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Tetrahedron 63 (2007) 7866–7873
Tetrahedron

An efficient route to vinyl substituted oxadiazoles and triazoles using phenylselanyl derivatives as precursor

Yu-Guang Wang,[a] Xian Huang[a,b,*] and Yu-Zhou Wu[a]

[a]*Department of Chemistry, Zhejiang University (Xixi Campus), Hangzhou 310028, PR China*
[b]*State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, PR China*

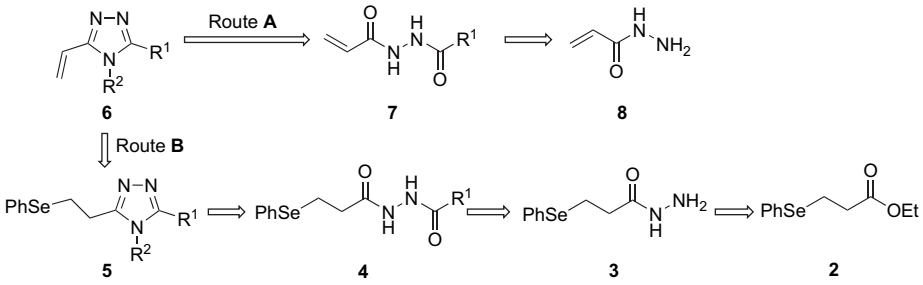
Received 13 March 2007; revised 21 May 2007; accepted 23 May 2007
Available online 26 May 2007

Abstract—Vinyl substituted oxadiazoles and triazoles were obtained from selenoxide *syn*-elimination of phenylselanylethyl substituted oxadiazoles and triazoles, which were prepared through hydrazinolysis, acylation, and cyclocondensation reactions of phenylselanylpropionate. Using phenylselanyl group as the precursor of terminal double bond is critical to the success of the reactions.

1. Introduction

Vinyl substituted heterocycles are versatile intermediates for the synthesis of complex natural products and biologically active compounds,[1] which are observed in many therapeutic agents. In addition, vinyl substituted heterocycles play an important role as useful additives in material chemistry.[2]

In view of the fact that vinyl substituted heterocycles have such a potential in organic synthesis, we wish to study the preparation of vinyl substituted oxadiazoles and triazoles. Therefore, we designed retrosynthetic Route **A** initially (Scheme 1). However, the preparation of α,β-unsaturated hydrazide **8** is difficult. When the conventional method for preparing acyl hydrazides was applied to the α,β-unsaturated ester, the predominant product was the pyrazolidinone due to hydrazinolysis and an undesired subsequent intramolecular Michael-type cyclization.[3] Alternatively, acyl hydrazides can be prepared by condensing carboxylic acids with hydrazine in the presence of coupling agents.[4] Nevertheless, most of these methods provide low yields and complicated product isolations.[5] Moreover, we failed to get the desired cyclocondensation product **6** from intermediate **7** by reaction with arylphosphazoanilide (Ar-N=P-NH-Ar).[10] Vinyl substituted heterocycle **6** has a highly reactive terminal double bond, which is directly connected to an electron withdrawing group (heterocycle),[6] and therefore is easily polymerized at high reaction temperature. In the search for alternative strategies to solve this problem, considering the protection of terminal double bond, we turned our attention to organoselenium. Diorganic selenides have attracted considerable interest because they are key intermediates[7] that can be efficiently introduced, manipulated, and removed under mild conditions and usually in good yields.



Scheme 1. Retrosynthetic route of the vinyl substituted 1,2,4-triazoles **6**.

* Corresponding author. Tel./fax: +86 571 88807077; e-mail: huangx@zju.edu.cn

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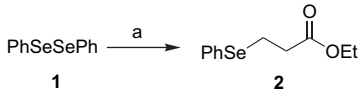
doi:10.1016/j.tet.2007.05.080

Fortunately, our careful investigation resulted in a high yielding Route **B**. We reasoned that the facile selenoxide *syn*-elimination[8] of the phenylselanyl group could be used to mask a vinylic functionality, thus serving as a 'pro-vinyl' group during the reaction and finally through facile selenoxide *syn*-elimination to get vinyl substituted heterocycles. Based on our continuous studies[9] on the application of selenium in solid- and solution-phase organic syntheses, here we reported an efficient protocol to prepare vinyl substituted oxadiazoles and triazoles via selenoxide *syn*-elimination of phenylselanylethyl substituted oxadiazoles and triazoles with the advantages of stability and good yield of the product.

2. Results and discussion

We began our experiment from diphenyl diselenide, which was treated with $NaBH_4$ and ethyl 3-chloro-propionate to get ethyl 3-phenylselanyl-propionate **2** almost quantitatively (Scheme 2).



Scheme 2. Reagents and conditions: (a) $NaBH_4$, THF/DMF, rt, 8 h; $ClCH_2CH_2COOEt$, rt, 4 h.

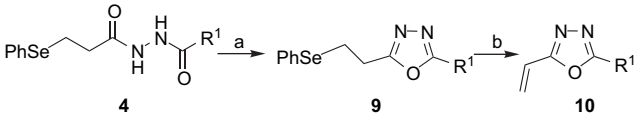
Since the direct reaction of phenylselanyl-propionate **2** and acylhydrazine did not occur, two-step reaction was adopted to synthesize hydrazide **4** (Scheme 3). Hydrazide **4** can undergo cyclocondensation reaction with arylphosphazoanilide (Ar-N=P-NH-Ar) to get phenylselanylethyl substituted 1,2,4-triazoles **5**.[10] Followed by the selenoxide *syn*-elimination, vinyl substituted 1,2,4-triazoles could be obtained in good yield regardless of whether R^1 and R^2 (in products **6**) are alkyl or aryl with an electron-donating group or an electron-withdrawing group (Scheme 3). Results are described in Table 1.

Besides vinyl substituted 1,2,4-triazoles, vinyl substituted 1,3,4-oxadiazoles[11] could also be obtained through hydrazinolysis, acylation, cyclocondensation, and elimination reaction of ethyl 3-phenylselanyl-propionate **2**. With this hydrazide **4** in hand, the cyclocondensation reaction was carried out in the presence of phosphorus oxychloride to form phenylselenoethyl substituted 1,3,4-oxazole **9**, which was then followed by selenoxide *syn*-elimination to obtain vinyl substituted 1,3,4-oxazole **10** in good yield (Scheme 4). The results are summarized in Table 2.

Table 1. Synthesis of the phenylselenoethyl substituted 1,2,4-triazoles **5** and the vinyl substituted 1,2,4-triazoles **6**

R^1	R^2	Product **5**	Yield **5**[a] (%)	Product **6**	Yield **6**[b] (%)
C_6H_5	2-$CH_3C_6H_4$	**5a**	71	**6a**	96
C_6H_5	3-$CH_3OC_6H_4$	**5b**	62	**6b**	95
C_6H_5	2,4-$(CH_3)_2C_6H_3$	**5c**	68	**6c**	97
C_6H_5	4-ClC_6H_4	**5d**	73	**6d**	98
$C_6H_5CH_2$	4-$CH_3C_6H_4$	**5e**	80	**6e**	97
$C_6H_5CH_2$	C_6H_5	**5f**	79	**6f**	98
4-$CH_3OC_6H_4$	4-$CH_3C_6H_4$	**5g**	71	**6g**	96
4-$CH_3OC_6H_4$	2-$CH_3C_6H_4$	**5h**	67	**6h**	97
4-$CH_3OC_6H_4$	4-ClC_6H_4	**5i**	72	**6i**	97
CH_3	4-$CH_3C_6H_4$	**5j**	82	**6j**	98
CH_3	α-Naphthalenyl	**5k**	70	**6k**	97
CH_3	3-$CH_3OC_6H_4$	**5l**	59	**6l**	97
i-C_3H_7	C_6H_5	**5m**	70	**6m**	96
i-C_3H_7	4-$CH_3C_6H_4$	**5n**	69	**6n**	97
i-C_3H_7	2-$CH_3C_6H_4$	**5o**	65	**6o**	98
n-C_6H_{13}	3-$CH_3C_6H_4$	**5p**	71	**6p**	97
n-C_6H_{13}	2-$CH_3C_6H_4$	**5q**	63	**6q**	97

[a] Yield of the product **5** is based on the compounds **2**.
[b] Yield of the product **6** is based on the compounds **5**.



Scheme 4. Reagents and conditions: (a) phosphorus oxychloride, reflux, 6 h; (b) H_2O_2, THF, 0 °C, 10 min, then rt, 1.5 h.

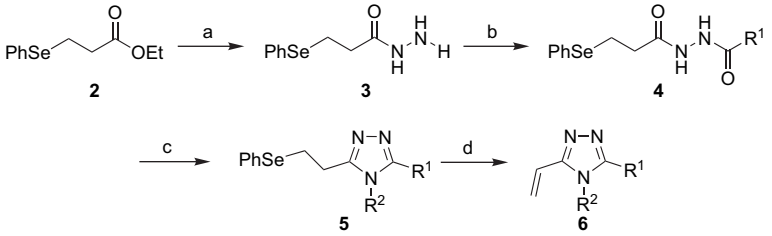
Table 2. Synthesis of the phenylselenoethyl substituted 1,3,4-oxadiazoles **9** and the vinyl substituted 1,3,4-oxadiazoles **10**

R^1	Product **9**	Yield **9**[a] (%)	Product **10**	Yield **10**[b] (%)
C_6H_5	**9a**	69	**10a**	98
4-$CH_3OC_6H_4$	**9b**	66	**10b**	97
CH_3	**9c**	71	**10c**	98
i-C_3H_7	**9d**	62	**10d**	97
n-C_6H_{13}	**9e**	58	**10e**	96

[a] Yield of the product **9** is based on the compounds **2**.
[b] Yield of the product **10** is based on the compounds **9**.

3. Conclusions

In summary, we have developed an efficient cyclocondensation route to phenylselanylethyl substituted oxadiazoles and triazoles, which followed by selenoxide *syn*-elimination gives vinyl substituted oxadiazoles and 1,2,4-triazoles, respectively. During the reaction, the phenylselanyl group acted as an efficient precursor of terminal double bond, which is critical to the success of the reactions.



Scheme 3. Reagents and conditions: (a) $NH_2NH_2H_2O$, CH_3OH, reflux; (b) R^1COCl, pyridine, CH_2Cl_2, 0 °C, then rt; (c) R^2–N=P-NH-R^2, *o*-dichlorobenzene, reflux, 3 h; (d) H_2O_2, THF, 0 °C, 10 min, then rt, 1.5 h.

4. Experimental

4.1. General

The melting points were uncorrected. THF and toluene were distilled from sodium/benzophenone immediately prior to use. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker Avance spectrometer, using $CDCl_3$ as the solvent and TMS as an internal standard. Mass spectra (EI, 70 eV) were recorded on an Agilent 5975 inert mass selective detector. Infrared spectra were recorded on a Bruker Vector 22 spectrometer. Elemental analyses were performed on a Flash EA 1112 instrument.

4.1.1. Typical procedure for the preparation of arylphosphazoanilide (Ar-N═P-NH-Ar). To a solution or suspension of the amine (78 mmol) in 100 mL toluene was slowly added phosphorus trichloride (15 mmol) dropwise. The mixture was stirred for 1.5 h at the reflux temperature. After completion of the reaction, the reaction mixture was filtered, and the filter cake was washed with hot toluene (2×30 mL). The filtrate was evaporated to dryness under vacuum to obtain the crude products, which were recrystallized via ethanol; the yield was 60–70%.

4.1.2. Typical procedure for the preparation of ethyl 3-phenylselanyl-propionate 2. Under a positive pressure of nitrogen, $NaBH_4$ (30.0 mmol) was added slowly to the reaction flask containing diphenyl diselenide **1** (3.12 g, 10.0 mmol) dissolved in anhydrous THF/DMF (60/12 mL). After 8 h of stirring at room temperature, ethyl 3-chloro-propionate (21.0 mmol) was added, and the mixture was stirred for 4.0 h at room temperature. The cooled mixture was partitioned between DCM and water. The organic layer was separated and the aqueous layer was extracted with DCM twice. The combined organic layers were washed with brine, dried over Mg_2SO_4, and concentrated in vacuo. The residual oil was loaded on a silica gel column and eluted with petroleum ether/ethyl acetate (20/1) to afford the product **2**.

4.1.3. Typical procedure for the preparation of the substituted acid *N*′-(3-phenylselanyl-propionyl)-hydrazide 4. The mixture of ethyl 3-phenylselanyl-propionate **2** (5.0 mmol) and hydrazine hydrate 85% (100 mmol) in methanol (40 mL) was refluxed under nitrogen. After the reaction was completed, monitored by TLC, the mixture was concentrated in vacuo to get the solid, which was washed with petroleum ether to give the 3-phenylselanyl-propionic acid hydrazide **3**.

Under a nitrogen atmosphere, acyl chloride in anhydrous DCM (5 mL) was added dropwise to the mixture of anhydrous pyridine (6.0 mmol) and compounds **3** (3.0 mmol) in anhydrous DCM (30 mL) at 0 °C. The mixture was stirred at room temperature. After the reaction was completed, monitored by TLC, the resulting precipitate was collected on a filter, washed with distilled water, petroleum ether, and cool DCM to give the product **4**.

4.1.4. Typical procedure for the preparation of the 5-phenylselenoethyl-3,4-disubstituted-1,2,4-triazoles (products 5a–q). Under a positive pressure of nitrogen, the compounds **4** (0.5 mmol) and arylphosphazoanilide (Ar-N═P-NH-Ar) (0.55 mmol) were dissolved in 1,2-dichlorobenzene (3 mL). The mixture was stirred for 3 h at reflux temperature and then cooled to room temperature. The reaction mixture was loaded on a silica gel column and eluted with petroleum ether/ethyl acetate to afford the product **5**.

4.1.4.1. 3-Phenyl-5-(2-phenylselanyl-ethyl)-4-*o*-tolyl-4*H*-[1,2,4]triazole (5a). Oil. ^{1}H NMR ($CDCl_3$) δ 7.41–7.39 (3H, m), 7.32–7.29 (5H, m), 7.26–7.24 (2H, m), 7.20–7.17 (4H, m), 3.19–3.17 (2H, m), 2.95–2.93 (2H, m), 1.85 (3H, s); ^{13}C NMR ($CDCl_3$) δ 154.8, 153.7, 135.5, 133.5, 132.5, 131.8, 130.2, 129.6, 129.2, 129.1, 128.5, 127.9, 127.7, 127.4, 127.1, 127.0, 26.5, 23.7, 17.3; MS *m*/*z* 338 (100), 419 (M^+); IR ν_{max} (cm^{-1}) 3057, 2925, 1579, 1500, 1473, 1441, 773, 736, 694; Anal. Calcd for $C_{23}H_{21}N_3Se$: C, 66.03%; H, 5.06%; N, 10.04%; Found: C, 66.11%; H, 5.10%; N, 10.09%.

4.1.4.2. 4-(3-Methoxy-phenyl)-3-phenyl-5-(2-phenylselanyl-ethyl)-4*H*-[1,2,4]triazole (5b). Oil. ^{1}H NMR ($CDCl_3$) δ 7.42–7.40 (2H, m), 7.34–7.24 (6H, m), 7.19–7.17 (3H, m), 7.02–7.00 (1H, m), 6.65–6.64 (2H, m), 3.72 (3H, s), 3.18–3.16 (2H, m), 3.06–3.04 (2H, m); ^{13}C NMR ($CDCl_3$) δ 160.4, 154.7, 153.7, 135.2, 132.4, 130.7, 129.4, 129.0, 128.9, 128.2, 128.0, 126.9, 126.6, 119.2, 115.2, 112.9, 55.4, 26.5, 23.8; MS *m*/*z* 354 (100), 435 (M^+); IR ν_{max} (cm^{-1}) 3057, 2938, 1604, 1492, 1476, 1231, 1023, 736, 692; Anal. Calcd for $C_{23}H_{21}N_3OSe$: C, 63.59%; H, 4.87%; N, 9.67%; Found: C, 63.48%; H, 4.95%; N, 9.71%.

4.1.4.3. 4-(2,4-Dimethyl-phenyl)-3-phenyl-5-(2-phenylselanyl-ethyl)-4*H*-[1,2,4]triazole (5c). White solid, mp 90–92 °C. ^{1}H NMR ($CDCl_3$) δ 7.43–7.41 (2H, m), 7.31–7.16 (8H, m), 7.08–7.02 (3H, m), 3.17–3.14 (2H, m), 2.94–2.92 (2H, m), 2.39 (3H, s), 1.78 (3H, s); ^{13}C NMR ($CDCl_3$) δ 154.7, 153.5, 140.1, 134.7, 132.2, 132.1, 130.5, 129.3, 129.0, 128.8, 128.2, 128.1, 127.4, 127.2, 126.9, 126.7, 26.4, 23.5, 21.0, 17.0; MS *m*/*z* 352 (100), 433 (M^+); IR ν_{max} (cm^{-1}) 3052, 2920, 1578, 1506, 1473, 1441, 738, 694; Anal. Calcd for $C_{24}H_{23}N_3Se$: C, 66.66%; H, 5.36%; N, 9.72%; Found: C, 66.54%; H, 5.53%; N, 9.81%.

4.1.4.4. 4-(4-Chloro-phenyl)-3-phenyl-5-(2-phenylselanyl-ethyl)-4*H*-[1,2,4]triazole (5d). White solid, mp 94–96 °C. ^{1}H NMR ($CDCl_3$) δ 7.38 (2H, d, *J*=8.4 Hz), 7.35–7.30 (5H, m), 7.27–7.18 (5H, m), 7.04 (2H, d, *J*=8.4 Hz), 3.15–3.11 (2H, m), 3.01–2.97 (2H, m); ^{13}C NMR ($CDCl_3$) δ 154.5, 153.6, 135.5, 132.6, 132.5, 130.1, 129.5, 128.9, 128.8, 128.4, 128.3, 128.0, 126.9, 126.2, 26.3, 23.8; MS *m*/*z* 358 (100), 439 (M^+); IR ν_{max} (cm^{-1}) 3058, 1577, 1496, 1416, 1094, 842, 739, 695; Anal. Calcd for $C_{22}H_{18}ClN_3Se$: C, 60.22%; H, 4.13%; N, 9.58%; Found: C, 60.31%; H, 4.29%; N, 9.41%.

4.1.4.5. 3-Benzyl-5-(2-phenylselanyl-ethyl)-4-*p*-tolyl-4*H*-[1,2,4]triazole (5e). White solid, mp 64–66 °C. ^{1}H NMR ($CDCl_3$) δ 7.26 (2H, d, *J*=8.0 Hz), 7.15–7.11 (8H, m), 6.92–6.90 (2H, m), 6.72 (2H, d, *J*=8.0 Hz), 3.94 (2H, s), 3.10–3.06 (2H, m), 2.91–2.89 (2H, m), 2.39 (3H, s); ^{13}C NMR ($CDCl_3$) δ 153.8, 153.4, 139.5, 135.3, 132.0, 130.1, 129.9, 128.8, 128.6, 128.1, 127.9, 126.5, 126.4, 126.2, 31.0, 26.0, 23.4, 20.8; MS *m*/*z* 352 (100), 433 (M^+); IR ν_{max} (cm^{-1}) 2972, 1579, 1516, 1431, 1217, 755, 550;

Anal. Calcd for $C_{24}H_{23}N_3Se$: C, 66.66%; H, 5.36%; N, 9.72%; Found: C, 66.73%; H, 5.33%; N, 9.81%.

4.1.4.6. 3-Benzyl-4-phenyl-5-(2-phenylselanyl-ethyl)-4*H*-[1,2,4]triazole (5f). Oil. ^{1}H NMR ($CDCl_3$) δ 7.46–7.44 (1H, m), 7.37–7.33 (2H, m), 7.27–7.26 (2H, m), 7.15–7.11 (6H, m), 6.89–6.83 (4H, m), 3.97 (2H, s), 3.13–3.09 (2H, m), 2.92–2.89 (2H, m); ^{13}C NMR ($CDCl_3$) δ 154.0, 153.5, 135.3, 133.0, 132.2, 129.6, 129.5, 128.9, 128.8, 128.3, 128.1, 127.0, 126.7, 126.5, 31.3, 26.2, 23.6; MS *m/z* 338 (100), 419 (M^+); IR ν_{max} (cm^{-1}) 3058, 2929, 1599, 1499, 1478, 1436, 733, 694; Anal. Calcd for $C_{23}H_{21}N_3Se$: C, 66.03%; H, 5.06%; N, 10.04%; Found: C, 65.90%; H, 5.20%; N, 10.09%.

4.1.4.7. 3-(4-Methoxy-phenyl)-5-(2-phenylselanyl-ethyl)-4-*p*-tolyl-4*H*-[1,2,4]triazole (5g). White solid, mp 86–88 °C. ^{1}H NMR ($CDCl_3$) δ 7.32 (2H, d, J=8.8 Hz), 7.30–7.28 (2H, m), 7.21 (2H, d, J=8.0 Hz), 7.17–7.14 (3H, m), 6.98 (2H, d, J=8.0 Hz), 6.74 (2H, d, J=8.8 Hz), 3.68 (3H, s), 3.15–3.11 (2H, m), 3.02–2.98 (2H, m), 2.39 (3H, s); ^{13}C NMR ($CDCl_3$) δ 159.9, 154.1, 153.2, 139.3, 132.0, 131.2, 130.2, 129.1, 128.7, 128.5, 126.5, 126.4, 118.6, 113.3, 54.6, 26.1, 23.4, 20.7; MS *m/z* 368 (100), 449 (M^+); IR ν_{max} (cm^{-1}) 3055, 2936, 1613, 1578, 1514, 1476, 1253, 1178, 1029, 835, 738; Anal. Calcd for $C_{24}H_{23}N_3OSe$: C, 64.28%; H, 5.17%; N, 9.37%; Found: C, 64.19%; H, 5.28%; N, 9.41%.

4.1.4.8. 3-(4-Methoxy-phenyl)-5-(2-phenylselanyl-ethyl)-4-*o*-tolyl-4*H*-[1,2,4]triazole (5h). Oil. ^{1}H NMR ($CDCl_3$) δ 7.45–7.41 (1H, m), 7.35 (2H, d, J=8.8 Hz), 7.30–7.28 (4H, m), 7.18–7.15 (4H, m), 6.76 (2H, d, J=8.8 Hz), 3.72 (3H, s), 3.17–3.15 (2H, m), 2.93–2.91 (2H, m), 1.83 (3H, s); ^{13}C NMR ($CDCl_3$) δ 160.3, 154.1, 153.2, 135.2, 133.2, 132.1, 131.6, 130.0, 129.1, 128.8, 128.6, 127.7, 127.5, 126.7, 119.1, 113.7, 54.9, 26.2, 23.4, 17.1; MS *m/z* 368 (100), 449 (M^+); IR ν_{max} (cm^{-1}) 3056, 2937, 1612, 1471, 1254, 1180, 1028, 838, 737; Anal. Calcd for $C_{24}H_{23}N_3OSe$: C, 64.28%; H, 5.17%; N, 9.37%; Found: C, 64.22%; H, 5.24%; N, 9.49%.

4.1.4.9. 4-(4-Chloro-phenyl)-3-(4-methoxy-phenyl)-5-(2-phenylselanyl-ethyl)-4*H*-[1,2,4]triazole (5i). Low point solid. ^{1}H NMR ($CDCl_3$) δ 7.38 (2H, d, J=8.4 Hz), 7.30–7.28 (2H, m), 7.25 (2H, d, J=8.8 Hz), 7.23–7.18 (3H, m), 7.05 (2H, d, J=8.4 Hz), 6.76 (2H, d, J=8.8 Hz), 3.72 (3H, s), 3.13–3.09 (2H, m), 2.99–2.95 (2H, m); ^{13}C NMR ($CDCl_3$) δ 160.3, 154.1, 153.4, 135.4, 132.5, 132.4, 130.0, 129.4, 128.8, 128.7, 128.4, 126.9, 118.2, 113.7, 54.9, 26.2, 23.7; MS *m/z* 311 (100), 469 (M^+); IR ν_{max} (cm^{-1}) 3055, 2937, 1678, 1612, 1499, 1254, 1180, 1028, 839, 738; Anal. Calcd for $C_{23}H_{20}ClN_3OSe$: C, 58.92%; H, 4.30%; N, 8.96%; Found: C, 59.0%; H, 4.35%; N, 9.04%.

4.1.4.10. 3-Methyl-5-(2-phenylselanyl-ethyl)-4-*p*-tolyl-4*H*-[1,2,4]triazole (5j). White solid, mp 87–89 °C. ^{1}H NMR ($CDCl_3$) δ 7.16–7.14 (4H, m), 7.04–7.02 (3H, m), 6.87–6.85 (2H, m), 2.99–2.95 (2H, m), 2.84–2.80 (2H, m), 2.30 (3H, s), 2.08 (3H, s); ^{13}C NMR ($CDCl_3$) δ 153.3, 151.2, 139.6, 132.1, 130.5, 130.2, 128.8, 128.5, 126.5, 126.1, 26.0, 23.5, 20.7, 10.6; MS *m/z* 276 (100), 357 (M^+); IR ν_{max} (cm^{-1}) 3052, 2930, 1582, 1518, 1435, 802, 695; Anal. Calcd for $C_{18}H_{19}N_3Se$: C, 60.67%; H, 5.37%; N, 11.79%; Found: C, 60.60%; H, 5.41%; N, 11.86%.

4.1.4.11. 3-Methyl-4-naphthalen-1-yl-5-(2-phenylselanyl-ethyl)-4*H*-[1,2,4]triazole (5k). Oil. ^{1}H NMR ($CDCl_3$) δ 8.06–7.99 (2H, m), 7.61–7.53 (3H, m), 7.32–7.30 (1H, d), 7.17–7.06 (6H, m), 3.09–3.02 (2H, m), 2.86–2.82 (2H, m), 2.16 (3H, s); ^{13}C NMR ($CDCl_3$) δ 154.6, 152.4, 134.3, 132.3, 130.6, 129.8, 129.6, 129.0, 128.9, 128.7, 128.4, 127.4, 126.8, 125.6, 125.4, 121.3, 26.4, 23.8, 10.7; MS *m/z* 312 (100), 393 (M^+); IR ν_{max} (cm^{-1}) 3057, 2929, 1520, 1473, 1426, 865, 779, 739; Anal. Calcd for $C_{21}H_{19}N_3Se$: C, 64.28%; H, 4.88%; N, 10.71%; Found: C, 64.36%; H, 4.79%; N, 10.78%.

4.1.4.12. 4-(3-Methoxy-phenyl)-3-methyl-5-(2-phenylselanyl-ethyl)-4*H*-[1,2,4]triazole (5l). Oil. ^{1}H NMR ($CDCl_3$) δ 7.43–7.39 (1H, m), 7.33–7.31 (2H, m), 7.19–7.17 (3H, m), 7.07–7.04 (1H, m), 6.72–6.70 (1H, m), 6.66–6.65 (1H, m), 3.81 (3H, s), 3.16–3.12 (2H, m), 3.00–2.96 (2H, m), 2.26 (3H, s); ^{13}C NMR ($CDCl_3$) δ 160.5, 153.6, 151.5, 134.5, 132.4, 130.7, 129.1, 128.9, 126.8, 118.8, 115.1, 112.6, 55.4, 26.4, 23.8, 10.9; MS *m/z* 292 (100), 373 (M^+); IR ν_{max} (cm^{-1}) 3059, 2935, 1601, 1492, 1424, 1226, 1026, 740, 693; Anal. Calcd for $C_{18}H_{19}N_3OSe$: C, 58.07%; H, 5.14%; N, 11.29%; Found: C, 58.18%; H, 5.23%; N, 11.20%.

4.1.4.13. 3-Isopropyl-4-phenyl-5-(2-phenylselanyl-ethyl)-4*H*-[1,2,4]triazole (5m). Oil. ^{1}H NMR ($CDCl_3$) δ 7.53–7.51 (3H, m), 7.28–7.26 (2H, m), 7.17–7.13 (5H, m), 3.13–3.09 (2H, m), 2.96–2.92 (2H, m), 2.81–2.74 (1H, m), 1.24–1.23 (6H, m); ^{13}C NMR ($CDCl_3$) δ 159.2, 153.3, 133.3, 132.2, 132.0, 129.8, 129.6, 128.7, 126.9, 126.6, 26.1, 24.8, 23.6, 20.8; MS *m/z* 290 (100), 371 (M^+); IR ν_{max} (cm^{-1}) 3054, 2971, 2931, 1578, 1500, 1436, 774, 738, 693; Anal. Calcd for $C_{19}H_{21}N_3Se$: C, 61.62%; H, 5.72%; N, 11.35%; Found: C, 61.51%; H, 5.81%; N, 11.40%.

4.1.4.14. 3-Isopropyl-5-(2-phenylselanyl-ethyl)-4-*p*-tolyl-4*H*-[1,2,4]triazole (5n). Oil. ^{1}H NMR ($CDCl_3$) δ 7.30 (2H, d, J=8.0 Hz), 7.28–7.26 (2H, m), 7.19–7.15 (3H, m), 7.02 (2H, d, J=8.0 Hz), 3.12–3.08 (2H, m), 2.96–2.92 (2H, m), 2.81–2.74 (1H, m), 2.45 (3H, s), 1.24 (3H, s), 1.23 (3H, s); ^{13}C NMR ($CDCl_3$) δ 159.3, 153.4, 139.8, 132.1, 130.6, 130.3, 128.9, 128.7, 126.7, 126.5, 26.1, 24.8, 23.6, 20.9, 20.8; MS *m/z* 304 (100), 385 (M^+); IR ν_{max} (cm^{-1}) 3052, 2972, 2930, 1578, 1515, 1434, 829, 738; Anal. Calcd for $C_{20}H_{23}N_3Se$: C, 62.49%; H, 6.03%; N, 10.93%; Found: C, 62.40%; H, 6.07%; N, 10.98%.

4.1.4.15. 3-Isopropyl-5-(2-phenylselanyl-ethyl)-4-*o*-tolyl-4*H*-[1,2,4]triazole (5o). Oil. ^{1}H NMR ($CDCl_3$) δ 7.48–7.44 (1H, m), 7.38–7.34 (2H, m), 7.28–7.25 (2H, m), 7.19–7.16 (3H, m), 7.08–7.06 (1H, m), 3.14–3.10 (2H, m), 2.95–2.89 (1H, m), 2.77–2.73 (1H, m), 2.63–2.59 (1H, m), 1.94 (3H, s), 1.27–1.21 (6H, m); ^{13}C NMR ($CDCl_3$) δ 159.2, 153.2, 135.2, 132.3, 132.1, 131.5, 130.1, 129.0, 128.9, 127.8, 127.3, 126.7, 26.2, 25.1, 23.4, 21.4, 20.5, 16.9; MS *m/z* 304 (100), 385 (M^+); IR ν_{max} (cm^{-1}) 3053, 2971, 2930, 1578, 1505, 1468, 1433, 774, 737; Anal. Calcd for $C_{20}H_{23}N_3Se$: C, 62.49%; H, 6.03%; N, 10.93%; Found: 62.38%; H, 6.12%; N, 11.00%.

4.1.4.16. 3-Hexyl-5-(2-phenylselanyl-ethyl)-4-*m*-tolyl-4*H*-[1,2,4]triazole (5p). Oil. ^{1}H NMR ($CDCl_3$) δ 7.39–7.24 (4H, m), 7.14–7.12 (3H, m), 6.91–6.89 (2H, m), 3.12–3.08 (2H, m), 3.96–3.92 (2H, m), 2.53–2.49 (2H, m), 2.36 (3H, s), 1.60–1.56 (2H, m), 1.23–1.14 (6H, m), 0.81–0.77 (3H, m); ^{13}C NMR ($CDCl_3$) δ 154.6, 153.0, 139.8, 133.0, 131.8, 130.1, 129.3, 128.8, 128.5, 126.9, 126.3, 123.5, 30.6, 28.1, 26.6, 26.0, 24.4, 23.4, 21.8, 20.7, 13.4; MS *m*/*z* 346 (100), 427 (M^+); IR ν_{max} (cm^{-1}) 3053, 2926, 2858, 1583, 1516, 1458, 794, 738, 694; Anal. Calcd for $C_{23}H_{29}N_3Se$: C, 64.78%; H, 6.85%; N, 9.85%; Found: C, 64.83%; H, 6.89%; N, 9.79%.

4.1.4.17. 3-Hexyl-5-(2-phenylselanyl-ethyl)-4-*o*-tolyl-4*H*-[1,2,4]triazole (5q). Oil. ^{1}H NMR ($CDCl_3$) δ 7.47–7.45 (1H, m), 7.40–7.34 (4H, m), 7.20–7.17 (3H, m), 7.08–7.06 (1H, m), 3.17–3.12 (2H, m), 2.95–2.77 (2H, m), 2.53–2.39 (2H, m), 1.96 (3H, s), 1.63–1.59 (2H, m), 1.28–1.18 (6H, m), 0.85–0.81 (3H, m); ^{13}C NMR ($CDCl_3$) δ 154.8, 153.2, 135.1, 132.1, 132.0, 131.4, 130.0, 128.9, 128.8, 127.6, 127.3, 126.7, 30.9, 28.5, 26.7, 26.2, 24.7, 23.3, 22.0, 16.8, 13.7; MS *m*/*z* 346 (100), 427 (M^+); IR ν_{max} (cm^{-1}) 3054, 2927, 2858, 1579, 1503, 1459, 736; Anal. Calcd for $C_{23}H_{29}N_3Se$: C, 64.78%; H, 6.85%; N, 9.85%; Found: C, 64.66%; H, 6.92%; N, 9.90%.

4.1.5. Typical procedure for the preparation of the 5-vinyl-3,4-disubstituted-1,2,4-triazoles (products 6a–q). Compounds **5** (0.3 mmol) were dissolved in THF (15 mL), 30% (aq) H_2O_2 (0.4 mL) was added, and the mixture was stirred for 10 min at 0 °C followed by 1.5 h at room temperature. The mixture was partitioned between DCM and water. The organic layer was separated and the aqueous layer was extracted with ethyl acetate twice. The combined organic layers were washed with brine, dried over Mg_2SO_4, and concentrated in vacuo. The residual compounds were loaded on a silica gel column and eluted with petroleum ether/ethyl acetate to afford the product **6**.

4.1.5.1. 3-Phenyl-4-*o*-tolyl-5-vinyl-4*H*-[1,2,4]triazole (6a). White solid, mp 125–127 °C. ^{1}H NMR ($CDCl_3$) δ 7.44–7.42 (3H, m), 7.36–7.34 (2H, m), 7.27–7.21 (4H, m), 6.20–6.18 (2H, m), 5.48–5.45 (1H, m), 1.93 (3H, s); ^{13}C NMR ($CDCl_3$) δ 153.7, 152.9, 135.8, 133.5, 131.7, 130.3, 129.7, 128.5, 128.1, 127.7, 127.6, 126.8, 122.0, 120.6, 17.4; MS *m*/*z* 261 (M^+, 100); IR ν_{max} (cm^{-1}) 3061, 2920, 1496, 1467, 1426, 1384, 980, 929, 781, 696; Anal. Calcd for $C_{17}H_{15}N_3$: C, 78.13%; H, 5.79%; N, 16.08%; Found: C, 78.02%; H, 5.83%; N, 16.15%.

4.1.5.2. 4-(3-Methoxy-phenyl)-3-phenyl-5-vinyl-4*H*-[1,2,4]triazole (6b). White solid, mp 81–83 °C. ^{1}H NMR ($CDCl_3$) δ 7.47–7.26 (6H, m), 7.05–7.03 (1H, m), 6.82–6.72 (2H, m), 6.34–6.32 (2H, m), 5.56–5.53 (1H, m), 3.79 (3H, s); ^{13}C NMR ($CDCl_3$) δ 160.7, 153.9, 153.1, 135.5, 130.8, 129.6, 128.4, 128.3, 126.7, 122.4, 120.6, 119.8, 115.5, 113.3, 55.6; MS *m*/*z* 277 (M^+, 100); IR ν_{max} (cm^{-1}) 2923, 2852, 1604, 1493, 1467, 1180, 1026, 695; Anal. Calcd for $C_{17}H_{15}N_3O$: C, 73.63%; H, 5.45%; N, 15.15%; Found: C, 73.52%; H, 5.42%; N, 15.24%.

4.1.5.3. 4-(2,4-Dimethyl-phenyl)-3-phenyl-5-vinyl-4*H*-[1,2,4]triazole (6c). White solid, mp 155–157 °C. ^{1}H NMR ($CDCl_3$) δ 7.47–7.45 (2H, m), 7.30–7.25 (3H, m), 7.16–7.06 (3H, m), 6.22–6.18 (2H, m), 5.46–5.43 (1H, m), 2.40 (3H, s), 1.88 (3H, s); ^{13}C NMR ($CDCl_3$) δ 153.7, 153.0, 140.5, 135.2, 132.3, 130.8, 129.6, 128.5, 128.3, 127.8, 127.5, 127.0, 121.6, 120.8, 21.2, 17.3; MS *m*/*z* 275 (M^+, 100); IR ν_{max} (cm^{-1}) 3055, 2921, 1505, 1471, 1445, 1427, 774, 694; Anal. Calcd for $C_{18}H_{17}N_3$: C, 78.52%; H, 6.22%; N, 15.26%; Found: C, 78.45%; H, 6.25%; N, 15.30%.

4.1.5.4. 4-(4-Chloro-phenyl)-3-phenyl-5-vinyl-4*H*-[1,2,4]triazole (6d). White solid, mp 158–160 °C. ^{1}H NMR ($CDCl_3$) δ 7.50 (2H, d, *J*=8.8 Hz), 7.40–7.38 (2H, m), 7.34–7.28 (3H, m), 7.19 (2H, d, *J*=8.8 Hz), 6.30–6.26 (2H, m), 5.55–5.52 (1H, m); ^{13}C NMR ($CDCl_3$) δ 153.7, 152.8, 135.7, 132.6, 130.1, 129.6, 128.7, 128.4, 128.2, 126.2, 122.5, 120.1; MS *m*/*z* 281 (M^+, 100); IR ν_{max} (cm^{-1}) 3091, 3063, 1493, 1468, 1426, 1092, 1009, 933, 844, 756, 700; Anal. Calcd for $C_{16}H_{12}ClN_3$: C, 68.21%; H, 4.29%; N, 14.91%; Found: C, 68.13%; H, 4.33%; N, 14.95%.

4.1.5.5. 3-Benzyl-4-*p*-tolyl-5-vinyl-4*H*-[1,2,4]triazole (6e). White solid, mp 99–101 °C. ^{1}H NMR ($CDCl_3$) δ 7.22 (2H, d, *J*=8.0 Hz), 7.15–7.13 (3H, m), 6.96–6.94 (2H, m), 6.84 (2H, d, *J*=8.0 Hz), 6.20–6.10 (2H, m), 5.40–5.37 (1H, m), 4.01 (2H, s), 2.42 (3H, s); ^{13}C NMR ($CDCl_3$) δ 153.7, 152.3, 139.7, 135.4, 130.3, 130.0, 128.2, 128.0, 126.8, 126.4, 121.0, 120.6, 31.0, 20.9; MS *m*/*z* 275 (M^+, 100); IR ν_{max} (cm^{-1}) 3037, 2924, 1516, 1443, 940, 829, 740, 698, 575; Anal. Calcd for $C_{18}H_{17}N_3$: C, 78.52%; H, 6.22%; N, 15.26%; Found: C, 78.60%; H, 6.25%; N, 15.15%.

4.1.5.6. 3-Benzyl-4-phenyl-5-vinyl-4*H*-[1,2,4]triazole (6f). White solid, mp 93–95 °C. ^{1}H NMR ($CDCl_3$) δ 7.48–7.40 (3H, m), 7.14–7.13 (3H, m), 9.96–9.91 (4H, m), 6.22–6.11 (2H, m), 5.42–5.39 (1H, m), 4.02 (2H, s); ^{13}C NMR ($CDCl_3$) δ 153.7, 152.3, 135.3, 133.1, 129.6, 129.5, 128.2, 128.1, 127.2, 126.5, 121.3, 120.6, 31.1; MS *m*/*z* 261 (M^+, 100); IR ν_{max} (cm^{-1}) 3055, 2921, 1597, 1500, 1455, 1441, 986, 930, 769, 738, 696; Anal. Calcd for $C_{17}H_{15}N_3$: C, 78.13%; H, 5.79%; N, 16.08%; Found: C, 78.03%; H, 5.83%; N, 16.14%.

4.1.5.7. 3-(4-Methoxy-phenyl)-4-*p*-tolyl-5-vinyl-4*H*-[1,2,4]triazole (6g). White solid, mp 141–143 °C. ^{1}H NMR ($CDCl_3$) δ 7.37 (2H, d, *J*=8.8 Hz), 7.31 (2H, d, *J*=8.0 Hz), 7.10 (2H, d, *J*=8.0 Hz), 6.79 (2H, d, *J*=8.8 Hz), 6.28–6.25 (2H, m), 5.48–4.45 (1H, m), 3.75 (3H, s), 2.44 (3H, s); ^{13}C NMR ($CDCl_3$) δ 160.2, 153.7, 152.7, 139.7, 131.6, 130.4, 129.5, 127.1, 121.4, 120.6, 118.9, 113.6, 55.0, 21.0; MS *m*/*z* 291 (M^+, 100); IR ν_{max} (cm^{-1}) 3037, 2933, 2838, 1613, 1515, 1466, 1438, 1254, 1179, 1031, 835; Anal. Calcd for $C_{18}H_{17}N_3O$: C, 74.20%; H, 5.88%; N, 14.42%; Found: C, 74.11%; H, 5.92%; N, 14.49%.

4.1.5.8. 3-(4-Methoxy-phenyl)-4-*o*-tolyl-5-vinyl-4*H*-[1,2,4]triazole (6h). White solid, mp 106–108 °C. ^{1}H NMR ($CDCl_3$) δ 7.48–7.44 (1H, m), 7.38–7.35 (4H, m), 7.22–7.20 (1H, m), 6.78–6.76 (2H, m), 6.21–6.15 (2H, m), 5.46–5.43 (1H, m), 3.75 (3H, s), 1.93 (3H, s); ^{13}C NMR ($CDCl_3$) δ 160.4, 153.4, 152.4, 135.6, 133.5, 131.6, 130.1,

128.9, 128.0, 127.5, 121.3, 120.6, 119.1, 113.8, 55.0, 17.2; MS *m/z* 291 (M^+, 100); IR ν_{max} (cm^{-1}) 2933, 2840, 1612, 1496, 1465, 1254, 1180, 1030, 838, 772; Anal. Calcd for $C_{18}H_{17}N_3O$: C, 74.20%; H, 5.88%; N, 14.42%; Found: C, 74.26%; H, 5.90%; N, 14.37%.

4.1.5.9. 4-(4-Chloro-phenyl)-3-(4-methoxy-phenyl)-5-vinyl-4*H*-[1,2,4]triazole (6i). White solid, mp 139–141 °C. ^1H NMR ($CDCl_3$) δ 7.50 (2H, d, J=8.8 Hz), 7.32 (2H, d, J=8.4 Hz), 7.20 (2H, d, J=8.8 Hz), 6.81 (2H, d, J=8.4 Hz), 6.27–6.25 (2H, m), 5.53–5.49 (1H, m), 3.77 (3H, s); ^{13}C NMR ($CDCl_3$) δ 160.5, 153.7, 152.5, 135.6, 132.8, 130.2, 129.7, 128.8, 122.2, 120.3, 118.5, 113.8, 55.1; MS *m/z* 311 (M^+, 100); IR ν_{max} (cm^{-1}) 3044, 2937, 2836, 1612, 1495, 1251, 1179, 1092, 1024, 834, 757, 596, 520; Anal. Calcd for $C_{17}H_{14}ClN_3O$: C, 65.49%; H, 4.53%; N, 13.48%; Found: C, 65.44%; H, 4.56%; N, 13.53%.

4.1.5.10. 3-Methyl-4-*p*-tolyl-5-vinyl-4*H*-[1,2,4]triazole (6j). White solid, mp 152–154 °C. ^1H NMR ($CDCl_3$) δ 7.36 (2H, d, J=8.0 Hz), 7.11 (2H, d, J=8.0 Hz), 6.20–6.09 (2H, m), 5.44–5.41 (1H, m), 2.46 (3H, s), 2.29 (3H, s); ^{13}C NMR ($CDCl_3$) δ 152.1, 151.8, 140.0, 131.1, 130.5, 126.7, 121.1, 120.0, 21.1, 10.9; MS *m/z* 199 (M^+, 100); IR ν_{max} (cm^{-1}) 3059, 3034, 2922, 1518, 1430, 932, 830; Anal. Calcd for $C_{12}H_{13}N_3$: C, 72.33%; H, 6.58%; N, 21.09%; Found: C, 72.25%; H, 6.61%; N, 21.14%.

4.1.5.11. 3-Methyl-4-naphthalen-1-yl-5-vinyl-4*H*-[1,2,4]triazole (6k). Pale yellow solid, mp 141–143 °C. ^1H NMR ($CDCl_3$) δ 8.06–8.00 (2H, m), 7.64–7.61 (2H, m), 7.56–7.54 (1H, m), 7.42–7.41 (1H, m), 7.22–7.20 (1H, m), 6.12–6.04 (2H, m), 5.34–5.32 (1H, m), 2.21 (3H, s); ^{13}C NMR ($CDCl_3$) δ 152.9, 152.7, 134.4, 130.7, 130.1, 129.8, 128.6, 128.4, 127.4, 125.8, 125.4, 121.6, 121.4, 120.9, 10.7; MS *m/z* 235 (M^+, 100); IR ν_{max} (cm^{-1}) 3057, 2925, 1596, 1518, 1427, 810, 780; Anal. Calcd for $C_{15}H_{13}N_3$: C, 76.57%; H, 5.57%; N, 17.86%; Found: C, 76.49%; H, 5.60%; N, 17.91%.

4.1.5.12. 4-(3-Methoxy-phenyl)-3-methyl-5-vinyl-4*H*-[1,2,4]triazole (6l). White solid, mp 145–147 °C. ^1H NMR ($CDCl_3$) δ 7.49–7.45 (1H, m), 7.10–7.07 (1H, m), 6.83–6.81 (1H, m), 6.76–6.75 (1H, m), 6.30–6.25 (1H, m), 6.15–6.10 (1H, m), 5.47–5.44 (1H, m), 3.87 (3H, s), 2.32 (3H, s); ^{13}C NMR ($CDCl_3$) δ 160.6, 152.0, 151.8, 134.7, 130.8, 121.4, 120.8, 119.1, 115.2, 112.9, 55.5, 10.9; MS *m/z* 215 (M^+, 100); IR ν_{max} (cm^{-1}) 3053, 2925, 1603, 1494, 1425, 1276, 1232, 1024, 801, 703; Anal. Calcd for $C_{12}H_{13}N_3O$: C, 66.96%; H, 6.09%; N, 19.52%; Found: C, 67.01%; H, 6.05%; N, 19.49%.

4.1.5.13. 3-Isopropyl-4-phenyl-5-vinyl-4*H*-[1,2,4]triazole (6m). White solid, mp 68–70 °C. ^1H NMR ($CDCl_3$) δ 7.55–7.54 (3H, m), 7.23–7.21 (2H, m), 6.20–5.99 (2H, m), 5.44–5.36 (1H, m), 2.83–2.76 (1H, m), 1.26 (3H, s), 1.24 (3H, s); ^{13}C NMR ($CDCl_3$) δ 159.8, 152.1, 133.9, 130.0, 129.9, 127.5, 121.3, 121.0, 25.1, 21.2; MS *m/z* 198 (100), 213 (M^+); IR ν_{max} (cm^{-1}) 3048, 2972, 2931, 1598, 1500, 1442, 926, 781, 707; Anal. Calcd for $C_{13}H_{15}N_3$: C, 73.21%; H, 7.09%; N, 19.70%; Found: C, 73.11%; H, 7.13%; N, 19.76%.

4.1.5.14. 3-Isopropyl-4-*p*-tolyl-5-vinyl-4*H*-[1,2,4]triazole (6n). White solid, mp 89–91 °C. ^1H NMR ($CDCl_3$) δ 7.31 (2H, d, J=8.0 Hz), 7.06 (2H, d, J=8.0 Hz), 6.21–6.14 (1H, m), 5.99–5.94 (1H, m), 5.34–5.31 (1H, m), 2.78–2.74 (1H, m), 2.41 (3H, s), 1.21 (3H, s), 1.20 (3H, s); ^{13}C NMR ($CDCl_3$) δ 159.9, 152.1, 140.1, 131.1, 130.5, 127.2, 121.1, 121.0, 25.0, 21.2; MS *m/z* 212 (100), 227 (M^+); IR ν_{max} (cm^{-1}) 3030, 2972, 2929, 1515, 1439, 931, 830, 762; Anal. Calcd for $C_{14}H_{17}N_3$: C, 73.98%; H, 7.54%; N, 18.49%; Found: C, 74.07%; H, 7.51%; N, 18.42%.

4.1.5.15. 3-Isopropyl-4-*o*-tolyl-5-vinyl-4*H*-[1,2,4]triazole (6o). Oil. ^1H NMR ($CDCl_3$) δ 7.48–7.46 (1H, m), 7.43–7.39 (2H, m), 7.19–7.17 (1H, d), 6.26–6.19 (1H, m), 5.93–5.89 (1H, m), 5.38–5.35 (1H, m), 2.70–2.66 (1H, m), 2.00 (3H, s), 1.30–1.26 (6H, m); ^{13}C NMR ($CDCl_3$) δ 159.5, 151.5, 135.7, 132.7, 131.5, 130.2, 127.8, 127.4, 121.1, 120.8, 25.0, 21.4, 20.7, 17.1; MS *m/z* 212 (100), 227 (M^+); IR ν_{max} (cm^{-1}) 3053, 2972, 2929, 1498, 1439, 1098, 1012, 778; Anal. Calcd for $C_{14}H_{17}N_3$: C, 73.98%; H, 7.54%; N, 18.49%; Found: C, 73.90%; H, 7.57%; N, 18.53%.

4.1.5.16. 3-Hexyl-4-*m*-tolyl-5-vinyl-4*H*-[1,2,4]triazole (6p). Oil. ^1H NMR ($CDCl_3$) δ 7.47–7.36 (2H, m), 7.04–7.03 (2H, m), 6.29–6.23 (1H, m), 6.11–6.06 (1H, m), 5.43–5.40 (1H, m), 2.62–2.58 (2H, m), 2.46 (3H, s), 1.64–1.61 (2H, m), 1.28–1.19 (6H, m), 0.85–0.81 (3H, m); ^{13}C NMR ($CDCl_3$) δ 155.1, 151.7, 140.0, 133.4, 130.3, 129.5, 127.4, 124.0, 120.8, 120.7, 30.9, 28.4, 27.0, 24.6, 22.0, 21.0, 13.7; MS *m/z* 198 (100), 269 (M^+); IR ν_{max} (cm^{-1}) 3049, 2926, 2857, 1609, 1493, 1456, 927, 797, 700; Anal. Calcd for $C_{17}H_{23}N_3$: C, 75.80%; H, 8.61%; N, 15.60%; Found: C, 75.68%; H, 8.65%; N, 15.67%.

4.1.5.17. 3-Hexyl-4-*o*-tolyl-5-vinyl-4*H*-[1,2,4]triazole (6q). Oil. ^1H NMR ($CDCl_3$) δ 7.44–7.35 (3H, m), 7.13–7.11 (1H, d), 6.23–6.16 (1H, m), 5.90–5.85 (1H, d), 5.34–5.31 (1H, d), 2.49–2.43 (2H, m), 1.96 (3H, s), 1.60–1.56 (2H, m), 1.25–1.16 (6H, m), 0.80–0.77 (3H, m); ^{13}C NMR ($CDCl_3$) δ 155.1, 151.6, 135.5, 132.6, 131.5, 130.2, 127.6, 127.4, 121.1, 120.6, 31.1, 28.6, 26.9, 24.7, 22.2, 17.1, 13.8; MS *m/z* 212 (100), 269 (M^+); IR ν_{max} (cm^{-1}) 3053, 2927, 2857, 1637, 1498, 1461, 1012, 928, 759; Anal. Calcd for $C_{17}H_{23}N_3$: C, 75.80%; H, 8.61%; N, 15.60%; Found: C, 75.71%; H, 8.66%; N, 15.63%.

4.1.6. Typical procedure for the preparation of the 5-phenylselenoethyl-2-substituted 1,3,4-oxadiazoles (products 9a–e). The mixture of compounds **4** (0.5 mmol) and 15 mL phosphorus oxychloride was refluxed for 6 h under nitrogen atmosphere. After completion of the reaction, the mixture was evaporated to dryness under vacuum. The residual compounds were loaded on a silica gel column and eluted with petroleum ether/ethyl acetate to afford the product **9**.

4.1.6.1. 2-Phenyl-5-(2-phenylselanyl-ethyl)-[1,3,4]oxadiazole (9a). Oil. ^1H NMR ($CDCl_3$) δ 7.98–7.95 (2H, m), 7.54–7.52 (2H, m), 7.48–7.45 (3H, m), 7.24–7.22 (3H, m), 3.29 (4H, s); ^{13}C NMR ($CDCl_3$) δ 165.4, 164.7, 133.6, 131.6, 129.2, 128.9, 128.5, 127.6, 126.7, 123.8, 26.9, 23.1;

MS *m/z* 249 (100), 330 (M^+); IR ν_{max} (cm^{-1}) 3057, 2931, 1727, 1575, 1478, 1177, 738, 691; Anal. Calcd for $C_{16}H_{14}N_2OSe$: C, 58.37%; H, 4.29%; N, 8.51%; Found: C, 58.31%; H, 4.34%; N, 8.59%.

4.1.6.2. 2-(4-Methoxy-phenyl)-5-(2-phenylselanyl-ethyl)-[1,3,4]oxadiazole (9b). White solid, mp 72–74 °C. ^1H NMR ($CDCl_3$) δ 7.82 (2H, d, J=8.8 Hz), 7.46–7.43 (2H, m), 7.16–7.14 (3H, m), 6.88 (2H, d, J=8.8 Hz), 3.73 (3H, s), 3.20–3.18 (4H, m); ^{13}C NMR ($CDCl_3$) δ 164.5, 164.2, 161.7, 133.1, 128.8, 128.2, 128.0, 127.1, 115.8, 113.9, 55.0, 26.5, 22.7; MS *m/z* 279 (100), 360 (M^+); IR ν_{max} (cm^{-1}) 2931, 2836, 1615, 1502, 1301, 1254, 1178, 1022, 959, 717; Anal. Calcd for $C_{17}H_{16}N_2O_2Se$: C, 56.83%; H, 4.49%; N, 7.80%; Found: C, 56.78%; H, 4.56%; N, 7.88%.

4.1.6.3. 2-Methyl-5-(2-phenylselanyl-ethyl)-[1,3,4]-oxadiazole (9c). Oil. ^1H NMR ($CDCl_3$) δ 7.41–7.39 (2H, m), 7.16–7.14 (3H, m), 3.11–3.07 (4H, m), 2.31 (3H, s); ^{13}C NMR ($CDCl_3$) δ 165.0, 163.1, 133.0, 128.7, 128.1, 127.0, 26.2, 22.5, 10.4; MS *m/z* 187 (100), 268 (M^+); IR ν_{max} (cm^{-1}) 3055, 2934, 1595, 1569, 1478, 1437, 1217, 1050, 740, 692; Anal. Calcd for $C_{11}H_{12}N_2OSe$: C, 49.45%; H, 4.53%; N, 10.48%; Found: C, 49.52%; H, 4.60%; N, 10.39%.

4.1.6.4. 2-Isopropyl-5-(2-phenylselanyl-ethyl)-[1,3,4]-oxadiazole (9d). Oil. ^1H NMR ($CDCl_3$) δ 7.44–7.41 (2H, m), 7.18–7.15 (3H, m), 3.14–3.08 (4H, m), 3.04–2.98 (1H, m), 1.26 (3H, s), 1.24 (3H, s); ^{13}C NMR ($CDCl_3$) δ 170.5, 165.0, 133.1, 128.8, 128.2, 127.2, 26.4, 25.8, 22.6, 19.5; MS *m/z* 215 (100), 296 (M^+); IR ν_{max} (cm^{-1}) 3055, 2975, 1587, 1563, 1478, 1437, 1022, 739, 692; Anal. Calcd for $C_{13}H_{16}N_2OSe$: C, 52.89%; H, 5.46%; N, 9.49%; Found: C, 52.98%; H, 5.50%; N, 9.46%.

4.1.6.5. 2-Hexyl-5-(2-phenylselanyl-ethyl)-[1,3,4]oxadiazole (9e). Oil. ^1H NMR ($CDCl_3$) δ 7.50–7.47 (2H, m), 7.24–7.22 (3H, m), 3.19–3.15 (4H, m), 2.73–2.70 (2H, m), 1.71–1.68 (2H, m), 1.33–1.24 (6H, m), 0.86–0.83 (3H, m); ^{13}C NMR ($CDCl_3$) δ 166.8, 165.1, 133.3, 128.9, 128.3, 127.3, 31.0, 28.3, 26.5, 26.0, 25.0, 22.7, 22.1, 13.7; MS *m/z* 257 (100), 338 (M^+); IR ν_{max} (cm^{-1}) 3056, 2930, 2858, 1590, 1566, 1478, 1437, 1173, 738, 692; Anal. Calcd for $C_{16}H_{22}N_2OSe$: C, 56.97%; H, 6.57%; N, 8.30%; Found: C, 56.85%; H, 6.66%; N, 8.39%.

4.1.7. Typical procedure for the preparation of the 5-vinyl-2-substituted 1,3,4-oxadiazoles (products 10a–e). Compounds **9** (0.3 mmol) were dissolved in THF (15 mL), 30% (aq) H_2O_2 (0.4 mL) was added, and the mixture was stirred for 10 min at 0 °C followed by 1.5 h at room temperature. The mixture was partitioned between DCM and water. The organic layer was separated and the aqueous layer was extracted with ethyl acetate twice. The combined organic layers were washed with brine, dried over Mg_2SO_4, and concentrated in vacuo. The residual compounds were loaded on a silica gel column and eluted with petroleum ether/ethyl acetate to afford the product **10**.

4.1.7.1. 2-Phenyl-5-vinyl-[1,3,4]oxadiazole (10a). Oil. ^1H NMR ($CDCl_3$) δ 8.10–8.08 (2H, m), 7.55–7.50 (3H, m), 6.83–6.76 (1H, m), 6.37–5.85 (2H, m); ^{13}C NMR ($CDCl_3$) δ 164.1, 163.5, 131.8, 129.0, 126.9, 124.8, 123.7, 120.0; MS *m/z* 172 (M^+, 100); IR ν_{max} (cm^{-1}) 3066, 2925, 1551, 1523, 1485, 1450, 781, 706, 690; Anal. Calcd for $C_{10}H_8N_2O$: C, 69.76%; H, 4.68%; N, 16.27%; Found: C, 69.66%; H, 4.73%; N, 16.35%.

4.1.7.2. 2-(4-Methoxy-phenyl)-5-vinyl-[1,3,4]oxadiazole (10b). White solid, mp 80–82 °C. ^1H NMR ($CDCl_3$) δ 7.89 (2H, d, J=8.8 Hz), 6.89 (2H, d, J=8.8 Hz), 6.71–6.64 (1H, m), 6.23–5.73 (2H, m), 3.75 (3H, s); ^{13}C NMR ($CDCl_3$) δ 163.5, 162.6, 161.8, 128.1, 123.9, 119.4, 115.5, 113.9, 54.9; MS *m/z* 135 (100), 202 (M^+); IR ν_{max} (cm^{-1}) 3107, 2999, 2951, 1615, 1501, 1311, 1264, 1182, 1088, 1019, 835, 696, 610; Anal. Calcd for $C_{11}H_{10}N_2O_2$: C, 65.34%; H, 4.98%; N, 13.85%; Found: C, 65.40%; H, 4.94%; N, 13.82%.

4.1.7.3. 2-Methyl-5-vinyl-[1,3,4]oxadiazole (10c). Oil. ^1H NMR ($CDCl_3$) δ 6.73–6.66 (1H, m), 6.23–5.78 (2H, m), 2.56 (3H, s); ^{13}C NMR ($CDCl_3$) δ 163.8, 163.2, 124.4, 119.9, 10.9; MS *m/z* 110 (M^+, 100); IR ν_{max} (cm^{-1}) 2926, 2855, 1719, 1563, 1271, 1072; Anal. Calcd for $C_5H_6N_2O$: C, 54.54%; H, 5.49%; N, 25.44%; Found: C, 54.40%; H, 5.55%; N, 25.49%.

4.1.7.4. 2-Isopropyl-5-vinyl-[1,3,4]oxadiazole (10d). Oil. ^1H NMR ($CDCl_3$) δ 6.74–6.67 (1H, m), 6.24–5.78 (2H, m), 3.23–3.18 (1H, m), 1.43 (3H, s), 1.41 (3H, s); ^{13}C NMR ($CDCl_3$) δ 170.3, 163.4, 124.2, 119.9, 26.1, 19.7; MS *m/z* 55 (100), 138 (M^+); IR ν_{max} (cm^{-1}) 2977, 2936, 1725, 1563, 1467, 1152, 1061; Anal. Calcd for $C_7H_{10}N_2O$: C, 60.85%; H, 7.30%; N, 20.28%; Found: C, 60.74%; H, 7.34%; N, 20.33%.

4.1.7.5. 2-Hexyl-5-vinyl-[1,3,4]oxadiazole (10e). Oil. ^1H NMR ($CDCl_3$) δ 6.74–6.67 (1H, m), 6.23–5.77 (2H, m), 2.88–2.84 (2H, m), 1.83–1.79 (2H, m), 1.41–1.31 (6H, m), 0.91–0.88 (3H, m); ^{13}C NMR ($CDCl_3$) δ 166.4, 163.4, 124.1, 119.8, 31.0, 28.4, 26.2, 25.1, 22.2, 13.7; MS *m/z* 110 (100), 180 (M^+); IR ν_{max} (cm^{-1}) 2931, 2860, 1572, 1529, 1462, 982; Anal. Calcd for $C_{10}H_{16}N_2O$: C, 66.63%; H, 8.95%; N, 15.54%; Found: C, 66.50%; H, 9.01%; N, 15.59%.

Acknowledgements

We are grateful to the National Natural Science Foundation of China (Project nos. 20672095 and 20332060).

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