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# Zn-promoted regio- and sequence-selective one-pot joining reactions of three components: vinylpyridines, alkyl iodides, and carbonyl compounds (or nitriles)

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ABSTRACT

Addition of alkyl iodides (**3**) into the solution containing 2-(or 4-)vinylpyridine (**1** or **2**) and carbonyl compounds (**6**) in the presence of Zn-powder (99.9%) in acetonitrile under refluxing brought about regio- and sequence-selective joining reaction of three components to give the corresponding (2-hydroxyethyl)pyridines (**7** or **8**) in good to moderate yields. On the other hand, 2-(2- or 4-pyridyl)ethyl alkyl ketones (**10** or **11**) were obtained from the similar joining reaction of three components by addition of alkyl iodides (**3**) into the solution of 2-(or 4-)vinylpyridine (**1** or **2**), and nitriles (**9**) in toluene containing Zn-powder (99.9%) under the similar reaction conditions.



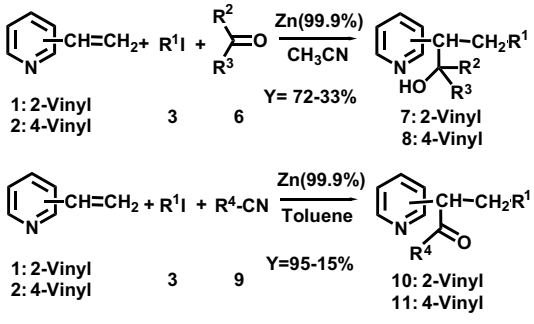
## 1. Introduction

Pyridine derivatives[1] have been of much importance and usefulness as bioactive natural products, pharmaceutical drugs, agrochemicals and various types of organic functional compounds such as electronic information materials, semi-conductors and battery materials, although only some reactions have been reported on carbon–carbon bond formation for pyridine derivatives, such as simple nucleophilic attack of stable carbanions to 2-vinylpyridine,[2] and similar attack of α-carbanions generated from 2-(or 4-)vinyl pyridine to styrene derivatives.[3,4]

On the other hand, conjugate addition of organozinc or organocopper reagents to α,β-unsaturated carbonyl compounds,[5] followed by the subsequent trapping of the anionic intermediates has been reported successfully to proceed using alkyl halides,[6] acid chlorides,[7] aldehydes,[8] and phenylselenyl halides.[9] However, the preparation and the handling of these organometallic reagents are troublesome and not necessarily simple, and these one-pot reactions, in principle, require two steps at low temperatures such as −78 °C.

We have already reported Zn-promoted one-pot joining reaction of three components among alkyl iodides, α,β-unsaturated esters (or α,β-unsaturated nitriles), and carbonyl compounds[10,11] (or nitriles or acid anhydrides).[12] It was instructive that the reactions proceeded regio- and sequence-selectively through the first alkylation to the β-carbons by alkyl iodide, and the following second C-acylation by acid anhydrides (or electrophilic attack by carbonyl compounds to the α-carbanions).

In this study, we wish to report Zn-promoted one-pot highly selective joining reactions of three components, 2-(or 4-)vinylpyridines (**1** or **2**), alkyl iodides (**3**), and carbonyl compounds (**6**) (or nitriles (**9**)) in regio- and sequence-selective manners to give the corresponding (2-hydroxyethyl)pyridines (**7** or **8**) or 2-(2- or 4-pyridyl) ethyl alkyl ketones (**10** or **11**) in good to moderate yields, as is shown in Scheme 1.




**Scheme 1.** Zn-promoted regio- and sequenceselective joining reaction of three components.

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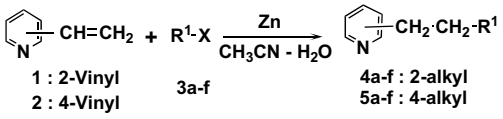
## 2. Results and discussion

As typical procedure for formation of (2-hydroxy) ethylpyridines (**7** or **8**), alkyl iodide (**3**) was added dropwise into a solution of 2-(or 4-)vinylpyridines (**1** or **2**) and carbonyl compounds (**6**) in acetonitrile under gentle refluxing to give the corresponding joining products of those three components in good to moderate yields. Interestingly, replacement of acetone (**6a**) by acetonitrile (**9a**) as the reagent and that of acetonitrile by toluene as the solvent in this reaction, brought about formation of 5-methyl-3-(2-pyridyl)hexan-2-one (**10a**;**a**) in a 82% yield as the almost single product, suggesting that acetone is more reactive than acetonitrile as an electrophile in the present Zn-promoted one-pot highly selective joining reaction of three components.

It may be quite noteworthy that complete regioselectivity was clearly observed that the alkyl groups of halides (**3**) form carbon–carbon bonds at β-position of the vinyl groups of 2-(or 4-)vinylpyridines (**1** or **2**), while the carbon atoms of the carbonyl groups of **6** or the cyano groups of nitriles (**9**) were attached with α-carbon of the vinyl groups of **1** or **2**.

As shown in Table 1, effect of halides (**3a**–**f**) on the yield of the products (**4a**–**f** and **5a**–**f**) in the joining reaction using water may indicate that secondary alkyl iodides were superior to primary or aryl iodides and activated bromides.

**Table 1**
Zn-promoted alkylation of 2- (or 4-) vinyl pyridines (**1** or **2**) and alkyl halides (**3**) in the presence of water




| Alkyl halides (**3**) | Isolated yield (%) | |
|---|---|---|
| | **4a**–**f**: 2-alkyl | **5a**–**f**: 4-alkyl |
| $(CH_3)_2CH$–I (**3a**) | **64** (**4a**) | **60** (**5a**) |
| $CH_3CH_2$–I (**3b**) | **25** (**4b**) | **5** (**5b**) |
| $CH_3(CH_2)_3$–I (**3c**) | **40** (**4c**) | **25** (**5c**) |
| $CH_3CH_2CH(CH_3)$–I (**3d**) | **47** (**4d**) | **31** (**5d**) |
| $C_6H_5CH_2$–Br (**3e**) | **23** (**4e**) | **13** (**5e**) |
| $H_5C_2OOCCH_2$–Br (**3f**) | **42** (**4f**) | **18** (**5f**) |

Reaction conditions: substrate **1** or **2** (10 mmol), alkyl halide (40 mmol), water (500 mmol), acetonitrile (50 ml), Zn (99.9% pure, 40 mmol), reflux for 0.5–1.0 h, $N_2$ atmosphere.

Furthermore, addition of isopropyl iodide (**3a**) into acetonitrile solution of 2-(or 4-)vinylpyridine (**1** or **2**) and a variety of carbonyl compounds (**6a**–**g**) under gentle reflux led to selective formation of the corresponding one-pot joining products of regioselective three components (**7a**; **a**–**g** or **8a**; **a**–**g**),[13] as shown in Table 2.

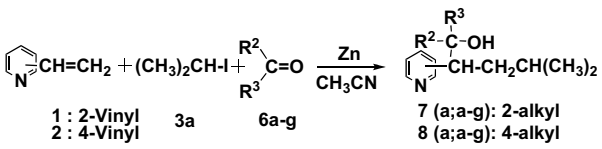
All of the products were characterized by comparison of their gas or liquid chromatographic behaviors with those of the authentic samples,[7] or their spectroscopic ($^1$H NMR, $^{13}$C NMR, MASS, and IR) and elemental analyses for new compounds.

It may be surprising that 2-(2- or 4-pyridyl)ethyl alkyl ketones (**10a**,**b**,**g**–**i**; **a**–**d** or **11a**,**g**–**i**; **a**–**d**) were formed as the predominant products from the similar one-pot joining reaction of three components by addition of alkyl iodides (**3a**,**b**,**g**–**i**) into the solution of 2-(or 4-)-vinylpyridine (**1** or **2**), and nitriles (**9a**–**d**) in toluene containing Zn-powder (99.9%)[14] under the similar reaction conditions, as shown in Table 3.

It was found that use of benzene or THF as the solvent of the reaction gave the same products even in lower yields whereas that of *n*-hexane, cyclohexane, DMF and NMP did not give the desired products at all.

It may be a common tendency that use of 2-vinylpyridine (**1**) as a starting compound in both of the coupling reactions of carbonyl compounds (**6a**–**g**) and nitriles (**9a**–**d**) resulted in formation of the

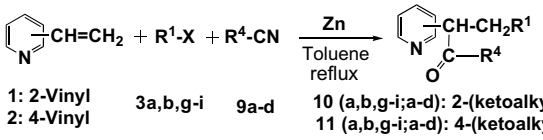
**Table 2**
Zn-promoted joining reaction of three components 2- (or 4-)vinylpyridine, isopropyl iodide and carbonyl compounds




| $R^2$ | $R^3$ | Yield (%) | |
|---|---|---|---|
| | | **7**(**a**; **a**–**g**): 2-alkyl | **8**(**a**; **a**–**g**): 4-alkyl |
| $CH_3$ | $CH_3$ | **60** (**7a**; **a**) | **48** (**8a**; **a**) |
| $CH_3CH_2$ | $CH_3CH_2$ | **63** (**7a**; **b**) | **51** (**8a**; **b**) |
| $(CH_3)_2CH$ | $(CH_3)_2CH$ | **72** (**7a**; **c**) | Trace |
| $-(CH_2)_5-$ | | **33** (**7a**; **d**) | **46** (**8a**; **d**) |
| $(CH_3)_2CH$ | H | **67** (**7a**; **e**) | **65** (**8a**; **e**) |
| $C_2H_5(CH_3)CH$ | H | **57** (**7a**; **f**) | **55** (**8a**; **f**) |
| $(C_2H_5)_2CH$ | H | **66** (**7a**; **g**) | **65** (**8a**; **g**) |

Reaction conditions: substrate **1** or **2** (10 mmol), isopropyl iodide **3** (40 mmol), carbonyl compound **4** (500 mmol), Zn (99.9% pure, 40 mmol), acetonitrile (100 ml), reflux for 0.5–1.0 h, $N_2$ atmosphere.

**Table 3**
Zn-promoted joining reaction of three components: 2-(or 4-) vinylpyridines (**1** or **2**), isopropyl iodide (**3a**,**b**, **g**–**i**) and nitriles (**9a**–**d**)



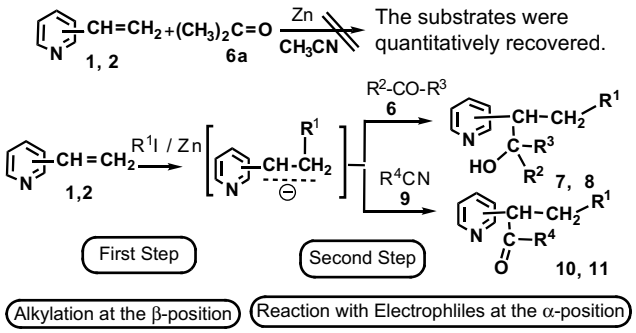

| $R^1$ of 3 | $R^4$ of 9 | Yield (%) | |
|---|---|---|---|
| | | **10**: 2-(ketoalkyl) | **11**: 4-(ketoalkyl) |
| $(CH_3)_2CH$ (**3a**) | $CH_3$ (**9a**) | **82** (**10a**; **a**) | **52** (**11a**; **a**) |
| $(CH_3)_2CH$ (**3a**) | $CH_2CH_3$ (**9b**) | **95** (**10a**; **b**) | **50** (**11a**; **b**) |
| $(CH_3)_2CH$ (**3a**) | $CH_3CH_2CH_2$ (**9c**) | **88** (**10a**; **c**) | **44** (**11a**; **c**) |
| $(CH_3)_2CH$ (**3a**) | $C_6H_5$ (**9d**) | **77** (**10a**; **d**) | **64** (**11a**; **d**) |
| $CH_3CH_2$ (**3b**) | $CH_3$ (**9a**) | **28** (**10b**; **a**) | 0 |
| Cyclo-$C_6H_{11}$ (**3g**) | $CH_3$ (**9a**) | **84** (**10g**; **a**) | **48** (**11g**; **a**) |
| $(CH_3)_3C$ (**3h**) | $CH_3$ (**9a**) | **90** (**10h**; **a**) | **70** (**11h**; **a**) |
| $CH_3CH_2CH_2$ (**3i**) | $CH_3$ (**9a**) | **24** (**10i**; **a**) | **15** (**11i**; **a**) |

Reaction conditions: substrate **1** or **2** (10 mmol), alkyl iodide **3** (40 mmol), alkyl nitrile **9** (500 mmol), Zn (99.9% pure, 40 mmol), toluene (100 ml), reflux for 0.5–1.0 h, $N_2$ atmosphere.

corresponding joining products of three components (**7a**; **a**–**g**) and (**10a**,**b**,**g**–**i**; **a**–**d**) in better yields than that of the products (**8a**; **a**–**g**) and (**11a**,**g**–**i**; **a**–**d**) formed from 4-vinylpyridine (**2**).

The present regioselective joining reaction of three components includes dual carbon–carbon bond formations in a one-pot operation, and their sequence is found to be distinctly selective by the following experimental fact. While the first addition of alkyl iodides (**3**) into the solution of acetonitrile containing Zn, 2- (or 4-)vinylpyridine (**1** or **2**), and carbonyl compounds (**6**) gave the corresponding joining products (**7** or **8**), any reaction did not take place without addition of alkyl iodides (**3**) under the similar conditions to result in quantitative recovery of **1** or **2**. This result clearly indicates that the addition of **3** initiates alkylation at the β-position of **1** or **2** at the first step, followed by electrophilic attack of **6** at the α-position of **1** or **2** at the second step, as shown in Scheme 2.

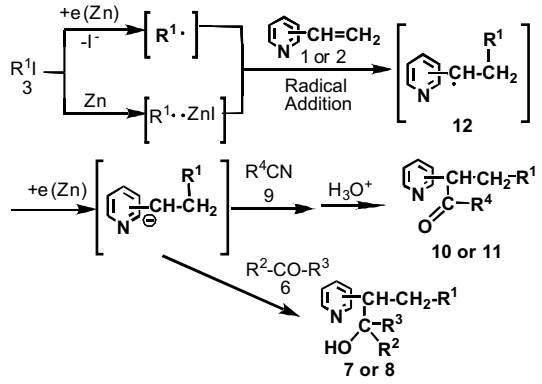
Some of control experiments provided us important information for proposal of reaction mechanism of the present one-pot regio- and sequence-selective joining reaction of three components. For example, use of EtZnI or $Et_2Zn$ reagent instead of combination of Zn (99.9%) and EtI led to no formation of the corresponding three-components joining products. Similarly, electroreduction of a mixture of 2- (or 4-) vinylpyridine (**1** or **2**), isopropyl




**Scheme 2.** Selectivity of reaction sequence in the Znpromoted one-pot regio- and sequenceselective joining reaction of three-components.

iodide (**3a**) and acetone (**6a**) in an acetonitrile solution containing $Et_4NOTs$ as a supporting electrolyte gave the corresponding dimer (1,4-di (2- or 4-)pyridinylbutane) as the almost sole product in 60–65% yields and no corresponding joining products of the three components.

From these experimental results and the reported fundamental reactivity as an alkyl radical generated from the combination of Zn metal and alkyl iodide, the following reaction scheme may be proposed as the most plausible reaction mechanism, as shown in Scheme 3.




**Scheme 3.** Proposed reaction mechanism.

Interaction of alkyl iodides (**3**) with Zn metal with 99.9% purity may generate radical pairs between zinc and alkyl radicals (or alkyl radical generated by one electron reduction by Zn metal, followed by elimination of $I^-$ anion), which may make radical attack to the β-positions of 2- (or 4-)vinylpyridine (**1** or **2**) to give the α-radical intermediates (**12**). Successive fast one-electron reduction from Zn metal may promptly form the corresponding carbanion species, which may react with electrophiles such as carbonyl compounds (**6**) and nitriles (**9**) to give the corresponding (2-hydroxyethyl)pyridines (**7** or **8**) and 2-(2- or 4-pyridyl)ethyl alkyl ketones (**10** or **11**), respectively, in moderate to good yields.

Because of high selectivity in regiochemistry and reaction-sequence, unique reaction pattern of joining condensation of three-components, simple one-pot procedure and satisfactory yield, the present three-components joining may be quite important, interesting and useful method in synthetic organic chemistry.

## 3. Experimental section

### 3.1. General procedure for Zn-promoted one-pot joining reaction of three components

Into a refluxing solution of 2-(or 4-) vinylpyridine (**1** or **2**) 1.05 g (10 mmol), an aliphatic ketone (or aldehyde) (**6a**–**g**) (40 mmol), and zinc powder (99.9% purity, 40 mmol)[14] in 100 ml of freshly distilled acetonitrile, was added several drops of an alkyl iodide **3** (40 mmol) under a nitrogen atmosphere. After a short period, an exothermic reaction took place. After the vigorous reflux subsided, the remaining alkyl iodide **3** added dropwise over 10 min to the stirred mixture, making refluxing violently by each addition of **3**. After the addition was completed, the reaction mixture was refluxed for 30 min with stirring. After the reaction, the mixture was poured into 200 ml of a saturated water of $NaHCO_3$. Then the mixture was filtered and extracted with three 100 ml portions of ethyl acetate. The combined ethereal solution was washed with saturated water of NaCl, and dried over anhydrous $MgSO_4$. After filtration of the drying agent and evaporation of the solvent under reduced pressure, preparative column chromatography of the crude product gave the corresponding joining product of three components (**7a**; **a**–**g** or **8a**; **a**–**g**) in a good to moderate yield, as shown in Table 2, in which isopropyl iodide was only used as an alkyl iodide.

Table 1 shows the results on formation of α-alkylation products (**4a**–**f** or **5a**–**f**), which were obtained when water was used in replace of an aliphatic ketone (or aldehyde) (**6a**–**g**). Replacement of an aliphatic ketone (or aldehyde) (**6a**–**g**) by an aliphatic or an aromatic nitriles (**9a**–**d**) as the reagent and that of acetonitrile by toluene as the solvent in this procedure, led to formation of new joining reaction of three components, that is vinylpyridine (**1** or **2**), an alkyl iodide (**3a**,**b**,**g**–**i**) and a nitriles (**9a**–**d**) in good to moderate yields, as shown in Table 3.

### 3.2. Analytical data for new compounds among the products

*3.2.1. 2,5-Dimethyl-3-(2-pyridyl)hexa-2-ol [**7a**; **a**]*

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 0.80 (d, $J$=6.6 Hz, 3H), 0.88 (d, $J$=6.6 Hz, 3H), 0.96 (s, 3H), 1.06–1.08 (m, 1H), 1.29 (s, 3H), 1.56–1.62 (m, 1H), 1.93–2.00 (m, 1H), 2.66 (dd, $J$=3.2, 11.5 Hz, 1H), 5.20 (s, 1H), 7.11–7.17 (m, 2H), 7.59–7.63 (m, 1H) and 8.53–8.54 (m, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 21.32, 24.13, 25.62, 27.63, 30.39, 39.03, 53.35, 72.35, 121.39, 124.70, 136.27, 148.90, and 164.08 ppm. IR (neat): 3393, 2869, 1594, 1470, and 1146 cm$^{-1}$. EIMS: $m/z$ 207 ($M^+$). Anal. Calcd for $C_{13}H_{21}NO$: C, 75.32; H, 10.21; N, 6.76. Found: C, 75.49; H, 10.07; N, 6.48.

*3.2.2. 2,5-Dimethyl-3-(4-pyridyl)hexa-2-ol [**8a**; **a**]*

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 0.80 (d, $J$=6.6 Hz, 3H), 0.84 (d, $J$=6.6 Hz, 3H), 1.14 (s, 3H), 1.17–1.18 (m, 1H), 1.21 (s, 3H), 1.50–1.57 (m, 1H), 1.80–1.87 (m, 1H), 2.65 (dd, $J$=3.2, 12.1 Hz, 1H), 7.18 (d, $J$=6.1 Hz, 2H) and 8.51 (d, $J$=5.9 Hz, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 20.86, 24.18, 25.57, 28.19, 28.27, 38.09, 54.25, 72.37, 125.04, 149.40 and 152.46 ppm. IR (neat): 3331, 2951, 1601, 1420, and 1131 cm$^{-1}$. EIMS: $m/z$ 208 ($M^+$). Anal. Calcd for $C_{13}H_{21}NO$: C, 75.32; H, 10.21; N, 6.76. Found: C, 75.54; H, 10.17; N, 6.33.

*3.2.3. 3-Ethyl-6-methyl-4-(2-pyridyl)hepta-3-ol [**7a**; **b**]*

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 0.74 (d, $J$=7.3 Hz, 3H), 0.77–0.85 (m, 6H), 0.88 (d, $J$=7.3 Hz, 3H), 1.03–1.16 (m, 2H), 1.47–1.54 (m, 1H), 1.57–1.74 (m, 3H), 1.92–1.99 (m, 1H), 2.66 (dd, $J$=3.2, 11.7 Hz, 1H), 5.34 (s, 1H), 7.11–7.16 (m, 2H), 7.58–7.62 (m, 1H) and 8.52–8.53 (m, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 7.86, 7.90, 21.29, 24.24, 25.41, 26.86, 30.33, 38.37, 48.96, 76.45, 121.28, 124.97, 136.20, 148.92 and 164.14 ppm. IR (neat): 3380, 2961, 1594, 1470, and 1438 cm$^{-1}$. EIMS: $m/z$ 236 ($M^+$). Anal. Calcd for $C_{15}H_{25}NO$: C, 76.55; H, 10.71; N, 5.95. Found: C, 76.59; H, 10.63; N, 5.82.

*3.2.4. 3-Ethyl-6-methyl-4-(4-pyridyl)hepta-3-ol [**8a**; **b**]*

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 0.79–0.90 (m, 12H), 1.08–1.13 (m, 1H), 1.15–1.23 (m, 1H), 1.24–1.34 (m, 1H), 1.39–1.46 (m, 1H), 1.59–1.65 (m, 2H), 1.82–1.89 (m, 1H), 2.70–2.74 (m, 1H), 7.21 (d,

$J$=5.9 Hz, 2H) and 8.47 (d, $J$=5.9 Hz, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 7.47, 7.95, 20.76, 24.24, 25.31, 28.05, 39.32, 37.66, 49.34, 76.02, 125.37, 149.21 and 151.37 ppm. IR (neat): 3291, 2958, 1602, 1463, and 1418 cm$^{-1}$. EIMS: $m/z$ 236 ($M^+$). Anal. Calcd for $C_{15}H_{25}NO$: C, 76.55; H, 10.71; N, 5.95. Found: C, 76.67; H, 10.54; N, 5.89.

*3.2.5. 2,6-Dimethyl-3-isopropyl-4-(2-pyridyl)hepta-3-ol [**7a**; **c**]*

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 0.51 (d, $J$=7.3 Hz, 3H), 0.77–0.95 (m, 10H), 1.07 (d, $J$=7.3 Hz, 3H), 1.09 (d, $J$=6.8 Hz, 3H), 1.51–1.58 (m, 1H), 1.61–1.68 (m, 2H), 1.97–2.04 (m, 1H), 2.23–2.30 (m, 1H), 3.23 (dd, $J$=3.2, 12.0 Hz, 1H), 5.92 (s, 1H), 7.13–7.18 (m, 2H), 7.57–7.62 (m, 1H) and 8.50–8.51 (m, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 18.58, 18.65, 19.00, 19.20, 21.09, 24.42, 25.21, 33.92, 35.23, 39.21, 46.11, 79.04, 121.24, 125.16, 136.12, 148.56 and 164.65 ppm. IR (neat): 3304, 2957, 1595, 1467, and 1439 cm$^{-1}$. EIMS: $m/z$ 264 ($M^+$). Anal. Calcd for $C_{17}H_{29}NO$: C, 77.51; H, 11.10; N, 5.32. Found: C, 77.78; H, 10.99; N, 4.93.

*3.2.6. 1-(3-Methyl-1-(2-pyridyl)butyl)cyclohexanol [**7a**; **d**]*

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 0.73 (d, $J$=6.6 Hz, 3H), 0.81 (d, $J$=6.6 Hz, 3H), 0.96–1.91 (m, 13H), 2.96 (dd, $J$=3.2, 11.5 Hz, 1H), 5.15 (s, 1H), 7.01–7.09 (m, 2H), 7.50–7.54 (m, 1H) and 8.46–8.47 (m, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 21.36, 21.37, 22.18, 22.30, 24.17, 25.51, 25.92, 35.56, 38.13, 38.41, 73.03, 121.27, 124.89, 136.19, 148.97 and 164.03 ppm. IR (neat): 3384, 2933, 1593, 1471 and 1437 cm$^{-1}$. EIMS: $m/z$ 248 ($M^+$). Anal. Calcd for $C_{16}H_{25}NO$: C, 77.68; H, 10.19; N, 5.66. Found: C, 77.62; H, 10.14; N, 5.61.

*3.2.7. 1-(3-Methyl-1-(4-pyridyl)butyl)cyclohexanol [**8a**; **d**]*

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 0.79 (d, $J$=6.6 Hz, 3H), 0.83 (d, $J$=6.6 Hz, 3H), 1.12–1.86 (m, 13H), 2.60–2.64 (m, 1H), 7.18 (d, $J$=6.1 Hz, 2H) and 8.49 (d, $J$=6.1 Hz, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 20.85, 21.78, 21.79, 21.88, 24.20, 25.43, 25.58, 35.72, 36.15, 37.29, 72.72, 125.23, 149.28 and 152.49 ppm. IR (neat): 3319, 2929, 1597, 1417, and 978 cm$^{-1}$. EIMS: $m/z$ 248 ($M^+$). Anal. Calcd for $C_{16}H_{25}NO$: C, 77.68; H, 10.19; N, 5.66. Found: C, 77.19; H, 10.01; N, 5.72.

*3.2.8. 2,6-Dimethyl-4-(2-pyridyl)hepta-3-ol [**7a**; **e**]*

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 0.81 (d, $J$=6.3 Hz, 3H), 0.91 (d, $J$=6.3 Hz, 3H), 0.91–1.05 (m, 6H), 1.13–1.15 (m, 1H), 1.41–1.48 (m, 1H), 1.76–1.84 (m, 1H), 1.89–1.96 (m, 1H), 2.94–2.98 (m, 1H), 3.41–3.43 (m, 1H), 5.23 (s, 1H), 7.10–7.17 (m, 2H), 7.59–7.63 (m, 1H) and 8.51–8.52 (m, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 18.99, 19.48, 21.37, 24.16, 25.22, 30.63, 36.82, 45.47, 79.96, 121.52, 123.62, 136.53, 148.91 and 164.74 ppm. IR (neat): 3233, 2952, 1595, 1484, and 997 cm$^{-1}$. EIMS: $m/z$ 222 ($M^+$). Anal. Calcd for $C_{14}H_{23}NO$: C, 75.97; H, 10.47; N, 6.33. Found: C, 76.16; H, 10.39; N, 5.98.

*3.2.9. 2,6-Dimethyl-4-(4-pyridyl)hepta-3-ol [**8a**; **e**]*

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 0.83 (d, $J$=6.6 Hz, 3H), 0.88 (d, $J$=6.6 Hz, 3H), 0.92 (d, $J$=6.8 Hz, 3H), 0.97 (d, $J$=6.8 Hz, 3H), 1.16–1.29 (m, 1H), 1.41–1.75 (m, 2H), 2.76–2.85 (m, 1H), 3.39–3.45 (m, 1H), 7.12–7.22 (m, 2H) and 8.49–8.50 (m, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 16.00, 16.67, 20.04, 24.17, 25.16, 30.63, 39.07, 46.22, 79.63, 123.87, 149.78 and 152.73 ppm. IR (neat): 3222, 2957, 1604, 1465, and 1054 cm$^{-1}$. EIMS: $m/z$ 222 ($M^+$). Anal. Calcd for $C_{14}H_{23}NO$: C, 75.97; H, 10.47; N, 6.33. Found: C, 76.00; H, 10.31; N, 6.31.

*3.2.10. 3,7-Dimethyl-5-(2-pyridyl)octa-4-ol [**7a**; **f**]*

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 0.80 (d, $J$=6.6 Hz, 3H), 0.87–0.91 (m, 6H), 0.98 (d, $J$=6.6 Hz, 3H), 1.13–1.20 (m, 2H), 1.47–1.53 (m, 3H), 1.87–1.94 (m, 1H), 2.98 (dt, $J$=3.4, 11.5 Hz, 1H), 3.59 (dd, $J$=3.4, 7.1 Hz, 1H), 4.59 (s, 1H), 7.10–7.16 (m, 2H), 7.58–7.63 (m, 1H) and 8.52–8.53 (m, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 11.01, 14.64, 21.41, 24.13, 25.34, 25.61, 36.70, 37.76, 46.03, 78.00, 121.45, 123.56, 136.46, 149.02 and 164.50 ppm. IR (neat): 3235, 2955, 1596, 1438, and 992 cm$^{-1}$. EIMS: $m/z$ 236 ($M^+$). Anal. Calcd for $C_{15}H_{25}NO$: C, 76.55; H, 10.71; N, 5.95. Found: C, 76.73; H, 10.70; N, 5.61.

*3.2.11. 3,7-Dimethyl-5-(4-pyridyl)octa-4-ol [**8a**; **f**]*

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 0.83 (d, $J$=4.4 Hz, 3H), 0.84 (d, $J$=4.4 Hz, 3H), 0.89–0.94 (m, 6H), 1.19–1.66 (m, 6H), 2.79–2.84 (m, 1H), 3.58–3.61 (dd, $J$=4.1, 7.6 Hz, 1H), 7.18–7.23 (m, 2H) and 8.48–8.51 (m, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 11.65, 12.43, 21.13, 23.87, 25.13, 26.74, 36.76, 40.82, 46.82, 77.55, 124.40, 149.69 and 152.22 ppm. IR (neat): 3204, 2959, 1603, 1463 and 1419 cm$^{-1}$. EIMS: $m/z$ 236 ($M^+$). Anal. Calcd for $C_{15}H_{25}NO$: C, 76.55; H, 10.71; N, 5.95. Found: C, 76.91; H, 10.69; N, 5.60.

*3.2.12. 3-Ethyl-7-methyl-5-(2-pyridyl)octa-4-ol [**7a**; **g**]*

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 0.81 (d, $J$=6.6 Hz, 3H), 0.83–0.88 (m, 6H), 0.91 (d, $J$=6.6 Hz, 3H), 1.13–1.16 (m, 1H), 1.31–1.50 (m, 5H), 1.68–1.72 (m, 1H), 1.90–1.97 (m, 1H), 2.96 (ddd, $J$=2.7, 2.9, 11.7 Hz, 1H), 3.69–3.70 (m, 1H), 4.88 (s, 1H), 7.10–7.17 (m, 2H), 7.59–7.63 (m, 1H) and 8.52–8.53 (m, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 10.17, 10.42, 20.38, 20.72, 21.41, 24.17, 25.33, 37.18, 41.93, 45.57, 75.44, 121.48, 123.56, 136.49, 148.97 and 164.81 ppm. IR (neat): 3244, 2955, 1595, 1438, and 1001 cm$^{-1}$. EIMS: $m/z$ 250 ($M^+$). Anal. Calcd for $C_{16}H_{27}NO$: C, 77.06; H, 10.91; N, 5.62. Found: C, 77.09; H, 10.86; N, 5.54.

*3.2.13. 3-Ethyl-7-methyl-5-(4-pyridyl)octa-4-ol [**8a**; **g**]*

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 0.83–0.85 (m, 6H), 0.88–0.92 (m, 6H), 1.22–1.70 (m, 8H), 2.84–2.90 (m, 1H), 3.67–3.70 (m, 1H), 7.21 (d, $J$=5.9 Hz, 2H) and 8.48 (d, $J$=5.9 Hz, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 11.11, 11.39, 20.00, 21.29, 22.10, 23.75, 25.20, 41.36, 42.96, 46.37, 75.84, 124.60, 149.37 and 152.39 ppm. IR (neat): 3206, 2959, 1603, 1464 and 1316 cm$^{-1}$. EIMS: $m/z$ 250 ($M^+$). Anal. Calcd for $C_{16}H_{27}NO$: C, 77.06; H, 10.91; N, 5.62. Found: C, 77.22; H, 10.89; N, 5.44.

*3.2.14. 5-Methyl-3-(2-pyridyl)hexa-2-one [**10a**; **a**]*

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 0.88 (d, $J$=6.8 Hz, 3H), 0.91 (d, $J$=6.6 Hz, 3H), 1.37–1.44 (m, 1H), 1.75–1.82 (m, 1H), 1.92–1.99 (m, 1H), 2.12 (s, 3H), 4.01 (dd, $J$=7.3, 7.8 Hz, 1H), 7.17–7.23 (m, 2H), 7.63–7.67 (m, 1H) and 8.57–8.58 (m, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 22.20, 22.87, 25.78, 29.11, 39.91, 60.08, 122.04, 122.79, 136.76, 149.63, 159.02 and 207.90 ppm. IR (neat): 2956, 1714, 1589, 1470, and 1434 cm$^{-1}$. EIMS: $m/z$ 191 ($M^+$). Anal. Calcd for $C_{12}H_{17}NO$: C, 75.35; H, 8.96; N, 7.32. Found: C, 75.48; H, 8.74; N, 7.00.

*3.2.15. 5-Methyl-3-(4-pyridyl)hexa-2-one [**11a**; **a**]*

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 0.88 (d, $J$=6.3 Hz, 3H), 0.89 (d, $J$=6.6 Hz, 3H), 1.32–1.42 (m, 1H), 1.78 (ddd, $J$=6.3, 8.3, 13.9 Hz, 1H), 1.86–1.93 (m, 1H), 2.12 (s, 3H), 3.73 (dd, $J$=7.6, 7.6 Hz, 1H), 7.17 (d, $J$=6.1 Hz, 2H) and 8.56 (d, $J$=6.1 Hz, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 21.98, 22.87, 25.59, 29.26, 40.47, 56.92, 123.47, 147.85, 150.27 and 206.84 ppm. IR (neat): 2957, 1714, 1595, 1414, and 1355 cm$^{-1}$. EIMS: $m/z$ 192 ($M^+$). Anal. Calcd for $C_{12}H_{17}NO$: C, 75.35; H, 8.96; N, 7.32. Found: C, 75.71; H, 8.92; N, 7.00.

*3.2.16. 6-Methyl-4-(2-pyridyl)hepta-3-one [**10a**; **b**]*

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 0.89 (d, $J$=7.8 Hz, 3H), 0.90 (d, $J$=7.0 Hz, 3H), 0.98 (t, $J$=7.3 Hz, 3H), 1.36–1.43 (m, 1H), 1.72–1.79 (m, 1H), 1.93–2.00 (m, 1H), 2.47 (q, $J$=7.3 Hz, 2H), 4.05 (dd, $J$=7.3, 7.8 Hz, 1H), 7.15–7.25 (m, 2H), 7.62–7.66 (m, 1H) and 8.55–8.56 (m, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 7.75, 22.30, 22.85, 25.86, 35.33, 40.31, 59.17, 121.98, 122.61, 136.72, 149.51, 159.29 and 210.57 ppm. IR (neat): 2956, 1716, 1587, 1470, and 1434 cm$^{-1}$. EIMS:

*m*/*z* 205 ($M^+$). Anal. Calcd for $C_{13}H_{19}NO$: C, 76.06; H, 9.33; N, 6.82. Found: C, 76.23; H, 9.13; N, 6.70.

*3.2.17. 6-Methyl-4-(4-pyridyl)hepta-3-one [**11a**; **b**]*

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 0.88 (d, *J*=6.6 Hz, 6H), 0.99 (t, *J*=7.3 Hz, 3H), 1.32–1.39 (m, 1H), 1.60–1.67 (m, 1H), 1.86–1.93 (m, 1H), 2.43 (q, *J*=7.3 Hz, 2H), 3.75 (dd, *J*=7.3, 7.6 Hz, 1H), 7.17 (d, *J*=5.9 Hz, 2H) and 8.54 (d, *J*=5.9 Hz, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 7.74, 22.06, 22.84, 25.67, 35.56, 40.98, 55.93, 123.47, 148.16, 150.17 and 209.62 ppm. IR (neat): 2957, 1716, 1596, 1467, and 1415 cm$^{-1}$. EIMS: *m*/*z* 205 ($M^+$). Anal. Calcd for $C_{13}H_{19}NO$: C, 76.06; H, 9.33; N, 6.82. Found: C, 76.24; H, 9.35; N, 6.91.

*3.2.18. 7-Methyl-5-(2-pyridyl)octa-4-one [**10a**; **c**]*

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 0.80 (t, *J*=7.3 Hz, 3H), 0.88 (d, *J*=6.6 Hz, 3H), 0.90 (d, *J*=6.6 Hz, 3H), 1.36–1.42 (m, 1H), 1.49–1.56 (m, 2H), 1.74–1.79 (m, 1H), 1.92–1.99 (m, 1H), 2.41 (t, *J*=7.3 Hz, 2H), 4.03 (dd, *J*=7.6, 7.6 Hz, 1H), 7.15–7.24 (m, 2H), 7.62–7.66 (m, 1H) and 8.55–8.56 (m, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 13.55, 17.04, 22.30, 22.84, 25.85, 40.19, 44.00, 59.43, 121.96, 122.64, 136.67, 149.50, 159.18 and 209.92 ppm. IR (neat): 2958, 1715, 1588, 1469, and 1434 cm$^{-1}$. EIMS: *m*/*z* 220 ($M^+$). Anal. Calcd for $C_{14}H_{21}NO$: C, 76.67; H, 9.65; N, 6.39. Found: C, 76.70; H, 9.46; N, 6.35.

*3.2.19. 7-Methyl-5-(4-pyridyl)octa-4-one [**11a**; **c**]*

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 0.80 (t, *J*=7.3 Hz, 3H), 0.88 (d, *J*=6.6 Hz, 6H), 1.32–1.39 (m, 1H), 1.48–1.56 (m, 2H), 1.59–1.66 (m, 1H), 1.85–1.93 (m, 1H), 2.39–2.42 (m, 2H), 3.74 (dd, *J*=7.3, 7.6 Hz, 1H), 7.17 (d, *J*=5.9 Hz, 2H) and 8.55 (d, *J*=5.9 Hz, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 13.50, 16.98, 22.07, 22.84, 25.65, 40.88, 44.24, 56.17, 123.50, 148.04, 150.18 and 209.00 ppm. IR (neat): 2959, 1715, 1595, 1467, and 1414 cm$^{-1}$. EIMS: *m*/*z* 220 ($M^+$). Anal. Calcd for $C_{14}H_{21}NO$: C, 76.67; H, 9.65; N, 6.39. Found: C, 76.43; H, 9.61; N, 6.36.

*3.2.20. 4-Methyl-1-phenyl-2-(2-pyridyl)penta-1-one [**10a**; **d**]*

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 0.90 (d, *J*=6.6 Hz, 3H), 0.96 (d, *J*=6.6 Hz, 3H), 1.48–1.54 (m, 1H), 1.79–1.86 (m, 1H), 2.11–2.18 (m, 1H), 5.00 (dd, *J*=7.3, 7.3 Hz, 1H), 7.10–7.62 (m, 6H), 8.07–8.09 (m, 2H) and 8.53–8.54 (m, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 22.47, 22.71, 42.14, 53.80, 54.96, 121.68, 122.18, 128.39, 128.60, 128.81, 128.97, 132.87, 136.73, 138.86, 149.40, 159.83 and 199.41 ppm. IR (neat): 2956, 1716, 1587, 1470, and 1434 cm$^{-1}$. EIMS: *m*/*z* 254 ($M^+$). Anal. Calcd for $C_{17}H_{19}NO$: C, 80.60; H, 7.56; N, 5.53. Found: C, 80.81; H, 7.65; N, 5.34.

*3.2.21. 4-Methyl-1-phenyl-2-(4-pyridyl)penta-1-one [**11a**; **d**]*

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 0.90 (d, *J*=6.8 Hz, 3H), 0.95 (d, *J*=6.6 Hz, 3H), 1.44–1.54 (m, 1H), 1.69–1.76 (m, 1H), 2.06–2.13 (m, 1H), 4.68 (dd, *J*=7.3, 7.3 Hz, 1H), 7.25–7.56 (m, 6H), 7.94–7.96 (m, 2H) and 8.51–8.53 (m, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 22.27, 22.75, 25.97, 42.77, 51.05, 123.35, 123.63, 128.39, 128.56, 128.66, 128.82, 133.33, 136.46, 148.64, 150.13, 150.22 and 198.81 ppm. IR (neat): 2954, 1677, 1592, 1466, and 1416 cm$^{-1}$. EIMS: *m*/*z* 206 ($M^+$). Anal. Calcd for $C_{17}H_{19}NO$: C, 80.60; H, 7.56; N, 5.53. Found: C, 80.92; H, 7.73; N, 5.01.

*3.2.22. 3-(2-Pyridyl)hexa-2-one [**10b**; **a**]*

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 0.91 (t, *J*=7.3 Hz, 3H), 1.18–1.30 (m, 2H), 1.79–1.88 (m, 1H), 2.02–2.14 (m, 1H), 2.12 (s, 3H), 3.90 (dd, *J*=7.3, 7.6 Hz, 1H), 7.17–7.23 (m, 2H), 7.63–7.68 (m, 1H) and 8.57–8.58 (m, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 13.92, 20.61, 29.18, 33.11, 62.39, 122.06, 122.75, 136.76, 149.70, 158.90 and 207.90 ppm. IR (neat): 2959, 1715, 1589, 1470, and 1434 cm$^{-1}$. EIMS: *m*/*z* 177 ($M^+$). Anal. Calcd for $C_{11}H_{15}NO$: C, 74.54; H, 8.53; N, 7.90. Found: C, 74.37; H, 8.11; N, 7.74.

*3.2.23. 4-Cyclohexyl-3-(2-pyridyl)buta-2-one [**10g**; **a**]*

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 0.92–1.66 (m, 10H), 1.72–1.79 (m, 2H), 1.95–2.09 (m, 1H), 2.11 (s, 3H), 4.03 (dd, *J*=7.3, 7.6 Hz, 1H), 7.16–7.22 (m, 2H), 7.63–7.67 (m, 1H) and 8.56–8.57 (m, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 26.09, 26.14, 26.44, 29.10, 32.97, 33.52, 35.24, 38.50, 59.35, 122.02, 122.76, 136.75, 149.62, 159.01 and 208.03 ppm. IR (neat): 2920, 1714, 1588, 1471, and 1434 cm$^{-1}$. EIMS: *m*/*z* 232 ($M^+$). Anal. Calcd for $C_{15}H_{21}NO$: C, 77.88; H, 9.15; N, 6.05. Found: C, 77.88; H, 9.05; N, 5.89.

*3.2.24. 4-Cyclohexyl-3-(4-pyridyl)buta-2-one [**11g**; **a**]*

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 0.84–1.73 (m, 12H), 1.89–1.96 (m, 1H), 2.09 (s, 3H), 3.77 (dd, *J*=7.6, 7.6 Hz, 1H), 7.16 (d, *J*=5.9 Hz, 2H) and 8.56 (d, *J*=5.9 Hz, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 25.98, 26.04, 26.29, 29.28, 32.79, 33.52, 35.04, 39.08, 56.51, 123.35, 123.57, 147.99, 150.21, 150.25 and 206.88 ppm. IR (neat): 2924, 1715, 1595, 1448, and 1415 cm$^{-1}$. EIMS: *m*/*z* 232 ($M^+$). Anal. Calcd for $C_{15}H_{21}NO$: C, 77.88; H, 9.15; N, 6.05. Found: C, 77.92; H, 9.08; N, 5.85.

*3.2.25. 5,5-Dimethyl-3-(2-pyridyl)hexa-2-one [**10h**; **a**]*

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 0.85 (s, 9H), 1.74 (m, 1H), 2.15 (s, 3H), 2.25–2.30 (m, 1H), 4.04–4.07 (m, 1H), 7.15–7.29 (m, 2H), 7.61–7.66 (m, 1H) and 8.54–8.56 (m, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 29.15, 29.50, 29.57, 29.63, 30.89, 44.11, 59.40, 121.82, 122.72, 136.77, 149.34, 160.05 and 207.71 ppm. IR (neat): 2954, 1718, 1589, 1471, and 1365 cm$^{-1}$. EIMS: *m*/*z* 206 ($M^+$). Anal. Calcd for $C_{13}H_{19}NO$: C, 76.06; H, 9.33; N, 6.82. Found: C, 76.14; H, 9.07; N, 6.82.

*3.2.26. 5,5-Dimethyl-3-(4-pyridyl)hexa-2-one [**11h**; **a**]*

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 0.86 (s, 9H), 1.49 (dd, *J*=4.9, 14.1 Hz, 1H), 2.13 (s, 3H), 2.33 (dd, *J*=7.3, 14.1 Hz, 1H), 3.75 (dd, *J*=4.9, 7.3 Hz, 1H), 7.17 (d, *J*=4.4 Hz, 2H) and 8.54 (d, *J*=4.4 Hz, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 29.19, 29.49, 30.91, 45.07, 55.47, 123.33, 149.33, 150.10 and 206.44 ppm. IR (neat): 2956, 1720, 1595, 1475, and 1415 cm$^{-1}$. EIMS: *m*/*z* 206 ($M^+$). Anal. Calcd for $C_{13}H_{19}NO$: C, 76.06; H, 9.33; N, 6.82. Found: C, 76.13; H, 9.30; N, 6.72.

*3.2.27. 3-(2-Pyridyl)hepta-2-one [**10i**; **a**]*

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 0.86 (t, *J*=7.3 Hz, 3H), 1.10–1.35 (m, 4H), 1.80–1.89 (m, 1H), 2.04–2.17 (m, 1H), 2.11 (s, 3H), 3.87 (dd, *J*=7.6, 7.6 Hz, 1H), 7.17–7.23 (m, 2H), 7.63–7.68 (m, 1H) and 8.57–8.58 (m, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 13.86, 22.59, 29.17, 29.61, 30.76, 62.10, 122.06, 122.74, 136.77, 149.64, 158.94 and 207.93 ppm. IR (neat): 2956, 1715, 1589, 1470, and 1434 cm$^{-1}$. EIMS: *m*/*z* 191 ($M^+$). Anal. Calcd for $C_{12}H_{17}NO$: C, 75.35; H, 8.96; N, 7.32. Found: C, 75.23; H, 8.68; N, 7.24.

*3.2.28. 3-(4-Pyridyl)hepta-2-one [**11i**; **a**]*

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 0.86 (t, *J*=7.3 Hz, 3H), 1.11–1.22 (m, 2H), 1.24–1.34 (m, 2H), 1.65–1.74 (m, 1H), 2.00–2.07 (m, 1H), 2.09 (s, 3H), 3.61 (dd, *J*=7.3, 7.6 Hz, 1H), 7.16 (dd, *J*=1.7, 4.4 Hz, 2H) and 8.56 (dd, *J*=1.7, 4.4 Hz, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 13.79, 22.48, 29.38, 29.50, 31.37, 59.25, 123.37, 123.52, 147.83, 150.25 and 206.91 ppm. IR (neat): 2957, 1715, 1596, 1414, and 1357 cm$^{-1}$. EIMS: *m*/*z* 192 ($M^+$). Anal. Calcd for $C_{12}H_{17}NO$: C, 75.35; H, 8.96; N, 7.32. Found: C, 75.68; H, 8.95; N, 7.13.

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13. For expression of the products **7**(**a**;**a**–**g**), **8**(**a**;**a**,**b**,**d**–**g**), **10**(**a**,**b**,**g**–**i**;**a**–**d**), and **11**(**a**, **g**–**i**; **a**–**d**) in Tables 2 and 3, the first alphabets correspond to those of alkyl halides **3a**,**b**,**g**–**i**, while the second ones are derived from those of carbonyl compounds **6a**–**g** and nitriles **9a**–**d**, respectively.
14. Zn powder with 99.9% purity was purchased from KOJUNDO CHEMICAL LABORATRY Co., Ltd.