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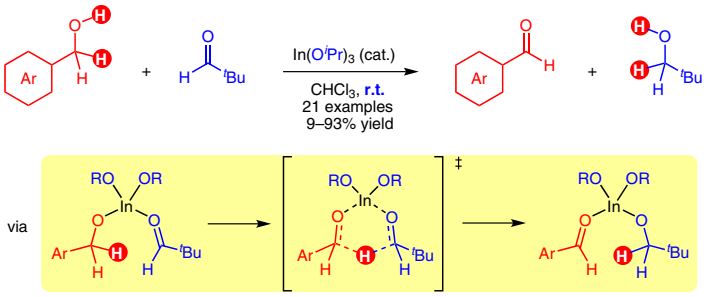
Indium(III) Isopropoxide as a Hydrogen Transfer Catalyst for Conversion of Benzylic Alcohols into Aldehydes or Ketones via Oppenauer Oxidation

Yohei Ogiwara
Yuji Ono
Norio Sakai*

Department of Pure and Applied Chemistry, Faculty of Science and Technology, Tokyo University of Science (RIKADAI), Noda, Chiba 278-8510, Japan
sakachem@rs.noda.tus.ac.jp



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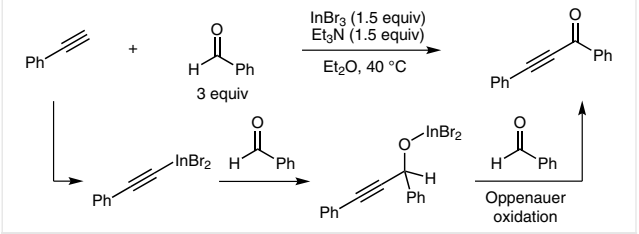
Abstract Indium(III) isopropoxide [In(O*i*-Pr)$_3$] was applicable as an Oppenauer oxidation catalyst, and the conversion of primary or secondary alcohols into the corresponding aldehydes or ketones was promoted at room temperature using pivalaldehyde as an oxidant.

Key words indium catalyst, Oppenauer oxidation, primary alcohol, secondary alcohol, aldehyde, ketone, room temperature

Oppenauer oxidation is a powerful method for the preparation of ketones or aldehydes from the corresponding secondary or primary alcohols. Because it can be performed under milder reaction conditions than other oxidation strategies, Oppenauer oxidations generally achieve a highly selective transformation of alcohols into carbonyl compounds bearing various functional groups.[1] Although a number of main-group- and transition-metal-based Oppenauer-type oxidations have been reported, the oxidation of primary alcohols to aldehydes remains a challenging transformation, because of either undesired side-reactions due to high reactivity of the oxidation product, aldehydes, as found in the Tishchenko reaction and aldol condensation, or a reverse Meerwein–Ponndorf–Verley (MPV) reduction.[2,3] In terms of substrate generality and catalytic efficiency for this transformation, the search for undiscovered metal catalysts that could be potentially applicable to Oppenauer oxidation is imperative.

In 2012, Lee and co-workers reported a pioneering example of an In(O*i*-Pr)$_3$-catalyzed MPV reduction of aldehydes leading to primary alcohols, which was the reverse of Oppenauer oxidation.[4] Kirillov and Carpentier et al. also discovered that a similar reduction of ligands is promoted with an indium complex, an indium imino-phenolate into an indium amido-phenolate, by *i*-PrOH.[5] Their studies revealed a new direction for indium complexes in MPV-type hydride transfer processes, and also suggested their potential for use in Oppenauer oxidation reactions. Very recently, our research group developed an indium(III) bromide promoted oxidative coupling of terminal alkynes with aldehydes leading to alkynyl ketones (Scheme 1).[6] In this reaction, the indium-mediated Oppenauer-type hydride transfer was considered a key oxidation step.[7] These results encouraged us to attempt the use of indium(III) compounds as catalysts for a simple Oppenauer oxidation of alcohols. We describe herein, indium(III) isopropoxide as a new Oppenauer oxidation catalyst, and how an oxidation series of primary and secondary alcohols effectively proceeded at room temperature, giving aldehydes and ketones.

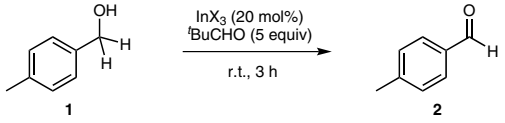


Scheme 1 Our previous result: indium-promoted oxidative coupling of terminal alkynes with aldehydes via Oppenauer oxidation

Initially, a catalyst screening for the Oppenauer oxidation of 4-methylbenzyl alcohol (**1**) was conducted (Table 1, entries 1–7). When the reaction of **1** with 20 mol% of InCl$_3$ using *t*-BuCHO as a hydrogen acceptor was performed in 0.33 M of dichloromethane at room temperature for three hours, the expected Oppenauer reaction was not observed by GC analysis (Table 1, entry 1). Also, no Oppenauer product was obtained using other indium(III) salts such as InBr$_3$, InI$_3$, In(OTf)$_3$, In(OAc)$_3$, and In(OH)$_3$ (entries 2–6). The use of In(O*i*-Pr)$_3$ as a catalyst, however, improved the results dras-

tically to form the corresponding benzaldehyde **2** in an 82% GC yield (entry 7). This result revealed that indium(III) alkoxide functions as an effective catalyst for Oppenauer oxidation, as well as for MPV reduction.[4] Solvents were next investigated for the reaction. Oxidation in chloroform led to a slightly increased yield of **2** (entry 8), and the use of other solvents, such as toluene, Et_2O, THF, and MeCN, also resulted in moderate to good yields of **2** (entries 9–12). Increasing the initial concentration of **1** in $CHCl_3$ from 0.33 to 0.5 M, resulted in an 88% increase in the GC yield of **2** (entry 13). Other oxidizing agents, such as acetone (3 equiv) in chloroform, or chloroform by itself as both an oxidizing agent and a solvent,[8] were not suitable for this In(O*i*-Pr)$_3$ catalyst system.

Table 1 Optimization for Oppenauer Oxidation of the Primary Alcohol **1**[a]

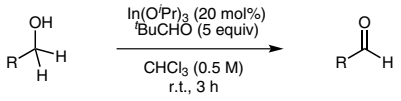


Entry	InX_3	Solvent	GC results (%)	
			Conv. of **1**	Yield of **2**
1	$InCl_3$	CH_2Cl_2 (0.33 M)	30	0
2	$InBr_3$	CH_2Cl_2 (0.33 M)	29	0
3	InI_3	CH_2Cl_2 (0.33 M)	20	0
4	$In(OTf)_3$	CH_2Cl_2 (0.33 M)	2	0
5	$In(OAc)_3$	CH_2Cl_2 (0.33 M)	1	0
6	$In(OH)_3$	CH_2Cl_2 (0.33 M)	98	0[b]
7	In(O*i*-Pr)$_3$	CH_2Cl_2 (0.33 M)	85	82
8	In(O*i*-Pr)$_3$	$CHCl_3$ (0.33 M)	>99	83
9	In(O*i*-Pr)$_3$	toluene (0.33 M)	97	81
10	In(O*i*-Pr)$_3$	Et_2O (0.33 M)	89	73
11	In(O*i*-Pr)$_3$	THF (0.33 M)	94	77
12	In(O*i*-Pr)$_3$	MeCN (0.33 M)	44	37
13	In(O*i*-Pr)$_3$	$CHCl_3$ (0.5 M)	>99	88 (87)[c]

[a] Reaction conditions: **1** (0.5 mmol), InX_3 (0.1 mmol), *t*-BuCHO (2.5 mmol), r.t., 3 h.
[b] Complex mixture.
[c] Isolated yield.

Examination of the Oppenauer oxidation of a variety of primary alcohols was then conducted under the optimal conditions (Table 2). The oxidation of a benzyl alcohol afforded benzaldehyde (**3**) in a 93% yield (Table 2, entry 1), and several benzyl alcohols bearing a carbon substituent at the aromatic ring, such as 4-*t*-Bu, 4-Ph, and 2-Me, were also applicable to the oxidation giving the corresponding products **4**–**6** in moderate yields (entries 2–4). Substrates with electron-donating alkoxy, aryloxy, and hydroxy groups at the 4- or 3-positions were converted into benzaldehydes **7**–**10**, respectively, in high yields (entries 5–8). Both nitrogen- and sulfur-containing functional groups were tolerated in the reaction, and the oxidation products **11** and **12** were obtained in good yields (entries 9 and 10). However, substrates with electron-deficient aromatic rings, which have halogen atoms as well as both cyano- and methoxycarbonyl groups, showed a relatively lower level of reactivity for the oxidation, giving **13**–**18** (entries 11–16). The reactions of benzyl alcohols, composed of a fused aromatic ring, a heterocycle, and a vinyl system, also afforded the corresponding aldehydes **19**–**22**, although a further optimization was necessary to improve the yields (entries 17–20). In contrast, when the other primary aliphatic alcohols, not benzylic ones, such as 1-decanol and 2-phenylethanol, were used as substrates for this procedure, unfortunately the corresponding aldehydes were not obtained and the starting alcohols were completely recovered.

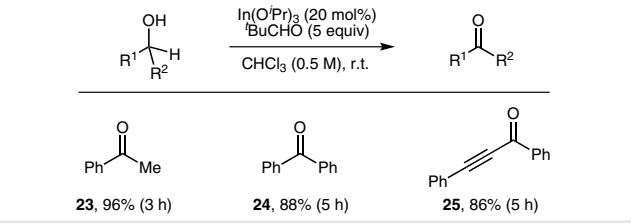
Table 2 Scope of the Oppenauer Oxidation of Primary Alcohols Leading to Aldehydes[a]



Entry	R	Product	Yield (%)[b]
1	Ph	**3**	93
2	4-*t*-BuC_6H_4	**4**	61
3	4-PhC_6H_4	**5**	50
4	2-MeC_6H_4	**6**	35
5	4-MeOC_6H_4	**7**	80
6	4-PrOC_6H_4	**8**	83
7	3-PhOC_6H_4	**9**	71
8	4-HOC_6H_4	**10**	85
9	4-$Me_2N$$C_6H_4$	**11**	71
10	4-MeSC_6H_4	**12**	80
11[c]	4-FC_6H_4	**13**	30
12	4-ClC_6H_4	**14**	50
13[c]	2-ClC_6H_4	**15**	9
14	4-BrC_6H_4	**16**	60
15	4-NCC_6H_4	**17**	13
16[c]	4-$MeO_2C$$C_6H_4$	**18**	40
17	1-naphthyl	**19**	68
18	2-naphthyl	**20**	51
19	2-pyridyl	**21**	21
20	(*E*)-cinnamyl	**22**	21

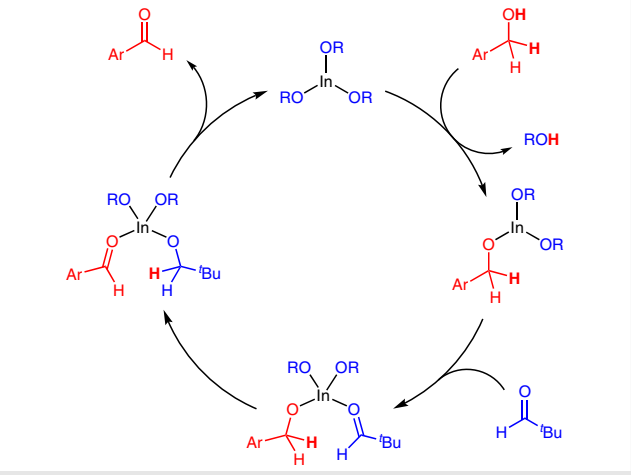
[a] Reaction conditions: alcohol (0.5 mmol), In(O*i*-Pr)$_3$ (0.1 mmol), *t*-BuCHO (2.5 mmol), $CHCl_3$ (1 mL), r.t., 3 h.
[b] Isolated yields.
[c] Reaction performed in 1.5 mmol scale.

Conversions of secondary alcohols into ketones were also achieved using the In(O*i*-Pr)$_3$/*t*-BuCHO oxidation system (Scheme 2). Acetophenone (**23**), benzophenone (**24**), and the alkynyl ketone **25** were obtained in high yields from their corresponding secondary alcohols.



Scheme 2 Oppenauer oxidation of several secondary alcohols leading to ketones. *Reagents and conditions*: alcohol (0.5 mmol), In(O*i*-Pr)$_3$ (0.1 mmol), *t*-BuCHO (2.5 mmol), $CHCl_3$ (1 mL), r.t. Isolated yields are shown.

The proposed catalytic cycle for the oxidation of primary alcohols is illustrated in Scheme 3. This was based on the assumption that the oxidation would proceed through a typical aluminum-based Oppenauer oxidation: (i) deprotonation of a benzyl alcohol by an indium alkoxide, (ii) coordination of the hydrogen acceptor, *t*-BuCHO, to the indium center, (iii) hydride transfer from the benzylic carbon to the aldehyde, and (iv) regeneration of the indium tri(alkoxide) catalyst with the release of the oxidation product.



Scheme 3 Proposed catalytic cycle

In summary, an indium-catalyzed Oppenauer oxidation of primary and secondary alcohols was achieved. A combination of indium(III) isopropoxide as a catalyst and pivalaldehyde as a hydrogen acceptor was found to be an effective oxidation tool for alcohols. Also, the oxidizing system produced not only a variety of benzaldehyde derivatives but also aromatic ketones at room temperature. Further improvements of the Oppenauer oxidation for aliphatic alcohols by In(O*i*-Pr)$_3$/*t*-BuCHO are now in progress.

^{1}H, ^{13}C{^{1}H} NMR spectra were recorded on a 300 or 500 MHz spectrometer. Chemical shifts in the ^{1}H, ^{13}C{^{1}H} NMR spectra were reported in ppm relative to residual solvent peaks such as that of $CHCl_3$ (δ = 7.26 for ^{1}H, and δ = 77.0 for ^{13}C) or of the internal reference TMS (δ = 0.00 for both ^{1}H and ^{13}C). GC analyses were performed using a DB-5 capillary column (30 m × 0.25 mm, film thickness = 0.25 μm). The substrates of alcohols were prepared via the reduction of the starting ketone or aldehyde using $NaBH_4$. The commercially available solid substrate, In(O*i*-Pr)$_3$, was purchased from Wako and purified by drying under reduced pressure vacuum prior to use. Pivalaldehyde was purchased and purified by vacuum transfer prior to use. $CHCl_3$ was dried and distilled over P_2O_5 and stored over molecular sieves. Unless otherwise noted, all reactions were performed under a N_2 atmosphere.

Oppenauer Oxidation of Alcohols Using In(*i*-OPr)$_3$; General Procedure

To a screw tube in a glovebox was added In(O*i*-Pr)$_3$ (29.2 mg, 0.1 mmol). The tube was then sealed and removed from the glovebox, and $CHCl_3$ (1 mL), alcohol (0.5 mmol), and pivalaldehyde (280 μL, 2.5 mmol) were added under N_2 in this order. After stirring the mixture at r.t. for 3 h, H_2O (1.0 mL) was added to the reaction mixture, which was then extracted with EtOAc. The organic phase was dried (Na_2SO_4), and evaporated under reduced pressure. The crude material was purified by silica gel column chromatography (Table 2 and Scheme 2).

4-Methylbenzaldehyde (2)[9]

General procedure was followed with 4-methylbenzyl alcohol (**1**) (61.1 mg, 0.5 mmol). Column chromatography (40:1 hexane/EtOAc) afforded **2** as a colorless oil (52.9 mg, 87%).

^{1}H NMR ($CDCl_3$, 500.2 MHz): δ = 2.44 (s, 3 H, CH_3), 7.33 (d, *J* = 8.0 Hz, 2 H, ArH), 7.78 (d, *J* = 8.0 Hz, 2 H, ArH), 9.97 (s, 1 H, CH).

^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 21.9, 129.7, 129.8, 134.2, 145.5, 192.0.

LRMS (EI): *m*/*z* (%) = 120 (M^+, 84), 106 (41), 91 (100), 79 (38), 77 (41), 65 (25).

Benzaldehyde (3)[10]

General procedure was followed with benzyl alcohol (54.1 mg, 0.5 mmol). Column chromatography (40:1 hexane/EtOAc) afforded **3** as a colorless oil (49.3 mg, 93%).

^{1}H NMR ($CDCl_3$, 500.2 MHz): δ = 7.54 (t, *J* = 8.0 Hz, 2 H, ArH), 7.62–7.65 (m, 1 H, ArH), 7.89 (d, *J* = 8.0 Hz, 2 H, ArH), 10.03 (s, 1 H, CHO).

^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 129.0, 129.7, 134.4, 136.4, 192.4.

LRMS (EI): *m*/*z* (%) = 106 (M^+, 100), 77 (97), 64 (19).

4-*tert*-Butylbenzaldehyde (4)[10]

General procedure was followed with 4-*tert*-butylbenzyl alcohol (82.1 mg, 0.5 mmol). Column chromatography (40:1 hexane/EtOAc) afforded **4** as a colorless oil (49.5 mg, 61%).

^{1}H NMR ($CDCl_3$, 500.2 MHz): δ = 1.36 (s, 9 H, CH_3), 7.56 (d, *J* = 8.0 Hz, 2 H, ArH), 7.82 (d, *J* = 8.0 Hz, 2 H, ArH), 9.98 (s, 1 H, CHO).

^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 31.1, 35.3, 126.0, 129.7, 134.1, 158.4, 192.1.

LRMS (EI): *m*/*z* (%) = 162 (M^+, 100), 147 (100), 119 (63), 103 (11), 91 (94), 77 (24).

4-Phenylbenzaldehyde (5)[9]

General procedure was followed with 4-phenylbenzyl alcohol (92.1 mg, 0.5 mmol). Column chromatography (40:1 hexane/EtOAc) afforded **5** as a colorless solid (45.6 mg, 50%); mp 59–60 °C.

^{1}H NMR ($CDCl_3$, 500.2 MHz): δ = 7.42 (t, *J* = 7.5 Hz, 1 H, ArH), 7.48 (t, *J* = 7.5 Hz, 2 H, ArH), 7.64 (d, *J* = 7.5 Hz, 2 H, ArH), 7.76 (d, *J* = 7.5 Hz, 2 H, ArH), 7.96 (d, *J* = 7.5 Hz, 2 H, ArH), 10.06 (s, 1 H, CHO).

^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 127.4, 127.7, 128.5, 129.0, 130.3, 135.2 139.7, 147.2, 191.9.

LRMS (EI): *m*/*z* (%) = 182 (M^+, 100), 151 (17), 126 (7), 90 (3), 75 (14), 64 (4).

2-Methylbenzaldehyde (6)[10]

General procedure was followed with 2-methylbenzyl alcohol (61.1 mg, 0.5 mmol). Column chromatography (40:1 hexane/EtOAc) afforded **6** as a colorless oil (21.0 mg, 35%).

^{1}H NMR ($CDCl_3$, 500.2 MHz): δ = 2.68 (s, 3 H, CH_3), 7.26 (d, *J* = 7.5 Hz, 1 H, ArH), 7.36 (t, *J* = 7.5 Hz, 1 H, ArH), 7.48 (t, *J* = 7.5 Hz, 1 H, ArH), 7.80 (d, *J* = 7.5 Hz, 1 H, ArH), 10.27 (s, 1 H, CHO).

^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 19.5, 126.3, 131.7, 132.0, 133.6, 134.1, 140.6, 192.8.

LRMS (EI): *m*/*z* (%) = 120 (M^+, 98), 108 (21), 91 (100), 77 (6), 66 (25).

4-Methoxybenzaldehyde (7)[10]

General procedure was followed with 4-methoxybenzyl alcohol (69.1 mg, 0.5 mmol). Column chromatography (40:1 hexane/EtOAc) afforded **7** as a colorless oil (54.5 mg, 80%).

^{1}H NMR ($CDCl_3$, 500.2 MHz): δ = 3.89 (s, 3 H, OCH_3), 7.00 (d, *J* = 8.5 Hz, 2 H, ArH), 7.84 (d, *J* = 8.5 Hz, 2 H, ArH), 9.88 (s, 1 H, CHO).

^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 55.5, 114.2, 129.9, 131.9, 164.5, 190.7.

LRMS (EI): *m*/*z* (%) = 136 (M^+, 100), 107 (33), 92 (36), 77 (66), 66 (19).

4-Propoxybenzaldehyde (8)[11]

General procedure was followed with 4-propoxybenzyl alcohol (83.1 mg, 0.5 mmol). Column chromatography (40:1 hexane/EtOAc) afforded **8** as a colorless oil (68.1 mg, 83%).

^{1}H NMR ($CDCl_3$, 500.2 MHz): δ = 1.53 (t, *J* = 7.5 Hz, 3 H, CH_3), 1.81–1.88 (m, 2 H, CH_2), 4.00 (t, *J* = 7.0 Hz, 2 H, CH_2), 6.99 (d, *J* = 8.0 Hz, 2 H, ArH), 7.82 (d, *J* = 8.0 Hz, 2 H, ArH), 9.87 (s, 1 H, CHO).

^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 10.4, 22.3, 69.7, 114.7, 129.6, 131.9, 164.2, 190.8.

LRMS (EI): *m*/*z* (%) = 164 (M^+, 58), 121 (100), 109 (41), 92 (13), 77 (9), 65 (17).

3-Phenoxybenzaldehyde (9)[12]

General procedure was followed with 4-phenoxybenzyl alcohol (100.1 mg, 0.5 mmol). Column chromatography (40:1 hexane/EtOAc) afforded **9** as a colorless oil (70.3 mg, 71%).

^{1}H NMR ($CDCl_3$, 500.2 MHz): δ = 7.03 (d, *J* = 8.0 Hz, 2 H, ArH), 7.16 (t, *J* = 8.0 Hz, 1 H, ArH), 7.27 (d, *J* = 8.0 Hz, 1 H, ArH), 7.36 (t, *J* = 8.0 Hz, 2 H, ArH), 7.50–7.45 (m, 2 H, ArH), 7.59 (d, *J* = 8.0 Hz, 1 H, ArH), 9.94 (s, 1 H, CHO).

^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 118.0, 119.4, 124.1, 124.5, 124.6, 130.0, 130.4 138.0, 156.1, 158.3, 191.5.

LRMS (EI): *m*/*z* (%) = 198 (M^+, 100), 181 (19), 169 (43), 141 (34), 114 (14), 77 (28).

4-Hydroxybenzaldehyde (10)[13]

General procedure was followed with 4-hydroxybenzyl alcohol (62.1 mg, 0.5 mmol). Column chromatography (20:1 hexane/EtOAc) afforded **10** as a colorless solid (51.9 mg, 85%); mp 110–111 °C.

^{1}H NMR ($CDCl_3$, 500.2 MHz): δ = 6.37 (s, 1 H, OH), 6.99 (d, *J* = 8.5 Hz, 2 H, ArH), 7.83 (d, *J* = 8.5 Hz, 2 H, ArH), 9.87 (s, 1 H, CHO).

^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 116.0, 129.8, 132.6, 161.6, 191.3.

LRMS (EI): *m*/*z* (%) = 122 (M^+, 93), 121 (100), 93 (39), 66 (30).

4-(Dimethylamino)benzaldehyde (11)[14]

General procedure was followed with 4-(dimethylamino)benzyl alcohol (75.6 mg, 0.5 mmol). Column chromatography (40:1 hexane/EtOAc) afforded **11** as a colorless solid (52.9 mg, 71%); mp 71–73 °C.

^{1}H NMR ($CDCl_3$, 500.2 MHz): δ = 3.09 (s, 6 H, NCH_3), 6.71 (d, *J* = 7.5 Hz, 2 H, ArH), 7.74 (d, *J* = 7.5 Hz, 2 H, ArH), 9.75 (s, 1 H, CHO).

^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 40.1, 110.9, 125.1, 132.0, 154.3, 190.3.

LRMS (EI): *m*/*z* (%) = 149 (M^+, 100), 132 (78), 120 (57), 105 (67), 91 (51), 77 (83), 64 (45).

4-(Methylthio)benzaldehyde (12)[3a]

General procedure was followed with 4-(methylthio)benzyl alcohol (77.1 mg, 0.5 mmol). Column chromatography (40:1 hexane/EtOAc) afforded **12** as a colorless oil (60.8 mg, 80%).

^{1}H NMR ($CDCl_3$, 500.2 MHz): δ = 2.54 (s, 3 H, SCH_3), 7.33 (d, *J* = 8.5 Hz, 2 H, ArH), 7.78 (d, *J* = 8.5 Hz, 2 H, ArH), 9.92 (s, 1 H, CHO).

^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 14.7, 125.2, 130.0, 132.9, 147.9, 191.2.

LRMS (EI): *m*/*z* (%) = 152 (M^+, 100), 123 (48), 108 (26), 79 (29), 77 (22), 69 (21), 66 (16).

4-Fluorobenzaldehyde (13)[15]

General procedure was followed with 4-fluorobenzyl alcohol (189.1 mg, 1.5 mmol). Column chromatography (40:1 hexane/EtOAc) afforded **13** as a colorless oil (55.8 mg, 30%).

^{1}H NMR ($CDCl_3$, 500.2 MHz): δ = 7.21–7.24 (m, 2 H, ArH), 7.91–7.93 (m, 2 H, ArH), 9.98 (s, 1 H, CHO).

^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 116.2 (d, *J* = 22.0 Hz), 132.1 (d, *J* = 9.9 Hz), 132.9 (d, *J* = 2.8 Hz), 166.4 (d, *J* = 255.1 Hz), 190.4.

LRMS (EI): *m*/*z* (%) = 124 (M^+, 97), 123 (100), 95 (86), 75 (25).

4-Chlorobenzaldehyde (14)[15]

General procedure was followed with 4-chlorobenzyl alcohol (71.3 mg, 0.5 mmol). Column chromatography (40:1 hexane/EtOAc) afforded **14** as a yellow solid (35.2 mg, 50%); mp 47–49 °C.

^{1}H NMR ($CDCl_3$, 500.2 MHz): δ = 7.52 (d, *J* = 8.5 Hz, 2 H, ArH), 7.82–7.84 (m, 2 H, ArH), 9.99 (s, 1 H, CHO).

^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 129.5, 130.9, 134.7, 140.9, 190.9.

LRMS (EI): *m*/*z* (%) = 140 (M^+, 93), 139 (100), 113 (22), 110 (66), 77 (17), 75 (30).

2-Chlorobenzaldehyde (15)[15]

General procedure was followed with 2-chlorobenzyl alcohol (213.8 mg, 1.5 mmol). Column chromatography (40:1 hexane/EtOAc) afforded **15** as a colorless oil (19.0 mg, 9%).

^{1}H NMR ($CDCl_3$, 500.2 MHz): δ = 7.40 (t, *J* = 7.5 Hz, 1 H, ArH), 7.46 (d, *J* = 7.5 Hz, 1 H, ArH), 7.54 (t, *J* = 7.5 Hz, 1 H, ArH), 7.93 (d, *J* = 7.5 Hz, 1 H, ArH), 10.50 (s, 1 H, CHO).

^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 127.3, 129.4, 130.6, 132.4, 135.1, 137.9, 189.8.

LRMS (EI): *m*/*z* (%) = 140 (M^+, 99), 139 (100), 128 (18), 111 (53), 77 (22), 75 (30).

4-Bromobenzaldehyde (16)[15]

General procedure was followed with 4-bromobenzyl alcohol (93.5 mg, 0.5 mmol). Column chromatography (40:1 hexane/EtOAc) afforded **16** as a colorless solid (54.9 mg, 60%); mp 56–58 °C.

^{1}H NMR ($CDCl_3$, 500.2 MHz): δ = 7.69 (d, *J* = 8.0 Hz, 2 H, ArH), 7.76 (d, *J* = 8.0 Hz, 2 H, ArH), 9.98 (s, 1 H, CHO).

^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 129.7, 131.0, 132.4, 135.1, 191.1.

LRMS (EI): *m*/*z* (%) = 186 (86), 185 (100), 184 (M^+, 87), 183 (99), 77 (25), 75 (29).

4-Cyanobenzaldehyde (17)[16]

General procedure was followed with 4-cyanobenzyl alcohol (66.6 mg, 0.5 mmol). Column chromatography (40:1 hexane/EtOAc) afforded **17** as a colorless solid (8.7 mg, 13%); mp 98–100 °C.

^{1}H NMR ($CDCl_3$, 500.2 MHz): δ = 7.86 (d, *J* = 8.5 Hz, 2 H, ArH), 8.01 (d, *J* = 8.5 Hz, 2 H, ArH), 10.11 (s, 1 H, CHO).

^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 117.6, 117.7, 129.9, 132.9, 138.7, 190.6.

LRMS (EI): *m*/*z* (%) = 131 (M^+, 93), 130 (100), 102 (82), 76 (51).

4-(Methoxycarbonyl)benzaldehyde (18)[17]

General procedure was followed with 4-(methoxycarbonyl)benzyl alcohol (249.3 mg, 1.5 mmol). Column chromatography (40:1 hexane/EtOAc) afforded **18** as a colorless solid (98.4 mg, 40%); mp 61–63 °C.

^{1}H NMR ($CDCl_3$, 500.2 MHz): δ = 3.97 (s, 3 H, CO_2CH_3), 7.96 (d, *J* = 8.5 Hz, 2 H, ArH), 8.21 (d, *J* = 8.5 Hz, 2 H, ArH), 10.11 (s, 1 H, CHO).

^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 52.6, 129.5, 130.2, 135.1, 139.1, 166.1, 191.6.

LRMS (EI): *m*/*z* (%) = 164 (M^+, 97), 133 (100), 123 (14), 105 (50), 77 (35).

1-Naphthaldehyde (19)[10]

General procedure was followed with 1-naphthylmethanol (79.1 mg, 0.5 mmol). Column chromatography (40:1 hexane/EtOAc) afforded **19** as a colorless oil (53.0 mg, 68%).

^{1}H NMR ($CDCl_3$, 500.2 MHz): δ = 7.56–7.62 (m, 2 H, ArH), 7.68 (t, *J* = 8.5 Hz, 1 H, ArH), 7.90 (d, *J* = 8.5 Hz, 1 H, ArH), 7.96 (d, *J* = 8.5 Hz, 1 H, ArH), 8.08 (d, *J* = 8.5 Hz, 1 H, ArH), 9.25 (d, *J* = 8.5 Hz, 1 H, ArH), 10.38 (s, 1 H, CHO).

^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 124.8 (2 C), 126.9, 128.4, 129.0, 130.5, 131.3, 133.7, 135.2, 136.6, 193.5.

LRMS (EI): *m*/*z* (%) = 156 (M^+, 100), 127 (89), 101 (9), 77 (13).

2-Naphthaldehyde (20)[10]

General procedure was followed with 2-naphthylmethanol (79.1 mg, 0.5 mmol). Column chromatography (40:1 hexane/EtOAc) afforded **20** as a colorless solid (39.8 mg, 51%); mp 60–61 °C.

^{1}H NMR ($CDCl_3$, 500.2 MHz): δ = 7.57–7.66 (m, 2 H, ArH), 7.90–8.02 (m, 4 H, ArH), 8.34 (s, 1 H, ArH), 10.16 (s, 1 H, CHO).

^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 122.7, 127.1, 128.1, 129.08, 129.10, 129.5, 132.6, 134.1, 134.5, 136.4, 192.3.

LRMS (EI): *m*/*z* (%) = 156 (M^+, 100), 127 (99), 101 (8), 77 (13).

2-Picolinaldehyde (21)[18]

General procedure was followed with 2-pyridylmethanol (54.6 mg, 0.5 mmol). Column chromatography (40:1 hexane/EtOAc) afforded **21** as a yellow oil (11.2 mg, 21%).

^{1}H NMR ($CDCl_3$, 500.2 MHz): δ = 7.53–7.55 (m, 1 H, ArH), 7.88–7.98 (m, 2 H, ArH), 8.79–8.82 (m, 1 H, ArH), 10.09 (s, 1 H, CHO).

^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 121.6, 127.8, 137.0, 150.2, 152.7, 193.4.

LRMS (EI): *m*/*z* (%) = 107 (M^+, 56), 79 (100), 55 (17).

Cinnamaldehyde (22)[3a]

General procedure was followed with cinnamyl alcohol (67.1 mg, 0.5 mmol). Column chromatography (40:1 hexane/EtOAc) afforded **22** as a yellow oil (13.9 mg, 21%).

^{1}H NMR ($CDCl_3$, 500.2 MHz): δ = 6.71–6.75 (m, 1 H, CH), 7.43–7.58 (m, 6 H), 9.70 (d, *J* = 8.5 Hz, 1 H, CHO).

^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 128.5, 128.6, 129.1, 131.3, 134.0, 152.8, 193.7.

LRMS (EI): *m*/*z* (%) = 132 (M^+, 91), 131 (100), 103 (63), 77 (46), 64 (8).

Acetophenone (23)[18]

General procedure was followed with 1-phenylethanol (61.1 mg, 0.5 mmol). Column chromatography (40:1 hexane/EtOAc) afforded **23** as a colorless oil (57.6 mg, 96%).

^{1}H NMR ($CDCl_3$, 500.2 MHz): δ = 2.60 (s, 3 H, CH_3), 7.46 (d, *J* = 8.5 Hz, 2 H, ArH), 7.56 (m, 1 H, ArH), 7.59 (d, *J* = 8.5 Hz, 2 H, ArH).

^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 26.5, 128.2, 128.5, 133.0, 137.0, 198.1.

LRMS (EI): *m*/*z* (%) = 120 (M^+, 44), 105 (100), 77 (94).

Benzophenone (24)[18]

General procedure was followed with 1,1-diphenylmethanol (92.1 mg, 0.5 mmol) for 5 h. Column chromatography (40:1 hexane/EtOAc) afforded **24** as a colorless solid (80.1 mg, 88%); mp 46–49 °C.

^{1}H NMR ($CDCl_3$, 500.2 MHz): δ = 7.49 (t, *J* = 7.5 Hz, 4 H, ArH), 7.56 (t, *J* = 7.5 Hz, 2 H, ArH), 7.81 (d, *J* = 7.5 Hz, 4 H, ArH).

^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 129.0, 129.7, 134.4, 136.4, 192.4.

LRMS (EI): *m*/*z* (%) = 182 (M^+, 94), 104 (100), 77 (94).

1,3-Diphenylprop-2-yn-1-one (25)[6]

General procedure was followed with 1,3-diphenylprop-2-yn-1-ol (104.1 mg, 0.5 mmol) for 5 h. Column chromatography (40:1 hexane/EtOAc) afforded **25** as yellow oil (88.6 mg, 86%).

^{1}H NMR ($CDCl_3$, 500.2 MHz): δ = 7.26–7.54 (m, 5 H, ArH), 7.26–7.54 (m, 3 H, ArH), 8.23 (d, *J* = 7.0 Hz, 2 H, ArH).

^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 86.9, 93.1, 120.1, 128.6, 128.7, 129.6, 130.8, 133.0, 134.1, 136.8, 178.0.

LRMS (EI): *m*/*z* (%) = 206 (M^+, 83), 178 (100), 129 (98), 105 (20), 89 (15), 77 (36).

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0035-1562542.

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