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Communication

Indium(I) bromide-mediated coupling of dibromoacetonitrile with aldehydes followed by Boord elimination of bromine and oxygen of β-bromo alkoxides for preparation of 3-organyl-2-alkenenitriles

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Abstract

The organoindium compound derived from indium monobromide and dibromoacetonitrile reacts with carbonyl compounds to afford the corresponding 2-bromo-2-cyano-indium(III) alkoxide. The action of a second equivalent of indium monobromide onto the alkoxides derived from aldehydes promotes the Boord elimination of the β-related oxygen and bromine atoms leading to 2-alkenenitriles.

Keywords: Indium; Organoindium; Carbon–carbon bond formation; Boord elimination; Oxygen extrusion; Sequenced chemical reactions

1. Introduction

Sequenced chemical reactions are an attractive new tool for the synthetic organic chemist. They provide a single-step process, normally carried out in one-pot, to a desired target molecule, whose formation needs several chemical transformations. The stored information acquired while studying the chemical properties of indium(I) compounds made possible the development of a new example of sequenced chemical reactions, mediated by indium(I) salts, leading to useful organic substances.

The most characteristic reaction of indium(I) compounds is the oxidative insertion into a suitable chemical bond [1]. Indium monohalides, for instance, are easily oxidized to the corresponding dihalogeno-α-halogenoalkyl-indium(III) compounds by insertion into one of the carbon–halogen bonds of *gem*-dihalogenoalkane derivatives (Scheme 1).

The electronic character of the α-halogenoalkylic carbon atom is determined by the nature of its substituents, R^1 and R^2 [1]. Organoindium species with electrophilic organyl substituents results from an interaction of the lone pairs of electrons on the α-halide substituent with an empty metal orbital ($R^1 = R^2 = H$; X = Br, I). α,α-Dihalogenonitriles [2] and α,α-dihalogenoketones [3] produce organometallics containing nucleophilic organyl substituents, and as such they conveniently couple with carbonyl compounds leading to new carbon–carbon bonds. In this work, we focus on the reaction involving InBr, dibromoacetonitrile and carbonyl compounds, which produced a novel example of sequenced chemical reactions promoted by InBr.

2. Results and discussion

Scheme 2 shows the sequenced reactions. We have demonstrated that the primary organometallic intermediate, (bromo-cyano-methyl)-dibromo-indium(III), **1** couples efficiently with selected carbonyl compounds, **2** to afford the indium(III) alkoxide, **3** [2]. The action of one molar equivalent of InBr on the alkoxide **3**, in refluxing THF, produces the organodimetallic intermediate, **4** believed to be the key intermediate leading to the alkenenitrile, **5**. The transformation **3** → **5**, which is verified only in reactions involving

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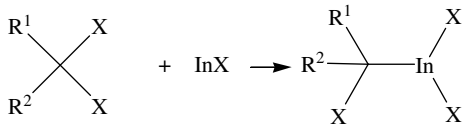
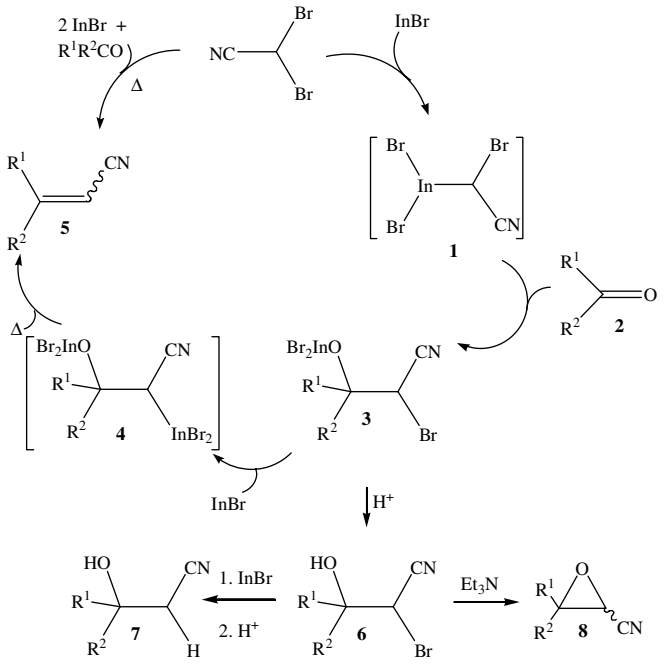


Scheme 1. Oxidative insertion of InX into the carbon–halogen bond of *gem*-dihaloalkanes.



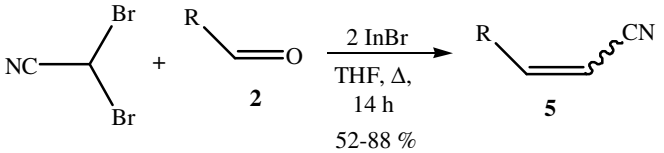
Scheme 2. Indium(I) bromide-promoted sequenced reactions between dibromoacetonitrile and carbonyl compounds.

aldehydes (see below), is equivalent to a Boord-type elimination of β-related bromine and oxygen atoms of the alkoxide **3** [4]. This reaction is very sensitive to moisture, which is in fact responsible for the alcohol side products **6** and **7**. As we have demonstrated, hydrolysis of alkoxide **3** gave 2-bromo-3-hydroxynitriles, **6** [2a]. The hydroxynitriles **7** are derived from **6** by reduction of their carbon–bromine bond promoted by InBr. Finally, compounds **6** are also easily transformed in the epoxides **8** [2a].

Of course, the conversion of the aldehyde **2** into the alkenenitrile **5** is more conveniently achieved by the direct action of two equivalents of InBr on a mixture containing equivalent quantities of the aldehyde **2** and dibromoacetonitrile. The results of these experiments are depicted in Table 1.

The efficiency of the reaction is governed by the primary coupling between the organoindium **1** and the carbonyl compounds leading to the alkoxide **3**. We have determined in previous studies that the best yields for this coupling occurred with aromatic aldehydes containing electron withdrawing groups [2a], which again offered superior yields of the alkenenitriles **5**. The reaction failed for acetophenone;

Table 1
Indium(I) bromide-promoted preparation of alkenenitriles



Entry	R	Yield (%)	*Z*/*E*
a	C_6H_5	88	1.4/1.0
b	*o*-Cl–C_6H_4	65	1.4/1.0
c	*p*-Cl–C_6H_4	80	1.0/1.2
	p-Cl–C_6H_4[a]	73	1.0/3.5
d	*o*-Br–C_6H_4	71	2.2/1.0
e	*p*-Br–C_6H_4	53	1.0/1.2
	p-Br–C_6H_4[a]	63	1.0/2.6
f	*p*-CH_3–C_6H_4	62	1.2/1.0
g	*o*-CH_3O–C_6H_4	62	1.0/1.5
h	*p*-CH_3O–C_6H_4	52	1.2/1.0
i	$^nC_6H_{13}$	60	1.3/1.0
j	$^nC_9H_{19}$	63	1.3/1.0
k	(*E*)–C_6H_5–CH=CH	55	1.8/1.0

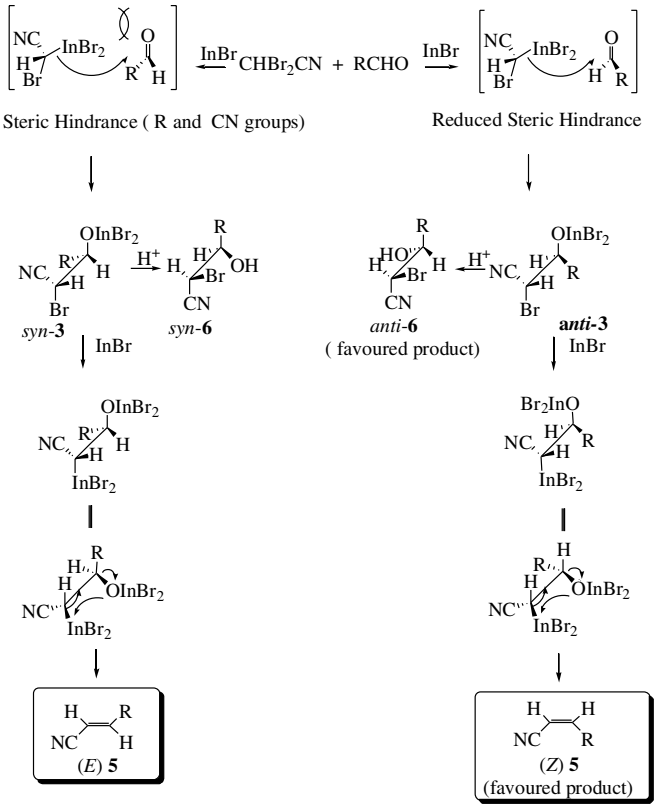
[a] Reaction with dichloroacetonitrile.

and since we have obtained the corresponding alcohol **6** from this ketone [2a], we attribute this drawback to the failure of InBr to insert into the carbon–bromine bond of the indium(III) alkoxide **3** to form the intermediate **4**.

The stereoselectivity of the process also depends on the primary coupling. In general, the *Z*/*E* diastereomeric ratios determined for compounds **5** follow closely the *syn*/*anti* ratio determined preliminarily for the alcohols **6** [2a]. Scheme 3 describes the direct relationship between stereoisomers **5** and the diastereoisomers **3**.

It is also possible to carry out the coupling followed by the elimination reactions with dichloroacetonitrile with comparable efficiency (Table 1, entries c and e), although in these cases significative enhancement of the stereoselectivity towards the *E*-isomer was observed.

In summary, this work shows how to use indium monohalides to produce reactive organoindium(III) species from *gem*-dihalogenoalkanes, capable of useful organic sequenced transformations. It establishes an attractive alternative to the Boord reaction to extrude oxygen from carbonyl compounds to generate olefins [5], in which the key step is the ejection of the β-related bromine and oxygen atoms of the 2-bromo-3-alkoxynitrile intermediates **3**. Further, the work offers a single step, one-pot, new protocol for preparing 3-organyl-2-alkenenitriles, **5**. Compounds **5** have been prepared by dehydration of β-hydroxynitriles promoted by strong bases [6]. The present method, which is conducted under neutral conditions, enhances significantly the formation of the *Z*-isomers in the resulting mixtures. Improvements on the stereoselectivity of the reaction, as dictated by the proposed mechanism, depend on the presence of a bulky substituent attached to the dihalogenonitrile, since it is expected that steric hindrance between this group and the organyl aldehyde substituent would determine the reaction stereoselectivity.



Scheme 3. Proposed reaction pathway of the indium(I) bromide-promoted sequenced reactions between dibromoacetonitrile and carbonyl compounds.

To this end, we would like to point out the differences between the present results with the very similar reaction between α,α-dibromoacetonitrile and benzaldehyde promoted by indium metal, which leads to a low yield of a complex mixture of products containing 2-cyano-phenyl-oxyrane (34%, *cis*:*trans* = 2:1), 2,2-dibromo-3-hydroxy-3-phenyl-propanenitrile (13%), 2-bromo-3-phenylpropenenitrile (4%) and 3-phenylpropenenitrile (4%) [7]. The nature of the products suggests that the reaction between metallic indium and $CHBr_2CN$ produces two distinct organoindium compounds carrying the organometallic units In–CBr_2CN, with the metal acting as a reducing agent and In–CHBrCN, produced by an oxidative insertion of the metal into one of the carbon–bromine bonds of $CHBr_2CN$. The organoindium product containing the In–CHBrCN unit is responsible for the generation of 2-cyano-phenyl-oxyrane and 3-phenyl-propenenitrile, while the product containing the In–CBr_2CN unit gives 2,2-dibromo-3-hydroxy-3-phenyl-propanenitrile and 2-bromo-3-phenylpropenenitrile. The chemioselectivity obtained from reactions promoted by InBr allows the selective production of the α-bromo-β-hydroxynitriles **6**, the oxiranes **8**, the β-hydroxynitriles **7**, and/or the alkenenitriles **5** via the organoindium intermediate **1**; and as also pointed in our earlier studies [3,8], the use of indium monobromide as the promoter of organic reactions may lead to different products than those obtained from reactions mediated by metallic indium.

3. Experimental

3.1. The intermolecular coupling of dibromoacetonitrile with aldehydes/Boord elimination of bromine and oxygen of β-bromo alkoxides for preparation of 3-organyl-2-alkenenitriles

A Schlenk test tube equipped with a condenser, truly dried under high vacuum, was charged with 2 mL of dry (sodium) THF, 195 mg (1.0 mmol) of the red solid InBr and dibromoacetonitrile (0.5 mmol). To this mixture was added 0.5 mmol of the aldehyde and the reaction was kept under reflux for l4 h. At the end of this period, the reaction was quenched with water. The organics were extracted with ethyl acetate. The extract was dried (Na_2SO_4) and evaporated to dryness. The alkenenitriles **5** were separated as a mixture of isomers by column chromatography with hexanes. The diastereomeric *Z*:*E* ratios were determined by ^1H NMR spectroscopy. TLC (in hexanes) allowed separation of the pure *Z* and *E* diastereoisomers. The only exception was the alkenenitriles derived from decanal, **5j** which could not be separated. Yields of reactions and diastereomeric ratios are given in Table 1.

3.2. The preparation of 3-(4′-chlorophenyl)-3-hydroxy-propanenitrile 7c

2-Bromo-3-(4′-chlorophenyl)-3-hydroxy-propanenitrile, **6c** was prepared according to the literature [2a]. Compound **6c** (1 mmol) was dissolved in 3 mL of THF:H_2O (2:1), at room temperature. To this solution was added InBr (1.2 mmol). After the dissolution of the red solid InBr, the reaction was stirred for 6 h, quenched with water, and then extracted with ethyl acetate. The product **7c** was purified by column chromatography on silica gel with hexane:acetate 4:1 (v/v). This procedure gave **7c** in 70% of yield.

3.3. Spectroscopic studies

The structures of the alkenenitriles **5a**–**k** and of the alcohol **7c** were determined by NMR (^1H and ^{13}C) spectroscopy and mass spectrometry. The spectroscopic data are summarized below.

(Z)-Cinnamonitrile, ***5a*** *[6a,9–11]:* yellowish oil; ^1H NMR ($CDCl_3$): $\delta = 5.34$ (d, $^3J = 12.1$ Hz, 1H), 7.02 (d, $^3J = 12.1$ Hz, 1H), 7.34 (m, 3H), 7.69 (m, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 95.10$, 117.29, 128.92, 129.00, 130.96, 133.59, 148.68; ^{13}C NMR (DEPT-135): $\delta = 95.10$, 128.92, 129.00, 130.96, 148.68.

(E)-Cinnamonitrile, ***5a*** *[6a,9,11,12]:* yellowish oil; ^1H NMR ($CDCl_3$): $\delta = 5.88$ (d, $^3J = 16.6$ Hz, 1H), 7.43 (m, 6H); ^{13}C NMR ($CDCl_3$): $\delta = 96.38$, 118.09, 127.34, 129.11, 131.20, 133.55, 150.56; ^{13}C NMR (DEPT-135): $\delta = 96.38$, 127.34, 129.11, 131.20, 150.56.

(Z)-2-Chlorocinnamonitrile, ***5b*** *[6a,9–11]:* yellowish oil; ^1H NMR ($CDCl_3$): $\delta = 5.54$ (d, $^3J = 12.0$ Hz, 1H), 7.31 (m, 3H), 7.47 (d, $^3J = 12.0$ Hz, 1H), 7.99 (m, 1H); ^{13}C NMR

($CDCl_3$): $\delta = 98.11$, 116.48, 127.18, 128.94, 129.84, 131.68, 134.32, 145.20, 145.23; MS (70 eV, EI, for ^{35}Cl): *m/z* (%):163 (M, 40), 128 (100), 101 (22), 75 (35).

(E)-2-Chlorocinnamonitrile, ***5b*** *[6a,9,11]:* yellowish oil; ^1H NMR ($CDCl_3$): $\delta = 5.83$ (d, $^3J = 16.7$ Hz, 1H), 7.35 (m, 4H), 7.76 (d, $^3J = 16.7$ Hz, 1H); ^{13}C NMR ($CDCl_3$): $\delta = 98.91$, 117.62, 126.82, 127.27, 130.33, 131.68, 131.94, 134.43, 146.50; MS (70 eV, EI, for ^{35}Cl): *m/z* (%): 163 (M, 94), 128 (100), 101 (48), 75 (41).

(Z)-4-Chlorocinnamonitrile, ***5c*** *[6a,10,11]:* colorless solid, m.p. >300 °C; ^1H NMR ($CDCl_3$): $\delta = 5.40$ (d, $^3J = 12.0$ Hz, 1H), 7.01 (d, $^3J = 12.0$ Hz, 1H), 7.34 (m, 2H), 7.67 (m, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 95.71$, 116.97, 129.21, 130.22, 131.98, 136.96, 147.21; MS (70 eV, EI, for ^{35}Cl): *m/z* (%): 163 (M, 100), 128 (98), 101 (31).

(E)-4-Chlorocinnamonitrile, ***5c*** *[6a,9–11]:* colorless solid, m.p. 84.1–86.2 °C; ^1H NMR ($CDCl_3$): $\delta = 5.79$ (d, $^3J = 16.6$ Hz, 1H), 7.27 (d, $^3J = 16.6$ Hz, 1H), 7.32 (s, 4H); ^{13}C NMR ($CDCl_3$): $\delta = 97.01$, 117.76, 128.51, 129.44, 131.98, 137.30, 149.10; ^{13}C NMR (DEPT-135) $\delta = 97.01$, 128.51, 129.44, 149.10; MS (70 eV, EI, for ^{35}Cl): *m/z* (%): 163 (M, 100), 128 (99), 114(10), 101 (37).

(Z)-2-Bromocinnamonitrile, ***5d*** *[11,13]:* greenish oil; ^1H NMR ($CDCl_3$): $\delta = 5.50$ (d, $^3J = 12.0$ Hz, 1H), 7.36 (m, 4H), 7.94 (d, 1H); ^{13}C NMR ($CDCl_3$): $\delta = 98.25$, 116.31, 124.43, 127.75, 129.18, 131.73, 133.07, 133.42, 147.72; MS (70 eV, EI, for ^{79}Br): *m/z* (%): 207 (M, 77), 180 (7), 128 (100), 101 (62), 75 (38).

(E)-2-Bromocinnamonitrile, ***5d*** *[11]:* greenish oil; ^1H NMR ($CDCl_3$): $\delta = 5.78$ (d, $^3J = 16.6$ Hz, 1H), 7.24 (m, 2H), 7.49 (m, 2H), 7.70 (d,$^3J = 16.6$ Hz, 1H); ^{13}C NMR ($CDCl_3$): $\delta = 98.96$, 117.53, 124.66, 126.89, 127.85, 132.06, 133.32, 133.50, 148.92; ^{13}C NMR (DEPT) $\delta = 98.96$, 126.89, 127.85, 132.06, 133.50, 148.92; MS (70 eV, EI, for ^{79}Br): *m/z* (%): 207 (M, 77), 180(8), 128 (100), 101 (62), 75 (38).

(Z)-4-Bromocinnamonitrile, ***5e*** *[6a]:* colorless solid, m.p. >300 °C; ^1H NMR ($CDCl_3$): $\delta = 5.42$ (d, $^3J = 12.0$ Hz, 1H), 7.00 (d, $^3J = 12.0$ Hz, 1 H), 7.56 (m, 4H); ^{13}C NMR ($CDCl_3$): $\delta = 95.84$, 116.95, 125.36, 130.35, 132.18, 133.37, 147.30; ^{13}C NMR (DEPT-135): 95.84, 130.35, 132.18, 147.30; MS (70 eV, EI, for ^{79}Br): *m/z* (%): 207 (M, 78), 180 (7), 128 (100), 101 (43), 75 (28).

(E)-4-Bromocinnamonitrile, ***5e*** *[6a]:* colorless solid, m.p. 105.0–105.8 °C; ^1H NMR ($CDCl_3$): $\delta = 5.77$ (d, $^3J = 16.7$ Hz, 1H), 7.25 (m, 3H), 7.48 (m, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 97.08$, 117.75, 125.60, 128.66, 132.34, 132.36, 149.17; ^{13}C NMR (DEPT-135): $\delta = 97.08$, 128.66, 132.34, 149.17; MS (70 eV, EI, for ^{79}Br): *m/z* (%): 207 (M, 79), 180(6), 128 (100), 101 (44), 75 (30).

(Z)-4-Methylcinnamonitrile, ***5f*** *[6a]:* yellowish oil; ^1H NMR ($CDCl_3$): $\delta = 2.31$ (s, 3H), 5.29 (d, $^3J = 12.2$ Hz, 1H), 7.00 (d, $^3J = 12.2$ Hz, 1H), 7.16 (d, 2H), 7.63 (d, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 21.48$, 93.70, 117.55, 129.00, 129.56, 130.94, 141.51, 148.55; ^{13}C NMR (DEPT-135): $\delta = 21.48$, 93.70, 129.00, 129.56, 148.55; MS (70 eV, EI): *m/z* (%): 143 (M, 100), 115 (83), 89 (25), 63 (26).

(E)-4-Methylcinnamonitrile, ***5f*** *[6a,9]:* yellowish oil; ^1H NMR ($CDCl_3$): $\delta = 2.30$ (s, 3H), 5.73 (d, $^3J = 16.6$ Hz, 1H), 7.21 (m, 5H); ^{13}C NMR ($CDCl_3$): $\delta = 21.43$, 94.98, 118.32, 127.25, 129.74, 130.75, 141.74, 150.42; ^{13}C NMR (DEPT-135): $\delta = 21.43$, 94.98, 127.25, 129.74, 150.42; MS (70 eV, EI): *m/z* (%): 143 (M, 100), 115 (77), 89 (21).

(Z)-2-Methoxycinnamonitrile, ***5g*** *[10,13]:* yellowish oil; ^1H NMR ($CDCl_3$): $\delta = 3.77$ (s, 3H), 5.33 (d, $^3J = 12.2$ Hz, 1H), 6.90 (m, 2H), 7.32 (m, 1H), 7.49 (d, $^3J = 12.2$ Hz, 1H) 8.00 (d, 1H); ^{13}C NMR ($CDCl_3$): $\delta = 55.53$, 94.65, 110.84, 117.55, 120.72, 122.71, 128.28, 132.26, 143.63, 157.46.

(E)-2-Methoxycinnamonitrile, ***5g****:* yellowish oil; ^1H NMR ($CDCl_3$): $\delta = 3.82$ (s, 3H), 5.98 (d, $^3J = 16.7$ Hz, 1H), 6.88 (m, 2H), 7.31 (m, 2H), 7.55 (d, $^3J = 16.7$ Hz, 1H); ^{13}C NMR ($CDCl_3$): $\delta = 55.52$, 96.97, 111.29, 118.93, 120.81, 122.56, 128.89, 132.27, 146.39, 158.22; MS (70 eV, EI): *m/z* (%): 159 (M, 75), 131 (100), 116 (53).

(Z)-4-Methoxycinnamonitrile, ***5h*** *[6a,9]:* yellowish oil; ^1H NMR ($CDCl_3$): $\delta = 3.78$ (s, 3H), 5.22 (d, $^3J = 12.0$ Hz, 1H), 6.87 (d, 2H), 6.96 (d, $^3J = 12.0$ Hz, 1H), 7.72 (d, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 55.56$, 91.93, 114.52, 117.95, 126.56, 130.93, 148.00, 161.66; ^{13}C NMR (DEPT-135): $\delta = 55.56$, 91.93, 114.52, 130.93, 148.00; MS (70 eV, EI): *m/z* (%): 159 (M, 100), 144 (39), 130 (10), 116 (56), 89 (51).

(E)-4-Methoxycinnamonitrile, ***5h*** *[6a,9,12]:* yellowish oil; ^1H NMR ($CDCl_3$): $\delta = 3.77$ (s, 3H), 5.64 (d, $^3J = 16.5$ Hz, 1H), 6.84 (d, 2H), 7.27 (m, 3H); ^{13}C NMR ($CDCl_3$): $\delta = 55.43$, 93.40, 114.52, 118.64, 126.37, 129.05, 150.00, 162.06; ^{13}C NMR (DEPT-135): $\delta = 55.43$, 93.40, 114.52, 129.05, 150.00; MS (70 eV, EI): *m/z* (%): 159 (M, 100), 144 (41), 129 (10), 116 (57), 89 (51).

(Z)-Non-2-enenitrile, ***5i****:* colorless oil; ^1H NMR ($CDCl_3$): $\delta = 0.81$ (t, $^3J = 7.1$ Hz, 3H), 1.15–1.43 (m, 8H), 2.34 (q, br, $^3J = 7.7$ Hz, 2H), 5.22 (dt, $^3J = 11.0$ Hz, $^3J = 1.2$ Hz, 1H), 6.40 (dt, $^3J = 11.0$ Hz, $^3J = 7.7$ Hz, 1 H); ^{13}C NMR ($CDCl_3$): $\delta = 13.96$, 22.47, 28.18, 28.66, 31.45, 31.85, 99.42, 116.02, 155.23; MS (70 eV, EI): *m/z* (%): 137 (M, 2), 136 (14), 122 (27), 108 (43), 94 (46), 80 (40), 67 (100), 55 (61).

(E)-Non-2-enenitrile, ***5i*** *[14]:* colorless oil; ^1H NMR ($CDCl_3$): $\delta = 0.81$ (t, $^3J = 6.9$ Hz, 3H), 1.13-1.40 (m, 8H), 2.13 (q, br, $^3J = 7.0$ Hz, 2H), 5.23 (dt, $^3J = 16.4$ Hz, $^3J = 1.4$ Hz, 1H), 6.64 (dt, $^3J = 16.4$ Hz, $^3J = 7.0$ Hz, 1H); ^{13}C NMR ($CDCl_3$): $\delta = 13.95$, 22.45, 27.58, 28.60, 31.44, 33.29, 99.64, 117.54, 156.12; MS (70 eV, EI): *m/z* (%): 137 (M, 2), 136 (17), 122 (34), 108 (57), 94 (52), 80 (35), 69 (100), 55 (86).

(Z + E)-Dodec-2-enenitrile, ***5j*** *(mixture Z:E = 4:3):* colorless oil; ^1H NMR ($CDCl_3$): $\delta = 0.82$ (t, $^3J = 6.7$ Hz, 21H), 1.20 (s, br, 98H), 2.14 (q, br, $^3J = 7.0$ Hz, 6H), 2.35 (q, br, $^3J = 7.6$ Hz, 8H), 5.23 (dt, $^3J = 10.8$ Hz, $^3J = 1.2$ Hz, 4H), 5.25 (dt, $^3J = 16.3$ Hz, $^3J = 1.6$ Hz, 3H), 6.40 (dt, $^3J = 10.8$ Hz, $^3J = 7.6$ Hz, 4H), 6.64 (dt, $^3J = 16.3$ Hz, $^3J = 6.9$ Hz, 3 H); MS (70 eV, EI): *m/z* (% *E,Z*): 178 (M, 10, 10), 164 (18, 16), 150 (56, 74), 136 (68,

98), 122 (67, 100), 108 (50, 40), 94 (79, 63), 80 (100, 64), 67 (96, 85), 54 (83, 94).

5-Phenyl-penta-2(Z),4(E)dienenitrile, ***5k*** *[10]:* yellow oil; ^{1}H NMR ($CDCl_3$): $\delta = 5.16$ (d, $^3J = 10.4$ Hz, 1H), 6.80–7.45 (m, 8H); ^{13}C NMR ($CDCl_3$): $\delta = 96.44$, 116.63, 124.04, 127.52, 128.83, 129.65, 135.19, 141.63, 149.19; ^{13}C NMR (DEPT-135): $\delta = 96.44$, 124.04, 127.52, 128.83, 129.65, 141.63, 149.19; MS (70 eV, EI): *m*/*z* (%): 154 (M−1, 100), 141 (88), 115 (97), 77 (48).

5-Phenyl-penta-2(E),4(E)dienenitrile; ***5k****:* yellow oil; ^{1}H NMR ($CDCl_3$): $\delta = 5.33$ (d, $^3J = 15.7$ Hz, 1H), 6.72–7.35 (m, 8H); ^{13}C NMR ($CDCl_3$): $\delta = 98.14$, 118.29, 125.33, 127.32, 128.83, 129.56, 135.15, 141.26, 150.23; ^{13}C NMR (DEPT-135): $\delta = 98.14$, 125.33, 127.32, 128.83, 129.56, 141.26, 150.23; MS (70 eV, EI): *m*/*z* (%): 155(100), 141 (72), 115(87), 77(41).

3-(4′-Chlorophenyl)-3-hydroxypropanenitrile, ***7c*** *[15]:* yellowish oil; ^{1}H NMR ($CDCl_3$): $\delta = 2.65$ (d, $^3J = 6.1$ Hz, 2H), 2.69 (s, br, 1H), 4.92 (t, $^3J = 6.1$ Hz, 1H), 7.27 (m, 4H); ^{13}C NMR ($CDCl_3$): $\delta = 29.91$, 69.20, 117.09, 126.91, 128.99, 134.46, 139.46.

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