Synthesis Y. M. Ivon et al. Paper

1-(Trimethylsilyl)vinyl MIDA Boronate: A Trifunctional C_2 Building Block

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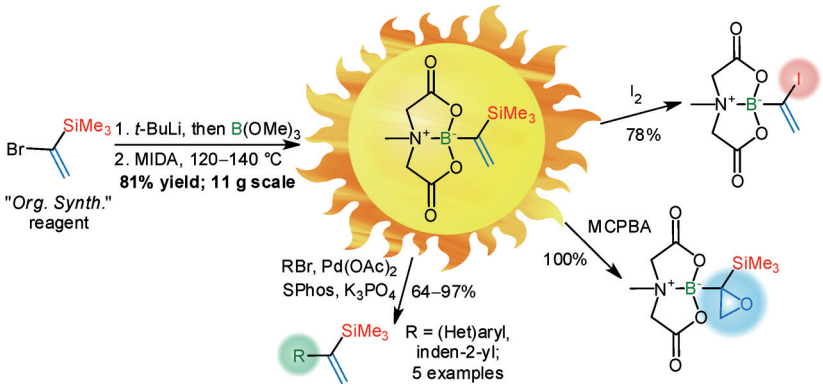


Received: 06.12.2017
Accepted after revision: 12.01.2018
Published online: 05.02.2018
DOI: 10.1055/s-0036-1591926; Art ID: ss-2017-t0790-op

Abstract 1-(Trimethylsilyl)vinyl MIDA boronate — a trifunctional C_2 building block — is prepared in only two laboratory steps and 54% overall yield starting from readily available trimethyl(vinyl)silane. The title compound undergoes orthogonal functionalization at either of the groups present in its structure, for example, iodination at the trimethylsilyl moiety, epoxidation at the double bond, and Suzuki–Miyaura coupling at the MIDA boronate.

Key words organosilicon compounds, organoboron compounds, alkenes, Suzuki–Miyaura coupling, orthogonal reactions

Vinyl boronic acids and their derivatives are versatile building blocks that are widely used in organic synthesis, initially as the coupling partners for Suzuki–Miyaura reactions.[1] α-Heteroatom-substituted vinyl boronic acid derivatives are of special interest since after coupling, functionalized alkenes are obtained in a regioselective manner; moreover, iterative chemoselective cross-coupling to form polysubstituted alkenes is possible.[2–4] Examples of these organoboron compounds include α- and β-(sulfon)amido,[5–8] α-alkoxy,[9–11] α-halogenoboronates,[12–14] α-boryl vinyl silanes[7,15–20] and α,α-diboryl alkenes.[21–23] Most of these compounds have a boronic acid ester as the boryl moiety, which is prone to oxidation, protodeborylation and polycondensation, and therefore provides limited possibilities for chemical manipulations at other functional groups. Trifluoroborates are widely recognized alternatives to boronate esters;[24,25] however, they have poor solubility in several typical organic solvents, which complicates their use in many routine transformations. On the contrary, *N*-methyliminodiacetic acid (MIDA) boronates have good chemical stability and solubility, and their utility for the synthesis of complex boronic acid derivatives and subsequent coupling reactions has been demonstrated.[26] To date, only a few α-heteroatom-substituted MIDA boronates have been described in the literature. In particular, bromide **1** (Figure 1) was prepared in two steps: borylation and bromination–elimination starting from vinyl magnesium bromide.[14] 2-Perfluoroalkyl-1-iodo derivatives **2** were obtained by Ru-catalyzed photoredox reactions of ethynyl MIDA boronate and perfluoroalkyl iodides.[27] Silyl enol ethers **3** were prepared by multistep synthesis via the corresponding acyl boronates.[9] Finally, α,α-diboryl derivatives **4** were synthesized via diborylation of alkynyl MIDA boronates and subsequent Suzuki–Miyaura reactions of intermediates **5**.[23]

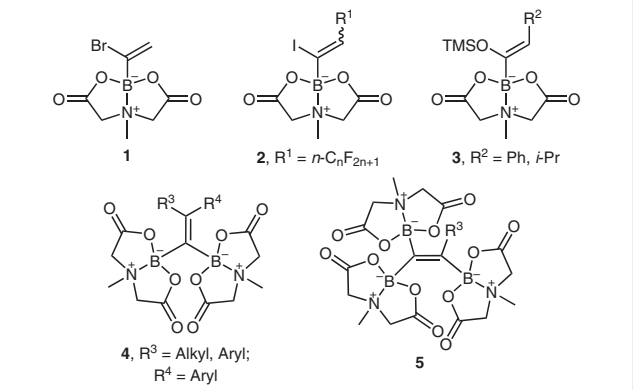
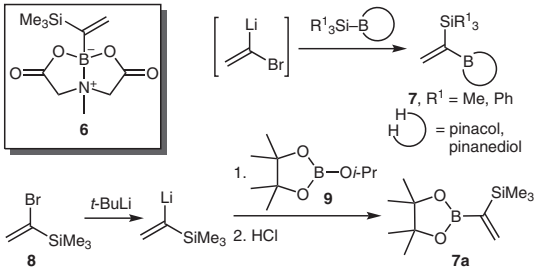


Figure 1 Known α-heteroatom-substituted vinyl MIDA boronates

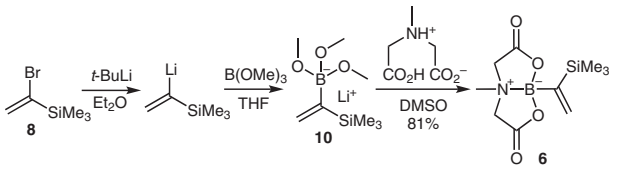
In this work, we describe a short and convenient synthesis, as well as some reactions of 1-(trimethylsilyl)vinyl MIDA boronate **6**, a promising building block possessing three functional groups per two main chain carbon atoms. It should be noted that to date, several boronic acid esters of general formula **7** have been described in the literature; they were prepared by alkylidene-type lithium carbenoid insertion into B–Si bonds (Scheme 1).[19,20] Compounds **7**

were also observed as minor by-products in the hydroboration of trimethylsilylacetylene.[28] Very recently, the synthesis of pinacol derivative **7a** via lithiation of bromide **8** [available in one step and 67% yield starting from trimethyl(vinyl)silane[29]], followed by transmetalation with pinacolate **9**, was reported on gram scale.[30]



Scheme 1 Synthesis of boronic acid esters **7**

Our approach to **6** started with a similar (but not identical) reaction sequence (Scheme 2). To install the boron functionality, lithiation with *t*-BuLi was used, followed by transmetalation with $B(OMe)_3$. It was found that the lithiation should be performed in Et_2O as the solvent, while the transmetalation proceeded smoothly only after addition of better solvating THF. The next step — ligand interchange from the ate-complex **10** to give MIDA boronate **6** — was challenging, probably due to protodeborylation. It was found that the method of Burke and co-workers, which relied on slow addition of the ate-complex to a hot solution of *N*-methyliminodiacetic acid in DMSO (110–160 °C), was beneficial.[14,31,32] In our case, optimization of the procedure showed that the addition should be performed at 120–140 °C, with simultaneous removal of volatiles by distillation (see Figure S1 in the Supporting Information). In this way, the target compound **6** was obtained in good yield (81% from **8**) on 11 g scale.[31] It should be noted that the counterion of the preformed ate-complex **10** (Li^+ vs Mg^{2+}) had a strong influence on the solubility of this salt. In particular, the magnesium salt (used in some of the previous work[14,32]) had limited solubility in THF (used for the metalation), while the lithium salt was well soluble, which was crucial for the addition step upon scale-up.



Scheme 2 Synthesis of 1-(trimethylsilyl)vinyl MIDA boronate **6**

Having in hand gram amounts of the compound **6**, we were interested in the possibility of its orthogonal functionalization at any of the groups present in the molecule (Scheme 3). It was found that:

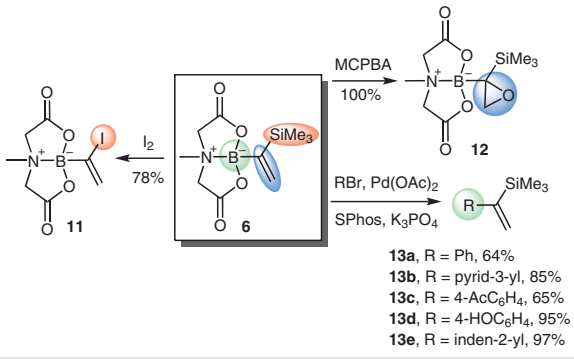
(1) The reaction with iodine proceeded smoothly to give the corresponding vinyl iodide **11** in 78% yield.

(2) Both the trimethylsilyl and MIDA boronate groups were stable toward deuterium exchange; the compound did not react with CF_3COOD or CF_3COOD/TBAF at ambient temperature.

(3) Reaction with *m*-chloroperbenzoic acid (MCPBA) gave epoxide **12** quantitatively. Surprisingly, the product **12** was stable toward the action of acids (aq H_2SO_4, $HClO_4$, HCOOH, CF_3COOH) and nucleophiles (NaN_3/NH_4Cl, $EtSH/Et_3N$, $EtSH/BF_3{\cdot}Et_2O$, Me_2CuLi and *n*-Bu_2CuLi, $Me_2CuLi/BF_3{\cdot}Et_2O$, PhMgBr/CuI, and Me_3Al).

(4) Cyclopropanations under Simmons–Smith reaction conditions (Et_2Zn/CH_2I_2 or $ClCH_2I$) and with ethyl diazoacetate/$Rh_2(OAc)_4$ or $Pd(OAc)_2$, as well as cross-metathesis reactions (allyltrimethylsilane, Grubbs' 2nd generation catalyst, various temperatures, CH_2Cl_2, benzene or toluene as the solvent) were unfruitful.

(5) Suzuki–Miyaura coupling under slow-release conditions was very efficient with either electron-rich or electron-poor aryl, hetaryl, and vinyl bromides, affording vinyl silanes **13a–e** in 64–97% yields. No desilylation was observed.



Scheme 3 Reactions of 1-(trimethylsilyl)vinyl MIDA boronate **6** (SPhos: 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl)

In conclusion, a convenient approach to 1-(trimethylsilyl)vinyl MIDA boronate **6**—a small, trifunctional C_2 building block—has been developed. It was shown that efficient orthogonal functionalization at either of the groups present in boronate **6** was possible. Compound **6**, as well as products **11** and **12** are shelf-stable at room temperature for at least six months, hence they are promising reagents for the construction of small molecules.

The solvents were purified according to standard procedures.[33] (1-Bromovinyl)trimethylsilane (**8**) was prepared according to the literature method.[29] All other starting materials were purchased from commercial sources. Analytical TLC was performed using Polychrom SI F254 plates. Column chromatography was performed using Kieselgel Merck 60 (230–400 mesh) as the stationary phase. Melting points were measured on a MPA100 OptiMelt automated melting point system. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 170 Avance 500 spectrometer [499.9 MHz (^{1}H) and 124.9 MHz (^{13}C)] and on a Varian Unity Plus 400 spectrometer [400.4 MHz (^{1}H) and 100.7 MHz (^{13}C)]. Chemical shifts are reported in ppm downfield from TMS as an internal standard. Mass spectra were recorded on an Agilent 1100 LCMSD SL instrument [chemical ionization (APCI), electrospray ionization (ESI)] and an Agilent 5890 Series II 5972 GCMS instrument [electron impact ionization (EI)]. Elemental analyses were performed at the Laboratory of Organic Analysis, Department of Chemistry, National Taras Shevchenko University of Kyiv.

1-(Trimethylsilyl)vinyl MIDA Boronate 6

All operations were carried out under an argon atmosphere. A solution of (1-bromovinyl)trimethylsilane (**8**) (10.0 g, 55.8 mmol) in Et_2O (110 mL) was cooled to –90 °C, after which a solution of *t*-BuLi in pentane (62 mL, 1.7 M, 0.105 mol) was added dropwise at –90 to –80 °C. The resulting mixture was stirred at this temperature for 30 min. Trimethyl borate (6.85 mL, 61.4 mmol) was added at –80 °C, followed by THF (110 mL) below –60 °C. The solution was stirred at –60 °C for an additional 40 min and allowed to warm to r.t. over 1 h. At this point, the solution was transferred via cannula to a dropping funnel connected to a second reaction vessel.

In another three-necked flask (fitted with a short distillation column, a thermometer and a dropping funnel with an argon inlet, see Figure S1 in the Supporting Information), a solution of *N*-methyliminodiacetic acid (26.3 g, 0.179 mmol) in DMSO (90 mL) was heated to 120 °C. Hexane (100 mL) was added dropwise with distillation, and the temperature in the flask was increased to 120–140 °C. The solution of ate complex **10** from the above-mentioned dropping funnel was added dropwise with simultaneous distilling of the ethereal solvents under vigorous stirring (the temperature in the reaction flask should be kept above 120 °C). After the addition was complete, the mixture was heated for an additional 20 min and then allowed to cool to r.t. The mixture was diluted with H_2O (400 mL) and extracted with EtOAc (2 × 200 mL). The combined extracts were washed with brine/H_2O (1:1) (2 × 200 mL), dried over Na_2SO_4 and evaporated in vacuo. The residue was recrystallized from $CHCl_3$/EtOAc to give MIDA boronate **6**.

Yield: 10.9 g (81%); colorless powder; mp 200–201 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 6.14 (s, 2 H), 4.24 (d, *J* = 17.3 Hz, 2 H), 4.00 (d, *J* = 17.3 Hz, 2 H), 2.65 (s, 3 H), 0.06 (s, 9 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 169.1 (C=O), 139.3 (CH_2), 61.8 (CH_2), 47.5 (CH_3), –0.4 (CH_3).

^{11}B NMR: (128 MHz, DMSO-d_6): δ = 11.1.

MS (CI): *m*/*z* = 256 [M + H]$^+$.

Anal. Calcd for $C_{10}H_{18}BNO_4Si$: C, 47.07; H, 7.11; N, 5.49. Found: C, 47.23; H, 6.89; N, 5.65.

1-Iodovinyl MIDA Boronate 11

Iodine (716 mg, 2.82 mmol) was added to a stirred solution of MIDA boronate **6** (600 mg, 2.35 mmol) in CH_2Cl_2 (25 mL) in one portion. The mixture was stirred at r.t. for 3 d and then quenched with 10% aq $Na_2S_2O_3$ (20 mL). The layers were separated and the aqueous phase was extracted with EtOAc (2 × 30 mL). The combined organic extracts were dried over Na_2SO_4 and evaporated. The residue was recrystallized from $CHCl_3$/EtOAc to give iodide **11**.

Yield: 565 mg (78%); colorless crystals; mp 183–184 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 6.84 (s, 1 H), 6.56 (s, 1 H), 4.36 (d, *J* = 17.1 Hz, 2 H), 4.07 (d, *J* = 17.1 Hz, 2 H), 2.89 (s, 3 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 168.4 (C=O), 150.8 (br s, C), 137.8 (CH_2), 62.5 (CH_2), 46.7 (CH_3).

^{11}B NMR: (128 MHz, DMSO-d_6): δ = 8.4.

MS (CI): *m*/*z* = 310 [M + H]$^+$.

Anal. Calcd for $C_7H_9BINO_4$: C, 27.22; H, 2.94; N, 4.53. Found: C, 27.45; H, 3.02; N, 4.67.

2-(Trimethylsilyl)oxiran-2-yl MIDA Boronate 12

MCPBA (70%, 2.24 g, 9.1 mmol) was added to a stirred solution of MIDA boronate **6** (1.16 g, 4.55 mmol) in CH_2Cl_2 (90 mL) at 0 °C, and the resulting mixture was stirred overnight at r.t. A second portion of MCPBA (70%, 0.60 g, 2.43 mmol) was added and the mixture was stirred at r.t. overnight, then quenched with 10% aq $Na_2S_2O_3$ (30 mL) and saturated aq $NaHCO_3$ (20 mL). The organic layer was separated, and the aqueous layer extracted with EtOAc (2 × 60 mL). The combined organic extracts were washed with 10% aq $Na_2S_2O_3$ (20 mL) and saturated aq $NaHCO_3$ (20 mL), dried over Na_2SO_4 and evaporated in vacuo. The residue was triturated with CH_2Cl_2 to give epoxide **12**.

Yield: 1.22 g (quant.); colorless crystals; mp 137–139 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 4.31 (d, *J* = 17.3 Hz, 1 H), 4.13 (d, *J* = 16.7 Hz, 1 H), 4.06 (d, *J* = 17.3 Hz, 1 H), 3.85 (d, *J* = 17.0 Hz, 1 H), 2.95 (s, 3 H), 2.75 (d, *J* = 5.8 Hz, 1 H), 2.62 (d, *J* = 5.8 Hz, 1 H), 0.00 (s, 9 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 169.4 (C=O), 168.1 (C=O), 62.2 (CH_2), 62.1 (CH_2), 51.5 (br s, C), 48.9 (CH_2), 46.3 (CH_3), –2.3 (CH_3).

^{11}B NMR (128 MHz, DMSO-d_6): δ = 10.4.

MS (CI): *m*/*z* = 272 [M + H]$^+$.

Anal. Calcd for $C_{10}H_{18}BNO_5Si$: C, 44.30; H, 6.69; N, 5.17. Found: C, 44.26; H, 6.72; N, 5.46.

Suzuki–Miyaura Coupling; General Procedure

The corresponding (het)aryl bromide (2.44 mmol) or 2-bromoindene (191 mg, 0.98 mmol), MIDA boronate **6** (500 mg, 1.96 mmol), K_3PO_4 (3.12 g, 14.7 mmol) and $Pd(OAc)_2$ (22 mg, 0.1 mmol) were mixed in dioxane/H_2O (6:1, 20 mL) under an argon atmosphere. SPhos (80 mg, 0.2 mmol) was added, and the solution was stirred at 60 °C overnight (ca.16 h), then cooled to r.t., diluted with H_2O (5 mL) (for **13a–c** and **13e**) or 0.5 M aq $NaHSO_4$ to pH = 3 (for **13d**), and extracted with *t*-BuOMe (for **13a–c**), EtOAc (for **13d**) or hexanes (for **13e**) (2 × 30 mL). The combined organic extracts were washed with brine (20 mL), dried over Na_2SO_4 and evaporated in vacuo.

Trimethyl(1-phenylvinyl)silane (13a)

Purified by column chromatography on silica gel using hexanes/CH_2Cl_2 (20:1) as eluent.

Yield: 220 mg (64%); colorless liquid [Lit.[32] bp 70–72 °C (10 mmHg)].

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33–7.16 (m, 5 H), 5.83 (d, *J* = 3.0 Hz, 1 H), 5.61 (d, *J* = 3.0 Hz, 1 H), 0.17 (s, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.7 (C), 144.9 (C), 128.3 (CH), 127.3 (CH_2), 126.8 (CH), 126.4 (CH), –0.74 (CH_3).

MS (EI): *m*/*z* = 176 [M]$^+$, 161 [M – CH_3]$^+$, 135, 73 [Me_3Si]$^+$.

Anal. Calcd for $C_{11}H_{16}Si$: C, 74.93; H, 9.15. Found: C, 75.10; H, 9.39.

3-[1-(Trimethylsilyl)vinyl]pyridine (13b)

Purified by column chromatography on silica gel using hexanes/*t*-BuOMe (4:1) as eluent.

Yield: 295 mg (85%); colorless liquid; R_f = 0.35 (hexanes/*t*-BuOMe, 4:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.47 (d, *J* = 4.8 Hz, 1 H), 8.43 (s, 1 H), 7.47 (d, *J* = 7.8 Hz, 1 H), 7.22 (dd, *J* = 7.8 Hz, 5.0 Hz, 1 H), 5.85 (d, *J* = 2.5 Hz, 1 H), 5.70 (d, *J* = 2.5 Hz, 1 H), 0.17 (s, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 150.3 (C), 147.9 (CH), 147.7 (CH), 140.4 (C), 134.0 (CH), 129.2 (CH_2), 123.1 (CH), –1.0 (CH_3).

MS (EI): *m*/*z* = 177 $[M]^+$, 176, 162 $[M - CH_3]^+$, 136, 73 $[Me_3Si]^+$.

Anal. Calcd for $C_{10}H_{15}NSi$: C, 67.74; H, 8.53; N, 7.90. Found: C, 67.71; H, 8.47; N, 7.87.

1-{4-[1-(Trimethylsilyl)vinyl]phenyl}ethanone (13c)

Purified by column chromatography on silica gel using hexanes/*t*-BuOMe (10:1) as eluent.

Yield: 280 mg (65%); yellowish liquid; R_f = 0.50 (hexanes/*t*-BuOMe, 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 (d, *J* = 8.0 Hz, 2 H), 7.24 (d, *J* = 8.0 Hz, 2 H), 5.85 (d, *J* = 2.5 Hz, 1 H), 5.67 (d, *J* = 2.5 Hz, 1 H), 2.59 (s, 3 H), 0.17 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.9 (C=O), 153.2 (C), 150.3 (C), 135.3 (C), 128.50 (CH_2), 128.48 (CH), 127.0 (CH), 26.7 (CH_3), –0.9 (CH_3).

MS (EI): *m*/*z* = 218 $[M]^+$, 203 $[M - CH_3]^+$, 177, 73 $[Me_3Si]^+$.

Anal. Calcd for $C_{13}H_{18}OSi$: C, 71.50; H, 8.31. Found: C, 71.86; H, 8.37.

4-[1-(Trimethylsilyl)vinyl]phenol (13d)

Purified by column chromatography on silica gel using hexanes/*t*-BuOMe (4:1) as eluent.

Yield: 360 mg (95%); colorless solid; mp 66–67 °C; R_f = 0.42 (hexanes/*t*-BuOMe, 4:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.10 (d, *J* = 8.7 Hz, 2 H), 6.79 (d, *J* = 8.7 Hz, 2 H), 5.80 (d, *J* = 2.9 Hz, 1 H), 5.55 (d, *J* = 2.9 Hz, 1 H), 4.89 (s, 1 H), 0.17 (s, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.2 (C), 152.6 (C), 137.5 (C), 128.1 (CH), 126.4 (CH_2), 115.2 (CH), –0.7 (CH_3).

MS (EI): *m*/*z* = 192 $[M]^+$, 177 $[M - CH_3]^+$, 161, 151, 119, 91, 73 $[Me_3Si]^+$.

Anal. Calcd for $C_{11}H_{16}OSi$: C, 68.69; H, 8.39. Found: C, 68.95; H, 8.39.

[1-(1*H*-Inden-2-yl)vinyl]trimethylsilane (13e)

Purified by column chromatography on silica gel using hexanes as eluent. Nearly a two-fold excess of **6** over 2-bromoindene should be used to ensure complete conversion of the bromide; otherwise, the product is not separable from unreacted 2-bromoindene.

Yield: 221 mg (97%); colorless liquid; R_f = 0.75 (hexanes).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 (d, *J* = 7.3 Hz, 1 H), 7.37 (d, *J* = 7.3 Hz, 1 H), 7.27 (t, *J* = 7.3 Hz, 1 H), 7.19 (t, *J* = 7.3 Hz, 1 H), 6.82 (s, 1 H), 6.01 (d, *J* = 2.5 Hz, 1 H), 5.56 (d, *J* = 2.5 Hz, 1 H), 3.62 (s, 2 H), 0.31 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.6 (C), 146.3 (C), 145.7 (C), 142.4 (C), 129.5 (CH), 126.6 (CH), 125.4 (CH_2), 124.9 (CH), 123.6 (CH), 121.0 (CH), 39.0 (CH_2), –0.4 (CH_3).

MS (EI): *m*/*z* = 214 $[M]^+$, 199 $[M - CH_3]^+$, 183, 141, 140, 139, 115, 73 $[Me_3Si]^+$.

Anal. Calcd for $C_{14}H_{18}Si$: C, 78.44; H, 8.46. Found: C, 78.75; H, 8.08.

Funding Information

This work was supported by Enamine Ltd.

Acknowledgment

The authors thank Dr. Andriy V. Tymtsunik for helpful discussions, Andriy V. Kozitsky for NMR measurements and Prof. Andrey A. Tolmachev for his encouragement and support.

Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0036-1591926.

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