Solid-phase organic synthesis of vinyl-substituted 1,2,4-triazoles based on polymer-supported α-selenopropionic acid

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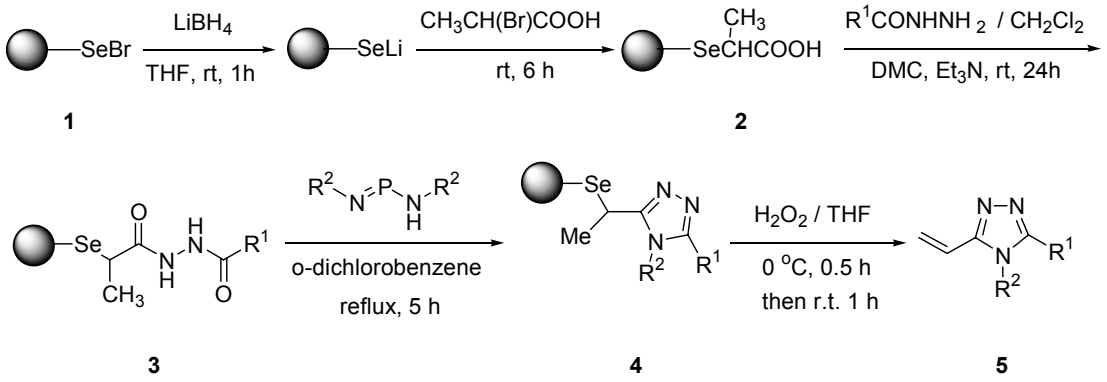
Abstract
Acylation of polystyrene-supported α-selenopropionic acid with acid hydrazides, followed by cyclocondensation with arylphosphazoanilides, and oxidation-elimination with 30 % hydrogen peroxide efficiently afforded vinyl-substituted 1,2,4-triazoles in good yield and purity, with advantages of decreased volatility and simplification of work-up procedure.

Keywords: Solid-phase organic synthesis, polystyrene-supported α-selenopropionic acid, vinyl-substituted 1,2,4-triazole

Introduction

Polymer-supported reagents have attracted growing interest because they can provide attractive and practical methods for combinatorial chemistry and solid-phase organic synthesis (SPOS) in recent years. [1] SPOS using insoluble solid supports such as polystyrene resins takes advantage of the simple removal of excess or consumed reagents by a simple filtration workup operation. Now, the design and synthesis of pharmacologically relevant heterocyclic molecules using SPOS methodology is recognized as a valuable tool for acceleration of drug discovery. The 1,2,4-triazole system has been known to be an important heterocycle in biologically active molecules. This five-numbered ring was also found in potent agonist or antagonist receptor ligands.[2] Furthermore, 1,2,4-triazole derivatives have been used as mimics [3] of the amide bond in order to increase bioavailability of the parent bioactive molecules. They have also been incorporated into peptides to surrogate *cis* amide bonds.[4] Among the 1,2,4-triazoles, vinyl substituted derivatives have now attracted considerable attention because of their biological properties,[5] such as antiallergic, antibacterial, and anti-HIV activity. However, to our knowledge, vinyl substituted 1,2,4-triazoles are seldom reported.[6] Although SPOS of 1,2,4-triazoles are investgated,[7] efforts are continuing for the development of more efficient methods with experimental simplicity.

Recently, we have reported vinyl-substituted 1,2,4-triazoles using polymer-supported ethyl β-phenylselenopropionate reagent.[8] In continuation of our interest in SPOS of biologically relevant heterocyclic compounds based on polymeric selenium reagent, we here wish to describe another simple and efficient traceless solid-phase synthetic approach to vinyl-substituted 1,2,4-triazoles based on polymer-supported α-selenopropionic acid (Scheme 1).



Scheme 1. SPOS of vinyl-substituted 1,2,4-triazoles.

Results and Discussions

Polymer-supported α-selenopropionic acid **2** was prepared by treatment of a THF-swollen suspension of cross-linked (1%) polystyrene bound selenium bromide **1** [9] with $LiBH_4$, followed by treatment with 2-bromopropionic acid according to our previous method.[10] The minimum loading of COOH of resin **2** verified by their FT-IR spectra showing a strong carbonyl absorption at 1726 cm^{-1} were determined by acid-base titration [11] to be 1.20 mmol/g. With resin **2** in hand, the acylation of the polymeric α-selenopropionic acid **2** with various acid hydrazides, the key for the success of this protocol was investigated. Here, the diacylhydrazination reaction was investigated starting from resin **2** and benzoic hydrazide. When DCC (dicyclohexyl carbodiimide) or HBTU (*O*-benzotriazol-1-yl-*N,N,N',N'*-tetramethyluronium hexafluorophosphate) was used as a coupling reagent to promote above reaction at room temperature or under reflux in CH_2Cl_2 or THF for 10 h or even for longer time, the diacylhydrazination on solid-phase was not complete as monitored by FT-IR study, which showed two strong peaks of carbonyl absorptions near 1726 and 1595 cm^{-1}. Interestingly, when DMC (2-chloro-1,3-dimethylimidazolinium chloride) [12] was added to the suspension of resin **2** with benzoic hydrazide in CH_2Cl_2 at room temperature, the conversion of resin **2** to polymer-bound diacyl hydrazide **3a** was complete. The FT-IR spectrum of resin **3a** showed a single strong carbonyl peak at 1595 cm^{-1}, with disappearance of the band at 1726 cm^{-1}. Next, the cyclocondensation of diacyl hydrazide resin **3** with arylphosphazoanilide (Ar-N=P-NH-Ar) [13] proceeded smoothly according our published method to furnish resin **4** (FT-IR spectra showed

C=N group absorptions at 1635-1641 cm^{-1}, with disappearance of the band at 1595 cm^{-1}), followed by selenoxide syn elimination with excess of 30 % hydrogen peroxide to afford the corresponding vinyl-substituted 1,2,4-triazoles **5** in moderate to good yields (74-83 %) and with good purities (88-94 %) of crude materials in all cases (Table 1). The residual resin, polystyrene-supported phenylseleninic acid, was obtained as a by-product, whose infrared data was identical to the previously reported data,[14] and showed no residual C=N group absorption indicating the oxidation-elimination was complete.

Table 1. The yields and purities of vinyl-substituted 1,2,4-trizoles **5a-5l**

Entry	R^1	R^2	Products	Yield (%) [a]	Purity (%) [b]
1	C_6H_5	C_6H_5	**5a**	82	94
2	C_6H_5	4-$CH_3C_6H_4$	**5b**	81	90
3	C_6H_5	3-$CH_3OC_6H_4$	**5c**	80	91
4	C_6H_5	4-ClC_6H_4	**5d**	78	89
5	$C_6H_5CH_2$	2-$CH_3C_6H_5$	**5e**	75	88
6	$C_6H_5CH_2$	3-$CH_3OC_6H_4$	**5f**	76	90
7	$C_6H_5CH_2$	2,4-$(CH_3)_2C_6H_3$	**5g**	80	92
8	$C_6H_5CH_2$	4-ClC_6H_4	**5h**	82	91
9	CH_3	C_6H_5	**5i**	83	92
10	CH_3	3-$CH_3OC_6H_4$	**5j**	80	91
11	CH_3	4-ClC_6H_4	**5k**	78	90
12	CH_3	1-naphthalenyl	**5l**	74	88

[a]Overall yields based on polystyrene-supported α-selenopropionic acid **2** (1.20 mmol COOH/g). [b]Determined by HPLC of crude cleavage product (λ = 254 nm).

In summary, a novel and efficient procedure for the solid-phase synthesis of vinyl-substituted 1,2,4-trizoles in moderate to good yields and with good purities using polymer-supported α-selenopropionic acid. The advantages of this method include straightforward operation, lack of odor, stability, and high purity of the product.

Experimental Section

General Procedure. Melting points were determined on X_4 melting point apparatus and are uncorrected. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker Avance (400 MHz) spectrometer using $CDCl_3$ as the solvent and TMS as an internal standard. FT-IR spectra were taken on a Perkin-Elmer SP One FT-IR spectrophotometer. Microanalyses were performed with a PE 2400 elemental analyzer. Mass spectra (EI, 70eV) were recorded on a HP5989B mass spectrometer. HPLC analysis was carried out on Agilent 1100 (250×4.6 mm C_{18}

Column, gradient elution 50/20/30 THF/CH_3OH/H_2O (v/v), 1 mL/min, UV detection at λ = 254 nm). Polystyrene (H 1000, 100-200 mesh, cross-linked with 1% divinylbenzene) for the preparation of polystyrene-supported selenium bromide [9] and other starting materials were purchased from commercial suppliers and used without further purification. CH_2Cl_2 was distilled from phosphorous pentoxide and THF was stilled from sodium-benzophenone immediately prior to use. Arylphosphazoanilide (Ar-N=P-NH-Ar)[8] and polystyrene-supported α-selenopropionic acid[10] were prepared in our laboratory according to the literature procedure

General procedure for the preparation of vinyl-substituted 1,2,4-triazole derivatives (5a-5l) Resin **2** (1.0 mmol) was swelled in anhydrous CH_2Cl_2 (20 mL) at room temperature for 30 min. Acid hydrazides (2.0 mmol), DMC (0.20 g, 1.2 mmol) and triethylamine (2.0 mmol) was added under nitrogen to the mixture. After 24 h with stirring at room temperature, the mixture was filtered and the resin was washed thoroughly successively with H_2O, THF, MeOH and CH_2Cl_2 (2×5 mL of each) and then dried under vacuum to afford resin **3**. Under a positive pressure of nitrogen, arylphosphazoanilide (3.0 mmol) was added to a suspension of the swollen resin **3** in 1,2-dichlorobenzene (15 mL). The mixture was stirred for 5 h at reflux. Resin **4** was collected by filtration and washed successively with DMF (3×10 mL), THF/H_2O (2:1) (2×10 mL), THF (2×10 mL), H_2O (2×10 mL), THF (2×10 mL), acetone (2×10 mL), THF (1×10 mL), CH_3OH (2×10 mL), and THF (1×10 mL). The washed resin **4** was then suspended in THF (15 mL), and 30 % hydrogen peroxide (0.5 mL, 5.8 mmol) was added; the mixture was stirred for 30 min at 0 °C, followed by 1 h at room temperature. The mixture was filtered, and the residual resin was washed with CH_2Cl_2 (3×10 mL). The filtrate was washed with H_2O (2×20 mL), dried over $MgSO_4$, and evaporated to dryness under vacuum to obtain the crude products **5**. Further purification was *via* flash chromatography with *n*-hexane/acetone (1:1, v/v) as the eluent for ^{1}H NMR, ^{13}C NMR, and microanalysis.

4,5-Diphenyl-3-vinyl-1,2,4-triazole (5a). White solid. Mp 114-115 °C; ^{1}H NMR: δ = 7.52-7.50 (m, 3H, Ar-*H*), 7.41-7.39 (m, 2H, Ar-*H*), 7.34-7.22 (m, 5H, Ar-*H*), 6.32-6.30 (m, 1H, =C*H*), 6.32-6.30 (m, 1H, =CH_2), 6.26-6.22 (m, 1H, =CH_2); ^{13}C NMR: δ = 154.1 (C3), 153.0 (C5), 134.5 (=*C*H), 130.0 (C), 129.7 (2 × *C*H), 129.5 (C), 128.2 (2 × *C*H), 128.1 (2 × *C*H), 127.5 (2 × *C*H), 126.8 (*C*H), 122.1 (*C*H), 120.4 (=*C*H_2); EIMS: *m/z* (%) = 247 (M^+); IR (KBr): ν = 3060, 1596, 1498, 1468, 1445, 1428, 1080, 780, 696 cm^{-1}; Anal. Calcd for $C_{16}H_{13}N_3$: C, 77.71; H, 5.30; N, 16.99. Found: C, 77.68; H, 5.36; N, 16.95.

4-(4-Methylphenyl)-5-phenyl-3-vinyl-1,2,4-triazole (5b). White solid. Mp 106-108 °C; ^{1}H NMR: δ = 7.45 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 7.34-7.26 (m, 5H, Ar-*H*), 7.09 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 6.31-6.29 (m, 1H, =C*H*), 6.26-6.22 (m, 1H, =CH_2), 5.52-5.50 (m, 1H, =CH_2), 2.45 (s, 3H, CH_3); ^{13}C NMR: δ = 154.0 (C3), 153.4 (C5), 140.1 (C), 131.6 (=*C*H), 130.6 (2 × *C*H), 129.6 (2 × *C*H), 128.5 (2 × *C*H), 128.3 (2 × *C*H), 127.2 (C), 126.9 (*C*H), 122.3 (*C*H), 120.5 (=*C*H_2), 21.1 (*C*H_3); EIMS: *m/z* (%) = 261 (M^+); IR (KBr): ν = 2920, 2851, 1632, 1515, 1470, 1449, 1430, 1395, 832, 760, 695 cm^{-1}; Anal. Calcd for $C_{17}H_{15}N_3$: C, 78.13; H, 5.79; N, 16.08. Found: C, 78.16; H, 5.84; N, 16.05.

4-(3-Methoxyphenyl)-5-phenyl-3-vinyl-1,2,4-triazole (5c). White solid. Mp 82-83 °C; ^{1}H NMR: δ = 7.48-7.40 (m, 2H, Ar-*H*), 7.34-7.32 (m, 1H, Ar-*H*), 7.30-7.27 (m, 3H, Ar-*H*), 7.08-7.05 (m, 1H, Ar-*H*), 6.84-6.81 (m, 1H, Ar-*H*), 6.72-6.70 (m, 1H, Ar-*H*), 6.35-6.32 (m, 1H, =C*H*), 6.22-6.18 (m, 1H, =CH_2), 5.55-5.52 (m, 1H, =CH_2), 3.80 (s, 3H, OCH_3); ^{13}C NMR: δ = 160.8 (C), 153.8 (C3), 153.1 (C5), 135.5 (=*C*H), 130.7 (C), 129.5 (2 × *C*H), 128.4 (C), 128.2 (*C*H), 126.7 (*C*H), 122.5 (*C*H), 120.5 (=*C*H_2), 120.0 (2 × *C*H), 115.3 (*C*H), 113.2 (*C*H), 55.5 (O*C*H_3); EIMS: *m/z* (%) = 277 (M^+); IR (KBr): ν = 3424, 3066, 2924, 2851, 1602, 1495, 1468, 1431, 1229, 1026, 695 cm^{-1}; Anal. Calcd for $C_{17}H_{15}N_3O$: C, 73.63; H, 5.45; N, 15.15. Found: C, 73.66; H, 5.48; N, 15.18.

4-(4-Chlorophenyl)-5-phenyl-3-vinyl-1,2,4-triazole (5d). White solid. Mp 159-161 °C; ^{1}H NMR: δ = 7.51 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 7.39-7.26 (m, 5H, Ar-*H*), 7.18 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 6.32-6.27 (m, 1H, =C*H*), 6.22-6.20 (m, 1H, =CH_2), 5.56-5.53 (m, 1H, =CH_2); ^{13}C NMR: δ = 153.6 (C3), 152.9 (C5), 135.7 (=*C*H), 132.5 (C), 130.2 (C), 129.5 (2 × *C*H), 128.8 (2 × *C*H), 128.5 (2 × *C*H), 128.1 (C), 126.3 (2 × *C*H), 122.6 (=*C*H_2), 120.0 (*C*H); EIMS: *m/z* (%) = 281 (M^+); IR (KBr): ν = 3091, 3065, 1495, 1466, 1428, 1090, 1010, 935, 846, 758, 699 cm^{-1}; Anal. Calcd for $C_{16}H_{12}ClN_3$: C, 68.21; H, 4.29; N, 14.91. Found: C, 68.24; H, 4.32; N, 14.96.

4-(2-Methylphenyl)-5-benzyl-3-vinyl-1,2,4-triazole (5e). White solid. Mp 71-73 °C; ^{1}H NMR: δ = 7.39-7.36 (m, 1H, Ar-*H*), 7.28-7.20 (m, 2H, Ar-*H*), 7.13-7.05 (m, 3H, Ar-*H*), 6.95-6.91 (m, 1H, Ar-*H*), 6.84-6.81 (m, 2H, Ar-*H*), 6.20-6.12 (m, 1H, =C*H*), 5.95-5.91 (m, 1H, =CH_2), 5.36-5.34 (m, 1H, =CH_2), 4.04-3.91 (m, 2H, CH_2), 1.52 (s, 3H, CH_3); ^{13}C NMR: δ = 153.7 (C3), 152.3 (C5), 136.0 (=*C*H), 135.1 (C), 132.2 (*C*H), 131.2 (C), 130.3 (2 × *C*H), 128.7 (2 × *C*H), 128.4 (C), 127.8 (*C*H), 127.3 (*C*H), 126.5 (*C*H), 121.1 (=*C*H_2), 120.8 (*C*H), 31.5 (*C*H_2), 16.7 (*C*H_3); EIMS: *m/z* (%) = 275 (M^+); IR (KBr): ν = 3036, 2925, 1498, 1460, 1441, 1018, 936, 770, 723, 699, 585 cm^{-1}; Anal. Calcd for $C_{18}H_{17}N_3$: C, 78.52; H, 6.22; N, 15.26. Found: C, 78.54; H, 6.26; N, 15.29.

4-(3-Methoxyphenyl)-5-benzyl-3-vinyl-1,2,4-triazole (5f). White solid. Mp 96-98 °C; ^{1}H NMR: δ = 7.36-7.28 (m, 1H, Ar-*H*), 7.18-7.15 (m, 3H, Ar-*H*), 7.03-6.97 (m, 3H, Ar-*H*), 6.61-6.58 (m, 1H, Ar-*H*), 6.34-6.32 (m, 1H, Ar-*H*), 6.26-6.20 (m, 1H, =C*H*), 6.15-6.11 (m, 1H, =CH_2), 5.46-5.43 (m, 1H, =CH_2), 4.02 (s, 2H, CH_2), 3.63 (s, 3H, OCH_3); ^{13}C NMR: δ = 160.2 (C), 153.8 (C3), 152.3 (C5), 135.7 (C), 134.2 (=*C*H), 130.3 (C), 128.5 (2 × *C*H), 128.3 (2 × *C*H), 126.6 (*C*H), 121.8 (=*C*H_2), 120.8 (*C*H), 119.5 (*C*H), 116.0 (*C*H), 112.7 (*C*H), 55.4 (O*C*H_3), 31.5 (*C*H_2); EIMS: *m/z* (%) = 291 (M^+); IR (KBr): ν = 3029, 2905, 1496, 1441, 1090, 1030, 845, 746, 733 cm^{-1}; Anal. Calcd for $C_{18}H_{17}N_3O$: C, 74.20; H, 5.88; N, 14.42. Found: C, 74.24; H, 5.93; N, 14.39.

4-(2,4-Dimethylphenyl)-5-benzyl-3-vinyl-1,2,4-triazole (5g). White solid. Mp 111-113 °C; ^{1}H NMR: δ = 7.14-7.06 (m, 5H, Ar-*H*), 6.91-6.80 (m, 3H, Ar-*H*), 6.22-6.16 (m, 1H), 5.96-5.93 (m, 1H, Ar-*H*), 5.36-5.33 (m, 1H, =C*H*), 4.02-3.88 (m, 2H, =CH_2), 2.40 (s, 3H, CH_3), 1.51 (s, 3H, CH_3); ^{13}C NMR: δ = 153.9 (C3), 152.3 (C5), 140.0 (C), 135.6 (=*C*H), 135.1 (C), 131.7 (C), 129.5 (2 × *C*H), 128.7 (2 × *C*H), 128.0 (C), 127.8 (*C*H), 127.2 (*C*H), 126.7 (*C*H), 121.0 (*C*H), 120.8 (=*C*H_2), 31.2 (*C*H_2), 21.1 (*C*H_3), 16.5 (*C*H_3); EIMS: *m/z* (%) = 289 (M^+); IR (KBr): ν =

3029, 2925, 1505, 1456, 1015, 940, 825, 728 cm^{-1}; Anal. Calcd for $C_{19}H_{19}N_3$: C, 78.86; H, 6.62; N, 14.52. Found: C, 78.89; H, 6.66; N, 14.56.

4-(4-Chlorophenyl)-5-benzyl-3-vinyl-1,2,4-triazole (5h). White solid. Mp 115-116 °C; ^{1}H NMR: δ = 7.40 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 7.18-7.15 (m, 3H, Ar-*H*), 6.95-6.91 (m, 2H, Ar-*H*), 6.91 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 6.23-6.18 (m, 1H, =C*H*), 6.12-6.07 (m, 1H, =CH_2), 5.46-5.43 (m, 1H, =CH_2), 4.03 (s, 2H, CH_2); ^{13}C NMR: δ = 153.8 (C3), 152.3 (C5), 135.7 (=*C*H), 135.2 (C), 131.8 (C), 129.7 (2 × *C*H), 128.8 (2 × *C*H), 128.4 (2 × *C*H), 128.2 (C), 126.7 (2 × *C*H), 122.1 (*C*H), 120.5 (=*C*H_2), 31.2 (*C*H_2); EIMS: *m/z* (%) = 295 (M^+); IR (KBr): ν = 3030, 1495, 1436, 1090, 946, 740, 567 cm^{-1}; Anal. Calcd for $C_{17}H_{14}ClN_3$: C, 69.03; H, 4.77; N, 14.21. Found: C, 68.98; H, 4.81; N, 14.24.

5-Methyl-4-phenyl-3-vinyl-1,2,4-triazole (5i). White solid. Mp 156-158 °C; ^{1}H NMR: δ = 7.61-7.55 (m, 3H, Ar-*H*), 7.25-7.22 (m, 2H, Ar-*H*), 6.31-6.23 (m, 1H, =C*H*), 6.13-6.09 (m, 1H, =CH_2), 5.47-5.44 (m, 1H, =CH_2), 2.30 (s, 3H, CH_3); ^{13}C NMR: δ = 152.2 (C3), 151.7 (C5), 133.8 (=*C*H), 130.1 (2 × *C*H), 129.7 (C), 127.0 (2 × *C*H), 121.4 (*C*H), 120.8 (=*C*H_2), 10.8 (*C*H_3); EIMS: *m/z* (%) = 185 (M^+); IR (KBr): ν = 3051, 1635, 1600, 1504, 1431, 942, 788, 699 cm^{-1}; Anal. Calcd for $C_{11}H_{11}N_3$: C, 71.33; H, 5.99; N, 22.69. Found: C, 71.27; H, 6.03; N, 22.65.

5-Methyl-4-(3-methoxyphenyl)-3-vinyl-1,2,4-triazole (5j). White solid. Mp 146-148 °C; ^{1}H NMR: δ = 7.49-7.45 (m, 1H, Ar-*H*), 7.09-7.05 (m, 1H, Ar-*H*), 6.81-6.80 (m, 1H, Ar-*H*), 6.75-6.73 (m, 1H, Ar-*H*), 6.30-6.25 (m, 1H, =C*H*), 6.15-6.09 (m, 1H, =CH_2), 5.45-5.43 (m, 1H, =CH_2), 3.85 (s, 3H, OCH_3), 2.32 (s, 3H, CH_3); ^{13}C NMR: δ = 160.6 (C), 152.0 (C3), 151.8 (C5), 134.8 (=*C*H), 130.8 (*C*H), 121.6 (CH), 121.0 (=*C*H_2), 119.3 (*C*H), 115.2 (*C*), 113.0 (*C*H), 55.5 (O*C*H_3), 10.9 (CH_3); EIMS: *m/z* (%) = 215 (M^+); IR (KBr): ν = 3055, 2931, 1605, 1495, 1460, 1430, 1280, 1221, 1023, 940, 841 cm^{-1}; Anal. Calcd for $C_{12}H_{13}N_3O$: C, 66.96; H, 6.09; N, 19.52. Found: C, 66.91; H, 6.13; N, 19.55.

5-Methyl-4-(4-chlorophenyl)-3-vinyl-1,2,4-triazole (5k). White solid. Mp 166-168 °C; ^{1}H NMR: δ = 7.52 (d, *J* = 8.1 Hz, 2H, Ar-*H*), 7.22 (d, *J* = 8.1 Hz, 2H, Ar-*H*), 6.24-6.19 (m, 1H, =C*H*), 6.09-6.05 (m, 1H, =CH_2), 6.44-6.41 (m, 1H, =CH_2), 2.27 (s, 3H, CH_3); ^{13}C NMR: δ = 152.0 (C3), 151.7 (C5), 136.0 (=*C*H), 132.1 (2 × *C*H), 130.2 (C), 128.2 (2 × *C*H), 121.7 (=*C*H_2), 120.4 (*C*H), 11.0 (*C*H_3); EIMS: *m/z* (%) = 219 (M^+); IR (KBr): ν = 3056, 1525, 1498, 1430, 1091, 1015, 936, 758 cm^{-1}; Anal. Calcd for $C_{11}H_{10}ClN_3$: C, 60.14; H, 4.59; N, 19.13. Found: C, 60.18; H, 4.63; N, 19.16.

5-Methyl-4-(1-naphthalenyl)-3-vinyl-1,2,4-triazole (5l). Pale yellow solid. Mp 141-143 °C; ^{1}H NMR: δ = 8.07-8.01 (m, 2H, Ar-*H*), 7.64-7.60 (m, 2H, Ar-*H*), 7.56-7.53 (m, 1H, Ar-*H*), 7.41-7.23 (m, 2H, Ar-*H*), 6.15-6.09 (m, 1H, =C*H*), 6.05-6.01 (m, 1H, =CH_2), 5.35-5.32 (m, 1H, =CH_2), 2.23 (s, 3H, CH_3); ^{13}C NMR: δ = 152.8 (C3), 152.6 (C5), 134.5 (=*C*H), 130.6 (C), 130.1 (C), 129.7 (C), 128.7 (*C*H), 128.4 (*C*H), 127.4 (*C*H), 125.8 (*C*H), 125.4 (*C*H), 121.6 (*C*H), 121.4 (*C*H), 120.8 (=*C*H_2), 10.9 (*C*H_3); EIMS: *m/z* (%) = 235 (M^+); IR (KBr): ν = 3420, 3060, 2925, 1600, 1520, 1470, 1071, 958, 812, 780 cm^{-1}; Anal. Calcd for $C_{15}H_{13}N_3$: C, 76.57; H, 5.57; N, 17.86. Found: C, 76.60; H, 5.62; N, 17.82.

Acknowledgements

We gratefully acknowledge financial support from the National Natural Science Foundation of China (No. 20562005), NSF of Jiangxi Province (No. 0620021 and No. 2007GZW0185) and the Research Program of Jiangxi Province Department of Education (No. GJJ08165).

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