A Mild Isomerization Reaction for β,γ-Unsaturated Ketone to α,β-Unsaturated Ketone

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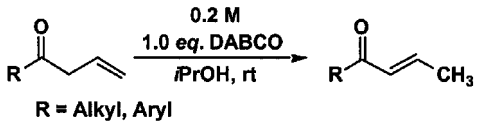
A series of β,γ-unsaturated ketones were isomerized to their corresponding α,β-unsaturated ketones by the introduction of DABCO in *i*PrOH at room temperature. The *endo*-cyclic double bond (β,γ-position) on ketone was rearranged to *exo*-cyclic double bond (α,β-position) under the reaction conditions.

Keywords: Isomerization; β,γ-unsaturated ketone; α,β-unsaturated ketone; DBU.

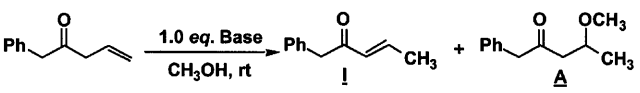
Rearrangement of carbon-carbon double bond is an important and useful method in organic synthesis.[1-4] α,β-Unsaturated carbonyl compounds play an important role and are ideal precursors for 1,4-addition reactions[5-7] and Diels-Alder reactions.[8-11] Isomerization reaction for β,γ-unsaturated ketone to α,β-unsaturated ketone is a prerequisite for the preparation of these synthetic intermediates in synthetic chemistry. The rearrangement reaction of β,γ-unsaturated ketone to α,β-unsaturated ketone is typically performed with acidic reagents such as HCl,[12] H_2SO_4[13] and *p*-TsOH[14] or with basic reagents such as Et_3N,[15] DBU,[16] NaOH[17] and *t*BuOK.[18] The yield of expected isomerized product usually is low and accompanied by side products when the α-protons exist on the β,γ-unsaturated ketone. Herewith, we wish to report a mild and an efficient double bond isomerization reaction for β,γ-unsaturated ketone by using DABCO (1,4-Diazabicyclo-[2.2.2]octane) as base, and the β,γ-double bond is rearranged to α,β-position at room temperature.

Scheme I



Our previous studies showed that β,γ-unsaturated ketones were synthesized by a Lewis acid promoted Barbier-type reaction.[19] It should be noted that the isomerized α,β-unsaturated ketone was not detected and obtained after acidic quenching. We think that a simple method for the synthesis of α,β-unsaturated ketones may be achieved by the isomerizations of β,γ-unsaturated ketones. Thus, we firstly investigated the double bond rearrangement reaction of 5-phenyl-pent-1-en-4-one under acidic reaction conditions. The very low yield of expected α,β-unsaturated ketone and some unidentified compounds as major products were obtained under these acidic reaction conditions. Therefore, we then investigated the isomerization reaction under basic reaction conditions and using methanol as solvent and as proton source (Scheme II). The β-methoxy ketone **A** was produced as the major product when amines such as Et_2NH, iPr_2NH and DBU (1,5-diazabicyclo[5.4.0]undec-5-ene) were introduced. The experimental results showed that DABCO was the best choice for the rearrangement reaction, and 80% yield of α,β-unsaturated ketone **I** was produced and without the formation of **A**. It should be noted that one equivalent of DABCO is necessary for the rearrangement reaction. The choice of solvent exhibits a tremendous impact for this rearrangement reaction; the yield of isomerized ketone increased to 89%, and fewer unidentified side products were observed when *i*PrOH was used instead of MeOH.

Scheme II



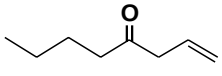
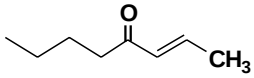
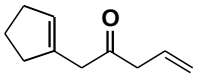
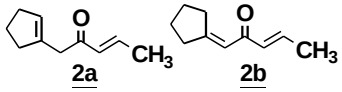
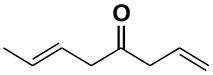
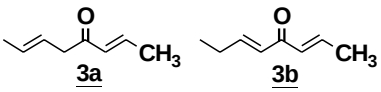
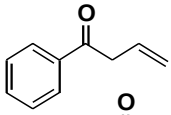
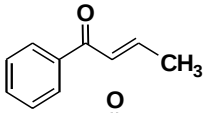
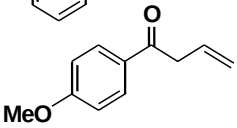
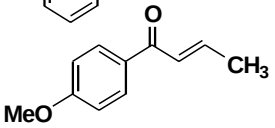
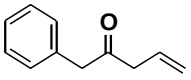
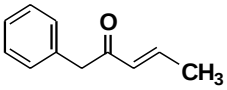
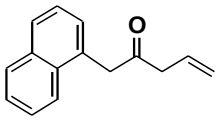
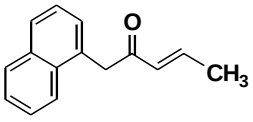
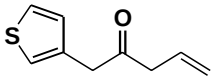
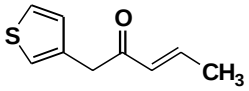
* $nBuNH_2$, rt, 42h	4% **I** + 16% **A** + Unknown
* Et_2NH, rt, 17h	20% **I** + 57% **A**
* iPr_2NH, rt, 44h	10% **I** + 41% **A**
* Et_3N, rt, 44h	51% **I** + 36% **A**
* DBU, rt, 2h	4% **I** + 60% **A** + Unknown
* DABCO, rt, 2h	80% **I**
* DABCO, *i*PrOH, rt, 2h	89% **I**

A series of β,γ-unsaturated ketones was investigated and transformed to α,β-unsaturated ketones under the reaction conditions, and the results are shown in Table 1. All the β,γ-unsaturated ketones were converted to α,β-unsaturated ketones with moderate to high yields under the reaction conditions. The β,γ-unsaturated ketones which exist α-protons on substituents also undergo isomerization reactions and convert to their corresponding α,β-unsaturated ketones with high yields (Table 1, Entries 1-3, 6-8).

The isomerization reaction for *endo*-cyclic double bond on β,γ-unsaturated ketone (Table 1, Entry 2) was further investigated under the optimum reaction conditions. The **2a**/**2b** ratio remained even when the reaction was proceeded at room temperature for a prolonged reaction time (72 hours) or under a higher temperature (refluxing reaction condition for 2 hours). The rearrangement reaction for oct-1,6-dien-4-one (Table 1, Entry 3) was also investigated and a higher yield (78%) and more isomerization completion (**3a**/**3b** = **1/5**) was achieved under refluxing reaction conditions.

The reaction mechanism for this mild isomerization is not clear. We think that DABCO (base) and alcohol (acid) as solvent and proton source may provide an acid-base complex to generate the isomerization process. Therefore, we believe that these mild isomerization reaction conditions can be further applied to some compounds which contain sensitive functionality such as a hydroxy group. The existing hydroxy group behaves as a proton source and then the isomerization reaction may proceed in aprotic solvent instead of protic sol-

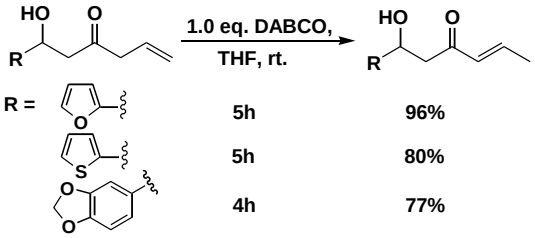
Table 1. Isomerizations for β,γ-Unsaturated Ketones to α,β-Unsaturated Ketones

Entry	Substrate	Product	Time (h)	Yield[a]
1			2	89%
2		 **2a** **2b**	4 1	76% (1/2)[b] 79% (1/2)[c]
3		 **3a** **3b**	2 1	47% (2/1)[d] 78% (1/5)[e]
4			1	74%
5			2	88%
6			2	89%
7			2	92%
8			2	86%

[a] The yields were determined after chromatographic purification.
[b] The **2a**/**2b** ratio was obtained under the optimum reaction conditions.
[c] The **2a**/**2b** ratio was obtained under refluxing reaction conditions.
[d] The **3a**/**3b** ratio was obtained under the optimum reaction conditions.
[e] The **3a**/**3b** ratio was obtained under refluxing reaction conditions.

vent. Thus, we synthesized β-hydroxy allyl ketone and investigated the isomerization reaction for its β,γ-position double bond under aprotic solvent (Scheme III). These compounds were transformed to their corresponding α,β-unsaturated ketones in good yields in THF instead of *i*PrOH and without the protection of a hydroxy group.

Scheme III



In conclusion, we demonstrated a mild and an efficient rearrangement reaction for the β,γ-unsaturated ketone to α,β-unsaturated ketone under DABCO/*i*PrOH reaction conditions. The β,γ-*endo*-cycilc double bond of ketone can be rearranged to α,β-*exo*-cyclic double bond under the reaction conditions. The β-hydroxy allyl ketone also was isomerized to its α,β-unsaturated ketone under DABCO/THF reaction conditions at room temperature and without the protection of a hydroxy group.

EXPERIMENTAL SECTION

The ^{1}H-NMR (proton nuclear magnetic resonance) spectra were recorded at 300 MHz (Bruker-AC300P) with deuteriochloroform ($CDCl_3$, Aldrich 99.8 atom% D) as the solvent and the internal standard. The ^{13}C-NMR (carbon nuclear magnetic resonance) spectra were recorded at 75.5 MHz (Bruker-AC300P) with $CDCl_3$ as the solvent and the internal standard. Chemical shifts are reported in parts per million and resonance patterns are reported with the notations of either s (singlet), d (doublet), t (triplet), q (quartet), or m (multiplet). Coupling constants (*J*) are reported in hertz (Hz). Mass spectra (MS) were recorded on JOEL SX-102A and VG 70-250S spectrophotometers and are reported in *m/e* units for the most abundant peaks. Infrared spectra (IR) were recorded on a BIO-RAD FTS-40 infrared spectrophotometer as a liquid film (neat) or a Nujol mull. Polystyrene was used as a standard, and the spectra are reported in reciprocal centimeters (cm^{-1}).

All experiments were carried out under a nitrogen atmosphere which was dried primarily by passing through a column of potassium hydroxide (KOH) layered with calcium sulfate ($CaSO_4$). Methanol and *i*-propanol were distilled from sodium and recirculated prior to use. Hexane and ethyl acetate were distilled from calcium hydride. Thin-layer chromatography (TLC) analysis was performed on a plastic plate (or aluminum sheet) precoated with silica gel (Merck, 5554 Silica gel 60F_{254}). Visualization was accomplished by UV light or developed by spraying with a 10% phosphomolybdic acid ethanol solution. Column chromatography was performed using silica gel (Merck 230-400 mesh) and ethyl acetate/hexane mixture as the eluent. All reagents (Table 1 and 2) were purchased from Aldrich, Merck and Riedel-deHaen and all were used directly without further purification. β,γ-Unsaturated ketones shown in Table 1 were prepared by the reported method.[19]

Typical procedure for isomerization reaction of β,γ-unsaturated ketone to α,β-unsaturated ketone

A reaction mixture of β,γ-unsaturated ketone (1.0 mmol) and DABCO (1.0 mmol) in anhydrous *i*PrOH (5.0 mL) was stirred at room temperature. After the reaction was complete (monitored by TLC), the organic solvent was removed directly under reduced pressure. Further purification was achieved on a flash chromatograph with silica gel and ethyl acetate/hexane as eluant. Isomerizations were investigated under the typical procedure, and the yields are the isolated yields after chromatography. All these β,γ-unsaturated ketones and α,β-unsaturated ketones were characterized by spectral analysis and by comparsion with the authentic compounds.

4-Methoxy-1-phenyl-pentan-2-one (Scheme II, A)

^{1}H-NMR: δ 1.13 (3H, d, *J* = 6.1 Hz), 2.43 (1H, dd, *J* = 15.9, 5.5 Hz), 2.74 (1H, dd, *J* = 15.9, 7.1 Hz), 3.28 (3H, s), 3.71 (2H, s), 3.78 (1H, ddq, *J* = 7.1, 5.5, 6.1 Hz), 7.18-7.35 (5H, m). ^{13}C-NMR: δ 19.0, 48.6, 50.9, 56.1, 73.1, 126.8, 128.5, 129.4, 133.9, 206.5. IR (neat): 3088 (sp^2-CH, w), 3064 (sp^2-CH, w), 3030 (sp^2-CH, w), 2974 (sp^3-CH, m), 2932 (sp^3-CH, m), 2824 (sp^3-CH, m), 1717 (C=O, s), 1603 (w), 1373 (w), 1193 (w), 1134 (C-O, s), 1088 (C-O, s), 902 (w), 751 (w), 701 (s) cm^{-1}. HRMS: 192.1142 (calcd. for $C_{12}H_{16}O_2$, 192.1150). MS: *m/z* 193 (3, M+1), 192 (17, M), 118 (10), 105

(12), 101 (17), 91 (28), 77 (6), 69 (12), 65 (6), 59 (base).

Oct-1-en-4-one (Table 1, Entry 1)

^{1}H-NMR: δ 0.90 (3H, t, *J* = 7.3), 1.31 (2H, m), 1.56 (2H, m), 2.43 (2H, t, *J* = 7.3 Hz), 3.16 (2H, d, *J* = 7.0 Hz), 5.10 (1H, dd, *J* = 16.9, 1.4 Hz), 5.17 (1H, dd, *J* = 9.5, 1.0 Hz), 5.92 (1H, m). ^{13}C-NMR: δ 13.8, 22.3, 25.8, 42.1, 47.7, 118.6, 130.7, 208.9. HRMS: 126.1045 (calcd. for $C_8H_{14}O$, 126.1044). MS: *m/z* 119 (34), 117 (31), 111 (21), 97 (21), 91 (33), 85 (44), 83 (24), 71 (42), 69 (69), 58 (50), 57 (base), 55 (42), 43 (93), 41 (79), 39 (29), 29 (52), 27 (25), 18 (86), 15 (26).

Oct-2-en-4-one (Table 1, Entry 1)

^{1}H-NMR: δ 0.90 (3H, t, *J* = 7.3), 1.26-1.39 (2H, m), 1.53-1.63 (2H, m), 1.88 (3H, dd, *J* = 6.9, 1.7 Hz), 2.51 (2H, t, *J* = 7.5 Hz), 6.11 (1H, dq, *J* = 15.8, 1.7 Hz), 6.83 (1H, dq, *J* = 15.8, 6.9 Hz). ^{13}C-NMR: δ 13.8, 18.1, 22.4, 26.4, 39.8, 132.0, 142.2, 200.7. HRMS: 126.1019 (calcd. for $C_8H_{14}O$, 126.1045). MS: *m/z* 127 (11, M+1), 126 (12, M), 125 (15), 111(25), 97 (35), 85 (57), 83 (35), 81 (30), 71 (55), 69 (49), 67 (23), 57 (base), 55 (52).

5-Cyclophentenylpent-1-en-4-one (Table 1, Entry 2)

^{1}H-NMR: δ 1.89 (2H, m), 2.24-2.38 (4H, m), 3.20-3.22 (4H, m), 5.13 (1H, dd, *J* = 15.0, 0.9 Hz), 5.18 (1H, dd, *J* = 11.6, 0.7 Hz), 5.52 (1H, t, *J* = 1.4 Hz), 5.90 (1H, m). ^{13}C-NMR: δ 23.5, 32.6, 35.3, 45.1, 118.8, 128.9, 130.6, 136.9, 206.6. HRMS: 150.1048 (calcd. for $C_{10}H_{14}O$, 150.1044). MS: *m/z* 135 (28), 109 (27), 107 (33), 81 (36), 79 (37), 77 (21), 69 (base), 67 (21), 53 (23), 43 (26), 41 (82), 39 (56). IR: (neat) 3098 (sp^2-CH, w), 3053 (sp^2-CH, w), 2974 (sp^3-CH, s), 2855 (sp^3-CH, s), 1717 (C=O, s), 1641 (C=C, m), 1410 (m), 1321 (m), 1053 (m), 860 (s) cm^{-1}.

1,6-Octdien-4-one (Table 1, Entry 3)

^{1}H-NMR: δ 1.70 (3H, dd, *J* = 4.6, 1.0 Hz), 3.12 (2H, dd, *J* = 5.0, 1.0 Hz), 3.19 (2H, dt, *J* = 7.0, 1.0 Hz), 5.13 (1H, dd, *J* = 17.5, 1.5 Hz), 5.18 (1H, dd, *J* = 11.0, 1.2 Hz), 5.90 (1H, m). ^{13}C-NMR: δ 18.0, 46.2, 47.0, 118.8, 122.7, 129.9, 130.5, 207.2. HRMS: 124.0847 (calcd. for $C_8H_{12}O$, 124.0888). MS: *m/z* 97 (27), 69 (60), 55 (22), 43 (base), 41 (40), 39 (42). IR: (neat) 3071 (sp^2-CH, m), 3035 (sp^2-CH, m), 2965 (sp^3-CH, m), 2919 (sp^3-CH, m), 1714 (C=O, s), 1641 (C=C, s), 975 (m), 914 (m), 744 (m) cm^{-1}.

Octa-2,6-dien-4-one (Table 1, Entry 3, 3a)

^{1}H-NMR: δ 1.68-1.70 (3H, m), 1.89 (3H, dd, *J* = 6.8, 1.5 Hz), 3.21 (2H, dd, *J* = 4.5, 1.8 Hz), 5.53-5.57 (2H, m), 6.13 (1H, dq, *J* = 15.6, 1.5 Hz), 6.86 (1H, dq, *J* = 15.6, 6.8 Hz). ^{13}C-NMR: δ 17.9, 18.1, 44.0, 123.3, 129.3, 131.2, 142.9, 198.4. HRMS: 124.0873 (calcd. for $C_8H_{12}O$, 124.0888). MS: *m/z* 124 (1, M), 99 (15), 97(17), 88 (11), 86 (68), 84 (base), 69 (60), 51 (45).

Octa-2,5-dien-4-one (Table 1, Entry 3, 3b)

^{1}H-NMR: δ 1.08 (3H, t, *J* = 7.4 Hz), 1.91 (3H, dd, *J* = 6.8, 1.3 Hz), 2.20-2.31 (2H, m), 6.30 (1H, dt, *J* = 15.0, 1.7 Hz), 6.35 (1H, dq, *J* = 15.6, 1.3 Hz), 6.85-6.98 (2H, m). ^{13}C-NMR: δ 12.2, 18.2, 25.6, 127.7, 130.2, 142.7, 149.0, 189.4. HRMS: 124.0878 (calcd. for $C_8H_{12}O$, 124.0888). MS: *m/z* 125 (6, M+1), 124 (8, M), 123 (9), 109(22), 97 (11), 95 (12), 83 (68), 69 (base), 57 (16), 55 (32), 53(10).

4-Phenylbut-1-en-4-one (Table 1, Entry 4)

^{1}H-NMR: δ 3.76 (2H, d, *J* = 6.6 Hz), 5.21 (1H, dd, *J* = 18.2, 1.5 Hz), 5.24 (1H, dd, *J* = 9.6, 1.5 Hz), 6.10 (1H, m), 7.47-7.75 (3H, m), 7.97 (1H, m). ^{13}C-NMR: δ 43.4, 118.7, 128.3, 128.6, 131.0, 133.1, 136.6, 198.0. HRMS: 146.0732 (calcd. for $C_{10}H_{10}O$, 146.0731). MS: *m/z* 146 (base), 145 (29), 131 (34), 105 (23). IR: (neat) 3071 (sp^2-CH, m), 2983 (sp^3-CH, w), 1684 (C=O, s), 1644 (C=C, m), 1598 (m), 1451 (m), 1232 (m), 911 (s), 750 (s), 697 (s) cm^{-1}.

1-Phenylbut-2-en-1-one (Table 1, Entry 4)

^{1}H-NMR: δ 2.00 (3H, dd, *J* = 6.6, 1.6 Hz), 6.90 (1H, dq, *J* = 15.5, 1.6 Hz), 7.07 (1H, dq, *J* = 15.5, 6.6 Hz), 7.42-7.48 (2H, m), 7.52-7.58 (1H, m), 7.90-7.94 (2H, m). ^{13}C-NMR: δ 18.5, 127.6, 128.5, 132.5, 137.9, 145.0, 190.8. HRMS: 146.0736 (calcd. for $C_{10}H_{10}O$, 146.0732). MS: *m/z* 147 (7, M+1), 146 (53, M), 145(17), 131 (50), 117 (16), 115 (11), 105 (base), 77 (89), 69 (49), 51 (40).

1-(4-Methoxy-phenyl)-but-2-en-1-one (Table 1, Entry 5)

^{1}H-NMR: δ 1.97 (3H, dd, *J* = 6.6, 1.4 Hz), 3.85 (3H, s), 6.87-6.95 (1H, m), 6.93 (2H, d, *J* = 8.7 Hz), 7.04 (1H, dq, *J* = 15.0, 6.6 Hz), 7.93 (2H, d, *J* = 8.7 Hz). ^{13}C-NMR: δ 18.5, 55.4, 113.7, 127.2, 130.8, 143.8, 163.3, 189.0. HRMS: 176.0836 (calcd. for $C_{11}H_{12}O_2$, 176.0837). MS: *m/z* 177 (60, M+1), 176 (59, M), 175(39), 161 (80), 145 (28), 136 (84), 135 (59), 107 (73), 92 (96), 77 (base), 69 (65), 64 (56), 63 (35).

5-Phenylpent-1-en-4-one (Table 1, Entry 6)

^{1}H-NMR: δ 3.21 (2H, dt, *J* = 7.0, 1.3 Hz), 3.72 (2H, s),

5.11 (1H, dd, *J* = 16.9, 1.5 Hz), 5.18 (1H, dd, *J* = 9.5, 1.4 Hz), 5.89 (1H, m), 7.19-7.37 (5H, m). ^{13}C-NMR: δ 46.8, 49.5, 119.0, 127.1, 128.7, 129.5, 130.4, 134.0, 206.0. HRMS: 160.0884 (calcd. for $C_{11}H_{12}O$, 160.0888). MS: *m/z* 160 (base), 151 (17), 150 (10), 136 (12), 122 (17). IR: (neat) 3089 (sp^2-CH, m), 3035 (sp^2-CH, w), 2983 (sp^3-CH, w), 2902 (sp^3-CH, w), 1714 (C=O, s), 1641 (C=C, s), 1494 (m), 1451 (m), 1339 (m), 911 (s), 750 (s), 697 (s) cm^{-1}.

1-Phenylpent-3-en-2-one (Table 1, Entry 6)

^{1}H-NMR: δ 1.88 (3H, dd, *J* = 6.8, 1.5 Hz), 3.81 (2H, s), 6.17 (1H, dq, *J* = 15.6, 1.5 Hz), 6.93 (1H, dq, *J* = 15.6, 6.8 Hz), 7.20-7.35 (5H, m). ^{13}C-NMR: δ 18.2, 47.4, 126.8, 128.6, 129.4, 131.0, 134.7, 143.6, 197.1. HRMS: 160.0888 (calcd. for $C_{11}H_{12}O$, 160.0888). MS: *m/z* 161 (13, M+1), 160 (18, M), 119 (35), 118 (61), 107 (44), 106 (22), 105 (93), 92 (47), 91 (75), 77 (88), 69 (base), 65 (30).

5-Naphthalenylpent-1-en-4-one (Table 1, Entry 7)

^{1}H-NMR: δ 3.19 (2H, d, *J* = 6.9 Hz), 4.15 (2H, s), 5.07 (1H, dd, *J* = 15.9, 1.7 Hz), 5.16 (1H, dd, *J* = 9.6, 1.3 Hz), 5.90 (1H, m), 7.38-7.55 (4H, m), 7.80-7.90 (3H, m). ^{13}C-NMR: δ 46.3, 47.8, 118.9, 123.8, 125.5, 125.9, 126.5, 128.1, 128.3, 128.8, 130.4, 130.7, 132.2, 133.9, 206.4. HRMS: 210.1044 (calcd. for $C_{15}H_{14}O$, 210.1044). MS: *m/z* 210 (base), 202 (5), 182 (5), 178 (6), 165 (9). IR: (neat) 3053 (sp^2-CH, w), 3035 (sp^2-CH, w) 2974 (sp^3-CH, w), 1714 (C=O, s), 1641 (C=C, m), 1598 (m), 1396 (m), 776 (s) cm^{-1}.

1-Naphthalen-1-yl-pent-3-en-2-one (Table 1, Entry 7)

^{1}H-NMR: δ 1.84 (3H, dd, *J* = 6.8, 1.5 Hz), 4.23 (2H, s), 6.23 (1H, dq, *J* = 15.5, 1.5 Hz), 6.98 (1H, dq, *J* = 15.5, 6.8 Hz), 7.36-7.54 (4H, m), 7.78-7.91 (3H, m). ^{13}C-NMR: δ 18.2, 46.1, 124.0, 125.5, 125.8, 126.4, 127.9, 128.1, 128.7, 130.2, 131.2, 132.4, 133.9, 143.5, 197.2. HRMS: 210.1058 (calcd. for $C_{15}H_{14}O$, 210.1045). MS: *m/z* 211 (48, M+1), 210 (base, M), 182 (19), 157 (18), 155 (82), 142 (84), 141 (80), 139 (85), 127 (43), 115 (35), 69 (29).

5-Thiopheneylpent-1-en-4-one (Table 1, Entry 8)

^{1}H-NMR: δ 3.22 (2H, d, *J* = 7.1 Hz), 3.76 (2H, s), 5.12 (1H, dd, *J* = 16.9, 1.5 Hz), 5.19 (1H, dd, *J* = 10.5, 1.4 Hz), 5.91 (1H, m), 6.96 (1H, d, *J* = 5.1 Hz), 7.09 (1H, d, *J* = 3.1 Hz), 7.30 (1H, dd, *J* = 5.1, 3.1). ^{13}C-NMR: δ 43.7, 46.7, 119.0, 123.0, 126.0, 128.5, 130.0, 133.6, 205.5. HRMS: 166.0449 (calcd. for $C_9H_{10}OS$, 166.0452). MS: *m/z* 166 (47), 165 (31), 162 (25), 124 (26), 113 (40), 112 (22), 111 (base). IR: (neat) 3089 (sp^2-CH, w), 2956 (sp^3-CH, w), 2884 (sp^3-CH, w), 1713 (C=O, s), 1641 (C=C, s), 1392 (m), 1330 (m), 1053 (m), 1005 (m), 920 (s), 776 (s), 742 (s) cm^{-1}.

1-Thiophen-3-yl-pent-3-en-2-one (Table 1, Entry 8)

^{1}H-NMR: δ 1.89 (3H, dd, *J* = 6.9, 1.7 Hz), 3.83 (2H, s), 6.17 (1H, dq, *J* = 15.7, 1.7 Hz), 6.93 (1H, dq, *J* = 15.7, 6.9 Hz), 6.96 (1H, dd, *J* = 4.9, 1.2 Hz), 7.08 (1H, dd, *J* = 3.2, 1.2 Hz), 7.28 (1H, dd, *J* = 4.9, 3.2 Hz). ^{13}C-NMR: δ 18.2, 41.9, 122.7, 125.8, 128.6, 130.8, 134.2, 13.6, 196.7; HRMS: 166.0443 (calcd. for $C_9H_{10}O$, 166.0452). MS: *m/z* 167 (8, M+1), 166 (55, M), 138 (27), 124 (16), 113 (15), 111 (38), 98 (24), 97 (base), 69 (61), 53 (20).

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