

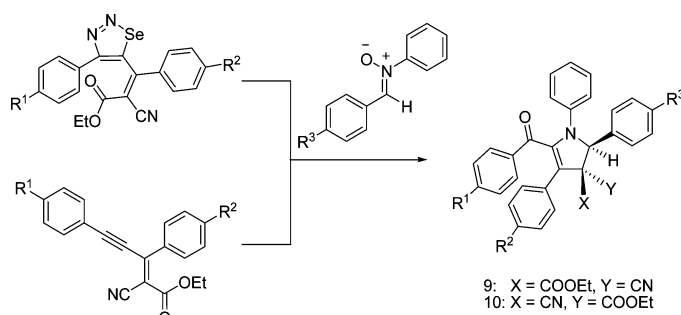
Synthesis of Highly Substituted 2,3-Dihydro-1*H*-pyrrole Derivatives via a Tandem Regioselective Addition of Nitrones to 1,3-Enynes with Subsequent Rearrangement

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A novel method for the synthesis of 1,3-enynes is described through oxidative cyclization of the semicarbazones of Michael adducts having potential nitrile functionality. Reaction of these 1,3-enynes with diaryl nitrones has yielded a diastereomeric mixture of highly substituted 2,3-dihydro-1*H*-pyrrole derivatives via a tandem regioselective addition with subsequent rearrangement.

Introduction

1,3-Enyne functionality can be found in many naturally occurring and biologically active compounds. The most potent antifungal agent possessing this substructure is terbinafine (commonly known as Lamisil), which is used to treat fungal infections of the toe and finger nails. It inhibits ergosterol synthesis by inhibiting squalene epoxidase, an enzyme that is involved in the fungal cell wall synthesis.¹ Although the palladium(0)-catalyzed Sonogashira coupling² of terminal alkynes with aryl or vinyl halides is one of the most widely employed methods for the synthesis of conjugated enynes, the other commonly utilized methodologies to access 1,3-enynes are copper(I)-catalyzed coupling³ and nickel-catalyzed alkynyl

boration of alkynes.⁴ Synthesis of 1,3-enynes through alk-1-enyldialkylborane,⁵ alkenyl nonaflates,⁶ phosphorane,⁷ and partial catalytic hydrogenation⁸ have also been reported. Herein, we report a novel method for the synthesis of tetrasubstituted 1,3-enynes through oxidative cyclization of the semicarbazones of Michael adducts and their subsequent reactivity toward diaryl nitrones yielding highly substituted pyrrole derivatives. Syntheses of highly substituted pyrroles via transition-metal-catalyzed multicomponent coupling have been reported recently.⁹ Highly substituted pyrrole derivatives have also been prepared by the cycloaddition of alkene with azalactones and oxazolones.¹⁰

Results and Discussion

The synthetic approach started by modifying the reported procedure¹¹ for the Michael addition of ethyl cyanoacetate (**2**)

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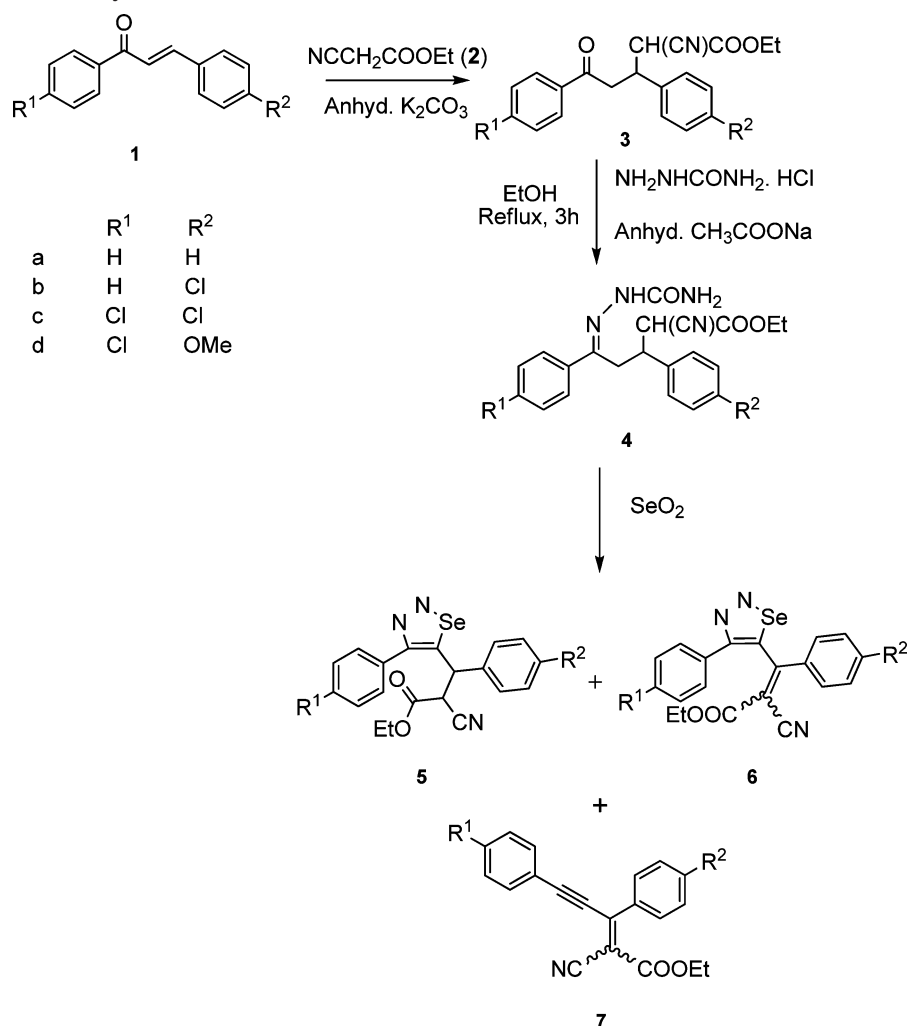
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SCHEME 1. Formation of Enyne and Oxidized Selenadiazole



to substituted benzylidene acetophenones (**1**) in the presence of an equimolar amount of potassium carbonate without any solvent at room temperature. It is also reported that the formation of cyclized products is quite common by the Michael addition of ethyl cyanoacetate with two molecules of benzylidene acetophenone followed by aldol condensation.¹² The members of the diastereomeric mixture of the Michael adduct have close R_f values, and hence, it is difficult to isolate the individual diastereomers (Scheme 1).

Without isolating the individual diastereomers, the ketones **3** were converted to their semicarbazones **4** by conventional methods.¹³ Quantitative conversion has been effected, and the diastereomeric pair has been obtained in the same ratio. It is to be noted that, of the two possible semicarbazone geometrical isomers, only one isomer has been obtained in all of the cases, probably the one in which the phenyl group and the NHCONH_2 are trans to each other. In these cases too, it is difficult to separate the diastereomers by column chromatography as they have close R_f values (Scheme 1).

Synthesis of 1,2,3-selenadiazoles is of recent interest as they are not only versatile intermediates for the preparation of alkynes and other selenium compounds¹⁴ but also have attracted much attention for their biological characteristics like antifungal, antibacterial, antimicrobial, and insecticidal activities.¹⁵ The semicarbazones **4** were then subjected to selenium dioxide treatment in THF to achieve the oxidative ring closure. Thus, when **4a** was subjected to selenium dioxide in THF, three products were formed as evident from TLC. These three fractions (**5a**, **6a**, **7a**) have been separated by column chromatography. The overall yield of these three products is 64%, and the ratio of **5a/6a/7a** is 48:27:25, as evident from the ^1H NMR spectrum of the crude mixture. The column-separated **5a**, **6a**, and **7a** have been analyzed for structure by spectral techniques. Thus, **5a** is an inseparable mixture of two diastereomeric forms of ethyl 2-cyano-3-phenyl-3-(4-phenyl-1,2,3-selenadiazol-5-yl)propanoate in the ratio 1:0.8, **6a** is ethyl 2-cyano-3-phenyl-3-(4-phenyl-1,2,3-selenadiazol-5-yl)-2-propenoate, and **7a** is the mixture of geometrical isomers of ethyl 2-cyano-3,5-diphenyl-2-penten-4-ynoate in a ratio of 5:1. The formation of the

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TABLE 1. Reaction of Semicarbazone **4** with Selenium Dioxide in Acetic Acid

entry	product	yield (%)	mp (°C)	product	yield (%)	mp (°C)
1	6a	36	125	7a	28	121
2	6b	31	127	7b	25	116
3	6c	34	138	7c	22	107
4	6d	32	viscous liquid	7d	23	viscous liquid

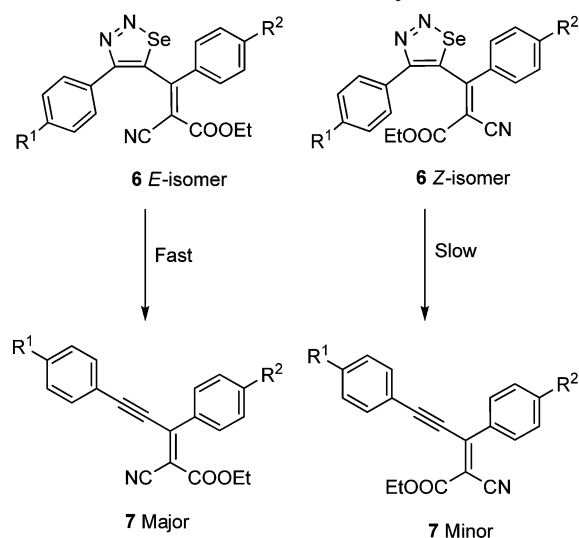
unexpected products, viz. **6a** and **7a**, can be rationalized considering the oxidation of the side chain by excess selenium dioxide and thermal decomposition of the alkene-substituted selenadiazole molecule. It is to be noted that such a dehydrogenation and elimination have not been observed in related reactions.¹⁶

The unexpected products **6** and **7** are ideally suited for the construction of heterocyclic compounds by cycloaddition strategies. Hence, the reaction of semicarbazone **4** with selenium dioxide was carried out in acetic acid with a 1:10 ratio of substrate and oxidizing agent to give compounds **6** and **7**, allowing **5** to react completely. The yields and melting points of the products are summarized in Table 1. An earnest attempt is made here to assign the correct stereochemistry of the major and minor isomers of **6** and **7** with the NMR data, and the following discussion offers a rationale for the formation of the major and minor isomers in the observed ratio.

In the *E* isomer of **6d**, the carbethoxy group and the aryl ring are cis to each other. Due to deshielding anisotropy of the aryl ring, the ethyl hydrogens are deshielded and, due to the deshielding effect of the carbonyl group, the aryl hydrogens of the *p*-methoxyphenyl ring are deshielded. The minor isomer of **6d** has its methylene hydrogens, methyl hydrogens, and *p*-methoxyphenyl hydrogens signals appearing at 4.4, 1.4, 7.8, and 7.0 ppm, respectively. The major isomer of **6d** has its methylene hydrogens, methyl hydrogens, and aromatic hydrogens signals appearing at 4.05, 1.12, 7.70, and 6.85 ppm, respectively. Hence, the major isomer has a *Z* configuration and the minor isomer has an *E* configuration. The *E* and *Z* isomers are in a ratio of 1:3 in **6d**. The structure of compound **6b** is unambiguously confirmed by single-crystal X-ray analysis (ORTEP 1, see the Supporting Information for more details).

Based on the same arguments, the stereochemistry for the major and minor isomers of **7d** can be assigned. The major isomer of **7d** has its methylene hydrogens, methyl hydrogens, and aromatic hydrogens at 4.40, 1.42, 7.85, and 7.00 ppm, respectively. The minor isomer has its methylene hydrogens, methyl hydrogens and aromatic hydrogens appearing at 4.25, 1.28, 7.50, and 6.94 ppm, respectively. It can be noticed that the isomer with deshielded hydrogens, which is supposed to be the *E* isomer, is the major isomer here and the isomer corresponding to the shielded hydrogens, the *Z* isomer, is the minor one. The *E* and *Z* isomers are in the ratio 2:1.

The observed ratio of *E* and *Z* isomers in **6d** and **7d** helps us to understand the course of the reaction. Selenium dioxide reacts initially with the α -methylene end of semicarbazone **4** to give selenadiazole **5**. In the presence of excess selenium dioxide, **5** is very reactive and gets further oxidized at the side chain to give an equal amount of the geometrical

SCHEME 2. Selective Formation of Enyne

isomers of **6**. The *E* form of **6** seems to be more vulnerable to thermolysis eliminating nitrogen and selenium to give the enyne than the other isomer. Hence, in the final reaction mixture consisting of **6** and **7**, the *E*-isomer dominates in **7** and *Z*-isomer dominates in **6** (Scheme 2). However, the reason for the preferential thermolysis of *E* form of **6** is not well understood.

It is well-known that 1,3-enynes behave as four electron donors in various intramolecular and intermolecular [4 + 2] cycloaddition reactions, which has found substantial application in experimental synthesis as an efficient and general route for ring construction of aromatic and dihydroaromatic compounds. The proposed mechanism of this reaction involves the formation of a six-membered allene (1,2,4-cyclohexatriene) and its derivatives.¹⁷ An inspection of the pertinent literature on the reactivity of 1,3-enynes revealed that the 1,3-dipolar addition of diazoalkane, chlorobenzylidene-*N*-phenylhydrazine, α ,*N*-diphenylnitrone, benzonitrile *N*-oxide 1,3-diphenylnitriloamine with various substituted enynes takes place at the double bond, not at the triple bond, leading to pyrazoline and isoxazolidine derivatives.¹⁸ As **7a–d** are good dipolorophiles, we effected the cycloaddition with nitrones (**8**) viz., α -(4-chlorophenyl)-*N*-phenyl nitron (**8a**) and α -(4-methoxyphenyl)-*N*-phenyl nitron (**8b**) expecting 1,3-dipolar addition to take place leading to isoxazoline derivatives.

However, the reaction proceeds smoothly, giving two isomeric products (**9** and **10**) in good yield in an almost equal ratio (Scheme 3). The *R_f* values of **9** and **10** are closer, but they have been successfully separated by column chromatography, and the structures of the products are deduced by two-dimensional NMR connectivity analysis to be isomeric pyrrole derivatives.

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SCHEME 3. Reaction of Enyne 7 with Dipole 8

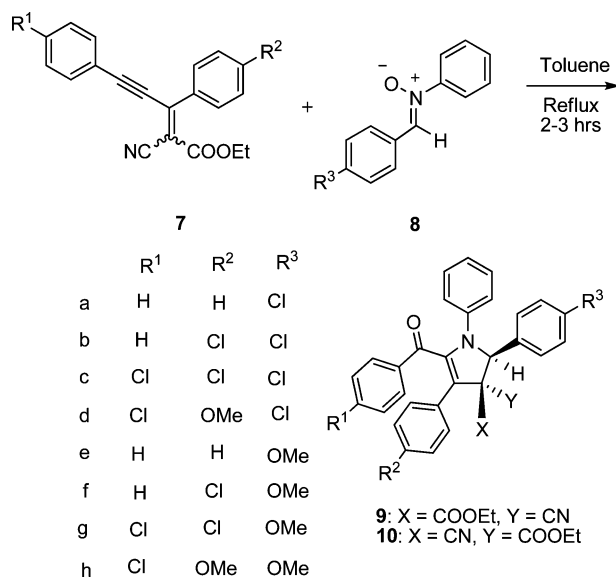


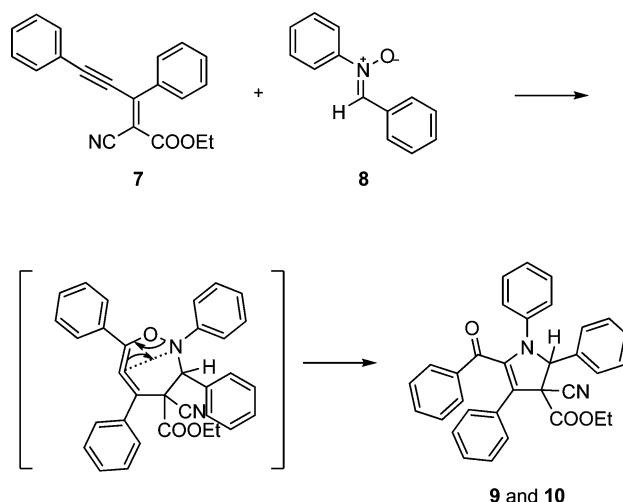
TABLE 2. Reaction of 1,3-Enyne 7 with Nitrone 8

entry	product	yield (%)	product	yield (%)
1	9a	43	10a	38
2	9b	34	10b	27
3	9c	40	10c	29
4	9d	36	10d	28
5	9e	35	10e	29
6	9f	33	10f	27
7	9g	46	10g	36
8	9h	28	10h	24

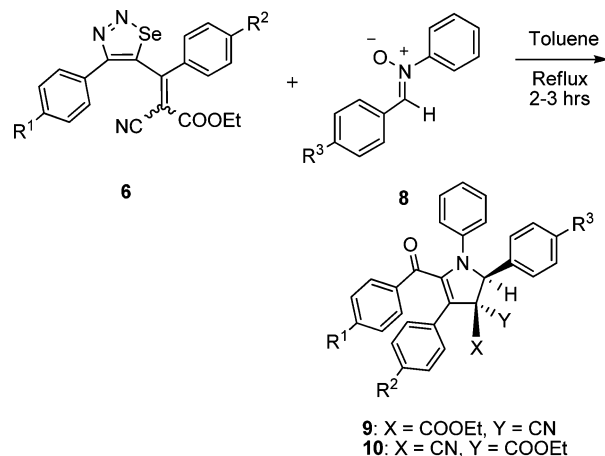
The fact that the expected cycloadducts were not formed has been inferred by the presence of carbonyl carbon signals beyond 190.0 ppm shown in the ^{13}C NMR spectra of both the products. Compounds **9** and **10** have a close ^1H NMR spectral pattern with small chemical shift differences due to the ortho hydrogens of benzoyl ring, methine, methylene, and methyl hydrogens. In the ^{13}C NMR spectra, the remarkable difference is that the methine carbon appears at 77.2 ppm in **9a** but at 75.5 ppm in **10a**. Obviously, these two compounds are stereoisomers arising due to a change in the orientation of the cyano and the carboxy groups with respect to the hydrogen and aryl group in the nearby carbon. However, the spectral data are not very helpful in distinguishing **9** and **10**, preventing the correct stereochemical assignment for **9** and **10**.

The reaction has been carried out with differently substituted enynes, and the results are summarized in Table 2. Fortunately, it was possible to grow a single crystal of **9g** to assign the structure unambiguously. It is clear from the crystal structure that compounds **9** are those diastereoisomers in which the aryl group at the C-2 position of the pyrrole and the cyano group at C-3 position are trans to each other, and hence, these two groups must have a cis relationship in **10**. From the crystal structure (ORTEP 2, see the Supporting Information for more details), it is clear that the methylene and methyl hydrogens of carboxy group at C-3 of **9** are in the shielding region of the aryl ring at the C-2 position, which is very much evident from the ^1H NMR data. For **9g**, the methyl and methylene hydrogens appear at 0.96 and 3.89 ppm, respectively, while for **10g**, these hydrogens appear at 1.24 and 4.32 ppm, respectively. The ortho hydrogens of the aryl ring at C-5 are deshielded in **9g** compared to **10g**,

SCHEME 4. Mechanism for the Formation of 9 and 10



SCHEME 5. Reaction of Selenadiazole 6 with Dipole 8



and this is due to the anisotropy of the ester carbonyl in the former, as supported by the crystal structure.

The formation of the product can be explained by considering the dipolar addition of the nitrone moiety with enyne, not in a [4 + 2] fashion but in a [3 + 4] fashion. Obviously, this reaction may not be concerted because a [3 + 4] reaction is not thermally allowed and hence stepwise. A very unstable seven membered allene type intermediate can be proposed which subsequently undergoes rearrangement as shown in the following scheme (Scheme 4).

This type of strained cyclic allene intermediate has already been proposed.¹⁹ An attempted cycloaddition of **6** instead of **7** with α -N-diarylnitrone has also been made. Here again, it is found that compounds **9** and **10** are formed in the same ratio. Elimination of nitrogen and selenium would have occurred in **6** prior to the cycloaddition and hence the reaction is very similar to that of **7** with nitrone (Scheme 5).

Conclusion

In summary, a novel method for the synthesis of 1,3-enynes is described starting from readily available precursors. Reaction

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of these 1,3-enynes with diaryl nitrones has been shown to give a diastereomeric mixture of highly substituted 2,3-dihydro-1H-pyrrole derivatives via a tandem regioselective addition with subsequent rearrangement.

Experimental Section

Typical Procedure for the Reaction of Semicarbazone (4) with Selenium Dioxide. A solution of semicarbazone **4** (0.005 mol) and powdered selenium dioxide (0.05 mol) in THF/acetic acid (15 mL) was gently heated on a water bath for 2 h. The selenium deposited on cooling was removed by filtration, and the filtrate was poured into crushed ice, extracted with chloroform, and purified by column chromatography using silica gel (60–120 mesh) with 97:3 petroleum ether/ethyl acetate as eluent to give an acetylene derivative (**7**) and the selenadiazoles (**5** and **6**), which were recrystallized from ethyl alcohol.

According to the typical procedure, semicarbazone **4a** was treated with selenium dioxide in THF to get 38% of **5a**, 14% of **6a**, and 13% of **7a**.

Ethyl 2-cyano-3-phenyl-3-(4-phenyl-1,2,3-selenadiazol-5-yl)-propanoate (5a): viscous liquid; IR (cm⁻¹) 2250, 1749, 1604, 1025; ¹H NMR (300 MHz, CDCl₃) δ 1.02 (t, *J* = 7.2 Hz, 3H), 1.07 (t, *J* = 7.2 Hz, 3H), 3.95–4.10 (m, 5H), 4.13 (d, *J* = 6.6 Hz, 1H), 5.27 (d, *J* = 7.5 Hz, 1H), 5.35 (d, *J* = 6.3 Hz, 1H), 7.26 (d, *J* = 7.5 Hz, 2H), 7.33–7.38 (m, 8H), 7.50–7.56 (m, 10H); ¹³C NMR (75 MHz, CDCl₃) δ 13.5, 13.6, 46.0, 46.1, 46.7, 47.5, 63.2, 63.3, 114.4, 114.7, 127.6, 127.8, 128.6, 128.8, 128.9, 129.0, 129.2, 129.3, 129.4, 129.6, 129.7, 131.0, 131.2, 136.8, 137.1, 156.1, 158.6, 160.2, 161.8, 163.3, 163.5. *One carbon has merged with another.

Ethyl 2-cyano-3-phenyl-3-(4-phenyl-1,2,3-selenadiazol-5-yl)-2-propenoate (6a): mp = 125 °C; IR (cm⁻¹) 2219, 1727, 1255, 1122; ¹H NMR (300 MHz, CDCl₃) δ (major isomer alone) 1.11 (t, *J* = 7.2 Hz, 3H), 4.05 (q, *J* = 7.2 Hz, 2H), 7.38–7.49 (m, 8H), 7.69 (dd, *J* = 9.0, 3.3 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 13.7, 62.9, 107.3, 115.6, 128.8, 128.9, 129.0, 129.2, 129.5, 130.7, 132.4, 136.1, 153.8, 159.4, 159.8, 160.9. Anal. Calcd for C₂₀H₁₅N₃O₂Se: C, 58.83; H, 3.70; N, 10.29. Found: C, 58.85; H, 3.71; N, 10.31.

Ethyl 2-cyano-3,5-diphenyl-2-penten-4-ynoate (7a): mp = 121 °C; IR (cm⁻¹) 2185, 1724, 1246, 1130; ¹H NMR (300 MHz, CDCl₃) δ (major isomer alone) 1.40 (t, *J* = 7.2 Hz, 3H), 4.41 (q, *J* = 7.2 Hz, 2H), 7.39–7.52 (m, 6H), 7.60 (dd, *J* = 8.1, 1.8 Hz, 2H), 7.81 (dd, *J* = 7.8, 1.8 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 14.2, 16.3, 88.7, 108.6, 113.8, 116.3, 121.6, 128.6, 128.7, 128.8, 130.7, 131.4, 132.6, 136.1, 149.5, 161.4. Anal. Calcd for C₂₀H₁₅NO₂: C, 79.72; H, 5.02; N, 4.65. Found: C, 79.75; H, 5.03; N, 4.65.

According to the typical procedure, semicarbazone **4b** was treated with selenium dioxide in acetic acid to give 31% of **6b** and 25% of **7b**.

Ethyl 3-(4-chlorophenyl)-2-cyano-3-(4-phenyl-1,2,3-selenadiazol-5-yl)-2-propenoate (6b): mp = 127 °C; IR (cm⁻¹) 2217, 1733, 1629, 1251; ¹H NMR (300 MHz, CDCl₃) δ 1.12 (t, *J* = 7.2 Hz, 3H), 4.07 (q, *J* = 7.2 Hz, 2H), 7.35–7.45 (m, 7H), 7.66 (dd, *J* = 7.8, 1.8 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 13.7, 63.0, 107.7, 115.4, 128.8, 129.0, 129.3, 129.6, 130.4, 130.6, 134.2, 138.7, 153.1, 158.5, 159.5, 160.7. Anal. Calcd for C₂₀H₁₄ClN₃O₂Se: C, 54.25; H, 3.19; N, 9.49. Found: C, 54.27; H, 3.20; N, 9.49.

Ethyl 3-(4-chlorophenyl)-2-cyano-5-phenyl-2-penten-4-ynoate (7b): mp = 116 °C; IR (cm⁻¹) 2192, 1727, 1535, 1241; ¹H NMR (300 MHz, CDCl₃) δ 1.41 (t, *J* = 7.2 Hz, 3H), 4.40 (q, *J* = 7.2 Hz, 2H), 7.35–7.50 (m, 5H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 8.7 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 14.3, 62.9, 88.8, 109.1, 114.5, 116.5, 121.8, 129.0, 129.5, 130.6, 131.3, 133.0, 134.8, 138.1, 148.4, 161.5. Anal. Calcd for C₂₀H₁₄ClNO₂: C, 71.54; H, 4.20; N, 4.17. Found: C, 71.55; H, 4.24; N, 4.19.

According to the typical procedure, semicarbazone **4c** was treated with selenium dioxide in acetic acid to give 34% of **6c** and 22% of **7c**.

Ethyl 3-(4-chlorophenyl)-3-[4-(4-chlorophenyl)-1,2,3-selenadiazol-5-yl]-2-cyano-2-propenoate (6c): mp = 138 °C; IR (cm⁻¹) 2215, 1739, 1587, 1253; ¹H NMR (300 MHz, CDCl₃) δ 1.15 (t, *J* = 6.9 Hz, 3H), 4.09 (q, *J* = 6.9 Hz, 2H), 7.35–7.45 (m, 6H), 7.62 (d, *J* = 8.4 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 13.7, 63.1, 107.7, 115.2, 129.0, 129.3, 129.4, 130.0, 130.5, 133.8, 135.7, 138.9, 153.4, 158.0, 158.2, 160.6. Anal. Calcd for C₂₀H₁₃Cl₂N₃O₂Se: C, 50.34; H, 2.75; N, 8.81. Found: C, 50.33; H, 2.75; N, 8.82.

Ethyl 3,5-bis(4-chlorophenyl)-2-cyano-2-penten-4-ynoate (7c): mp = 107 °C; IR (cm⁻¹) 2192, 1724, 1535, 1243; ¹H NMR (300 MHz, CDCl₃) δ 1.41 (t, *J* = 7.2 Hz, 3H), 4.40 (q, *J* = 7.2 Hz, 2H), 7.37 (d, *J* = 9.0 Hz, 2H), 7.47 (d, *J* = 8.7 Hz, 2H), 7.53 (d, *J* = 8.7 Hz, 2H), 7.74 (d, *J* = 9.0 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 14.1, 62.5, 89.1, 109.0, 112.5, 114.6, 119.8, 129.1, 129.2, 129.8, 133.8, 134.2, 137.2, 137.8, 147.7, 161.0. Anal. Calcd for C₂₀H₁₃Cl₂NO₂: C, 64.88; H, 3.54; N, 3.78. Found: C, 64.91; H, 3.54; N, 3.79.

According to the typical procedure, semicarbazone **4d** was treated with selenium dioxide in acetic acid to give 32% of **6d** and 23% of **7d**.

Ethyl 3-[4-(4-chlorophenyl)-1,2,3-selenadiazol-5-yl]-2-cyano-3-(4-methoxyphenyl)-2-propenoate (6d): viscous liquid; IR (cm⁻¹) 2188, 1729, 1577, 1336; ¹H NMR (300 MHz, CDCl₃) δ (major isomer alone) 1.12 (t, *J* = 7.2 Hz, 3H), 3.83 (s, 3H), 4.05 (q, *J* = 7.2 Hz, 2H), 6.85 (d, *J* = 9.0 Hz, 2H), 7.38 (d, *J* = 8.7 Hz, 2H), 7.48 (d, *J* = 9 Hz, 2H), 7.70 (d, *J* = 8.7 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 13.7, 55.5, 62.6, 104.3, 114.4, 116.2, 127.7, 128.5, 129.3, 131.0, 133.6, 135.4, 154.6, 157.9, 158.7, 161.2, 163.2.

Ethyl 5-(4-chlorophenyl)-2-cyano-3-(4-methoxyphenyl)-2-penten-4-ynoate (7d): viscous liquid; IR (cm⁻¹) 2188, 1735, 1507, 1336; ¹H NMR (300 MHz, CDCl₃) δ (major isomer alone) 1.42 (t, *J* = 6.9 Hz, 3H), 3.88 (s, 3H), 4.40 (q, *J* = 6.9 Hz, 2H), 7.00 (d, *J* = 8.7 Hz, 2H), 7.38 (d, *J* = 8.7 Hz, 2H), 7.54 (d, *J* = 8.7 Hz, 2H), 7.85 (d, *J* = 8.7 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 14.2, 55.5, 62.2, 89.4, 106.4, 111.3, 114.1, 116.9, 120.1, 128.0, 129.1, 131.1, 133.7, 136.9, 148.5, 162.4.

Typical Procedure for the Reaction of Ethyl 2-Cyano-3,5-diaryl-2-penten-4-ynoate (7) with α-Aryl-N-phenylnitrone (8). A solution of ethyl 2-cyano-3,5-diaryl-2-penten-4-ynoate **7** (0.0005 mol) and α-(4-chlorophenyl)-N-phenylnitrone **8a** (4-methoxyphenyl)-N-phenylnitrone **8b** (0.0006 mol) in toluene (20 mL) was refluxed for 2–3 h. After completion of the reaction, the solvent was evaporated under reduced pressure and the products **9** and **10** were separated by column chromatography using silica gel (60–120 mesh) with 97:3 petroleum ether/ethyl acetate as eluent.

Ethyl 5-benzoyl-3-cyano-2-(4-chlorophenyl)-1,4-diphenyl-2,3-dihydro-1H-pyrrole-3-carboxylate (9a) was obtained by following the typical procedure with **7a** and **8a** (yield = 43%; viscous liquid): IR (cm⁻¹) 2225, 1743, 1671; ¹H NMR (300 MHz, CDCl₃) δ 0.94 (t, *J* = 7.2 Hz, 3H), 3.85 (q, *J* = 7.2 Hz, 2H), 5.74 (s, 1H), 6.87 (d, *J* = 7.8 Hz, 2H), 7.00–7.70 (m, 15H), 8.15 (d, *J* = 7.8 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 13.4, 61.3, 63.2, 77.2, 114.4, 117.9, 124.2, 125.9, 127.2, 128.5, 128.6, 128.8, 129.1, 129.5, 129.6, 129.7, 131.0, 132.0, 134.2, 135.2, 135.4, 141.7, 148.0, 164.4, 190.1.

Ethyl 5-benzoyl-3-cyano-2-(4-chlorophenyl)-1,4-diphenyl-2,3-dihydro-1H-pyrrole-3-carboxylate (10a) was obtained by following the typical procedure with **7a** and **8a** (yield = 38%; viscous liquid): IR (cm⁻¹) 2242, 1743, 1668; ¹H NMR (300 MHz, CDCl₃) δ 1.21 (t, *J* = 7.2 Hz, 3H), 4.33 (q, *J* = 7.2 Hz, 2H), 5.70 (s, 1H), 6.83 (d, *J* = 7.2 Hz, 2H), 7.00–7.70 (m, 15H), 7.98 (d, *J* = 7.8 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 13.9, 62.7, 64.0, 75.5, 114.6, 115.7, 123.0, 125.9, 128.0, 128.4, 128.5, 128.7, 129.2, 129.3, 129.5, 129.6, 130.8, 133.1, 134.2, 135.4, 135.7, 141.7, 146.8, 166.9, 190.1.

Ethyl 5-benzoyl-3-cyano-2,4-bis(4-chlorophenyl)-1-phenyl-2,3-dihydro-1H-pyrrole-3-carboxylate (9b) was obtained by following the typical procedure with **7b** and **8a** (yield = 34%; mp = 139 °C): IR (cm⁻¹) 2244, 1741, 1673, 1592, 1230; ¹H NMR (300 MHz, CDCl₃) δ 0.95 (t, *J* = 7.2 Hz, 3H), 3.86 (m, 2H), 5.48 (s, 1H) 6.86 (d, *J* = 7.2 Hz, 2H), 7.00–7.86 (m, 14H), 8.15 (d, *J* = 7.5 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 13.5, 61.1, 63.4, 77.0, 112.9, 117.7, 124.4, 126.2, 128.5, 128.7, 128.8, 128.9, 129.2, 129.7, 131.7, 133.4, 134.5, 135.4, 135.5, 141.5, 148.8, 164.7, 190.7. Anal. Calcd for C₃₃H₂₄Cl₂N₂O₃: C, 69.85; H, 4.26; N, 4.94. Found: C, 69.84; H, 4.28; N, 4.96.

Ethyl 5-benzoyl-3-cyano-2,4-bis(4-chlorophenyl)-1-phenyl-2,3-dihydro-1H-pyrrole-3-carboxylate (10b) was obtained by following the typical procedure with **7b** and **8a** (yield = 27%; viscous liquid): IR (cm⁻¹) 2238, 1743, 1670, 1598, 1213; ¹H NMR (300 MHz, CDCl₃) δ 1.24 (t, *J* = 7.2 Hz, 3H), 4.34 (m, 2H), 5.73 (s, 1H) 6.84 (d, *J* = 7.5 Hz, 2H), 6.98 (d, *J* = 7.5 Hz, 2H), 7.09 (t, *J* = 7.8 Hz, 2H), 7.14 (d, *J* = 7.4 Hz, 2H), 7.22 (d, *J* = 8.7 Hz, 2H), 7.35–7.55 (m, 6H), 7.99 (d, *J* = 7.5 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 13.9, 62.4, 64.0, 76.5, 112.8, 115.6, 123.2, 125.6, 128.6, 128.8, 129.2, 129.3, 129.4, 129.5, 132.7, 133.7, 134.5, 135.4, 135.5, 141.3, 147.4, 166.7, 189.9.

Ethyl 5-(4-chlorobenzoyl)-3-cyano-2,4-bis(4-chlorophenyl)-1-phenyl-2,3-dihydro-1H-pyrrole-3-carboxylate (9c) was obtained by following the typical procedure with **7c** and **8a** (yield = 40%; mp = 147 °C): IR (cm⁻¹) 2244, 1743, 1671, 1587, 1093; ¹H NMR (300 MHz, CDCl₃) δ 0.95 (t, *J* = 7.2 Hz, 3H), 3.87 (m, 2H), 5.69 (s, 1H), 6.87 (d, *J* = 7.2 Hz, 2H), 7.02–7.20 (m, 7H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.7 Hz, 2H), 7.50 (d, *J* = 8.7 Hz, 2H), 8.11 (d, *J* = 8.4 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 13.4, 61.1, 63.6, 77.6, 113.3, 117.5, 124.7, 126.5, 128.5, 128.9, 129.0, 129.3, 129.4, 129.6, 129.7, 131.0, 131.5, 133.7, 133.9, 135.5, 141.1, 141.4, 148.5, 164.7, 189.5. Anal. Calcd for C₃₃H₂₃Cl₃N₂O₃: C, 65.85; H, 3.85; N, 4.65. Found: C, 65.86; H, 3.87; N, 4.66.

Ethyl 5-(4-chlorobenzoyl)-3-cyano-2,4-bis(4-chlorophenyl)-1-phenyl-2,3-dihydro-1H-pyrrole-3-carboxylate (10c) was obtained by following the typical procedure with **7c** and **8a** (yield = 29%; viscous liquid): IR (cm⁻¹) 2227, 1745, 1670, 1589, 1093; ¹H NMR (300 MHz, CDCl₃) δ 1.23 (t, *J* = 6.9 Hz, 3H), 4.32 (m, 2H), 5.68 (s, 1H), 6.82 (d, *J* = 7.2 Hz, 2H), 7.00 (t, *J* = 7.2 Hz, 1H), 7.09 (t, *J* = 7.8 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 6.9 Hz, 2H), 7.40 (d, *J* = 8.7 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.92 (d, *J* = 8.7 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 13.9, 22.3, 64.1, 75.6, 113.2, 115.5, 123.3, 125.8, 128.7, 129.2, 129.3, 129.4, 130.7, 130.8, 132.5, 133.8, 134.0, 135.6, 141.1, 142.2, 147.0, 166.6, 188.7.

Ethyl 5-(4-chlorobenzoyl)-3-cyano-2-(4-chlorophenyl)-4-(4-methoxyphenyl)-1-phenyl-2,3-dihydro-1H-pyrrole-3-carboxylate (9d) was obtained by following the typical procedure with **7d** and **8a** (yield = 36%; mp = 116 °C): IR (cm⁻¹) 2246, 1741, 1671, 1590, 1249; ¹H NMR (300 MHz, CDCl₃) δ 0.95 (t, *J* = 7.2 Hz, 3H), 3.79 (s, 3H), 3.85 (disturbed multiplet, 2H), 5.60 (s, 1H), 6.73 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 7.2 Hz, 2H), 6.99 (t, *J* = 7.2 Hz, 1H), 7.08 (t, *J* = 7.2 Hz, 2H), 7.19 (d, *J* = 9.0 Hz, 2H), 7.38 (d, *J* = 9.0 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 8.12 (d, *J* = 7.2 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 13.5, 55.1, 61.8, 63.1, 78.2, 114.1, 115.4, 117.8, 123.1, 124.6, 126.2, 128.8, 128.9, 129.1, 129.3, 129.7, 131.0, 131.7, 134.2, 135.3, 140.7, 142.2, 147.1, 159.2, 164.9, 190.0. Anal. Calcd for C₃₄H₂₆Cl₂N₂O₄: C, 68.35; H, 4.39; N, 4.69. Found: C, 68.36; H, 4.41; N, 4.68.

Ethyl 5-(4-chlorobenzoyl)-3-cyano-2-(4-chlorophenyl)-4-(4-methoxyphenyl)-1-phenyl-2,3-dihydro-1H-pyrrole-3-carboxylate (10d) was obtained by following the typical procedure with **7d** and **8a** (yield = 28%; viscous liquid): IR (cm⁻¹) 2246, 1741, 1671, 1590, 1249; ¹H NMR (300 MHz, CDCl₃) δ 1.27 (t, *J* = 7.2 Hz, 3H), 3.72 (s, 3H), 4.32 (disturbed multiplet, 2H), 5.62 (s, 1H), 6.71 (d, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 7.2 Hz, 2H), 6.98 (d, *J* = 7.5 Hz, 2H), 7.09 (d, *J* = 7.5 Hz, 2H), 7.18 (d, *J* = 9.0 Hz, 2H), 7.34 (d, *J* = 8.7 Hz, 2H), 7.41 (d, *J* = 8.7 Hz, 2H) 7.54 (d, *J* = 8.7

Hz, 2H), 7.93 (d, *J* = 8.7 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 13.9, 55.1, 62.8, 63.9, 75.5, 113.9, 115.5, 115.6, 122.8, 122.9, 125.3, 129.1, 129.2, 129.3, 129.4, 129.6, 130.8, 131.2, 134.1, 135.4, 140.6, 141.8, 145.5, 159.4, 166.9, 188.9.

Ethyl 5-benzoyl-3-cyano-2-(4-methoxyphenyl)-1,4-diphenyl-2,3-dihydro-1H-pyrrole-3-carboxylate (9e) was obtained by following the typical procedure with **7a** and **8b** (yield = 35%; mp = 99 °C): IR (cm⁻¹) 2223, 1745, 1671, 1606, 1025; ¹H NMR (300 MHz, CDCl₃) δ 0.95 (t, *J* = 7.2 Hz, 3H), 3.80 (s, 3H), 3.84 (m, 2H), 5.71 (s, 1H), 6.85–5.55 (m, 17H), 8.17 (d, *J* = 8.4 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 13.4, 55.2, 61.5, 63.0, 77.8, 113.9, 118.2, 124.2, 125.2, 125.6, 127.2, 127.4, 128.2, 128.4, 128.6, 129.0, 129.6, 129.7, 131.4, 134.1, 135.8, 142.0, 148.1, 160.2, 165.1, 191.0. Anal. Calcd for C₃₄H₂₈N₂O₄: C, 77.25; H, 5.34; N, 5.30. Found: C, 77.28; H, 5.37; N, 5.33.

Ethyl 5-benzoyl-3-cyano-2-(4-methoxyphenyl)-1,4-diphenyl-2,3-dihydro-1H-pyrrole-3-carboxylate (10e) was obtained by following the typical procedure with **7a** and **8b** (yield = 29%; viscous liquid): IR (cm⁻¹) 2244, 1741, 1670, 1610, 1031; ¹H NMR (300 MHz, CDCl₃) δ 1.22 (t, *J* = 7.2 Hz, 3H), 3.80 (s, 3H), 4.30 (m, 2H), 5.67 (s, 1H), 6.85–7.55 (m, 17H), 8.00 (d, *J* = 8.7 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 13.8, 55.1, 62.9, 63.7, 75.9, 114.2, 115.9, 122.0, 124.9, 127.2, 127.7, 127.9, 128.2, 128.4, 128.6, 129.0, 129.3, 129.5, 131.1, 134.1, 135.7, 141.8, 146.8, 160.2, 167.2, 190.3.

Ethyl 5-benzoyl-3-cyano-4-(4-chlorophenyl)-2-(4-methoxyphenyl)-1-phenyl-2,3-dihydro-1H-pyrrole-3-carboxylate (9f) was obtained by following the typical procedure with **7b** and **8b** (yield = 33%; mp = 157 °C): IR (cm⁻¹) 2244, 1739, 1668, 1255; ¹H NMR (300 MHz, CDCl₃) δ 0.96 (t, *J* = 7.2 Hz, 3H), 3.79 (s, 3H), 3.86 (m, 2H), 5.70 (s, 1H), 6.85–7.60 (m, 16H), 8.16 (d, *J* = 8.4 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 13.5, 55.2, 61.3, 63.2, 77.9, 112.8, 113.9, 118.0, 124.5, 124.9, 125.9, 128.5, 128.7, 128.8, 129.1, 129.6, 129.7, 130.0, 133.2, 134.4, 135.6, 141.7, 148.9, 160.3, 165.0, 190.9. Anal. Calcd for C₃₄H₂₇ClN₂O₄: C, 72.53; H, 4.83; N, 4.98. Found: C, 72.53; H, 4.84; N, 4.99.

Ethyl 5-benzoyl-3-cyano-4-(4-chlorophenyl)-2-(4-methoxyphenyl)-1-phenyl-2,3-dihydro-1H-pyrrole-3-carboxylate (10f) was obtained by following the typical procedure with **7b** and **8b** (yield = 27%; mp = 107 °C): IR (cm⁻¹) 2337, 1741, 1668, 1247; ¹H NMR (300 MHz, CDCl₃) δ 1.24 (t, *J* = 7.2 Hz, 3H), 3.80 (s, 3H), 4.33 (m, 2H), 5.68 (s, 1H), 6.82–7.60 (m, 16H), 8.00 (d, *J* = 8.4 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 13.9, 55.2, 62.7, 63.8, 75.9, 112.7, 114.3, 115.9, 123.2, 125.3, 126.0, 128.5, 128.8, 129.0, 129.1, 129.3, 129.4, 129.7, 133.4, 134.4, 135.6, 141.5, 147.5, 160.3, 166.9, 190.2. Anal. Calcd for C₃₄H₂₇ClN₂O₄: C, 72.53; H, 4.83; N, 4.98. Found: C, 72.55; H, 4.83; N, 4.99.

Ethyl 5-(4-chlorobenzoyl)-3-cyano-4-(4-chlorophenyl)-2-(4-methoxyphenyl)-1-phenyl-2,3-dihydro-1H-pyrrole-3-carboxylate (9g) was obtained by following the typical procedure with **7c** and **8b** (yield = 46%; mp = 153 °C): IR (cm⁻¹) 2360, 1668, 1610, 1376; ¹H NMR (300 MHz, CDCl₃) δ 0.96 (t, *J* = 7.2 Hz, 3H), 3.80 (s, 3H), 3.89 (m, 2H), 5.66 (s, 1H), 6.85–7.50 (m, 15H), 8.12 (d, *J* = 8.4 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 13.5, 55.2, 61.3, 63.3, 78.1, 113.2, 113.9, 117.8, 124.6, 124.7, 126.6, 128.4, 128.8, 129.1, 129.2, 129.6, 129.7, 131.0, 133.4, 133.9, 140.9, 141.7, 148.6, 160.3, 164.9, 189.7. Anal. Calcd for C₃₄H₂₆Cl₂N₂O₄: C, 68.35; H, 4.39; N, 4.69. Found: C, 68.36; H, 4.41; N, 4.70.

Ethyl 5-(4-chlorobenzoyl)-3-cyano-4-(4-chlorophenyl)-2-(4-methoxyphenyl)-1-phenyl-2,3-dihydro-1H-pyrrole-3-carboxylate (10g) was obtained by following the typical procedure with **7c** and **8b** (yield = 36%; viscous liquid): IR (cm⁻¹) 2246, 1741, 1670, 1211; ¹H NMR (300 MHz, CDCl₃) δ 1.24 (t, *J* = 7.2 Hz, 3H), 3.80 (s, 3H), 4.32 (m, 2H), 5.65 (s, 1H), 6.80–7.55 (m, 15H), 7.95 (d, *J* = 8.7 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 13.9, 55.1, 62.7, 63.9, 76.1, 113.1, 114.3, 115.7, 123.3, 125.5, 125.9, 128.6, 129.1, 129.2, 129.3, 129.5, 130.7, 133.7, 133.9, 140.9, 141.5, 147.1, 160.4, 166.9, 188.9.

Ethyl 5-(4-chlorobenzoyl)-3-cyano-2,4-bis-(4-methoxyphenyl)-1-phenyl-2,3-dihydro-1H-pyrrole-3-carboxylate (9h) was obtained by following the typical procedure with **7d** and **8b** (yield = 28%; mp = 158 °C): IR (cm⁻¹) 2238, 1737, 1666, 1589, 1255; ¹H NMR (300 MHz, CDCl₃) δ 0.95(t, *J* = 7.2 Hz, 3H), 3.72 (s, 3H), 3.80 (s, 3H), 3.85 (m, 2H), 5.60 (s, 1H), 6.70–7.50 (m, 15H), 8.12 (d, *J* = 8.7 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 13.5, 55.1, 55.3, 61.8, 63.1, 78.2, 113.9, 114.0, 115.3, 118.1, 123.4, 124.5, 125.1, 125.9, 128.9, 129.0, 129.1, 129.6, 131.6, 134.3, 140.5, 142.5, 147.2, 159.1, 160.2, 165.1, 189.9. Anal. Calcd for C₃₅H₂₉ClN₂O₅: C, 70.88; H, 4.93; N, 4.72. Found: C, 70.90; H, 4.95; N, 4.75.

Ethyl 5-(4-chlorobenzoyl)-3-cyano-2,4-bis-(4-methoxyphenyl)-1-phenyl-2,3-dihydro-1H-pyrrole-3-carboxylate (10h) was obtained by following the typical procedure with **7d** and **8b** (yield = 24%; viscous liquid): IR (cm⁻¹) 2244, 1741, 1668, 1178; ¹H NMR (300 MHz, CDCl₃) δ 1.26 (t, *J* = 7.2 Hz, 3H), 3.71 (s, 3H), 3.80 (s, 3H), 4.33 (m, 2H), 5.58 (s, 1H), 6.70–7.55 (m, 15H), 7.95 (d, *J* = 8.4 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 13.9, 55.0, 55.1, 63.1, 63.7, 76.0, 113.8, 114.0, 115.5, 115.9, 122.9, 123.1, 124.9, 126.5, 128.9, 129.0, 129.5, 129.6, 130.8, 134.2, 140.5, 142.2, 145.5, 159.3, 160.3, 167.1, 189.1.

Reaction of Ethyl 2-Cyano-3-phenyl-3-(4-phenyl-1,2,3-selenadiazol-5-yl)-2-propenoate (6a) with α-(4-Chlorophenyl)-N-

phenylnitrone (8a). A solution of ethyl 2-cyano-3-phenyl-3-(4-phenyl-1,2,3-selenadiazol-5-yl)-2-propenoate **6a** (0.06 g, 0.00015 mol) and α-(4-chlorophenyl)-N-phenylnitrone **8a** (0.046 g, 0.0002 mol) in toluene (20 mL) was refluxed for 2–3 h. After completion of the reaction, the solvent was evaporated under reduced pressure, and the products were separated by column chromatography using silica gel (60–120 mesh) with 97:3 petroleum ether: ethyl acetate as eluent. Yield of **9a**: 42%. Yield of **10a**: 35%.

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Supporting Information Available: General experimental procedures, ¹H and ¹³C NMR spectra for synthesized compounds, and crystallographic information files (CIF) for compounds **6b** and **9g**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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