

Scheme 1 Synthesis of α -aminophosphonates.

Table 1 Synthesis of α -aminophosphonates in the presence of ZnI_2 .

Entry	R	R'	Product	Time (min)	Yield (%)	mp ($^{\circ}\text{C}$)
1	C_6H_5	C_6H_5	3a	15	96	87–89
2	$2\text{-NO}_2\text{C}_6\text{H}_4$	C_6H_5	3b	15	75	155–158
3	$4\text{-MeC}_6\text{H}_4$	C_6H_5	3c	5	80	113–115
4	$4\text{-MeOC}_6\text{H}_4$	C_6H_5	3d	5	95	130–135
5	$4\text{-HOC}_6\text{H}_4$	C_6H_5	3e	20	80	Viscous oil
6	$4\text{-ClC}_6\text{H}_4$	C_6H_5	3f	5	90	60–62
7	$3\text{-NO}_2\text{C}_6\text{H}_4$	C_6H_5	3g	15	75	130–135
8	$3\text{-MeOC}_6\text{H}_4$	C_6H_5	3h	5	70	Viscous oil
9	$4\text{-MeC}_6\text{H}_4$	$4\text{-ClC}_6\text{H}_4$	3i	15	65	60–62
10	$4\text{-MeOC}_6\text{H}_4$	$4\text{-ClC}_6\text{H}_4$	3j	20	50	Viscous oil
11	$4\text{-HOC}_6\text{H}_4$	$4\text{-BrC}_6\text{H}_4$	3k	15	78	154–156
12	$2,3\text{-Cl}_2\text{C}_6\text{H}_3$	C_6H_5	3l	5	55	Viscous oil

In conclusion, we have reported herein a zinc iodide catalyzed novel and eco-friendly method for the synthesis of α -aminophosphonates at room temperature under solvent-free conditions. The advantages of the present protocol are mild heterogeneous reaction conditions, shorter reaction times and easy work-up; inexpensive and ready availability of the catalyst makes the procedure an attractive alternative to the existing methods for the synthesis of α -aminophosphonates.

3. Experimental

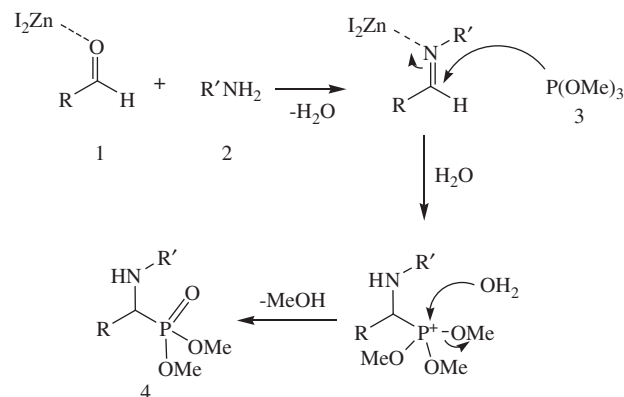
A mixture of aldehyde (1 mmol), amine (1 mmol), trimethylphosphite (1 mmol) and zinc iodide (20 mol%) was stirred at room temperature for the specified time (Table 1). After thin layer chromatography indicated the disappearance of starting materials, chloroform (10 ml) was added and the insoluble material was filtered to separate the catalyst. The filtrate was concentrated. The crude solid residue was purified by crystallization in ethanol, and in the case of the liquid product it was purified by chromatography on a short column of silica gel to afford pure α -aminophosphonates.

Compound **3a**: ^1H NMR (CDCl_3): δ 3.51 (d, 3H, $J=10.5$ Hz, OCH_3), 3.81 (d, 3H, $J=10.6$ Hz, OCH_3), 4.82 (d, 1H, $J=24$ Hz, CHP), 6.64 (d, 2H, $J=8.0$ Hz, ArH), 6.74 (t, 1H, $J=7.2$ Hz, ArH), 7.10 (t, 2H, $J=7.7$ Hz, ArH), 7.30 (t, 1H,

$J=7.5$ Hz, ArH), 7.39 (t, 2H, $J=7.4$ Hz, ArH), 7.50 (d, 2H, $J=7.3$ Hz, ArH); ^{13}C NMR (CDCl_3): δ 54.1 (d, $J=7.0$ Hz), 54.2 (d, $J=6.8$ Hz), 56.2 (d, $J=150$ Hz), 114.3 (CH), 119.0, 128.2 (d, $J=5.8$ Hz), 128.4 (d, $J=3.1$ Hz), 129.1, 131.2, 136.0, 146.6 (d, $J=14.5$ Hz).

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**Scheme 2** Proposed mechanism.

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