Palladium-Catalyzed Chemoselective Intramolecular Cyclization of 2-Bromoaryl Alkenenitriles

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The chemoselectivity in the palladium-catalyzed intramolecular cyclization of 2-(*o*-bromoaryl)-alkenenitriles depends on the nature of α–substitutents. 2-(*o*-Bromoanilino)alkenenitriles attacked the cyano group, followed by the cyano group transposition and hydrolysis, to give *o*-(methylamino)benzonitrile. 2-(*o*-Bromobenzyl)alkenenitriles, 2-(*o*-bromophenylthio)alkenenitriles and 2-(*o*-bromophenoxy)-alkenenitriles attacked the olefinic double bonds and led to 1-vinyl-2-indancecarbonitrile, 1,2,3,4-tetrahydronaphthalene-2-carbonitriles, 3,4-dihydro-2*H*-benzo[*b*]thiine-2-carbonitriles, and 3,4-dihydro-2*H*-benzo-[*b*]oxine-2-carbonitriles. A general mechanism for the palladium-catalyzed arylations is proposed.

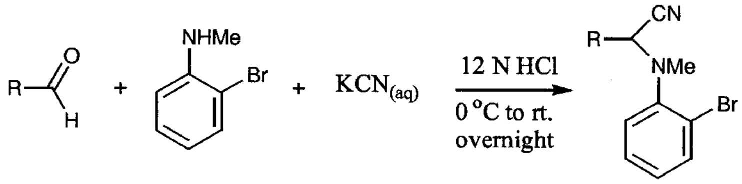
INTRODUCTION

Heck reactions are important palladium-catalyzed reactions for carbon-carbon bond formation such as the well documented arylation of olefins.[1] The corresponding arylation of the cyano group is, however, uncommon except for a few examples.[2] We demonstrated previously[2] that intramolecular and intermolecular palladium-catalyzed arylations at the cyano groups were feasible for some carefully designed compounds. Using this method, a series of α-(*o*-bromoanilino)-2-alkenenitriles were converted to various γ-carbolines, and α-amino alkenenitriles reacted with iodobenzene to give amides and benzonitrile. In these reactions, the intermediary organopalladium complexes underwent intramolecular cyclizations[2a,b] and intermolecular arylations[2c] chemoselectively by attacking the cyano group but not the olefinic double bonds.

A series of *N*-methyl-2-(*o*-bromoanilino)alk-3-enenitriles **1a-e**, *N*-methyl-2-(*o*-bromoanilino)-2-cyclopropylacetonitrile **1f**, 2-(*o*-bromobenzyl)alk-3-enenitrile **2**, 2-(*o*-bromobenzyl)alk-4-enenitriles (**5a**, **5c**, **5d** and **6a-c**), 2-(*o*-bromophenylthio) alk-4-enenitriles (**9a-d** and **10a-d**), and 2-(*o*-bromophenoxy)alk-4-enenitriles (**11a**, **11c**, **11d** and **12a**) have been prepared [Eq. (1)-(4)]. Most of these compounds have olefin and cyano groups oriented in similar proximity to the arylpalladium complex. The palladium-catalyzed cyclization may occur by two competitive pathways, either attack on the double bond or on the cyano group. This study indicated that the chemoselectivity of palladium-catalyzed arylation was controlled by the α-substituents of the starting materials of alkenenitriles. Thus, 2-(*o*-bromoanilino)-alkenenitriles **1a-f** with α-amino substituents underwent arylations selectively at the cyano groups in most cases to afford *o*-(methylamino)benzonitrile **16**. Other compounds with arakyl, phenylsulfanyl or phenoxy substituents attacked the olefinic positions selectively to give 1-vinyl-2-indanecarbonitrile **24**, 1,2,3,4-tetrahydronaphthalene-2-carbonitriles (**25a**, **25c**, **25d** and **26a-c**), 3,4-dihydro-2*H*-benzo[*b*]thiine-2-carbonitriles (**27a-d** and **28a-d**), and 3,4-dihydro-2*H*-benzo[*b*]oxine-2-carbonitriles (**29a**, **29c**, **29d** and **30a**).

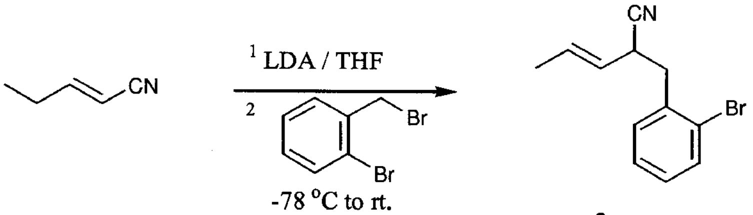
RESULTS AND DISCUSSION

As shown in Table 1, α-(*o*-bromoanilino)-3-alkenenitriles **1a-e** were prepared [Eq. (1)] by condensation of equimolar amounts of an appropriate unsaturated aldehyde, potassium cyanide, and *N*-methyl-*o*-bromoaniline[3] in the presence of hydrochloric acid (12 M).[4] α-Amino(cyclopropyl)acetonitrile **1f** was prepared similarly from cyclopropanecarbaldehyde. 2-(*o*-Bromobenzyl)-3-pentenenitrile **2** was prepared from 2-pentenenitrile by treatments with lithium diisopropylamide (LDA) and *o*-bromobenzyl bromide [Eq. (2)].[5] 3-(*o*-Bromophenyl)propanenitrile **3** and 3-(*o*-bromopheny)-2-phenylpropanenitrile **4** were prepared similarly from acetonitrile and phenylacetonitrile. 2-(*o*-Bromophenylthio)acetonitrile **7** and 2-(o-bromophenoxy) acetonitrile **8** were prepared, respectively, from the reactions of *o*-bromophenylthiol and *o*-bromophenol with 2-chloroacetonitrile in the presence of a strong base *t*-BuOK.[6] Compounds **7** and **8** were then treated with LDA and 1-bromo-2-alkenes at −78 °C to give monosubstituted 2-(*o*-bromobenzyl)-4-alkenenitriles (**5a**, **5c**, **5d** and **6a-c**), 2-(*o*-bromophenylthio)-4-alkenenitriles **9a-d**, 2-(*o*-bromophenoxy)-4-alkenenitriles (**11a**, **11c** and **11d**), disutituted 2-alkenyl-2-(*o*-bromophenylthio)alk-4-enenitriles **10a-d**, and 2-alkenyl-2-(*o*-bromophenoxy) alkenenitriles **12a** [Eq. 3 and 4)]. The monosubstituted products were isolated as the major products when the reaction solutions



1a R = MeCH=CH
1b R = PrCH=CH
1c R = Me_2C=CH
1d R = PhCH=CH
1e R = MeCH=CHCH=CH
1f R = $(CH_2)_2CH$

(1)



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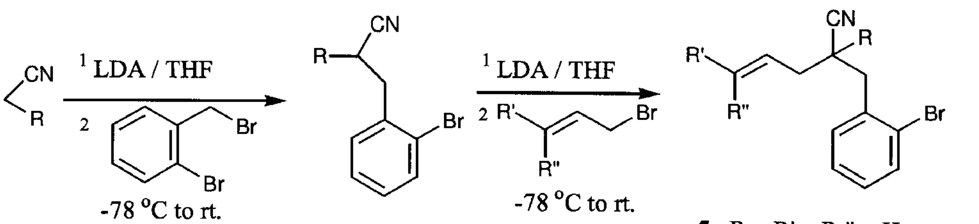
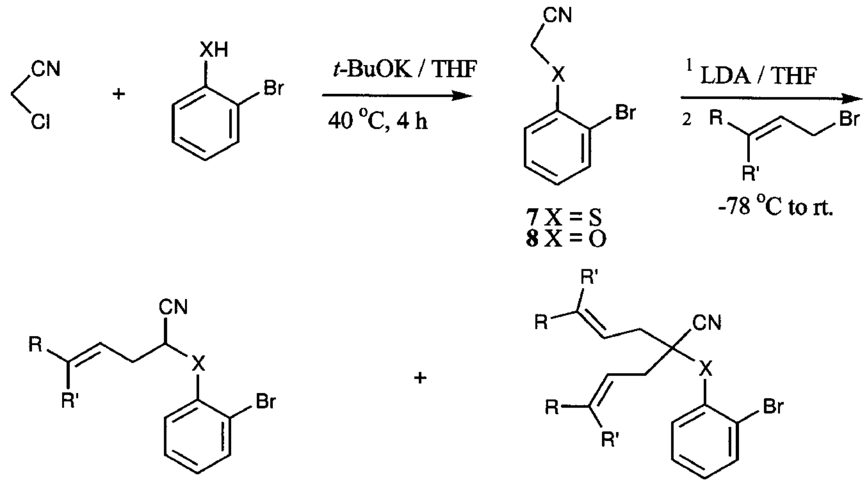
(2)



3 R = H
4 R = Ph

5a R = R' = R" = H
5c R = H, R' = R" = Me
5d R = R" = H, R' = Ph
6a R = Ph, R' = R' = H
6b R = Ph, R' = Me, R" = H
6c R = Ph, R' = R" =Me

(3)



7 X = S
8 X = O

(4)

9a X = S, R = R' = H
9b X = S, R = Me, R' = H
9c X = S, R = R' = Me
9d X = S, R = Ph, R' = H
11a X = O, R = R' = H
11b X = O, R = Me, R' = H
11c X = O, R = R' = Me
11d X = O, R = Ph, R' = H

10a X = S, R = R' = H
10b X = S, R = Me, R' = H
10c X = S, R = R' = Me
10d X = S, R = Ph, R' = H
12a X = O, R = R' = H

Table 1. Preparation of 2-Bromoaryl Alkenenitriles (o-BrC_6H_4X)C(CN)RY

Entry	X	Y	R	Products (yield, %)[a]
1	NMe	MeCH=CH	H	**1a** (59)
2	NMe	PrCH=CH	H	**1b** (78)
3	NMe	Me_2C=CH	H	**1c** (83)
4	NMe	PhCH=CH	H	**1d** (86)
5	NMe	MeCH=CHCH=CH	H	**1e** (83)
6	NMe	$(CH_2)_2CH$	H	**1f** (78)
7	CH_2	CH_2=CH	H	**2** (76)
8	CH_2	CH_2=$CHCH_2$	H	**5a** (72)
9	CH_2	$(CH_3)_2C$=$CHCH_2$	H	**5c** (75)
10	CH_2	PhCH=$CHCH_2$	H	**5d** (80)
11	CH_2	CH_2=$CHCH_2$	Ph	**6a** (81)
12	CH_2	CH_3CH=$CHCH_2$	Ph	**6b** (73)
13	CH_2	$(CH_3)_2C$=$CHCH_2$	Ph	**6c** (65)
14	S	CH_2=$CHCH_2$	H	**9a** (32)
	S	CH_2=$CHCH_2$	CH_2=$CHCH_2$	**10a** (27)
15	S	CH_3CH=$CHCH_2$	H	**9b** (30)
	S	CH_3CH=$CHCH_2$	CH_3CH=$CHCH_2$	**10b** (25)
16	S	$(CH_3)_2C$=$CHCH_2$	H	**9c** (32)
	S	$(CH_3)_2C$=$CHCH_2$	$(CH_3)_2C$=$CHCH_2$	**10c** (28)
17	S	PhCH=$CHCH_2$	H	**9d** (30)
	S	PhCH=$CHCH_2$	PhCH=$CHCH_2$	**10d** (26)
18	O	CH_2=$CHCH_2$	H	**11a** (20)
	O	CH_2=$CHCH_2$	CH_2=$CHCH_2$	**12a** (25)
19	O	$(CH_3)_2C$=$CHCH_2$	H	**11c** (46)
20	O	PhCH=$CHCH_2$	H	**11d** (52)

[a] The monosubstituted products were found as major products when the reaction solution was warmed quickly back to room temperature.

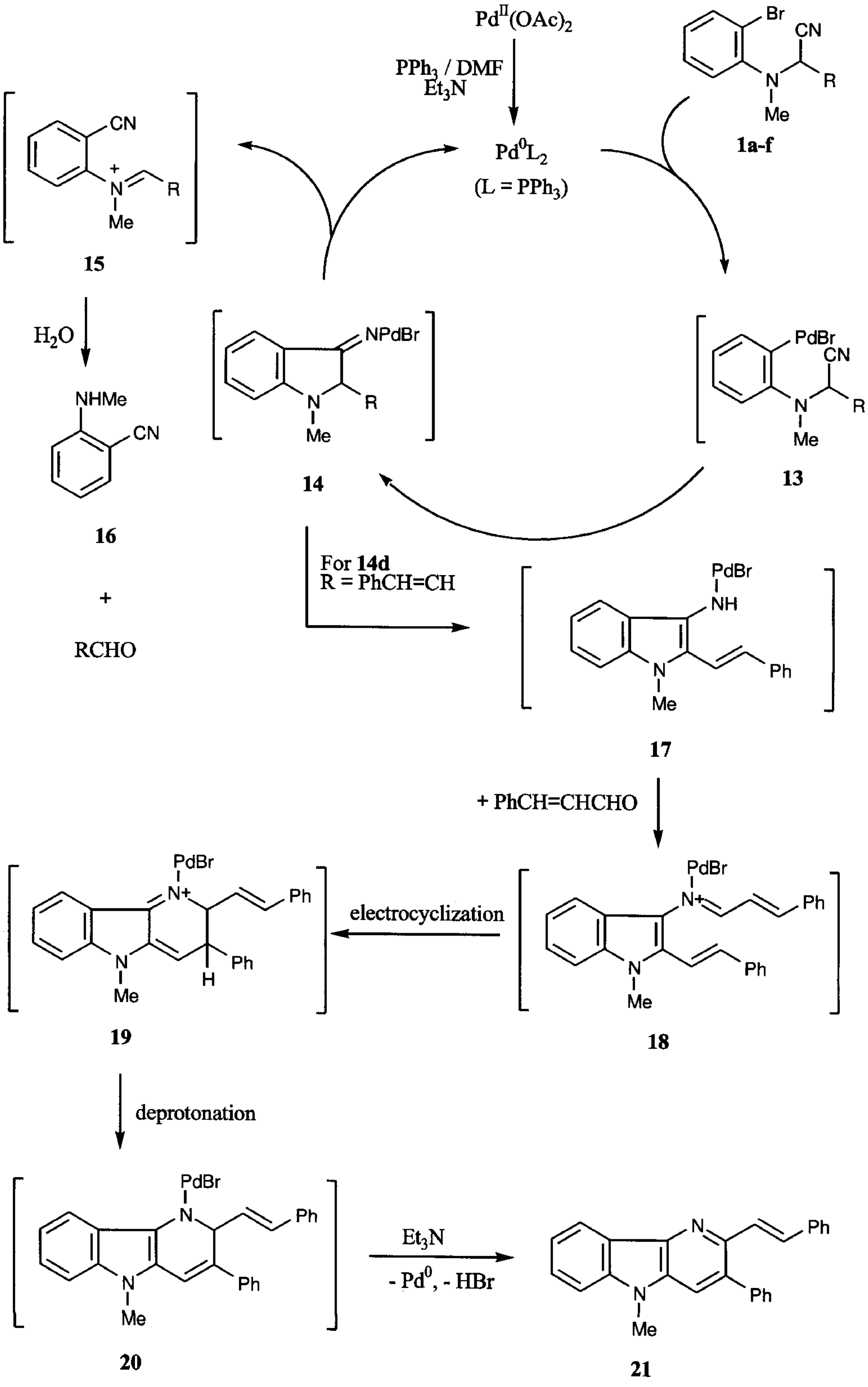
were quickly warmed back to room temperature.

In a typical procedure[7] (Table 2), α-(o-bromoanilino)-alkenenitrile **1d** (1 mmol) in DMF (15 mL) was treated with $Pd(OAc)_2$ (0.1 mmol), PPh_3 (0.2 mmol), and Et_3N (1.2 mmol) for 6 h at 100 °C under an argon atmosphere to give 2-(methylamino)benzonitrile **16** and γ-carboline **21** in 38 and 36% yields, respectively (entry 4). The reactions of **1a-c**, **1e** and **1f** (entries 1-3 and 5-6) gave the benzonitrile **16** (60–85%) and the aldehydes RCHO.

A possible mechanism for the palladium-catalyzed reaction[8] is proposed for the formation of the benzonitrile **16** (Scheme I). The reactions were presumably initiated by oxidative insertion of Pd^0 into the bromophenyl groups of **1a-f**. The organopalladium complex **13** underwent cyclization by attacking selectively on the cyano group, giving **14**, but not on the olefinic double bonds. The iminoindoline **14** might yield an iminium ion **15**, which was subsequently hydrolyzed to give 2-(methylamino)benzonitrile **16** and the aldehydes RCHO. When R was a styryl group, the palladium amide **14d** reacted further with the in-site generated cinnamaldehyde to give γ-carboline **21**, presumably via the iminium intermediate **18**.[9] This process might involve electrocyclization, deprotonation, and elimination of palladium and HBr. It might be argued that an alternative pathway led to **16** from the arypalladium bromide **13** after a ligand exchange with the cyano group. The resulting arylpalladium cyanide could undergo reductive elimination to give **15** and then end up with the product **16**. We prefer the reaction mechanism with the intermidate **14**, as it could explain the formation of γ-carboline **21** as well.

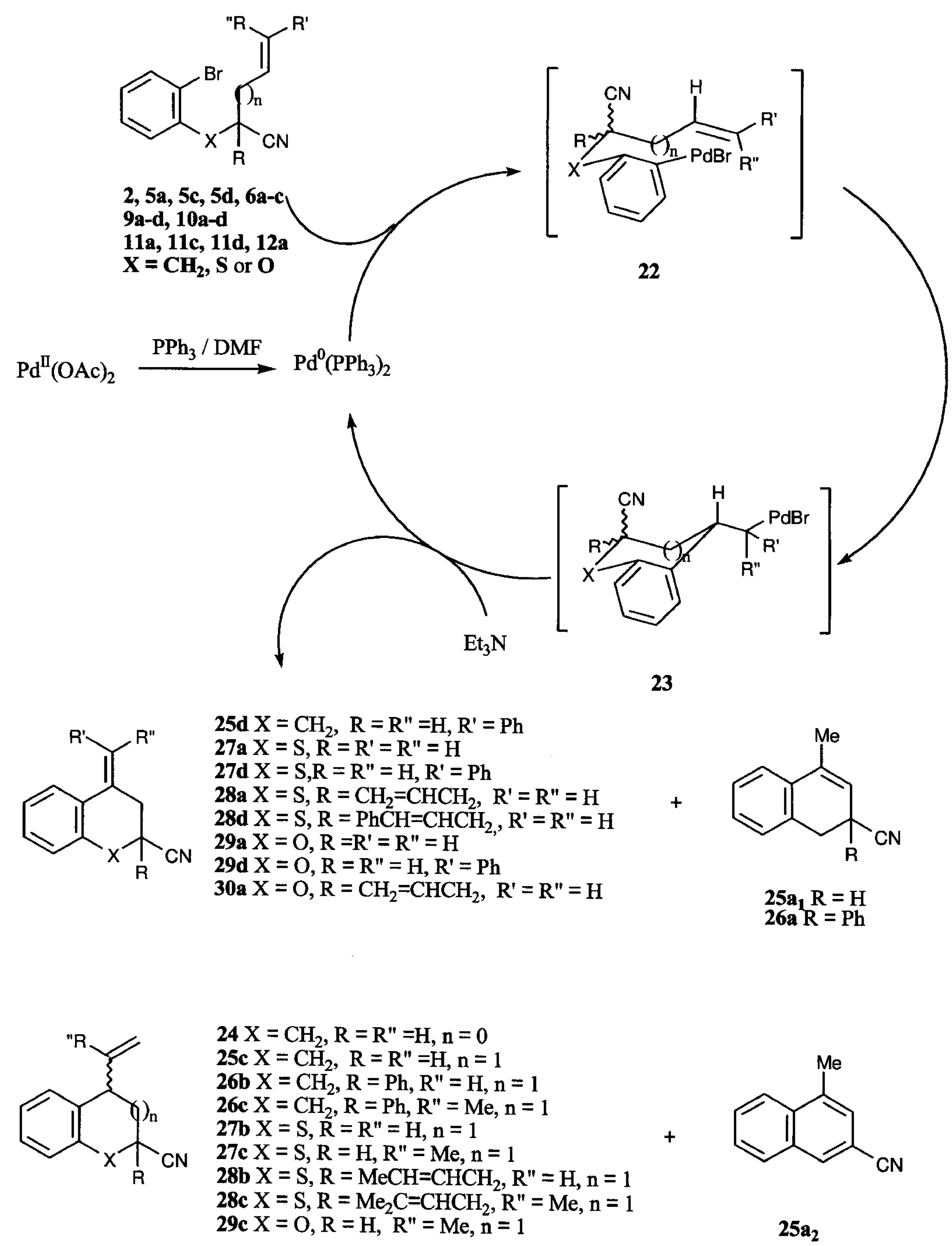
Under similar reaction conditions, the palladium-catalyzed reactions of alkylnitriles (**2**, **5a**, **5c**, **5d** and **6a-c**), phenylsulfenylnitriles (**9a-d** and **10a-d**) and phenoxynitriles (**11a**, **11c**, **11d**, and **12a**) proceeded, however, differently from anilinonitriles **1a-f**. The reaction of 2-(o-bromophenylsulfenyl)-4-hexenenitrile **9b** (entry 15, Table 2) afforded 4-vinyl-3,4-dihydro-2H-benzo[b]thiine-2-carbonitrile **27b** (80%) as a mixture of *cis* and *trans* isomers in a ratio of 4 : 1 as determination by analysis of the 2D ^{1}H NMR spectrum. This result showed that the arylpalladium intermediate **22** attacked selectively the olefinic double bond instead of the cyano group (Scheme II). When two stereomers were possibly obtained in individual cyclisation, the R or cyano group substitutions at the 2-position of **23** might dispose at either the equatorial or axial orientation. Thus, the organopalladium intermediate 23 upon elimination of palladium and HBr would

Scheme I



give the *cis and trans* dihydrobenzothiines **27b**$_1$ and **27b**$_2$. The reactions of **2**, **5a**, **5c**, **5d**, **6a-c**, **9a-d**, **10a-d** **11a**, **11c**, **11d** and **12a** proceeded with similar chemoselectivity on the olefinic double bonds to give the 2-indanecarbonitrile **24**, 1,2,3,4-

Scheme II



tetrahydronaphthalene-2-carbonitriles (**25a**, **25c**, **25d**, and **26a-c**), 3,4-dihydro-2*H*-benzo[*b*]thiine-2-carbonitriles (**27a-d**, and **28a-d**), and 3,4-dihydro-2*H*-benzo[*b*]oxine-2-carbonitriles (**29a**, **29c**, **29d**, **30a**), as shown in Table 2.

Depending on the α-substituents, the palladium-catalyzed intramolecular cyclization of 2-(*o*-bromoaryl)-alkenenitriles might proceed on two different pathways, either attacking the cyano group or the olefinic double bond (Scheme III). When the α-position with respect to the cyano group had a strong electron-donating group of the amino substitution, the organopalladium **13** attacked the cyano group to give iminoindoline intermediates **14**. Upon elimination of palladium, it would give an iminium ion **15**, which was subsequently hydrolyzed to afford 2-(methylamino)benzonitrile **16**

Table 2. Palladium-Catalyzed Chemoselective Intramolecular Cyclization of 2-Bromoaryl Alkenenitriles, (o-BrC_6H_4X)C(CN)RY

Entry	Substrate	X	Products (yields, %) Addition to CN	Addition to C=C
1	**1a**	NMe	**16** (81)	–
2	**1b**	NMe	**16** (60)	–
3	**1c**	NMe	**16** (85)	–
4	**1d**	NMe	**16** (38) + **21** (36)	–
5	**1e**	NMe	**16** (72)	–
6	**1f**	NMe	**16** (80)	–
7	**2**	CH_2	–	**24** (71)
8	**5a**	CH_2	–	**25a₁** (42) + **25a₂** (22)
9	**5c**	CH_2	–	**25c** (68)
10	**5d**	CH_2	–	**25d** (75)
11	**6a**	CH_2	–	**26a** (62)
12	**6b**	CH_2	–	**26b** (60)
13	**6c**	CH_2	–	**26c** (58)
14	**9a**	S	–	**27a** (76)
15	**9b**	S	–	**27b₁** (64) + **27b₂** (16)[a]
16	**9c**	S	–	**27c₁** (60) + **27c₂** (10)[a]
17	**9d**	S	–	**27d** (78)
18	**10a**	S	–	**28a** (65)
19	**10b**	S	–	**28b₁** (8) + **28b₂** (64)[a]
20	**10c**	S	–	**28c** (62)
21	**10d**	S	–	**28d** (61)
22	**11a**	O	–	**29a** (46)
23	**11c**	O	–	**29c** (58)
24	**11d**	O	–	**29d** (52)
25	**12a**	O	–	**30a** (64)

[a] Compounds **27b₁**, **27c₁** and **28b₁** have *cis* configuration, whereas **27b₂**, **27c₂** and **28b₂** have *trans* configuration.

and the aldehydes RCHO. On the other hand, the organopalladium **22** with α-substituents of alkyl, sulfenyl and phenoxy groups with mild electron-donating power attacked the olefinic double bonds.

CONCLUSIONS

Our studies of the palladium-catalyzed reactions showed the following common features: (i) 2-(o-bromoaryl)-alkenenitriles underwent palladium-catalyzed chemoselective intramolecular cyclizations depending on the substitution at α–position; (ii) the organopalladium intermediate **13** underwent cyclization by selective attack on the cyano group rather than the olefinic double bond; (iii) the iminopalladium complex **14** underwent transposition of cyano group when the α-position had an amino group with strong electron-donating power; (iv) the organopalladium intermediate **22** underwent cyclization by selectively attacking the olefinic double bond. The subsequent elimination of palladium and HBr from **14** and **23** finally gave the observed products.

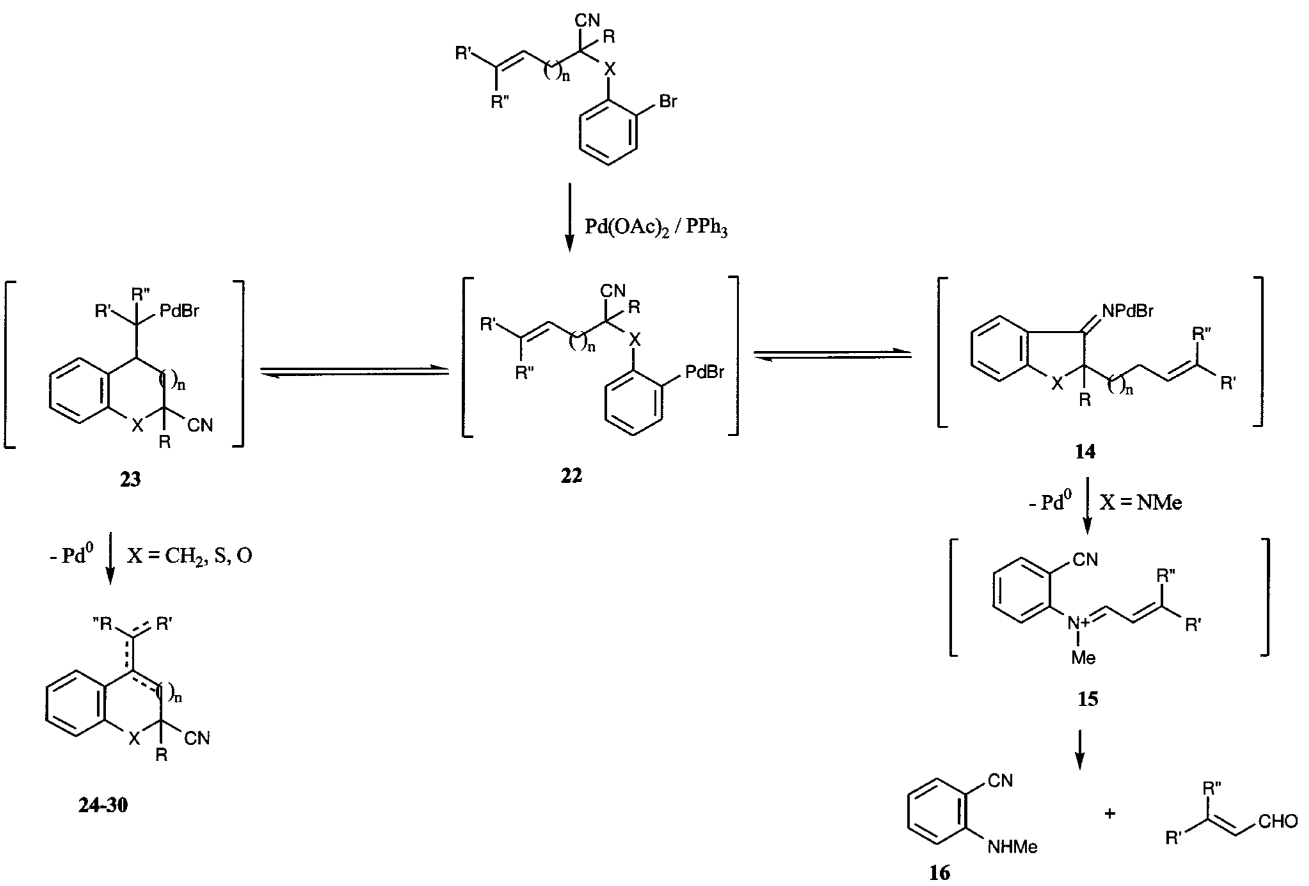
EXPERIMENTAL

Melting points are uncorrected. ^1H NMR spectra were recorded at 200 or 300 MHz. TMS was used as an internal standard. ^{13}C NMR spectra were recorded at 50 or 75 MHz, $CDCl_3$ was used as an internal standard. Mass spectra were recorded at an ionizing voltage of 70 eV. Merck silica gel 60F sheets were used for analytical thin-layer chromatography. Column chromatography was performed on SiO_2 (70-230 mesh); gradients of EtOAc and hexane were used as eluents. DMF, Et_3N, and CH_2Cl_2 were distilled over CaH_2, whilst THF was distilled from sodium benzophenone ketyl under nitrogen.

Preparation of 2-(*N*-Methyl-*o*-bromoanilino)-3-alkenenitriles 1a-f

To a mixture of *N*-methyl-*o*-bromoaniline (15.0 mmol) and aqueous HCl (12.5 mL of 12 M solution) was added dropwise an appropriate unsaturated aldehyde (18 mmol) at 0 °C, followed by aqueous KCN (1.05 g in 5 mL solution, 16.2 mmol). The mixture was stirred for 12 h at room temperature;

Scheme III



the aqueous phase was separated and extracted with EtOAc. The combined organic phase was washed with aqueous HCl (1 M) and brine, dried (Na_2SO_4) and concentrated under reduced pressure to give the title compound. The aminonitrile compounds **1a-f** decomposed, giving the corresponding aniline and aldehydes, on silica gel column chromatography.

2-(*N*-Methyl-*o*-bromoanilino)-3-pentenenitrile 1a

Yield 59%; oil; TLC [EtOAc-hexane (2:98)] R_f 0.28; ν_{max} (neat)/cm^{-1} 2960, 2800, 2240, 1590, 1476, 970, 760; δ_H ($CDCl_3$) 1.73 (3 H, ddd, *J* = 6, 1, 1 Hz), 2.65 (3 H, s), 4.80 (1 H, br s), 6.56 (1 H, ddq, *J* = 15, 3, 1 Hz), 6.06 (1 H, dqd, *J* = 15, 6, 1 Hz), 6.88-6.96 (1 H, m), 7.20-7.23 (2 H, m), 7.48 (1 H, dd, *J* = 8, 1.5 Hz); δ_C ($CDCl_3$) 17.4 (q), 35.0 (q), 58.3 (d), 115.4 (s), 120.3 (s), 123.2 (d), 123.6 (d), 126.1 (d), 128.4 (d), 131.8 (d), 133.7 (d), 147.9 (s); *m/z* 266 (28), 264 (32), 185 (68), 157 (100), 105 (52), 77 (74) (Found: M, 266.0238. $C_{12}H_{13}N_2{}^{81}Br$ requires *M*, 266.0242).

2-(*N*-Methyl-*o*-bromoanilino)-3-heptenenitrile 1b

Yield 78%; oil; TLC [EtOAc-hexane (2:98)] R_f 0.25; ν_{max} (neat)/cm^{-1} 2960, 2800, 2240, 1590, 1490, 970, 760; δ_H ($CDCl_3$) 0.90 (3 H, t, *J* = 7 Hz), 1.35-1.50 (2 H, m), 2.08 (2 H, dt, *J* = 7, 7, Hz), 2.72 (3 H, s), 4.89 (1 H, br dd, *J* = 2, 1 Hz), 5.57 (1 H, dd, *J* = 16, 2 Hz), 6.10 (1 H, dtd, *J* = 16, 7, 1 Hz), 6.93-7.02 (1 H, m), 7.23-7.34 (2 H, m), 7.55 (1 H, dd, *J* = 8, 1 Hz); δ_C ($CDCl_3$) 13.5 (q), 21.8 (t), 33.9 (t), 35.0 (q), 58.3 (d), 115.4 (s), 120.3 (s), 122.5 (d), 123.2 (d), 126.1 (d), 128.4 (d), 133.6 (d), 136.9 (d), 147.9 (s); *m/z* 294 (9), 292 (11), 185 (64), 157 (100), 105 (50), 77 (76) (Found: M, 292.0574. $C_{14}H_{17}N_2{}^{79}Br$ requires *M*, 292.0575).

4-Methyl-2-(*N*-methyl-*o*-bromoanilino)-3-pentenenitrile 1c

Yield 83%; oil; TLC [EtOAc-hexane (2:98)] R_f 0.29; ν_{max} (neat)/cm^{-1} 2920, 2200, 1600, 1490, 770, 740, 670; δ_H ($CDCl_3$) 1.68 (3 H, d, *J* = 1 Hz), 1.81 (3 H, d, *J* = 1 Hz), 2.84 (3 H, s), 4.91 (1 H, d, *J* = 8 Hz), 5.34 (1 H, br d, *J* = 8 Hz), 6.95-7.06 (1 H, m), 7.26-7.35 (2 H, m), 7.56 (1 H, d, *J* = 8 Hz); δ_C ($CDCl_3$) 18.6 (q), 25.8 (q), 36.6 (q), 54.0 (d), 116.0 (s), 117.1 (s), 120.7 (s), 123.7 (d), 126.3 (d), 128.3 (d), 133.7 (d), 140.7 (d), 148.0 (s); *m/z* 280 (7), 278 (7), 265 (14), 263 (13), 185 (69), 157 (100), 105 (51) (Found: M, 278.0421.

$C_{13}H_{15}N_2{}^{79}Br$ requires *M*, 278.0419).

2-(*N*-Methyl-*o*-bromoanilino)-4-phenyl-3-pentenenitrile 1d

Yield 86%; white solid, mp 86-88 °C; TLC [EtOAc-hexane (2:98)] R_f 0.20; ν_{max} (KBr)/cm^{-1} 3054, 2234, 1582, 1469, 968, 741, 695; δ_H ($CDCl_3$) 2.78 (3 H, s), 5.11 (1 H, dd, *J* = 4, 1 Hz), 6.32 (1 H, dd, *J* = 16, 4 Hz), 6.97-7.08 (2 H, m), 7.26-7.30 (5 H, m), 7.45 (2 H, dd, *J* = 8, 1 Hz), 7.59 (1 H, dd, *J* = 8, 1 Hz); δ_C ($CDCl_3$) 35.4 (q), 58.6 (d), 115.1 (s), 120.4 (s), 121.6 (d), 123.3 (d), 126.3 (d), 126.8 (2 x d), 128.5 (d), 128.6 (d), 128.7 (2 x d), 133.7 (d), 134.9 (d), 135.1 (s), 147.8 (s); *m/z* 328 (7), 326 (8), 247 (28), 157 (82), 142 (100), 115 (55), 77 (14) (Found: M, 326.0420. $C_{17}H_{15}N_2{}^{79}Br$ requires *M*, 326.0419).

2-(*N*-Methyl-*o*-bromoanilino)-3,5-heptadienenitrile 1e

Yield 83%; white solid, mp 65-67 °C;; TLC [EtOAc-hexane (2:98)] R_f 0.19; ν_{max} (KBr)/cm^{-1} 2955, 2811, 2230, 1595, 1508, 990, 743; δ_H ($CDCl_3$) 1.79 (3 H, d, *J* = 7 Hz), 2.73 (3 H, s), 4.98 (1 H, d, *J* = 4 Hz), 5.66 (1 H, dd, *J* = 15, 4 Hz), 5.87 (1 H, dq, *J* = 15, 7 Hz), 6.12 (1 H, dd, *J* = 15, 10 Hz), 6.59 (1 H, dd, *J* = 15, 10 Hz), 6.97-7.04 (1 H, m), 7.29-7.31 (2 H, m), 7.57 (1 H, d, *J* = 8 Hz); δ_C ($CDCl_3$) 18.1 (q), 35.2 (q), 58.2 (d), 115.2 (s), 120.3 (s), 121.8 (d), 123.2 (d), 126.1 (d), 128.4 (d), 129.4 (d), 132.9 (d), 133.7 (d), 135.2 (d), 147.9 (s); *m/z* 292 (26), 290 (29), 277 (21), 275 (20), 211 (51), 185 (74), 157 (100), 106 (50), 77 (60) (Found: M, 290.0417. $C_{14}H_{15}N_2{}^{79}Br$ requires *M*, 290.0419).

2-Cyclopropyl-2-(*N*-methyl-*o*-bromoanilino)ethanenitrile 1f

Yield 78%; oil; TLC [EtOAc-hexane (5:95)] R_f 0.22; ν_{max} (neat)/cm^{-1} 2960, 2210, 1590, 1480, 1280, 760; δ_H ($CDCl_3$) 0.61-.083 (4 H, m), 1.32-1.43 (1 H, m), 2.91 (3 H, s), 4.15 (1 H, d, *J* = 9 Hz), 6.96-7.04 (1 H, m), 7.30 (2 H, dd, *J* = 8, 8 Hz), 7.56 (1 H, dd, *J* = 8, 1 Hz); δ_C ($CDCl_3$) 2.1 (t), 4.1 (t), 11.8 (d), 36.1 (q), 60.2 (d), 115.4 (s), 120.5 (s), 123.6 (d), 126.2 (d), 128.4 (d), 133.6 (d), 147.9 (s); *m/z* 266 (68), 264 (72), 240 (18), 238 (20), 225 (82), 223 (92), 186 (70), 184 (83), 105 (68), 77 (68), 49 (100) (Found: M, 264.0268. $C_{12}H_{13}N_2{}^{79}Br$ requires *M*, 264.0262).

Preparation of 2-(*o*-Bromobenzyl)-3-pentenenitrile 2 and 3-(*o*-Bromophenyl) propanenitriles 3 and 4

Under an atmosphere of argon, a solution of diisopropylamine (0.9 mL, 5.5 mmol) in THF (10 mL) was cooled to 5 °C, and a solution of BuLi (1.6 M solution in hexane, 3.5 mL, 5.5 mmol) was added dropwise to it. After 15 min, the LDA solution was cooled to 8 °C, and a solution of the appropriate alkenenitrile (5 mmol) in THF (5 mL) was added dropwise to it. The resulting orange-colored solution was stirred for 45 min after which a solution of *o*-bromobenzyl bromide (1.5 g, 6 mmol) in THF (5 mL) was added dropwise to it. The reaction was removed from a dry ice bath quickly, warmed to room temperature, and kept for an additional 6 h before being quenched with saturated aqueous NH_4Cl. The mixture was concentrated under reduced pressure, and the residue was taken up with EtOAc. The resulting solution was washed with brine, dried (Na_2SO_4) and concentrated under reduced pressure. The crude product was purified by chromatography on a silica gel column with gradients of EtOAc and hexane to give the title compounds.

2-(*o*-Bromobenzyl)-3-pentenenitrile 2

Oil; TLC [EtOAc-hexane (2:98)] R_f 0.14; ν_{max} (neat)/cm^{-1} 3050, 2960, 2230, 1560, 1450, 965, 750; δ_H ($CDCl_3$) 1.71 (3 H, dd, *J* = 6, 1 Hz), 3.00-3.10 (2 H, m), 3.52-3.60 (1 H, m), 5.38 (1 H, ddq, *J* = 15, 7, 1 Hz), 5.83 (1 H, dqd, *J* = 15, 6, 1 Hz), 7.09-7.17 (1 H, m), 7.26-7.30 (2 H, m), 7.54 (1 H, d, *J* = 8 Hz); δ_C ($CDCl_3$) 17.6 (q), 34.4 (d), 38.9 (t), 119.7 (s), 124.0 (d), 124.3 (s), 127.7 (d), 129.1 (d), 130.1 (d), 131.7 (d), 133.0 (d), 136.0 (s); *m/z* 251 ([16), 249 (17), 171 (98), 169 (100), 90 (27), 89 (19) (Found: M, 249.0150. $C_{12}H_{12}N^{79}Br$ requires *M*, 249.0153).

3-(*o*-Bromophenyl)propanenitrile 3

Oil; TLC [EtOAc-hexane (2:98)] R_f 0.09; ν_{max} (neat)/cm^{-1} 3040, 2920, 2230, 1550, 750; δ_H ($CDCl_3$) 2.65 (2 H, t, *J* = 7.6 Hz), 3.06 (2 H, t, *J* = 7.6 Hz), 7.08-7.17 (1 H, m), 7.23-7.30 (2 H, m), 7.54 (1 H, d, *J* = 8 Hz); δ_C ($CDCl_3$) 17.4 (t), 31.9 (t), 118.7(s), 123.9 (s), 127.8 (d), 129.0 (d), 130.7 (d), 133.0 (d), 137.0 (s); *m/z* 211 (25), 209 (25), 171 (98), 169 (100), 119 (15), 117 (15), 90 (24) (Found: M, 208.9847. $C_9H_8N^{79}Br$ requires *M*, 208.9840).

3-(*o*-Bromophenyl)-2-phenylpropanenitrile 4

Oil; TLC [EtOAc-hexane (2:98)] R_f 0.11; ν_{max} (neat)/cm^{-1} 3050, 2960, 2220, 1550, 750; δ_H ($CDCl_3$) 3.10-3.35 (2 H, m), 4.21 (1 H, dd, *J* = 9.5, 6 Hz), 7.12-7.26 (2 H, m), 7.37-7.40 (6 H, m), 7.58 (1 H, d, *J* = 8 Hz); δ_C ($CDCl_3$) 37.6 (d), 42.7 (t), 119.9 (s), 124.3 (s), 127.2 (2 x d), 127.7 (d), 128.2 (d), 129.0 (2 x d), 129.2 (d), 131.8 (d), 133.0 (d), 135.2 (s), 135.7 (s); *m/z* 287(22), 285 (22), 171 (98), 169 (100), 90 (35), 89 (31) (Found: M, 285.0159. $C_{15}H_{12}N^{79}Br$ requires *M*, 285.0153).

Preparation of 2-(*o*-Bromoaryl)acetonitrile 7 and 8

Under an atmosphere of argon, a solution of *t*-BuOK (4.04 g, 36 mmol) in THF (30 mL) was cooled to -5 °C, and *o*-bromophenol (or *o*-bromothiophenol) (30 mmol) was added dropwise to it. The resulting orange-colored solution was stirred for 45 min, after which 2-chloroacetonitrile (2.28 mL, 36 mmol) was added dropwise to it. The reaction was warmed to 50 °C, and kept for an additional 6 h before being quenched with saturated aqueous NH_4Cl. The mixture was concentrated under reduced pressure, and the residue was taken up with EtOAc. The resulting solution was washed with brine, dried (Na_2SO_4) and concentrated under reduced pressure. The crude product was purified by chromatography on a silica gel column with gradients of EtOAc and hexane to give the title compounds.

2-(*o*-Bromophenylsulfanyl)acetonitrile 7

Oil; TLC [EtOAc-hexane (5:95)] R_f 0.11; ν_{max} (neat)/cm^{-1} 3010, 2210, 1480, 1050, 760; δ_H ($CDCl_3$) 3.61 (2 H, s), 7.12 (1 H, dd, J = 8, 8 Hz), 7.28 (1 H, dd, J = 8, 8 Hz), 7.45 (1 H, d, J = 8 Hz), 7.55 (1 H, d, J = 8 Hz); δ_C($CDCl_3$) 19.1 (t), 115.7 (s), 125.5 (s), 128.1 (d), 129.2 (d), 131.4 (d), 132.8 (s), 133.2 (d); *m/z* 229 (63), 227 (60), 189 (60), 187 (59), 108 (100), 69 (24) (Found: M, 226.9401. $C_8H_6NS^{79}Br$ requires *M*, 226.9404).

2-(*o*-Bromophenoxyl)acetonitrile 8

Solid, mp 46-47 °C; TLC [EtOAc-hexane (2:98)] R_f 0.09; ν_{max} (KBr)/cm^{-1} 3030, 2940, 2220, 1500, 1050, 750; δ_H ($CDCl_3$) 4.78 (2 H, s), 6.96 (1 H, ddd, J = 8, 8, 1 Hz), 7.00 (1 H, dd, J = 8, 1 Hz), 7.28 (1 H, ddd, J = 8, 8, 1 Hz), 7.55 (1 H, dd, J = 8, 1 Hz); δ_C ($CDCl_3$) 54.8 (t), 112.9 (s), 114.8(s), 115.2 (d), 124.8 (d), 128.8 (d), 134.0 (d), 153.1 (s) ; *m/z* 213 (83), 211 (85), 173 (97), 171 (100), 145 (86) 143 (88) (Found: M, 210.9643. $C_8H_6NO^{79}Br$ requires *M*, 210.9633).

Preparation of 2-(*o*-Bromoaryl)-4-alkenenitriles 5a, 5c, 5d, 6a-c, 9a-d, 10a-d, 11a-d and 12a

Under an atmosphere of argon, a solution of diisopropylamine (0.54 mL, 3.3 mmol) in THF (10 mL) was cooled to 5 °C, and a solution of BuLi (1.6 M solution in hexane; 2.1 mL, 3.3 mmol) was added dropwise to it. After 15 min, the LDA solution was cooled to 8 °C, and a solution of the appropriate 2-(*o*-bromoaryl)acetonitrile (3 mmol) in THF (5 mL) was added dropwise to it. The resulting orange-colored solution was stirred for 45 min, after which a solution of 2-alkenyl bromide (3.6 mmol) in THF (5 mL) was added dropwise to it. The reaction was removed from a dry ice bath quickly, warmed to room temperature, and kept for an additional 6 h before quenched with saturated aqueous NH_4Cl. The mixture was concentrated under reduced pressure, and the residue was taken up with EtOAc. The resulting solution was washed with brine, dried (Na_2SO_4) and concentrated under reduced pressure. The crude product was purified by chromatography on a silica gel column with gradients of EtOAc and hexane to give the title compounds.

2-(*o*-Bromobenzyl)-4-pentenenitrile 5a

Oil; TLC [EtOAc-hexane (1:99)] R_f 0.07; ν_{max} (neat)/cm^{-1} 2960, 2930, 2220, 1645, 1560, 750; δ_H ($CDCl_3$) 2.48 (2H, t, J = 6 Hz), 2.94-3.17 (3 H, m), 5.28 (1 H, d, J = 11 Hz), 5.32 (1 H, dd, J = 5, 1 Hz), 5.83-5-6.04 (1 H, m), 7.16-7.24 (1 H, m), 7.30-7.40 (2 H, m), 7.61 (1 H, d, J = 8 Hz); δ_C ($CDCl_3$) 31.8 (d), 36.1 (t), 38.2 (t), 119.4 (t), 120.9 (s), 124.3 (s), 127.8 (d), 129.2 (d), 131.6 (d), 132.7 (d), 133.1 (d), 136.3 (s); *m/z* 251 (13), 249 (14), 171 (100), 169 (95), 128 (12), 90 (34) (Found: M, 249.0514. $C_{12}H_{12}N^{79}Br$ requires *M*, 249.0513).

2-(*o*-Bromobenzyl)-5-methyl-4-hexenenitrile 5c

Oil; TLC [EtOAc-hexane (1:99)] R_f 0.09; ν_{max} (neat)/cm^{-1} 2920, 2230, 1440, 1020, 750; δ_H ($CDCl_3$) 1.64 (3 H, s), 1.74 (3 H, s), 2.37 (2 H, t, J = 6 Hz), 2.89-3.09 (3 H, m), 5.23 (1 H, brt, J = 6 Hz), 7.08-7.16 (1 H, m), 7.24-7.31 (2 H, m), 7.54 (1 H, dd, J = 8, 1 Hz); δ_C ($CDCl_3$) 18.0 (q), 25.3 (q), 30.5 (t), 32.3 (d), 38.2 (t), 118.6 (d), 121.4 (s), 124.3 (s), 127.7 (d), 129.0 (d), 131.5 (d), 133.0 (d), 136.4 (s), 136.6 (s); *m/z* 279 (2), 277 (2), 198 (22), 171 (11), 169 (11), 119 (27), 117 (28), 69 (100) (Found: M, 277.0458. $C_{14}H_{16}N^{79}Br$ requires *M*, 277.0466).

2-(*o*-Bromobenzyl)-5-phenyl-4-pentenenitrile 5d

Oil; TLC [EtOAc-hexane (2:98)] R_f 0.08; ν_{max} (neat)/cm^{-1} 3040, 2920, 2210, 1460, 750; δ_H ($CDCl_3$) 2.60 (2 H, t, J = 6 Hz), 3.00-3.18 (3 H, m), 6.28 (1 H, dt, J = 16, 7 Hz), 6.60 (1 H, d, J = 16 Hz), 7.13-7.20 (1 H, m), 7.24-7.45 (7 H, m), 7.60 (1 H, d, J = 8 Hz); δ_C ($CDCl_3$) 32.1 (d), 35.3 (t), 38.1 (t), 120.9 (s), 124.0 (d), 124.3 (s), 126.3 (2 x d), 127.7 (d), 127.8 (d), 128.6 (2 x d), 129.1 (d), 131.6 (d), 133.0 (d), 134.2 (d), 136.3 (s), 136.6 (s); *m/z* 327 (4), 325 (4), 246 (34), 118 (16), 117 (100), 115 (28), 91 (24) (Found: M, 325.0467. $C_{18}H_{16}N^{79}Br$ requires *M*, 325.0466).

2-(*o*-Bromobenzyl)-2-phenyl-4-pentenenitrile 6a

Oil; TLC [EtOAc-hexane (2:98)] R_f 0.12; ν_{max} (neat)/cm^{-1} 3050, 2230, 1635, 1590, 990, 910, 750, 720, 690; δ_H ($CDCl_3$) 2.71 (1 H, dd, J = 14, 8 Hz), 2.95 (1 H, dd, J = 14, 6 Hz), 3.27 (1 H, d, J = 14 Hz), 3.60 (1 H, d, J = 14 Hz), 5.12 (1 H, dt, J = 10, 1 Hz), 5.15 (1 H, dd, J = 10, 1 Hz), 5.56-5.65 (1 H, m), 7.08-7.32 (3 H, m), 7.33-7.41 (5 H, m), 7.52 (1 H, dd, J = 8, 1 Hz); δ_C ($CDCl_3$) 43.1 (t), 45.2 (t), 48.9 (s), 120.2 (t), 121.3 (s), 126.1 (s), 126.6 (2 x d), 127.2 (d), 128.0 (d), 128.8 (2 x d), 128.9 (d), 131.6 (d), 131.8 (d), 133.0 (d), 134.7 (s), 137.4 (s); m/z 327 (38), 325 (39), 205 (25), 170 (97), 169 (100), 156 (28), 129 (24), 89 (30) (Found: M, 325.0469. $C_{18}H_{16}N^{79}Br$ requires *M*, 325.0466).

2-(*o*-Bromobenzyl)-2-phenyl-4-hexenenitrile 6b

Oil; TLC [EtOAc-hexane (2:98)] R_f 0.13; ν_{max} (neat)/cm^{-1} 3020, 2960, 2220, 1550, 965, 750, 690; **major isomer** δ_H ($CDCl_3$) 1.59 (3 H, dd, J = 6, 2 Hz), 2.63-2.95 (2 H, m), 3.61 (1 H, d, J = 14 Hz), 3.65 (1 H, d, J = 14 Hz), 5.28-5.38 (1 H, m), 5.52-5.65 (1 H, m), 7.07-7.21 (3 H, m), 7.33 -7.75 (6 H, m); δ_C ($CDCl_3$) 17.9 (q), 42.1 (t), 45.0 (t), 49.1 (s), 121.5 (s), 124.1 (d), 126.1 (s), 126.6 (2 x d), 127.2 (d), , 127.8 (d), 128.7 (3 x d), 128.8 (d), 131.7 (d), 132.9 (d), 134.8 (s), 137.7 (s); *m/z* 341 (23), 339 (23), 287 (32), 285 (35), 205 (38), 171 (96), 169 (100), 105 (51) (Found: M, 339.0625. $C_{19}H_{18}N^{79}Br$ requires *M*, 339.0623); **minor isomer** δ_H ($CDCl_3$) 1.59 (3 H, dd, J = 6, 2 Hz), 2.63-2.95 (2 H, m), 3.27 (1 H, d, J = 11 Hz), 3.34 (1 H, d, J = 11 Hz), 5.28-5.38 (1 H, m), 5.52-5.65 (1 H, m), 7.07-7.21 (3 H, m), 7.33 -7.75 (6 H, m); δ_C ($CDCl_3$) 13.1 (q), 36.2 (t), 45.0 (t), 48.7 (s), 121.6 (s), 123.5 (d), 126.1 (s), 126.6 (2 x d), 127.2 (d), 128.7 (3 x d), 128.8 (d), 131.1 (d), 131.7 (d), 132.9 (d), 134.8 (s), 137.7 (s).

2-(*o*-Bromobenzyl)—5-methyl-2-phenyl-4-hexenenitrile 6c

Oil; TLC [EtOAc-hexane (1:99)] R_f 0.09; ν_{max} (neat)/cm^{-1} 2960, 2220, 1450, 1020, 750, 690; δ_H ($CDCl_3$) 1.58 (3 H, s), 1.66 (3 H, d, J = 1 Hz), 2.82 (2 H, d, J = 8 Hz), 3.28 (1 H, d, J = 14 Hz), 3.62 (1 H, d, J = 14 Hz), 5.10 (1 H, tq, J = 8, 1 Hz), 7.08-7.20 (3 H, m), 7.32-7.42 (5 H, m), 7.53 (1 H, d, J = 7.5 Hz); δ_C ($CDCl_3$) 18.1 (q), 25.7 (q), 37.6 (t), 44.8 (t), 48.9 (s), 117.6 (d), 1221.8 (s), 126.1 (s), 126.6 (2 x d), 127.1 (d), 127.8 (d), 128.6 (2 x d), 128.7 (d), 131.6 (d), 132.9 (d), 134.9 (s), 136.7 (s), 137.9 (s); *m/z* 355 (7), 353 (8), 287 (66), 285 (68), 206 (23), 171 (22), 169 (23), 119 (60), 117 (63), 69 (100); (Found: M, 353.0783. $C_{20}H_{20}N^{79}Br$ requires *M*, 353.0779).

2-(*o*-Bromobenzyl)-2,5-diphenyl-4-pentenenitrile 6d

Solid; mp 98-99 °C; TLC [EtOAc-hexane (2:98)] R_f 0.14; ν_{max} (KBr)/cm^{-1} 3040, 2920, 2230, 1590. 1500, 965, 750, 695; δ_H ($CDCl_3$) 2.82 (1 H, dd, J = 14, 8 Hz), 3.03 (1 H, dd, J = 14, 6 Hz), 3.26 (1 H, d, J = 14 Hz), 3.59 (1 H, d, J = 14 Hz), 5.90 (1 H, ddd, J = 15, 8, 6 Hz), 6.40 (1 H, dd, J = 15, 1 Hz), 7.00-7.10 (1 H, m), 7.12-7.18 (6 H, m), 7.27-7.40 (6 H, m), 7.45 (1 H, dd, J = 8, 1 Hz); δ_C ($CDCl_3$) 42.4 (t), 45.2 (t), 49.3 (s), 121.4 (s), 123.0 (d), 126.2 (s), 126.3 (2 x d), 126.6 (2 x d), 127.3 (d), 127.5 (d), 128.1 (d), 128.4 (2 x d), 128.9 (2 x d), 129.0 (d), 131.8 (d), 133.0 (d), 134.8 (s), 135.1 (d), 136.7 (s), 137.6 (s); *m/z* 403 (4), 401 (3), 205, (9), 169 (14), 118 (30), 117 (100), 115 (39) (Found: M, 401.0774. $C_{24}H_{20}N^{79}Br$ requires *M*, 401.0779).

2-(*o*-Bromophenylsulfenyl)-4-pentenenitrile 9a

Oil; TLC [EtOAc-hexane (2:98)] R_f 0.12; ν_{max} (neat)/cm^{-1} 3050, 2210, 1630, 1430, 1000, 910, 730; δ_H ($CDCl_3$) 3.52-3.78 (2 H, m), 3.98 (1 H, t, J = 6.8 Hz), 5.24-5.34 (2 H, m), 5.79-5.96 (1 H, m), 7.22 (1 H, ddd, J = 8, 8, 1 5 Hz), 7.34 (1 H, ddd, J = 8, 8, 1.5 Hz), 7.62-7.69 (2 H, m); δ_C ($CDCl_3$) 36.7 (d), 36.1 (t), 118.2 (s), 120.2 (t), 128.1 (s), 128.4 (d), 130.5 (d), 131.4 (d), 132.3 (s), 133.6 (d), 135.2 (d); *m/z* 269 (38), 267 (37) 228 (62), 226 (61), 147 (63), 108 (100), 69 (30) (Found: M, 269.9722. $C_{11}H_{10}NS^{81}Br$ requires *M*, 269.9717).

2-(*o*-Bromophenylsulfenyl)-4-hexenenitrile 9b

Oil; TLC [EtOAc-hexane (1:99)] R_f 0.19; ν_{max} (neat)/cm^{-1} 2900, 2220, 1450, 1020, 965, 750; δ_H ($CDCl_3$) 1.71 (3 H, dd, J = 6, 1 Hz), 2.54-2.63 (2 H, m), 3.91 (1 H, dd, J = 6.5, 6 Hz), 5.45-5.65 (1 H, m), 5.65-5.76 (1 H, m), 7.19 (1 H, ddd, J = 8, 8, 2 Hz), 7.32 (1 H, ddd, J = 8, 8, 2 Hz), 7.60-7.66 (2 H, m); δ_C ($CDCl_3$) 17.8 (q), 35.0 (t), 36.1 (d), 118.3 (s), 123.9 (d), 127.9 (s), 128.2 (d), 130.1 (d), 131.1 (d), 132.6 (s), 133.4 (d), 134.6 (d); *m/z* 283 (60), 281 (56), 229 (75), 148 (290, 108 (84), 55 (100) (Found: M, 280.9881. $C_{12}H_{12}NS^{79}Br$ requires *M*, 280.9874).

2-(*o*-Bromophenylsulfenyl)-5-methyl hexenenitrile 9c

Oil; TLC [EtOAc-hexane (0.5:99.5)] R_f 0.09; ν_{max} (neat)/cm^{-1} 2950, 2210, 1650, 1440, 1010, 750; δ_H ($CDCl_3$) 1.64 (3 H, s), 1.72 (3 H, s), 2.59 (2 H, t, J = 7 Hz), 3.87 (1 H, t, J = 7 Hz), 5.22 (1 H, brtd, J = 7, 1 Hz), 7.16 (1 H, ddd, J = 8, 8, 1 Hz), 7.29 (1 H, ddd, J = 8, 8, 1 Hz), 7.58-7.64 (2 H, m); δ_C ($CDCl_3$) 18.0 (q), 25.6 (q), 30.6 9t), 36.1 (d), 117.4 (d), 118.6 (s), 128.0 (s), 128.2 (d), 130.2 (d), 132.7 (s), 133.4 (d), 134.6 (d), 137.6 (s); *m/z* 297 (21), 2950(21), 229 (53), 227 (52), 108 (56), 69 (100) (Found: M, 295.0019. $C_{13}H_{14}NSBr$ requires *M*, 295.0030).

***E*-2-(*o*-Bromophenylsulfenyl)-5-phenyl-4-pentenenitrile 9d**

Oil; TLC [EtOAc-hexane (1:99)] R_f 0.05; ν_{max} (neat)/cm^{-1} 3040, 2220, 1450, 965, 750, 690; δ_H ($CDCl_3$) 2.80 (2 H, t, J = 7 Hz), 4.00 (1 H, t, J = 7 Hz), 6.22 (1 H, dt, J = 16, 7 Hz), 6.58 (1 H, d, J = 16 Hz), 7.19-7.35 (5 H, m), 7.63 (1 H, dd, J = 8, 1 Hz), 7.67 (1 H, d, J = 7.5 Hz); δ_C ($CDCl_3$) 35.4 (t), 36.0 (d), 118.2 (s), 122.4 (d), 126.3 (2 x d), 127.8 (d), 128.3 (d), 128.3 (s), 128.5 (2 x d), 130.5 (d), 132.2 (s), 133.5 (d), 134.9 (d), 135.1 (d), 136.1 (s); m/z 345 (3), 343 (3), 117 (100), 115 (11), 108 (11), 91 (8) (Found: M, 343.0035. $C_{17}H_{14}N^{79}Br$ requires *M*, 343.0030).

1-Allyl-2-(*o*-Bromophenylsulfenyl)-4-pentenenitrile 10a

Oil; TLC [EtOAc-hexane (2:98)] R_f 0.24; ν_{max} (neat)/cm^{-1} 3040, 2200, 1620, 1420, 1000, 910, 740; δ_H ($CDCl_3$) 2.50 (2 H, ddd, J = 14, 7.5, 1 Hz), 2.67 (2 H, ddd, J = 14, 7, 1 Hz), 5.23 (2 H, dd, J = 15, 1.5 Hz), 5.27 (2 H, dd, J = 10, 1 Hz), 5.80-6.01 (2 H, m), 7.27 (1 H, ddd, J = 8, 8, 1 Hz), 7.38, (1 H, ddd, $J = 8, 8, 1.5$ Hz), 7.70 (1 H, dd, $J = 8, 1.5$ Hz), 7.93 (1 H, dd, $J = 7.5, 2$ Hz); δ_C ($CDCl_3$) 40.9 (2 x t), 49.0 (s), 119.9 (s), 120.9 (2 x t), 128.1 (d), 130.4 (2 x d), 130.7 (s), 131.3 (d), 131.5 (s), 133.6 (d), 138.4 (d); m/z 309 (6), 307 (5), 268 (53), 266 (52), 227 (31), 108 (100) (Found: M, 307.0038. $C_{14}H_{14}NS^{79}Br$ requires *M*, 307.0030).

2-(*o*-Bromophenylsulfenyl)-2-(2-butenyl)-4-hexenenitrile 10b

Oil; TLC [EtOAc-hexane (1:99)] R_f 0.26; ν_{max} (neat)/cm^{-1} 2920, 2220, 1450, 965, 750; δ_H ($CDCl_3$) 1.69 (6 H, dd, $J = 6, 1$ Hz), 2.40 (2 H, dd, $J = 14, 7$ Hz), 2.56 (2 H, dd, $J = 14, 6$ Hz), 5.40-5.70 (4 H, m), 7.22 (1 H, ddd, $J = 8, 8, 2$ Hz), 7.34 (1 h, ddd, $J = 8, 8, 2$ Hz), 7.66 (1 H, dd, $J = 8, 2$ Hz), 7.92 (1 H, dd, $J = 8, 2$ Hz); δ_C ($CDCl_3$) 18.0 (2 x q), 40.1 (2 x t), 49.9 (s), 120.4 (s), 123.2 (2 x d), 128.0 (d), 131.0 (d), 131.3 (2 x s), 131.7 (2 x d), 133.6 (d), 138.1 (d); *m/z* 337 (7), 335 (7), 202 (24), 146 (8), 109 (100), 67 (26) (Found: M, 335.0349. $C_{16}H_{18}NS^{79}Br$ requires *M*, 335.0343).

2-(*o*-Bromophenylsulfenyl)-5-methyl-2-(methyl-2-butenyl)-4-hexenenitrile 10c

Oil; TLC [EtOAc-hexane (0.5:99.5)] R_f 0.11; ν_{max} (neat)/cm^{-1} 2900, 2210, 1660, 1440, 1020, 750; δ_H($CDCl_3$) 1.60 (6 H, d, $J = 1$ Hz), 1.75 (6 H, d, $J = 1$ Hz), 2.45 (2 H, dd, $J = 15, 7.5$ Hz), 2.58 (2 H, dd, $J = 15, 7.5$ Hz), 5.26 (2 H, tqq, $J = 7.5, 1, 1$ Hz), 7.23 (1 H, ddd, $J = 8, 8, 1.5$ Hz), 7.35 (1 H, ddd, $J = 8, 8, 1.5$ Hz), 7.68 (1 H, dd, $J = 8, 1.5$ Hz), 7.94 (1 H, dd, $J = 8, 1.5$ Hz); δ_C ($CDCl_3$) 18.1 (2 x q), 25.8 (2 x q), 35.4 (2 x t), 50.6 (s), 116.7 (2 x d), 120.7 (s), 127.9 (d), 130.9 (d), 131.4 (s), 133.4 (d), 137.2 (3 x s), 138.0 (d); *m/z* 365 (24), 363 (24), 297 (58), 295 (57), 216 (51), 108 (49), 69 (100) (Found: M, 363.0655. $C_{18}H_{22}NS^{79}Br$ requires *M*, 363.0656).

***E*-2-(*o*-Bromophenylsulfenyl)-5-phenyl-2-[(*E*)-3-phenylpropenyl]-4-pentenenitrile 10d**

Oil; TLC [EtOAc-hexane (1:99)] R_f 0.06; ν_{max} (neat)/cm^{-1} 3020, 2220, 1590, 965, 750, 690; δ_H ($CDCl_3$) 2.71 (2 H, dd, $J = 14, 7$ Hz), 2.86 (2 H, dd, $J = 14, 7$ Hz), 6.30 (2 H, dt, $J = 16, 7$ Hz), 6.56 (2 H, d, $J = 16$ Hz), 7.20-7.41 (12 H, m), 7.69 (1 H, d, $J = 8,$ Hz), 8.00 (1 H, dd, $J = 8, 1$ Hz); δ_C ($CDCl_3$) 40.6 (2 x t), 49.8 (s), 120.2 (s), 121.8 (2 x d), 126.3 (4 x d), 127.8 (2 x d), 128.2 (d), 128.5 (4 x d), 130.9 (s), 131.4 (d), 131.5 (s), 133.7 (d), 135.6 (2 x d), 136.3 (2 x s), 138.4 (d); m/z 462 (7), 460 (7), 380 (35), 271 (17), 205 (35), 117 (100), 91 (23) (Found: M, 459.0651. $C_{26}H_{22}NS^{79}Br$ requires *M*, 459.0656).

2-(*o*-Bromophenoxy)-4-pentenenitrile 11a

Oil; TLC [EtOAc-hexane (1:99)] R_f 0.08; ν_{max} (neat)/cm^{-1} 3020, 2210, 1580, 990, 910, 750; δ_H ($CDCl_3$) 2.76 (2 H, ddd, $J = 7, 7, 1$ Hz), 4.70 (1 H, t, $J = 7$ Hz), 5.22 (1 H, dd, $J = 10, 1$ Hz), 5.25 (1 H, dd, $J = 16, 0.6$ Hz), 5.77-5.95 (1 H, m), 6.88 (1 H, ddd, $J = 8, 8, 1$ Hz), 7.01 (1 H, d, $J = 8$ Hz), 7.20 (1 H, ddd, $J = 8, 8, 1$ Hz), 7.46 (1 H, dd, $J = 8, 1$ Hz); δ_C ($CDCl_3$) 37.6 (t), 68.0 (d), 113.7 (s), 116.7 (s), 117.1 (d), 120.9 (t), 125.0 (d), 128.7 (d), 129.8 (d), 13.8 (d), 152.9 (s); m/z 253 (4), 251 (3), 212 (58), 210 (59), 172 (100), 131 (60) (Found: M, 250.9952. $C_{11}H_{10}NO^{79}Br$ requires *M*, 250.9946).

2-(*o*-Bromophenoxy)-5-methyl-2-(methyl-2-butenyl)-4-hexenenitrile 12c

Oil; TLC [EtOAc-hexane (1:99)] R_f 0.08; ν_{max} (neat)/cm^{-1} 3020, 2220, 1590, 750; δ_H ($CDCl_3$) 1.61 (6 H, d, $J = 0.8$ Hz), 1.75 (6 H, d, $J = 1$ Hz), 2.68 (4 H, d, $J = 7$ Hz), 5.28 (2 H, brt, $J = 7$ Hz), 6.96 (1 H, ddd, $J = 8, 8, 1$ Hz), 7.27 (1 H, ddd, $J = 8, 8, 1$ Hz), 7.55 (2 H, dd, $J = 8, 1$ Hz); δ_C ($CDCl_3$) 18.0 (2 x q), 25.8 (2 x q), 35.5 (2 x t), 79.6 (s), 115.7 (2 x d), 116.7 (s), 119.7 (s), 120.8 (d), 125.0 (d), 128.2 (d), 133.6 (d), 137.4 (2 x s), 151.6 (s); *m/z* 349 (7), 347 (8), 201 (16), 175 (26), 173 (26), 161 (18), 109 (44), 69 (100) (Found: M, 347.0892. $C_{18}H_{22}NO^{79}Br$ requires *M*, 347.0885).

2-(*o*-Bromophenoxy)-5-methyl-4-hexenenitrile 11c

Oil; TLC [EtOAc-hexane (1:99)] R_f 0.04; ν_{max} (neat)/cm^{-1} 3020, 2210, 1590, 750; δ_H ($CDCl_3$) 1.73 (3 H, s), 1.78 (3 H, s), 2.83 (1 H, dd, $J = 7, 7,$ Hz), 4.71 (2 H, dd, $J = 7, 7$ Hz), 5.31 (1 H, brt, $J = 7$ Hz), 6.98 (1 H, ddd, $J = 8, 8, 1$ hz), 7.11 (1 H, dd, $J = 8, 1$ Hz), 7.30 (1 H, ddd, $J = 8, 8, 1$ Hz), 7.57 (1 H, dd, $J = 8, 1$ Hz); δ_C ($CDCl_3$) 18.0 (q), 25.7 (q), 32.1 (t), 68.1 (d), 113.5 (s), 115.3 (d), 116.8 (d), 117.1 (s), 124.6 (d), 128.6 (d), 133.7 (d), 138.1 (s), 153.0 (s); *m/z* 281 (6), 279 (6), 174 (81), 172 (83), 108 (25), 81 (37), 69 (100) (Found: M, 279.0258. $C_{13}H_{14}NO^{79}Br$ requires *M*, 279.0259).

***E*-2-(*o*-Bromophenoxy)-5-phenyl-4-pentenenitrile 11d**

Oil; TLC [EtOAc-hexane (1:99)] R_f 0.04; ν_{max} (neat)/cm^{-1} 3020, 2220, 1660, 1580, 970, 760, 690; δ_H ($CDCl_3$) 2.92 (2 H, ddd, $J = 7, 7, 1$ Hz), 4.75 (1 H, t, $J = 7$ Hz), 6.24 (1 H, dt, $J = 16, 7$ Hz), 6.59 (1 H, d, $J = 16$ Hz), 6.90 (1 H, ddd, $J = 8, 8, 1$ Hz), 7.05 (1 H, dd, $J = 8, 1$ Hz), 7.15-7.31 (6 H, m), 7.49 (1 H, dd, $J = 8, 1$ Hz); δ_C ($CDCl_3$) 37.0 (t), 68.3 (d), 113.8 (s), 116.8 (s), 117.3 (d), 120.9 (d), 125.0 (d), 126.4 (2 x d), 127.8 (d), 128.5 (2 x d), 128.7 (d), 133.9 (d), 135.7 (d), 136.4 (s), 153.0 (s); *m/z* 329 (2), 327 (2), 248 (120, 156 (18), 129 (16), 117 (100) (Found: M, 327.0262. $C_{17}H_{14}NO^{79}Br$ requires *M*, 327.0259).

2-Allyl-2-(*o*-bromophenoxy)-4-pentenenitrile 12a

Oil; TLC [EtOAc-hexane (1:99)] R_f 0.11; ν_{max} (neat)/cm^{-1} 3020, 2220, 1580, 1220, 990, 910, 760; δ_H ($CDCl_3$)

2.66-2.85 (4 H, m), 5.24 (2 H, dd, *J* = 18, 1.5 Hz), 5.26 (2 H, dd, *J* = 9, 1 Hz), 5.81-6.00 (2 H, m), 6.99 (1 H, ddd, *J* = 8, 8, 1 Hz), 7.29 (1 H, ddd, *J* = 8, 8, 1 Hz), 7.52 (1 H, dd, *J* = 8, 1 Hz), 7.56 (1 H, dd, *J* = 8, 1 Hz); δ_C ($CDCl_3$) 41.2 (2 x t), 78.8 (s), 116.9 (s), 118.9 (s), 121.1 (d), 121.3 (2 x t), 125.5 (d), 128.5 (d), 129.8 (2 x d), 133.8 (d), 151.3 (s); *m/z* 293 (7), 291 (7), 174 (96), 172 (100), 145 (13), 143 (13) (Found: M, 291.0262. $C_{14}H_{14}NO^{79}Br$ requires *M*, 291.0259).

General Procedure for the Palladium-Catalyzed Reactions (Table 2)

To a stirred solution of compound **1** (1 mmol) in DMF (10 mL) were sequentially added Et_3N (0.167 mL), PPh_3 (0.52 mg, 0.2 mmol), and $Pd(OAc)_2$ (22.5 mg, 0.1 mmol) at room temperature under an argon atmosphere. The reaction mixture was stirred and heated at 100 °C for 10−12 h and then cooled to room temperature, diluted with EtOAc (50 mL), washed with water (3 ×15 mL), dried (Na_2SO_4), filtered and concentrated under reduced pressure. The residue was separated by chromatography on a silica gel column with gradients of EtOAc and hexane to give the products shown in Table 2.

2-(Methylamino)benzonitrile 16

Solid, mp 62-64 °C; TLC [EtOAc-hexane (5:95)] R_f 0.13; ν_{max} (KBr)/cm^{-1} 3280, 3020, 2250, 1576, 1480, 1210, 743; δ_H ($CDCl_3$) 2.77 (3 H, d, *J* = 7 Hz), 4.65 (1 H, br s), 6.52 (1 H, d, *J* = 8 Hz), 6.56 (1 H, d, *J* = 8 Hz), 7.28 (2 H, ddd, *J* = 8, 8, 1 Hz); δ_C ($CDCl_3$) 29.7 (q), 95.2 (s), 109.9 (d), 116.0 (d), 117.8 (s), 132.4 (d), 134.1 (d), 151.0 (s); *m/z* 132 (84), 131 (100), 104 (48), 77 (24).

5-Methyl-2-phenyl-3-(2*E*-phenylethenyl)-γ-carboline 21

Solid, mp 197-199 °C; TLC [EtOAc-hexane (5:95)] R_f 0.23; ν_{max} (neat)/cm^{-1} 2960, 1630, 1496, 965, 815, 750; δ_H ($CDCl_3$) 3.83 (3 H, s), 7.21-7.61 (15 H, m), 7.97 (1 H, d, *J* = 16 Hz), 8.51 (1 H, d, *J* = 8 Hz); δ_C ($CDCl_3$) 29.1 (q), 108.7 (d), 116.7 (d), 119.8 (d), 121.4 (d), 122.3 (s), 126.6 (d), 127.0 (2 x d), 127.4 (2 x d), 127.8 (d), 128.3 (2 x d), 128.5 (2 x d), 130.2 (d), 131.0 (d), 134.2 (s), 137.8 (s), 140.5 (s), 141.2 (s), 142.7 (s), 145.2 (s), 151.0 (s); *m/z* 360 (100), 359 (89), 283 (74), 268 (22), 91 (31), 77 (75) (Found: C, 86.47; H, 5.57; N,7.74 %; M, 360.1634. $C_{26}H_{20}N_2$ requires C, 86.63; H, 5.60; N, 7.78 %. *M*, 360.1626).

1-Vinyl-2-indanecarbonitrile 24

Oil; TLC [EtOAc-hexane (1:99)] R_f 0.05; ν_{max} (neat)/cm^{-1} 3040, 2960, 2210, 1550, 990, 900, 750; δ_H ($CDCl_3$) 3.02 (1H, dd, *J* = 14, 10 Hz), 3.21-3.45 (2 H, m), 4.08 (1 H, t, *J* = 10 Hz), 5.40 (1 H, dd, *J* = 10, 1 Hz), 5.48 (1 H, dd, *J* = 17, 1 Hz), 5.85 (1 H, ddd, *J* = 17, 10, 10 Hz), 7.12-7.21 (1 H, m), 7.29-7.31 (3 H, m); δ_C ($CDCl_3$) 36.1 (t), 36.2 (d), 54.5 (d), 119.4 (t), 121.2 (s), 124.3 (d), 124.4 (d), 127.5 (d), 127.8 (d), 136.3 (d), 139.4 (s), 141.9 (s); *m/z* 169 (80), 154 (62), 142 (100), 129 (36), 115 (51) (Found: M, 169.0895. $C_{12}H_{11}N$ requires *M*, 169.0891).

2-(4-Methyl-1,2-dihydronaphthalene)carbonitrile 25a₁

Oil; TLC [EtOAc-hexane (1:99)] R_f 0.03; ν_{max} (neat)/cm^{-1} 2940, 2220, 1450, 750; δ_H ($CDCl_3$) 2.10 (3 H, d, *J* = 1.5 Hz), 3.07 (2 H, d, *J* = 8 Hz), 3.45-3.56 (1 H, m), 5.72-5.75 (1 H, m), 7.14-7.30 (4 H, m); δ_C ($CDCl_3$) 19.1 (q), 25.7 (d), 31.7 (t), 117.6 (d), 120.7 (s), 123.6 (d), 127.5 (d), 127.6 (d), 128.0 (d), 132.0 (s), 133.7 (s), 136.2 (s); *m/z* 169 (63), 167 (13), 154 (100), 140 (25), 129 (35) (Found: M, 169.0896. $C_{12}H_{11}N$ requires *M*, 169.0891).

2-(4-Methylnaphthalene)carbonitrile 25a₂

Solid, mp 58-60 °C; TLC [EtOAc-hexane (1:99)] R_f 0.07; ν_{max} (KBr)/cm^{-1} 3030, 2940, 2220, 1550, 1490, 750; δ_H ($CDCl_3$) 2.67 (3 H, s), 7.39 (1 H, s), 7.56-7.66 (2 H, m), 7.84 (1 H, dd, *J* = 8, 1 Hz), 7.96-7.8.04 (2 H, m); δ_C ($CDCl_3$) 19.1 (q), 108.8 (s), 119.3 (s), 124.2 (d), 126.4 (d), 127.2 (d), 128.8 (d), 129.0 (d), 132.2 (s), 132.5 (d), 133.9 (s), 136.2 (s); *m/z* 167 (100), 166 (59), 140 (30), 139 (21) (Found: M, 167.0736. $C_{12}H_9N$ requires *M*, 167.0735).

2-(4-Isopropenyl-1,2,3,4-tetrahydronaphthalene)carbonitrile 25c

Solid, mp 51-53 °C; TLC [EtOAc-hexane (1:99)] R_f 0.10; ν_{max} (KBr)/cm^{-1} 2920, 2220, 1635, 990, 750; δ_H ($CDCl_3$) 1.73 (3 H, s), 2.10-2.16 (2 H, m), 3.05-3.12 (3 H, m), 3.69 (1 H, t, *J* = 6 Hz), 4.44 (1 H, d, *J* = 1 Hz), 4.97 (1H, d, *J* = 1 Hz), 7.04-7.17 (4 H, m); δ_C ($CDCl_3$) 20.7 (q), 22.8 (d), 30.0 (t), 32.4 (t), 44.5 (d), 115.6 (t), 112.2 (s), 126.6 (2 x d), 128.7 (d), 129.8 (d), 132.6 (s), 136.1 (s), 147.4 (s); *m/z* 197 (100), 182 (53), 144 (64), 129 (91), 115 (33) (Found: M, 197.1210. $C_{14}H_{15}N$ requires *M*, 197.1204).

2-[4-(*E*)-Phenylmethylidene-1,2,3,4-tetrahydronaphthalene]-carbonitrile 25d

Solid, mp 89-91 °C; TLC [EtOAc-hexane (1:99)] R_f 0.09; ν_{max} (neat)/cm^{-1} 2940, 2220, 1550, 1450, 750, 690; δ_H ($CDCl_3$) 2.84-3.00 (2 H, m), 3.10-3.25 (3 H, m), 7.05-7.10 (1 H, m), 7.20-7.42 (8 H, m), 7.68-7.75 (1 H, m); δ_C($CDCl_3$) 26.1 (d), 30.6 (t), 33.1 (t), 121.5 (s), 124.4 (d), 126.6 (d), 127.2 (d), 127.4 (d), 128.0 (d), 128.4 (2 x d), 129.0 (d), 129.3 (2 x d), 132.0 (s), 132.9 (s), 134.5 (s), 137.0 (s); *m/z* 245 (45), 169 (31), 155 (76), 154 (100), 117 (31), 115 (30), 91 (29), 69 (58)

(Found: M, 245.1205. $C_{18}H_{15}N$ requires *M*, 245.1204).

2-(4-Methyl-2-phenyl-1,2-dihydronaphthalene)carbonitrile 26a

Solid, mp 118-120 °C; TLC [EtOAc-hexane (2:98)] R_f 0.11; ν_{max} (KBr)/cm^{-1} 2940, 2220, 1590, 1490, 750, 690; δ_H ($CDCl_3$) 2.26 (3 H, d, *J* = 1.4 Hz), 3.30 (1 H, d, *J* = 15.5 Hz), 3.41 (1 H, d, *J* = 15.5 Hz), 5.91 (1 H, br s), 7.15 (1 H, d, *J* = 8 Hz), 7.18-7.43 (6 H, m), 7.62 (2 H, dd, *J* = 8, 1 Hz); δ_C ($CDCl_3$) 19.2 (q), 42.6 (s), 42.7 (t), 121.7 (s), 123.3(d), 123.7 (d), 126.1 (2 x d), 127.6 (d), 127.7 (d), 128.0 (d), 128.4 (d), 128.8 (2 x d), 131.3 (s), 133.1 (s), 136.8 (s), 139.7 (s); m/z 246 (14), 245 (74), 230 (76), 168 (22), 129 (100) (Found: M, 245.1214. $C_{18}H_{15}N$ requires *M*, 245.1204).

2-(4-Vinyl-2-phenyl-1,2,3,4-tetrahydronaphthalene)-carbonitrile 26b

Oil; TLC [EtOAc-hexane (2:98)] R_f 0.12; ν_{max} (neat)/cm^{-1} 3060, 2910, 2230, 1600, 1495, 990, 910, 740, 700; δ_H ($CDCl_3$) 2.07 (1 H, dd, *J* = 13, 12 Hz), 2.38 (1 H, ddd, *J* = 13, 6, 1.5 Hz), 3.25 (2 H, s), 3.90-4.02 (1 H, m), 5.21 (1 H, dd, *J* = 14, 1.5 Hz), 5.28 (1 H, dd, *J* = 20, 1.5 Hz), 5.65-5.83 (1 H, m), 7.04-7.18 (3 H, m), 7.24-7.40 (4 H, m), 7.41-7.50 (2 H, m); δ_C ($CDCl_3$) 40.2 (t), 42.0 (s), 42.2 (t), 43.1 (d), 117.6 (t), 122.2 (s), 125.5 (2 x d), 126.6 (d), 127.1 (d), 128.3 (d), 128.9 (d), 129.0 (d), 129.2 (2 x d), 132.3 (s), 135.9 (s), 140.2 (d), 140.2 (s); *m/z* 259 (32), 130 (100), 129 (44), 115 (28), 91 (68) (Found: M, 259.1369. $C_{19}H_{17}N$ requires *M*, 259.1361).

2-(4-Isopropenyl-2-phenyl-1,2,3,4-tetrahydronaphthalene)-carbonitrile 26c

Oil; TLC [EtOAc-hexane (2:98)] R_f 0.13; ν_{max} (neat)/cm^{-1} 3050, 2210, 1490, 900, 760, 690; δ_H ($CDCl_3$) 1.58 (3 H, s), 2.21 ((1 H, dd, *J* = 13, 12 Hz), 2.38 (1 H, dd, *J* = 13, 6 Hz), 3.30 (2 H, s), 4.10-4.21 (1 H, m), 5.02(1 H, dd, *J* = 1.5, 1.5 Hz), 5.10 (1 H, br s), 7.07-7.45 (7 H, m), 7.55-7.60 (2 H, m); δ_C ($CDCl_3$) 18.2 (q), 39.0 (t), 42.1 (t), 46.5 (s), 46.8 (d), 115.4 (t), 122.1 (s), 125.5 (2 x d), 126.6 (d), 127.2 (d), 128.2 (d), 128.3 (d), 129.0 (d), 129.1 (2 x d), 132.7 (s), 135.5 (s), 140.2 (s), 145.8 (s); *m/z* 273 (M^+, 49), 144 (92), 129 (100), 115 (25), 91 (29) (Found: M, 273.1525. $C_{20}H_{19}N$ requires *M*, 273.1517).

4-Methylene-3,4-dihydro-2*H*-benzo[*b*]thiine-2-carbonitrile 27a

Oil; TLC [EtOAc-hexane (1:99)] R_f 0.08; ν_{max} (neat)/cm^{-1} 3060, 2950, 2230, 1640, 1070, 760, 740; δ_H ($CDCl_3$) 3.01-3.06 (2 H, m), 4.13 (1 H, dd, *J* = 5, 4 Hz), 5.22 (1 H, s), 5.74 (1 H, s), 7.07-7.21 (3 H, m), 7.61 (1 H, dd, *J* = 8, 1 Hz); δ_C ($CDCl_3$) 28.6 (d), 35.7 (t), 115.8 (t), 118.3 (s), 125.6 (d), 126.3 (d), 126.4 (d), 128.7 (d), 131.4 (s), 136.0 (2 x s); *m/z* 187 (M^+, 100), 186 (64), 172 (33), 147 (28), 134 (68), 115 (19) (Found: M, 187.0459. $C_{11}H_9NS$ requires *M*, 187.0456).

***Cis*-4-Vinyl-3,4-dihydro-2*H*-benzo[*b*]thiine-2-carbonitrile 27b$_1$**

Oil; TLC [EtOAc-hexane (1:99)] R_f 0.06; ν_{max} (neat)/cm^{-1} 2900, 2205, 1625, 985, 910, 750; δ_H ($CDCl_3$) 2.34-2.58 (2 H, m), 3.86 (1 H, dd, *J* = 12, 7.5 Hz), 4.21 (1 H, dd, *J* = 7.5, 4 Hz), 5.16 (1 H, ddd, *J* = 16, 1.2, 1.2 Hz), 5.38 (1 H, ddd, *J* = 10, 1.2, 1.2 Hz), 5.92 (1 H, ddd, *J* = 15, 10, 7.5 Hz), 7.16-7.34 (4 H, m); δ_C ($CDCl_3$) 27.0 (d), 33.8 (t), 42.7 (d), 118.2 (t), 119.2 (s), 126.2 (d), 127.3 (d), 127.5 (d), 128.8 (d), 129.6 (s), 136.0 (s), 138.1 (d); *m/z* 201 (100), (27), 147 (85), 115 (30) (Found: M, 285.0145. $C_{12}H_{11}NS$ requires *M*, 285.0153).

***Trans*-4-Vinyl-3,4-dihydro-2*H*-benzo[*b*]thiine-2-carbonitrile 27b$_2$**

Oil; TLC [EtOAc-hexane (1:99)] R_f 0.04; ν_{max} (neat)/cm^{-1} 2920, 2220, 1640, 990, 920, 750; δ_H ($CDCl_3$) 2.21-2.37 (1 H, m), 2.62-2.74 (1 H, m), 3.50-3.62 (1H, m), 4.28 (1 H, dd, *J* = 8, 6 Hz), 5.31 (1 H, ddd, *J* = 17, 1.2, 1.2 Hz), 5.40 (1 H, ddd, *J* = 10, 1.2, 1.2 Hz), 6.03-6.20 (1 H, m), 7.23-7.35 (4 H, m); δ_C ($CDCl_3$) 26.0 (d), 32.4 (t), 40.7 (d), 118.8 (s), 118.8 (t), 125.4 (d), 126.3 (d), 127.5 (d), 129.0 (s), 130.4 (d), 133.0 (s), 138.6 (d); m/z 201 (50), 186 (19), 168 (19), 147 (100), 117 (6) (Found: M, 201.0612. $C_{12}H_{11}NS$ requires *M*, 201.0612).

***Cis*-4-Isopropenyl-3,4-dihydro-2*H*-benzo[*b*]thiine-2-carbonitrile 27c$_1$**

This compound was a mixture of two isomers, *cis*/*trans* = 6 : 1. *Cis*-Isomer : oil; TLC [EtOAc-hexane (2:98)] R_f 0.14; ν_{max} (neat)/cm^{-1} 2960, 2260, 1545, 910, 760; δ_H ($CDCl_3$) 1.70 (3 H, s), 2.33-2.45 (2 H, m), 3.78 (1 H, dd, *J* = 8, 5 Hz), 4.08 (1 H, dd, *J* = 7, 4 Hz), 4.71 (1 H, d, *J* = 0.6 Hz), 5.05 (1 H, d, *J* = 1 Hz), 7.04-7.17 (4 H, m); δ_C ($CDCl_3$) 19.5 (q), 26.0 (d), 30.6 (t), 44.1 (d), 116.3 (t), 118.7 (s), 125.3 (d), 126.0 (d), 127.2 (d), 129.0 (s), 130.0 (s), 133.0 (d), 144.6 (s); *m/z* 215 (48), 172 (28), 162 (41), 147 (100) (Found: M, 215.0765. $C_{13}H_{13}NS$ requires *M*, 215.0769).

***Trans*-4-Isopropenyl-3,4-dihydro-2*H*-benzo[*b*]thiine-2-carbonitrile 27c$_2$**

δ_H ($CDCl_3$) 1.75 (3 H, s), 3.52 (1 H, dd, *J* = 8, 5 Hz), 4.21 (1 H, dd, *J* = 8, 5 *Hz)*, 4.89 (1 H, s), 5.08 (1 H, s); δ_C ($CDCl_3$) 19.4 (q),27.4 (d), 32.4 (t), 46.2 (d), 115.9 (t), 118.7 (s), 125.9 (d), 126.9 (d), 128.5 (d), 129.5 (s), 130.1 (d), 135.2 (s), 144.0 (s).

4-[(*E*)-1-Phenylmethylidene]-3,4-dihydro-2*H*-benzo[*b*]thiine-2-carbonitrile 27d

Solid, mp 163-164 °C; TLC [EtOAc-hexane (0.5:99.5)] R_f 0.03; ν_{max} (KBr)/cm^{-1} 2920, 2230, 1640, 900, 760, 690; δ_H ($CDCl_3$) 3.14 (1 H, ddd, *J* = 14, 4, 2 Hz), 3.61 (1 H, ddd, *J* = 14, 6, 1 Hz), 4.13 (1 H, ddd, *J* = 6, 4, 1 Hz), 7.21-7.49 (9 H, m), 7.72-7.81 (1 H, m); δ_C ($CDCl_3$) 28.6 (d), 30.2 (t), 118.3 (s), 126.2 (d), 126.9 (2 x d), 127.5 (d), 128.4 (s), 128.5 (3 x d), 129.2 (2 x d), 130.3 (s), 130.6 (d), 133.6 (s), 136.5 (s); m/z 263 (100), 235 (26), 134 (16), 91 (31) (Found: C, 77.62; H, 5.02; N, 5.29%; M, 263.0772. $C_{17}H_{14}NS$ requires C, 77.54; H, 4.98; N, 5.32%. *M*, 263.0769).

2-Allyl-4-methylene-3,4-dihydro-2*H*-benzo[*b*]thiine-2-carbonitrile 28a

Oil; TLC [EtOAc-hexane (1:99)] R_f 0.06; ν_{max} (neat)/cm^{-1} 3050, 2960, 2230, 1640, 990, 900, 750; δ_H ($CDCl_3$) 2.68-2.83 (3 H, m), 3.04 (1 H, dd, *J* = 14, 0.5 Hz), 5.21 (1 H, t, *J* = 1 Hz), 5.31-5.40 (2 H, m), 5.76 (1 H, t, *J* = 1 Hz), 5.90-6.10 (1 H, m), 7.09-7.23 (3 H, m), 7.62 (1 H, dd, *J* = 8, 1 Hz); δ_C ($CDCl_3$) 42.4 (t), 42.6 (s), 43.4 (t), 115.8 (t), 119.9 (s), 121.7 (d), 125.5 (d), 125.7 (d), 125.9 (d), 129.6 (d), 130.0 (d), 131.0 (s), 137.0 (2 x s); *m/z* 227 (38), 186 (100), 147 (21), 115 (5) (Found: M, 227.0772. $C_{14}H_{13}NS$ requires *M*, 227.0769).

***Cis*-2-[(*E*)-2-Butenyl]-4-vinyl-3,4-dihydro-2*H*-benzo[*b*]thiine-2-carbonitrile 28b$_1$**

Oil; TLC [EtOAc-hexane (1:99)] R_f 0.05; ν_{max} (neat)/cm^{-1} 2950, 2220, 990, 965, 900, 750; δ_H ($CDCl_3$) 1.75 (3 H, d, *J* = 6 Hz), 2.39 (2 H, dd, *J* = 14, 5 Hz), 2.56-2.70 (2 H, m), 3.76-3.89 (1 H, m), 5.26-5.31 (1 H, m), 5.35 (1 H, d, *J* = 15 Hz), 5.57-5.80 (3 H, m), 7.02-7.13 (3 H, m), 7.23-7.30 (1 H, m); δ_C ($CDCl_3$) 18.0 (q), 40.2 (t), 41.9 (s), 42.4 (d), 43.2 (t), 118.3 (t), 120.9 (s), 122.3 (d), 125.5 (d), 126.2 (d), 127.2 (d), 129.5 (d), 132.7 (d), 133.4 (s), 139.2 (d); *m/z* 255 (36), 200 (100), 147 (70), 116 (25) (Found: M, 255.1088. $C_{16}H_{17}NS$ requires *M*, 255.1082).

***Trans*-2-[(*E*)-2-Butenyl]-4-vinyl-3,4-dihydro-2*H*-benzo[*b*]-thiine-2-carbonitrile 28b$_2$**

Oil; TLC [EtOAc-hexane (1:99)] R_f 0.03; ν_{max} (neat)/cm^{-1} 2920, 2220, 1640, 1435, 990, 965, 900, 750; δ_H ($CDCl_3$) 1.75 (3 H, d, *J* = 6 Hz), 2.26-2.32 (2 H, m), 2.64 (2 H, d, *J* = 6 Hz), 3.50 (1 H, dd, *J* = 14, 7.5 Hz), 5.12-5.28 (2 H, m), 5.60-5.80 (2 H, m), 5.98-6.15 (1 H, m), 7.12-7.24 (4 H, m); δ_C ($CDCl_3$) 18.0 (q), 40.2 (t), 41.4 (s), 41.7 (d), 43.6 (t), 117.6 (t), 122.8 (d), 126.2 (d), 127.3 (d), 127.6 (d), 128.6 (d), 130.5 (s), 132.5 (d), 136.5 (s), 138.4 (d); *m/z* 255 (27), 200 (100), 173 (19), 147 (75), 134 (22), 116 (45) (Found: M, 255.1086. $C_{16}H_{172}NS$ requires *M*, 255.1082).

4-Isopropenyl-2-(3-methyl-2-buthenyl)-3,4-dihydro-2*H*-benzo[*b*]thiine-2-carbonitrile 28c

Oil; TLC [EtOAc-hexane (1:99)] R_f 0.08; ν_{max} (neat)/cm^{-1} 2920, 2240, 1520, 900, 750; δ_H ($CDCl_3$) 1.59 (3 H, s), 1.73 (3 H, s), 1.83 (3 H, s), 2.09 (1 H, dd, *J* = 13, 13 Hz), 2.40 (1 H, dd, *J* = 13, 5 Hz), 2.66 (2 H, d, *J* = 7.5 Hz), 4.00 (1 H, dd, *J* = 13, 5 Hz), 5.08 (1 H, d, *J* = 1.5 Hz), 5.12 (1 H, d, *J* = 1.5 Hz), 5.38 (1 H, tq, *J* = 7.5, 1 Hz), 7.05-7.28 (4 H, m); δ_C ($CDCl_3$) 17.9 (q), 18.3 (q), 25.9 (q), 38.4 (t), 39.0 (t), 42.4 (s), 46.0 (d), 115.7 (d), 115.9 (t), 120.8 (s), 125.5 (d), 126.3 (d), 127.0 (d), 129.0 (d), 130.0 (s), 132.7 (s), 138.5 (s), 145.0 (s); *m/z* 283 (48), 215 (100), 172 (24), 147 (44), 69 (78) (Found: M, 283.1399. $C_{18}H_{21}NS$ requires *M*, 283.1395).

4-[(*E*)-1-Phenylmethylidene]-2-[(*E*)-3-phenyl-2-propenyl]-3,4-dihydro-2*H*-benzo[*b*]thiine-2-carbonitrile 28d

Soild, mp 133-134 °C; TLC [EtOAc-hexane (0.5:99.5)] R_f 0.03; ν_{max} (KBr)/cm^{-1} 3040, 2920, 2230, 1640, 965, 900, 750; δ_H ($CDCl_3$) 2.82 (2 H, dd, *J* = 7, 4 Hz), 2.89 (1 H, d, *J* = 14 Hz), 3.64 (1 H, d, *J* = 14 Hz), 6.24 (1 H, dt, *J* = 16, 7 Hz), 6.62 (1 H, d, *J* = 16 Hz), 7.18-7.43 (14 H, m), 7.71-7.76 (1 H, m); δ_C($CDCl_3$) 36.2 (t), 42.8 (t), 43.2 (s), 120.3 (s), 121.0 (d), 125.9 (d), 126.5 (3 x d), 126.6 (d), 127.5 (d), 128.0 (d), 128.6 (5 x d), 129.3 (2 x d), 130.1 (s), 130.6 (d), 130.9 (s), 132.8 (s), 136.4 (d), 136.5 (s); *m/z* 379 (36), 262 (36), 117 (100), 91 (11) (Found: C, 82.11; H, 5.60; N, 3.68 %; M, 379.1340. $C_{26}H_{21}NS$ requires C, 82.29; H, 5.58; N, 3.69 %. *M*, 379.1395).

4-Methylene-3,4-dihydro-2*H*-benzo[*b*]oxine-2-carbonitrile 29a

Oil; TLC [EtOAc-hexane (1:99)] R_f 0.08; ν_{max} (neat)/cm^{-1} 3040, 2920, 2220, 1450, 910, 750; δ_H ($CDCl_3$) 2.79-3.05 (2 H, m), 5.06 (1 H, s), 5.11 (1 H, dd, *J* = 5.5, 5 Hz), 5.68 (1 H, s), 6.88 (1 H, dd, *J* = 8, 1 Hz), 6.97 (1 H, ddd, *J* = 8, 8, 1 Hz), 7.19 (1 H, ddd, *J* = 8, 8, 1 Hz), 7.55 (1 H, dd, *J* = 8, 1 Hz); δ_C ($CDCl_3$) 34.6 (t), 64.1 (d), 111.0 (t), 116.8 (s), 117.7 (d), 120.8 (s), 122.5 (d), 124.5 (d), 130.1 (d), 132.2 (s), 151.2 (s); *m/z* 171 (100), 170 (46), 156 (36), 131 (48), 118 (51), 90 (24) (Found: M, 171.0681. $C_{11}H_9NO$ requires *M*, 171.0684).

4-Isopropenyl-3,4-dihydro-2*H*-benzo[*b*]oxine-2-carbonitrile 29c

Oil; TLC [EtOAc-hexane (1:99)] R_f 0.13; ν_{max} (neat)/cm^{-1} 3040, 2960, 2230, 1590, 910, 750; δ_H ($CDCl_3$) 1.69 (3 H, d, *J* = 0.4 Hz), 2.23-2.32 (2 H, m), 3.82 (1 H, t, *J* = 7.5 Hz), 4.83 (1 H, s), 5.09 (1 H, s), 5.10 (1 H, t, *J* = 4 Hz), 6.89 (1 H, d, *J* = 8 Hz), 6.98 (1 H, dd, *J* = 8, 8 Hz), 7.12 (1 H, dd, *J* = 8, 8 Hz), 7.17 (1 H, dd, *J* = 8, 1 Hz); δ_C ($CDCl_3$) 19.1 (q), 29.8 (t), 40.5 (d), 62.0 (d), 116.4 (t), 117.1 (t), 117.5 (s), 122.1 (d), 128.3 (d), 129.5 (d), 145.1 (2 x s), 151.9 (s); *m/z* 199 (100), 184 (53), 173 (32), 157 (48), 131 (57), 103 (27), 77 (29) (Found: M, 199.0992. $C_{13}H_{13}NO$ requires *M*, 199.0997).

4-[(*E*)-1-Phenylmethylidene]-3,4-dihydro-2*H*-benzo[*b*]oxine-2-carbonitrile 29d

Solid, mp 82-83 °C; TLC [EtOAc-hexane (1:99)] R_f 0.09; ν_{max} (KBr)/cm^{-1} 3040, 2920, 2230, 1590, 1450, 750, 695; δ_H ($CDCl_3$) 3.15-3.231 (2 H, m), 5.05 (1 H, dd, *J* = 5.6, 4.6 Hz), 6.94 (1 H, dd, *J* = 8, 1 Hz), 7.05 (1 H, ddd, *J* = 8, 8, 1 Hz), 7.21-7.41 (7 H, m), 7.69 (1 H, dd, *J* = 8, 1 Hz); δ_C ($CDCl_3$) 29.7 (t), 63.8 (d), 116.8 (s), 117.8 (d), 121.7 (s), 122.7 (d), 124.4 (d), 125.5 (d), 125.8 (s), 127.5 (d), 128.5 (2 x d), 129.3 (2 x d), 129.7 (d), 136.0 (s), 151.5 (s); *m/z* 247 (31), 155 (100), 154 (73), 140 (29), 128 (29), 115 (48), 91 (22), 77 (25) (Found: M, 247.0995. $C_{17}H_{13}NO$ requires *M*, 247.0997).

2-Allyl-4-methylene-3,4-dihydro-2*H*-benzo[*b*]oxine-2-carbonitrile 30a

Oil; TLC [EtOAc-hexane (0.5:99.5)] R_f 0.05; ν_{max} (neat)/cm^{-1} 3040, 2960, 2230, 1640, 990, 900, 750; δ_H ($CDCl_3$) 2.73-2.89 (4 H, m), 5.09 (1 H, bt, *J* = 1.6 Hz), 5.33 (1 H, brd, *J* = 16 Hz), 5.34 (1 H, brd, *J* = 10 Hz), 5.72 (1 H, br s), 5.85-6.10 (1 H, m), 6.91 (1 H, dd, *J* = 8, 1 Hz), 7.00 (1 H, ddd, *J* = 8, 8, 1 Hz), 7.23 (1 H, ddd, *J* = 8, 8, 1 Hz), 7.59 (1 H, dd, *J* = 8, 1 Hz); δ_C ($CDCl_3$) 39.2 (t), 43.2 (t), 74.7 (s), 111.2 (t), 117.7 (d), 118.3 (s), 120.6 (s), 121.5 (t), 122.4 (d), 124.4 (d), 129.5 (d), 130.1 (d), 132.7 (s), 151.3 (s); *m/z* 211 (46), 170 (100), 115 (36), 89 (12), 63 (12) (Found: C, 82.49; H, 5.33; N, 5.64 %; M, 211.1001. $C_{14}H_{13}NO$ requires C, 82.57; H, 5.30; N, 5.67 %. *M*, 211.0997).

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