

**Supplementary Materials:**

**Experimental Procedure**

To a solution of aldehyde (0.5 mmol) in acetic anhydride (1.5 mmol) was added tetrabutylammonium tribromide (TBATB) (0.05 mmol) and the reaction mixture was stirred at room temperature. Aliquots (5  $\mu$ L) were removed at appropriate time points, quenched by adding it to a saturated solution of  $NaHCO_3$  (50  $\mu$ L). The reaction mixture was extract with ethyl acetate (100  $\mu$ L) and injected into gas chromatography (Model GC 2000) using capillary TIPO BP-1 column (Length 30m x diameter 0.25 mm). Percentage of product formed was calculated from the chromatogram using Chromcard 32 software.

**Supplementary Table S1: The experimental values of the ‘percentage of un-reacted substrates at different time intervals’ for 9 chosen chemical systems (for details see the text).**

| S. No. | Chemical Systems    | Reaction time (min) | % of unreacted substrate |
|--------|---------------------|---------------------|--------------------------|
| 1      | $C_6H_5CHO$         | 0                   | 100                      |
|        |                     | 11                  | 99.1                     |
|        |                     | 26                  | 98                       |
|        |                     | 34                  | 97.2                     |
|        |                     | 48                  | 96.4                     |
|        |                     | 60                  | 94.4                     |
|        |                     | 78                  | 91.7                     |
| 2      | $4-(CH_3)C_6H_4CHO$ | 0                   | 100                      |
|        |                     | 1                   | 98.5                     |
|        |                     | 2                   | 97.7                     |
|        |                     | 5                   | 94.8                     |
|        |                     | 10                  | 89.9                     |
|        |                     | 15                  | 86.17                    |
|        |                     |                     |                          |
| 3      | $4-(Cl)C_6H_4CHO$   | 0                   | 100                      |
|        |                     | 10                  | 99.75                    |
|        |                     | 20                  | 99                       |
|        |                     | 30                  | 97.1                     |
|        |                     | 40                  | 96.8                     |
|        |                     | 50                  | 96.1                     |
|        |                     | 60                  | 95.8                     |
| 4      | $2-(NO_2)C_6H_4CHO$ | 0                   | 100                      |
|        |                     | 240 (4h)            | 99.75                    |
|        |                     | 360 (6h)            | 99.65                    |
|        |                     | 480 (8h)            | 99.25                    |
|        |                     | 600 (10h)           | 98.5                     |
|        |                     | 900 (15h)           | 96.4                     |

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(Supplementary Table S1 continuing)

| S. No. | Chemical Systems         | Reaction time (min) | % of unreacted substrate |
|--------|--------------------------|---------------------|--------------------------|
| 5      | $3-(NO_2)C_6H_4CHO$      | 0                   | 100                      |
|        |                          | 240 (4h)            | 99.5                     |
|        |                          | 360 (6h)            | 99.1                     |
|        |                          | 480 (8h)            | 91.7                     |
|        |                          | 600 (10h)           | 88.6                     |
|        |                          | 900 (15h)           | 72                       |
|        |                          |                     |                          |
| 6      | $4-(NO_2)C_6H_4CHO$      | 0                   | 100                      |
|        |                          | 240 (4h)            | 99.5                     |
|        |                          | 360 (6h)            | 99                       |
|        |                          | 480 (8h)            | 94.3                     |
|        |                          | 600 (10h)           | 92.2                     |
|        |                          | 900 (15h)           | 76.2                     |
|        |                          |                     |                          |
| 7      | $4-(OMe)C_6H_4CHO$       | 0                   | 100                      |
|        |                          | 0.5 (30 sec)        | 97.2                     |
|        |                          | 1.25 (75 sec)       | 90.4                     |
|        |                          | 1.5 (90sec)         | 89.12                    |
|        |                          | 3 (180 sec)         | 80                       |
|        |                          |                     |                          |
| 8      | $3,4-(OMe)_2C_6H_3CHO$   | 0                   | 100                      |
|        |                          | 1                   | 97.9                     |
|        |                          | 2                   | 94.6                     |
|        |                          | 3                   | 90.5                     |
|        |                          | 4                   | 84.1                     |
|        |                          | 5                   | 81.3                     |
|        |                          | 6                   | 74                       |
|        |                          |                     |                          |
| 9      | $3,4,5-(OMe)_3C_6H_2CHO$ | 0                   | 100                      |
|        |                          | 1                   | 98.4                     |
|        |                          | 2                   | 96.5                     |

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(Supplementary Table S1 continuing)

| S. No. | Chemical Systems   | Reaction time (min) | % of unreacted substrate |
|--------|--|---------------------|--------------------------|
|        | 3,4,5-(OMe) <sub>3</sub> C <sub>6</sub> H <sub>2</sub> CHO | 3                   | 94.5                     |
|        |  | 4                   | 93.7                     |
|        |  | 6                   | 87.4                     |
|        |  | 8                   | 82.9                     |
|        |  | 10                  | 77.3                     |