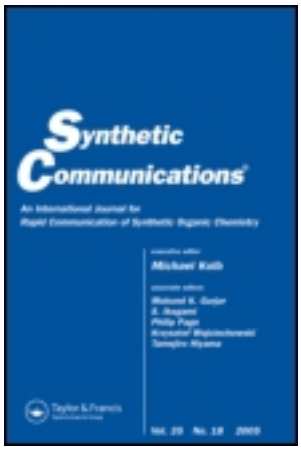

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Synthesis of 5- and 6-Acyl-1-cyano and -1-ethoxycarbonyl Cycloalkenes

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ABSTRACT

Conjugated addition of primary nitroalkanes to the functional acetates **3** and **4** in basic medium, leads to the cyclic nitroesters **5** and nitronitriles **6**. These derivatives are easily converted via the Nef reaction to the corresponding γ-ketoestesrs **7** and γ-ketonitriles **8** in good yields.

Key Words: Functional cycloalkenols; Nitroalkanes; Conjugated addition.

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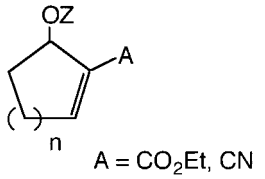
The five and six membered ring synthesis of functional cycloalkenols has been achieved by the Wittig–Horner reaction on aliphatic 1,4- and 1,5-dialdehydes, stable in water, in heterogeneous medium in the presence of potassium carbonates as base.[1] The electrophilic behavior of cycloalkenols **1** and **2** and their derivatives (Sch. 1) toward various organometallic reagents provided 1,4-addition products as well as the substitution of OZ group, where both served as precursors in the synthesis of natural products.[2–5]

In continuation to our interest in the synthesis of some functionalized molecules, we report here the electrophilic reactivity of the allylic acetates **3** and **4** toward nitroalkanes anions to obtain the corresponding compounds which are considered as a potential intermediates in organic synthesis, where it is very well known that nitro groups can be converted into various functional groups such as carbonyl which is was well documented.[6–10] Conjugate addition of nitroalkanes to α,β-unsaturated carbonyl compounds, provides a convenient method for preparing the corresponding nitro compound.[11–14]

In the present work we showed that, the substitution reaction of functional allyl acetate with nitroalkanes can be carried out not only in the case of acyclic molecules,[15,16] but also with cyclic acetates. Indeed the condensation reaction of nitroalkanes under basic conditions with the allyl acetates **3** and **4** provided, via a S_N2'substitution, cyclo nitroesters **5** and nitronitriles **6** (Sch. 2). However, appropriate solvents and bases were chosen according to the nature of the group A and the size of the ring, as described in Table 1.

Due to the existence of two asymmetric centers in the molecules of cycloalkanes nitroesters **5** and nitronitriles **6**, a mixture of two diastereoisomers (a,a′-d,d′) was obtained in each case and which were confirmed by chromatography, ^{1}H NMR and ^{13}C spectra.

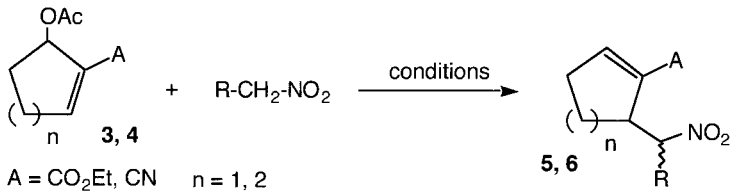
The transformation of cyclic nitroesters **5** and nitronitriles **6** into cyclic γ-ketoesters **7** and γ-ketonitriles **8** was achieved by using Nef reaction, an appropriate method for further transformation of **5** and **6** by addition of their nitronate anions to a methanolic solution of concentrated



1 : n = 1, Z = H ; **3 :** n = 1, Z = Ac

2 : n = 2, Z = H ; **4 :** n = 2, Z = Ac

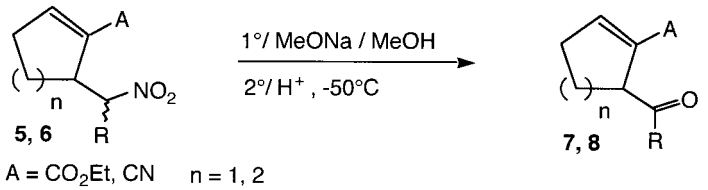
Scheme 1.



Scheme 2.

Table 1. Synthesis of cycloalkenic nitroesters **5** and **6′** nitronitriles.

Product	A	*n*	R	Base (equiv.)/solvent	Time (h)	Yield (%)
5a,a′	CO_2Et	1	Me	DBU (1)/THF	8	59
5b,b′	CO_2Et	1	Et	DBU (1)/THF	6	60
5c,c′	CO_2Et	2	Me	DBU (1.5)/THF	8	55
5d,d′	CO_2Et	2	Et	DBU (1.5)/THF	6	58
6a,a′	CN	1	Me	NaOH (2)/THF	96	58
6b,b′	CN	1	Et	NaOH (2)/THF	72	53
6c,c′	CN	2	Me	DBU (1)/CH_3CN	18	66
6d,d′	CN	2	Et	DBU (1)/CH_3CN	12	80



Scheme 3.

sulfuric acid at $-50^{\circ}C$, leading to the pure cyclic γ-ketoesters **7** and γ-ketonitriles **8** (Sch. 3).

In conclusion, we showed that the reaction of nitroalkanes with alicyclic acetates of type **3** and **4** in basic medium provides an easy way to synthesize a new family of cycloalkenic nitroesters **5** and nitronitriles **6** which can be converted via the Nef reaction in highly acidic medium and at low temperature, to the corresponding cycloalkenic γ-ketoesters **7** and γ-ketonitriles **8**.

Table 2. Synthesis of cycloalkenic γ-ketoesters and γ-ketonitriles.

Product	N	A	R	Yield (%)
7a	1	CO_2Et	Me	38
7b	1	CO_2Et	Et	33
7c	2	CO_2Et	Me	30
7d	2	CO_2Me	Et	35
8a	1	CN	Me	72
8b	1	CN	Et	80
8c	2	CN	Me	55
8d	2	CN	Et	68

EXPERIMENTAL

Synthesis of Cyclopentenic and Cyclohexenic Nitroesters 5a,a′-d,d′

General procedure. To a solution of cyclic allyl acetate **3** (A=CO_2Et, $n=1$) or **4** (A=CO_2Et, $n=2$) (5 mmol) in THF (15 mL) and suitable amount nitroalkane, DBU was added at room temperature (Table 1). After stirring for an appropriate time, the solvent was removed to give an oil which was purified by column chromatography on silica gel (EtOAc/hexane, 3:7).

5-(1-Nitroethyl) cyclopent-1-ene carboxylic acid ethyl ester 5a,a′. IR ($CHCl_3$, $\nu\,cm^{-1}$): 1705 (C=O); 1631 (C=C); 1547 (C-NO_2). ^{1}H NMR (300 MHz, $CDCl_3$): 6.97, 6.87 (2m, 2H); 5.18 (m, 2H); 4.23 (2q, 4H, $J=7.2$ Hz, $J=7.2$ Hz); 3.88, 3.40 (2m, 2H); 2.53, 2.47 (2m, 4H); 2.20, 2.04 (2m, 4H); 1.55, 1.33 (2dd, 6H, $J=6.9$ Hz, $J=1.5$ Hz); 1.32, 1.31 (2t, 6H, $J=7.2$ Hz, $J=7.2$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$): 164.4, 164.0 (<u>C</u>=O); 147.5, 146.2 (<u>C</u>=CH); 135.0, 134.8 (C=<u>C</u>H); 82.8, 82.7 (<u>C</u>HNO_2); 60.5, 60.4 (CO_2<u>C</u>H_2CH_3); 48.3, 48.0 (<u>C</u>HCHNO_2); 32.2, 31.3 (<u>C</u>H_2CH=C); 23.9, 23.8 (<u>C</u>H_2CH_2CH=); 16.7, 12.1 (<u>C</u>H_3CHNO_2); 14.1 (CO_2CH_2<u>C</u>H_3). MS, *m/z*: 166 (18, 51); 137 (22, 16); 120 (41, 100); 93 (100, 74); 29 (31, 25); exact mass M^+ 213.2345 (Calcd. for $C_{10}H_{15}NO_4$ 213.2336).

5-(1-Nitropropyl) cyclopent-1-ene carboxylic acid ethyl ester 5 b,b′. IR ($CHCl_3$ ν cm^{-1}): 1705 (C=O); 1630 (C=C); 1547 (C-NO_2). ^{1}H NMR (300 MHz, $CDCl_3$): 6.96, 6.85 (2m, 2H); 5.01 (m, 2H); 4.23 (2q, 4H, $J=7.2$ Hz, $J=7.2$ Hz); 3.69, 3.40 (2m, 2H); 2.44 (m, 4H); 2.12 (m, 4H); 1.74 (m, 4H); 1.32, 1.31 (2t, 6H, $J=7.2$ Hz, $J=7.2$ Hz); 0.99, 0.96 (2t, 6H, $J=7.4$ Hz, $J=7.4$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$): 164.3, 164.0 (<u>C</u>=O);

147.5, 146.4 (C=CH); 135.0, 134.9 (C=CH); 90.5, 89.9 ($CHNO_2$); 60.4, 60.3 ($CO_2CH_2CH_3$); 48.3, 48.2 ($CHCHNO_2$); 32.1, 31.5 ($CH_2CH=C$); 24.6, 23.6 ($CH_2CH_2CH=$); 20.3 (CH_2CHNO_2); 14.1 ($CO_2CH_2CH_3$); 10.8, 10.5 ($CH_3CH_2CHNO_2$). MS, *m/z*: 180 (38, 17); 151 (30, 41); 134 (100, 54); 107 (37, 75); 79 (42, 100); 29 (40, 99); exact mass M^+ 227.2614 (Calcd. for $C_{11}H_{17}NO_4$ 227.2631).

6-(1-Nitroethyl) cyclohex-1-ene carboxylic acid ethyl ester 5c,c′. IR ($CHCl_3$, ν cm^{-1}): 1702 (C=O); 1643 (C=C); 1549 (C-NO_2). ^{1}H NMR (300 MHz, $CDCl_3$): 7.12, 7.06 (2t, 2H, $J = 4$ Hz, $J = 4$ Hz); 5.05, 4.85 (2qt, 2H, $J = 6.6$ Hz, $J = 6.6$ Hz); 4.14 (2q, 4H, $J = 7.0$ Hz, $J = 7$ Hz); 3.36, 3.08 (2m, 2H); 2.14 (m, 4H); 1.60–1.47 (m, 8H); 1.43, 1.32 (2d, 6H, $J = 7.0$ Hz, $J = 7.0$ Hz); 1.24, 1.22 (2t, 6H, $J = 7.0$ Hz, $J = 7.0$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$): 167.0, 166.3 (C=O); 143.8, 143.2 (C=CH); 129.5, 129.4 (C=CH); 84.3, 84.0 ($CHNO_2$); 60.9, 60.6 ($CO_2CH_2CH_3$); 37.3, 37.2 ($CHCHNO_2$); 25.3, 25.5 ($CH_2CH=C$); 22.6, 22.5 ($CH_2CH_2CH=$); 18.3, 18.4 (CH_2CH_2CH); 16.8, 17.5 (NO_2CHCH_3) 14.1, 14.0 ($CO_2CH_2CH_3$). MS, *m/z*: 180 (44,100); 152 (47,55); 107 (76,85); 79 (100,86); 29 (40,28); exact mass M^+ 227.2620 (Calcd. for $C_{11}H_{17}NO_4$ 227.2625).

6-(1-Nitropropyl) cyclohex-1-ene carboxylic acid ethyl ester 5d,d′. IR ($CHCl_3$, ν cm^{-1}): 1713 (C=O); 1632 (C=C); 1555 (C-NO_2). ^{1}H NMR (300 MHz, $CDCl_3$): 7.09, 7.15 (2m, 2H); 4.82, 4.71 (2m, 2H); 4.23 (2q, 4H, $J = 6.9$ Hz, $J = 6.9$ Hz); 3.32, 3.18 (2m, 2H); 2.00–2.30 (m, 8H); 1.45–1.85 (m, 8H); 1.32, 1.30 (2t, 6H, $J = 6.9$ Hz, $J = 6.9$ Hz); 0.93, 0.92 (2t, 6H, $J = 7.0$ Hz, $J = 7.2$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$): 166.7, 166.8 (C=O); 143.3, 143.2 (C=CH); 129.5, 129.6 (C=CH); 92.1, 91.4 ($CHNO_2$); 60.6 ($CO_2CH_2CH_3$); 37.1, 36.3 ($CHCHNO_2$); 25.2, 25.3 ($CH_2CH=C$); 24.2, 23.4 ($CH_2CH_2CH=$); 23.0, 22.0 (CH_2CHNO_2); 18.3, 17.40 (CH_2CH_2CH); 14.1, 14.0 ($CO_2CH_2CH_3$) 11.2, 10.7 ($NO_2CHCH_2CH_3$). MS, *m/z*: 194 (68,43); 165 (42,100); 148 (100,58); 121 (54,82); 29 (34,16); exact mass M^+ 241.2847 (Calcd. for $C_{12}H_{19}NO_4$ 241.2833).

Synthesis of Cyclopentenic Nitronitriles 6a,a′-b,b′

Typical procedure. To a mixture of cyclic allyl acetate **3** (A=CN, $n = 1$) (5 mmol) and nitroalkane (20 mmol) dissolved in THF (25 mL), cooled at 0°C with an ice-bath, was added a solution of NaOH (18 mL, 0.6 N). After the addition was complete, the mixture was stirred at 50°C for the appropriate time given in Table 1. The mixture was diluted with H_2O and extracted with ether (3×30 mL). The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$. The solvent

was removed to leave an oil which was purified by column chromatography on silica gel (EtOAc/hexane, 2:8).

5-(1-Nitroethyl) cyclopent-1-ene carbonitrile 6a,a′. IR ($CHCl_3$, $\nu\,cm^{-1}$): 2223 (C≡N); 1642 (C=C); 1552 (C-NO_2). ^1H NMR (300 MHz, $CDCl_3$): 6.86 (m, 2H); 4.78 (m, 2H); 3.70, 3.41 (2m, 2H); 2.6 (m, 4H); 2.17, 1.93 (2m, 4H); 1.68, 1.54 (2d, 6H, $J = 6.9$ Hz, $J = 6.7$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$): 152.6, 152.5 (C=CH); 115.5, 114.9 (C=CH); 113.9, 113.6 (C≡N); 83.7, 82.9 ($CHNO_2$); 50.7, 49.8 ($CHCHNO_2$); 32.8, 32.0 (CH_2CH=C); 24.8, 23.8 (CH_2CH_2CH=); 16.8, 13.7 (CH_3CHNO_2). MS, *m*/*z*: 119 (69,100); 93 (100,68); 92 (74,71); 65 (51,49); exact mass M^+ 166.1844 (Calcd. for $C_8H_{10}N_2O_2$ 166.1829).

5-(1-Nitropropyl) cyclopent-1-ene carbonitrile 6b,b′. IR ($CHCl_3$, $\nu\,cm^{-1}$): 2223 (C≡N); 1641 (C=C); 1552 (C-NO_2). ^1H NMR (300 MHz, $CDCl_3$): 6.84 (m, 2H); 4.58 (m, 2H); 3.52, 3.40 (2m, 2H); 2.56 (m, 4H); 2.18 (m, 4H); 1.98 (m, 4H); 1.01 (t, 6H, $J = 7.4$ Hz, $J = 7.4$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$): 152.7, 152.6 (C=CH); 115.6, 115.2 (C=CH); 114.0, 113.2 (C≡N); 91.0, 90.8 ($CHNO_2$); 49.8, 49.4 ($CHCHNO_2$); 32.6, 32.1 (CH_2CH=C); 25.1, 24.8 (CH_2CH_2CH=); 22.8 (CH_2CHNO_2); 10.2, 10.1 (CH_3CH_2). MS, *m*/*z*: 133 (13); 104 (7); 92 (100); 65 (22); exact mass M^+ 180.2018 (Calcd. for $C_9H_{12}N_2O_2$ 180.2023).

Synthesis of Cyclohexenic Nitronitriles 6c,c′-d,d′

Typical procedure: DBU (5 mmol) was added at room temperature to a solution of nitroalkane (5 mmol) and acetate **4** (A=CN, $n = 2$) in acetonitrile (25 mL). The solution was stirred for the time mentioned in Table 1. After evaporation of the solvent the residue was purified by chromatography (EtOAc/hexane, 2:8) giving the pure product **6c,c′-d,d′**.

6-(1-Nitroethyl) cyclohex-1-ene carbonitrile 6c,c′. IR ($CHCl_3$, $\nu\,cm^{-1}$): 2217 (C≡N); 1631 (C=C); 1552 (C-NO_2). ^1H NMR (300 MHz, $CDCl_3$): 6.85 (t, 2H, $J = 4$ Hz, $J = 4$ Hz); 4.85 (qt, 2H, $J = 6.2$ Hz, $J = 6.2$ Hz); 3.25, 2.80 (2m, 2H); 2.23 (m, 4H) 1.86, 1.73 (2m, 4H), 1.52 (m, 4H); 1.70, 1.54 (2d, 6H, $J = 7$ Hz, $J = 7$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$): 149.8, 149.4 (C=CH); 118.6, 117.4 (C=CH); 112.4, 112.0 (C≡N); 83.9, 82.4 ($CHNO_2$); 39.9, 39.3 ($CHCHNO_2$); 25.8, 25.7 (CH_2CH=C); 22.6, 21.3 (CH_2CH_2CH=); 19.4, 18.2 (CH_2CH_2CH), 16.2, 12.7 (CH_3CHNO_2). MS, *m*/*z*: 133 (70); 118 (63); 106 (66); 92 (100), 79 (58); exact mass M^+ 180.2041 (Calcd. for $C_9H_{12}N_2O_2$ 180.2034).

6-(1-Nitropropyl) cyclohex-1-ene carbonitrile 6d,d′. IR ($CHCl_3$, $\nu\,cm^{-1}$): 2217 (C≡N); 1631 (C=C); 1552 (C-NO_2). ^1H NMR (300 MHz, $CDCl_3$): 6.84 (m, 2H); 4.60 (m, 2H); 3.06, 2.80 (2m, 2H); 1.90–2.28

(m, 8H); 1.83–1.53 (m, 8H); 1.03, 1.02 (2t, 6H, $J = 7.3$ Hz, $J = 7.3$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$): 149.8, 149.8 (C=CH); 112.2, 112.1 (C=CH); 118.8, 117.6 (C≡N); 91.5, 91.1 ($CHNO_2$); 39.4, 38.1 ($CHCHNO_2$); 25.8, 25.7 (CH_2CH=C); 24.6 (CH_2CH_2CH=); 22.6, 21.3 (CH_2CHNO_2; 19.2, 17.9 (CH_2CH_2CH); 11.2, 10.4 (CH_3CH_2). MS, *m*/*z*: 147 (48); 132 (33); 106 (68), 79 (100).

Synthesis of Cycloalkenic Ketoesters and Ketonitriles 7,8a–d

Typical procedure. To a solution of MeOH (15 mL) and Na (15 mmol), was added the nitro derivative **5** or **6** (5 mmol) to obtain the corresponding nitronate. After stirring for 1h, a mixture of MeOH (15 mL) and concentrated H_2SO_4 (3 mL) was added at -50°C. After 1 h, H_2O (30 mL) was added and the solution was concentrated in order to partially remove MeOH. The mixture was extracted with CH_2Cl_2 (3×30 mL), washed with 1% NaOH (10 mL), brine (10 mL) and dried ($MgSO_4$). The solvent was evaporated under reduced pressure to obtain a crude product, which was purified by chromatography (EtOAc/hexane, 2:8).

5-Acetyl cyclopent-1-ene carboxylic acid ethyl ester 7a. IR ($CHCl_3$, ν cm^{-1}): 1710 (C=O); 1631 (C=C). ^{1}H NMR (300 MHz, $CDCl_3$): 6.97 (m, 1H); 4.18 (q, 2H, $J = 7.2$ Hz); 3.90 (m, 1H); 2,60 (m,2H); 2.23 (s, 3H); 2.00, 2.28 (2m, 2H); 1.27 (t, 3H, $J = 7.2$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$): 206.6 (CH_3C=O); 164.2 ($CO_2C_2H_5$); 146.6 (CH=C); 135.8 (CH=C); 60.4 ($CO_2CH_2CH_3$); 56.5 ($CHCOCH_3$); 32.5 (CH_2CH=C); 28.8 (CH_3C=O); 27.7 (CH_2CH_2CH=); 14 ($CO_2CH_2CH_3$). MS, *m*/*z*: 182 ($M^{+\cdot}$, 5); 140 (76); 112 (47); 67 (88); 43 (100); exact mass M^+ 182.2217 (Calcd. for $C_{10}H_{14}O_3$ 182.2209).

5-Propionyl cyclopent-1-ene carboxylic acid ethyl ester 7b. IR ($CHCl_3$, ν cm^{-1}): 1710 (C=O); 1631 (C=C). ^{1}H NMR (300 MHz, $CDCl_3$): 6.95 (m, 1H); 4.15 (q, 2H, $J = 7.2$ Hz); 3.92 (m, 1H); 2.64 (m, 2H); 2.52 (q, 2H, $J = 6.9$ Hz); 2.25, 1.94, (2m, 2H); 1.28 (t, 3H, $J = 7.2$ Hz); 1.09 (t, 3H, $J = 6.9$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$): 222.2 (CH_3CH_2C=O); 164.2 ($CO_2C_2H_5$); 146.4 (CH=C); 135.6 (CH=C); 60.3 ($CO_2CH_2CH_3$); 55.4 ($CHCOCH_2$); 35.2 (CH_2C=O); 28.1 (CH_2CH_2CH =); 14 ($CO_2CH_2CH_3$); 7.6 (CH_3CH_2C=O). MS, *m*/*z*: 196 ($M^{+\cdot}$, 4); 140 (33); 111 (22); 57 (100); 29 (46); exact mass M^+ 196.2455 (Calcd. for $C_{11}H_{16}O_3$ 196.2413).

6-Acetyl cyclohex-1-ene carboxylic acid ethyl ester 7c. IR ($CHCl_3$, ν cm^{-1}): 1707 (C=O); 1651 (C=C). ^{1}H NMR (300 MHz, $CDCl_3$): 7.20 (t, 1H, $J = 4.1$ Hz); 4.17 (q, 2H, $J = 7.2$ Hz); 3.61 (m, 1H); 2.25 (s, 3H); 2,23

(m, 2H); 1.84 (m, 2H); 1.59 (m, 2H); 1.26 (t, 3H, $J = 7.2$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$): 209.6 ($CH_3\underline{C}{=}O$); 166.0 ($\underline{C}O_2C_2H_5$); 142.1 (CH=$\underline{C}$); 129.1 ($\underline{C}H{=}C$); 60.4 ($CO_2\underline{C}H_2CH_3$); 47.4 ($\underline{C}HCOCH_3$); 28.5 ($\underline{C}H_2CH{=}C$); 25.7 ($\underline{C}H_3C{=}O$); 25.0 ($\underline{C}H_2CH_2CH{=}$) 18.6 ($CH_2\underline{C}H_2CH$); 14.1 ($CO_2CH_2\underline{C}H_3$). MS, *m*/*z*: 154 (100); 108 (53); 79 (53); 43 (52); exact mass M^+ 196.2433 (Calcd. for $C_{11}H_{16}O_3$ 196.2446).

6-Propionyl cyclohex-1-ene carboxylic acid methyl ester 7d. IR ($CHCl_3$, ν cm^{-1}): 1708 (C=O); 1650 (C=C). ^{1}H NMR (300 MHz, $CDCl_3$): 7.12 (t, 1H, $J = 4$ Hz); 3.61 (s, 3H); 3.53 (m, 1H); 2,54 (q, 2H, $J = 7.4$ Hz); 2.17 (m, 2H); 1.77 (m, 2H), 1.51 (m, 2H); 1.03 (t, 3H, $J = 7.2$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$): 212.0 ($CH_3CH_2\underline{C}{=}O$); 167.0 ($\underline{C}O_2C_2H_5$); 142.0 (CH=$\underline{C}$); 128.8 ($\underline{C}H{=}C$); 60.3 ($CO_2\underline{C}H_3$); 51.4 ($\underline{C}HCOCH_2$); 46.5 ($\underline{C}H_2CH{=}O$); 34.4 ($\underline{C}H_2CH{=}C$); 25.2 ($\underline{C}H_2CH_2CH{=}$); 18.5 ($CH_2\underline{C}H_2CH$); 7.7 ($COCH_2\underline{C}H_3$). MS, *m*/*z*: 164 (22); 140 (32); 108 (30); 79 (30); 57 (100); 29 (23); exact mass M^+ 210.2746 (Calcd. for $C_{12}H_{18}O_3$ 210.2736).

5-Acetyl cyclopent-1-ene carbonitrile 8a. IR ($CHCl_3$, ν cm^{-1}): 2224 (C≡N); 1717 (C=O); 1612 (C=C). ^{1}H NMR (300 MHz, $CDCl_3$): 6.84 (m, 1H); 3.87 (m, 1H); 2,61 (m,2H); 2.28 (s, 3H); 2.35, 2.17 (2m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 205.6 ($CH_3\underline{C}{=}O$); 152.1 (CH=$\underline{C}$); 115.6 ($\underline{C}H{=}C$); 112.9 ($\underline{C}{\equiv}N$); 58.7 ($\underline{C}HCOCH_3$); 32.6 ($\underline{C}H_2CH{=}C$); 28.3 ($\underline{C}H_3C{=}O$); 26.1 ($\underline{C}H_2CH_2CH{=}$). MS, *m*/*z*: 135 ($M^{+\cdot}$, 6); 92 (10); 43 (100); exact mass M^+ 135.1654 (Calcd. for C_8H_9NO 135.1635).

5-Propionyl cyclopent-1-ene carbonitrile 8b. IR ($CHCl_3$, ν cm^{-1}): 2223 (C≡N); 1717 (C=O); 1611 (C=C). ^{1}H NMR (300 MHz, $CDCl_3$): 6.84 (m, 1H); 3.87 (m, 1H); 2.65–2.57 (m, q, 4H, $J = 7.2$ Hz); 2.3–2.12 (m, 2H); 1.10 (t, 2H, $J = 7.2$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$): 208.4 ($CH_3CH_2\underline{C}{=}O$); 152.1 (CH=$\underline{C}$); 115.7 ($\underline{C}H{=}C$); 113.2 ($\underline{C}{\equiv}N$); 57.9 ($\underline{C}HCOCH_2$); 34.7 ($\underline{C}H_2C{=}O$); 32.8 ($\underline{C}H_2CH{=}C$); 26.5 ($\underline{C}H_2CH_2CH{=}$); 7.3 ($COCH_2\underline{C}H_3$). MS, *m*/*z*: 149 ($M^{+\cdot}$, 2); 92 (9); 57 (100); 29 (39); exact mass M^+ 149.1965 (Calcd. for $C_9H_{11}NO$ 149.1924).

6-Acetyl cyclohex-1-ene carbonitrile 8c. IR ($CHCl_3$, ν cm^{-1}): 2220 (C≡N); 1715 (C=O); 1633 (C=C). ^{1}H NMR (300 MHz, $CDCl_3$): 6.84 (td, 1H, $J = 4$ Hz, $J = 1.8$ Hz); 3.37 (m, 1H); 2.28 (s, 3H); 2.24 (m, 2H); 1.91 (m, 2H); 1.65 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 206.5 ($CH_3\underline{C}{=}O$); 148.5 (CH=$\underline{C}$); 118.9 ($\underline{C}H{=}C$); 110.6 ($\underline{C}{\equiv}N$); 49.5 ($\underline{C}HCOCH_3$); 28.5 ($\underline{C}H_2CH{=}C$); 25.7 ($\underline{C}H_3C{=}O$); 24.5 ($\underline{C}H_2CH_2CH{=}$); 18.4 ($CH_2\underline{C}H_2CH$). MS, *m*/*z*: 149 ($M^{+\cdot}$, 3); 106 (23); 43 (100); exact mass M^+ 149.1944 (Calcd. for $C_9H_{11}NO$ 149.1948).

6-Propionyl cyclohex-1-ene carbonitrile 8d. IR ($CHCl_3$, ν cm^{-1}): 2220 (C≡N); 1717 (C=O); 1622 (C=C). ^{1}H NMR (300 MHz, $CDCl_3$): 6.83 (td, 1H, $J = 4$ Hz, $J = 1.5$ Hz); 3.39 (m, 1H); 2,60 (q, 2H, $J = 7.3$ Hz); 2.22 (m,

2H); 1.77, 1.65 (2m, 4H); 1.09 (t, 3H, $J = 7.3$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$): 209.3 ($CH_3CH_2\underline{C}$=O); 148.2 (CH=$\underline{C}$); 118.9 ($\underline{C}$H=C); 48.6 ($\underline{C}$HCOCH_2); 34.6 ($\underline{C}H_2$CH=O); 26.07 ($\underline{C}H_2$CH=C); 24.5 ($\underline{C}H_2CH_2$CH=); 18.5 ($CH_2\underline{C}H_2$CH); 7.8 (CO$CH_2\underline{C}H_3$). MS, *m*/*z*: 106 (8); 57 (100); 29 (28); exact mass M^+ 163.2241 (Calcd. for $C_{10}H_{13}NO$ 163.2228).

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