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ORIGINAL PAPER

Synthesis of novel α-acyloxycarboxamides containing vinylbis(silanes) through three-component Passerini reactions

Vahideh Raeisdasteh Hokmabad[1] · Hassan Abbasi[1] · Kazem D. Safa[1]

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Abstract A three-component efficient procedure is described for the synthesis of novel α-acyloxycarboxamides containing bis(trimethylsilyl)ethenyl group from 4-[2,2-bis(trimethylsilyl) ethenyl]benzaldehyde, aromatic carboxylic acids and isocyanides, via the Passerini reaction. This reaction proceeds smoothly and cleanly under mild conditions in H_2O and [bmim]BF_4 at room temperature and led to products in good yields. The silylated aldehyde was obtained via Peterson olefination reaction of terephthalaldehyde with tris(trimethylsilyl) methyllithium in THF at 0 °C.

Keywords Passerini reaction · 4-[2,2-bis(trimethylsilyl) ethenyl]benzaldehyde · Carboxylic acid · Isocyanide · Water · [bmim]BF_4

Introduction

Since the discovery of the high biological potential of several classes of organosilicon compounds, in the 1960s, it is obvious that the organosilicon compounds, in principle, can exhibit high and specific biological activity. In the meantime, some biologically active organosilicon compounds have already found practical application as therapeutic agents in medicine and as reference drugs in experimental pharmacology [1–6]. Vinylsilanes and vinylbis(silanes) are important synthetic reagents in organic synthesis [7–9] because the C(sp^2)–Si bonds undergo numerous transformations [8]. Vinylbis(silanes) are useful reagents for the preparation of ketones and isoxazoline derivatives as well as for a variety of important organosilicon reagents, such as acylsilanes, epoxysilanes, silanols [10–15]. Recently, we described the synthesis of new organosilicon compounds containing the vinylbis(silane) group and converted them to amines [16]. Multicomponent reactions are special types of synthetically useful organic reactions in which three or more reagents are combined to react in a one-pot procedure [17, 18]. This allows for high atom economy, a minimization of the formation of by-products, and decreases costs and is less time consuming [19]. They have been extensively studied over the past few years, since these processes represent an efficient way of assembling complex molecules in one pot, thus exemplifying many of the desired features of an ideal synthesis. Among MCRs, isocyanide-based multicomponent reactions (IMCRs) have attracted much attention because of the advantages that they offer to the field of the combinatorial chemistry [20–23]. The IMCRs are particularly interesting because they are more versatile and diverse than the remaining MCRs [24, 25]. The Passerini reaction (first described in 1921, Scheme 1) [26] is the most fundamental MCR involving isocyanides that provide α-acyloxycarboxamides by combining three building blocks in one step: a carboxylic acid, an aldehyde and an isocyanide. This reaction has been involved as a key step in the total synthesis of natural products due to the fact that the α-acyloxycarboxamide is a frequently recurring motif in many pharmacologically interesting natural products [27–30].

Experimental

Materials and instruments

4-[2,2-Bis(trimethylsilyl)ethenyl]benzaldehyde and [bmim]BF_4 were prepared based on the reported procedures [16,

✉ Kazem D. Safa
dsafa@tabrizu.ac.ir

[1] Organosilicon Research Laboratory, Faculty of Chemistry, University of Tabriz, Tabriz 5166616471, Iran

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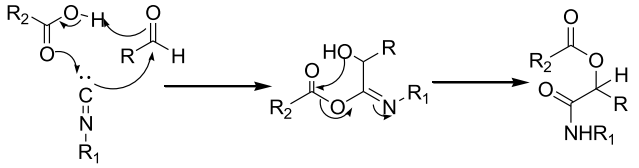


Scheme 1 Mechanism of Passerini reaction

31, 32]. Other starting materials and solvents were purchased from Merck and were used without further purification. The FTIR spectra were recorded on a Bruker-Tensor 270 spectrometer. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker FT-400 MHz spectrometer at room temperature and with $CDCl_3$ as the solvent for ^{1}H NMR, tetramethylsilane (TMS) served as internal standard ($\delta = 0$). Mass spectra were obtained with a GC-Mass Agilent, quadrupole model 5973 N instrument, operating at 70 eV. Melting points were measured with Barnstead international capillary melting point apparatus. Elemental analyses were carried out with an Elementar Vario EL III instrument.

General procedure for synthesis of 4a–4k

1. A mixture of 4-[2,2-bis(trimethylsilyl)ethenyl]benzaldehyde (1a, 1 mmol), a carboxylic acid derivative (2, 1 mmol) and an isocyanide (3, 1 mmol) in 2 ml [bmim]BF_4 was stirred at room temperature for a certain period of time (Table 1) to complete the reaction (monitored by TLC). The product was extracted three times with 10 ml portions of diethyl ether, and the combined ethereal phases were washed with brine and dried over sodium sulfate. The solvent was removed under reduced pressure, and the product was purified by column chromatography on silica gel using an ethyl acetate–hexane eluent. The rest of the viscous ionic liquid was further washed with DCM and dried at 80 °C under reduced pressure to reuse in subsequent runs.
2. A mixture of 4-[2,2-bis(trimethylsilyl)ethenyl]benzaldehyde (1a, 1 mmol), a carboxylic acid derivative (2, 1 mmol) and an isocyanide (3, 1 mmol) in 2 ml H_2O was stirred at room temperature for a certain period of time (Table 1) to complete the reaction (monitored by TLC). The precipitate was collected by suction, subsequently rinsed with *n*-hexane and dried to give product.

Analyses and spectra

(tert-Butylcarbamoyl)(4-(2,2-bis(trimethylsilyl)vinyl)phenyl) methyl 2-chlorobenzoate **(4a)** White powder (silica gel, *n*-hexane/ethyl acetate 10:2, $R_f = 0.6$), m.p. 72–76 °C. FTIR (KBr, cm^{-1}): 838.77, 1256.87 (Si–CH_3), 1695.24, 1724.89 (CO), 2890, 2961.39, 3072.29 (CH), 3308.68 (NH). ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): −0.08 (*s*, 9H, $SiMe_3$), 0.17 (*s*, 9H, $SiMe_3$), 1.35 (*s*, 9H, *t*-Bu), 6.20 (*s*, 1H, CH=), 6.31 (*s*, 1H, NH), 7.18 (*d*, $J = 8$ Hz, 1H, Ar), 7.35–7.49 (*m*, 5H, Ar), 7.70 (*s*, 1H, CH =), 7.90 (*d*, $J = 8$ Hz, 1H, Ar). ^{13}C NMR (400 MHz, $CDCl_3$, δ/ppm): −0.53, 0.95 ($SiMe_3$), 27.60 (CH_3), 50.58 (N–C), 74.86 (CH), 125.70, 127.24, 127.44, 127.57, 128.70, 129.17, 132.50, 132.68, 133.57, 142.51 (Ar), 146.50, 152.92 (vinyl. C), 164.07 (CO of amide), 166.42 (CO of ester). MS (m/z (EI), %): 515 ($[M]^+$), 139 (100), 213 (61.02), 73.10 (42.84, $[SiMe_3]^+$), 416.10 (39.01). Anal. Calc. for $C_{27}H_{38}ClNO_3Si_2$: C 62.82, H 7.42, N, 2.71. Found: C 62.61, H 7.29, N 2.63%.

(tert-Butylcarbamoyl)(4-(2,2-bis(trimethylsilyl)vinyl) phenyl) methyl benzoate **(4b)** White powder (silica gel, *n*-hexane/ethyl acetate 9:1, $R_f = 0.5$), m.p. 71–74 °C. FTIR (KBr, cm^{-1}): 837.62, 1256.40 (Si–CH_3), 1666, 1725 (CO), 2844.62, 2958.44, 3083.91 (CH), 3283 (NH). ^{1}H NMR

Table 1 Synthesis of α-acyloxycarboxamides containing 2,2-bis(trimethylsilyl)ethenyl group **(4a–k)**

Entry	R_1	R_2	Product	Yield (%)/H_2O	Time (h)/H_2O	Yield (%)/[bmim]BF_4	Time (h)/[bmim]BF_4
1	*t*-Bu	2-Cl	4*a*	95	2	83	10
2	*t*-Bu	H	4*b*	94	2	85	13
3	*t*-Bu	2-Me	4*c*	95	4	75	12
4	*t*-Bu	3,4,5-trimethoxy	4*d*	97	2	87	10
5	*t*-Bu	2-NO_2	4*e*	95	3	87	18
6	*t*-Bu	4-NO_2	4*f*	93	3	72	15
7	Cyclohexyl	3-Cl	4*g*	97	1.5	87	9
8	Cyclohexyl	4-Cl	4*h*	96	3	85	9
9	Cyclohexyl	3-F	4*i*	98	1.5	90	12
10	Cyclohexyl	3-NO_2	4*j*	97	2	85	15
11	Cyclohexyl	4-Br	4*k*	92	5	75	18

(400 MHz, $CDCl_3$, δ/ppm): −0.08 (*s*, 9H, $SiMe_3$), 0.17 (*s*, 9H, $SiMe_3$), 1.35 (*s*, 9H, *t*-Bu), 6.21 (*s*, 1H, CH), 6.33 (*s*, 1H, NH), 7.1 (*d*, $J = 8$ Hz, 2H, Ar), 7.30 (*m*, 1H, Ar), 7.40 (*m*, 5H, Ar), 7.7 (*s*, 1H, CH =), 7.89 (*d*, $J = 8$ Hz, 1H, Ar); ^{13}C NMR (400 MHz, $CDCl_3$, δ/ppm): −0.5, −0.91 ($SiMe_3$), 27.58 (CH_3), 50.60 (N–C), 75.90 (CH), 125.7, 125.9, 127.14, 130.2, 131.08, 131.9, 133.45, 142.4 (Ar), 146.42, 152.95 (vinyl. C), 163.09 (CO of amide), 166.11 (CO of ester); MS (m/z (EI), %): 481 ($[M]^+$), 105.10 (100), 179.10 (79.02), 382.20 (61.61), 73.10 (42.56, $[SiMe_3]^+$). Anal. Calc. for $C_{27}H_{39}NO_3Si_2$: C 67.31, H 8.16, N, 2.91. Found: C, 67.15, H 7.97, N 2.77%.

(tert-Butylcarbamoyl)(4-(2,2-bis(trimethylsilyl)vinyl)phenyl) methyl 2-methyl benzoate **(4c)** White powder (silica gel, *n*-hexane/ethyl acetate, 9:1, $R_f = 0.6$), m.p. 84–87 °C. FTIR (KBr, cm^{-1}), 838.8, 1249.95 (Si–CH_3), 1658.04, 1724.49 (CO), 2910, 2960.9, 3081.28 (CH), 3283.97 (NH). ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): −0.07 (*s*, 9H, $SiMe_3$), 0.18 (*s*. 9H, $SiMe_3$), 1.33 (*s*, 9H, *t*-Bu), 2.60 (*s*, 3H, CH_3), 5.83 (*s*, 1H, NH), 6.16 (*s*, 1H, CH), 7.20 (*d*, $J = 8$ Hz, 2H, Ar), 7.28 (t, $J = 8$ Hz, 2H, Ar), 7.44 (t, $J = 8$ Hz, 3H, Ar), 7.72 (*s*, 1H, CH =), 7.9 (*d*, $J = 8$ Hz, 1H, Ar). ^{13}C NMR (400 MHz, $CDCl_3$, δ/ppm): −0.53, 0.90 ($SiMe_3$), 20.70 (CH_3), 27.6 (CH_3), 50.5 (N–C), 74.9 (CH), 124.88, 125.79, 127.23, 129.50, 130.48, 130.80, 131.42, 131.80, 133.72, 142.50 (Ar), 146.5, 152.9 (vinyl. C), 164 (CO of amide), 166.4 (CO of ester). MS (m/z (EI), %): 495 ($[M]^+$), 119.10 (100), 193.10 (57.89), 396.20 (45.04), 73.10 (30.28, $[SiMe_3]^+$). Anal. Calc. for $C_{28}H_{41}NO_3Si_2$: C 67.83, H 8.34, N 2.83. Found: C 67.43, H 8.09, N 2.69%.

(tert-Butylcarbamoyl)(4-(2,2-bis(trimethylsilyl)vinylphenyl) methyl 3,4,5-trimethoxy benzoate **(4d)** White powder (silica gel, *n*-hexane/ethyl acetate 10:1, $R_f = 0.6$), m.p. 131–133 °C. FTIR (KBr, cm^{-1}): 840.87, 1255.72 (Si–CH_3), 1665.60, 1723.48 (CO), 2860.8, 2959.7, 3082 (CH), 3308.59 (NH). ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): −0.15 (*s*, 9H, $SiMe_3$), 0.10 (*s*, 9H, $SiMe_3$), 1.25 (*s*, 9H, *t*-Bu), 3.82 (*s*, 9H, OMe), 5.64 (*s*, 9H, NH), 6.05 (*s*, 1H, CH), 7.13 (*d*, $J = 8$ Hz, 2H, Ar), 7.26 (*s*, 2H, Ar), 7.36 (*d*, $J = 8$ Hz, 2H, Ar), 7.63 (*s*, 1H, CH=). ^{13}C NMR (400 MHz, $CDCl_3$, δ/ppm): −0.54, 0.9 ($SiMe_3$), 27.62 (CH_3), 50.5 (N–C), 55.23, 59.9 (O–CH_3), 75.01 (CH), 106.08, 123.32, 125.84, 127.29, 133.48, 142.62, 152.02 (Ar), 146.6, 152.8 (vinyl. C), 163.8 (CO of amide), 166.2 (CO of ester). MS (m/z (EI), %): 571 ($[M]^+$), 195.10 (100), 269.10 (38.44), 472.20 (27.03), 73.10 (20.74, $[SiMe_3]^+$). Anal. Calc. for $C_{30}H_{45}NO_6Si_2$: C 63.01, H 7.93, N 2.45. Found: C 62.78, H 7.73, N 2.34%.

(tert-Butylcarbamoyl)(4-(2,2-bis(trimethylsilyl)vinyl)phenyl)methyl 2-nitrobenzoate **(4e)** White powder (silica gel, *n*-hexane/ethyl acetate 10:2, $R_f = 0.4$), m.p. 111–113 °C. FTIR (KBr, cm^{-1}): 839.21, 1253.31 (Si–CH_3), 1675.58, 1740.9 (CO), 2960.87, 3076.38 (CH), 3329.39 (NH). ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): −0.08 (*s*, 9H, $SiMe_3$), 0.17 (*s*, 9H, $SiMe_3$), 1.36 (*s*, 9H, *t*-Bu), 6.02 (*s*, 1H, NH), 6.15 (*s*, 1H, CH), 7.18 (*d*, $J = 8$ Hz, 2H, Ar), 7.36 (*d*, $J = 8$ Hz, 2H, Ar), 7.69 (*m*, 3H, Ar, CH =), 7.85 (*m*, 2H, Ar). ^{13}CNMR (400 MHz, $CDCl_3$, δ/ppm): −0.56, 0.91 ($SiMe_3$), 27.47 (CH_3), 50.78 (N–C), 76.50 (CH), 122.81, 125.2, 125.8, 127.19, 129.83, 131.44, 132.02, 147.19 (Ar), 146.5, 152.8 (vinyl. C), 162.61 (CO of amide), 165.63 (CO of ester). MS (m/z (EI), %): 526 ($[M]^+$), 73.10 (100, $[SiMe_3]^+$), 182.90 (68.67), 184.90 (67.18), 261.10 (59.13). Anal. Calc. for $C_{27}H_{38}N_2O_5Si_2$: C 61.56, H, 7.27, N 5.32. Found: C 61.37, H 7.04, N 5.12%.

(tert-Butylcarbamoyl)(4-(2,2-bis(trimethylsilyl)vinyl)phenyl) methyl 4-nitrobenzoate **(4f)** White powder (silica gel, *n*-hexane/ethyl acetate 10:2, $R_f = 0.4$), m.p. 146–149 °C. FTIR (KBr, cm^{-1}): 839.63, 1258.8 (Si–CH_3), 1662.70, 1731.56 (CO), 2863.49, 2961.58, 3086.81 (CH), 3429.12 (NH). ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): −0.07 (*s*, 9H, $SiMe_3$), 0.18 (*s*, 9H, $SiMe_3$), 1.30 (*s*, 9H, *t*-Bu), 5.48 (*s*, 1H, NH), 6.14 (*s*, 1H, CH), 7.23 (*d*, $J = 8$ Hz, 2H, Ar), 7.45 (*d*, $J = 8$ Hz, 2H, Ar), 7.7 (*s*, 1H, CH =), 8.28 (q, $J = 20$ Hz, 4H, Ar). ^{13}C NMR (400 MHz, $CDCl_3$, δ/ppm): −0.57, 0.93 ($SiMe_3$), 27.5 (CH_3), 50.8 (N–C), 75.5 (CH), 122.6, 126.05, 127.51, 130, 132.70, 133.89, 143.15, 149.70 (Ar), 147.06, 152.5 (vinyl. C), 162.6 (CO of amide), 165.6 (CO of ester). MS (m/z (EI), %): 526 ($[M]^+$), 73.10 (100, $[SiMe_3]^+$), 182.90 (68.67), 184.90 (67.18), 261.10 (59.13). Anal. Calc. for $C_{27}H_{38}N_2O_5Si_2$: C 61.56, H, 7.27, N, 5.32. Found: C 61.33, H 7.19, N 5.15%.

(Cyclohexylcarbamoyl)(4-(2,2-bis(trimethylsilyl)vinyl) phenyl) methyl 3-chlorobenzoate **(4g)** White powder (silica gel, *n*-hexane/ethyl acetate 10:2, $R_f = 0.5$), m.p. 141–143 °C. FTIR (KBr, cm^{-1}): 839.97, 1251.14 (Si–CH_3), 1657.88, 1731.61 (CO), 2856.34, 2933.28, 3084.54 (CH), 3308.68 (NH). ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): −0.06 (*s*, 9H, $SiMe_3$), 0.18 (*s*, 9H, $SiMe_3$), 1.05–1.92 (*m*, 10H, 5 CH_2 of cyclohexyl), 3.81 (*m*, 1H, CH of cyclohexyl), 5.75 (*d*, $J = 8$ Hz, 1H, NH), 6.24 (*s*, 1H, CH), 7.21 (*d*, $J = 8$ Hz, 2H, Ar), 7.42 (*m*, 3H, Ar), 7.56 (*d*, $J = 8$ Hz, 1H, Ar), 7.70 (*s*, 1H, CH =), 7.98 (*d*, $J = 8$ Hz, 1H, Ar), 8.05 (*s*, 1H, Ar). ^{13}C NMR (400 MHz, $CDCl_3$, δ/ppm): −0.55, 0.95 ($SiMe_3$), 23.62, 24.37, 31.76 (CH_2 of cyclohexyl), 47.29 (N–C), 75.08 (CH), 125.88, 126.96, 127.34, 128.82, 128.89,

130.11, 132.54, 132.93, 133.71, 142.78 (Ar), 146.71, 152.73 (vinyl. C), 163.05 (CO of amide), 165.99 (CO of ester). MS (*m*/z (EI), %): 541 ($[M]^+$), 139 (100), 73.10 (86.99, $[SiMe_3]^+$), 213 (71.80), 141 (33.80). Anal. Calc. for $C_{29}H_{40}ClNO_3Si_2$: C, 64.23, H, 7.44, N, 2.58. Found: C 64.09, H 7.38, N 2.46%.

(Cyclohexylcarbamoyl)(4-(2,2-bis(trimethylsilyl)vinyl) phenyl) methyl 4-chlorobenzoate **(4h)** White powder (silica gel, *n*-hexane/ethyl acetate 10:1, $R_f = 0.5$), m.p. 112–114 °C. FTIR (KBr, cm^{-1}): 843.11, 1260.99 (Si–CH_3), 1686.10, 1727.15 (CO), 2855.23, 2935.06, 3083.6 (CH), 3284.06 (NH). ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): −0.07 (*s*, 9H, $SiMe_3$), 0.18 (*s*, 9H, $SiMe_3$), 1.02–1.92 (*m*, 10H, 5 CH_2 of cyclohexyl), 3.80 (*m*, 1H, CH of cyclohexyl), 5.76 (*d*, $J = 8$ Hz, 1H, NH), 6.23 (*s*, 1H, CH), 7.2 (*d*, $J = 8$ Hz, 2H, Ar), 7.44 (*d*, $J = 8$ Hz, 4H, Ar), 7.7 (*s*, 1H, CH =), 8.02 (*d*, $J = 8$ Hz, 2H, Ar). ^{13}C NMR (400 MHz, $CDCl_3$, δ/ppm): −0.66, 0.8 ($SiMe_3$), 23.49, 24.26, 31.66 (CH_2 of cyclohexyl), 47.17 (N–C), 74.81 (CH), 125.74, 126.68, 127.70, 130.08, 130.40, 132.90, 138.95, 142.64 (Ar), 146.60, 152.62 (vinyl. C), 163.26 (CO of amide), 166.03 (CO of ester). MS (m/z (EI), %): 541 ($[M]^+$), 139 (100), 73.10 (86.99, $[SiMe_3]^+$), 213 (71.80), 141 (33.80). Anal. Calc. for $C_{29}H_{40}ClNO_3Si_2$: C, 64.23, H, 7.44, N, 2.58. Found: C 64.03, H 7.32, N 2.41%.

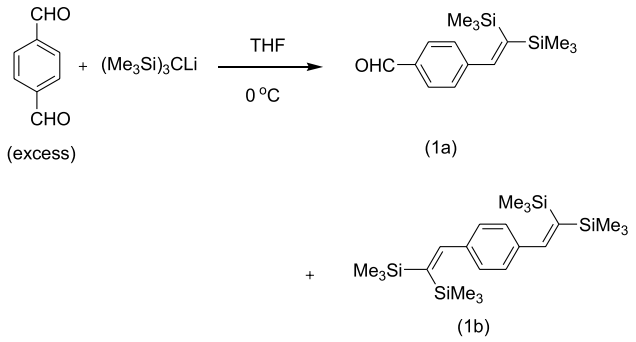
(Cyclohexylcarbamoyl)(4-(2,2-bis(trimethylsilyl)vinyl) phenyl) methyl 3-fluorobenzoate **(4i)** White powder (silica gel, *n*-hexane/ethyl acetate 10:2, $R_f = 0.5$), m.p. 122–124 °C. FTIR (KBr, cm^{-1}): 840.34, 1269.03 (Si–CH_3), 1657.60, 1728.69 (CO), 2856.38, 2935.60, 3082.12 (CH), 3269.08 (NH). ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): −0.03 (*s*, 9H, $SiMe_3$), 0.22 (*s*, 9H, $SiMe_3$), 1.06–1.96 (*m*, 10H, 5 CH_2 of cyclohexyl), 3.84 (*m*, 1H, CH of cyclohexyl), 5.80 (*d*, $J = 8$ Hz, NH), 6.28 (*s*, 1H, CH), 7.24 (*d*, $J = 8$ Hz, 2H, Ar), 7.32 (*m*, 1H, Ar), 7.49 (*m*, 3H, Ar), 7.74 (*s*, 1H, CH =), 7.80 (*s*, $J = 8$ Hz, 1H, Ar), 7.93 (*d*, $J = 8$ Hz, 1H, Ar). ^{13}C NMR (400 MHz, $CDCl_3$, δ/ppm): −0.54, 0.96 ($SiMe_3$), 23.62, 24.62, 31.78 (CH_2 of cyclohexyl), 47.28 (N–C), 75.08 (CH), 115.58, 115.8, 119.51, 119.72, 124.55, 125.8, 127.33, 129.22, 133.03, 142.76 (Ar), 146.71, 152.76 (vinyl. C), 162.79 (CO of amide), 165.99 (CO of ester). MS (m/z (EI), %): 525 ($[M]^+$), 123 (100), 197 (87.50), 73.10 (63.51, $[SiMe_3]^+$), 188.10 (26.83). Anal. Calc. for $C_{29}H_{40}FNO_3Si_2$: C, 66.24 H, 7.67, N, 2.66. Found: C 66.02, H 7.57, N 2.59%.

(Cyclohexylcarbamoyl)(4-(2,2-bis(trimethylsilyl)vinyl) phenyl) methyl 3-nitrobenzoate **(4j)** White powder (silica gel, *n*-hexane/ethyl acetate 10:2, $R_f = 0.5$), m.p. 129–132 °C. FTIR (KBr, cm^{-1}): 839.97, 1251.13 (Si–CH_3), 1655.73, 1732.42 (CO), 2858.58, 2934.96, 3086.25 (CH), 3265.11 (NH). ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): −0.06 (*s*, 9H, $SiMe_3$), 0.18 (*s*, 9H, $SiMe_3$), 1.2–1.93 (*m*, 10H, 5 CH_2 of cyclohexyl), 3.81 (*m*, 1H, CH of cyclohexyl), 5.62 (*d*, $J = 8$ Hz, 1H, NH), 6.25 (*s*, 1H, CH), 7.24 (t, $J = 8$ Hz, 2H, Ar), 7.46 (*d*, $J = 8$ Hz, 2H, Ar), 7.69 (t, $J = 8$ Hz, 2H, Ar), 8.43 (t, $J = 8$ Hz, 2H, Ar), 8.90 (*s*, 1H, Ar). ^{13}C NMR (400 MHz, $CDCl_3$, δ/ppm): −0.55, 0.95 ($SiMe_3$), 23.62, 24.35, 31.8 (CH_2 of cyclohexyl), 47.47 (N–C), 75.5 (CH), 123.77, 125.9, 126.09, 127.7, 130.22, 132.47, 143.15, 147.02 (Ar), 147.2, 152.5 (vinyl. C), 163 (CO of amide), 165.67 (CO of ester). MS (m/z (EI), %): 552 ($[M]^+$), 73.10 (100, $[SiMe_3]^+$), 261.10 (53.32), 187.10 (30.92), 276.10 (23.38), 203.10 (20.12). Anal. Calc. for $C_{29}H_{40}N_2O_5Si_2$: C, 63.01, H, 7.29, N, 5.07. Found: C 62.84, H 7.07, N 4.91%.

(Cyclohexylcarbamoyl)(4-(2,2-bis(trimethylsilyl)vinyl) phenyl) methyl 4-bromobenzoate **(4K)** Yellow powder (silica gel, *n*-hexane/ethyl acetate 10:2, $R_f = 0.5$), m.p. 182–184 °C. FTIR (KBr, cm^{-1}): 814.25, 1248.46 (Si–CH_3), 1684.42, 1728.67 (CO), 2856.60, 2934.16, 3066.35 (CH), 3304.75 (NH). ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): −0.074 (*s*, 9H, $SiMe_3$), 0.18 (*s*, 9H, $SiMe_3$), 1.2–1.92 (*m*, 10H, 5 CH_2 of cyclohexyl), 3.79 (*m*, 1H, CH of cyclohexyl), 5.74 (*d*, $J = 8$ Hz, 1H, NH), 6.23 (*s*, 1H, CH), 7.20 (*d*, $J = 8$ Hz, 2H, Ar), 7.43 (*d*, $J = 8$ Hz, 2H, Ar), 7.61 (*d*, $J = 8$ Hz, 2H, Ar), 7.7 (*s*, 1H, CH =), 7.95 (*d*, $J = 8$ Hz, 2H, Ar). ^{13}C NMR (400 MHz, $CDCl_3$, δ/ppm): −0.53, 0.97 ($SiMe_3$), 23.65, 24.39, 31.79 (CH_2 of cyclohexyl), 47.28 (N–C), 74.95 (CH), 125.86, 127.34, 130.31, 130.65, 130.87, 130.95, 134,157 (Ar), 142.7, 152.7 (vinyl. C), 166.09 (CO of ester). MS (m/z (EI), %): 587 ($[M^{+2}]^+$), 73.10 (100, $[SiMe_3]^+$), 207 (85.6), 182.9 (43.87), 184.90 (42.48), 281 (41.84). Anal. Calc. for $C_{29}H_{40}BrNO_3Si_2$: C, 59.37 H, 6.87, N, 2.39. Found: C 58.98, H 6.68, N 2.19%.

Results and discussion

α-Acyloxycarboxamides are precursors in the synthesis of natural products. Recently Pirrung and Sarma reported the acceleration of the Passerini reaction in water and in aqueous solutions compared to organic solvents. Similar results in terms of reaction time and yields were obtained when ionic liquid such as $[bmim]BF_4$ was used as solvent for most reactions [33, 34]. Due to interesting properties of silicon-containing organic compounds

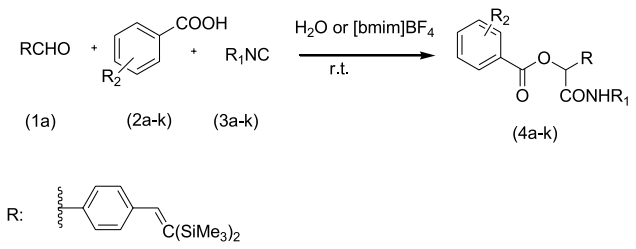


Scheme 2 Preparation of 4-[2,2 bis(trimethylsilyl)ethenyl]benzaldehyde via Peterson protocol

and in connection with our continued research on environmentally benign methodologies in organic synthesis, we were interested in inserting a silicon atom into α-acyloxycarboxamides via the Passerini reaction. Therefore, we apply this methodology to the versatile and efficient one-pot synthesis of α-acyloxycarboxamide derivatives containing the organosilicon groups in H_2O and [bmim]BF_4 as solvents at room temperature. Previously, we reported the synthesis of 4-[2,2-bis(trimethylsilyleth enyl)]benzaldehyde **(1a)** by the reaction of $(Me_3Si)_3CLi$ with terephthalaldehyde via the Peterson olefination reaction (Scheme 2) [16].

The one-pot three-component condensation reactions of aldehyde **1a** with aromatic carboxylic acids **2** and isocyanides **3** proceeded smoothly and cleanly under mild conditions in H_2O and [bmim]BF_4 and led to products in good yields (Table 1). All of the pure products **(4a–4k)** were stable at room temperature for a long time. Elemental analyses and spectroscopic data clearly indicated the formation of products. Full results are given in Experimental section (Scheme 3).

We also tested the effect of different solvents on the efficiency of the Passerini reaction using synthesis of **4a** as a model reaction. The results are given in Table 2. According to the results, it is observed that water and [bmim]BF_4 are suitable solvents for this type of reaction.



Scheme 3 Passerini reaction of 4-[2,2-bis(trimethylsilylethenyl)]benzaldehyde (**1a**) with aromatic carboxylic acids **2** and isocyanides **3**

Table 2 Effect of different solvents on one-pot synthesis of **4a**

Entry	Solvent	Time/h	Temp/°C	Yield/%
1	CH_2Cl_2	48	25	–
2	CH_2Cl_2	48	Reflux	45
3	THF	48	25	–
4	THF	48	Reflux	40
5	PEG	42	25	25
6	PEG	48	60	34
7	[bmim]BF_4	10	25	83
8	H_2O	2	25	95

Conclusions

In summary, we have synthesized and characterized novel α-acyloxycarboxamides containing an organosilicon groups by the Passerini three-component reaction between 4-[2,2-bis(trimethylsilyl)ethenyl]benzaldehyde, an isocyanide and carboxylic acids in [bmim]BF_4 and H_2O as solvents. This reaction is smoothly and efficiently carried out under mild conditions, and no side reactions were observed, rendering it a useful protocol for the synthesis of these compounds.

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