

## SUPPORTING INFORMATION

Title: **Utility of Polymer-supported Reagents in the Total Synthesis of Lamellarins**

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## Supporting Information

### General Experimental Methods

Unless otherwise noted: Reactions were run in oven-dried round-bottomed flasks. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl while dichloromethane (DCM) from calcium hydride prior to use. All other compounds were used as received from the suppliers. The crude reaction mixtures were concentrated under reduced pressure by removing organic solvents on rotary evaporator. Column chromatography was performed using silica gel 60 (particle size 0.06-0.2 mm; 70-230 mesh ASTM). Analytical thin-layer chromatography (TLC) was performed with silica gel 60 F<sub>254</sub> aluminum sheets. Chemical shifts for <sup>1</sup>H nuclear magnetic resonance (NMR) spectra were reported in parts per million (ppm,  $\delta$ ) downfield from tetramethylsilane. Splitting patterns are described as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), broad (br), doublet of doublet (dd), and doublet of doublet of doublet (ddd). Resonances for infrared (IR) spectra were reported in wavenumbers (cm<sup>-1</sup>). Low resolution (LRMS) and high resolution (HRMS) mass spectra were obtained using electron ionization (EI) and fast atom bombardment (FAB) techniques, respectively. Melting points were uncorrected.

**Table.**  $\alpha$ -Keto bromination<sup>a</sup> of acetophenone carbonate derivatives (**9a** and **9b**)

entry	R	brominating agent <sup>b</sup>	Solvent <sup>c</sup>	time (h)	ratio (mono:di)	yield (%) <sup>d</sup>	purity (%) <sup>e</sup>
1	H	A	DCM	18	14:1	96	93
2 <sup>f</sup>	H	B	DCM	18	1.5:1	67	60
3	H	B	DCM	18	5:1	83	83
4 <sup>g</sup>	H	B	DCM	7	--	trace	--
5	H	B	CH <sub>3</sub> CN	18	3.5:1	85	78
6	H	B	hexane	18	2:1	66	66
7	H	B	toluene	18	8:1	92	89
8 <sup>h</sup>	H	B	THF	18	100:0	--	--
9 <sup>f</sup>	H	C	DCM	18	6.5:1	87	87
10 <sup>i</sup>	H	C	DCM	48	12.5:1	--	--
11 <sup>g</sup>	H	C	toluene	18	--	0	--
12	H	C	toluene	72	33:1	98	97
13	H	C	toluene	120	25:1	97	96
14	OMe	A	DCM	18	10:1	90	91
15	OMe	B	toluene	18	5:1	85	83
16	OMe	C	DCM	18	4.6:1	86	82
17	OMe	C	toluene	72	7:1	88	88

<sup>a</sup>Unless otherwise noted, the reactions were performed at 0 °C to room temperature.<sup>b</sup>A = BnNMe<sub>3</sub>Br<sub>3</sub>; B = Amberlyst A-26 Br<sub>3</sub><sup>-</sup>-form; C = PVPHP.<sup>c</sup>DCM = dichloromethane; THF = tetrahydrofuran.<sup>d</sup>Yield of monobromination was determined by <sup>1</sup>H NMR of the crude material. Isolated and estimated yields (<sup>1</sup>H NMR) were comparable. The crude mixture contained only monobromination and dibromination products and could be used in the subsequent step without further purification.<sup>e</sup>Purity of the monobromination product was calculated based on the ratio of the monobromination to dibromination product.<sup>f</sup>The reactions were performed at room temperature.<sup>g</sup>The reactions were not complete; virtually all starting material was observed by <sup>1</sup>H NMR.<sup>h</sup>There were some unidentifiable inseparable contaminants with the monobromination product.<sup>i</sup>The reaction was performed at 0 °C but was incomplete; large amount of starting material (*ca.* 50%) remained.



















