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Addition of Reformatsky Reagents to 1,1-Dicyanoalkenes

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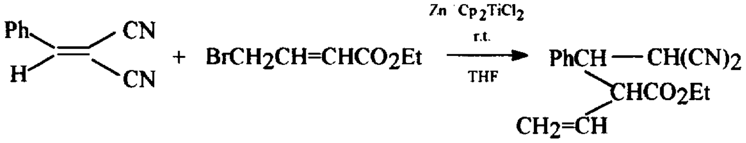
Abstract: Reformatsky reagents are found to react with different 1,1-dicyanoalkenes to afford addition products, and the reaction can be conducted more efficiently in the presence of a catalytic amount of Cp_2TiCl_2. There is strong evidence to support a SET process in the course of Reformatsky reagent formation. © 1997 Published by Elsevier Science Ltd. All rights reserved.

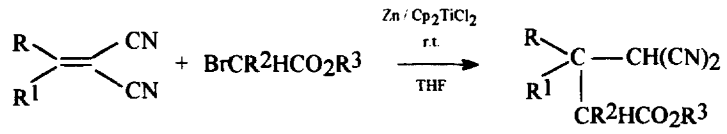
The Reformatsky reaction between a α-haloester and a carbonyl compound constitutes a widely used methodology for carbon-carbon bond formation.[1] Unfortunately, its classical form has many limits such as low yield, and long reaction time.[2] To overcome these problems, a number of researchers have modified the reaction by use of activated zinc dust,[3] other metals[4] or additives[5] instead of zinc. We also have reported[6] that this reaction can be conducted much more efficiently in the presence of a catalytic amount of titanium biscyclopentadienyl dichloride (Cp_2TiCl_2).

Generally speaking, when α,β-unsaturated carbonyl compounds react with α-bromoacetates under Reformatsky reaction conditions, 1,2-addition products dominate Michael addition products.[7] However, to the best of our knowledge, only one paper reported the Reformatsky reagent addition to a Michael acceptor other than α,β-unsaturated carbonyl compounds.[8] Here we would like to report a new case of this addition (Scheme 1 and 2).



1a 4 5

Scheme 1



1 2 3

1a, R=Ph, R^1=H
1b, R=4-F-Ph, R^1=H
1c, R=4-O$_2$N-Ph, R^1=H
1d, R=Styryl, R^1=H
1e, R=4-MeO-Ph, R^1=H
1f, R=i-Pr, R^1=H
1g, R=Ph, R^1=Me
1h, R, R^1= -(CH$_2$)$_5$-
1i, R=2-furyl, R^1=H

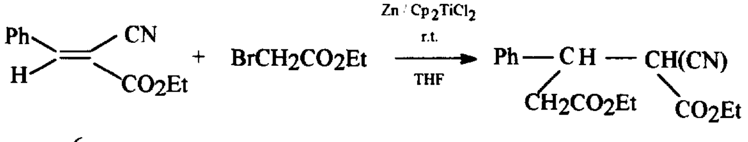
2a, R^2=H, R^3=Et
2b, R^2=Me, R^3=Et
2c, R^2=H, R^3=Cinnamyl

3a, R=Ph, R^1=R^2=H, R^3=Et
3b, R=4-F-Ph, R^1=R^2=H, R^3=Et
3c, R=4-O$_2$N-Ph, R^1=R^2=H, R^3=Et
3d, R=Styryl, R^1=R^2=H, R^3=Et
3e, R=4-MeO-Ph, R^1=R^2=H, R^3=Et
3f, R=i-Pr, R^1=R^2=H, R^3=Et
3g, R=Ph, R^1=Me, R^2=H, R^3=Et
3h, R, R^1 = -(CH$_2$)$_5$-, R^2=H, R^3=Et
3i, R=2-Furyl, R^1=R^2=H, R^3=Et
3j, R=Ph, R^1=H, R^2=Me, R^3=Et
3k, R=Ph, R^1=R^2=H, R^3=Cinnamyl

Scheme 2

RESULTS AND DISCUSSION

The results (Table 1) suggest that Reformatsky reagents can react smoothly with 1,1-dicyanoalkenes in moderate to excellent yields. Other electron-deficient alkenes, such as 1,1-diethoxycarbonylstyrene, diethylmaleate, and cinnamyl cyanide fail to react under our conditions. Fortunately, we do find that compound **6** can react with Reformatsky reagent to give the addition product 7 (Scheme 3).



6 7

Scheme 3

The Reformatsky reaction of alkyl 4-bromocrotonates with carbonyl compounds generally led to α-substituted products under kinetic conditions, i.e., low-boiling solvent and short reaction time.[9] Our results (Entry 17) follow this rule very well.

Although the cyano group has been proven to be a good Reformatsky acceptor.[10] Our experimental results indicate that the cyano group in the substrates **1** and **6** remains unchanged. Clearly, the carbon-carbon double bonds in those substrates are more reactive than the carbon-nitrogen triple bond. However, when a 1:1 mixture of **1a** and benzaldehyde were subjected to a Reformatsky reagent, the latter acted exclusively as an acceptor. That is to say, the carbonyl group is more reactive than the electron-deficient carbon-carbon double bond.

It was reported that nitrobenzaldehyde can inhibit the formation of Reformatsky reagent.[11] Similarly, we also found that in a one-step procedure (Entry 6) the substrate **1c** cannot furnish any addition product. But in a two-step procedure (Entry 7), the normal product **3c** was obtained in an isolated yield of 51.6%.

Table 1. Addition of Reformatsky Reagents to Electron-deficient Alkenes

Run	Substrate		Method [a]	Product	Yield% [b] (Syn/Anti) [c]
1	1a	2a	A	3a	82.9
2			B	3a	66.9
3			C	3a	66.1
4			D	3a	61.1
5	1b	2a	A	3b	58.5
6	1c	2a	A	3c	0
7			C	3c	51.6
8	1d	2a	A	3d	50.7
9	1e	2a	A	3e	63.6
10	1f	2a	A	3f	76.0
11	1g	2a	A	3g	43.2[d]
12	1h	2a	A	3h	55.6
13	1i	2a	A	3i	68.1
14	1a	2b	A	3j	92.7(43/57)
15	1a	2c	A	3k	82.3[e]
16	6	2a	A	7	62.3[f]
17	1a	4	A	5	65.7(29/71)[g]

a, For the details of Methods A-D, see Experimental Section. b, All yields refer to isolated yields; c, The isomer ratios were determined by ^{1}H NMR (300 MHz) integrations on the combined products; d, This yield was based on the conversion of **1g**; e, 36.8% (based on **2c**) of cinnamyl acetate was also isolated; f, The ratio of Syn/Anti was not determined. g, None of γ-substituted product was detected.

To gain more information, the following experiments were conducted. In one experiment, a mixture of an equal molar of activated zinc powder[12] and ethyl bromoacetate, and 10% molar amount of *p*-dinitrobenzene was stirred in dry THF at room temperature. After stirring for fifteen minutes, no reaction was observed. Then the mixture was stirred and refluxed for another thirty minutes, and filtered. 95% of the zinc powder was recovered. In the other, the mixture, in the abscence of *p*-dinitrobenzene, was stirred in dry THF at room temperature. Within five minutes, zinc powder was consumed to give a yellowish solution, i.e. Reformatsky reagent solution. Obviously, *p*-dinitrobenzene, which is a known radical anion inhibitor,[13] did inhibit the reaction completely. Besides *p*-dinitrobenzene, we found that a catalytic amount of *p*-chloronitrobenzene could inhibit this reaction.

Furthermore, the course of Reformatsky reagent formation was also studied by ESR using spin trapping techniques. Thus, to a well stirred mixture of ethyl bromoacetate (10 mmol), and Cp_2TiCl_2 (0.5 mmol) in dry THF (8 mL) was added commercial zinc powder (5mmol) at room temperature. After three minutes, 1 mg of spin trap 2-methyl-2-nitropropane (MNP) was added to the solution. A sample of the mixture was transferred to an ESR tube, and the ESR spectra were recorded at room temperature. The spectra (Figure 1, left, a_N=1.44 mT, a_H=0.84 mT, g=2.0047) are consistent with the radical **8** (Scheme 4). In order to see if Cp_2TiCl_2 is the key additive to the SET process, the above mixture, in the abscence of Cp_2TiCl_2, was immersed into a 55°C oil bath and stirred for four minutes. To which was added 1 mg of N-tert-butyl-α-phenyl nitrone. A sample of the solution was placed in an ESR tube and the ESR spectra were recorded at room temperature. The spectra (Figure 1, right, a_N=1.45 mT, a_H=0.36 mT, g=2.0069), which may be due to the radical **9** (Scheme 4), indicate that zinc powder can act as a single-electron donor. In addition, when zinc powder was activated according to the literature,[12] Reformatsky reagent was found to be formed in dry THF even at room temperature (*vide ante*). These findings suggest that a SET mechanism is involved in the course of Reformatsky reagent formation.[14]

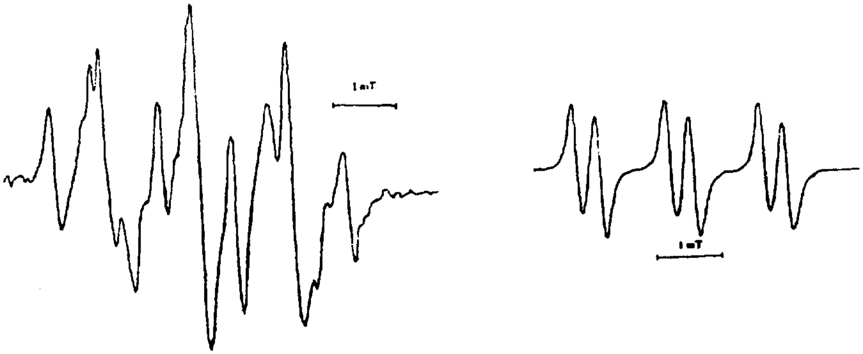
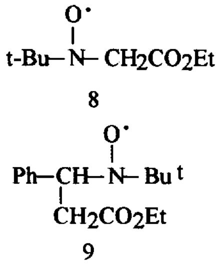


Figure 1

On the other hand, when **2c** reacted with **1a** (Entry 15), the reduced product and the addition product were isolated in yields of 36.8% (based on **2c**) and 82.3% respectively. No cyclized product, which might be formed through a radical intermediate, was detected. Moreover, when **1a** and **2a** were subjected to Method A conditions in the presence of 20% molar of hydroquinone, zinc powder was nearly consumed. After usual work-up, **3a** was isolated in a yield of 47.1%. These results fail to agree with a radical chain mechanism.

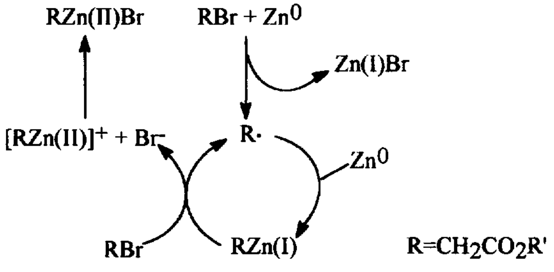
With the above facts in hand, also enlightened by the work of Chanon and co-workers,[15] the authors tend to believe that the formation of Reformatsky reagent is similar to that of Grignard reagent (Scheme 5):



$\text{t-Bu–}\overset{\displaystyle O^{\bullet}}{\overset{|}{N}}\text{–CH}_2\text{CO}_2\text{Et}$ **8**

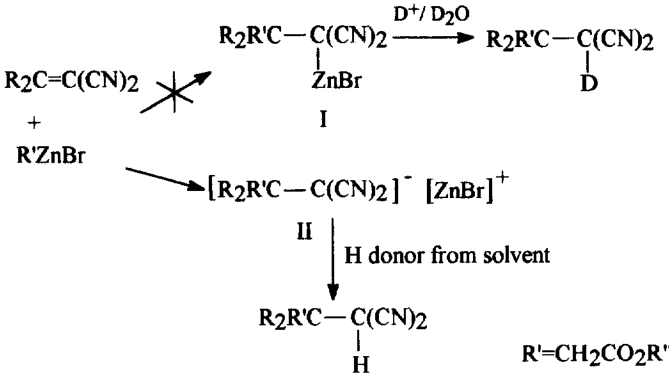
$\text{Ph–}\underset{\displaystyle CH_2CO_2Et}{\underset{|}{CH}}\text{–}\overset{\displaystyle O^{\bullet}}{\overset{|}{N}}\text{–Bu}^t$ **9**

Scheme 4



Scheme 5

The fact that the addition can be conducted with Reformatsky reagent prepared either prior to use (Method B and C) or *in situ* (Method A and D) suggest that the addition does occur between the substrate and the Reformatsky reagent. Now two questions arise. One is how the addition proceeded? In order to answer this question, the reaction was quenched with a 1:1 mixture of D_2O/CF_3CO_2D, no deuterated product was isolated. According to the classic mechanism of Reformatsky reaction,[16] species **I** (Scheme 6) should be the key intermediate. However, the above result is not in favour of the possibility of species **I** as the intermediate. Alternatively, we would like to consider species **II** as the key intermediate, which can abstract a hydrogen atom from solvent before acid work-up to give the product.



Scheme 6

The other question is what role a catalytic amount of Cp_2TiCl_2 plays in the reaction. We have observed the following facts. When zinc powder was added to the reaction mixture (Method A), the red solution usually turned into grey-green. This solution contained a mixture of Ti^{2+} and Ti^{3+}, which had been proven by their characteristic ESR spectra. After the solution was stirred for several minutes, the reaction would take place vigorously. Because of Ti^{3+} species, Cp_2TiCl, is likely to be a good electron donor,[17] and there seems to be a possibility of Cp_2TiCl_2 participation in the SET process. On the other hand, since the reduction of Cp_2TiCl_2 repuires the oxidation of zinc, the surface of zinc powder would actually be activated. At this time, unfortunately, not enough evidence was obtained to see whether it simply activates zinc powder, or if it participates in the SET process or the further process.[18] However, by comparing Method A with Method B and method D (Table 1, entries 1, 3 and 4), we find that a catalytic amount of Cp_2TiCl_2 was very useful to the addition.

Anyway, this work has widened the scope of Reformatsky reaction, and more significantly, strong evidence has been found to support a SET mechanism in the course of Reformatsky reagent formation. Finally, Cp_2TiCl_2 has proven to be an efficient catalyst in the Reformatsky type reaction.

EXPERIMENTAL

^1H- and ^{13}C-NMR spectra were obtained on Bruker AMX-300 (300 MHz) or AMX-400 (400 MHz) spectrometers using $CDCl_3$ solution, peak positions are given in ppm with TMS as internal standard and *J* values are given in Hz. IR spectra were recorded on a Shimadzu IR-440 spectrometer and only the strongest or structurally most important peaks are listed. MS data were measured on HP-5898A instrument (low resolution) or Finnigan MAT-95 spectrometer (HRMS), both operating at 70 eV. ESR spectra were recorded on Varian E-112 spectrometer with X-band, field modulation 100 kHz, response time 0.25 second and sweep width 10 mT. Elemental analyses were carried out at the Analytical Department of this Institute. Flash chromatography was performed on silica gel H (400 mesh).

Dry THF was distilled from sodium. 1,1-Dicyanoalkenes were prepared according to the literature.[19] Commercial zinc powder (A. R.) was activated, if noted, according to the method of Tsuda.[12]

Typical procedure: Method A -To a solution of 1,1-dicyanoalkene (5 mmol), α-bromoester (10 mmol), and Cp_2TiCl_2 (0.5 mmol) in dry THF (10 mL) at room temperature was added commercial zinc powder (10 mmol). After vigorously stirring for 30 minutes, the reaction was quenched by addition of water and dilute aqueous hydrogen chloride solution successively. The mixture was extracted with ethyl acetate (2×20 mL), and the combined organic layer was washed with brine and dried over anhydrous $MgSO_4$. The solvents were removed by rotary evaporation, and the residue was chromatographed over silica gel (light petroleum ether / ethyl acetate) to give the product.

Method B - To a solution of α-bromoester (20 mmol) in dry THF (20 mL) at room temperature was added activated zinc powder (20 mmol) and the mixture stirred. After the zinc powder was consumed, 1,1-dicyanoalkene (5 mmol) was immediately added, and the mixture was stirred for another 30 minutes. Other work-up was the same as with Method A.

Method C - To a solution of α-bromoester (10 mmol), Cp_2TiCl_2 (0.5 mmol) in dry THF (20 mL) at room temperature was added commercial zinc powder (10 mmol) and the mixture stirred. Other procedures were the same as with Method B.

Method D -A mixture of α-bromoester (10 mmol), 1,1-dicyanoalkene (5 mmol) and commercial zinc powder (10 mmol) in dry THF (20 mL) was stirred and refluxed for another sixty minutes. Work-up was the same as with Method A.

***Ethyl 4,4-dicyano-3-phenylbutyrate* (3a)**: IR (neat): 2264, 1735, 703 cm^{-1}. δ_H (300 MHz): 1.18 (3H, t, *J* 7.08), 2.89-3.07 (2H, m), 3.74 (1H, m), 4.10 (2H, q, *J* 7.10), 4.48 (1H, d, *J* 5.35), 7.33-7.43 (5H, m). δ_C (300 MHz): 13.8, 28.7, 36.3, 42.1, 61.2, 111.5, 111.7, 127.7, 128.9, 135.9, 170.0. m/z (%): 242 (M^+, 11.99), 213 (100), 197 (43.84), 143 (42.14), 135 (98.69), 105 (56.77). Anal. Calcd for $C_{14}H_{14}N_2O_2$: C, 69.41; H, 5.82; N, 11.59. Found: C, 69.43; H, 5.87; N, 11.59.

***Ethyl 4,4-dicyano-3-(4-fluorophenyl)butyrate* (3b)**: IR (neat): 2234, 1728, 838 cm^{-1}.δ_H (400 MHz): 1.20 (3H, t, *J* 7.14), 2.88-3.02 (2H, m), 3.75 (1H, m), 4.12 (2H, q, *J* 7.14), 4.47 (1H, dd, *J* 0.58, 5.65), 7.10 (2H, m), 7.36 (2H, m). m/z (%): 261 (M^++1, 100), 260 (M^+, 14.12), 233 (26.77), 231 (53.40), 195 (27.76), 153 (92.93), 122 (29.64). HRMS m/z, calcd for $C_{14}H_{13}FN_2O_2$: 260.0961, found: 260.0921.

***Ethyl 4,4-dicyano-3-(4-nitrophenyl)butyrate* (3c)**: IR (neat): 3117, 2991, 2257, 1730, 1526, 1351, 860 cm^{-1}. δ_H (300 MHz): 1.12 (3H, t, *J* 7.24), 2.84-3.03 (2H, m), 3.79 (1H, m), 4.04 (2H, q, *J* 7.11), 4.50 (1H, d, *J* 5.52), 7.49 (2H, m), 8.18 (2H, m). m/z (%): 287 (M^+, 3.17), 258 (100.0), 242 (30.22), 213 (16.29), 188 (25.72), 180 (32.86), 150 (21.94), 103 (18.73). HRMS m/z, calcd for $C_{14}H_{13}N_3O_4$: 287.0906, found: 287.0863.

***Ethyl 4,4-dicyano-3-styrylbutyrate* (3d)**: IR (neat): 2239, 1728, 696 cm^{-1}. δ_H (300 MHz): 1.23 (3H, t, *J* 7.05), 2.73 (2H, d, *J* 6.89), 3.29 (1H, m), 4.15 (2H, q, *J* 7.06), 4.38(1H, d, *J* 4.98), 6.10 (1H, dd, *J* 8.60, 15.8), 6.71 (1H, d, *J* 15.8), 7.23-7.40 (5H, m). m/z (%): 268 (M^+, 15.21), 239 (19.06), 203 (18.89), 157 (39.88), 129 (100), 115 (64.07). Anal. Calcd for $C_{16}H_{16}N_2O_2$: C, 71.63; H, 6.01; N, 10.44. Found: C, 71.60; H, 6.01; N, 10.28.

Ethyl 4,4-dicyano-3-(4-methoxyphenyl)butyrate **(3e)**: IR (neat): 2238, 1728, 836 cm^{-1}. δ_H (300 MHz): 1.19 (3H, t, *J* 7.13), 2.85-3.04 (2H, m), 3.70 (1H, m), 3.77 (3H, s), 4.10 (2H, q, *J* 7.13), 4.44 (1H, d, *J* 5.74), 6.91 (2H, m), 7.28 (2H, m). m/z (%): 272 (M$^+$, 15.95), 207 (100), 185 (26.93), 165 (89.49), 137 (19.37), 134 (34.56). Anal. Calcd for $C_{15}H_{16}N_2O_3$: C, 66.20; H, 5.92; N, 10.29. Found: C, 66.04; H, 5.93; N, 10.17.

Ethyl 4,4-dicyano-3-isopropanylbutyrate **(3f)**: IR (neat): 2232, 1728 cm^{-1}. δ_H (300 MHz): 1.02 (3H, d, *J* 6.84), 1.08 (3H, d, *J* 6.81), 1.29 (3H, t, *J* 7.09), 2.11 (1H, m), 2.49 (2H, m), 2.64 (1H, m), 4.19 (2H, q, *J* 7.09), 4.34 (1H, d, *J* 5.03). m/z (%): 207 (M$^+$-1, 1.95), 165 (14.24), 163 (76.09), 137 (67.96), 119 (36.11), 69 (59.23), 43 (100). Anal. Calcd for $C_{11}H_{16}N_2O_2$: C, 63.44; H, 7.74; N, 13.45. Found: C, 63.38; H, 7.78; N, 13.30.

Ethyl 4,4-dicyano-3-phenyl-3-methylbutyrate **(3g)**: IR (neat): 2235, 1728, 697 cm^{-1}. δ_H (300 MHz): 1.13 (3H, t, *J* 7.16), 1.81 (3H, s), 2.84-3.02 (2H, m), 4.06 (2H, q, *J* 7.13), 4.96 (1H, s), 7.33-7.43 (5H, m). m/z (%): 256 (M$^+$, 8.39), 211 (17.54), 191 (89.65), 168 (47.29), 145 (100), 117 (83.75), 91 (49.77). HRMS m/z, calcd for $C_{15}H_{16}N_2O_2$: 256.1212, found: 256.1235.

Ethyl (1-malononitrilyl)cyclohexanylacetate **(3h)**: IR (neat): 2930, 2226, 1722 cm^{-1}. δ_H (300 MHz): 1.28 (3H, t, *J* 7.12), 1.60-1.84 (10H, m), 2.68 (2H, s), 4.17 (2H, q, *J* 7.12), 4.78 (1H, s). m/z (%): 235 (M$^+$+1, 1.95), 207 (17.41), 189 (51.61), 123 (54.29), 95 (100), 88 (68.23), 81 (71.36). HRMS m/z, calcd for $C_{13}H_{18}N_2O_2$: 234.1368, found: 234.1391.

Ethyl 4,4-dicyano-3-(2-furyl)butyrate **(3i)**: IR (neat): 2986, 2912, 2258, 1733, 747 cm^{-1}. δ_H (300 MHz): 1.26 (3H, t, *J* 7.11), 2.97 (2H, d, *J* 7.25), 3.92 (1H, m), 4.18 (2H, q, *J* 7.13), 4.52 (1H, d, *J* 5.55), 6.40 (2H, m), 7.44 (1H, m). m/z (%): 232 (M$^+$, 6.01), 205 (67.30), 203 (73.03), 167 (49.39), 145 (100.0), 133 (34.4), 125 (41.05), 94 (55.84). HRMS m/z, calcd for $C_{12}H_{12}N_2O_3$: 232.0848, found: 232..0873.

Ethyl Anti-4,4-dicyano-3-phenyl-2-methylbutyrate **(anti-3j)**: IR (KBr): 2268, 1722, 710 cm^{-1}. δ_H (300 MHz): 1.06 (3H, d, *J* 7.05), 1.27 (3H, t, *J* 7.20), 3.14 (1H, m), 3.40 (1H, m), 4.23 (2H, q, *J* 7.05), 4.52 (1H, d, *J* 4.96), 7.35-7.45 (5H, m). m/z (%): 256 (M$^+$, 12.07), 227 (49.93), 155 (58.65), 135 (100), 117 (91.54), 102 (89.70), 91 (58.65). Anal. Calcd for $C_{15}H_{16}N_2O_2$: C, 70.30; H, 6.29; N, 10.93. Found: C, 70.33; H, 6.50; N, 10.64.

Ethyl Syn-4,4-dicyano-3-phenyl-2-methylbutyrate **(syn-3j)**: IR (neat): 2246, 1730, 700 cm^{-1}. δ_H (300 MHz): 1.03 (3H, t, *J* 7.30), 1.27 (3H, d, *J* 6.87), 3.22 (1H, m), 3.41 (1H, m), 3.98 (2H, q, *J* 7.14), 4.52 (1H, d, *J* 7.05), 7.27-7.42 (5H, m). m/z (%): 256 (M$^+$, 24.26), 211 (47.60), 155 (21.25), 135 (100), 117 (80.64), 91 (79.09). Anal. Calcd for $C_{15}H_{16}N_2O_2$: C, 70.30; H, 6.29; N, 10.93. Found: C, 70.15; H, 6.50; N, 10.57.

Cinnamyl 4,4-dicyano-3-phenylbutyrate **(3k)**: IR (neat): 3032, 2908, 2259, 1733, 700 cm^{-1}. δ_H (300 MHz): 2.94-3.14 (2H, m), 3.74 (1H, m), 4.45 (1H, d, *J* 5.61), 4.73 (2H, d, *J* 6.57), 6.17 (1H, dt, *J* 6.52, 15.87), 6.61 (1H, d, *J*, 15.88), 7.25-7.43 (10H, m). m/z (%): 330 (M$^+$+1, 6.24), 330 (M$^+$, 24.35), 197 (17.17), 134 (32.95), 131 (33.76), 117 (100.0), 115 (51.32), 104 (26.61), 91 (22.79). HRMS m/z, calcd for $C_{21}H_{18}N_2O_2$: 330.1369, found: 330.1367.

Diethyl 2-cyano-3-phenylpentanedioate **(7)**: IR (neat): 2985, 2246, 1743, 702 cm^{-1}. δ_H (300 MHz): 1.08-1.21 (6H, m), 2.82-3.03 (2H, m), 3.81-3.90 (1.3H, m), 4.01-4.21 (4.7H, m), 7.27-7.33 (5H, m). δ_c (400 MHz): 13.75, 13.76, 13.95, 14.01, 36.95, 37.56, 41.19, 41.87, 43.37, 43.85, 60.79, 60.96, 62.76, 62.89, 115.16, 115.31, 127.59, 127.91, 128.17, 128.29, 128.74, 128.87, 137.51, 138.26, 164.79, 170.44, 170.78. m/z (%): 289 (M$^+$, 9.35), 260 (12.70), 244 (35.37), 215 (100.0), 143 (86.90), 135 (52.76), 105 (37.39), 77 (19.97). HRMS m/z, calcd for $C_{16}H_{19}NO_4$: 289.1314, found: 289.1318.

Ethyl Anti-4,4-dicyano-3-phenyl-2-vinylbutyrate **(anti-5)**: IR (neat): 2233, 1729, 708 cm^{-1}. δ_H (300 MHz): 1.28 (3H, t, *J* 7.14), 3.76 (2H, m), 4.22 (2H, q, *J* 7.15), 4.37 (1H, d, *J* 6.08), 5.21 (2H, m), 5.59 (1H, m), 7.27-7.44 (5H, m). m/z (%): 268 (M^+, 1.57), 239 (17.03), 195 (30.93), 155 (54.91), 130 (62.09), 129 (100), 115 (31.69). HRMS m/z, calcd for $C_{16}H_{16}N_2O_2$: 268.1212, found: 268.1261.

Ethyl Syn-4,4-dicyano-3-phenyl-2-vinylbutyrate **(syn-5)**: IR (neat): 2248, 1732, 703 cm^{-1}. δ_H (300 MHz): 0.92 (3H, t, *J* 7.11), 3.56 (1H, m), 3.79 (1H, m), 3.90 (2H, m), 4.22 (1H, d, *J* 6.80), 5.46 (1H, d, *J* 10.32), 5.61 (1H, d, *J* 16.85), 5.84 (1H, m), 7.30-7.49 (5H, m). m/z (%): 268 (M^+, 5.11), 239 (9.47), 195 (32.62), 155 (58.44), 129 (100), 114 (37.71). HRMS m/z, calcd for $C_{16}H_{16}N_2O_2$: 268.1212, found: 268.1202.

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