical properties, such as thermal stability and solubility. Furthermore, the specific features of the adamantyl scaffold, including lipophilicity, steric demand, dispersion attraction, and conformational stability and rigidity expanded their presence and influence in several other important areas of research, such as supramolecular chemistry, and molecular syntheses. Despite the great importance of adamantyl-substituted organic compounds, the incorporation of adamantyl group into organic molecules largely relies on conventional nucleophilic substitution reactions with adamantyl halides. Recently, selected examples of C–H adamantylation were reported as the part of the scope of transition-metal-catalyzed C–H alkylation protocols. However, no specific methods have as of yet been reported for the C–H adamantylation of heteroarenes, in detail delineating its scope and limitations. Within our program on transition-metal-catalyzed C–H alkylation and photoredox catalysis, we have now devised an exceedingly mild method for the C–H adamantylation of azoles by a photoinduced decarboxylative C–H alkylation strategy. Notable features of our approach include (i) expedient C–H adamantylation on diversely decorated azoles, (ii) non-directing group-assisted C–H functionalization, (iii) easily accessible and inexpensive 1-adamantanecarboxylic acid as reagent, (iv) visible-light-promoted C–H functionalization, (v) no stoichiometric oxidants and iridium or ruthenium photocatalysts, and (vi) key mechanistic insights, and (vii) ambient reaction temperature (Scheme 1).

We initiated our studies by examining suitable photocatalysts (PCs) (Figure 1), bases, and solvents under oxidant-free conditions, using an easily accessible cobaloxime complex as cocatalyst for the envisioned decarboxylative C–H adamantylation of benzothiazole (1a) with adamantane carboxylic acid (2) (Table 1). Thus, among a set of representative photocatalysts, 9-mesityl-10-methylacridinium perchlorate (PC1) provided optimal results in a mixture of...
DCE/H₂O (3:1) as the reaction medium (Table 1, entry 1). While a variety of bases could be utilized, the photoinduced C–H adamantylation was most effective in the presence of K₂HPO₄. The key importance of the photocatalyst, base, and light irradiation in the decarboxylative C–H adamantylation manifold was verified by probing the transformation in the absence of each component under otherwise identical reaction conditions (entries 17–19). Notably, the use of blue light was found beneficial to realize satisfactory yields (entries 20 and 21).

With the optimized reaction conditions in hand, we probed the scope of the reaction with a range of azoles 1 (Scheme 2). To our delight, the visible-light-enabled decarboxylative C–H adamantylation proved broadly applicable towards a range of azoles. Thus, differently substituted benzothiazoles 1a–h and benzoxazoles 1i–p were efficiently transformed into the desired adamantyl-substituted products 3a–p in satisfactory yields. Notably, the challenging benzimidazole 1q and caffeine derivatives 1r,s were successfully functionalized under identical reaction conditions.

In consideration of the unique reactivity of the photoinduced decarboxylative C–H functionalization, we were attracted to delineate its mode of action. To probe the catalyst’s working mode, we performed an intermolecular competition experiment, which revealed electron-deficient benzothiazole 1e to be preferentially converted (Scheme 3a). Further, we investigated a SET-type regime by the use of typical radical scavengers TEMPO, galvinoxyl, and BHT (Scheme 3b), which significantly suppressed the catalytic efficacy.

To further elucidate the reaction mechanism of the photoinduced C–H adamantylation, we performed a series of additional experiments (Figure 2). First, we monitored the conversion profile of the photocatalytic reaction of 1a and 2 to give 3a, which revealed the reaction being completely suppressed in the absence of light (Figure 2a). These findings provided strong evidence for the beneficial influence of visible-light irradiation. Second, fluorescence-quenching experiments (Figure 2b–d) revealed no quenching of the free acid 2, while both benzothiazole and the carbamate salt quenched the excited state of acridinium photocatalyst.
Based on these observations, we propose the single-electron transfer to occur from PC1* to adamantane carboxylate as the key step. In light of these mechanistic findings, a plausible catalytic cycle for the photoinduced decarboxylative C–H adamantylation protocol is elaborated in Scheme 4. The acridinium photocatalyst [Arc-Mes+] is initially excited to [Arc-Mes+] by blue light absorption, which oxidizes the adamantan carboxylate anion to the oxygen-centered carboxyl radical. Then, decarboxylation forms the adamantyl radical. Subsequently, the [Arc-Mes•] radical is re-oxidized to [Arc-Mes+] by the cobalt(III) species to complete the photo-
catalytic cycle. In the meantime, the attack of the adamantyl radical at the electrophilic C2 position of benzothiazole (1a) generates radical intermediate A. Upon deprotonation, reduction of the cobalt(II) species to cobalt(I) through SET from species A then delivers the adamantlylated product 3a. Concurrently, the cobalt(III)-hydride species could be formed from the cobalt(I) species by capturing a proton generated in the reaction. Release of H2 through a reaction with another proton will regenerate the cobalt(III) species.16–f

In summary, we have reported on the unprecedented visible-light-enabled decarboxylative C–H adamantylation of azoles at ambient reaction temperature. The oxidant-free decarboxylative adamantylolation was efficiently achieved by the aid of catalytic amounts of easily available cobalt oxime derivatives, were well tolerated, providing a new general strategy to access adamantlylated-substituted heterocycles motifs.

Catalytic reactions were carried out in pre-dried 10 mL vials under N2 atmosphere. In cases wherein air- or moisture-sensitive reagents were used, reactions were performed under N2 atmosphere using standard Schlenk techniques. The following substrates were prepared according to previously described procedures: Benzothiazoles 1b–h,17 benzoxazoles 11–p,18 benzimidazole 1q,19 [Co(dmgH)(dmgH2)Cl2]20 and tetrabutylammonium adamantane carboxylate.21 Other chemicals were obtained from commercial sources and were used without further purification, unless otherwise noted. Yields refer to isolated products.

Visible-Light-Promoted Decarboxylative C–H Adamantylation; General Procedure

To an oven-dried 10 mL vial were added the heterocycle 1 (0.40 mmol, 1.0 equiv), 1-adamantanezcarboxylic acid (2; 216 mg, 1.20 mmol, 3.0 equiv), K2HPO4 (209 mg, 1.20 mmol, 3.0 equiv), 9-mesityl-10-methylacridinium perchlorate (8.2 mg, 50 μmol), and [Co(dmgH)(dmgH2)Cl2] (11.6 mg, 8.0 mol%). After the vial was capped with a septum, it was evacuated and refilled with N2 for three times before DCE (1.5 mL) and H2O (0.5 mL) were added sequentially. If the heterocyclic substrate 1 was a liquid, it was added at this point. The mixture was degassed and stirred for 24 h under visible light irradiation (Kessil A360N, see Figure S-1 in the Supporting Information). After 24 h, the mixture was diluted with CH2Cl2 (10 mL) and H2O (10 mL), and the phases were separated. The aqueous layer was extracted with CH2Cl2 (2 × 10 mL), the combined organic phases were dried (Na2SO4), and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (n-pentane or n-hexane/EtO2 20:1 to 2:1) affording the corresponding product 3.

2-[(3R,5R,7R)-Adamantan-1-yl]benzo[d]thiazole (3a)

The general procedure was followed using benzothiazole (1a; 54.1 mg, 0.40 mmol) and 1-adamantanezcarboxylic acid (2; 216 mg, 1.20 mmol) for 24 h. After aqueous workup, purification by column chromatography on silica gel (n-pentane/EtO2 30:1) afforded 3a; yield: 89.3 mg (331 μmol, 83%); white solid; mp 103–104 °C.

IR (ATR): 2898, 2845, 1506, 1434, 1168, 999, 963, 754, 725, 680 cm–1.

1H NMR (400 MHz, CDCl3): δ = 8.00 (ddd, J = 8.2, 1.2, 0.7 Hz, 1 H), 7.86 (ddd, J = 7.2, 1.2, 0.7 Hz, 1 H), 7.44 (ddd, J = 8.2, 7.2, 1.2 Hz, 1 H), 7.32 (ddd, J = 8.2, 7.2, 1.2 Hz, 1 H), 2.18–2.12 (m, 9 H), 1.86–1.81 (m, 6 H).

13C NMR (101 MHz, CDCl3): δ = 182.3 (Cq), 153.3 (Cq), 134.5 (Cq), 125.8 (CH), 124.5 (CH), 122.8 (CH), 121.7 (CH), 43.1 (CH2), 40.3 (Cq), 36.7 (CH2), 28.7 (CH).

MS (ESI): m/z (%) = 270 ([M + H]+, 100).

HRMS (ESI): m/z calcld for C18H20NS+: [M + H]+: 270.1311; found: 270.1313.

The analytical data are in accordance with those reported in the literature.20c

2-[(3R,5R,7R)-Adamantan-1-yl]-6-methylbenzo[d]thiazole (3b)

The general procedure was followed using benzothiazole (1b; 59.7 mg, 0.40 mmol) and 1-adamantanezcarboxylic acid (2; 216 mg, 1.20 mmol) for 24 h. After aqueous workup, purification by column chromatography on silica gel (n-pentane/EtO2 30:1) afforded 3b; yield: 60.6 mg (214 μmol, 53%); white solid; mp 132–133 °C.

IR (ATR): 2899, 2845, 1500, 1449, 1164, 1000, 835, 812, 569 cm–1.

1H NMR (400 MHz, CDCl3): δ = 7.87 (d, J = 8.3 Hz, 1 H), 7.65–7.62 (m, 1 H), 7.24 (ddd, J = 8.2, 1.7, 0.6 Hz, 1 H), 2.46 (s, 3 H), 2.16–2.11 (m, 9 H), 1.83–1.80 (m, 6 H).

13C NMR (101 MHz, CDCl3): δ = 181.2 (Cq), 151.4 (Cq), 134.6 (Cq), 134.5 (Cq), 127.3 (CH), 122.2 (CH), 121.4 (CH), 43.1 (CH2), 40.2 (Cq), 36.7 (CH2), 28.7 (CH), 21.6 (CH3).

MS (ESI): m/z (%) = 284 ([M + H]+, 100).

HRMS (ESI): m/z calcld for C19H22NS+: [M + H]+: 284.1467; found: 284.1471.

The analytical data are in accordance with those reported in the literature.21

2-[(3R,5R,7R)-Adamantan-1-yl]-6-methoxybenzo[d]thiazole (3c)

The general procedure was followed using benzothiazole (1c; 66.1 mg, 0.40 mmol) and 1-adamantanezcarboxylic acid (2; 216 mg, 1.20 mmol) for 24 h. After aqueous workup, purification by column chromatography on silica gel (n-pentane/EtO2 25:1) afforded 3c; yield: 70.2 mg (234 μmol, 59%); white solid; mp 118–119 °C.

IR (neat): 2904, 1467, 1450, 1435, 1261, 1223, 1028, 1000, 834, 827 cm–1.
The general procedure was followed using benzothiazole (3g) for 24 h. After aqueous workup, purification by column chromatography on silica gel (n-pentane/Et2O 15:1) afforded 3d; yield: 60.0 mg (176 mmol, 54%); white solid; mp 107–108 °C.

IR (ATR): 3049, 1710, 1279, 1185, 1001, 800, 772, 740, 680 cm⁻¹.


1H NMR (400 MHz, CDCl₃): δ = 7.87 (dd, J = 8.9, 0.4 Hz, 1 H), 7.31 (d, J = 2.5 Hz, 1 H), 7.03 (dd, J = 8.9, 2.5 Hz, 1 H), 3.85 (s, 3 H), 2.15–2.11 (m, 9 H), 1.82–1.79 (m, 6 H).

13C NMR (101 MHz, CDCl₃): δ = 179.8 (C₆), 157.3 (C₄), 147.8 (C₈), 135.7 (C₂), 123.2 (CH), 114.9 (CH), 104.4 (CH), 55.9 (CH₂), 43.1 (CH₂), 40.1 (CH₂), 36.7 (CH₂), 28.7 (CH). MS (ESI): m/z (%) = 304 (M + H⁺, 99). HRMS (ESI): m/z calcd for C₁₉H₁₉ClNS⁺ [M + H]⁺: 304.0921; found: 304.0924.

The analytical data are in accordance with those reported in the literature.²²

2-[(3R,5R,7R)-Adamantan-1-yl]-6-(trifluoromethyl)benz[d]thiazole (3d)
The general procedure was followed using benzothiazole 1d (81.3 mg, 0.40 mmol) and 1-adamantaneacarbonylic acid (2; 216 mg, 1.20 mmol) for 24 h. After aqueous workup, purification by column chromatography on silica gel (n-pentane/Et₂O 30:1) afforded 3d; yield: 96.3 mg (285 μmol, 71%); white solid; mp 183–184 °C.

IR (ATR): 2911, 1317, 1278, 1163, 1112, 1085, 1001, 880, 829, 681 cm⁻¹.

1H NMR (400 MHz, CDCl₃): δ = 8.15 (dq, J = 1.8, 0.7 Hz, 1 H), 8.07 (dt, J = 8.6, 0.7 Hz, 1 H), 7.68 (ddd, J = 8.6, 1.8, 0.7 Hz, 1 H), 2.19–2.14 (m, 9 H), 1.87–1.80 (m, 6 H).

13C NMR (101 MHz, CDCl₃): δ = 185.7 (C₆), 155.4 (C₄), 134.7 (C₈), 126.8 (q, 3JCF = 32.7 Hz, C₆), 124.4 (q, 3JCF = 272.0 Hz, C₄), 123.0 (CH), 122.8 (q, 3JCF = 5.3 Hz, CH₂), 119.2 (q, 3JCF = 4.2 Hz, CH₂) (CH₃) 43.0 (CH₂), 36.6 (CH₂), 28.7 (CH). MS (ESI): m/z (%) = 338 (M + H⁺, 13), 300 (100).


2-[(3R,5R,7R)-Adamantan-1-yl]-6-fluorobenzo[d]thiazole (3f)
The general procedure was followed using benzothiazole 1e (61.3 mg, 0.40 mmol) and 1-adamantaneacarbonylic acid (2; 216 mg, 1.20 mmol) for 24 h. After aqueous workup, purification by column chromatography on silica gel (n-pentane/Et₂O 30:1) afforded 3e; yield: 62.1 mg (216 μmol, 54%); white solid; mp 107–108 °C.

IR (ATR): 2911, 2889, 1454, 1245, 1161, 1001, 915, 836, 800, 791 cm⁻¹.

1H NMR (400 MHz, CDCl₃): δ = 7.91 (ddd, J = 8.9, 4.8, 0.4 Hz, 1 H), 7.52 (ddd, J = 8.2, 2.6, 0.4 Hz, 1 H), 7.16 (ddd, J = 8.9, 8.2, 2.6 Hz, 1 H), 2.16–2.12 (m, 9 H), 1.83–1.79 (m, 6 H).

13C NMR (101 MHz, CDCl₃): δ = 182.0 (d, 3JCF = 3.1 Hz, C₆), 160.2 (d, 3JCF = 244.2 Hz, C₄), 149.9 (d, 3JCF = 1.6 Hz, C₆), 135.5 (d, 3JCF = 11.2 Hz, C₄), 123.6 (d, 3JCF = 9.4 Hz, CH₃), 114.3 (d, 3JCF = 24.6 Hz, CH₃), 107.8 (d, 3JCF = 26.4 Hz, CH₃), 43.1 (CH₃), 40.4 (CH₂), 36.6 (CH₂), 28.7 (CH). MS (ESI): m/z (%) = 288 (M + H⁺, 100).


2-[(3R,5R,7R)-Adamantan-1-yl]-6-chlorobenzo[d]thiazole (3f)
The general procedure was followed using benzothiazole 1f (67.9 mg, 0.40 mmol) and 1-adamantaneacarbonylic acid (2; 216 mg, 1.20 mmol) for 24 h. After aqueous workup, purification by column chromatography on silica gel (n-pentane/Et₂O 30:1) afforded 3f; yield: 71.8 mg (236 μmol, 59%); white solid; mp 145–146 °C.

IR (ATR): 2898, 2844, 1514, 1435, 1259, 1097, 999, 802, 768, 680 cm⁻¹.

1H NMR (400 MHz, CDCl₃): δ = 7.88 (dd, J = 8.7, 0.4 Hz, 1 H), 7.81 (dd, J = 2.1, 0.4 Hz, 1 H), 7.38 (dd, J = 8.7, 2.1 Hz, 1 H), 2.16–2.11 (m, 9 H), 1.84–1.79 (m, 6 H).

13C NMR (101 MHz, CDCl₃): δ = 182.8 (C₆), 151.9 (C₄), 135.8 (C₈), 130.4 (C₂), 126.6 (CH), 123.5 (CH), 121.3 (CH), 43.1 (CH₂), 40.4 (C₆), 36.6 (CH₂), 28.7 (CH). MS (ESI): m/z (%) = 304 (M + H⁺, 100).

HRMS (EI): m/z calcd for C₁₉H₁₉ClNS⁺ [M + H]⁺: 304.0921; found: 304.0924.

The analytical data are in accordance with those reported in the literature.²²
IR (ATR): 2906, 2851, 1557, 1451, 1264, 1044, 801, 739, 704 cm⁻¹.

IR (ATR): 2902, 2849, 1561, 1452, 1103, 40.2 (CH₂), 36.5 (CH₂), 36.0 (C₆H₅), 27.9 (CH).

MS (EI): m/z (%) = 254 ([M + H]⁺, 100), 276 ([M + Na⁺]², 15).

HRMS (EI): m/z calcld for C₁₇H₁₈NO⁺ [M + H]⁺: 267.1539; found: 267.1540.

The analytical data are in accordance with those reported in the literature.

2-[(3R,5R,7R)-Adamantan-1-yl]-5-methylbenzodioxazole (3j)
The general procedure was followed using 5-methylbenzoxazole 1k (53.3 mg, 0.40 mmol) and 1-adamantanecarboxylic acid (2; 216 mg, 1.20 mmol) for 24 h. After aqueous workup, purification by column chromatography on silica gel (n-hexane/EtOAc 10:1) afforded 3j; yield: 61.0 mg (228 µmol, 57%); white solid; mp 112–114 °C.

HRMS (EI): m/z calcld for C₁₇H₂₁NO⁺ [M + H]⁺: 268.1696; found: 268.1702.

2-[(3R,5R,7R)-Adamantan-1-yl]-5-chlorobenzodioxazole (3k)
The general procedure was followed using 5-chlorobenzoxazole 1l (61.4 mg, 0.40 mmol) and 1-adamantanecarboxylic acid (2; 216 mg, 1.20 mmol) for 24 h. After aqueous workup, purification by column chromatography on silica gel (n-hexane/EtOAc 10:1) afforded 3k; yield: 68.0 mg (236 µmol, 59%); white solid; mp 115–116 °C.

IR (ATR): 2908, 2851, 1557, 1451, 1264, 1044, 801, 739, 704 cm⁻¹.

1H NMR (600 MHz, CDCl₃): δ = 7.26 (d, J = 2.1 Hz, 1 H), 7.37 (d, J = 8.6 Hz, 1 H), 7.23 (dd, J = 8.6, 2.1 Hz, 1 H), 2.19–2.08 (m, 6 H), 1.95–1.78 (m, 6 H).

13C NMR (126 MHz, CDCl₃): δ = 117.3 (C₆H₅), 149.0 (C₆H₅), 142.3 (C₆H₅), 129.3 (C₆H₅), 124.5 (CH), 119.7 (CH), 110.9 (CH), 40.2 (CH₂), 36.5 (CH₂), 36.3 (C₆H₅), 28.0 (CH).

MS (EI): m/z (%) = 287 ([M⁺]⁺, 100), 276 ([M + Na⁺]², 15).

HRMS (EI): m/z calcld for C₁₇H₁₇ClNO⁺ [M + H⁺]: 289.1155; found: 289.1158.

2-[(3R,5R,7R)-Adamantan-1-yl]-5-(tert-butyl)benzodioxazole (3l)
The general procedure was followed using benzoxazole 1m (50.2 mg, 0.40 mmol) and 1-adamantanecarboxylic acid (2; 216 mg, 1.20 mmol) for 48 h. After aqueous workup, purification by column chromatography on silica gel (n-pentane/EtOAc 10:1) afforded 3l; yield: 56.0 mg (182 µmol, 45%); white solid; mp 159–160 °C.

IR (ATR): 2906, 2849, 1561, 1480, 1452, 1272, 1041, 924, 800 cm⁻¹.

1H NMR (600 MHz, CDCl₃): δ = 7.34 (dd, J = 2.0, 0.6 Hz, 1 H), 7.39 (dd, J = 8.6, 0.6 Hz, 1 H), 7.26 (dd, J = 8.5, 2.0 Hz, 1 H), 2.16–2.10 (m, 6 H), 2.12–1.0 (m, 3 H), 1.81 (t, J = 2.9 Hz, 6 H), 1.36 (s, 9 H).

13C NMR (126 MHz, CDCl₃): δ = 173.8 (C₆H₅), 145.3 (C₆H₅), 136.6 (C₆H₅), 136.3 (C₆H₅), 124.7 (CH), 120.3 (CH), 111.2 (CH), 40.3 (CH₂), 36.6 (CH₂), 36.3 (C₆H₅), 28.0 (CH).

MS (EI): m/z (%) = 288 ([M + H⁺]⁺, 60).
tert-Butyl 2-((3R,5R,7R)-Adamantan-1-yl)benzoz[d]oxazole-6-carboxylate (3p)

The general procedure was followed using benzoxazole 1p (87.7 mg, 0.40 mmol) and 1-adamantanecarboxylic acid (2; 216 mg, 1.20 mmol) for 48 h. After aqueous workup, purification by column chromatography on silica gel (n-pentane/Et2O 10:1) afforded 3p; yield: 52.8 mg (161 μmol, 40%); white solid; mp 185–187 °C.

IR (ATR): 2904, 1710, 1291, 1268, 1244, 1154, 1044, 943, 777 cm–1.

HRMS (ESI): m/z (%) = 354 (M + H)+, 100.


The general procedure was followed using substrate 2-

The general procedure was followed using benzothiazole (1q), 1-phenylbenzimidazole (3q), and 1-adamantanecarboxylic acid (3r), 1-phenyl-1H-benzo[d]imidazole (3s) and 1-adamantanecarboxylic acid (2; 162 mg, 0.90 mmol) for 48 h. After aqueous workup, purification by column chromatography on silica gel (n-pentane/Et2O 10:1) afforded 3s; yield: 53.5 mg (129 μmol, 43%); white solid; mp 147–148 °C.

IR (ATR): 2890, 1165, 1536, 1426, 1382, 1137, 1105, 1035, 743 cm–1.


HRMS (ESI): m/z calcd for C_{17}H_{25}N_{4}O_{2} [M + Na]+: 354.2064; found: 354.2064.

2-[(3R,5R,7R)-Adamantan-1-yl]-1-phenyl-1H-benzo[d]imidazole (3q)

The general procedure was followed using 1-phenylbenzimidazole 1q (78.0 mg, 0.40 mmol) and 1-adamantanecarboxylic acid (2; 216 mg, 1.20 mmol) for 48 h. After aqueous workup, purification by column chromatography on silica gel (n-pentane/Et2O 10:2) afforded 3q; yield: 80.0 mg (244 μmol, 61%); white solid; mp 185–187 °C.

IR (ATR): 2904, 2850, 1498, 1454, 1375, 1264, 737, 700 cm–1.

HRMS (ESI): m/z (%) = 328 ([M]+), 70, 327 (100), 271 (30).

HRMS (ESI): m/z calcd for C_{22}H_{32}N_{4}O_{4}Na+ [M + Na]+: 439.2316; found: 439.2319.

Reaction in the Presence of Radical Scavengers

The general procedure was followed using benzothiazoles 1a (54.1 mg, 0.40 mmol), 1-benzothiazole (2; 216 mg, 1.20 mmol) and radical scavengers (1–3 equiv) for 24 h. After aqueous workup, purification by column chromatography on silica gel (n-pentane/Et2O 10:1) yielded 3a.

On/Off Plot

According to the general procedure, five independent reactions were set up and placed in front of the blue LEDs. The reaction mixtures were sequentially stirred under visible light irradiation and in the absence of light. Every 2 h a reaction vial was removed from the setup and workup was performed according to the general procedure. After a total of 10 h, the obtained isolated yields were plotted with respect to the reaction time.

Fluorescence Quenching Experiments

Sample solutions were prepared in DCE with [Acr-Mes]([ClO4]) concentration of c = 1.6 × 10–7 M and varying concentrations of the respective quencher (added to each sample from a stock solution). The sample solutions were degassed prior to measurement by sparging with N2. Stern–Volmer experiments were conducted with a fixed excitation wavelength of 430 nm and detection at 518 nm (emission maximum). Plotting of the I0/I value against the concentration of the potential quencher resulted in the graphs (Figures 2b–d).
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Supporting Information

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