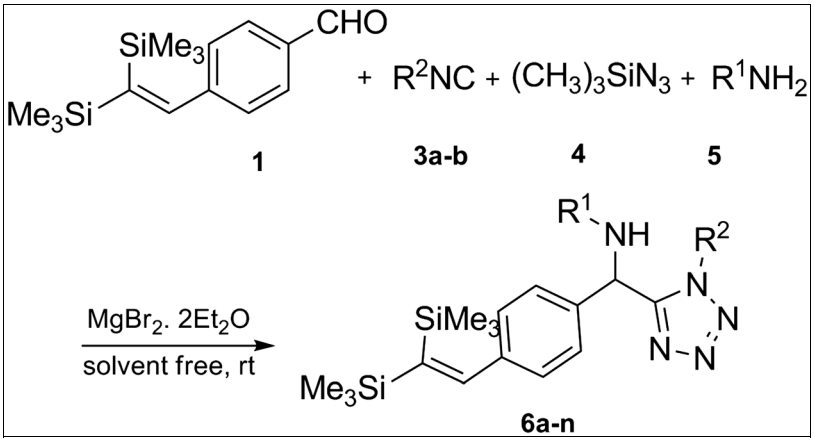
One-Pot Synthesis of New 1,5-Disubstituted Tetrazoles Bearing 2,2-Bis (trimethylsilyl)ethenyl Groups via The Ugi Four-Component Condensation Reaction Catalyzed by $MgBr_2{\cdot}2Et_2O$

Kazem D. Safa,* Tohid Shokri, Hassan Abbasi, and Reza Teimuri-Mofrad

Organosilicon Research Laboratory, Faculty of Chemistry, University of Tabriz, 5166616471 Tabriz, Iran
*E-mail: dsafa@tabrizu.ac.ir

Received June 11, 2012
DOI 10.1002/jhet.1858
Published online 00 Month 2013 in Wiley Online Library (wileyonlinelibrary.com).



A simple one-pot Ugi four-component condensation reaction has been developed for the synthesis of tetrazoles bearing 2,2-bis(trimethylsilyl)ethenyl groups from the synthesized 4-[2,2-bis(trimethylsilyl) ethenyl] benzaldehyde (**1**), various amines, isocyanides, and trimethylsilylazide at room temperature, without solvent, and in the presence of catalytic amounts of $MgBr_2{\cdot}2Et_2O$ as catalyst.

J. Heterocyclic Chem., **00,** 00 (2013).

INTRODUCTION

Tetrazoles are an important class of heterocycles with wide-ranging applications in medicinal and synthetic chemistry. The nitrogen-rich ring system is used in propellants [1], trigger explosives, components of mixed propellants, gas-generating mixtures [2,3], information recording systems [4], and pharmaceuticals [5]. Tetrazoles are also used as monodentate or bidentate ligands in coordination chemistry [6].

The synthesis of monocyclic tetrazoles was originally reported in 1961 [7,8]. It is by use of a variation of classical Ugi reaction that condensation of an aldehyde or ketone with a primary or secondary amine, an isocyanide, and an azide affords the desired tetrazole [9]. Also, synthesis of tetrazoles from a cycloaddition reaction between a nitrile and an azide is well documented [10]. Organosilicon reagents and compounds are valuable in organic synthesis [11]. Because $C(sp^2)$–Si bonds in organosilicon compounds undergo numerous transformations [12, 11c], 2,2-bis (trimethylsilyl)ethenyl compounds are used as precursors for the preparation of ketones and isoxazoline derivatives, as well as a variety of important organosilicon intermediates, such as acylsilanes, epoxysilanes, and silanols [13,14]. We have recently reported new organosilicon compounds containing 2,2-bis(trimethylsilyl)ethenyl groups and their conversion into amines [15].

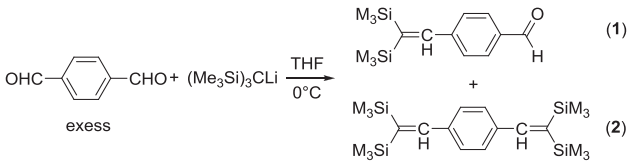
In recent years, it is found that magnesium bromide ethyl etherate ($MgBr_2{\cdot}2Et_2O$) has many applications as a mild Lewis acid because of its ease of preparation, oxophilic nature, and coordinating ability for bidentate chelation that makes various chelation-controlled organic transformations easier [16]. These results prompted us to use this catalyst in the synthesis of new tetrazoles via multicomponent reaction. Although multicomponent reaction based on isocyanide has been applied to the synthesis of 1,5-disubstituted tetrazoles [17,18], our literature survey revealed that this synthetic strategy had not been applied to the synthesis of tetrazoles containing 2,2-bis (trimethylsilyl)ethenyl moiety.

RESULTS AND DISCUSSION

Various heterocyclic compounds have been obtained by the Ugi reaction, either directly [19] or by the post-condensation modification [20]. We used Ugi four-component condensation (Ugi-4CC) to synthesize new tetrazoles bearing 2,2-bis (trimethylsilyl)ethenyl groups from the reaction of bissilylated aldehyde (**1**), which was prepared by the reaction of $(Me_3Si)_3CLi$ with terephthalaldehyde in a Peterson olefination [15] and primary aminese, trimethylsilylazide, and isocyanides (Scheme 1).

To obtain the expected tetrazoles, the reactions were carried out with excess amount of primary amines,

Scheme 1. The preparation of 4-[2,2-bis(trimethylsilyl)ethenyl]benzaldehyde (**1**) via Peterson protocol.

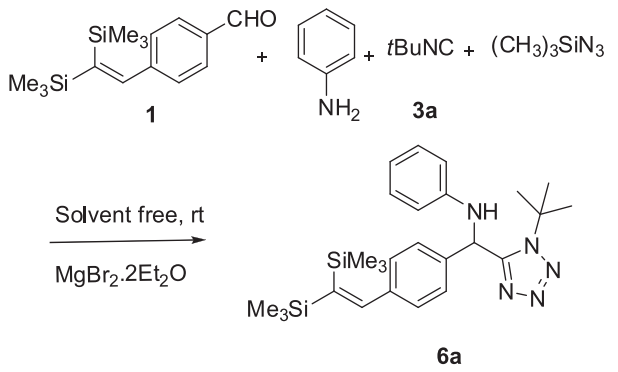


trimethylsilylazide, and isocyanides (**3a**,**b**) under mild conditions, without solvent, and at room temperature in the presence of Lewis acid as a catalyst.

Although $MgBr_2{\cdot}2Et_2O$ has recently been used as a catalyst for the synthesis of various organic compounds [21], we decided to examine its catalytic activity for the synthesis of tetrazoles via Ugi-4CC. Initially, aldehyde (**1**) was reacted with aniline, trimethylsilylazide, and *tert*-butyl isocyanide (**3a**) in the absence of catalyst in methanol as a solvent. In this condition, the reaction took place smoothly to afford the expected adduct (**6a**) in 30% yield at 24 h. $MgBr_2{\cdot}2Et_2O$ catalyst has a significant effect on the reaction rate and yield. In the presence of $MgBr_2{\cdot}2Et_2O$ in methanol as solvent, 65% yield was obtained after 90 min. The reactions were conducted in different solvents such as ethanol, acetonitrile, THF, or CH_2Cl_2. As shown in Table 1, the best result (87% yield) was obtained under solvent-free conditions.

Table 1

One-pot synthesis of the tetrazole **6a** in various organic solvents in the presence of $MgBr_2{\cdot}2Et_2O$.



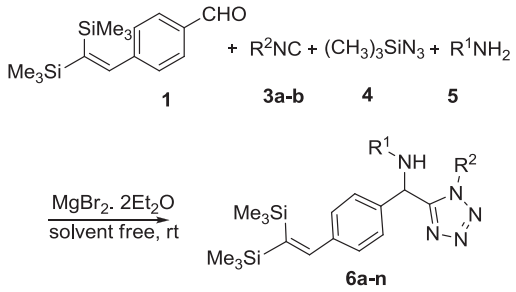
Entry	Solvent	Time (min)	Yield (%)
1	Methanol	90	65
2	THF	60	62
3	Ethanol	50	67
4	CH_3CN	60	69
5	CH_2Cl_2	45	71
6	Neat	30	87

Fortunately, desired products (**6a–6n**) were isolated in excellent yields when the reaction was performed in the solvent-free conditions in the presence of $MgBr_2{\cdot}2Et_2O$. The optimum amount of catalyst was 5 mol% for aromatic and hetrocyclic amines and 10 mol% for aliphatic amines (Scheme 2).

We have not established a detailed mechanism for the formation of **6**; however, a reasonable possibility is shown in Scheme 3 [22]. To prove the efficiency of the conditions, we studied the Ugi-4CC reaction of aldehyde (**1**) and trimethylsilylazide with different amines and isocyanides under similar conditions. The results are presented in Table 2. Primary aromatic amines with electron-donating groups such as methoxy and methyl gave the tetrazole derivatives **6b** and **6d** in slightly higher yield than amines with electron-withdrawing groups such as nitro (**6g**), obtained after 80 min. Heterocyclic amines reacted slowly under these conditions. 2-Aminopyridine gave only 42% yield (**6j**) after 5 h, and 2-aminopyrimidine gave no product even after 3 days. The best results (96% yield) were obtained with *para*-fluoroaniline (**6e**) under the same conditions.

Using cyclohexylisocyanide (**3b**) instead of *tert*-butyl isocyanide (**3a**) gave the similar products (**6m** and **6n**), but the reaction times increased. In continuation of our work, we attempted to synthesize epoxide derivatives of **6a** and **6n** by the reaction of MCPBA in CH_2Cl_2 at room temperature [13], but unfortunately, the ^1H NMR of the products showed that the expected epoxides have not been prepared.

Scheme 2. Synthesis of new tetrazoles (**6**).



Scheme 3. Proposed mechanism.

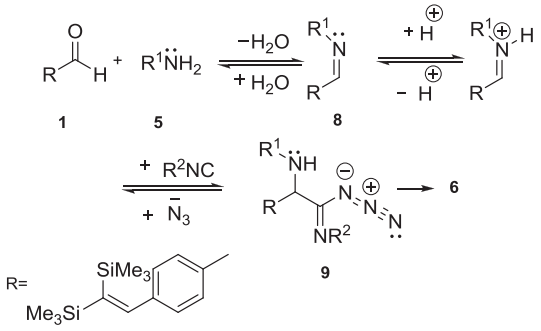


Table 2

Reaction of aldehyde (**1**) with various amines, trimethylsilylazide, and isocyanides in the presence of $MgBr_2{\cdot}2Et_2O$.

Entry	R^1	R^2	Yield (%)	Time	Product
1	C_6H_5	3a	87	30 min	**6a**
2	4-MeC_6H_4	3a	93	40 min	**6b**
3	4-ClC_6H_4	3a	81	35 min	**6c**
4	4-$MeOC_6H_4$	3a	90	30 min	**6d**
5	4-FC_6H_4	3a	96	20 min	**6e**
6	3-ClC_6H_4	3a	78	25 min	**6f**
7	4-$NO_2C_6H_4$	3a	65	80 min	**6g**
8	2-ClC_6H_4	3a	54	20 min	**6h**
9	2-BrC_6H_4	3a	63	15 min	**6i**
10	2-Pyridyl	3a	42	5 h	**6j**
11	$CH_3(CH_2)_2CH_2$	3a	60	2h	**6k**
12	$CH_3(CH_2)_3CH_2$	3a	67	70min	**6l**
13	4-FC_6H_4	3b	75	60min	**6m**
14	C_6H_5	3b	69	90min	**6n**

CONCLUSION

In summary, treatment of aldehyde (**1**) with amines, trimethylsilylazide, and isocyanides gave a series of new tetrazoles containing the 2,2-bis(trimethylsilyl)ethenyl group. The use of $MgBr_2{\cdot}2Et_2O$ as a catalyst decreased the reaction times and increased the yields. We have described a successful route for the convenient synthesis of new tetrazoles bearing 2,2-bis(trimethylsilyl)ethenyl groups via the Ugi-4CC reaction. The method offers several advantages including operational simplicity, mild reaction conditions, good yields, short time reaction, and easy work-up.

EXPERIMENTAL

Reactions involving organolithium reagents were carried out under dry argon. Solvents were dried by standard methods. Substrates for the preparation of 4-[2,2-bis(trimethylsilyl)ethenyl]benzaldehyde (**1**) and also all amines used in the synthesis of tetrazoles, via trimethylsilylazide, *tert*-butyl isocyanide, cyclohexylisocyanide, and $MgBr_2{\cdot}2Et_2O$, were purchased from Merck and Fluka and used without further purification. FTIR spectra were recorded on a Bruker-Tensor 270 spectrometer. ^1H and ^{13}C NMR spectra were recorded with a Bruker FT-400 MHz spectrometer at room temperature and with $CDCl_3$ as solvent. For ^1H NMR, TMS served as internal standard. Mass spectra were obtained with a GC-Mass Agilent quadrupole model 5973N instrument, operating at 70 eV. Melting points were measured with a Barnstead international capillary melting point apparatus.

General procedure for the synthesis of new tetrazole containing 2,2-bis(trimethylsilyl)ethenyl groups (6a–6n). 4-[2,2-Bis(trimethylsilyl)ethenyl]benzaldehyde (0.36 mmol), amine (0.43 mmol), and $MgBr_2{\cdot}2Et_2O$ (mol%) were mixed, and trimethylsilylazide (0.36 mmol) and isocyanide (0.36 mmol) were added after 5 min. The mixture was stirred at room temperature until the reaction was complete (as monitored by TLC). When the reaction was complete, the mixture was poured into water (20 mL) and extracted with dichloromethane (3 × 5 mL). The organic layer was washed with saturated NaCl solution and dried over Na_2SO_4. The solvent was evaporated and the residue purified by preparative TLC (*n*-hexane/ethyl acetate; 10:2) to give the tetrazole.

***N*-{[4-(2,2-Bis(trimethylsilyl)ethenyl)phenyl](1-tert-butyl-1H-tetrazol-5-yl)methyl}aniline (6a).** White solid, mp 143–145°C; FTIR (potassium bromide): 1251, 821, (Si–CH_3), 1622, 1514 (ph), 3320 (NH) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ −0.11 (s, 9H, $SiMe_3$), 0.16 (s, 9H, $SiMe_3$), 1.68 (s, 9H, $C(CH_3)$), 4.77 (d, 1H, J = 9.6 Hz, 1H, NH), 6.12 (d, J = 9.6 Hz, 1H, CH), 6.66 (d, J = 8 Hz, 2H, Ar), 6.76 (t, J = 7.6 Hz, 1H, Ar), 7.13–7.25 (m, 6H, Ar), 7.67 (s, 1H, HC═); ^{13}C NMR (100 MHz, $CDCl_3$): δ −0.56, 0.93 ($SiMe_3$), 29.08)C($\underline{C}H_3$((, 53.67(CH), 61.7($\underline{C}$(CH_3((, 113.54, 118.35, 126.25, 127.6, 128.34, 135.76, 142.32, 144.78, 146.81, 152.57, (Ar, vinyl), 154.07 (tetrazole-C-5) ppm; GC–MS, (EI): *m/z*, 477 (66%, $[M]^+$), 421 (23%, $[M - t\text{-Bu}]^+$), 352 (94%, $[M - C_5H_9N_4]^+$), 73 (100%, $[SiMe_3]^+$).

***N*-{[4-(2,2-Bis(trimethylsilyl)ethenyl)phenyl](1-tert-butyl-1H-tetrazol-5-yl)methyl}4-methylaniline (6b).** Light yellow solid, mp 135–137°C; FTIR (potassium bromide): 1250, 840, (Si–CH_3), 1517 (C_6H_4), 3384 (NH) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ −0.11 (s, 9H, $SiMe_3$), 0.16 (s, 9H, $SiMe_3$), 1.66 (s, 9H, $C(CH_3)$), 2.2 (s, 3H, CH_3), 4.66 (d, 1H, J = 9.6 Hz, 1H, NH), 6.08 (d, J = 9.6 Hz, 1H, CH), 6.59 (d, J = 8 Hz, 2H, Ar), 6.95 (d, J = 8 Hz, 2H, Ar), 7.14 (d, J = 8.0 Hz, 2H, Ar), 7.22 (d, J = 8.0 Hz, 2H, Ar), 7.66 (s, 1H, HC═), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ −0.5, 0.9 ($SiMe_3$), 19.4 (Me), 28.6 ($C(\underline{C}H_3)$), 54.2 (CH), 60.6)$\underline{C}$(CH_3)(, 113.9, 114.2, 126.24, 127.5, 127.7, 128.8, 135.9, 142.2, 142.5, 152.6 (Ar, vinyl), 154.1 (tetrazole-C-5) ppm; GC–MS, (EI): *m/z*, 491 (66%, $[M]^+$), 435 (10% $[M - t\text{-Bu}]^+$), 366 (76%, $[M - C_5H_9N_4]^+$), 207 (100%, $[C_{15}H_{13}N]^+$), 73 (90%, $[SiMe_3]^+$).

***N*-{[4-(2,2-Bis(trimethylsilyl)ethenyl)phenyl](1-tert-butyl-1H-tetrazol-5-yl)methyl}4-chloroaniline (6c).** Yellow solid, mp 135–137°C; FTIR (potassium bromide): 1249, 839 (Si–CH_3), 1597, 1489 (C_6H_4), 3319 (NH) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ −0.11 (s, 9H, $SiMe_3$), 0.16 (s, 9H, $SiMe_3$), 1.67 (s, 9H, $C(CH_3)$), 4.85 (d, 1H, J = 9.6 Hz, 1H, NH), 6.08 (d, J = 9.6 Hz, 1H, CH), 6.58 (d, J = 8.8 Hz, 2H, Ar), 7.09 (d, J = 8.4 Hz, 1H, Ar), 7.15 (d, J = 8.0 Hz, 2H, Ar), 7.24 (d, J = 8.0 Hz, 2H, Ar), 7.66 (s, 1H, HC═); ^{13}C NMR (100 MHz, $CDCl_3$): δ −0.58, 0.91, ($SiMe_3$), 29.0 $C(\underline{C}H_3)$, 53.8 (CH), 60.7 ($\underline{C}(CH_3)$), 114.7, 123.04, 126.23, 127.65, 128.2, 135.2, 142.4, 143.3, 146.9, 152.4 (Ar, vinyl), 153.7 (tetrazole-C-5) ppm; GC–MS, (EI): *m/z*, 512 (7%, $[M]^+$), 455 (7%, $[M - t\text{-Bu}]^+$), 207 (100%, $[C_{15}H_{13}N]^+$); 73 (35%, $[SiMe_3]^+$).

***N*-{[4-(2,2-Bis(trimethylsilyl)ethenyl)phenyl](1-tert-butyl-1H-tetrazol-5-yl)methyl}4-methoxyaniline (6d).** Yellow solid, mp 121–123°C; FTIR (potassium bromide): 1245, 837 (Si–CH_3), 1624, 1512 (C_6H_4), 3441 (NH) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ −0.11 (s, 9H, $SiMe_3$), 0.16 (s, 9H, $SiMe_3$), 1.64 (s, 9H, $C(CH_3)$), 3.7 (s, 3H, OCH_3), 4.52 (d, J = 12 Hz, 1H, NH), 5.99 (d, J = 12 Hz, 1H,CH), 6.67 (d, J = 12 Hz, 2H, Ar), 6.73 (d, J = 12 Hz, 2H, Ar), 7.14 (d, J = 8 Hz, 2H, Ar), 7.21 (d, J = 8 Hz, 2H, Ar), 7.6 (s, 1H, HC═); ^{13}C NMR (100 MHz, $CDCl_3$): δ −0.5, 0.9, ($SiMe_3$), 29.0 ($C(\underline{C}H_3)$), 54.5(CH), 55.5 (OMe), 60.5 ($\underline{C}(CH_3)$), 113.7, 116.2, 126.3, 127.5, 135.9, 142.2, 146.7, 152.6 (Ar, vinyl), 154.1 (tetrazole-C-5) ppm; GC–MS, (EI): *m/z*, 507 (8%, $[M]^+$), 451 (5% $[M - t\text{-Bu}]^+$), 73 (42%, $[SiMe_3]^+$), 207 (100%, $[C_{15}H_{13}N]^+$).

***N*-{[4-(2,2-Bis(trimethylsilyl)ethenyl)phenyl](1-tert-butyl-1H-tetrazol-5-yl)methyl}4-flouroaniline (6e).** Yellow solid, mp 120–123°C; FTIR (potassium bromide): 1249, 836 (Si–CH_3),

1605, 1504 (C_6H_4), 3322 (NH) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ −0.11 (s, 9H, $SiMe_3$), 0.16 (s, 9H, $SiMe_3$), 1.65 (s, 9H, $C(CH_3)$), 4.71 (d, 1H, J = 8.4 Hz, 1H, NH), 6.03 (d, J = 8.4 Hz,1H, CH), 6.64–6.61 (m, 2H, Ar), 6.82–6.87 (m, 2H, Ar), 7.15 (d, J = 8.0 Hz, 2H, Ar), 7.21 (d, J = 8.0 Hz, 2H, Ar), 7.6 (s, 1H, HC═); ^{13}C NMR (100 MHz, $CDCl_3$): δ −0.57, 0.92, ($SiMe_3$), 29.0 ($C(\underline{C}H_3)$), 54.8 (CH), 60.6 ($\underline{C}(CH_3)$), 114.7, 114.9, 126.2, 127.6, 135.5, 141.1, 142.4, 146.9, 152.4, 153.9 (Ar, vinyl), 154.0 (tetrazole-C-5) ppm; GC–MS, (EI): *m/z*, 495 (20%, $[M]^+$), 439 (10% $[M - t\text{-Bu}]^+$), 370 (35%, $[M - C_5H_9N_4]^+$), 207 (100%, $[C_{15}H_{13}N]^+$), 73 (62%, $[SiMe_3]^+$).

N-{[4-(2,2-Bis(trimethylsilyl)ethenyl)phenyl](1-tert-butyl-1H-tetrazol-5-yl)methyl}3-chloroaniline (6f). Yellow solid, mp 144–146°C; FTIR (potassium bromide): 1249, 848 (Si–CH_3), 1600,1497 (C_6H_4), 3448 (NH) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ −0.11 (s, 9H, $SiMe_3$), 0.16 (s, 9H, $SiMe_3$), 1.68 (s, 9H, $C(CH_3)$), 4.9 (d, 1H, J = 9.2 Hz, 1H, NH), 6.07 (d, J = 9.2 Hz, 1H, CH), 6.52 (dd, J = 1.6, 9.1 Hz, 1H, Ar), 6.61 (t, J = 1.6 Hz, 1H, Ar), 6.71 (dd, J = 1.6, 9.1 Hz, 1H, Ar), 7.04 (t, J = 9.2 Hz, 1H, Ar), 7.16 (d, J = 8 Hz, 2H, Ar), 7.23 (d, J = 8 Hz, 1H, Ar), 7.6 (s, 1H, HC═); ^{13}C NMR (100 MHz, $CDCl_3$): δ −0.570, 0.91, ($SiMe_3$), 28.06 ($C(\underline{C}H_3)$), 53.3 (CH), 60.8 ($\underline{C}(CH_3)$), 111.7, 113.01, 118.1, 126.2, 127.6, 129.3, 134.0, 135.1, 142.5, 145.8, 147.03, 152.4 (Ar, vinyl), 153.7 (tetrazole-C-5) ppm; GC–MS, (EI): *m/z*, 511(15%, $[M]^+$), 386 (25%, $[M - C_5H_9N_4]^+$), 207 (100%, $[C_{15}H_{13}N]^+$), 73 (70%, $[SiMe_3]^+$).

N-{[4-(2,2-Bis(trimethylsilyl)ethenyl)phenyl](1-tert-butyl-1H-tetrazol-5-yl)methyl}4-nitroaniline (6g). Yellow solid, mp 70–71°C; FTIR (potassium bromide): 1256, 842 (Si–CH_3), 1643, 1592, 1510 (C_6H_4), 3394 (NH) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ −0.01 (s, 9H, $SiMe_3$), 0.20 (s, 9H, $SiMe_3$), 1.4 (s, 9H, $C(CH_3)$), 4.94 (d, 1H, NH), 5.57 (s, 1H, CH), 6.57 (d, J = 8.4 Hz, 2H, Ar), 6.64 (d, J = 8.4 Hz, 2H, Ar), 7.68 (s, 1H, HC═), 7.97 (d, J = 8.6 Hz, 2H, Ar), 8.18 (d, J = 8.6 Hz, 2H, Ar); ^{13}CNMR (100 MHz, $CDCl_3$): δ −0.550, 1.07 ($SiMe_3$), 27.21 (C($\underline{C}H_3$)), 50.83 (CH), 58.2 ($\underline{C}(CH_3)$), 111.4, 120.9, 123.8, 126.14, 127.9, 135.03, 139.2, 143.7, 147.4, 152.05 (Ar, vinyl), 155.8 (tetrazole-C-5) ppm; GC–MS, (EI), *m/z*: 522 (10%, $[M]^+$), 446 (30%), 207 (100%, $[C_{15}H_{13}N]^+$).

N-{[4-(2,2-Bis(trimethylsilyl)ethenyl)phenyl](1-tert-butyl-1H-tetrazol-5-yl)methyl}2-chloroaniline (6h). White solid, mp 164–166°C; FTIR (potassium bromide): 1248, 839 (Si–CH_3), 1597, 1506 (C_6H_4), 3425 (NH) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ −0.18 (s, 9H, $SiMe_3$), 0.10 (s, 9H, $SiMe_3$), 1.62 (s, 9H, $C(CH_3)$), 5.32 (d, J = 8 Hz, 1H, NH), 6.09 (d, J = 8 Hz, 1H,CH), 6.51 (dd, J = 7.3, 0.8 Hz, 1H, Ar), 6.57–6.63 (m, 1H, Ar), 6.95–6.99 (m, 1H, Ar), 7.10 (d, J = 8.0 Hz, 2H, Ar), 7.18–7.22 (m, 3H, Ar), 7.6 (s, 1H, HC═); ^{13}C NMR (100 MHz, $CDCl_3$): δ −0.50, 0.9, ($SiMe_3$), 29.0 ($C(\underline{C}H_3)$), 53.0 (CH), 60.8 ($\underline{C}(CH_3)_3$), 111.8, 118.2, 119.7, 126.15, 126.5, 127.6, 128.6, 135.11, 140.6, 142.4, 146.8, 152.5 (Ar, vinyl), 153.6 (tetrazole-C-5) ppm; GC–MS (EI): *m/z*, 511 (14%, $[M]^+$), 386 (25%, $[M - C_5H_9N_4]^+$), 207 (100%, $[C_{15}H_{13}N]^+$), 73 (67%, $[SiMe_3]^+$).

N-{[4-(2,2-Bis(trimethylsilyl)ethenyl)phenyl](1-tert-butyl-1H-tetrazol-5-yl)methyl}2-boromoaniline (6i). White solid, mp 153–155°C; FTIR (potassium bromide): 1247, 841 (Si–CH_3), 1593, 1503 (C_6H_4), 3411 (NH) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ −0.12 (s, 9H, $SiMe_3$), 0.16 (s, 9H, $SiMe_3$), 1.70 (s, 9H, $C(CH_3)$), 5.4 (d, J = 8 Hz, 1H, NH), 6.15 (d, J = 8 Hz, 1H, CH), 6.55 (d, J = 8 Hz, 1H, Ar), 6.59–6.63 (m, 1H, Ar), 7.07 (t, J = 8.0 Hz, 1H, Ar), 7.16 (d, J = 8.0 Hz, 2H, Ar), 7.28 (d, J = 8.0 Hz, 2H, Ar), 7.43 (dd, J = 8.0, 1.2 Hz, 1H, Ar), 7.6 (s, 1H, HC═); ^{13}C NMR (100 MHz, $CDCl_3$): δ −0.5, 0.9 ($SiMe_3$), 0.89, 29.0 ($C(\underline{C}H_3)_3$), 53.0 (CH), 60.8 ($\underline{C}(CH_3)$), 111.8, 118.7, 126.12, 127.2, 127.6, 131.8, 135.05, 141.6, 142.43, 146.81, 152.49 (Ar, vinyl), 153.6 (tetrazole-C-5) ppm; GC–MS, (EI); *m/z*, 555 (7%, $[M]^+$), 432 (12%, $[M - C_5H_9N_4]^+$), 207 (100%, $[C_{15}H_{13}N]^+$), 73 (38%, $[SiMe_3]^+$).

N-{[4-(2,2-Bis(trimethylsilyl)ethenyl)phenyl](1-tert-butyl-1H-tetrazol-5-yl)methyl}pyridin-2-amine (6j). Yellow viscous liquid; FTIR (potassium bromide): 837.9, 1257.9 (Si–CH_3), 1559.8, 1603.4 (Ph), 3423.1 (N–H) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ −0.10 (s, 9H, $SiMe_3$), 0.16 (s, 9H, $SiMe_3$), 1.71 (s, 9H, $C(CH_3)$), 4.47 (d, J = 9.2 Hz, 1H, NH), 6.49 (d, J = 8.4 Hz, 1H, CH), 6.59 (t, J = 6.8 Hz, 1H, Ar), 7.06 (d, J = 9.2 Hz, 1H, Ar), 7.14 (d, J = 8.0 Hz, 2H, Ar), 7.22 (d, J = 8.0 Hz, 2H, Ar), 7.35–7.39 (m, 1H, Ar), 7.67 (s, 1H, HC═), 8.0 (d, J = 4.3 Hz, 1H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ −0.55, 0.93 ($SiMe_3$), 28.8($C(\underline{C}H_3)_3$), 49.55 (CH), 60.61 ($\underline{C}(CH_3)$), 108.86, 113.29, 126.61, 127.48, 136.13, 136.3, 142.1, 146.3, 146.6, 152.7, 154.7 (Ar, vinyl), 155.7 (tetrazole-C-5) ppm; GC–MS, (EI): *m/z*, 478 (52%, $[M]^+$), 422 (36% $[M - t\text{-Bu}]^+$), 207 (100%, $[C_{15}H_{13}N]^+$), 73 (85%, $[SiMe_3]^+$).

N-{[4-(2,2-Bis(trimethylsilyl)ethenylphenyl](1-tert-butyl-1H-tetrazol-5-yl)methyl}butan-1-amine (6k). mp 126–130°C; FTIR (potassium bromide); 1250, 840 (Si–CH_3), 1597, 1489 (C_6H_4), 3325 (NH) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ −0.11 (s, 9H, $SiMe_3$), 0.16 (s, 9H, $SiMe_3$), 0.84–0.87 (t, J = 8 Hz, 3H, CH_3), 1.24–1.35 (m, 4H, CH_2), 1.61 (s, 9H, C(CH_3)), 1.83 (s, 1H, NH), 2.47–2.53 (m, 2H, CH_2), 5.2 (s, 1H, (CH)), 7.12–7.20 (m, 4H, Ar), 7.67 (s, 1H, HC═); ^{13}C NMR (100 MHz, $CDCl_3$): δ −0.56, 0.92 ($SiMe_3$), 12.8 (CH_3), 19.32 (CH_2), 28.95 ($C(\underline{C}H_3)_3$), 29.89 (CH_2), 46.69 (CH_2), 57.86 (CH_2), 60.26 ($\underline{C}(CH_3)$), 126.47, 127.3, 136.4, 141.8, 146.4, 152.7 (Ar, vinyl), 154.65 (tetrazole-C-5) ppm; GC–MS, (EI): *m/z*, 457 (25%, $[M]^+$), 401 (20%, $M - t\text{-Bu}]^+$), 429 (95%), 207 (100%, $[C_{15}H_{13}N]^+$), 386 (20%), 73 (35%, $[SiMe_3]^+$).

N-{[(4-(2,2-Bis(trimethylsilyl)ethenyl)phenyl](1-tert-butyl-1H-tetrazol-5-yl)methyl}pentan-1-amine (6l). mp 131–134°C; FTIR (potassium bromide); 838, 1248 (Si–CH_3), 1498, 1615 (C_6H_4), 3339 (N–H) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ −0.11 (s, 9H, $SiMe_3$), 0.16 (s, 9H, $SiMe_3$), 0.85–1.51 (m, 11H, CH_3), 1.61 (s, 9H, $C(CH_3)$), 2.46–2.52 (m, 2H, CH_2), 5.2 (s, 1H, (CH)), 7.13 (d, J = 8.0 Hz, 2H, Ar), 7.19 (d, J = 8.0 Hz, 2H, Ar), 7.67 (s, 1H, HC═); ^{13}C NMR (100 MHz, $CDCl_3$):): δ −0.54, 0.94 ($SiMe_3$), 12.9(CH_3),21.49(CH_2), 28.37, 28.62, 28.69(CH_2) 28.98 ($C(\underline{C}H_3)_3$), 30.42–30.49 (CH_2), 47.04 (CH), 57.89 ($\underline{C}(CH_3)$–), 126.4, 127.4, 136.5, 141.9, 152.8 (Ar, vinyl), 154.6 (tetrazole-C-5) ppm; GC–MS, (EI): *m/z*, 471 (25%, $[M]^+$), 444 (20%), 405 (37%), 386 (20%), 207 (100%, $[C_{15}H_{13}N]^+$), 73 (70%, $[SiMe_3]^+$).

N-{[4-(2,2-Bis(trimethylsilyl)ethenyl)phenyl](1-cyclohexyl-1H-tetrazol-5-yl)methyl}-4-fluoroaniline (6m). mp 155–157°C; FTIR (potassium bromide); 838, 1248 (Si–CH_3), 1498, 1615 (C_6H_4), 3339 (N–H) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ−0.01 (s, 9H, $SiMe_3$), 0.197 (s, 9H, $SiMe_3$), 1.28–1.33(m, CH_2 of c-hex), 1.35–1.45 (m, CH_2 of c-hex), 1.61(m, CH_2 of c-hex), 1.71–1.74 (m, CH_2 of c-hex), 2.025 (d. J = 12.0 Hz, 2H, CH_2 of c-hex), 2.13 (d, J = 12.0 Hz, 2H, CH_2 of c-hex), 3.94 (m, 1H, CH of c-hex), 4.85 (s, 1H, NH), 5.97 (d, J = 8.0 Hz, 1H, CH),6.74 (t, J = 8.0 Hz, 2H, Ar), 6.94 (t, J = 8.0 Hz, Ar), 7.04–7.11 (dd,

J = 12, 8.0 Hz, 4H, Ar), 7.68 (s, 1H, HC=); ^{13}C NMR (100 MHz, $CDCl_3$): δ −0.52, 1.08 ($SiMe_3$), 23.7, 24.7, 28.6, 31.5 32.07 (CH_2 of C-hex), 47.5 (CH of C-hex), 58.8 (CH), 113.9, 114.9, 122.6, 126.3, 127.4, 136.9, 145.99, 146.5, 152.7, (Ar, vinyl), 154.6 (tetrazole-C-5) ppm; 521 (25%, $[M]^+$), 412 (45%), 207 (90%, $[C_{15}H_{13}N]^+$), 73 (100%, $[SiMe_3]^+$).

N-{[4-(2,2-Bis(trimethylsilyl)ethenyl)phenyl](1-cyclohexyl-1H-tetrazol-5-yl)methyl}aniline (6n). mp 131–134°C; FTIR (potassium bromide); 840, 1248 (Si–CH_3), 1560, 1604 (Ph), 3374 (N–H) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ−0.004 (s, 9H, $SiMe_3$), 0.197 (s, 9H, $SiMe_3$), 1.25–1.41 (CH_2 of C-hex), 3.68 (s, 1H, NH), 5.94 (d, J = 8.0 Hz, 1H, CH),6.69 (d, J = 8.0 Hz, 2H, Ar), 6.85 (t, J = 8.0 Hz, Ar), 7.05–7.10 (m, 4H, Ar), 7.24(d, J = 8.0 Hz, 2H, Ar) 7.67 (s, 1H, HC=); ^{13}C NMR (100 MHz, $CDCl_3$): δ −0.52, 1.06 ($SiMe_3$), 23.7–32.07 (C-hex), 47.4 (CH of C-hex), 58.4 (CH), 113.5, 118.34, 120.52, 121.77, 126.37, 127.26, 127.46, 128.26, 145.99, 152.92, (Ar, vinyl), 154.05 (tetrazole-C-5) ppm; GC–MS, (EI): *m/z*, 503 (30%, $[M]^+$), 429 (45%), 207 (90%, $[C_{15}H_{13}N]^+$), 73 (100%, $[SiMe_3]^+$).

Acknowledgment. Financial support of this work by the Tabriz University is gratefully appreciated, and also we thank Dr. J. D. Smith for his helpful comments.

REFERENCES AND NOTES

[1] Brown, M.; US Patent 1967, 3, 338, 915; Chem Abstr 1968, 87299.

[2] Ostrovskii, V. A.; Koldobskii, G. I. Ros Khim Zh 1997, 41(2), 84.

[3] Ilyushin, M. A.; Tselinskii, I. V.; Chernai, A. V. Ros Khim Zh 1997, 41(4), 81.

[4] Koldobskii, G. I.; Ostrovskii, V. A. Usp Khim 1994, 63, 847–865.

[5] Bradbury, R. H. et al. J Med Chem 1993, 36, 1245; (b) Carini, D. J. *et al*. J Med Chem 1991, 34, 2525.

[6] (a) Stassen, A. F.; Grunert, M.; Mills, A. M.; Spek, A. L.; Haasnoot, J. G.; Reedijk, J.; Linert, W. Dalton Trans 2003, 3628–3633; (b) Wu, T.; Yi, B.-H.; Li, D. Inorg Chem 2005, 44,; (c) Wu, T.; Zhou, R.; Li, D. Inorg Chem Commun 2006, 9, 341; (d) Yu, Z.; Wang, X.; Feng, Y.; Zhong, X. Inorg Chem Commun 2004, 7, 492.

[7] Ugi, I. Angew Chem Int Ed Engl 1962, 1, 8.

[8] Ugi, I.; Steinbruckner, C. Chem Ber 1961, 94, 734.

[9] Mayer, J.; Umkehrer, M.; Kalinski, C.; Ross, G.; Kolb, J.; Burdacka, C.; Hiller, W. Tetrahedron Lett 2005, 46, 7393.

[10] (a) Butler, R. N.; Comprehensive Heterocyclic Chemistry; Katritzky, A. R.; Rees, C. W.; Scriven, E. F. V., Eds; Permagon: Oxford, UK, 1996, Vol. 4; (b) Demko, Z. P.; Sharpless, K. B. Org Lett 2002, 4, 2525.

[11] (a) Rendler, S.; Oestreich, M. Synthesis 2005, 11, 1727–1747; (b) Wan, J. P.; Liu, Y. Curr Org Chem 2011, 15, 2758; (c) Dilman, A. D.; Ioffe, S. L. Chem Rev 2003, 103, 733.

[12] (a) Pawluc, P.; Hreczycho, G.; Marciniec, B. J Org Chem 2006, 71, 8676–8679; (b) Mise, T.; Takaguchi, Y.; Wakatsuki, Y.; Takaguchi, Y.; Umemiya, T.; Shimizu, S., Y. Chem Commun 1998, 6, 699.

[13] (a) Pawluc, P.; Hreczycho, G.; Walkowia, J.; Marciniec, B. Synlett 2007, 2061; (b) Hreczycho, G.; Pawluc, P.; Marciniec, B.; Synthesis 2006, 1370

[14] (a) Safa, K. D.; Ghorbanpour, K.; Hassanpour, A.; Tofangdarzadeh, S. J Organomet Chem 2009, 694, 1907; (b) Safa, K. D.; Behmagham, F.; Ghorbanpour, K. J Organomet Chem 2011, 696, 1840.

[15] Safa, K. D., Vahid Mardipour, J.; Mosaei Oskoei, Y. J Organomet Chem 2011, 696, 802.

[16] Mojtahedi, M. M.; Abaee, M. S., Abbasi, H. Can J Chem 2006, 84, 429.

[17] Thorman, M.; Almstetter, M.; Tremi, A.; Heiser, U.; Buchholz, M. WO patent. 2008, 55950. Chem Abstr 2008, 148, P55950.

[18] Kalinski, C.; Umkehrer, M.; Gonnard, S.; Jager, N.; Ross, G.; Hiller, W. Tetrahedron Lett 2006, 47, 2041.

[19] (a) Short, K. M.; Ching, B. W.; Mjalli, A. M. M. Tetrahedron 1997, 53, 6653; (b) Hanusch-Kompa, C.; Ugi, I. Tetrahedron Lett 1998, 39, 2725; (c) Zhang, J.; Jacobson, A.; Rusche, J. R.; Herlihy, W. J Org Chem 1999, 64, 1074; (d) Marcaccini, S.; Miguel, D.; Torroba, T.; Garcia-Valverde, M. J Org Chem 2003, 68, 3315.

[20] (a) Lee, D.; Sello, J. K.; Schreiber, S. L. Org Lett 2000, 2, 709; (b) Tempest, P.; Pettus, L.; Gore, V.; Hulme, C. Tetrahedron Lett 2003, 44, 1947; (c) Faggi, C.; Garcia-Valverde, M.; Marcaccini, S.; Pepino, R.; Pozo, M. C. Synthesis 2003, 1553; (d) Marcaccini, S.; Pepino, R.; Pozo, M. C.; Basurto, S.; Garcia-Valverde, M.; Torroba, T. Tetrahedron Lett 2003, 44, 3999; (e) Beck, B.; Picard, A.; Herdtweck, E.; Dömling, A. Org Lett 2004, 6, 39.

[21] (a) Mojtahedi, M. M.; Abaee, M. S., Abbasi H. Can J Chem 2006, 84, 429–432; (b) Mojtahedi, M. M.; Abbasi H.; Abaee, M. S. J Mol Catal A: Chem 2006, 250, 6.

[22] Amanpour, T.; Mirzaei, P.; Bazgir, A. Tetrahedron Lett 2012, 53, 1421.