1.

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$$R^{3} = \begin{pmatrix} R^{2} & S_{2}O_{8}^{2} & SO_{4}^{-1} & SO_{4}^$$

doi: 10.1021/acs.orglett.9b00968.

$$t$$
-Bu
 O
 $N=O$
 t -Bu·O + ·N=O

$$\begin{bmatrix} H & C_1 & C_2 & C_2 & C_3 & C_4 & C_4 & C_4 & C_5 & C_5 & C_6 & C_6$$

4.

1) MnO₂, CH₂Cl₂, rt, 71%

2) $\mathrm{CH_3CN}$, reflux, 20%

Org. Lett. **2019**, 21, 7209–7212.

General procedure for the generation of diazo compounds:

was necessary for analytically pure products.

Conditioning phase: A solution of hydrazone (1 mmol, 0.1 M) and Hünig's base (2 equiv.) in CH₂Cl₂ (10 mL) was passed through the column reactor (Omnifit® column³, 6.6 mm i.d. × 50 mm length), packed with activated MnO₂ (0.86 g),⁴ at a flow rate of 0.5 mL min⁻¹ for 20 min (*phase 1*) and the reactor output was monitored using a Flow-IR® device.² The flow was switched to solvent (Hünig base, 0.2 M in CH₂Cl₂) for 10 min (*phase 2*). The column was then ready for the generation of the diazo compound.

Generation phase: A solution of hydrazone (2 mmol, 0.1 M) and Hünig's base (2 equiv.) in CH₂Cl₂ (20 mL) was passed through a conditioned column reactor (Omnifit® column³, 6.6 mm i.d. × 50 mm length)(phase 3). When the FlowIR® showed that the intensity of the diazo peak (region 2050-2100 cm⁻¹. Figure S1) was stable (0.2 A.U.),² the reactor output was collected every 6 min (0.3 mmol) or 9 min (0.45 mmol, excess of diazo compound) in a vial containing the appropriate reagent (0.6 mmol of carboxylic acid or 0.3 mmol of boronic acid) equipped with a stirring bar. The mixture was stirred until the gas evolution ceased and the colour of diazo compound disappeared. The reaction mixture was diluted with EtOAc and washed with water. After evaporation of dried organic layer, the desired product was obtained. In few cases, purification over silica gel

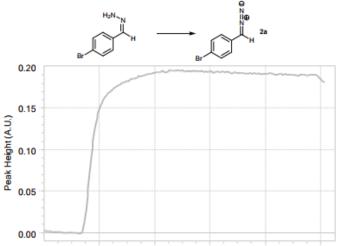


Figure S1. FlowIR® data (peak at 2069 cm-1) for the generation of 2a.

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