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TMSCl Promoted Direct sp^3 C-H Alkenylation to Construct (*E*)-2-Styryl-tetrahydrobenzo[*d*]thiazoles

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A high-efficient and stereo-specific approach for the preparation of biologically important (*E*)-2-styryl-tetrahydrobenzo[*d*]thiazoles has been developed via TMSCl promoted direct sp^3 C-H alkenylation of 2-methyl-5,6-dihydrobenzo[*d*]thiazol-7(4*H*)-one under metal-free conditions. Seventeen target compounds were synthesized in excellent yields of 82%—98% under the optimal conditions of 300 mol% TMSCl at 110 ℃ for 2 h, and their chemical structures were elucidated by IR, NMR, ESI-MS, elemental analyses and X-ray crystallography analysis. A plausible mechanism was also proposed, and this method provided a good functional group conversion for the sp^3 C-H substrates.

Keywords (*E*)-2-styryl-tetrahydrobenzo[*d*]thiazole, sp^3 C-H alkenylation, TMSCl, synthesis

Introduction

Benzo[*d*]thiazole, especially tetrahydrobenzo[*d*]thiazole, constitutes one of the key core units in various natural products, potent pharmaceutical compounds and functional materials, which could be used as neuroprotective,[1,2] antimicrobial,[3,4] antileukemic,[5,6] antioxidant and antitumor[7,8] agents. As a versatile synthetic protocol, the styryl group allows a broad range of transformations including addition, oxidation, reduction, cyclization and metathesis.[9-11] Therefore, the introduction of the styryl group to the tetrahydrobenzo[*d*]thiazole skeleton gains more and more attention due to their recognized importance in biology, pharmacology, and organic synthesis.

The sp^3 C—H bond is usually regarded as the low-reactive functional group with high thermodynamic stabilities, and directly constructing C—C bonds form C—H bonds is highly desirable due to the streamline synthetic scheme, high efficiency and atom economy.[12,13] In recent years, the direct sp^3 C—H bond functionalization of methylhetarenes has attracted tremendous attentions employing a variety of unique transition metal catalysts, such as Au,[14,15] Pd,[16,17] Ir,[18] Rh,[19] Ni,[20,21] Cu[22,23] or hypervalent iodine agent.[24] However, the complex precursors, sensitive catalysts, tedious multi-step synthesis and purification usually limited the further application of direct functionalization of sp^3 C—H bond. Due to the importance of 2-styryl substituted heterocycles as pharmaceutical agents and building blocks in organic synthesis, a new methodology was therefore described by an efficient and direct sp^3 C-H alkenylation of 2-methyl-5,6-dihydrobenzo[*d*]thiazol-7(4*H*)-one to construct 2-styryl-tetrahydrobenzo[*d*]thiazole under metal-free conditions in this work.

Experimental

Reagents and instruments

All chemical reagents and materials were purchased from commercial suppliers and used without further purification. The solvents of dichloromethane, ethyl acetate (EtOAc) and *n*-hexane were dried by $CaCl_2$ and distilled immediately before use. *N*,*N*′-Dimethylformamide (DMF) and trimethylsilyl chloride (TMSCl) were dried over calcium hydride (CaH_2) and distilled under dry nitrogen atmosphere, respectively. Flash column chromatography for purification was performed in a glass column by using 200—300 mesh silica gel. Analytical thin layer chromatography (TLC) was conducted using Kieselgel-G (Merck Si 245 F) layers (0.25 mm thick) visualized in UV-cabinet (λ_{max}=254 and 365 nm). Solvents were evaporated under reduced pressure at 50 ℃ in EYELA Rotavapor. Melting points were determined with an uncorrected X-4 digital melting point apparatus. Infrared radiation spectra (IR) were recorded on a PE-983 infrared spectrometer as KBr pellets with absorption in cm^{-1}. Nuclear magnetic resonance spectra (NMR) were recorded in deuterated chloroform ($CDCl_3$) as solvent employing tetramethylsilane (TMS) as internal standard on Bruker AVANCE III 400 MHz Plus

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NMR spectrometer. Mass spectrometry (MS) data were measured on API 4000 LC-MS/MS system. Elemental analyses were carried out with a Vario EL III elementary analysis instrument. The single-crystal X-ray diffraction analysis was performed on a Rigaku Mecury CCD diffractometer.

General procedure for the synthesis of 2-methyl-5,6-dihydrobenzo[*d*]thiazol-7(4*H*)-one (2)

In a round-bottomed flask (250 mL) equipped with a stir bar, the mixture of 2-bromocyclohexan-1,3-dione (19.1 g, 100 mmol) and thioacetamide (7.51 g, 100 mmol) were dissolved in anhydrous pyridine (120 mL) and stirred at 115 ℃ for 8 h under the protection of nitrogen atmosphere. The progress of the reaction was monitored by TLC (eluent: *n*-hexane/EtOAc＝3∶1, *V*/*V*). After disappearance of starting materials, the solution was cooled to room temperature, and 10% NaCl solution (200 mL) was added, then the product was extracted with dichloromethane (80 mL×3). The organic phase was separated, washed with saturated NaCl solution (100 mL×2) and dried over anhydrous sodium sulphate. Removal of the solvent on a rotary evaporator under high vacuum gave a viscous dark-red oil, which was purified by flash column chromatography on silica gel (eluent: *n*-hexane/EtOAc＝5∶1, *V*/*V*) to yield the title compound as yellow oil[25] in 66% yield (11.15 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.02 (t, J＝6.0 Hz, 2H), 2.75 (s, 3H), 2.61 (t, J＝6.8 Hz, 2H), 2.42－2.17 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.3, 173.3, 166.8, 130.9, 37.8, 27.1, 23.0, 20.0.

General procedure for the synthesis of 2-styryl-tetrahydrobenzo[*d*]thiazoles (3a–3q)

To the cold solution of aromatic aldehyde (1.0 mmol) and 2-methyl-5,6-dihydrobenzo[*d*]thiazol-7(4*H*)-one (1.0 mmol) in anhydrous DMF (10 mL) was added TMSCl (3.0 mmol) successively. The mixture was allowed to heat to 110 ℃ for 2 h under a glass Serpentine condenser until reached completion (monitored by TLC, eluent: *n*-hexane/EtOAc＝1∶1, *V*/*V*). After cooling to room temperature, the mixture was diluted in water (50 mL), and the product was extracted with dichloromethane (30 mL×3). The organic phase was separated, washed with saturated NaCl solution (50 mL×2), dried over anhydrous sodium sulphate and evaporated. The crude product was purified by flash column chromatography on silica gel (eluent: *n*-hexane/EtOAc＝2∶1, *V*/*V*) to give the target compound.

(*E*)-2-Styryl-5,6-dihydrobenzo[*d*]thiazol-7(4*H*)-one (3a) Yellow solids, yield 97%, m.p. 101－102 ℃.[26] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.61 (d, J＝16.0 Hz, 1H), 7.58－7.55 (m, 2H), 7.43－7.35 (m, 3H), 7.26 (d, J＝16.0 Hz, 1H), 3.07 (t, J＝6.4 Hz, 2H), 2.64 (t, J＝6.8 Hz, 2H), 2.27－2.20 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.3, 172.5, 167.6, 137.7, 134.9, 129.9, 129.8, 128.9, 127.6, 120.7, 37.9, 27.2, 23.0; IR (KBr) *v*: 3039, 2939, 1661, 1514, 1361, 1307, 951, 760, 689; MS (ESI) *m/z*: 533.05 [2M＋Na]. Anal. calcd for $C_{15}H_{13}NOS$: C 70.56, H 5.13, N 5.49; found C 70.48, H 5.07, N 5.39.

(*E*)-2-(2-Fluorostyryl)-5,6-dihydrobenzo[*d*]thiazol-7(4*H*)-one (3b) Yellow solids, yield 84%, m.p. 111－112 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.73 (d, J＝16.0 Hz, 1H), 7.61－7.56 (m, 1H), 7.38－7.31 (m, 2H), 7.18 (t, J＝7.2 Hz, 1H), 7.14－7.09 (m, 1H), 3.07 (t, J＝6.0 Hz, 2H), 2.65 (t, J＝6.4 Hz, 2H), 2.27－2.21 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.2, 172.3, 167.6, 161.1 (d, J＝51.8 Hz), 131.1 (d, J＝8.7 Hz), 130.3 (d, J＝2.3 Hz), 128.5 (d, J＝2.7 Hz), 124.5 (d, J＝3.6 Hz), 123.2 (d, J＝7.2 Hz), 123.1, 116.2 (d, J＝21.8 Hz), 37.9, 27.3, 23.0; IR (KBr) *v*: 1940, 1664, 1366, 960, 756; MS (ESI) *m/z*: 274.02 [M＋H]. Anal. calcd for $C_{15}H_{12}FNOS$: C 65.91, H 4.43, N 5.12; found C 65.80, H 4.36, N 5.02.

(*E*)-2-(2-Chlorostyryl)-5,6-dihydrobenzo[*d*]thiazol-7(4*H*)-one (3c) Yellow solids, yield 91%, m.p. 124－126 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.01 (d, J＝16.0 Hz, 1H), 7.69 (t, J＝9.2 Hz, 1H), 7.43 (t, J＝9.2 Hz, 1H), 7.31－7.23 (m, 3H), 3.07 (t, J＝6.0 Hz, 2H), 2.65 (t, J＝6.4 Hz, 2H), 2.24 (t, J＝6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.3, 172.0, 167.7, 134.5, 133.4, 133.2, 130.5, 130.3, 130.2, 127.1, 127.0, 123.1, 37.9, 27.2, 23.0; IR (KBr) *v*: 2947, 1659, 1364, 1324, 1305, 957, 757; MS (ESI) *m/z*: 290.27 [M＋H]. Anal. calcd for $C_{15}H_{12}ClNOS$: C 62.17, H 4.17, N 4.83; found C 62.02, H 4.12, N 4.77.

(*E*)-2-(2-Bromostyryl)-5,6-dihydrobenzo[*d*]thiazol-7(4*H*)-one (3d) Yellow solids, yield 92%, m.p. 128－129 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.97 (d, J＝16.0 Hz, 1H), 7.67 (dd, J＝8.0, 1.6 Hz, 1H), 7.62 (dd, J＝8.0, 0.8 Hz, 1H), 7.37－7.33 (m, 1H), 7.24－7.19 (m, 2H), 3.08 (t, J＝6.4 Hz, 2H), 2.65 (t, J＝6.4 Hz, 2H), 2.25 (q, J＝6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.2, 172.0, 167.7, 136.1, 135.0, 133.5, 130.7, 130.4, 127.8, 127.2, 125.0, 123.4, 38.0, 27.3, 23.0; IR (KBr) *v*: 2946, 1660, 1364, 956, 755; MS (ESI) *m/z*: 355.71 [M＋Na]. Anal. calcd for $C_{15}H_{12}BrNOS$: C 53.90, H 3.62, N 4.19; found C 53.80, H 3.56, N 4.11.

(*E*)-2-(2-Methoxystyryl)-5,6-dihydrobenzo[*d*]thiazol-7(4*H*)-one (3e) Yellow solids, yield 87%, m.p. 171－173 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.89 (d, J＝16.4 Hz, 1H), 7.55 (dd, J＝7.6, 1.6 Hz, 1H), 7.38 (d, J＝16.0 Hz, 1H), 7.36－7.32 (m, 1H), 7.00－6.92 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.3, 173.8, 167.6, 158.0, 133.5, 130.9, 129.6, 128.4, 123.9, 121.6, 120.8, 111.1, 55.4, 37.9, 27.3, 23.0; IR (KBr) *v*: 2944, 1657, 1364, 1242, 1114, 967, 759; MS (ESI) *m/z*: 593.48 [2M＋Na]. Anal. calcd for $C_{16}H_{15}NO_2S$: C 67.34, H 5.30, N 4.91; found C 67.26, H 5.24, N 4.85. Anal. calcd for $C_{16}H_{15}NO_2S$: C 67.34, H 5.30, N 4.91; found C 67.26, H 5.24, N 4.85.

(E)-2-(3-Chlorostyryl)-5,6-dihydrobenzo[*d*]thiazol-7(4H)-one (3f) Yellow solids, yield 88%, m.p. 130－131 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54 (t, J＝8.0 Hz, 2H), 7.44－7.42 (m, 1H), 7.35－7.33 (m, 2H),

7.24 (d, *J*=16.4 Hz, 1H), 3.07 (t, *J*=6.4 Hz, 2H), 2.65 (t, *J*=6.4 Hz, 2H), 2.27−2.21 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 192.2, 171.7, 167.7, 136.8, 135.8, 135.0, 130.3, 130.1, 129.5, 127.3, 125.7, 121.9, 37.9, 27.2, 22.9; IR (KBr) *v*: 2943, 1655, 1364, 1324, 966, 788, 684; MS (ESI) *m/z*: 290.27 [M+H]. Anal. calcd for $C_{15}H_{12}ClNOS$: C 62.17, H 4.17, N 4.83; found C 62.06, H 4.13, N 4.78.

(*E*)-2-(3-Bromostyryl)-5,6-dihydrobenzo[*d*]thiazol-7(4*H*)-one (3g) Yellow solids, yield 95%, m.p. 125−126 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.71 (s, 1H), 7.53 (d, *J*=16.0 Hz, 1H), 7.50−7.46 (m, 2H), 2.28 (d, *J*=8.0 Hz, 1H), 2.23 (d, *J*=16.4 Hz, 1H), 3.07 (t, *J*=6.4 Hz, 2H), 2.65 (t, *J*=6.4 Hz, 2H), 2.27−2.21 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 192.2, 171.7, 167.7, 137.1, 135.7, 132.5, 130.4, 130.3, 130.2, 126.1, 123.1, 121.9, 37.9, 27.2, 23.0; IR (KBr) *v*: 2941, 1655, 1509, 1365, 966, 786, 682; MS (ESI) *m/z*: 355.68 [M+Na]. Anal. calcd for $C_{15}H_{12}BrNOS$: C 53.90, H 3.62, N 4.19; found C 53.79, H 3.58, N 4.12.

(*E*)-2-(3-Hydroxystyryl)-5,6-dihydrobenzo[*d*]thiazol-7(4*H*)-one (3h) Yellow solids, yield 90%, m.p. 118−119 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.54 (d, *J*=16.0 Hz, 1H), 7.28−7.20 (m, 2H), 7.09 (t, *J*=8.4 Hz, 2H), 6.88 (dd, *J*=8.0, 0.8 Hz, 1H), 6.36 (brs, 1H), 3.06 (t, *J*=6.0 Hz, 2H), 2.66 (t, *J*=6.4 Hz, 2H), 2.27−2.20 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 192.6, 172.8, 167.8, 156.4, 137.8, 136.4, 130.2, 129.8, 120.7, 120.4, 117.3, 113.9, 37.9, 27.2, 22.9; IR (KBr) *v*: 3349, 2935, 1644, 1592, 1451, 1366, 957, 781, 686; MS (ESI) *m/z*: 269.79 [M–H]. Anal. calcd for $C_{15}H_{13}NO_2S$: C 66.40, H 4.83, N 5.16; found C 66.31, H 4.79, N 5.09.

(*E*)-2-(4-Fluorostyryl)-5,6-dihydrobenzo[*d*]thiazol-7(4*H*)-one (3i) Yellow solids, yield 89%, m.p. 144−145 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.57−7.53 (m, 3H), 7.17 (d, *J*=16.0 Hz, 1H), 7.10 (t, *J*=8.4 Hz, 2H), 3.07 (t, *J*=6.4 Hz, 2H), 2.67−2.63 (m, 2H), 2.28−2.20 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 192.3, 172.3, 167.6, 163.5 (d, *J*=249.6 Hz), 136.3, 131.3 (d, *J*=3.4 Hz), 129.8, 129.3 (d, *J*=8.2 Hz), 120.4 (d, *J*=2.5 Hz), 116.2 (d, *J*=21.8 Hz), 37.9, 27.3, 23.0; IR (KBr) *v*: 2962, 1655, 1509, 1363, 1224, 1165, 976, 830; MS (ESI) *m/z*: 274.02 [M+H]. Anal. calcd for $C_{15}H_{12}FNOS$: C 65.91, H 4.43, N 5.12; found C 65.80, H 4.38, N 5.05.

(*E*)-2-(4-Chlorostyryl)-5,6-dihydrobenzo[*d*]thiazol-7(4*H*)-one (3j) Yellow solids, yield 98%, m.p. 176−177 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.56 (d, *J*=16.0 Hz, 1H), 7.49 (d, *J*=8.4 Hz, 2H), 7.37 (d, *J*=8.4 Hz, 2H), 7.21 (d, *J*=16.0 Hz, 1H), 3.06 (t, *J*=6.0 Hz, 2H), 2.64 (t, *J*=6.4 Hz, 2H), 2.25 (q, *J*=6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 192.2, 172.0, 167.7, 136.1, 135.6, 133.5, 130.2, 129.2, 128.7, 121.2, 37.9, 27.2, 23.0; IR (KBr) *v*: MS (ESI) *m/z*: 290.27 [M+H]. Anal. calcd for $C_{15}H_{12}ClNOS$: C 62.17, H 4.17, N 4.83; found C 62.06, H 4.13, N 4.77.

(*E*)-2-(4-Bromostyryl)-5,6-dihydrobenzo[*d*]thiazol-7(4*H*)-one (3k) Yellow solids, yield 97%, m.p. 170−171 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.54 (t, *J*=8.0 Hz, 3H), 7.42 (d, *J*=8.4 Hz, 2H), 7.23 (d, *J*=16.0 Hz, 1H), 3.06 (t, *J*=6.4 Hz, 2H), 2.64 (t, *J*=6.4 Hz, 2H), 2.27−2.19 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 192.2, 172.0, 167.7, 136.2, 133.9, 132.2, 131.7, 131.2, 130.2, 128.9, 123.9, 121.2, 37.9, 27.2, 23.0; IR (KBr) *v*: 2942, 1664, 1488, 1362, 1325, 1068, 815; MS (ESI) *m/z*: 355.71 [M+Na]. Anal. calcd for $C_{15}H_{12}BrNOS$: C 53.90, H 3.62, N 4.19; found C 53.79, H 3.57, N 4.15.

(*E*)-2-(4-Methylstyryl)-5,6-dihydrobenzo[*d*]thiazol-7(4*H*)-one (3l) Yellow solids, yield 85%, m.p. 161−162 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.58 (d, *J*=16.0 Hz, 1H), 7.46 (dd, *J*=8.0, 3.6 Hz, 2H), 7.21 (dd, *J*=8.4, 4.0 Hz, 3H), 3.06 (t, *J*=6.4 Hz, 2H), 2.64 (t, *J*=6.8 Hz, 2H), 2.38 (s, 3H), 2.26−2.20 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 192.2, 172.9, 167.6, 140.2, 137.8, 132.3, 129.7, 128.2, 127.5, 119.8, 37.9, 27.3, 23.0, 21.4; IR (KBr) *v*: 2942, 1658, 1511, 1363, 1181, 805; MS (ESI) *m/z*: 270.79 [M+H]. Anal. calcd for $C_{16}H_{15}NOS$: C 71.34, H 5.61, N 5.20; found C 71.28, H 5.57, N 5.15.

(*E*)-2-[4-(Trifluoromethyl)styryl]-5,6-dihydrobenzo[*d*]thiazol-7(4*H*)-one (3m) Yellow solids, yield 88%, m.p. 203−204 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.67−7.61 (m, 5H), 7.32 (d, *J*=16.0 Hz, 1H), 3.08 (t, *J*=5.6 Hz, 2H), 2.66 (t, *J*=6.0 Hz, 2H), 2.25 (t, *J*=5.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 192.3, 171.4, 167.7, 138.4, 135.6, 130.6, 127.6, 125.9 (d, *J*=3.7 Hz), 122.9, 122.5, 37.9, 27.2, 22.9; IR (KBr) *v*: 2951, 1665, 1363, 1323, 1162, 1120, 1066, 829; MS (ESI) *m/z*: 669.13 [2M+Na]. Anal. calcd for $C_{16}H_{12}F_3NOS$: C 59.43, H 3.74, N 4.33; found C 59.37, H 3.70, N 4.28.

(*E*)-2-[2-(Thiophen-2-yl)vinyl]-5,6-dihydrobenzo-[*d*]thiazol-7(4*H*)-one (3n) Yellow solids, yield 82%, m.p. 94−96 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.74 (d, *J*=15.6 Hz, 1H), 7.37 (d, *J*=4.8 Hz, 1H), 7.26 (s, 1H), 7.07−7.02 (m, 2H), 3.05 (t, *J*=6.4 Hz, 2H), 2.64 (t, *J*=6.4 Hz, 2H), 2.26−2.20 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 192.2, 172.0, 167.7, 140.4, 130.3, 129.9, 129.8, 128.2, 127.8, 119.7, 37.9, 27.2, 23.0; IR (KBr) *v*: 2934, 1658, 1610, 1360, 938, 715; MS (ESI) *m/z*: 545.00 [2M+Na]. Anal. calcd for $C_{13}H_{11}NOS_2$: C 59.74, H 4.24, N 5.36; found C 59.68, H 4.20, N 5.29.

(*E*)-2-[2-(Pyridin-2-yl)vinyl]-5,6-dihydrobenzo[*d*]-thiazol-7(4*H*)-one (3o) Yellow solids, yield 85%, m.p. 123−125 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 8.65 (d, *J*=4.0 Hz, 1H), 7.79 (d, *J*=15.6 Hz, 1H), 7.74−7.69 (m, 1H), 7.65 (d, *J*=15.6 Hz, 1H), 7.43 (d, *J*=7.6 Hz, 1H), 7.27−7.23 (m, 1H), 3.08 (t, *J*=6.4 Hz, 2H), 2.65 (t, *J*=6.4 Hz, 2H), 2.27−2.21 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 192.3, 171.6, 167.7, 153.3, 150.1, 136.8, 135.9, 130.8, 124.2, 124.0, 123.6, 37.9, 27.3, 23.0; IR (KBr) *v*: 2943, 1660, 1363, 990, 769; MS (ESI) *m/z*: 256.8 [M+H]. Anal. calcd for $C_{14}H_{12}N_2OS$: C 65.60, H 4.72, N 10.93; found C 65.51, H 4.69, N 10.87.

(*E*)-2-[2-(Pyridin-3-yl)vinyl]-5,6-dihydrobenzo[*d*]-thiazol-7(4*H*)-one (3p) Yellow solids, yield 89%, m.p. 115−116 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 8.79 (s,

1H), 8.60 (s, 1H), 7.88 (d, J=8.0 Hz, 1H), 7.60 (d, J=16.0 Hz, 1H), 7.37−7.33 (m, 1H), 7.28 (d, J=8.0 Hz, 1H), 3.08 (t, J=6.0 Hz, 2H), 2.66 (t, J=6.4 Hz, 2H), 2.28−2.22 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.2, 171.3, 167.7, 150.3, 149.3, 133.6, 133.5, 130.9, 130.5, 123.8, 122.5, 37.9, 27.2, 22.9; IR (KBr) v: 2943, 1664, 1511, 1362, 1326, 973, 803, 704; MS (ESI) m/z: 535.00 [2M+Na]. Anal. calcd for $C_{14}H_{12}N_2OS$: C 65.60, H 4.72, N 10.93; found C 65.49, H 4.66, N 10.87.

(*E*)-2-[2-(Naphthalen-1-yl)vinyl]-5,6-dihydrobenzo[*d*]thiazol-7(4*H*)-one (3q) Yellow solids, yield 88%, m.p. 52−54 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.46 (d, J=16.0 Hz, 1H), 8.23 (d, J=8.0 Hz, 1H), 7.89 (d, J=8.4 Hz, 2H), 7.83 (d, J=7.2 Hz, 1H), 7.60−7.49 (m, 3H), 7.34 (d, J=15.6 Hz, 1H), 3.10 (t, J=6.4 Hz, 2H), 2.66 (t, J=6.4 Hz, 2H), 2.26 (t, J=6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.3, 172.5, 167.7, 134.5, 133.7, 132.3, 131.3, 130.1, 128.8, 126.8, 126.2, 125.5, 124.5, 123.3, 123.1, 38.0, 27.3, 23.0; IR (KBr) v: 2944, 1659, 1363, 1303, 793, 771; MS (ESI) m/z: 632.98 [2M+Na]. Anal. calcd for $C_{19}H_{15}NOS$: C 74.72, H 4.95, N 4.59; found C 74.65, H 4.90, N 4.52.

Crystal structure determination by X-ray diffraction crystallography

Single crystals of compound **3e** ($C_{16}H_{15}NO_2S$, M_r=285.35) were obtained by slow evaporation from a 50∶50 mixture of ethyl acetate and *n*-hexane at 4 ℃. A colorless prism crystal with dimensions of 0.21 mm×0.19 mm×0.18 mm was selected for measurement. Diffraction data of the single crystal were collected at 296 K on a Rigaku Mecury CCD diffractometer equipped with a graphite-monochromatic Mo Kα radiation (λ=0.71073 Å) by Crystal clear software. In an asymmetric unit the molecule crystallized in monoclinic space group $P2_1/c$ with a=13.366(15) Å, b=7.161(7) Å, c=18.195(14) Å, Z=4, V=1417(2) Å^3, D_{calc}=1.337 gm/cm^3, F(000)=600. A total of 14079 reflections were collected in the range of 1.87°≤θ≤27.44° by using an ω-scan mode, of which 3222 were unique with R_{int}=0.1556 and 2577 were observed with $I>2\sigma(I)$. Empirical absorption corrections were applied. The structure was solved by direct methods using *SHELXS*-97 programs.[27] All of the non-hydrogen atoms were located from difference Fourier maps, and then refined anisotropically with *SHELXL*-97 via a full-matrix least-squares procedure.[28] The hydrogen atoms were added according to the theoretical model. The final R=0.0664, wR=0.1805, $(\Delta/\sigma)_{max}$=0.000, S=1.057, $(\Delta\rho)_{max}$=0.644 and $(\Delta\rho)_{min}$=−0.415 e/Å^3. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 1051976. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (Fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

Results and Discussion

Optimization of conditions for the model reaction

Firstly, 2-methyl-5,6-dihydrobenzo[*d*]thiazol-7(4*H*)-one (**2**)[25] was prepared according to the known Hantzsch thiazole synthesis from the starting materials of 2-bromocyclohexan-1,3-dione (**1**)[29] and thioacetamide in refluxing pyridine. In the preliminary experiments, the sp^3 C−H alkenylation reaction of 2-methyl-5,6-dihydrobenzo[*d*]thiazol-7(4*H*)-one (**2**) with aromatic aldehydes was conducted in *N*,*N*′-dimethylformamide (DMF) at 80 ℃ for 12 h under the 20 mol% of transition metal halide catalyst, for example, $PdCl_2$, $TiCl_4$, $SrCl_2$, $FeCl_3$, $CoCl_2$ and $ZnCl_2$. However, the McMurry olefination product of *trans*-stilbene was isolated when $TiCl_4$ and zinc power were used[30] (Table 1, Entry 2), and the others showed no catalytic effect except $FeCl_3$ with 31% isolated yield (Entry 6). Subsequently, several representative protic acids, such as sulfuric acid and hydrochloric acid were screened as additives, but no superior results were obtained (Entries 7−8). Interestingly, when $FeCl_3$ and *p*-toluenesulfonic acid (*p*-TsOH) were added together, the promising 2-styryl-tetrahydrobenzo[*d*]thiazole (**3**) was obtained with yield of 55% with two diastereomeric isomers mixture (Entry 9). Although the dark-colored reaction

Table 1 Optimization of the reaction conditions

Entry	Catalyst (equiv.)	Solvent	Condition[a]	Yield[b]/%
1	$PdCl_2$ (20 mol%)	DMF	80 ℃, 12 h	0
2	$TiCl_4$ (20 mol%)	DMF	80 ℃, 12 h	0
3	$SrCl_2$ (20 mol%)	DMF	80 ℃, 12 h	0
4	$CoCl_2$ (20 mol%)	DMF	80 ℃, 12 h	0
5	$ZnCl_2$ (20 mol%)	DMF	80 ℃ 12 h	0
6	$FeCl_3$ (20 mol%)	DMF	80 ℃, 12 h	31
7	$FeCl_3$ (20 mol%) +H_2SO_4 (20 mol%)	DMF	80 ℃, 12 h	28
8	$FeCl_3$ (20 mol%) +HCl (20 mol%)	DMF	80 ℃, 12 h	20
9	$FeCl_3$ (20 mol%) +*p*-TsOH (20 mol%)	DMF	80 ℃, 12 h	55
10	$FeCl_3$ (20 mol%) +TMSCl (20 mol%)	DMF	80 ℃, 12 h	73
11	TMSCl (100 mol%)	DMF	80 ℃, 12 h	85
12	TMSCl (100 mol%)	THF	80 ℃, 12 h	0
13	TMSCl (100 mol%)	$CHCl_3$	80 ℃, 12 h	0
14	TMSCl (100 mol%)	CH_3CN	80 ℃, 12 h	0
15	TMSCl (100 mol%)	DMSO	80 ℃, 12 h	0
16	TMSCl (100 mol%)	EtOH	80 ℃, 12 h	23
17	TMSCl (100 mol%)	Toluene	80 ℃, 12 h	20

[a] Unless otherwise noted, all reactions were performed with **2** (0.1 mmol), benzaldehyde (0.1 mmol) in solvent (1.0 mL). [b] The yield of the product **3** was monitored by ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) after the model reaction finished.

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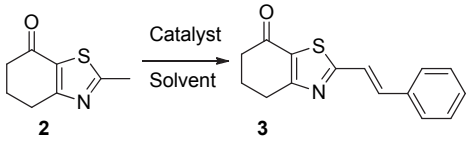
mixture was difficult to separate, the result did encourage us for seeking more efficient catalyst (Scheme 1).

Scheme 1 Model reaction for the sp^3 C-H alkenylation reaction



As a mild useful and inexpensive Lewis acid catalyst, trimethylsilyl chloride (TMSCl) has been widespread used in many organic transformations because of the near neutral conditions, more reactivity and commercial viability,[31-34] and many biologically important compounds were successfully prepared by the promotion of TMSCl in recent literatures.[35-38] Thus, TMSCl was chosen as the co-catalyst with $FeCl_3$ for constructing the (*E*)-2-styryl-tetrahydrobenzo[*d*]thiazole (**3**), and 73% yield of the target product was obtained (Table 1, Entry 10). Considering the dark color and separating difficulties caused by the $FeCl_3$ catalyst, searching for ideal conditions included shortening the reaction time, convenient isolation and high yields was the goal of optimizing the model reaction. Fortunately, we found 80% yield of **3** could also be obtained by increasing the load of TMSCl to three equivalents without the presence of $FeCl_3$ (Entry 11), which indicated TMSCl might be an efficient catalyst in this transformation instead of $FeCl_3$.

Furthermore, the best solvent was screened from tetrahydrofuran (THF), chlrorform ($CHCl_3$), acetonitrile (CH_3CN), dimethyl sulfoxide (DMSO), ethanol (EtOH) and toluene. The reaction mixture became black viscous mixture when DMSO was used, which might be relate to the oxidation property of the solvent (Entry 15). Besides the poor yield of ethanol and toluene, the other solvent seemed to inhibit the catalytic activity of TMSCl (Entries 12—14). Finally, DMF was proved to be the most suitable solvent in the TMSCl-promoted sp^3 C-H alkenylation.

To find the effects of the catalyst dosage on the yields of the product, the reaction of 2-methyl-5,6-dihydrobenzo[*d*]thiazol-7(4*H*)-one (**2**) with benzaldehyde was performed under the 100 mol% to 300 mol% of TMSCl, and the reaction temperature was increased from 90 to 110 ℃ with aim of shortening the reaction time within 4 h. Therefore, a group of orthogonal experiments[39,40] was designed and carried out in sequence to search the optimal conditions. The orthogonal design table L_9 (3^4) was obtained by SPSS software[41] (Statistical Product and Service Solutions), and calculated results were given in Table 2. The results indicated the main factor influencing the yields of sp^3 C-H alkenylation was the catalyst dosage, and the order of significance in decreasing order was: catalyst dosage＞reaction temperature＞reaction time. Ultimately, the most optimal conditions for the model reaction were confirmed as 300 mol% TMSCl at 110 ℃ for 2 h.

Table 2 Optimization of the reaction conditions

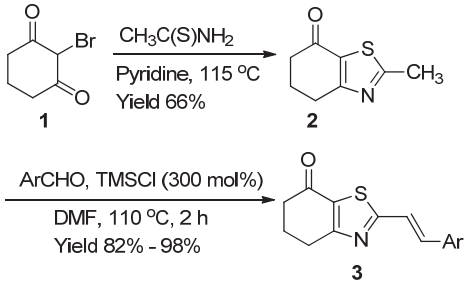
Factor level	Catalyst dosage	Temperature	Time	Yield/%
1	1 (100 mol%)	1 (90 ℃)	1 (2 h)	85
2	1 (100 mol%)	2 (100 ℃)	2 (3 h)	89
3	1 (100 mol%)	3 (110 ℃)	3 (4 h)	90
4	2 (200 mol%)	1 (90 ℃)	2 (3 h)	88
5	2 (200 mol%)	2 (100 ℃)	3 (4 h)	93
6	2 (200 mol%)	3 (110 ℃)	1 (2 h)	95
7	3 (300 mol%)	1 (90 ℃)	3 (4 h)	94
8	3 (300 mol%)	2 (100 ℃)	1 (2 h)	98
9	3 (300 mol%)	3 (110 ℃)	2 (3 h)	99
k_1[a]	88.0	89.0	92.7	—
k_2[a]	92.0	93.3	92.0	—
k_3[a]	97.0	94.7	92.3	—
R	9.0	5.7	0.7	—

[a] k_i was the average scores of each factor at its different level (*i* equals 1, 2, and 3, respectively).

The sp^3 C-H alkenylation reaction and possible mechanism

With the optimized conditions in hand, the scope of sp^3 C-H alkenylation reaction of 2-methyl-5,6-dihydrobenzo[*d*]thiazol-7(4*H*)-one (**2**) was extended to various aromatic or heteroaromatic aldehydes (Scheme 2). Finally, seventeen (*E*)-2-styryl-tetrahydrobenzo[*d*]thiazoles (**3a**—**3q**) were successfully prepared in the high yields of 82%—98% (Table 3), and their chemical structures were confirmed by IR, NMR, ESI-MS, elemental analyses and X-ray crystallography analysis. The reaction showed perfect stereo-selectivity of (*E*)-isomer with the coupling constant of 15.6—16.4 Hz for the olefinic double bond in ^{1}H NMR spectra. Application of this method in the synthesis of bioactive antitumor agents is currently in progress.

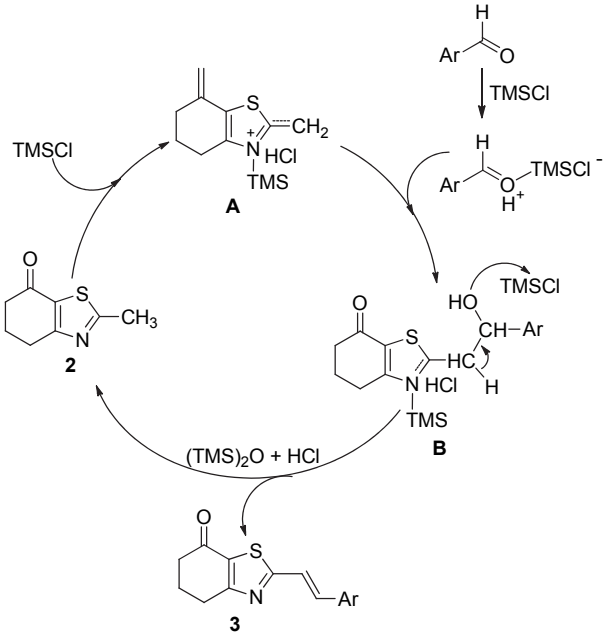
Scheme 2 Synthetic routes for the 2-styryl-tetrahydrobenzo[*d*]thiazoles



According to some related literatures,[31,42,43] a possible mechanism of the TMSCl-promoted sp^3 C-H alkenylation reaction for constructing 2-styryl-tetrahydrobenzo[*d*]thiazoles could be tentatively explained as shown in Scheme 3, which might involve: (i) TMSCl induced the 2-methyl-5,6-dihydrobenzo[*d*]thiazol-7(4*H*)-

one (**2**) to give the thioenol tautomer (A), and also activated aldehyde by coordinating to the carbonyl group; (ii) then a similar reaction of Adol-type condensation occurred between the two intermediates, and resulted in the corresponding addition product (B); (iii) finally adduct (B) was aromatized to generate the product (**3**) through the dehydration of TMSCl.

Scheme 3 Proposed mechanism for the TMSCl-promoted sp^3 C-H alkenylation reaction



Spectroscopy and X-ray crystal structural analysis

The structure of compound **3e** was confirmed by the X-ray crystallographic analysis, and its ORTEP drawing with common atom numbering scheme was shown in Figure 1. The crystallographic data, selected bond lengths, bond angles and torsion angles were listed in the supporting materials. The 6-membered ring (A) of C(1)-C(2)-C(3)-C(4)-C(5)-C(6) in Figure 1 shows a distorted chair conformation [Φ=302.1382(7145)°, θ=123.90(61)°, puckering amplitude (Q)=0.3480(44)°]. The olefinic double bond C(8)=C(9) is in a (*Z*)-conformation with the bond length of 1.335(3) Å (see Table 3), which formed a long-ranged conjugated system with the thiazole system (B) of S(1)-C(6)-C(5)-N(1)-C(7) and benzene ring (C) of C(10)-C(11)-C(12)-C(13)-C(14)-C(15). All ring atoms in the thiazole system (B) were essentially coplanar with a maximum deviation of –0.0050(29) Å from the plane for C(7). The intermolecular weak π-π stacking interactions between the ring B and C helped to stabilize the 3D supramolecular architecture of the crystal (Figure 2), and the centroid-to-centroid distance of two rings was 3.9657(47) Å with the interplanar angle of 6.921(80)° and perpendicular distance of 3.467 Å.

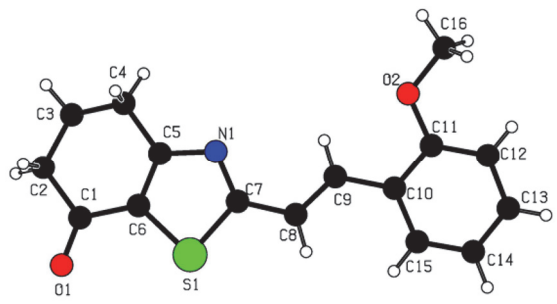


Figure 1 The ORTEP drawing of **3e** with numbered atoms.

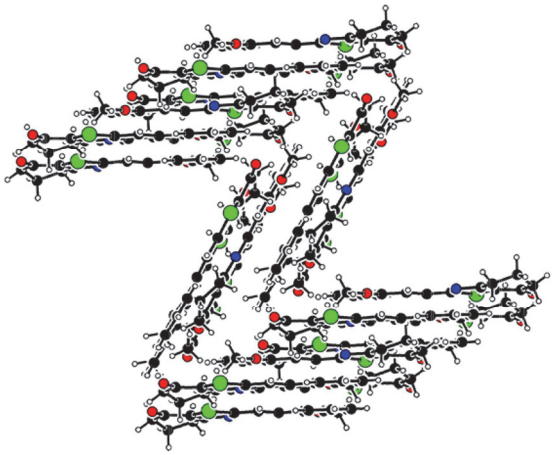


Figure 2 Packing diagram of **3e**.

Table 3 Synthesis of the 2-styryl-tetrahydrobenzo[*d*]thiazole **3**

No.	Substituent (Ar)	State	Yield[a]/%	Melting point/℃
3a	Ph	Yellow solids	97	101—102
3b	2-FPh	Yellow solids	84	111—112
3c	2-ClPh	Yellow solids	91	124—125
3d	2-BrPh	Yellow solids	92	128—129
3e	2-CH_3OPh	Yellow solids	87	171—172
3f	3-ClPh	Yellow solids	88	130—131
3g	3-B-Ph	Yellow solids	95	125—126
3h	3-HOPh	Yellow solids	90	118—119
3i	4-FPh	Yellow solids	89	144—145
3j	4-ClPh	Yellow solids	98	176—177
3k	4-BrPh	Yellow solids	97	170—171
3l	4-CH_3Ph	Yellow solids	85	161—162
3m	4-CF_3Ph	Yellow solids	88	203—204
3n	Thiophen-2-yl	Yellow solids	82	94—95
3o	Pyridin-2-yl	Yellow solids	85	123—124
3p	Pyridin-3-yl	Yellow solids	89	115—116
3q	Naphthalen-1-yl	Yellow solids	88	52—53

[a] Isolated yields.

Conclusions

In summary, an efficient strategy of TMSCl-promoted sp^3 C-H alkenylation reaction for the stereo-specific synthesis of (*E*)-2-styryl-tetrahydrobenzo[*d*]thia-

zoles has been developed in this work. This facial and straightforward process has attractive features of high selectivity, easy work-up and excellent conversion of substrates. The proposed mechanism of this reaction suggested that the alkenylation of other sp^3 C-H substrates will be further investigated in our laboratory.

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References

[1] Modi, G.; Antonio, T.; Reith, M.; Dutta, A. *J. Med. Chem*. **2014**, *57*, 1557.
[2] Johnson, M.; Antonio, T.; Reith, M. E.; Dutta, A. K. *J. Med. Chem*. **2012**, *55*, 5826.
[3] Shams, H. Z.; Mohareb, R. M.; Helal, M. H.; Mahmoud, A. E.-S. *Molecules* **2011**, *16*, 6271.
[4] Ouf, S. A.; Taleb, A. M.; Tharwat, N. A.; Geweely, N. S. *J. Mycol. Med*. **2013**, *23*, 230.
[5] Prasanna, D. S.; Kavitha, C. V.; Vinaya, K.; Ranganatha, S. R.; Raghavan, S. C.; Rangappa, K. S. *Eur. J. Med. Chem*. **2010**, *45*, 5331.
[6] Prasanna, D. S.; Kavitha, C. V.; Raghava, B.; Vinaya, K.; Ranganatha, S. R.; Raghavan, S. C.; Rangappa, K. S. *Invest. New Drugs* **2010**, *28*, 454.
[7] Shams, H. Z.; Mohareb, R. M.; Helal, M. H.; Mahmoud, A. E. *Molecules* **2010**, *16*, 52.
[8] Gouda, M. A.; Abu-Hashem, A. A. *Arch. Pharm*. **2011**, *344*, 170.
[9] Kamal, A.; Rahim, A.; Riyaz, S.; Poornachandra, Y.; Balakrishna, M.; Kumar, C. G.; Hussaini, S. M.; Sridhar, B.; Machiraju, P. K. *Org. Biomol. Chem*. **2015**, *13*, 1347.
[10] Alagoez, O.; Yilmaz, M.; Pekel, A. T.; Graiff, C.; Maggi, R. *RSC Adv*. **2014**, *4*, 14644.
[11] Deliomeroglu, M. K.; Dengiz, C.; Çalışkan, R.; Balci, M. *Tetrahedron* **2012**, *68*, 5838.
[12] Campos, K. R. *Chem. Soc. Rev*. **2007**, *36*, 1069.
[13] Yoo, W. J.; Li, C. J. *Top. Curr. Chem*. **2010**, *292*, 281.
[14] Xie, J.; Pan, C.; Abdukader, A.; Zhu, C. *Chem. Soc. Rev*. **2014**, *43*, 5245.
[15] Ma, Y.; Zhang, S.; Yang, S.; Song, F.; You, J. *Angew Chem., Int. Ed*. **2014**, *53*, 7870.
[16] Pedroni, J.; Boghi, M.; Saget, T.; Cramer, N. *Angew Chem., Int. Ed*. **2014**, *53*, 9064.
[17] Chan, K. S.; Wasa, M.; Chu, L.; Laforteza, B. N.; Miura, M.; Yu, J. Q. *Nat. Chem*. **2014**, *6*, 146.
[18] Kawamorita, S.; Murakami, R.; Iwai, T.; Sawamura, M. *J. Am. Chem. Soc*. **2013**, *135*, 2947.
[19] Kawamorita, S.; Miyazaki, T.; Iwai, T.; Ohmiya, H.; Sawamura, M. *J. Am. Chem. Soc*. **2012**, *134*, 12924.
[20] Wu, X.; Zhao, Y.; Ge, H. *J. Am. Chem. Soc*. **2014**, *136*, 1789.
[21] Aihara, Y.; Chatani, N. *J. Am. Chem. Soc*. **2014**, *136*, 898.
[22] Wu, X.; Zhao, Y.; Ge, H. *Chem. Asian J*. **2014**, *9*, 2736.
[23] Li, Q.; Huang, Y.; Chen, T.; Zhou, Y.; Xu, Q.; Yin, S. F.; Han, L. B. *Org. Lett*. **2014**, *16*, 3672.
[24] Zhang, N.; Cheng, R.; Zhang-Negrerie, D.; Du, Y.; Zhao, K. *J. Org. Chem*. **2014**, *79*, 10581.
[25] McIntyre, N. A.; McInnes, C.; Griffiths, G.; Barnett, A. L.; Kontopidis, G.; Slawin, A. M.; Jackson, W.; Thomas, M.; Zheleva, D. I.; Wang, S.; Blake, D. G.; Westwood, N. J.; Fischer, P. M. *J. Med. Chem*. **2010**, *53*, 2136.
[26] Macdonald, G. J.; Tresadern, G. J.; Trabanco-Suarez, A. A.; Pastor-Fernandez, J. *WO073347*, **2011** [*Chem. Abstr*. **2011**, *155*, 791275].
[27] Sheldrick, G. M. *SHELXS-97*, A program for automatic solution of crystal structures, University of Göttingen, Göttingen, Germany, **1997**.
[28] Sheldrick, G. M. *SHELXL-97*, A program for crystal structure refinement, University of Göttingen, Göttingen, Germany, **1997**.
[29] Blond, G.; Bour, C.; Salem, B.; Suffert, J. *Org. Lett*. **2008**, *10*, 1075.
[30] Geng, W.; Wang, H.; Wang, Z.; Zhang, S.; Zhang, W.-X.; Xi, Z. *Tetrahedron* **2012**, *68*, 5283.
[31] Song, X. R.; Han, Y. P.; Qiu, Y. F.; Qiu, Z. H.; Liu, X. Y.; Xu, P. F.; Liang, Y. M. *Chem. Eur. J*. **2014**, *20*, 12046.
[32] Song, X. R.; Song, B.; Qiu, Y. F.; Han, Y. P.; Qiu, Z. H.; Hao, X. H.; Liu, X. Y.; Liang, Y. M. *J. Org. Chem*. **2014**, *79*, 7616.
[33] More, S. V.; Sastry, M. N. V.; Yao, C.-F. *Synlett* **2006**, *9*, 1399.
[34] Liu, C. R.; Li, M. B.; Yang, C. F.; Tian, S. K. *Chem. Eur. J*. **2009**, *15*, 793.
[35] Wei, G.; Chalker, J. M.; Cohen, T. *J. Org. Chem*. **2011**, *76*, 7912.
[36] Wan, J.; Zhou, Y.; Liu, Y.; Fang, Z.; Wen, C. *Chin. J. Chem*. **2014**, *32*, 219.
[37] Wang, M.; Gao, M.; Miller, K. D.; Zheng, Q. H. *Bioorg. Med. Chem. Lett*. **2013**, *23*, 1017.
[38] Soeta, T.; Tamura, K.; Fujinami, S.; Ukaji, Y. *Org. Biomol. Chem*. **2013**, *11*, 2168.
[39] Othman, N.; Kamarudin, S. K.; Takriff, M. S.; Rosli, M. I.; Engku, C. E. M.; Adnan, M. A. *Sci. World J*. **2014**, 242658.
[40] Jin, L.; Wang, W.; Cao, C.; Huang, N.; Wang, J.; Zou, K. *Arkivoc* **2014**, *4*, 252.
[41] Wang, Y.; Harrison, M.; Clark, B. J. *J. Chromatogr. A* **2006**, *1105*, 77.
[42] Bahrami, K.; Khodaei, M. M.; Yousefi, B. H.; Arabi, M. S. *Tetrahedron Lett*. **2010**, *51*, 6939.
[43] Liu, C.; Cheng, D.; Yang, F. *Chin. J. Chem*. **2014**, *32*, 1095.

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