DOI: 10.1002/ejoc.200800385

Sequential Double Olefination of 2-(Arylmethylidene)-2-phosphonoacetonitrile with Dimsyl Lithium and Aldehydes: A Domino Route to Densely Substituted 1,3-Butadienes

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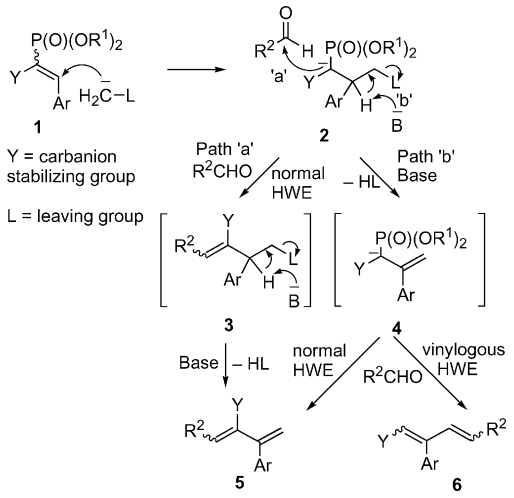
Keywords: Domino reactions / Olefination / Michael addition / Elimination

An efficient and highly stereoselective synthesis of densely substituted 1,3-dienes has been achieved which entails a sequential double olefination of 2-(arylmethylidene)-2-phosphonoacetonitriles by a one-pot domino process involving Michael addition of dimsyllithium to 2-(arylmethylidene)-2-phosphonoacetonitrile, Horner–Wadsworth–Emmons reaction of the resulting phosphonate ylide with the added aldehyde followed by base induced methylsulfenoxy elimination. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2008)

Introduction

Aryl-substituted conjugated dienes possess special photochemical and photophysical properties[1] and are widely used as advanced materials in nonlinear optics as well as liquid crystals.[2] Substituted 1,3-butadienes also enjoy widespread use in the synthesis owing to their ready participation in the Diels–Alder (DA) reaction for building skeleton of complex molecules.[3] There are numerous methods presently available to prepare 1,3-dienes. However, diversity-oriented synthetic (DOS) strategies[4] for selective syntheses of densely substituted regio- and/or stereoisomers from the same starting material merely by slight modification of reaction conditions[5] are preferred.

A multicomponent domino approach[6] to highly and differentially substituted regio- and stereoisomeric 1,3-dienes could be envisaged from simple building blocks viz. an activated vinyl phosphonate, a carbenoid and an aldehyde as shown in (Scheme 1). Carbanion with a leaving group attached to that carbon in combination with a base can be considered as 'carbenoid' equivalent. Therefore, the addition of a nucleophilic L–H_2C^- carbanion (L is a leaving group) (Scheme 1) to a Michael acceptor containing a phosphonate activating group **1** is expected to lead to the adduct **2**. In the presence of a base and an aldehyde, this adduct could subsequently provide the dienes **5** and/or **6** by two routes via intermediates **3** (Path 'a') and **4** (Path 'b'). In Path 'a', the adduct **2** would first undergo a Horner–Wadsworth–Emmons (HWE) reaction with the added aldehyde followed by a base induced elimination to give **5** only. Path 'b' would follow a reverse sequence of reactions where the base induced elimination would precede to give the intermediate allylic phosphonate ylide **4**. Unlike Path 'a', the mesomeric forms of ylide **4** in Path 'b' can, in principle, serve as a precursor for diverse products either by enduring a normal HWE reaction[7,8] (α-attack) or a vinylogous[9] HWE reaction (γ-attack) with the aldehyde to provide **5** or **6**, respectively.



Scheme 1. Proposed path for synthesis of isomeric 1,3-dienes.

Our recent work has shown that dimethylsulfonium methylide **7**[10] in combination with a base[11] or excess of itself[12] can act as an equivalent of a carbenoid. We have demonstrated that this ylide-base combination on reaction with vinyl phosphonate **1** and subsequently with an aldehyde leads to a sequential tandem double olefination to provide di and tri substituted 1,3-dienes **5** or **6** with very high regio- and stereoselectivity.[13,14] The regioselectivity

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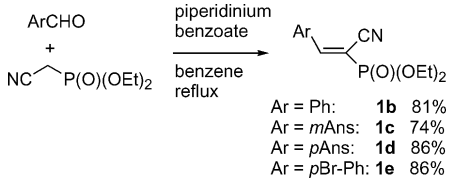
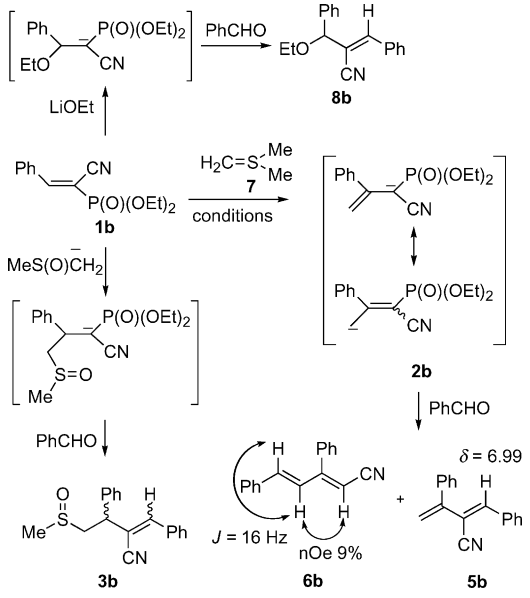
depended essentially on the activating groups; for example, while 2-(arylmethylidene)-2-phosphonoacetate **1a** (Ar = Ph, $R^1 = CF_3CH_2$; Y = CO_2Et; Scheme 1) favoured a normal HWE olefination,[13] the phosphonoacetonitrile **1b** (Ar = Ph, R^1 = Et; Y = CN) gave diene **6** via an unusual vinylogous HWE reaction.[14] This posed a challenge to make dienes of type **5** and **6** from the same starting material. We present here a unique solution of the tandem double olfination of phosphonoacetonitriles **1b**–**e** to give the regioisomeric dienes **5** by using lithium dimsylate–lithium ethoxide as the carbenoid equivalent.

Results and Discussion

Arylmethylidene phosphonoacetonitriles **1b**–**e** were prepared in very good yields using diethyl (cyanomethyl)phosphonate and the corresponding aromatic aldehydes by a Knoevenagel type reaction[15] as shown in Scheme 2. As we had already addressed[14] the synthesis of dienes **6** from **1b** using methylide **7**, we focussed our attention to the synthesis of regioisomeric dienes **5**. We initially planned to achieve our goal by changing methylide generation conditions using trimethylsulfonium iodide and different bases/solvents.[16] When the ylide was generated using 3 equiv. each of Me_3SI and *n*BuLi in THF,[12] and reacted with **1b** followed by quenching the intermediate with benzaldehyde, diene **6b**



Scheme 2. Synthesis of 2-(arylmethylidene)-2-phosphonoacetonitriles.



Scheme 3. Reaction of **1b** with ylide **7**/dimsylate ion/LiOEt and then with PhCHO.

was obtained, albeit in poor yield (ca. 13%) associated with a large amount of polar unidentified material (Scheme 3 and Table 1, entry 1). While screening a few ylide generation conditions, we observed an interesting and dramatic change in the regioselectivity of the sequential olefinations when *n*BuLi was used as the base and DMSO as the co-solvent. We were delighted to see the formation of the desired diene **5b** albeit in moderate yield (25–35%) when the methylide was generated using 1.5–3.0 equiv. of Me_3SI and 2.5–3.0 equiv. of *n*BuLi in THF containing 1–1.5 equiv. of DMSO and subsequent reaction with **1b** and benzaldehyde (1.2–1.5 equiv.) (Table 1, entries 2–4). Although the yield was moderate, both the regio- and the stereoselectivities were very high. The (*Z*)-stereochemistry of the trisubstituted double bond in diene **5b** was ascertained from the chemical shift value of the proton[17] attached therein. The main byproduct of the reaction was found to be **3b**[18] (Scheme 3), which was formed due to conjugate addition of dimsylate anion on **1b** followed by normal HWE reaction with benzaldehyde. The sulfoxide **3b** was isolated as a mixture of diastereoisomers and the individual stereoisomers could not be isolated in pure form because of the lability of its stereogenic centres. The formation of **3b** suggests that the ylide **7** generated under the condition is less nucleophilic than lithium dimsylate. To prevent the formation of **3b**, we next decided to add a proton source like alcohol into the reaction medium to tap on the concentration of dimsylate anion. We were gratified to see that addition of ethanol into the reaction medium did the trick to get **5b** (Table 1, entries 5–7). A gradual increase in ethanol quantity initially increased the yield of **5b** with simultaneous decrease in **3b** formation. The optimum quantity of ethanol was found to be 1.5 equiv. beyond which a side product **8b** (Table 1, entry 7) started forming due to ethoxide addition on **1b** followed by HWE reaction with PhCHO (Scheme 3). To know the

Table 1. Optimization of the double olefination of **1b** and PhCHO.

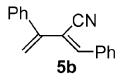
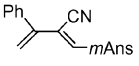
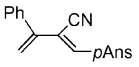
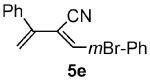
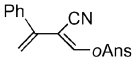
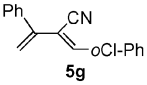
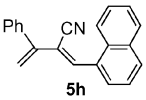
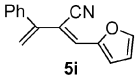
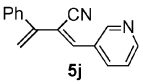
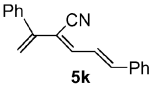
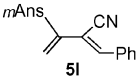
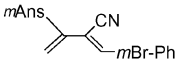
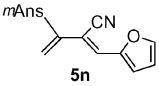
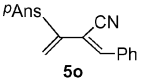
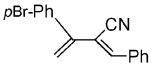
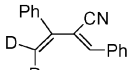
Entry	*n*BuLi/Me_3SI (equiv.)	DMSO/EtOH (equiv.)	**5b**/**6b**/**3b**[a]	Yield of **5b** [%][b]
1	3/3	0/0	3:97:00	–[c,d]
2	3/3	1.5/0	70:00:30	35[d]
3	2.5/3	1.0/0	45:00:55	30[d]
4	2.5/1.5	1.5/0	40:00:60	25[d,e]
5	2.5/1.5	1.5/1.0	80:00:20	51[d]
6	2.5/1.5	1.5/1.5	100:00:00	62[d]
7	2.5/1.5	1.5/2	100:00:00	48[d,f]
8	2.5/0	2.5/0	65:00:35	53[g]
9	2.5/0	1.5/1.5	100:00:00	82[g]

[a] The ratio was found from the crude product by ^1H NMR spectroscopy. [b] Yield refers to pure product obtained after column chromatography. [c] Instead of **5b**, **6b** was isolated in 13% yield. [d] *n*BuLi was added to Me_3SI suspension in THF/DMSO/EtOH at –10 °C. After 15 min, **1b** (1 equiv.) was added and the reaction mixture was brought to room temperature. PhCHO (1.2 equiv.) was added to the reaction mixture and stirred for 3 h. [e] 40% of **3b** was isolated. [f] 26% of **8b** was isolated. [g] *n*BuLi was added to THF/DMSO/EtOH at 0 °C. After 2 min, **1b** (1 equiv.) was added, followed by PhCHO (1.2–2.5 equiv.), and stirred at room temperature for 3 h.

exact role of lithium dimsylate and lithium ethoxide in this reaction, we carried out this olefination reaction omitting Me_3SI (Table 1, entries 8 and 9). When **1b** was treated with lithium dimsylate generated using 2.5 equiv. each of *n*BuLi and DMSO followed by addition of 2.5 equiv. of benzaldehyde, resulted in a clean reaction leading to the formation of **5b** associated with significant amount of **3b** (**3b**/**5b** = 35:65). Finally, the quantities of DMSO and benzaldehyde could be reduced to 1.5 and 1.2 equiv., respectively, by adding 1.5 equiv. of EtOH into the reaction medium. The desired diene **5b** was formed in excellent yield, with very high regio- and stereoisomeric purity, and also free of **3b**. This confirmed that the lithium dimsylate–lithium ethoxide combination is equivalent to carbenoid acting as the olefination reagent, and is an excellent surrogate for dimethylsulfonium methylide **7**. Although, Michael addition[19] of carbon nucleophiles, stabilized by positively charged S, As and Te is well known, dimsylate anion (methylsulfinyl carbanion) has not received much attention over the years especially as a substitute for sulfonium or sulfoxonium ylides.[20] Earlier reports[21–23] on the reaction of dimsylate ion with electrophiles (carbonyls, olefins) provided products like sulfonium or sulfoxonium ylides produced with those electrophiles. But, the reactions were performed under harsh conditions. The yields were also poor and accompanied by many side products. In our study, the optimized conditions (Table 1, entry 9), required the use of 1.5 equiv. each of DMSO, EtOH and 2.5 equiv. of *n*BuLi with respect to vinyl phophonate **1b** or benzaldehyde in THF at ambient temperature giving **5b** in 82% yield. The stereoisomeric purity of **5b** was found to be >97% (GC), while the other regioisomer **6b** was not detected. The scope of this one-pot sequential tandem double olefination for the synthesis of substituted 1,3-dienes was investigated under the optimized reaction conditions (Table 2). For this, a wide range of aldehydes bearing aryl, heteroaryl and alkenyl groups were treated with vinyl phosphonates **1b**–**e** leading to the desired products in very good yields, with excellent regio and stereoselectivity. 2-Furaldehyde, benzaldehydes having an *ortho* substituent and 1-naphthaldehyde (Table 2; entries 5–8 and 13) also gave the desired products with slightly erroded stereoselectivity, but no regioisomers were detected. The (*Z*)-isomers of the olefinic products were formed with consistent and reproducible ratios, thus suggesting their direct formation in the HWE reaction. The method can be used for the synthesis of 4,4-dideuterated dienes using [D_6]DMSO. Thus **5b-*d*$_2$** (Table 2, entry 16) was synthesised in excellent yield and purity[24] from **1b** and benzaldehyde.

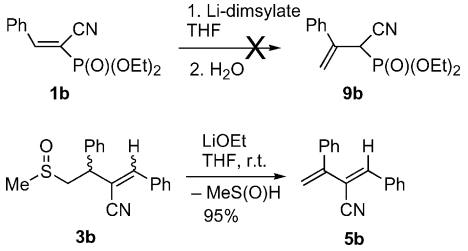
To establish the elementary steps by which this domino process is operating, we carried out two reactions as depicted in Scheme 4. When the reaction of **1b** and lithium dimsylate–lithium ethoxide was carried out without adding PhCHO, no olefination product **9b** was isolated. However, when **3b** was treated with lithium ethoxide (generated in-situ by the reaction of *n*BuLi and EtOH) in THF at room temperature, **5b** was formed in nearly quantitative yield indicating its intermediacy in the reaction. Therefore, the domino process follows Path 'a' (Scheme 1) involving first the Michael addition of dimsyllithium to **1**, HWE reaction of the resulting phosphonate ylide with the added aldehyde

Table 2. Stereoselective sequential tandem double olefination of **1b**–**e** with aldehydes.

Entry	Substrate / Aldehyde	Product[a,b]	Yield [%][c]
1.	**1b** / Benzaldehyde	 **5b**	82[d]
2.	**1b** / *m*-Anisaldehyde	 **5c**	79[d]
3.	**1b** / *p*-Anisaldehyde	 **5d**	81[d]
4.	**1b** / *m*-Bromo-benzaldehyde	 **5e**	82[d]
5	**1b** / *o*-Anisaldehyde	 **5f**	76[d]
6.	**1b** / *o*-Chloro-benzaldehyde	 **5g**	80[e]
7.	**1b** / 1-Naphthaldehyde	 **5h**	74[f]
8.	**1b** / 2-Furaldehyde	 **5i**	82[g]
9.	**1b** / 3-Pyridine carboxaldehyde	 **5j**	81[d]
10.	**1b** / *trans*-Cinnam-aldehyde	 **5k**	85[d]
11.	**1c** / Benzaldehyde	 **5l**	80[d]
12.	**1c** / *m*-Bromo-benzaldehyde	 **5m**	85[d]
13.	**1c** / 2-Furaldehyde	 **5n**	76[h]
14.	**1d** / Benzaldehyde	 **5o**	84[d]
15.	**1e** / Benzaldehyde	 **5p**	80[d]
16.	**1b** / Benzaldehyde	 **5b-*d*$_2$**	82[i]

[a] Optimized procedure is provided in the experimental section. [b] Isolated yield of TLC homogeneous material. [c] Isomeric purity determined by capillary GC/^{1}H NMR of crude product (see Supporting Information). [d] Isomeric purity >94%. [e] Isomeric purity >95%. [f] Isomeric purity >87%. [g] Isomeric purity >93%. [h] Isomeric purity >97%. [i] Isotopic purity >91%.

to give the intermediate **3** which then undergoes lithium ethoxide induced methylsulfenoxy elimination resulting in the diene **5**.



Scheme 4. Establishment of elementary steps of domino reaction.

Conclusions

In conclusion, we have developed a new regio- and stereoselective one-pot three component sequential double olefination reaction of lithium dimsylate, 2-(arylmethylidene)-2-phosphonoacetonitriles and aldehydes leading to the syntheses of differentially functionalized trisubstituted 1,3-dienes[25,26] in very good yields. Lithium dimsylate–lithium ethoxide system can be treated as a surrogate of dimethylsulfonium methylide base combination and equivalent to a "carbenoid". As the process described herein is simple, it could be easily adopted for DOS to synthesize regioisomeric olefins from the same substrate.

Experimental Section

Materials and Methods: All reactions were performed in oven-dried (120 °C) or flame-dried glass apparatus under dry N_2 or argon atmosphere. Tetrahydrofuran (THF) was dried from sodium/benzophenone while DMSO from CaH_2 followed by storage over 4-Å molecular sieves. The aldehydes were crystallized or distilled prior to use. *n*BuLi (1.6 M in hexane) was purchased from Aldrich. The column chromatography was performed on silica gel (230–400 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker 200 MHz spectrometer. Spectra were referenced to residual chloroform (^{1}H: δ = 7.25 ppm, ^{13}C: δ = 77.00 ppm). The mass spectra were recorded on a Fisons VG Quatro II mass spectrometer (EI 70 V, CI 30 V, ESI 3.5 kV). High resolution mass spectra were recorded at 60–70 eV with a Waters Micromass Q-TOF spectrometer (ESI, Ar). Infrared spectra (IR) were recorded on a JASCO FT IR spectrophotometer in NaCl cells or in KBr discs. Peaks are reported in cm^{-1}. Melting points (mp) were determined on a Fischer John's melting point apparatus and are uncorrected. Gas chromatography (GC) studies were carried out using Younglin Acme 6000M Gas Chromatograph fitted with a capillary column (WCOT Fused Silica, CP-SIL-5-CB, 50 m × 0.25 mm/0.39 mm, 0.25 μm; Carrier: helium 1 mL/min; split 5 mL/min).

General Procedure I. Preparation of 2-(Arylmethylidene)-2-phosphonoacetonitriles 1: Following the reported procedure,[15] a solution of an aromatic aldehyde (12 mmol), diethyl (cyanomethyl)-phosphonate (1.6 mL, 10 mmol) and piperidinium benzoate (415 mg, 2 mmol) in benzene (80 mL) was heated under reflux fitted with a Dean–Stark apparatus for 2 days. The reaction mixture was cooled, washed with water and brine, dried ($MgSO_4$) and the solvents evaporated. The residue was purified on silica gel using hexane/ethyl acetate to give the corresponding 2-(arylmethylidene)-2-phosphonoacetonitrile **1** (74–86%).

General Procedure II. Preparation of 1,3-Dienes 5: *n*BuLi (1.6 mL, 2.5 mmol, 1.6 M hexane solution) was added to a stirred solution of DMSO (0.11 mL, 1.5 mmol) and EtOH (0.09 mL, 1.5 mmol) in THF (4 mL) at 0 °C. After 2 min, 2-(arylmethylidene)-2-phosphonoacetonitrile **1** (1.0 mmol) in THF (2 mL) was added to the reaction mixture followed by the addition of the aldehyde (1.2 mmol). The reaction mixture was brought to room temperature and stirred for 3–12 h. The reaction mixture was diluted with water and extracted with diethyl ether. The combined extract was washed with brine, dried with magnesium sulfate, filtered and concentrated under vacuum. The residue was purified on silica gel using hexane/ethyl acetate to give the corresponding diene **5**.

Diethyl [(*E*)-1-Cyano-2-phenylethenyl]phosphonate (1b): Yield 2.15 g (81%) as viscous oil. IR (neat): $\tilde{\nu}$ = 2985, 2935, 2909, 2212, 1595, 1572, 1449, 1392, 1369, 1260, 1211, 1163, 1015, 973, 831, 787, 762 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.40 (t, J = 7 Hz, 6 H, 2× CH_3CH_2O), 4.30–4.14 (m, 4 H, 2× CH_3CH_2O), 7.58–7.44 (m, 3 H, Ar), 7.97–7.93 (m, 2 H, Ar), 8.00 (d, J = 21.4 Hz, 1 H, ArC*H*) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 15.6 (d, J = 5.9 Hz), 62.9 (d, J = 4.4 Hz), 99.6 (d, J = 195 Hz), 114.7 (d, J = 10.2 Hz), 128 ppm. 6 (2 C), 129.7 (2 C), 131.8 (d, J = 17.7 Hz), 132.4, 158.1 ppm.

Diethyl [(*E*)-1-Cyano-2-(3-methoxyphenyl)ethenyl]phosphonate (1c): Yield 2.18 g (74%) as viscous oil. IR (neat): $\tilde{\nu}$ = 3007, 2939, 2910, 2213, 1599, 1576, 1491, 1483, 1465, 1433, 1264, 1216, 1173, 1162, 1023, 978, 754, 684 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.39 (t, J = 7.2 Hz, 6 H, 2× CH_3CH_2O), 3.84 (s, 3 H, O*Me*), 4.15 (q, J = 7.2 Hz, 2 H, CH_3CH_2O), 4.23 (q, J = 7.2 Hz, 2 H, CH_3CH_2O), 7.07 (d, J = 8 Hz, 1 H, Ar), 7.33–7.54 (m, 3 H, Ar), 8.00 (d, J = 21.4 Hz, 1 H, ArC*H*) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 16.2 (d, J = 6.2 Hz), 55.3, 63.5 (d, J = 5.8 Hz), 100.2 (d, J = 195 Hz), 114.0, 115.4 (d, J = 10.1 Hz), 119.8, 123.4, 130.1, 133.6 (d, J = 17.7 Hz), 158.8 (d, J = 7 Hz), 159.9 ppm.

Diethyl [(*E*)-1-Cyano-2-(4-methoxyphenyl)ethenyl]phosphonate (1d): Yield 2.54 g (86%) as viscous oil. IR (neat): $\tilde{\nu}$ = 3063, 3016, 2988, 2938, 2908, 2842, 2210, 1588, 1562, 1512, 1427, 1309, 1264, 1180, 1065, 1024, 974, 834, 794, 756 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.36 (t, J = 7 Hz, 6 H, 2× CH_3CH_2O), 3.88 (s, 3 H, O*Me*), 4.22 (q, J = 7 Hz, 2 H, CH_3CH_2O), 4.19 (q, J = 7.1 Hz, 2 H, CH_3CH_2O), 6.97 (d, J = 8.8 Hz, 2 H, Ar), 7.92 (d, J = 23 Hz, 1 H, ArC*H*), 7.96 (d, J = 8.7 Hz, 2 H, Ar) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 16.2 (d, J = 5.8 Hz), 55.5, 63.3 (d, J = 5.6 Hz), 95.5 (d, J = 198 Hz), 114.6 (2 C), 116.0 (d, J = 10.3 Hz), 125.4 (d, J = 14 Hz), 132.9 (2 C), 158.2, 163.5 ppm.

Diethyl [(*E*)-1-Cyano-2-(4-bromophenyl)ethenyl]phosphonate (1e): Yield 2.96 g (86%) as viscous oil. IR (neat): $\tilde{\nu}$ = 2985, 2933, 2908, 2212, 1586, 1558, 1487, 1443, 1403, 1369, 1262, 1163, 1098, 1022, 975, 824, 783, 751 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.40 (t, J = 7 Hz, 6 H, 2× CH_3CH_2O), 4.29–4.09 (m, 4 H, 2× CH_3CH_2O), 7.62 (d, J = 8.4 Hz, 2 H, Ar), 7.81 (d, J = 8.6 Hz, 2 H, Ar), 7.93 (d, J = 21 Hz, 1 H, ArC*H*) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 15.9 (d, J = 6 Hz), 63.4 (d, J = 5.6 Hz), 100.6 (d, J = 196 Hz), 114.8 (d, J = 9.9 Hz), 127.5, 130.9 (d, J = 18 Hz), 131.4 (2 C), 132.2 (2 C), 156.9 (d, J = 7.1 Hz) ppm.

2-[2-(Methylsulfinyl)-1-phenylethyl]-3-phenylacrylonitrile (3b) (mixture of diastereoisomers): Yield 118 mg (40%) as viscous oil. IR (film): $\tilde{\nu}$ = 3063, 3016, 2210, 1615, 1494, 1452, 1408, 1215, 1049, 966, 931, 889, 700, 666 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): (nonpolar isomer): δ = 2.69 (s, 3 H, CH_3S), 3.18 (dd, J = 12.6 and

2.6 Hz, 1 H, CH_AH$_B$S), 3.47 (dd, J = 12.6 and 12.6 Hz, 1 H, CH$_A$$H_B$S), 4.36 (dd, J = 12.6 and 2.6 Hz, 1 H, CHCH$_2$S), 7.33 (s, 1 H, ArCH), 7.37–7.40 (m, 8 H, Ar), 7.72–7.78 (m, 2 H, Ar) ppm. ^{1}H NMR (200 MHz, $CDCl_3$): (polar isomer): δ = 2.63 (s, 3 H, CH_3S), 3.12–3.52 (m, 2 H, CH$_2$S), 4.32 (dd, J = 5.0 and 10.4 Hz, 1 H, CHCH$_2$S), 7.17 (s, 1 H, ArCH), 7.35–7.41 (m, 8 H, Ar), 7.70–7.76 (m, 2 H, Ar) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, mixture of isomers): δ = 39.3, 45.5, 58.2, 58.8, 111.3, 112.9, 117.3, 117.7, 127.2, 127.8, 128.2, 128.4, 128.9, 129.1, 129.2, 129.3, 130.7, 130.8, 132.9, 137.9, 139.1, 144.8, 146.2 ppm.

(3*RS*,1*E*)-2-Cyano-1,3-diphenyl-3-ethoxy-1-propene (8b): Yield 68 mg (26%) as viscous oil. IR ($CHCl_3$ film): $\tilde{\nu}$ = 3019, 2975, 2836, 2216, 1600, 1561, 1488, 1268, 1098, 760 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.30 (t, J = 7 Hz, 3 H, CH_3CH$_2$O), 3.43–3.74 (m, 2 H, CH$_3$C$H_A$$H_B$O), 5.01 (s, 1 H, PhC$H$O), 7.22 (s, 1 H, ArC$H$), 7.27–7.48 (m, 8 H, Ar), 7.72–7.79 (m, 2 H, Ar) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 15.2, 65.0, 82.7, 113.6, 126.9 (2 C), 128.5, 128.7 (2 C), 128.8 (2 C), 129.1 (2 C), 133.1, 138.6, 143.0 ppm. EI MS: m/z (%) = 264 (80) [M$^+$ + H], 235 (82), 217 (98), 206 (50), 190 (97), 179 (92), 158 (55), 140 (98), 136 (93), 128 (100), 106 (99), 102 (100), 91 (48), 78 (98).

(1*Z*,3*E*)-1-Cyano-2,4-diphenyl-1,3-butadiene (6b): Yield 30 mg (13%). M.p. 57 °C. IR ($CHCl_3$): $\tilde{\nu}$ = 3034, 2209, 1615, 1581, 1561, 1491, 1449, 1375, 1199, 1071, 1005, 966, 803, 779, 753, 705, 690 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.55 (s, 1 H, CHCN), 6.59 (d, J = 16 Hz, 1 H, CH=CH-Ph), 7.04 (d, J = 16 Hz, 1 H, CH=CH-Ph), 7.31–7.52 (m, 10 H, 2×Ph) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 97.4, 117.7, 127.3 (2 C), 128.1, 128.6 (2 C), 128.7 (2 C), 128.8 (2 C), 129.3 (2 C), 135.0, 135.4, 139.8, 160.7 ppm. ESI MS: m/z (%) = 232 (2) [M$^+$ + 1], 124 (100). GC: (260 °C isothermal) t_R = 9.025 min (100%). HRMS: calcd. for $C_{17}H_{14}N$ (M$^+$ + H) 232.1126, found 232.1122. $C_{17}H_{13}N$ (231.3): calcd. C 88.28, H 5.67, N 6.06; found C 88.04, H 5.74, N 5.92.

(1*Z*)-2-Cyano-1,3-diphenyl-1,3-butadiene (5b): Yield 190 mg (82%). M.p. 51–52 °C. IR ($CHCl_3$): $\tilde{\nu}$ = 3054, 2211, 1607, 1570, 1493, 1445, 1209, 1100, 1072, 1029, 936, 908, 754, 682 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.49 (s, 1 H, C=CH_AH$_B$), 5.92 (s, 1 H, C=CH$_A$$H_B$), 6.99 (s, 1 H, PhC$H$=C), 7.30–7.43 (m, 8 H, Ar), 7.73–7.78 (m, 2 H, Ar) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 113.0, 117.4, 119.2, 128.4, 128.6 (2 C), 128.7 (2 C), 128.8 (2 C), 129.3 (2 C), 130.5, 133.4, 138.2, 144.6, 145.2 ppm. ESI MS: m/z (%) = 232 (60) [M$^+$ + 1], 148 (100). GC: (260 °C isothermal) t_R = 7.642 min (100%). $C_{17}H_{13}N$ (231.3): calcd. C 88.28, H 5.67, N 6.06; found C 88.11, H 5.82, N 5.80.

(1*Z*)-2-Cyano-1-(3-methoxyphenyl)-3-phenyl-1,3-butadiene (5c): Yield 206 mg (79%) as thick gum. IR (neat): $\tilde{\nu}$ = 2935, 2220, 1600, 1491, 1040, 928 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.83 (s, 3 H, OMe), 5.47 (s, 1 H, C=CH_AH$_B$), 5.90 (s, 1 H, C=CH$_A$$H_B$), 6.94 (s, 1 H, ArC$H$=C), 6.92–6.96 (m, 1 H, Ar), 7.25–7.42 (m, 8 H, Ar) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 55.4, 113.2, 113.5, 117.1, 117.4, 119.3, 122.2, 128.4, 128.6 (2 C), 128.7 (2 C), 129.8, 134.7, 138.3, 144.5, 145.2, 159.8 ppm. EI MS: m/z (%) = 230 (100) [M$^+$ – OMe], 216 (22), 203 (27), 190 (16), 178 (16), 153 (56), 115 (32), 101 (24), 91 (67), 77 (56), 63 (15). GC: (200 °C – 10 °C/min – 260 °C – 5 °C/min – 300 °C) t_R = 12.46 min (100%). $C_{18}H_{15}NO$ (261.32): calcd. C 82.73, H 5.79, N 5.36; found C 82.34, H 5.83, N 5.20.

(1*Z*)-2-Cyano-3-(4-methoxyphenyl)-3-phenyl-1,3-butadiene (5d): Yield 212 mg (81%) as thick gum. IR (neat): $\tilde{\nu}$ = 3019, 2935, 2838, 2215, 1602, 1511, 1308, 1260, 1279, 1031, 904, 832, 764 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.84 (s, 3 H, OMe), 5.41 (s, 1 H, C=CH_AH$_B$), 5.83 (s, 1 H, C=CH$_A$$H_B$), 6.89 (s, 1 H, ArC$H$=C), 6.90 (d, J = 8.8 Hz, 2 H, Ar), 7.28–7.43 (m, 5 H, Ph), 7.73 (d, J = 8.8 Hz, 2 H, Ar) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 55.4, 110.1, 114.2 (2 C), 117.9, 118.0, 126.1, 128.3, 128.5 (2 C), 128.7 (2 C), 131.2 (2 C), 138.5, 144.1, 145.4, 161.4 ppm. ESI MS: m/z (%) = 262 (18) [M$^+$ + 1], 261 (100) [M$^+$], 260 (52) [M$^+$ – 1], 245 (17), 230 (55), 217 (25), 184 (46), 169 (17), 91 (36), 77 (28). GC: (200 °C – 10 °C/min – 260 °C – 5 °C/min – 300 °C) t_R = 13.29 min (100%). $C_{18}H_{15}NO$ (261.32): calcd. C 82.73, H 5.79, N 5.36; found C 82.41, H 5.86, N 5.23.

(1*Z*)-2-Cyano-1-(3-bromophenyl)-3-phenyl-1,3-butadiene (5e): Yield 254 mg (82%) as thick gum. IR (neat): $\tilde{\nu}$ = 3019, 2935, 2221, 1593, 1569, 1493, 1474, 1444, 1426, 1075, 914 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.50 (s, 1 H, C=CH_AH$_B$), 5.93 (s, 1 H, C=CH$_A$$H_B$), 6.87 (s, 1 H, ArC$H$=C), 7.27–7.43 (m, 6 H, Ph and Ar), 7.51 (d, J = 8 Hz, 1 H, Ar), 7.73 (s, 1 H, Ar), 7.79 (d, J = 8 Hz, 1 H, Ar) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 114.7, 116.8, 120.1, 122.8, 127.2, 128.6, 128.7 (4 C), 130.3, 132.4, 133.3, 135.4, 137.9, 142.6, 144.9 ppm. ESI MS: m/z (%) = 311 (6) [$C_{17}H_{12}{}^{81}BrN^+$], 309 (6) [$C_{17}H_{12}{}^{79}BrN^+$], 230 (100), 202 (13), 101 (19), 77 (26). GC: (200 °C – 10 °C/min – 260 °C – 5 °C/min – 300 °C) t_R = 13.08 min (100%). $C_{17}H_{12}BrN$ (310.19): calcd. C 65.83, H 3.90, N 4.52; found C 65.59, H 4.01, N 4.38.

(1*Z*)-2-Cyano-1-(2-methoxyphenyl)-3-phenyl-1,3-butadiene (5f): Yield 198 mg (76%). M.p. 81–82 °C. IR ($CHCl_3$ film): $\tilde{\nu}$ = 3019, 2219, 1599, 1491, 1466, 1437, 1251, 1179, 1027, 908 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.75 (s, 3 H, OMe), 5.46 (s, 1 H, C=CH_AH$_B$), 5.85 (s, 1 H, C=CH$_A$$H_B$), 6.86 (d, J = 8.4 Hz, 1 H, Ar), 7.03 (t, J = 7.4 Hz, 1 H, Ar), 7.30–7.43 (m, 7 H, Ph, Ar and ArCH=C), 8.06 (d, J = 7.4 Hz, 1 H, Ar) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 55.5, 110.6, 113.1, 117.6, 118.5, 120.7, 122.8, 128.3, 128.4 (2 C), 128.6 (3 C), 131.8, 138.4, 140.3, 145.4, 157.7 ppm. EI MS: m/z (%) = 262 (44) [M$^+$ + H], 261 (100) [M$^+$], 246 (32), 230 (92), 219 (30), 218 (29), 202 (21), 184 (68), 169 (23), 108 (29), 91 (63), 77 (90), 63 (23). GC: (200 °C – 10 °C/min – 260 °C – 5 °C/min – 300 °C) t_R = 11.97 min (1.5%), t_R = 12.21 min (98.5%). HRMS: calcd. for $C_{18}H_{16}NO$ (M$^+$ + H) 262.1232, found 262.1237.

(1*Z*)-2-Cyano-1-(2-chlorophenyl)-3-phenyl-1,3-butadiene (5g): Yield 212 mg (80%). M.p. 62–63 °C. IR ($CHCl_3$ film): $\tilde{\nu}$ = 3058, 3027, 2925, 2222, 1612, 1588, 1574, 1493, 1466, 1441, 1053, 1036, 906, 762, 752 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.54 (s, 1 H, C=CH_AH$_B$), 5.95 (s, 1 H, C=CH$_A$$H_B$), 7.30–7.46 (m, 9 H, Ph, Ar and ArCH=C), 8.00–8.05 (m, 1 H, Ar) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 116.1, 116.6, 120.1, 127.1, 128.5 (2 C), 128.6 (4 C), 129.4, 129.7, 131.2, 134.7, 137.8, 141.4, 144.9 ppm. ESI MS: m/z (%) = 288 (12) [M$^+$ + Na], 266 (100) [M$^+$ + H], 154 (7). GC: (200 °C–10 °C/min – 260 °C–5 °C/min – 300 °C) t_R = 11.72 min (100%). HRMS: calcd. for $C_{17}H_{13}ClN$ (M$^+$ + H) 266.0737, found 266.0740.

(1*Z*)-2-Cyano-1-(1-naphthyl)-3-phenyl-1,3-butadiene (5h): Yield 208 mg (74%). M.p. 81–82 °C. IR ($CHCl_3$ film): $\tilde{\nu}$ = 3062, 3019, 2223, 1598, 1575, 1509, 1495, 1444, 1051, 1027, 912 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.55 (s, 1 H, C=CH_AH$_B$), 5.97 (s, 1 H, C=CH$_A$$H_B$), 7.46–7.64 (m, 9 H, Ph and Ar), 7.70 (s, 1 H, =CHNp), 7.88 (t, J = 7.4 Hz, 2 H, Ar), 8.05 (d, J = 7.4 Hz, 1 H, Ar) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 116.5, 117.1, 119.7, 123.2, 125.5, 126.3, 126.9, 127.0, 128.5, 128.7 (2 C), 128.8 (2 C), 128.9, 130.7, 130.8, 131.4, 133.4, 138.3, 143.0, 145.0 ppm. ESI MS: m/z (%) = 282 (100) [M$^+$ + H]. HRMS: calcd. for $C_{21}H_{16}N$ (M$^+$ + H) 282.1283, found 282.1276.

(1*Z*)-2-Cyano-1-(2-fuyrl)-3-phenyl-1,3-butadiene (5i): Yield 181 mg (82%) as thick gum. IR (neat): $\tilde{\nu}$ = 3140, 3056, 2929, 2218, 1592, 1493, 1469, 1444, 1151, 1088, 1025, 899, 886, 782, 754 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.41 (s, 1 H, C=CH_AH$_B$), 5.87 (s, 1

H, C=CH$_A$H$_B$), 6.51 (d, J = 1.6 Hz, 1 H, Fur), 6.75 (s, 1 H, ArC*H*=C), 7.07 (d, J = 3.4 Hz, 1 H, Fur), 7.26–7.33 (m, 2 H, Ar), 7.35–7.43 (m, 3 H, Ar), 7.54 (s, 1 H, Fur) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 109.2, 112.8, 115.6, 117.2, 118.9, 128.4, 128.6 (2 C), 128.7 (2 C), 130.4, 138.0, 144.6, 145.0, 149.8 ppm. EI MS: *m*/*z* (%) = 222 (13) [M$^+$ + H], 221 (62) [M$^+$], 192 (42), 165 (100), 140 (28), 139 (29), 115 (30), 89 (35), 77 (87), 63 (65). GC: (200 °C – 10 °C/min – 260 °C – 5 °C/min – 300 °C) t_R = 9.48 min (98.3%), t_R = 10.16 min (1.7%). HRMS: calcd. for $C_{15}H_{12}NO$ (M$^+$ + H) 222.0919, found 222.0916.

(1*Z*)-2-Cyano-3-phenyl-1-(3-pyridyl)-1,3-butadiene (5j): Yield 188 mg (81%) as thick gum. IR ($CHCl_3$ film): $\tilde{\nu}$ = 3019, 2222, 1582, 1493, 1481, 1412, 1215, 1024, 913 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.54 (s, 1 H, C=C*H$_A$*H$_B$), 5.96 (s, 1 H, C=CH$_A$*H$_B$*), 6.95 (s, 1 H, PyC*H*=C), 7.27–7.33 (m, 2 H, Ph), 7.38–7.49 (m, 4 H, Ph and Py), 8.44 (d, J = 8 Hz, 1 H, Py), 8.60 (d, J = 8 Hz, 1 H, Py), 8.62 (s, 1 H, Py) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 115.8, 116.8, 120.5, 123.7, 128.7 (3 C), 128.8 (2 C), 129.6, 135.0, 137.7, 140.3, 144.8, 150.7, 151.0 ppm. ESI MS: *m*/*z* (%) = 233 (100) [M$^+$ + H]. GC: (200 °C–10 °C/min – 260 °C–5 °C/min – 300 °C) t_R = 10.92 min (99%). HRMS: calcd. for $C_{16}H_{13}N_2$ (M$^+$ + H) 233.1079, found 233.1084.

(1*E*,2*Z*)-4-Cyano-1,5-diphenyl-1,3,5-hexatriene (5k): Yield 219 mg (85%). M.p. 93 °C. IR (neat): $\tilde{\nu}$ = 3019, 2222, 1603, 1577, 1495, 1447, 1215 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.40 (s, 1 H, C=C*H$_A$*H$_B$), 5.83 (s, 1 H, C=CH$_A$*H$_B$*), 6.76 (d, J = 10.8 Hz, 1 H, CH=CCN), 6.77 (d, J = 16.4 Hz, 1 H, PhC*H*=CH), 7.23–7.45 (m, 11 H, 2 × Ph, C=CH) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 114.7, 116.5, 119.1, 124.8, 127.5 (2 C), 128.3, 128.6 (2 C), 128.7 (2 C), 128.9 (2 C), 129.5, 135.7, 138.2, 141.5, 144.3, 144.5 ppm. ESI MS: *m*/*z* (%) = 258 (100) [M$^+$ + H]. HRMS: calcd. for $C_{19}H_{16}N$ (M$^+$ + H) 258.1283, found 258.1283.

(1*Z*)-2-Cyano-3-(3-methoxyphenyl)-1-phenyl-1,3-butadiene (5l): Yield 209 mg (80%) as thick gum. IR (neat): $\tilde{\nu}$ = 3062, 3020, 2958, 2938, 2834, 2218, 1597, 1577, 1448, 1321, 1286, 1239, 1044, 754, 690 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.83 (s, 3 H, OMe), 5.47 (s, 1 H, C=C*H$_A$*H$_B$), 5.89 (s, 1 H, C=CH$_A$*H$_B$*), 6.85–6.97 (m, 3 H, Ar), 7.00 (s, 1 H, ArC*H*=C), 7.25–7.41 (m, 4 H, Ph, Ar), 7.73–7.77 (m, 2 H, Ar) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 55.3, 112.8, 113.8, 114.4, 117.4, 119.1, 121.1, 128.8 (2 C), 129.3 (2 C), 129.6, 130.5, 133.4, 139.6, 144.6, 145.0, 159.7 ppm. ESI MS: *m*/*z* (%) = 262 (100) [M$^+$ + H], 184 (31). GC: (200 °C – 10 °C/min – 260 °C – 5 °C/min – 300 °C) t_R = 12.43 min (100%). HRMS: calcd. for $C_{18}H_{16}NO$ (M$^+$ + H) 262.1232, found 262.1224.

(1*Z*)-2-Cyano-1-(3-bromophenyl)-3-(3-methoxyphenyl)-1,3-butadiene (5m): Yield 289 mg (85%) as thick gum. IR (neat): $\tilde{\nu}$ = 3019, 2962, 2836, 2220, 1596, 1576, 1486, 1474, 1427, 1321, 1287, 1215, 1042 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.83 (s, 3 H, OMe), 5.51 (s, 1 H, C=C*H$_A$*H$_B$), 5.91 (s, 1 H, C=CH$_A$*H$_B$*), 6.82–6.96 (m, 3 H, Ar), 6.90 (s, 1 H, ArC*H*=C), 7.26 (d, J = 8 Hz, 1 H, Ar), 7.35 (d, J = 8 Hz, 1 H, Ar), 7.51 (d, J = 8 Hz, 1 H, Ar), 7.74 (s, 1 H, Ar), 7.79 (d, J = 8 Hz, 1 H, Ar) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 55.3, 112.0, 113.9, 114.5, 116.8, 120.0, 121.1, 122.8, 127.3, 129.8, 130.4, 132.4, 133.3, 135.4, 139.3, 142.7, 144.8, 159.8 ppm. EI MS: *m*/*z* (%) = 341 (23) [$C_{18}H_{14}{}^{81}$BrNO$^+$], 339 (23) [$C_{18}H_{14}{}^{79}$BrNO$^+$], 260 (100), 245 (43), 217 (45). GC: (200 °C – 10 °C/min – 260 °C – 5 °C/min – 300 °C) t_R = 15.14 min (100%). HRMS: calcd. for $C_{18}H_{15}NO^{79}Br$ (M$^+$ + H) 340.0337, found 340.0334.

(1*Z*)-2-Cyano-1-(2-fuyrl)-3-(3-methoxyphenyl)-1,3-butadiene (5n): Yield 191 mg (76%) as thick gum. IR ($CHCl_3$ film): $\tilde{\nu}$ = 3018, 2219, 1596, 1578, 1467, 1428, 1233, 1042, 903 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.82 (s, 3 H, OMe), 5.41 (s, 1 H, C=C*H$_A$*H$_B$), 5.85 (s, 1 H, C=CH$_A$*H$_B$*), 6.51–6.53 (m, 1 H, Fur), 6.77 (s, 1 H, ArC*H*=C), 6.79–6.95 (m, 3 H, Ar and Fur), 7.07 (d, J = 3.2 Hz, 1 H, Fur), 7.31 (t, J = 8 Hz, 1 H, Ar), 7.54 (s, 1 H, Ar) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 55.3, 109.0, 112.8, 113.8, 114.4, 115.6, 117.1, 118.8, 121.1, 129.7, 130.5, 139.4, 144.5, 145.0, 149.8, 159.7 ppm. EI MS: *m*/*z* (%) = 252 (17) [M$^+$ + H], 251 (100) [M$^+$], 222 (47), 207 (21), 195 (51), 190 (36), 180 (24), 165 (28), 152 (33), 140 (15), 127 (16), 89 (21), 77 (18), 63 (27). GC: (200 °C–10 °C/min – 260 °C–5 °C/min – 300 °C) t_R = 10.99 min (100%). HRMS: calcd. for $C_{16}H_{14}NO_2$ (M$^+$ + H) 252.1025, found 252.1032.

(1*Z*)-2-Cyano-1-phenyl-3-(4-methoxyphenyl)-1,3-butadiene (5o): Yield 219 mg (84%) as thick gum. IR (neat): $\tilde{\nu}$ = 3018, 2960, 2935, 2838, 2217, 1608, 1509, 1451, 1290, 1250, 1215, 1179, 1029, 837, 754 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.84 (s, 3 H, OMe), 5.42 (s, 1 H, C=C*H$_A$*H$_B$), 5.82 (s, 1 H, C=CH$_A$*H$_B$*), 6.92 (d, J = 8.2 Hz, 2 H, Ar), 7.00 (s, 1 H, ArC*H*=C), 7.20–7.27 (m, 2 H, Ph), 7.37–7.41 (m, 3 H, Ph), 7.74 (d, J = 8.2 Hz, 2 H, Ar) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 55.3, 113.2, 114.0 (3 C), 117.5, 118.3, 128.8 (2 C), 129.3 (2 C), 129.8 (2 C), 130.4, 133.5, 144.5, 144.8, 159.7 ppm. EI MS: *m*/*z* (%) = 262 (35) [M$^+$ + H], 261 (67) [M$^+$], 246 (29), 230 (38), 218 (34), 217 (66), 190 (30), 140 (36), 127 (41), 121 (50), 108 (60), 89 (69), 77 (100), 63 (78). GC: (200 °C – 10 °C/min – 260 °C – 5 °C/min – 300 °C) t_R = 12.80 min (100%). HRMS: calcd. for $C_{18}H_{16}NO$ (M$^+$ + H) 262.1232, found 262.1233.

(1*Z*)-3-(4-Bromophenyl)-2-cyano-1-phenyl-1,3-butadiene (5p): Yield 248 mg (80%) as thick gum. IR (neat): $\tilde{\nu}$ = 3062, 3029, 2217, 1588, 1571, 1485, 1447, 1392, 1210, 1068, 1010, 832 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.46 (s, 1 H, C=C*H$_A$*H$_B$), 5.90 (s, 1 H, C=CH$_A$*H$_B$*), 6.93 (s, 1 H, PhC*H*=C), 7.21 (d, J = 8.4 Hz, 2 H, Ar), 7.37–7.43 (m, 3 H, Ph), 7.55 (d, J = 8.4 Hz, 2 H, Ar), 7.64–7.77 (m, 2 H, Ph) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 112.6, 117.2, 119.5, 122.6, 128.9 (2 C), 129.4 (2 C), 130.3 (2 C), 130.7, 131.9 (2 C), 133.2, 137.2, 144.2, 144.7 ppm. ESI MS: *m*/*z* (%) = 312 (51) [$C_{17}H_{13}N^{81}$Br, M$^+$ + H], 310 (58) [$C_{17}H_{13}N^{79}$Br, M$^+$ + H], 231 (100). GC: (200 °C – 10 °C/min – 260 °C – 5 °C/min – 300 °C) t_R = 13.31 min (100%). HRMS: calcd. for $C_{17}H_{13}N^{79}Br$ (M$^+$ + H) 310.0231, found 310.0237.

(1*Z*)-2-Cyano-1,3-diphenyl-1,3-butadiene (5b-*d*$_2$): Yield 191 mg (82%). M.p. 49–51 °C. IR (neat): $\tilde{\nu}$ = 3019, 2219, 1598, 1572, 1491, 1445, 1215 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.99 (s, 1 H, PhC*H*=C), 7.30–7.43 (m, 8 H, Ar), 7.73–7.78 (m, 2 H, Ar) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 112.9, 117.4, 118.1–119.4 (m), 128.4, 128.6 (2 C), 128.7 (2 C), 128.8 (2 C), 129.3 (2 C), 130.5, 133.4, 138.2, 144.6, 145.0 ppm. EI MS: *m*/*z* (%) = 233 (90) [M$^+$], 232 (100), 231 (45), 217 (15), 204 (22), 155 (42), 129 (17), 116 (24), 92 (32), 77 (24), 63 (8).

Supporting Information (see also the footnote on the first page of this article): Copies of ^{1}H and ^{13}C NMR, and GC traces of dienes **5**.

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Received: April 17, 2008
Published Online: June 18, 2008

