A general α-cyanoformylation using α-litho-β-ethoxyacrylonitrile: application to the syntheses of new 6-cyano-2,4-bis(phenylthio)- and 4-cyano-2,6-bis(phenylthio)hepta-2,4,6-trienals

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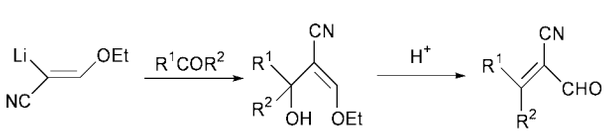
A new α-cyanoformylation of aldehydes and ketones proceeds in good to high yields using α-lithioacrylonitrile. This novel α-cyanoformylation is successfully applied to the preparation of two kinds of hepta-2,4,6-trienals, bearing a 6-cyano group (**10**) and a 4-cyano group (**12**).

α-Cyanocinnamaldehydes have been one of the most important classes of synthons for the syntheses of various biologically active and heterocyclic compounds.[1]

Mostly, the cyanoethenes have been synthesized from the Knoevenagel condensation using active methylene compounds such as malonodinitrile,[2] cyanoacetate,[3] and cyanoacetic acid, and their derivatives.[4] However, cyanoacetaldehyde is highly reactive to base, so that Knoevenagel conditions are not suitable for the preparation of α-cyanoacrolein derivatives. There are a few other synthetic approaches to α-cyanoacrolein; for example, the oxidation of 2-cyanoprop-1-en-3-ols with PCC,[5] and the reduction of ethylenemalonodinitriles with DIBAL-H.[6] Recently, a convenient α-cyanoformylation of aromatic aldehydes with 3,3-dimethoxypropiononitrile–NaOMe and successive hydration with 6 M HCl has been reported; however, this method has not been further investigated.[1b]

Results and discussion

Recently, we have reported a versatile olefination of carbonyl compounds using 2-alkoxy-1-chalcogen-substituted alkenyllithiums. In particular, we have shown the following two types of olefinations: (i) a formyl olefination bearing a chalcogen functional group at the α-position of the formyl group,[7] and (ii) a perfluoroacyl olefination bearing a chalcogen or non-chalcogen functional group at the α-position to the perfluoroacyl group.[8] Since β-alkoxyacrylonitriles have been easily and regioselectively lithiated,[9] a general olefination process using its alkenyllithium will provide a novel α-cyanoformylation (Scheme 1). As far as we know, no one has reported the general

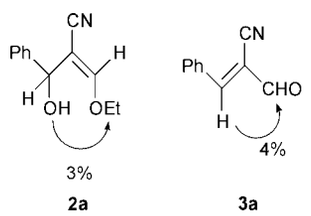


2 **3**

Scheme 1

α-cyanoformylation of carbonyl compounds. If the olefination using β-alkoxyacrylonitrile is accomplished, it will provide useful synthons for the preparation of bioactive or heterocyclic compounds. Here, we report the novel α-cyanoformylation of carbonyl compounds and their application to the syntheses of new cyano-substituted hepta-2,4,6-trienals.

β-Ethoxyacrylonitrile **1** was easily lithiated by treatment with lithium 2,2,6,6-tetramethylpiperidide (LTMP) at −78 °C, and successive reaction with benzaldehyde gave (*Z*)-2-cyano-3-ethoxy-1-phenylprop-3-en-1-ol **2a** in 65% yield. We next examined the dehydration of **2a** with several kinds of acid and found that trifluoromethanesulfonic acid trimethylsilyl ester (TMSOTf) was effective for the olefination process. Reaction of **2a** with TMSOTf afforded (*E*)-2-cyano-3-phenylprop-2-enal **3a** as a single stereoisomer. The stereostructures of **2a** and **3a** were determined by NOE experiments as shown in Fig. 1. α-Cyanoformylation of various aldehydes proceeded in good to high yields (Table 1, Entries 2–5). The easily enolizable 4-*tert*-butylcyclohexanone gave **2f** exclusively, and the successive dehydration with TMSOTf afforded **3f** in high yield; however, the reaction with cyclohex-2-enone was accompanied by a Michael addition product **4** (Entry 7). The bulky benzophenone also gave the cyanoolefination product **3h** in good yield (Entry 8). This novel olefination has been found to be applicable to the various aldehydes and ketones tested.



2a **3a**

Fig. 1

Advantages of this olefination include introducing the cyano group, which is less hindered and is strongly capable of electron-withdrawing, retaining the formyl group, which could be easily converted to other useful functional groups. Our next approaches are the tandem α-cyanoformylation or the preparations of the photo-sensitive hepta-2,4,6-trienal, which would undergo the tandem cyclization to afford the oxabicyclo[3.3.0]octa-3,7-diene. Our previous report has shown that the photoreaction of 2,4,6-tris(phenylthio)-2,4,6-heptatrienal afforded the new heterocycles, 2-oxa- or aza-bicyclic compounds.[10] First, a tandem olefination was examined as shown in Scheme 2. Reaction of **2b** with α-lithiated acrylonitrile gave 2,4-dicyano-1-ethoxy-6,6-dimethylhepta-1,4-dien-3-ol **5** in 35% yield; however, attempted dehydration with TMSOTf to give the aldehyde **6** did not succeed.

Next, we attempted to prepare the cyano-substituted hepta-2,4,6-trienals. α-Thioformylation of **2b** with PhSCH=CHOEt–*n*-BuLi afforded the penta-2,4-dienal **8** *via* the intermediate

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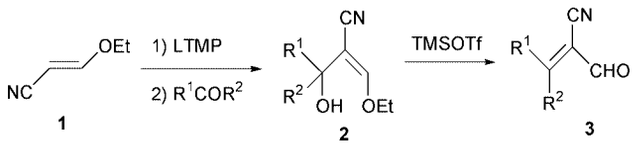
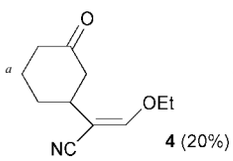
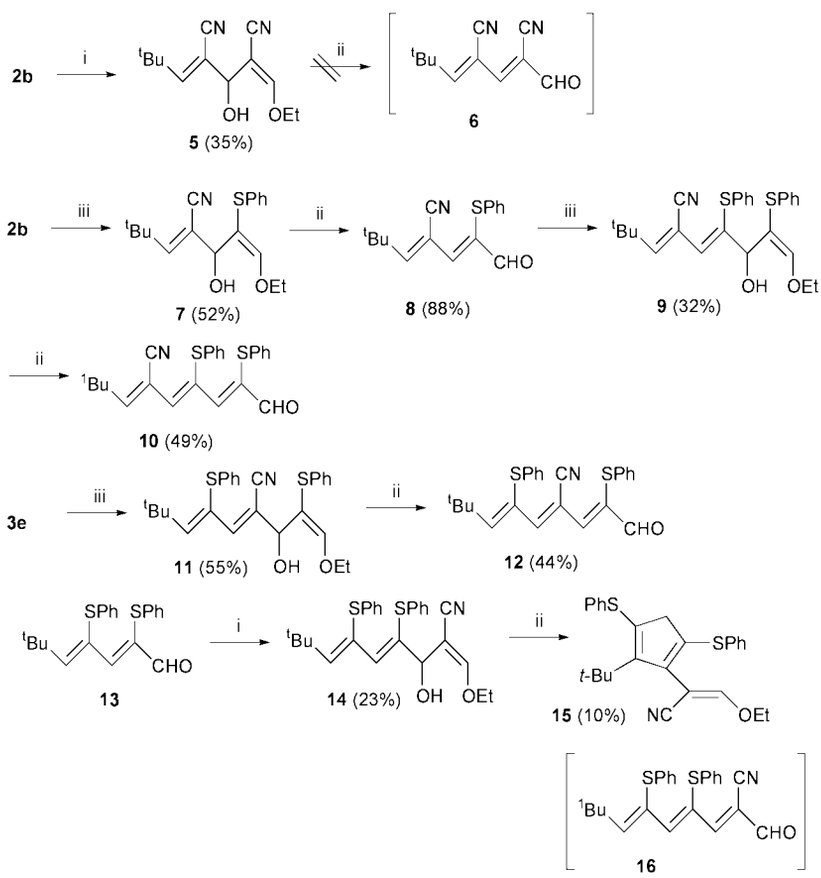
Table 1 α-Cyanoformyl olefination of aldehydes and ketones



	Carbonyl compound			
Entry	R^1	R^2	Alcohol (% yield)	Product (% yield)
1	Ph	H	(*Z*)-**2a** (65)	(*E*)-**3a** (91)
2	^{t}Bu	H	(*Z*)-**2b** (quant.)	(*E*)-**3b** (91)
3	Phenylethynyl	H	(*Z*)-**2c** (54)	(*E*)-**3c** (83)
4	(*E*)-PhCH=CH	Me	(*Z*)-**2d** (76)	(*E*)-**3d** (99)
5	^{t}BuCH=C(SPh)	H	(*Z*)-**2e** (55)	(*E*)-**3e** (99)
6	$(CH_2)_2CH(t\text{-Bu})(CH_2)_2$		**2f** (59)	**3f** (99)
7	$CH{=}CH(CH_2)_3$		**2g** (28)[a]	**3g** (99)
8	Ph	Ph	(*Z*)-**2h** (53)	**3h** (99)

[a]  was also produced.



Scheme 2 *Reagents and conditions*: i, **1**, LTMP, −78 °C; ii, TMSOTf. −78 °C; iii, PhSCH=CHOEt, *n*-BuLi, −78 °C.

alcohol **7** in good yield. The second olefination afforded the desired hepta-2,4,6-trienal **10**. Furthermore, we conducted the olefination of **3e** in order to prepare the 4-cyano-substituted hepta-2,4,6-trienal **12**. The 4-cyano-2,6-bis(phenylthio)hepta-2,4,6-trienal **12** was obtained in moderate yield; however, α-cyanoformylation of **13** did not produce the trienal **16**, but instead gave 3-*tert*-butyl-2-(1-cyano-2-ethoxyethenyl)-1,4-bis-(phenylthio)cyclopenta-1,3-diene **15** *via* cationic cyclization. The reaction of **8** with α-lithioacrylonitrile gave the hepta-1,4,6-trien-3-ol **17**; however, treatment of **17** with TMSOTf did not give the desired trienal **19**, but instead the cyclized 2-oxabicyclo[3.3.0]octa-3,7-diene **18** (Scheme 3). The structure was determined by the existence of the two cyano groups in the IR spectrum, which showed ν 2040 and 2160 cm^{-1}; by the existence of the two characteristic kinds of methine protons and the olefinic protons in the ^{1}H NMR spectrum, which exhibited δ 2.88 (t, *J* 2 Hz, 5-H), 3.54 (t, *J* 2 Hz, 6-H), 6.42 (d, *J* 2 Hz, 3-H), 6.95 (d, *J* 2 Hz, 8-H), which is determined by the correlations of the H–H COSY (Fig. 2); and the molecular formula $C_{19}H_{18}N_2OS$ (*m*/*z* 322). The stereochemistry of **18** was

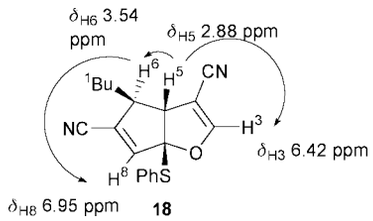


Fig. 2

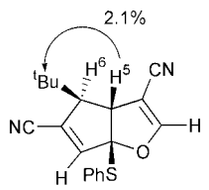
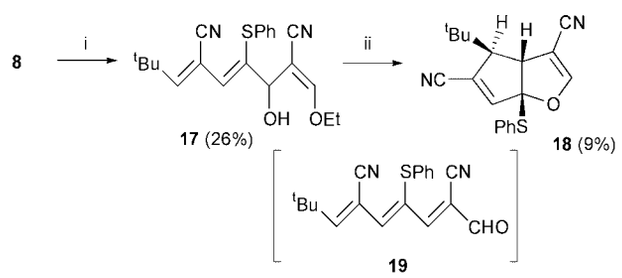
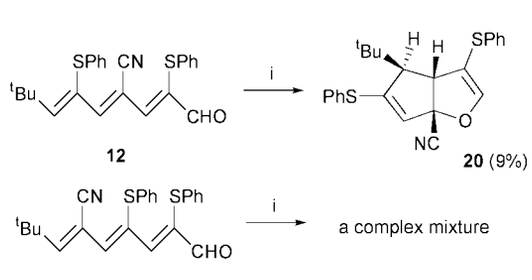


Fig. 3



Scheme 3 *Reagents and conditions*: i, **1**, LTMP, −78 °C; ii, TMSOTf, −78 °C.

determined by NOE experiments (Fig. 3). Irradiation of 5-H at δ 2.88 increased the intensity of the *t*-Bu group, not that of 6-H. The plausible mechanism for formation of the oxabicyclic compound is considered to be the same as that in the previous report; however, the fact that the 2,6-dicyano-4-(phenylthio)-hepta-2,4,6-trienal **19** could not be isolated, and instead directly afforded the 2-oxabicyclo[3.3.0]octa-3,7-diene **18**, shows that the cyano group at the 2-position of the trienal accelerates this tandem cyclization of the hepta-2,4,6-trienals. We also performed the photocyclizations of the hepta-2,4,6-trienals **12** and **10**; however, the 2-oxabicyclic compounds gave rise to only low yields or a complex mixture (Scheme 4).



Scheme 4 *Conditions*: i, MeCN, *hν* (500–600 nm).

In summary, α-cyanoformylation is considered to be one of the good methods for the preparation of various α-cyanoacrolein derivatives. In addition, we could carry out syntheses of some cyano-substituted hepta-2,4,6-trienals. Now we are examining other transformations of the new 2,4,6-trienals and their derivatives. These results will be reported elsewhere.

Experimental

Mps were determined on a Yanagimoto micro-melting-point apparatus and are uncorrected. Elemental analyses were performed at the Microanalytical Laboratory of Gifu Pharmaceutical University. ^{1}H and ^{13}C NMR spectra were determined with a Varian Inova 400 (400 MHz) spectrometer at the Center of Instrumentation of Gifu University. Chemical shifts (δ) are expressed in parts per million (ppm) with respect to tetramethylsilane as internal standard. Splitting patterns are designated as follows: s = singlet, d = doublet, t = triplet, q = quartet. *J*-Values are given in Hz. IR spectra of solids (KBr) and liquids (film) were recorded on a JASCO IR A-100 infrared spectrometer. EI Mass spectra (MS) were obtained using a JMS-SX102A spectrometer with a direct-insertion probe at an ionization voltage of 70 eV. Ether refers to diethyl ether.

Preparation of 3-ethoxy-2-cyanoprop-2-en-1-ols 2a–i, 5, 14, 17 using α-lithio-2-ethoxyacrylonitrile: typical procedure

(*Z*)-2-Cyano-3-ethoxy-1-phenylprop-2-en-1-ol 2a. Under an Ar atmosphere, a THF (2.00 ml) solution of 3-ethoxyacrylonitrile **1** (0.30 g, 3.10 mmol) was added dropwise to a THF (5.00 ml) solution of lithium 2,2,6,6-tetramethylpiperidide [prepared from *n*-BuLi (3.10 ml, 4.65 mmol) and 2,2,6,6-tetramethylpiperidine (0.88 g, 6.20 mmol)] at −78 °C. Then, a THF (1.00 ml) solution of benzaldehyde (0.49 g, 4.65 mmol) was added dropwise to the reaction mixture. The whole was poured into water (50.0 ml), the organic layer was separated, and the aqueous layer was extracted with ether. The combined organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel and development with AcOEt–hexane (1 : 5) to give the title compound **2a** (0.41 g, 65%) as a yellow oil, IR (film; cm^{-1}) 3600–3100 (OH), 2170 (CN); ^{1}H NMR (400 MHz; $CDCl_3$) δ 1.30 (3H, t, *J* 7, Me), 3.02 (1H, br s, OH), 4.04 (2H, q, *J* 7, OCH_2), 5.71 (1H, s, 1-H), 6.85 (1H, s, olefinic H), 7.25–7.34 (3H, m, ArH), 7.41–7.44 (2H, m, ArH); ^{13}C NMR (100 MHz; $CDCl_3$) δ 15.30 (q), 66.68 (d), 71.41 (t), 97.58 (s), 117.85 (s), 125.78 (2d), 128.01 (2d), 128.58 (2d), 141.34 (s), 158.78 (d); MS *m*/*z* 203 (M^+) (Calc. for $C_{12}H_{13}NO_2$: C, 70.92; H, 6.45; N, 6.89. Found: C, 70.58; H, 6.53; N, 7.02%).

(*Z*)-2-Cyano-1-ethoxy-4,4-dimethylpent-en-3-ol 2b. A brown oil, IR (film; cm^{-1}) 3820–3080 (OH), 2240 (CN); ^{1}H NMR (400 MHz; $CDCl_3$) δ 0.98 (9H, s, Me × 3), 1.32 (3H, t, *J* 7, Me), 2.11 (1H, d, *J* 6, OH), 4.06 (2H, q, *J* 7, OCH_2), 4.27 (1H, d, *J* 6, 3-H), 6.92 (1H, s, olefinic H); ^{13}C NMR (100 MHz; $CDCl_3$) δ 15.45 (q), 25.78 (3q), 36.95 (s), 71.30 (t), 73.32 (d), 95.04 (s), 119.14 (s), 159.45 (d); MS *m*/*z* 183 (M^+). (Calc. for $C_{10}H_{17}NO_2$: C, 65.54; H, 9.35; N, 7.64. Found: C, 65.14; H, 9.49; N, 7.62%).

(*Z*)-2-Cyano-1-ethoxy-5-phenylpent-1-en-4-yn-3-ol 2c. Yellow needles, mp 30 °C; IR (film; cm^{-1}) 3800–3150 (OH), 2230 (CN); ^{1}H NMR (400 MHz; $CDCl_3$) δ 1.36 (3H, t, *J* 7, Me), 2.68 (1H, d, *J* 6, OH), 4.13 (2H, q, *J* 7, OCH_2), 5.56 (1H, d, *J* 6, 3-H), 6.95 (1H, d, *J* 1, olefinic H), 7.26–7.38 (3H, m, ArH), 7.43–7.52 (2H, m, ArH); ^{13}C NMR (100 MHz; $CDCl_3$) δ 15.35 (q), 56.53 (t), 71.90 (d), 86.32 (s), 95.40 (s), 117.47 (s), 122.11 (s), 124.66 (s), 128.45 (2d), 128.99 (d), 132.10 (2d), 159.69 (d); MS *m*/*z* 227 (M^+) (Calc. for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77; N, 6.16. Found: C, 73.66; H, 5.85; N, 6.15%).

(1*Z*,4*E*)-2-Cyano-1-ethoxy-3-methyl-5-phenylpenta-1,4-dien-3-ol 2d. Yellow needles, mp 30 °C; IR (film; cm^{-1}) 3650–3150 (OH), 2220 (CN); ^{1}H NMR (400 MHz; $CDCl_3$) δ 1.31 (3H, t, *J* 7, Me), 1.63 (3H, s, Me), 3.33 (1H, s, OH), 4.05–4.10 (2H, m, OCH_2), 6.36 (1H, d, *J* 16, 4-H), 6.63 (1H, d, *J* 16, 5-H), 6.88 (1H, s, 1-H), 7.22–7.39 (5H, m, ArH); ^{13}C NMR (100 MHz; $CDCl_3$) δ 15.40 (q), 28.14 (q), 72.05 (t), 72.49 (s), 100.17 (s), 118.30 (s), 126.76 (2d), 127.79 (d), 127.88 (d), 128.73 (2d), 133.37 (d), 136.58 (s), 158.52 (d); MS *m*/*z* 200 (M^+ − Ph), 166 (M^+ − OH, CN) (Calc. for $C_{15}H_{17}NO_2$: C, 74.05; H, 7.04; N, 5.76. Found: C, 74.30; H, 6.83; N, 6.01%).

(1*Z*,4*E*)-2-Cyano-1-ethoxy-6,6-dimethyl-4-(phenylthio)hepta-1,4-dien-3-ol 2e. Mp 96–97 °C, IR (film; cm^{-1}) 3600–3300 (OH), 2240 (CN); ^1H NMR (400 MHz; $CDCl_3$) δ 1.21 (3H, t, *J* 7, Me), 1.30 (9H, s, Me × 3), 2.37 (1H, d, *J* 5, OH), 3.92–3.99 (2H, m, OCH_2), 4.94 (1H, d, *J* 5, 3-H), 6.62 (1H, d, *J* 1, 5-H), 6.87 (1H, s, 1-H), 7.15–7.29 (5H, m, ArH); ^{13}C NMR (100 MHz; $CDCl_3$) δ 15.28 (q), 30.76 (3q), 33.77 (s), 67.53 (d), 71.29 (t), 96.56 (s), 117.47 (s), 126.22 (d), 128.83 (2d), 129.09 (2d), 129.55 (s), 135.52 (s), 148.70 (d), 160.10 (d); MS *m*/*z* 317 (M^+) (Calc. for $C_{18}H_{23}NO_2S$: C, 68.11; H, 7.30; N, 4.11. Found: C, 67.82; H, 7.36; N, 4.27%).

(*Z*)- and (*E*)-4-*tert*-Butyl-1-(1-cyano-2-ethoxyethenyl)cyclohexanol 2f. The *Z*-isomer was obtained as colorless prisms, mp 64–66 °C; IR (film; cm^{-1}) 3650–3300 (OH), 2210 (CN); ^1H NMR (400 MHz; $CDCl_3$) δ 0.87 (9H, s, Me × 3), 1.01–1.02 (1H, m, 4-H), 1.36 (3H, t, *J* 7, Me), 1.42–1.46 (2H, m, CH_2), 1.58–1.61 (2H, m, CH_2), 1.65–1.72 (2H, m, CH_2), 1.95–1.99 (2H, m, CH_2), 2.76 (1H, s, OH), 4.09 (2H, q, *J* 7, OCH_2), 6.82 (1H, s, olefinic H); ^{13}C NMR (100 MHz; $CDCl_3$) δ 15.38 (q), 22.23 (2t), 27.64 (3q), 32.52 (s), 37.17 (2t), 47.26 (d), 71.20 (s), 71.85 (t), 102.53 (s), 118.57 (s), 158.22 (d); MS *m*/*z* 251 (M^+) (Calc. for $C_{15}H_{25}NO_2$: C, 71.67; H, 10.02; N, 5.57. Found: C, 71.39; H, 10.28; N, 5.50%).

The *E*-isomer was obtained as a brown oil, IR (film; cm^{-1}) 3700–3130 (OH), 2220 (CN); ^1H NMR (400 MHz; $CDCl_3$) δ 0.85 (9H, s, Me × 3), 1.00–1.25 (3H, m, 4-H and CH_2), 1.37 (3H, t, *J* 7, Me), 1.39–1.56 (2H, m, CH_2), 1.73–1.76 (2H, m, CH_2), 2.32–2.41 (2H, m, CH_2), 2.71 (1H, br s, OH), 4.13 (2H, q, *J* 7, OCH_2), 6.91 (1H, s, olefinic H); ^{13}C NMR (100 MHz; $CDCl_3$) δ 15.44 (q), 24.72 (2t), 27.72 (3q), 32.38 (s), 38.52 (2t), 47.08 (d), 72.05 (t), 72.44 (s), 98.45 (s), 119.56 (s), 160.47 (d); MS *m*/*z* 251 (M^+).

(*E*)- and (*Z*)-1-(1-Cyano-2-ethoxyethenyl)cyclohex-2-en-1-ol 2g. A yellow oil, *E* : *Z* = 80 : 20; IR (film; cm^{-1}) 3750–3150 (OH), 2230 (CN); ^1H NMR (400 MHz; $CDCl_3$) δ 1.34 (t, *J* 7, *Z*-Me), 1.37 (t, *J* 7, *E*-Me), 1.65–2.07 (m, *E*- and *Z*-CH_2), 2.68 (br s, *Z*-OH), 3.12 (s, *E*-OH), 4.07 (q, *J* 7, *Z*-OCH_2), 4.12 (q, *J* 7, *E*-OCH_2), 5.61 (m, *Z*-CH), 5.82 (d, *J* 10, *E*-CH), 5.88–5.98 (m, *E*- and *Z*-CH), 6.89 (s, *E*-olefinic H), 6.98 (s, *Z*-olefinic H); ^{13}C NMR (100 MHz; $CDCl_3$) δ 15.29 (*E*-q), 18.84 (*Z*-t), 24.72 (*E*-t), 24.84 (*Z*-t), 35.71 (*E*-t), 36.37 (*Z*-t), 69.42 (*Z*-s), 69.64 (*E*-s), 70.69 (*Z*-t), 71.90 (*E*-t), 97.84 (*Z*-s), 100.84 (*E*-s), 116.07 (*Z*-s), 118.58 (*E*-s), 129.68 (*Z*-d), 129.73 (*E*-d), 131.01 (*E*-d), 132.33 (*Z*-d), 158.86 (*E*-d), 160.41 (*Z*-d); MS *m*/*z* 193 (M^+) (Calc. for $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82; N, 7.25. Found: C, 67.98; H, 7.87; N, 7.33%).

(*E*)-3-(1-Cyano-2-ethoxyethenyl)cyclohexanone 4. A yellow oil, IR (film; cm^{-1}) 2230 (CN), 1720 (CO); ^1H NMR (400 MHz; $CDCl_3$) δ 1.33 (3H, t, *J* 7, Me), 1.67–1.80 (2H, m, CH_2), 1.88–1.91 (1H, m, CH_2), 2.11–2.19 (2H, m, CH_2), 2.28–2.40 (3H, m, CH_2), 2.94–3.02 (1H, m, 3-H), 4.07 (2H, q, *J* 7, OCH_2), 6.86 (1H, s, olefinic H); ^{13}C NMR (100 MHz; $CDCl_3$) δ 15.24 (q), 24.95 (t), 34.34 (d), 40.85 (t), 45.87 (t), 95.61 (s), 118.27 (s), 158.12 (d), 209.74 (s); MS *m*/*z* 193 (M^+) (Calc. for $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82; N, 7.25. Found: C, 67.93; H, 7.97; N, 7.15%).

(*E*)- and *(Z)*-2-Cyano-3-ethoxy-1,1-diphenylprop-2-en-1-ol 2h. *E* : *Z* = 95 : 5, White powder, mp 57–60 °C; IR (KBr; cm^{-1}) 3630–3500 (OH), 2210 (CN); ^1H NMR (400 MHz; $CDCl_3$) δ 1.13 (t, *J* 7, *E*-Me), 1.25 (t, *J* 7, *Z*-Me), 2.03 (s, *E*-OH), 2.15 (s, *Z*-OH), 3.97 (q, *J* 7, *E*-OCH_2), 4.11 (q, *J* 7, *Z*-OCH_2), 6.63 (s, *Z*-olefinic H), 7.01 (s, *E*-olefinic H), 7.25–7.41 (m, *E*- and *Z*-ArH); ^{13}C NMR of *(E)*-**2h** (100 MHz; $CDCl_3$) δ 15.27 (q), 72.19 (t), 79.34 (s), 102.09 (s), 118.47 (s), 127.20 (4d), 128.07 (2d), 128.21 (4d), 144.45 (2s), 159.13 (d); MS *m*/*z* 279 (M^+) (Calc. for $C_{18}H_{17}NO_2$: C, 77.40; H, 6.13; N, 5.01. Found: C, 77.37; H, 6.16; N, 4.98%).

(1*Z*,4*E*)-2,4-Dicyano-1-ethoxy-6,6-dimethylhepta-1,4-dien-3-ol 5. A brown oil, IR (film; cm^{-1}) 3750–3100 (OH), 2220 (CN); ^1H NMR (400 MHz; $CDCl_3$) δ 1.26 (9H, s, Me × 3), 1.37 (3H, t, *J* 7, Me), 3.11 (1H, s, OH), 4.15 (2H, q, *J* 7, OCH_2), 5.19 (1H, s, olefinic H), 6.61 (1H, d, *J* 1, CH), 7.05 (1H, s, olefinic H); ^{13}C NMR (100 MHz; $CDCl_3$) δ 15.37 (q), 29.62 (3q), 34.41 (s), 66.21 (d), 72.12 (t), 94.26 (s), 110.84 (s), 116.29 (s), 116.77 (s), 157.64 (d), 160.79 (d) (Calc. for $C_{13}H_{18}N_2O_2$: *M*, 234.1368. Found: M^+, 234.1352).

Hydrolysis of 2-cyano-3-ethoxyprop-2-en-1-ols 2a–h. Typical procedure

Trimethylsilyl trifluoromethanesulfonate (TMSOTf) (0.36 ml, 2.00 mmol) was added dropwise to a CH_2Cl_2 (2.00 ml) solution of **2a** (0.20 g, 1.00 mmol) at −78 °C under an Ar atmosphere. After stirring for 10 min, the reaction mixture was poured into saturated aq. $NaHCO_3$ (50 ml). The organic layer was separated and the aqueous layer was extracted with $CHCl_3$. The combined organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was crystallized from hexane. The orange powder was filtered off and recrystallized from ether–hexane to give *(E)*-2-cyano-3-phenylprop-2-enal **3a** (0.14 g, 91%) as colorless needles, mp 85–86 °C; IR (KBr; cm^{-1}) 2220 (CN), 1690 (CO); ^1H NMR (400 MHz; $CDCl_3$) δ 7.54–7.65 (3H, m, ArH), 7.97 (1H, s, olefinic H), 8.04–8.06 (2H, m, ArH), 9.61 (1H, s, CHO); ^{13}C NMR (100 MHz; $CDCl_3$) δ 112.54 (s), 114.25 (s), 129.69 (2d), 131.38 (s), 131.51 (2d), 134.52 (d), 159.59 (d), 187.27 (d); MS *m*/*z* 157 (M^+) (Calc. for $C_{10}H_7NO$: C, 76.42; H, 4.49; N, 8.91. Found: C, 76.27; H, 4.59; N, 8.98%).

(*E*)-2-Cyano-4,4-dimethylpent-2-enal 3b. White powder, mp 30 °C; IR (KBr; cm^{-1}) 2240 (CN), 1710 (CO); ^1H NMR (400 MHz; $CDCl_3$) δ 1.37 (9H, s, Me × 3), 7.36 (1H, s, olefinic H), 9.40 (1H, s CHO); ^{13}C NMR (100 MHz; $CDCl_3$) δ 28.91 (3q), 36.22 (s), 94.57 (s), 112.80 (s), 177.49 (d), 187.43 (d); MS *m*/*z* 138 (M^+) (Calc. for $C_8H_{11}NO$: C, 70.04; H, 8.08; N, 10.21. Found: C, 69.88; H, 8.23; N, 10.10%).

(*E*)-2-Cyano-5-phenylpent-2-en-4-ynal 3c. Colorless needles (from ether–hexane), mp 59–60 °C; IR (KBr; cm^{-1}) 2190 (CN), 1690 (CO); ^1H NMR (400 MHz; $CDCl_3$) δ 7.34 (1H, s, olefinic H), 7.41–7.53 (3H, m, ArH), 7.62–7.65 (2H, m, ArH), 9.55 (1H, s, CHO); ^{13}C NMR (100 MHz; $CDCl_3$) δ 85.76 (s), 113.02 (s), 116.42 (s), 120.61 (s), 123.22 (s), 129.05 (2d), 131.88 (d), 133.37 (2d), 140.02 (d), 185.33 (d); MS *m*/*z* 181 (M^+) (Calc. for $C_{12}H_7NO$: C, 79.55; H, 3.89; N, 7.73. Found: C, 79.31; H, 3.99; N, 7.71%).

(2*E*,4*E*)-2-Cyano-3-methyl-5-phenylpenta-2,4-dienal 3d. Yellow needles, mp 56–58 °C; IR (KBr; cm^{-1}) 2230 (CN), 1680 (CO); ^1H NMR (400 MHz; $CDCl_3$) δ 2.60 (3H, s, Me), 7.43–7.49 (4H, m, ArH and 4-H), 7.56 (1H, d, *J* 16, 5-H), 7.62–7.64 (2H, m, ArH), 10.04 (1H, s, CHO); ^{13}C NMR (100 MHz; $CDCl_3$) δ 14.55 (q), 114.86 (s), 127.23 (d), 128.79 (2d), 129.43 (2d), 131.46 (d), 134.85 (s), 143.71 (d), 185.34; MS *m*/*z* 197 (M^+) (Calc. for $C_{13}H_{11}NO$: C, 79.17; H, 5.62; N, 7.10. Found: C, 79.01; H, 5.72; N, 7.10%).

(2*E*,4*E*)-2-Cyano-6,6-dimethyl-4-(phenylthio)hepta-2,4-dienal 3e. Brown powder, mp 68–72 °C; IR (KBr; cm^{-1}) 2230 (CN), 1700 (CO); ^1H NMR (400 MHz; $CDCl_3$) δ 1.38 (9H, s, Me × 3), 7.14 (1H, s, 3-H), 7.23–7.32 (5H, m, ArH), 7.42 (1H, s, 5-H), 9.27 (1H, s, CHO); ^{13}C NMR (100 MHz; $CDCl_3$) δ 30.07 (3q), 113.29 (s), 114.85 (s), 127.19 (d), 127.41 (s), 129.02 (2d), 129.62 (2d), 133.98 (s), 162.92 (d), 163.99 (d), 186.48 (d) (Calc. for $C_{16}H_{17}NOS$: *M*, 271.1031. Found: M^+, 271.1022).

2-(4-*tert*-Butylcyclohexylidene)-2-cyanoethanal 3f. Pale yellow powder, mp 103–105 °C; IR (KBr; cm^{-1}) 2230 (CN),

1670 (CO); ^{1}H NMR (400 MHz; $CDCl_3$) δ 0.90 (9H, s, Me × 3), 1.28–1.48 (3H, m, CH and CH_2), 2.14–2.18 (2H, m, CH_2), 2.26–2.44 (2H, m, CH_2), 3.13–3.14 (1H, m, CH_2), 3.17–3.18 (1H, m, CH_2), 9.95 (1H, s, CHO); ^{13}C NMR (100 MHz; $CDCl_3$) δ 27.60 (3q), 29.37 (d), 30.75 (s), 37.13 (2t), 47.41 (2t), 112.55 (s), 114.06 (s), 181.91 (s), 184.16 (d); MS *m*/*z* 205 (M^+) (Calc. for $C_{13}H_{19}NO$: C, 76.06; H, 9.33; N, 6.82. Found: C, 75.78; H, 9.35; N, 6.75%).

(*E*)-2-Cyano-2-(cyclohex-2-enylidene)ethanal 3g. A brown oil, *E* : *Z* = 59 : 41; IR (film; cm^{-1}) 2230 (CN), 1670 (CO); ^{1}H NMR (400 MHz; $CDCl_3$) δ 1.89–1.98 (m, CH_2), 2.42–2.47 (m, CH_2), 2.86–2.89 (m, CH_2), 3.06–3.09 (m, CH_2), 6.80–6.91 (m, olefinic H), 7.31–7.35 (m, olefinic H), 9.98 (s, *E*-CHO), 10.00 (s, *Z*-CHO); MS *m*/*z* 146 ($M^+ - 1$) (Calc. for C_9H_9NO: C, 73.45; H, 6.16; N, 9.52. Found: C, 73.19; H, 6.23; N, 9.48%).

2-Cyano-3,3-diphenylprop-2-enal 3h. Pale yellow needles, mp 140–142 °C; IR (KBr; cm^{-1}) 2230 (CN), 1670 (CO); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.26–7.28 (2H, m, ArH), 7.45–7.63 (8H, m, ArH), 9.42 (1H, s, CHO); ^{13}C NMR (100 MHz; $CDCl_3$) δ 113.34 (s), 115.58 (s), 128.91 (2d), 128.95 (2d), 130.80 (2d), 131.70 (2d), 132.20 (d), 132.71 (d), 135.81 (s), 137.66 (s), 173.34 (s), 187.12 (d); MS *m*/*z* 233 (M^+) (Calc. for $C_{16}H_{11}NO$: C, 82.38; H, 4.75; N, 6.00. Found: C, 82.20; H, 4.73; N, 5.91%).

Preparation of (2*Z*,4*Z*,6*Z*)-6-cyano-8,8-dimethyl-2,4-bis(phenylthio)nona-2,4,6-trienal 10

(1*E*,4*E*)-4-Cyano-1-ethoxy-6,6-dimethyl-2-(phenylthio)hepta-1,4-dien-3-ol 7. Under an Ar atmosphere, a THF (1.50 ml) solution of *(E)*-2-cyano-4,4-dimethylpent-1-en-3-ol **2b** (0.14 g, 1.00 mmol) was added dropwise to a THF (2.00 ml) solution of PhSCLi=CHOEt [prepared from 2-ethoxyvinyl phenyl sulfide (0.27 g, 1.50 mmol) and *n*-BuLi (0.80 ml, 1.20 mmol)] at −78 °C. After stirring for 10 min, the reaction mixture was poured into water (50 ml). The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel and development with AcOEt–*n*-hexane (1 : 5) to give the title compound **7** (0.17 g, 52%) as a yellow oil, IR (film; cm^{-1}) 3700–3200 (OH), 2240 (CN); ^{1}H NMR (400 MHz; $CDCl_3$) δ 1.04 (9H, s, Me × 3), 1.37 (3H, t, *J* 7, Me), 3.28 (1H, d, *J* 9, OH), 4.06 (2H, q, *J* 7, OCH_2), 5.14 (1H, dd, *J* 9 and 1, CH), 6.28 (1H, d, *J* 1, olefinic H), 6.85 (1H, s, olefinic H), 7.13–7.16 (1H, m, ArH), 7.22–7.27 (2H, m, ArH), 7.31–7.34 (2H, m, ArH); ^{13}C NMR (100 MHz; $CDCl_3$) δ 15.41 (q), 29.34 (3q), 33.98 (s), 70.23 (t), 71.17 (d), 107.93 (s), 112.29 (s), 116.82 (s), 126.16 (d), 127.24 (2d), 129.08 (2d), 137.08 (s), 156.14 (d), 156.92 (d) (Calc. for $C_{18}H_{23}NO_2S$: *M*, 317.1449. Found: M^+, 317.1444).

(2*Z*,4*Z*)-4-Cyano-6,6-dimethyl-2-(phenylthio)hepta-2,4-dienal 8. TMSOTf (0.06 ml, 0.32 mmol) was added dropwise to a CH_2Cl_2 (2.00 ml) solution of **7** (0.10 g, 0.32 mmol) at −78 °C. The mixture was stirred for 10 min. The work-up procedure afforded the title compound **8** (76 mg, 88%) as a yellow powder, mp 64–68 °C; IR (film; cm^{-1}) 2250 (CN), 1710 (CO); ^{1}H NMR (400 MHz; $CDCl_3$) δ 1.32 (9H, s, Me × 3), 6.91 (1H, s, olefinic H), 7.20 (1H, s, olefinic H), 7.21–7.34 (5H, m, ArH), 9.34 (1H, s, CHO); ^{13}C NMR (100 MHz; $CDCl_3$) δ 29.40 (3q), 35.67 (s), 108.20 (s), 115.35 (s), 127.66 (d), 129.50 (2d), 130.43 (2d), 132.98 (s), 135.62 (s), 142.83 (d), 170.44 (d), 189.84 (d) (Calc. for $C_{16}H_{17}NOS$: *M*, 271.1031. Found: M^+, 271.1020).

(1*E*,4*Z*,6*Z*)-6-Cyano-1-ethoxy-8,8-dimethyl-2,4-bis(phenylthio)nona-1,4,6-trien-3-ol 9. Under an Ar atmosphere, a THF (1.50 ml) solution of compound **8** (0.12 g, 0.43 mmol) was added dropwise to a THF (2.00 ml) solution of PhSCLi=CHOEt [prepared from PhSCH=CHOEt (0.16 g, 0.86 mmol) and *n*-BuLi (0.43 ml, 0.65 mmol)] at −78 °C. The work-up procedure afforded the title compound **9** (65 mg, 32%) as a yellow oil, IR (film; cm^{-1}) 3650–3150 (OH), 2230 (CN); ^{1}H NMR (400 MHz; $CDCl_3$) δ 1.14 (9H, s, Me × 3), 1.24 (3H, t, *J* 7, Me), 2.81 (1H, d, *J* 7, OH), 3.89–4.00 (2H, m, OCH_2), 5.22 (1H, d, *J* 5, CH), 5.96 (1H, d, *J* 1, olefinic H), 6.55 (1H, t, *J* 1, olefinic H), 6.80 (1H, t, *J* 12, CH), 7.09–7.39 (6H, m, ArH), 7.42–7.45 (4H, m, ArH); ^{13}C NMR (100 MHz; $CDCl_3$) δ 15.43 (q), 29.49 (3q), 34.59 (s), 69.83 (t), 70.72 (d), 107.28 (s), 108.48 (s), 116.64 (s), 126.10 (d), 126.74 (d), 127.17 (2d), 128.99 (2d), 129.04 (2d), 129.94 (d), 130.15 (2d), 134.79 (s), 137.94 (s), 138.16 (s), 157.51 (d), 163.06 (d); MS *m*/*z* 452 ($M^+ + 1$). This compound was too labile to be isolated at room temperature, so it was taken to the next (hydration) step without purification.

Hydration of 9. TMSOTf (0.10 ml, 0.55 mmol) was added dropwise to a CH_2Cl_2 (2.00 ml) solution of **9** (50 mg, 0.11 mmol) at −78 °C. The work-up procedure afforded (2*Z*,4*Z*,6*Z*)-6-cyano-8,8-dimethyl-2,4-bis(phenylthio)nona-2,4,6-trienal **10** (22 mg, 49%) as a yellow oil, IR (film; cm^{-1}) 2240 (CN), 1710 (CO); ^{1}H NMR (400 MHz; $CDCl_3$) δ 1.32 (9H, s, Me × 3), 6.45 (1H, s, olefinic H), 6.55 (1H, d, *J* 1, olefinic H), 6.62 (1H, d, *J* 1, olefinic H), 7.07–7.10 (2H, m, ArH), 7.20–7.31 (6H, m, ArH), 7.36–7.38 (2H, m, ArH), 9.18 (1H, s, CHO); ^{13}C NMR (100 MHz; $CDCl_3$) δ 29.60 (3q), 35.29 (s), 108.55 (s), 116.01 (s), 127.57 (d), 127.94 (d), 129.35 (2d), 129.48 (2d), 130.09 (2d), 131.44 (2d), 133.20 (s), 136.16 (d), 137.80 (s), 148.12 (d), 166.41 (d), 189.11 (d) (Calc. for $C_{24}H_{23}NO_2S_2$: *M*, 421.1170. Found: M^+, 421.1168).

Preparation of (2*Z*,4*Z*,6*Z*)-4-cyano-8,8-dimethyl-2,6-bis(phenylthio)nona-2,4,6-trienal 12

(1*E*,4*E*,6*Z*)-4-Cyano-1-ethoxy-8,8-dimethyl-2,6-bis(phenylthio)nona-1,4,6-trien-3-ol 11. Under an Ar atmosphere, a THF (1.00 ml) solution of 2-cyano-6,6-dimethyl-4-(phenylthio)-hepta-2,4-dienal **3e** (0.27 g, 1.00 mmol) was added dropwise to a THF (5.00 ml) solution of PhSCLi=CHOEt [prepared from PhSCH=CHOEt (0.36 g, 2.00 mmol) and *n*-BuLi (1.00 ml, 1.50 mmol)] at −78 °C. The work-up procedure afforded the title compound **11** (0.25 g, 55%) as a brown oil, IR (film; cm^{-1}) 3480 (OH), 2250 (CN); ^{1}H NMR (400 MHz; $CDCl_3$) δ 1.27 (9H, s, Me × 3), 1.32 (3H, t, *J* 7, Me), 2.92 (1H, d, *J* 8, OH), 3.98 (2H, q, *J* 7, CH_2), 5.03 (1H, d, *J* 8, CH), 6.25 (1H, s, olefinic H), 6.48 (1H, s, olefinic H), 6.75 (1H, s, olefinic H), 7.12–7.29 (10H, m, ArH); ^{13}C NMR (100 MHz; $CDCl_3$) δ 15.46 (q), 30.36 (3q), 34.59 (s), 70.34 (t), 107.97 (s), 116.30 (s), 116.73 (s), 126.44 (s), 126.48 (d), 126.57 (d), 127.57 (2d), 129.21 (2d), 129.24 (2d), 129.64 (2d), 134.80 (s), 137.02 (s), 145.59 (d), 153.44 (d), 156.64 (d) (Calc. for $C_{26}H_{29}NO_2S_2$: *M*, 451.1640. Found: M^+, 451.1631).

(2*Z*,4*Z*,6*Z*)-4-Cyano-8,8-dimethyl-2,6-bis(phenylthio)nona-2,4,6-trienal 12. TMSOTf (0.04 ml, 0.22 mmol) was added dropwise to a CH_2Cl_2 (2.00 ml) solution of **11** (0.10 g, 0.22 mmol) at −78 °C. The work-up procedure afforded the title compound **12** (39 mg, 44%) as a yellow powder, mp 95–98 °C (decomp.); IR (film; cm^{-1}) 2230 (CN), 1700 (CO); ^{1}H NMR (400 MHz; $CDCl_3$) δ 1.36 (9H, s, Me^3), 6.80 (1H, s, olefinic H), 7.02 (1H, d, *J* 1, olefinic H), 7.04 (1H, d, *J* 1, olefinic H), 7.14–7.30 (10H, m, ArH), 9.24 (1H, s, CHO); ^{13}C NMR (100 MHz; $CDCl_3$) δ 30.29 (3q), 35.23 (s), 109.56 (s), 115.76 (s), 127.20 (d), 127.35 (s), 127.78 (d), 129.49 (2d), 129.54 (2d), 129.94 (2d), 130.55 (2d), 132.84 (s), 134.17 (s), 136.31 (s), 140.71 (d), 156.59 (d), 156.86 (d), 189.55 (d); MS *m*/*z* 405 (M^+) (Calc. for $C_{24}H_{23}NOS_2$: C, 71.08; H, 5.72; N, 3.45. Found: C, 70.85; H, 5.68; N, 3.41%).

Attempted preparation of (2*E*,4*Z*,6*Z*)-2-cyano-8,8-dimethyl-4,6-bis(phenylthio)nona-2,4,6-trienal 16

Preparation of (1*Z*,4*Z*,6*Z*)-2-cyano-1-ethoxy-8,8-dimethyl-4,6-bis(phenylthio)nona-1,4,6-trien-3-ol 14. Under an Ar atmosphere, a THF (1.00 ml) solution of 3-ethoxyacrylonitrile **1** (0.29 g, 3.00 mmol) was added dropwise to a THF (5.00 ml) solution of lithium 2,2,6,6-tetramethylpiperidide [prepared from 2,2,6,6-tetramethylpiperidine (0.17 g, 1.20 mmol) and *n*-BuLi (0.80 ml, 1.20 mmol)] at −78 °C. After 10 min of stirring, a THF (1.00 ml) solution of 6,6-dimethyl-2,4-bis(phenylthio)hepta-2,4-dienal **13** (0.51 g, 1.50 mmol) was added dropwise to the reaction mixture. The work-up procedure afforded the title compound **14** (0.16 g, 23%) as a yellow oil, IR (film; cm^{-1}) 3450 (OH), 2230 (CN); ^{1}H NMR (400 MHz; $CDCl_3$) δ 1.09 (9H, s, Me × 3), 1.32 (3H, t, *J* 7, Me), 2.92 (1H, d, *J* 8, OH), 3.98 (2H, q, *J* 7, CH_2), 5.03 (1H, d, *J* 8, CH), 6.25 (1H, s, olefinic H), 6.48 (1H, s, olefinic H), 6.75 (1H, s, olefinic H), 7.12–7.29 (10H, m, ArH); ^{13}C NMR (100 MHz; $CDCl_3$) δ 15.46 (q), 30.36 (3q), 34.59 (s), 70.34 (t), 107.97 (s), 116.30 (s), 116.73 (s), 126.44 (s), 126.48 (d), 126.57 (d), 127.57 (2d), 129.21 (2d), 129.24 (2d), 129.64 (2d), 134.80 (s), 137.02 (s), 145.59 (d), 153.44 (d), 156.64 (d) (Calc. for $C_{26}H_{29}NO_2S_2$: *M*, 451.1640. Found: M^+, 451.1650).

Reaction of 14 with TMSOTf. TMSOTf (0.06 ml, 0.11 mmol) was added dropwise to a CH_2Cl_2 (2.0 ml) solution of **14** (0.05 g, 0.11 mmol) at −78 °C. The work-up procedure afforded 2-*tert*-butyl-3-[(*Z*)-1-cyano-2-ethoxyethenyl]-1,4-bis(phenylthio)cyclopentadiene **15** (0.05 g, 10%) as a yellow oil, IR (film; cm^{-1}) 2200 (CN); ^{1}H NMR (400 MHz; $CDCl_3$) δ 1.36 (9H, s, Me × 3), 1.44 (3H, t, *J* 7, Me), 2.68 (2H, s, CH_2), 4.42 (2H, q, *J* 7, OCH_2), 5.89 (1H, s, olefinic H), 7.13–7.44 (10H, m, ArH) (Calc. for $C_{26}H_{27}NOS_2$: *M*, 433.1534. Found: *M*, 433.1538).

Attempted preparation of 2,6-dicyano-8,8-dimethyl-4-(phenylthio)nona-2,4,6-trienal 19

(1*Z*,4*Z*,6*Z*)-2,6-Dicyano-1-ethoxy-8,8-dimethyl-4-(phenylthio)nona-1,4,6-trien-3-ol 17. Under an Ar atmosphere, a THF (1.00 ml) solution of 3-ethoxyacrylonitrile **1** (0.08 g, 0.83 mmol) was added dropwise to a THF solution of lithium 2,2,6,6-tetramethylpiperidide [prepared from 2,2,6,6-tetramethylpiperidine (0.117 g, 0.83 mmol) and *n*-BuLi (0.48 ml, 0.72 mmol)] at −78 °C. Then, a THF (1.50 ml) solution of (2*Z*,4*Z*)-4-cyano-6,6-dimethyl-2-(phenylthio)hepta-2,4-dienal **8** (0.15 g, 0.55 mmol) was added dropwise to the reaction mixture. The work-up procedure afforded the title compound **17** (53 mg, 26%) as a brown oil, IR (film; cm^{-1}) 3750–3150 (OH), 2240 (CN); ^{1}H NMR (400 MHz; $CDCl_3$) δ 1.21 (3H, t, *J* 7, Me), 1.25 (9H, s, Me × 3), 2.17 (1H, s, OH), 3.99 (2H, q, *J* 7, OCH_2), 5.10 (1H, s, CH), 6.52 (1H, d, *J* 1, olefinic H), 6.82 (1H, t, *J* 1, olefinic H), 6.92 (1H, s, CH), 7.22–7.37 (5H, m, ArH); ^{13}C NMR (100 MHz; $CDCl_3$) δ 15.27 (q), 29.56 (3q), 34.87 (s), 66.84 (d), 71.58 (t), 95.30 (s), 107.50 (s), 116.48 (s), 117.37 (s), 127.36 (d), 129.22 (2d), 129.64 (d), 130.84 (2d), 133.43 (s), 137.02 (s), 160.52 (d), 164.53 (d) (Calc. for $C_{21}H_{24}N_2O_2S$: *M*, 368.1558. Found: M^+, 368.1551).

Reaction of 17 with TMSOTf. TMSOTf (0.06 ml, 0.32 mmol) was added dropwise to a CH_2Cl_2 (2.00 ml) solution of **17** (0.100 g, 0.27 mmol) at −78 °C. The reaction mixture was poured into saturated aq. $NaHCO_3$ (50.0 ml). The work-up procedure afforded (1*R**,5*S**,6*S**)-6-*tert*-butyl-4,7-dicyano-1-(phenylthio)-2-oxabicyclo[3.3.0]octa-3,7-diene **18** (8 mg, 9%) as colorless needles, mp 118–120 °C; IR (film; cm^{-1}) 2160 (CN), 2040 (CN); ^{1}H NMR (400 MHz; $CDCl_3$) δ 1.14 (9H, s, Me × 3), 2.88 (1H, t, *J* 2, CH), 3.54 (1H, t, *J* 2, CH), 6.42 (1H, d, *J* 2, olefinic H), 6.95 (1H, d, *J* 2, olefinic H), 7.39–7.50 (3H, m, ArH), 7.55–7.58 (2H, m, ArH); ^{13}C NMR (100 MHz; $CDCl_3$) δ 28.13 (3q), 34.96 (s), 53.32 (d), 65.61 (d), 92.61 (s), 108.79 (s), 113.97 (s), 116.08 (s), 120.92 (s), 128.30 (s), 129.76 (2d), 130.53 (d), 135.86 (2d), 144.73 (d), 156.48 (d); MS *m*/*z* 322 (M^+) (Calc. for $C_{19}H_{18}N_2OS$: 70.98; H, 5.63; N, 8.69. Found: C, 70.59; H, 5.60; N, 8.53%).

Photoreaction of (2*Z*,4*Z*,6*Z*)-4-cyano-8,8-dimethyl-2,6-bis(phenylthio)nona-2,4,6-trienal 12

Under an Ar atmosphere, a MeCN (150 ml) solution of **12** (60 mg, 0.15 mmol) was stirred for 2 days under irradiation with a 40 W fluorescent daylight lamp. The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel with AcOEt–*n*-hexane (1 : 10) as developer to give (1*R**,5*R**,6*S**)-6-*tert*-butyl-1-cyano-4,7-bis(phenylthio)-2-oxabicylo[3.3.0]octa-3,7-diene **20** (6 mg, 9%) as a white powder, IR (film; cm^{-1}) 2250 (CN); ^{1}H NMR (400 MHz; $CDCl_3$) δ 0.91 (9H, s, Me × 3), 2.90 (1H, t, *J* 1, CH), 3.74 (1H, t, *J* 1, CH), 4.91 (1H, d, *J* 1, olefinic H), 6.55 (1H, d, *J* 2, olefinic H), 7.12–7.44 (10H, m, ArH) (Calc. for $C_{24}H_{23}NOS_2$: *M*, 405.1121. Found: M^+, 405.1137).

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