Silylcupration and Copper-Catalyzed Carbomagnesiation of Ynamides: Application to Aza-Claisen Rearrangement

Hiroto Yasui, Hideki Yorimitsu,* and Koichiro Oshima*

Department of Material Chemistry, Graduate School of Engineering, Kyoto University,
Kyoto-daigaku Katsura, Nishikyo-ku, Kyoto 615-8510

Received October 29, 2007; E-mail: yori@orgrxn.mbox.media.kyoto-u.ac.jp

Treatment of ynamides with silylcopper reagents resulted in silylcupration to afford (*E*)-β-silylenamides, after protonolysis, in good yields with high regio- and stereoselectivity. Reaction of ynamides having an allyl group on the nitrogen with Grignard reagents in the presence of a copper catalyst resulted in carbomagnesiation across the alkynyl unit and subsequent heating provided 4-pentenenitriles via aza-Claisen rearrangement.

Ynamides are ynamines having sufficient stability to prepare and handle due to the electron-withdrawing group on the nitrogen. Since direct and convenient synthesis of ynamides was accomplished, organic reactions of ynamides have been studied actively.[1] Among them, addition reactions of organometallic reagents to ynamides have been well investigated.[2] We report here highly regio- and stereoselective silylcupration of ynamides. We also describe copper-catalyzed carbomagnesiation reactions of ynamides having an allyl group followed by aza-Claisen rearrangement.[3]

Silylcupration of Ynamides

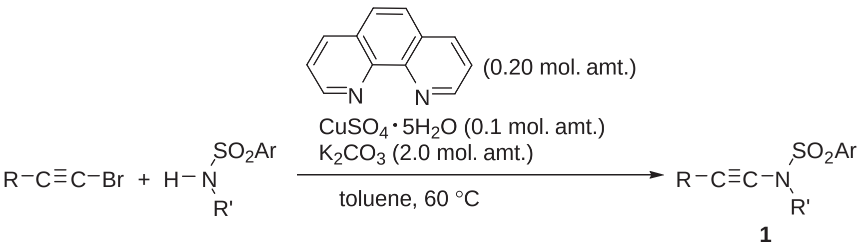
Vinylsilanes play an important role as synthetic building blocks because they react with various electrophiles in the presence or absence of Lewis acid and they are used widely for palladium-catalyzed cross-coupling reactions.[4] Silylmetalation of alkynes is one of the most general methods for synthesis of multi-substituted vinylsilanes.[5] We report herein silylcupration of ynamides with high regio- and stereoselectivity.[6]

Preparation of internal ynamides **1** was performed according to Hsung's method.[7] Treatment of *N*-monosubstituted arenesulfonamides and 1-bromo-1-alkyne in the presence of potassium carbonate and catalytic amounts of $CuSO_4 \cdot 5H_2O$ and 1,10-phenanthroline at 60 °C in toluene provided the corresponding ynamides **1** in good yields (Scheme 1).

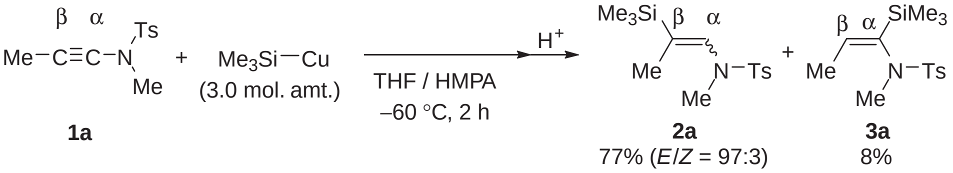
Reaction of *N*-1-propynylamide **1a** with Me_3SiCu, prepared by Me_3SiLi and $CuBr \cdot SMe_2$, furnished the corresponding products **2a** and **3a** in 77% and 8% yields, respectively (Scheme 2). It was revealed that the silyl group was mainly attached to the β carbon of the ynamide. The directing effect of the sulfonyl group of ynamides would play an important role in determining the regiochemistry of the silylcupration.[8]

Reaction of *N*-phenylethynylamides **1b** with Me_3SiCu provided the desired product **2b** with high regio- and stereoselectivity (Scheme 3). Ynamide having an allyl group **1c** underwent reaction to furnish the silylated product **2c** without difficulty. Silylcupration of **1b** with dimethylphenylsilylcopper ($PhMe_2SiCu$) also proceeded smoothly to afford **2d**.

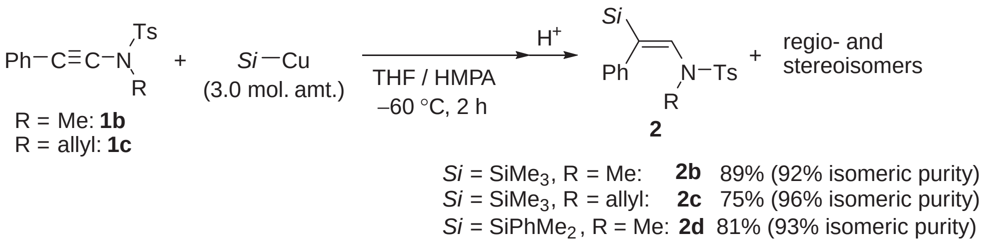
The vinylcopper generated by the silylcupration reacted with allyl bromide to provide the corresponding product **4** in high yield (Scheme 4).



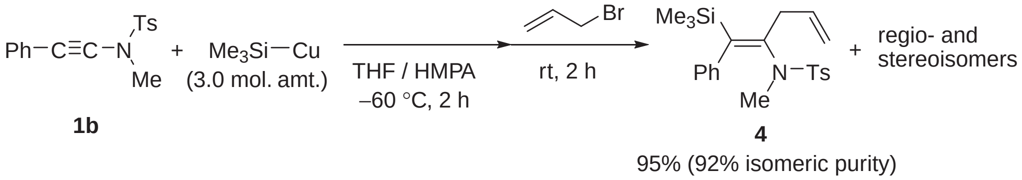
Scheme 1.



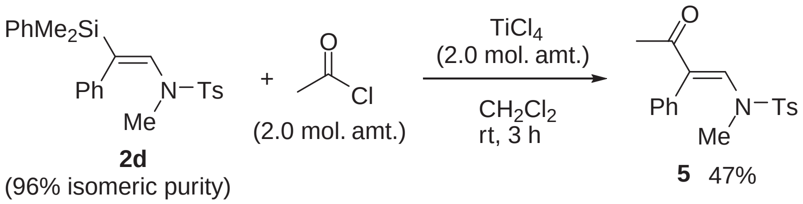
Scheme 2.



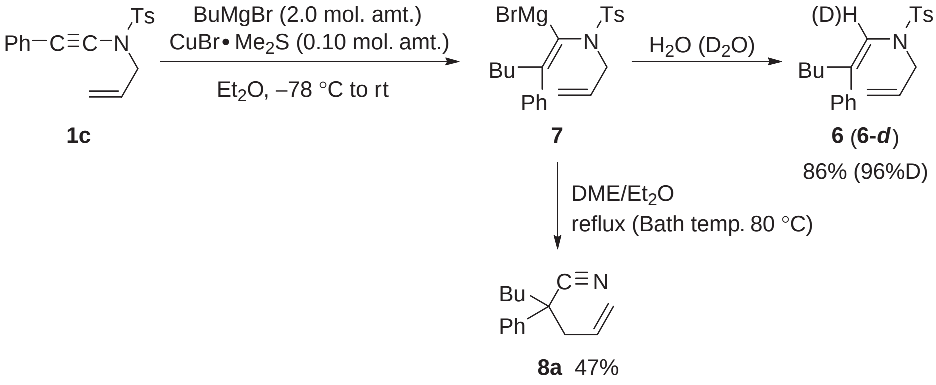
Scheme 3.



Scheme 4.



Scheme 5.



Scheme 6.

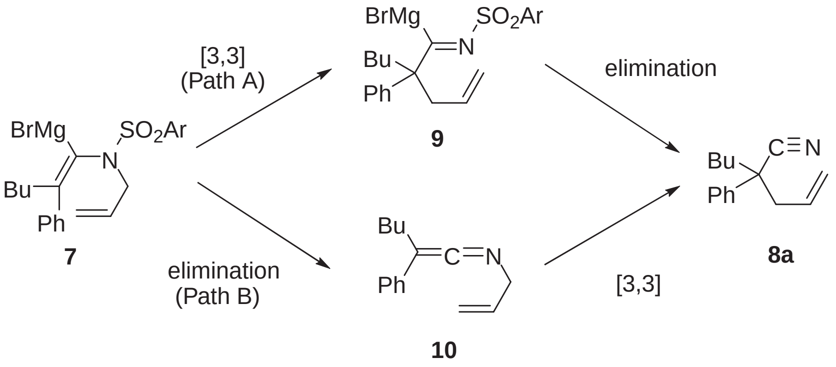
Then, Lewis acid-catalyzed reaction of (*E*)-β-silylenamide with an electrophile was examined. Treatment of (*E*)-β-silylenamide **2d** with acetyl chloride in the presence of titanium tetrachloride ($TiCl_4$) in CH_2Cl_2 at room temperature afforded the corresponding product **5** in 47% NMR yield with regio- and stereoselectivity (Scheme 5).

Carbomagnesiation Reactions of Ynamides Followed by Aza-Claisen Rearrangement

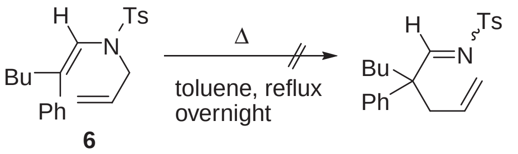
The [3,3] sigmatropic rearrangement of 3-aza-1,5-hexadienes is called an aza-Claisen rearrangement and plays an important role in organic synthesis.[9] We describe herein carbomagnesiation reactions of *N*-allyl-*N*-(phenylethynyl)arenesulfonamides and the subsequent aza-Claisen rearrangement. The transformation offers a new protocol to the repertoire of chemistry towards the synthesis of 4-pentenenitriles.

The initial carbomagnesiation proceeded smoothly by using Grignard reagents and a copper catalyst.[10] Treatment of *N*-allyl-*N*-phenylethynyl-*p*-toluenesulfonamide (**1c**) with 2.0 molar amounts of butylmagnesium bromide in the presence of $CuBr{\cdot}Me_2S$ (0.1 mol. amt.) in diethyl ether at ambient temperature afforded **6** in 86% yield after hydrolysis.[11] Quenching the reaction with deuterium oxide provided the corresponding deuterium-labeled product **6-*d*** (96%D). Hence, it is suggested that intermediate **7** was formed in the reaction flask. When organomagnesium **7** was heated in a mixed solvent of 1,2-dimethoxyethane (DME) and diethyl ether, pentenenitrile **8a** was obtained in 47% yield, along with 34% of **6** (Scheme 6).

There are two possible mechanisms of the formation of nitrile **8a** (Scheme 7). The [3,3] sigmatropic rearrangement of the organomagnesium **7** and subsequent elimination of magnesium sulfinate from **9** would afford **8a** (Path A). The other



Scheme 7.



Scheme 8.

mechanism (Path B) is as follows. First, elimination of magnesium sulfinate from organomagnesium **7** could take place to give ketene imine intermediate **10**. Then, [3,3] sigmatropic rearrangement of **10** could proceed to furnish nitrile **8a**. The [3,3] sigmatropic rearrangement of 3-aza-1,2,5-hexatrienes has been known to proceed smoothly.[12] It is worth noting that heating **6** in boiling toluene resulted in complete recovery of **6** (Scheme 8).

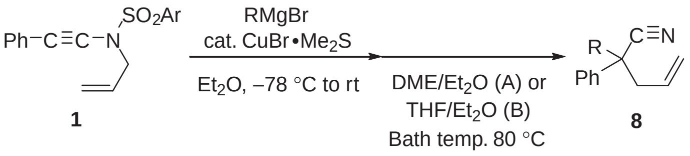
Table 1 summarizes the results of the synthesis of 4-pentenenitriles starting from Grignard reagents and ynamides having an allyl group on the nitrogen. Primary alkyl Grignard reagents including a bulky neopentylmagnesium reagent participated in the reaction. When phenyl and secondary alkyl Grignard reagents were used, the yields of desired products were much lower (Entries 4 and 7). Ynamides **1d**, having a *p*-fluorophenylsulfonyl group on the nitrogen, improved the yields (Entries 5 and 6).

The scope of substrates was investigated (Table 2). *N*-(2-Methyl-2-propenyl)amides **1e** and **1f** and *N*-(2-phenyl-2-propenyl)amide **1g** participated in the reaction (Entries 1–3). Due to the inherent regiospecificity of the aza-Claisen rearrangement, 2,2,3,3-tetrasubstituted 4-pentenenitrile **8h** was obtained in the reaction of *N*-(3-methyl-2-butenyl)amide **1h** (Entry 4). It is difficult to synthesize such a sterically congested nitrile by conventional nitrile synthesis. The reactions of *N*-2-butenyl- and *N*-cinnamylamides **1i** and **1j** afforded mixtures of diastereomers (Entries 5 and 6). The reactions of **1k** and **1l** with butylmagnesium bromide gave the corresponding nitriles **8k** and **8l** in lower yields of 33% and 34%, respectively (Entries 7 and 8). The phenyl group at the acetylenic terminus proved to be indispensable for the success of the reaction. A similar reaction of *N*-allyl-*N*-1-octynyl-*p*-toluenesulfonamide resulted in formation of a complex mixture containing 6% of the anticipated nitrile and 31% of *N*-allyl-*p*-toluenesulfonamide. Unfortunately, silylcupration of ynamide **1c** followed by heating gave no desired aza-Claisen rearrangement product.

Experimental

General. ^{1}H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra were taken on a Varian UNITY INOVA 500 spectrometer unless otherwise noted. ^{1}H NMR and ^{13}C NMR spectra were obtained in $CDCl_3$ with tetramethylsilane as an internal standard. Chemical shifts (δ) are in parts per million relative to tetramethylsilane at 0.00 ppm for ^{1}H and relative to $CDCl_3$ at 77.20 ppm for ^{13}C unless otherwise noted. IR spectra were determined on a SHIMADZU FTIR-8200PC spectrometer. Mass spectra were determined on a JEOL Mstation 700 spectrometer. TLC analyses were performed on commercial glass plates bearing 0.25-mm layer of Merck Silica gel $60F_{254}$. Silica gel (Wakogel 200 mesh)

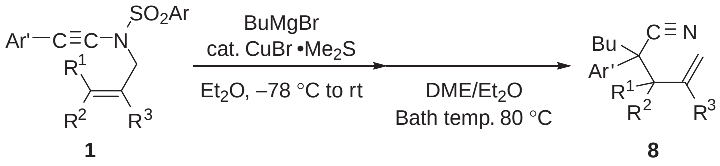
Table 1. Carbomagnesiation of Ynamides Followed by Aza-Claisen Rearrangement

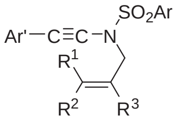
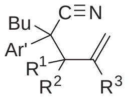
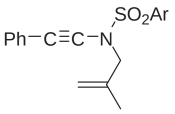
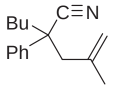
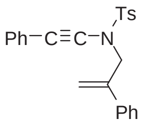
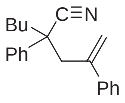
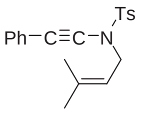
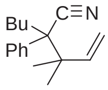
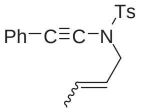
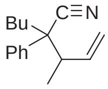
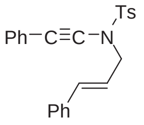
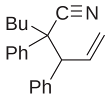
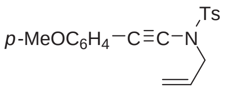
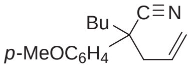
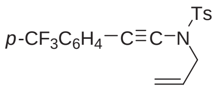
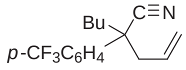


Entry	1	Ar	RMgBr	Solvent	Time[a)]/h	8	Yield[b)]/%
1	**1c**	*p*-Tolyl	BuMgBr	A	5	**8a**	47
2	**1c**	*p*-Tolyl	EtMgBr	B	4	**8b**	47
3	**1c**	*p*-Tolyl	^{t}BuCH$_2$MgBr	B	18	**8c**	46
4	**1c**	*p*-Tolyl	PhMgBr	B	4	**8d**	27
5	**1d**	*p*-FC$_6$H$_4$	BuMgBr	A	4	**8a**	61
6	**1d**	*p*-FC$_6$H$_4$	EtMgBr	B	4	**8b**	50
7	**1d**	*p*-FC$_6$H$_4$	^{i}PrMgBr	B	19	**8e**	23

a) Time for the rearrangement. b) Isolated yield.

Table 2. Scope and Limitation of Carbomagnesiation Followed by Aza-Claisen Rearrangement



Entry	1		8		Yield[a)]/%
1	**1e** (Ar = *p*-tolyl)		**8f**		48 (from **1e**)
2	**1f** (Ar = *p*-FC$_6$H$_4$)				58 (from **1f**)
3	**1g**		**8g**		37
4	**1h**		**8h**		61
5	**1i**[b)]		**8i**[c)]		57
6	**1j**		**8j**[d)]		49
7	**1k**		**8k**		33
8	**1l**		**8l**		34

a) Isolated yield. b) E/Z = 4:1. c) Diastereomer ratio = 1.4:1. d) Diastereomer ratio = 1.6:1.

was used for column chromatography. The analyses were carried out at the Elemental Analysis Center of Kyoto University.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. THF and ether were purchased from Kanto Chemical Co., stored under nitrogen, and used as provided. Ynamides **1** were prepared by copper-catalyzed alkynylation of amides.[7] Trimethylsilyllithium and dimethylphenylsilyllithium were prepared by conventional methods.[13]

Typical Procedure for Silylcupration of Ynamides. A solution of methyllithium (1.1 mL, 1.1 mol L^{-1} diethyl ether solution, 1.2 mmol) was added to hexamethyldisilane (0.37 mL, 1.8 mmol) in freshly distilled hexamethylphosphoric triamide (1.2 mL) at 0 °C under argon. The mixture was stirred at 0 °C for 15 min. After THF (3 mL) was added, the reaction mixture was cooled to −60 °C. CuBr•SMe$_2$ (247 mg, 1.8 mmol) was added and the resulting mixture was stirred at −60 °C for 15 min. A solution of ynamide **1b** (114 mg, 0.40 mmol) in THF (3 mL) was added. After stirring at −60 °C for 2 h, allyl bromide (0.17 mL, 2.0 mmol) was added and the reaction mixture was stirred at room temperature for 2 h. A saturated aqueous solution of ammonium chloride (2 mL) was added. The organic compounds were extracted with a mixture of ethyl acetate and hexane twice. The combined organic portion was dried over anhydrous sodium sulfate and concentrated in vacuo. Chromatographic purification on silica gel afforded **2b** (151 mg, 0.38 mmol, 92% isomeric purity) in 95% yield.

Typical Procedure for Carbomagnesiation Reaction of Ynamides Followed by Aza-Claisen Rearrangement. CuBr•SMe$_2$ (6 mg, 0.03 mmol) and *N*-allyl-*N*-phenylethynyl-*p*-fluorobenzenesulfonamide (**1d**, 95 mg, 0.30 mmol) were placed in a 20-mL reaction flask under argon. Diethyl ether (3 mL) was added. A solution of butylmagnesium bromide (0.53 mL, 1.13 mol L^{-1} diethyl ether solution, 0.60 mmol) was added at −78 °C. The mixture was stirred at room temperature for 1 h. DME (5 mL) was added, and the reaction mixture was refluxed for 4 h (bath temp, 80 °C). A saturated aqueous solution of ammonium chloride (2 mL) was added. The organic compounds were extracted with a mixture of ethyl acetate and hexane twice. The combined organic portion was dried over anhydrous sodium sulfate and concentrated in vacuo. Chromatographic purification on silica gel afforded **8a** (39 mg, 0.18 mmol) in 61% yield.

Characterization Data. The ^{1}H and ^{13}C NMR spectral data of compounds **1c**,[7] **8a**,[3] and **8d**[14] can be found in the literature.

***N*-Methyl-*N*-1-propynyl-*p*-toluenesulfonamide (1a):** IR (nujol) 2924, 2855, 2265, 1456, 1355, 1168, 1158, 1042, 816, 677, 566, 545 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.88 (s, 3H), 2.46 (s, 3H), 3.01 (s, 3H), 7.34–7.39 (m, 2H), 7.76–7.81 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 3.39, 21.83, 39.43, 64.26, 73.90, 127.97, 129.87, 133.49, 144.64; Found: C, 59.16; H, 5.82%. Calcd for $C_{11}H_{13}NO_2S$: C, 59.17; H, 5.87%; Mp 99–100 °C.

***N*-Methyl-*N*-phenylethynyl-*p*-toluenesulfonamide (1b):** IR (nujol) 2924, 2233, 1595, 1365, 1164, 764, 676, 546 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.46 (s, 3H), 3.15 (s, 3H), 7.27–7.31 (m, 3H), 7.34–7.38 (m, 4H), 7.83–7.85 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 21.85, 39.49, 69.19, 84.11, 122.87, 128.02, 128.04, 128.44, 129.98, 131.57, 133.40, 144.97; Found: C, 67.07; H, 5.25%. Calcd for $C_{16}H_{15}NO_2S$: C, 67.34; H, 5.30%; Mp 85–86 °C.

***N*-Phenylethynyl-*N*-2-propenyl-*p*-fluorobenzenesulfonamide (1d):** IR (nujol) 2925, 2855, 2235, 1492, 1367, 1181, 545 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.08 (dt, $J = 6.5$, 1.0 Hz, 2H), 5.24–5.33 (m, 2H), 5.79 (ddt, $J = 16.5$, 10.0, 6.5 Hz, 1H), 7.23–7.30 (m, 5H), 7.34–7.36 (m, 2H), 7.97–8.00 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 54.67, 71.30, 81.99, 116.66 (d, $J = 22.4$ Hz), 120.51, 122.68, 128.19, 128.48, 130.74, 130.82, 131.61, 133.85, 165.93 (d, $J = 254.8$ Hz). Found: C, 64.97; H, 4.70%. Calcd for $C_{17}H_{14}NO_2FS$: C, 64.75; H, 4.47%; Mp 77.7–79.6 °C.

***N*-(2-Methyl-2-propenyl)-*N*-phenylethynyl-*p*-toluenesulfonamide (1e):** IR (neat) 2976, 2920, 2235, 1597, 1366, 1169, 756, 691, 589 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.75 (s, 3H), 2.43 (s, 3H), 3.94 (s, 2H), 4.97 (s, 2H), 7.25–7.27 (m, 3H), 7.32–7.35 (m, 4H), 7.84 (d, $J = 8.5$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 19.82, 21.74, 58.05, 70.85, 82.43, 115.98, 122.95, 127.79, 127.81, 128.32, 129.86, 131.32, 134.60, 138.80, 144.81. Found: C, 69.96; H, 6.07%. Calcd for $C_{19}H_{19}NO_2S$: C, 70.13; H, 5.88%.

***N*-(2-Methyl-2-propenyl)-*N*-phenylethynyl-*p*-fluorobenzenesulfonamide (1f):** IR (neat) 3081, 2237, 1592, 1495, 1368, 1175, 1156, 837, 756, 589 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.76 (s, 3H), 3.98 (s, 2H), 4.98 (s, 1H), 4.99 (s, 1H), 7.23–7.34 (m, 7H), 7.97–8.00 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 19.91, 58.26, 71.13, 82.05, 116.28, 116.63 (d, $J = 22.5$ Hz), 122.76, 128.10, 128.46, 128.60, 130.71 (d, $J = 9.6$ Hz), 131.53, 138.68, 165.89 (d, $J = 255.3$ Hz); HRMS (FAB) Found: 330.0958. Calcd for $C_{18}H_{17}NO_2FS$: 330.0964 [MH$^+$].

***N*-Phenylethynyl-*N*-(2-phenyl-2-propenyl)-*p*-toluenesulfonamide (1g):** IR (nujol) 2924, 2854, 2248, 1362, 1174, 915, 758, 608, 550 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.43 (s, 3H), 4.43 (s, 2H), 5.33 (s, 1H), 5.53 (s, 1H), 7.24–7.33 (m, 10H), 7.40–7.41 (m, 2H), 7.78 (d, $J = 8.5$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.81, 55.50, 71.43, 82.29, 117.94, 122.95, 126.52, 127.84, 127.93, 128.23, 128.33, 128.56, 129.87, 131.40, 134.40, 138.16, 141.44, 144.83. Found: C, 74.33; H, 5.43%. Calcd for $C_{24}H_{21}NO_2S$: C, 74.39%; H, 5.46%. Mp 100.7–101.0 °C.

***N*-(3-Methyl-2-butenyl)-*N*-phenylethynyl-*p*-toluenesulfonamide (1h):** IR (neat) 2360, 2235, 1363, 1169, 1091, 754, 691, 584 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.68 (d, $J = 1.0$ Hz, 3H), 1.70 (d, $J = 1.0$ Hz, 3H), 2.44 (s, 3H), 4.05 (d, $J = 8.0$ Hz, 2H), 5.20 (tsept, $J = 8.0$, 1.0 Hz, 1H), 7.24–7.35 (m, 7H), 7.81–7.84 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 18.20, 21.81, 25.91, 49.80, 70.68, 83.05, 117.21, 123.26, 127.72, 127.92, 128.39, 129.80, 131.28, 135.07, 139.45, 144.65; HRMS (EI) Found: 339.1293. Calcd for $C_{20}H_{21}NO_2S$: 339.1293 [M$^+$].

***N*-2-Butenyl-*N*-phenylethynyl-*p*-toluenesulfonamide (1i, a 8:2 Mixture of Stereoisomers):** IR (neat) 2919, 2234, 1366, 1171, 1091, 937, 756, 582, 546 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.65–1.68 (m, 3H), 2.43 (s, 3H), 3.96–3.98 (m, 2 × 0.8H), 4.11 (d, $J = 6.5$ Hz, 2 × 0.2H), 5.40–5.46 (m, 1H), 5.68–5.75 (m, 1H), 7.23–7.35 (m, 7H), 7.81–7.85 (m, 2H); ^{13}C NMR ($CDCl_3$) (*E*-isomer) δ 17.80, 21.71, 54.10, 71.04, 82.73, 123.10, 123.74, 127.78, 127.89, 128.34, 129.79, 131.31, 132.28, 134.96, 144.70; HRMS (FAB) Found: 325.1138. Calcd for $C_{19}H_{19}NO_2S$: 325.1136 [M$^+$].

***N*-Phenylethynyl-*N*-[(*E*)-3-phenyl-2-propenyl]-*p*-toluenesulfonamide (1j):** IR (neat) 3029, 2235, 1597, 1495, 1363, 1169, 1090, 753, 692, 586 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.38 (s, 3H), 4.21 (dd, $J = 7.0$, 1.5 Hz, 2H), 6.07 (dt, $J = 16.0$, 7.0 Hz, 1H), 6.55 (d, $J = 16.0$ Hz, 1H), 7.20–7.33 (m, 12H), 7.84–7.86 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 21.68, 54.34, 71.16, 82.66, 121.84, 122.86, 126.69, 127.84, 127.92, 128.20, 128.33, 128.65, 129.86, 131.37, 134.83, 135.34, 136.09, 144.85; HRMS (EI) Found: 387.1291. Calcd for $C_{24}H_{21}NO_2S$: 387.1293 [M$^+$].

***N*-*p*-Methoxyphenylethynyl-*N*-2-propenyl-*p*-toluenesulfonamide (1k):** IR (neat) 2935, 2839, 2237, 1606, 1512, 1363, 1250, 1171, 664 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.46 (s, 3H), 3.81 (s, 3H), 4.04 (dt, $J = 6.5$, 1.5 Hz, 2H), 5.20–5.24 (m, 1H), 5.24–5.32 (m, 1H), 5.79 (ddt, $J = 17.0$, 10.0, 6.5 Hz, 1H), 6.80–6.85 (m, 2H), 7.28–7.34 (m, 2H), 7.34–7.39 (m, 2H), 7.82–7.87 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 21.76, 54.56, 55.40, 70.61, 80.94, 114.00, 114.80, 120.05, 127.90, 129.84, 131.11, 133.47, 134.80, 144.85, 159.61; HRMS (FAB) Found: 341.1082. Calcd for $C_{19}H_{19}NO_3S$: 341.1086 [M$^+$].

***N*-2-Propenyl-*N*-[*p*-(trifluoromethyl)phenylethynyl]-*p*-toluenesulfonamide (1l):** IR (neat) 2929, 2235, 1615, 1370, 1323, 1171, 1126, 1105, 1066, 842, 664 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.47 (s, 3H), 4.08 (dt, $J = 6.5$, 1.5 Hz, 2H), 5.26–5.34 (m, 2H), 5.80 (ddt, $J = 17.0$, 10.0, 6.5 Hz, 1H), 7.38 (d, $J = 8.5$ Hz, 2H), 7.43 (d, $J = 8.5$ Hz, 2H), 7.54 (d, $J = 8.0$ Hz, 2H), 7.84–7.86 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 21.89, 54.53, 70.61, 85.19, 120.55, 124.21 (q, $J = 270.7$ Hz), 125.41 (q, $J = 3.9$ Hz), 127.13, 128.01, 129.47 (q, $J = 32.5$ Hz), 130.11, 130.97, 131.21, 134.91, 145.22; HRMS (FAB) Found: 380.0936. Calcd for $C_{19}H_{17}NO_2F_3S$: 380.0932 [MH$^+$].

***N*-Methyl-*N*-[(*E*)-2-(trimethylsilyl)propenyl]-*p*-toluenesulfonamide (2a):** IR (neat) 2955, 1614, 1349, 1250, 1166, 839, 713 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.07 (s, 9H), 1.77 (s, 3H), 2.43 (s, 3H), 2.80 (s, 3H), 5.88 (s, 1H), 7.31 (d, $J = 8.0$ Hz, 2H), 7.64 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ −2.04, 14.86, 21.69, 37.57, 127.31, 127.77, 129.56, 129.66, 132.41, 143.64; Found: C, 56.69, 7.80%. Calcd for $C_{14}H_{23}NO_2SiS$: C, 56.52; H, 7.79%.

***N*-Methyl-*N*-[(*E*)-2-phenyl-2-(trimethylsilyl)ethenyl]-*p*-toluenesulfonamide (2b):** IR (neat) 2955, 1607, 1353, 1248, 1169, 838, 758, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.06 (s, 9H), 2.42 (s, 3H), 2.47 (s, 3H), 6.69–6.71 (m, 2H), 6.73 (s, 1H), 7.09–7.16 (m, 3H), 7.35 (d, $J = 8.0$ Hz, 2H), 7.66 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ −1.20, 21.77, 35.76, 125.96, 126.67, 127.23, 127.97, 128.52, 129.90, 131.48, 135.24, 140.00, 143.87; Found: C, 63.37; H, 6.93%. Calcd for $C_{19}H_{25}NO_2SiS$: C, 63.47; H, 7.01%.

***N*-[(*E*)-2-Phenyl-2-(trimethylsilyl)ethenyl]-*N*-2-propenyl-*p*-toluenesulfonamide (2c):** IR (neat) 2956, 1605, 1353, 1249, 1167, 1092, 837, 770 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.06 (s, 9H), 2.46 (s, 3H), 3.53–3.55 (m, 2H), 4.77–4.81 (m, 1H), 4.91–4.93 (m, 1H), 5.29 (ddt, $J = 17.0$, 10.5, 6.0 Hz, 1H), 6.54 (s, 1H), 6.71–6.73 (m, 2H), 7.12–7.18 (m, 3H), 7.33 (d, $J = 8.5$ Hz, 2H), 7.68 (d, $J = 8.5$ Hz, 2H); ^{13}C NMR (CDCl$_3$) δ −1.20, 21.73, 49.58, 117.29, 126.21, 127.32, 127.93, 128.23, 129.54, 129.80, 131.30, 132.80, 136.71, 139.73, 143.76; Found: C, 65.50; H, 7.00%. Calcd for $C_{21}H_{27}NO_2SiS$: C, 65.41; H, 7.06%.

_N_-[(_E_)-2-Dimethylphenylsilyl-2-phenylethenyl]-_N_-methyl-_p_-toluenesulfonamide (2d): IR (neat) 2957, 1594, 1354, 1248, 1168, 936, 810, 754, 702 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.32 (s, 6H), 2.43 (s, 3H), 2.47 (s, 3H), 6.67–6.69 (m, 2H), 6.75 (s, 1H), 7.10–7.12 (m, 3H), 7.34 (d, $J = 8.0$ Hz, 2H), 7.38–7.44 (m, 3H), 7.51–7.52 (m, 2H), 7.59 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (CDCl$_3$) δ −2.82, 21.69, 35.67, 124.36, 126.01, 127.14, 127.86, 127.89, 128.65, 129.32, 129.83, 133.34, 134.22, 134.99, 137.59, 139.49, 143.84; Found: C, 67.97; H, 6.49%. Calcd for $C_{24}H_{27}NO_2SiS$: C, 68.37; H, 6.45%.

_N_-Methyl-_N_-{(_E_)-1-[α-(trimethylsilyl)benzylidene]-3-butenyl}-_p_-toluenesulfonamide (4): IR (neat) 2954, 1600, 1344, 1251, 1151, 840, 718, 701 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.13 (s, 9H), 2.39 (s, 3H), 2.57 (s, 3H), 3.38 (d, $J = 6.5$ Hz, 2H), 4.93–4.96 (m, 1H), 4.99–5.02 (m, 1H), 5.76 (ddt, $J = 17.0$, 10.5, 6.5 Hz, 1H), 7.01 (br, 2H), 7.18–7.19 (m, 3H), 7.24–7.28 (m, 2H), 7.47 (d, $J = 8.5$ Hz, 2H); ^{13}C NMR (CDCl$_3$) δ 0.43, 21.51, 38.77, 40.35, 117.60, 125.68, 127.51, 127.90 (br, 2C), 129.36, 135.09, 137.45, 141.90, 142.92, 143.98, 146.09; Found: C, 65.85; H, 7.37%. Calcd for $C_{22}H_{29}NO_2SiS$: C, 66.12; H, 7.31%.

_N_-Methyl-_N_-[(_E_)-3-oxo-2-phenyl-1-butenyl]-_p_-toluenesulfonamide (5): IR (nujol) 2924, 2854, 1657, 1613, 1357, 1347, 1292, 1169, 1155, 971, 754, 724, 702, 664 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.16 (s, 3H), 2.46 (s, 6H), 7.00–7.02 (m, 2H), 7.27–7.29 (m, 3H), 7.37 (d, $J = 8.0$ Hz, 2H), 7.71–7.73 (m, 2H), 8.10 (s, 1H); ^{13}C NMR (CDCl$_3$) δ 21.83, 28.00, 35.14, 123.49, 127.43, 128.12, 128.34, 130.34, 131.01, 134.55, 135.29, 138.07, 144.99, 197.89; HRMS (EI) Found: 329.1085. Calcd for $C_{18}H_{19}NO_3S$: 329.1086 [M^{+}].

_N_-[(_Z_)-2-Phenyl-1-hexenyl]-_N_-2-propenyl-_p_-toluenesulfonamide (6): IR (nujol) 2924, 2855, 1347, 1159, 934, 770, 664 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.84 (t, $J = 7.5$ Hz, 3H), 1.21–1.30 (m, 4H), 2.33 (m, 2H), 2.45 (s, 3H), 3.51 (dt, $J = 6.5$, 1.5 Hz, 2H), 4.84–4.88 (m, 1H), 4.95–4.98 (m, 1H), 5.41 (ddt, $J = 17.0$, 10.5, 6.5 Hz, 1H), 5.88 (s, 1H), 6.97–6.98 (m, 2H), 7.21–7.24 (m, 3H), 7.32 (d, $J = 8.0$ Hz, 2H), 7.67 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (CDCl$_3$) δ 13.93, 21.72, 22.09, 30.18, 36.25, 52.08, 118.22, 121.06, 127.46, 127.64, 128.13, 128.22, 129.72, 133.13, 136.09, 138.45, 140.79, 143.58. Found: C, 71.57; H, 7.36%. Calcd for $C_{22}H_{27}NO_2S$: C, 71.51; H, 7.36%. Mp 81.2–81.7 °C.

_N_-[(_Z_)-1-Deuterio-2-phenyl-1-hexenyl]-_N_-2-propenyl-_p_-toluenesulfonamide (6-_d_): IR (nujol) 2925, 2855, 1340, 1158, 935, 822, 771, 703 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.84 (t, $J = 7.5$ Hz, 3H), 1.21–1.30 (m, 4H), 2.33 (t, $J = 7.5$ Hz, 2H), 2.45 (s, 3H), 3.51 (dt, $J = 6.5$, 1.0 Hz, 2H), 4.84–4.88 (m, 1H), 4.95–4.98 (m, 1H), 5.41 (ddt, $J = 17.0$, 10.0, 6.5 Hz, 1H), 6.95–6.97 (m, 2H), 7.21–7.23 (m, 3H), 7.32 (d, $J = 8.0$ Hz, 2H), 7.67 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (CDCl$_3$) δ 13.94, 21.73, 22.09, 30.19, 36.22, 52.01, 118.20, 120.75 (t, $J = 26.3$ Hz), 127.46, 127.63, 128.13, 128.23, 129.73, 133.16, 136.16, 138.46, 140.46, 143.58. Found: C, 71.58; H + D, 7.58%. Calcd for $C_{22}H_{26}DNO_2S$: C, 71.31; H + D, 7.61%. Mp 81.1–82.3 °C.

2-Ethyl-2-phenyl-4-pentenenitrile (8b): IR (neat) 2973, 2938, 2236, 1495, 1449, 925, 762, 699 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.92 (t, $J = 7.5$ Hz, 3H), 1.94 (dq, $J = 14.5$, 7.5 Hz, 1H), 2.08 (dq, $J = 14.5$, 7.5 Hz, 1H), 2.67–2.69 (m, 2H), 5.10–5.15 (m, 2H), 5.65 (ddt, $J = 17.5$, 10.5, 7.0 Hz, 1H), 7.29–7.33 (m, 1H), 7.37–7.41 (m, 4H); ^{13}C NMR (CDCl$_3$) δ 9.75, 33.26, 45.17, 48.97, 120.04, 122.15, 126.35, 127.90, 128.99, 132.08, 137.96. Found: C, 84.17; H, 8.37%. Calcd for $C_{13}H_{15}N$: C, 84.28; H, 8.16%.

2-Neopentyl-2-phenyl-4-pentenenitrile (8c): IR (neat) 2956, 2909, 2236, 1642, 1601, 1449, 924, 702 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.82 (s, 9H), 1.98 (d, $J = 14.5$ Hz, 1H), 2.06 (d, $J = 14.5$ Hz, 1H), 2.67 (d, $J = 7.0$ Hz, 2H), 5.09–5.14 (m, 2H), 5.56–5.64 (m, 1H), 7.29–7.32 (m, 1H), 7.36–7.40 (m, 2H), 7.46–7.48 (m, 2H); ^{13}C NMR (CDCl$_3$) δ 31.03, 32.18, 45.97, 48.95, 52.37, 120.25, 122.78, 126.61, 127.80, 128.82, 131.83, 138.58. Found: C, 84.24; H, 9.26%. Calcd for $C_{16}H_{21}N$: C, 84.53; H, 9.31%.

2-Isopropyl-2-phenyl-4-pentenenitrile (8e): IR (neat) 2967, 2235, 1495, 1449, 923, 761, 699 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.81 (d, $J = 6.5$ Hz, 3H), 1.21 (d, $J = 6.5$ Hz, 3H), 2.18 (sept, $J = 6.5$ Hz, 1H), 2.65 (ddt, $J = 14.0$, 7.0, 1.0 Hz, 1H), 2.86 (ddt, $J = 14.0$, 7.5, 1.0 Hz, 1H), 5.01–5.04 (m, 1H), 5.06–5.10 (m, 1H), 5.43–5.51 (m, 1H), 7.28–7.31 (m, 1H), 7.36–7.38 (m, 4H); ^{13}C NMR (CDCl$_3$) δ 18.70, 18.95, 37.24, 42.26, 53.89, 119.62, 121.07, 126.89, 127.78, 128.80, 132.39, 137.74. Found: C, 84.53; H, 8.67%. Calcd for $C_{14}H_{17}N$: C, 84.37; H, 8.60%.

2-Butyl-4-methyl-2-phenyl-4-pentenenitrile (8f): IR (neat) 3078, 2958, 2864, 2236, 1647, 1495, 1449, 900, 699 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.85 (t, $J = 7.5$ Hz, 3H), 1.05–1.12 (m, 1H), 1.24–1.34 (m, 2H), 1.41–1.49 (m, 1H), 1.53 (s, 3H), 1.92 (dt, $J = 13.5$, 4.5 Hz, 1H), 2.01 (dt, $J = 12.5$, 4.5 Hz, 1H), 2.60 (d, $J = 14.0$ Hz, 1H), 2.70 (d, $J = 14.0$ Hz, 1H), 4.71 (s, 1H), 4.83 (s, 1H), 7.26–7.31 (m, 1H), 7.36–7.42 (m, 4H); ^{13}C NMR (CDCl$_3$) δ 13.98, 22.74, 23.83, 27.42, 41.06, 47.81, 49.17, 116.65, 122.75, 126.31, 127.79, 128.89, 138.51, 140.17. Found: C, 84.76; H, 9.46%. Calcd for $C_{16}H_{21}N$: C, 84.53; H, 9.31%.

2-Butyl-2,4-diphenyl-4-pentenenitrile (8g): IR (neat) 2958, 2933, 2236, 1686, 1627, 1600, 1495, 1448, 907, 778, 698 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.79 (t, $J = 7.5$ Hz, 3H), 1.01–1.42 (m, 4H), 1.87 (dt, $J = 13.5$, 4.5 Hz, 1H), 1.95 (dt, $J = 12.0$, 4.5 Hz, 1H), 3.07 (d, $J = 13.5$ Hz, 1H), 3.16 (d, $J = 13.5$ Hz, 1H), 5.09 (s, 1H), 5.28 (s, 1H), 7.15–7.33 (m, 10H); ^{13}C NMR (CDCl$_3$) δ 13.88, 22.67, 27.42, 40.22, 46.50, 48.64, 118.84, 122.18, 126.38, 126.67, 127.53, 127.66, 128.26, 128.68, 138.12, 141.81, 143.72; HRMS (FAB) Found: 290.1901. Calcd for $C_{21}H_{24}N$: 290.1908 [MH^{+}].

2-Butyl-3,3-dimethyl-2-phenyl-4-pentenenitrile (8h): IR (neat) 2961, 2934, 2874, 2233, 1469, 1448, 922, 750, 703 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.84 (t, $J = 7.5$ Hz, 3H), 1.02 (s, 3H), 1.17 (s, 3H), 1.27–1.39 (m, 4H), 1.94–2.00 (m, 1H), 2.05–2.12 (m, 1H), 5.02 (d, $J = 18.0$ Hz, 1H), 5.15 (d, $J = 10.5$ Hz, 1H), 5.89 (dd, $J = 18.0$, 10.5 Hz, 1H), 7.29–7.39 (m, 5H); ^{13}C NMR (CDCl$_3$) δ 14.03, 23.03, 23.14, 24.48, 28.03, 32.39, 43.23, 56.06, 115.13, 122.71, 127.81, 127.96, 128.77, 134.95, 142.87. Found: C, 84.49; H, 9.76%. Calcd for $C_{17}H_{23}N$: C, 84.59; H, 9.60%.

2-Butyl-3-methyl-2-phenyl-4-pentenenitrile (8i, a 59:41 Mixture of Diastereomers): IR (neat) 2959, 2933, 2865, 2235, 1714, 1601, 1495, 1449, 923, 762, 701 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.78–1.52 (m, 4H), 0.80 (t, $J = 7.5$ Hz, 3×0.59H), 0.84 (t, $J = 7.5$ Hz, 3×0.41H), 0.87 (d, $J = 6.5$ Hz, 3×0.59H), 1.21 (d, $J = 7.0$ Hz, 3×0.41H), 1.71–1.82 (m, 1×0.59H), 1.90–1.99 (m, 1×0.41H), 1.99–2.12 (m, 1H), 2.52–2.60 (m, 1×0.59H), 2.62–2.72 (m, 1×0.41H), 4.88–5.00 (m, 2×0.41H), 5.18–5.26 (m, 2×0.59H), 5.50 (ddd, $J = 17.0$, 10.0, 8.0 Hz, 1×0.41H), 5.88–5.98 (m, 1×0.59H), 7.20–7.39 (m, 5H); ^{13}C NMR (CDCl$_3$) δ 13.93, 13.96, 16.37, 17.23, 22.70, 22.82, 27.59, 27.61, 37.14, 38.87, 47.10, 48.51, 52.51, 52.62, 117.12, 117.61, 121.26, 121.97, 126.52, 127.10, 127.71, 127.74, 128.60, 128.94, 137.03, 137.93, 138.09, 139.18. Found: C, 84.65; H, 9.55%. Calcd for $C_{16}H_{21}N$: C, 84.53; H, 9.31%.

2-Butyl-2,3-diphenyl-4-pentenenitrile (8j, a 60:40 Mixture of Diastereomers): IR ($CDCl_3$) 2958, 2932, 2865, 2234, 1602, 1494, 1449, 925, 724, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.75 (t, $J = 7.0$ Hz, 3×0.60H), 0.84 (t, $J = 7.0$ Hz, 3×0.40H), 0.86–1.06 (m, 1H), 1.09–1.47 (m, 3H), 1.68 (ddd, $J = 13.5$, 12.0, 4.5 Hz, 1×0.60H), 1.89 (ddd, $J = 14.0$, 12.5, 4.5 Hz, 1×0.60H), 1.96 (ddd, $J = 14.0$, 12.5, 4.5 Hz, 1×0.40H), 2.24 (ddd, $J = 12.5$, 12.5, 4.5 Hz, 1×0.40H), 3.54 (d, $J = 9.5$ Hz, 1×0.40H), 3.64 (d, $J = 8.5$ Hz, 1×0.60H), 4.77–4.81 (m, 1×0.60H), 4.98–5.01 (m, 1×0.60H), 5.26–5.32 (m, 2×0.40H), 6.05 (ddd, $J = 17.0$, 10.5, 8.5 Hz, 1×0.60H), 6.41 (ddd, $J = 16.5$, 10.0, 9.5 Hz, 1×0.40H), 6.90–6.95 (m, 2×0.40H), 7.06–7.10 (m, 2×0.60H), 7.12–7.24 (m, 2H), 7.28–7.42 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 14.01, 14.08, 22.77, 22.88, 27.60, 27.68, 37.92, 38.53, 52.99, 53.13, 60.14, 60.84, 118.96, 119.26, 121.85, 121.88, 127.08, 127.21, 127.23, 127.71, 127.89, 127.99, 128.19, 128.59, 128.74, 128.79, 128.83, 129.45, 135.94, 136.71, 136.78, 137.46, 139.06, 139.23. Found: C, 86.95; H, 8.27%. Calcd for $C_{21}H_{23}N$: C, 87.15; H, 8.01%.

2-Butyl-2-*p*-methoxylphenyl-4-pentenenitrile (8k): IR (neat) 2937, 2863, 2235, 1611, 1514, 1253, 1185, 1036, 830 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.85 (t, $J = 7.0$ Hz, 3H), 1.07–1.16 (m, 1H), 1.21–1.46 (m, 3H), 1.84 (dt, $J = 13.5$, 4.5 Hz, 1H), 1.97 (dt, $J = 12.5$, 4.5 Hz, 1H), 2.59–2.68 (m, 2H), 3.82 (s, 3H), 5.099–5.104 (m, 1H), 5.12–5.14 (m, 1H), 5.60–5.69 (m, 1H), 6.89–6.92 (m, 2H), 7.28–7.32 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 13.97, 22.72, 27.44, 39.97, 45.63, 47.47, 55.45, 114.26, 119.91, 122.60, 127.37, 130.34, 132.22, 159.08. Found: C, 78.72; H, 8.59%. Calcd for $C_{16}H_{21}NO$: C, 78.97; H, 8.70%.

2-Butyl-2-*p*-(trifluoromethyl)phenyl-4-pentenenitrile (8l): IR (neat) 2962, 2936, 2866, 2238, 1620, 1329, 1169, 1122, 1071, 1018, 927, 839 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.85 (t, $J = 7.5$ Hz, 3H), 1.03–1.12 (m, 1H), 1.22–1.38 (m, 2H), 1.41–1.49 (m, 1H), 1.90 (dt, $J = 13.5$, 4.5 Hz, 1H), 2.03 (dt, $J = 12.0$, 4.5 Hz, 1H), 2.63–2.74 (m, 2H), 5.10–5.14 (m, 2H), 5.58–5.66 (m, 1H), 7.53 (d, $J = 8.5$ Hz, 2H), 7.65 (d, $J = 8.5$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.86, 22.64, 27.40, 39.79, 45.37, 48.30, 120.65, 121.64, 124.02 (q, $J = 270.6$ Hz), 126.03 (m), 126.81, 130.0 (q, $J = 32.6$ Hz), 131.36, 142.40. Found: C, 68.37; H, 6.45%. Calcd for $C_{16}H_{18}NF_3$: C, 68.31; H, 6.45%.

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