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A CONVENIENT STEREOSELECTIVE SYNTHESIS OF CONJUGATED DIENOIC ESTERS AND AMIDES †

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Abstract: (2E,4E)-Dienoic esters and amides could be synthesized via the stereoselective isomerization of the corresponding 2-ynoic esters and amides, respectively, under the catalysis of ruthenium or iridium complexes.

The stereoselective synthesis of conjugated dienes is one of the important problems in organic and natural product chemistry.[1] The isomerization of alkynes to conjugated dienes can represent a useful synthetic approach due to the ready accessibility and elaboration of alkynes. Recently, there have appeared several reports about the highly stereoselective synthesis of (E,E)-α,β-γ,δ-dienones via isomerization of α,β-ynones effected by transition metal complexes.[2] In our results,[2a,2b] it was found that an activation group, carbonyl group, at the α-position of the triple bond is important for this reaction, which led us to study the isomerization of acetylenic derivatives with other electron withdrawing groups and the carboxyl group was tried. In a preliminary communication,[3] we have reported the isomerization of 2-ynoic esters to (2E,4E)-dienoic esters catalyzed by $RuH_2(Ph_3P)_4$ or $IrH_5(i\text{-}Pr_3P)_2$. Herein, we wish to describe in detail the reactions of 2-ynoic esters, 2-ynoic amides and 2-ynoic acids catalyzed by $RuH_2(Ph_3P)_4$ or $IrH_5(i\text{-}Pr_3P)_2$.

(2E,4E)-Dienoic esters

(2E,4E)-Dienoic esters are valuable synthetic intermediates.[4] Many naturally occurring compounds such as insecticides and insect pheromones were synthesized using (2E,4E)-dienoic esters as starting materials. Some (2E,4E)-dienoic esters such as (2E,4E)-decadienoic esters are also aromatic substances.[4a,5] Representative literature procedures to synthesize these compounds involves Wittig reaction[4a,4b] and the elimination reactions,[4c,4d] but only a few of them gave exclusively (2E,4E)-dienoic esters by a simple procedure.[4]

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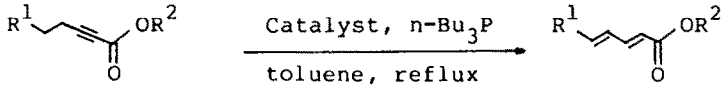
† Respectfully dedicated to Professor Yu Wang on the occasion of his 80th birthday.

2-Ynoic esters (**1**) can be readily prepared by the reaction of an acetylenic carbanion with carbon dioxide followed by esterification with an alcohol in high yield.[6] Heating **1** with 1 mol% of a ruthenium or iridium hydride complex in the presence of n-Bu_3P in toluene at reflux led to the formation of dienoic esters (**2**):



1 **2**

a: R^1=CH_3, R^2=CH_3; **b**: R^1=CH_3, R^2=C_2H_5; **c**: R^1=C_2H_5, R^2=CH_3;
d: R^1=C_2H_5, R^2=C_2H_5; **e**: R^1=n-C_3H_7, R^2=CH_3; **f**: R^1=n-C_3H_7, R^2=C_2H_5;
g: R^1=n-C_5H_{11}, R^2=CH_3; **h**: R^1=n-C_5H_{11}, R^2=C_2H_5.

Table 1. Isomerization of 2-ynoic esters to (2E,4E)-dienoic esters catalyzed by $IrH_5(i\text{-}Pr_3P)_2$

Entry	2-Ynoic ester **1**	n-Bu_3P/cat.	Solvent	Temp. (°C)	Time (h)	Yield of **2**[a] (%)
1	**1c**	0	benzene	80	24	48[b]
2	**1c**	4	benzene	80	30	87
3	**1g**	4	benzene	80	24	92
4	**1a**	4	toluene	110	24	85
5	**1e**	4	toluene	110	24	89
6	**1f**	4	toluene	110	24	90

a: Isolated yield. All products gave satisfactory IR, ^1H NMR and MS data.

b: Determined by ^1H NMR spectra.

The representative results using $IrH_5(i\text{-}Pr_3P)_2$ or $RuH_2(Ph_3P)_4$ as the catalyst are shown in Table 1 and 2, respectively. Alkyl phosphine ligands are also important for this reaction.[2b] In the absence of n-Bu_3P, the $IrH_5(i\text{-}Pr_3P)_2$ catalyzed isomerization of methyl 2-heptynoate (**1c**) gave poor yield, but the same reaction gave complete conversion by adding 4 mol% of n-Bu_3P (compare entries 1 and 2). Complex $IrH_5(i\text{-}Pr_3P)_2$ has higher catalytic activity than $RuH_2(Ph_3P)_4$ (compare entries 1 and 7). The presence of different phosphine ligands in these two complexes may be the major reason of the different reactivity.[2b] 2-Ynoic esters have lower reactivity than α,β-ynones, for example, under the catalysis of 1 mol% of $IrH_5(i\text{-}Pr_3P)_2$, 3-octyn-2-one gave almost quantitative conversion at 60°C for 24 h,[2b] while methyl hep-

Table 2. Isomerization of 2-ynoic esters to (2E,4E)-dienoic esters catalyzed by $RuH_2(Ph_3P)_4$

Entry	2-Ynoic esters 1	n-Bu_3P/cat.	Solvent	Temp. (°C)	Time (h)	Yield of 2[a] (%)
7	**1c**	0	benzene	80	24	0[b]
8	**1c**	6	benzene	80	24	58[b]
9	**1g**	0	toluene	110	36	93[c]
10	**1h**	6	toluene	110	28	90
11	**1d**	6	toluene	110	30	86
12	**1b**	6	toluene	110	30	88

a: Isolated yield. All products gave satisfactory IR, ^1H NMR and MS data.

b: Determined by ^1H NMR spectra.

c: Five equivalents of basic alumica were added.

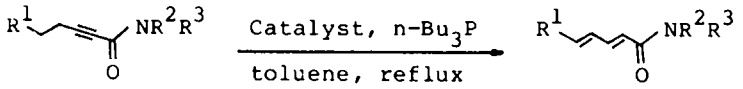
tynoate gave only 48% conversion at 80°C for 24 h (entry 1). Alumina can also influence this reaction,[7] thus, in the presence of 5 equivalents of basic alumina, $RuH_2(Ph_3P)_4$ could catalyze the isomerization of methyl 2-decynoate (**1g**) yielding quantitatively isomerized product even in the absence of n-Bu_3P (entry 9).

Similar to (E,E)-α,β-γ,δ-dienones,[2a,2b] while using $CDCl_3$ or CCl_4 as solvent, the ^1H NMR gave difficultly recognized spin-spin coupling constant of H_γ and H_δ.[4a,4b] The stereochemistry of (2E,4E)-dienoic esters can be determined by ^1H NMR using C_6D_6 as solvent, which showed that the reaction is highly stereoselective. Therefore, our results may provide a useful method for the stereoselective synthesis of (2E,4E)-dienoic esters.

(2E,4E)-Dienoic amides

(2E,4E)-Dienoic amides are important structural features of a number of natural products, which have been reported to be physiologically active and can be used as insecticides. Some well known examples of them include Pellitrorine,[4c] Achillea,[8] and Trichonine.[9] There are several novel methods for their synthesis involving the successful Wittig reaction,[10] elimination reaction,[11] and amidation of corresponding dienoic acids[4c] or esters.[9]

2-Ynoic amides can also form (2E,4E)-dienoic amides under the catalysis of $IrH_5(i\text{-}Pr_3P)_2$ or $RuH_2(Ph_3P)_4$ by lengthening the reflux time. These reactions usually gave products in good isolated yield as shown in Table 3. It is shown that 2-ynoic amides are less active than the corresponding 2-ynoic esters. A dilute solution should be used for the monosubstituted amides in order to prevent the polymerization (entries 19 and 20), and the yield is lower.



3 **4**

a: $R^1=C_2H_5$, $R^2,R^3=-(CH_2)_4-$; **b**: $R^1=C_2H_5$, $R^2,R^3=-(CH_2)_5-$;
c: $R^1=n-C_5H_{11}$, $R^2,R^3=-(CH_2)_5-$; **d**: $R^1=n-C_9H_{19}$, $R^2,R^3=-(CH_2)_4-$;
e: $R^1=n-C_5H_{11}$, $R^2,R^3=-(CH_2)_5-$; **f**: $R^1=n-C_5H_{11}$, $R^2=i-C_4H_9$, $R^3=H$;
g: $R^1=n-C_9H_{19}$, $R^2=i-C_4H_9$, $R^3=H$.

Table 3. Isomerization of 2-ynoic amides[a] to (2E,4E)-dienoic amides catalyzed by $IrH_5(i-Pr_3P)_2$ or $RuH_2(Ph_3P)_4$

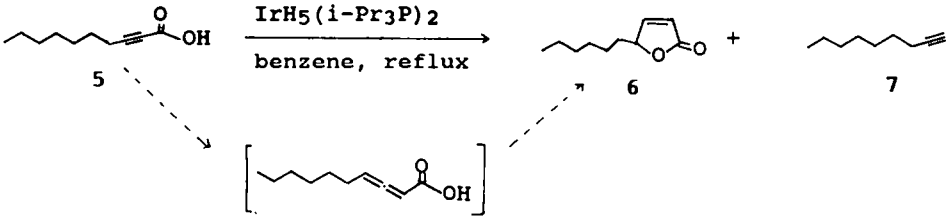
Entry	2-Ynoic amides 3	Catalyst	Time (h)	Yield of 4[b] (%)
13	**3a**	$RuH_2(Ph_3P)_4$	48	92
14	**3b**	$RuH_2(Ph_3P)_4$	48	90
15	**3b**	$IrH_5(i-Pr_3P)_2$	48	88
16	**3c**	$IrH_5(i-Pr_3P)_2$	48	91
17	**3d**	$IrH_5(i-Pr_3P)_2$	52	90
18	**3e**	$IrH_5(i-Pr_3P)_2$	52	90
19	**3f**	$IrH_5(i-Pr_3P)_2$	40	80
20	**3g**	$IrH_5(i-Pr_3P)_2$	40	78

a: Reaction condition: entries 13-18: 2-ynoic amide (3 mmol), catalyst (0.06 mmol), $n-Bu_3P$ (0.24 mmol) and toluene (5 ml) at reflux; entries 19 and 20: 2-ynoic amide (3 mmol), catalyst (0.03 mmol), $n-Bu_3P$ (0.12 mmol) and toluene (10 mmol) at reflux.

b: Isolated yield.

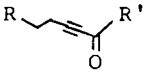
The stereochemistry of the products can be determined by ^1H NMR in C_6D_6 as trans-trans geometry. Using this isomerization reaction, the following dienoic amides have been synthesized: N-(2E,4E-decadienoyl)-piperidine (**4c**, Achillea amide[8a]), N-(2E,4E-tetradecadienoyl)-pyrrolidine (**4d**, Achillea amide[8b]), N-(2E,4E-tetradecadienoyl)-piperidine(**4e**, isolated from Otanthus Maritimus[12]), N-isobutyl-N-(2E,4E-decadienoyl)-amide (**4f**, Pellitrorine[4c]) and N-isobutyl-N-(2E,4E-tetradecadienoyl)-amide (**4g**, occurred in Leuocylus Formosus[13]).

The mechanism of the present reaction may be similar to that we have proposed for the reaction of α,β-ynones.[2a,2b] In the transition metal complexes catalyzed isomerization reaction of α,β-ynone, allenone was proposed to be the possible intermediate, but no direct evidence has been found.[2] On further study of the transition metal complexes catalyzed isomerization of substituted alkynes, some results were found supporting this mechanism. Under the catalysis of $IrH_5(i\text{-}Pr_3P)_2$, 2-decynoic acid (**5**) was heated in benzene at reflux for 24 h to give a mixture of 5-hexyl-2(5H)-furanone (**6**) and 1-nonyne (**7**) in the ratio of 2:3. A similar result was obtained by using $RuH_2(Ph_3P)_4$ as the catalyst. Allenoic acid, either free or still complexed to the metal complex, appears to be the possible intermediate, lactonization of which may take place to give **6**.[14,15] The alkyne (**7**) may result from the decarboxylation of alkynoic acid. Tsuji's work about the isomerization of 2,3-dienoic ester to 2,4-dienoic ester[16] gives another evidence to this mechanism.



From above results, it is obvious that in order to carry out the isomerization of the triple bond, a carbonyl group is necessary at the α-position of the triple bond and excess phosphine is important for this reaction. In most cases, catalysts with aliphatic phosphines are more active than that with aromatic phosphines. The addition of excess phosphine may increase the electron density of the transition metal and make the triple bond more active.

It was shown that the order of reactivity for the isomirization of the substituted alkynes to substituted dienes is:



R': alkyl group > alkoxyl group > amino group

Experimental

All the transition metal complexes catalyzed reactions were carried out under a prepurified nitrogen atmosphere. Benzene was distilled from sodium and benzophenone under nitrogen immediately before use. The boiling and melting points are uncorrected. ^1H NMR spectra were recorded on an EM-360, Varian XL-200 or Bruker MSL-300 spectrometer. Chemical shifts are reported as values in parts per million with Me_4Si as an internal standard. Infrared

spectra were recorded as liquid film or KBr disc on Shimadzu IR-440 spectrometer. Mass spectra were obtained on a Finnigan 4021 GC/MS/DC instrument. High resolution mass spectral data were determined on Finnigan-MAT 8430 spectrometer.

Materials: 2-Ynoic esters were prepared according to the reported methods,[6,17] compound and boiling point are as follows: methyl 2-hexynoate (**1a**), 89-90°C/19 mm (literature:[17] 65°C/10 mm); ethyl 2-hexynoate (**1b**),[18] 116-118°C/19 mm; methyl 2-heptynoate (**1c**), 82-83°C/14 mm (literature:[17] 72°C/10 mm); ethyl 2-heptynoate (**1d**),[18] 82-84°C/8 mm; methyl 2-octynoate (**1e**), 80-81°C/6 mm(literature:[17] 94°C/10 mm); ethyl 2-octynoate (**1f**), 84-85°C/6 mm.

General procedure for the isomerization of 2-ynoic esters to (2E,4E)-dienoic esters catalyzed by $IrH_5(i\text{-}Pr_3P)_2$ + 4n-Bu_3P or $RuH_2(Ph_3P)_4$ + 6n-Bu_3P:

A mixture of **1** (4 mmol), catalyst (0.04 mmol) and n-Bu_3P (0-0.24 mmol) in toluene (or benzene) was heated at reflux for 24-30 h. After cooling and removal of solvent, the red residue was distilled under reduced pressure and **2** was obtained by short-path distillation as a colorless oil. The analytical data of products are as follows:

Methyl (2E,4E)-hexadienoate (**2a**): Colorless liquid; IR(neat): 3050, 1720, 1640, 1620 cm^{-1}; ^1H NMR(C_6D_6, 200 MHz): 1.48(d, 3H), 4.01(s, 3H), 5.60(dq, J_{54}=15.2 Hz, J_{56}=7.3 Hz, 1H), 5.72(dd, J_{43}=10.8 Hz, J_{45}=15.2 Hz, 1H), 5.78(d, J_{23}=15.5 Hz, 1H), 7.65(dd, J_{32}=15.5 Hz, J_{34}=10.8 Hz, 1H); MS(m/e): 126(M^+), 111, 81.

Ethyl (2E,4E)-hexadienoate (**2b**): Colorless liquid; IR(neat): 3050, 1720, 1640, 1620 cm^{-1}; ^1H NMR(C_6D_6, 200 MHz): 1.05(t, 3H), 1.45(d, 3H), 4.10(q, 2H), 5.65(dq, J_{54}=15.0 Hz, J_{56}=6.8 Hz, 1H), 5.85(dd, J_{43}=10.8 Hz, J_{45}=15.0 Hz, 1H), 5.90(d, J_{23}=15.2 Hz, 1H), 7.40(dd, J_{32}=15.2 Hz, J_{34}=10.8 Hz, 1H); MS(m/e): 140(M^+), 125, 95, 67.

Methyl (2E,4E)-heptadienoate (**2c**): Colorless liquid; IR(neat): 2960, 1720, 1642, 1618 cm^{-1}; ^1H NMR(C_6D_6, 200 MHz): 0.73(t, 3H), 1.80(m, 2H), 3.48 (s, 3H), 5.66(dt, J_{54}=15.0 Hz, J_{56}=7.0 Hz, 1H), 5.78(dd, J_{43}=10.8 Hz, J_{45}=15.0 Hz, 1H), 5.83(d, J_{23}=15.4 Hz, 1H), 7.45(dd, J_{32}=15.4 Hz, J_{34}=10.8 Hz, 1H); MS(m/e): 140(M^+), 111, 109.

Ethyl (2E,4E)-heptadienoate (**2d**): Colorless liquid; IR(neat): 3050, 1720, 1640, 1620 cm^{-1}; ^1H NMR(C_6D_6, 200 MHz): 0.83(t, 3H), 1.0(t, 3H), 1.82 (m, 2H), 4.12(q, 2H), 5.62(dt, J_{54}=15.3 Hz, J_{56}=7.2 Hz, 1H), 5.74(dd, J_{43}= 10.8 Hz, J_{45}=15.3 Hz, 1H), 5.80(d, J_{23}=15.5 Hz, 1H), 7.50(dd, J_{32}=15.5 Hz, J_{34}=10.8 Hz); MS(m/e): 154(M^+), 109, 81.

Methyl (2E,4E)-octadienoate (**2e**): Colorless liquid; IR(neat): 3045, 1720, 1640, 1620 cm^{-1}; ^1H NMR(C_6D_6, 200 MHz): 0.81(t, 3H), 1.20(m, 2H), 1.75

(m, 2H), 3.50(s, 3H), 5.68(dt, J_{54}=15.0 Hz, J_{56}=7.0 Hz, 1H), 5.85(dd, J_{43}=10.6 Hz, J_{45}=15.0 Hz, 1H), 5.90(d, J_{23}=15.4 Hz, 1H), 7.45(dd, J_{32}=15.4 Hz, J_{34}=10.6 Hz, 1H); MS(m/e): 154(M^+), 123, 111, 95, 81.

Ethyl (2E,4E)-octadienoate (**2f**): Colorless liquid; IR(neat): 3050, 1720, 1640, 1620 cm^{-1}; ^1H NMR(C_6D_6, 200 MHz): 0.80(t, 3H), 1.0(t, 3H), 1.2(m, 2H), 1.80(m, 2H), 4.12(q, 2H), 5.70(dt, J_{54}=15.2 Hz, J_{56}=7.0 Hz, 1H), 5.85(dd, J_{43}=10.8 Hz, J_{45}=15.2 Hz, 1H), 5.92(d, J_{23}=15.4 Hz, 1H), 7.50(dd, J_{32}=15.4 Hz, J_{34}=10.8 Hz, 1H); MS(m/e): 168(M^+), 123, 111, 95, 81.

Methyl (2E,4E)-decadienoate (**2g**): Colorless liquid; IR(neat): 3050, 1720, 1640, 1620 cm^{-1}; ^1H NMR(C_6D_6, 200 MHz); 0.71(t, 3H), 1.0(m, 6H), 1.60(m, 2H), 3.25(s, 3H), 5.49(dt, J_{54}=15.0 Hz, J_{56}=7.2 Hz, 1H), 5.66(dd, J_{45}=15.0 Hz, J_{43}=11.0 Hz, 1H), 5.70(d, J_{23}=15.4 Hz, 1H), 7.21(dd, J_{32}=15.4 Hz, J_{34}=11.0 Hz, 1H); MS(m/e): 182(M^+), 151, 111, 81.

Ethyl (2E,4E)-decadienoate (**2h**): Colorless liquid; IR(neat): 3050, 1720, 1640, 1620 cm^{-1}; ^1H NMR(C_6D_6, 200 MHz): 0.85(t, 3H), 1.0(t, 3H), 1.20(m, 6H), 1.80(m, 2H), 4.10(q, 2H), 5.70(dt, J_{54}=15.2 Hz, J_{56}=7.0 Hz, 1H), 5.85(dd, J_{43}=10.8 Hz, J_{45}=15.2 Hz, 1H), 5.90(d, J_{23}=15.4 Hz, 1H), 7.52(dd, J_{32}=15.4 Hz, J_{34}=10.8 Hz, 1H); MS(m/e): 198(M^+), 151, 125, 81.

N-(2-heptynoyl)piperidine (**3b**): Prepared by a similar procedure reported by Paphael.[20] A mixture of 2-heptynoic acid (10 g, 79 mmol) and oxalyl chloride (29.6 g, 231 mmol) was heated at reflux for about 40 min (the gas evolution ceased after about 10 min). The excess oxalyl chloride was removed under vacuum and the residue was flashly distilled to give 2-heptynoyl chloride.

A solution of piperidine (2.53 g, 215 mmol) and ether (40 ml) was added dropwise to the acid chloride prepared above at 0°C. After stirring for 1 h at room temperature, the reaction mixture was diluted with ether and washed with dilute sulfuric acid, sodium bicarbonate and water. The ether layer was dried over anhydrous sodium sulfate. After removal of ether, the residue was distilled at reduced pressure as a colorless liquid in 65% yield; bp 114-115°C/0.05 mm (literature[21]: 135°C/0.1 mm); IR(neat): 2240, 1650 cm^{-1}; ^1H NMR(CCl_4, 60 MHz): 1.0(t, 3H), 1.4(m, 4H), 1.8(m, 6H), 2.1(m, 2H), 3.6(m, 4H).

Following 2-ynoic amides were prepared using above method, compound, yield, boiling point and spectra data are as follows:

3a[21], 62%, 135-136°C/0.1 mm(literature: 135°C/0.1 mm); IR: 2240, 1650 cm^{-1}; ^1H NMR(CCl_4, 60 MHz): 1.0(t, 3H), 1.4(m, 4H), 1.9(m, 4H), 2.1(m, 2H), 3.6(m, 4H).

3c, 68%, 103-104°C/0.02 mm; IR(neat): 2240, 1650 cm^{-1}; ^1H NMR(CCl_4, 60 MHz): 1.0(t, 3H), 1.4-1.8(m, 16H), 2.1(m,2H), 3.6(m, 4H); MS(m/e): 235(M^+), 164, 150, 127, 84, 55; calculated exact mass for $C_{15}H_{25}ON$: 235.194, found:

235.193.

3d, 70%, 180°C/0.01 mm; IR(neat): 2240, 1650 cm^{-1}; ^1H NMR(CCl_4, 60 MHz): 1.0(t, 3H), 1.4-1.8(m, 22H), 2.21(t, 2H), 3.61(m, 4H); MS(m/e): 277(M^+), 193, 136, 98; calculated exact mass for $C_{18}H_{31}ON$: 277.240, found: 277.242.

3e, 73%, 179-181°C/0.01 mm; IR(neat): 2240, 1650 cm^{-1}; ^1H NMR(CCl_4, 60 MHz): 1.0(t, 3H), 1.4-1.8(m, 24H), 2.1(m, 2H), 3.6(m, 4H); MS(m/e): 291(M^+), 207, 150, 55; calculated exact mass for $C_{19}H_{33}ON$: 291.156, found: 291.258.

Compounds **3f** and **3g** were prepared according to the known method:

3f, 95%, mp 61-62°C; IR(KBr): 2240, 1650 cm^{-1}; ^1H NMR(CCl_4, 60 MHz): 1.0 (m, 9H), 1.2-1.8(m, 11H), 2.2(t, 2H), 3.0(m, 2H), 6.0(br. 1H); MS(m/e): 223 (M^+), 208, 168, 151, 81; calculated exact mass for $C_{14}H_{25}ON$: 223.196, found: 223.196.

3g, 88%, mp 48-49°C; IR(KBr): 2240, 1650 cm^{-1}; ^1H NMR(CCl_4, 60 MHz): 1.0 (m, 9H), 1.2-1.8(m, 19H), 2.2(t, 2H), 3.0(m, 2H), 6.0(br. 1H); MS(m/e): 279 (M^+), 264, 207, 152, 81; calculated exact mass for $C_{18}H_{33}ON$: 279.258, found: 279.258.

General procedure for the isomerization of 2-ynoic amides catalyzed by $IrH_5(i\text{-}PrP)_2$ + 4n-BuP_3 or $RuH_2(PhP)_4$ + 4n-BuP_3:

A solution of **3** (3 mmol), catalyst (0.06 mmol) and n-BuP_3(0.24 mmol) in toluene was heated at reflux for about 50 h. After cooling and removal of solvent, the red residue was distilled under reduced pressure or purified by passing through a short column of silica gel to give the product.

N-(2E,4E-Heptadienoyl)-pyrrolidine (**4a**): Colorless liquid, bp 110°C/0.01 mm(bath temperature); IR(neat): 3050, 1650 cm^{-1}; ^1H NMR(C_6D_6, 200 MHz): 0.7(t, 3H), 1.2(m, 4H), 1.85(m, 2H), 3.20(m, 4H), 5.75(dt, J_{54}=15.0 Hz, J_{56}= 7.5 Hz, 1H), 6.05(dd, J_{43}=10.8 Hz, J_{45}=15.0 Hz, 1H), 6.15(d, J_{23}=15.1 Hz, 1H), 7.60(dd, J_{32}=15.1 Hz, J_{34}=10.8 Hz, 1H); MS(m/e): 179(M^+), 150, 136, 81; calculated exact mass for $C_{11}H_{17}ON$: 179.131, found: 179.131.

N-(2E,4E-Heptadienoyl)-piperidine (**4b**): Colorless liquid, bp 110°C/0.01 mm(bath temperature); IR(neat): 3050, 1650 cm^{-1}; ^1H NMR(C_6D_6, 200 MHz): 0.7(t, 3H), 1.2(m, 6H), 1.90(m, 2H), 3.20(m, 4H), 5.80(dt, J_{54}=14.8 Hz, J_{56}= 7.3 Hz, 1H), 6.10(dd, J_{43}=11.0 Hz, J_{45}=14.8 Hz, 1H), 6.20(d, J_{23}=15.0 Hz, 1H), 7.67(dd, J_{32}=15.0 Hz, J_{34}=11.0 Hz, 1H); MS(m/e): 193(M^+), 150, 81, 55; calculated exact mass for $C_{12}H_{19}ON$: 193.147, found: 193.146.

N-(2E,4E-Decadienoyl)-piperidine (**4c**): Colorless liquid; IR(neat): 3050, 1650 cm^{-1}; ^1H NMR(C_6D_6, 300 MHz): 0.7(t, 3H), 1.1(m, 12H), 1.84(m, 2H), 3.20 (m, 4H), 5.75(dt, J_{54}=15.0 Hz, J_{56}=7.4 Hz, 1H), 6.13(dd, J_{43}=11.0 Hz, J_{45}= 15.0 Hz, 1H), 6.17(d, J_{23}=15.0 Hz, 1H), 7.69(dd, J_{32}=15.0 Hz, J_{34}=11.0 Hz, 1H); MS(m/e); 235(M^+), 150, 81, 55.

N-(2E,4E-Tetradecadienoyl)-pyrrolidine (**4d**): Pale yellow liquid; IR

(neat): 3050, 1650 cm^{-1}; ^1H NMR(C_6D_6, 300 MHz): 0.7(t, 3H), 1.1(m, 18 H), 1.82(m, 2H), 3.20(m, 4H), 5.74(dt, J_{54}=15.0 Hz, J_{56}=7.5 Hz, 1H), 6.09(dd, J_{43}=10.7 Hz, J_{45}=15.0 Hz, 1H), 6.15(d, J_{23}=14.9 Hz, 1H), 7.61(dd, J_{32}=14.9 Hz, J_{34}=10.7 Hz, 1H); MS(m/e): 277(M^+), 150, 81.

N-(2E,4E-Tetradecadienoyl)-piperidine (**4e**): Pale yellow liquid; IR (neat): 3050, 1650 cm^{-1}; 1H NMR(C_6D_6, 300 MHz): 0.7(t, 3H), 1.1(m, 20H), 1.80(m, 2H), 3.20(m, 4H), 5.75(dt, J_{54}=14.9 Hz, J_{56}=7.3 Hz, 1H), 6.10(dd, J_{43}=10.8 Hz, J_{45}=14.9 Hz, 1H), 6.15(d, J_{23}=15.1 Hz, 1H), 7.60(dd, J_{32}=15.1 Hz, J_{34}=10.8 Hz, 1H); MS(m/e); 291(M^+), 150, 81, 55.

N-Isobutyl-N-(2E,4E-decadienoyl)amide (**4f**): Pale yellow solid; mp 91-92°C; IR(KBr): 3050, 1650 cm^{-1}; ^1H NMR(C_6D_6, 300 MHz): 0.8(m, 9H), 1.2(m, 7H), 1.8(t, 2H), 3.35(t, 2H), 5.76(m, 1H), 5.85(dt, J_{54}=14.8 Hz, 1H), 6.18 (dd, J_{43}=11.0 Hz, J_{45}=14.8 Hz, 1H), 6.20(dd, J_{23}=15.0 Hz, 1H), 7.60(dd, J_{32}= 15.0 Hz, J_{34}=11.0 Hz, 1H); MS(m/e): 223(M^+), 207, 151, 81.

N-Isobutyl-N-(2E,4E-tetradecadienoyl)amide (**4g**): Pale yellow solid; mp 52-54°C; IR(KBr): 3050, 1650 cm^{-1}; ^1H NMR(C_6D_6, 300 MHz): 0.8(m, 9H), 1.2(m, 15H), 1.8(t, 2H), 3.35(t, 2H), 5.78(m, 1H), 5.83(dt, J_{54}=15.0 Hz, 1H), 6.16(dd, J_{43}=10.8 Hz, J_{45}=15.0 Hz, 1H), 6.20(dd, J_{23}=15.1 Hz, 1H), 7.59(dd, J_{32}=15.1 Hz, J_{34}=10.8 Hz, 1H); MS(m/e): 279(M^+), 263, 219, 183, 152, 81.

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