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Cyanation of nucleophilic alkynes: easy approach to element-substituted α-cyanoenamines

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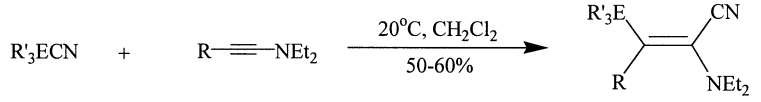
Abstract—The reactions of trimethylsilyl cyanide and tributyltin cyanide with ynamines proceeds as a regioselective *syn*-addition and provide previously unknown β-elementosubstituted α-cyanoenamines as pure *E*-isomers. The reaction of cyanogen bromide with ynamines as well the hydrocyanation of phosphorus substituted *N*,*N*-diethylaminoacetylenes by acetone cyanohydrin also proceeds as regioselective *syn*-addition, though the initially formed *Z*-isomers undergo an easy transformation into *E*-isomers. Cross-coupling reaction of β-bromo-α-cyanoenamine with arylboronic acids were shown to be an easy and convenient approach to α-dialkylaminosubstituted cynnamonitriles.

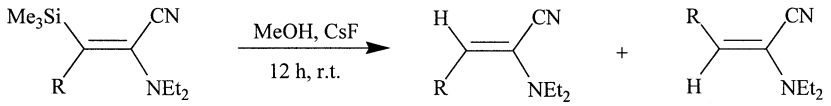
α-Cyanoenamines have been shown to be of great utility in organic synthesis as demonstrated by their conversion into 1,4-diones, 1,2-diones, ketenimines, amides, α-haloimidoyl cyanides, acyl cyanides, carboxylic acids, lactones, and dihydropyrazines. The anions of α-cyanoenamines have also been used for α- or γ-alkylation, 1,2- or 1,4-addition to enones and as β-carboxylvinyl anion equivalents.[1] Presently, more than 10 synthetic approaches to α-cyanoenamines are known. However, α-cyanoenamines bearing heteroatom substituents at the double bond are unknown. During our research on the electrophilic addition of organoelement reagents to the triple bond of nucleophilic alkynes,[2] we found an easy approach to the element-substituted α-cyanoenamines, which could serve both as convenient synthons in cross-coupling reactions for introduction of α-cyanoenamine moiety, and for hydrogenation leading to valuable saturated element-substituted α-aminonitriles and diamines.

Ni- or Pd-catalysed addition of trimethylsilyl cyanide to alkynes has recently been shown to lead to the formation of *syn*-adducts.[3,4] We have found that in the presence of such catalysts the reaction of Me_3SiCN with amino- and alkoxyacetylenes leads to complex mixtures of products. In the absence of transition metal or electrophilic catalysts, Me_3SiCN does not react with alkoxyacetylenes. On the other hand, the addition of Me_3SiCN (**1a**) to ynamines (**2a**,**b**) was discovered to take place slowly (1–2 weeks) at



1a,b **2a,b** ***E*-3a-d**

Scheme 1. 1: **a**, R′$_3$E=Me_3Si; **b**, R′$_3$E=Bu_3Sn; **2**: **a**, R=Me; **b**, R=*i*-Pr; **3**: **a**, R=Me, R′$_3$E=Me_3Si; **b**, R = *i*-Pr, R′$_3$E = Me_3Si; **c**, R=Me, R′$_3$E=Bu_3Sn; **d**, R = *i*-Pr, R′$_3$E = Bu_3Sn.



3a,b 68-72% ***Z*-4a,b** 8-12% ***E*-4a,b**

Scheme 2.

Keywords: ynamines; electrophilic addition; trimethylsilyl cyanide; cyanogens bromide; α-cyanoenamines; cross-coupling.
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Table 1. Isomer ratio, isolated yield and the most important NMR data for α-cyanoenamines

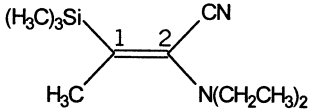
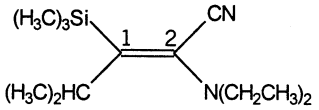
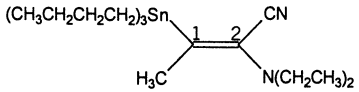
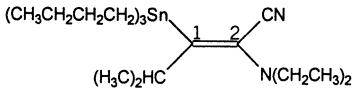
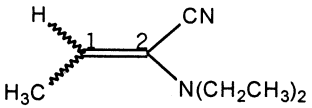
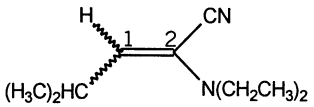
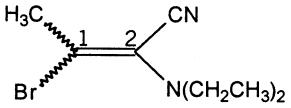
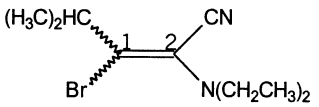
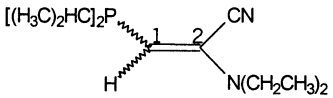
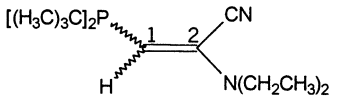
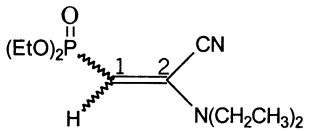
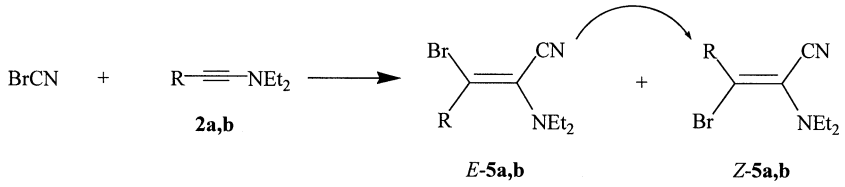
	Product	*Z*/*E* ratio	Time, h (yield, %)	δ_{C1} (ppm); *J* (Hz)	δ_{C2} (ppm); *J* (Hz)	δ_{CN} (ppm); *J* (Hz)	$\delta_{H-C=}$ (ppm)
3a		0:100	15 (59)	153.9; $^{1}J_{SiC}$=61.1	130.4	113.4	–
3b		0:100	24 (52)	164.0	129.3	113.5	–
3c		0:100	3 (57)	162.5; $^{1}J_{^{119}SnC}$=329.6	128.5; $^{2}J_{SnC}$=29.0	113.0; $^{3}J_{SnC}$=60.1	–
3d		0:100	49 (49)	174.1; $^{1}J_{^{119}SnC}$=323.5	126.7; $^{2}J_{SnC}$=30.5	113.1; $^{3}J_{SnC}$=62.3	–
4a		87:13	1 (72)	*Z*: 139.8; $^{1}J_{CH}$=157.5 *E*: 116.1; $^{1}J_{CH}$=156.8	*Z*: 123.4 *E*: 114.4	*Z*: 115.1; $^{3}J_{CH}$=5.6 *E*: 114.8; $^{3}J_{CH}$=12.5	*Z*: 6.19 q; *J*=6.9 Hz *E*: 5.21 q; *J*=6.9 Hz
4b		91:9	2.5 (65)	*Z*: 152.2; $^{1}J_{CH}$=155.0 *E*: 128.9; $^{1}J_{CH}$=155.5	*Z*: 120.5 *E*: 114.3	*Z*: 114.9; $^{3}J_{CH}$ 6.5 *E*: 114.8; $^{3}J_{CH}$=13.1	*Z*: 5.96 d; *J*=10.1 Hz *E*: 4.99 d; *J*=9.7 Hz
5a		54:46	2 (78)	*Z*: 137.6 *E*: 138.5	*Z*: 121.9 *E*: 124.1	*Z*: 112.8 *E*: 113.4	– –
5b		63:37	2 (67)	*Z*: 152.7 *E*: 153.7	*Z*: 119.7 *E*: 122.7	*Z*: 112.7 *E*: 113.2	– –
7a		9:91	2 (78)	*Z*: 109.9; $^{1}J_{CH}$=152.7; $^{1}J_{PC}$=27.1 *E*: 102.7, $^{1}J_{CH}$=151.9; $^{1}J_{PC}$=15.9	*Z*: 130.6; $^{2}J_{PC}$=18.3 *E*: 132.8; $^{2}J_{PC}$=41.4	*Z*: 116.8; $^{3}J_{PC}$=8.1 *E*: 114.3; $^{3}J_{CH}$=13.4; $^{3}J_{PC}$=3.1	*Z*: 4.82 d; $^{2}J_{PH}$=5.5 Hz *E*: 4.76 d; $^{2}J_{PH}$=5.5 Hz
	δ_P -8.1 (*Z**), -1.0 (*E*)						

Table 1. (*continued*)

	Product	*Z*/*E* ratio	Time, h (yield, %)	δ_{C1} (ppm); *J* (Hz)	δ_{C2} (ppm); *J* (Hz)	δ_{CN} (ppm); *J* (Hz)	$\delta_{H-C=}$ (ppm)
7b	 δ_P 6.0 (*Z**), 15.9 (*E*)	0:100 (after long storage)	3 (80)	*Z*: 108.9; $^1J_{CH}$=151.9; $^1J_{PC}$=27.5 *E*: 102.7; $^1J_{CH}$=152.0; $^1J_{PC}$=16.8	*Z*: 130.3; $^2J_{PC}$=20.8, *E*: 132.7; $^2J_{PC}$=44.3	*Z*: 117.0; $^3J_{CH}$=7.3; $^3J_{PC}$=9.2 *E*: 114.4; $^3J_{CH}$=13.4; $^3J_{PC}$=3.7	*Z*: 5.16 d; $^2J_{PH}$=4.9 Hz *E*: 4.97 d; $^2J_{PH}$=4.9 Hz
9	 δ_P 13.5 (*Z*), 16.2 (*E*)	0:100 (after long storage	36 (76)	*Z*: 86.7; $^1J_{CH}$=156.9; $^1J_{PC}$=206.0 *E*: 87.1; $^1J_{CH}$=155.9; $^1J_{PC}$=212.1	*Z*: 132.7; $^2J_{PC}$=9.2 *E*: 132.3; $^2J_{PC}$=12.2	*Z*: 115.0; $^3J_{CH}$=8.4; $^3J_{PC}$=27.5 *E*: 111.8; $^3J_{CH}$=12.9; $^3J_{PC}$=8.5	*Z*: 4.50 d; $^2J_{PH}$=2.3 Hz *E*: 4.54 d; $^2J_{PH}$=5.6 Hz

* Distant couplings for *Z*-isomers of **7a**,**b** have been found: $^4J_{PC}$=12.3 Hz, $^5J_{PC}$=3.1 Hz and $^5J_{PH}$=2.2 Hz (*Z*-**7a**); $^4J_{PC}$=12.1 Hz, $^5J_{PC}$=3.0 Hz and $^5J_{PH}$=2.4 Hz (*Z*-**7b**).

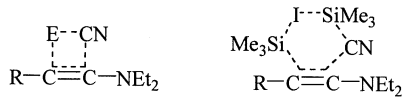


Scheme 3. a, R=Me; **b**, R=*i*-Pr.

room temperature in CH_2Cl_2 in the absence of catalysts to give α-cyanoenamines (**3a**,**b**) as individual regio- and stereoisomers in 50–60% yields. In this case, the addition of a catalytic amount of electrophilic catalyst—Me_3SiI—accelerates the reaction and decreases the reaction time to several hours at rt. We have shown that Bu_3SnCN (**1b**) can also add to aminoacetylenes (**2a**,**b**) in regio- and stereoselective mode. In this case, the reaction proceeds smoothly at rt without any catalyst (Scheme 1).

The determination of the configuration of tetrasubstituted alkenes **3a**–**d** is a difficult problem, particularly in those cases when only one isomer can be detected and direct comparison of the spectra of respective isomers could not be done. We investigated a differential Overhauser's effect for the confirmation of the structure of compound **3a**. NOEDIF showed a definite though weak response of CH_3 protons on irradiation of NCH_2 protons which can be interpreted as an evidence in favour of spatial proximity of these groups in *syn*-position. It could thus be concluded, that the data given above speaks in favour of the *syn*-addition pathway for the reaction of **1a** and possibly for the addition of **1b** to the ynamines **2a**,**b**. The structure of the adducts **3a**,**b** was also confirmed by their transformation into trisubstituted alkenes by treatment with an equivalent amount of CsF in a methanolic solution. After 12 h at rt the protodesilylation procedure gave the isomers *Z*-**4a**,**b** in 68–72% yields along with the corresponding *E*-isomers of **4a**,**b** in 12 and 8% yields, respectively (Scheme 2).

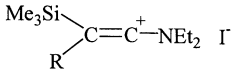
^{1}H NMR spectroscopic data for the compound *Z*-**4a** is consistent with the data reported earlier for the same compound.[5] It is known that the protodesilylation at a sp^2 carbon atom in the presence of fluoride anion commonly proceeds with retention of the configuration of the alkene.[6] However in some cases, especially in the presence of electron withdrawing substituents at the double bond, partial



"A"

"B"

E=Me_3Si; Bu_3Sn; Br



"C"

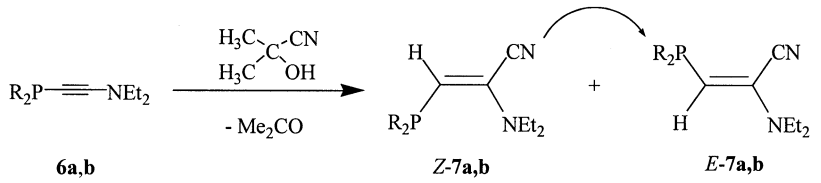
Scheme 4. E=Me_3Si; Bu_3Sn; Br.

inversion can be observed.[7] So the data obtained for protodesilylation of **1a** is also consistent with the proposed *E*-structure of α-cyanoenamine **3a**. The regiochemistry of the adducts **3c**,**d** should be similar to that of the adducts **3a**,**b** which has been confirmed by the values of $^1J_{^{119}SnC}$=323–330 Hz and $^2J_{^{119}SnC}$=29–30 Hz for corresponding olefin carbon atoms in ^{13}C NMR spectra (see Table 1).

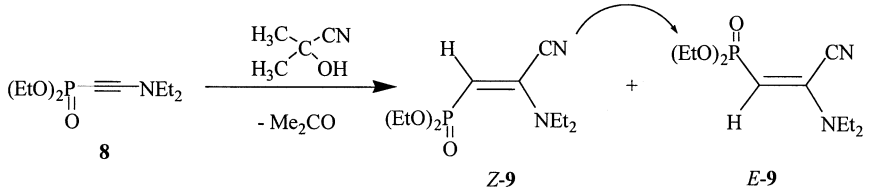
It was interesting to test other electrophilic cyanides in the addition reactions to nucleophilic aminoacetylenes. We have found that the addition of cyanogen bromide to ynamines **2a**,**b** was complete within 1–2 h at rt in CH_2Cl_2 to give β-bromo-α-cyanoenamines **5a**,**b** in 67 and 78% yields, respectively. Monitoring of this reaction by ^{1}H NMR spectroscopy showed that *E*-isomer **5a** (as a result of *syn*-addition) was the primary product. However, the individual *E*-isomers **5a**,**b** cannot be obtained in pure form, because a fast isomerisation of the *E*-isomers into *Z*-isomers took place simultaneously with the addition. It was shown that cyanogen bromide itself can catalyse this isomerisation. As a result, after the purification by column chromatography mixtures of 46–37% of *E*-**5a**,**b** and 54–63% *Z*-**5a**,**b** were obtained (Scheme 3).

The assignment of the signals in the ^{13}C NMR spectra of the *E*/*Z*-isomer mixture and the determination of the structure of the initial isomer also have been made based on the investigation of the differential nuclear Overhauser's effect. We observed a definite though weak response of CH_3 protons on irradiation of NCH_2 protons the *E*-**5a** isomer, which can be interpreted as evidence in favour of spatial proximity of these groups in *syn*-position.

The regioselectivity of addition of Me_3SiCN, Bu_3SnCN and BrCN to nucleophilic alkynes is typical for an electrophilic mechanism. The formation of exclusively *syn*-adducts in an electrophilic addition reaction is, though more rare than *anti*-addition, nevertheless a well documented phenomenon. For example, the addition of boron[8] and aluminium hydrides,[9] a series of boron chlorides[10] to alkynes gives exclusively *syn*-adducts. The addition of hydrogen chloride or chlorine to alkynes has been reported to give both *E*- and *Z*-dichloroalkenes.[11] From recent publications the *syn*-addition of aryltellurium trichloride to alkynes should be mentioned.[12] *syn*-Addition is favoured for the addition of covalent electrophilic reagents not capable to give irenium cations, as well as for the strongly polarised triple bond.[13] Therefore, the hypothesis that in our case the addition of silyl cyanide, tin cyanide and cyanogen bromide to ynamine is realised via a four-membered mechanism 'A' seems perfectly justified. Less clear is the reason for the stereoselective formation of *syn*-adduct in the reaction of Me_3SiCN and dimethylaminopropyne (**2a**) in the presence



Scheme 5. **a**, R=*i*-Pr; **b**, R=*t*-Bu.



Scheme 6.

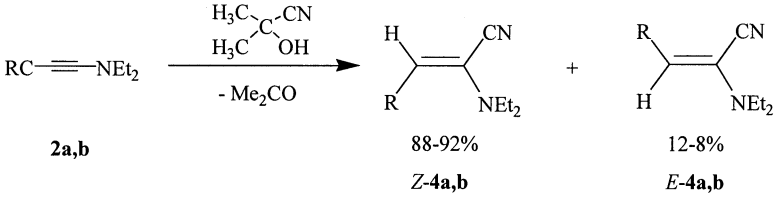
of catalytic amounts of Me_3SiI. We suggest a trimolecular process shown in scheme 'B'. Less likely is a two step reaction involving *syn*-addition of Me_3SiI followed by a nucleophilic displacement of iodine by cyano group. In a separate experiment, we have shown that the reaction of Me_3SiI with ynamine **2a**, both in absence or in presence of AgCN is not selective and gives a complex mixture of products. The formation of vinyl cation 'C' stabilised by NR_2 group and its subsequent reaction with cyanide should be rejected as this pathway should lead to a mixture of *syn*- and *anti*-adducts (Scheme 4).[13]

The attempts to synthesize the β-phosphinosubstituted α-cyanoenamines by a non-catalytic and catalytic reaction of trimethylsilyl cyanide **1a** with phosphorus substituted aminoacetylenes (**6a**,**b**),[14] or by the reaction of cyanophosphine *i*-Pr_2PCN with aminoacetylene **2a** failed. In the former case, a complex mixture of products was obtained, in the latter case no reaction has been observed. Nevertheless, β-phosphinosubstituted α-cyanoenamines can be obtained in the reaction of phosphorus substituted aminoacetylenes (**6a**,**b**) with acetone cyanohydrin as a source of hydrogen cyanide. In this case, the formation of both *E*- and *Z*-isomers has been detected. We measured the isomer ratio at low conversions and found that *Z*-isomers **7a**,**b** are the primary products, while on further exposure the *Z*-isomers transformed into the more stable *E*-isomers, to provide 80–100% of *E*-isomer after 24 h at rt. It was shown that acetone cyanohydrin can act as the catalyst of this isomerisation (Scheme 5).

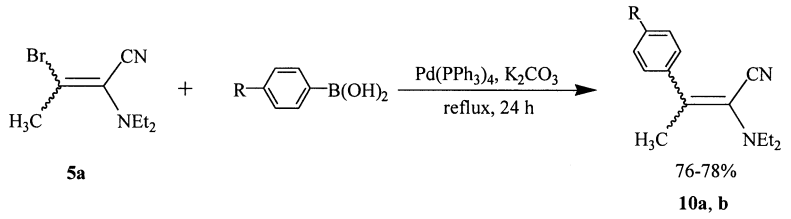
Further, we investigated the possibility of the hydrocyanation of less nucleophilic phosphorus(IV) substituted ynamine **8** with the acetone cyanohydrin. We also observed an easy *syn*-addition of hydrogen cyanide at rt, followed by slow isomerisation (1–2 weeks) of initially formed *Z*-isomer into 90–100% of the *E*-isomer (Scheme 6).

Earlier the only example of the HCN addition to ynamine with formation of the adduct *Z*-**4a** was described.[5] This compound was obtained as a side product as a result of *syn*-addition to ynamine **2a** of hydrogen cyanide, generated from 1,2,4-triazine. To the best of our knowledge other examples of HCN addition to aminoacetylenes are unknown. We have realised the hydrocyanation of aminoacetylenes **2a**,**b** with acetone cyanohydrin to give *Z*/*E*-isomers in an approximate 9:1 ratio. It this case, the amount of minor isomer E-**4a** increases after heating of the reaction mixtures of products. Thus during vacuum distillation the ratio *Z*-**4a**/*E*-**4a** changes from 9:1 to 3:1, while after heating for 2 h at 90°C this ratio becomes 1:3 (with partial decomposition). It could therefore be concluded that kinetically controlled *syn*-addition with the primary formation of *Z*-isomer took place also in this reaction (Scheme 7).

The *Z*-geometry of the major isomers **4**, **7** and **9** was assigned based on the $^3J_{HCCC(N)}$ values[15] and the downfield shift of the hydrogen atom at the double bond in the case where the CN group is in the *Z*-position to hydrogen.[16] For phosphorus(III) substituted adducts **7**, the proposed structure has been additionally confirmed by: (1) higher values of $^2J_{PC=C}$ in the case of the amino group and the phosphorus atom are in the *E*-position (compare with Ref. 17), (2) long-distance spin–spin coupling of NCH_2 protons and phosphorus(III) atom in the minor isomer **7b**.[18] The ^{13}C NMR chemical shifts of the sp^2 carbon atoms in α-cyanoenamines give evidence for opposite polarisation of the double bond in compounds **3**, **4** and **7**, **9**. For **3** and **4**, the electron withdrawing effect of the CN group is dominating,



Scheme 7.



Scheme 8.

while in the case of **7**, **9**—the electron donor effect of the Et_2N group prevails.

β-Bromo-α-cyanoenamines can be used for further substitution of bromine atom by cross-coupling or Heck reactions to give α-dialkylaminosubstituted cynnamonitriles. We have found that the reaction of the compound **5a** with tolyl- and anisylboronic acids under standard Suzuki cross-coupling conditions provided 2-(diethylamino)-3-(4-methylphenyl)-2-butenenitrile **10a** and 2-(diethylamino)-3-(4-methoxyphenyl)-2-butenenitrile **10b** with 78 and 76% yield, respectively. Optimization of the reaction procedure and synthesis of a series of new α-dialkylaminosubstituted cinnamonitriles is now underway (Scheme 8).

1. Experimental

NMR spectra were recorded on Varian spectrometer VXR-400 using TMS as internal standard. J_{SiC} and J_{SnC} couplings were presented for satellite peaks, J_{CH} were obtained by ^{13}C NMR without ^{1}H decoupling. IR spectra were recorded on IKS-22 spectrophotometer. Column chromatography was carried out with silica gel 60 from Merck using anhydrous dichloromethane as eluent. Trimethylsilyl cyanide and tributyltin cyanide were obtained commercially from Merck and Aldrich, respectively. Starting *N*,*N*-diethyl-1-propyn-1-amine and *N*,*N*-diethyl-3-methyl-1-butyn-1-amine were produced following the methods[19,20], respectively. 2-(Diisopropylphosphino)-*N*,*N*-diethyl-1-acetylenamine and 2-[di(*tert*-butyl)phosphino]-*N*,*N*-diethyl-1-acetylenamine were prepared as discribed.[7] *O*,*O*-diethyl 2-(diethylamino)ethynylphosphonate was synthesised according to procedure.[21] Acetone cyanohydrin was obtained commercially from Reachim and used without further purification.

1.1. General procedure

A solution of 1.2 mmol of corresponding cyanide was added dropwise at rt to a solution of 1 mmol of ynamine in 2 mL of dry dichloromethane. In the case of trimethylsilyl cyanide addition, catalytic amount of trimethylsilyl iodide (about 5 mol%) is desirable. After the reaction was complete (IR spectroscopy control) the solvent was evaporated in vacuo. The residue was distilled or chromatographed on silica.

1.1.1. (*E*)-2-(Diethylamino)-3-(trimethylsilyl)-2-butenenitrile (3a). A yellow-pale oil (0.125 g, 59%); bp 61–62°C/0.9 mmHg; [Found: C, 62.55; H, 10.73; N, 13.41. $C_{11}H_{22}N_2Si$ requires C, 62.80; H, 10.54; N, 13.31%]; ν_{max}(liquid film) 2920–2680 (br), 2145, 1575 cm^{-1}; δ_H (400 MHz, $CDCl_3$): 2.63 (4H, q, *J*=7.1 Hz, NCH_2), 2.01 (3H, s, CH_3C=), 1.01 (6H, t, *J*=7.1 Hz, CH_2CH_3), 0.16 (9H, s, Me_3Si); δ_C (100.6 MHz, $CDCl_3$): 153.9 ($^1J_{SiC}$=61.1 Hz, Si*C*=), 130.4 (*C*=, 113.4 (*C*N), 48.3 (NCH_2), 19.5 (CH_3C=), 12.7 (CH_2CH_3), −0.5 (Me_3Si).

1.1.2. (*E*)-2-(Diethylamino)-4-methyl-3-(trimethylsilyl)-2-pentenenitrile (3b). A colourless oil (0.124 g, 52%); [Found: C, 66.23; H, 10.21; N, 11.24. $C_{13}H_{26}N_2Si$ requires C, 65.48; H, 10.99; N, 11.78%]; ν_{max}(liquid film) 2930–2680 (br), 2150, 1580 cm^{-1}; δ_H (400 MHz, $CDCl_3$)[†]: 2.98 (1H, m, C*H*Me_2), 2.63 (4H, q, *J*=7.1 Hz, NCH_2), 1.19 (6H, d, *J*=7.2 Hz, $CHMe_2$), 1.01 (6H, t, *J*=7.1 Hz, CH_2CH_3), 0.21 (9H, s, Me_3Si); δ_C (100.6 MHz, $CDCl_3$): 164.0 (Si*C*=), 129.3 (*C*=), 113.5 (*C*N), 48.1 (NCH_2), 29.7 (*C*HMe_2), 21.3 (CHMe_2), 12.4 (CH_2CH_3), 1.4 (Me_3Si).

1.1.3. (*E*)-2-(Diethylamino)-3-(tributylstannyl)-2-butenenitrile (3c). A yellow-pale oil (0.243 g, 57%); [Found: C, 55.78; H, 8.97; N, 7.21. $C_{20}H_{40}N_2Sn$ requires C, 55.22; H, 9.27; N, 6.78%]; ν_{max}(liquid film) 2950–2800 (br), 2190, 1585 cm^{-1}; δ_H (400 MHz, $CDCl_3$): 2.63 (4H, q, *J*=7.2 Hz, NCH_2), 2.15 (3H, s, CH_3C=), 1.45 (6H, m, $CH_3CH_2CH_2$), 1.29 (6H, m, CH_2CH_2Sn), 1.02 (6H, m, CH_2Sn), 0.99 (6H, t, *J*=7.2 Hz, NCH_2CH_3), 0.88 (9H, t, *J*=7.3 Hz, $CH_3CH_2CH_2$); δ_C (100.6 MHz, $CDCl_3$): 162.54 ($^1J_{119}$SnC=329.6 Hz, Sn*C*=), 128.5 ($^2J_{SnC}$=29.0 Hz, *C*=), 113.0 ($^3J_{SnC}$=60.1 Hz, *C*N), 48.3 (NCH_2), 29.0 ($^3J_{SnC}$=19.2 Hz, $CH_3CH_2CH_2$), 27.3 ($^2J_{SnC}$=62.5 Hz, CH_2CH_2Sn), 21.4 ($^2J_{SnC}$=26.6 Hz, CH_3C=), 13.6 ($CH_3CH_2CH_2$), 12.5 (NCH_2CH_3), 10.6 ($^1J_{119}$SnC=347.9 Hz, CH_2Sn).

1.1.4. (*E*)-2-(Diethylamino)-4-methyl-3-(tributylstannyl)-2-pentenenitrile (3d). A colourless oil (0.223 g, 49%); [Found: C, 57.23; H, 9.98; N, 6.70. $C_{22}H_{44}N_2Sn$ requires C, 57.16; H, 9.59; N, 6.35%]; ν_{max}(liquid film) 2950–2790 (br), 2190, 1580; δ_H (400 MHz, $CDCl_3$): 3.21 (1H, m, C*H*Me_2), 2.63 (4H, q, *J*=7.2 Hz, NCH_2), 1.45 (6H, m, $CH_3CH_2CH_2$), 1.31 (6H, m, CH_2CH_2Sn), 1.06 (6H, d, *J*=7.0 Hz, $CHMe_2$), 1.02 (6H, t, *J*=7.2 Hz, NCH_2CH_3), 1.00 (6H, m, CH_2Sn), 0.89 (9H, t, *J*=7.2 Hz, $CH_3CH_2CH_2$); δ_C (100.6 MHz, $CDCl_3$): 174.1 ($^1J_{119}$SnC=323.5 Hz, Sn*C*=), 126.7 ($^2J_{SnC}$=30.5 Hz, *C*=); 113.1 ($^3J_{SnC}$=62.3 Hz, *C*N), 48.1 (NCH_2), 34.9 ($^2J_{SnC}$=22.9 Hz, *C*HMe_2), 29.0 ($^3J_{SnC}$=18.3 Hz, $CH_3CH_2CH_2$), 28.4 ($^3J_{SnC}$ 10.7 Hz, CHMe_2), 27.3 ($^2J_{SnC}$=67.1 Hz, CH_2CH_2Sn), 13.5 ($CH_3CH_2CH_2$), 12.4 ($^1J_{119}$SnC=347.9 Hz, CH_2Sn), 12.2 (NCH_2CH_3).

1.1.5. 2-(Diethylamino)-2-butenenitrile (4a). Mixture of *Z*/*E* isomers with 87:13 ratio; a yellow oil (0.100 g, 72%);

[†] According to ^1H NMR after column chromatography compound **3b** contained about 5% desilylated product **4b**.

bp 64–65°C/8 mmHg; [Found: C, 69.59; H, 10.04; N, 20.36. $C_8H_{14}N_2$ requires C, 69.52; H, 10.21; N, 20.27%]; ν_{max}(liquid film) 2970–2780 (br), 2195, 1620 cm^{-1}.

1.1.6. (*Z*)-2-(Diethylamino)-2-butenenitrile (*Z*-4a). δ_H (400 MHz, $CDCl_3$): 6.19 (1H, q, *J*=6.9 Hz, *H*C═), 2.65 (4H, q, *J*=7.2 Hz, NC*H*$_2$); 1.82 (3H, d, *J*=6.9 Hz, C*H*$_3$C═), 0.99 (6H, t, *J*=7.2 Hz, CH$_2$C*H*$_3$); δ_C (100.6 MHz, $CDCl_3$): 139.8 ($^1J_{CH}$=157.5 Hz, H*C*═), 123.4 (*C*═), 115.1 ($^3J_{CH}$=5.6 Hz, *C*N), 48.4 (N*C*H$_2$), 13.3 (*C*H$_3$C═), 12.9 (CH$_2$*C*H$_3$).

1.1.7. (*E*)-2-(Diethylamino)-2-butenenitrile (*E*-4a). δ_H (400 MHz, $CDCl_3$): 5.21 (1H, q, *J*=6.9 Hz, *H*C═), 2.98 (4H, q, *J*=7.2 Hz, NC*H*$_2$); 1.90 (3H, d, *J*=6.9 Hz, C*H*$_3$C═); 1.02 (6H, t, *J*=7.2 Hz, CH$_2$C*H*$_3$); δ_C (100.6 MHz, $CDCl_3$): 116.1 ($^1J_{CH}$=156.8 Hz, H*C*═), 114.8 ($^3J_{CH}$=12.5 Hz, *C*N); 114.4 (*C*═), 44.4 (N*C*H$_2$), 14.8 (*C*H$_3$C═), 11.9 (CH$_2$*C*H$_3$).

1.1.8. 2-(Diethylamino)-4-methyl-2-pentenenitrile (4b). Mixture of *Z*/*E* isomers with 91:9 ratio; a yellow-pale oil (0.108 g, 65%); [Found: C, 72.36; H, 11.20; N, 17.02. $C_{10}H_{18}N_2$ requires C, 72.24; H, 10.91; N, 16.85]; ν_{max}(liquid film) 2980–2690 (br), 2180, 1610 cm^{-1}.

1.1.9. (*Z*)-2-(Diethylamino)-4-methyl-2-pentenenitrile (*Z*-4b). δ_H (400 MHz, $CDCl_3$): 5.96 (1H, d, *J*=10.1 Hz, *H*C═), 3.09 (1H, m, C*H*Me$_2$), 2.64 (4H, q, *J*=7.1 Hz, NC*H*$_2$), 0.99 (6H, t, *J*=7.1 Hz, CH$_2$C*H*$_3$), 0.96 (6H, d, *J*=6.9 Hz, CH*Me*$_2$); δ_C (100.6 MHz, $CDCl_3$): 152.2 ($^1J_{CH}$=155.0 Hz, H*C*═), 120.5 (*C*═), 114.9 ($^3J_{CH}$=6.5 Hz, *C*N), 48.6 (N*C*H$_2$), 26.3 (*C*HMe$_2$), 21.5 (CH*Me*$_2$), 13.1 (CH$_2$*C*H$_3$).

1.1.10. (*E*)-2-(Diethylamino)-4-methyl-2-pentenenitrile (*E*-4b). δ_H (400 MHz, $CDCl_3$): 4.99 (1H, d, *J*=9.7 Hz, *H*C═), 3.10 (1H, m, C*H*Me$_2$), 3.01 (4H, q, *J*=7.1 Hz, NC*H*$_2$); 1.03 (6H, d, *J*=6.7 Hz, CH*Me*$_2$), 1.00 (6H, t; *J*=7.1 Hz, CH$_2$C*H*$_3$); δ_C (100.6 MHz, $CDCl_3$): 128.9 ($^1J_{CH}$=155.5 Hz, H*C*═), 114.8 ($^3J_{CH}$=13.1 Hz, *C*N), 114.3 (C═), 44.3 (N*C*H$_2$), 29.7 (*C*HMe$_2$), 23.4 (CH*Me*$_2$), 11.7 (CH$_2$*C*H$_3$).

1.1.11. 3-Bromo-2-(diethylamino)-2-butenenitrile (5a). Mixture of *Z*/*E* isomers with 54:46 ratio; a brown oil (0.17 g, 78%); [Found: C, 44.05; H, 5.87; N, 12.37. $C_8H_{13}BrN_2$ requires C, 44.26; H, 6.04; N, 12.90%]; ν_{max}(liquid film) 2980, 2820, 2195, 1640 cm^{-1}.

1.1.12. (*E*)-3-Bromo-2-(diethylamino)-2-butenenitrile (*E*-5a). δ_H (400 MHz, $CDCl_3$): 2.68 (4H, q, *J*=7.2 Hz, NC*H*$_2$), 2.48 (3H, s, C*H*$_3$C═), 0.98 (6H, t, *J*=7.2 Hz, CH$_2$C*H*$_3$); δ_C (100.6 MHz, $CDCl_3$): 138.5 (Br*C*═), 124.1 (*C*═), 113.4 (*C*N), 48.8 (N*C*H$_2$), 23.8 (*C*H$_3$C═), 12.9 (CH$_2$*C*H$_3$).

1.1.13. (*Z*)-3-Bromo-2-(diethylamino)-2-butenenitrile (*Z*-5a). δ_H (400 MHz, $CDCl_3$): 2.77 (4H, q, *J*=7.2 Hz, NC*H*$_2$), 2.59 (3H, s, C*H*$_3$C═), 1.03 (6H, t, *J*=7.2 Hz, CH$_2$C*H*$_3$); δ_C (100.6 MHz, $CDCl_3$): 137.6 (Br*C*═), 121.9 (*C*═), 112.8 (*C*N), 48.1 (N*C*H$_2$), 25.7 (*C*H$_3$C═), 12.8 (CH$_2$*C*H$_3$).

1.1.14. 3-Bromo-2-(diethylamino)-4-methyl-2-pentenenitrile (5b). Mixture of *Z*/*E* isomers with 63:37 ratio; a brown oil (0.163 g, 67%); [Found: N, 12.04. $C_{10}H_{17}BrN_2$ requires N, 11.66%]; ν_{max}(liquid film) 3000–2800 (br), 2180, 1640 cm^{-1}.

1.1.15. (*E*)-3-Bromo-2-(diethylamino)-4-methyl-2-pentenenitrile (*E*-5b). δ_H (400 MHz, $CDCl_3$): 3.71 (1H, sept, *J*=6.6 Hz, C*H*Me$_2$), 2.67 (4H, q, *J*=7.1 Hz, NC*H*$_2$), 1.00 (6H, d, *J*=6.6 Hz, CH*Me*$_2$), 0.98 (6H, t, *J*=7.1 Hz, CH$_2$C*H*$_3$); δ_C (100.6 MHz, $CDCl_3$): 153.7 (Br*C*═), 122.7 (*C*═), 113.2 (*C*N), 48.8 (N*C*H$_2$), 30.7 (*C*HMe$_2$), 20.7 (CH*Me*$_2$), 13.1 (CH$_2$*C*H$_3$).

1.1.16. (*Z*)-3-Bromo-2-(diethylamino)-4-methyl-2-pentenenitrile (*Z*-5b). δ_H (400 MHz, $CDCl_3$): 3.30 (1H, sept, *J*=6.6 Hz, C*H*Me$_2$), 2.76 (4H, q, *J*=7.1 Hz, NC*H*$_2$); 1.14 (6H, d, *J*=6.6 Hz, CH*Me*$_2$); 1.04 (6H, t, *J*=7.1 Hz, CH$_2$C*H*$_3$); δ_C (100.6 MHz, $CDCl_3$): 152.7 (Br*C*═), 119.7 (*C*═), 112.7 (*C*N), 48.0 (N*C*H$_2$), 35.0 (*C*HMe$_2$), 21.7 (CH*Me*$_2$), 12.6 (CH$_2$*C*H$_3$).

1.1.17. 2-(Diethylamino)-3-(diisopropylphosphino)-2-propenenitrile (7a). A colourless oil (0.187 g, 78%); [Found: P, 12.55. $C_{13}H_{25}N_2P$ requires P, 12.89]; ν_{max}(liquid film) 3030–2750 (br), 2210, 1555 cm^{-1}.

1.1.18. (*E*)-2-(Diethylamino)-3-(diisopropylphosphino)-2-propenenitrile (*E*-7a). δ_H (400 MHz, $CDCl_3$): 4.76 (1H, d, $^2J_{PH}$=5.5 Hz, *H*C═), 3.21 (4H, q, *J*=7.1 Hz, NC*H*$_2$), 1.70 (2H, m, PC*H*), 1.05 (6H, t, *J*=7.1 Hz, CH$_2$C*H*$_3$), 0.99 (6H, dd, $^3J_{PH}$=15.8 Hz, *J*=7.1 Hz, PCH*Me*$_2$); 0.92 (6H, dd; $^3J_{PH}$=10.8 Hz, *J*=6.9 Hz, PCH*Me*$_2$); δ_C (100.6 MHz, $CDCl_3$): 132.8 (d, $^2J_{PC}$=41.4 Hz, *C*═), 114.3 (d, $^3J_{PC}$= 3.1 Hz, $^3J_{CH}$=13.4 Hz, *C*N), 102.7 (d, $^1J_{PC}$=15.9 Hz, $^1J_{CH}$=151.9 Hz, H*C*═), 44.6 (N*C*H$_2$), 24.1 (d, $^1J_{PC}$=9.1 Hz, P*C*HMe$_2$), 19.7 (d, $^2J_{PC}$=18.3 Hz, PCH*Me*$_2$), 18.2 (d, $^2J_{PC}$=7.7 Hz, PCH*Me*$_2$), 12.3 (CH$_2$*C*H$_3$); δ_P (161.9 MHz, $CDCl_3$): −1.0.

1.1.19. (*Z*)-2-(Diethylamino)-3-(diisopropylphosphino)-2-propenenitrile (*Z*-7a). δ_H (400 MHz, $CDCl_3$): 4.82 (1H, d, $^2J_{PH}$=5.5 Hz, *H*C═), 3.32 (4H, dq; *J*=7.1 Hz, $^5J_{PH}$=2.2 Hz, NC*H*$_2$)[‡]; δ_C (100.6 MHz, $CDCl_3$): 130.6 (d, $^2J_{PC}$=18.3 Hz, *C*═), 116.8 (d, $^3J_{PC}$=8.1 Hz, *C*N), 109.9 (d, $^1J_{PC}$=27.1 Hz, $^1J_{CH}$=152.7 Hz, H*C*═), 46.1 (d, $^4J_{PC}$=12.3 Hz, N*C*H$_2$), 25.0 (d, $^1J_{PC}$=9.1 Hz, P*C*HMe$_2$), 19.6 (d, $^2J_{PC}$=18.3 Hz, PCH*Me*$_2$), 18.1 (d, $^2J_{PC}$=7.6 Hz, PCH*Me*$_2$), 12.8 (d; $^5J_{PC}$=3.1 Hz; CH$_2$*C*H$_3$); δ_P (161.9 MHz, $CDCl_3$): −8.1.

1.1.20. 3-[Di(*tert*-butyl)phosphino]-2-(diethylamino)-2-propenenitrile (7b). A colourless oil (0.215 g, 80%); [Found: C, 66.89; H, 11.41; P, 11.73. $C_{15}H_{29}N_2P$ requires C, 67.13; H, 10.89; P, 11.54%]; ν_{max}(liquid film) 3080–2800 (br), 2210, 1560 cm^{-1}.

1.1.21. (*E*)-3-[Di(*tert*-butyl)phosphino]-2-(diethylamino)-2-propenenitrile (*E*-7b). δ_H (400 MHz, $CDCl_3$): 4.97 (1H, d, $^2J_{PH}$=4.9 Hz, *H*C═), 3.20 (4H, q, *J*=7.0 Hz, NC*H*$_2$), 1.03

[‡] Other signals of minor isomer *Z*-**7a** cannot be seen with certainty.

(18H, d, $^3J_{PH}$=11.5 Hz; PC*Me*$_3$); 1.01 (6H, t, *J*=7.0 Hz, CH_2CH_3); δ_C (100.6 MHz, $CDCl_3$): 132.7 (d, $^2J_{PC}$= 44.3 Hz, *C*═), 114.4 (d, $^3J_{PC}$=3.2 Hz, $^3J_{CH}$=13.4 Hz, *C*N), 102.8 (d, $^1J_{PC}$=16.8 Hz, $^1J_{CH}$=152.0 Hz, H*C*═), 44.5 (N*C*H$_2$), 31.8 (d, $^1J_{PC}$=17.6 Hz, P*C*Me$_3$), 29.3 (d, $^2J_{PC}$=13.7 Hz, PC*Me*$_3$), 12.4 (CH_2CH3); δ_P (161.9 MHz, $CDCl_3$): 15.9.

1.1.22. (*Z*)-3-[Di(*tert*-butyl)phosphino]-2-(diethylamino)-2-propenenitrile (*Z*-7b). δ_H (400 MHz, $CDCl_3$): 5.16 (1H, d, $^2J_{PH}$=4.9 Hz, *H*C═), 3.34 (4H, dq, *J*=6.9 Hz, $^5J_{PH}$= 2.4 Hz, NC*H*$_2$), 1.11 (18H, d, $^3J_{PH}$=11.6 Hz; PC*Me*$_3$), 1.09 (6H, t, *J*=6.9 Hz, CH_2CH_3); δ_C (100.6 MHz, $CDCl_3$): 130.3 (d, $^2J_{PC}$=20.8 Hz, *C*═), 117.0 (d, $^3J_{PC}$=9.1 Hz, $^3J_{CH}$= 7.3 Hz, *C*N), 108.9 (d, $^1J_{PC}$=27.5 Hz, $^1J_{CH}$=151.9 Hz, H*C*═), 45.9 (d, $^4J_{PC}$=12.1 Hz, N*C*H$_2$), 32.5 (d, $^1J_{PC}$= 18.3 Hz, P*C*Me$_3$), 29.1 (d, $^2J_{PC}$=15.2 Hz, PC*Me*$_3$), 12.9 (d, $^5J_{PC}$=3.0 Hz, CH_2CH_3); δ_P (161.9 MHz, $CDCl_3$): 6.1.

1.1.23. *O*,*O*-Diethyl 2-cyano-2-(diethylamino)ethenylphosphonate (9). A colourless oil (0.198 g, 76%); [Found: C, 51.13; H, 7.98; P, 12.32. $C_{11}H_{21}N_2O_3P$ requires C, 50.76; H, 8.13; P, 11.90%]; ν_{max}(liquid film) 2970–2850 (br), 2275, 1565 cm^{-1}.

1.1.24. *O*,*O*-Diethyl (*E*)-2-cyano-2-(diethylamino)ethenylphosphonate (*E*-9). δ_H (400 MHz, $CDCl_3$): 4.54 (1H, d, $^2J_{PH}$=5.6 Hz, *H*C═), 4.11 (4H, dq, *J*=7.1 Hz, $^3J_{PH}$= 1.5 Hz, POC*H*$_2$), 3.34 (4H, q, *J*=7.2 Hz, NC*H*$_2$), 1.34 (6H, t, *J*=7.1 Hz, OCH_2CH_3), 1.17 (6H, t, *J*=7.2 Hz, NCH_2CH_3); δ_C (100.6 MHz, $CDCl_3$): 132.3 (d, $^2J_{PC}$=12.2 Hz, *C*═), 111.8 (d, $^3J_{PC}$=8.5 Hz, $^3J_{CH}$=12.9 Hz, *C*N), 87.1 (d, $^1J_{PC}$= 212.1 Hz, $^1J_{CH}$=155.9 Hz, H*C*═), 61.9 (d, $^2J_{PC}$=6.1 Hz, O*C*H$_2$), 45.3 (N*C*H$_2$), 15.9 (d, $^3J_{PC}$=7.6 Hz, OCH_2CH_3), 12.2 (NCH_2CH_3); δ_P (161.9 MHz, $CDCl_3$): 16.2.

1.1.25. *O*,*O*-Diethyl (*Z*)-2-cyano-2-(diethylamino)ethenylphosphonate (*Z*-9). δ_H (400 MHz, $CDCl_3$): 4.50 (1H, d, $^2J_{PH}$=2.3 Hz, *H*C═), 4.08 (4H, dq, *J*=7.0 Hz, $^3J_{PH}$= 1.4 Hz, OC*H*$_2$), 3.58 (4H, q, *J*=7.1 Hz, NC*H*$_2$), 1.35 (6H, t, *J*=7.0 Hz, OCH_2CH_3), 1.24 (6H, t, *J*=7.1 Hz, NCH_2CH_3); δ_C (100.6 MHz, $CDCl_3$): 132.7 (d, $^2J_{PC}$=9.2 Hz, *C*═), 115.0 (d, $^3J_{PC}$=27.5 Hz, $^3J_{CH}$=8.4 Hz, *C*N), 86.7 (d, $^1J_{PC}$= 206.0 Hz, $^1J_{CH}$=156.9 Hz, H*C*═), 61.8 (d, $^2J_{PC}$=6.1 Hz, O*C*H$_2$), 45.6 (N*C*H$_2$), 15.6 (d, $^3J_{PC}$=7.6 Hz, OCH_2CH_3), 13.0 (NCH_2CH_3); δ_P (161.9 MHz, $CDCl_3$): 13.5.

1.2. Suzuki coupling of 3-bromo-2-(diethylamino)-2-butenenitrile with arylboronic acids—general procedure

In a flask equipped with reflux condenser and gas inlet 0.3 mmol of **5a**, 0.33 mmol of arylboronic acid, 0.9 mmol K_2CO_3 were dissolved in 3 mL of THF and 1 mL of water under atmosphere of Ar. 12.0 μmol $Pd(PPh_3)_4$ (4 mol%) was added and the solution was stirred at reflux for 24 h. Solvents were evaporated in vacuum and the residue was purified by column chromatography on silica with benzene as eluent.

1.2.1. 2-(Diethylamino)-3-(4-methylphenyl)-2-butenenitrile (10a). Mixture of *Z*/*E* isomers with 61:39 ratio; a colourless oil (0.054 g, 78%); [Found: C, 78.67; H, 9.10; N, 12.09. $C_{15}H_{20}N_2$ requires C, 78.90; H, 8.83; N, 12.27%], R_f (benzene) 0.35; ν_{max}(luqiud film) 2850–2830 (br), 2190, 1625, 1600.

1.2.2. (*E*)-2-(Diethylamino)-3-(4-methylphenyl)-2-butenenitrile (*E*-10a). δ_H (400 MHz, $CDCl_3$): 7.35 (2H, m, C*H*$_{Ar}$), 7.13 (2H, m, C*H*$_{Ar}$), 2.64 (4H, q, *J*=7.2 Hz, NC*H*$_2$), 2.33 (3H, s, *Me*Ar); 2.32 (3H, s, CH_3C═); 0.93 (6H, t, *J*=7.2 Hz, CH_2CH_3); δ_C (100.6 MHz, $CDCl_3$): 146.5 (Ar*C*═), 138.0 (Me*C*$_{Ar}$), 135.7 (*C*$_{Ar}$C═), 128.6 (*C*H$_{Ar}$), 127.9 (*C*H$_{Ar}$), 119.7 (N*C*═), 115.1 (*C*N), 48.1 (N*C*H$_2$), 21.9 (CH_3C═), 21.2 (*Me*Ar), 12.9 (CH_2CH_3).

1.2.3. (*Z*)-2-(Diethylamino)-3-(4-methylphenyl)-2-butenenitrile (*Z*-10a). δ_H (400 MHz, $CDCl_3$): 7.28 (2H, m, C*H*$_{Ar}$), 7.18 (2H, m, C*H*$_{Ar}$), 2.74 (4H, q, *J*=7.2 Hz, NC*H*$_2$), 2.35 (3H, s, *Me*Ar), 2.23 (3H, s, CH_3C═), 1.05 (6H, t, *J*=7.2 Hz, CH_2CH_3). δ_C (100.6 MHz, $CDCl_3$): 153.2 (Ar*C*═), 138.9 (Me*C*$_{Ar}$), 136.0 (*C*$_{Ar}$C═), 129.1 (*C*H$_{Ar}$), 127.5 (*C*H$_{Ar}$), 119.0 (N*C*═), 114.7 (*C*N), 48.8 (N*C*H$_2$), 21.2 (*Me*Ar), 19.9 (CH_3C═); 13.1 (CH_2CH_3).

1.2.4. 2-(Diethylamino)-3-(4-methoxyphenyl)-2-butenenitrile (10b). Mixture of *Z*/*E* isomers with 60:40 ratio; a colourless oil (0.055 g, 76%); [Found: C, 74.10; H, 8.34; N, 11.02. $C_{15}H_{20}N_2O$ requires C, 73.74; H, 8.25; N, 11.47%]; R_f 0.27 (benzene); ν_{max}(liquid film) 2960–2850 (br), 2190, 1625, 1605.

1.2.5. (*E*)-2-(Diethylamino)-3-(4-methoxyphenyl)-2-butenenitrile (*E*-10b). δ_H (400 MHz, $CDCl_3$): 7.52 (2H, m, C*H*$_{Ar}$), 6.85 (2H, m, C*H*$_{Ar}$), 3.80 (3H, s, O*CH*$_3$), 2.66 (4H, q, *J*=7.2 Hz, NC*H*$_2$), 2.33 (3H, s, CH_3C═), 0.94 (6H, t, *J*=7.2 Hz, CH_2CH_3); δ_C (100.6 MHz, $CDCl_3$): 159.4 (MeO*C*$_{Ar}$), 145.8 (Ar*C*═), 130.7 (*C*$_{Ar}$C═), 129.7 (*C*H$_{Ar}$), 119.1 (N*C*═), 115.3 (*C*N), 113.2 (*C*H$_{Ar}$), 55.2 (*Me*OAr), 48.1 (N*C*H$_2$), 21.7 (CH_3C═), 12.8 (CH_2CH_3).

1.2.6. (*Z*)-2-(Diethylamino)-3-(4-methoxyphenyl)-2-butenenitrile (*Z*-10b). δ_H (400 MHz, $CDCl_3$): 7.36 (2H, m, C*H*$_{Ar}$), 6.90 (2H, m, C*H*$_{Ar}$), 3.81 (3H, s, O*CH*$_3$); 2.73 (4H, q, *J*=7.3 Hz, NC*H*$_2$), 2.23 (3H, s, CH_3C═), 1.04 (6H, t, *J*= 7.3 Hz, CH_2CH_3); δ_C (100.6 MHz, $CDCl_3$): 160.1 (MeO*C*$_{Ar}$), 152.8 (Ar*C*═), 131.1 (*C*$_{Ar}$C═), 129.0 (*C*H$_{Ar}$), 118.5 (N*C*═), 114.9 (*C*N), 113.8 (*C*H$_{Ar}$), 55.3 (*Me*OAr), 48.8 (N*C*H$_2$), 19.9 (CH_3C═), 13.1 (CH_2CH_3).

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