

Supporting Information

A Photoactivable Fluorophore Based on Thiadiazolidinedione as Caging Group

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Synthesis of 4-thia-2,6-diazatricyclo[5.2.2.0^{2,6}]undecane-3,5-dione **1** (ref 10):

A stirred solution of 55 mg (0.47 mmol) 1-thia-3,4-diazolidine-2,5-dione **1** (gift from Novartis Agro) in 20 mL of acetone was cooled to $-78\text{ }^{\circ}\text{C}$ under nitrogen and kept in the dark. Dropwise addition of a small portion of an acetone solution (2 mL) of 68 mg (0.63 mmol) *tert*-butyl hypochlorite through a syringe afforded the purple and thermally unstable thiadiazoline as oxidation product. A sufficient fraction of an acetone solution (2 mL) of 75 mg (0.94 mmol) 1,3-cyclohexadiene was immediately added by a second syringe to cause the red color to disappear (within a few seconds). This procedure of alternate addition of the two reagents was repeated until no further coloring could be observed upon addition of the oxidizing reagent. The solution was allowed to warm up, filtered, and the solvent was removed under reduced pressure. The resulting solid was purified by column chromatography (silica gel, $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH} = 96:4$) to yield 47 mg (0.24 mmol, 54% yield) of 4-thia-2,6-diazatricyclo[5.2.2.0^{2,6}]undec-8-ene-3,5-dione as colorless crystals: mp $143\text{ }^{\circ}\text{C}$ (ref 10: $144\text{--}145\text{ }^{\circ}\text{C}$), ^1H NMR (300 MHz, CDCl_3) δ 1.68 (m, 2H, CH_2), 2.21 (m, 2H, CH_2), 5.20 (m, 2H, CH), 6.60 (m, 2H, CH=).

The hydrogenation was carried out by stirring a solution of 40 mg (0.200 mmol) 4-thia-2,6-diazatricyclo[5.2.2.0^{2,6}]undec-8-ene-3,5-dione in 10 mL of ethanol containing 40 mg 5% palladium on activated carbon under hydrogen at atmospheric pressure. After 2 h the mixture was filtered and the solvent evaporated to give 39 mg (0.197 mmol, 98% yield) of **1** as a colorless solid: mp $130\text{--}132\text{ }^{\circ}\text{C}$ (ref 10: $137\text{ }^{\circ}\text{C}$), ^1H NMR (500 MHz, CDCl_3) δ 1.92 (m, 4H, H of CH_2), 2.15 (m, 4H, H of CH_2), 4.68 (m, 2H, CH). HRMS (M^+) calcd for $\text{C}_8\text{H}_{10}\text{N}_2\text{O}_2\text{S}$ 198.0463, found 198.0461.