



Figure 2. Substrate scopes for the photocatalytic reactions between an electron-deficient alkene **1** and C-H partners **2**. Isolated yields and diastereomeric ratios (dr, determined based on $^1\text{H-NMR}$ spectra) are shown under each product. rt: room temperature.

protocol is compatible with various electron-deficient cyanoaromatics (**6a** – **6e**) and amides (**6f**–**6l**), yielding their corresponding arylated products in good to excellent yields of 30% – 96%. Impressively, all cyclic amides (**6j** – **6l**) reacted exclusively at its α -N-CH₂ position.

We next explored the coupling reaction between amide **5** and various aromatic carbonyl compounds **7**, including aldehyde, ketone, and ester (**Figure 3b**). Attaching photogenerated radical intermediates to C=O bonds is challenging and was achieved only in limited instances, for example, via the reaction between an organochromium-type carbanion species and aldehydes.¹⁹ Using CdS QD gels as the photocatalyst, we successfully coupled *N,N*-dimethylacetamide (DMA) with benzaldehyde (**8a**), acetophenone (**8b**), 4-fluorobenzophenone (**8c**), and dimethyl terephthalate (**8d**) in moderate to excellent yields of 28% to 78%. The reaction between *N,N*-dimethylacetamide and dimethyl terephthalate also led to 6% of ketone product (**Figure S7**). Most impressively, we observed an unusual three-component reaction between *N,N*-dimethylacetamide, acetone, and dimethylterephthalate, forming an alkylated pinacol C–C cou-

pling product **9** at a good yield of 42%. The above results have clearly demonstrated that CdS QD gels are a versatile photocatalyst for activating C-H bonds and efficiently utilizing the generated intermediates for coupling reactions.

Mechanistic understanding

To understand the C-H bond activation mechanism, we started with detecting in situ generated radical intermediates during the photocatalytic reactions. We used 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) as the radical scavenger. We confirmed the formation of α -ethereal, α -amido, acyl, and benzylic radicals from THF, DMA, benzaldehyde, and toluene by detecting their TEMPO adducts using high-resolution mass spectrometry (**Figures 4a** and **S8**). Reactions were also completely inhibited due to the presence of TEMPO (**Figure 4a**). Similar reaction inhibition was observed after exposing the reaction to another common radical scavenger, oxygen molecules (entry 2 in **Figure 4b**). Both observations indicate that QD gel-catalyzed C-H bond activation led to neutral radical formation. The kinetic